Supporting Information

Forging Structural Complexity: Diastereoselective Synthesis of Densely Substituted β–Lactams with Dual Functional Handles for Enhanced Core Modifications

Agustin M. Rodriguez Treviño,[a] Pierre Loch-Temzelides, †[a] Sanjay Pandiri, †[a] Justin K. Kirkland,[b] Michael T. Davenport,[b] Ulises Aguinaga,[c] Muhammed Yousufuddin,[c] Daniel H. Ess,[b] László Kürti*[a]

[a] Department of Chemistry, Rice University, Houston, Texas 77030, USA. E-mail: kurti.laszlo@rice.edu

[b] Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84604, USA.

[c] Department of Natural Sciences, University of North Texas at Dallas, Dallas, Texas 75241, USA.

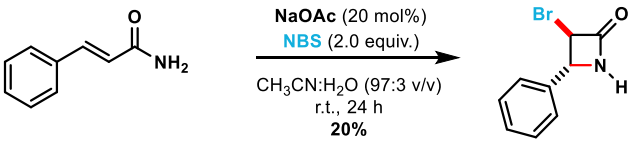
TABLE OF CONTENTS

1. General Information

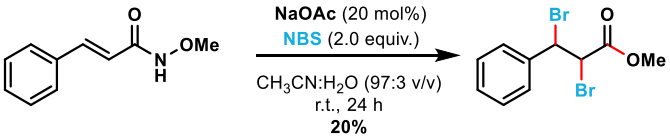
All reactions were carried out in oven-dried glassware unless otherwise noted. When needed, nonaqueous reagents were transferred under argon *via* syringe or cannula and dried prior to use. Dry solvents were obtained by passing deoxygenated solvents through activated alumina columns (MBraun SPS-800 series Solvent Purification System). Other solvents and reagents were used as obtained from the supplier unless otherwise noted. 1,1,1,3,3,3-Hexafluoroisopropanol (>99.5%) was purchased from Oakwood Chemicals. Analytical TLC was performed using Merck silica gel F254 (230–400 mesh) plates and analyzed by UV light or by staining upon heating with $KMnO_4$ solution (1 g of $KMnO_4$, 6.7 g of K_2CO_3, 1.7 mL of 1 M NaOH, 100 mL of H_2O). Flash column chromatography was performed using Biotage Isolera One automated chromatograph with pre-packed KP-Sil cartridges using p.a. grade solvents unless otherwise noted. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-*d*6 on a Bruker Avance DRX-600 spectrometer. The chemical shifts are reported in ppm relative to residual $CHCl_3$ (δ 7.26) or DMSO (2.50 ppm) for ^1H NMR and $CDCl_3$ (δ 77.16) DMSO-*d*6 (39.52) for ^{13}C NMR. The diastereomeric ratios were determined by ^1H NMR analysis of crude reaction mixtures. Melting points (MP) were determined in open capillaries using a Mettler Toledo MP50 melting point system and are uncorrected. High-resolution mass spectrometric data were measured using Agilent 1290/6230 LCMS-TOF system with electrospray ionization (ESI) in negative/positive mode.

2. Preliminary experimental results:

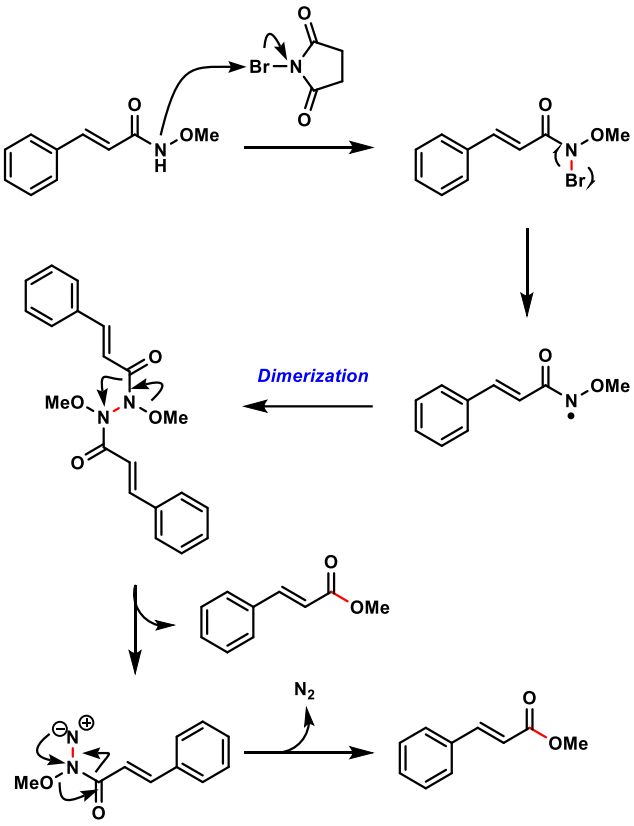
***Naskar et al.*, 1999:**



Our results:



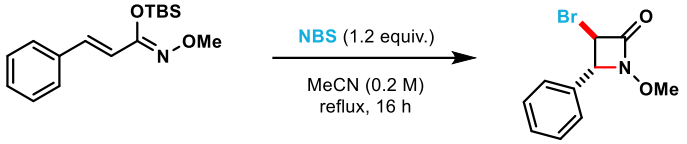
Proposed mechanism by *Zhato et al.* and *Chattopadhyay et al.*:



3. Optimization of the reaction conditions

To an oven-dried 8-mL vial equipped with a magnetic stir bar was added the silyl imino ether **1** (0.5 mmol). The starting material was suspended in the indicated solvent at concentration, followed by the addition of *N*-Bromo succinimide (indicated equivalents). The reaction mixture was then either kept at room temperature or heated to the given temperature for the given time. Finally, excess solvent was evaporated under vacuum and the crude mixture was purified by flash column chromatography to obtain the pure β-lactam **2**. The full optimization table is shown next:

Table 1. Optimization of the cyclization reaction to afford monocyclic *N*-alkoxy/aryloxy β-lactams.

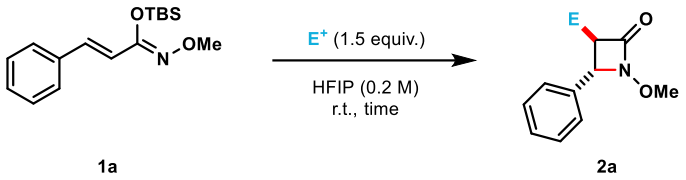


1a **2a**

entry[a]	Solvent	NBS equivalents	Concentration (M)	Temperature (°C)	Time (h)	Yield (%)
1	CH_3CN	1.2	0.2	r.t.	16	0[a]
2	CH_3CN	1.2	0.2	Reflux (82)	16	30
3	Toluene	1.2	0.2	Reflux (110)	16	0[a]
4	Dioxane	1.2	0.2	Reflux (110)	16	0[b]
5	HFIP	1.2	0.2	r.t.	1	67
6	Isopropanol	1.2	0.2	r.t.	0.5	0[b]
7	THF	1.2	0.2	r.t.	3	0[a]
8	THF	1.2	0.2	40	16	0[b]
9	CF_3CH_2OH	1.2	0.2	r.t.	16	31
10	DMF	1.2	0.2	r.t.	1	0[b]
11	DCM	1.2	0.2	Reflux (40)	16	0[a]
12	2-Me-THF	1.2	0.2	r.t.	16	0[b]
13	Diethyl Ether	1.2	0.2	r.t.	16	0[a]
14	Ethanol	1.2	0.2	r.t.	4	0[b]
15	HFIP	1.0	0.2	r.t.	1	61
16	HFIP	1.5	0.2	r.t.	1	80
17	HFIP	2.0	0.2	r.t.	1	76
18	HFIP	1.5	0.1	r.t.	1	80
19	HFIP	1.5	0.5	r.t.	1	68
20	HFIP	1.5	1.0	r.t.	1	47
21	HFIP:MeCN	1.5	0.2	Reflux (40)	16	15
22	HFIP:Toluene	1.5	0.2	r.t.	1	trace
23	HFIP:DCM	1.5	0.2	r.t.	1	70

[a]The silyl imino ether **1** remained unreacted and no desired product **2** was observed. [b]The silyl imino ether **1** was consumed and no desired product **2** was observed.

Table 2. Screening of different electrophiles for the cyclization reaction from optimized reaction conditions.

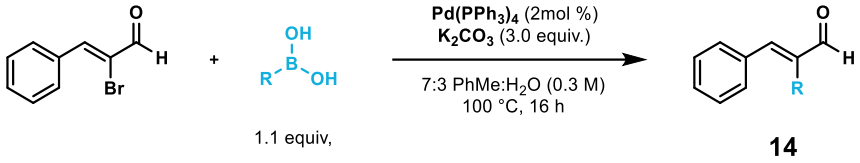


1a **2a**

entry[a]	Reagent	Time (h)	Yield (%)
1	NBS	1	80
2	DBI	1	78
3	Br_2	0.5	42
4	NCS	1	21
5	DCDMH	6	20
6	TCCA	6	31
7	I_2	16	0[a]
8	NIS	6	39
9	Select Fluor	6	0[a]
10	mCPBA	3	0[a]

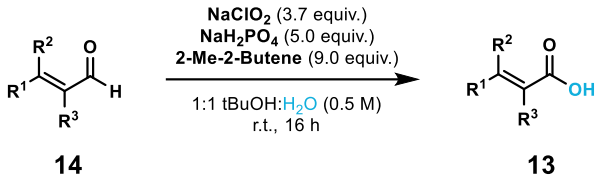
[a]The silyl imino ether **1** was consumed and no desired product **2** was observed.

4. General procedures for the synthesis of α,ß–unsaturated aldehydes

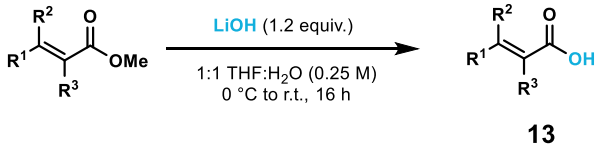


Method A: Following a modified literature procedure.[1] In a round-bottom flask under Argon atmosphere, α–bromo cinnamaldehyde (1.0 equiv.), boronic acid (1.1 equiv.), $Pd(PPh_3)_4$ (2 mol%) and K_2CO_3 (3.0 equiv.) were dissolved in toluene-H_2O (7:3, 0.3 M) mixture. The reaction mixture was heated to 100 °C overnight. After completion of the reaction, the reaction was diluted with EtOAc and partitioned with H_2O. It was extracted twice with EtOAc and the combined organic layers were dried over Na_2SO_4. The reaction mixture was then concentrated *in vacuo* and it was purified by column chromatography on silica gel (hexanes:EtOAc) to afford the corresponding α,ß–unsaturated aldehydes.

5. General procedures for the synthesis of carboxylic acids



Method A: Following a modified literature procedure.[2] In a round-bottom flask open to air, the corresponding cinnamaldehyde (1.0 equiv.) was dissolved in *t*-BuOH (0.5 M) at room temperature. Then $NaClO_2$ (3.7 equiv.) was added, followed by H_2O (0.5 M) and 2-methyl-2-butene (9.0 equiv.). Finally, NaH_2PO_4 (5.0 equiv.) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, saturated NH_4Cl was added, and the reaction mixture was extracted with EtOAc three times. The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted three times with $NaHCO_3$. The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted three times with DCM. The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded the corresponding α,ß–unsaturated carboxylic acids without further purification.

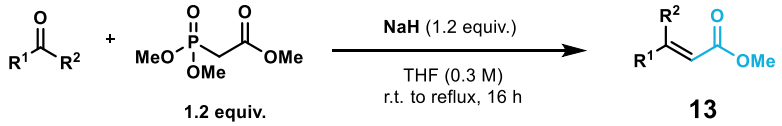


Method B: Following a modified literature procedure.[3] In a round-bottom flask open to air, LiOH (1.2 equiv.) was dissolved in THF:H_2O (1:1, 0.25 M) at room temperature. The reaction mixture was then cooled down to 0 °C using an ice-water bath. Then the corresponding methyl ester (1.0 equiv.) was added slowly.

[1] Matsuda, T., Sakurai, Y. *Eur. J. Org. Chem.* **2013**, 2013, 4219–4222.
[2] Yang, C., Li, F., Wu, T.R., Cui, R., Wu, B.B., Jin, R.X., Li, Y., Wang, X.S. *Org. Lett.* **2021**, 23, 8132–8137.
[3] Niwayama, S. Cho, H., Lin, C. *Tetrahedron Lett.* **2008**, 49, 4434–4436.

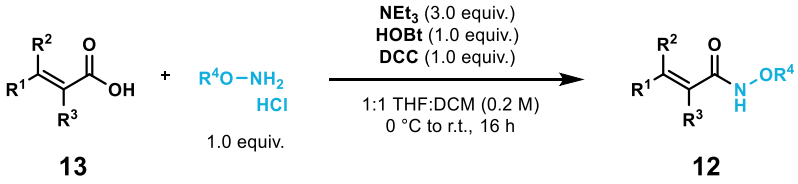
After complete addition, the reaction mixture was allowed to worm to room temperature, and it was monitored by TLC. After full consumption of the starting material, the solvent was removied *in vacuo* and conc. $NaHCO_3$ was added to the reaction mixture. It was then partitioned in DCM, and it was extracted three times with DCM. The aqueous layer was then carefully acidified with 3 M HCl, and it was extracted three times with DCM. The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded the corresponding carboxylic acids without further purification.

6. General procedures for the synthesis of α,ß–unsaturated esters



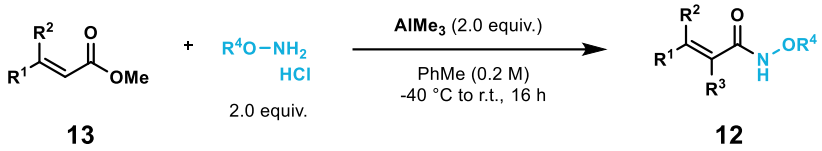
Method A: Following a modified literature procedure.[4] In a flame-dried round bottom flask under Argon atmosphere, sodium hydride (60% dispersion in mineral oil, 1.2 equiv.) was suspended in dry THF (0.3 M). Trimethyl phosphonoacetate (1.2 equiv.) was then added slowly at room temperature. After 5 min, the appropriate aldehyde or ketone (1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature; it was partitioned with H_2O and extracted three times with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (hexanes:EtOAc) to afford the corresponding α,ß–unsaturated methyl esters.

7. General procedures for the synthesis of hydroxamate esters



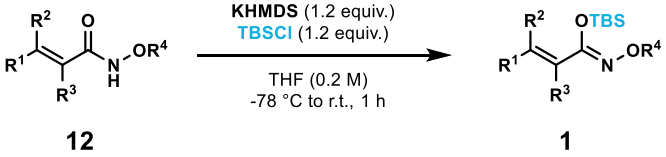
Method A: In an oven-dried round-bottom flask under Argon atmosphere, the hydroxylamine hydrochloride (1.0 equiv.) was suspended in THF:DCM (1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (1.5 equiv.) was added, and the reaction mixture was allowed to stir for 20 min at 0 °C. HOBt hydrate (1.0 equiv.) and the carboxylic acid (1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was washed once with HCl (3 M), followed by one wash with conc. $NaHCO_3$ and finally with H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (hexanes:EtOAc) to afford the corresponding hydroxamate esters.

[4] Duan, Z.C., Hu, X.P., Zhang, C., Zheng, Z. *J. Org. Chem.* **2010**, 75, 8319–8321.



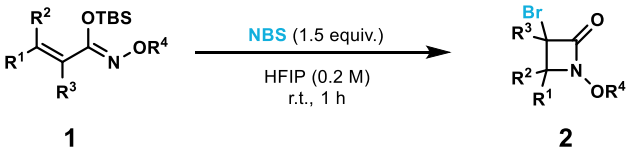
Method B: In a flame-dried round-bottom flask under Argon atmosphere, the hydroxylamine hydrochloride (2.0 equiv.) was suspended in dry Toluene (0.2 M). The reaction mixture was then cooled down to –40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, the corresponding ester (1.0 equiv.) was added, and the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with HCl (3M) until gas evolution ceased. The reaction mixture was then partitioned with H_2O and extracted three times with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (hexanes:EtOAc) to afford the corresponding hydroxamate esters.

8. General procedures for the synthesis of silyl imino ethers



In a flame-dried round bottom flask under Argon atmosphere, the corresponding hydroxamate ester (1.0 equiv.) was dissolved in dry THF (0.2 M) at room temperature. The reaction mixture was then cooled down to –78 °C using an acetone-dry ice bath. A solution of KHMDS (1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 30 to 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with H_2O and extracted with EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (hexanes:EtOAc) to afford the corresponding silyl imino ethers.

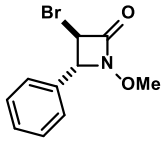
9. General procedures for the synthesis of β–lactams



In an 8-mL scintillation vial open to air, the corresponding silyl imino ether (0.5 mmol) was dissolved in HFIP (0.2 M). NBS (1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (hexanes:EtOAc) to afford the corresponding β-lactam.

10. Synthesis and characterization of lactams (2) and indolenes (3):

Rac 3-bromo-1-methoxy-4-phenylazetidin-2-one (2a)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1a** (145.7 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford rac 3-bromo-1-methoxy-4-phenylazetidin-2one **2a** as a colorless oil (102 mg, 80%).

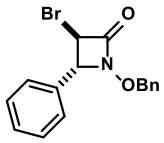
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 3H), 7.40 – 7.38 (m, 2H), 4.93 (d, *J* = 1.7 Hz, 1H), 4.33 (d, *J* = 1.7 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.4, 134.4, 129.9, 129.4, 126.7, 70.6, 64.1, 46.2.

HRMS: Calculated $[M+H]^+$ for $C_{10}H_{11}BrNO_2^+$: 255.9968, found: 255.9959.

FTIR (cm^{-1}): 3005, 2939, 2825, 1780, 1497, 1456, 1364, 1204, 11146, 1035, 975, 724, 696.

***rac* 1-(benzyloxy)-3-bromo-4-pehnylazetidin-2-one (2b)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1b** (183.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4-pehnylazetidin-2-one **2b** as a colorless oil (132.9 mg, 80%).

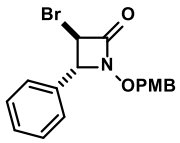
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 8H), 7.22 – 7.19 (m, 2H), 5.03 (d, *J* = 11.3, 1H), 4.94 (d, *J* = 11.3, 1H), 4.42 (d, *J* = 1.6, 1H), 4.24 (d, *J* = 1.6, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7, 134.5, 134.3, 129.7, 129.6, 129.4, 129.3, 128.9, 126.7, 78.7, 72.0, 46.1.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{15}BrNO_2^+$: 332.0281, found: 332.0288

FTIR (cm^{-1}): 3033, 3005, 2948, 1785, 1522, 1497, 1456, 1360, 1204, 1076, 1034, 956, 907, 740, 696.

***rac* 3-bromo-1-((4-methoxybenzyl)oxy)-4-phenylazetidin-2-one (2c)**



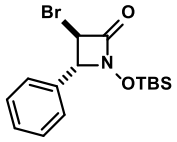
Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1c** (198.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 3-bromo-1-((4-methoxybenzyl)oxy)-4-phenylazetidin-2-one **2c** as a colorless oil (72.5 mg, 40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.37 (m 3H), 7.27 – 7.24 (m, 2H), 7.22 – 7.20 (m, 2H), 6.89 – 6.86 (m 2H), 4.98 (d, *J* = 11.1 Hz, 1H), 4.87 (d, *J* = 11.1 Hz, 1H), 4.43 (d, *J* = 1.6 Hz, 1H), 4.24 (d, *J* = 1.6 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.7, 160.6, 134.4, 131.4, 129.7, 129.2, 129.2, 126.7, 126.5, 114.2, 78.3, 72.0, 55.5, 46.1.

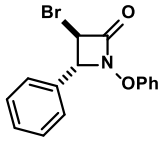
HRMS: Calculated $[M+H]^+$ for $C_{17}H_{17}BrNO_3^+$: 362.0386, found: 362.0386
FTIR (cm^{-1}): 3033, 3003, 2937, 2837, 1781. 1611, 1513, 1456, 1303, 1250, 1175, 1029, 953, 849, 819, 725, 696.

***rac* 3-bromo-1-((*tert*-butyldimethylsilyl)-oxy)-4-phenylazetidin-2-one (2d)**



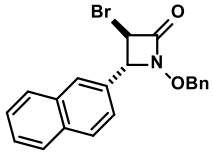
Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1d** (195.9 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 3-bromo-1-((*tert*-butyldimethylsilyl)-oxy)-4-phenylazetidin-2-one **2d** as a colorless oil (121.2 mg, 68%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 3H), 7.35 – 7.34 (m, 2H), 4.81 (d, *J* = 1.5 Hz, 1H), 4.34 (d, *J* = 1.5 Hz, 1H), 0.89 (s, 9H), 0.22 (s, 3H), 0.16 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.3, 134.2 129.7, 129.3, 126.9, 126.9, 73.1, 46.2, 25.6, -4.8, -4.8.
HRMS: Calculated $[M+H]^+$ for $C_{15}H_{23}BrNO_2Si^+$: 356.0676, found: 356.0683
FTIR (cm^{-1}): 2952, 2931, 2886, 2886, 1785, 1472, 1457. 1255, 1033, 958, 833, 788, 734, 696.

***rac* 3-bromo-1-phenoxy-4-phenylazetidin-2-one (2e)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1e** (176.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 3-bromo-1-phenoxy-4-phenylazetidin-2-one **2e** as a pale-pink solid (79.5 mg, 50%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 5H), 736 – 7.35 (m, 3H), 6.96 – 6.95 (m, 2H), 5.08 (d, *J* = 1.8 Hz, 1H), 4.48 (d, *J* = 1.9 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 157.3, 133.6, 132.9, 130.0, 129.5, 126.8, 117.2, 116.7, 71.8, 45.5.
HRMS: Calculated $[M+H]^+$ for $C_{15}H_{13}BrNO_2^+$: 318.0124, found: 318.0126
Melting Point: 96.2 – 97.2 °C
FTIR (cm^{-1}): 3093, 3065, 3018, 2938, 1797, 1580, 1479, 1456, 1365, 1192, 1166, 1154, 1144, 1073, 1036, 1006, 949, 848, 820, 754 725, 696.

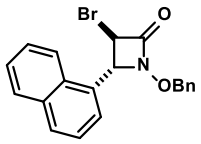
***rac* 1-(benzyloxy)-3-bromo-4-(naphthalen-2-yl)azetidin-2-one (2f)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1f** (208.8.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4-(naphthalen-2-yl)azetidin-2-one **2f** as a white solid (91.7 mg, 48%).

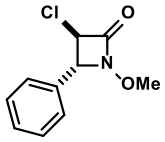
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 3H), 7.67 (s, 1H), 7.59 – 7.52 (m, 2H), 7.39 – 7.30 (m, 5H), 7.28 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.05 (d, *J* = 11.3 Hz, 1H), 4.96 (d, *J* = 11.3 Hz, 1H), 4.59 (d, *J* = 1.6 Hz, 1H), 4.33 (d, *J* = 1.7 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 134.5, 133.9, 133.2, 131.6, 129.7, 129.6, 129.4, 129.4, 128.9, 128.2, 128.0, 127.1, 127.0, 123.1, 78.7, 72.3, 46.1.
HRMS: Calculated $[M+H]^+$ for $C_{20}H_{17}BrNO_2^+$: 404.0257, found: 404.0257
Melting Point: 95.6 – 98.5 °C
FTIR (cm^{-1}): 33.94, 32.65, 3059, 3031, 2942, 1780, 1455, 1310, 1209, 1180, 1159, 1031, 967, 946, 905, 785, 750, 695.

***rac* 1-(benzyloxy)-3-bromo-4-(naphthalen-1-yl)azetidin-2-one (2g)**



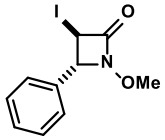
Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1g** (208.8.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4-(naphthalen-2-yl)azetidin-2-one **2g** as a colorless oil (91.7 mg, 48%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.90 (m, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.80 (m, 1H), 7.60 – 7.58 (m, 1H), 7.57 – 7.55 (m, 2H), 7.48 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.38 – 7.33 (m, 3H), 5.19 (s, 1H), 5.18 (d, *J* = 11.1 Hz, 1H), 5.08 (d, *J* = 11.1 Hz, 1H), 4.20 (d, *J* = 1.6 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 134.2, 133.8, 131.1, 130.6, 129.9, 129.8, 129.6, 129.6, 129.2, 129.0, 129.0, 127.2, 126.5, 125.6, 123.5, 122.8, 78.5, 69.3, 46.1.
HRMS: Calculated $[M+H]^+$ for $C_{20}H_{17}BrNO_2^+$: 404.0257, found: 404.0261
FTIR (cm^{-1}): 3090, 3062, 3033, 3007, 2945, 2881, 1785, 1497, 1455, 1324, 1180, 1044, 947, 797, 792, 780, 766, 698.

***rac* 3-chloro-1-methoxy-4-phenylazetidin-2-one (2h)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1a** (145.7 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NCS (100.1 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford rac 3-chloro-1-methoxy-4-phenylazetidin-2one **2h** as a colorless oil (22.2 mg, 21%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 3H), 7.39 – 7.38 (m, 2H), 4.85 (d, *J* = 1.7 Hz, 1H), 4.35 (d, *J* = 1.7 Hz, 1H), 3.81 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 134.2, 129.9, 129.4, 126.8, 70.6, 64.2, 59.8.
HRMS: Calculated $[M+H]^+$ for $C_{10}H_{11}ClNO_2^+$: 212.0473, found: 212.0477.
FTIR (cm^{-1}): 3033, 2990, 2940, 1789, 1498, 1457, 1365, 1076, 1040, 980, 740, 698.

***rac* 3-iodo-1-methoxy-4-phenylazetidin-2-one (2i)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1a** (145.7 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NIS (168.7 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford rac 3-iodo-1-methoxy-4-phenylazetidin-2one **2i** as a colorless oil (59.1 mg, 39%).

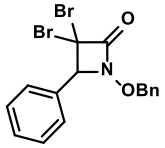
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 3H), 7.41 – 7.39 (m, 2H), 4.99 (d, *J* = 1.9 Hz, 1H), 4.36 (d, *J* = 1.9 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 135.1, 129.8, 129.4, 126.5, 71.8, 63.9. 17.4

HRMS: Calculated $[M+H]^+$ for $C_{10}H_{11}INO_2^+$: 303.9829, found: 303.9832.

FTIR (cm^{-1}): 3032, 2991, 2937, 1773, 1496, 1456, 1363, 1305, 1284, 1126, 1031, 972, 840, 713, 695.

***rac* 1-(benzyloxy)-3,3-dibromo-4-phenylazetidin-2-one (2j)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1j** (223.23 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3,3-dibromo-4-phenylazetidin-2-one **2j** as a yellow crystals (129.5 mg, 63%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 4H), 7.39 – 7.36 (m, 4H), 7.23 – 7.32 (m, 2H), 5.14 (d, *J* = 11.2 Hz, 1H), 5.03 (d, *J* = 11.2 Hz, 1H), 4.90 (s, 1H).

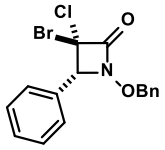
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 134.0, 132.6, 130.1, 129.8, 129.7, 129.0, 128.8, 128.0, 79.5, 78.7, 53.0.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{14}Br_2NO_2^+$: 411.9366, found: 411.9372.

Melting Point: 77.4 – 81.3 °C

FTIR (cm^{-1}): 3066, 0325, 2954, 2891, 1782, 1498, 1454, 1377, 1365, 1216, 1150, 1052, 942, 908, 844, 767, 748, 695.

***rac* 1-(benzyloxy)-3-bromo-3-chloro-4-phenylazetidin-2-one (2k)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1k** (223.23 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3,3-dibromo-4-phenylazetidin-2-one **2k** as a white solid (129.5 mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 4H), 7.37 – 7.36 (m, 2H), 7.24 – 7.22 (m, 2H), 5.13 (d, *J* = 11.2 Hz, 1H), 5.01 (d, *J* = 11.2 Hz, 1H), 4.93 (s, 1H).

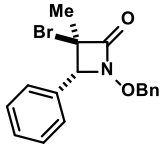
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 133.9, 131.2, 130.0, 129.6, 129.6, 128.9, 128.7, 128.1, 79.8, 78.6, 66.7.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{14}BrClNO_2^+$: 365.9891, found: 365.9898.

Melting Point: 67.9 – 70.5 °C

FTIR (cm^{-1}): 3066, 3035, 2955, 2893, 1784, 1498, 1455, 1379, 1218, 1151, 1001, 948, 757, 749, 696.

***rac* 1-(benzyloxy)-3-bromo-3-methyl-4-phenylazetidin-2-one (2l)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1l** (190.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-3-methyl-4-phenylazetidin-2-one **2l** as a white crystals (90 mg, 52%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 8H), 7.22 – 7.20 (m, 2H), 5.10 (d, *J* = 11.1 Hz, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 4.84 (s, 1H), 1.35 (s, 3H).

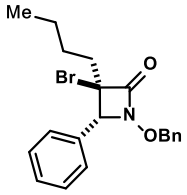
^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4, 134.4, 132.9, 129.7, 129.4, 129.3, 129.0, 129.0, 128.9, 127.2, 78.3, 76.8, 59.4, 21.9.

HRMS: Calculated $[M+H]^+$ for $C_{17}H_{17}BrNO_2^+$: 347.0438, found: 347.0439.

Melting Point: 82.2 – 84.2 °C

FTIR (cm^{-1}): 3034, 2985, 2891, 1771, 1497, 1456, 1439, 1383, 1217, 1157, 1057, 957, 909, 752, 741, 697.

***rac* 1-(benzyloxy)-3-bromo-3-butyl-4-phenylazetidin-2-one (2m)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1m** (211.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-3-butyl-4-phenylazetidin-2-one **2m** as a colorless oil (110 mg, 57%).

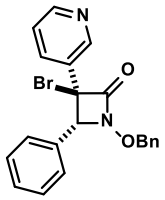
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 8H), 7.25 – 7.21 (m, 2H), 5.08 (d, *J* = 11.2 Hz, 1H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.84 (s, 1H), 1.59 – 1.54 (m, 1H), 1.45 – 1.34 (m, 2H), 1.07 – 0.99 (m, 2H), 0.97 – 0.90 (m, 1H), 0.63 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 134.5, 132.8, 129.7, 129.3, 129.3, 128.9, 128.8, 127.6, 78.2, 76.9, 65.9, 33.5, 27.2, 22.3, 13.6.

HRMS: Calculated $[M+H]^+$ for $C_{20}H_{23}BrNO_2^+$: 388.0907, found: 388.0915.

FTIR (cm^{-1}): 3065, 3033, 2956, 2872, 1781, 1497, 1455, 1358, 1213, 1169, 971, 942, 907, 745, 696.

***rac* 1-(benzyloxy)-3-bromo-4-phenyl-3-(pyrdin-3-yl)azetidin-2-one (2n)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1n** (204.6 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column

chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4-phenyl-3-(pyrdin-3-yl)azetidin-2-one **2n** as a colorless oil (61.4 mg, 30%).

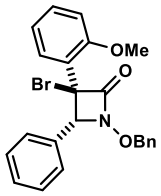
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 2.4, 0.8 Hz, 1H), 8.31 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.1, 2.4, 1.6 Hz, 1H), 7.42 – 7.38 (m, 5H), 7.21 – 7.18 (m, 1H), 7.17 – 7.14 (m, 2H), 6.99 (ddd, *J* = 8.1, 4.8, 0.9 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 5.14 (d, *J* = 11.2 Hz, 1H), 5.09 (s, 1H), 5.03 (d, *J* = 11.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 149.7, 149.6, 135.8, 134.4, 132.1, 131.0, 129.7, 129.7, 129.6, 129.0, 128.9, 127.9, 122.0, 78.7, 78.7, 60.1.

HRMS: Calculated $[M+H]^+$ for $C_{21}H_{18}BrN_2O_2^+$: 409.0546, found: 409.0552.

FTIR (cm^{-1}): 3034, 2932, 1786, 1497, 1456, 1417, 1364, 1060, 1029, 945, 749, 698.

rac 1-(benzyloxy)-3-(2-methoxyphenyl)-4-phenylazetidin-2-one (2o)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1o** (237 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-3-(2-methoxyphenyl)-4-phenylazetidin-2-one **2o** as a white crystalline solid (109 mg, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.44 – 7.42 (m, 3H), 7.36 – 7.35 (m, 2H), 7.30 – 7.27 (m, 1H), 7.24 – 7.18 (m, 4H), 6.80 (d, *J* = 8.8 Hz, 1H), 5.05 (d, *J* = 11.1 Hz, 1H), 4.90 (d, *J* = 11.1 Hz, 1H), 4.64 (s, 1H), 3.83 (s, 3H).

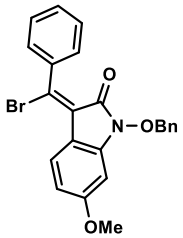
^{13}C NMR (150 MHz, $CDCl_3$) δ 161.8, 155.9, 134.2, 134.1, 133.6, 130.5, 129.7, 129.4, 129.3, 129.2, 128.7, 128.6, 128.1, 113.3, 113.1, 78.2, 74.1, 61.8, 55.5.

HRMS: Calculated $[M+H]^+$ for $C_{23}H_{21}BrNO_3^+$: 438.0699, found: 438.0700.

Melting Point: 114.2 – 115.5 °C

FTIR (cm^{-1}): 3061, 3038, 2940, 1783, 1489, 1456, 1394, 1379, 1265, 1235, 1021, 886, 749, 697.

(*E*)-1-(benzyloxy)-3-(bromo(phenyl)methylene)-6-methoxyindolin-2-one (3p)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1p** (236.9 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (95:5 Hexanes:EtOAc) to afford (*E*)-1-(benzyloxy)-3-(bromo(phenyl)methylene)-6-methoxyindolin-2-one **3p** as an orange crystalline solid (108 mg, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.71 (s, 1H), 7.63 – 7.61 (m, 2H), 7.51 – 7.47 (m, 4H), 7.46 – 7.43 (m, 1H), 7.40 – 7.37 (m, 3H), 6.08 (s, 1H), 5.24 (s, 2H), 3.71 (s, 3H).

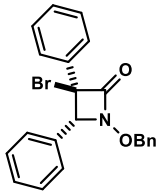
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 157.2, 142.3, 136.7, 135.0, 134.6, 130.3, 130.1, 129.6 129.4, 129.0, 127.3, 123.6, 111.3, 103.8, 93.2, 79.1, 56.5.

HRMS: Calculated $[M+H]^+$ for $C_{23}H_{19}BrNO_3^+$: 436.0543, found: 403.0552.

Melting Point: 162.0 – 167.0 °C

FTIR (cm^{-1}): 3061, 3030, 2958, 2899, 1703, 1611, 1474, 1446, 1385, 1224, 1204, 1173, 1049, 1014, 957, 906, 821, 746, 692.

***rac* 1-(benzyloxy)-3-bromo-3,4-diphenylazetidin-2-one (2q)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1q** (221.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-3,4-diphenylazetidin-2-one **2q** as a pale-yellow oil (32.1 mg, 16%).

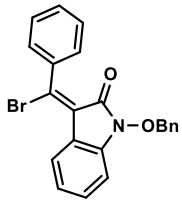
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 5H), 7.19 – 7.16 (m, 1H), 7.15 – 7.11 (m, 4H), 7.08 – 7.03 (m, 3H), 6.91 – 6.89 (m, 2H), 5.12 (d, *J* = 11.1 Hz, 1H), 5.10 (s, 1H), 5.01 (d, *J* = 11.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 134.5, 134.5, 132.8, 129.7, 129.4, 129.2, 128.9, 128.8, 128.5, 128.5, 128.3, 128.2, 79.1, 78.5, 63.1.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{19}BrNO_2^+$: 409.0594, found: 408.0596.

FTIR (cm^{-1}): 3063, 3032, 2940, 1780, 1497, 1455, 1448, 1364, 1047, 944, 743, 693, 656.

(*E*)-1-(benzyloxy)-3-(bromo(phenyl)methylene)indolin-2-one (3q)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1q** (221.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (95:5 Hexanes:EtOAc) to afford (*E*)-1-(benzyloxy)-3-(bromo(phenyl)methylene)indolin-2-one **3q** as a yellow solid (89 mg, 44%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.52 -7.46 (m, 5H), 7.39 – 7.38 (m, 3H), 7.28 – 7.26 (m, 1H), 6.60 (d, *J* =- 8.3 Hz, 1H), 5.24 (s, 2H).

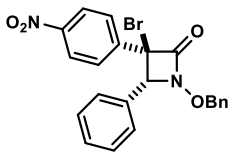
^{13}C NMR (150 MHz, $CDCl_3$) δ 164.1, 140.0, 139.8, 134.4, 134.4, 134.2, 132.5, 130.5, 130.1, 129.5, 129.5, 129.1, 128.9, 125.5, 124.0, 119.8, 115.0, 109.4, 78.7.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{17}BrNO_2^+$: 406.0437, found: 406.0437.

Melting Point: 138.1 – 140.5 °C

FTIR (cm^{-1}): 3064, 3034, 2919, 2850, 1709, 1603, 1446, 1379, 1309, 1266, 1205, 1107, 1056, 942, 902, 801, 744, 691..

***rac* 1-(benzyloxy)-3-bromo-3-(4-nitrophenyl)-4-phenylazetidin-2-one (2r)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1r** (244 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in*

vacuo and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-3-(4-nitrophenyl)-4-phenylazetidin-2-one **2r** as a yellow oil (147 mg, 65%).

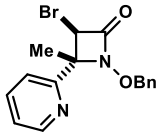
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.43 – 7.41 (m, 1H), 7.39 – 7.38 (m, 4H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.20 (m, 1H), 7.17 – 7.14 (m, 2H), 6.90 – 6.89 (m, 2H), 5.13 (d, *J* = 11.2 Hz, 1H), 5.07 (s, 1H), 5.03 (d, *J* = 11.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.1, 147.4, 141.5, 134.2, 131.8, 139.7, 129.6, 129.5, 129.4, 128.8, 128.8, 127.7, 123.2, 78.6, 78.6, 60.3.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{18}BrN_2O_4^+$: 453.044, found: 453.0456

FTIR (cm^{-1}): 3060, 3032, 2943, 2875, 1783, 1604, 1519, 1456, 1343, 1212, 1149, 1045, 943, 851, 742, 694.

***rac* 1-(benzyloxy)-3-bromo-4-methyl-4-(pyrdin-2-yl)azetidin-2-one (2s)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1s** (204.6 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4-methyl-4-(pyrdin-2-yl)azetidin-2-one **2s** as a colorless oil (112.8 mg, 65%).

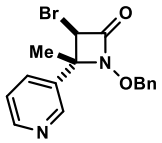
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 7.70 (td, *J* = 7.8, 1.9 Hz, 1H), 7.40 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.46 – 7.32 (m, 5H), 7.27 – 7.25 (m, 1H), 5.08 (d, *J* = 11.0 Hz, 1H), 5.02 (d, 11.0 Hz, 1H), 4.94 (s, 1H), 1.66 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 158.2, 149.8, 137.1, 135.1, 129.6, 129.3, 128.7, 123.5, 120.7, 79.4, 71.2, 51.9, 20.2.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{16}BrN_2O_2^+$: 347.0390, found: 347.0395.

FTIR (cm^{-1}): 3059, 3028, 3004, 2940, 1784, 1588, 1470, 1434, 1380, 1294, 1213, 1062, 909, 750, 698.

***rac* 1-(benzyloxy)-3-bromo-4-methyl-4-(pyrdin-3-yl)azetidin-2-one (2t)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1t** (204.6 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4-methyl-4-(pyrdin-3-yl)azetidin-2-one **2t** as a colorless oil (119.8 mg, 69%).

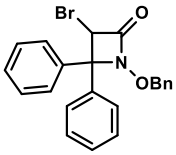
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 – 8.61 (m, 2H), 7.64 (ddd, *J* = 8.1, 2.5, 1.5 Hz, 1H), 7.37 (s, 5H), 7.31 (t, 6.6 Hz), 1H), 5.10 (s, 2H), 4.54 (s, 1H), 1.63 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 149.9, 147.1, 134.7, 133.2, 130.0, 129.6, 129.5, 128.9, 213.8, 79.5, 69.2, 52.8, 21.7.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{16}BrN_2O_2^+$: 347.0390, found: 347.0394.

FTIR (cm^{-1}): 3032, 2987, 2936, 1778, 1574, 1481, 1418, 1381, 1283, 1187, 1060, 1021, 907, 818, 742, 696.

***rac* 1-(benzyloxy)-3-bromo-4,4-diphenylazetidin-2-one (2u)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1u** (221.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4,4-diphenylazetidin-2-one **2u** as a white crystalline solid (181 mg, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 5H), 7.19 – 7.16 (m, 1H), 7.15 – 7.13 (m, 4H), 7.08 – 7.03 (m, 3H), 6.91 – 6.89 (m, 2H), 5.12 (d, *J* = 11.1 Hz, 1H), 5.10 (s, 1H), 5.01 (d, *J* = 11.1 Hz, 1H).

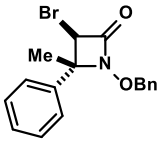
^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 134.5, 134.5, 132.8, 129.7, 129.4, 129.2, 128.9, 128.8, 128.5, 128.3, 128.2, 79.1, 78.5, 63.1.

HRMS: Calculated $[M+Na]^+$ for $C_{22}H_{18}BrNO_2Na^+$: 430.0413, found: 430.0409.

Melting Point: 98.4 – 100.2 °C

FTIR (cm^{-1}): 3062, 3033, 2955, 1778, 1496, 1447, 1374, 1216, 1180, 965, 906, 848, 731, 694.

***rac* 1-(benzyloxy)-3-bromo-4-methyl-4-phenylazetidin-2-one (2v)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1v** (190.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4-phenyl-3-(pyrdin-3-yl)azetidin-2-one **2v** as a colorless oil (138.5 mg, 80%).

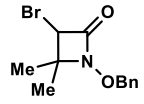
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 10H), 5.09 (dd, *J* = 13.3, 2.4 Hz, 2H), 4.54 (s, 1H), 1.64 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 140.3, 134.8, 129.6, 129.3, 129.1, 128.8, 128.7, 125.4, 79.3, 70.8, 53.3, 21.9.

HRMS: Calculated $[M+H]^+$ for $C_{17}H_{17}BrNO_2^+$: 346.0437, found: 346.0442.

FTIR (cm^{-1}): 3063, 3032, 2993, 1779, 1497, 1448, 1361, 1276, 1219, 1057, 907, 807, 735, 662.

***rac* 1-(benzyloxy)-3-bromo-4,4-dimethylazetidin-2-one (2w)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1w** (160 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-4,4-dimethylazetidin-2-one **2w** as a colorless oil (110.3mg, 78%).

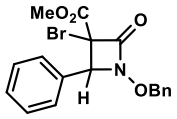
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 5H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.97 (d, *J* = 11.2 Hz, 1H), 4.34 (s, 1H), 1.33 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 135.3, 129.6, 129.4, 128.8, 79.3, 66.6, 51.2, 23.7, 22.7.

HRMS: Calculated $[M+H]^+$ for $C_{12}H_{15}BrNO_2^+$: 284.0281, found: 284.0282.

FTIR (cm^{-1}): 3032, 2972, 2932, 1774, 1455, 1387, 1373, 1268, 1248, 1110, 1016, 954, 819, 748, 696.

***rac* methyl 1-(benzyloxy)-3-bromo-2-oxo-4-phenylazetidine-3-carboxylate (2x)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1x** (212.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* methyl 1-(benzyloxy)-3-bromo-2-oxo-4-phenylazetidine-3-**2x** as a pale-yellow oil (72 mg, 37%) as a 1:1 mixture of diastereomers.

One diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 5H), 7.23 – 7.20 (m, 2H), 5.16 (d, *J* = 11.1 Hz, 1H), 5.06 – 5.04 (m, 1H), 4.71 (s, 1H), 3.30 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.9, 158.3, 134.2, 131.3, 129.9, 129.6, 129.5, 129.0, 128.8, 127.3, 76.3, 70.3, 59.2, 53.3.

Second diastereomer:

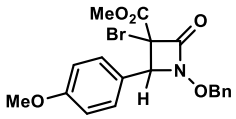
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 5H), 7.23 – 7.20 (m, 2H), 5.11 (d, *J* = 11.1 Hz, 1H), 5.06 – 5.04 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 158.4, 134.3, 132.6, 129.8, 129.7, 129.5, 128.8, 128.6, 128.2, 78.8, 70.3, 61.8, 54.4.

HRMS: Calculated $[M+H]^+$ for $C_{18}H_{17}BrNO_4^+$: 390.0335, found: 390.0336.

FTIR (cm^{-1}): 3065, 3034, 2954, 1796, 1753, 1732, 1497, 1455, 1434, 1264, 1200, 1002, 748, 697.

***rac* methyl 1-(benzyloxy)-3-bromo-2-(4-methoxyphenyl)-4-oxoazetidine-3-carboxylate (2y)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1y** (227.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* methyl 1-(benzyloxy)-3-bromo-2-(4-methoxyphenyl)-4-oxoazetidine-3-carboxylate **2y** as a colorless oil (168 mg, 80%).

One diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 5H), 7.15 – 7.12 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.09 (d, *J* = 11.2 Hz, 1H), 5.03 (d, *J* = 11.1 Hz, 1H), 5.00 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 160.7, 158.5, 134.4, 129.8, 129.6, 129.5, 128.8, 124.3, 114.0, 78.7, 70.2, 62.6, 55.5, 54.4.

Second diastereomer:

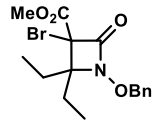
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 5H), 7.15 – 7.12 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.13 (d, *J* = 11.2 Hz, 1H), 5.03 (d, *J* = 11.1 Hz, 1H), 4.66 (s, 1H), 3.80 (s, 3H), 3.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 160.8, 158.4, 134.2, 129.8, 129.5, 129.0, 128.8, 123.0, 114.2, 78.7, 76.1, 59.2, 55.5, 53.4.

HRMS: Calculated $[M+H]^+$ for $C_{19}H_{19}BrNO_5^+$: 420.0441, found: 420.0444.

FTIR (cm^{-1}): 3064, 3033, 3007, 2954, 2839, 1793, 1750, 1611, 1514, 1456, 1249, 1176, 1027, 1009, 950, 837, 746, 697.

methyl *rac* 1-(benzyloxy)-3-bromo-2,2-diethyl-4-oxazetidine-3-carboxylate (2z)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1z** (183 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford methyl *rac* 1-(benzyloxy)-3-bromo-2,2-diethyl-4-oxazetidine-3-carboxylate **2z** as a colorless oil (92 mg, 55%).

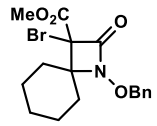
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 5H), 5.05 (q_{AB}, *J* = 13.5 Hz, 2H), 3.82 (s, 3H), 1.87 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.80 – 1.71 (m, 3H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 158.5, 134.5, 129.8, 129.4, 128.7, 79.5, 75.8, 63.2, 53.7, 26.7, 25.0, 8.9, 8.7.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{21}BrNO_4^+$: 370.0648, found: 370.0651.

FTIR (cm^{-1}): 3032, 2979, 2950, 2886, 1788, 1740, 1522, 1456, 1436, 1376, 1234, 1203, 1186, 1100, 1027, 947, 907, 748, 697.

methyl *rac* 1-(benzyloxy)-3-bromo-2-oxo-1-azaspiro[3.5]nonane-3-carboxylate (2aa)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1aa** (235.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford methyl *rac* 1-(benzyloxy)-3-bromo-2-oxo-1-azaspiro[3.4]nonane carboxylate **2aa** as a colorless oil (105 mg, 55%).

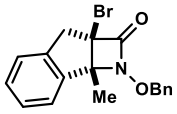
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.38 (m , 5H), 5.08 (s, 2H), 3.83 (s, 3H), 1.94 – 1.90 (m, 1H), 1.74 – 1.68 (m, 2H), 1.62 – 1.59 (m, 4H), 1.51 (ddt, *J* = 12.6, 6.8, 3.7 Hz, 1H), 1.43 (dddd, *J* = 13.8, 11.7, 6.6, 3.2 Hz, 1H), 1.33 – 1.25 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 158.2, 134.4, 129.9, 129.5, 128.7, 79.7, 72.5, 64.7, 53.8, 33.5, 31.2, 24.5, 23.5, 23.1.

HRMS: Calculated $[M+H]^+$ for $C_{17}H_{21}BrNO_4^+$: 382.0648, found: 382.0656.

FTIR (cm^{-1}): 3033, 2939, 2863, 1788, 1745, 1455, 1435, 1245, 1014, 1002, 943, 908, 849, 744, 697.

***rac* 1-(benzyloxy)-2a-bromo-7b-methyl-1,2a,3,7b-tetrahydro-2H-indeno[1,2-b]azet-2-one (2ab)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ab** (196.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford rac 1-(benzyloxy)-2a-bromo-7b-methyl-1,2a,3,7b-tetrahydro-2H-indeno[1,2-b]azet-2-one **2ab** as a white solid (125 mg, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 3H), 7.35 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.26 (m, 1H), 7.22 (dt, *J* = 7.5, 1.0 Hz, 1H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.84 (d, *J* = 11.1 Hz, 1H), 3.85 (d, *J* = 17.8 Hz, 1H), 3.37 (d, *J* = 17.8 Hz, 1H), 1.50 (s, 3H).

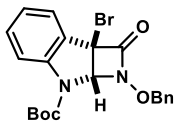
^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 140.3, 139.5, 135.3, 129.9, 129.7, 129.3, 128.8, 127.7, 125.9, 124.9, 80.6, 79.2, 64.4, 42.2, 18.5.

HRMS: Calculated $[M+H]^+$ for $C_{18}H_{17}BrNO_2^+$: 358.0437, found: 358.0442.

Melting Point: 89.7 – 93.9 °C

FTIR (cm^{-1}): 3062, 3033, 3008, 2984, 2889, 1770, 1487, 1455, 1378, 1251, 1214, 1126, 1114, 970, 891, 741, 694.

tert-butyl *rac* 1-(benzyloxy)-7b-bromo-2-oxo-1,2,2a,7b-tetrahydro-3H-azeto[3,2-b]indole-3-carboxylate (2ac)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ac** (240 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *tert*-butyl *rac* 1-(benzyloxy)-7b-bromo-2-oxo-1,2,2a,7b-tetrahydro-3H-azeto[3,2-b]indole-3-carboxylate **2ac** as a white solid (95.5 mg, 43%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.42 (dd, *J* = 7.2, 2.3 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.16 (td, *J* = 7.6, 1.0 Hz, 1H), 5.25 (d, *J* = 1.6 Hz, 2H), 1.65 (s, 9H).

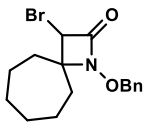
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9, 150.0, 141.3, 133.7, 131.7, 129.7, 129.5, 128.7, 126.7, 124.7, 122.2, 115.7, 88.1, 84.8, 79.2, 70.5, 28.3.

HRMS: Calculated $[M+H]^+$ for $C_{21}H_{22}BrN_2O_4^+$: 445.0757, found: 445.0761.

Melting Point: 106.9 – 109.4 °C

FTIR (cm^{-1}): 3110, 3072, 3039, 2977, 2929, 1803, 1714, 1473, 1463, 1344, 1153, 1110, 1071, 956, 858, 7388, 697.

rac 1-(benzyloxy)-3-bromo-1-azaspiro[3.6]decan-2-one (2ad)



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ad** (187 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bormo-1-azaspiro[3.9]decan-2-one **2ad** as a white solid (128 mg, 74%).

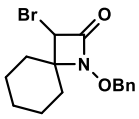
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 5H), 5.00 (q, *J* = 10.8 Hz, 2H), 4.34 (s, 1H), 2.05 – 1.98 (m, 2H), 1.77 – 1.71 (m, 2H), 1.68 – 1.62 (m, 1H), 1.59 – 1.38 (m, 7H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 134.7, 129.6, 129.3, 128.7, 79.4, 72.7, 52.0, 36.7, 35.1, 29.6, 29.5, 22.9, 22.8.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{21}BrNO_2^+$: 338.0750, found: 358.0761.

FTIR (cm^{-1}): 3032, 2928, 2857, 1774, 1455, 1368, 1231, 1193, 1101, 954, 908, 745, 695.

***rac* 1-(benzyloxy)-3-bromo-1-azaspiro[3.5]nonan-2-one (2ae)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ae** (178.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bormo-1-azaspiro[3.5]nonan-2-one **2ae** as a colorless oil (113.2 mg, 70%).

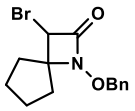
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 5H), 5.03 (d, *J* = 10.8 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.28 (s, 1H), 1.86 (ddd, *J* = 13.5, 12.1, 4.1 Hz, 1H), 1.82 – 1.77 (m, 2H), 1.69 – 1.65 (m, 1H), 1.61 – 1.57 (m, 2H), 1.55 – 1.46 (m, 2H), 1.33 (dtt, *J* = 13.5, 12.0, 3.6 Hz, 1H), 1.18 (dddd, *J* = 16.4, 15.0, 9.6, 3.7, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3, 134.9, 129.7, 129.3, 128.8, 79.5, 69.4, 50.2, 34.2, 31.7, 24.5, 24.0, 23.5.

HRMS: Calculated $[M+H]^+$ for $C_{15}H_{19}BrNO_2^+$: 324.0594, found: 324.0602.

FTIR (cm^{-1}): 3032, 2934, 2856, 1775, 1453, 1364, 1168, 1051, 950, 905, 849, 740, 696.

***rac* 1-(benzyloxy)-3-bromo-1-azaspiro[3.4]octan-2-one (2af)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1af** (172.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bormo-1-azaspiro[3.4]octan-2-one **2af** as a colorless oil (64.6 mg, 414%).

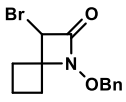
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.39 (m, 5H), 5.03 (d, *J* = 10.9 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.45 (s, 1H), 2.00 – 1.90 (m, 2H), 1.73 – 1.68 (m, 2H), 1.62 – 1.56 (m, 3H), 1.55 – 1.50 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.0, 134.9, 129.8, 129.4, 128.8, 79.2, 76.6, 51.4, 33.3, 31.9, 24.1, 24.0.

HRMS: Calculated $[M+H]^+$ for $C_{14}H_{17}BrNO_2^+$: 310.0437, found: 310.0438.

FTIR (cm^{-1}): 3032, 2959, 2874, 1775, 1497, 1454, 1369, 1335, 1188, 1049, 950, 907, 848, 743, 696.

***rac* 1-(benzyloxy)-3-bromo-1-azaspiro[3.3]heptan-2-one (2ag)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ag** (166 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bormo-1-azaspiro[3.3]hepoctan-2-one **2ag** as a colorless oil (61 mg, 41%).

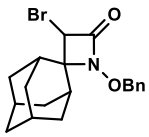
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 5H), 5.03 (m, 2H), 4.46 (s, 1H), 2.35 (dt, *J* = 12.5, 9.5 Hz, 1H), 2.30 (ddt, *J* = 12.9, 8.6, 4.0 Hz, 1H), 2.03 (ddt, *J* = 12.4, 8.5, 3.8 Hz, 1H), 1.92 (dt, *J* = 12.9, 9.6 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.57 (dt, *J* = 11.3, 8.9 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.2, 135.0, 129.9, 129.5, 128.8, 79.1, 70.3, 50.5, 29.8, 28.3, 13.2.

HRMS: Calculated $[M+H]^+$ for $C_{13}H_{15}BrNO_2^+$: 296.0281, found: 296.0284.

FTIR (cm^{-1}): 3064, 3032, 2989, 2945, 2881, 1775, 1455, 1362, 1294, 1212, 1054, 906, 848, 741, 696.

***rac* (1r,3r,5r,7r)-1'-(benzyloxy)-3'-bromospiro[adamantine-2,2'-azetidin]-4'-one (2ah)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ah** (205.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* (1r,3r,5r,7r)-1'-(benzyloxy)-3'-bromospiro[adamantine-2,2'-azetidin]-4'-one **2ah** as a white crystalline solid (174.9 mg, 93%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.39 – 7.37 (m, 3H), 5.15 (s, 2H), 4.27 (s, 1H), 2.34 (ddd, *J* = 12.8, 3.7, 2.0 Hz, 1H), 2.15 (dd, *J* = 13.5, 3.2 Hz, 1H), 2.10 (dq, *J* = 6.6 3.6, 3.5 Hz, 2H), 1.96 – 1.93 (m, 2H), 1.88 (p, *J* = 3.2 Hz, 1H), 1.83 (dq, *J* = 13.0, 3.0 Hz, 1H), 1.77 (dq, *J* = 13.4, 3.1 Hz, 1H), 1.74 – 1.68 (m, 5H).

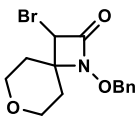
^{13}C NMR (150 MHz, $CDCl_3$) δ 161.5, 134.2, 129.7, 129.3, 128.7, 79.4, 76.8, 50.8, 38.4, 37.0, 36.5, 35.4, 34.6, 34.3, 34.2, 26.9, 26.3.

HRMS: Calculated $[M+H]^+$ for $C_{19}H_{23}BrNO_2^+$: 376.0907, found: 376.0911.

Melting Point: 42.3 – 51.4 °C

FTIR (cm^{-1}): 3032, 2906, 2857, 1773, 1498, 1471, 1453, 1375, 1228, 1051, 994, 878, 737, 695.

***rac* 1-(benzyloxy)-3-bromo-7-oxa-1-azaspiro[3.5]nonan-2-one (2ai)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ai** (180.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-3-bromo-7-oxa-1-azaspiro[3.5]nonan-2-one **2ai** as a colorless oil (128.2 mg, 79%).

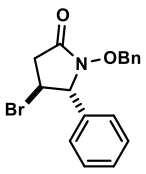
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (s, 5H), 5.02 (d, *J* = 10.9 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.36 (s, 1H), 3.92 – 3.89 (m, 1H), 3.81 (dddd, *J* = 12.0, 4.8, 3.8, 1.1 Hz, 1H), 3.53 (ddd, *J* = 12.0, 10.5, 3.0 Hz, 1H), 3.44 (ddd, *J* = 12.0, 10.8, 2.8 Hz, 1H), 2.08 (ddd, *J* = 13.7, 10.8, 4.5 Hz, 1H), 1.74 (dtd, *J* = 13.9, 3.2, 3.1, 2.2 Hz, 1H), 1.67 (ddd, *J* = 13.8, 10.5, 4.7 Hz, 1H), 1.52 (ddt, *J* = 13.7, 3.7, 2.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 134.6, 129.8, 129.5, 128.8, 79.4, 66.5, 66.2, 65.1, 49.6, 34.2, 31.7.

HRMS: Calculated $[M+H]^+$ for $C_{14}H_{17}BrNO_3^+$: 326.0386, found: 326.0389.

FTIR (cm^{-1}): 3032, 2906, 2857, 1773, 1498, 1471, 1453, 1375, 1228, 1051, 994, 878, 737, 695.

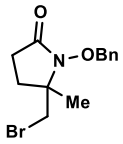
***rac* 1-(benzyloxy)-4-bromo-5-phenylpyrrolidin-2-one (2aj)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ai** (190.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (90:10 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-4-bromo-5-phenylpyrrolidin-2-one **2aj** as a colorless crystal (117.7 mg, 68%).

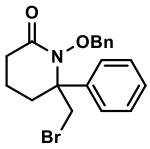
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 3H), 7.34 – 7.30 (m, 3H), 7.28 – 7.26 (m, 2H), 7.24 – 7.22 (m, 2H), 5.05 (d, *J* 10.6 Hz, 1H), 4.85 (d, *J* = 10.6 Hz, 1H), 4.65 (d, 4.2 Hz, 1H), 4.15 (dt, *J* = 7.6, 4.5 Hz, 1H), 3.14 (dd, *J* = 17.9, 7.7 Hz, 1H), 2.78 (dd, *J* = 17.9, 4.7 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 136.1, 134.7, 129.8, 129.3, 129.1, 128.7, 126.9, 77.8, 72.0, 42.4, 38.5.
HRMS: Calculated $[M+H]^+$ for $C_{17}H_{17}BrNO_2^+$: 346.0437, found: 346.0441.
FTIR (cm^{-1}): 3058, 3034, 2956, 2892, 1681, 1453, 1367, 1267, 1160, 1030, 974, 841, 759.

***rac* 1-(benzyloxy)-5-(bromoethyl)-5-methylpyrrolidin-2-one (2ak)**



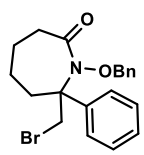
Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1ak** (166.8 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (70:30 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-5-(bromoethyl)-5-methylpyrrolidin-2-one **2ak** as a colorless oil (142.1 mg, 95%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.39 – 7.34 (m, 3H), 5.12 (s, 2H), 3.50 (d, *J* = 10.8 Hz, 1H), 3.38 (d, *J* = 10.8 Hz, 1H), 2.47 (ddd, *J* = 17.4, 10.4, 6.0 Hz, 1H), 2.35 (ddd, *J* = 17.4, 10.4, 5.5 Hz, 1H), 2.22 (ddd, *J* = 13.1, 10.4, 5.5 Hz, 1H), 1.84 (ddd, *J* = 13.1, 10.4, 5.9 Hz, 1H), 1.35 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 135.3, 129.7, 129.0, 128.7, 78.6, 63.1, 39.0, 27.78, 26.5, 23.0.
HRMS: Calculated $[M+H]^+$ for $C_{13}H_{17}BrNO_2^+$: 298.0437, found: 298.0445.
FTIR (cm^{-1}): 3063, 3032, 2973, 2886, 1704, 1454, 1376, 1249, 1058, 912, 752, 716, 695.

***rac* 1-(benzyloxy)-6-(bromoethyl)-6-phenylpiperidin-2-one (2al)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1al** (42 mg, 0.1 mmol) was dissolved in HFIP (0.5 mL, 0.2 M). NBS (27.4 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (70:30 Hexanes:EtOAc) to afford *rac* 1-(benzyloxy)-6-(bromoethyl)-6-phenylpiperidin-2-one **2al** as a white crystalline solid (28.2 mg, 73%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.43 (m, 2H), 7.36 – 7.27 (m, 8H), 5.40 (d, *J* = 9.4 Hz, 1H), 5.16 (d, *J* = 9.4 Hz, 1H), 4.18 (d, *J* = 11.3 Hz, 1H), 3.95 (d, *J* = 11.3 Hz, 1H), 2.72 (td, *J* = 13.4, 3.4 Hz, 1H), 2.63 (ddd, *J* = 17.0, 12.5, 6.6 Hz, 1H), 2.51 (ddt, *J* = 17.0, 5.5, 2.3 Hz, 1H), 2.13 (dddd, *J* = 13.5, 4.1, 3.2, 2.2 Hz, 1H), 1.68 – 1.63 (m, 1H), 1.43 – 1.35 (m, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 141.0, 135.7, 129.4, 129.0, 128.5, 128.5, 128.1, 126.8, 77.7, 72.3, 38.8, 36.1, 33.7, 17.0.
HRMS: Calculated $[M+H]^+$ for $C_{19}H_{21}BrNO_2^+$: 374.0750, found: 374.0754.
FTIR (cm^{-1}): 3030, 2957, 1678, 1496, 1446, 1356, 1331, 1207, 1048, 974, 750.

***rac* 1-(benzyloxy)-7-(bromoethyl)-7-phenylazepan-2-one (2am)**



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1am** (119 mg, 0.3 mmol) was dissolved in HFIP (0.5 mL, 0.2 M). NBS (75 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column chromatography on silica gel (DCM as the sole eluent) to afford *rac* 1-(benzyloxy)-7-(bromoethyl)-7-phenylazepan-2-one **2am** as a colorless oil (33.1 mg, 31%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.37 – 7.33 (m, 5H), 7.30 – 7.27 (m, 3H), 5.35 (d, *J* = 8.9 Hz, 1H), 5.24 (d, *J* = 8.9 Hz, 1H), 4.20 (d, *J* = 10.8 Hz, 1H), 3.62 (d, *J* = 10.8 Hz, 1H), 2.60 – 2.56 (m, 2H), 2.48 (dt, *J* = 15.5, 3.8 Hz, 1H), 1.98 (ddd, *J* = 15.6, 9.4, 3.8 Hz, 1H), 1.87 (dtd, *J* = 12.2, 9.0, 7.7, 4.7 Hz, 1H), 1.65 – 1.59 (m, 4H).

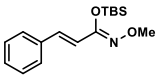
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.3, 141.2, 135.8, 129.6, 129.1, 128.6, 128.5, 128.1, 126.9, 78.0, 71.7, 43.2, 37.1, 36.5, 23.6, 22.0.

HRMS: Calculated $[M+H]^+$ for $C_{20}H_{23}BrNO_2^+$: 388.0907, found: 388.0912.

FTIR (cm^{-1}): 3062, 3032, 2936, 2865, 1666, 1497, 1447, 1313, 1215, 1015, 909, 763, 742.

11. Synthesis and characterization of silyl imino ethers (1):

***tert*butyl dimethylsilyl (*Z*)-*N*-methoxycinnanimidate (1a)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12a** (695 mg, 3.92 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to –78 °C using an acetone-dry ice bath. A solution of KHMDS (5.1 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (706 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 30 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-methoxycinnanimidate **1a** as a colorless oil (646 mg, 60%).

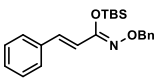
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.35 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 1.02 (s, 9H), 0.25 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.9, 136.0, 134.3, 128.9, 128.7, 1272.2, 120.3, 61.2, 26.1, 19.1, -3.7.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{26}NO_2Si^+$: 292.1727, found: 292.1735.

FTIR (cm^{-1}): 3061, 6027, 2956, 2931, 2898, 2858, 1581, 1471, 1463, 1449, 1346, 1251, 1062, 1018, 921, 823. 784, 752, 690.

***tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)cinnamimidate (1b)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12b** (12.55 g, 49.54 mmol, 1.0 equiv.) was dissolved in dry THF (250 mL, 0.2 M) at room temperature. The reaction

mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (64.5 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (9.6 g, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 200 mL of H_2O and extracted with 250 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-(benzyloxy)cinnamimidate **1b** as a crystalline white solid (13.38 g, 74%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 4H), 7.38 – 7.31 (m, 5H), 7.29 – 7.26 (m, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 5.04 (s, 2H), 0.98 (s, 9H), 0.16 (s, 6H).

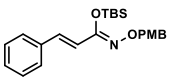
^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 137.1, 136.1, 134.2, 129.0, 129.0, 128.9, 128.6, 128.5, 128.2, 127.2, 120.6, 76.3, 26.1, 19.1, -3.6.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{30}NO_2Si^+$: 368.2040, found: 368.2049.

Melting Point: 58.1 – 61.4 °C

FTIR (cm^{-1}): 3085, 3063, 3031, 2959, 2949, 2879, 2857, 1577, 1448, 1360, 1346, 1250, 1054, 1009, 1000, 964, 783, 750, 738, 689.

*tert*butyl dimethylsilyl (*Z*)-*N*-((4-methoxybenzyloxy)oxy)cinnamimidate (1c)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12c** (2.0 g, 7.06 mmol, 1.0 equiv.) was dissolved in dry THF (35 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (7.8 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (1.20 g, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 40 mL of H_2O and extracted with 50 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-((4-methoxybenzyloxy)oxy)cinnamimidate **1c** as a white solid (1.88 g, 67%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.35 – 7.32 (4H), 7.29 – 7.26 (m, 1H), 7.12 (d, *J* = 16.0 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.97 (s, 2H), 3.82 (s, 3H), 0.97 (s, 9H), 0.13 (s, 6H).

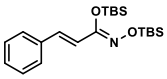
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 152.7, 136.1, 134.1, 130.8, 129.2, 128.9, 128.6, 127.2, 120.6, 113.8, 76.0, 55.4, 26.1, 26.1, 19.1, .01, -3.6.

HRMS: Calculated $[M+H]^+$ for $C_{23}H_{32}NO_3Si^+$: 398.2146, found: 398.2153.

Melting Point: 82.0 – 85.0 °C

FTIR (cm^{-1}): 3031, 2929, 2885, 2857, 1611, 1588, 1514, 1377, 1347, 1249, 1174, 1051, 1031, 999, 969, 825, 786, 751, 692.

***tert*butyl dimethylsilyl (*Z*)-*N*-((tert-butyldimethylsilyl)oxy)cinnamimidate (1d)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12d** (3.73 g, 22.88 mmol, 1.0 equiv.) was dissolved in dry THF (115 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (47 mL, 2.05 equiv., 1.0 M in THF) was then added slowly. TBSCl (7.213 g, 2.1 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 30 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 100 mL of H_2O and extracted with 100 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-((tert-butyldimethylsilyl)oxy)cinnamimidate **1d** as a yellow oil (3.209 g, 36%).

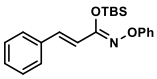
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.35 – 7.32 (m, 2H), 7.28 – 7.26 (m, 1H), 7.12 (d, *J* = 16.1 Hz, 1H), 6.54 (d, *J* = 16.1 Hz, 1H), 1.02 (s, 9H), 0.97 (s, 9H), 0.28 (s, 6H), 0.20 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 136.3, 133.7, 128.8, 128.8, 128.8, 128.5, 127.8, 127.2, 121.5, 26.5, 26.1, -3.3, -4.9.

HRMS: Calculated $[M+H]^+$ for $C_{21}H_{38}NO_2Si_2^+$: 392.2436, found: 392.2444.

FTIR (cm^{-1}): 3028, 2955, 2929, 2885, 2857, 1582, 1347, 1250, 1038, 958, 871, 836, 780, 753, 690.

***tert*butyl dimethylsilyl (*Z*)-*N*-phenoxycinnamimidate (1e)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12e** (1.0 g, 4.18 mmol, 1.0 equiv.) was dissolved in dry THF (21 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (5.0 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (753 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 25 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-phenoxycinnamimidate **1e** as a white solid (1.102 g, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.39 – 7.37 (m, 2H), 7.34 – 7.30 (m, 3H), 7.27 – 7.23 (m, 3H), 7.03 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 1.07 (s, 9H), 0.36 (s, 6H).

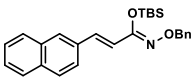
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 155.0, 135.8, 129.5, 129.0, 129.0, 127.4, 122.3, 120.1, 114.8, 26.1, 19.1, -3.6.

HRMS: Calculated $[M+H]^+$ for $C_{21}H_{28}NO_2Si^+$: 354.1884, found: 384.1890.

Melting Point: 59.4 – 62.9 °C

FTIR (cm^{-1}): 3059, 3027, 2958, 2927, 2854, 1593, 1578, 1488, 1349, 1250, 1209, 1034, 1022, 959, 806, 787, 752, 688.

***tert*butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(naphthalen-2-yl)acrylamidate (1f)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12f** (1.0 g, 3.3 mmol, 1.0 equiv.) was dissolved in dry THF (17 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.3 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (646 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(naphthalen-2-yl)acrylamidate **1f** as a white solid (1.035 g, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 4H), 7.62 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.43 – 7.42 (m, 2H), 7.39 – 7.36 (m, 2H), 7.34 – 7.31 (m, 1H), 7.28 (d, *J* = 16.0 Hz, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 5.06 (s, 2H), 1.02 (s, 9H), 0.18 (s, 6H).

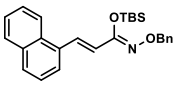
^{13}C NMR (150 MHz, $CDCl_3$) δ 152.9, 137.1, 134.2, 133.6, 133.6, 133.5, 139.1, 128.6, 125.8, 128.3, 128.2, 127.9, 127.8, 126.6, 126.5, 123.6, 120.9, 76.3, 26.1, 19.1, -3.6.

HRMS: Calculated $[M+H]^+$ for $C_{26}H_{32}NO_2Si^+$: 418.2197, found: 418.2201.

Melting Point: 79.4 – 82.8 °C

FTIR (cm^{-1}): 3057, 3034, 2956, 2927, 2879, 1580, 1468, 1461, 1364, 1321, 1247, 1054, 1008, 958, 836, 811, 746, 696.

***tert*butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(naphthalen-1-yl)acrylamidate (1g)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12g** (303.4 mg, 1.0 mmol, 1.0 equiv.) was dissolved in dry THF (5 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (1.2 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (180 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 5 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(naphthalen-1-yl)acrylamidate **1g** as a colorless oil (324 mg, 69%).

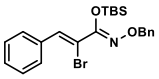
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 1H), 7.94 (d, *J* = 15.7 Hz, 1H), 7.78 – 7.85 (m, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.70 (dt, *J* = 7.3, 1.0 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.47 – 7.45 (m, 1H), 7.44 – 7.42 (m, 2H), 7.38 (tt, *J* = 6.5, 1.0 Hz, 2H), 7.35 – 7.32 (m, 1H), 6.63 (d, *J* = 15.7 Hz, 1H), 5.07 (s, 2H), 1.05 (s, 9H), 0.21 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.8, 137.1, 133.9, 133.5, 131.4, 131.0, 129.1, 129.0, 128.8, 128.5, 128.2, 126.5, 126.0, 125.8, 124.1, 123.5, 123.1, 76.4, 26.2, 19.1, -3.5.

HRMS: Calculated $[M+H]^+$ for $C_{26}H_{32}NO_2Si^+$: 418.2197, found: 418.2201.

FTIR (cm^{-1}): 3061, 3034, 2954, 229, 2857, 1582, 1362, 1350, 1329, 1251, 1053, 1001, 959, 786, 770, 696.

***tert*butyl dimethylsilyl (1*Z*,2*Z*)-*N*-(benzyloxy)-2-bromo-3-phenylacrylamide (1j)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12j** (1.33 g, 4.0 mmol, 1.0 equiv.) was dissolved in dry THF (40 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.8 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (721 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 40 mL of H_2O and extracted with 50 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*Z*)-*N*-(benzyloxy)-2-bromo-3-phenylacrylamide **1j** as a pale-yellow oil (1.130 g, 64%).

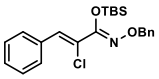
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 – 7.70 (m, 2H), 7.66 (s, 1H), 7.45 – 7.43 (m, 2H), 7.40 – 7.32 (m, 6H), 5.10 (s, 2H), 0.95 (s, 9H), 0.14 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.3, 136.7, 135.0, 133.2, 129.9, 129.5, 128.9, 128.5, 128.4, 128.4, 114.3, 26.0, -3.5.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{29}BrNO_2Si^+$: 446.1145, found: 446.1145.

FTIR (cm^{-1}): 3064, 3033, 2954, 2930, 2858, 1580, 1339, 1253, 1197, 1049, 991, 809, 786, 754, 688.

***tert*butyl dimethylsilyl (1*Z*,2*Z*)-*N*-(benzyloxy)-2-chloro-3-phenylacrylamide (1k)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12k** (575.5 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.6 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (390 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*Z*)-*N*-(benzyloxy)-2-chloro-3-phenylacrylamide **1k** as a pale-yellow solid (344 mg, 43%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (ddd, *J* = 8.5, 1.3, 0.6 Hz, 2H), 7.44 – 7.42 (m, 2H), 7.41 – 7.32 (m, 7H), 5.11 (s, 2H), 0.96 (s, 9H), 0.14 (s, 6H).

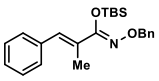
^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 136.7, 134.2, 130.1, 129.6, 129.5, 128.9, 128.5, 128.4, 123.7, 26.0, 19.0, -3.6.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{29}ClNO_2Si^+$: 402.1651, found: 402.1659.

Melting Point: 65.5 – 68.7 °C

FTIR (cm^{-1}): 3093, 3071, 3054, 2938, 2928, 2855, 1587, 1491, 1467, 1446, 1318, 1252, 1078, 1067, 1014, 973, 793, 744, 688.

***tert*butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-methyl-3-phenylacrylimidate (1l)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12l** (575.5 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.6 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (390 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-methyl-3-phenylacrylimidate **1l** as a white pale-yellow solid (344 mg, 43%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 2H), 7.37 – 7.34 (m, 4H), 7.33 – 7.31 (m, 3H), 7.26 – 7.24 (m, 1H), 7.23 (s, 1H), 5.04 (s, 2H), 2.06 (d, *J* = 1.3 Hz, 3H), 0.96 (s, 9H), 0.13 (s, 6H).

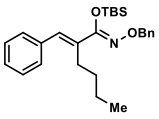
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 137.4, 137.3, 130.8, 129.9, 129.5, 129.3, 128.4, 128.3, 128.1, 127.2, 76.3, 26.1, 19.1, 14.1, -3.5.

HRMS: Calculated $[M+H]^+$ for $C_{23}H_{32}NO_2Si^+$: 382.2197, found: 382.2209.

Melting Point: 45.1 – 46.7 °C

FTIR (cm^{-1}): 3066, 3030, 2958, 2929, 2856, 1586, 1466, 1361, 1246, 1129, 1050, 960, 837, 785, 748, 694.

***tert*butyl dimethylsilyl (*Z*)-2-((*E*)-benzylidene)-*N*-(benzyloxy)pentanimidate (1m)**



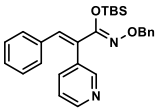
Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12m** (773.5 mg, 2.5 mmol, 1.0 equiv.) was dissolved in dry THF (12.5 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (3.0 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (450 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 15 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-2-((*E*)-benzylidene)-*N*-(benzyloxy)pentanimidate **1m** as a colorless oil (568 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.36 – 7.33 (m, 4H), 7.33 – 7.30 (m, 1H), 7.29 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 5.02 (s, 2H), 2.48 – 2.46 (m, 2H), 1.53 – 1.48 (m, 2H), 1.35 (h, *J* = 7.4 Hz, 2H), 0.95 (s, 9H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.15 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.5, 137.7, 137.3, 135.3, 130.5, 129.4, 129.1, 128.4, 128.3, 128.0, 127.2, 76.2, 31.8, 27.2, 26.1, 23.1, 19.1, 14.0, -3.6.

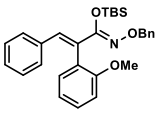
HRMS: Calculated $[M+H]^+$ for $C_{26}H_{38}NO_2Si^+$: 424.2666, found: 424.2675.
FTIR (cm^{-1}): 3063, 3030, 2955, 2929, 2858, 1585, 1470, 1455, 1362, 1333, 1276, 1251, 1060, 1021, 993, 823, 784, 695.

***tert*butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-phenyl-2-(pyridin-3-yl)acrylimidate (1n)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12n** (120 mg, 0.36 mmol, 1.0 equiv.) was dissolved in dry THF (4 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (0.43 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (61 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 5 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-phenyl-2-(pyridin-3-yl)acrylimidate **1n** as a colorless oil (94 mg, 58%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (m, 1H), 8.40 (s, 1H), 7.47 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.40 (s, 1H), 7.34 – 7.30 (m, 3H), 7.28 – 7.26 (m, 2H), 7.24 – 7.22 (m, 1H), 7.14 – 7.12 (m, 3H), 4.87 (s, 2H), 0.95 (s, 9H), 0.16 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.1, 151.3, 148.4, 138.2, 137.0, 135.5, 133.1, 132.9, 131.4, 130.0, 129.6, 128.4, 128.4, 128.3, 128.2, 128.0, 123.1, 76.4, 26.1, 19.1, -3.5.
HRMS: Calculated $[M+H]^+$ for $C_{27}H_{33}N_2O_2Si^+$: 445.2306, found: 445.2308.
FTIR (cm^{-1}): 3031, 2929, 2857, 1670, 1586, 1472, 1363, 1253, 1058, 1039, 1002, 838, 787, 751.

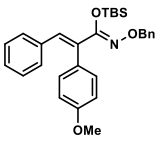
***tert*butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-(2-methoxyphenyl)-3-phneylacrylimidate (1o)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12o** (359 mg, 1.0 mmol, 1.0 equiv.) was dissolved in dry THF (5 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (1.2 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (180 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 5 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-(2-methoxyphenyl)-3-phneylacrylimidate **1o** as a colorless oil (382 mg, 81%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 7H), 7.11 – 7.09 (m, 3H), 7.01 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.96 (dd, *J* = 6.8, 2.9 Hz, 1H), 6.90 (ddd, *J* = 6.4, 3.4, 2.3 Hz, 2H), 4.87 (s, 2H), 3.62 (s, 3H), 0.90 (s, 9H), 0.13 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 153.5, 137.6, 136.4, 132.0, 131.7, 131.3, 129.6, 129.5, 129.0, 128.2, 128.1, 127.9, 127.5, 126.4, 120.8, 111.2, 76.1, 55.5, 26.0, 19.0, -3.7.

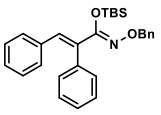
HRMS: Calculated $[M+H]^+$ for $C_{29}H_{36}NO_3Si^+$: 474.2469, found: 474.2461.
FTIR (cm^{-1}): 3029, 2958, 2930, 2884, 1598, 1582, 1470, 1461, 1295, 1247, 1055, 1003, 907, 751, 728, 693.

***tert*butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-(4-methoxyphenyl)-3-phenylacrylimidate (1p)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12p** (1.08 g, 3.0 mmol, 1.0 equiv.) was dissolved in dry THF (30 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (3.6 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (540 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 30 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-(4-methoxyphenyl)-3-phenylacrylimidate **1p** as a pale-yellow oil (1.33 g, 94%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.3 – 7.31 (m, 5H), 7.23 (s, 1H), 7.13 – 7.10 (m, 3H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.97 – 6.95 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.92 (s, 2H), 3.84 (s, 3H), 0.91 (s, 9H), 0.13 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 154.1, 137.3, 136.3, 134.3, 131.6, 131.5, 130.0, 129.6, 129.0, 128.3, 128.1, 127.5, 113.7, 76.5, 55.4, 26.0, 19.0, -3.6.
HRMS: Calculated $[M+H]^+$ for $C_{29}H_{36}NO_3Si^+$: 474.2459, found: 474.2463.
FTIR (cm^{-1}): 3062, 3032, 2954, 2929, 2857,. 1605, 1579, 1512, 1287, 1244, 1171, 1002, 823, 784, 693.

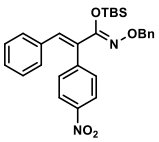
***tert*butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2,3-diphenylacrylimidate (1q)**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12q** (988.2 mg, 3.0 mmol, 1.0 equiv.) was dissolved in dry THF (15 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (3.6 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (496 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 15 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2,3-diphenylacrylimidate **1q** as a colorless oil (882 mg, 66%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 8H), 7.27 (s, 1H), 7.18 – 7.16 (m, 2H), 7.12 – 7.09 (m, 3H), 6.93 – 6.91 (m, 2H), 4.90 (s, 2H), 0.91 (s, 9H), 0.13 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.9, 137.2, 136.9, 136.1, 134.7, 131.7, 130.4, 130.0, 139.6, 128.3, 128.3, 128.1, 127.6, 127.4, 76.3, 26.0, 19.0, -3.6.
HRMS: Calculated $[M+H]^+$ for $C_{28}H_{34}NO_2Si^+$: 444.2353, found: 444.2358.
Melting Point: 81.7 – 84.5 °C

FTIR (cm^{-1}): 3057, 3030, 2952, 2930, 2882, 2854, 1599, 1583, 1491, 1470, 1443, 1360, 1301, 1250, 1055, 1012, 964, 839, 778, 696, 690.

_tert_butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-(4-nitrophenyl)-3-phenylacrylimidate (1r)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12r** (1.3 g, 3.5 mmol, 1.0 equiv.) was dissolved in dry THF (35 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.2 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (576 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 40 mL of H_2O and extracted with 40 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-2-(4-nitrophenyl)-3-phenylacrylimidate **1r** as a colorless oil (1.05 g, 55%).

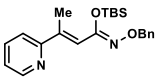
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.38 (s, 1H), 7.33 – 7.30 (m, 5H), 7.26 – 7.24 (m, 1H), 7.16 – 7.11 (m, 3H), 6.89 – 6.87 (m, 2H), 4.85 (s, 2H), 0.96 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.7, 147.2, 144.4, 137.0, 135.1, 133.0, 132.8, 131.7, 129.9, 129.6, 128.4, 128.3, 128.3, 128.3, 123.4, 76.4, 26.1, 19.1, -3.5.

HRMS: Calculated $[M+H]^+$ for $C_{28}H_{33}N_2O_4Si^+$: 489.2204, found: 489.2209.

FTIR (cm^{-1}): 2931, 1598, 1520, 1318, 1253, 1053, 104, 852, 787, 750, 697.

_tert_butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(pyridine-2-yl)but-2-enimidate (1s)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12s** (2.0 g, 7.45 mmol, 1.0 equiv.) was dissolved in dry THF (37 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (9.0 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (1.35 g, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 40 mL of H_2O and extracted with 40 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(pyridine-2-yl)but-2-enimidate) **1s** as a colorless oil (497.1 mg, 17%).

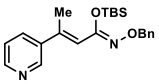
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.65 (td, *J* = 7.6 Hz, 1H), 7.47 – 7.46 (m, 1H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.32 – 7.30 (m, 1H), 7.17 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 6.60 (d, *J* = 1.4 Hz, 1H), 5.05 (s, 2H), 2.40 (d, *J* = 1.4 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 152.1, 149.1, 142.5, 137.6, 136.5, 129.1, 128.4, 128.1, 122.5, 121.4, 120.5, 76.2, 25.8, 18.8, 16.8, -3.8.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{31}N_2O_2Si^+$: 383.2149, found: 383.2150.

FTIR (cm^{-1}): 3206, 3033, 2953, 2929, 2857, 1635, 1584, 1465, 1432, 1360, 1250, 1054, 1003, 870, 833, 779, 696.

_tert_butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(pyridine-3-yl)but-2-enimidate (1t)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12t** (658.8 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (360 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-(pyridine-3-yl)but-2-enimidate) **1t** as a light yellow crystalline solid (482.8 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 2.5, 0.9 Hz, 1H), 8.52 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.69 (ddd, *J* = 8.0, 2.4, 1.6 Hz, 1H), 7.42 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 7.33 – 7.30 (m, 1H), 7.27 – 7.25 (m, 2H), 5.99 (q, *J* = 1.4 Hz, 1H), 5.04 (s, 2H), 2.33 (d, *J* = 1.4 Hz, 3H), 0.92 (s, 9H), 0.15 (s, 6H).

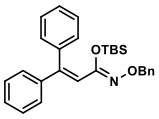
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.4, 149.1, 147.6, 140.9, 138.5, 137.5, 133.4, 129.1, 128.4, 128.1, 123.3, 120.6, 76.3, 25.8, 18.7, 18.4, -3.8.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{31}N_2O_2Si^+$: 383.2149, found: 383.2151.

Melting Point: 101.7 – 109.8 °C

FTIR (cm^{-1}): 3143, 3063, 3033, 2930, 2874, 1675, 1633, 1528, 1454, 1357, 1286, 1205, 1052, 943, 863, 752, 699.

_tert_butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-3,3-diphenylacrylimidate (1u)

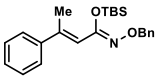


Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12u** (533 mg, 1.62 mmol, 1.0 equiv.) was dissolved in dry THF (8 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.0 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (292 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-(benzyloxy)-3,3-diphenylacrylimidate **1u** as a white solid (607 mg, 84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 8H), 7.27 (s, 1H), 7.18 – 7.16 (m, 2H), 7.12 – 7.09 (m, 3H), 6.93 – 6.91 (m, 2H), 4.90 (s, 2H), 0.91 (s, 9H), 0.13 (s, 6H).

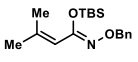
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.9, 137.2, 136.9, 136.1, 134.7, 131.7, 130.4, 130.0, 139.6, 128.3, 128.3, 128.1, 128.1, 127.6, 127.4, 76.3, 26.0, 19.0, -3.6.
HRMS: Calculated $[M+H]^+$ for $C_{28}H_{34}NO_2Si^+$: 444.2353, found: 444.2360.
Melting Point: 111.0 – 112.1 °C
FTIR (cm^{-1}): 3107, 3052, 2959, 1629, 1595, 1491, 1348, 1289, 1065, 970, 765, 739, 631.

_tert_butyl dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-phenylbut-2-enimidate (1v)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12v** (1.0 g, 3.74 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.86 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (733 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (1*Z*,2*E*)-*N*-(benzyloxy)-3-phenylbut-2-enimidate **1v** as a pale yellow oil (200 mg, 49%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 4H), 7.37 – 7.27 (m, 6H), 5.97 (q, *J* = 1.4 Hz, 1H), 5.04 (s, 2H), 2.33 (d, *J* = 1.4 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 144.3, 143.1, 137.7, 129.1, 128.5, 128.4, 128.0, 126.2, 119.0, 76.1, 25.8, 18.7, 18.6, -3.8.
HRMS: Calculated $[M+H]^+$ for $C_{23}H_{32}NO_2Si^+$: 382.2202, found: 382.2203.
FTIR (cm^{-1}): 3063, 3032, 2953, 2929, 2857, 1634, 1577, 1471, 1349, 1289, 1251, 1233, 1053, 1003, 837, 784, 694.

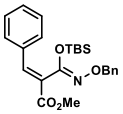
_tert_butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-3-methylbut-2-enimidate (1w)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12w** (821 mg, 4.0 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.8 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (721 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-(benzyloxy)-3-methylbut-2-enimidate **1w** as a colorless oil (340 mg, 27%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.28 (m, 1H), 5.46 (p, *J* = 1.4 Hz, 1H), 4.99 (s, 2H), 1.90 (d, *J* = 1.4 Hz, 3H), 1.80 (d, *J* = 1.4 Hz, 3H), 0.90 (s, 9H), 0.11 (s, 6H).

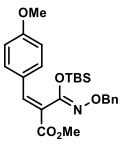
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 143.6, 137.8, 129.0, 128.3, 127.9, 117.1, 75.9, 26.8, 25.8, 20.6, 18.7, -3.9.
HRMS: Calculated $[M+H]^+$ for $C_{18}H_{30}NO_2Si^+$: 320.2040, found: 320.2040.
FTIR (cm^{-1}): 3032, 2954, 2930, 2858, 1655, 1598, 1454, 1362, 1352, 1272, 1250, 1076, 1045, 996, 825, 784, 696.

methyl (*E*)-3-phenyl-2-((*Z*)-6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)acrylate (1x)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12x** (623 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (362 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford methyl (*E*)-3-phenyl-2-((*Z*)-6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)acrylate **1x** as a light yellow oil (351.5 mg, 41%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.51 – 7.49 (m, 2H), 7.35 – 7.28 (m, 8H), 4.99 (s, 2H), 3.81 (s, 3H), 0.82 (s, 9H), 0.15 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 147.8, 144.8, 137.8, 133.5, 130.5, 130.4, 128.7, 128.6, 128.4, 127.9, 124.4, 75.9, 52.4, 25.6, 18.6, -3.7.
HRMS: Calculated $[M+H]^+$ for $C_{24}H_{32}NO_4Si^+$: 426.2095, found: 426.2096.
FTIR (cm^{-1}): 3064, 3031, 2952, 2929, 2857, 1719, 1619, 1435, 2145, 1199, 1082, 1069, 837, 786, 690.

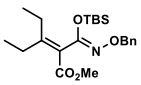
methyl (*E*)-3-(4-methoxyphenyl)-2-((*Z*)-6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)acrylate (1y)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12y** (682.7 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (362 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford methyl (*E*)-3-(4-methoxyphenyl)-2-((*Z*)-6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)acrylate **1y** as a light yellow oil (533.5 mg, 59%).

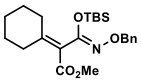
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 6.77 (d, *J* = 8.9 Hz, 2H), 5.01 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 0.83 (s, 9H), 0.16 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 161.5, 148.1, 144.6, 138.0, 132.6, 128.8, 128.4, 127.9, 126.1, 121.6, 114.1, 75.9, 55.5, 52.2, 25.6, 18.6, -3.8.
HRMS: Calculated $[M+H]^+$ for $C_{25}H_{34}NO_5Si^+$: 456.2201, found: 456.2204.
FTIR (cm^{-1}): 2952, 2930, 2857, 1715, 1602, 1512, 1434, 1241, 1201, 1172, 1073, 1032, 824, 785, 697.

methyl (*Z*)-3-ethyl-2-(6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)pent-2-enoate (1z)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12z** (582.7 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (362 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford methyl (*Z*)-3-ethyl-2-(6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)pent-2-enoate **1z** as a colorless oil (191.2 mg, 24%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 5.01 (s, 2H), 3.69 (s, 3H), 2.49 (q, *J* = 7.5 Hz, 2H), 2.14 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.85 (s, 9H), 0.15 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 166.0, 150.0, 138.1, 128.7, 128.3, 127.8, 121.8, 75.7, 51.5, 28.4, 25.9, 25.6, 18.6, 13.0, -3.8.
HRMS: Calculated $[M+H]^+$ for $C_{22}H_{36}NO_4Si^+$: 406.2408, found: 406.2408.
FTIR (cm^{-1}): 3036, 2956, 2931, 2859, 1724, 1619, 1456, 1250, 1228, 1069, 841, 786, 697.

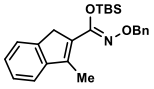
methyl (*Z*)-3-((benzyloxy(imino)-3-((tert-butyldimethylsilyl)oxy)-2-cyclohexylidenepropanoate (1aa)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12aa** (602 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (362 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford methyl (*Z*)-3-((benzyloxy(imino)-3-((tert-butyldimethylsilyl)oxy)-2-cyclohexylidenepropanoate **1aa** as a colorless oil (785 mg, 95%).

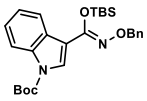
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 5.01 (s, 2H), 3.70 (s, 3H), 2.68 – 2.66 (m, 2H), 2.22 (t, *J* = 5.8 Hz, 2H), 1.64 (dd, *J* = 7.8, 4.1 Hz, 2H), 1.55 (m, 4H), 0.85 (s, 9H), 0.13 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 162.1, 150.0, 138.0, 128.9, 128.3, 127.9, 120.0, 75.8, 51.6, 34.1, 32.0, 28.6, 28.3, 26.3, 25.6, 18.6, -3.9.
HRMS: Calculated $[M+H]^+$ for $C_{23}H_{36}NO_4Si^+$: 406.2408, found: 418.2414.
FTIR (cm^{-1}): 3032, 2929, 2857, 1722, 1618, 1325, 1242, 1203, 1061, 1012, 843, 823, 811, 785, 696.

*tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-3-methyl-1*H*-indene-1-carbimidate (1ab)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ab** (559 mg, 2.0 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (362 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-3-methyl-1*H*-indene-1-carbimidate **1ab** as a pale-brown solid (554.4 mg, 70%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 3H), 7.38 – 7.36 (m, 3H), 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 5.05 (s, 2H), 3.58 (d, *J* = 2.3 Hz, 2H), 2.34 (s, 3H), 0.93 (s, 9H), 0.16 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2, 146.6, 142.6, 141.0, 137.5, 131.9, 129.4, 128.4, 128.1, 126.5, 125.8, 123.6, 119.9, 76.2, 39.5, 26.0, 19.0, 12.8, -3.3.
HRMS: Calculated $[M+H]^+$ for $C_{24}H_{32}NO_2Si^+$: 394.2197, found: 394.2209.
FTIR (cm^{-1}): 3066, 2952, 2927, 2880, 2855, 1567, 1469, 1459, 1384, 1366, 1272, 1249, 1192, 1121, 1029, 984, 963, 786, 759, 767, 699.

*tert*butyl (*Z*)-3-(6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)-1*H*-indole-1-carboxylate (1ac)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ac** (500 mg, 1.4 mmol, 1.0 equiv.) was dissolved in dry THF (7 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (1.8 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (267 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to

afford *tert*butyl (*Z*)-3-(6,6,7,7-tetramethyl-1-phenyl-2,5-dioxa-3-aza-6-silaoct-3-en-4-yl)-1*H*-indole-1-carboxylate **1ac** as a pale-brown solid (460 mg, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 1H), 8.14 (d, *J* = 7.1 Hz, 1H), 7.92 (s, 1H), 7.49 – 7.48 (m, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.26 (m, 1H), 5.14 (s, 2H), 1.66 (s, 9H), 0.99 (s, 9H), 0.18 (s, 6H).

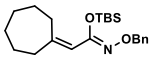
^{13}C NMR (150 MHz, $CDCl_3$) δ 148.5, 137.5, 129.3, 128.4, 128.2, 127.1, 127.0, 125.0, 123.5, 123.1, 115.0, 114.9, 84.1, 76.5, 28.3, 26.1, 19.0, -3.7.

HRMS: Calculated $[M+H]^+$ for $C_{27}H_{37}N_2O_4Si^+$: 481.2523, found: 481.2529.

Melting Point: 114.4 – 114.7 °C

FTIR (cm^{-1}): 3060, 3034, 2959, 2933, 2886, 2856, 1730, 1613, 1554, 1450, 1399, 1361, 1284, 1211, 1146, 1072, 1004, 965, 785, 762, 703, 676.

*tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cycloheptyldeneacetimidate (1ad)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ad** (1.6 g, 6.17 mmol, 1.0 equiv.) was dissolved in dry THF (31 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (7.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (1.11 g, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 30 mL of H_2O and extracted with 30 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cycloheptyldeneacetimidate **1ad** as a colorless oil (527 mg, 23%).

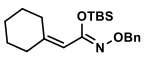
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 5.43 (p, *J* = 1.3 Hz, 1H), 4.98 (s, 2H), 2.56 – 2.54 (m, 2H), 2.30 – 2.27 (m, 2H), 1.61 –1.55 (m, 4H), 1.52 – 1.47 (m, 4H), 0.90 (s, 9H), 0.10 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 151.4, 138.0, 129.1, 128.3, 127.9, 116.9, 75.9, 38.6, 32.5, 29.8, 29.6, 28.7, 27.0, 25.8, 18.7, -3.9.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{36}NO_2Si^+$: 374.2510, found: 374.2515.

FTIR (cm^{-1}): 3032, 2927, 2856, 1641, 1594, 1472, 1456, 1251, 1056, 1005, 837, 824, 785, 969.

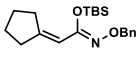
*tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cyclohexyldeneacetimidate (1ae)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ae** (400 mg, 1.6 mmol, 1.0 equiv.) was dissolved in dry THF (16 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (1.9 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (288 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc

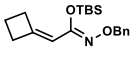
three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cyclohexyldeneacetimidate **1ae** as a colorless oil (260 mg, 45%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.38 (m, 2H), 7.35 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 5.41 (p, *J* = 1.3 Hz, 1H), 4.98 (s, 2H), 2.47 – 2.45 (m, 2H), 2.14 – 2.12 (m, 2H), 1.60 – 1.49 (m, 6H), 0.89 (s, 9H), 0.10 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 151.1, 137.8, 129.1, 128.3, 127.9, 113.9, 75.9, 37.6, 30.5, 28.5, 27.7, 26.5, 25.8, 18.7, -3.9.
HRMS: Calculated $[M+H]^+$ for $C_{21}H_{34}NO_2Si^+$: 360.2353, found: 360.2357.
FTIR (cm^{-1}): 3065, 3032, 2928, 2856, 1653, 1602, 1448, 1362, 1281, 1249, 1226, 1050, 1002, 823, 783, 695.

*tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cyclopentyldeneacetimidate (1af)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12f** (925 mg, 4.0 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.8 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (781 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cyclopentyldeneacetimidate **1af** as a colorless oil (912 mg, 66%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.28 (m, 1H), 5.58 (p, *J* = 2.4 Hz, 1H), 4.97 (s, 2H), 2.49 (tdt, *J* = 7.2, 2.8, 1.5 Hz, 2H), 2.35 (tdq, *J* = 7.1, 1.6 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.62 – 1.58 (m, 2H), 0.90 (s, 9H), 0.11 (s, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 155.4, 152.3, 137.9, 129.1, 128.3, 127.9, 112.7, 75.9, 35.5, 32.6, 26.8, 26.1, 25.9, 18.8, -3.7.
HRMS: Calculated $[M+H]^+$ for $C_{20}H_{32}NO_2Si^+$: 346.2197, found: 346.2200.
FTIR (cm^{-1}): 3032, 2954, 2930, 2858, 1656, 1583, 1454, 1362, 1304, 1251, 1054, 998, 835, 784, 695.

*tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cyclobutyldeneacetimidate (1ag)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ag** (700 mg, 3.22 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.2 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (631 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction

crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-cyclobutyldeneacetimidate **1ag** as a colorless oil (370 mg, 35%).

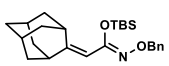
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27 (s, 1H), 5.43 (p, *J* = 2.4 Hz, 1H), 4.94 (s, 2H), 2.92 (tp, *J* = 8.1, 1.4, 1.3 Hz, 2H), 2.74 (ddt, *J* = 8.2, 7.4, 2.4 Hz, 2H), 1.99 (h, *J* = 7.7 Hz, 2H), 0.98 (s, 9H), 0.10 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.9, 152.1, 137.6, 129.1, 128.3, 127.9, 113.1, 75.9, 33.5, 32.3, 25.9, 18.9, 17.9, -3.4.

HRMS: Calculated $[M+H]^+$ for $C_{19}H_{30}NO_2Si^+$: 332.2040, found: 332.2096.

FTIR (cm^{-1}): 3032, 2953, 2929, 2857, 1679, 1584, 1471, 1351, 1252, 1052, 1000, 836, 823, 810, 784, 695.

*tert*butyl dimethylsilyl (*Z*)-2-((1r,3r,5R,7S)-adamant-2-ylidene)-*N*-(benzyloxy)acetimidate (1ah)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ahg** (892 mg, 3.0 mmol, 1.0 equiv.) was dissolved in dry THF (15 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.0 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (586 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-2-((1r,3r,5R,7S)-adamant-2-ylidene)-*N*-(benzyloxy)acetimidate **1ah** as a white solid (567 mg, 46%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.38 (m, 2H), 7.34 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 5.37 (s, 1H), 4.95 (s, 2H), 3.40 (br, 1H), 2.37 (br, 1H), 1.93 – 1.77 (m, 12H), 0.89 (s, 9H), 0.10 (s, 6H).

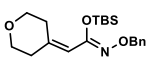
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.0, 151.6, 137.9, 129.2, 128.3, 127.9, 109.2, 75.9, 41.0, 39.9, 39.1, 37.2, 33.2, 28.3, 25.8, 18.8, -3.7.

Melting Point: 53.4 – 87.8 °C

HRMS: Calculated $[M+H]^+$ for $C_{25}H_{38}NO_2Si^+$: 412.2666, found: 412.2667.

FTIR (cm^{-1}): 3032, 2953, 2922, 2901, 2849, 1651, 1593, 1366, 1262, 1243, 1211, 1054, 989, 959, 813, 783, 695.

*tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-(tetrahydro-4*H*-pyran-4-ylidene)acetimidate (1ai)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ai** (742 mg, 3.0 mmol, 1.0 equiv.) was dissolved in dry THF (15 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (4.0 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (586 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc

three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-2-(tetrahydro-4H-pyran-4-ylidene)acetimidate **1ai** as a white solid (512 mg, 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.37 (m, 2H), 7.35 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 5.50 (p, *J* = 1.3 Hz, 1H), 4.97 (s, 2H), 3.72 (t, *J* = 5.5 Hz, 2H), 3.63 (t, *J* = 5.5 Hz, 2H), 2.64 (ddd, *J* = 6.2, 5.0, 1.3 Hz, 2H), 2.26 (ddd, *J* = 6.2, 5.0, 1.3 Hz, 2H), 0.90 (s, 9H), 0.11 (s, 6H).

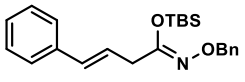
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.0, 145.1, 137.6, 129.1, 128.4, 128.0, 115.7, 76.0, 69.3, 68.6, 37.4, 31.7, 25.8, 18.7, -3.8.

Melting Point: 44.3 – 46.3 °C

HRMS: Calculated $[M+H]^+$ for $C_{20}H_{32}NO_3Si^+$: 362.2146, found: 362.2148.

FTIR (cm^{-1}): 3032, 2955, 2930, 2856, 1658, 1601, 1386, 1362, 1273, 1251, 1099, 1051, 1003, 835, 810, 784, 696.

tertbutyl dimethylsilyl (1*Z*,3*E*)-*N*-(benzyloxy)-4-phenylbut-3-enimidate (1aj)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12aj** (1.01 g, 3.78 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (7.6 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (1.134 g, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-4-phenylbut-3-enimidate **1aj** as a pale yellow oil (1.158 g, 80%).

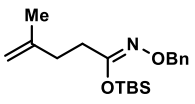
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 10H), 6.49 (dd, *J* = 15.8, 1.6 Hz, 1H), 6.22 (dt, *J* = 15.9, 7.0 Hz, 1H), 4.95 (s, 2H), 3.05 (dd, *J* = 7.0, 1.5 Hz, 2H), 0.88 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.3, 137.3, 133.0, 129.4, 128.9, 128.5, 128.3, 127.3, 126.4, 126.2, 124.1, 75.7, 36.7, 25.7, 18.6, -3.9.

HRMS: Calculated $[M+H]^+$ for $C_{23}H_{32}NO_2Si^+$: 382.2197, found: 382.2203.

FTIR (cm^{-1}): 3030, 2929, 2857, 1635, 1362, 1252, 1055, 966, 787, 696.

tertbutyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-4-methylpent-4-enimidate (1ak)



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12ak** (948 mg, 4.33 mmol, 1.0 equiv.) was dissolved in dry THF (22 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (5.2 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (780 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full

conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-4-methylpent-4-enimidate **1ak** as a colorless oil (984 mg, 68%).

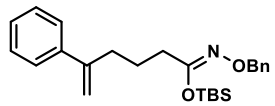
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 7.35 – 7.32 (m, 2H), 7.31 – 7.28 m (1H), 4.92 (s, 2H), 4.72 (m, 1H), 4.70 (m, 1H), 2.26 (s, 4H), 1.72 (t, *J* = 1.72 Hz, 3H), 0.89 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.6, 144.7, 137.6, 128.9, 128.4, 128.0, 110.6, 75.6, 34.2, 31.6, 25.8, 22.5, 18.7, -3.8.

HRMS: Calculated $[M+H]^+$ for $C_{19}H_{32}NO_2Si^+$: 334.2197, found: 334.2203.

FTIR (cm^{-1}): 3068, 3033, 2955, 2930, 2858, 1635, 1472, 1362, 1251, 1052, 1003, 889, 822, 811, 696.

tertbutyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-5-phenylhex-5-enimidate (1al)



In a flame-dried round-bottom flask under Argon atmosphere, methyltriphenylphosphonium bromide (186 mg, 1.2 equiv.) was suspended in dry Et_2O (2.2 mL, 0.2 M). The reaction mixture was then cooled down to 0 °C using an ice-water cooling bath under vigorous stirring. Then *n*-BuLi (0.19 mL, 1.1 equiv., 2.5 M solution in hexanes) was added dropwise with vigorous stirring. The reaction turned bright yellow and was allowed to stir for 5 min. Then compound **1al'** was added slowly and the reaction was allowed to warm to room temperature and stirred overnight. The bright yellow color disappeared, and a white precipitate was formed. After the 16h, the reaction mixture was allowed to cool down to room temperature. The solids were filtered and washed thrice with Et_2O (10 mL). The filtrate was then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (97/03 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-5-phenylhex-5-enimidate **1al** as colorless oil (50 mg, 28%).

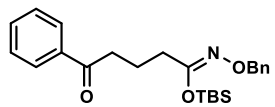
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 4H), 7.34 – 7.28 (m, 5H), 7.25 – 7.24 (m, 1H),
7.38 (s, 5H), 5.02 (d, *J* = 10.9 Hz, 1H), 4.98 (d, *J* = 10.9 Hz, 1H), 4.36 (s, 1H), 3.92 – 3.89 (m, 1H), 3.81 (dddd, *J* = 12.0, 4.8, 3.8, 1.1 Hz, 1H), 3.53 (ddd, *J* = 12.0, 10.5, 3.0 Hz, 1H), 3.44 (ddd, *J* = 12.0, 10.8, 2.8 Hz, 1H), 2.08 (ddd, *J* = 13.7, 10.8, 4.5 Hz, 1H), 1.74 (dtd, *J* = 13.9, 3.2, 3.1, 2.2 Hz, 1H), 1.67 (ddd, *J* = 13.8, 10.5, 4.7 Hz, 1H), 1.52 (ddt, *J* = 13.7, 3.7, 2.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.6, 147.9, 141.1, 137.6, 129.4, 128.9, 128.5, 128.4, 128.4, 128.0, 127.5, 126.3, 112.8, 75.6, 34.7, 32.4, 25.8, 24.7, 18.6, -3.9.

HRMS: Calculated $[M+H]^+$ for $C_{25}H_{36}NO_2Si^+$: 410.2510, found: 410.2515.

FTIR (cm^{-1}): 3024, 2930, 2858, 1635, 1495, 1456, 1364, 1216, 1055, 837, 779, 698.

tertbutyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-5-oxo-5-phenylpentanimidate (1al')



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12al** (569 mg, 1.91 mmol, 1.0 equiv.) was dissolved in dry THF (10 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (2.1 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (316 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left

stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 10 mL of H_2O and extracted with 10 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-5-oxo-5-pehnylpentanimidate **1al'** as a colorless oil (178 mg, 23%).

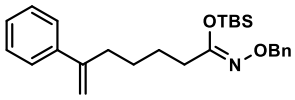
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.57 – 7.54 (m, 1H), 7.46 – 7.43 (m, 2H), 7.37 – 7.36 (m, 2H), 7.33 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 4.92 (s, 2H), 2.97 (dd, *J* = 7.8, 7.0 Hz, 2H), 2.24 (t, *J* = 7.1 Hz, 2H), 2.01 (p, *J* – 7.2 Hz, 2H), 0.89 (s, 9H), 0.10 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 199.9, 154.2, 137.7, 137.1, 133.1, 128.9, 128.7, 128.4, 128.2, 128.0, 75.6, 37.6, 32.8, 25.8, 20.5, 18.7, -3.9.

HRMS: Calculated $[M+H]^+$ for $C_{24}H_{34}NO_3^+$: 412.2302, found: 412.2310.

FTIR (cm^{-1}): 3064, 3031, 2954, 2930, 2858, 1738, 1634, 1449, 1363, 1251, 1228, 1054, 824, 786.

tertbutyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-6-phenylhept-6-enimidate (1am)



In a flame-dried round-bottom flask under Argon atmosphere, methyltriphenylphosphonium bromide (397 mg, 1.2 equiv.) was suspended in dry Et_2O (4.6 mL, 0.2 M). The reaction mixture was then cooled down to 0 °C using an ice-water cooling bath under vigorous stirring. Then *n*-BuLi (0.41 mL, 1.1 equiv., 2.5 M solution in hexanes) was added dropwise with vigorous stirring. The reaction turned bright yellow and was allowed to stir for 5 min. Then compound **1am'** was added slowly and the reaction was allowed to warm to room temperature and stirred overnight. The bright yellow color disappeared, and a white precipitate was formed. After the 16h, the reaction mixture was allowed to cool down to room temperature. The solids were filtered and washed thrice with Et_2O (10 mL). The filtrate was then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (97/03 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-6-phenylhept-6-enimidate **1am** as colorless oil (124 mg, 32%).

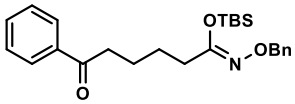
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.37 – 7.27 (m, 7H), 7.26 – 7.24 (m, 1H), 5.26 (d, *J* = 1.5 Hz, 1H), 5.05 (q, *J* = 1.4 Hz, 1H), 4.91 (s, 2H), 2.51 (dt, *J* = 7.5, 1.3 Hz, 2H), 2.13 – 2.10 (m, 2H), 1.59 (dtd, *J* = 8.7, 7.5, 6.2 Hz, 2H), 1.50 – 1.45 (m, 2H), 0.88 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 148.4, 141.4, 137.5, 129.0, 128.4, 128.4, 128.0, 127.4, 126.3, 112.5, 75.6, 35.1, 32.7, 27.7, 25.8, 18.7, -3.9.

HRMS: Calculated $[M+H]^+$ for $C_{26}H_{32}NO_2Si^+$: 424.2666, found: 424.2672.

FTIR (cm^{-1}): 3028, 2970, 2930, 2858, 1634, 1455, 1206, 1055, 786, 698.

tertbutyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-6-oxo-6-phenylhexanimidate (1am')



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12am** (955 mg, 3.07 mmol, 1.0 equiv.) was dissolved in dry THF (16 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (3.4 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (506 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned

with 20 mL of H_2O and extracted with 20 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford *tert*butyl dimethylsilyl (*Z*)-*N*-(benzyloxy)-6-oxo-6-phenylhexanimidate **1am'** as a colorless oil (394 mg, 30%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.94 (m, 2H), 7.57 – 7.54 (m, 1H), 7.47 – 7.44 (m, 2H), 7.37 – 7.35 (m, 2H), 7.34 – 7.31 (m, 2H), 7.29 – 7.27 (m, 1H), 4.91 (s, 2H), 2.98 – 2.95 (m, 2H), 2.19 – 2.16 (m, 2H), 1.79 – 1.74 (m, 2H), 1.69 – 1.64 (m, 2H), 0.92 (s, 9H), 0.10 (s 6H).

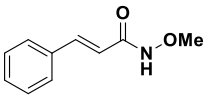
^{13}C NMR (150 MHz, $CDCl_3$) δ 200.2, 154.6, 137.5, 137.1, 133.1, 129.0, 128.7, 128.4, 128.2, 128.0, 75.6, 38.3, 32.7, 25.8, 23.7, 18.7, 18.1, -3.9.

HRMS: Calculated $[M+H]^+$ for $C_{25}H_{36}NO_3Si^+$: 426.2459, found: 426.2463.

FTIR (cm^{-1}): 3064, 3032, 2953, 2930, 2858, 1728, 1634, 1450, 1362, 1276, 1252, 1055, 1002, 787.

12. Synthesis and characterization of hydroxamate esters (12):

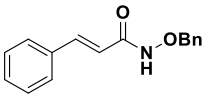
N-methoxycinnamamide (12a)



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $MeONH_2{\cdot}HCl$ (958 mg, 11.47 mml, 2.0 equiv.) was suspended in dry Toluene (29 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (5.7 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, methyl cinnamate (930 mg, 5.74 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80:20 hexanes:EtOAc) to afford *N*-methoxycinnamamide **12a** as a white crystalline solid. The NMR data matches the one reported in the literature.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (br, 1H), 7.76 (d, *J* = 15.8 Hz, 1H), 7.53 (m, 2H), 7.37 (m, 3H), 6.42 (brs, 1H), 3.84 (s, 3H).

N-methoxycinnamamide (12b)



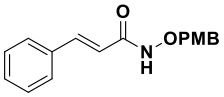
Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (1.0 equiv.) was suspended in THF:DCM (226 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (26 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 60 min at 0 °C. HOBt hydrate (10.36 g, 1.0 equiv.) and cinnamic acid (10 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 60 min at 0 °C. Finally, NEt_3 (26 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir for 48 h. The reaction was then filtered, and the obtained

[5] K. Inamoto, J. Kawasaki, K. Hiroya, Y. Kondo, T. Doi. *Chem. Commun.* **2012**, *48,* 4332−4334.

filtrate was diluted with 100 mL of EtOAc and then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-benzyloxycinnamide **12b** as a white powder (12.55 g, 73%). The NMR data matches the one reported in the literature.[6]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (br, 1H), 7.74 (d, *J* = 15.5 Hz, 1H), 7.50 – 7.49 (m, 2H), 7.44 – 7.36 (m, 8H), 4.97 (s, 2H).

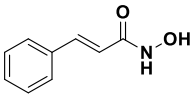
N-((4-methoxybenzyl)oxy)cinnamamide (12c)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, *O*-(4-methoxybenzyl)hydroxylamine (3.1g, 1.0 equiv.) was suspended in THF:DCM (100 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (4.2 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (3.1 g, 1.0 equiv.) and cinnamic acid (3.0 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (4.2 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and then washed once with 25 mL HCl (3 M), followed by one wash with 25 mL conc. $NaHCO_3$ and finally with 25 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-((4-methoxybenzyl)oxy)cinnamamide **12c** as a white powder (4.6 g, 80%). The NMR data matches the one reported in the literature.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (br, 1H), 7.75 – 7.71 (d, *J* = 15.7 Hz, 1H), 7.50 – 7.49 (m, 2H), 7.38 – 7.35 (m, 5H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.27 (bs, 1H), 4.91 (s, 2H), 3.80 (s, 3H).

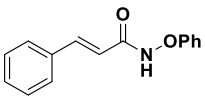
N-hydroxycinamamide (12d)



Following a known literature procedure[8] *N*-hydroxycinnamamide **12d** was prepared as a pale pink powder. The NMR data matches the one reported in the literature.[9]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (bs, 1H), 7.48 (bs, 2H), 7.35 (bs, 3H), 6.37 (bs, 1H).

N-phenoxycinnamamide (12e)



In an oven-dried round-bottom flask under Argon atmosphere, *O*-phenylhydroxylamine hydrochloride (1.95 g, 1.0 equiv.) was suspended in DCM (66,

[6] Gissot, A., Volonterio, A., Zanda, M. *J. Org. Chem.* **2005**, *70*(17), 6925−6928.
[7] Zhang, N., Yang, R., Zhang-Negrerie, D., Du, Y., Zhao, K. *J. Org. Chem.* **2012**, *78*(17), 8705−8711.
[8] Usachova, N., Leitis, G., Jirgensons, A., Kalvinsh, I. *Synthn. Commun.* **2010**, *40*, 927–935.
[9] Porcheddu, A., Giacomelli, G. *J. Org. Chem.* **2006**, *71*(18), 7057–7059.

0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. EDCI·HCl (3.8 g, 1.5 equiv.) and DMAP (1.93 g, 1.2 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, cinnamic acid (1.95 g, 13.17 mmol) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then washed once with 50 mL H_2O and extracted with DCM 3 x 70 mL. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (60/40 hexanes:EtOAc) to afford *N*-phenoxycinnamamide **12e** as a white powder (1.1 g, 35%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 12.03 (bs, 1H), 7.65 – 7.64 (m, 2H), 7.60 (d, *J* = 16.0 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.36 – 7.33 (m, 2H), 7.06 – 7.03 (m, 3H), 6.62 (d, *J* = 16.0 Hz, 1H).

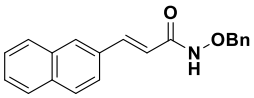
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 140.8, 134.4, 130.0, 129.5, 129.0, 127.9, 122.4, 117.6, 112.9.

HRMS: Calculated $[M+H]^+$ for $C_{15}H_{14}NO_2^+$: 240.1019, found: 240.1025.

Melting Point: 149.9 – 151.8 °C

FTIR (cm^{-1}): 3118, 3055, 2925, 2857, 1667, 1625, 1589, 1487, 1343, 1118, 1044, 979, 750.

(*E*)-*N*-(benzyloxy)-3-(naphthalen-2-yl)acrylamide (12f)



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2$·HCl (1.81 g, 11.32 mml, 2.0 equiv.) was suspended in dry Toluene (28 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (5.7 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13f** (1.2 g, 5.66 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80:20 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-3-(naphthalene-2-yl)acrylamide **12f** as a white crystalline solid (601 mg, 54%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.32 (s, 1H), 8.10 (s, 1H), 7.96 – 7.92 (m, 3H), 7.72 – 7.71 (m, 1H), 7.67 (d, *J* = 15.8 Hz, 1H), 7.56 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.45 – 7.35 (m, 5H), 6.58 (d, *J* = 15.8 Hz, 1H), 4.90 (s, 2H).

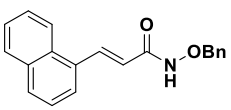
^{13}C NMR (150 MHz, DMSO-d_6) δ 163.0, 139.6, 136.0, 133.5, 133.0, 132.2, 129.0, 128.8, 128.6, 128.4, 128.3, 127.7, 127.0, 126.7, 123.5, 119.0, 77.0.

HRMS: Calculated $[M+H]^+$ for $C_{20}H_{18}NO_2^+$: 304.1332, found: 304.1342.

Melting Point: 140.6 – 141.2 °C

FTIR (cm^{-1}): 3193, 3058, 3035, 2994, 1648, 1622, 1509, 1497, 1050, 976, 962, 739, 694.

(*E*)-*N*-(benzyloxy)-3-(naphthalen-2-yl)acrylamide (12g)



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2$·HCl (1.81 g, 11.32 mml, 2.0 equiv.) was suspended in dry Toluene (28 mL, 0.2 M). The

reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (5.7 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13g** (1.2 g, 5.66 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80:20 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-3-(naphthalene-2-yl)acrylamide **14g** as a white crystalline solid (453 mg, 26%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.41 (s, 1H), 8.28 (d, *J* = 15.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.60 – 7.55 (m, 2H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 4.92 (s, 2H).

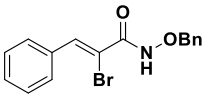
^{13}C NMR (150 MHz, DMSO-d_6) δ 162.8, 136.0, 133.3, 131.7, 130.7, 129.8, 128.8, 128.7, 128.4, 128.3, 127.0, 126.3, 125.7, 124.6, 123.1, 121.6, 77.1.

HRMS: Calculated $[M+H]^+$ for $C_{20}H_{18}NO_2^+$: 304.1332, found: 304.1332.

Melting Point: 157.8 – 160.0 °C

FTIR (cm^{-1}): 3230, 3059, 2990, 1656, 1618, 1506, 1348, 1051, 967, 790, 774, 750.

(*Z*)-*N*-(benzyloxy)-2-bromo-3-pehnylacrylamide (12j)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (1.27 g, 1.0 equiv.) was suspended in THF:DCM (40 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (1.7 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 630 min at 0 °C. HOBt hydrate (1.22 g, 1.0 equiv.) and compound **15j** (1.8 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (1.7 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford (*Z*)-*N*-(benzyloxy)-2-bromo-3-phenylacrylamide **12j** as a yellow powder (1.6 g, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.32 (s, 1H), 7.75 – 7.74 (m, 2H), 7.46 – 7.43 (m, 2H), 7.42 – 7.39 (m, 6H), 5.02 (s, 2H).

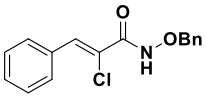
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.5, 138.7, 134.9, 133.7, 130.2, 130.1, 129.6, 129.2, 128.9, 128.6, 110.8, 78.7.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{15}BrNO_2^+$: 332.0281, found: 332.0283.

Melting Point: 55.1 – 56.1 °C

FTIR (cm^{-1}): 3228, 3057, 3033, 2954, 1654, 1610, 1481, 1445, 1268, 1082, 1064, 738, 688.

(*Z*)-*N*-(benzyloxy)-2-chloro-3-pehnylacrylamide (12k)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (1.05 g, 1.0 equiv.) was suspended in THF:DCM (32 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.5 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 630 min at 0 °C. HOBt hydrate (1.0 g, 1.0 equiv.) and compound **13k** (1.2 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.5 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford (*Z*)-*N*-(benzyloxy)-2-chloro-3-phenylacrylamide **12k** as a white powder (728 mg, 38%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.09 (bs, 1H), 8.02 (s, 1H), 7.77 – 7.75 (m, 2H), 7.46 – 7.39 (m, 8H), 5.02 (s, 2H).

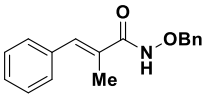
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.6, 135.0, 134.9, 132.9, 130.7, 130.2, 129.6, 129.2, 128.9, 128.7, 120.4, 78.7.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{15}ClNO_2^+$: 288.0786, found: 288.0787.

Melting Point: 89.8 – 91.6 °C

FTIR (cm^{-1}): 3239, 3092, 3036, 2883, 1656, 1614, 1482, 1444, 1272, 1262, 1085, 1067, 739, 690.

(*E*)-*N*-(benzyloxy)-2-methyl-3-pehnylacrylamide (12l)



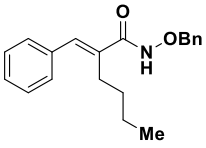
Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (1.5 g, 1.0 equiv.) was suspended in THF:DCM (46 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.0 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (1.42 g, 1.0 equiv.) and compound **13l** (1.5 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.0 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-2-methyl-3-phenylacrylamide **12l** as a white powder (1.0 g, 40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (bs, 1H), 7.45 – 7.43 (m, 2H), 7.40 – 7.35 (m, 5H), 7.30 – 7.28 (m, 3H), 7.17 (s, 1H), 5.00 (s, 2H), 2.04 (d, *J* = 1.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 135.6, 135.5, 134.6, 129.9, 129.4, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 78.3, 14.2.

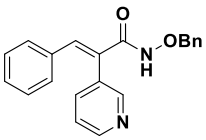
HRMS: Calculated $[M+H]^+$ for $C_{17}H_{18}NO_2^+$: 268.1332, found: 268.1346.
Melting Point: 89.8 – 93.0 °C
FTIR (cm^{-1}): 3221, 3059, 2930, 1652, 1618, 1498, 1448, 1278, 1004, 910, 694.

(*E*)-2-benzylidene-*N*-(benzyloxy)hexanamide (12m)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (860 mg, 1.0 equiv.) was suspended in THF:DCM (28 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.1 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (827 mg, 1.0 equiv.) and compound **13m** (1.1 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.1 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 40 mL of EtOAc and then washed once with 40 mL HCl (3 M), followed by one wash with 40 mL conc. $NaHCO_3$ and finally with 40 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford (*E*)-2-benzylidene-*N*-(benzyloxy)hexanamide **12l** as a colorless oil (1.01 g, 61%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.46 – 7.44 (m, 2H), 7.41 – 7.34 (m, 5H), 7.30 – 7.27 (m, 1H), 7.24 – 7.23 (m, 2H), 6.93 (s, 1H), 5.01 (s, 2H), 2.49 – 2.47 (m, 2H), 1.43 (ddt, *J* = 12.1, 8.0, 3.9 Hz, 2H), 1.32 (h, 7.3 Hz, 2H), 0.87 (t, *J* = 7.3 Hz).
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 136.6, 135.6, 135.5, 133.1, 129.5, 129.0, 128.9, 128.7, 128.5, 128.1, 78.2, 30.9, 27.8, 22.8, 13.9.
HRMS: Calculated $[M+H]^+$ for $C_{20}H_{24}NO_2^+$: 310.1802, found: 310.1809.
FTIR (cm^{-1}): 3189, 3029, 2956, 2929, 2871, 1738, 1648, 1621, 1494, 1455, 1365, 1217, 910, 731, 694.

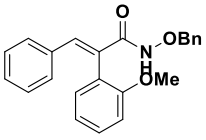
(*E*)-*N*-(benzyloxy)-3-phenyl-2-(pyridin-3-yl)acrylamide (12n)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (184.2 mg, 1.0 equiv.) was suspended in THF:DCM (12 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (0.24 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (176.8 mg, 1.0 equiv.) and compound **15n** (260 mg, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (0.24 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 10 mL of EtOAc and then washed once with 10 mL HCl (3 M), followed by one wash with 10 mL conc. $NaHCO_3$ and finally with 1 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-3-phenyl-2-(pyridine-3-yl)acylamide **12n** as a white powder (1.0 g, 40%).

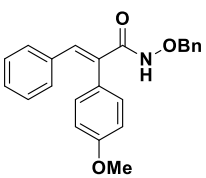
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (bs, 1H), 8.28 (bs, 1H), 8.16 (s, 1H), 7.86 (s, 1H), 7.47 – 7.45 (m, 1H), 7.37 – 7.33 (m, 5H), 7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 2H), 6.95 – 6.93 (m, 2H), 4.97 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0, 150.4, 149.7, 139.8, 137.6 135.1, 134.0, 131.2, 130.5, 129.6, 129.4, 129.1, 128.9, 128.8, 128.7, 128.6, 124.1, 78.3.
HRMS: Calculated $[M+H]^+$ for $C_{21}H_{19}N_2O_2^+$: 331.1441, found: 331.1449.
Melting Point: 153.8 – 155.8 °C
FTIR (cm^{-1}): 3139, 3033, 2929, 1667, 1616, 1494, 1265, 1209, 1057, 1037, 905, 730.

(*E*)-*N*-(benzyloxy)-2-(2-methoxyphenyl)-3-phenylacrylamide (12o)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (1.57 mg, 1.0 equiv.) was suspended in THF:DCM (50 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.1 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (1.51 g, 1.0 equiv.) and compound **13o** (2.5 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.1 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-2-(2-methoxyphenyl)-3-phenylacrylamide **12o** as an off-white powder (2.57 g, 44%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.83 (s, 1H), 7.37 – 7.32 (m, 6H), 7.19 – 7.16 (m, 1H), 7.14 – 7.12 (m, 2H), 7.01 – 6.99 (m, 3H), 6.93 – 6.90 (m, 2H), 4.95 (m, 2H), 3.67 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 157.3, 138.3, 135.4, 135.1, 131.3, 130.6, 130.2, 129.4, 129.2, 128.8, 128.8, 128.7, 128.3, 123.8, 121.8, 111.6, 78.3, 55.7.
HRMS: Calculated $[M+H]^+$ for $C_{23}H_{22}NO_3^+$: 360.1594, found: 360.1599.
Melting Point: 104.8 – 107.0 °C
FTIR (cm^{-1}): 3193, 3065, 3022, 2960, 1644, 1597 1487, 1461, 1242, 1021, 762, 691.

(*E*)-*N*-(benzyloxy)-2-(4-methoxyphenyl)-3-phenylacrylamide (12p)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (942 mg, 1.0 equiv.) was suspended in THF:DCM (30 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.2 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (905 mg, 1.0 equiv.) and compound **13p** (1.5 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.2 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and

then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-2-(4-methoxyphenyl)-3-phenylacrylamide **12p** as an off-white powder (1.12 g, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.81 (s, 1H), 7.37 – 7.34 (m, 5H), 7.20 – 7.17 (m, 1H),7.16 – 7.13 (m, 2H), 7.04 – 7.01 (m, 4H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.96 (s, 2H), 3.83 (s, 3H).

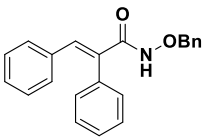
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 137.8, 135.2, 134.8, 131.6, 130.9, 130.6, 129.5, 128.9, 128., 128.4, 126.8, 115.1, 78.3, 55.4.

HRMS: Calculated $[M+H]^+$ for $C_{23}H_{22}NO_3^+$: 360.1594, found: 360.1608.

Melting Point: 104.6 – 106.4 °C

FTIR (cm^{-1}): 3180, 3029, 2996, 2967, 1655, 1616, 1489, 1450, 1239, 1173, 1050, 907, 830, 751, 692.

(*E*)-*N*-(benzyloxy)-2,3-diphenylacrylamide (12q)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (6.38 mg, 1.0 equiv.) was suspended in THF:DCM (200 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (8.4 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (6.12 g, 1.0 equiv.) and compound **13q** (8.96 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (8.4 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 100 mL of EtOAc and then washed once with 100 mL HCl (3 M), followed by one wash with 100 mL conc. $NaHCO_3$ and finally with 100 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-2,3-diphenylacrylamide **12q** as a white powder (4.64 g, 36%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.79 (s, 1H), 7.37 – 7.33 (m, 7H), 7.20 – 7.17 (m, 1H), 7.14 – 7.12 (m, 4H), 6.99 – 6.97 (s, 2H), 4.96 (s, 2H).

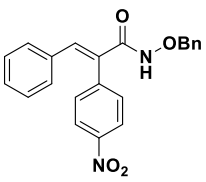
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 138.0, 135.1, 135.0, 134.6, 131.9, 130.6, 129.7, 129.7, 129.5, 129.0, 128.9, 128.8, 128.7, 128.4, 78.3.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{20}NO_2^+$: 330.1489, found: 330.1492.

Melting Point: 106.7 – 108.8 °C

FTIR (cm^{-1}): 3131, 3058, 3026, 2934, 1651, 1614, 1495, 146, 1370, 1282, 1083, 1064, 754, 689.

(*E*)-*N*-(benzyloxy)-2-(4-nitrophenyl)-3-phenylacrylamide (12r)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (543 mg, 1.0 equiv.) was suspended in THF:DCM (20 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (0.8 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for

30 min at 0 °C. HOBt hydrate (568 mg, 1.0 equiv.) and compound **13r** (1.0 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (0.8 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 20 mL of EtOAc and then washed once with 20 mL HCl (3 M), followed by one wash with 20 mL conc. $NaHCO_3$ and finally with 20 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-2-(4-nitrophenyl)-3-phenylacrylamide **12r** as a white powder (1.3 g, 94%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.81 (s, 1H), 7.69 (s, 1H), 7.37 (m, 5H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.18 – 7.16 (m, 2H), 6.95 – 6.94 (m, 2H), 4.97 (s, 2H).

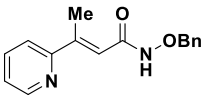
^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 148.0, 142.2, 139.5, 134.9, 137.7, 131.1, 130.5, 130.4, 129.7, 129.5, 129.2, 128.9, 128.7, 128.6, 128.5, 124.6, 78.4.

HRMS: Calculated $[M+H]^+$ for $C_{22}H_{19}N_2O_4^+$: 330.1489, found: 330.1492.

Melting Point: 126.2 – 130.6 °C

FTIR (cm^{-1}): 3244, 3070, 2932, 1664, 1618, 1593, 1514, 1446, 1340, 1047, 750, 693.

(*E*)-*N*-(benzyloxy)-3-(pyridin-2-yl)but-2-enamide (12s)



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (3.6 g, 22.57 mmol, 2.0 equiv.) was suspended in dry Toluene (56 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (11.3 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13s** (2.0 g, 11.3 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 60 mL H_2O and extracted three times with 60 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-3-(pyridin-2-yl)but-2-enamide **12s** as a white powder (1.17 g, 77%).

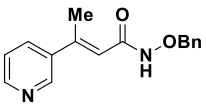
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.31 (s, 1H), 8.60 (d, *J* = 4.1 Hz, 1H), 7.85 (td, *J* = 7.7, 1.9 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.34 (m, 6H), 6.71 (s, 1H), 4.87 (s, 2H), 2.52 (s, 3H).

^{13}C NMR (150 MHz, DMSO-d_6) δ 164.0, 156.8, 149.0, 147.6, 137.2, 136.1, 128.8, 128.3, 128.2, 123.7, 120.6, 118.5, 76.9, 15.0.

HRMS: Calculated $[M+H]^+$ for $C_{15}H_{17}N_2O_2^+$: 269.1285, found: 269.1290.

Melting Point: 65.4 – 69.8 °C

(*E*)-*N*-(benzyloxy)-3-(pyridin-3-yl)but-2-enamide (12t)



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (1.92 g, 12.0 mml, 2.0 equiv.) was suspended in dry Toluene (30 mL, 0.2 M). The

reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (6 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13t** (1.06 g, 6.0 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-3-(pyridin-3-yl)but-2-enamide **12t** as a white powder (790 mg, 49%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.18 (s, 1H), 8.69 (d, *J* = 2.4 Hz, 1H), 8.56 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.88 (dt, *J* = 8.1, 2.1 Hz, 1H), 7.44 – 7.34 (m, 6H), 6.06 (s, 1H), 4.87 (s, 2H), 2.50 (s, 3H).

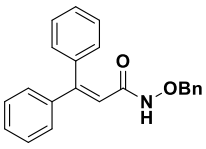
^{13}C NMR (150 MHz, DMSO-d_6) δ 163.7, 149.6, 146.9, 137.3, 136.1, 133.5, 128.8, 128.3, 128.3, 118.1, 77.0, 16.6.

HRMS: Calculated $[M+H]^+$ for $C_{15}H_{17}N_2O_2^+$: 269.1285, found: 269.1292.

Melting Point: 121.3 – 122.1 °C

FTIR (cm^{-1}): 3142, 2931, 2874, 1675, 1633, 1527, 1454, 1356, 1204, 1052, 943, 863, 752, 699.

(*E*)-*N*-(benzyloxy)-3,3-diphenylacrylamide (12u)

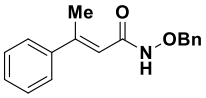


Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (6.38 g, 1.0 equiv.) was suspended in THF:DCM (200 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (8.4 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 60 min at 0 °C. HOBt hydrate (6.12 g, 1.0 equiv.) and β-phenyl cinnamic acid **13u** (8.96 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 60 min at 0 °C. Finally, NEt_3 (8.4 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir for 48 h. The reaction was then filtered, and the obtained filtrate was diluted with 100 mL of EtOAc and then washed once with 100 mL HCl (3 M), followed by one wash with 100 mL conc. $NaHCO_3$ and finally with 100 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-3,3-diphenylacrylamide **12u** as a white powder (4.64 g, 35%). The NMR data is in agreement with the one reported in the literature.[10]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.78 (bs, 1H), 7.36 – 7.34 (m, 8H), 7.20 – 7.17 (m, 1H), 7.14 – 7.12 (m, 4H), 6.99 – 6.97 (m, 2H), 4.96 (s, 2H).

[10] Ghosh, S., Chattopadyay. S. K. *Adv. Synth. Catal.* **2019**, *361*, 4727−4738.

(*E*)-*N*-(benzyloxy)-3-methyl-phenylacrylamide (12v)



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (1.81 g, 11.3 mml, 2.0 equiv.) was suspended in dry Toluene (30 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (5.7 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, methyl β-methyl cinnamate **13v** (1.0 g, 5.67 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford (*E*)-*N*-(benzyloxy)-3-methyl-3-phenylacrylamide **12v** as a white powder (1.11 g, 73%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.13 (s, 1H), 7.49 – 7.48 (m, 2H), 7.44 – 7.35 (m, 8H), 6.01 (s, 1H), 4.987 (s, 2H), 2.50 (s, 3H).

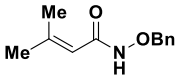
^{13}C NMR (150 MHz, DMSO-d_6) δ 164.1, 149.9, 141.9, 136.1, 128.8, 128.7, 128.6, 128.3, 128.2, 125.9, 116.7, 77.0, 16.9.

HRMS: Calculated $[M+H]^+$ for $C_{17}H_{18}NO_2^+$: 268.1338, found: 268.1340.

Melting Point: 68.7 – 71.0 °C

FTIR (cm^{-1}): 3086, 3062, 3035, 2955, 1639, 1610, 1510, 1493, 1384, 1274, 1058, 969, 745, 688.

***N*-(benzyloxy)-3-methyl-but-2-enamide (12w)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (4.6 g, 28.8 mmol, 2.0 equiv.) was suspended in dry Toluene (72 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (14.4 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13w** (1.84 g, 14.4 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 60 mL H_2O and extracted three times with 60 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-3-methyl-3-but-2-enamide **12w** as a white powder (1.115 g, 38%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.88 (s, 1H), 7.40 – 7.33 (m, 5H), 5.45 (s, 1H), 4.79 (s, 2H), 2.08 (s, 3H), 1.79 (s, 3H).

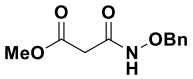
^{13}C NMR (150 MHz, DMSO-d_6) δ 164.2, 150.7, 136.2, 128.7, 128.3, 128.2, 115.1, 76.9, 26.9, 19.5

HRMS: Calculated $[M+H]^+$ for $C_{12}H_{16}NO_2^+$: 206.1176, found: 206.1185.

Melting Point: 71.8 – 73.2 °C

FTIR (cm^{-1}): 3194, 2974, 2938, 1637, 1496, 1453, 1360, 1250, 1026, 745, 696.

Methyl 3-((benzyloxy)amino)-3-oxopropanoate (12')



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (6.76 g, 1.0 equiv.) was suspended in THF:DCM (212 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (9.0 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (6.76 g, 1.0 equiv.) and compound **13'** (5 g, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (9.0 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 150 mL of EtOAc and then washed once with 100 mL HCl (3 M), followed by one wash with 100 mL conc. $NaHCO_3$ and finally with 100 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford methyl 3-((benzyloxy)amino)-3-oxopropanoate **12'** as a white powder (6.16 g, 65%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.24 (s, 1H), 7.40 – 7.35 (m, 5H), 4.80 (s, 2H), 3.63 (s, 3H), 3.14 (s, 2H).

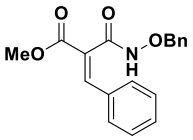
^{13}C NMR (150 MHz, DMSO-d_6) δ 167.8, 162.3, 135.8, 128.9, 128.3, 76.9, 52.0

HRMS: Calculated $[M+H]^+$ for $C_{11}H_{14}NO_4^+$: 224.0917, found: 224.0921.

Melting Point: 81.6 – 82.6 °C

FTIR (cm^{-1}): 3149, 2995, 2941, 2850, 1736, 1649, 1532, 1432, 1346, 1309, 1197, 1170, 1061, 1009, 950, 795, 725, 685.

Methyl (*E*)-(2-(benzyloxy)carbamoyl)-3-phenylacrylate (12x)



In a flame-dried round-bottom flask under Argon atmosphere, compound **12'** (2.0 g, 8.96 mmol) was dissolved in dry THF (30 mL, 0.3M). The reaction was cooled down to 0 °C using a water cooling bath. $TiCl_4$ neat (1.14 mL, 1.20 equiv.) was then added dropwise and was left stirring for 30 at the same temperature. Then, benzaldehyde (0.91 mL, 1.0 equiv.) was added, followed by *N*-methyl morpholine (2.96 mL, 3.0 equiv.). The reaction was allowed to slowly warm up to room temperature, and it was allowed to stirr overnight. After completion, the reaction was quenched with 30 mL H_2O and extracted three times with 40 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford methyl (*E*)-(2-(benzyloxy)carbamoyl)-3-phenylacrylate **12x** as a white powder (1.21 g, 43%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.58 (s, 1H), 7.70 (s, 1H), 7.63 – 7.61 (m, 2H), 7.46 – 7.42 (m, 3H), 7.37 – 7.35 (m, 5H), 4.85 (s, 2H), 3.76 (s, 3H).

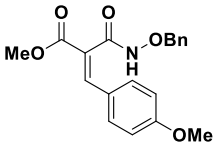
^{13}C NMR (150 MHz, DMSO-d_6) δ 164.8, 162.3, 142.2, 135.8, 132.7, 13.08, 129.9, 128.9, 128.9, 128.3, 128.3, 126.2, 79.2, 76.5, 52.4.

HRMS: Calculated $[M+H]^+$ for $C_{18}H_{18}NO_4^+$: 268.1338, found: 268.1340.

Melting Point: 99.5 – 100.7 °C

FTIR (cm^{-1}): 3218, 2950, 1732, 1651, 1626, 1496, 1449, 1433, 1263, 1199, 1027, 768, 752, 689.

Methyl (*E*)-(2-(benzyloxy)carbamoyl)-3-(4-methoxyphenyl)acrylate (12y)



In a flame-dried round-bottom flask under Argon atmosphere, compound **12'** (2.0 g, 8.96 mmol) was dissolved in dry THF (30 mL, 0.3M). The reaction was cooled down to 0 °C using a water cooling bath. $TiCl_4$ neat (1.14 mL, 1.20 equiv.) was then added dropwise and was left stirring for 30 at the same temperature. Then, *p*-anisaldehyde (1.09 mL, 1.0 equiv.) was added, followed by *N*-methyl morpholine (2.96 mL, 3.0 equiv.). The reaction was allowed to slowly warm up to room temperature, and it was allowed to stirr overnight. After completion, the reaction was quenched with 30 mL H_2O and extracted three times with 40 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford methyl (*E*)-(2-(benzyloxy)carbamoyl)-3-(4-methoxyphenyl)acrylate **12y** as a white powder (1.442 g, 36%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.56 (s, 1H), 7.63 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.35 (m, 5H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.88 (s, 2H), 3.79 (s, 3H), 3.73 (s, 3H).

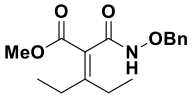
^{13}C NMR (150 MHz, DMSO-d_6) δ 165.1, 162.8, 161.3, 142.0, 135.9, 132.0, 1288, 128.8, 128.3, 125.1, 123.3, 114.4, 76.5, 55.4, 52.2.

HRMS: Calculated $[M+H]^+$ for $C_{19}H_{20}NO_5^+$: 342.1336, found: 342.1345.

Melting Point: 95.6 – 96.2 °C

FTIR (cm^{-1}): 3122, 2956, 2883, 1715, 1637, 1603, 1514, 1267, 1247, 1201, 1175, 1090, 1013, 828, 693.

Methyl 2-((benzyloxy)carbamoyl)-3-ethylpent-2-enoate (12z)



In a flame-dried round-bottom flask under Argon atmosphere, compound **12'** (2.0 g, 8.96 mmol) was dissolved in dry THF (30 mL, 0.3M). The reaction was cooled down to 0 °C using a water cooling bath. $TiCl_4$ neat (1.14 mL, 1.20 equiv.) was then added dropwise and was left stirring for 30 at the same temperature. Then, 3-pentanone (0.95 mL, 1.0 equiv.) was added, followed by *N*-methyl morpholine (2.96 mL, 3.0 equiv.). The reaction was allowed to slowly warm up to room temperature, and it was allowed to stirr overnight. After completion, the reaction was quenched with 30 mL H_2O and extracted three times with 40 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford methyl 2-((benzyloxy)carbamoyl)-3-ethylpent-2-enoate **12z** as a white powder (1.027 g, 39%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.24 (s, 1H), 7.42 – 7.34 (m, 5H), 4.84 (s, 2H), 3.63 (s, 3H), 2.49 – 2.46 (m, 2H), 2.06 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H).

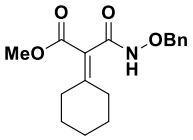
^{13}C NMR (150 MHz, DMSO-d_6) δ 164.8, 164.2, 163.2, 136.1, 128.7, 128.2, 128.2, 123.3, 76.4, 51.4, 27.6, 24.4, 12.7, 12.6.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{22}NO_4^+$: 292.1543, found: 292.1552.

Melting Point: 70.7 – 80.7 °C

FTIR (cm^{-1}): 3167, 2974, 2879, 1715, 1635, 1606, 1501, 1431, 1268, 1229, 1094, 1020, 1000, 751, 695.

Methyl 3-((benzyloxy)amino)-2-cyclohexylidene-3-oxopropanoate (12aa)



In a flame-dried round-bottom flask under Argon atmosphere, compound **12'** (2.0 g, 8.96 mmol) was dissolved in dry THF (30 mL, 0.3M). The reaction was cooled down to 0 °C using a water cooling bath. $TiCl_4$ neat (1.14 mL, 1.20 equiv.) was then added dropwise and was left stirring for 30 at the same temperature. Then, cyclohexanone (0.93 mL, 1.0 equiv.) was added, followed by *N*-methyl morpholine (2.96 mL, 3.0 equiv.). The reaction was allowed to slowly warm up to room temperature, and it was allowed to stirr overnight. After completion, the reaction was quenched with 30 mL H_2O and extracted three times with 40 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (50/50 hexanes:EtOAc) to afford methyl 2-((benzyloxy)carbamoyl)-3-ethylpent-2-enoate **12aa** as a white powder (1.478 g, 54%).

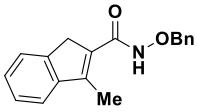
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.24 (s, 1H), 7.40 – 7.34 (m, 5H), 4.83 (s, 2H), 3.62 (s, 3H), 2.68 – 2.66 (m, 2H), 2.10 (s, 2H), 1.56 – 1.53 (m, 6H).

^{13}C NMR (150 MHz, DMSO-d_6) δ 164.6, 12.9, 161.0, 136.1, 128.8, 128.2, 128.2, 121.3, 76.4, 51.5, 40.1, 33.5, 30.3, 27.9, 27.7, 25.4.

HRMS: Calculated $[M+H]^+$ for $C_{17}H_{22}NO_4^+$: 304.1543, found: 304.1548.

FTIR (cm^{-1}): 3176, 2932, 2856, 1719, 1650, 1452, 1433, 1266, 1204, 1095, 1024, 746, 697.

***N*-(benzyloxy)-3-methyl-1*H*-indene-2-carboxamide (12ab)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (916 mg, 1.0 equiv.) was suspended in THF:DCM (29 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (1.2 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (879 mg, 1.0 equiv.) and compound **13ab** (1.0 g, 5.74 mmol, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (1.2 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 30 mL of EtOAc and then washed once with 20 mL HCl (3 M), followed by one wash with 20 mL conc. $NaHCO_3$ and finally with 20 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-3-methyl-1*H*-indene-2-carboxamide **12ab** as a white powder (1.03 g, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62(s, 1H), 7.44 – 7.31 (m, 9H), 5.01 (s, 2H), 3.47 (s, 2H), 2.45 (s, 3H).

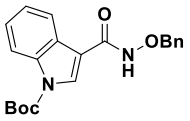
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 148.6, 145.1, 142.3, 135.5, 129.4, 129.3, 128.7, 128.6, 127.4, 126.8, 123.9, 120.8, 78.4, 37.9, 12.4

HRMS: Calculated $[M+H]^+$ for $C_{18}H_{18}NO_2^+$: 280.1332, found: 280.1338.

Melting Point: 143.1 – 145.1 °C

FTIR (cm^{-1}): 3178, 2033, 2949, 1631, 1495, 1351, 1267, 1008, 899, 754, 717, 696.

***tert*-butyl-3-((benzyloxy)carbamoyl)-1*H*-indole-1-carboxylate (12ac)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (611 mg, 1.0 equiv.) was suspended in THF:DCM (20 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (0.8 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (586 mg, 1.0 equiv.) and compound **13ac** (1.0 g, 5.74 mmol, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (0.8 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 30 mL of EtOAc and then washed once with 20 mL HCl (3 M), followed by one wash with 20 mL conc. $NaHCO_3$ and finally with 20 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *tert*-butyl-3-((benzyloxy)carbamoyl)-1*H*-indole-1-carboxylate **12ac** as a white powder (675 mg, 48%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.08 (s, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.47 (m, 2H), 7.43 – 7.38 (m, 4H), 7.31 – 7.29 (m, 1H), 5.07 (m, 2H), 1.67 (m, 9H).

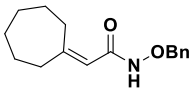
^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 149.1, 135.3, 135.3, 129.3, 128.8, 128.7, 128.6, 128.6, 127.5, 125.3, 123.9, 121.3, 115.2, 112.7, 78.6, 28.1.

HRMS: Calculated $[M+H]^+$ for $C_{21}H_{23}N_2O_4^+$: 367.1658, found: 367.1665.

Melting Point: 52.6 – 58.7 °C

FTIR (cm^{-1}): 3145, 2979, 2935, 1739, 1641, 1450, 1248, 1217, 1147, 1081, 838, 744, 695.

***N*-(benzyloxy)-2-cycloheptylideneacetamide (12ad)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (2.164 g, 13.56 mmol, 2.0 equiv.) was suspended in dry Toluene (34 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (6.8 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13ad** (1.6 g, 6.78 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-2-cycloheptylideneacetamide **12ad** as a colorless oil (1.7 mg, 94%).

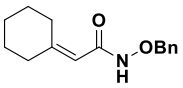
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.66 (bs, 1H), 7.41 – 7.32 (m, 5H), 5.51 (bs, 1H), 4.80 (s, 2H), 2.81 – 2.79 (m, 2H), 2.29 – 2.27 (m, 2H), 1.62 – 1.57 (m, 4H), 1.51 – 1.48 (m, 4H).

^{13}C NMR (150 MHz, DMSO-d_6) δ 164.2, 160.3, 136.2, 128.7, 128.3, 128.1, 114.8, 76.8, 38.3, 30.9, 29.3, 27.5, 26.4.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{22}NO_2^+$: 260.1645, found: 260.1651.

FTIR (cm^{-1}): 3181, 2922, 2852, 1650, 1630, 1496, 1453, 1051, 736.

***N*-(benzyloxy)-2-cyclohexylideneacetamide (12ae)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (1.24 g, 7.78 mmol, 2.0 equiv.) was suspended in dry Toluene (20 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (3.9 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13ae** (600 mg, 6.78 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-2-cyclohexylideneacetamide **12ae** as white powder (750 mg, 79%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.91 (s, 1H), 7.40 – 7.34 (m, 5H), 5.38 (s, 1H), 4.79 (m, 2H), 2.76 (t, *J* = 5.8 Hz, 2H), 2.10 (t, *J* = 5.8 Hz, 2H), 1.58 – 1.50 (m, 6H).

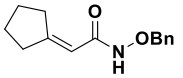
^{13}C NMR (150 MHz, DMSO-d_6) δ 164.2, 157.6, 136.2, 128.7, 128.3, 128.2, 112.4, 76.8, 37.2, 28.9, 28.1, 27.3, 25.8.

HRMS: Calculated $[M+H]^+$ for $C_{15}H_{20}NO_2^+$: 246.1489, found: 246.1495.

Melting Point: 71.9 – 73.5 °C

FTIR (cm^{-1}): 3174, 2992, 2930, 2853, 1636, 1524, 1446, 1229, 1047, 980, 840, 751, 699.

***N*-(benzyloxy)-2-cyclopentylideneacetamide (12af)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2 \cdot HCl$ (2.28 g, 14.27 mmol, 2.0 equiv.) was suspended in dry Toluene (36 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (7.13 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13af** (1.0 m, 7.13 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 35 mL H_2O and extracted three times with 35 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-2-cyclopentylideneacetamide **12af** as white powder (1.38 g, 84%).

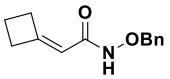
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.63 (bs, 1H), 7.41 – 7.33 (m, 5H), 5.67 (bs, 1H), 4.80 (m, 2H), 2.71 – 2.68 (m, 2H), 2.37 – 2.34 (m, 2H), 1.67 (p, *J* = 7.0 Hz, 2H), 1.59 (q, *J* = 7.2 Hz, 2H).

^{13}C NMR (150 MHz, DMSO-d_6) δ 164.2, 162.7, 136.2, 128.7, 128.3, 128.2, 110.5, 76.9, 35.1, 31.7, 26.1, 24.9.

HRMS: Calculated $[M+H]^+$ for $C_{14}H_{18}NO_2^+$: 232.1332, found: 232.1342.

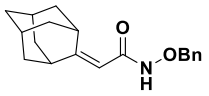
Melting Point: 78.0 – 79.6 °C
FTIR (cm^{-1}): 3215, 1964, 2946, 2866, 1630, 1507, 1497, 1242, 1067, 852, 730.

***N*-(benzyloxy)-2-cyclobutylideneacetamide (12ag)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (442.8 mg, 2.78 mmol, 2.0 equiv.) was suspended in dry Toluene (7 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (1.4 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13ag** (175 mg, 1.39 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 10 mL H_2O and extracted three times with 10 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-2-cyclobutylideneacetamide **12ag** as colorless oil (202 mg, 67%).
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.84 (bs, 1H), 7.39 – 7.34 (m, 5H), 5.60 (bs, 1H), 4.78 (s, 2H), 3.03 (t, *J* = 8.1 Hz, 2H), 2.75 (t, *J* = 7.9 Hz, 2H), 2.01 (p, *J* = 7.9 Hz, 2H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 163.5, 161.2, 136.2, 128.7, 128.3, 128.2, 76.9, 33.1, 31.9, 17.7.
HRMS: Calculated $[M+H]^+$ for $C_{13}H_{16}NO_2^+$: 218.1176, found: 218.1180.
FTIR (cm^{-1}): 3182, 2956, 1682, 1633, 1496, 1360, 1250, 1209, 1046, 846, 741.

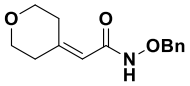
2-((1r,3r,3R,7S)-adamant-2-ylidene)-*N*-(benzyloxy)acetamide (12ah)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $OBnNH_2{\cdot}HCl$ (996 mg, 1.0 equiv.) was suspended in THF:DCM (32 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.4 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (957 mg, 1.0 equiv.) and compound **13ah** (1.2 g, 6.24 mmol, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.4 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 30 mL of EtOAc and then washed once with 30 mL HCl (3 M), followed by one wash with 30 mL conc. $NaHCO_3$ and finally with 30 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford 2-((1r,3r,3R,7S)-adamant-2-ylidene)-*N*-(benzyloxy)acetamide **12ah** as white solid (1.4 g, 75%).
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.89 (bs, 1H), 7.40 – 7.34 (m, 5H), 5.37 (s, 1H), 4.80 (s, 2H), 4.08 (bs, 1H), 2.32 (bs, 1H), 1.92 – 1.89 (m, 6H), 1.82 (bs, 2H), 1.76 – 1.70 (m, 4H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 165.9, 164.4, 136.2, 128.7, 128.3, 128.1, 108.0, 76.9, 40.4, 40.1, 39.5, 38.5, 36.3, 31.7, 27.3.
HRMS: Calculated $[M+H]^+$ for $C_{19}H_{24}NO_2^+$: 298.1802, found: 298.1808.

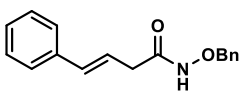
Melting Point: 111.1 – 113.8 °C
FTIR (cm^{-1}): 3272, 2908, 2850, 1652, 1633, 1499, 1447, 1252, 1187, 1055, 951, 747, 738, 697.

***N*-(benzyloxy)-2-(tetrahydro-4*H*-pyran-4-ylidene)acetamide (12ai)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2{\cdot}HCl$ (1.756 g, 11.0 mmol, 2.0 equiv.) was suspended in dry Toluene (28 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (5.5 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13ai** (859 mg, 5.5 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)- 2-(tetrahydro-4*H*-pyran-4-ylidene)acetamide **12ai** as colorless oil (1.184 g, 87%).
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.02 (bs, 1H), 7.41 – 7.35 (m, 5H), 5.49 (bs, 1H), 4.81 (s, 2H), 3.65 (t, *J* = 5.5 Hz, 2H), 3.60 (t, *J* = 5.5 Hz, 2H), 2.92 (t, *J* = 5.6 Hz, 2H), 2.21 (t, *J* = 5.6 Hz, 2H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 163.8, 152.5, 138.3, 128.7, 128.3, 113.5, 76.9, 68.4, 67.7, 36.9, 30.4.
HRMS: Calculated $[M+H]^+$ for $C_{14}H_{18}NO_3^+$: 248.1281, found: 248.1290.
FTIR (cm^{-1}): 3197, 2961, 2850, 1662, 1638, 1231, 1096, 1053, 982, 909, 729, 696.

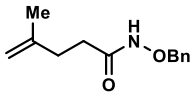
(*E*)-*N*-(benzyloxy)-4-phenylbut-3-enamide (12aj)



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $OBnNH_2{\cdot}HCl$ (985 mg, 1.0 equiv.) was suspended in THF:DCM (30 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (1.3 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (947 mg, 1.0 equiv.) and (E)-4-phenylbut-3-enoic acid (1.0 g, 6.17 mmol, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (1.3 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 30 mL of EtOAc and then washed once with 30 mL HCl (3 M), followed by one wash with 30 mL conc. $NaHCO_3$ and finally with 30 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to (E)-N-(benzyloxy)-4-phenylbut-3-enamide **12aj** as white solid (1.5 g, 95%).
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.12 (s, 1H), 7.41 – 7.22 (m, 10H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 7.1 Hz, 1H), 4.80 (s, 2H), 2.95 – 2.94 (m, 2H).

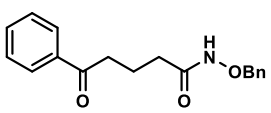
^{13}C NMR (150 MHz, DMSO-d_6) δ 167.2, 136.7, 136.0, 132.4, 128.8, 128.6, 128.3, 128.2, 127.4, 126.0, 123.5, 76.8, 36.7.
HRMS: Calculated $[M+H]^+$ for $C_{17}H_{18}NO_2^+$: 268.1332, found: 268.1336.
Melting Point: 81.7 – 85.7 °C
FTIR (cm^{-1}): 3126, 3062, 3028, 2928, 2851, 1667, 1626, 1487, 1449, 1039, 1016, 963, 747, 693.

***N*-(benzyloxy)-4-methylpent-4-enamide (12ak)**



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $BnONH_2$·HCl (1.6 g, 10.0 mmol, 2.0 equiv.) was suspended in dry Toluene (25 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (5 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13ak** (711 mg, 5 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-4-methylpent-4-enamide **12ak** as colorless oil (949 g, 87%).
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.98 (s, 1H), 7.38 – 7.31 (m, 5H), 4.76 (s, 2H), 4.69 (s, 1H), 4.65 (s, 1H), 2.19 (t, *J* = 7.6 Hz, 2H), 2.08 (dd, *J* = 8.6, 6.6 Hz, 2H), 1.67 (s, 3H).
^{13}C NMR (150 MHz, DMSO-d_6) δ 174.0, 149.5, 141.3, 134.0, 133.5, 133.4, 115.5, 82.0, 37.9, 35.8, 27.5.
HRMS: Calculated $[M+H]^+$ for $C_{13}H_{18}NO_2^+$: 220.1332, found: 220.1338.
FTIR (cm^{-1}): 3185, 3068, 3031, 2969, 2938, 1648, 1497, 1454, 1069, 1028, 975, 888, 745.

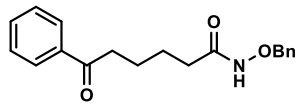
***N*-(benzyloxy)-5-oxo-5-phenylpentanamide (12al)**



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $OBnNH_2$·HCl (869 mg, 1.0 equiv.) was suspended in THF:DCM (52 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.2 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (1.6 g, 1.0 equiv.) and 5-oxo-5phenylpentanoic acid (2.0 g, 10.4 mmol, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.2 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-5-oxo-pehnylpentanamide **12al** as white solid (1.1 g, 36%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.94 – 7.93 (m, 2H), 7.65 – 7.62 (m, 1H), 7.54 - 7.52 (m, 2H), 7.39 – 7.32 (m, 5H), 4.78 (s, 2H), 3.01 (t, *J* = 7.1 Hz, 2H), 2.04 (t, *J* = 7.3 Hz, 2H), 1.84 (t, *J* = 7.2 Hz, 2H).
^{13}C NMR (150 MHz, DMSO-d6) δ 199.5, 169.1, 136.6, 136.1, 133.1, 128.7, 128.7, 128.3, 128.2, 127.8, 76.7, 37.0, 31.4, 19.6.
HRMS: Calculated $[M+H]^+$ for $C_{18}H_{20}NO_3^+$: 298.1438, found: 298.1442.
Melting Point: 78.5 – 79.6 °C
FTIR (cm^{-1}): 3220, 3060, 3041, 2970, 2929, 2851, 1738, 1655, 1513, 1448, 1373, 1198, 968, 727, 687.

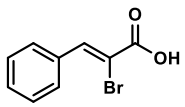
***N*-(benzyloxy)-6-oxo-6-phenylhexanamide (12am)**



Following **Method A** from the general procedures for the synthesis of hydroxamate esters, in an oven-dried round-bottom flask under Argon atmosphere, $OBnNH_2 \cdot HCl$ (810 mg, 1.0 equiv.) was suspended in THF:DCM (48 mL, 1:1, 0.2 M) at room temperature. The reaction mixture was cooled down to 0 °C using a water-ice bath. NEt_3 (2.1 mL, 1.5 equiv.) was added, and the reaction mixture was allowed to stir for 30 min at 0 °C. HOBt hydrate (1.5 g, 1.0 equiv.) and 6-oxo-6-phenylhexanoic acid (2.0 g, 10.4 mmol, 1.0 equiv.) were added subsequently, and the reaction was allowed to stir for an additional 30 min at 0 °C. Finally, NEt_3 (2.1 mL, 1.5 equiv.) were added, reaction was allowed to warm up to room temperature and it was allowed to stir overnight. The reaction was then filtered, and the obtained filtrate was diluted with 50 mL of EtOAc and then washed once with 50 mL HCl (3 M), followed by one wash with 50 mL conc. $NaHCO_3$ and finally with 50 mL H_2O. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford *N*-(benzyloxy)-6-oxo-6-pehnylhexanamide **12al** as white solid (1.5 g, 50%).
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.96 (s, 1H), 7.97 – 7.95 (m, 2H), 7.64 – 7.62 (m, 1H), 7.54 – 7.51 (m, 2H), 7.40 – 7.32 (m, 5H), 4.77 (s, 2H), 3.02 (t, *J* = 6.7 Hz, 2H), 1.99 (t, *J* = 6.7 Hz, 2H), 1.59 – 1.55 (m, 4H).
^{13}C NMR (150 MHz, DMSO-d6) δ 199.9, 169.2, 136.7, 136.1, 133.1, 128.8, 128.7, 128.3, 128.2, 127.9, 76.8, 37.5, 32.1, 24.5, 23.2.
HRMS: Calculated $[M+H]^+$ for $C_{19}H_{22}NO_3^+$: 312.1594, found: 312.1601.
Melting Point: 58.6 – 60.1 °C
FTIR (cm^{-1}): 3239, 3059, 2997, 2970, 2956, 2870, 1738, 1649, 1446, 1372, 1218, 1017, 955, 754, 696.

13. Synthesis and characterization carboxylic acids (13):

(*Z*)-2-bromo-3-phenylacrylic acid (13j)



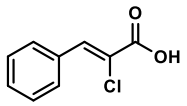
Following **Method A** from the general procedures for the synthesis of carboxylic acids, (*Z*)-2-bromo-3-phenylacrylaldehyde (3.5 g, 16.6 mmol) was dissolved in *t*-BuOH (33 mL, 0.5 M). Then $NaClO_2$ (5.6 g, 61.4 mmol) was added, followed by H_2O (33 mL, 0.5 M) and 2-methyl-2-butene (15.8 mL, 150 mmol). Finally, NaH_2PO_4 (9.96 g, 83 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 50 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (50 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (50 mL x 4). The combined aqueous layers were then carefully acidified with 3 M

HCl, and it was extracted with DCM (60 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*Z*)-2-bromo-3-phenylacrylic acid **13j** as a white solid (2.632 g, 70%). NMR data matches the ones reported in the literature.[11]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.92 – 7.91 (m, 2H), 7.47 – 7.46 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 143.5, 133.5, 131.0, 130.8, 128.7, 111.6.

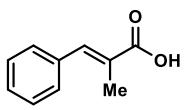
(*Z*)-2-chloro-3-phenylacrylic acid (13k)



In a flame-dried round-bottom flask, benzaldehyde (1.684 g, 15.87 mmol) and 2-chloroacetaldehyde (1.000 g, 10.6 mmol) were dissolved in dry THF (53 mL, 0.2 M) under Argon atmosphere. The reaction mixture was cooled down to 0 °C, using an ice-water bath. Neat $TiCl_4$ (2.3 mL, 2.0 equiv.) was added slowly and the reaction mixture was left stirring for 30 min at the same temperature. NEt_3 (5.9 mL, 4.0 equiv.) was then added and the reaction mixture was allowed to warm to room temperature. The reaction was left stirring overnight. After completion, the reaction was quenched with 50 mL of conc. NH_4Cl and it was extracted with EtOAc (60 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 50/50) to afford (Z)-2-chloro-3-phenylacrylalic acid **13k** as a white crystalline solid (1.553 g, 54%). NMR data matches the ones reported in the literature.[12]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.90 – 7.89 (m, 2H), 7.47 – 7.45 (m, 3H).

(*E*)-2-methyl-3-phenylacrylic acid (13l)



Following **Method A** from the general procedures for the synthesis of carboxylic acids, (*Z*)-2-methyl-3-phenylacrylaldehyde (10.47 g, 71.6 mmol) was dissolved in *t*-BuOH (145 mL, 0.5 M). Then $NaClO_2$ (23.97 g, 265 mmol) was added, followed by H_2O (145 mL, 0.5 M) and 2-methyl-2-butene (69 mL, 645 mmol). Finally, NaH_2PO_4 (42.97 g, 358 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 100 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (8100 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (100 mL x 4). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (150 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-2-methyl-3-phenylacrylic acid **13l** as a white solid (1.818 g, 47%). NMR data matches the ones reported in the literature.[13]

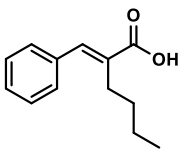
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.46 – 7.41 (m, 4H), 7.38 – 7.34 (m, 1H), 2.16 (s, 3H).

[11] Ma, X., Li, W., Li, X., Tao, X., Fan, W., Xie, X., Ayad, T., Ratovelomanana-Vidal, V., Zhang, Z. *Chem. Commun.* **2012**, 48, 5352–5354.

[12] Ma, X., Li, W., Li, X., Tao, X., Fan, W., Xie, X., Ayad, T., Ratovelomanana-Vidal, V., Zhang, Z. *Chem. Commun.* **2012**, 48, 5352–5354.

[13] Su, M.D., Liu, Y.F., Nie, Z.W., Yang, T.L., Cao, Z.Z., Li, H., Luo, W.P., Liu, Q., Guo, C.C. *J. Org. Chem.* **2022**, 87, 7022–7032.

(*E*)-2-benzylidenehexanoic acid (13m)

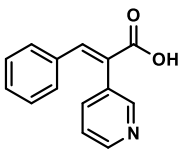


Following **Method A** from the general procedures for the synthesis of carboxylic acids, compound **14m** (1.36 g, 7.22 mmol) was dissolved in *t*-BuOH (14 mL, 0.5 M). Then $NaClO_2$ (1.96 g, 21.66 mmol) was added, followed by H_2O (14 mL, 0.5 M) and 2-methyl-2-butene (6.9 mL, 65 mmol). Finally, NaH_2PO_4 (4.33 g, 36 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 25 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (25 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (25 mL x 3). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (50 mL x 3). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-2-benzylidenehexanoic acid **13m** as a pale yellow crystalline solid (905 mg, 61%). NMR data matches the ones reported in the literature.[14]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.42 – 7.40 (m, 4H), 7.37 – 7.34 (m, 1H), 2.56 – 2.53 (m, 2H), 1.61 – 1.56 (tt, *J* = 8.0, 6.3 Hz, 2H), 1.44 – 1.38 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 174.0, 141.1, 135.7, 129.6, 128.8, 128.7, 31.5, 27.2, 23.0, 14.0.

(*E*)-3-phenyl-2-(pyridin-3-yl)acrylic acid (13n)



Following **Method A** from the general procedures for the synthesis of carboxylic acids, compound **14n** (750 mg, 3.58 mmol) was dissolved in *t*-BuOH (7 mL, 0.5 M). Then $NaClO_2$ (1.62 g, 17.9 mmol) was added, followed by H_2O (7 mL, 0.5 M) and 2-methyl-2-butene (3.4 mL, 32 mmol). Finally, NaH_2PO_4 (946 mg, 7.9 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 7 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (25 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (25 mL x 3). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (50 mL x 3). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-3-phenyl-2-(pyridine-3-yl)acrylic acid **13n** as a white crystalline solid (260 mg, 32%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.93 (s, 1H), 8.54 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.32 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.89 (s, 1H), 7.64 (ddd, *J* = 7.8, 2.3, 1.7 Hz, 1H), 7.42 (ddd, *J* = 7.8, 4.9, 0.9 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.07 – 7.05 (m, 2H).

^{13}C NMR (150 MHz, DMSO-d_6) δ 167.9, 149.9, 148.5, 140.6, 137.6, 134.1, 132.2, 130.2, 10.2, 129.3, 128.5, 123.5.

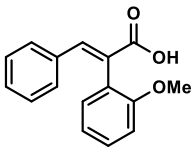
HRMS: Calculated $[M+H]^+$ for $C_{14}H_{12}NO_2^+$: 226.0868, found: 226.0884

Melting Point: 236.7 – 239.5 °C

FTIR (cm^{-1}): 3055, 3028, 2422, 1671, 1627, 1591, 1572, 1410, 1239, 1192, 1174, 1009, 776, 718, 690.

[14] Fujihara, T., Xu, T., Semba, K., Terao, Tsuji, Y. *Angew. Chem. Int. Ed.* **2011**, 50, 523–527.

(*E*)-2-(2-methoxyphenyl)-2-phenylacrylic acid (13o)



Following **Method A** from the general procedures for the synthesis of carboxylic acids, compound **14o** (3.6 g, 15.1 mmol) was dissolved in *t*-BuOH (30 mL, 0.5 M). Then $NaClO_2$ (4.1 g, 45.3 mmol) was added, followed by H_2O (30 mL, 0.5 M) and 2-methyl-2-butene (14.4 mL, 136 mmol). Finally, NaH_2PO_4 (9.07 g, 75.6 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 30 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (50 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (50 mL x 4). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (60 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-2-(2-methoxyphenyl)-3-phenylacrylic acid **13o** as a white solid (3.646 g, 95%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.38 – 7.36 (m, 1H), 7.24 – 7.21 (m, 1H), 7.19 – 7.16 (m, 2H), 7.12 – 7.10 (m, 2H), 7.08 – 7.06 (m, 1H), 6.99 – 6.97 (m, 2H), 6.96 – 6.93 (m, 2H), 3.76 (s, 3H).

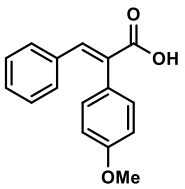
^{13}C NMR (150 MHz, $CDCl_3$) δ 129.9, 157.6, 142.5, 134.8, 131.0, 130.7, 130.7, 130.6, 130.0, 129.5, 128.9, 128.4, 128.4, 124.8, 121.2, 111.4, 55.8.

HRMS: Calculated $[M-H]^+$ for $C_{16}H_{13}O_2^-$: 253.0870, found: 253.0876.

Melting Point: 146.9 – 147.7 °C

FTIR (cm^{-1}): 3059, 3016, 2962, 2938, 2622, 1670, 1490, 1461, 1447, 1433, 1417, 1274, 1245, 749

(*E*)-2-(4-methoxyphenyl) 2-phenylacrylic acid (13p)

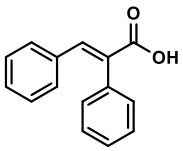


Following **Method A** from the general procedures for the synthesis of carboxylic acids, compound **14p** (2.0 g, 8.4 mmol) was dissolved in *t*-BuOH (8 mL, 0.5 M). Then $NaClO_2$ (2.3 g, 25.2 mmol) was added, followed by H_2O (8 mL, 0.5 M) and 2-methyl-2-butene (8 mL, 76 mmol). Finally, NaH_2PO_4 (5.0 g, 42 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 15 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (30 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (30 mL x 4). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (40 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-2-(4-methoxyphenyl)-3-phenylacrylic acid **13p** as a white solid (1.912 g, 90%). NMR data matches the ones reported in the literature.[15]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.16 (m, 4H), 7.12 – 7.10 (m, 2H), 6.92 – 6.91 (m, 2H), 3.84 (s, 3H).

[15] Zhou, Z., Dixon, D.D., Jolit, A., Tius, M.A. *Chem. Eur. J.* **2016**, *22*, 15929–15936.

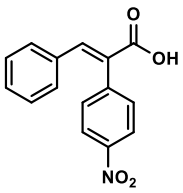
(*E*)-2,3-diphenylacrylic acid (13q)



Following **Method A** from the general procedures for the synthesis of carboxylic acids, compound **14q** (3.75 g, 18.02 mmol) was dissolved in *t*-BuOH (18 mL, 0.5 M). Then $NaClO_2$ (4.89 g, 54.05 mmol) was added, followed by H_2O (18 mL, 0.5 M) and 2-methyl-2-butene (17.2 mL, 162 mmol). Finally, NaH_2PO_4 (10.8 g, 90.1 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 30 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (50 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (50 mL x 4). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (60 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-2,3-diphenylacrylic acid **13q** as a white solid (3.82 g, 94%). NMR data matches the ones reported in the literature.[16]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.41 – 7.37 (m, 3H), 7.26 – 7.22 (m, 3H), 7.18 – 7.16 (m, 2H), 7.08 – 7.06 (m, 2H).

(*E*)-2-(4-nitrophenyl)-3-phenylacrylic acid (13r)

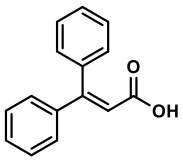


Following **Method A** from the general procedures for the synthesis of carboxylic acids, compound **14r** (2.0 g, 7.9 mmol) was dissolved in *t*-BuOH (9 mL, 0.5 M). Then $NaClO_2$ (2.14 g, 29.23 mmol) was added, followed by H_2O (9 mL, 0.5 M) and 2-methyl-2-butene (7.53 mL, 71.71 mmol). Finally, NaH_2PO_4 (4.74 g, 39.5 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight. After full conversion, 10 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (20 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (20 mL x 4). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (30 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-2-(4-nitrophenyl)-3-phenylacrylic acid **13r** as a white solid (1.7 g, 80%). NMR data matches the ones reported in the literature.[17]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 8.07 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.31 – 7.28 (m, 1H), 7.23 – 7.20 (m, 2H), 7.05 – 7.04 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 147.7, 144.5, 142.5, 133.5, 131.4, 130.9, 130.4, 129.6, 128.8, 124.0.

(*E*)-3-phenylbut-2-enoic acid (13u)



Following **Method A** from the general procedures for the synthesis of carboxylic acids, compound **14u** (1.0 g, 4.8 mmol) was dissolved in *t*-BuOH (5 mL, 0.5 M). Then $NaClO_2$ (1.3 g, 14.4 mmol) was added, followed by H_2O (5 mL, 0.5 M) and 2-methyl-2-butene (4.6 mL, 43.2 mmol). Finally, NaH_2PO_4 (2.88 g, 24.0 mmol) was added, and the reaction mixture was loosely capped. It was stirred vigorously at room temperature overnight.

[16] Wang, X., Nakajima, M., Martin, R. *J. Am. Chem. Soc.* **2015**, 137, 8924–8927.

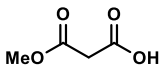
[17] Song, C., Chen, P., Tang, Y. *RSC. Adv.* **2017**, *7*, 11233–11243.

After full conversion, 10 mL saturated NH_4Cl were added, and the reaction mixture was extracted with EtOAc (20 mL x 3). The combined organic layers partitioned with conc. $NaHCO_3$ until the aqueous layer was basic. It was extracted $NaHCO_3$ (20 mL x 4). The combined aqueous layers were then carefully acidified with 3 M HCl, and it was extracted with DCM (30 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded (*E*)-3-phenylbut-2-enoic acid **13u** as a white solid (1.7 g, 80%). NMR data matches the ones reported in the literature.[18]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 4H), 7.34 – 7.32 (m, 2H), 7.29 – 7.27 (m, 2H), 7.23 – 7.21 (m, 2H), 6.35 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 158.9, 140.7, 138.4, 129.8, 129.2, 128.5, 128.4, 128.3, 128.0, 116.1.

Methyl 3-oxopropanoate (13')

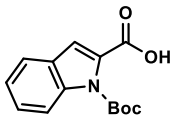


Following a modified literature procedure[19], dimethyl malonate (20 g, 151.4 mmol) was suspended in a mixture MeCN:H_2O (15 mL, 10 M) and then cooled down to 0 °C using an ice/water bath. Then 30 mL of a 5M solution of KOH were added over 20 min (1.0 equiv.) via an addition funnel. The reaction was left stirring at 0 °C for one hour. Then it was warmed to room temperature, diluted with 50 mL of distilled H_2O and extracted with EtOAc (50 mL x 3). The aqueous layer wwas then carefully acidified with 3 M HCl, and it was extracted with EtOAc (50 mL x 4). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded methyl 3-oxopropanoate **13'** as a colorless oil (12.571 g, 70%). NMR data matches the ones reported in the literature.[20]

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.45 (s, 2H).

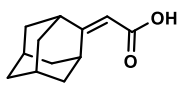
^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 167.7, 53.0, 40.5.

1-(*tert*-butoxycarbonyl)-1*H*-indole-3-carboxylic acid (13ac)



Following a known literature procedure[21] *N*-hydroxycinnamamide **13ac** was prepared as a pale pink powder. The NMR data matches the one reported in the literature.[22]

2-((1r,3r,5*R*,7*S*)-adamantan-2-ylidene)acetic acid (13ah)



Following **Method B** from the general procedures for the synthesis of carboxylic acids, in a round-bottom flask open to air, LiOH (336 mg, 14 mmol, 1.2 equiv.) was dissolved in THF:H_2O (12:12 mL, 0.5 M) at room temperature. The reaction mixture was then cooled down to 0 °C using an ice-water bath. Then methyl 2-((1r,3r,5R,7S)-adamantan-2-ylidene)acetate (2.4 g, 11.6 mmol, 1.0 equiv.) was added slowly. After complete addition, the reaction mixture was allowed to worm to room temperature, and it was monitored by TLC. After full consumption of the starting material, the solvent was removed *in vacuo* and conc. $NaHCO_3$ (20 mL) was added to the reaction mixture.

[18] Tanaka, S., Watanabe, K., Tanaka, Y., Hattori, T. *Org. Lett.* **2016**, *18*, 2576−2579.
[19] Niwayama, S., Cho, H., Lin, C. *Tett. Lett.* **2008**, *49*, 4434–4436.
[20] Niwayama, S., Cho, H., Lin, C. *Tett. Lett.* **2008**, *49*, 4434–4436.
[21] Usachova, N., Leitis, G., Jirgensons, A., Kalvinsh, I. *Synthn. Commun.* **2010**, *40*, 927–935.
[22] Shen, Q-K, Deng, H., Wang, S-B., Tian Y-S., Quan, Z-S. *Eur. J. Med. Chem.* **2019**, *173*, 15–31.

It was then partitioned in DCM (50 mL), and it was extracted with DCM (3 x 50 mL). The aqueous layer was then carefully acidified with 3 M HCl, and it was extracted with DCM (3 x 50 mL). The combined organic layers were then dried over Na_2SO_4. Evaporation of the solvent afforded 2-((1r,3r,5*R*,7*S*)-adamantan-2-ylidene)acetic acid **13ah** as a white crystalline solid (1.79 g, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.53 (brs, 1H), 5.61 (s, 1H), 4.06 (s, 1H), 2.48 (d, *J* = 2.75 Hz, 1H), 1.98 – 1.94 (m, 5H), 1.88 – 1.81 (m, 5Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 175.5, 172.4, 108.3, 41.8, 40.3, 39.4, 36.9, 33.3, 28.0.

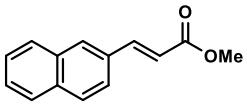
HRMS: Calculated $[M-H]^+$ for $C_{12}H_{15}O_2^-$: 191.1078, found: 191.1078.

Melting Point: 138.0 – 141.0 °C

FTIR (cm^{-1}): 2999, 2920, 2898, 2849, 2569, 1682, 1671, 1629, 1450, 1416, 1250, 1209, 1189, 931, 867, 701.

14. Synthesis and characterization of α,ß–unsaturated esters (13):

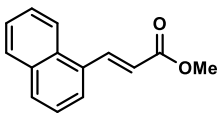
Methyl (*E*)-3-(naphthalene-2-yl)acrylate (13f)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (462 mg, 11.53 mmol, 1.2 equiv.) was suspended in dry THF (32 mL, 0.3 M). Trimethyl phosphonoacetate (1.67 mL, 11.53 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, 2-naphthaldehyde (1.5 g, 9.6 mmol, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford methyl (*E*)-3-(naphthalene-2-yl)acrylate **13f** as a colorless oil (1.2 g, 59%). NMR data matches the ones reported in the literature.[23]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.88 – 7.83 (m, 4H), 7.67 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.54 – 7.50 (m, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H).

Methyl (*E*)-3-(naphthalene-1-yl)acrylate (13g)



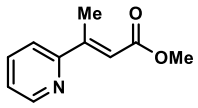
Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (462 mg, 11.53 mmol, 1.2 equiv.) was suspended in dry THF (32 mL, 0.3 M). Trimethyl phosphonoacetate (1.67 mL, 11.53 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, 2-naphthaldehyde (1.5 g, 9.6 mmol, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc)

[23] Rozsar, D., Farley, A. J.M., McLauchlan, I., Shennan, B.D.A., Yamazaki, K., Dixon, D.J. *Angew. Chem. Int. Ed.* **2023**, *62*, e2023033.

to afford methyl (*E*)-3-(naphthalene-1-yl)acrylate **13g** as a colorless oil (1.7 g, 84%). NMR data matches the ones reported in the literature.[24]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (d, *J* = 15.8 Hz, 1H), 8.21 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.89 (m, 2H), 7.88 (dt, *J* = 7.2, 1.0 Hz, 1H), 7.59 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.49 (ddd, *J* = 7.98, 7.7, 0.5 Hz, 1H), 6.54 (d, *J* 15.7 Hz, 1H), 3.86 (s, 3H).

Methyl (*E*)-3-(pyridine-2-yl)but-2-enoate (13s)



Following **Method A** from the general procedures for the synthesis of α,ß–unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (594 mg, 24.76 mmol, 1.2 equiv.) was suspended in dry THF (70 mL, 0.3 M). Trimethyl phosphonoacetate (3.6 mL, 24.76 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, 1-(pyridine-2-yl)ethan-1-one (2.3 mL, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (40 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (60:40 hexanes:EtOAc) to afford methyl (*E*)-3-(pyridine-2-yl)but-2-enoate **13s** as a colorless oil (2.34 g, 64%).

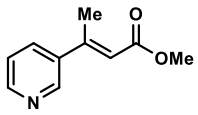
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 4.7, 1.9, 1.0, 1H), 7.71 (td, *J* = 7.8, 7.7, 1.8 Hz, 1H), 7.55 (td, *J* 8.0, 1.0 Hz, 1H), 7.28 – 7.25 (m, 1H), 6.70 (m, 1H), 3.78 (s, 3H), 2.63 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 158.1, 153.6, 149.4, 136.8, 123.7, 121.1, 118.9, 51.4, 16.2.

HRMS: Calculated $[M\text{-}H]^+$ for $C_{10}H_{12}NO_2^+$: 178.0863, found: 178.0870.

FTIR (cm^{-1}): 3053, 3001, 2949, 1713, 1634, 1581, 1567, 1432, 1345, 1278, 1167, 1152, 1031, 785, 744.

Methyl (*E*)-3-(pyridine-3-yl)but-2-enoate (13t)



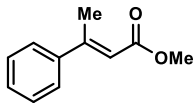
Following **Method A** from the general procedures for the synthesis of α,ß–unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (594 mg, 24.76 mmol, 1.2 equiv.) was suspended in dry THF (70 mL, 0.3 M). Trimethyl phosphonoacetate (3.6 mL, 24.76 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, 1-(pyridine-2-yl)ethan-1-one (2.3 mL, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (40 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (60:40 hexanes:EtOAc) to afford methyl (*E*)-3-(pyridine-3-yl)but-2-enoate **13t** as a light yellow oil (2.127 g, 58%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 2.4, 0.9 Hz, 1H), 8.60 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.75 (ddd, *J* = 8.0, 2.5, 1.6 Hz, 1H), 7.31 (ddd, *J* = 8.0, 4.8, 0.9 Hz, 1H), 6.15 (d, *J* = 1.4 Hz, 1H), 3.77 (s, 3H), 2.59 (d, *J* = 1.34Hz, 3H).

[24] Martinez, A.M., Puet, A., Dominguez, G., Alonso, I., Castro-Biondo, R., Perez-Castells, J. *Org. Let.* **2023**, *25*, 5923–5928.

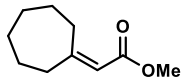
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.9, 152.6, 150.2, 147.7, 137.8, 133.7, 123.4, 118.3m, 51.5, 17.9.
HRMS: Calculated $[M-H]^+$ for $C_{10}H_{12}NO_2^+$: 178.0863, found: 178.0870.
FTIR (cm^{-1}): 3033, 2950, 1713, 1627, 1435, 1347, 1279, 1193, 1164, 1020, 872, 807, 705.

Methyl (*E*)-3-phenylbut-2-enoate (13v)



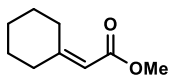
Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (400 mg, 10 mmol, 1.2 equiv.) was suspended in dry THF (30 mL, 0.3 M). Trimethyl phosphonoacetate (1.33 mL, 10 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, acetophenone (1.0 g, 8.3 mmol, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (50 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford methyl (*E*)-3-phenylbut-2-enoate **13v** as a yellow oil (1.1 g, 75%). NMR data matches the ones reported in the literature.[25]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.47 (m, 2H), 7.69 – 7.36 (m, 3H), 6.14 (d, *J* = 1.3 Hz, 1H), 3.76 (s, 3H), 2.58 (d, *J* = 1.3 Hz, 3H).

Methyl 2-cyloheptylideneacetate (13ad)



Following **Method A** from the general procedures for the synthesis of α,ß–unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (614 mg, 15.3 mmol, 1.2 equiv.) was suspended in dry THF (42 mL, 0.3 M). Trimethyl phosphonoacetate (2.2 mL, 15.3 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, cycloheptanone (1.5 mL, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (40 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford methyl 2-cycloheptylideneacetate **13ad** as a colorless oil (1.704 g, 80%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.67 (p, *J* = 1.3 Hz, 1H), 3.67 (s, 3H), 2.88 – 2.86 (m, 2H), 2.38 – 2.36 (m, 2H), 1.70 – 1.62 (m, 4H), 1.95 – 1.49 (m, 4H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 167.2, 115.3, 50.9, 39.1, 32.2, 30.0, 29.2, 28.2, 26.7.
HRMS: Calculated $[M-H]^+$ for $C_{10}H_{17}O_2^+$: 169.1123, found: 169.1225.
FTIR (cm^{-1}): 2924, 2853, 1714, 1634, 1433, 1379, 1194, 1174, 1145, 1027, 722.

Methyl 2-cylohexylideneacetate (13ae)



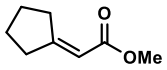
Following **Method A** from the general procedures for the synthesis of α,ß–unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride

[25] Pugliese, G., Vaghi, F., Lonardi, G., Licini, G., Orlandi, M., *Eur. J. Org. Chem.* **2023**, *26*, e202201492.

(1.53 g, 38.2 mmol, 1.2 equiv.) was suspended in dry THF (250 mL, 0.1 M). Trimethyl phosphonoacetate (5.5 mL, 38.2 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, cyclohexanone (2.64 mL, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (200 mL) and extracted with EtOAc (3 x 300 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford methyl 2-cyclohexylideneacetate **13ae** as a colorless oil (1.7 g, 43%). NMR data matches the ones reported in the literature.[26]

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.60 (p, *J* = 1.2 Hz, 1H), 3.68 (s, 3H), 2.83 – 2.81 (m, 2H), 2.20 – 2.18 (m, 2H), 1.67 – 1.57 (m, 6H).

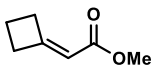
Methyl 2-cylopentylideneacetate (13af)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (541 mg, 13.5 mmol, 1.2 equiv.) was suspended in dry THF (38 mL, 0.3 M). Trimethyl phosphonoacetate (2.0 mL, 13.5 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, cyclopentanone (1.0 mL, 11.3 mmol, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (40 mL) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford methyl 2-cyclopentylideneacetate **13af** as a colorless oil (1.473 g, 93%). NMR data matches the ones reported in the literature.[27]

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.81 (s, 1H), 3.68 (s, 3H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.77 – 1.72 (m, 2H), 1.68 – 1.64 (m, 2H).

Methyl 2-cylobutylideneacetate (13ag)

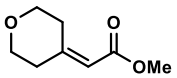


Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (1.72 g, 42.8 mmol, 1.2 equiv.) was suspended in dry THF (119 mL, 0.3 M). Trimethyl phosphonoacetate (6.2 mL, 42.8 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, cyclobutanone (2.67 mL, 35.67 mmol, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (100 mL) and extracted with EtOAc (3 x 120 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford methyl 2-cyclobutylideneacetate **13ag** as a colorless oil (1.8 g, 40%). NMR data matches the ones reported in the literature.[28]

[26] Jager, C., Haase, M., Koschorreck, K., Urlacher, V.B., DEska, J., *Angew. Chem. Int. Ed.* **2023**, *62*, e202213671.
[27] Tadros, J., Dankers, C., Aldrich-Wright, J.R., Polyzos, A., Gordon, C.P. *Eur. J. Org., Chem.* **2021**. 4184–4194.
[28] Goti, A., Brandi, A., De Sarlo, F., Guarna, A. *Tetrahedron.* **1992**, *48*, 5283–5300.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.59 (p, *J* = 2.3 Hz, 1H), 3.68 (s, 3H), 3.12 (dddd, *J* = 8.0, 7.0, 2.4, 1.2 Hz, 2H), 2.84 (dddd, *J* = 9.3, 6.9, 2.2, 1.1 Hz, 2H), 2.09 (p, *J* = 8.0 Hz, 2H).

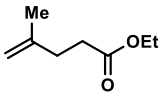
Methyl 2-(tetrahydro-4*H*-pyran-4-ylidene)acetate (13ai)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated esters, in a flame-dried round bottom flask under Argon atmosphere, sodium hydride (719 mg, 18 mmol, 1.2 equiv.) was suspended in dry THF (50 mL, 0.3 M). Trimethyl phosphonoacetate (2.6 mL, 18 mmol, 1.2 equiv.) was then added slowly at room temperature. After 5 min, tetrahydro-4*H*-pyran-4-one (1.03 mL, 15 mmol, 1.0 equiv.) was added to reaction mixture. The reaction mixture was then heated to reflux (66 °C) overnight. After completion, the reaction was allowed to cool down to room temperature, it was partitioned with H_2O (50 mL) and extracted with EtOAc (3 x 60 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (95:5 hexanes:EtOAc) to afford methyl 2-(tetrahydro-4*H*-pyran-4-ylidene)acetate **13ai** as a colorless oil (1.051 g, 45%). NMR data matches the ones reported in the literature.[29]

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.68 (s, 1H), 3.77 (t, *J* = 5.5 Hz, 2H), 3.73 (t, *J* = 5.5 Hz, 2H), 3.69 (s, 3H), 3.01 (t, *J* = 5.6 Hz, 2H), 2.33 (t, *J* = 5.6 Hz, 2H).

Ethyl 4-methylpent-4-enoate (13ak)



In a flame-dried round-bottom flask under Argon atmosphere, NaH (720 mg, 60% in mineral oil, 1.2 equiv.) was suspended in dry Et_2O (75 mL, 0.2 M). The reaction mixture was then cooled down to 0 °C using an ice-water cooling bath under vigorous stirring. Methyltriphenylphosphonium bromide (6.43 g, 1.2 equiv.) was added and allowed to stir for 30 min until bubbling ceased. The reaction was mixture was then heated to reflux overnight (16 h). The reaction turned bright yellow. Then levulinic acid ethyl ester (2.16 g, 15 mmol) was added and the reaction was left heating at reflux for 16 h. The bright yellow color disappeared and a white precipitate was formed. The reaction mixture was allowed to cool down to room temperature. The solids were filtered and washed thrice with Et_2O (10 mL). The filtrate was then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (95/05 hexanes:Et_2O) to afford Ethyl 4-methylpent-4-enoate **12ak** as colorless oil (1.43 g, 67%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.69 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.45 (dd, *J* = 8.8, 6.4 Hz, 2H), 2.34 (dd, *J* = 9.0, 6.5 Hz, 2H), 1.74 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 144.3, 110.5, 60.5, 32.8, 32.8, 22.6, 14.4.

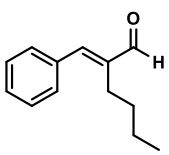
HRMS: Calculated $[M-H]^+$ for $C_8H_{15}O_2^+$: 143.1067, found: 143.1065.

FTIR (cm^{-1}): 3078, 2952, 2924, 2855, 1737, 1446, 1371, 1231, 1154, 1030, 888.

[29] Kuehne, M.E., Bornmann, W.G., Marko,, I., Qin, Y., LeBoulluec, K.L., Frasier, D.A., Xu, F., Mulamba, T., Ensinger, C.L., Borman, L.S., Huot, A.E., Exon, C., Bizzaro, F.T., Cheung, J.B., Bane, S.L. *Org. Biomol. Chem.* **2003**, 1, 2120–2136.

15. Synthesis and characterization of α,ß-unsaturated aldehydes (14):

(*E*)-2-benzylidenehexanal (14m)

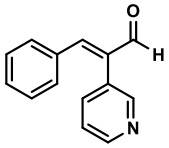


Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated aldehydes, (*Z*)-2-bromo-3-phenylacryaldehyde (5.0 g, 23.7 mmol), *n*–butylboronic acid (3.87 g, 37.9 mmol, 1.6 equiv.), K_2CO_3 (9.83 g, 71.1 mmol, 3.0 equiv.) and $Pd(PPh_3)_4$ (548 mg, 0.474 mmol, 2 mol%) were dissolved in a 7:3 mixture of Toluene:H_2O (80 mL, 0.3 M) and heated to 100 °C overnight under Argon atmosphere. After completion, the reaction was quenched with 50 mL of H_2O and extracted with EtOAc (50 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 90/10) to afford (*E*)-2-benzylidenehexanal **14m** as a yellow-orange oil (1.360 g, 30%). NMR data matches the ones reported in the literature.[30]

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.51 – 7.49 (m, 2H), 7.46 – 7.44 (m, 2H), 7.41 – 7.38 (m, 1H), 7.21 (s, 1H), 2.55 – 2.52 (m, 2H), 1.51 – 1.46 (m, 2H), 1.44 – 1.38 (m, 2H), 0.93 (t, 3H, *J* = 7.24 Hz).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.9, 149.9, 129.8, 129.7, 128.9, 30.6, 24.7, 23.2, 14.0.

(*E*)-3-phenyl-2-(pyridine-3-yl)acrylaldehyde (14n)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated aldehydes, (*Z*)-2-bromo-3-phenylacryaldehyde (3.0 g, 14.21 mmol), pyridin-3-ylboronic acid (1.92 g, 15.64 mmol, 1.1 equiv.), K_2CO_3 (5.9 g, 42.6 mmol, 3.0 equiv.) and $Pd(PPh_3)_4$ (329 mg, 0.284 mmol, 2 mol%) were dissolved in a 7:3 mixture of Toluene:H_2O (47 mL, 0.3 M) and heated to 100 °C overnight under Argon atmosphere. After completion, the reaction was quenched with 40 mL of H_2O and extracted with EtOAc (50 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 50/50) to afford (*E*)-3-phenyl-2-(pyridine-3-yl)acrylaldehyde **14n** as a white-off solid (1.4 g, 47%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.63 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.43 (d, *J* = 1.4 Hz), 7.58 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.51 (s, 1H), 7.36 (ddd, *J* = 7.8, 4.9, 0.9 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.28 – 7.26 (m, 2H), 7.21 – 7.20 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.3, 151.9, 150.4, 149.6, 148.4, 137.5, 133.6, 130.8, 130.8, 129.0, 128.9, 123.7.

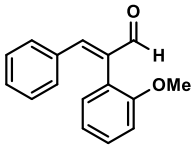
HRMS: Calculated $[M+H]^+$ for $C_{14}H_{12}NO^+$: 210.0913, found: 210.0916

Melting Point: 93.8 – 96.2 °C

FTIR (cm^{-1}): 3056, 2948, 2845, 2727, 1676, 1623, 1563, 1406, 1313, 1223, 1099, 1070, 1024, 931, 732.

[30] Liu, J., Wen, X., Qin, C., Li, X., Luo, X., Sun, A., Zhu, B., Song, S., Jiao, N. *Angew. Chem. Int. Ed.* **2017**, 56, 11940–11944.

(*E*)-2-(2-methoxyphenyl)-3-phenylacrylaldehyde (14o)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated aldehydes, (*Z*)-2-bromo-3-phenylacryaldehyde (5.0 g, 23.07 mmol), (2-methoxyphenyl)boronic acid (3.96 g, 26.07 mmol, 1.1 equiv.), K_2CO_3 (9.83 g, 71.1 mmol, 3.0 equiv.) and $Pd(PPh_3)_4$ (548 mg, 0.474 mmol, 2 mol%) were dissolved in a 7:3 mixture of Toluene:H_2O (80 mL, 0.3 M) and heated to 100 °C overnight under Argon atmosphere. After completion, the reaction was quenched with 50 mL of H_2O and extracted with EtOAc (50 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 90/10) to afford (*E*)-2-(2-methoxyphenyl)-3-phenylacrylaldehyde **14o** as a colorless oil (3.71 g, 68%).

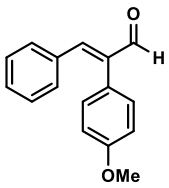
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.47 (s, 1H), 7.41 – 7.38 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.21 (m, 4H), 7.04 (ddd, *J* = 7.3, 2.0, 0.7 Hz, 1H), 7.01 – 6.98 (m, 2H), 3.69 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 157.2, 149.8, 139.1, 134.7, 130.8, 130.5, 130.2, 130.1, 128.6, 123.0, 121.3, 121.3, 111.6, 55.8.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{15}O_2^+$: 239.1067, found: 239.1078

FTIR (cm^{-1}): 3059, 3008, 2938, 2835, 1679, 1624, 1596, 1492, 1245, 1067, 1023, 749, 688.

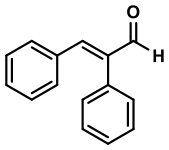
(*E*)-2-(4-methoxyphenyl)-3-phenylacrylaldehyde (14p)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated aldehydes, (*Z*)-2-bromo-3-phenylacryaldehyde (5.0 g, 23.07 mmol), (4-methoxyphenyl)boronic acid (3.96 g, 26.07 mmol, 1.1 equiv.), K_2CO_3 (9.83 g, 71.1 mmol, 3.0 equiv.) and $Pd(PPh_3)_4$ (548 mg, 0.474 mmol, 2 mol%) were dissolved in a 7:3 mixture of Toluene:H_2O (80 mL, 0.3 M) and heated to 100 °C overnight under Argon atmosphere. After completion, the reaction was quenched with 50 mL of H_2O and extracted with EtOAc (50 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 90/10) to afford (*E*)-2-(4-methoxyphenyl)-3-phenylacrylaldehyde **14p** as an off-white solid (3.26 g, 59%). NMR data matches the ones reported in the literature.[31]

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.35 (s, 1H), 7.32 – 7.29 (m, 1H), 7.28 – 7.25 (m, 4H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H).

(*E*)-2,3-diphenylacrylaldehyde (14q)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated aldehydes, (*Z*)-2-bromo-3-phenylacryaldehyde (1.0 g, 4.74 mmol), phenylboronic acid (595 mg, 4.88 mmol, 1.1 equiv.), K_2CO_3 (1.965 g, 14.22 mmol, 3.0 equiv.) and $Pd(PPh_3)_4$ (110 mg, 0.095 mmol, 2 mol%) were dissolved in a 7:3 mixture of Toluene:H_2O (16 mL, 0.3 M) and heated to 100 °C overnight under Argon atmosphere. After completion, the reaction was quenched with 5 mL of H_2O and extracted with EtOAc (20 mL x 3). The combined organic

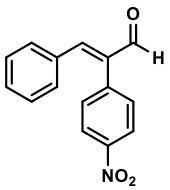
[31] Chuang, T.H., Chang, W.Y., Li, C.F., Wen, T.C., Tsai, C.C. *J. Org. Chem.* **2011**, *76*, 9678–9686.

layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 90/10) to afford (*E*)-2,3-diphenylacrylaldehyde **14q** as a white solid (756 mg, 76%). NMR data matches the ones reported in the literature.[32]

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.43 – 7.39 (m, 4H), 7.31 – 7.28 (m, 1H), 7.25 – 7.19 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 194.1, 150.3, 142.0, 134.2, 133.5, 130.9, 130.4, 1219.5, 129.0, 1128.7, 128.5.

(*E*)-2-(4-nitrophenyl)-3-phenylacrylaldehyde (14r)



Following **Method A** from the general procedures for the synthesis of α,ß-unsaturated aldehydes, (*Z*)-2-bromo-3-phenylacryaldehyde (5.0 g, 23.07 mmol), (2-nitrophenyl)boronic acid (4.35 g, 26.07 mmol, 1.1 equiv.), K_2CO_3 (9.83 g, 71.1 mmol, 3.0 equiv.) and $Pd(PPh_3)_4$ (548 mg, 0.474 mmol, 2 mol%) were dissolved in a 7:3 mixture of Toluene:H_2O (80 mL, 0.3 M) and heated to 100 °C overnight under Argon atmosphere. After completion, the reaction was quenched with 50 mL of H_2O and extracted with EtOAc (50 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 60/40) to afford (*E*)-2-(2-nitrophenyl)-3-phenylacrylaldehyde **14r** as a white solid (2.42 g, 40%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.27 (d, *J* = 8.9 Hz, 2H), 7.52 (s, 1H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.29 – 7.27 (m, 2H), 7.18 – 7.17 (m, 2H).

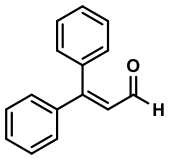
^{13}C NMR (150 MHz, $CDCl_3$) δ 192.7, 151.9, 147.9, 140.5, 139.9, 133.3, 131.1, 130.9, 130.8, 129.0, 124.1.

HRMS: Calculated $[M+H]^+$ for $C_{15}H_{12}NO_3^+$: 254.0812, found: 254.0817

Melting Point: 131.9 – 135.9 °C

FTIR (cm^{-1}): 3113, 3053, 2836, 1667, 1632, 1510, 1343, 1322, 1107, 1088, 931, 857, 716, 687.

3,3-diphenylacrylaldehyde (14u)



Following a modified literature procedure[33], bromobezene (1.47 g, 1.4 mmol, 1.05 equiv.), sodium acetate (843 mg, 10.3 mmol, 1.1 equiv.), and $Pd(OAc)_2$ (20 mg, 1 mol%) and were dissolved in *N*-methylpyrrolidine (12 mL, 0.75 M) and then cinnamaldehyde (1.182 g, 8.94 mmol, 1.0 equiv.) was added. The reaction mixture was heated to 120 °C overnight under Argon atmosphere. After completion, the reaction was quenched with 10 mL of H_2O and extracted with EtOAc (25 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 90/10) to afford 3,3-diphenylacrylaldehyde **14u** as a white solid (686 mg, 37%). NMR data matches the ones reported in the literature.[34]

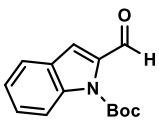
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.53 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.42 (d, 4H), 7.40 – 7.35 (m, 4H), 7.32 – 7.30 (d, 2H), 6.60 (d, *J* = 8.0 Hz, 1H)

[32] Liu, J., Wen, X., Qin, C., Li, X., Luo, X., Sun, A., Zhu, B., Song, S., Jiao, N. *Angew. Chem. Int. Ed.* **2017**, 56, 11940–11944.

[33] Zhdanko, A., Schmauder, A., Ma, C.I., Sibley, L. D., Sept, D., Sasse, F., Maier, M.E. *Chem. Eur. J.* **2011**, *17*, 13349–13357.

[34] Li, J., Tan, C., Gong, J., Yang, Z. *Org. Lett.* **2014**, *61*, 5370–5373.

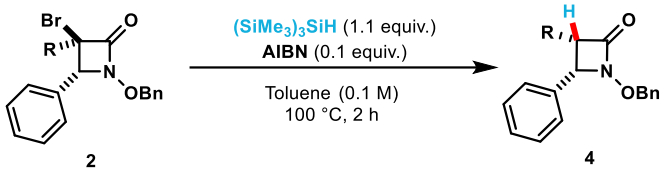
***tert*-Butyl 3-formyl-1*H*-indole-1-carboxylate (14ac)**



Indole-3-carboxaldehyde (5 g, 34.4 mmol) was dissolved in dry MeCN (344 mL, 0.2 M). Then Boc_2O (9.77 g, 44.8 mmol, 1.3 eq.) and DMAP (1.4 h, 11.5 mmol, 0.33 eq.) were added. The reaction was left stirring for 1 hour at room temperature. After completion, the reaction mixture was partitioned in 500 mL of a 1:1 mixture of DCM:H_2O and the organic layer was separated. The organic layer was dried over Na_2SO_4. Evaporation of the solvent afforded *tert*-Butyl 3-formyl-1*H*-indole-1-carboxylate **14ac** as an off-white solid (7.67 g, 41%). NMR data matches the ones reported in the literature.[35]

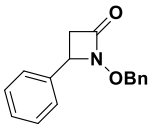
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.29 (m, 1H), 8.24 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.42 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 7.2, 1.1 Hz, 1H), 1.71 (s, 9H).

16. Procedures and characterization of functionalized β–lactams:



2 4

***rac*-1-(benzyloxy)-4-phenylazetidin-2-one (4b)**



In a flame-dried round-bottom flask, compound **2b** (332 mg, 1.0 mmol) and AIBN (16 mg, 0.1 equiv.) were dissolved in dry Toluene (10 mL, 0.1 M) under Argon atmosphere. $(SiMe)_3SiH$ (0.34 mL, 1.1 equiv.) was added and the reaction mixture was heated to 100 °C for 2 h. After completion, the reaction was allowed to cool down to room temperature, and then it was concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford rac-1-(benzyloxy)-4-phenylazetidin-2-one **4b** as a pale-yellow oil (189 mg, 79%).

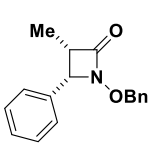
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 8H), 7.26 – 7.25 (m, 2H), 4.94 (d, *J* = 11.3 Hz, 1H), 4.86 (d, *J* = 11.3 Hz, 1H), 4.50 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.08 (dd, *J* = 13.9, 5.5 Hz, 1H), 2.60 (dd, *J* = 13.9, 2.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 137.3, 135.3, 129.1, 129.0, 129.0, 128.8, 128.7, 126.7, 78.2, 60.6, 42.2.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{16}NO_2^+$: 254.1176, found: 254.11777.

FTIR (cm^{-1}): 3080, 3062, 3033, 2953, 2881, 1766, 1496, 1455, 1365, 1036, 971, 742, 694.

***rac*-1-(benzyloxy)-3-methyl-4-phenylazetidin-2-one (4m)**



In a flame-dried round-bottom flask, compound **2m** (509 mg, 1.5 mmol) and AIBN (24 mg, 0.1 equiv.) were dissolved in dry Toluene (15 mL, 0.1 M) under Argon atmosphere. $(SiMe)_3SiH$ (0.50 mL, 1.1 equiv.) was added and the reaction mixture was heated to 100 °C

[35] Loy, N.S.Y., Singh, A., Xu, X., Park, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 2212–2216.

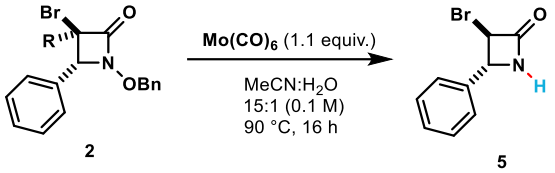
for 2 h. After completion, the reaction was allowed to cool down to room temperature, and then it was concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford rac-1-(benzyloxy)-3-methyl-4-phenylazetidin-2-one **4m** as a colorless oil (308 mg, 78%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 8H), 7.20 – 7.18 (m, 2H), 5.05 (d, *J* = 11.2 Hz, 1H), 4.99 (d, *J* = 11.1 Hz, 1H), 4.69 (d, *J* = 5.6 Hz, 1H), 3.20 (qd, *J* = 7.3, 5.2 Hz, 1H), 0.78 (d, *J* = 7.4 Hz, 3H).

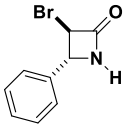
^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 135.3, 134.7, 129.1, 128.7, 128.6, 128.3, 127.4, 77.9, 65.1, 45.5, 9.8.

HRMS: Calculated $[M+H]^+$ for $C_{17}H_{18}NO_2^+$: 268.1332, found: 268.1337.

FTIR (cm^{-1}): 3063, 3033, 2973, 2932, 1761, 1496, 1455, 1378, 1365, 1061, 950, 736, 696.



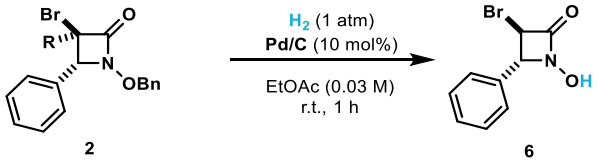
***rac*-3-bromo-4-phenylazetidin-2-one (5b)**



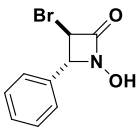
In a flame-dried round-bottom flask, compound **2b** (166 mg, 0.5 mmol) and $Mo(CO)_6$ (158 mg, 1.2 equiv.) were dissolved in a 1:1 mixture of MeCN:H_2O (2.5 mL, 0.2 M). The reaction mixture was heated to 100 °C for 16 h. After completion, the reaction was allowed to cool down to room temperature, and then it was concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford rac-3-bromo-4-phenylazetidin-2-one **5b** as an off-white solid (49 mg, 43%). NMR data matches the ones reported in the literature.[36]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.38 (m, 5H), 6.31 (bs, 1H), 4.83 (d, *J* = 2.0 Hz, 1H), 4.57 (t, *J* = 2.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 137.3, 129.4, 129.3, 125.8, 62.5, 51.5.



***rac*-3-bromo-1-hydroxy-4-phenylazetidin-2-one (6b)**



In a round-bottom flask, compound **2b** (332 mg, 1.0 mmol) was dissolved in EtOAc (33 mL, 0.03 M) and then 10 wt% Pd/C (77 mg) was added. The reaction mixture was purged with N_2 for 30 min. Then it was evacuated and filled with 1 balloon of H_2 (1 atm). The reaction was left stirring for 1 h. After completion, it was filtered over celite and the solvent was

[36] Bandini, E., Favi, G., Martelli, G., Panuzio, M., Piersanti, G. *Org. Lett.* **2000**, *2*, 1077−1079.

concentrated *in vacuo* to afford rac-3-bromo-1-hydroxy-4-phenylazetidin-2-one **6b** as a pale-orange solid (160 mg, 66%) without further purification.

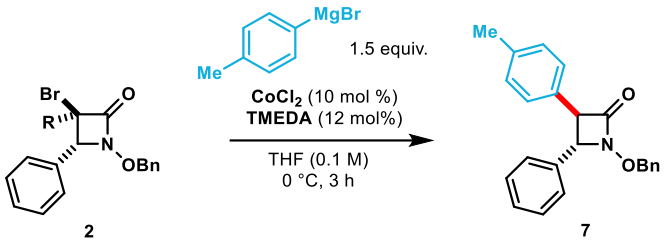
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 3H), 7.41 – 7.39 (m, 2H), 5.02 (d, *J* = 1.4 Hz, 1H), 4.36 (d, *J* = 1.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 133.6, 130.0, 129.5, 126.6, 72.9, 45.5.

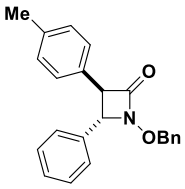
Melting Point: 100.8 – 105.3 °C

HRMS: Calculated $[M+H]^+$ for $C_9H_9BrNO_2^+$: 241.9812, found: 241.9813.

FTIR (cm^{-1}): 3059, 3030, 2956, 2888, 2812, 1761, 1453, 1351, 1200, 1172, 1053, 956, 789, 756, 726, 692.



***rac*-1-(benzylox)-4-phenyl-3-(*p*-tolyl)azetidin-2-one (7b)**



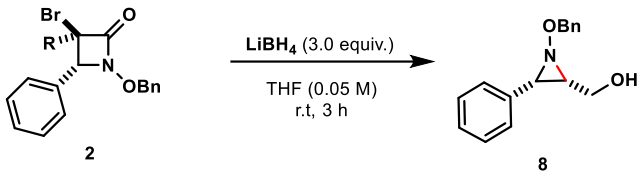
In a flame-dried round-bottom flask under Argon atmosphere, compound **2b** (166 mg, 0.5 mmol) was dissolved in dry THF (5.0 mL, 0.1 M). Then 1.0 mL of a 0.05 M solution of $CoCl_2$ in THF (10 mol%) was added, followed by TMEDA (9 µL, 12 mol%). The reaction mixture was cooled down to 0 °C using an ice/water bath. Then *p*-tolylmagnesium bromide (0.67 mL, 1.12 M in THF) was added *via* syringe pump (rate of addition = 40 µL/min). The reaction was then left stirring for 3 h after the addition was done still at 0 °C. After completion, the reaction was quenched with 5 mL of conc. NH_4Cl and extracted with EtOAc (15 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford rac-1-(benzyloxy)-4-phenyl-3-(*p*-tolyl)azetidin-2-one **7b** as a colorless oil (96 mg, 54%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 8H), 7.30 – 7.28 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.06 (d, *J* = 11.4 Hz, 1H), 4.95 (d, *J* = 11.4 Hz, 1H), 4.40 (d, *J* = 2.2 Hz, 1H), 3.85 (d, *J* = 2.2 Hz, 1H), 2.33 (s, 3H).

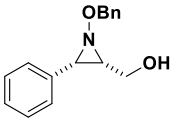
^{13}C NMR (150 MHz, $CDCl_3$) δ 165.3, 137.7, 136.6, 135.3, 131.0, 129.7, 129.3, 129.1, 128.9, 128.7, 127.4, 126.7, 78.2, 70.1, 60.6, 21.3.

HRMS: Calculated $[M+H]^+$ for $C_{23}H_{22}NO_2^+$: 344.1645, found: 344.1653.

FTIR (cm^{-1}): 3063, 3031, 2924, 1771, 1515, 1455, 1365, 1034, 957, 809, 742, 696.



***rac*-(1-(benzylox)-3-phenylaziridin-2-yl)methanol (8b)**



In a flame-dried round-bottom flask under Argon atmosphere, compound **2b** (166 mg, 0.5 mmol) was dissolved in dry THF (10.0 mL, 0.05 M). The reaction mixture was cooled down to 0 °C using an ice/water bath. Then a solution of $LiBH_4$ (0.27 mL, 4 M in THF) was added slowly. The reaction mixture was allowed to warm up to room temperature and was left stirring for 3 h. After completion, the reaction was quenched with 5 mL of distilled H_2O and extracted with EtOAc (20 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (70/30 hexanes:EtOAc) to afford rac-(1-(benzyloxy)- 3-phenylaziridin-2yl)methanol **8b** as a white crystalline solid (52.2 mg, 41%).

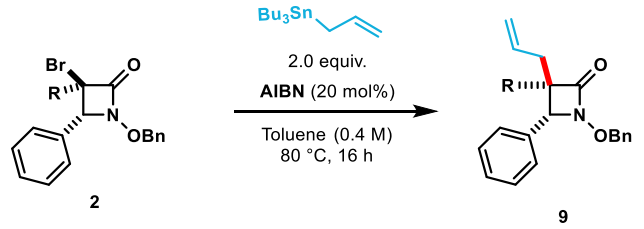
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.43 (m, 2H), 7.36 – 7.33 (m,3H), 7.21 – 7.18 (m, 3H), 6.89 – 6.87 (m, 2H), 4.90 (t, *J* = 5.7 Hz, 1H), 4.48 (d, *J* = 10.7 Hz, 1H), 4.13 (d, *J* = 10.7, 1H), 3.51 (ddd, *J* = 11.9, 5.6, 4.6 Hz, 1H), 3.41 (dt, *J* = 12.1, 6.2 Hz, 1H), 3.10 (d, *J* = 6.5 Hz, 1H), 2.95 (td, *J* = 6.5, 4.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 136.6, 132.4, 130.1, 128.4, 127.9, 127.6, 127.6, 127.5, 73.2, 60.9, 48.0, 47.1.

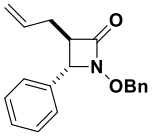
Melting Point: 89.8 – 91.0 °C

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{17}NO_2^+$: 256.1332, found: 256.1336.

FTIR (cm^{-1}): 3310, 3060, 3033, 2935, 2918, 2876, 1454, 1375, 1217, 1056, 1017, 978, 871, 751, 697.



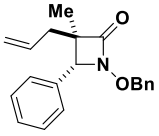
***rac*-3-allyl-1-(benzyloxy)-4-phenylazetidin-2-one (9b)**



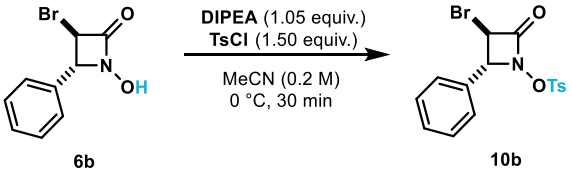
In a flame-dried round-bottom flask under Argon atmosphere, compound **2m** (69.2 mg, 0.2 mmol), AIBN (5.0 mg, 15 mol%) and allyltributyltin (132 mg, 2.0 equiv.) were dissolved in dry Toluene (0.5 mL, 0.4 M). Then the reaction was heated to 80 °C and left heating overnight. After completion, the reaction was allowed to cool down to room temperature and it was quenched with 1 mL of H_2O. The reaction mixture was extracted with EtOAc (5 mL x 3) and the combined organic layers were dried over Na_2SO_4. The reaction mixture was then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford rac-3-allyl-1-(benzyloxy)-4-phenylazetidin-2-one **9b** as a colorless oil (51 mg, 82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 8H), 7.23 – 7.22 (m, 2H), 5.72 (ddt, *J* = 17.0, 10.4, 6.7 Hz, 1H), 5.05 – 5.01 (m, 2H), 4.97 (d, *J* = 11.3 Hz, 1H), 4.87 (d, *J* = 11.3 Hz, 1H), 4.16 (d, *J* = 2.1 Hz, 1H), 2.82 (ddd, *J* = 9.0, 5.1, 2.2 Hz, 1H), 2.54 (dddt, *J* = 14.5, 6.4, 5.1, 1.4 Hz, 1H), 2.36 – 2.30 (m, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 137.0, 135.3, 134.0, 129.3, 129.3, 129.0, 128.7, 128.7, 126.7, 117.8, 78.1, 68.8, 54.7, 32.6.
HRMS: Calculated $[M+H]^+$ for $C_{19}H_{20}NO_2^+$: 294.1489, found: 294.1493.
FTIR (cm^{-1}): 3065, 3032, 3007, 2930, 1767, 1641, 1497, 1455, 1368, 995, 971, 911, 742, 696.

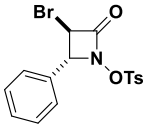
***rac*-3-allyl-1-(benzyloxy)-3-methyl-4-phenylazetidin-2-one (9m)**



In a flame-dried round-bottom flask under Argon atmosphere, compound **2m** (69.2 mg, 0.2 mmol), AIBN (5.0 mg, 15 mol%) and allyltributyltin (132 mg, 2.0 equiv.) were dissolved in dry Toluene (0.5 mL, 0.4 M). Then the reaction was heated to 80 °C and left heating overnight. After completion, the reaction was allowed to cool down to room temperature and it was quenched with 1 mL of H_2O. The reaction mixture was extracted with EtOAc (5 mL x 3) and the combined organic layers were dried over Na_2SO_4. The reaction mixture was then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford rac-3-allyl-1-(benzyloxy)-3-methyl-4-phenylazetidin-2-one **9m** as a colorless oil (51 mg, 82%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 7H), 7.32 – 7.29 (m, 1H), 7.18 – 7.16 (m, 2H), 5.75 (ddt, *J* = 16.8, 10.2, 7.3 Hz, 1H), 5.15 – 5.11 (m, 2H), 5.06 (d, *J* = 11.2 Hz, 1H), 5.00 (d, *J* = 11.3 Hz, 1H), 4.45 (s, 1H), 2.37 (ddt, *J* = 13.9, 7.3, 1.1 Hz, 2H), 2.30 (ddt, *J* = 14.0, 7.4, 1.2 Hz, 1H), 0.75 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 135.3, 135.3, 133.1, 129.3, 129.1, 128.7, 128.6, 128.2, 127.1, 119.3, 77.8, 70.0, 55.0, 40.5, 15.9.
HRMS: Calculated $[M+H]^+$ for $C_{20}H_{22}NO_2^+$: 308.1645, found: 308.1650.
FTIR (cm^{-1}): 3064, 3032, 3007, 2976, 2928, 1764, 1497, 1454, 1378, 1216, 1099, 983, 950, 914, 743, 696.

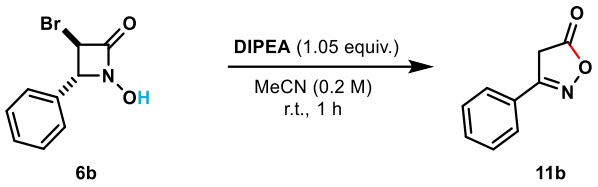


***rac*-3-bromo-2-oxo-4-phenylazetidin-1-yl 4-methylbenzenesulfonate (10b)**



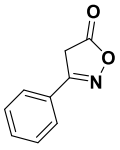
In a flame-dried round-bottom flask under Argon atmosphere, compound **6b** (711 mg, 3.0 mmol) and TsCl (841 mg, 1.5 equiv.) were dissolved in dry MeCN (15.0 mL, 0.2 M) and cooled down to 0 °C using an ice/water bath. Then Hunig's base (0.51 mL, 1.0 equiv.) was added slowly. After 30 min, the reaction was allowed to warm up to room temperature and it was then concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80/20 hexanes:EtOAc) to afford rac-3-bromo-2-oxo-4-phenylazetidin-1-yl 4-methylbenzenesulfonate **10b** as a pale-yellow solid (1.03 g, 88%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.40 (m, 5H), 7.30 – 7.28 (m, 2H), 5.14 (d, *J* = 1.8 Hz, 1H), 4.34 (d, *J* = 1.8 Hz, 1H), 2.49 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 147.3, 132.9, 130.5, 130.3, 130.2, 129.5, 129.5, 126.9, 73.4, 45.5, 22.1.
HRMS: Calculated $[M+H]^+$ for $C_{16}H_{15}BrNO_4S^+$: 395.9900, found: 395.9902.
FTIR (cm^{-1}): 3032, 2997, 2925, 1804, 1594, 1497, 1457, 1385, 1193, 1177, 1089, 1028, 941, 810, 765, 708, 695.



6b **11b**

3-phenylisoxazol-5(4*H*)-one (11b)

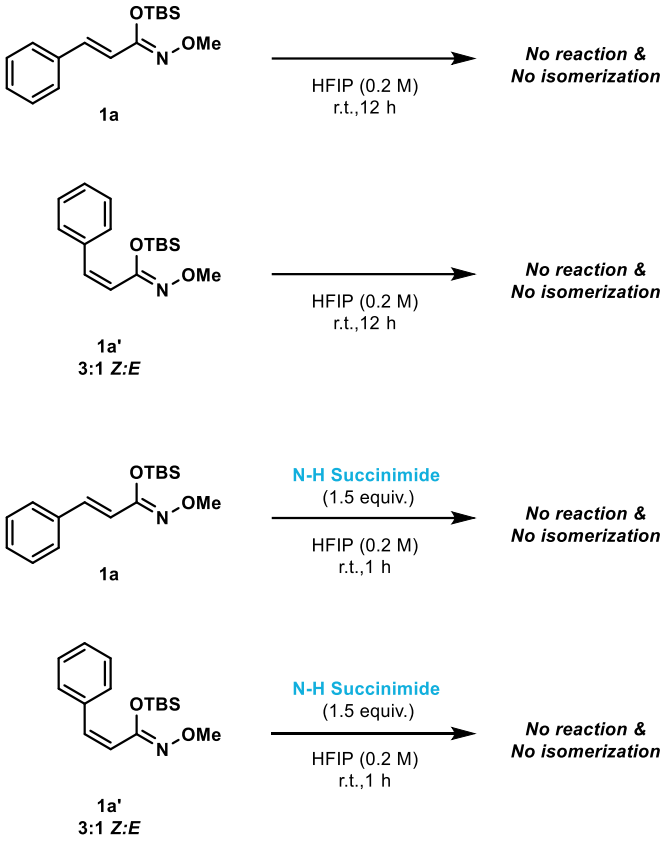


In a flame-dried round-bottom flask, compound **2b** (166 mg, 0.5 mmol) was dissolved in dry MeCN (2.5 mL, 0.2 M). Then Hunig's base (0.51 mL, 1.0 equiv.) was added slowly and it was left stirring at room temperature for 1 h. After completion, the reaction was concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (60/40 hexanes:EtOAc) to afford 3-phenylisoxazolo-5(4*H*)-one **10b** as a white powder (53 mg, 66%). NMR data matches the ones reported in the literature.[37]
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.67 (m, 2H), 7.56 – 7.53 (m, 1H), 7.50 – 7.47 (m, 2H), 3.81 (s, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 163.2, 132.3, 129.4, 127.8, 126.7, 34.2.

[37] Chang, M-Y., Chen, H-y., Tsai, Y-L. *Org. Lett.* **2019**, *21*, 1832−1836.

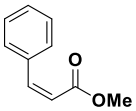
17. Control experiments and procedures and characterization for the synthesis of compound 2a':

Control Experiments:



Procedures and characterization for the synthesis of compound 2a':

(*Z*)-Methyl cinnamate (13a')

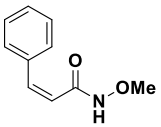


Following a modified literature procedure[38], (*E*)-methyl cinnamate (1.5 g, 1.0 equiv.) was dissolved in DCM (77 mL, 0.12 M) under Argon atmosphere. BF_3 etherate (1.3 mL, 0.5 equiv.) was added. The reaction was shone with 2 white desk lamps for 3 days at room temperature. After 3 days, the reaction was quenched with 80 mL of H_2O and extracted with DCM (80 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (Hexane/EtOAc = 97/3) to afford (*Z*)-Methyl cinnamate **13a'** as a colorless oil (942 mg, 63%). NMR data matches the ones reported in the literature.[39]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.38 – 7.32 (m, 3H), 6.96 (d, *J* = 12.6 Hz, 1H), 5.96 (d, *J* = 12.6 Hz, 1H), 3.72 (s, 3H).

[38] Lewis, F.D., Oxman, J. D., Gibson, L.L., Hampsoch, H. L., Quillen, S.L. *J. Am. Chem. Soc.* **1986**, *108(11)*, 3005–3015.
[39] Li, J., Tan, C., Gong, J., Yang, Z. *Org. Lett.* **2014**, *61*, 5370–5373.

(*Z*)-*N*-methoxycinnamamide (12a')



Following **Method B** from the general procedures for the synthesis of hydroxamate esters, in a flame-dried round-bottom flask under Argon atmosphere, $MeONH_2 \cdot HCl$ (958 mg, 11.47 mml, 2.0 equiv.) was suspended in dry Toluene (29 mL, 0.2 M). The reaction mixture was then cooled down to −40 °C using an acetone cooling bath. Then a solution of $AlMe_3$ (5.7 mL, 2M in toluene, 2.0 equiv.) was added dropwise avoiding a spike in temperature greater than 20 °C. After the addition was done, compound **13a'** (930 mg, 5.74 mmol, 1.0 equiv.) was added, the reaction was allowed to warm to room temperature, and it was allowed to stir overnight. The reaction was then quenched with 3M HCl until gas evolution ceased. The reaction mixture was then partitioned with 30 mL H_2O and extracted three times with 30 mL EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80:20 hexanes:EtOAc) to afford *N*-methoxycinnamamide **12a'** as a colorless oil (731 mg, 72%).

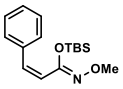
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.27 (s, 1H), 7.59 – 7.58 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.30 (m, 1H), 6.76 (d, *J* = 12.7 Hz, 1H), 5.87 (d, *J* = 12.7 Hz, 1H), 3.61 (s, 3H).

^{13}C NMR (150 MHz, DMSO-d_6) δ 163.3, 137.5, 135.0, 129.3, 128.5, 128.1, 121.1, 62.9.

HRMS: Calculated $[M+H]^+$ for $C_{10}H_{12}NO_2^+$: 178.0863, found: 178.0863.

FTIR (cm^{-1}): 3173, 2974, 2935, 1650, 1622, 1495, 1225, 1065, 978, 930, 852, 769, 691.

***tert*butyl dimethylsilyl (1*Z*,2*Z*)-*N*-methoxycinnanimidate (1a')**



Following the general procedures for the synthesis of silyl imino ethers, in a flame-dried round bottom flask under Argon atmosphere, compound **12a'** (695 mg, 3.92 mmol, 1.0 equiv.) was dissolved in dry THF (20 mL, 0.2 M) at room temperature. The reaction mixture was then cooled down to −78 °C using an acetone-dry ice bath. A solution of KHMDS (5.1 mL, 1.2 equiv., 1.0 M in THF) was then added slowly. TBSCl (706 mg, 1.2 equiv.) was then added, and the reaction was allowed to warm to room temperature. The reaction was left stirring for 60 min until full conversion was overserved by TLC. The reaction mixture was then partitioned with 20 mL of H_2O and extracted with 30 mL of EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The reaction crude was then purified by column chromatography on silica gel (93:7 hexanes:EtOAc) to afford *terbutyl* dimethylsilyl (*Z*)-*N*-methoxycinnanimidate **1a'** and compound **1a** as a colorless oil (646 mg, 60%) in a 3:1 mixture of inseparable diastereomers.

Data for 1a':

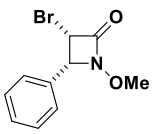
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 2H), 7.29 – 7.27 (m, 2H), 7.24 – 7.22 (m, 1H), 6.66 (d, *J* = 12.5 Hz, 1H), 5.94 (d, *J* = 12.5 Hz, 1H), 3.80 (s, 3H), 0.70 (s, 9H), -0.01 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 136.2, 135.6, 129.7, 128.0, 127.9, 120.7, 61.2, 25.5, 18.6, -4.3.

HRMS: Calculated $[M+H]^+$ for $C_{16}H_{26}NO_2Si^+$: 292.1727, found: 292.1732.

FTIR (cm^{-1}): 3060, 3028, 2952, 2931, 2898, 1579, 1471, 1463, 1297, 1252, 993, 823, 783, 693.

rac-3-bromo-1-methoxy-4-phenylazetidin-2-one (2a')



Following the general procedures for the synthesis of β–lactams, in an 8-mL scintillation vial open to air, compound **1a'** (145.7 mg, 0.5 mmol) was dissolved in HFIP (2.5 mL, 0.2 M). NBS (134.9 mg, 1.5 equiv.) was then added, and the reaction mixture was stirred for 60 min. After completion, the reaction was concentrated *in vacuo* and purified by column czhromatography on silica gel (90:10 Hexanes:EtOAc) to afford rac-3-bromo-1-methoxy-4-phenylazetidin-2one **2a'** as a white crystalline solid (22 mg, 18%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 3H), 7.36 – 7.35 (m, 2H), 5.26 (d, *J* = 5.2 Hz, 1H), 4.98 (d, *J* = 5.2 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 161.4, 133.3, 129.6, 128.6, 128.6, 128.2, 64.8, 64.2, 47.0.

HRMS: Calculated $[M+H]^+$ for $C_{10}H_{11}BrNO_2^+$: 255.9968, found: 255.9969.

Melting Point: 109.2 – 113.4 °C

FTIR (cm^{-1}): 3064, 3036, 3007, 2918, 1779, 1541, 1456, 1367, 1035, 968, 843, 750, 695.

18. X-Ray Data:

Data for **2j, 2k and 2a'** were collected using a Bruker APEX II diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The cell parameters were obtained from the least squares refinement of the spots (from 36 collected frames) using APEX 4 (Bruker-AXS, 2022). Data collection and absorption correction were performed using APEX 4 (Bruker-AXS, 2022) and refined by least squares methods using SHELXL2018 (Sheldrick, 2015). Initial atomic positions for XXX were located using intrinsic phasing. Calculated hydrogen atom positions were input and refined in a riding manner along with attached carbons. The crystallographic details for **2j, 2k and 2a'** are summarized below.

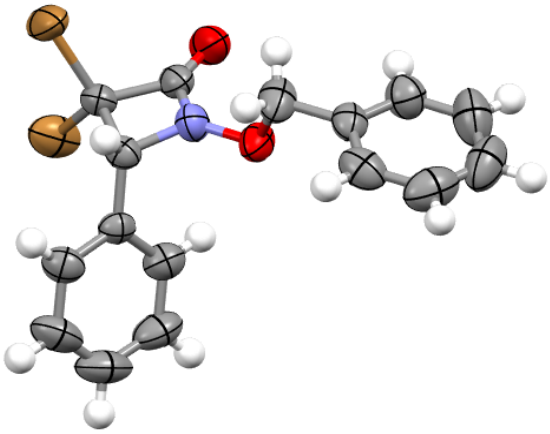


Table 3. Crystal data and structure refinement for C16 H13 Br2 N O2 (**2j**).

Identification code	**2j, CCDC: 2301303**	
Empirical formula	C16 H13 Br2 N O2	
Formula weight	411.09	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.9175(14) Å	a= 90°.
	b = 17.323(3) Å	b= 115.609(2)°.
	c = 10.7669(15) Å	g = 90°.
Volume	1668.1(4) $Å^3$	
Z	4	
Density (calculated)	1.637 Mg/m^3	
Absorption coefficient	4.862 mm^{-1}	
F(000)	808	

Crystal size	0.300 x 0.250 x 0.050 mm^3
Theta range for data collection	2.336 to 29.146°.
Index ranges	-13<=h<=13, -23<=k<=23, -14<=l<=14
Reflections collected	18321
Independent reflections	4466 [R(int) = 0.0367]
Completeness to theta = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.441
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4466 / 0 / 190
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1051
R indices (all data)	R1 = 0.0852, wR2 = 0.1234
Largest diff. peak and hole	0.798 and -0.763 e.$Å^{-3}$

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C16 H13 Br2 N O2 (**2j**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	7714(1)	990(1)	3078(1)	85(1)
Br(2)	7015(1)	492(1)	5556(1)	86(1)
O(1)	9537(3)	2027(2)	6164(3)	78(1)
O(2)	7070(3)	3253(1)	5095(3)	64(1)
N(1)	7126(3)	2486(2)	4797(3)	57(1)
C(1)	7183(3)	1338(2)	4502(3)	50(1)
C(2)	8248(4)	1980(2)	5355(4)	54(1)
C(3)	5904(4)	1953(2)	4015(3)	48(1)
C(4)	7352(6)	3744(2)	4137(4)	75(1)
C(5)	7397(4)	4546(2)	4634(4)	55(1)
C(6)	8668(5)	4823(3)	5697(4)	71(1)
C(7)	8718(7)	5550(3)	6191(6)	98(2)
C(8)	7515(8)	6018(3)	5671(6)	97(2)
C(9)	6236(7)	5766(3)	4609(6)	92(2)
C(10)	6168(5)	5027(3)	4093(4)	74(1)
C(11)	4698(3)	1899(2)	4496(3)	46(1)

C(12)	4951(4)	2121(2)	5814(4)	59(1)
C(13)	3829(6)	2066(3)	6235(5)	76(1)
C(14)	2448(5)	1784(3)	5350(6)	85(1)
C(15)	2197(5)	1559(3)	4056(5)	80(1)
C(16)	3308(4)	1620(2)	3622(4)	61(1)

Table 5. Bond lengths [Å] and angles [°] for C16 H13 Br2 N O2 (**2j**).

Br(1)-C(1)	1.922(3)
Br(2)-C(1)	1.904(3)
O(1)-C(2)	1.199(4)
O(2)-N(1)	1.375(4)
O(2)-C(4)	1.454(5)
N(1)-C(2)	1.337(5)
N(1)-C(3)	1.466(4)
C(1)-C(2)	1.536(5)
C(1)-C(3)	1.562(5)
C(3)-C(11)	1.498(4)
C(3)-H(3)	0.9800
C(4)-C(5)	1.482(5)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.372(5)
C(5)-C(10)	1.380(6)
C(6)-C(7)	1.361(7)
C(6)-H(6)	0.9300
C(7)-C(8)	1.348(8)
C(7)-H(7)	0.9300
C(8)-C(9)	1.361(8)
C(8)-H(8)	0.9300
C(9)-C(10)	1.386(7)
C(9)-H(9)	0.9300
C(10)-H(10)	0.9300
C(11)-C(16)	1.377(5)
C(11)-C(12)	1.385(5)

C(12)-C(13)	1.374(6)
C(12)-H(12)	0.9300
C(13)-C(14)	1.376(7)
C(13)-H(13)	0.9300
C(14)-C(15)	1.363(7)
C(14)-H(14)	0.9300
C(15)-C(16)	1.374(6)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
N(1)-O(2)-C(4)	111.1(3)
C(2)-N(1)-O(2)	129.6(3)
C(2)-N(1)-C(3)	99.6(3)
O(2)-N(1)-C(3)	129.6(3)
C(2)-C(1)-C(3)	87.5(2)
C(2)-C(1)-Br(2)	114.6(2)
C(3)-C(1)-Br(2)	117.2(2)
C(2)-C(1)-Br(1)	110.5(2)
C(3)-C(1)-Br(1)	114.1(2)
Br(2)-C(1)-Br(1)	111.00(17)
O(1)-C(2)-N(1)	134.6(4)
O(1)-C(2)-C(1)	136.5(4)
N(1)-C(2)-C(1)	89.0(3)
N(1)-C(3)-C(11)	115.2(3)
N(1)-C(3)-C(1)	83.5(2)
C(11)-C(3)-C(1)	119.7(3)
N(1)-C(3)-H(3)	111.8
C(11)-C(3)-H(3)	111.8
C(1)-C(3)-H(3)	111.8
O(2)-C(4)-C(5)	106.0(3)
O(2)-C(4)-H(4A)	110.5
C(5)-C(4)-H(4A)	110.5
O(2)-C(4)-H(4B)	110.5
C(5)-C(4)-H(4B)	110.5
H(4A)-C(4)-H(4B)	108.7
C(6)-C(5)-C(10)	117.8(4)
C(6)-C(5)-C(4)	120.1(4)

C(10)-C(5)-C(4)	122.1(4)
C(7)-C(6)-C(5)	121.0(5)
C(7)-C(6)-H(6)	119.5
C(5)-C(6)-H(6)	119.5
C(8)-C(7)-C(6)	121.2(5)
C(8)-C(7)-H(7)	119.4
C(6)-C(7)-H(7)	119.4
C(7)-C(8)-C(9)	119.5(5)
C(7)-C(8)-H(8)	120.2
C(9)-C(8)-H(8)	120.2
C(8)-C(9)-C(10)	119.9(5)
C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0
C(5)-C(10)-C(9)	120.6(4)
C(5)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(16)-C(11)-C(12)	118.8(3)
C(16)-C(11)-C(3)	119.9(3)
C(12)-C(11)-C(3)	121.3(3)
C(13)-C(12)-C(11)	120.3(4)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(14)	120.1(4)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	119.8(4)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	120.4(4)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-C(11)	120.6(4)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7

Symmetry transformations used to generate equivalent atoms:

Table 6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C16 H13 Br2 N O2 (**2j**). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	67(1)	116(1)	82(1)	-45(1)	43(1)	-14(1)
Br(2)	79(1)	63(1)	123(1)	33(1)	52(1)	19(1)
O(1)	49(2)	103(2)	73(2)	-32(2)	18(1)	-6(1)
O(2)	90(2)	44(1)	76(2)	-4(1)	53(2)	-10(1)
N(1)	57(2)	45(2)	71(2)	-4(1)	29(2)	-6(1)
C(1)	42(2)	54(2)	57(2)	-3(2)	24(2)	-2(1)
C(2)	49(2)	64(2)	52(2)	-12(2)	25(2)	-6(2)
C(3)	47(2)	51(2)	44(2)	4(1)	20(1)	-2(1)
C(4)	113(3)	58(2)	70(2)	-4(2)	56(3)	-17(2)
C(5)	71(2)	49(2)	51(2)	2(2)	33(2)	-10(2)
C(6)	71(3)	66(3)	70(2)	2(2)	25(2)	-2(2)
C(7)	120(4)	79(4)	82(3)	-15(3)	31(3)	-32(3)
C(8)	160(6)	57(3)	92(4)	-6(3)	70(4)	-5(3)
C(9)	116(4)	76(3)	105(4)	31(3)	69(4)	32(3)
C(10)	67(2)	88(3)	62(2)	17(2)	24(2)	-8(2)
C(11)	45(2)	43(2)	51(2)	8(1)	23(1)	9(1)
C(12)	63(2)	61(2)	59(2)	5(2)	31(2)	8(2)
C(13)	99(3)	76(3)	79(3)	13(2)	62(3)	22(2)
C(14)	76(3)	89(3)	119(4)	34(3)	69(3)	24(2)
C(15)	49(2)	93(3)	100(3)	22(3)	35(2)	5(2)
C(16)	50(2)	69(2)	61(2)	7(2)	21(2)	4(2)

Table 7. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^{\ 3}$) for C16 H13 Br2 N O2 (**2j**).

	x	y	z	U(eq)

H(3)	5495	2046	3021	57
H(4A)	6562	3687	3213	90
H(4B)	8297	3610	4127	90
H(6)	9508	4508	6085	86
H(7)	9599	5728	6901	117
H(8)	7559	6509	6035	117
H(9)	5408	6090	4230	110
H(10)	5289	4854	3376	88
H(12)	5885	2307	6418	71
H(13)	4003	2220	7119	92
H(14)	1688	1748	5635	102
H(15)	1268	1362	3462	96
H(16)	3120	1473	2732	73

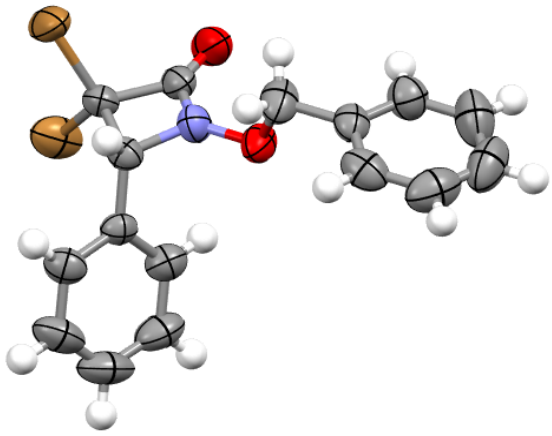


Table 8. Crystal data and structure refinement for C16 H13 Br Cl N O2 (**2k**).

Identification code	**2k, CCDC: 2301304**	
Empirical formula	C16 H13 Br Cl N O2	
Formula weight	366.63	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.915(3) Å	a= 90°.
	b = 17.251(6) Å	b= 115.375(5)°.
	c = 10.682(3) Å	g = 90°.
Volume	1650.8(9) $Å^3$	
Z	4	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	2.654 mm^{-1}	
F(000)	736	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.347 to 31.775°.	
Index ranges	-14<=h<=14, -25<=k<=25, -15<=l<=15	
Reflections collected	20864	
Independent reflections	5570 [R(int) = 0.0363]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.602	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5570 / 0 / 190
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1286
R indices (all data)	R1 = 0.0992, wR2 = 0.1519
Extinction coefficient	n/a
Largest diff. peak and hole	0.745 and -0.663 e.Å^{-3}

Table 9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for C16 H13 Br Cl N O2 (**2k**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2269(1)	904(1)	6744(1)	91(1)
Cl(1)	3019(1)	542(1)	4334(1)	86(1)
O(1)	485(2)	2002(2)	3689(2)	86(1)
O(2)	2927(2)	3235(1)	4845(2)	66(1)
N(1)	2872(2)	2456(1)	5105(2)	61(1)
C(1)	2822(3)	1299(2)	5337(3)	54(1)
C(2)	1769(3)	1951(2)	4513(3)	58(1)
C(3)	4103(3)	1918(1)	5881(3)	51(1)
C(4)	5309(3)	1878(1)	5398(2)	50(1)
C(5)	5086(3)	2131(2)	4093(3)	63(1)
C(6)	6217(5)	2083(2)	3673(4)	82(1)
C(7)	7568(4)	1781(2)	4533(5)	91(1)
C(8)	7807(4)	1524(2)	5829(4)	89(1)
C(9)	6689(3)	1574(2)	6278(3)	66(1)
C(10)	2587(4)	3705(2)	5809(3)	74(1)
C(11)	2584(3)	4522(2)	5362(3)	58(1)
C(12)	3829(4)	4992(2)	5946(3)	78(1)
C(13)	3793(6)	5744(2)	5465(5)	98(1)
C(14)	2528(6)	6019(2)	4411(5)	102(1)
C(15)	1307(6)	5565(2)	3838(4)	101(1)
C(16)	1326(4)	4821(2)	4299(3)	76(1)

Table 10. Bond lengths [Å] and angles [°] for C16 H13 Br Cl N O2 (**2k**).

Br(1)-C(1)	1.930(3)
Cl(1)-C(1)	1.752(3)
O(1)-C(2)	1.202(3)
O(2)-N(1)	1.377(3)
O(2)-C(10)	1.459(3)
N(1)-C(2)	1.327(3)
N(1)-C(3)	1.474(3)
C(1)-C(2)	1.531(4)
C(1)-C(3)	1.569(3)
C(3)-C(4)	1.493(3)
C(3)-H(3)	0.9800
C(4)-C(5)	1.386(4)
C(4)-C(9)	1.389(4)
C(5)-C(6)	1.377(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.362(6)
C(6)-H(6)	0.9300
C(7)-C(8)	1.374(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.386(5)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-C(11)	1.488(4)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(16)	1.378(4)
C(11)-C(12)	1.382(4)
C(12)-C(13)	1.391(6)
C(12)-H(12)	0.9300
C(13)-C(14)	1.362(6)
C(13)-H(13)	0.9300
C(14)-C(15)	1.349(6)
C(14)-H(14)	0.9300
C(15)-C(16)	1.371(5)

C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
N(1)-O(2)-C(10)	111.0(2)
C(2)-N(1)-O(2)	129.8(2)
C(2)-N(1)-C(3)	99.7(2)
O(2)-N(1)-C(3)	129.3(2)
C(2)-C(1)-C(3)	87.47(19)
C(2)-C(1)-Cl(1)	115.06(19)
C(3)-C(1)-Cl(1)	116.70(17)
C(2)-C(1)-Br(1)	110.87(17)
C(3)-C(1)-Br(1)	114.01(17)
Cl(1)-C(1)-Br(1)	110.87(14)
O(1)-C(2)-N(1)	134.4(3)
O(1)-C(2)-C(1)	136.2(3)
N(1)-C(2)-C(1)	89.4(2)
N(1)-C(3)-C(4)	115.3(2)
N(1)-C(3)-C(1)	82.95(18)
C(4)-C(3)-C(1)	118.8(2)
N(1)-C(3)-H(3)	112.2
C(4)-C(3)-H(3)	112.2
C(1)-C(3)-H(3)	112.2
C(5)-C(4)-C(9)	119.1(3)
C(5)-C(4)-C(3)	121.8(2)
C(9)-C(4)-C(3)	119.1(2)
C(6)-C(5)-C(4)	120.5(3)
C(6)-C(5)-H(5)	119.7
C(4)-C(5)-H(5)	119.7
C(7)-C(6)-C(5)	120.4(3)
C(7)-C(6)-H(6)	119.8
C(5)-C(6)-H(6)	119.8
C(6)-C(7)-C(8)	119.9(3)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(7)-C(8)-C(9)	120.7(3)
C(7)-C(8)-H(8)	119.6
C(9)-C(8)-H(8)	119.6

C(8)-C(9)-C(4)	119.4(3)
C(8)-C(9)-H(9)	120.3
C(4)-C(9)-H(9)	120.3
O(2)-C(10)-C(11)	105.6(2)
O(2)-C(10)-H(10A)	110.6
C(11)-C(10)-H(10A)	110.6
O(2)-C(10)-H(10B)	110.6
C(11)-C(10)-H(10B)	110.6
H(10A)-C(10)-H(10B)	108.8
C(16)-C(11)-C(12)	118.0(3)
C(16)-C(11)-C(10)	119.8(3)
C(12)-C(11)-C(10)	122.2(3)
C(11)-C(12)-C(13)	120.3(3)
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-H(12)	119.9
C(14)-C(13)-C(12)	119.9(4)
C(14)-C(13)-H(13)	120.0
C(12)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	120.2(4)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(14)-C(15)-C(16)	120.6(4)
C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7
C(15)-C(16)-C(11)	121.0(4)
C(15)-C(16)-H(16)	119.5
C(11)-C(16)-H(16)	119.5

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C16 H13 Br Cl N O2 (**2k**). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	71(1)	120(1)	90(1)	46(1)	42(1)	9(1)
Cl(1)	81(1)	67(1)	119(1)	-34(1)	51(1)	-22(1)
O(1)	50(1)	115(2)	79(1)	32(1)	13(1)	2(1)
O(2)	90(1)	50(1)	77(1)	3(1)	52(1)	10(1)
N(1)	56(1)	51(1)	74(1)	5(1)	26(1)	7(1)
C(1)	50(1)	58(1)	57(1)	5(1)	26(1)	-2(1)
C(2)	50(1)	72(2)	56(1)	15(1)	25(1)	4(1)
C(3)	50(1)	54(1)	48(1)	-2(1)	20(1)	1(1)
C(4)	49(1)	49(1)	51(1)	-9(1)	22(1)	-9(1)
C(5)	69(2)	65(2)	58(2)	-5(1)	31(1)	-9(1)
C(6)	101(3)	87(2)	80(2)	-19(2)	61(2)	-27(2)
C(7)	82(2)	106(3)	111(3)	-39(2)	67(2)	-28(2)
C(8)	53(2)	106(3)	106(3)	-22(2)	32(2)	0(2)
C(9)	52(2)	78(2)	66(2)	-4(1)	22(1)	0(1)
C(10)	105(2)	66(2)	68(2)	9(1)	51(2)	22(2)
C(11)	71(2)	56(1)	50(1)	-3(1)	31(1)	10(1)
C(12)	74(2)	90(2)	66(2)	-17(2)	26(2)	6(2)
C(13)	119(3)	83(2)	110(3)	-36(2)	65(3)	-31(2)
C(14)	162(5)	62(2)	95(3)	-1(2)	68(3)	2(2)
C(15)	126(3)	88(3)	80(2)	21(2)	35(2)	41(2)
C(16)	77(2)	73(2)	70(2)	2(2)	24(2)	9(2)

Table 12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for C16 H13 Br Cl N O2 (**2k**).

	x	y	z	U(eq)
H(3)	4500	1995	6885	61
H(5)	4166	2335	3496	75
H(6)	6058	2258	2797	98
H(7)	8328	1749	4243	109
H(8)	8728	1315	6411	107
H(9)	6862	1405	7161	80
H(10A)	3338	3631	6751	89
H(10B)	1619	3566	5765	89
H(12)	4694	4804	6664	94
H(13)	4632	6059	5862	118
H(14)	2506	6521	4086	122
H(15)	444	5757	3124	122
H(16)	477	4514	3888	91

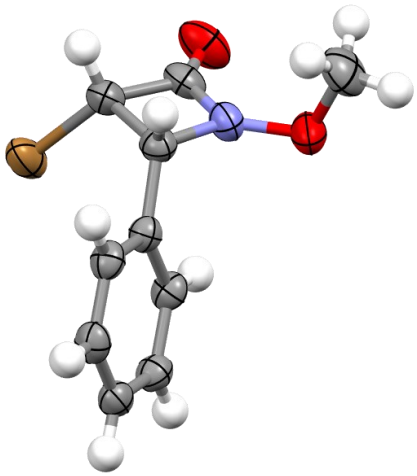


Table 13. Crystal data and structure refinement for C10 H10 Br N O2 (**2a'**).

Identification code	**2a', CCDC: 2302628**	
Empirical formula	C10 H10 Br N O2	
Formula weight	256.10	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.6110(6) Å	a= 90°.
	b = 7.1772(8) Å	b= 90°.
	c = 25.602(3) Å	g = 90°.
Volume	1031.0(2) $Å^3$	
Z	4	
Density (calculated)	1.650 Mg/m^3	
Absorption coefficient	3.959 mm^{-1}	
F(000)	512	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.948 to 31.875°.	
Index ranges	-8<=h<=8, -10<=k<=10, -37<=l<=37	
Reflections collected	13720	
Independent reflections	3540 [R(int) = 0.0290]	
Completeness to theta = 25.000°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.741 and 0.546
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3540 / 0 / 129
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0807
R indices (all data)	R1 = 0.0547, wR2 = 0.0873
Absolute structure parameter	0.272(14)
Extinction coefficient	n/a
Largest diff. peak and hole	0.691 and -0.528 e.$Å^{-3}$

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C10 H10 Br N O2 (**2a'**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2011(1)	10502(1)	3815(1)	62(1)
O(1)	6339(6)	8912(4)	4718(1)	66(1)
O(2)	7023(5)	5146(4)	4155(1)	58(1)
N(1)	5240(5)	6449(4)	4166(1)	44(1)
C(1)	5044(7)	8069(5)	4430(1)	44(1)
C(2)	2502(6)	8278(5)	4221(1)	43(1)
C(3)	2871(6)	6396(5)	3924(1)	39(1)
C(4)	2805(6)	6341(4)	3335(1)	34(1)
C(5)	4634(5)	7105(5)	3040(1)	38(1)
C(6)	4497(6)	7100(5)	2502(1)	40(1)
C(7)	2541(5)	6320(4)	2255(1)	39(1)
C(8)	732(5)	5542(5)	2546(1)	41(1)
C(9)	872(5)	5550(5)	3086(1)	38(1)
C(10)	6678(10)	3740(6)	4536(2)	65(1)

Table 15. Bond lengths [Å] and angles [°] for C10 H10 Br N O2 (**2a'**).

Br(1)-C(2)	1.925(3)
O(1)-C(1)	1.199(4)
O(2)-N(1)	1.369(4)
O(2)-C(10)	1.417(5)
N(1)-C(1)	1.350(5)
N(1)-C(3)	1.466(4)
C(1)-C(2)	1.531(5)
C(2)-C(3)	1.564(5)
C(2)-H(2)	0.9800
C(3)-C(4)	1.508(4)
C(3)-H(3)	0.9800
C(4)-C(9)	1.380(4)
C(4)-C(5)	1.388(4)
C(5)-C(6)	1.378(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.385(5)
C(6)-H(6)	0.9300
C(7)-C(8)	1.378(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.386(4)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600

N(1)-O(2)-C(10)	111.9(3)
C(1)-N(1)-O(2)	131.1(3)
C(1)-N(1)-C(3)	99.2(3)
O(2)-N(1)-C(3)	129.5(3)
O(1)-C(1)-N(1)	133.9(4)
O(1)-C(1)-C(2)	136.9(4)
N(1)-C(1)-C(2)	89.2(3)
C(1)-C(2)-C(3)	87.8(3)

C(1)-C(2)-Br(1)	113.8(2)
C(3)-C(2)-Br(1)	118.2(2)
C(1)-C(2)-H(2)	111.7
C(3)-C(2)-H(2)	111.7
Br(1)-C(2)-H(2)	111.7
N(1)-C(3)-C(4)	116.4(3)
N(1)-C(3)-C(2)	83.8(2)
C(4)-C(3)-C(2)	120.3(3)
N(1)-C(3)-H(3)	111.2
C(4)-C(3)-H(3)	111.2
C(2)-C(3)-H(3)	111.2
C(9)-C(4)-C(5)	119.5(3)
C(9)-C(4)-C(3)	119.4(3)
C(5)-C(4)-C(3)	121.1(3)
C(6)-C(5)-C(4)	120.1(3)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(5)-C(6)-C(7)	120.1(3)
C(5)-C(6)-H(6)	119.9
C(7)-C(6)-H(6)	119.9
C(8)-C(7)-C(6)	120.0(3)
C(8)-C(7)-H(7)	120.0
C(6)-C(7)-H(7)	120.0
C(7)-C(8)-C(9)	119.8(3)
C(7)-C(8)-H(8)	120.1
C(9)-C(8)-H(8)	120.1
C(4)-C(9)-C(8)	120.5(3)
C(4)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
O(2)-C(10)-H(10A)	109.5
O(2)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(2)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C10 H10 Br N O2 (**2a'**). The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	91(1)	51(1)	43(1)	-1(1)	-12(1)	26(1)
O(1)	77(2)	63(2)	58(2)	4(1)	-28(2)	-13(2)
O(2)	48(1)	68(2)	57(1)	18(1)	7(1)	19(1)
N(1)	40(1)	49(2)	43(1)	4(1)	-7(1)	5(1)
C(1)	52(2)	45(2)	35(2)	11(1)	-6(1)	-3(2)
C(2)	47(2)	49(2)	33(1)	2(1)	-2(1)	5(1)
C(3)	36(1)	43(2)	37(1)	4(1)	1(1)	-2(1)
C(4)	34(1)	31(1)	38(1)	-2(1)	0(1)	0(1)
C(5)	31(2)	38(2)	44(2)	-2(1)	2(1)	-5(1)
C(6)	39(2)	38(2)	42(2)	1(1)	7(1)	0(1)
C(7)	44(2)	36(1)	37(1)	-4(1)	-2(1)	4(1)
C(8)	35(2)	40(2)	48(2)	-7(2)	-7(1)	-1(2)
C(9)	31(1)	37(1)	47(2)	2(1)	3(1)	-2(1)
C(10)	84(3)	46(2)	66(2)	14(2)	-10(2)	6(2)

Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for C10 H10 Br N O2 (**2a'**).

	x	y	z	U(eq)
H(2)	1317	8158	4500	51
H(3)	1890	5403	4075	47
H(5)	5955	7620	3205	45
H(6)	5720	7620	2305	48
H(7)	2449	6323	1892	47
H(8)	-579	5013	2380	49
H(9)	-345	5018	3283	46
H(10A)	7140	4205	4873	98
H(10B)	7632	2673	4450	98
H(10C)	5027	3388	4544	98

19. Computational Studies:

In the main manuscript geometry optimizations were performed in Gaussian 16 revision B.01[40] with M06-2X[41]/6-31G**[LANL2DZ for Br][42,43] with SMD[44] solvation model for acetonitrile. In Figure S1 below the same method and basis set was used, but the SMD model for trifluoroethanol was used instead of acetonitrile. Conformational structure searching was carried out using the CREST[45] code (6.2.3) with GFN2-xTB[46] and the lowest 10 were then optimized with M06-2X. Vibrational frequencies were calculated for verification of minima or transition states. The carbocation C-C bond rotation transition state was located using the nudged elastic band (NEB) method in ORCA 5.0[47] with M06-2X/def2-SVP (see Figure below for NEB profile). The resulting NEB structure was then further optimized in Gaussian 16 keeping the dihedral angle restrained. This provided the ability to have a M06-2X/6-31G**[LANL2DZ for Br] energy with SMD solvation.

Because HFIP solvent is not available in Gaussian 16, for an estimate of a fluorinated alcohol solvent we re-optimized all structures presented in the main manuscript with the SMD solvent model for trifluoroethanol. The energy surface is shown in Figure S1. Comparison with the main manuscript shows very small energy differences compared to acetonitrile solvent.

[40] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision B.01; Gaussian Inc., Wallingford CT, 2016.

[41] Y. Zhao and D. G. Truhlar., *Theor. Chem. Acc.*, **2008**, 120, 215–241.

[42] R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, **1971**, 54, 724–728.

[43] P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, **1985**, 82, 270–283.

[44] A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B.*, **2009**, 113, 6378–6396.

[45] P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, **2020**, 22, 7169–7192.

[46] C. Bannwarth, S. Ehlert and S. Grimme, *J. Chem. Theory Comput.*, **2019**, 15, 1652–1671.

[47] F. Neese, Software update: The ORCA program system—Version 5.0, WIREs Computational Molecular Science, 2022, 12, e1606.

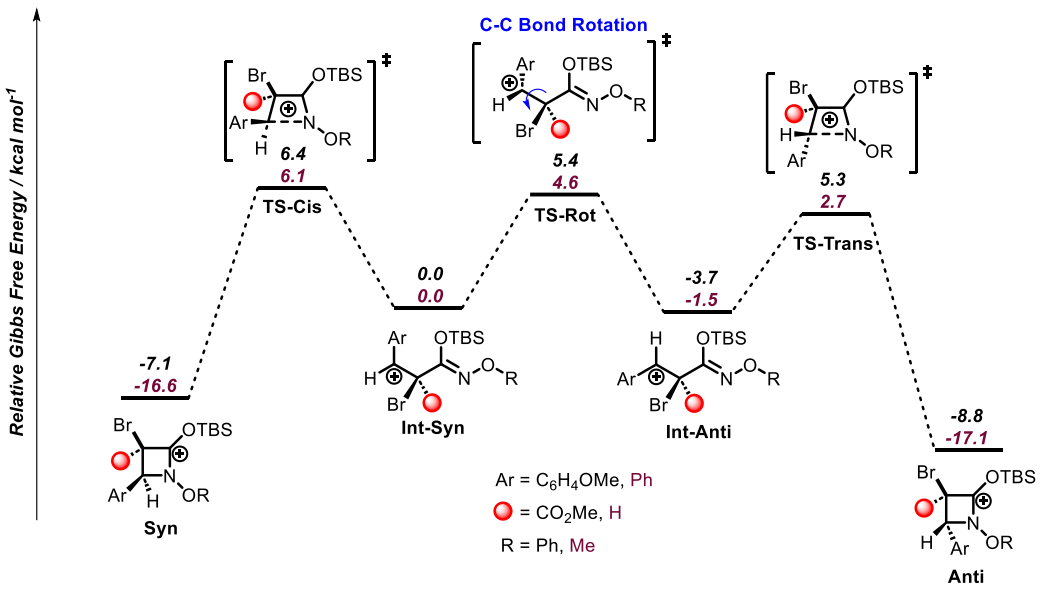


Figure S1. Energy surface for ring closing transition states and C–C bond rotation (derived from 1y and 1a') using the SMD trifluoroethanol solvent model.

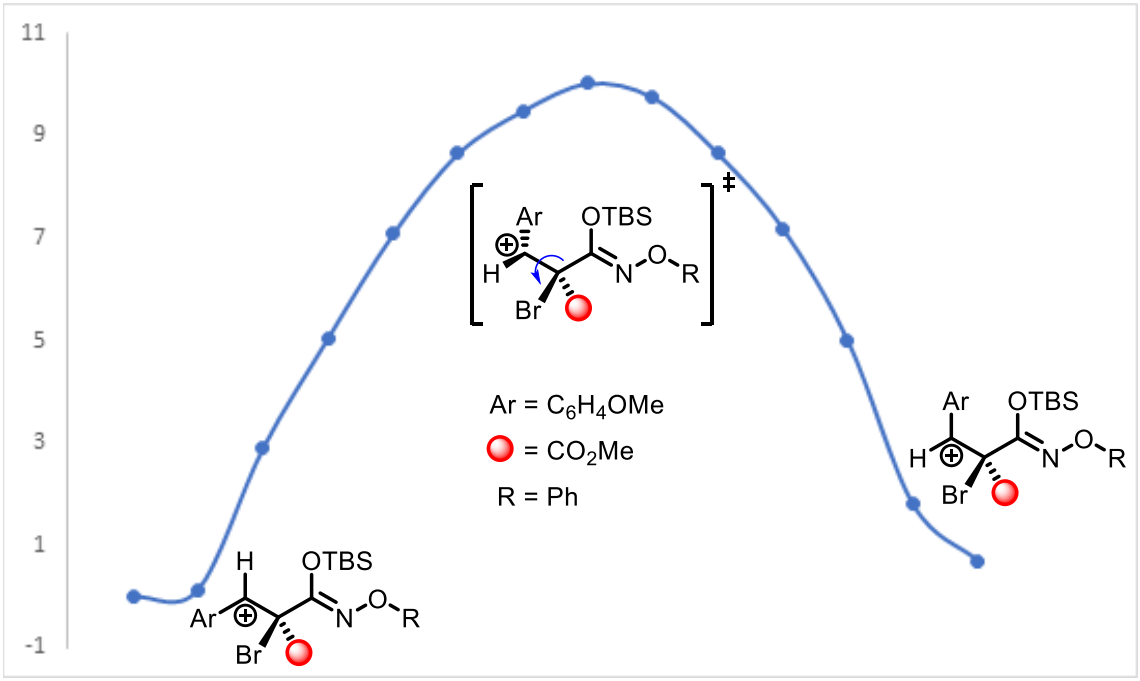


Figure S2. Lowest energy structure profile obtained from nudge elastic band calculations for C⍰C bond rotation.

Because there is no HFIP continuum solvent model in Gaussian, for the bromination reaction step we evaluated the thermodynamics for generating the carbocation intermediate. Assuming NBS is a source of Br_2, Figure S3a shows the energy for forming the benzylic cation in the gas phase and implicit trifluoroethanol. Figure S3b shows the energy using two explicit HFIP molecules, which shows 16 kcal/mol reduction in the thermodynamic energy change that is likely linked to the kinetics of bromination.

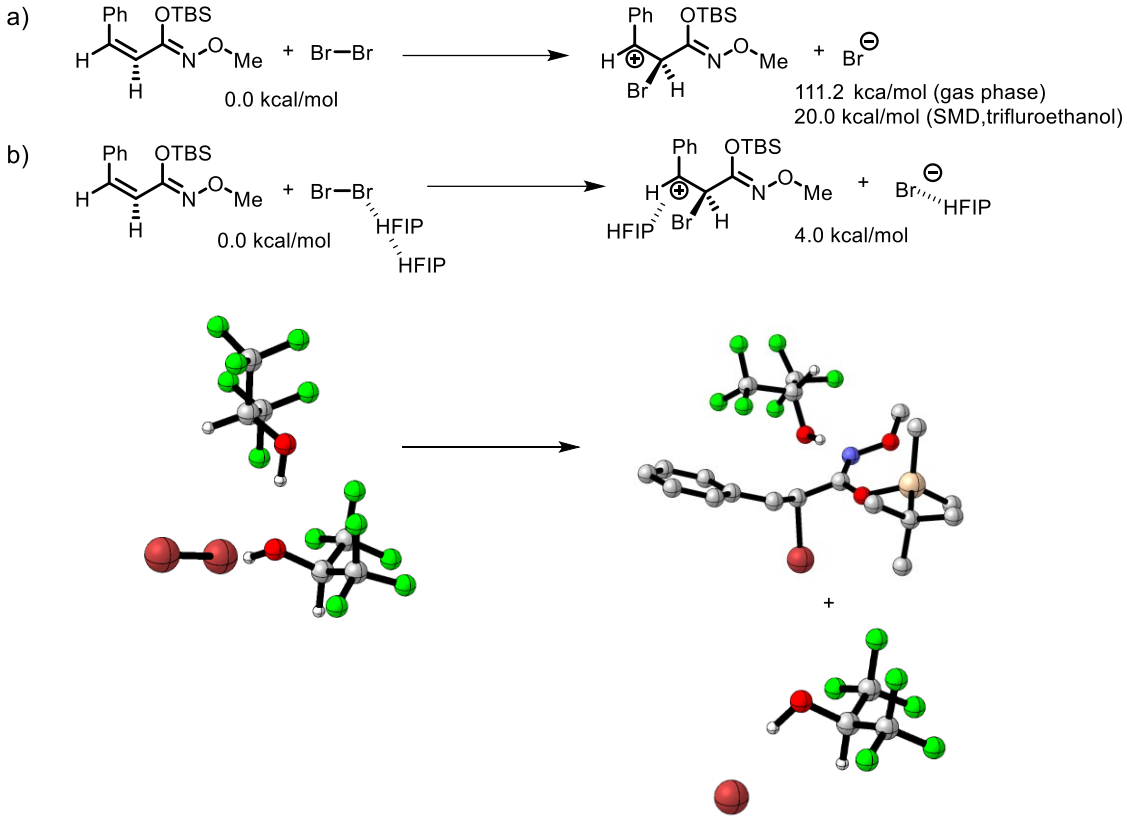


Figure S3. a) Thermodynamics for formation of the benzylic carbocation from 1a' in the gas phase and implicit trifluoroethanol b) with 2 explicit HFIP moleucles. 3D depiction of explicitly solvated Br2 and benzylic carbocation are included.

Absolute Energies and Xyz Structures

1a' Int-Syn

Zero-point correction= 0.384761 (Hartree/Particle)
Thermal correction to Energy= 0.410480
Thermal correction to Enthalpy= 0.411424
Thermal correction to Gibbs Free Energy= 0.326391
Sum of electronic and zero-point Energies= -1131.605445
Sum of electronic and thermal Energies= -1131.579727
Sum of electronic and thermal Enthalpies= -1131.578782
Sum of electronic and thermal Free Energies= -1131.663815

C	4.321136000000	1.505084000000	-0.557945000000
C	5.632573000000	1.284832000000	-0.206830000000
C	3.309019000000	0.563565000000	-0.180379000000
H	6.407233000000	1.988247000000	-0.487149000000
C	5.957825000000	0.132063000000	0.520907000000
C	3.670301000000	-0.605225000000	0.565365000000
H	2.916624000000	-1.323242000000	0.867498000000
C	4.984529000000	-0.807738000000	0.906488000000
H	5.276852000000	-1.684858000000	1.471368000000
H	4.030360000000	2.385201000000	-1.123237000000
C	2.014248000000	0.852571000000	-0.562785000000
C	0.822377000000	0.008189000000	-0.336338000000
C	-0.387610000000	0.768900000000	0.105755000000
N	-0.276262000000	2.043732000000	0.147989000000
O	-1.417919000000	2.624570000000	0.647745000000
Br	0.483101000000	-0.739821000000	-2.210427000000
C	-1.416729000000	4.015728000000	0.346100000000
H	-0.537753000000	4.499323000000	0.781778000000
H	-1.433761000000	4.175640000000	-0.736024000000
O	-1.424153000000	0.023671000000	0.443288000000
Si	-3.118750000000	0.365352000000	0.255287000000
C	-3.807525000000	-1.377136000000	0.020523000000
C	-3.782426000000	1.118328000000	1.830225000000
H	-3.277680000000	0.689667000000	2.702063000000
H	-3.638679000000	2.200779000000	1.850874000000
H	-4.852924000000	0.909107000000	1.929560000000
C	-3.338856000000	1.413164000000	-1.280985000000
H	-3.595912000000	2.443200000000	-1.017841000000
H	-2.415961000000	1.440753000000	-1.871818000000
H	-4.129802000000	1.014958000000	-1.924055000000
C	-3.130505000000	-2.049220000000	-1.180315000000
H	-2.056646000000	-2.179244000000	-1.012199000000
H	-3.566850000000	-3.042014000000	-1.353862000000
H	-3.257073000000	-1.466125000000	-2.100649000000
C	-5.320233000000	-1.292370000000	-0.231072000000
H	-5.733634000000	-2.301365000000	-0.359946000000
H	-5.850602000000	-0.825706000000	0.606645000000
H	-5.554224000000	-0.724322000000	-1.138577000000
C	-3.551271000000	-2.211285000000	1.283201000000
H	-4.059550000000	-1.788931000000	2.157450000000
H	-3.928261000000	-3.233302000000	1.143876000000
H	-2.481887000000	-2.280054000000	1.512212000000
H	1.834920000000	1.780410000000	-1.102997000000
H	-2.325282000000	4.416453000000	0.797116000000

H	6.993372000000	-0.042089000000	0.797678000000
H	0.974122000000	-0.873621000000	0.282343000000

1a' Int-Anti

Zero-point correction= 0.384861 (Hartree/Particle)
Thermal correction to Energy= 0.410583
Thermal correction to Enthalpy= 0.411527
Thermal correction to Gibbs Free Energy= 0.326780
Sum of electronic and zero-point Energies= -1131.605187
Sum of electronic and thermal Energies= -1131.579465
Sum of electronic and thermal Enthalpies= -1131.578521
Sum of electronic and thermal Free Energies= -1131.663268

C	-0.211787000000	0.749717000000	-0.009867000000
C	1.142242000000	0.782287000000	-0.603926000000
N	-0.011046000000	-1.584707000000	-0.248678000000
C	-0.775918000000	-0.629588000000	0.127356000000
H	1.283719000000	0.152675000000	-1.480370000000
O	-1.970719000000	-0.694519000000	0.684950000000
Br	-1.294323000000	1.786989000000	-1.397210000000
C	2.211023000000	1.546778000000	-0.179997000000
C	2.170739000000	2.394095000000	0.974553000000
C	3.413587000000	1.459004000000	-0.954399000000
C	3.286881000000	3.114754000000	1.320820000000
C	4.521454000000	2.188881000000	-0.591546000000
C	4.453290000000	3.011945000000	0.540839000000
H	1.272025000000	2.464428000000	1.577002000000
H	3.426395000000	0.810196000000	-1.825030000000
H	3.276348000000	3.760212000000	2.190968000000
H	5.436109000000	2.132513000000	-1.169248000000
O	-0.565726000000	-2.811886000000	0.024025000000
Si	-3.264424000000	-1.827472000000	0.446488000000
C	-3.161938000000	-3.179124000000	1.728509000000
H	-3.958637000000	-3.910445000000	1.552758000000
H	-2.203340000000	-3.700070000000	1.678290000000
H	-3.290536000000	-2.781319000000	2.740089000000
C	-3.218140000000	-2.443386000000	-1.318972000000
H	-4.234439000000	-2.583538000000	-1.702378000000
H	-2.715329000000	-1.722746000000	-1.974264000000
H	-2.688736000000	-3.396799000000	-1.393249000000
C	-4.777698000000	-0.738423000000	0.749551000000
C	-4.948840000000	0.256540000000	-0.405397000000
H	-5.828642000000	0.890139000000	-0.230670000000
H	-4.078450000000	0.914938000000	-0.500100000000

H	-5.092882000000	-0.252377000000	-1.365135000000
C	-6.018085000000	-1.641043000000	0.831204000000
H	-6.149367000000	-2.243312000000	-0.075910000000
H	-5.967917000000	-2.323839000000	1.686573000000
H	-6.920754000000	-1.027373000000	0.949930000000
C	-4.628222000000	0.036560000000	2.065214000000
H	-4.501828000000	-0.634237000000	2.922673000000
H	-3.769650000000	0.715582000000	2.035761000000
H	-5.526741000000	0.640525000000	2.249319000000
C	0.137659000000	-3.823412000000	-0.689275000000
H	-0.329921000000	-4.765565000000	-0.400964000000
H	0.041400000000	-3.672039000000	-1.768461000000
H	5.327993000000	3.588323000000	0.827274000000
H	1.193713000000	-3.826527000000	-0.404938000000
H	-0.341776000000	1.316100000000	0.910008000000

1a' TS-Rot

Zero-point correction= 0.384213 (Hartree/Particle)
Thermal correction to Energy= 0.409082
Thermal correction to Enthalpy= 0.410026
Thermal correction to Gibbs Free Energy= 0.328648
Sum of electronic and zero-point Energies= -1131.600073
Sum of electronic and thermal Energies= -1131.575204
Sum of electronic and thermal Enthalpies= -1131.574260
Sum of electronic and thermal Free Energies= -1131.655637

Frequency = -34.3262

C	4.533932000000	1.011820000000	-1.953724000000
C	5.657970000000	1.332422000000	-1.227569000000
C	3.394396000000	0.442478000000	-1.296684000000
H	6.525112000000	1.766231000000	-1.710582000000
C	5.667526000000	1.088893000000	0.151579000000
C	3.433558000000	0.201322000000	0.116743000000
H	2.583745000000	-0.244720000000	0.623640000000
C	4.564615000000	0.523551000000	0.821770000000
H	4.618065000000	0.345192000000	1.889056000000
H	4.485948000000	1.186302000000	-3.024386000000
C	2.298576000000	0.159136000000	-2.082746000000
C	1.028444000000	-0.449534000000	-1.594259000000
C	0.225606000000	0.464833000000	-0.709364000000
N	0.487666000000	1.714183000000	-0.808205000000
O	-0.288934000000	2.450283000000	0.059579000000
Br	-0.129004000000	-1.011658000000	-3.149739000000

C	-0.262563000000	3.819830000000	-0.326622000000
H	0.762813000000	4.200474000000	-0.312943000000
H	-0.695053000000	3.948818000000	-1.323343000000
O	-0.671168000000	-0.129520000000	0.055333000000
Si	-2.270794000000	0.423980000000	0.457439000000
C	-3.181585000000	-1.221478000000	0.623458000000
C	-2.228912000000	1.308749000000	2.101937000000
H	-1.475936000000	0.861013000000	2.758577000000
H	-1.991543000000	2.368258000000	1.983890000000
H	-3.199296000000	1.224523000000	2.602849000000
C	-2.910794000000	1.443159000000	-0.976966000000
H	-2.963661000000	2.502385000000	-0.708894000000
H	-2.250584000000	1.351938000000	-1.847461000000
H	-3.909034000000	1.116258000000	-1.284420000000
C	-3.050900000000	-2.026405000000	-0.675294000000
H	-2.006974000000	-2.280451000000	-0.885527000000
H	-3.617251000000	-2.964184000000	-0.597333000000
H	-3.440791000000	-1.474507000000	-1.539158000000
C	-4.666544000000	-0.951320000000	0.906496000000
H	-5.203151000000	-1.902321000000	1.021701000000
H	-4.811518000000	-0.379591000000	1.830121000000
H	-5.145834000000	-0.401614000000	0.088643000000
C	-2.584106000000	-2.027595000000	1.785142000000
H	-2.700361000000	-1.506433000000	2.742175000000
H	-3.092857000000	-2.996840000000	1.873162000000
H	-1.517061000000	-2.225448000000	1.633433000000
H	2.402182000000	0.329763000000	-3.153229000000
H	-0.866525000000	4.347243000000	0.412785000000
H	6.555067000000	1.340054000000	0.724882000000
H	1.237183000000	-1.382146000000	-1.060835000000

1a' TS-Cis

Zero-point correction= 0.384020 (Hartree/Particle)
Thermal correction to Energy= 0.409057
Thermal correction to Enthalpy= 0.410001
Thermal correction to Gibbs Free Energy= 0.326401
Sum of electronic and zero-point Energies= -1131.595511
Sum of electronic and thermal Energies= -1131.570474
Sum of electronic and thermal Enthalpies= -1131.569530
Sum of electronic and thermal Free Energies= -1131.653130

Frequency = -211.8450

C	-0.766525000000	0.753003000000	-1.097925000000

C	-2.052326000000	-0.017125000000	-1.222313000000
N	-0.444365000000	-1.411147000000	-0.598316000000
C	0.221639000000	-0.327317000000	-0.810115000000
H	-0.548226000000	1.223751000000	-2.059508000000
H	-2.210722000000	-0.366972000000	-2.242008000000
O	1.501606000000	-0.117562000000	-0.897407000000
Br	-0.657875000000	2.263915000000	0.213293000000
C	-3.138191000000	-0.153105000000	-0.341194000000
C	-3.057269000000	0.075130000000	1.058625000000
C	-4.364771000000	-0.581508000000	-0.913933000000
C	-4.180454000000	-0.090092000000	1.839804000000
C	-5.491320000000	-0.712060000000	-0.123287000000
C	-5.396086000000	-0.465287000000	1.247850000000
H	-2.110123000000	0.330993000000	1.516946000000
H	-4.408402000000	-0.780360000000	-1.980410000000
H	-4.125868000000	0.065917000000	2.910986000000
H	-6.435413000000	-1.015751000000	-0.560254000000
H	-6.276517000000	-0.579409000000	1.872679000000
O	0.309864000000	-2.544870000000	-0.547805000000
Si	2.833099000000	-0.952524000000	-0.123289000000
C	3.424686000000	-2.302453000000	-1.261264000000
H	3.738940000000	-1.901782000000	-2.229672000000
H	4.284442000000	-2.810535000000	-0.810804000000
H	2.640468000000	-3.044835000000	-1.428465000000
C	2.245775000000	-1.552690000000	1.546395000000
H	3.030304000000	-1.412662000000	2.297527000000
H	1.364873000000	-0.993127000000	1.882246000000
H	1.987371000000	-2.614559000000	1.518631000000
C	4.078705000000	0.452270000000	0.028577000000
C	3.542734000000	1.508764000000	1.004145000000
H	3.386741000000	1.095719000000	2.007167000000
H	4.259508000000	2.335468000000	1.093983000000
H	2.591282000000	1.928848000000	0.658778000000
C	5.400200000000	-0.118699000000	0.564182000000
H	6.128479000000	0.691275000000	0.700372000000
H	5.271996000000	-0.611008000000	1.535323000000
H	5.839555000000	-0.844294000000	-0.129422000000
C	4.323063000000	1.101084000000	-1.340391000000
H	4.718330000000	0.382730000000	-2.067274000000
H	3.404721000000	1.532860000000	-1.752145000000
H	5.058317000000	1.910663000000	-1.243497000000
C	-0.365487000000	-3.541256000000	0.224569000000
H	-0.519673000000	-3.189440000000	1.248382000000
H	-1.324231000000	-3.788265000000	-0.238942000000

H 0.292142000000 -4.410361000000 0.216374000000

1a' TS-Trans

Zero-point correction= 0.384227 (Hartree/Particle)
Thermal correction to Energy= 0.409231
Thermal correction to Enthalpy= 0.410175
Thermal correction to Gibbs Free Energy= 0.327484
Sum of electronic and zero-point Energies= -1131.600322
Sum of electronic and thermal Energies= -1131.575318
Sum of electronic and thermal Enthalpies= -1131.574374
Sum of electronic and thermal Free Energies= -1131.657065

Frequency = -202.2218

C	-0.533693000000	1.330441000000	-0.314670000000
C	0.826108000000	1.025259000000	-0.880170000000
N	-0.064984000000	-0.839599000000	-0.250545000000
C	-1.022670000000	-0.034749000000	0.043349000000
H	0.850852000000	0.682791000000	-1.911342000000
O	-2.179985000000	-0.236901000000	0.598572000000
Br	-1.696200000000	2.175204000000	-1.716250000000
C	2.054900000000	1.370832000000	-0.290126000000
C	2.162845000000	1.898733000000	1.023301000000
C	3.224618000000	1.155390000000	-1.064853000000
C	3.408189000000	2.206085000000	1.530423000000
C	4.464901000000	1.472967000000	-0.546281000000
C	4.552070000000	1.995279000000	0.747623000000
H	1.278168000000	2.057729000000	1.630709000000
H	3.125878000000	0.746741000000	-2.066299000000
H	3.504838000000	2.609692000000	2.531654000000
H	5.362319000000	1.318149000000	-1.133878000000
O	-0.221276000000	-2.136998000000	0.139948000000
Si	-3.207697000000	-1.654909000000	0.545845000000
C	-2.783229000000	-2.738028000000	1.999695000000
H	-3.425054000000	-3.625788000000	1.996345000000
H	-1.743470000000	-3.070471000000	1.948333000000
H	-2.936163000000	-2.214166000000	2.948032000000
C	-2.970976000000	-2.467997000000	-1.119825000000
H	-3.930665000000	-2.832649000000	-1.501094000000
H	-2.574735000000	-1.758052000000	-1.855174000000
H	-2.285317000000	-3.316995000000	-1.056795000000
C	-4.908765000000	-0.863895000000	0.711239000000
C	-5.202793000000	-0.014426000000	-0.532463000000
H	-6.192593000000	0.452069000000	-0.443337000000

H	-4.466228000000	0.787736000000	-0.654401000000
H	-5.201991000000	-0.617210000000	-1.447695000000
C	-5.957738000000	-1.979536000000	0.832600000000
H	-5.944692000000	-2.653703000000	-0.031960000000
H	-5.806772000000	-2.581811000000	1.735472000000
H	-6.962528000000	-1.541443000000	0.891699000000
C	-4.965895000000	0.025088000000	1.960665000000
H	-4.773571000000	-0.545787000000	2.875873000000
H	-4.238105000000	0.841741000000	1.908717000000
H	-5.963943000000	0.472781000000	2.054611000000
C	0.512118000000	-2.999092000000	-0.735311000000
H	0.356338000000	-4.005390000000	-0.346927000000
H	0.129047000000	-2.921584000000	-1.756425000000
H	5.526597000000	2.243487000000	1.156833000000
H	1.574773000000	-2.743660000000	-0.708647000000
H	-0.542842000000	2.021369000000	0.526390000000

1a' Int-Cis

Zero-point correction= 0.387358 (Hartree/Particle)
Thermal correction to Energy= 0.411966
Thermal correction to Enthalpy= 0.412910
Thermal correction to Gibbs Free Energy= 0.331670
Sum of electronic and zero-point Energies= -1131.632348
Sum of electronic and thermal Energies= -1131.607740
Sum of electronic and thermal Enthalpies= -1131.606795
Sum of electronic and thermal Free Energies= -1131.688035

C	0.760346000000	1.024842000000	0.112468000000
C	1.370963000000	-0.151907000000	0.954566000000
N	0.042783000000	-0.780605000000	0.733018000000
C	-0.473424000000	0.171378000000	0.000913000000
O	-1.568710000000	0.338902000000	-0.604004000000
Br	1.582020000000	1.425064000000	-1.636529000000
C	2.532499000000	-0.941694000000	0.435831000000
C	3.797774000000	-0.689369000000	0.968218000000
C	2.372628000000	-1.900089000000	-0.567232000000
C	4.904718000000	-1.382691000000	0.487176000000
C	3.480658000000	-2.599124000000	-1.037361000000
C	4.746381000000	-2.338815000000	-0.514492000000
H	3.911498000000	0.049707000000	1.756503000000
H	1.388403000000	-2.112280000000	-0.977124000000
H	5.887843000000	-1.182622000000	0.900656000000
H	3.354363000000	-3.348314000000	-1.812102000000
O	-0.445595000000	-1.984802000000	1.080731000000

Si	-2.955229000000	-0.711038000000	-1.032204000000
C	-3.538276000000	0.138905000000	-2.575207000000
H	-2.811867000000	0.008995000000	-3.383248000000
H	-4.490987000000	-0.288244000000	-2.905451000000
H	-3.683358000000	1.209981000000	-2.407910000000
C	-2.284409000000	-2.415987000000	-1.349022000000
H	-2.174403000000	-3.006915000000	-0.437592000000
H	-2.980575000000	-2.935472000000	-2.017265000000
H	-1.315424000000	-2.369884000000	-1.857917000000
C	-4.138227000000	-0.572192000000	0.418999000000
C	-4.711095000000	0.849637000000	0.494192000000
H	-5.273239000000	1.108145000000	-0.409333000000
H	-5.397282000000	0.925916000000	1.347011000000
H	-3.924321000000	1.599955000000	0.632760000000
C	-5.276889000000	-1.576658000000	0.173902000000
H	-4.909555000000	-2.608483000000	0.141130000000
H	-6.007586000000	-1.509459000000	0.989659000000
H	-5.809678000000	-1.372533000000	-0.762061000000
C	-3.430543000000	-0.914887000000	1.735902000000
H	-2.614746000000	-0.214433000000	1.955324000000
H	-4.146014000000	-0.849897000000	2.565339000000
H	-3.023869000000	-1.932017000000	1.727792000000
C	-0.305353000000	-2.196364000000	2.505422000000
H	-0.791542000000	-3.153794000000	2.684923000000
H	0.753814000000	-2.255641000000	2.767924000000
H	1.501208000000	0.137882000000	1.999363000000
H	-0.804976000000	-1.396528000000	3.055515000000
H	5.608120000000	-2.885714000000	-0.883657000000
H	0.626043000000	1.961442000000	0.650240000000

1a' Int-Trans

Zero-point correction= 0.387039 (Hartree/Particle)
Thermal correction to Energy= 0.411987
Thermal correction to Enthalpy= 0.412932
Thermal correction to Gibbs Free Energy= 0.330380
Sum of electronic and zero-point Energies= -1131.631974
Sum of electronic and thermal Energies= -1131.607025
Sum of electronic and thermal Enthalpies= -1131.606081
Sum of electronic and thermal Free Energies= -1131.688632

C	0.602329000000	-0.740447000000	0.715812000000
C	1.720682000000	0.295124000000	1.070731000000
N	0.576537000000	1.241091000000	1.189001000000
C	-0.373154000000	0.395635000000	0.899094000000

O	-1.622955000000	0.581083000000	0.845750000000
Br	0.313225000000	-2.207444000000	2.015409000000
C	2.715004000000	0.661899000000	0.011495000000
C	2.290131000000	1.088919000000	-1.250560000000
C	4.076998000000	0.576714000000	0.299908000000
C	3.230162000000	1.420100000000	-2.220119000000
C	5.015662000000	0.905710000000	-0.675534000000
C	4.592783000000	1.326997000000	-1.933812000000
H	1.228650000000	1.168049000000	-1.477302000000
H	4.398149000000	0.252833000000	1.285922000000
H	2.900536000000	1.753282000000	-3.198698000000
H	6.074720000000	0.837136000000	-0.449644000000
O	0.523149000000	2.576222000000	1.313094000000
Si	-2.909661000000	-0.343187000000	0.019022000000
C	-2.077572000000	-1.662878000000	-0.993961000000
H	-1.337499000000	-1.250120000000	-1.686833000000
H	-1.603474000000	-2.432297000000	-0.377591000000
H	-2.847921000000	-2.163036000000	-1.591917000000
C	-3.949424000000	-0.984388000000	1.414684000000
H	-4.879917000000	-1.408123000000	1.022185000000
H	-3.427502000000	-1.771850000000	1.966876000000
H	-4.207365000000	-0.182710000000	2.112624000000
C	-3.706742000000	1.004437000000	-1.016206000000
C	-4.740279000000	0.348001000000	-1.945639000000
H	-5.506824000000	-0.200911000000	-1.386192000000
H	-5.251687000000	1.122740000000	-2.530507000000
H	-4.270227000000	-0.344484000000	-2.652241000000
C	-4.407457000000	2.019006000000	-0.102062000000
H	-5.215506000000	1.554481000000	0.473122000000
H	-3.709158000000	2.484290000000	0.602767000000
H	-4.848617000000	2.819173000000	-0.709626000000
C	-2.638474000000	1.717156000000	-1.857878000000
H	-1.901537000000	2.230959000000	-1.230064000000
H	-2.104387000000	1.022130000000	-2.515901000000
H	-3.115217000000	2.473382000000	-2.494031000000
C	1.214179000000	2.998726000000	2.511532000000
H	2.274453000000	2.742426000000	2.441131000000
H	1.088082000000	4.079698000000	2.529363000000
H	2.187277000000	0.115941000000	2.041195000000
H	0.754147000000	2.538150000000	3.387932000000
H	5.323711000000	1.587631000000	-2.692561000000
H	0.663984000000	-1.164852000000	-0.285568000000

1y Int-Syn

Zero-point correction= 0.543235 (Hartree/Particle)
Thermal correction to Energy= 0.580046
Thermal correction to Enthalpy= 0.580991
Thermal correction to Gibbs Free Energy= 0.470530
Sum of electronic and zero-point Energies= -1704.696240
Sum of electronic and thermal Energies= -1704.659429
Sum of electronic and thermal Enthalpies= -1704.658485
Sum of electronic and thermal Free Energies= -1704.768945

C	2.967431000000	-2.323894000000	-0.633967000000
C	4.209765000000	-2.082233000000	-0.139094000000
C	1.792524000000	-1.650214000000	-0.120268000000
H	5.076810000000	-2.586145000000	-0.545937000000
C	4.341006000000	-1.156110000000	0.936503000000
C	1.969641000000	-0.712211000000	0.974290000000
H	1.115769000000	-0.202327000000	1.399219000000
C	3.199412000000	-0.496538000000	1.495453000000
H	3.365009000000	0.190428000000	2.317036000000
H	2.836001000000	-3.031820000000	-1.446840000000
C	0.609261000000	-1.957163000000	-0.720176000000
C	-0.742067000000	-1.381965000000	-0.398542000000
C	-0.769125000000	0.128677000000	-0.273676000000
N	0.118241000000	0.777021000000	-0.919854000000
O	0.002204000000	2.133768000000	-0.720293000000
Br	-1.987718000000	-1.827626000000	-1.938777000000
C	1.039212000000	2.799069000000	-1.452801000000
H	0.960896000000	2.527755000000	-2.510266000000
H	0.803490000000	3.859566000000	-1.334665000000
O	-1.729063000000	0.590925000000	0.511096000000
Si	-2.757644000000	1.977582000000	0.339690000000
C	-4.294994000000	1.350098000000	1.237225000000
C	-2.002510000000	3.434632000000	1.229363000000
H	-1.504693000000	3.108644000000	2.148285000000
H	-1.265662000000	3.945207000000	0.605038000000
H	-2.780174000000	4.154226000000	1.506566000000
C	-3.058604000000	2.251870000000	-1.481720000000
H	-2.201262000000	2.737687000000	-1.954881000000
H	-3.245884000000	1.303618000000	-1.996287000000
H	-3.938261000000	2.888365000000	-1.627224000000
C	-5.364652000000	2.449943000000	1.278280000000
H	-6.264254000000	2.078924000000	1.786956000000
H	-5.020719000000	3.335525000000	1.823929000000
H	-5.663961000000	2.766137000000	0.272290000000

C	-3.911858000000	0.954771000000	2.670310000000
H	-3.127091000000	0.189330000000	2.679386000000
H	-3.551323000000	1.815428000000	3.245484000000
H	-4.784918000000	0.546470000000	3.196874000000
C	-4.852981000000	0.123606000000	0.502953000000
H	-5.724407000000	-0.273299000000	1.041181000000
H	-5.178349000000	0.374219000000	-0.513491000000
H	-4.108584000000	-0.677214000000	0.430684000000
O	5.477747000000	-0.845952000000	1.483840000000
C	6.709572000000	-1.376026000000	0.955298000000
H	6.810119000000	-1.099547000000	-0.096403000000
H	7.495471000000	-0.913393000000	1.547425000000
H	6.729800000000	-2.460571000000	1.077127000000
H	0.629351000000	-2.719353000000	-1.495191000000
C	-1.264498000000	-1.970120000000	0.940987000000
O	-0.574191000000	-1.899139000000	1.926710000000
O	-2.468204000000	-2.485955000000	0.876942000000
C	-3.004808000000	-2.962478000000	2.126607000000
H	-4.005631000000	-3.318515000000	1.892710000000
H	-2.384016000000	-3.774146000000	2.509076000000
H	-3.043711000000	-2.146908000000	2.850304000000
C	2.411855000000	2.484122000000	-0.914968000000
C	3.279507000000	1.647700000000	-1.620089000000
C	2.827902000000	3.030221000000	0.303423000000
C	4.560374000000	1.386252000000	-1.133356000000
C	4.104336000000	2.768534000000	0.793831000000
C	4.976902000000	1.954263000000	0.069605000000
H	2.951965000000	1.211772000000	-2.560555000000
H	2.150206000000	3.675037000000	0.858060000000
H	5.233569000000	0.746288000000	-1.696789000000
H	4.424327000000	3.206645000000	1.734249000000
H	5.977362000000	1.760638000000	0.445546000000

1y Int-Anti

Zero-point correction= 0.543476 (Hartree/Particle)
Thermal correction to Energy= 0.580226
Thermal correction to Enthalpy= 0.581170
Thermal correction to Gibbs Free Energy= 0.472730
Sum of electronic and zero-point Energies= -1704.698285
Sum of electronic and thermal Energies= -1704.661535
Sum of electronic and thermal Enthalpies= -1704.660591
Sum of electronic and thermal Free Energies= -1704.769031

C	3.068240000000	-2.003696000000	0.939408000000

C	4.270908000000	-1.812965000000	0.333118000000
C	1.833862000000	-1.543561000000	0.344754000000
H	5.187863000000	-2.144691000000	0.802290000000
C	4.292834000000	-1.178458000000	-0.941939000000
C	1.896694000000	-0.903440000000	-0.954383000000
H	0.989305000000	-0.569660000000	-1.444143000000
C	3.085035000000	-0.741216000000	-1.579720000000
H	3.166908000000	-0.277361000000	-2.555707000000
H	3.018147000000	-2.497221000000	1.905236000000
C	0.692383000000	-1.733822000000	1.064814000000
C	-0.689315000000	-1.275038000000	0.708694000000
C	-0.796019000000	0.182726000000	0.303537000000
N	0.145279000000	0.932045000000	0.733056000000
O	-0.048923000000	2.243984000000	0.361143000000
Br	-1.315240000000	-2.459066000000	-0.834835000000
C	1.024991000000	3.035792000000	0.879375000000
H	0.735023000000	4.061433000000	0.636816000000
H	1.065051000000	2.921414000000	1.967277000000
O	-1.848499000000	0.519858000000	-0.410999000000
Si	-2.850716000000	1.931631000000	-0.343598000000
C	-4.508730000000	1.194702000000	-0.869074000000
C	-2.888358000000	2.581706000000	1.408183000000
H	-2.653918000000	1.775718000000	2.110600000000
H	-2.160182000000	3.384990000000	1.547030000000
H	-3.882305000000	2.967357000000	1.658020000000
C	-2.246335000000	3.161461000000	-1.614571000000
H	-1.412960000000	3.754294000000	-1.229913000000
H	-1.910370000000	2.646280000000	-2.520256000000
H	-3.053617000000	3.844892000000	-1.899485000000
C	-4.386226000000	0.620626000000	-2.287314000000
H	-3.609695000000	-0.150903000000	-2.341802000000
H	-5.335825000000	0.160869000000	-2.592581000000
H	-4.145934000000	1.398789000000	-3.020753000000
C	-5.586951000000	2.287407000000	-0.854675000000
H	-5.346402000000	3.111083000000	-1.536386000000
H	-6.549829000000	1.867468000000	-1.174652000000
H	-5.729806000000	2.708141000000	0.147022000000
C	-4.907686000000	0.073085000000	0.098222000000
H	-4.990468000000	0.434834000000	1.129663000000
H	-5.882501000000	-0.343395000000	-0.189898000000
H	-4.174869000000	-0.740676000000	0.089119000000
O	5.379709000000	-0.962620000000	-1.620284000000
C	6.665772000000	-1.294335000000	-1.060411000000
H	6.813393000000	-0.748771000000	-0.125740000000

H	6.734517000000	-2.371479000000	-0.897104000000
H	7.391036000000	-0.975877000000	-1.805134000000
H	0.772083000000	-2.280881000000	2.001648000000
C	-1.696365000000	-1.548034000000	1.837196000000
O	-2.486056000000	-0.720984000000	2.218099000000
O	-1.568629000000	-2.770421000000	2.322439000000
C	-2.479841000000	-3.114575000000	3.383119000000
H	-3.507230000000	-3.054145000000	3.020471000000
H	-2.229766000000	-4.135689000000	3.661640000000
H	-2.341499000000	-2.438096000000	4.227752000000
C	2.347858000000	2.680815000000	0.249739000000
C	3.342358000000	2.040030000000	0.990361000000
C	2.586596000000	2.990183000000	-1.093261000000
C	4.575558000000	1.743966000000	0.409251000000
C	3.813508000000	2.689912000000	-1.678069000000
C	4.814586000000	2.075551000000	-0.923402000000
H	3.152288000000	1.785438000000	2.030077000000
H	1.808933000000	3.480619000000	-1.674084000000
H	5.349410000000	1.259081000000	0.998079000000
H	3.995180000000	2.943167000000	-2.718032000000
H	5.776466000000	1.852418000000	-1.375773000000

1y TS-Rot

Zero-point correction= 0.543543 (Hartree/Particle)
Thermal correction to Energy= 0.579371
Thermal correction to Enthalpy= 0.580315
Thermal correction to Gibbs Free Energy= 0.474301
Sum of electronic and zero-point Energies= -1704.685564
Sum of electronic and thermal Energies= -1704.649736
Sum of electronic and thermal Enthalpies= -1704.648792
Sum of electronic and thermal Free Energies= -1704.754806

Frequency = -15.4802

C	1.870288000000	-3.736398000000	-1.705677000000
C	3.171450000000	-3.730620000000	-2.099763000000
C	1.222683000000	-2.554687000000	-1.169408000000
H	3.623516000000	-4.616814000000	-2.525660000000
C	3.924839000000	-2.533341000000	-1.933352000000
C	2.042240000000	-1.379960000000	-0.957946000000
H	1.631672000000	-0.516506000000	-0.458622000000
C	3.345872000000	-1.375548000000	-1.325724000000
H	3.980849000000	-0.511423000000	-1.158639000000
H	1.277350000000	-4.638173000000	-1.825943000000

C	-0.105984000000	-2.698673000000	-0.889471000000
C	-1.183299000000	-1.759339000000	-0.436027000000
C	-0.967077000000	-0.263354000000	-0.323234000000
N	-0.321613000000	0.318701000000	-1.257715000000
O	-0.332393000000	1.688729000000	-1.085876000000
Br	-2.660756000000	-2.030216000000	-1.812025000000
C	0.548874000000	2.305342000000	-2.018145000000
H	0.374336000000	1.894609000000	-3.017658000000
H	0.246582000000	3.357510000000	-2.016964000000
O	-1.587210000000	0.281458000000	0.709962000000
Si	-2.334473000000	1.823562000000	0.990298000000
C	-3.492933000000	1.345318000000	2.402843000000
C	-1.061770000000	3.064923000000	1.558316000000
H	-0.366099000000	2.612973000000	2.272864000000
H	-0.485985000000	3.463482000000	0.719675000000
H	-1.558028000000	3.901472000000	2.062180000000
C	-3.283524000000	2.321122000000	-0.539194000000
H	-2.656292000000	2.888333000000	-1.230908000000
H	-3.661526000000	1.438009000000	-1.065649000000
H	-4.146951000000	2.937929000000	-0.267142000000
C	-4.203760000000	2.593105000000	2.945217000000
H	-4.909328000000	2.307782000000	3.736742000000
H	-3.497228000000	3.309979000000	3.377556000000
H	-4.777338000000	3.109471000000	2.166559000000
C	-2.680065000000	0.694745000000	3.531017000000
H	-2.125026000000	-0.182012000000	3.178590000000
H	-1.957674000000	1.397323000000	3.962827000000
H	-3.347937000000	0.369178000000	4.340050000000
C	-4.541234000000	0.352908000000	1.880686000000
H	-5.174640000000	0.000760000000	2.706247000000
H	-5.197597000000	0.817494000000	1.135790000000
H	-4.075840000000	-0.524003000000	1.417222000000
O	5.170824000000	-2.410620000000	-2.286095000000
C	5.867436000000	-3.515198000000	-2.897547000000
H	5.369164000000	-3.799765000000	-3.826064000000
H	6.867645000000	-3.141189000000	-3.102342000000
H	5.910316000000	-4.356560000000	-2.203480000000
H	-0.466639000000	-3.727187000000	-0.890051000000
C	-1.598745000000	-2.272703000000	0.965533000000
O	-0.751024000000	-2.345773000000	1.820300000000
O	-2.863173000000	-2.600404000000	1.093399000000
C	-3.252425000000	-3.061271000000	2.402341000000
H	-4.315052000000	-3.281331000000	2.326267000000
H	-2.688126000000	-3.958913000000	2.659910000000

H	-3.072122000000	-2.280145000000	3.142717000000
C	1.999789000000	2.173394000000	-1.620411000000
C	2.996332000000	2.245179000000	-2.595601000000
C	2.363430000000	2.035501000000	-0.278371000000
C	4.341450000000	2.203895000000	-2.233718000000
C	3.708790000000	1.982607000000	0.083328000000
C	4.701311000000	2.076430000000	-0.892436000000
H	2.716381000000	2.339590000000	-3.641828000000
H	1.588319000000	1.967063000000	0.481064000000
H	5.108394000000	2.265960000000	-2.999662000000
H	3.981947000000	1.874197000000	1.128542000000
H	5.748803000000	2.042089000000	-0.609698000000

1y TS-Cis

Zero-point correction= 0.542897 (Hartree/Particle)
Thermal correction to Energy= 0.579045
Thermal correction to Enthalpy= 0.579989
Thermal correction to Gibbs Free Energy= 0.472917
Sum of electronic and zero-point Energies= -1704.684359
Sum of electronic and thermal Energies= -1704.648211
Sum of electronic and thermal Enthalpies= -1704.647266
Sum of electronic and thermal Free Energies= -1704.754338

Frequency = -281.9809

C	0.569175000000	1.444180000000	-0.490421000000
C	-0.767932000000	1.227893000000	-1.196454000000
N	0.134176000000	-0.605018000000	-1.051065000000
C	0.985805000000	0.010062000000	-0.311644000000
H	-0.723997000000	1.440624000000	-2.262246000000
O	1.987769000000	-0.398674000000	0.394647000000
Br	0.530739000000	2.485410000000	1.219505000000
C	-2.052224000000	1.144507000000	-0.634389000000
C	-2.314631000000	0.791477000000	0.721229000000
C	-3.149955000000	1.331484000000	-1.511674000000
C	-3.600761000000	0.675845000000	1.166272000000
C	-4.451037000000	1.226380000000	-1.071762000000
C	-4.683426000000	0.887031000000	0.275061000000
H	-1.500173000000	0.569052000000	1.400962000000
H	-2.954528000000	1.575877000000	-2.551713000000
H	-3.825415000000	0.387710000000	2.186801000000
H	-5.271036000000	1.385050000000	-1.760083000000
O	0.292119000000	-1.940478000000	-1.265284000000
Si	3.174723000000	-1.640963000000	0.045494000000

C	3.496087000000	-1.528695000000	-1.786709000000
H	2.612447000000	-1.826344000000	-2.359179000000
H	3.772013000000	-0.509176000000	-2.075197000000
H	4.318672000000	-2.195057000000	-2.067428000000
C	2.492074000000	-3.280379000000	0.611604000000
H	3.299054000000	-4.019435000000	0.664242000000
H	2.052329000000	-3.195010000000	1.610295000000
H	1.729308000000	-3.656512000000	-0.074298000000
C	4.619710000000	-1.072386000000	1.107786000000
C	4.191868000000	-1.032857000000	2.581615000000
H	5.030820000000	-0.695597000000	3.204158000000
H	3.358771000000	-0.339451000000	2.742374000000
H	3.888369000000	-2.021473000000	2.943714000000
C	5.780387000000	-2.064415000000	0.937164000000
H	6.117936000000	-2.123039000000	-0.104083000000
H	6.636669000000	-1.741097000000	1.543060000000
H	5.508352000000	-3.073993000000	1.264454000000
C	5.075672000000	0.325268000000	0.668687000000
H	4.268393000000	1.060181000000	0.758419000000
H	5.912025000000	0.658814000000	1.296890000000
H	5.422565000000	0.324467000000	-0.371220000000
C	1.521238000000	2.227678000000	-1.404115000000
O	1.129202000000	3.017716000000	-2.224212000000
O	2.779783000000	1.915131000000	-1.158925000000
C	3.759890000000	2.612402000000	-1.951821000000
H	3.614185000000	2.380471000000	-3.008026000000
H	3.670535000000	3.687443000000	-1.787999000000
H	4.725180000000	2.249898000000	-1.605443000000
O	-5.887168000000	0.720216000000	0.800784000000
C	-7.034452000000	0.877357000000	-0.038911000000
H	-7.086546000000	1.896845000000	-0.429956000000
H	-7.008083000000	0.158364000000	-0.862173000000
H	-7.894129000000	0.680365000000	0.598695000000
C	-0.950758000000	-2.508949000000	-1.706149000000
H	-1.290714000000	-1.978763000000	-2.601535000000
H	-0.677853000000	-3.530910000000	-1.981828000000
C	-2.002290000000	-2.494967000000	-0.626554000000
C	-3.347166000000	-2.349952000000	-0.970830000000
C	-1.649764000000	-2.683716000000	0.713174000000
C	-4.335248000000	-2.425049000000	0.009634000000
C	-2.637231000000	-2.750672000000	1.693221000000
C	-3.981826000000	-2.630021000000	1.342353000000
H	-3.619930000000	-2.184552000000	-2.010243000000
H	-0.601073000000	-2.784944000000	0.982708000000

H	-5.379985000000	-2.313604000000	-0.266136000000
H	-2.357412000000	-2.899974000000	2.731515000000
H	-4.750927000000	-2.684132000000	2.106825000000

1y TS-Trans

Zero-point correction= 0.542720 (Hartree/Particle)
Thermal correction to Energy= 0.579123
Thermal correction to Enthalpy= 0.580067
Thermal correction to Gibbs Free Energy= 0.471041
Sum of electronic and zero-point Energies= -1704.684588
Sum of electronic and thermal Energies= -1704.648185
Sum of electronic and thermal Enthalpies= -1704.647241
Sum of electronic and thermal Free Energies= -1704.756267

Frequency = -242.5638

C	-0.614811000000	1.312169000000	-0.263051000000
C	0.752615000000	0.937738000000	-0.831007000000
N	-0.122482000000	-0.814191000000	-0.226195000000
C	-1.097809000000	-0.054578000000	0.124041000000
H	0.759471000000	0.724275000000	-1.896553000000
O	-2.252920000000	-0.311079000000	0.646832000000
Br	-1.799878000000	2.003790000000	-1.746859000000
C	2.001717000000	1.148030000000	-0.231334000000
C	2.199506000000	1.373291000000	1.162925000000
C	3.140879000000	1.029508000000	-1.070020000000
C	3.461854000000	1.503071000000	1.667380000000
C	4.415873000000	1.174767000000	-0.575769000000
C	4.584143000000	1.402745000000	0.804754000000
H	1.357539000000	1.390546000000	1.848083000000
H	2.994692000000	0.833051000000	-2.128460000000
H	3.638917000000	1.655289000000	2.726078000000
H	5.268275000000	1.090237000000	-1.237478000000
O	-0.228433000000	-2.150616000000	0.024125000000
Si	-3.262830000000	-1.738722000000	0.518781000000
C	-2.780381000000	-2.913264000000	1.879822000000
H	-2.942516000000	-2.469739000000	2.866781000000
H	-3.388062000000	-3.822205000000	1.812733000000
H	-1.729449000000	-3.201552000000	1.795407000000
C	-3.046306000000	-2.426080000000	-1.204013000000
H	-3.984860000000	-2.875624000000	-1.546096000000
H	-2.781368000000	-1.638334000000	-1.918260000000
H	-2.269090000000	-3.193865000000	-1.234520000000
C	-4.963794000000	-0.978623000000	0.783554000000

C	-5.319661000000	-0.085884000000	-0.412803000000
H	-6.306953000000	0.369284000000	-0.260608000000
H	-4.594662000000	0.726462000000	-0.537729000000
H	-5.357234000000	-0.654130000000	-1.348986000000
C	-5.993016000000	-2.112345000000	0.905672000000
H	-6.006303000000	-2.753873000000	0.016511000000
H	-5.797089000000	-2.745144000000	1.778488000000
H	-6.999905000000	-1.690926000000	1.021487000000
C	-4.975108000000	-0.137451000000	2.067363000000
H	-4.734894000000	-0.738922000000	2.951248000000
H	-4.259219000000	0.689731000000	2.012852000000
H	-5.973526000000	0.292099000000	2.221755000000
C	-0.617316000000	2.431840000000	0.780900000000
O	-0.017011000000	3.462579000000	0.623082000000
O	-1.362676000000	2.112086000000	1.822436000000
C	-1.456351000000	3.123534000000	2.845082000000
H	-1.886973000000	4.033601000000	2.424828000000
H	-2.107639000000	2.704198000000	3.608419000000
H	-0.465556000000	3.332203000000	3.252178000000
O	5.762006000000	1.517156000000	1.394881000000
C	6.948104000000	1.412962000000	0.600022000000
H	7.777147000000	1.523558000000	1.296175000000
H	6.997196000000	0.435867000000	0.112631000000
H	6.978857000000	2.210415000000	-0.147124000000
C	0.702585000000	-2.872426000000	-0.792950000000
H	0.465389000000	-3.919179000000	-0.582983000000
H	0.493565000000	-2.669201000000	-1.848360000000
C	2.137912000000	-2.559455000000	-0.447567000000
C	3.131089000000	-2.746334000000	-1.411785000000
C	2.496109000000	-2.138809000000	0.835470000000
C	4.471121000000	-2.540968000000	-1.090397000000
C	3.835991000000	-1.926613000000	1.153570000000
C	4.826749000000	-2.134254000000	0.194934000000
H	2.852460000000	-3.060090000000	-2.414634000000
H	1.725253000000	-1.980357000000	1.584834000000
H	5.236184000000	-2.692236000000	-1.845623000000
H	4.106982000000	-1.597425000000	2.152511000000
H	5.870628000000	-1.973145000000	0.447517000000

1y Int-Cis

Zero-point correction= 0.544849 (Hartree/Particle)
Thermal correction to Energy= 0.581008
Thermal correction to Enthalpy= 0.581952
Thermal correction to Gibbs Free Energy= 0.475462

Sum of electronic and zero-point Energies= -1704.705682
Sum of electronic and thermal Energies= -1704.669523
Sum of electronic and thermal Enthalpies= -1704.668579
Sum of electronic and thermal Free Energies= -1704.775069

C	-0.442496000000	1.094004000000	-0.978419000000
C	0.792989000000	0.195817000000	-0.539052000000
N	-0.245092000000	-0.536295000000	0.263502000000
C	-1.251485000000	0.247468000000	-0.026385000000
O	-2.441662000000	0.320225000000	0.378584000000
Br	-1.040708000000	0.980254000000	-2.846262000000
C	1.584759000000	-0.596578000000	-1.516729000000
C	2.941684000000	-0.296794000000	-1.676358000000
C	1.033110000000	-1.658013000000	-2.233285000000
C	3.732358000000	-1.047882000000	-2.529244000000
C	1.815911000000	-2.428279000000	-3.084810000000
C	3.176846000000	-2.129199000000	-3.226743000000
H	3.382352000000	0.521953000000	-1.114221000000
H	-0.014167000000	-1.922365000000	-2.105413000000
H	4.788522000000	-0.833689000000	-2.652509000000
H	1.367758000000	-3.262537000000	-3.610196000000
O	-0.145033000000	-1.414506000000	1.281746000000
Si	-3.103634000000	0.590793000000	2.031423000000
C	-1.651610000000	0.550266000000	3.190571000000
H	-0.810915000000	1.126021000000	2.789738000000
H	-1.953904000000	1.024710000000	4.131111000000
H	-1.315160000000	-0.465739000000	3.409798000000
C	-3.889099000000	2.263822000000	1.866248000000
H	-4.484371000000	2.489056000000	2.757713000000
H	-3.124178000000	3.038100000000	1.759762000000
H	-4.549705000000	2.303540000000	0.995238000000
C	-4.319721000000	-0.819552000000	2.244000000000
C	-5.513176000000	-0.639613000000	1.296338000000
H	-5.200668000000	-0.615260000000	0.246103000000
H	-6.210036000000	-1.478728000000	1.416026000000
H	-6.063411000000	0.282842000000	1.509880000000
C	-3.630237000000	-2.160267000000	1.962957000000
H	-4.331541000000	-2.983725000000	2.147926000000
H	-3.302404000000	-2.234140000000	0.920068000000
H	-2.760693000000	-2.315224000000	2.611954000000
C	-4.806524000000	-0.786890000000	3.702478000000
H	-5.292712000000	0.163439000000	3.951688000000
H	-5.542493000000	-1.584839000000	3.862088000000
H	-3.984640000000	-0.947174000000	4.409285000000

C	-0.337223000000	-2.801838000000	0.884819000000
H	-0.678926000000	-3.264091000000	1.814740000000
H	-1.147254000000	-2.851565000000	0.151358000000
O	4.028052000000	-2.833893000000	-4.000410000000
C	3.516641000000	-3.977232000000	-4.671429000000
H	3.115848000000	-4.705505000000	-3.957714000000
H	2.736575000000	-3.700248000000	-5.388227000000
H	4.359705000000	-4.416061000000	-5.204220000000
C	0.916696000000	-3.461729000000	0.375722000000
C	2.185774000000	-2.950513000000	0.645712000000
C	0.787665000000	-4.633604000000	-0.372917000000
C	3.316776000000	-3.591975000000	0.143736000000
C	1.919256000000	-5.285907000000	-0.855432000000
C	3.186968000000	-4.760181000000	-0.606402000000
H	2.290333000000	-2.037800000000	1.225679000000
H	-0.202640000000	-5.028652000000	-0.585554000000
H	4.300869000000	-3.176749000000	0.338685000000
H	1.810949000000	-6.195179000000	-1.438774000000
H	4.069609000000	-5.257073000000	-0.997344000000
H	1.440254000000	0.759170000000	0.138703000000
C	-0.356485000000	2.519187000000	-0.446994000000
O	-0.661218000000	2.749530000000	0.702130000000
O	0.107647000000	3.379877000000	-1.317903000000
C	0.258804000000	4.731826000000	-0.835211000000
H	-0.710425000000	5.119339000000	-0.518627000000
H	0.962009000000	4.749185000000	-0.001491000000
H	0.644747000000	5.297679000000	-1.679560000000

1y Int-Trans

Zero-point correction= 0.545269 (Hartree/Particle)
Thermal correction to Energy= 0.581390
Thermal correction to Enthalpy= 0.582334
Thermal correction to Gibbs Free Energy= 0.475293
Sum of electronic and zero-point Energies= -1704.710277
Sum of electronic and thermal Energies= -1704.674156
Sum of electronic and thermal Enthalpies= -1704.673212
Sum of electronic and thermal Free Energies= -1704.780253

C	-0.153826000000	1.361531000000	-0.736397000000
C	0.961311000000	0.422602000000	-0.123515000000
N	-0.178895000000	-0.106091000000	0.687515000000
C	-1.111065000000	0.665272000000	0.194478000000
O	-2.344040000000	0.810251000000	0.408040000000
Br	-0.584600000000	1.064954000000	-2.640769000000

C	2.067822000000	1.045271000000	0.660477000000
C	1.838996000000	1.656445000000	1.901755000000
C	3.356966000000	1.023172000000	0.135087000000
C	2.888246000000	2.230441000000	2.596760000000
C	4.419251000000	1.607023000000	0.820582000000
C	4.185043000000	2.211554000000	2.059723000000
H	0.845025000000	1.666209000000	2.342921000000
H	3.539417000000	0.537927000000	-0.820005000000
H	2.732314000000	2.694871000000	3.564560000000
H	5.413462000000	1.572529000000	0.392311000000
O	-0.251362000000	-0.944113000000	1.737674000000
Si	-3.311955000000	0.594143000000	1.909099000000
C	-2.170923000000	1.183589000000	3.253505000000
H	-1.782032000000	2.177232000000	3.007660000000
H	-2.733415000000	1.268435000000	4.190102000000
H	-1.333524000000	0.502247000000	3.426993000000
C	-4.686696000000	1.783210000000	1.539212000000
H	-5.410946000000	1.801967000000	2.359542000000
H	-4.284534000000	2.793295000000	1.414324000000
H	-5.216731000000	1.505583000000	0.623037000000
C	-3.835220000000	-1.223800000000	1.991724000000
C	-3.460666000000	-1.952671000000	0.692865000000
H	-2.376428000000	-1.981780000000	0.535390000000
H	-3.812509000000	-2.990544000000	0.742617000000
H	-3.917979000000	-1.486589000000	-0.186827000000
C	-3.166853000000	-1.917274000000	3.188306000000
H	-3.492262000000	-2.964104000000	3.232886000000
H	-2.075493000000	-1.907756000000	3.111937000000
H	-3.441844000000	-1.442545000000	4.136599000000
C	-5.361506000000	-1.283546000000	2.176303000000
H	-5.894432000000	-0.836699000000	1.330876000000
H	-5.675831000000	-2.331701000000	2.254582000000
H	-5.684069000000	-0.772761000000	3.090488000000
C	0.331444000000	-2.252394000000	1.433223000000
H	-0.067879000000	-2.871777000000	2.239568000000
H	-0.063822000000	-2.598428000000	0.474625000000
O	5.140311000000	2.792983000000	2.814028000000
C	6.471956000000	2.777340000000	2.319160000000
H	6.832040000000	1.751177000000	2.188730000000
H	6.546797000000	3.314580000000	1.367738000000
H	7.078280000000	3.282729000000	3.070205000000
C	1.833146000000	-2.193267000000	1.449618000000
C	2.494308000000	-1.686695000000	2.573617000000
C	2.571188000000	-2.624483000000	0.348000000000

C	3.882384000000	-1.605757000000	2.589291000000
C	3.964568000000	-2.554880000000	0.368398000000
C	4.618938000000	-2.042734000000	1.485932000000
H	1.915773000000	-1.343869000000	3.427777000000
H	2.053933000000	-3.011599000000	-0.526218000000
H	4.391671000000	-1.202419000000	3.459095000000
H	4.535008000000	-2.892374000000	-0.491077000000
H	5.702656000000	-1.978131000000	1.498433000000
H	1.318030000000	-0.322804000000	-0.836762000000
C	0.028303000000	2.832137000000	-0.393877000000
O	-0.586386000000	3.349754000000	0.507096000000
O	0.951389000000	3.393939000000	-1.141000000000
C	1.292408000000	4.748954000000	-0.786079000000
H	0.413126000000	5.388961000000	-0.869799000000
H	1.679134000000	4.771069000000	0.234660000000
H	2.058666000000	5.050679000000	-1.496079000000

Br_2 with 2 HFIP

Zero-point correction= 0.130886 (Hartree/Particle)
Thermal correction to Energy= 0.155061
Thermal correction to Enthalpy= 0.156005
Thermal correction to Gibbs Free Energy= 0.069030
Sum of electronic and zero-point Energies= -1605.179315
Sum of electronic and thermal Energies= -1605.155140
Sum of electronic and thermal Enthalpies= -1605.154196
Sum of electronic and thermal Free Energies= -1605.241171

C	0.260215000000	-0.302466000000	-0.463167000000
H	-0.348732000000	-1.204767000000	-0.350243000000
C	-0.347171000000	0.554468000000	-1.565875000000
F	0.458836000000	1.578550000000	-1.869345000000
F	-0.514099000000	-0.173360000000	-2.670842000000
F	-1.532381000000	1.046948000000	-1.206079000000
C	0.292861000000	0.423851000000	0.879778000000
F	0.896428000000	-0.346961000000	1.789219000000
F	0.972120000000	1.573141000000	0.796743000000
F	-0.936211000000	0.697322000000	1.320266000000
O	1.574352000000	-0.581005000000	-0.878627000000
H	1.928737000000	-1.332056000000	-0.376196000000
C	4.390421000000	1.583851000000	-0.462745000000
H	4.925342000000	0.677055000000	-0.773300000000
C	4.193232000000	1.504174000000	1.046373000000
F	3.578852000000	2.587660000000	1.527701000000
F	3.424659000000	0.442512000000	1.331029000000

F	5.349833000000	1.358100000000	1.700338000000
C	5.239653000000	2.777774000000	-0.866849000000
F	5.429335000000	2.775617000000	-2.188892000000
F	4.650262000000	3.932920000000	-0.543048000000
F	6.438605000000	2.746667000000	-0.276225000000
O	3.156237000000	1.757254000000	-1.086397000000
H	2.643898000000	0.931836000000	-1.013789000000
Br	2.557622000000	-0.950883000000	-3.526020000000
Br	3.691514000000	-1.279436000000	-5.716329000000

Br with 1 HFIP

Zero-point correction= 0.064092 (Hartree/Particle)
Thermal correction to Energy= 0.075126
Thermal correction to Enthalpy= 0.076071
Thermal correction to Gibbs Free Energy= 0.023271
Sum of electronic and zero-point Energies= -802.773377
Sum of electronic and thermal Energies= -802.762343
Sum of electronic and thermal Enthalpies= -802.761398
Sum of electronic and thermal Free Energies= -802.814198

C	4.319987000000	1.677138000000	-0.283701000000
H	4.326355000000	0.799157000000	-0.943247000000
C	5.018512000000	1.296525000000	1.011401000000
F	5.043032000000	2.316103000000	1.880098000000
F	4.369529000000	0.285790000000	1.598482000000
F	6.284041000000	0.907578000000	0.807972000000
C	5.035113000000	2.808207000000	-1.006868000000
F	4.405636000000	3.083647000000	-2.153568000000
F	5.050829000000	3.932107000000	-0.277911000000
F	6.305112000000	2.498639000000	-1.300973000000
O	3.028826000000	2.095405000000	0.023502000000
H	2.419758000000	1.500923000000	-0.496143000000
Br	1.637713000000	-0.037232000000	-1.805126000000

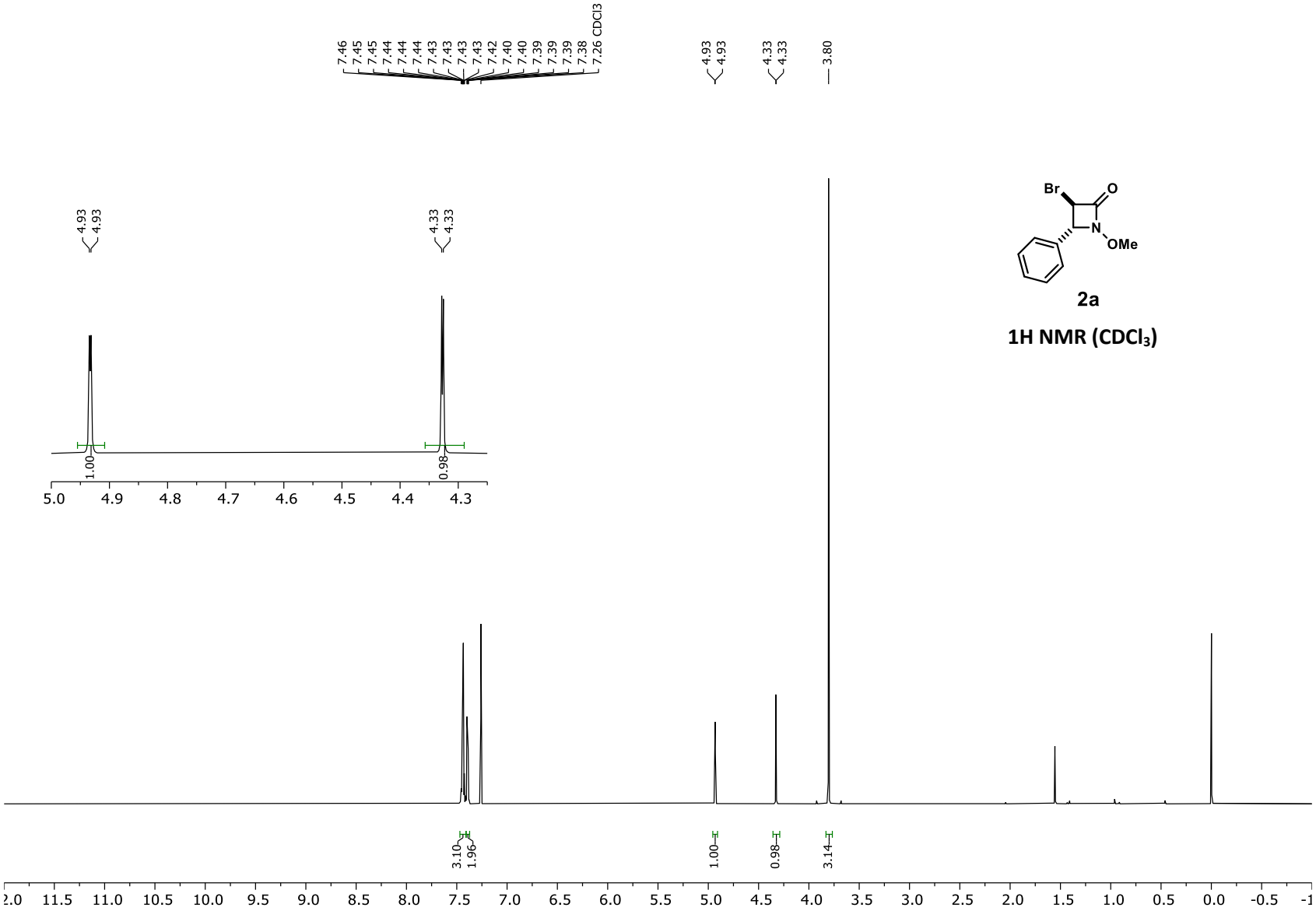
1a with 1 HFIP

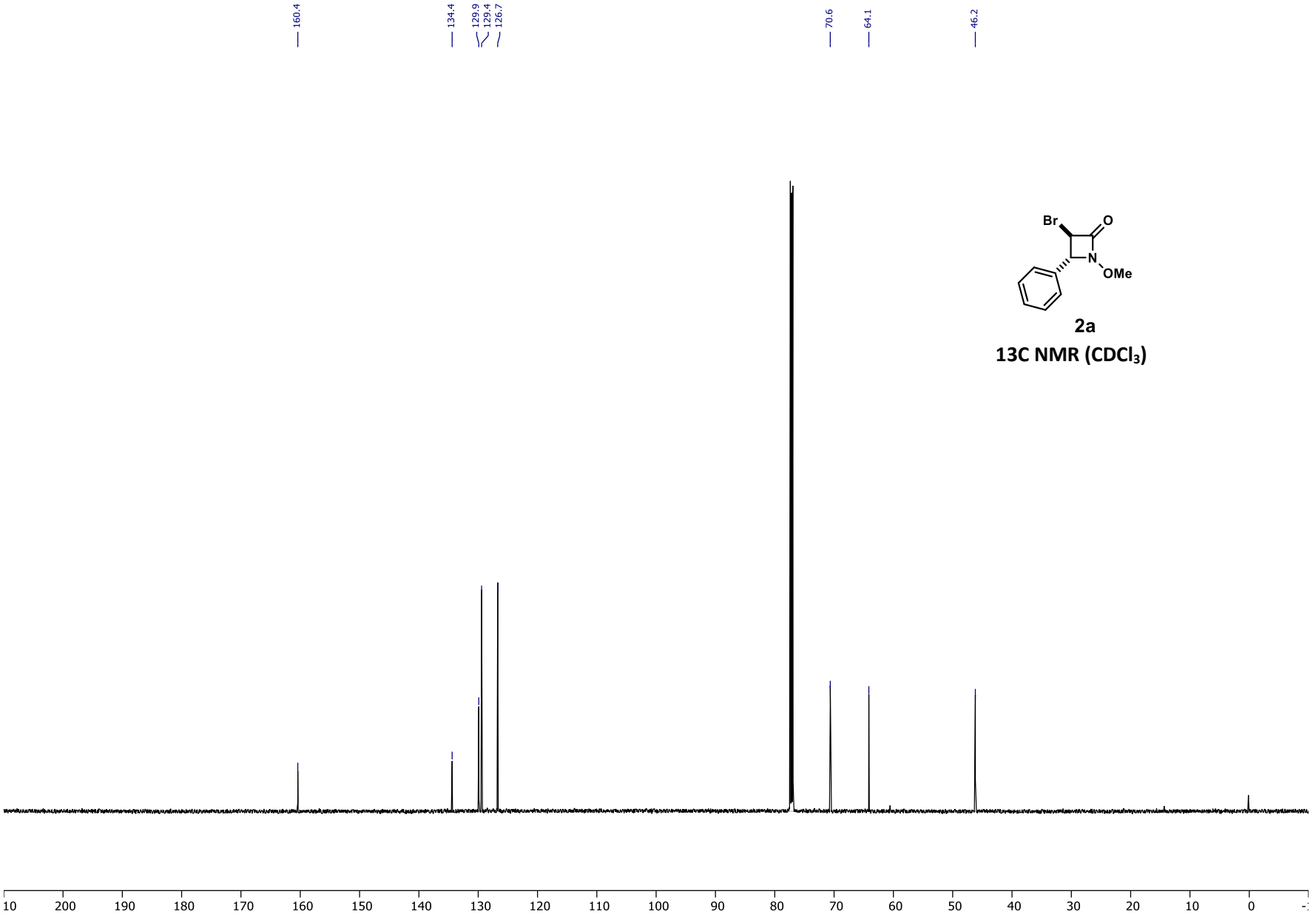
Zero-point correction= 0.451228 (Hartree/Particle)
Thermal correction to Energy= 0.487043
Thermal correction to Enthalpy= 0.487987
Thermal correction to Gibbs Free Energy= 0.382895
Sum of electronic and zero-point Energies= -1921.098964
Sum of electronic and thermal Energies= -1921.063150
Sum of electronic and thermal Enthalpies= -1921.062206
Sum of electronic and thermal Free Energies= -1921.167298

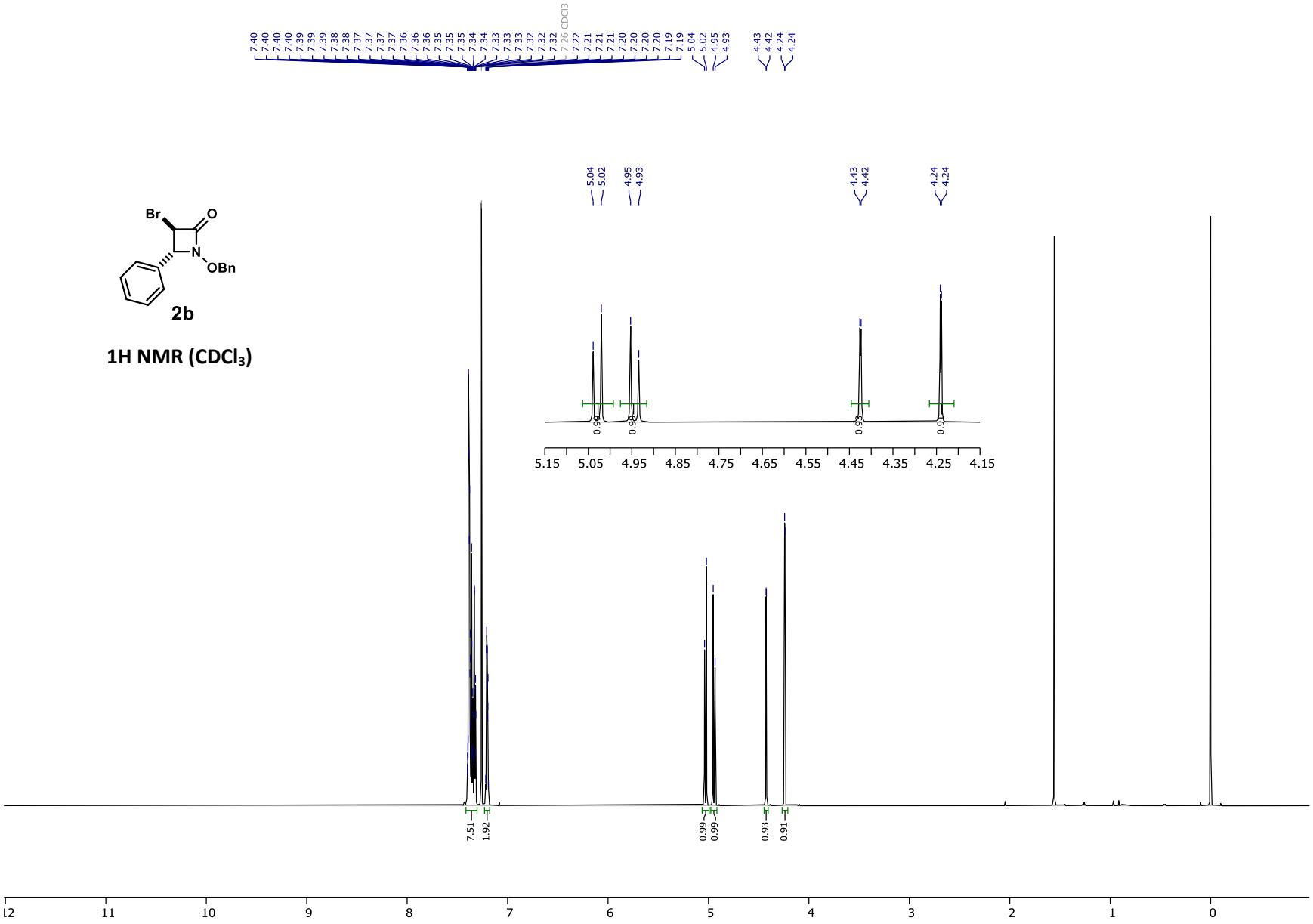
C	1.947668000000	0.055189000000	-0.754194000000
C	1.146824000000	-0.709728000000	0.220868000000
H	1.692358000000	-1.369141000000	0.889409000000
H	1.392631000000	0.801989000000	-1.319395000000
C	3.294947000000	-0.114839000000	-1.033775000000
C	4.118172000000	-1.068375000000	-0.362869000000
C	3.867635000000	0.763541000000	-2.002714000000
C	5.456804000000	-1.137885000000	-0.670168000000
C	5.212465000000	0.688511000000	-2.289446000000
C	5.998052000000	-0.262807000000	-1.626556000000
H	3.696108000000	-1.738586000000	0.378006000000
H	3.226815000000	1.490509000000	-2.493539000000
H	6.096692000000	-1.859176000000	-0.175562000000
H	5.661175000000	1.353757000000	-3.017686000000
H	7.057704000000	-0.325627000000	-1.855883000000
C	0.148415000000	0.108443000000	0.968178000000
N	0.056334000000	-0.168102000000	2.213516000000
O	-0.874873000000	0.636817000000	2.825137000000
C	-0.922684000000	0.349911000000	4.218056000000
H	-1.234267000000	-0.685087000000	4.385199000000
H	0.052142000000	0.526906000000	4.679699000000
H	-1.663765000000	1.033589000000	4.634276000000
O	-0.515090000000	0.999679000000	0.254394000000
Si	-1.680072000000	2.228422000000	0.618720000000
C	-0.978241000000	3.448090000000	1.850907000000
H	-1.291173000000	4.469290000000	1.609222000000
H	-1.300302000000	3.219121000000	2.869950000000
H	0.115749000000	3.415571000000	1.828540000000
C	-1.816636000000	3.020530000000	-1.092391000000
C	-3.288841000000	1.422301000000	1.119088000000
H	-3.404127000000	0.456736000000	0.615246000000
H	-3.332264000000	1.250001000000	2.197387000000
H	-4.140215000000	2.050225000000	0.835592000000
C	-0.450916000000	3.582074000000	-1.510614000000
H	-0.084652000000	4.333226000000	-0.798792000000
H	0.301760000000	2.788687000000	-1.594245000000
H	-0.522116000000	4.069627000000	-2.491983000000
C	-2.273520000000	1.973839000000	-2.117038000000
H	-2.341638000000	2.423984000000	-3.116479000000
H	-1.572956000000	1.133102000000	-2.176695000000
H	-3.262601000000	1.571454000000	-1.869064000000
C	-2.837911000000	4.166056000000	-1.050469000000
H	-2.920579000000	4.630468000000	-2.042038000000
H	-3.837142000000	3.814370000000	-0.770243000000

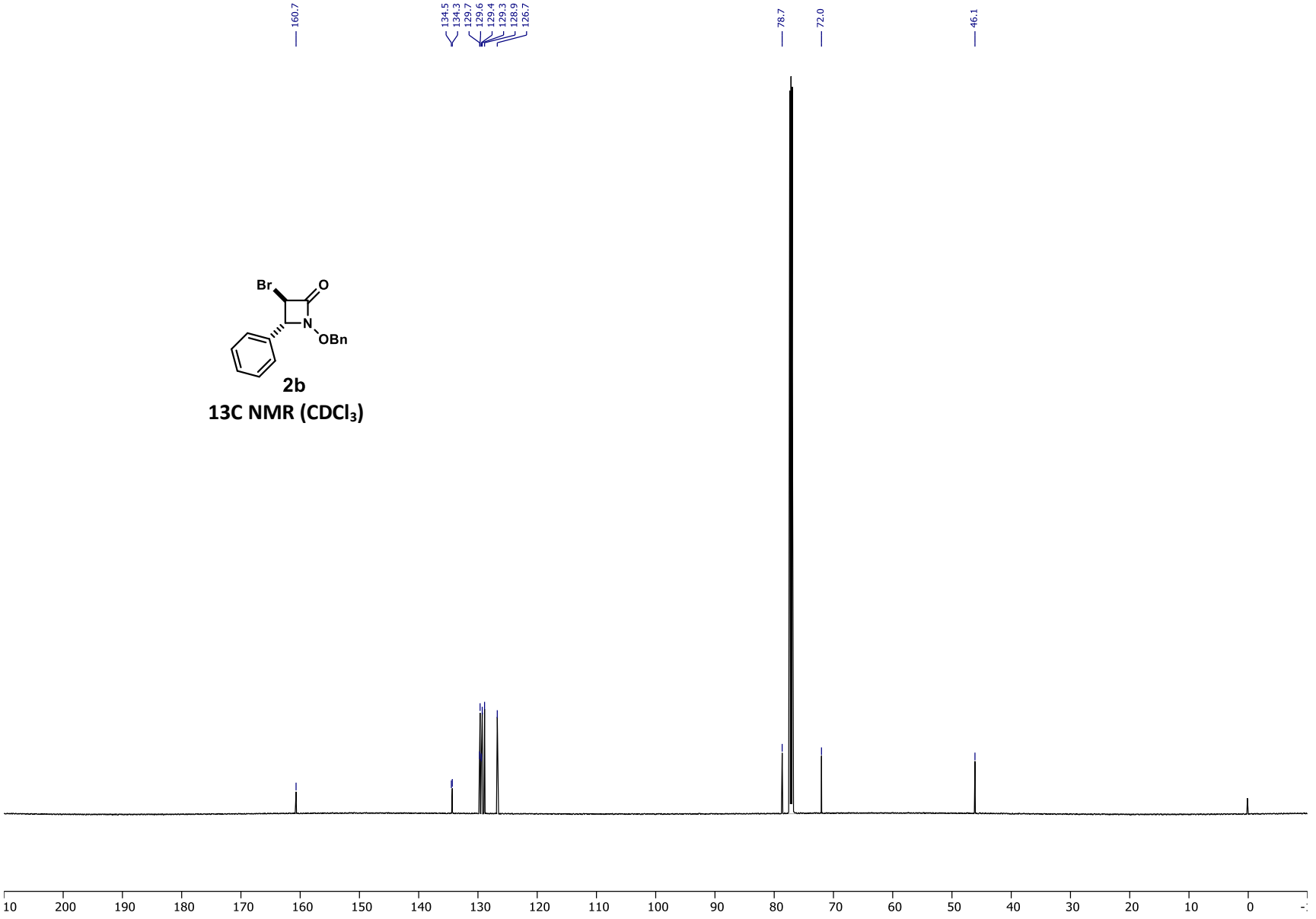
H	-2.546055000000	4.952083000000	-0.344822000000
Br	0.149823000000	-1.942021000000	-1.086144000000
C	3.009997000000	2.768776000000	1.521840000000
H	2.767847000000	3.751201000000	1.940752000000
C	4.424142000000	2.843504000000	0.945572000000
F	4.948151000000	1.627208000000	0.735116000000
F	4.404016000000	3.483054000000	-0.226568000000
F	5.246867000000	3.498774000000	1.768246000000
C	2.926001000000	1.745763000000	2.644635000000
F	1.757851000000	1.852815000000	3.281380000000
F	3.020620000000	0.495895000000	2.169377000000
F	3.908313000000	1.921510000000	3.532580000000
O	2.106532000000	2.351408000000	0.542657000000
H	1.738228000000	3.123830000000	0.088315000000

20. Spectroscopic Data:



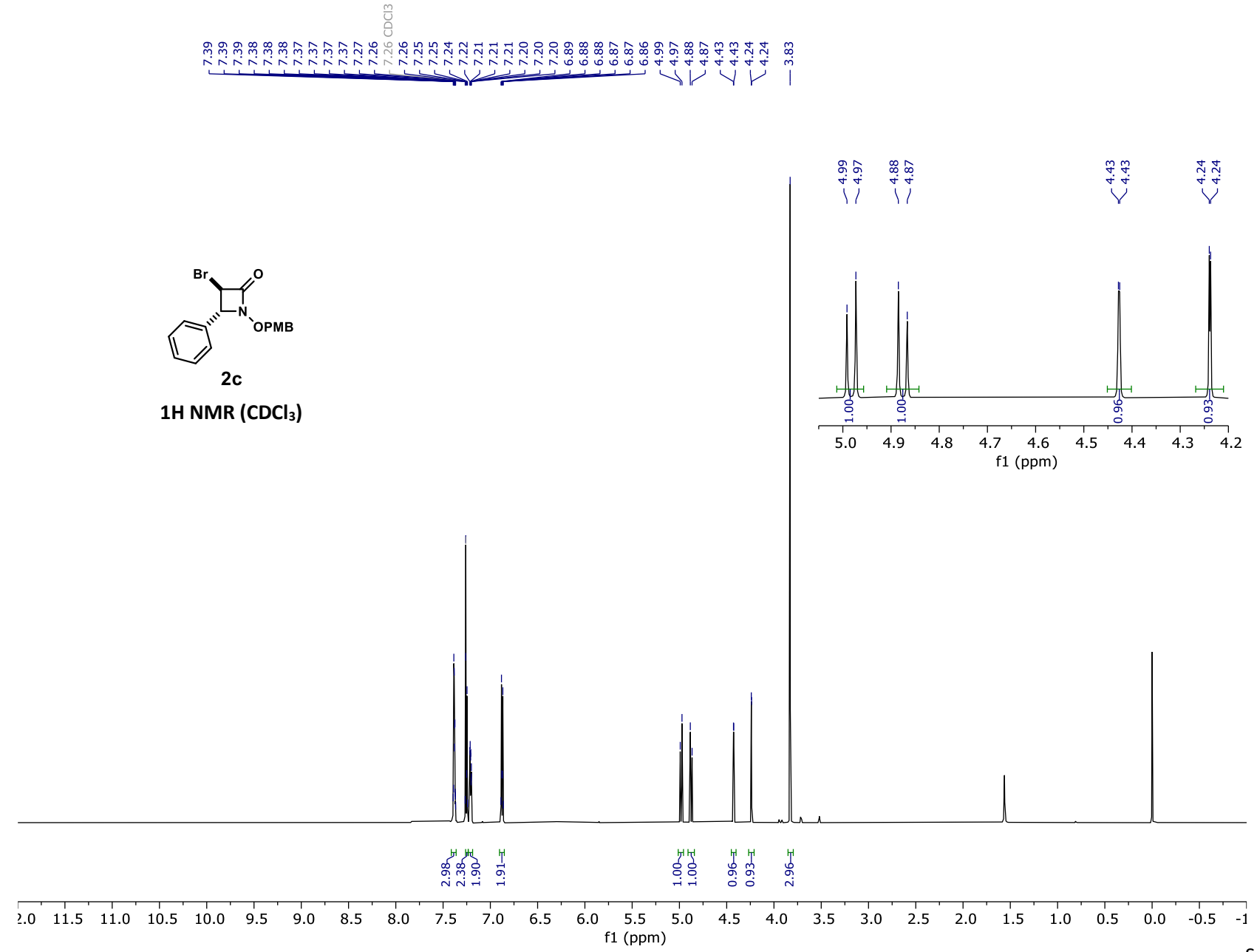

160.4
134.4
129.9
129.4
126.7
70.6
64.1
46.2
Br
O
N
OMe
2a
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

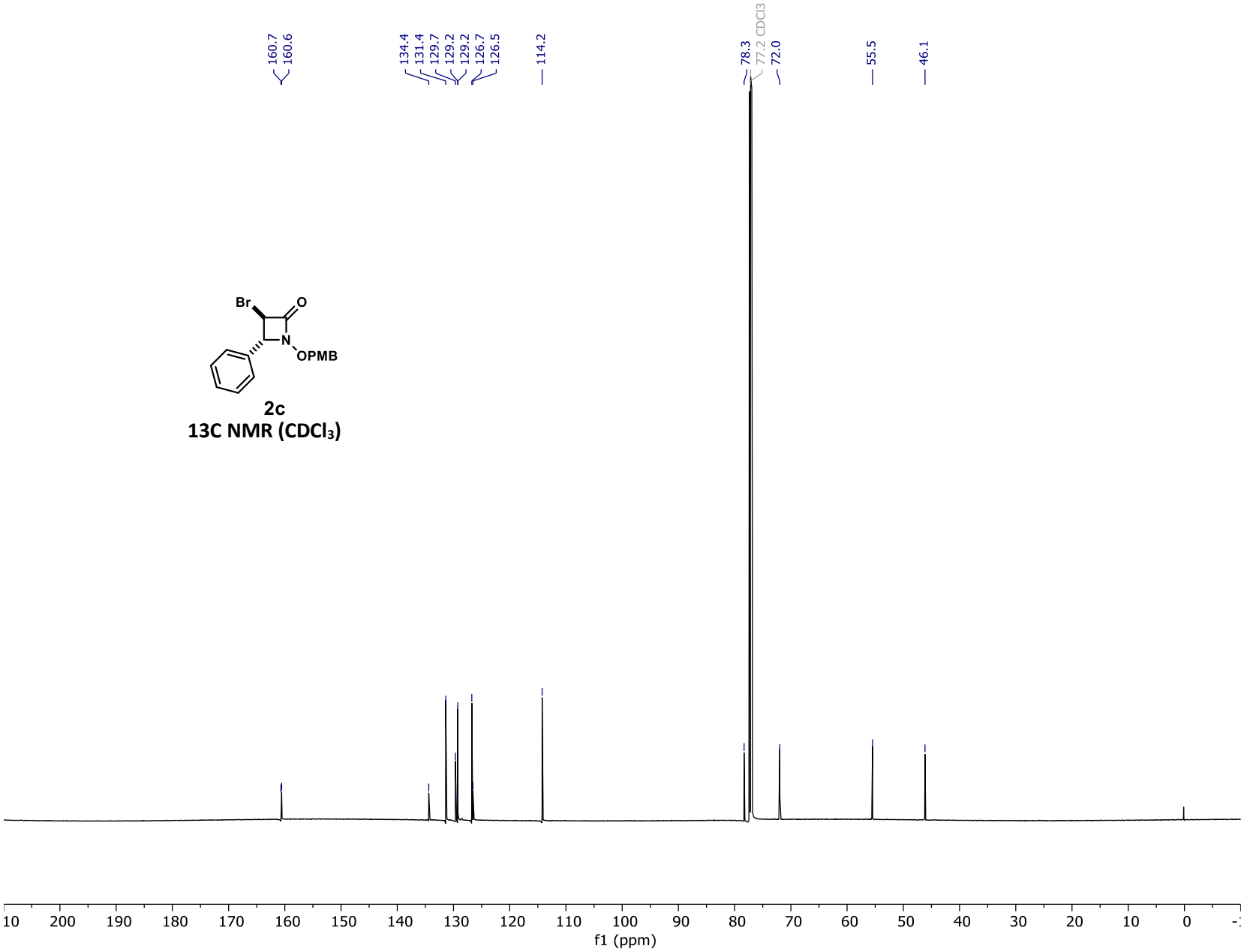

Br
O
N
OBn
2b
1H NMR (CDCl3)
7.26 CDCl3
5.04
5.02
4.95
4.93
4.43
4.42
4.24
4.24
7.51
1.92
0.99
0.99
0.93
0.91



2b

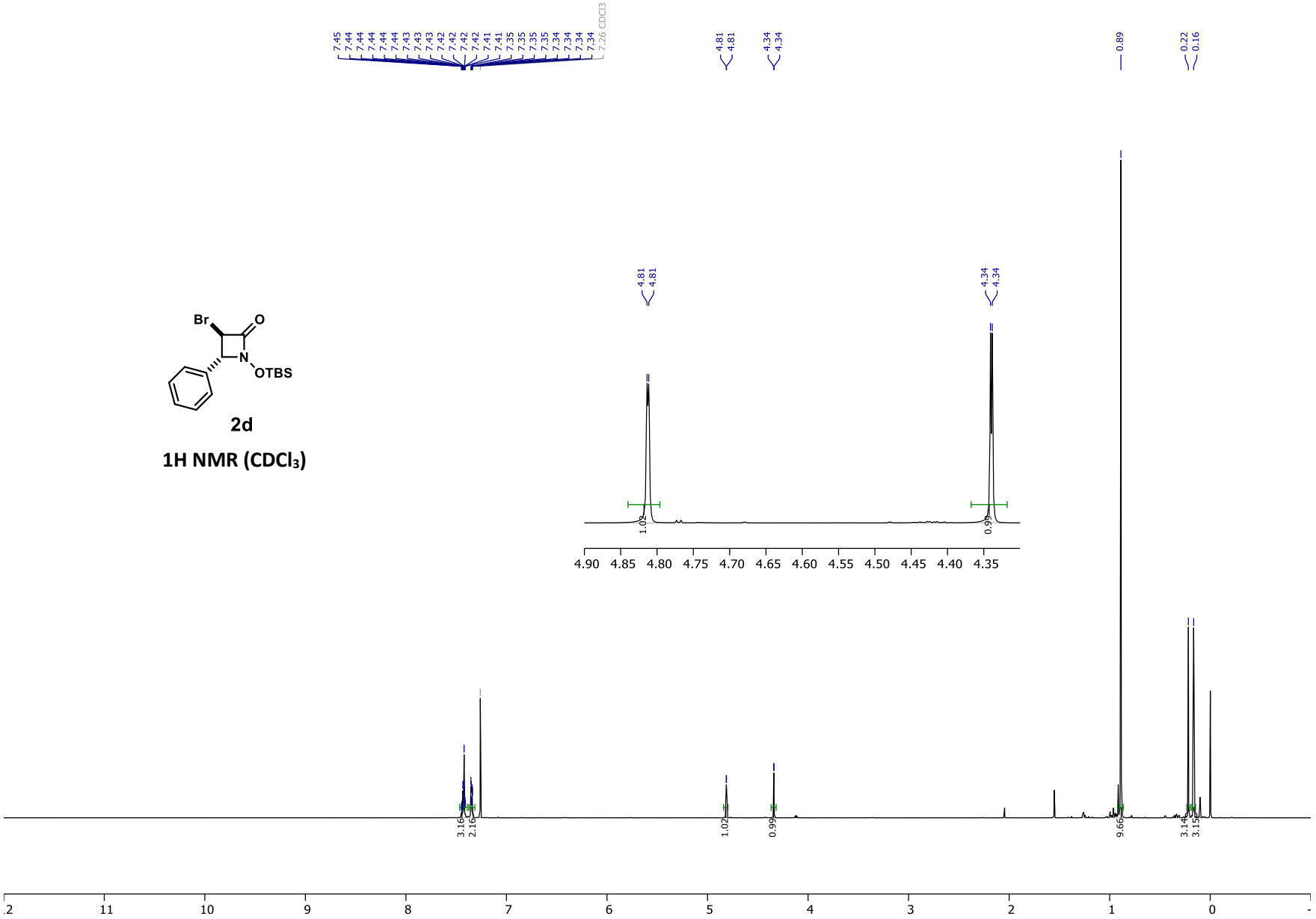
13C NMR ($CDCl_3$)

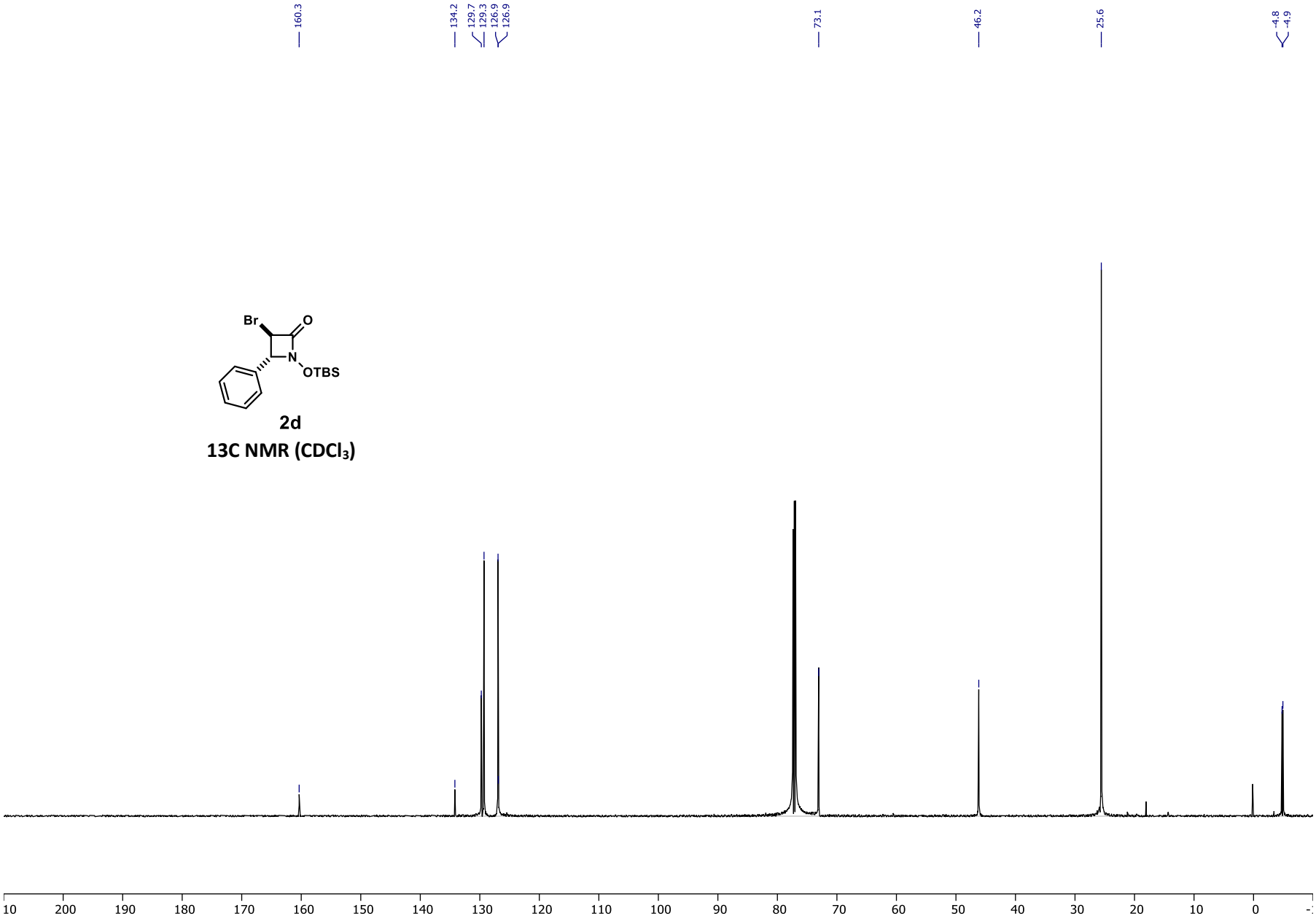

7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.37 7.27 7.26 7.26 CDCl3 7.26 7.25 7.25 7.24 7.22 7.21 7.21 7.21 7.20 7.20 7.20 6.89 6.88 6.88 6.87 6.87 6.86 4.99 4.97 4.88 4.87 4.43 4.43 4.24 4.24 3.83
Br
O
N
OPMB
2c
1H NMR (CDCl3)
4.99 4.97 4.88 4.87 4.43 4.43 4.24 4.24
1.00 1.00 0.96 0.93
5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2
f1 (ppm)
2.98 2.38 1.90 1.91 1.00 1.00 0.96 0.93 2.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



2c

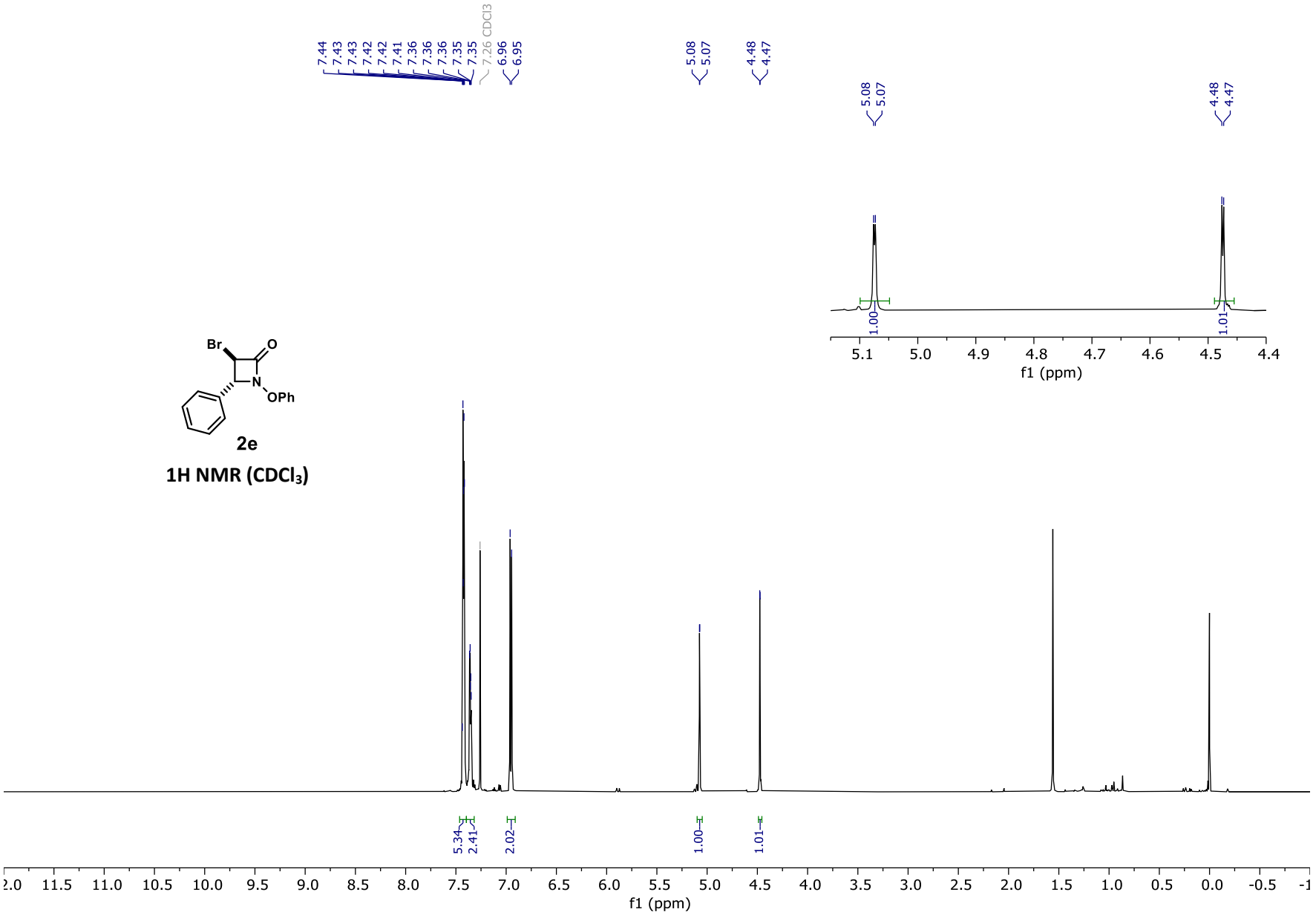
13C NMR ($CDCl_3$)

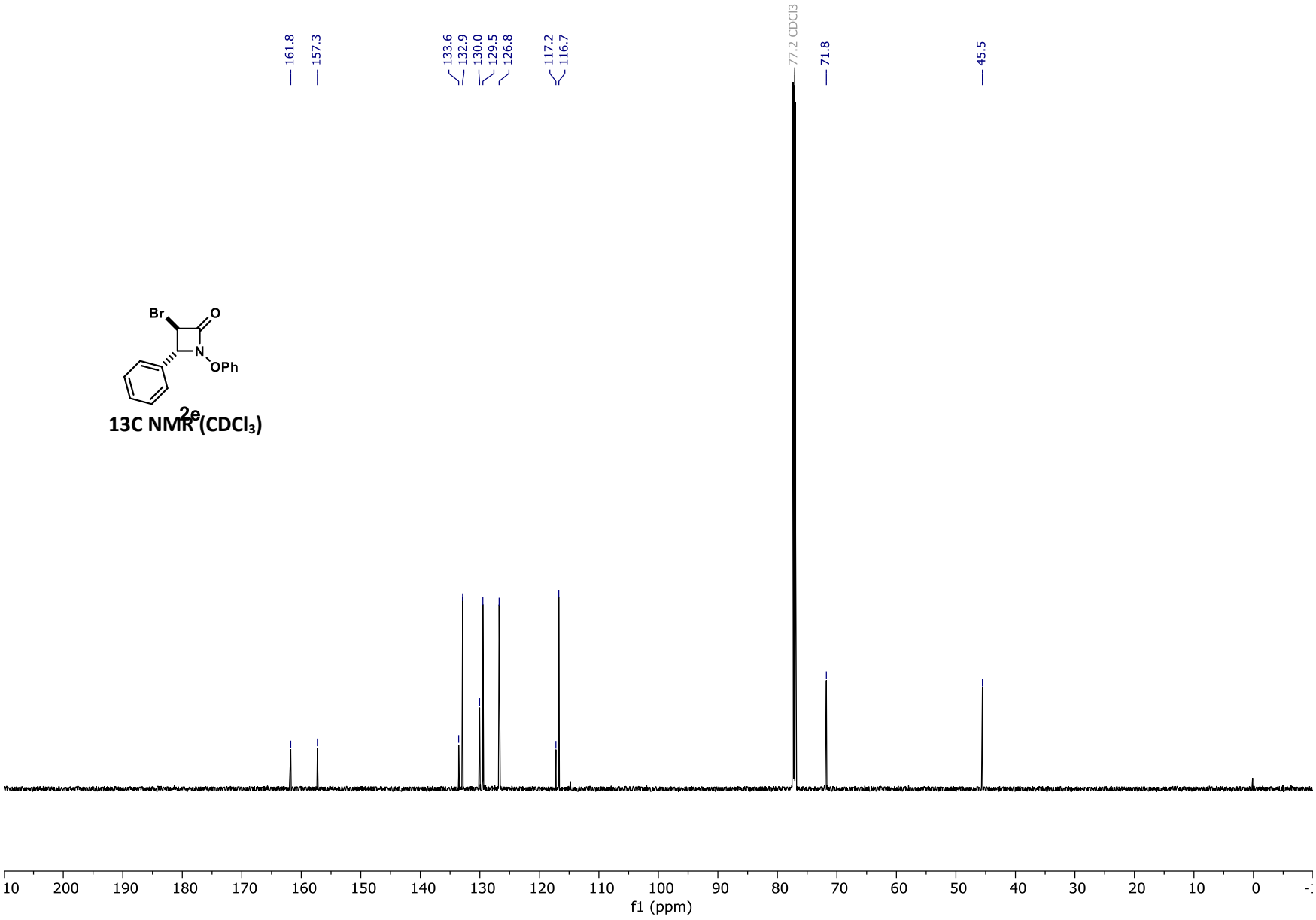

Br
O
N
OTBS
2d
1H NMR (CDCl3)
7.45 7.44 7.44 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.35 7.35 7.35 7.35 7.34 7.34 7.34 7.34 7.26 CDCl3
4.81 4.81
4.34 4.34
0.89
0.22 0.16
4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35
3.16 2.16 1.02 0.99 9.66 3.14 3.15
.2 11 10 9 8 7 6 5 4 3 2 1 0 -

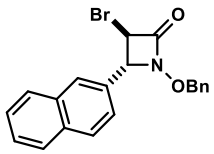


2d

13C NMR ($CDCl_3$)

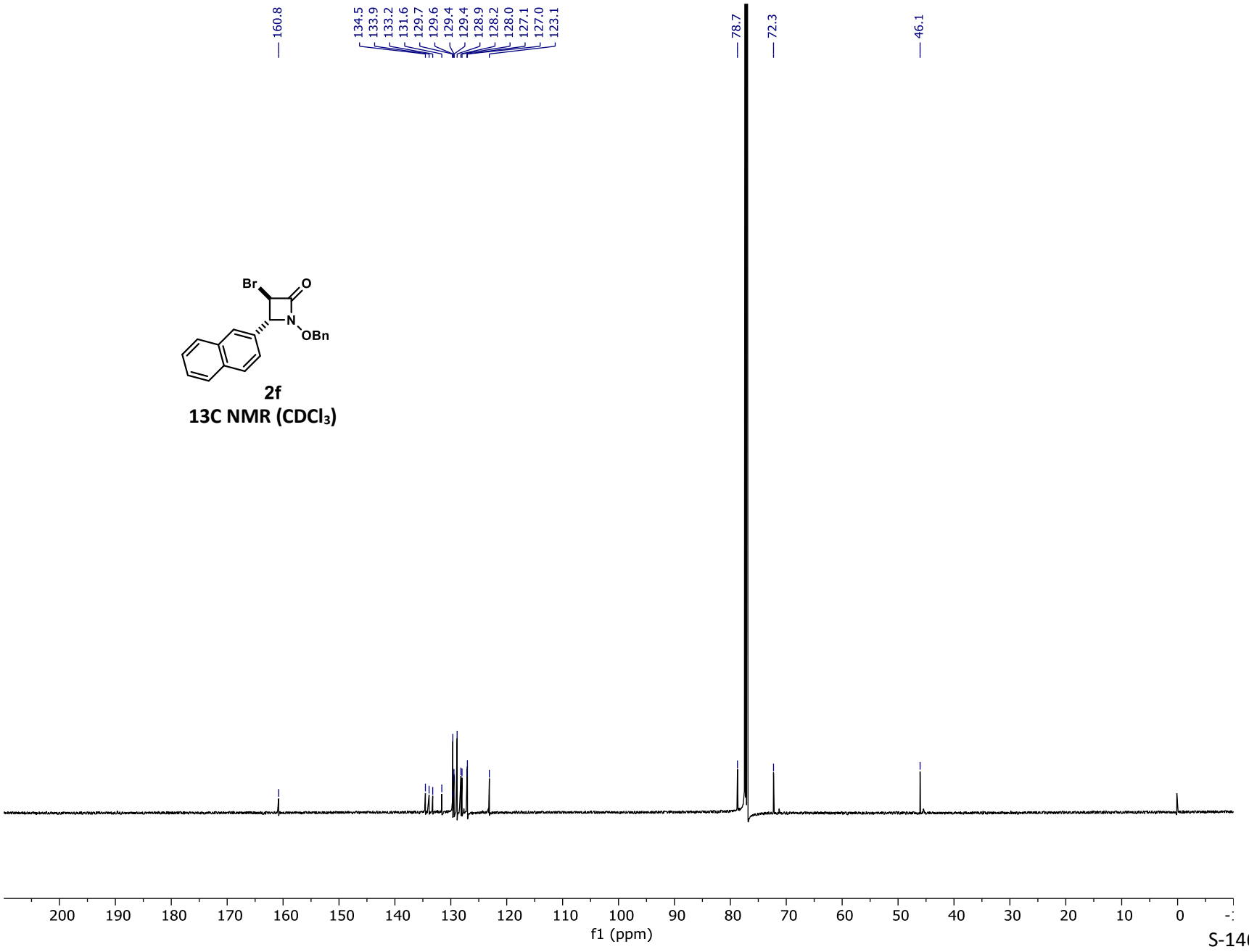

7.44
7.43
7.43
7.42
7.42
7.41
7.36
7.36
7.36
7.35
7.35
7.26 CDCl3
6.96
6.95
5.08
5.07
4.48
4.47
Br
O
N
OPh
2e
1H NMR (CDCl3)
1.00
1.01
f1 (ppm)
5.34
2.41
2.02
1.00
1.01
f1 (ppm)


161.8
157.3
133.6
132.9
130.0
129.5
126.8
117.2
116.7
77.2 CDCl3
71.8
45.5
Br
O
N
OPh
2e
13C NMR (CDCl3)
f1 (ppm)



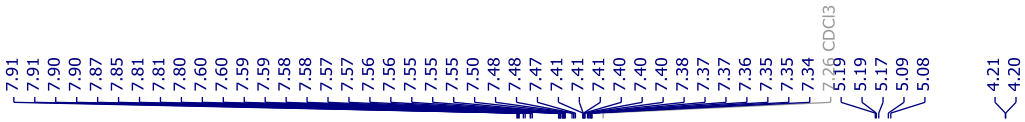
2f

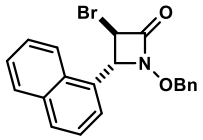
1H NMR ($CDCl_3$)



2f

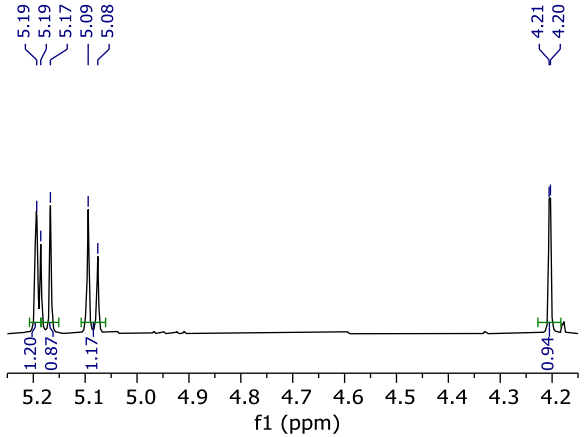
13C NMR ($CDCl_3$)

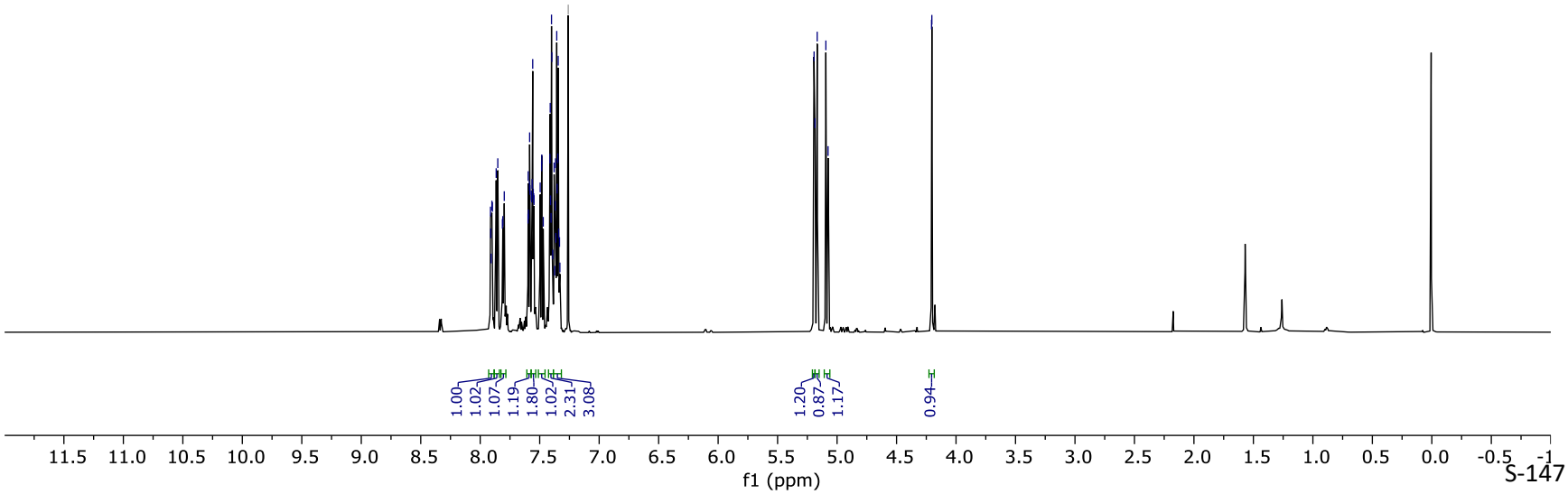


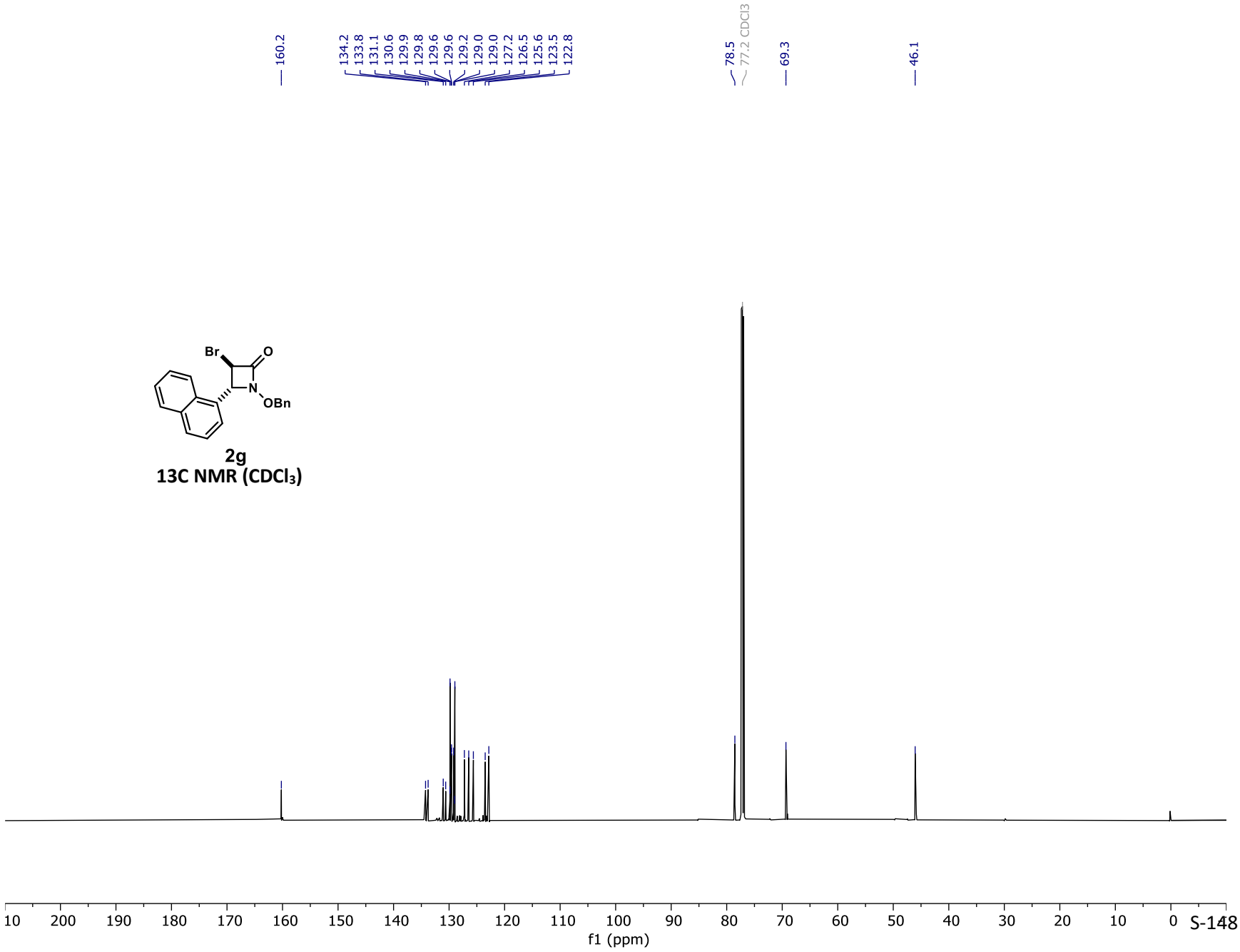


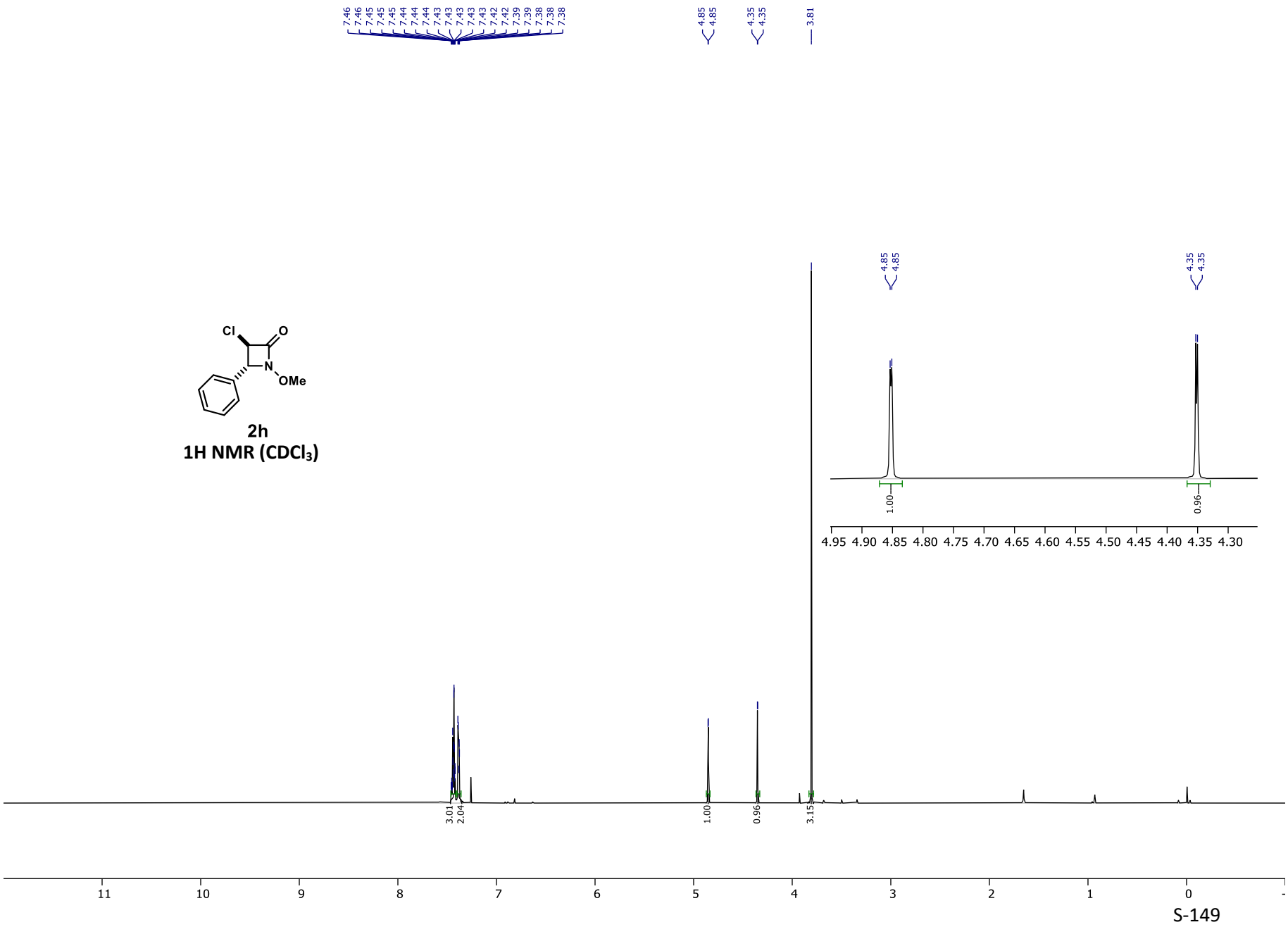
2g

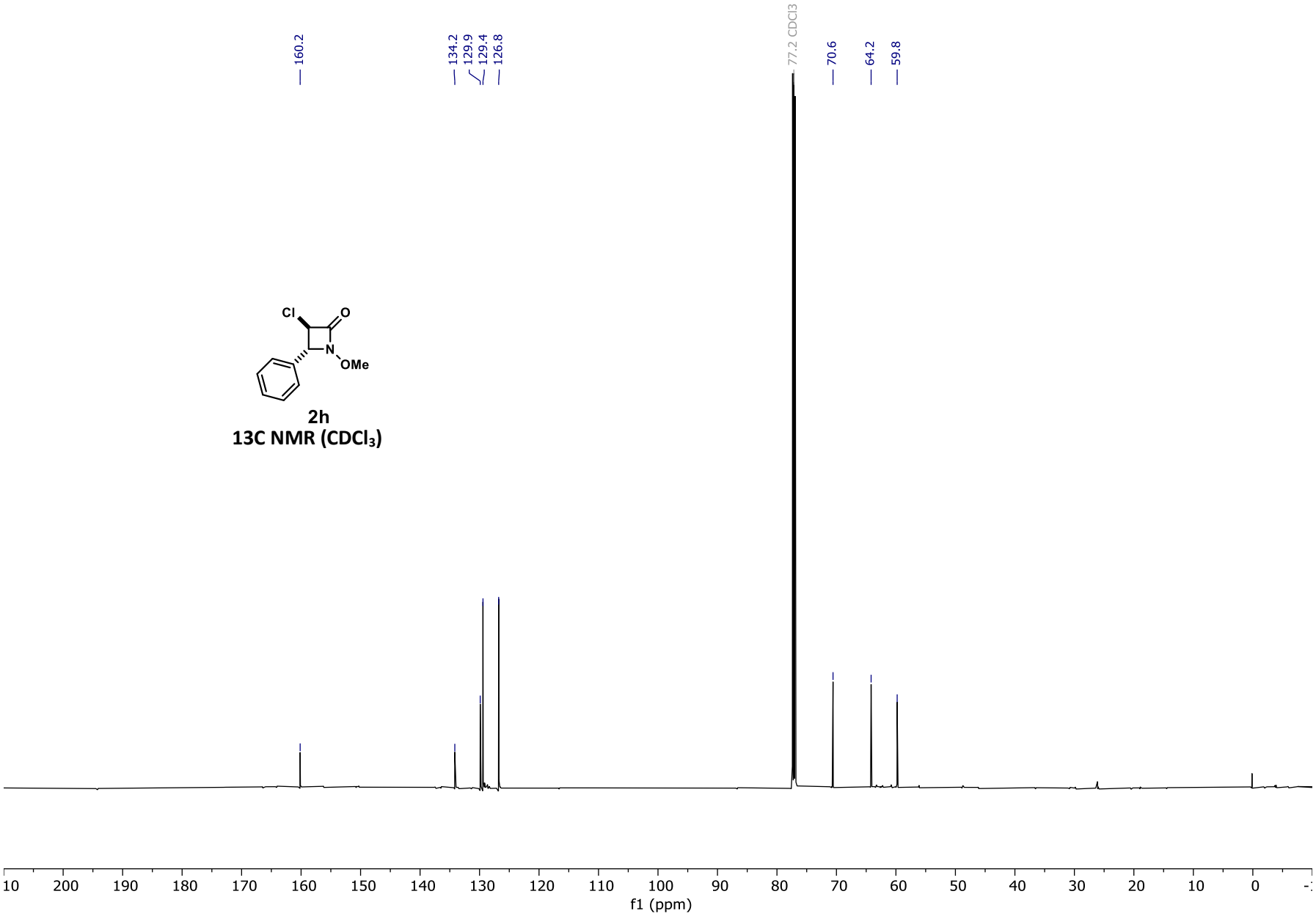
1H NMR ($CDCl_3$)



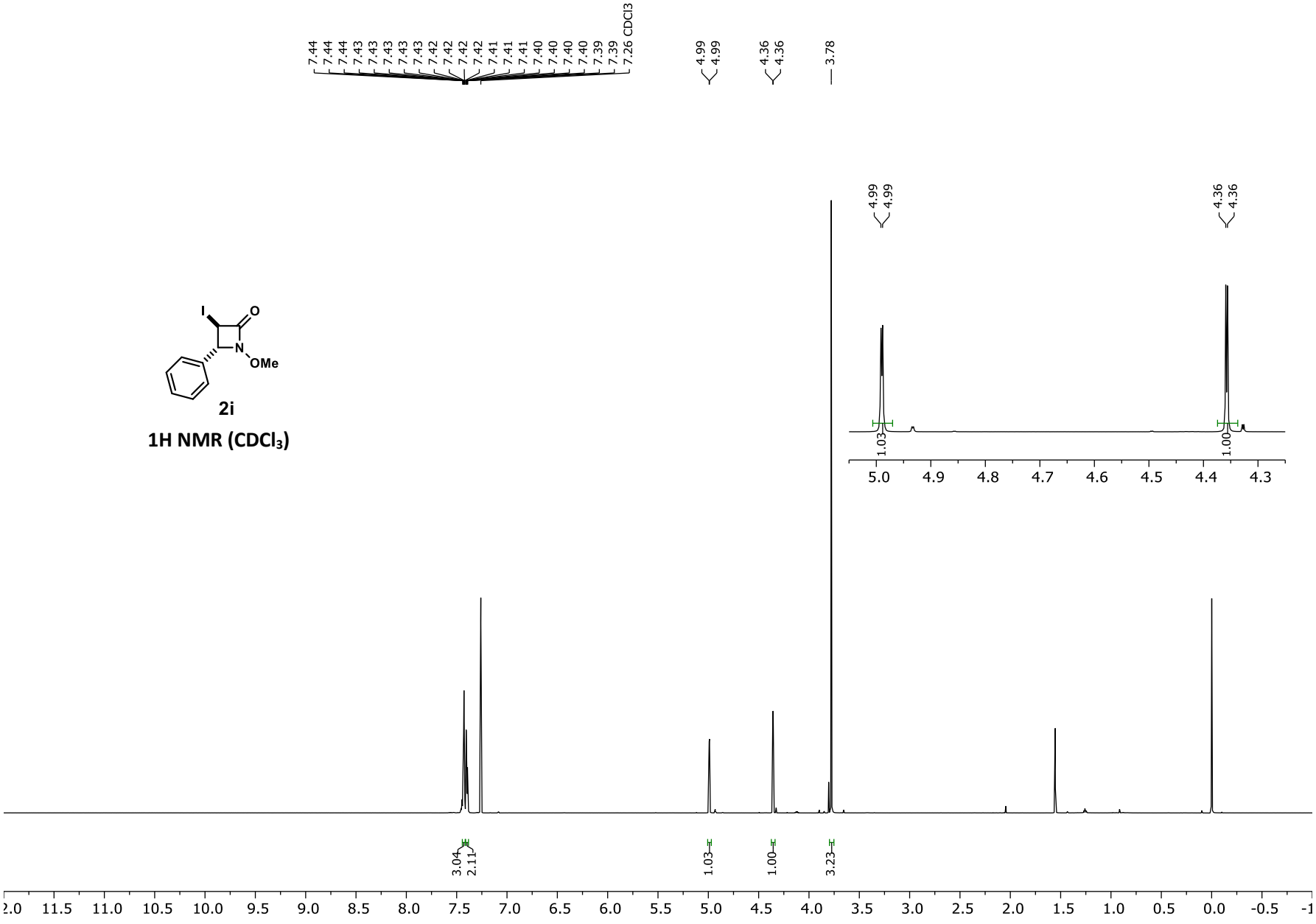


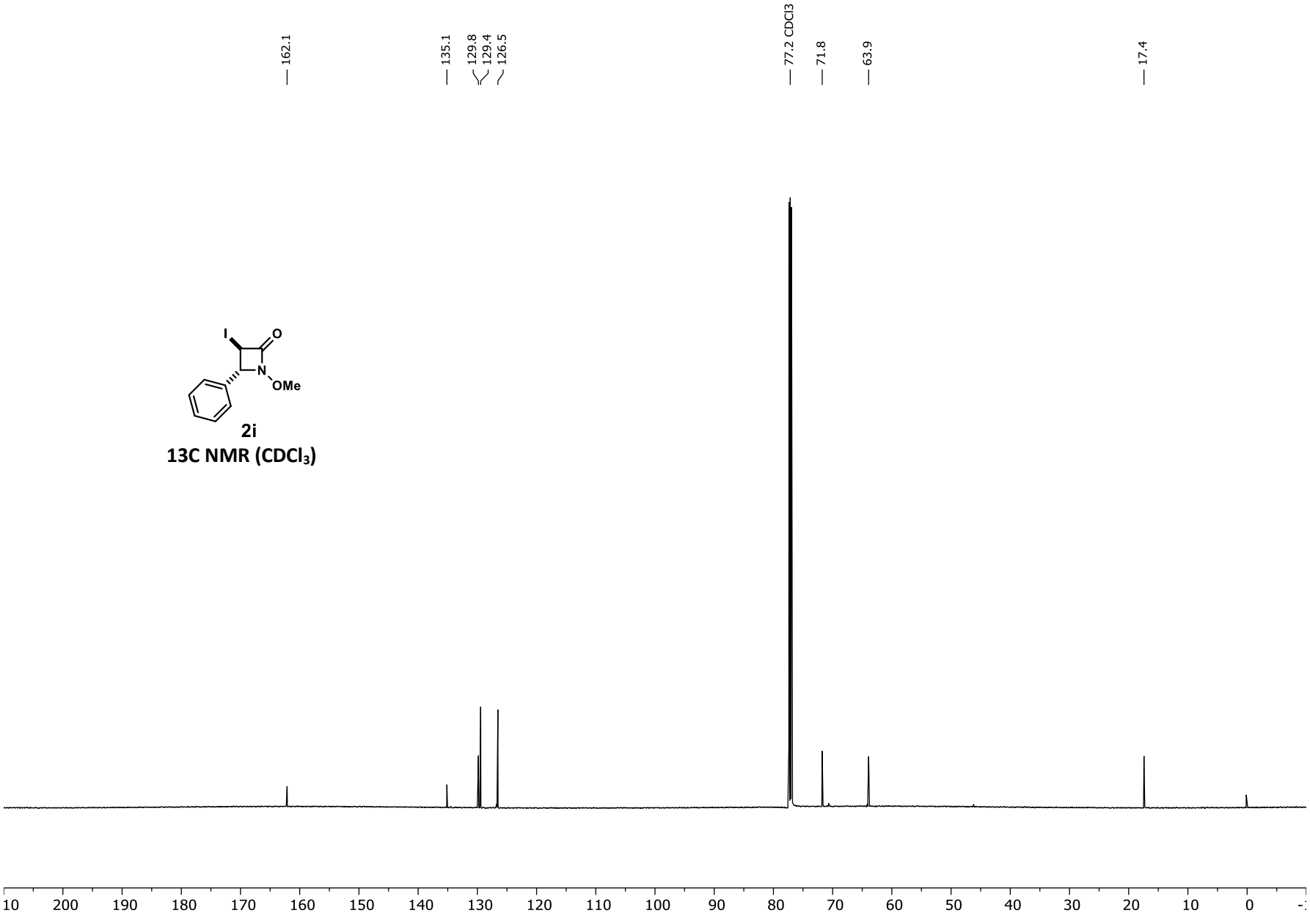

160.2
134.2
133.8
131.1
130.6
129.9
129.8
129.6
129.6
129.2
129.0
129.0
127.2
126.5
125.6
123.5
122.8
78.5
77.2 CDCl3
69.3
46.1
Br
O
N
OBn
2g
13C NMR (CDCl3)
f1 (ppm)

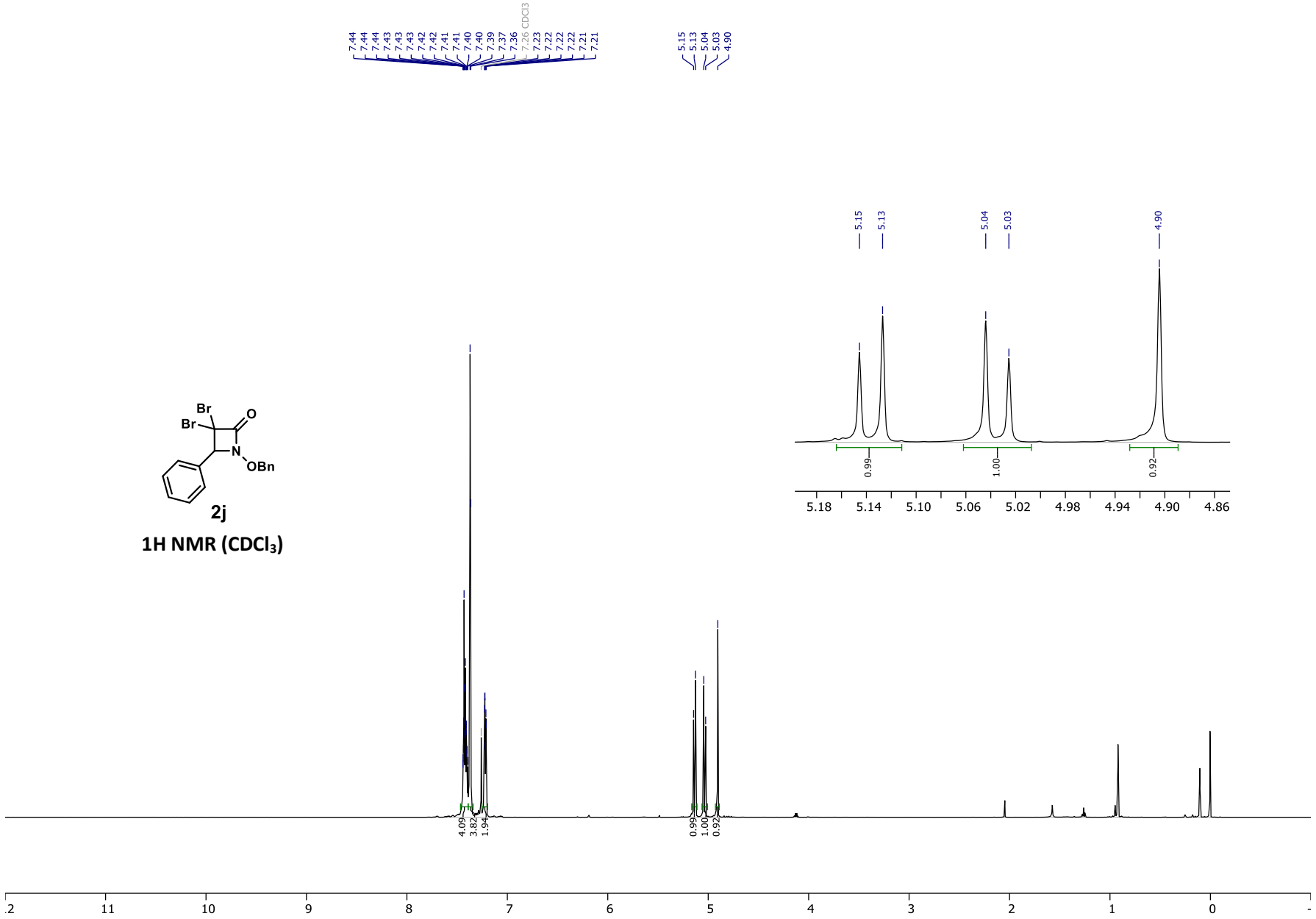

7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.43 7.43 7.42 7.42 7.39 7.39 7.38 7.38 7.38
4.85 4.85
4.35 4.35
3.81
Cl
O
N
OMe
2h
1H NMR (CDCl3)
4.85 4.85
4.35 4.35
1.00
0.96
4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30
3.01
2.04
1.00
0.96
3.15
11 10 9 8 7 6 5 4 3 2 1 0

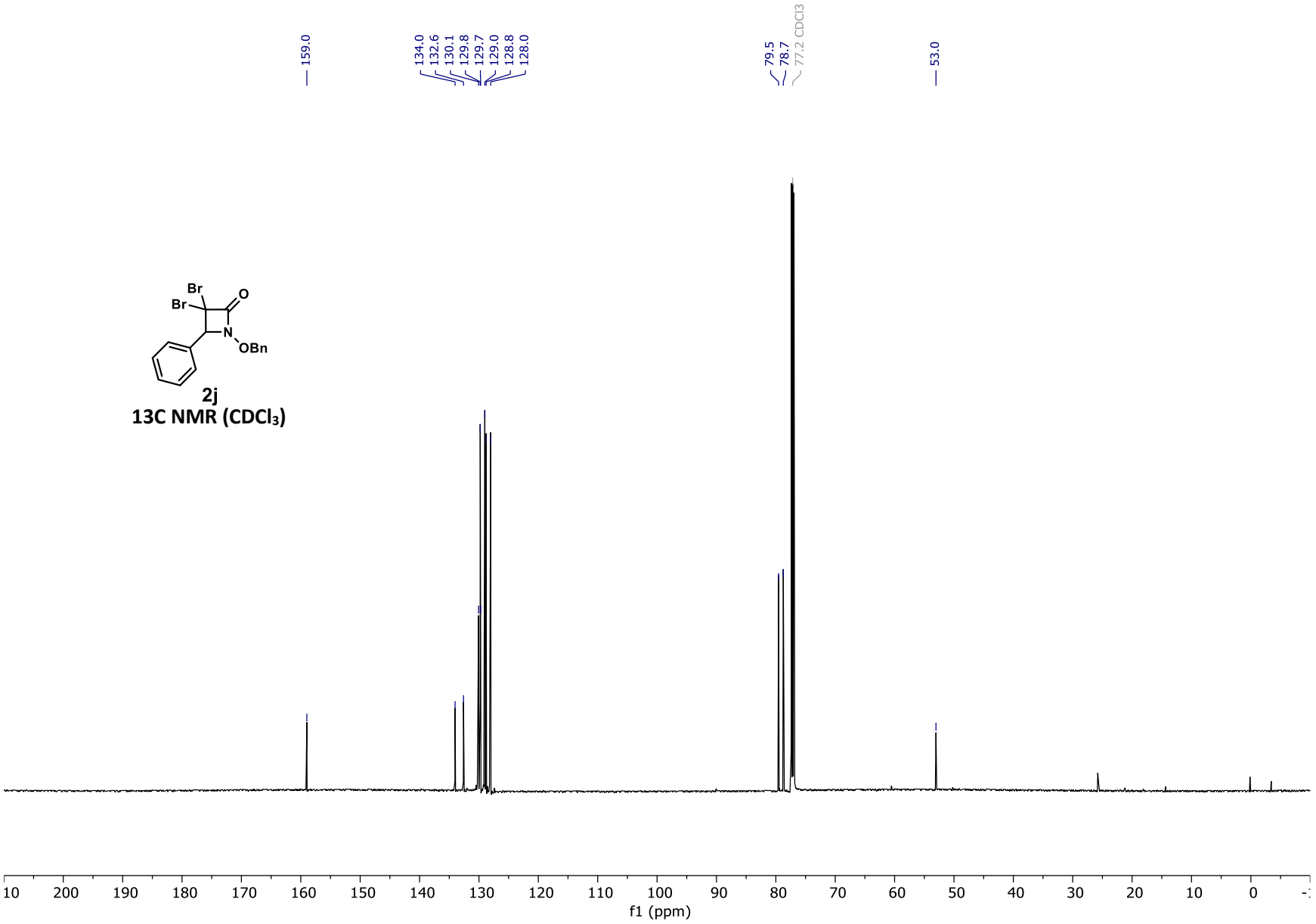


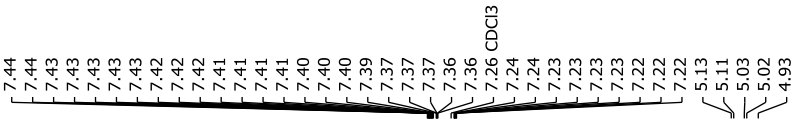
2h
13C NMR ($CDCl_3$)

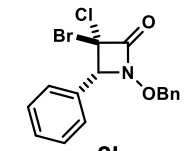

7.44
7.44
7.44
7.43
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.26 CDCl3
4.99
4.99
4.36
4.36
3.78
I
O
N
OMe
2i
1H NMR (CDCl3)
4.99
4.99
4.36
4.36
1.03
1.00
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
3.04
2.11
1.03
1.00
3.23
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1


162.1
135.1
129.8
129.4
126.5
77.2 CDCl3
71.8
63.9
17.4
I
O
N
OMe
2i
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.37
7.36
7.26 CDCl3
7.23
7.22
7.22
7.22
7.21
7.21
5.15
5.13
5.04
5.03
4.90
Br
Br
O
N
OBn
2j
1H NMR (CDCl3)
0.99
1.00
0.92
4.09
3.82
1.94

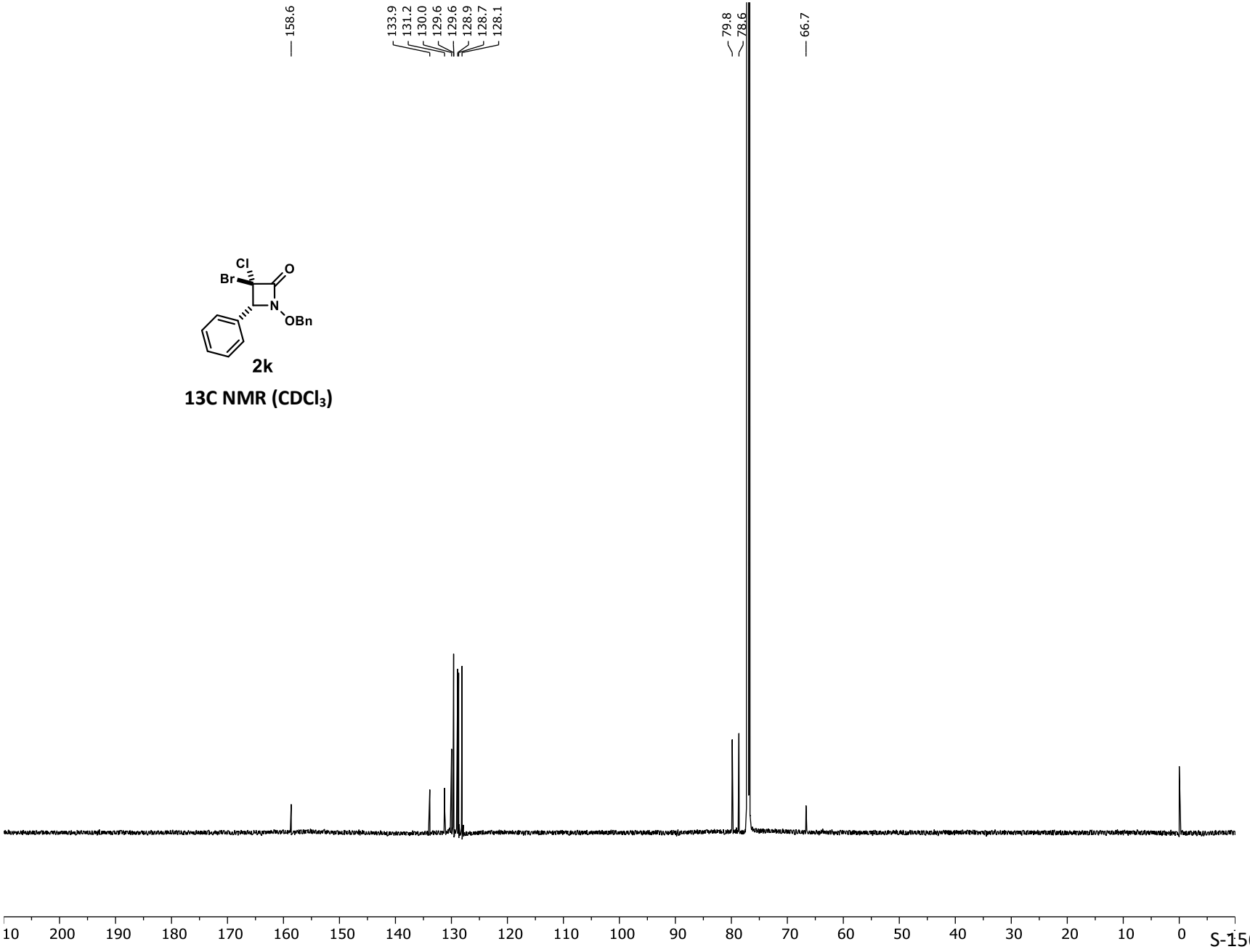

159.0
134.0
132.6
130.1
129.8
129.7
129.0
128.8
128.0
79.5
78.7
77.2 CDCl3
53.0
Br
Br
O
N
OBn
2j
13C NMR (CDCl3)
f1 (ppm)





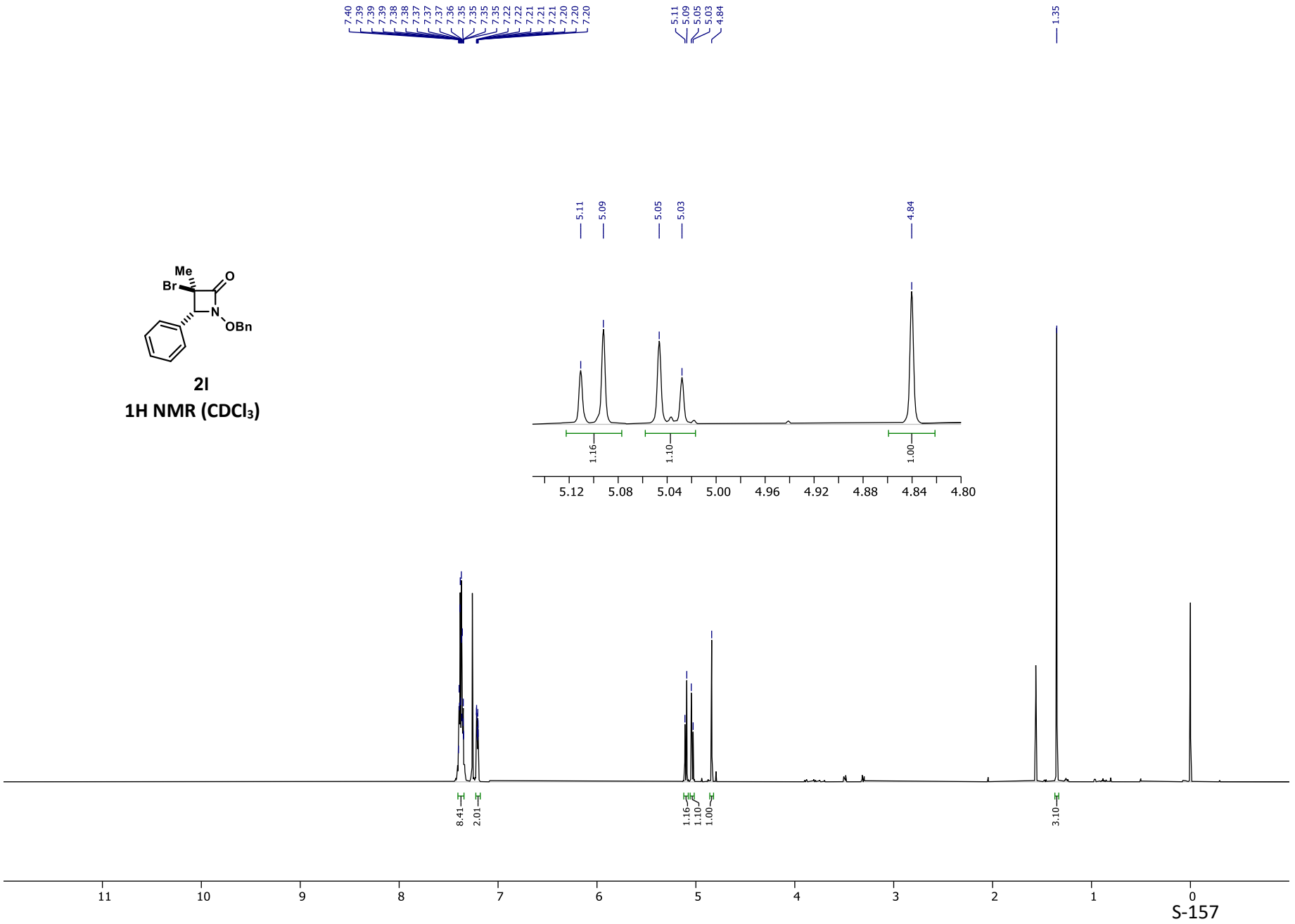
2k

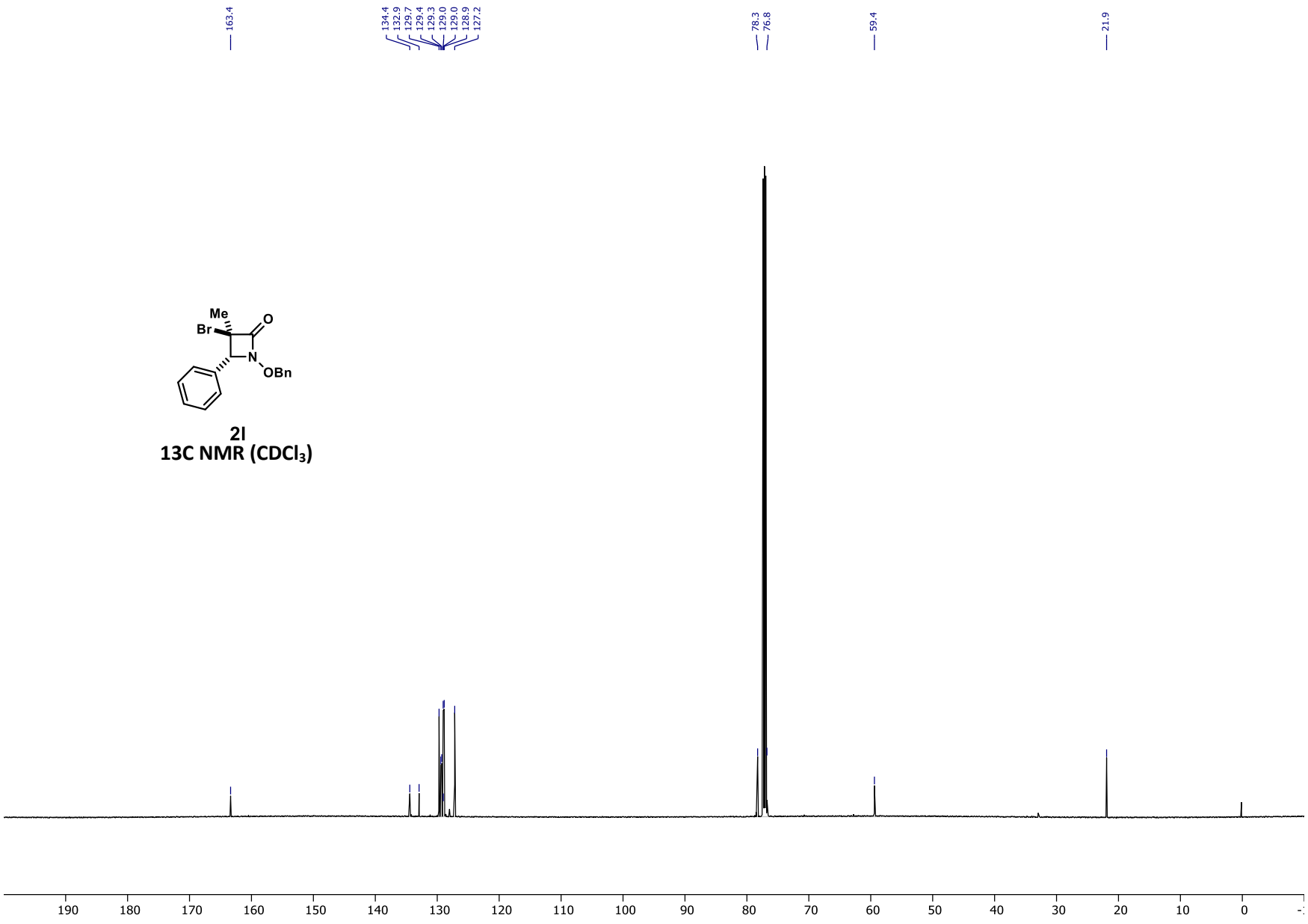
1H NMR ($CDCl_3$)



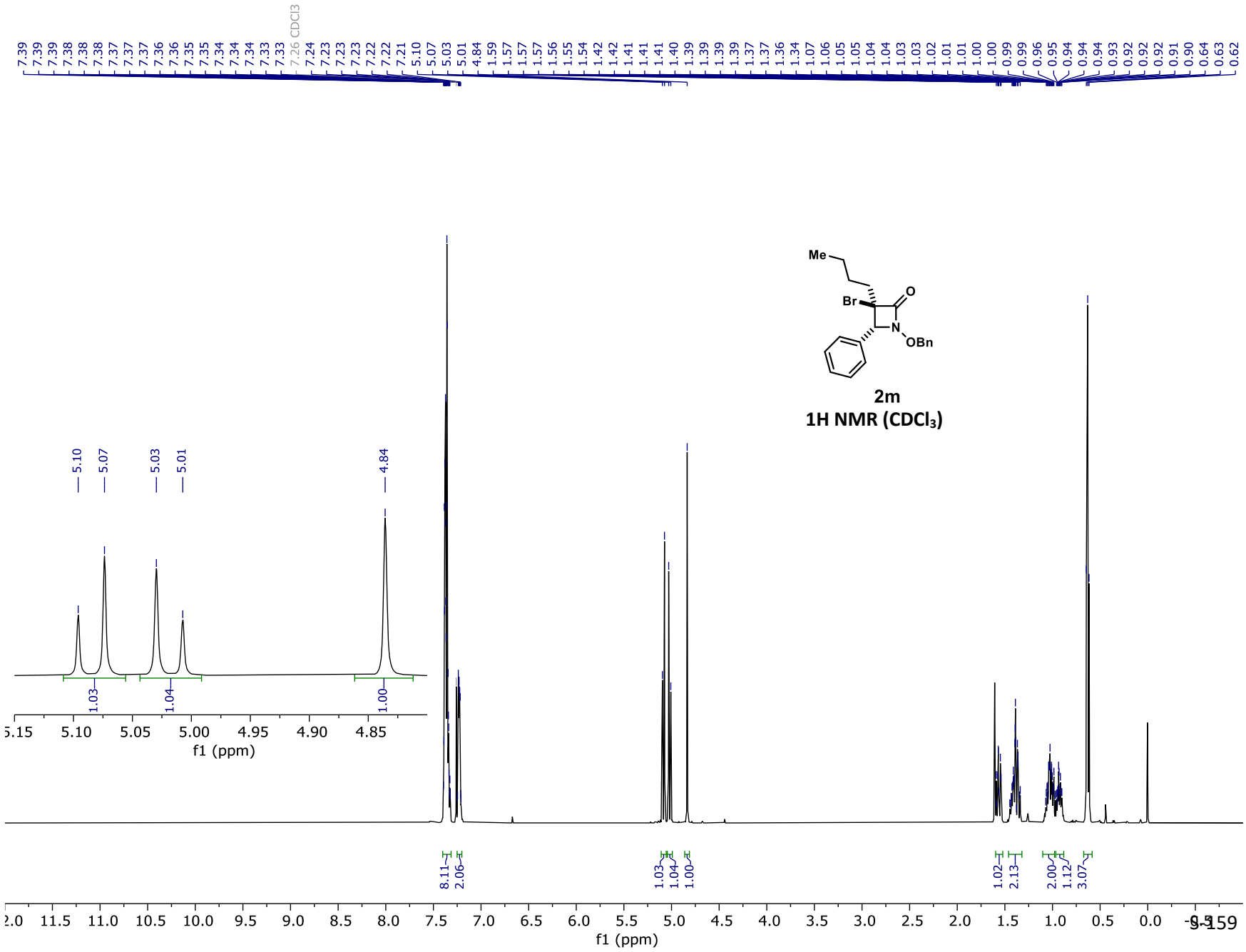
2k

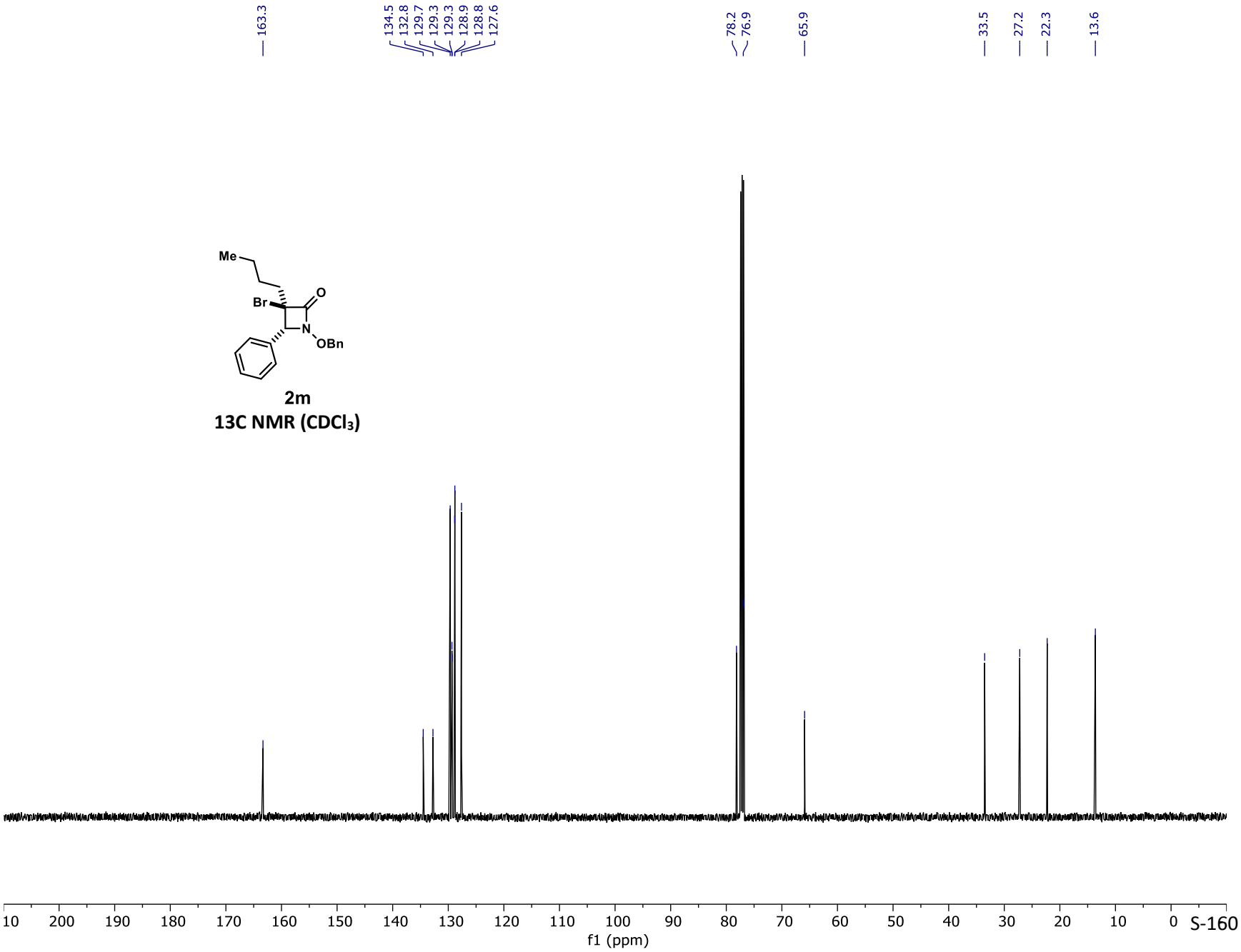
13C NMR ($CDCl_3$)

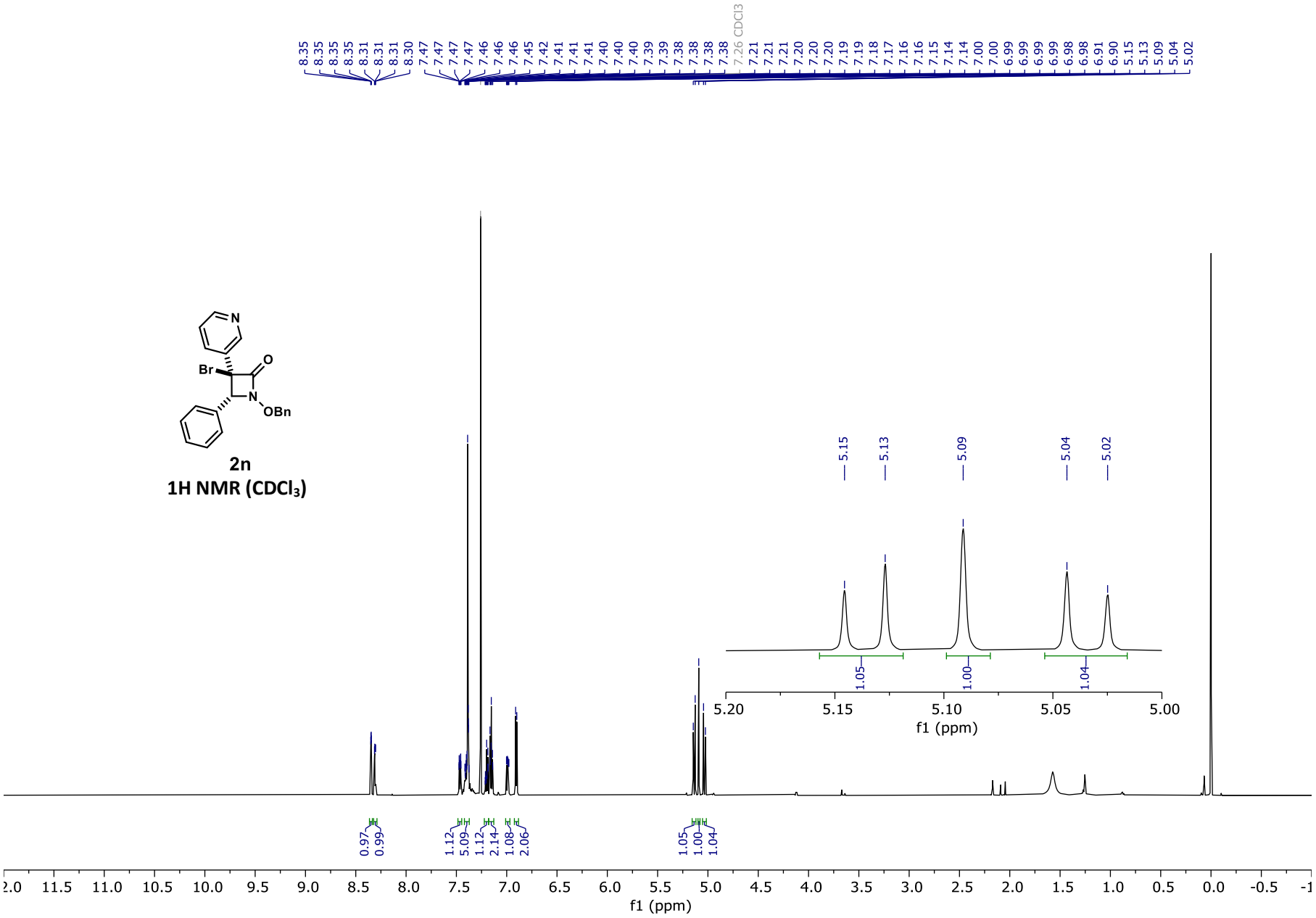

7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.35
7.35
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.20
5.11
5.09
5.05
5.03
4.84
1.35
Me
Br
O
N
OBn
2l
1H NMR (CDCl3)
1.16
1.10
1.00
5.12
5.08
5.04
5.00
4.96
4.92
4.88
4.84
4.80
8.41
2.01
1.16
1.10
1.00
3.10
11
10
9
8
7
6
5
4
3
2
1
0

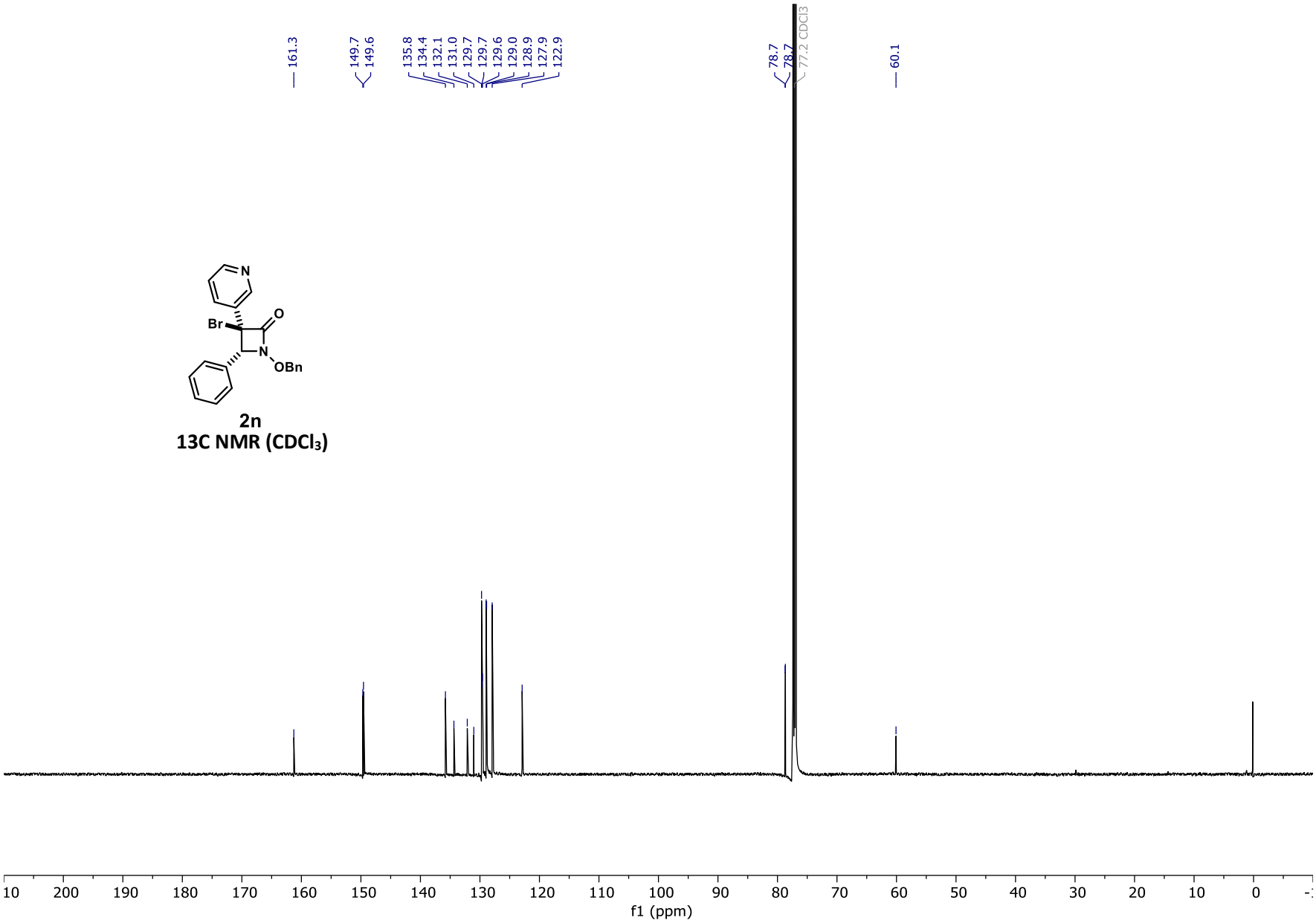


2l
13C NMR ($CDCl_3$)

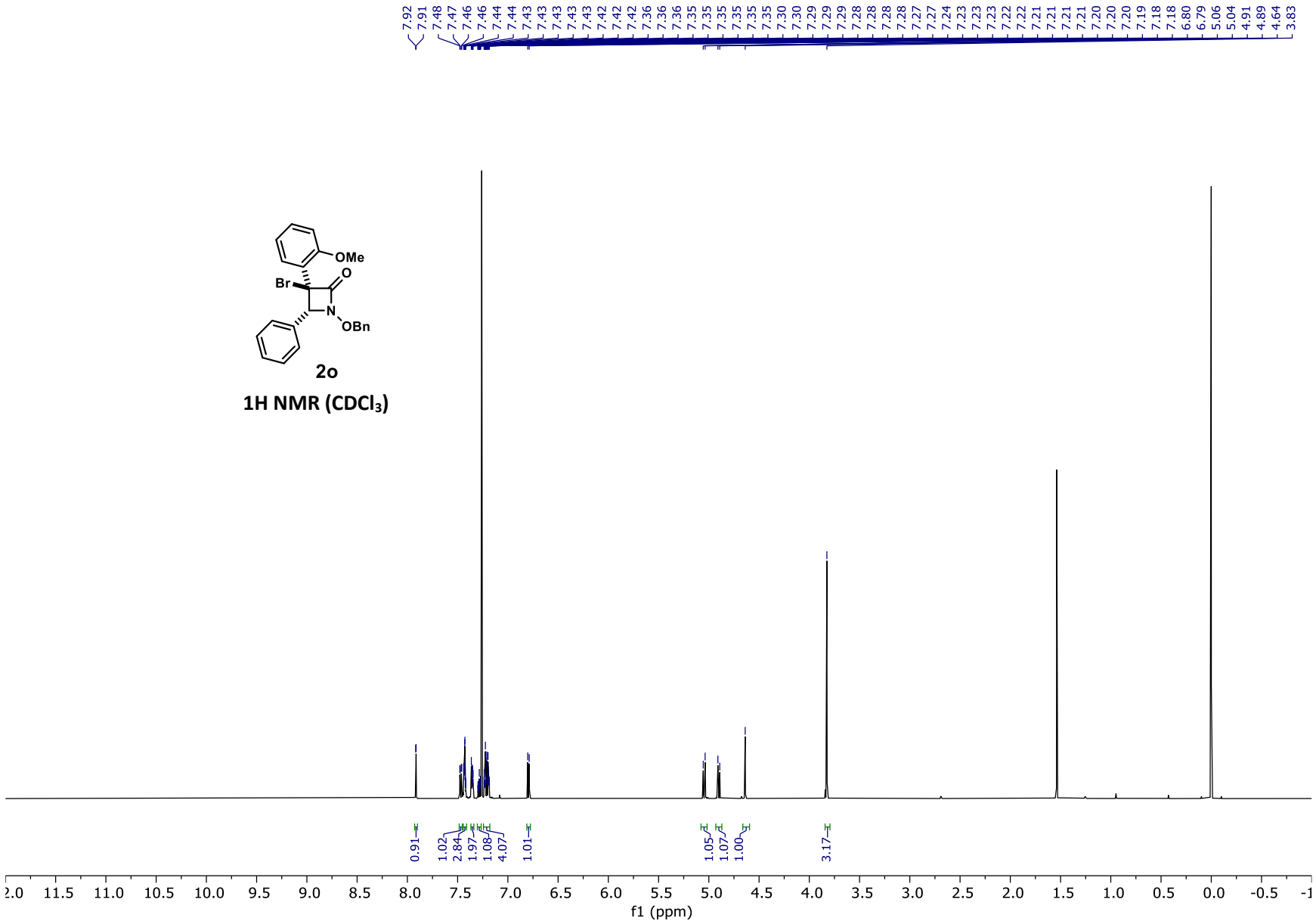

Me
Br
O
N
OBn
2m
1H NMR (CDCl3)
f1 (ppm)

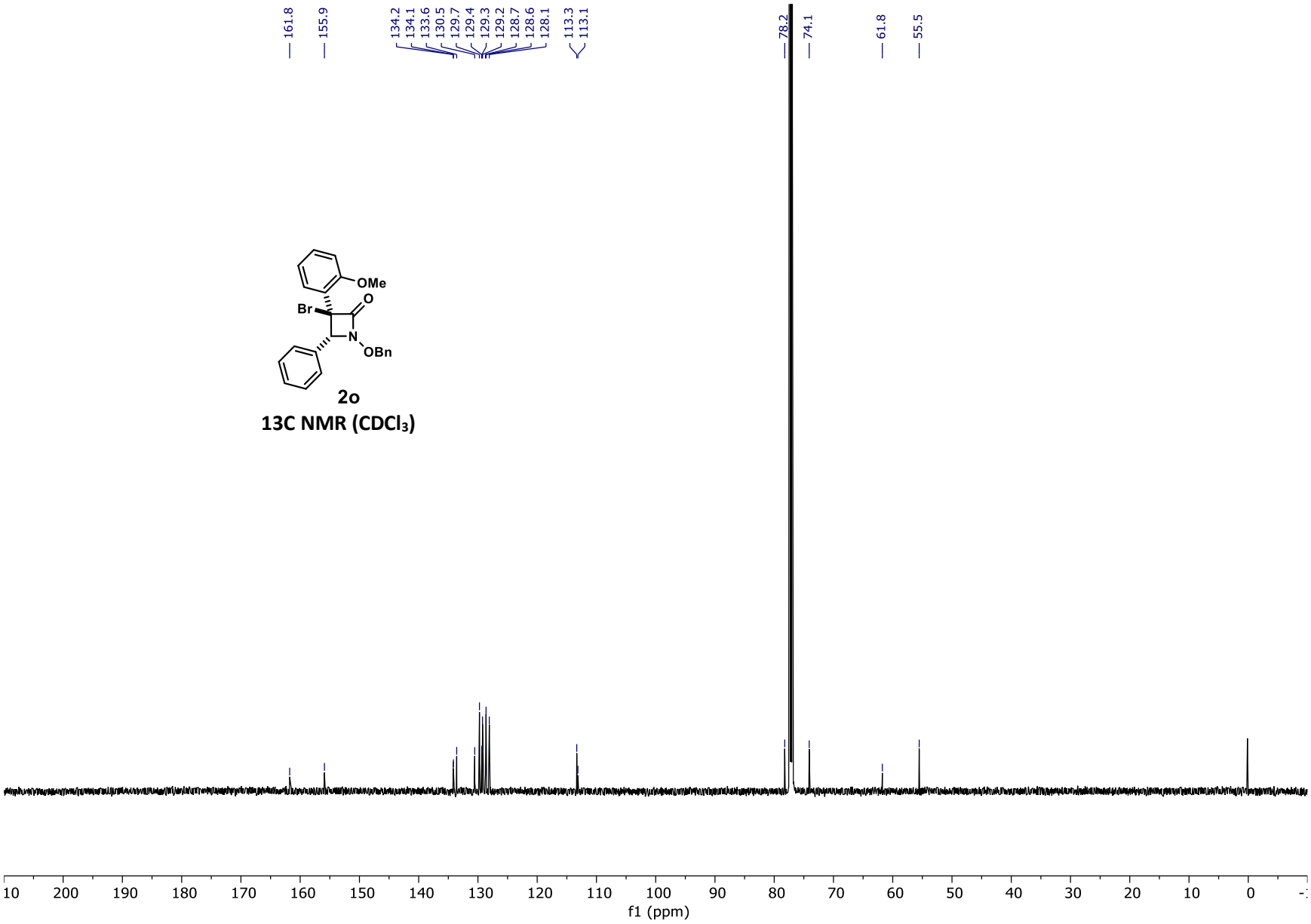

163.3
134.5
132.8
129.7
129.3
129.3
128.9
128.8
127.6
78.2
76.9
65.9
33.5
27.2
22.3
13.6
Me
Br
O
N
OBn
2m
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

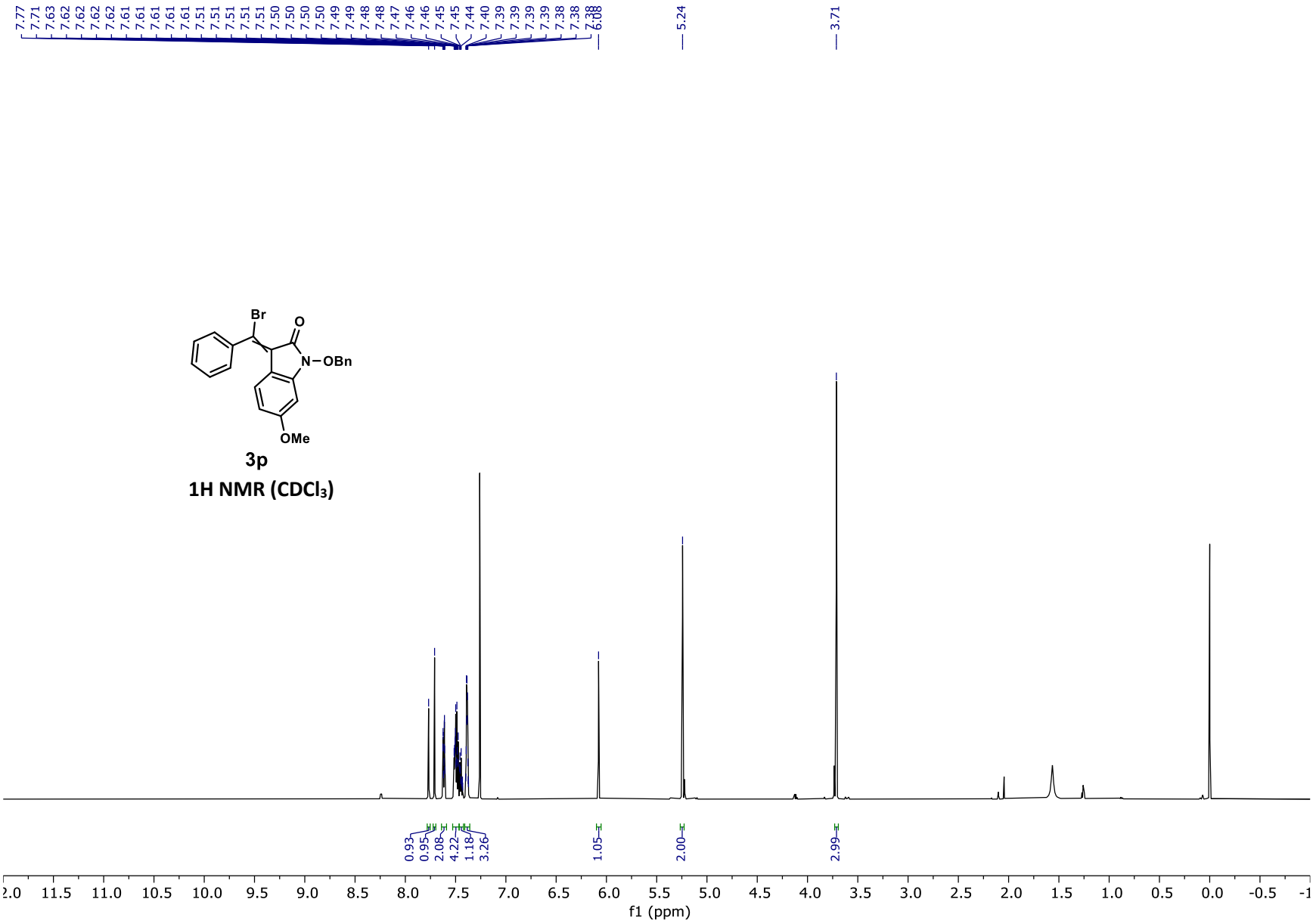

8.35 8.35 8.35 8.31 8.31 8.31 8.30 7.47 7.47 7.47 7.47 7.46 7.46 7.46 7.45 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.38 7.26 CDCl3 7.21 7.21 7.21 7.20 7.20 7.20 7.19 7.19 7.18 7.17 7.16 7.16 7.15 7.14 7.14 7.00 7.00 6.99 6.99 6.99 6.99 6.98 6.98 6.91 6.90 5.15 5.13 5.09 5.04 5.02
N
Br
O
N
OBn
2n
1H NMR (CDCl3)
5.15 5.13 5.09 5.04 5.02
1.05 1.00 1.04
5.20 5.15 5.10 5.05 5.00
f1 (ppm)
0.97 0.99 1.12 5.09 1.12 2.14 1.08 2.06 1.05 1.00 1.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

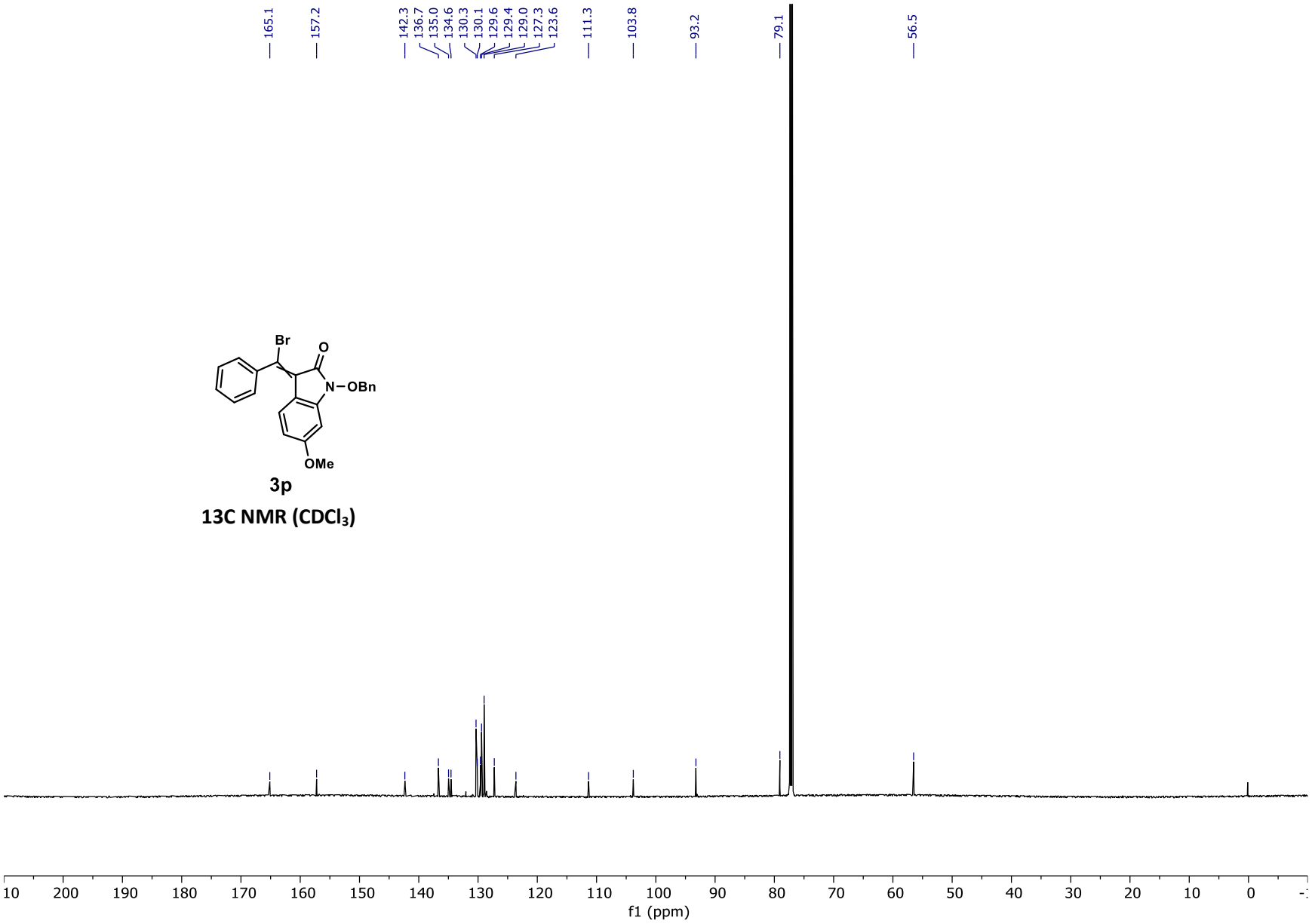


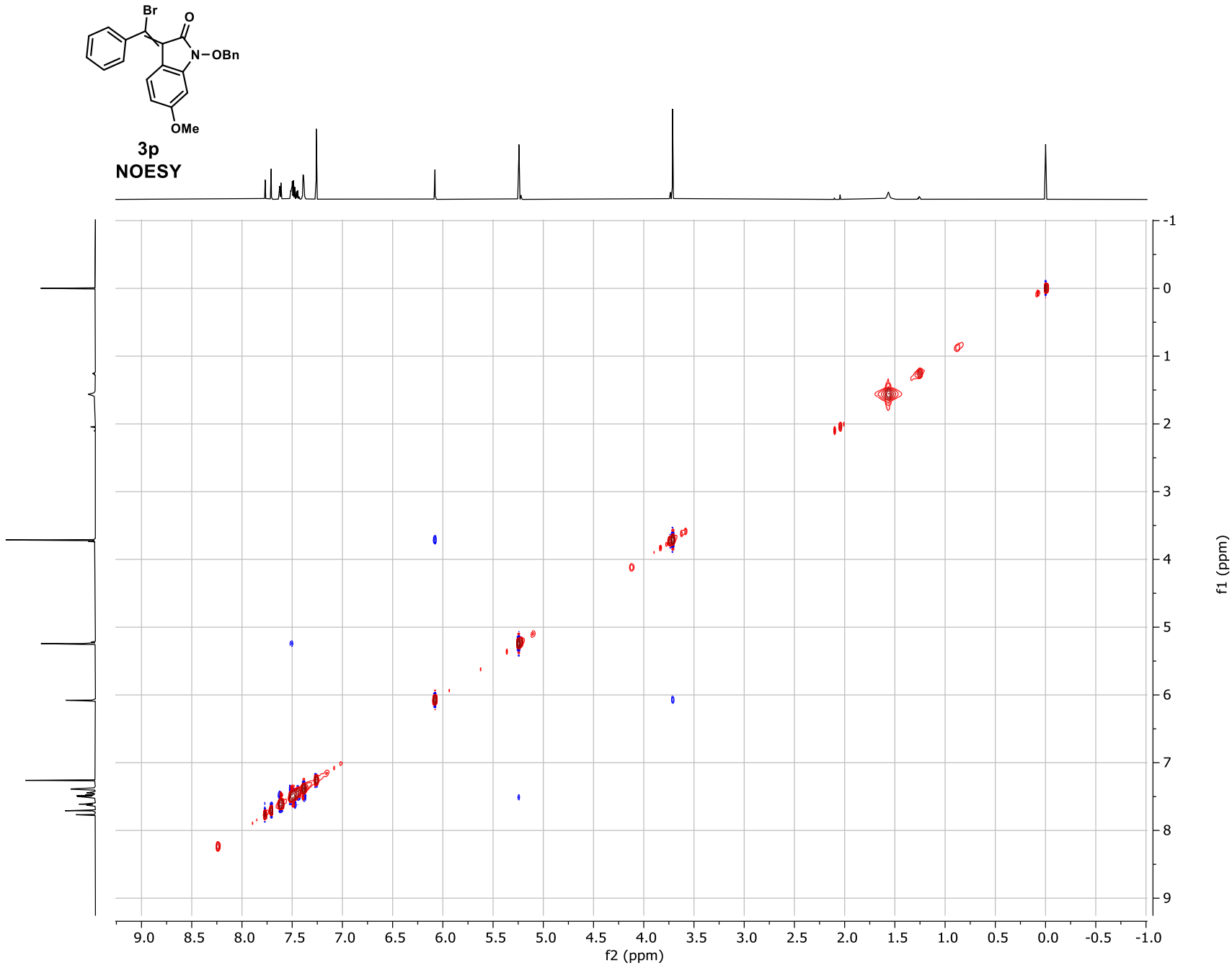
2n
13C NMR ($CDCl_3$)

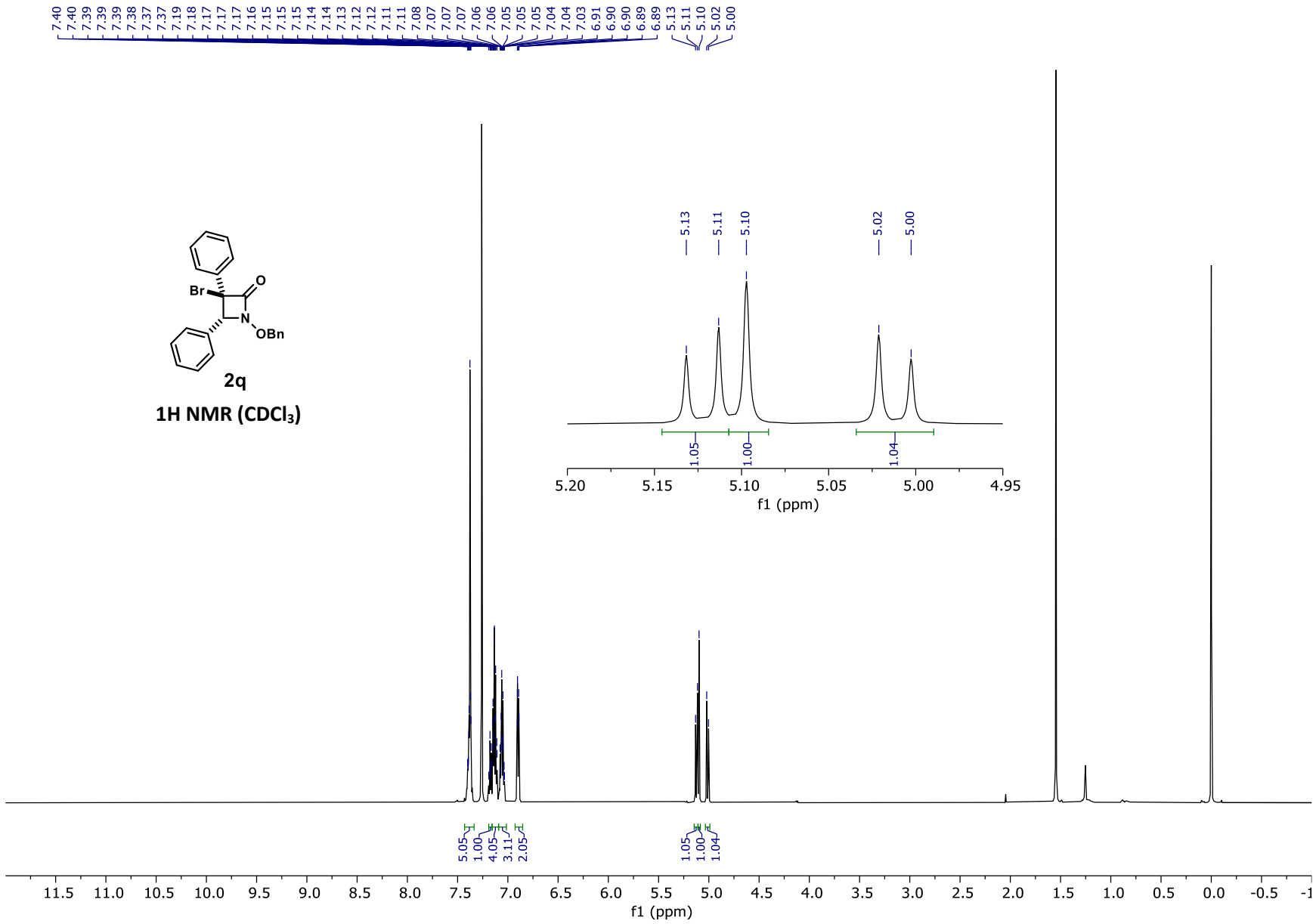

OMe
O
Br
N
OBn
2o
1H NMR (CDCl3)
f1 (ppm)

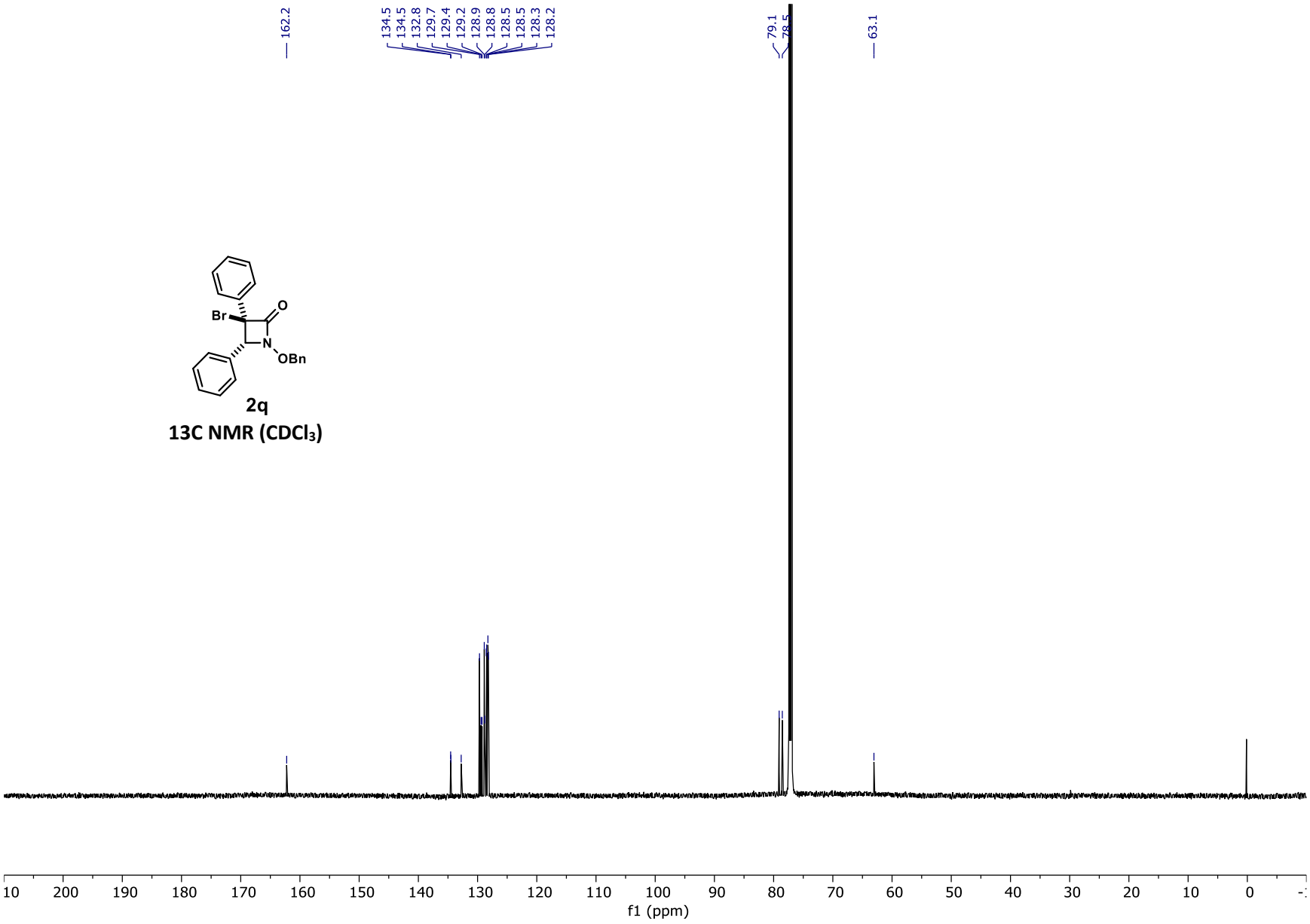

161.8
155.9
134.2
134.1
133.6
130.5
129.7
129.4
129.3
129.2
128.7
128.6
128.1
113.3
113.1
78.2
74.1
61.8
55.5
OMe
Br
O
N
OBn
2o
13C NMR (CDCl3)
f1 (ppm)

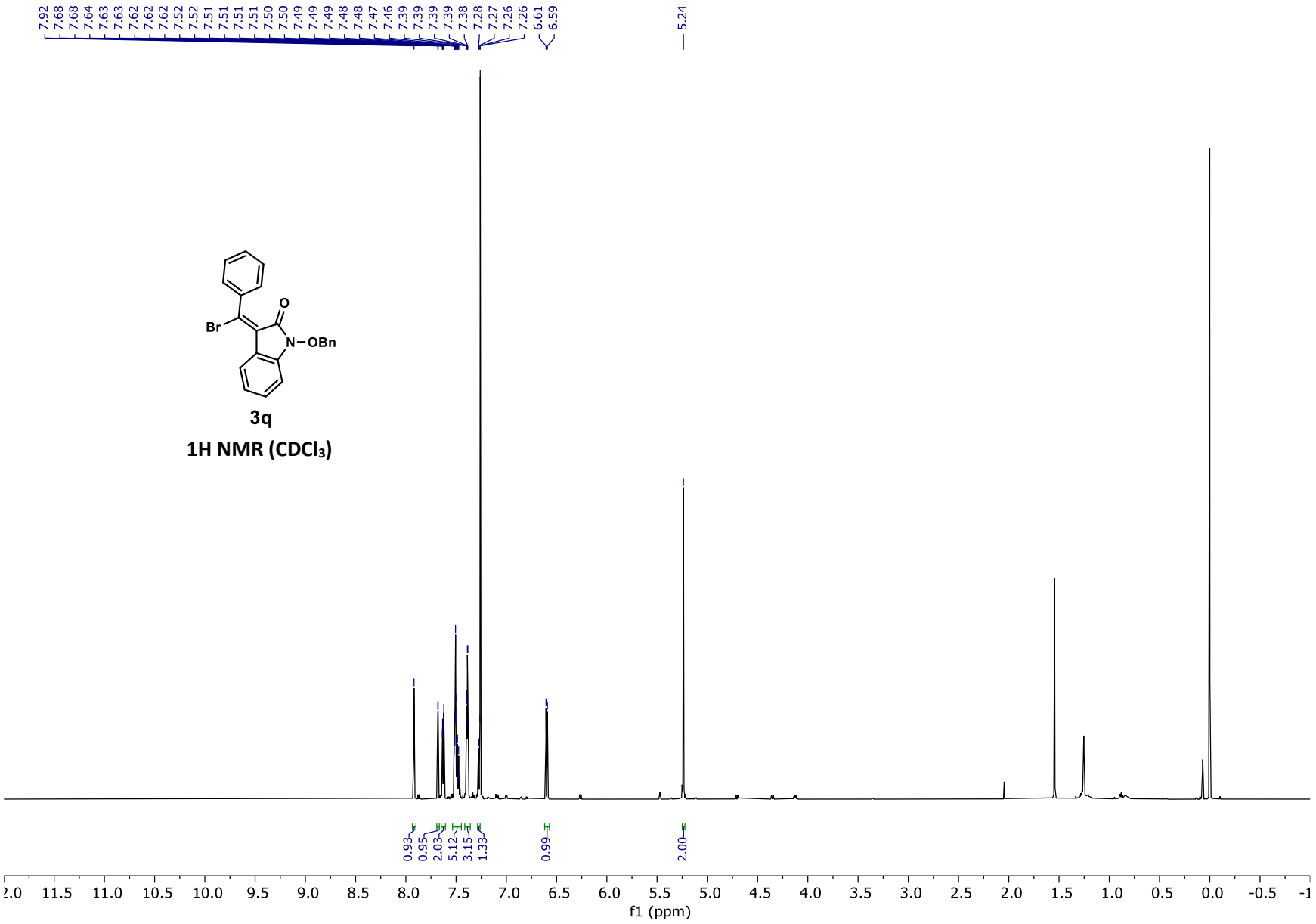

7.77
7.71
7.63
7.62
7.62
7.62
7.62
7.61
7.61
7.61
7.61
7.61
7.51
7.51
7.51
7.51
7.50
7.50
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.38
6.08
5.24
3.71
Br
O
N−OBn
OMe
3p
1H NMR (CDCl3)
0.93
0.95
2.08
4.22
1.18
3.26
1.05
2.00
2.99
f1 (ppm)

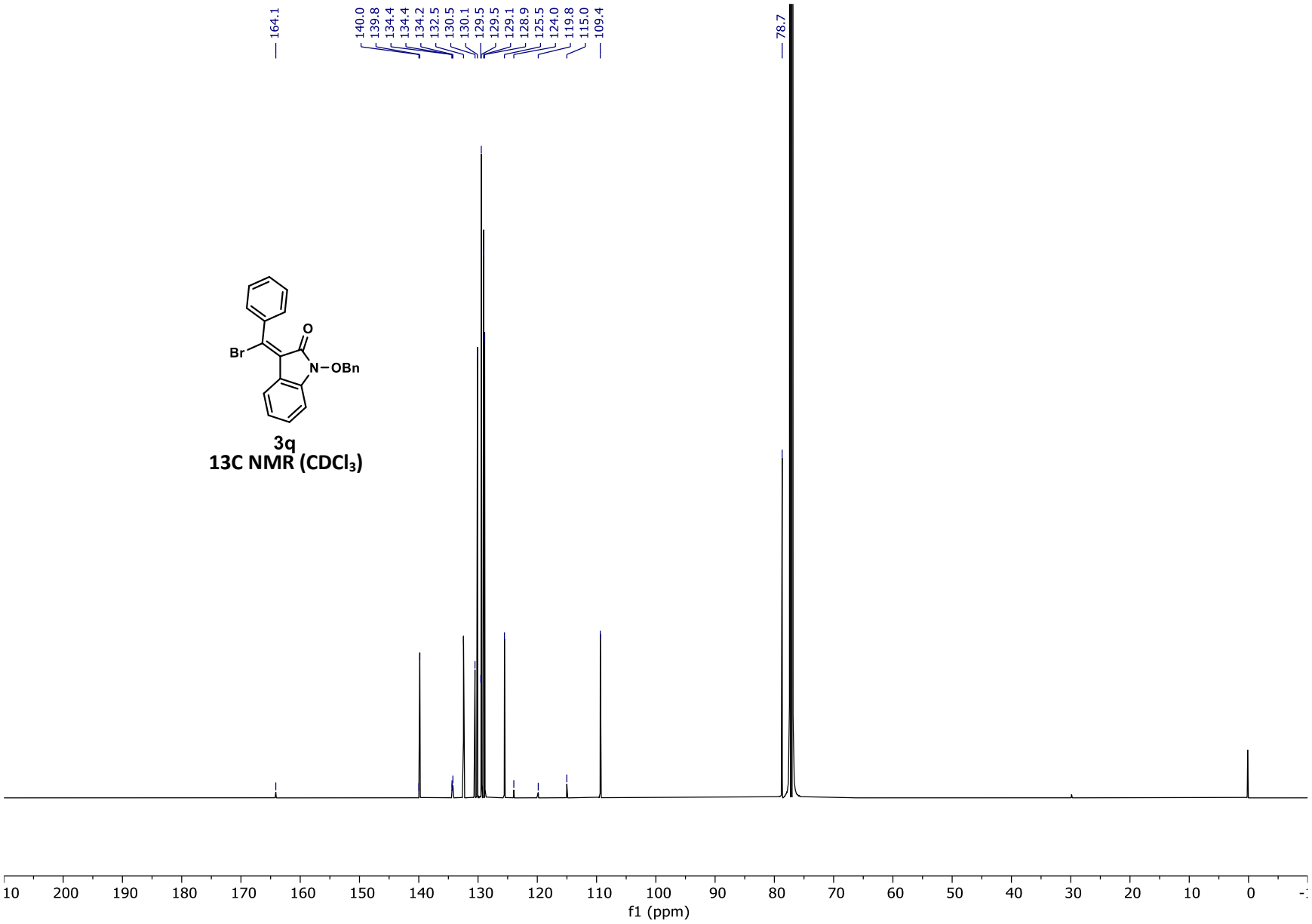

165.1
157.2
142.3
136.7
135.0
134.6
130.3
130.1
129.6
129.4
129.0
127.3
123.6
111.3
103.8
93.2
79.1
56.5
Br
O
N–OBn
OMe
3p
13C NMR (CDCl3)
f1 (ppm)


Br
O
N–OBn
OMe
3p
NOESY
f2 (ppm)
f1 (ppm)

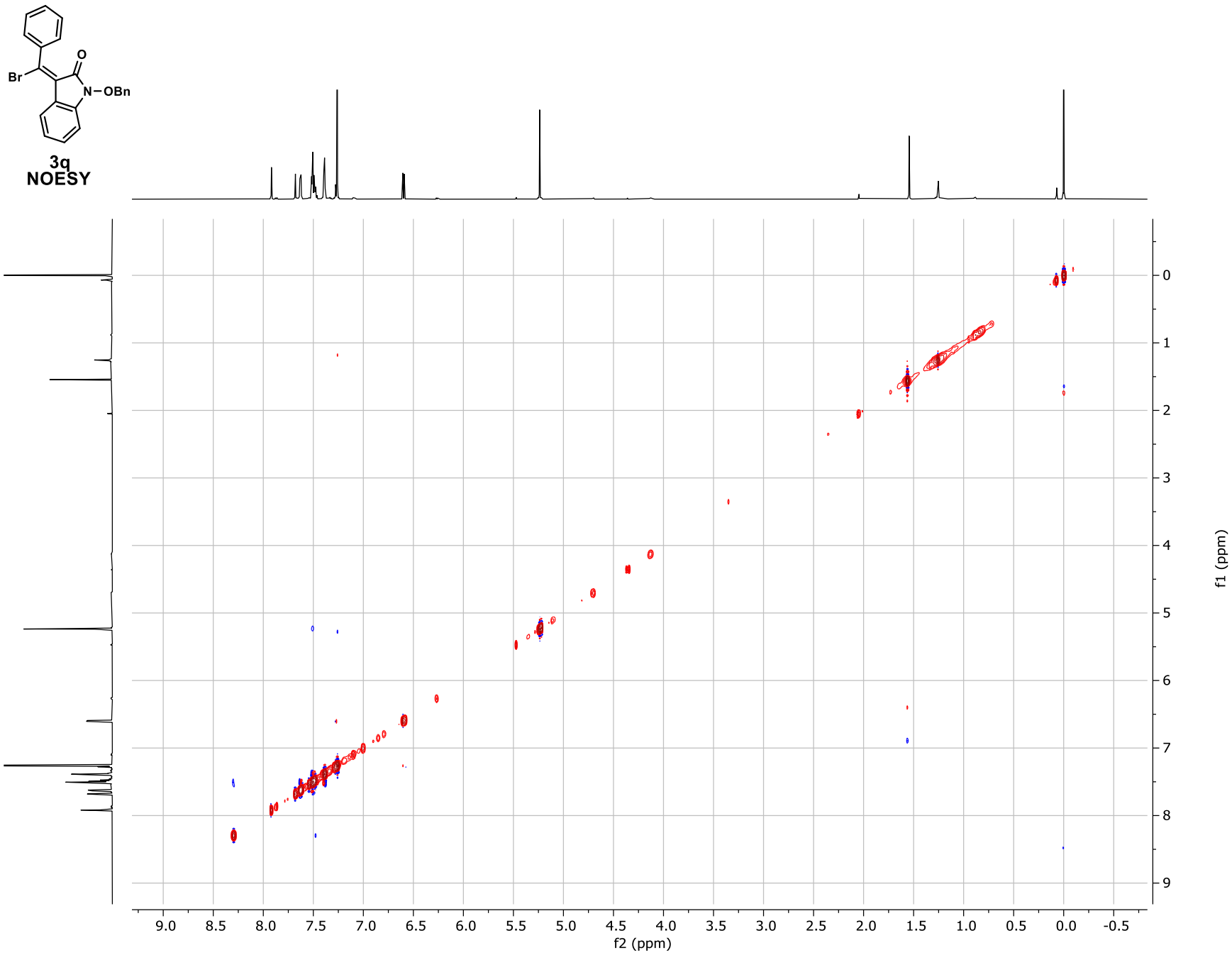

7.40 7.40 7.39 7.39 7.39 7.38 7.37 7.37 7.19 7.18 7.17 7.17 7.17 7.16 7.15 7.15 7.15 7.14 7.14 7.13 7.12 7.12 7.11 7.11 7.08 7.07 7.07 7.07 7.06 7.06 7.05 7.05 7.05 7.04 7.04 7.03 6.91 6.90 6.90 6.89 6.89 5.13 5.11 5.10 5.02 5.00
Br
O
N
OBn
2q
1H NMR (CDCl3)
5.13 5.11 5.10 5.02 5.00
1.05 1.00 1.04
5.20 5.15 5.10 5.05 5.00 4.95
f1 (ppm)
5.05 1.00 4.05 3.11 2.05
1.05 1.00 1.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

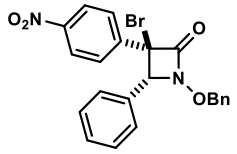

162.2
134.5
134.5
132.8
129.7
129.4
129.2
128.9
128.8
128.5
128.5
128.3
128.2
79.1
78.5
63.1
Br
O
N
OBn
2q
13C NMR (CDCl3)
f1 (ppm)


7.92
7.68
7.68
7.64
7.63
7.63
7.62
7.62
7.62
7.52
7.52
7.51
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.47
7.46
7.39
7.39
7.39
7.39
7.38
7.28
7.27
7.26
7.26
6.61
6.59
5.24
Br
O
N–OBn
3q
1H NMR (CDCl3)
0.93
0.95
2.03
5.12
3.15
1.33
0.99
2.00
f1 (ppm)



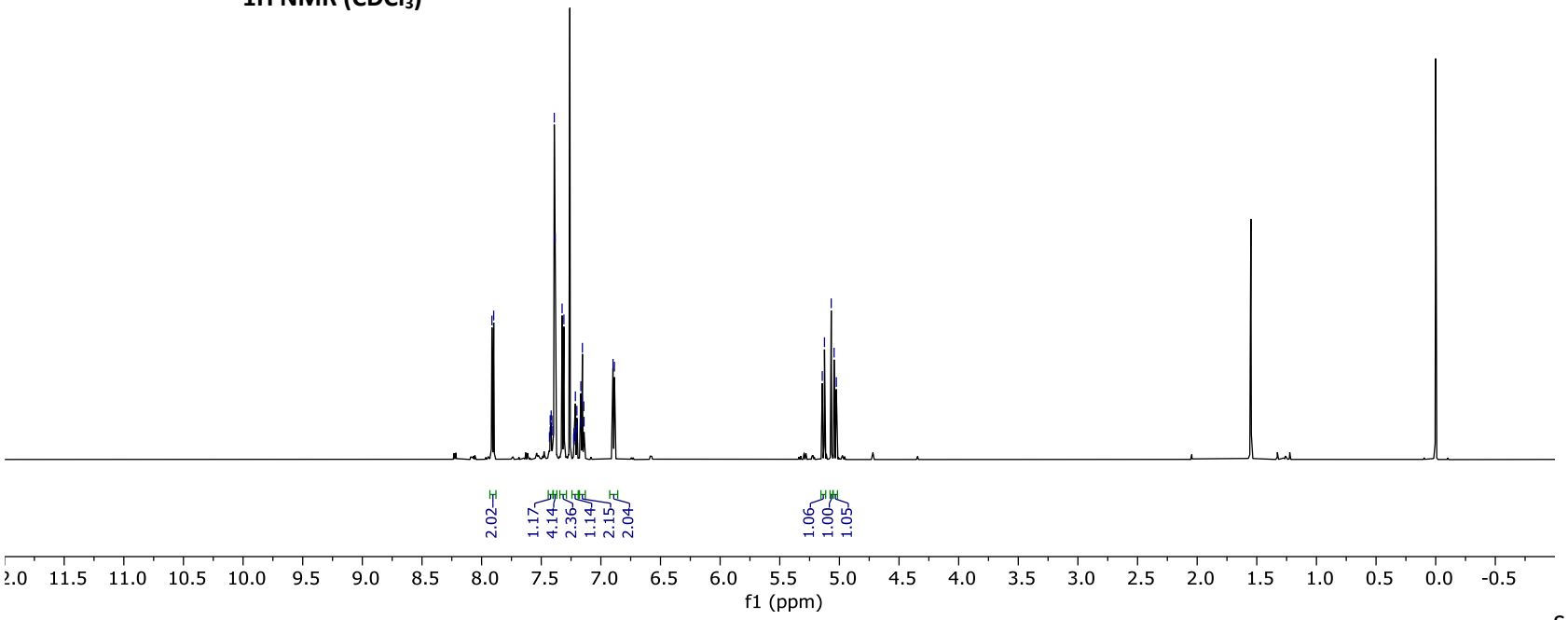
3q
13C NMR ($CDCl_3$)

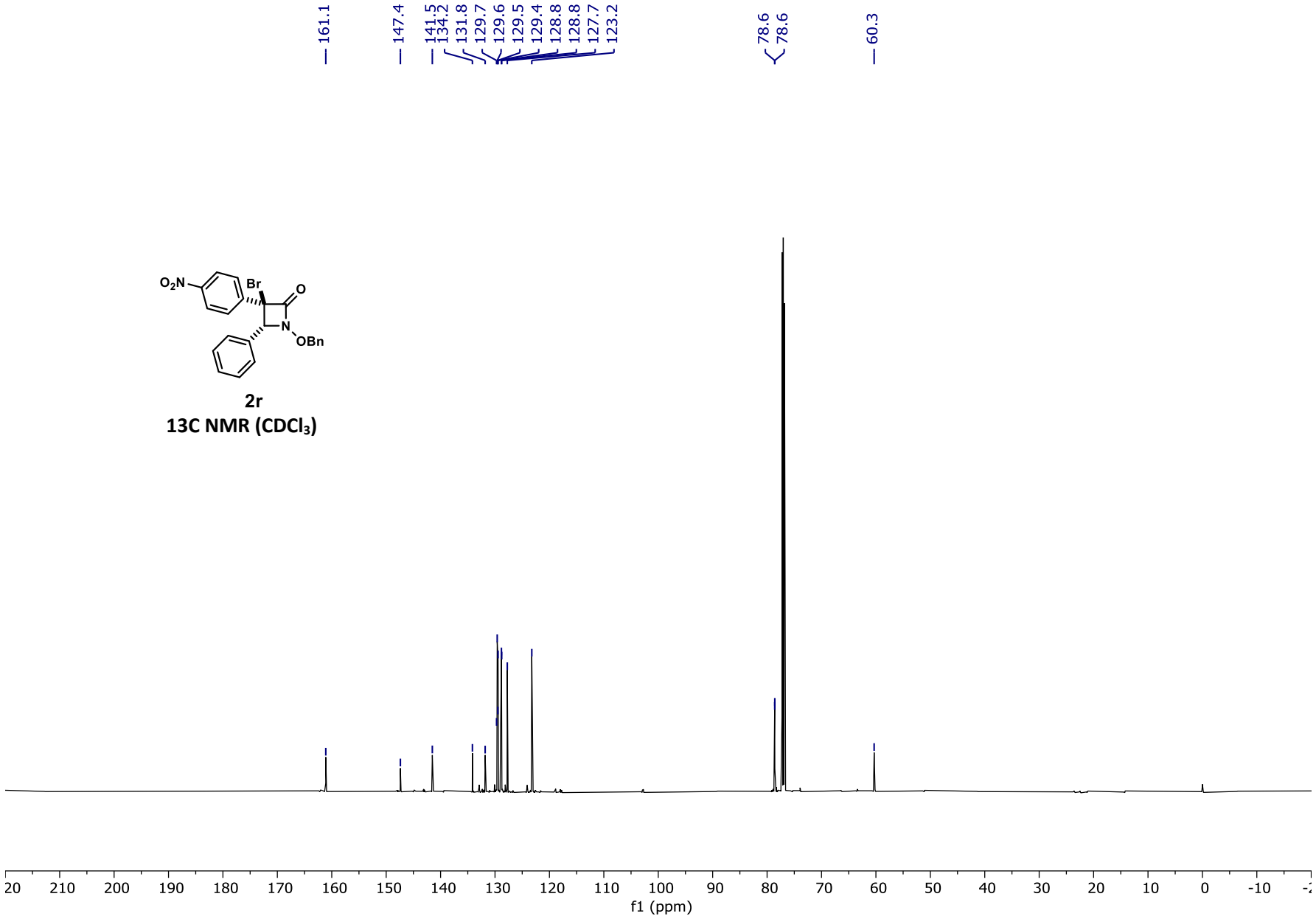

Br
O
N–OBn
3q
NOESY
f2 (ppm)
f1 (ppm)

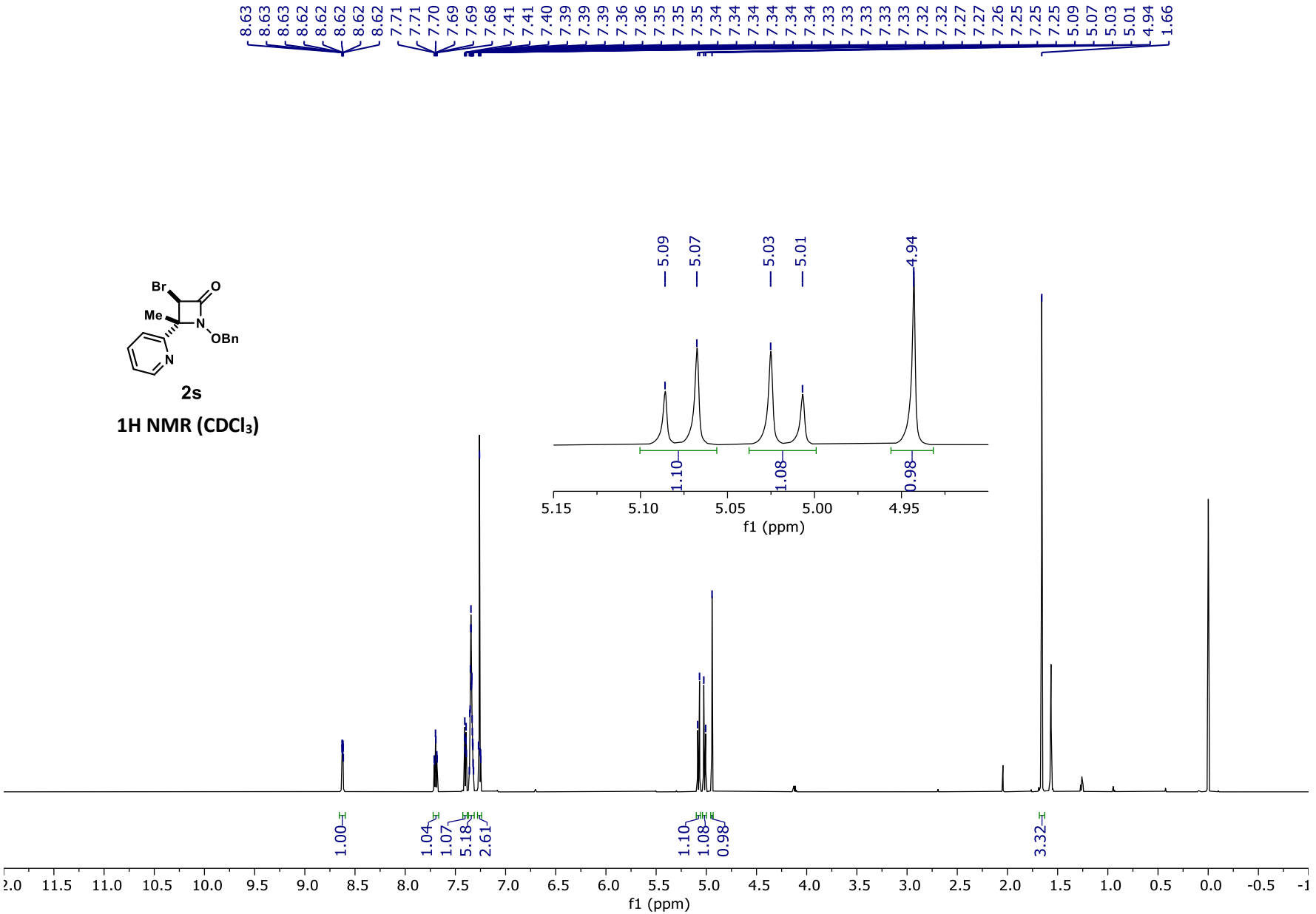


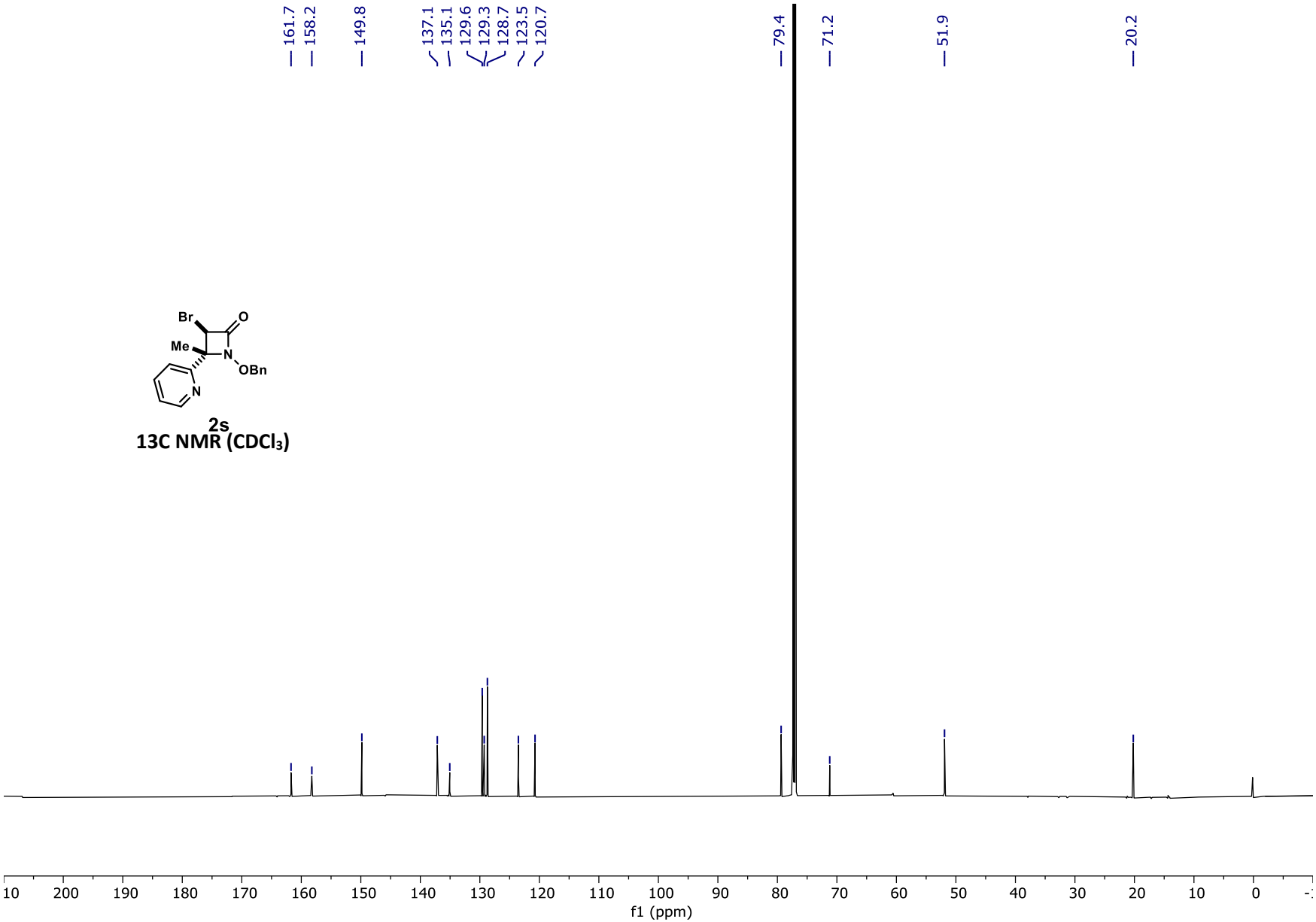
2r

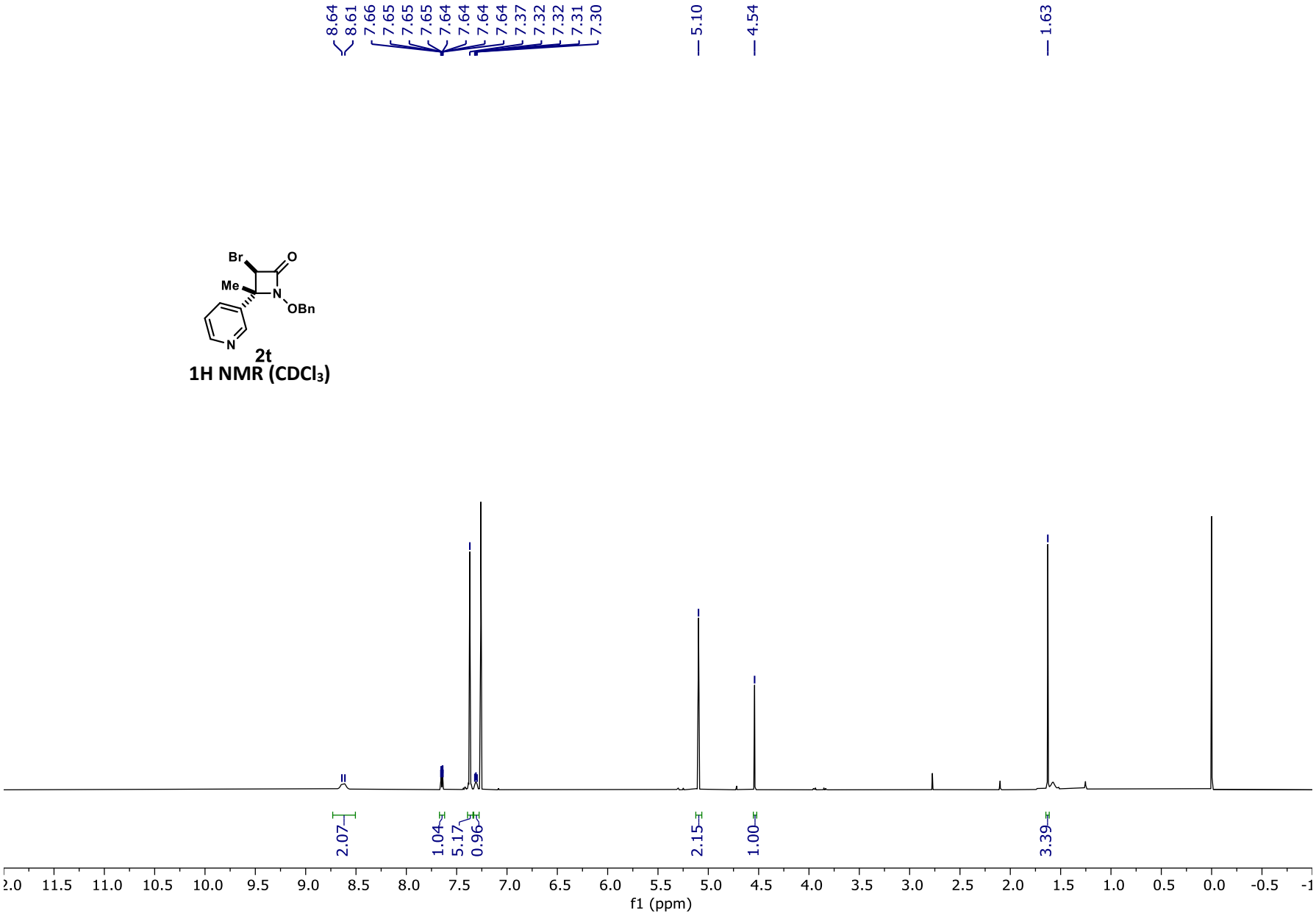
1H NMR ($CDCl_3$)

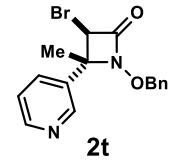



161.1
147.4
141.5
134.2
131.8
129.7
129.6
129.5
129.4
128.8
128.8
127.7
123.2
78.6
78.6
60.3
O2N
Br
O
N
OBn
2r
13C NMR (CDCl3)
f1 (ppm)


8.63 8.63 8.63 8.62 8.62 8.62 8.62 7.71 7.71 7.70 7.69 7.69 7.68 7.41 7.41 7.40 7.39 7.39 7.39 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.33 7.32 7.32 7.27 7.27 7.26 7.25 7.25 7.25 5.09 5.07 5.03 5.01 4.94 1.66
Br
O
Me
N
OBn
N
2s
1H NMR (CDCl3)
5.09 5.07 5.03 5.01 4.94
1.10 1.08 0.98
5.15 5.10 5.05 5.00 4.95
f1 (ppm)
1.00 1.04 1.07 5.18 2.61 1.10 1.08 0.98 3.32
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

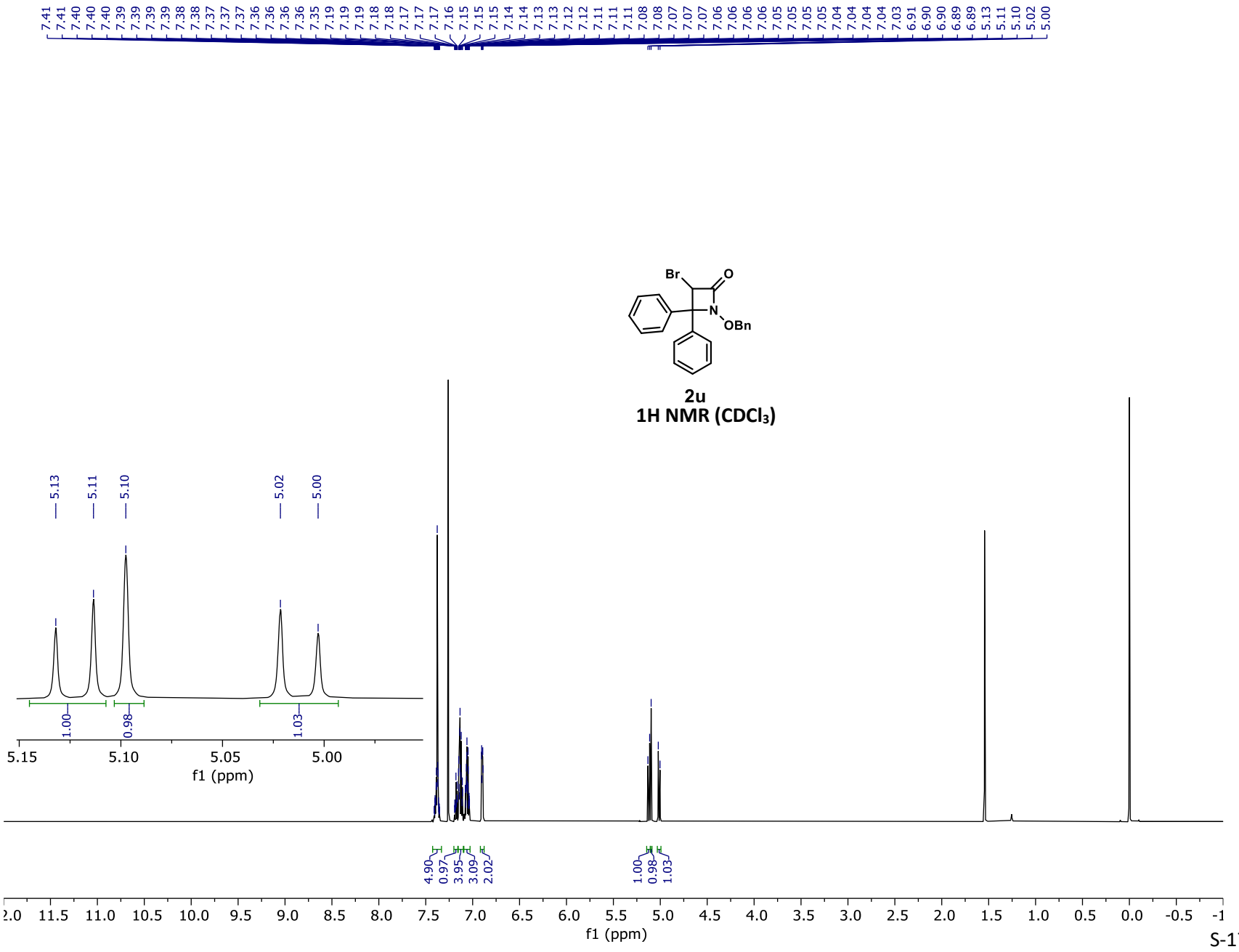

161.7
158.2
149.8
137.1
135.1
129.6
129.3
128.7
123.5
120.7
79.4
71.2
51.9
20.2
Br
O
Me
N
OBn
N
2s
13C NMR (CDCl3)
f1 (ppm)

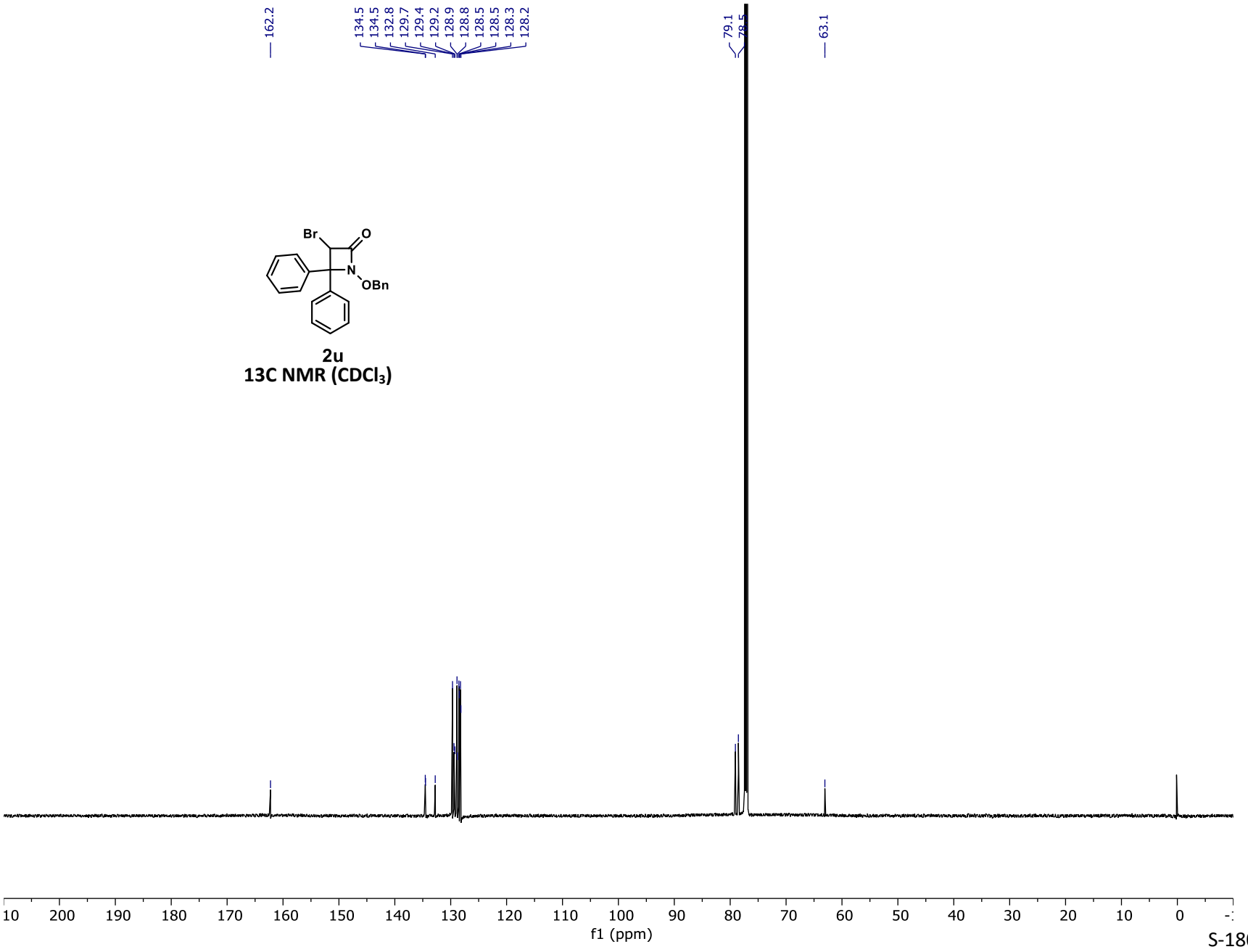

8.64
8.61
7.66
7.65
7.65
7.65
7.64
7.64
7.64
7.64
7.37
7.32
7.32
7.31
7.30
5.10
4.54
1.63
Br
O
Me
N
OBn
N
2t
1H NMR (CDCl3)
2.07
1.04
5.17
0.96
2.15
1.00
3.39
f1 (ppm)



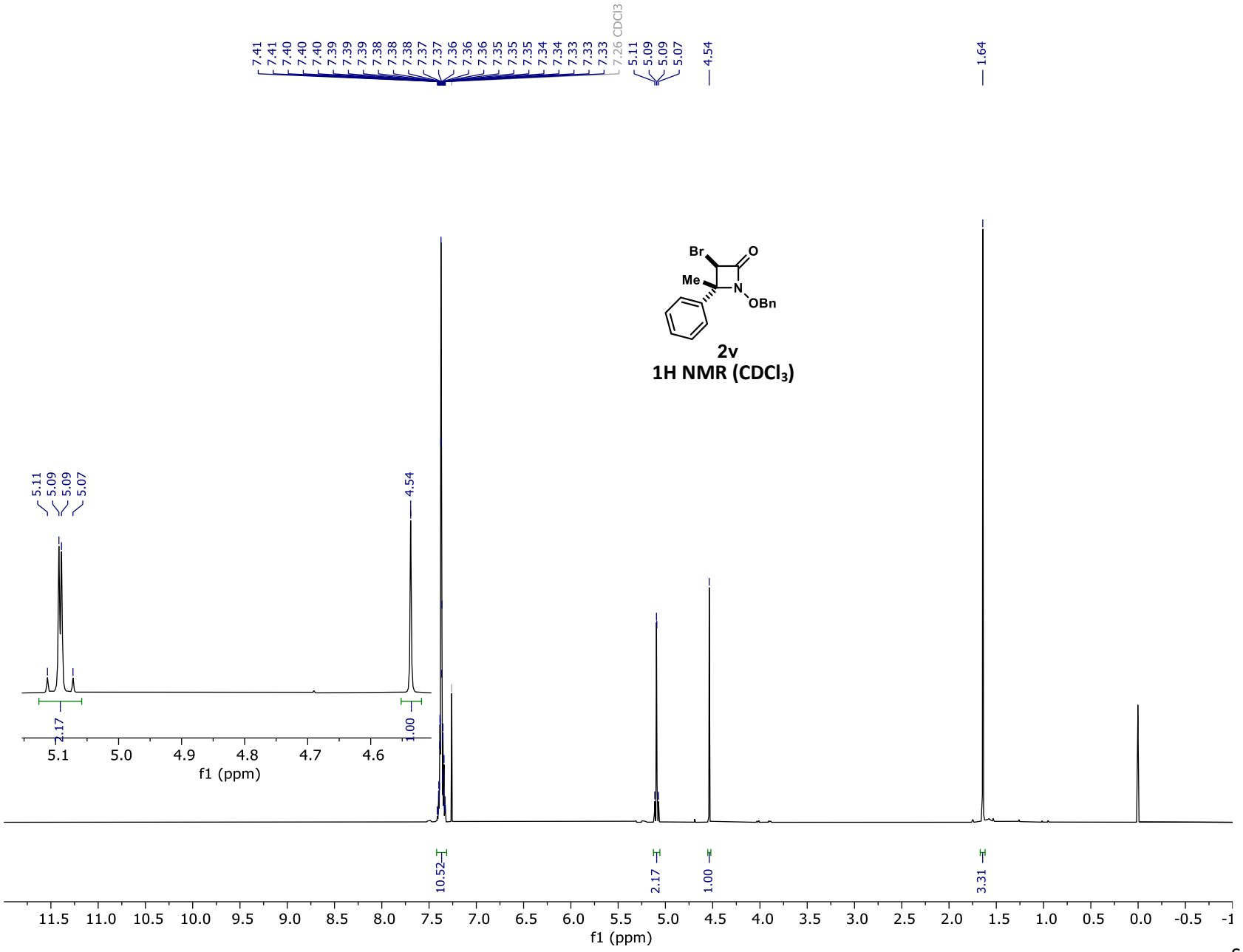
2t

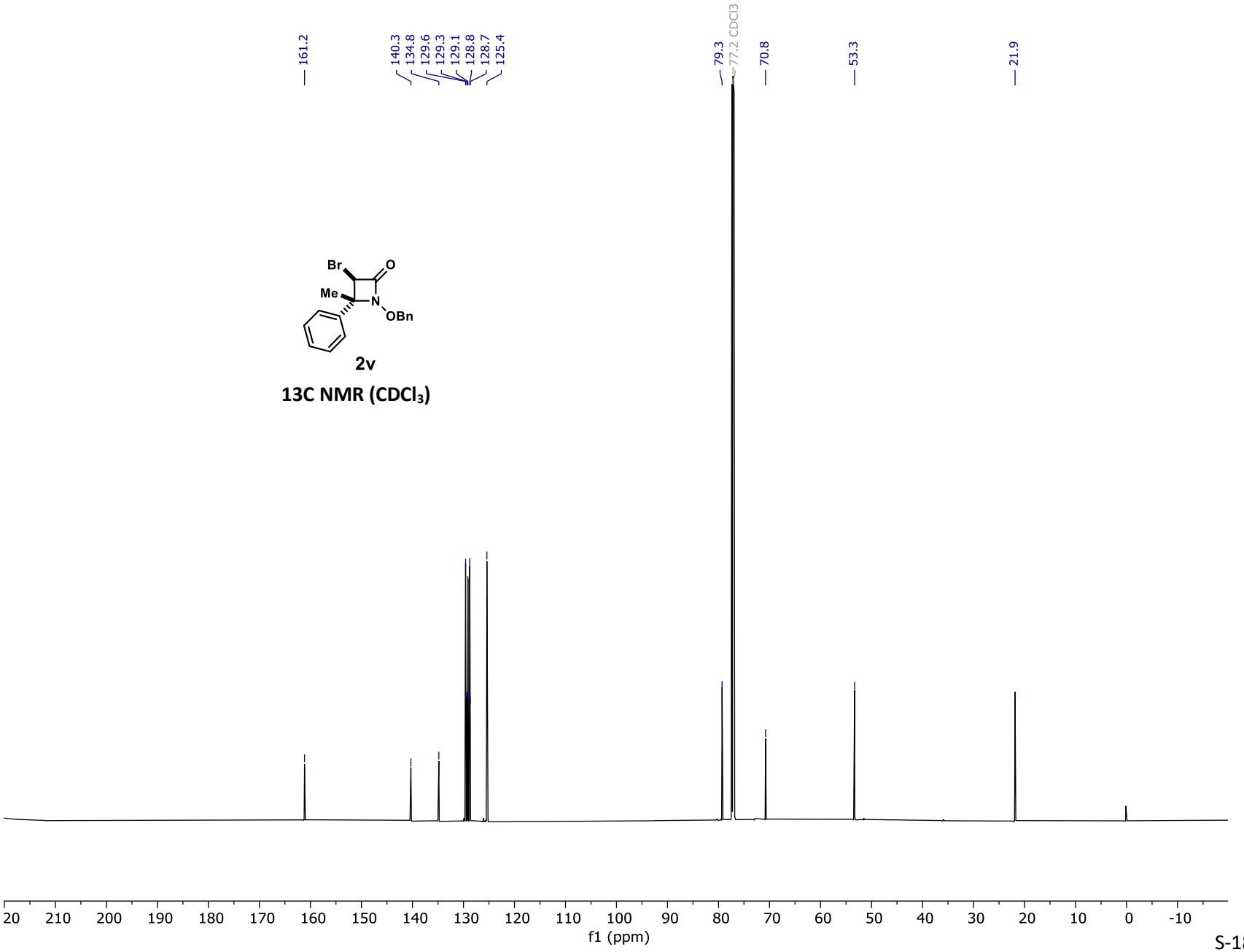
13C NMR ($CDCl_3$)

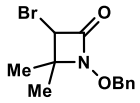

Br
O
N
OBn
2u
1H NMR (CDCl3)
f1 (ppm)



2u
13C NMR ($CDCl_3$)

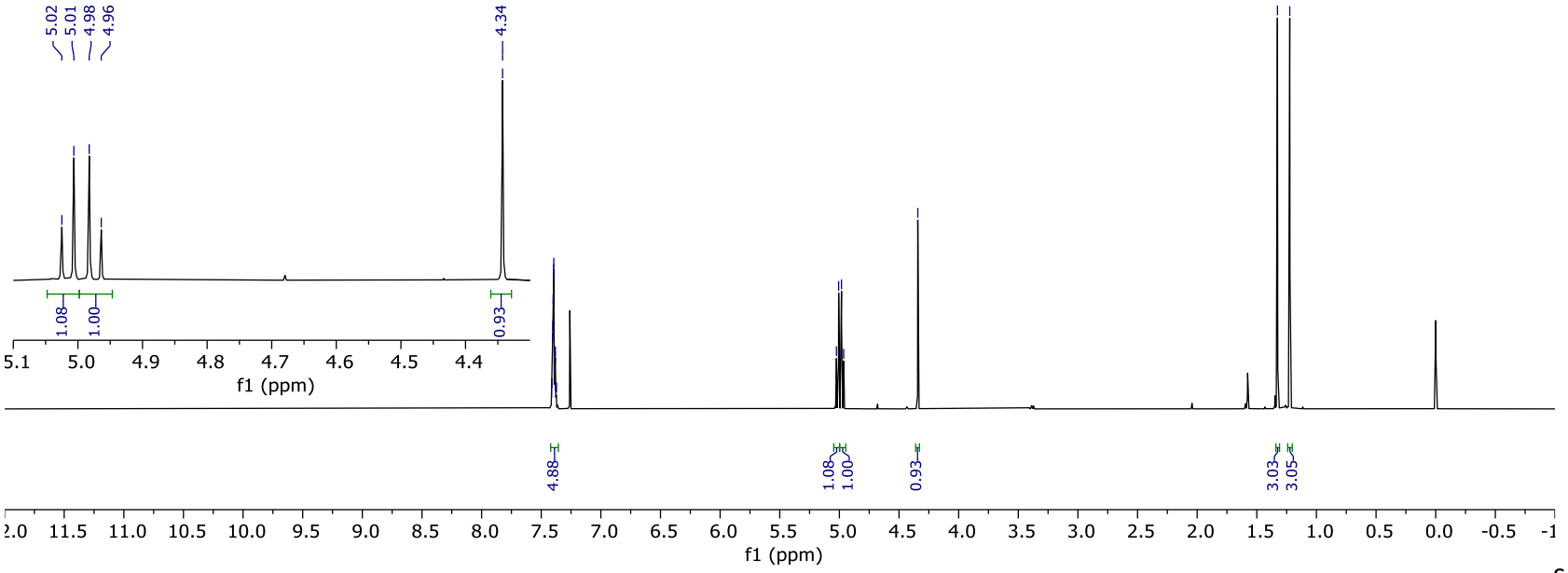

7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.26 CDCl3
5.11 5.09 5.09 5.07
4.54
1.64
Br
O
Me
N
OBn
2v
1H NMR (CDCl3)
5.11 5.09 5.09 5.07
4.54
2.17
1.00
5.1 5.0 4.9 4.8 4.7 4.6
f1 (ppm)
10.52
2.17
1.00
3.31
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

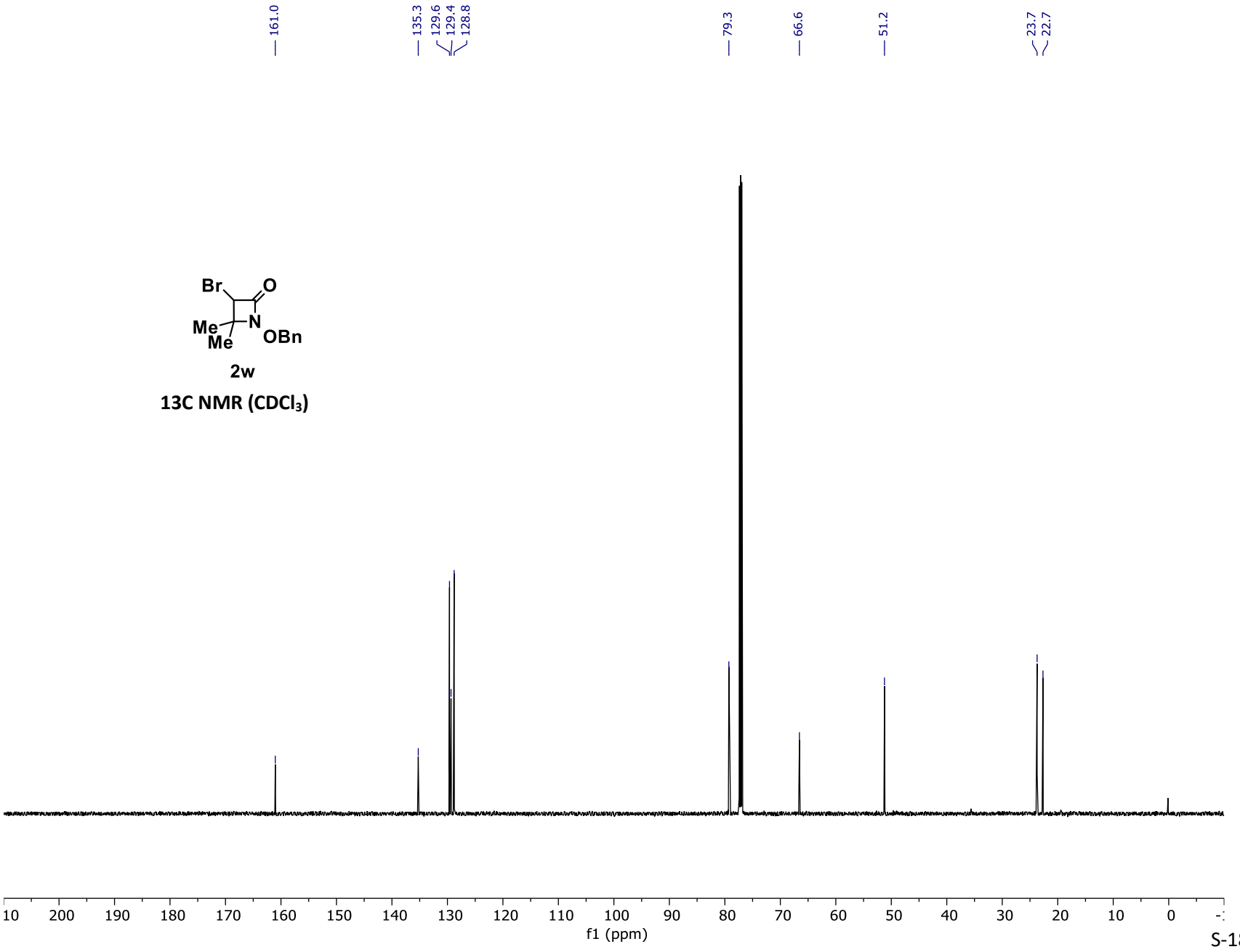

161.2
140.3
134.8
129.6
129.3
129.1
128.8
128.7
125.4
79.3
77.2 CDCl3
70.8
53.3
21.9
Br
O
Me
N
OBn
2v
13C NMR (CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

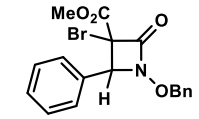


2w

1H NMR ($CDCl_3$)

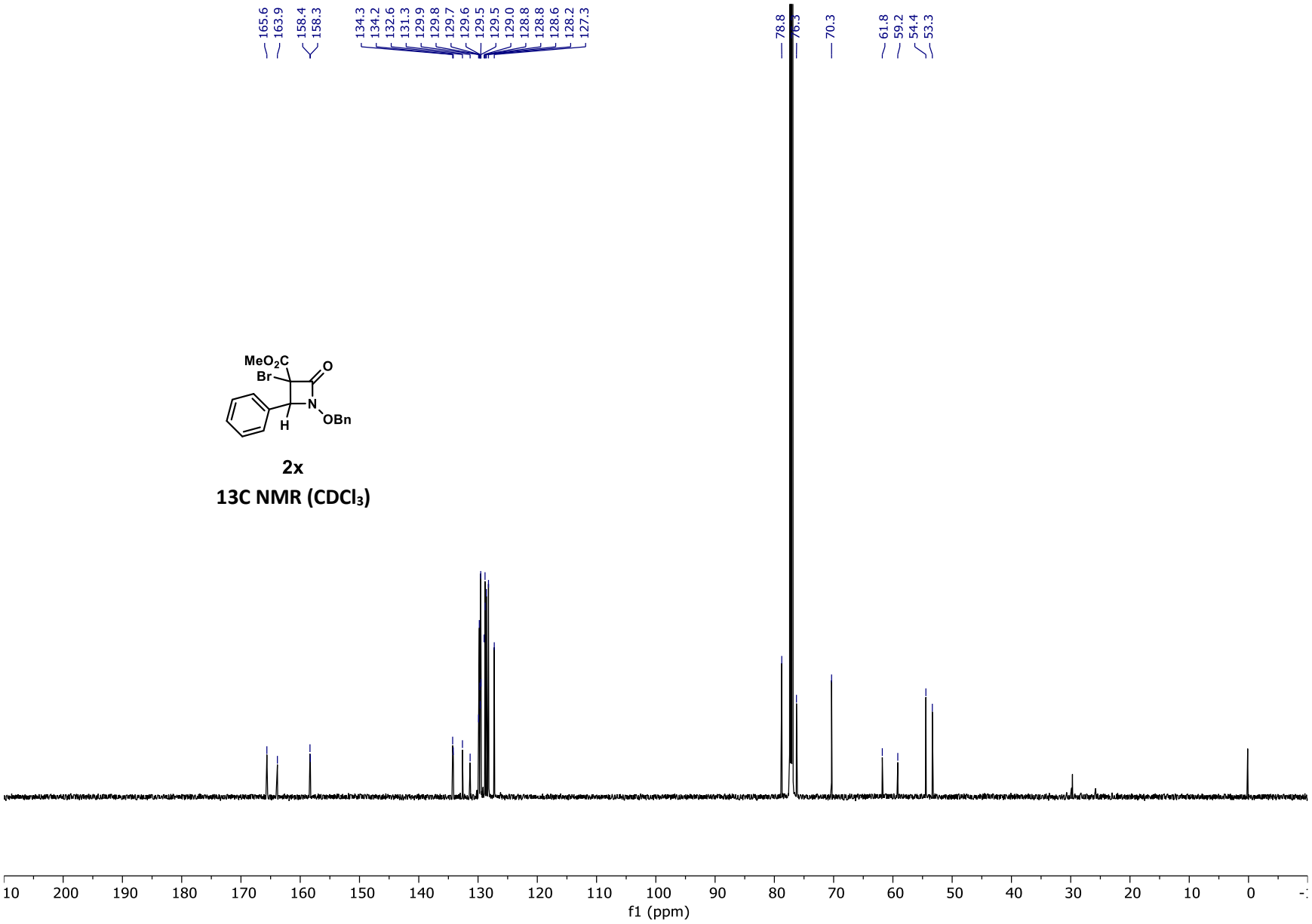



161.0
135.3
129.6
129.4
128.8
79.3
66.6
51.2
23.7
22.7
Br
O
N
Me
Me
OBn
2w
13C NMR (CDCl3)
f1 (ppm)



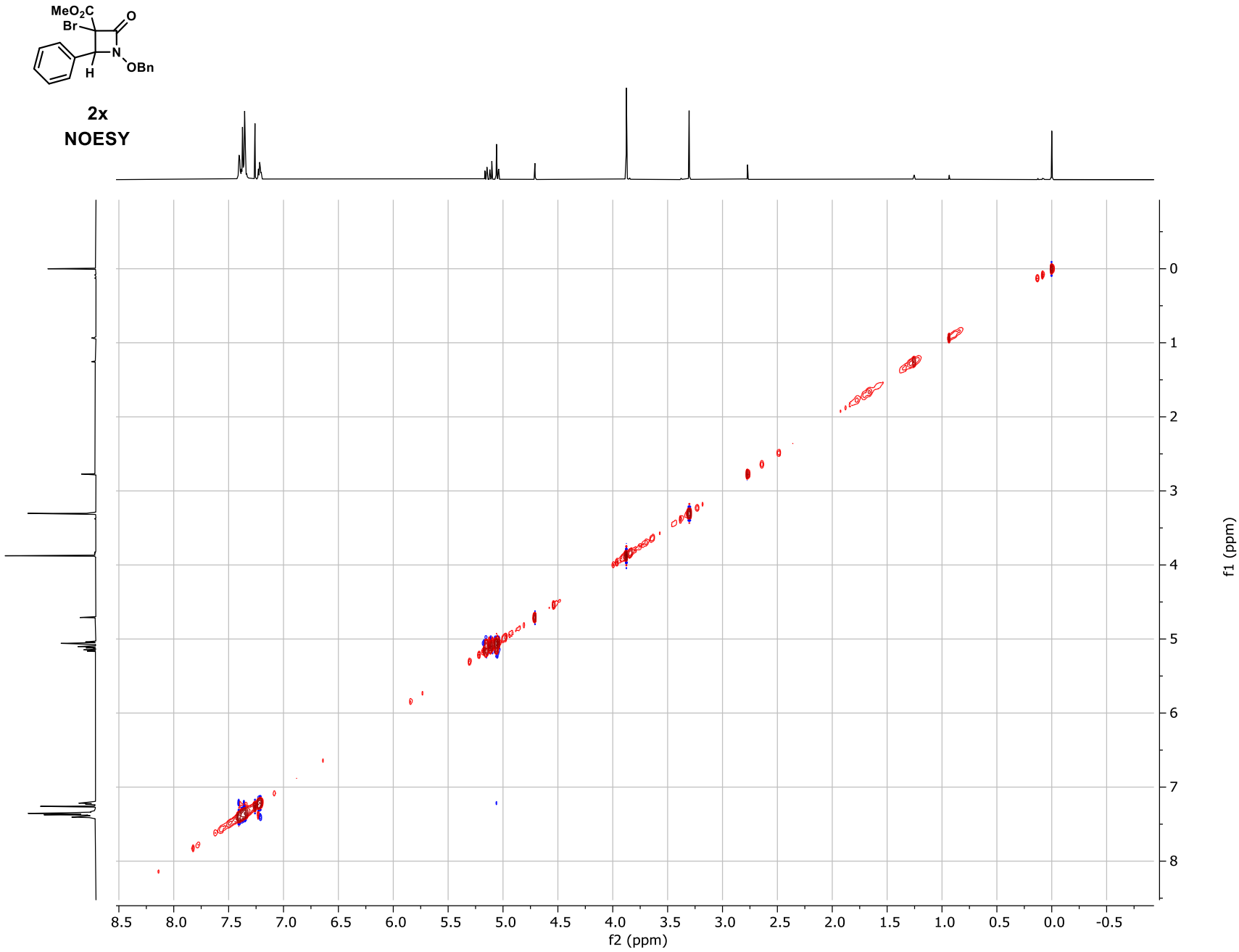
2x

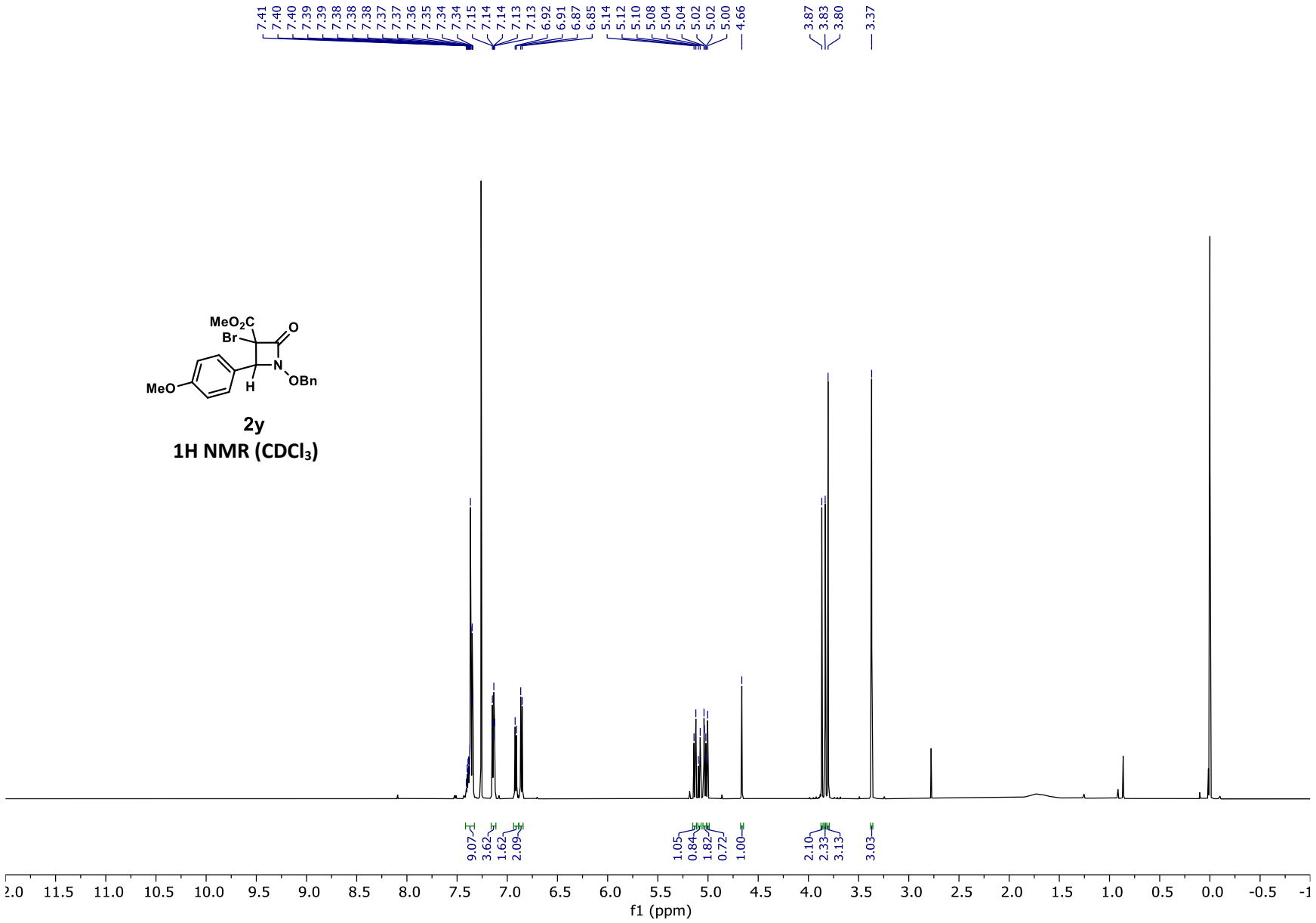
1H NMR ($CDCl_3$)

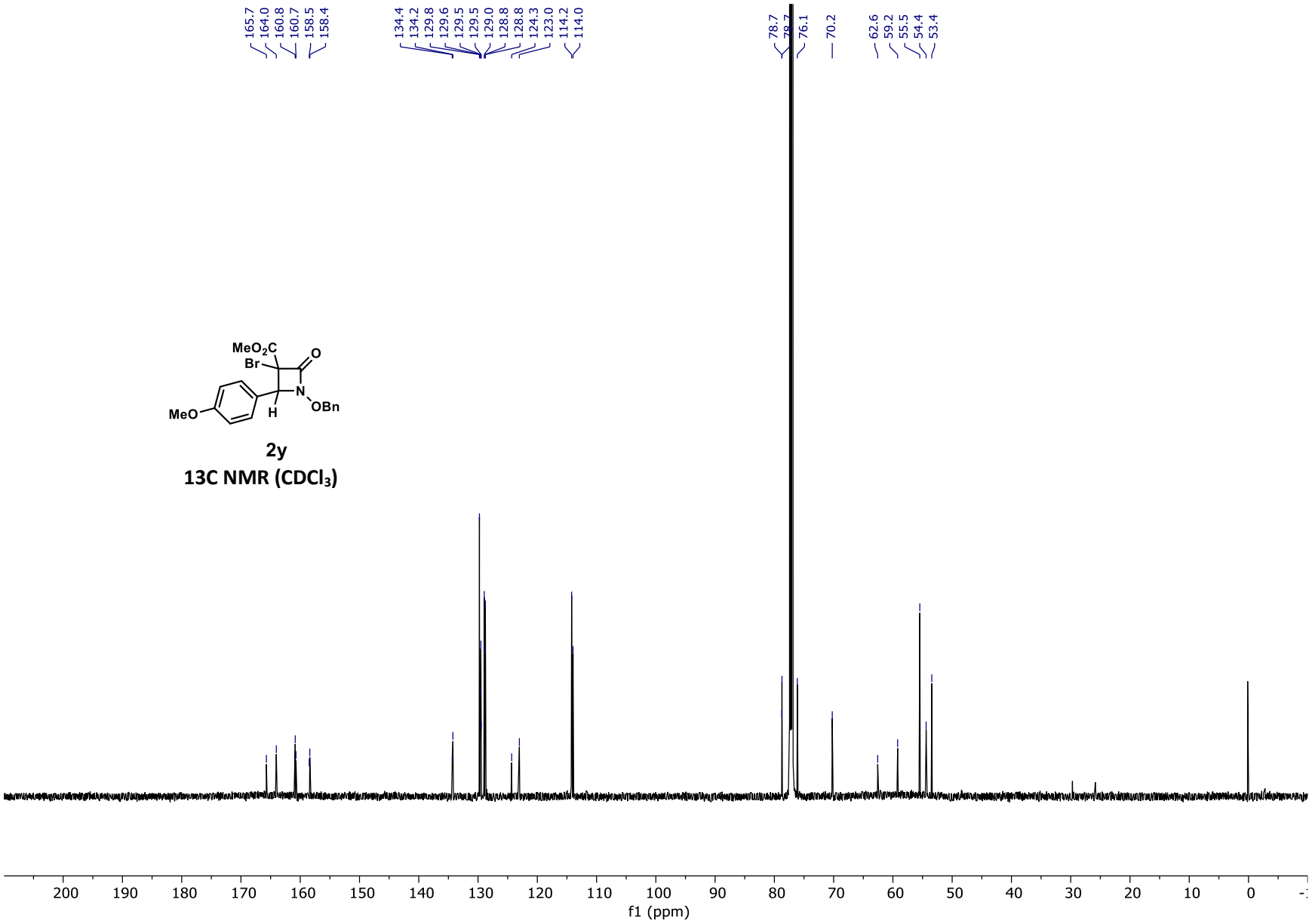


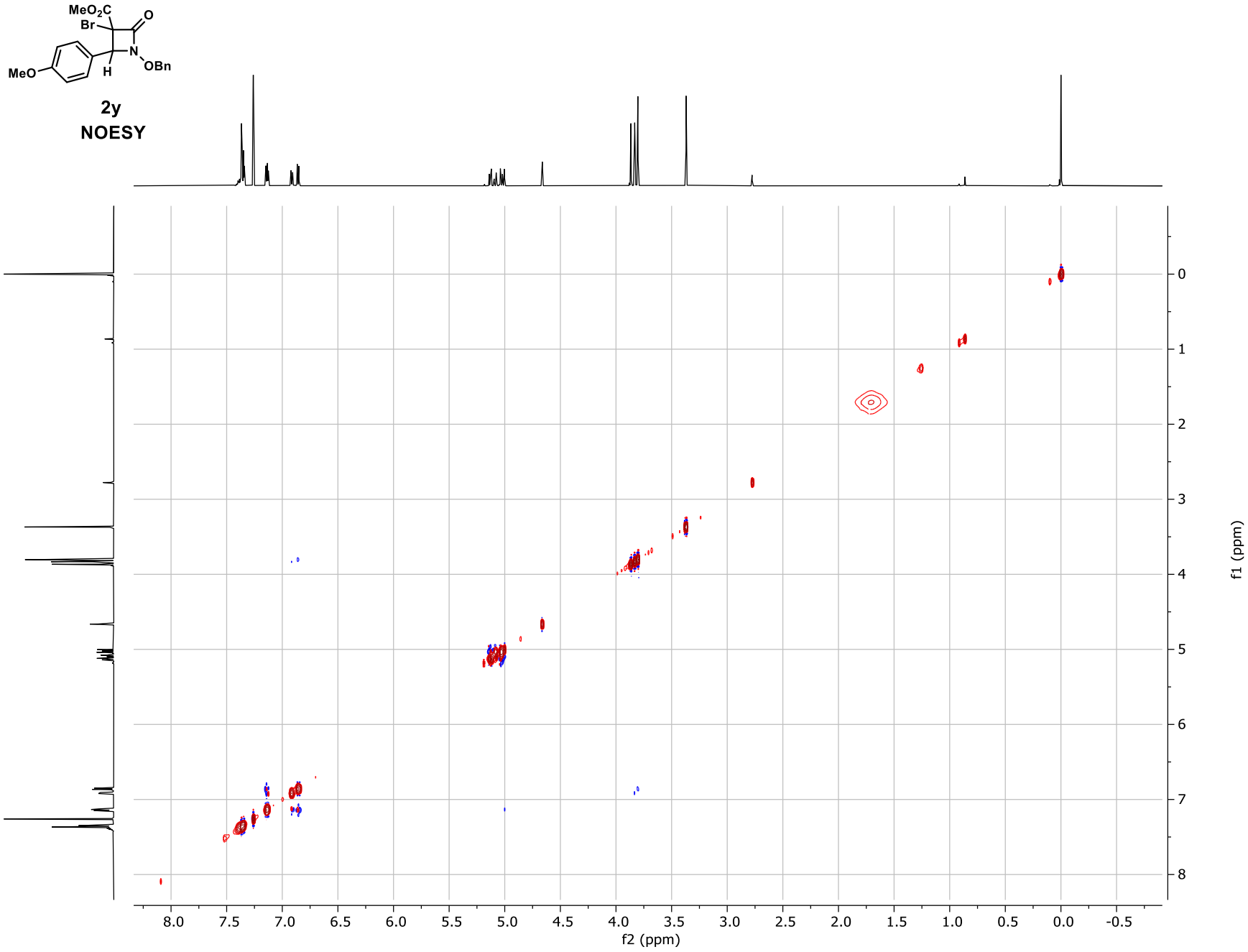
2x

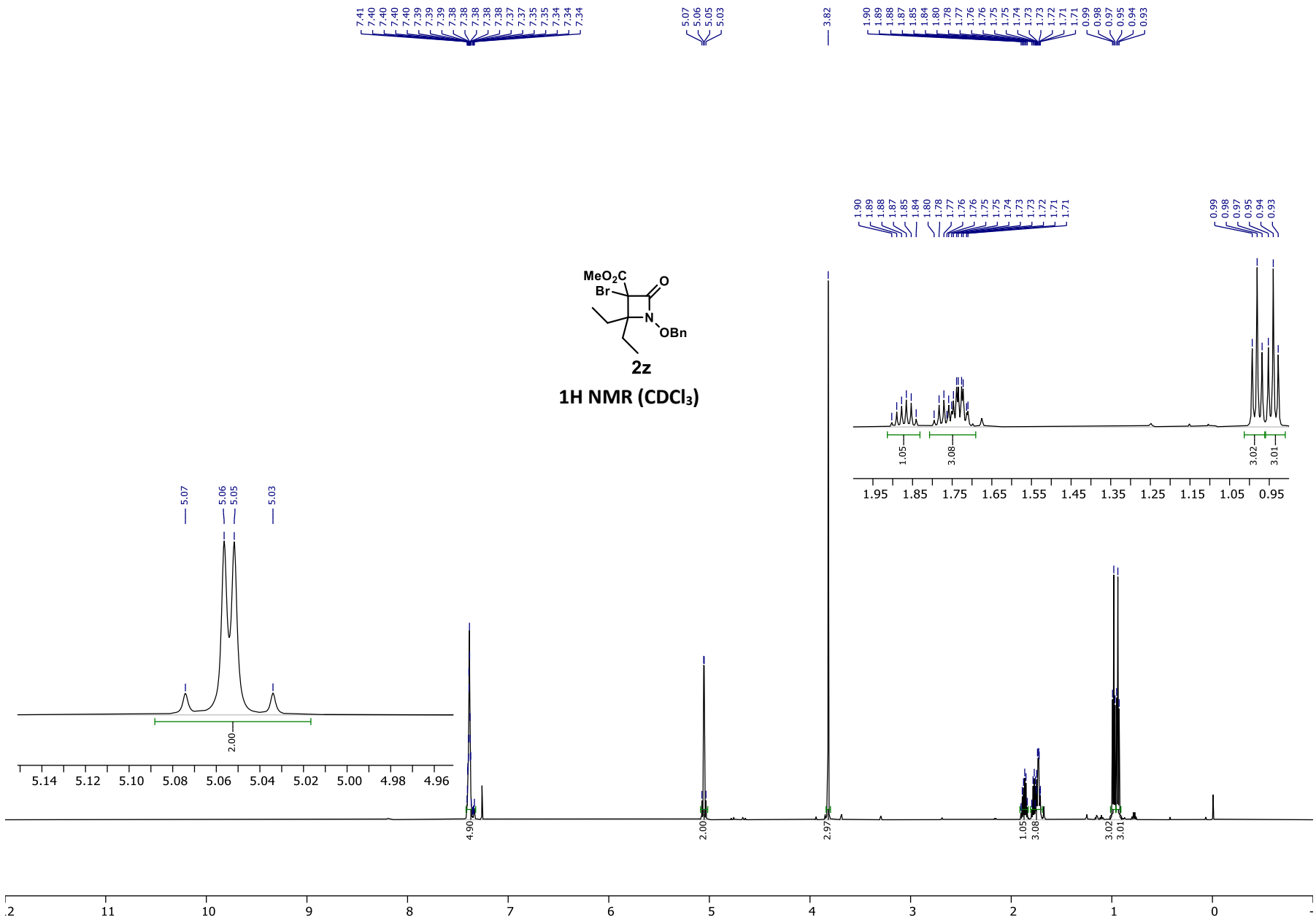
13C NMR ($CDCl_3$)

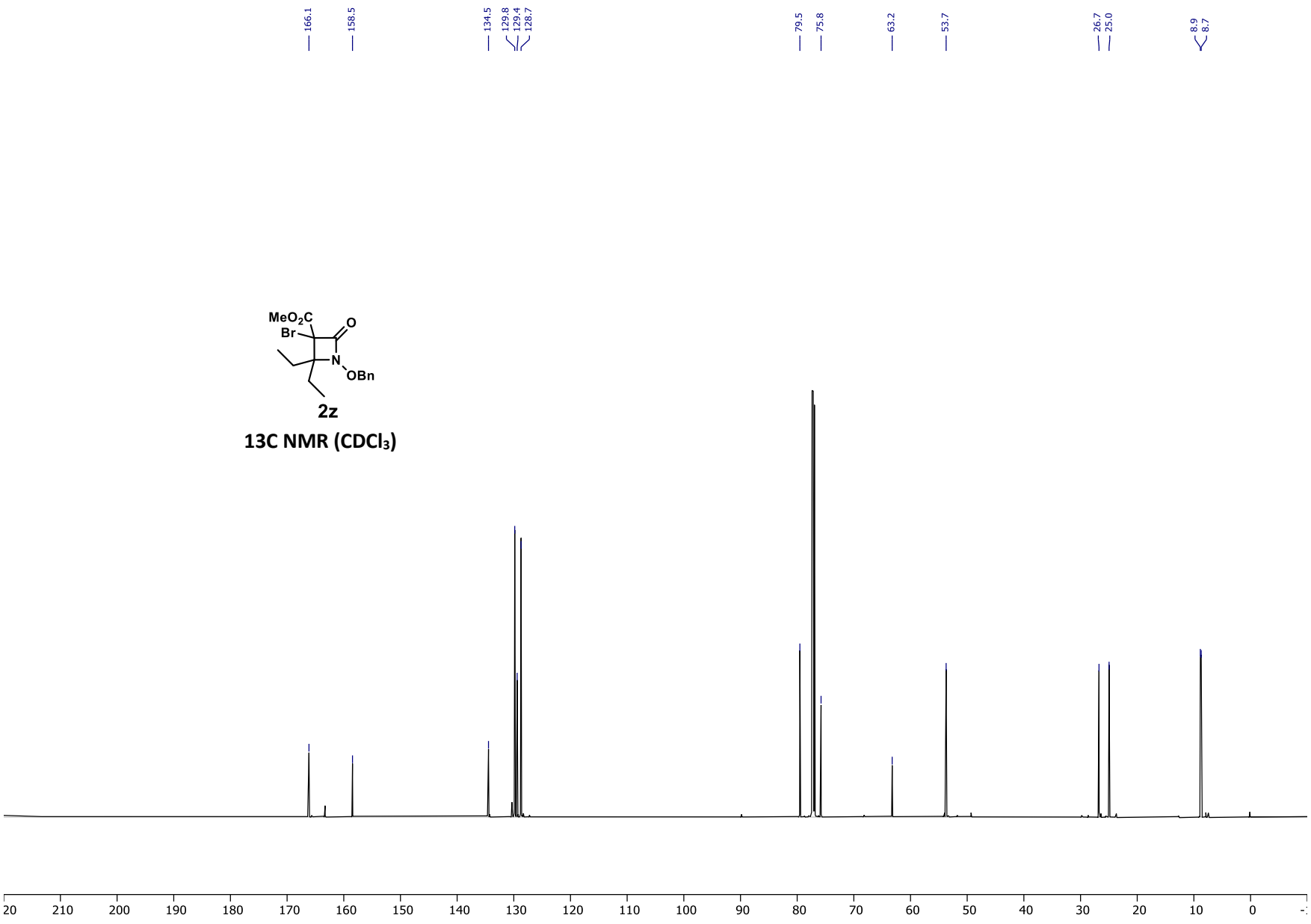

MeO2C
Br
O
N
OBn
H
2x
NOESY
f2 (ppm)
f1 (ppm)

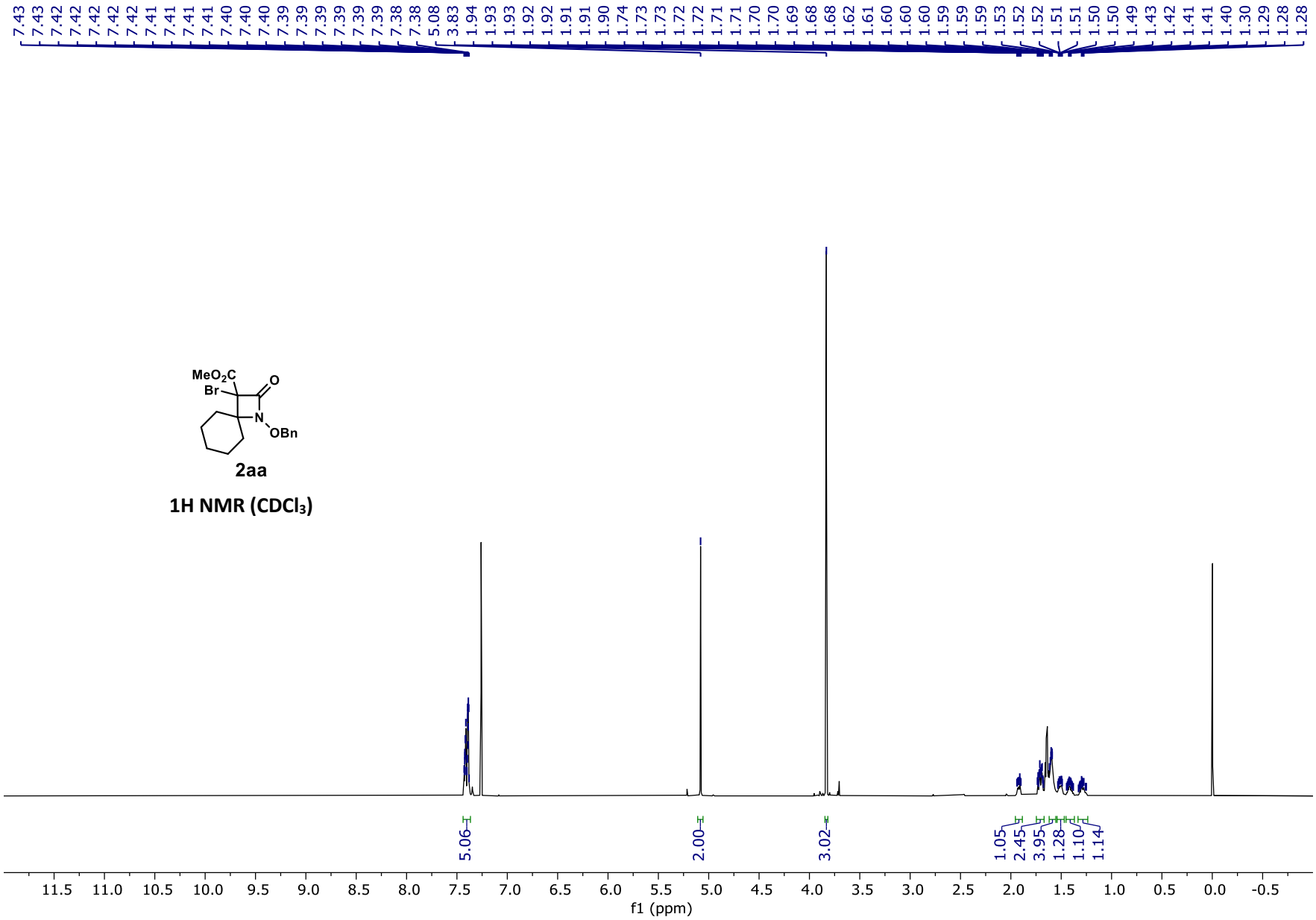

7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.34
7.15
7.14
7.14
7.13
7.13
6.92
6.91
6.87
6.85
5.14
5.12
5.10
5.08
5.04
5.04
5.02
5.02
5.00
4.66
3.87
3.83
3.80
3.37
MeO2C
Br
O
N
OBn
MeO
H
2y
1H NMR (CDCl3)
9.07
3.62
1.62
2.09
1.05
0.84
1.82
0.72
1.00
2.10
2.33
3.13
3.03
f1 (ppm)

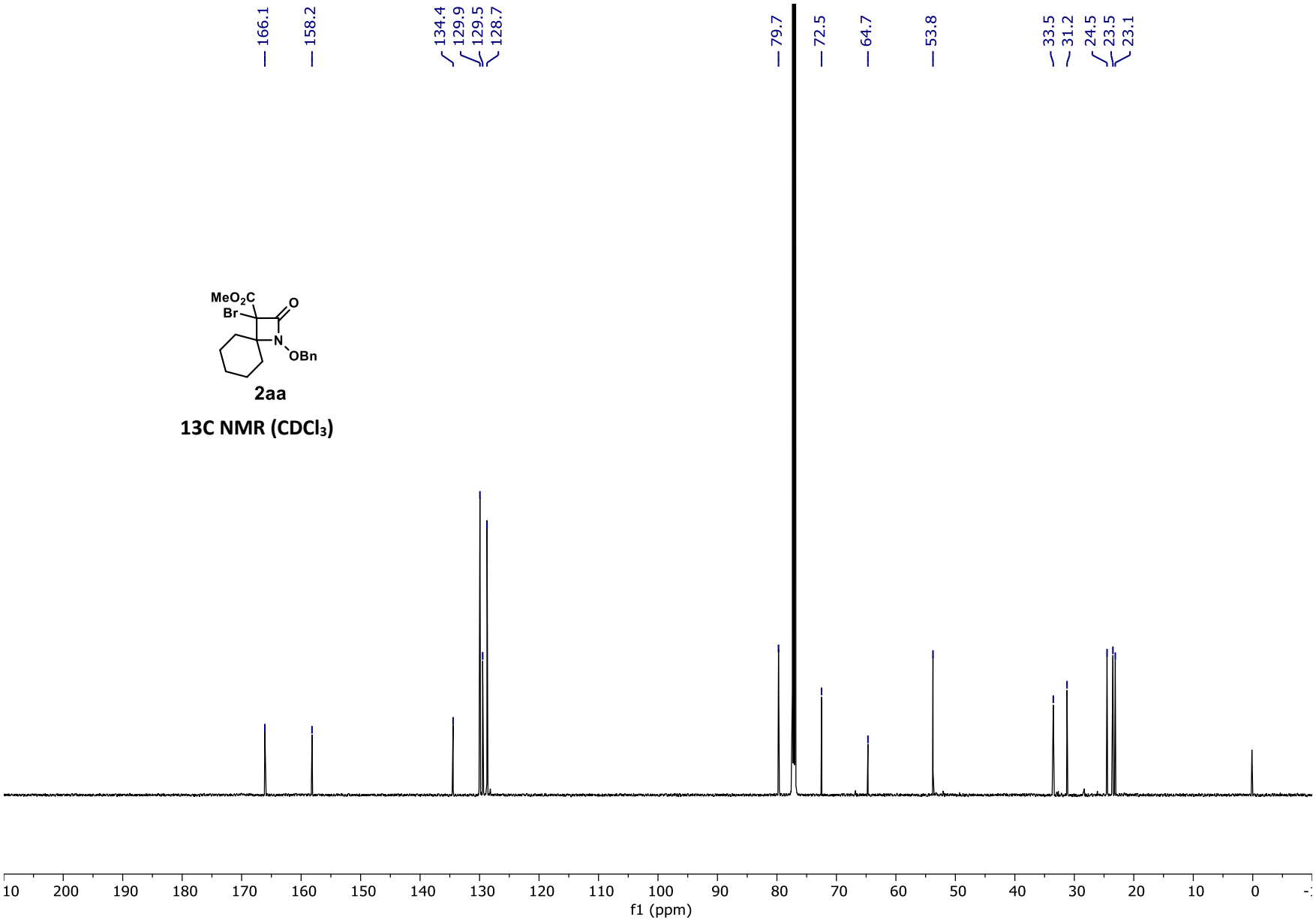

165.7
164.0
160.8
160.7
158.5
158.4
134.4
134.2
129.8
129.6
129.5
129.5
129.0
128.8
128.8
124.3
123.0
114.2
114.0
78.7
78.7
76.1
70.2
62.6
59.2
55.5
54.4
53.4
MeO2C
Br
O
N
OBn
H
MeO
2y
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

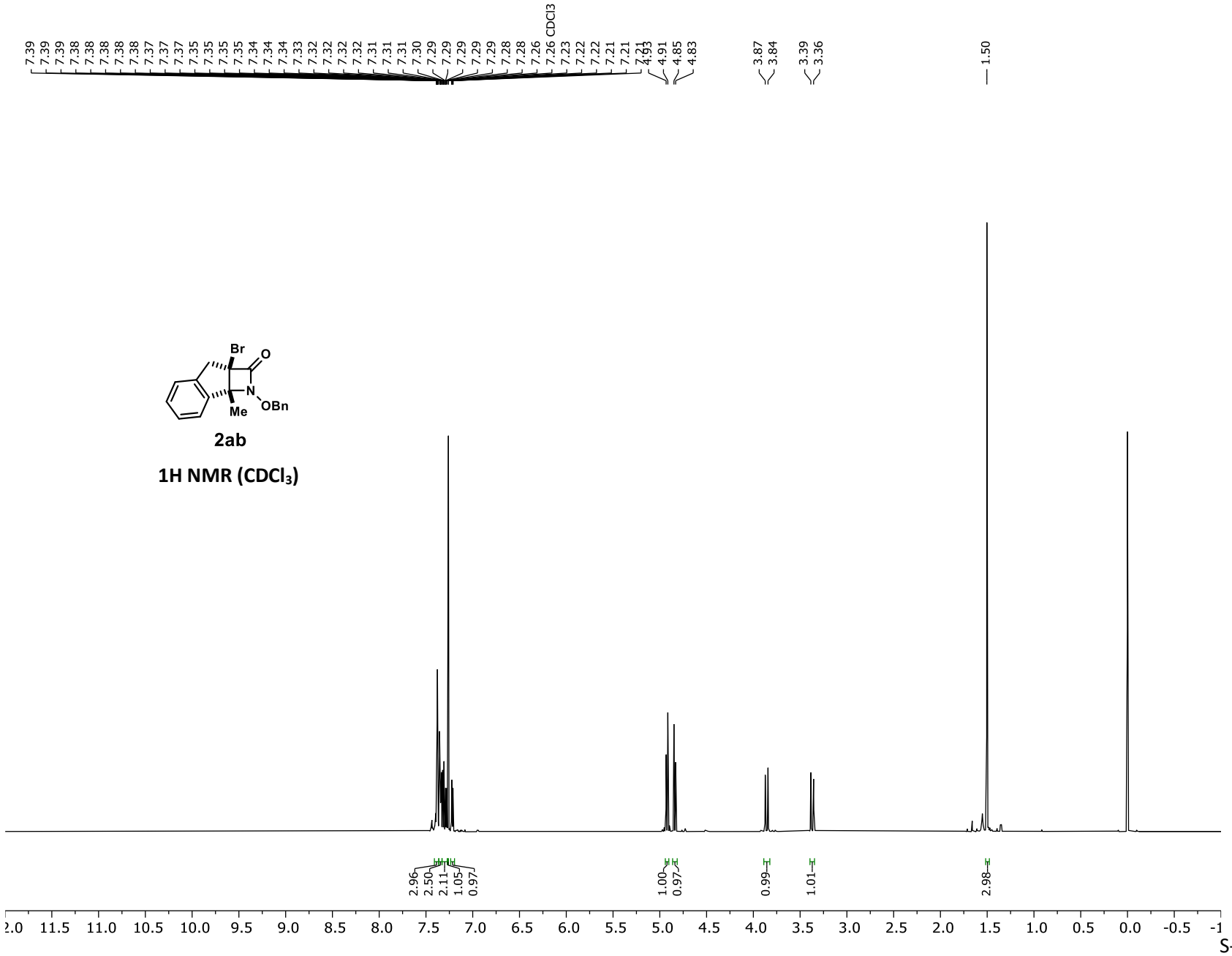

MeO2C
Br
O
N
OBn
H
MeO
2y
NOESY
f2 (ppm)
f1 (ppm)

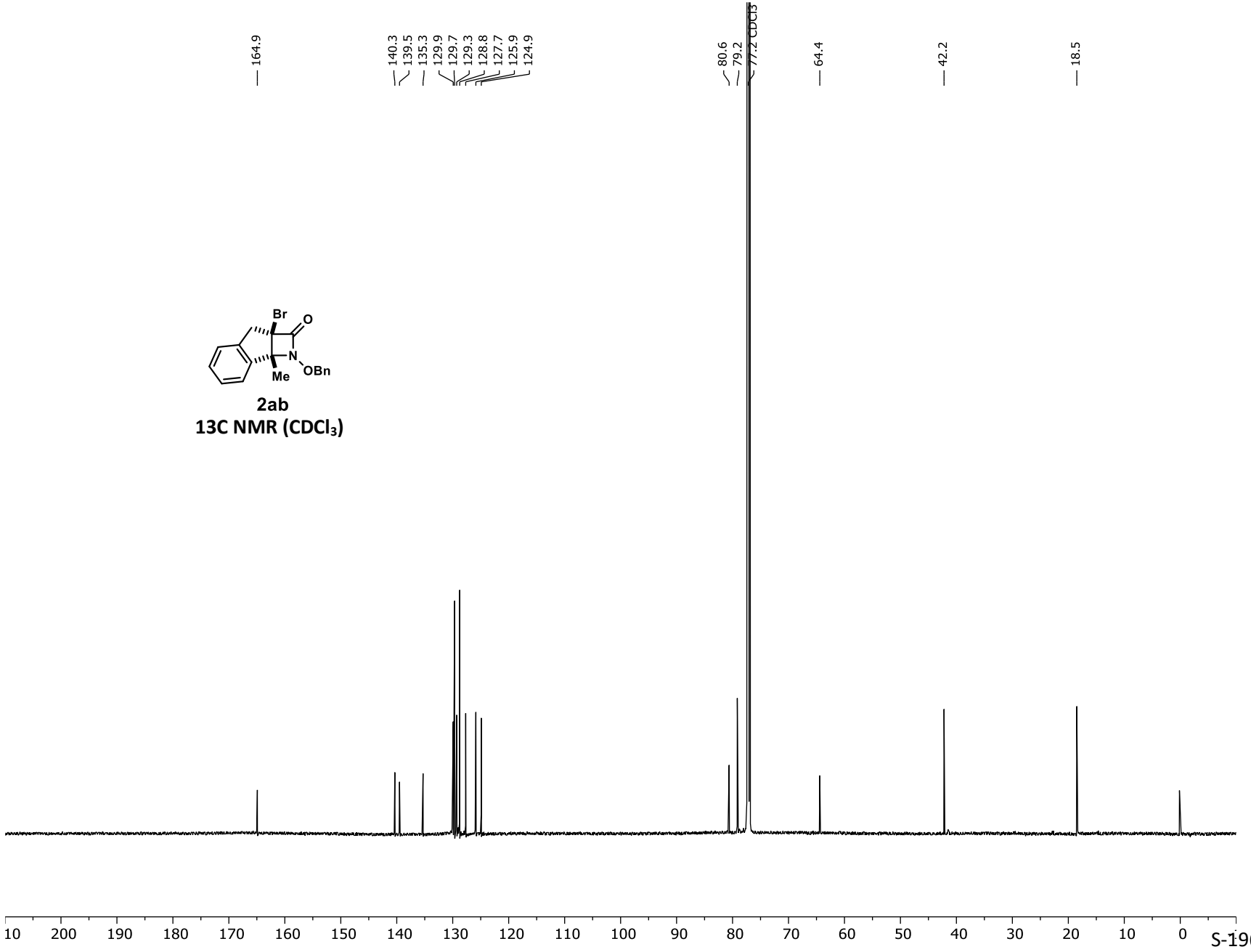

MeO2C
Br
O
N
OBn
2z
1H NMR (CDCl3)

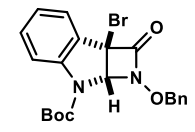

166.1
158.5
134.5
129.8
129.4
128.7
79.5
75.8
63.2
53.7
26.7
25.0
8.9
8.7
MeO2C
Br
O
N
OBn
2z
13C NMR (CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.38 5.08 3.83 1.94 1.93 1.93 1.92 1.92 1.91 1.91 1.90 1.74 1.73 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.68 1.68 1.62 1.61 1.60 1.60 1.60 1.59 1.59 1.59 1.53 1.52 1.52 1.51 1.51 1.50 1.50 1.49 1.43 1.42 1.41 1.41 1.40 1.30 1.29 1.28 1.28
MeO2C
Br
O
N
OBn
2aa
1H NMR (CDCl3)
5.06
2.00
3.02
1.05
2.45
3.95
1.28
1.10
1.14
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.1
158.2
134.4
129.9
129.5
128.7
79.7
72.5
64.7
53.8
33.5
31.2
24.5
23.5
23.1
MeO2C
Br
O
N
OBn
2aa
13C NMR (CDCl3)
f1 (ppm)

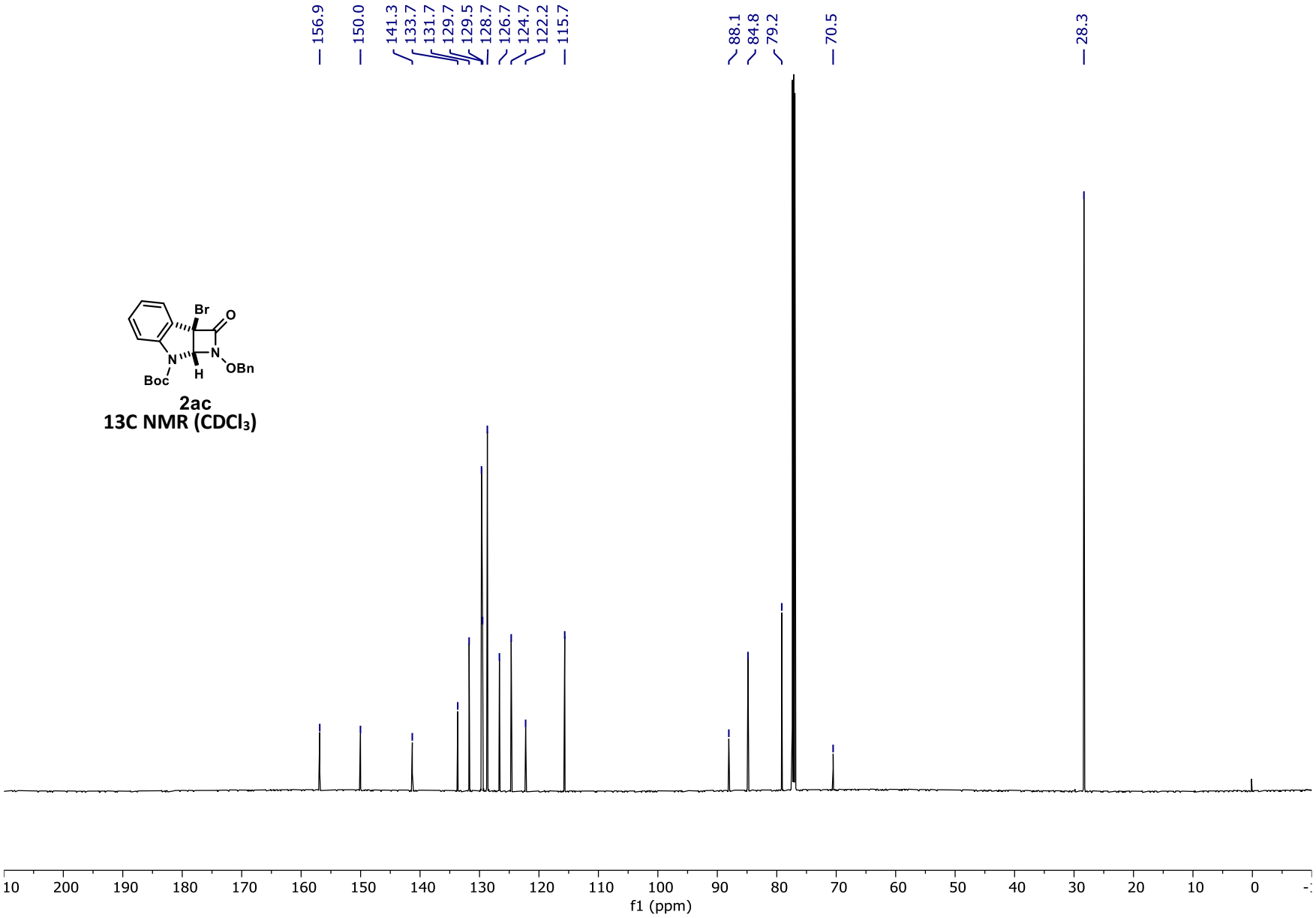

7.39 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.37 7.35 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.29 7.29 7.28 7.28 7.26 7.26 CDCl3 7.23 7.22 7.22 7.21 7.21 7.21 4.93 4.91 4.85 4.83 3.87 3.84 3.39 3.36 1.50
Br
O
N
OBn
Me
2ab
1H NMR (CDCl3)
2.96 2.50 2.11 1.05 0.97 1.00 0.97 0.99 1.01 2.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

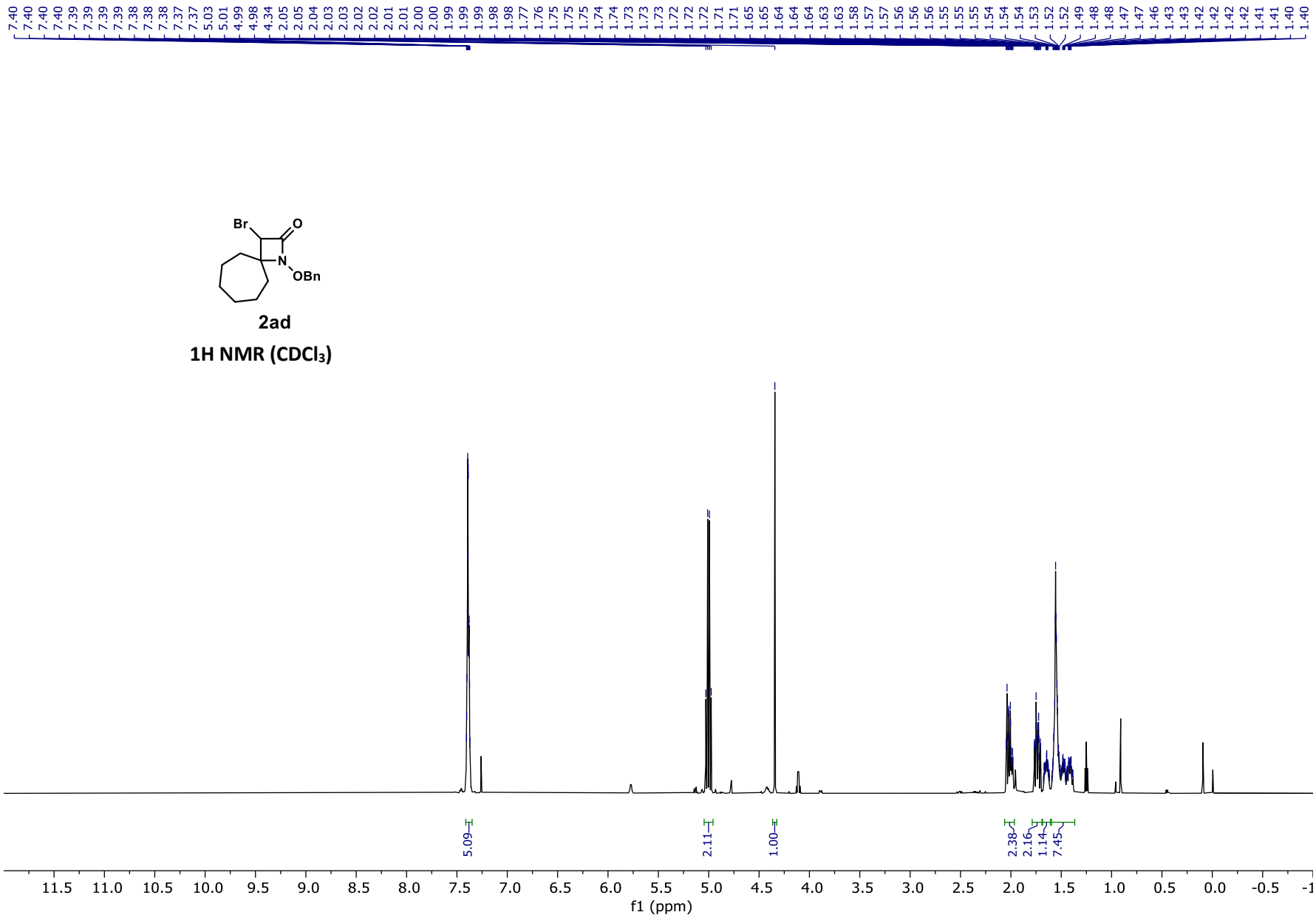

164.9
140.3
139.5
135.3
129.9
129.7
129.3
128.8
127.7
125.9
124.9
80.6
79.2
77.2 CDCl3
64.4
42.2
18.5
Br
O
N
OBn
Me
2ab
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

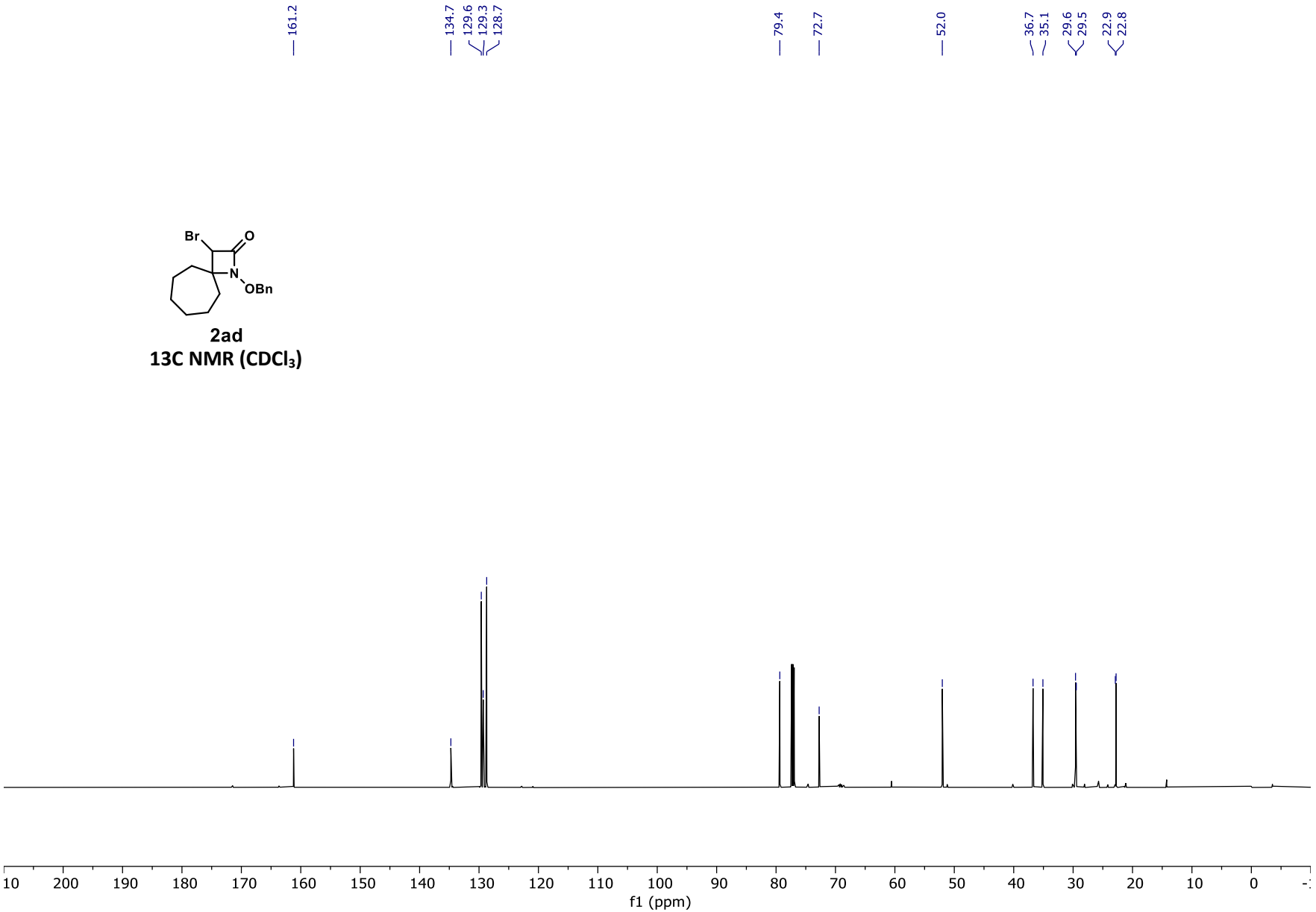


2ac

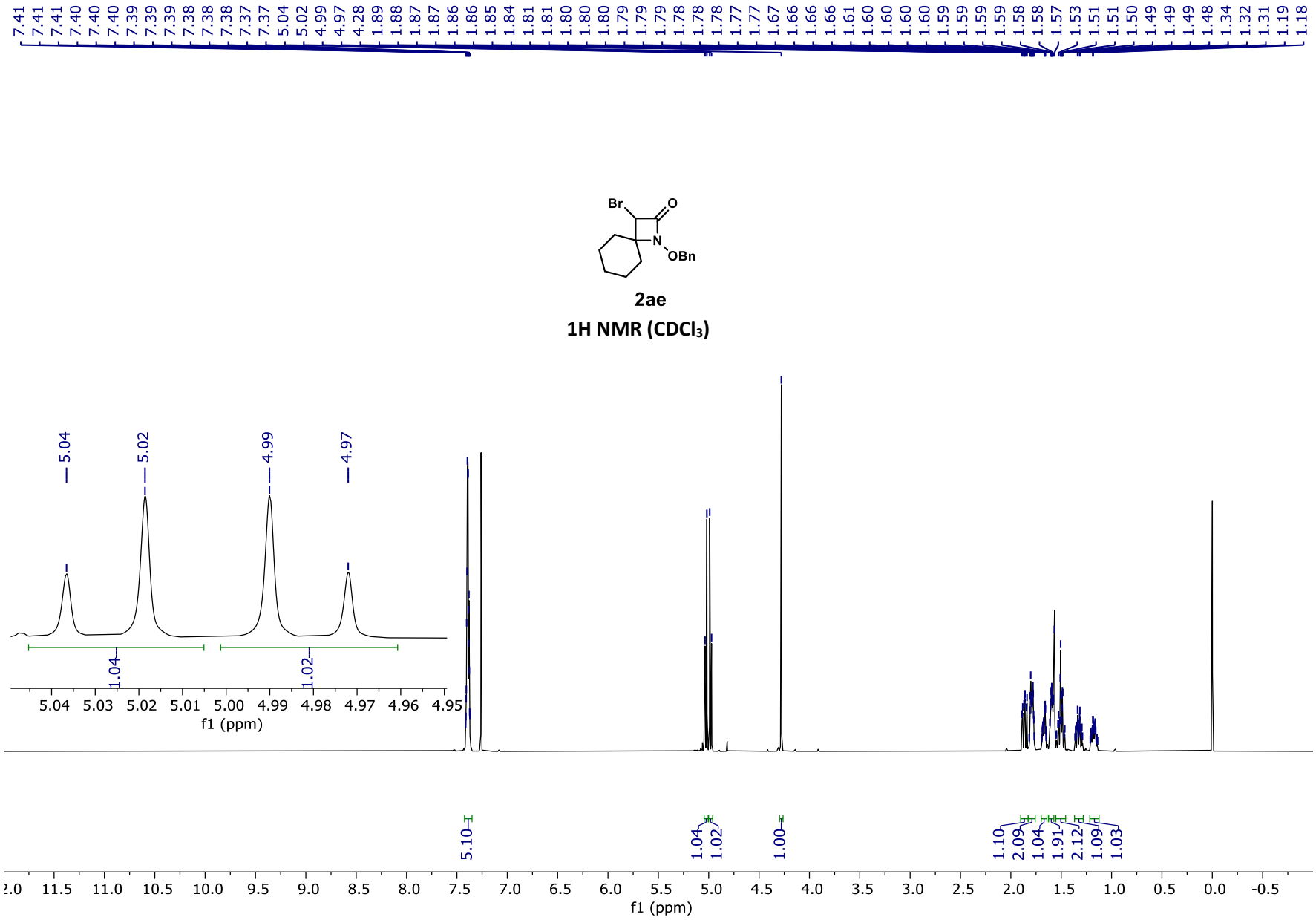
1H NMR ($CDCl_3$)

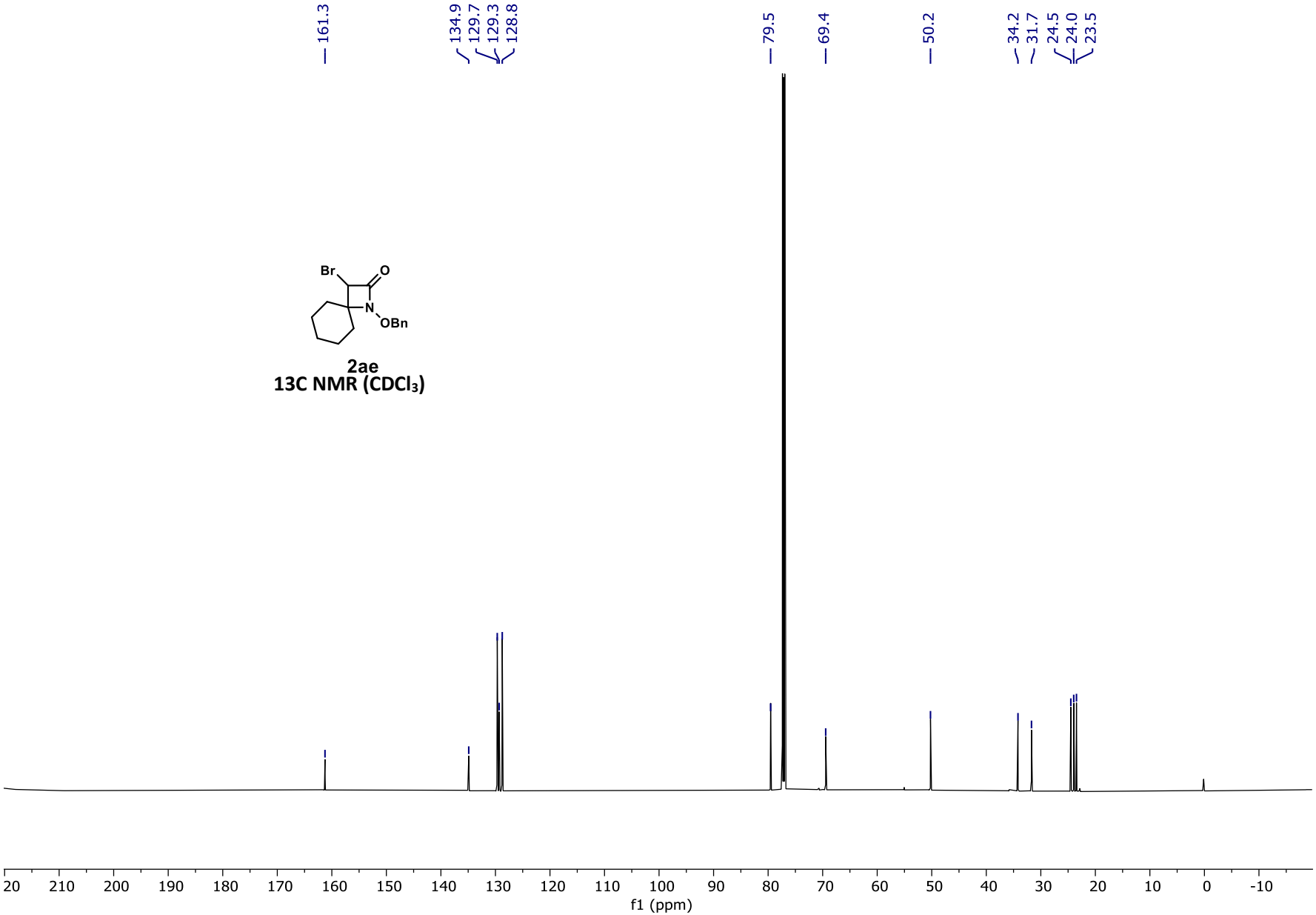

156.9
150.0
141.3
133.7
131.7
129.7
129.5
128.7
126.7
124.7
122.2
115.7
88.1
84.8
79.2
70.5
28.3
Br
O
N
N
OBn
Boc
H
2ac
13C NMR (CDCl3)
f1 (ppm)

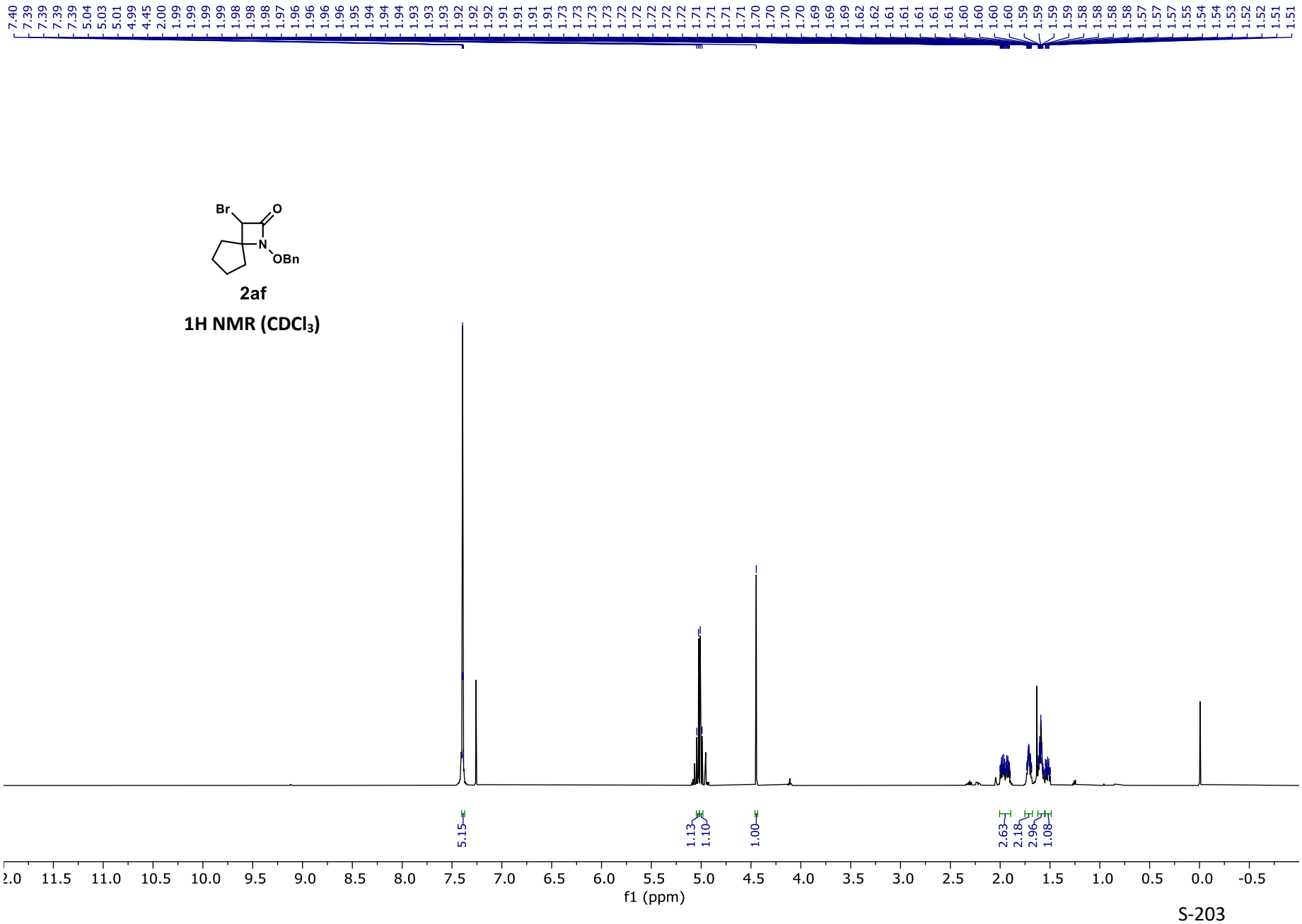

7.40 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 5.03 5.01 4.99 4.98 4.34 2.05 2.05 2.04 2.03 2.03 2.02 2.02 2.01 2.01 2.00 2.00 1.99 1.99 1.99 1.98 1.98 1.77 1.76 1.75 1.75 1.75 1.74 1.74 1.73 1.73 1.73 1.72 1.72 1.72 1.71 1.71 1.65 1.65 1.64 1.64 1.64 1.63 1.63 1.58 1.57 1.57 1.56 1.56 1.56 1.55 1.55 1.55 1.54 1.54 1.54 1.53 1.52 1.52 1.49 1.48 1.48 1.47 1.47 1.46 1.43 1.43 1.42 1.42 1.42 1.42 1.41 1.41 1.40 1.40
Br
O
N
OBn
2ad
1H NMR (CDCl3)
5.09
2.11
1.00
2.38
2.16
1.14
7.45
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

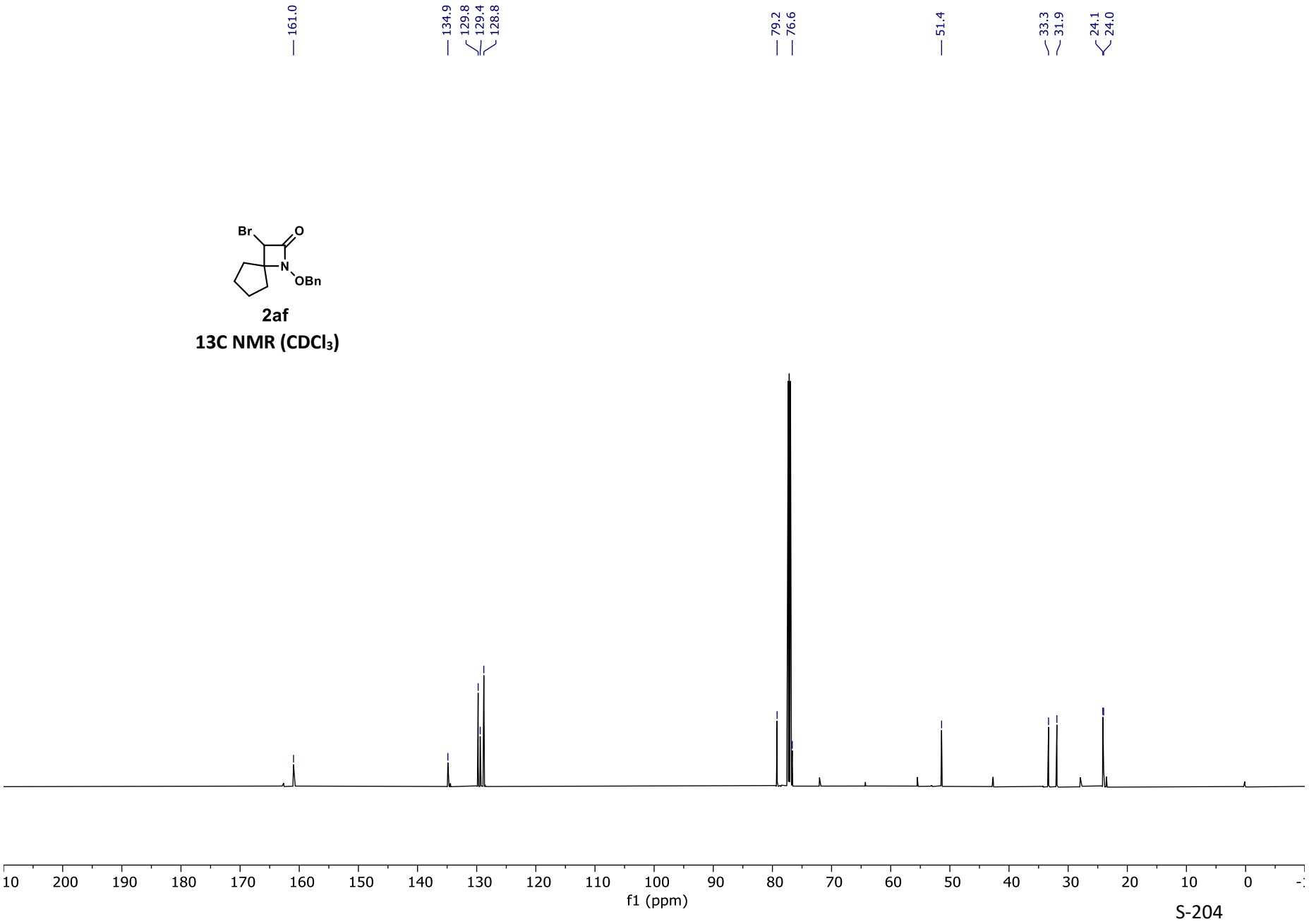


2ad
13C NMR ($CDCl_3$)


7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 5.04 5.02 4.99 4.97 4.28 1.89 1.88 1.87 1.87 1.86 1.86 1.85 1.84 1.81 1.81 1.80 1.80 1.80 1.79 1.79 1.79 1.78 1.78 1.77 1.77 1.67 1.66 1.66 1.66 1.61 1.60 1.60 1.60 1.59 1.59 1.59 1.59 1.58 1.58 1.57 1.53 1.51 1.51 1.50 1.49 1.49 1.49 1.48 1.34 1.32 1.31 1.19 1.18
Br
O
N
OBn
2ae
1H NMR (CDCl3)
5.04
5.02
4.99
4.97
1.04
1.02
5.04 5.03 5.02 5.01 5.00 4.99 4.98 4.97 4.96 4.95
f1 (ppm)
5.10
1.04
1.02
1.00
1.10
2.09
1.04
1.91
2.12
1.09
1.03
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

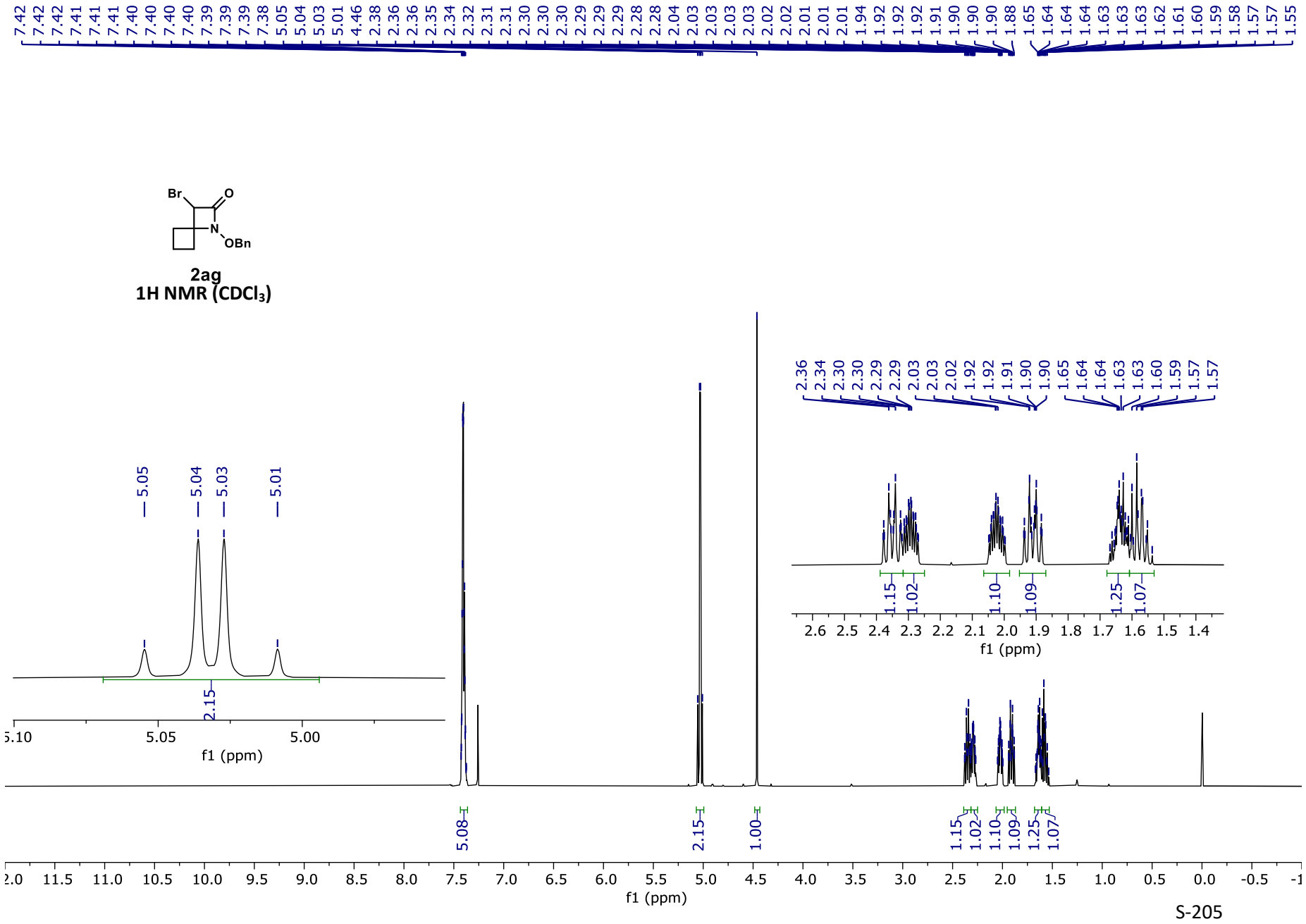

161.3
134.9
129.7
129.3
128.8
79.5
69.4
50.2
34.2
31.7
24.5
24.0
23.5
Br
O
N
OBn
2ae
13C NMR (CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

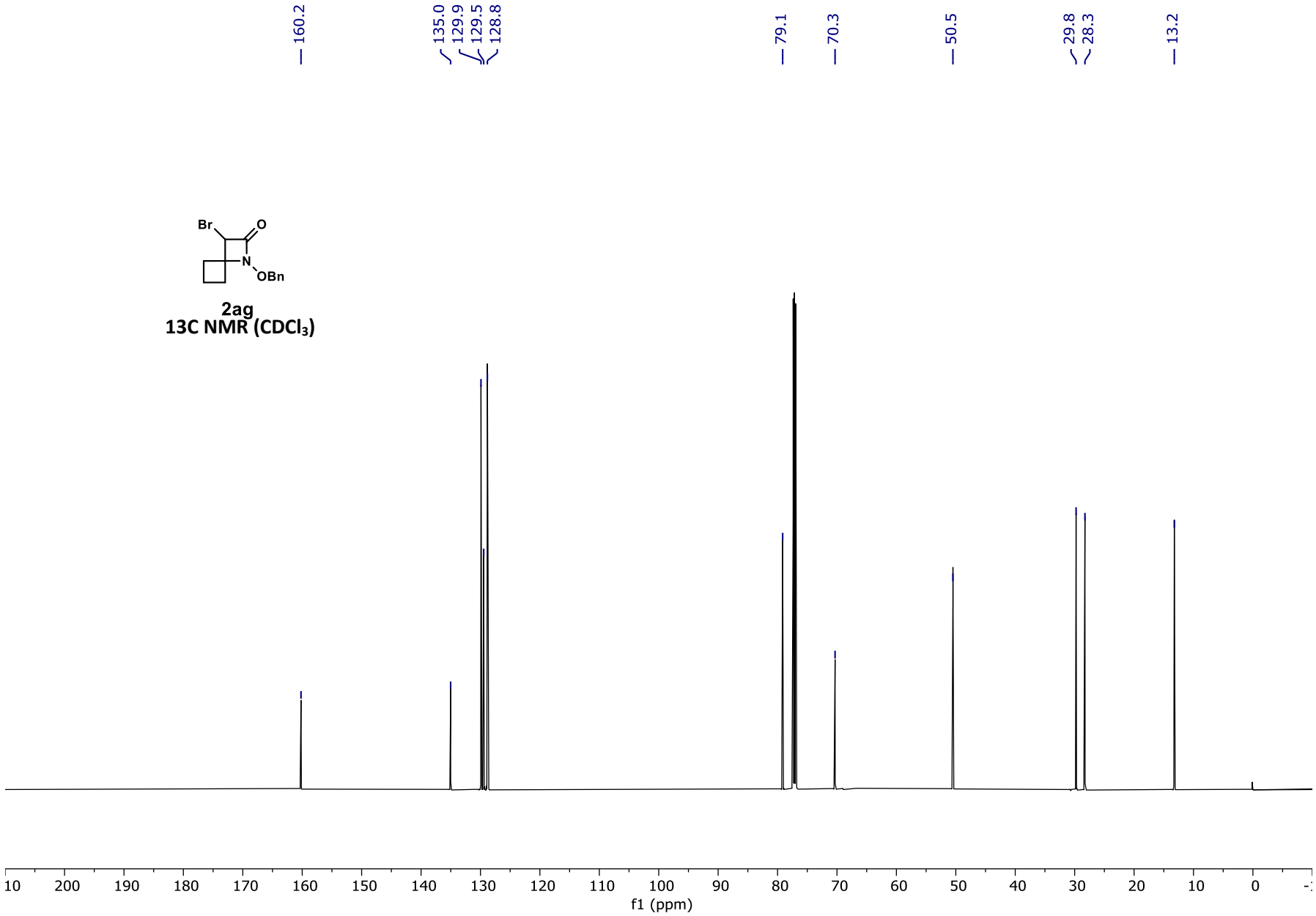

7.40 7.39 7.39 7.39 7.39 5.04 5.03 5.01 4.99 4.45 2.00 1.99 1.99 1.99 1.99 1.98 1.98 1.98 1.97 1.96 1.96 1.96 1.96 1.95 1.94 1.94 1.94 1.93 1.93 1.93 1.92 1.92 1.92 1.91 1.91 1.91 1.91 1.73 1.73 1.73 1.72 1.72 1.72 1.72 1.72 1.71 1.71 1.71 1.71 1.70 1.70 1.70 1.70 1.69 1.69 1.69 1.62 1.62 1.61 1.61 1.61 1.61 1.61 1.60 1.60 1.60 1.60 1.59 1.59 1.59 1.59 1.58 1.58 1.58 1.58 1.57 1.57 1.57 1.55 1.54 1.54 1.53 1.52 1.52 1.51 1.51
Br
O
N
OBn
2af
1H NMR (CDCl3)
5.15
1.13
1.10
1.00
2.63
2.18
2.96
1.08
f1 (ppm)

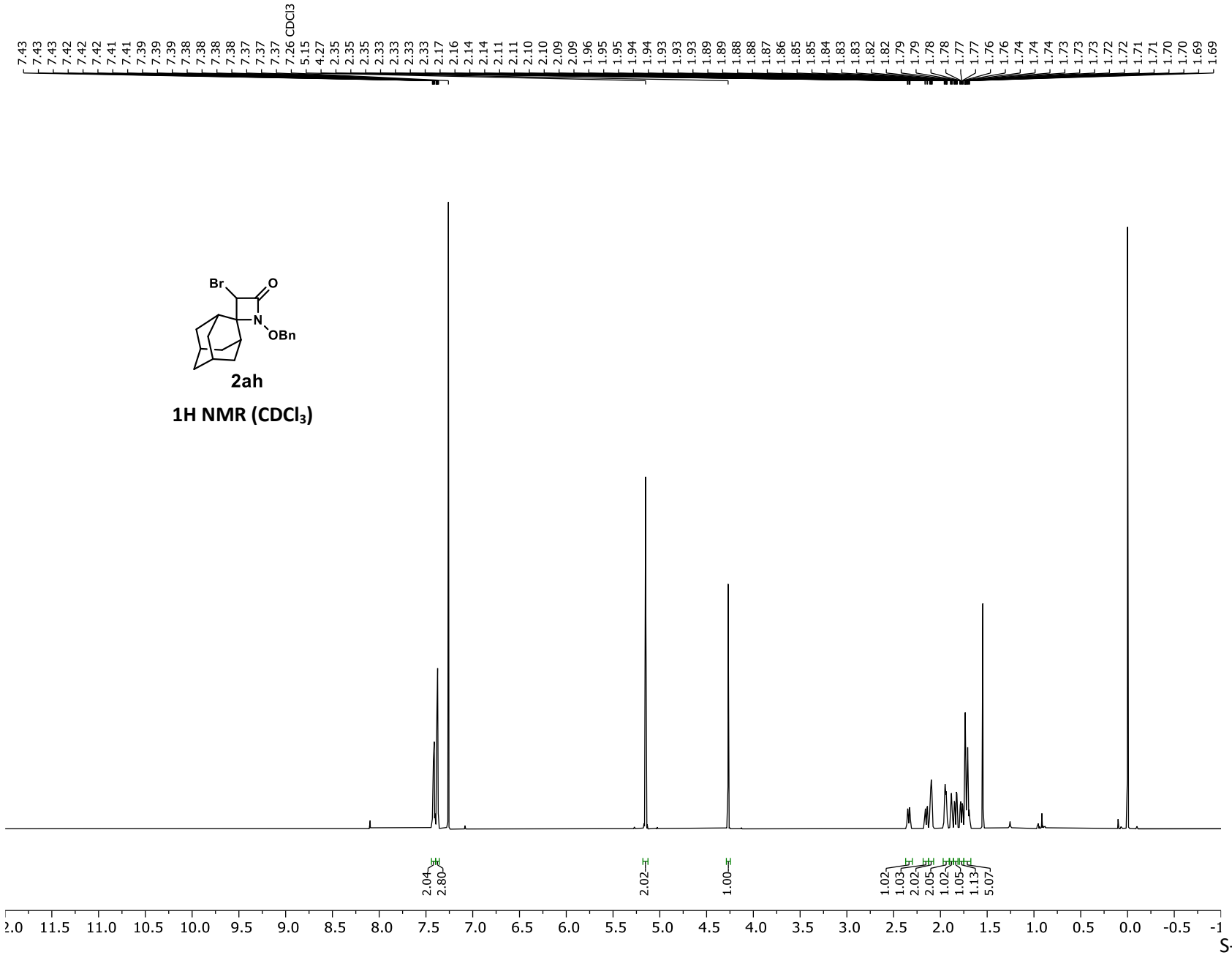


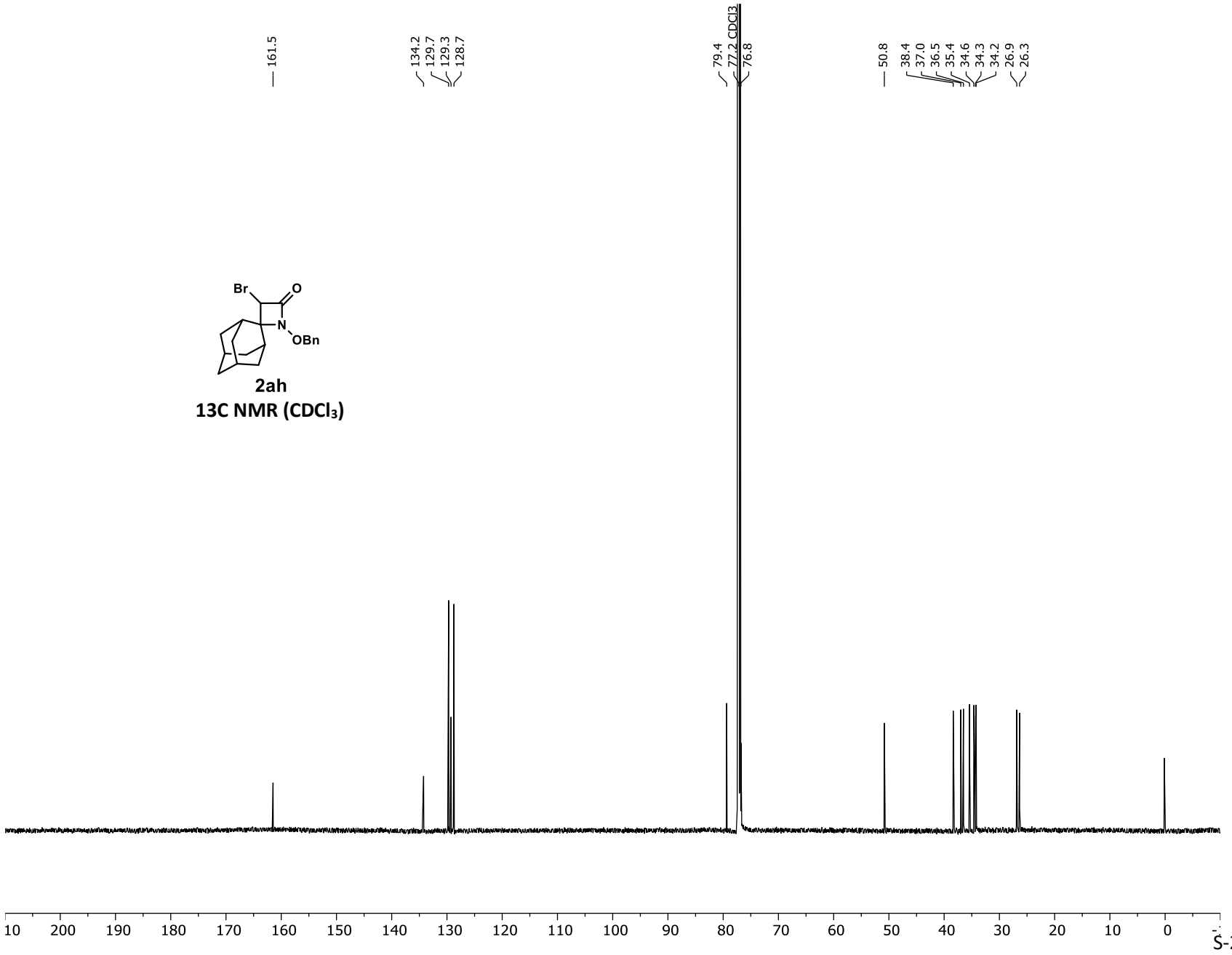
2af

13C NMR ($CDCl_3$)


Br
O
N
OBn
2ag
1H NMR (CDCl3)
f1 (ppm)
S-205

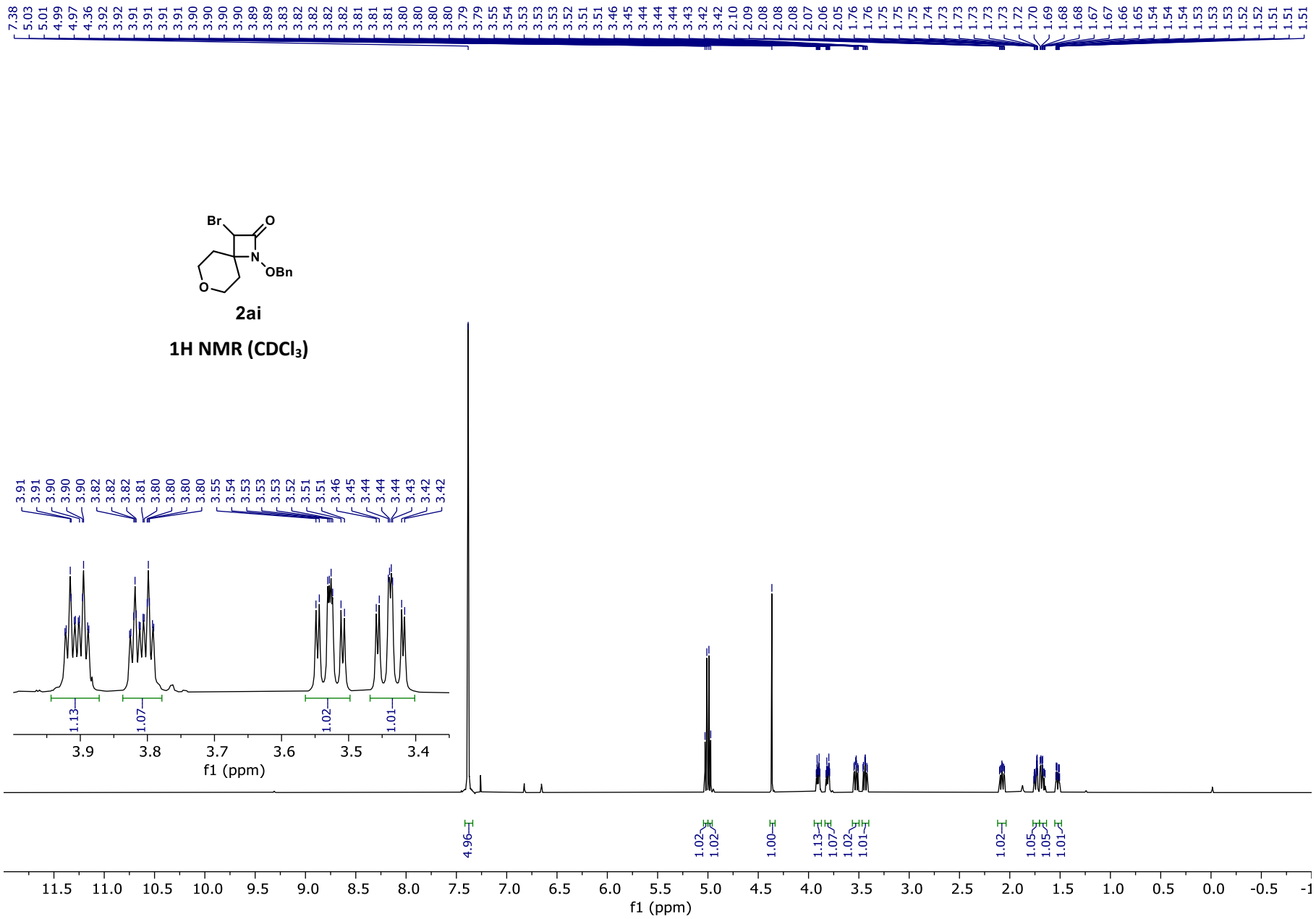

160.2
135.0
129.9
129.5
128.8
79.1
70.3
50.5
29.8
28.3
13.2
Br
O
N
OBn
2ag
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

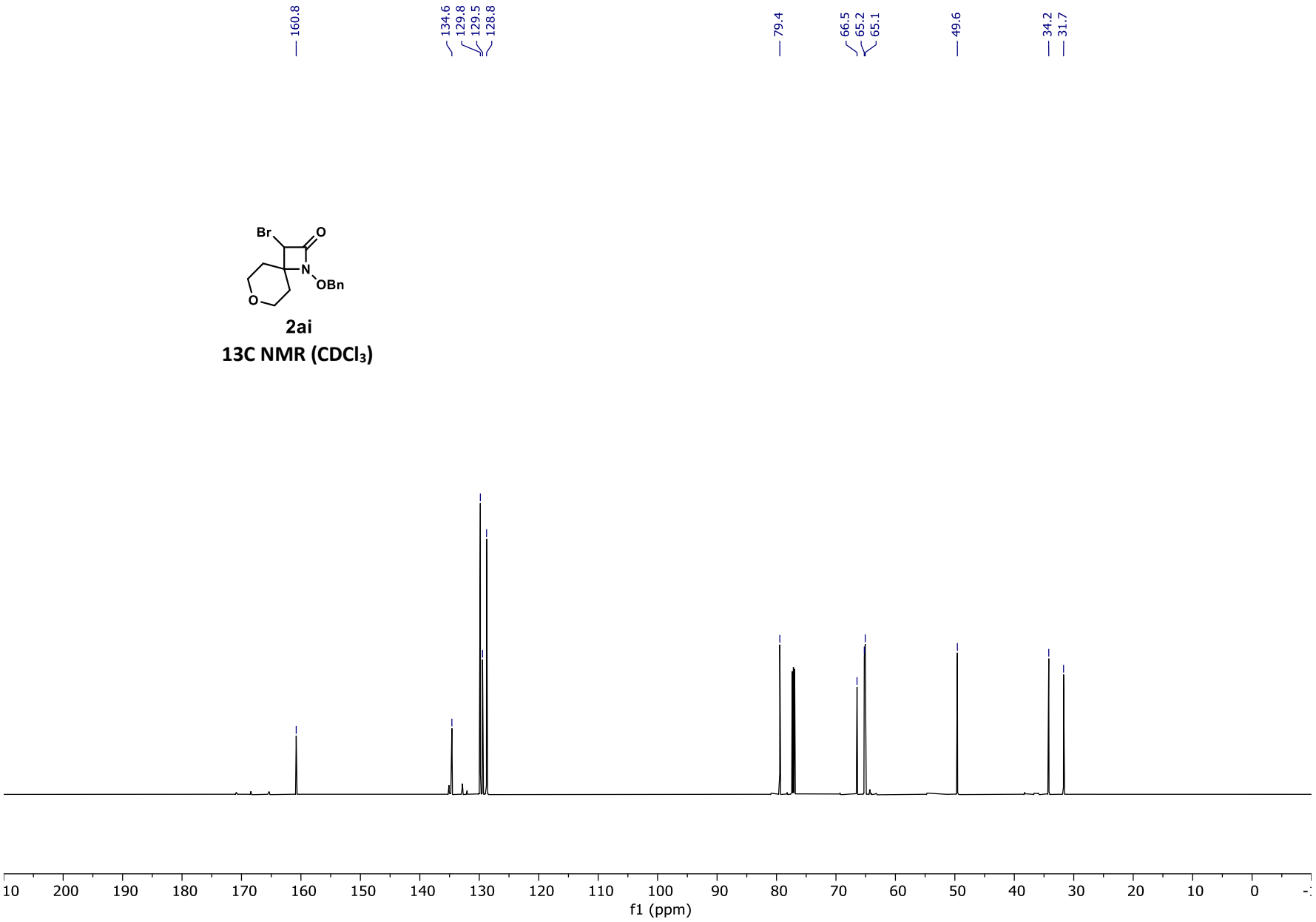

7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.39 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.37 CDCl3 7.26 5.15 4.27 2.35 2.35 2.35 2.33 2.33 2.33 2.33 2.17 2.16 2.14 2.14 2.11 2.11 2.10 2.10 2.09 2.09 1.96 1.95 1.95 1.94 1.94 1.93 1.93 1.93 1.89 1.89 1.88 1.88 1.87 1.86 1.85 1.85 1.84 1.83 1.83 1.82 1.82 1.79 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.74 1.74 1.73 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.69
Br
O
N
OBn
2ah
1H NMR (CDCl3)
2.04
2.80
2.02
1.00
1.02
1.03
2.02
2.05
1.02
1.05
1.13
5.07
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1



2ah

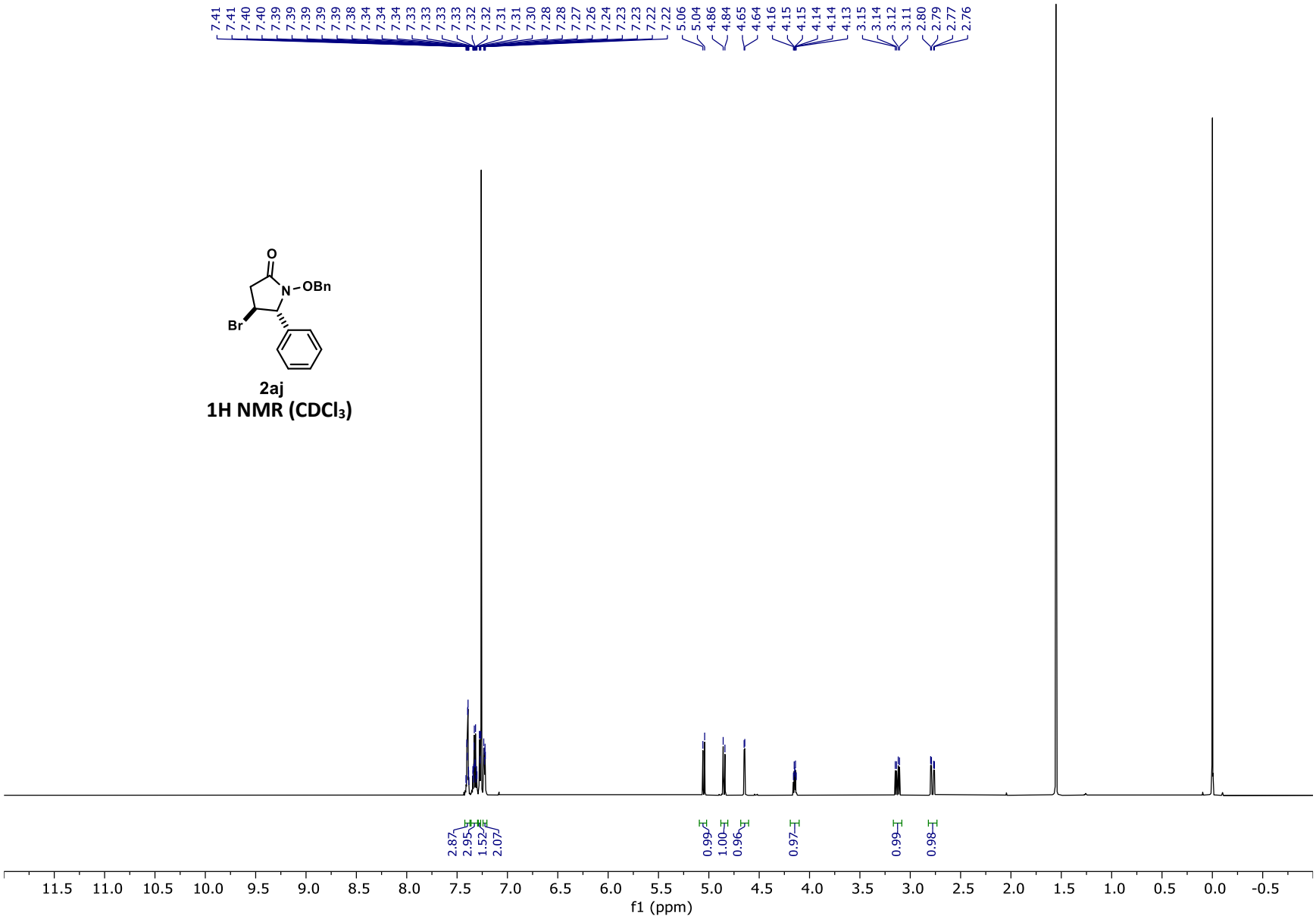
13C NMR ($CDCl_3$)

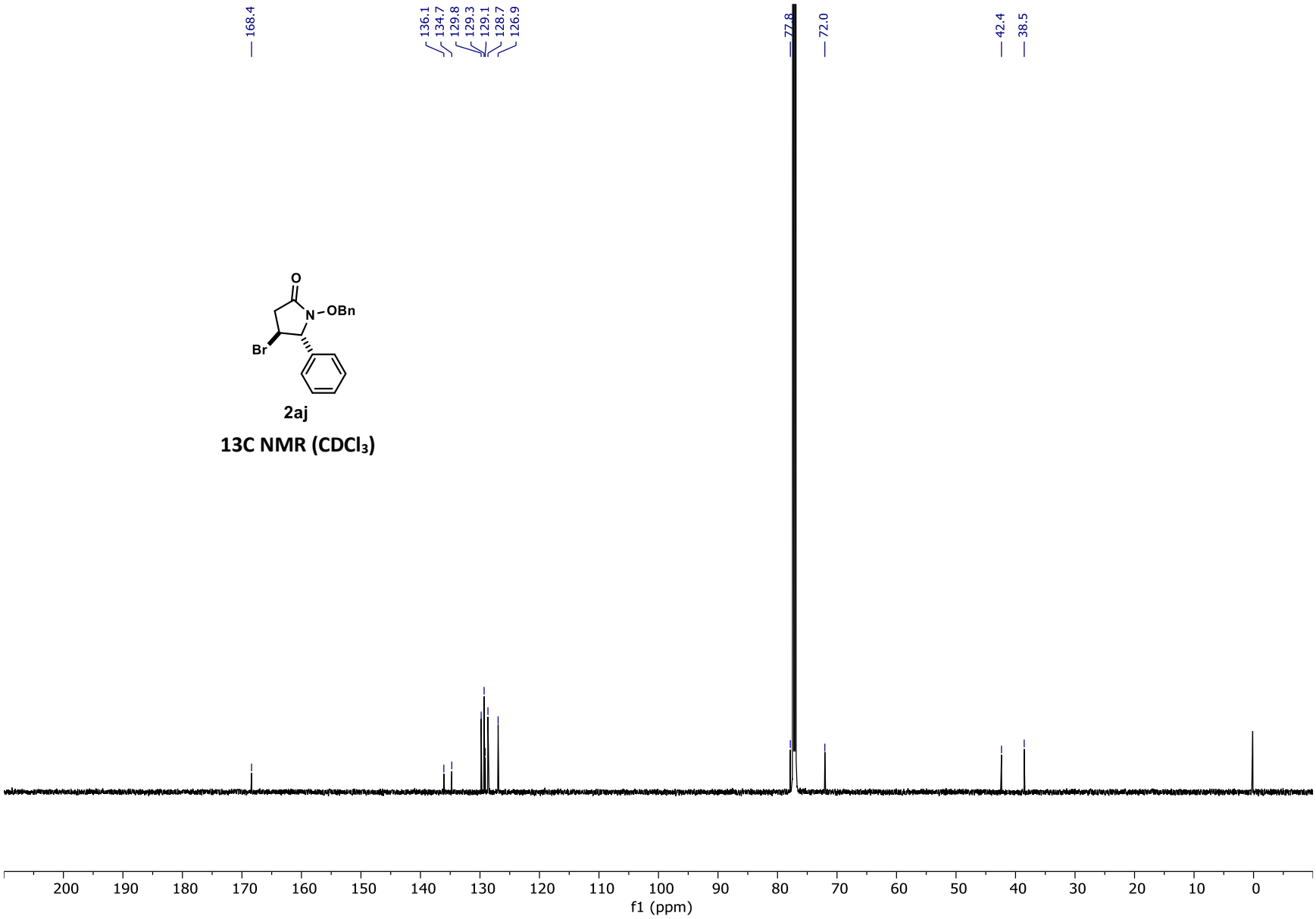

Br
O
N
OBn
O
2ai
1H NMR (CDCl3)
f1 (ppm)

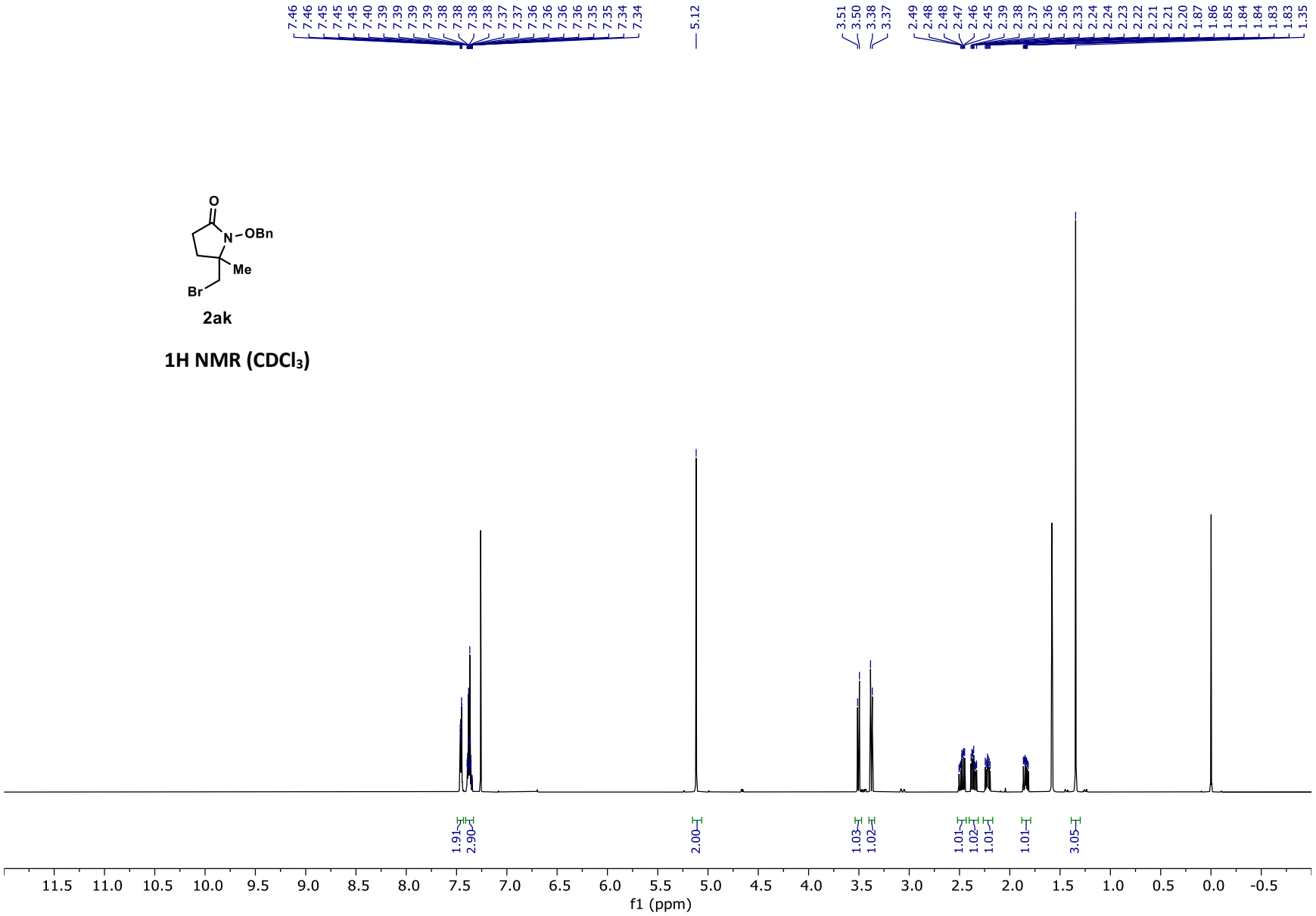


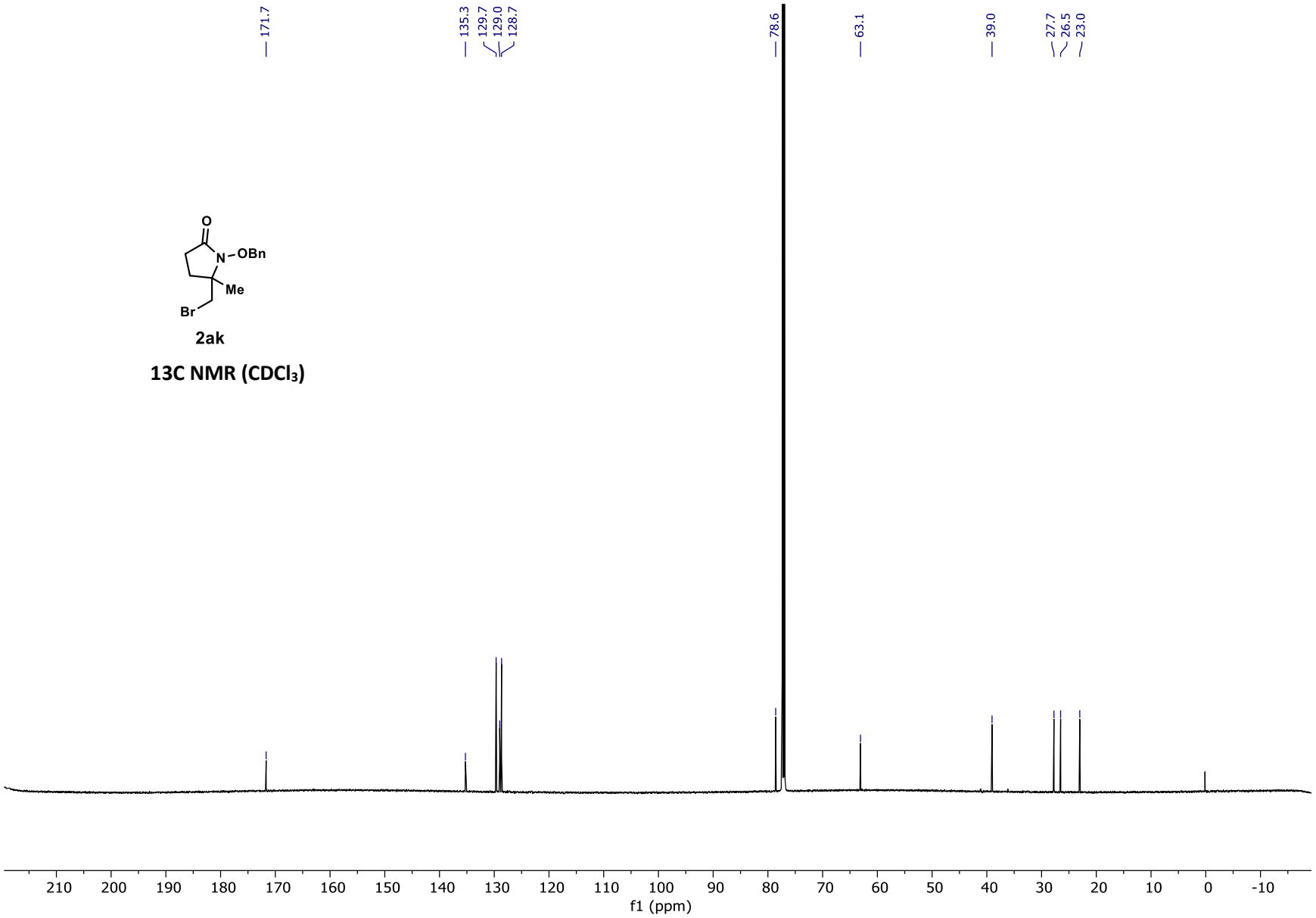
2ai

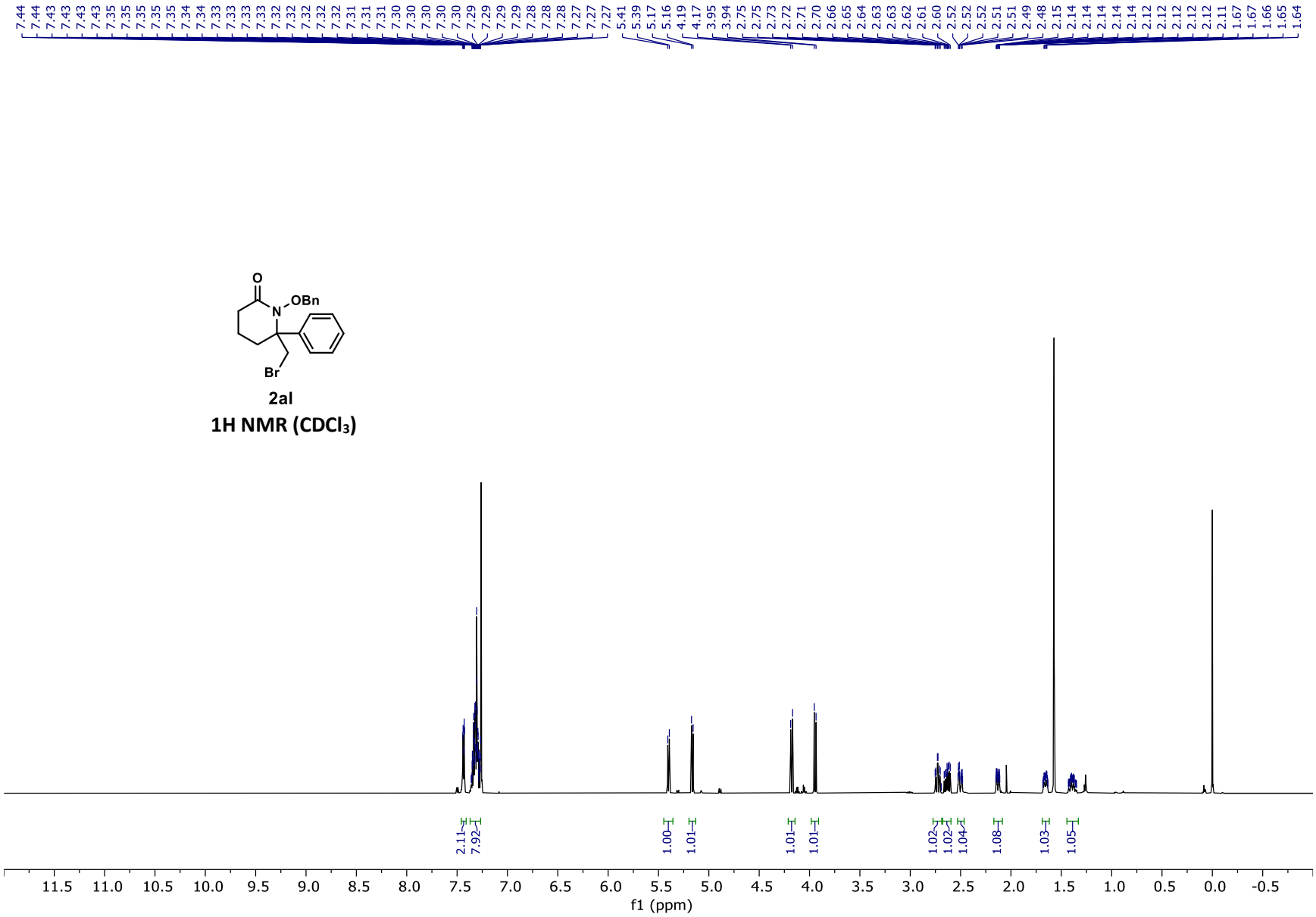
13C NMR ($CDCl_3$)

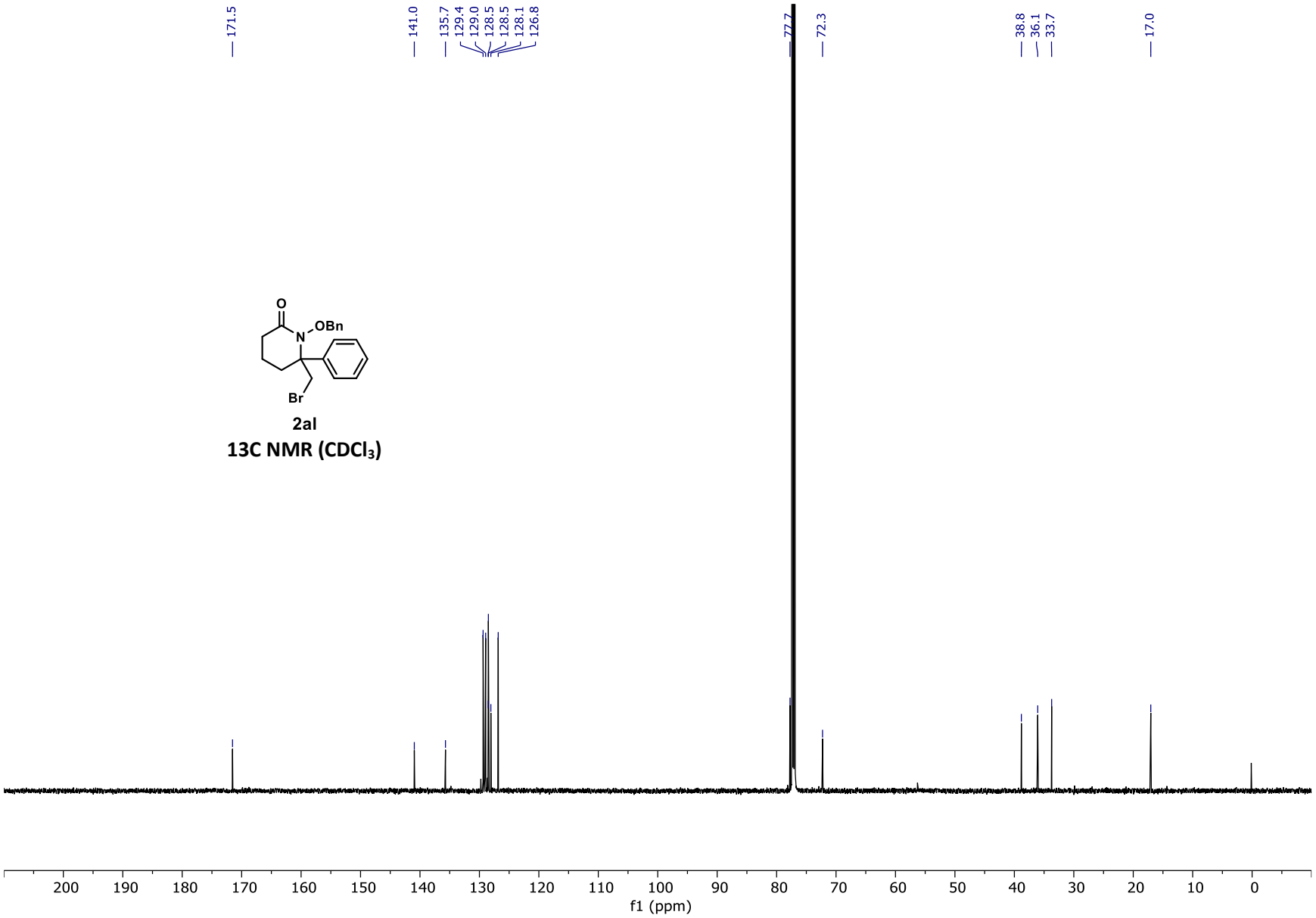

7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.28 7.27 7.26 7.24 7.23 7.23 7.22 5.06 5.04 4.86 4.84 4.65 4.64 4.16 4.15 4.15 4.14 4.14 4.13 3.15 3.14 3.12 3.11 2.80 2.79 2.77 2.76
O
N
OBn
Br
2aj
1H NMR (CDCl3)
2.87 2.95 1.52 2.07 0.99 1.00 0.96 0.97 0.99 0.98
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.4
136.1
134.7
129.8
129.3
129.1
128.7
126.9
77.8
72.0
42.4
38.5
O
N
OBn
Br
2aj
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.46
7.46
7.45
7.45
7.45
7.45
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.35
7.34
7.34
5.12
3.51
3.50
3.38
3.37
2.49
2.48
2.48
2.47
2.46
2.45
2.39
2.38
2.37
2.36
2.36
2.33
2.24
2.24
2.23
2.22
2.21
2.21
2.20
1.87
1.86
1.85
1.84
1.84
1.83
1.83
1.35
O
N
OBn
Me
Br
2ak
1H NMR (CDCl3)
1.91
2.90
2.00
1.03
1.02
1.01
1.02
1.01
1.01
3.05
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

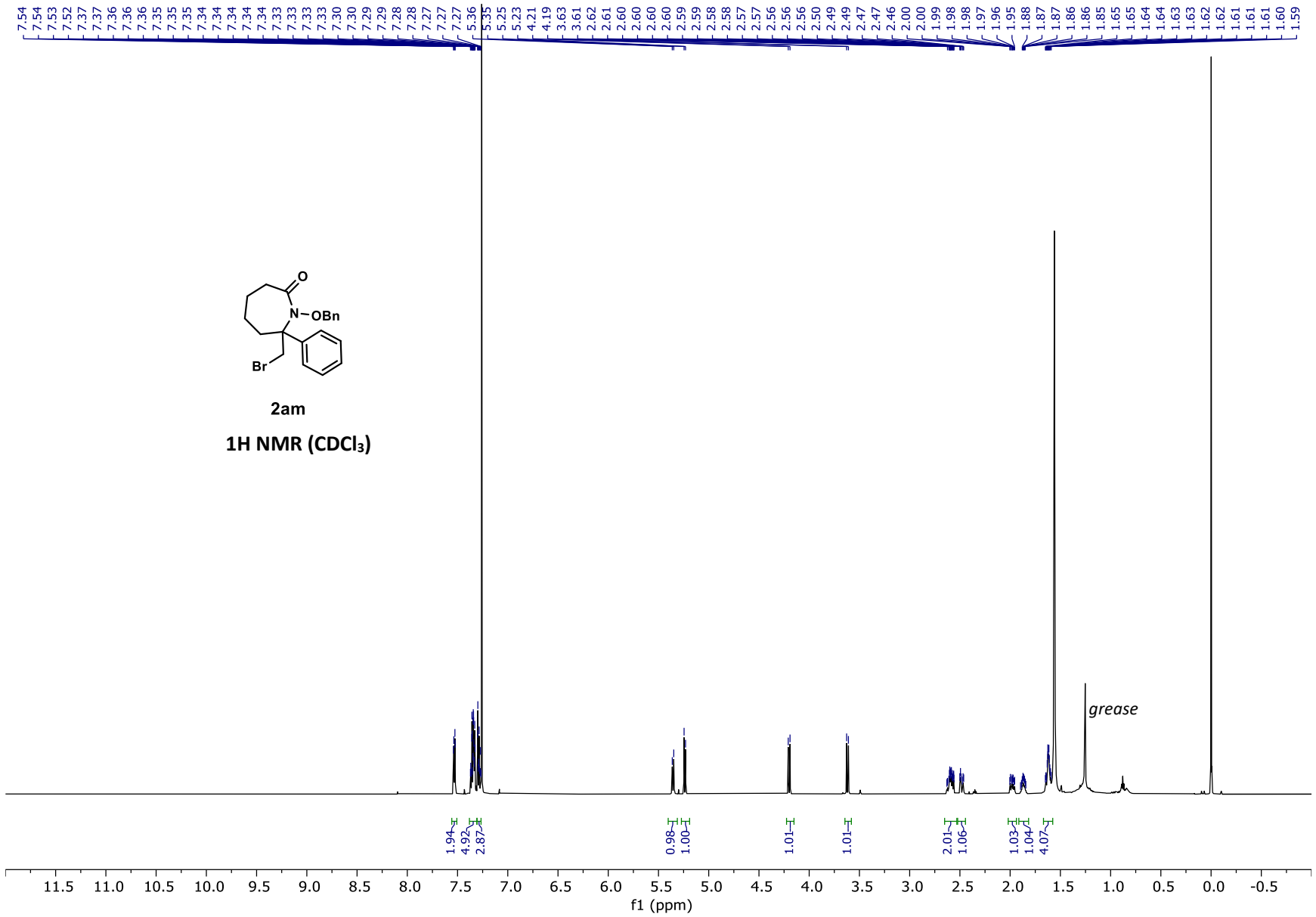

171.7
135.3
129.7
129.0
128.7
78.6
63.1
39.0
27.7
26.5
23.0
O
N
OBn
Me
Br
2ak
13C NMR (CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

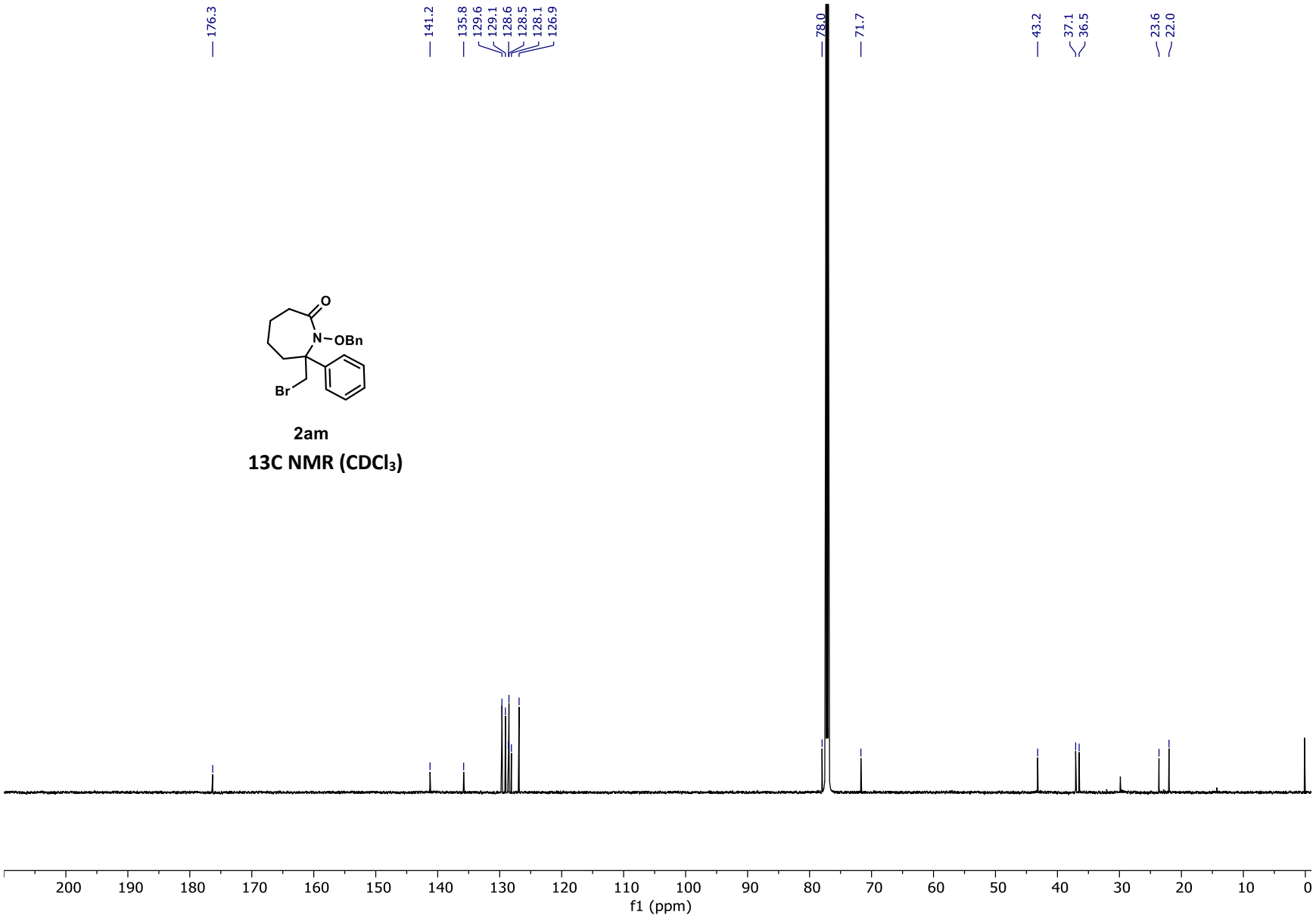

7.44 7.44 7.43 7.43 7.43 7.43 7.35 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.30 7.30 7.29 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27
5.41 5.39 5.17 5.16 4.19 4.17 3.95 3.94 2.75 2.75 2.73 2.72 2.71 2.70 2.66 2.65 2.64 2.63 2.63 2.62 2.61 2.60 2.52 2.52 2.52 2.51 2.51 2.49 2.48 2.15 2.14 2.14 2.14 2.14 2.14 2.12 2.12 2.12 2.12 2.11 1.67 1.67 1.66 1.65 1.64
O
N
OBn
Br
2al
1H NMR (CDCl3)
2.11 7.92 1.00 1.01 1.01 1.01 1.02 1.02 1.04 1.08 1.03 1.05
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



2al

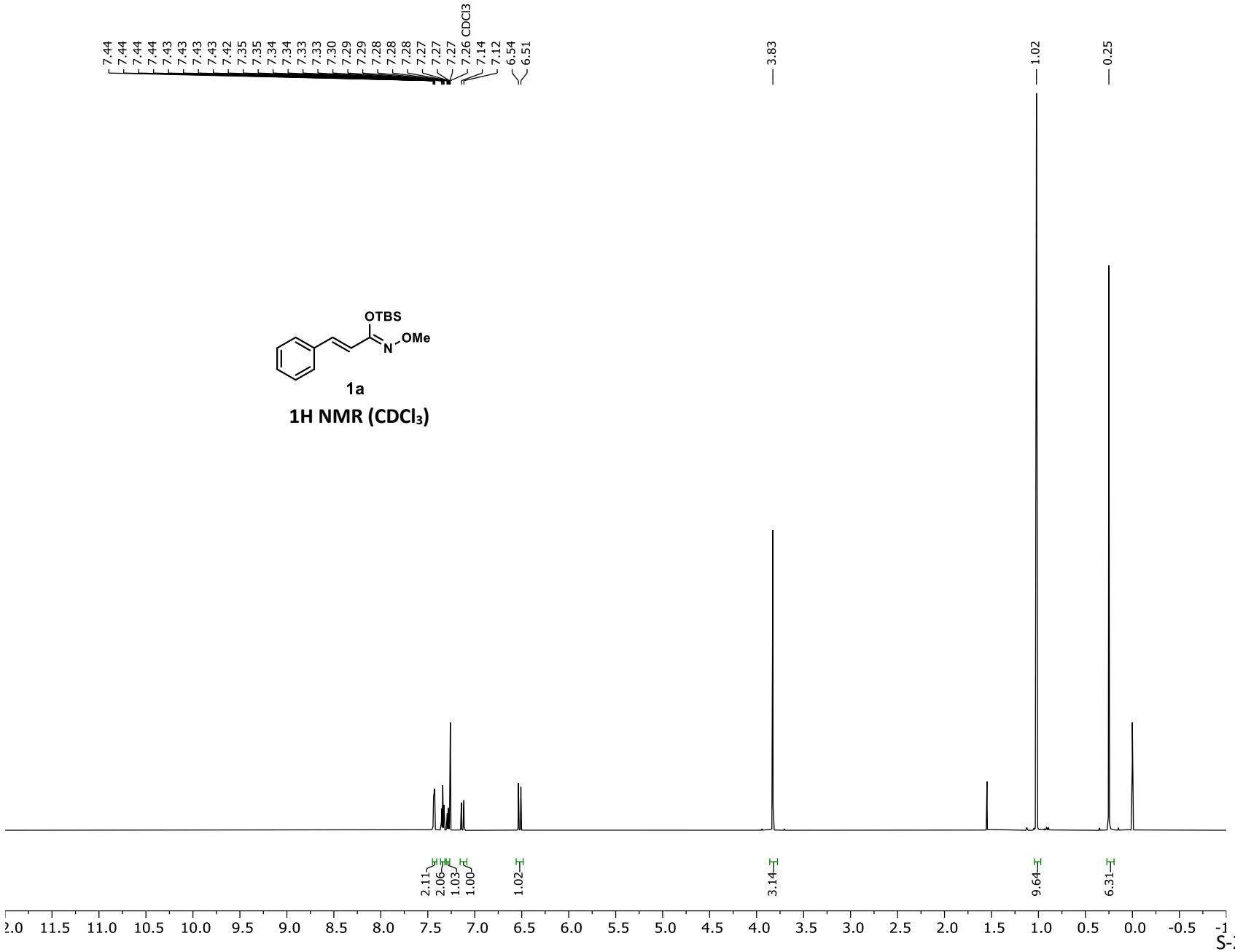
13C NMR ($CDCl_3$)

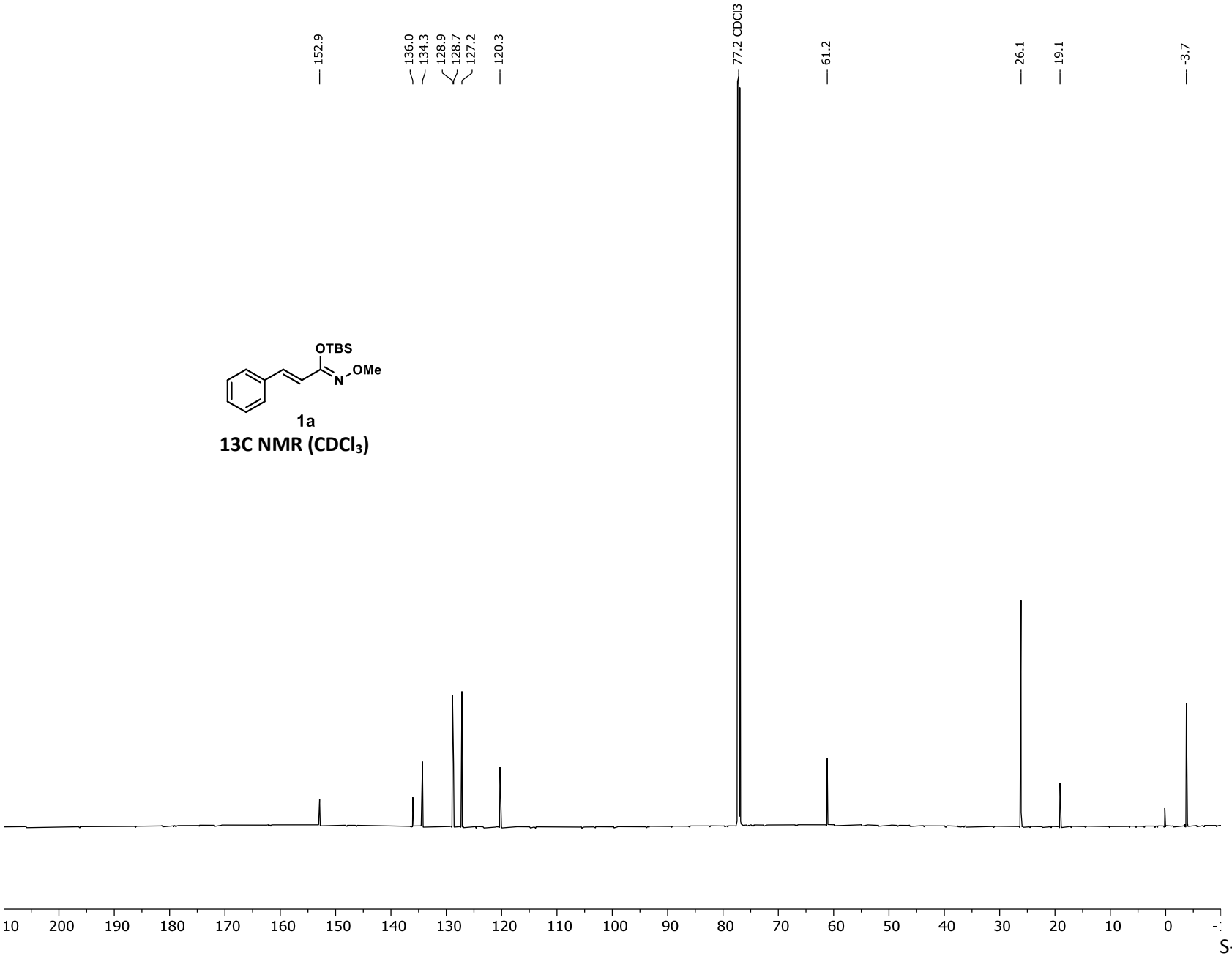

O
N–OBn
Br
2am
1H NMR (CDCl3)
grease
f1 (ppm)

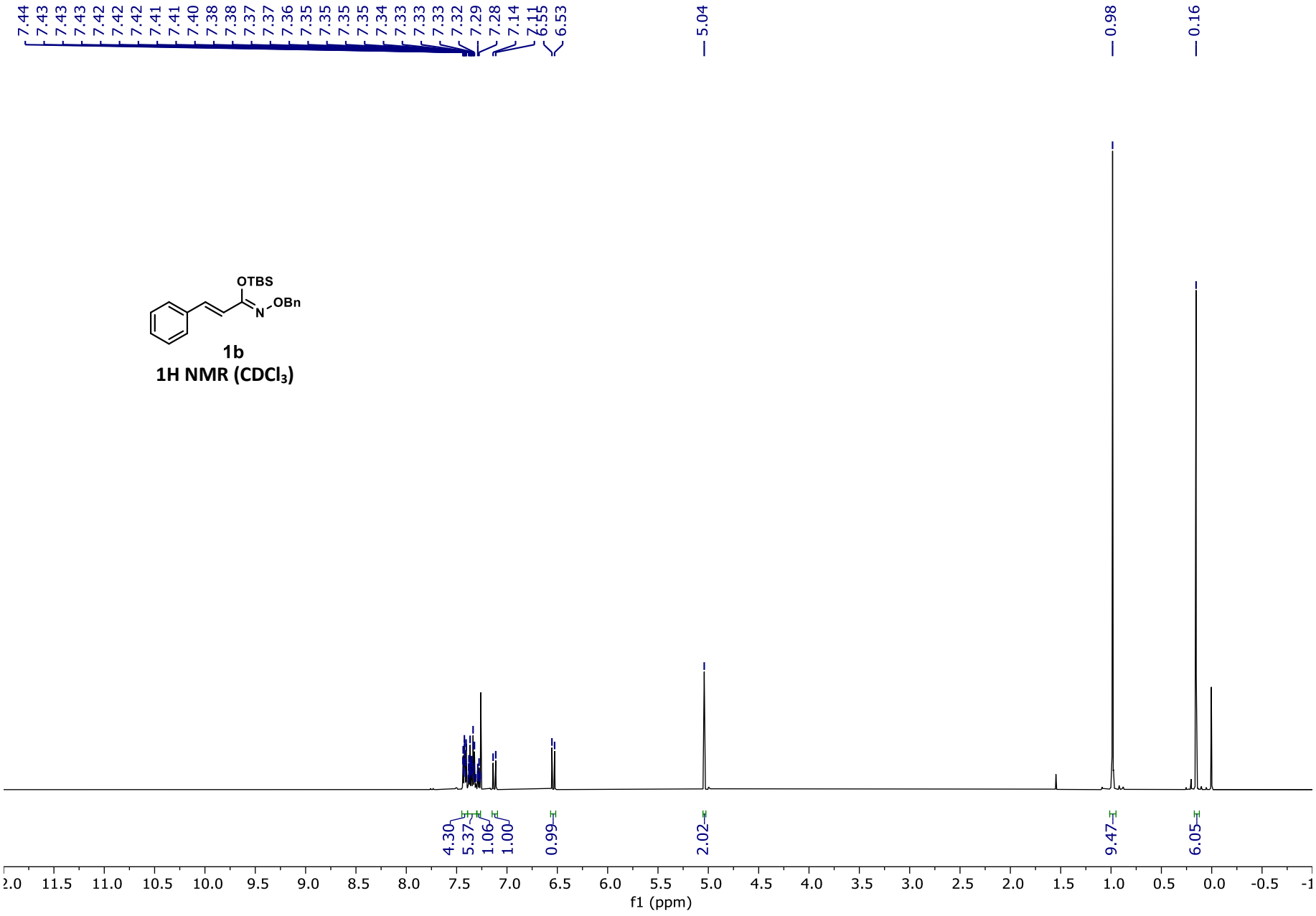


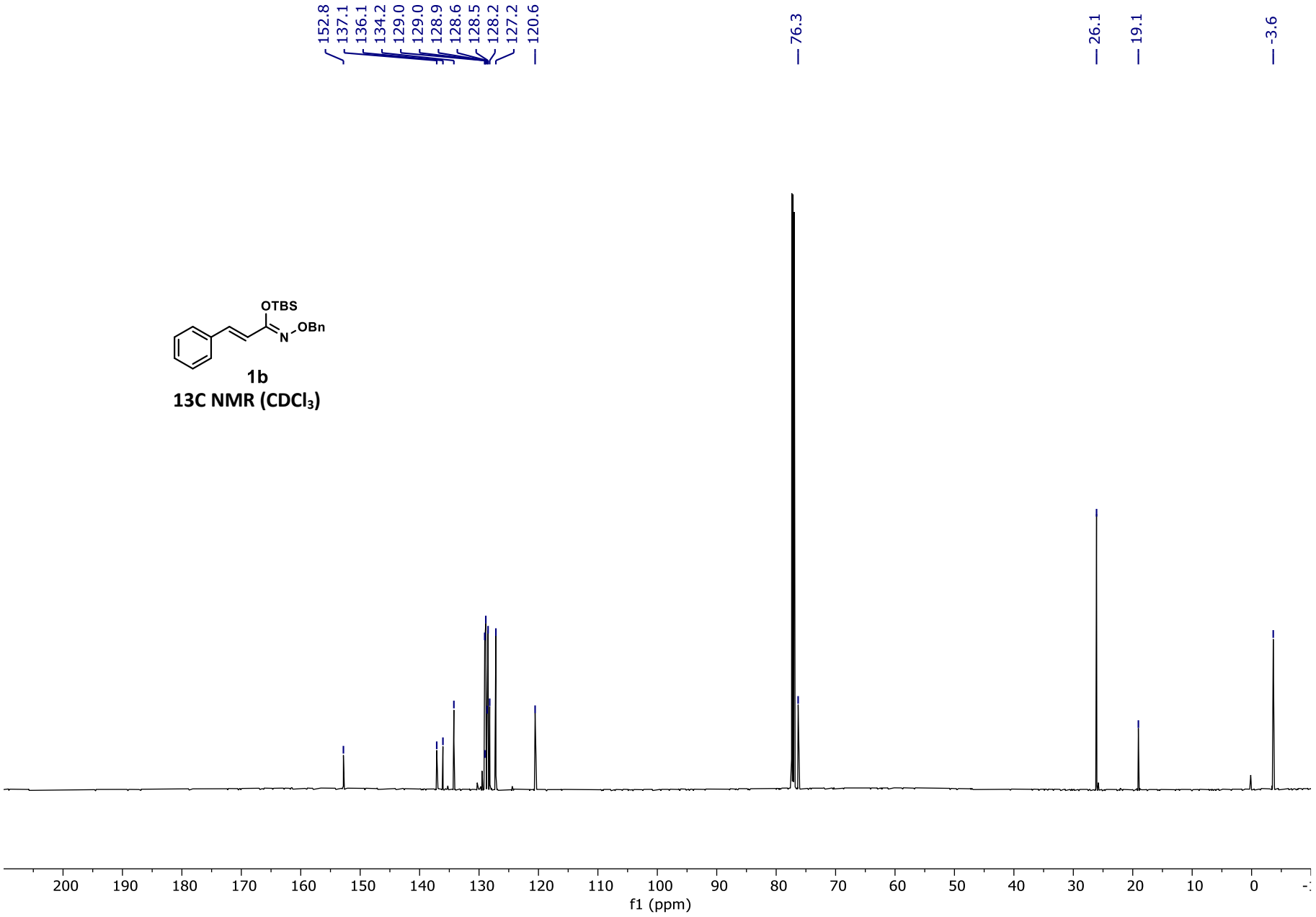
2am

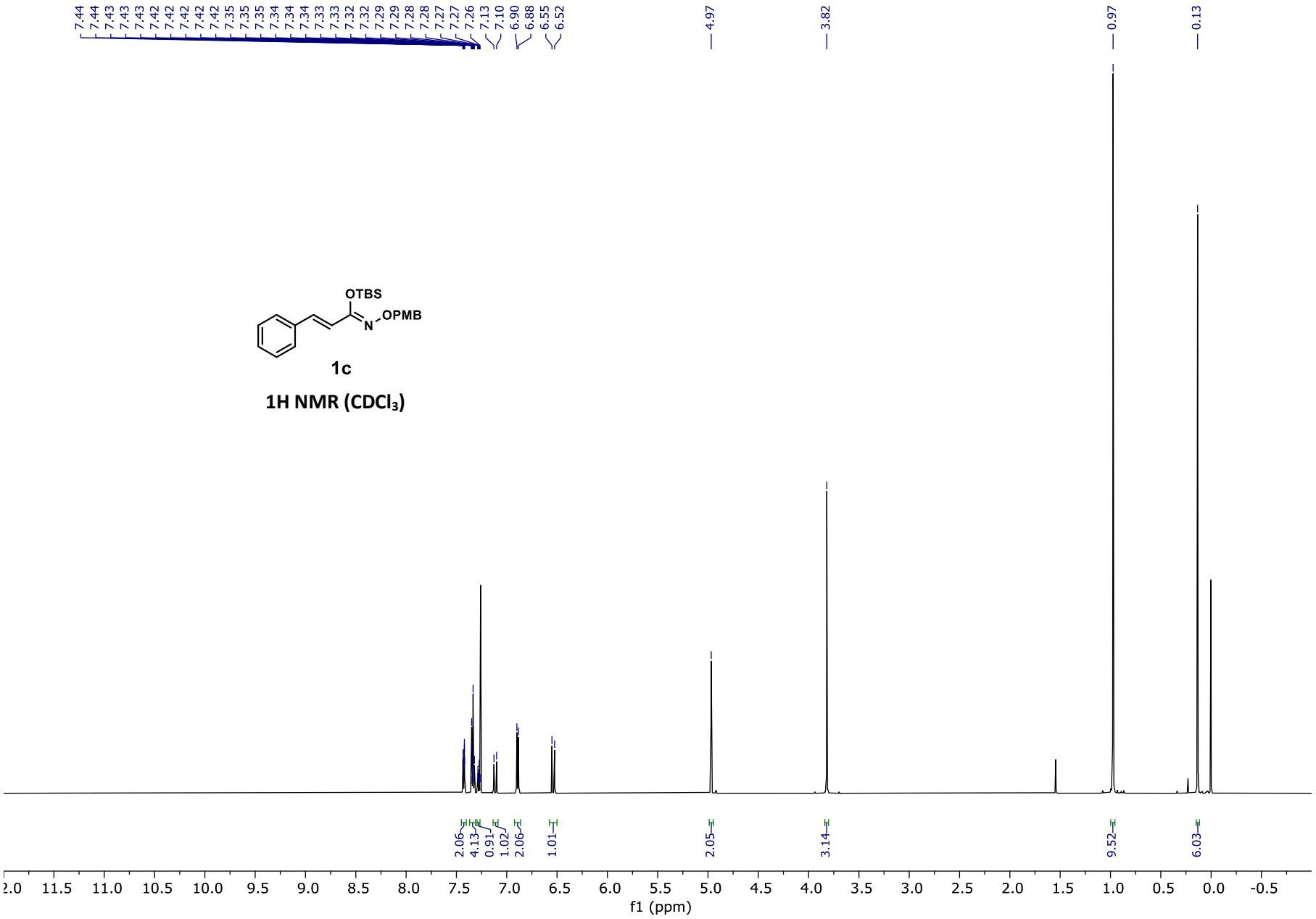
13C NMR ($CDCl_3$)

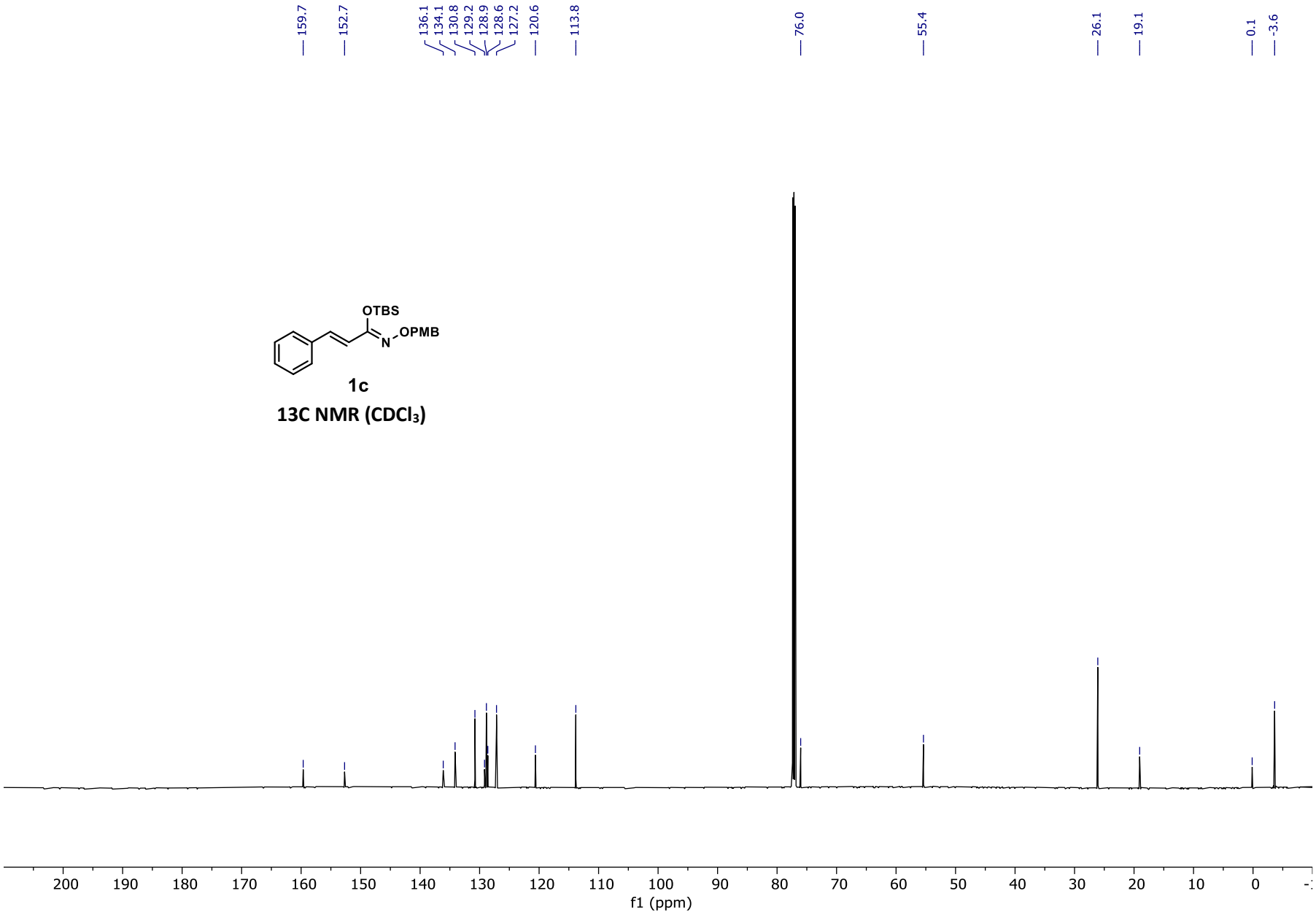

7.44
7.44
7.44
7.44
7.43
7.43
7.43
7.43
7.42
7.35
7.35
7.34
7.34
7.33
7.33
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.27
7.26 CDCl3
7.14
7.12
6.54
6.51
3.83
1.02
0.25
OTBS
N
OMe
1a
1H NMR (CDCl3)
2.11
2.06
1.03
1.00
1.02
3.14
9.64
6.31


152.9
136.0
134.3
128.9
128.7
127.2
120.3
77.2 CDCl3
61.2
26.1
19.1
-3.7
OTBS
N
OMe
1a
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.29
7.28
7.14
7.11
6.55
6.53
5.04
0.98
0.16
OTBS
N
OBn
1b
1H NMR (CDCl3)
4.30
5.37
1.06
1.00
0.99
2.02
9.47
6.05
f1 (ppm)

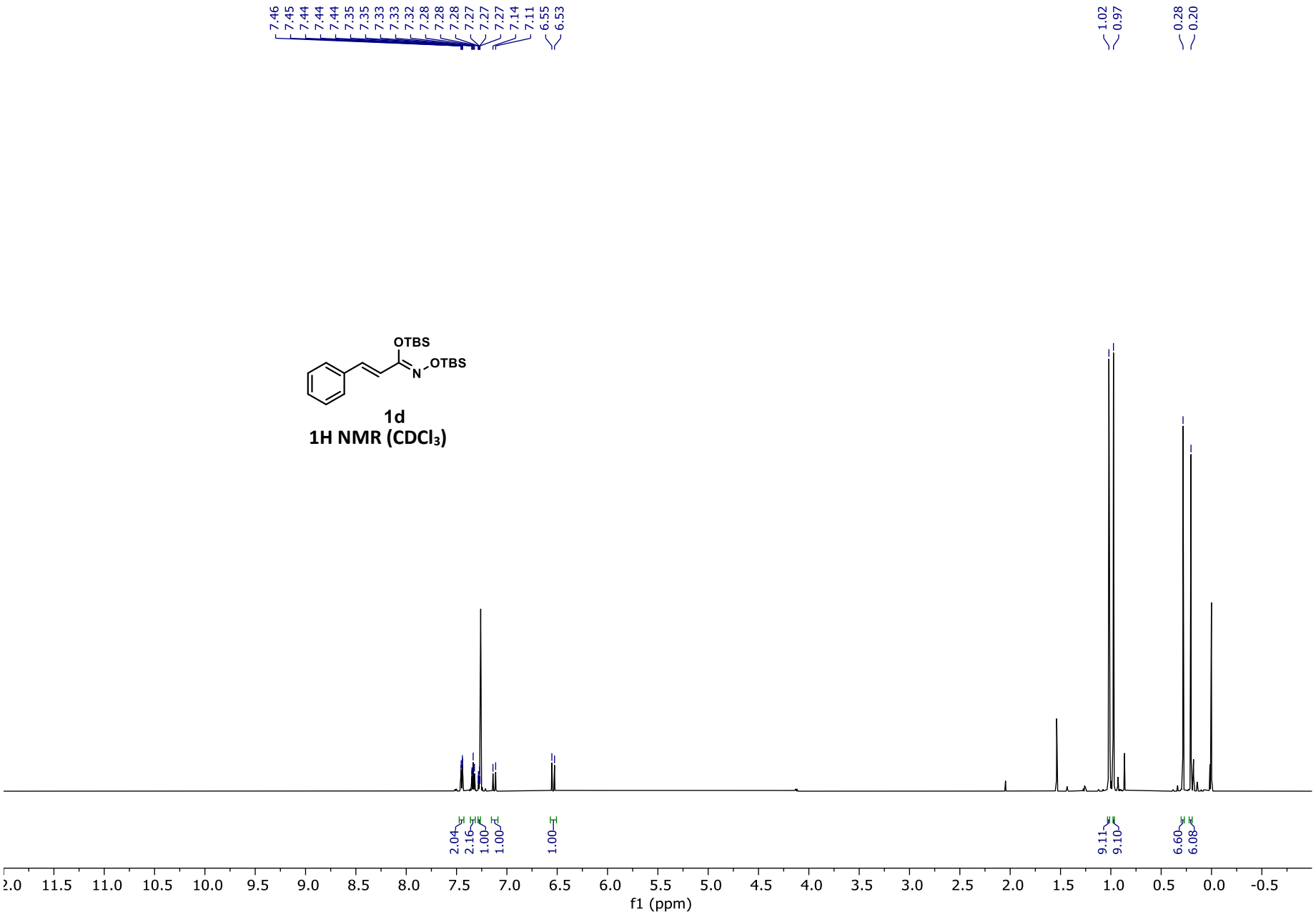

152.8
137.1
136.1
134.2
129.0
129.0
128.9
128.6
128.5
128.2
127.2
120.6
76.3
26.1
19.1
-3.6
OTBS
N
OBn
1b
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

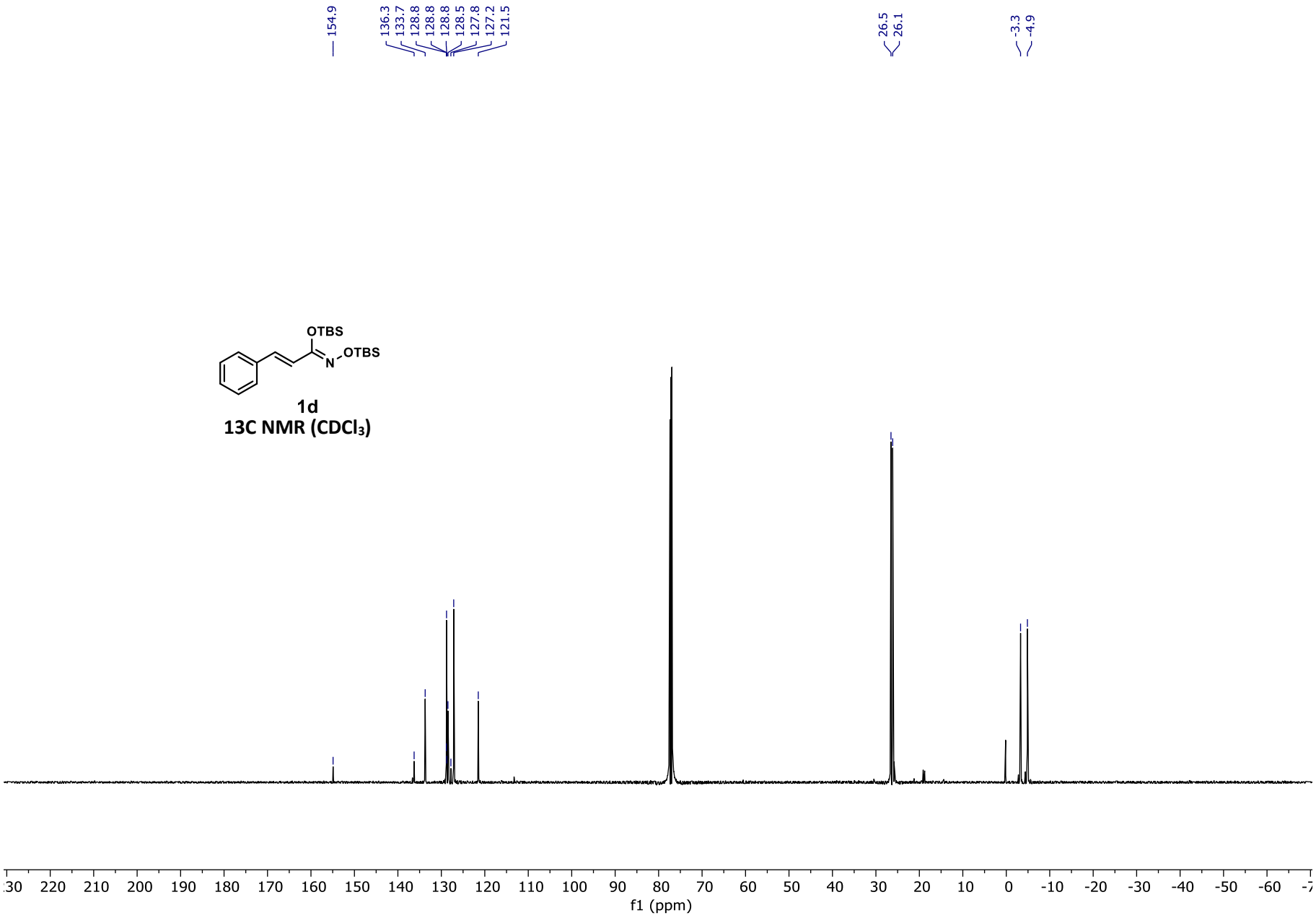

7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.42
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.29
7.28
7.28
7.27
7.27
7.26
7.13
7.10
6.90
6.88
6.55
6.52
4.97
3.82
0.97
0.13
OTBS
N
OPMB
1c
1H NMR (CDCl3)
2.06
4.13
0.91
1.02
2.06
1.01
2.05
3.14
9.52
6.03
f1 (ppm)

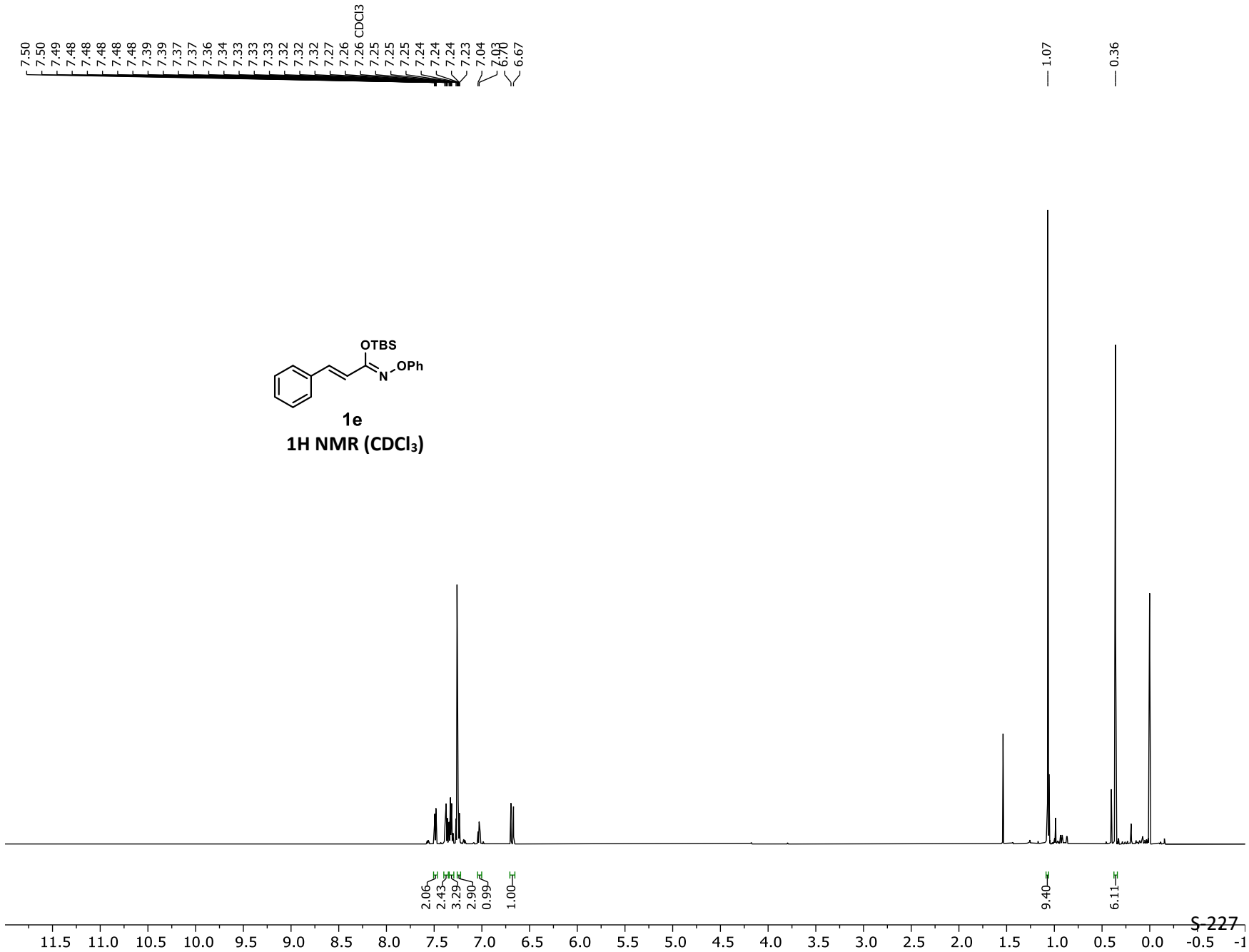


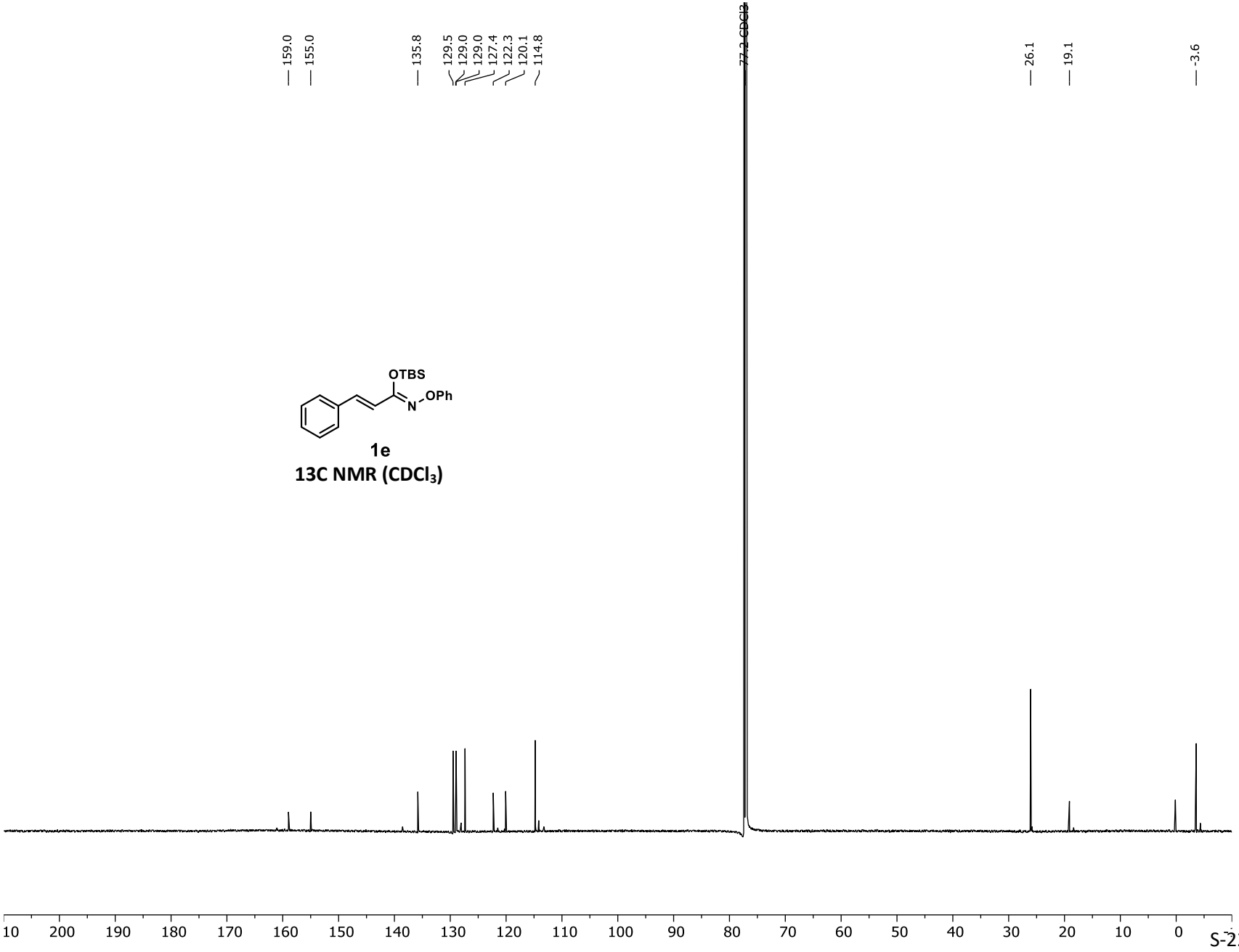
1c

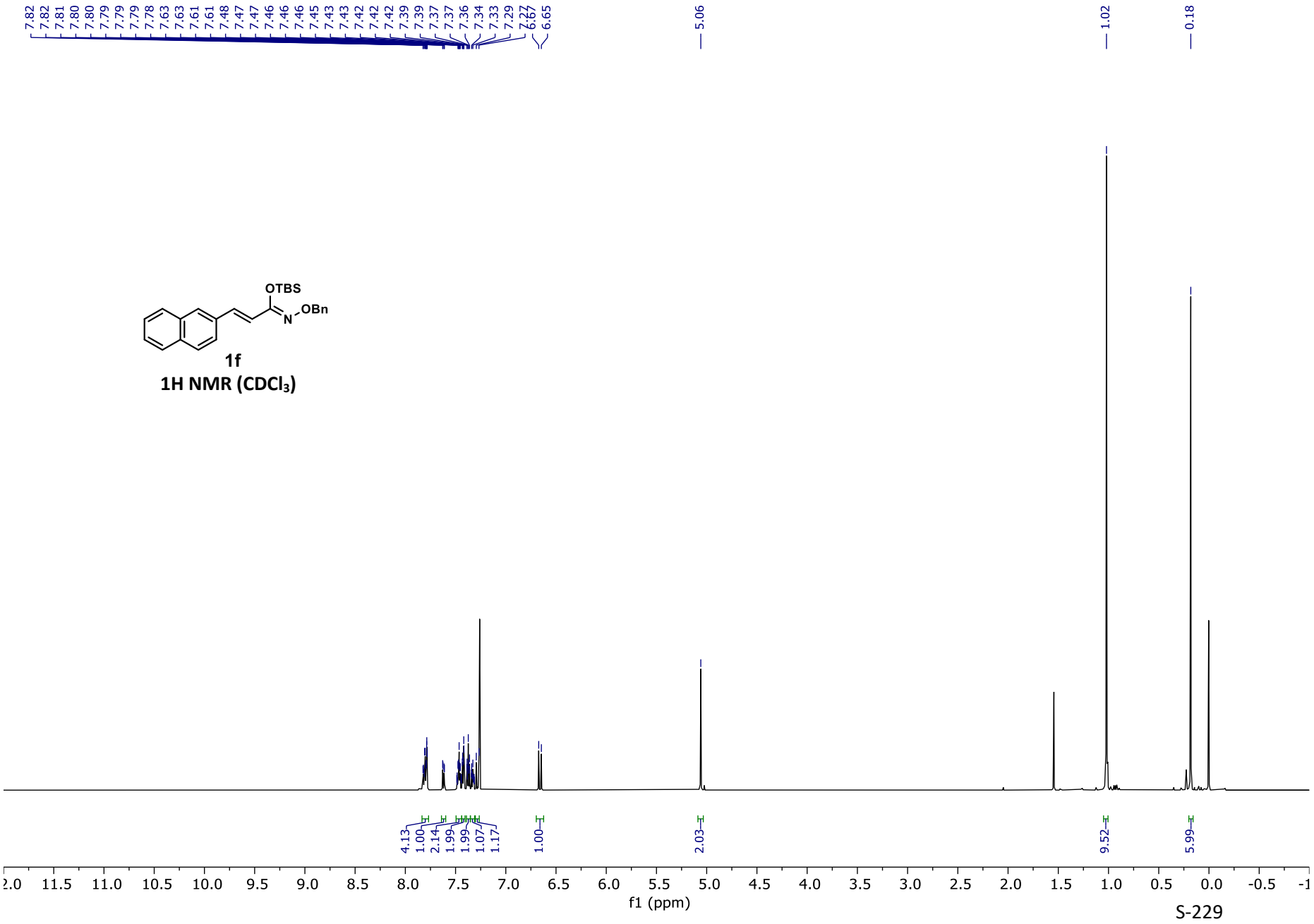
13C NMR ($CDCl_3$)

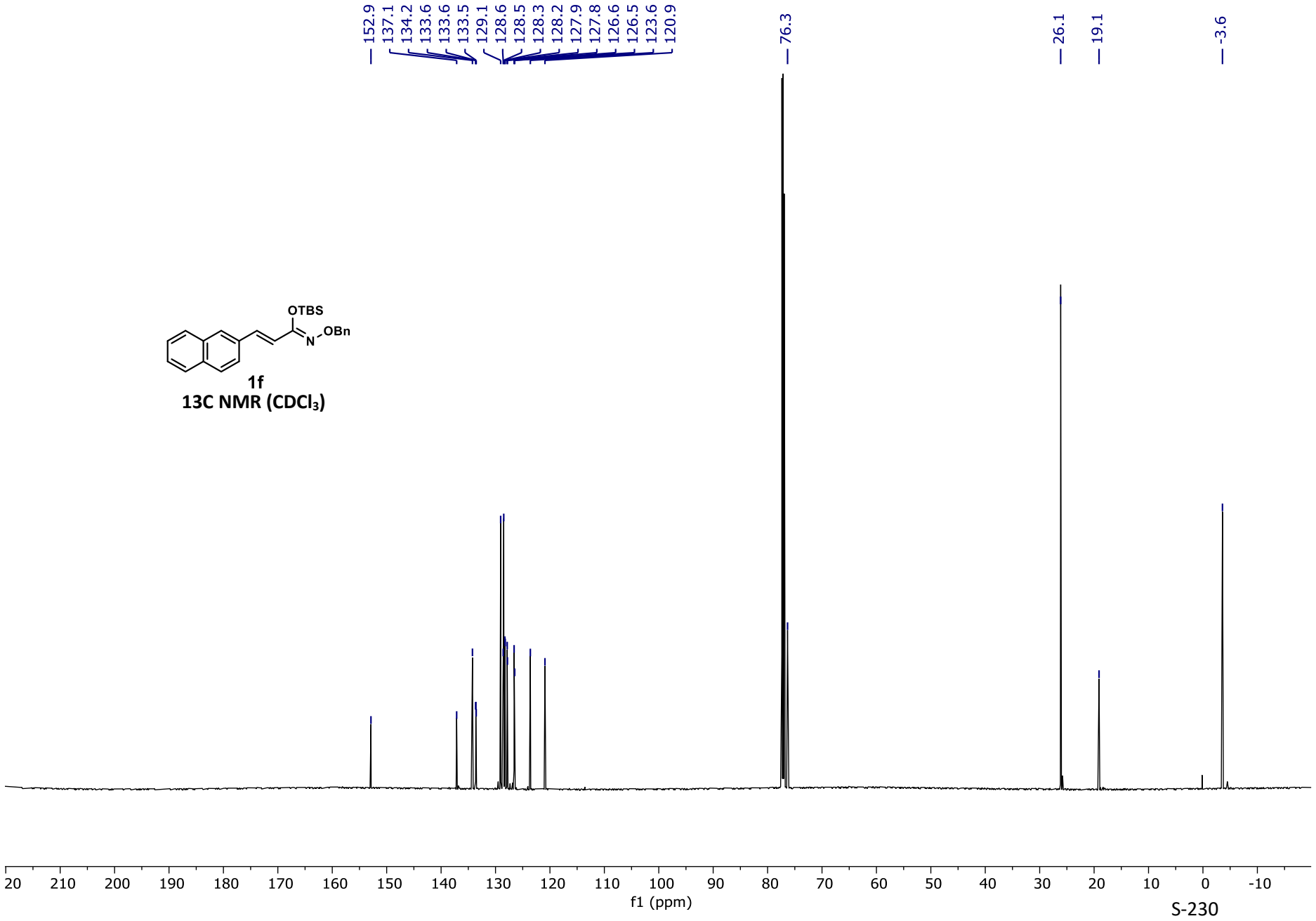

7.46
7.45
7.44
7.44
7.44
7.35
7.35
7.33
7.33
7.32
7.28
7.28
7.28
7.27
7.27
7.27
7.14
7.11
6.55
6.53
1.02
0.97
0.28
0.20
OTBS
N
OTBS
1d
1H NMR (CDCl3)
2.04
2.16
1.00
1.00
1.00
9.11
9.10
6.60
6.08
f1 (ppm)

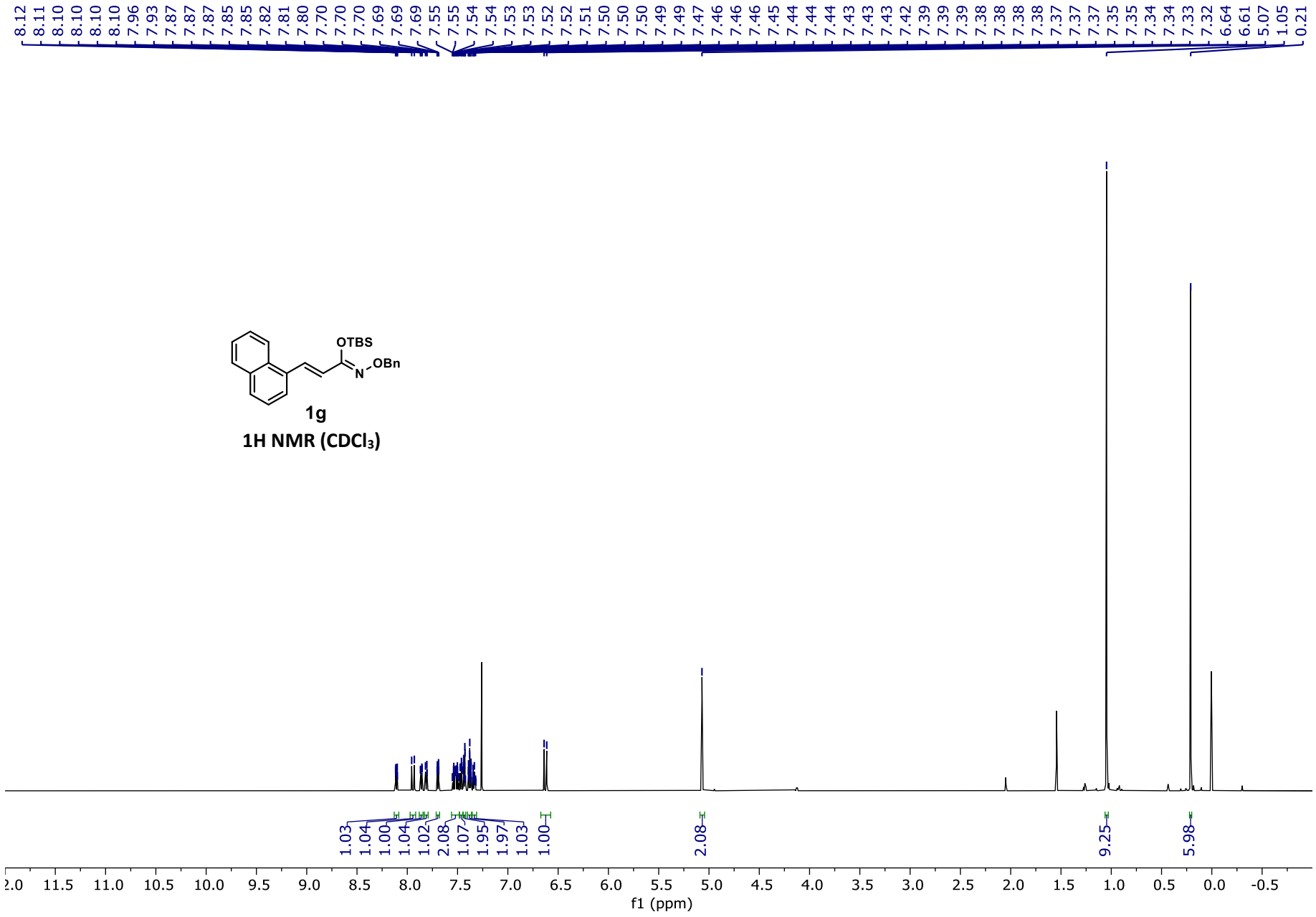

154.9
136.3
133.7
128.8
128.8
128.8
128.5
127.8
127.2
121.5
26.5
26.1
-3.3
-4.9
OTBS
N
OTBS
1d
13C NMR (CDCl3)
f1 (ppm)

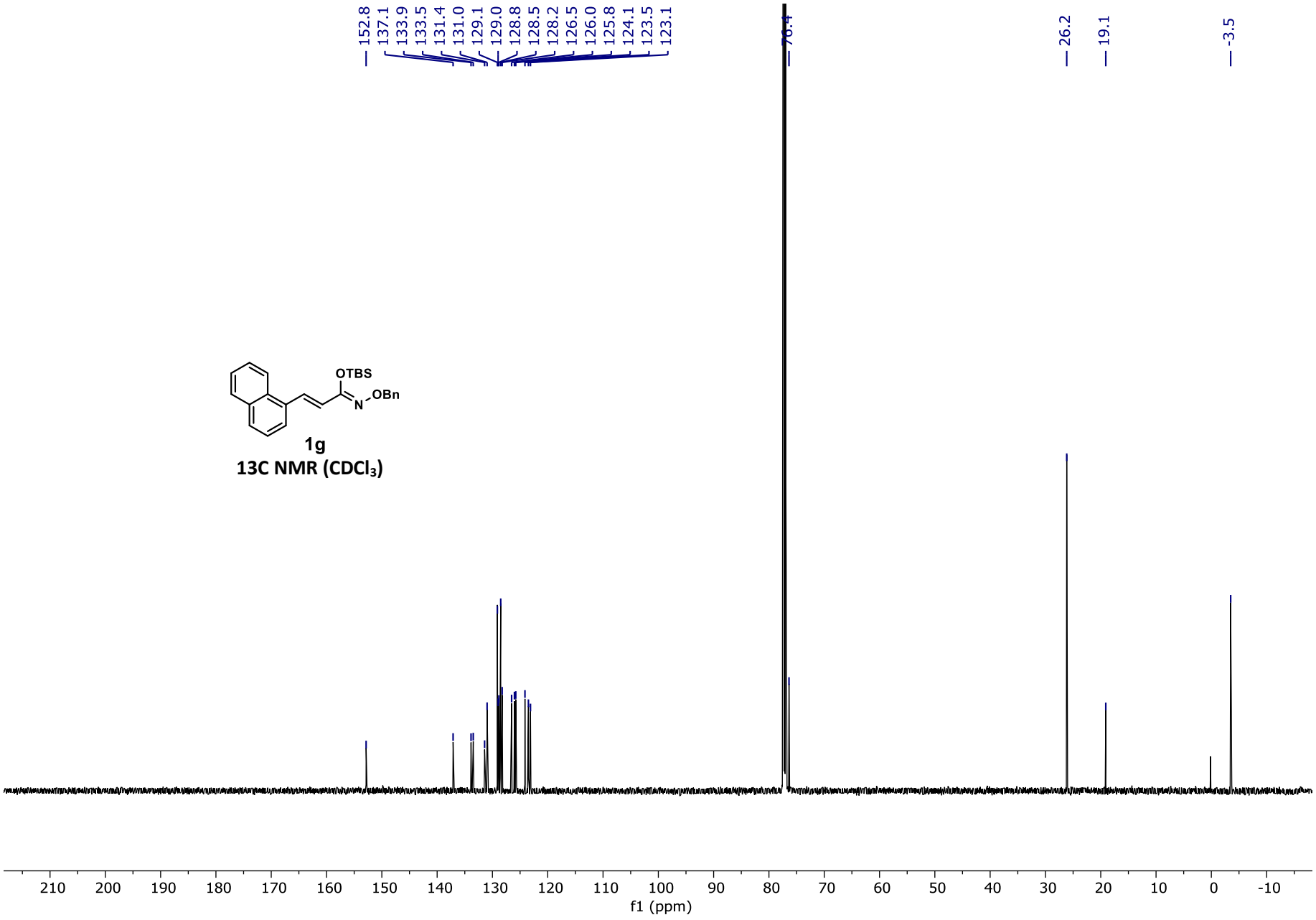

7.50
7.50
7.49
7.48
7.48
7.48
7.48
7.48
7.39
7.39
7.37
7.37
7.36
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.27
7.26
7.26 CDCl3
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.04
7.03
6.70
6.67
1.07
0.36
OTBS
N
OPh
1e
1H NMR (CDCl3)
2.06
2.43
3.29
2.90
0.99
1.00
9.40
6.11
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1

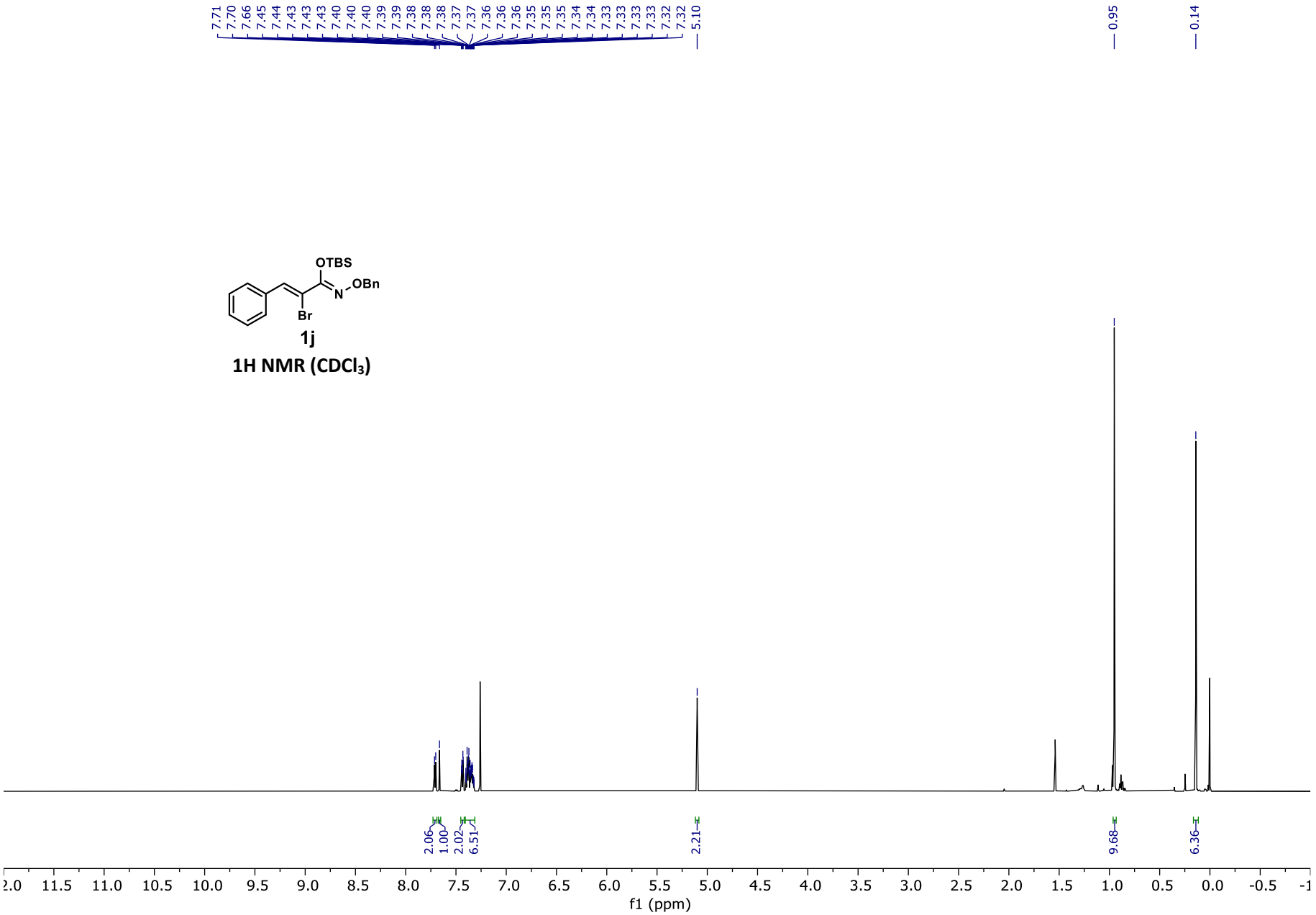

159.0
155.0
135.8
129.5
129.0
129.0
127.4
122.3
120.1
114.8
77.3 CDCl3
26.1
19.1
-3.6
OTBS
N
OPh
1e
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

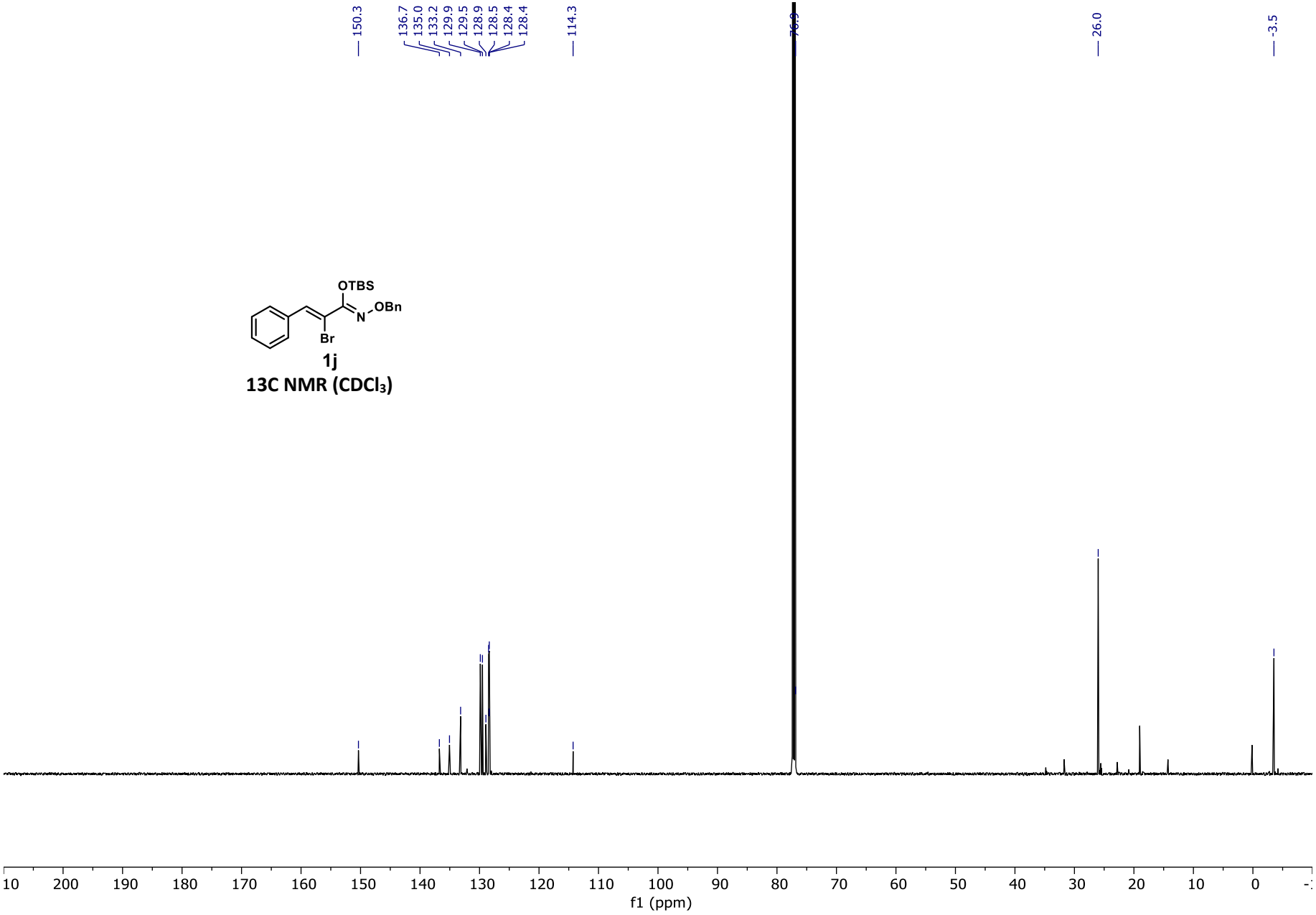

7.82
7.82
7.81
7.80
7.80
7.79
7.79
7.79
7.78
7.63
7.63
7.61
7.61
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.43
7.43
7.42
7.42
7.42
7.39
7.39
7.37
7.37
7.36
7.34
7.33
7.29
6.67
6.65
5.06
1.02
0.18
OTBS
OBn
N
1f
1H NMR (CDCl3)
4.13
1.00
2.14
1.99
1.99
1.07
1.17
1.00
2.03
9.52
5.99
f1 (ppm)

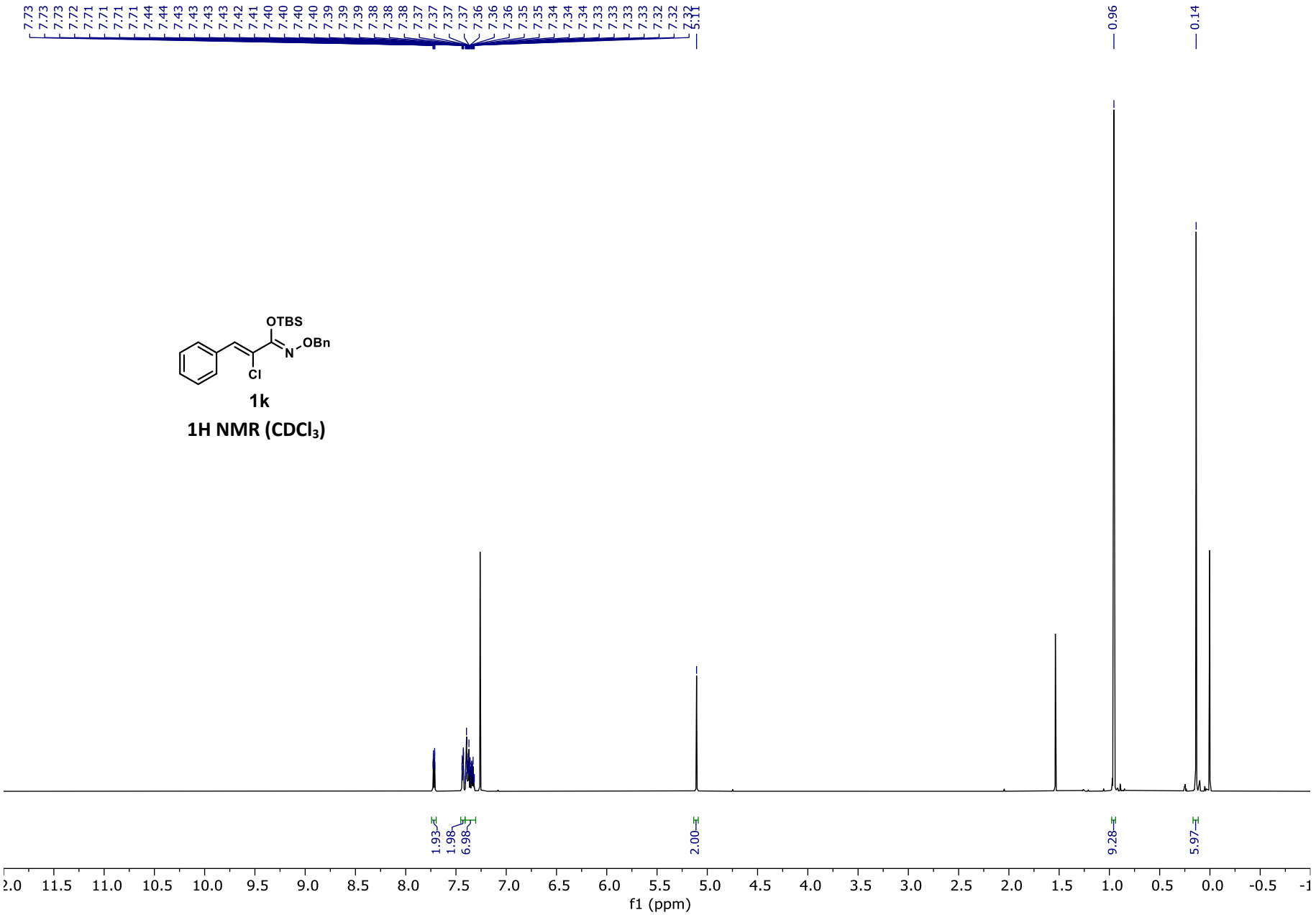

152.9
137.1
134.2
133.6
133.6
133.5
129.1
128.6
128.5
128.3
128.2
127.9
127.8
126.6
126.5
123.6
120.9
76.3
26.1
19.1
-3.6
OTBS
N
OBn
1f
13C NMR (CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

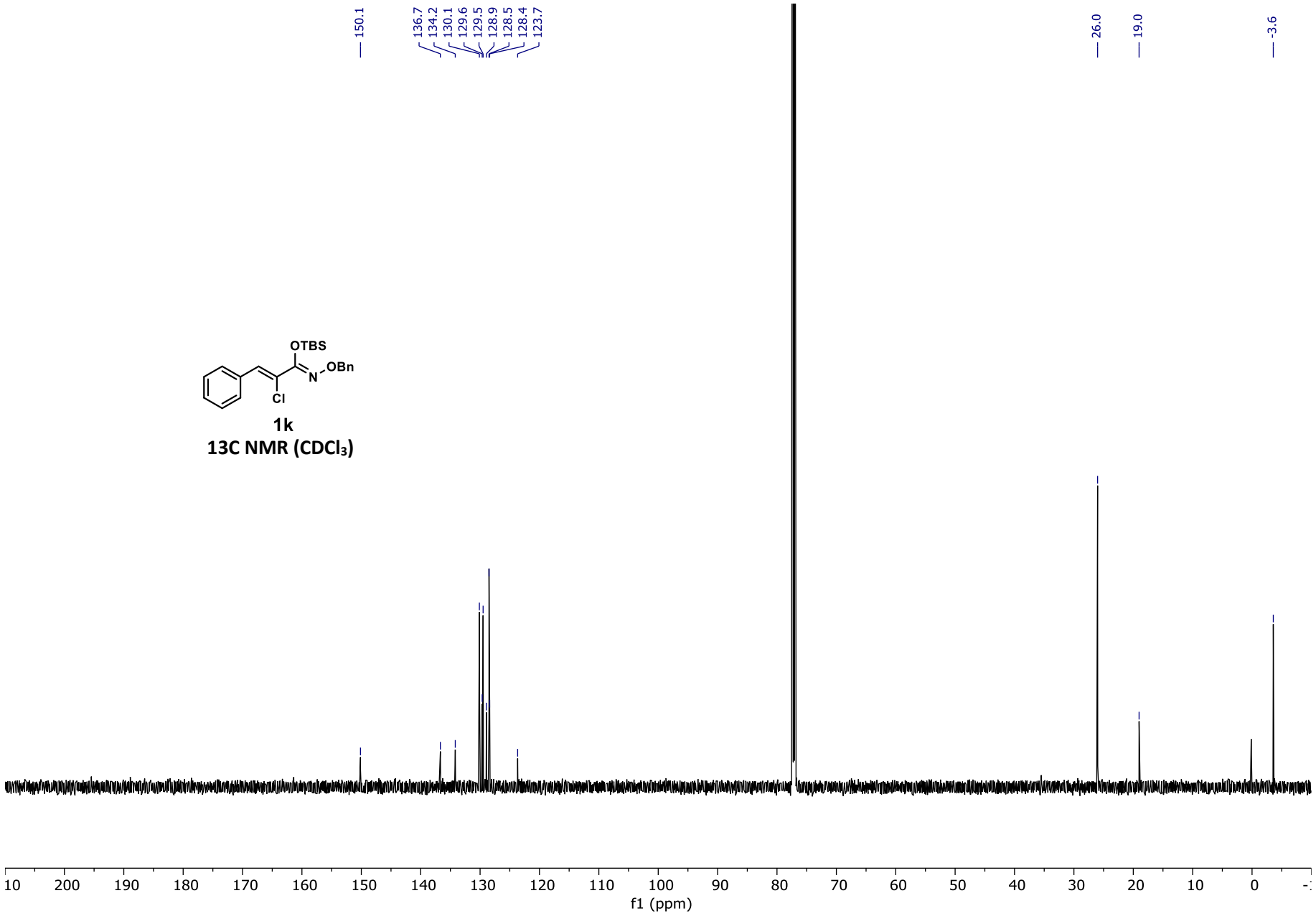

8.12 8.11 8.10 8.10 8.10 8.10 7.96 7.93 7.87 7.87 7.87 7.85 7.85 7.82 7.81 7.80 7.70 7.70 7.70 7.69 7.69 7.69 7.55 7.55 7.54 7.54 7.53 7.53 7.52 7.52 7.51 7.50 7.50 7.50 7.49 7.49 7.47 7.46 7.46 7.46 7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.42 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.35 7.35 7.34 7.34 7.33 7.32 6.64 6.61 5.07 1.05 0.21
OTBS
N
OBn
1g
1H NMR (CDCl3)
1.03 1.04 1.00 1.04 1.02 2.08 1.07 1.95 1.97 1.03 1.00 2.08 9.25 5.98
f1 (ppm)

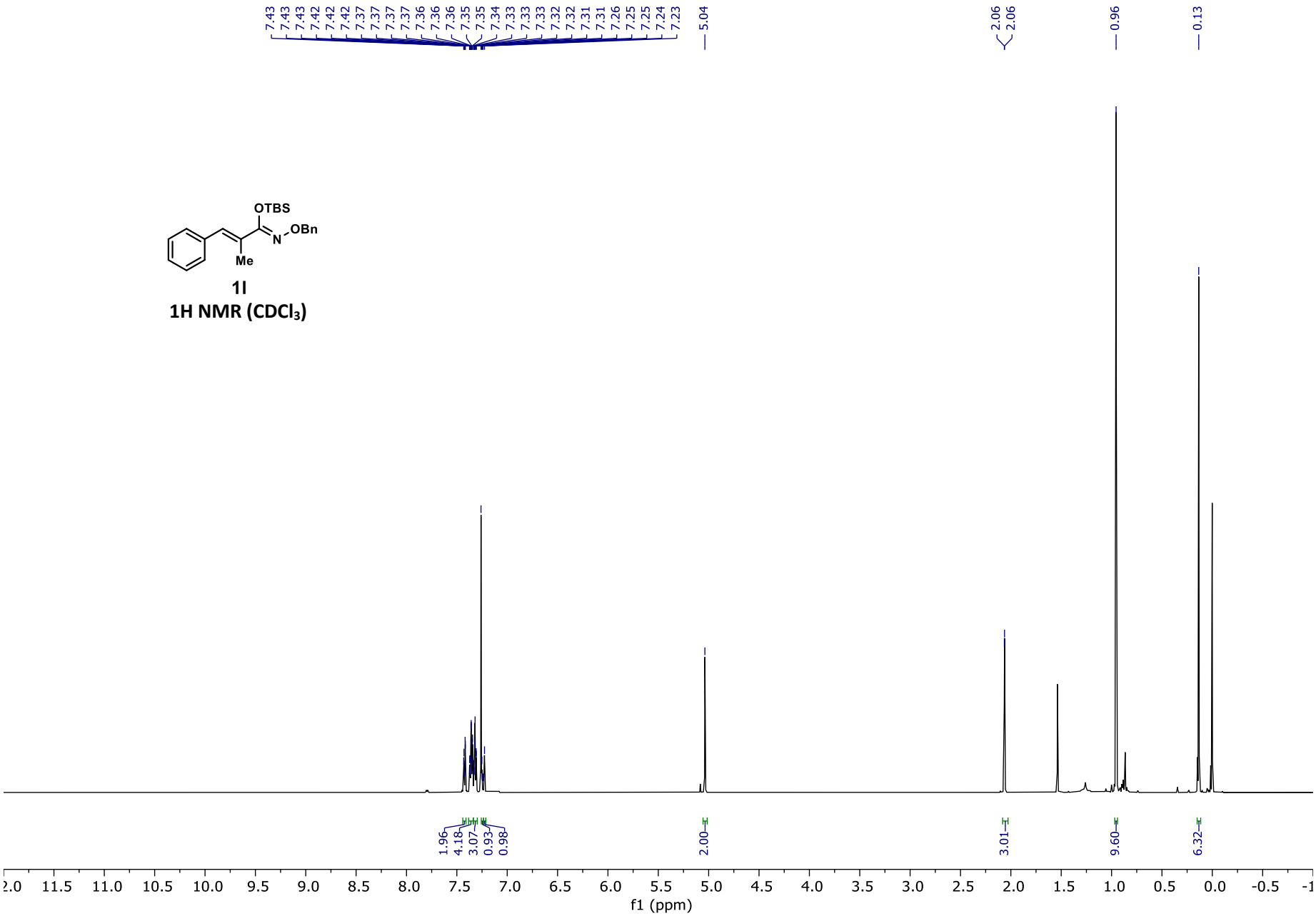

152.8
137.1
133.9
133.5
131.4
131.0
129.1
129.0
128.8
128.5
128.2
126.5
126.0
125.8
124.1
123.5
123.1
76.4
26.2
19.1
-3.5
OTBS
N
OBn
1g
13C NMR (CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

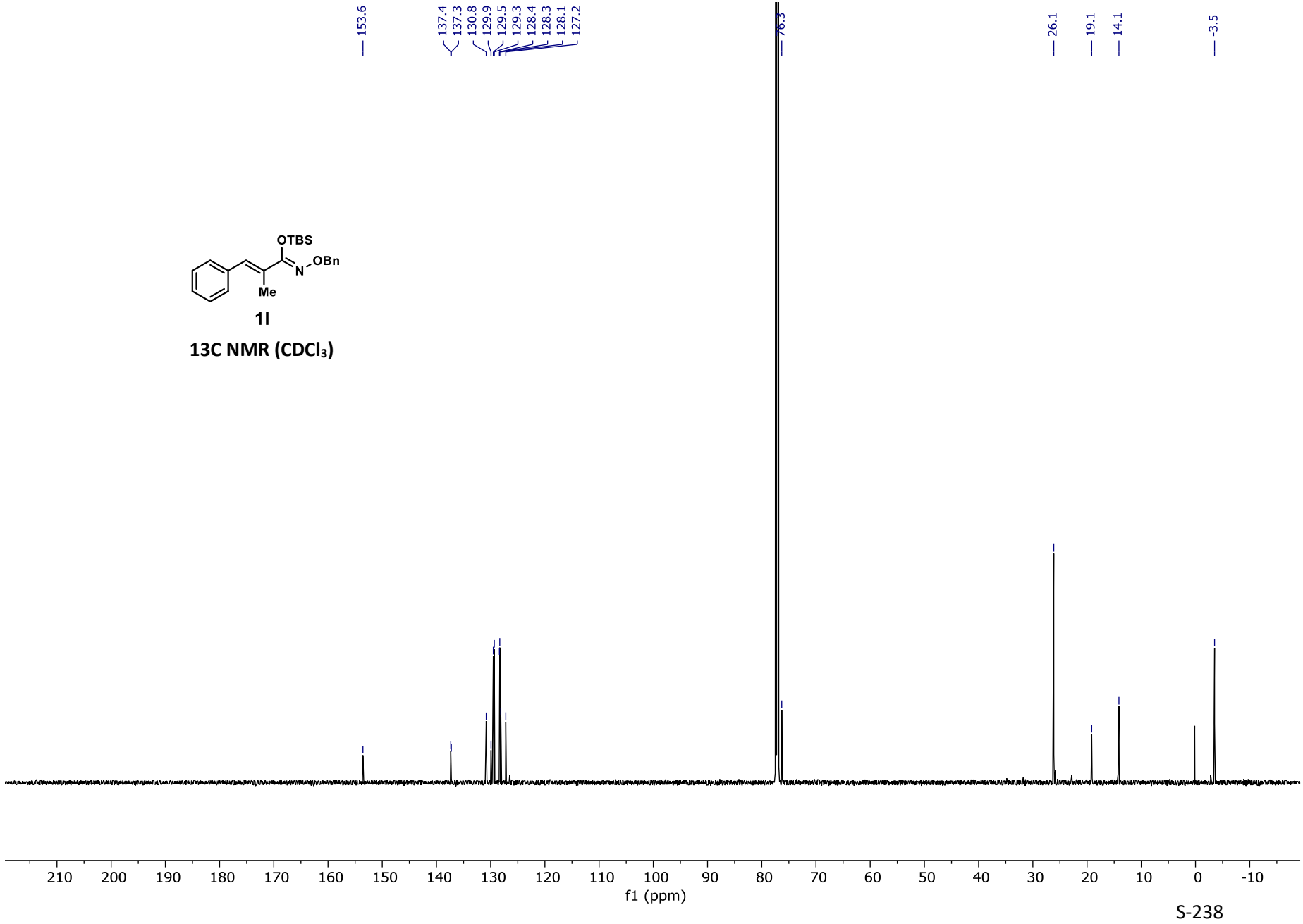

7.71
7.70
7.66
7.45
7.44
7.43
7.43
7.43
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
5.10
0.95
0.14
OTBS
N
OBn
Br
1j
1H NMR (CDCl3)
2.06
1.00
2.02
6.51
2.21
9.68
6.36
f1 (ppm)

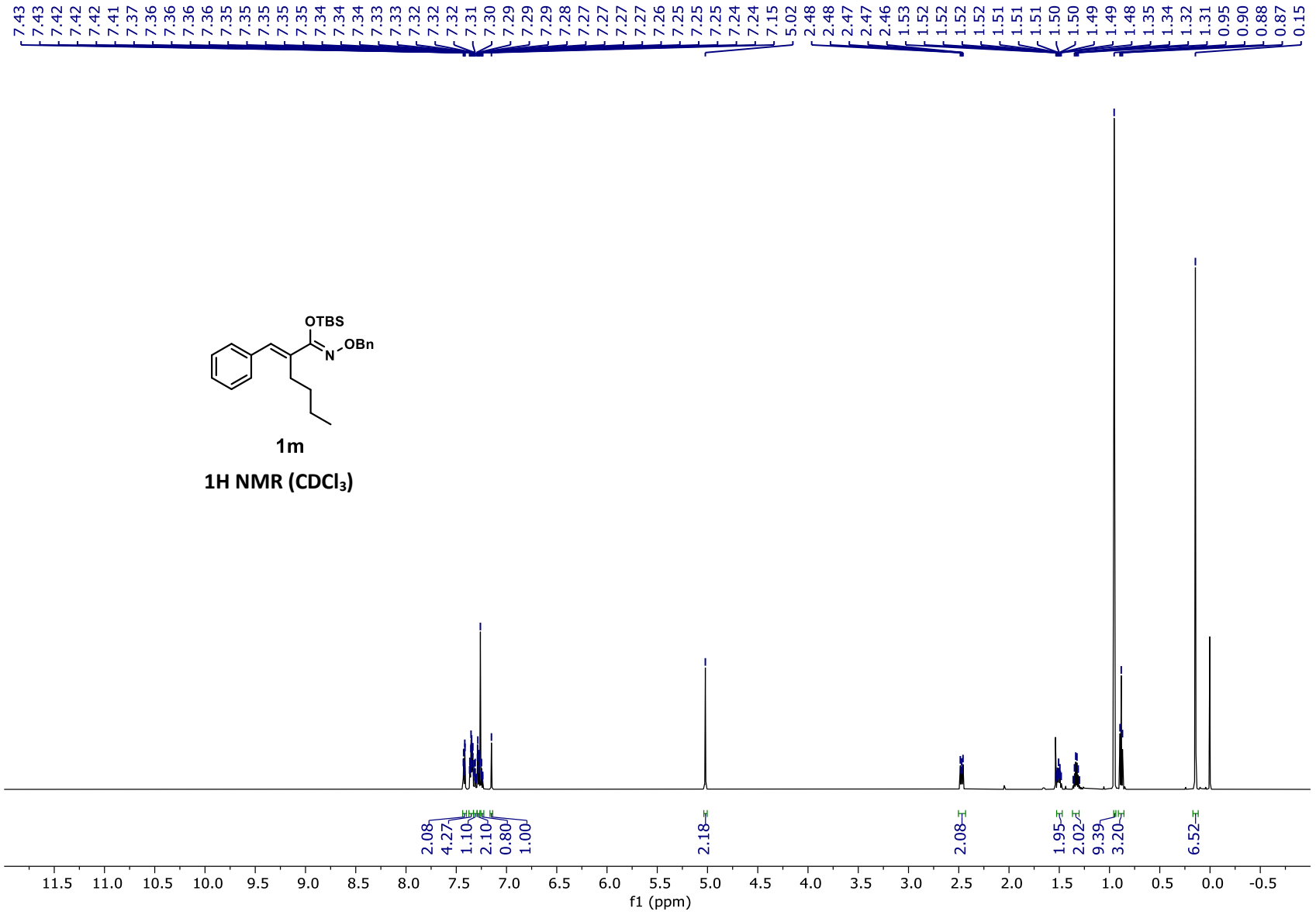

150.3
136.7
135.0
133.2
129.9
129.5
128.9
128.5
128.4
128.4
114.3
76.9
26.0
-3.5
OTBS
N
OBn
Br
1j
13C NMR (CDCl3)
f1 (ppm)

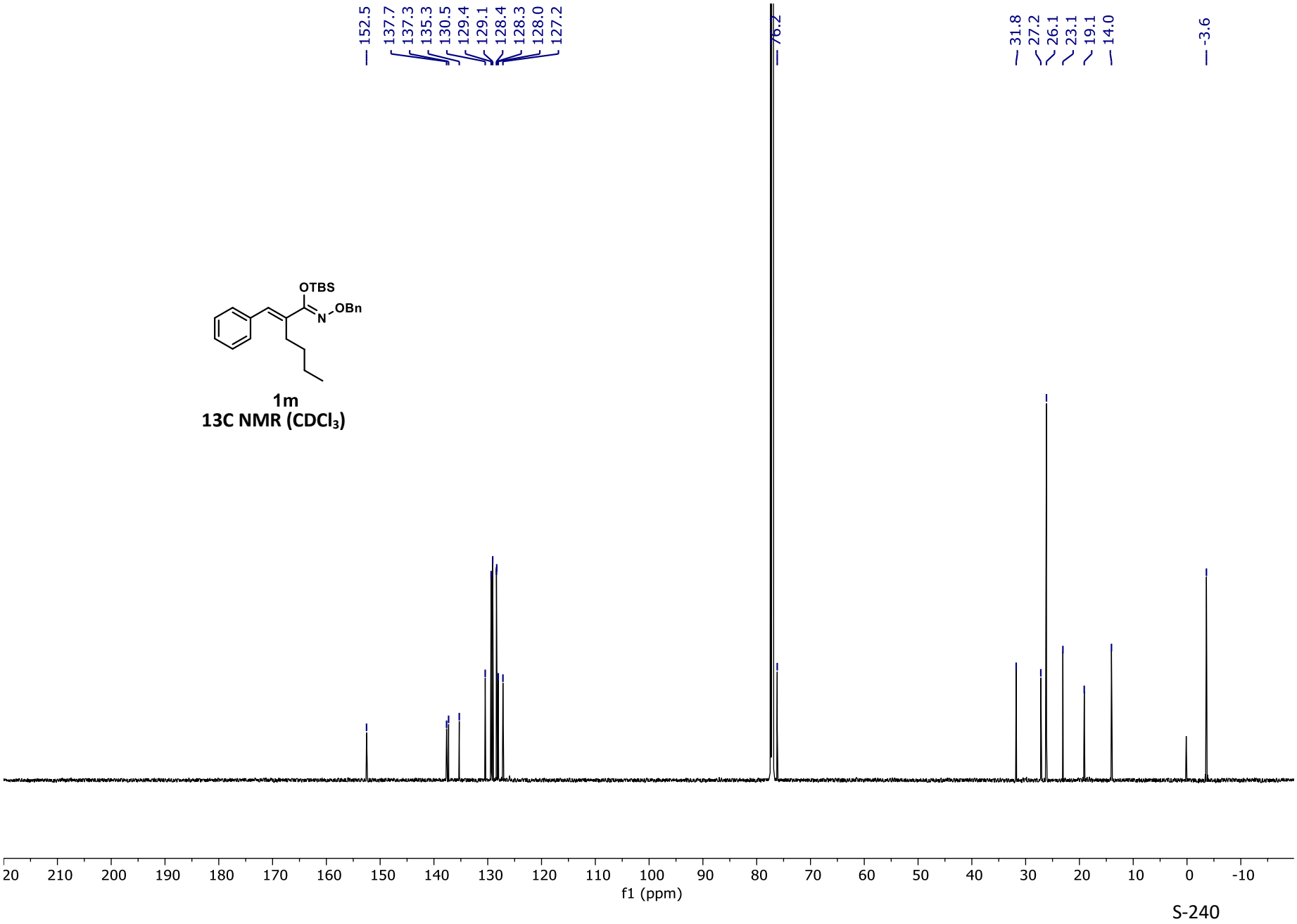

7.73 7.73 7.73 7.72 7.71 7.71 7.71 7.71 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.40 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32
5.11
0.96
0.14
OTBS
N
OBn
Cl
1k
1H NMR (CDCl3)
1.93
1.98
6.98
2.00
9.28
5.97
f1 (ppm)

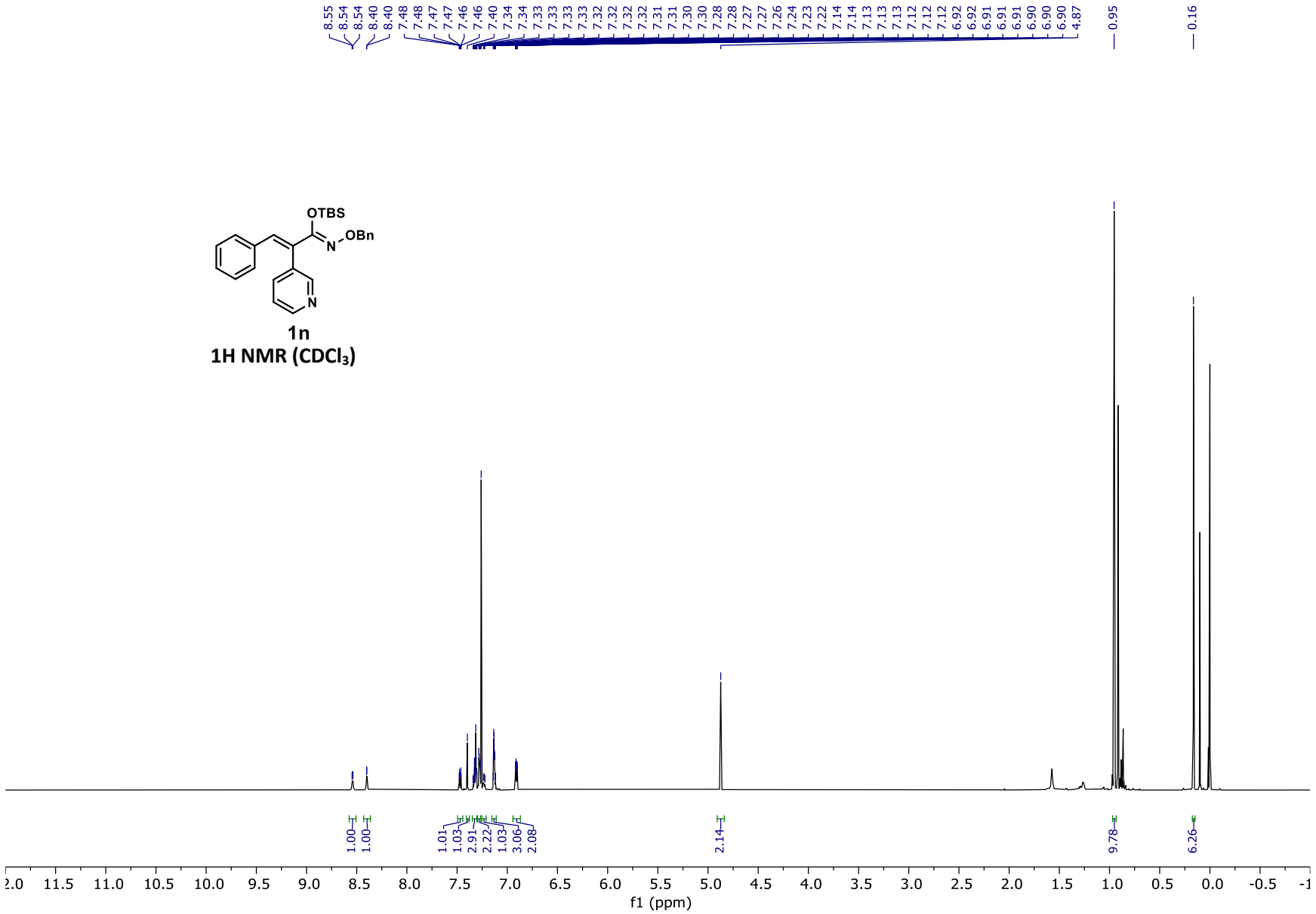

150.1
136.7
134.2
130.1
129.6
129.5
128.9
128.5
128.4
123.7
26.0
19.0
-3.6
OTBS
OBn
N
Cl
1k
13C NMR (CDCl3)
f1 (ppm)

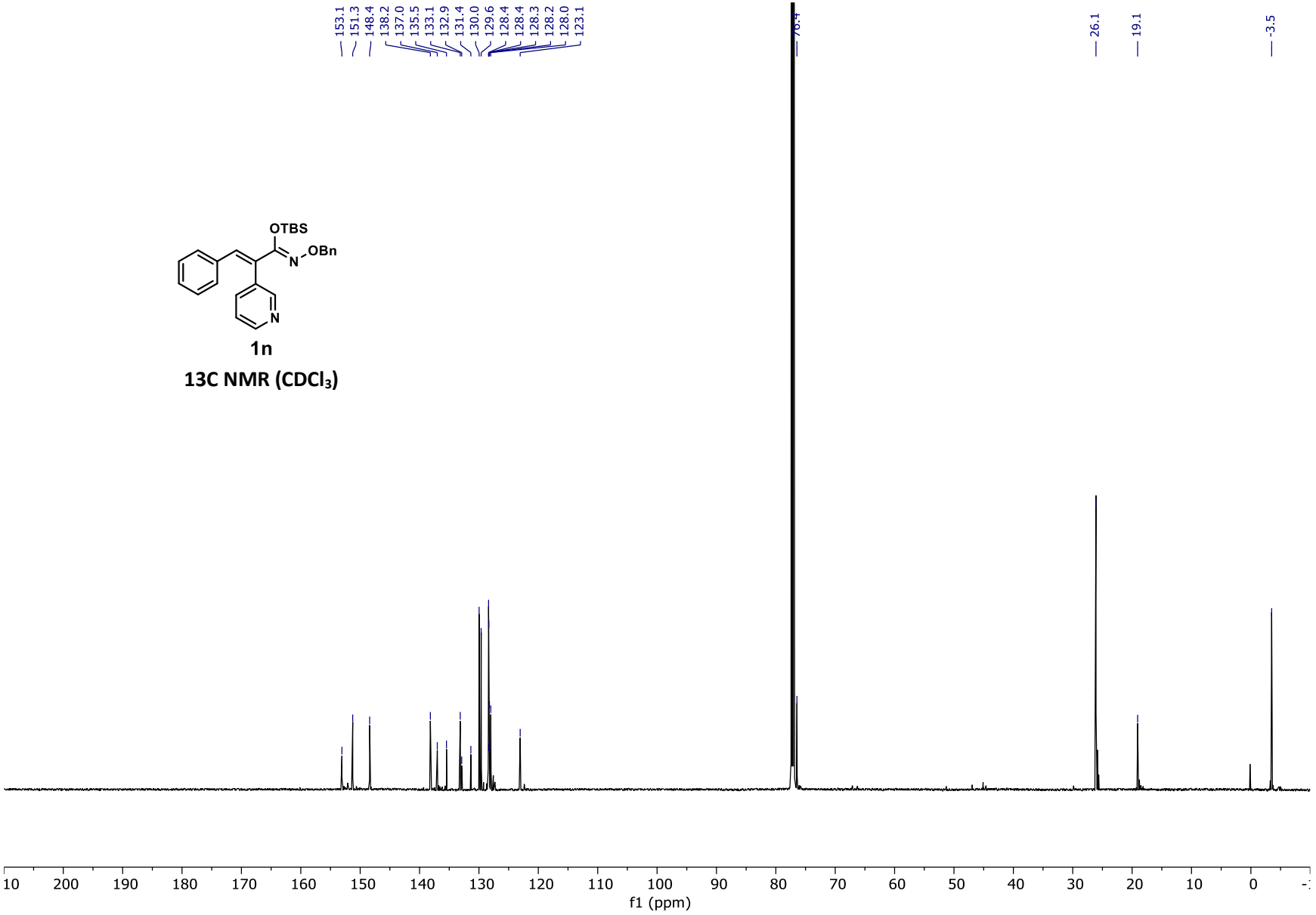

OTBS
N
OBn
Me
1I
1H NMR (CDCl3)
7.43 7.43 7.43 7.42 7.42 7.42 7.37 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.26 7.25 7.25 7.24 7.23
5.04
2.06 2.06
0.96
0.13
1.96 4.18 3.07 0.93 0.98
2.00
3.01
9.60
6.32
f1 (ppm)

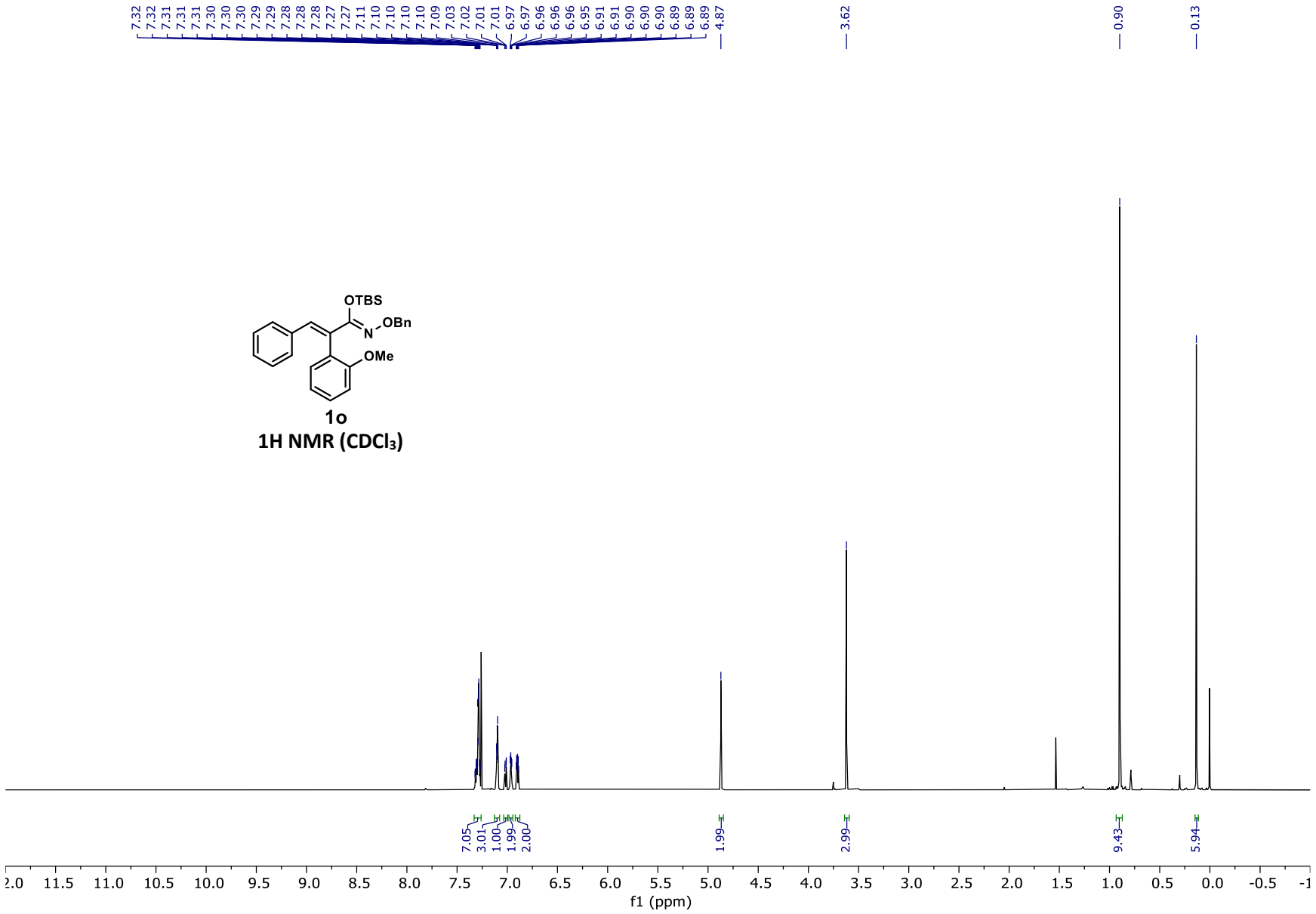

153.6
137.4
137.3
130.8
129.9
129.5
129.3
128.4
128.3
128.1
127.2
76.3
26.1
19.1
14.1
-3.5
OTBS
N
OBn
Me
1l
13C NMR (CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

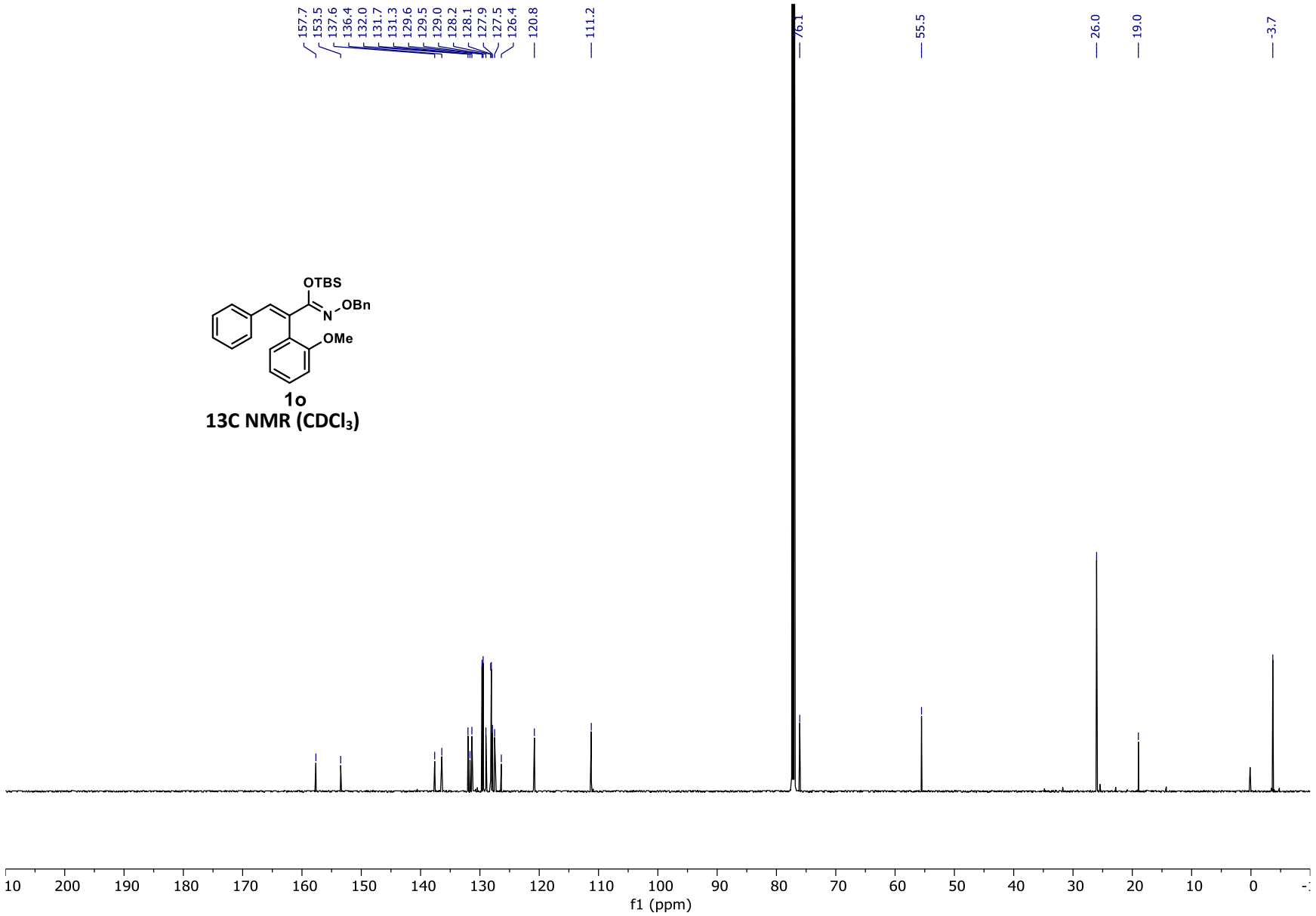

7.43 7.43 7.42 7.42 7.42 7.41 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.30 7.29 7.29 7.29 7.28 7.27 7.27 7.27 7.27 7.26 7.25 7.25 7.25 7.24 7.24 7.15 5.02 2.48 2.48 2.47 2.47 2.46 1.53 1.52 1.52 1.52 1.52 1.51 1.51 1.51 1.50 1.50 1.49 1.49 1.48 1.35 1.34 1.32 1.31 0.95 0.90 0.88 0.87 0.15
OTBS
N
OBn
1m
1H NMR (CDCl3)
2.08 4.27 1.10 2.10 0.80 1.00 2.18 2.08 1.95 2.02 9.39 3.20 6.52
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

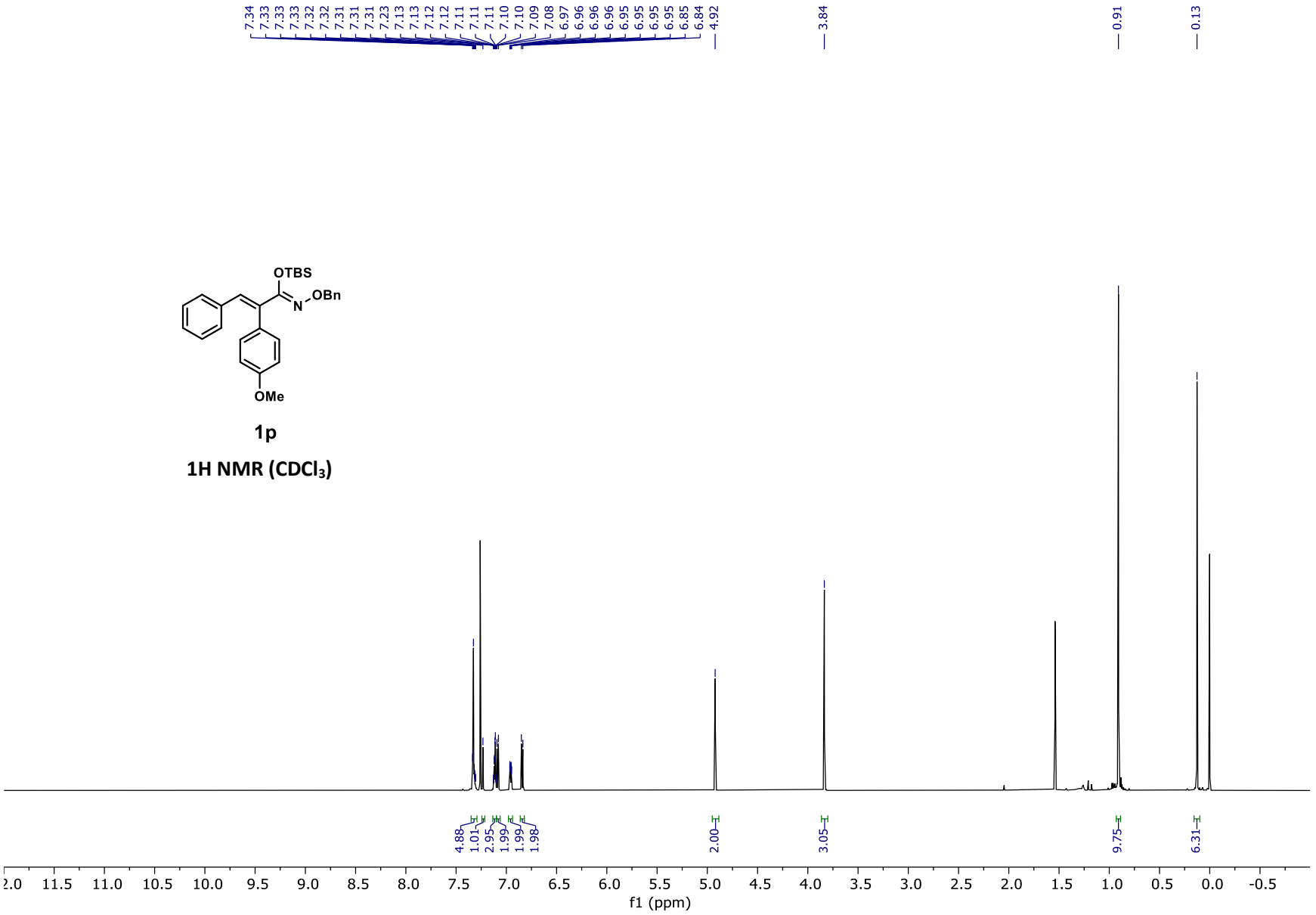

152.5
137.7
137.3
135.3
130.5
129.4
129.1
128.4
128.3
128.0
127.2
76.2
31.8
27.2
26.1
23.1
19.1
14.0
-3.6
OTBS
N
OBn
1m
13C NMR (CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

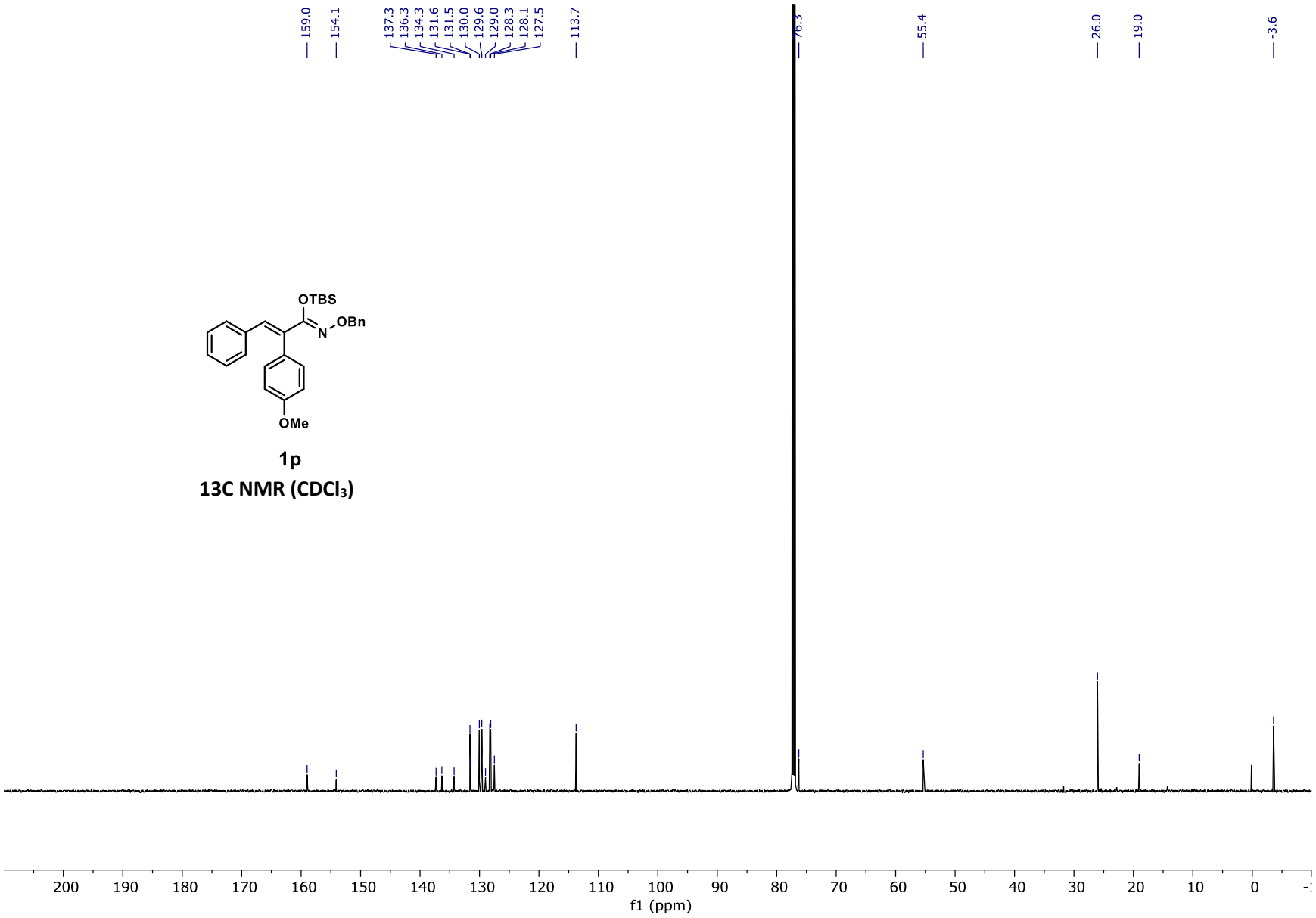

8.55
8.54
8.54
8.40
8.40
7.48
7.48
7.47
7.47
7.46
7.46
7.40
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.28
7.28
7.27
7.27
7.26
7.24
7.23
7.22
7.14
7.14
7.13
7.13
7.13
7.12
7.12
7.12
6.92
6.92
6.91
6.91
6.91
6.90
6.90
6.90
4.87
0.95
0.16
OTBS
N
OBn
N
1n
1H NMR (CDCl3)
1.00
1.00
1.01
1.03
2.91
2.22
1.03
3.06
2.08
2.14
9.78
6.26
f1 (ppm)


153.1
151.3
148.4
138.2
137.0
135.5
133.1
132.9
131.4
130.0
129.6
128.4
128.4
128.3
128.2
128.0
123.1
26.1
19.1
-3.5
OTBS
N
OBn
N
1n
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.11 7.10 7.10 7.10 7.09 7.03 7.02 7.01 7.01 6.97 6.97 6.96 6.96 6.96 6.95 6.91 6.91 6.90 6.90 6.89 6.89 6.89 4.87
3.62
0.90
0.13
OTBS
N
OBn
OMe
1o
1H NMR (CDCl3)
7.05 3.01 1.00 1.99 2.00
1.99
2.99
9.43
5.94
f1 (ppm)

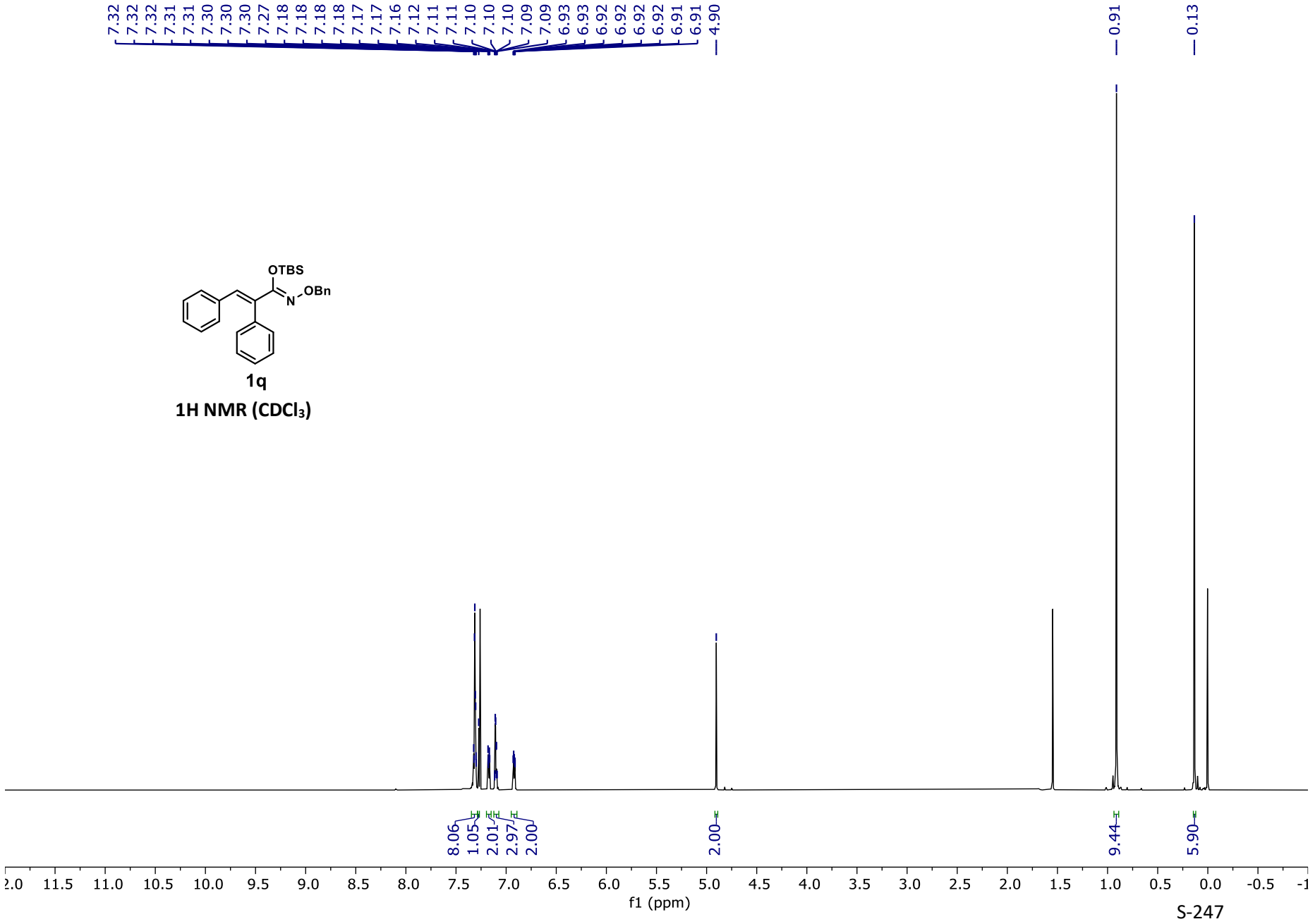

157.7
153.5
137.6
136.4
132.0
131.7
131.3
129.6
129.5
129.0
128.2
128.1
127.9
127.5
126.4
120.8
111.2
76.1
55.5
26.0
19.0
-3.7
OTBS
N
OBn
OMe
1o
13C NMR (CDCl3)
f1 (ppm)


7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.23
7.13
7.13
7.12
7.12
7.11
7.11
7.11
7.10
7.10
7.09
7.08
6.97
6.96
6.96
6.96
6.95
6.95
6.95
6.85
6.84
4.92
3.84
0.91
0.13
OTBS
N
OBn
OMe
1p
1H NMR (CDCl3)
4.88
1.01
2.95
1.99
1.99
1.98
2.00
3.05
9.75
6.31
f1 (ppm)



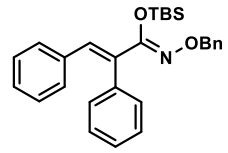
1p

13C NMR ($CDCl_3$)



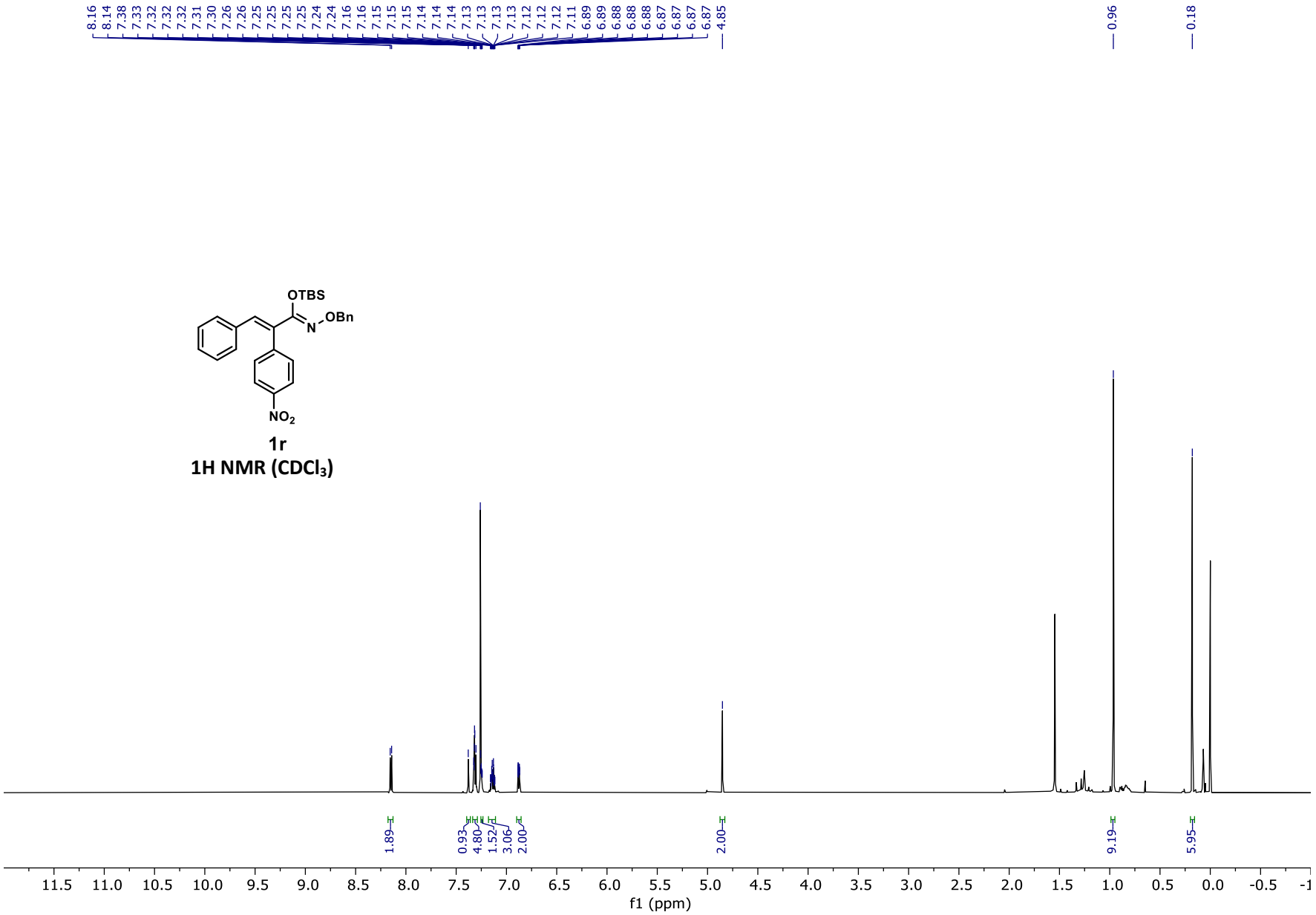
1q

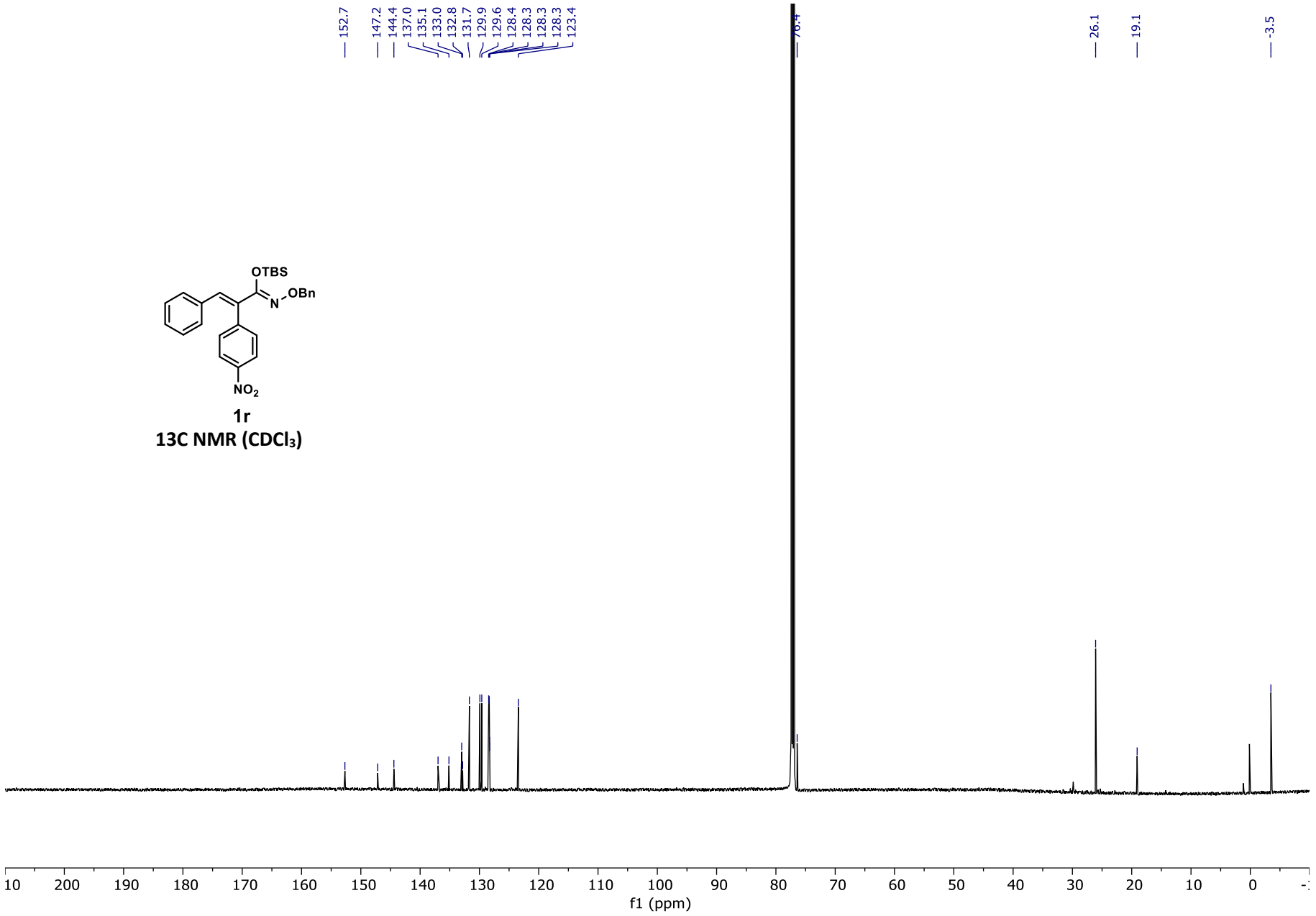
1H NMR ($CDCl_3$)



1q

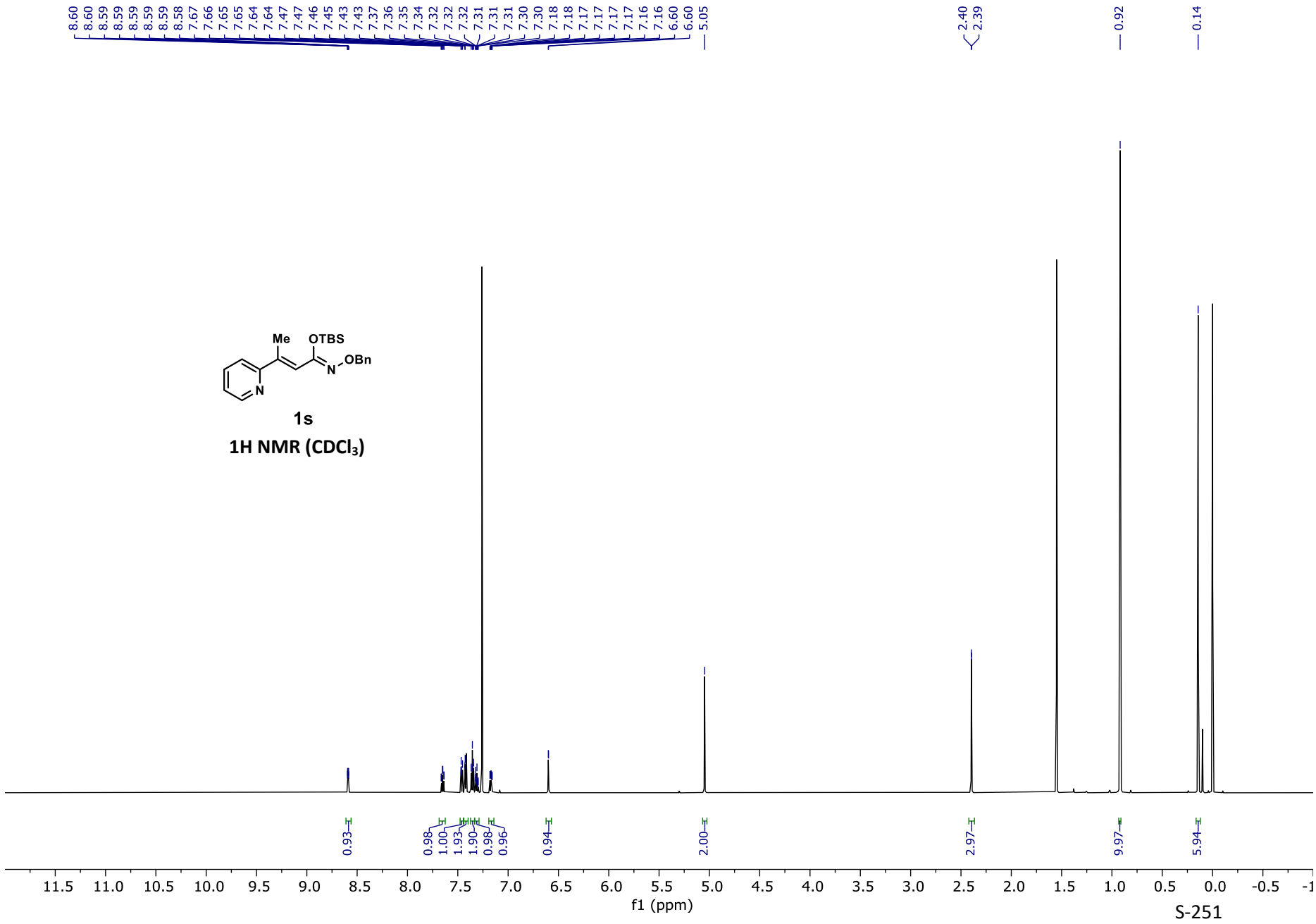
13C NMR ($CDCl_3$)

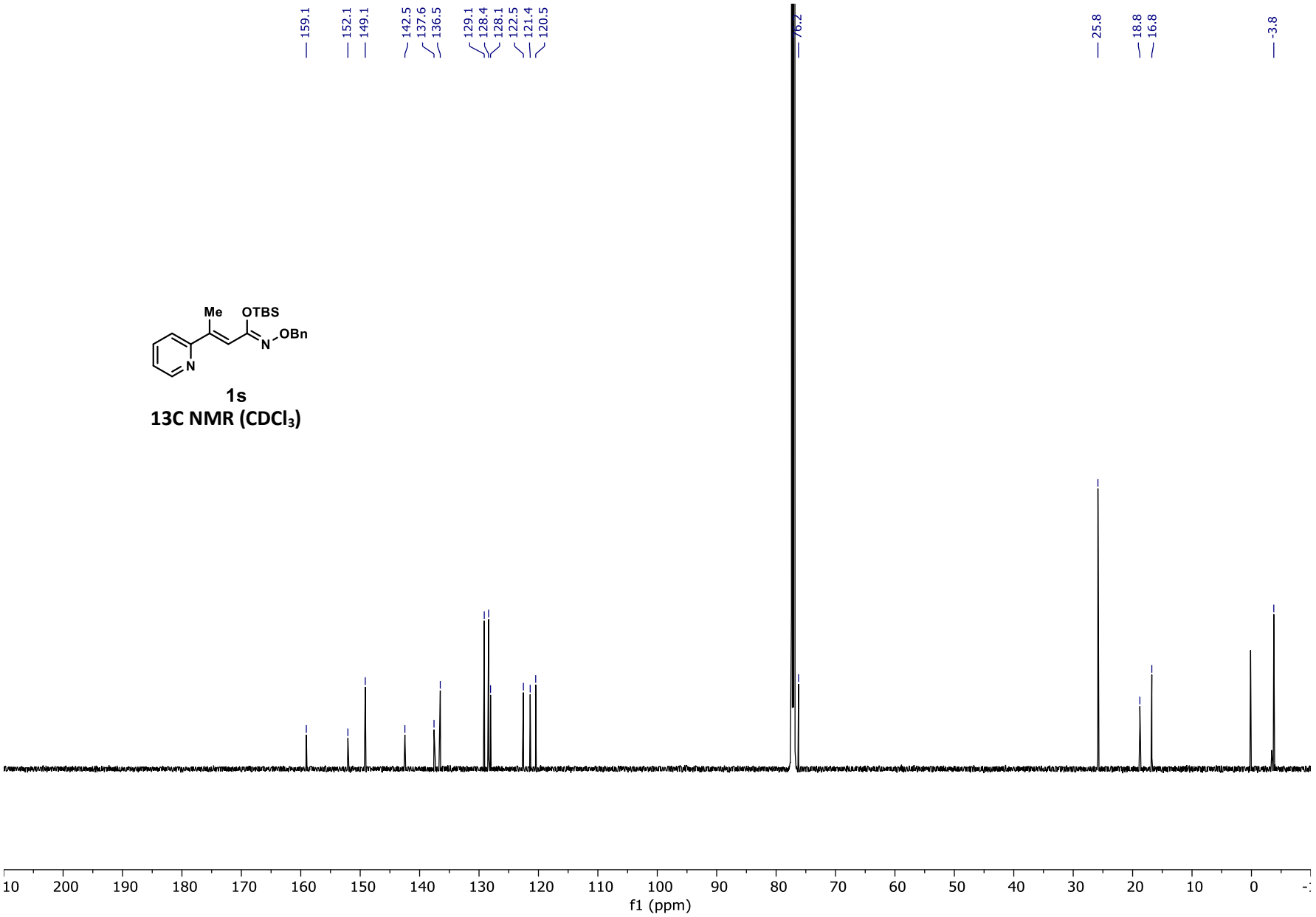

8.16
8.14
7.38
7.33
7.32
7.32
7.32
7.31
7.30
7.26
7.26
7.25
7.25
7.25
7.25
7.24
7.24
7.16
7.16
7.15
7.15
7.15
7.14
7.14
7.14
7.13
7.13
7.13
7.13
7.12
7.12
7.12
7.11
6.89
6.89
6.88
6.88
6.88
6.87
6.87
6.87
6.87
4.85
0.96
0.18
OTBS
N
OBn
NO2
1r
1H NMR (CDCl3)
1.89
0.93
4.80
1.52
3.06
2.00
2.00
9.19
5.95
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

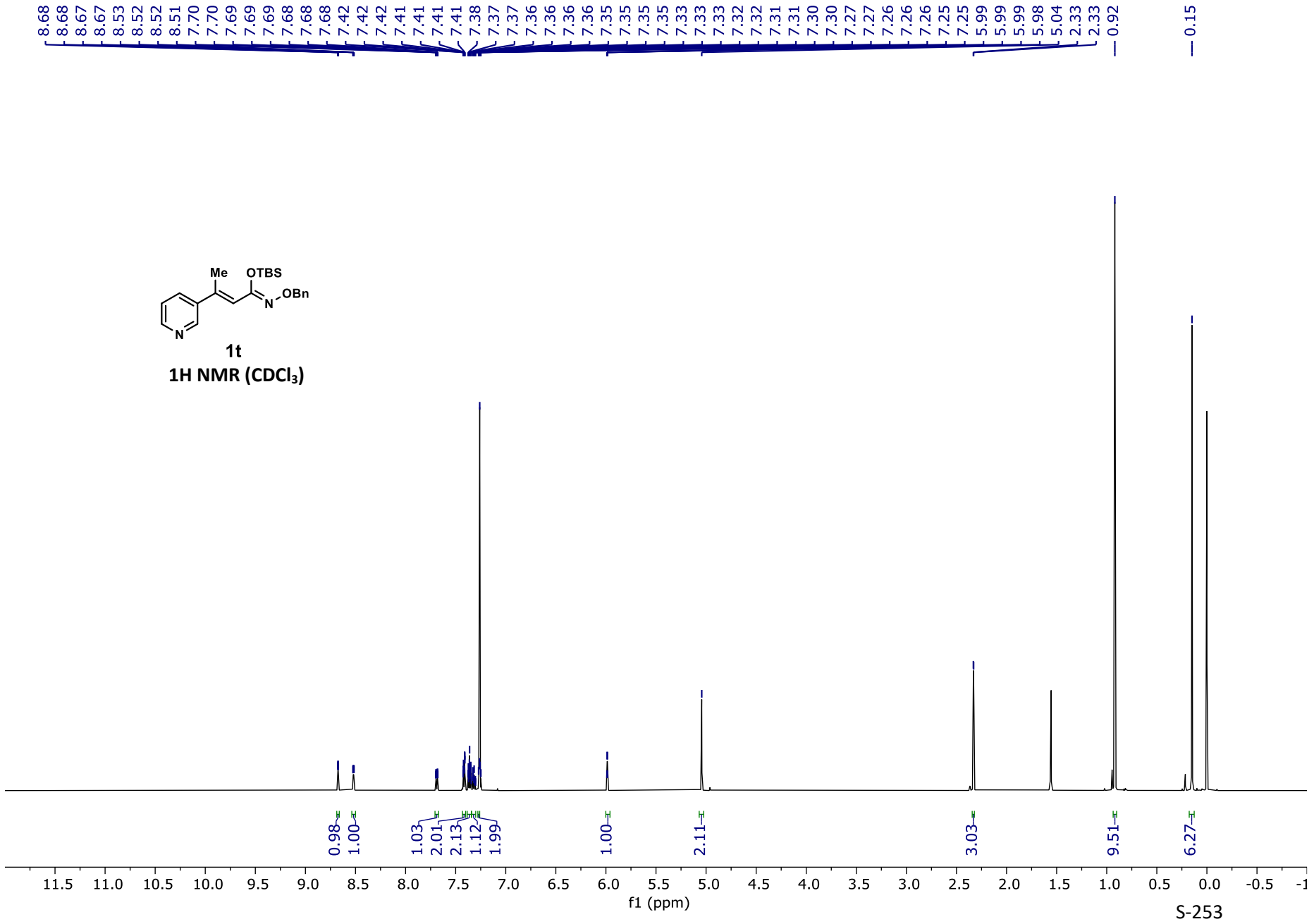


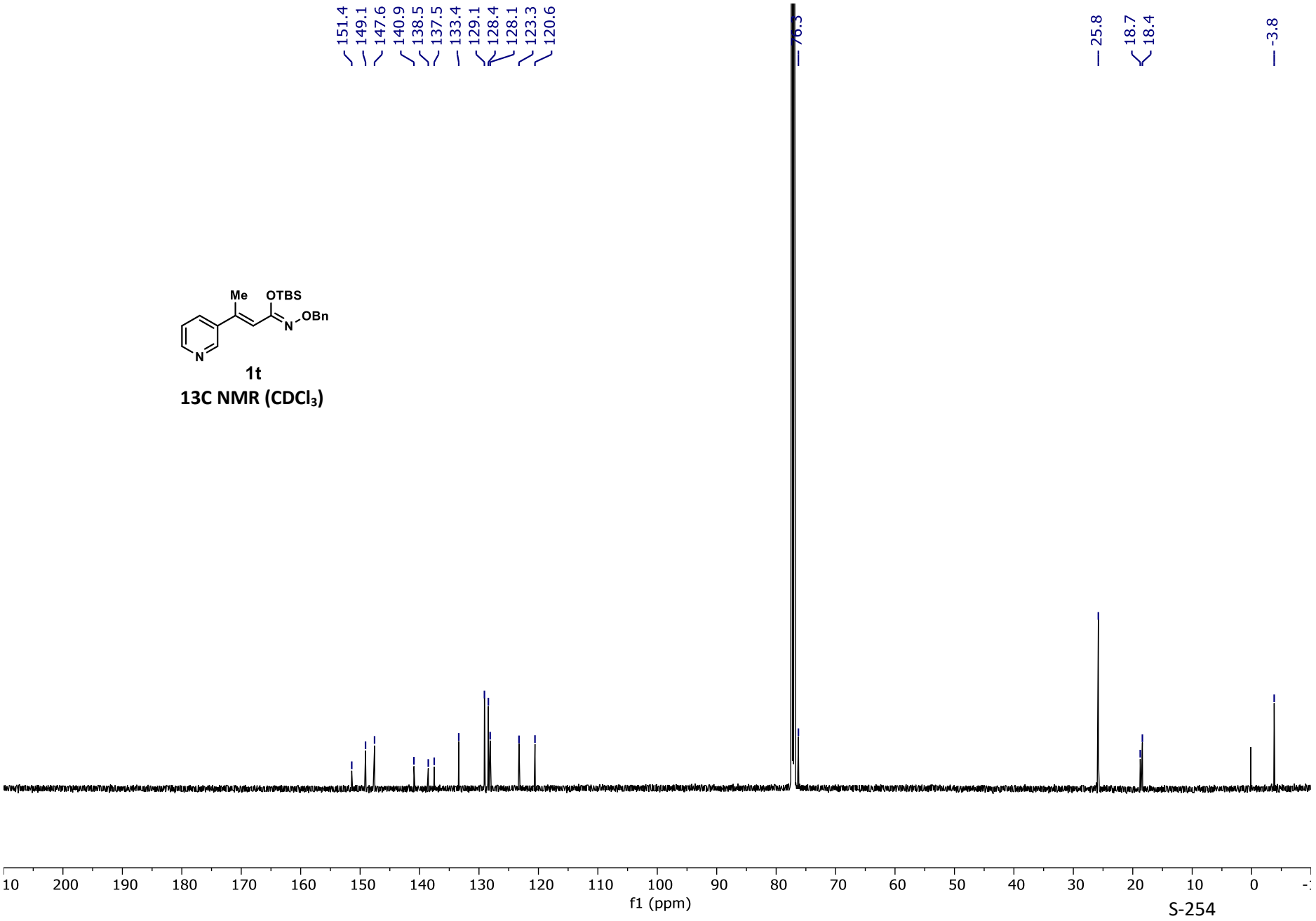
1r

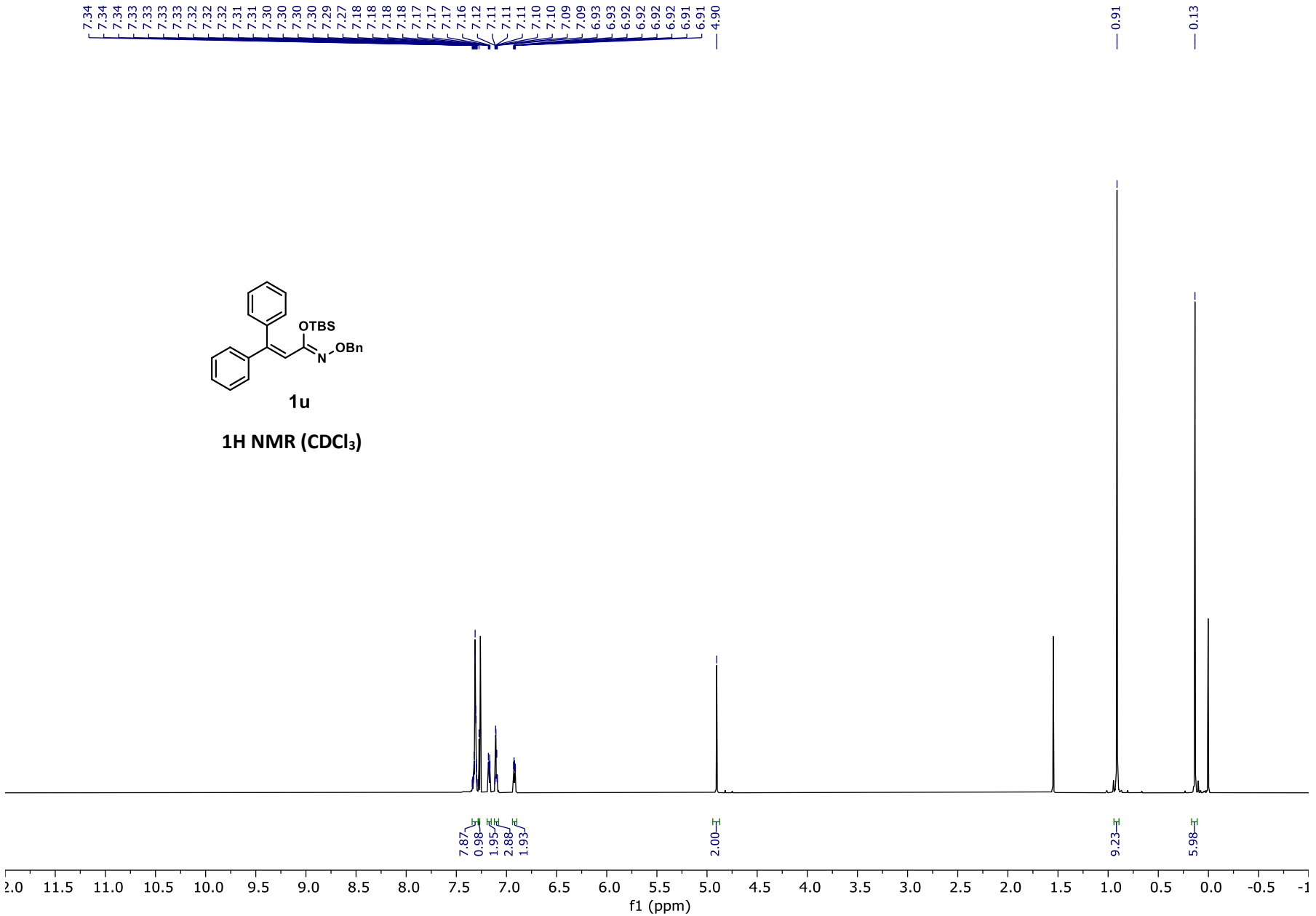
13C NMR ($CDCl_3$)


8.60 8.60 8.59 8.59 8.59 8.59 8.59 8.58 7.67 7.66 7.65 7.65 7.64 7.64 7.47 7.47 7.46 7.45 7.43 7.43 7.37 7.36 7.35 7.34 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.18 7.18 7.17 7.17 7.17 7.17 7.16 6.60 6.60 5.05
2.40 2.39
0.92
0.14
Me
OTBS
N
OBn
N
1s
1H NMR (CDCl3)
0.93 0.98 1.00 1.93 1.90 0.98 0.96 0.94 2.00 2.97 9.97 5.94
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


159.1
152.1
149.1
142.5
137.6
136.5
129.1
128.4
128.1
122.5
121.4
120.5
76.2
25.8
18.8
16.8
-3.8
Me
OTBS
N
OBn
N
1s
13C NMR (CDCl3)
f1 (ppm)

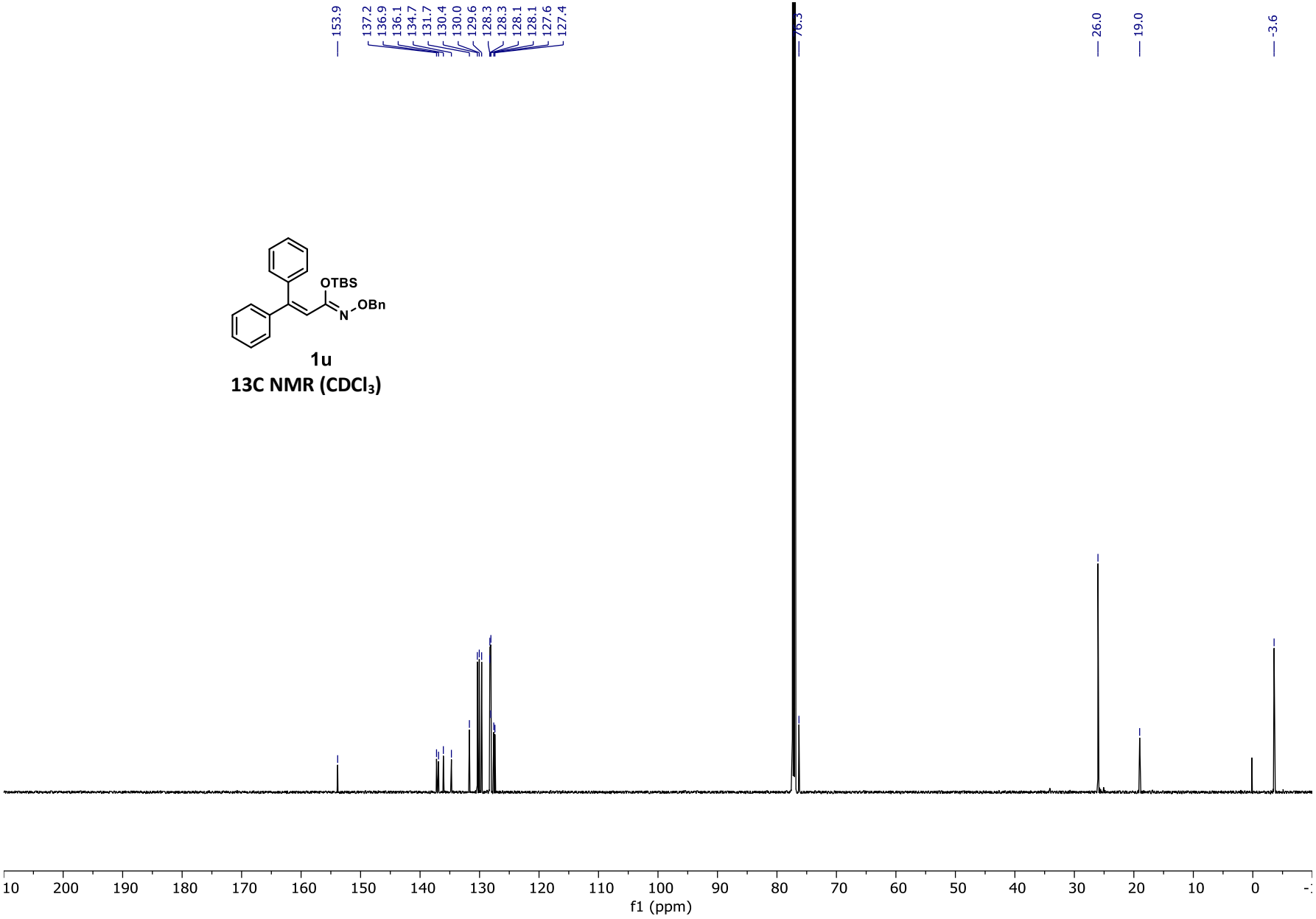

8.68 8.68 8.67 8.67 8.53 8.52 8.52 8.51 7.70 7.70 7.69 7.69 7.69 7.68 7.68 7.68 7.42 7.42 7.42 7.41 7.41 7.41 7.41 7.38 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.35 7.35 7.35 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.27 7.27 7.26 7.26 7.26 7.25 7.25 5.99 5.99 5.98 5.04 2.33 2.33 0.92 0.15
Me
OTBS
OBn
N
N
1t
1H NMR (CDCl3)
0.98 1.00 1.03 2.01 2.13 1.12 1.99 1.00 2.11 3.03 9.51 6.27
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

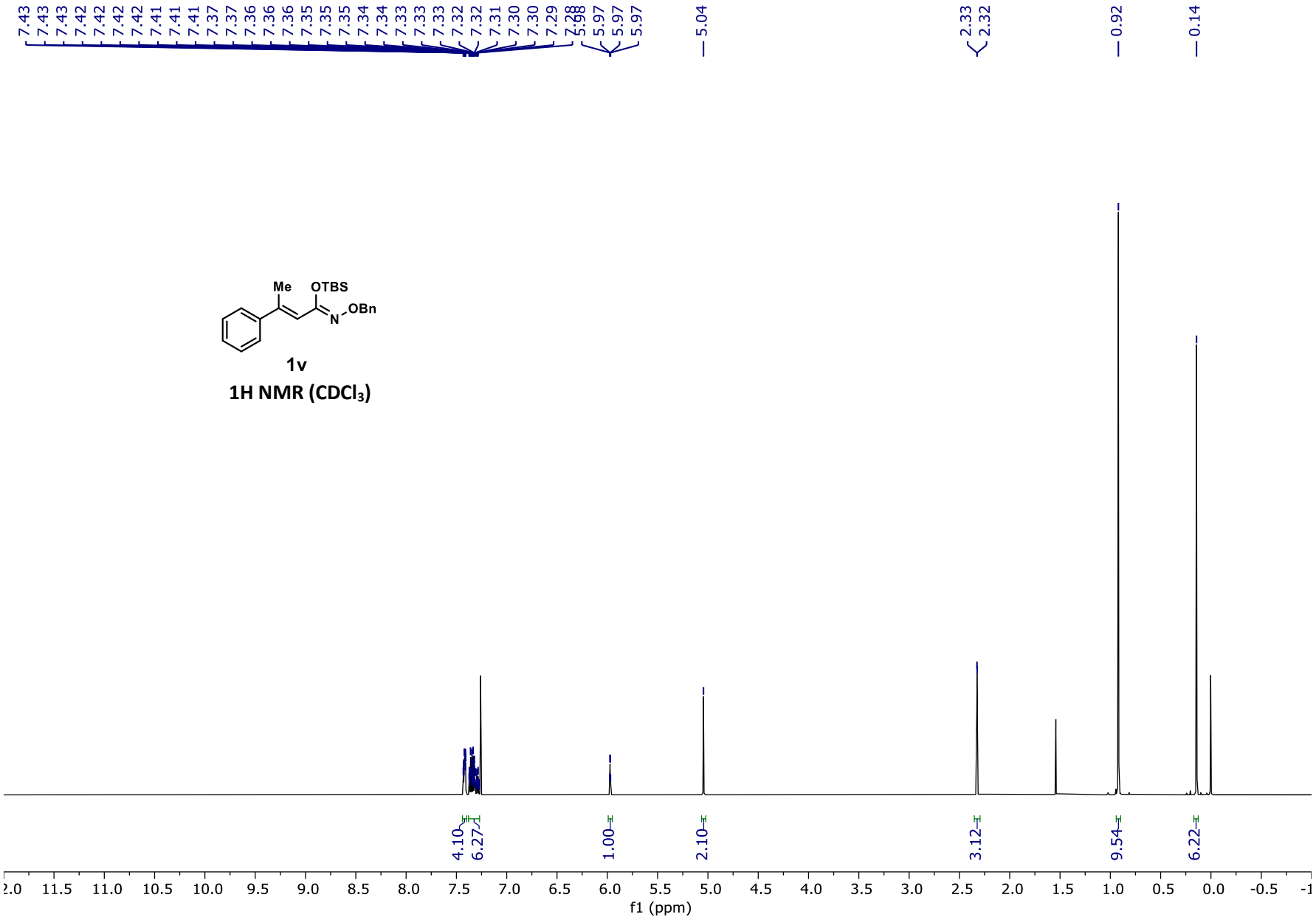

151.4
149.1
147.6
140.9
138.5
137.5
133.4
129.1
128.4
128.1
123.3
120.6
25.8
18.7
18.4
-3.8
Me
OTBS
OBn
N
N
1t
13C NMR (CDCl3)
f1 (ppm)

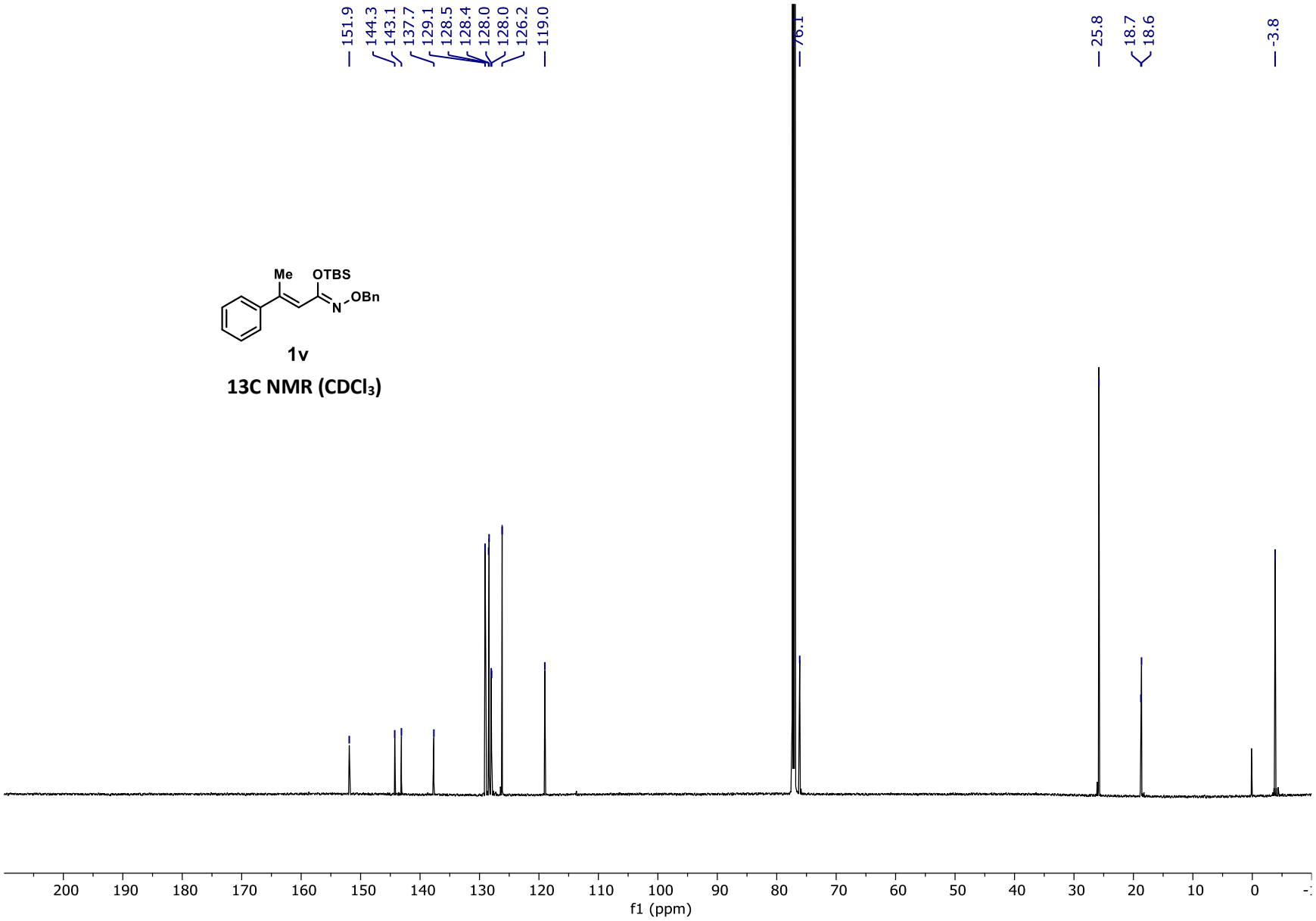


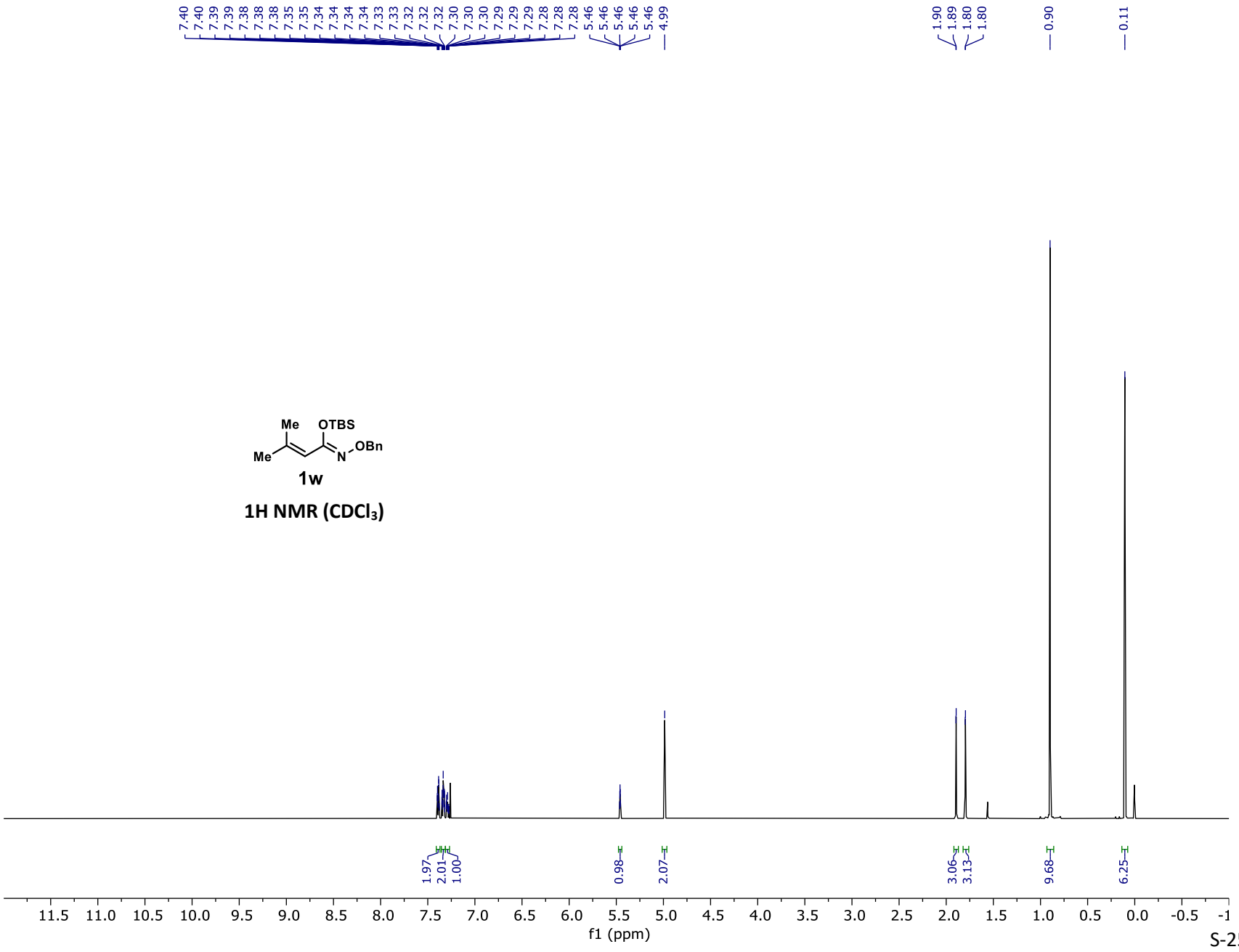
1u

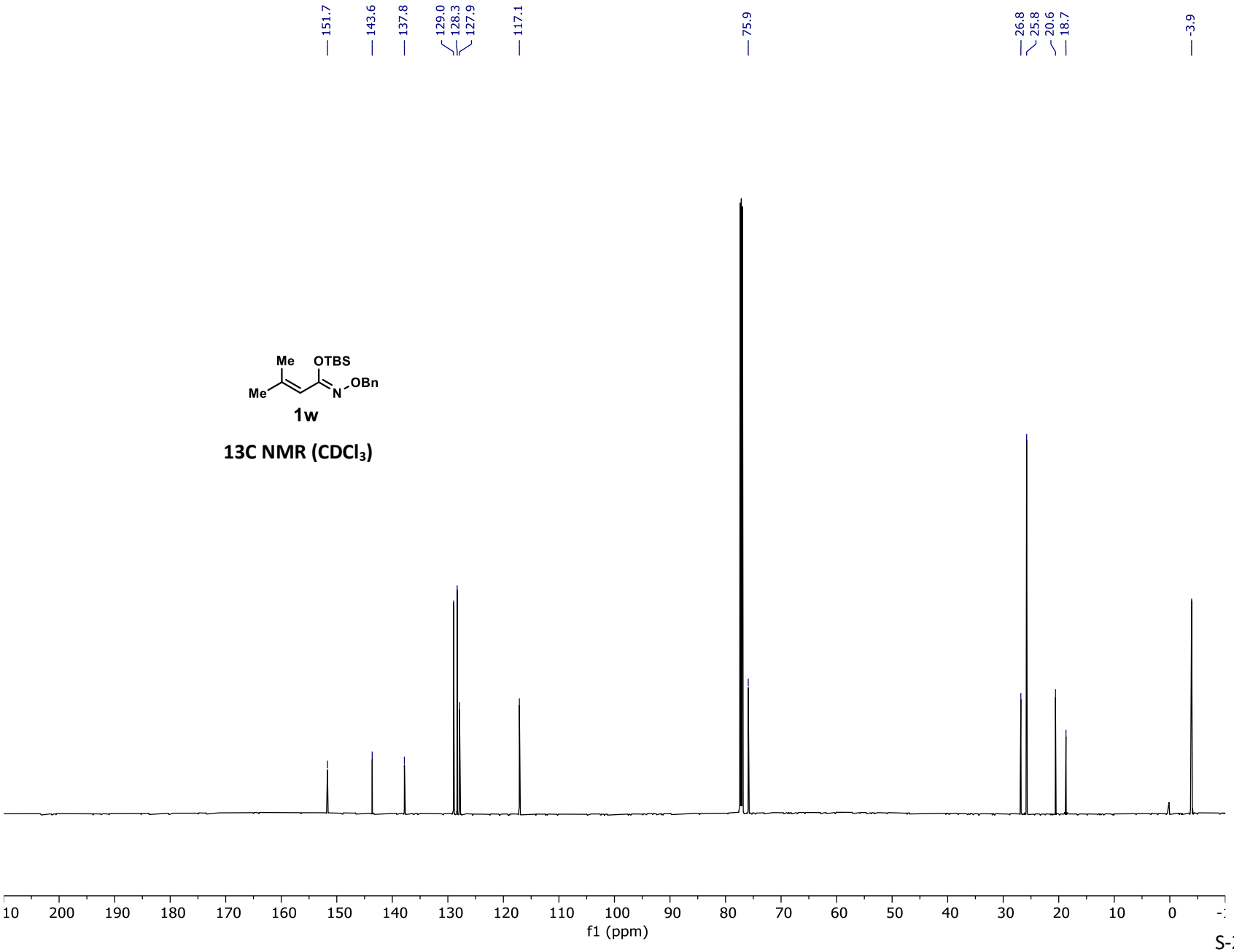
1H NMR ($CDCl_3$)

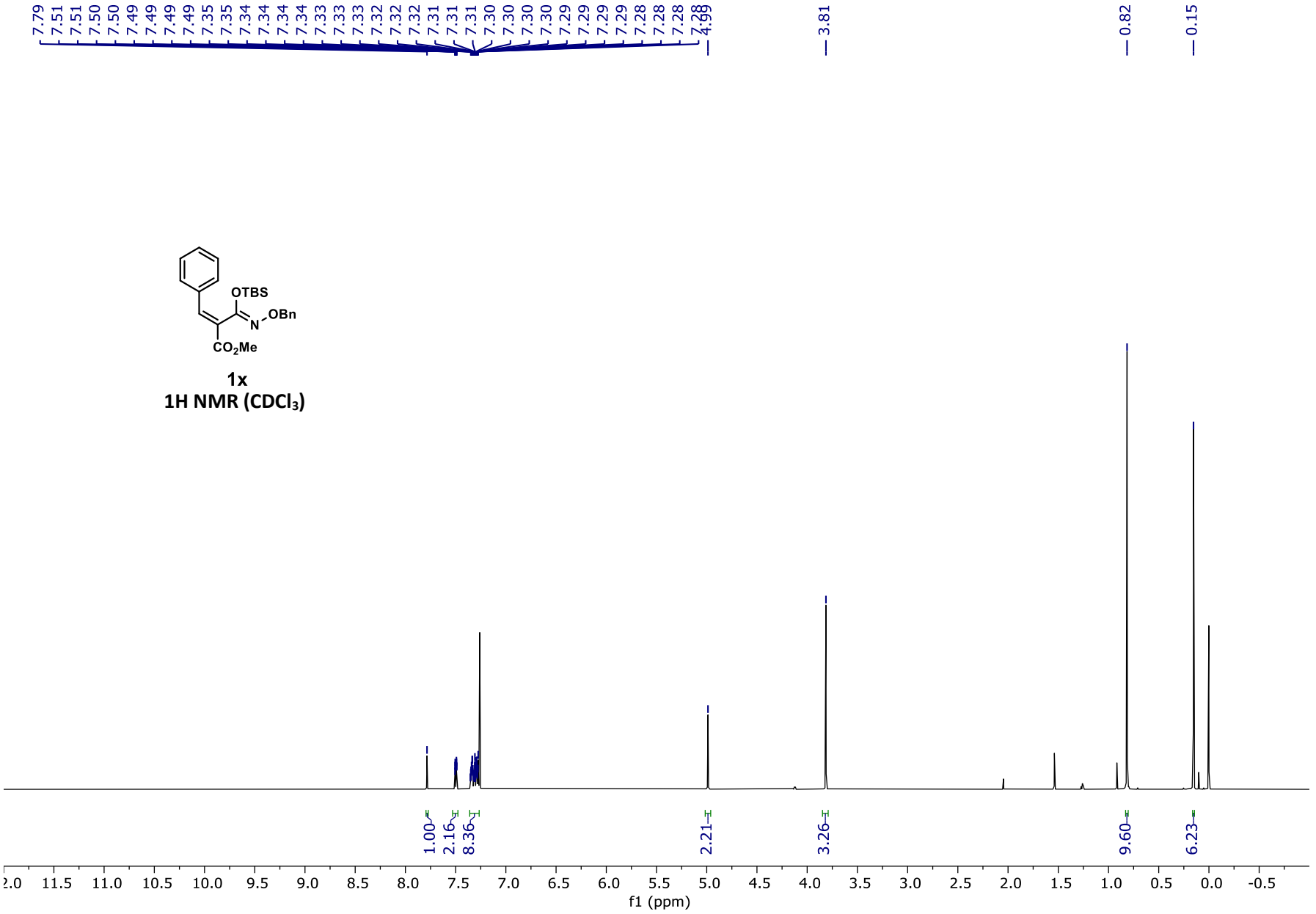

153.9
137.2
136.9
136.1
134.7
131.7
130.4
130.0
129.6
128.3
128.3
128.1
128.1
127.6
127.4
76.3
26.0
19.0
-3.6
OTBS
N
OBn
1u
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

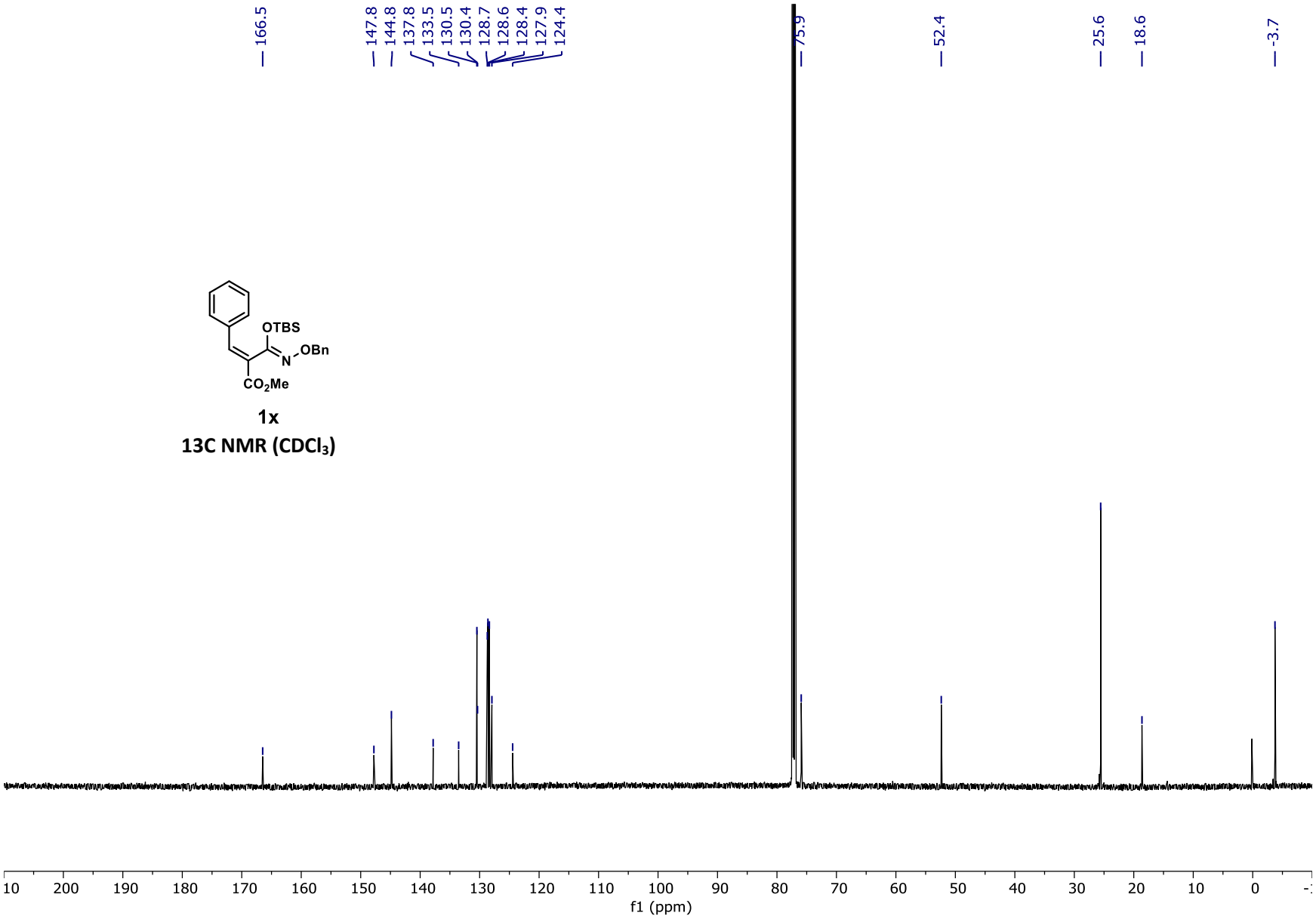

7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.41 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.28 5.98 5.97 5.97 5.97
5.04
2.33 2.32
0.92
0.14
Me
OTBS
N
OBn
1v
1H NMR (CDCl3)
4.10
6.27
1.00
2.10
3.12
9.54
6.22
f1 (ppm)

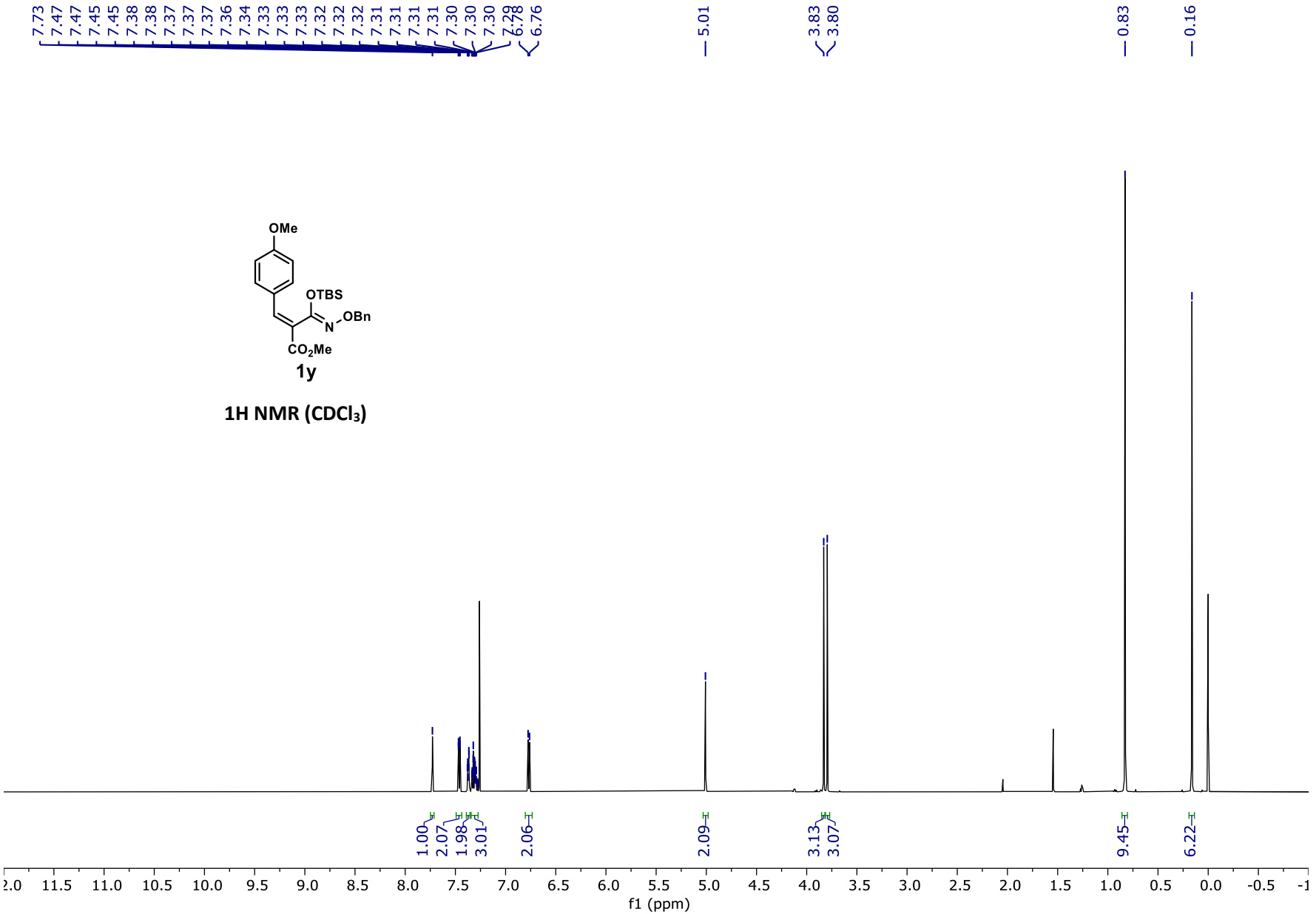

151.9
144.3
143.1
137.7
129.1
128.5
128.4
128.0
128.0
126.2
119.0
76.1
25.8
18.7
18.6
-3.8
Me
OTBS
N
OBn
1v
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

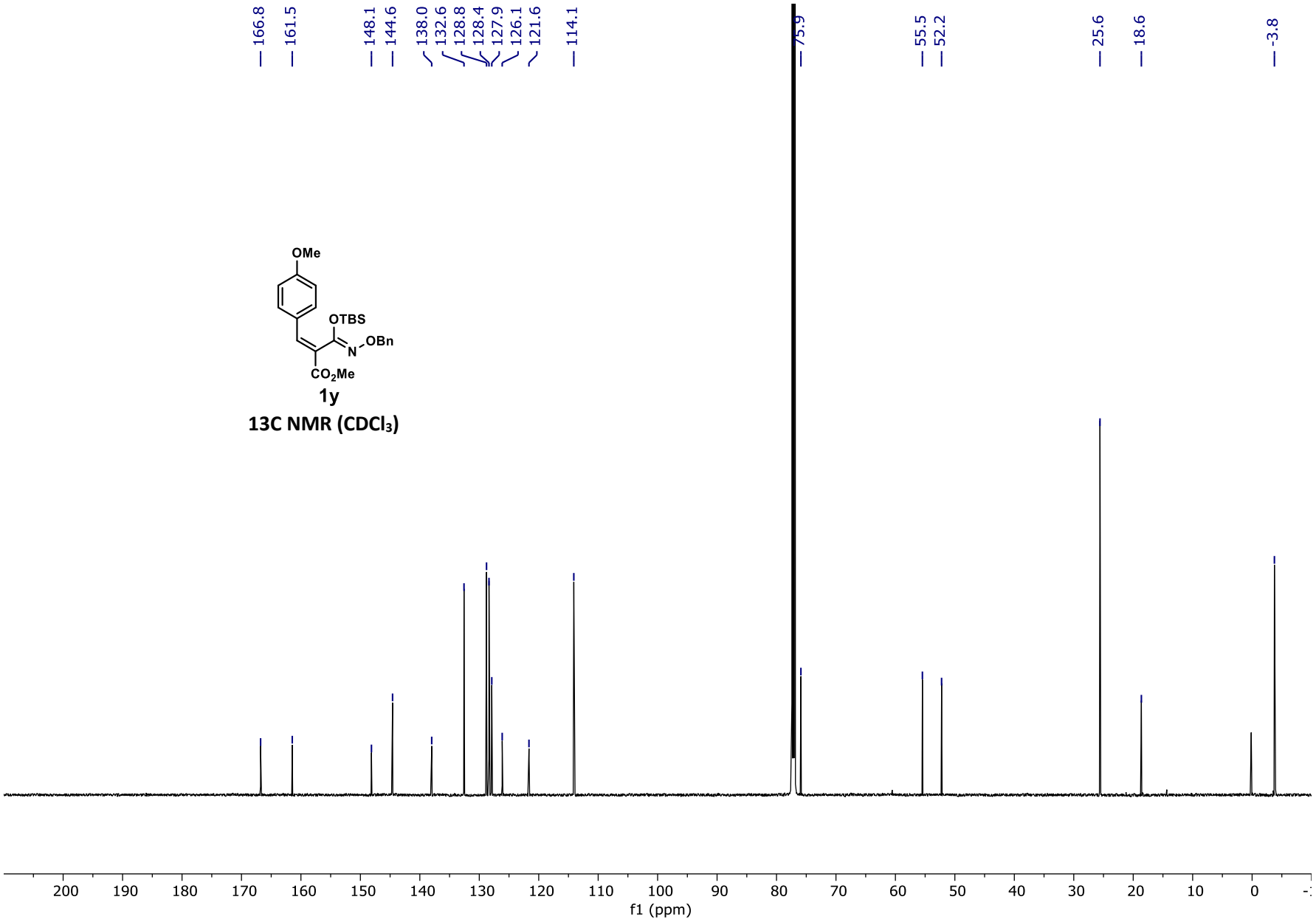

7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.28
5.46
5.46
5.46
5.46
4.99
1.90
1.89
1.80
1.80
0.90
0.11
Me
OTBS
OBn
Me
N
1w
1H NMR (CDCl3)
1.97
2.01
1.00
0.98
2.07
3.06
3.13
9.68
6.25
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

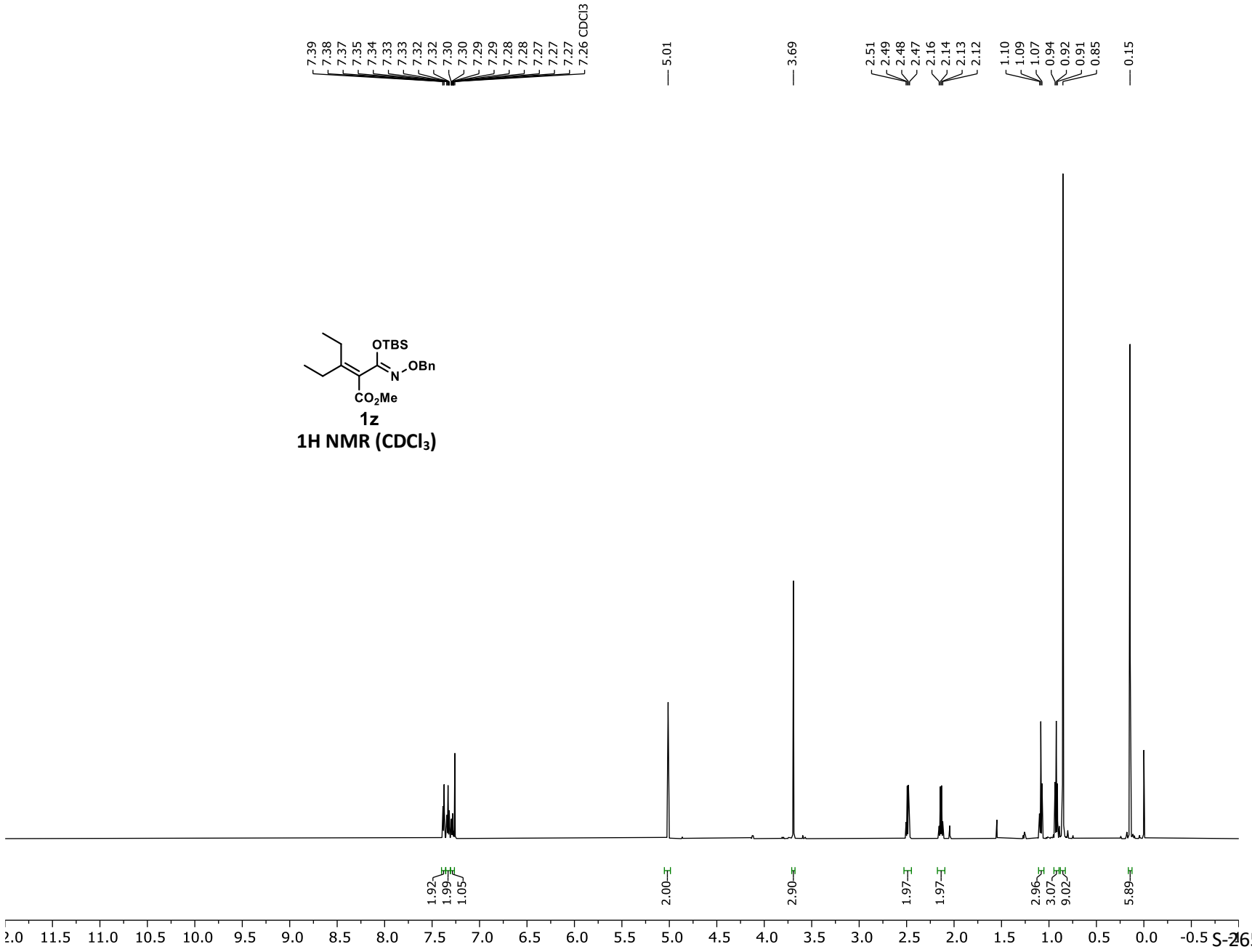

151.7
143.6
137.8
129.0
128.3
127.9
117.1
75.9
26.8
25.8
20.6
18.7
-3.9
Me
OTBS
OBn
Me
N
1w
13C NMR (CDCl3)
f1 (ppm)

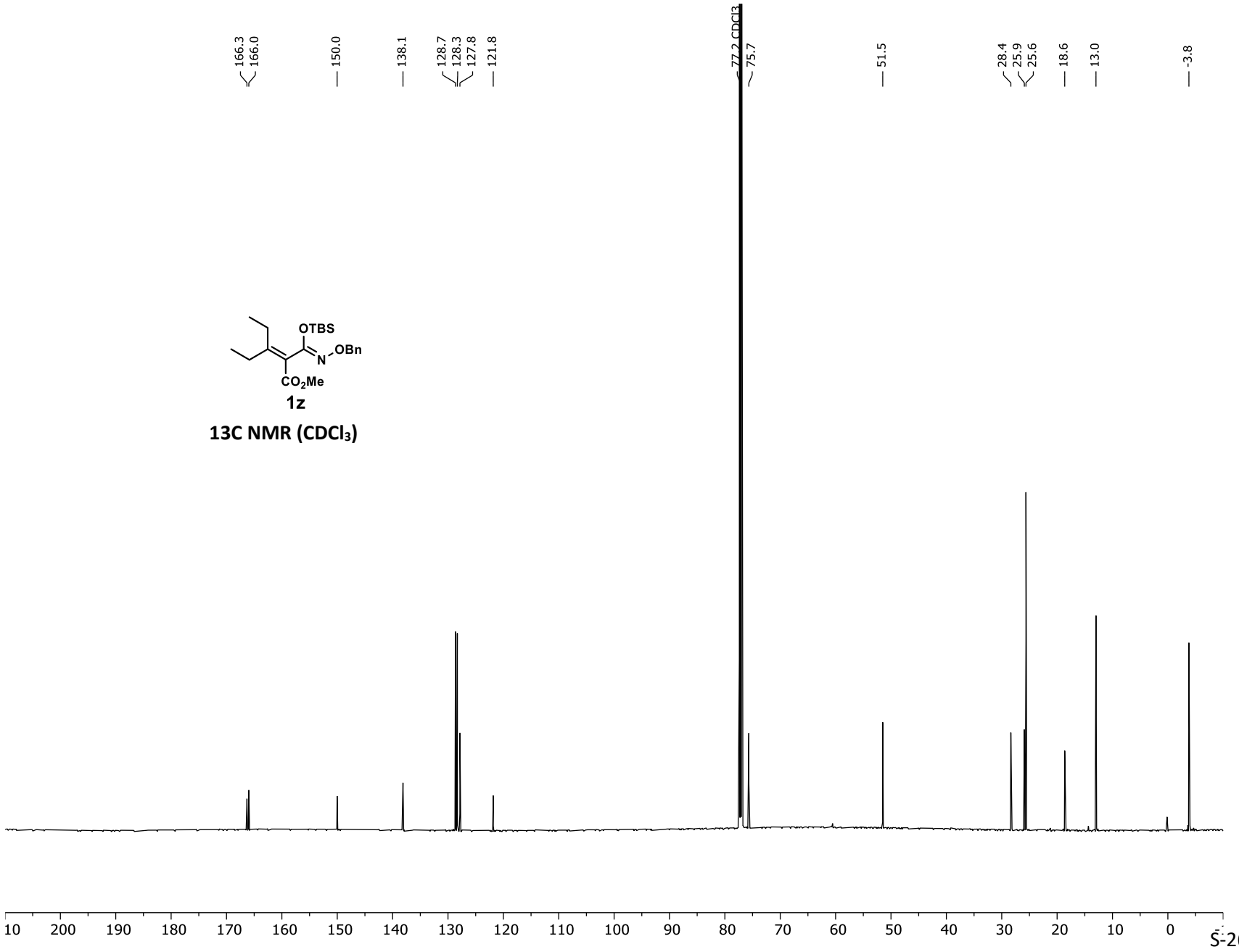

7.79
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.49
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.30
7.29
7.29
7.29
7.29
7.28
7.28
7.28
7.28
4.99
3.81
0.82
0.15
OTBS
OBn
N
CO2Me
1x
1H NMR (CDCl3)
1.00
2.16
8.36
2.21
3.26
9.60
6.23
f1 (ppm)

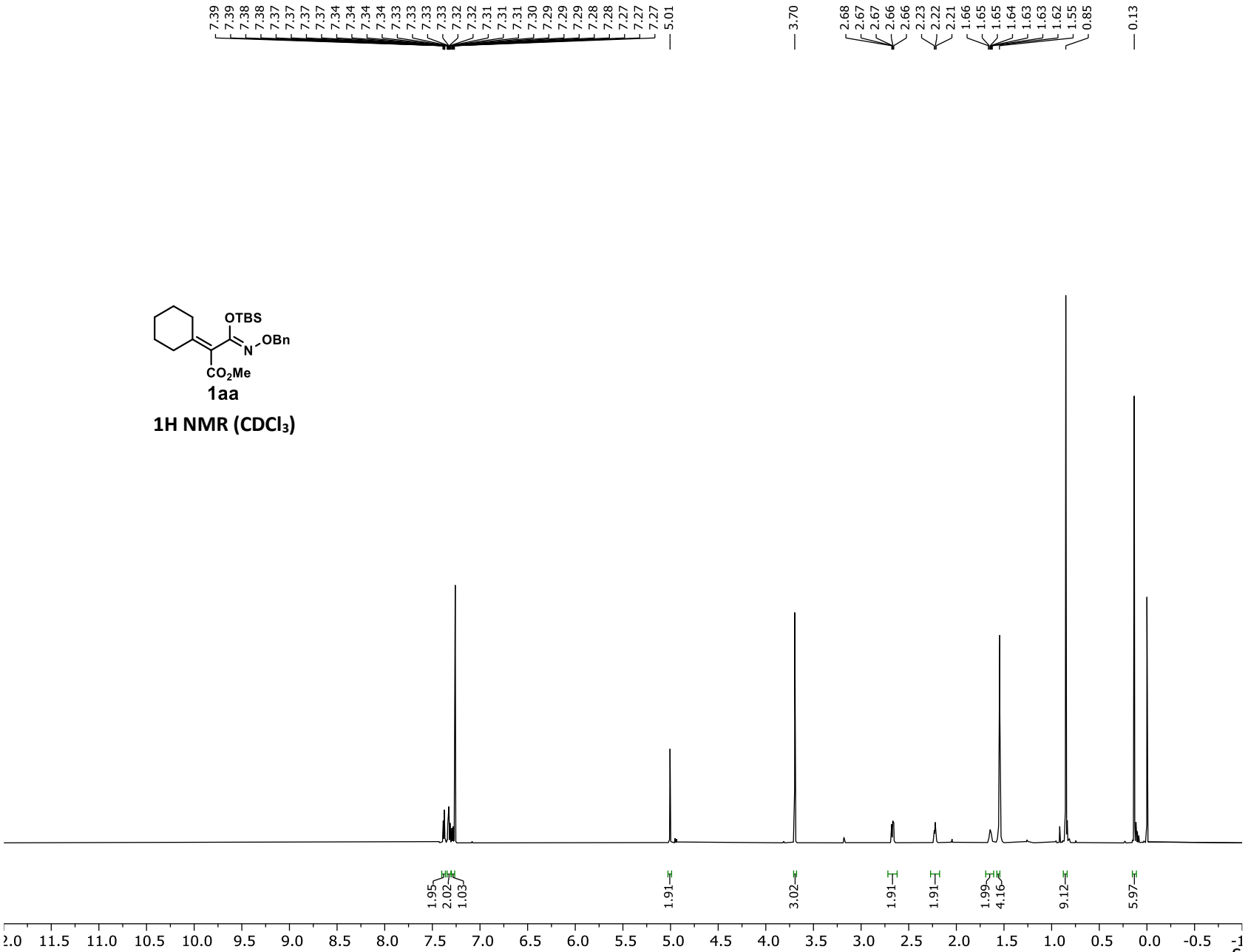

166.5
147.8
144.8
137.8
133.5
130.5
130.4
128.7
128.6
128.4
127.9
124.4
75.9
52.4
25.6
18.6
-3.7
OTBS
N
OBn
CO2Me
1x
13C NMR (CDCl3)
f1 (ppm)

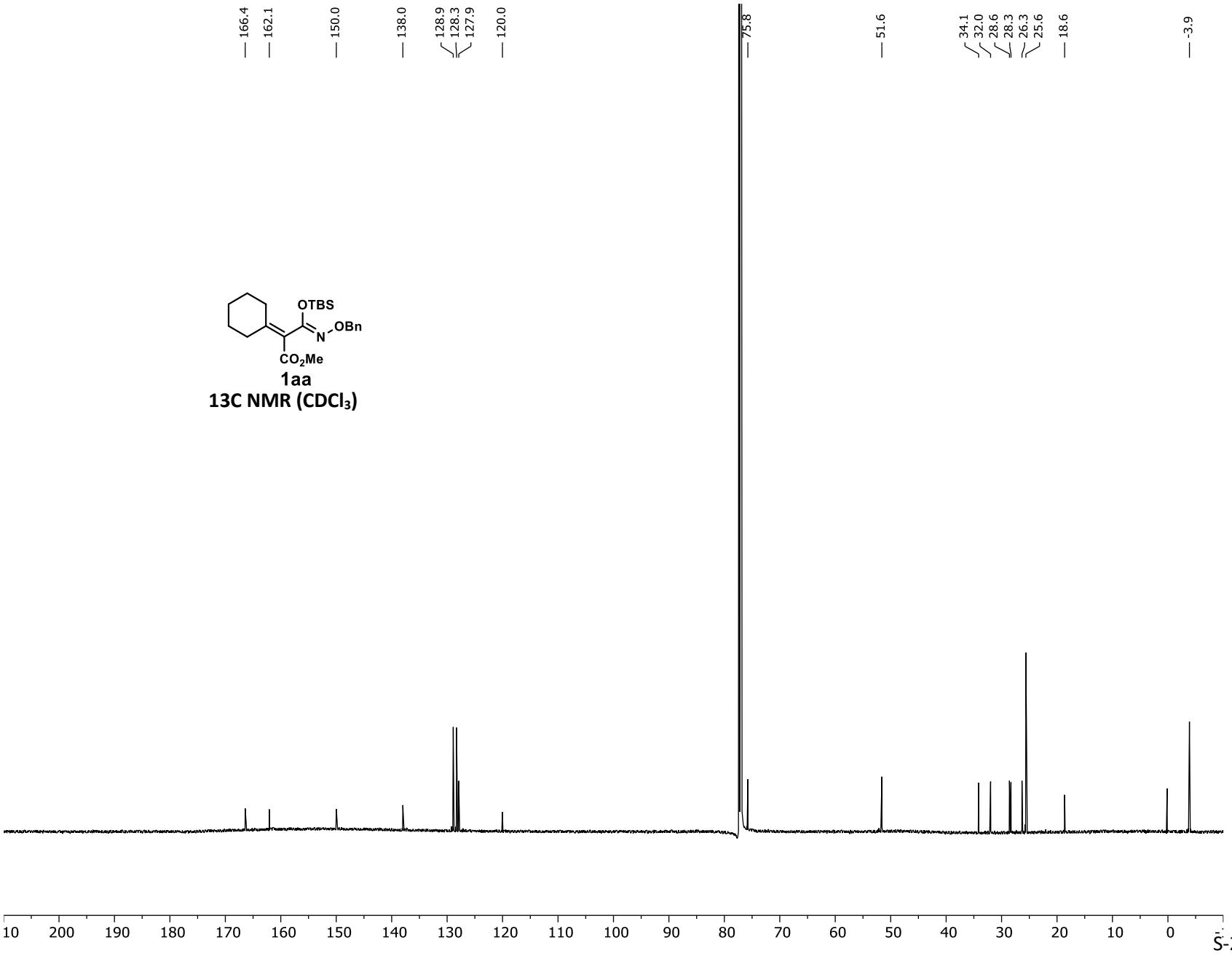

7.73
7.47
7.47
7.45
7.45
7.38
7.38
7.37
7.37
7.37
7.36
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.30
7.29
6.78
6.76
5.01
3.83
3.80
0.83
0.16
OMe
OTBS
OBn
N
CO2Me
1y
1H NMR (CDCl3)
1.00
2.07
1.98
3.01
2.06
2.09
3.13
3.07
9.45
6.22
f1 (ppm)

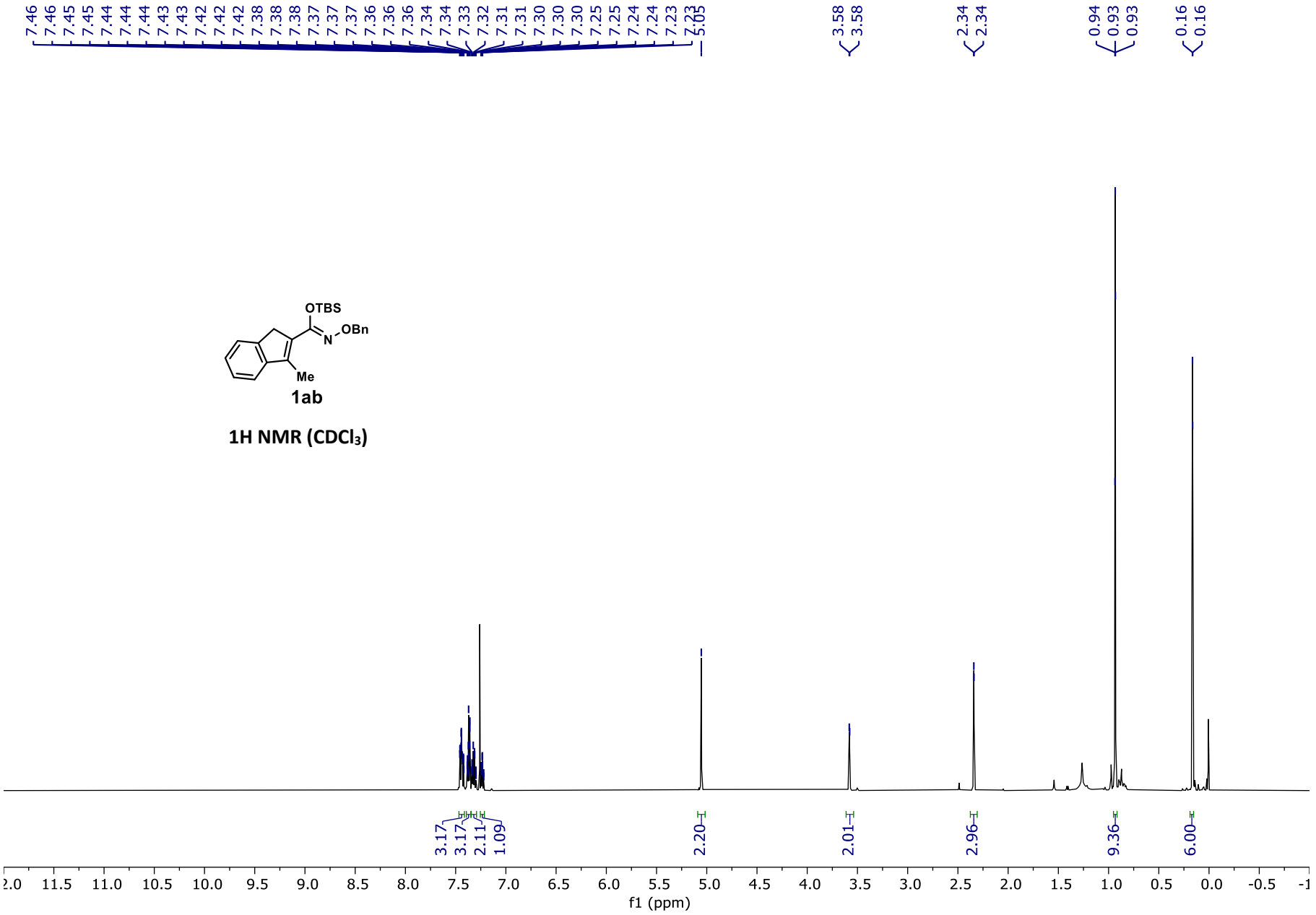

166.8
161.5
148.1
144.6
138.0
132.6
128.8
128.4
127.9
126.1
121.6
114.1
77.9
55.5
52.2
25.6
18.6
-3.8
OMe
OTBS
N
OBn
CO2Me
1y
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

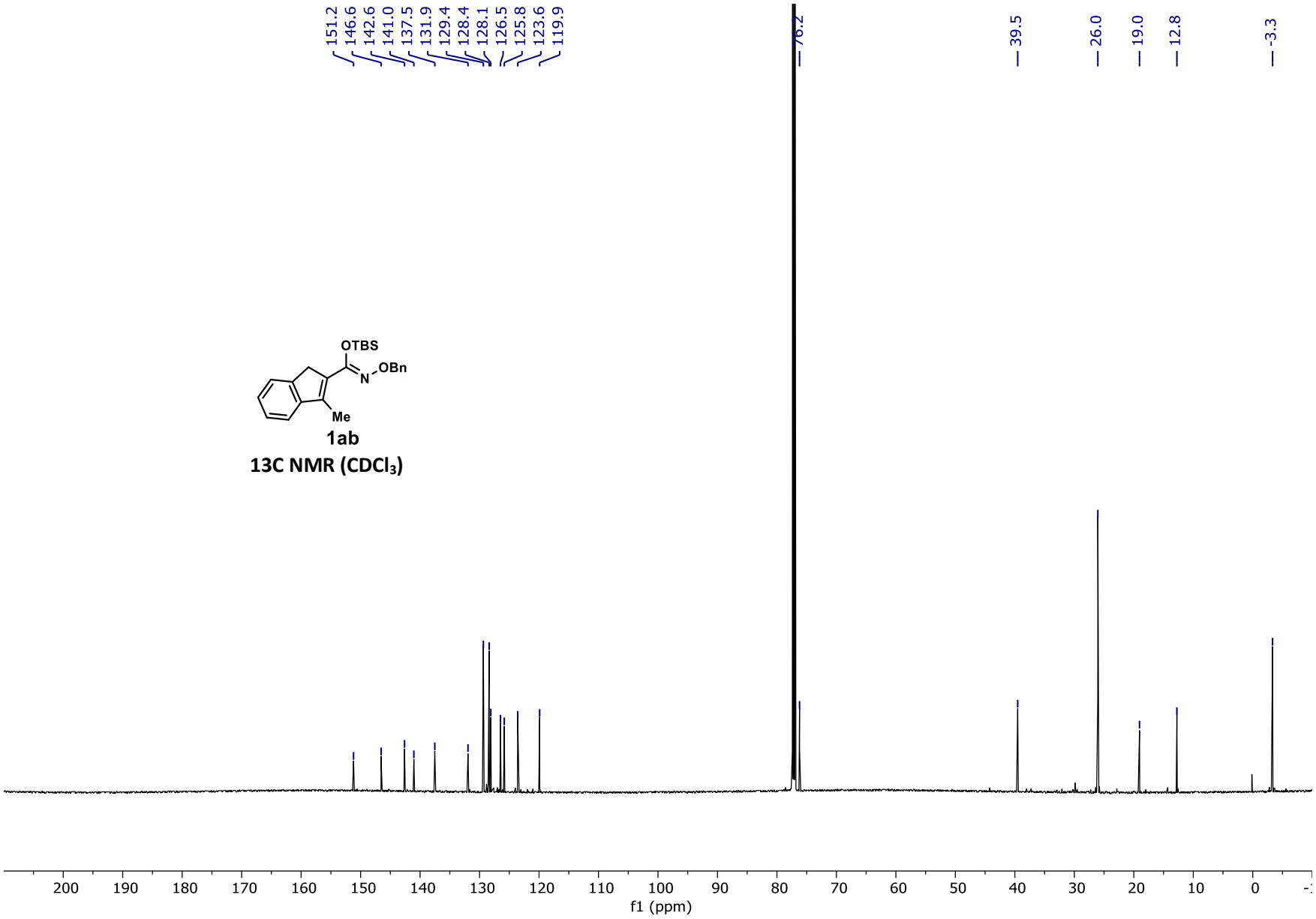

7.39
7.38
7.37
7.35
7.34
7.33
7.33
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26 CDCl3
5.01
3.69
2.51
2.49
2.48
2.47
2.16
2.14
2.13
2.12
1.10
1.09
1.07
0.94
0.92
0.91
0.85
0.15
OTBS
OBn
N
CO2Me
1z
1H NMR (CDCl3)
1.92
1.99
1.05
2.00
2.90
1.97
1.97
2.96
3.07
9.02
5.89
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

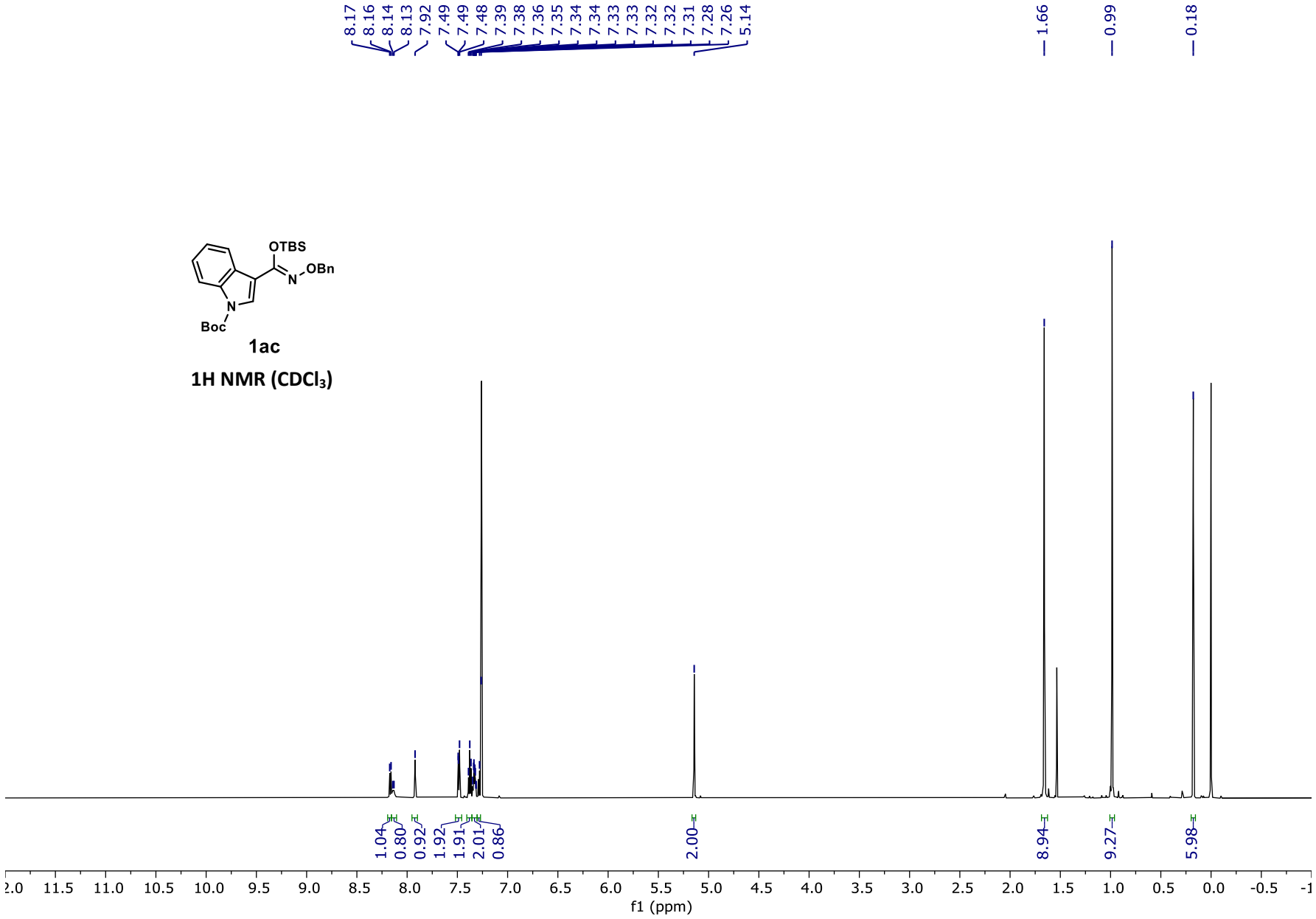

166.3
166.0
150.0
138.1
128.7
128.3
127.8
121.8
77.2 CDCl3
75.7
51.5
28.4
25.9
25.6
18.6
13.0
-3.8
OTBS
N
OBn
CO2Me
1z
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

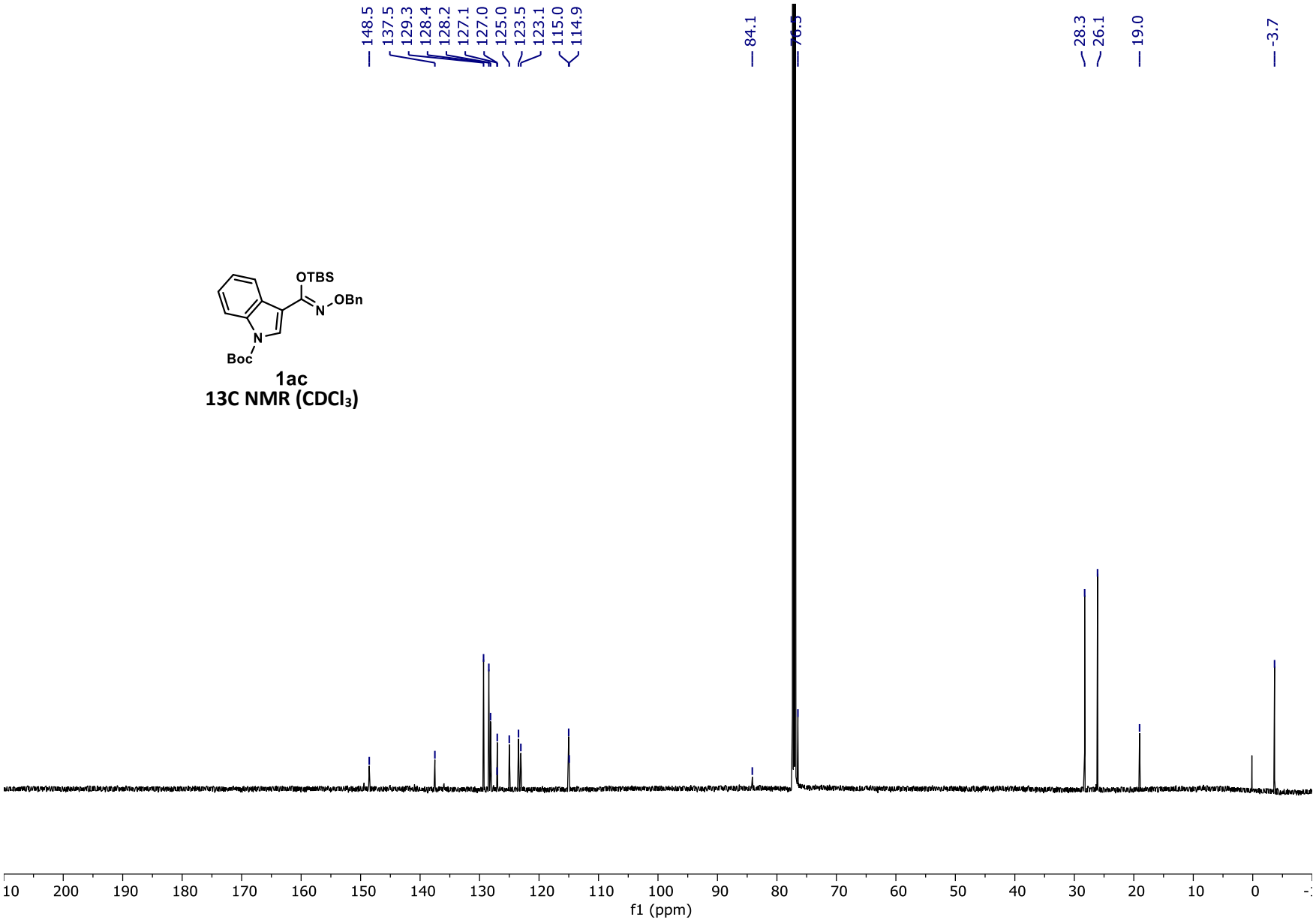

7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.34 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.27 5.01
3.70
2.68 2.67 2.67 2.66 2.66 2.23 2.22 2.21 1.66 1.65 1.65 1.64 1.63 1.63 1.62 1.55 0.85
0.13
OTBS
N
OBn
CO2Me
1aa
1H NMR (CDCl3)
1.95 2.02 1.03 1.91 3.02 1.91 1.91 1.99 4.16 9.12 5.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


166.4
162.1
150.0
138.0
128.9
128.3
127.9
120.0
75.8
51.6
34.1
32.0
28.6
28.3
26.3
25.6
18.6
-3.9
OTBS
OBn
N
CO2Me
1aa
13C NMR (CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

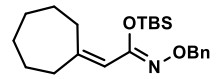

7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.30 7.30 7.25 7.25 7.24 7.24 7.23 7.23 5.05
3.58 3.58
2.34 2.34
0.94 0.93 0.93
0.16 0.16
OTBS
N
OBn
Me
1ab
1H NMR (CDCl3)
3.17 3.17 2.11 1.09
2.20
2.01
2.96
9.36
6.00
f1 (ppm)


151.2
146.6
142.6
141.0
137.5
131.9
129.4
128.4
128.1
126.5
125.8
123.6
119.9
76.2
39.5
26.0
19.0
12.8
-3.3
OTBS
N
OBn
Me
1ab
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.17
8.16
8.14
8.13
7.92
7.49
7.49
7.48
7.39
7.38
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.28
7.26
5.14
1.66
0.99
0.18
OTBS
N
OBn
N
Boc
1ac
1H NMR (CDCl3)
1.04
0.80
0.92
1.92
1.91
2.01
0.86
2.00
8.94
9.27
5.98
f1 (ppm)

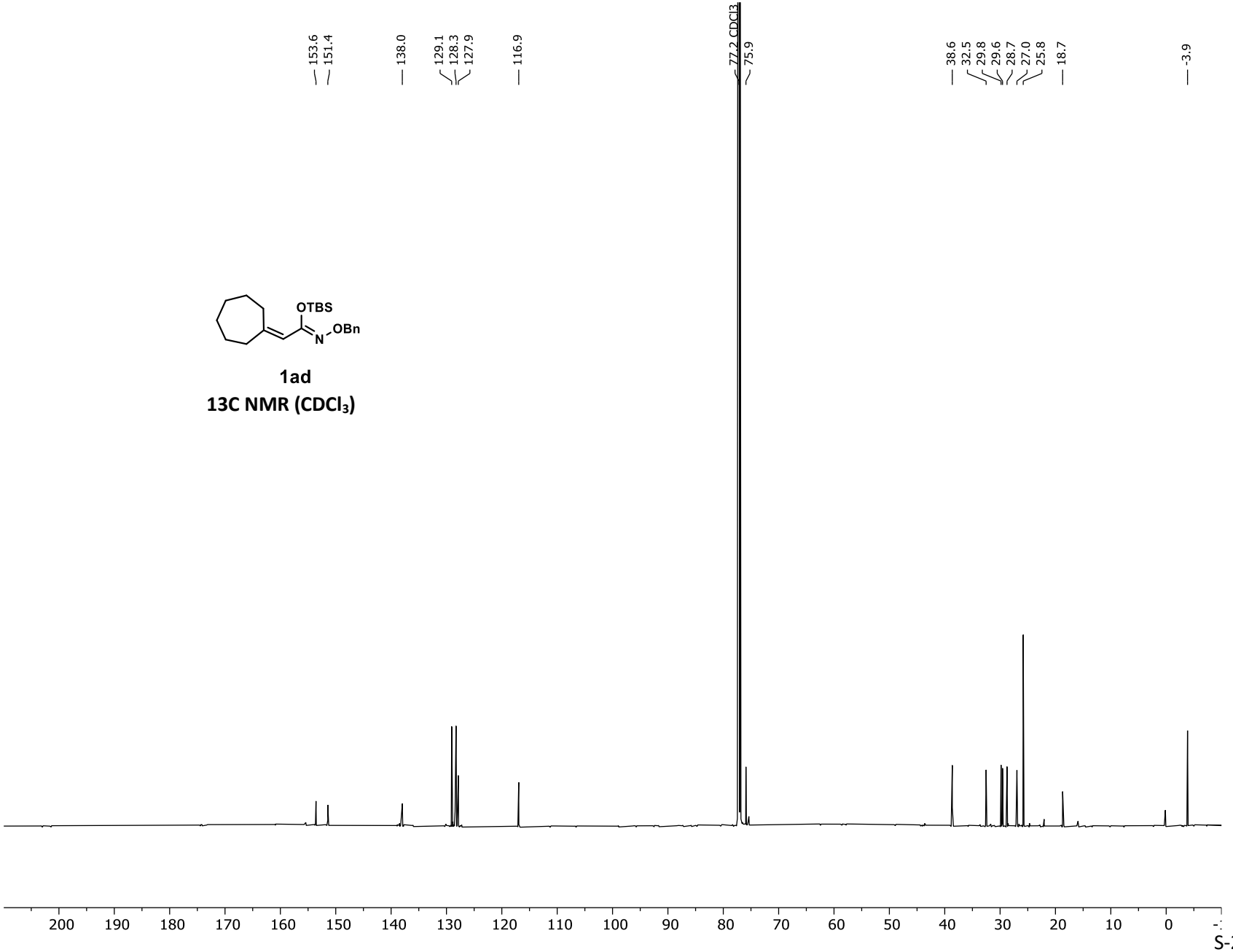


1ac
13C NMR ($CDCl_3$)



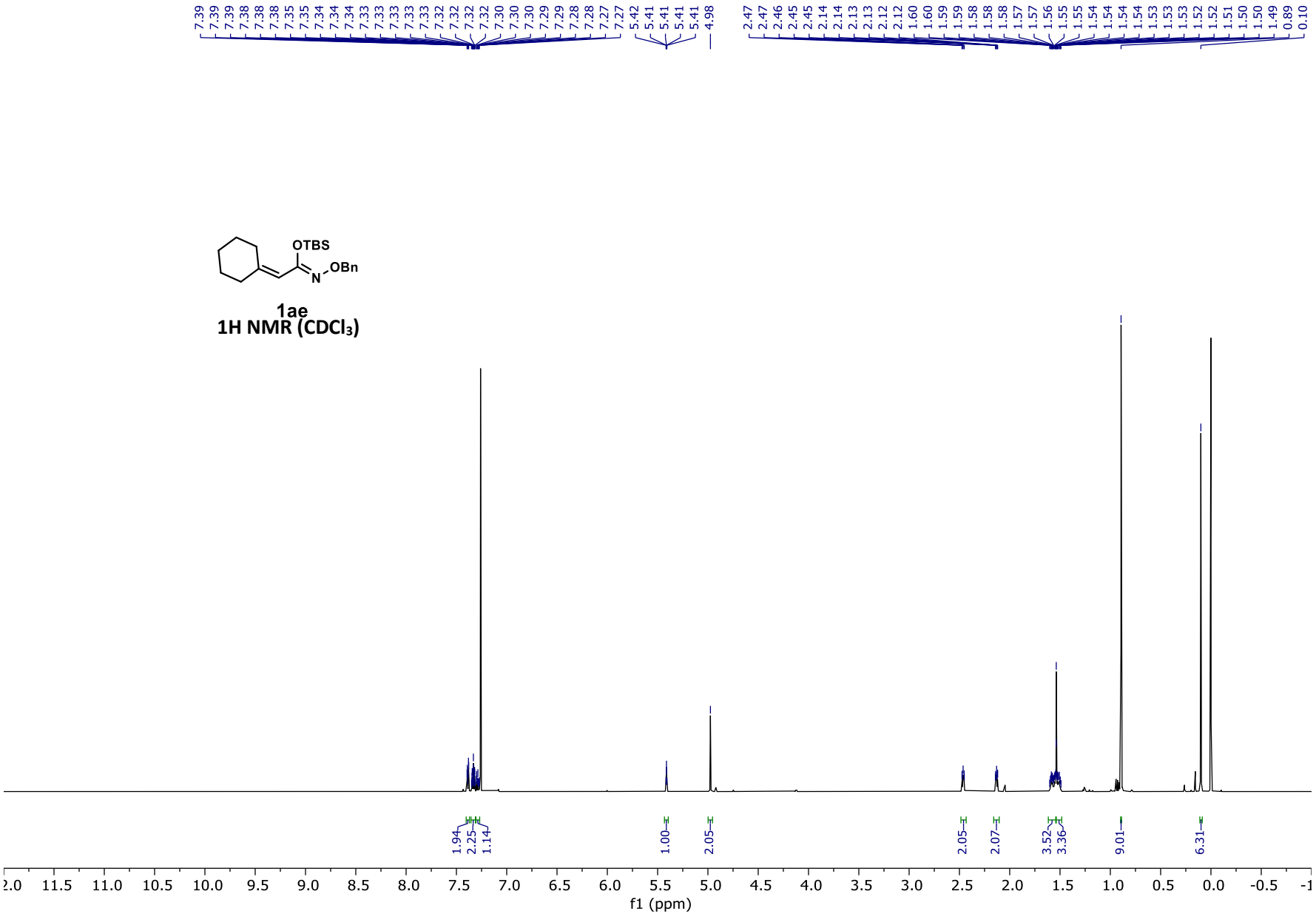
1ad

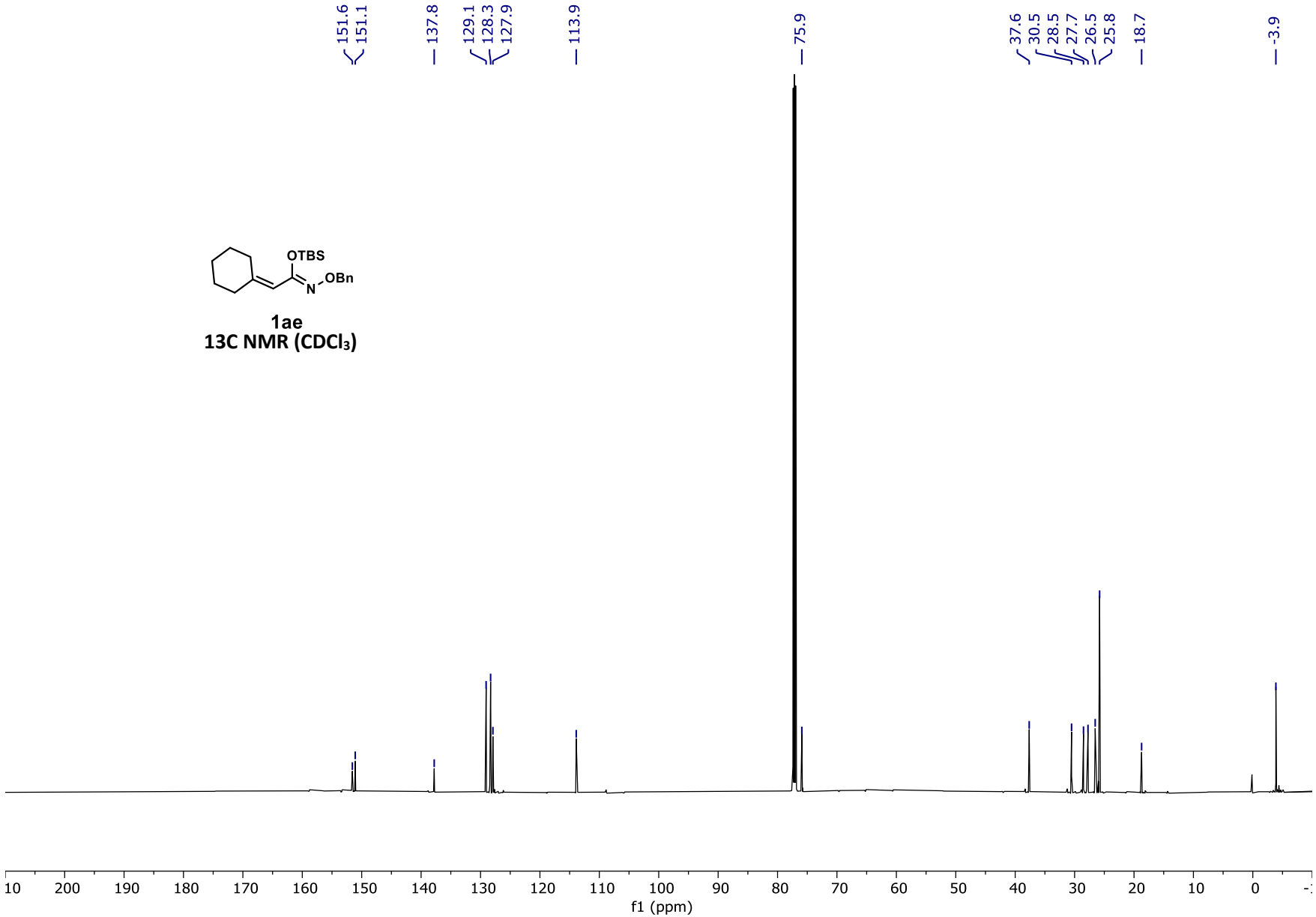
1H NMR ($CDCl_3$)

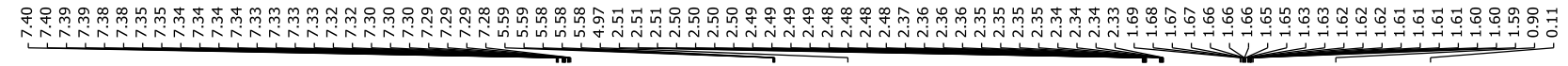


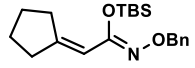
1ad

13C NMR ($CDCl_3$)


7.39 7.39 7.39 7.38 7.38 7.38 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 5.42 5.41 5.41 5.41 5.41 4.98
2.47 2.47 2.46 2.45 2.45 2.14 2.14 2.13 2.13 2.12 2.12 1.60 1.60 1.59 1.59 1.58 1.58 1.58 1.57 1.57 1.56 1.55 1.55 1.54 1.54 1.54 1.54 1.53 1.53 1.53 1.52 1.52 1.51 1.50 1.50 1.49 0.89 0.10
OTBS
OBn
N
1ae
1H NMR (CDCl3)
1.94 2.25 1.14 1.00 2.05 2.05 2.07 3.52 3.36 9.01 6.31
f1 (ppm)

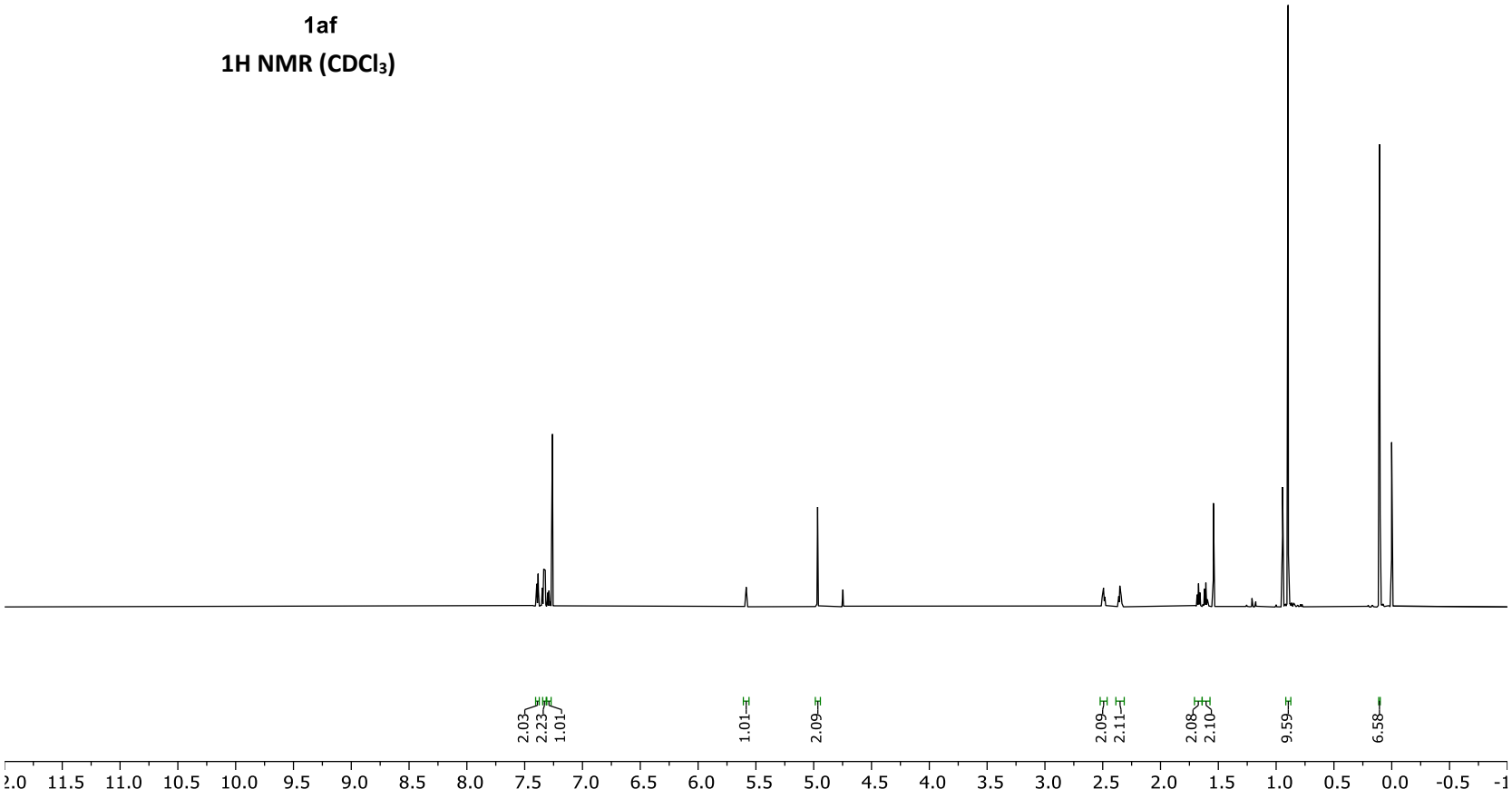

151.6
151.1
137.8
129.1
128.3
127.9
113.9
75.9
37.6
30.5
28.5
27.7
26.5
25.8
18.7
-3.9
OTBS
N
OBn
1ae
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

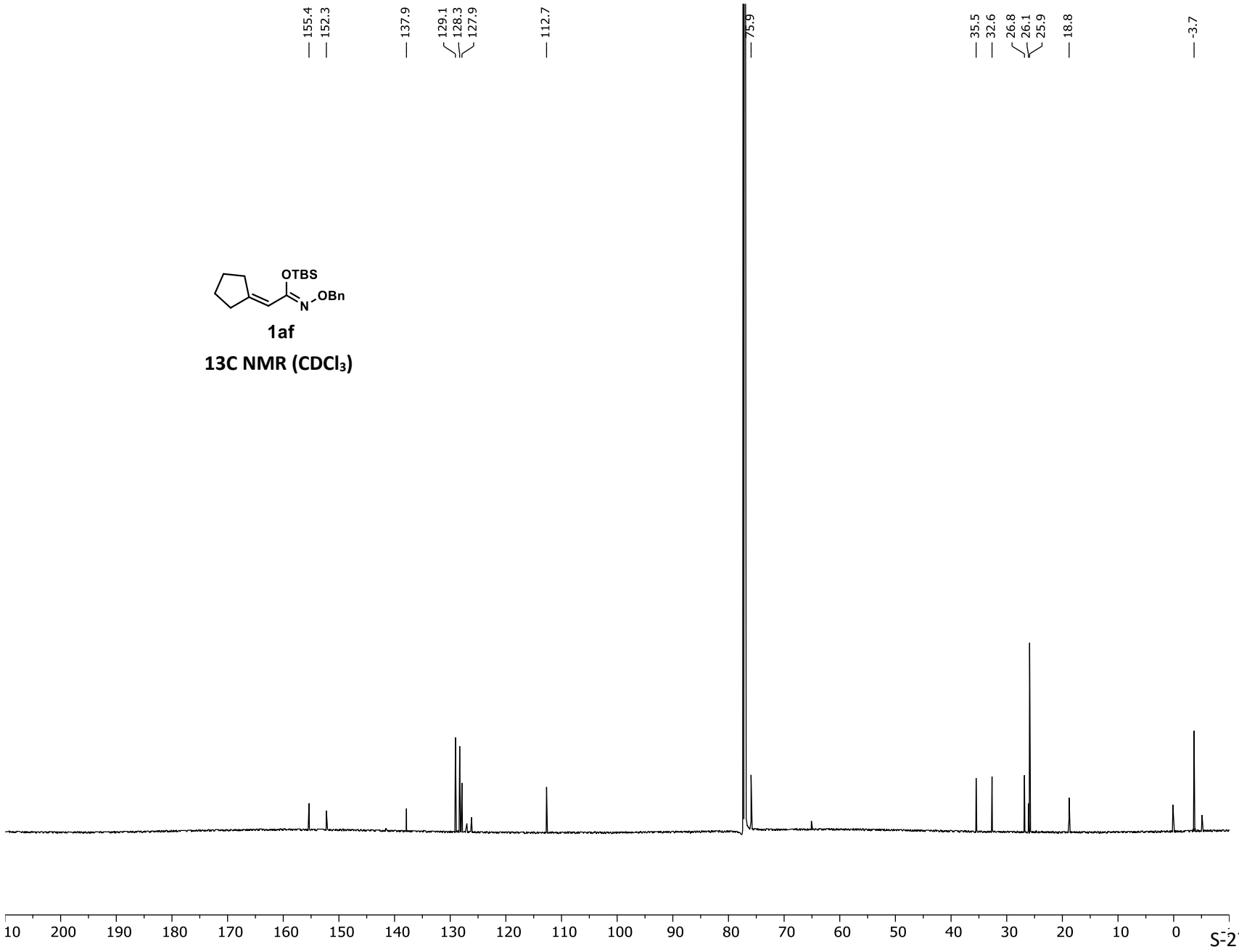


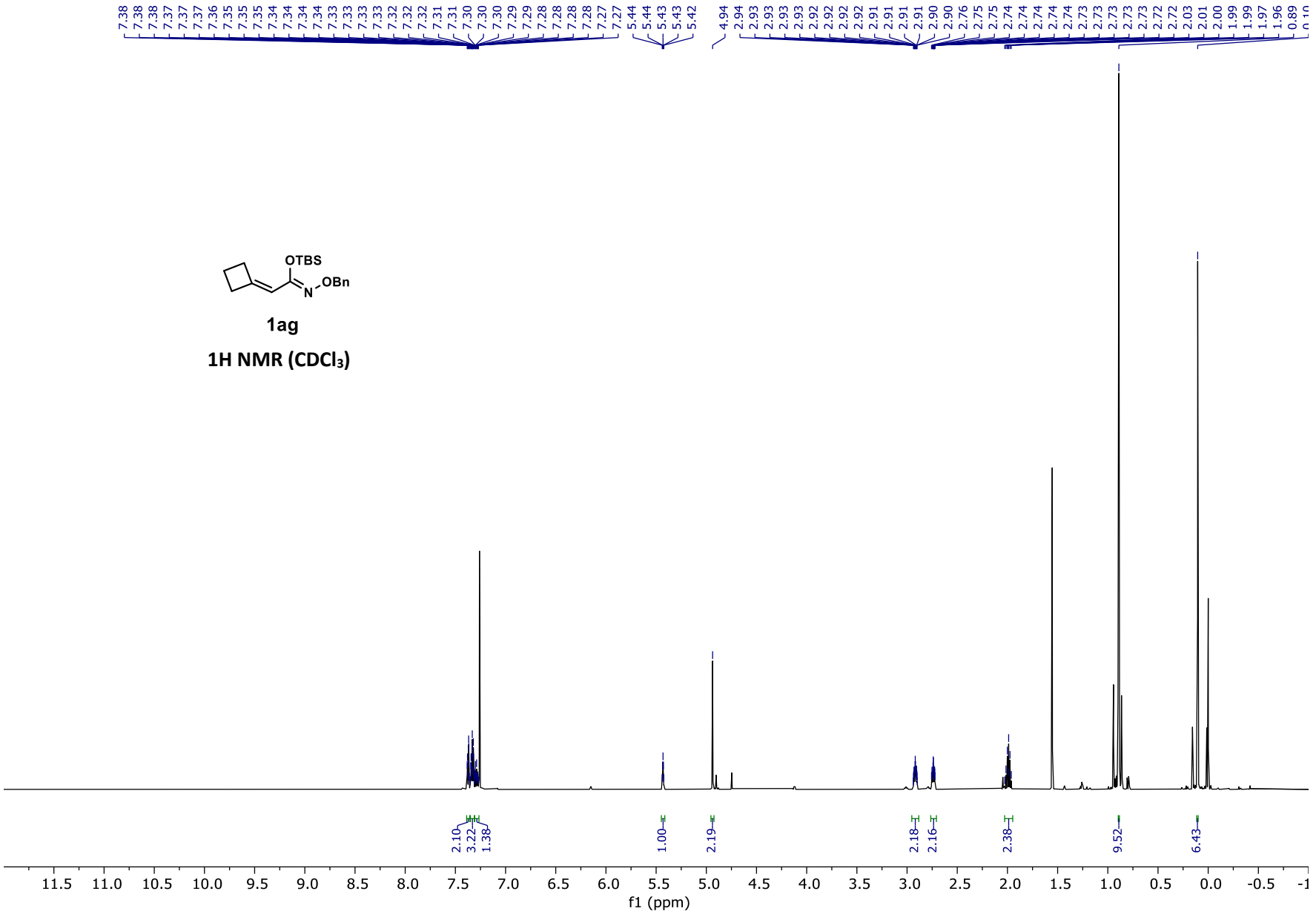


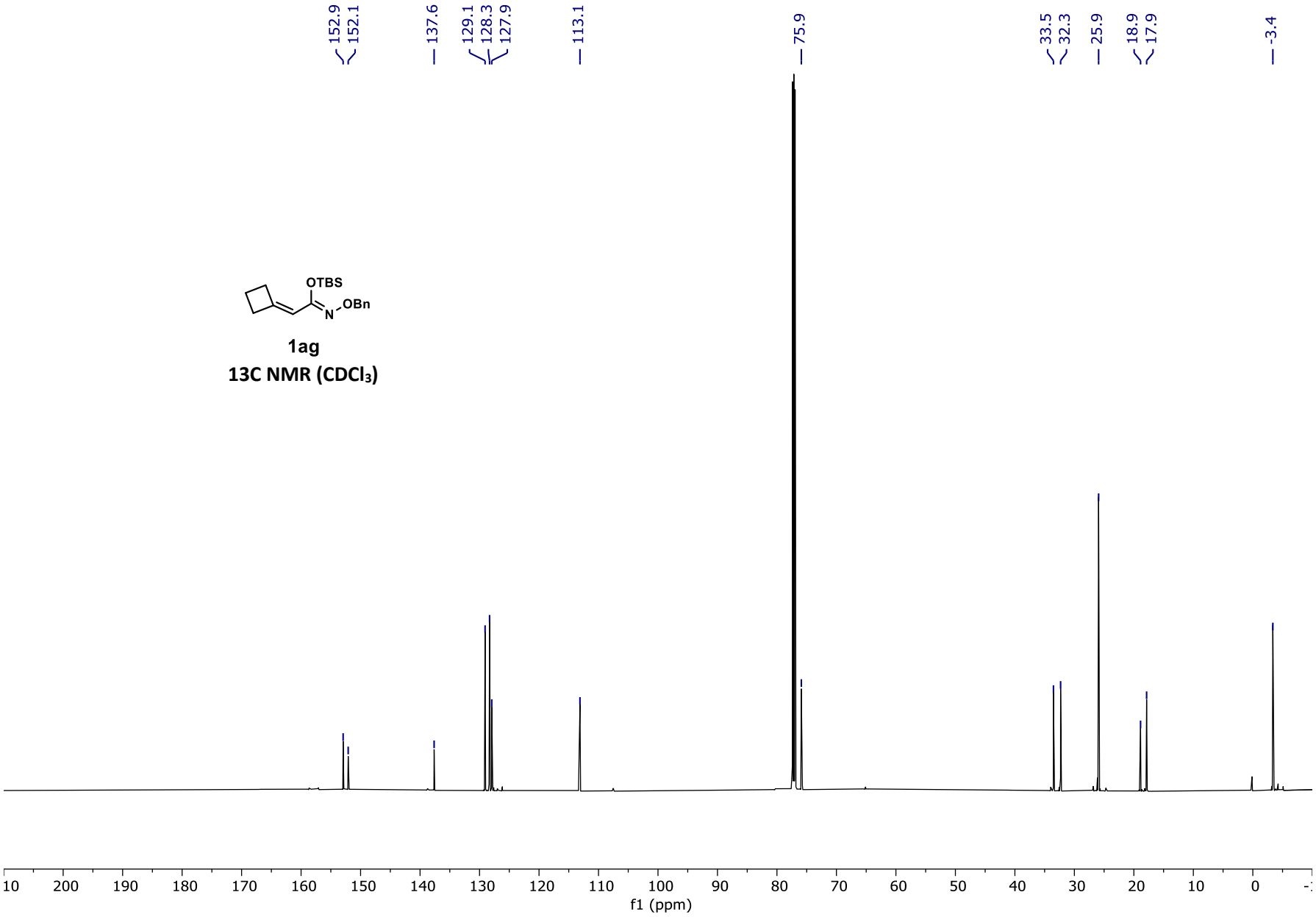
1af

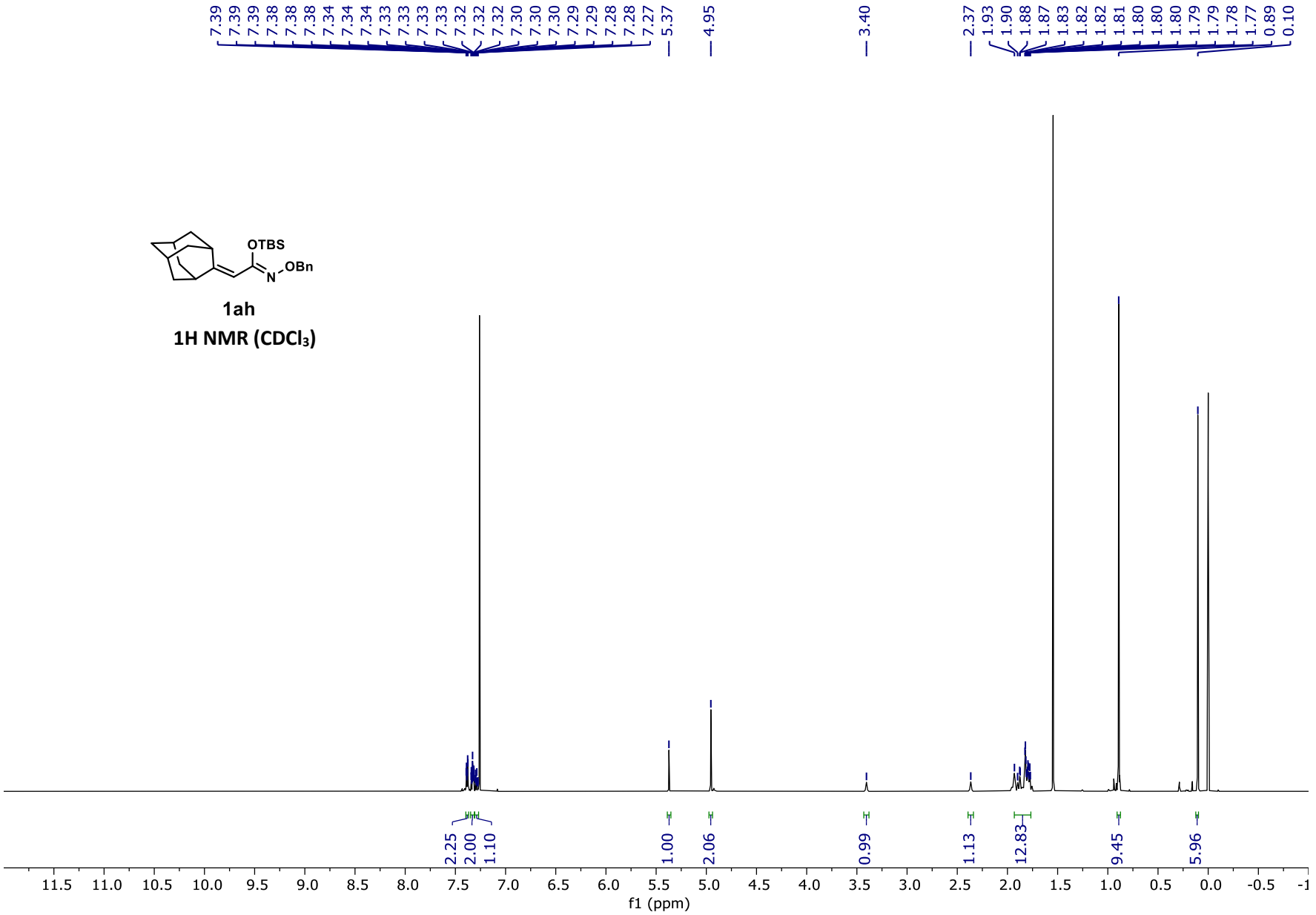
1H NMR ($CDCl_3$)

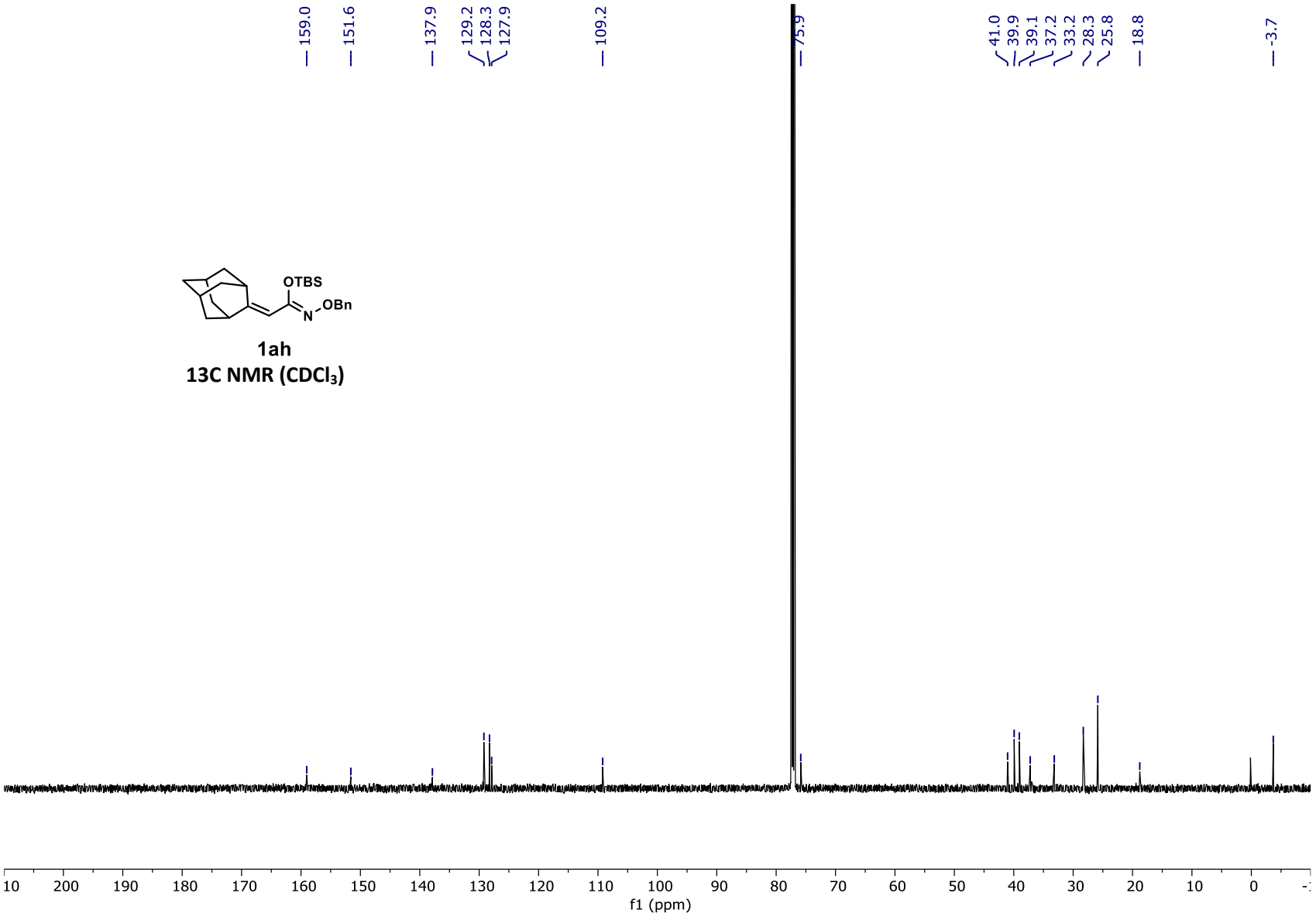


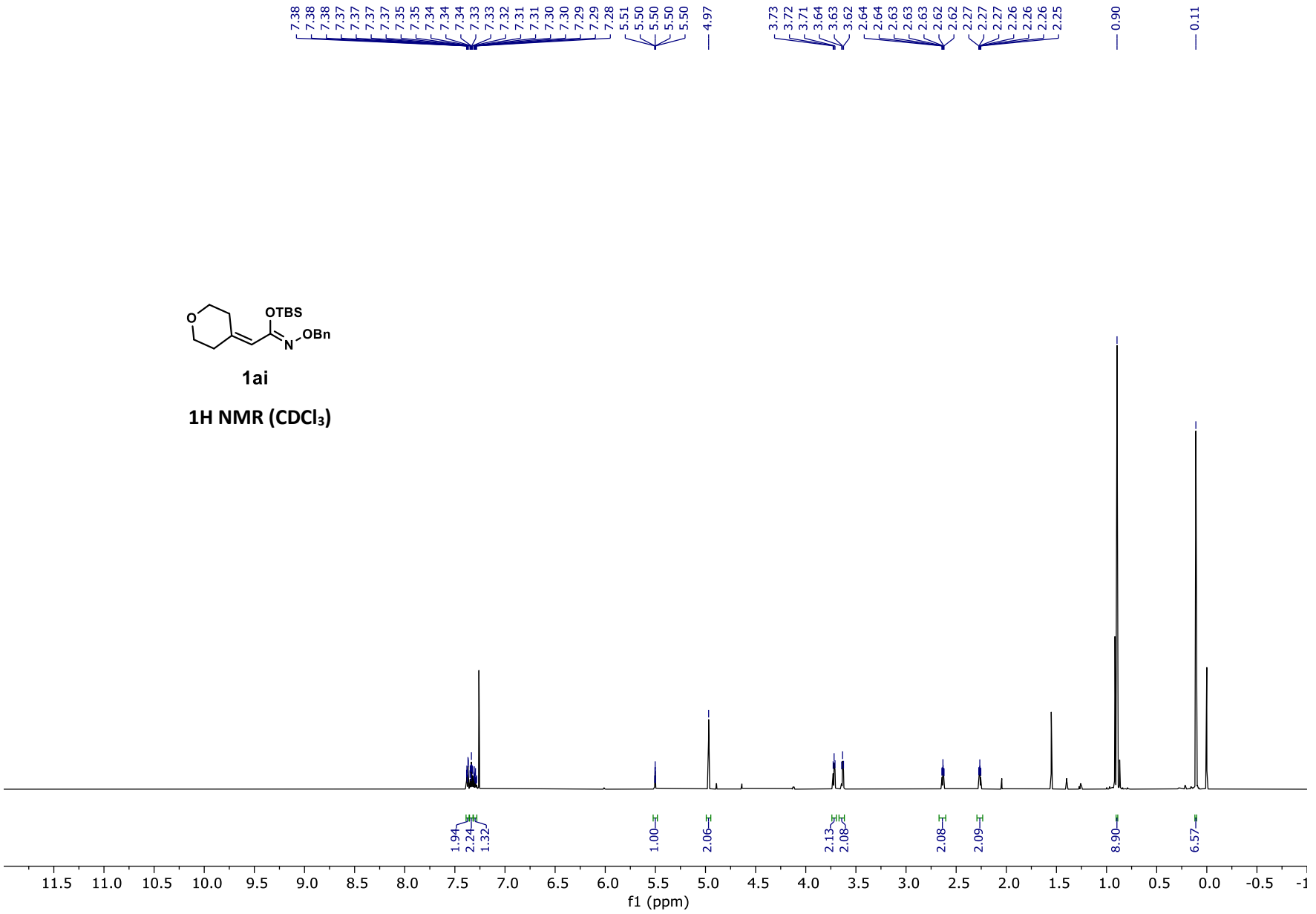

155.4
152.3
137.9
129.1
128.3
127.9
112.7
75.9
35.5
32.6
26.8
26.1
25.9
18.8
-3.7
OTBS
N
OBn
1af
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

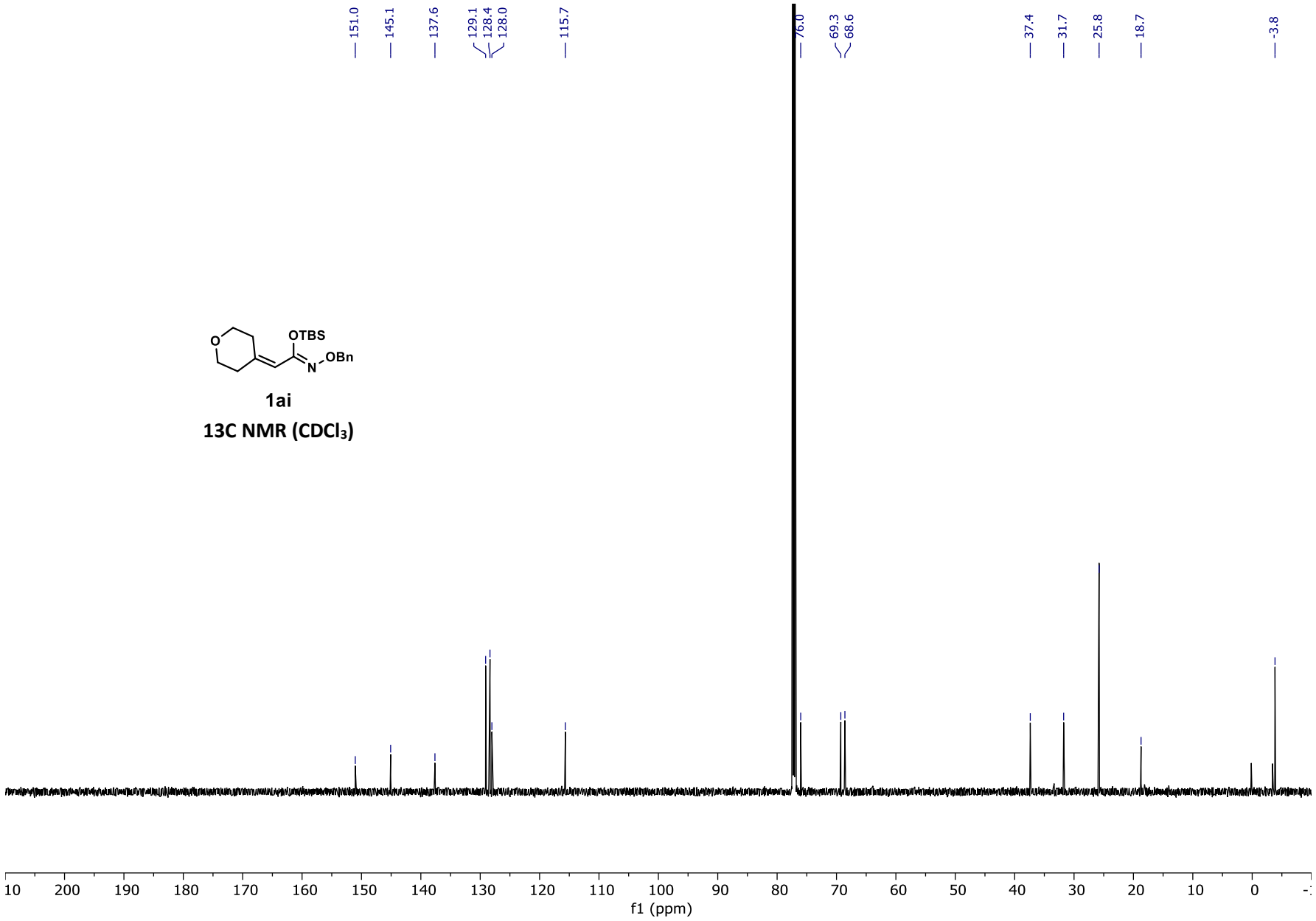

OTBS
N
OBn
1ag
1H NMR (CDCl3)
f1 (ppm)

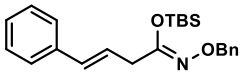

152.9
152.1
137.6
129.1
128.3
127.9
113.1
75.9
33.5
32.3
25.9
18.9
17.9
-3.4
OTBS
N
OBn
1ag
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.39 7.39 7.39 7.38 7.38 7.38 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.27 5.37 4.95 3.40 2.37 1.93 1.90 1.88 1.87 1.83 1.82 1.82 1.81 1.80 1.80 1.80 1.79 1.79 1.78 1.77 0.89 0.10
OTBS
N
OBn
1ah
1H NMR (CDCl3)
2.25 2.00 1.10 1.00 2.06 0.99 1.13 12.83 9.45 5.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


159.0
151.6
137.9
129.2
128.3
127.9
109.2
75.9
41.0
39.9
39.1
37.2
33.2
28.3
25.8
18.8
-3.7
OTBS
N
OBn
1ah
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

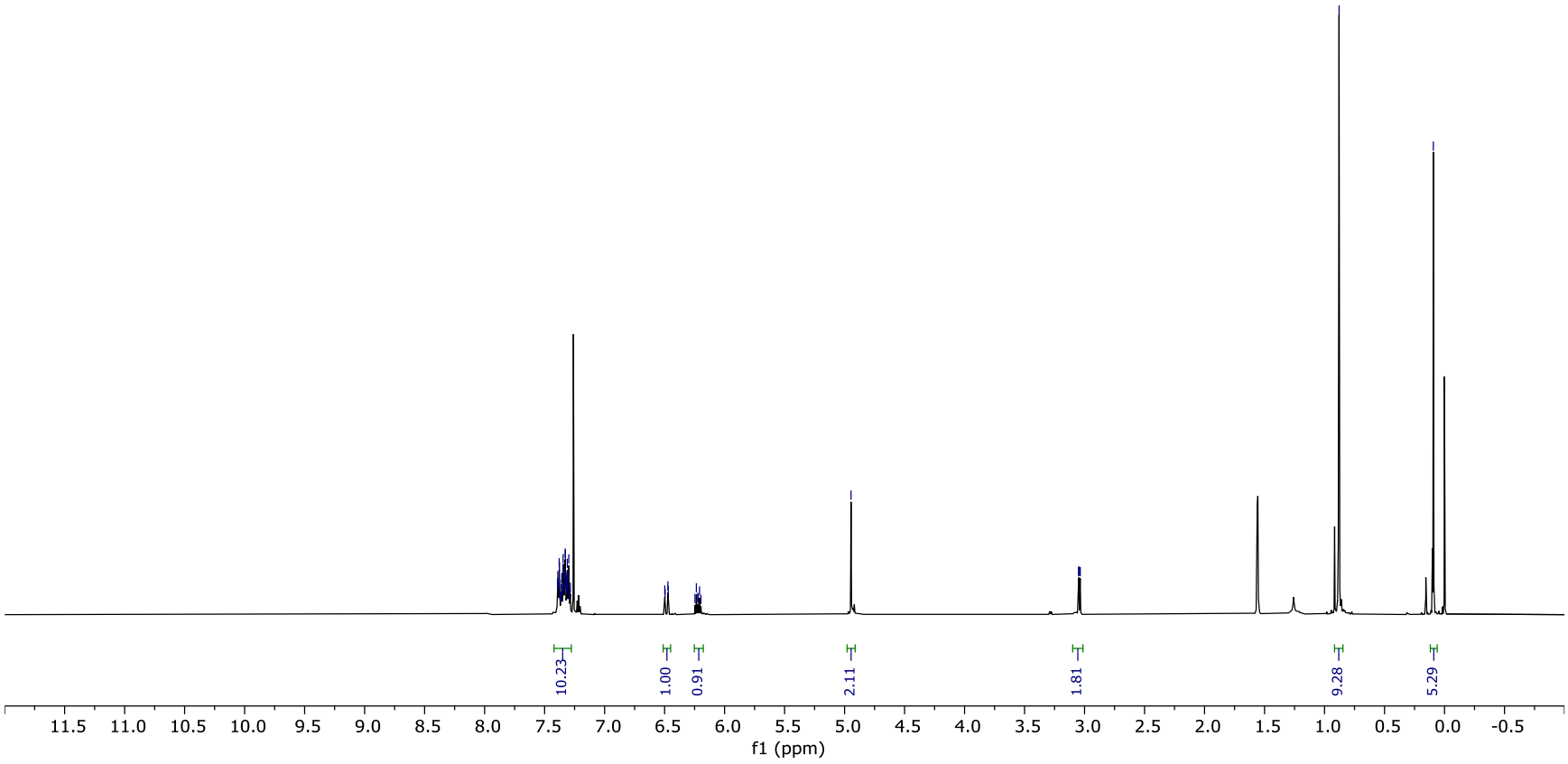

7.38 7.38 7.38 7.37 7.37 7.37 7.37 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28
5.51 5.50 5.50 5.50
4.97
3.73 3.72 3.71 3.64 3.63 3.62
2.64 2.64 2.63 2.63 2.63 2.62 2.62
2.27 2.27 2.27 2.26 2.26 2.25
0.90
0.11
O
OTBS
N
OBn
1ai
1H NMR (CDCl3)
1.94 2.24 1.32 1.00 2.06 2.13 2.08 2.08 2.09 8.90 6.57
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

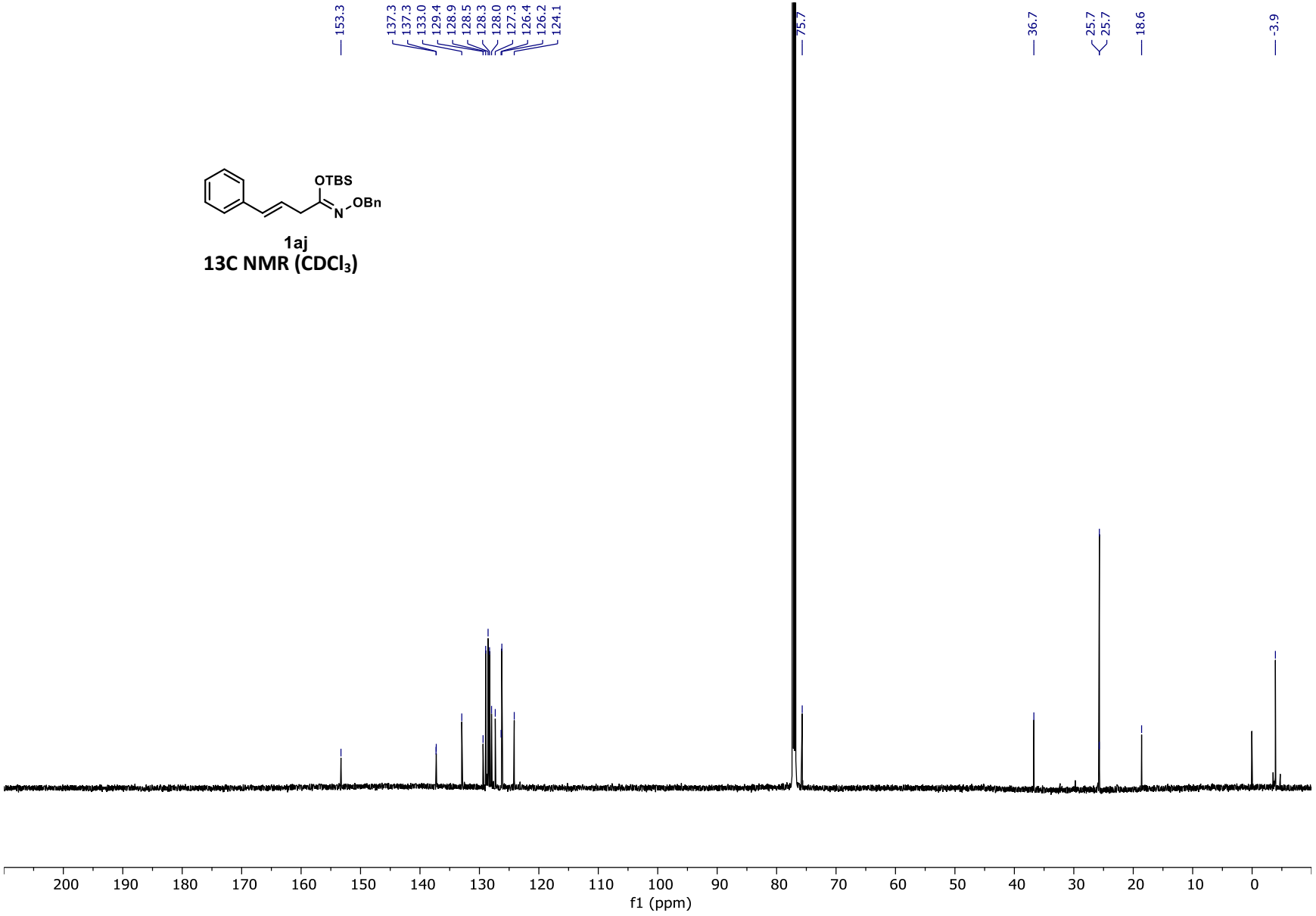

151.0
145.1
137.6
129.1
128.4
128.0
115.7
76.0
69.3
68.6
37.4
31.7
25.8
18.7
-3.8
OTBS
OBn
N
O
1ai
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

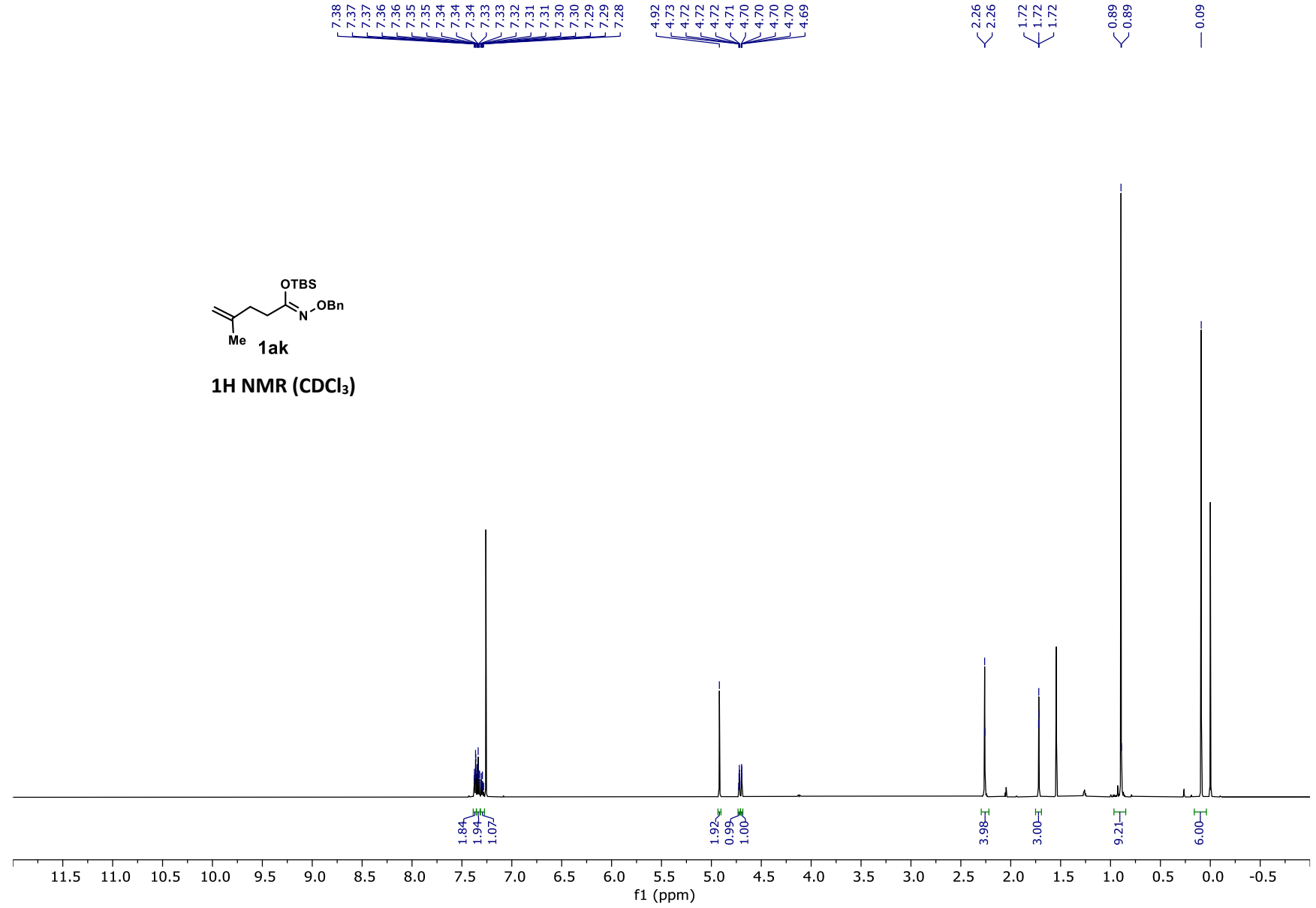


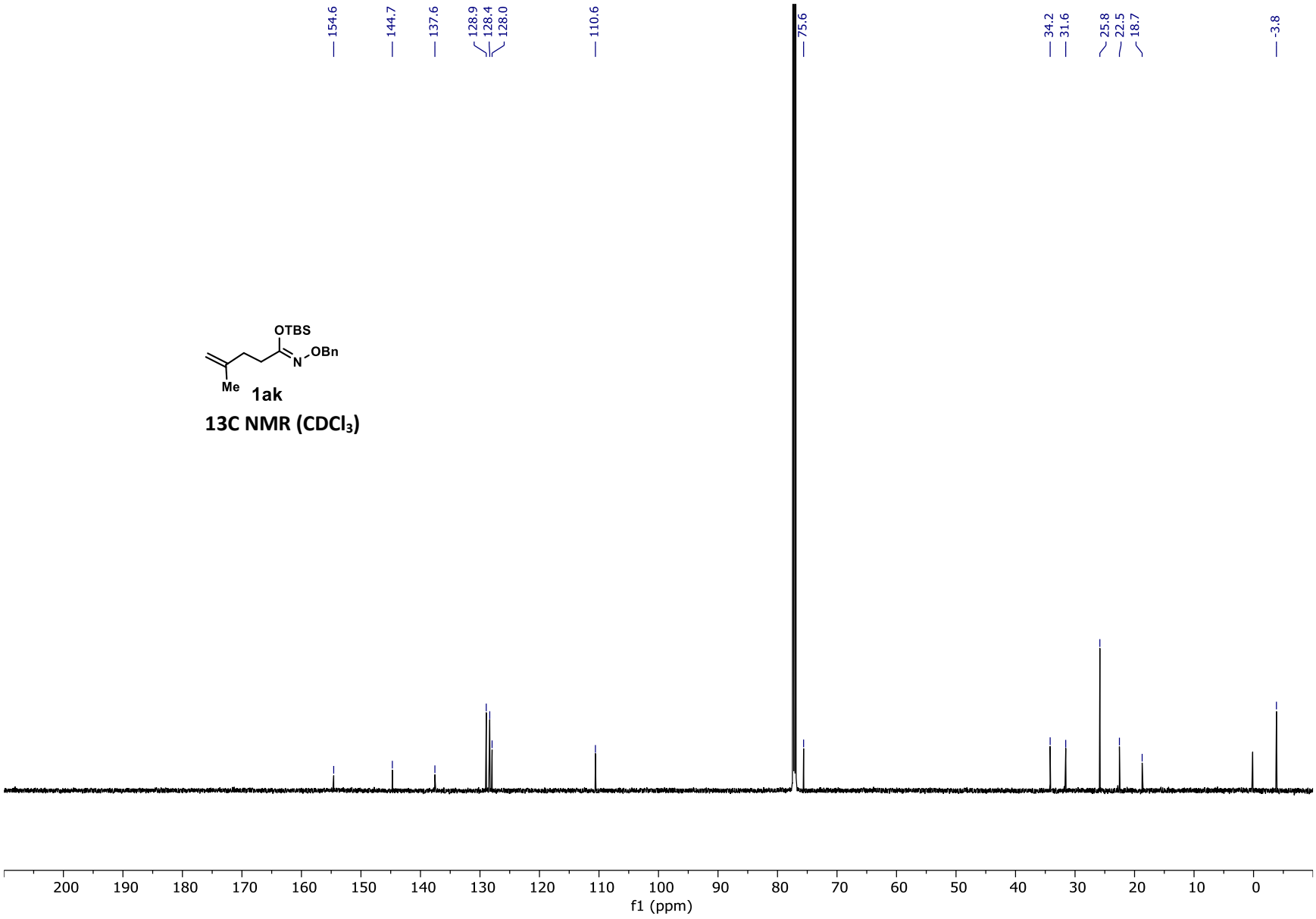
1aj

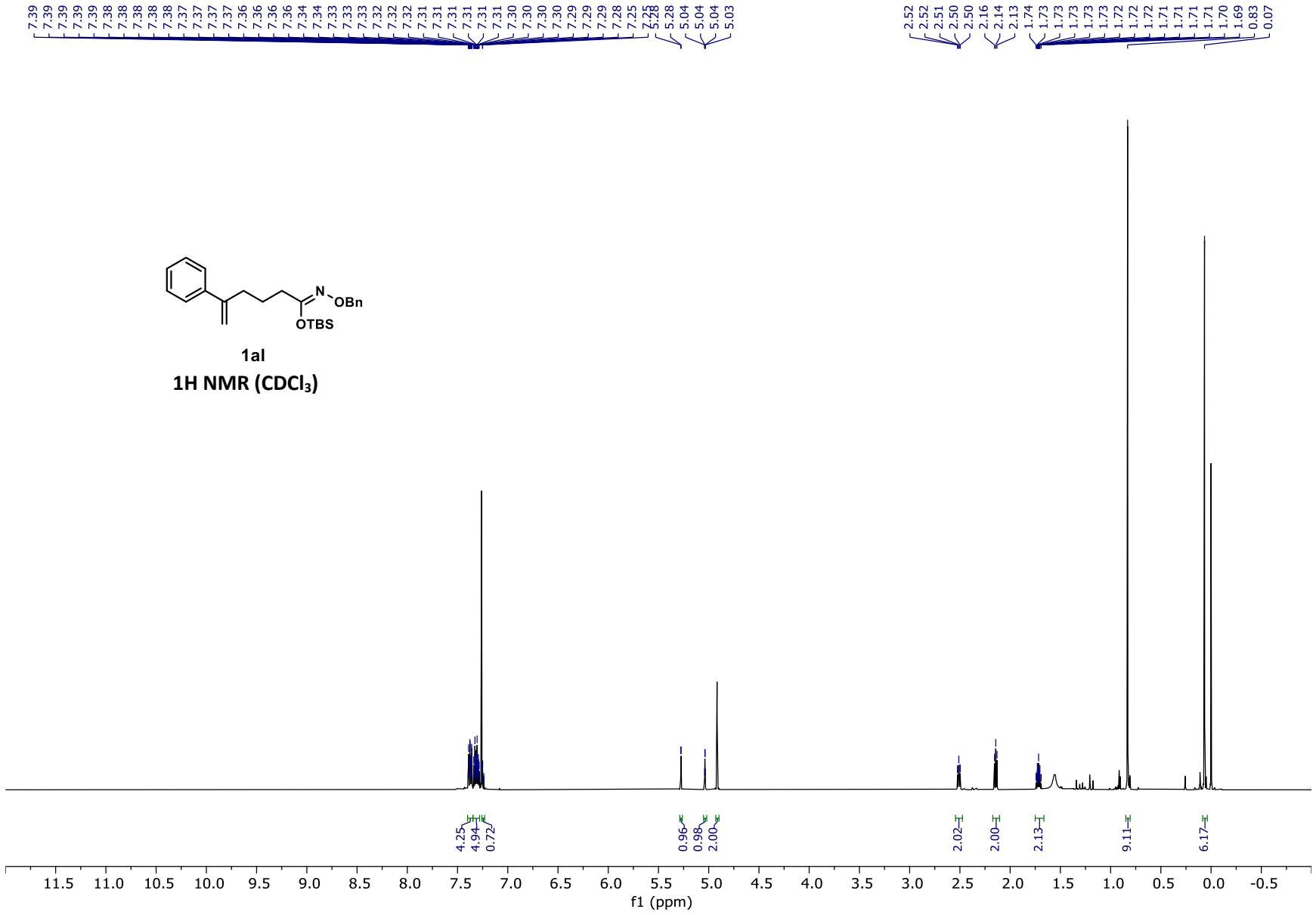
1H NMR ($CDCl_3$)

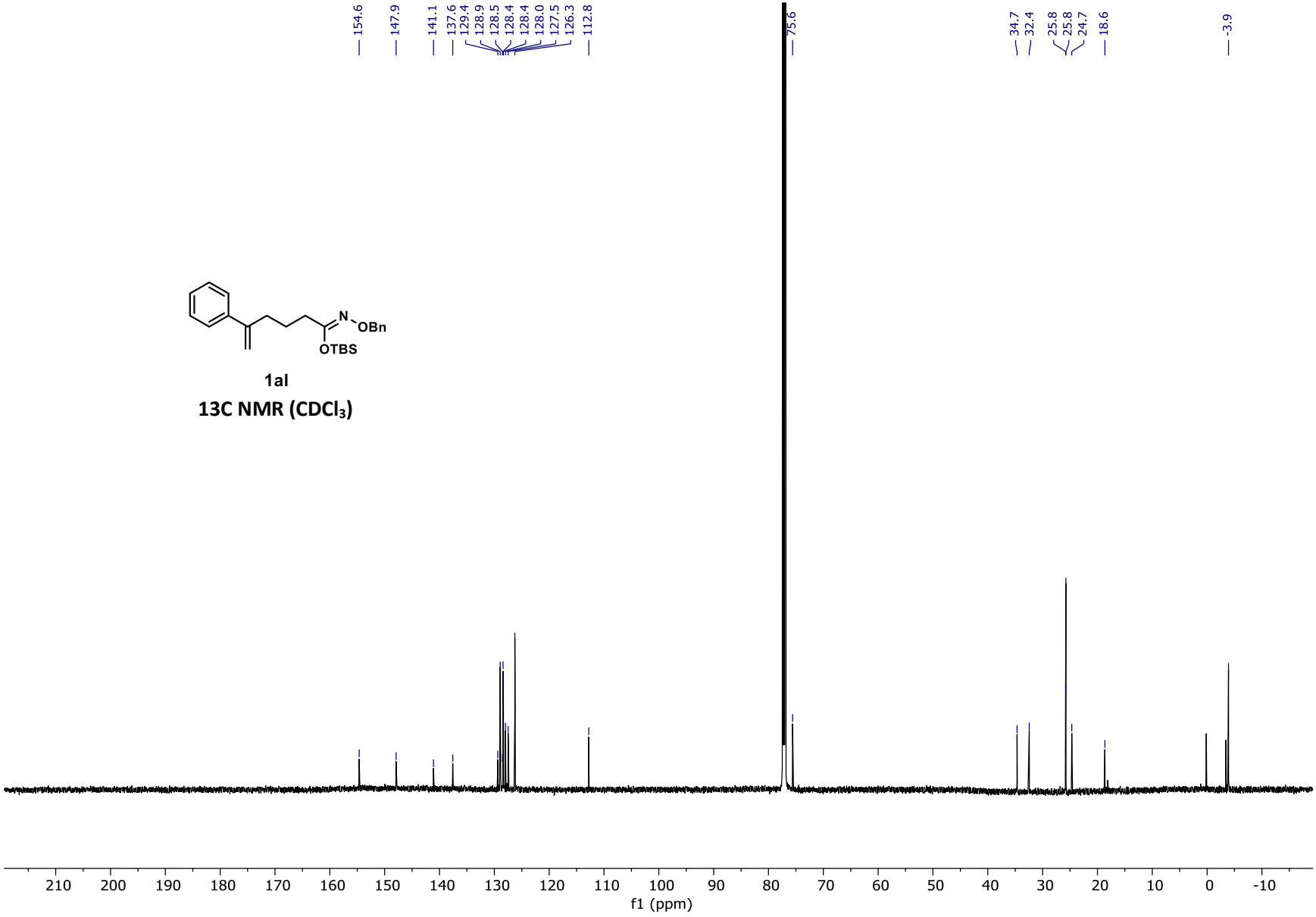



153.3
137.3
137.3
133.0
129.4
128.9
128.5
128.3
128.0
127.3
126.4
126.2
124.1
75.7
36.7
25.7
25.7
18.6
-3.9
OTBS
N
OBn
1aj
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
4.92
4.73
4.72
4.72
4.72
4.71
4.70
4.70
4.70
4.70
4.69
2.26
2.26
1.72
1.72
1.72
0.89
0.89
0.09
OTBS
N
OBn
Me
1ak
1H NMR (CDCl3)
1.84
1.94
1.07
1.92
0.99
1.00
3.98
3.00
9.21
6.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

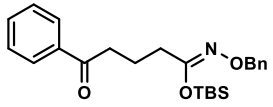

154.6
144.7
137.6
128.9
128.4
128.0
110.6
75.6
34.2
31.6
25.8
22.5
18.7
-3.8
OTBS
N
OBn
Me
1ak
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.39 7.39 7.39 7.39 7.38 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.31 7.31 7.30 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.25 5.28 5.04 5.04 5.04 5.03
2.52 2.52 2.51 2.50 2.50 2.16 2.14 2.13 1.74 1.73 1.73 1.73 1.73 1.72 1.72 1.72 1.71 1.71 1.71 1.71 1.70 1.69 0.83 0.07
N
OBn
OTBS
1al
1H NMR (CDCl3)
4.25
4.94
0.72
0.96
0.98
2.00
2.02
2.00
2.13
9.11
6.17
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



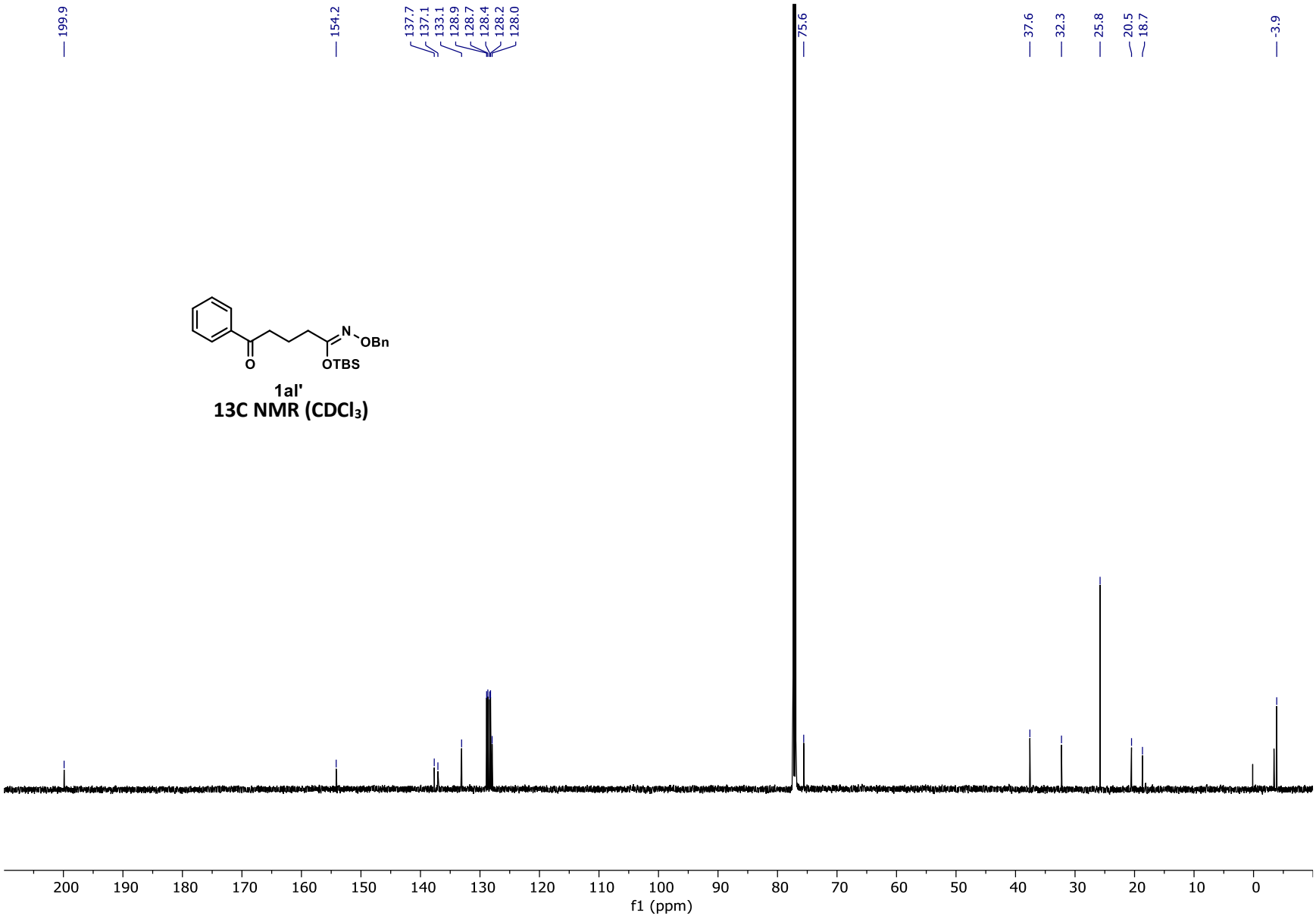
1al

13C NMR ($CDCl_3$)



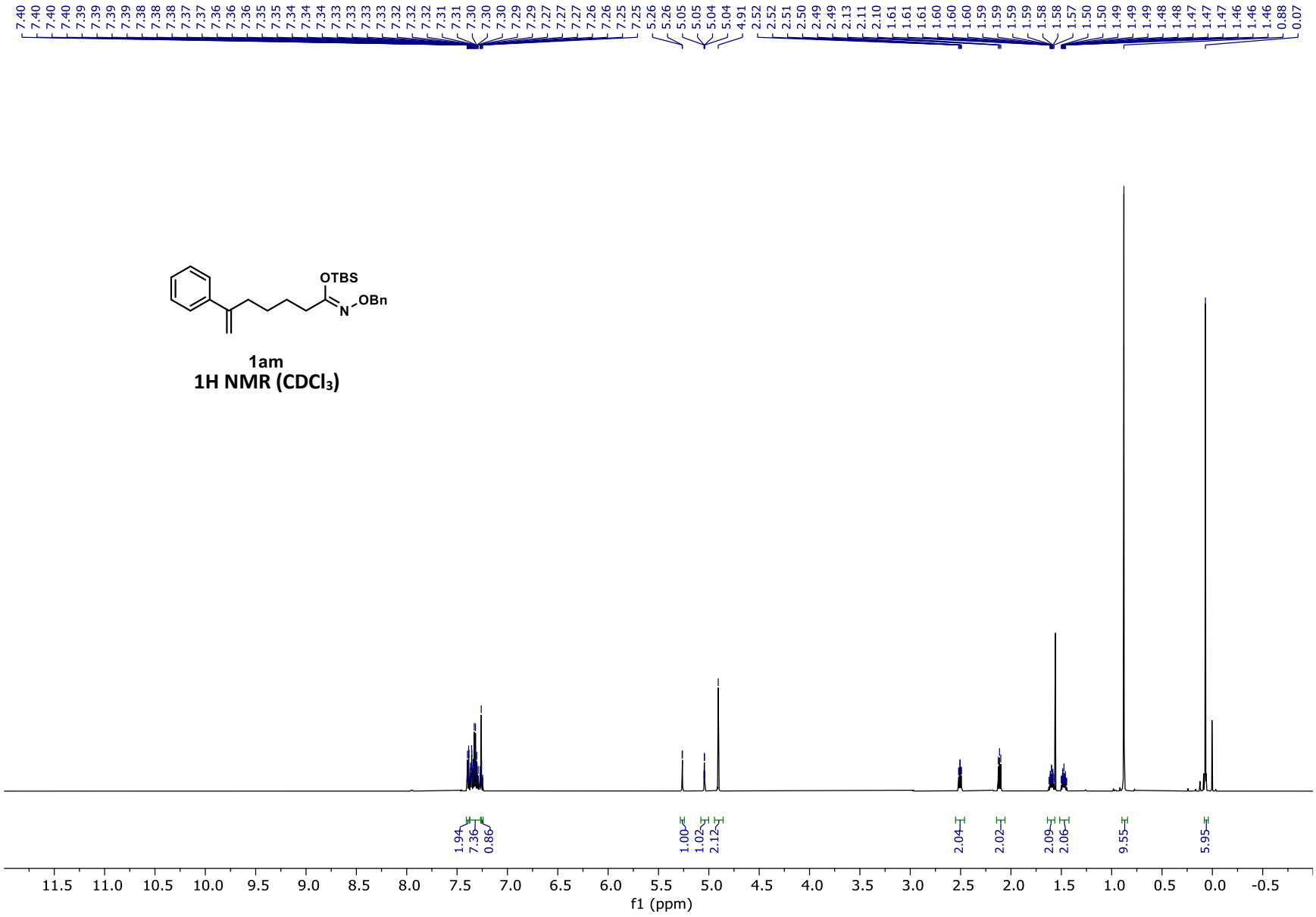
1al'

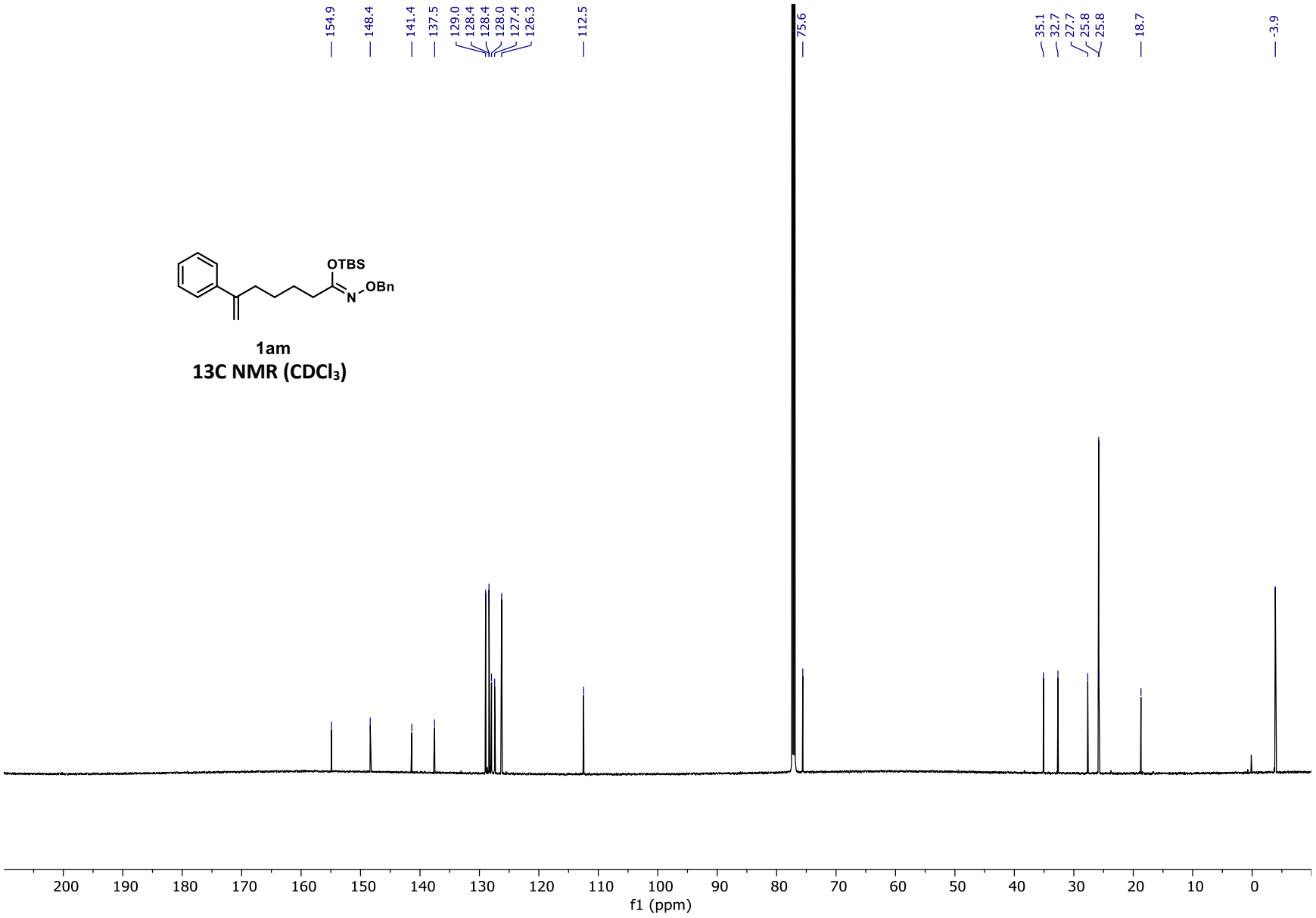
1H NMR ($CDCl_3$)



1al'

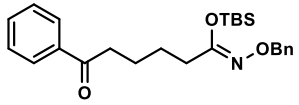
13C NMR ($CDCl_3$)


OTBS
N
OBn
1am
1H NMR (CDCl3)
f1 (ppm)



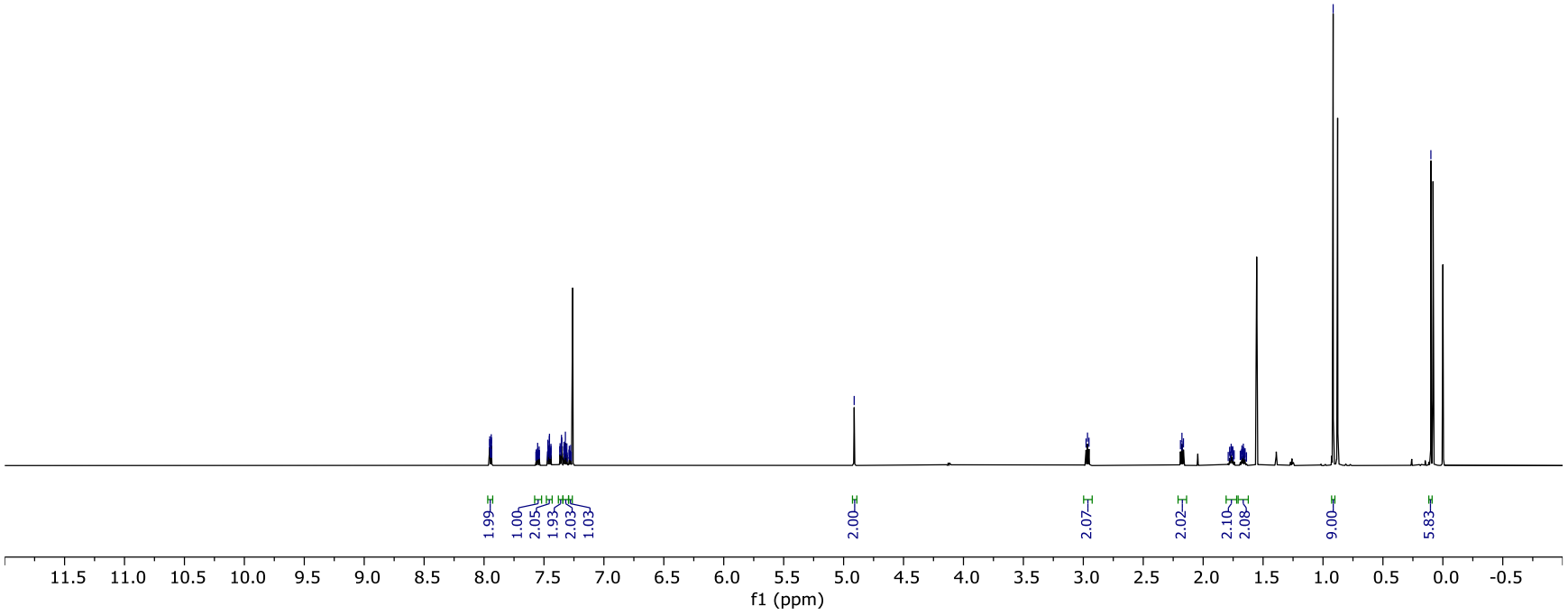
1am

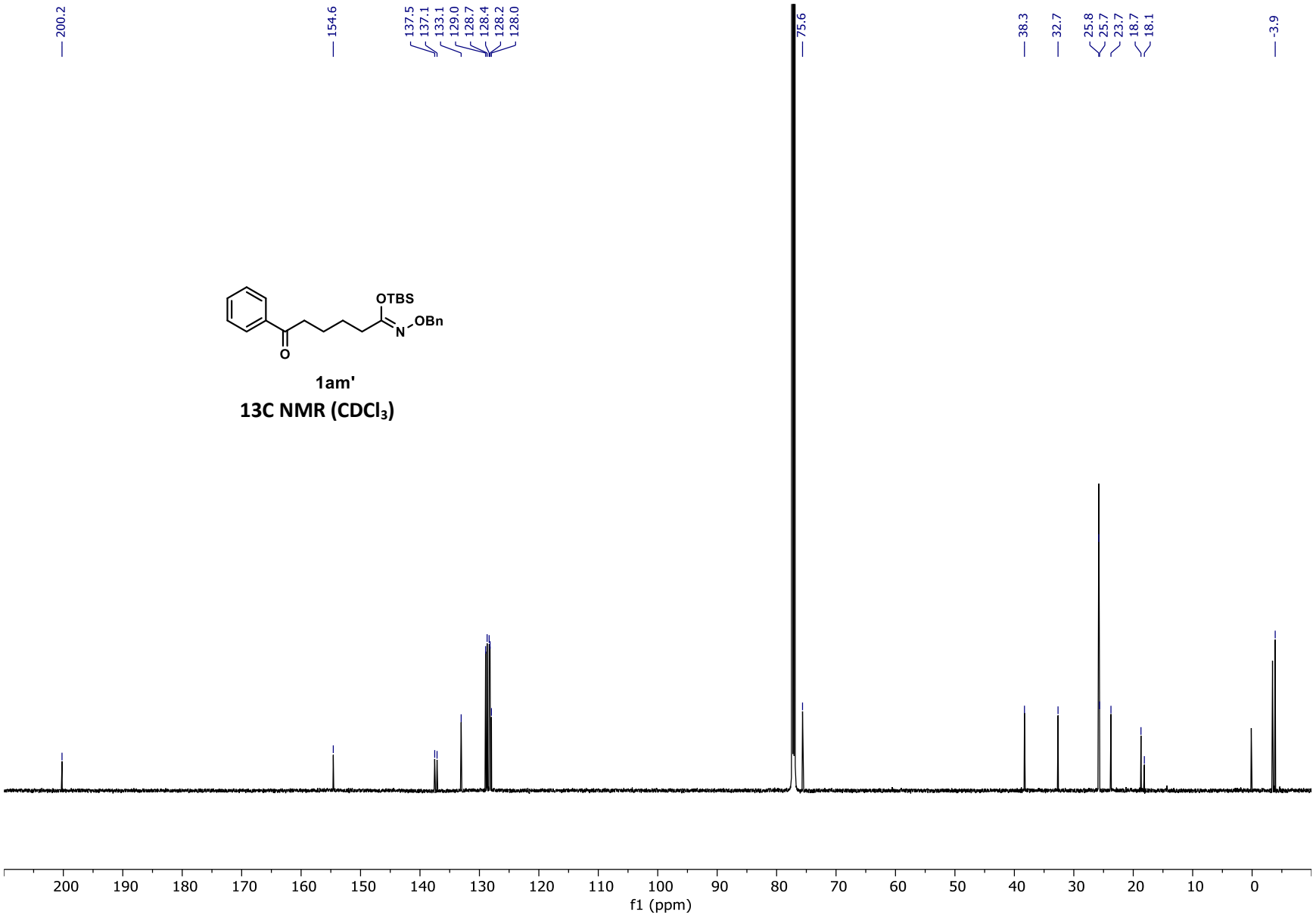
13C NMR ($CDCl_3$)

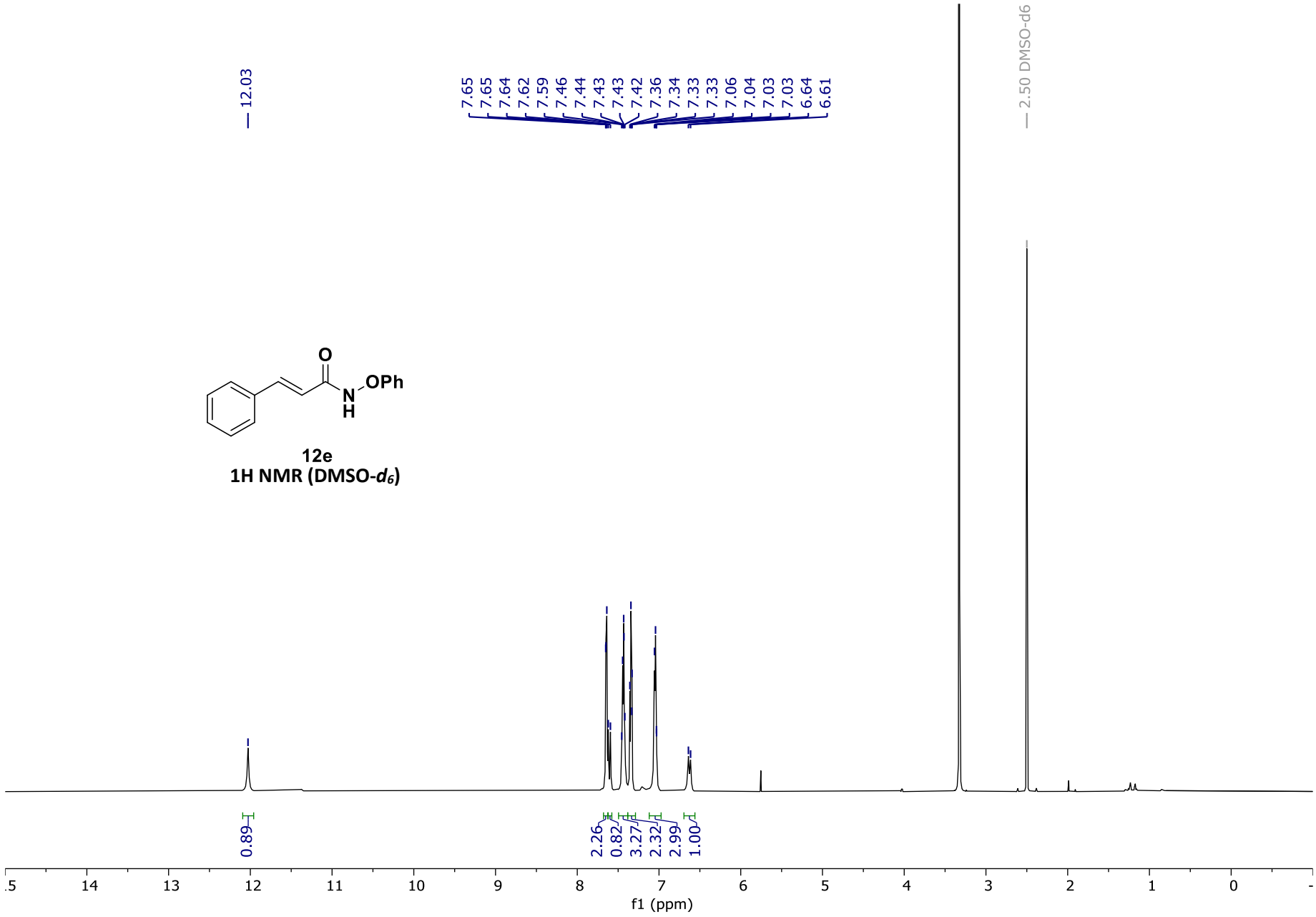


1am'

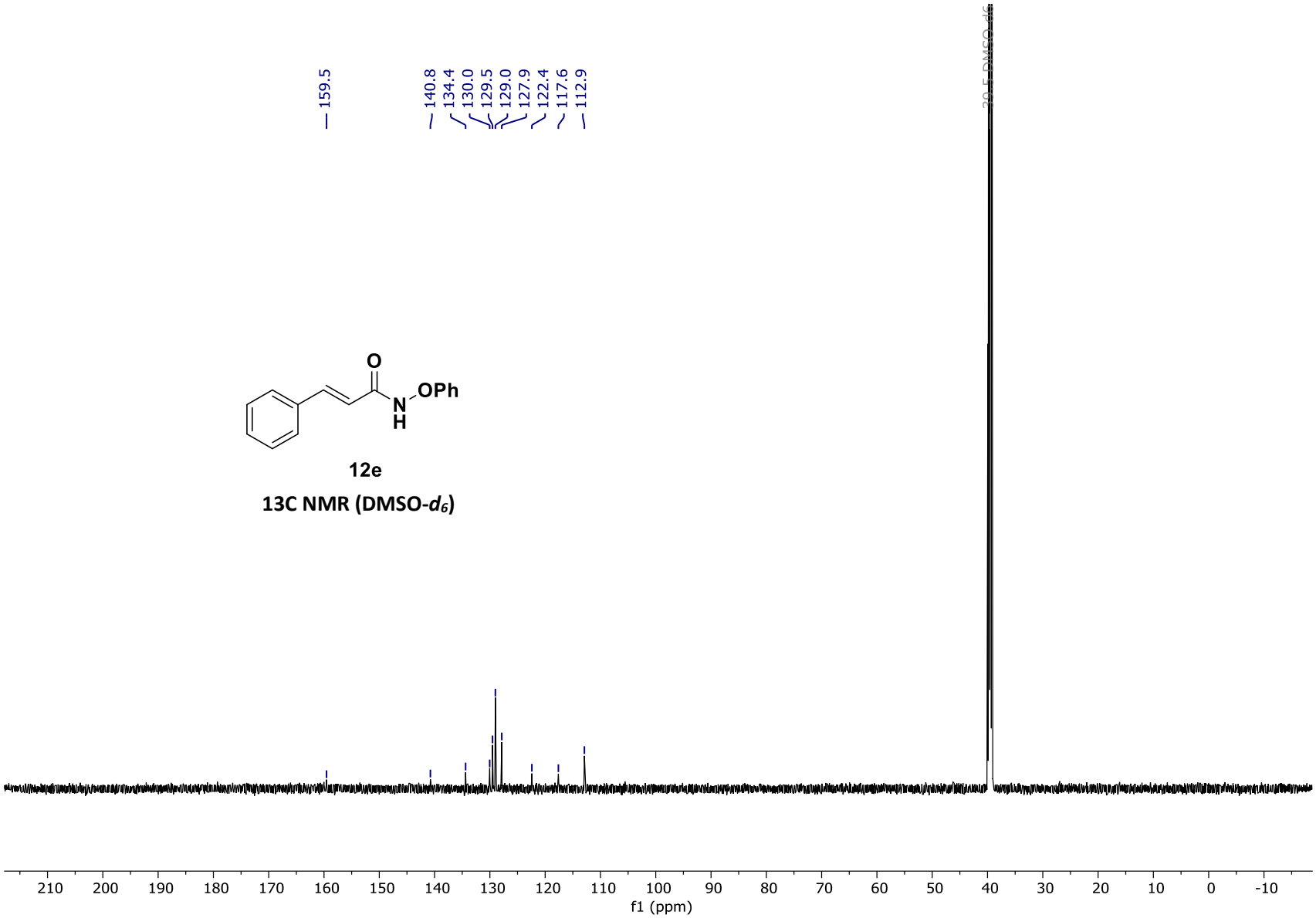
1H NMR ($CDCl_3$)




200.2
154.6
137.5
137.1
133.1
129.0
128.7
128.4
128.2
128.0
75.6
38.3
32.7
25.8
25.7
23.7
18.7
18.1
-3.9
OTBS
N
OBn
O
1am'
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

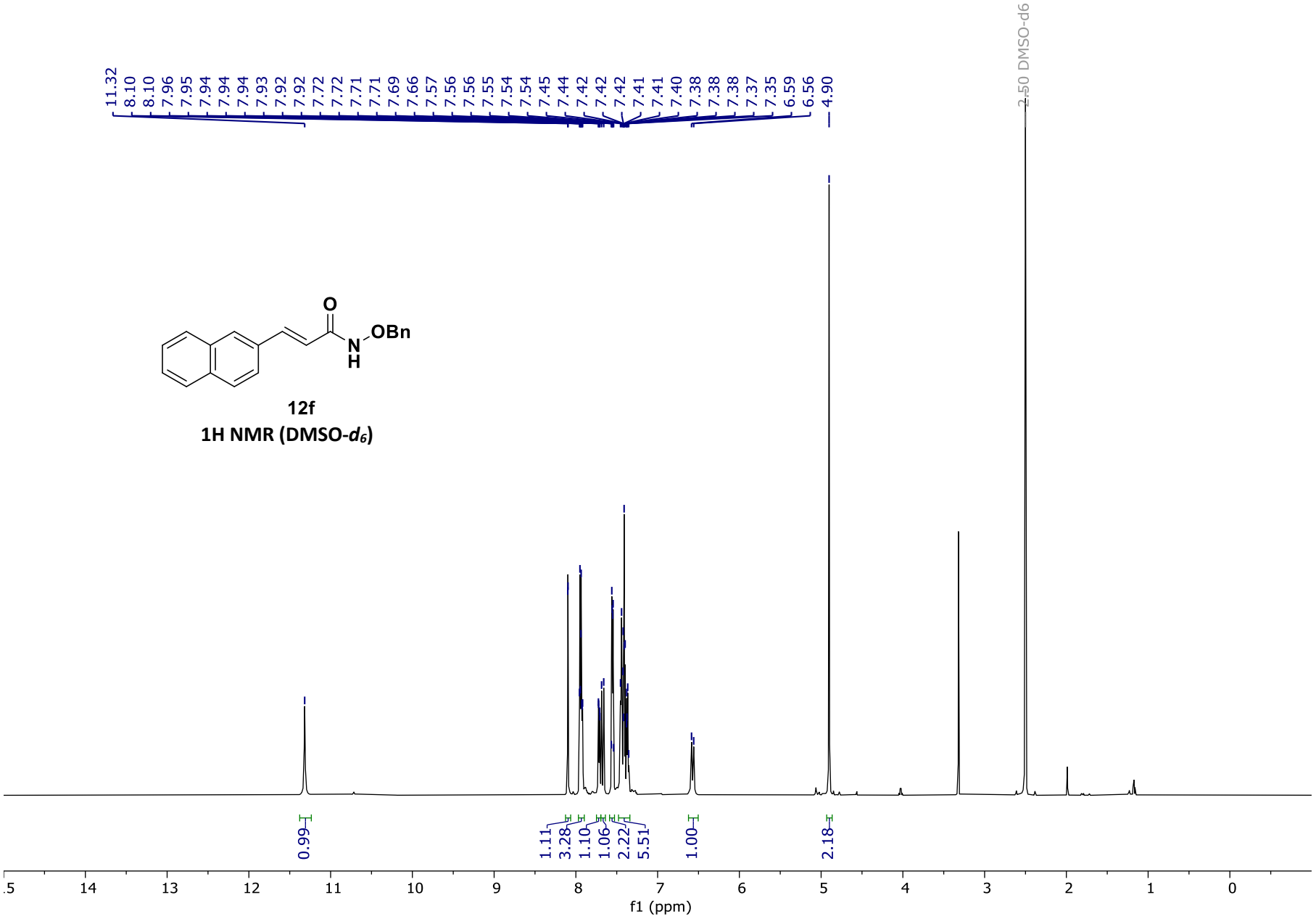


12e
1H NMR (DMSO-d_6)



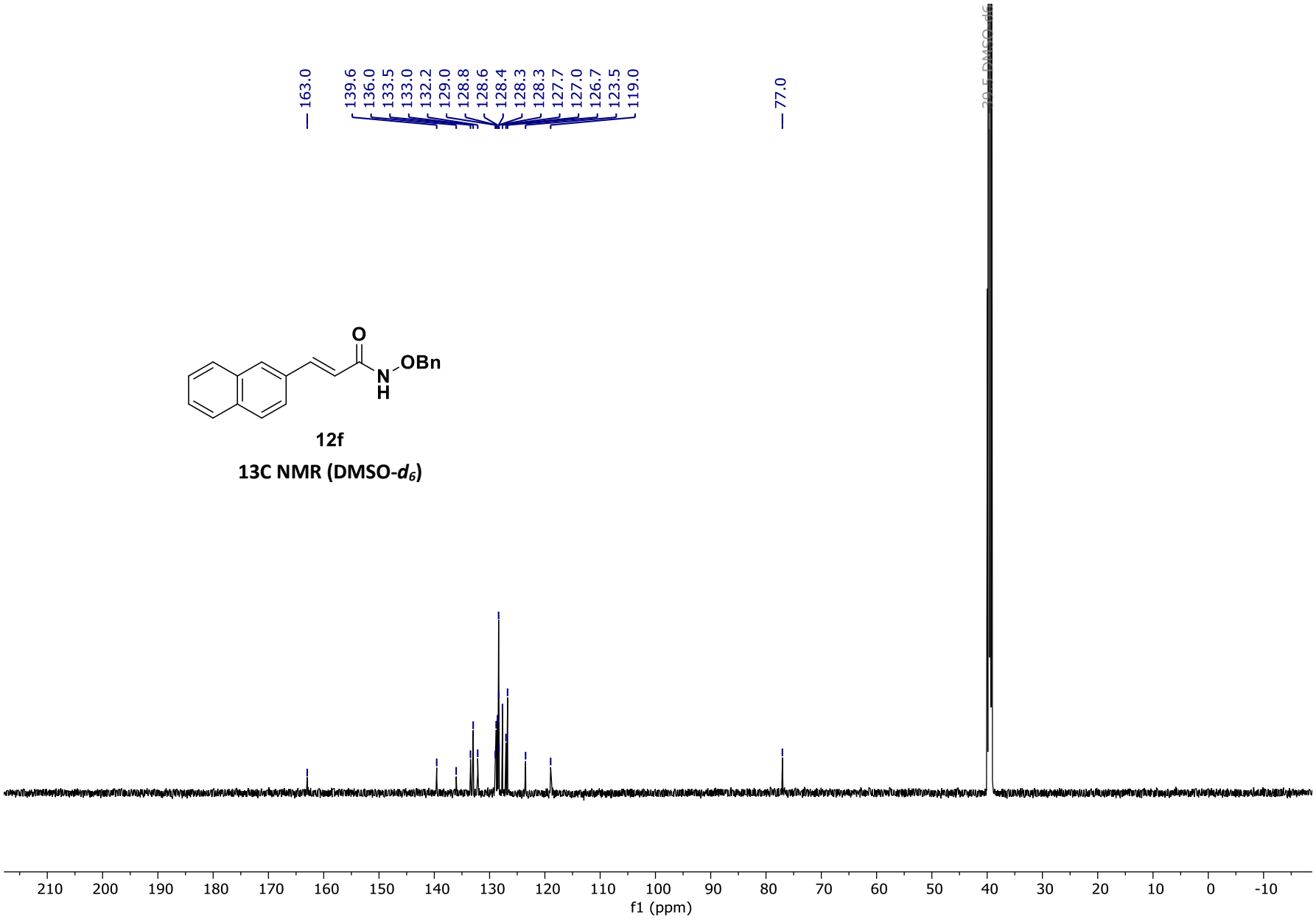
12e

13C NMR (DMSO-d_6)



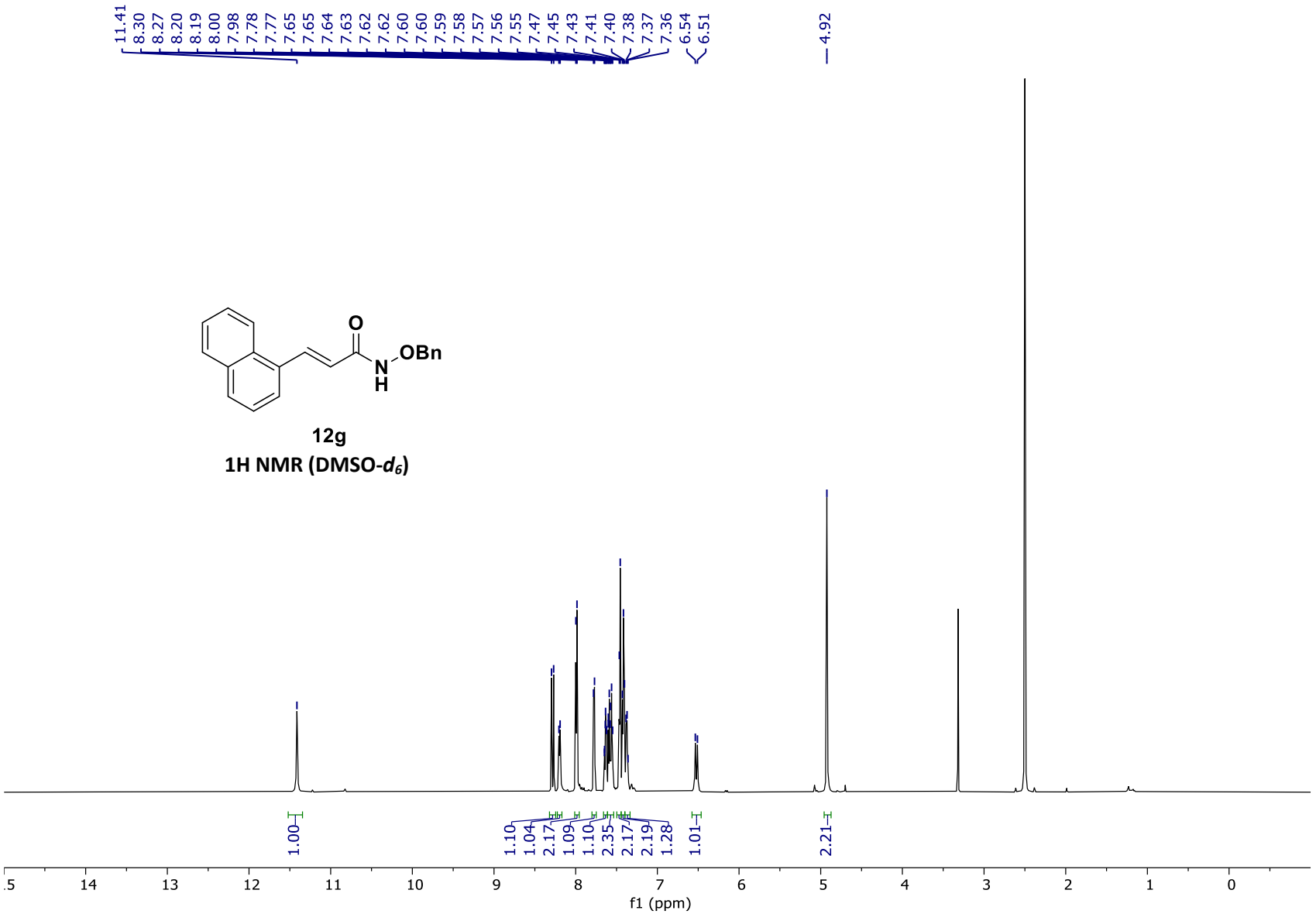
12f

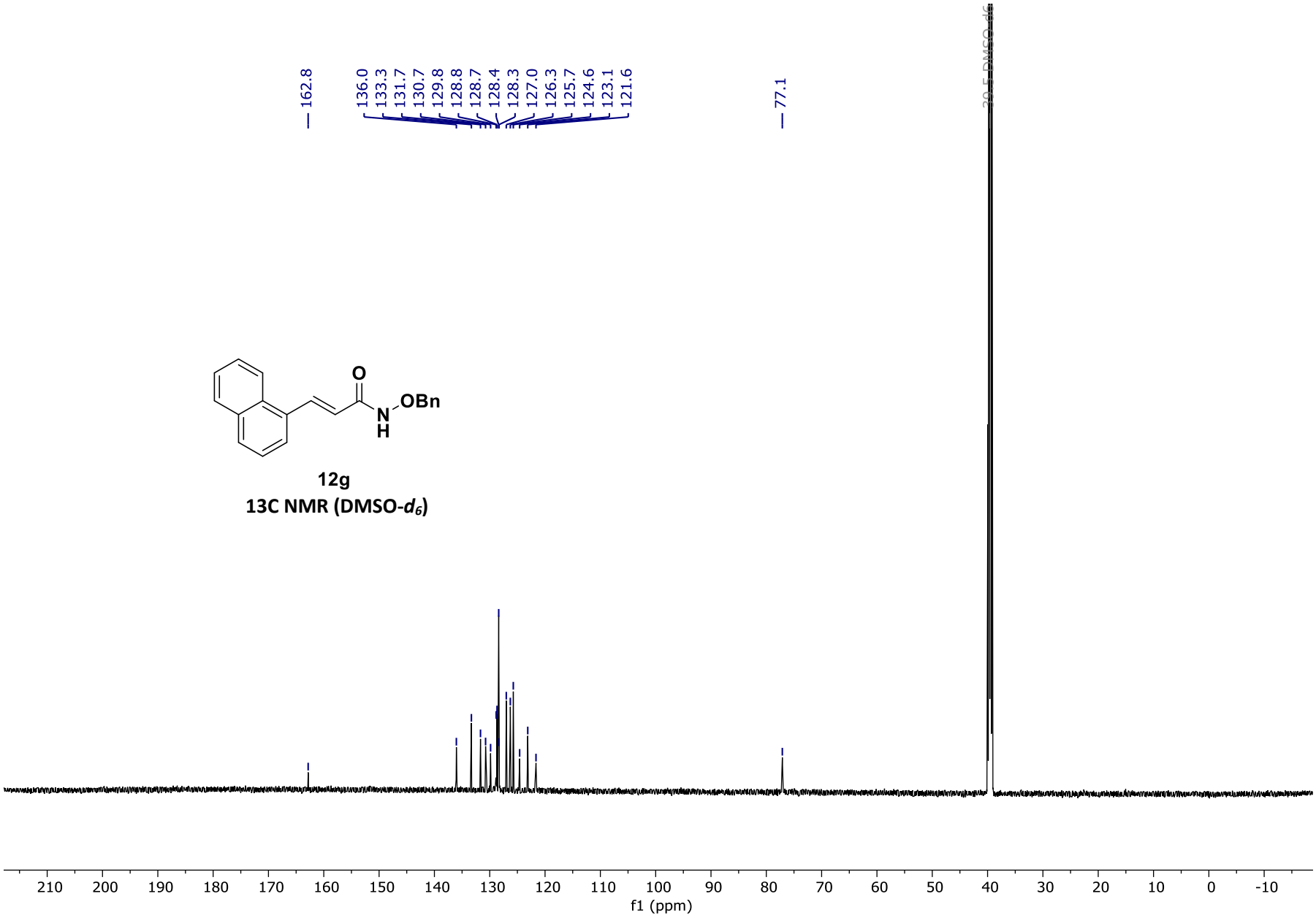
1H NMR (DMSO-d_6)



12f

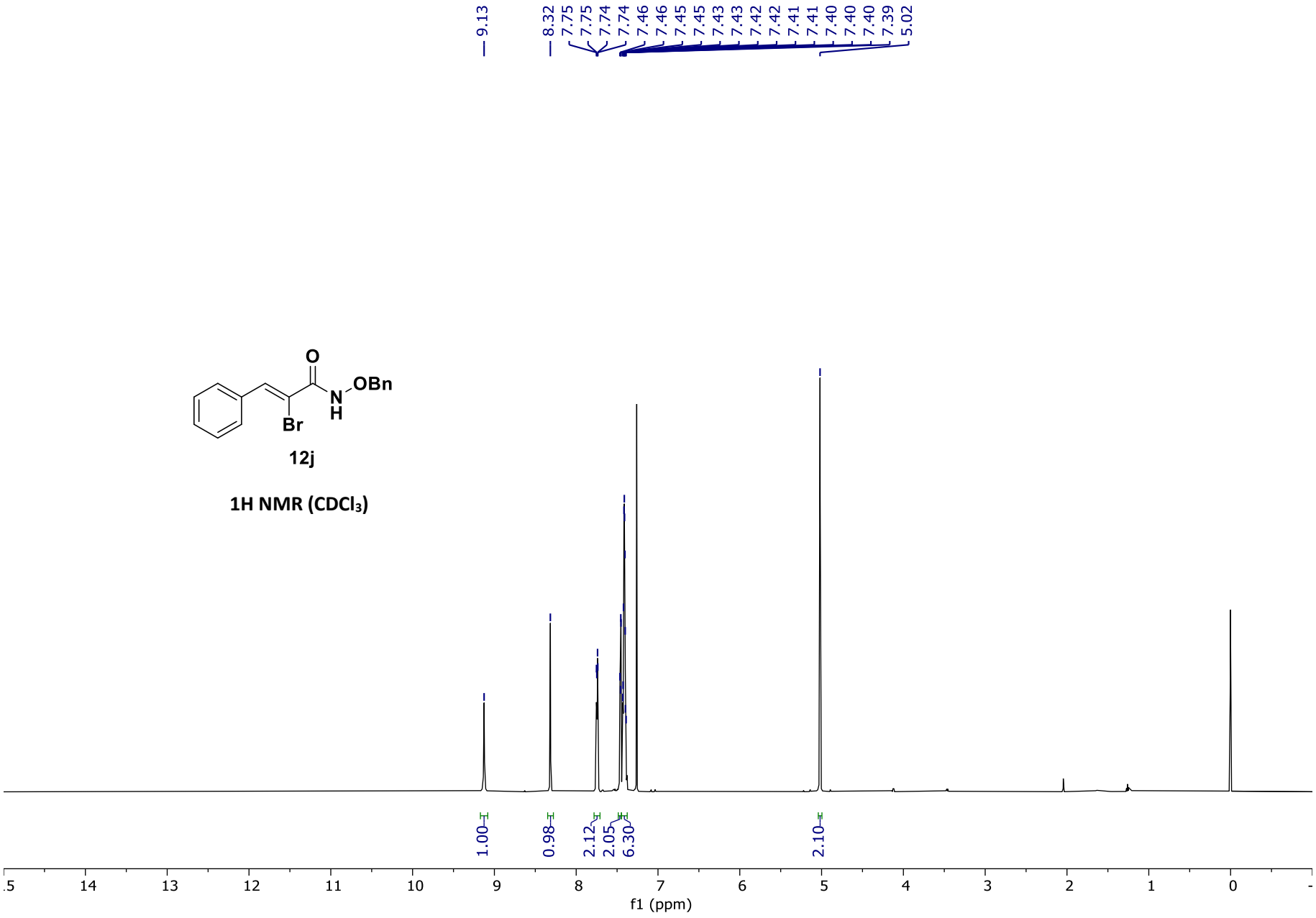
13C NMR (DMSO-d_6)

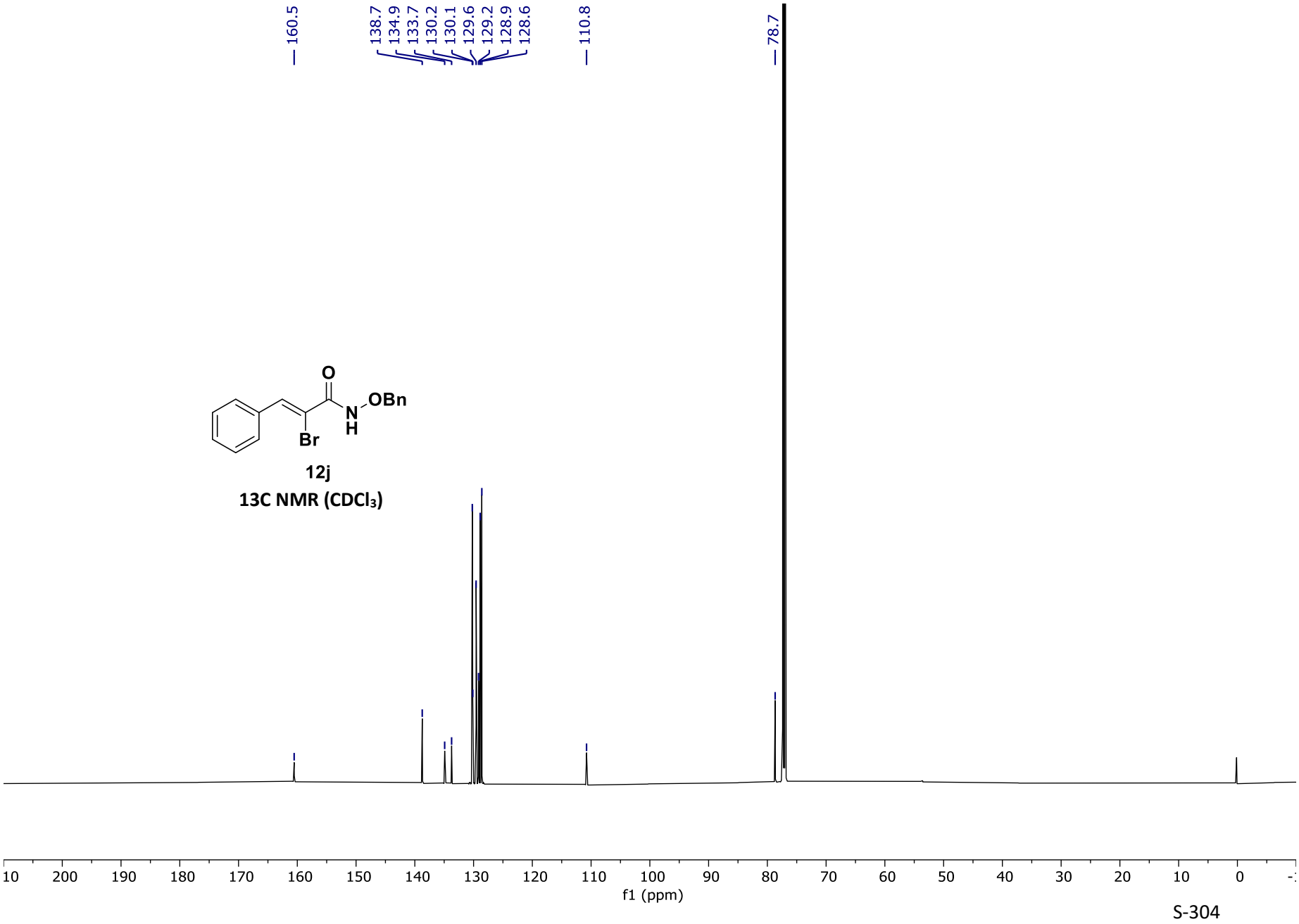

11.41
8.30
8.27
8.20
8.19
8.00
7.98
7.78
7.77
7.65
7.65
7.64
7.63
7.62
7.62
7.60
7.60
7.59
7.58
7.57
7.56
7.55
7.47
7.45
7.43
7.41
7.40
7.38
7.37
7.36
6.54
6.51
4.92
O
N
H
OBn
12g
1H NMR (DMSO-d6)
1.00
1.10
1.04
2.17
1.09
1.10
2.35
2.17
2.19
1.28
1.01
2.21
f1 (ppm)

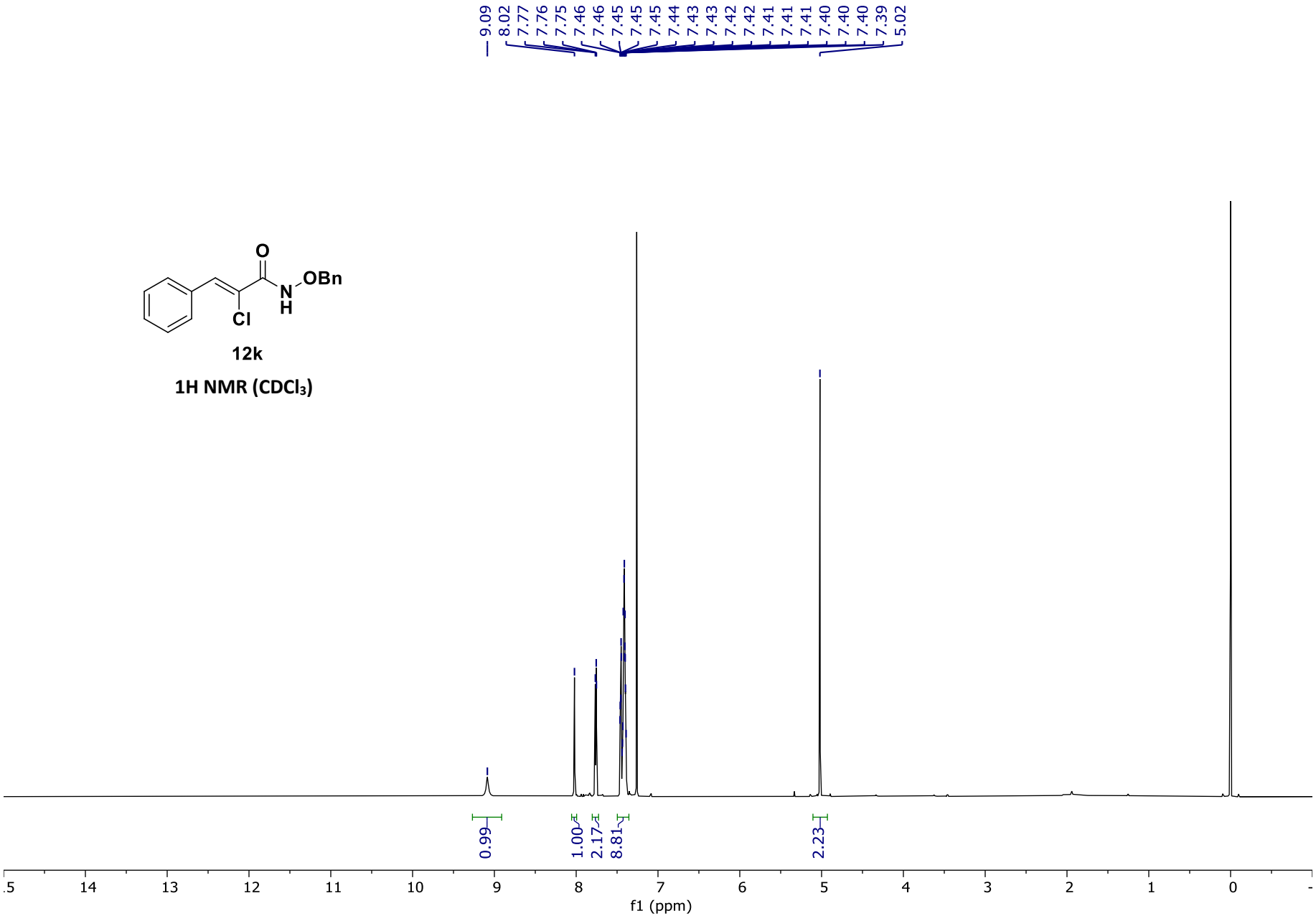


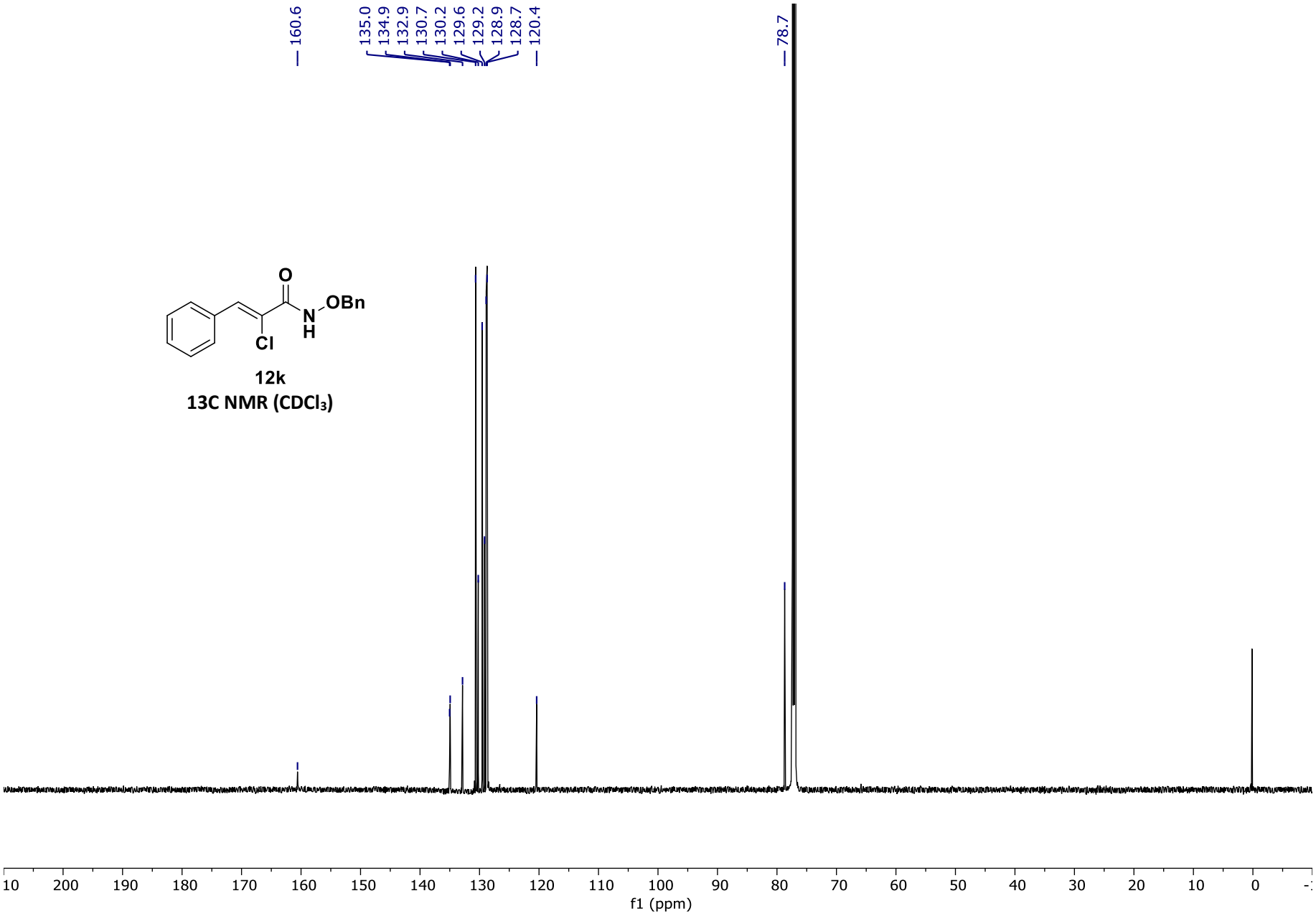
12g

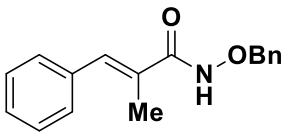
13C NMR (DMSO-d_6)


9.13
8.32
7.75
7.75
7.74
7.74
7.46
7.46
7.45
7.45
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
5.02
O
N
H
OBn
Br
12j
1H NMR (CDCl3)
1.00
0.98
2.12
2.05
6.30
2.10
f1 (ppm)


160.5
138.7
134.9
133.7
130.2
130.1
129.6
129.2
128.9
128.6
110.8
78.7
O
OBn
N
H
Br
12j
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

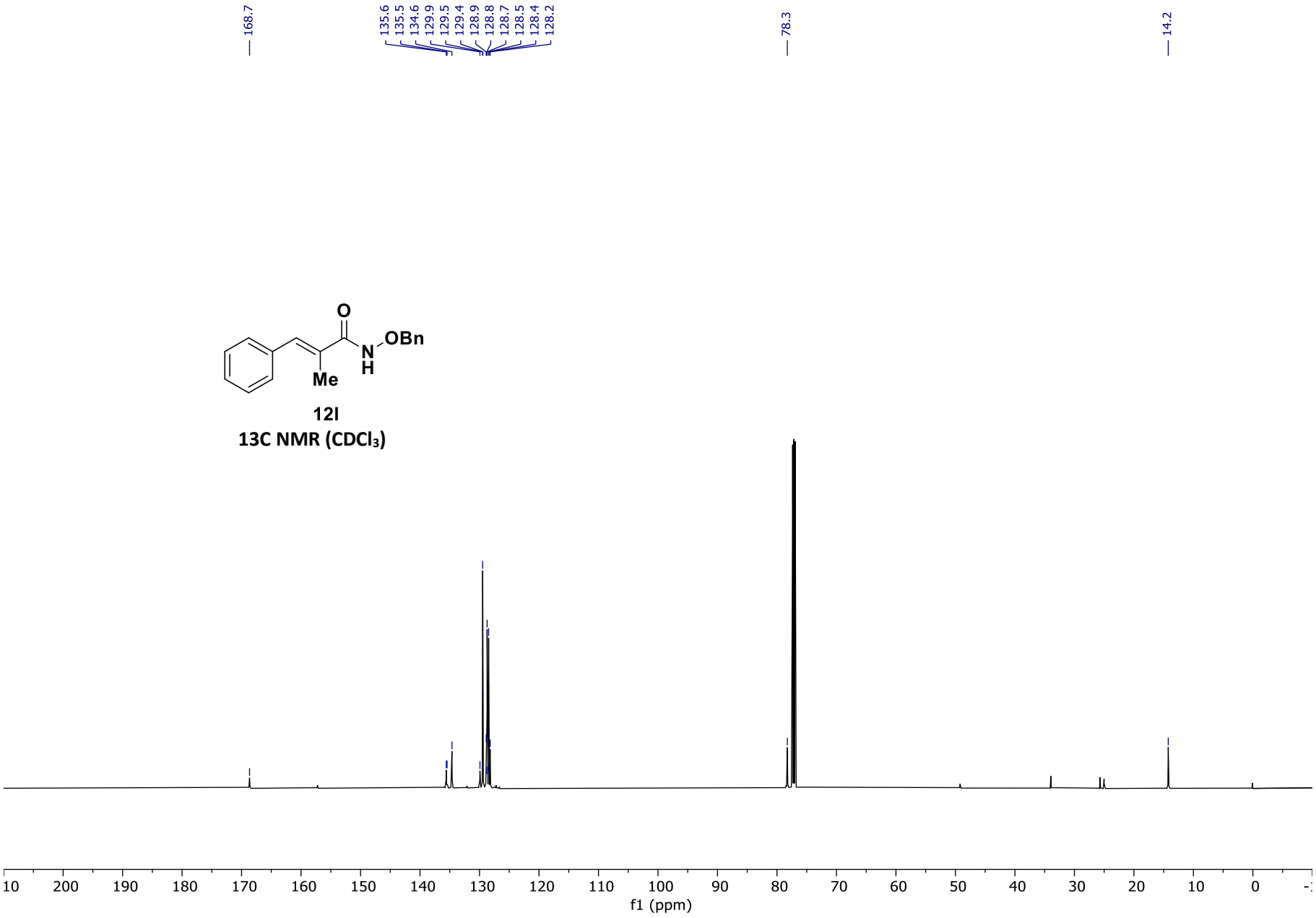

9.09
8.02
7.77
7.76
7.75
7.46
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
5.02
O
OBn
N
H
Cl
12k
1H NMR (CDCl3)
0.99
1.00
2.17
8.81
2.23
f1 (ppm)

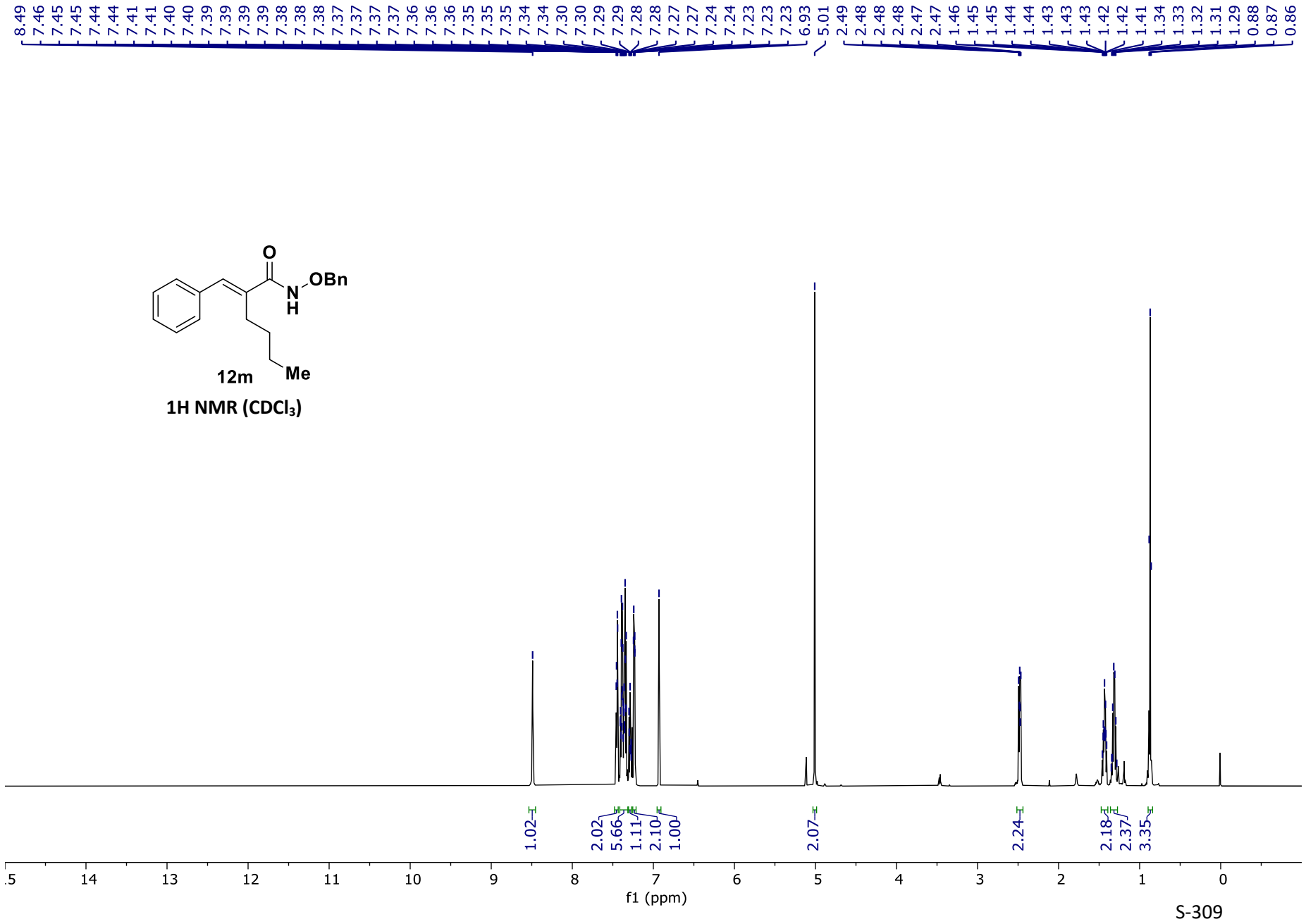

160.6
135.0
134.9
132.9
130.7
130.2
129.6
129.2
128.9
128.7
120.4
78.7
O
OBn
N
H
Cl
12k
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

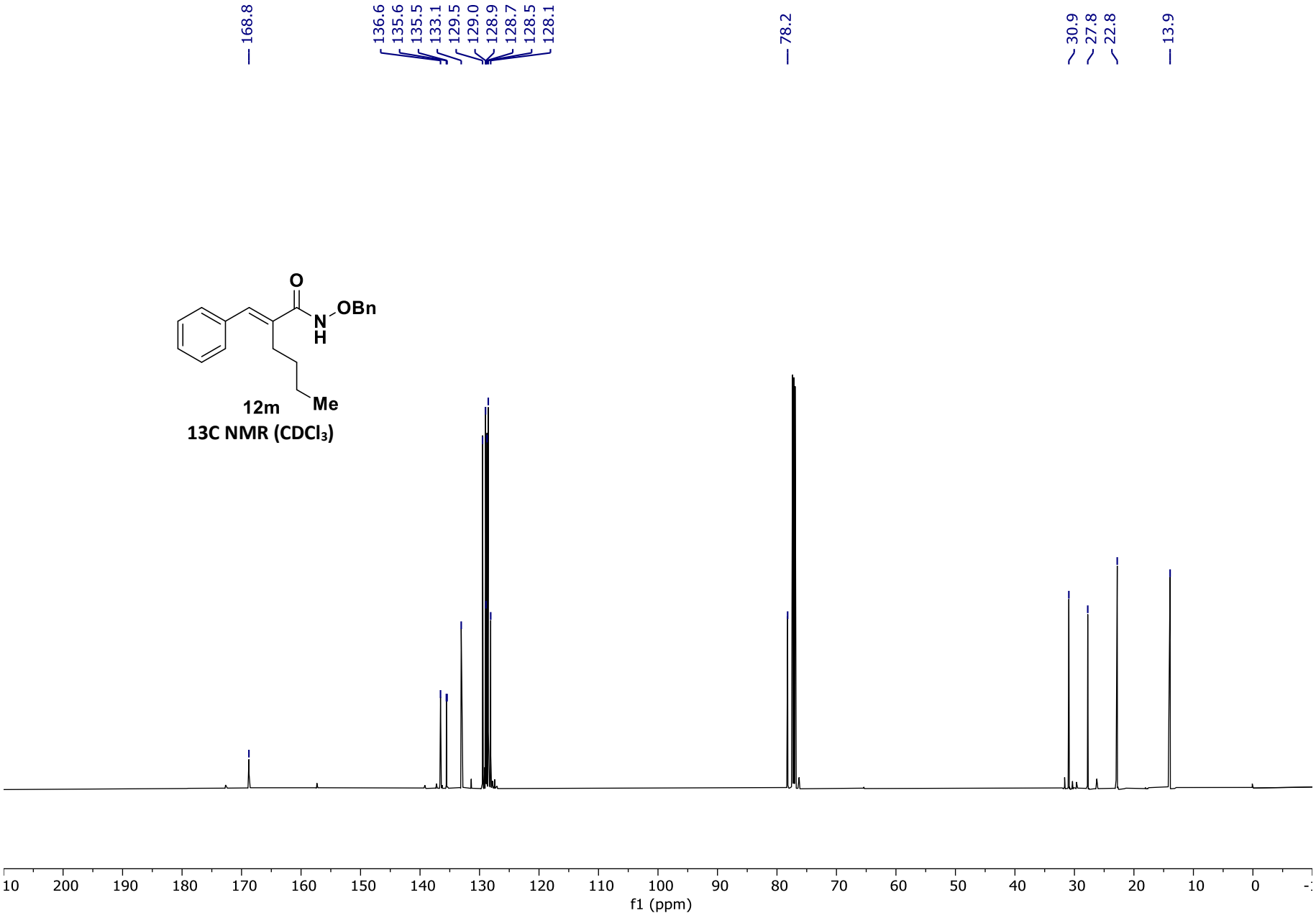


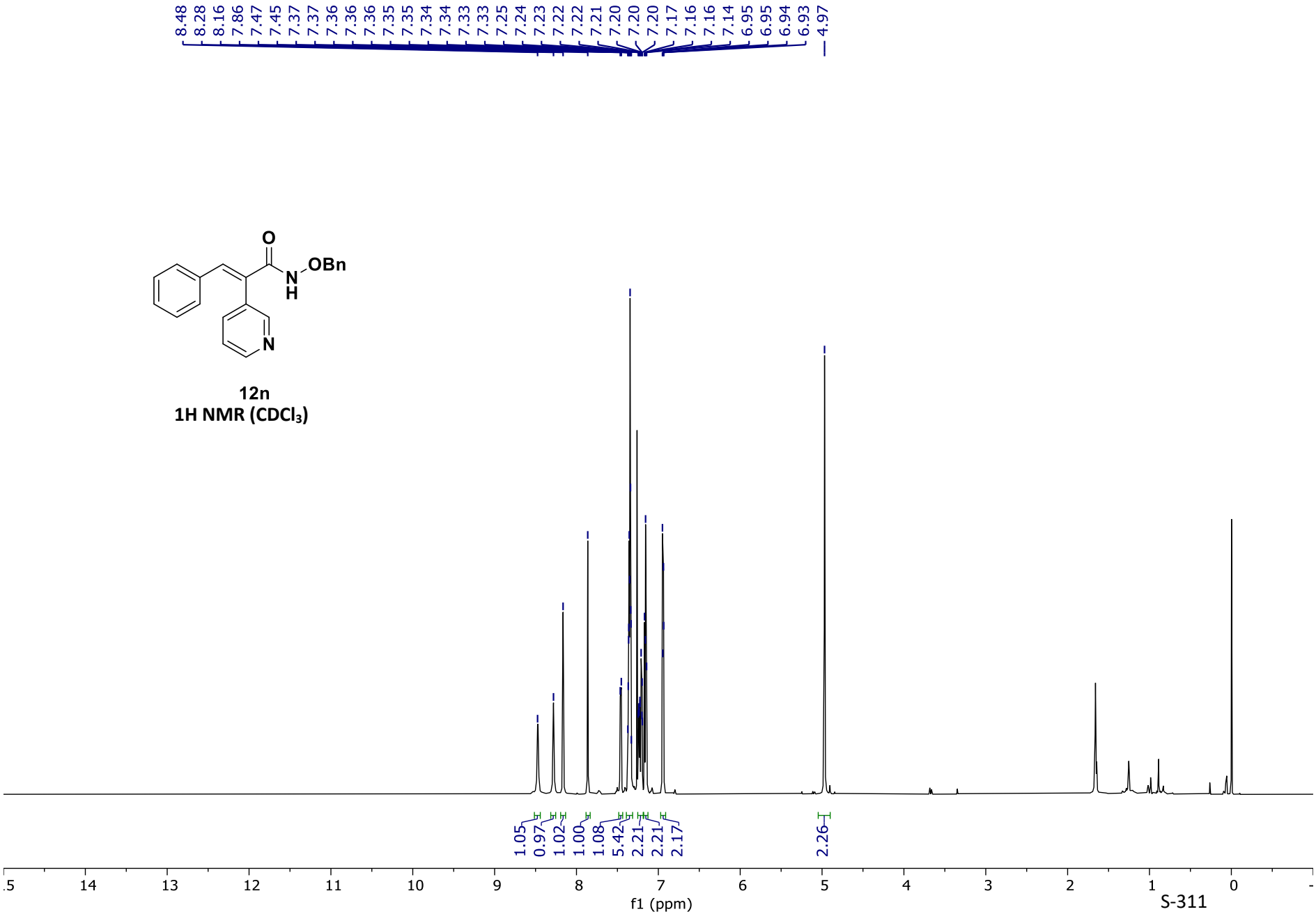
12l

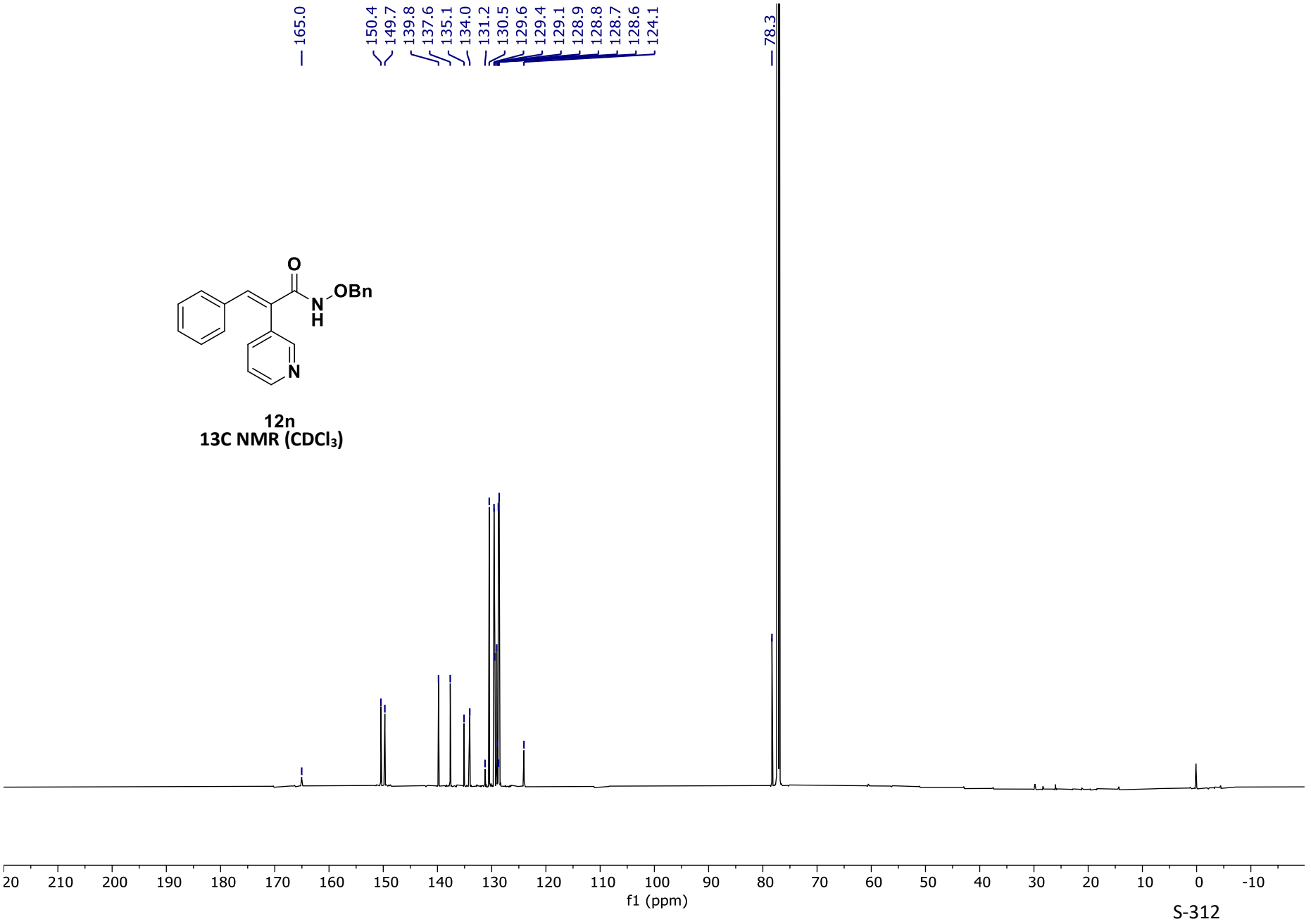
1H NMR ($CDCl_3$)


168.7
135.6
135.5
134.6
129.9
129.5
129.4
128.9
128.8
128.7
128.5
128.4
128.2
78.3
14.2
O
N
H
OBn
Me
12l
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

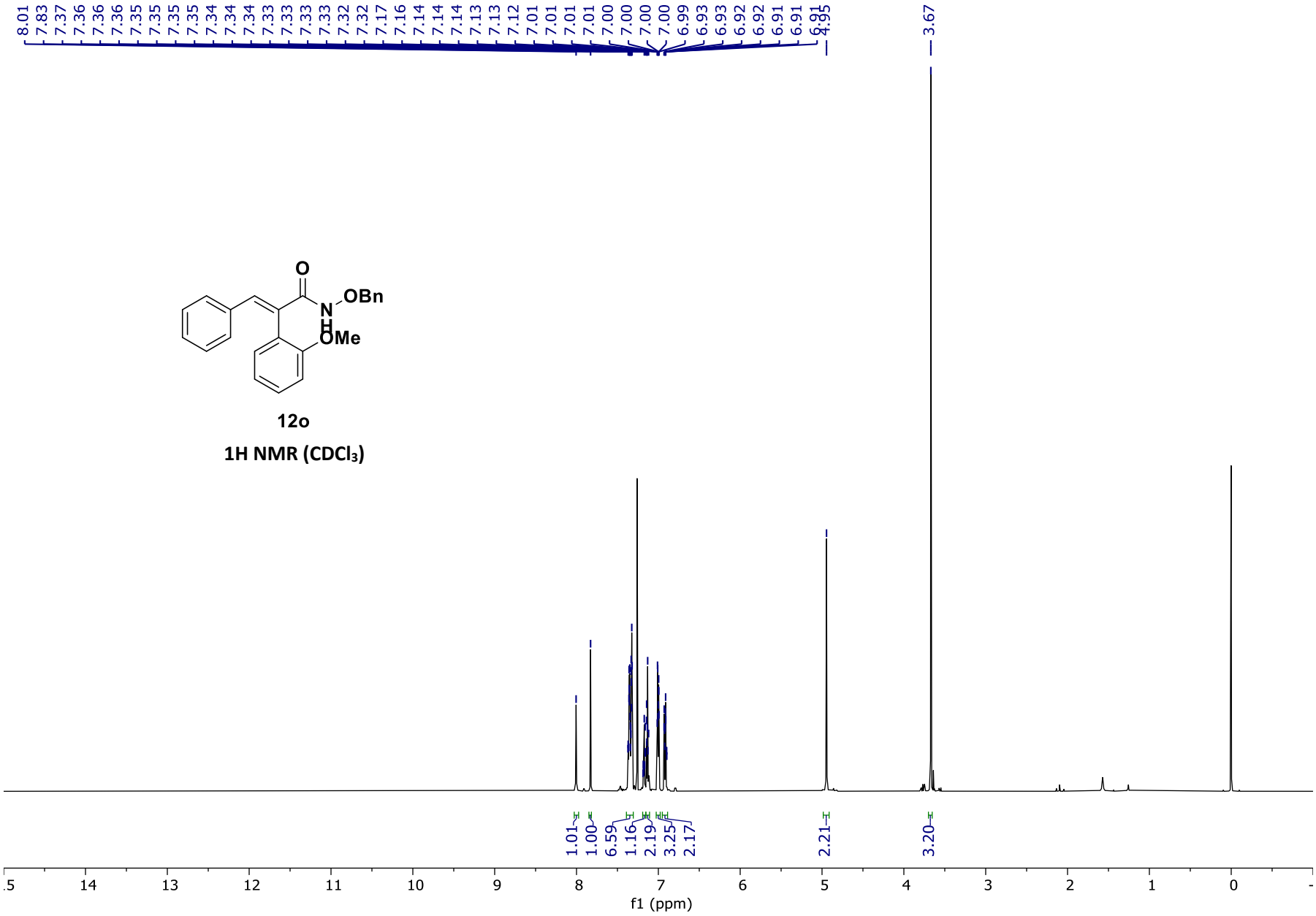

8.49 7.46 7.45 7.45 7.44 7.44 7.41 7.41 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.24 7.24 7.23 7.23 7.23 6.93 5.01 2.49 2.48 2.48 2.48 2.47 2.47 1.46 1.45 1.45 1.44 1.44 1.43 1.43 1.43 1.42 1.42 1.41 1.34 1.33 1.32 1.31 1.29 0.88 0.87 0.86
O
N
H
OBn
Me
12m
1H NMR (CDCl3)
1.02 2.02 5.66 1.11 2.10 1.00 2.07 2.24 2.18 2.37 3.35
.5 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


168.8
136.6
135.6
135.5
133.1
129.5
129.0
128.9
128.7
128.5
128.1
78.2
30.9
27.8
22.8
13.9
O
N
H
OBn
Me
12m
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.48
8.28
8.16
7.86
7.47
7.45
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.25
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.20
7.17
7.16
7.16
7.14
6.95
6.95
6.94
6.93
4.97
O
N
H
OBn
N
12n
1H NMR (CDCl3)
1.05
0.97
1.02
1.00
1.08
5.42
2.21
2.21
2.17
2.26
f1 (ppm)

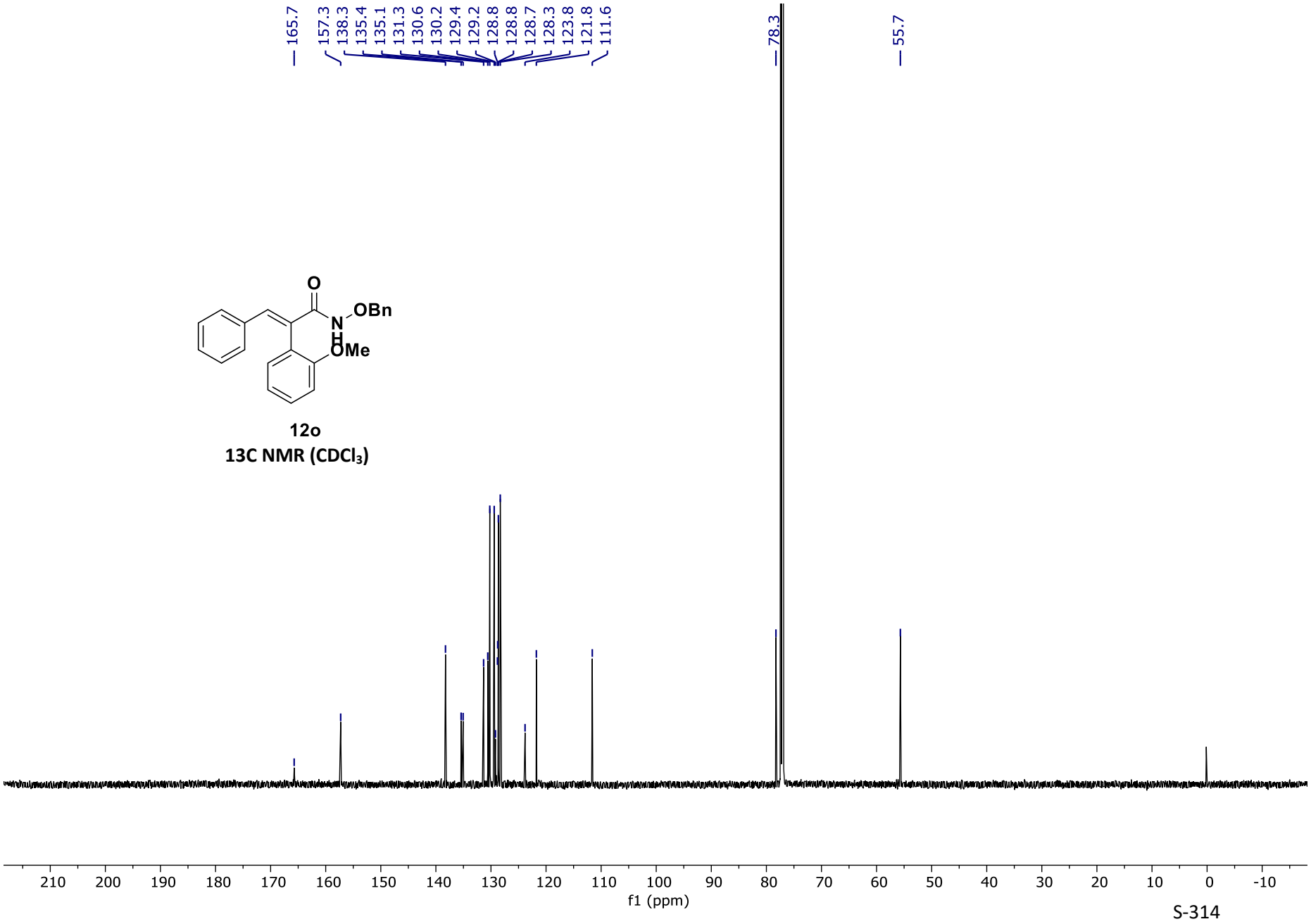


12n
13C NMR ($CDCl_3$)



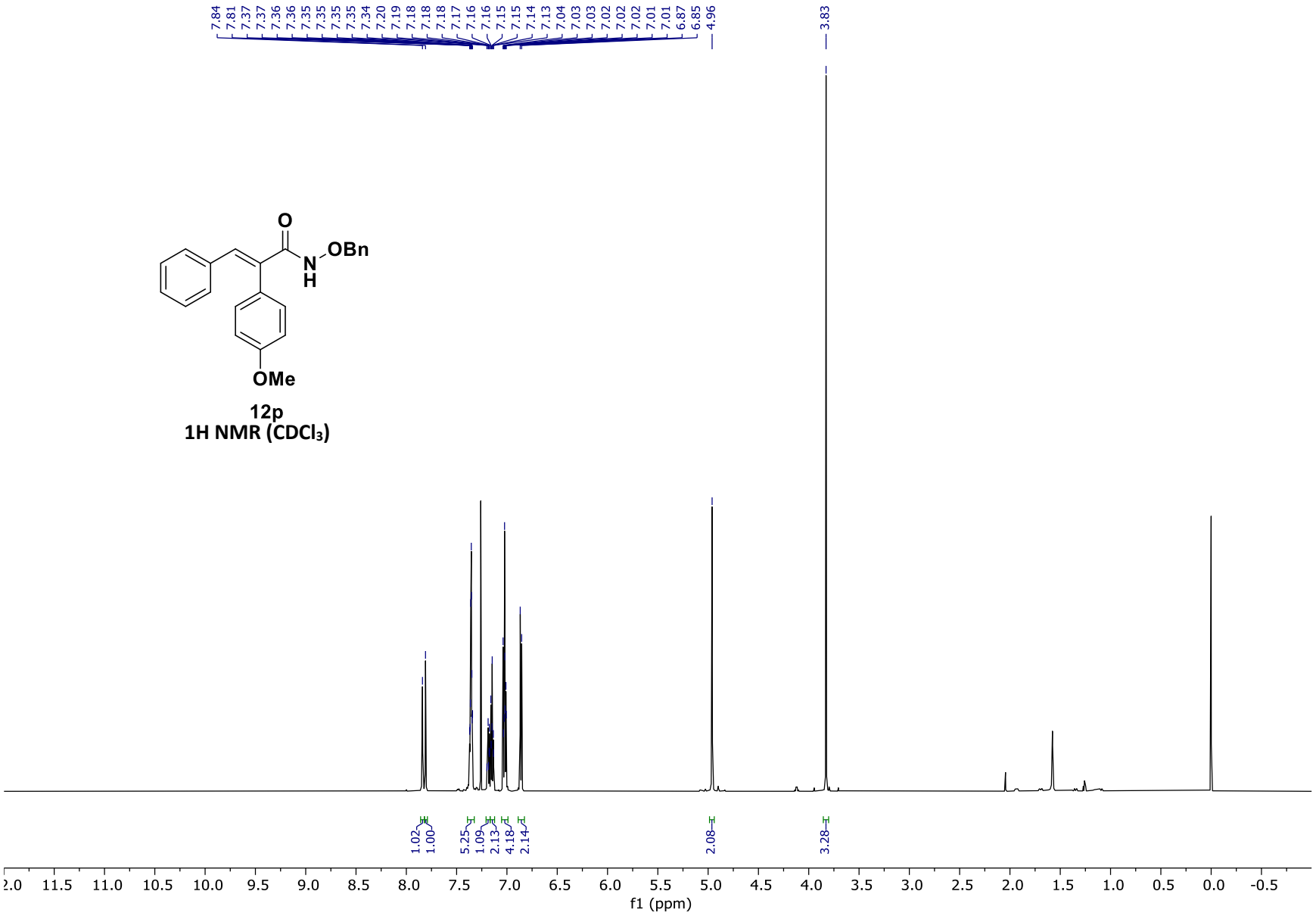
12o

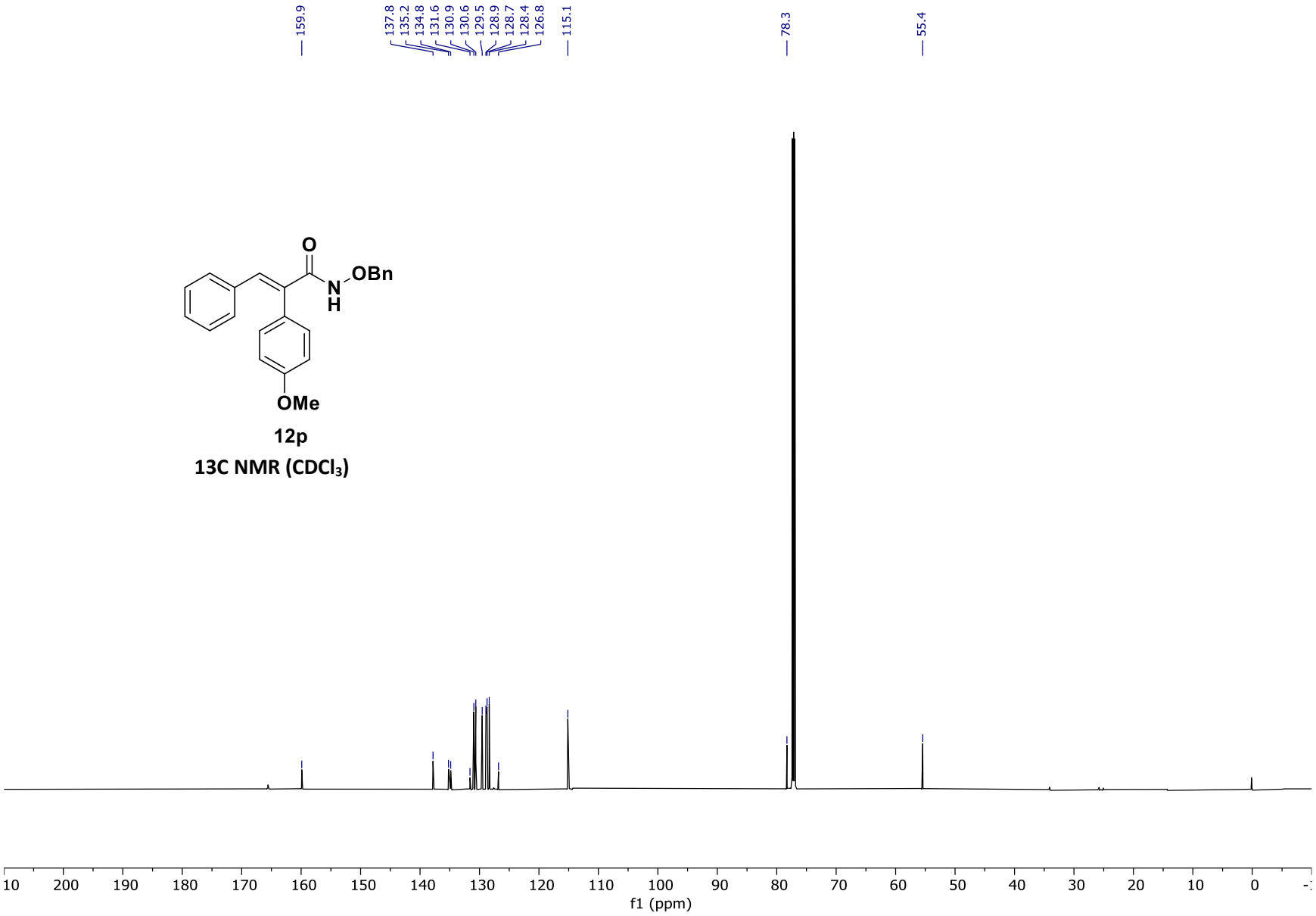
1H NMR ($CDCl_3$)

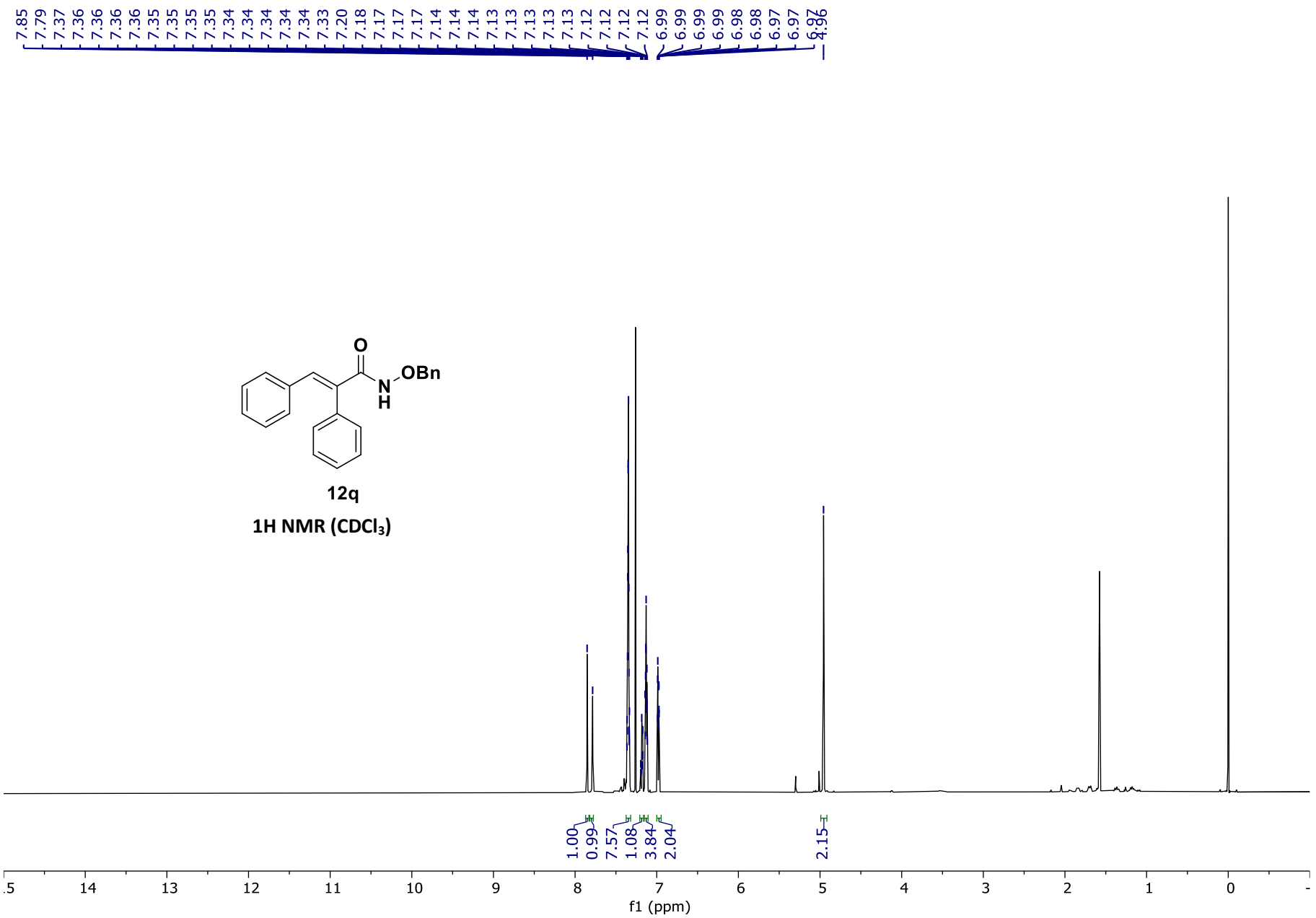


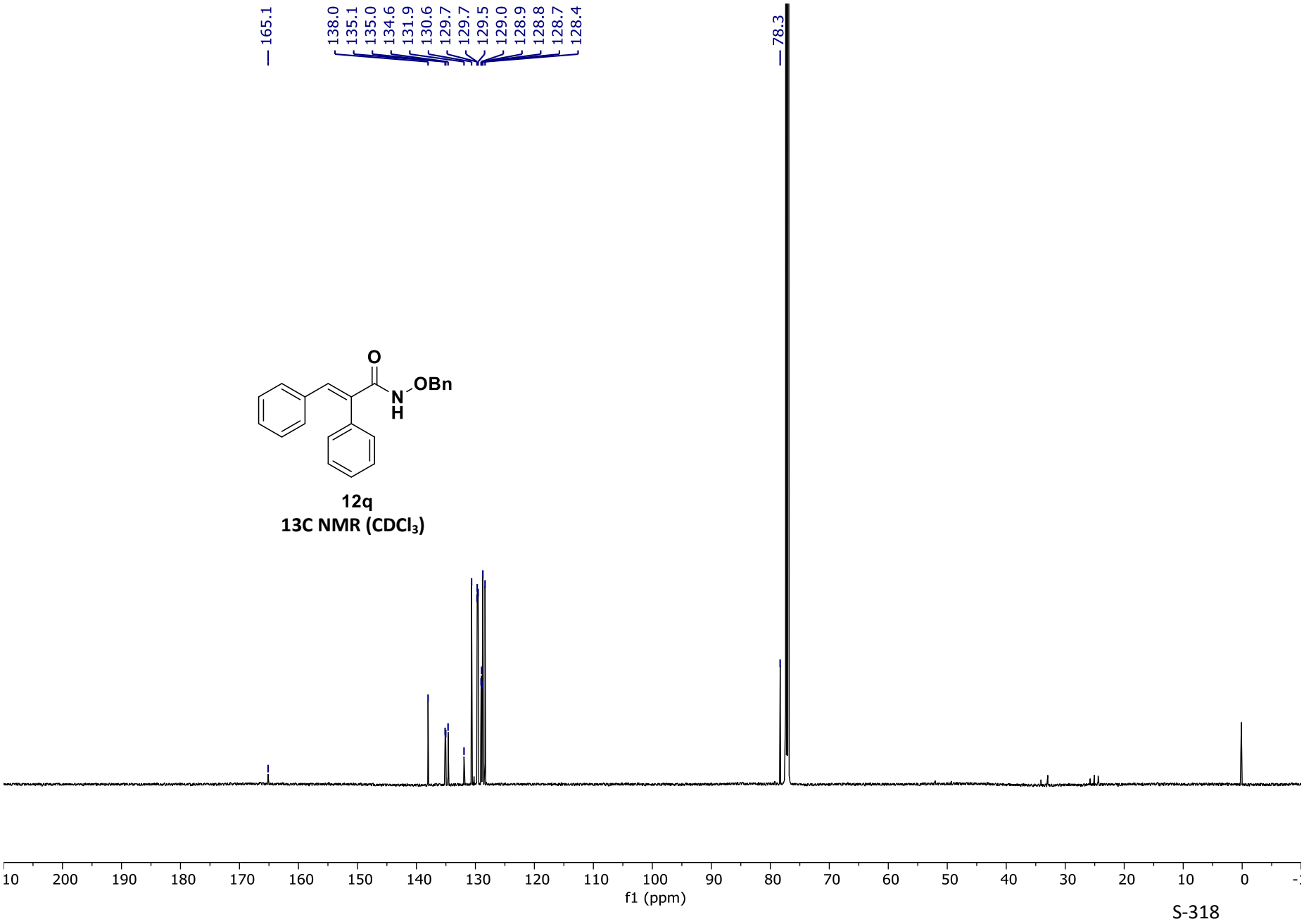
12o

13C NMR ($CDCl_3$)

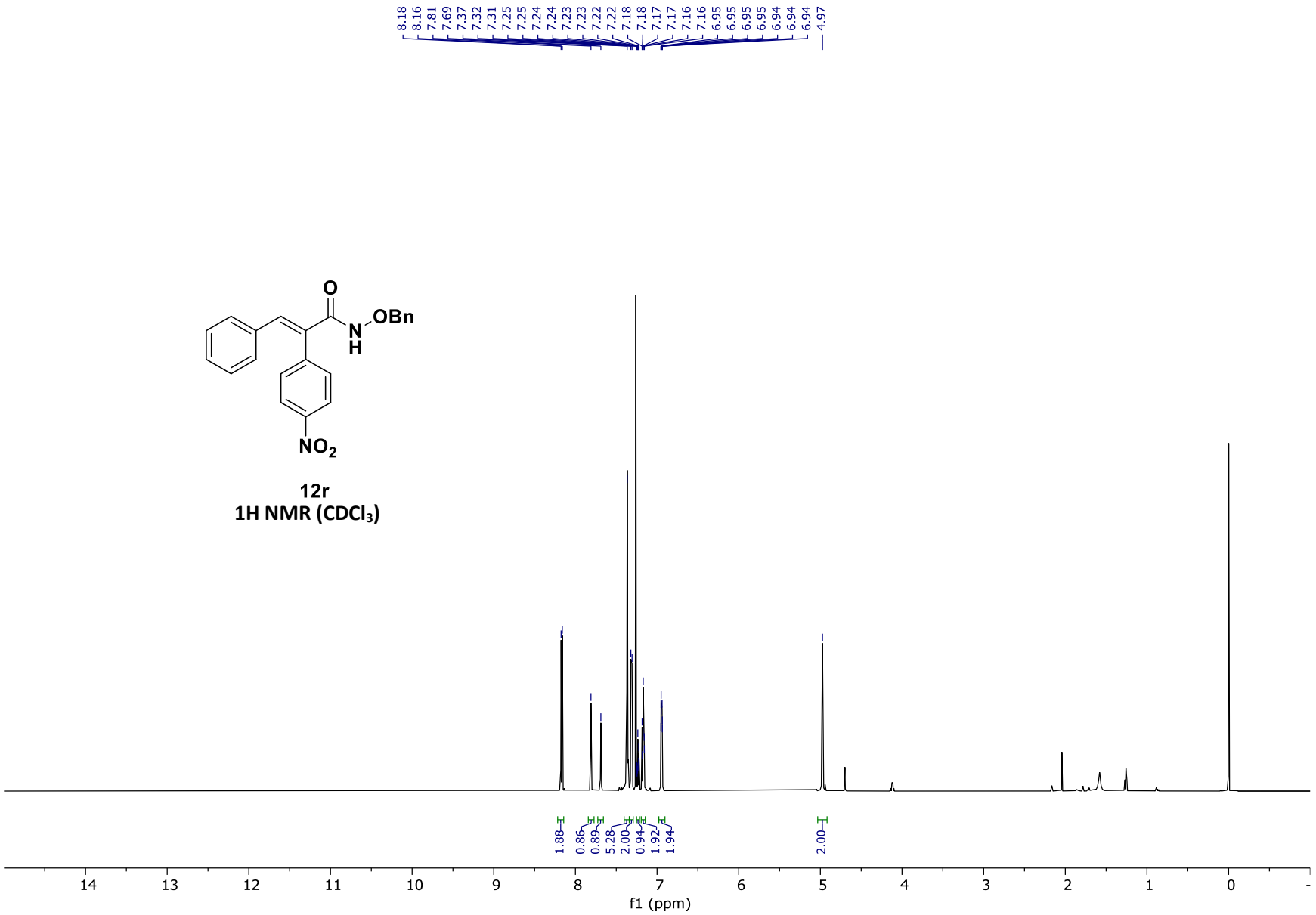

7.84
7.81
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.35
7.34
7.20
7.19
7.18
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.04
7.03
7.03
7.02
7.02
7.02
7.01
7.01
6.87
6.85
4.96
3.83
O
N
H
OBn
OMe
12p
1H NMR (CDCl3)
1.02
1.00
5.25
1.09
2.13
4.18
2.14
2.08
3.28
f1 (ppm)

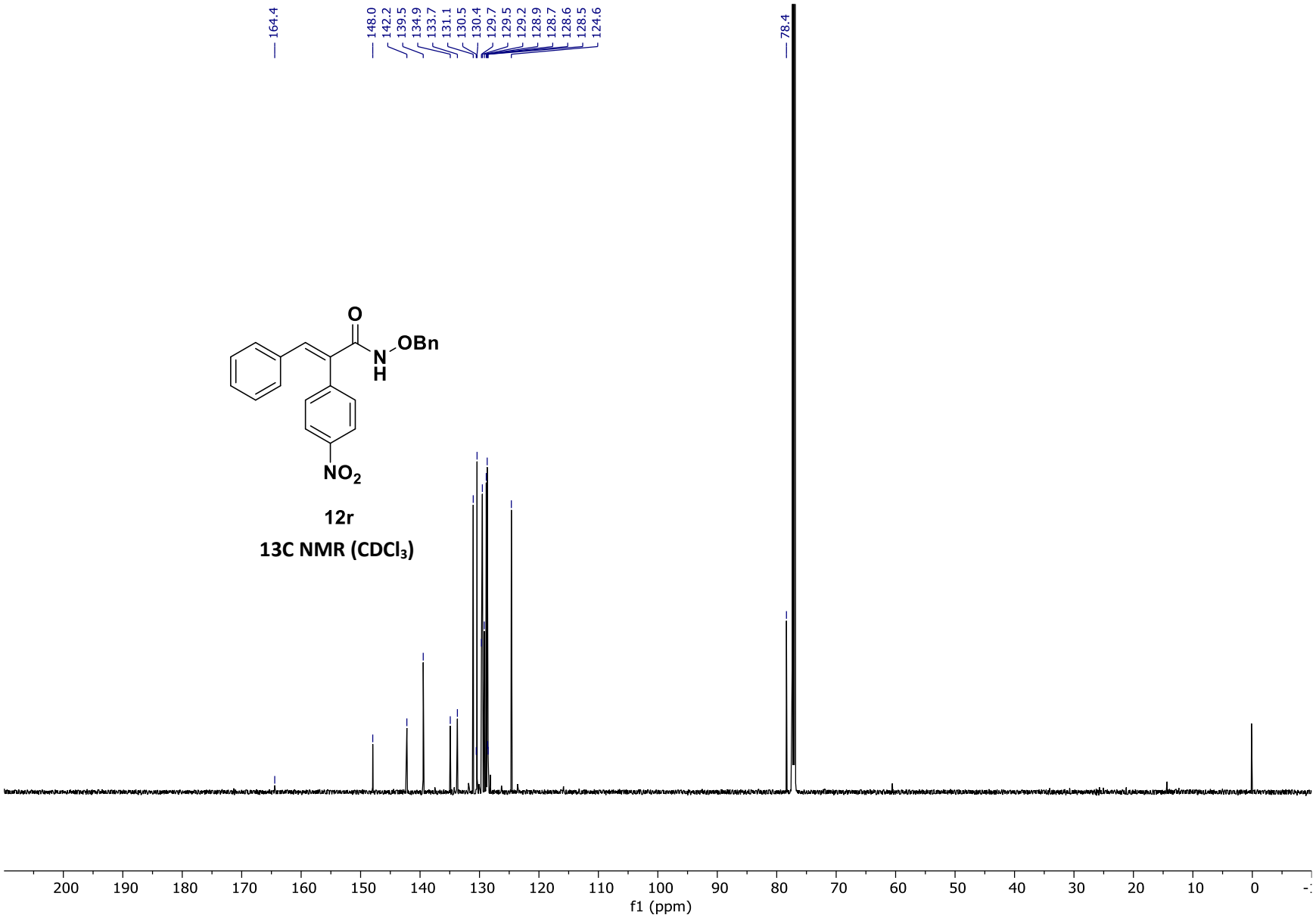

159.9
137.8
135.2
134.8
131.6
130.9
130.6
129.5
128.9
128.7
128.4
126.8
115.1
78.3
55.4
O
N
H
OBn
OMe
12p
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

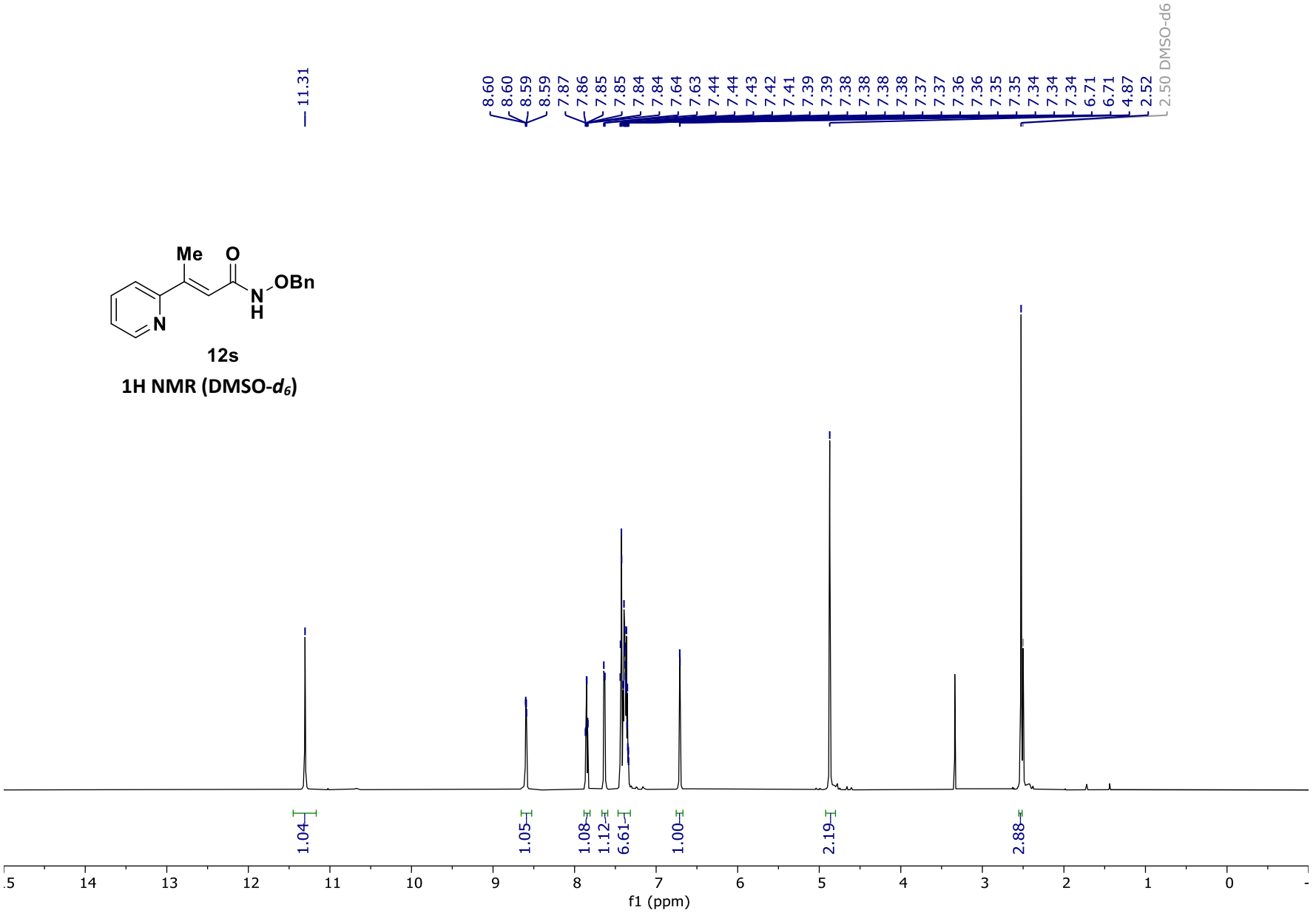

7.85
7.79
7.37
7.36
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.34
7.34
7.33
7.20
7.18
7.17
7.17
7.17
7.14
7.14
7.14
7.13
7.13
7.13
7.13
7.13
7.12
7.12
7.12
7.12
6.99
6.99
6.99
6.98
6.98
6.97
6.97
6.97
4.96
O
N
H
OBn
12q
1H NMR (CDCl3)
1.00
0.99
7.57
1.08
3.84
2.04
2.15
f1 (ppm)

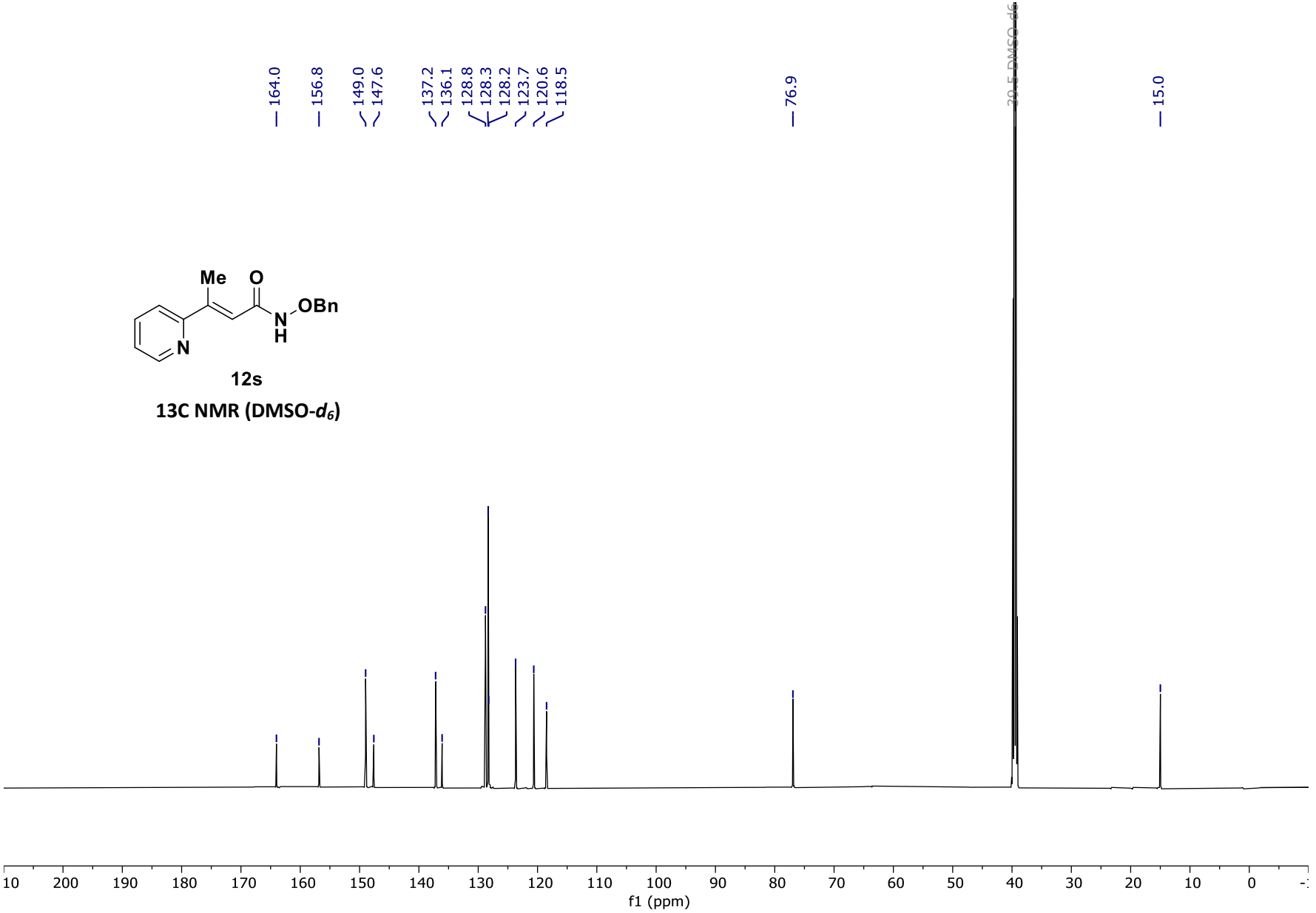


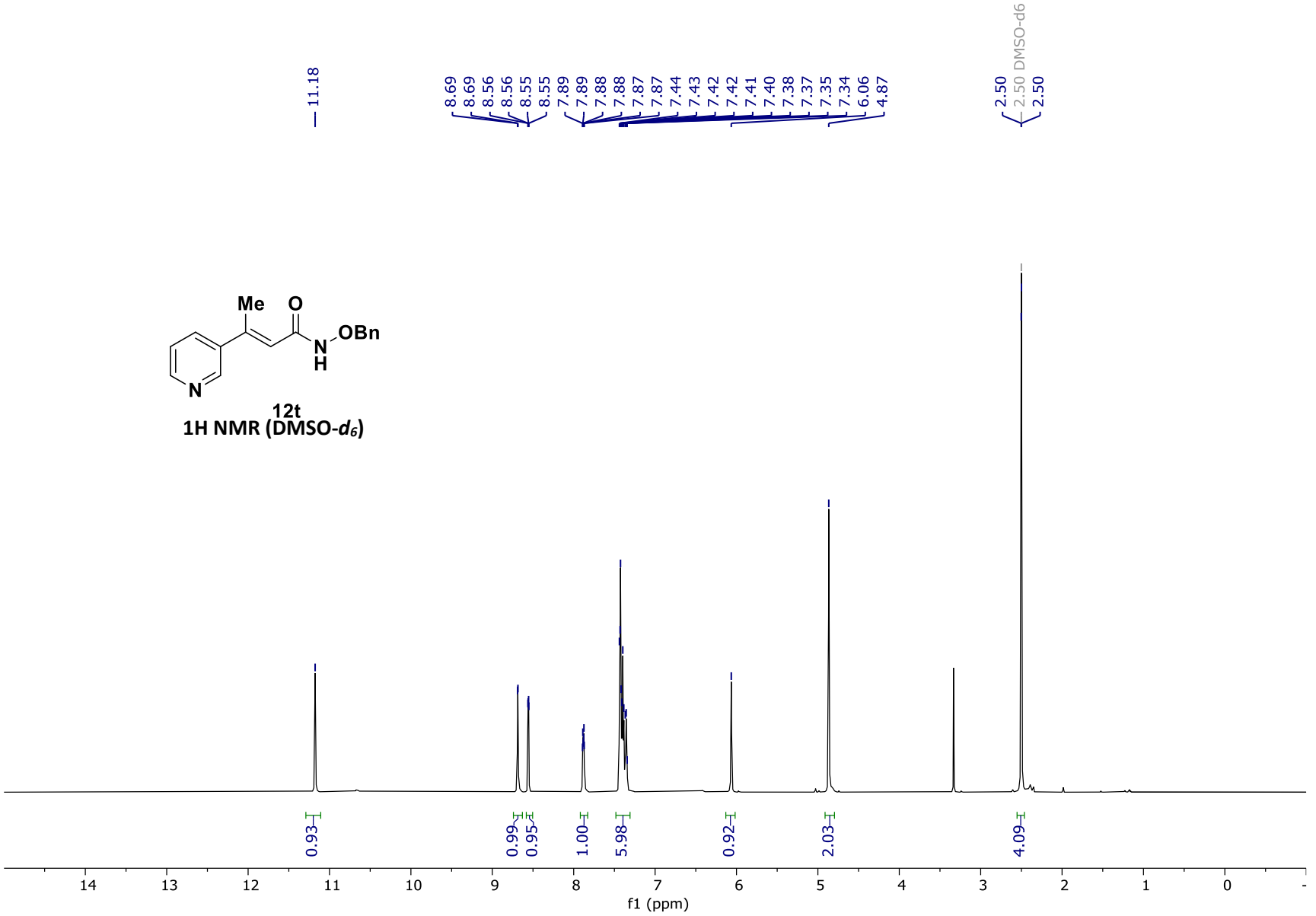
12q
13C NMR ($CDCl_3$)

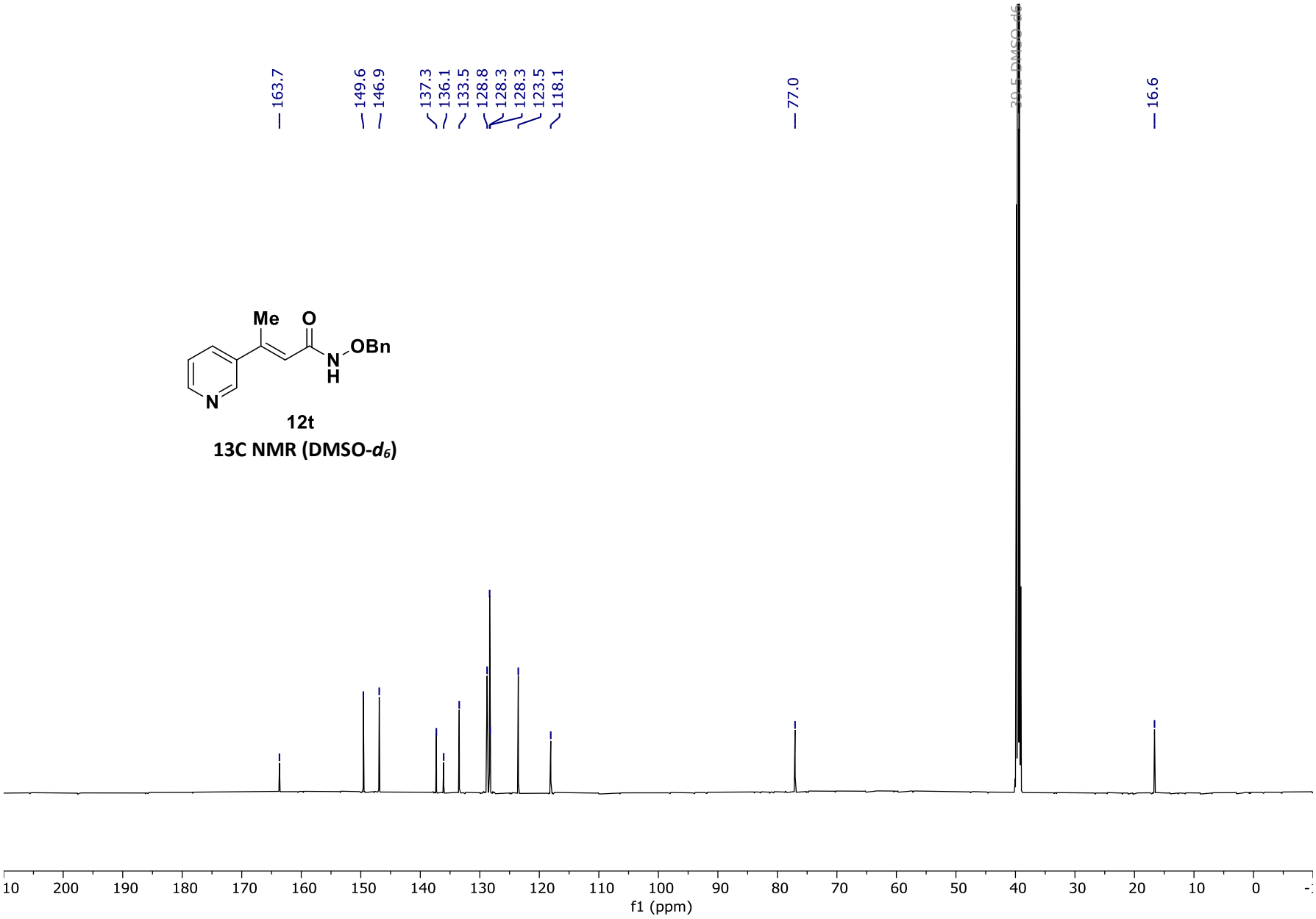

8.18
8.16
7.81
7.69
7.37
7.32
7.31
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.18
7.18
7.17
7.17
7.16
7.16
6.95
6.95
6.95
6.94
6.94
6.94
4.97
O
N
H
OBn
NO2
12r
1H NMR (CDCl3)
1.88
0.86
0.89
5.28
2.00
0.94
1.92
1.94
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-
f1 (ppm)


164.4
148.0
142.2
139.5
134.9
133.7
131.1
130.5
130.4
129.7
129.5
129.2
128.9
128.7
128.6
128.5
124.6
78.4
O
N
H
OBn
NO2
12r
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11.31
8.60
8.60
8.59
8.59
7.87
7.86
7.85
7.85
7.84
7.84
7.64
7.63
7.44
7.44
7.43
7.42
7.41
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.34
6.71
6.71
4.87
2.52
2.50 DMSO-d6
Me
O
N
OBn
H
N
12s
1H NMR (DMSO-d6)
1.04
1.05
1.08
1.12
6.61
1.00
2.19
2.88
f1 (ppm)

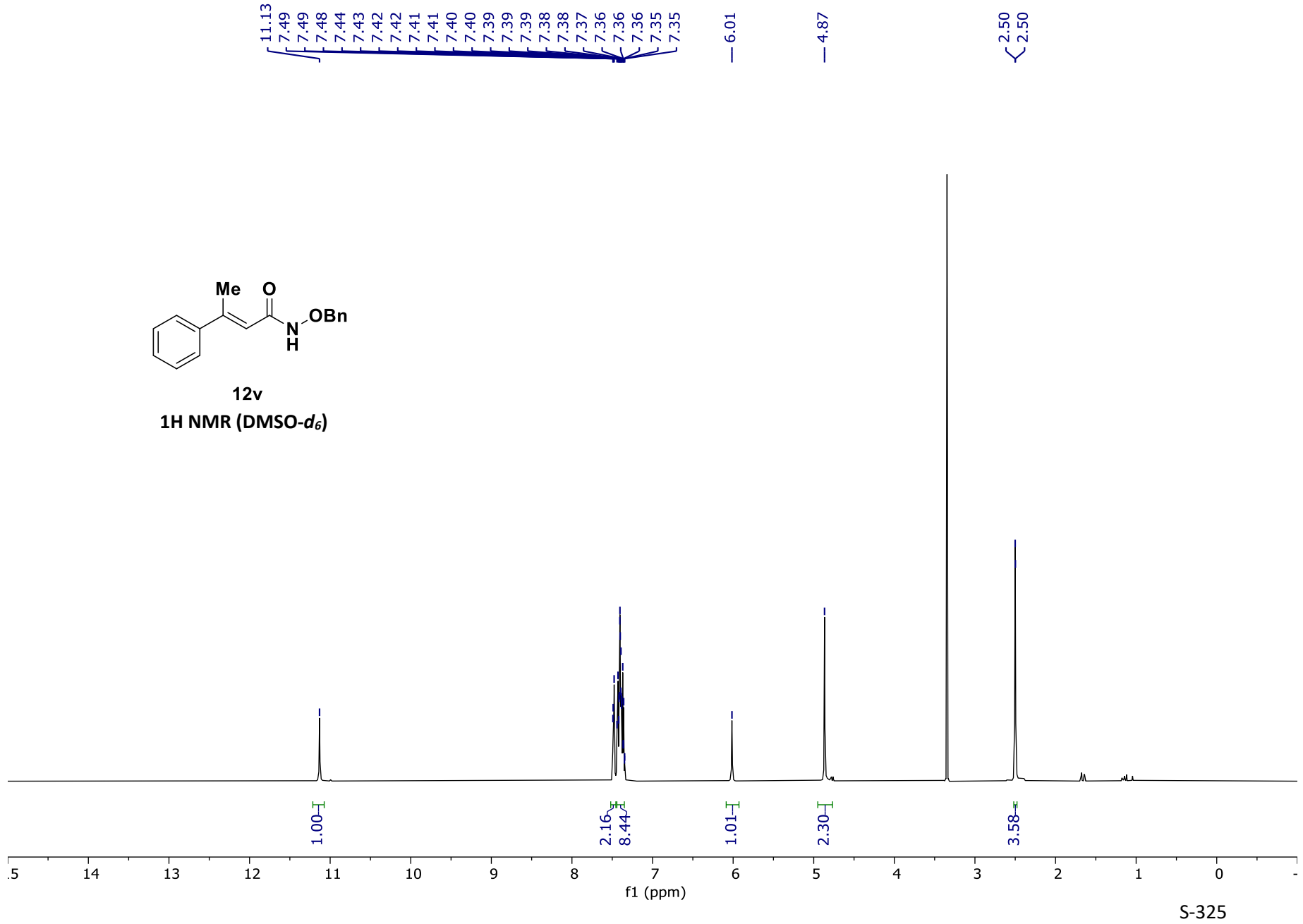

164.0
156.8
149.0
147.6
137.2
136.1
128.8
128.3
128.2
123.7
120.6
118.5
76.9
39.5 DMSO-d6
15.0
Me
O
OBn
N
H
N
12s
13C NMR (DMSO-d6)
f1 (ppm)

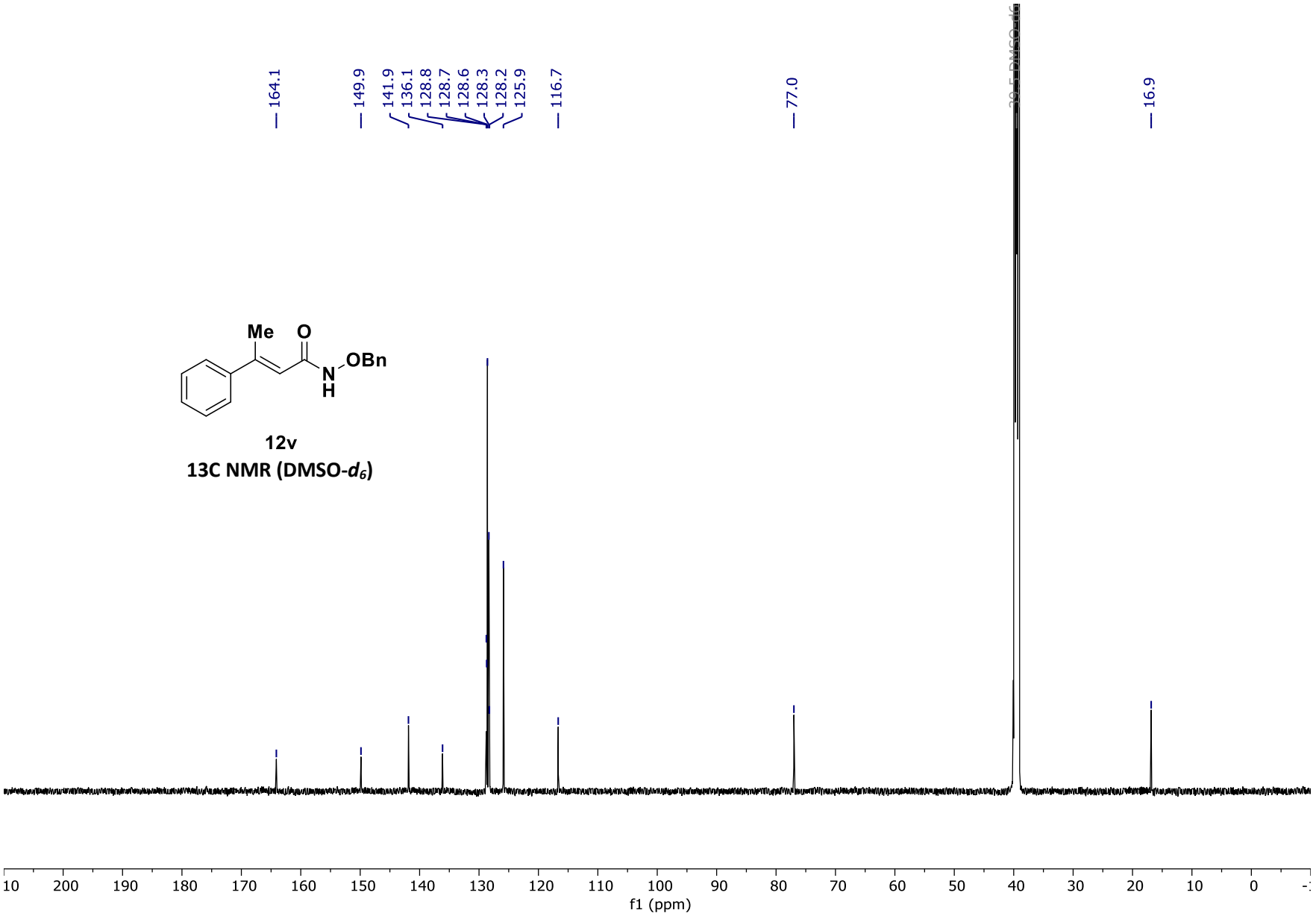

11.18
8.69
8.69
8.56
8.56
8.55
8.55
7.89
7.89
7.88
7.88
7.87
7.87
7.44
7.43
7.42
7.42
7.41
7.40
7.38
7.37
7.35
7.34
6.06
4.87
2.50
2.50 DMSO-d6
2.50
Me
O
N
H
OBn
N
12t
1H NMR (DMSO-d6)
0.93
0.99
0.95
1.00
5.98
0.92
2.03
4.09
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-
f1 (ppm)

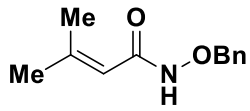


12t

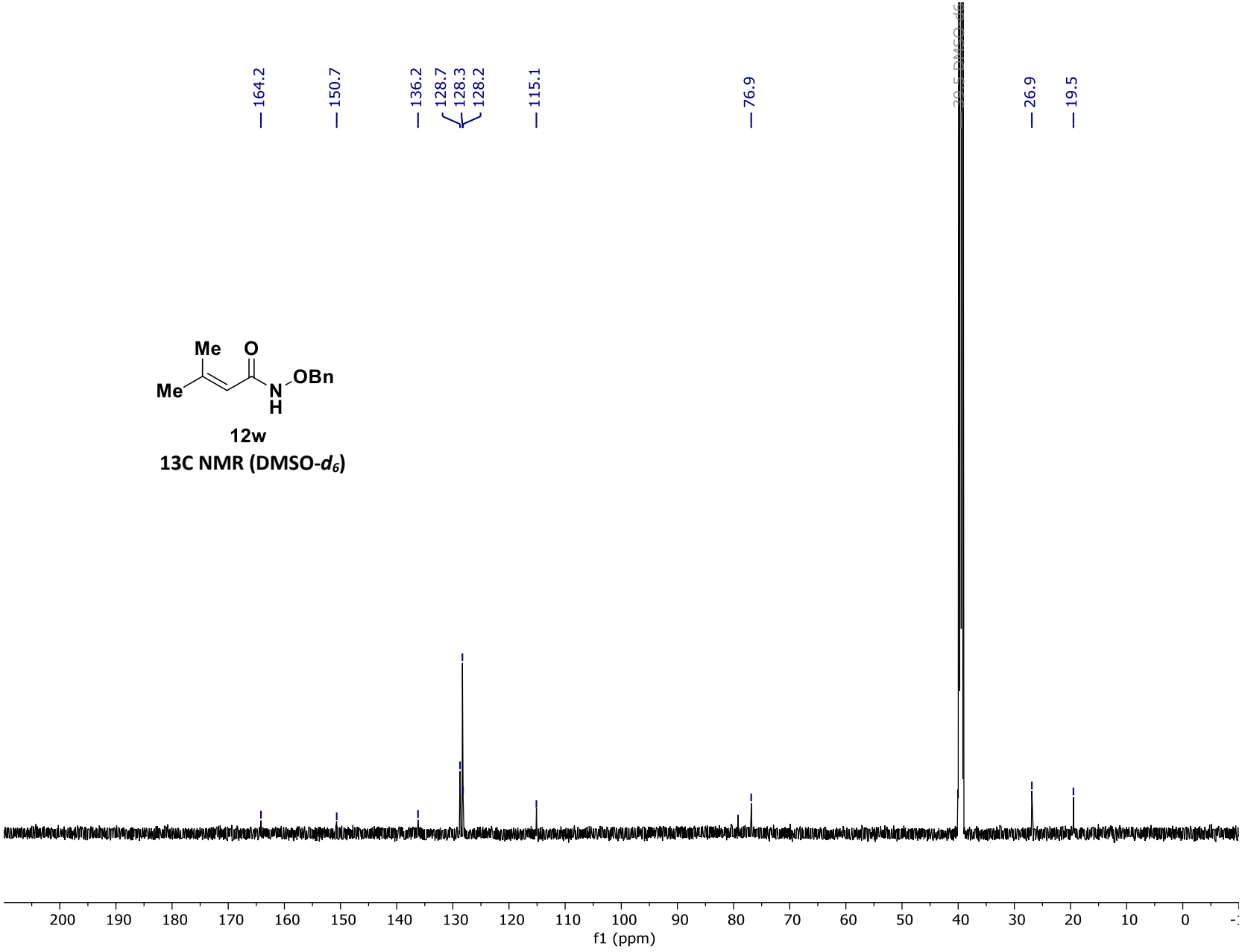
13C NMR (DMSO-d_6)

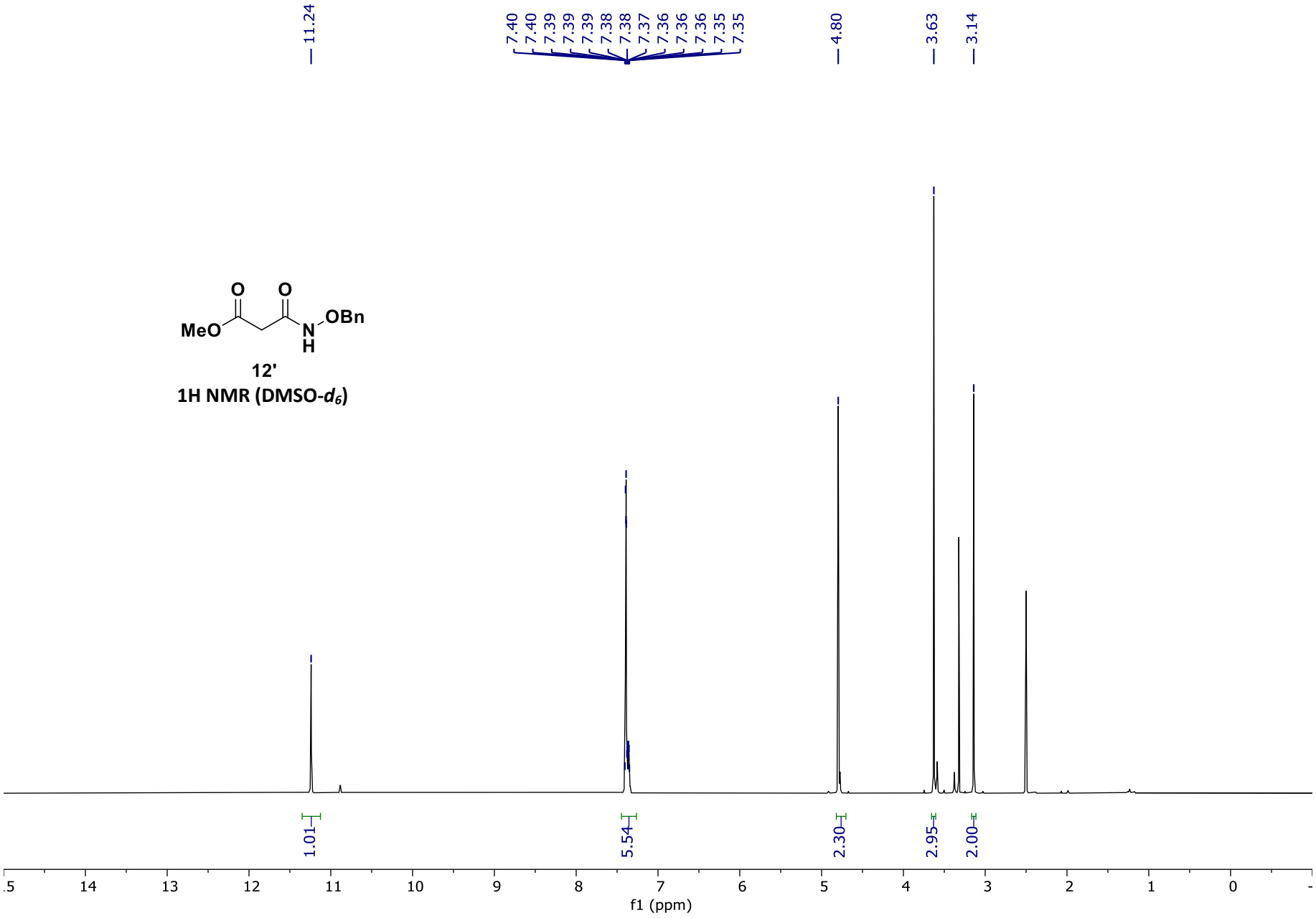

11.13
7.49
7.49
7.48
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.35
6.01
4.87
2.50
2.50
Me
O
N
H
OBn
12v
1H NMR (DMSO-d6)
1.00
2.16
8.44
1.01
2.30
3.58
f1 (ppm)

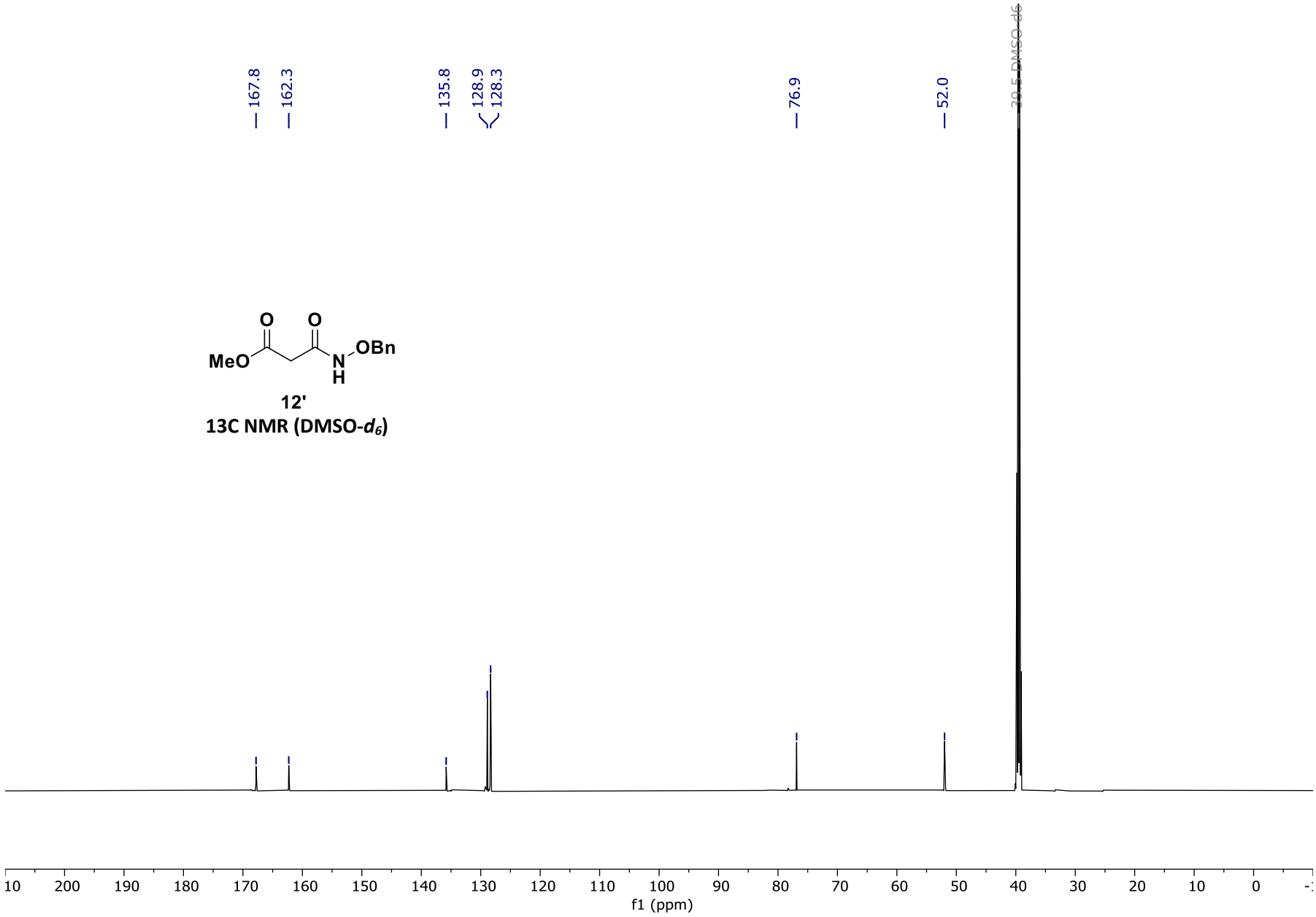

164.1
149.9
141.9
136.1
128.8
128.7
128.6
128.3
128.2
125.9
116.7
77.0
16.9
Me
O
OBn
N
H
12v
13C NMR (DMSO-d6)
f1 (ppm)

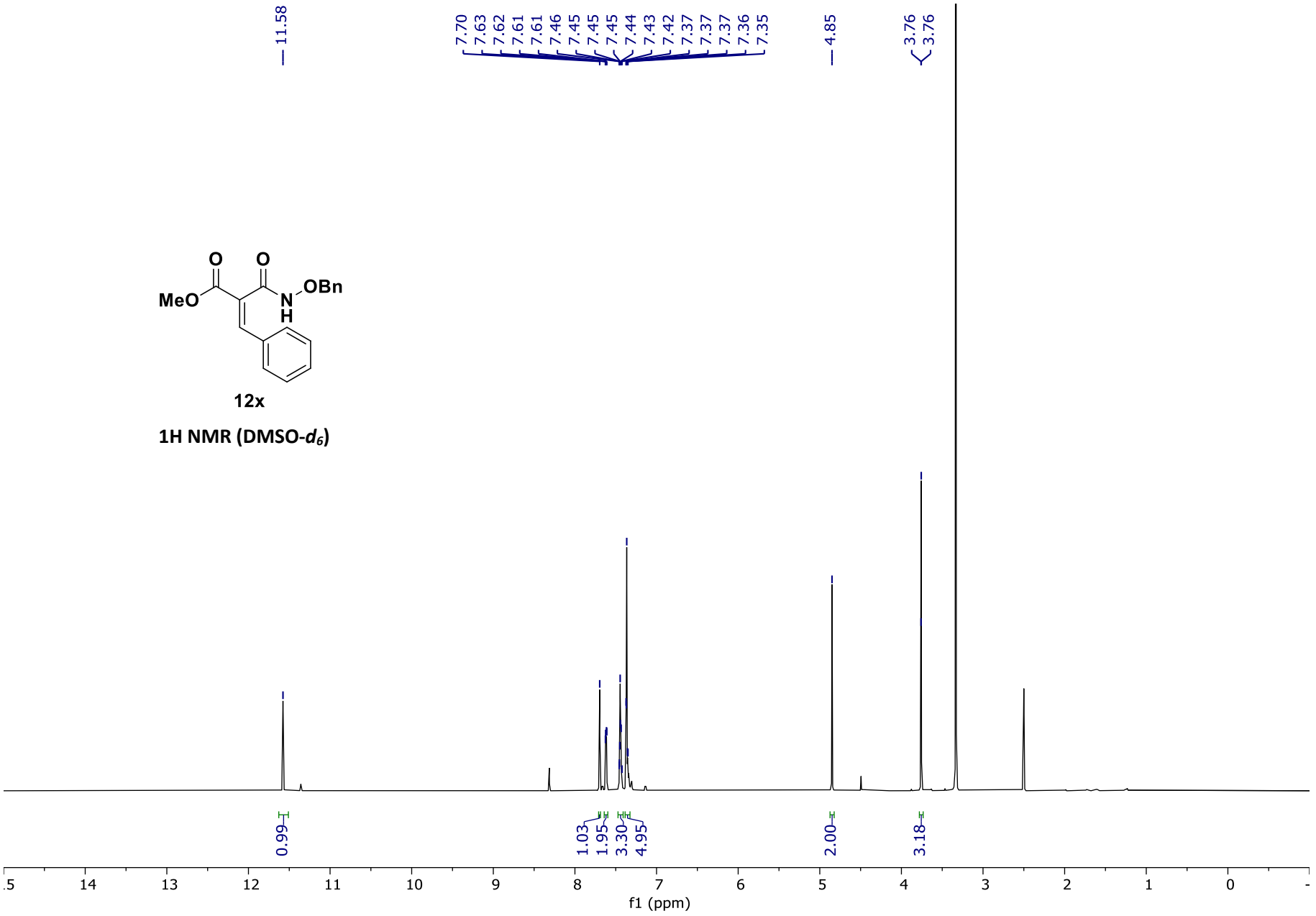


12w
1H NMR (DMSO-d_6)


164.2
150.7
136.2
128.7
128.3
128.2
115.1
76.9
39.5 DMSO-d6
26.9
19.5
Me
O
OBn
Me
N
H
12w
13C NMR (DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

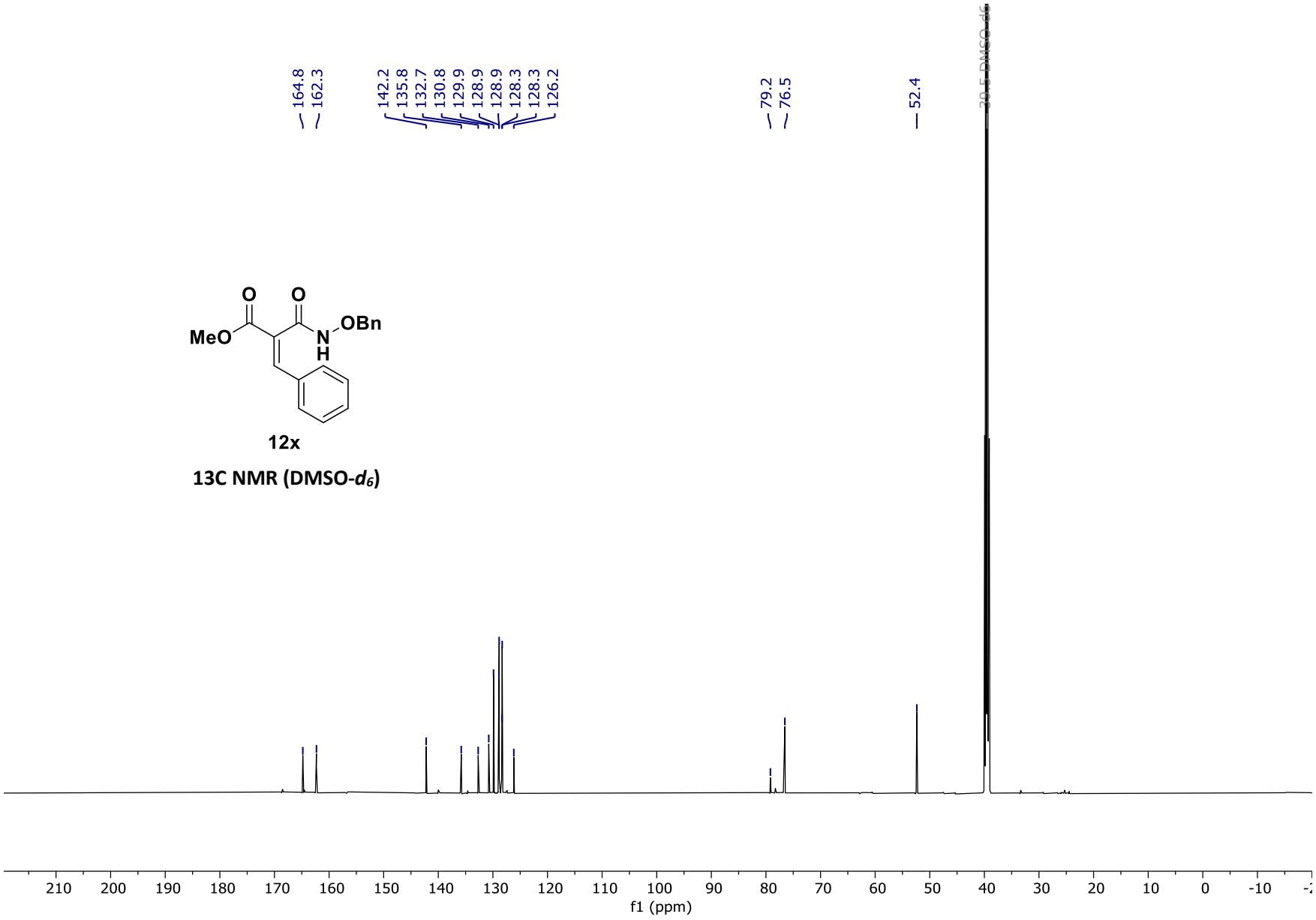

11.24
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.35
4.80
3.63
3.14
MeO
O
O
N
H
OBn
12'
1H NMR (DMSO-d6)
1.01
5.54
2.30
2.95
2.00
f1 (ppm)


167.8
162.3
135.8
128.9
128.3
76.9
52.0
39.5 DMSO-d6
O
O
MeO
N
H
OBn
12'
13C NMR (DMSO-d6)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



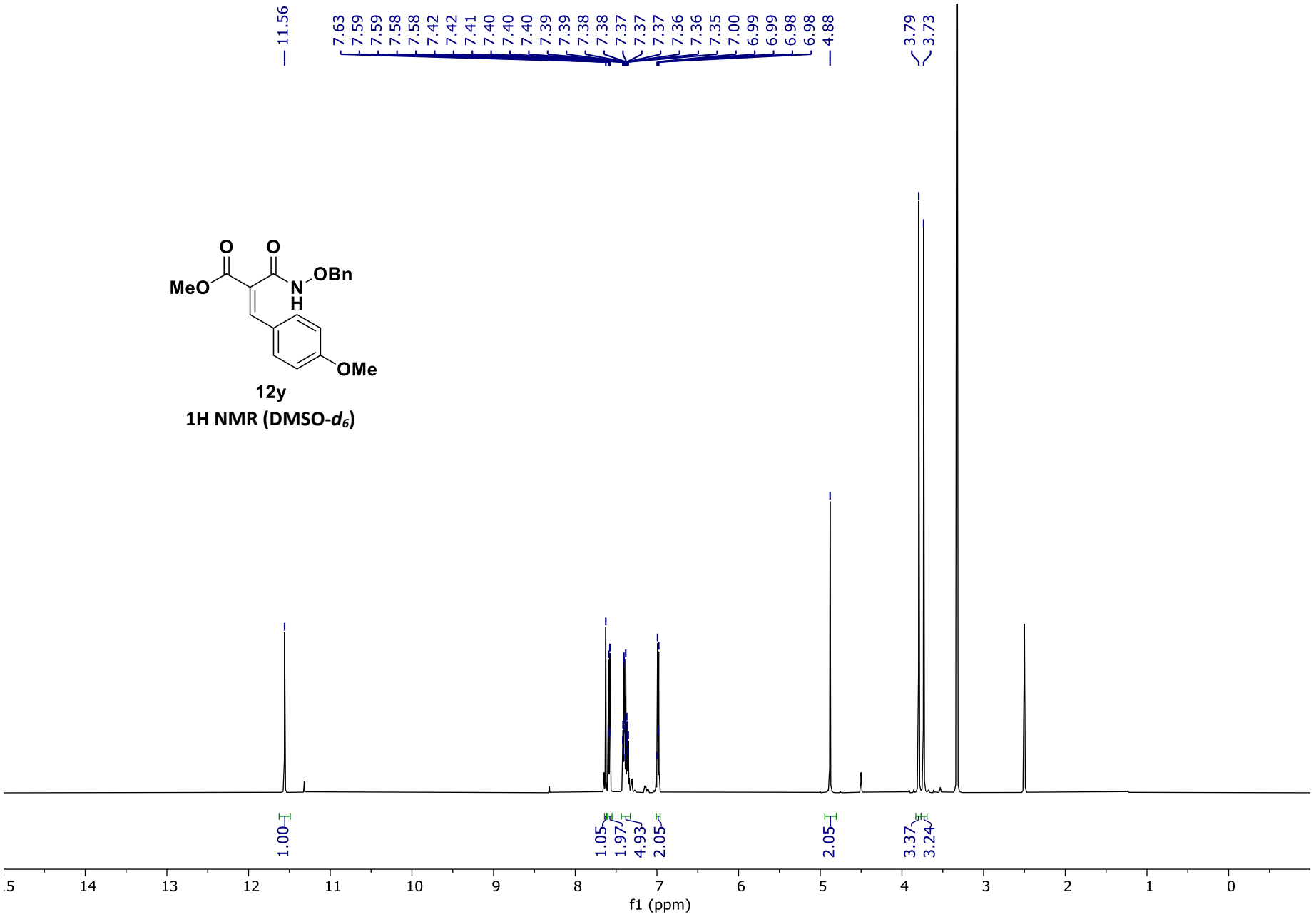
12x

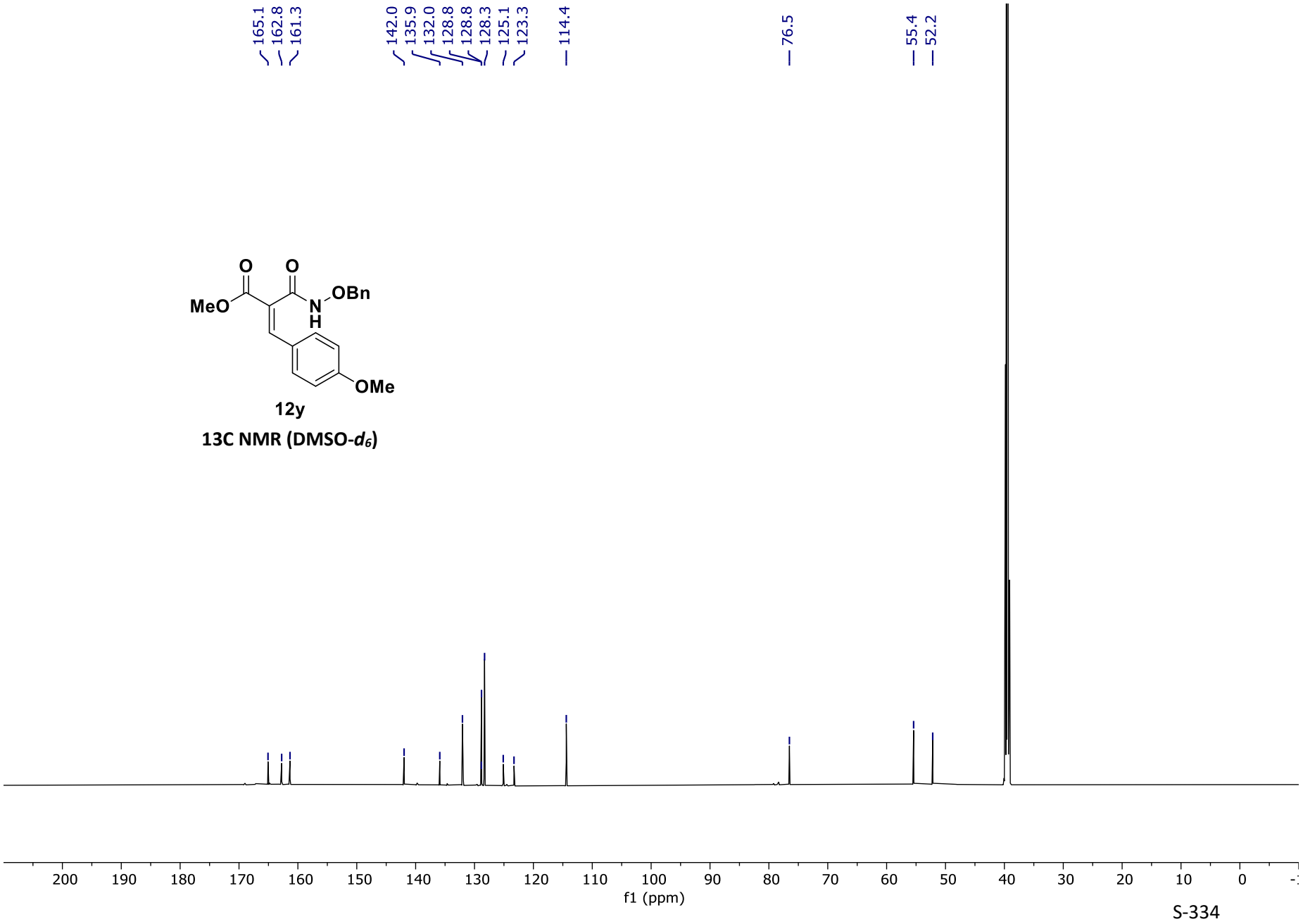
1H NMR (DMSO-d_6)



12x

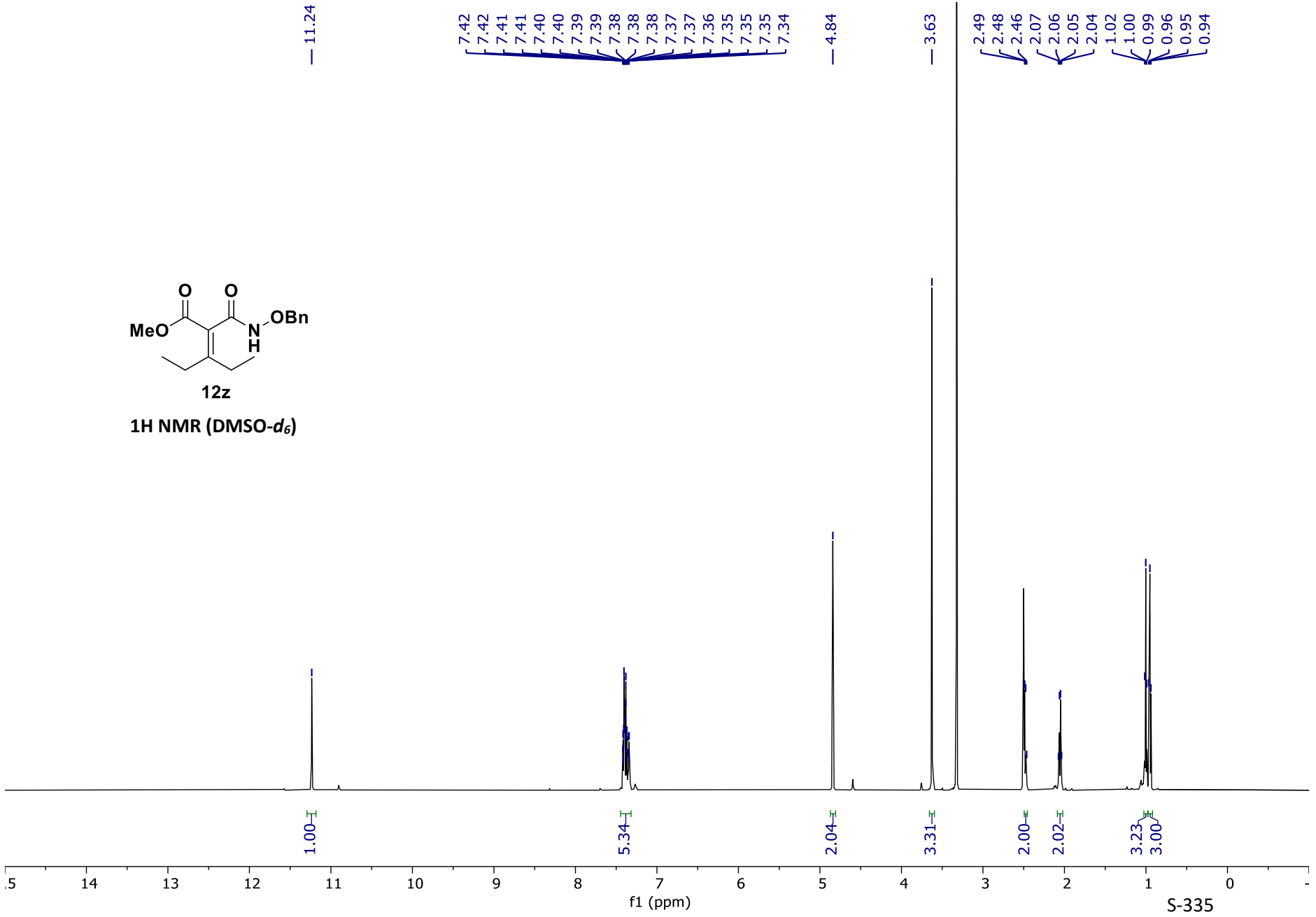
13C NMR (DMSO-d_6)

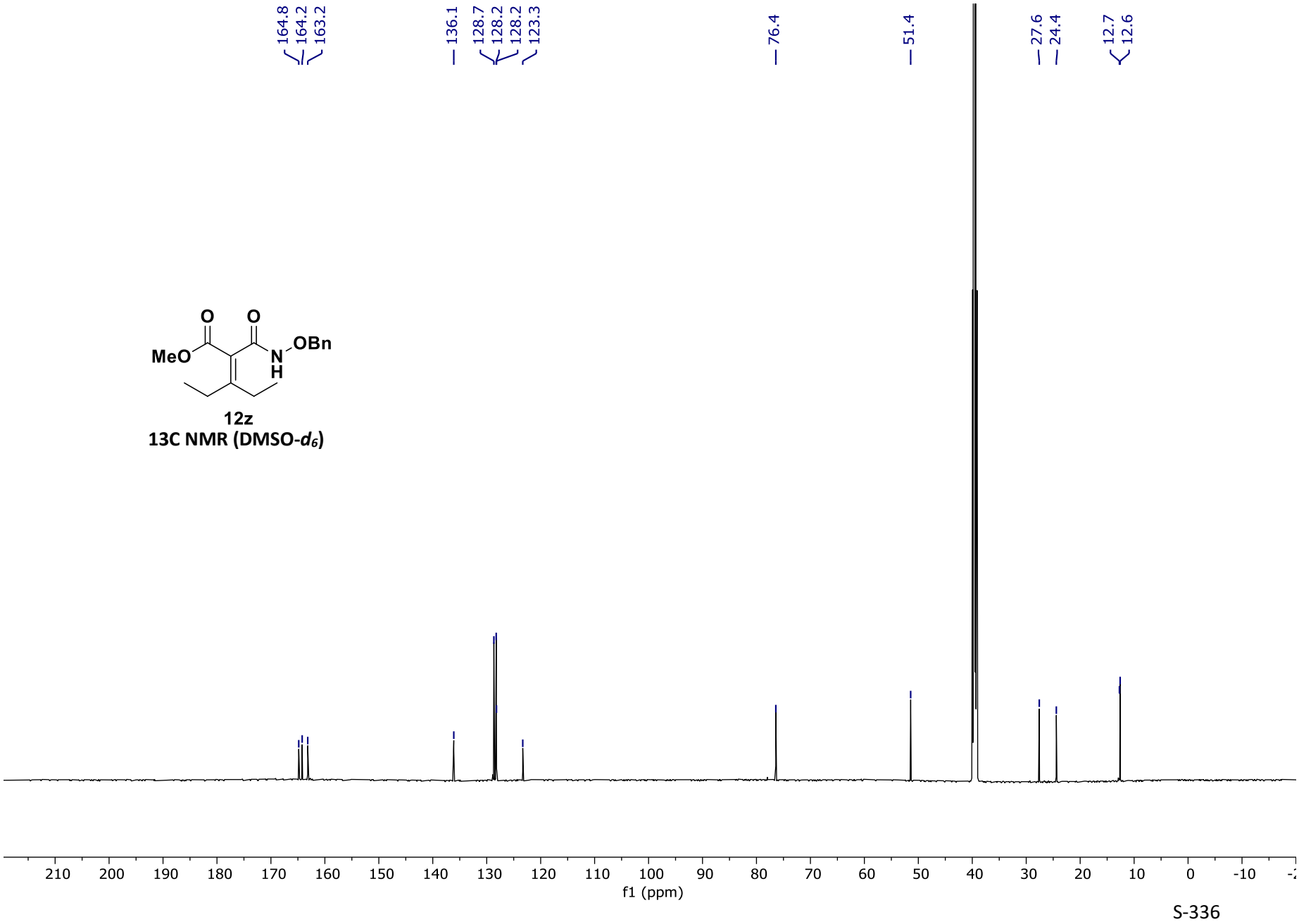

11.56
7.63
7.59
7.59
7.58
7.58
7.42
7.42
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.00
6.99
6.99
6.98
6.98
4.88
3.79
3.73
O
O
MeO
N
H
OBn
OMe
12y
1H NMR (DMSO-d6)
1.00
1.05
1.97
4.93
2.05
2.05
3.37
3.24
.5
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



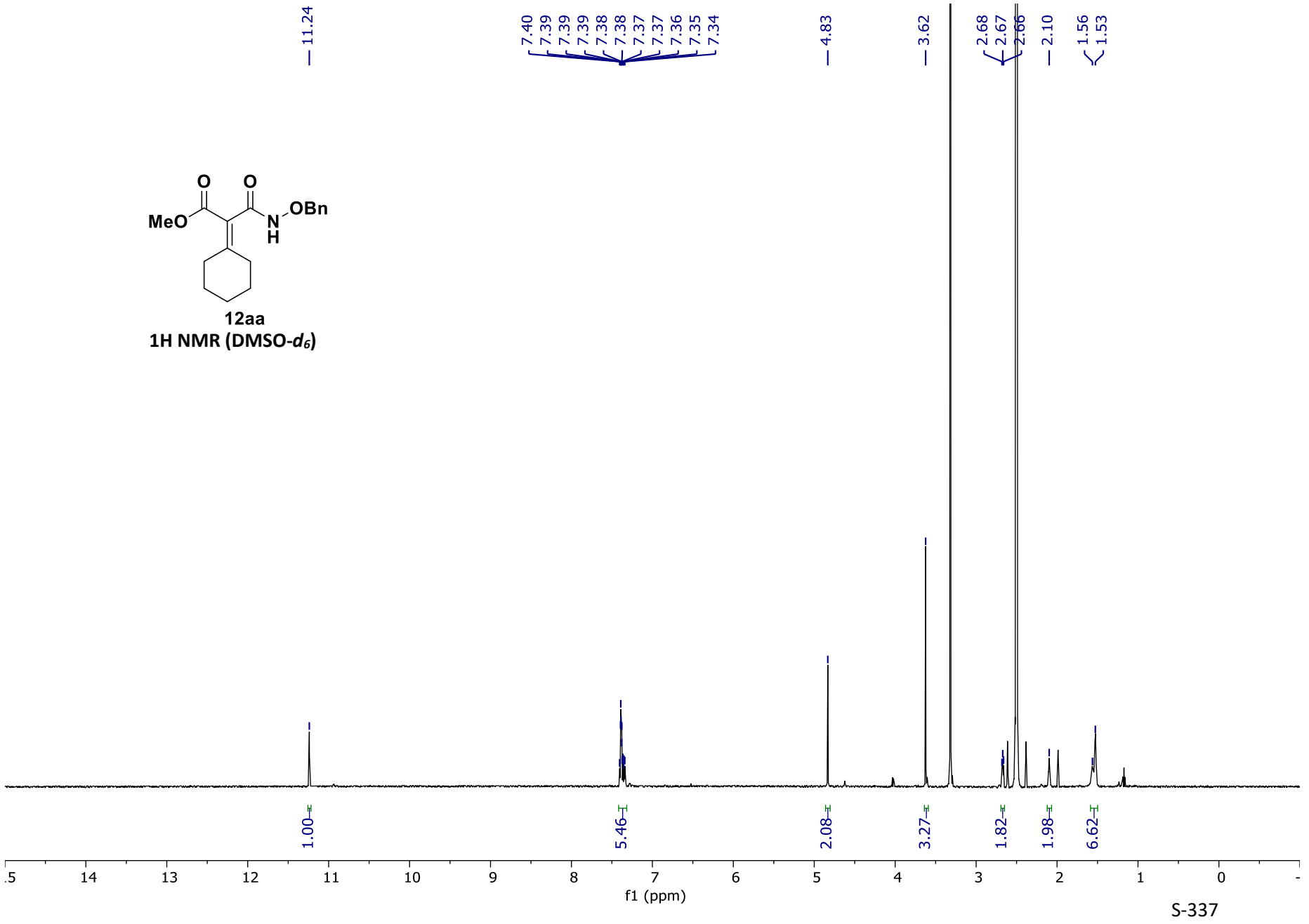
12y

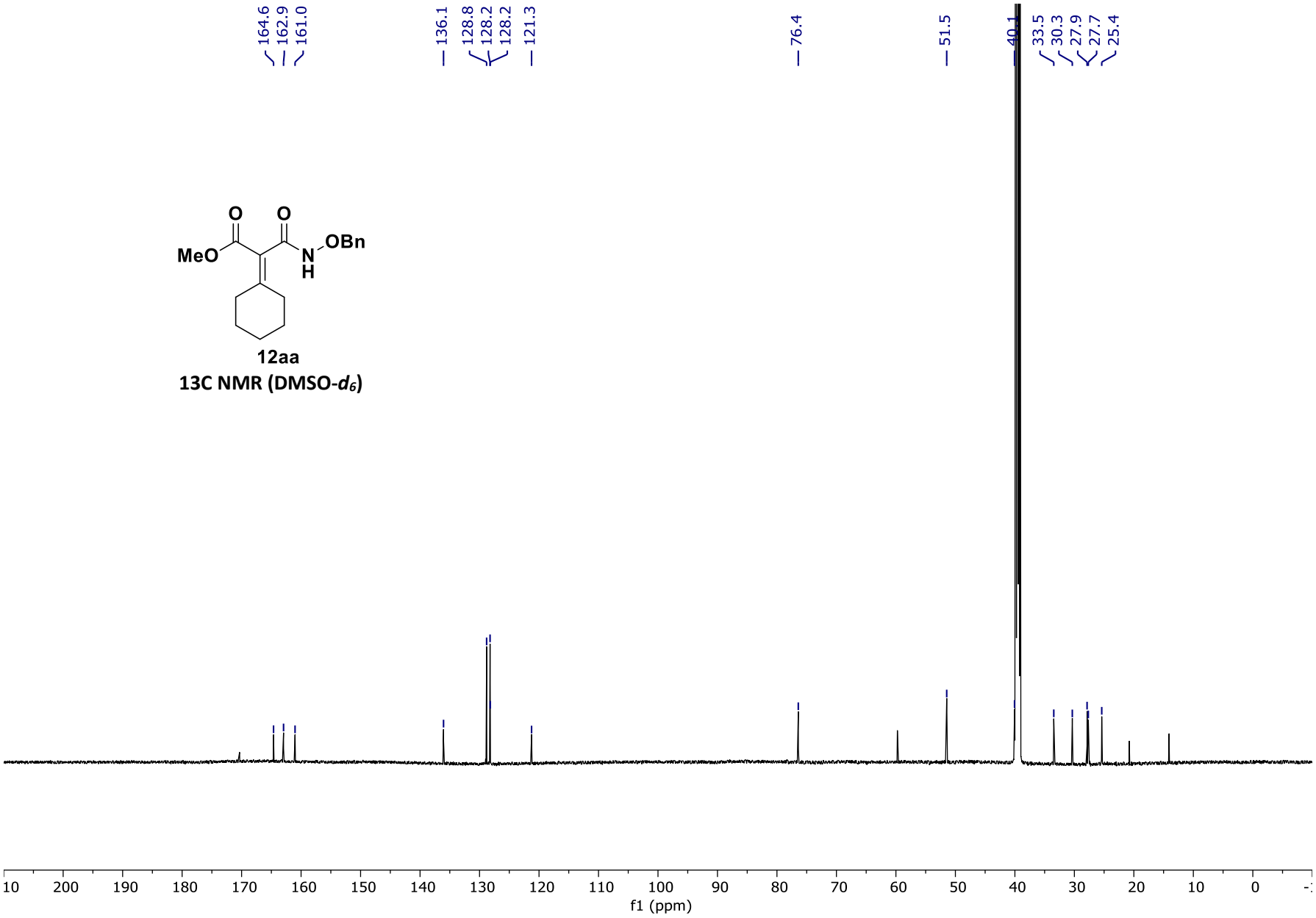
13C NMR (DMSO-d_6)


11.24
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.35
7.34
4.84
3.63
2.49
2.48
2.46
2.07
2.06
2.05
2.04
1.02
1.00
0.99
0.96
0.95
0.94
O
O
MeO
N
H
OBn
12z
1H NMR (DMSO-d6)
1.00
5.34
2.04
3.31
2.00
2.02
3.23
3.00
f1 (ppm)



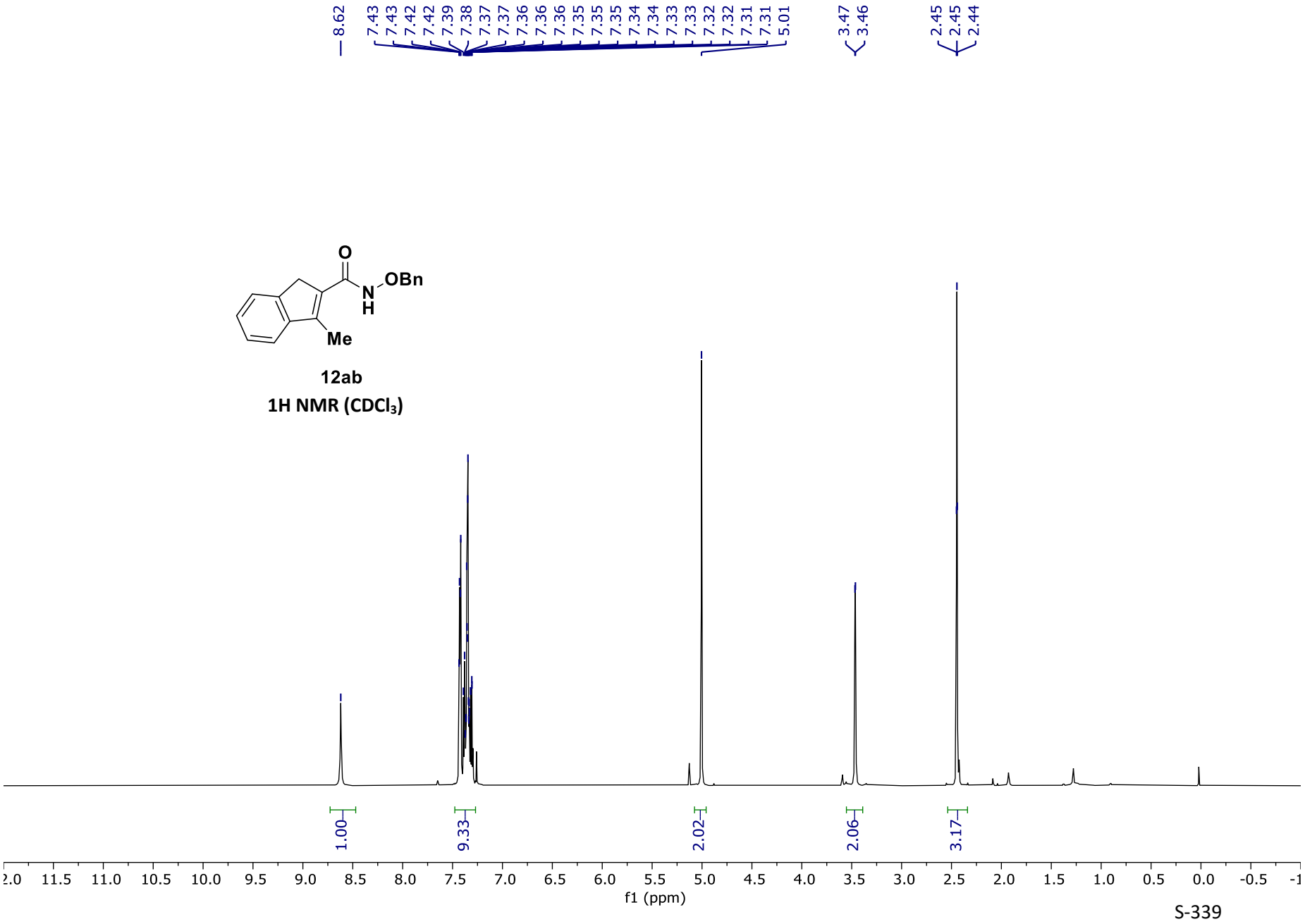
12z
13C NMR (DMSO-d_6)

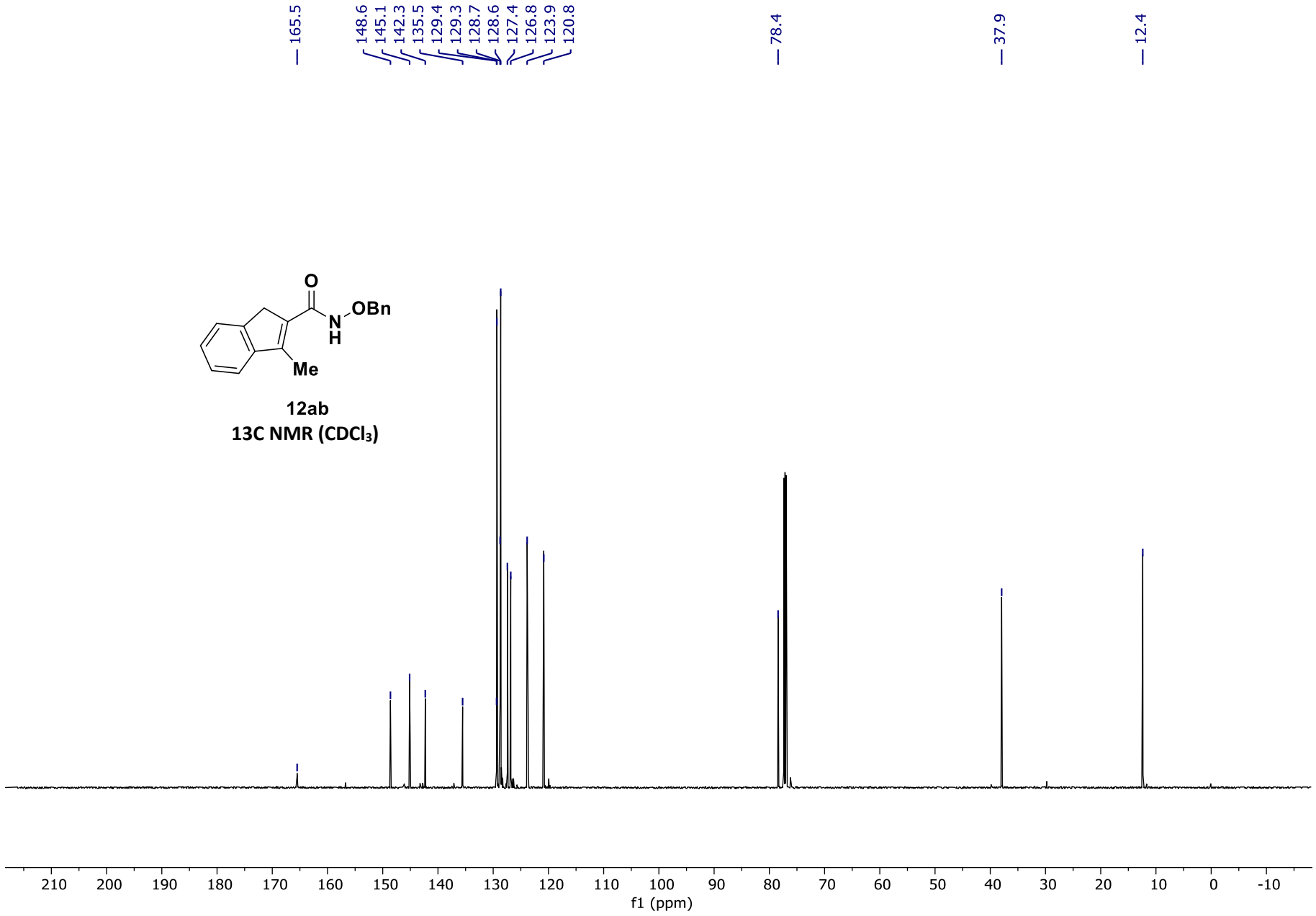

11.24
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.34
4.83
3.62
2.68
2.67
2.66
2.10
1.56
1.53
MeO
O
O
N
H
OBn
12aa
1H NMR (DMSO-d6)
1.00
5.46
2.08
3.27
1.82
1.98
6.62
f1 (ppm)

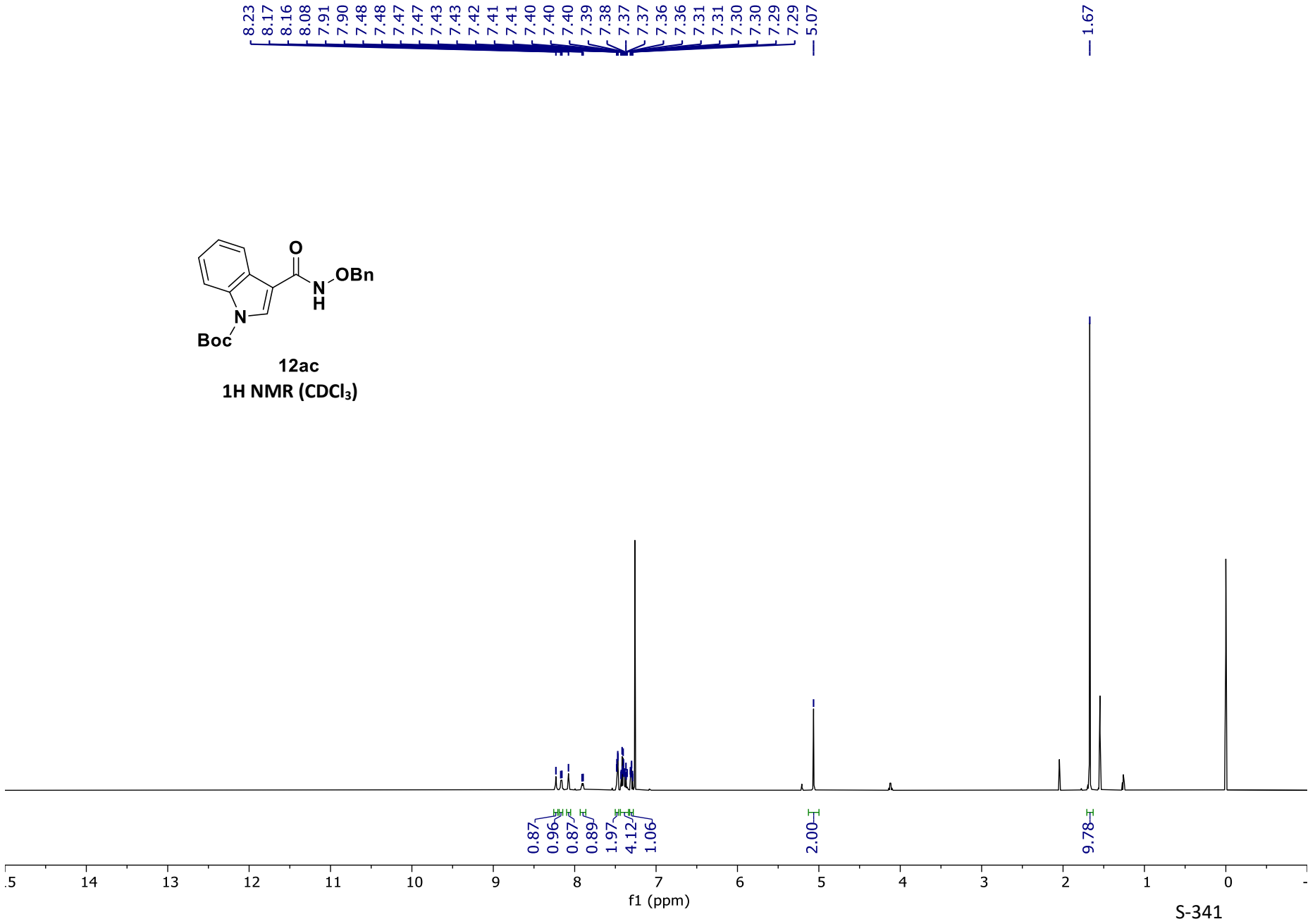


12aa

13C NMR (DMSO-d_6)

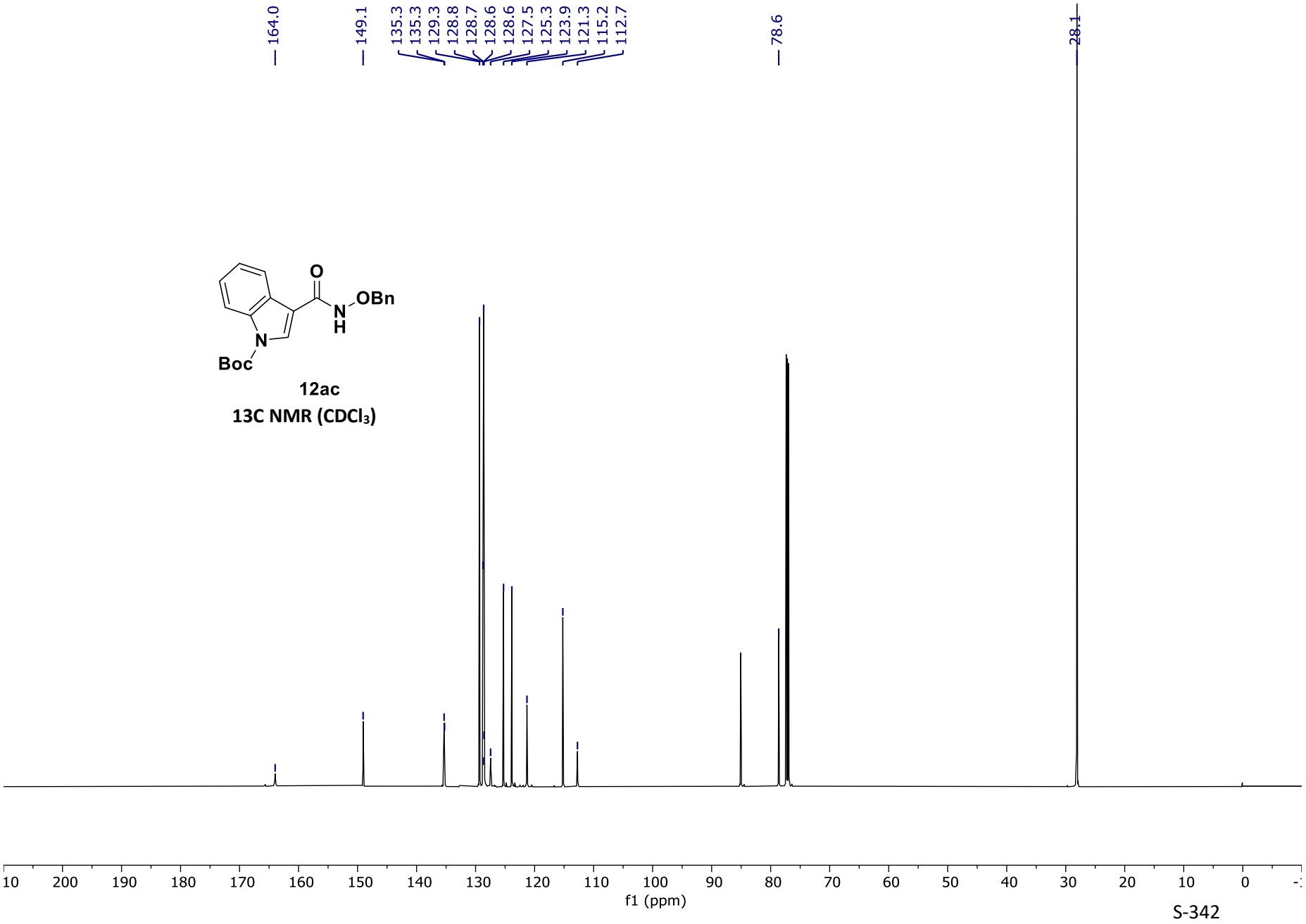

8.62
7.43
7.43
7.42
7.42
7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
5.01
3.47
3.46
2.45
2.45
2.44
O
N
H
OBn
Me
12ab
1H NMR (CDCl3)
1.00
9.33
2.02
2.06
3.17
f1 (ppm)

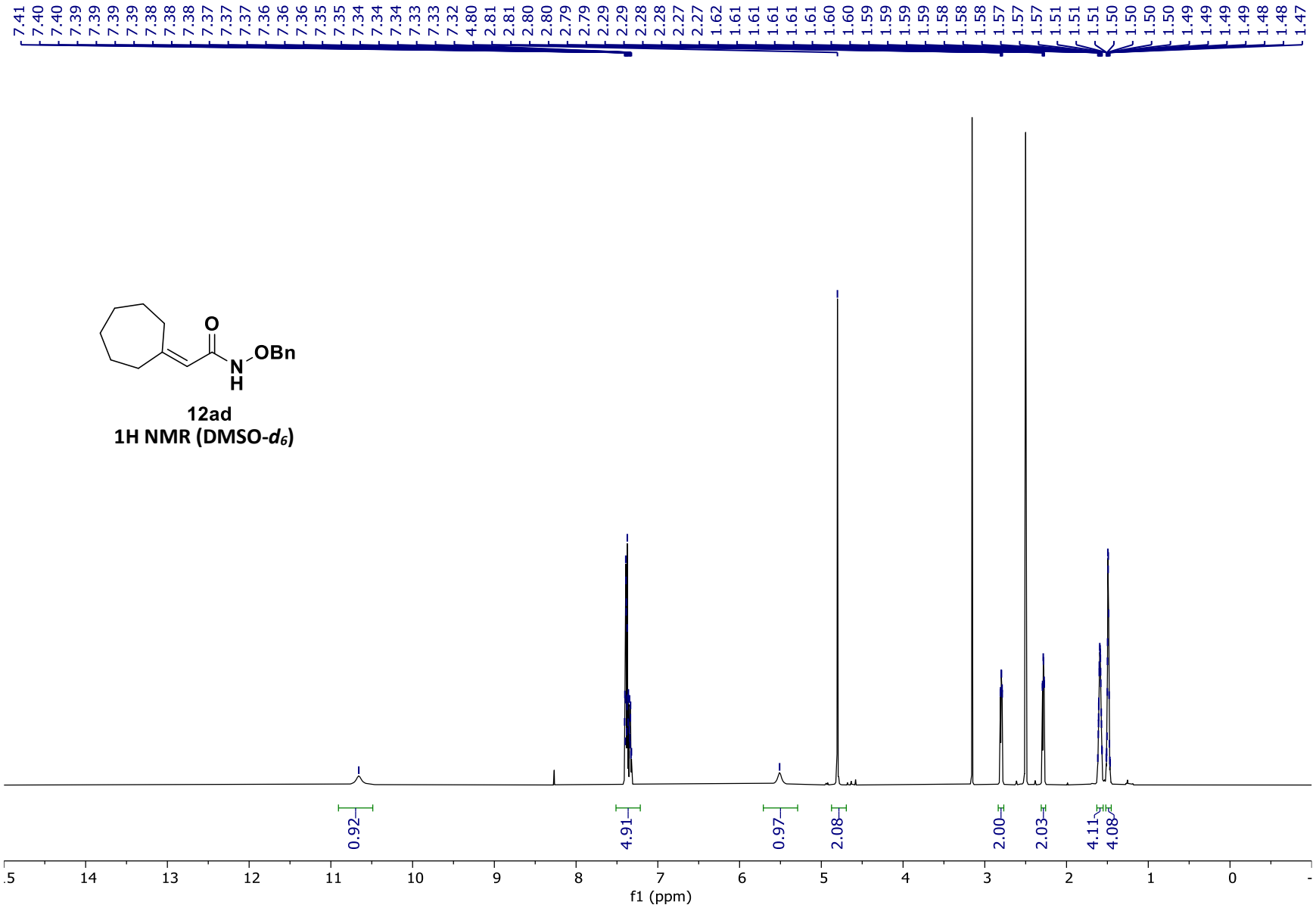

165.5
148.6
145.1
142.3
135.5
129.4
129.3
128.7
128.6
127.4
126.8
123.9
120.8
78.4
37.9
12.4
O
N
H
OBn
Me
12ab
13C NMR (CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

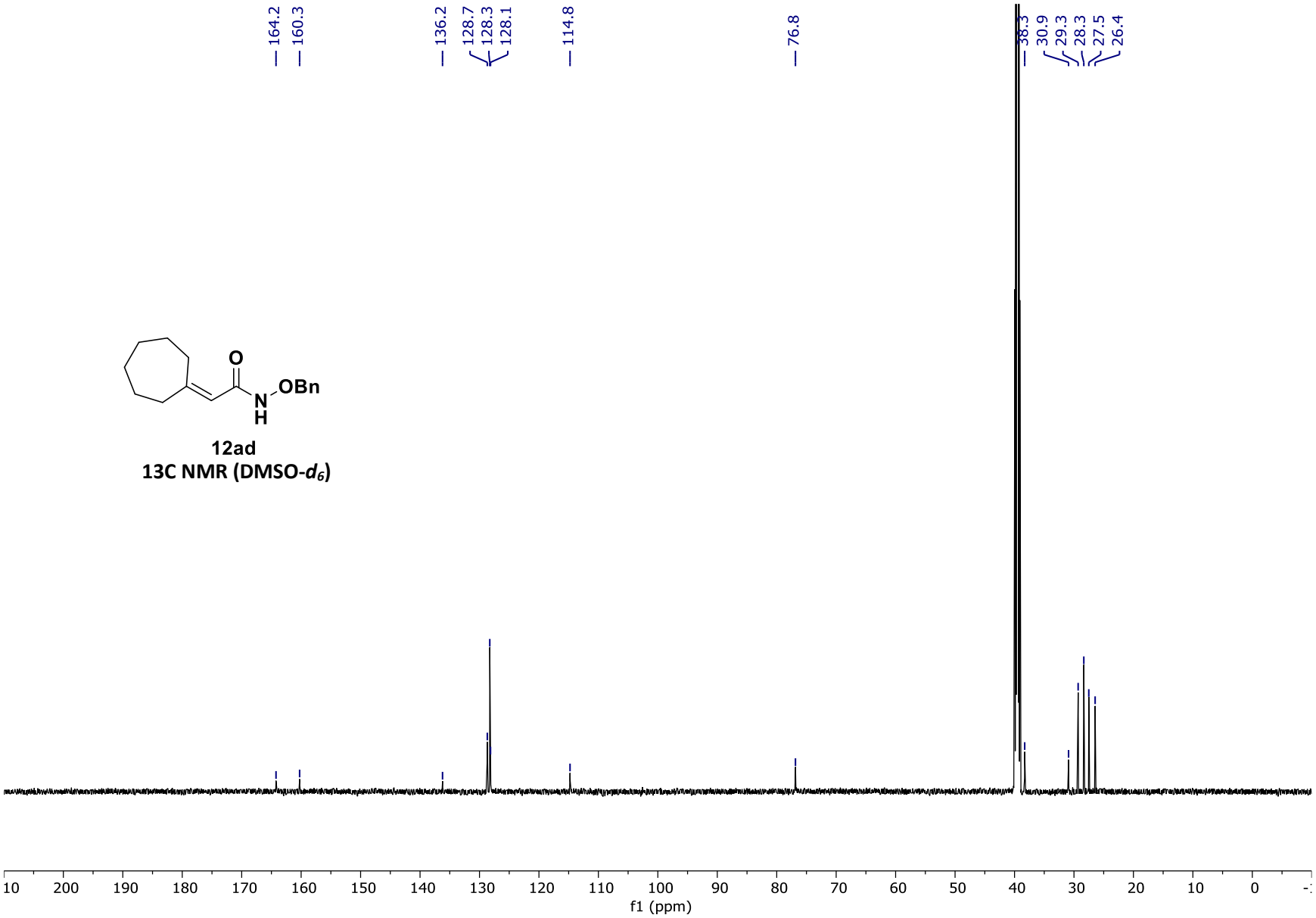


12ac

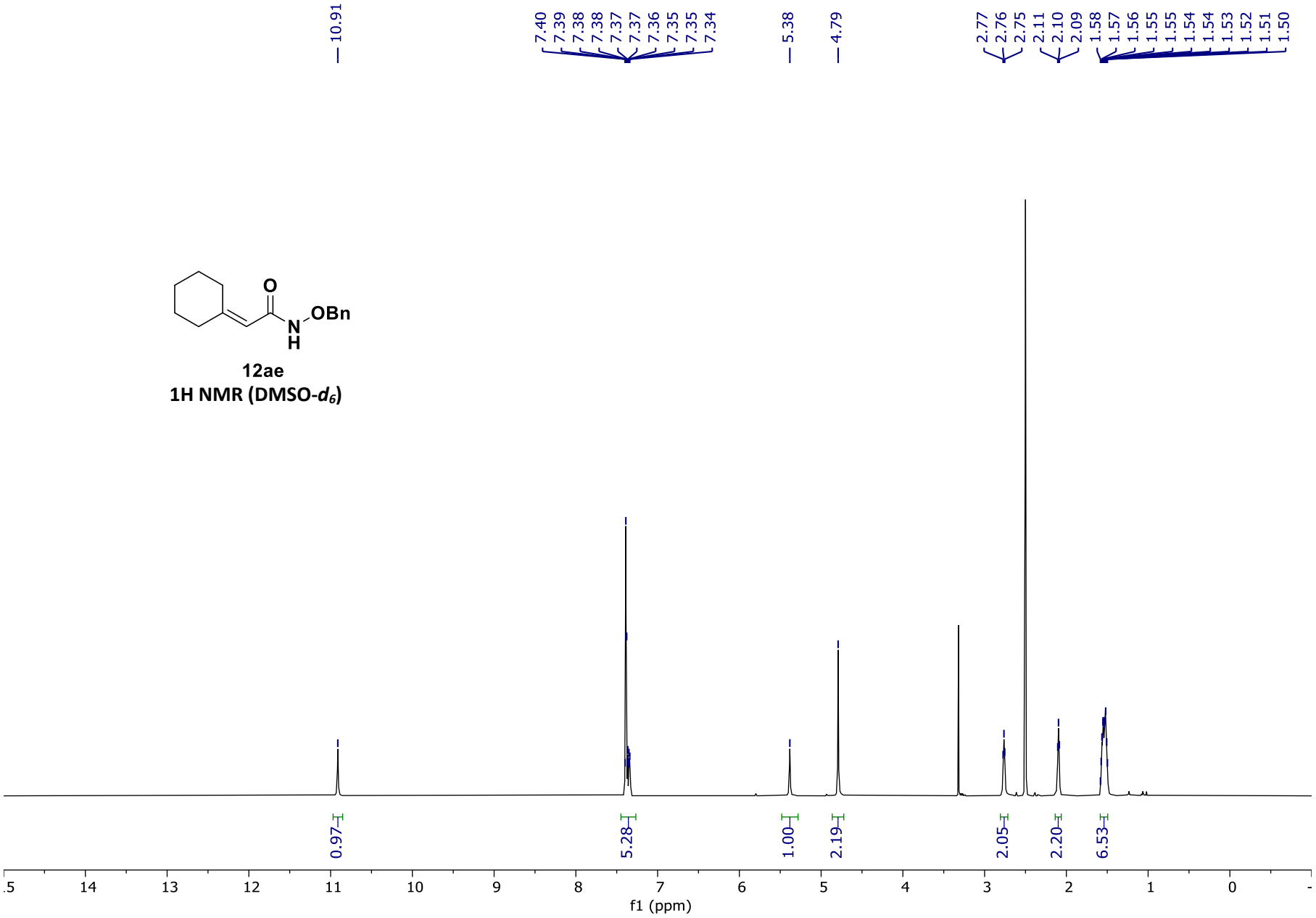
1H NMR ($CDCl_3$)

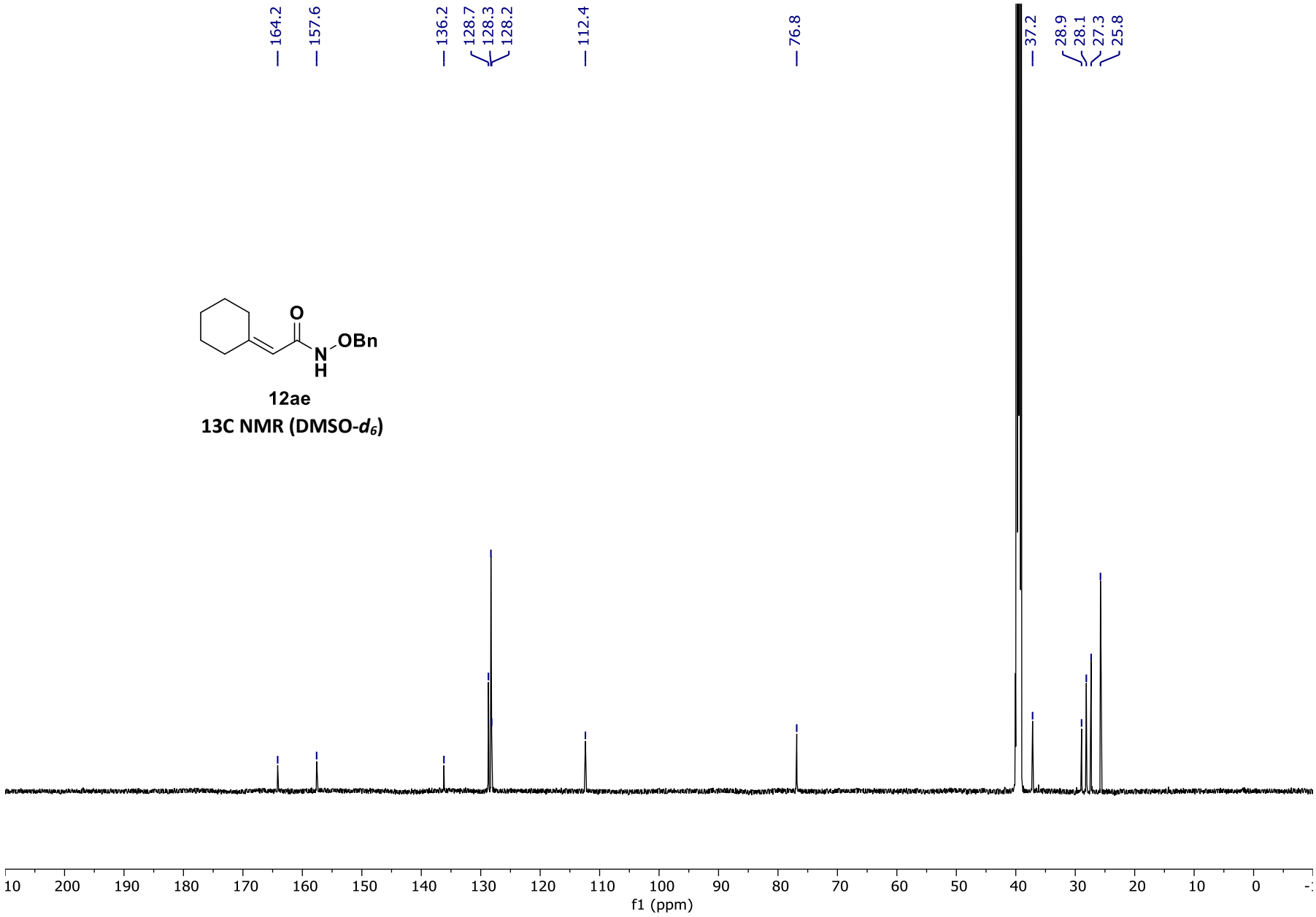

164.0
149.1
135.3
135.3
129.3
128.8
128.7
128.6
128.6
127.5
125.3
123.9
121.3
115.2
112.7
78.6
28.1
O
N
OBn
H
N
Boc
12ac
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

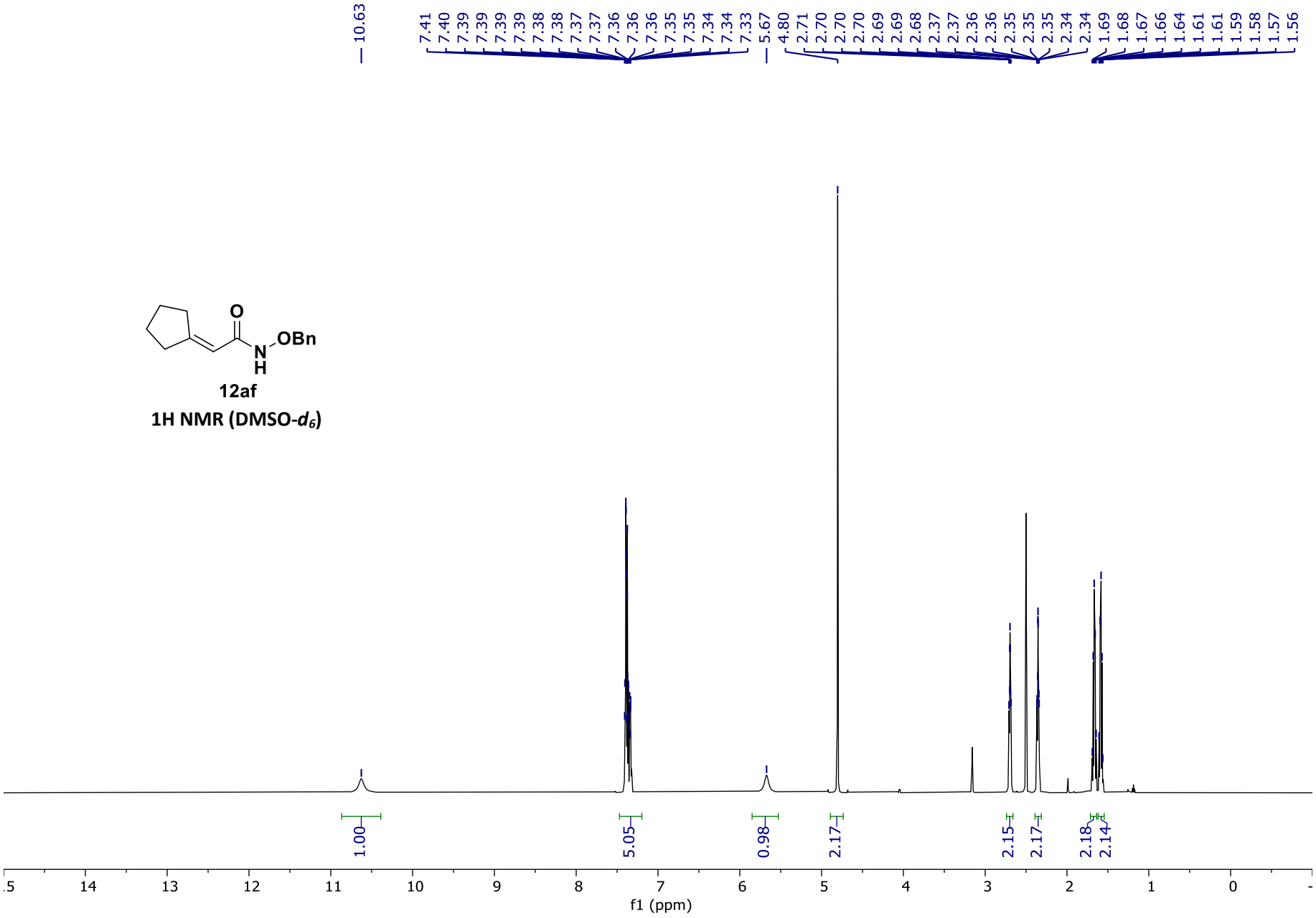

7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 4.80 2.81 2.81 2.80 2.80 2.79 2.29 2.29 2.28 2.28 2.27 2.27 1.62 1.61 1.61 1.61 1.61 1.61 1.60 1.60 1.59 1.59 1.59 1.59 1.58 1.58 1.58 1.57 1.57 1.57 1.51 1.51 1.51 1.50 1.50 1.50 1.50 1.49 1.49 1.49 1.49 1.48 1.48 1.47
O
N
H
OBn
12ad
1H NMR (DMSO-d6)
0.92
4.91
0.97
2.08
2.00
2.03
4.11
4.08
.5 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -
f1 (ppm)

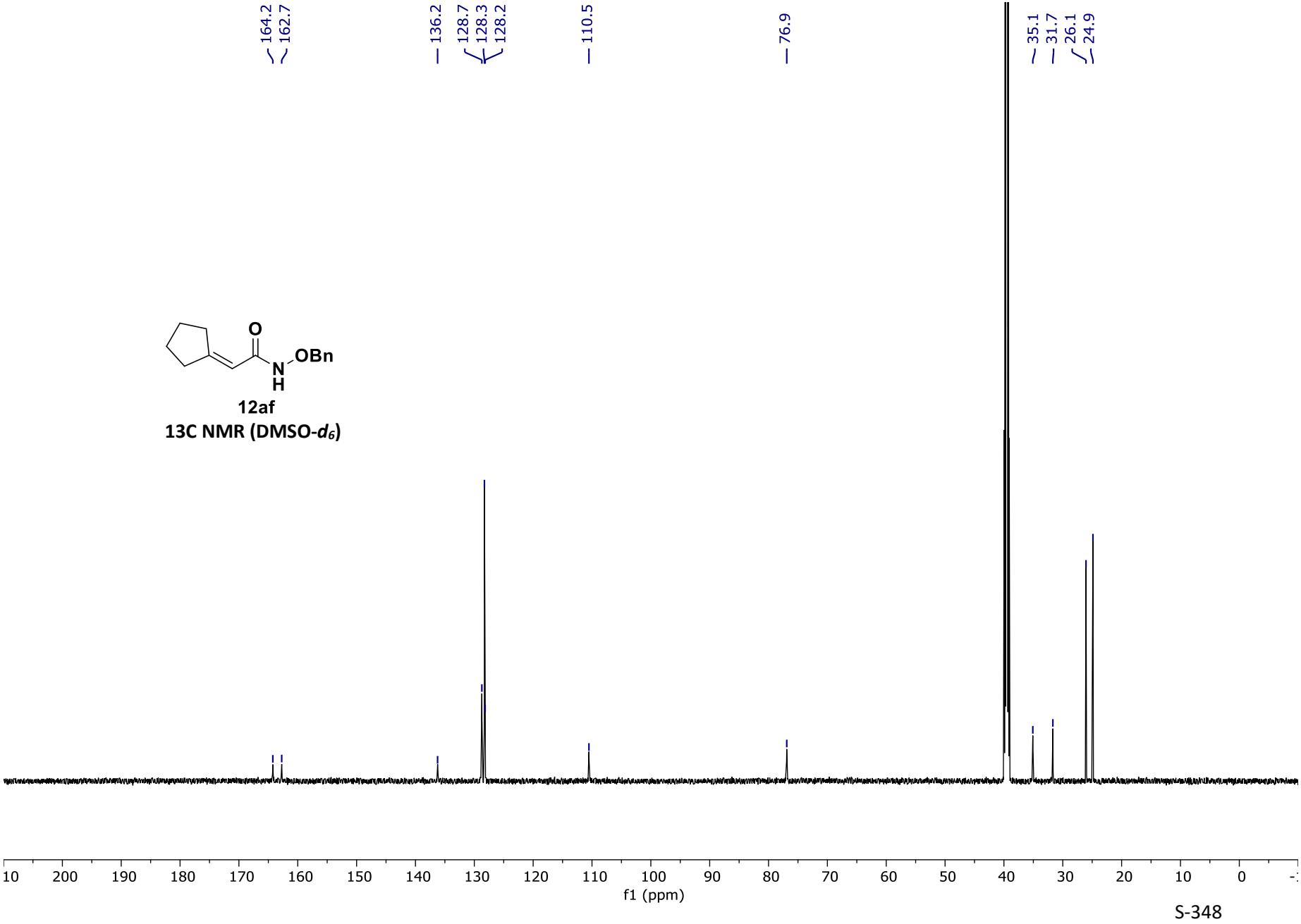


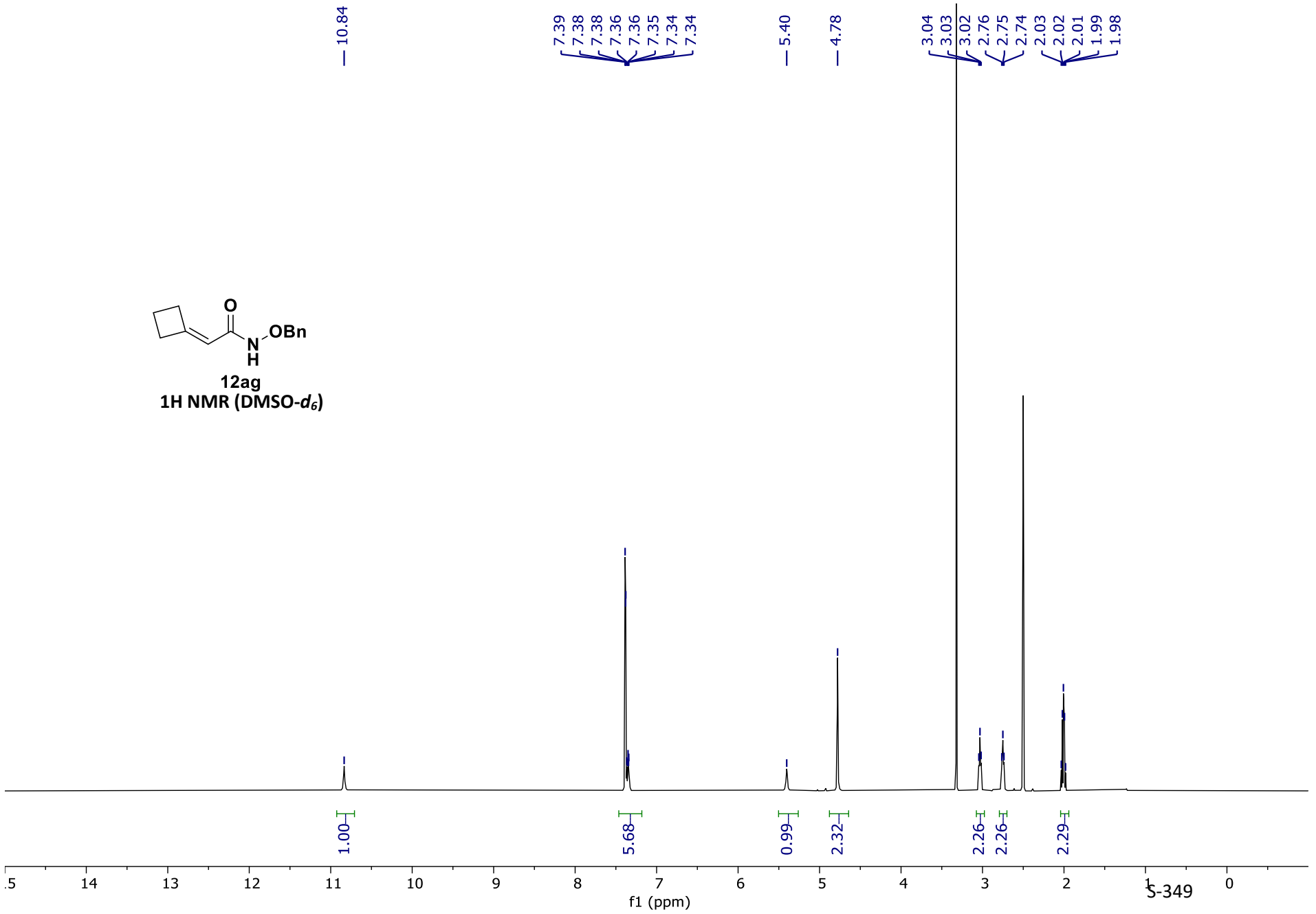
12ad
13C NMR (DMSO-d_6)

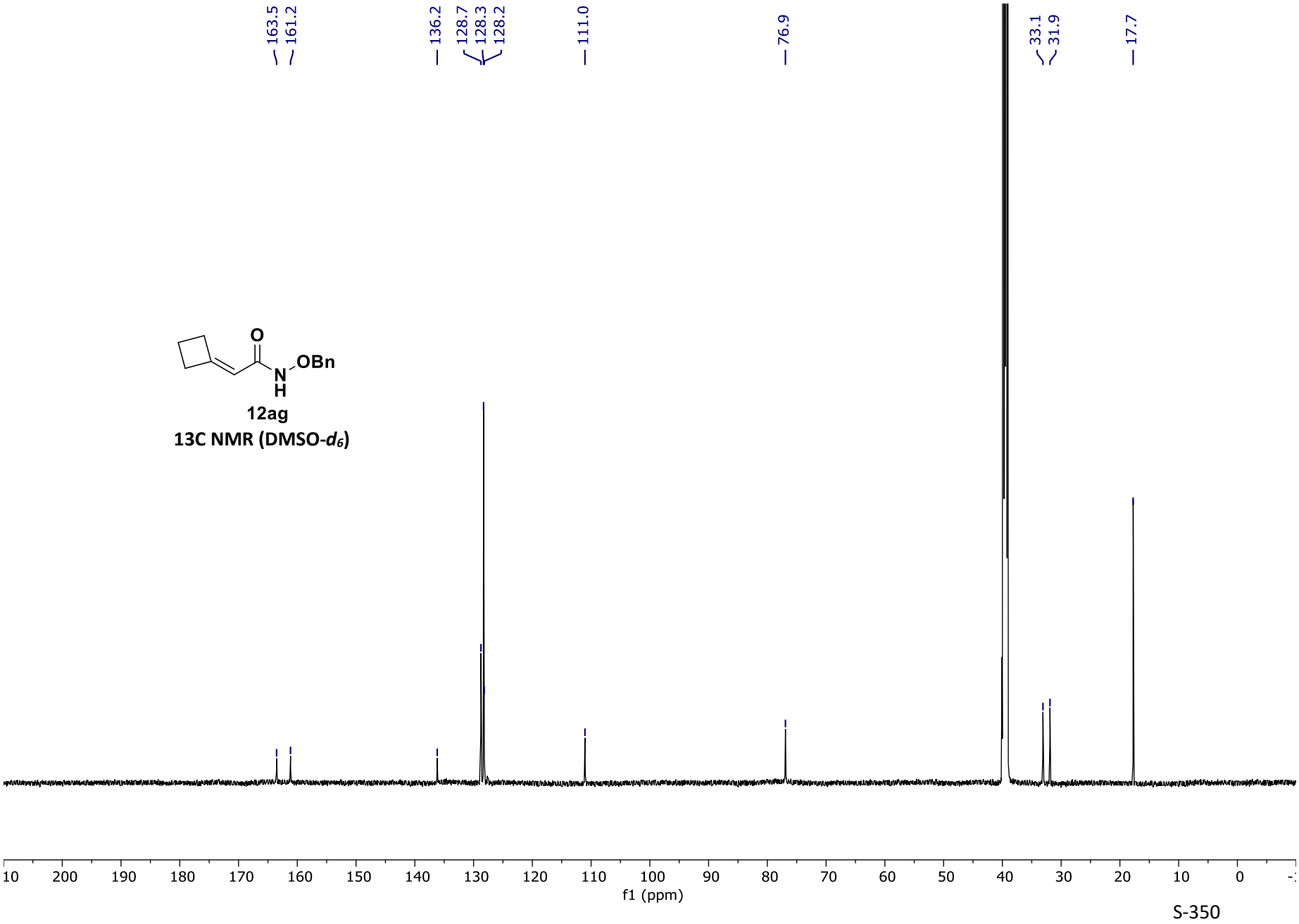

10.91
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
5.38
4.79
2.77
2.76
2.75
2.11
2.10
2.09
1.58
1.57
1.56
1.55
1.55
1.54
1.54
1.53
1.52
1.51
1.50
O
N
H
OBn
12ae
1H NMR (DMSO-d6)
0.97
5.28
1.00
2.19
2.05
2.20
6.53
f1 (ppm)

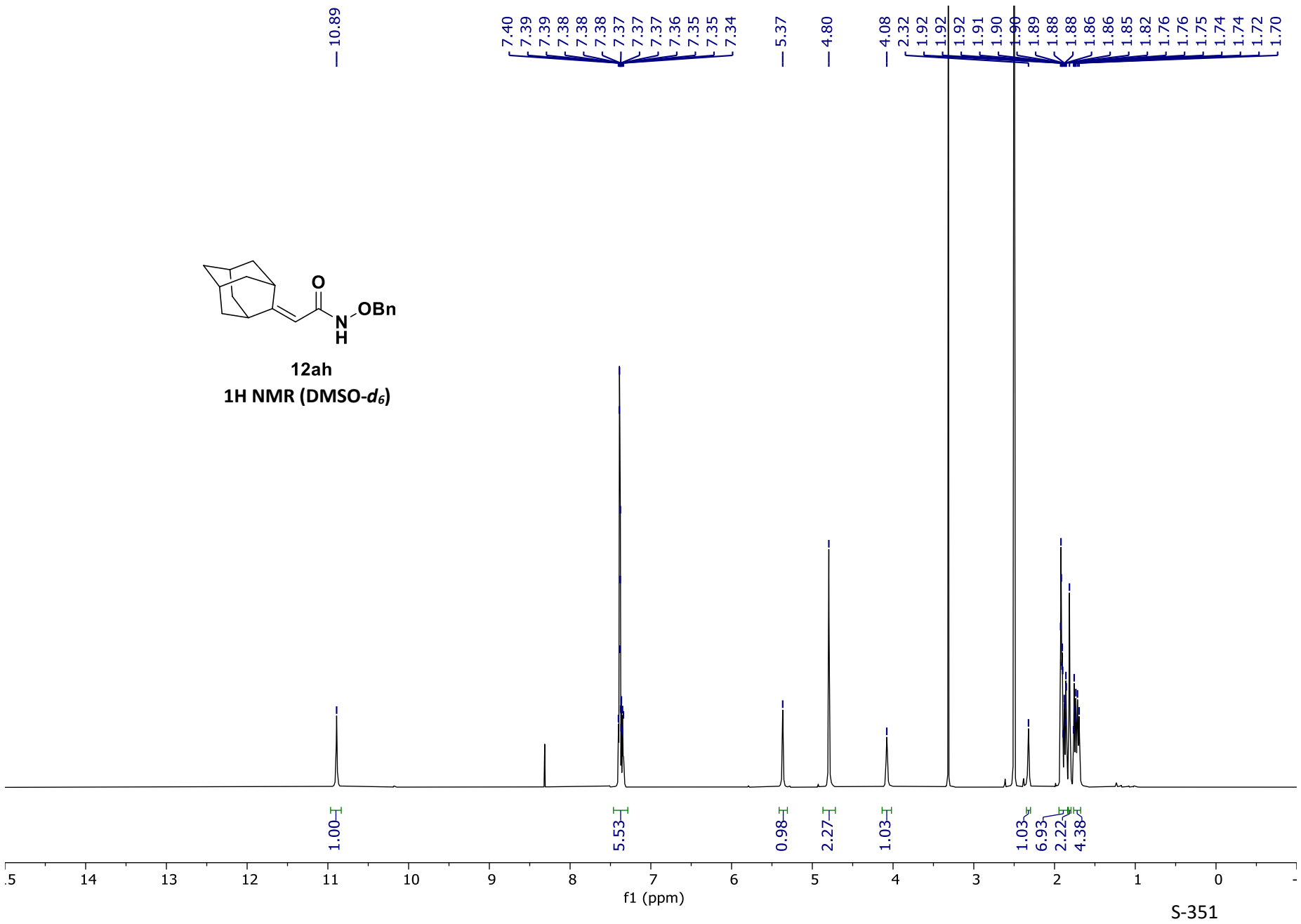

164.2
157.6
136.2
128.7
128.3
128.2
112.4
76.8
37.2
28.9
28.1
27.3
25.8
O
N
H
OBn
12ae
13C NMR (DMSO-d_6)
f1 (ppm)

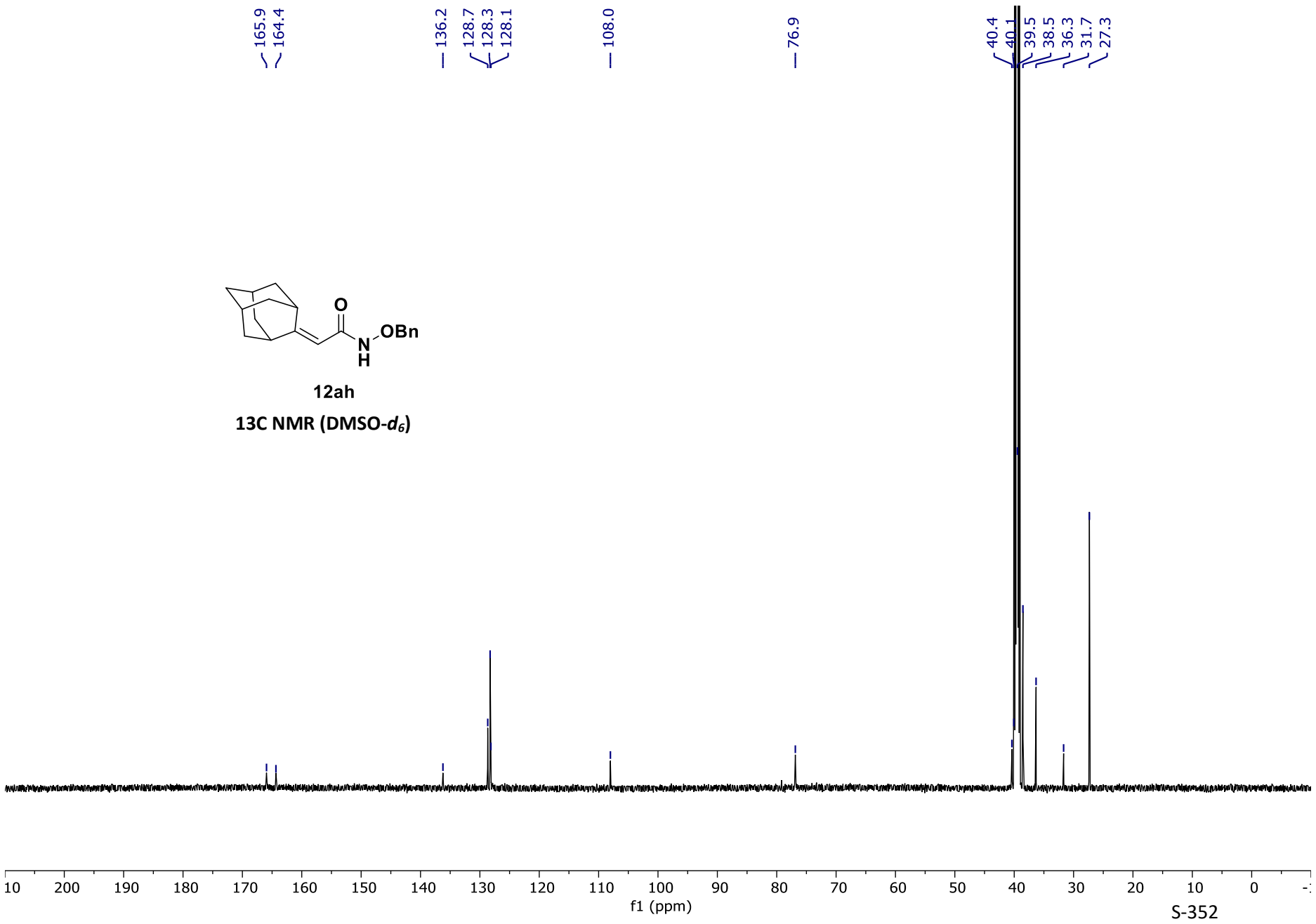

10.63
7.41
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
5.67
4.80
2.71
2.70
2.70
2.70
2.69
2.69
2.68
2.37
2.37
2.36
2.36
2.35
2.35
2.35
2.34
2.34
1.69
1.68
1.67
1.66
1.64
1.61
1.61
1.59
1.58
1.57
1.56
O
OBn
N
H
12af
1H NMR (DMSO-d6)
1.00
5.05
0.98
2.17
2.15
2.17
2.18
2.14
f1 (ppm)

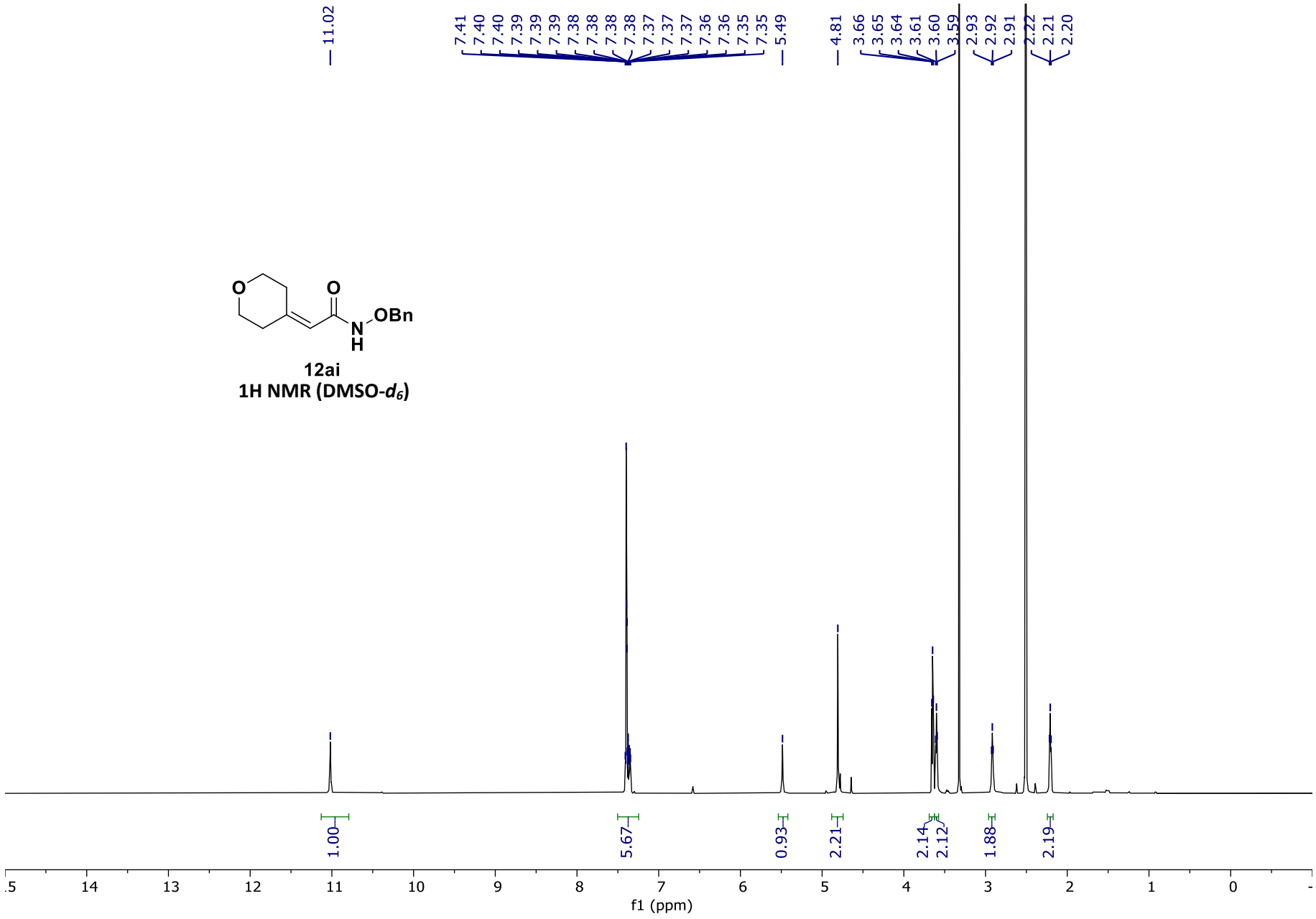

164.2
162.7
136.2
128.7
128.3
128.2
110.5
76.9
35.1
31.7
26.1
24.9
O
N
H
OBn
12af
13C NMR (DMSO-d_6)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

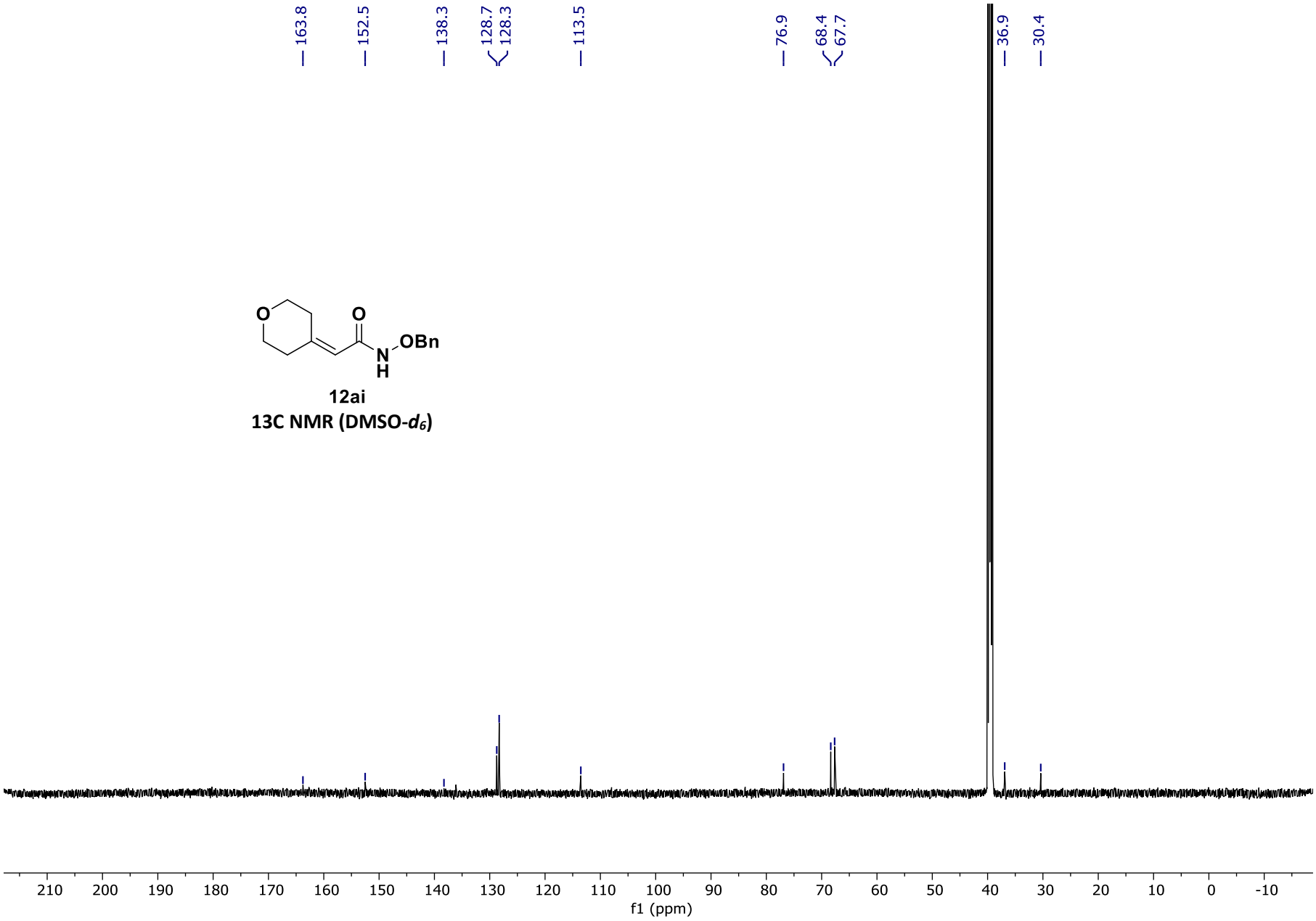

10.84
7.39
7.38
7.38
7.36
7.36
7.35
7.34
7.34
5.40
4.78
3.04
3.03
3.02
2.76
2.75
2.74
2.03
2.02
2.01
1.99
1.98
O
N
H
OBn
12ag
1H NMR (DMSO-d6)
1.00
5.68
0.99
2.32
2.26
2.26
2.29
f1 (ppm)

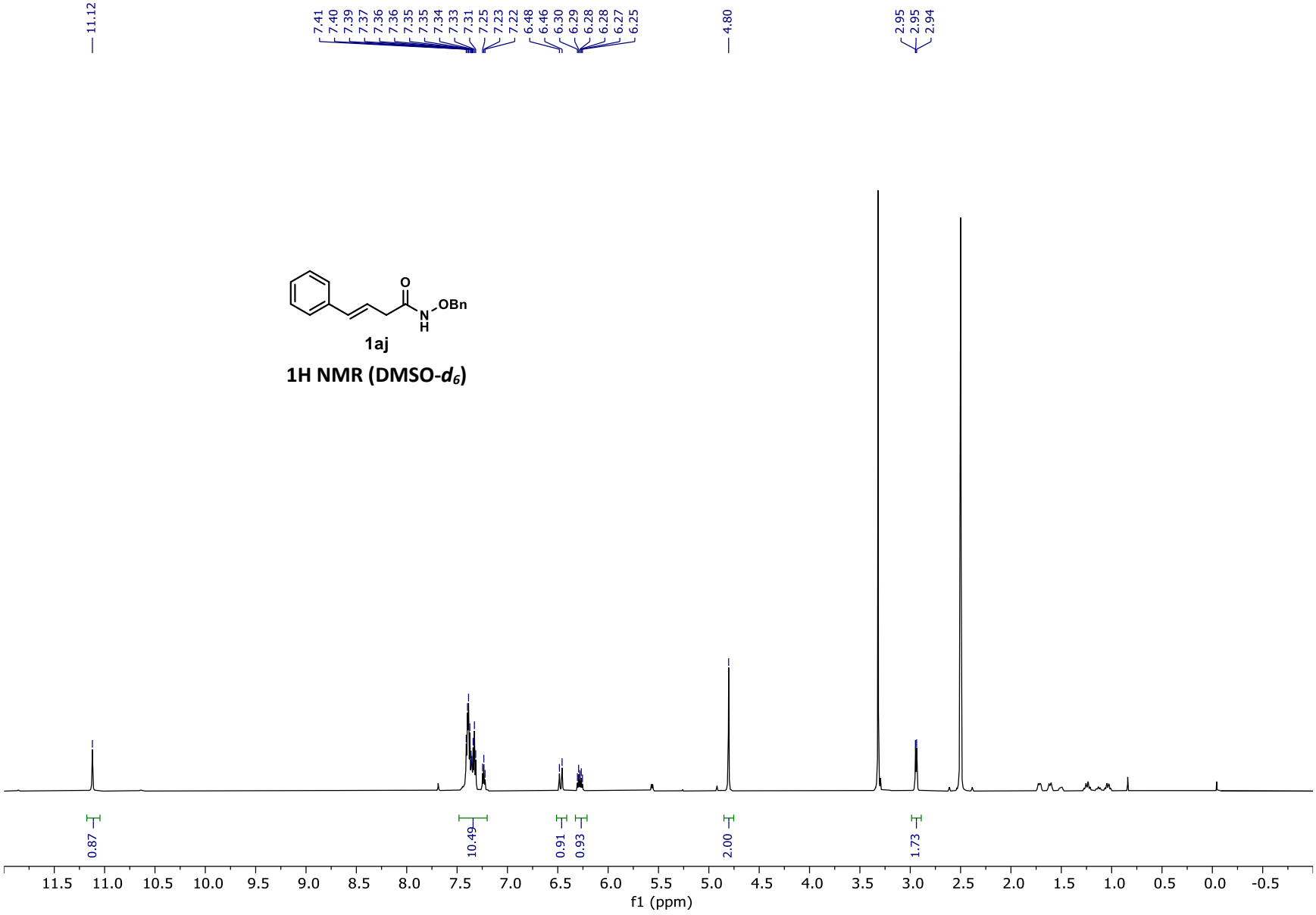

163.5
161.2
136.2
128.7
128.3
128.2
111.0
76.9
33.1
31.9
17.7
O
N
H
OBn
12ag
13C NMR (DMSO-d_6)
f1 (ppm)

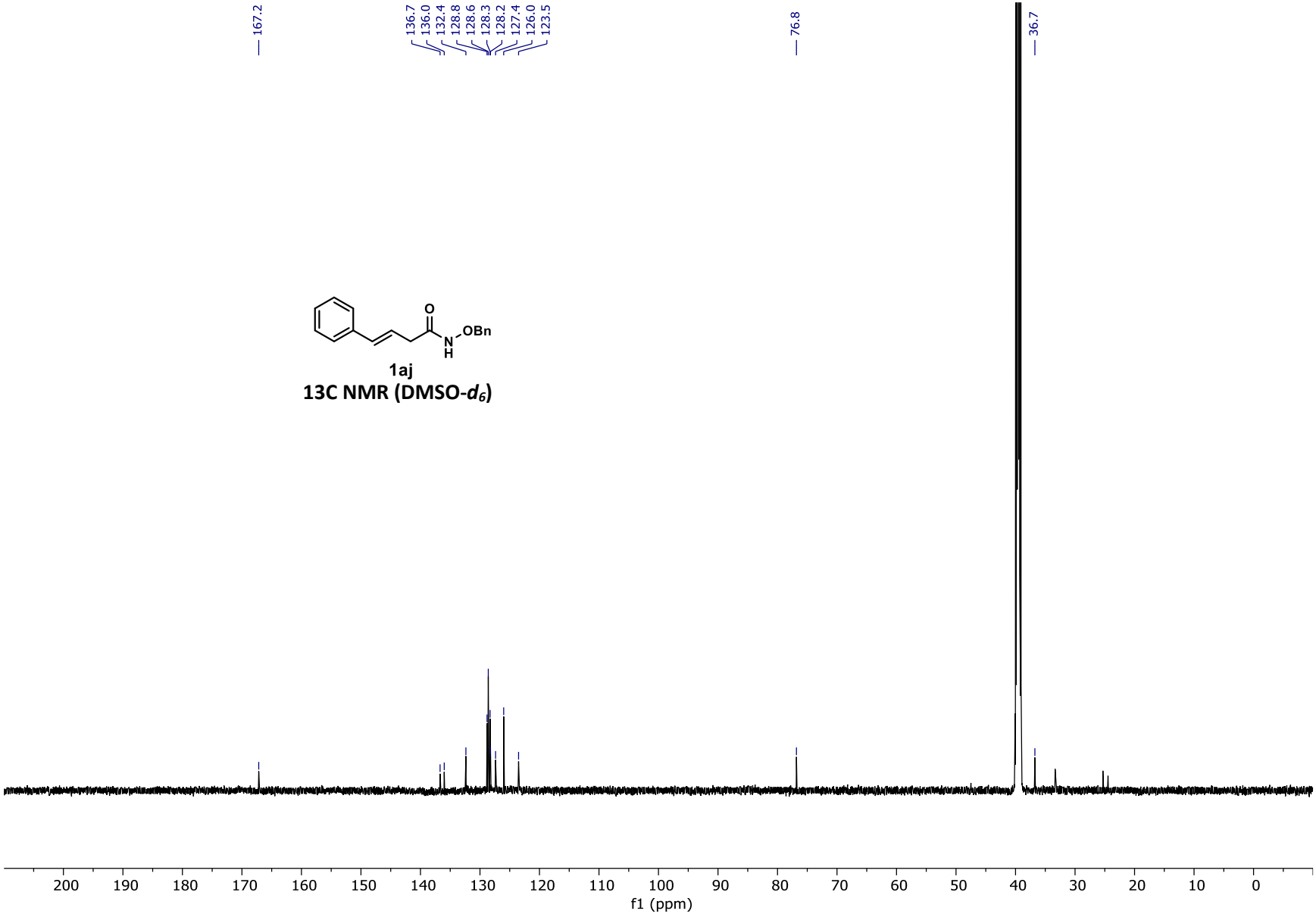

10.89
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.34
5.37
4.80
4.08
2.32
1.92
1.92
1.92
1.91
1.90
1.90
1.89
1.88
1.88
1.86
1.86
1.85
1.82
1.76
1.76
1.75
1.74
1.74
1.72
1.70
O
N
H
OBn
12ah
1H NMR (DMSO-d6)
1.00
5.53
0.98
2.27
1.03
1.03
6.93
2.22
4.38
f1 (ppm)


165.9
164.4
136.2
128.7
128.3
128.1
108.0
76.9
40.4
40.1
39.5
38.5
36.3
31.7
27.3
O
N
H
OBn
12ah
13C NMR (DMSO-d_6)
f1 (ppm)


11.02
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
5.49
4.81
3.66
3.65
3.64
3.61
3.60
3.59
2.93
2.92
2.91
2.22
2.21
2.20
O
O
N
H
OBn
12ai
1H NMR (DMSO-d6)
1.00
5.67
0.93
2.21
2.14
2.12
1.88
2.19
f1 (ppm)

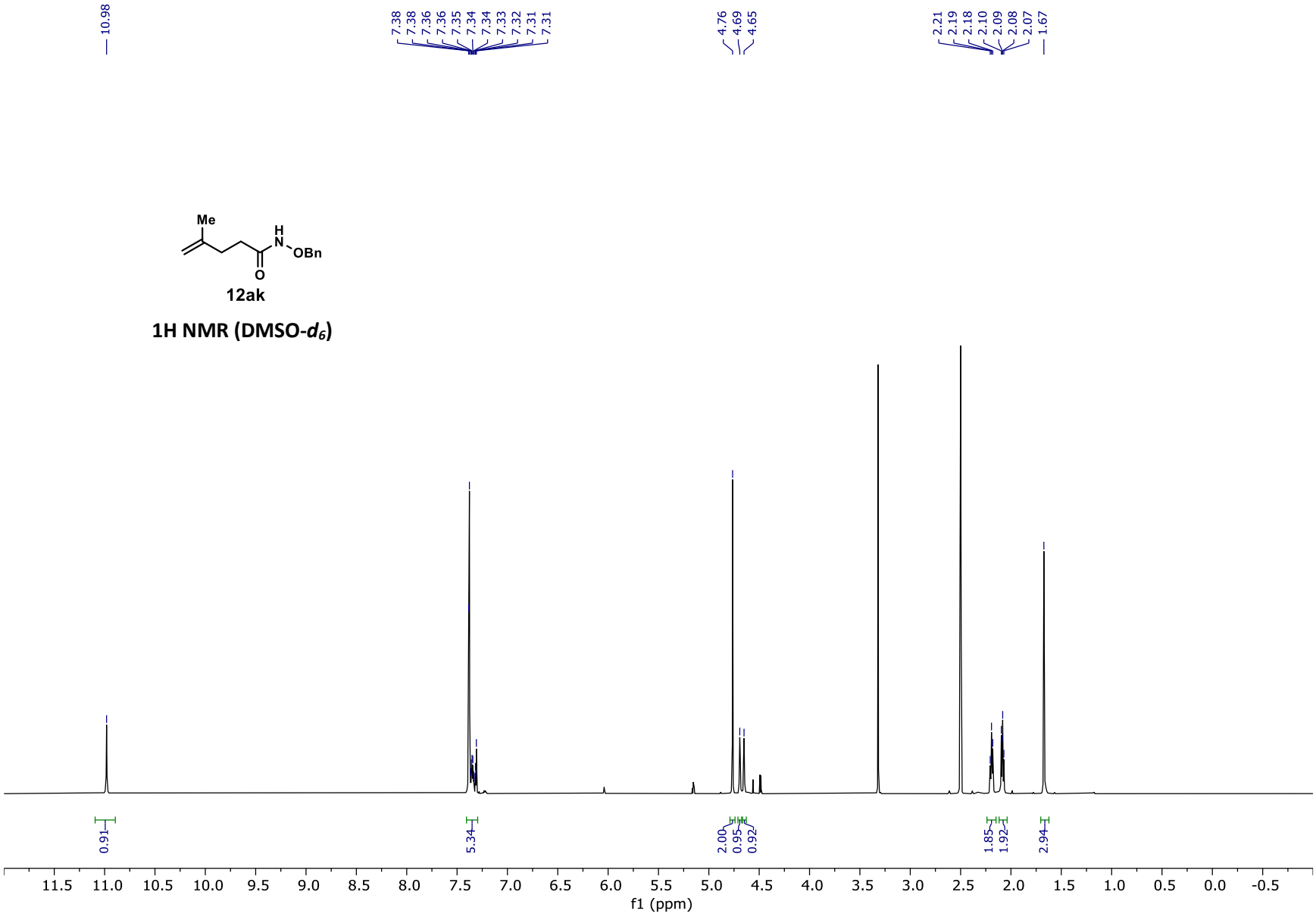

163.8
152.5
138.3
128.7
128.3
113.5
76.9
68.4
67.7
36.9
30.4
O
O
N
H
OBn
12ai
13C NMR (DMSO-d_6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

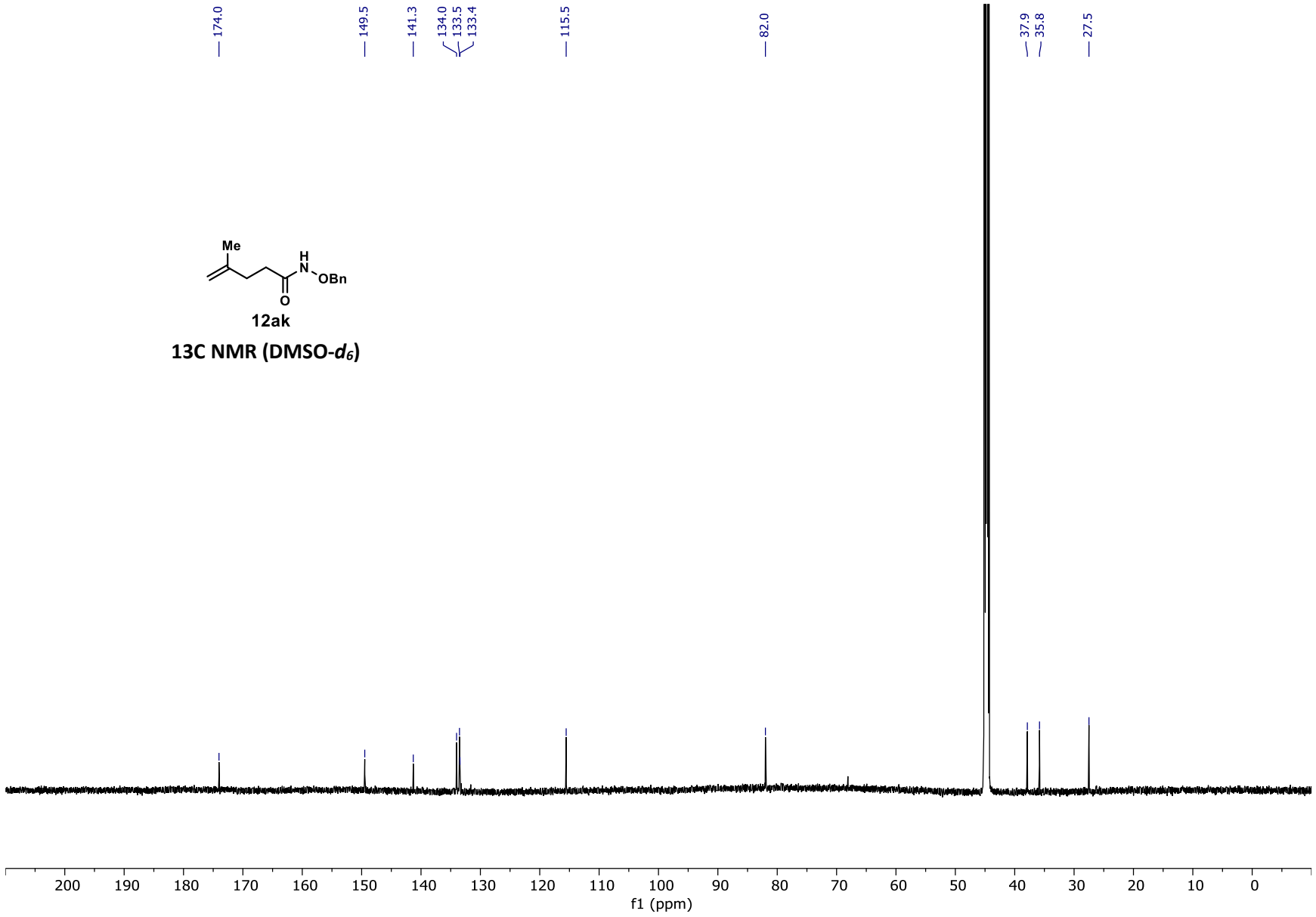

11.12
7.41
7.40
7.39
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.31
7.25
7.23
7.22
6.48
6.46
6.30
6.29
6.28
6.28
6.27
6.25
4.80
2.95
2.95
2.94
O
N
H
OBn
1aj
1H NMR (DMSO-d6)
0.87
10.49
0.91
0.93
2.00
1.73
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



1aj

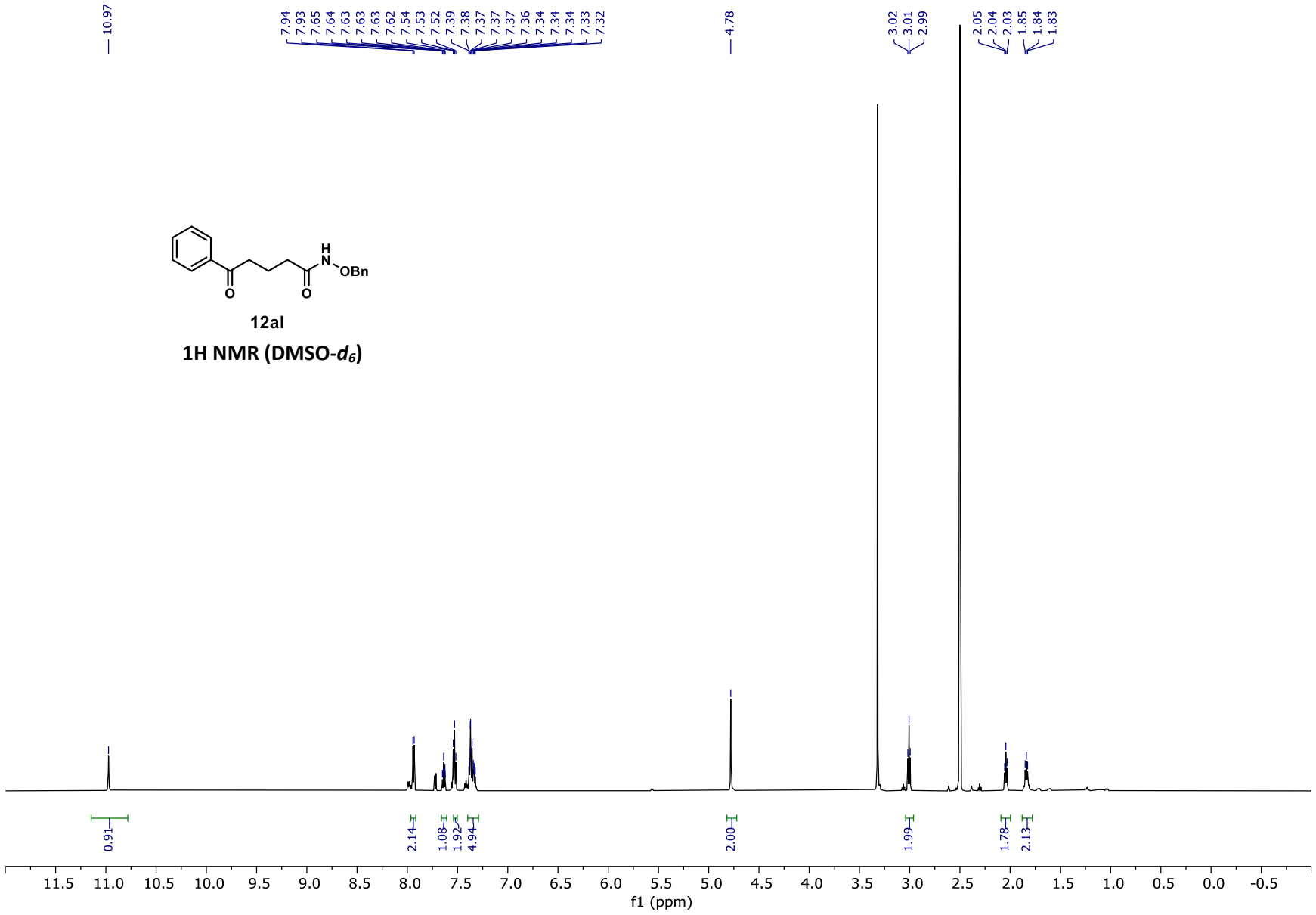
13C NMR (DMSO-d_6)


10.98
7.38
7.38
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.31
4.76
4.69
4.65
2.21
2.19
2.18
2.10
2.09
2.08
2.07
1.67
Me
H
N
OBn
O
12ak
1H NMR (DMSO-d6)
0.91
5.34
2.00
0.95
0.92
1.85
1.92
2.94
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



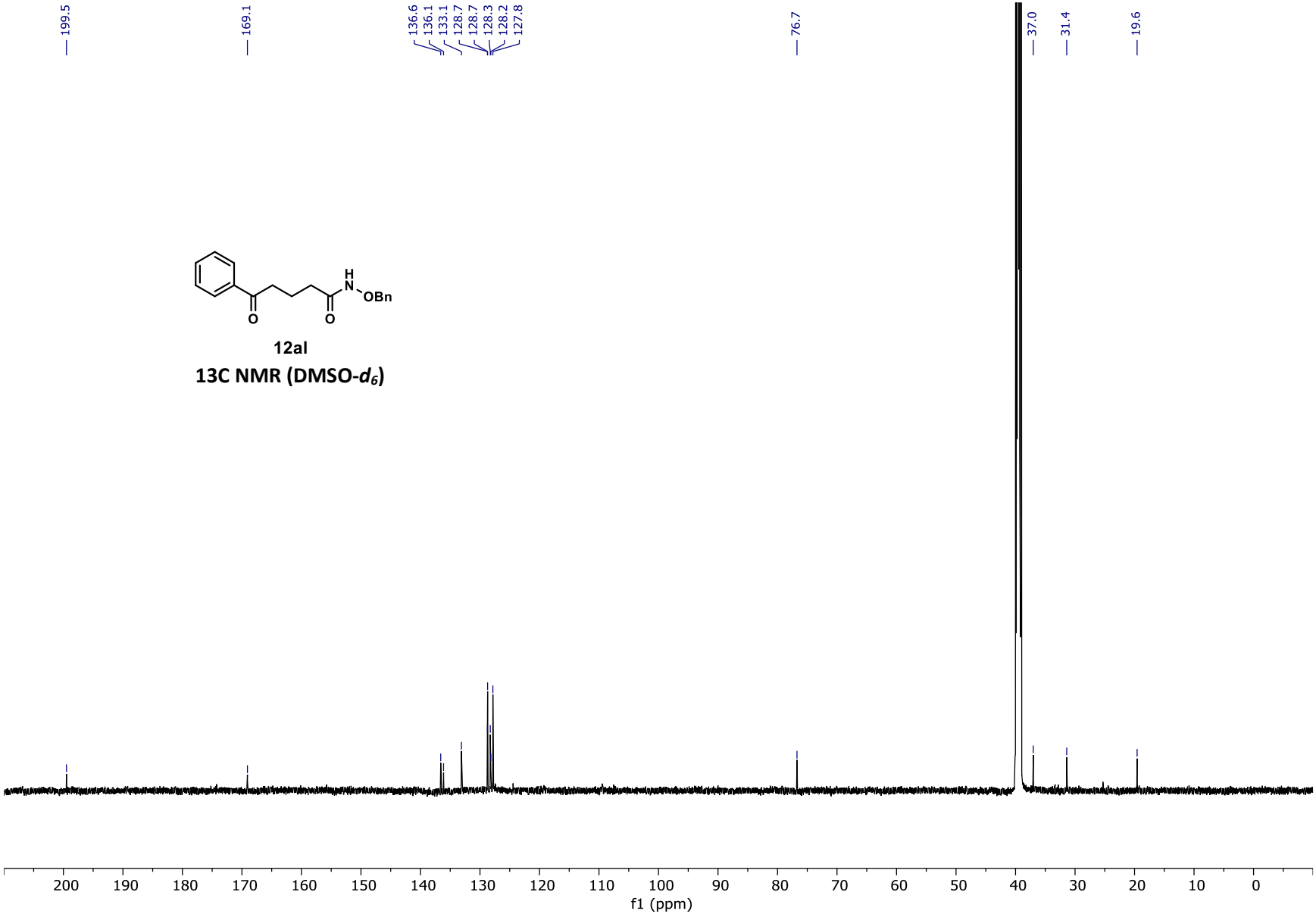
12ak

13C NMR (DMSO-d_6)



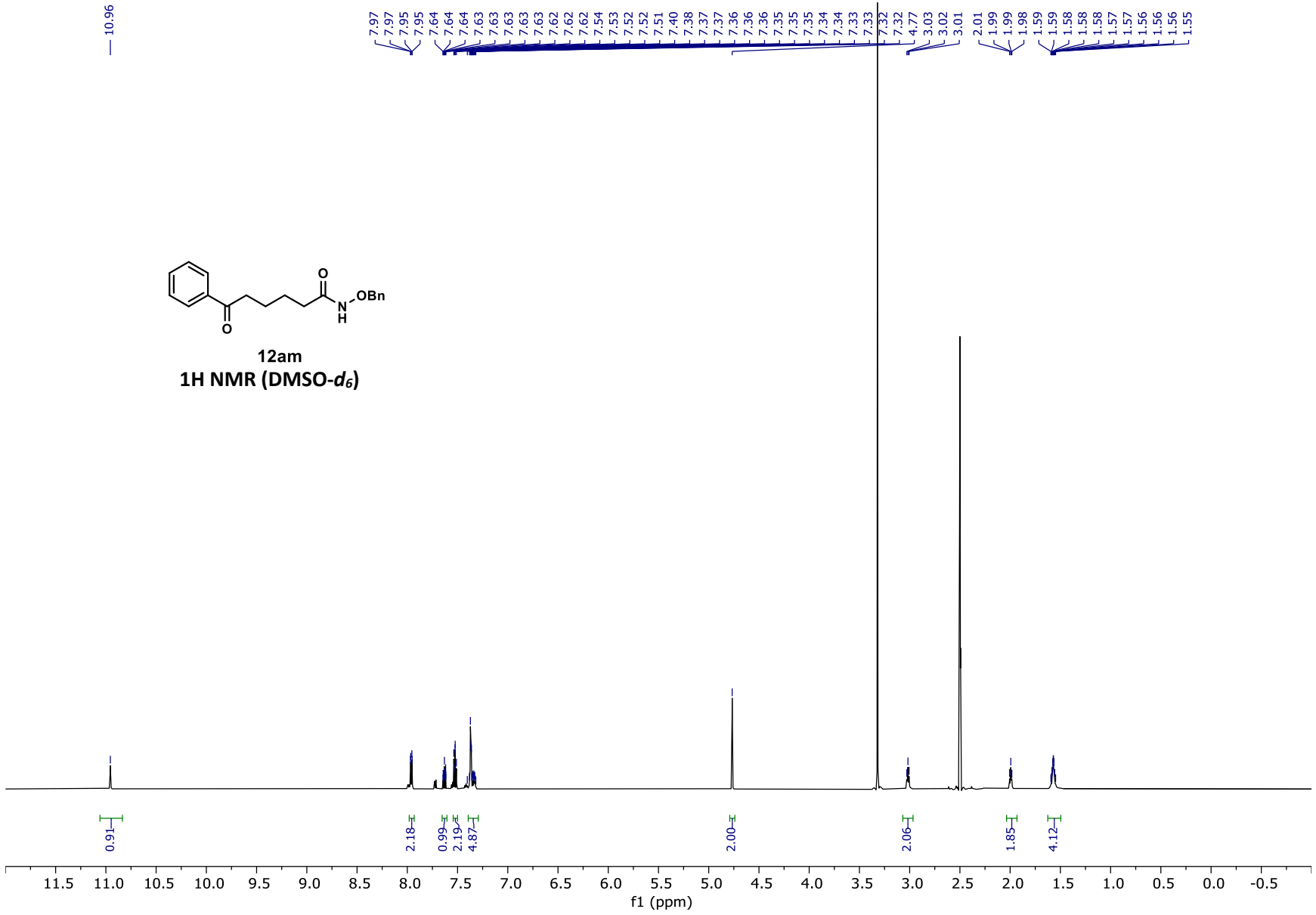
12al

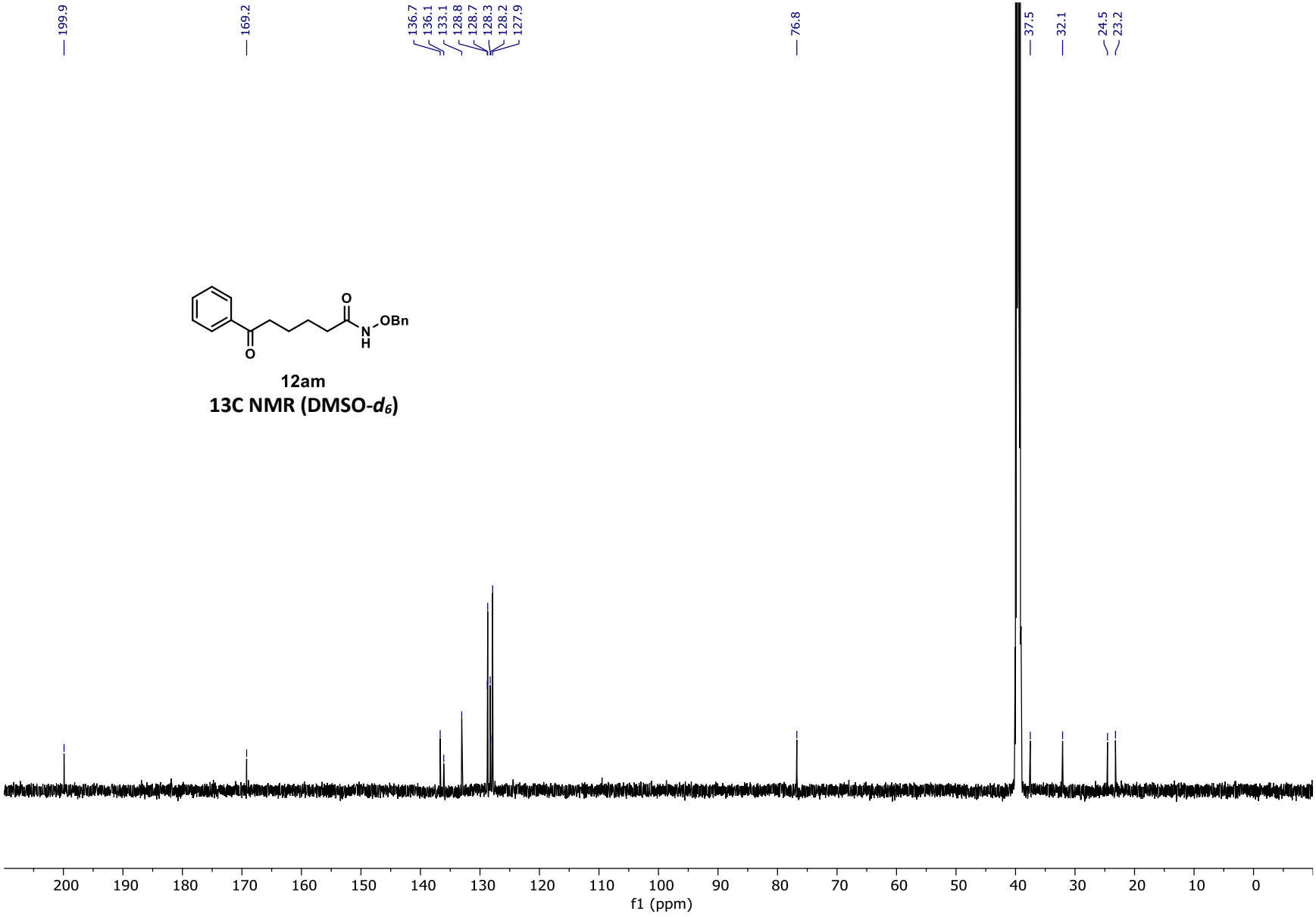
1H NMR (DMSO-d_6)



12al

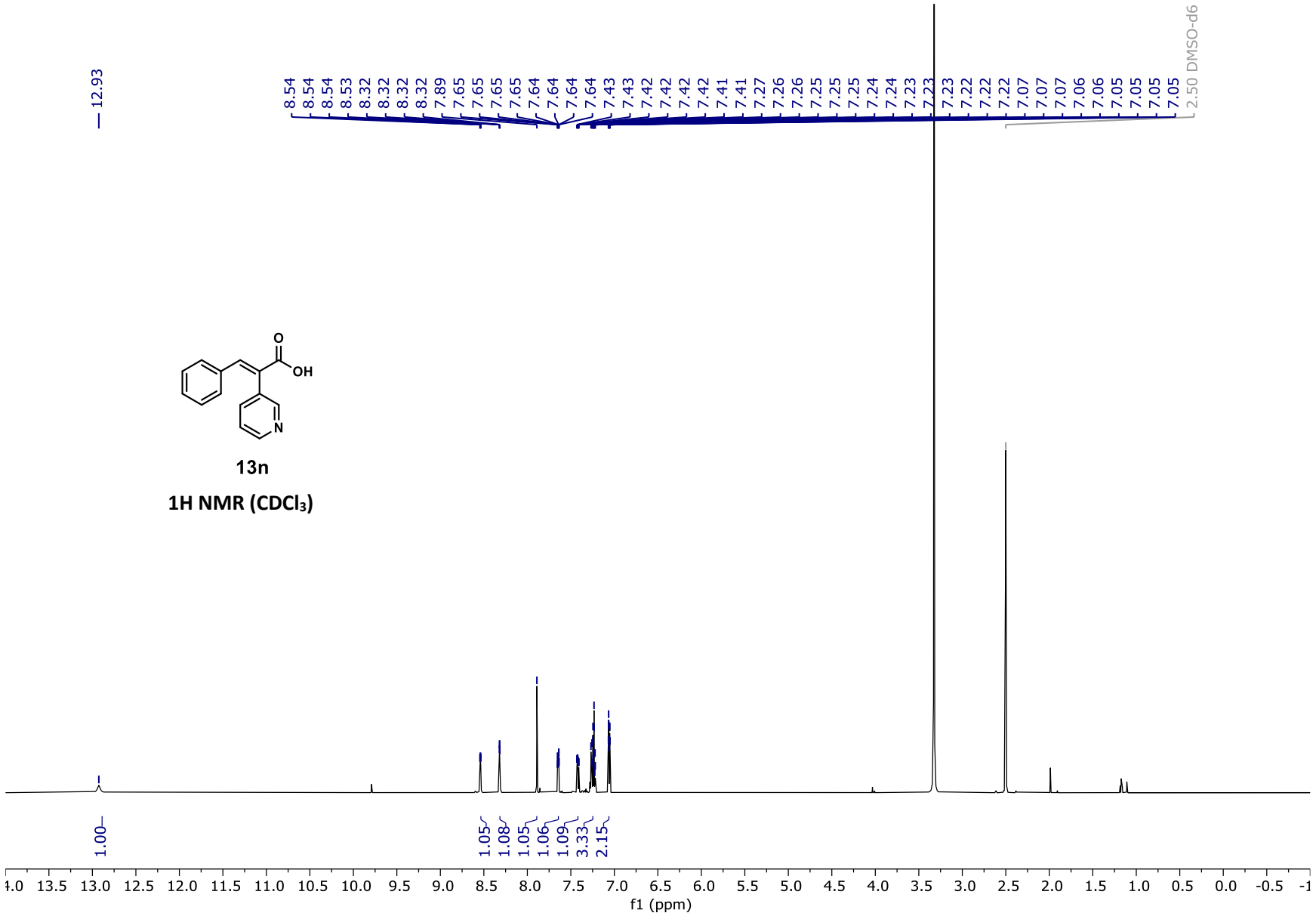
13C NMR (DMSO-d_6)

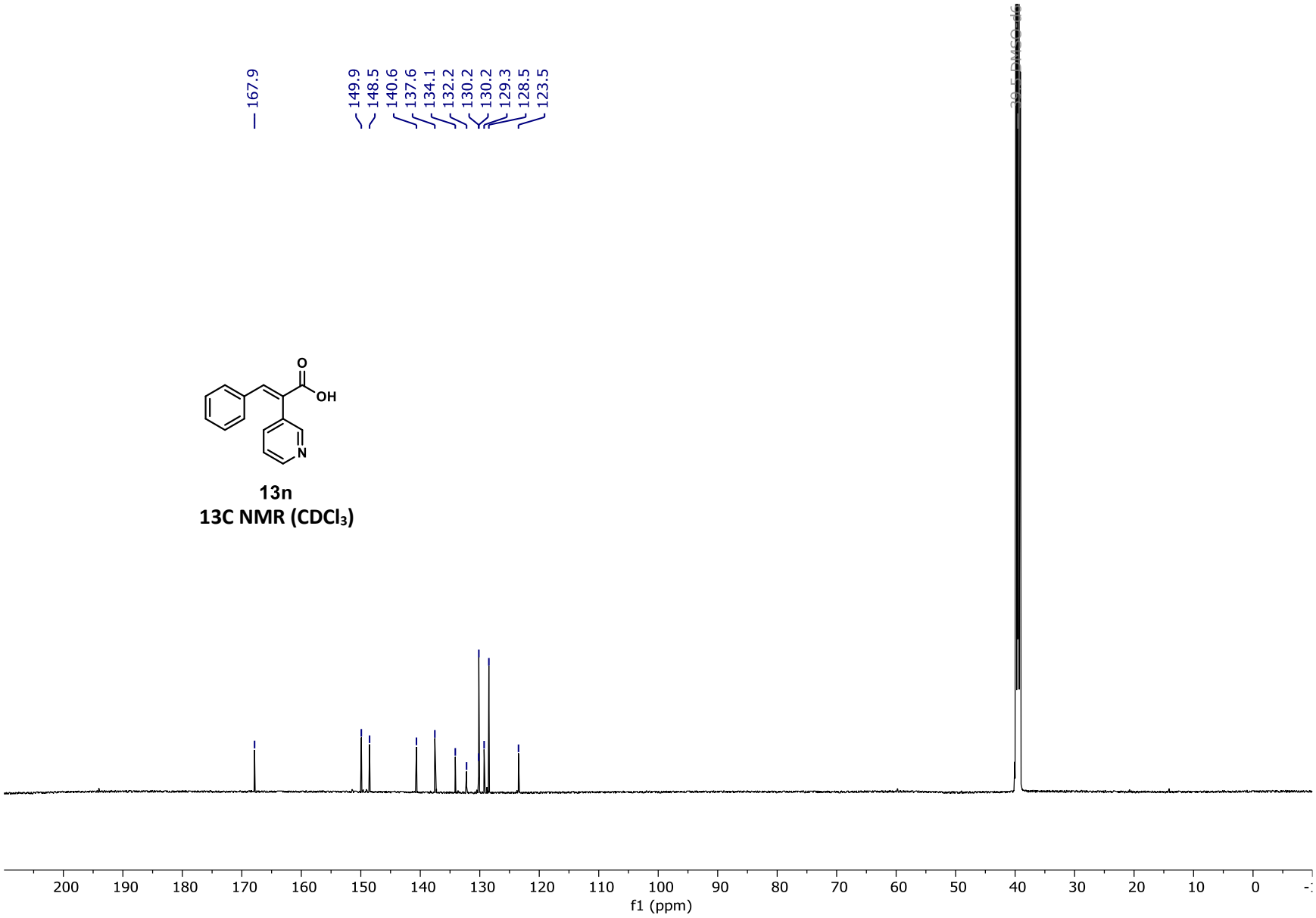

10.96
7.97 7.97 7.95 7.95 7.64 7.64 7.64 7.63 7.63 7.63 7.63 7.62 7.62 7.62 7.54 7.53 7.52 7.52 7.51 7.40 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 4.77 3.03 3.02 3.01 2.01 1.99 1.99 1.98 1.59 1.59 1.58 1.58 1.58 1.57 1.57 1.56 1.56 1.56 1.55
O
OBn
N
H
O
12am
1H NMR (DMSO-d6)
0.91 2.18 0.99 2.19 4.87 2.00 2.06 1.85 4.12
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



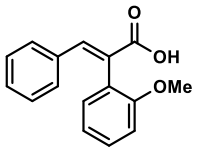
12am

13C NMR (DMSO-d_6)


12.93
8.54
8.54
8.54
8.53
8.32
8.32
8.32
8.32
7.89
7.65
7.65
7.65
7.64
7.64
7.64
7.64
7.43
7.43
7.42
7.42
7.42
7.42
7.41
7.41
7.27
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.07
7.07
7.07
7.06
7.06
7.05
7.05
7.05
2.50 DMSO-d6
O
OH
N
13n
1H NMR (CDCl3)
1.00
1.05
1.08
1.05
1.06
1.09
3.33
2.15
f1 (ppm)

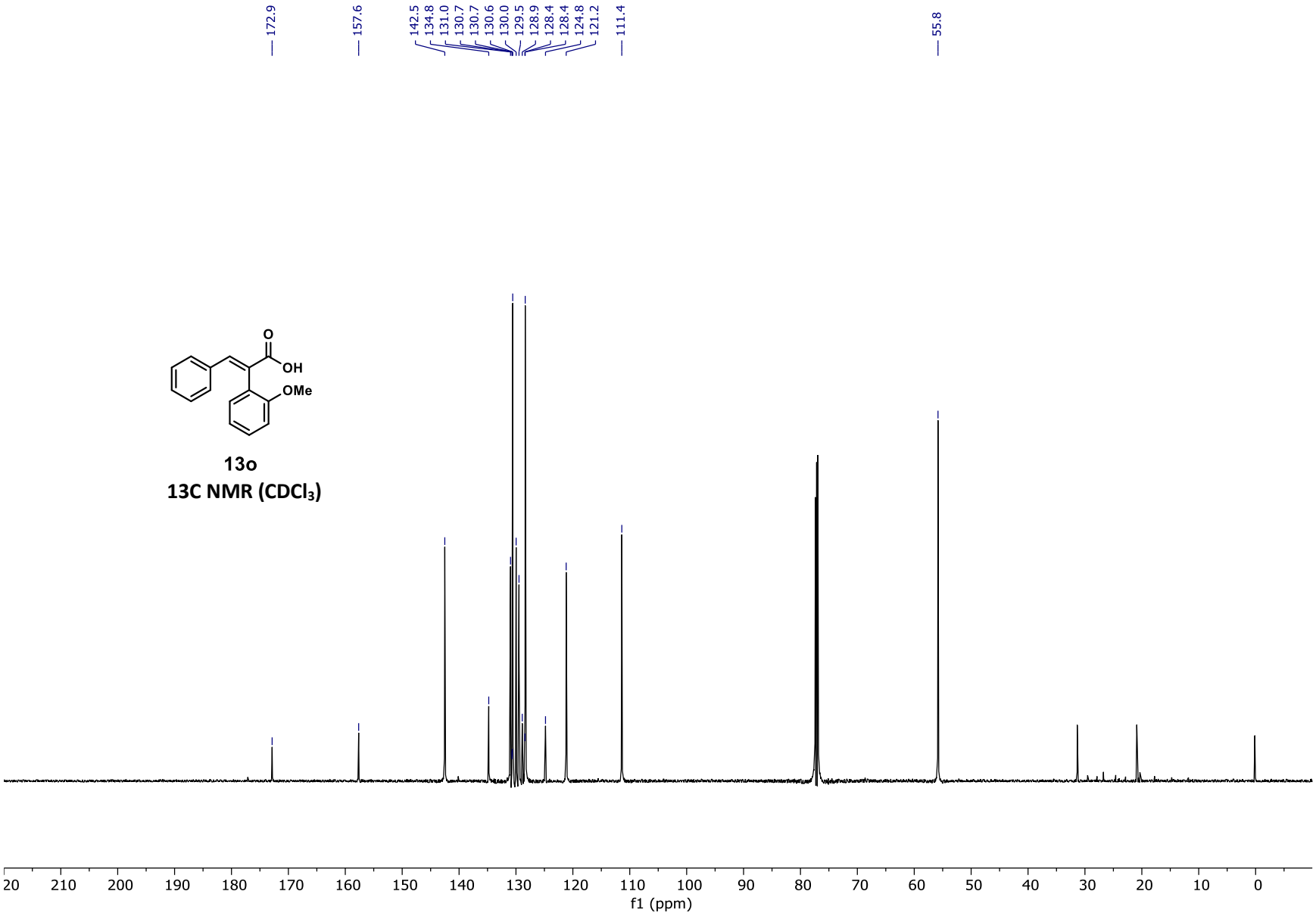


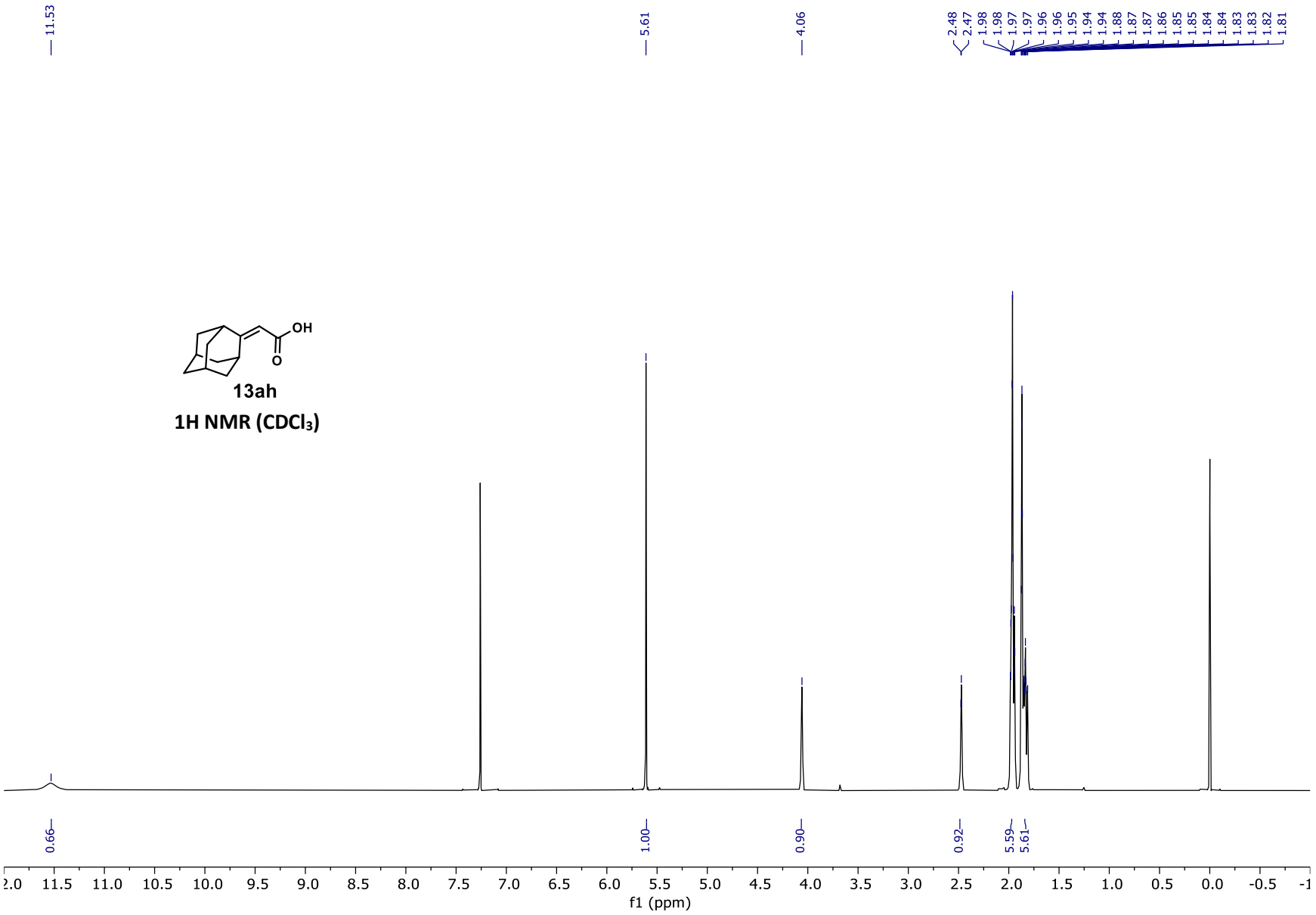
13n
13C NMR ($CDCl_3$)

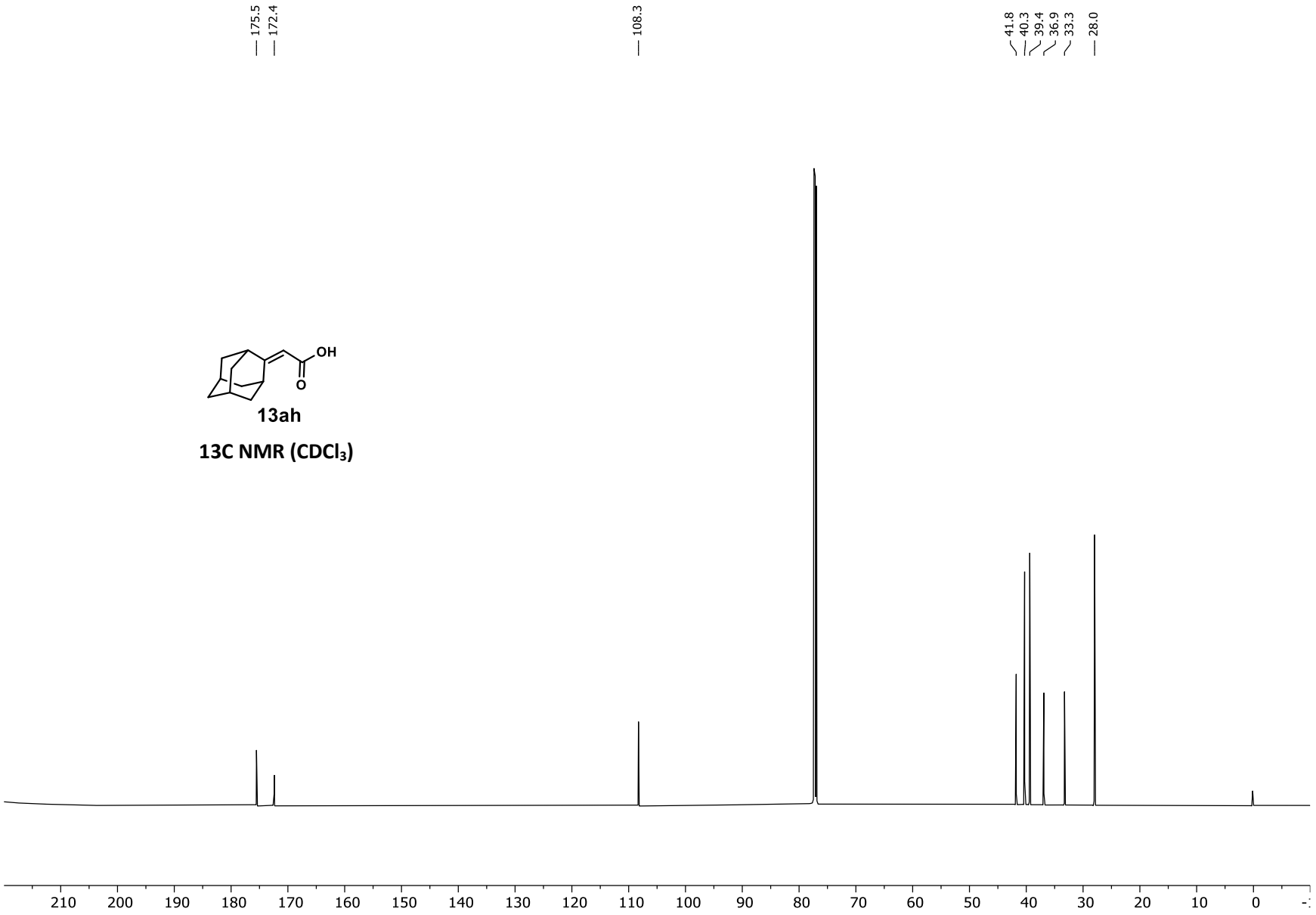


13o

1H NMR ($CDCl_3$)

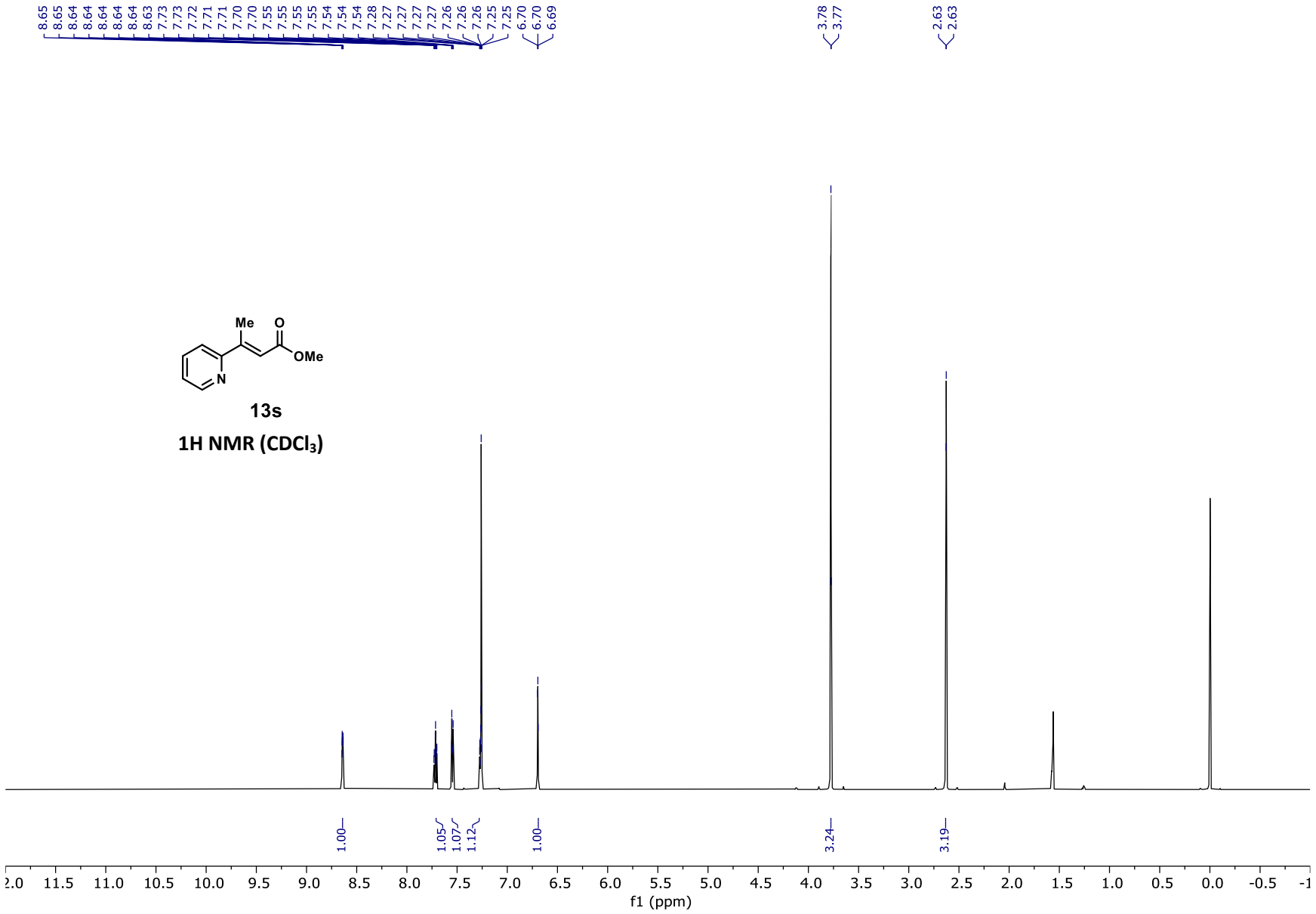

172.9
157.6
142.5
134.8
131.0
130.7
130.7
130.6
130.0
129.5
128.9
128.4
128.4
124.8
121.2
111.4
55.8
O
OH
OMe
13o
13C NMR (CDCl3)
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

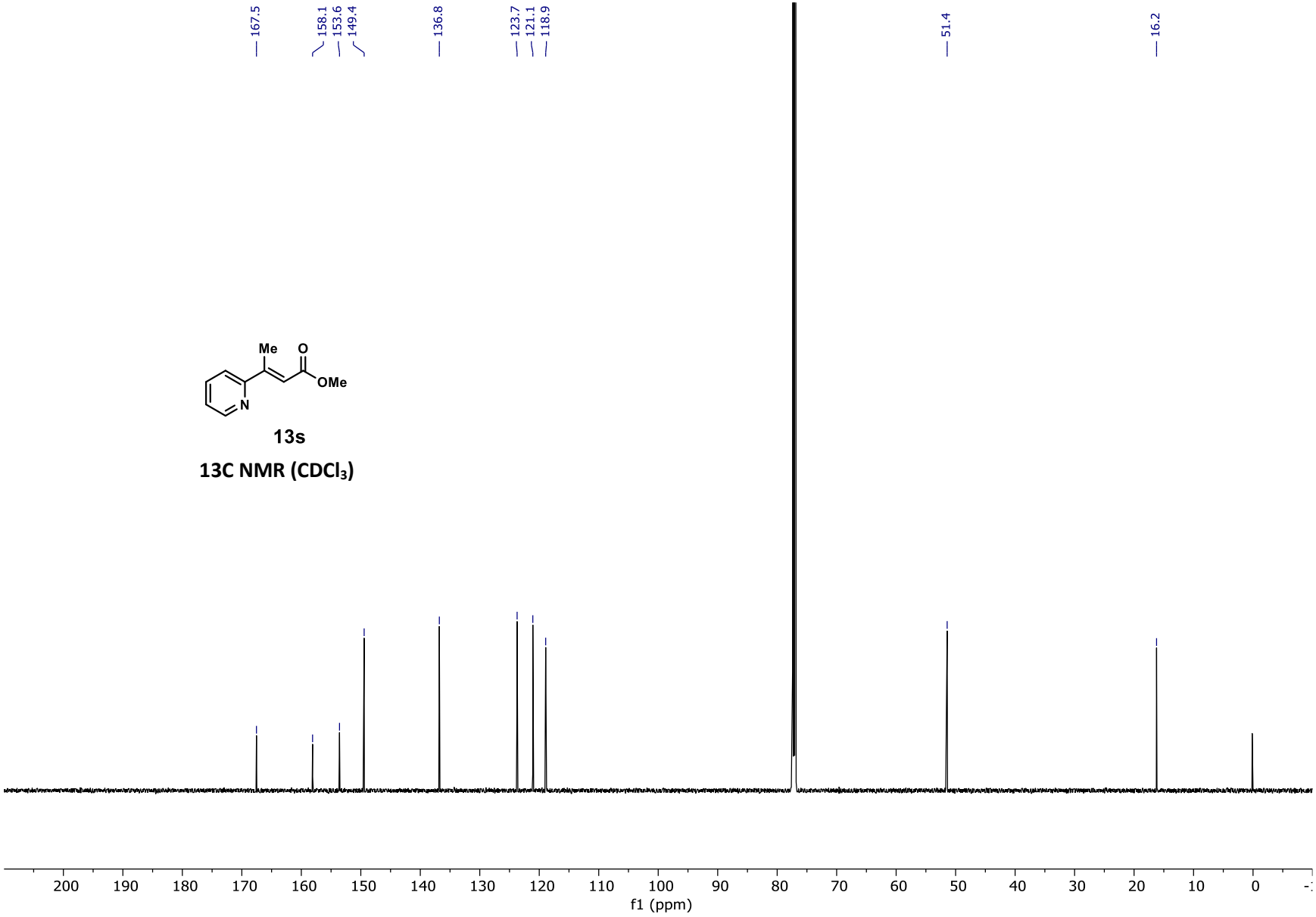

11.53
5.61
4.06
2.48
2.47
1.98
1.98
1.97
1.97
1.96
1.96
1.95
1.94
1.94
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.82
1.81
OH
O
13ah
1H NMR (CDCl3)
0.66
1.00
0.90
0.92
5.59
5.61
f1 (ppm)



13ah

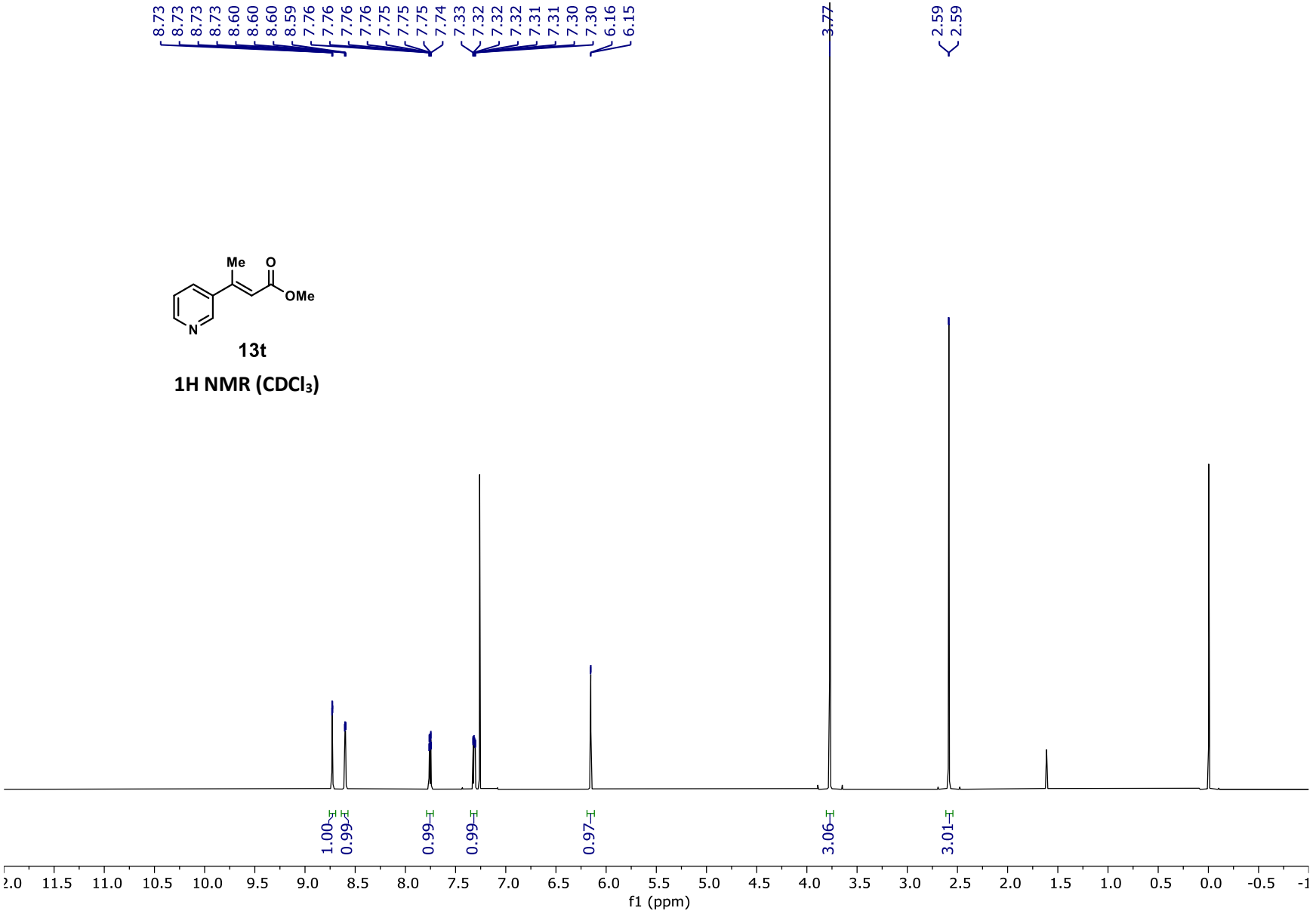
13C NMR ($CDCl_3$)

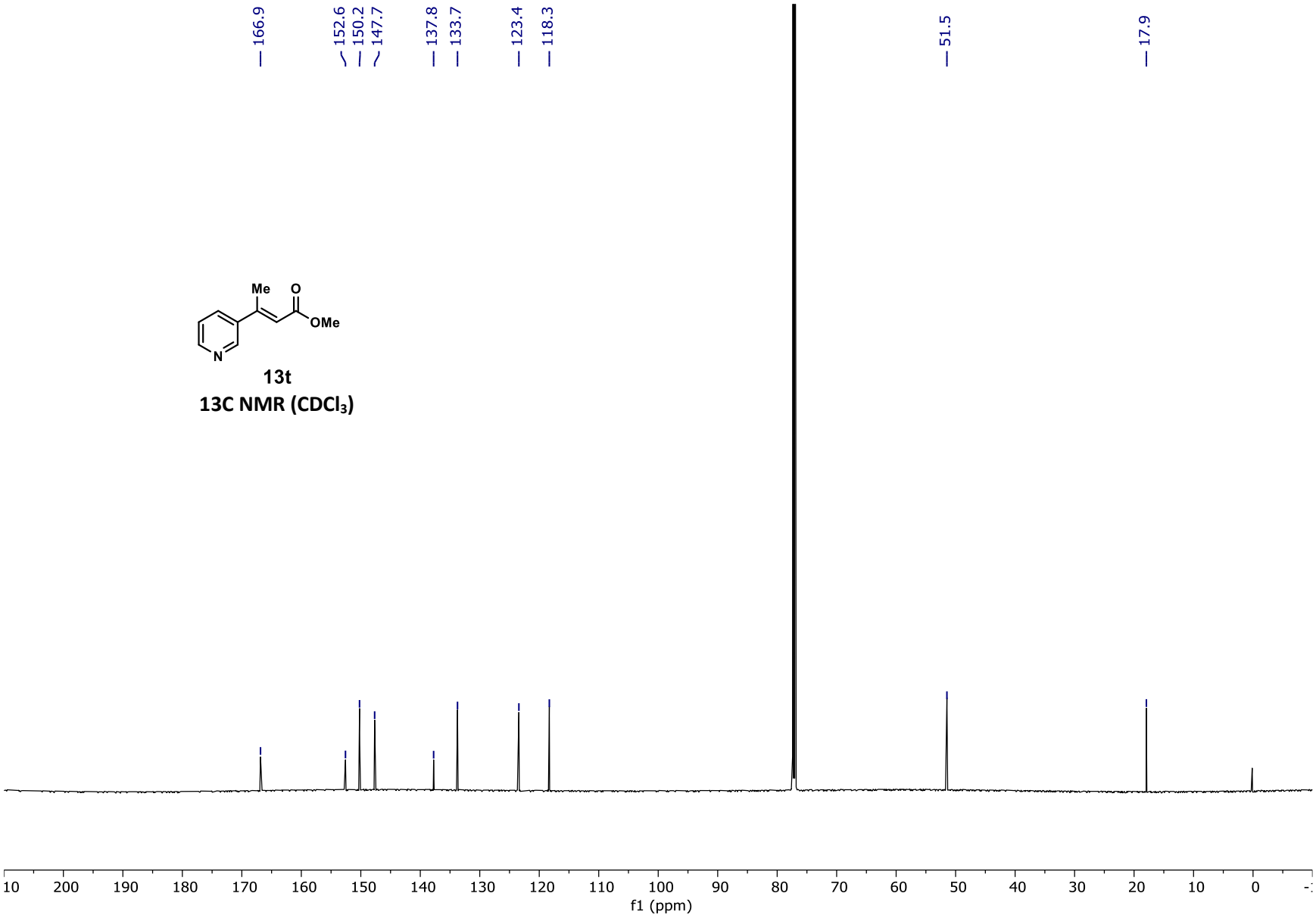

8.65
8.65
8.64
8.64
8.64
8.64
8.64
8.63
7.73
7.73
7.72
7.71
7.71
7.70
7.70
7.55
7.55
7.55
7.55
7.54
7.54
7.54
7.28
7.27
7.27
7.27
7.27
7.26
7.26
7.25
7.25
6.70
6.70
6.69
3.78
3.77
2.63
2.63
Me
O
OMe
N
13s
1H NMR (CDCl3)
1.00
1.05
1.07
1.12
1.00
3.24
3.19
f1 (ppm)

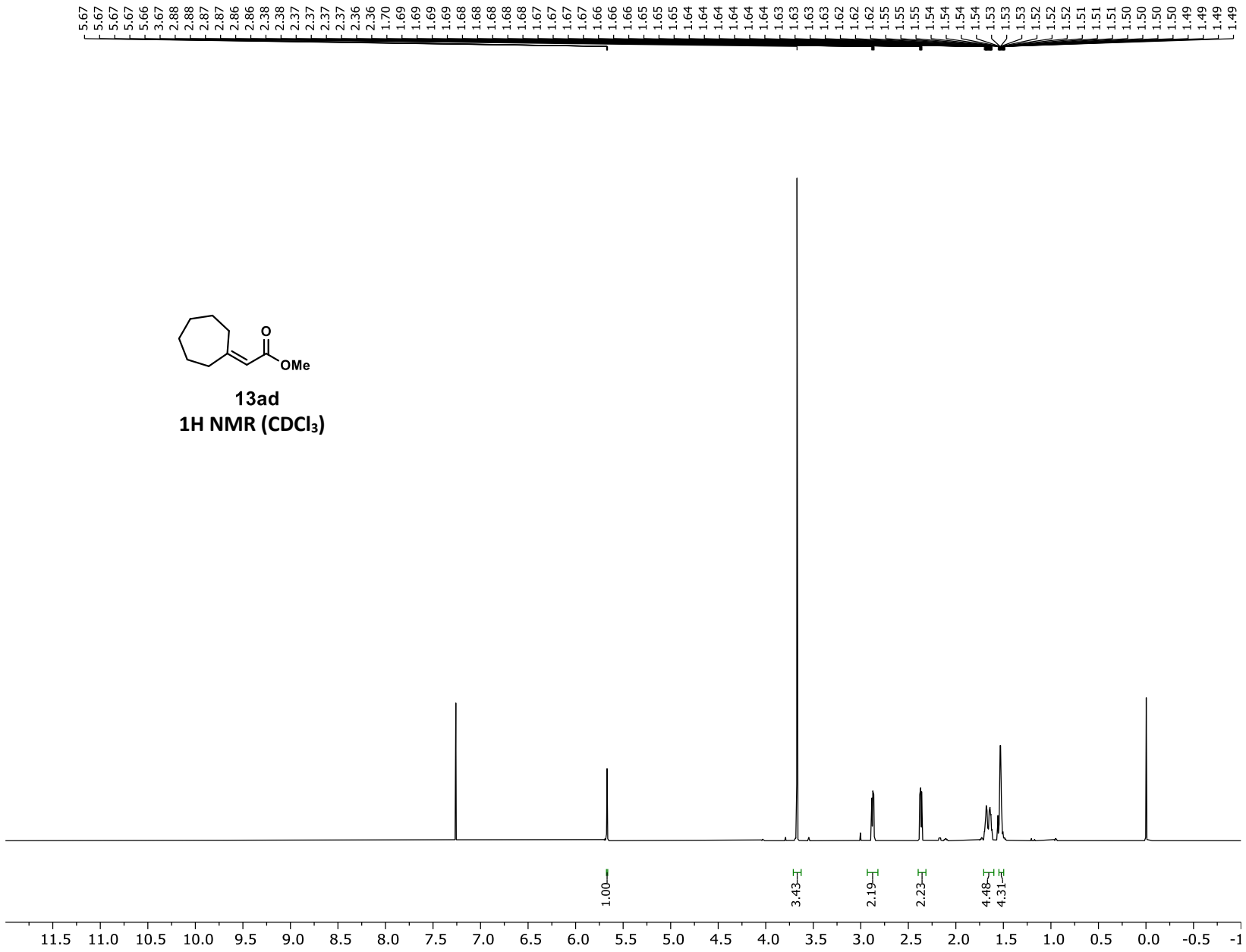


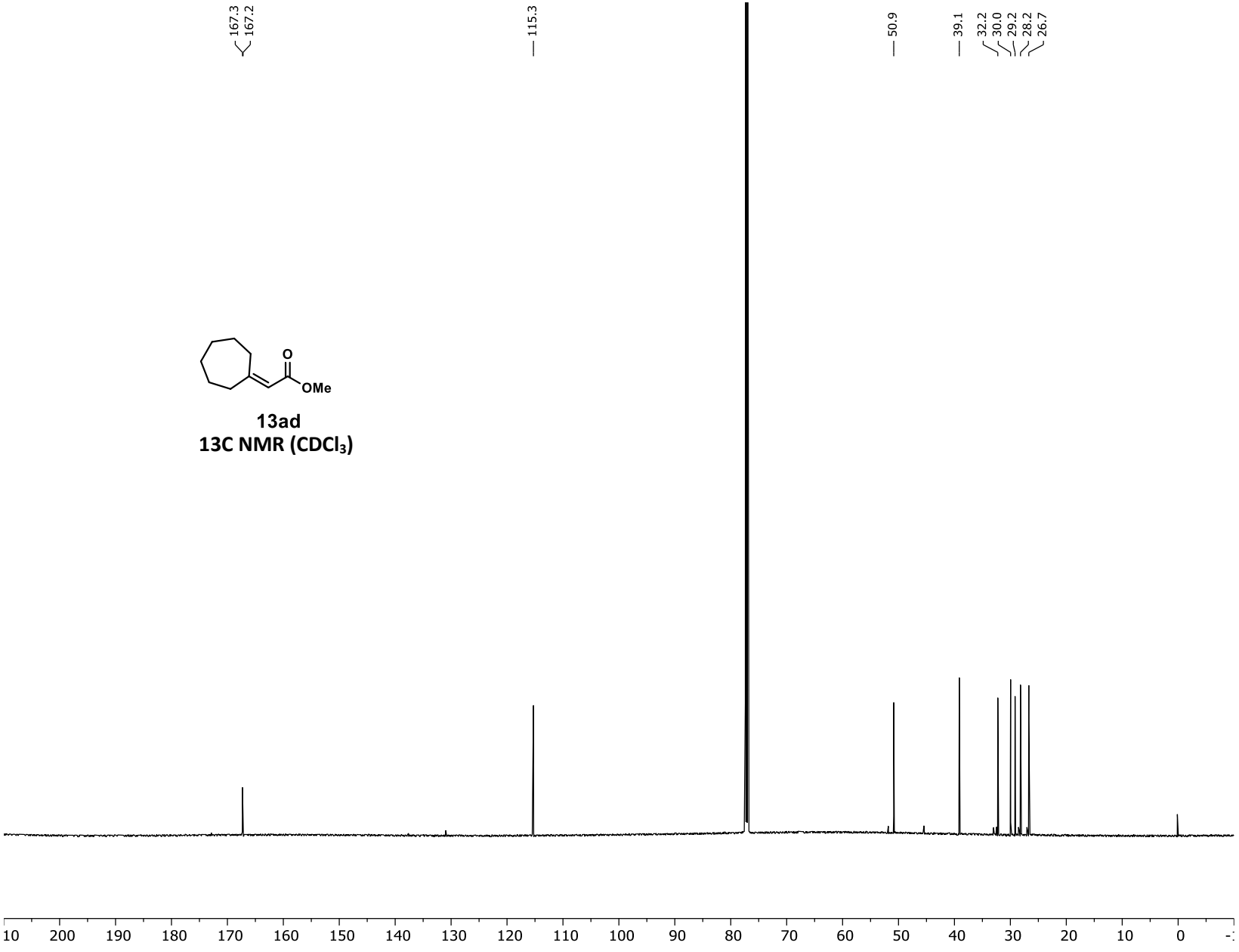
13s

13C NMR ($CDCl_3$)

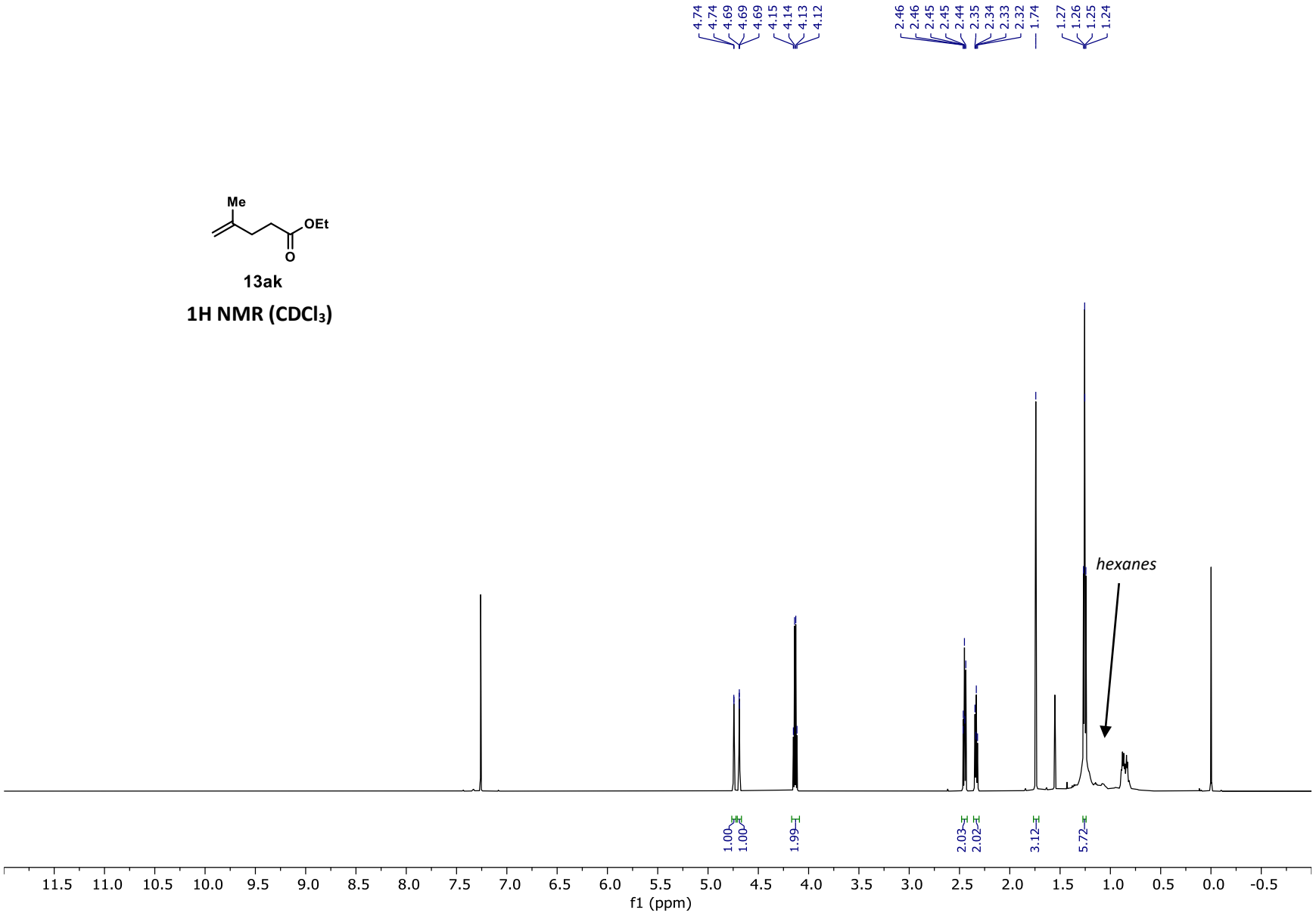

8.73
8.73
8.73
8.73
8.60
8.60
8.60
8.59
7.76
7.76
7.76
7.76
7.75
7.75
7.75
7.74
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
6.16
6.15
3.77
2.59
2.59
Me
O
OMe
N
13t
1H NMR (CDCl3)
1.00
0.99
0.99
0.99
0.97
3.06
3.01
f1 (ppm)

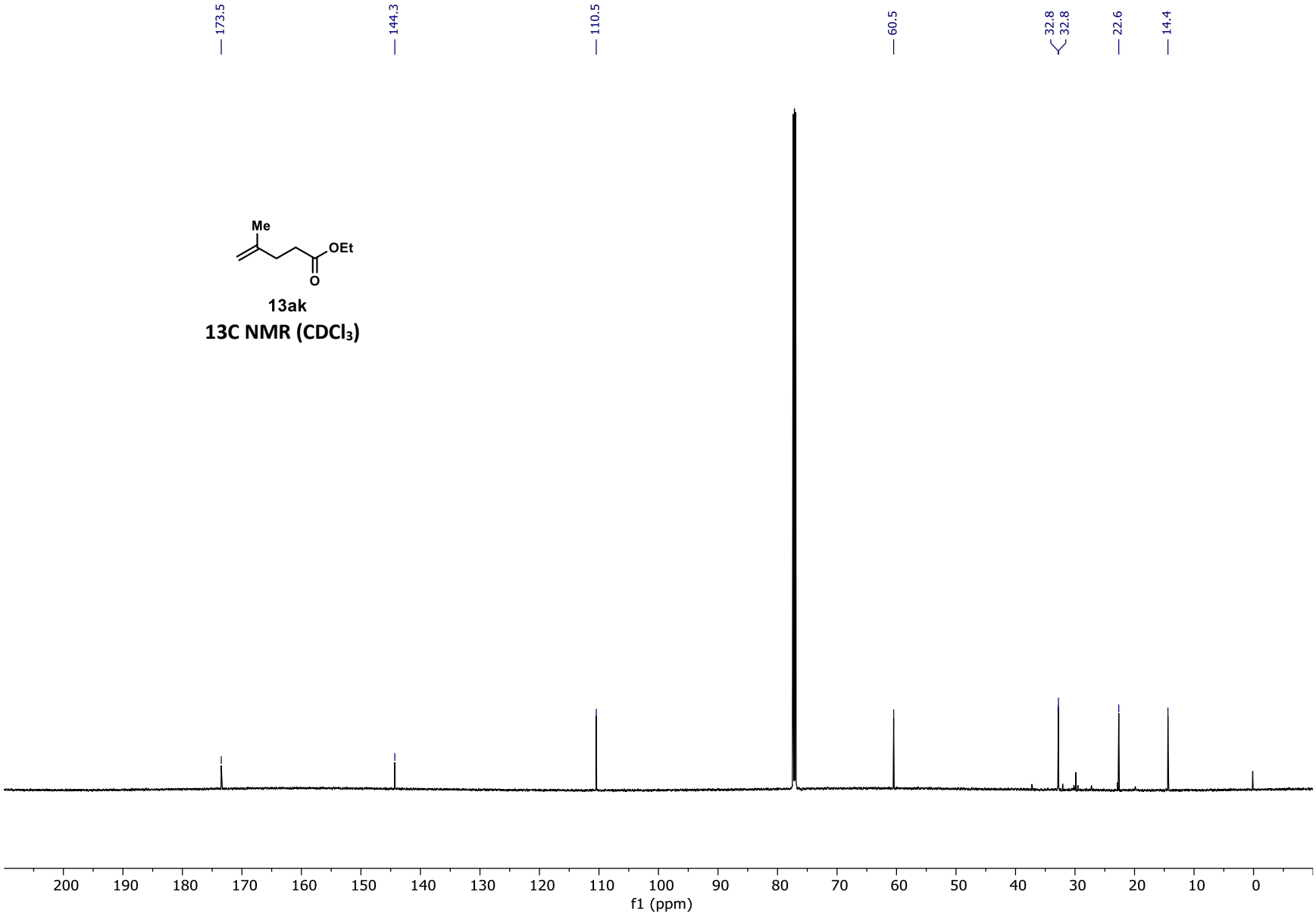

166.9
152.6
150.2
147.7
137.8
133.7
123.4
118.3
51.5
17.9
Me
O
OMe
N
13t
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

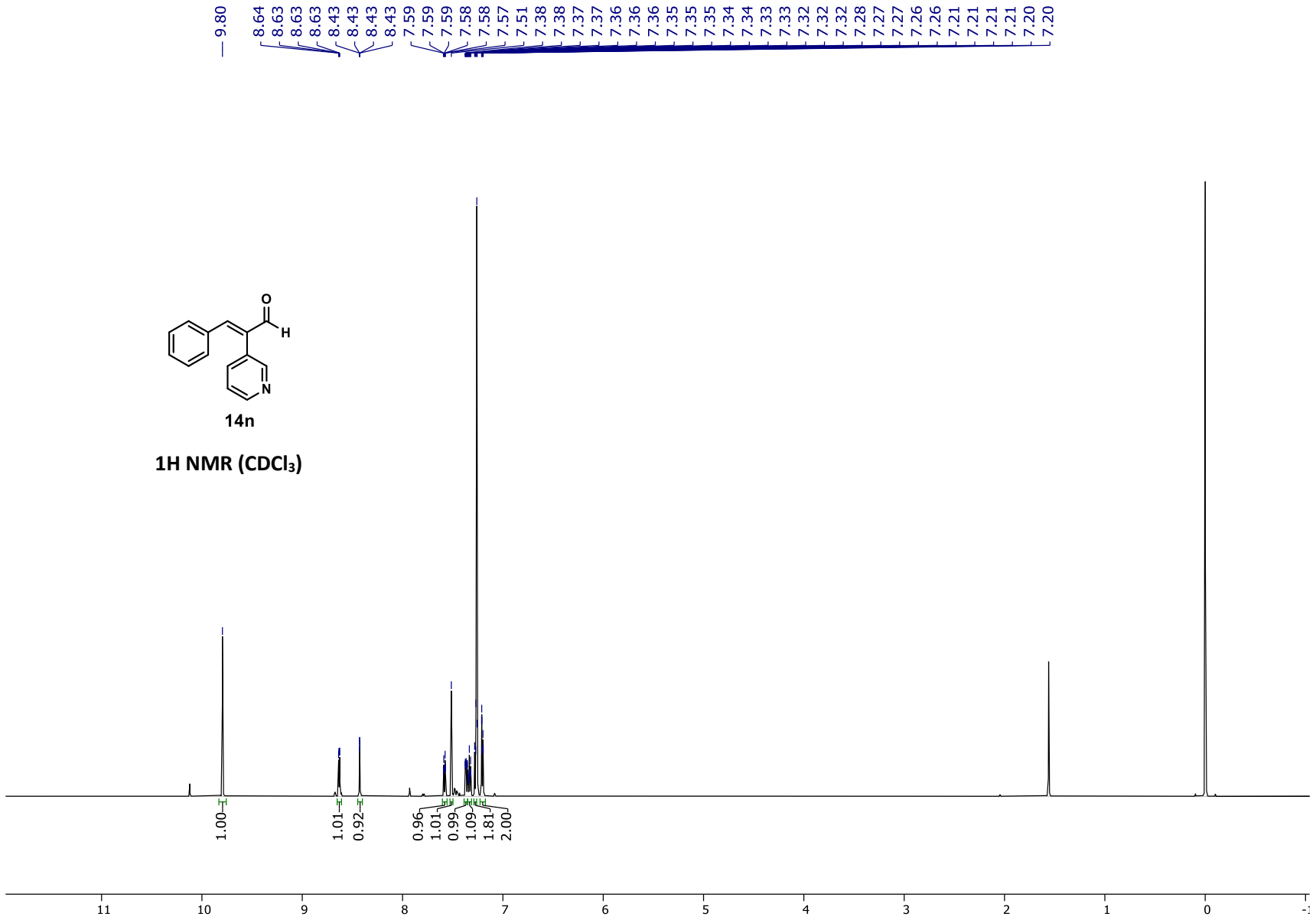

5.67 5.67 5.67 5.67 5.66 3.67 2.88 2.88 2.87 2.87 2.86 2.86 2.38 2.38 2.37 2.37 2.37 2.36 2.36 1.70 1.69 1.69 1.69 1.69 1.68 1.68 1.68 1.68 1.68 1.67 1.67 1.67 1.67 1.66 1.66 1.66 1.65 1.65 1.65 1.64 1.64 1.64 1.64 1.64 1.64 1.63 1.63 1.63 1.63 1.62 1.62 1.62 1.55 1.55 1.54 1.54 1.54 1.54 1.53 1.53 1.53 1.52 1.52 1.52 1.51 1.51 1.51 1.50 1.50 1.50 1.50 1.49 1.49 1.49
O
OMe
13ad
1H NMR (CDCl3)
1.00
3.43
2.19
2.23
4.48
4.31
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

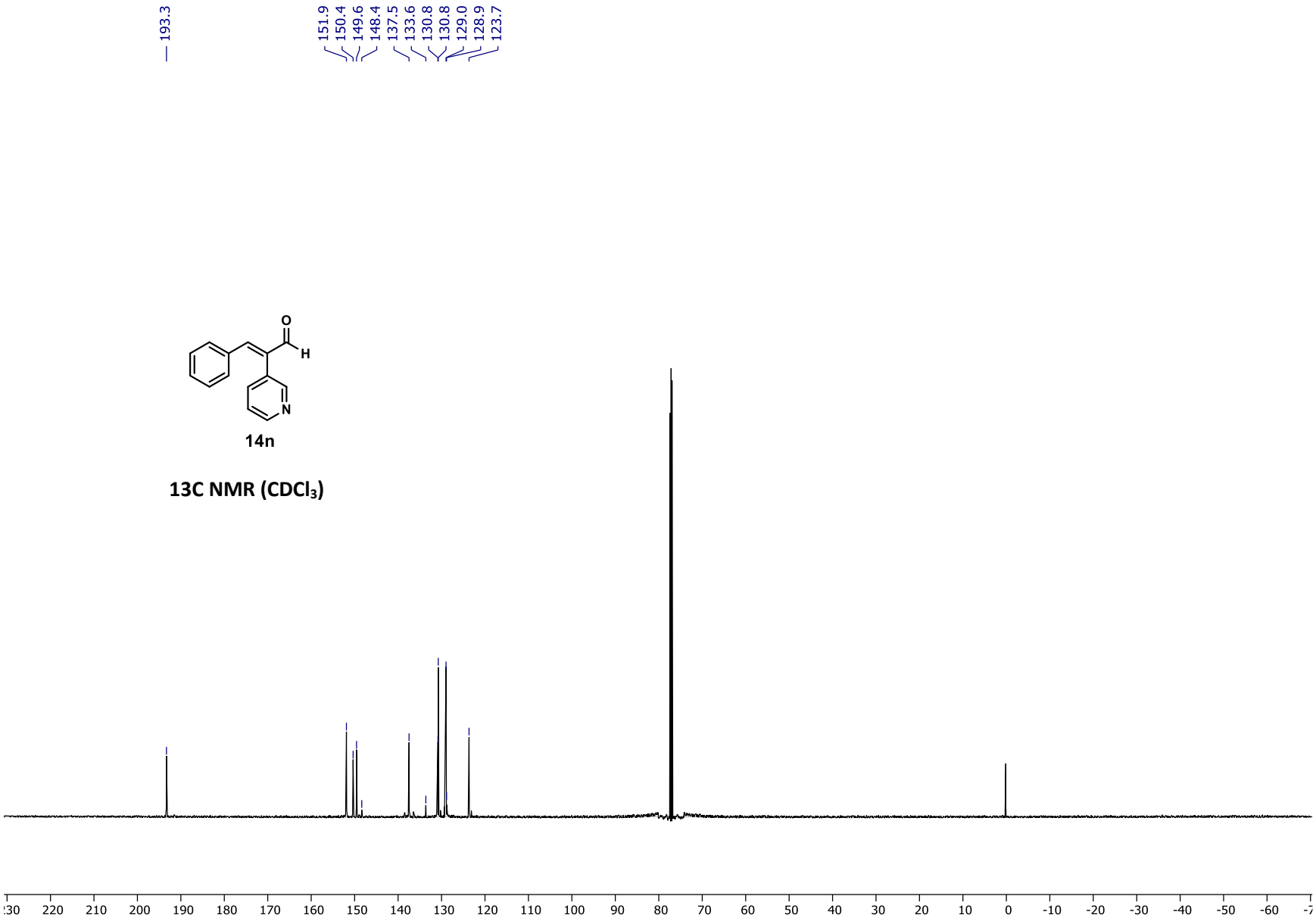


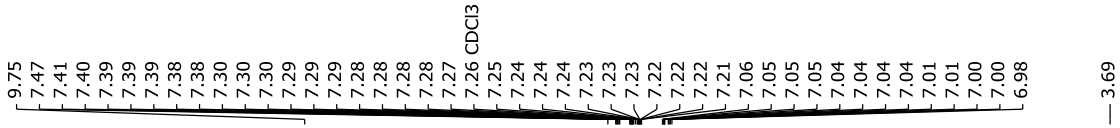
13ad
13C NMR ($CDCl_3$)

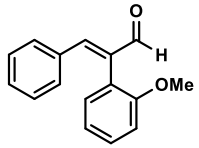

Me
OEt
O
13ak
1H NMR (CDCl3)
4.74
4.74
4.69
4.69
4.69
4.15
4.14
4.13
4.12
2.46
2.46
2.45
2.45
2.44
2.35
2.34
2.33
2.32
1.74
1.27
1.26
1.25
1.24
hexanes
1.00
1.00
1.99
2.03
2.02
3.12
5.72
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


173.5
144.3
110.5
60.5
32.8
32.8
22.6
14.4
Me
OEt
O
13ak
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.80
8.64
8.63
8.63
8.63
8.43
8.43
8.43
8.43
7.59
7.59
7.59
7.58
7.58
7.57
7.51
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.28
7.27
7.27
7.26
7.26
7.21
7.21
7.21
7.21
7.20
7.20
O
H
N
14n
1H NMR (CDCl3)
1.00
1.01
0.92
0.96
1.01
0.99
1.09
1.81
2.00
11
10
9
8
7
6
5
4
3
2
1
0

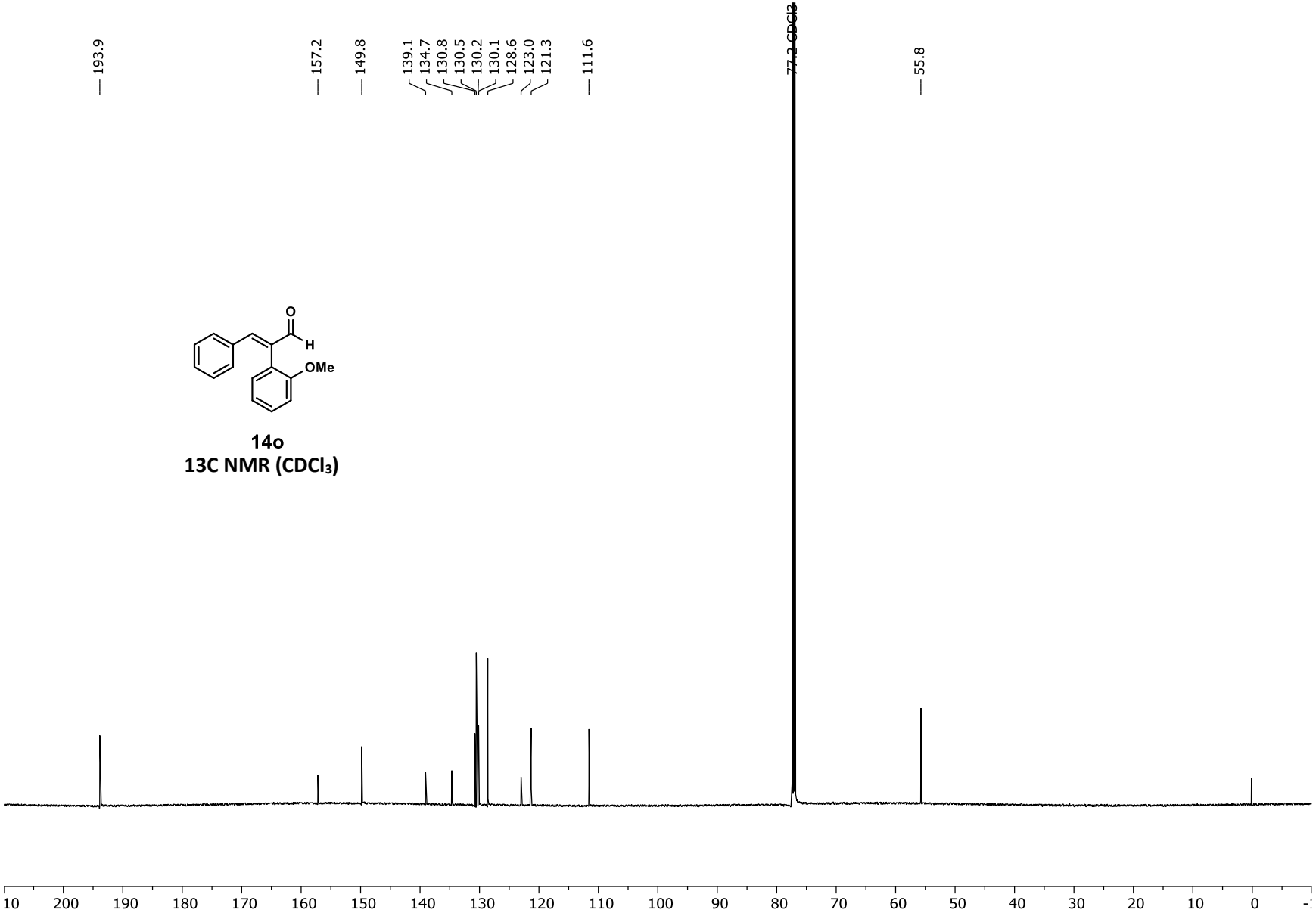

193.3
151.9
150.4
149.6
148.4
137.5
133.6
130.8
130.8
129.0
128.9
123.7
O
H
N
14n
13C NMR (CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60



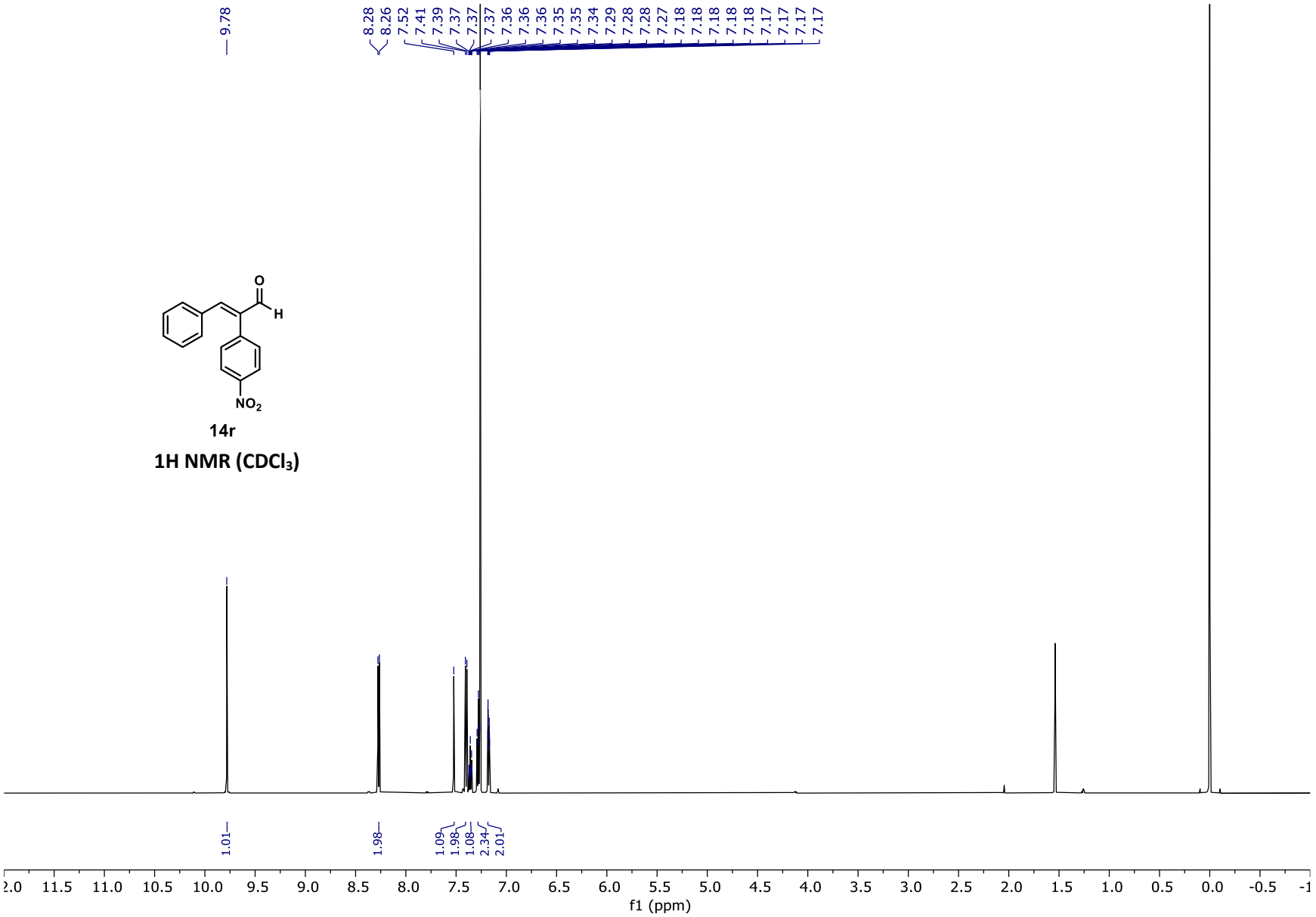


14o

1H NMR ($CDCl_3$)

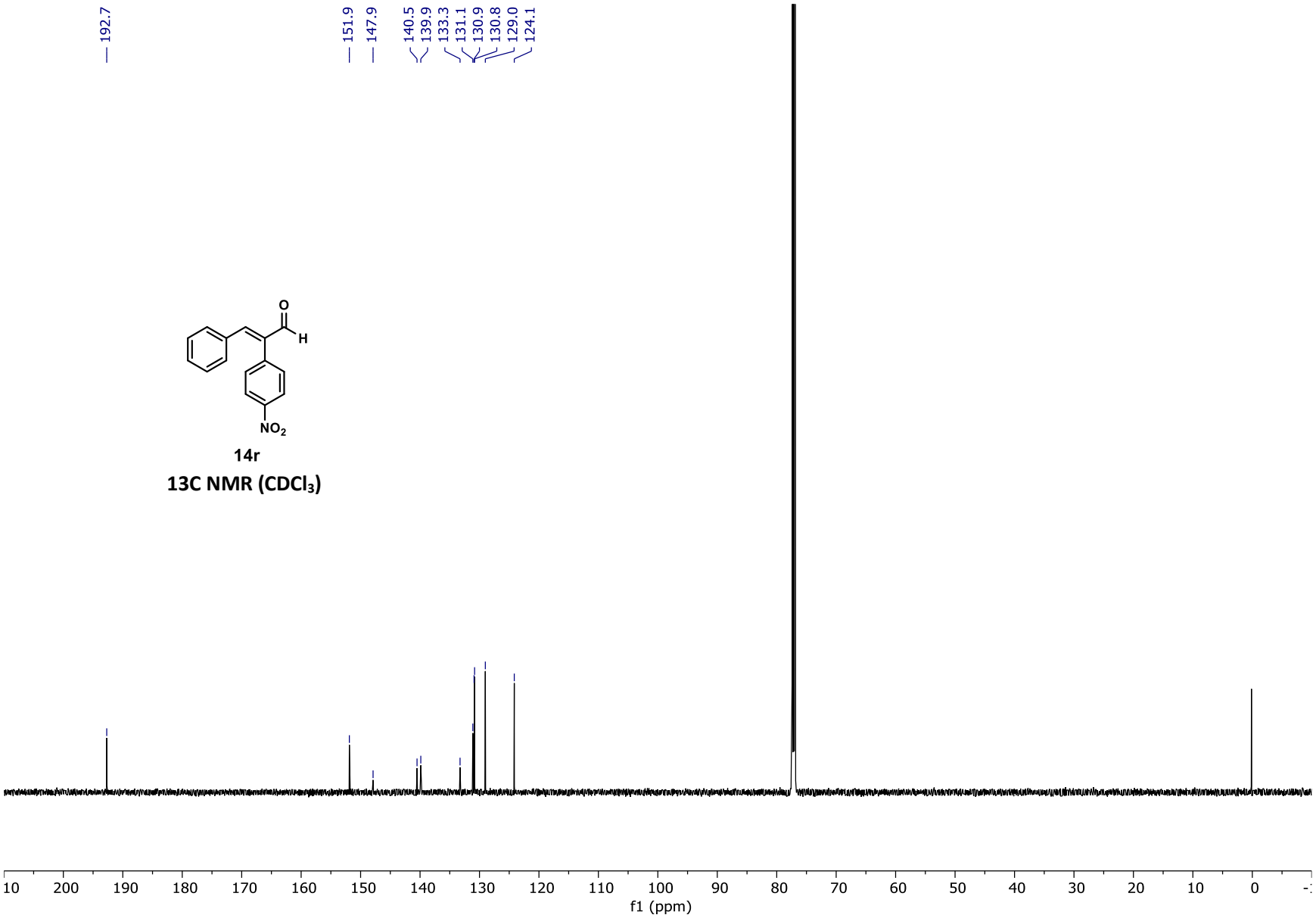


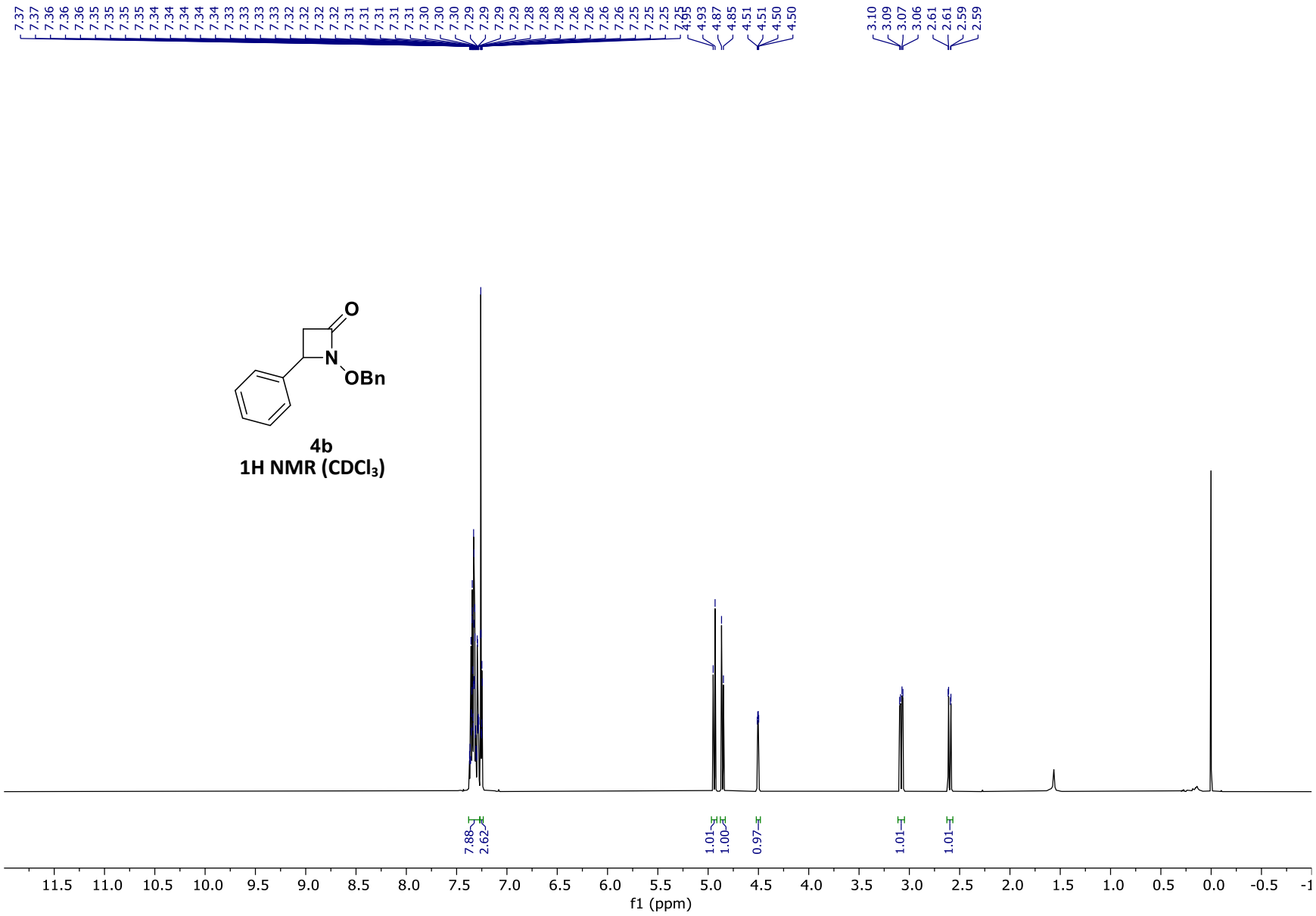
14o
13C NMR ($CDCl_3$)

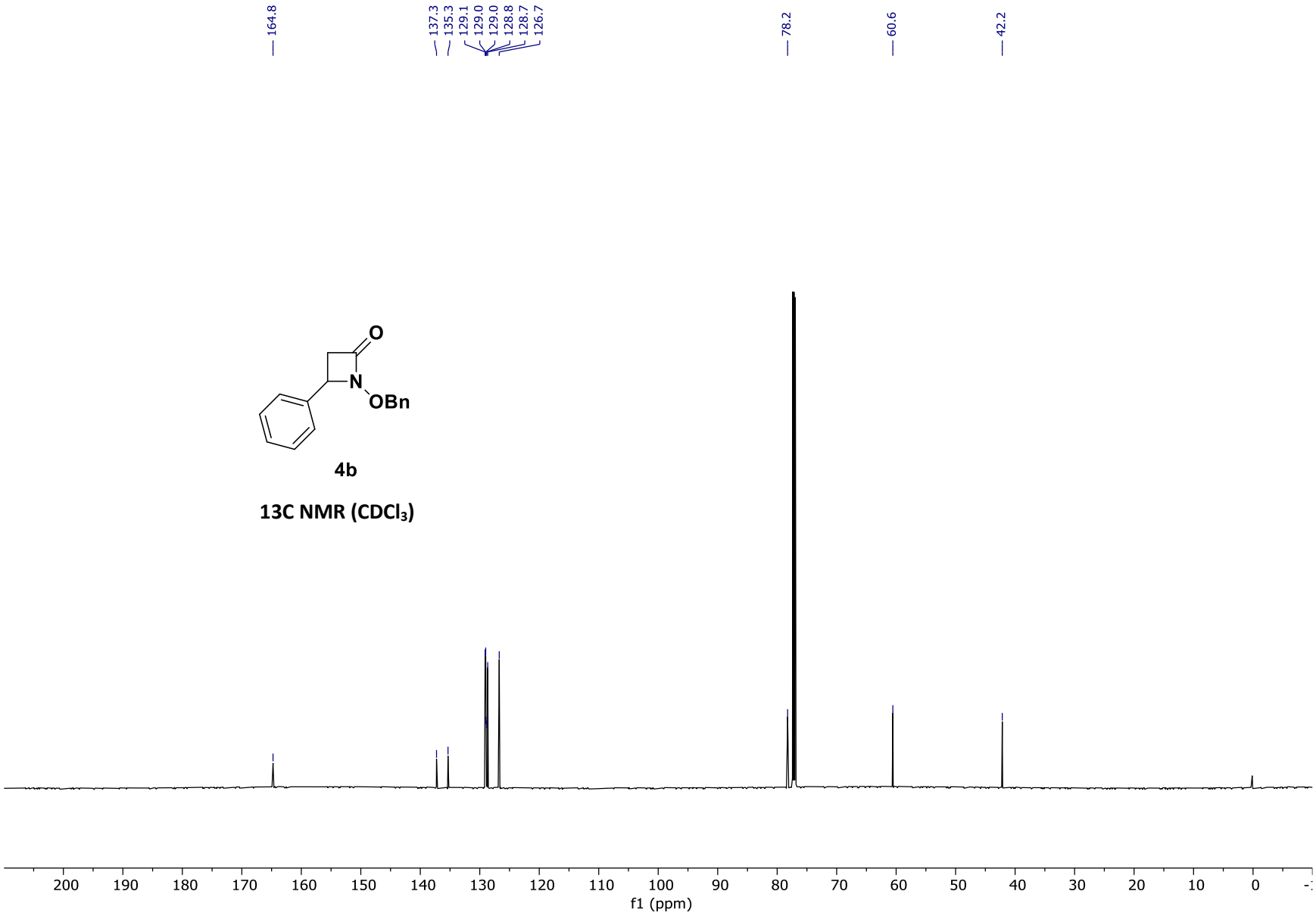


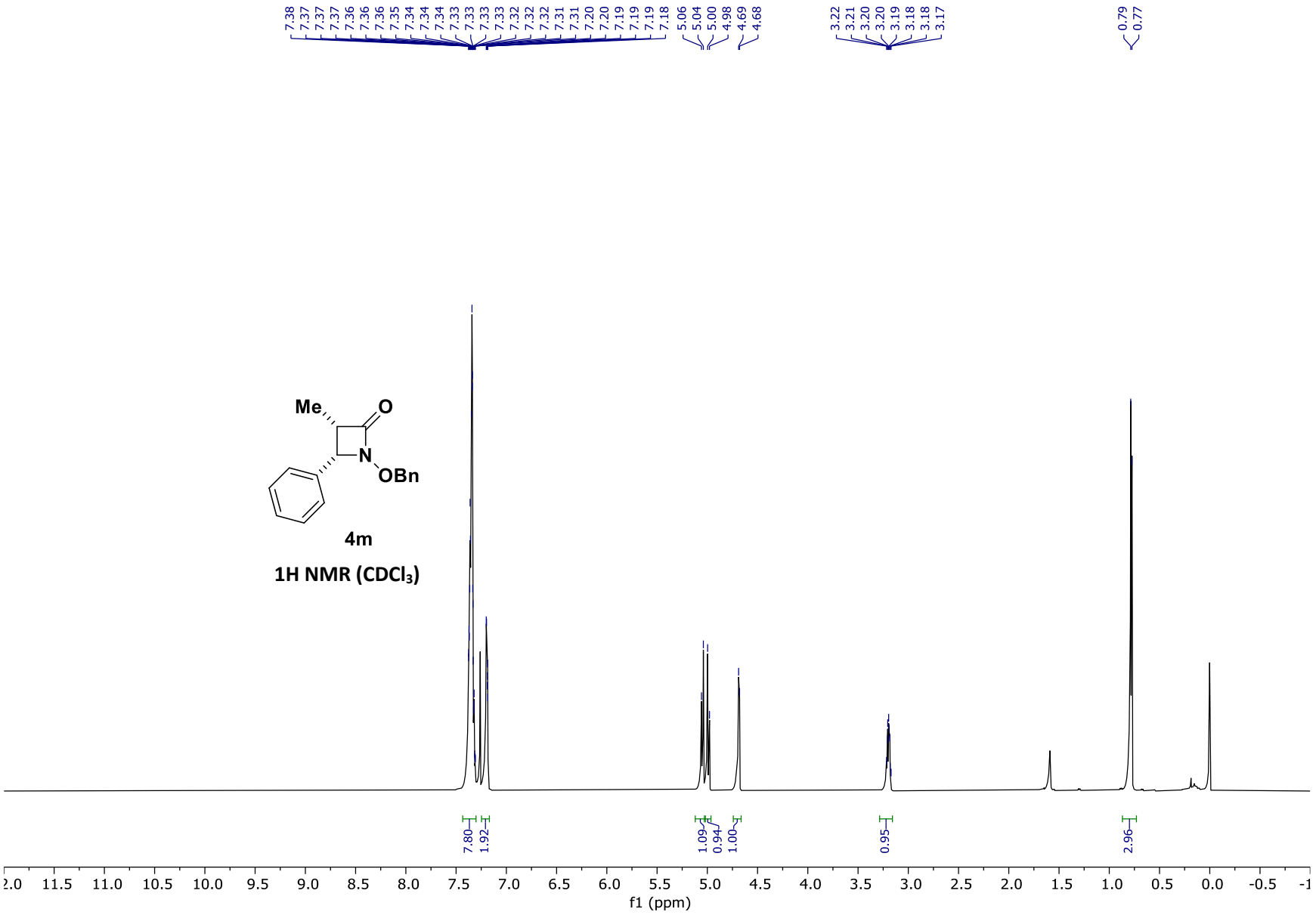
14r

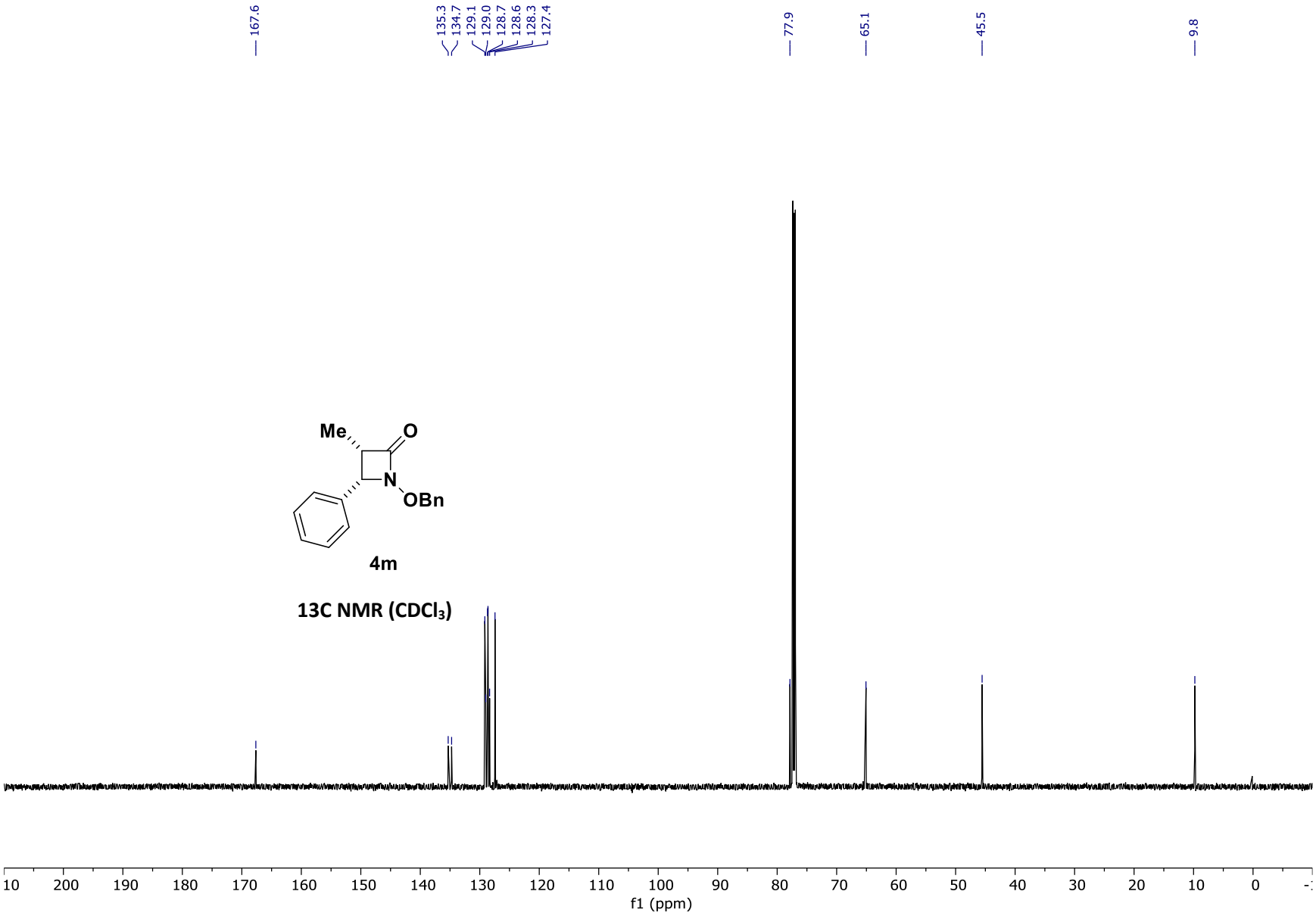
1H NMR ($CDCl_3$)

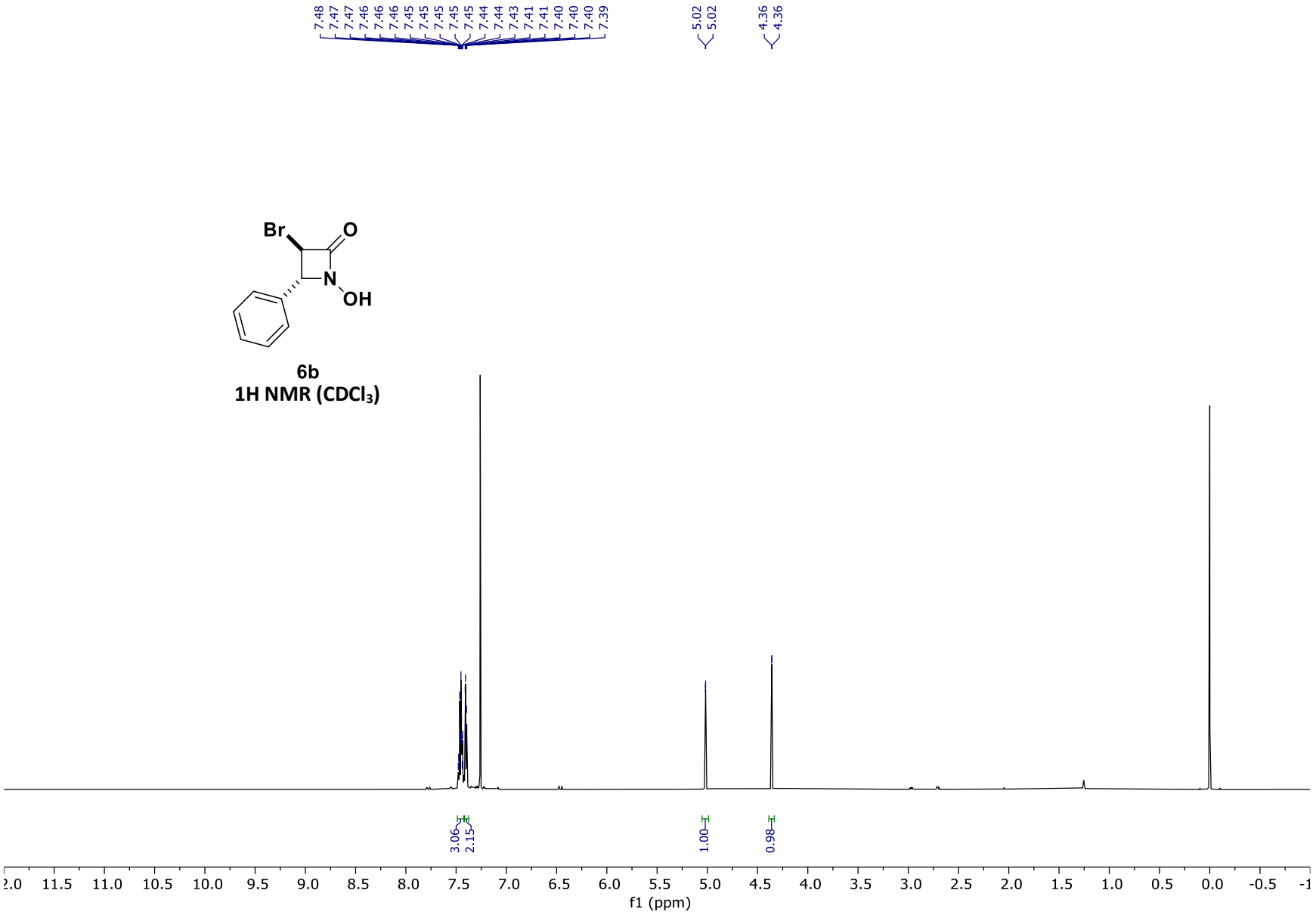

192.7
151.9
147.9
140.5
139.9
133.3
131.1
130.9
130.8
129.0
124.1
O
H
NO2
14r
13C NMR (CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.29 7.28 7.28 7.28 7.26 7.26 7.26 7.26 7.25 7.25 7.25 4.95 4.93 4.87 4.85 4.51 4.51 4.50 4.50
3.10 3.09 3.07 3.06 2.61 2.61 2.59 2.59
O
N
OBn
4b
1H NMR (CDCl3)
7.88 2.62 1.01 1.00 0.97 1.01 1.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

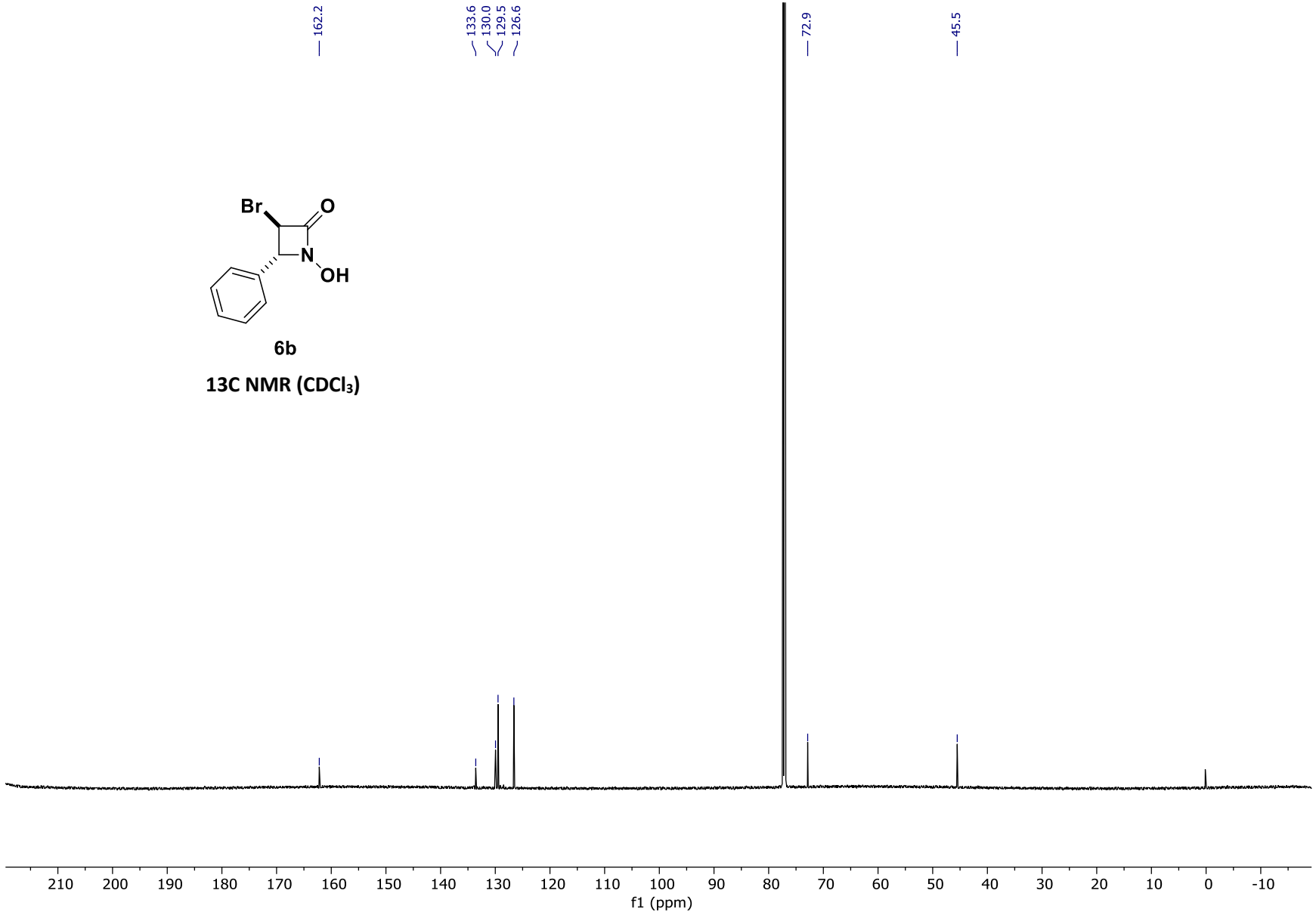

164.8
137.3
135.3
129.1
129.0
129.0
128.8
128.7
126.7
78.2
60.6
42.2
O
N
OBn
4b
13C NMR (CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

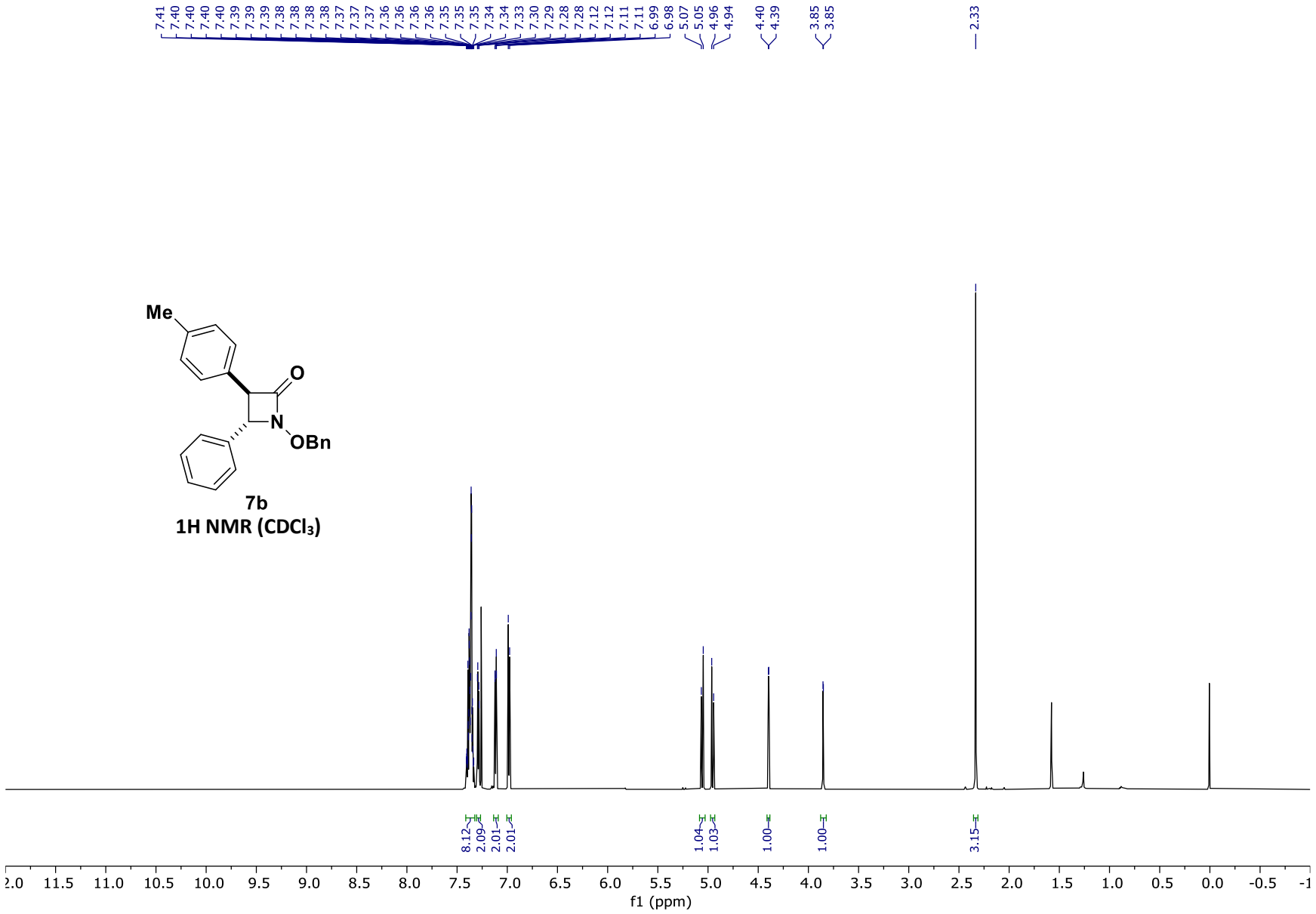

7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.20 7.20 7.19 7.19 7.19 7.18 5.06 5.04 5.00 4.98 4.69 4.68
3.22 3.21 3.20 3.20 3.19 3.18 3.18 3.17
0.79 0.77
Me
O
N
OBn
4m
1H NMR (CDCl3)
7.80 1.92 1.09 0.94 1.00 0.95 2.96
f1 (ppm)

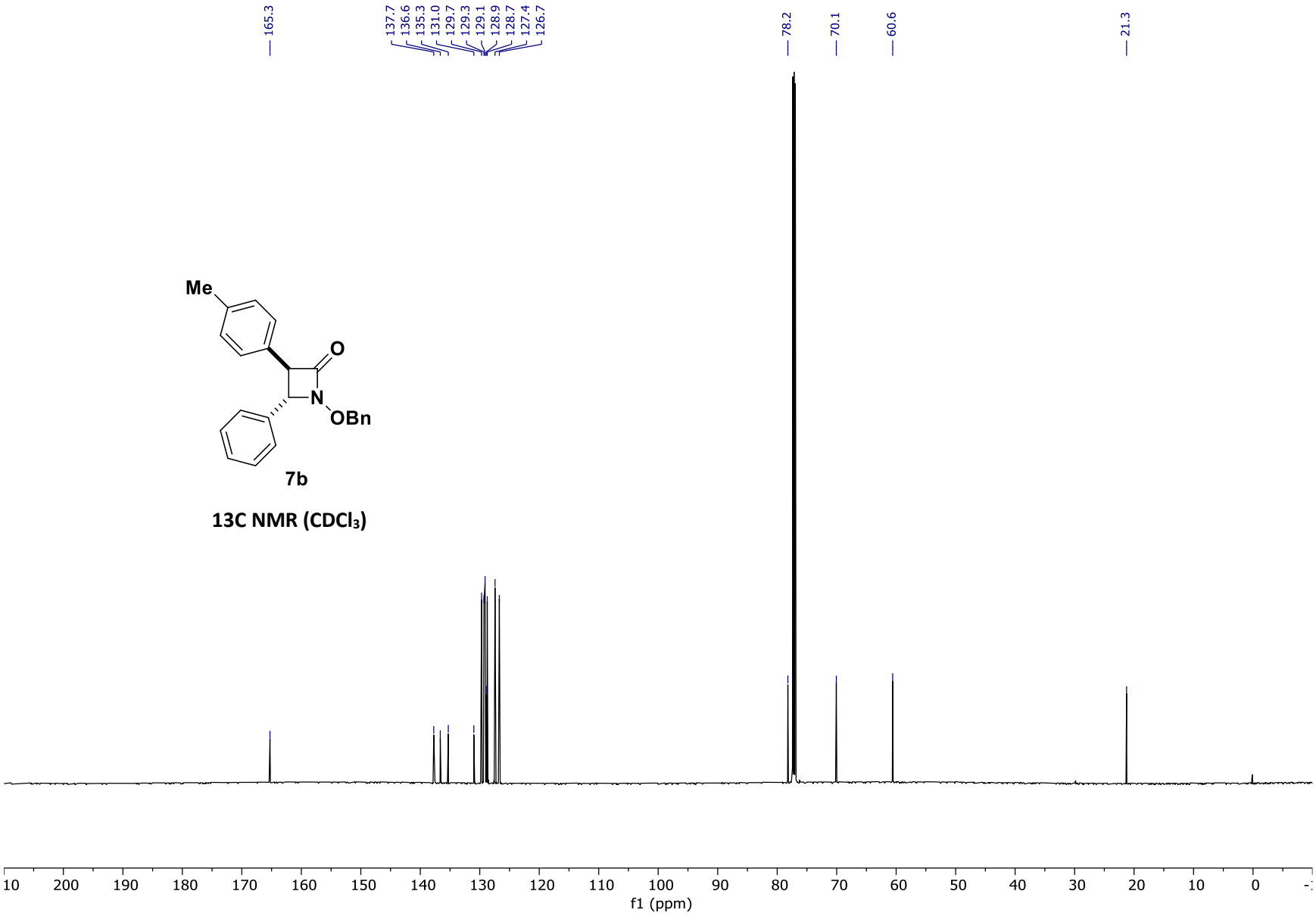

167.6
135.3
134.7
129.1
129.0
128.7
128.6
128.3
127.4
77.9
65.1
45.5
9.8
Me
O
N
OBn
4m
13C NMR (CDCl3)
f1 (ppm)

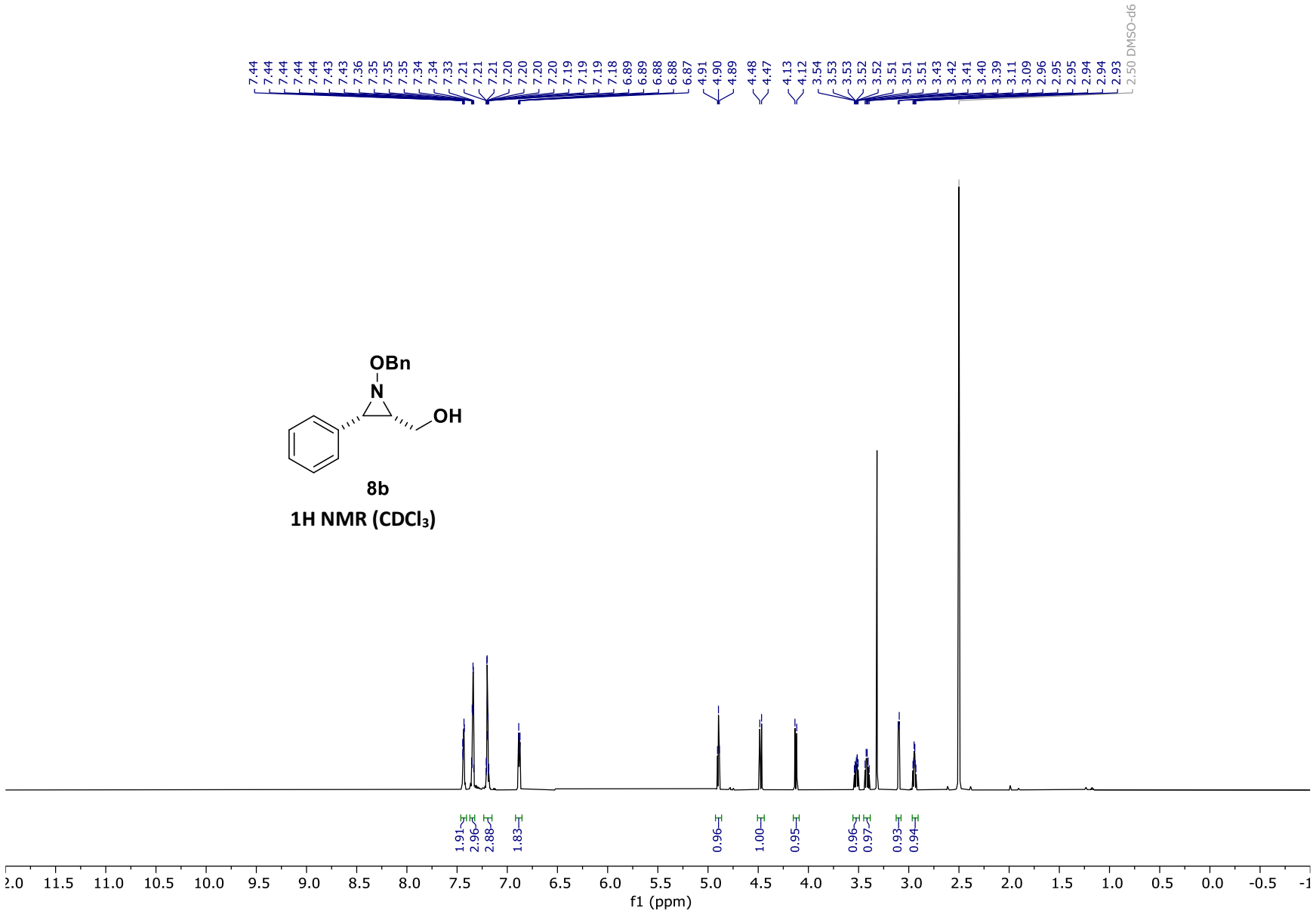


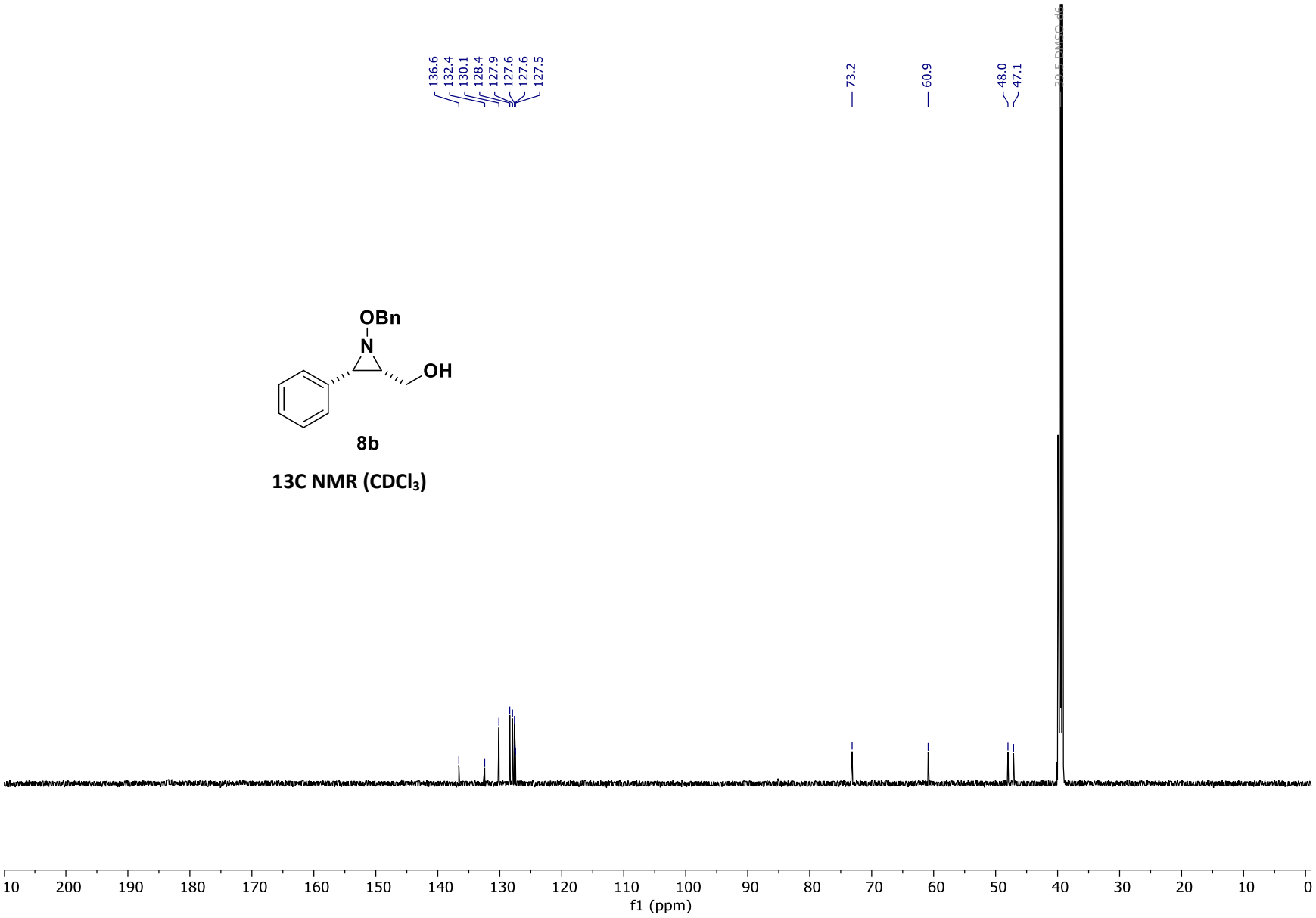
6b
1H NMR ($CDCl_3$)


162.2
133.6
130.0
129.5
126.6
72.9
45.5
Br
O
N
OH
6b
13C NMR (CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

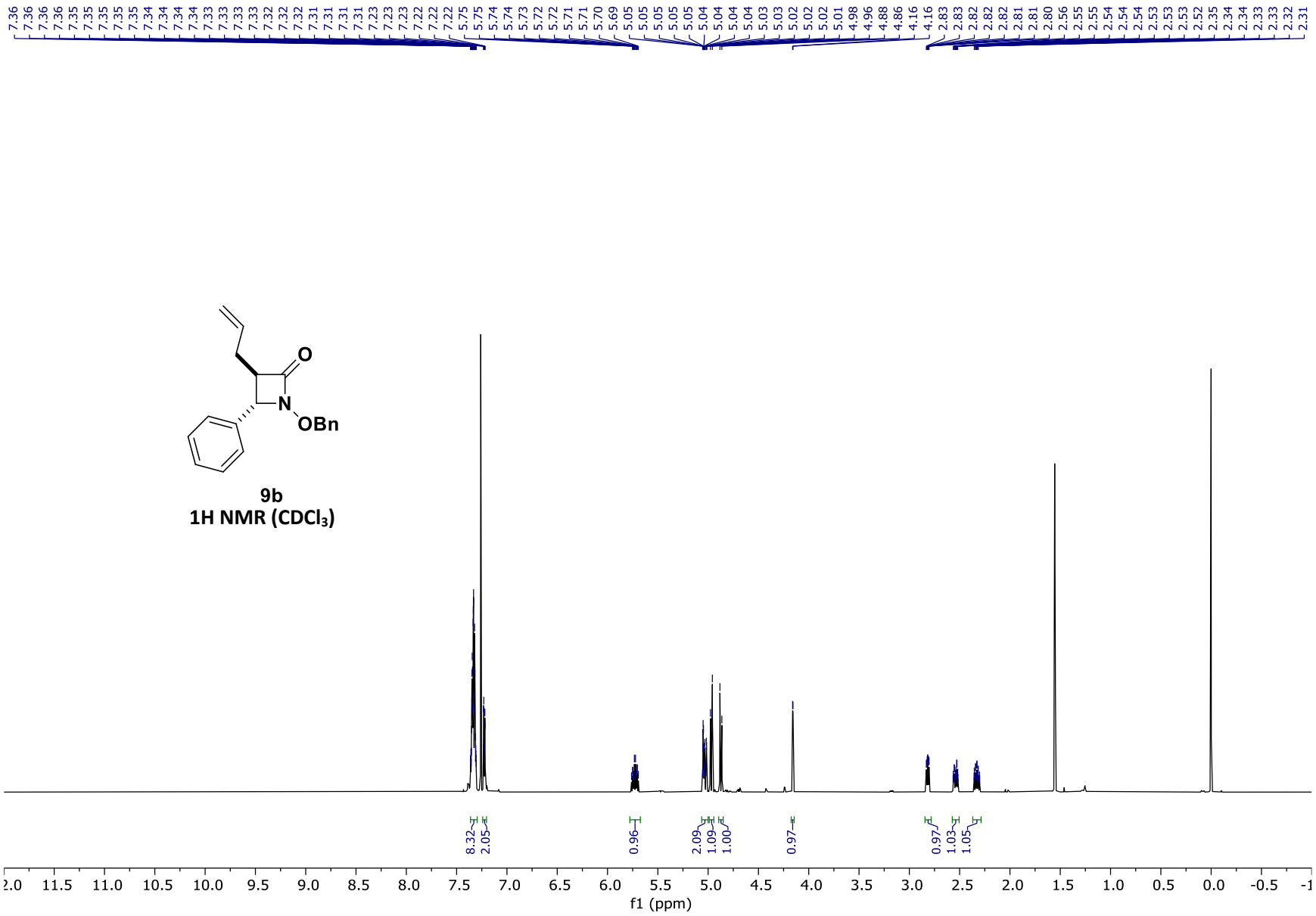

7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.30
7.29
7.28
7.28
7.12
7.12
7.11
7.11
6.99
6.98
5.07
5.05
4.96
4.94
4.40
4.39
3.85
3.85
2.33
Me
O
N
OBn
7b
1H NMR (CDCl3)
8.12
2.09
2.01
2.01
1.04
1.03
1.00
1.00
3.15
f1 (ppm)

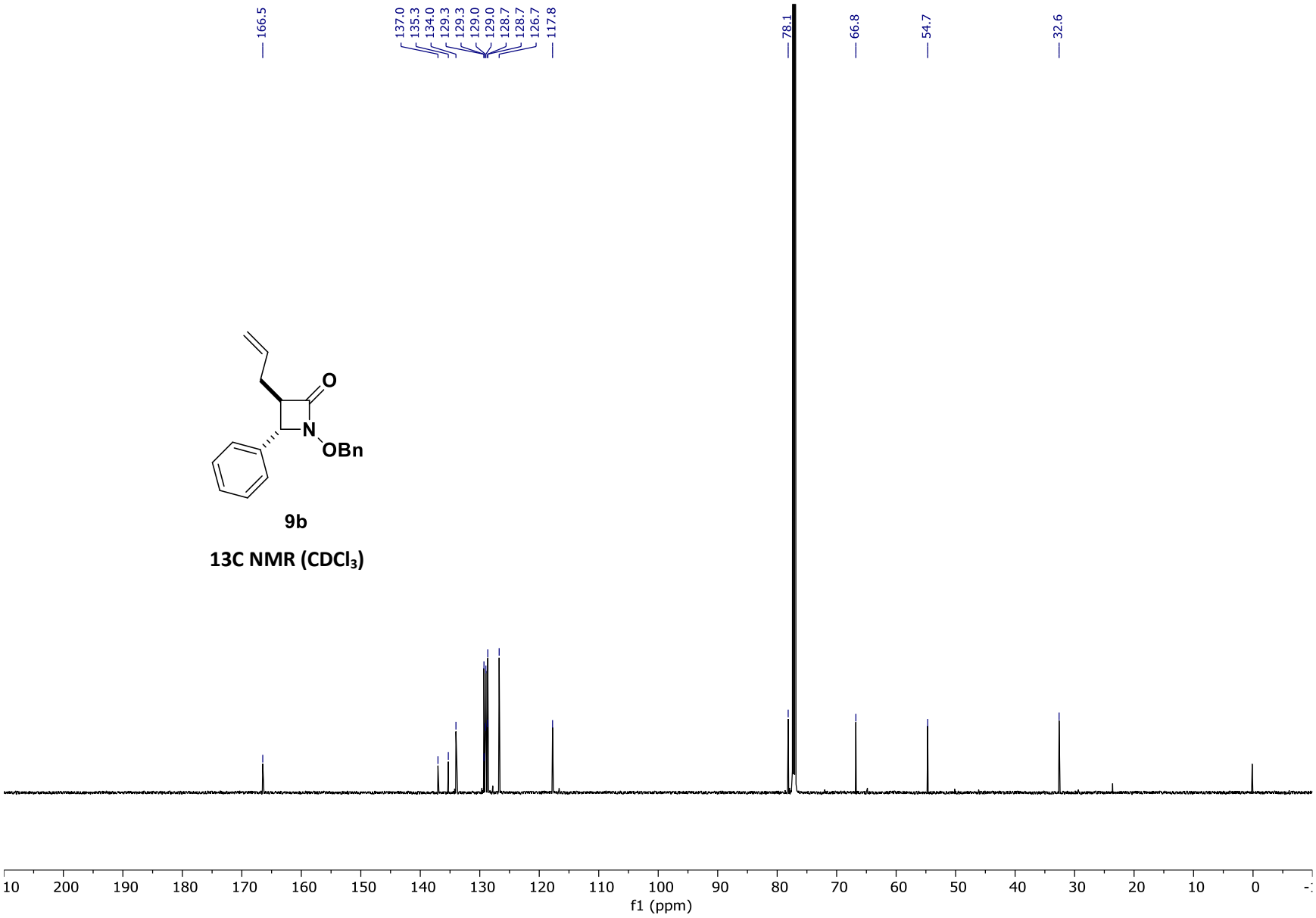

165.3
137.7
136.6
135.3
131.0
129.7
129.3
129.1
128.9
128.7
127.4
126.7
78.2
70.1
60.6
21.3
Me
O
N
OBn
7b
13C NMR (CDCl3)
f1 (ppm)


OBn
N
OH
8b
1H NMR (CDCl3)
f1 (ppm)


136.6
132.4
130.1
128.4
127.9
127.6
127.6
127.5
73.2
60.9
48.0
47.1
OBn
N
OH
8b
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

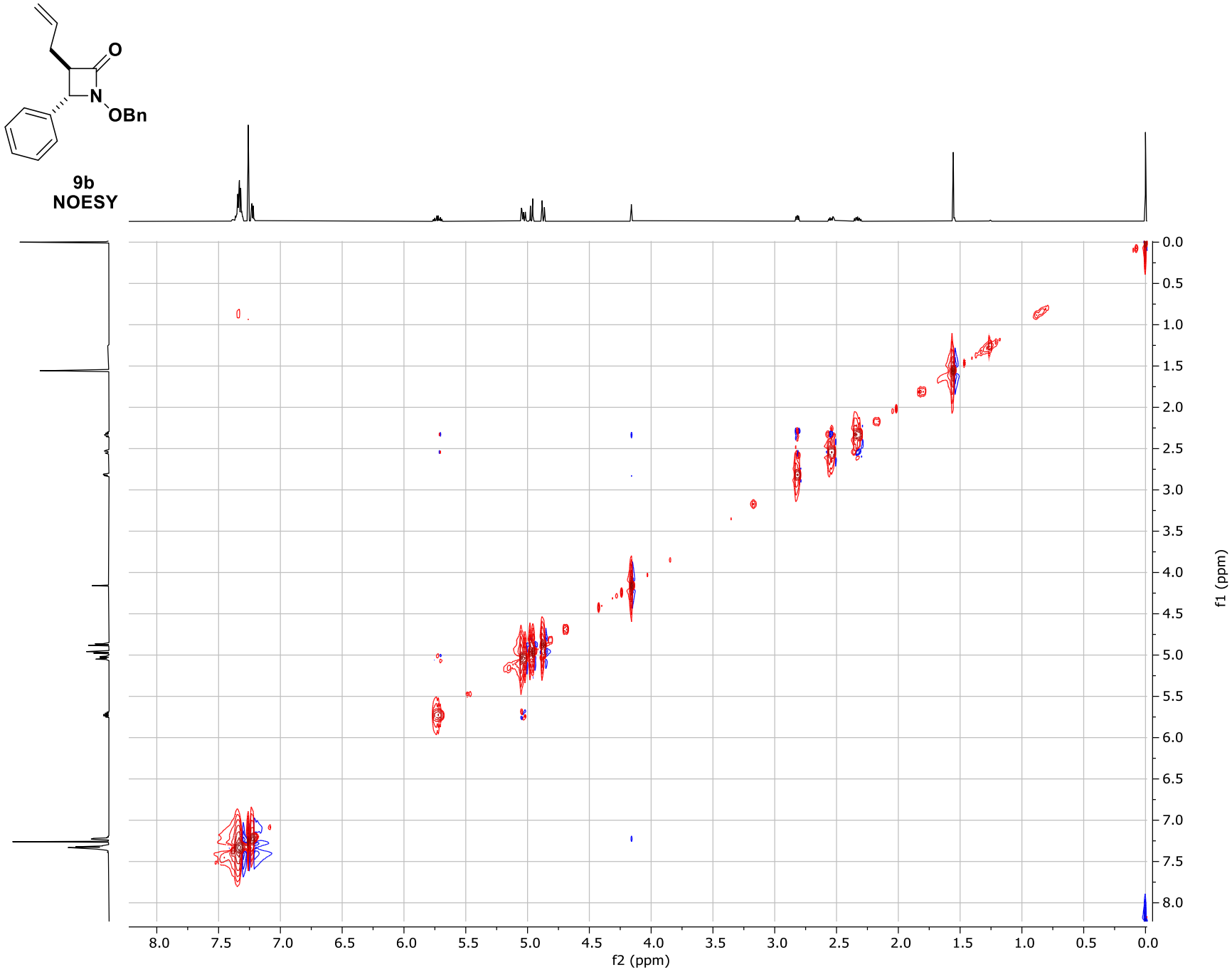

OBn
N
OH
8b
NOESY
{2.50,2.50}DMSO-d6
f2 (ppm)
f1 (ppm)

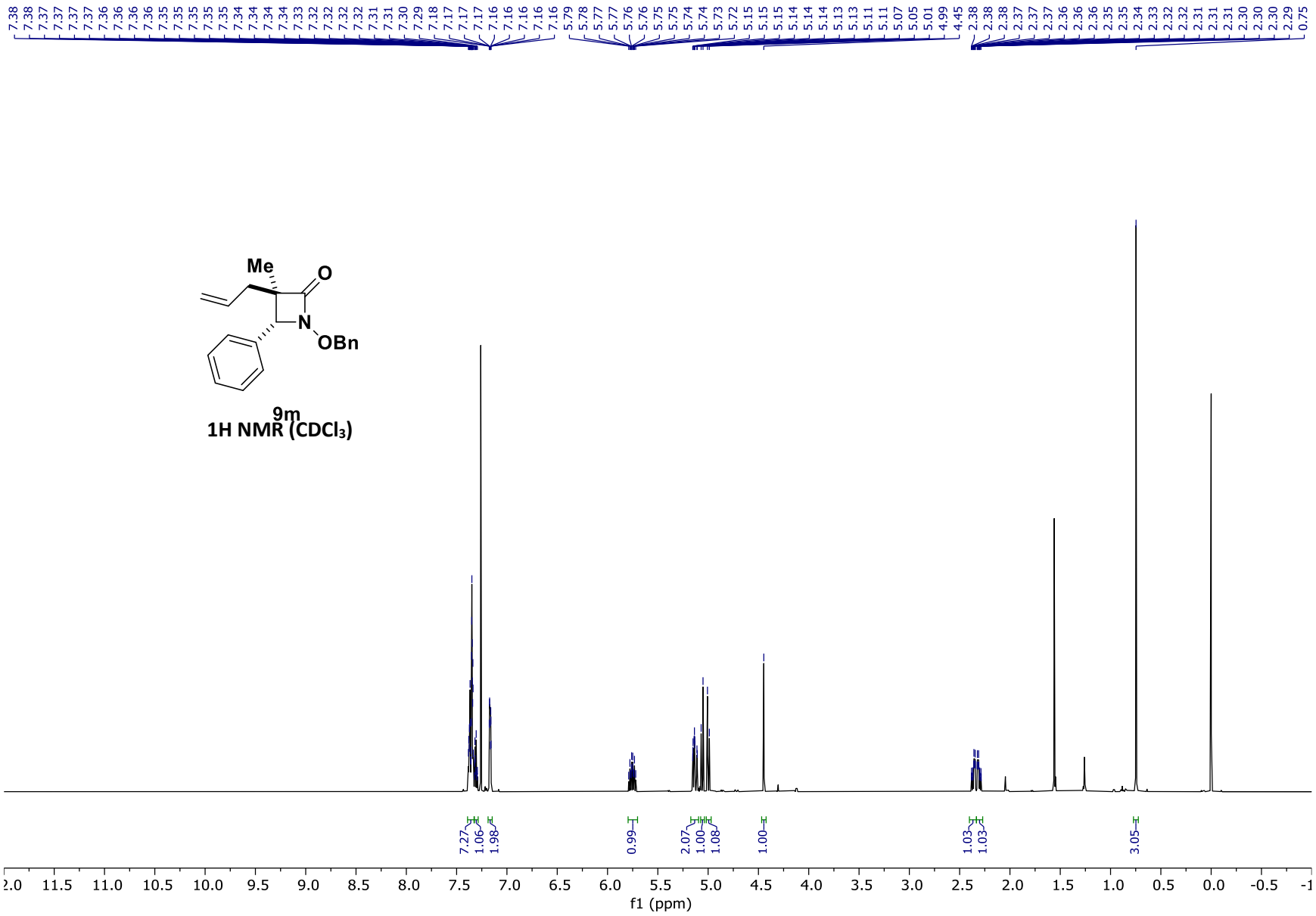

O
N
OBn
9b
1H NMR (CDCl3)
f1 (ppm)

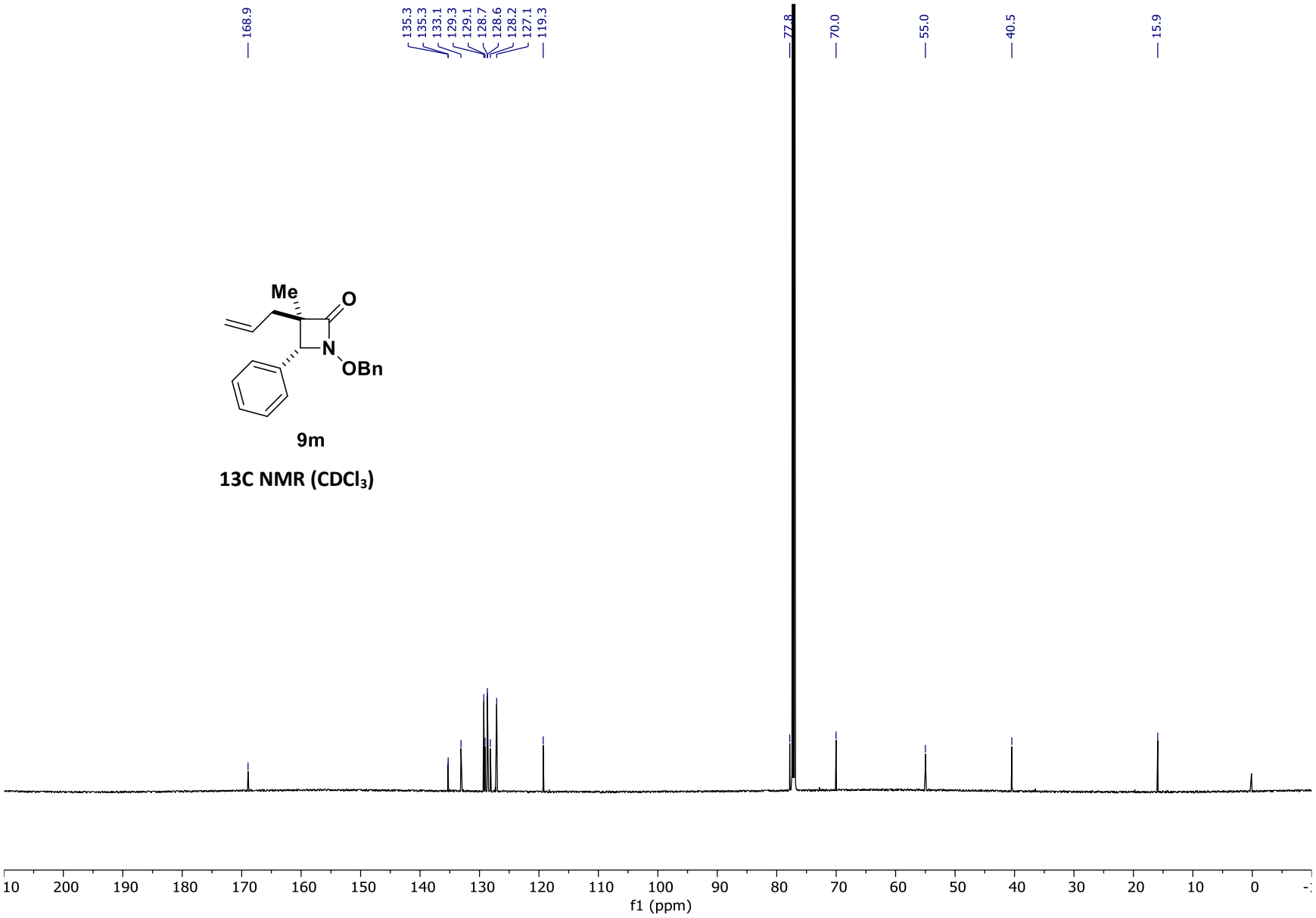


9b

13C NMR ($CDCl_3$)

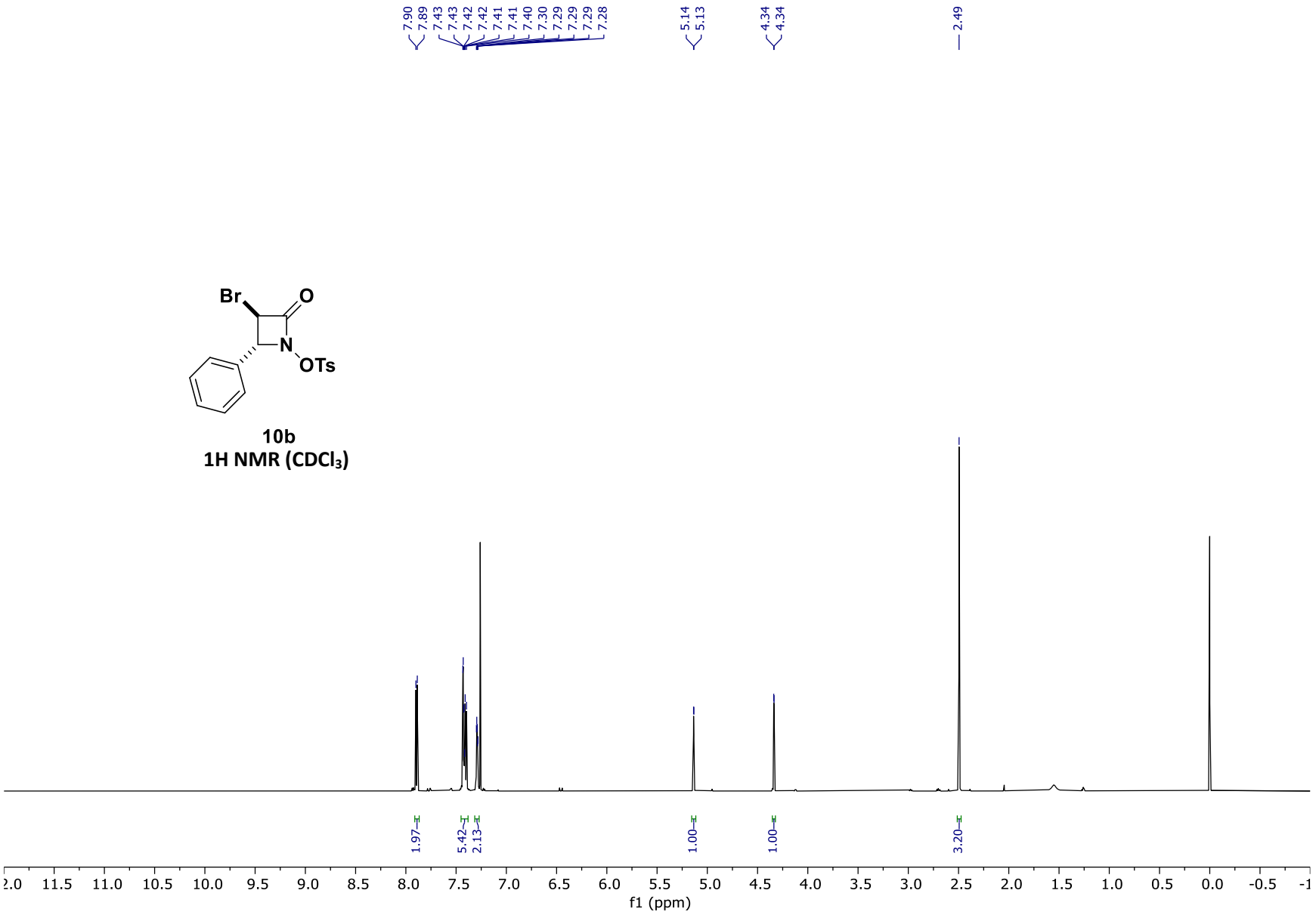

O
N
OBn
9b
NOESY
f2 (ppm)
f1 (ppm)

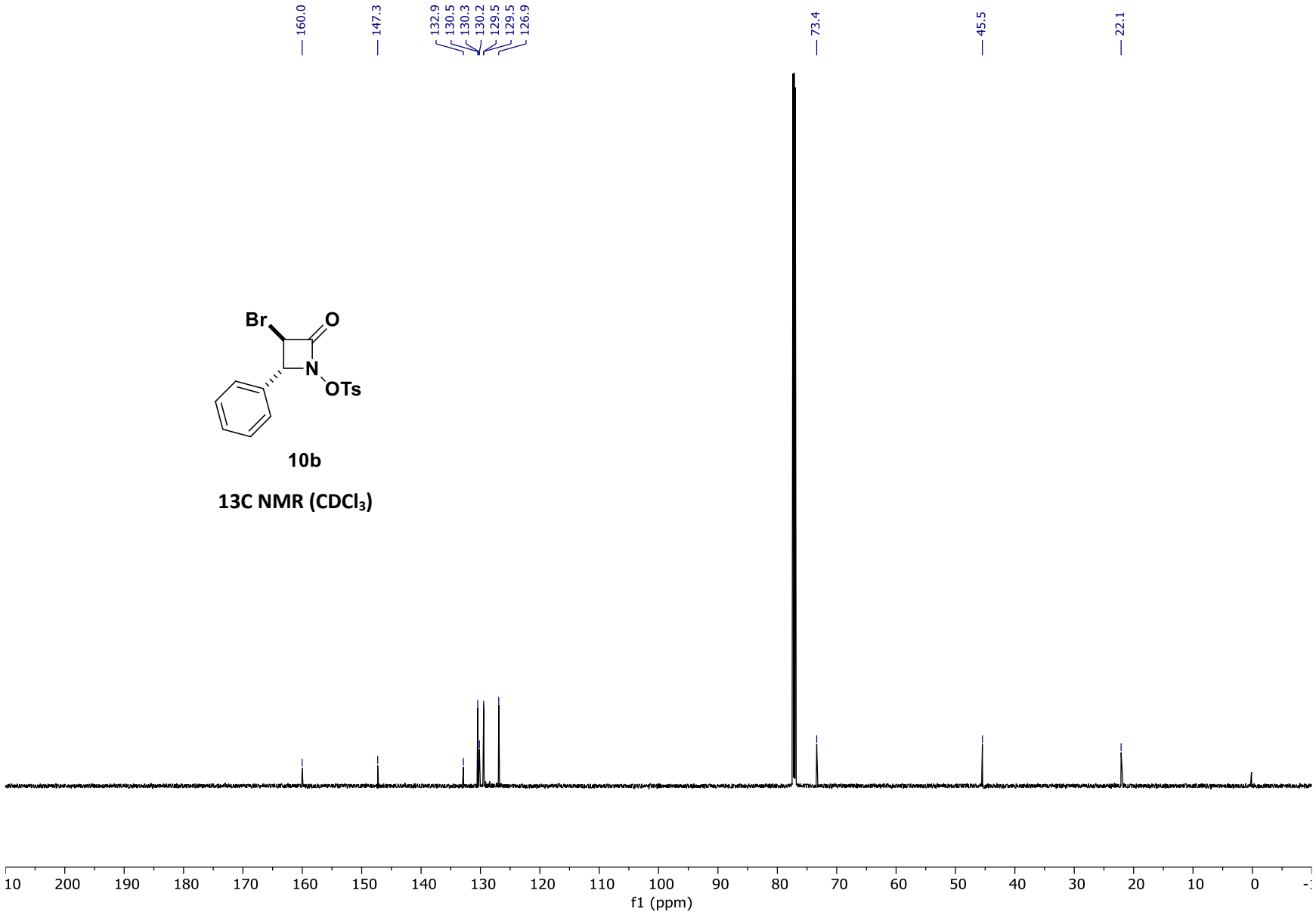

Me
O
N
OBn
9m
1H NMR (CDCl3)
f1 (ppm)

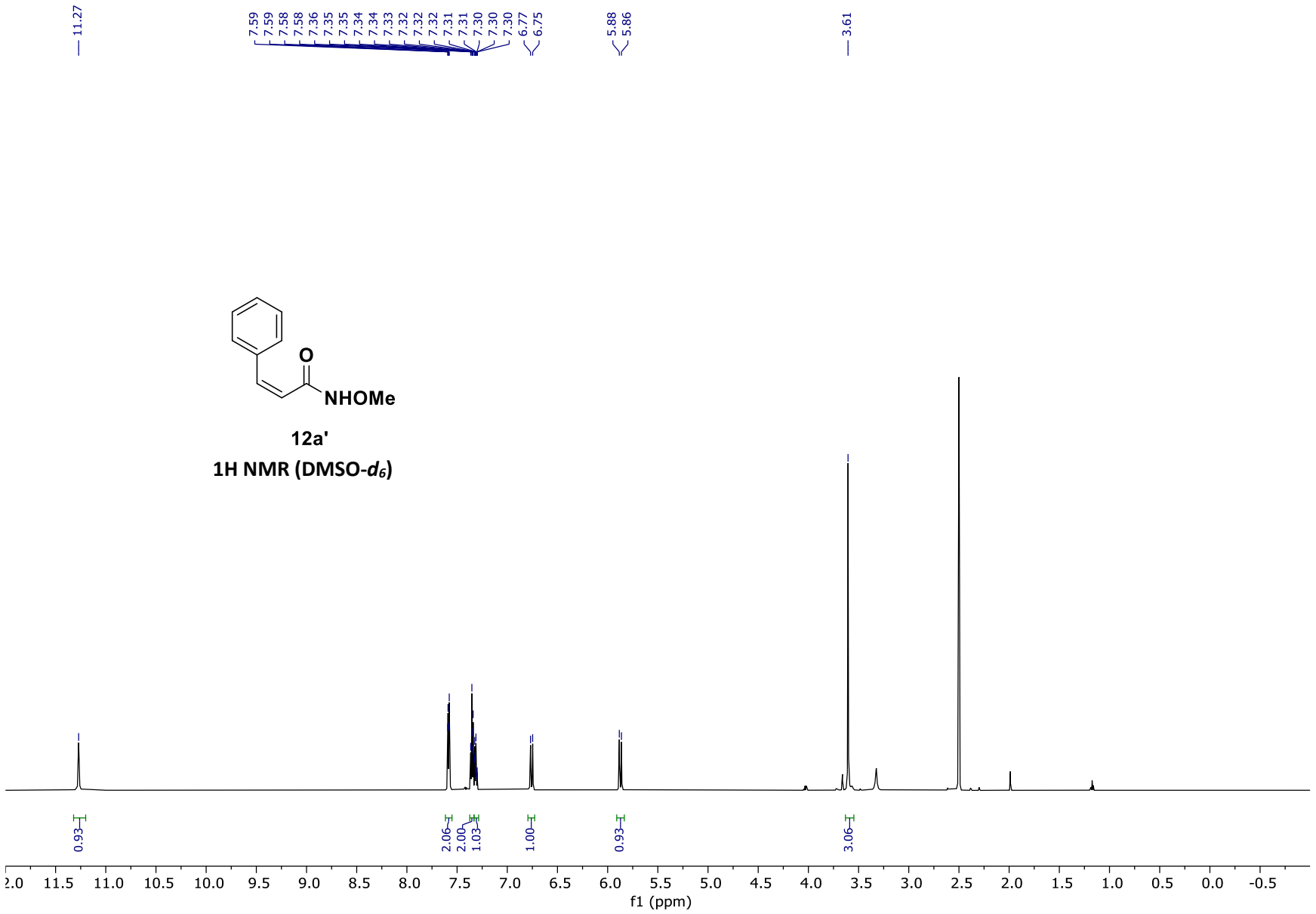


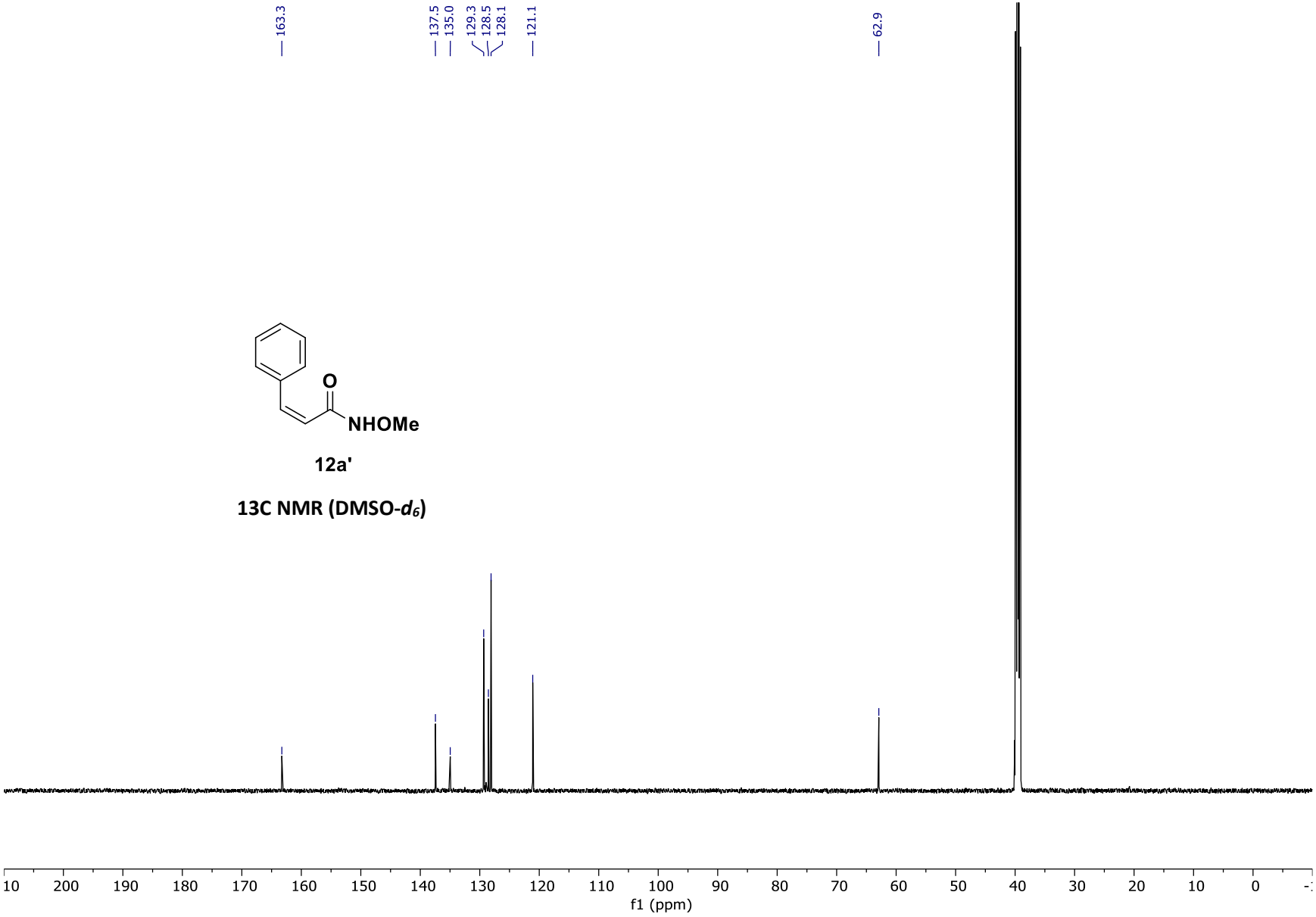
9m

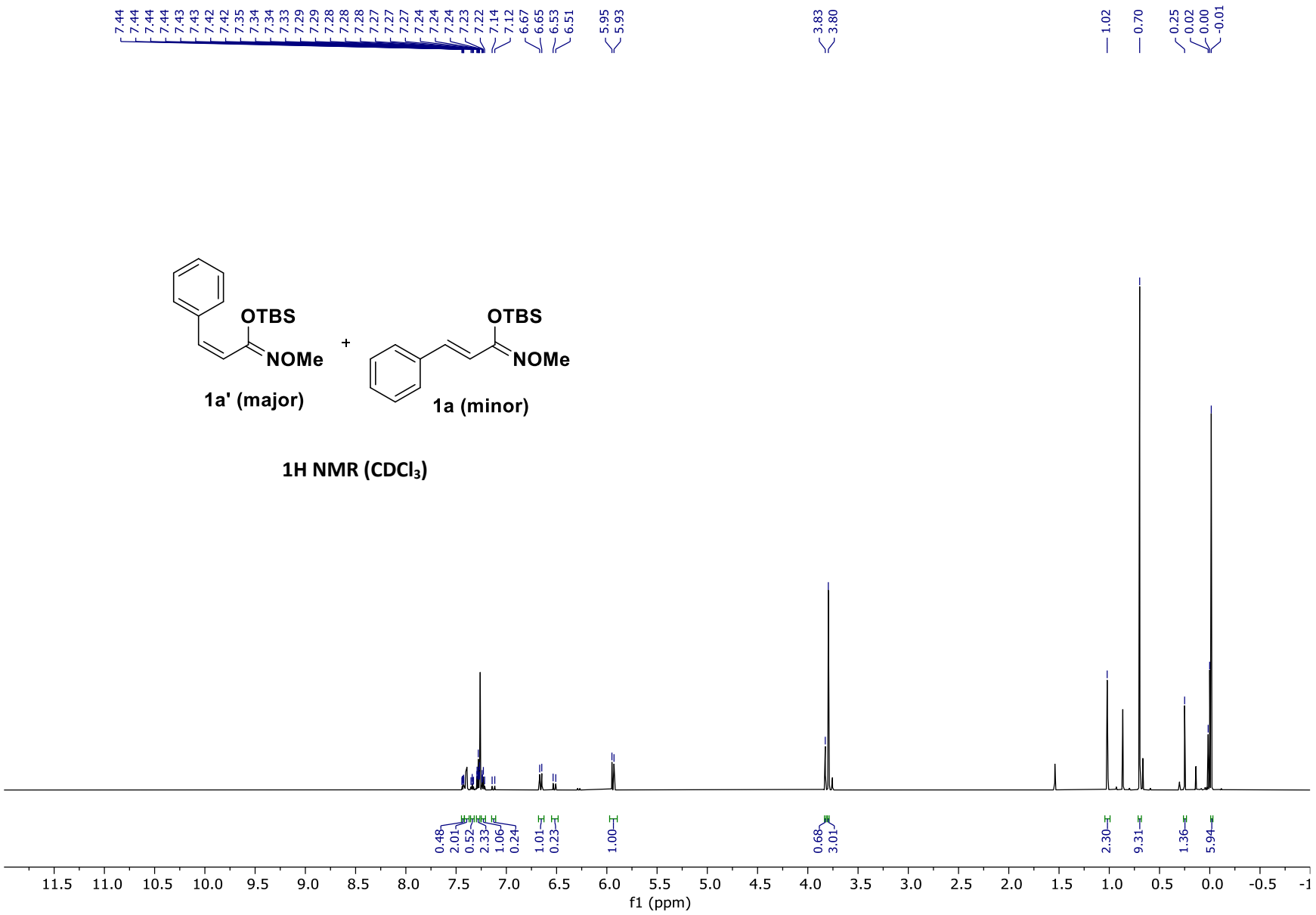
13C NMR ($CDCl_3$)

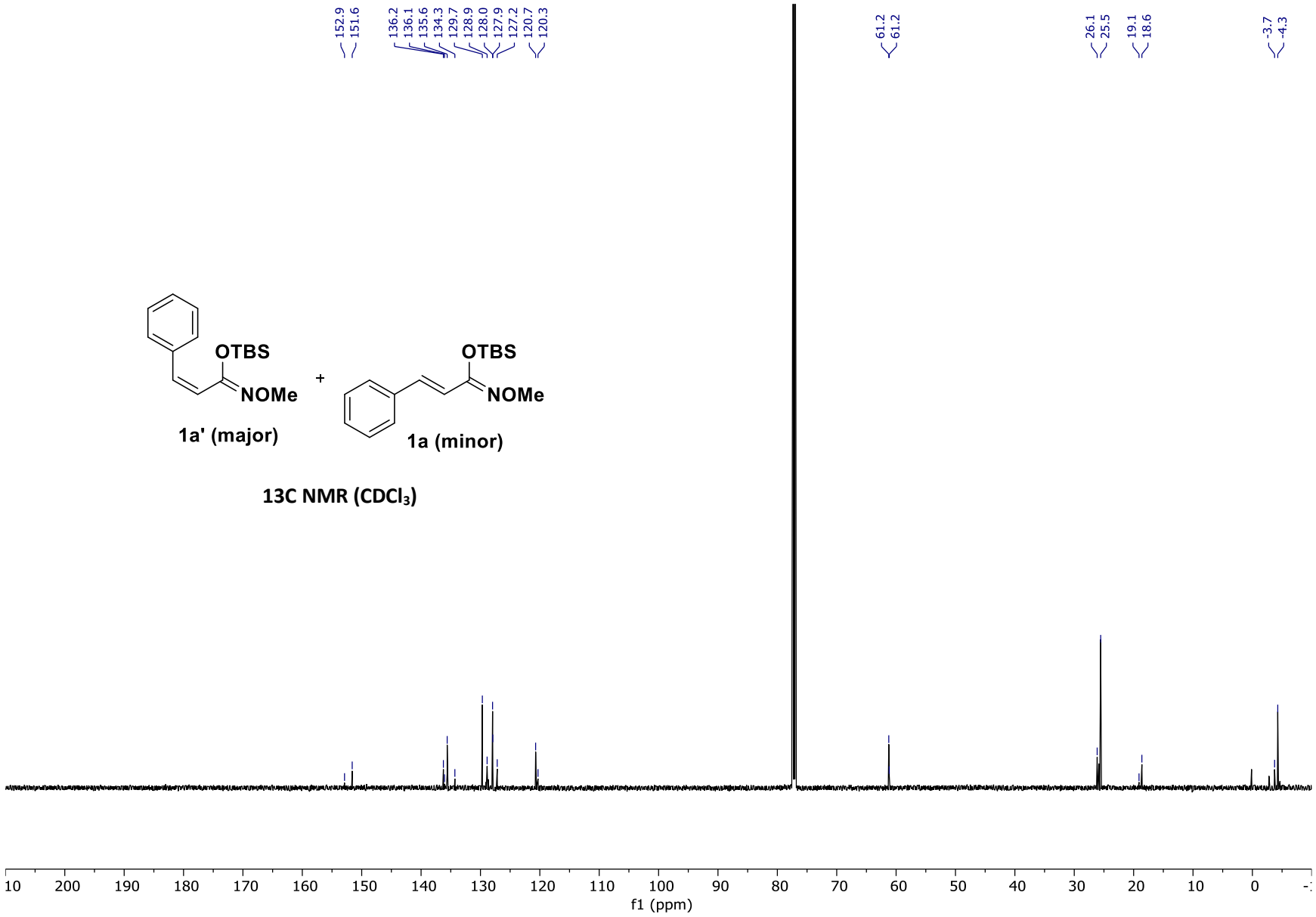

7.90
7.89
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.30
7.29
7.29
7.29
7.28
5.14
5.13
4.34
4.34
2.49
Br
O
N
OTs
10b
1H NMR (CDCl3)
1.97
5.42
2.13
1.00
1.00
3.20
f1 (ppm)

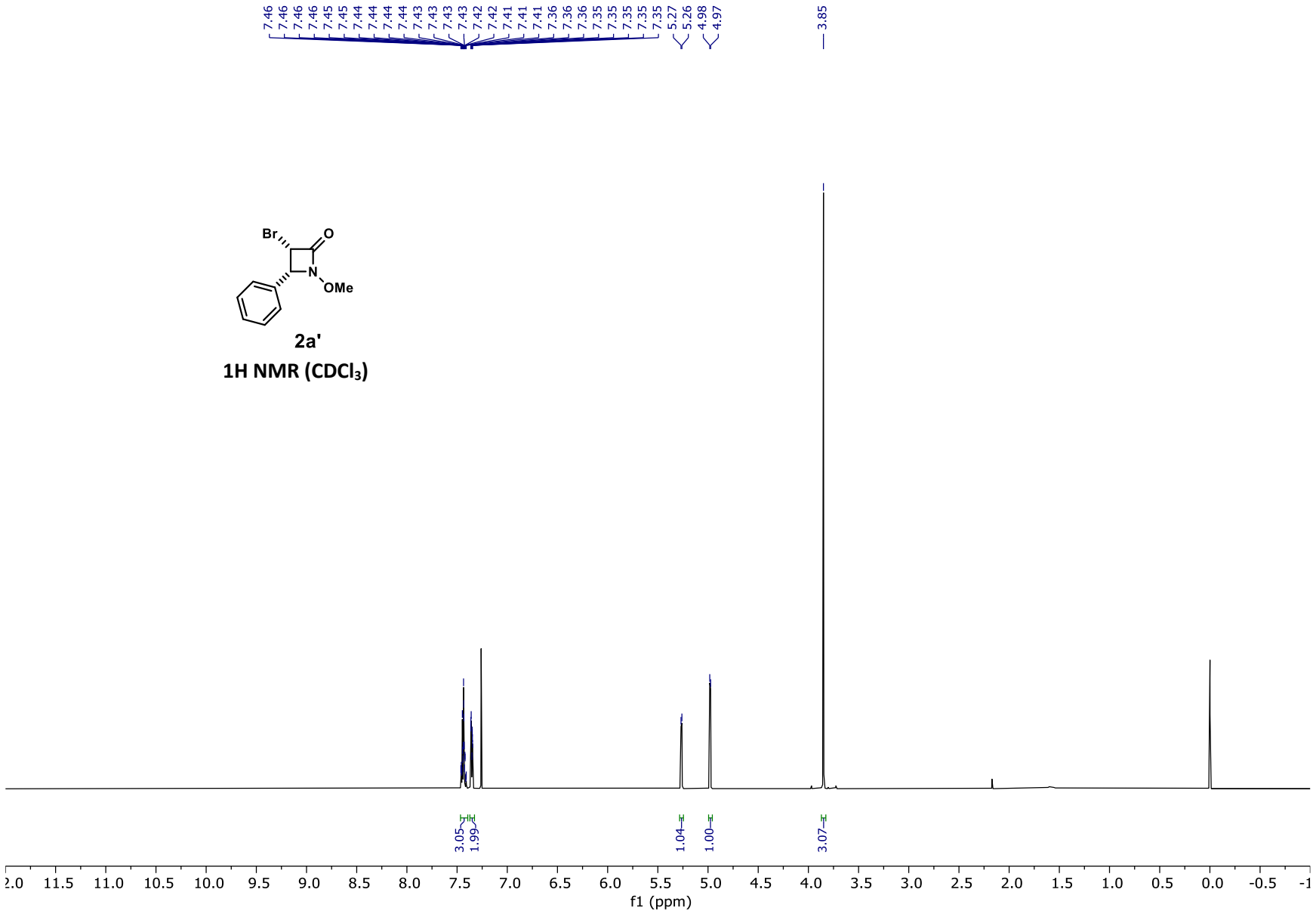

160.0
147.3
132.9
130.5
130.3
130.2
129.5
129.5
126.9
73.4
45.5
22.1
Br
O
N
OTs
10b
13C NMR (CDCl3)
f1 (ppm)

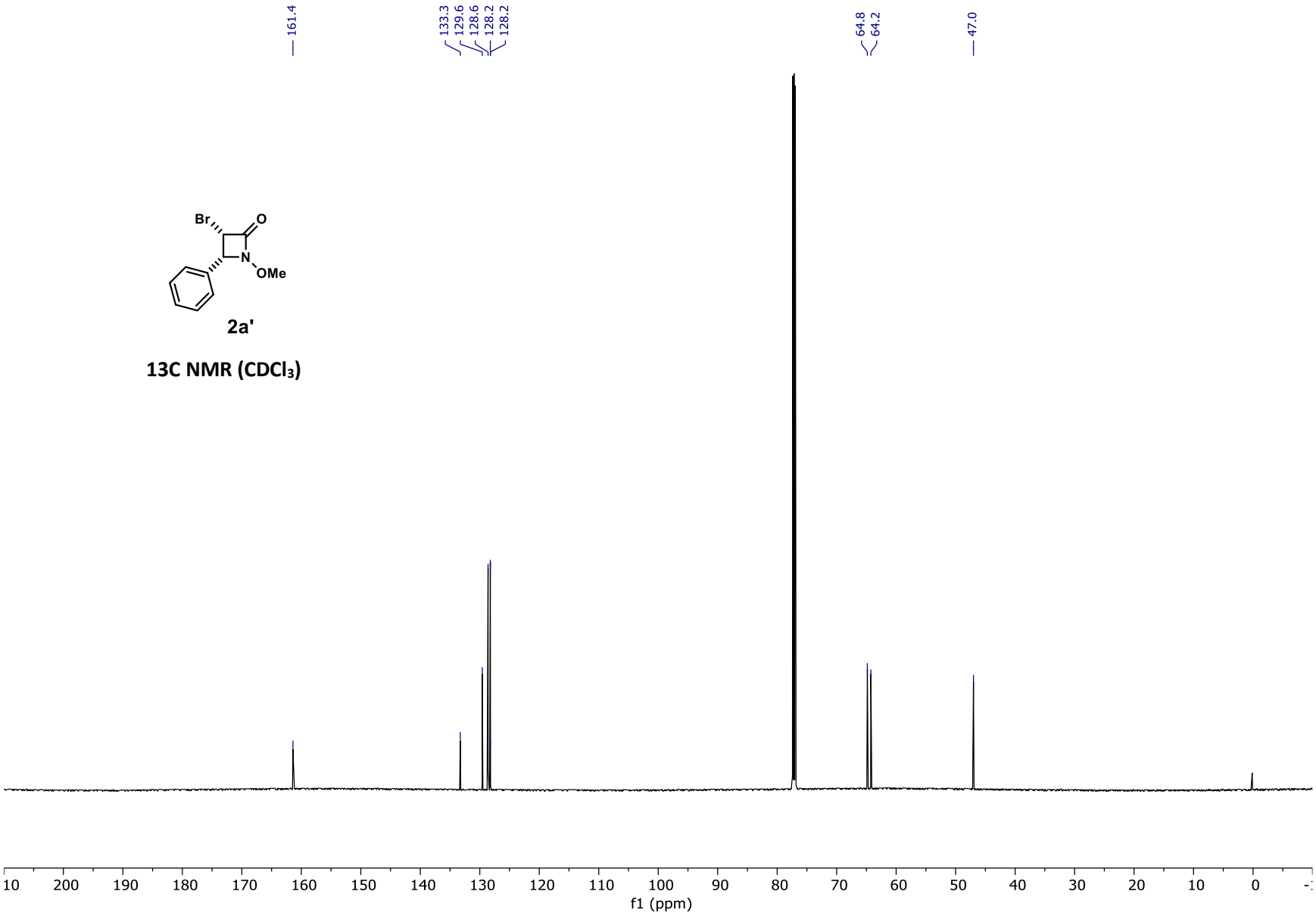

11.27
7.59
7.59
7.58
7.58
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.30
6.77
6.75
5.88
5.86
3.61
O
NHOMe
12a'
1H NMR (DMSO-d6)
0.93
2.06
2.00
1.03
1.00
0.93
3.06
f1 (ppm)


163.3
137.5
135.0
129.3
128.5
128.1
121.1
62.9
O
NHOMe
12a'
13C NMR (DMSO-d_6)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.44
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.35
7.34
7.34
7.33
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.27
7.24
7.24
7.24
7.23
7.22
7.14
7.12
6.67
6.65
6.53
6.51
5.95
5.93
3.83
3.80
1.02
0.70
0.25
0.02
0.00
-0.01
OTBS
NOMe
1a' (major)
+
OTBS
NOMe
1a (minor)
1H NMR (CDCl3)
0.48
2.01
0.52
2.33
1.06
0.24
1.01
0.23
1.00
0.68
3.01
2.30
9.31
1.36
5.94
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


152.9
151.6
136.2
136.1
135.6
134.3
129.7
128.9
128.0
127.9
127.2
120.7
120.3
61.2
61.2
26.1
25.5
19.1
18.6
-3.7
-4.3
OTBS
NOMe
1a' (major)
+
OTBS
NOMe
1a (minor)
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.46
7.46
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.44
7.43
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.36
7.36
7.36
7.35
7.35
7.35
7.35
7.35
5.27
5.26
4.98
4.97
3.85
Br
O
N
OMe
2a'
1H NMR (CDCl3)
3.05
1.99
1.04
1.00
3.07
f1 (ppm)


161.4
133.3
129.6
128.6
128.2
128.2
64.8
64.2
47.0
Br
O
N
OMe
2a'
13C NMR (CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)