Aryne-mediated [2,3]-sigmatropic rearrangement of tertiary 2,3-allenylamines bearing an electron-withdrawing group at the α-position

Lu Han, Xue-Ting Zhang, Dong Xie and Shi-Kai Tian*

Hefei National Laboratory for Physical Sciences at the Microscale, Center for Excellence in Molecular Synthesis (CAS), and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China
E-mail: tiansk@ustc.edu.cn

Supporting information

Table of contents

General information

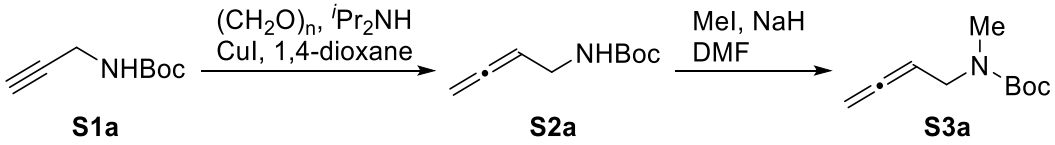
The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer or on a Bruker AC-500 FT spectrometer. The chemical shifts of ^{1}H NMR and ^{13}C NMR spectra were referenced internally with tetramethylsilane (δ H 0.00 and δ C 0.0), or residual protio solvent signals $CDCl_3$ (δ C 77.2). Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). ESI-mass data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump, using a Daicel Chiralpak column (AD-H, OJ, OD, 250 × 4.6 mm) with isopropanol/hexane as the mobile phase, and the UV detection was monitored at 254 nm. Optical rotations were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\,^{\circ}C}$ (c = g/100 mL, solvent).

Chemicals were purchased from Adamas, Energy Chemical, Acros, Accela, Alfa Aesar, and TCI, and used as received.

Abbreviations: Boc = *tert*-butoxycarbonyl, DCE = 1,2-dichloroethane, DCM = dichoromethane, DMF = *N*,*N*-dimethylformamide, rt = room temperature, TBAF = tetrabutylammonium fluoride, Tf = trifluoromethanesulfonyl, TFA = trifluoroacetic acid, THF = tetrahydrofuran, TMS = trimethylsilyl.

Preparation of tertiary 2,3-allenylamines

(1) Preparation of Boc-protected 2,3-allenylamines **S2a** and **S3a**



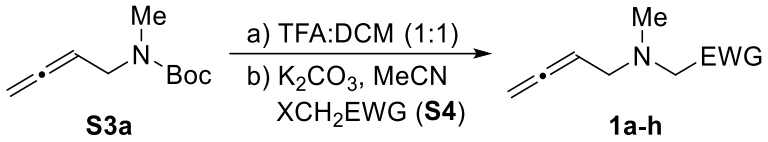
S1a **S2a** **S3a**

To a solution of CuI (4.76 g, 25.0 mmol) in 1,4-dioxane (60 mL) were added *tert*-butyl prop-2-yn-1-ylcarbamate (**S1a**) (7.76 g, 50.0 mmol), diisopropylamine (9.12 g, 90.0 mmol), and paraformaldehyde (3.75 g, 125 mmol). The mixture was stirred under reflux conditions for 2 hours, cooled to room temperature, filtered through a pad of silica gel, and washed with ethyl acetate (30 mL). The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (15:1) as the eluent, to give *tert*-butyl buta-2,3-dien-1-ylcarbamate (**S2a**) (5.50 g, 65% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.23-5.18 (m, 1H), 4.84-4.82 (m, 2H), 4.71 (s, br, 1H), 3.75-3.70 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.0, 155.8, 88.6, 79.5, 77.5, 38.9, 28.5. HRMS (ESI) calcd for $C_9H_{16}NO_2^+$ $(M + H)^+$ 170.1176, found 170.1172.

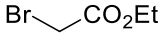
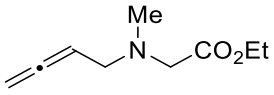
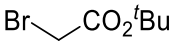
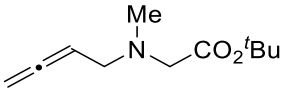
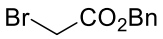
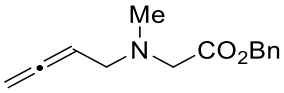
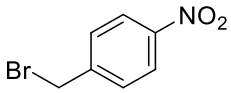
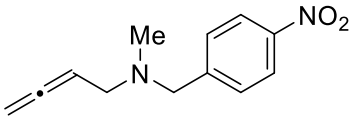
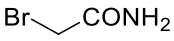
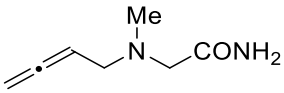
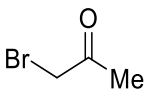
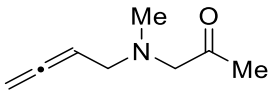
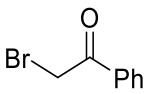
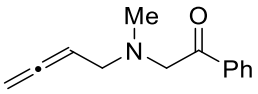
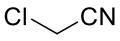
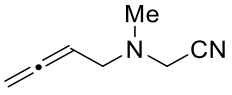
To a solution of compound **S2a** (5.50 g, 32.5 mmol) in dry *N*,*N*-dimethylformamide (60 mL) at 0 °C was added portionwise NaH (1.56 g, 39.0 mmol, 60% dispersion in mineral oil). The mixture was stirred at 0 °C for 30 minutes, added dropwise methyl iodide (5.54 g, 39.0 mmol), and stirred at room temperature for 12 hours. The reaction was quenched with saturated aqueous ammonium chloride (60 mL), extracted with diethyl ether (3 × 60 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (20:1) as the eluent, to give *tert*-butyl buta-2,3-dien-1-

yl(methyl)carbamate (**S3a**) (5.66 g, 95% yield) as a colorless oil. The spectral data of **S3a** are in agreement with those reported in the literature.[1]

(2) Method A

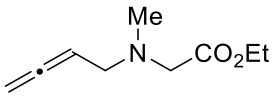


S3a **1a-h**

Entry	**S4**	**1a-h**
1	 **S4a**	 **1a**
2	 **S4b**	 **1b**
3	 **S4c**	 **1c**
4	 **S4d**	 **1d**
5	 **S4e**	 **1e**
6	 **S4f**	 **1f**
7	 **S4g**	 **1g**
8	 **S4h**	 **1h**

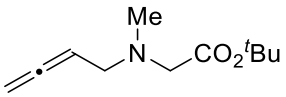
To a solution of *tert*-butyl buta-2,3-dien-1-yl(methyl)carbamate (**S3a**) (916 mg, 5.0 mmol) in

dichloromethane (2.0 mL) at 0 ℃ was added trifluoroacetic acid (2.0 mL). The mixture was stirred at 0 ℃ for 30 minutes, and concentrated under reduced pressure. The residue was dissolved in acetonitrile (10.0 mL), cooled to 0 ℃, and added portionwise K_2CO_3 (2.07 g, 15.0 mmol). The mixture was stirred at 0 ℃ for 10 minutes, and added alkyl halide **S4** (5.0 mmol). The mixture was stirred at room temperature for 8 hours, diluted with water (10 mL), extracted with ethyl acetate (3 × 10 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (5:1 to 2:1) as the eluent, to give 2,3-allenylamine **1a-h**.



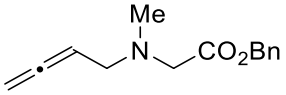
1a

Ethyl *N*-(buta-2,3-dien-1-yl)-*N*-methylglycinate (**1a**) was obtained (677 mg, 80% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20-5.13 (m, 1H), 4.73-4.72 (m, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.28 (s, 2H), 3.21-3.18 (m, 2H), 2.40 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 170.9, 86.5, 75.0, 60.6, 57.4, 56.1, 42.2, 14.3. HRMS (ESI) calcd for $C_9H_{16}NO_2^+$ $(M + H)^+$ 170.1176, found 170.1177.



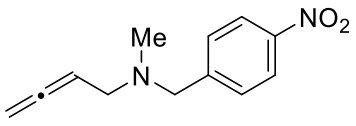
1b

tert-Butyl *N*-(buta-2,3-dien-1-yl)-*N*-methylglycinate (**1b**) was obtained (690 mg, 70% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.14 (m, 1H), 4.74-4.71 (m, 2H), 3.23-3.20 (m, 4H), 2.41 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 170.1, 86.7, 81.1, 75.0, 58.1, 56.0, 42.1, 28.3. HRMS (ESI) calcd for $C_{11}H_{20}NO_2^+$ $(M + H)^+$ 198.1489, found 198.1490.



1c

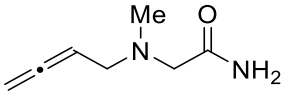
Benzyl *N*-(buta-2,3-dien-1-yl)-*N*-methylglycinate (**1c**) was obtained (833 mg, 72% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 5.19-5.12 (m, 3H), 4.71-4.69 (m, 2H), 3.33 (s, 2H), 3.21-3.18 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 170.7, 135.8, 128.6, 128.4, 128.3, 86.5, 75.0, 66.3, 57.3, 56.1, 42.2. HRMS (ESI) calcd for $C_{14}H_{18}NO_2^+$ $(M + H)^+$ 232.1332, found 232.1333.



1d

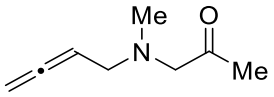
N-Methyl-*N*-(4-nitrobenzyl)buta-2,3-dien-1-amine (**1d**) was obtained (949 mg, 87% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 5.23-5.16

(m, 1H), 4.76-4.73 (m, 2H), 3.64 (s, 2H), 3.14-3.11 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 147.2, 147.1, 129.5, 123.6, 86.6, 75.2, 60.2, 56.2, 42.1. HRMS (ESI) calcd for $C_{12}H_{15}N_2O_2^+$ $(M + H)^+$ 219.1128, found 219.1127.



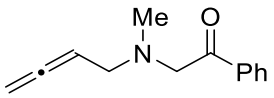
1e

2-(Buta-2,3-dien-1-yl(methyl)amino)acetamide (**1e**) was obtained (406 mg, 58% yield) as a yellow solid. m.p. 50-52 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, br, 1H), 6.38 (s, br, 1H), 5.16-5.09 (m, 1H), 4.78-4.75 (m, 2H), 3.14-3.11 (m, 2H), 3.06 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 174.5, 86.6, 75.5, 59.9, 56.6, 43.0. HRMS (ESI) calcd for $C_7H_{13}N_2O^+$ $(M + H)^+$ 141.1022, found 141.1024.



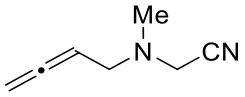
1f

1-(Buta-2,3-dien-1-yl(methyl)amino)propan-2-one (**1f**) was obtained (313 mg, 45% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20-5.13 (m, 1H), 4.75-4.72 (m, 2H), 3.25 (s, 2H), 3.14-3.11 (m, 2H), 2.33 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 207.4, 86.6, 75.1, 66.3, 56.7, 42.7, 27.8. HRMS (ESI) calcd for $C_8H_{14}NO^+$ $(M + H)^+$ 140.1070, found 140.1066.



1g

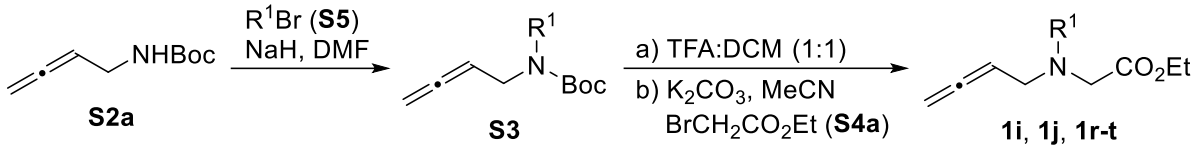
2-(Buta-2,3-dien-1-yl(methyl)amino)-1-phenylethan-1-one (**1g**) was obtained (483 mg, 48% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 5.27-5.20 (m, 1H), 4.74-4.72 (m, 2H), 3.90 (s, 2H), 3.28-3.25 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 197.1, 136.1, 133.4, 128.7, 128.2, 86.4, 75.1, 62.2, 56.7, 42.6. HRMS (ESI) calcd for $C_{13}H_{16}NO^+$ $(M + H)^+$ 202.1226, found 202.1226.

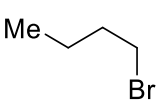
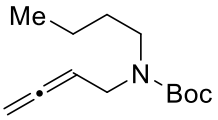
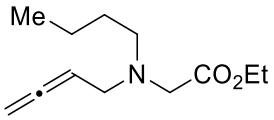
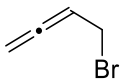
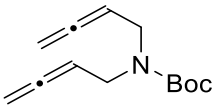
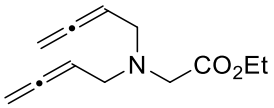
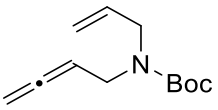
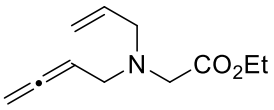
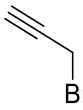
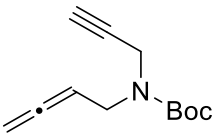
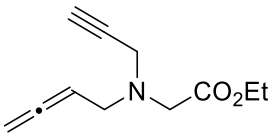
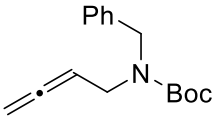
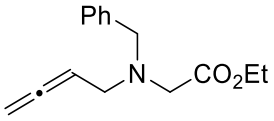


1h

2-(Buta-2,3-dien-1-yl(methyl)amino)acetonitrile (**1h**) was obtained (519 mg, 85% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14-5.07 (m, 1H), 4.83-4.80 (m, 2H), 3.60 (s, 2H), 3.13-3.12 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 114.6, 86.4, 76.0, 54.9, 44.1, 42.0. HRMS (ESI) calcd for $C_7H_{11}N_2^+$ $(M + H)^+$ 123.0917, found 123.0916.

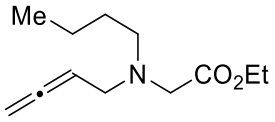
(3) Method B



Entry	S5	S3	1i, 1j, 1r-t
1	 **S5a**	 **S3b**	 **1i**
2	 **S5b**	 **S3c**	 **1j**
3	 **S5c**	 **S3d**	 **1r**
4	 **S5d**	 **S3e**	 **1s**
5	 **S5e**	 **S3f**	 **1t**

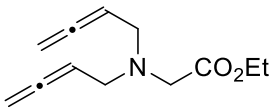
To a solution of *tert*-butyl buta-2,3-dien-1-ylcarbamate (**S2a**) (846 mg, 5.0 mmol) in *N*,*N*-dimethylformamide (10 mL) at 0 ℃ was added portionwise NaH (240 mg, 6.0 mmol, 60% dispersion in mineral oil). The mixture was stirred at room temperature for 30 minutes, cooled to 0 ℃, and added dropwise alkyl halide **S5** (5.0 mmol). The mixture was stirred at room temperature for 8 hours, quenched with saturated aqueous ammonium chloride (10 mL), extracted with diethyl ether (3 × 10 mL), washed with brine (20 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Crude compound **S3** was used in the next step without purification.

To a solution of crude compound **S3** in dichloromethane (2.0 mL) at 0 ℃ was added trifluoroacetic acid (2.0 mL). The mixture was stirred at 0 ℃ for 30 minutes, and concentrated under reduced pressure. The residue was dissolved in acetonitrile (10.0 mL), cooled to 0 ℃, and added portionwise K_2CO_3 (2.07 g, 15.0 mmol). The mixture was stirred at 0 ℃ for 10 minutes, and added ethyl bromoacetate (**S4a**) (835 mg, 5.0 mmol). The mixture was stirred at room temperature for 8 hours, diluted with water (10 mL), extracted with ethyl acetate (3 × 10 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (3:1) as the eluent, to give 2,3-allenylamine **1i**, **1j**, or **1r**-**1t**.



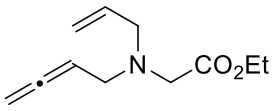
1i

Ethyl *N*-(buta-2,3-dien-1-yl)-*N*-butylglycinate (**1i**) was obtained (687 mg, 65% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19-5.12 (m, 1H), 4.72-4.71 (m, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.36 (s, 2H), 3.32-3.31 (m, 2H), 2.63-2.59 (m, 2H), 1.48-1.46 (m, 2H), 1.33-1.29 (m, 5H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 171.4, 86.4, 74.9, 60.6, 54.7, 53.9, 53.4, 29.5, 20.6, 14.4, 14.1. HRMS (ESI) calcd for $C_{12}H_{22}NO_2^+$ $(M + H)^+$ 212.1645, found 212.1644.



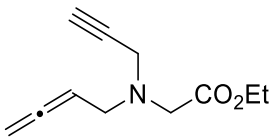
1j

Ethyl di(buta-2,3-dien-1-yl)glycinate (**1j**) was obtained (808 mg, 78% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19-5.12 (m, 2H), 4.74-4.71 (m, 4H), 4.18 (q, J = 7.2 Hz, 2H), 3.39 (s, 2H), 3.34-3.31 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 171.1, 86.4, 74.9, 60.7, 54.0, 53.1, 14.4. HRMS (ESI) calcd for $C_{12}H_{18}NO_2^+$ $(M + H)^+$ 208.1332, found 208.1331.



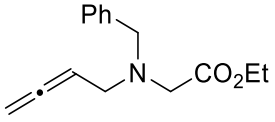
1r

Ethyl *N*-allyl-*N*-(buta-2,3-dien-1-yl)glycinate (**1r**) was obtained (859 mg, 88% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92-5.82 (m, 1H), 5.18-5.15 (m, 3H), 4.73-4.71 (m, 2H), 4.10 (q, J = 7.2 Hz, 2H), 3.28 (s, 2H), 3.33-3.26 (m, 4H), 1.20 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 171.3, 135.1, 118.5, 86.4, 75.0, 60.6, 57.2, 54.0, 53.2, 14.4. HRMS (ESI) calcd for $C_{11}H_{18}NO_2^+$ $(M + H)^+$ 196.1332, found 196.1334.



1s

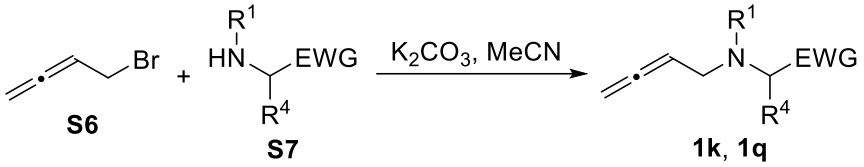
Ethyl *N*-(buta-2,3-dien-1-yl)-*N*-(prop-2-yn-1-yl)glycinate (**1s**) was obtained (841 mg, 87% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24-5.17 (m, 1H), 4.79-4.76 (m, 2H), 4.21 (q, J = 7.2 Hz, 2H), 3.63 (d, J = 2.4 Hz, 2H), 3.45 (s, 2H), 3.30-3.28 (m, 2H), 2.26 (t, J = 2.4 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 170.7, 86.9, 78.1, 75.4, 74.0, 60.9, 53.7, 53.3, 42.7, 14.4. HRMS (ESI) calcd for $C_{11}H_{16}NO_2^+$ $(M + H)^+$ 194.1176, found 194.1179.



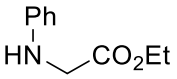
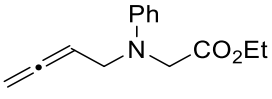
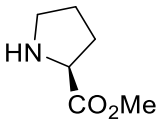
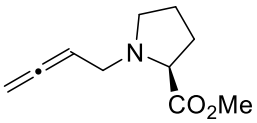
1t

Ethyl *N*-benzyl-*N*-(buta-2,3-dien-1-yl)glycinate (**1t**) was obtained (1.09 g, 89% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.22 (m, 5H), 5.21-5.14 (m, 1H), 4.73-4.71 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.81 (s, 2H), 3.35 (s, 2H), 3.33-3.30 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 209.8, 171.4, 138.5, 129.2, 128.4, 127.3, 86.9, 75.1, 60.4, 57.6, 53.9, 52.8, 14.4. HRMS (ESI) calcd for $C_{15}H_{20}NO_2^+$ $(M + H)^+$ 246.1489, found 246.1490.

(4) Method C

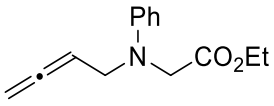


S6 **S7** **1k**, **1q**

Entry	**S7**	**1k**, **1q**
1	 **S7a**	 **1k**
2	 **S7b**	 **1q**

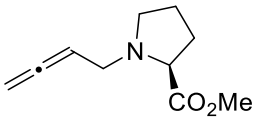
4-Bromobuta-1,2-diene (**S6**) was prepared according to the literature.[2]

To a solution of amine **S7** (5.0 mmol) in acetonitrile (10 mL) were added K_2CO_3 (830 mg, 6.0 mmol) and 4-bromobuta-1,2-diene (**S6**) (665 mg, 5.0 mmol). The mixture was stirred at room temperature for 8 hours, diluted with water (10 mL), extracted with ethyl acetate (3 × 10 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (10:1 to 3:1) as the eluent, to give 2,3-allenylamine **1k** or **1q**.



1k

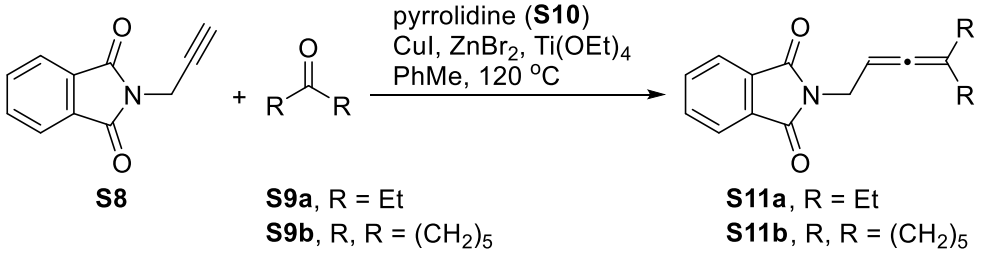
Ethyl *N*-(buta-2,3-dien-1-yl)-*N*-phenylglycinate (**1k**) was obtained (508 mg, 44% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.20 (m, 2H), 6.76-6.71 (m, 1H), 6.70-6.68 (m, 2H), 5.26-5.21 (m, 1H), 4.78-4.77 (m, 2H), 4.20 (q, J = 7.2 Hz, 2H), 4.07-4.04 (m, 4H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 171.3, 147.9, 129.3, 117.8, 112.9, 86.9, 76.4, 61.1, 52.6, 50.7, 14.4. HRMS (ESI) calcd for $C_{14}H_{18}NO_2^+$ $(M + H)^+$ 232.1332, found 232.1332.

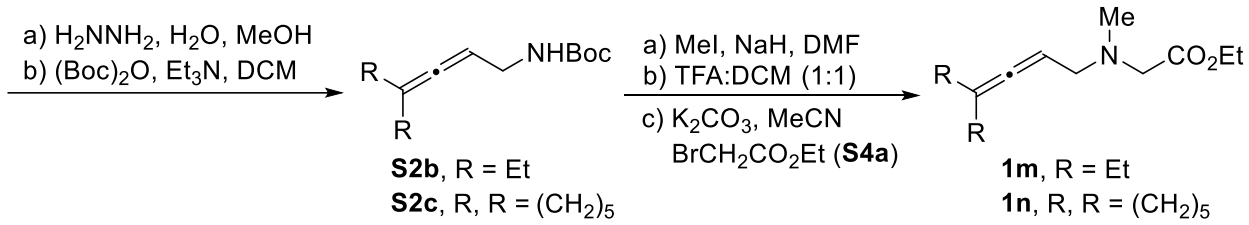


1q

Methyl buta-2,3-dien-1-yl-*L*-prolinate (**1q**) was obtained (589 mg, 65% yield) as a yellow oil. >99% ee. $[\alpha]_D^{20}$ = -109 (*c* = 1.70, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22-5.19 (m, 1H), 4.73-4.70 (m, 2H), 3.73 (s, 3H), 3.36-3.16 (m, 4H), 2.50-2.48 (m, 1H), 2.16-2.12 (m, 1H), 1.98-1.92 (m, 2H), 1.83-1.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 174.7, 86.7, 75.1, 64.7, 53.3, 53.1, 52.0, 29.7, 23.3. HRMS (ESI) calcd for $C_{10}H_{16}NO_2^+$ $(M + H)^+$ 182.1176, found 182.1174.

(5) Method D[3]



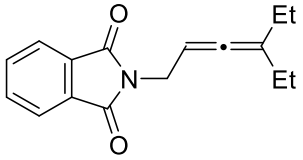


$ZnBr_2$ (901 mg, 4.0 mmol) was added to a dried Schlenk tube with a stirring bar under nitrogen atmosphere and dried under vacuum with a heating gun. After cooling to room temperature under nitrogen atmosphere, toluene (15 mL), CuI (95.2 mg, 0.50 mmol), $Ti(OEt)_4$ (2.28 g, 10 mmol), 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (**S8**) (926 mg, 5.0 mmol), ketone **S9** (8.0 mmol), and pyrrolidine (**S10**) (392 mg, 5.5 mmol) were added sequentially. The Schlenk tube was then sealed by screwing the polytetrafluoroethylene plug tightly and placed in a pre-heated oil bath of 120 ℃ with vigorous stirring for 12 hours. After cooling to room temperature, the crude reaction mixture was filtered through a short pad of basic aluminum oxide eluted with acetone (60 mL). After evaporation, the residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (10:1) as the eluent, to give protected 2,3-allenylamine **S11**.

To a solution of protected 2,3-allenylamine **S11** (2.5 mmol) in methanol (15 mL) was added hydrazine monohydrate (2.0 mL, 85%). The mixture was stirred at 80 ℃ (oil bath) for 1 hour, cooled to room temperature, filtered, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (10 mL), cooled to 0 ℃, and added triethylamine (304 mg, 3.0 mmol) and *tert*-butyldicarbonate (655 mg, 3.0 mmol). The mixture was stirred at room temperature for 2 hours, concentrated under reduced pressure, and the residue was purified by silica gel column chromatography, using petroleum ether and ethyl acetate (10:1) as the eluent, to give Boc-protected 2,3-allenylamine **S2**.

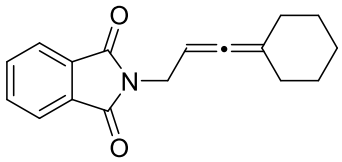
To a solution of Boc-protected 2,3-allenylamine **S2** (2.5 mmol) in dry *N*,*N*-dimethylformamide

(10 mL) at 0 ℃ was added portionwise NaH (120 mg, 3.0 mmol, 60% dispersion in mineral oil). The mixture was stirred at room temperature for 30 minutes, cooled to 0 ℃, and added dropwise methyl iodide (426 mg, 3.0 mmol). The mixture was stirred at room temperature for 12 hours, quenched with saturated aqueous ammonium chloride (10 mL), extracted by diethyl ether (3 × 10 mL), washed with brine (20 mL), dried over with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (1.0 mL), cooled to 0 ℃, and added trifluoroacetic acid (1.0 mL). The mixture was stirred at 0 ℃ for 30 minutes and concentrated under reduced pressure. The residue was dissolved in acetonitrile (5.0 mL), cooled to 0 ℃, and added portionwise K_2CO_3 (1.04 g, 7.5 mmol). The mixture was stirred at 0 ℃ for 10 minutes, and added ethyl bromoacetate (**S4a**) (420 mg, 2.5 mmol). The mixture was stirred at room temperature for 8 hours, diluted with water (5.0 mL), extracted with ethyl acetate (3 × 5.0 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (3:1) as the eluent, to give 2,3-allenylamine **1m** or **1n**.



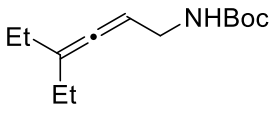
S11a

2-(4-Ethylhexa-2,3-dien-1-yl)isoindoline-1,3-dione (**S11a**) was obtained (702 mg, 55% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.83 (m, 2H), 7.73-7.69 (m, 2H), 5.29-5.24 (m, 1H), 4.27 (d, J = 5.0 Hz, 2H), 1.89-1.79 (m, 4H), 0.88 (t, J = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1, 168.0, 134.0, 132.4, 123.3, 112.3, 88.8, 37.3, 25.5, 12.1. HRMS (ESI) calcd for $C_{16}H_{18}NO_2^+$ $(M + H)^+$ 256.1332, found 256.1332.



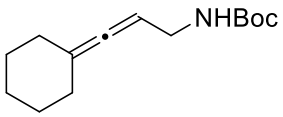
S11b

2-(3-Cyclohexylideneallyl)isoindoline-1,3-dione (**S11b**) was obtained (628 mg, 47% yield) as a white solid. The spectral data of **S11b** are in agreement with those reported in the literature.[3]



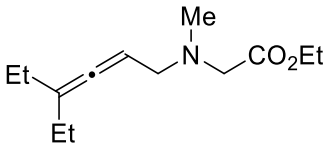
S2b

tert-Butyl (4-ethylhexa-2,3-dien-1-yl)carbamate (**S2b**) was obtained (558 mg, 99% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24-5.22 (m, 1H), 4.56 (s, br, 1H), 3.71-3.65 (m, 2H), 2.00-1.95 (m, 4H), 1.45 (s, 9H), 0.99 (t, J = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 155.9, 111.6, 91.2, 79.3, 39.9, 28.5, 25.7, 12.5. HRMS (ESI) calcd for $C_{13}H_{24}NO_2^+$ $(M + H)^+$ 226.1802, found 226.1797.



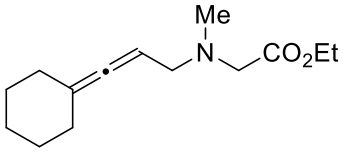
S2c

tert-Butyl (3-cyclohexylideneallyl)carbamate (**S2c**) was obtained (587 mg, 99% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04-5.01 (m, 1H), 4.60 (s, br, 1H), 3.69-3.64 (m, 2H), 2.14-2.09 (m, 4H), 1.62-1.50 (m, 6H), 1.45 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 155.9, 105.9, 87.0, 79.3, 39.9, 31.7, 28.6, 27.6, 26.2. HRMS (ESI) calcd for $C_{14}H_{24}NO_2^+$ $(M + H)^+$ 238.1802, found 238.1800.



1m

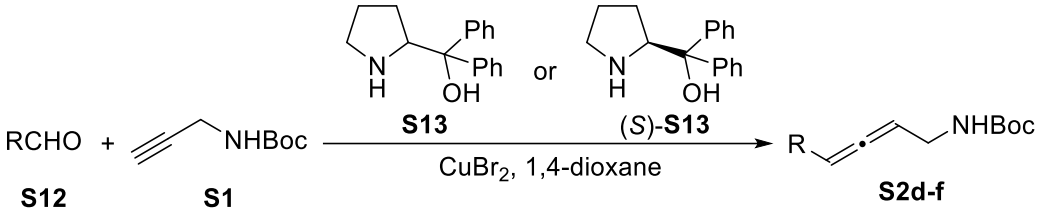
Ethyl *N*-(4-ethylhexa-2,3-dien-1-yl)-*N*-methylglycinate (**1m**) was obtained (484 mg, 86% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23-5.18 (m, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.32 (s, 2H), 3.18 (d, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.97-1.95 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 171.0, 108.5, 89.4, 60.7, 57.7, 57.4, 42.3, 25.7, 14.4, 12.6. HRMS (ESI) calcd for $C_{13}H_{24}NO_2^+$ $(M + H)^+$ 226.1802, found 226.1804.

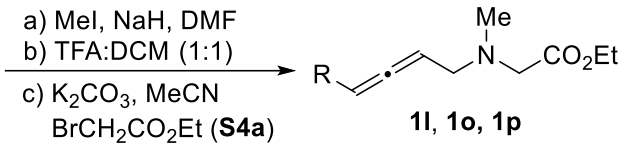


1n

Ethyl *N*-(3-cyclohexylideneallyl)-*N*-methylglycinate (**1n**) was obtained (498 mg, 84% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02-4.97 (m, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.29 (s, 2H), 3.14 (d, J = 7.2 Hz, 2H), 2.40 (s, 3H), 2.12-2.09 (m, 4H), 1.60-1.52 (m, 6H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 171.1, 102.5, 84.8, 60.7, 57.6, 57.3, 42.3, 31.5, 27.4, 26.2, 14.4. HRMS (ESI) calcd for $C_{14}H_{24}NO_2^+$ $(M + H)^+$ 238.1802, found 238.1805.

(6) Condition E[4]



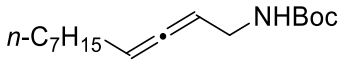


Entry	S12	S13 or (*S*)-S13	S2d-f	1
1	*n*-C_7H_{15}CHO **S12a**	**S13**	*n*-C_7H_{15} NHBoc **S2d**	*n*-C_7H_{15} Me N CO_2Et **1l**
2	CHO **S12b**	(*S*)-**S13**	H NHBoc H **S2e**	H Me N CO_2Et H **1o**
3	PhCHO **S12c**	(*S*)-**S13**	Ph H NHBoc H **S2f**	Ph H Me N CO_2Et H **1p**

To a dried Schlenk tube with a stirring bar under nitrogen atmosphere were added $CuBr_2$ (223 mg, 1.0 mmol), β-amino alcohol **S13** or (*S*)-**S13** (2.54 g, 10.0 mmol), 1,4-dioxane (20 mL), aldehyde **S12** (15.0 mmol), and *tert*-butyl prop-2-yn-1-ylcarbamate (**S1**) (2.33 g, 15.0 mmol). The Schlenk tube was then sealed by screwing the polytetrafluoroethylene plug tightly. The mixture was stirred in an oil bath preheated at 130 ℃ for 12 hours, cooled to room temperature, diluted with diethyl ether (100 mL), washed with hydrochloric acid (3.0 M, 50 mL), extracted with diethyl ether (100 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (10:1) as the eluent, to give Boc-protected 2,3-allenylamine **S2d-f**.

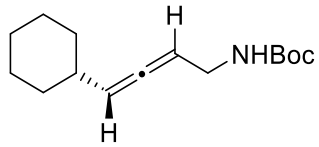
To a solution of Boc-protected 2,3-allenylamine **S2d-f** (5.0 mmol) in dry *N*,*N*-dimethylformamide (10 mL) at 0 ℃ was added portionwise NaH (240 mg, 6.0 mmol, 60% dispersion in mineral oil). The mixture was stirred at room temperature for 30 minutes, cooled to 0 °C, and added dropwise methyl iodine (852 mg, 6.0 mmol). The mixture was stirred at room temperature for 12 hours, quenched with saturated aqueous ammonium chloride (10 mL), extracted by diethyl ether (3 × 10 mL), washed with brine, dried over with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (2.0 mL), cooled to 0 ℃, and added trifluoroacetic acid (2.0 mL).

The mixture was stirred at 0 ℃ for 30 minutes, and concentrated under reduced pressure. The residue was dissolved in acetonitrile (10 mL), cooled to 0 ℃, and added portionwise K_2CO_3 (2.08 g, 15.0 mmol). The mixture was stirred at 0 ℃ for 10 minutes, and added ethyl bromoacetate (**S4a**) (840 mg, 5.0 mmol). The mixture was stirred at room temperature for 8 hours, diluted with water (10 mL), extracted with ethyl acetate (3 × 10 mL), washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (3:1) as the eluent, to give 2,3-allenylamine **1l**, **1o**, or **1p**.



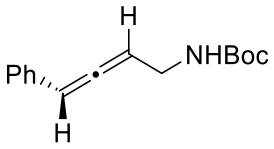
S2d

tert-Butyl undeca-2,3-dien-1-ylcarbamate (**S2d**) was obtained (1.74 g, 65% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28-5.23 (m, 1H), 5.18-5.13 (m, 1H), 4.60 (s, br, 1H), 3.71-3.67 (m, 2H), 2.02-1.98 (m, 2H), 1.45 (s, 9H), 1.41-1.37 (m, 2H), 1.35-1.25 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 155.9, 94.3, 89.2, 39.5, 32.0, 29.4, 29.3, 29.2, 28.8, 28.5, 22.8, 14.2. HRMS (ESI) calcd for $C_{16}H_{29}NO_2Na^+$ $(M + Na)^+$ 290.2091, found 290.2091.



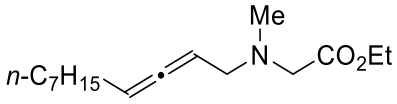
S2e

tert-Butyl (*R*)-(4-cyclohexylbuta-2,3-dien-1-yl)carbamate (**S2e**) was obtained (1.68 g, 67% yield) as a yellow solid. m.p. 61-63 ºC. >99% ee (see below for the ee determination). $[\alpha]_D^{20}$ = -11.4 (c = 2.10, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.27-5.24 (m, 1H), 5.22-5.18 (m, 1H), 4.60 (s, br, 1H), 3.72-3.65 (m, 2H), 2.01-1.95 (m, 1H), 1.76-1.70 (m, 4H), 1.65-1.62 (m, 1H), 1.45 (s, 9H), 1.32-1.04 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 155.9, 100.3, 90.2, 37.2, 33.2, 33.1, 28.6, 26.2, 26.1. HRMS (ESI) calcd for $C_{15}H_{25}NO_2Na^+$ $(M + Na)^+$ 274.1778, found 274.1777.



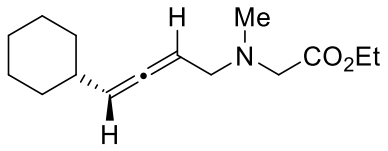
S2f

tert-Butyl (*R*)-(4-phenylbuta-2,3-dien-1-yl)carbamate (**S2f**) was obtained (1.30 g, 53% yield) as a yellow oil. 98% ee (see below for the ee determination). $[\alpha]_D^{20}$ = -250 (c = 0.50, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.27 (m, 4H), 7.23-7.18 (m, 1H), 6.39-6.27 (m, 1H), 5.66-5.62 (m, 1H), 4.74 (s, br, 1H), 3.90-3.78 (m, 2H), 1.41 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.5, 155.8, 134.0, 128.7, 127.3, 127.0, 97.5, 93.6, 79.6, 39.2, 28.5. HRMS (ESI) calcd for $C_{15}H_{19}NO_2Na^+$ $(M + Na)^+$ 268.1308, found 268.1305.



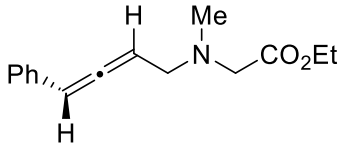
1l

Ethyl *N*-methyl-*N*-(undeca-2,3-dien-1-yl)glycinate (**1l**) was obtained (896 mg, 67% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16-5.09 (m, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.29 (s, 2H), 3.19-3.17 (m, 2H), 2.41 (s, 3H), 2.02-1.96 (m, 2H), 1.44-1.32 (m, 2H), 1.30-1.26 (m, 11H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 170.9, 91.4, 87.1, 60.7, 57.4, 57.0, 42.3, 32.0, 29.3, 29.2, 29.1, 28.8, 22.8, 14.4, 14.2. HRMS (ESI) calcd for $C_{16}H_{30}NO_2^+$ $(M + H)^+$ 268.2271, found 268.2273.



1o

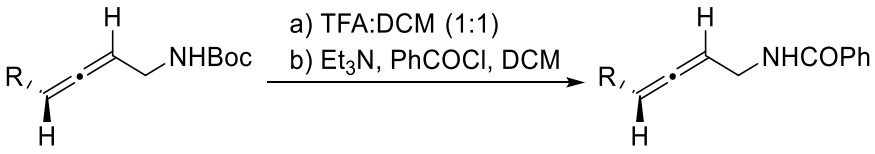
Ethyl (*R*)-*N*-(4-cyclohexylbuta-2,3-dien-1-yl)-*N*-methylglycinate (**1o**) was obtained (930 mg, 74% yield) as a yellow oil. >99% ee (see below for the ee determination). $[\alpha]_D^{20}$ = -90.0 (c = 2.00, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20-5.11 (m, 2H), 4.22-4.16 (m, 2H), 3.29 (d, J = 2.0 Hz, 2H), 3.18-3.16 (m, 2H), 2.40 (s, 3H), 2.01-1.93 (m, 1H), 1.76-1.69 (m, 4H), 1.65-1.61 (m, 1H), 1.30-1.03 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 171.0, 97.3, 88.2, 60.6, 57.4, 57.2, 42.4, 37.2, 33.2, 33.1, 26.2, 26.1, 14.3. HRMS (ESI) calcd for $C_{15}H_{26}NO_2^+$ $(M + H)^+$ 252.1958, found 252.1955.



1p

Ethyl (*R*)-*N*-methyl-*N*-(4-phenylbuta-2,3-dien-1-yl)glycinate (**1p**) was obtained (785 mg, 64% yield) as a yellow oil. 98% ee (see below for the ee determination). $[\alpha]_D^{20}$ = -269 (c = 1.80, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 4H), 7.22-7.18 (m, 1H), 6.21-6.18 (m, 1H), 5.62 (q, J = 6.8 Hz, 1H), 4.21-4.15 (m, 2H), 3.35-3.32 (m, 4H), 2.47 (s, 3H), 1.26 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 170.8, 134.2, 128.8, 127.1, 126.9, 95.0, 91.3, 60.8, 57.5, 56.3, 42.4, 14.4. HRMS (ESI) calcd for $C_{15}H_{20}NO_2^+$ $(M + H)^+$ 246.1489, found 246.1487.

(7) Determination of the ee of compounds **S2e** and **S2f**

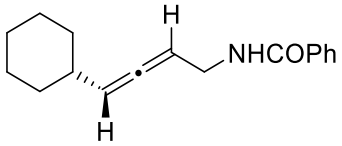


S2e, R = Cy
S2f, R = Ph

S14a, R = Cy
S14b, R = Ph

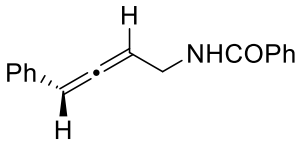
To a solution of Boc-protected 2,3-allenylamine **S2e** or **S2f** (0.20 mmol) in dichloromethane (0.50

mL) at 0 ℃ was added trifluoroacetic acid (0.50 mL). The mixture was stirred at 0 ℃ for 30 minutes, and concentrated under reduced pressure. The residue was dissolved in dichloromethane (1.0 mL), cooled to 0 ℃, and added triethylamine (60.1 mg, 0.60 mmol) and benzoyl chloride (33.7 mg, 0.24 mmol). The mixture was stirred at room temperature for 1 hour, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using petroleum ether and ethyl acetate (10:1) as the eluent, to give amide **S14a** or **S14b**.



S14a

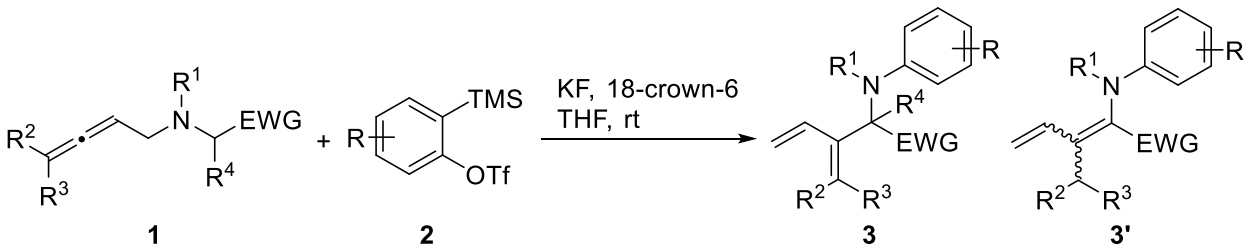
(*R*)-*N*-(4-Cyclohexylbuta-2,3-dien-1-yl)benzamide (**S14a**) was obtained (49.0 mg, 96% yield) as a yellow oil. The ee value was determined to be >99% by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (2:98), 1.0 mL/min, λ = 254 nm, tR (major) = 42.4 min, tR (minor) = 37.4 min]. $[\alpha]_D^{20}$ = -48.4 (*c* = 1.50, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.51-7.47 (m, 1H), 7.44-7.41 (m, 2H), 6.37 (s, br, 1H), 5.36-5.31 (m, 2H), 4.07-3.97 (m, 2H), 2.04-1.96 (m, 1H), 1.75-1.68 (m, 4H), 1.64-1.60 (m, 1H), 1.30-1.22 (m, 2H), 1.18-1.02 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.0, 167.3, 134.6, 131.5, 128.6, 126.9, 100.8, 89.5, 38.4, 37.1, 33.1, 33.0, 26.1, 26.0, 25.9. HRMS (ESI) calcd for $C_{17}H_{22}NO^+$ $(M + H)^+$ 256.1696, found 256.1693.



S14b

(*R*)-*N*-(4-Phenylbuta-2,3-dien-1-yl)benzamide (**S14b**) was obtained (46.4 mg, 93% yield) as a yellow solid. m.p. 91-93 ºC. The ee value was determined to be 98% by chiral stationary phase HPLC analysis [Daicel Chiralpak AD-H, isopropanol/hexane (15:85), 2.0 mL/min, λ = 254 nm, tR (major) = 5.2 min, tR (minor) = 4.7 min]. $[\alpha]_D^{20}$ = -210 (*c* = 2.30, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.0 Hz, 2H), 7.47-7.44 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.32-7.29 (m, 4H), 7.24-7.19 (m, 1H), 6.42 (s, br, 1H), 6.35-6.32 (m, 1H), 5.80-5.76 (m, 1H), 4.18-4.16 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 167.6, 134.6, 133.8, 131.6, 128.8, 128.7, 127.5, 127.0, 126.9, 97.9, 93.0, 38.4. HRMS (ESI) calcd for $C_{17}H_{16}NO^+$ $(M + H)^+$ 250.1226, found 250.1223.

General procedure for the aryne-mediated [2,3]-sigmatropic rearrangement of tertiary 2,3-allenylamines

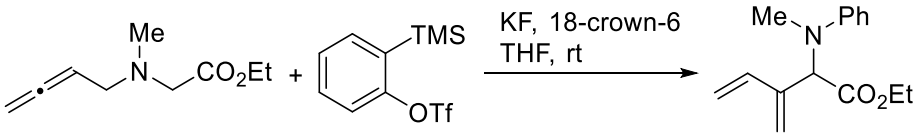


1 **2** **3** **3'**

To a mixture of tertiary 2,3-allenylamine **1** (0.20 mmol), KF (23.3mg, 0.40 mmol), and 18-crown-6 (105 mg, 0.40 mmol) in tetrahydrofuran (1.0 mL) was added 2-(trimethylsilyl)aryl triflate **2** (0.24 mmol). The mixture was stirred at room temperature for 3 hours, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using a mixture of petroleum ether and ethyl acetate (10:1 to 3:1) as the eluent, to give 2-vinylallyamine **3** or 1-amino-1,3-diene **3'**.

The alkene configuration of compounds **3a'**, **3f'**, **3h'**, **3l**, and **3o** was determined by 2D-NOESY spectroscopic analysis.

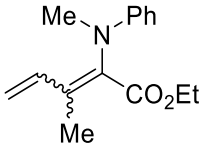
A gram-scale reaction



1a **2a** **3a**

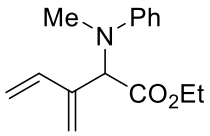
To a mixture of ethyl *N*-(buta-2,3-dien-1-yl)-*N*-methylglycinate (**1a**) (1.02 g, 6.0 mmol), KF (700 mg, 12.0 mmol), and 18-crown-6 (3.17 g, 12.0 mmol) in tetrahydrofuran (30 mL) was added 2-(trimethylsilyl)aryl triflate (**2a**) (2.15 g, 7.2 mmol). The mixture was stirred at room temperature for 3 hours, filtered, washed with ethyl acetate (5.0 mL × 3), and concentrated under reduced pressure. The residue was purified by silica gel chromatography, using ethyl petroleum ether and acetate (10:1) as the eluent, to give ethyl 2-(methyl(phenyl)amino)-3-methylenepent-4-enoate (**3a**) (1.15 g, 78% yield) as a yellow oil.

Analytical data for the products (Tables 1-3 and Scheme 3)



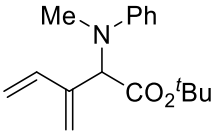
3a'

Ethyl 3-methyl-2-(methyl(phenyl)amino)penta-2,4-dienoate (**3a'**) was obtained (39.3 mg, 80% yield, 53:47 *Z*/*E*) as a yellow oil (Table 1, entry 6). ^{1}H NMR (500 MHz, $CDCl_3$) for the (*Z*)-isomer: δ 7.22-7.18 (m, 2H), 6.82 (dd, J = 17.6, 11.0 Hz, 1H), 6.79-6.74 (m, 1H), 6.66-6.63 (m, 2H), 5.64-5.55 (m, 1H), 5.39-5.36 (m, 1H), 4.07-4.01 (m, 2H), 3.08 (s, 3H), 2.24 (s, 3H), 0.99 (t, J = 7.0 Hz, 3H). ^{1}H NMR (500 MHz, $CDCl_3$) for the (*E*)-isomer: δ 7.43 (dd, J = 17.5, 11.0 Hz, 1H), 7.22-7.18 (m, 2H), 6.79-6.74 (m, 1H), 6.66-6.63 (m, 2H), 5.64-5.55 (m, 1H), 5.39-5.36 (m, 1H), 4.07-4.01 (m, 2H), 3.08 (s, 3H), 1.96 (s, 3H), 1.00 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 166.4, 148.7, 148.3, 142.4, 142.3, 135.5, 135.1, 134.6, 134.5, 129.2, 129.1, 119.9, 118.8, 118.1, 117.9, 113.2, 113.1, 60.6, 60.5, 39.8, 38.9, 14.5, 14.1, 13.8. HRMS (ESI) calcd for $C_{15}H_{20}NO_2^+$ $(M + H)^+$ 246.1489, found 246.1481.



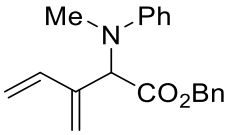
3a

Ethyl 2-(methyl(phenyl)amino)-3-methylenepent-4-enoate (**3a**) was obtained (37.3 mg, 76% yield) as a yellow oil (Table 2, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 6.79-6.75 (m, 3H), 6.39 (dd, J = 17.6, 11.2 Hz, 1H), 5.43 (s, 1H), 5.20-5.15 (m, 3H), 5.07 (d, J = 11.2 Hz, 1H), 4.28-4.15 (m, 2H), 2.90 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 149.2, 141.5, 136.7, 129.3, 119.4, 117.5, 115.4, 112.5, 62.8, 61.0, 33.1, 14.3. HRMS (ESI) calcd for $C_{15}H_{20}NO_2^+$ $(M + H)^+$ 246.1489, found 246.1489.



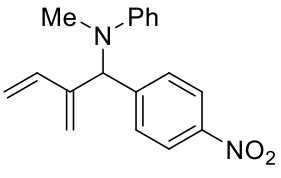
3b

tert-Butyl 2-(methyl(phenyl)amino)-3-methylenepent-4-enoate (**3b**) was obtained (35.5 mg, 65% yield) as a yellow oil (Table 2, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 6.79-6.73 (m, 3H), 6.38 (dd, J = 17.6, 11.2 Hz, 1H), 5.42 (s, 1H), 5.22 (s, 1H), 5.17 (d, J = 17.6 Hz, 1H), 5.08-5.05 (m, 2H), 2.89 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 149.5, 141.9, 137.1, 129.4, 119.4, 117.3, 115.4, 112.7, 81.9, 63.5, 33.2, 28.2. HRMS (ESI) calcd for $C_{17}H_{24}NO_2^+$ $(M + H)^+$ 274.1802, found 274.1804.



3c

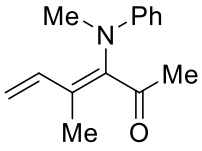
Benzyl 2-(methyl(phenyl)amino)-3-methylenepent-4-enoate (**3c**) was obtained (44.9 mg, 73% yield) as a yellow oil (Table 2, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 5H), 7.26-7.22 (m, 2H), 6.79-6.75 (m, 3H), 6.36 (dd, J = 17.6, 11.2 Hz, 1H), 5.38 (s, 1H), 5.26 (s, 1H), 5.22-5.14 (m, 3H), 5.07-5.04 (m, 2H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 149.1, 141.3, 136.8, 135.6, 129.5, 128.7, 128.5, 128.4, 119.8, 117.8, 115.6, 112.8, 66.8, 63.0, 33.3. HRMS (ESI) calcd for $C_{20}H_{22}NO_2^+$ $(M + H)^+$ 308.1645, found 308.1644.



3d

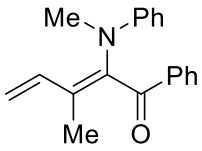
N-Methyl-*N*-(2-methylene-1-(4-nitrophenyl)but-3-en-1-yl)aniline (**3d**) was obtained (28.3 mg, 48% yield) as a yellow oil (Table 2, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.17 (m, 2H), 7.43-7.41

(m, 2H), 7.25-7.20 (m, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.49 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.72 (s, 1H), 5.45 (s, 1H), 5.10-5.02 (m, 2H), 4.84 (s, 1H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 148.3, 147.3, 145.0, 137.6, 129.4, 129.3, 123.9, 121.0, 117.5, 115.6, 112.6, 63.6, 33.9. HRMS (ESI) calcd for $C_{18}H_{19}N_2O_2^+$ $(M + H)^+$ 295.1441, found 295.1443.



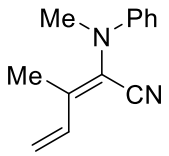
3f'

(*Z*)-4-Methyl-3-(methyl(phenyl)amino)hexa-3,5-dien-2-one (**3f'**) was obtained (21.1 mg, 49% yield, >99:1 *Z*/*E*) as a yellow oil (Table 2, entry 6). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.22 (m, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 6.57 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.67 (d, *J* = 17.5 Hz, 1H), 5.43 (d, *J* = 11.0 Hz, 1H), 3.17 (s, 3H), 2.19 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.2, 147.7, 141.0, 140.8, 135.6, 129.6, 121.2, 118.0, 112.5, 39.6, 29.1, 13.9. HRMS (ESI) calcd for $C_{14}H_{18}NO^+$ $(M + H)^+$ 216.1383, found 216.1382.



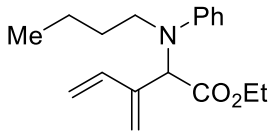
3g'

(*Z*)-3-Methyl-2-(methyl(phenyl)amino)-1-phenylpenta-2,4-dien-1-one (**3g'**) was obtained (24.4 mg, 44% yield, >99:1 *Z*/*E*) as a yellow oil (Table 2, entry 7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.47-7.44 (m, 1H), 7.36-7.32 (m, 2H), 7.16-7.12 (m, 2H), 6.78-6.66 (m, 4H), 5.56 (d, *J* = 17.6 Hz, 1H), 5.37 (d, *J* = 11.6 Hz, 1H), 3.14 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 147.6, 141.0, 139.2, 136.2, 135.4, 132.5, 129.1, 128.5, 128.4, 118.6, 118.5, 114.3, 40.7, 14.9. HRMS (ESI) calcd for $C_{19}H_{20}NO^+$ $(M + H)^+$ 278.1539, found 278.1539.



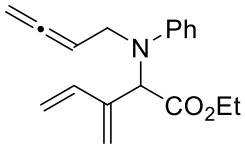
3h'

(*E*)-3-Methyl-2-(methyl(phenyl)amino)penta-2,4-dienenitrile (**3h'**) was obtained (36.1 mg, 91% yield, 25:75 *Z*/*E*) as a yellow oil (Table 2, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$) for the (*E*)-isomer: δ 7.30-7.27 (m, 2H), 7.04 (dd, *J* = 17.2, 10.8 Hz, 1H), 6.91-6.87 (m, 1H), 6.75-6.73 (m, 2H), 5.69 (d, *J* = 17.2 Hz, 1H), 5.55 (d, *J* = 10.8 Hz, 1H), 3.11 (s, 3H), 1.91 (s, 3H). ^{1}H NMR (400 MHz, $CDCl_3$) for the (*Z*)-isomer: δ 7.30-7.27 (m, 2H), 6.91-6.87 (m, 1H), 6.82 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.75-6.73 (m, 2H), 5.68- 5.64 (m, 1H), 5.46 (d, *J* = 10.8 Hz, 1H), 3.08 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.6, 146.9, 146.5, 134.1, 131.9, 129.5, 129.4, 122.1, 121.6, 119.9, 119.8, 117.9, 117.3, 116.1, 115.4, 114.4, 114.3, 38.7, 38.3, 15.6, 13.0. HRMS (ESI) calcd for $C_{13}H_{14}N_2Na^+$ $(M + Na)^+$ 221.1049, found 221.1049.



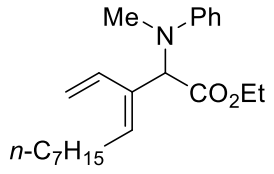
3i

Ethyl 2-(butyl(phenyl)amino)-3-methylenepent-4-enoate (**3i**) was obtained (42.0 mg, 73% yield) as a yellow oil (Table 2, entry 9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.77-6.73 (m, 3H), 6.41 (dd, J = 17.6, 11.2 Hz, 1H), 5.44 (s, 1H), 5.22-5.17 (m, 3H), 5.10 (d, J = 11.2 Hz, 1H), 4.26-4.15 (m, 2H), 3.42-3.20 (m, 2H), 1.62-1.41 (m, 2H), 1.31-1.22 (m, 5H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 148.4, 141.7, 137.2, 129.4, 119.8, 117.5, 115.6, 113.3, 62.9, 61.1, 47.0, 30.3, 20.5, 14.3, 14.0. HRMS (ESI) calcd for $C_{18}H_{26}NO_2^+$ $(M + H)^+$ 288.1958, found 288.1959.



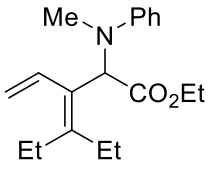
3j

Ethyl 2-(buta-2,3-dien-1-yl(phenyl)amino)-3-methylenepent-4-enoate (**3j**) was obtained (36.8 mg, 65% yield) as a yellow oil (Table 2, entry 10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 6.84-6.77 (m, 3H), 6.40 (dd, J = 17.6, 11.2 Hz, 1H), 5.46 (s, 1H), 5.24-5.19 (m, 3H), 5.16-5.11 (m, 2H), 4.73-4.70 (m, 2H), 4.27-4.09 (m, 3H), 4.00-3.93 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 172.0, 148.1, 141.5, 136.8, 129.3, 120.1, 118.2, 115.7, 113.7, 89.3, 76.0, 62.6, 61.3, 46.2, 14.3. HRMS (ESI) calcd for $C_{18}H_{22}NO_2^+$ $(M + H)^+$ 284.1645, found 284.1645.



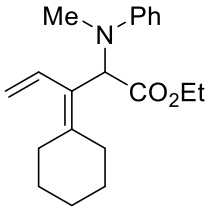
3l

Ethyl (*E*)-2-(methyl(phenyl)amino)-3-vinylundec-3-enoate (**3l**) was obtained (61.8 mg, 90% yield, 10:90 *Z*/*E*) as a yellow oil (Table 2, entry 12). ^{1}H NMR (400 MHz, $CDCl_3$) for the (*E*)-isomer: δ 7.26-7.22 (m, 2H), 6.77-6.72 (m, 3H), 6.68 (dd, J = 17.6, 11.2 Hz, 1H), 5.51 (t, J = 7.2 Hz, 1H), 5.22 (s, 1H), 5.11-5.05 (m, 2H), 4.26-4.16 (m, 2H), 2.88 (s, 3H), 2.35-2.21 (m, 2H), 1.47-1.40 (m, 2H), 1.33-1.21 (m, 11H), 0.89 (t, J = 6.8 Hz, 3H). ^{1}H NMR for the (*Z*)-isomer: δ 7.26-7.22 (m, 2H), 6.77-6.72 (m, 3H), 6.28 (dd, J = 17.6, 11.2 Hz, 1H), 5.92 (t, J = 7.6 Hz, 1H), 5.20 (s, 1H), 5.19-5.15 (m, 1H), 4.95 (d, J = 11.2 Hz, 1H), 4.20-4.09 (m, 2H), 2.89 (s, 3H), 2.12-1.99 (m, 2H). 1.47-1.40 (m, 2H), 1.33-1.21 (m, 11H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) for the (*E*)-isomer: δ 172.7, 149.4, 135.2, 132.2, 131.5, 129.4, 117.3, 115.0, 112.5, 63.7, 60.9, 32.8, 31.9, 29.5, 29.3, 29.2, 27.9, 22.8, 14.4, 14.2. Partial ^{13}C NMR for the (*Z*)-isomer: δ 149.6, 138.8, 138.2, 132.8, 129.3, 117.7, 113.1, 112.9, 61.2, 60.7, 34.1, 31.9, 29.4, 28.5, 14.3. HRMS (ESI) calcd for $C_{22}H_{34}NO_2^+$ $(M + H)^+$ 344.2584, found 344.2586.



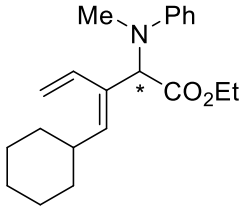
3m

Ethyl 4-ethyl-2-(methyl(phenyl)amino)-3-vinylhex-3-enoate (**3m**) was obtained (38.0 mg, 63% yield) as a yellow oil (Table 2, entry 13). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 2H), 6.76-6.72 (m, 3H), 6.52 (dd, J = 17.6, 11.6 Hz, 1H), 5.24 (s, 1H), 5.22-5.10 (m, 2H), 4.19-4.06 (m, 2H), 2.92 (s, 3H), 2.39-2.20 (m, 2H), 2.13-1.99 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.6 Hz, 3H), 0.98 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 150.5, 149.5, 134.6, 129.3, 126.2, 117.3, 115.8, 112.7, 62.4, 60.9, 34.1, 25.6, 25.4, 14.3, 13.5, 12.4. HRMS (ESI) calcd for $C_{19}H_{28}NO_2^+$ $(M + H)^+$ 302.2115, found 302.2113.



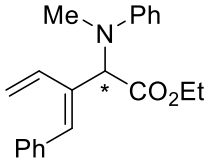
3n

Ethyl 3-cyclohexylidene-2-(methyl(phenyl)amino)pent-4-enoate (**3n**) was obtained (43.3 mg, 69% yield) as a yellow oil (Table 2, entry 14). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 2H), 6.76-6.72 (m, 3H), 6.45 (dd, J = 17.6, 11.2 Hz, 1H), 5.25 (s, 1H), 5.17-5.11 (m, 2H), 4.20-4.06 (m, 2H), 2.93 (s, 3H), 2.56-2.51 (m, 1H), 2.33-2.26 (m, 1H), 2.19-2.13 (m, 1H), 2.08-2.02 (m, 1H), 1.71-1.36 (m, 6H), 1.20 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 149.4, 146.4, 134.6, 129.3, 124.1, 117.3, 116.8, 112.6, 62.4, 60.9, 33.9, 31.9, 31.8, 28.4, 27.9, 26.6, 14.3. HRMS (ESI) calcd for $C_{20}H_{28}NO_2^+$ $(M + H)^+$ 314.2115, found 314.2113.



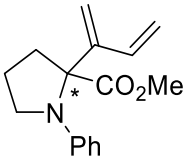
3o

Ethyl (*E*)-3-(cyclohexylmethylene)-2-(methyl(phenyl)amino)pent-4-enoate (**3o**) was obtained (55.7 mg, 85% yield, <1:99 *Z*/*E*, 70% ee) as a yellow oil (Table 2, entry 15). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak OJ, isopropanol/hexane (10:90), 0.8 mL/min, λ = 254 nm, tR (major) = 7.4 min, tR (minor) = 4.7 min]. $[\alpha]_D^{20}$ = +20.4 (c = 0.80, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 2H), 6.78-6.73 (m, 3H), 6.72-6.66 (m, 1H), 5.33 (d, J = 9.2 Hz, 1H), 5.21 (s, 1H), 5.09-5.03 (m, 2H), 4.28-4.13 (m, 2H), 2.87 (s, 3H), 2.59-2.49 (m, 1H), 1.76-1.66 (m, 5H), 1.40-1.04 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 149.4, 140.7, 131.7, 130.5, 129.4, 117.2, 114.9, 112.4, 63.4, 60.8, 36.9, 33.0, 32.8, 32.6, 26.0, 25.8, 25.7, 14.4. HRMS (ESI) calcd for $C_{21}H_{30}NO_2^+$ $(M + H)^+$ 328.2271, found 328.2266.



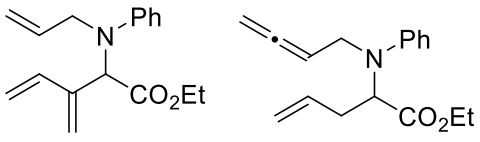
3p

Ethyl (*E*)-3-benzylidene-2-(methyl(phenyl)amino)pent-4-enoate (**3p**) was obtained (47.6 mg, 74% yield, <1:99 *Z/E*, 81% ee) as a yellow oil (Table 2, entry 16). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak OJ, isopropanol/hexane (10:90), 0.8 mL/min, λ = 254 nm, tR (major) = 11.1 min, tR (minor) = 7.4 min]. $[\alpha]_D^{20}$ = +30.3 (*c* = 0.60, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 7H), 6.84-6.76 (m, 4H), 6.59 (s, 1H), 5.40 (s, 1H), 5.25 (d, *J* = 17.6 Hz, 1H), 5.15 (d, *J* = 11.2 Hz, 1H), 4.32-4.20 (m, 2H), 2.98 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 149.3, 136.2, 133.9, 132.7, 132.6, 129.7, 129.5, 128.4, 127.8, 117.7, 116.7, 112.8, 64.2, 61.2, 33.4, 14.4. HRMS (ESI) calcd for $C_{21}H_{24}NO_2^+$ $(M + H)^+$ 322.1802, found 322.1797.



3q

Methyl 2-(buta-1,3-dien-2-yl)-1-phenylpyrrolidine-2-carboxylate (**3q**) was obtained (20.1 mg, 39% yield, 90% ee) as a yellow oil (Table 2, entry 17). The ee value was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak OD, isopropanol/hexane (2:98), 1.0 mL/min, λ = 254 nm, tR (major) = 6.1 min, tR (minor) = 5.3 min]. $[\alpha]_D^{20}$ = -29.4 (*c* = 1.70, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.12 (m, 2H), 6.70-6.66 (m, 1H), 6.64-6.61 (m, 2H), 6.39 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.48 (s, 1H), 5.47-5.42 (m, 1H), 5.10-5.07 (m, 2H), 3.57-3.52 (m, 5H), 2.54-2.47 (m, 1H), 2.32-2.26 (m, 1H), 2.04-1.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 146.1, 145.1, 136.0, 128.7, 117.0, 115.1, 114.7, 113.5, 74.1, 52.3, 50.2, 39.5, 22.8. HRMS (ESI) calcd for $C_{16}H_{19}NO_2Na^+$ $(M + Na)^+$ 280.1308, found 280.1307.

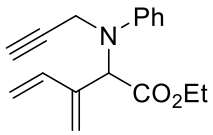


3r **4a**

3r:**4a** = 43:57

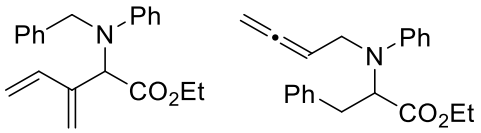
A 43:57 mixture of ethyl 2-(allyl(phenyl)amino)-3-methylenepent-4-enoate (**3r**) and ethyl 2-(buta-2,3-dien-1-yl(phenyl)amino)pent-4-enoate (**4a**) was obtained (41.2 mg, 76% yield) as a yellow oil (Scheme 3a). ^{1}H NMR (400 MHz, $CDCl_3$) for compound **3r**: δ 7.25-7.20 (m, 2H), 6.84-6.75 (m, 3H), 6.40 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.87-5.76 (m, 1H), 5.43 (s, 1H), 4.23-4.12 (m, 2H), 4.10-3.92 (m, 2H), 1.26 (t, *J* = 6.8 Hz, 3H). ^{1}H NMR for compound **4a**: δ 7.25-7.20 (m, 2H), 6.84-6.75 (m, 3H), 5.87-5.76 (m, 1H), 5.25-5.05 (m, 3H), 4.77-4.74 (m, 2H), 4.38 (t, *J* = 7.6 Hz, 1H), 4.23-4.12 (m, 2H), 4.10-3.92 (m, 2H), 2.79-2.72 (m, 1H), 2.68-2.60 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 172.5, 172.0, 148.8, 148.4, 141.5, 137.1, 136.7, 134.4, 129.3, 129.2, 119.9, 118.3,

118.0, 117.9, 115.7, 115.5, 114.6, 113.6, 88.8, 76.4, 62.6, 61.8, 61.2, 61.1, 50.1, 46.7, 34.7, 14.4, 14.3. HRMS (ESI) calcd for $C_{17}H_{22}NO_2^+$ $(M + H)^+$ 272.1645, found 272.1649.



3s

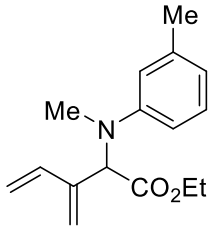
Ethyl 3-methylene-2-(phenyl(prop-2-yn-1-yl)amino)pent-4-enoate (**3s**) was obtained (28.6 mg, 53% yield) as a yellow oil (Scheme 3b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.84 (t, J = 7.2 Hz, 1H), 6.43 (dd, J = 17.6, 11.2 Hz, 1H), 5.48 (s, 1H), 5.28 (d, J = 17.6 Hz, 1H), 5.23-5.20 (m, 2H), 5.13 (d, J = 11.2 Hz, 1H), 4.25-4.17 (m, 3H), 4.07-4.01 (m, 1H), 2.16 (t, J = 2.4 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 147.7, 141.3, 136.5, 129.4, 120.0, 119.1, 116.0, 114.2, 81.1, 71.7, 62.6, 61.3, 37.1, 14.3. HRMS (ESI) calcd for $C_{17}H_{20}NO_2^+$ $(M + H)^+$ 270.1489, found 270.1492.



3t **6a**

3t:**6a** = 80:20

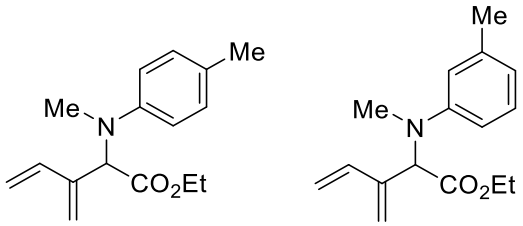
A 80:20 mixture of ethyl 2-(benzyl(phenyl)amino)-3-methylenepent-4-enoate (**3t**) and ethyl *N*-(buta-2,3-dien-1-yl)-*N*-phenylphenylalaninate (**6a**) was obtained (48.2 mg, 75% yield) as a yellow oil (Scheme 3c). ^{1}H NMR (400 MHz, $CDCl_3$) for compound **3t**: δ 7.28-7.14 (m, 7H), 6.78-6.74 (m, 3H), 6.37 (dd, J = 17.6, 11.2 Hz, 1H), 5.43 (s, 1H), 5.39 (s, 1H), 5.32 (d, J = 17.6 Hz, 1H), 5.20 (s, 1H), 5.14 (d, J = 11.2 Hz, 1H), 4.76-4.58 (m, 2H), 4.19-4.06 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H). ^{1}H NMR (400 MHz, $CDCl_3$) for compound **6a**: 7.28-7.14 (m, 7H), 6.78-6.74 (m, 3H), δ 5.08-5.05 (m, 1H), 4.73-4.70 (m, 2H), 4.53 (t, J = 7.6 Hz, 1H), 4.19-4.06 (m, 2H) 4.04-4.00 (m, 2H), 3.33 (dd, J = 14.0, 7.2 Hz, 1H), 3.17 (dd, J = 14.0, 7.2 Hz, 1H), 1.13 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 172.5, 171.9, 149.0, 148.2, 141.1, 139.8, 138.0, 137.2, 129.3, 129.2, 129.1, 128.6, 128.2, 126.9, 126.7, 126.4, 120.2, 118.4, 118.1, 115.4, 114.5, 114.2, 88.7, 76.3, 63.9, 62.8, 61.2, 61.0, 51.8, 47.4, 36.3, 14.2. HRMS (ESI) calcd for $C_{21}H_{24}NO_2^+$ $(M + H)^+$ 322.1802, found 322.1797.



3u

Ethyl 2-(methyl(*m*-tolyl)amino)-3-methylenepent-4-enoate (**3u**) was obtained (47.7 mg, 92% yield) as a yellow oil (Table 3, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.12 (m, 1H), 6.61-6.59 (m, 3H), 6.38 (dd, J = 17.6, 11.2 Hz, 1H), 5.43 (s, 1H), 5.21-5.16 (m, 3H), 5.07 (d, J = 11.2 Hz, 1H),

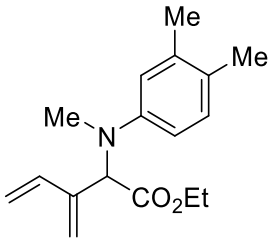
4.29-4.14 (m, 2H), 2.90 (s, 3H), 2.32 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.4, 141.7, 139.1, 136.8, 129.3, 119.5, 118.5, 115.6, 113.4, 109.7, 62.9, 61.0, 33.2, 22.1, 14.4. HRMS (ESI) calcd for $C_{16}H_{22}NO_2^+$ $(M + H)^+$ 260.1645, found 260.1646.



3v **3u**

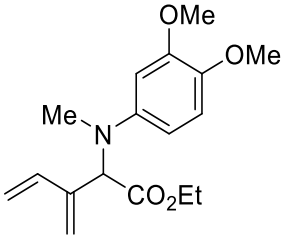
3v:**3u** = 45:55

A 45:55 mixture of ethyl 2-(methyl(*p*-tolyl)amino)-3-methylenepent-4-enoate (**3v**) and ethyl 2-(methyl(*m*-tolyl)amino)-3-methylenepent-4-enoate (**3u**) was obtained (31.1 mg, 60% yield) as a yellow oil (Table 3, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$) for compound **3v**: δ 7.06 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 6.38 (dd, J = 17.6, 11.2 Hz, 1H), 5.43 (s, 1H), 5.15-5.13 (m, 3H), 5.07 (d, J = 11.2 Hz, 1H), 4.29-4.14 (m, 2H), 2.88 (s, 3H), 2.26 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.4, 147.2, 141.7, 139.1, 136.9, 136.8, 130.0, 129.3, 126.8, 119.4, 118.5, 115.6, 115.5, 113.4, 112.9, 109.8, 63.2, 63.0, 61.0, 60.9, 33.4, 33.2, 22.1, 20.4, 14.4. HRMS (ESI) calcd for $C_{16}H_{22}NO_2^+$ $(M + H)^+$ 260.1645, found 260.1641.



3w

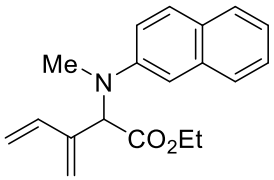
Ethyl 2-((3,4-dimethylphenyl)(methyl)amino)-3-methylenepent-4-enoate (**3w**) was obtained (39.4 mg, 72% yield) as a yellow oil (Table 3, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J = 8.4 Hz, 1H), 6.60 (d, J = 2.8 Hz, 1H), 6.55 (dd, J = 8.4, 2.8 Hz, 1H), 6.38 (dd, J = 17.6, 11.2 Hz, 1H), 5.42 (s, 1H), 5.20 (d, J = 17.6 Hz, 1H), 5.19-5.14 (m, 2H), 5.07 (d, J = 11.2 Hz, 1H), 4.28-4.13 (m, 2H), 2.88 (s, 3H), 2.23 (s, 3H), 2.17 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 147.6, 141.8, 137.4, 136.9, 130.5, 125.5, 119.3, 115.5, 114.4, 110.2, 63.1, 61.0, 33.3, 20.6, 18.7, 14.4. HRMS (ESI) calcd for $C_{17}H_{24}NO_2^+$ $(M + H)^+$ 274.1802, found 274.1799.



3x

Ethyl 2-((3,4-dimethoxyphenyl)(methyl)amino)-3-methylenepent-4-enoate (**3x**) was obtained

(46.4 mg, 76% yield) as a yellow oil (Table 3, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, J = 8.8 Hz, 1H), 6.44-6.36 (m, 2H), 6.31 (dd, J = 8.8, 2.8 Hz, 1H), 5.43 (s, 1H), 5.23 (d, J = 17.6 Hz, 1H), 5.18-5.09 (m, 3H), 4.28-4.15 (m, 2H), 3.87 (s, 3H), 3.82 (s, 3H), 2.89 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 149.8, 144.5, 141.7, 141.5, 136.8, 119.5, 115.6, 113.0, 104.5, 99.0, 63.9, 61.0, 56.6, 55.9, 33.9, 14.4. HRMS (ESI) calcd for $C_{17}H_{24}NO_4^+$ $(M + H)^+$ 306.1700, found 306.1702.

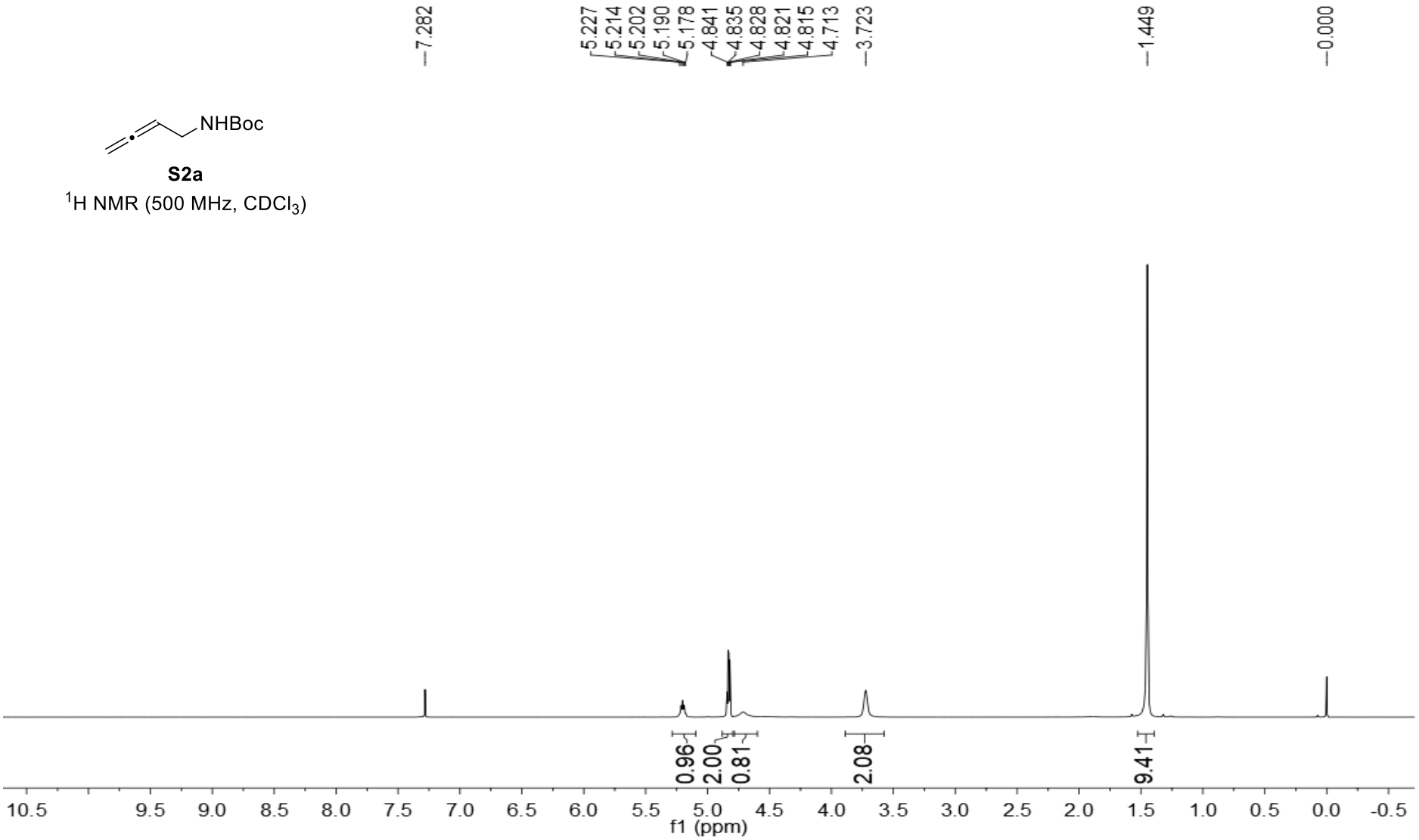


3y

Ethyl 2-(methyl(naphthalen-2-yl)amino)-3-methylenepent-4-enoate (**3y**) was obtained (41.4 mg, 70% yield) as a yellow oil (Table 3, entry 5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.64 (m, 3H), 7.39-7.35 (m, 1H), 7.24-7.16 (m, 2H), 7.00 (d, J = 2.4 Hz, 1H), 6.41 (dd, J = 17.6, 11.2 Hz, 1H), 5.46 (s, 1H), 5.35 (s, 1H), 5.18 (d, J = 17.6 Hz, 2H), 5.07 (d, J = 11.2 Hz, 1H), 4.30-4.16 (m, 2H), 3.01 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 147.2, 141.5, 136.8, 135.0, 129.2, 127.5, 127.3, 126.5, 122.5, 119.7, 115.8, 115.6, 106.9, 63.2, 61.2, 33.5, 14.4. HRMS (ESI) calcd for $C_{19}H_{22}NO_2^+$ $(M + H)^+$ 296.1645, found 296.1643.

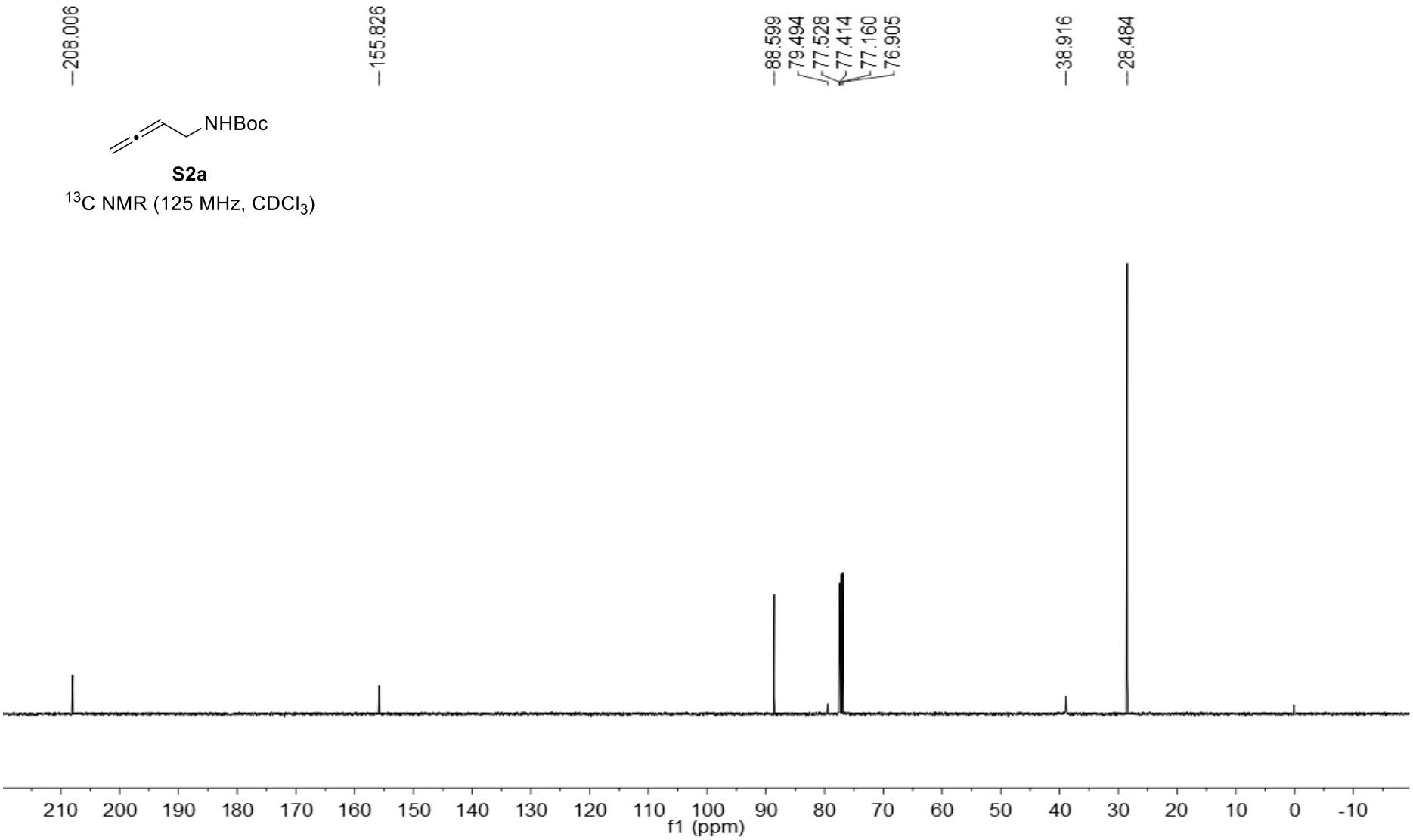
References

(1) R. K. Dieter, N. Chen, H. Yu, L. E. Nice and V. K. Gore, *J. Org. Chem.*, 2005, **70**, 2109−2119.
(2) C. P. Grugel and B. Breit, *Org. Lett*., 2019, **21**, 9672−9676.
(3) Q. Liu, X. Tang, Y. Cai and S. Ma, *Org. Lett*., 2017, **19**, 5174−5177.
(4) X. Huang, T. Cao, Y. Han, X. Jiang, W. Lin, J. Zhang and S. Ma, *Chem. Commun*., 2015, **51**, 6956−6959.



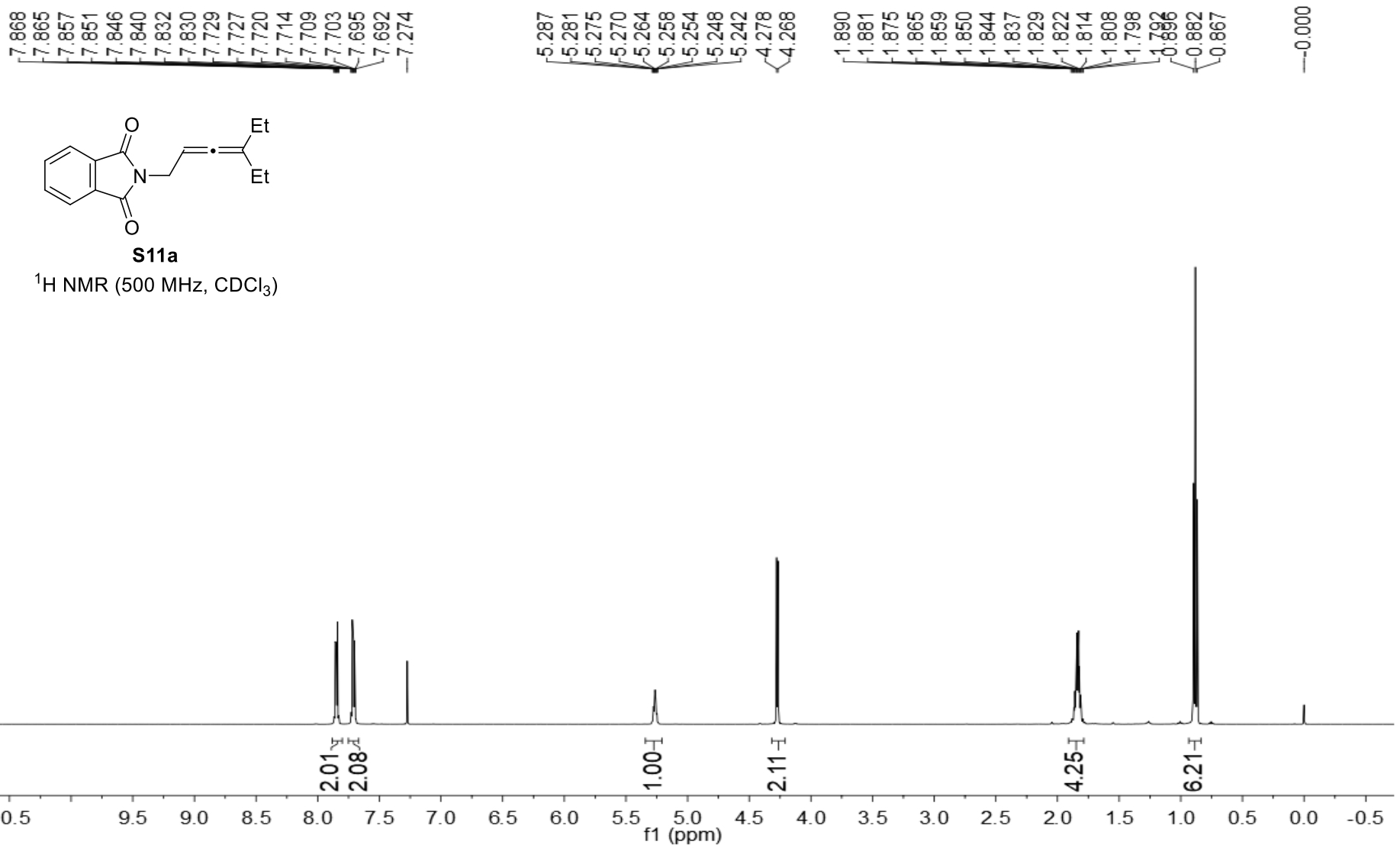
S2a

^{1}H NMR (500 MHz, $CDCl_3$)



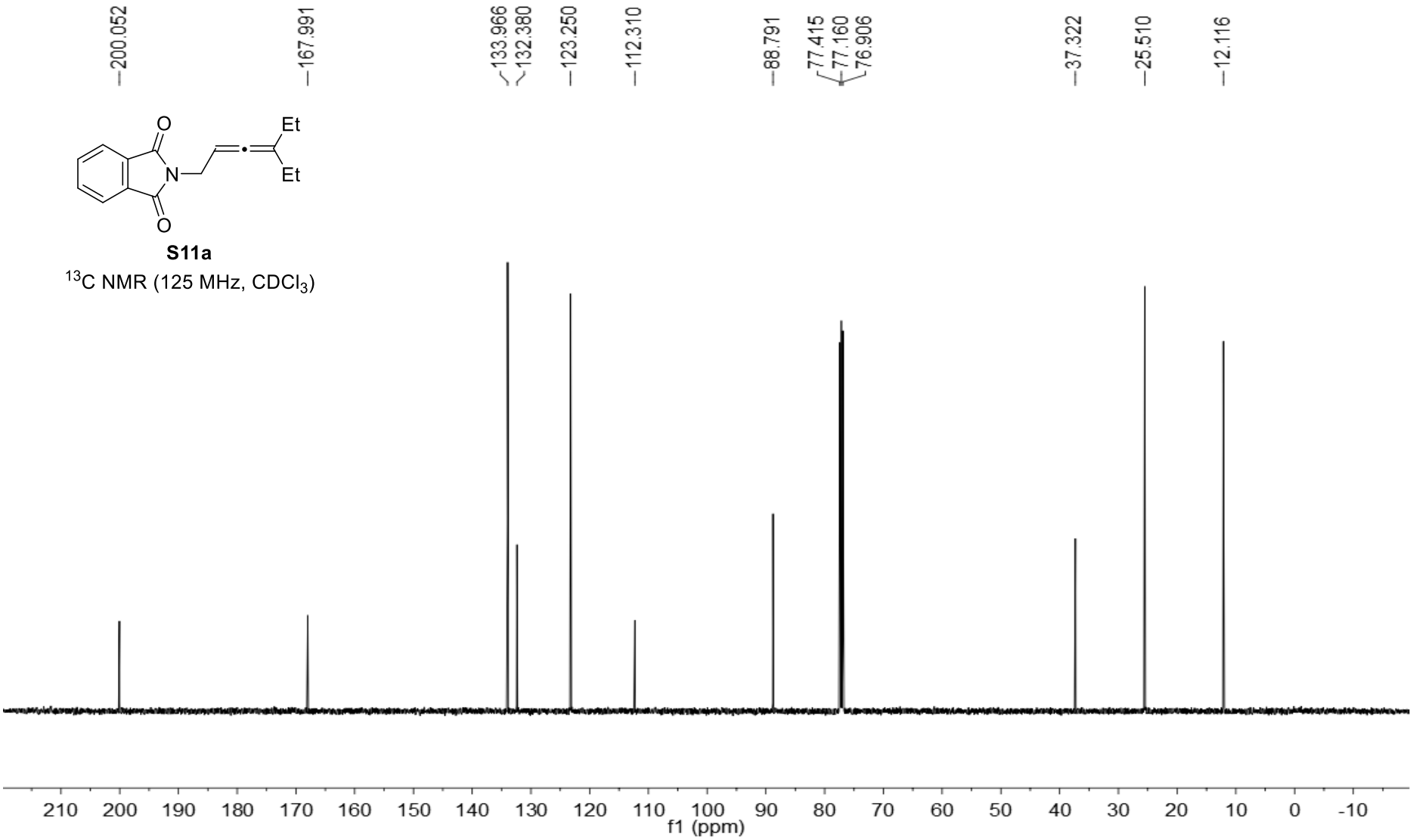
S2a

^{13}C NMR (125 MHz, $CDCl_3$)



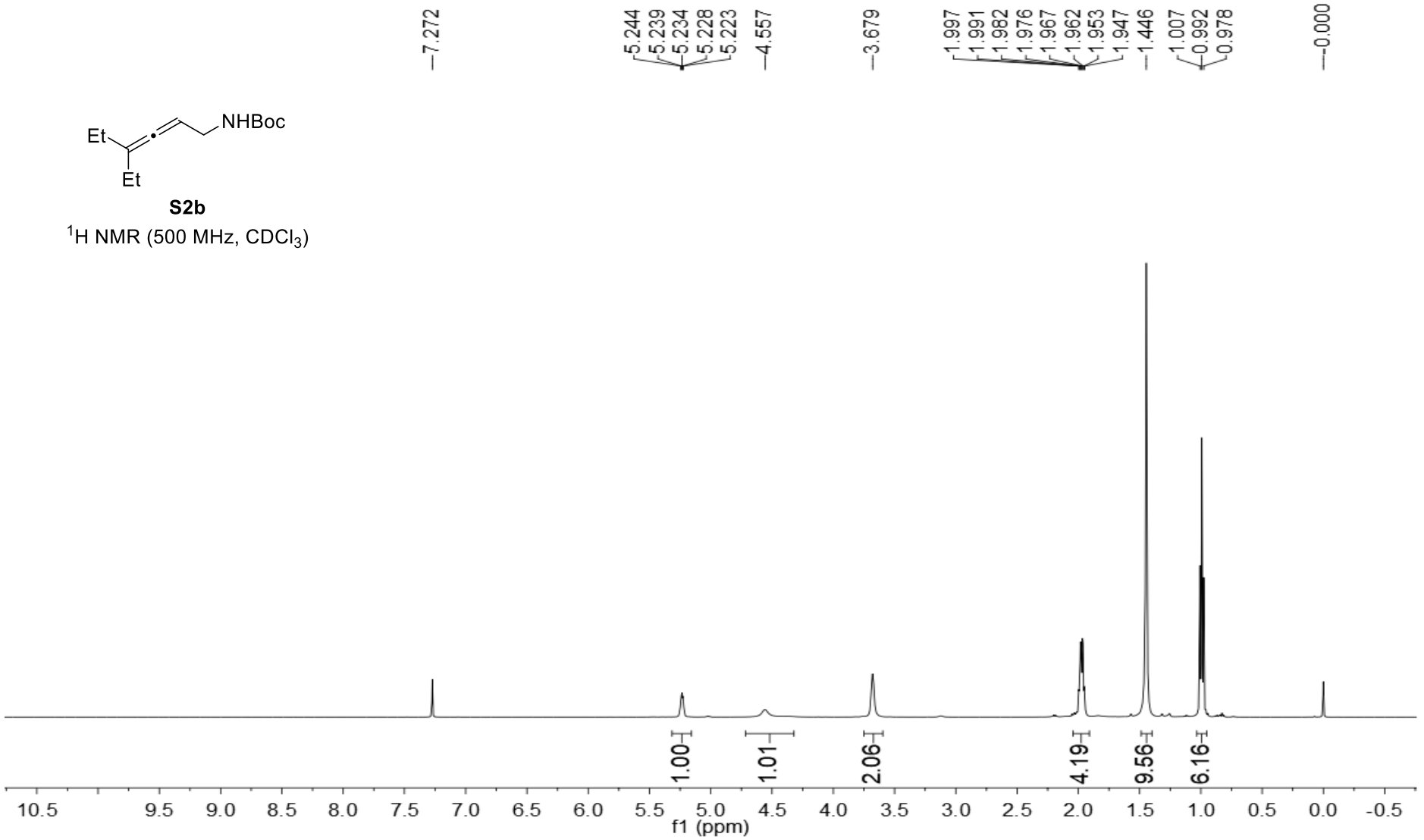
S11a

^{1}H NMR (500 MHz, $CDCl_3$)



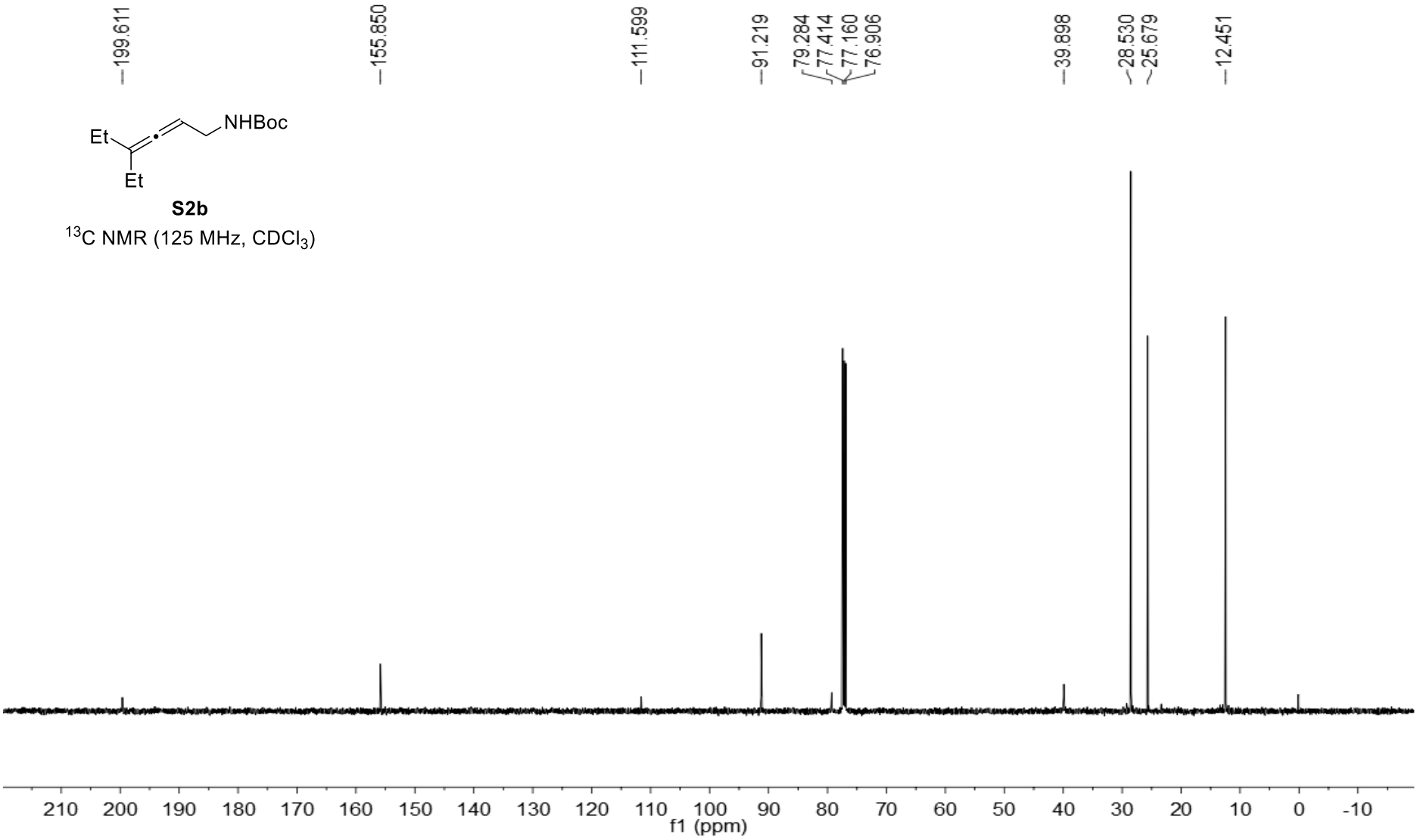
S11a

^{13}C NMR (125 MHz, $CDCl_3$)



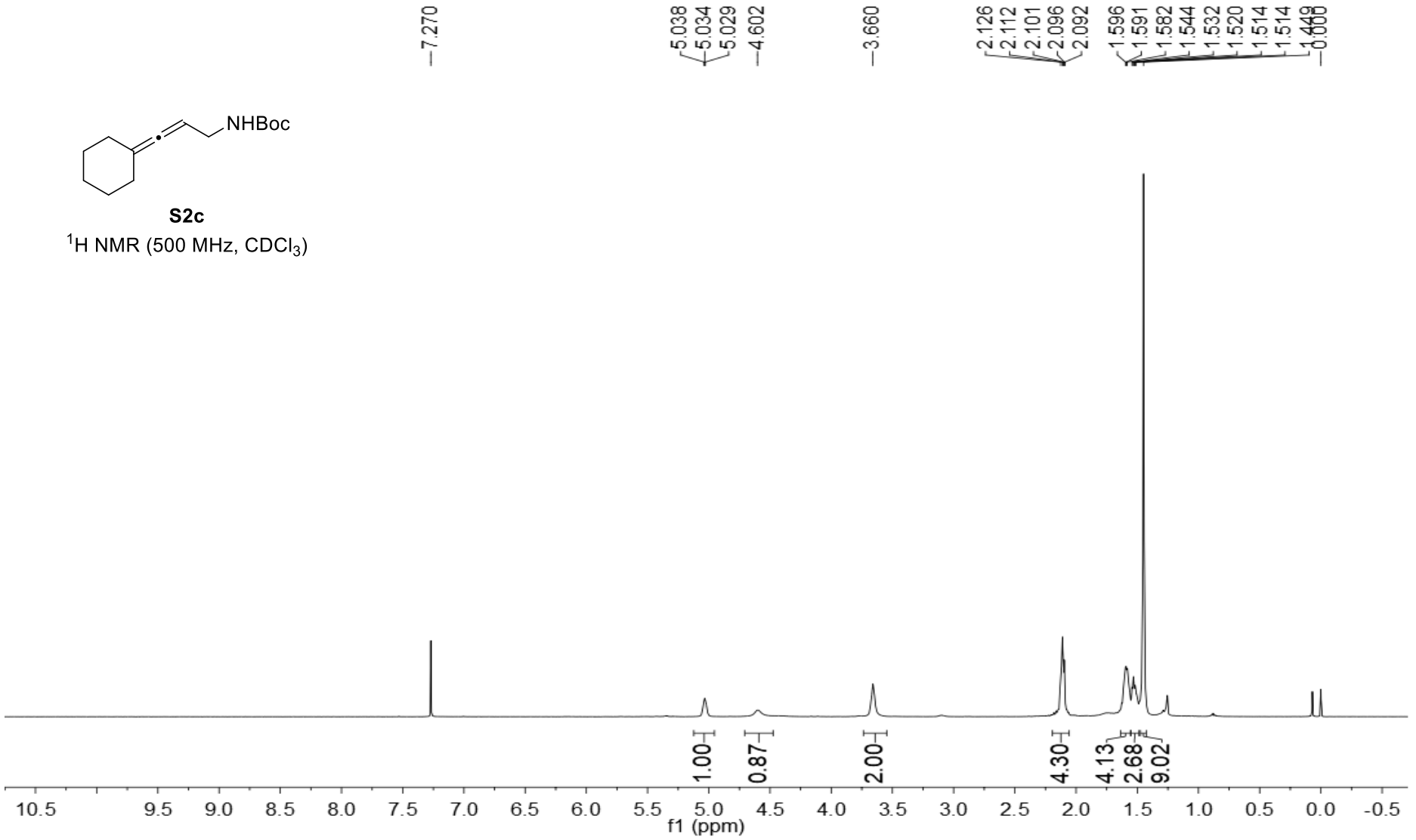
S2b

^{1}H NMR (500 MHz, $CDCl_3$)



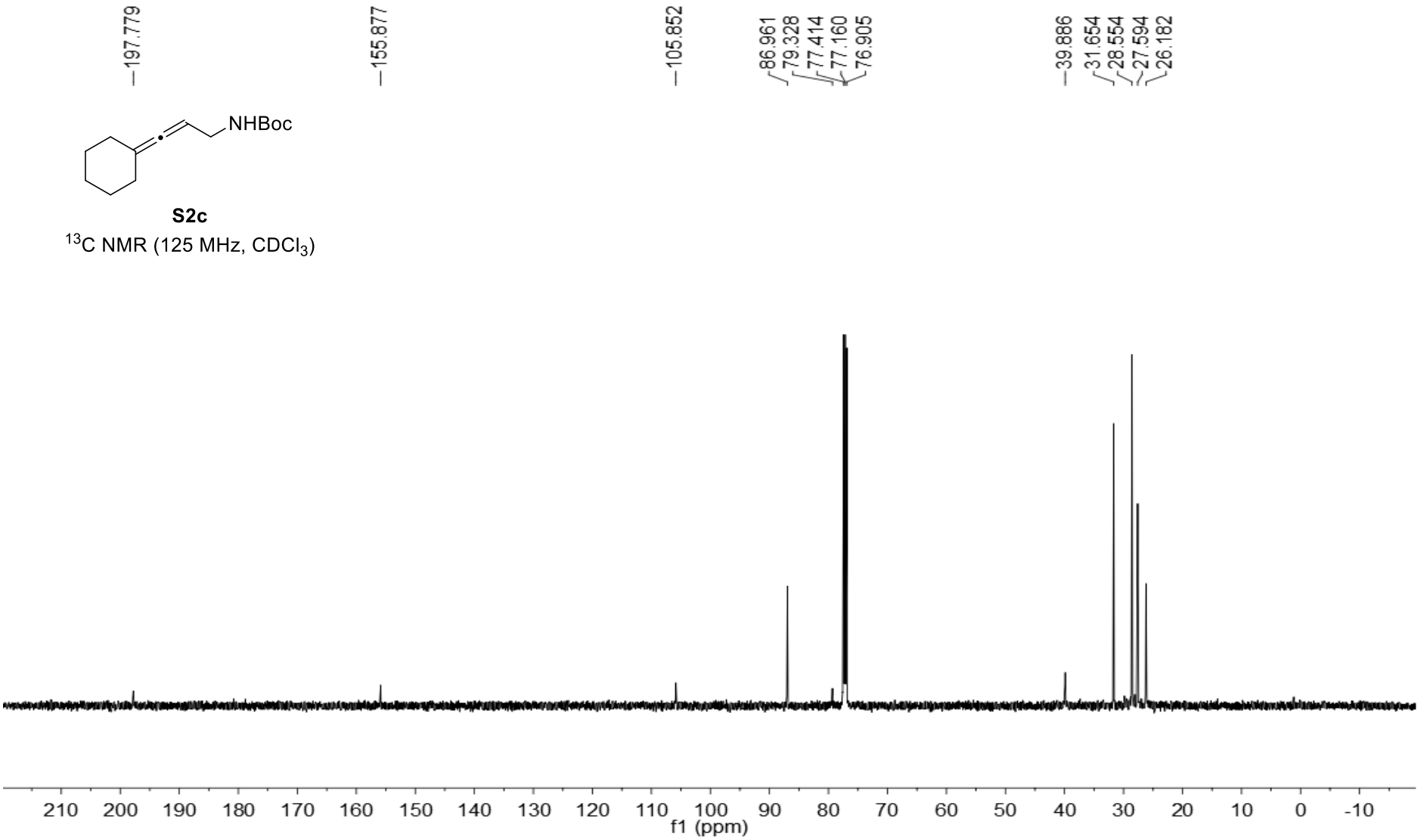
S2b

^{13}C NMR (125 MHz, $CDCl_3$)



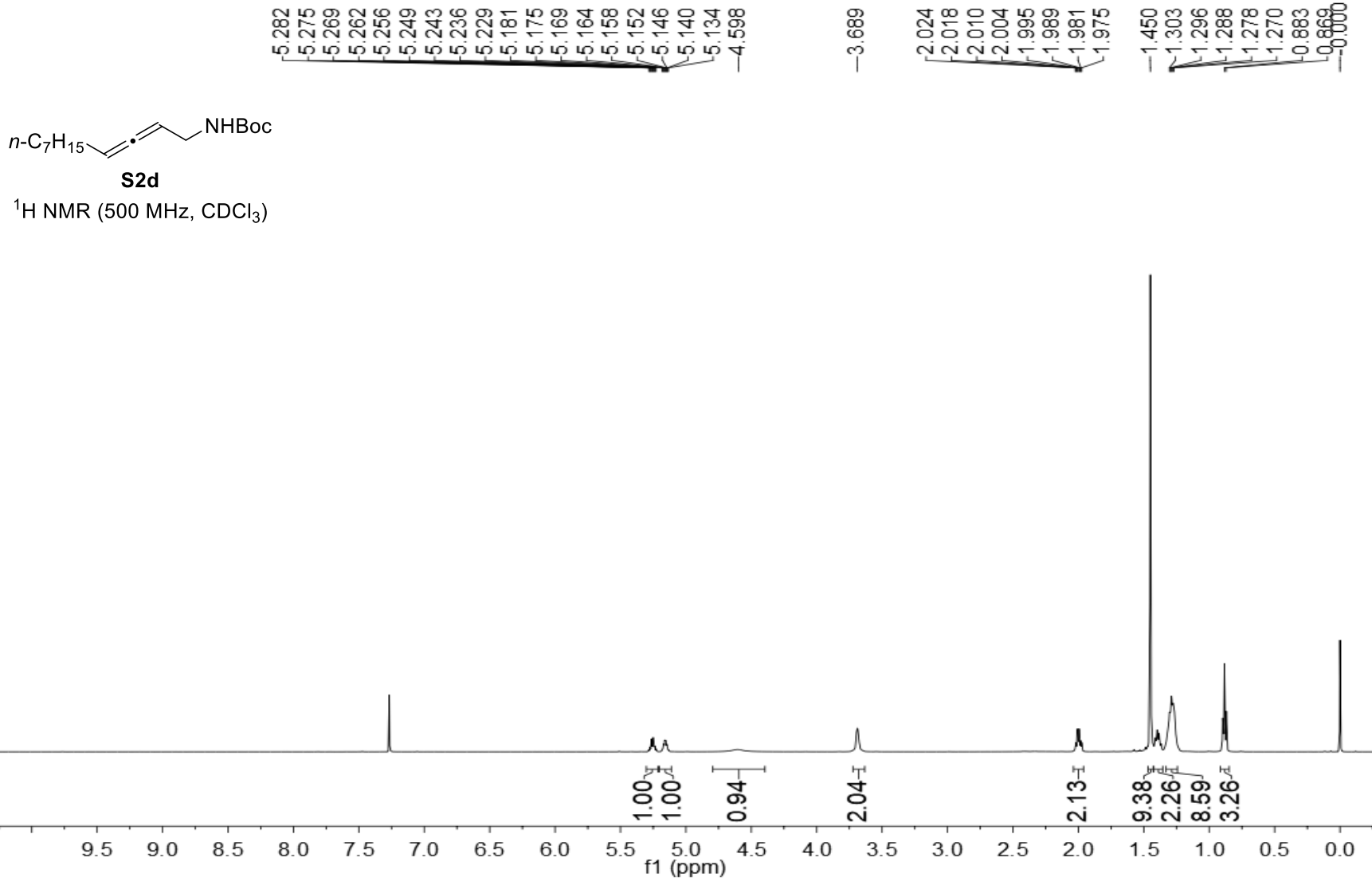
S2c

^{1}H NMR (500 MHz, $CDCl_3$)



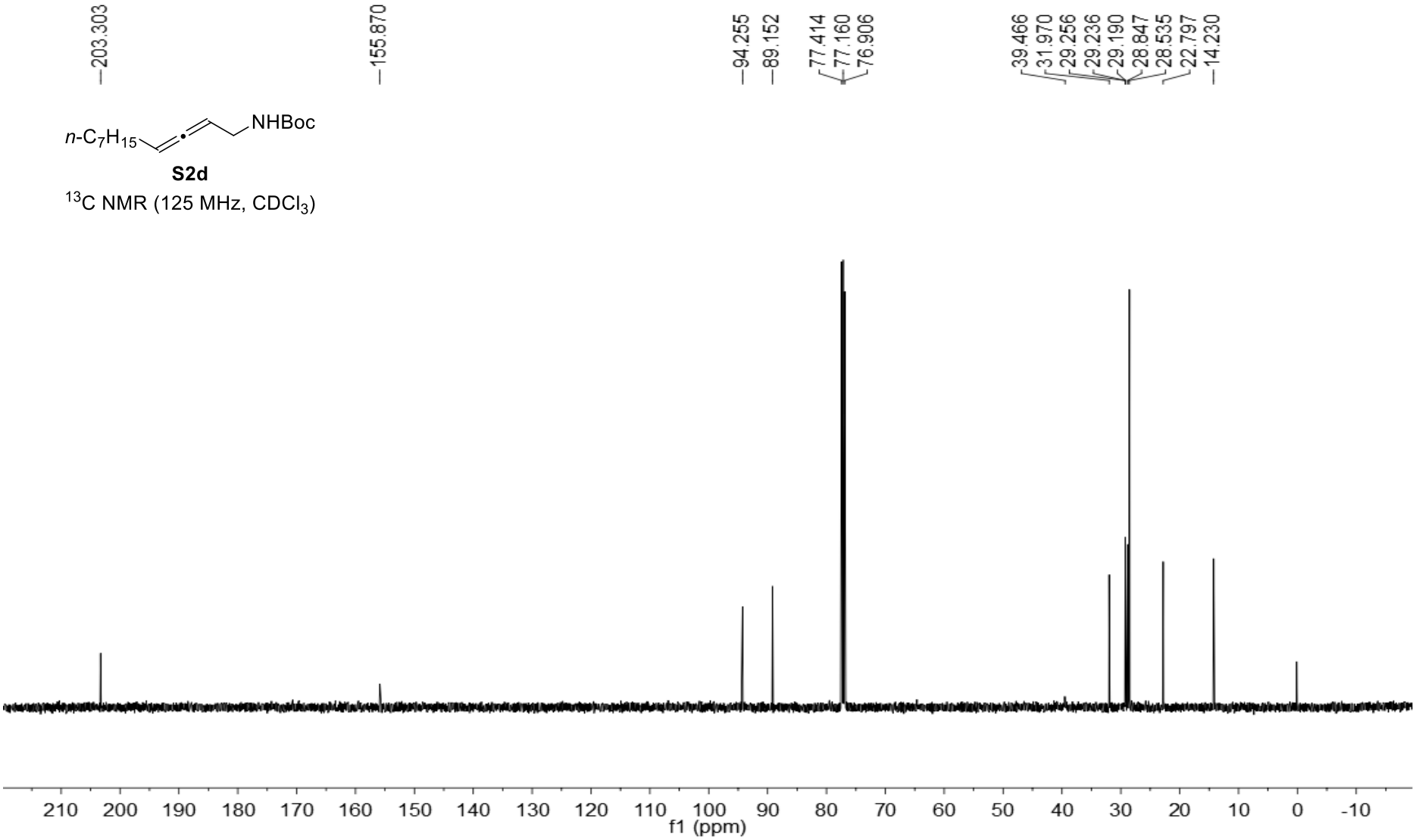
S2c

^{13}C NMR (125 MHz, $CDCl_3$)



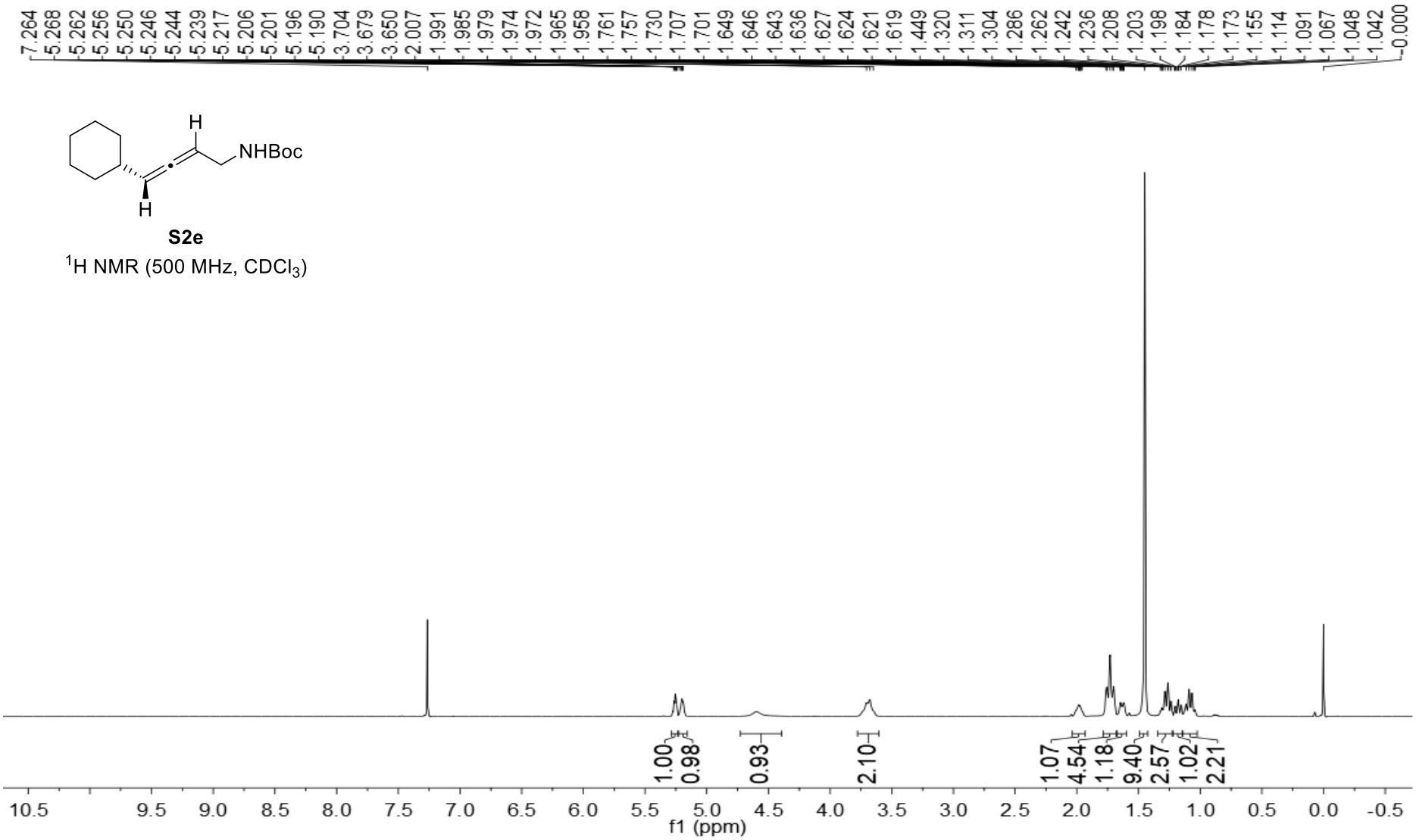
S2d

^{1}H NMR (500 MHz, $CDCl_3$)



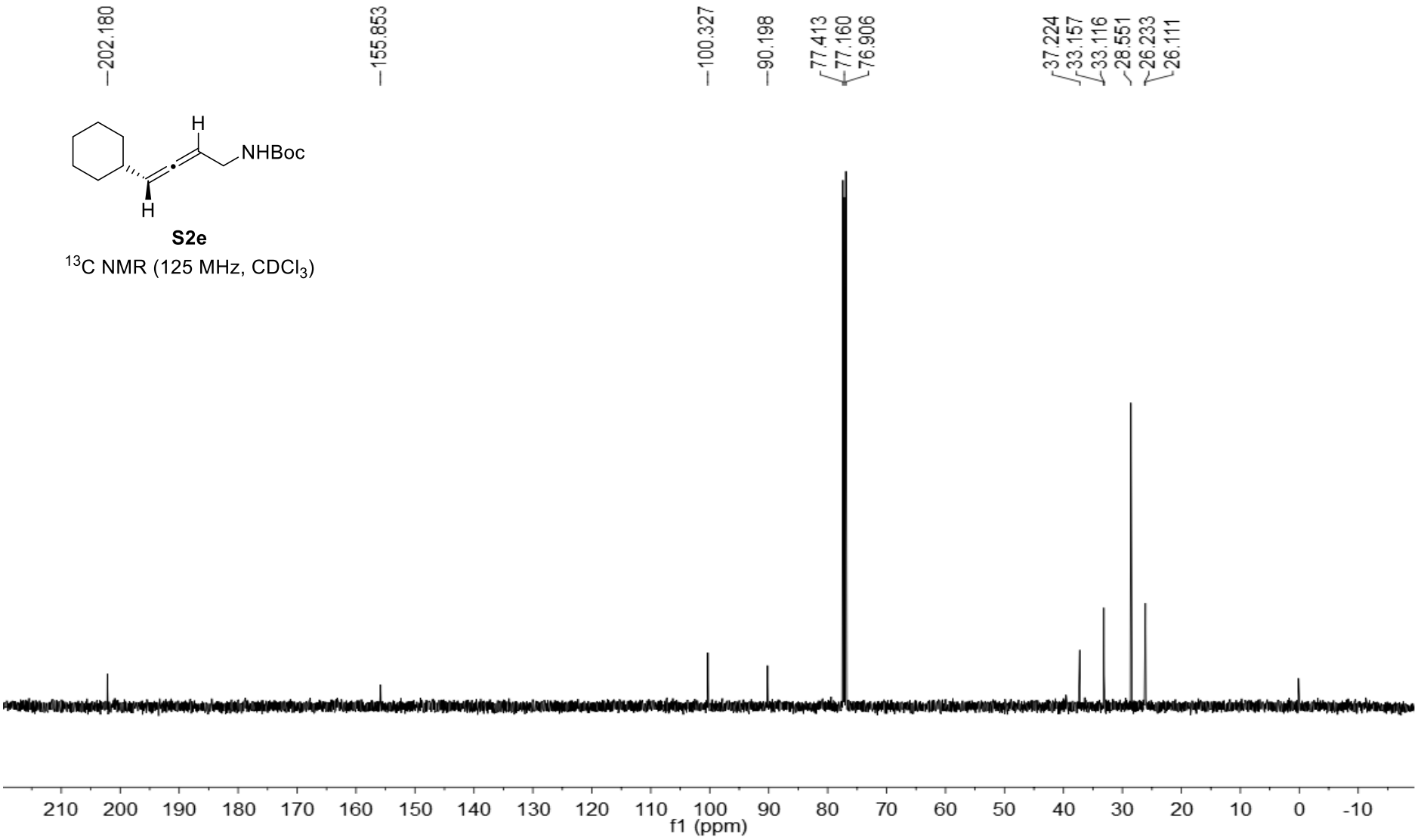
S2d

^{13}C NMR (125 MHz, $CDCl_3$)



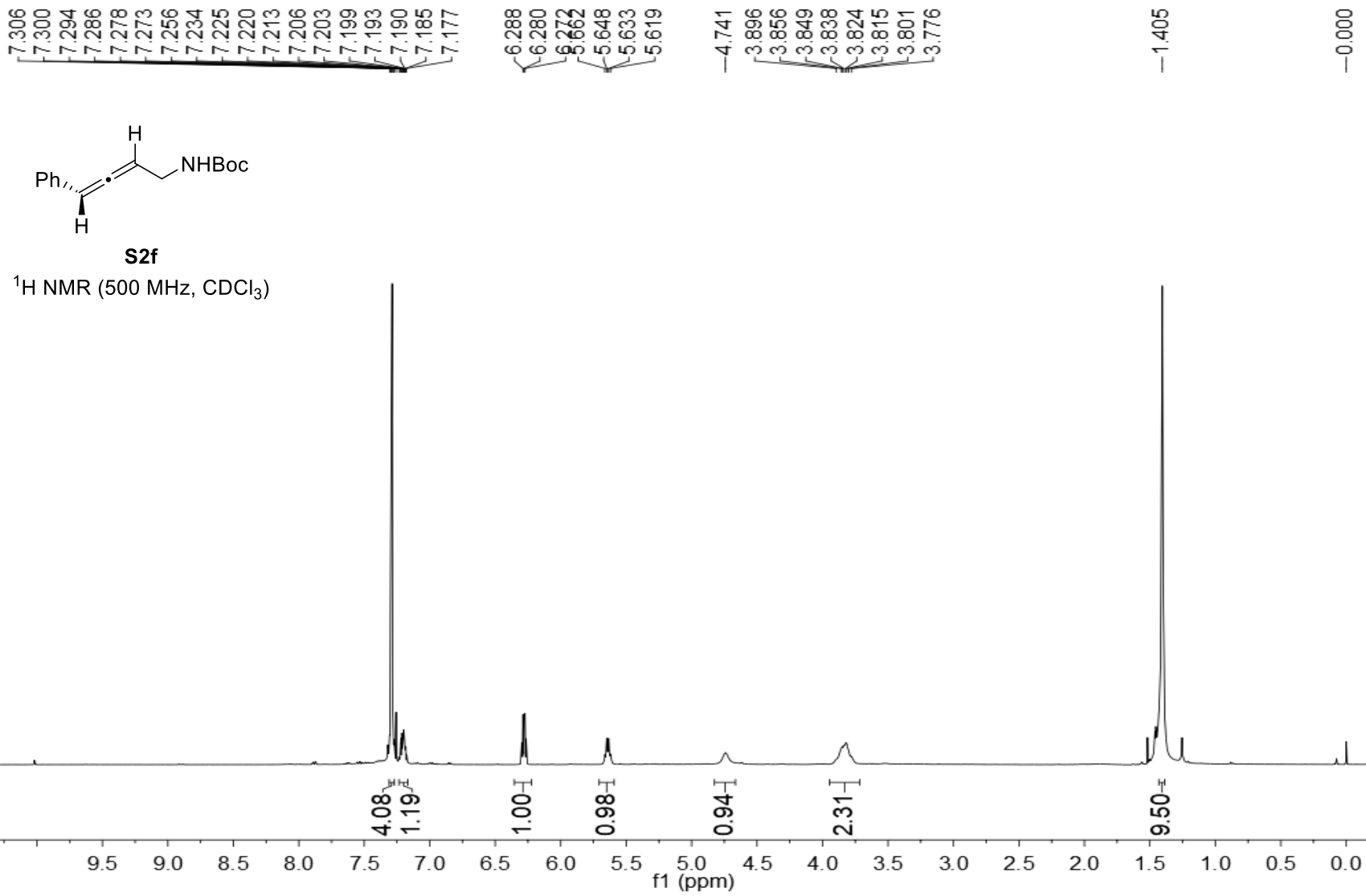
S2e

^{1}H NMR (500 MHz, $CDCl_3$)



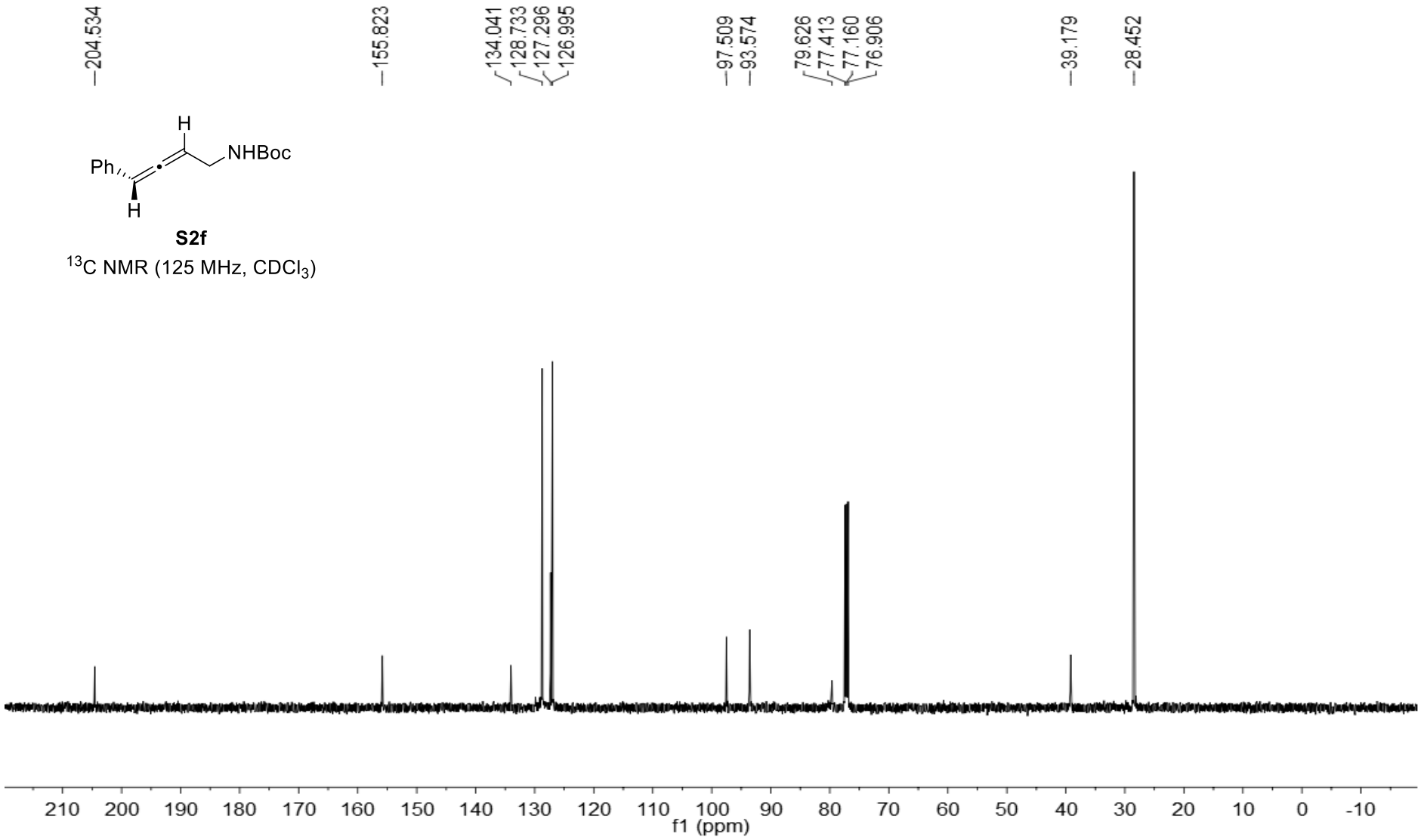
S2e

^{13}C NMR (125 MHz, $CDCl_3$)



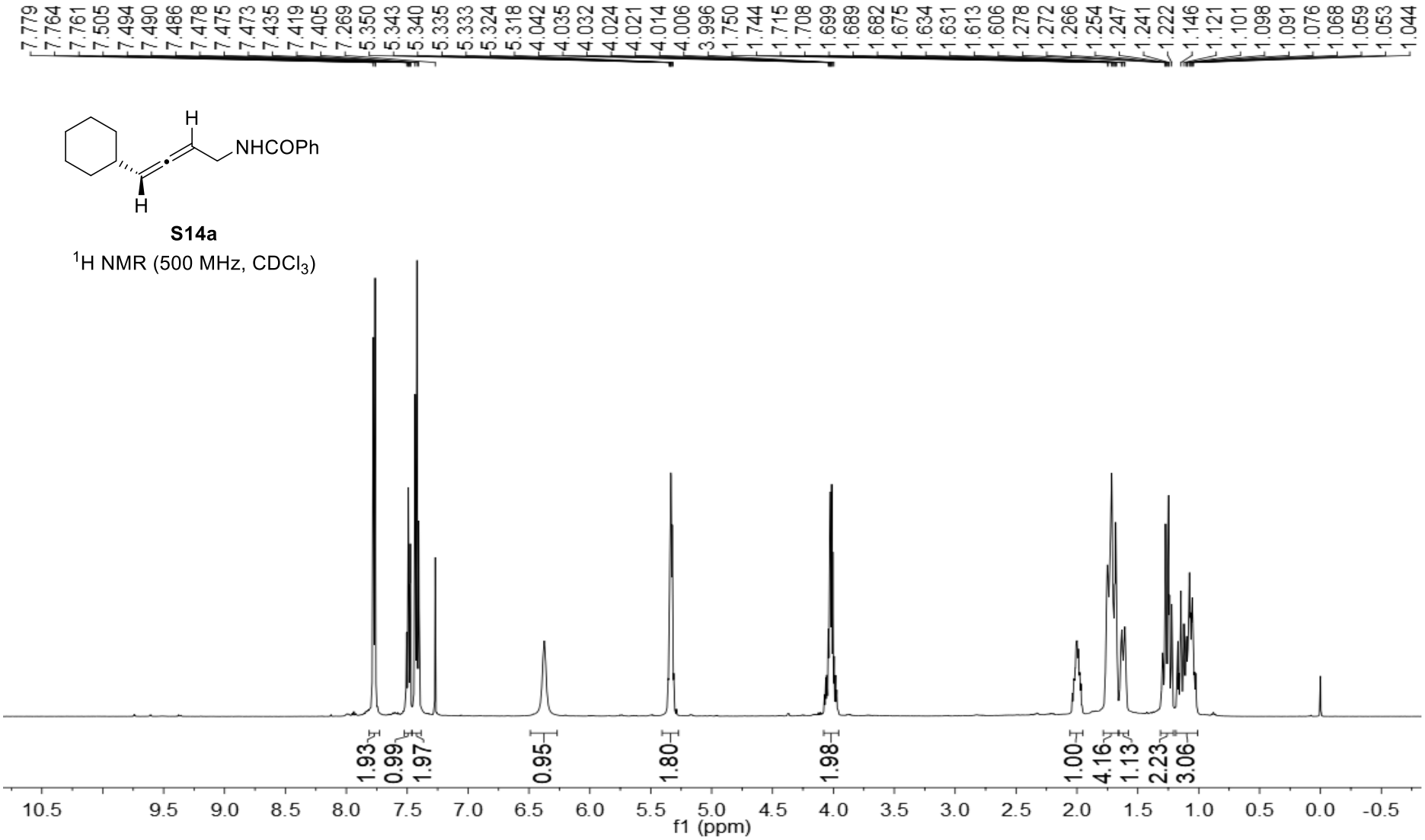
S2f

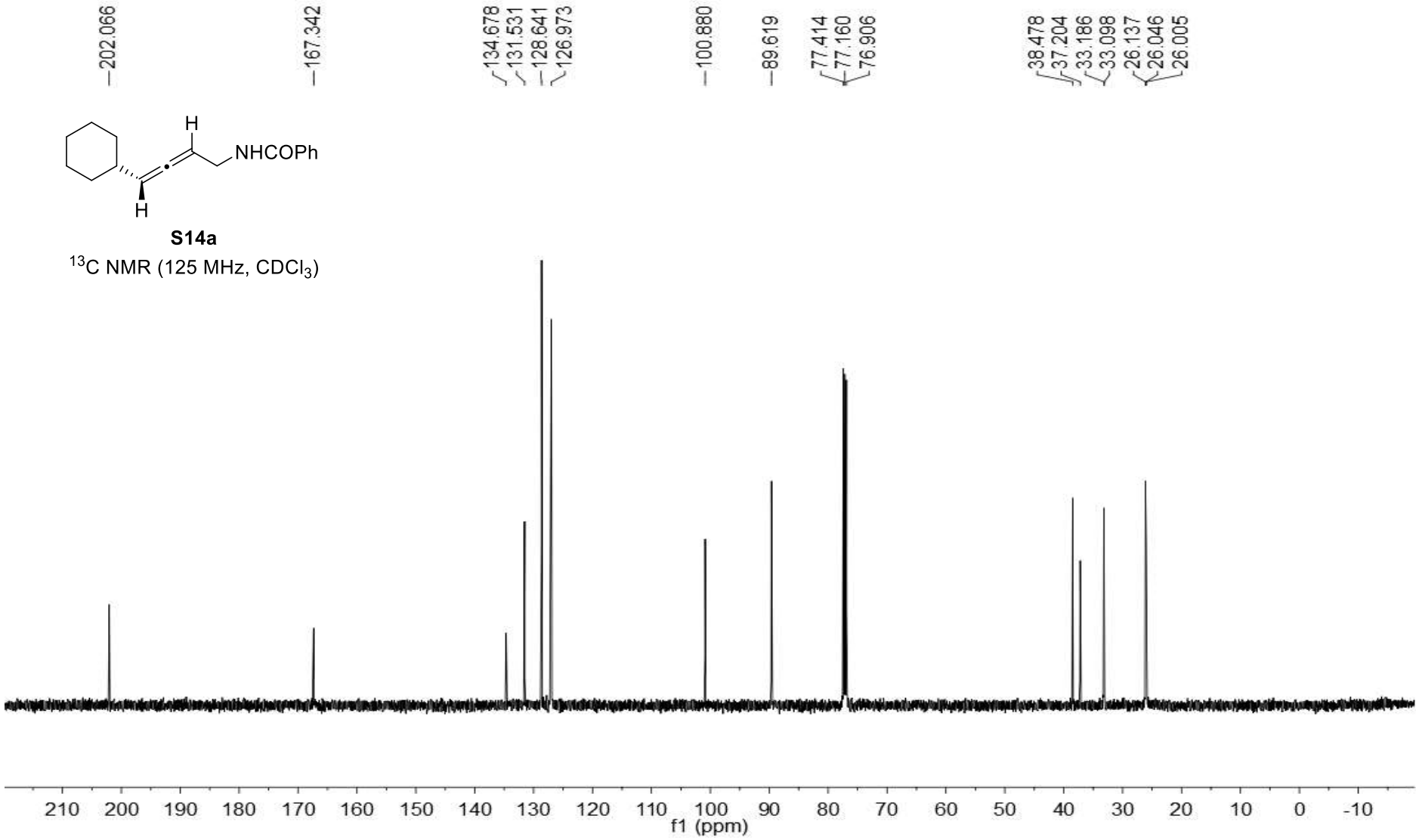
^{1}H NMR (500 MHz, $CDCl_3$)



S2f

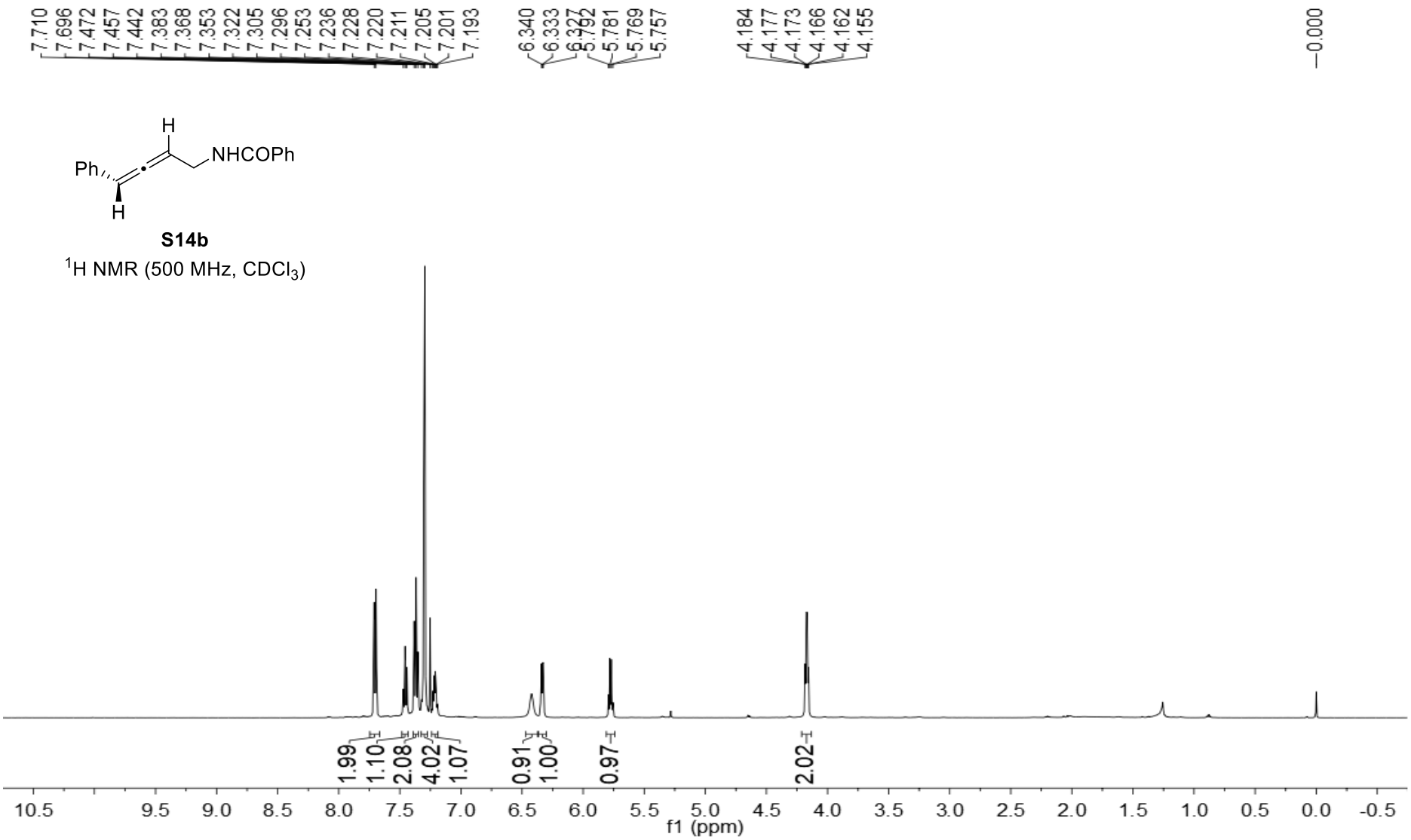
^{13}C NMR (125 MHz, $CDCl_3$)


7.779
7.764
7.761
7.505
7.494
7.490
7.486
7.478
7.475
7.473
7.435
7.419
7.405
7.269
5.350
5.343
5.340
5.335
5.333
5.324
5.318
4.042
4.035
4.032
4.024
4.021
4.014
4.006
3.996
1.750
1.744
1.715
1.708
1.699
1.689
1.682
1.675
1.634
1.631
1.613
1.606
1.278
1.272
1.266
1.254
1.247
1.241
1.222
1.146
1.121
1.101
1.098
1.091
1.076
1.068
1.059
1.053
1.044
H
NHCOPh
H
S14a
1H NMR (500 MHz, CDCl3)
1.93
0.99
1.97
0.95
1.80
1.98
1.00
4.16
1.13
2.23
3.06
10.5
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)



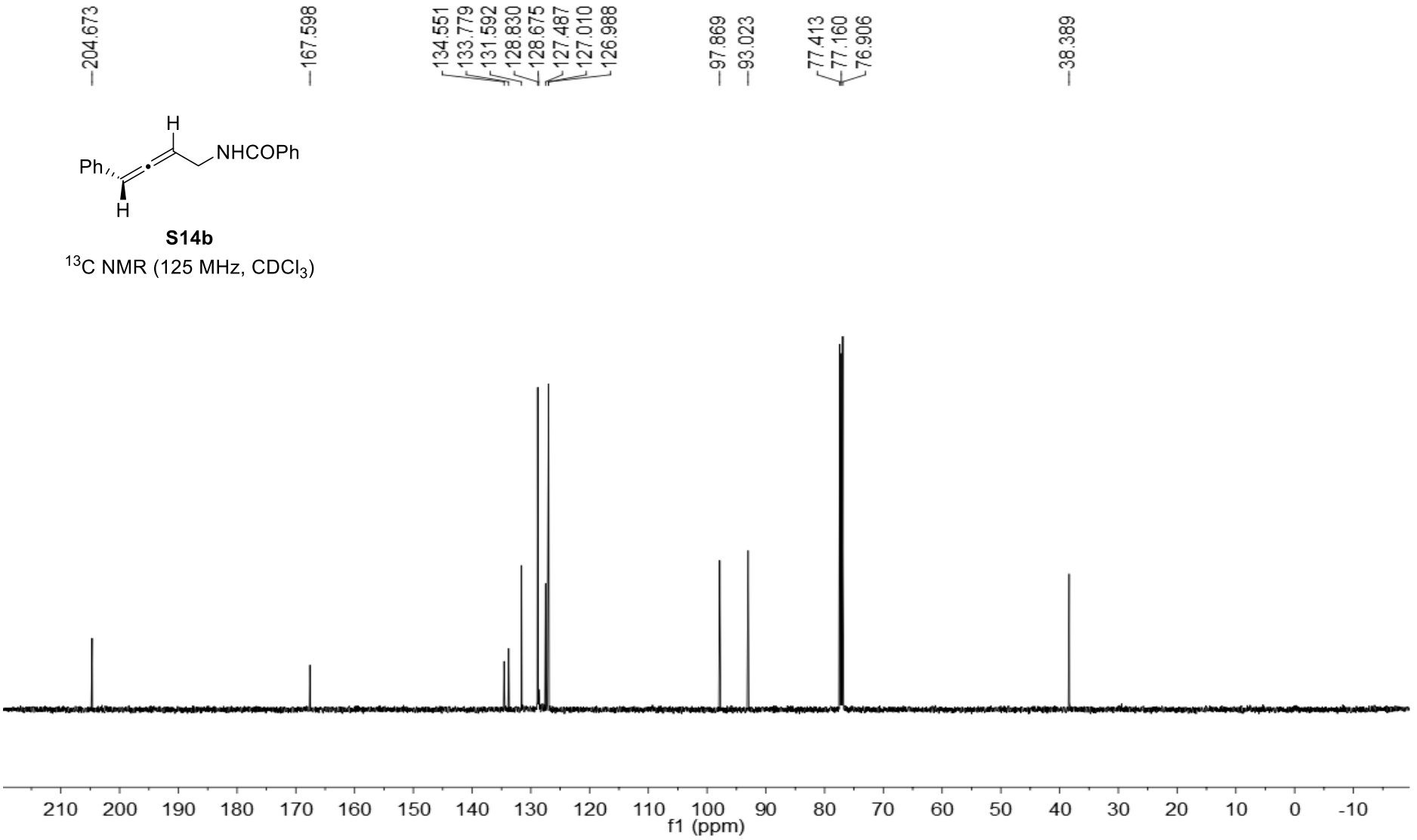
S14a

^{13}C NMR (125 MHz, $CDCl_3$)



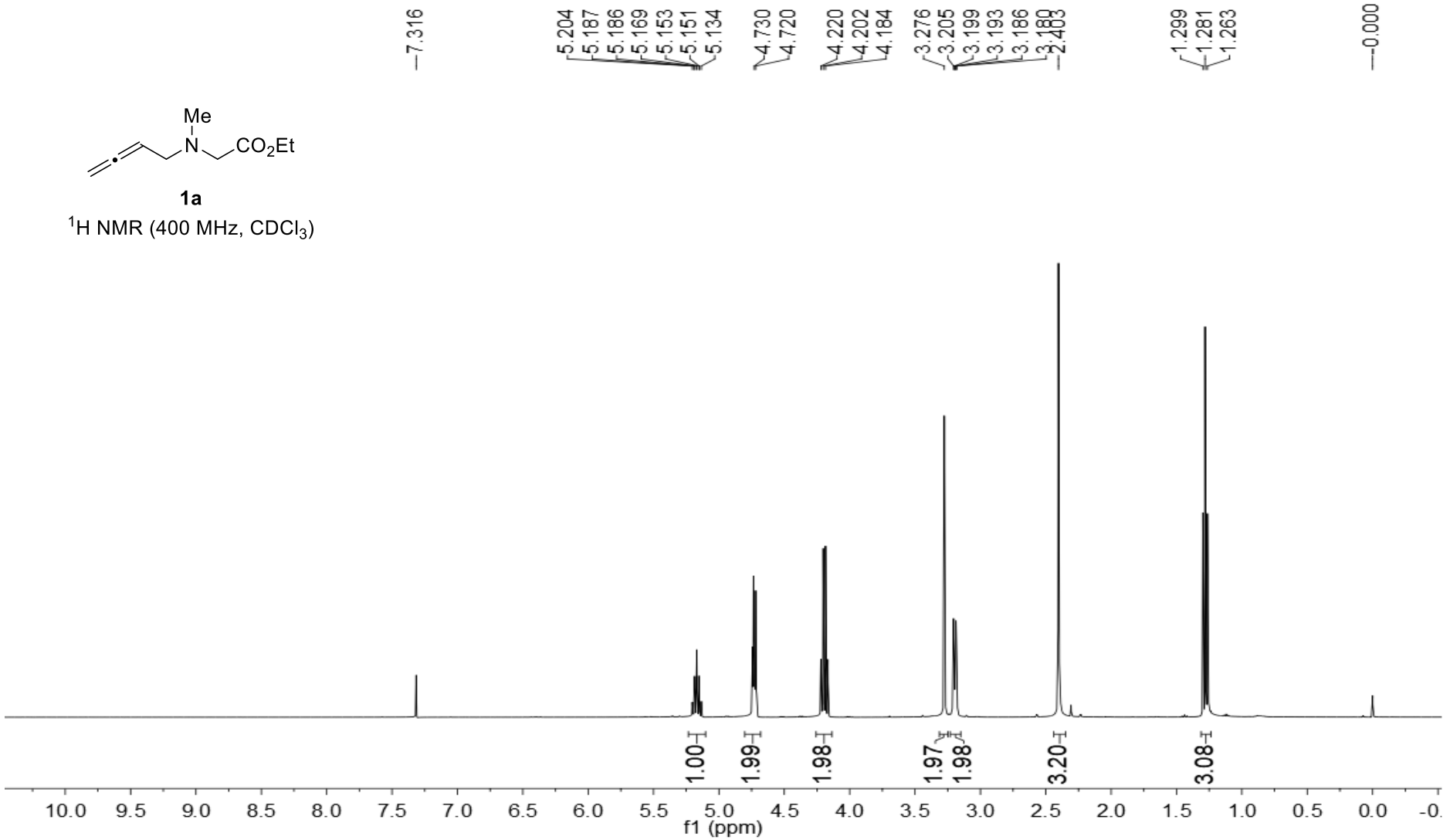
S14b

^{1}H NMR (500 MHz, $CDCl_3$)



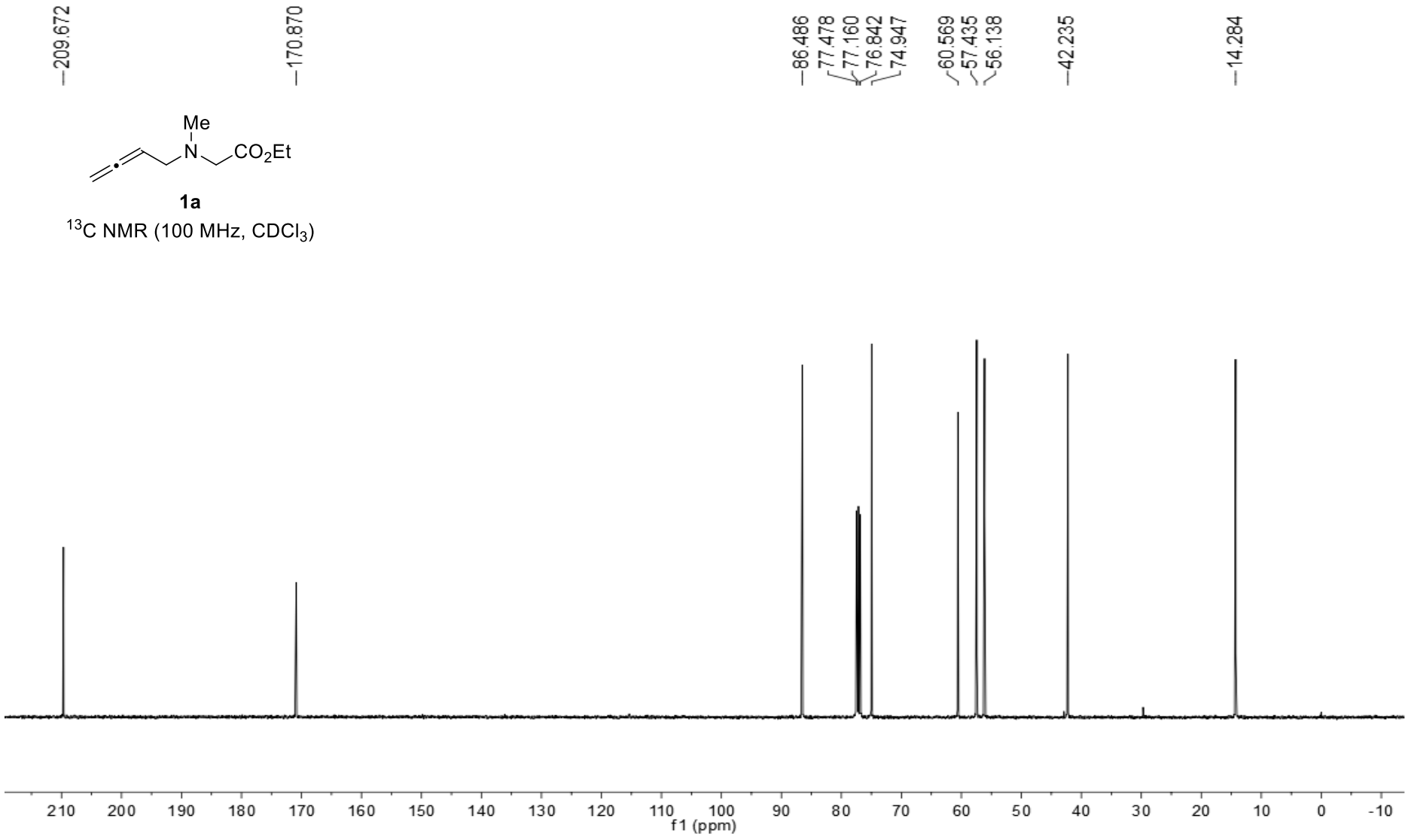
S14b

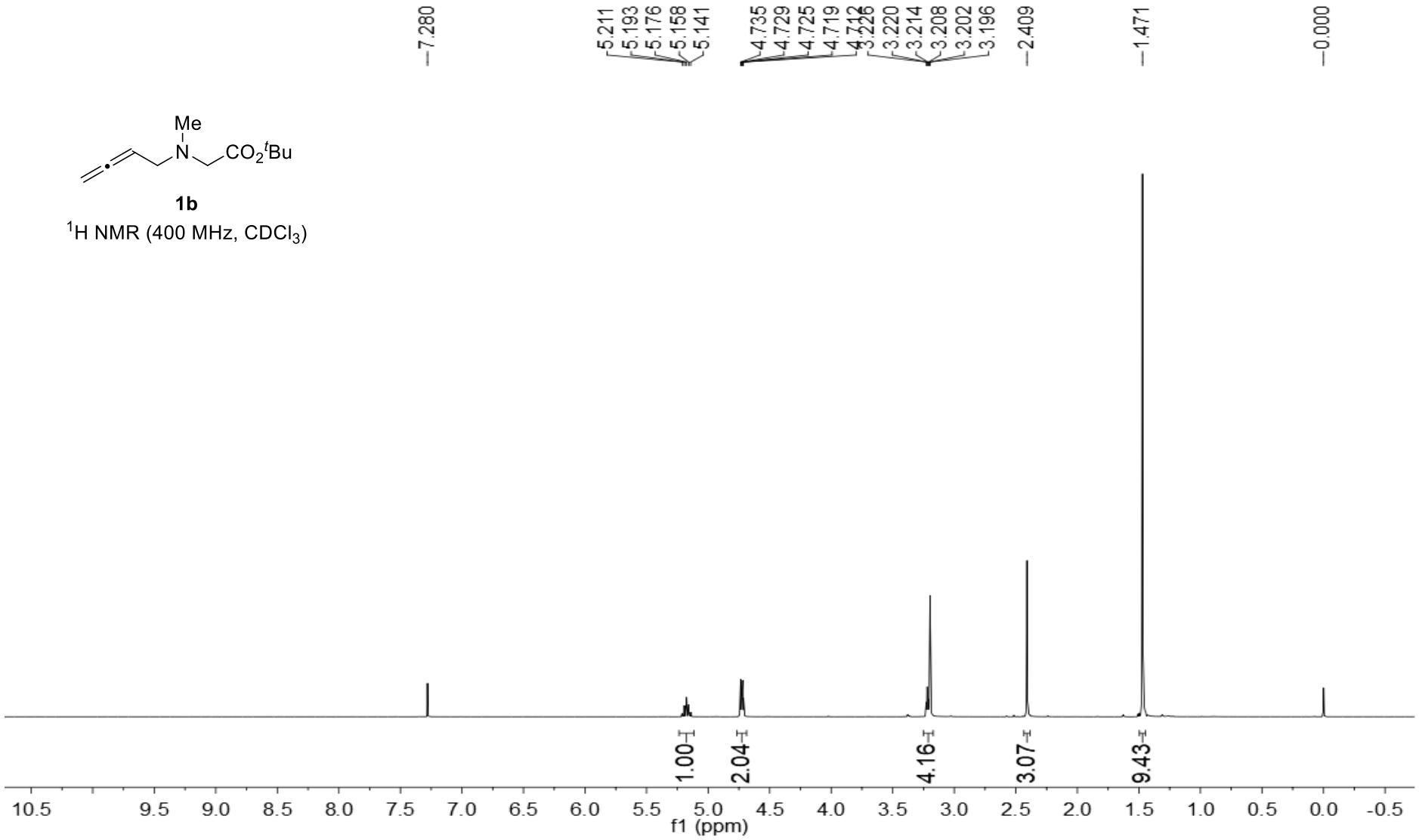
^{13}C NMR (125 MHz, $CDCl_3$)



1a

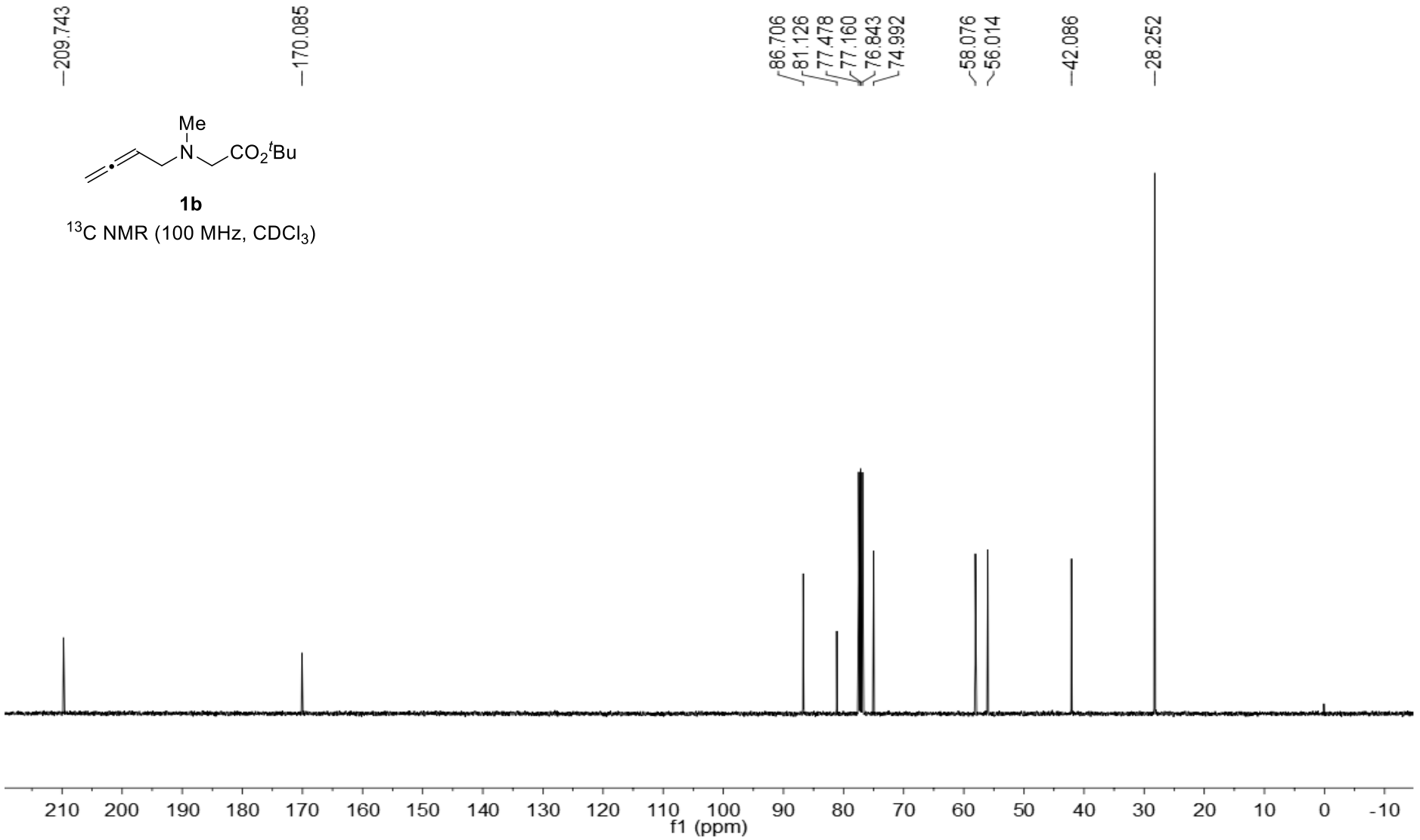
^{1}H NMR (400 MHz, $CDCl_3$)


209.672
170.870
86.486
77.478
77.160
76.842
74.947
60.569
57.435
56.138
42.235
14.284
Me
N
CO2Et
1a
13C NMR (100 MHz, 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)



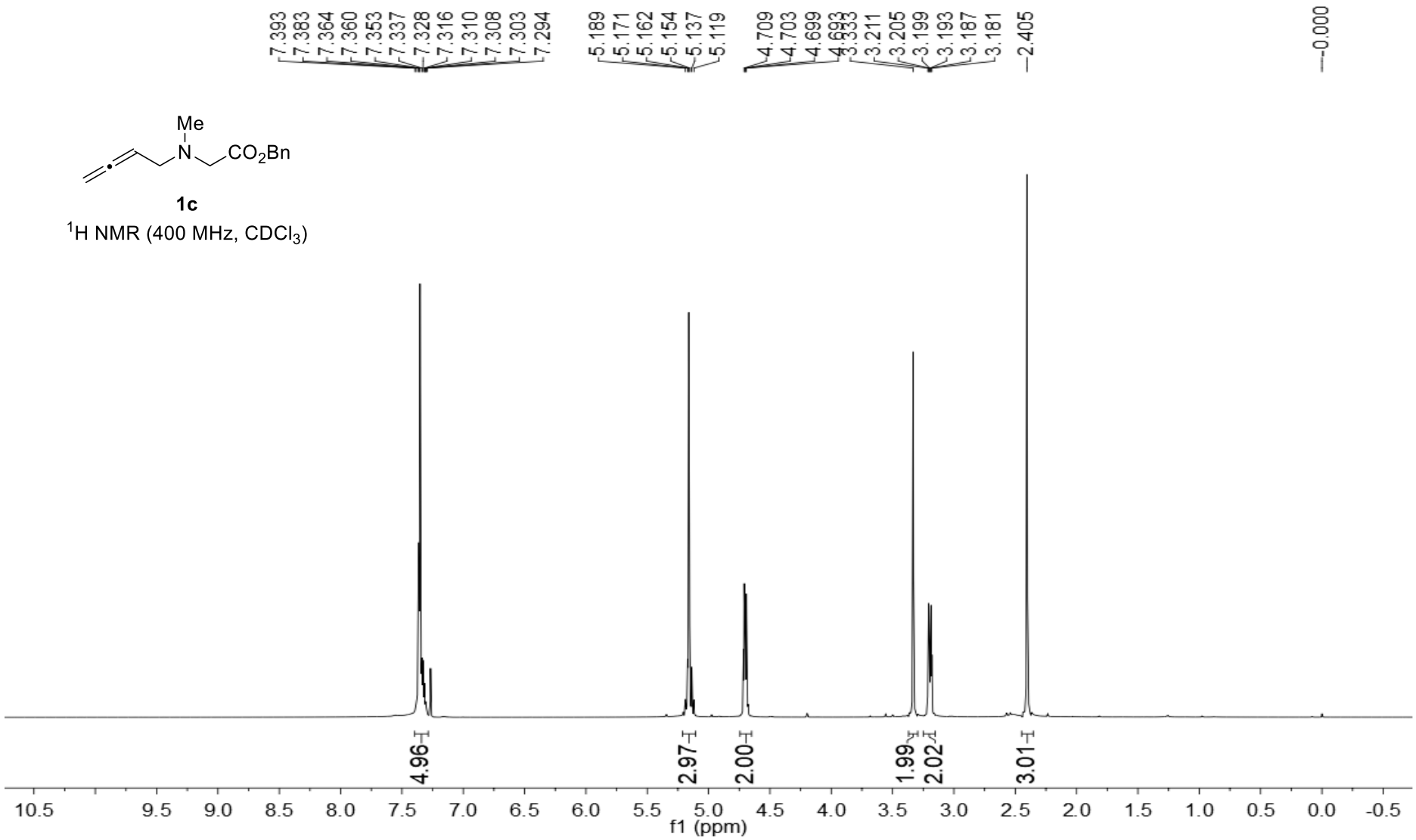
1b

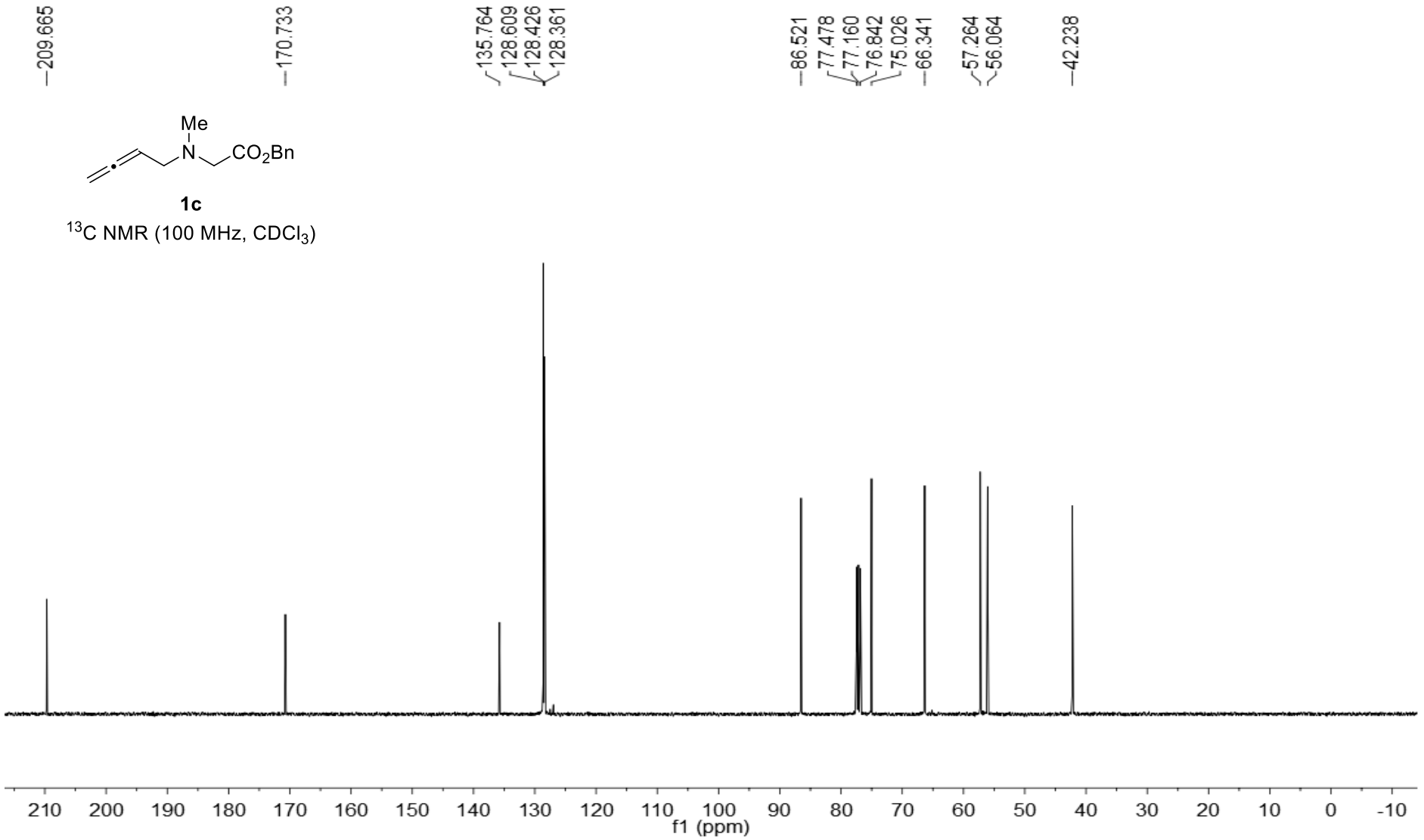
^{1}H NMR (400 MHz, $CDCl_3$)



1b

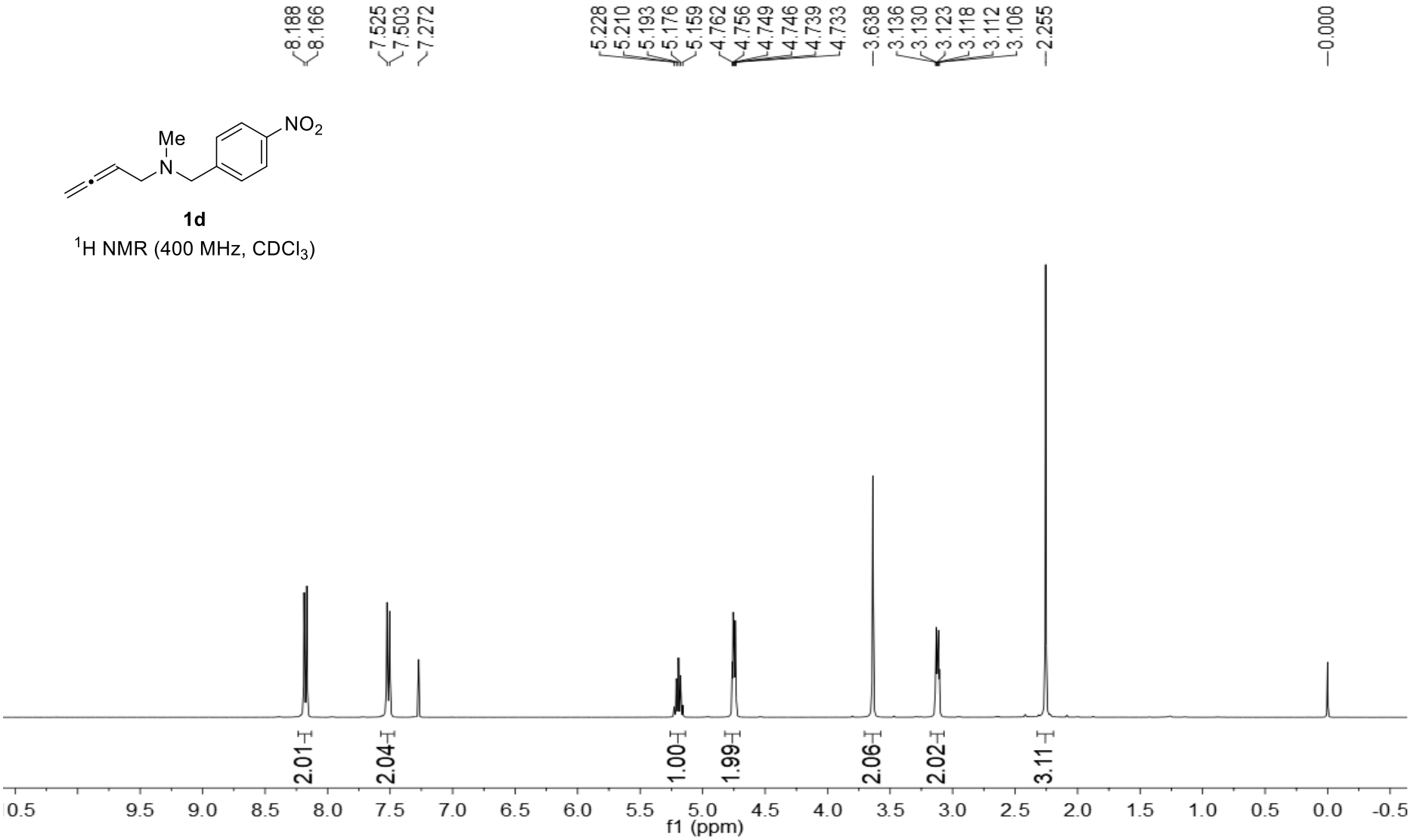
^{13}C NMR (100 MHz, $CDCl_3$)


7.393
7.383
7.364
7.360
7.353
7.337
7.328
7.316
7.310
7.308
7.303
7.294
5.189
5.171
5.162
5.154
5.137
5.119
4.709
4.703
4.699
4.693
3.333
3.211
3.205
3.199
3.193
3.187
3.181
2.405
0.000
Me
N
CO2Bn
1c
1H NMR (400 MHz, CDCl3)
4.96
2.97
2.00
1.99
2.02
3.01
10.5
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)



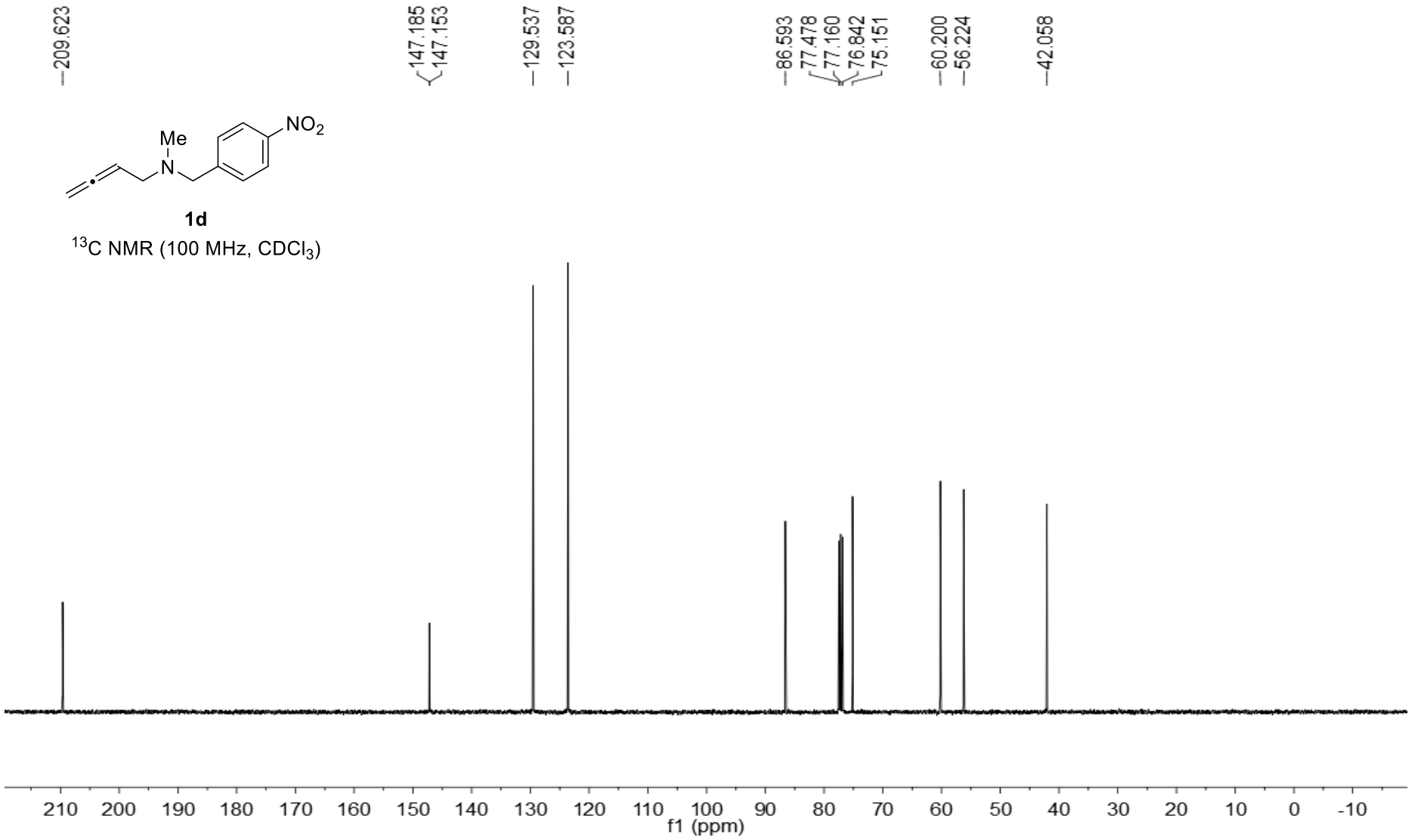
1c

^{13}C NMR (100 MHz, $CDCl_3$)



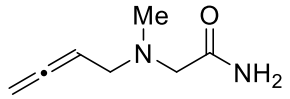
1d

^{1}H NMR (400 MHz, $CDCl_3$)



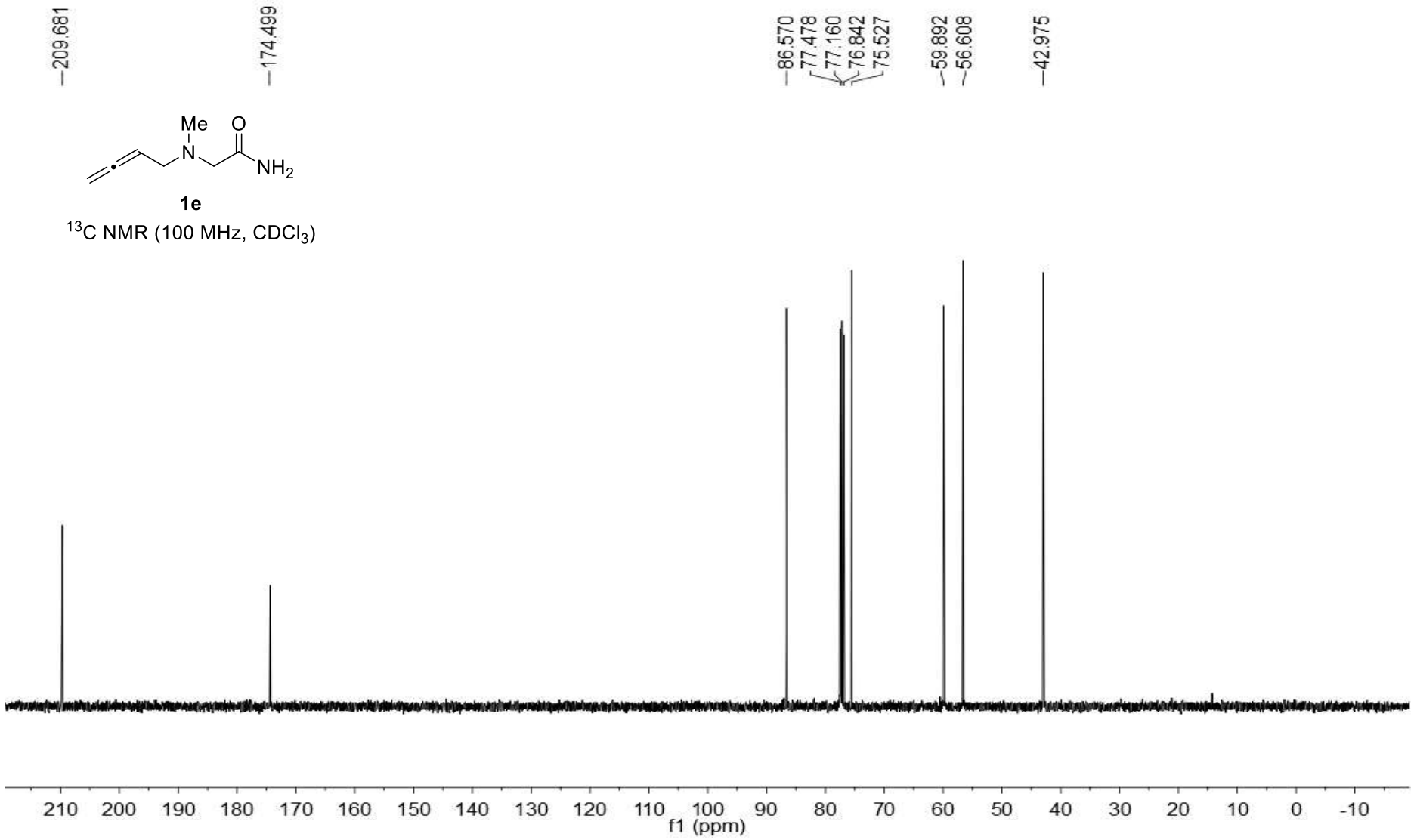
1d

^{13}C NMR (100 MHz, $CDCl_3$)



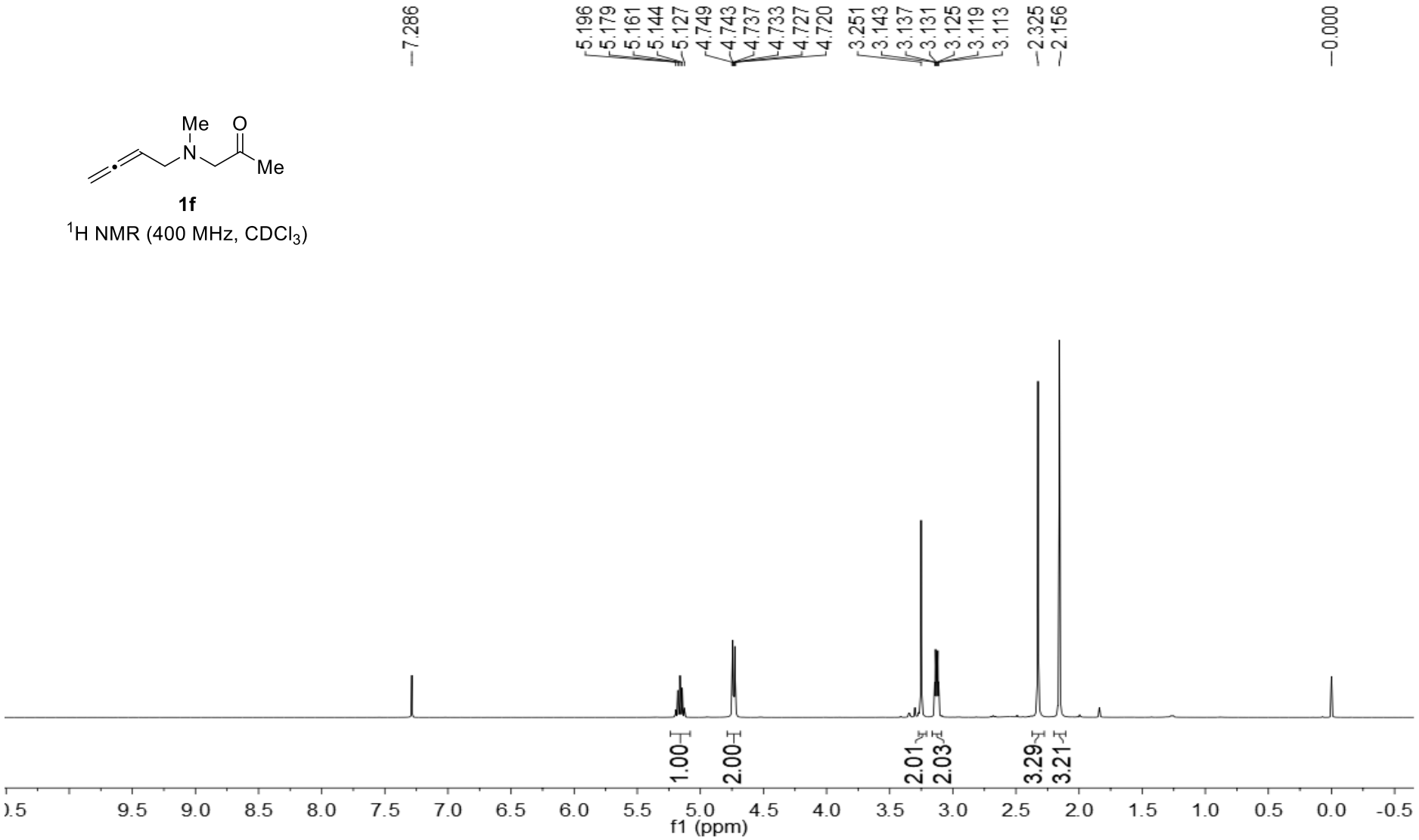
1e

^{1}H NMR (400 MHz, $CDCl_3$)



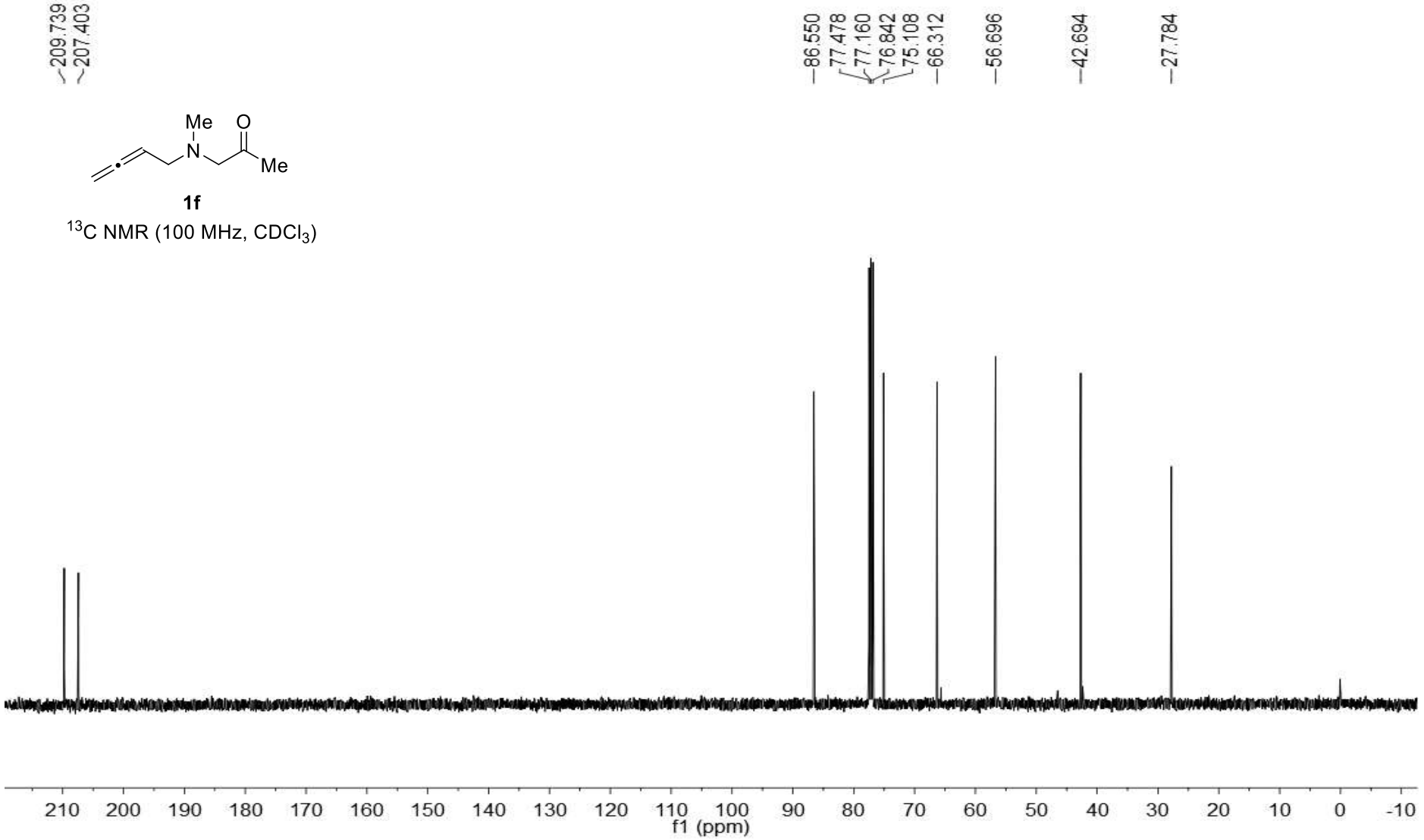
1e

^{13}C NMR (100 MHz, $CDCl_3$)



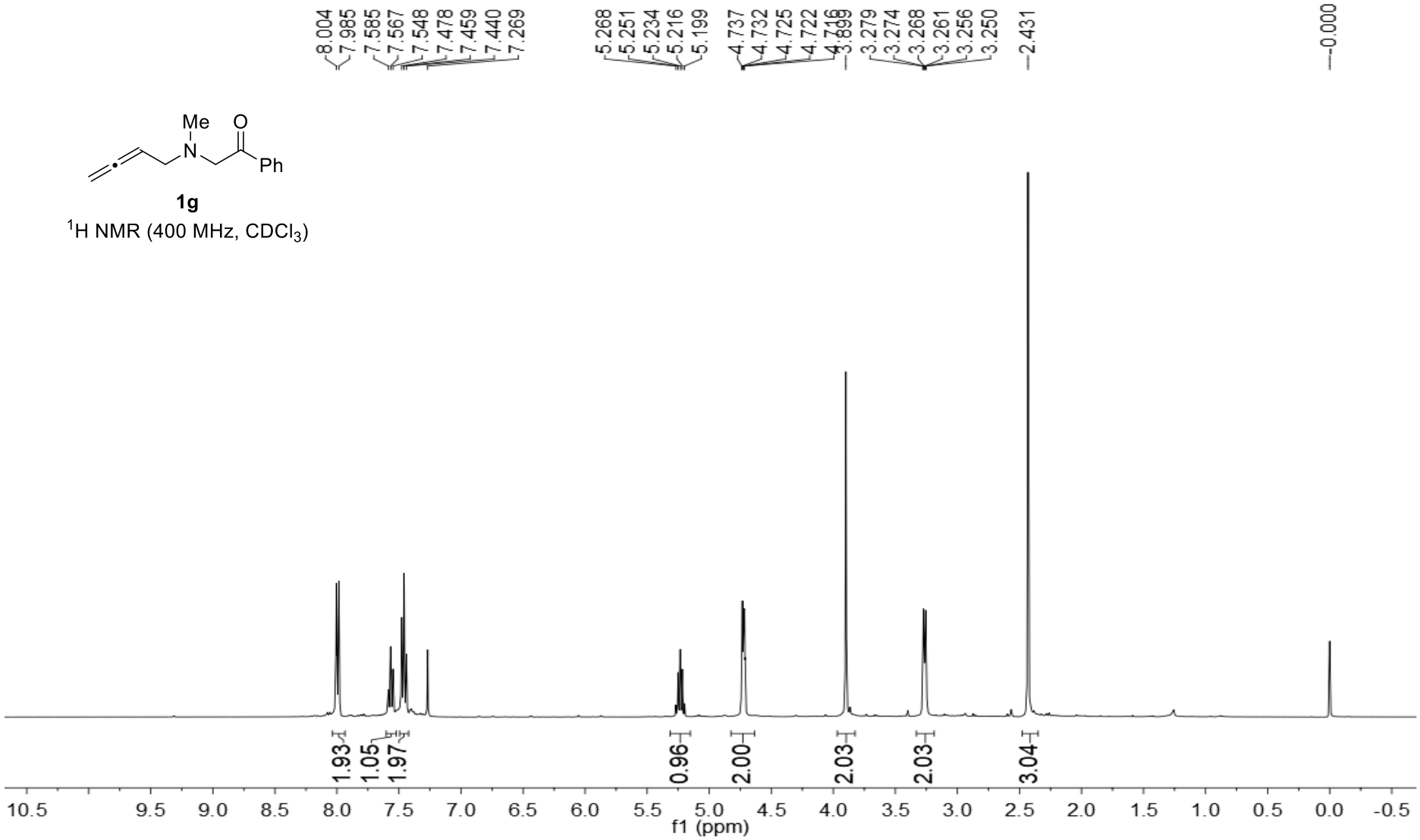
1f

^{1}H NMR (400 MHz, $CDCl_3$)



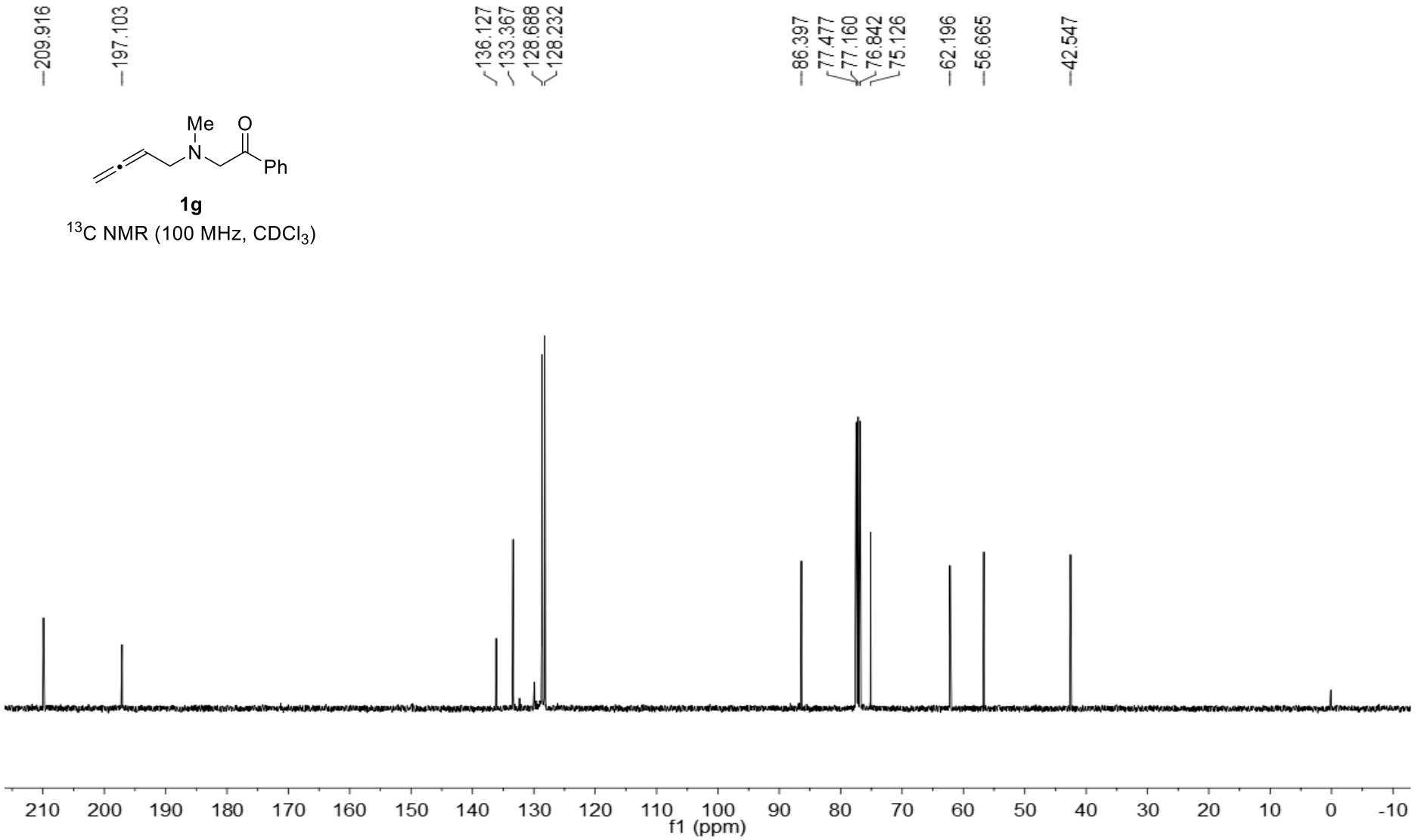
1f

^{13}C NMR (100 MHz, $CDCl_3$)



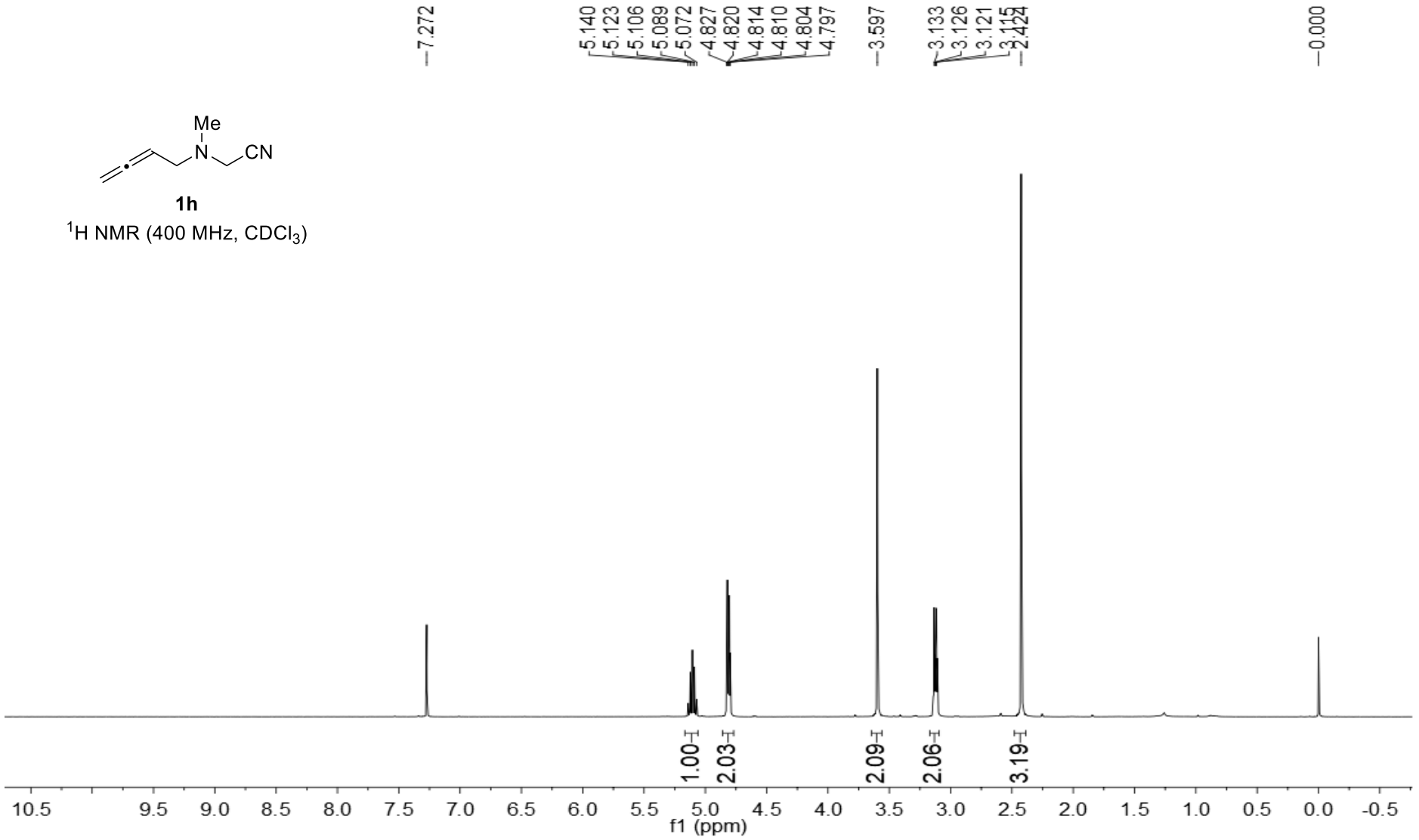
1g

^{1}H NMR (400 MHz, $CDCl_3$)



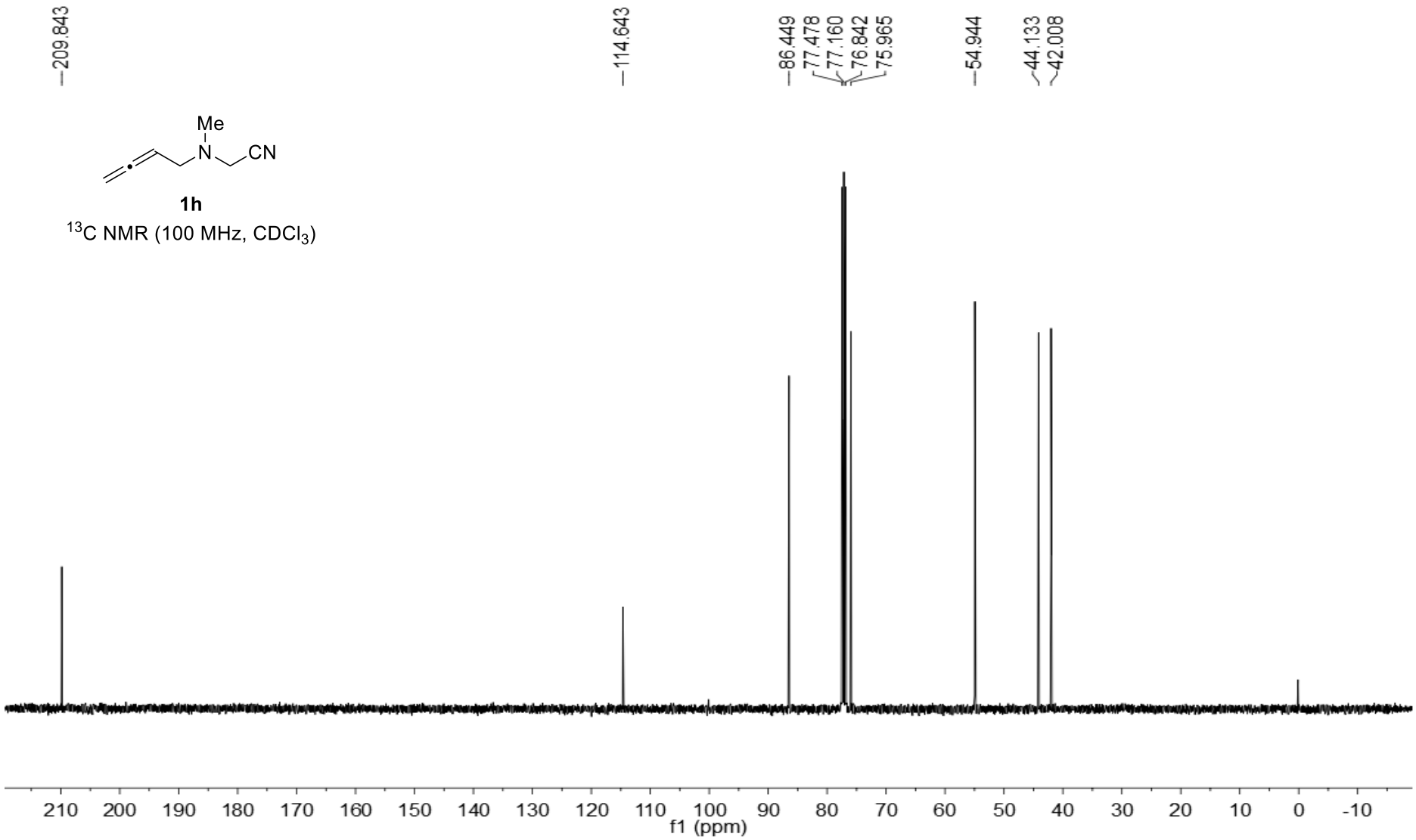
1g

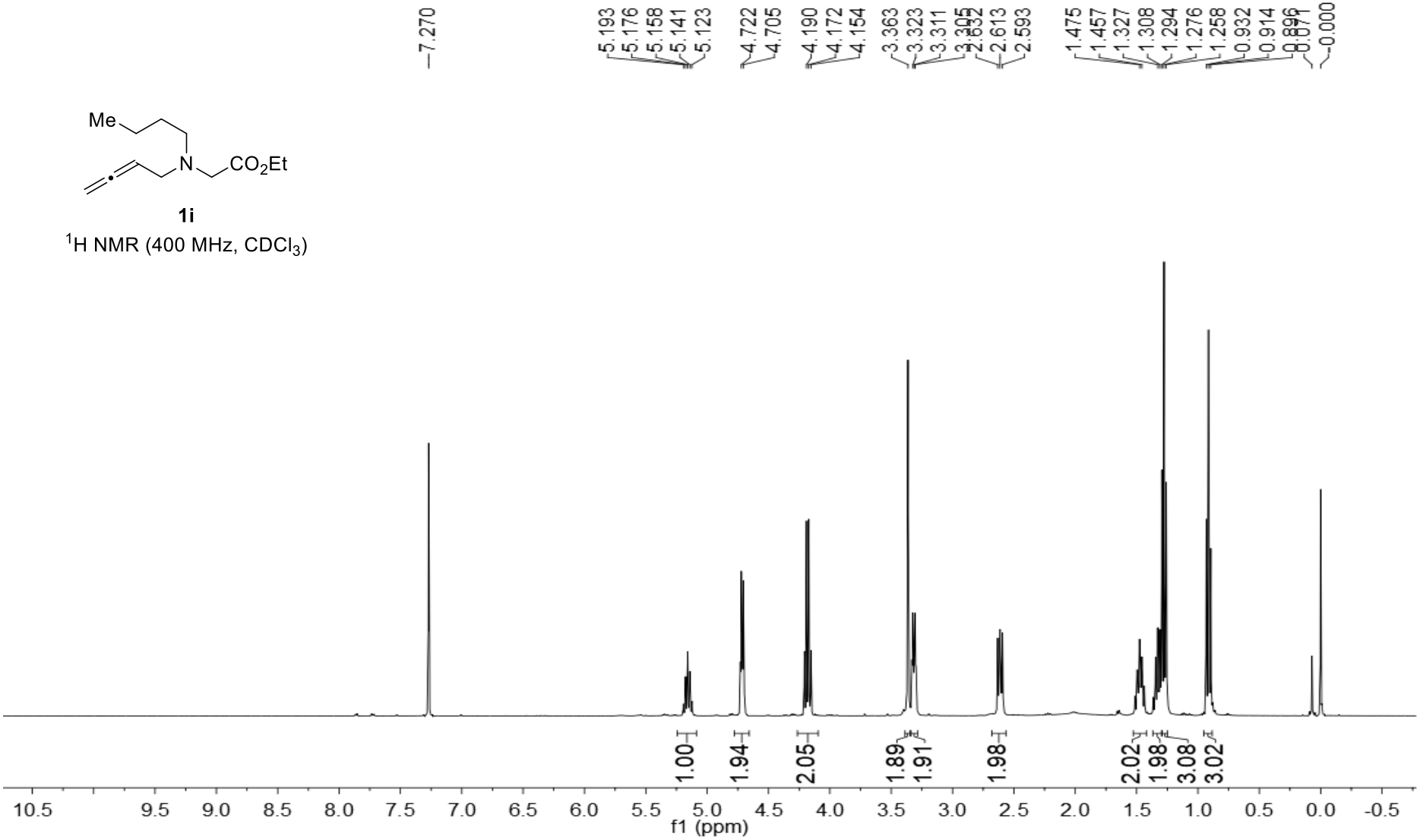
^{13}C NMR (100 MHz, $CDCl_3$)

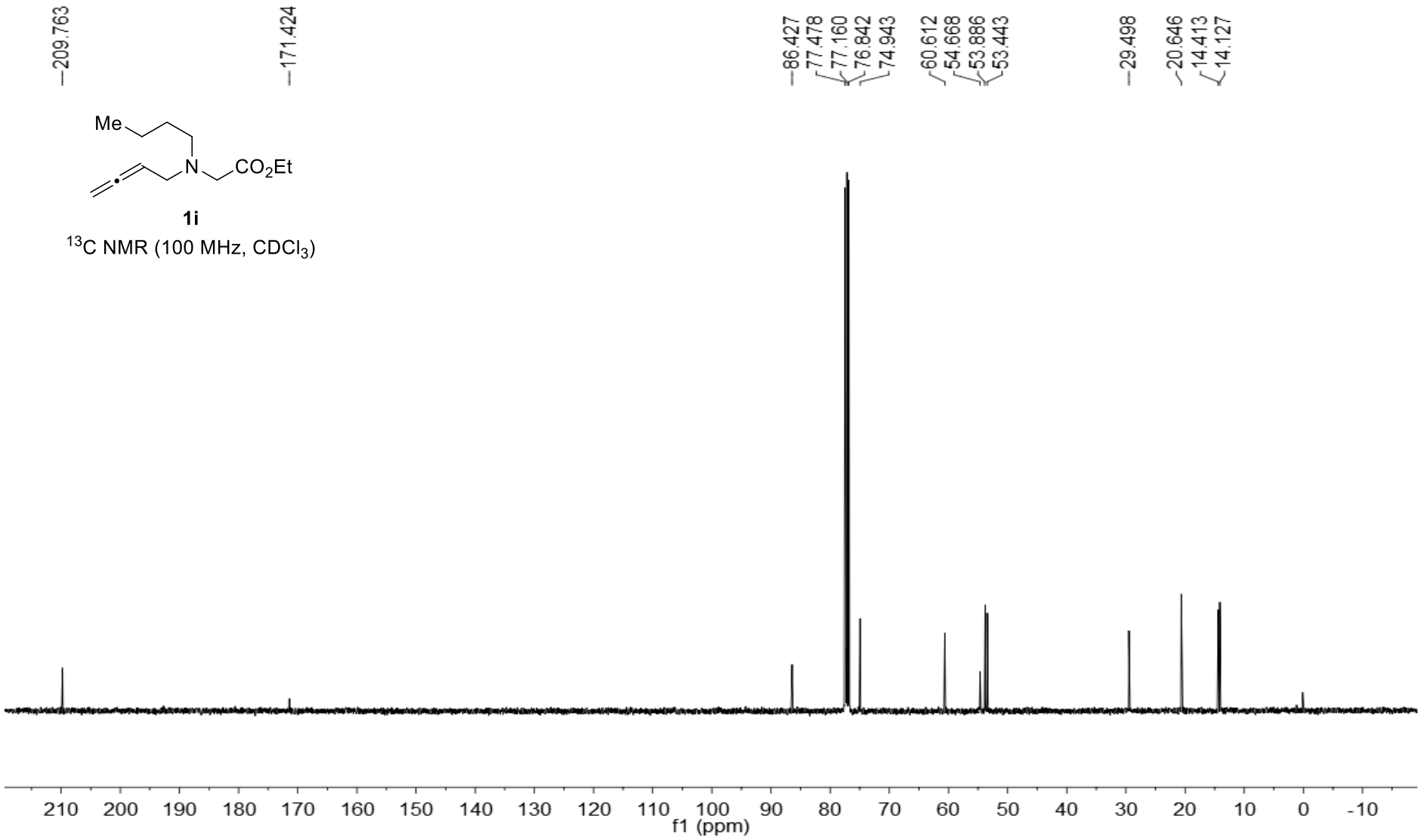


1h

^{1}H NMR (400 MHz, $CDCl_3$)

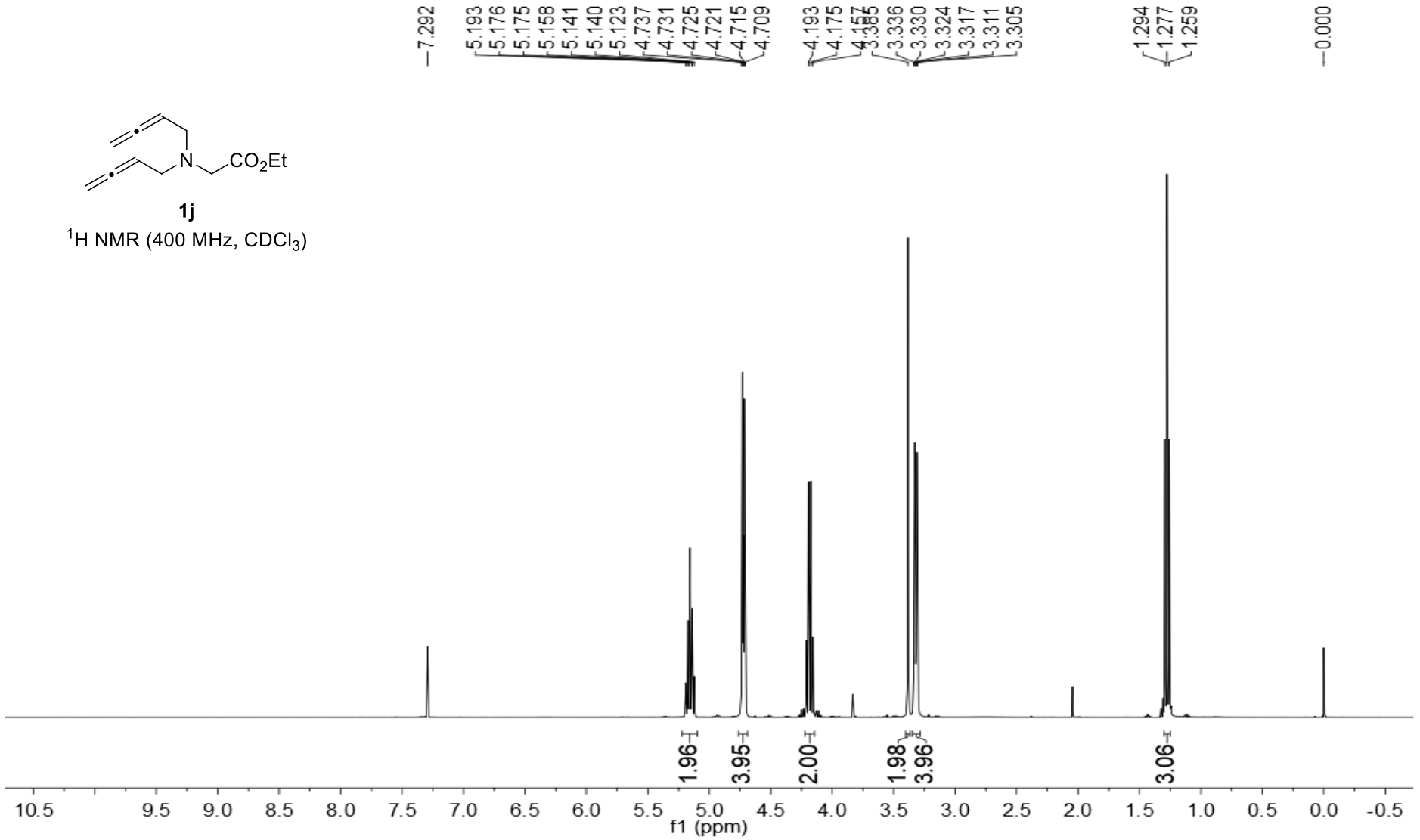

209.843
114.643
86.449
77.478
77.160
76.842
75.965
54.944
44.133
42.008
Me
N
CN
1h
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
N
CO2Et
1i
1H NMR (400 MHz, CDCl3)
7.270
5.193
5.176
5.158
5.141
5.123
4.722
4.705
4.190
4.172
4.154
3.363
3.323
3.311
2.613
2.593
1.475
1.457
1.327
1.308
1.294
1.276
1.258
0.932
0.914
0.000
1.00
1.94
2.05
1.89
1.91
1.98
2.02
1.98
3.08
3.02
f1 (ppm)



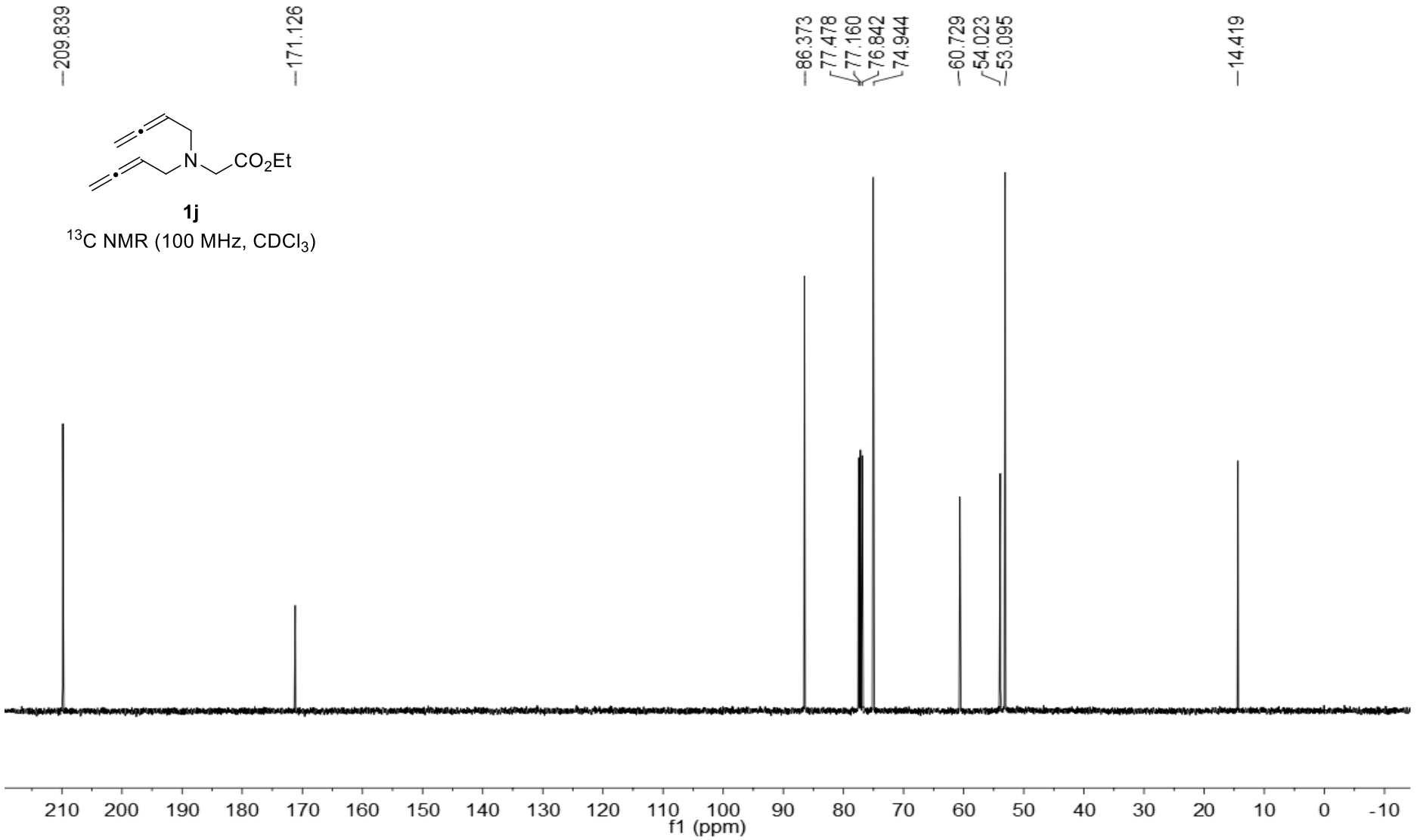
1i

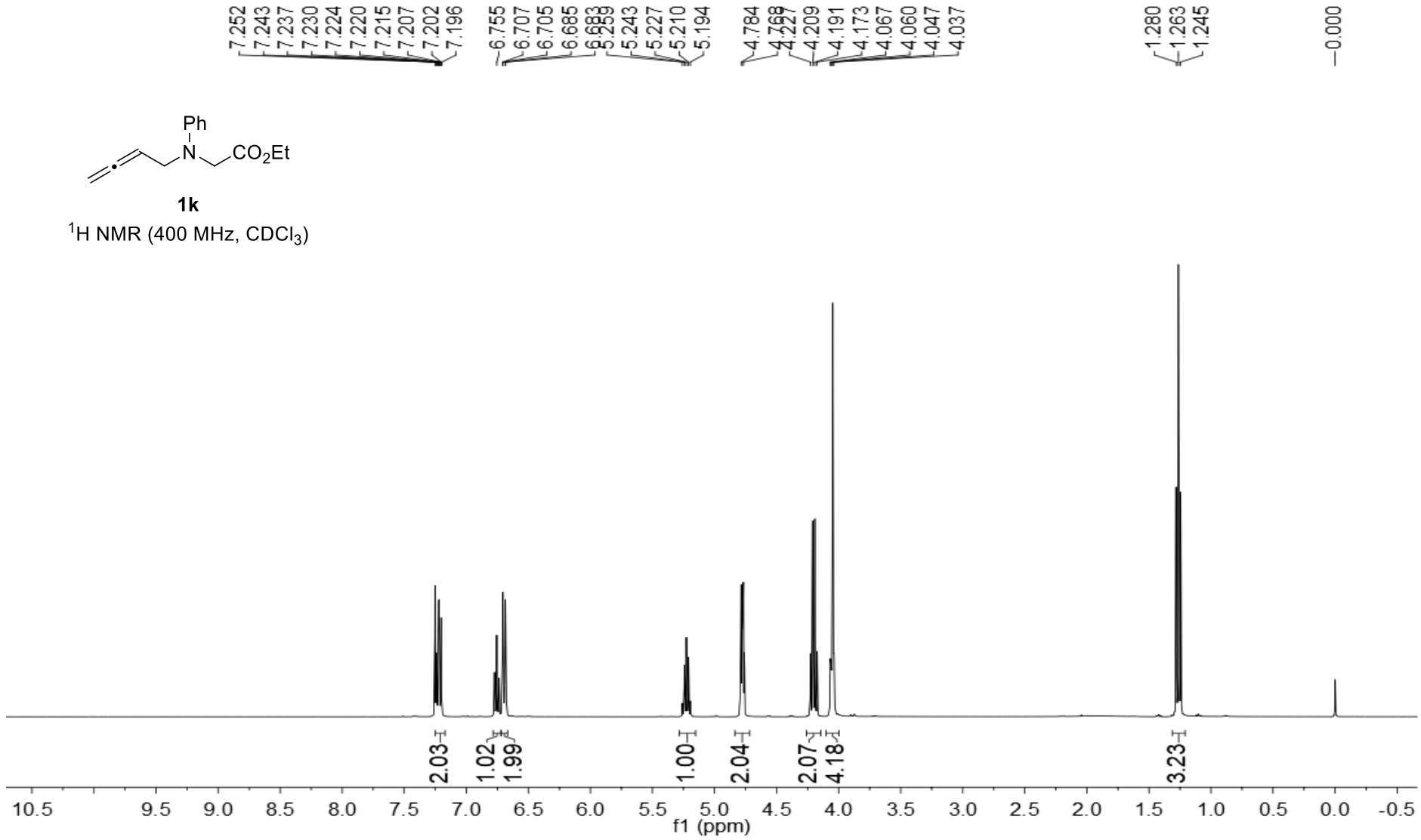
^{13}C NMR (100 MHz, $CDCl_3$)



1j

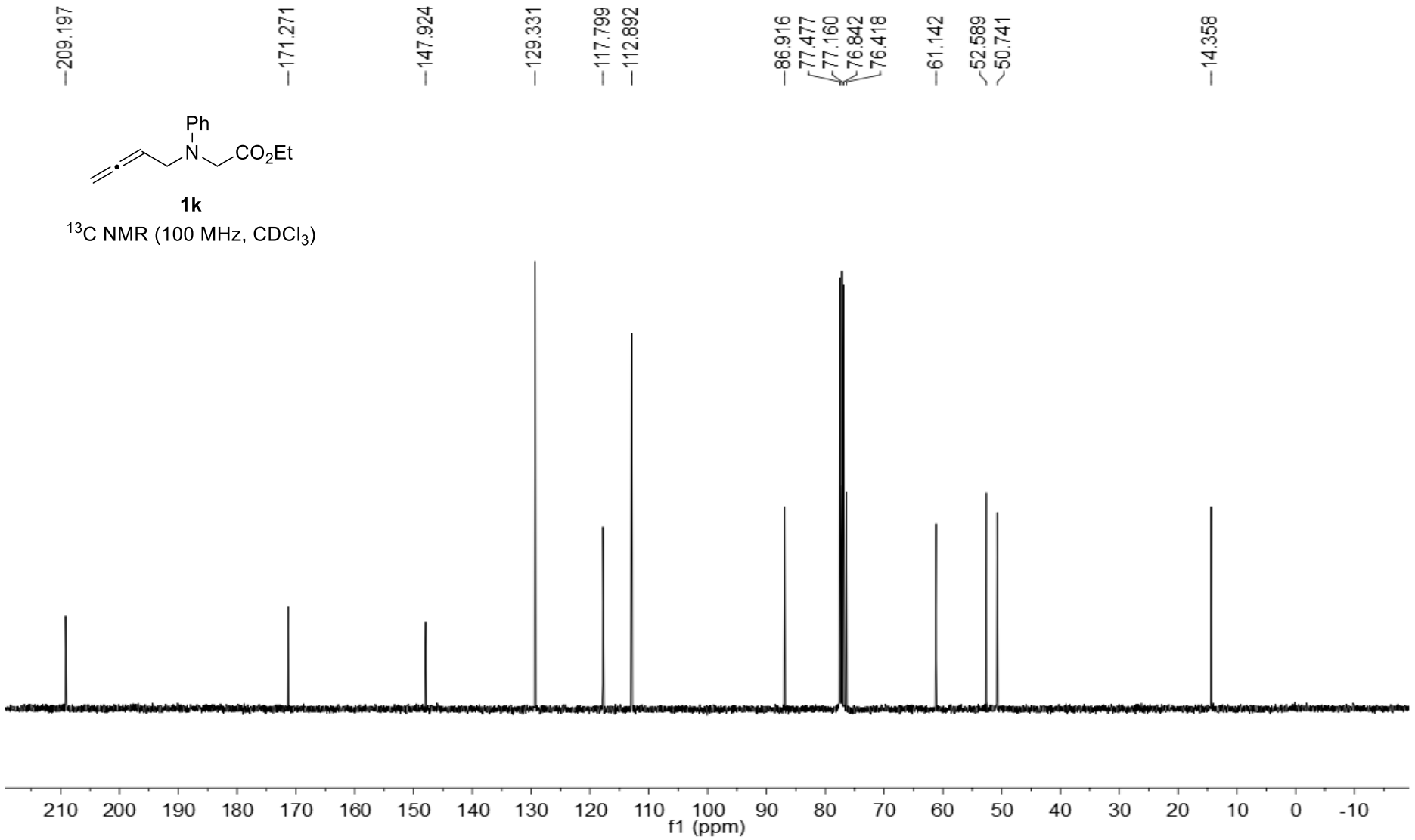
^{1}H NMR (400 MHz, $CDCl_3$)

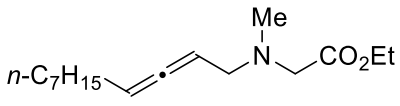

209.839
171.126
86.373
77.478
77.160
76.842
74.944
60.729
54.023
53.095
14.419
N
CO2Et
1j
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



1k

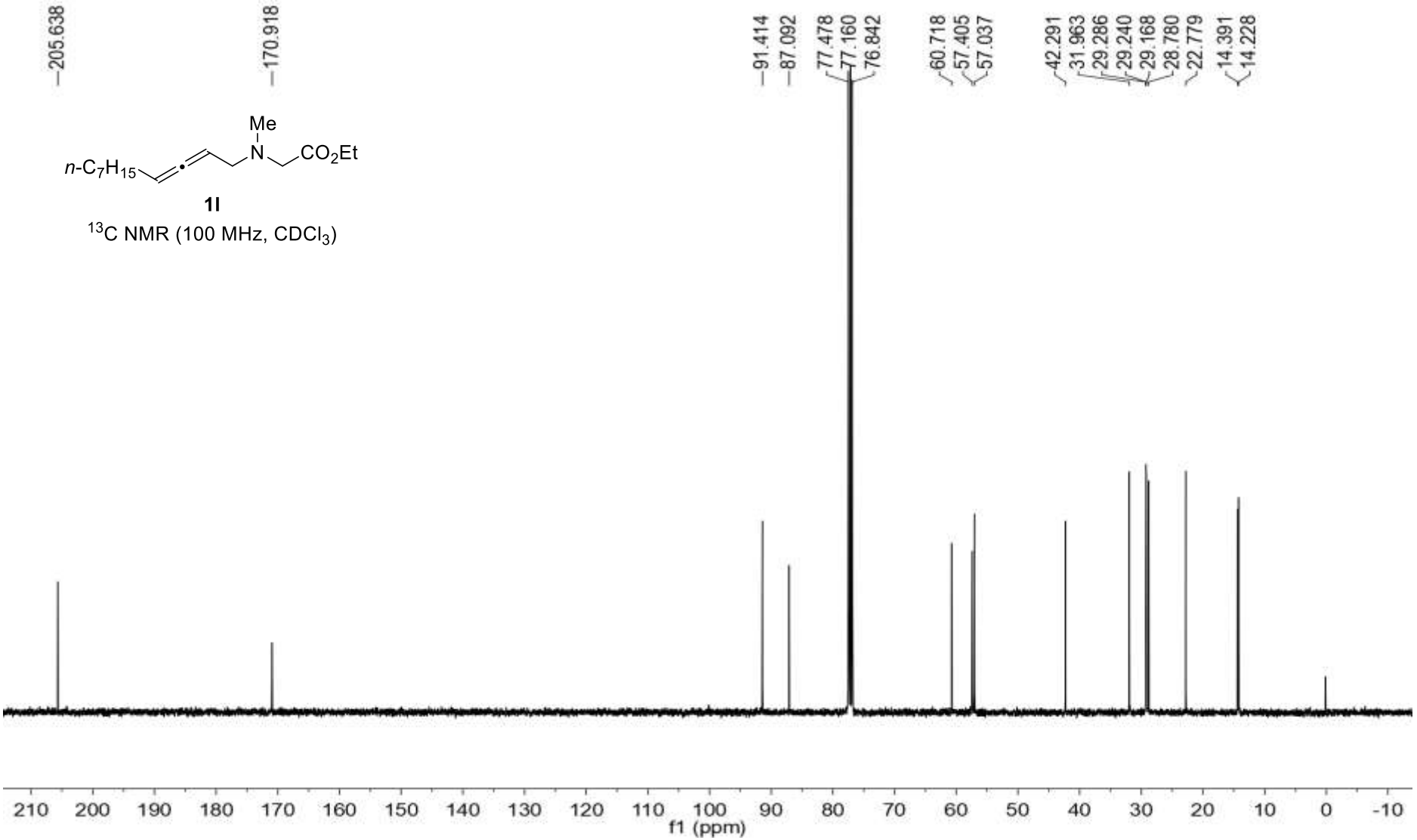
^{1}H NMR (400 MHz, $CDCl_3$)


209.197
171.271
147.924
129.331
117.799
112.892
86.916
77.477
77.160
76.842
76.418
61.142
52.589
50.741
14.358
Ph
N
CO2Et
1k
13C NMR (100 MHz, 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)



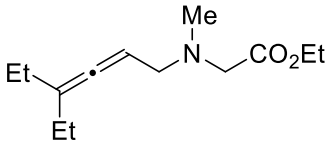
1l

^{1}H NMR (400 MHz, $CDCl_3$)



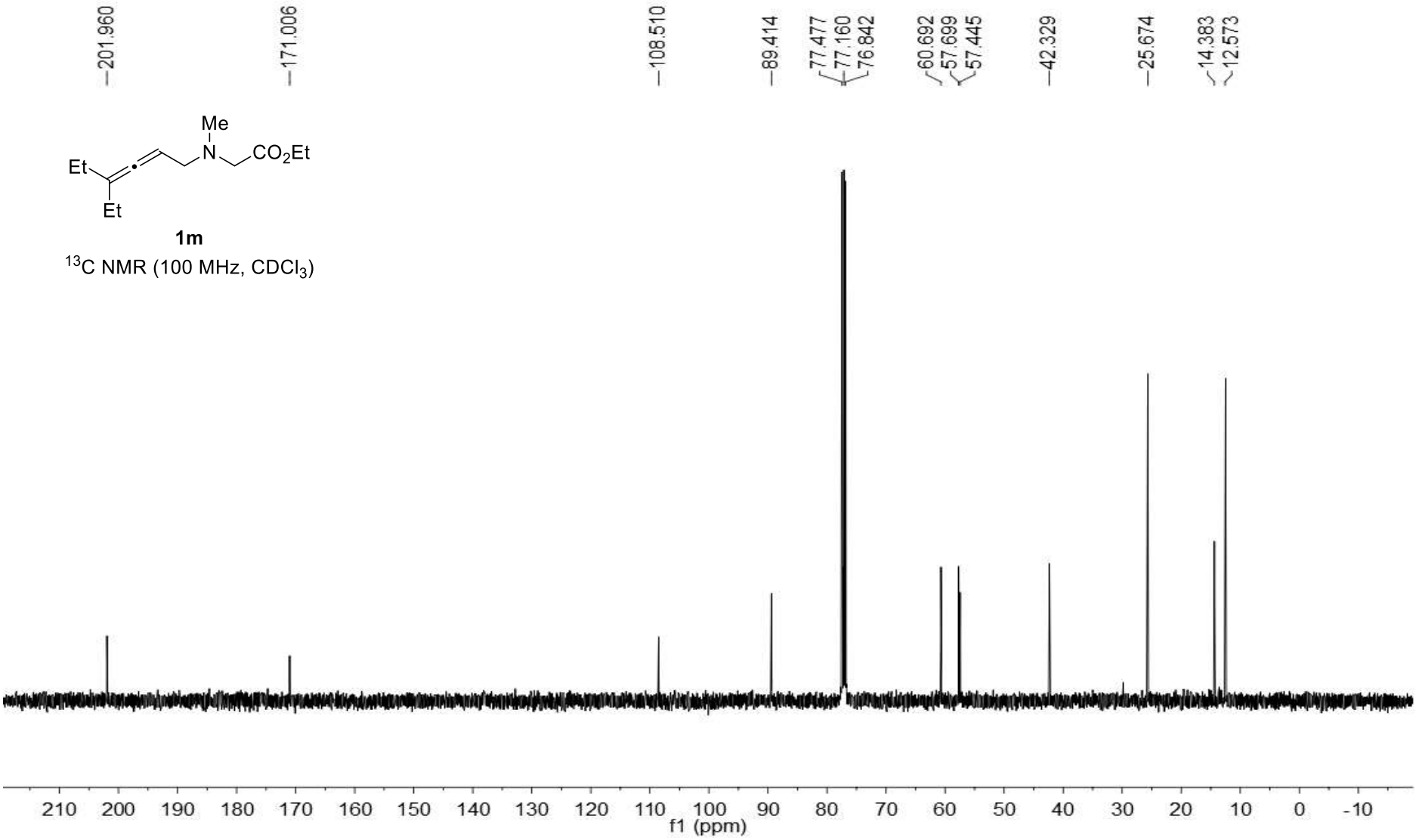
1l

^{13}C NMR (100 MHz, $CDCl_3$)



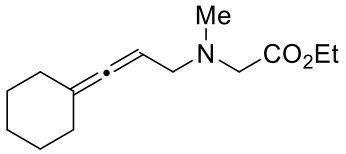
1m

^{1}H NMR (400 MHz, $CDCl_3$)



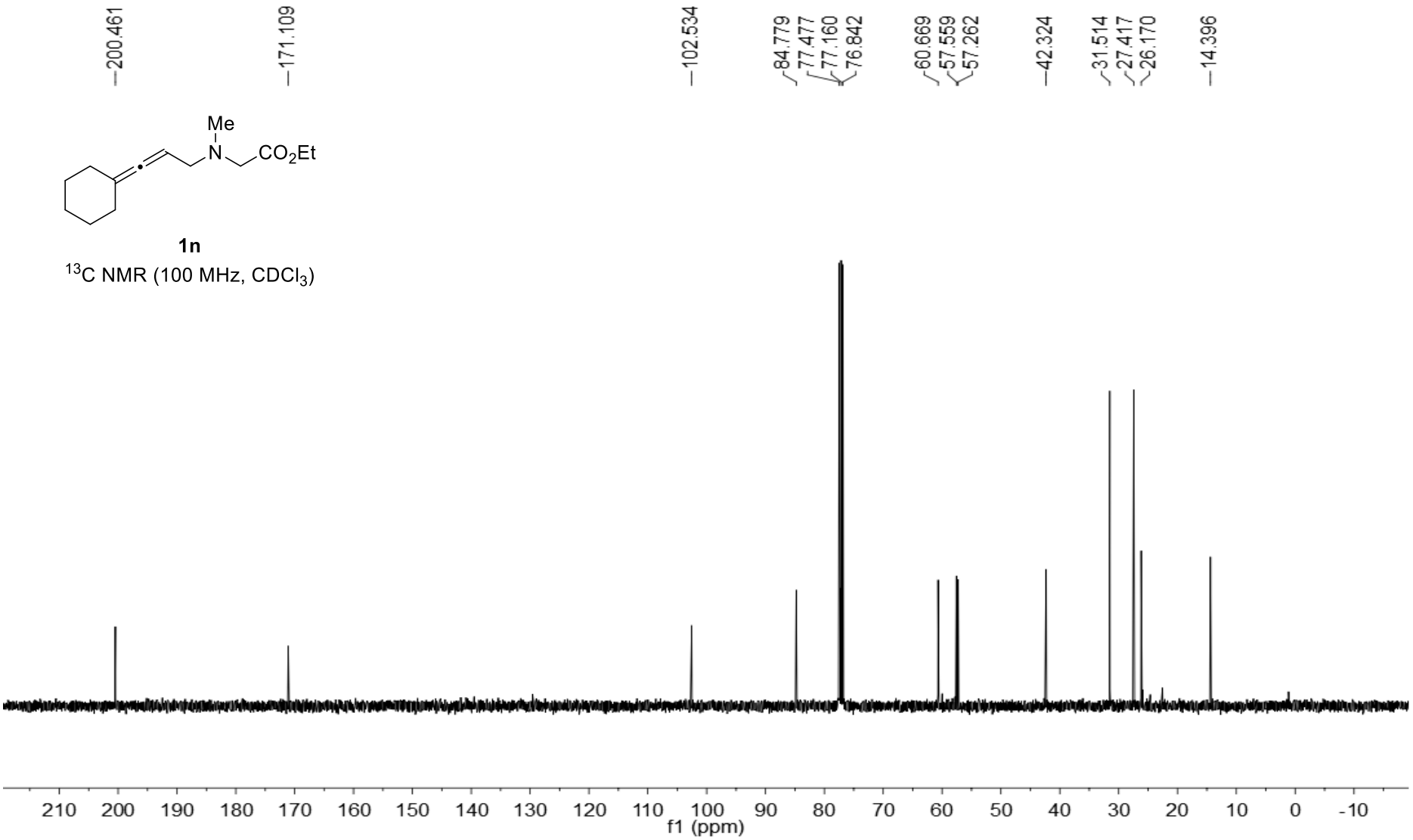
1m

^{13}C NMR (100 MHz, $CDCl_3$)



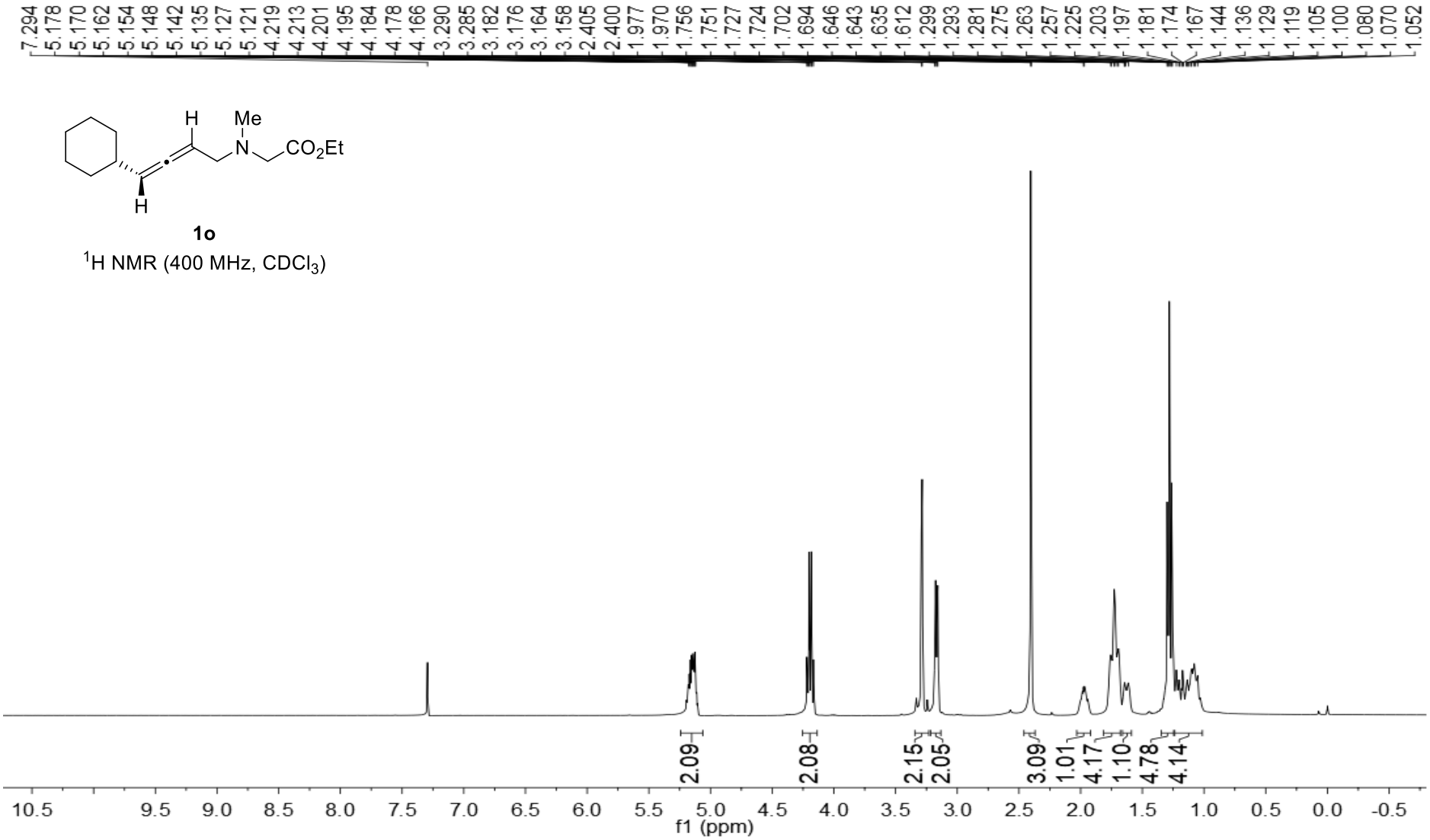
1n

^{1}H NMR (400 MHz, $CDCl_3$)



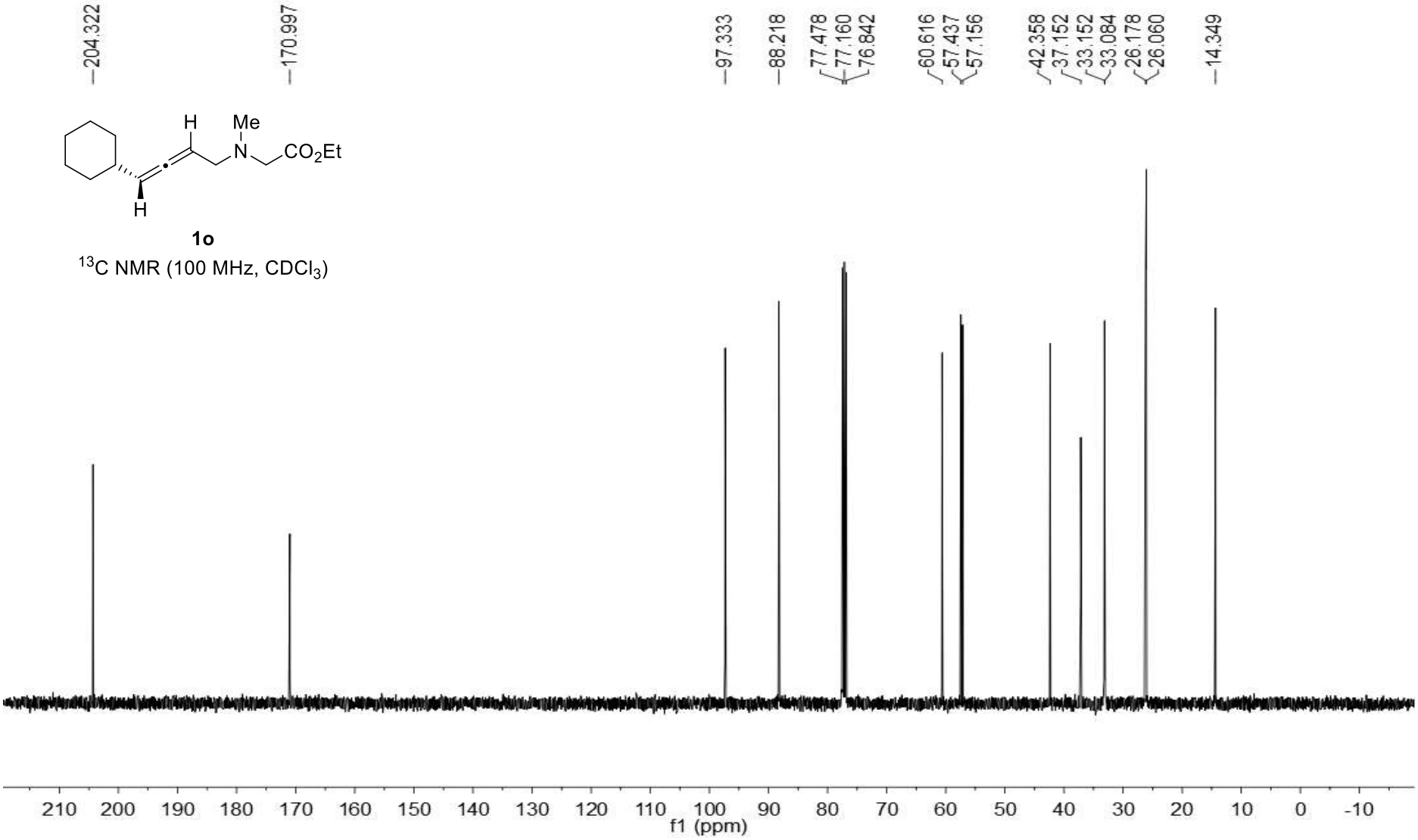
1n

^{13}C NMR (100 MHz, $CDCl_3$)



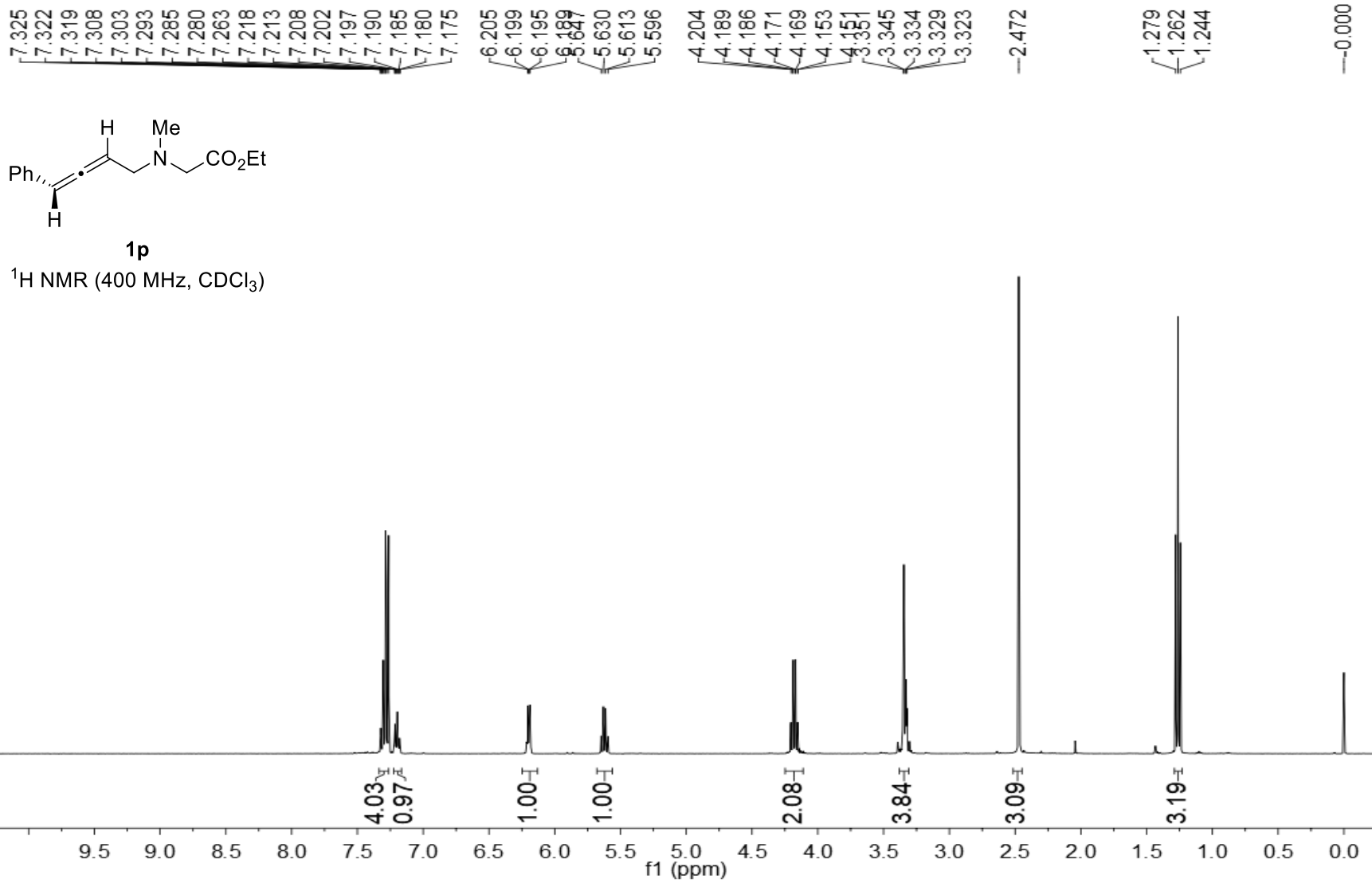
1o

^{1}H NMR (400 MHz, $CDCl_3$)



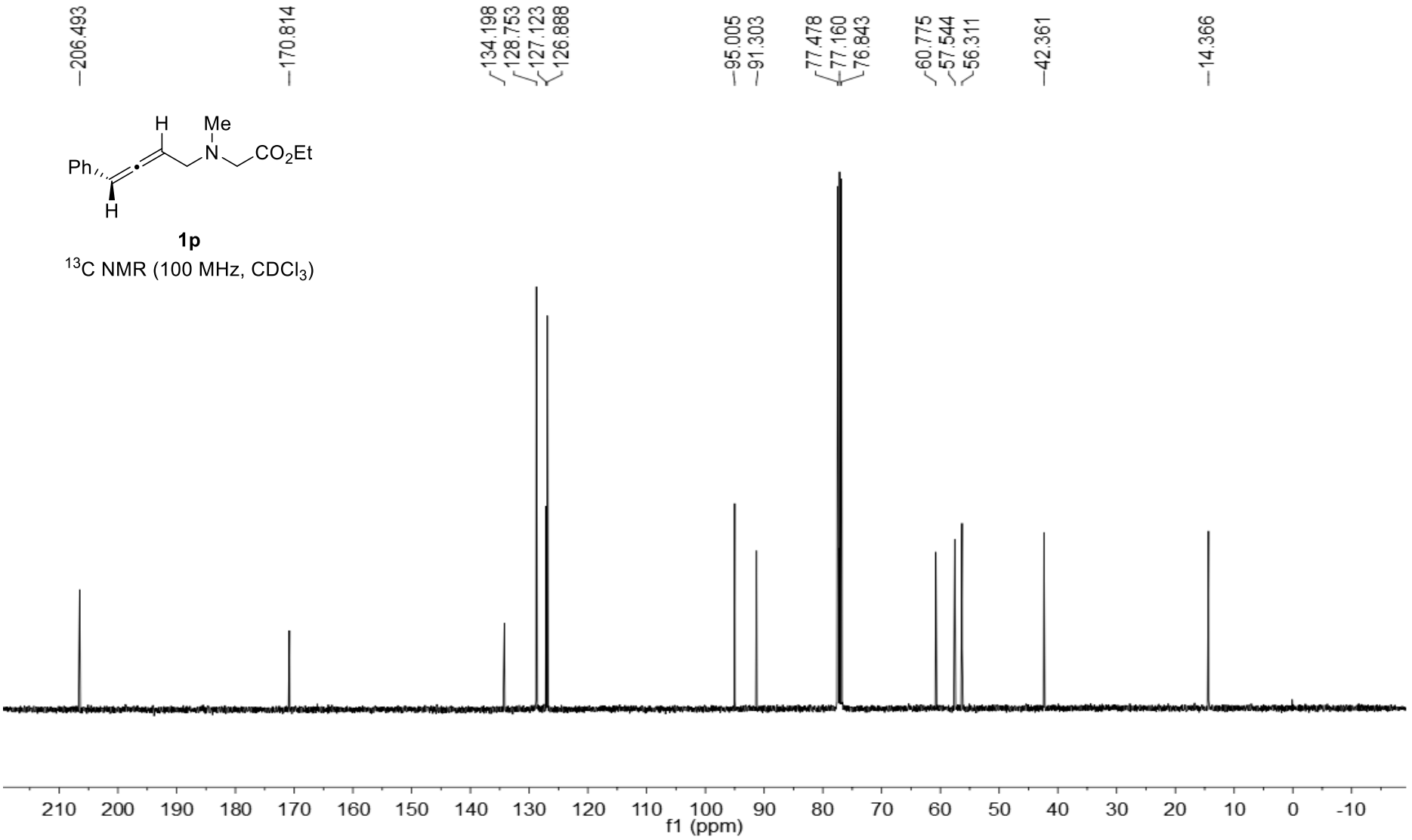
1o

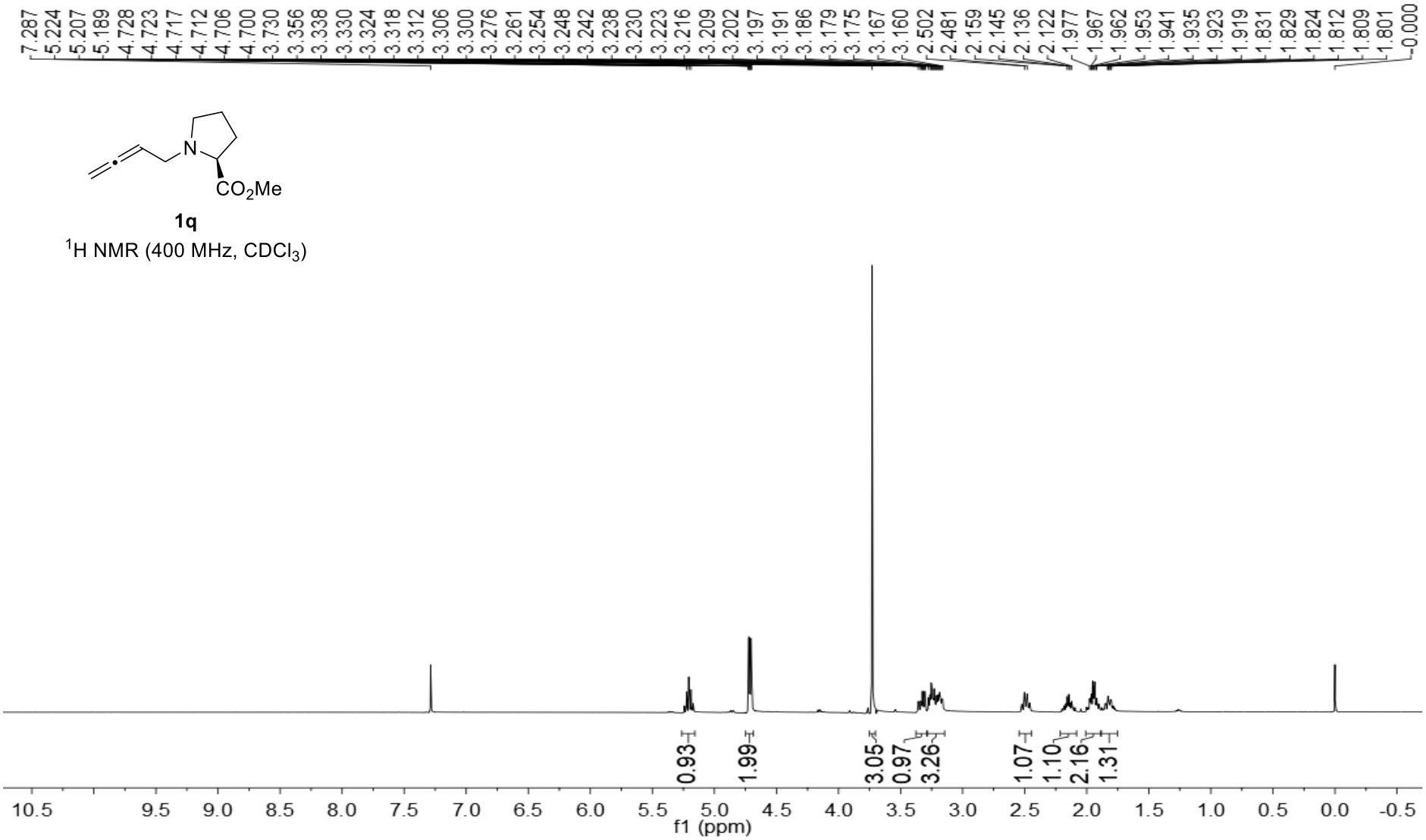
^{13}C NMR (100 MHz, $CDCl_3$)



1p

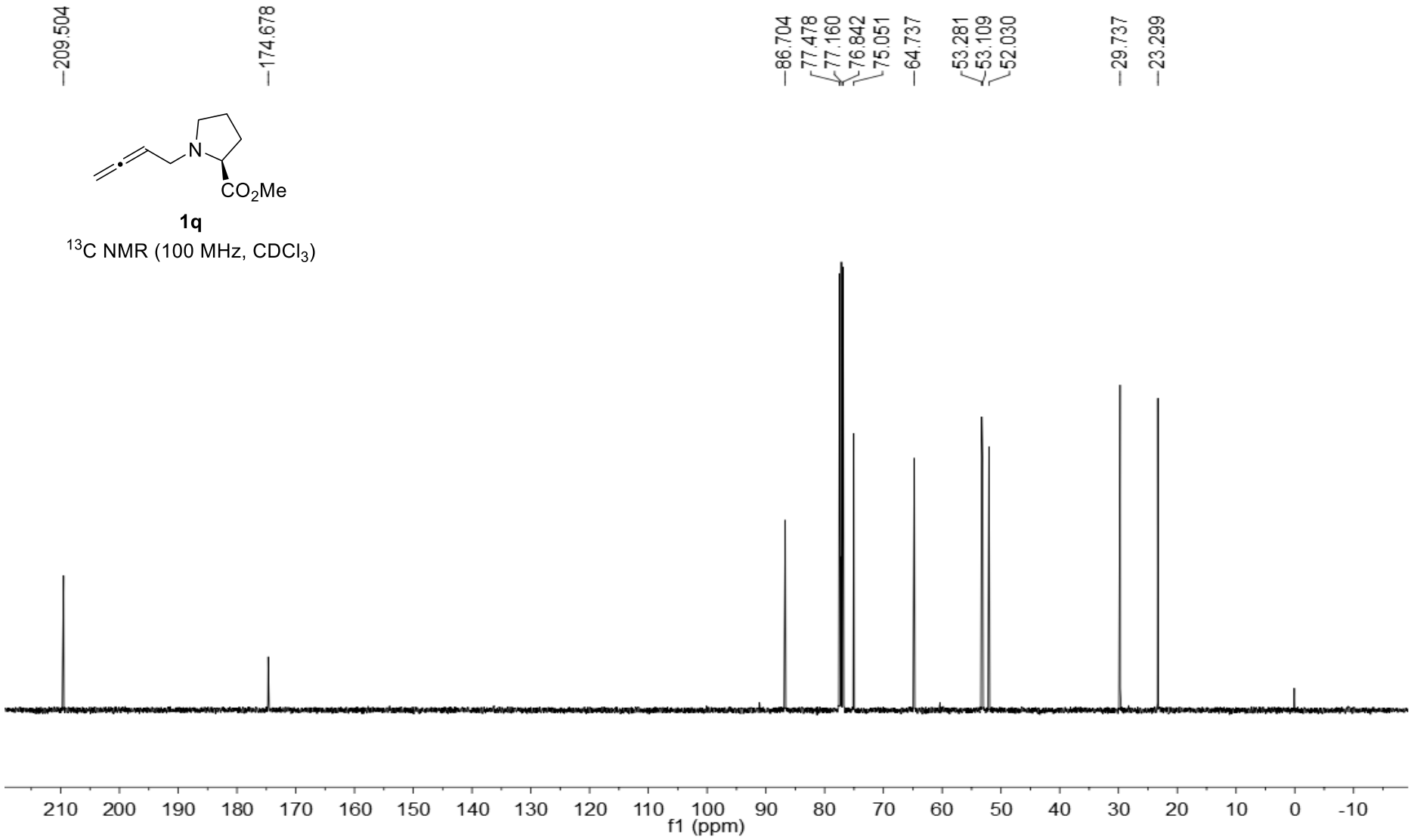
^{1}H NMR (400 MHz, $CDCl_3$)


206.493
170.814
134.198
128.753
127.123
126.888
95.005
91.303
77.478
77.160
76.843
60.775
57.544
56.311
42.361
14.366
H
Me
N
CO2Et
Ph
H
1p
13C NMR (100 MHz, 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)



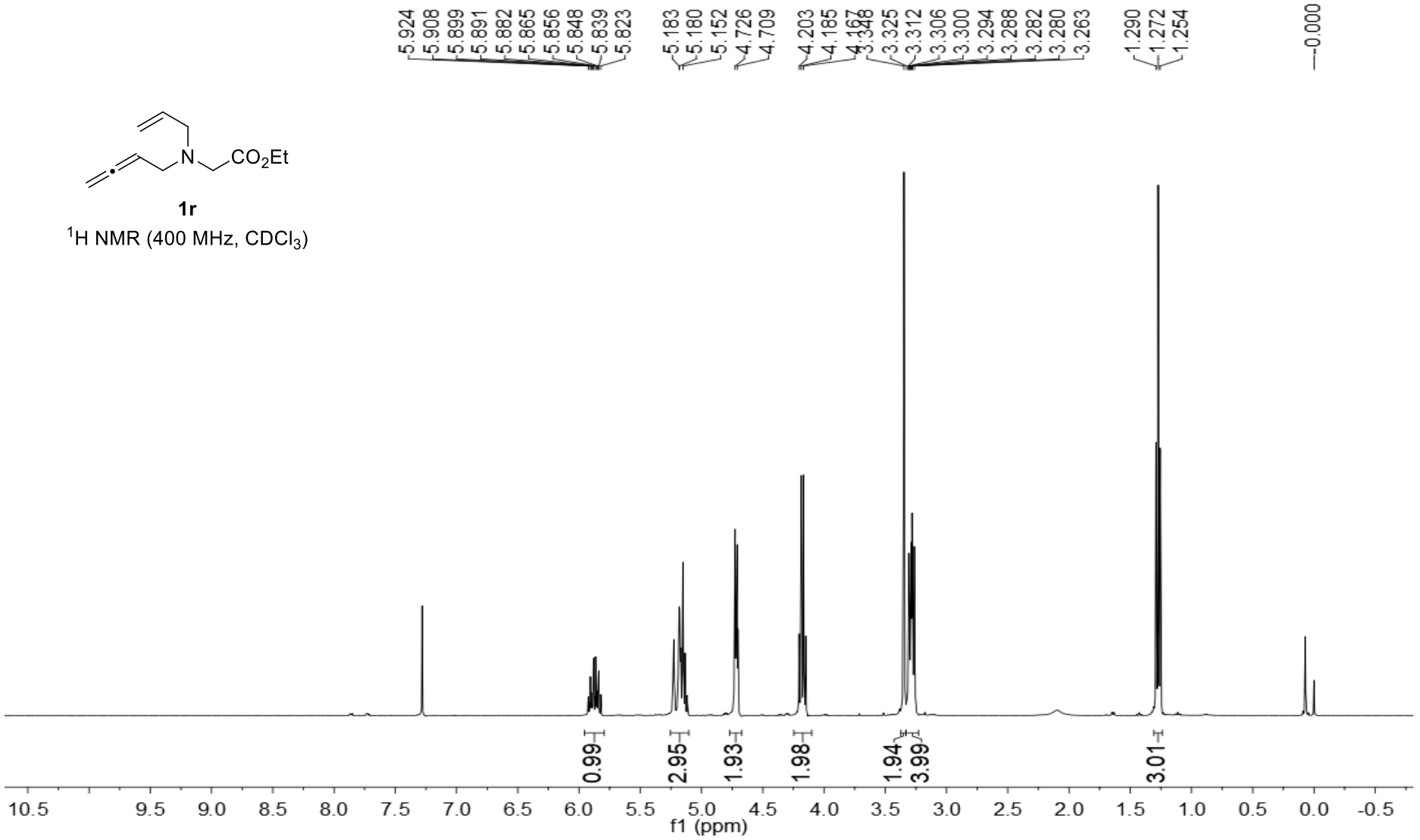
1q

^{1}H NMR (400 MHz, $CDCl_3$)



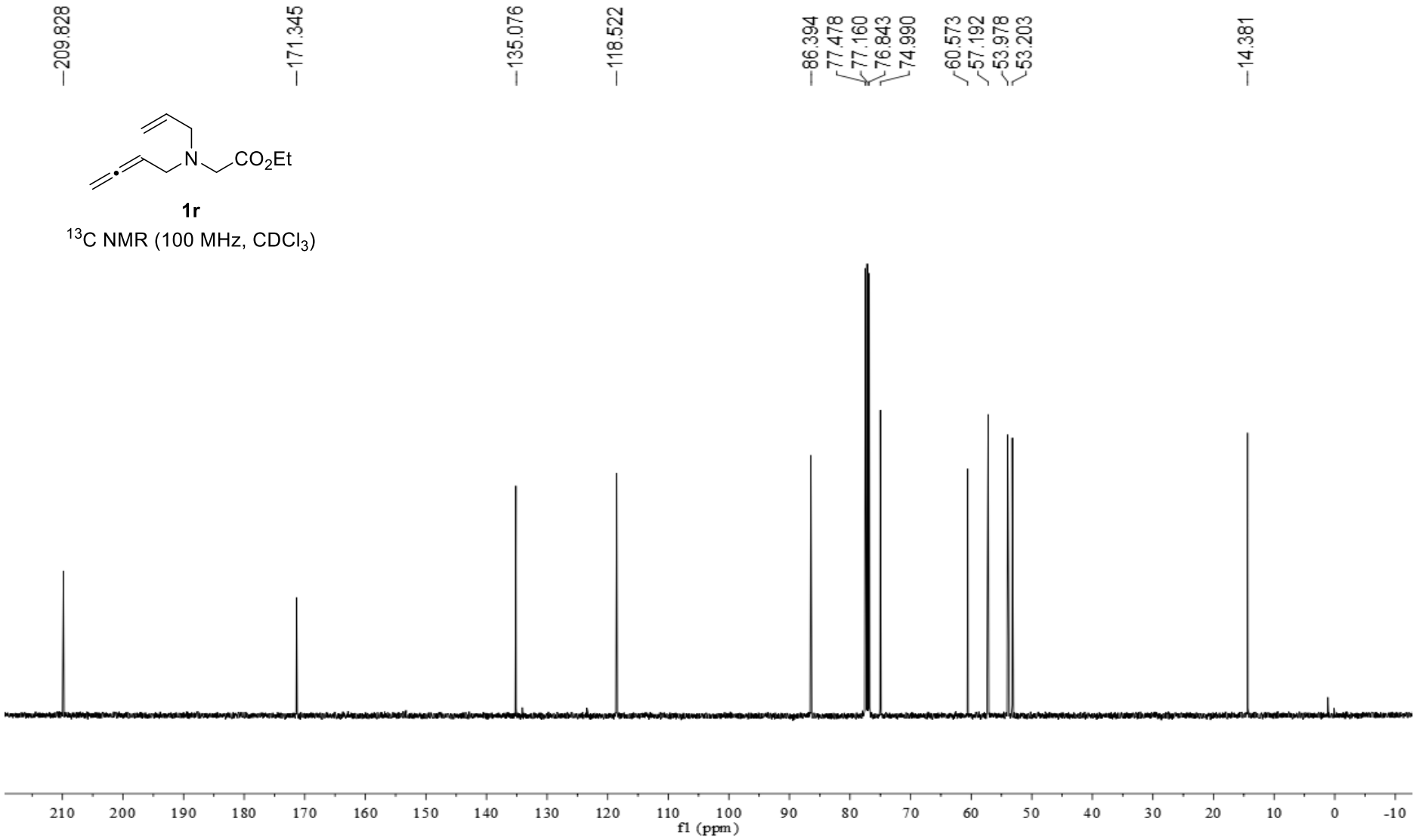
1q

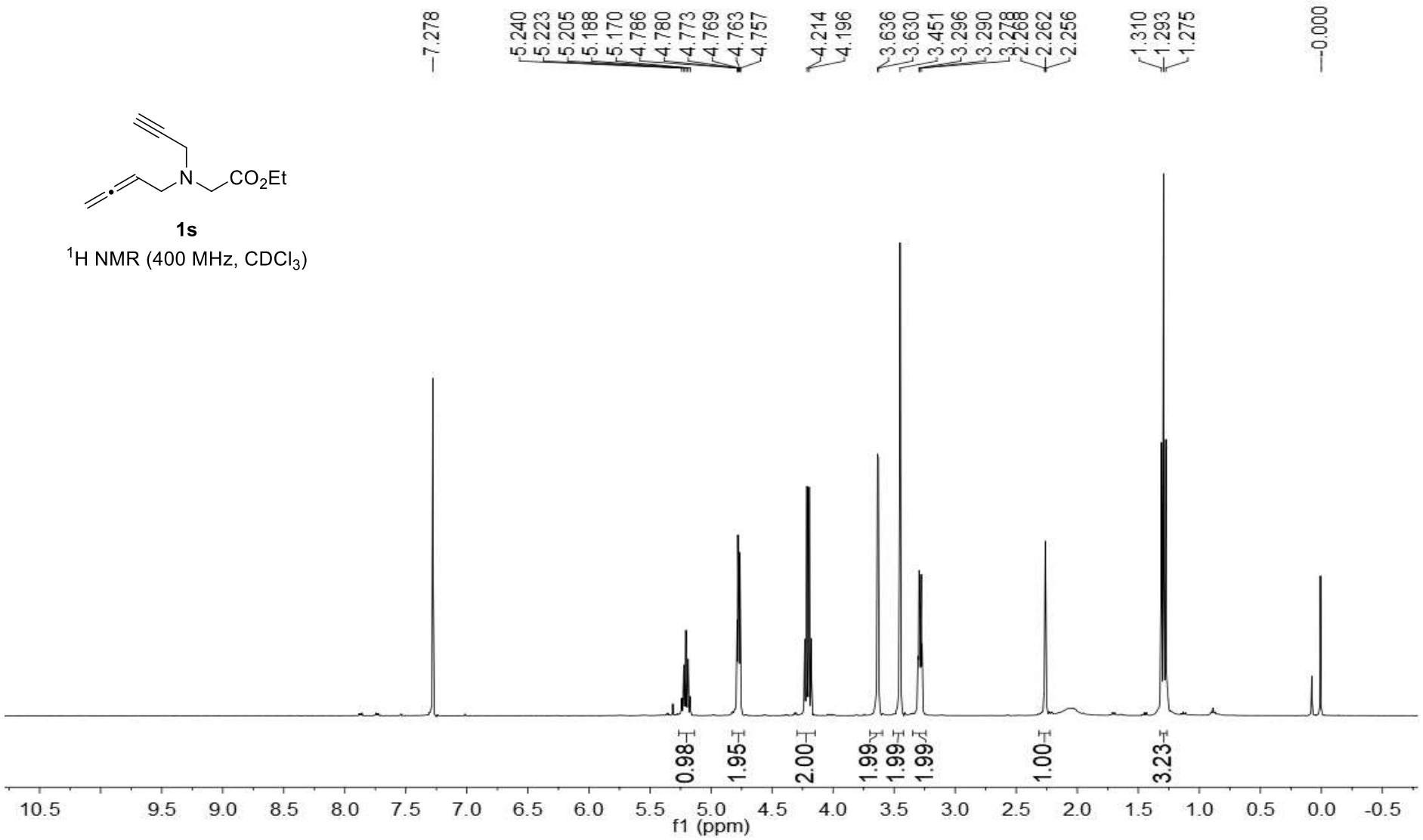
^{13}C NMR (100 MHz, $CDCl_3$)



1r

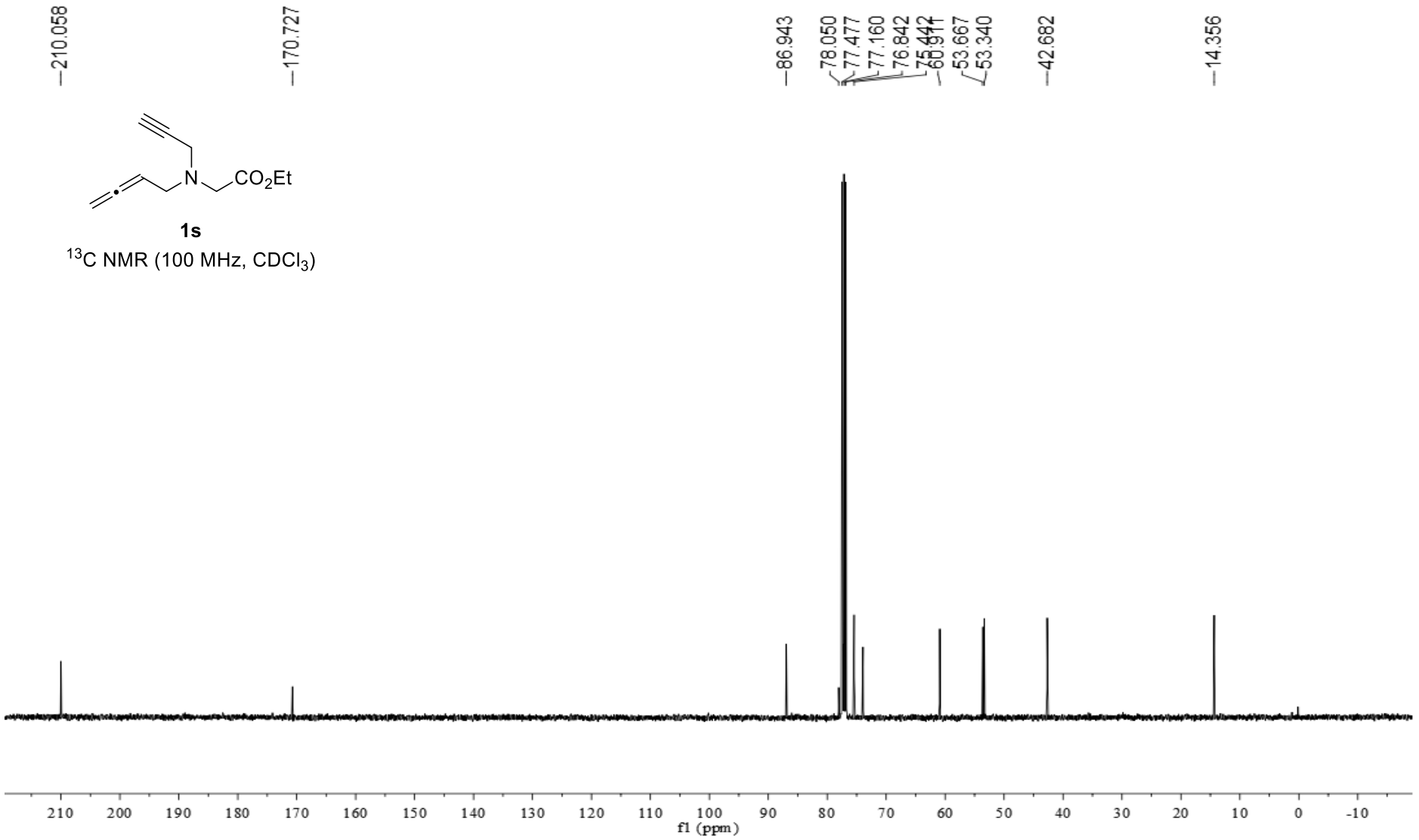
^{1}H NMR (400 MHz, $CDCl_3$)


209.828
171.345
135.076
118.522
86.394
77.478
77.160
76.843
74.990
60.573
57.192
53.978
53.203
14.381
N
CO2Et
1r
13C NMR (100 MHz, 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)



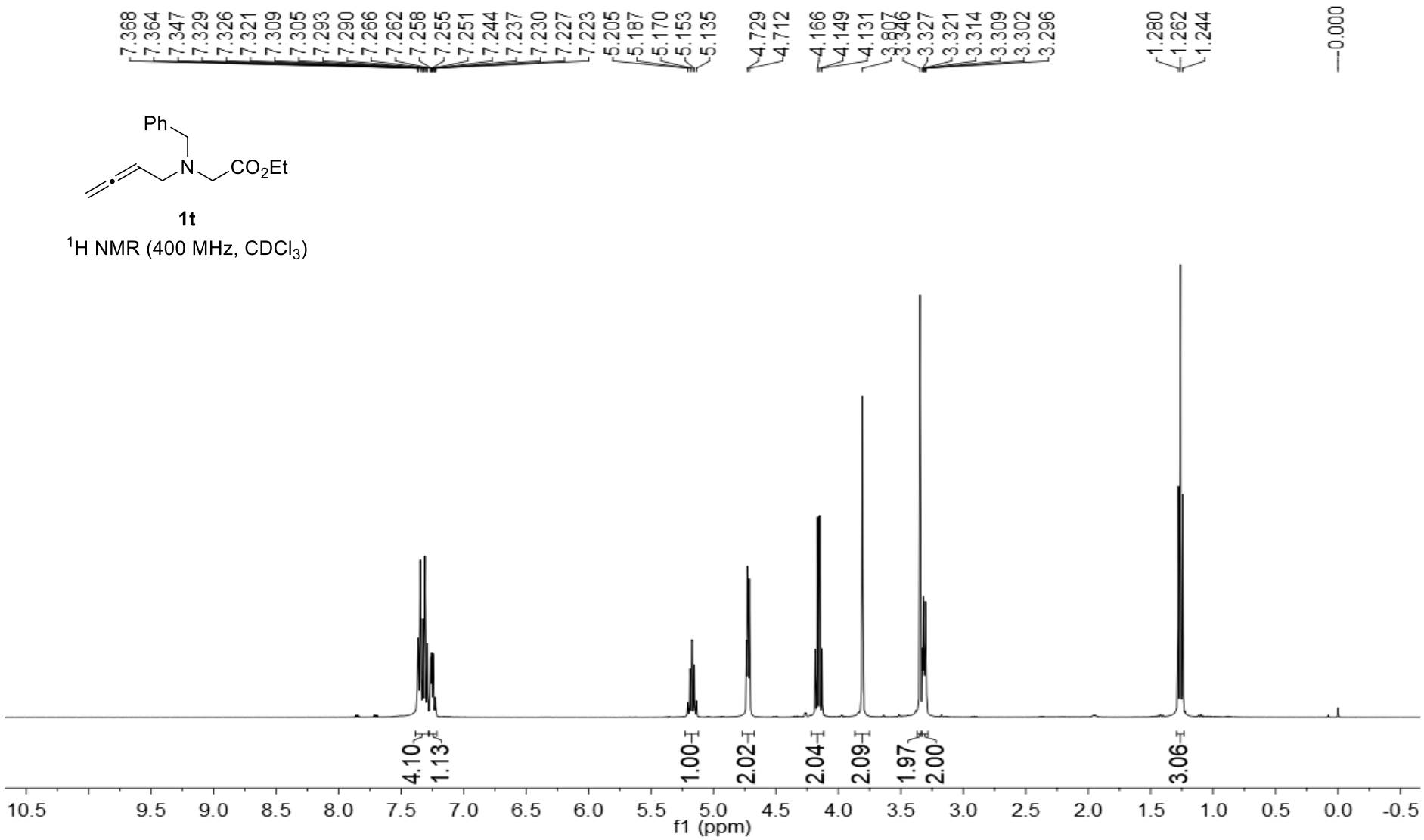
1s

^{1}H NMR (400 MHz, $CDCl_3$)



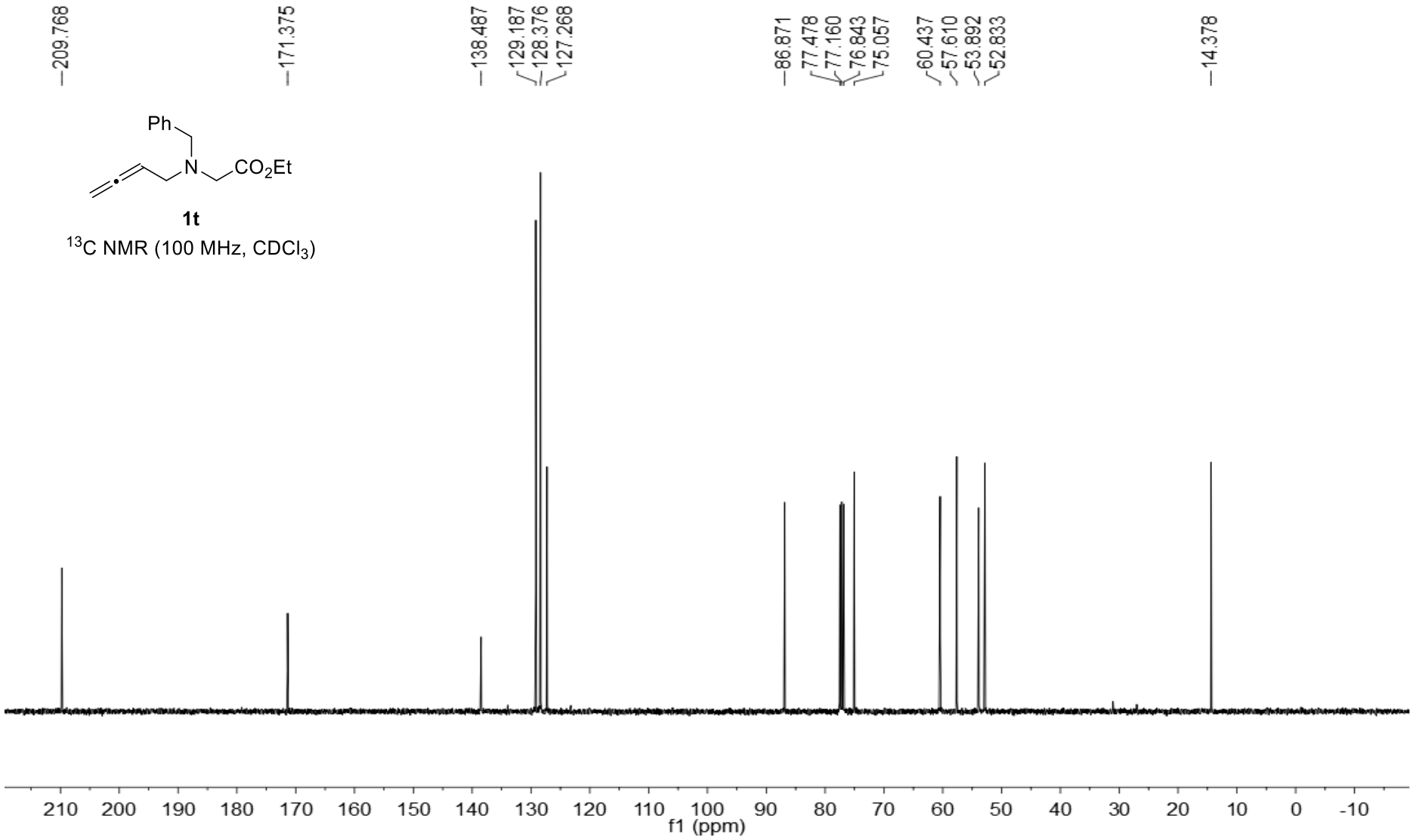
1s

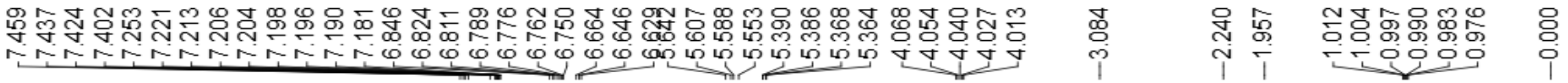
^{13}C NMR (100 MHz, $CDCl_3$)

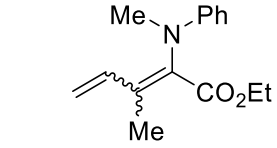


1t

^{1}H NMR (400 MHz, $CDCl_3$)

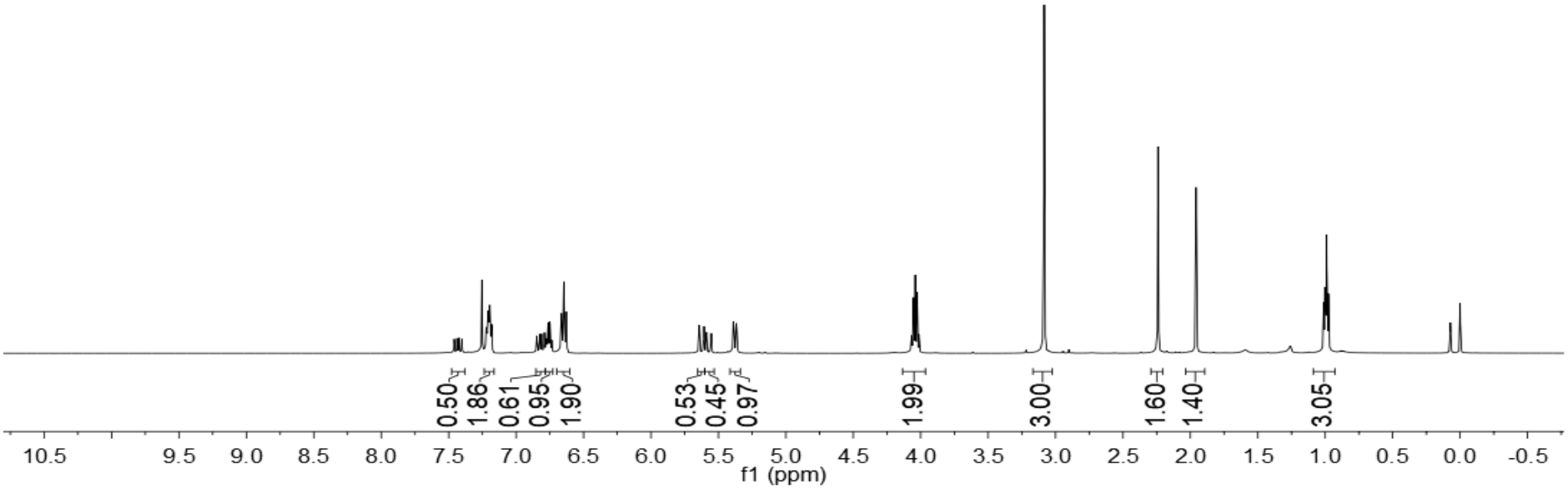

209.768
171.375
138.487
129.187
128.376
127.268
86.871
77.478
77.160
76.843
75.057
60.437
57.610
53.892
52.833
14.378
Ph
N
CO2Et
1t
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

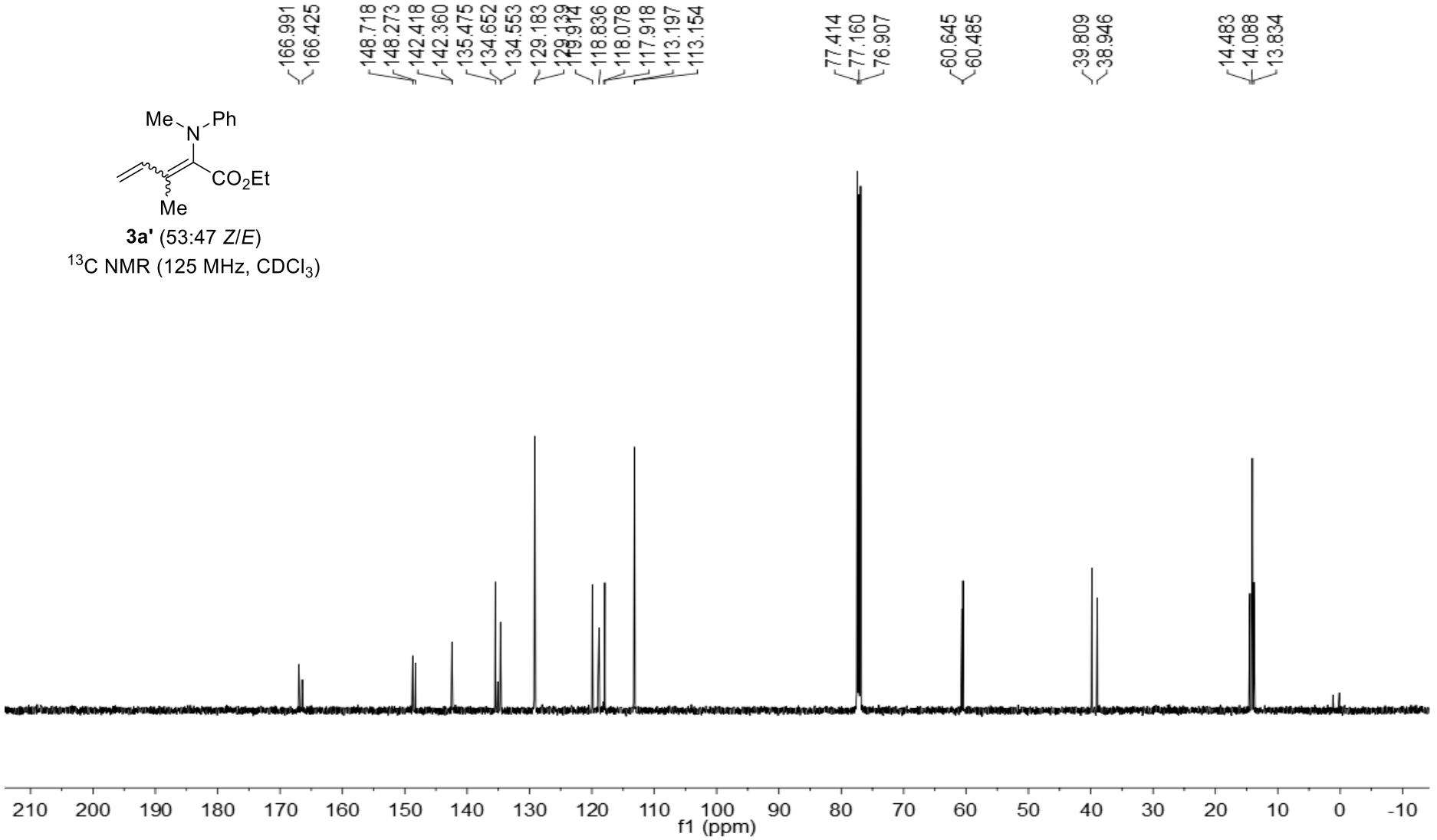




3a' (53:47 *Z*/*E*)

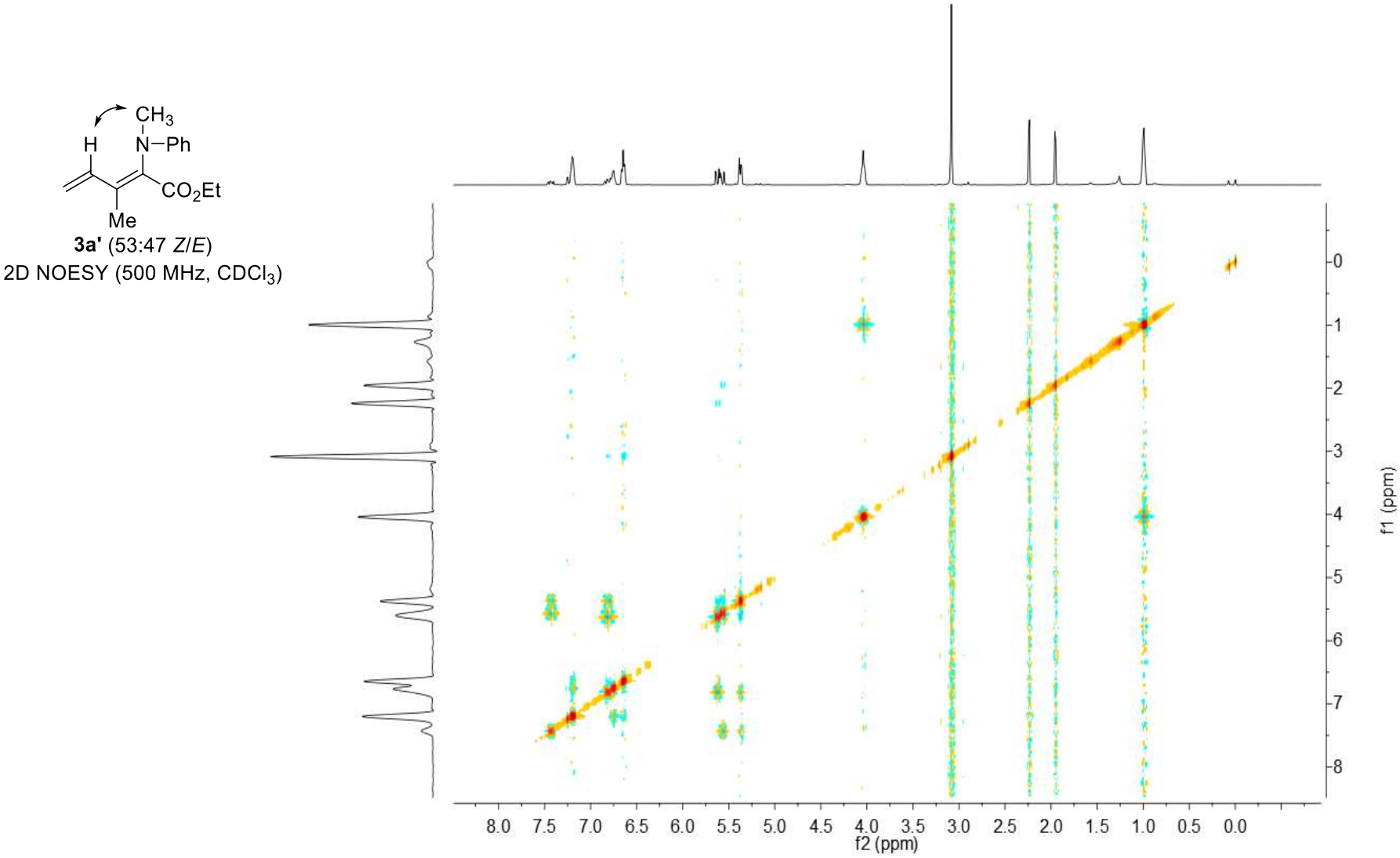
^{1}H NMR (500 MHz, $CDCl_3$)

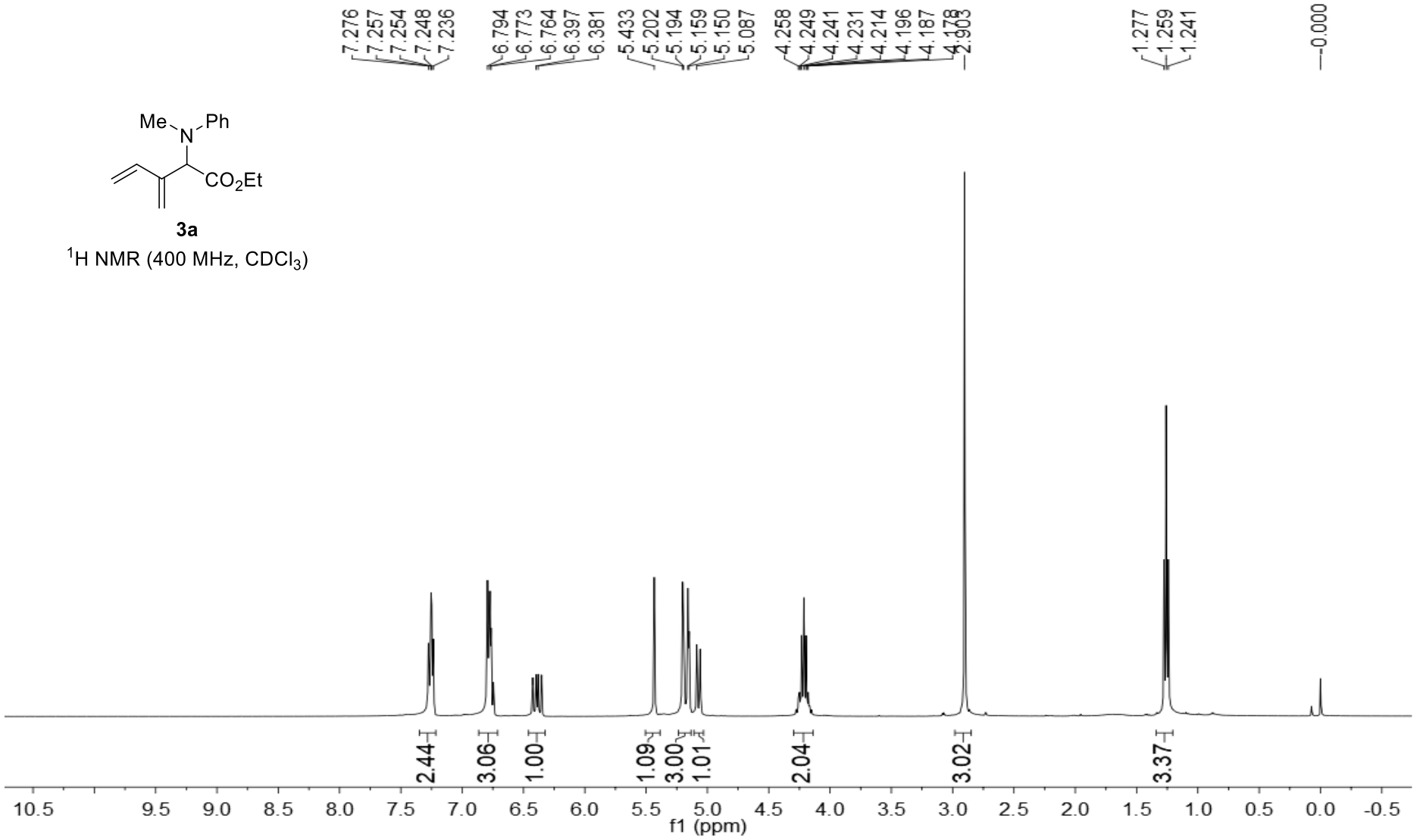




3a' (53:47 *Z*/*E*)

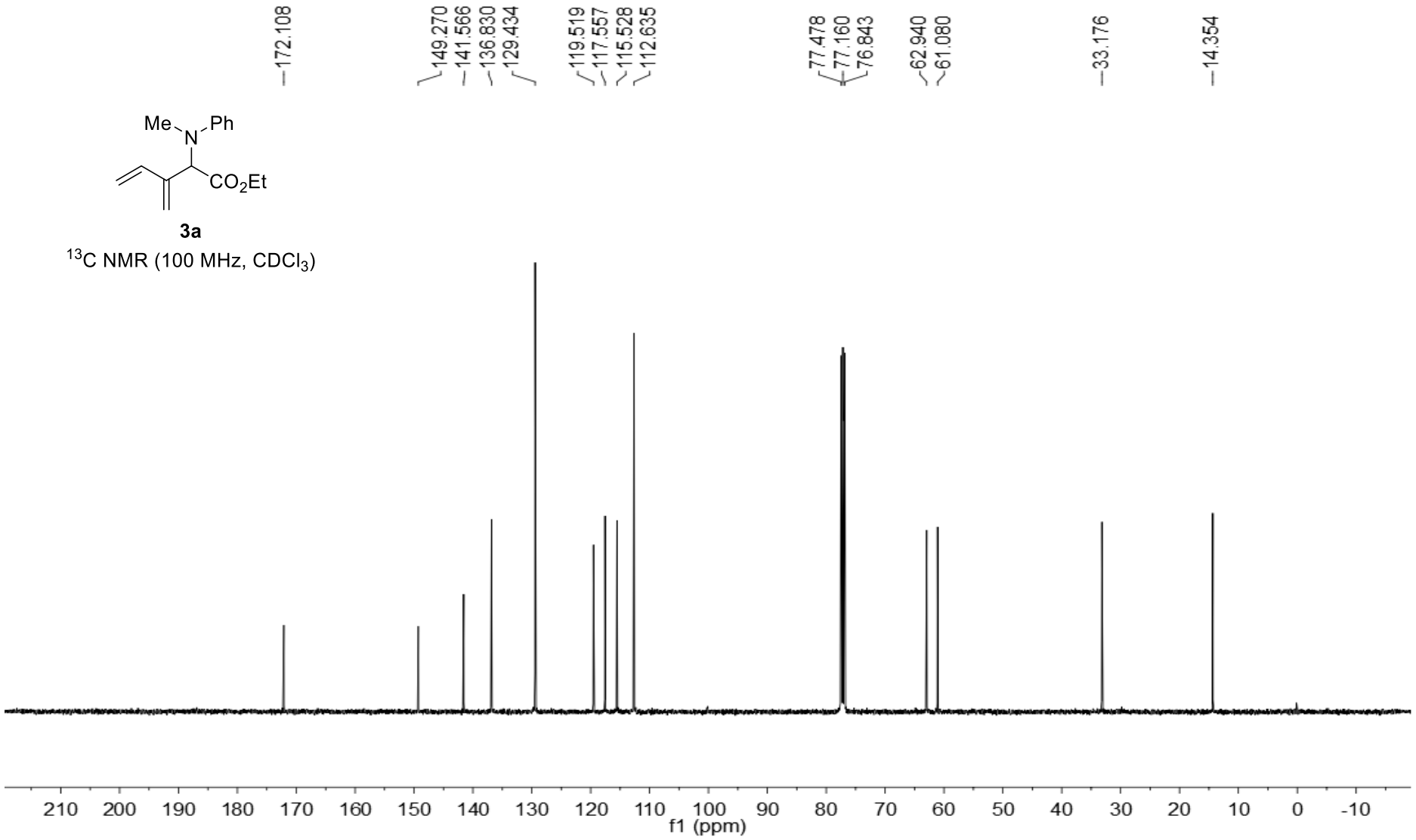
^{13}C NMR (125 MHz, $CDCl_3$)

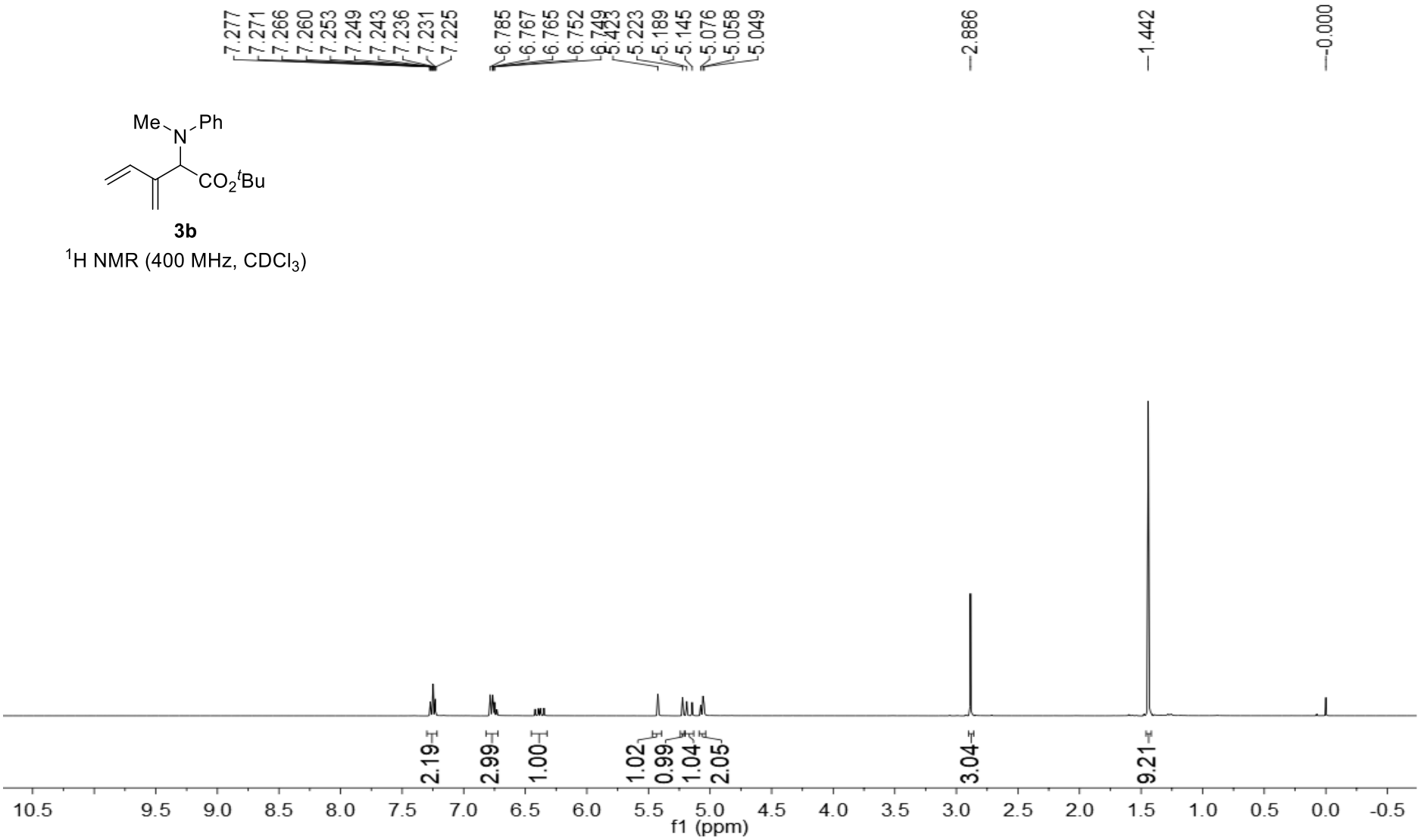

CH3
H
N–Ph
CO2Et
Me
3a' (53:47 Z/E)
2D NOESY (500 MHz, CDCl3)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)



3a

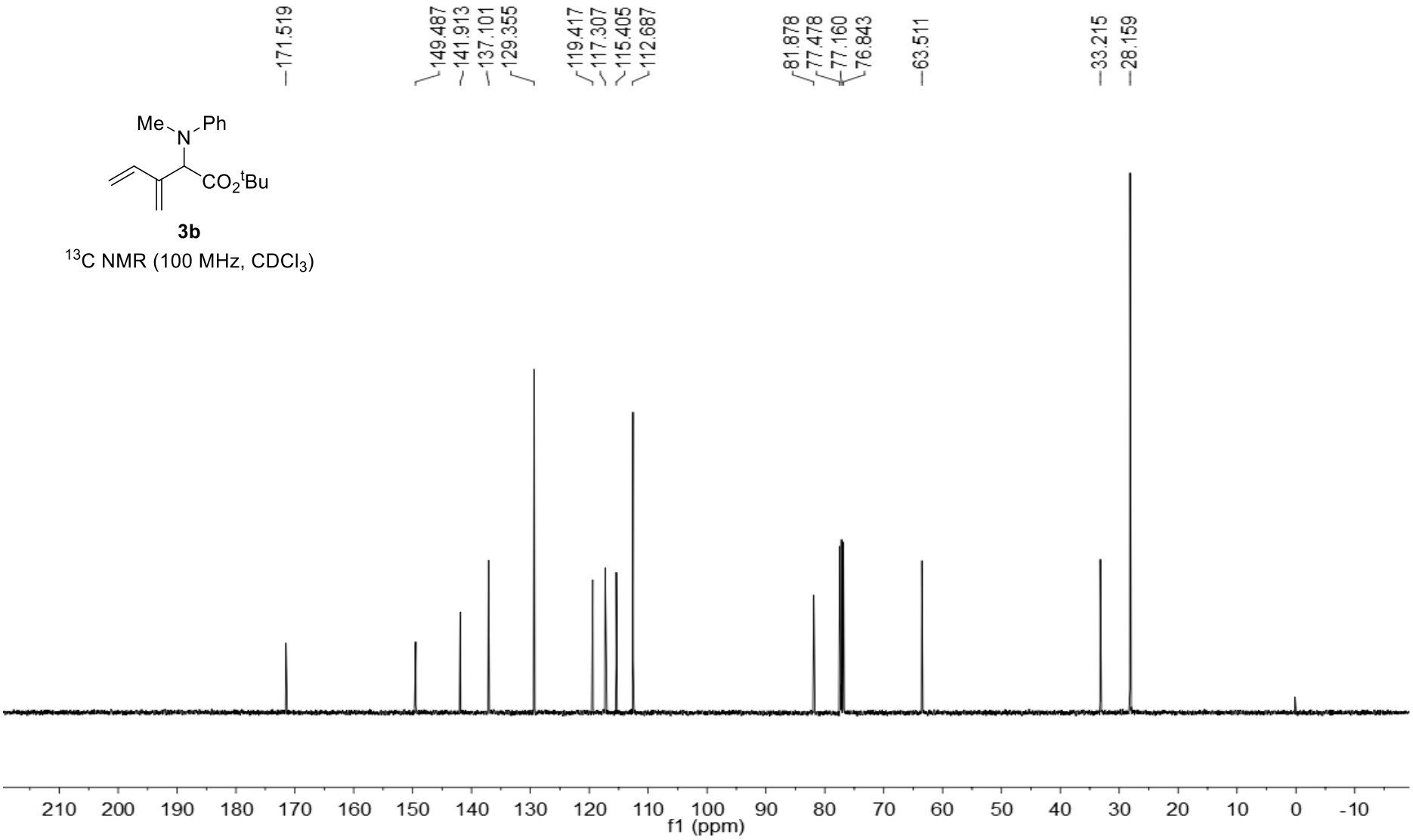
^{1}H NMR (400 MHz, $CDCl_3$)

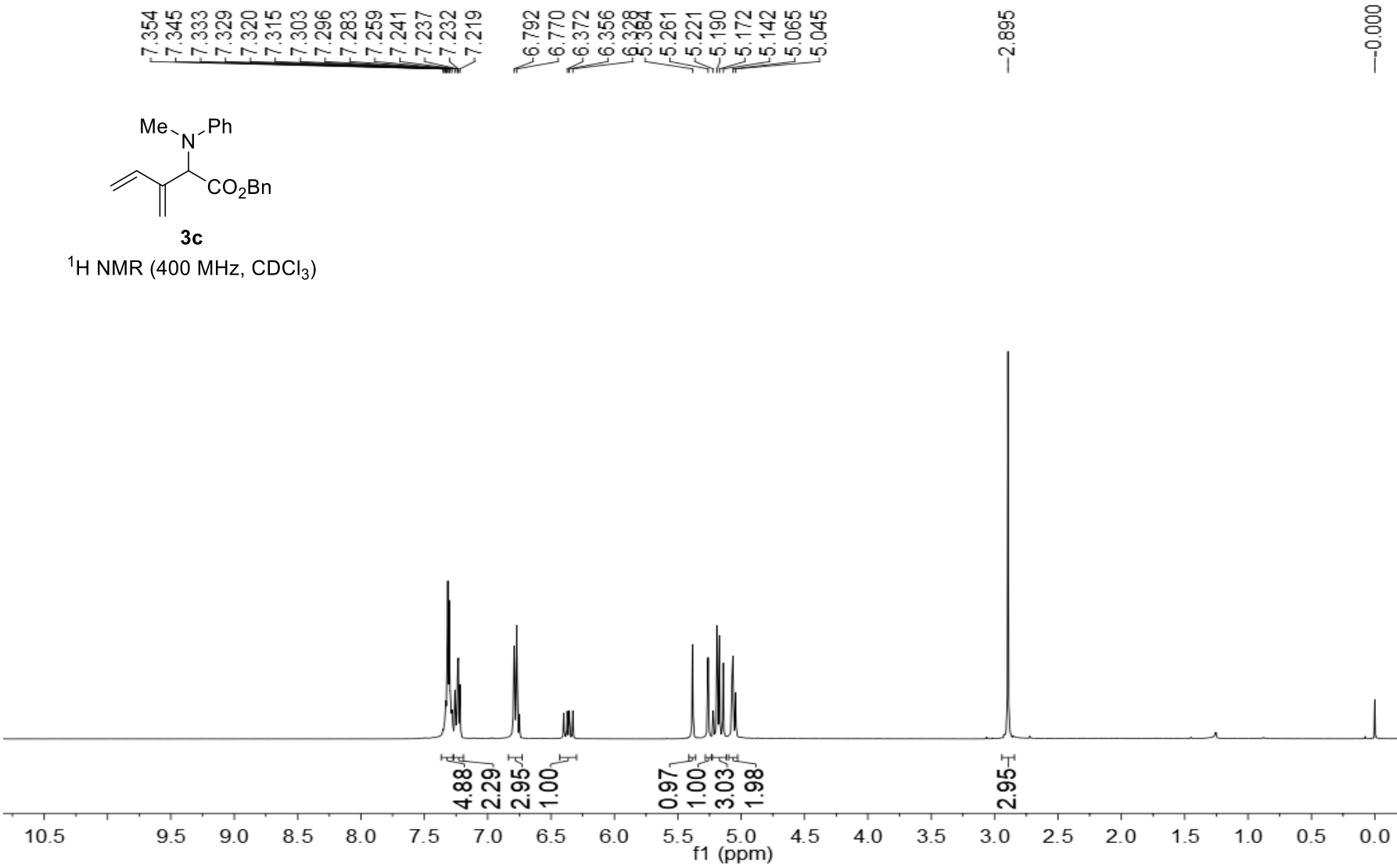

172.108
149.270
141.566
136.830
129.434
119.519
117.557
115.528
112.635
77.478
77.160
76.843
62.940
61.080
33.176
14.354
Me
N
Ph
CO2Et
3a
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3b

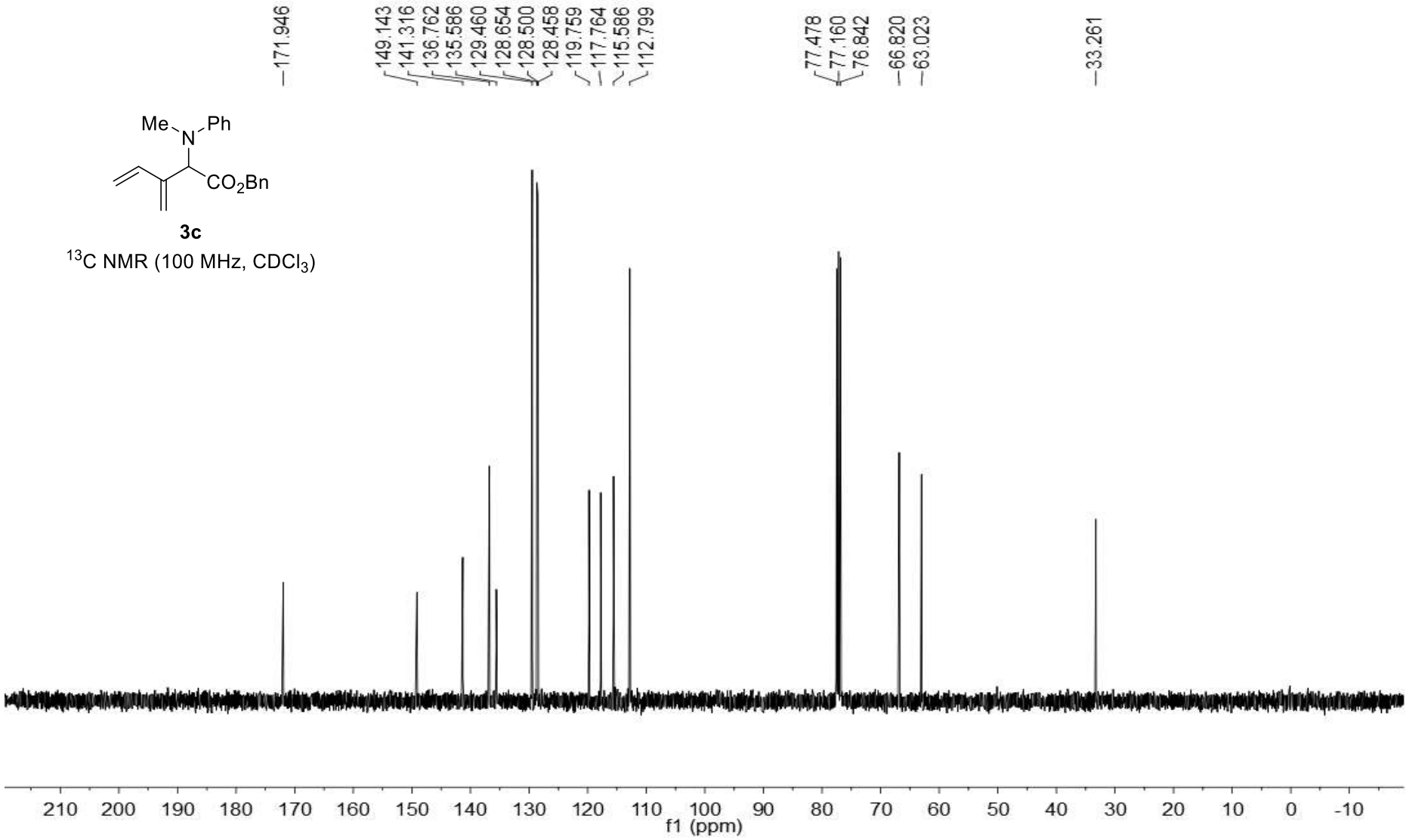
^{1}H NMR (400 MHz, $CDCl_3$)

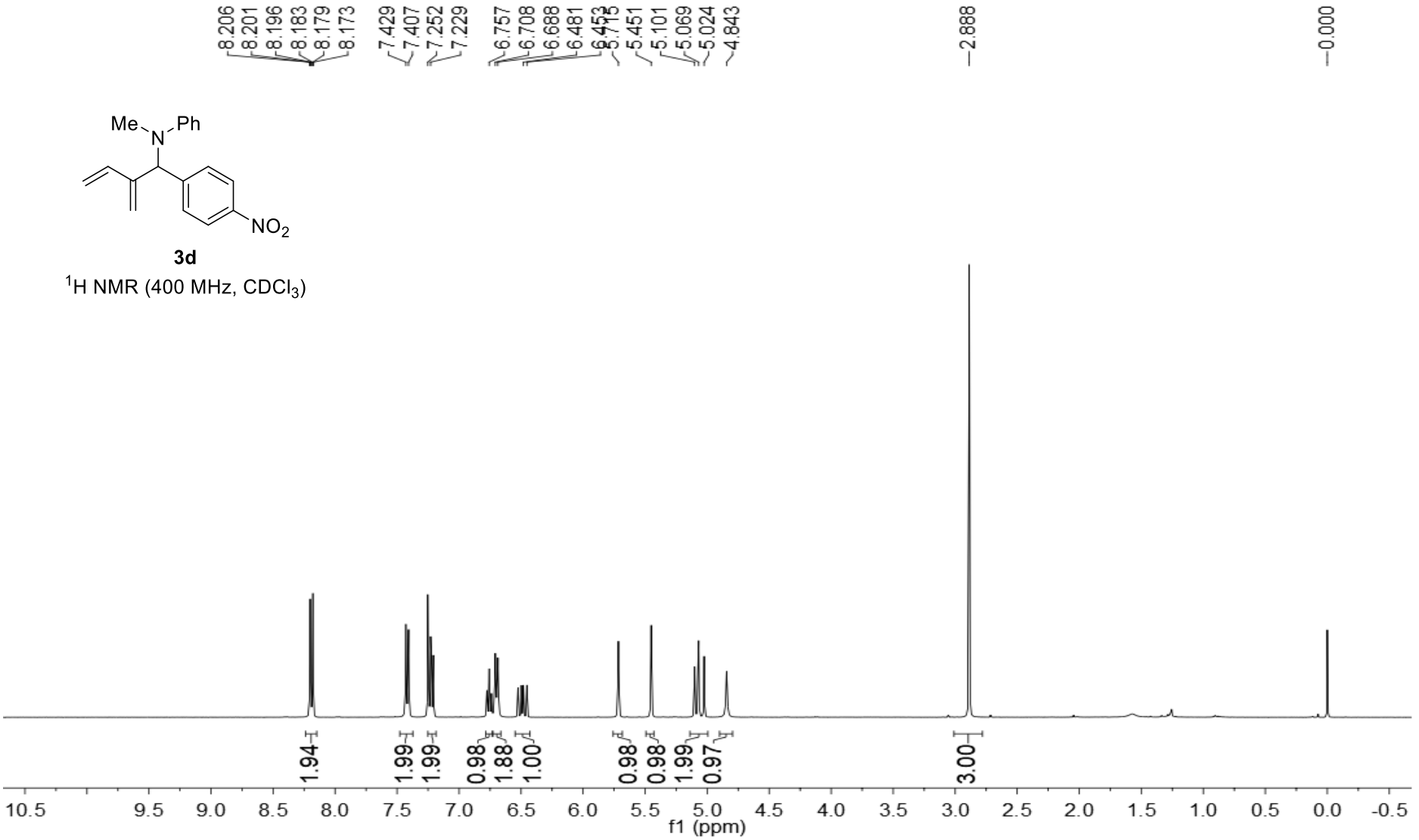

171.519
149.487
141.913
137.101
129.355
119.417
117.307
115.405
112.687
81.878
77.478
77.160
76.843
63.511
33.215
28.159
Me
N
Ph
CO2tBu
3b
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3c

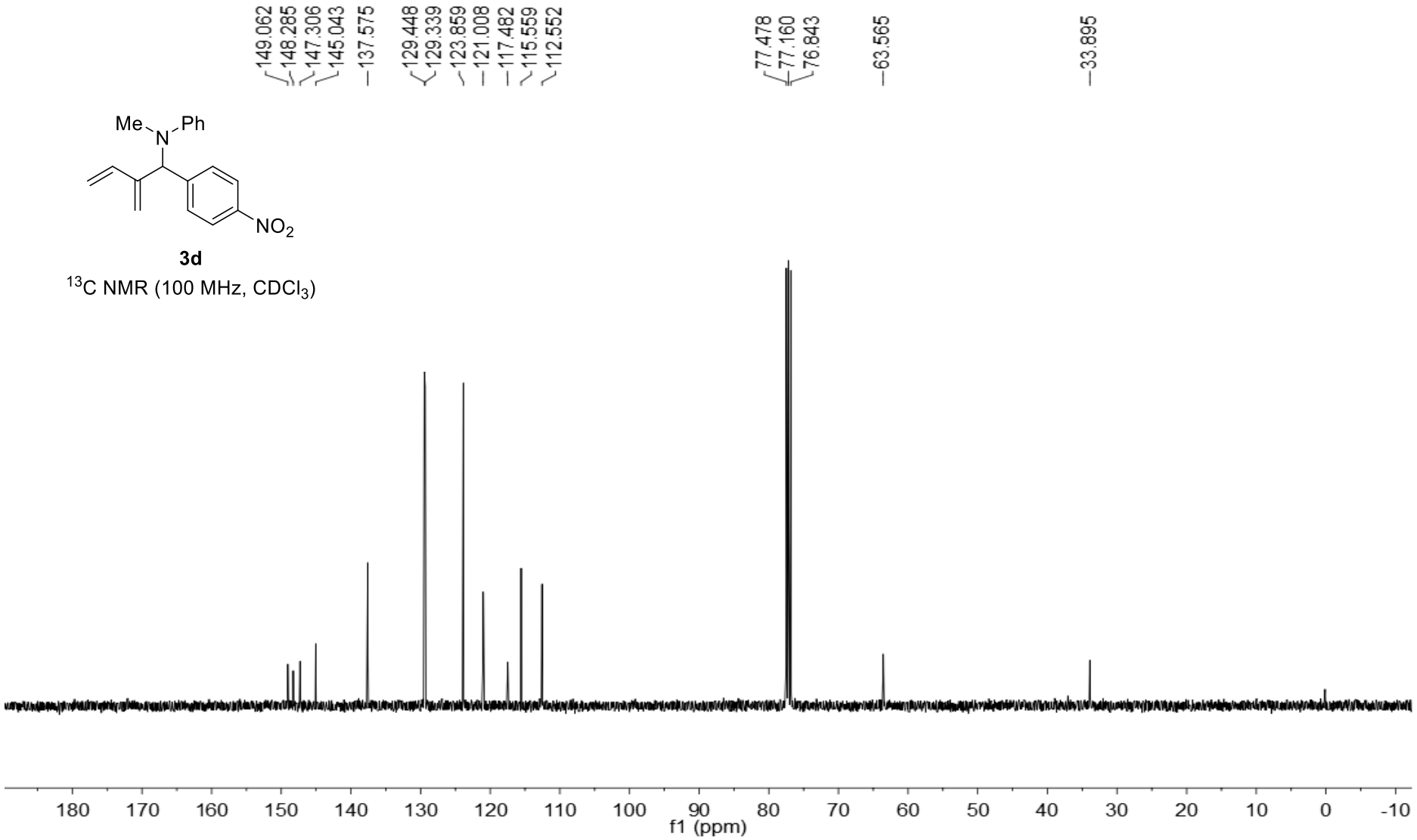
^{1}H NMR (400 MHz, $CDCl_3$)


171.946
149.143
141.316
136.762
135.586
129.460
128.654
128.500
128.458
119.759
117.764
115.586
112.799
77.478
77.160
76.842
66.820
63.023
33.261
Me
N
Ph
CO2Bn
3c
13C NMR (100 MHz, 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)



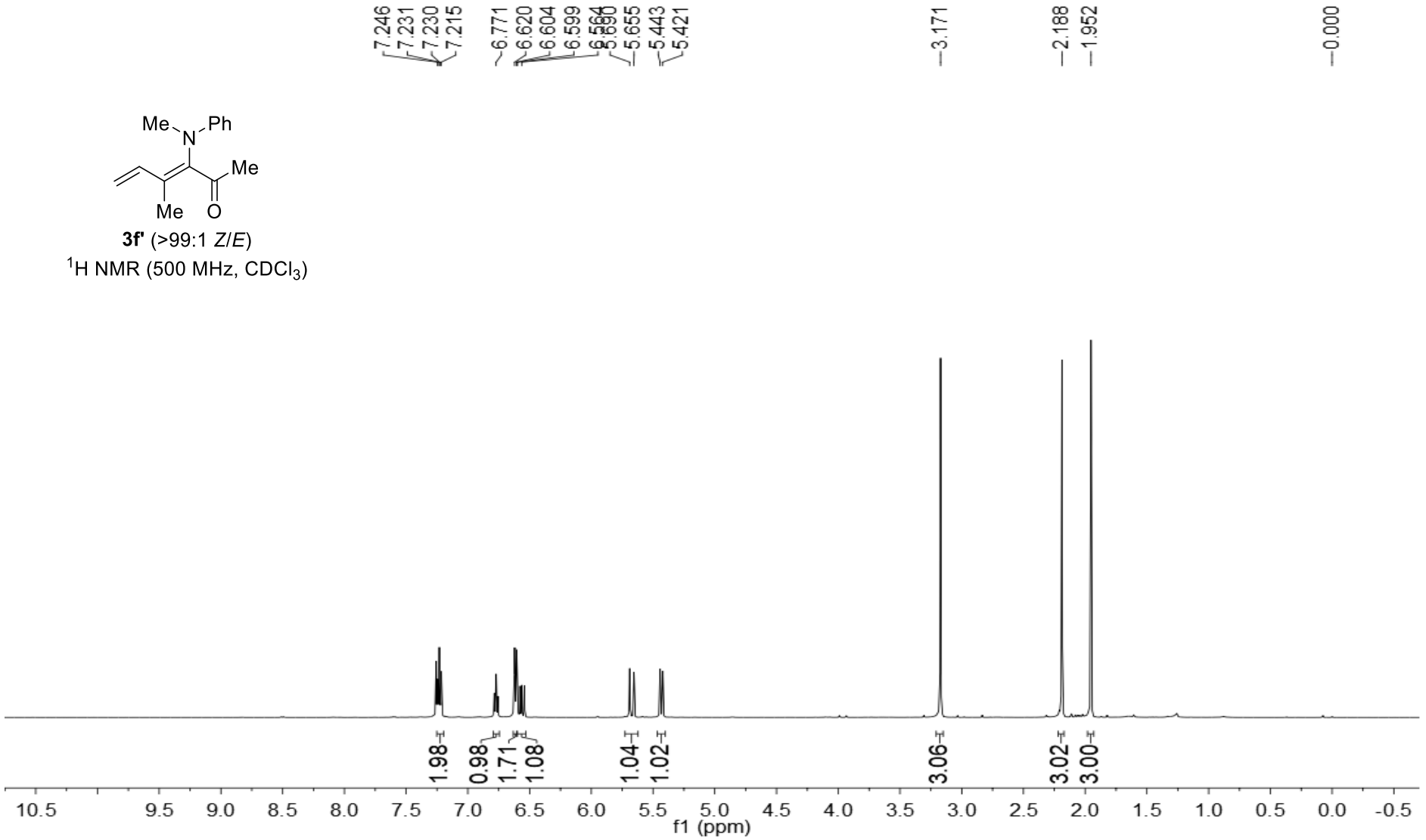
3d

^{1}H NMR (400 MHz, $CDCl_3$)



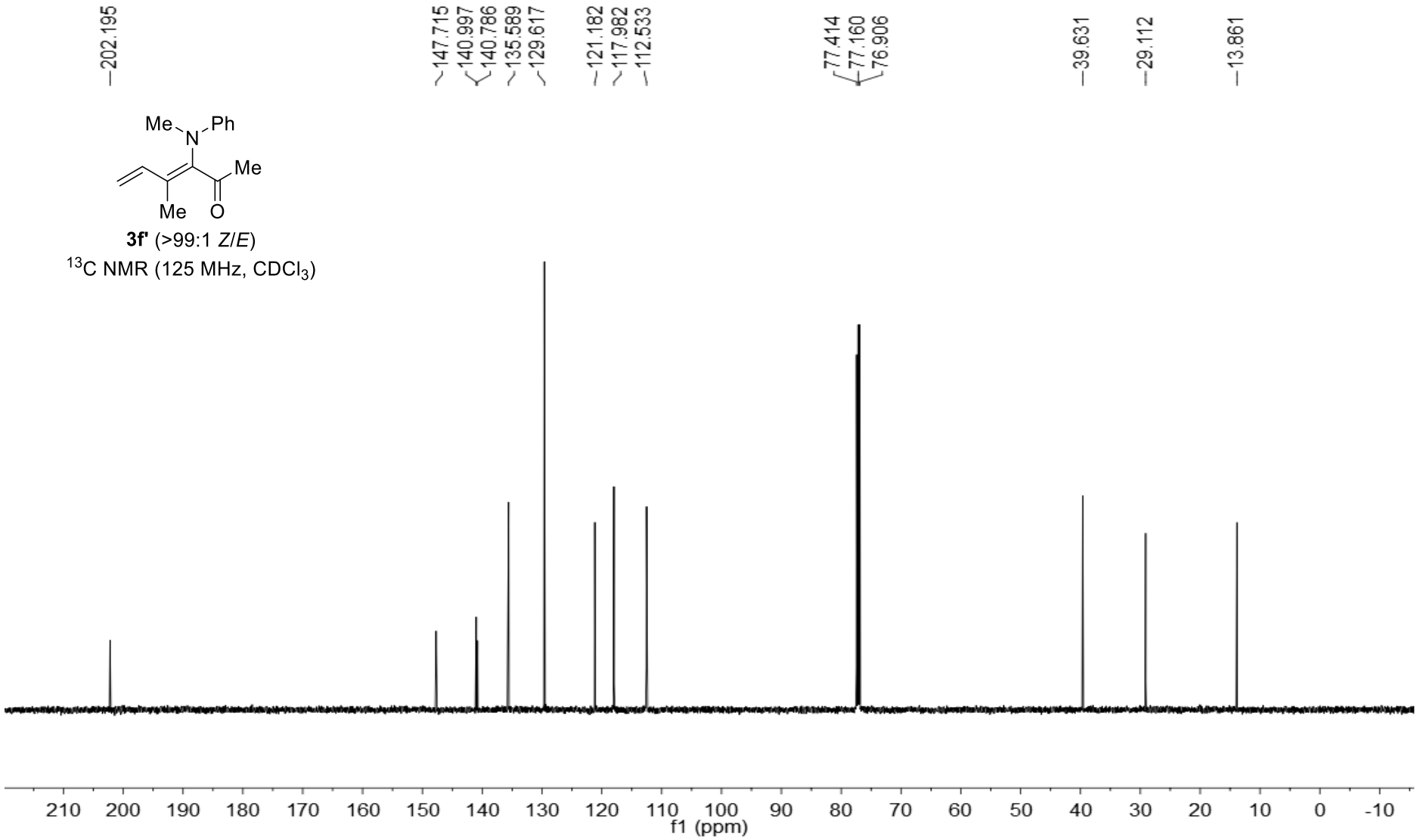
3d

^{13}C NMR (100 MHz, $CDCl_3$)



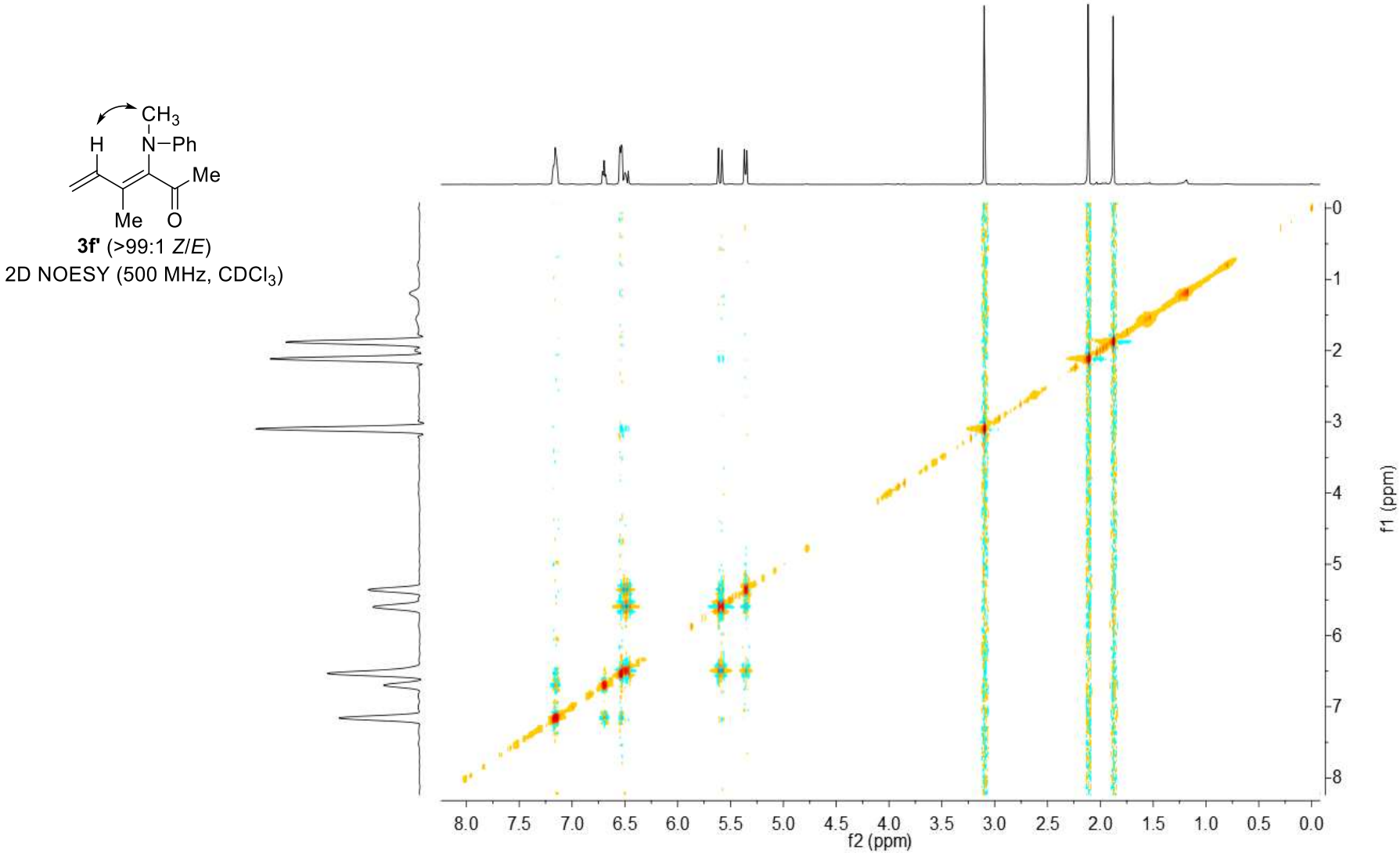
3f' (>99:1 *Z*/*E*)

^{1}H NMR (500 MHz, $CDCl_3$)

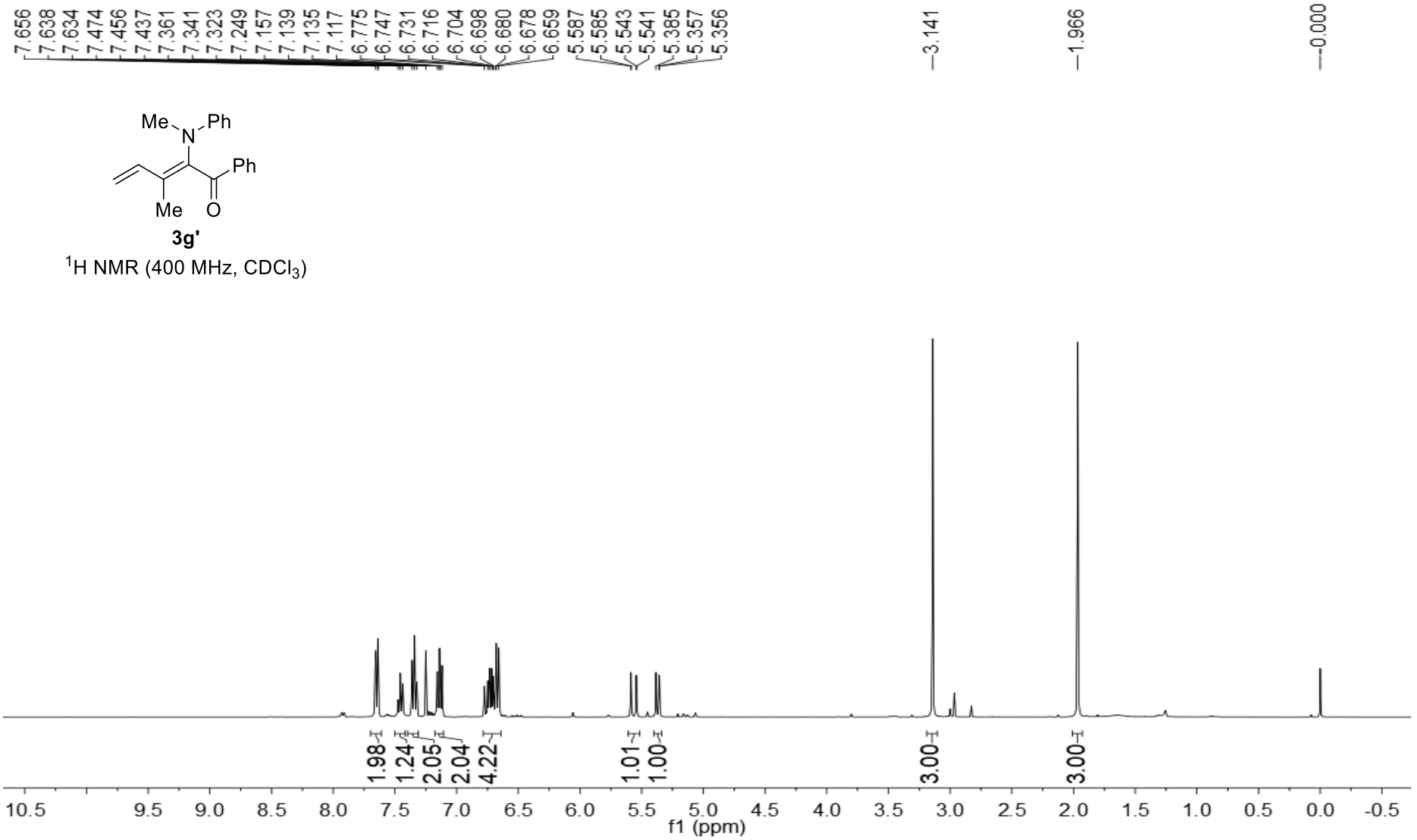


3f' (>99:1 *Z*/*E*)

^{13}C NMR (125 MHz, $CDCl_3$)

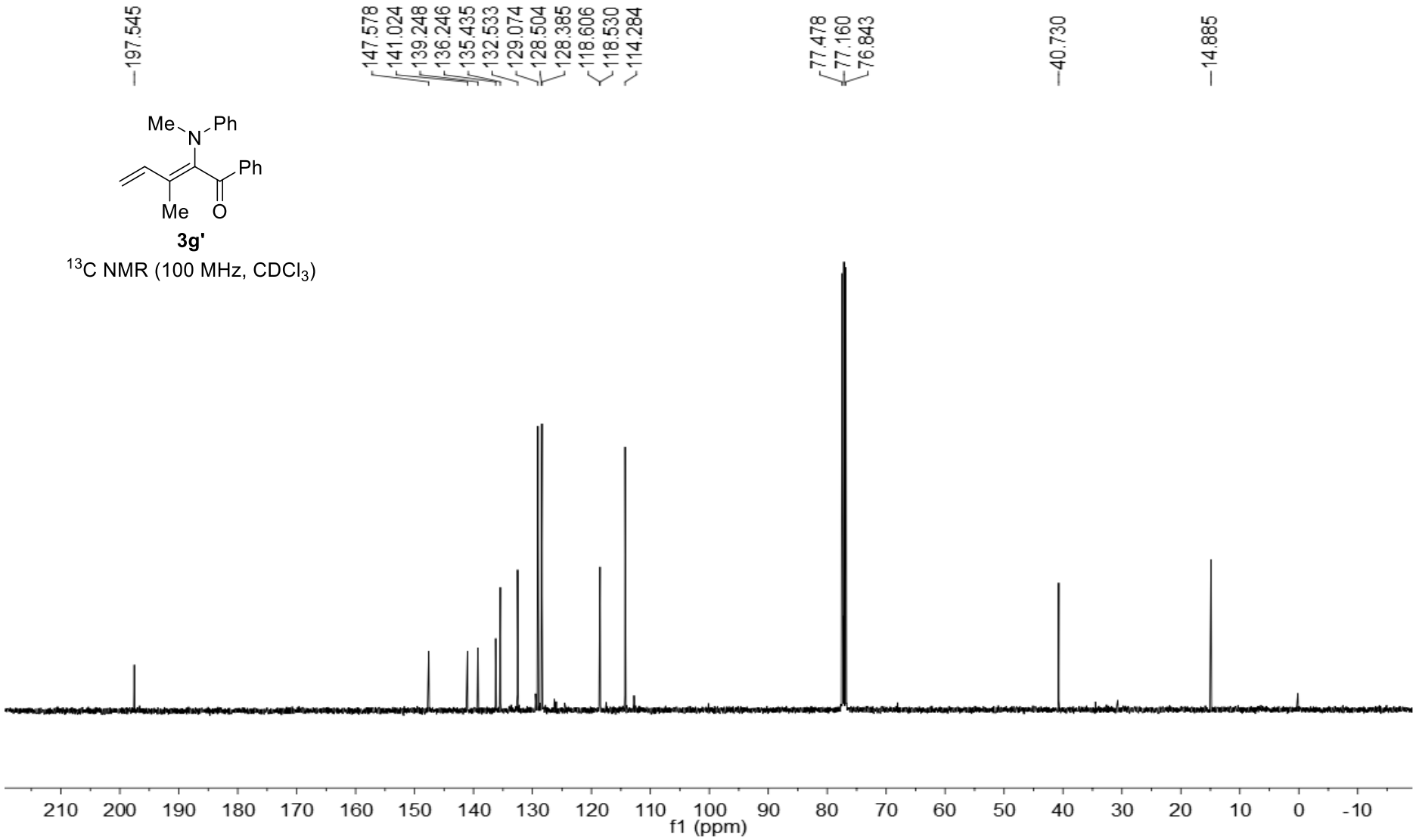


3f' (>99:1 *Z*/*E*)
2D NOESY (500 MHz, $CDCl_3$)



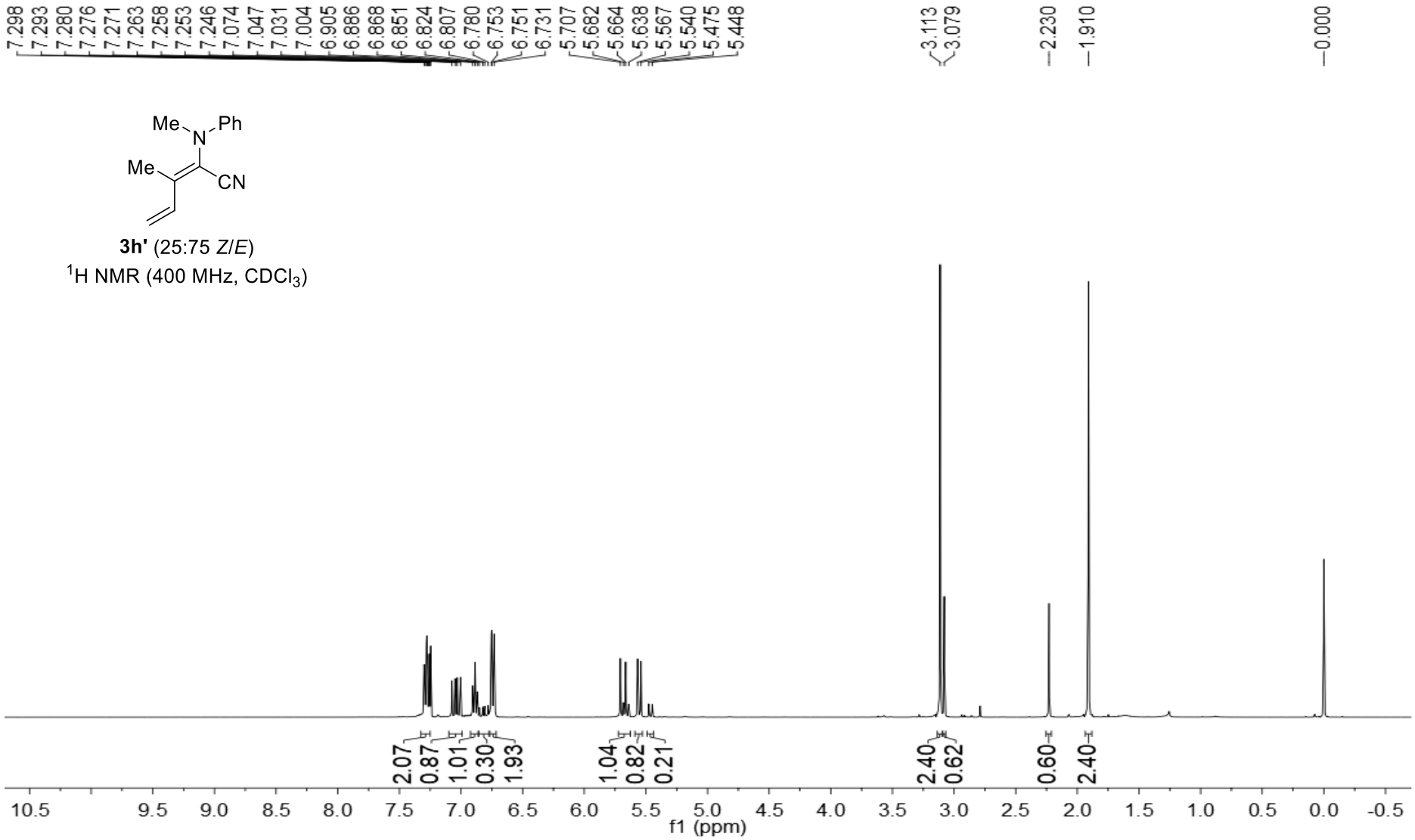
3g'

^{1}H NMR (400 MHz, $CDCl_3$)



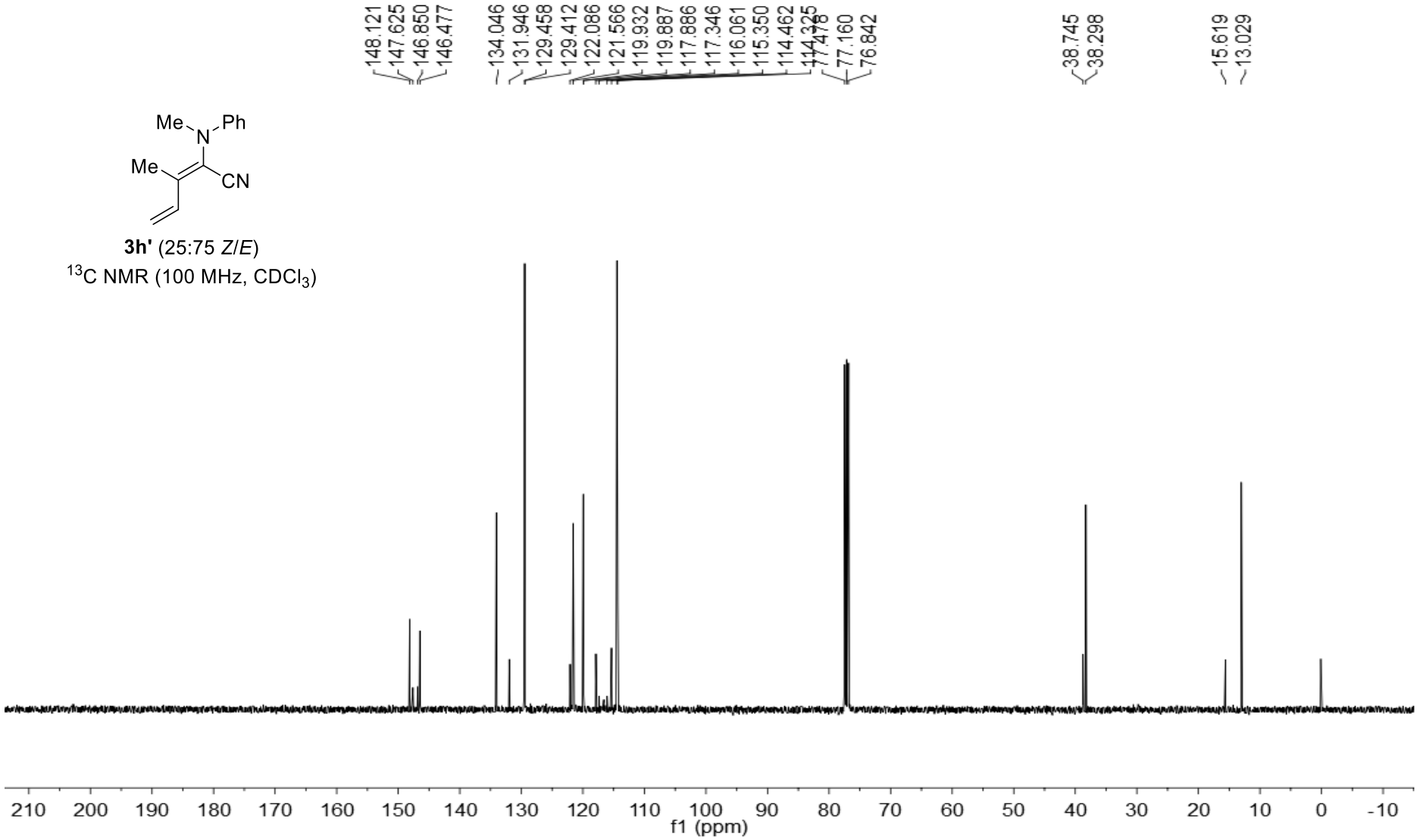
3g'

^{13}C NMR (100 MHz, $CDCl_3$)



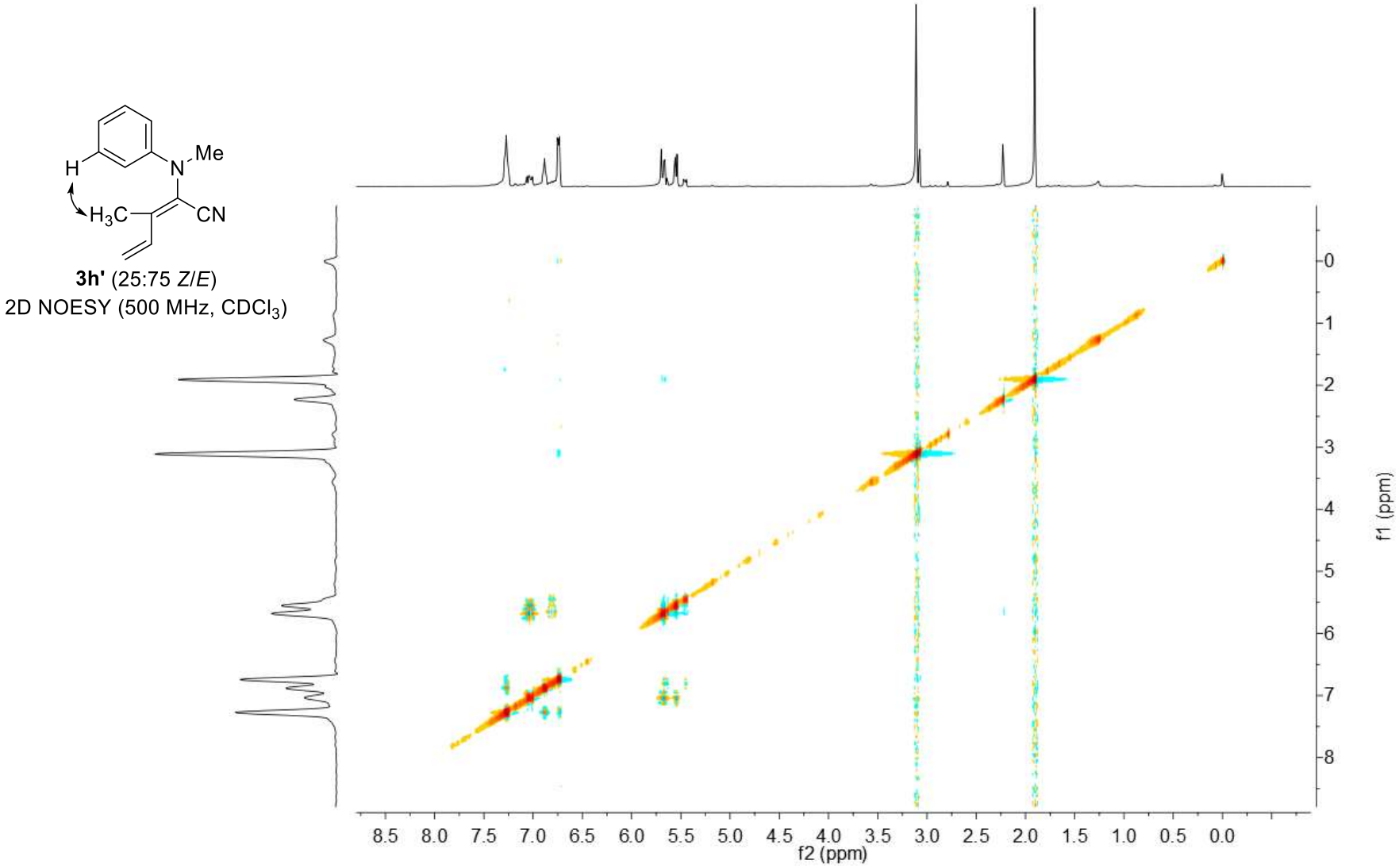
3h' (25:75 *Z*/*E*)

^{1}H NMR (400 MHz, $CDCl_3$)

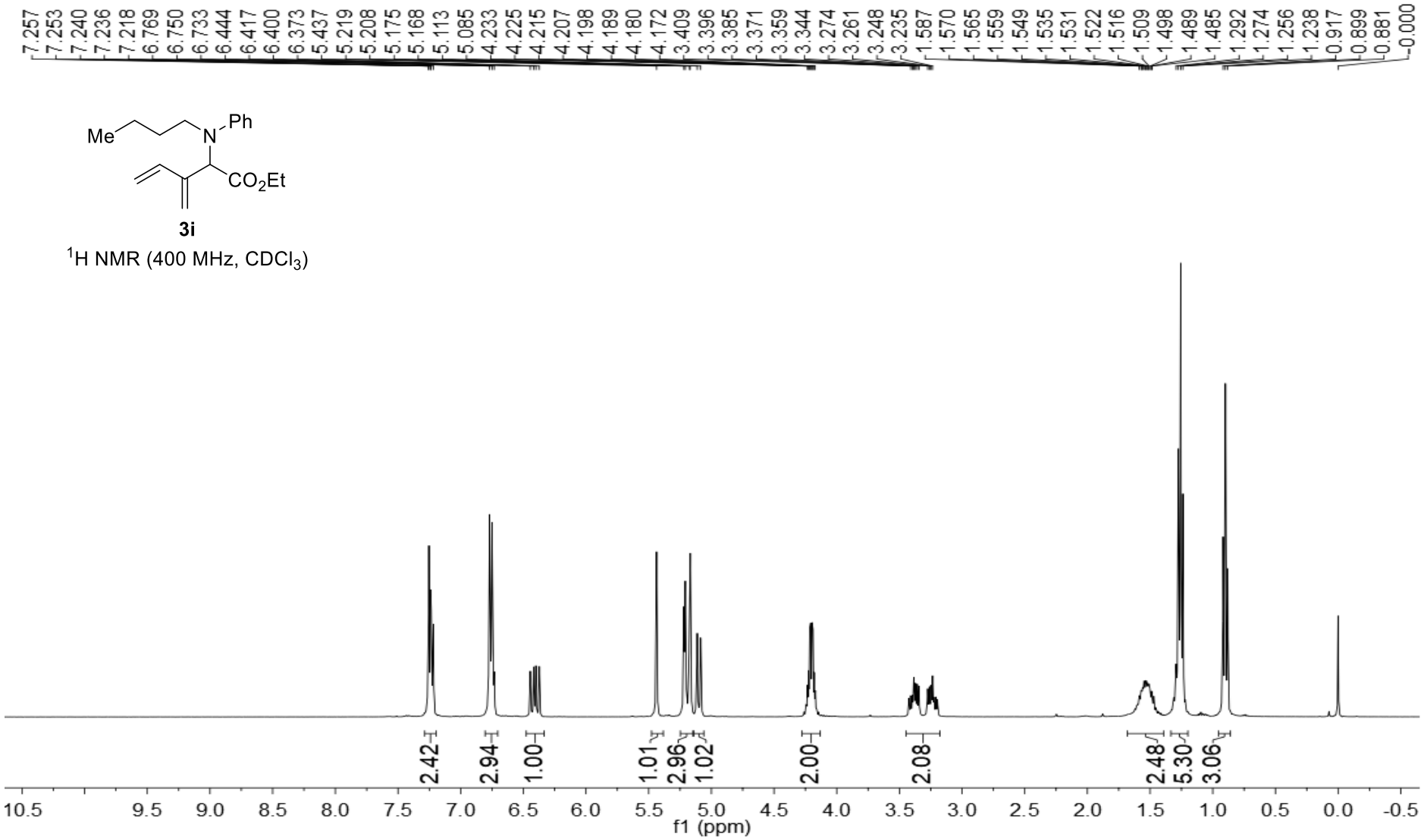


3h' (25:75 *Z*/*E*)

^{13}C NMR (100 MHz, $CDCl_3$)

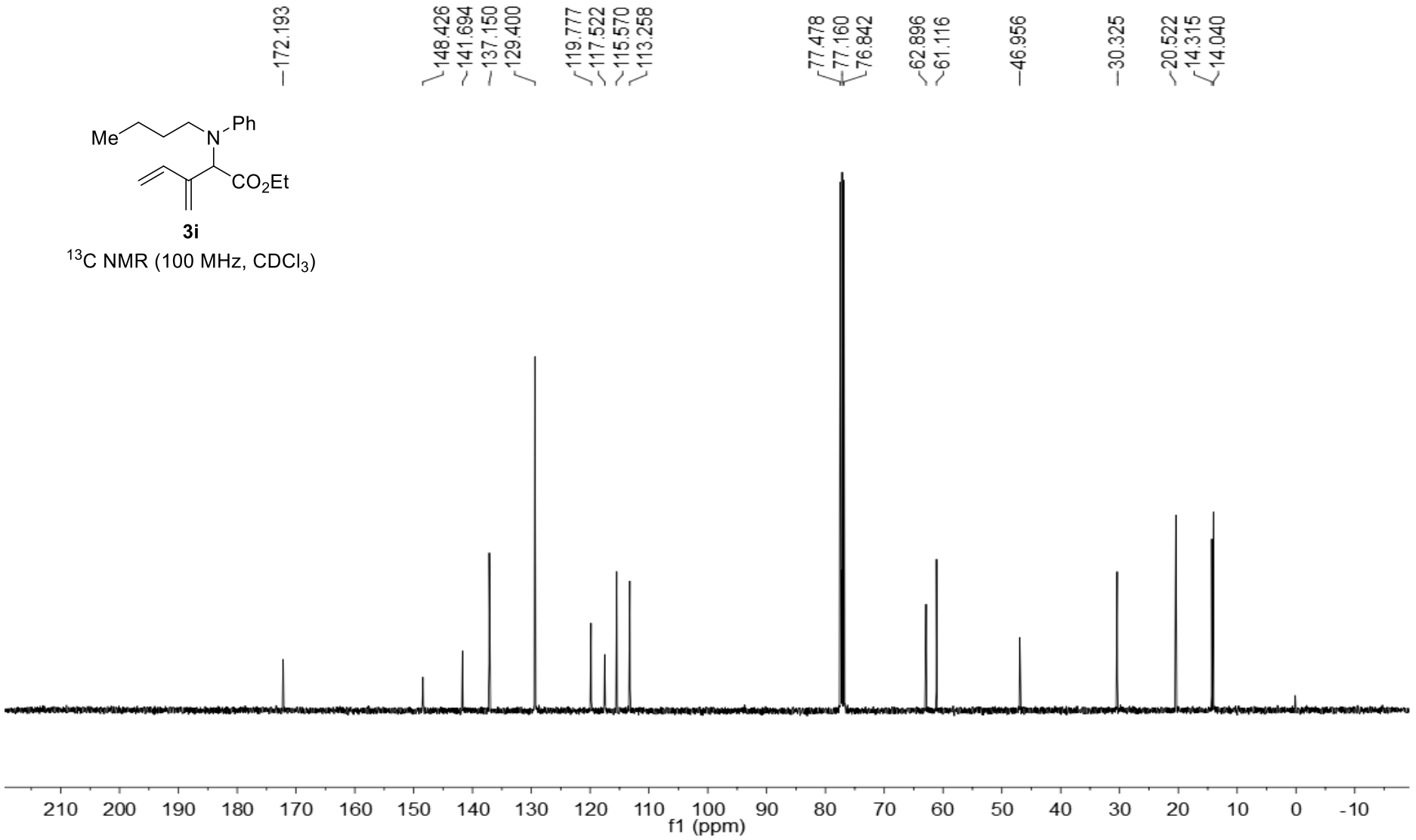


3h' (25:75 *Z*/*E*)
2D NOESY (500 MHz, $CDCl_3$)



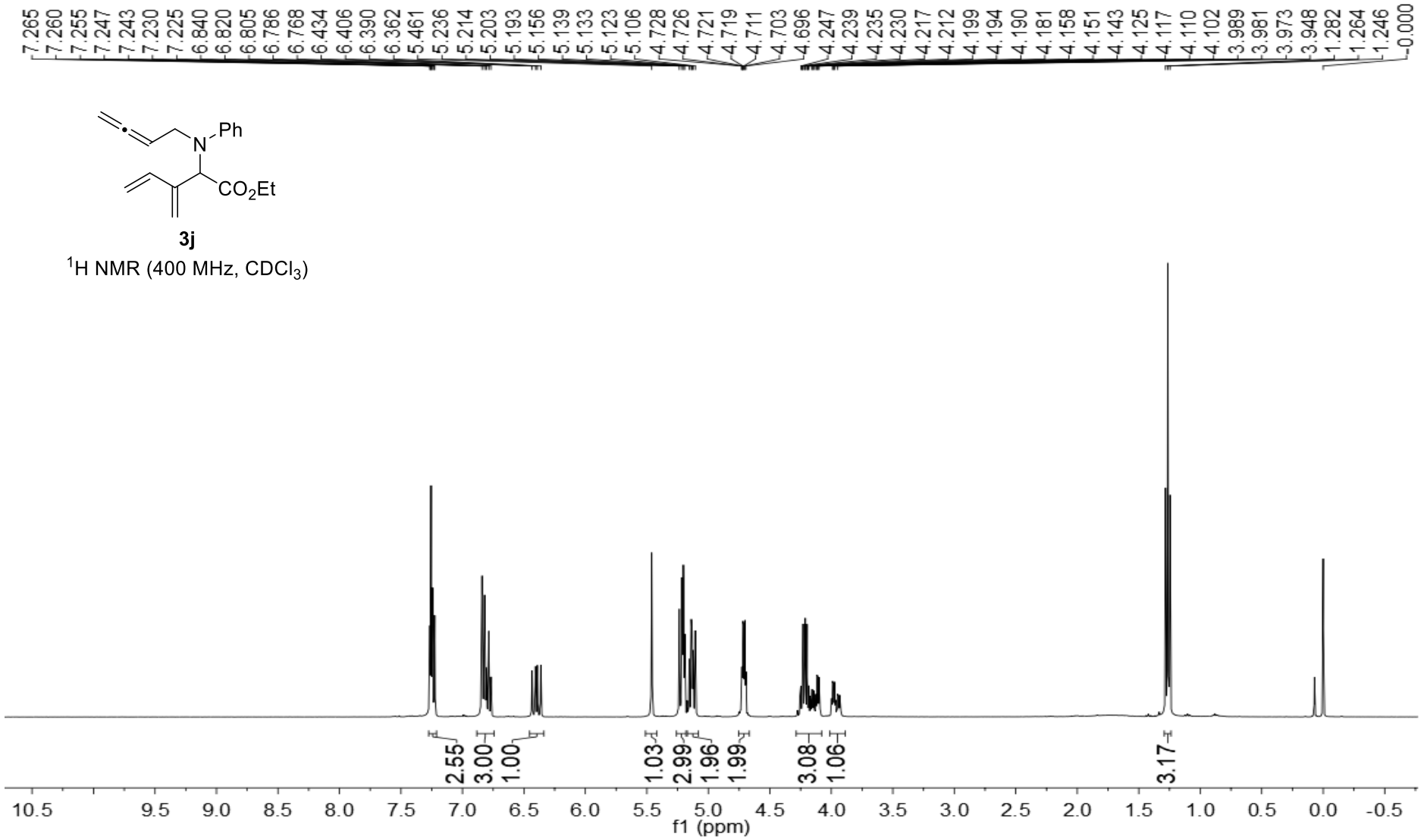
3i

^{1}H NMR (400 MHz, $CDCl_3$)



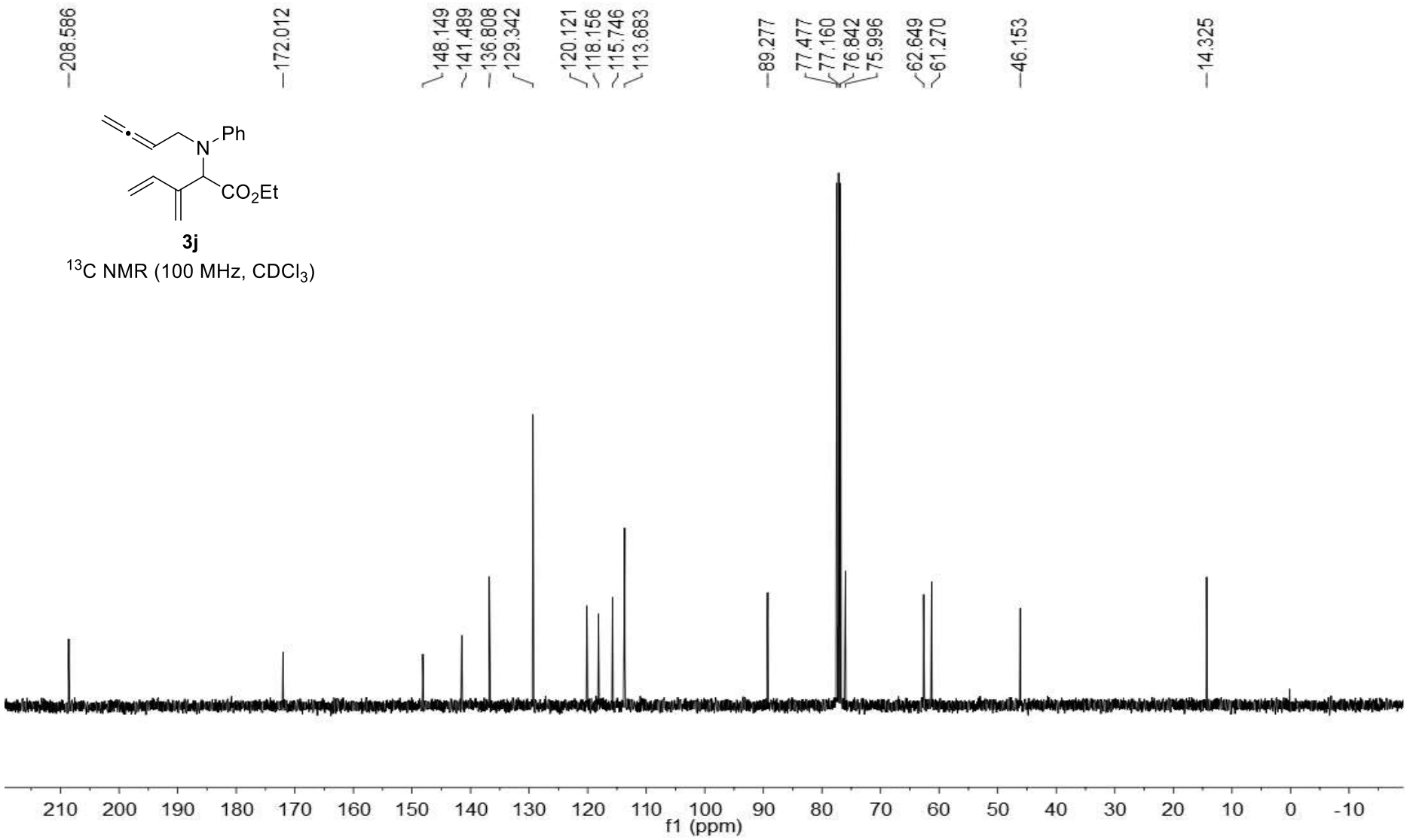
3i

^{13}C NMR (100 MHz, $CDCl_3$)



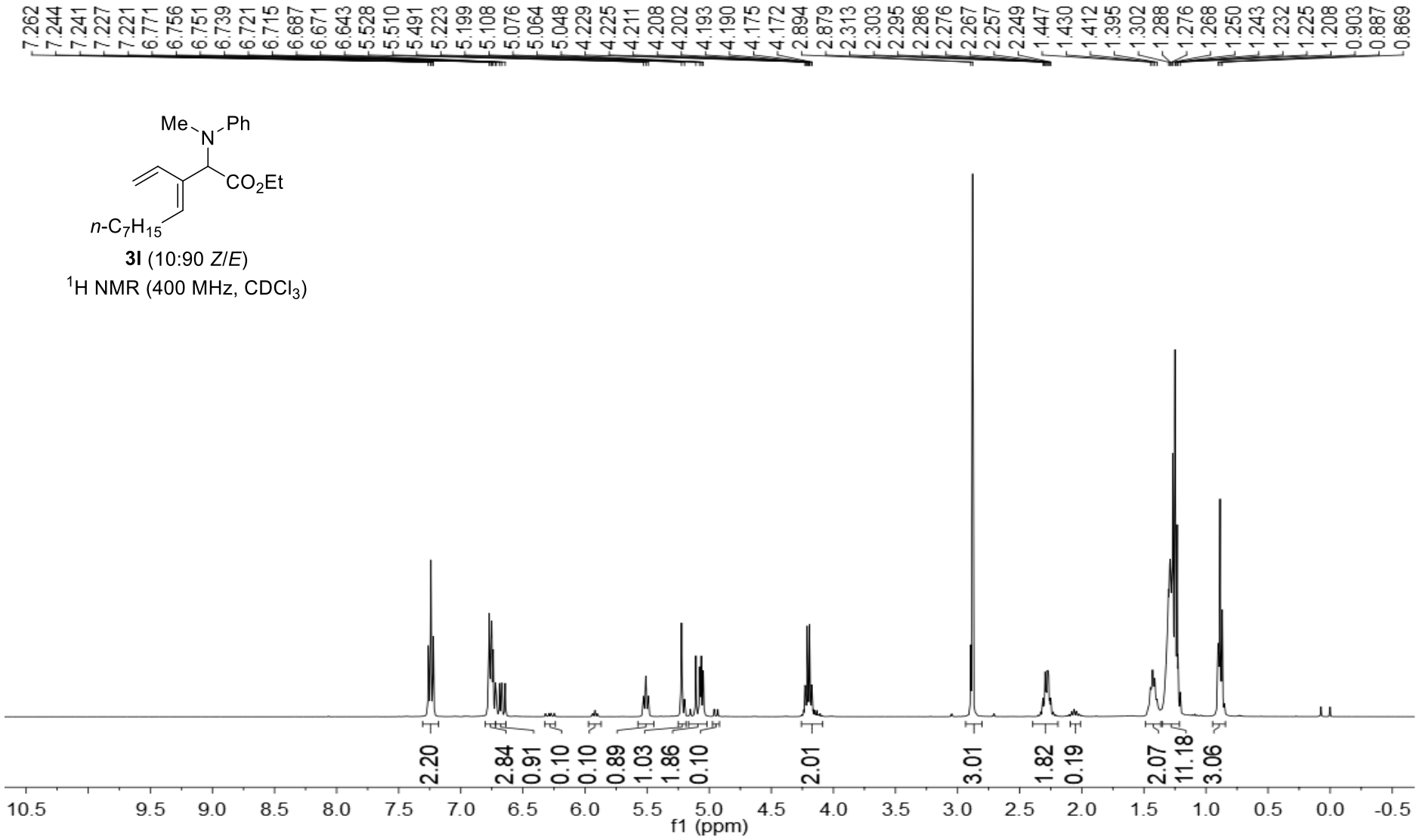
3j

^{1}H NMR (400 MHz, $CDCl_3$)



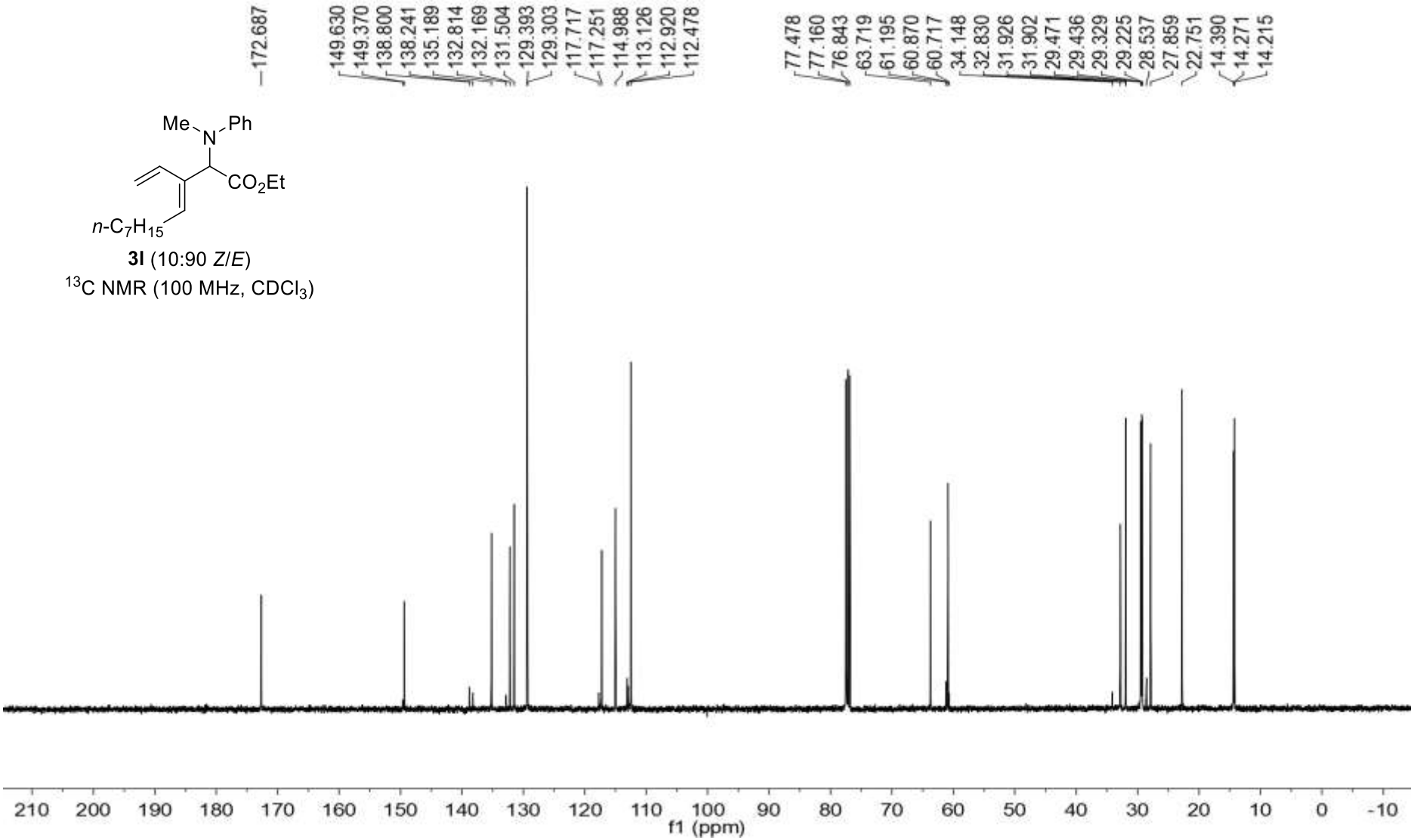
3j

^{13}C NMR (100 MHz, $CDCl_3$)



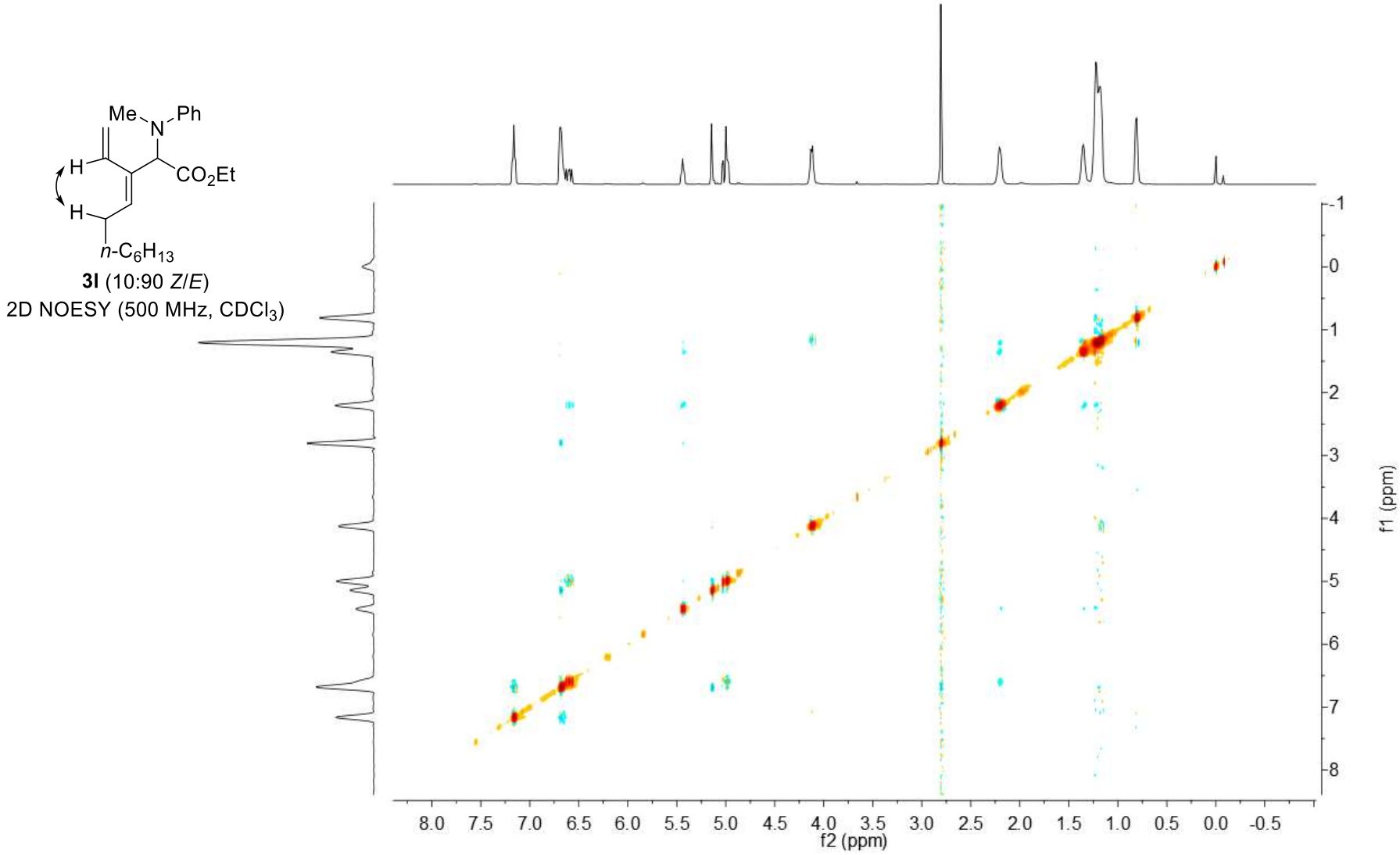
3l (10:90 *Z*/*E*)

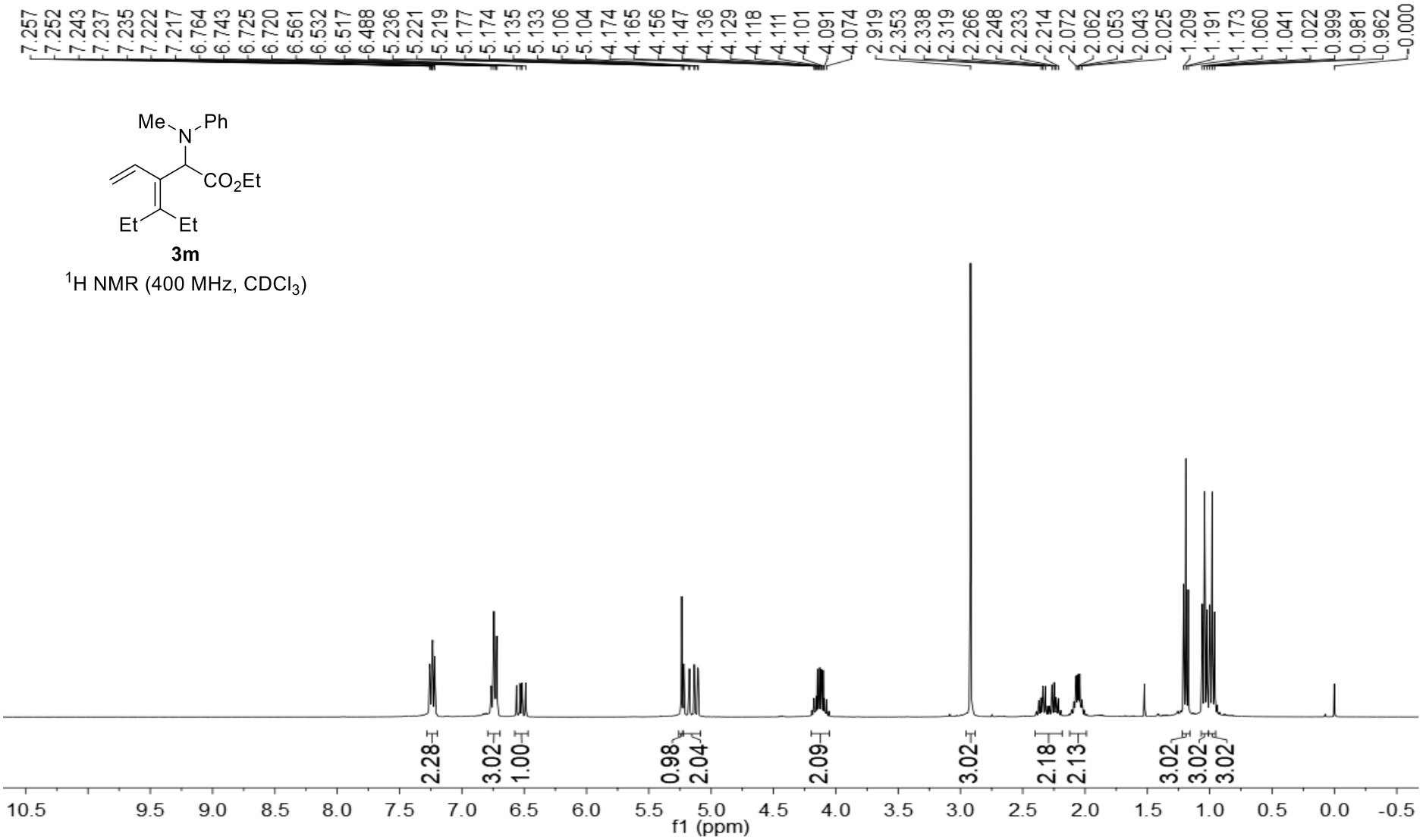
^{1}H NMR (400 MHz, $CDCl_3$)



3l (10:90 *Z*/*E*)

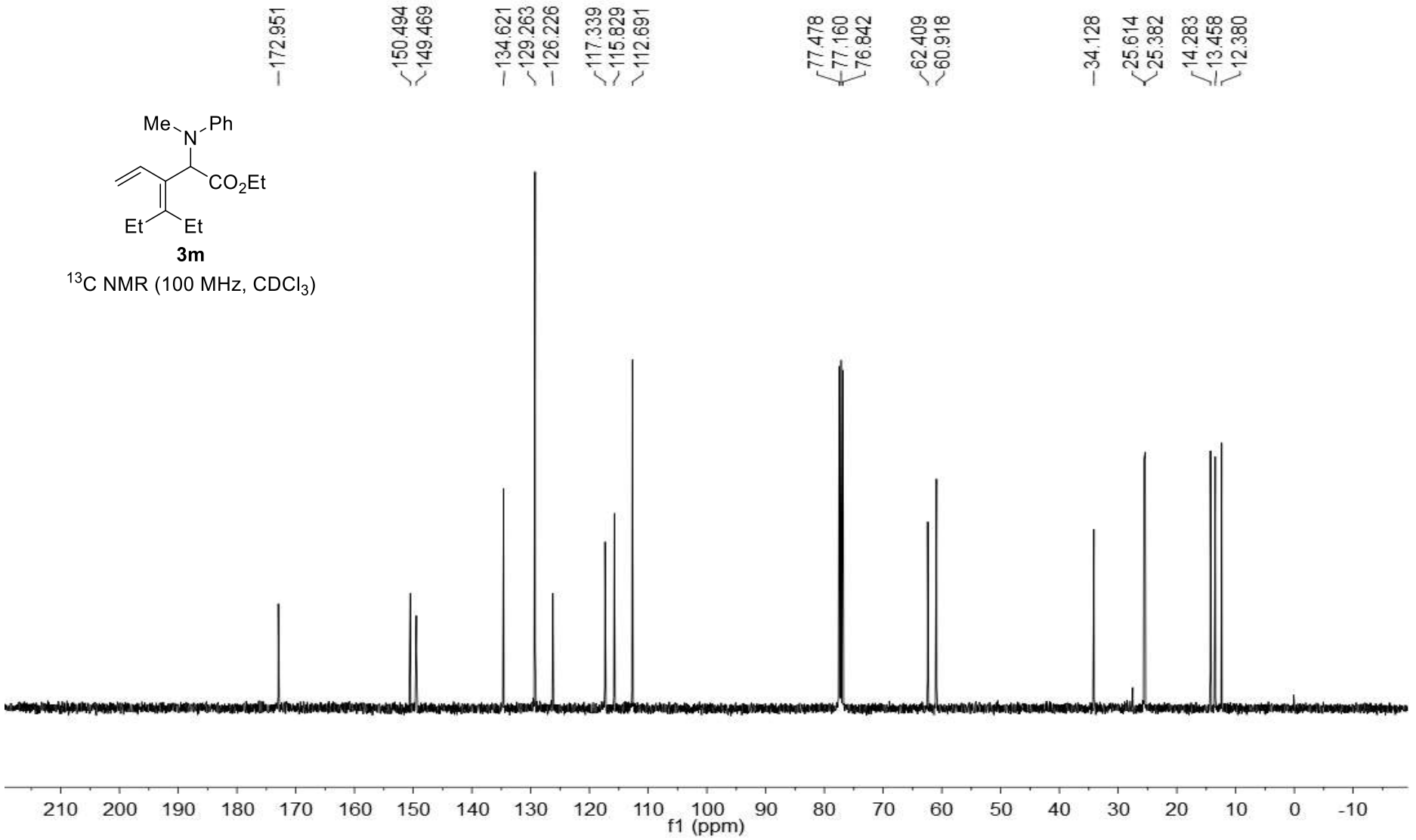
^{13}C NMR (100 MHz, $CDCl_3$)


Me
N
Ph
H
CO2Et
H
n-C6H13
3l (10:90 Z/E)
2D NOESY (500 MHz, CDCl3)
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
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8
f1 (ppm)



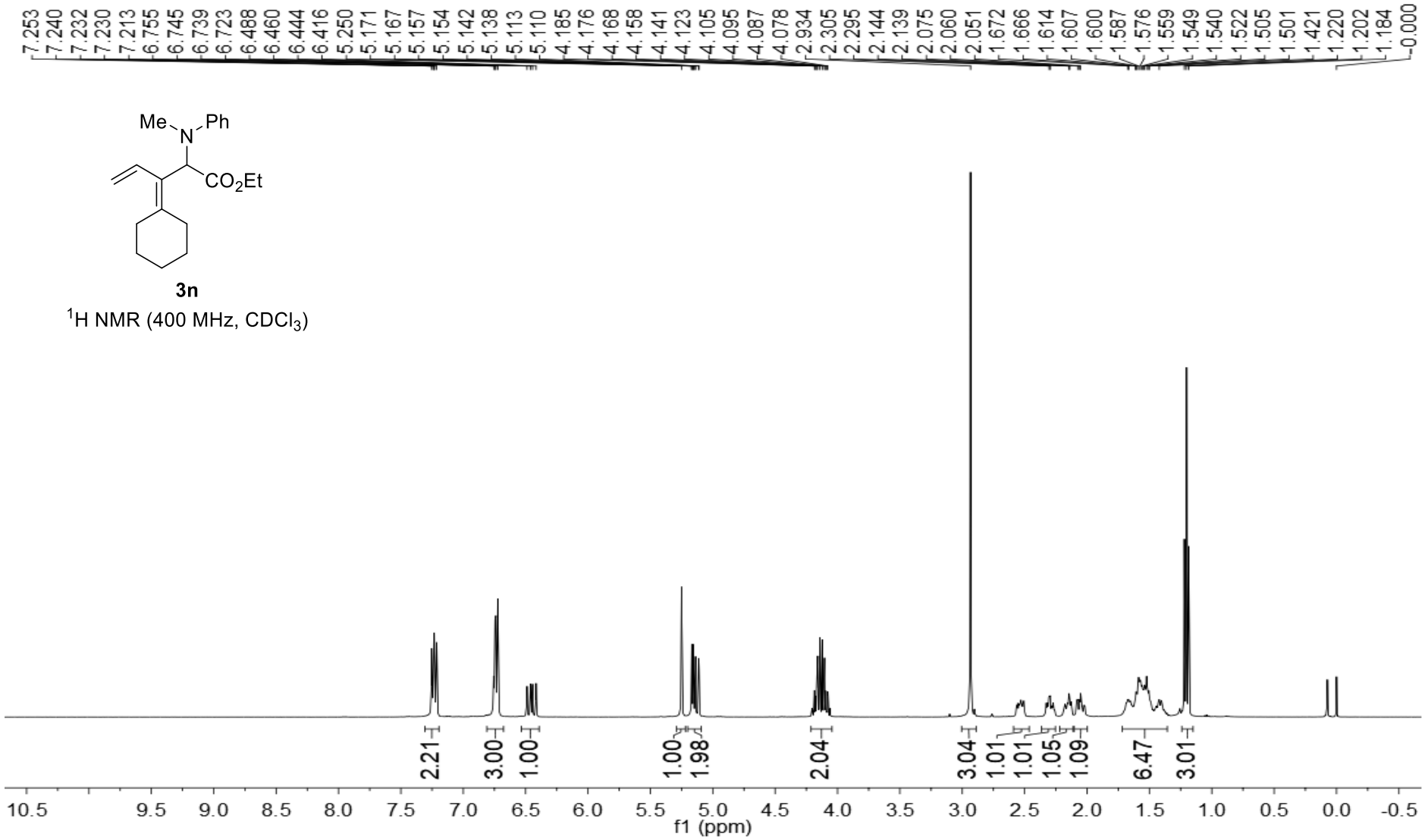
3m

^{1}H NMR (400 MHz, $CDCl_3$)



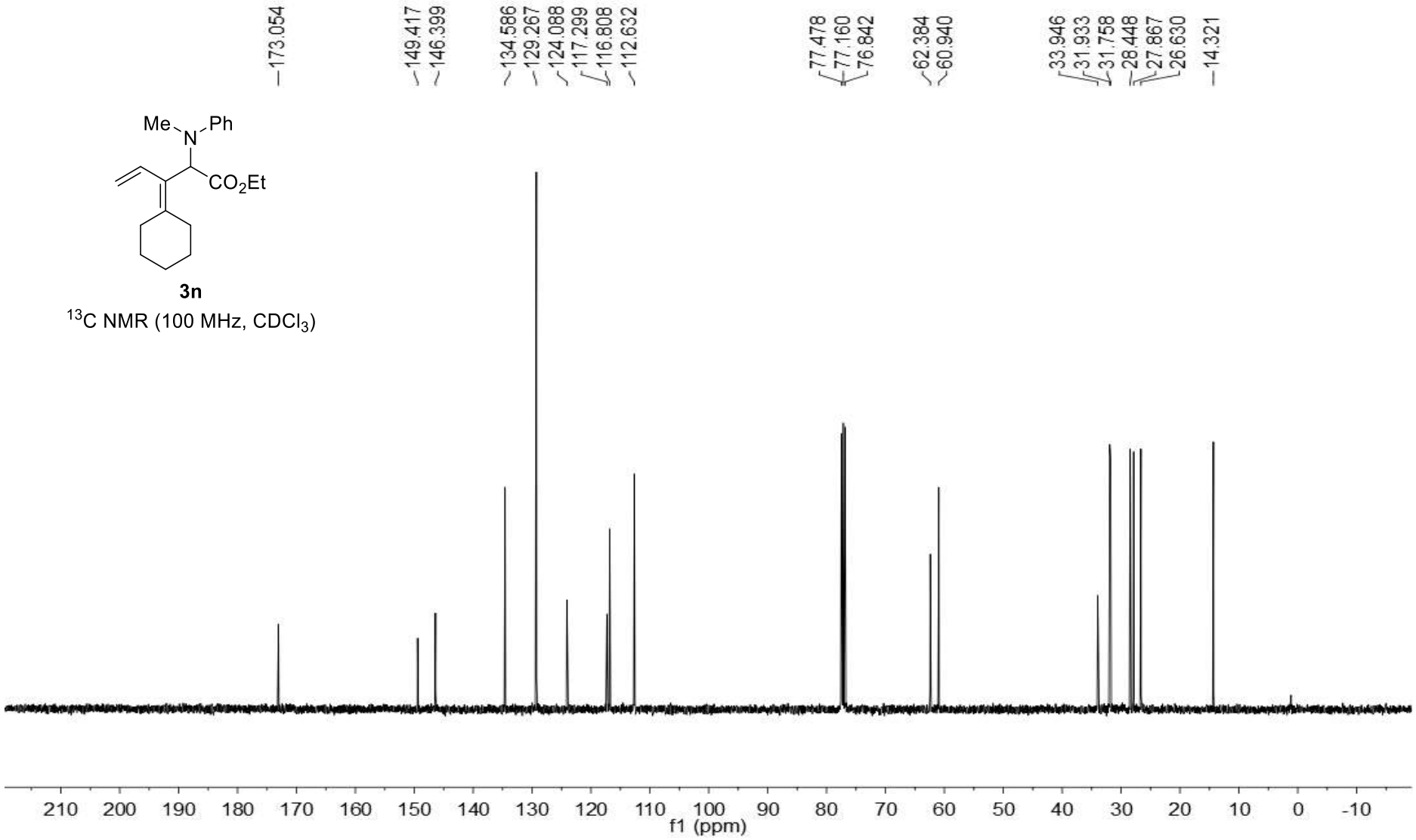
3m

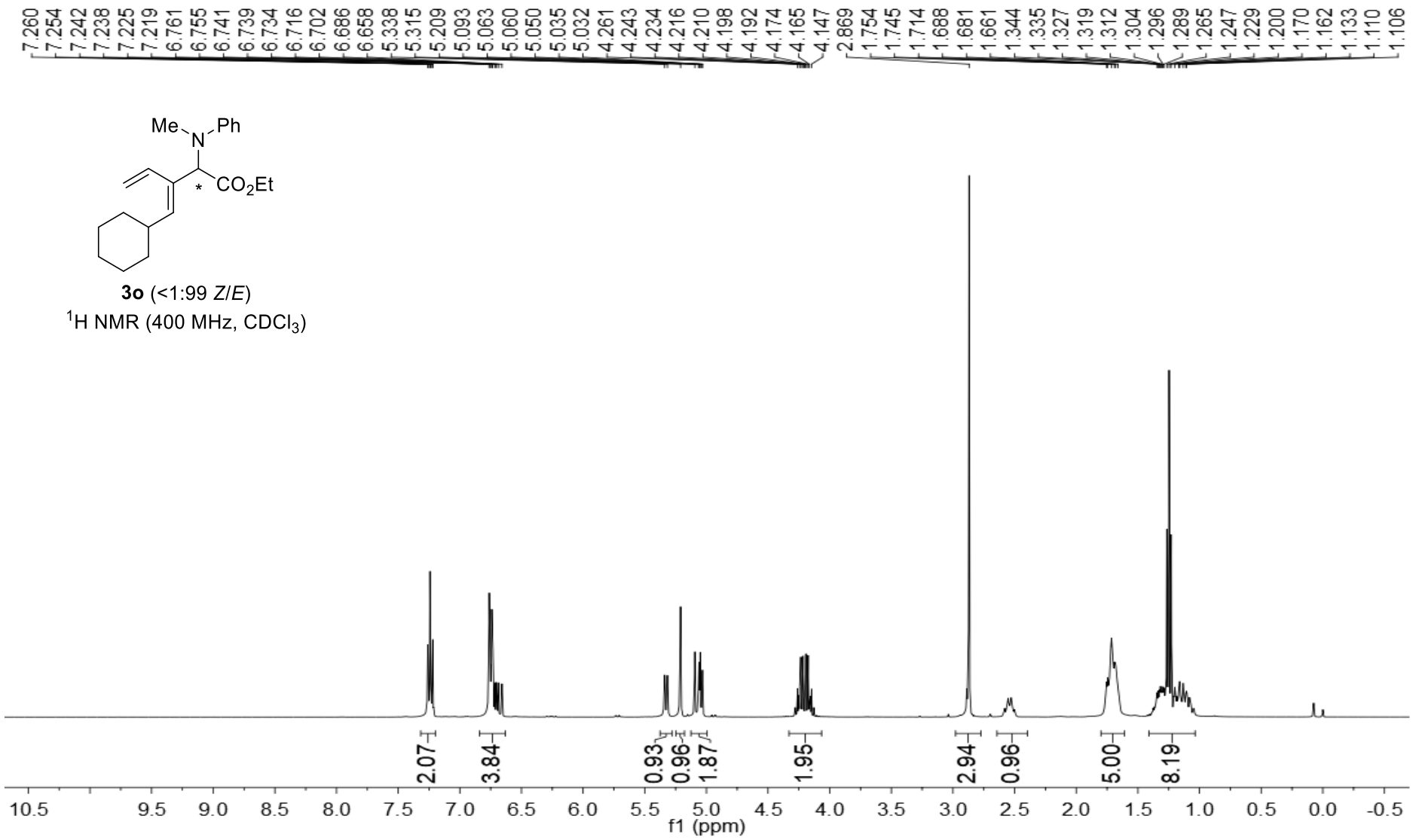
^{13}C NMR (100 MHz, $CDCl_3$)



3n

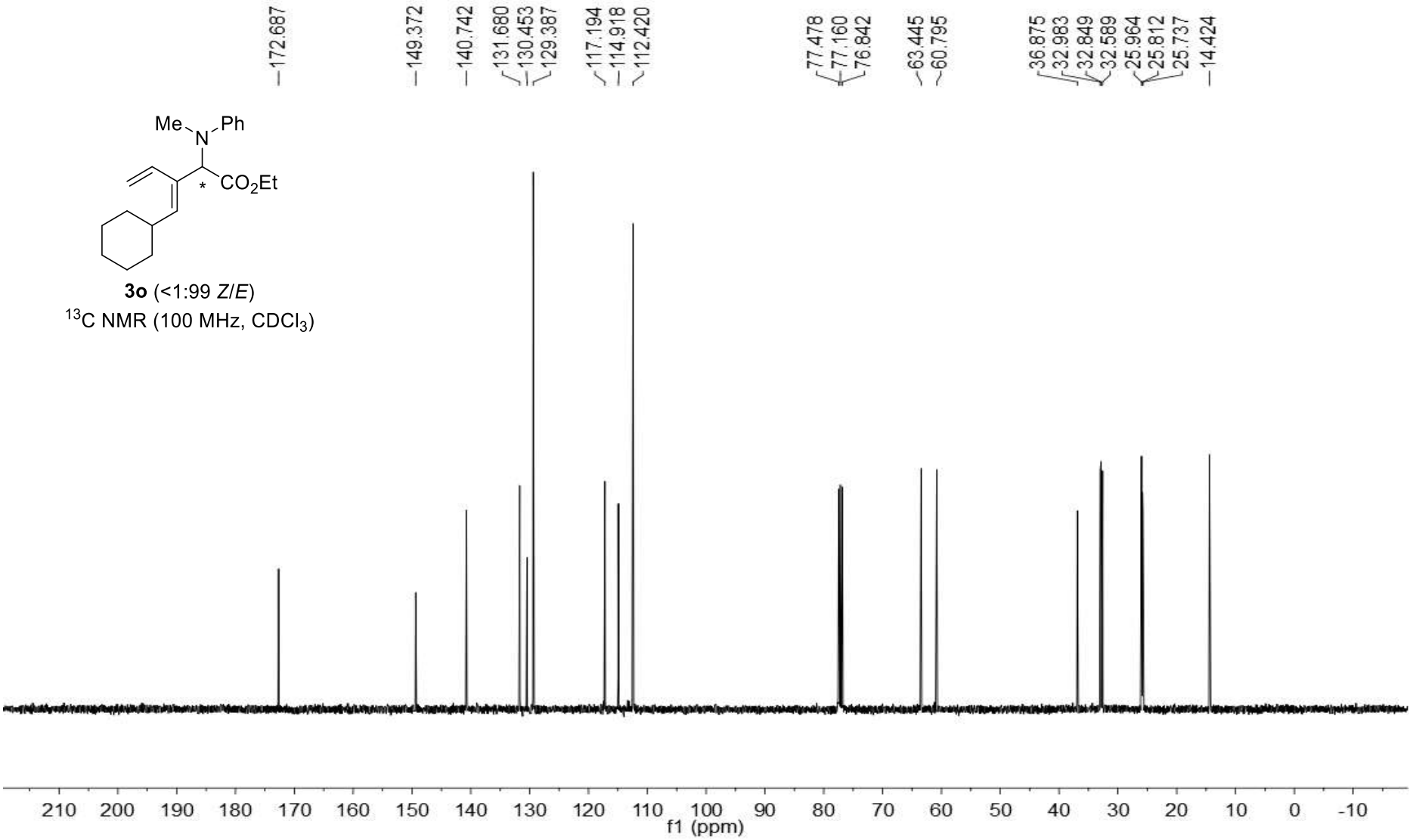
^{1}H NMR (400 MHz, $CDCl_3$)


173.054
149.417
146.399
134.586
129.267
124.088
117.299
116.808
112.632
77.478
77.160
76.842
62.384
60.940
33.946
31.933
31.758
28.448
27.867
26.630
14.321
Me
N
Ph
CO2Et
3n
13C NMR (100 MHz, 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)



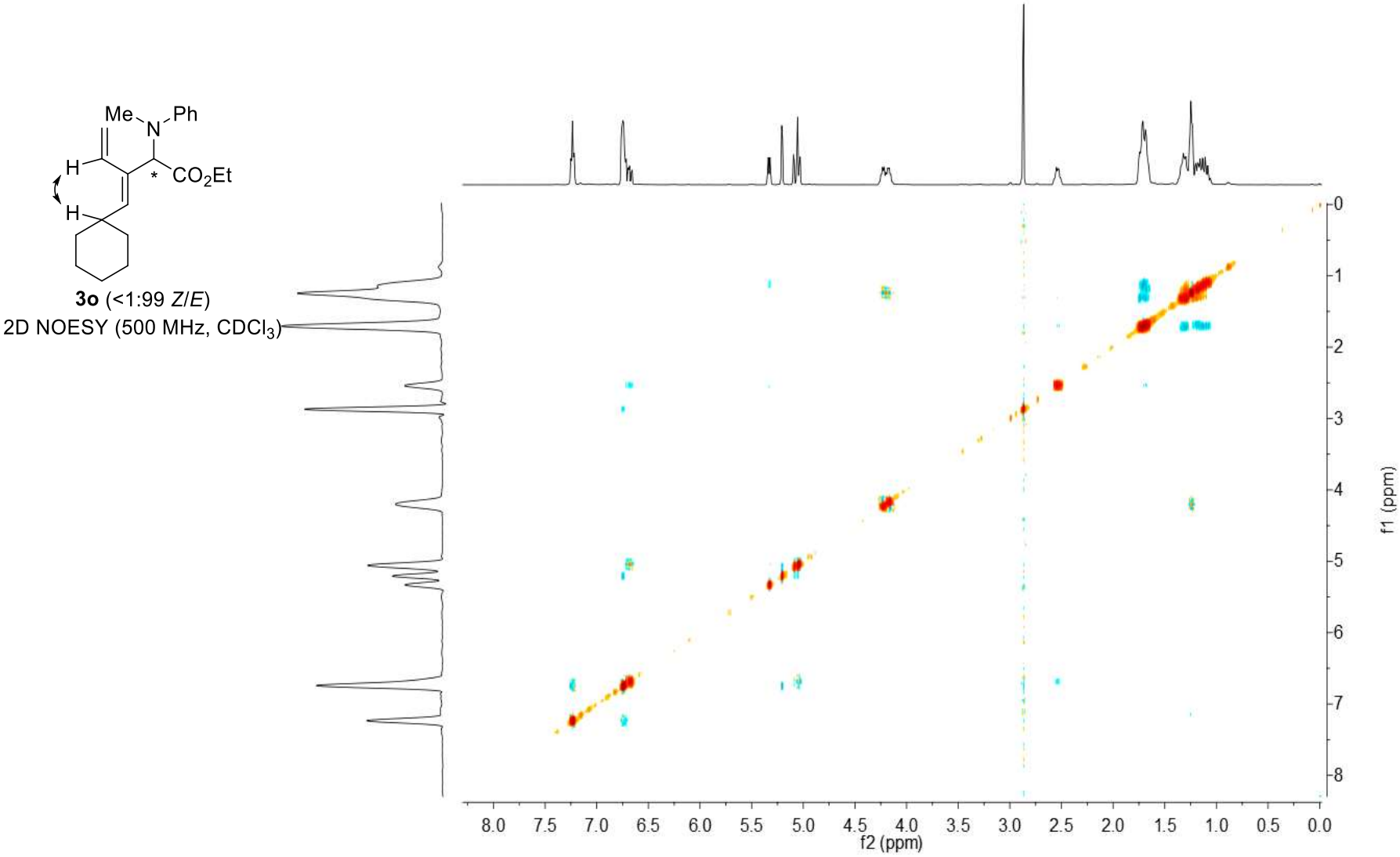
3o (<1:99 *Z*/*E*)

^{1}H NMR (400 MHz, $CDCl_3$)

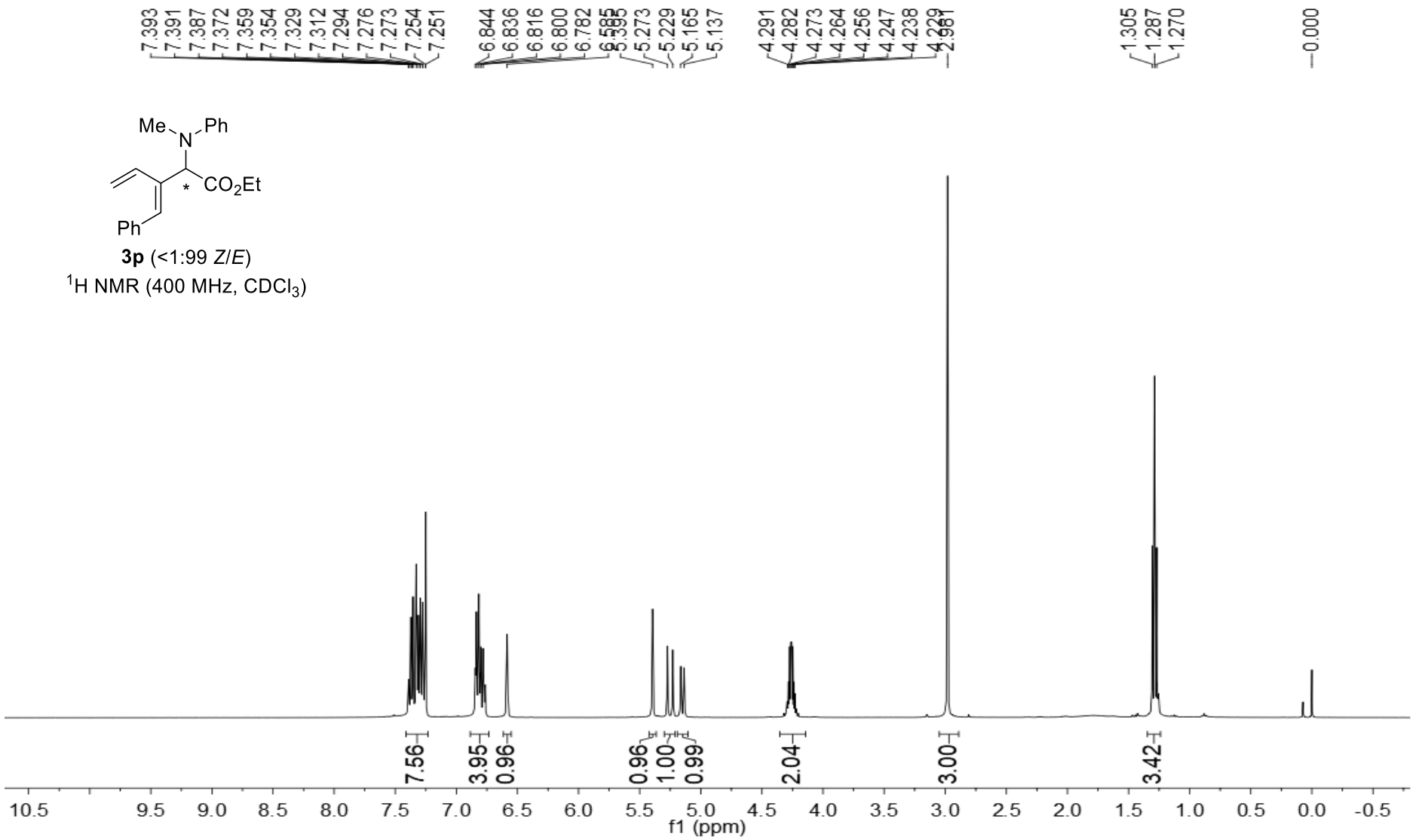


3o (<1:99 *Z*/*E*)

^{13}C NMR (100 MHz, $CDCl_3$)

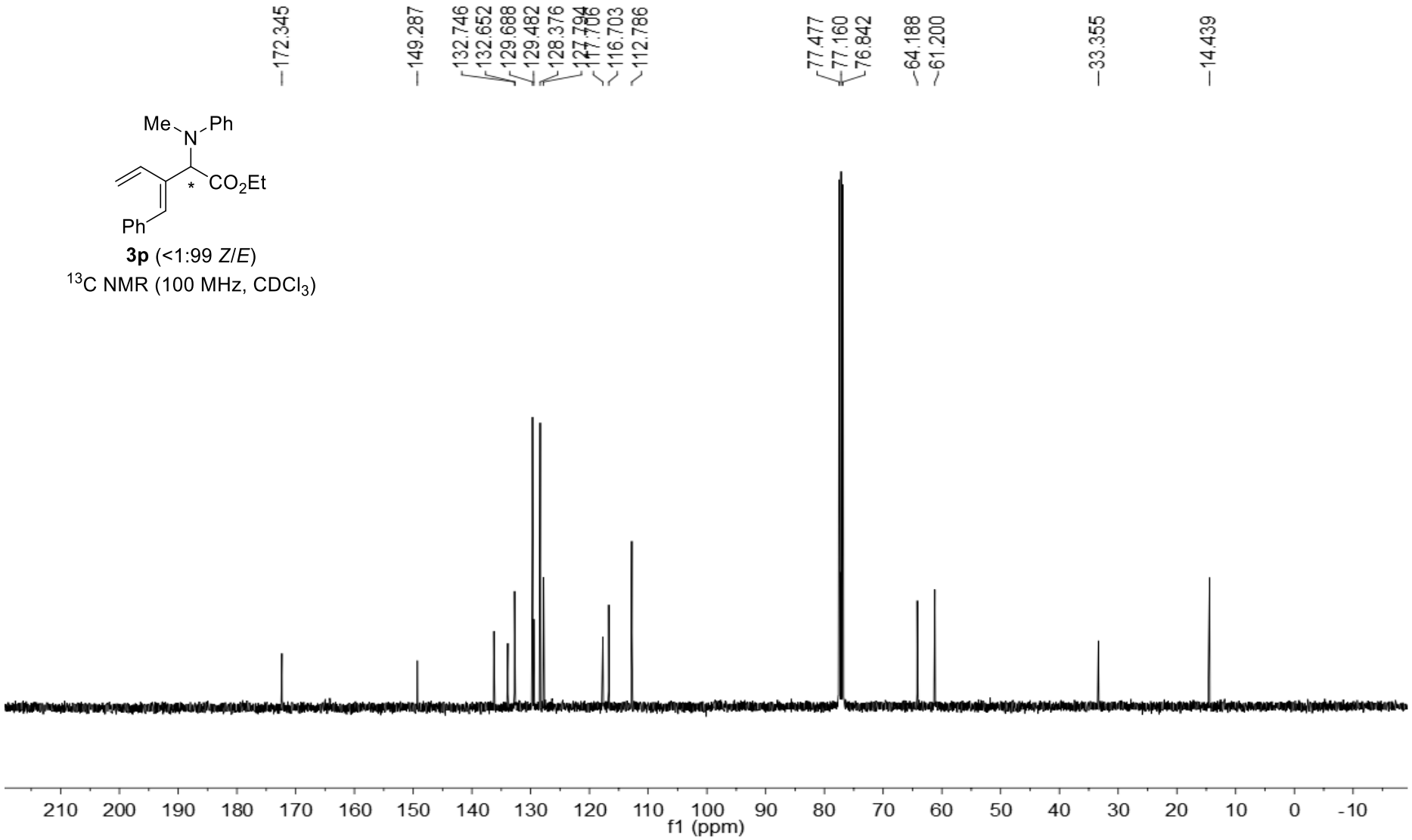


3o (<1:99 *Z*/*E*)
2D NOESY (500 MHz, $CDCl_3$)



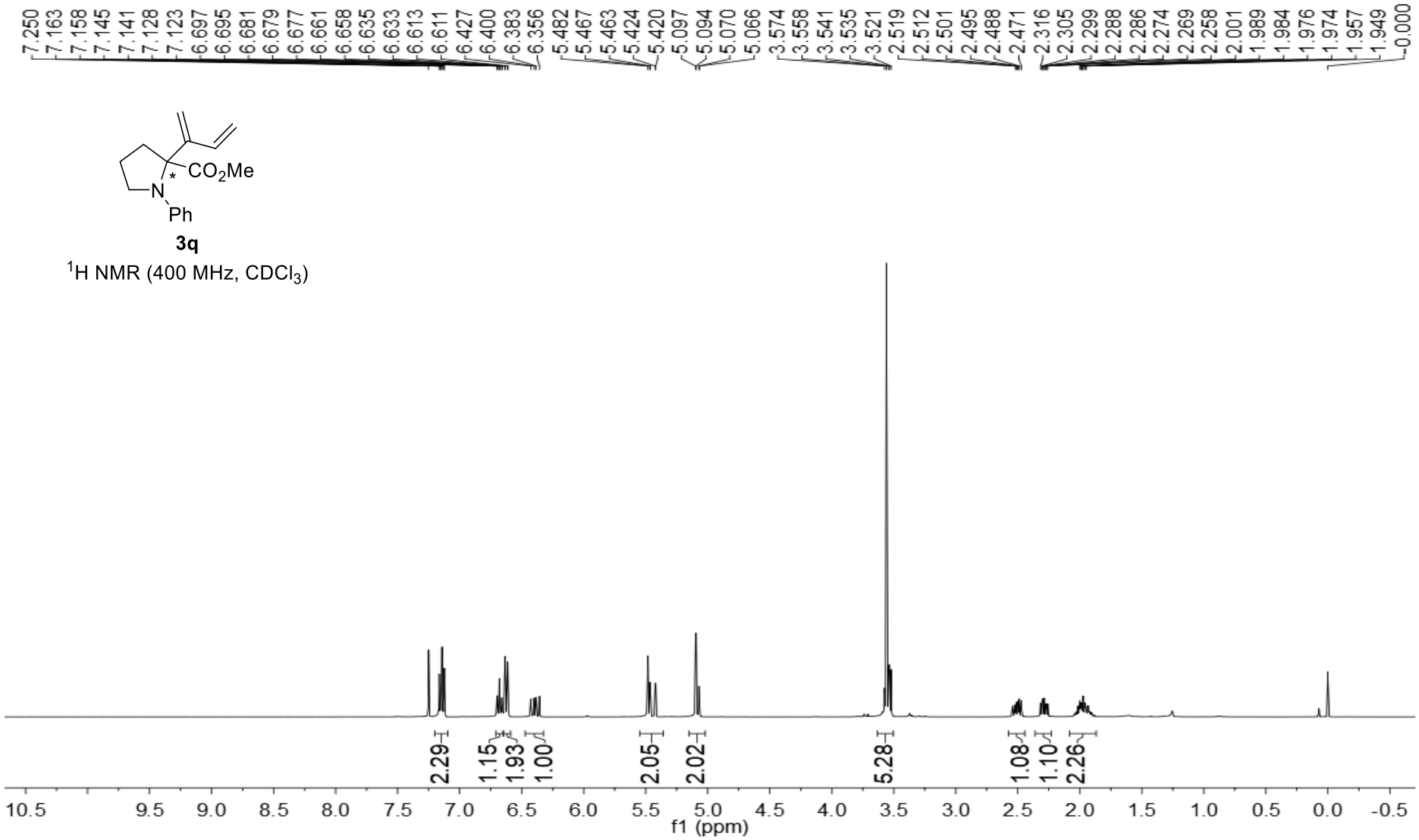
3p (<1:99 *Z*/*E*)

^{1}H NMR (400 MHz, $CDCl_3$)



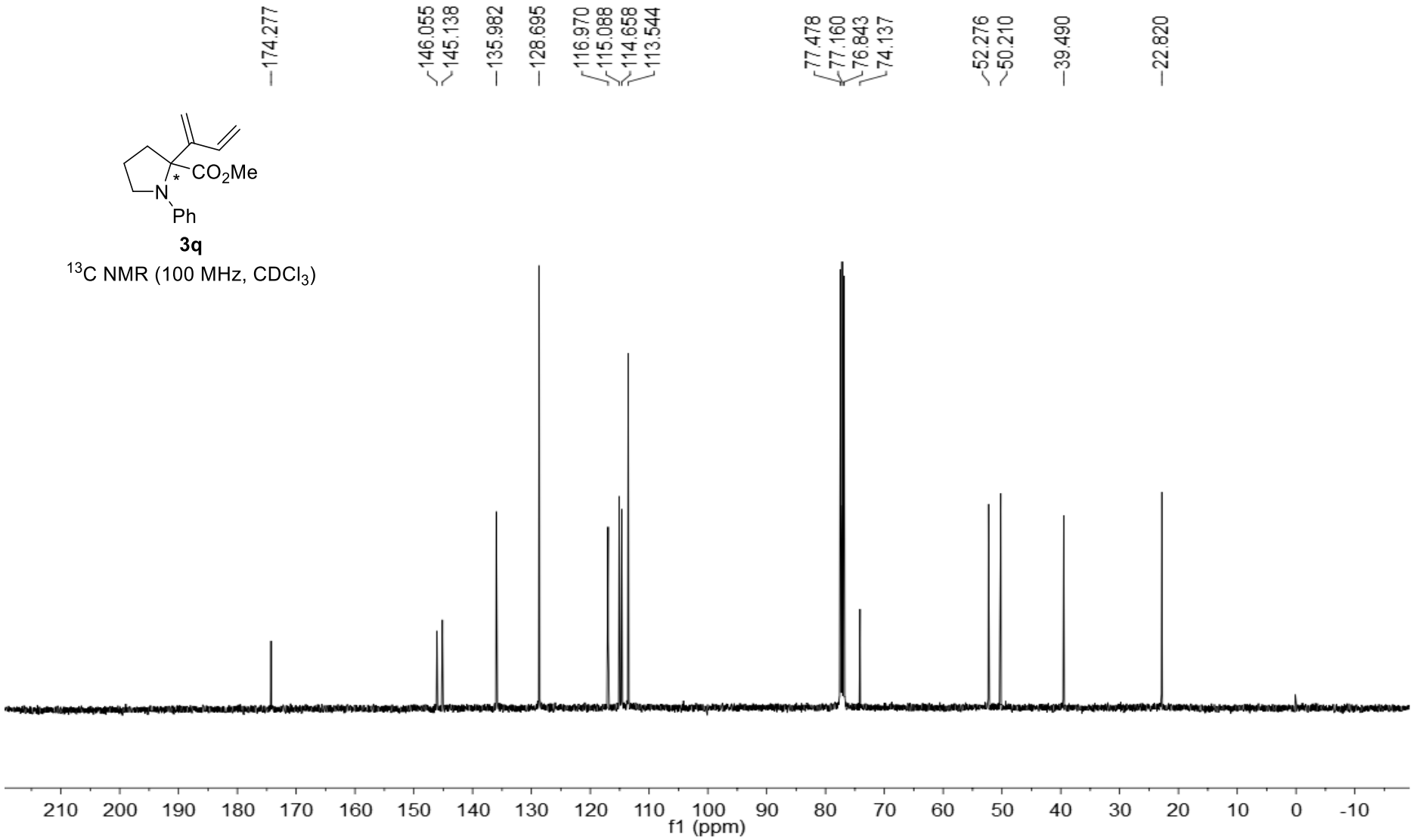
3p (<1:99 *Z*/*E*)

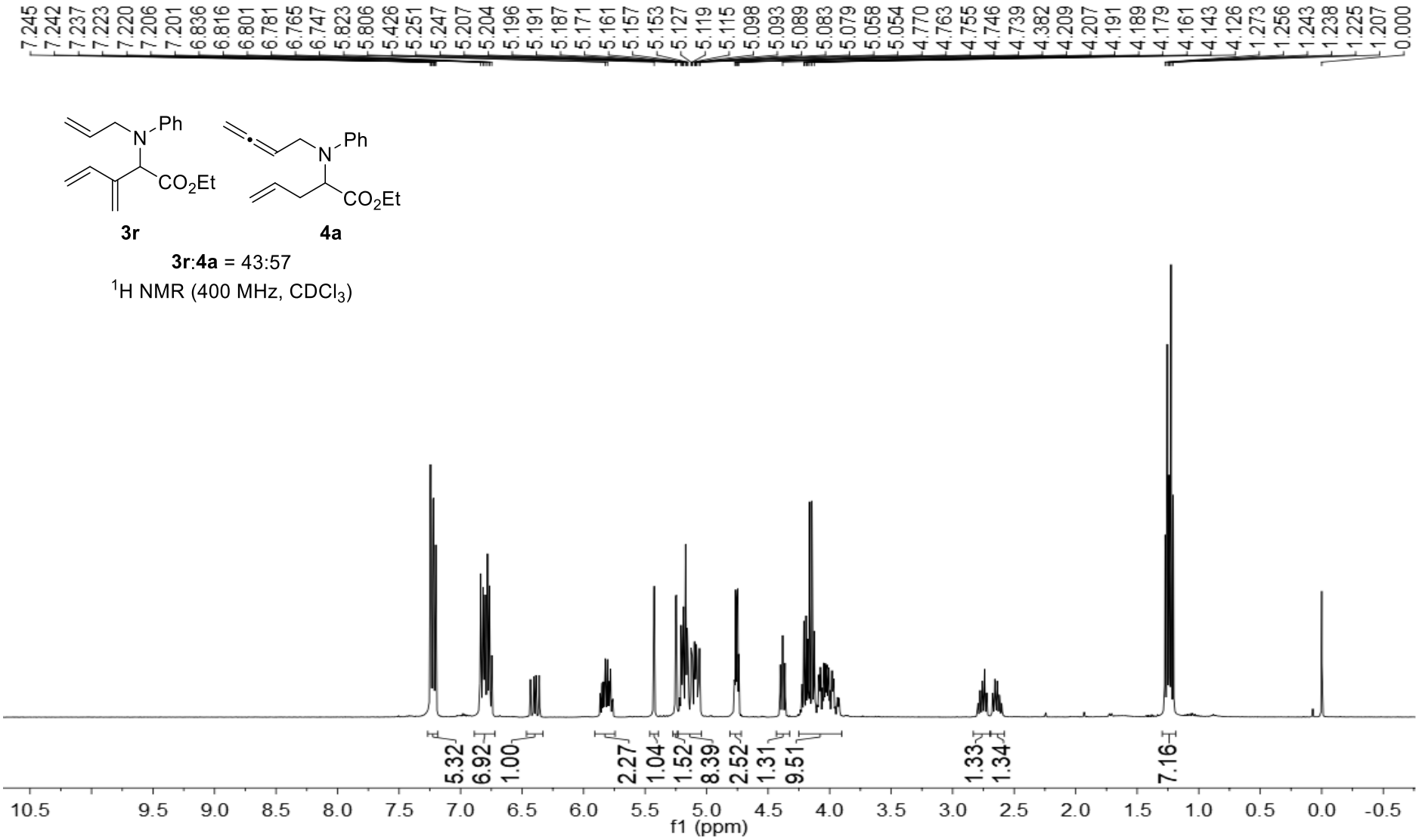
^{13}C NMR (100 MHz, $CDCl_3$)

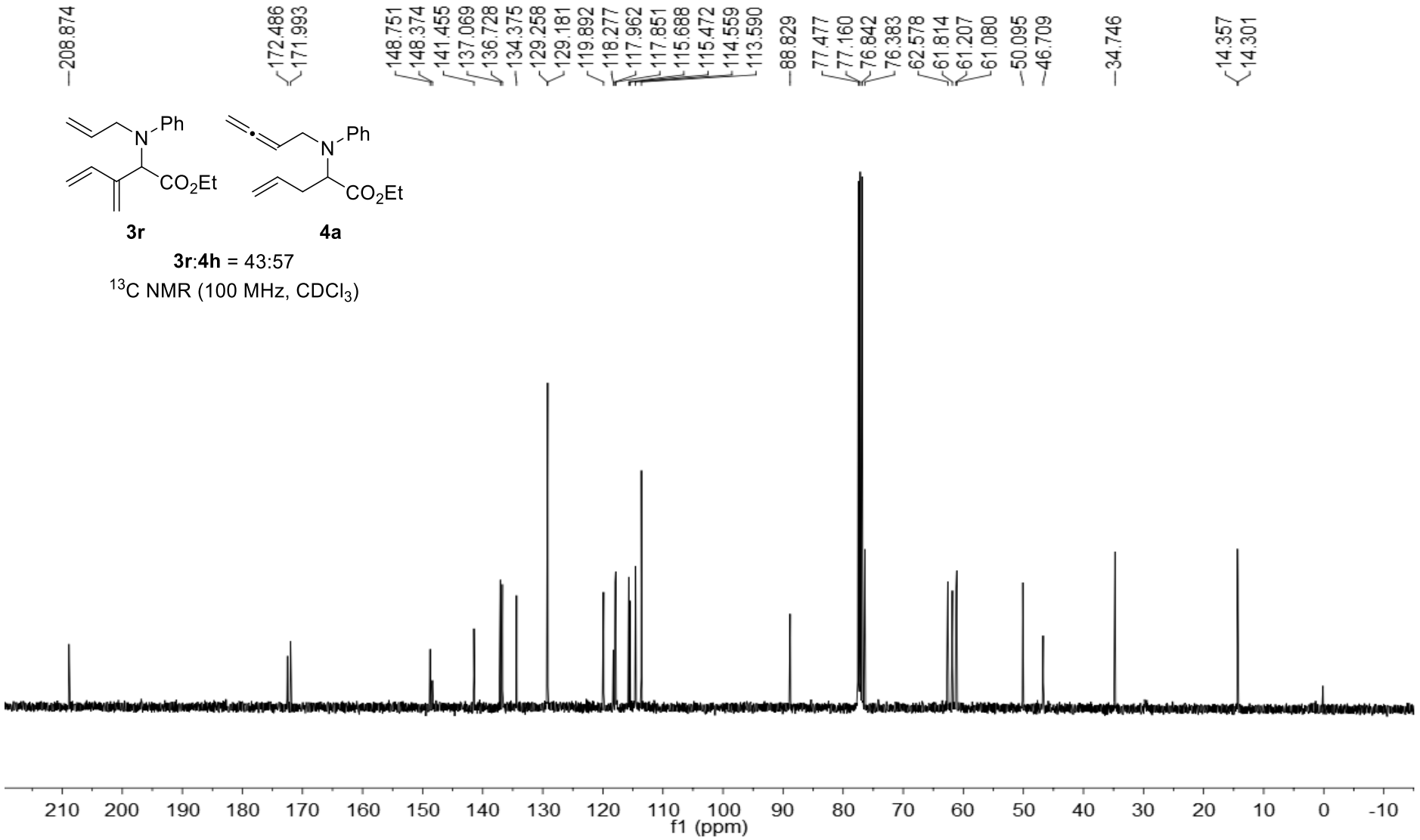


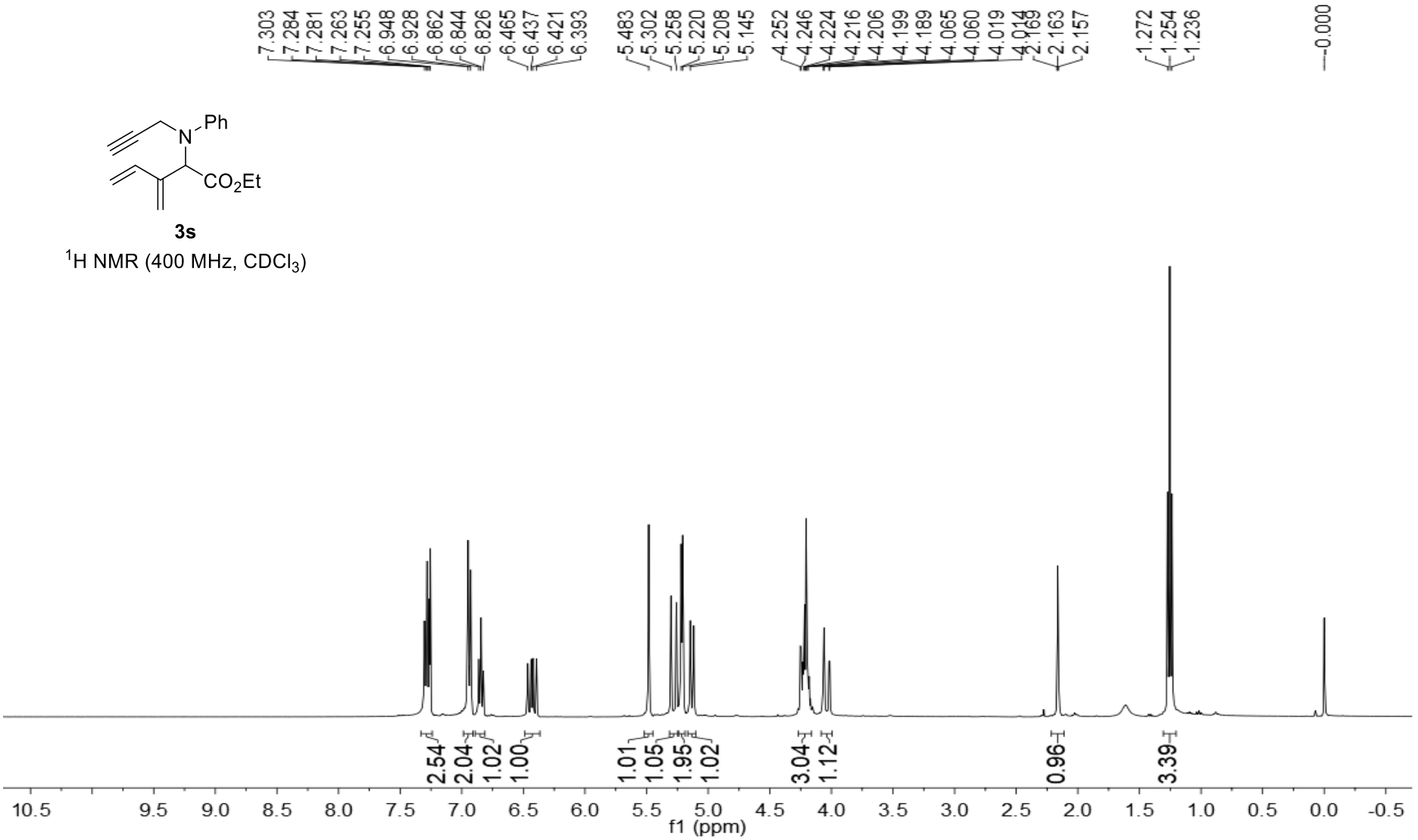
3q

^{1}H NMR (400 MHz, $CDCl_3$)


174.277
146.055
145.138
135.982
128.695
116.970
115.088
114.658
113.544
77.478
77.160
76.843
74.137
52.276
50.210
39.490
22.820
CO2Me
N
Ph
3q
13C NMR (100 MHz, 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)

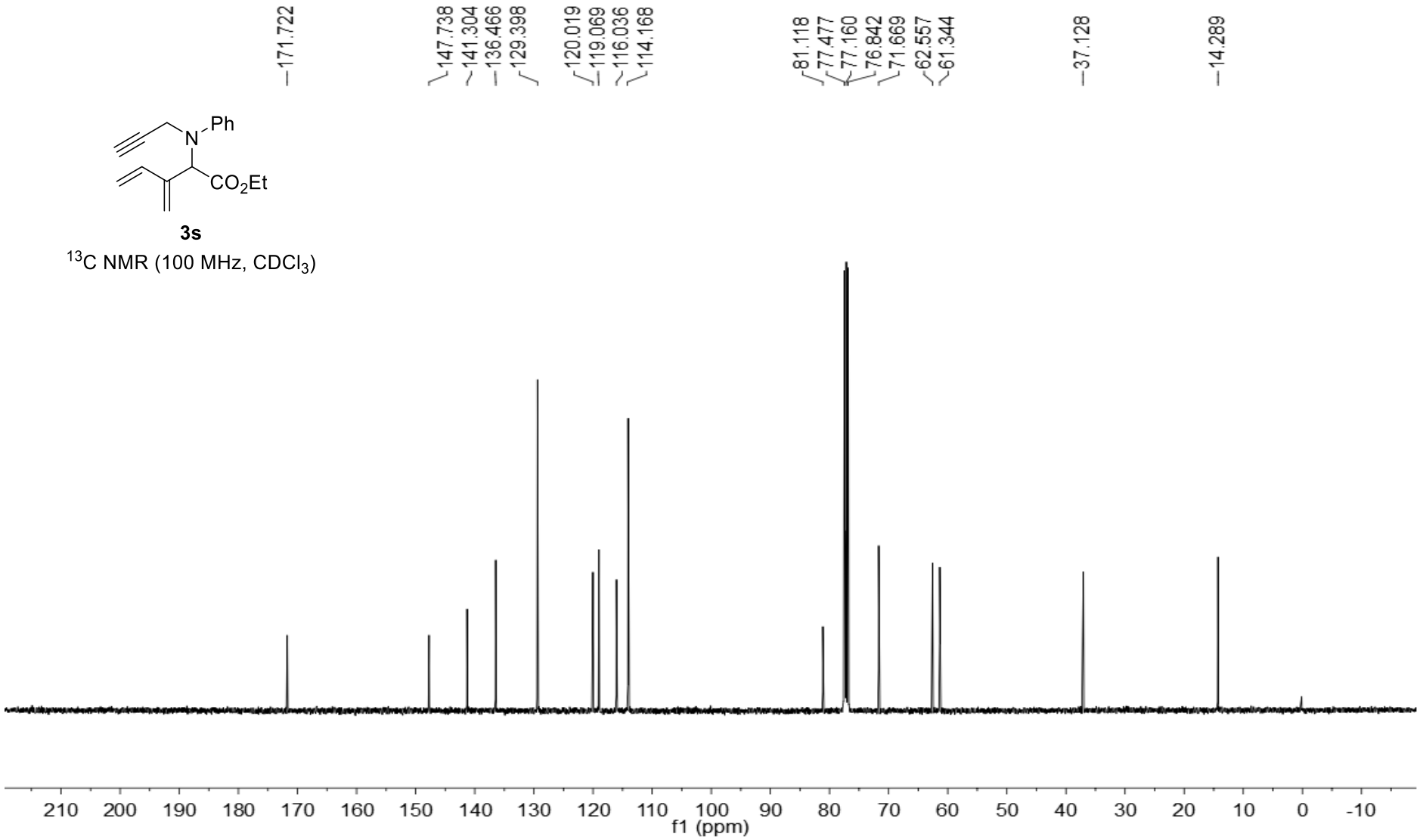

7.245
7.242
7.237
7.223
7.220
7.206
7.201
6.836
6.816
6.801
6.781
6.765
6.747
5.823
5.806
5.426
5.251
5.247
5.207
5.204
5.196
5.191
5.187
5.171
5.161
5.157
5.153
5.127
5.119
5.115
5.098
5.093
5.089
5.083
5.079
5.058
5.054
4.770
4.763
4.755
4.746
4.739
4.382
4.209
4.207
4.191
4.189
4.179
4.161
4.143
4.126
1.273
1.256
1.243
1.238
1.225
1.207
0.000
Ph
N
CO2Et
Ph
N
CO2Et
3r
4a
3r:4a = 43:57
1H NMR (400 MHz, CDCl3)
5.32
6.92
1.00
2.27
1.04
1.52
8.39
2.52
1.31
9.51
1.33
1.34
7.16
10.5
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)


208.874
172.486
171.993
148.751
148.374
141.455
137.069
136.728
134.375
129.258
129.181
119.892
118.277
117.962
117.851
115.688
115.472
114.559
113.590
88.829
77.477
77.160
76.842
76.383
62.578
61.814
61.207
61.080
50.095
46.709
34.746
14.357
14.301
Ph
N
CO2Et
3r
4a
3r:4h = 43:57
13C NMR (100 MHz, 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)



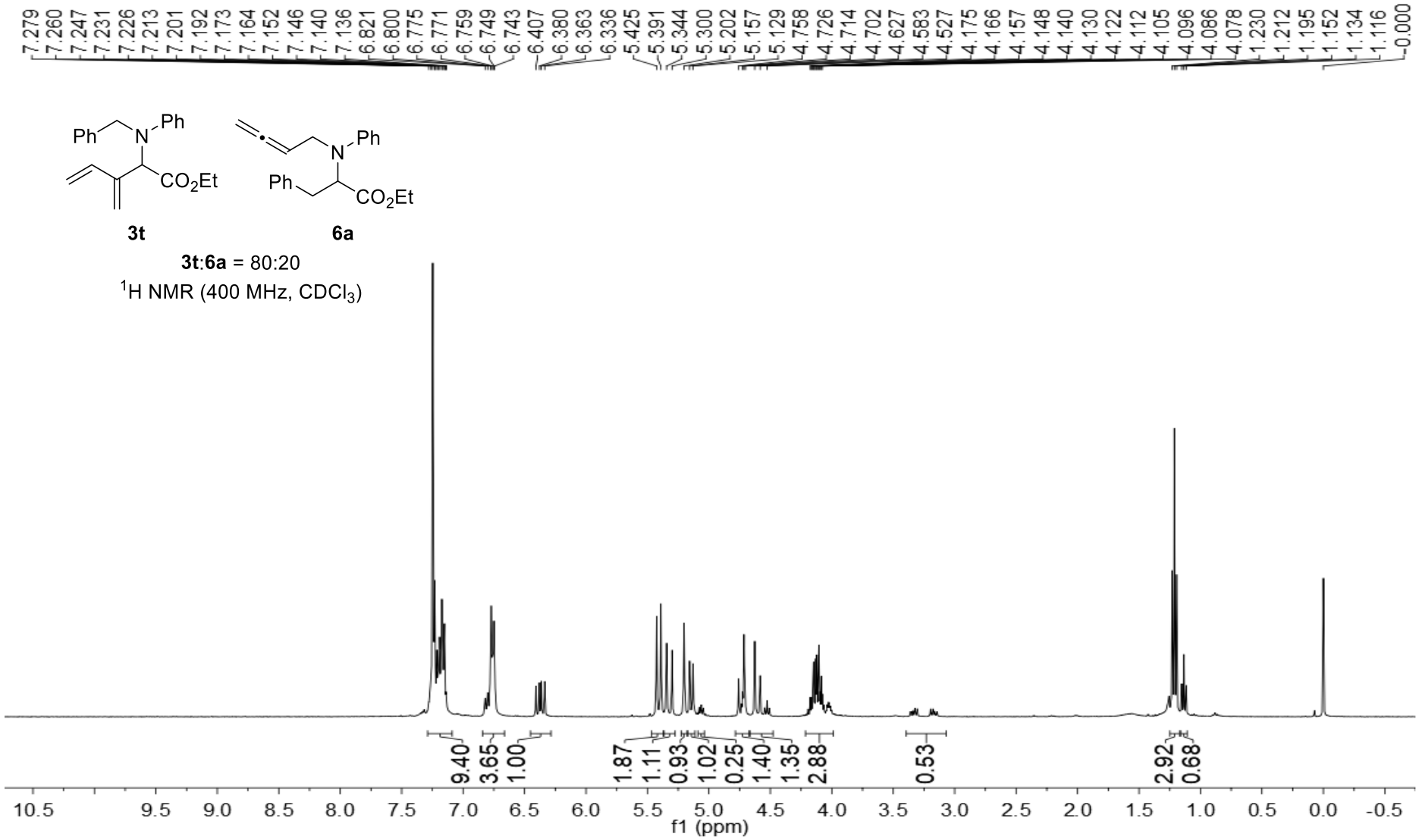
3s

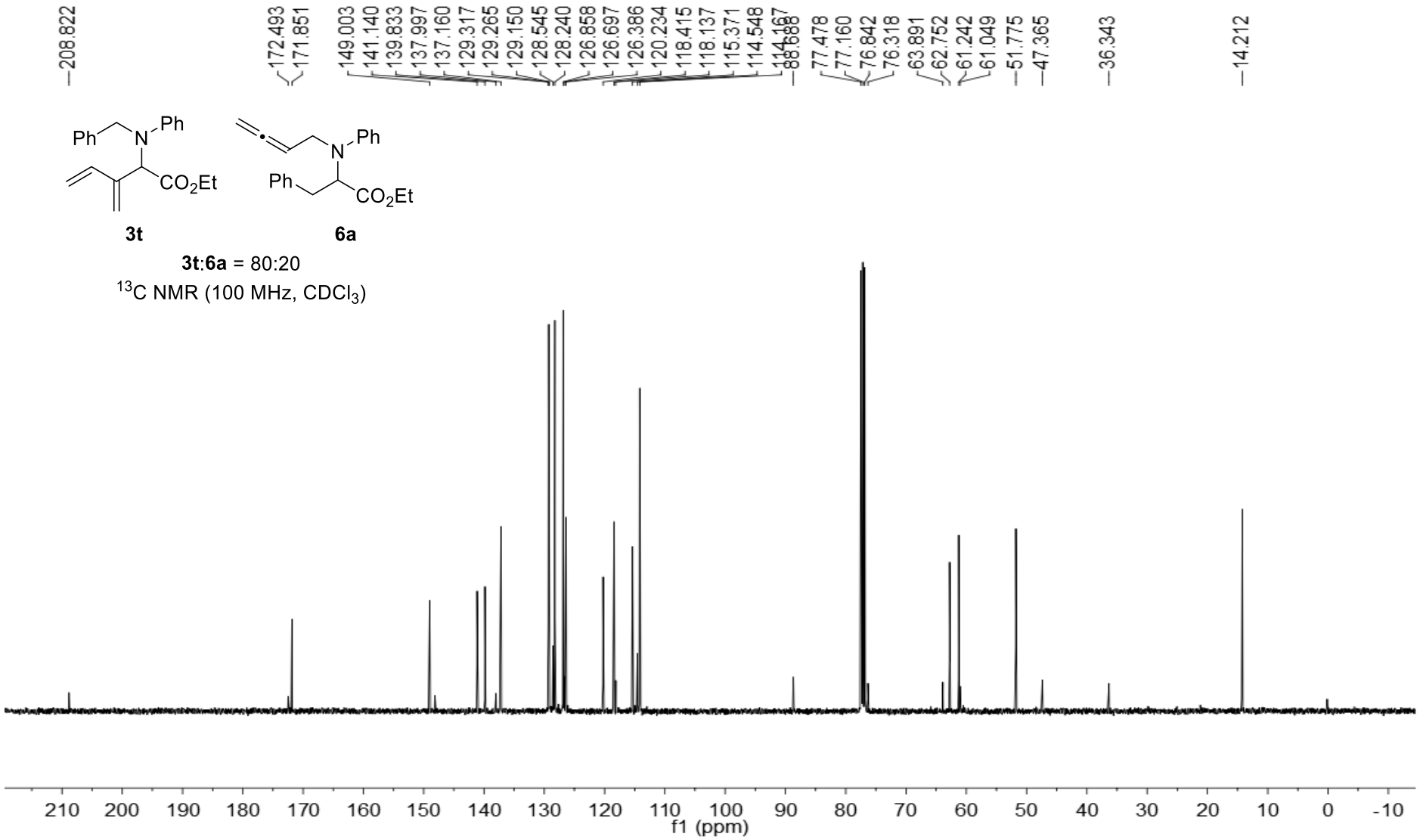
^{1}H NMR (400 MHz, $CDCl_3$)

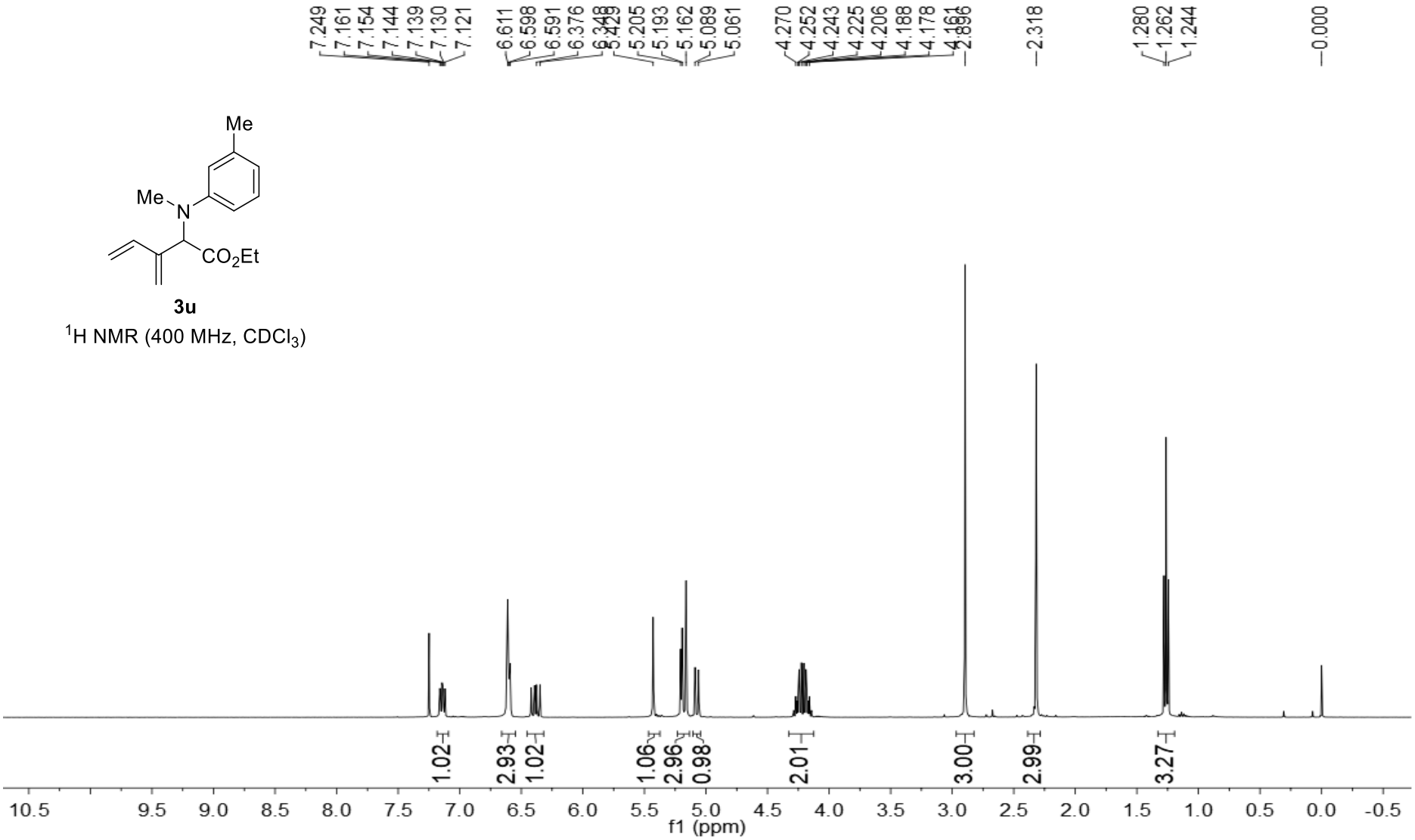


3s

^{13}C NMR (100 MHz, $CDCl_3$)

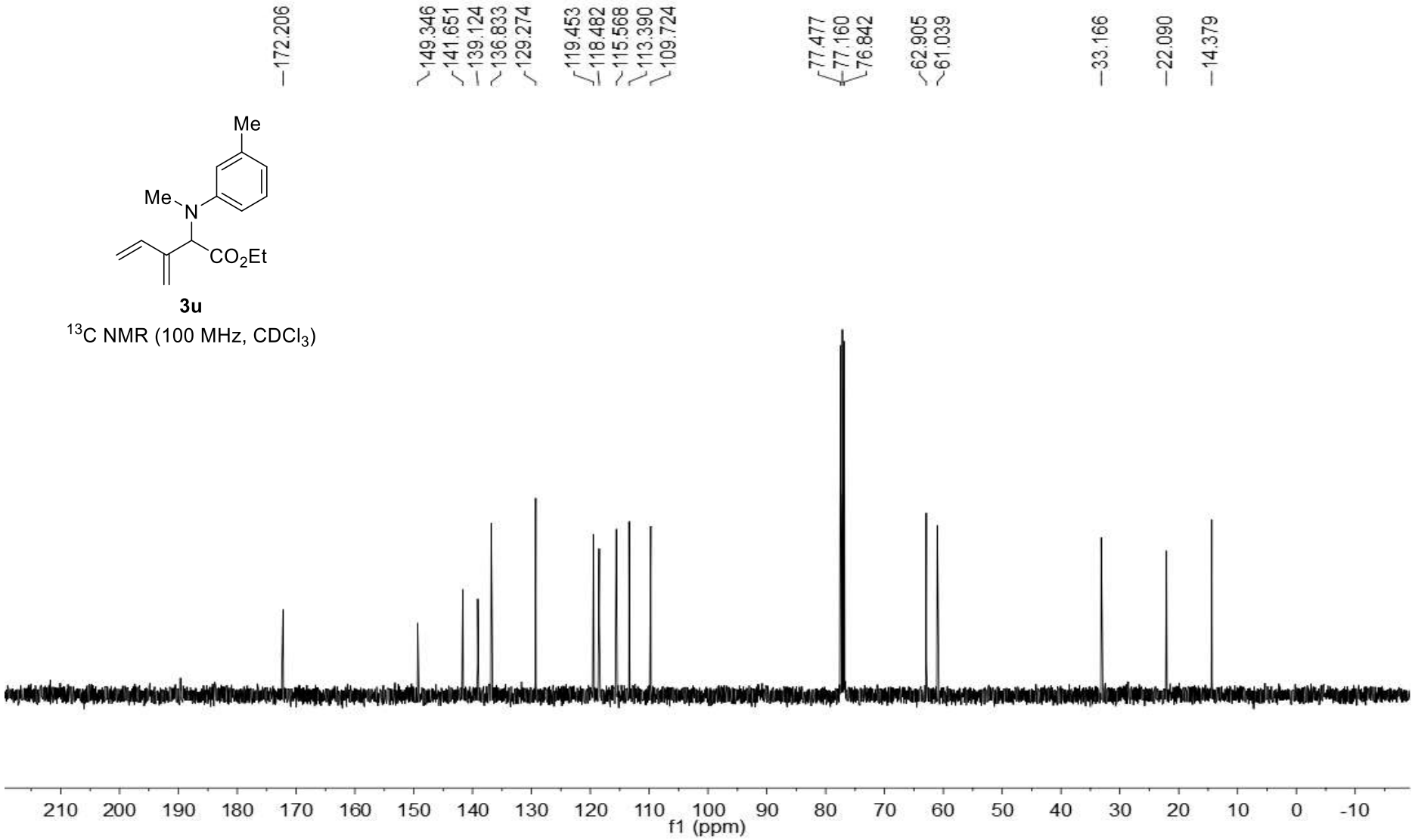

7.279
7.260
7.247
7.231
7.226
7.213
7.201
7.192
7.173
7.164
7.152
7.146
7.140
7.136
6.821
6.800
6.775
6.771
6.759
6.749
6.743
6.407
6.380
6.363
6.336
5.425
5.391
5.344
5.300
5.202
5.157
5.129
4.758
4.726
4.714
4.702
4.627
4.583
4.527
4.175
4.166
4.157
4.148
4.140
4.130
4.122
4.112
4.105
4.096
4.086
4.078
1.230
1.212
1.195
1.152
1.134
1.116
0.000
Ph
N
Ph
CO2Et
Ph
N
Ph
Ph
CO2Et
3t
6a
3t:6a = 80:20
1H NMR (400 MHz, CDCl3)
9.40
3.65
1.00
1.87
1.11
0.93
1.02
0.25
1.40
1.35
2.88
0.53
2.92
0.68
10.5
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)


208.822
172.493
171.851
149.003
141.140
139.833
137.997
137.160
129.317
129.265
129.150
128.545
128.240
126.858
126.697
126.386
120.234
118.415
118.137
115.371
114.548
114.167
88.688
77.478
77.160
76.842
76.318
63.891
62.752
61.242
61.049
51.775
47.365
36.343
14.212
Ph
N
Ph
CO2Et
Ph
N
Ph
CO2Et
3t
6a
3t:6a = 80:20
13C NMR (100 MHz, 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)



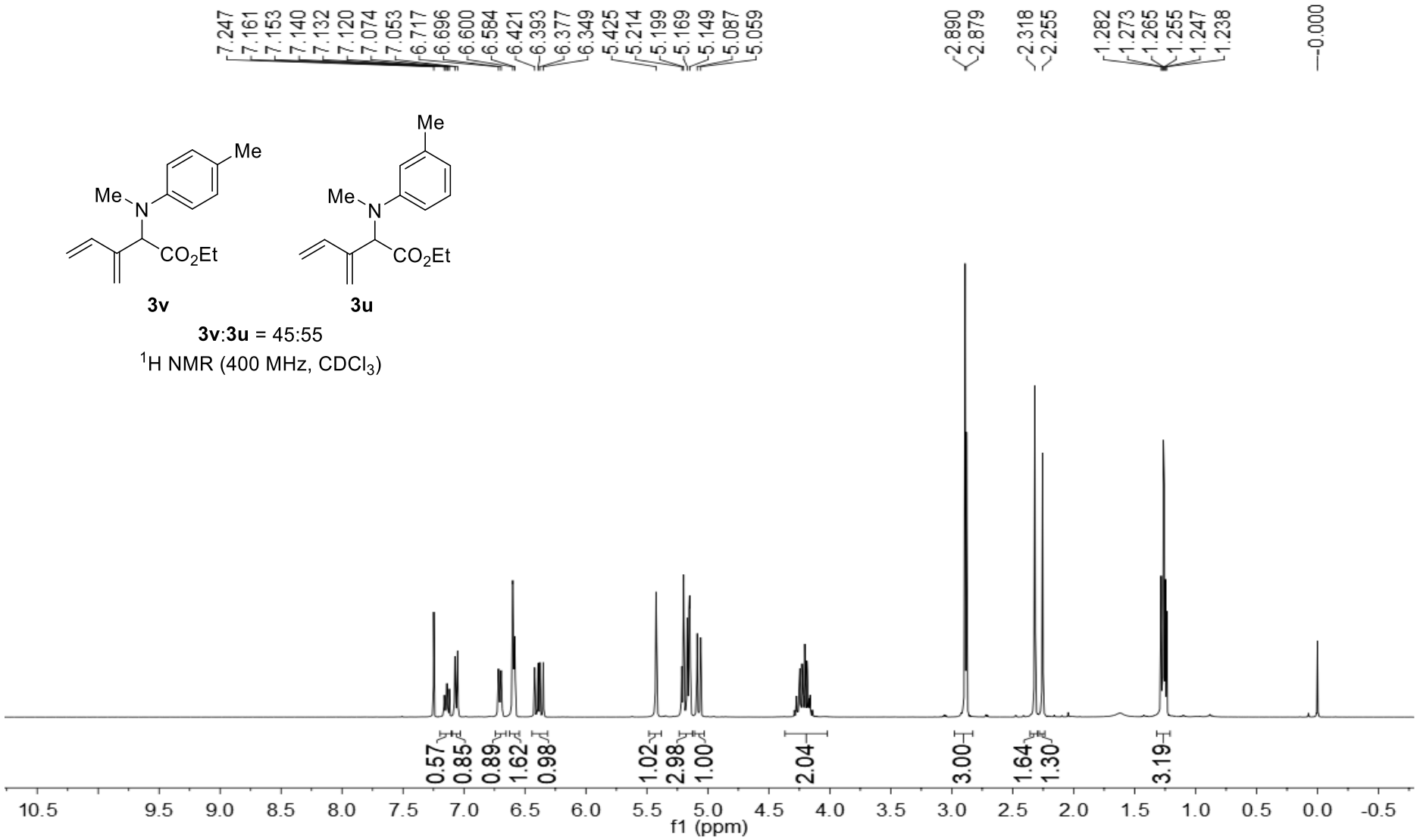
3u

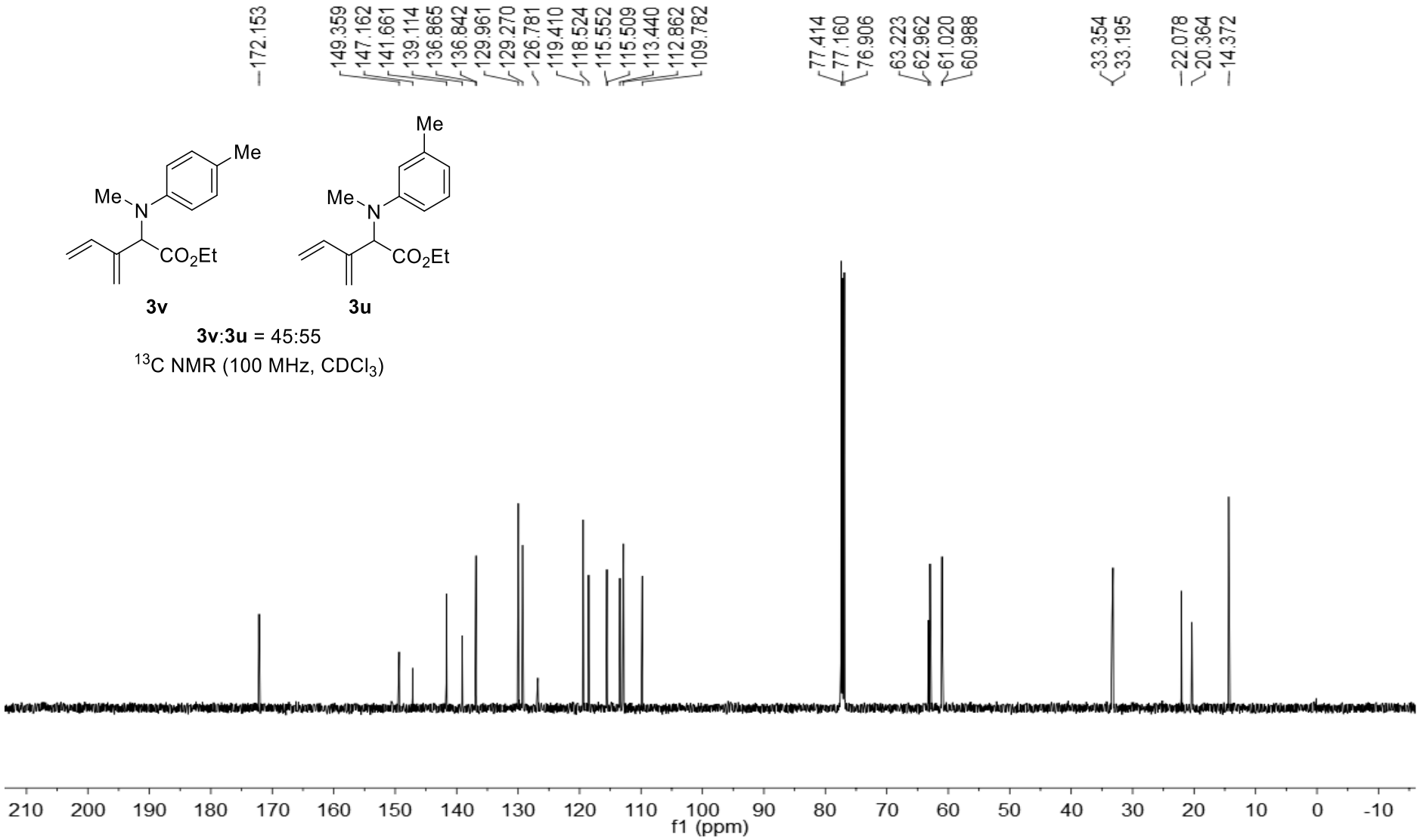
^{1}H NMR (400 MHz, $CDCl_3$)

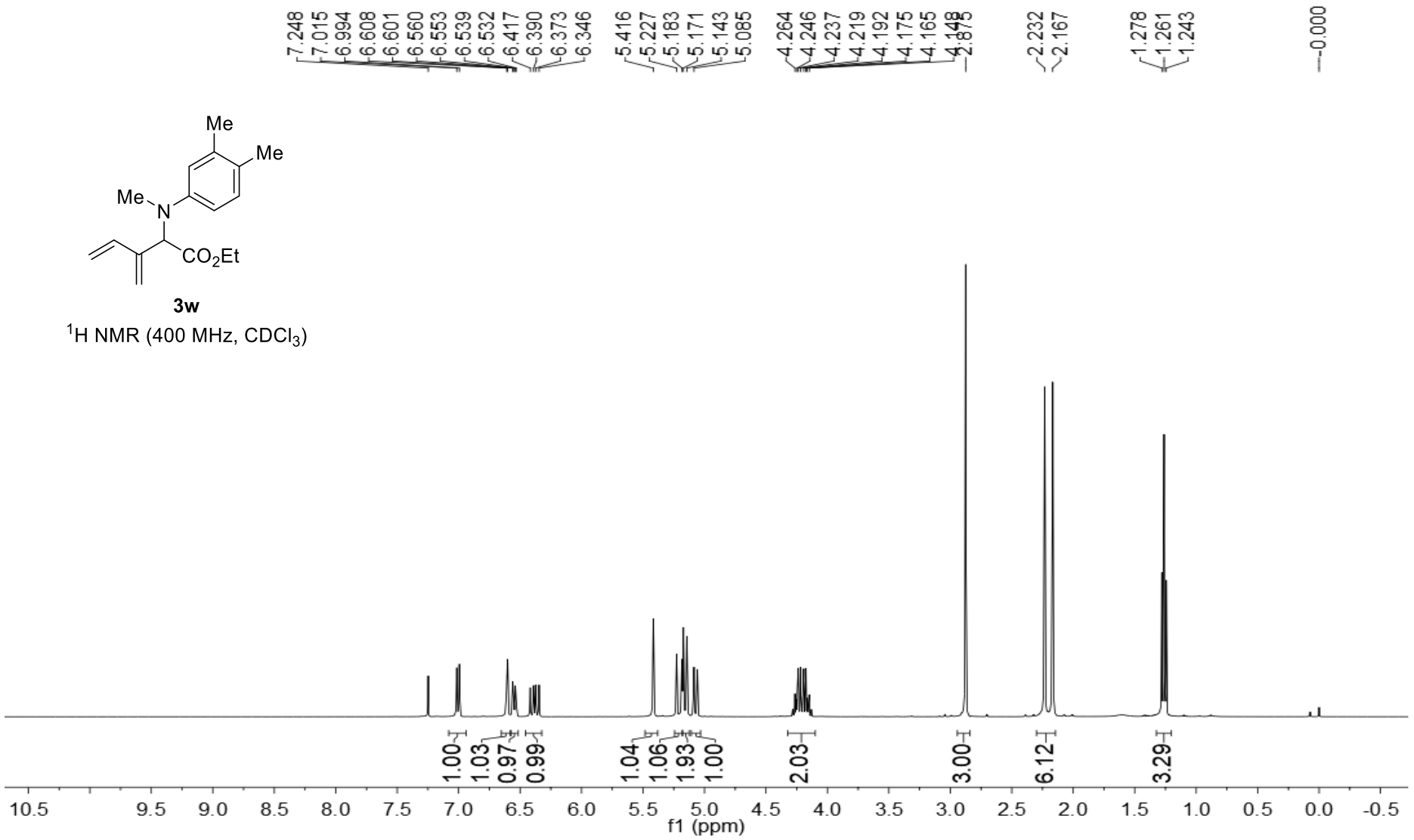


3u

^{13}C NMR (100 MHz, $CDCl_3$)

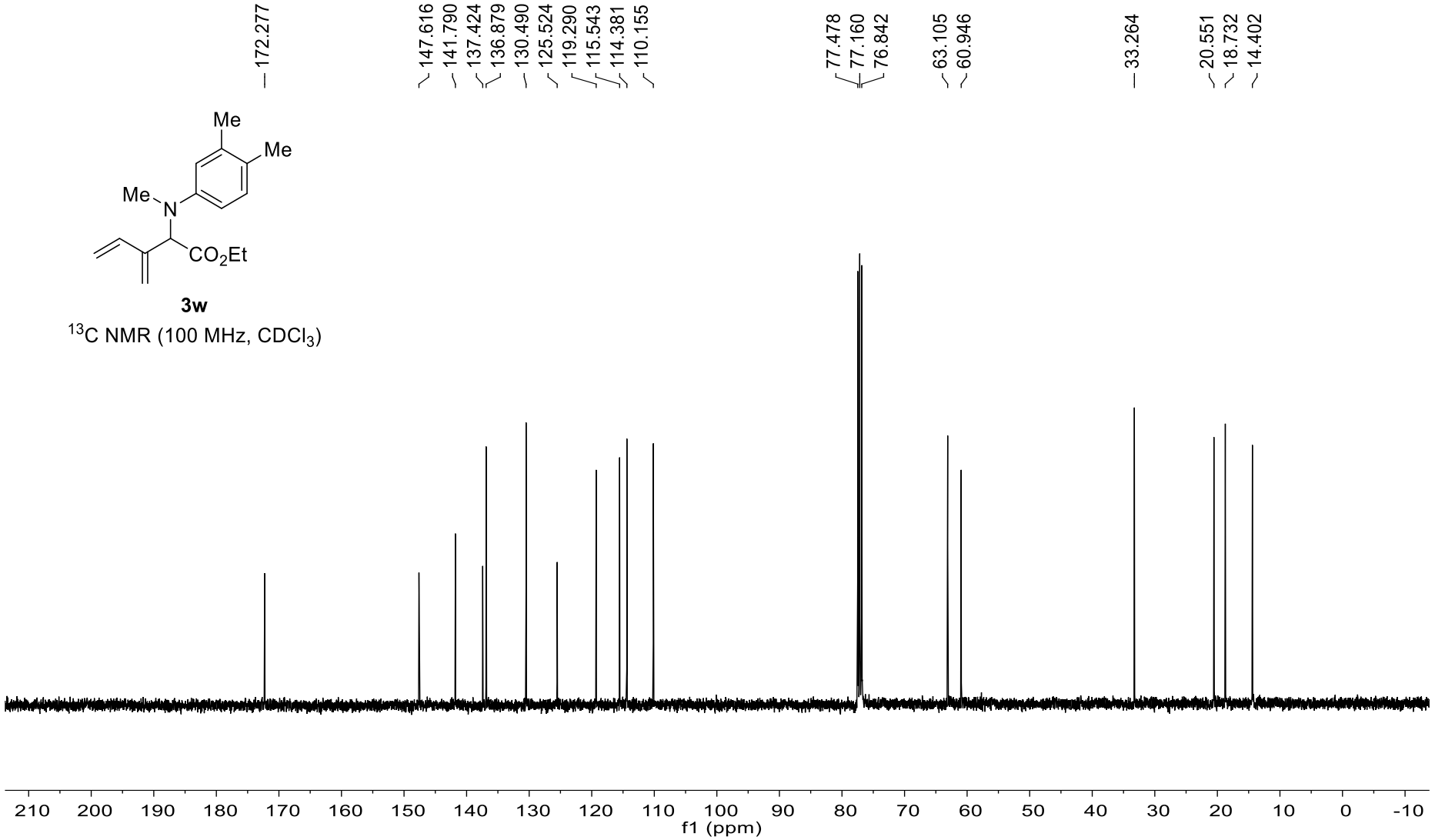

7.247
7.161
7.153
7.140
7.132
7.120
7.074
7.053
6.717
6.696
6.600
6.584
6.421
6.393
6.377
6.349
5.425
5.214
5.199
5.169
5.149
5.087
5.059
2.890
2.879
2.318
2.255
1.282
1.273
1.265
1.255
1.247
1.238
0.000
Me
Me
N
CO2Et
3v
Me
Me
N
CO2Et
3u
3v:3u = 45:55
1H NMR (400 MHz, CDCl3)
0.57
0.85
0.89
1.62
0.98
1.02
2.98
1.00
2.04
3.00
1.64
1.30
3.19
10.5
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)

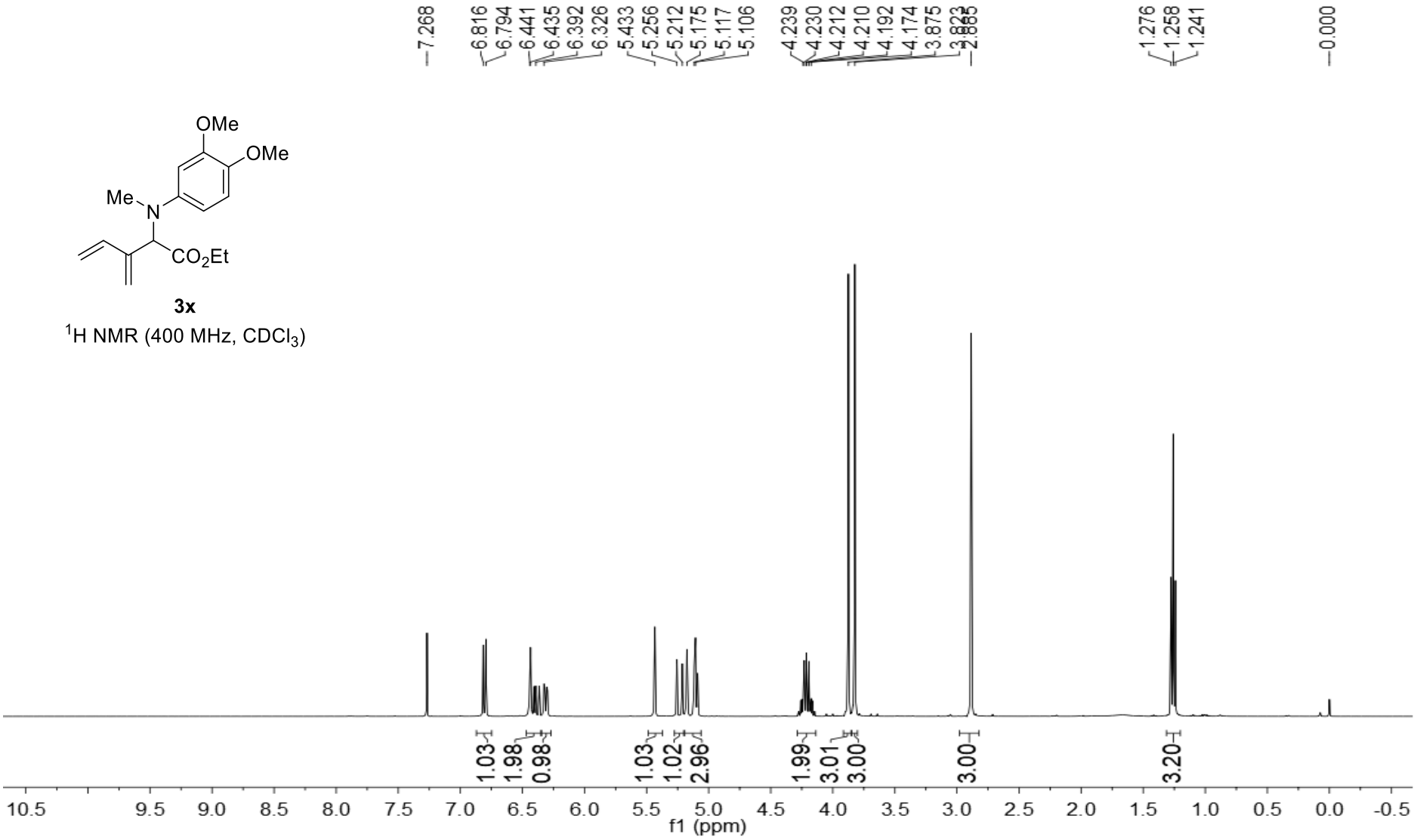

172.153
149.359
147.162
141.661
139.114
136.865
136.842
129.961
129.270
126.781
119.410
118.524
115.552
115.509
113.440
112.862
109.782
77.414
77.160
76.906
63.223
62.962
61.020
60.988
33.354
33.195
22.078
20.364
14.372
Me
Me
N
CO2Et
Me
Me
N
CO2Et
3v
3u
3v:3u = 45:55
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3w

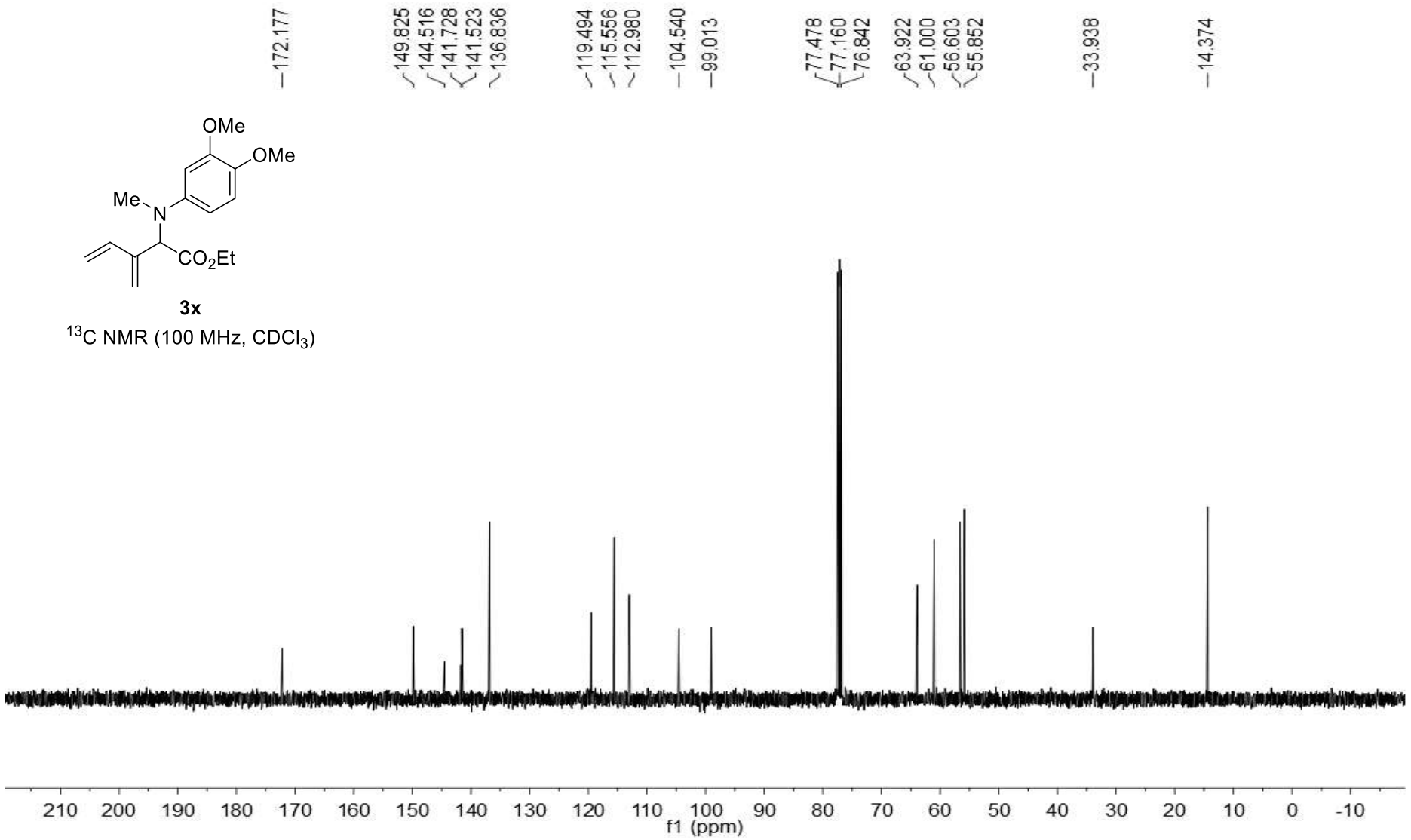
^{1}H NMR (400 MHz, $CDCl_3$)


172.277
147.616
141.790
137.424
136.879
130.490
125.524
119.290
115.543
114.381
110.155
77.478
77.160
76.842
63.105
60.946
33.264
20.551
18.732
14.402
Me
Me
Me
N
CO2Et
3w
13C NMR (100 MHz, 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)



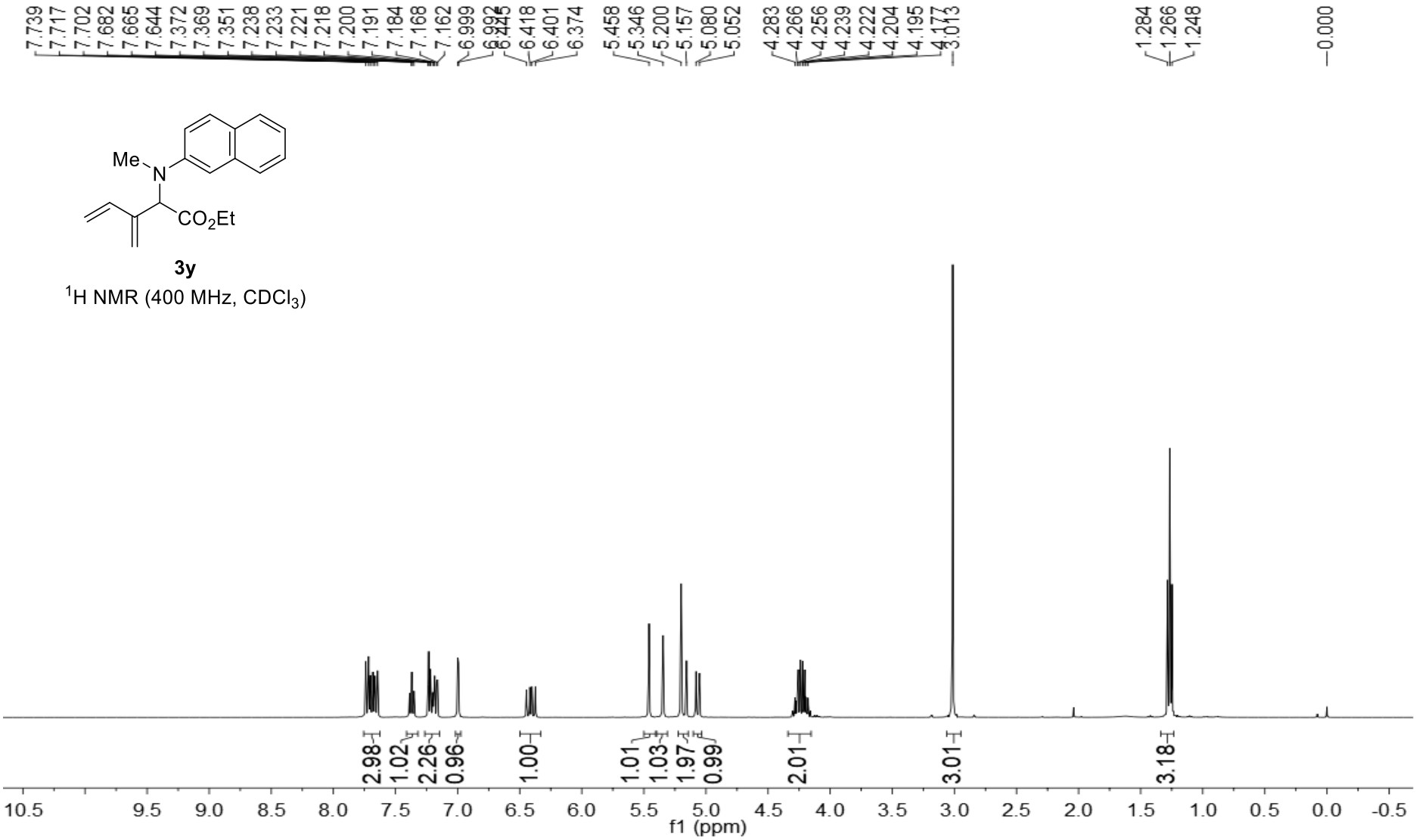
3x

^{1}H NMR (400 MHz, $CDCl_3$)



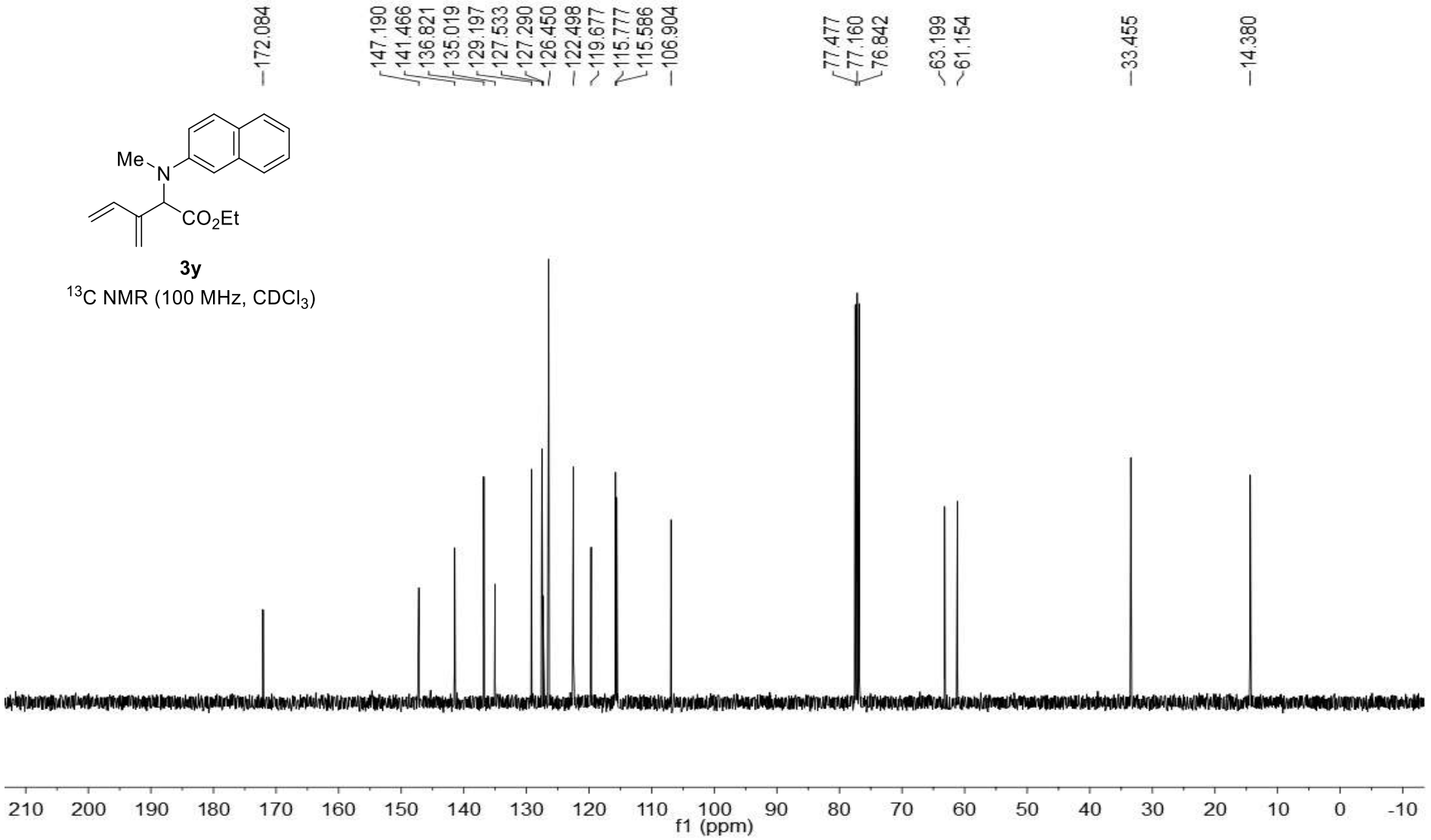
3x

^{13}C NMR (100 MHz, $CDCl_3$)



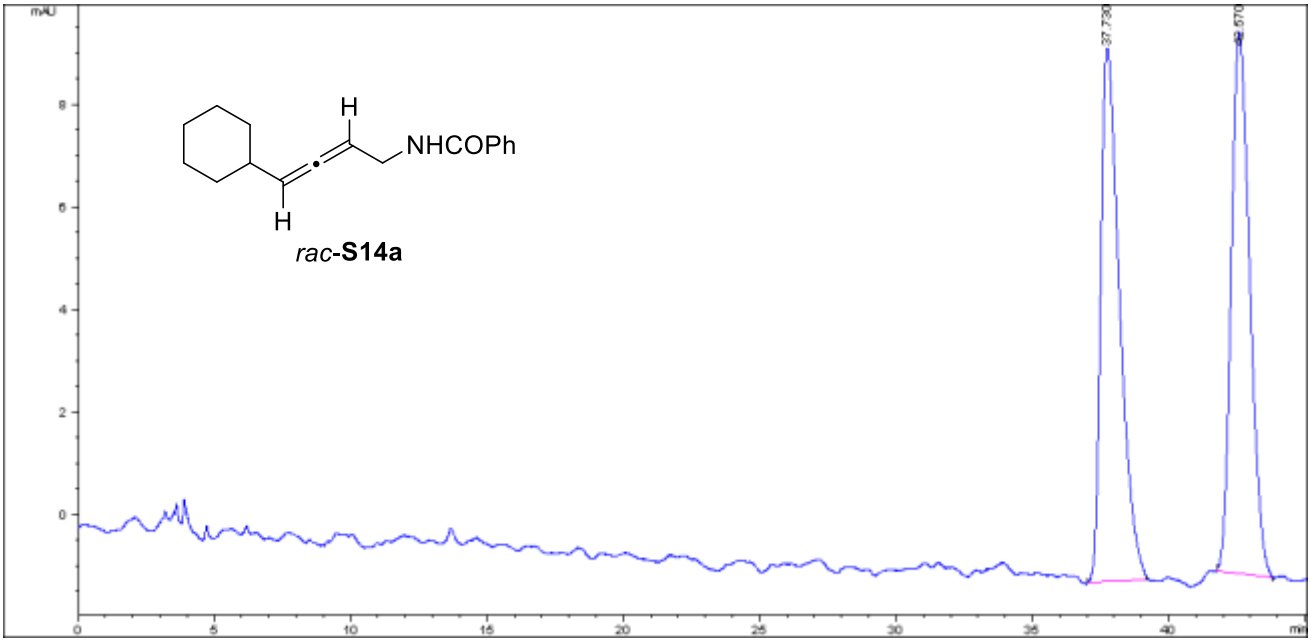
3y

^{1}H NMR (400 MHz, $CDCl_3$)



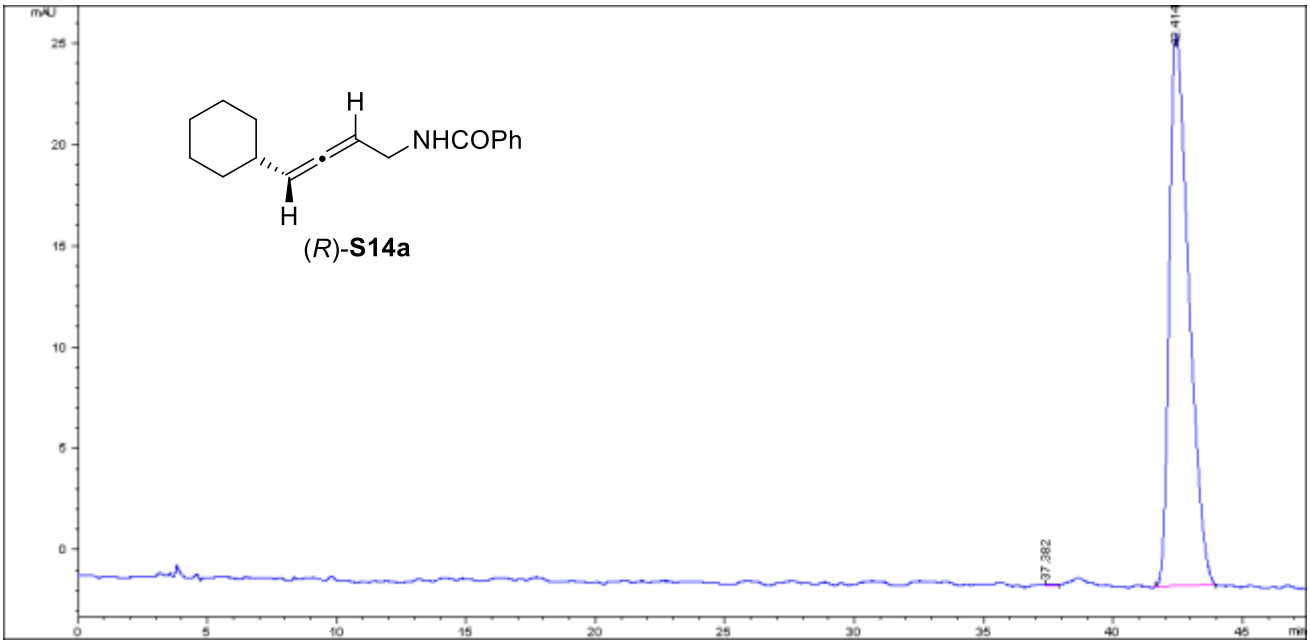
3y

^{13}C NMR (100 MHz, $CDCl_3$)



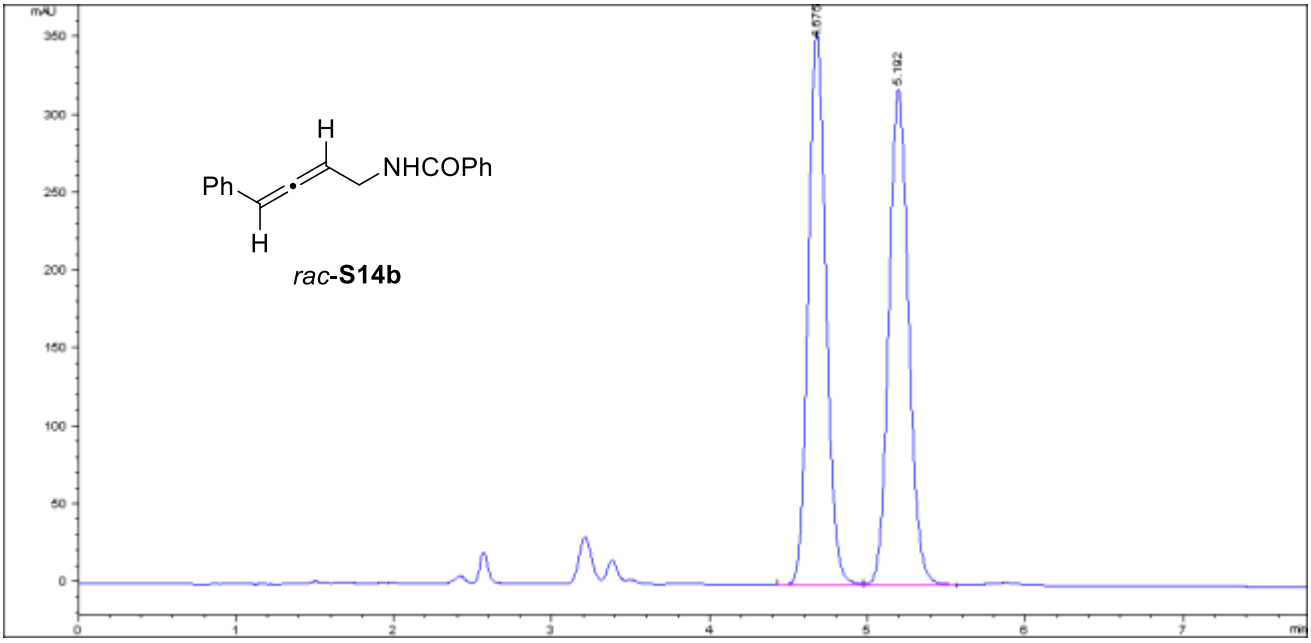
rac-**S14a**

Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	37.73	502.6	10.4	0.6902	0.499	50.212
2	42.57	498.3	10.6	0.7069	0.729	49.788



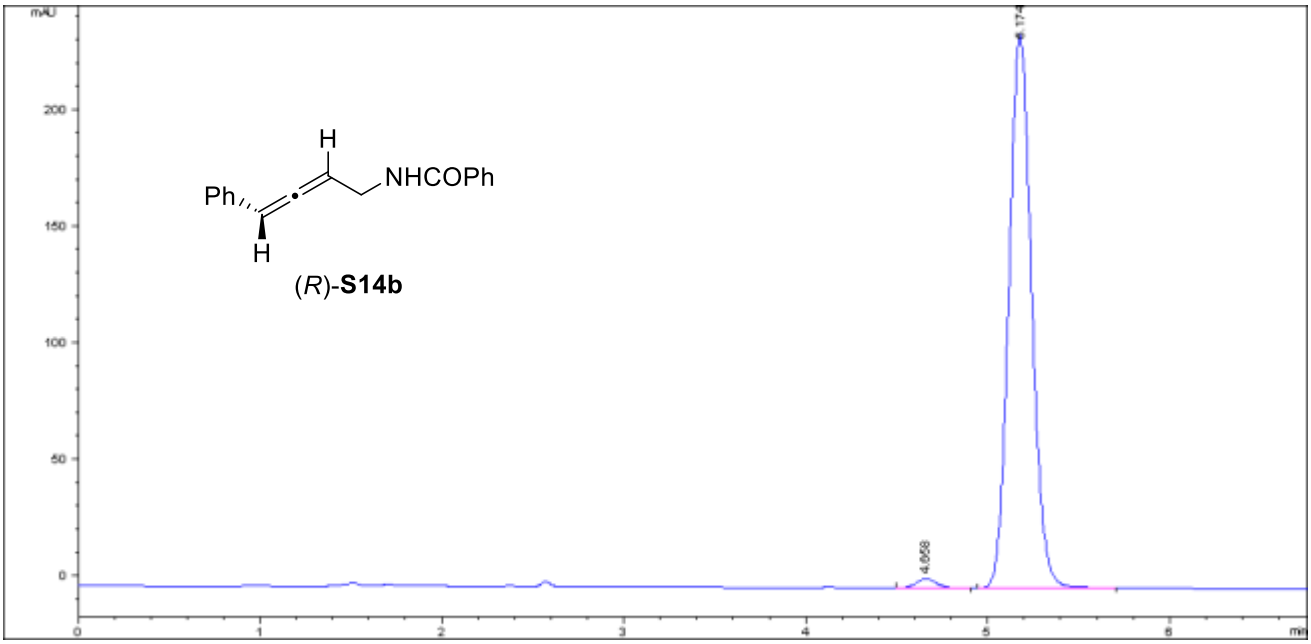
(*R*)-**S14a**

Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	37.382	2	5.3E-2	0.4704	0.2.59E-2	0.137
2	42.414	1426.1	27.3	0.7597	0.5	99.863



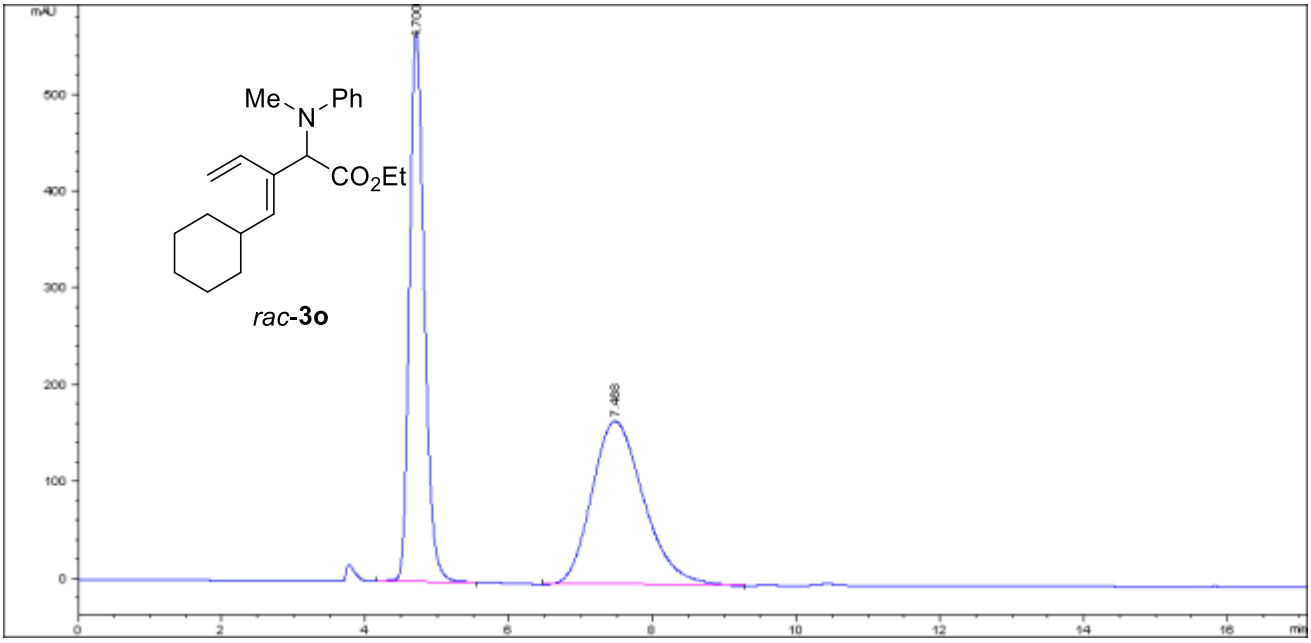
rac-**S14b**

Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	4.675	2775.5	355.2	0.1217	0.883	49.975
2	5.192	2778.3	318.2	0.1354	0.889	50.025

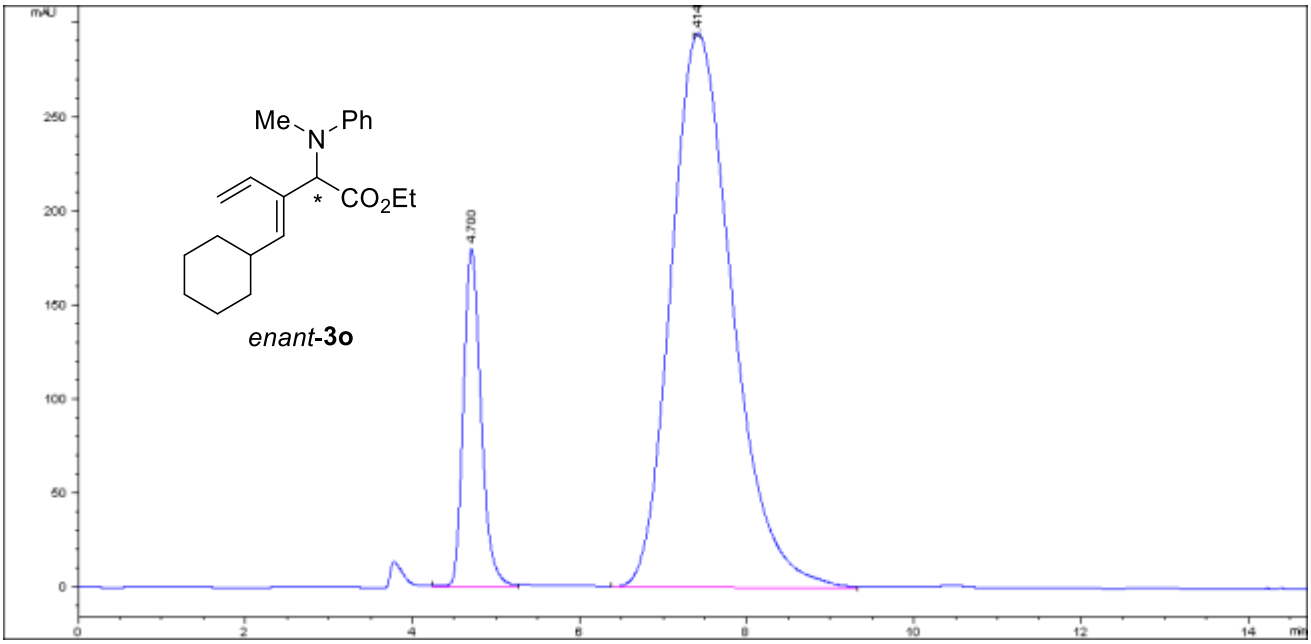


(*R*)-**S14b**

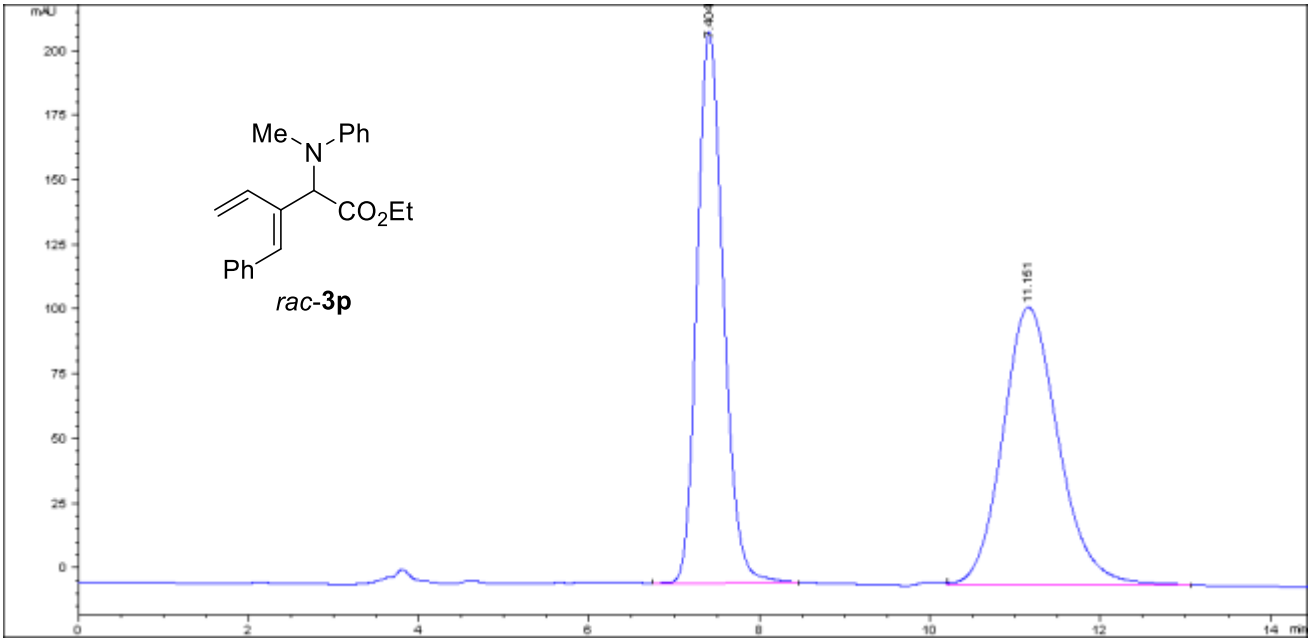
Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	4.658	31.5	4	0.1224	0.902	1.499
2	5.174	2066.3	238	0.1348	0.884	98.501



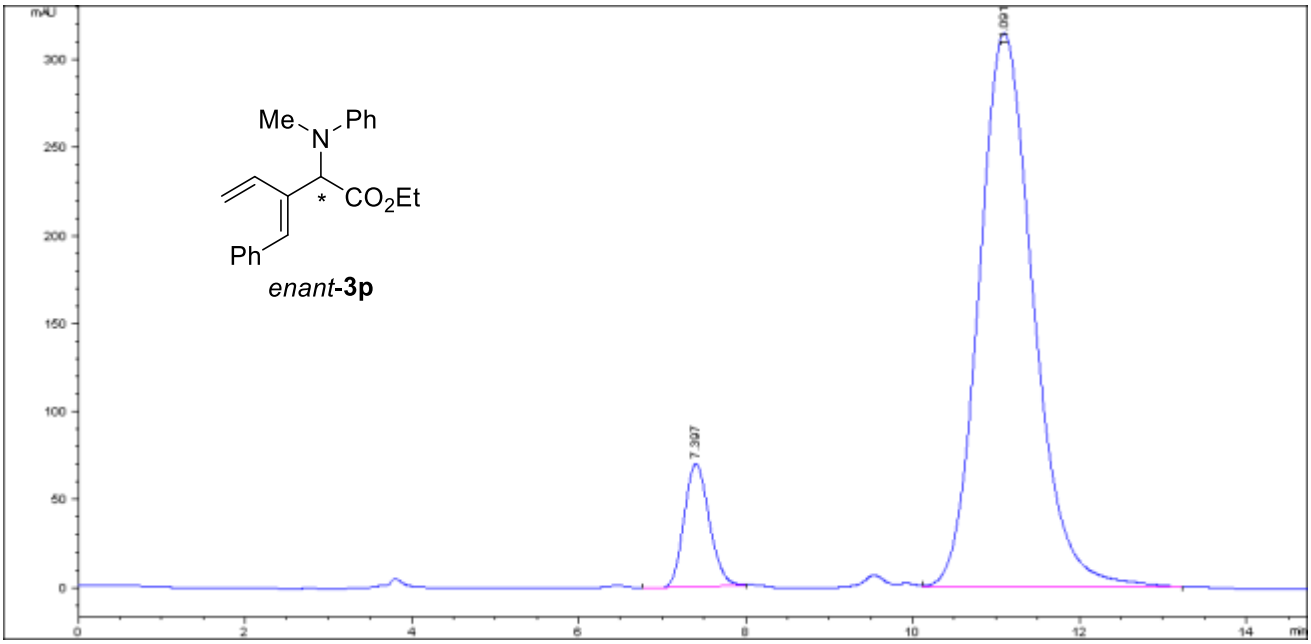
Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	4.7	8235.4	568.5	0.2243	0.778	49.100
2	7.468	8537.2	169.2	0.781	0.768	50.900



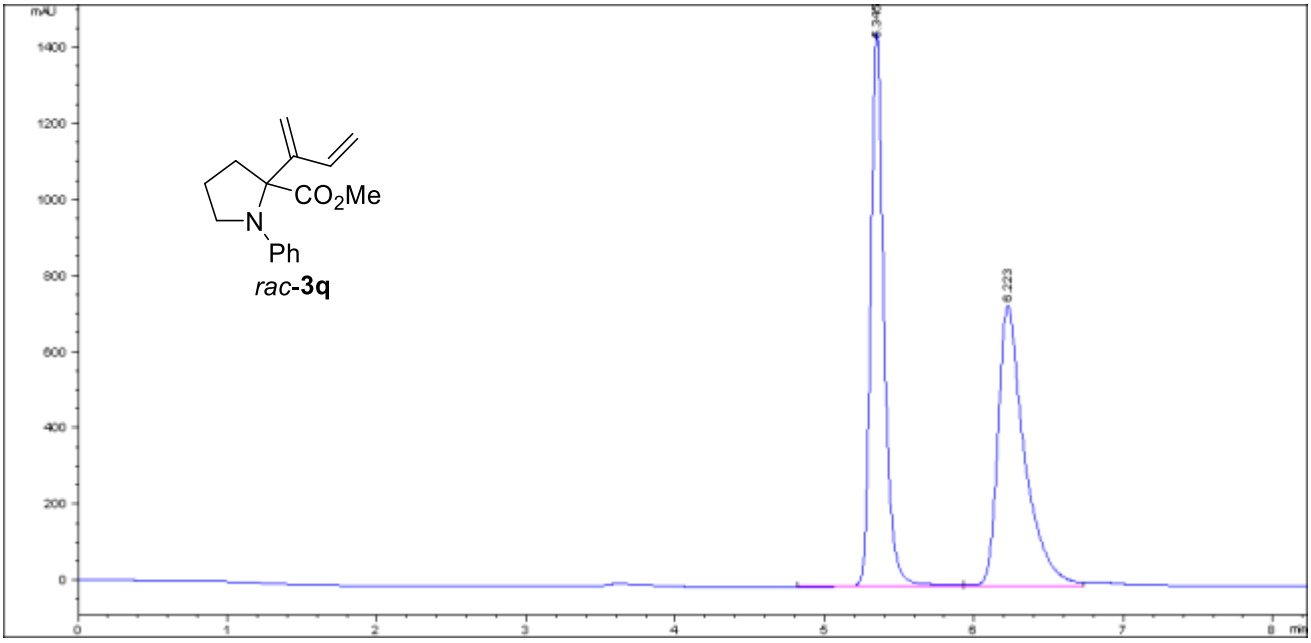
Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	4.7	2682.5	180.7	0.2285	0.772	15.080
2	7.414	15105.8	295.1	0.7894	0.751	84.920



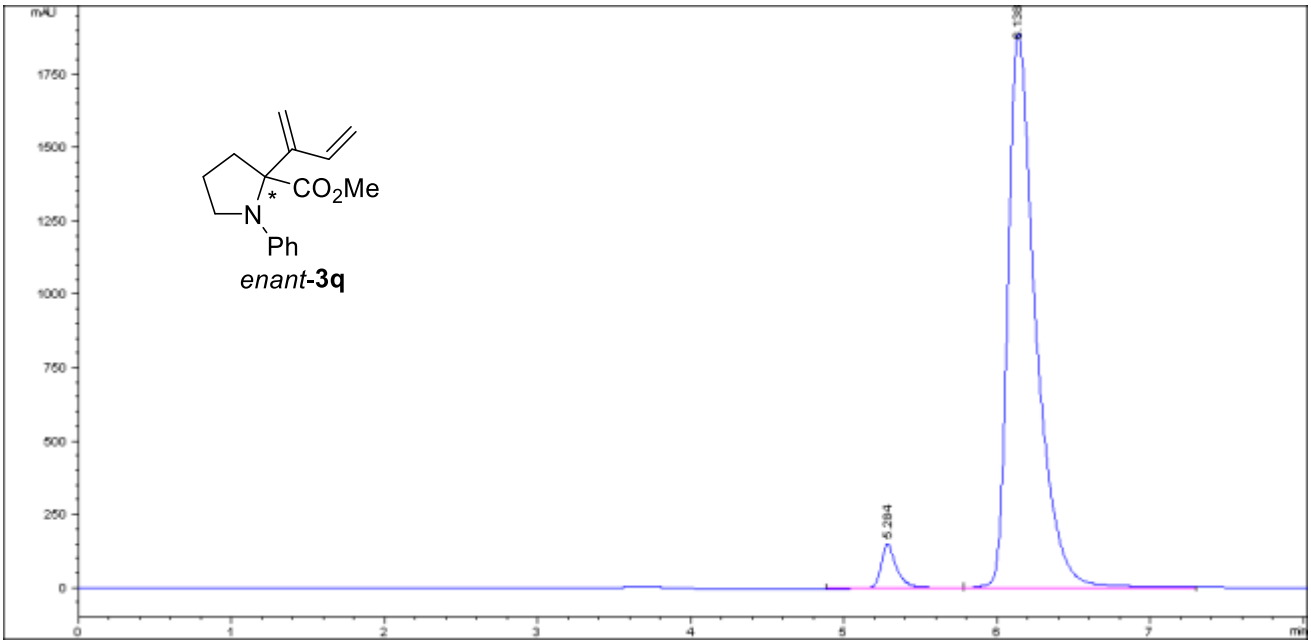
Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.404	4581	213	0.3324	0.811	48.230
2	11.151	4917.3	107.6	0.7007	0.82	51.770



Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.397	1471.2	70.1	0.3263	0.83	9.338
2	11.091	14283.3	314.8	0.6983	0.809	90.662



Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.345	9192.6	1457.9	0.0954	0.735	49.834
2	6.223	9253.9	738.2	0.1812	0.551	50.166



Number	Time (min)	Area (mAU.s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.284	1215.2	155.1	0.1118	0.616	4.795
2	6.138	24129.5	1893.6	0.1894	0.55	95.205