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Supporting Information

Diastereo- and Enantioselective Rhodium(III)-Catalyzed Reductive Cyclization of Cyclohexadienone-Containing 1,6-Dienes

Yun-Xuan Tan, Pei-Ying Peng, Ya-Jie Wang, Xi-Liang Liu, Wenbo Ye,* Dingding Gao,* Guo-Qiang Lin, and Ping Tian*

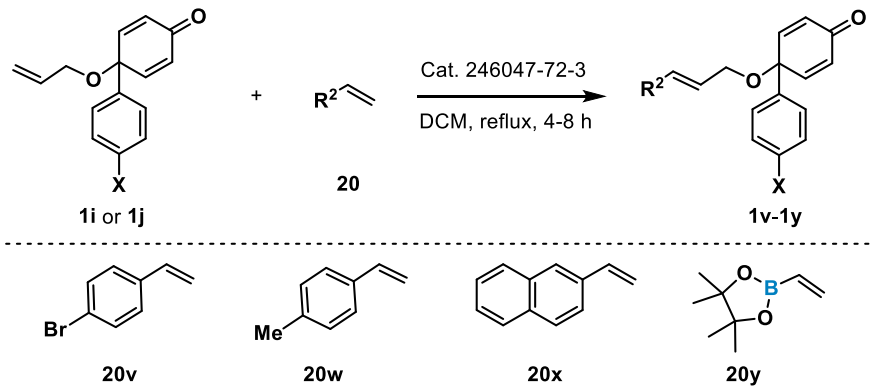
Contents

1. General information

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 MHz, Bruker AV-500 MHz and Bruker AV-600 MHz in the indicated solvents. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz. Optical rotations were measured on Anton Paar MCP 5500. ESI mass spectra were recorded on Agilent 1200/G6100A. EI mass spectra were recorded on Waters Micromass DCT Premier.

2. Substrate preparation

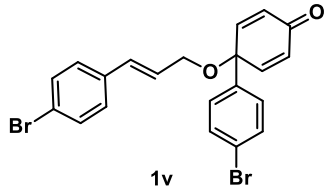
Note: Substrates **1a−1u**, **1z**, **1ab**, and **1ac** were synthesized according to our previous reports.[1]



General procedure for preparation of substrates 1v-1y: A dried bottle was charged with **1i** or **1j** (2.0 mmol, 1.0 equiv) and Cat. 246047-72-3 (84.9 mg, 5 mol%), backfilled with argon. Then substrate **20** (10 mmol, 5.0 equiv) and DCM (10 mL) were added. After the mixture was stirred at 50 °C for 4 to 8 h, the reaction mixture was cooled to room temperature. The reaction mixture was concentrated in vacuo and the residue was purified by flash silica gel chromatography to afford the desired product **1v−1y**.

[1] For the preparation of substrates **1a**-**1k**, **1m**-**1t**, and **1ab**, see: (a) Y.-X. Tan, F. Zhang, P.-P. Xie, S.-Q. Zhang, Y.-F. Wang, Q.-H. Li, P. Tian, X. Hong and G.-Q. Lin, *J. Am. Chem. Soc.*, 2019, **141**, 12770. For the preparation of substrates **1l** and **1u**, see: (b) C.-Y. He, Q.-H. Li, X. Wang, F. Wang, P. Tian, and Lin, G.-Q. *Adv. Synth. Catal.*, 2020, **362**, 765. For the preparation of substrate **1z**, see: (c) J.-L. Zhang, D. Gao, Y.-X. Tan, C.-Y. He, P.-Y. Peng, G.-Q. Lin, Q.-H. Li and P. Tian, *Org. Lett.*, 2020, **22**, 3661. For the preparation of substrate **1ac**, see: (d) B. F. Sels, D. E. De Vos, and P. A. Jacobs, *Angew. Chem., Int. Ed.*, 2005, **44**, 310.

(*E*)-4'-Bromo-1-((3-(4-bromophenyl)allyl)oxy)-[1,1'-biphenyl]-4(1*H*)-one (1v)



1v

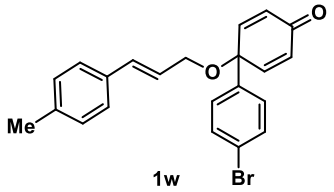
R_f = 0.3 (PE/EA = 10/1), yellow solid (200 mg, 22% yield), m.p. = 128 – 129 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 10.2 Hz, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.42 (d, *J* = 10.2 Hz, 2H), 6.31 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.23 (dd, *J* = 5.8, 1.5 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 185.3, 149.9, 137.3, 135.5, 132.0, 131.8, 131.4, 130.1, 128.1, 127.6, 126.5, 122.7, 121.8, 76.2, 65.9.

FT-MS: $[M+H]^{\oplus}$ 459.0; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{21}H_{17}{}^{79}Br_2O_2^{\oplus}$ 458.9590, found 458.9584.

(*E*)-4'-Bromo-1-((3-(p-tolyl)allyl)oxy)-[1,1'-biphenyl]-4(1*H*)-one (1w)



1w

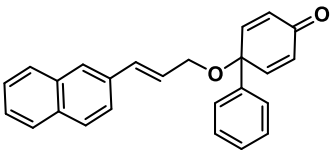
R_f = 0.3 (PE/EA = 10/1), yellow solid (140 mg, 18% yield), m.p. = 105 – 106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 10.1 Hz, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.41 (d, *J* = 10.1 Hz, 2H), 6.27 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.23 (dd, *J* = 6.0, 1.1 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 185.5, 150.8, 137.9, 137.4, 133.7, 132.8, 132.0, 130.0, 129.4, 127.7, 126.5, 124.6, 122.6, 76.2, 66.3, 21.3.

FT-MS: $[M+H]^{\oplus}$ 395.1; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{22}H_{20}{}^{79}BrO_2^{\oplus}$ 395.0641, found 395.0635.

(*E*)-1-((3-(Naphthalen-2-yl)allyl)oxy)-[1,1'-biphenyl]-4(1*H*)-one (1x)



1x

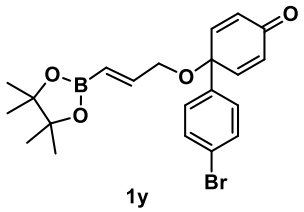
R_f = 0.3 (PE/EA = 15/1), yellow oil (152 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 – 7.74 (m, 4H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.47 (d, *J* = 5.0 Hz, 2H), 7.38 (dd, *J* = 15.7, 8.0 Hz, 3H), 6.92 (d, *J* = 9.9 Hz, 2H), 6.83 (d, *J* = 16.1 Hz, 1H), 6.52 – 6.41 (m, 3H), 4.32 (d, *J* = 5.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 185.7, 150.7, 138.2, 134.1, 133.6, 133.2, 132.5, 129.8, 128.9, 128.5, 128.4, 128.1, 127.8, 126.7, 126.4, 126.4, 126.1, 125.9, 123.6, 76.6, 66.1.

FT-MS: $[M+H]^{\oplus}$ 353.2; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{25}H_{21}O_2^{\oplus}$ 353.1536, found 353.1529.

(*E*)-4'-Bromo-1-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)-[1,1'-biphenyl]-4(1*H*)-one (1y)



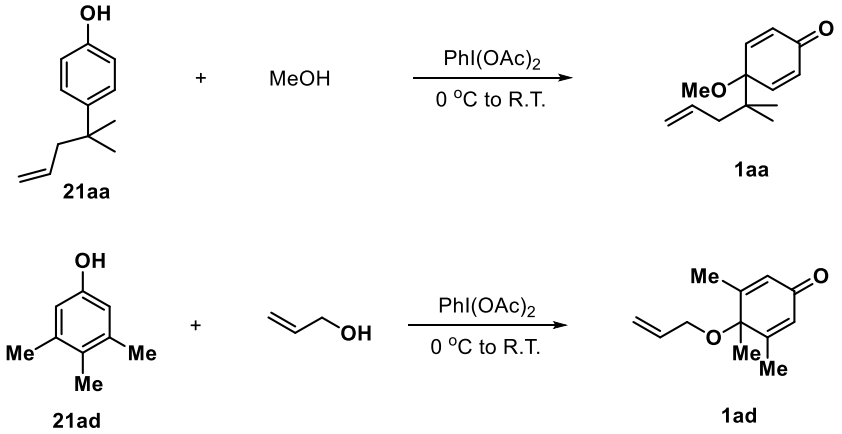
1y

R_f = 0.5 (PE/EA = 5/1), yellow oil (150 mg, 17% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 10.0 Hz, 2H), 6.66 (dt, *J* = 18.2, 4.0 Hz, 1H), 6.36 (d, *J* = 10.0 Hz, 2H), 5.83 (d, *J* = 18.1 Hz, 1H), 4.13 (d, *J* = 2.1 Hz, 2H), 1.27 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 185.3, 149.9, 148.5, 137.2, 132.0, 130.1, 127.7, 122.6, 83.5, 76.1, 66.5, 24.9.

FT-MS: $[M+H]^{\oplus}$ 430.1; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{21}H_{25}{}^{79}Br^{10}BO_4^{\oplus}$ 430.1060, found 430.1053.

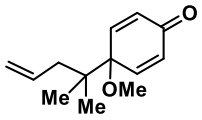


General procedure for preparation of substrates 1aa and **1ad**: A well-stirred solution of substituted phenol **21aa**[2] or **21ad** (1.0 eq) in alcohol (5.0 eq) was cooled to 0 °C and treated with phenyliodine (III) diacetate (PIDA, 1.5 eq) in several portions. The resulting mixture was warmed

[2] For the preparation of substrate **21aa**, see: J. A. Cella, *J. Org. Chem.*, 2002, **47**, 2125.

to room temperature and stirred overnight. Then it was diluted with water and extracted with dichloroethane. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate eluent to afford the desired product **1aa** or **1ad**.

4-Methoxy-4-(2-methylpent-4-en-2-yl)cyclohexa-2,5-dien-1-one (1aa)



1aa

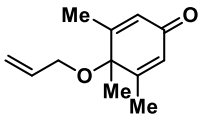
R_f = 0.5 (PE/EA = 9/1), colorless oil (300 mg, 29% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.90 (d, *J* = 10.5 Hz, 2H), 6.42 (d, *J* = 10.5 Hz, 2H), 5.78 (ddt, *J* = 17.5, 10.1, 7.4 Hz, 1H), 5.07 – 4.97 (m, 2H), 3.20 (s, 3H), 2.15 (d, *J* = 7.4 Hz, 2H), 0.97 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.2, 150.4, 134.8, 132.5, 117.8, 80.1, 53.1, 42.4, 41.9, 22.1.

ESI-MS: $[M+H]^{\oplus}$ 207.1; **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1379.

4-(Allyloxy)-3,4,5-trimethylcyclohexa-2,5-dien-1-one (1ad)



1ad

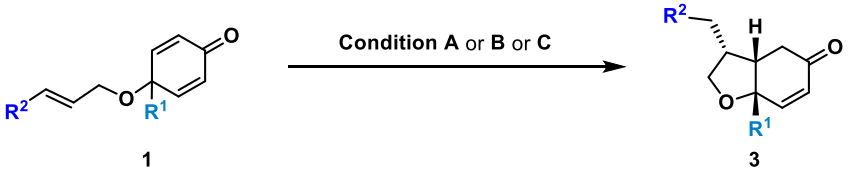
R_f = 0.5 (PE/EA = 9/1), colorless oil (38% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.17 (s, 2H), 5.87 (ddt, *J* = 17.1, 10.6, 5.4 Hz, 1H), 5.29 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.4, 1.4 Hz, 1H), 3.53 (dt, *J* = 5.4, 1.4 Hz, 2H), 2.02 (s, 6H), 1.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.3, 161.0, 134.0, 129.1, 117.1, 76.7, 65.9, 25.1, 18.0.

ESI-MS: $[M+H]^{\oplus}$ 193.2; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{12}H_{17}O_2^{\oplus}$ 193.1223, found 193.1221.

3. Substrate scope of cyclohexadienone-tethered alkenes



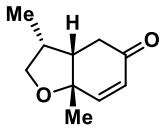
1 3

Condition A: A dried Schlenk flask was charged with **C3** (5.66 mg, 5 mol%), *t*-BuONa (2.0 mg, 10 mol%), and substrate **1** (if **1** is a solid, 0.2 mmol, 1.0 equiv), backfilled with argon. Then anhydrous DCE (2 mL), Et_3SiH (0.3 mmol, 1.5 equiv) and substrate **1** (if **1** is a liquid, 0.2 mmol, 1.0 equiv) were added. After the mixture was stirred at 40 ^oC for 10 h, the reaction mixture was cooled to room temperature. Then NH_4F (0.5M in MeOH) was added to quench the reaction and stirred for 10 min. Finally, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography to afford the desired product **3**.

Condition B: A dried Schlenk flask was charged with **C3** (5.66 mg, 5 mol%) and substrate **1** (if **1** is a solid, 0.2 mmol, 1.0 equiv), backfilled with argon. Then anhydrous DCE (2 mL), HBpin (0.5 mmol, 2.5 equiv) and substrate **1** (if **1** is a liquid, 0.2 mmol, 1.0 equiv) were added. After the mixture was stirred at room temperature for 10 h. Then, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography to afford the desired product **3**.

Condition C: A dried Schlenk flask was charged with **C3** (2.8 mg, 5 mol%), *t*-BuONa (1.0 mg, 10 mol%), and substrate **1** (if **1** is a solid, 0.1 mmol, 1.0 equiv), backfilled with argon. Then anhydrous DCE (1 mL), Et_3SiH (0.15 mmol, 1.5 equiv) and substrate **1** (if **1** is a liquid, 0.1 mmol, 1.0 equiv) were added. After the mixture was stirred at 50 ^oC for 2 h, the reaction mixture was cooled to room temperature. Then NH_4F (0.5M in MeOH) was added to quench the reaction and stirred for 10 min. Finally, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography to afford the desired product **3**.

(3*R*,3a*S*,7a*S*)-3,7a-Dimethyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3a)



3a

Condition A, R_f = 0.25 (PE/EA = 10/1), light yellow oil (32 mg, 96% yield).

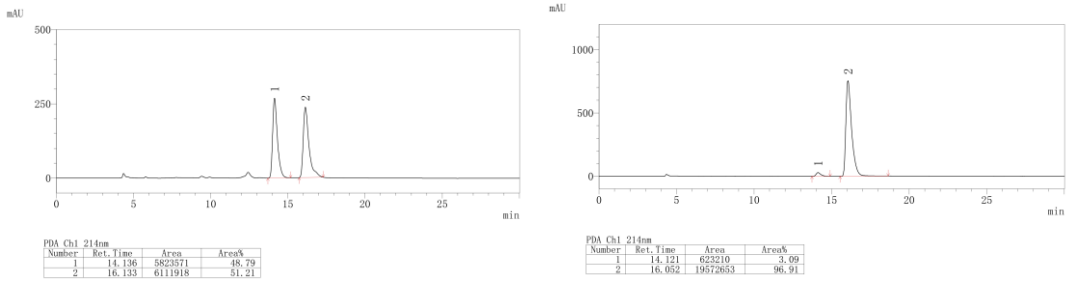
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (d, *J* = 10.3 Hz, 1H), 5.98 (d, *J* = 10.3 Hz, 1H), 4.08 (dd, *J* = 8.7, 7.5 Hz, 1H), 3.37 (dd, *J* = 8.7, 7.4 Hz, 1H), 2.65 – 2.48 (m, 4H), 1.46 (s, 3H), 0.90 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.5, 152.6, 129.0, 78.9, 73.6, 45.6, 36.7, 35.7, 25.8, 13.8.

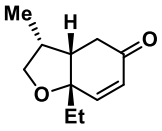
EI-MS: $[M]^{\oplus}$ 166; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{11}H_{14}O_2^{\oplus}$ 166.0994, found 166.0997.

Specific Rotation: $[\alpha]_D^{25.0}$ 78.5 (*c* 1.9, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 16.0 min (major), 14.1 min (minor).



(3*R*,3a*S*,7a*S*)-7a-Ethyl-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3b)



3b

Condition A, R_f = 0.3 (PE/EA = 15/1), colorless oil (33.72 mg, 94% yield).

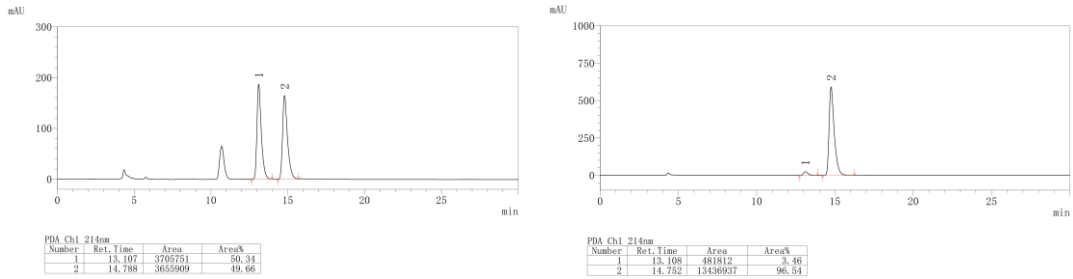
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (dd, *J* = 10.4, 0.7 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.01 (dd, *J* = 8.6, 6.9 Hz, 1H), 3.38 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.62 – 2.47 (m, 4H), 1.85 – 1.68 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.8, 151.8, 129.7, 81.4, 73.3, 43.0, 37.2, 36.1, 32.3, 13.8, 8.4.

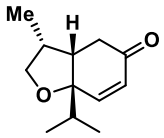
EI-MS: $[M]^{\oplus}$ 180; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{11}H_{16}O_2^{\oplus}$ 180.1150, found 180.1147.

Specific Rotation: $[\alpha]_D^{25.0}$ 91.3 (*c* 1.57, $CHCl_3$) for 93% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 14.8 min (major), 13.1 min (minor).



(3*R*,3a*S*,7a*S*)-7a-Isopropyl-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3c)



3c

Condition A, R_f = 0.3 (PE/EA = 15/1), colorless oil (33.2 mg, 86% yield).

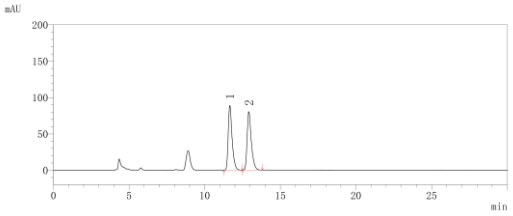
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.61 (d, *J* = 10.4 Hz, 1H), 6.11 (d, *J* = 10.4 Hz, 1H), 3.93 (dd, *J* = 8.5, 6.8 Hz, 1H), 3.35 (dd, *J* = 8.5, 6.5 Hz, 1H), 2.70 – 2.42 (m, 4H), 2.04 – 1.93 (m, 1H), 1.06 – 0.94 (m, 6H), 0.89 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 150.5, 130.3, 83.4, 72.8, 40.9, 38.2, 37.1, 36.8, 17.7, 17.0, 13.8.

EI-MS: $[M]^{\oplus}$ 194; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{12}H_{18}O_2^{\oplus}$ 194.1307, found 194.1314.

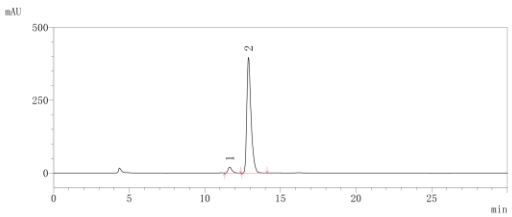
Specific Rotation: $[\alpha]_D^{25.0}$ 89.2 (*c* 1.35, $CHCl_3$) for 91% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 12.9 min (major), 11.6 min (minor).



PDA Ch1 214nm

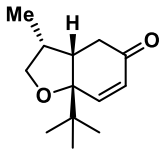
Number	Ret.Time	Area	Area%
1	11.660	1577575	50.42
2	12.918	1551385	49.58



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	11.642	358610	4.41
2	12.887	7766386	95.59

(3*R*,3a*S*,7a*S*)-7a-(Tert-butyl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3d)



3d

Condition A, R_f = 0.5 (PE/EA = 10/1), colorless oil (36 mg, 87% yield).

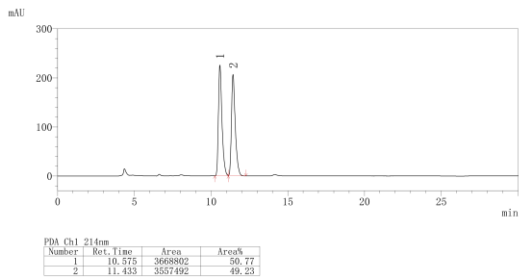
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.75 (dd, *J* = 10.6, 1.4 Hz, 1H), 6.11 (dd, *J* = 10.6, 0.4 Hz, 1H), 3.89 (dd, *J* = 8.6, 6.5 Hz, 1H), 3.33 (dd, *J* = 8.6, 5.7 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.63 – 2.50 (m, 2H), 2.49 – 2.36 (m, 1H), 1.04 (s, 9H), 0.88 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.7, 150.7, 130.0, 84.8, 73.1, 39.2, 38.6, 38.6, 37.3, 25.4, 14.2.

EI-MS: $[M]^{\oplus}$ 208; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{13}H_{20}O_2^{\oplus}$ 208.1463, found 208.1457.

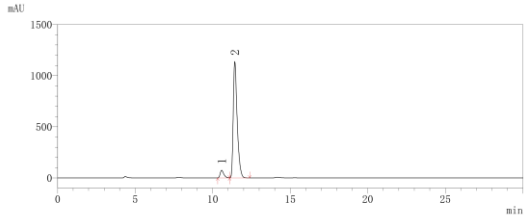
Specific Rotation: $[\alpha]_D^{25.0}$ 103.2 (*c* 1.55, $CHCl_3$) for 89% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 11.4 min (major), 10.6 min (minor).



PDA Ch1 214nm

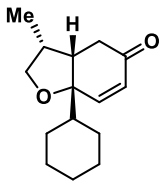
Number	Ret.Time	Area	Area%
1	10.575	3668802	50.77
2	11.433	3557492	49.23



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	10.580	1190587	5.61
2	11.426	20013644	94.39

(3*R*,3a*S*,7a*S*)-7a-Cyclohexyl-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3e)



3e

Condition A, R_f = 0.35 (PE/EA = 15/1), colorless oil (42.8 mg, 91% yield).

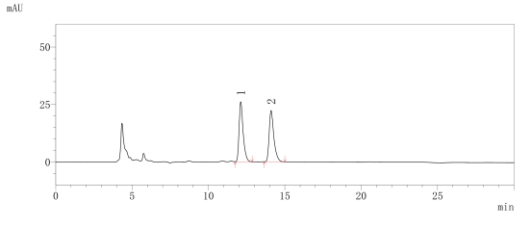
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.59 (dd, *J* = 10.4, 1.1 Hz, 1H), 6.08 (d, *J* = 10.4 Hz, 1H), 3.91 (dd, *J* = 8.6, 6.6 Hz, 1H), 3.35 (dd, *J* = 8.6, 6.2 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.60 – 2.41 (m, 3H), 1.91 – 1.75 (m, 4H), 1.69 – 1.58 (m, 2H), 1.33 – 1.21 (m, 2H), 1.18 – 1.00 (m, 3H), 0.88 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 151.1, 129.9, 83.0, 72.8, 47.3, 41.1, 38.2, 37.1, 27. 9, 27.1, 26.6, 26.5, 26.4, 13.8.

EI-MS: $[M]^{\oplus}$ 234; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{15}H_{22}O_2^{\oplus}$ 234.1620, found 234.1629.

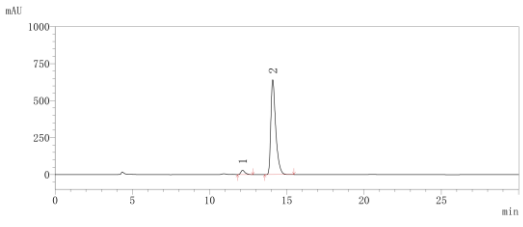
Specific Rotation: $[\alpha]_D^{25.0}$ 40.3 (*c* 1.9, $CHCl_3$) for 93% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 14.1 min (major), 12.1 min (minor).



PDA Ch1 214nm

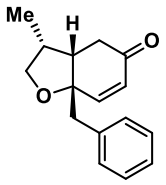
Number	Ret.Time	Area	Area%
1	12.116	486424	50.53
2	14.101	476216	49.47



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	12.134	545015	3.73
2	14.087	14060100	96.27

(3*R*,3a*S*,7a*S*)-7a-Benzyl-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3f)



3f

Condition A, R_f = 0.35 (PE/EA = 12/1), colorless oil (46 mg, 95% yield).

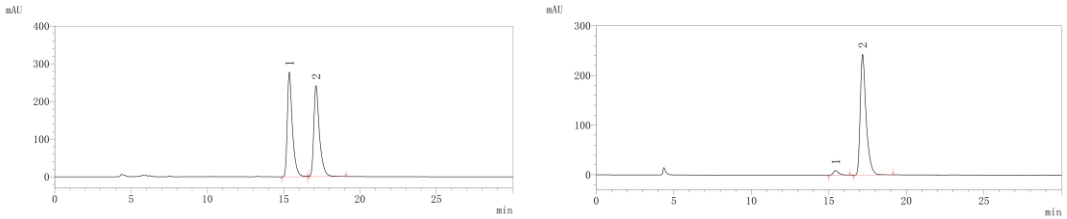
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31 – 7.20 (m, 5H), 6.58 (dd, *J* = 10.4, 1.3 Hz, 1H), 5.99 (dd, *J* = 10.4, 0.6 Hz, 1H), 3.96 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.37 (dd, *J* = 8.7, 6.1 Hz, 1H), 3.01 (s, 2H), 2.67 – 2.58 (m, 1H), 2.51 – 2.39 (m, 2H), 2.16 (dd, *J* = 17.5, 7.1 Hz, 1H), 0.86 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.5, 151.6, 135.8, 130.4, 129. 6, 128.3, 127.0, 81.1, 73.3, 45.6, 43.3, 37.2, 35.9, 14.2.

EI-MS: $[M]^{\oplus}$ 242; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{16}H_{18}O_2^{\oplus}$ 242.1307, found 242.1302.

Specific Rotation: $[\alpha]_D^{25.0}$ 35.2 (*c* 2.05, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 17.2 min (major), 15.4 min (minor).



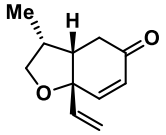
PDA Ch1 214nm

Number	Ret. Time	Area	Area%
1	15.369	6380813	50.65
2	17.118	6217764	49.35

PDA Ch1 214nm

Number	Ret. Time	Area	Area%
1	15.437	211047	3.19
2	17.179	6395356	96.81

(3*R*,3a*S*,7a*S*)-3-Methyl-7a-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3g)



3g

Condition A, R_f = 0.3 (PE/EA = 15/1), colorless oil (32.5 mg, 91% yield).

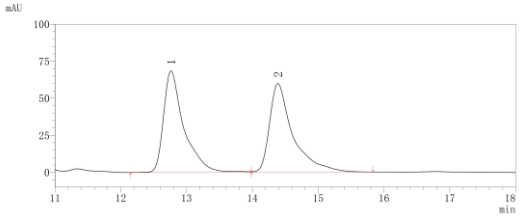
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.56 (d, *J* = 10.3 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 5.93 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.31 (dd, *J* = 17.4, 0.8 Hz, 1H), 5.24 (dd, *J* = 10.6, 0.7 Hz, 1H), 4.13 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.51 (dd, *J* = 8.6, 6.7 Hz, 1H), 2.66 – 2.47 (m, 4H), 0.93 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.6, 149.2, 139.7, 130.1, 115.4, 81.4, 74.0, 45.3, 36.2, 35.0, 13.6.

EI-MS: $[M]^{\oplus}$ 178; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{11}H_{14}O_2^{\oplus}$ 178.0994, found 178.0997.

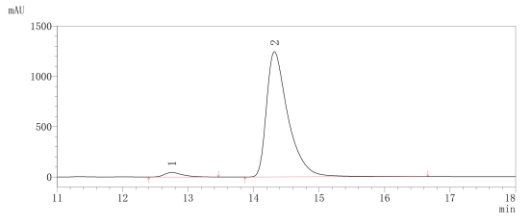
Specific Rotation: $[\alpha]_D^{25.0}$ 1.6 (*c* 1.07, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 14.3 min (major), 12.7 min (minor).



PDA Ch1 214nm

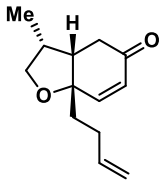
Number	Ret.Time	Area	Area%
1	12.763	1471014	49.99
2	14.387	1471996	50.01



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	12.749	867042	2.96
2	14.317	28468453	97.04

(3*R*,3a*S*,7a*S*)-7a-(But-3-en-1-yl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3h)



3h

Condition A, R_f = 0.3 (PE/EA = 10/1), light yellow oil (39 mg, 95% yield).

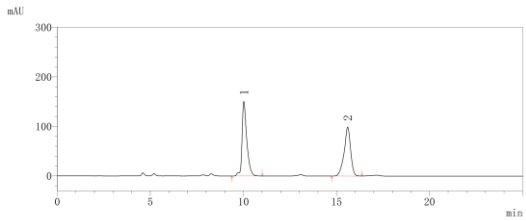
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.65 (d, *J* = 10.4 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 5.83 (ddt, *J* = 16.7, 10.2, 6.5 Hz, 1H), 5.12 – 4.91 (m, 2H), 4.03 (dd, *J* = 8.4, 7.1 Hz, 1H), 3.38 (dd, *J* = 8.5, 6.6 Hz, 1H), 2.65 – 2.48 (m, 4H), 2.25 – 2.14 (m, 2H), 1.91 – 1.74 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.6, 151.6, 137.9, 129.6, 115.0, 80.8, 73.3, 43.6, 38.6, 37.1, 35.9, 28.3, 13.9.

EI-MS: $[M]^{\oplus}$ 206; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{13}H_{18}O_2^{\oplus}$ 206.1307, found 206.1299.

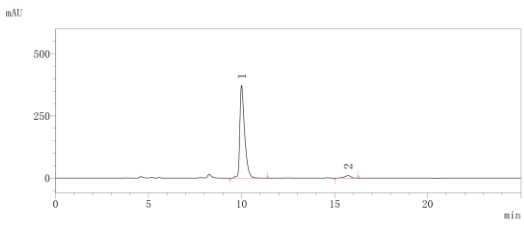
Specific Rotation: $[\alpha]_D^{25.0}$ 40.3 (*c* 1.88, $CHCl_3$) for 93% *ee*.

Chiral HPLC analysis: Chiralpak AS-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 10.0 min (major), 15.7 min (minor).



PDA Ch1 214nm

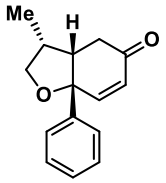
Number	Ret.Time	Area	Area%
1	10.023	2660350	52.68
2	15.600	2389957	47.32



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	9.997	6657380	96.64
2	15.721	231817	3.36

(3*R*,3a*S*,7a*S*)-3-Methyl-7a-phenyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one



3i

Condition A, R_f = 0.4 (PE/EA = 20/1), colorless oil (42.5 mg, 93% yield).

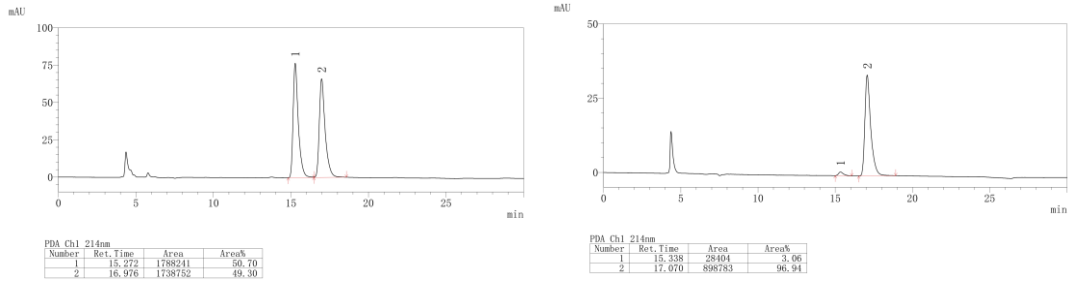
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 6.63 (d, *J* = 10.2 Hz, 1H), 6.16 (d, *J* = 10.2 Hz, 1H), 4.29 (dd, *J* = 8.4, 7.7 Hz, 1H), 3.75 – 3.69 (m, 1H), 2.78 (dd, *J* = 14.3, 7.0 Hz, 1H), 2.61 – 2.52 (m, 3H), 0.95 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 149.4, 143.8, 129.2, 128.7, 127.7, 125.0, 82.8, 74.2, 48.3, 36.4, 35.4, 12.9.

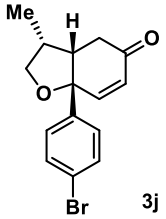
EI-MS: $[M]^{\oplus}$ 228; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{15}H_{16}O_2^{\oplus}$ 228.1150, found 228.1151.

Specific Rotation: $[\alpha]_D^{25.0}$ -108.9 (*c* 1.87, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 17.1 min (major), 15.3 min (minor).



(3*R*,3a*S*,7a*S*)-7a-(4-Bromophenyl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3j)



3j

Condition A, R_f = 0.35 (PE/EA = 15/1), colorless oil (56 mg, 92% yield).

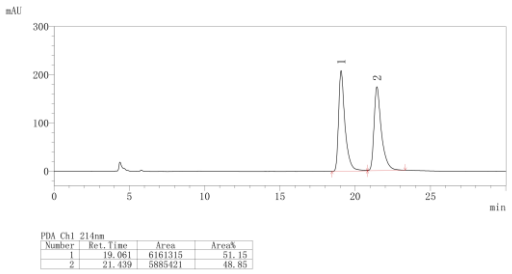
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.17 (d, *J* = 10.2 Hz, 1H), 4.27 (t, *J* = 8.1 Hz, 1H), 3.74 – 3.68 (m, 1H), 2.73 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.62 – 2.49 (m, 3H), 0.95 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.6, 148.7, 142.9, 131.8, 129.4, 126.9, 121.8, 82.5, 74.2, 48.3, 36.4, 35.3, 12.8.

EI-MS: $[M]^{\oplus}$ 306; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{15}H_{15}O_2{}^{79}Br^{\oplus}$ 306.0255, found 306.0261.

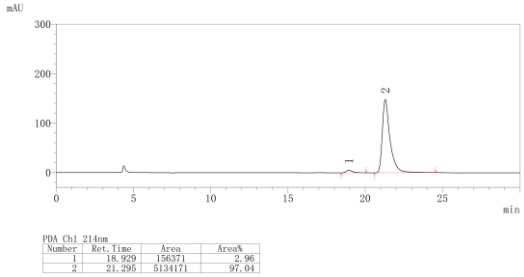
Specific Rotation: $[\alpha]_D^{25.0}$ -110.4 (*c* 2.7, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 21.3 min (major), 18.9 min (minor).



PDA Ch1 214nm

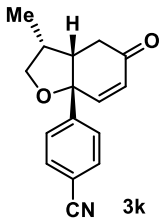
Number	Ret.Time	Area	Area%
1	19.061	6161315	51.15
2	21.439	5885421	48.85



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	18.929	156571	2.96
2	21.295	5134171	97.04

4-((3*R*,3a*S*,7a*S*)-3-Methyl-5-oxo-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)benzonitrile (3k)



3k

Condition A, R_f = 0.3 (PE/EA = 5/1), colorless oil (48 mg, 95% yield).

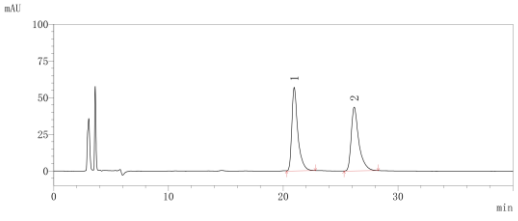
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.69 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 10.2 Hz, 1H), 6.21 (d, *J* = 10.2 Hz, 1H), 4.30 (t, *J* = 8.1 Hz, 1H), 3.79 – 3.73 (m, 1H), 2.79 – 2.72 (m, 1H), 2.64 – 2.52 (m, 3H), 0.97 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 149.2, 147.7, 132.5, 129.8, 125.9, 118.5, 111.7, 82.5, 74.3, 48.2, 36.5, 35.1, 12.7.

EI-MS: $[M]^{\oplus}$ 253; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{16}H_{15}NO_2{}^{\oplus}$ 253.1103, found 253.1098.

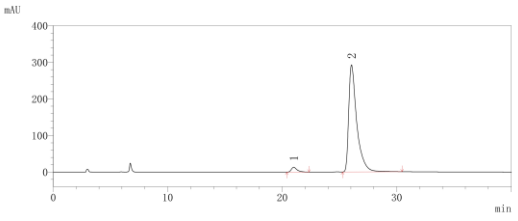
Specific Rotation: $[\alpha]_D^{25.0}$ -129.1 (*c* 2.4, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.0 mL/min; Retention time: 26.1 min (major), 21.0 min (minor).



PDA Ch1 214nm

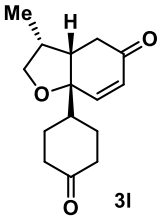
Number	Ret.Time	Area	Area%
1	20.967	2065218	50.83
2	26.184	1997913	49.17



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	21.002	470001	3.19
2	26.051	14283773	96.81

(3*R*,3a*S*,7a*S*)-3-Methyl-7a-(4-oxocyclohexyl)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3l)



3l

Condition B, R_f = 0.3 (PE/EA = 5/2), light yellowe oil (32.1mg, 65% yield).

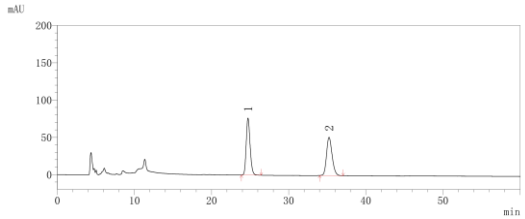
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.61 (dd, *J* = 10.4, 1.1 Hz, 1H), 6.12 (d, *J* = 10.3 Hz, 1H), 3.96 (dd, *J* = 8.7, 6.7 Hz, 1H), 3.39 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.64 – 2.30 (m, 7H), 2.27 – 2.18 (m, 2H), 2.16 – 2.07 (m, 1H), 1.67 – 1.50 (m, 2H), 0.91 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.7, 198.1, 149.6, 130.6, 82.3, 73.0, 45.4, 41.3, 40.9, 40.6, 38.1, 36.8, 27.5, 26.8, 13.7.

EI-MS: $[M]^{\oplus}$ 248; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{15}H_{20}O_3^{\oplus}$ 248.1412, found 248.1416.

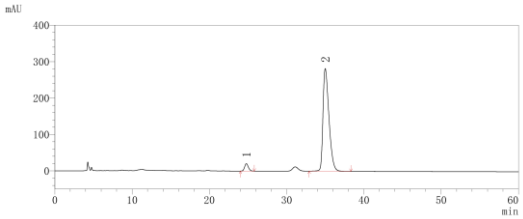
Specific Rotation: $[\alpha]_D^{25.0}$ 27.7 (*c* 1.36, $CHCl_3$) for 91% *ee*.

Chiral HPLC analysis: Chiralpak OD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 85/15; flow rate = 0.7 mL/min; Retention time: 35.0 min (major), 24.8 min (minor).



PDA Ch1 214nm

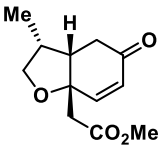
Number	Ret.Time	Area	Area%
1	24.721	2679441	50.96
2	35.232	2578582	49.04



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	24.785	686265	4.34
2	34.993	15132866	95.66

Methyl 2-((3R,3aS,7aS)-3-methyl-5-oxo-3,3a,4,5-tetrahydrobenzofuran-7a(2H)-yl) acetate (3m)



3m

Condition A, R_f = 0.3 (PE/EA = 4/1), colorless oil (30.5 mg, 68% yield).

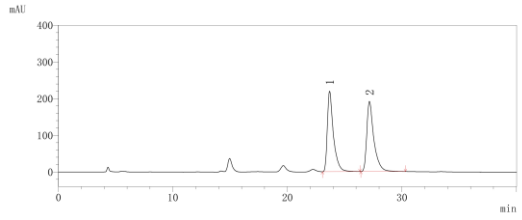
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.75 (dd, *J* = 10.4, 1.0 Hz, 1H), 6.05 (d, *J* = 10.4 Hz, 1H), 4.05 (dd, *J* = 8.7, 7.2 Hz, 1H), 3.69 (s, 3H), 3.43 (dd, *J* = 8.7, 6.9 Hz, 1H), 2.92 – 2.85 (m, 1H), 2.76 (s, 2H), 2.65 – 2.52 (m, 3H), 0.92 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 170.0, 149.4, 129.8, 78.9, 73.5, 52.0, 44.1, 43.8, 37.0, 35.6, 13.7.

EI-MS: $[M]^{\oplus}$ 224; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{12}H_{16}O_4^{\oplus}$ 224.1049, found 224.1041.

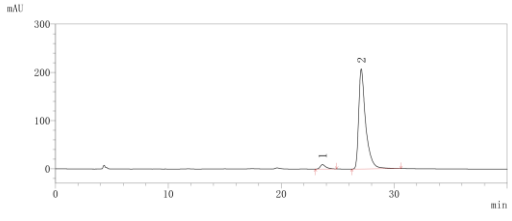
Specific Rotation: $[\alpha]_D^{25.0}$ 51.6 (*c* 1.35, $CHCl_3$) for 93% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 27.1 min (major), 23.7 min (minor).



PDA Ch1 214nm

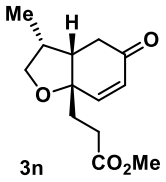
Number	Ret.Time	Area	Area%
1	23.685	8094411	49.64
2	27.164	8212688	50.36



PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	23.654	322342	3.50
2	27.087	8900288	96.50

Methyl 3-((3R,3aS,7aS)-3-methyl-5-oxo-3,3a,4,5-tetrahydrobenzofuran-7a(2H)-yl) propanoate (3n)



3n

Condition A, R_f = 0.3 (PE/EA = 7/2), yellow oil (46.5 mg, 98% yield).

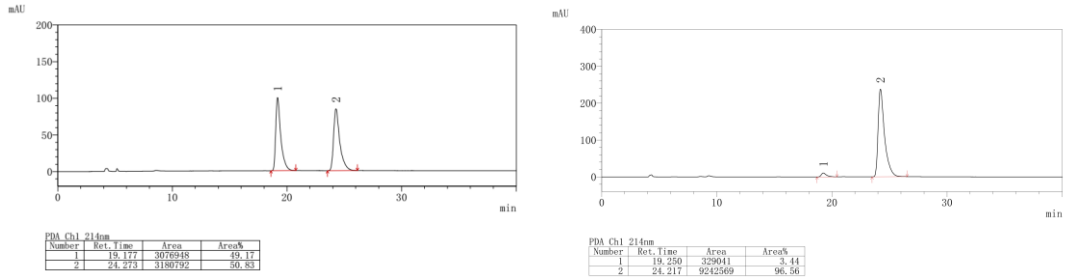
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.61 (d, *J* = 10.4 Hz, 1H), 6.03 (d, *J* = 10.4 Hz, 1H), 4.01 (dd, *J* = 8.6, 7.0 Hz, 1H), 3.69 (s, 3H), 3.38 (dd, *J* = 8.7, 6.1 Hz, 1H), 2.62 – 2.43 (m, 6H), 2.15 – 2.01 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.1, 173.5, 150.6, 129.78, 80.0, 73.5, 51.8, 43.5, 36.9, 35.7, 33.8, 28.7, 13.8.

EI-MS: $[M]^{\oplus}$ 238; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{13}H_{18}O_4^{\oplus}$ 238.1205, found 238.1202.

Specific Rotation: $[\alpha]_D^{24.9}$ 50.2 (*c* 2.02, $CHCl_3$) for 93% *ee*.

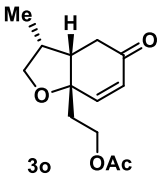
Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.7 mL/min; Retention time: 24.2 min (major), 19.2 min (minor).



Number	Ret.Time	Area	Area%
1	19.177	3076948	49.17
2	24.273	3180792	50.83

Number	Ret.Time	Area	Area%
1	19.250	329041	3.44
2	24.217	9242569	96.56

2-((3*R*,3a*S*,7a*S*)-3-Methyl-5-oxo-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)ethyl acetate (3o)



Condition A, R_f = 0.35 (PE/EA = 4/1), yellow oil (40.2 mg, 84% yield).

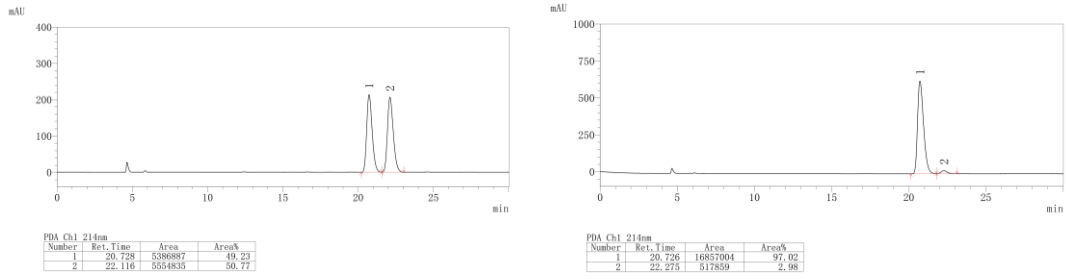
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.64 (dd, *J* = 10.4, 1.1 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.32 – 4.17 (m, 2H), 4.04 (dd, *J* = 8.7, 7.2 Hz, 1H), 3.37 (dd, *J* = 8.8, 6.9 Hz, 1H), 2.69 – 2.51 (m, 4H), 2.17 – 2.01 (m, 5H), 0.91 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 170.9, 150.9, 129.8, 79.8, 73.4, 60.3, 44.0, 37.9, 36.9, 35.6, 21.0, 13.9.

EI-MS: $[M]^{\oplus}$ 238; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{13}H_{18}O_4^{\oplus}$ 238.1205, found 238.1205.

Specific Rotation: $[\alpha]_D^{25.0}$ 64.3 (*c* 1.67, $CHCl_3$) for 94% *ee*.

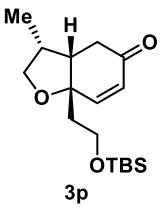
Chiral HPLC analysis: Chiralpak OD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 20.1 min (major), 22.3 min (minor).



Number	Ret.Time	Area	Area%
1	20.728	5386887	49.23
2	22.116	5554835	50.77

Number	Ret.Time	Area	Area%
1	20.726	16857004	97.02
2	22.275	517859	2.98

(3*R*,3a*S*,7a*S*)-7a-(2-((Tert-butyldimethylsilyl)oxy)ethyl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3p)



Condition A, R_f = 0.3 (PE/EA = 8/1), colorless oil (55.2 mg, 89% yield).

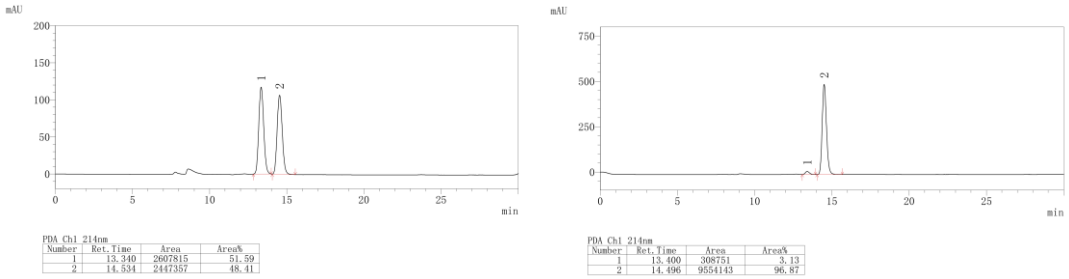
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.64 (dd, *J* = 10.4, 1.0 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 4.03 (dd, *J* = 8.6, 7.4 Hz, 1H), 3.85 – 3.73 (m, 2H), 3.37 (dd, *J* = 8.6, 7.1 Hz, 1H), 2.81 – 2.72 (m, 1H), 2.69 – 2.50 (m, 3H), 2.07 – 1.89 (m, 2H), 0.94 – 0.86 (m, 12H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.9, 151.9, 129.4, 80.5, 73.3, 58.8, 43.9, 42.2, 37.0, 35.8, 25.9, 18.2, 14.0, -5.4.

EI-MS: $[M]^{\oplus}$ 310; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{17}H_{30}O_3Si^{\oplus}$ 310.1964, found 310.1964.

Specific Rotation: $[\alpha]_D^{25.0}$ 41.3 (*c* 2.38, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Chiralpak OD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 98/2; flow rate = 0.4 mL/min; Retention time: 14.5 min (major), 13.4 min (minor).



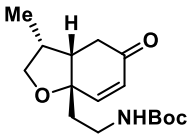
PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	13.340	2607815	51.59
2	14.534	2447357	48.41

PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	13.400	308751	3.13
2	14.496	9554143	96.87

Tert-butyl (2-((3*R*,3a*S*,7a*S*)-3-methyl-5-oxo-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)ethyl) carbamate (3q)



3q

Condition A, R_f = 0.3 (PE/EA = 3/1), yellow oil (20 mg, 68% yield, 0.1 mmol scale).

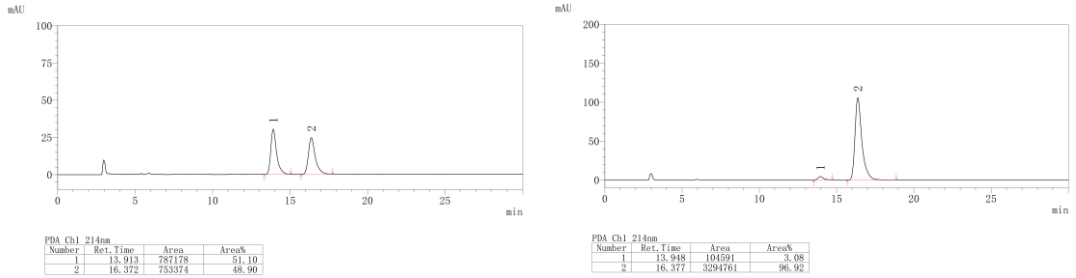
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.66 (d, *J* = 10.3 Hz, 1H), 6.03 (d, *J* = 10.4 Hz, 1H), 5.06 (s, 1H), 4.09 – 4.01 (m, 1H), 3.41 – 3.21 (m, 3H), 2.69 – 2.45 (m, 4H), 2.04 – 1.85 (m, 2H), 1.45 (s, 9H), 0.90 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.1, 155.9, 150.9, 129.9, 80.6, 79.4, 73.6, 44.1, 38.5, 36.6, 36.4, 35.7, 28.5, 14.1.

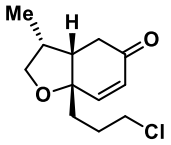
EI-MS: $[M]^{\oplus}$ 295; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{16}H_{25}NO_4^{\oplus}$ 295.1784, found 295.1788.

Specific Rotation: $[\alpha]_D^{25.0}$ 33.0 (*c* 1.0, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.0 mL/min; Retention time: 16.4 min (major), 13.9 min (minor).



(3*R*,3a*S*,7a*S*)-7a-(3-Chloropropyl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3r)



3r

Condition A, R_f = 0.4 (PE/EA = 5/1), colorless oil (41 mg, 90% yield).

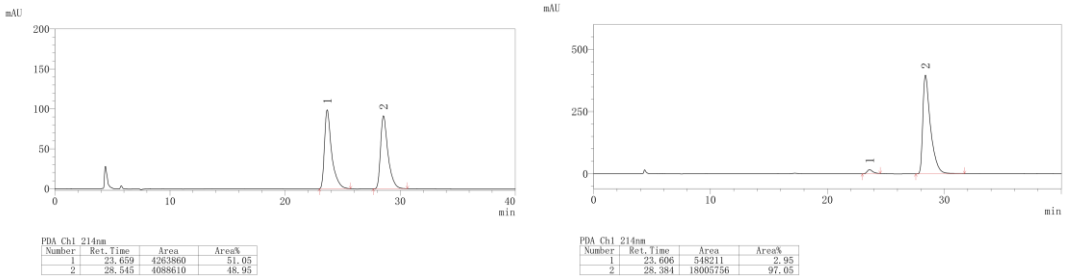
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (dd, *J* = 10.4, 0.8 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.03 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H), 3.38 (dd, *J* = 8.7, 6.4 Hz, 1H), 2.63 – 2.48 (m, 4H), 1.97 – 1.79 (m, 4H), 0.90 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.3, 151.2, 129.8, 80.5, 73.5, 45.1, 43.8, 37.0, 36.7, 35.9, 27.3, 13.9.

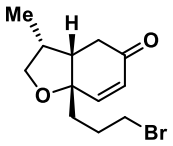
EI-MS: $[M]^{\oplus}$ 228; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{12}H_{17}{}^{35}ClO_2{}^{\oplus}$ 228.0917, found 228.0923.

Specific Rotation: $[\alpha]_D^{25.0}$ 53.2 (*c* 1.77, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 28.4 min (major), 23.6 min (minor).



(3*R*,3a*S*,7a*S*)-7a-(3-Bromopropyl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3s)



3s

Condition A, R_f = 0.35 (PE/EA = 5/1), colorless oil (46.3 mg, 85% yield).

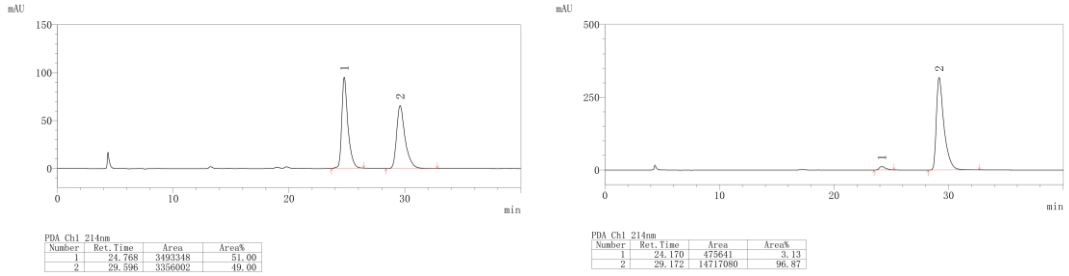
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (dd, *J* = 10.4, 0.5 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.03 (dd, *J* = 8.7, 7.0 Hz, 1H), 3.45 (t, *J* = 6.5 Hz, 2H), 3.38 (dd, *J* = 8.7, 6.3 Hz, 1H), 2.63 – 2.47 (m, 4H), 2.07 – 1.78 (m, 4H), 0.90 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 151.2, 129.8, 80.5, 73.5, 43.7, 37.9, 37.0, 35.9, 33.7, 27.4, 13.9.

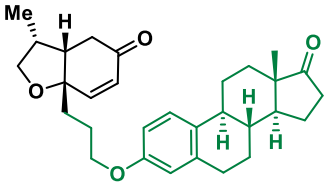
EI-MS: $[M]^{\oplus}$ 272; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{12}H_{17}{}^{79}BrO_2{}^{\oplus}$ 272.0412, found 272.0409.

Specific Rotation: $[\alpha]_D^{25.0}$ 35.0 (*c* 1.77, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 29.1 min (major), 24.1 min (minor).



(3*R*,3a*S*,7a*S*)-3-Methyl-7a-(3-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)propyl)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3t)



3t

Condition A, **C2** was used instead of **C3**, R_f = 0.3 (PE/EA = 5/2), white solid (43.3 mg, 94% yield, 0.1 mmol scale). m.p. = 172°C–173°C.

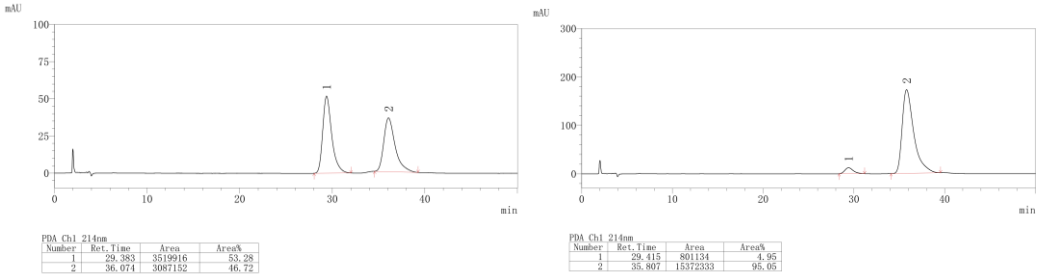
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.19 (d, *J* = 8.6 Hz, 1H), 6.72 – 6.61 (m, 3H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.04 (dd, *J* = 8.6, 7.1 Hz, 1H), 3.96 (t, *J* = 5.3 Hz, 2H), 3.38 (dd, *J* = 8.6, 6.6 Hz, 1H), 2.93 – 2.83 (m, 2H), 2.64 – 2.45 (m, 5H), 2.43 – 2.35 (m, 1H), 2.28 – 2.21 (m, 1H), 2.19 – 1.82 (m, 8H), 1.65 – 1.40 (m, 6H), 0.93 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 221.0, 198.5, 156.9, 151.6, 137.8, 132.1, 129.7, 126.4, 114.5, 112.0, 80.8, 73.4, 67.7, 50.4, 48.0, 44.0, 43.5, 38.4, 37.0, 35.9, 35.9, 31.6, 29.7, 26.6, 25.9, 24.1, 21.6, 13.9, 13.9.

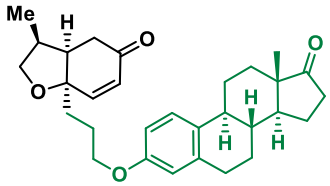
ESI-MS: $[M+H]^{\oplus}$ 463.3; **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd for $C_{30}H_{39}O_4^{\oplus}$ 463.2843, found 463.2846.

Specific Rotation: $[\alpha]_D^{25.0}$ 100.0 (*c* 1.45, $CHCl_3$) for 95:5 dr.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.5 mL/min; Retention time: 35.8min (major), 29.4 min (minor).



(3*S*,3a*R*,7a*R*)-3-Methyl-7a-(3-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)propyl)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3t')



3t'

Condition A, *ent*-**C2** was used instead of **C3**, R_f = 0.3 (PE/EA = 5/2), white solid (44 mg, 95% yield, 0.1 mmol scale). m.p. = 176°C–177°C.

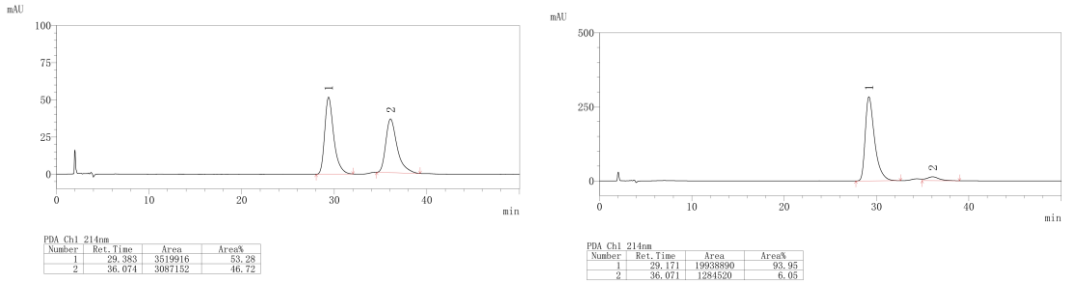
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.19 (d, *J* = 8.6 Hz, 1H), 6.73 – 6.61 (m, 3H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.04 (dd, *J* = 8.6, 7.1 Hz, 1H), 3.96 (t, *J* = 5.6 Hz, 2H), 3.38 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.93 – 2.82 (m, 2H), 2.66 – 2.46 (m, 5H), 2.42 – 2.35 (m, 1H), 2.28 – 2.20 (m, 1H), 2.18 – 1.82 (m, 8H), 1.68 – 1.38 (m, 6H), 0.93 – 0.88 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 221.0, 198.5, 156.9, 151.6, 137.8, 132.1, 129.7, 126.4, 114.5, 112.1, 80.8, 73.4, 67.7, 50.4, 48.0, 44.0, 43.6, 38.4, 37.0, 36.0, 35.9, 31.6, 29.7, 26.6, 25.9, 24.1, 21.6, 13.9, 13.9.

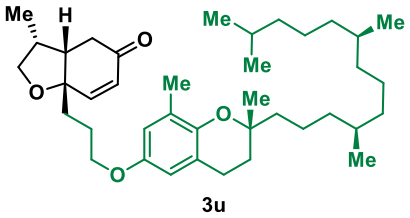
ESI-MS: $[M+H]^{\oplus}$ 463.3; **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd for $C_{30}H_{39}O_4^{\oplus}$ 463.2843, found 463.2846.

Specific Rotation: $[\alpha]_D^{25.0}$ 75.0 (*c* 1.83, $CHCl_3$) for 6:94 dr.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.5 mL/min; Retention time: 29.2min (major), 36.1 min (minor).



(3*R*,3a*S*,7a*S*)-7a-(3-(((*R*)-2,8-Dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)propyl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3u)



3u

Condition A, **C2** was used instead of **C3**, R_f = 0.4 (PE/EA = 10/1), light yellow oil (35.8 mg, 60% yield, 0.1 mmol scale).

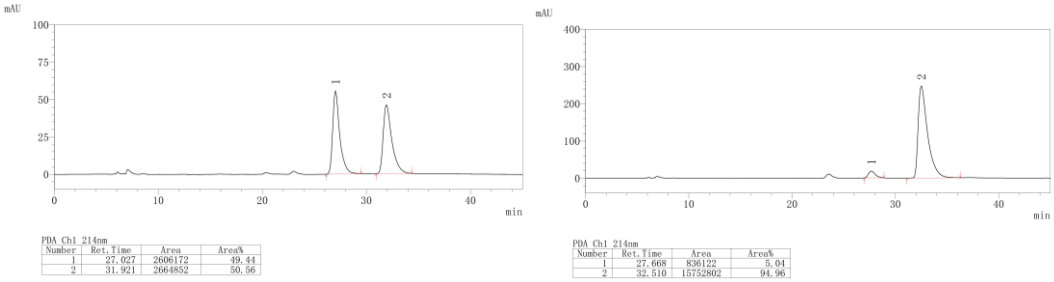
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.65 (d, *J* = 10.4 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 6.42 (d, *J* = 2.7 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.03 (dd, *J* = 8.6, 7.1 Hz, 1H), 3.90 (t, *J* = 5.5 Hz, 2H), 3.38 (dd, *J* = 8.6, 6.7 Hz, 1H), 2.77 – 2.66 (m, 2H), 2.66 – 2.50 (m, 4H), 2.13 (s, 3H), 1.97 – 1.69 (m, 6H), 1.58 – 1.46 (m, 3H), 1.43 – 1.20 (m, 15H), 1.17 – 1.02 (m, 6H), 0.92 – 0.81 (m, 15H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.6, 151.7, 151.4, 146.3, 129.7, 127.3, 121.0, 115.5, 111.9, 80.9, 75.6, 73.4, 68.3, 43.6, 40.0, 39.4, 37.5, 37.5, 37.3, 37.1, 36.0, 32.9, 32.8, 31.4, 28.1, 24.9, 24.5, 24.3, 24.2, 22.8, 22.7, 22.7, 21.1, 19.8, 19.7, 16.3, 13.9.

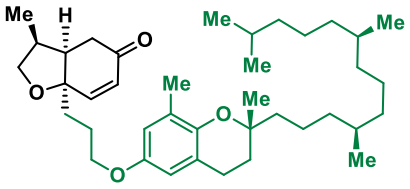
ESI-MS: $[M+H]^{\oplus}$ 595.5; **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd for $C_{39}H_{63}O_4^{\oplus}$ 595.4721, found 595.4729.

Specific Rotation: $[\alpha]_D^{24.9}$ 11.9 (*c* 1.43, $CHCl_3$) for 95:5 dr.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 98/2; flow rate = 0.5 mL/min; Retention time: 32.5 min (major), 27.7 min (minor).



(3S,3aR,7aR)-7a-(3-(((R)-2,8-dimethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy) propyl)-3-methyl-2,3,3a,7a-tetrahydrobenzofuran-5(4H)-one (3u')



3u'

Condition A, *ent*-**C2** was used instead of **C3**, R_f = 0.4 (PE/EA = 10/1), light yellow oil (35 mg, 59% yield, 0.1 mmol scale).

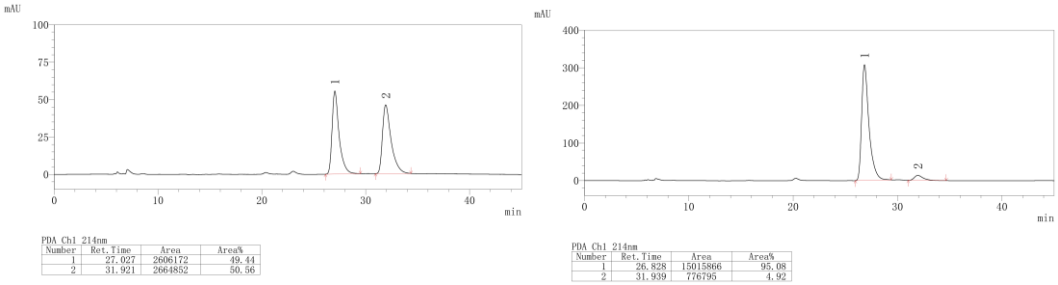
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.65 (d, *J* = 10.4 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 6.42 (d, *J* = 2.7 Hz, 1H), 6.04 (d, *J* = 10.4 Hz, 1H), 4.03 (dd, *J* = 8.6, 7.1 Hz, 1H), 3.90 (t, *J* = 5.6 Hz, 2H), 3.38 (dd, *J* = 8.6, 6.7 Hz, 1H), 2.74 – 2.67 (m, 2H), 2.66 – 2.50 (m, 4H), 2.13 (s, 3H), 1.98 – 1.69 (m, 6H), 1.58 – 1.47 (m, 3H), 1.43 – 1.20 (m, 15H), 1.16 – 1.02 (m, 6H), 0.92 – 0.82 (m, 15H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.6, 151.7, 151.4, 146.3, 129.7, 127.3, 121.0, 115.5, 111.9, 80.9, 75.6, 73.4, 68.3, 43.6, 40.0, 39.4, 37.5, 37.5, 37.3, 37.1, 36.0, 32.9, 32.8, 31.4, 28.1, 24.9, 24.5, 24.3, 24.2, 22.8, 22.7, 22.7, 21.1, 19.8, 19.7, 16.3, 13.9.

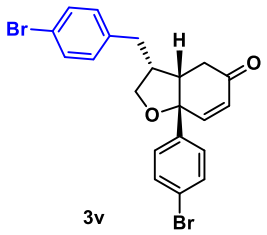
ESI-MS: $[M+H]^{\oplus}$ 595.5; **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd for $C_{39}H_{63}O_4^{\oplus}$ 595.4721, found 595.4729.

Specific Rotation: $[\alpha]_D^{25.0}$ -2.9 (*c* 1.45, $CHCl_3$) for 5: 95 dr.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 98/2; flow rate = 0.5 mL/min; Retention time: 26.8 min (major), 31.9 min (minor).



(3*R*,3a*S*,7a*S*)-3-(4-Bromobenzyl)-7a-(4-bromophenyl)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3v)



3v

Condition C, R_f = 0.4 (PE/EA = 5/1), colorless oil (35.2 mg, 77% yield).

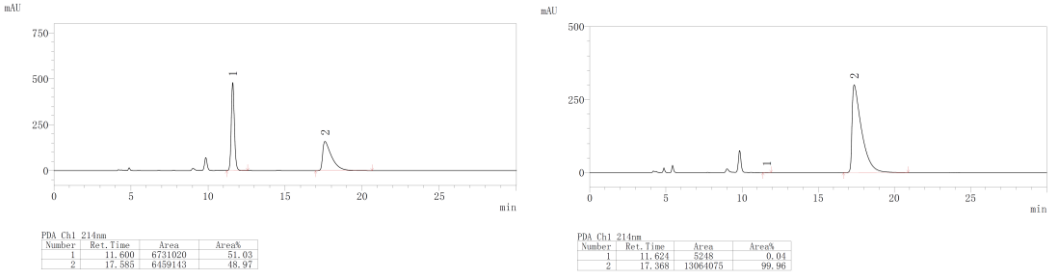
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 10.1 Hz, 1H), 6.18 (d, *J* = 10.1 Hz, 1H), 4.11 (dd, *J* = 8.7, 7.5 Hz, 1H), 3.89 – 3.83 (m, 1H), 2.82 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.75 – 2.46 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 148.3, 142.8, 138.5, 131.9, 131.9, 130.2, 129.2, 126.9, 122.0, 120.4, 82.7, 72.3, 47.5, 43.3, 35.5, 33.4.

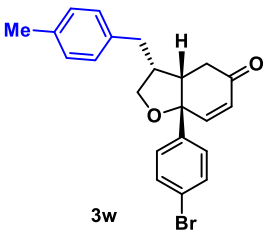
FT-MS: $[M+H]^{\oplus}$ 461.0; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{21}H_{19}{}^{79}Br_2O_2^{\oplus}$ 460.9746, found 460.9736.

Specific Rotation: $[\alpha]_D^{25.0}$ -107.3 (*c* 0.88, $CHCl_3$) for >99% *ee*.

Chiral HPLC analysis: Chiralpak IA Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 85/15; flow rate = 0.7 mL/min; Retention time: 17.4 min (major), 11.6 min (minor).



(3*R*,3a*S*,7a*S*)-7a-(4-Bromophenyl)-3-(4-methylbenzyl)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3w)



3w

Condition C, R_f = 0.3 (PE/EA = 9/1), colorless oil (19.5 mg, 49% yield).

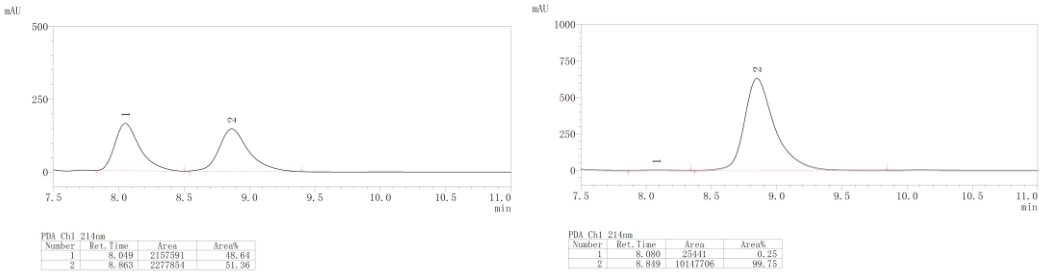
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 10.1 Hz, 1H), 6.16 (d, *J* = 10.1 Hz, 1H), 4.17 – 4.09 (m, 1H), 3.93 – 3.86 (m, 1H), 2.81 (dd, *J* = 14.7, 6.8 Hz, 1H), 2.75 – 2.47 (m, 5H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.5, 148.3, 143.1, 136.4, 136.1, 131.8, 129.4, 129.1, 128.3, 126.9, 121.9, 82.7, 72.6, 47.5, 43.4, 35.5, 33.5, 21.1.

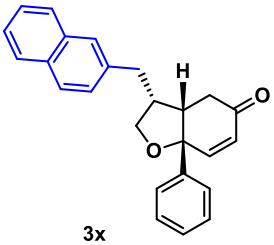
FT-MS: $[M+H]^{\oplus}$ 397.1; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{22}H_{22}{}^{79}BrO_2{}^{\oplus}$ 397.0798, found 397.0790.

Specific Rotation: $[\alpha]_D^{25.0}$ -117.8 (*c* 0.74, $CHCl_3$) for >99% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.0 mL/min; Retention time: 8.8 min (major), 8.1 min (minor).



(3*R*,3a*S*,7a*S*)-3-(Naphthalen-2-ylmethyl)-7a-phenyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3x)



3x

Condition C, R_f = 0.5 (PE/EA = 5/1), colorless oil (21.7 mg, 61% yield).

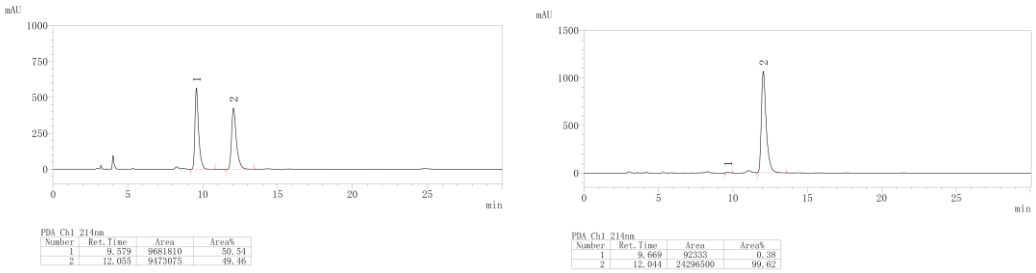
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 – 7.73 (m, 3H), 7.55 (s, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 7.22 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.65 (d, *J* = 10.1 Hz, 1H), 6.20 (d, *J* = 10.2 Hz, 1H), 4.14 (dd, *J* = 8.5, 7.1 Hz, 1H), 4.00 – 3.92 (m, 1H), 2.95 – 2.83 (m, 3H), 2.78 – 2.65 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.7, 149.1, 143.8, 137.2, 133.6, 132.2, 128.9, 128.8, 128.4, 127.8, 127.7, 127.5, 126.9, 126.8, 126.2, 125.6, 125.0, 83.0, 72.4, 47.6, 43.5, 35.7, 34.3.

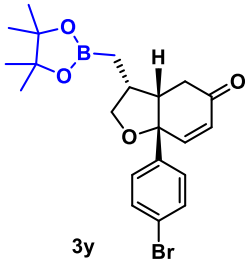
FT-MS: $[M+H]^{\oplus}$ 355.2; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{25}H_{23}O_2{}^{\oplus}$ 355.1693, found 355.1685.

Specific Rotation: $[\alpha]_D^{25.0}$ -90.2 (*c* 0.9, $CHCl_3$) for >99% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.0 mL/min; Retention time: 12.0 min (major), 9.7 min (minor).



(3*R*,3a*S*,7a*S*)-7a-(4-Bromophenyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3y)



Condition C, R_f = 0.5 (PE/EA = 5/1), colorless oil (21.8 mg, 50% yield).

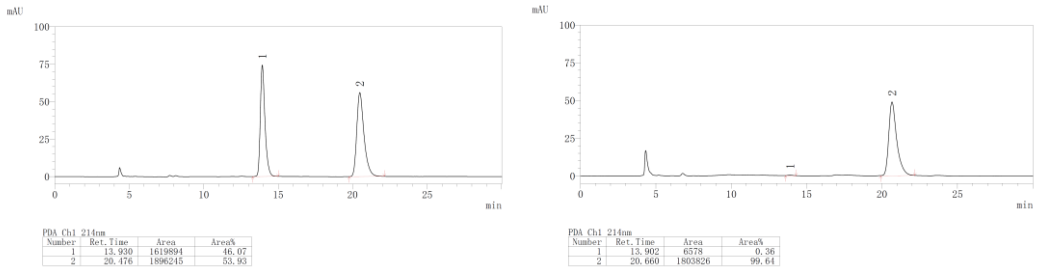
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 8.5 Hz, 2H), 7.28 (s, 2H), 6.54 (d, *J* = 10.1 Hz, 1H), 6.13 (d, *J* = 10.1 Hz, 1H), 4.32 – 4.27 (m, 1H), 3.72 – 3.67 (m, 1H), 2.76 (dd, *J* = 14.5, 7.2 Hz, 1H), 2.61 (dd, *J* = 15.8, 7.8 Hz, 1H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.21 (s, 12H), 0.78 (qd, *J* = 15.8, 8.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.8, 148.4, 143.3, 131.7, 129.3, 127.0, 121.7, 83.5, 82.5, 74.3, 48.3, 37.6, 35.4, 24.9, 24.8.

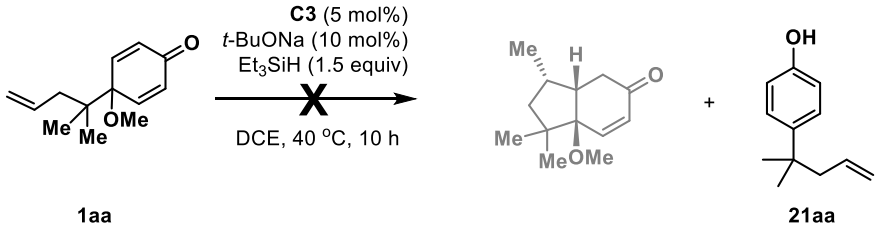
FT-MS: $[M+H]^{\oplus}$ 432.1; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{21}H_{27}{}^{79}Br^{10}BO_4{}^{\oplus}$ 432.1217, found 432.1210.

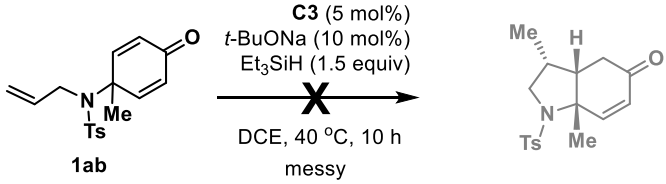
Specific Rotation: $[\alpha]_D^{25.0}$ -93 (*c* 0.25, $CHCl_3$) for >99% *ee*.

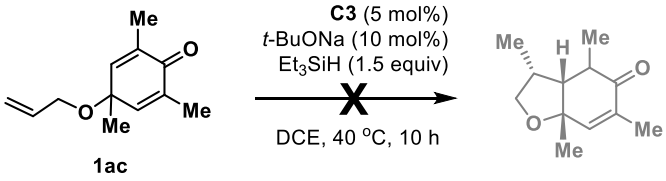
Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 20.6 min (major), 13.9 min (minor).

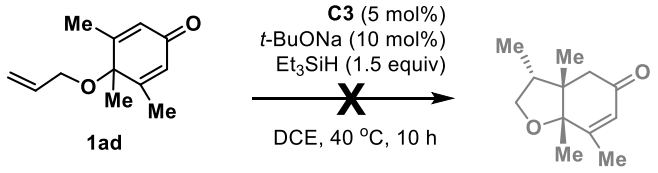


Unsuccessful substrates:

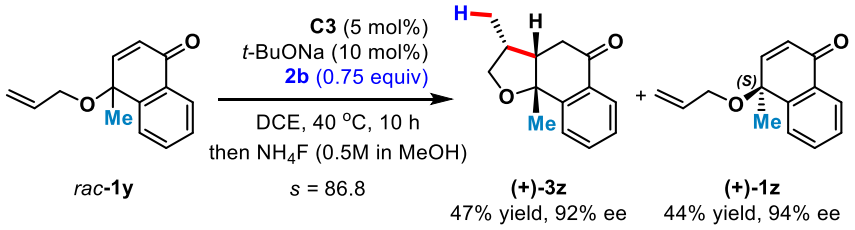






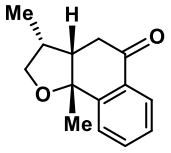


4. Kinetic resolution of *rac*-1z



A dried Schlenk flask was charged with **C3** (5.66 mg, 5 mol%) and *t*-BuONa (2.0 mg, 10 mol%), backfilled with argon. Then anhydrous DCE (1 mL), Et_3SiH (0.15 mmol, 0.75 equiv) and *rac*-**1z** (0.2 mmol, 1.0 equiv) were added. After the mixture was stirred at 40 °C for 10 h, the reaction mixture was cooled to room temperature. Then NH_4F (0.5M in MeOH) was added to quench the reaction and stirred for 10 min. Finally, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography to afford product **(+)-3z** and **(+)-1z**.

(3*R*,3a*S*,9b*R*)-3,9b-Dimethyl-2,3,3a,9b-tetrahydronaphtho[1,2-b]furan-5(4*H*)-one ((+)-3z)



(+)-3z

R_f = 0.3 (PE/EA = 4/1), colorless oil (20.3 mg, 47% yield).

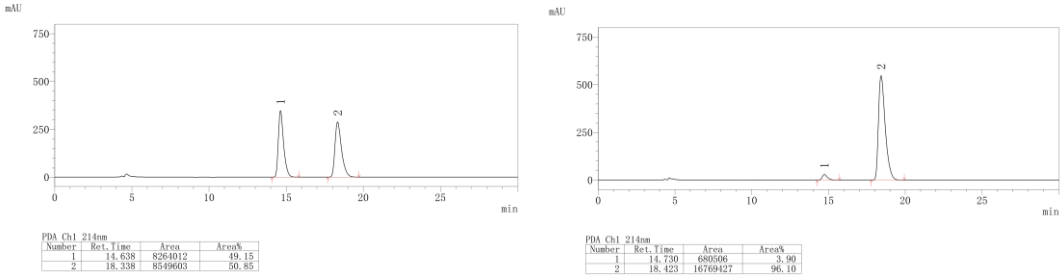
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.70 – 7.57 (m, 2H), 7.41 – 7.34 (m, 1H), 4.16 – 4.09 (m, 1H), 3.12 (dd, *J* = 8.8, 6.7 Hz, 1H), 2.91 – 2.77 (m, 2H), 2.72 – 2.58 (m, 2H), 1.64 (s, 3H), 0.74 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.3, 147.4, 134.6, 131.5, 127.7, 127.0, 125.8, 80.4, 73.5, 46.5, 36.4, 36.2, 29.2, 14.7.

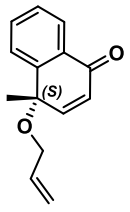
EI-MS: $[M]^{\oplus}$ 216; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{14}H_{16}O_2^{\oplus}$ 216.1150, found 216.1158.

Specific Rotation: $[\alpha]_D^{25.0}$ 22.5 (*c* 0.86, $CHCl_3$) for 92% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 98/2; flow rate = 0.7 mL/min; Retention time: 18.4 min (major), 14.7 min (minor).



(*S*)-4-(Allyloxy)-4-methylnaphthalen-1(4*H*)-one ((+)-1z)



(+)-1z

R_f = 0.6 (PE/EA = 4/1), colorless oil (19 mg, 44% yield).

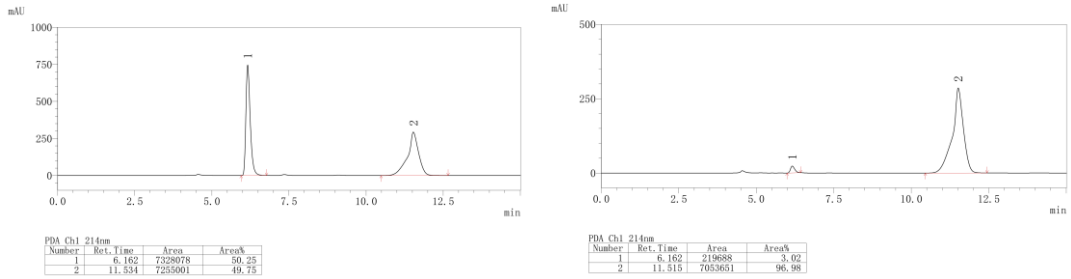
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.72 – 7.60 (m, 2H), 7.50 – 7.41 (m, 1H), 6.98 (d, *J* = 10.3 Hz, 1H), 6.49 (d, *J* = 10.3 Hz, 1H), 5.84 (ddd, *J* = 22.7, 10.7, 5.5 Hz, 1H), 5.27 – 5.19 (m, 1H), 5.13 (dd, *J* = 10.4, 1.4 Hz, 1H), 3.72 (ddt, *J* = 12.1, 5.6, 1.3 Hz, 1H), 3.53 (ddt, *J* = 12.2, 5.4, 1.4 Hz, 1H), 1.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.3, 152.7, 145.2, 134.6, 133.3, 131.3, 130.1, 128.2, 126.8, 126.3, 116.9, 73.8, 66.4, 30.6.

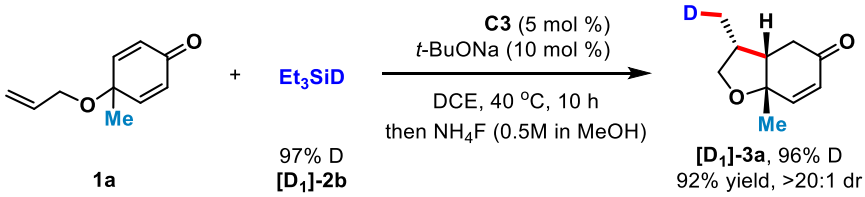
ESI-MS: $[M+H]^{\oplus}$ 215.1; **HRMS (ESI)**: $[M+H]^{\oplus}$ calcd for $C_{14}H_{15}O_2^{\oplus}$ 215.1067, found 215.1067.

Specific Rotation: $[\alpha]_D^{25.0}$ 76.6 (*c* 0.89, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Chiralpak OD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 11.5 min (major), 6.2 min (minor).



5. Deuterium-labelling experiment



(3*R*,3a*S*,7a*S*)-7a-Methyl-3-(methyl-d)-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one ([D$_1$]-3a) A dried Schlenk flask was charged with **C3** (5.66 mg, 5 mol%) and *t*-BuONa (2.0 mg, 10 mol%), backfilled with argon. Then anhydrous DCE (2 mL), Et_3SiD (0.276 mmol, 1.5 equiv) and **1a** (0.184 mmol, 1.0 equiv) were added. After the mixture was stirred at 40 °C for 10 h, the reaction mixture was cooled to room temperature. Then NH_4F (0.5M in MeOH) was added to quench the reaction and stirred for 10 min. Finally, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography (PE/EA = 5/1) to afford product **[D$_1$]-3a**.

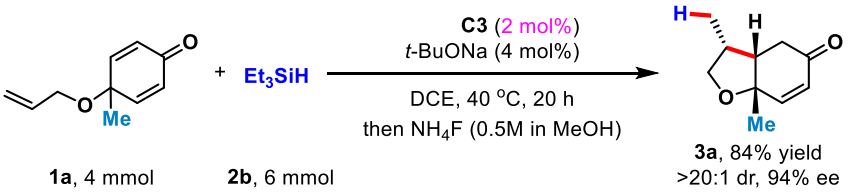
light yellow oil (28.2 mg, 92% yield, 96% D).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (d, *J* = 10.3 Hz, 1H), 5.98 (d, *J* = 10.3 Hz, 1H), 4.08 (dd, *J* = 8.6, 7.6 Hz, 1H), 3.37 (dd, *J* = 8.6, 7.4 Hz, 1H), 2.66 – 2.48 (m, 4H), 1.46 (s, 3H), 0.89 (dt, *J* = 5.3, 1.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.5, 152.6, 129.0, 78.9, 73.5, 45.6, 36.6, 35.7, 25.8, 13.50 (t, *J* = 19.0 Hz).

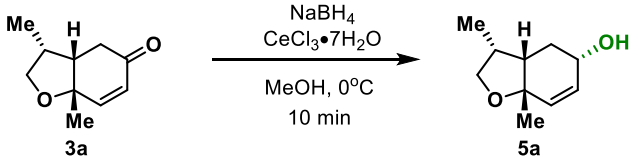
EI-MS: $[M]^{\oplus}$ 167; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{10}H_{13}DO_2^{\oplus}$ 167.1057, found 167.1063.

6. Subgram-scale experiment



A dried Schlenk flask was charged with **C3** (45.3 mg, 2 mol%) and *t*-BuONa (15.4 mg, 4 mol%), backfilled with argon. Then anhydrous DCE (10 mL), Et_3SiH (6.0 mmol, 1.5 equiv) and **1a** (4.0 mmol, 1.0 equiv) were added. After the mixture was stirred at 40 °C for 20 h, the reaction mixture was cooled to room temperature. Then NH_4F (0.5M in MeOH) was added to quench the reaction and stirred for 10 min. Finally, the reaction mixture was filtered, washed with EtOAc (100 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography (PE/EA = 5/1) to afford product **3a** (556 mg, 84% yield).

7. Transformations of cyclization product



(3*R*,3a*S*,5*S*,7a*S*)-3,7a-Dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran-5-ol (5a) A dried Schlenk flask was charged with **3a** (33.2 mg, 0.2 mmol, 1.0 equiv), $CeCl_3·7H_2O$ (89 mg, 1.2 equiv) and MeOH (2.0 mL). It was cooled to 0°C and $NaBH_4$ (9.12 mg, 1.2 equiv) was added carefully. The reaction mixture was stirred at 0°C for 10 mins. Then it was concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate eluent (PE/EA = 2:1) to afford the desired product **5a** as colorless oil (24.5 mg, 73% yield, >20:1 dr).

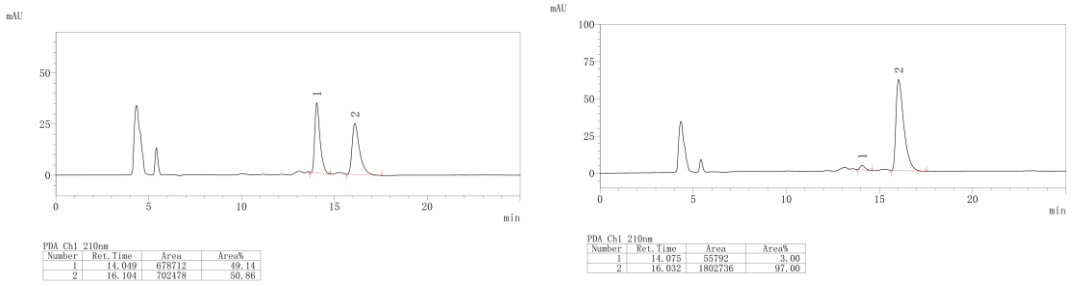
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.79 (d, *J* = 10.0 Hz, 1H), 5.68 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.21 – 4.12 (m, 1H), 3.97 (t, *J* = 8.0 Hz, 1H), 3.48 (dd, *J* = 10.7, 8.2 Hz, 1H), 2.83 – 2.69 (m, 1H), 2.15 (s, 1H), 1.98 (ddd, *J* = 13.5, 6.7, 4.8 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.26 – 1.16 (m, 4H), 0.98 (d, *J* = 6.9 Hz, 3H).

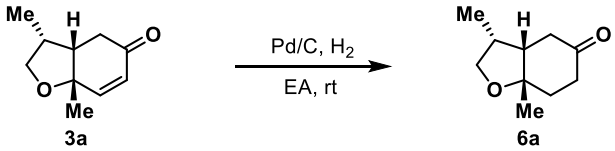
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 133.3, 132.1, 79.6, 72.4, 67.6, 44. 4, 35.7, 30.8, 28.4, 11.2.

EI-MS: $[M]^{\oplus}$ 168; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{10}H_{16}O_2^{\oplus}$ 168.1150, found 168.1145.

Specific Rotation: $[\alpha]_D^{25.0}$ 16.2 (*c* 1.2, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 16.0 min (major), 14.1 min (minor).





(3*R*,3a*S*,7a*S*)-3,7a-Dimethylhexahydrobenzofuran-5(4*H*)-one (6a) A dried Schlenk flask was charged with **3a** (33.2 mg, 0.2 mmol, 1.0 equiv), Pd/C (31.8 mg, 15 mol%) and EA (2.0 mL), backfilled with hydrogen. The reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate eluent (PE/EA = 4:1) to afford the desired product **6a** as colorless oil (28.3 mg, 84% yield).

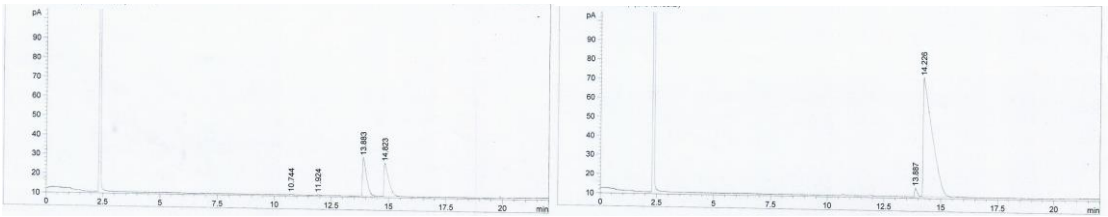
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.04 – 3.97 (m, 1H), 3.43 (t, *J* = 9.2 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.53 – 2.42 (m, 1H), 2.38 – 2.07 (m, 5H), 1.99 (dt, *J* = 18.7, 6.7 Hz, 1H), 1.31 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 213.3, 82.0, 72.7, 46.3, 38.1, 36.7, 35.8, 34.2, 27.5, 11.9.

EI-MS: $[M]^{\oplus}$ 168; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{10}H_{16}O_2^{\oplus}$ 168.1150, found 168.1149.

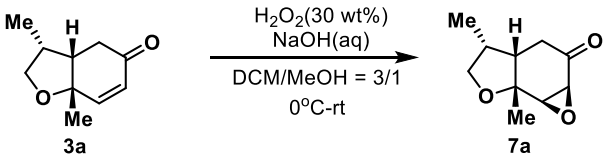
Specific Rotation: $[\alpha]_D^{25.0}$ -21.7 (*c* 0.81, $CHCl_3$) for 96% *ee*.

Chiral GC analysis: The enantiomeric ratio was determined by GC using Cyclosil-B (30m×0.25mm×0.25um) column (150 ºC – 260 ºC). He carrier gas at 1.0 mL/min. Retention time: 14.2 min (major), 13.9 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.744	PBA	0.0995	3.56317	4.44534e-1	0.72320
2	11.924	BBA	0.1016	3.36487	4.10573e-1	0.68295
3	13.883	PBA	0.1658	243.06203	19.99786	49.33301
4	14.823	BB	0.1867	242.70645	16.98354	49.26084
Totals :				492.69651	37.83651	

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.887	PB	0.1172	34.80628	4.35784	2.02732
2	14.226	BBA	0.3319	1682.05396	62.12404	97.97268
Totals :				1716.86024	66.48188	



(1a*S*,3a*S*,4*R*,6a*R*,6b*R*)-4,6a-Dimethylhexahydrooxireno[2,3-g]benzofuran-2(1a*H*)-one (7a) A dried Schlenk flask was charged with **3a** (33.2 mg, 0.2 mmol, 1.0 equiv), DCM/MeOH (0.2 mL/0.6 mL). It was cooled to 0°C, then 30%wt H_2O_2 (0.4 mL) and 20%wt NaOH (0.2 mL) were added carefully. The reaction mixture was stirred at room temperature for 30 min. $Na_2S_2O_3$ was added to quench the reaction. Then it was diluted with water (20 mL) and extracted with DCM (20 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate eluent (PE/EA = 4:1) to afford the desired product **7a** as colorless oil (22.5 mg, 62% yield).

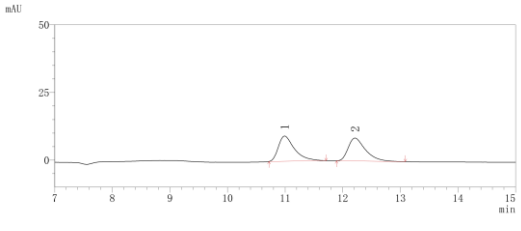
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.91 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.46 (d, *J* = 3.8 Hz, 1H), 3.38 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.29 (d, *J* = 3.8 Hz, 1H), 2.80 (dd, *J* = 15.2, 7.3 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.22 (dd, *J* = 15.2, 1.3 Hz, 1H), 1.55 (s, 3H), 0.94 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 207.2, 78.4, 73.4, 64.4, 55.5, 48.5, 38.7, 33.1, 25.4, 12.6.

EI-MS: $[M]^{\oplus}$ 182; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{10}H_{14}O_3^{\oplus}$ 182.0943, found 182.0941.

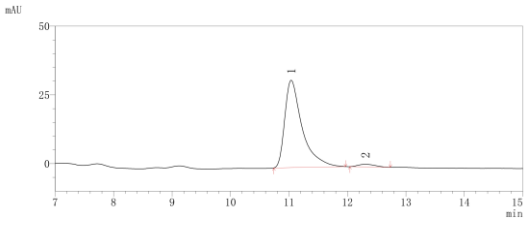
Specific Rotation: $[\alpha]_D^{25.0}$ 16.9 (*c* 0.77, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 11.0 min (major), 12.3 min (minor).



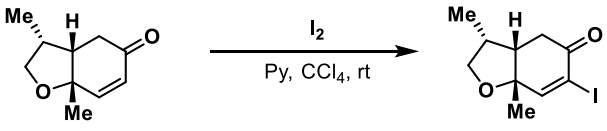
PDA Ch1 214nm

Number	Ret.Time	Area	Area%
1	10.990	181990	50.70
2	12.212	176983	49.30



PDA Ch1 210nm

Number	Ret.Time	Area	Area%
1	11.037	656953	97.22
2	12.306	18817	2.78



(3*R*,3a*S*,7a*R*)-6-iodo-3,7a-Dimethyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (8a) A dried Schlenk flask was charged with **3a** (33.2 mg, 0.2 mmol, 1.0 equiv), I_2 (114.3 mg, 0.45 mmol, 3.0 equiv), pyridine/CCl_4 (1.5 mL/1.5 mL). The reaction mixture was stirred at room temperature overnight. Then, the reaction mixture was concentrated under reduced pressure and purified by flash column chromatography using petroleum ether/ethyl acetate eluent (PE/EA = 4:1) to afford the desired product **8a** as colorless oil (25 mg, 57% yield).

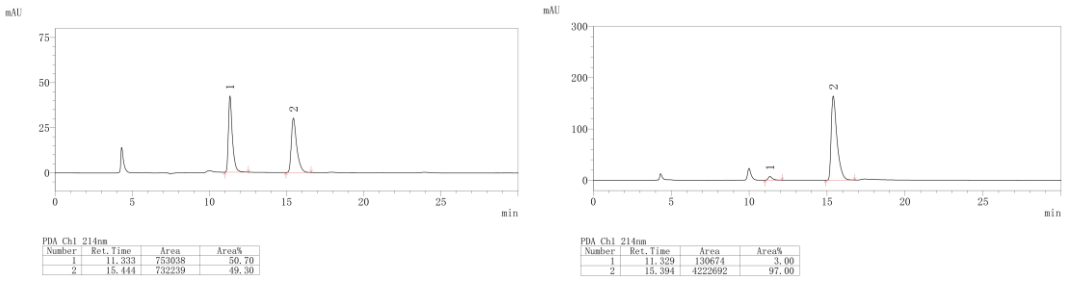
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 0.7 Hz, 1H), 4.10 (dd, *J* = 8.8, 7.4 Hz, 1H), 3.40 (dd, *J* = 8.8, 7.3 Hz, 1H), 2.83 (dd, *J* = 17.0, 4.0 Hz, 1H), 2.72 – 2.53 (m, 3H), 1.46 (s, 3H), 0.88 (d, *J* = 7.0 Hz, 3H).

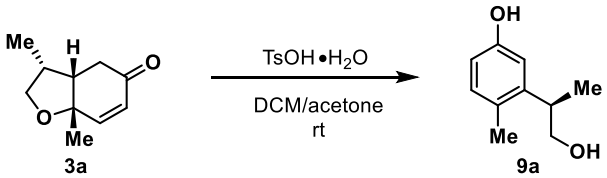
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.3, 161.2, 104.0, 82.2, 73.9, 46.1, 36.5, 34.4, 25.4, 13.8.

EI-MS: $[M]^{\oplus}$ 292; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{10}H_{13}O_2I^{\oplus}$ 291.9960, found 291.9966.

Specific Rotation: $[\alpha]_D^{25.0}$ -27.5 (*c* 0.93, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 15.4 min (major), 11.3 min (minor).





(*R*)-3-(1-Hydroxypropan-2-yl)-4-methylphenol (9a) A dried Schlenk flask was charged with **3a** (33.2 mg, 0.2 mmol, 1.0 equiv), *p*-toluenesulfonic acid monohydrate (76 mg, 2.0 equiv) and DCM/acetone (1.0 mL/1.0 mL). The reaction mixture was stirred at room temperature for 3 h. Then, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate eluent (PE/EA = 2:1) to afford the desired product **9a** as colorless oil (16 mg, 48% yield).

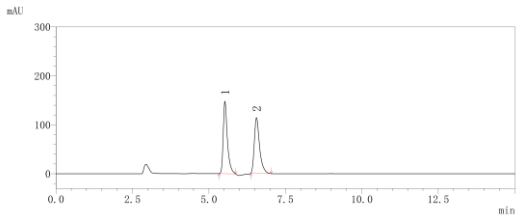
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.00 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 6.59 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.98 (s, 1H), 3.73 – 3.60 (m, 2H), 3.24 – 3.11 (m, 1H), 2.24 (s, 3H), 1.95 (s, 1H), 1.18 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 154.3, 143.1, 131.6, 128.2, 113.3, 112.7, 67.8, 37.3, 18.7, 17.5.

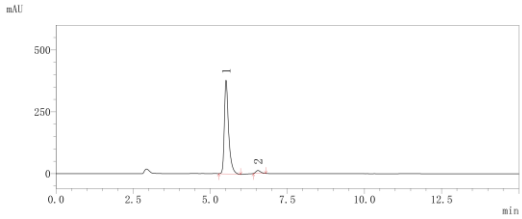
EI-MS: $[M]^{\oplus}$ 168; **HRMS (EI)**: $[M]^{\oplus}$ calcd for $C_{10}H_{14}O_2^{\oplus}$ 166.0994, found 166.0999.

Specific Rotation: $[\alpha]_D^{25.0}$ 12.5 (*c* 0.54, $CHCl_3$) for 93% *ee*.

Chiral HPLC analysis: Phenomenex Lux 5u Cellulose-2 (PC-2) (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.0 mL/min; Retention time: 5.5 min (major), 6.6 min (minor).

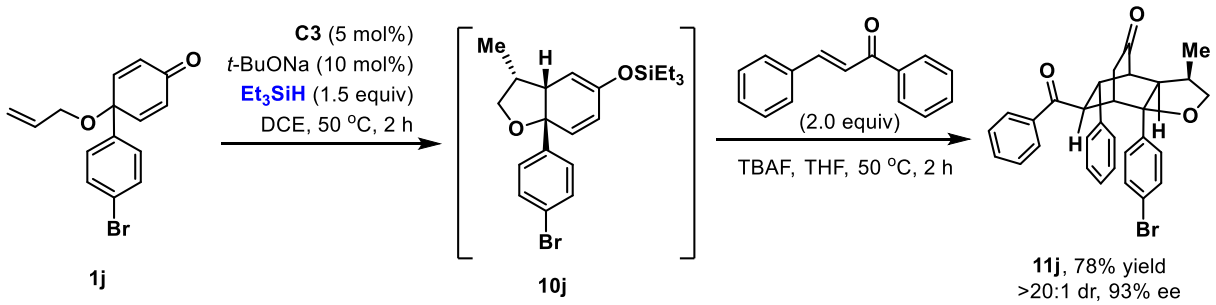


PDA Ch1 214nm			
Number	Ret. Time	Area	Area%
1	5.525	1404585	50.66
2	6.558	1367754	49.34



PDA Ch1 214nm			
Number	Ret. Time	Area	Area%
1	5.515	3627633	96.61
2	6.550	127343	3.39

8. One-pot process to polycyclic products



(3*R*,3a*R*,4*R*,7*S*,7a*S*,8*S*,9*R*)-8-Benzoyl-7a-(4-bromophenyl)-3-methyl-9-phenylhexahydro-4,7-ethanobenzofuran-5(4*H*)-one (11j) A dried Schlenk flask was charged with **C3** (2.8 mg, 5 mol%), *t*-BuONa (1.0 mg, 10 mol%), and substrate **1j** (0.1 mmol, 1.0 equiv), backfilled with argon. Then anhydrous DCE (1 mL), Et_3SiH (0.15 mmol, 1.5 equiv) were added. After the mixture was stirred at 50 °C for 2 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. Then (*E*)-chalcone (0.2 mmol, 2.0 equiv), TBAF (2.0 equiv, 0.2 mL, 1.0M in THF) and THF (1.0 mL) were added and the mixture was stirred at 50 °C for another 2 h. Finally, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography (PE/EA = 9:1) to afford the desired product **11j** (white solid, 40 mg, 78% yield, m.p. = 95 – 96 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.45 – 7.41 (m, 1H), 7.29 – 7.25 (m, 4H), 7.24 – 7.16 (m, 7H), 6.98 (d, *J* = 8.7 Hz, 2H), 4.47 (dd, *J* = 5.9, 2.2 Hz, 1H), 3.81 (t, *J* = 8.5 Hz, 1H), 3.68 (dd, *J* = 5.9,

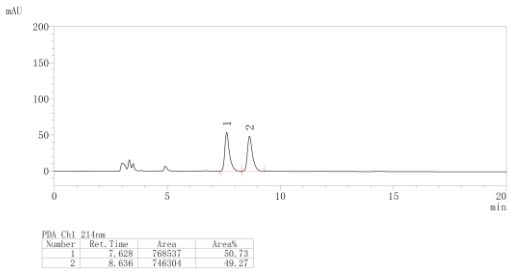
2.5 Hz, 1H), 3.33 (dd, *J* = 6.1, 2.5 Hz, 1H), 3.29 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.24 (dd, *J* = 10.0, 8.7 Hz, 1H), 3.17 (dd, *J* = 18.9, 3.5 Hz, 1H), 3.12 (t, *J* = 2.2 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.43 (dd, *J* = 18.8, 2.3 Hz, 1H), 1.13 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 215.6, 199.0, 143.6, 140.6, 135.6, 132.9, 130.9, 129.0, 128.7, 128.2, 127.4, 127.0, 126.9, 121.9, 85.9, 74.4, 52.9, 50.2, 49.9, 45.6, 41.7, 40.8, 36.9, 11.9.

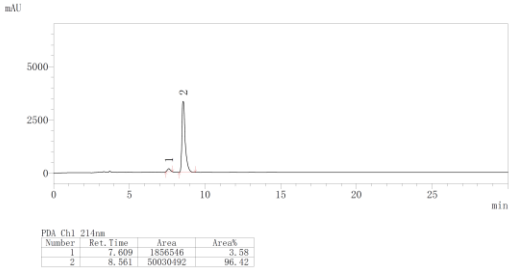
FT-MS: $[M+H]^{\oplus}$ 515.1; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{30}H_{28}O_3{}^{79}Br^{\oplus}$ 515.1216, found 515.1201.

Specific Rotation: $[\alpha]_D^{25.0}$ 57.7 (*c* 1.65, $CHCl_3$) for 93% *ee*.

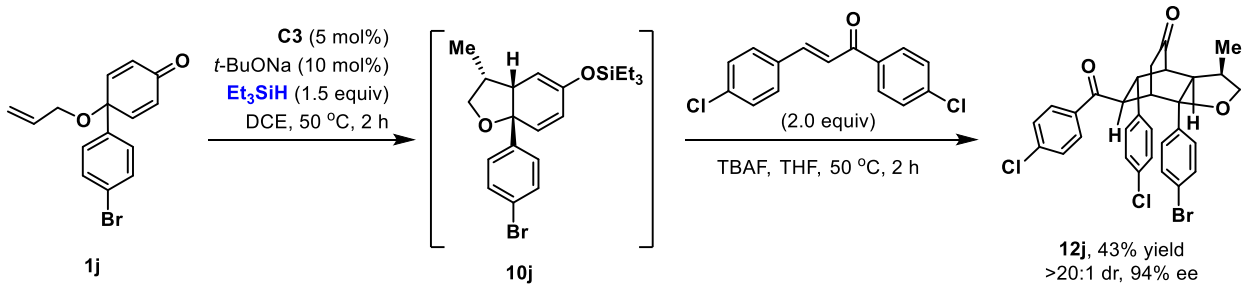
Chiral HPLC analysis: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.0 mL/min; Retention time: 8.6 min (major), 7.6 min (minor).



PDA Ch1 214nm			
Number	Ret. Time	Area	Area%
1	7.628	768537	50.73
2	8.636	746304	49.27



PDA Ch1 214nm			
Number	Ret. Time	Area	Area%
1	7.609	1856546	3.58
2	8.561	50030492	96.42



(3*R*,3a*R*,4*R*,7*S*,7a*S*,8*S*,9*R*)-7a-(4-Bromophenyl)-8-(4-chlorobenzoyl)-9-(4-chlorophenyl)-3-methylhexahydro-4,7-ethanobenzofuran-5(4*H*)-one (12j) A dried Schlenk flask was charged with **C3** (2.8 mg, 5 mol%), *t*-BuONa (1.0 mg, 10 mol%), and substrate **1j** (0.1 mmol, 1.0 equiv), backfilled with argon. Then anhydrous DCE (1 mL), Et_3SiH (0.15 mmol, 1.5 equiv) were added. After the mixture was stirred at 50 °C for 2 h, the reaction mixture was cooled to room temperature and concentrated in vacuo. Then (*E*)-1,3-bis(4-chlorophenyl)prop-2-en-1-one (0.2 mmol, 2.0 equiv), TBAF (2.0 equiv, 0.2 mL, 1.0M in THF) and THF (1.0 mL) were added and the mixture was stirred at 50 °C for another 2 h. Finally, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography (PE/EA = 9:1) to afford the desired product **12j** (yellow solid, 25 mg, 43% yield, m.p. = 109 – 110 °C).

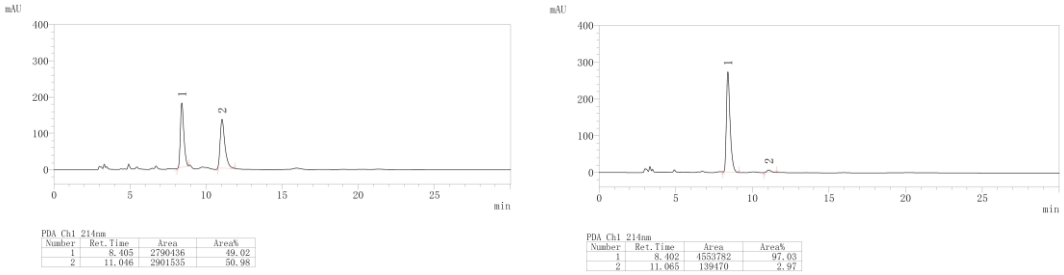
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27 – 7.18 (m, 6H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.41 (d, *J* = 4.4 Hz, 1H), 3.81 (t, *J* = 8.4 Hz, 1H), 3.51 (d, *J* = 3.8 Hz, 1H), 3.22 (dd, *J* = 24.5, 13.9 Hz, 4H), 3.08 (s, 1H), 2.53 (dt, *J* = 15.7, 7.7 Hz, 1H), 2.38 (d, *J* = 18.8 Hz, 1H), 1.12 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 214.9, 197.7, 142.0, 140.6, 139.4, 134.0, 132.9, 131.1, 129.1, 128.7, 128.6, 128.4, 122.2, 85.8, 74.5, 53.2, 50.2, 49.8, 45.7, 41.7, 40.3, 36.9, 12.0.

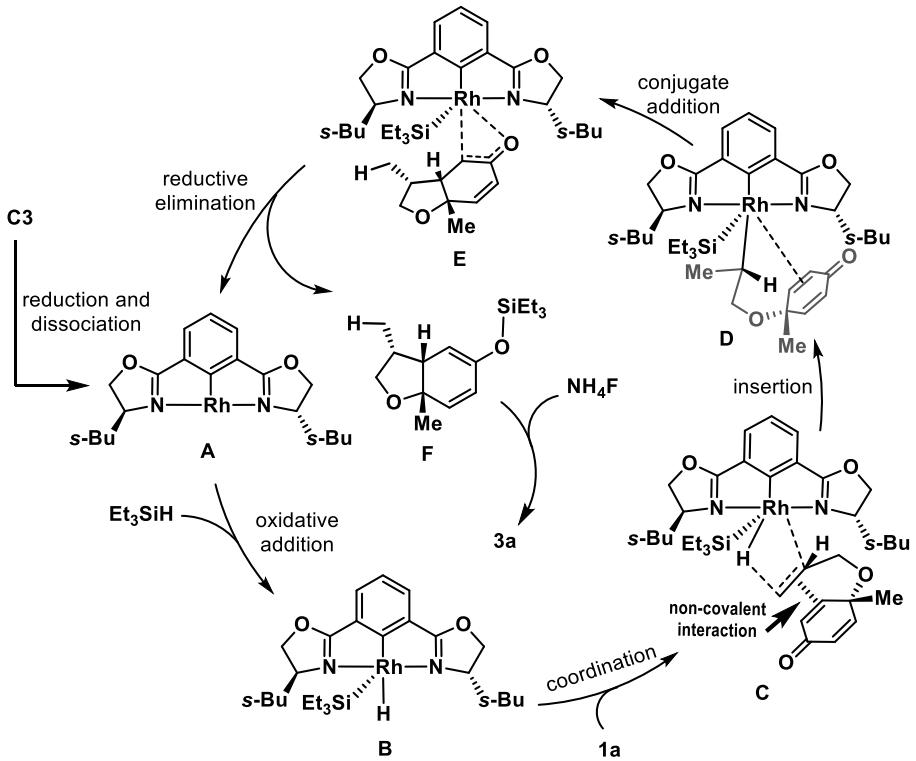
FT-MS: $[M+H]^{\oplus}$ 583.0; **HRMS (DART)**: $[M+H]^{\oplus}$ calcd for $C_{30}H_{26}O_3{}^{79}Br^{35}Cl_2{}^{\oplus}$ 583.0473, found 583.0427.

Specific Rotation: $[\alpha]_D^{25.0}$ 71.6 (*c* 0.8, $CHCl_3$) for 94% *ee*.

Chiral HPLC analysis: Chiralpak AD-H Column (250 mm); detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 1.0 mL/min; Retention time: 8.4 min (major), 11.1 min (minor).

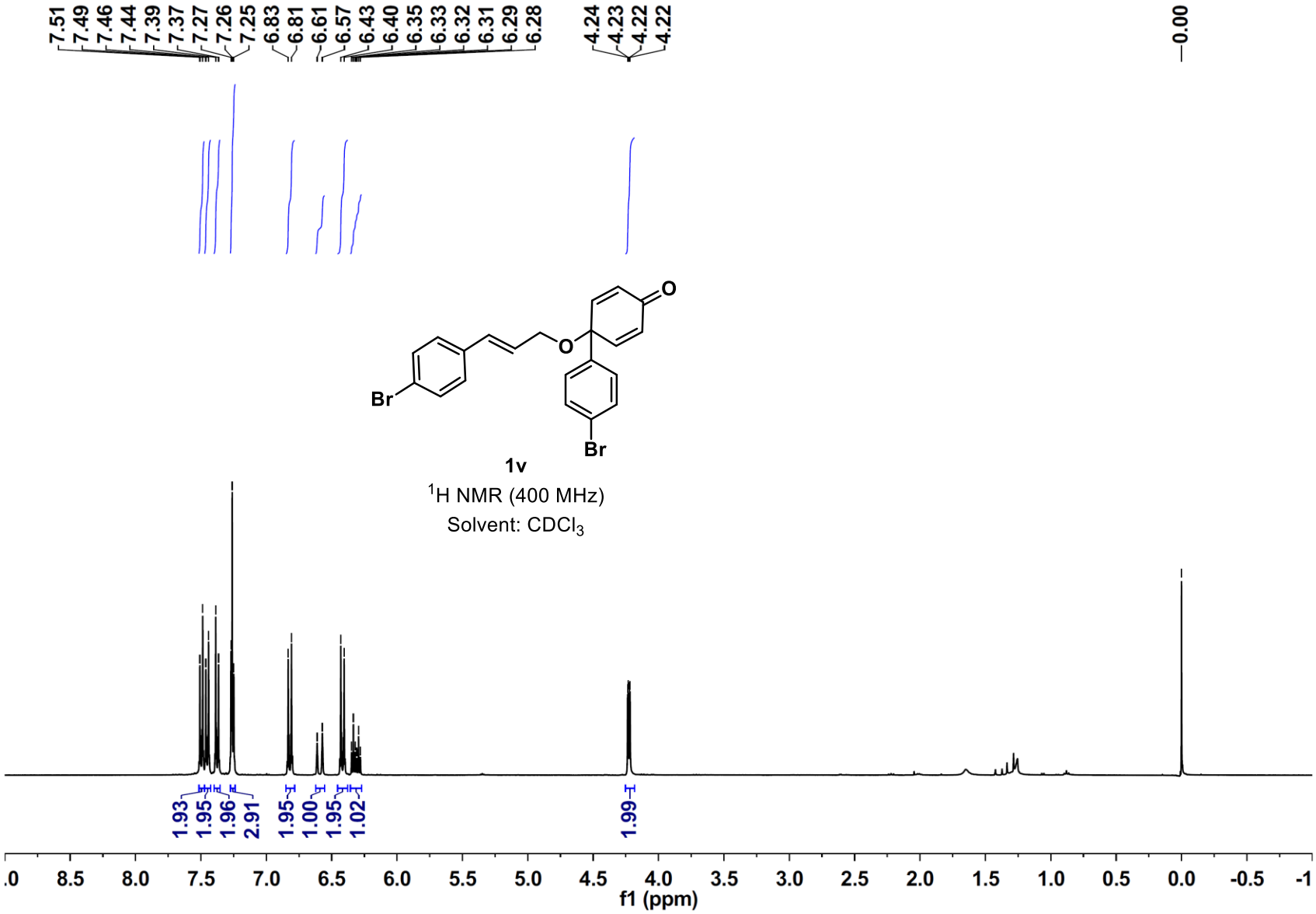


9. Proposed reaction mechanism



The reduction of rhodium precatalyst **C3** by triethylsilane and dissociation of water lead to the formation of Rh(I)-complex **A**, which may be the catalytic active species and triggers the Rh(I)/Rh(III) catalytic cycle. The oxidative addition of the Rh(I)-complex **A** with triethylsilane affords the Rh(III)-hydride complex **B**. Then, the coordination and *anti*-Markovnikov insertion of the cyclohexadienone-tethered terminal alkene **1a** to the Rh(III)-hydride complex **B** provides the Rh(III)-complex **D**, which subsequently undergoes conjugate addition and reductive elimination to offer the enol silyl ether product **F** and regenerates the Rh(I)-complex **A**. Finally, quenching silyl ether product **F** with ammonium fluoride produces the corresponding reductive cyclization product **3a**. Notably, the non-covalent interaction between the enone moiety and the terminal alkene may enhance the reactivity of the terminal alkene to some extent, which would avoid the direct reduction of the enone.

10. ^{1}H NMR, ^{13}C NMR, HMQC, and NOE Copies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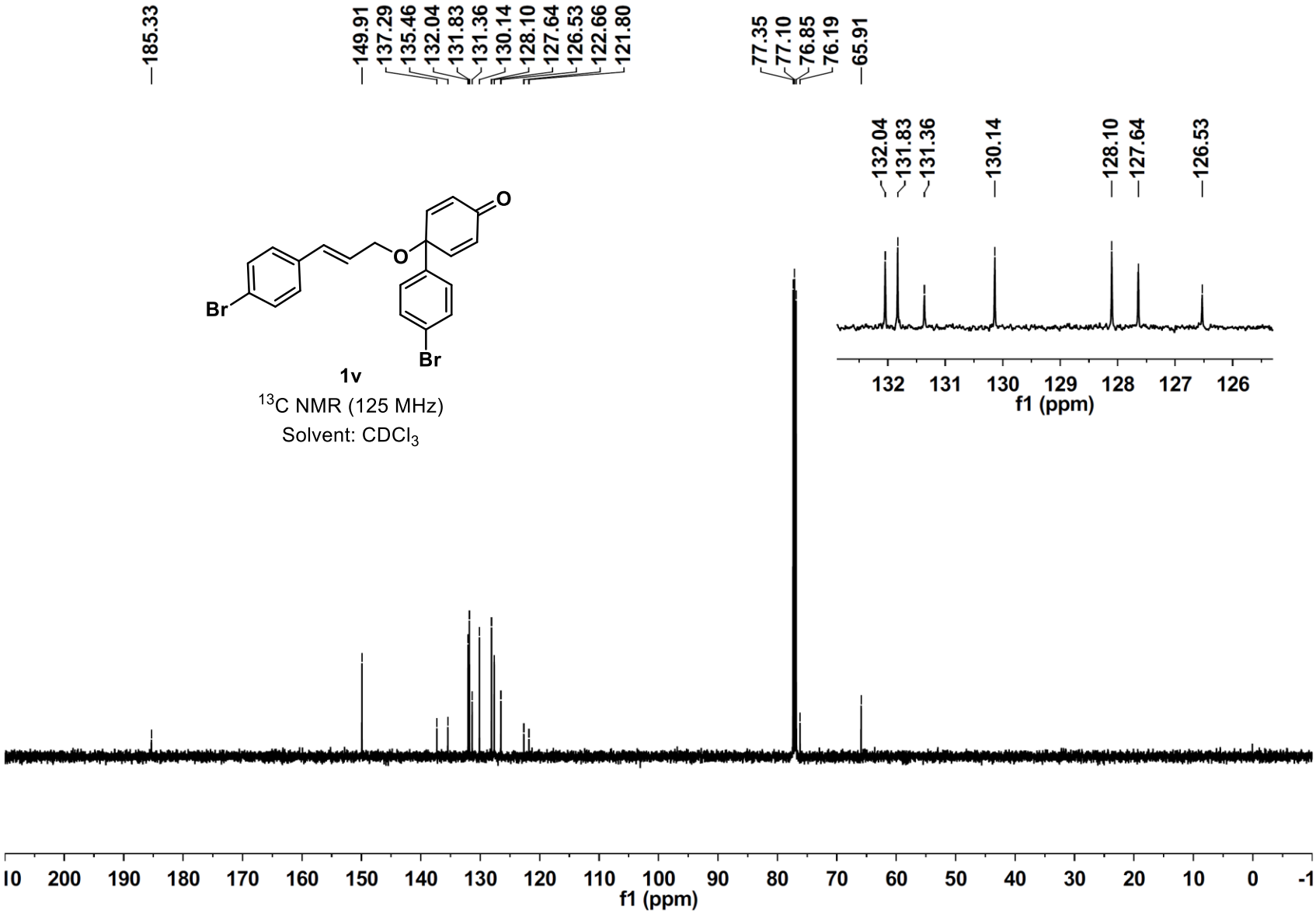
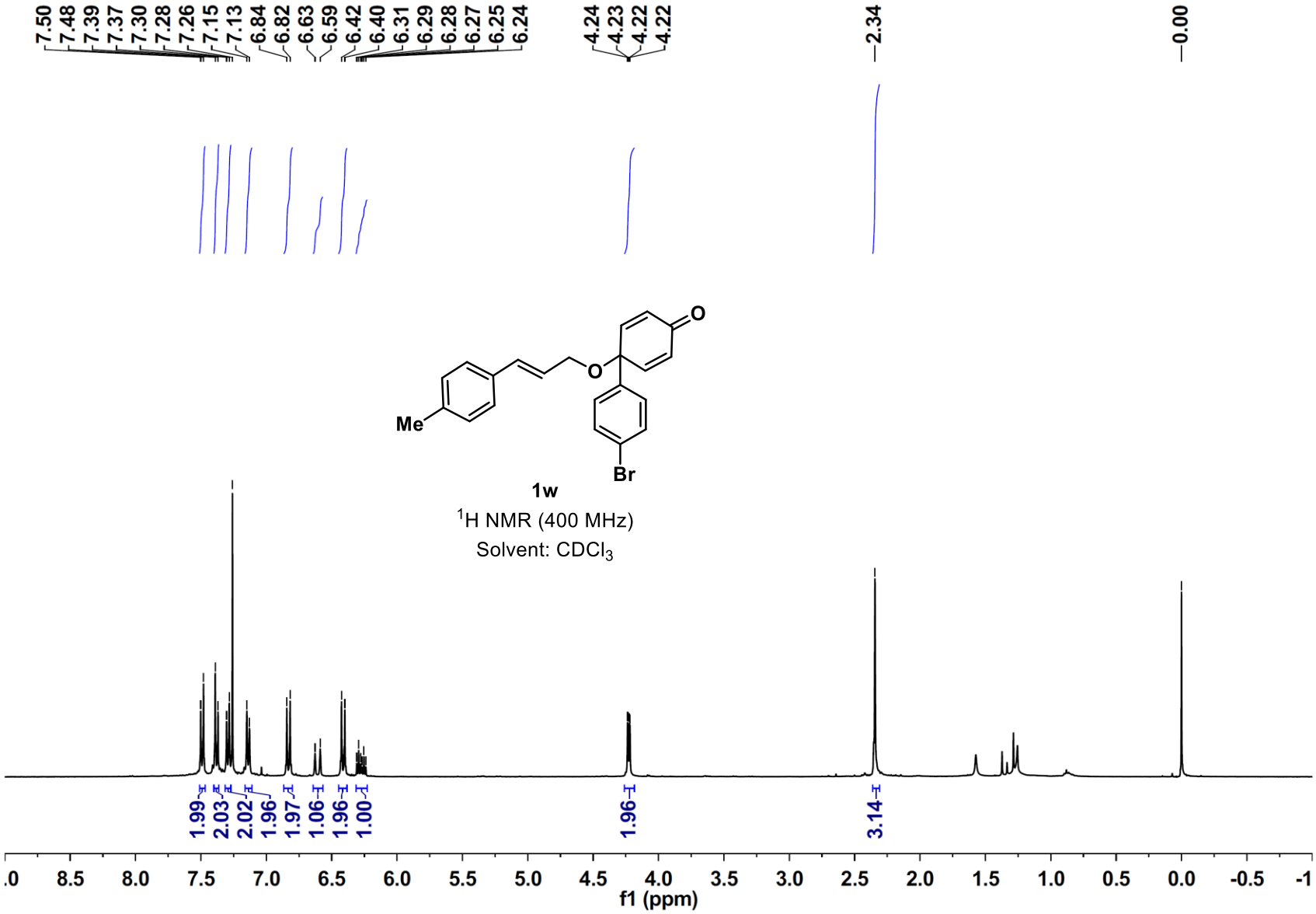
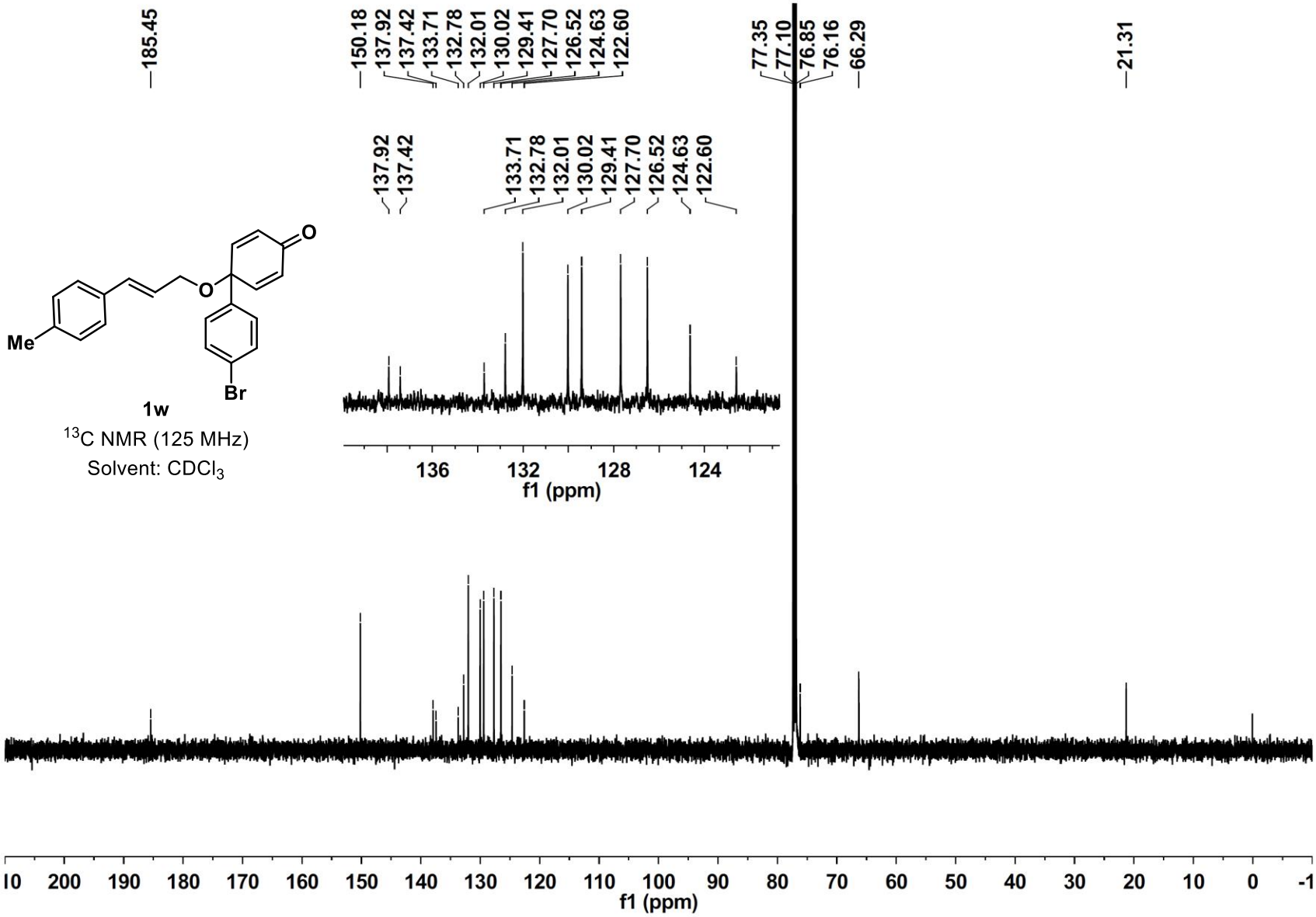
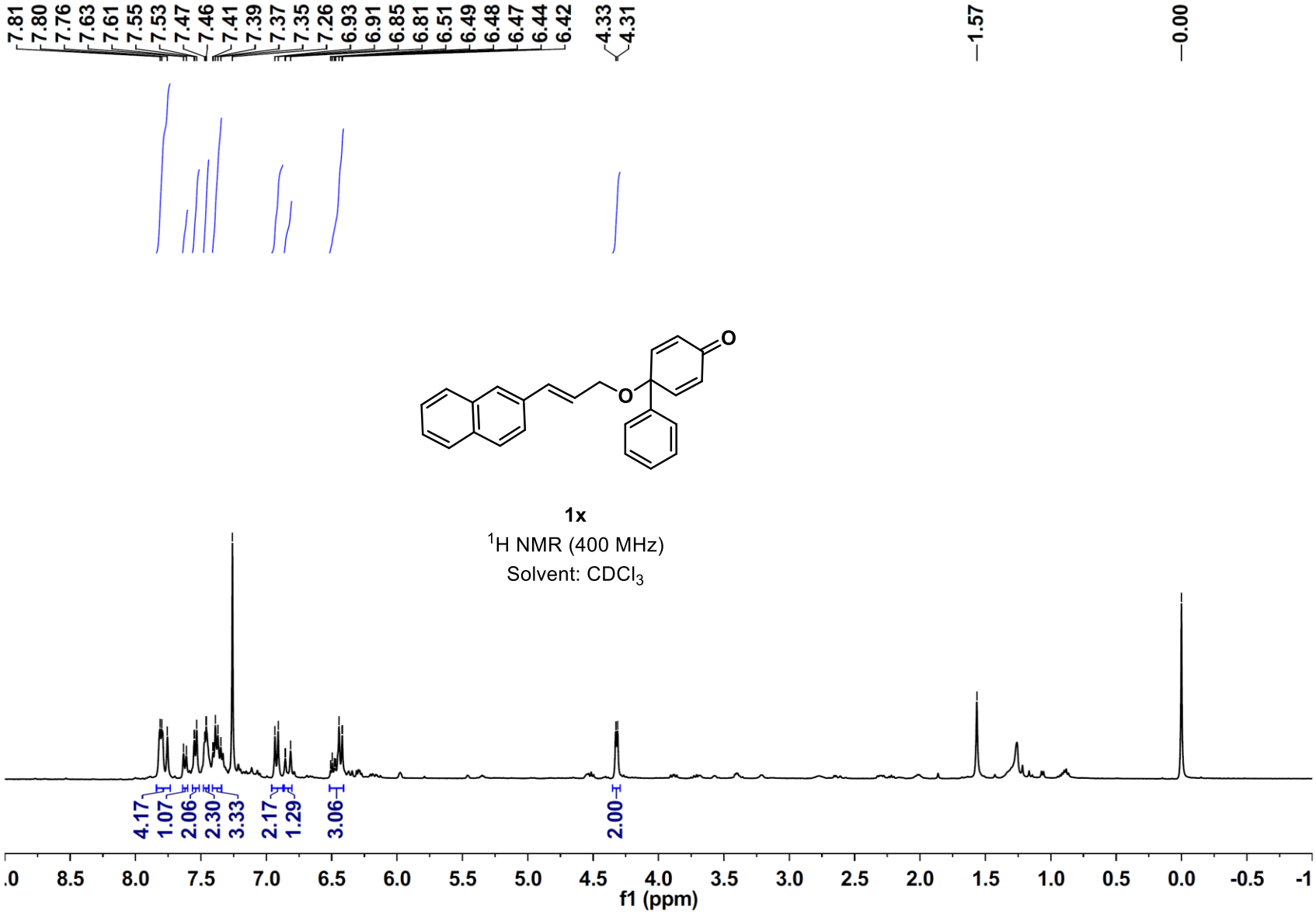
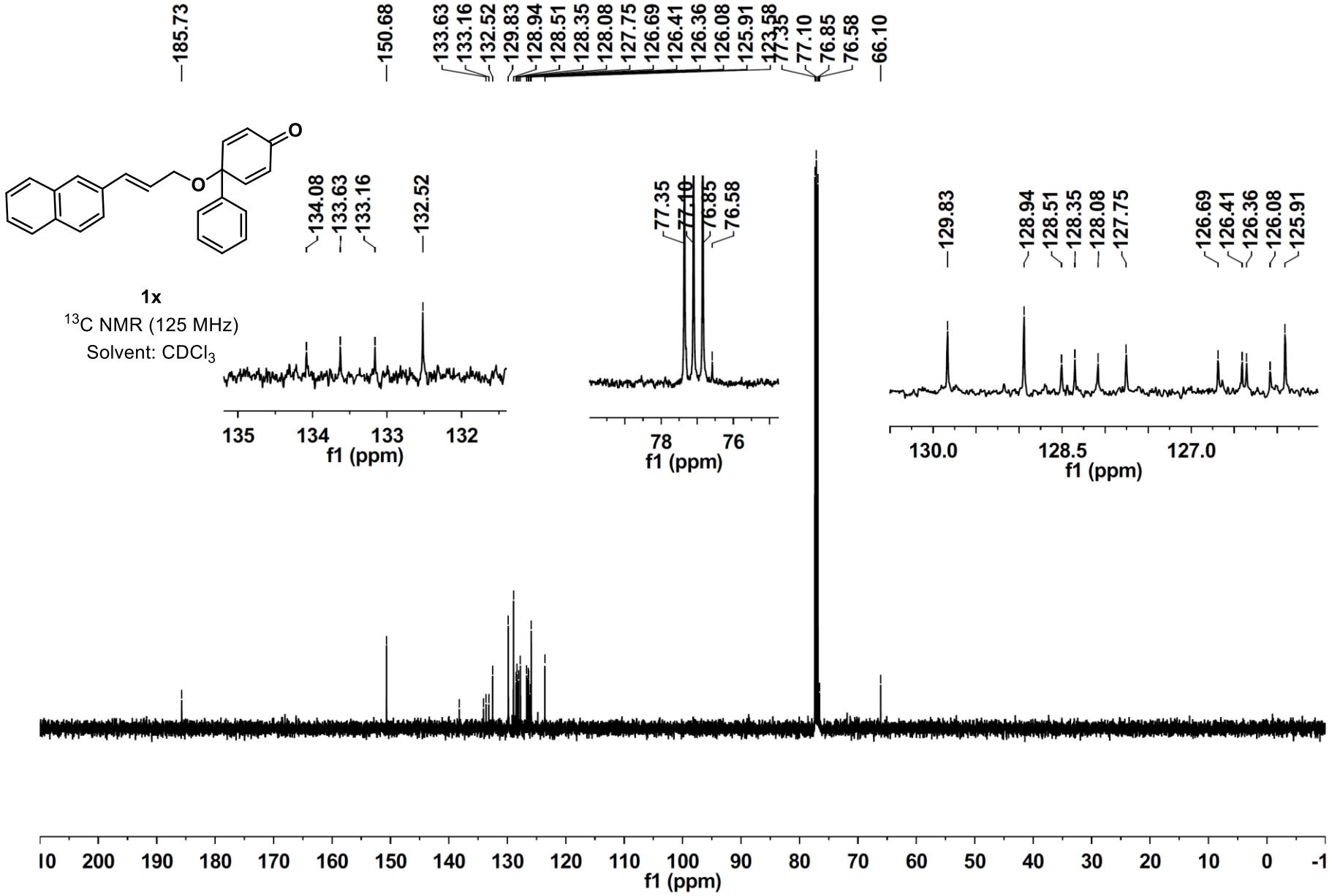
7.49
7.46
7.44
7.39
7.37
7.27
7.26
7.25
6.83
6.81
6.61
6.57
6.43
6.40
6.35
6.33
6.32
6.31
6.29
6.28
4.24
4.23
4.22
4.22
0.00
O
O
Br
Br
1v
1H NMR (400 MHz)
Solvent: CDCl3
1.93
1.95
1.96
2.91
1.95
1.00
1.95
1.02
1.99
f1 (ppm)

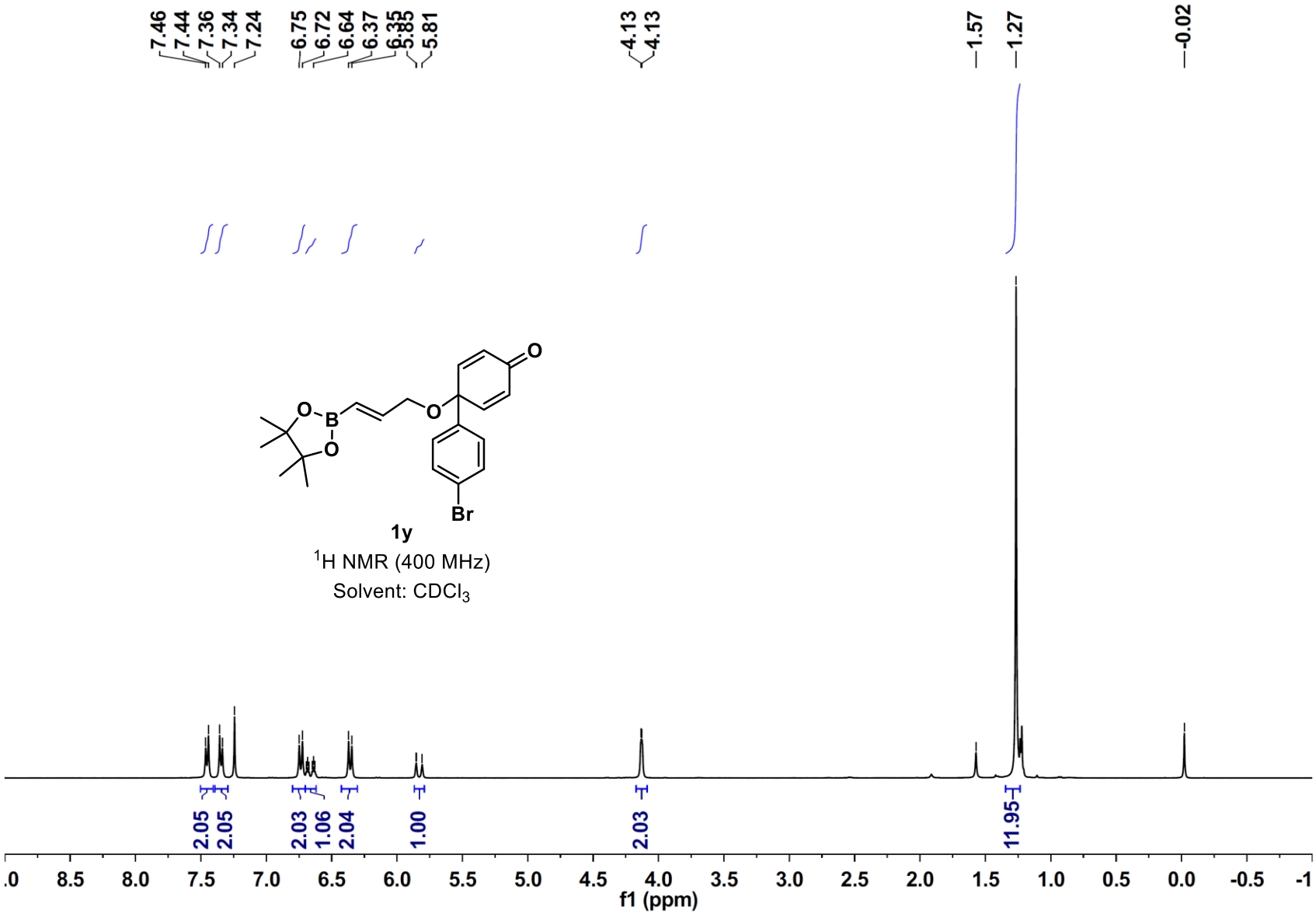

185.33
149.91
137.29
135.46
132.04
131.83
131.36
130.14
128.10
127.64
126.53
122.66
121.80
77.35
77.10
76.85
76.19
65.91
O
O
Br
Br
1v
13C NMR (125 MHz)
Solvent: CDCl3
132.04
131.83
131.36
130.14
128.10
127.64
126.53
132 131 130 129 128 127 126
f1 (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.50
7.48
7.39
7.37
7.30
7.28
7.26
7.15
7.13
6.84
6.82
6.63
6.59
6.42
6.40
6.31
6.29
6.28
6.27
6.25
6.24
4.24
4.23
4.22
4.22
2.34
0.00
O
O
Me
Br
1w
1H NMR (400 MHz)
Solvent: CDCl3
1.99
2.03
2.02
1.96
1.97
1.06
1.96
1.00
1.96
3.14
f1 (ppm)


185.45
150.18
137.92
137.42
133.71
132.78
132.01
130.02
129.41
127.70
126.52
124.63
122.60
77.35
77.10
76.85
76.16
66.29
21.31
Me
O
O
Br
1w
13C NMR (125 MHz)
Solvent: CDCl3
136
132
128
124
f1 (ppm)
f1 (ppm)


7.81
7.80
7.76
7.63
7.61
7.55
7.53
7.47
7.46
7.41
7.39
7.37
7.35
7.26
6.93
6.91
6.85
6.81
6.51
6.49
6.48
6.47
6.44
6.42
4.33
4.31
1.57
0.00
O
O
1x
1H NMR (400 MHz)
Solvent: CDCl3
4.17
1.07
2.06
2.30
3.33
2.17
1.29
3.06
2.00
f1 (ppm)

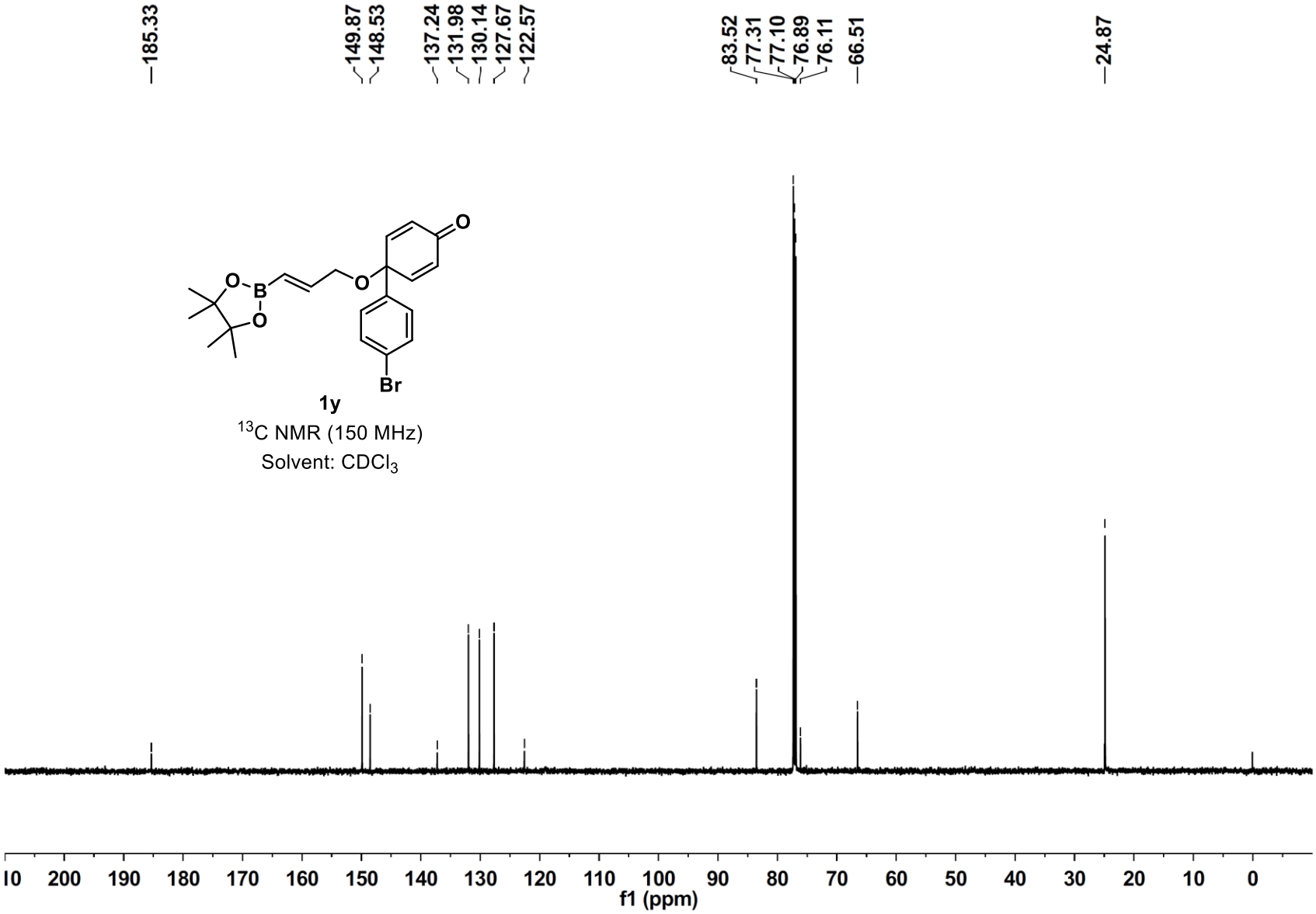

185.73
150.68
133.63
133.16
132.52
129.83
128.94
128.51
128.35
128.08
127.75
126.69
126.41
126.36
126.08
125.91
123.58
77.35
77.10
76.85
76.58
66.10
O
O
1x
13C NMR (125 MHz)
Solvent: CDCl3
134.08
133.63
133.16
132.52
135
134
133
132
f1 (ppm)
77.35
77.10
76.85
76.58
78
76
f1 (ppm)
129.83
128.94
128.51
128.35
128.08
127.75
126.69
126.41
126.36
126.08
125.91
130.0
128.5
127.0
f1 (ppm)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

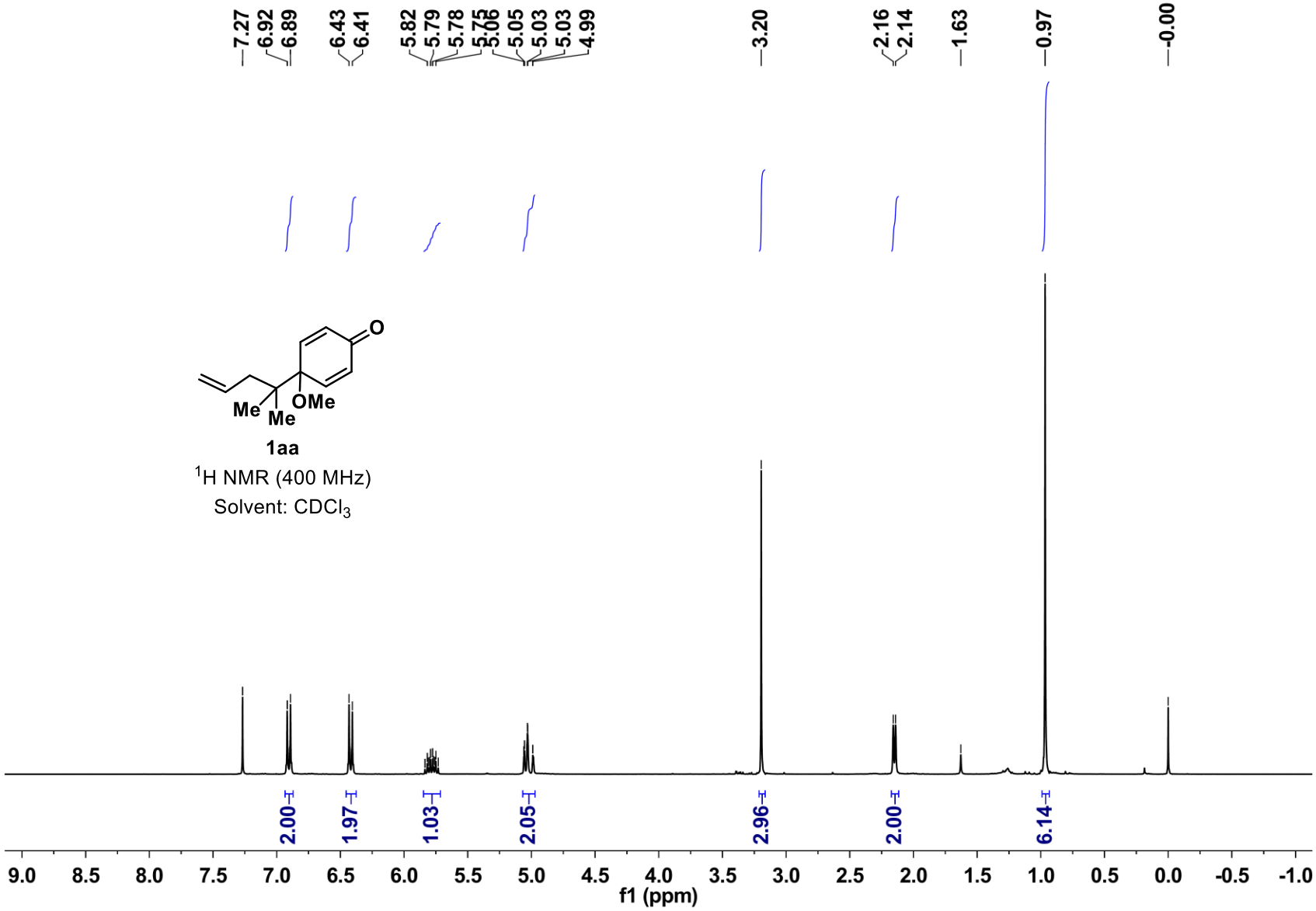


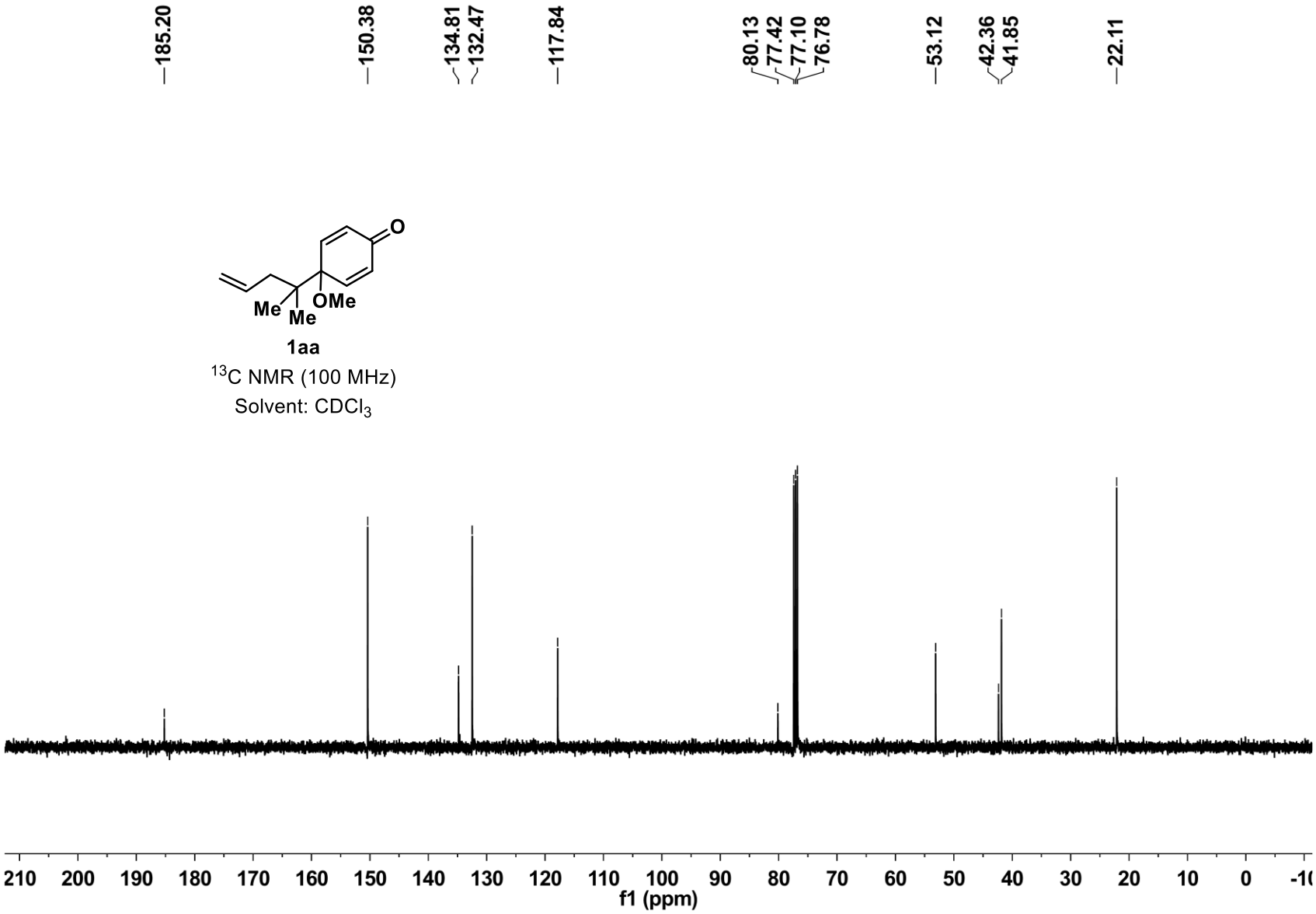
1y

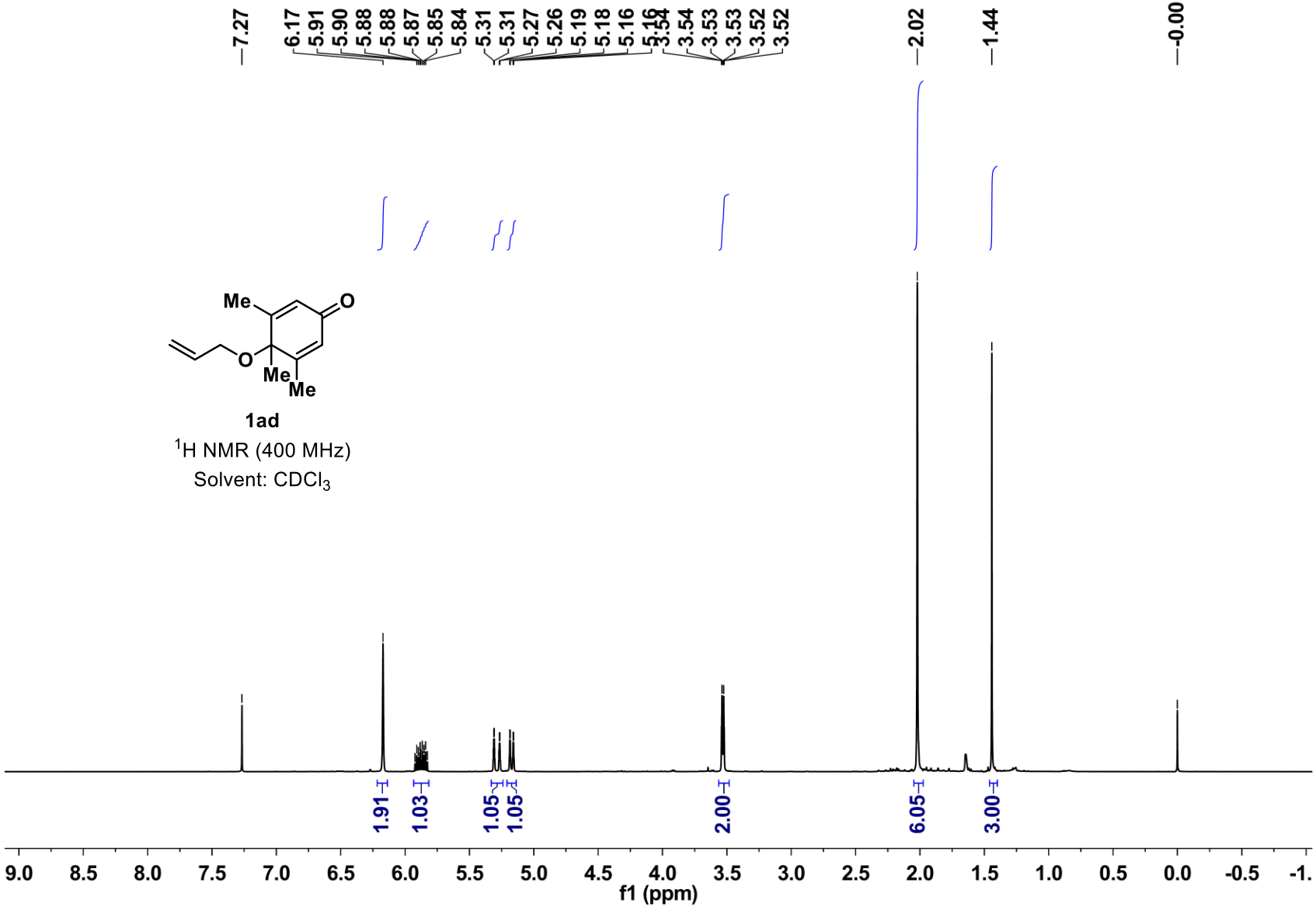
^{1}H NMR (400 MHz)

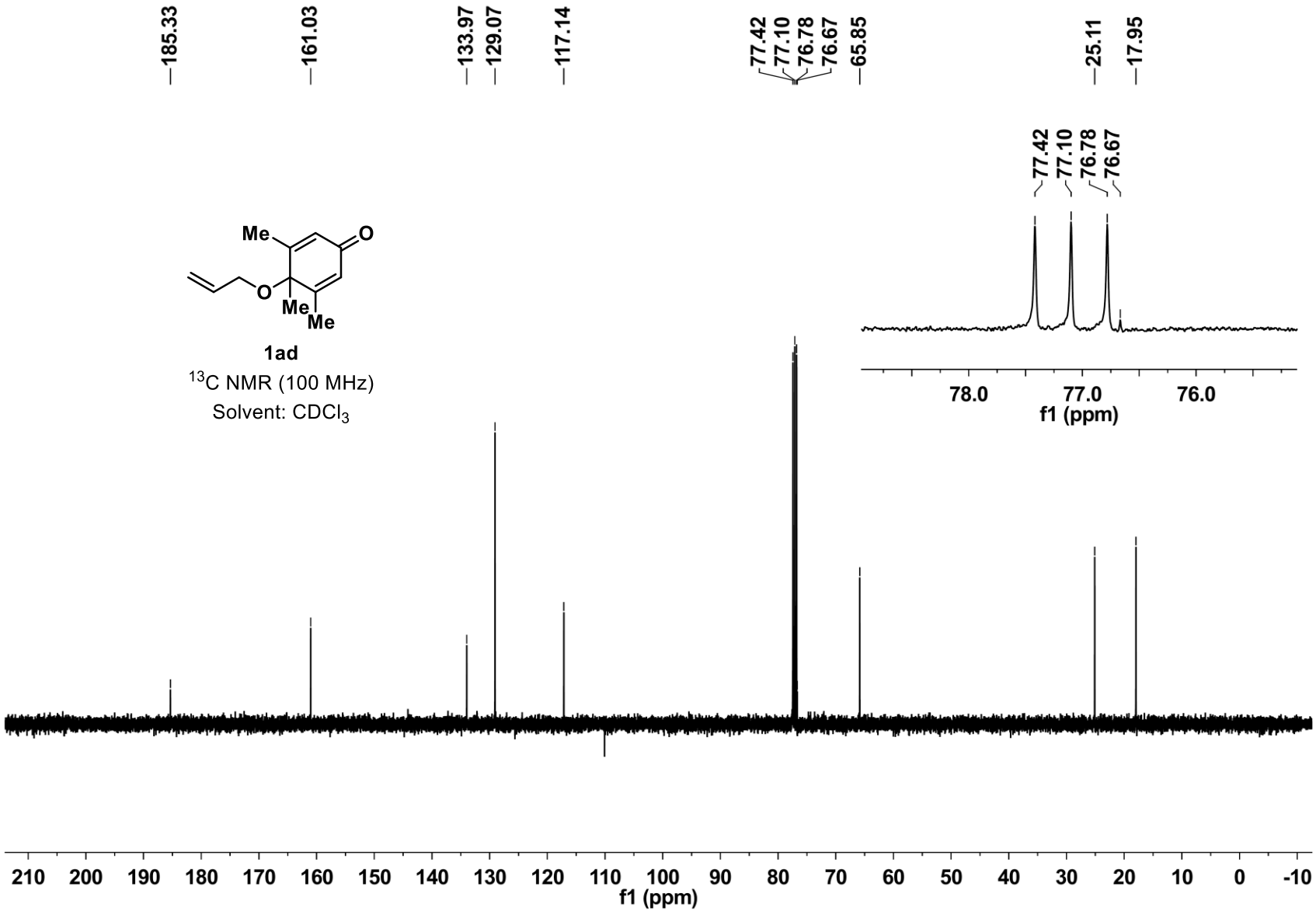
Solvent: $CDCl_3$

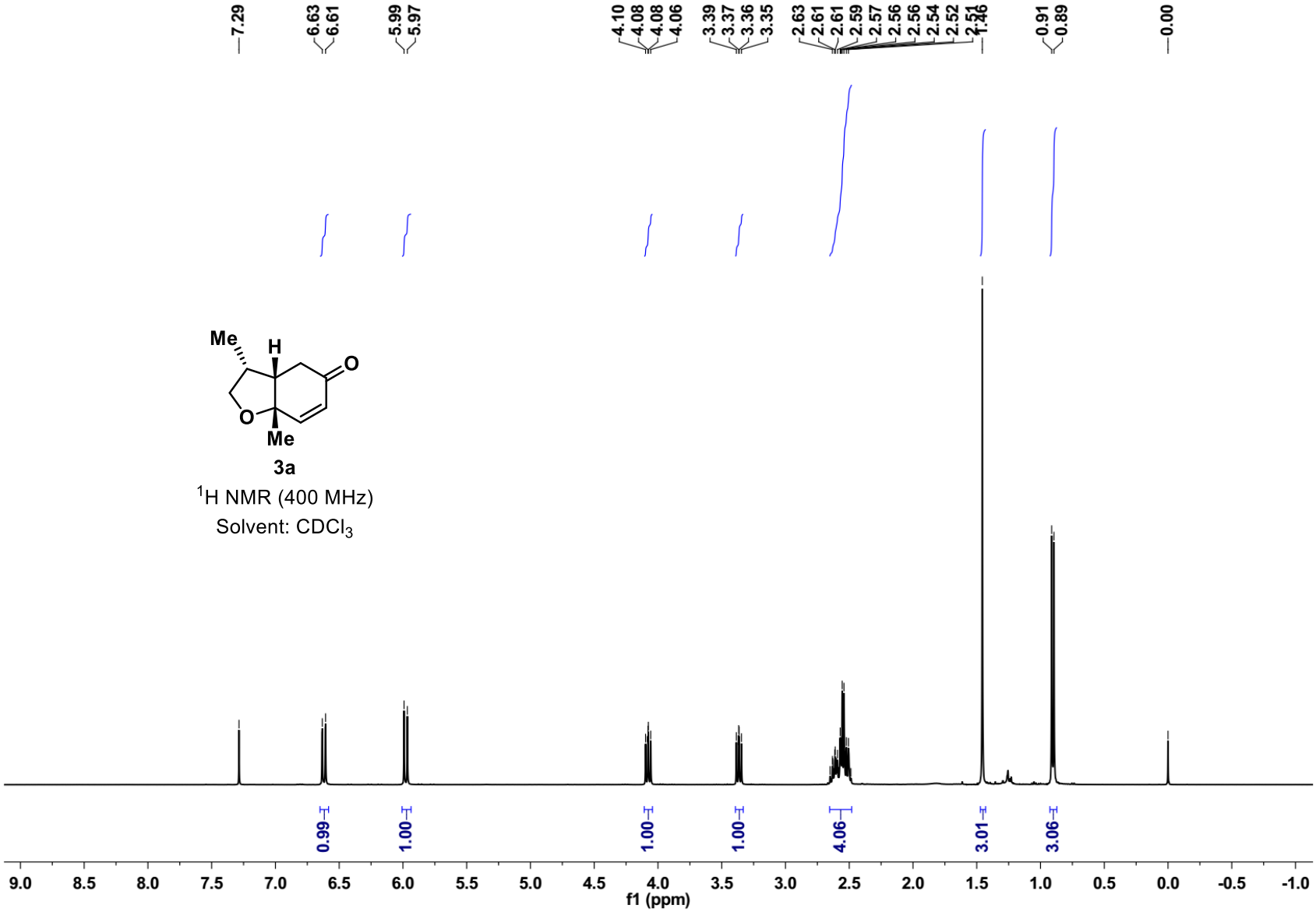

185.33
149.87
148.53
137.24
131.98
130.14
127.67
122.57
83.52
77.31
77.10
76.89
76.11
66.51
24.87
O
O
B
O
O
Br
1y
13C NMR (150 MHz)
Solvent: CDCl3
f1 (ppm)

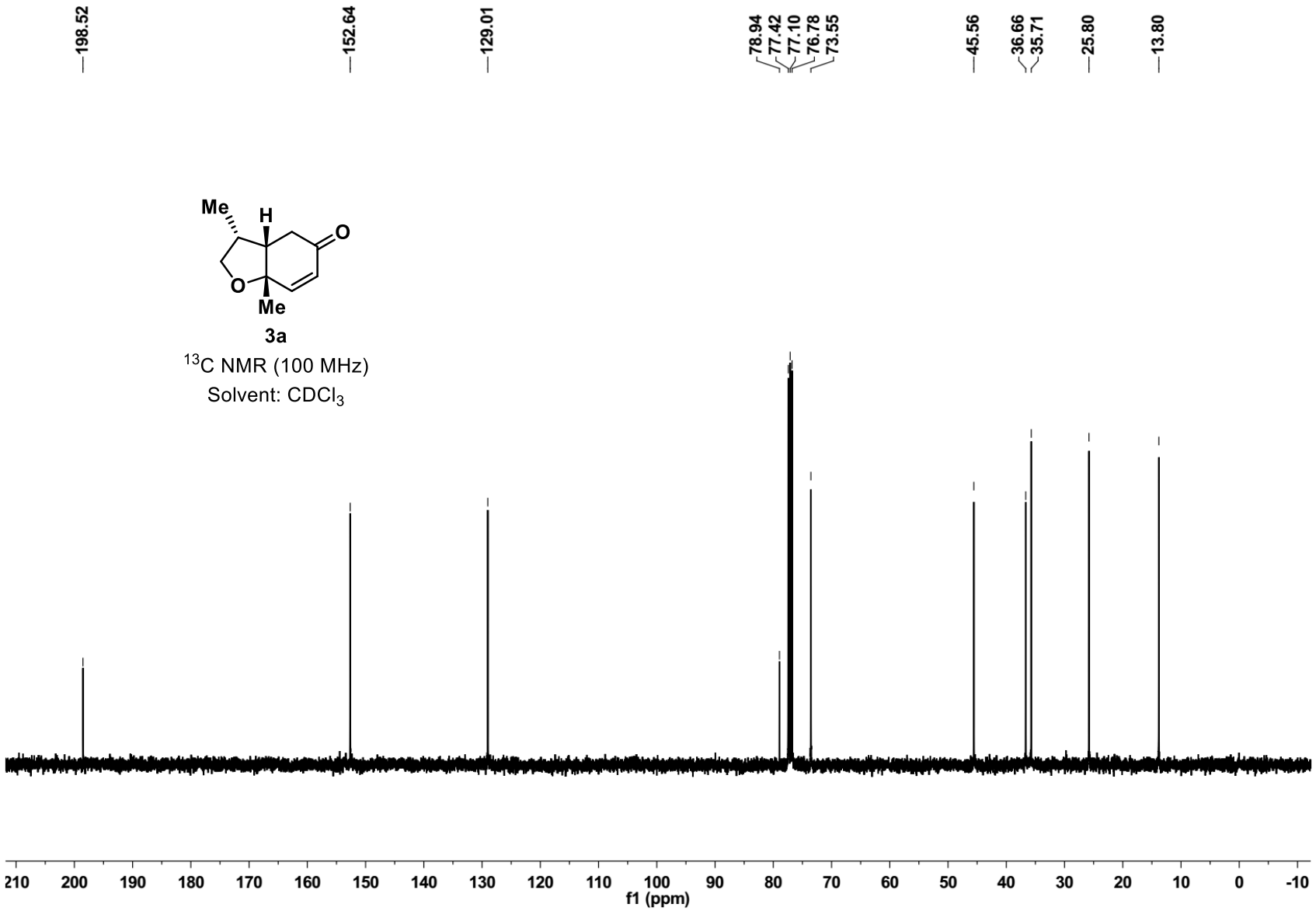

7.27
6.92
6.89
6.43
6.41
5.82
5.79
5.78
5.75
5.06
5.05
5.03
5.03
4.99
3.20
2.16
2.14
1.63
0.97
0.00
O
Me
Me
OMe
1aa
1H NMR (400 MHz)
Solvent: CDCl3
2.00
1.97
1.03
2.05
2.96
2.00
6.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

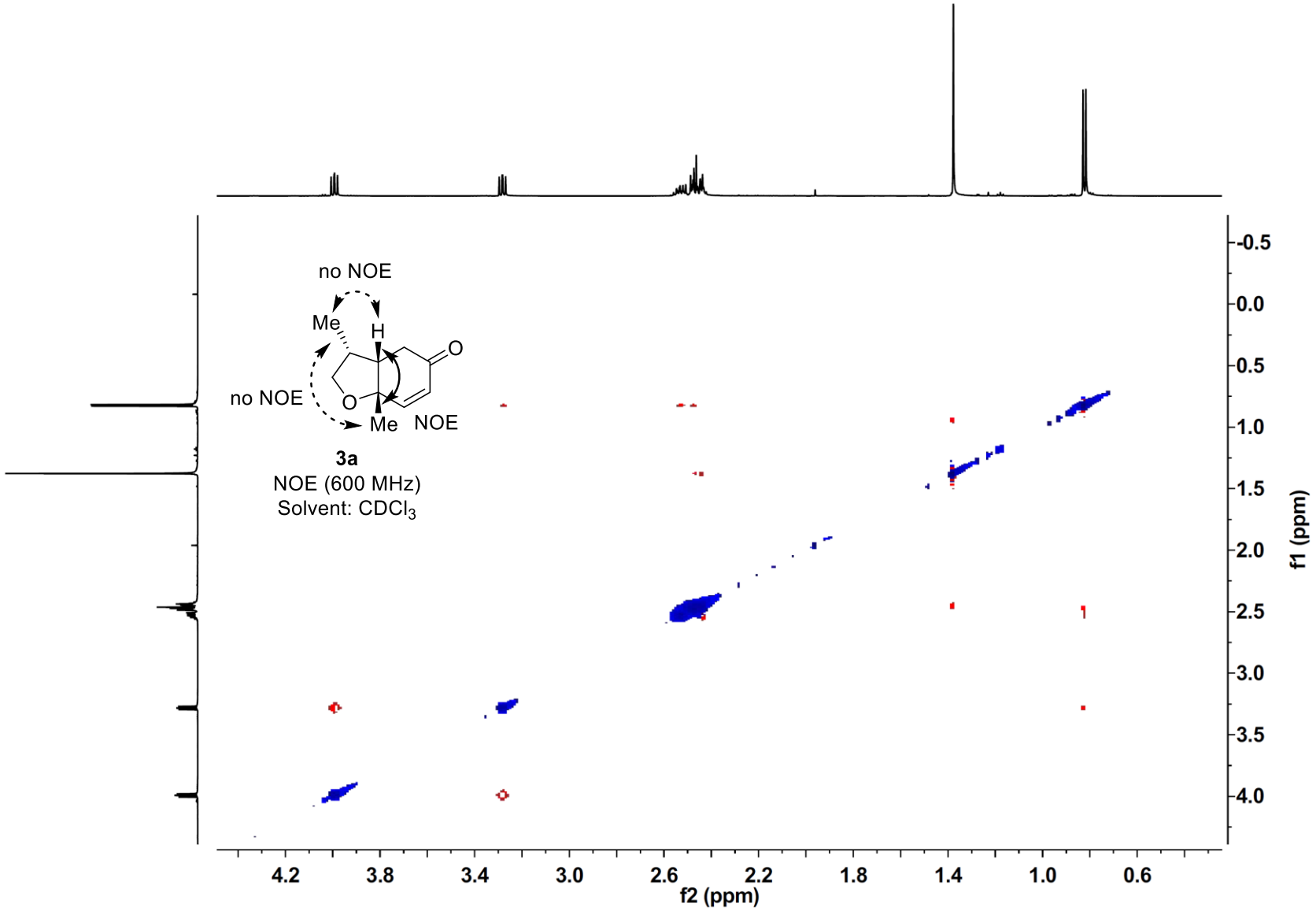

185.20
150.38
134.81
132.47
117.84
80.13
77.42
77.10
76.78
53.12
42.36
41.85
22.11
O
Me
Me
OMe
1aa
13C NMR (100 MHz)
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1(
f1 (ppm)

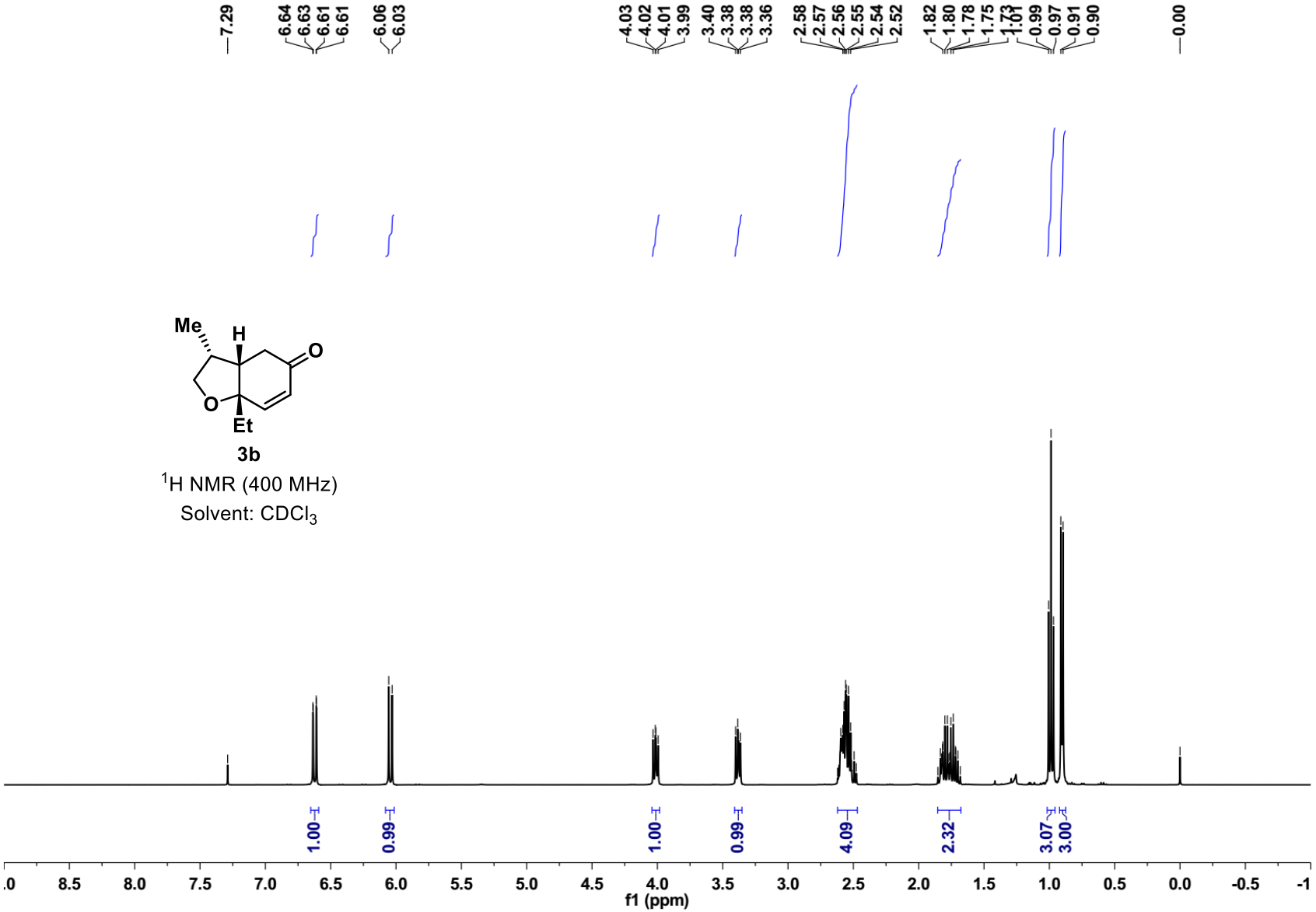

7.27
6.17
5.91
5.90
5.88
5.88
5.87
5.85
5.84
5.31
5.31
5.27
5.26
5.19
5.18
5.16
5.16
3.54
3.54
3.53
3.53
3.52
3.52
2.02
1.44
0.00
Me
O
O
Me
Me
1ad
1H NMR (400 MHz)
Solvent: CDCl3
1.91
1.03
1.05
1.05
2.00
6.05
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

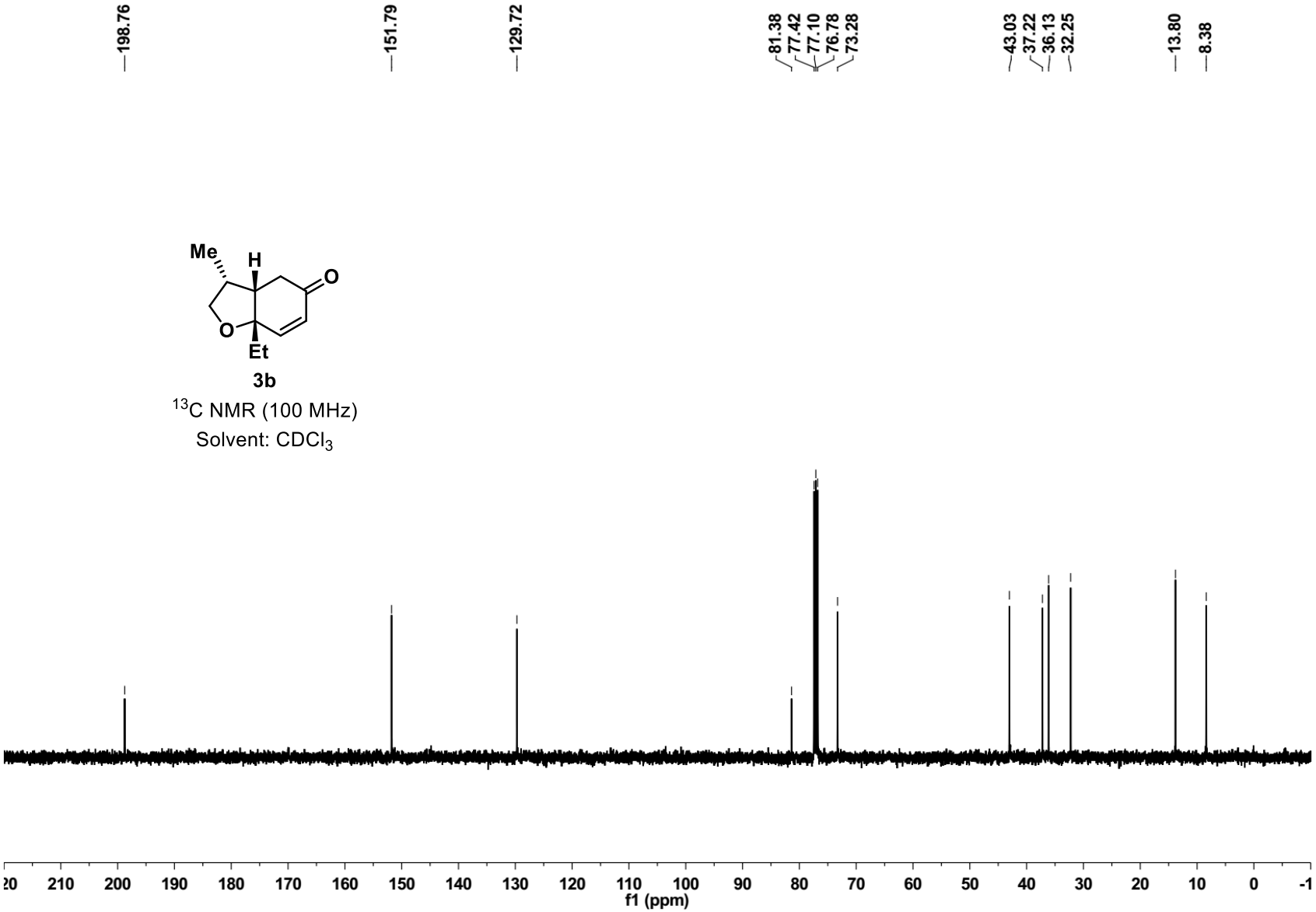

185.33
161.03
133.97
129.07
117.14
77.42
77.10
76.78
76.67
65.85
25.11
17.95
Me
O
O
Me
Me
1ad
13C NMR (100 MHz)
Solvent: CDCl3
78.0
77.0
76.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.29
6.63
6.61
5.99
5.97
4.10
4.08
4.08
4.06
3.39
3.37
3.36
3.35
2.63
2.61
2.61
2.59
2.57
2.56
2.56
2.54
2.52
2.51
1.46
0.91
0.89
0.00
Me
H
O
O
Me
3a
1H NMR (400 MHz)
Solvent: CDCl3
0.99
1.00
1.00
1.00
4.06
3.01
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


198.52
152.64
129.01
78.94
77.42
77.10
76.78
73.55
45.56
36.66
35.71
25.80
13.80
Me
H
O
O
Me
3a
13C NMR (100 MHz)
Solvent: 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)


no NOE
Me
H
O
no NOE
O
Me
NOE
3a
NOE (600 MHz)
Solvent: CDCl3
f2 (ppm)
f1 (ppm)
4.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

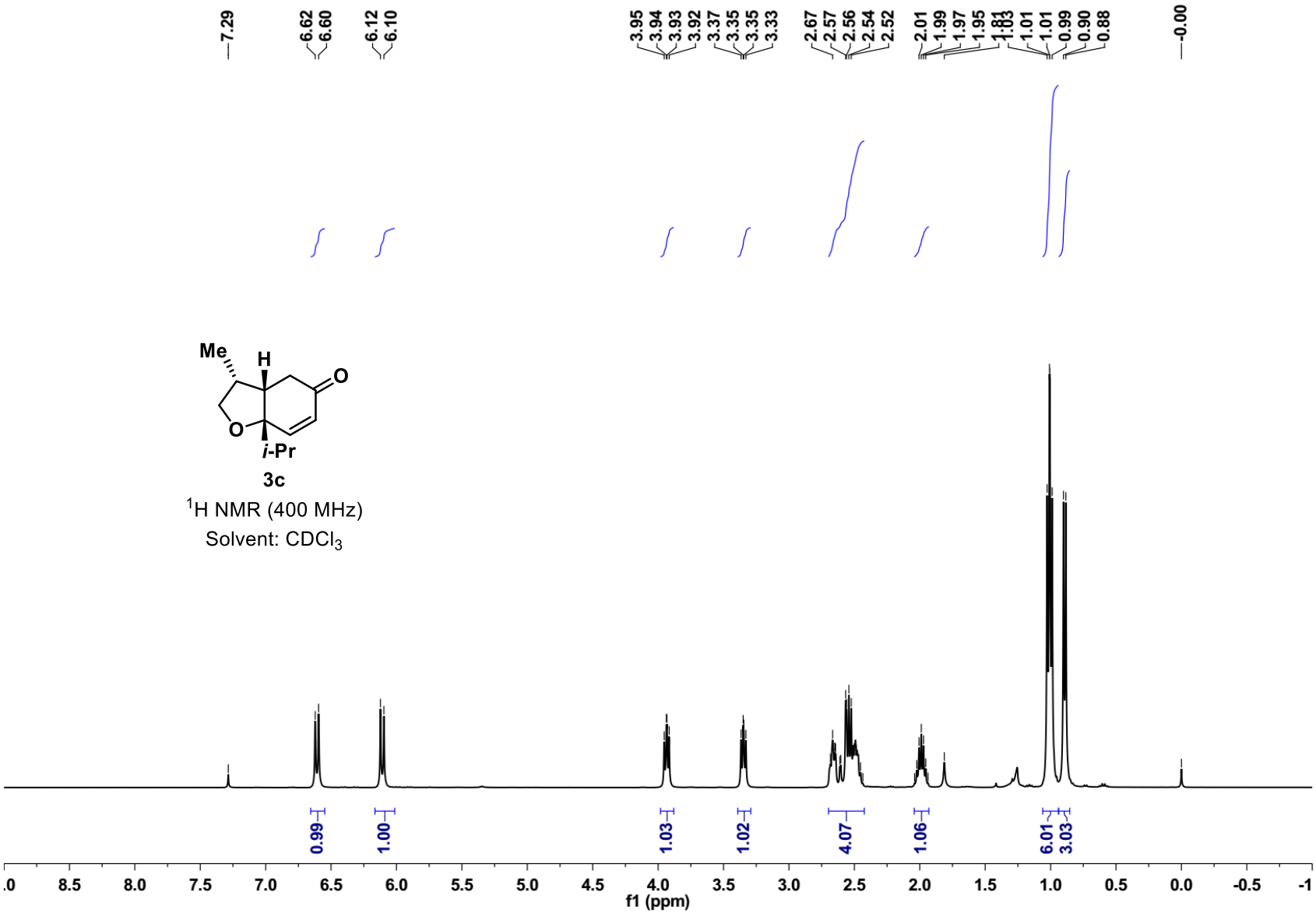

7.29
6.64
6.63
6.61
6.61
6.06
6.03
4.03
4.02
4.01
3.99
3.40
3.38
3.38
3.36
2.58
2.57
2.56
2.55
2.54
2.52
1.82
1.80
1.78
1.75
1.73
1.01
0.99
0.97
0.91
0.90
0.00
Me
H
O
O
Et
3b
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.99
1.00
0.99
4.09
2.32
3.07
3.00
f1 (ppm)

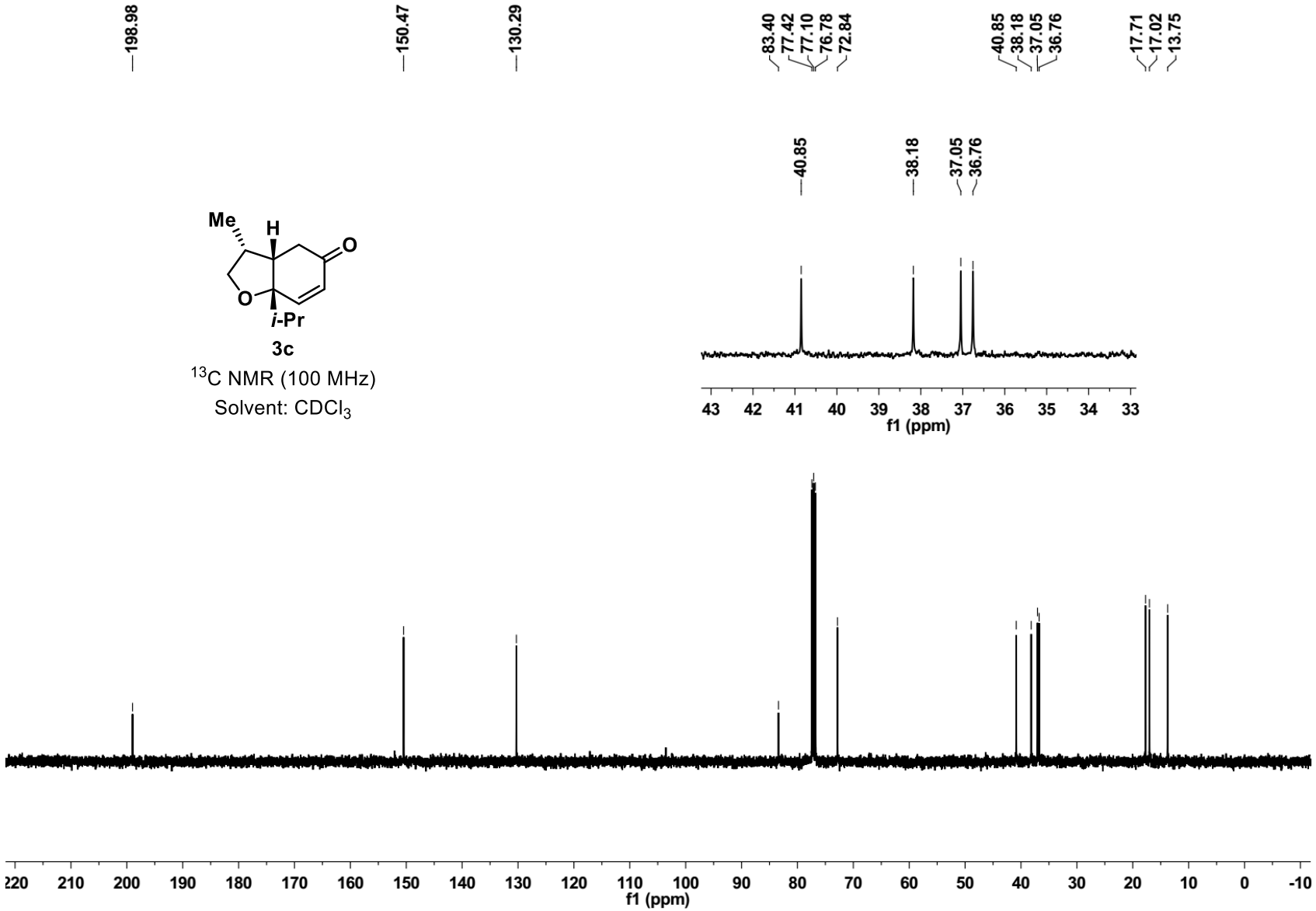


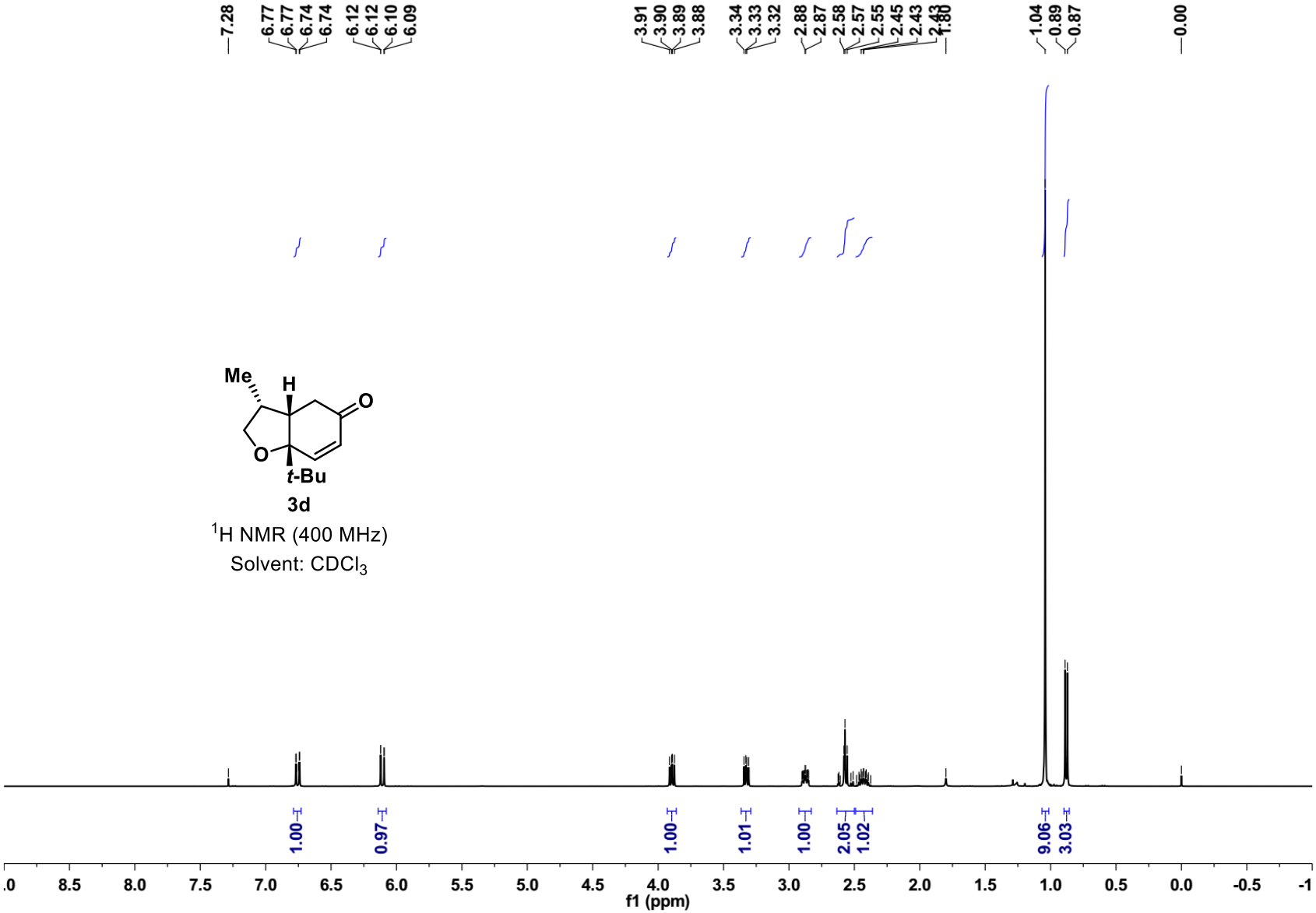
3b

^{13}C NMR (100 MHz)

Solvent: $CDCl_3$


7.29
6.62
6.60
6.12
6.10
3.95
3.94
3.93
3.92
3.37
3.35
3.35
3.33
2.67
2.57
2.56
2.54
2.52
2.01
1.99
1.97
1.95
1.83
1.81
1.03
1.01
1.01
0.99
0.90
0.88
-0.00
Me
H
O
O
i-Pr
3c
1H NMR (400 MHz)
Solvent: CDCl3
0.99
1.00
1.03
1.02
4.07
1.06
6.01
3.03
f1 (ppm)

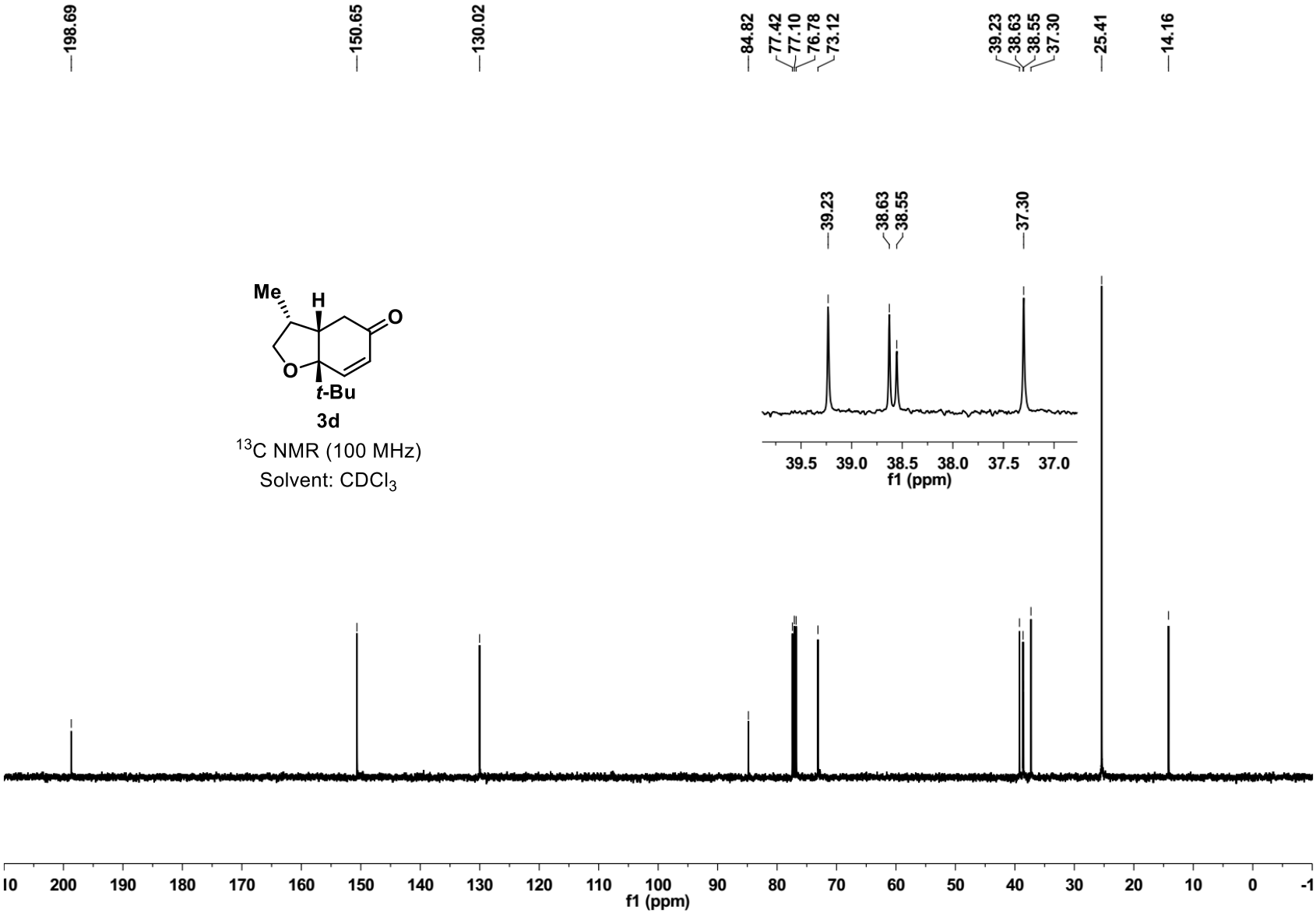

198.98
150.47
130.29
83.40
77.42
77.10
76.78
72.84
40.85
38.18
37.05
36.76
17.71
17.02
13.75
Me
H
O
O
i-Pr
3c
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

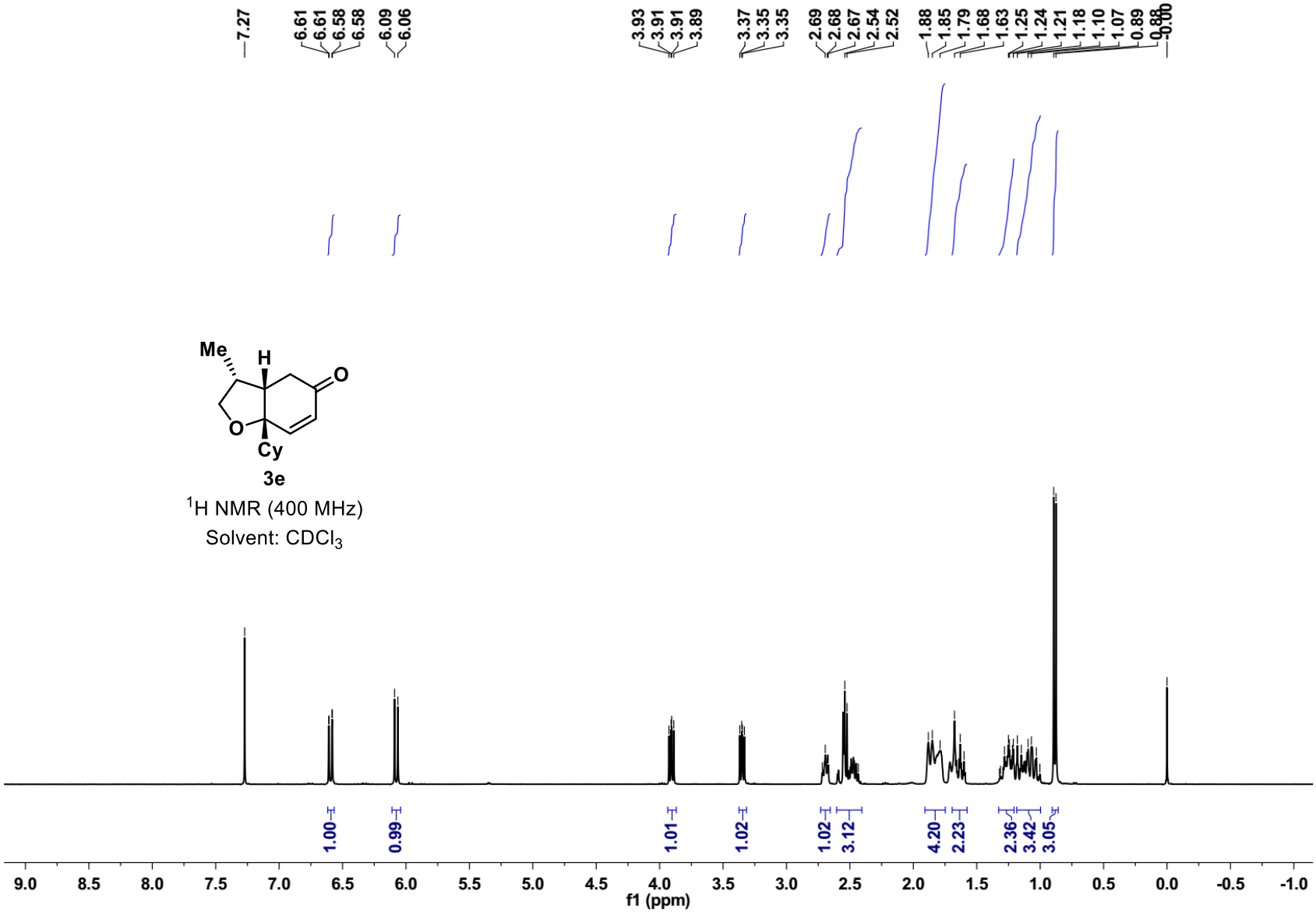


3d

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$


198.69
150.65
130.02
84.82
77.42
77.10
76.78
73.12
39.23
38.63
38.55
37.30
25.41
14.16
Me
H
O
O
t-Bu
3d
13C NMR (100 MHz)
Solvent: CDCl3
39.5 39.0 38.5 38.0 37.5 37.0
f1 (ppm)
f1 (ppm)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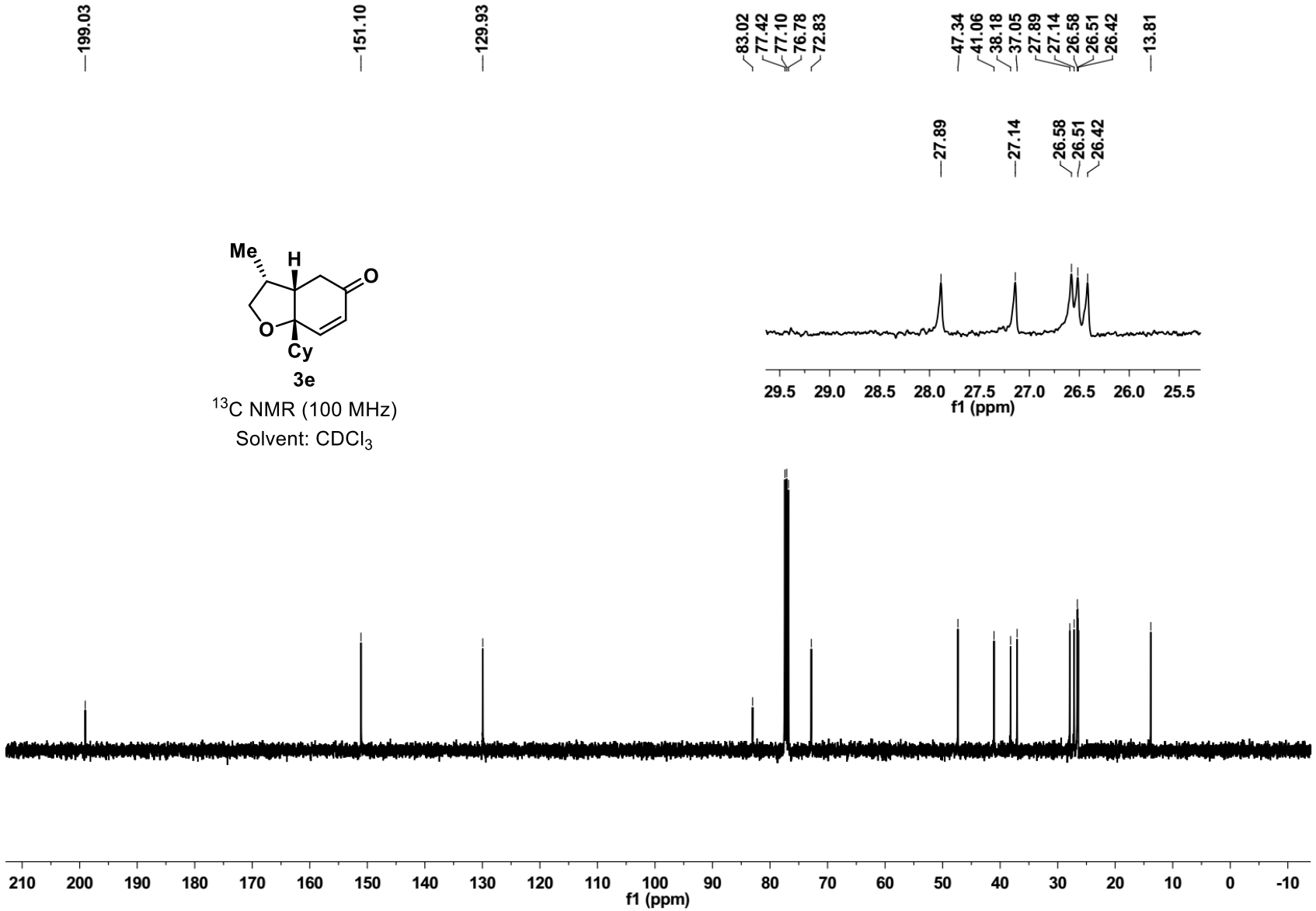
6.61
6.61
6.58
6.58
6.09
6.06
3.93
3.91
3.91
3.89
3.37
3.35
3.35
2.69
2.68
2.67
2.54
2.52
1.88
1.85
1.79
1.68
1.63
1.25
1.24
1.21
1.18
1.10
1.07
0.89
0.88
0.00
Me
H
O
O
Cy
3e
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.99
1.01
1.02
1.02
3.12
4.20
2.23
2.36
3.42
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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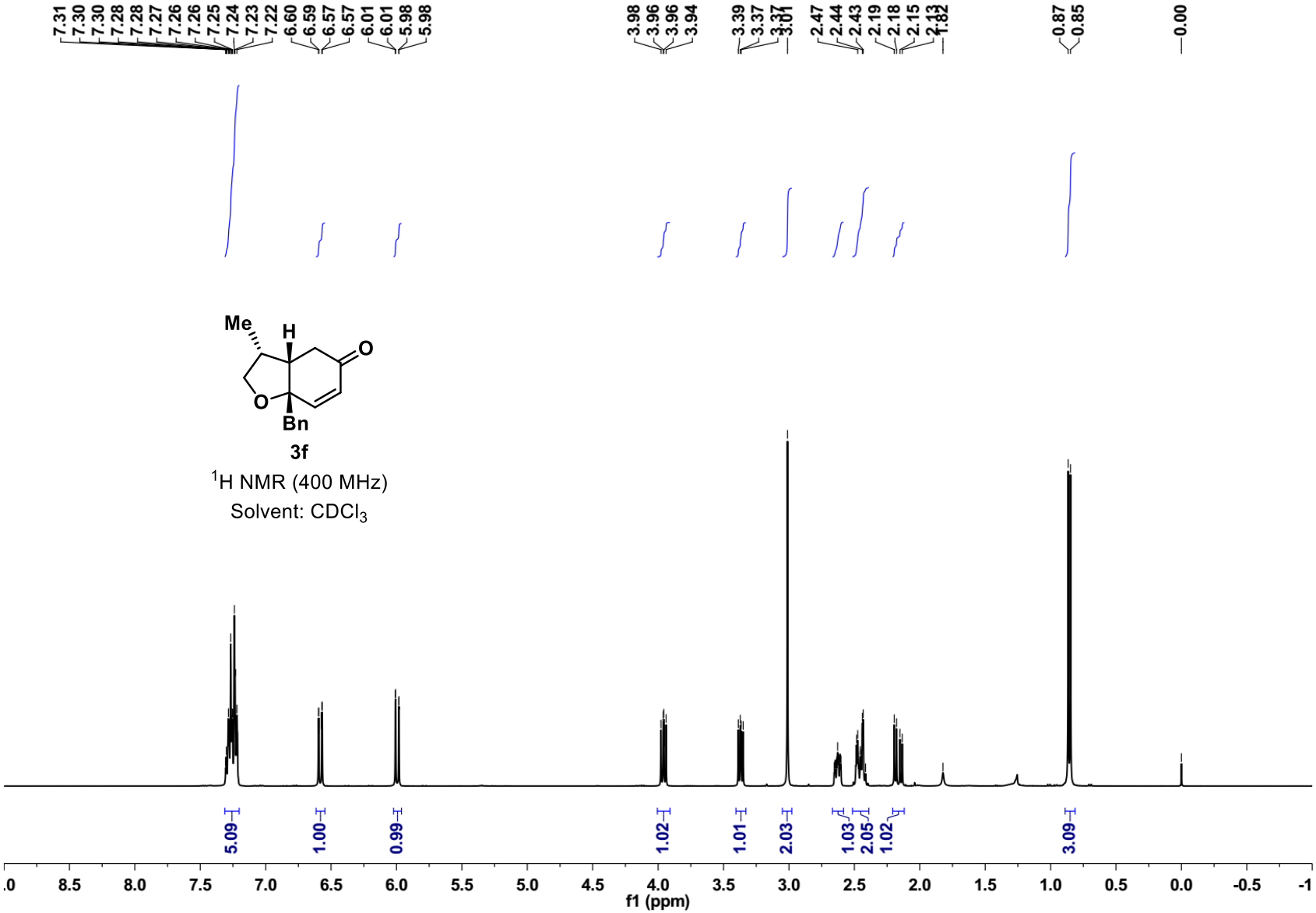
77.10
76.78
72.83
47.34
41.06
38.18
37.05
27.89
27.14
26.58
26.51
26.42
13.81
Me
H
O
O
Cy
3e
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)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7.30
7.30
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7.28
7.27
7.26
7.26
7.25
7.24
7.23
7.22
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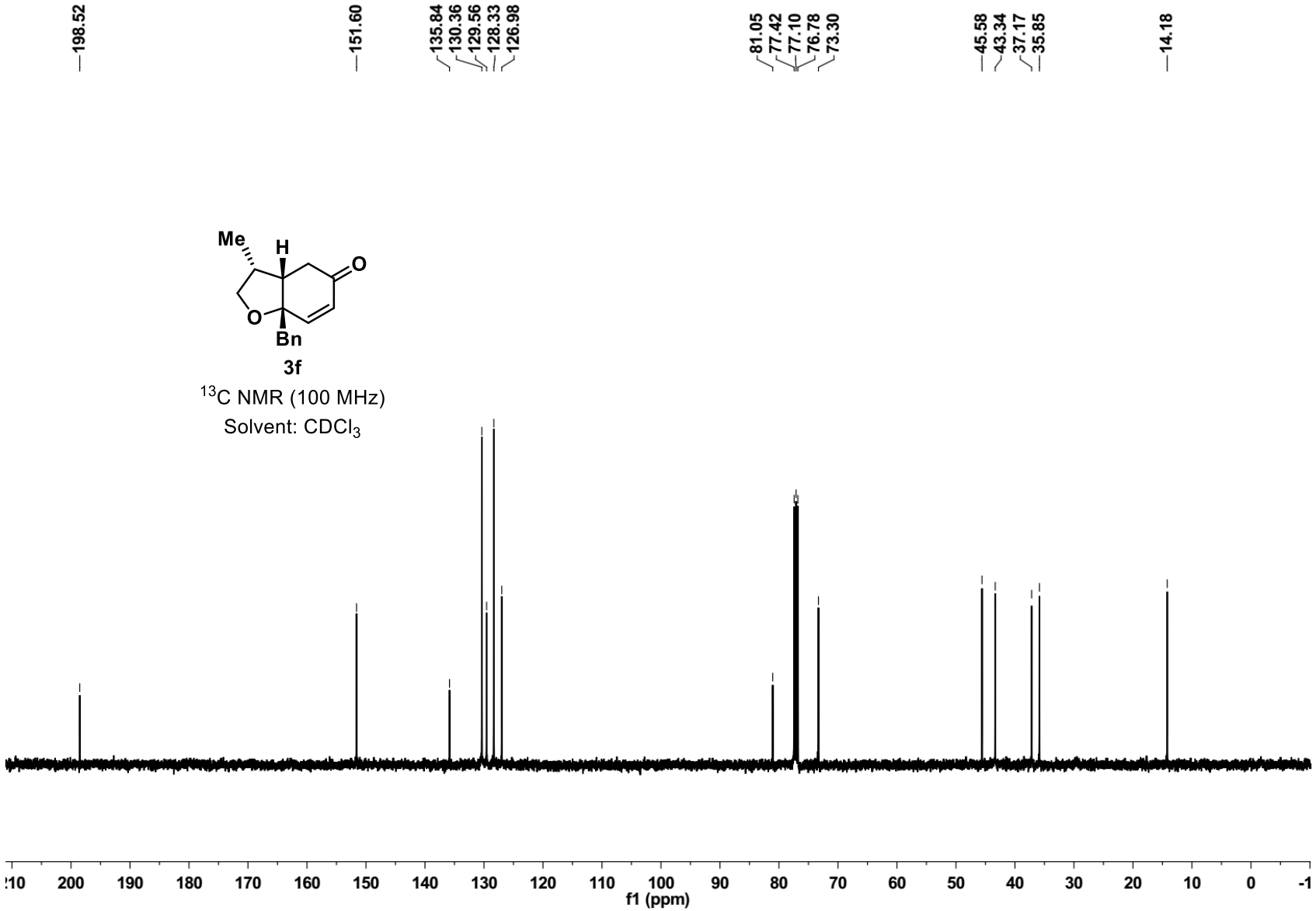
6.59
6.57
6.57
6.01
6.01
5.98
5.98
3.98
3.96
3.96
3.94
3.39
3.37
3.37
3.01
2.47
2.44
2.43
2.19
2.18
2.15
2.13
1.82
0.87
0.85
0.00
Me
H
O
O
Bn
3f
1H NMR (400 MHz)
Solvent: CDCl3
5.09
1.00
0.99
1.02
1.01
2.03
1.03
2.05
1.02
3.09
f1 (ppm)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151.60
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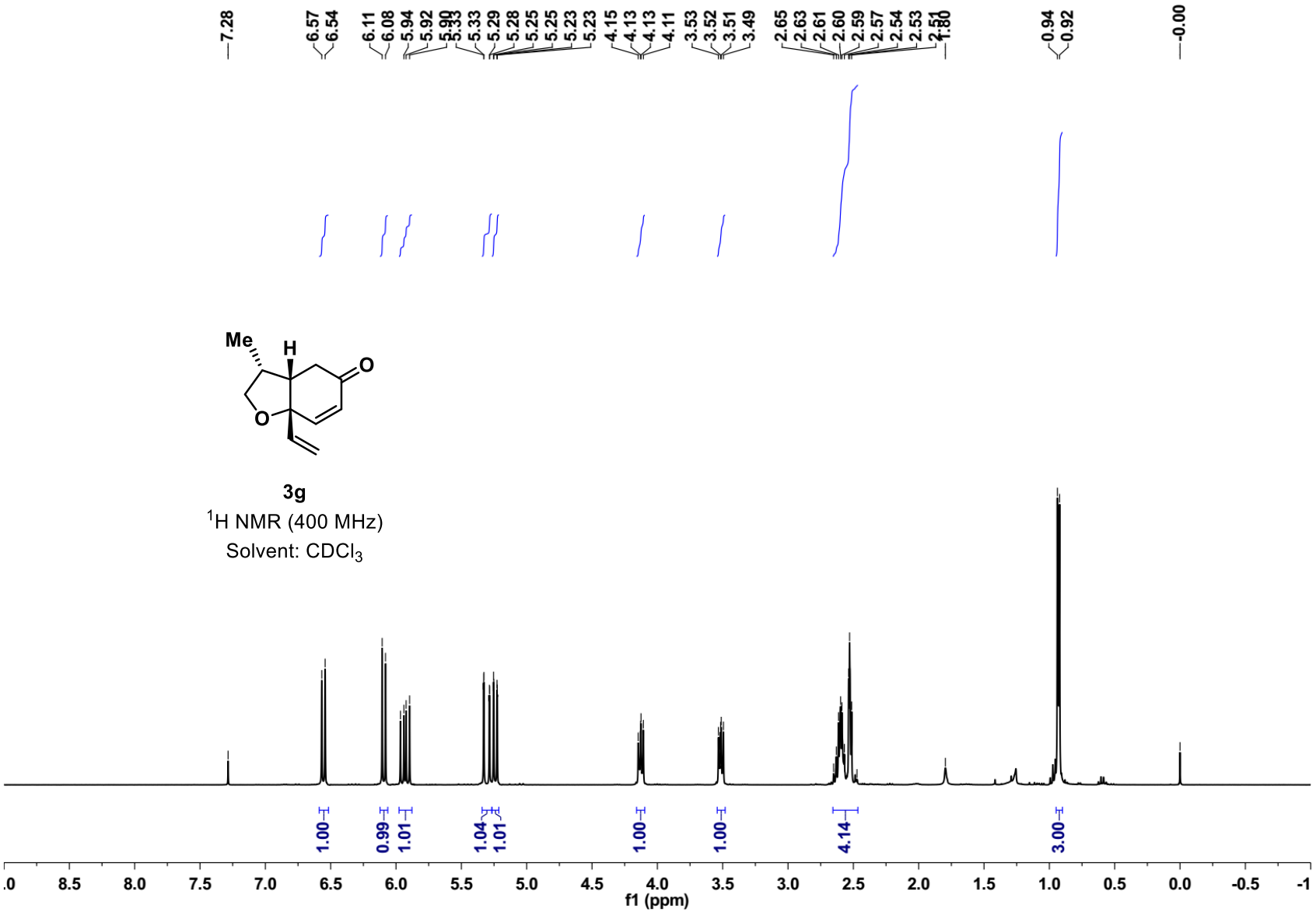
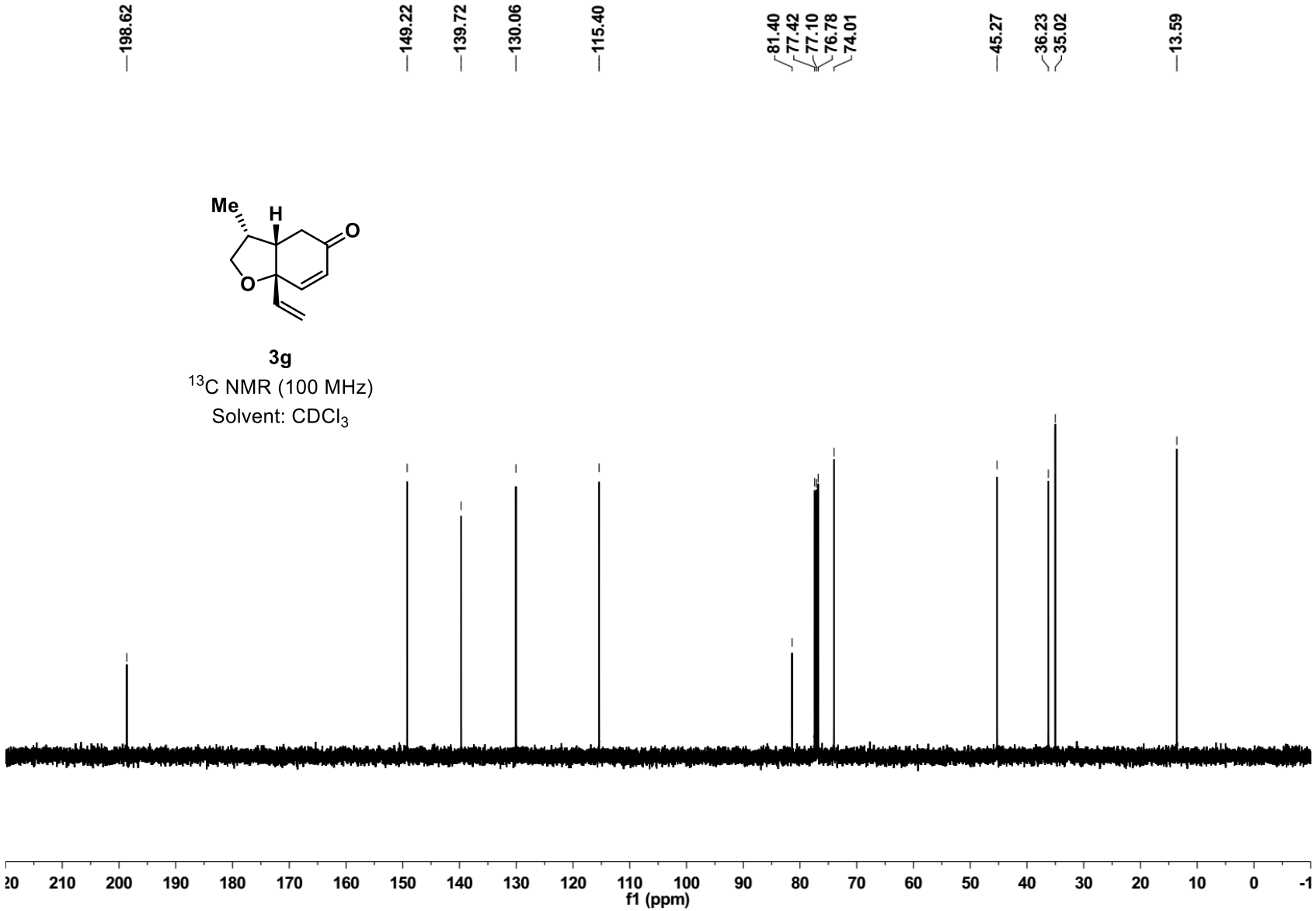
129.56
128.33
126.98
81.05
77.42
77.10
76.78
73.30
45.58
43.34
37.17
35.85
14.18
Me
H
O
O
Bn
3f
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)



3g

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$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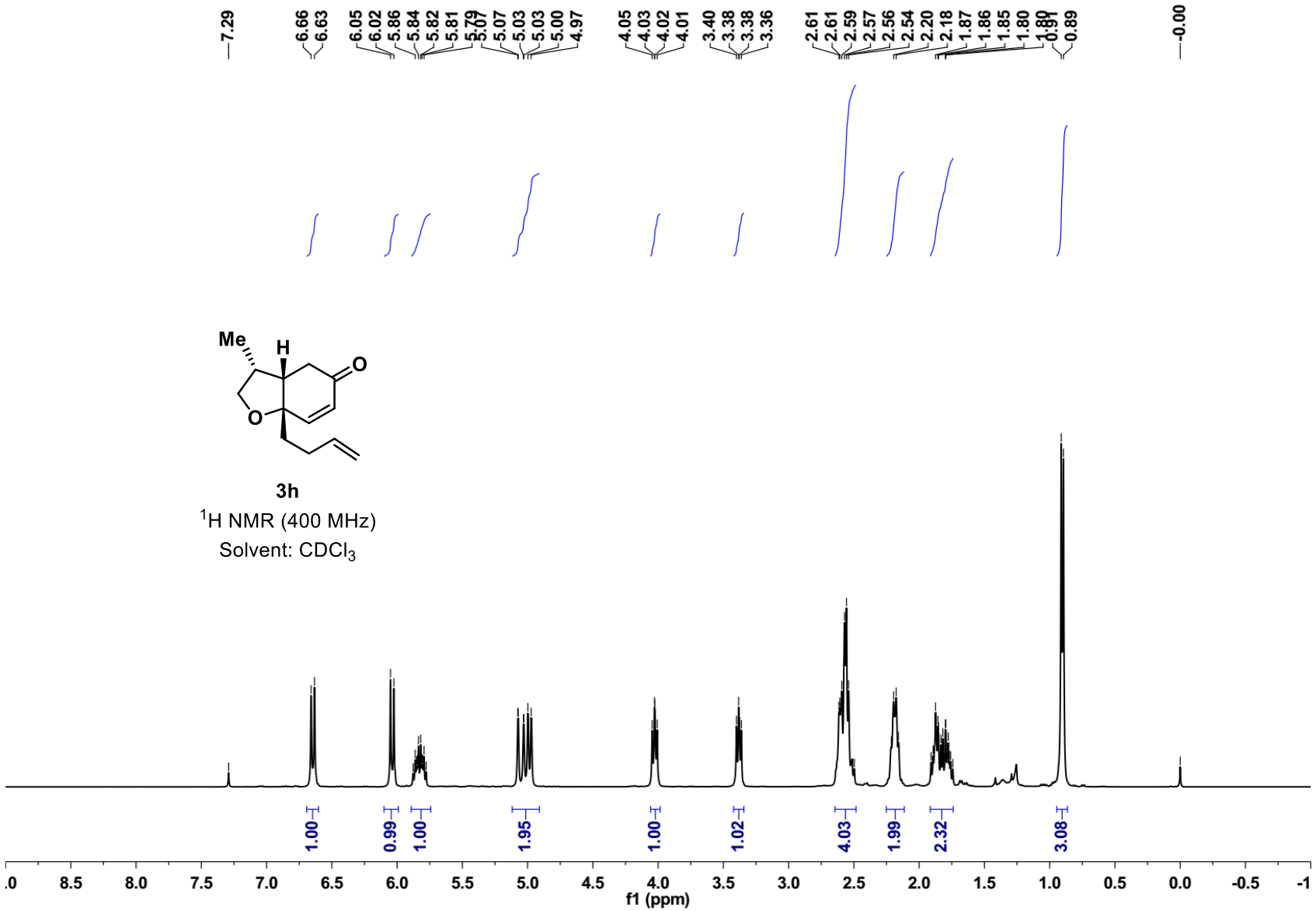
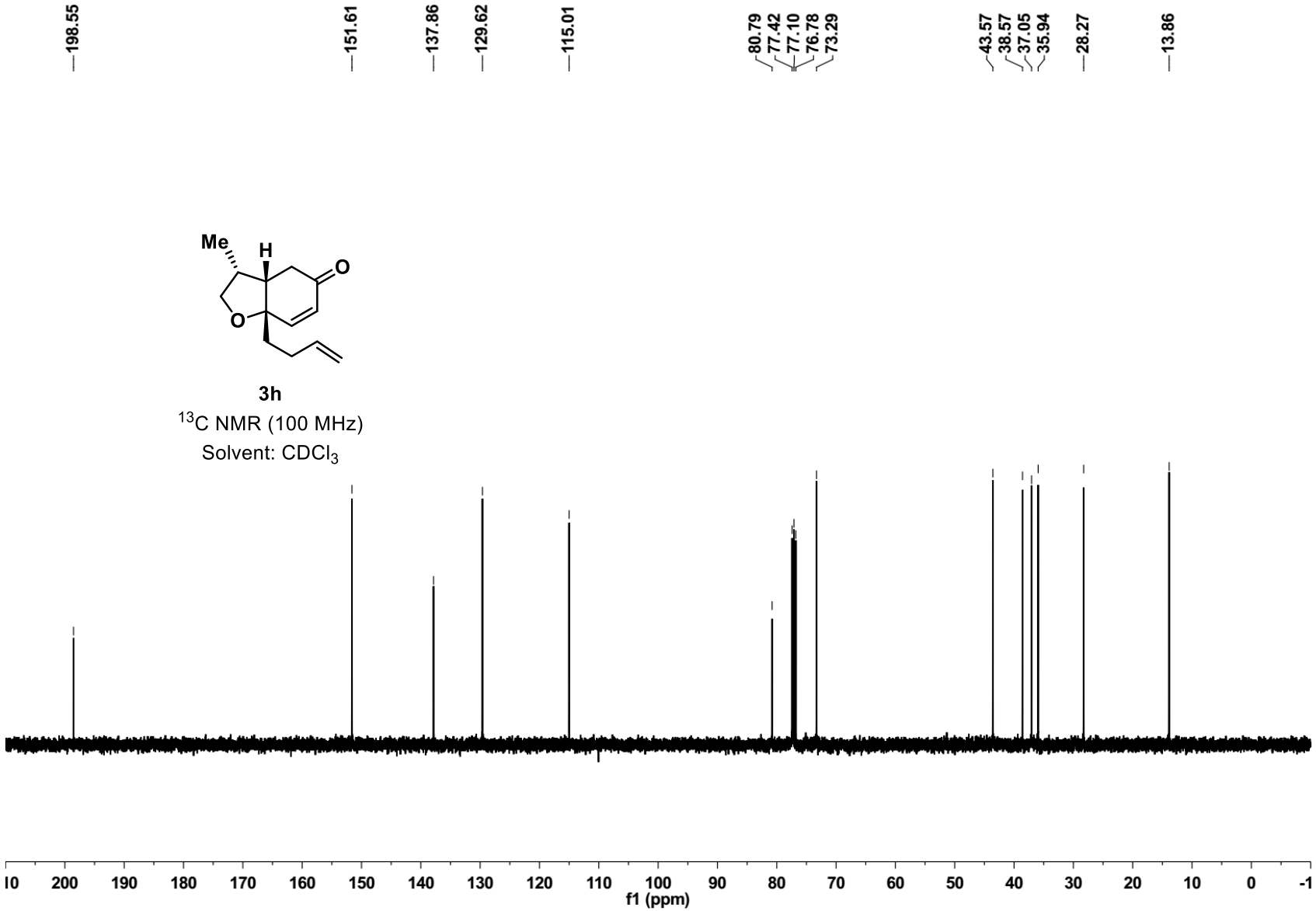
149.22
139.72
130.06
115.40
81.40
77.42
77.10
76.78
74.01
45.27
36.23
35.02
13.59
Me
H
O
O
3g
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


7.29
6.66
6.63
6.05
6.02
5.86
5.84
5.82
5.81
5.79
5.07
5.07
5.03
5.03
5.00
4.97
4.05
4.03
4.02
4.01
3.40
3.38
3.38
3.36
2.61
2.61
2.59
2.57
2.56
2.54
2.20
2.18
1.87
1.86
1.85
1.80
1.80
0.91
0.89
-0.00
Me
H
O
O
3h
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.99
1.00
1.95
1.00
1.02
4.03
1.99
2.32
3.08
f1 (ppm)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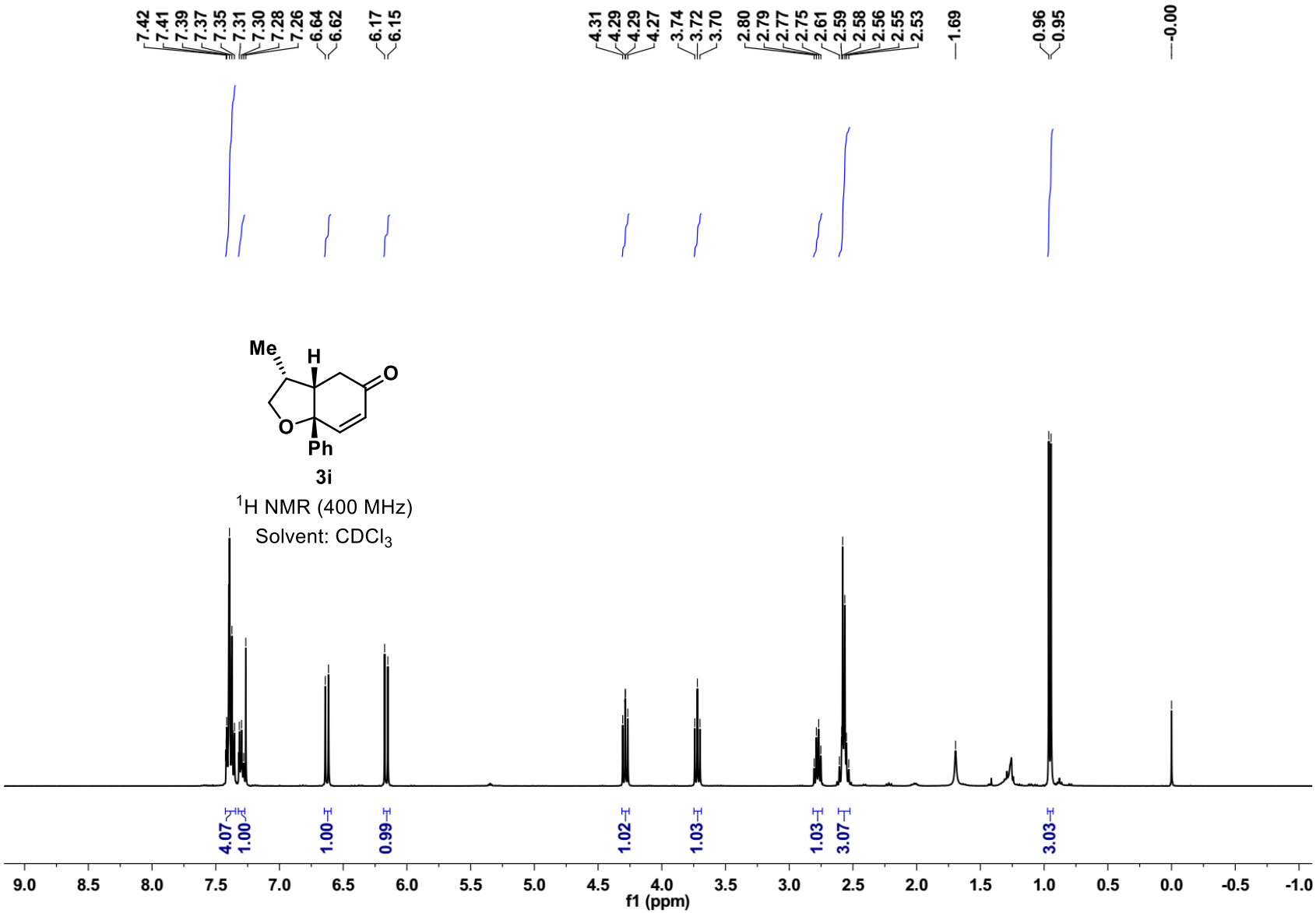
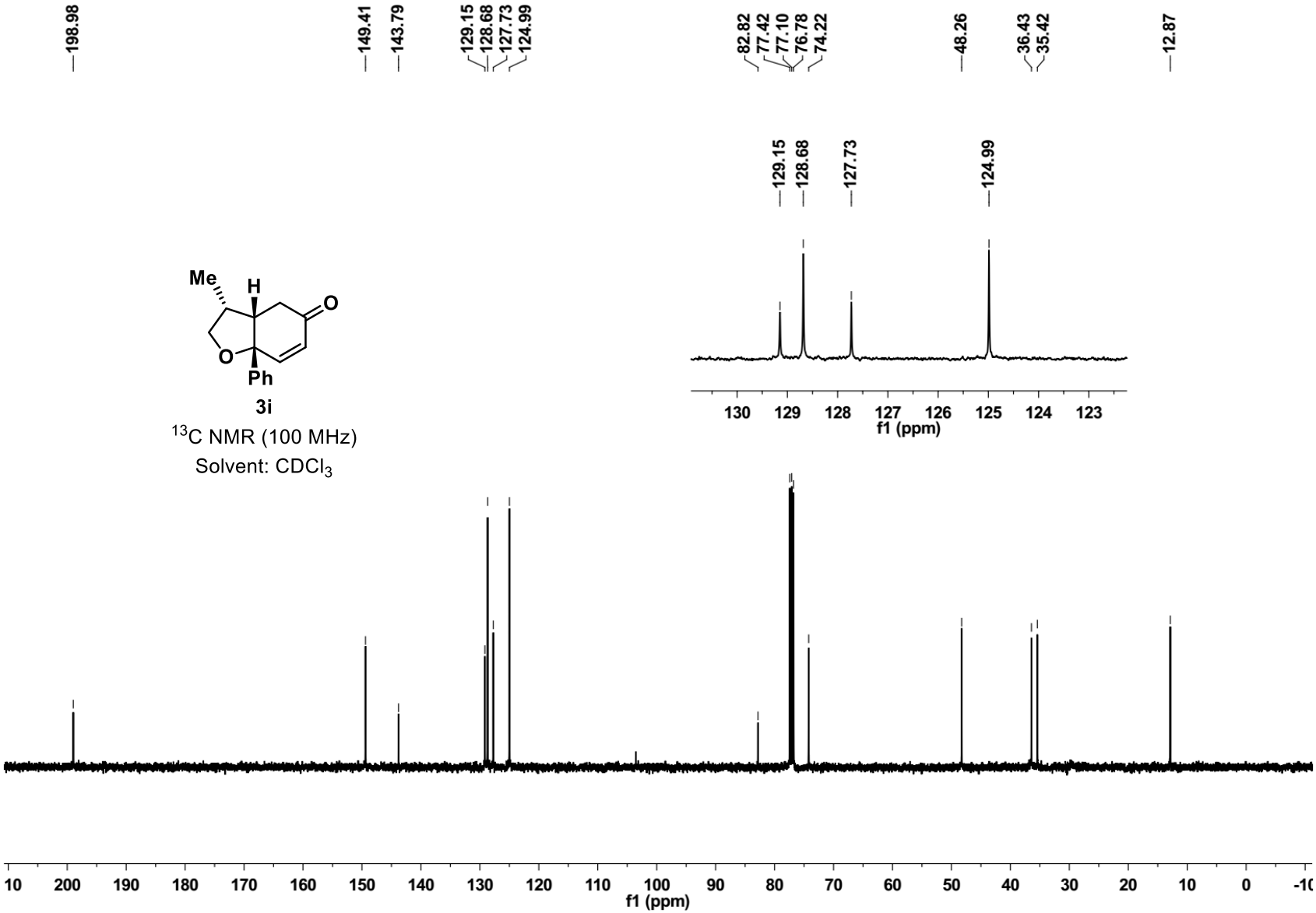
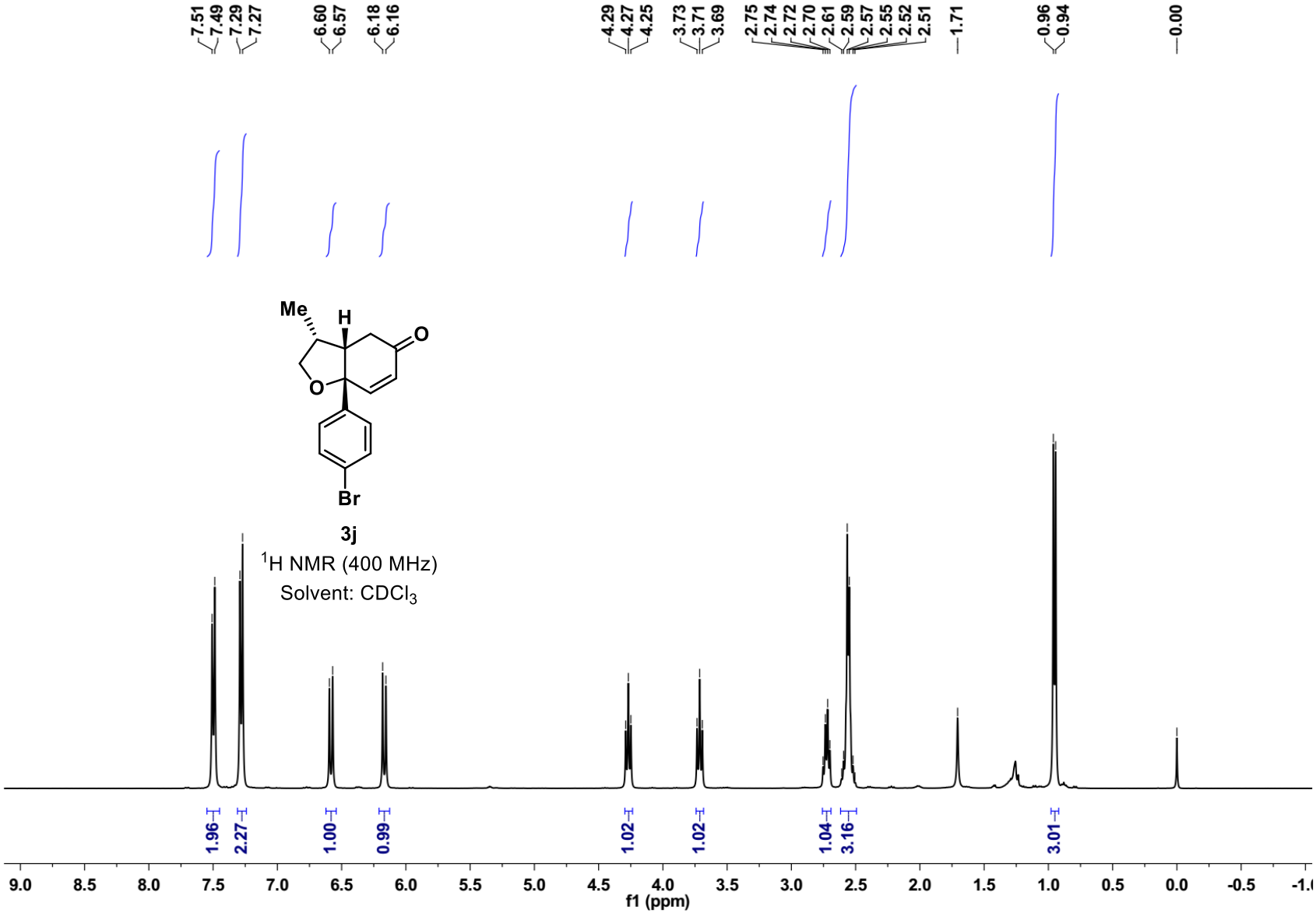
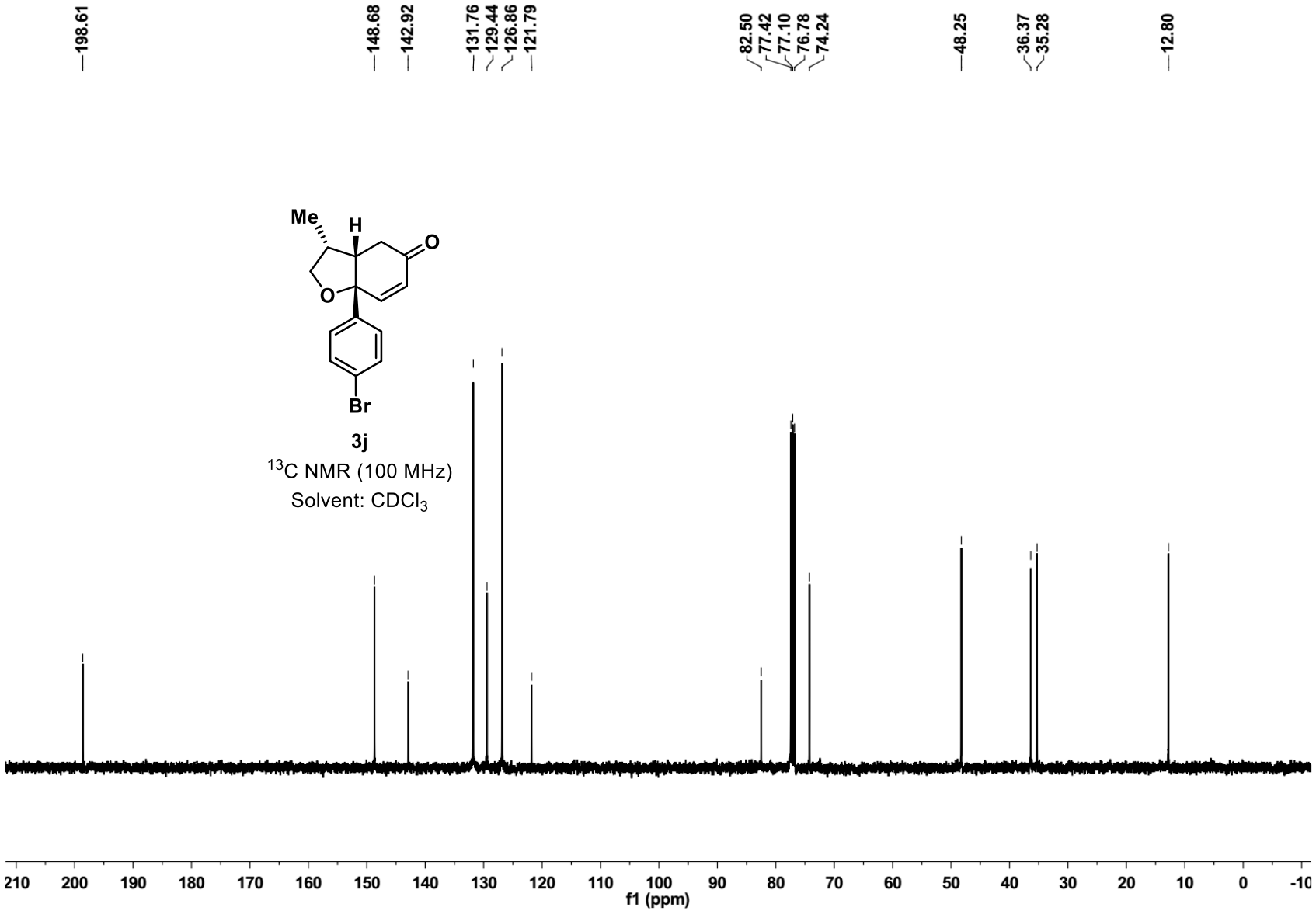
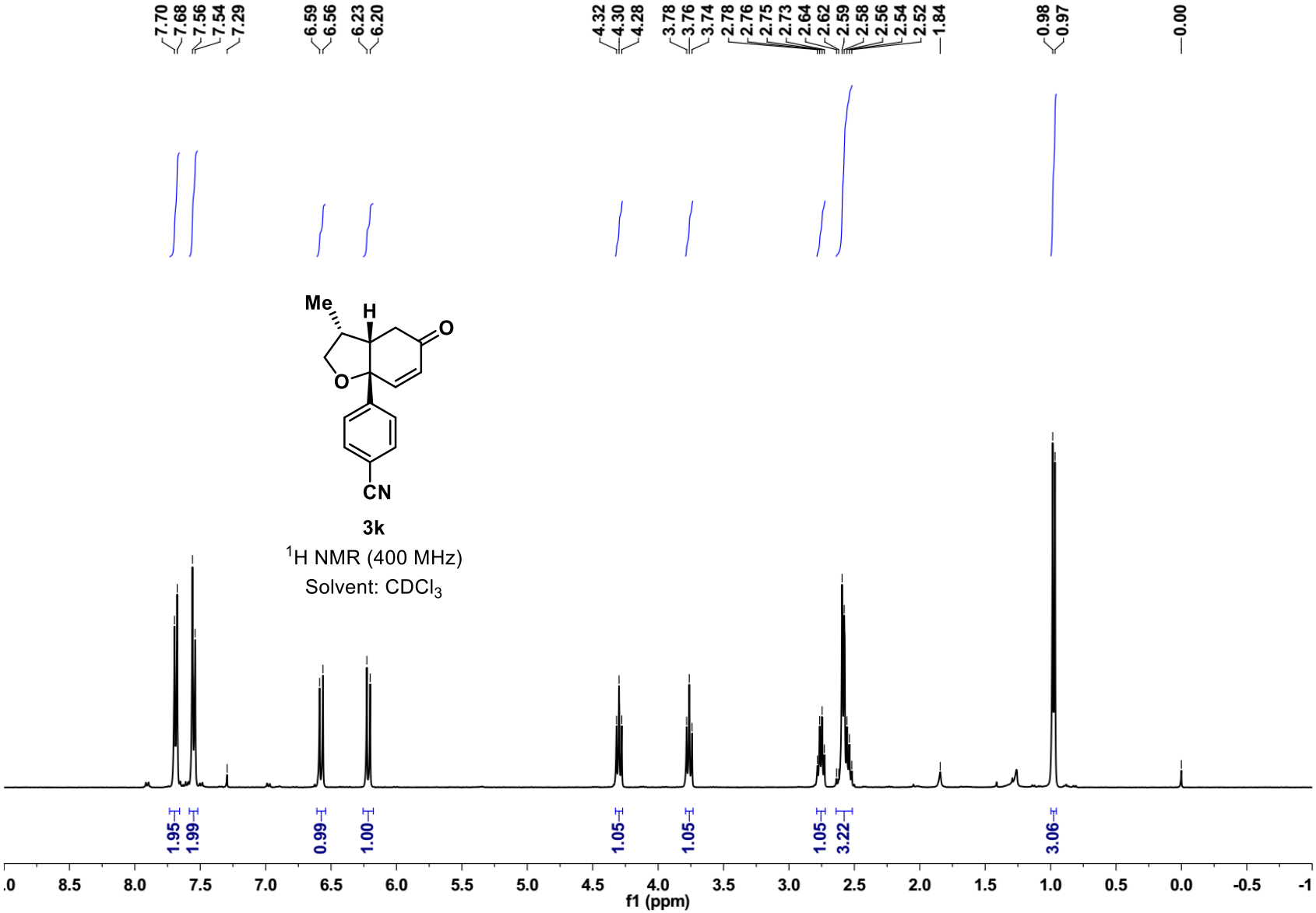
137.86
129.62
115.01
80.79
77.42
77.10
76.78
73.29
43.57
38.57
37.05
35.94
28.27
13.86
Me
H
O
O
3h
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

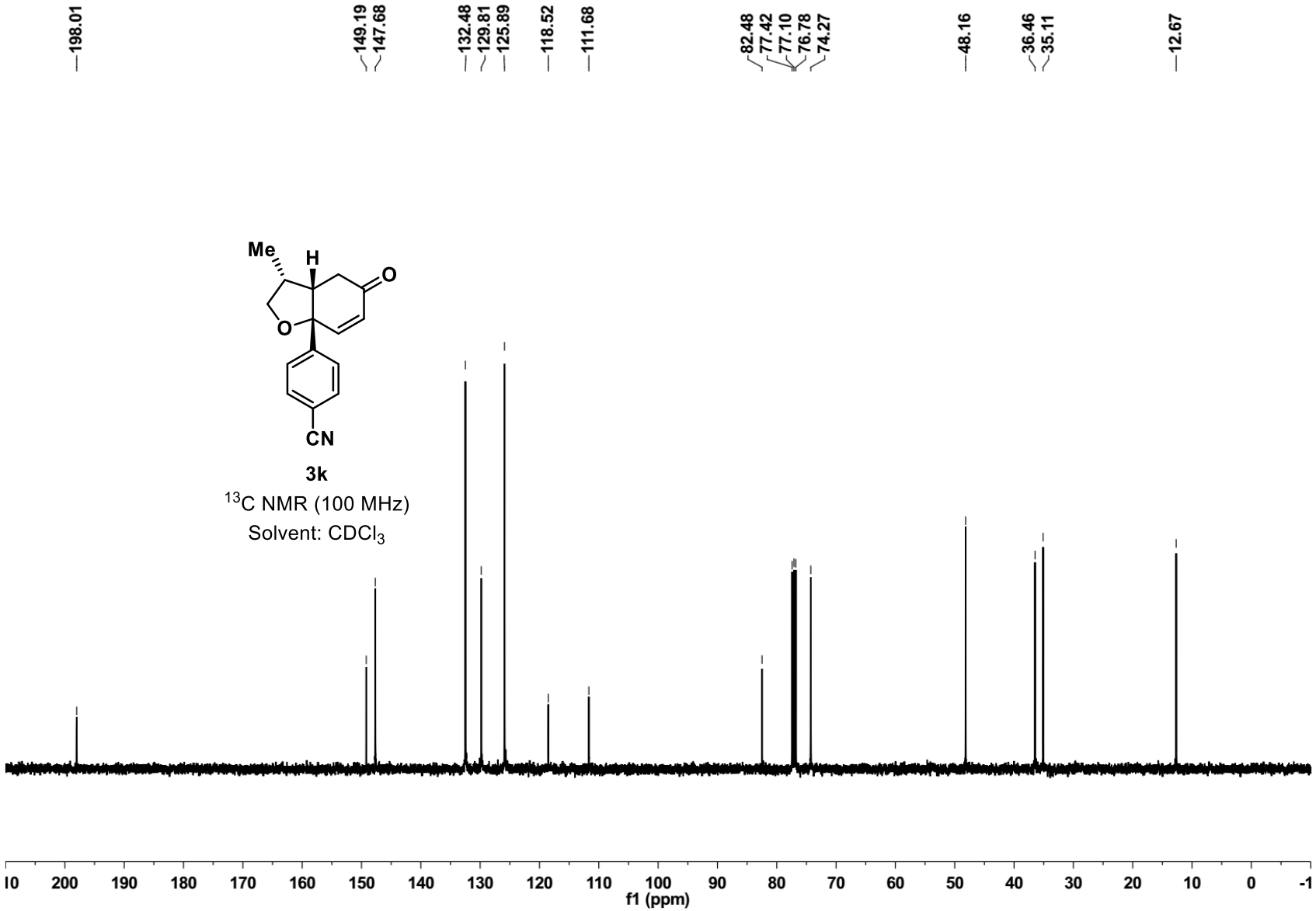

7.42
7.41
7.39
7.37
7.35
7.31
7.30
7.28
7.26
6.64
6.62
6.17
6.15
4.31
4.29
4.29
4.27
3.74
3.72
3.70
2.80
2.79
2.77
2.75
2.61
2.59
2.58
2.56
2.55
2.53
1.69
0.96
0.95
0.00
Me
H
O
O
Ph
3i
1H NMR (400 MHz)
Solvent: CDCl3
4.07
1.00
1.00
0.99
1.02
1.03
1.03
3.07
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

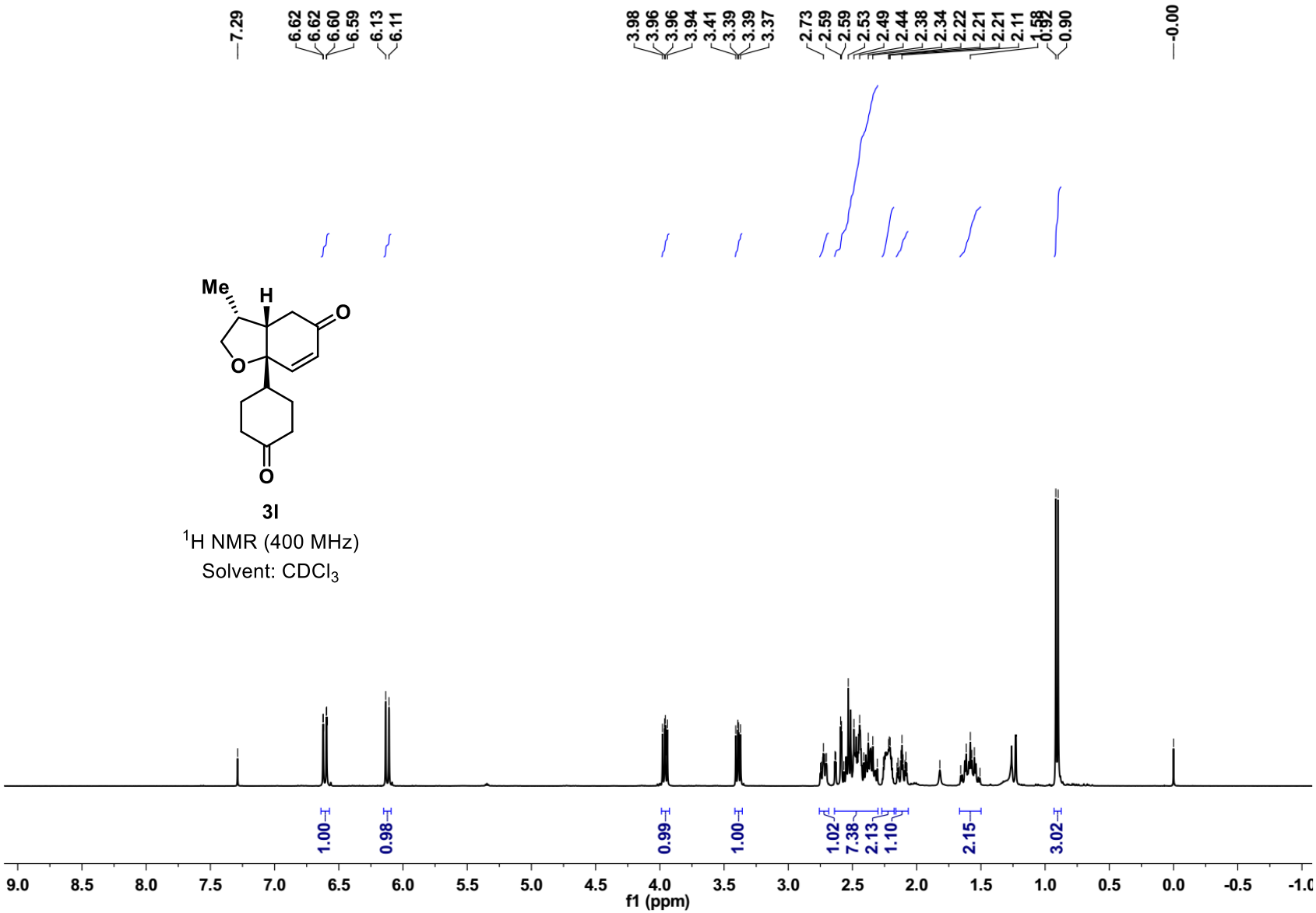

198.98
149.41
143.79
129.15
128.68
127.73
124.99
82.82
77.42
77.10
76.78
74.22
48.26
36.43
35.42
12.87
Me
H
O
O
Ph
3i
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


7.51
7.49
7.29
7.27
6.60
6.57
6.18
6.16
4.29
4.27
4.25
3.73
3.71
3.69
2.75
2.74
2.72
2.70
2.61
2.59
2.57
2.55
2.52
2.51
1.71
0.96
0.94
0.00
Me
H
O
O
Br
3j
1H NMR (400 MHz)
Solvent: CDCl3
1.96
2.27
1.00
0.99
1.02
1.02
1.04
3.16
3.01
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)


198.61
148.68
142.92
131.76
129.44
126.86
121.79
82.50
77.42
77.10
76.78
74.24
48.25
36.37
35.28
12.80
Me
H
O
O
Br
3j
13C NMR (100 MHz)
Solvent: 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)


7.70
7.68
7.56
7.54
7.29
6.59
6.56
6.23
6.20
4.32
4.30
4.28
3.78
3.76
3.74
2.78
2.76
2.75
2.73
2.64
2.62
2.59
2.58
2.56
2.54
2.52
1.84
0.98
0.97
0.00
Me
H
O
O
CN
3k
1H NMR (400 MHz)
Solvent: CDCl3
1.95
1.99
0.99
1.00
1.05
1.05
1.05
3.22
3.06
f1 (ppm)

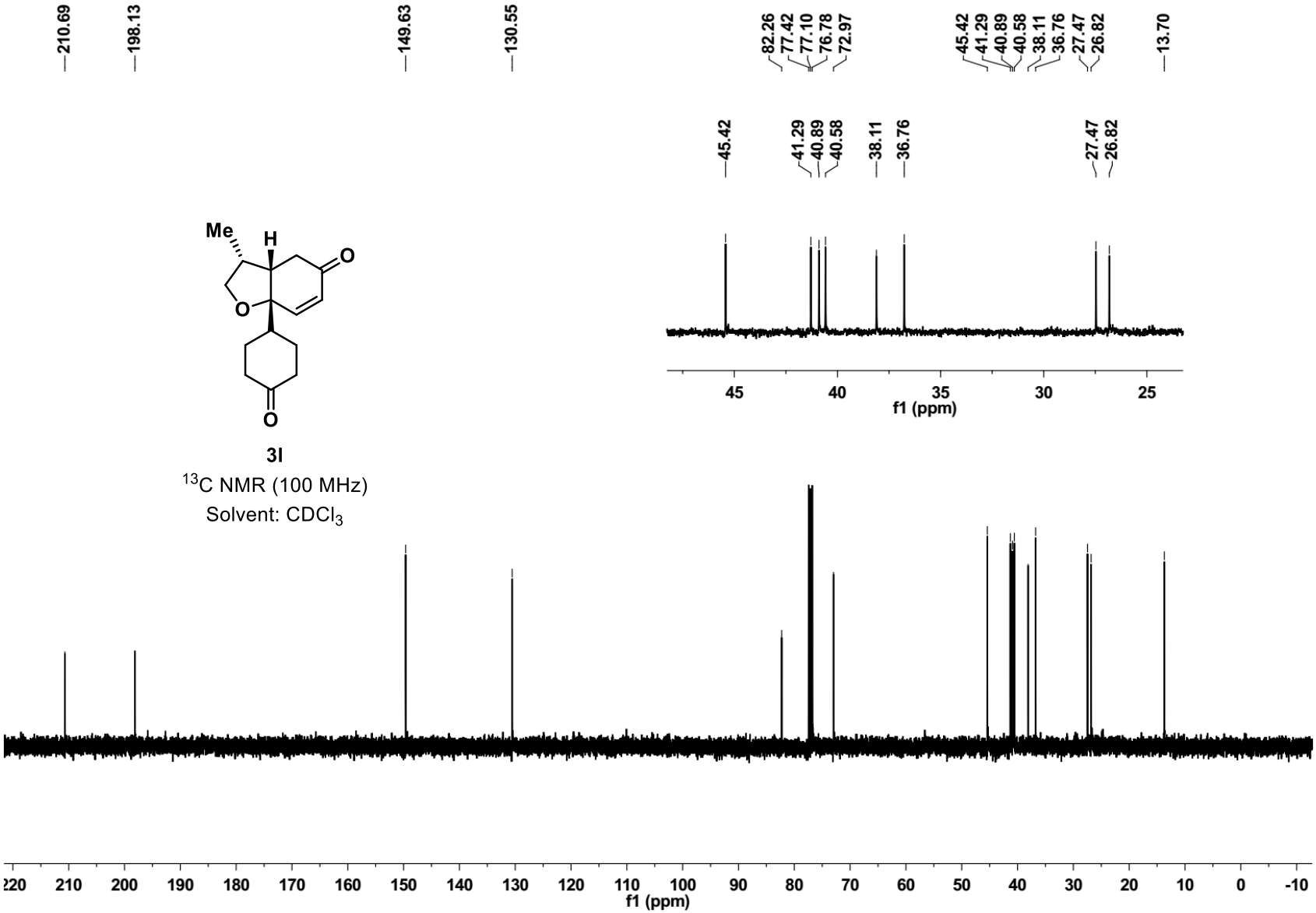

198.01
149.19
147.68
132.48
129.81
125.89
118.52
111.68
82.48
77.42
77.10
76.78
74.27
48.16
36.46
35.11
12.67
Me
H
O
O
CN
3k
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)



3l

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$


210.69
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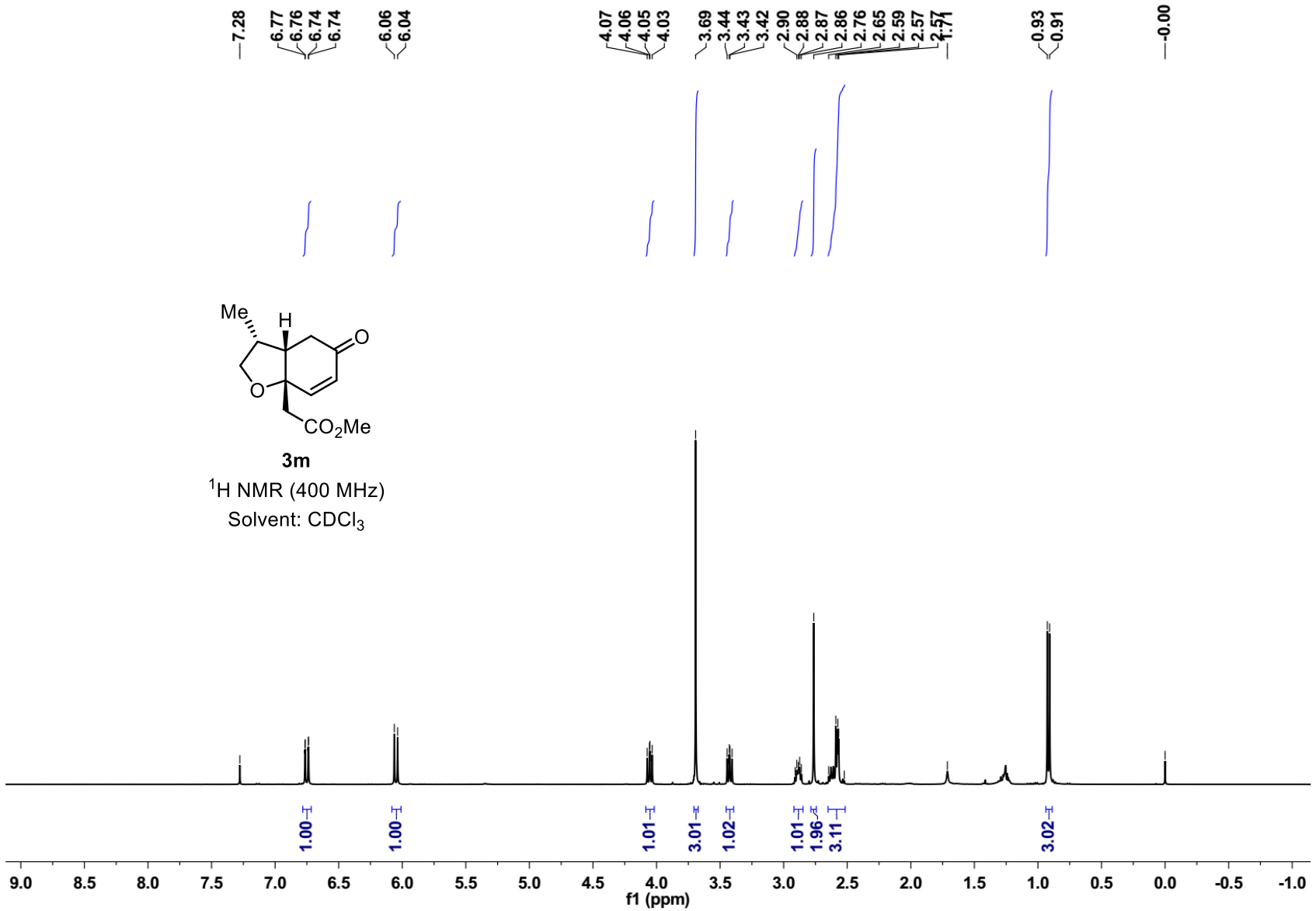
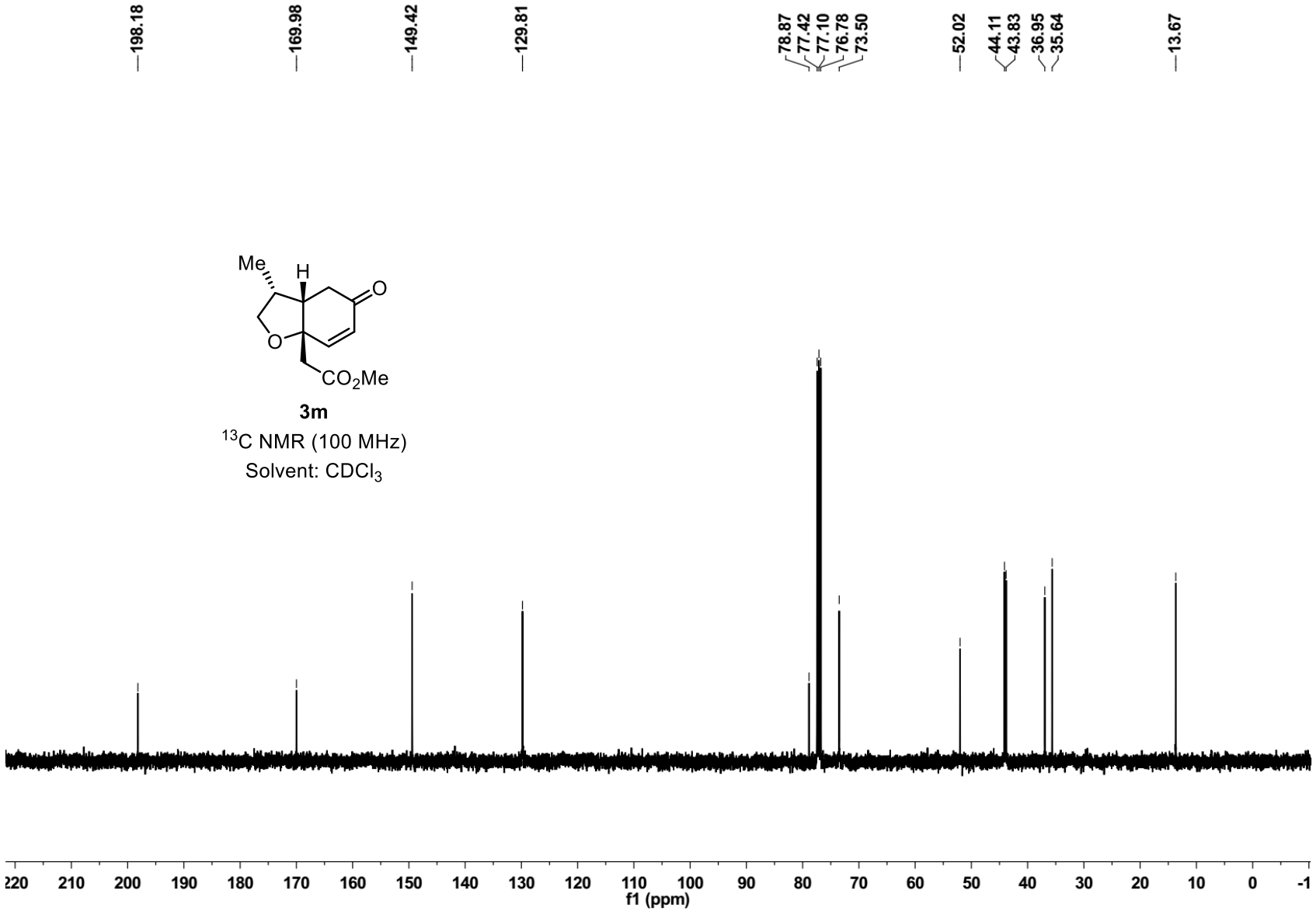
82.26
77.42
77.10
76.78
72.97
45.42
41.29
40.89
40.58
38.11
36.76
27.47
26.82
13.70
Me
H
O
O
O
3l
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)


7.28
6.77
6.76
6.74
6.74
6.06
6.04
4.07
4.06
4.05
4.03
3.69
3.44
3.43
3.42
2.90
2.88
2.87
2.86
2.76
2.65
2.59
2.57
2.57
1.71
0.93
0.91
-0.00
Me
H
O
O
CO2Me
3m
1H NMR (400 MHz)
Solvent: CDCl3
1.00
1.00
1.01
3.01
1.02
1.01
1.96
3.11
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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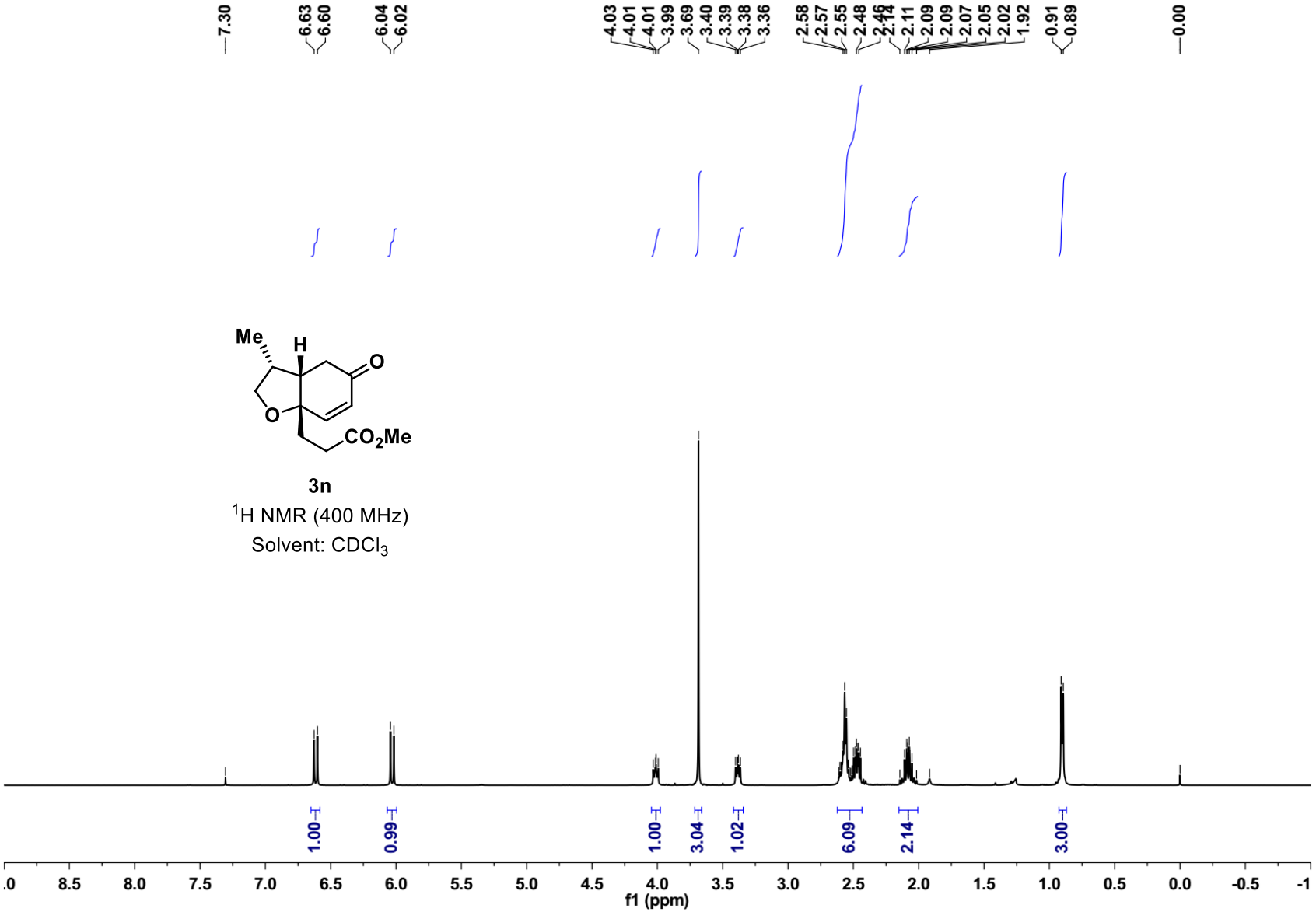
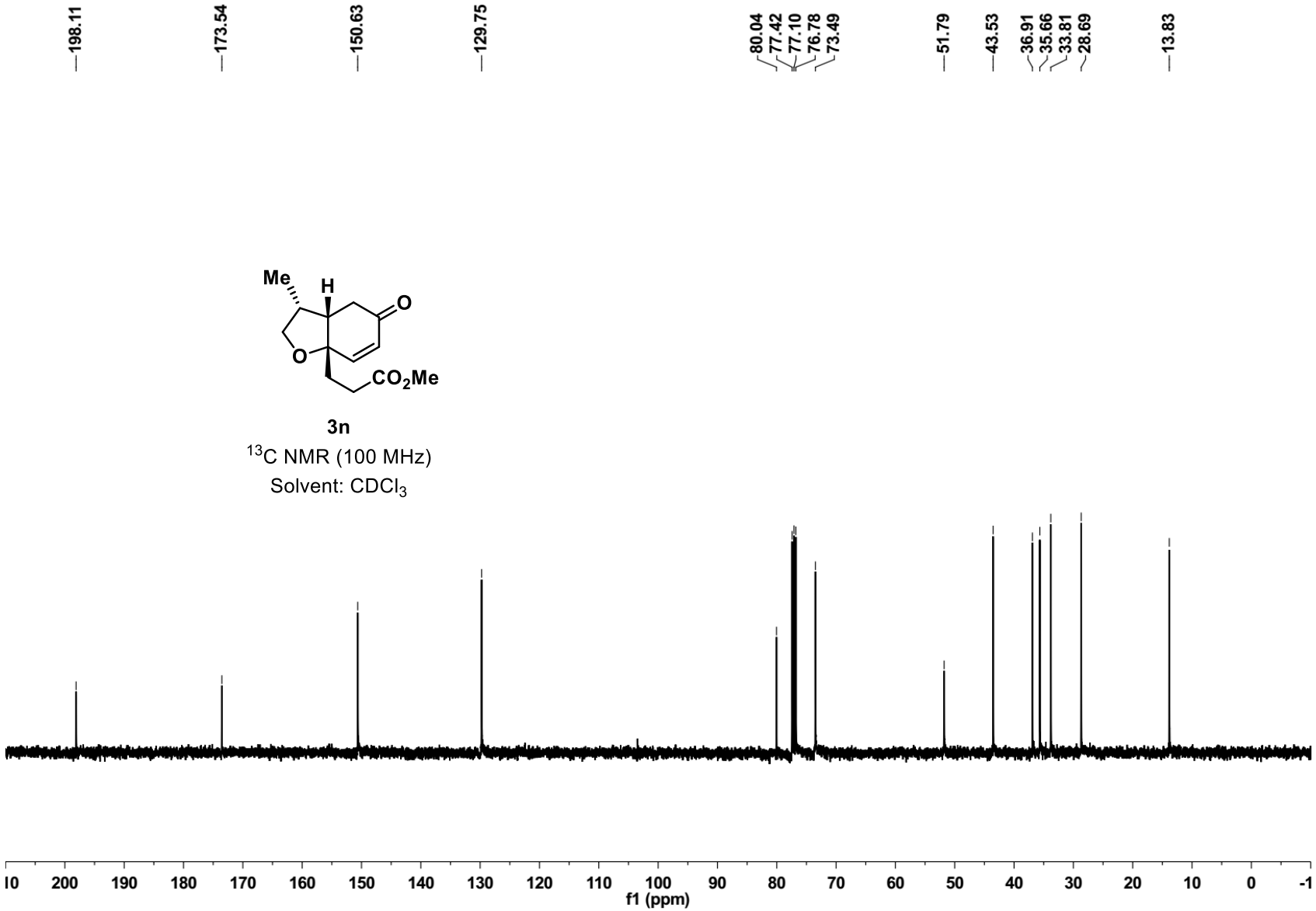
78.87
77.42
77.10
76.78
73.50
52.02
44.11
43.83
36.95
35.64
13.67
Me
H
O
O
CO2Me
3m
13C NMR (100 MHz)
Solvent: CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



3n

^{1}H NMR (400 MHz)

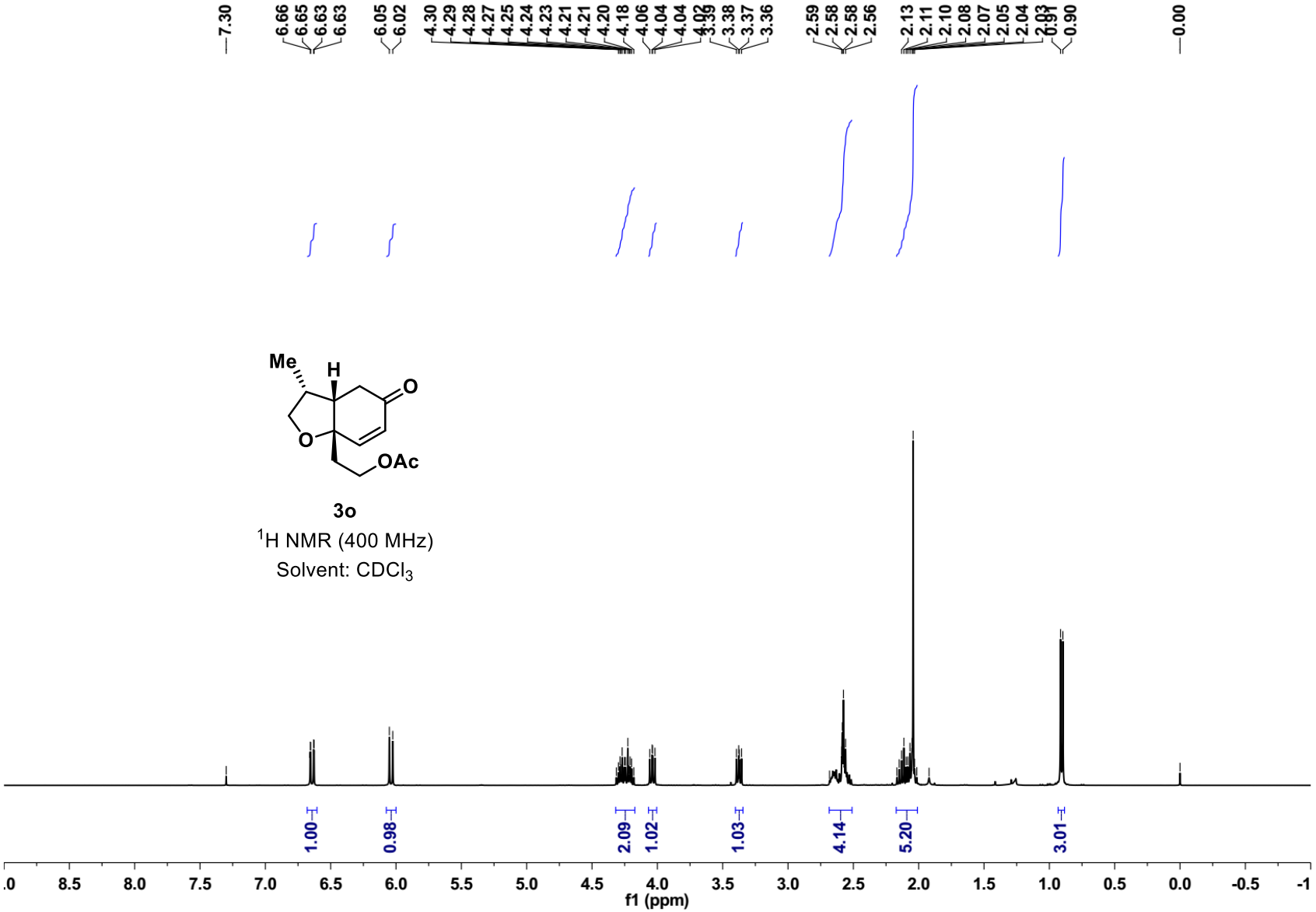
Solvent: $CDCl_3$



3n

^{13}C NMR (100 MHz)

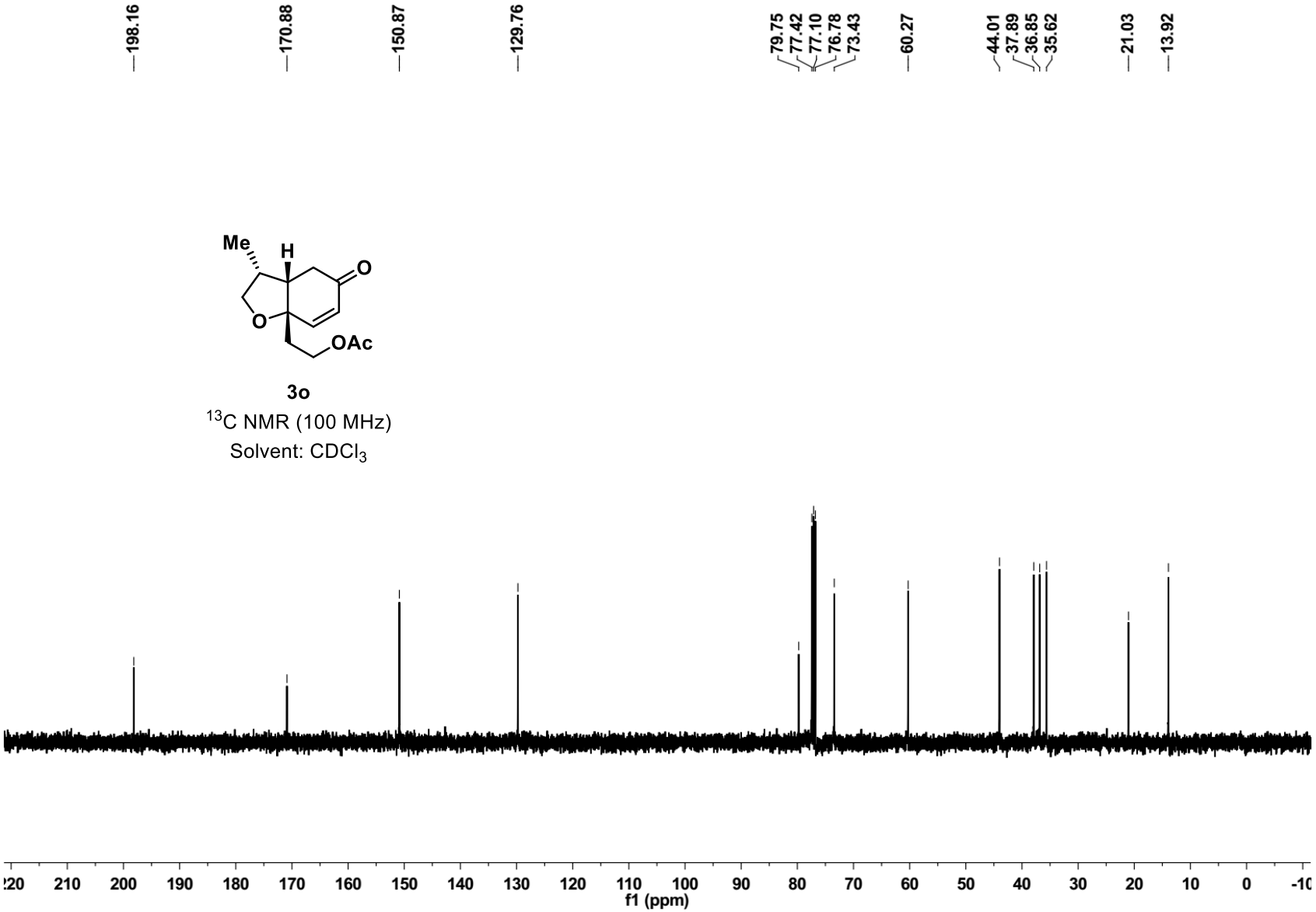
Solvent: $CDCl_3$



3o

^{1}H NMR (400 MHz)

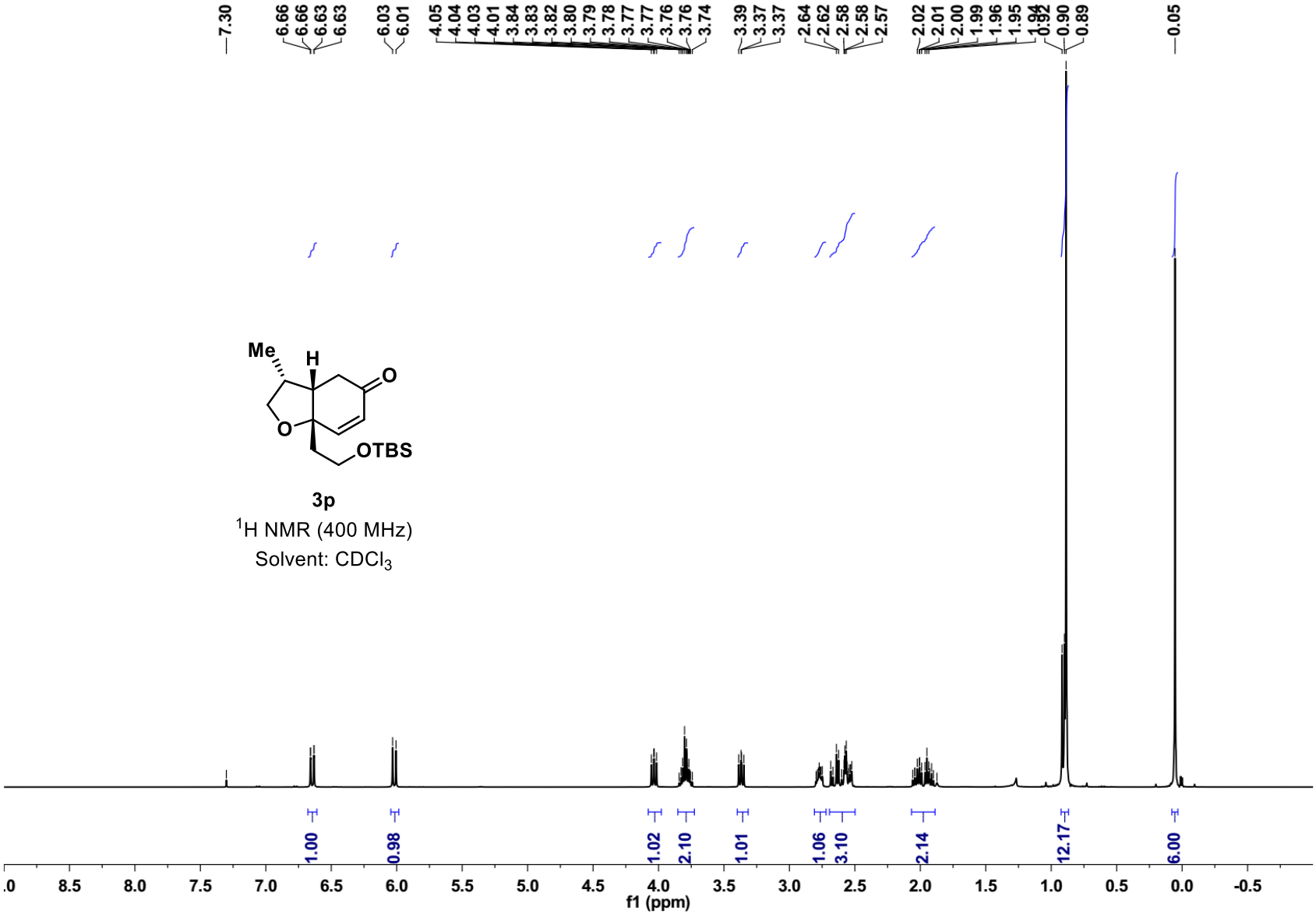
Solvent: $CDCl_3$



3o

^{13}C NMR (100 MHz)

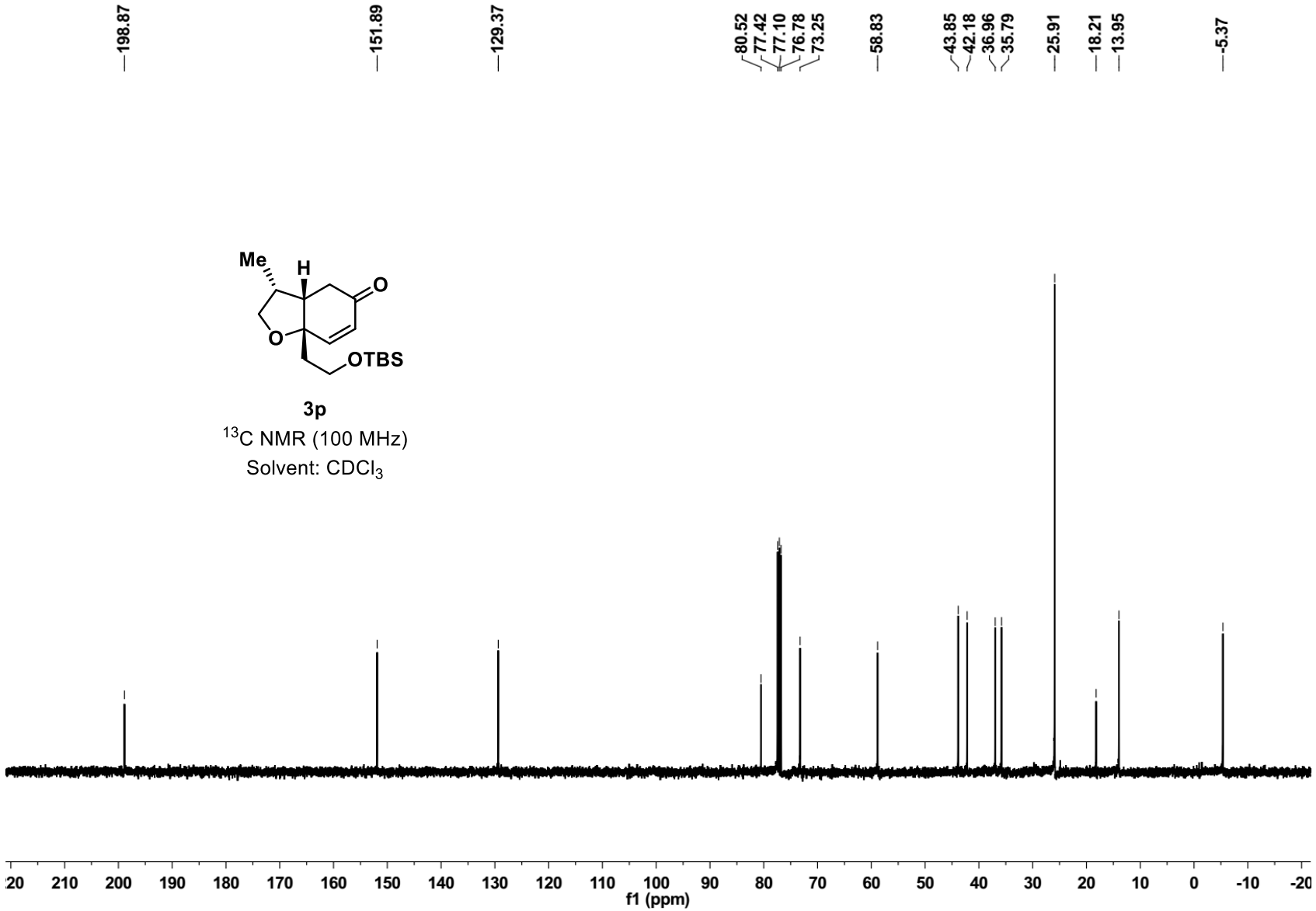
Solvent: $CDCl_3$



3p

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$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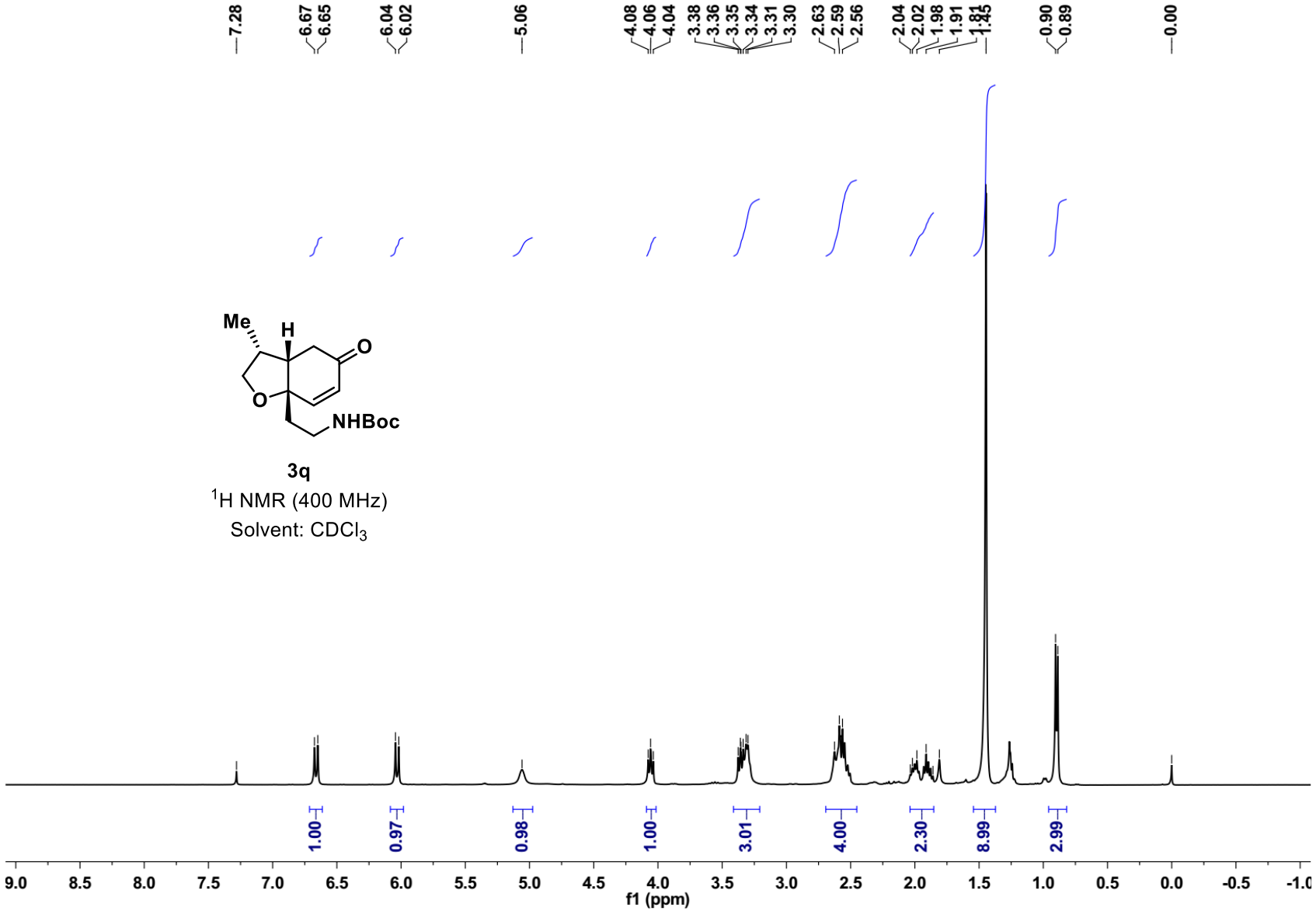
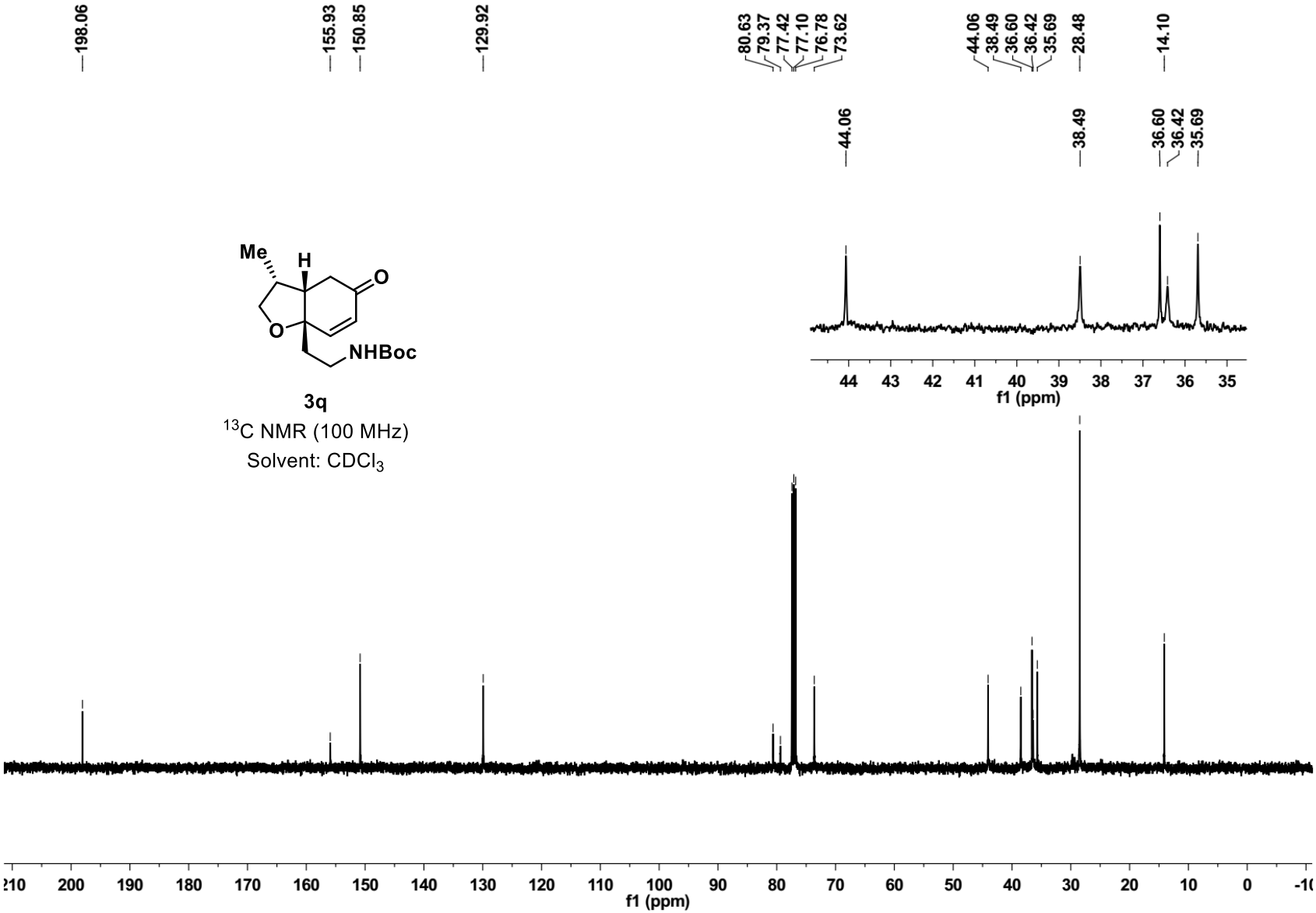
80.52
77.42
77.10
76.78
73.25
58.83
43.85
42.18
36.96
35.79
25.91
18.21
13.95
-5.37
Me
H
O
O
OTBS
3p
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

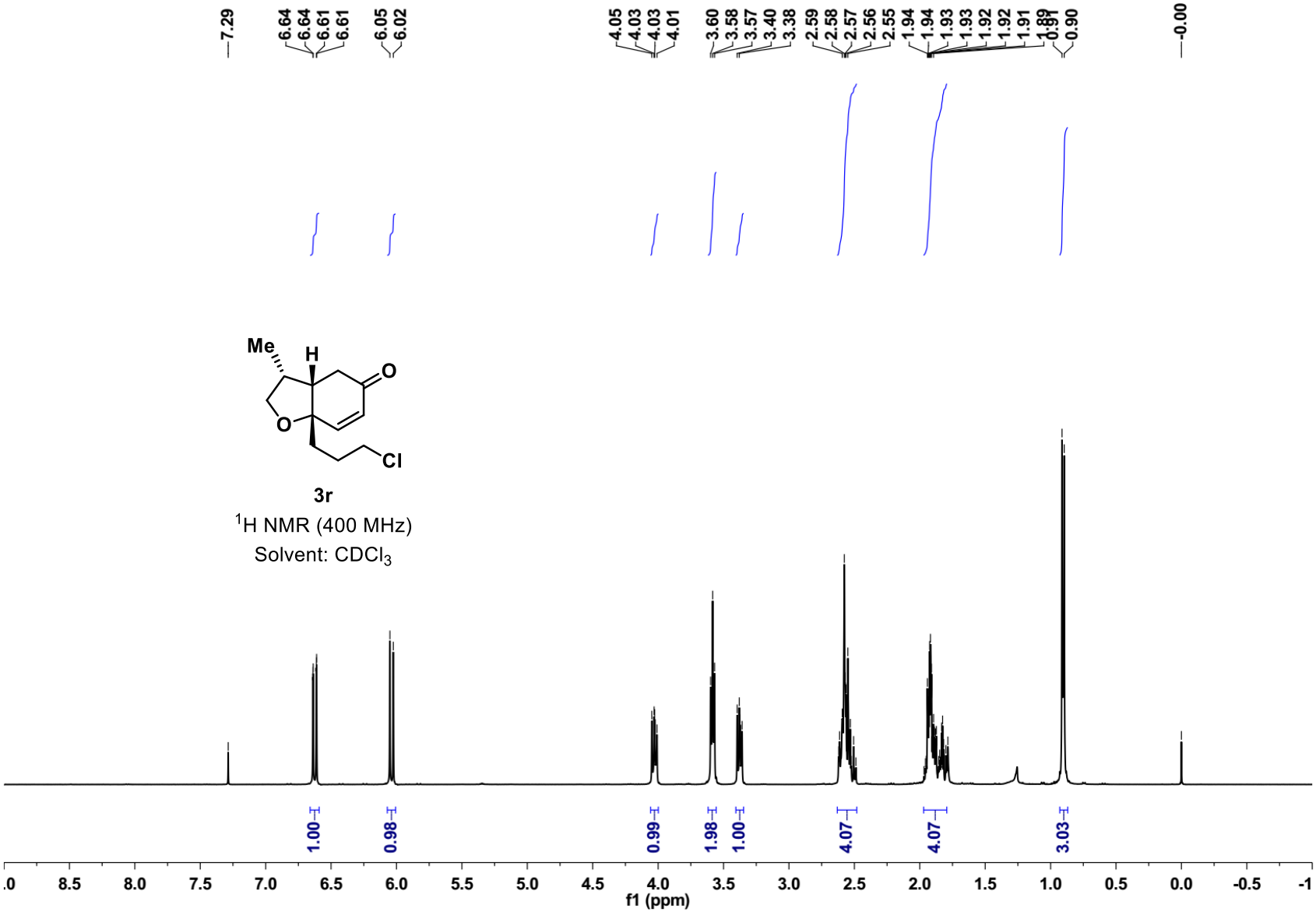


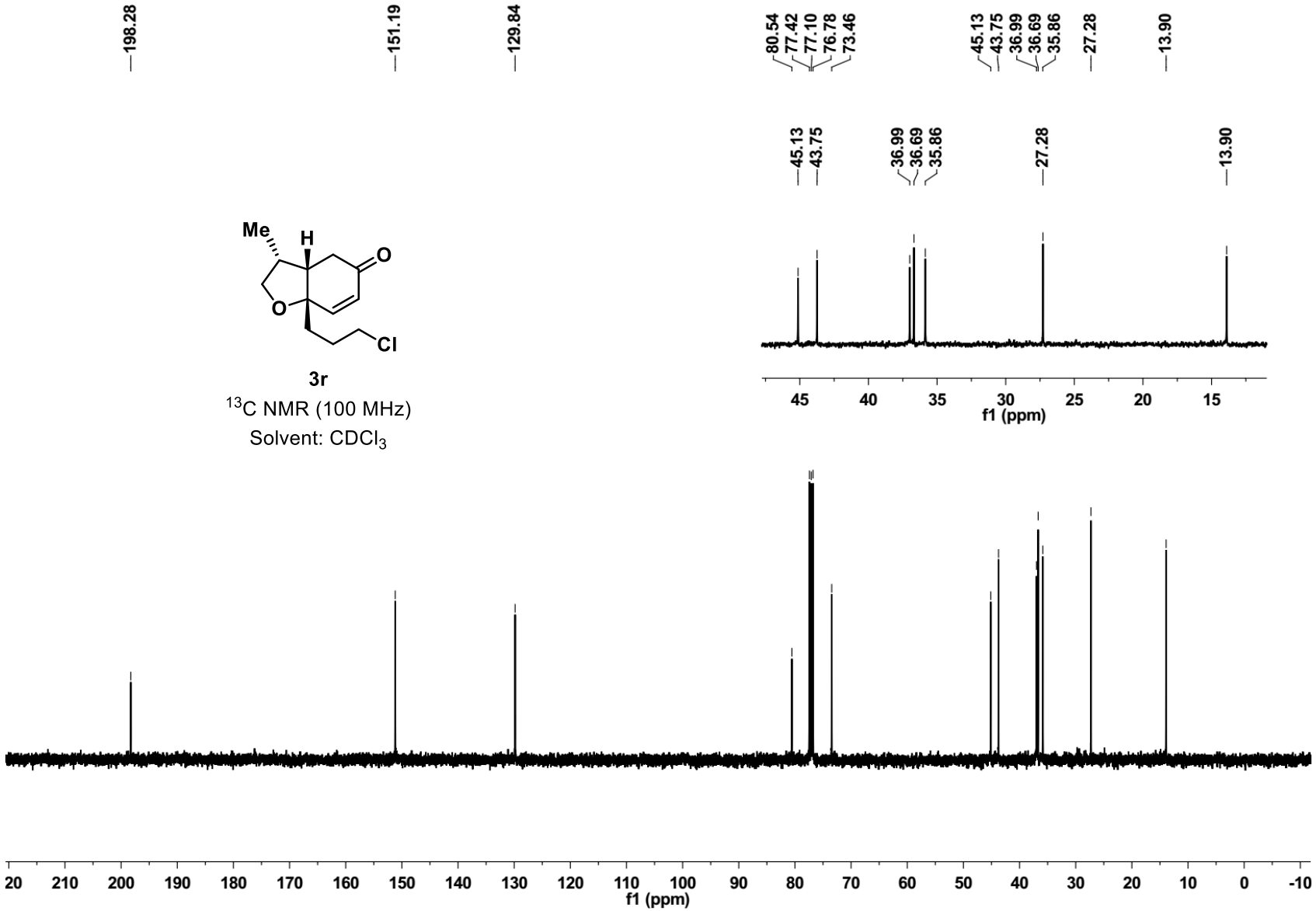
3q

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$


198.06
155.93
150.85
129.92
80.63
79.37
77.42
77.10
76.78
73.62
44.06
38.49
36.60
36.42
35.69
28.48
14.10
Me
H
O
O
NHBoc
3q
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


7.29
6.64
6.64
6.61
6.61
6.05
6.02
4.05
4.03
4.03
4.01
3.60
3.58
3.57
3.40
3.38
2.59
2.58
2.57
2.56
2.55
1.94
1.94
1.93
1.93
1.92
1.92
1.91
1.89
0.91
0.90
-0.00
Me
H
O
O
Cl
3r
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.98
0.99
1.98
1.00
4.07
4.07
3.03
f1 (ppm)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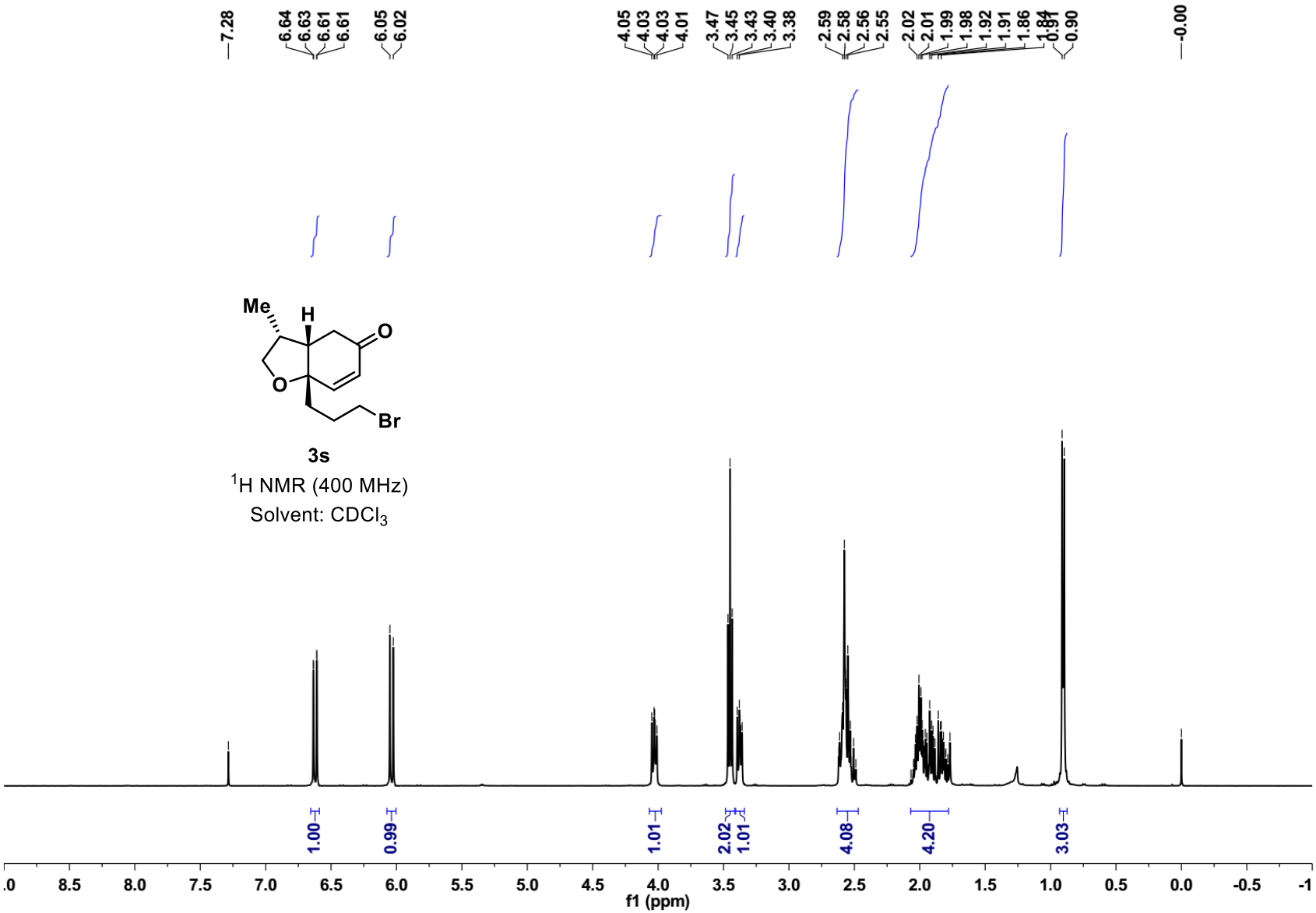
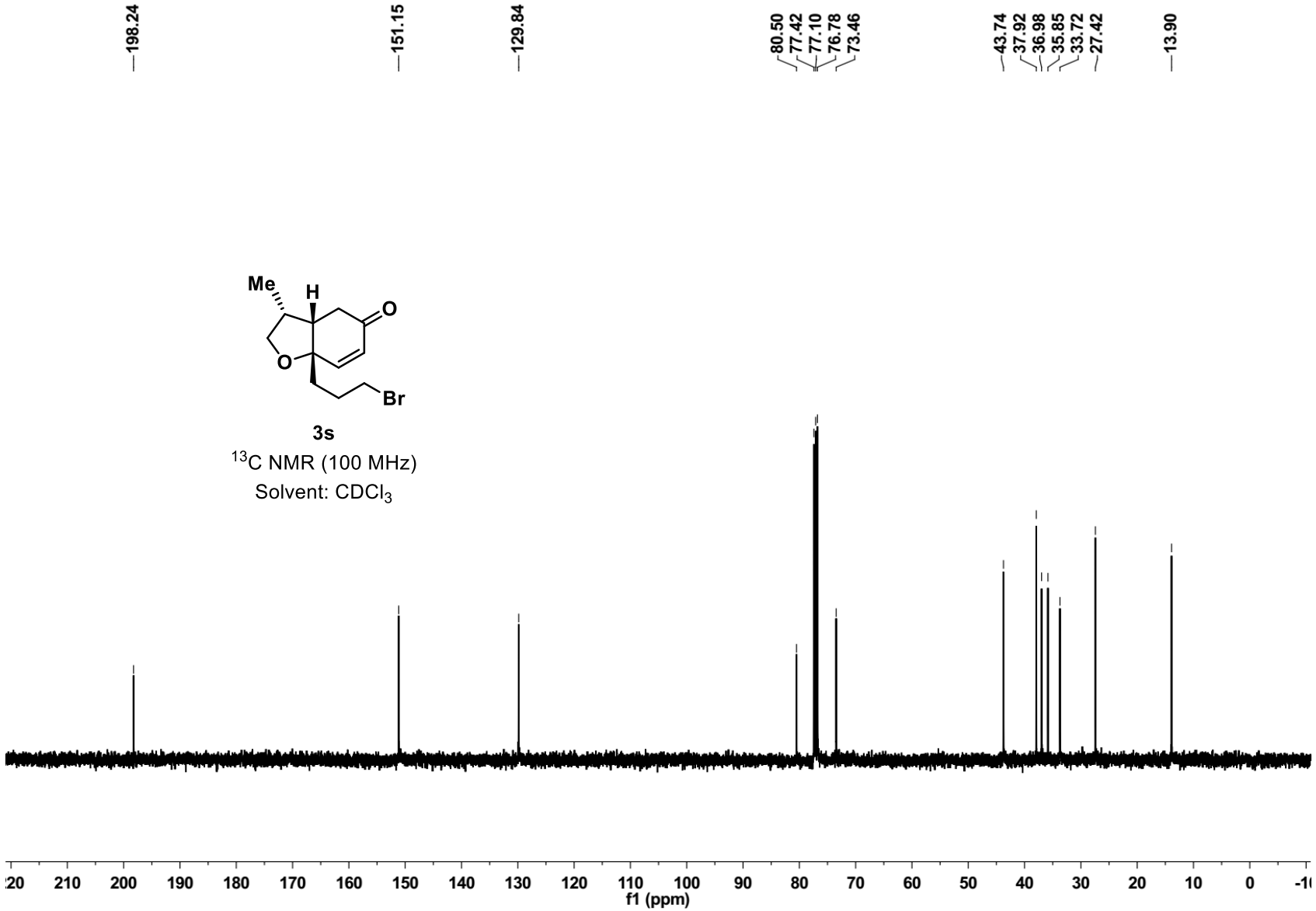
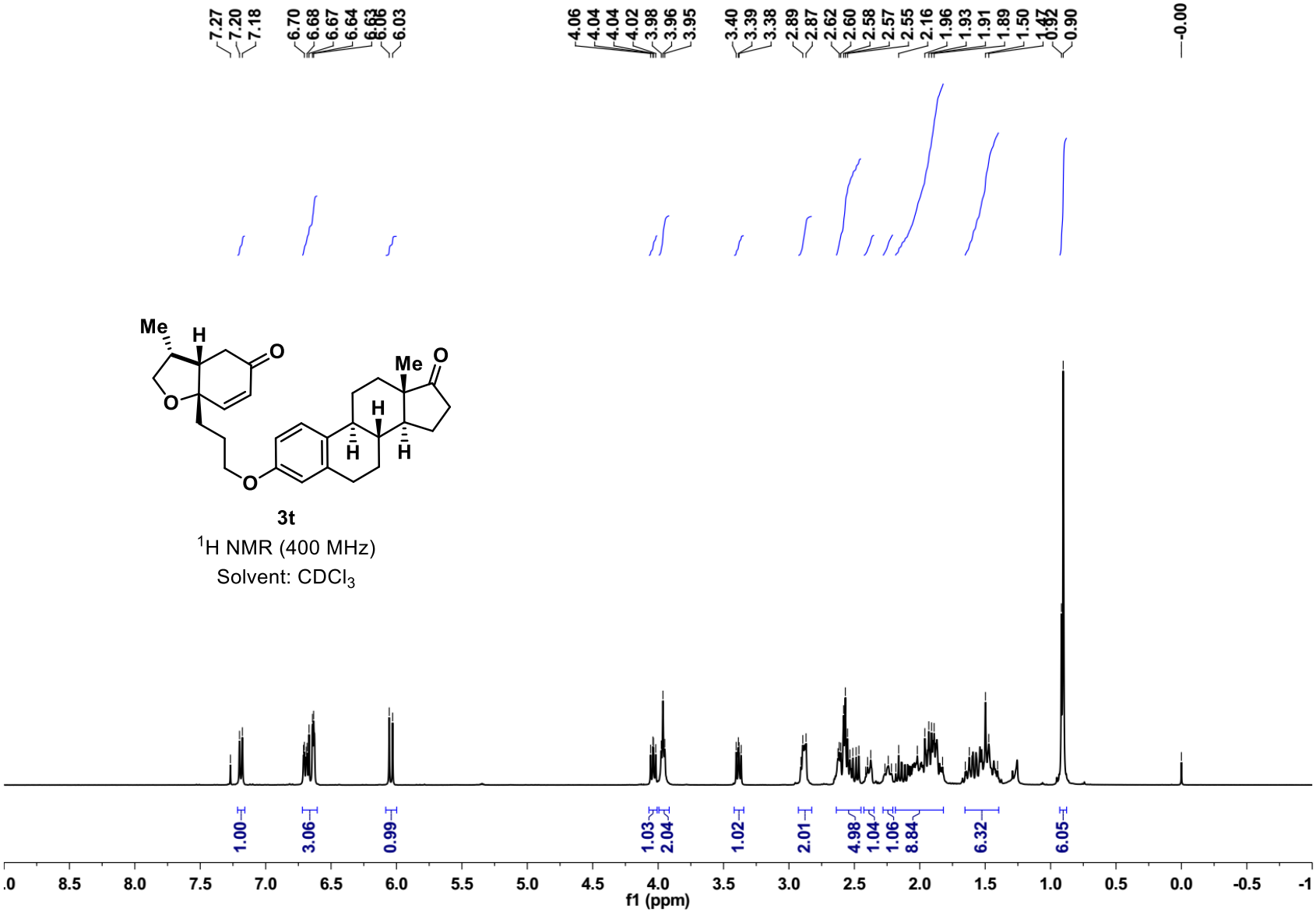
151.19
129.84
80.54
77.42
77.10
76.78
73.46
45.13
43.75
36.99
36.69
35.86
27.28
13.90
Me
H
O
O
Cl
3r
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)


7.28
6.64
6.63
6.61
6.61
6.05
6.02
4.05
4.03
4.03
4.01
3.47
3.45
3.43
3.40
3.38
2.59
2.58
2.56
2.55
2.02
2.01
1.99
1.98
1.92
1.91
1.86
0.91
0.90
-0.00
Me
H
O
O
Br
3s
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.99
1.01
2.02
1.01
4.08
4.20
3.03
f1 (ppm)

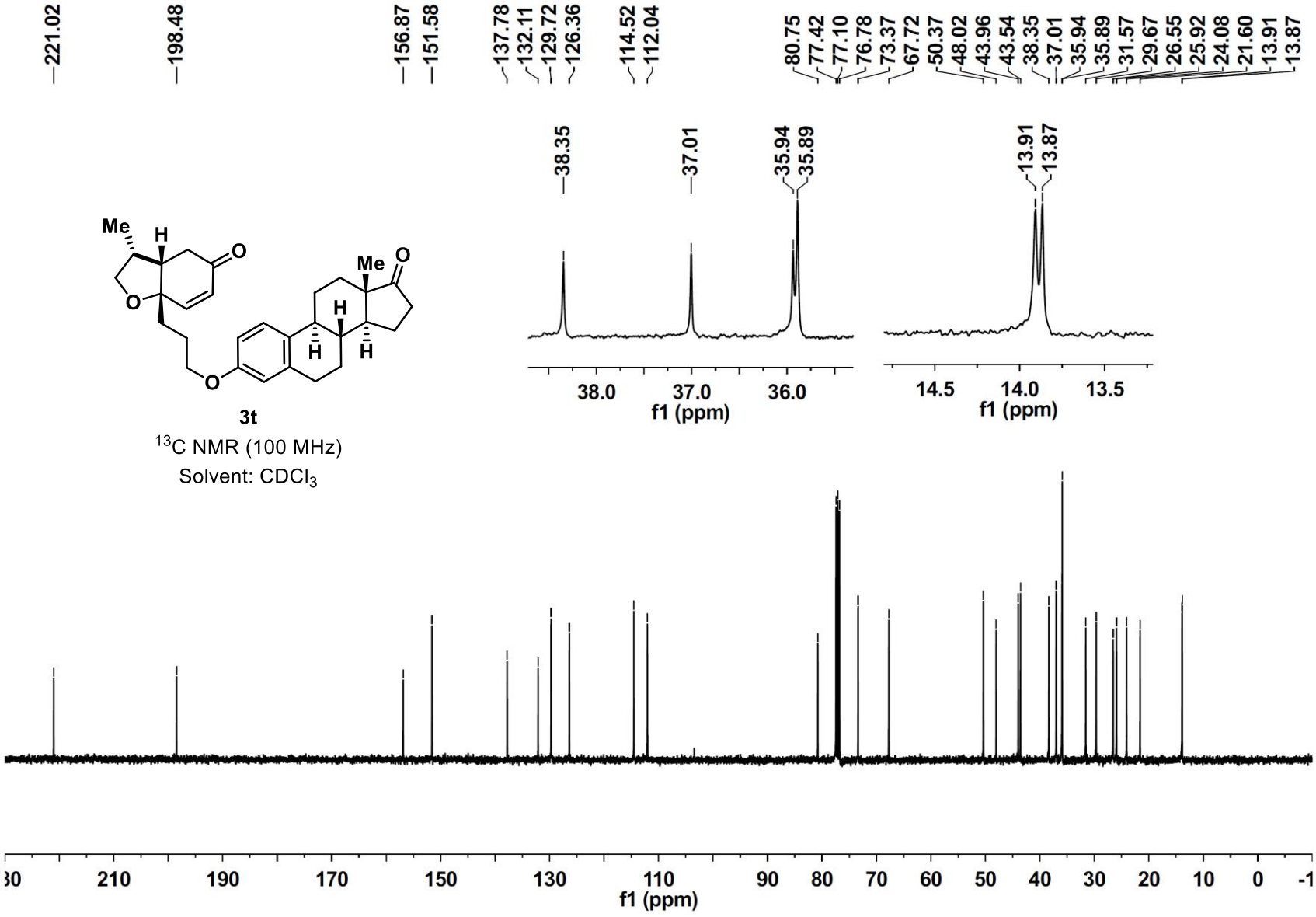

198.24
151.15
129.84
80.50
77.42
77.10
76.78
73.46
43.74
37.92
36.98
35.85
33.72
27.42
13.90
Me
H
O
O
Br
3s
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)



3t

^{1}H NMR (400 MHz)

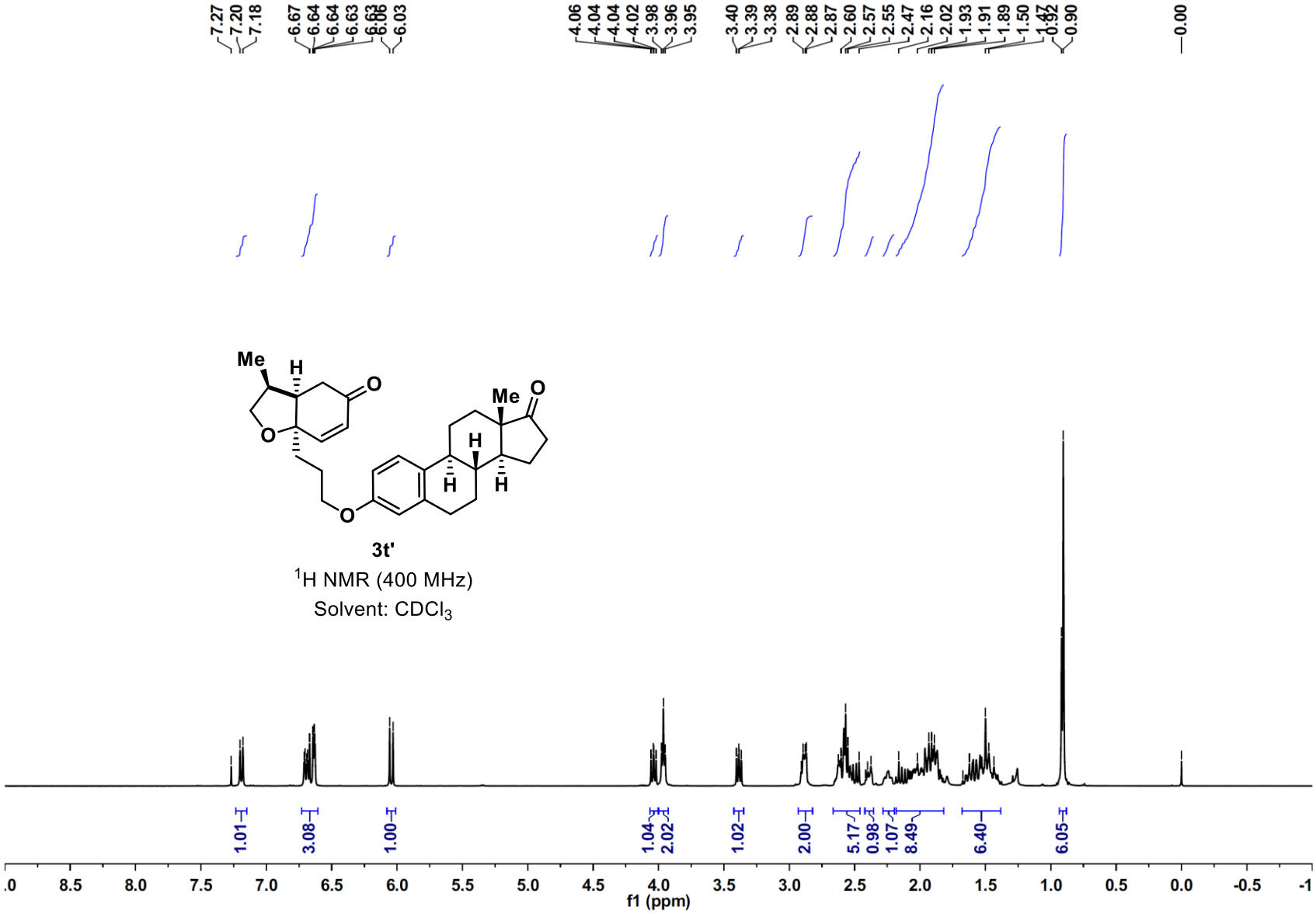
Solvent: $CDCl_3$



3t

^{13}C NMR (100 MHz)

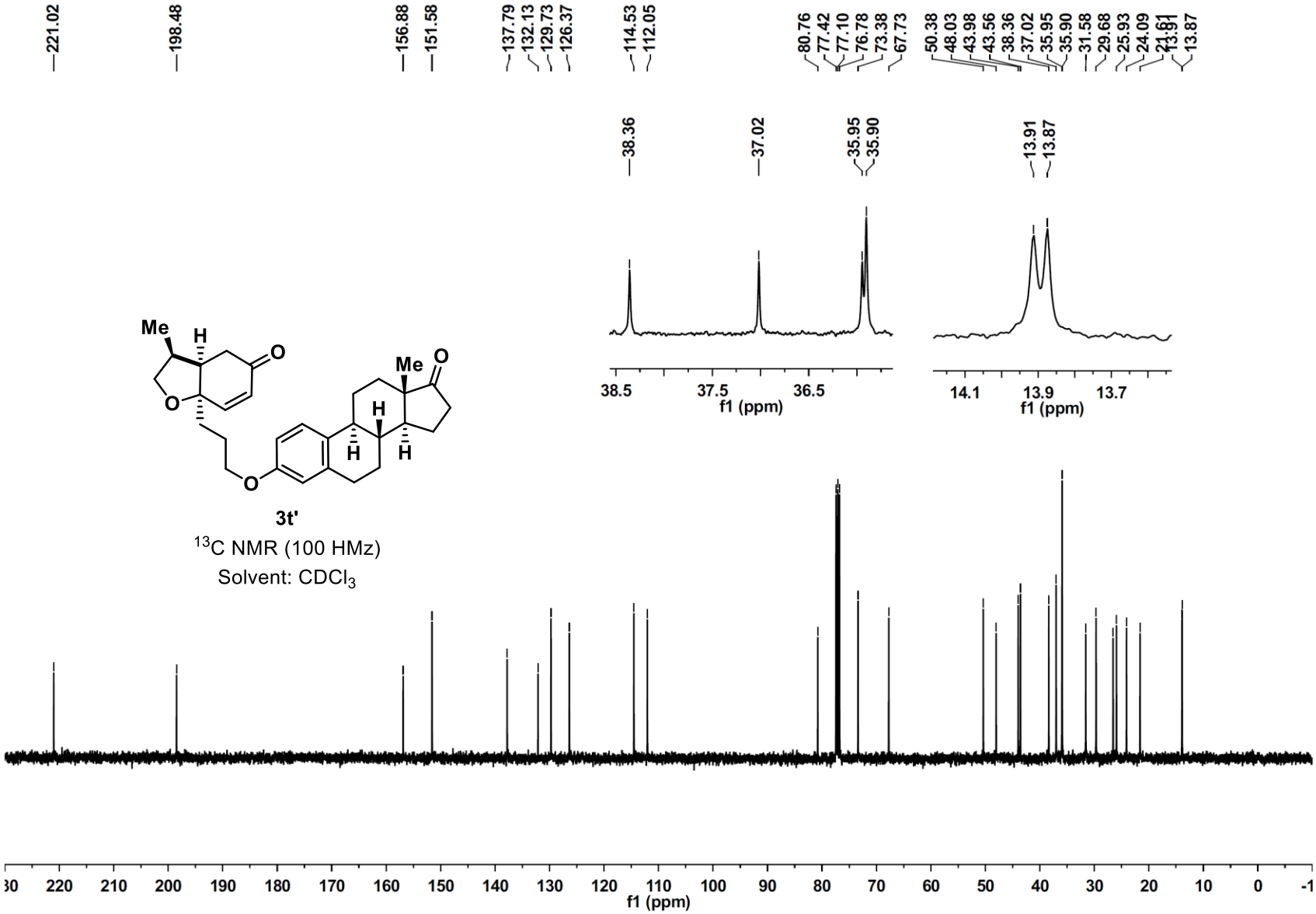
Solvent: $CDCl_3$

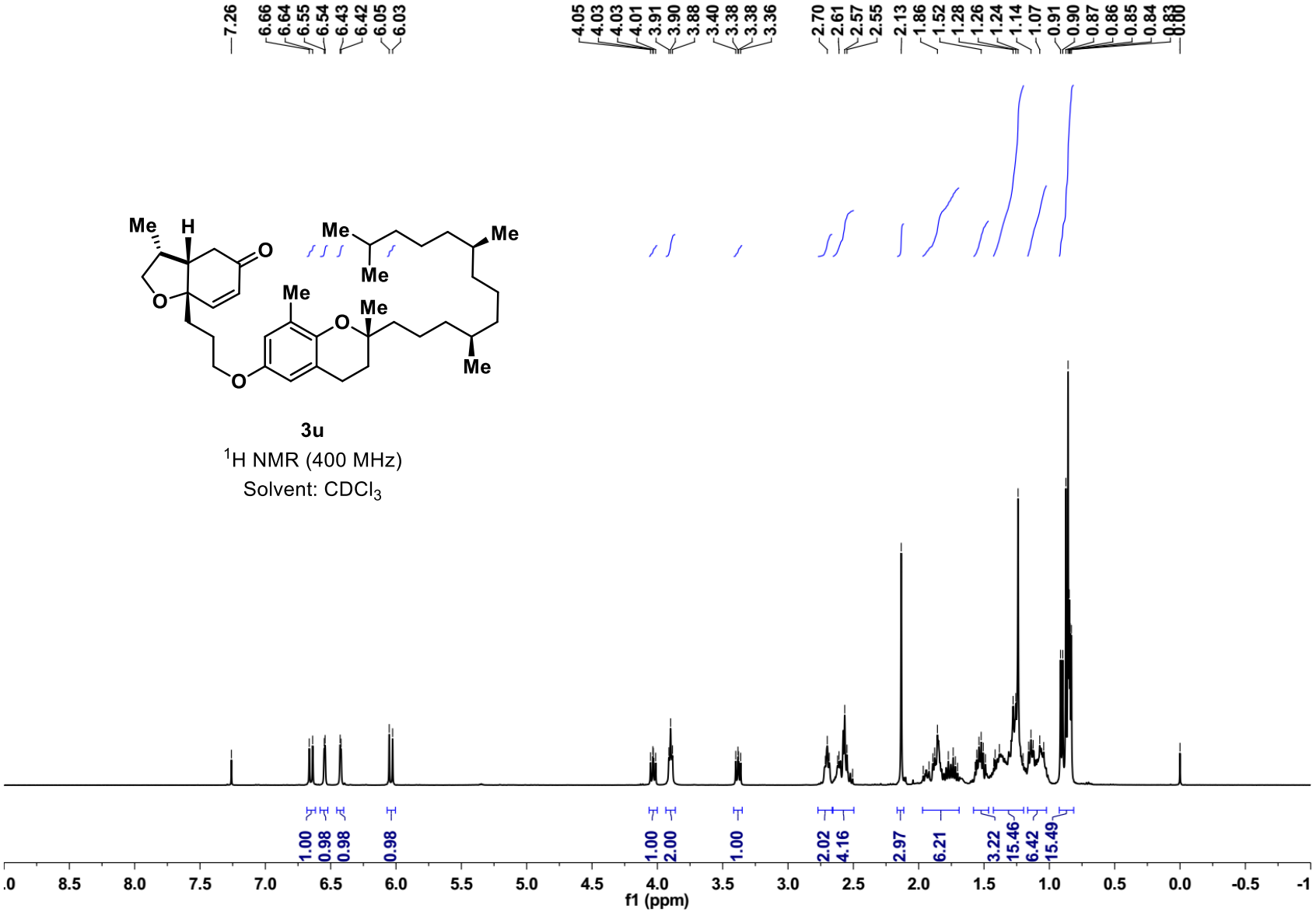


3t'

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$

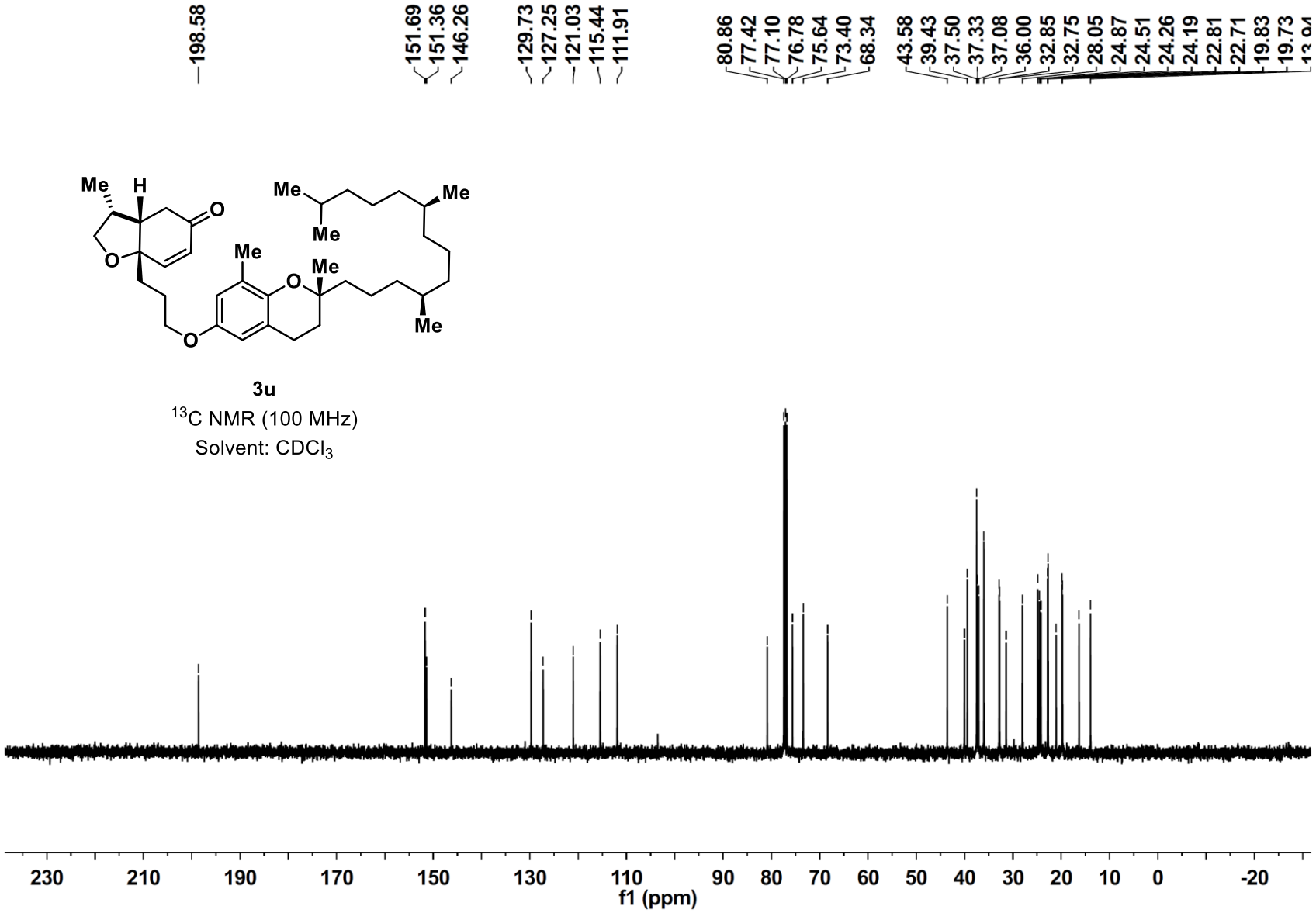

221.02
198.48
156.88
151.58
137.79
132.13
129.73
126.37
114.53
112.05
80.76
77.42
77.10
76.78
73.38
67.73
50.38
48.03
43.98
43.56
38.36
37.02
35.95
35.90
31.58
29.68
25.93
24.09
21.61
13.91
13.87
38.36
37.02
35.95
35.90
13.91
13.87
38.5
37.5
36.5
f1 (ppm)
14.1
13.9
13.7
f1 (ppm)
Me
H
O
O
Me
O
H
H
H
O
3t'
13C NMR (100 HMz)
Solvent: CDCl3
f1 (ppm)

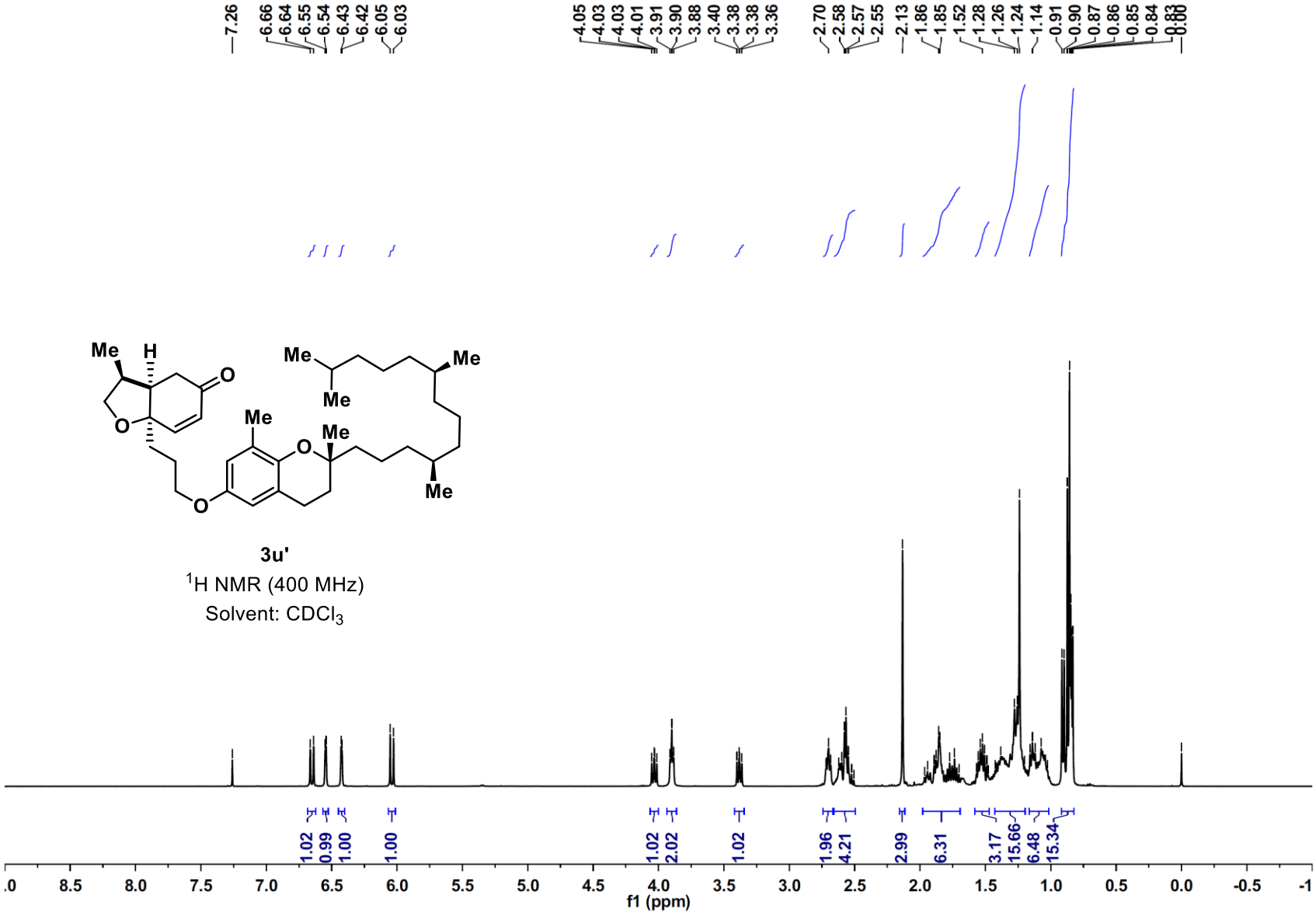


3u

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$

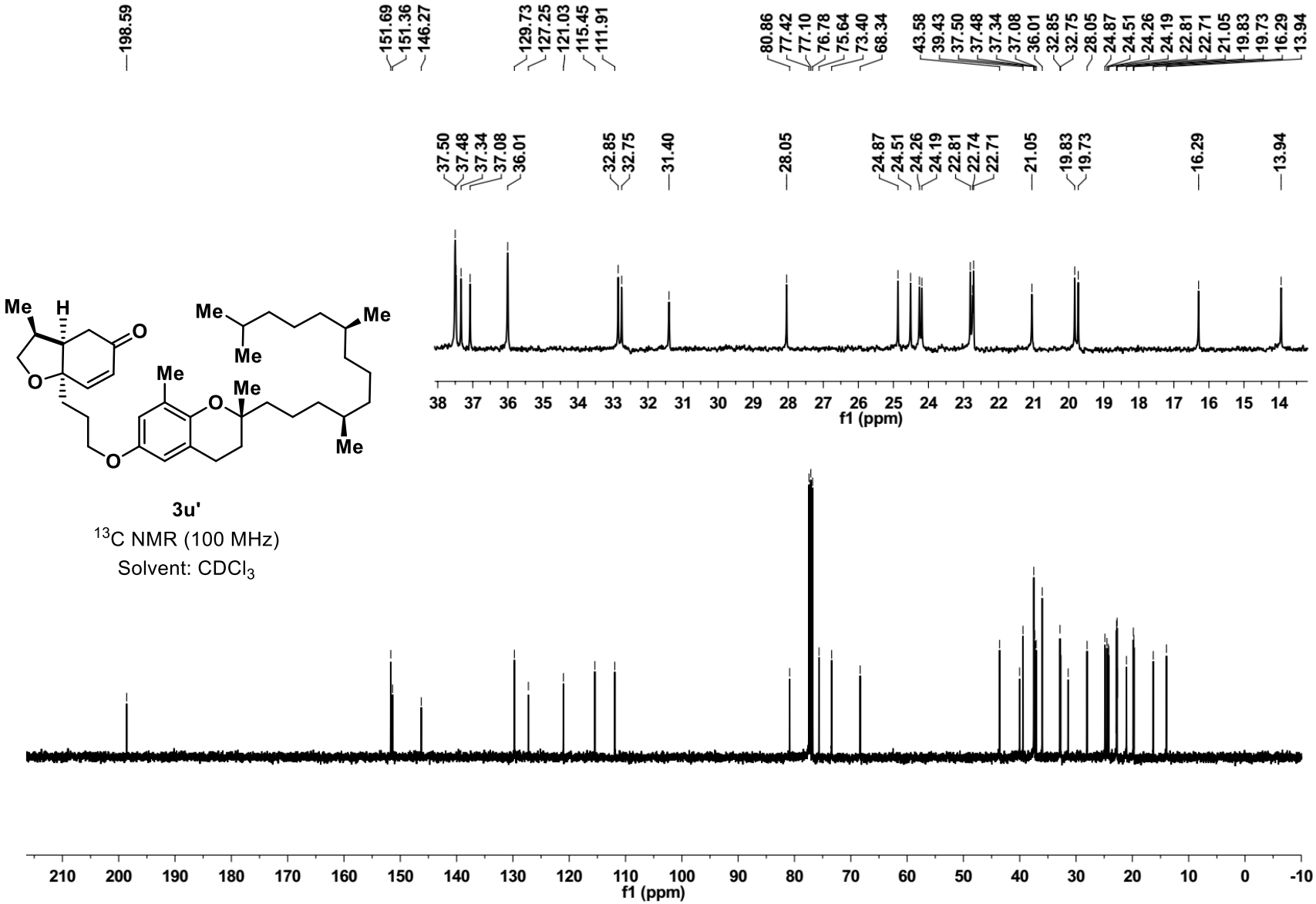

198.58
151.69
151.36
146.26
129.73
127.25
121.03
115.44
111.91
80.86
77.42
77.10
76.78
75.64
73.40
68.34
43.58
39.43
37.50
37.33
37.08
36.00
32.85
32.75
28.05
24.87
24.51
24.26
24.19
22.81
22.71
19.83
19.73
Me
H
O
O
Me
Me
Me
Me
O
Me
O
Me
3u
13C NMR (100 MHz)
Solvent: CDCl3
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
f1 (ppm)

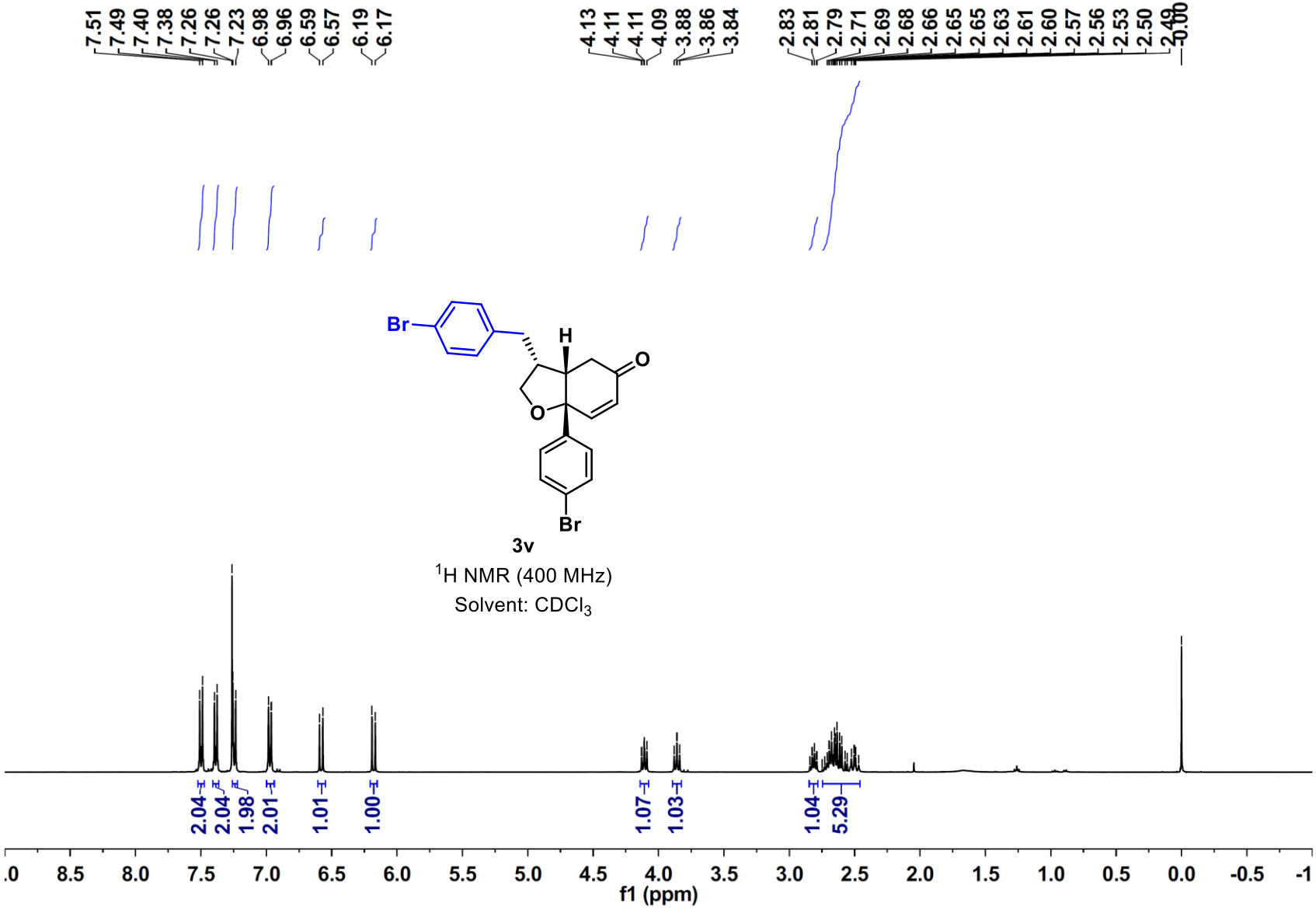


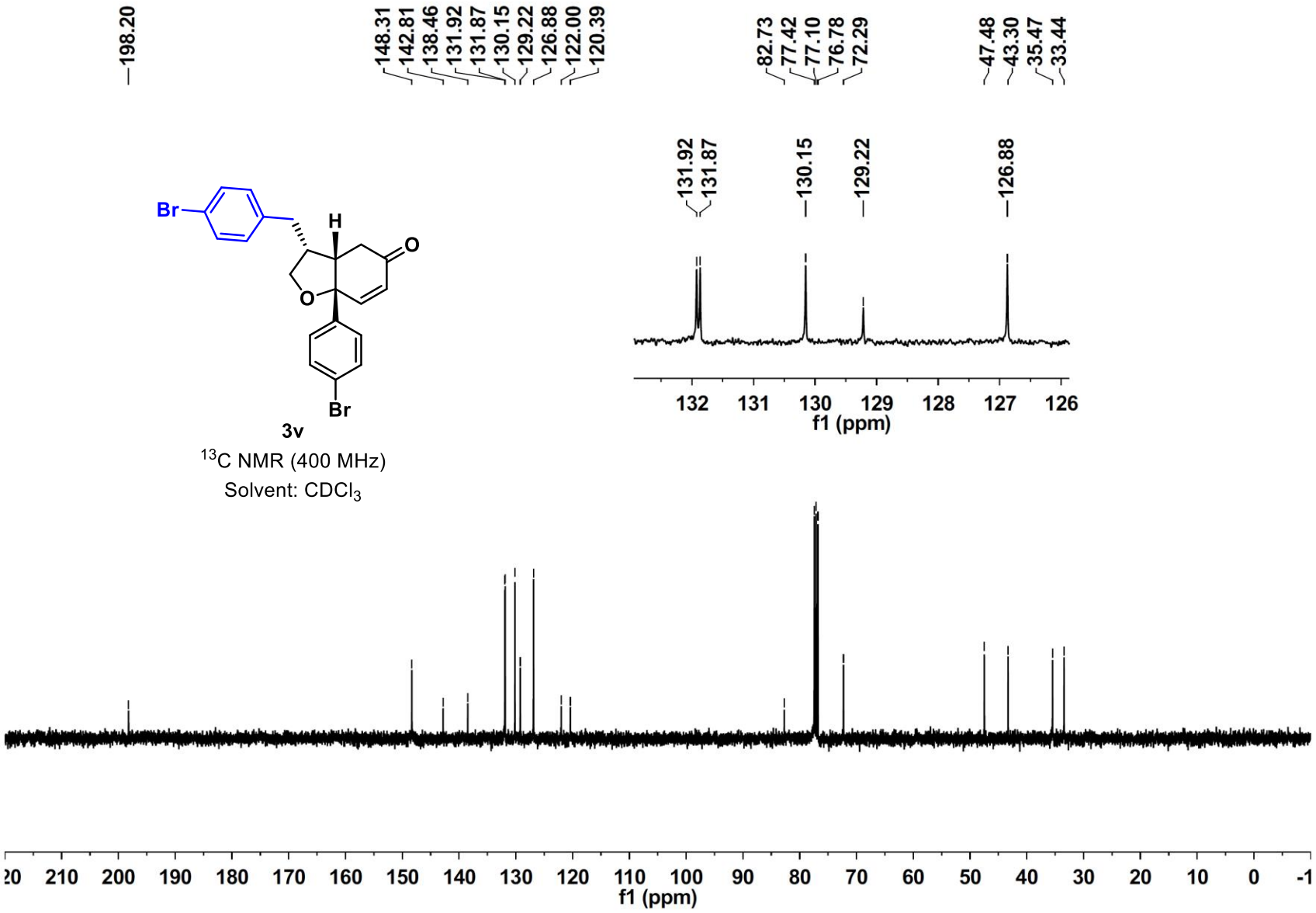
3u'

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$


198.59
151.69
151.36
146.27
129.73
127.25
121.03
115.45
111.91
80.86
77.42
77.10
76.78
75.64
73.40
68.34
43.58
39.43
37.50
37.48
37.34
37.08
36.01
32.85
32.75
28.05
24.87
24.51
24.26
24.19
22.81
22.71
21.05
19.83
19.73
16.29
13.94
Me
H
O
Me
Me
Me
Me
O
O
Me
3u'
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)

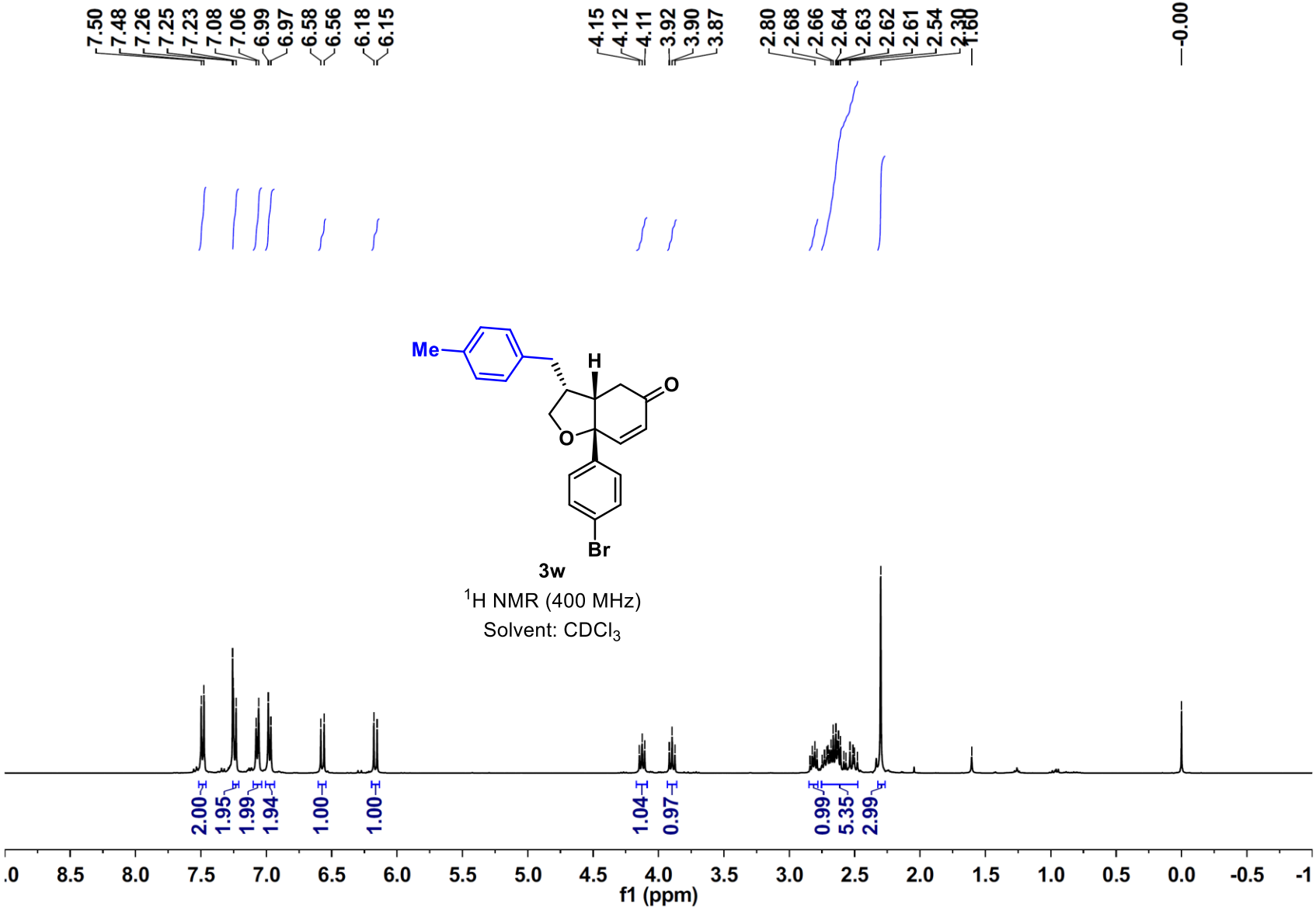

7.51
7.49
7.40
7.38
7.26
7.26
7.23
6.98
6.96
6.59
6.57
6.19
6.17
4.13
4.11
4.11
4.09
3.88
3.86
3.84
2.83
2.81
2.79
2.71
2.69
2.68
2.66
2.65
2.65
2.63
2.61
2.60
2.57
2.56
2.53
2.50
2.49
0.00
Br
H
O
O
Br
3v
1H NMR (400 MHz)
Solvent: CDCl3
2.04
2.04
1.98
2.01
1.01
1.00
1.07
1.03
1.04
5.29
f1 (ppm)

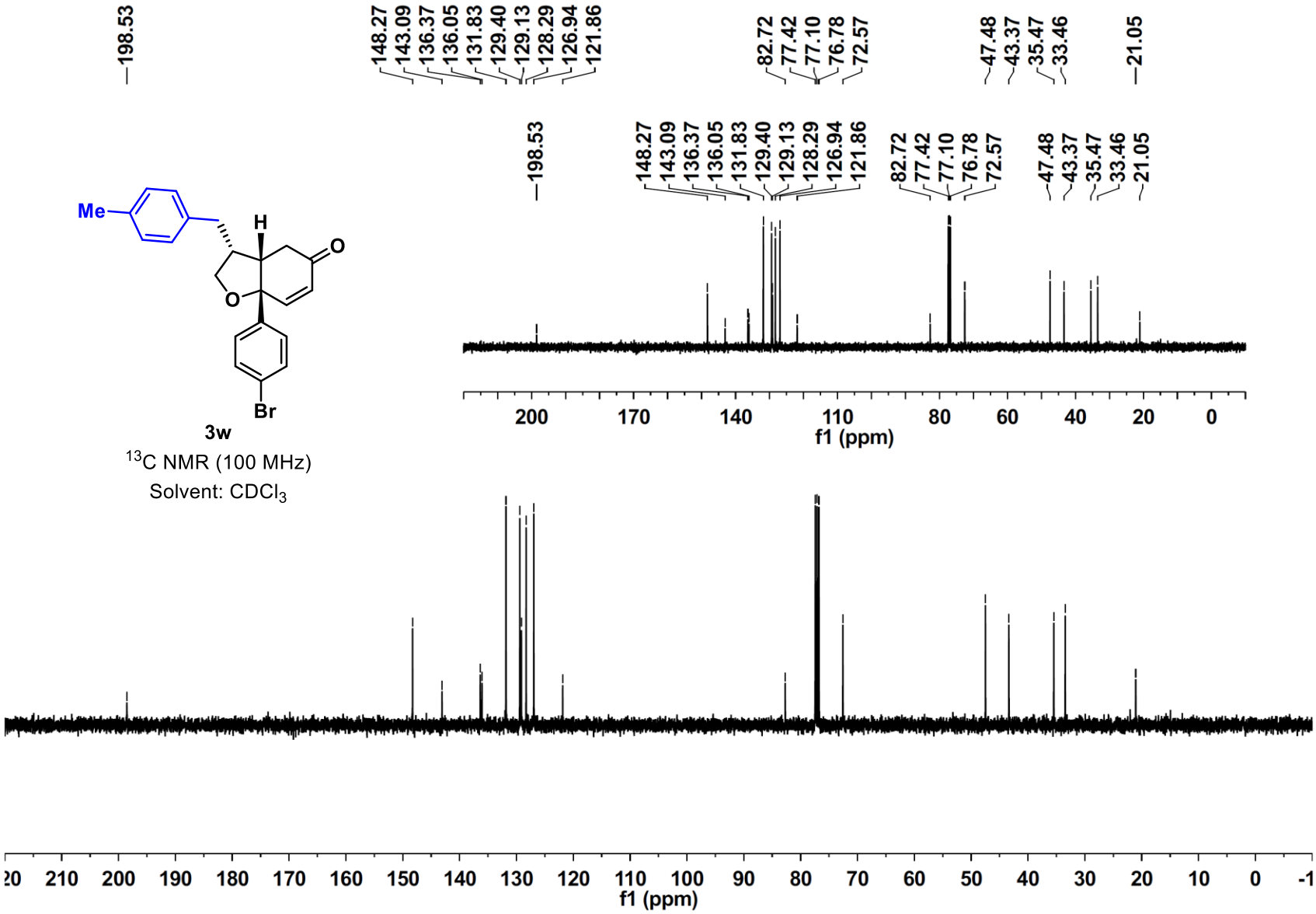


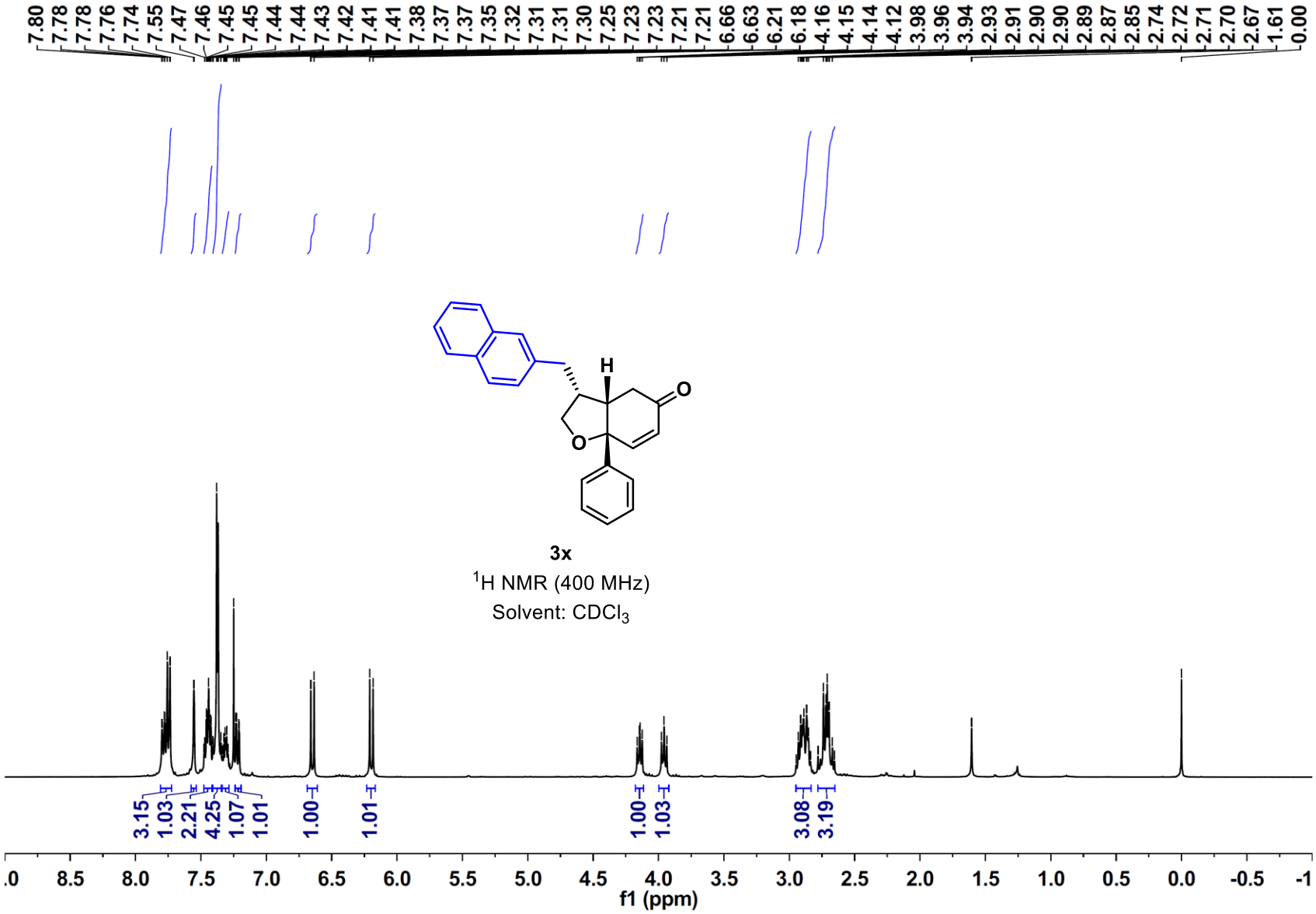
3v

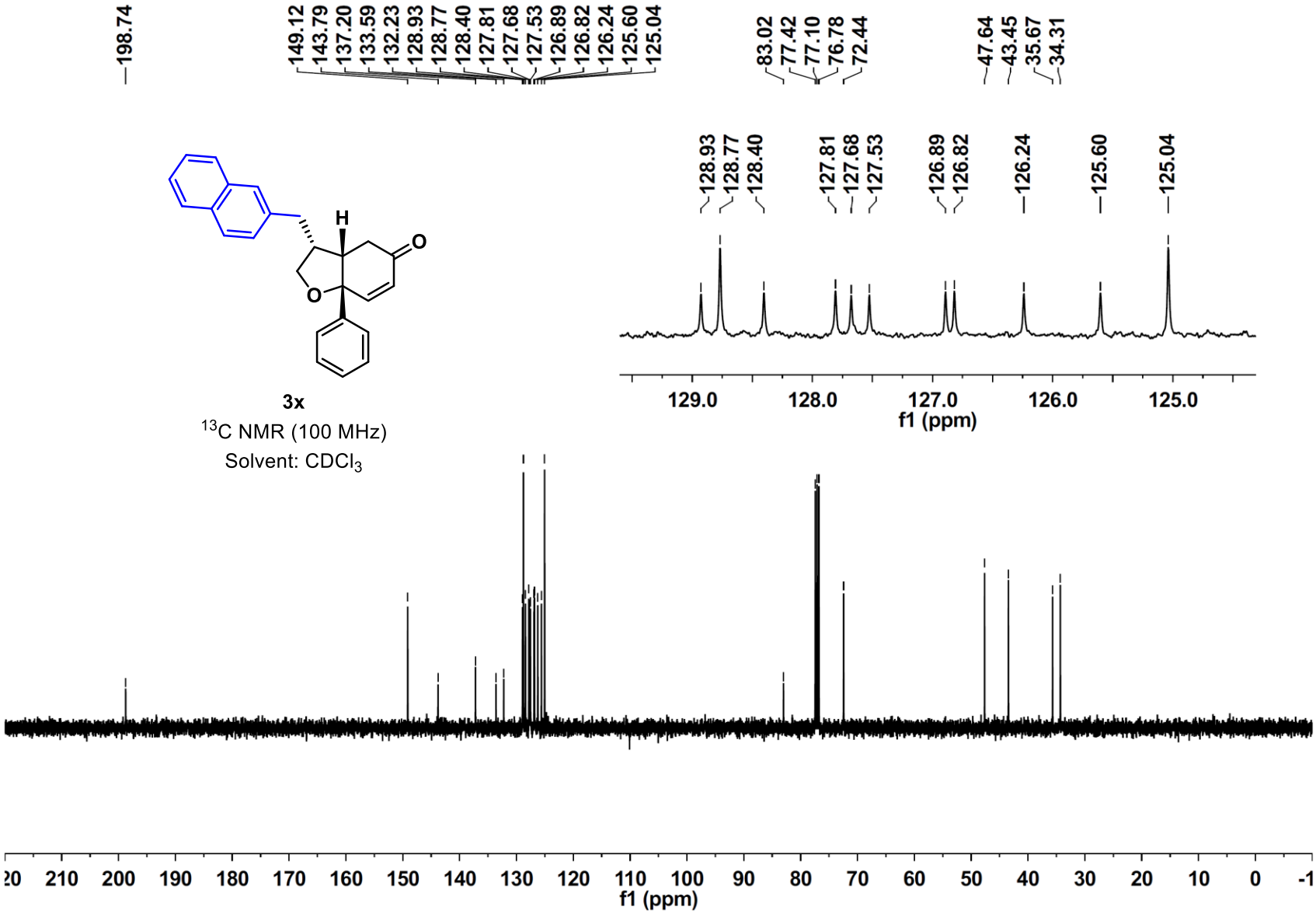
^{13}C NMR (400 MHz)

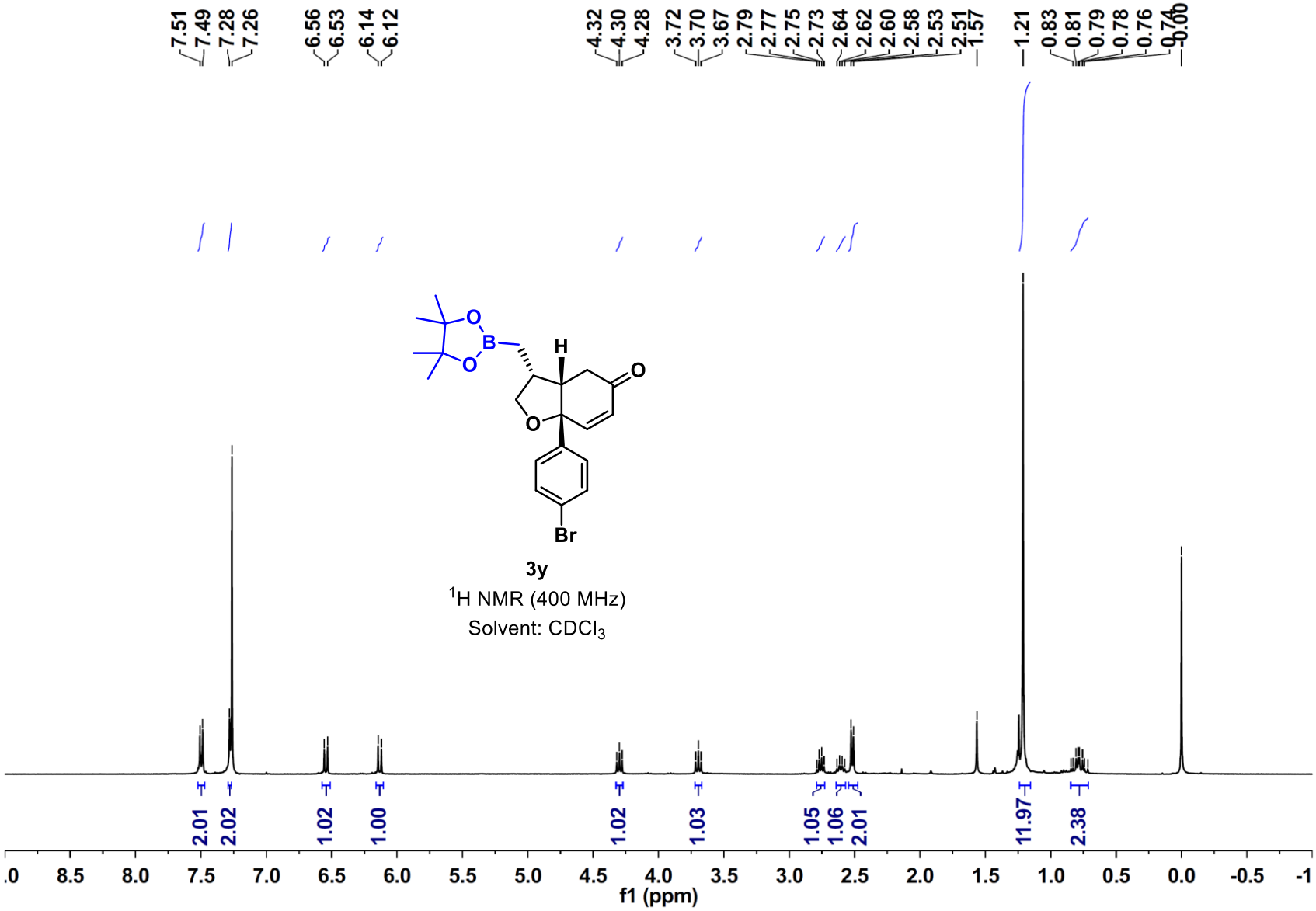
Solvent: $CDCl_3$

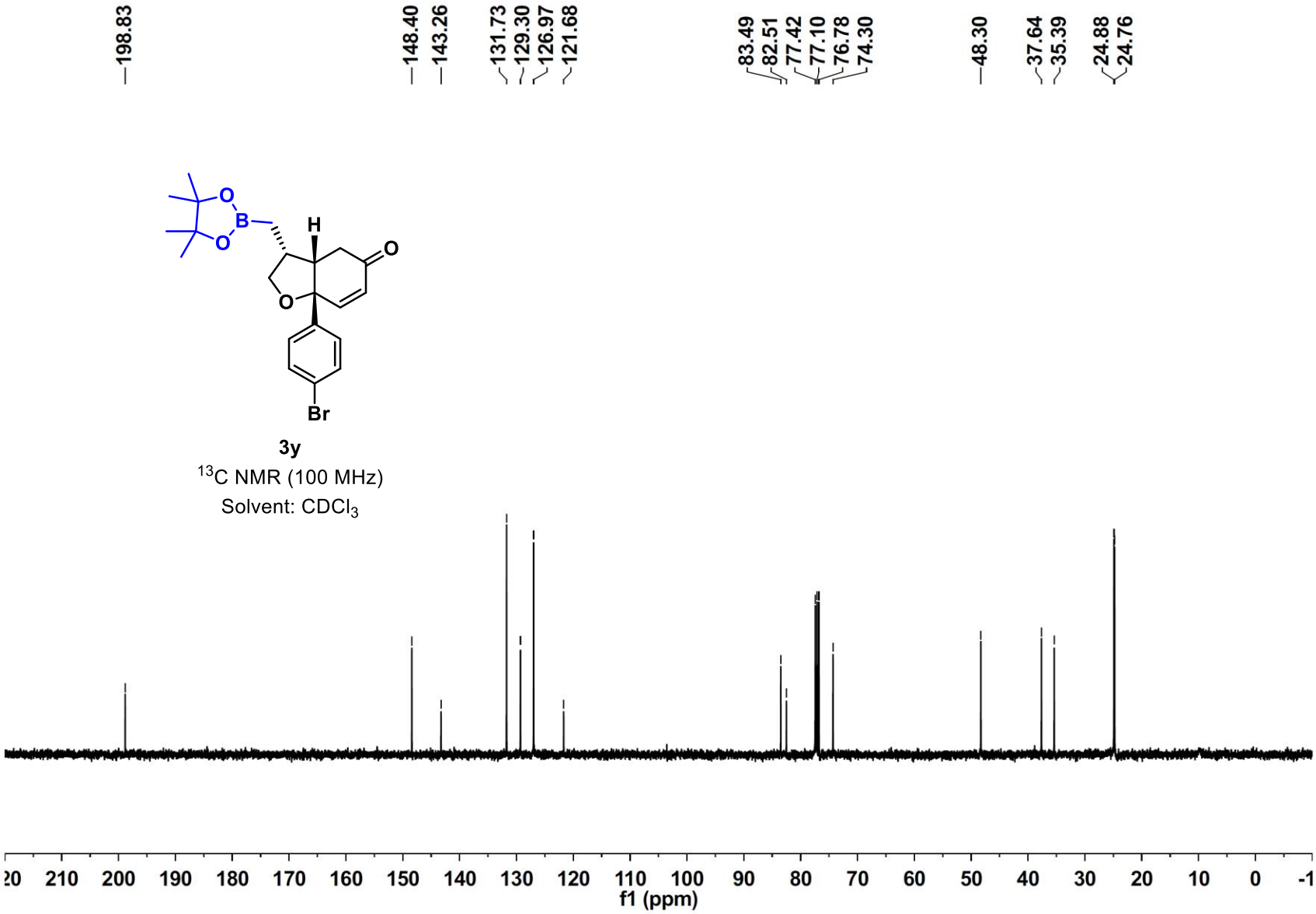

7.50
7.48
7.26
7.25
7.23
7.08
7.06
6.99
6.97
6.58
6.56
6.18
6.15
4.15
4.12
4.11
3.92
3.90
3.87
2.80
2.68
2.66
2.64
2.63
2.62
2.61
2.54
2.30
1.60
0.00
Me
H
O
O
Br
3w
1H NMR (400 MHz)
Solvent: CDCl3
2.00
1.95
1.99
1.94
1.00
1.00
1.04
0.97
0.99
5.35
2.99
f1 (ppm)


198.53
148.27
143.09
136.37
136.05
131.83
129.40
129.13
128.29
126.94
121.86
82.72
77.42
77.10
76.78
72.57
47.48
43.37
35.47
33.46
21.05
Me
H
O
O
Br
3w
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


7.80 7.78 7.78 7.76 7.74 7.55 7.47 7.46 7.45 7.45 7.44 7.44 7.43 7.42 7.41 7.41 7.38 7.37 7.37 7.35 7.32 7.31 7.31 7.30 7.25 7.23 7.23 7.21 7.21 6.66 6.63 6.21 6.18 4.16 4.15 4.14 4.12 3.98 3.96 3.94 2.93 2.91 2.90 2.90 2.89 2.87 2.85 2.74 2.72 2.71 2.70 2.67 1.61 0.00
H
O
O
3x
1H NMR (400 MHz)
Solvent: CDCl3
3.15 1.03 2.21 4.25 1.07 1.01 1.00 1.01 1.00 1.03 3.08 3.19
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


198.74
149.12
143.79
137.20
133.59
132.23
128.93
128.77
128.40
127.81
127.68
127.53
126.89
126.82
126.24
125.60
125.04
83.02
77.42
77.10
76.78
72.44
47.64
43.45
35.67
34.31
H
O
O
3x
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)

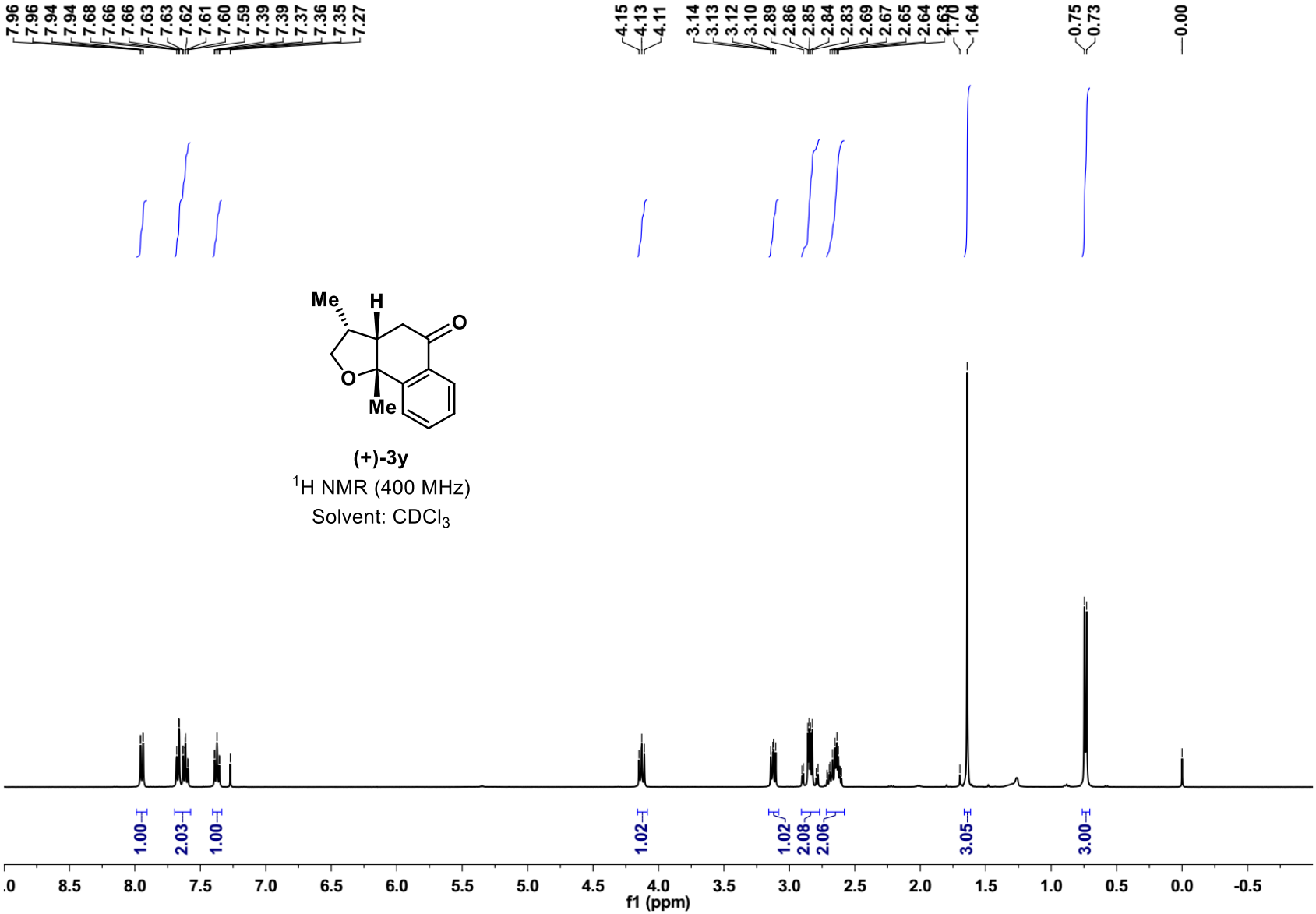

7.51
7.49
7.28
7.26
6.56
6.53
6.14
6.12
4.32
4.30
4.28
3.72
3.70
3.67
2.79
2.77
2.75
2.73
2.64
2.62
2.60
2.58
2.53
2.51
1.57
1.21
0.83
0.81
0.79
0.78
0.76
0.74
0.00
O
B
O
H
O
O
Br
3y
1H NMR (400 MHz)
Solvent: CDCl3
2.01
2.02
1.02
1.00
1.02
1.03
1.05
1.06
2.01
11.97
2.38
f1 (ppm)



3y

^{13}C NMR (100 MHz)

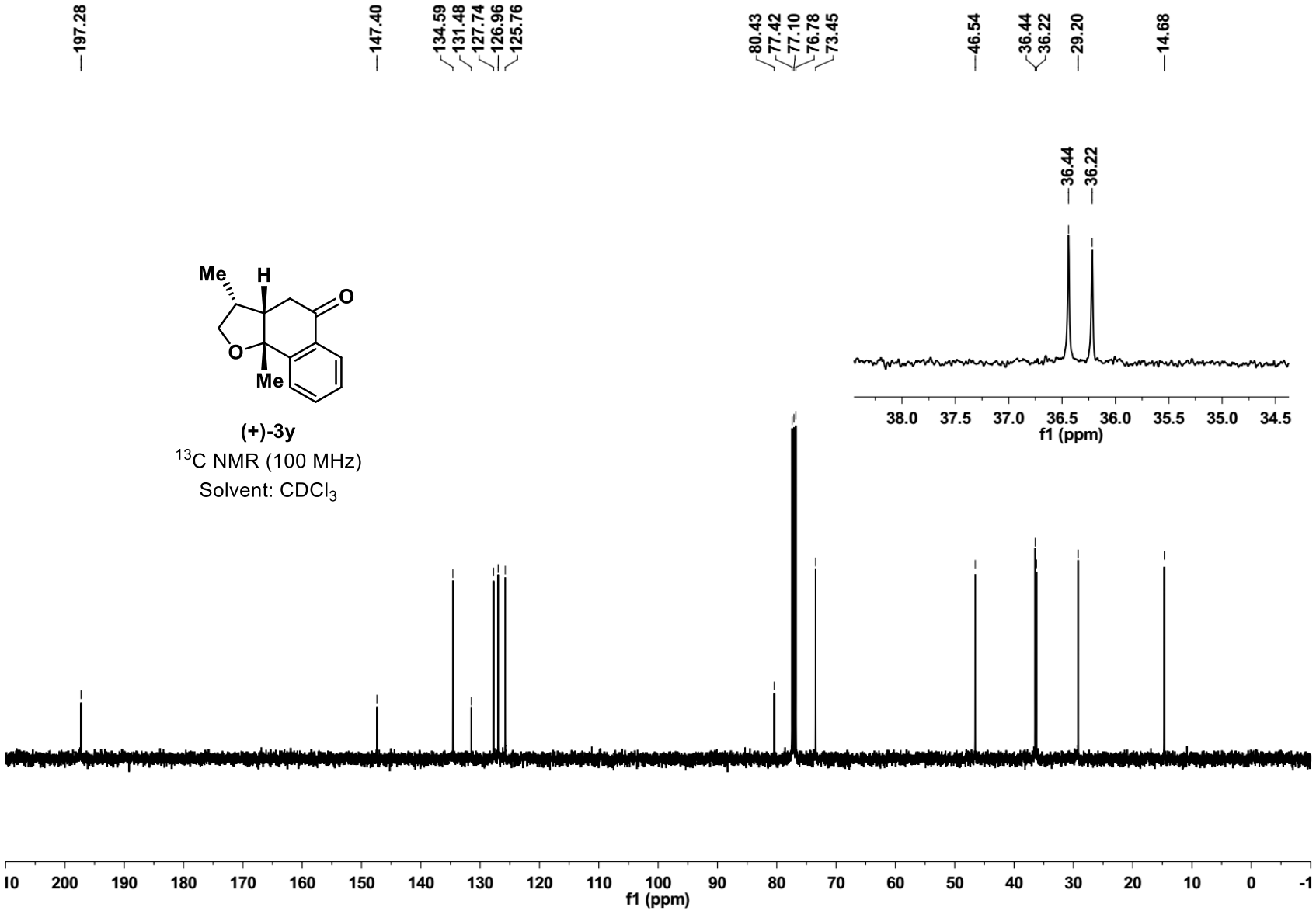
Solvent: $CDCl_3$

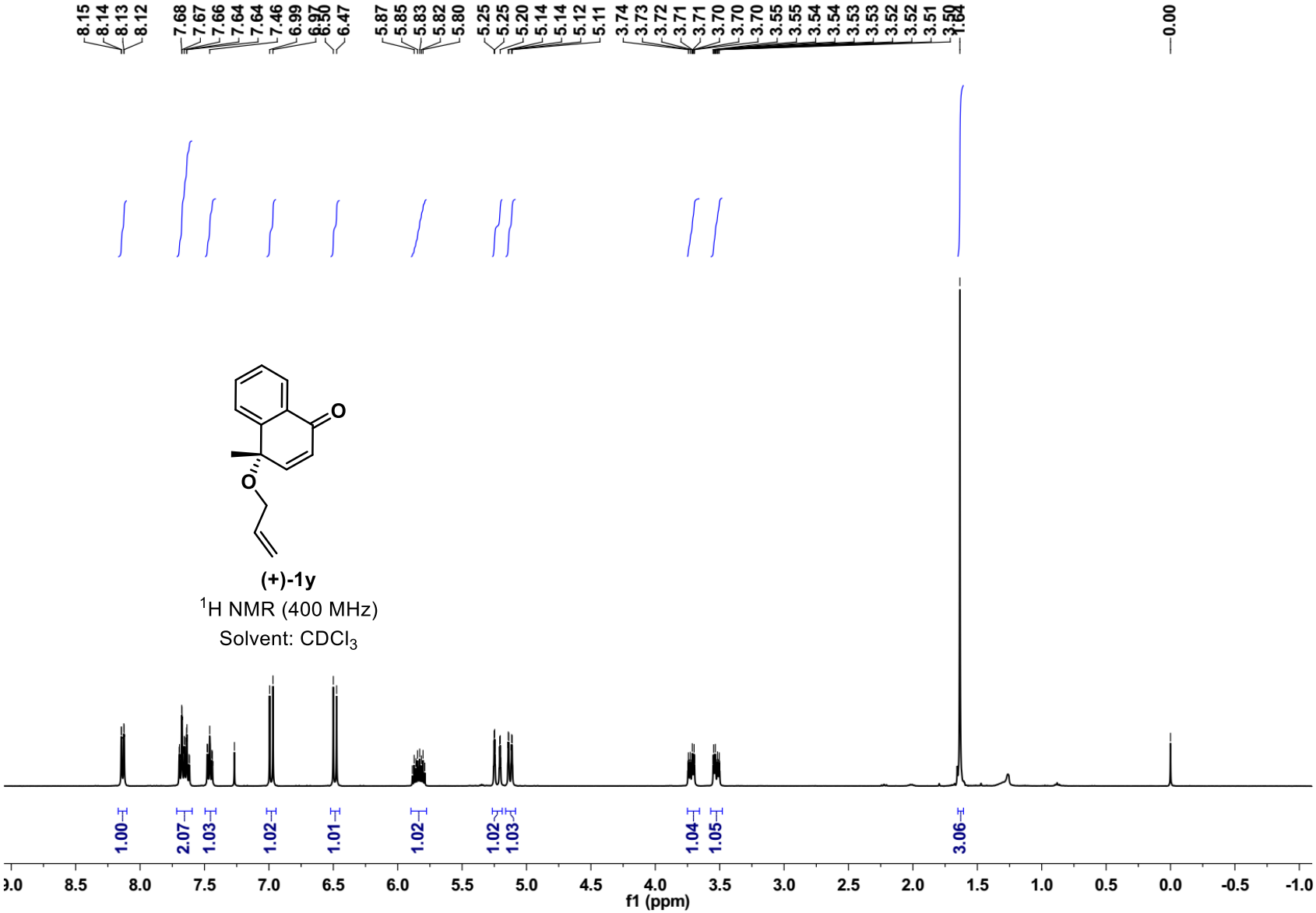


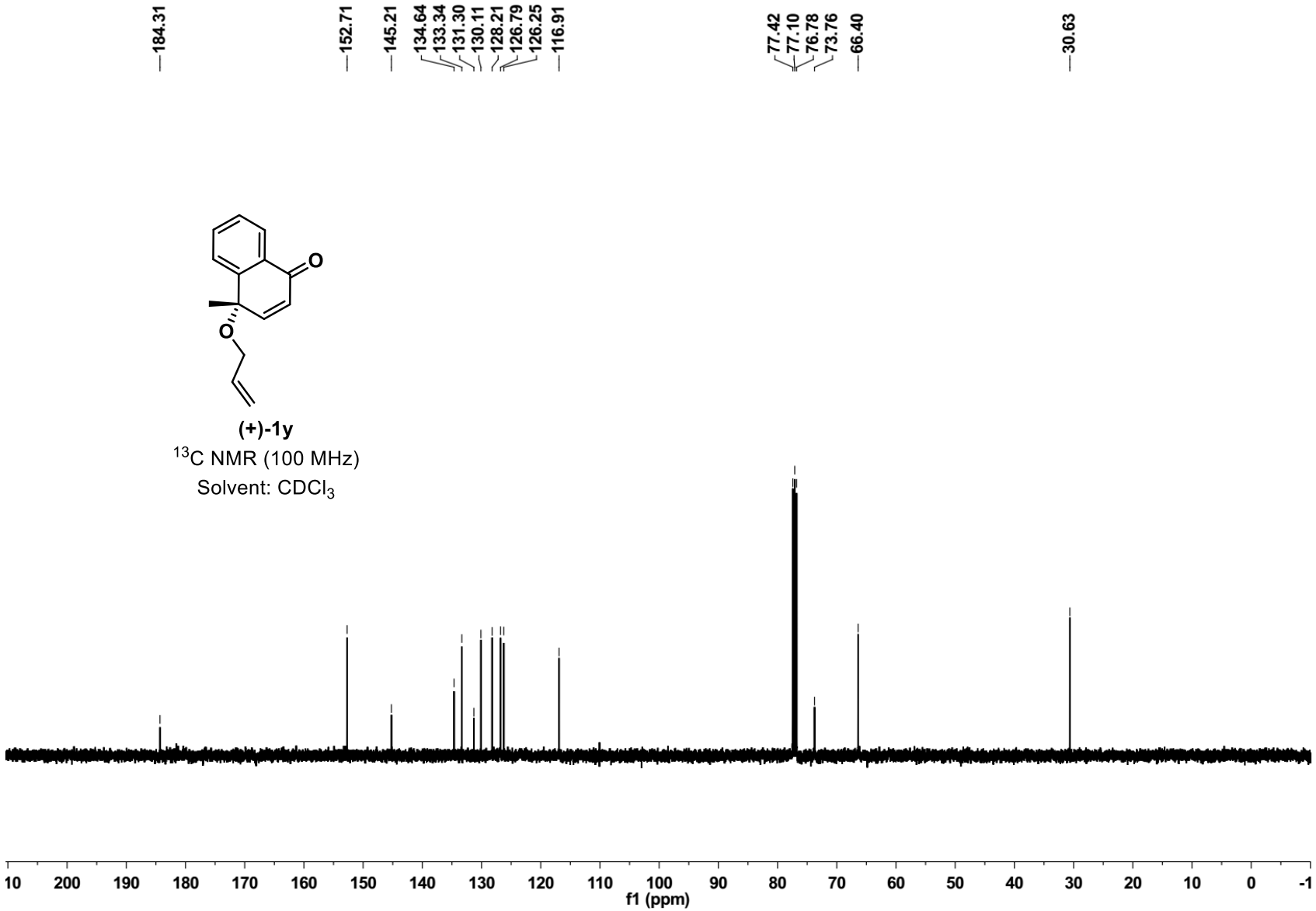
(+)-3y

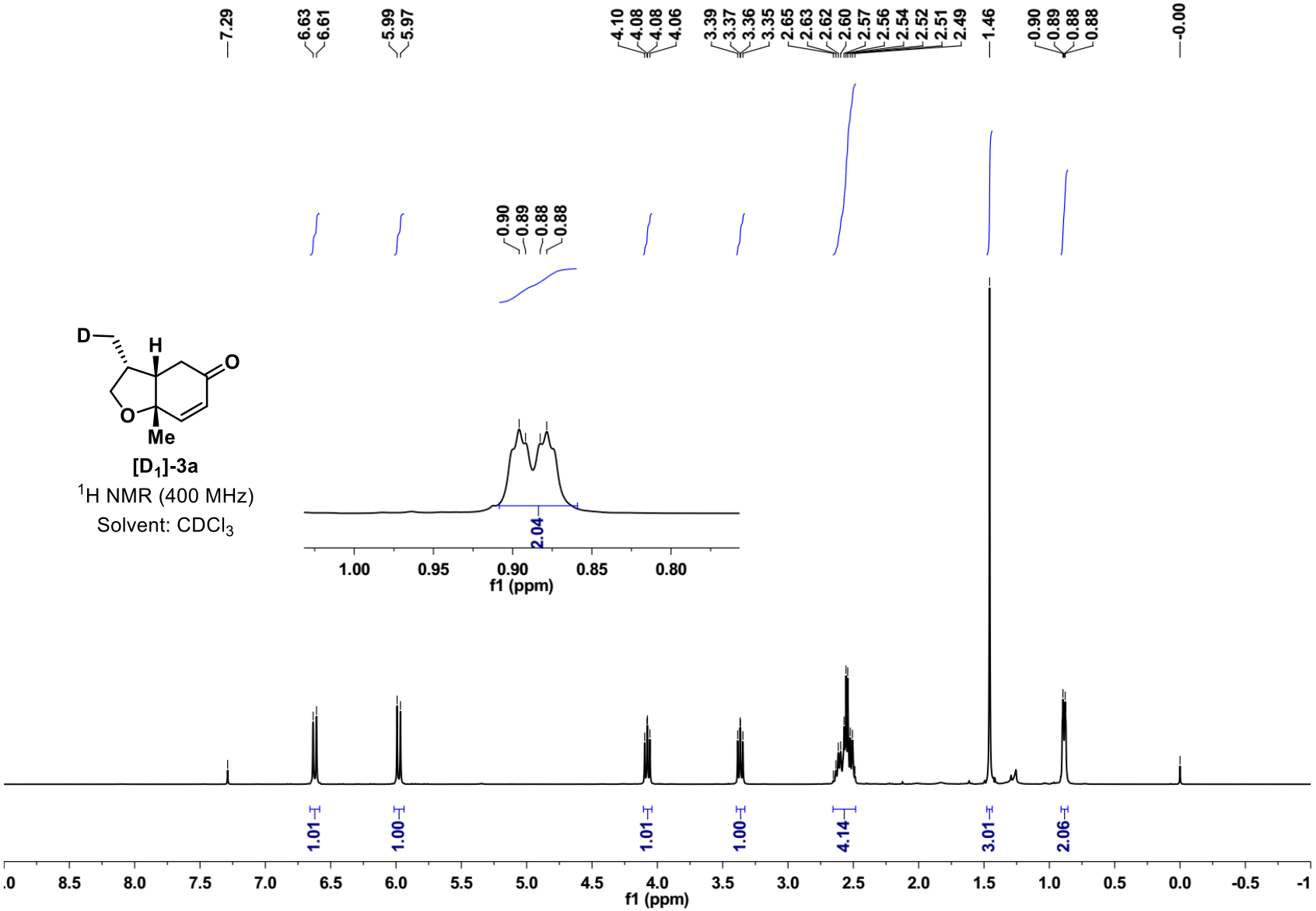
^{1}H NMR (400 MHz)

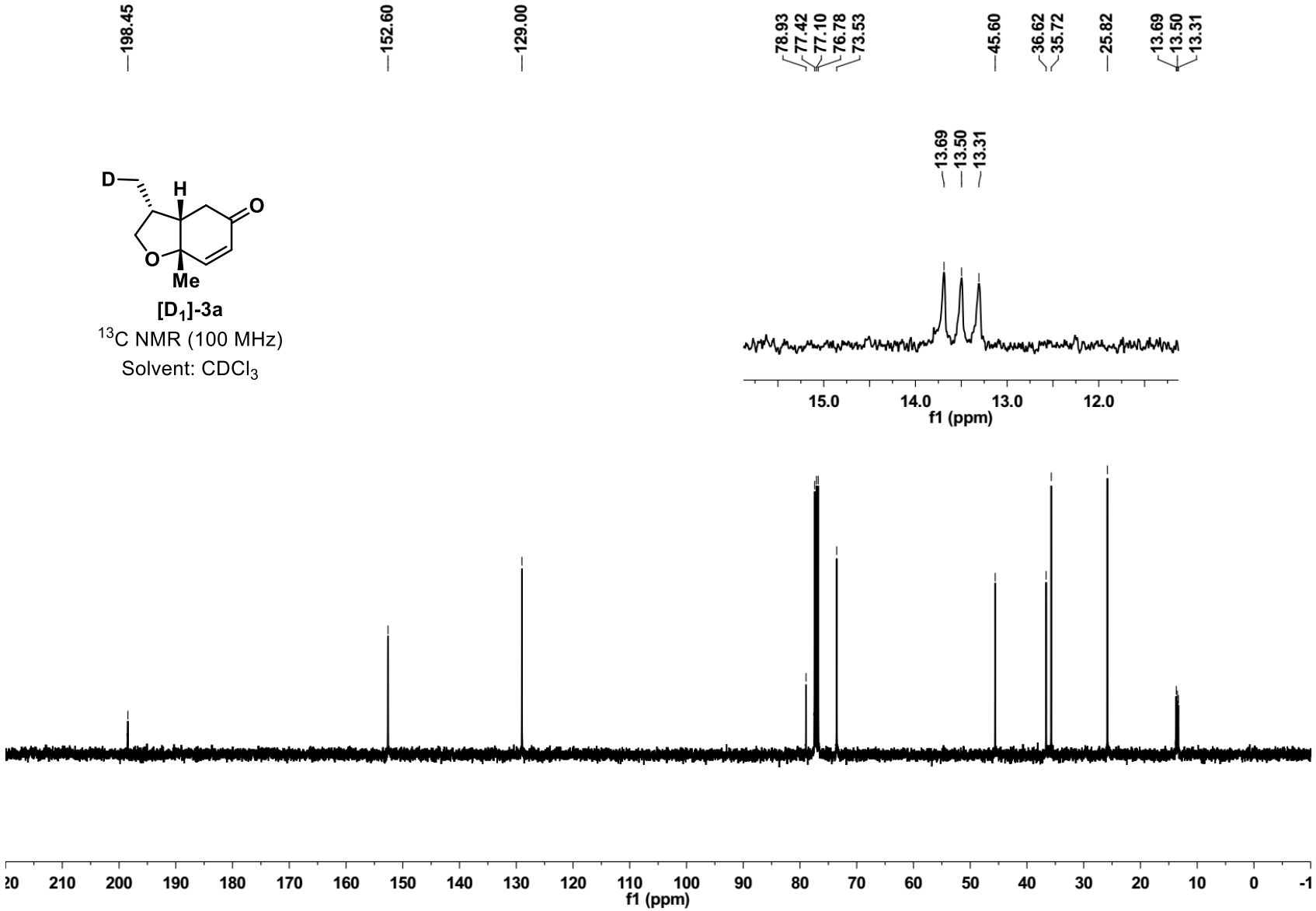
Solvent: $CDCl_3$

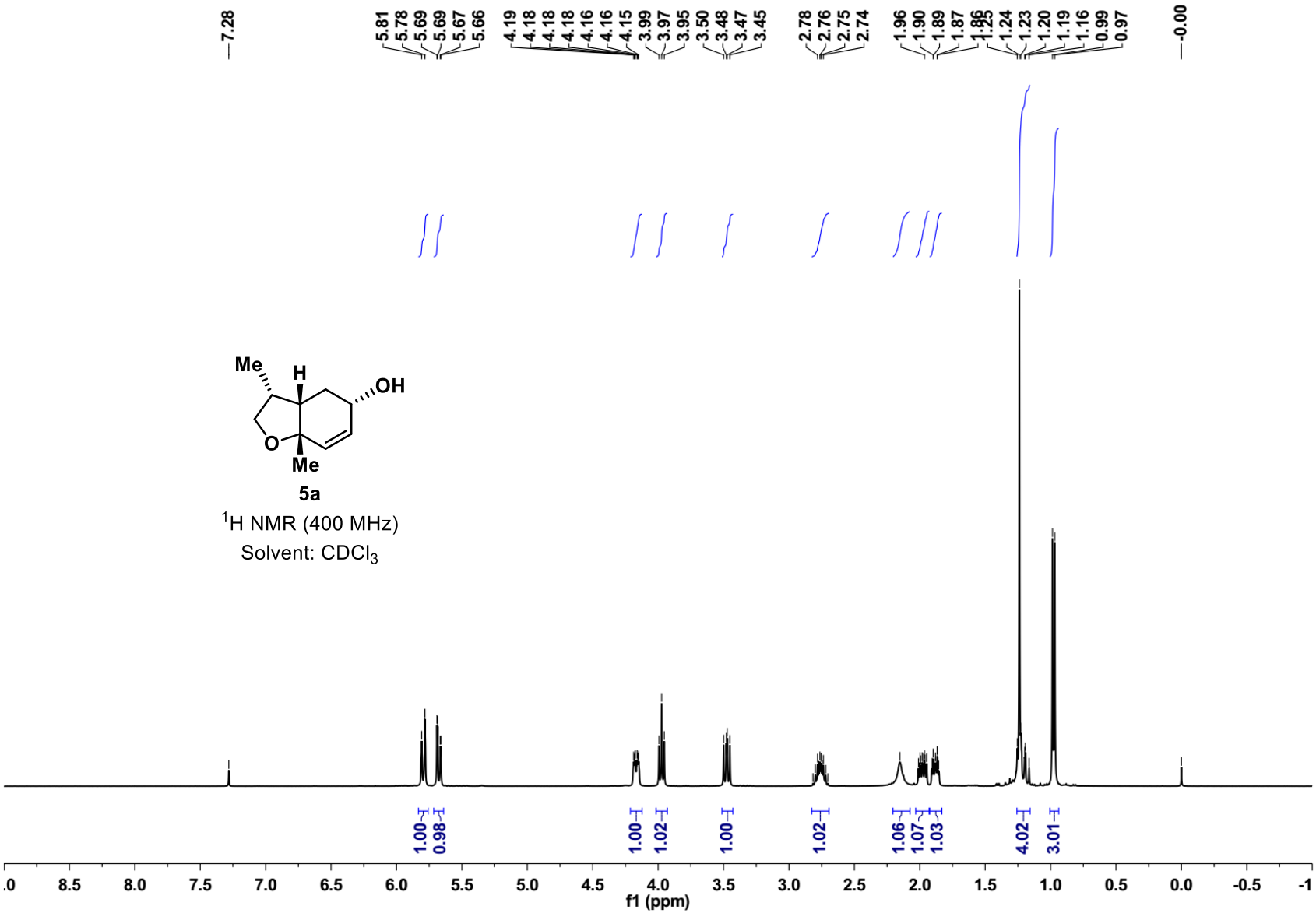

197.28
147.40
134.59
131.48
127.74
126.96
125.76
80.43
77.42
77.10
76.78
73.45
46.54
36.44
36.22
29.20
14.68
Me
H
O
O
Me
(+)-3y
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

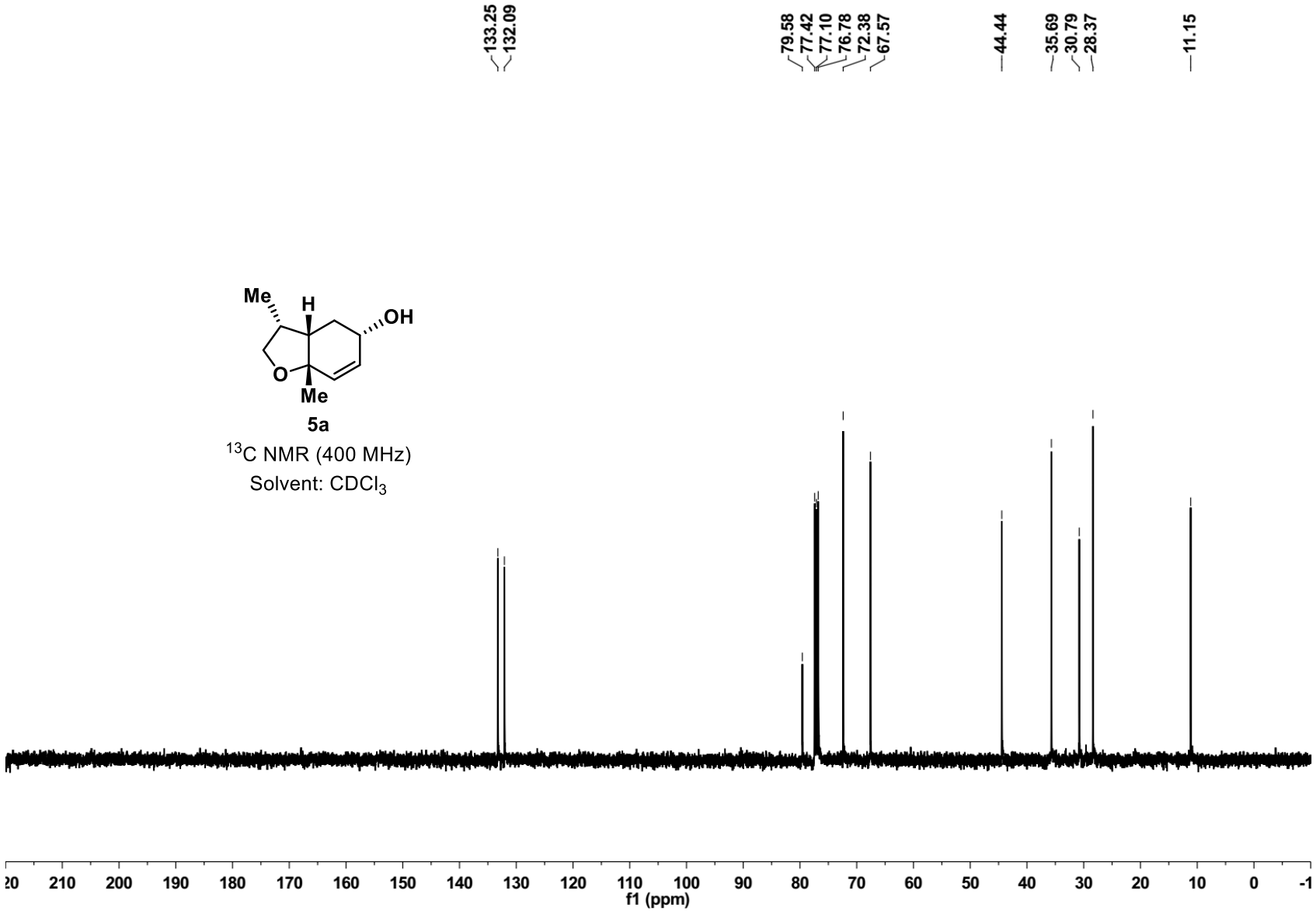

8.15
8.14
8.13
8.12
7.68
7.67
7.66
7.64
7.64
7.46
6.99
6.97
6.50
6.47
5.87
5.85
5.83
5.82
5.80
5.25
5.25
5.20
5.14
5.14
5.12
5.11
3.74
3.73
3.72
3.71
3.71
3.70
3.70
3.70
3.55
3.55
3.54
3.54
3.53
3.53
3.52
3.52
3.51
3.50
1.64
0.00
O
O
(+)-1y
1H NMR (400 MHz)
Solvent: CDCl3
1.00
2.07
1.03
1.02
1.01
1.02
1.02
1.03
1.04
1.05
3.06
f1 (ppm)

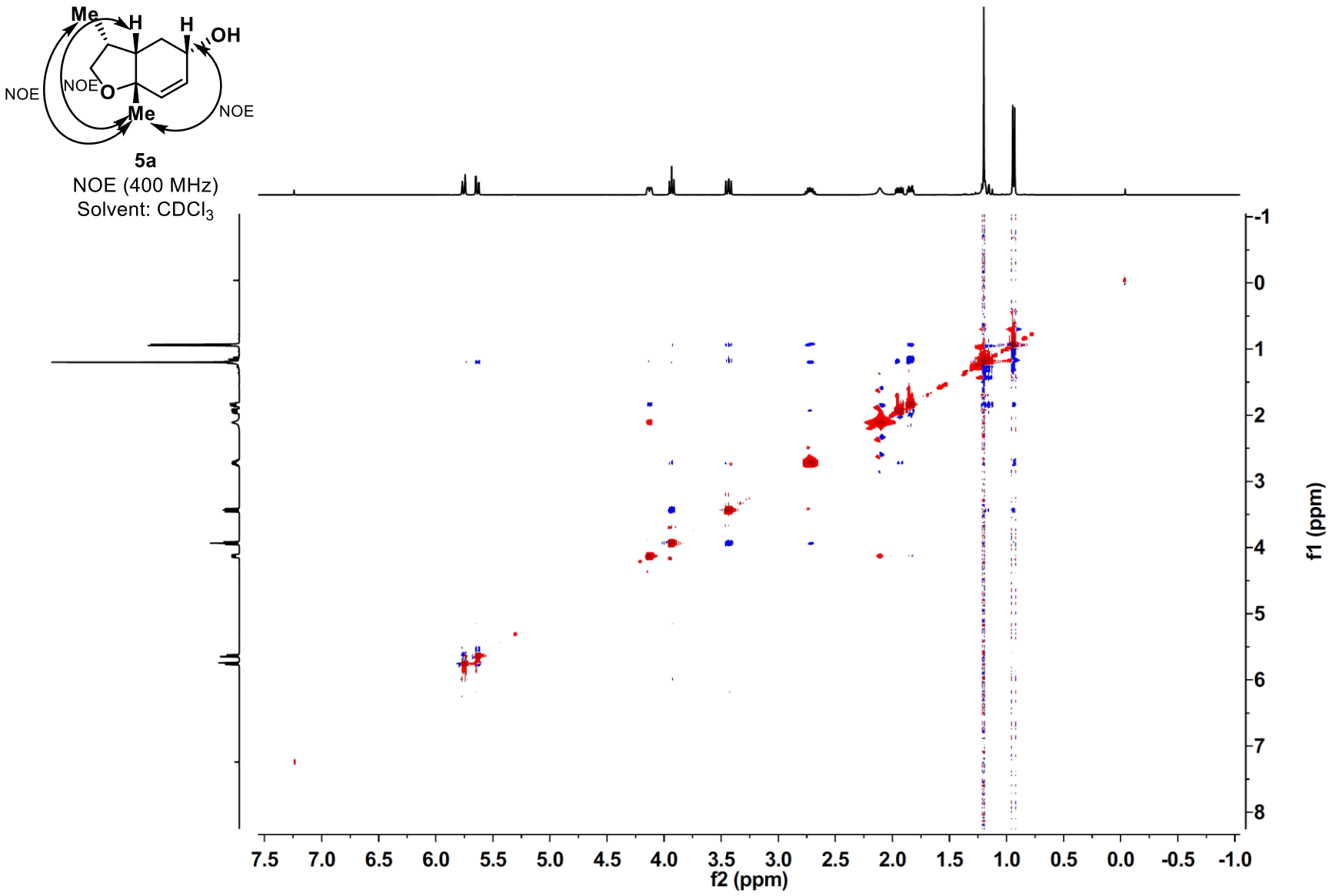

184.31
152.71
145.21
134.64
133.34
131.30
130.11
128.21
126.79
126.25
116.91
77.42
77.10
76.78
73.76
66.40
30.63
O
O
(+)-1y
13C NMR (100 MHz)
Solvent: CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

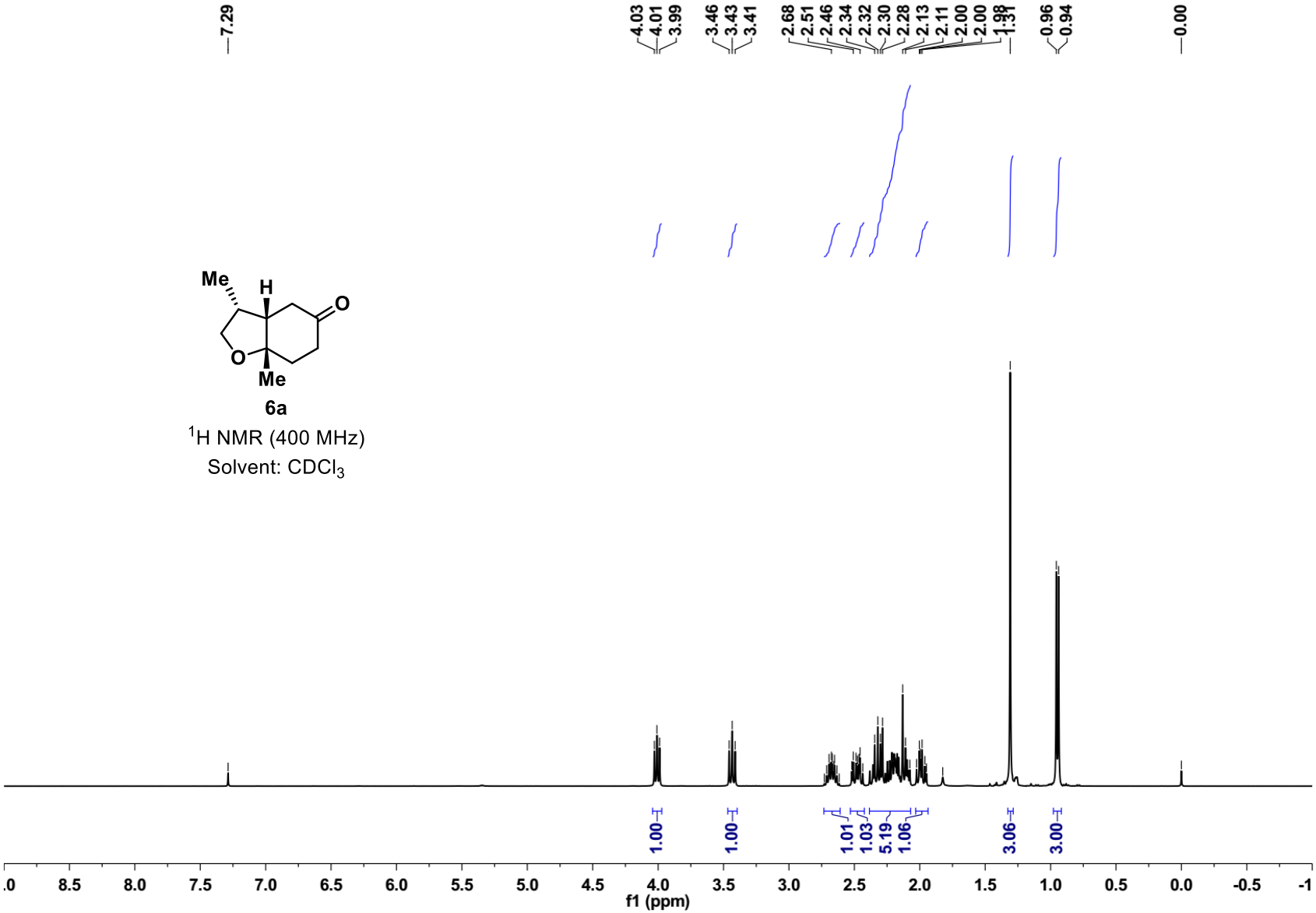

7.29
6.63
6.61
5.99
5.97
4.10
4.08
4.08
4.06
3.39
3.37
3.36
3.35
2.65
2.63
2.62
2.60
2.57
2.56
2.54
2.52
2.51
2.49
1.46
0.90
0.89
0.88
0.88
-0.00
D
H
O
O
Me
[D1]-3a
1H NMR (400 MHz)
Solvent: CDCl3
2.04
1.00
0.95
0.90
0.85
0.80
f1 (ppm)
1.01
1.00
1.01
1.00
4.14
3.01
2.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


198.45
152.60
129.00
78.93
77.42
77.10
76.78
73.53
45.60
36.62
35.72
25.82
13.69
13.50
13.31
D
H
O
O
Me
[D1]-3a
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)


7.28
5.81
5.78
5.69
5.69
5.67
5.66
4.19
4.18
4.18
4.18
4.16
4.16
4.15
3.99
3.97
3.95
3.50
3.48
3.47
3.45
2.78
2.76
2.75
2.74
1.96
1.90
1.89
1.87
1.86
1.85
1.24
1.23
1.20
1.19
1.16
0.99
0.97
0.00
Me
H
OH
O
Me
5a
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.98
1.00
1.02
1.00
1.02
1.06
1.07
1.03
4.02
3.01
f1 (ppm)


133.25
132.09
79.58
77.42
77.10
76.78
72.38
67.57
44.44
35.69
30.79
28.37
11.15
Me
H
OH
O
Me
5a
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)

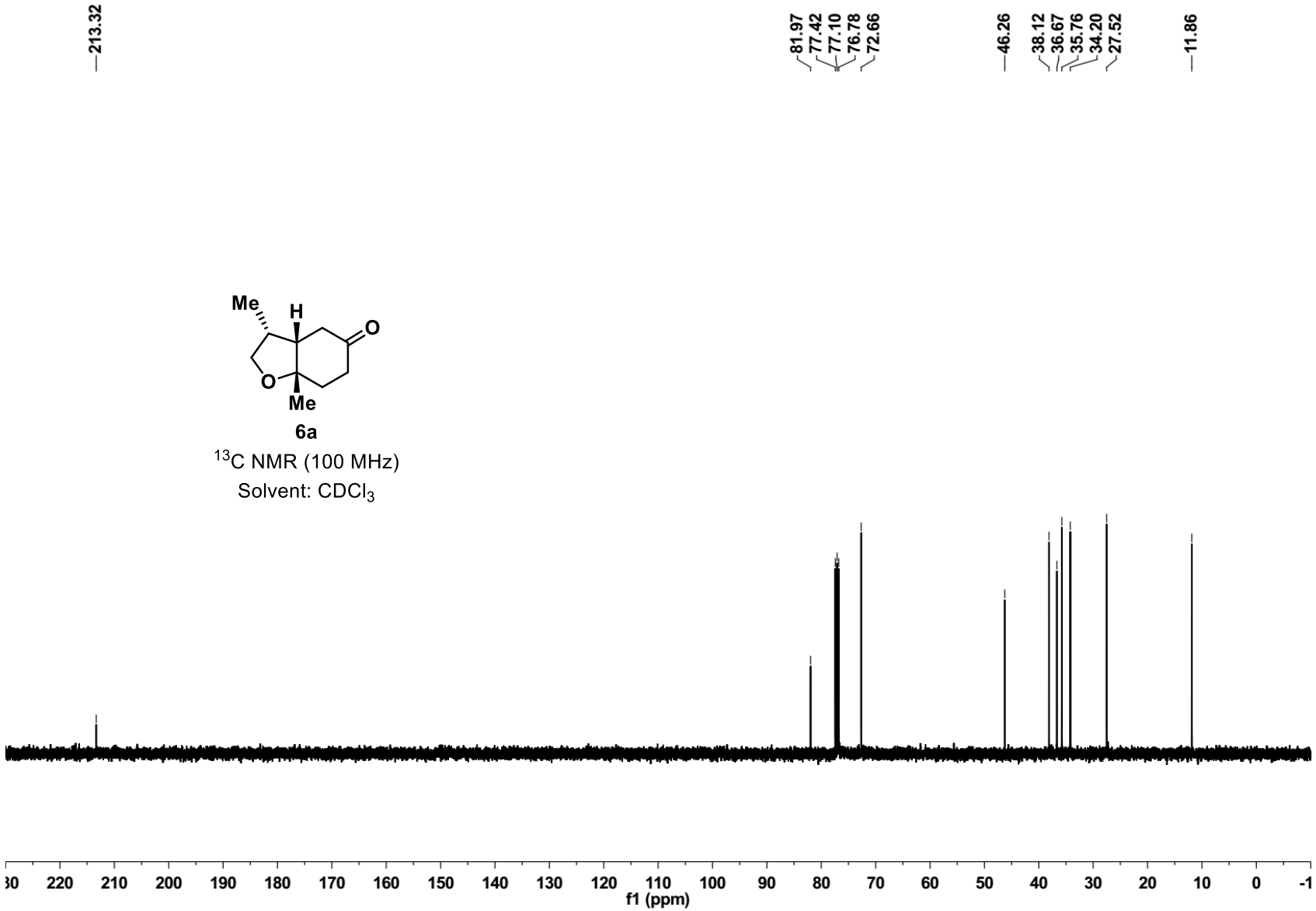

Me
H
H
OH
NOE
NOE
O
Me
NOE
5a
NOE (400 MHz)
Solvent: CDCl3
f2 (ppm)
f1 (ppm)

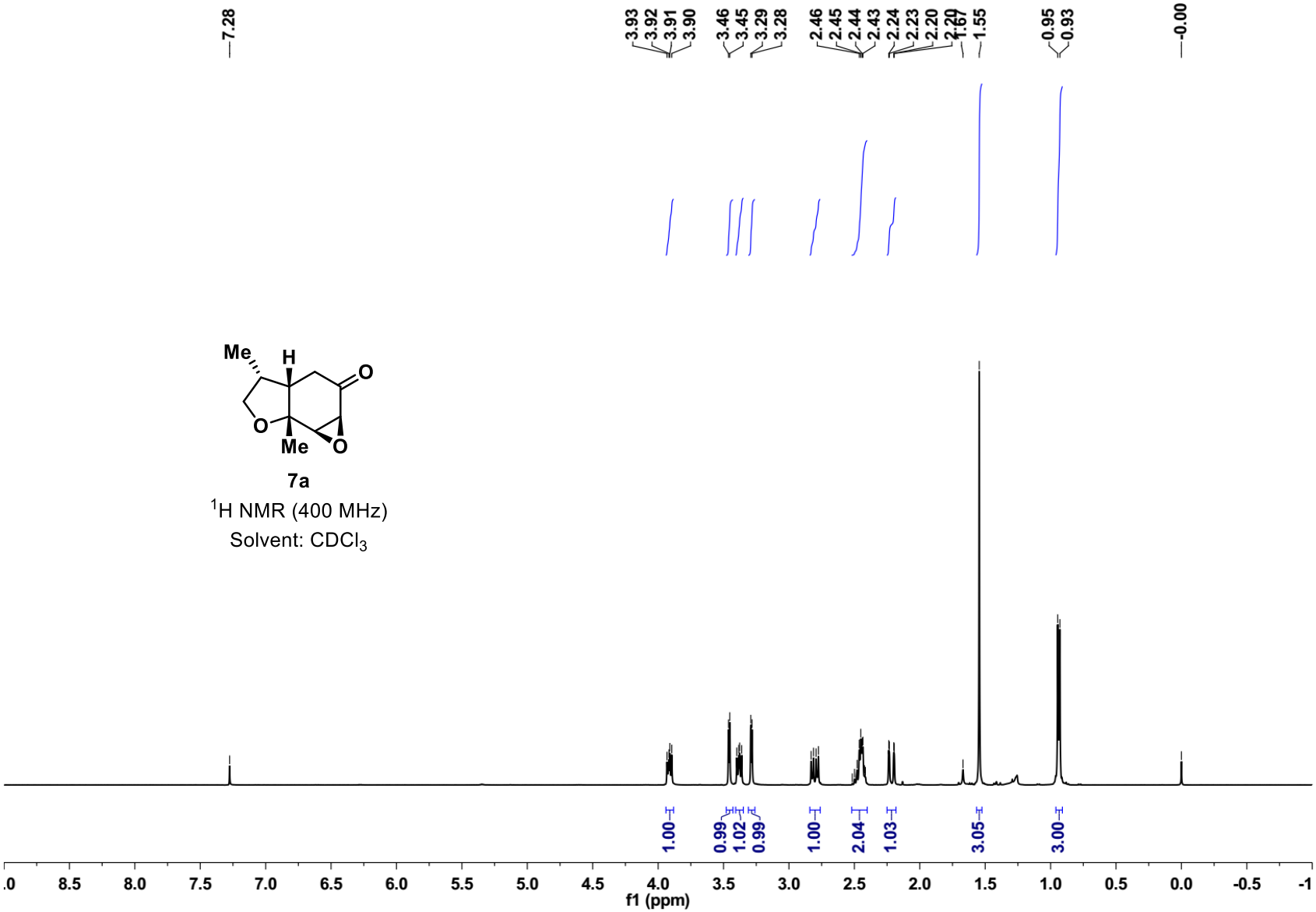


6a

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$

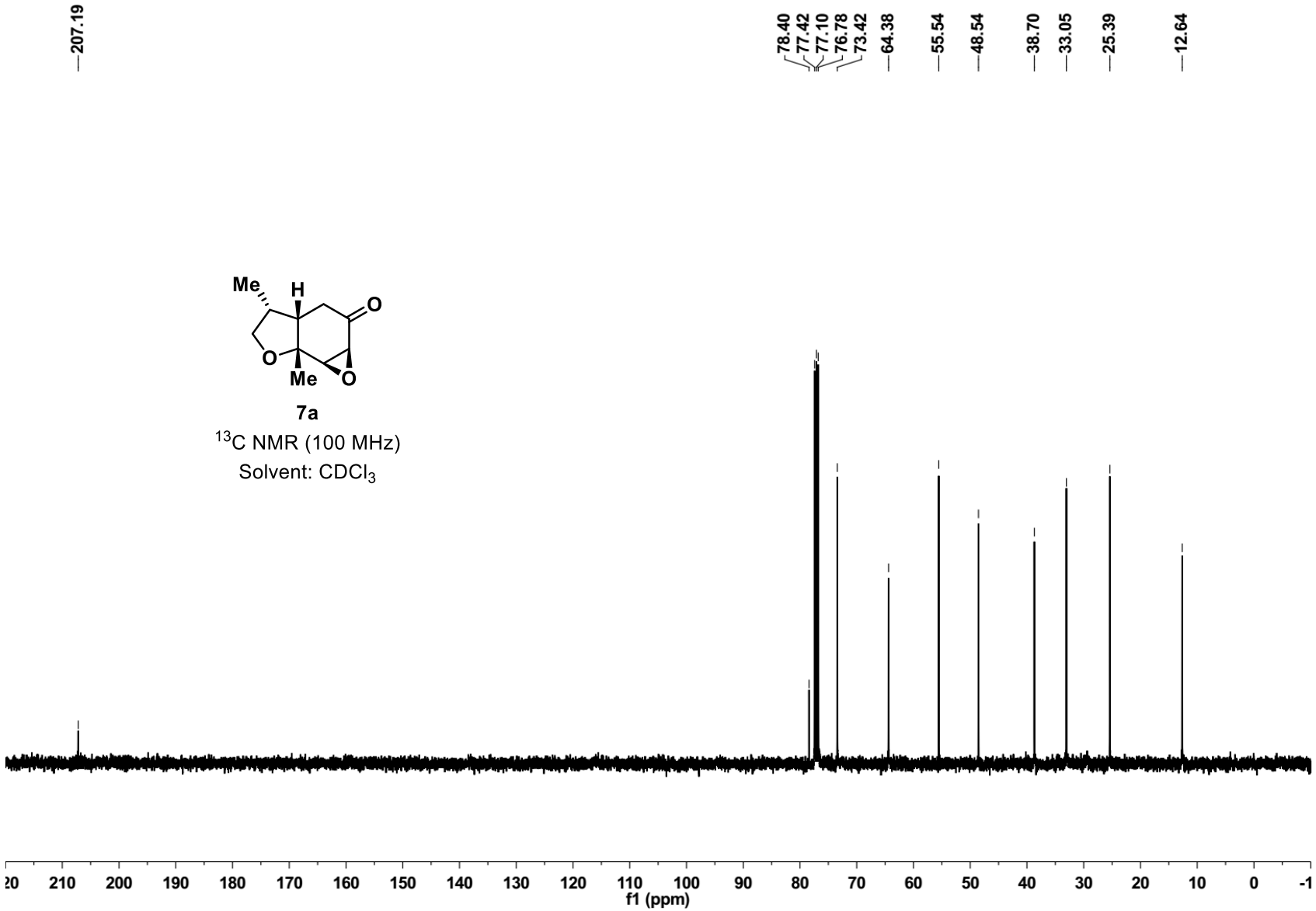

213.32
81.97
77.42
77.10
76.78
72.66
46.26
38.12
36.67
35.76
34.20
27.52
11.86
Me
H
O
O
Me
6a
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

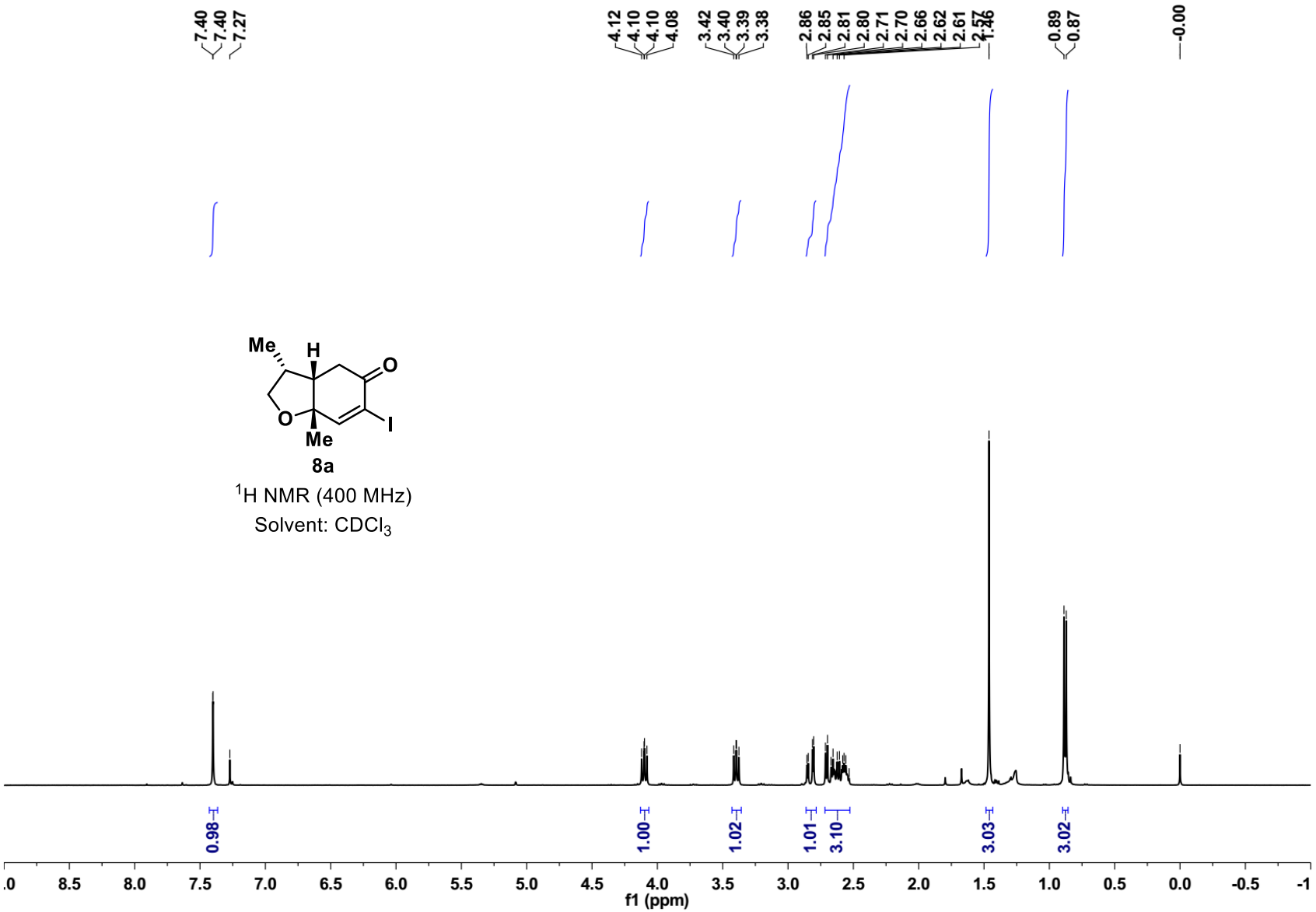


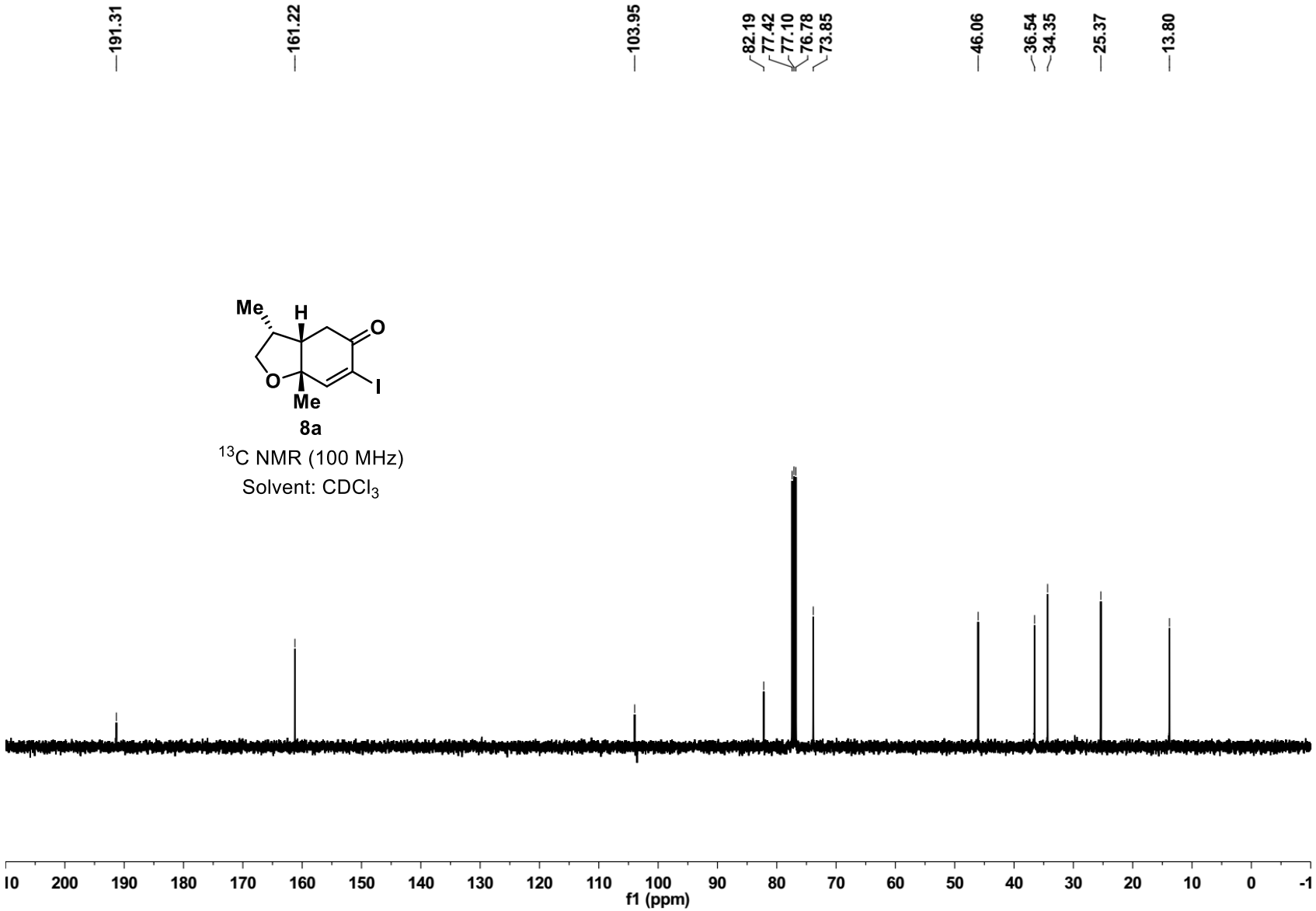
7a

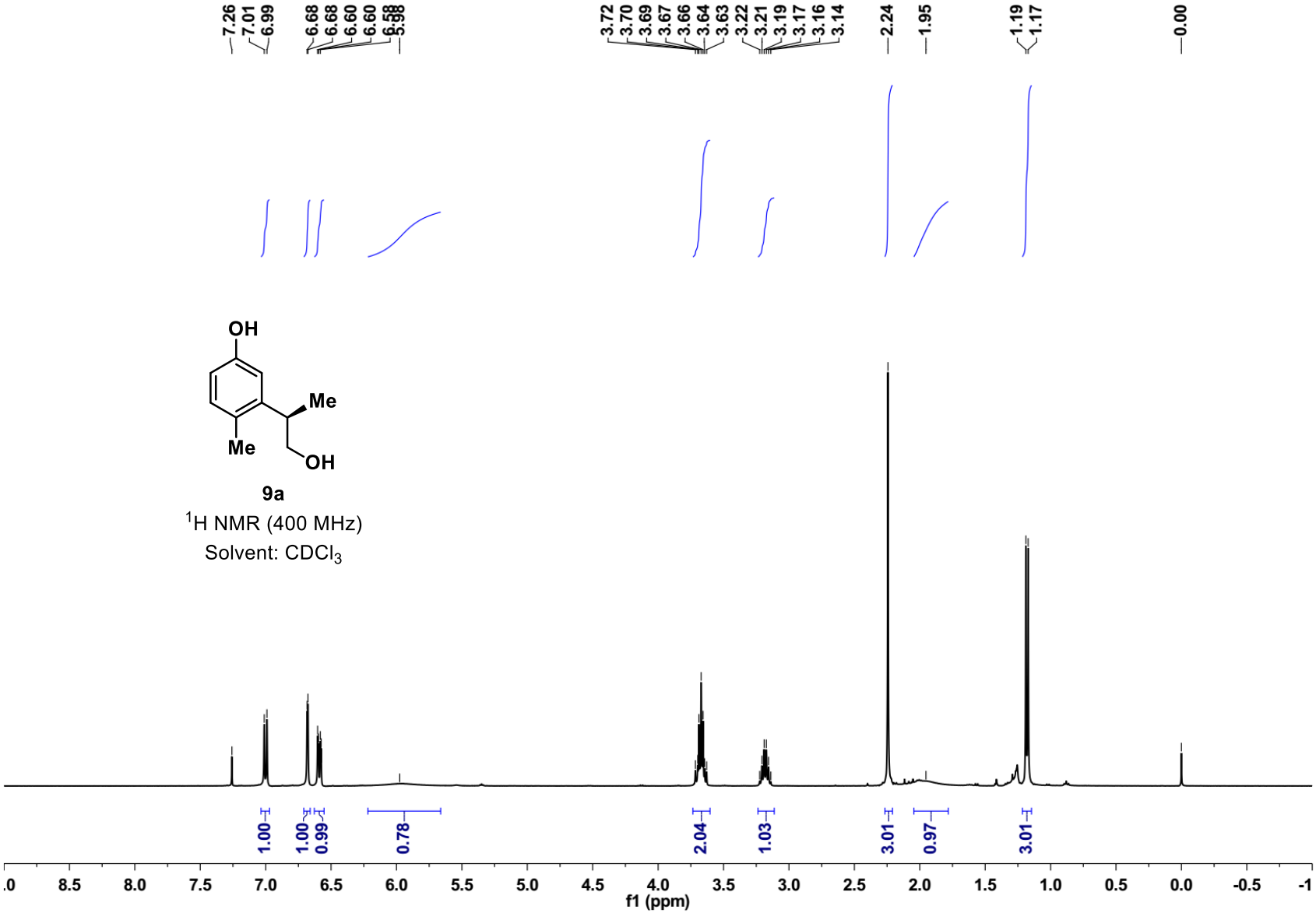
^{1}H NMR (400 MHz)

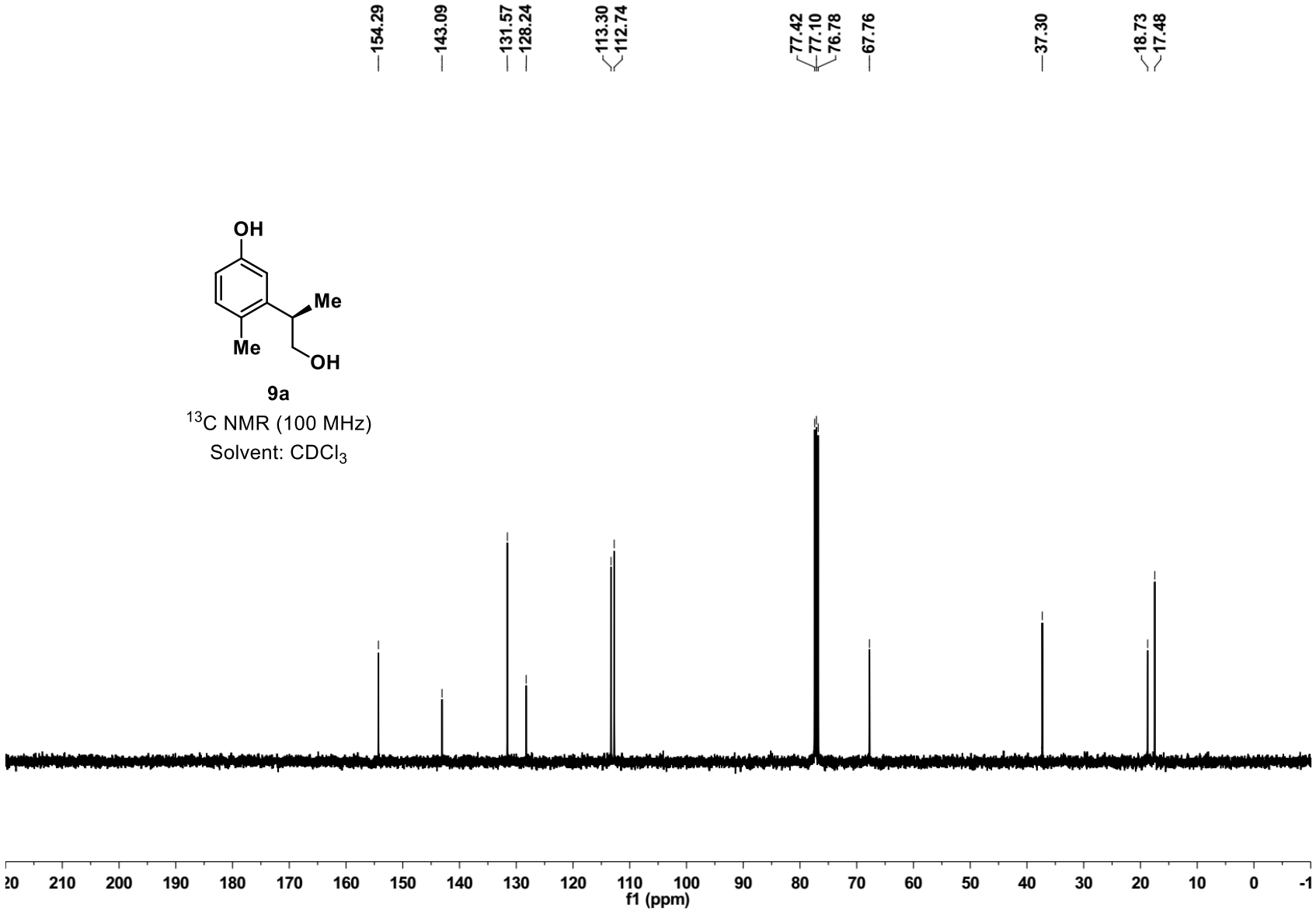
Solvent: $CDCl_3$

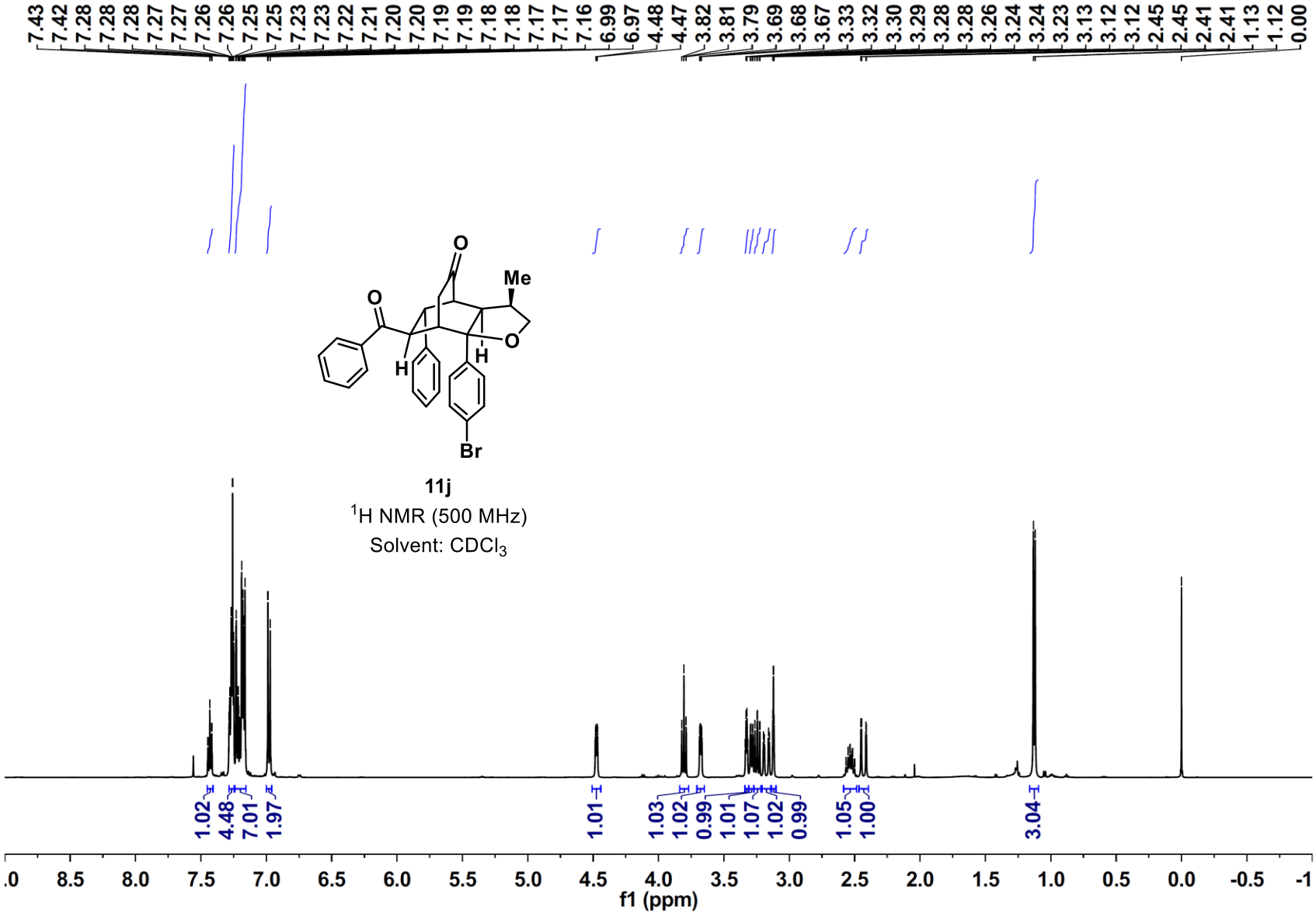

207.19
78.40
77.42
77.10
76.78
73.42
64.38
55.54
48.54
38.70
33.05
25.39
12.64
Me
H
O
O
Me
O
7a
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

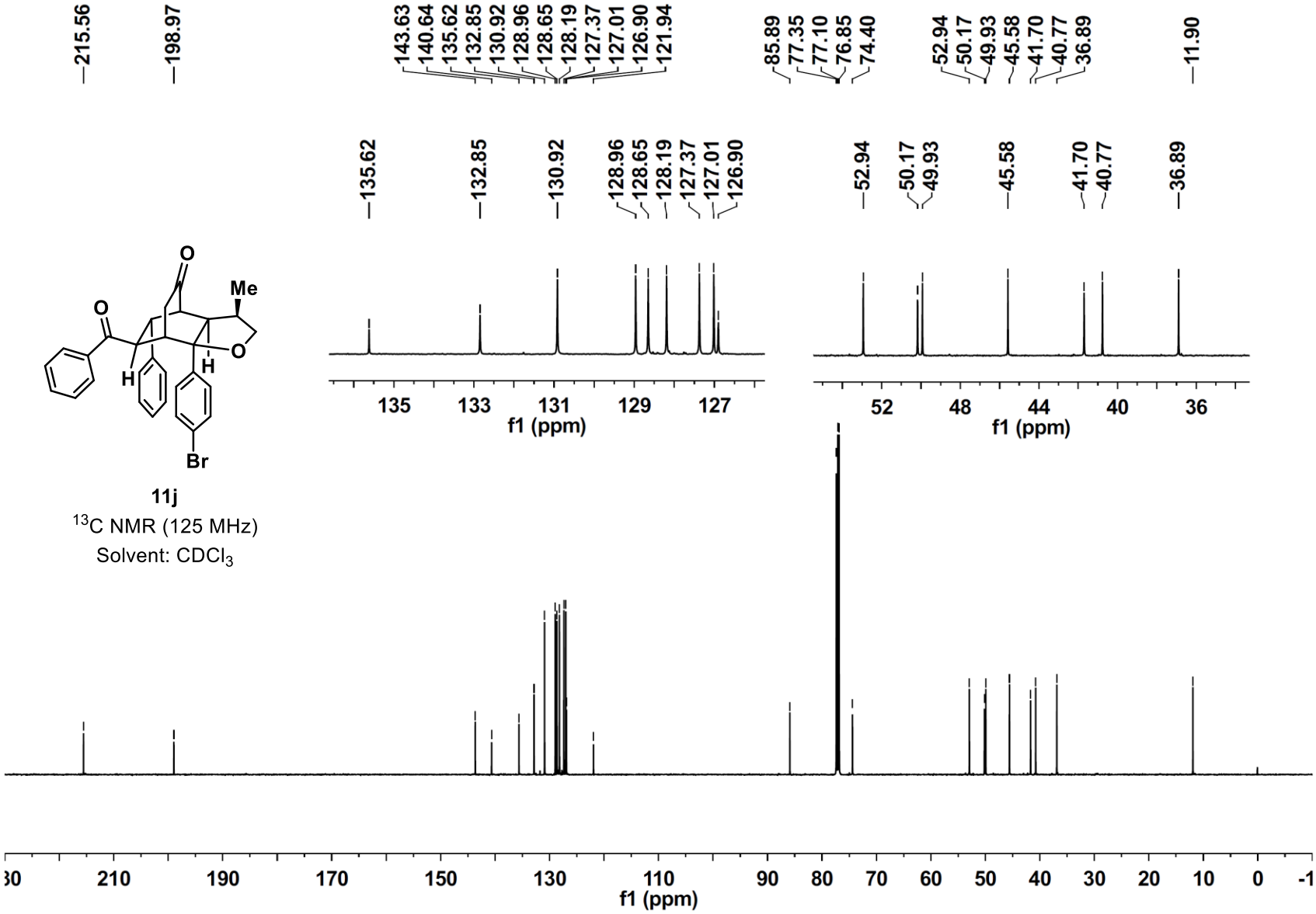

7.40
7.40
7.27
4.12
4.10
4.10
4.08
3.42
3.40
3.39
3.38
2.86
2.85
2.81
2.80
2.71
2.70
2.66
2.62
2.61
1.46
0.89
0.87
-0.00
Me
H
O
O
Me
I
8a
1H NMR (400 MHz)
Solvent: CDCl3
0.98
1.00
1.02
1.01
3.10
3.03
3.02
f1 (ppm)


191.31
161.22
103.95
82.19
77.42
77.10
76.78
73.85
46.06
36.54
34.35
25.37
13.80
Me
H
O
O
I
Me
8a
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)


7.26
7.01
6.99
6.68
6.68
6.60
6.60
6.58
5.98
3.72
3.70
3.69
3.67
3.66
3.64
3.63
3.22
3.21
3.19
3.17
3.16
3.14
2.24
1.95
1.19
1.17
0.00
OH
Me
Me
OH
9a
1H NMR (400 MHz)
Solvent: CDCl3
1.00
1.00
0.99
0.78
2.04
1.03
3.01
0.97
3.01
f1 (ppm)


154.29
143.09
131.57
128.24
113.30
112.74
77.42
77.10
76.78
67.76
37.30
18.73
17.48
OH
Me
Me
OH
9a
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)

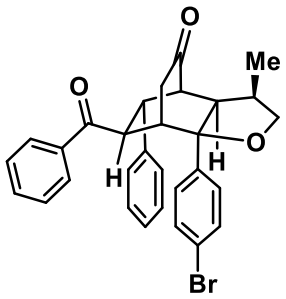

7.43 7.42 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.23 7.23 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.16 6.99 6.97 4.48 4.47 3.82 3.81 3.79 3.69 3.68 3.67 3.33 3.32 3.30 3.29 3.28 3.28 3.26 3.24 3.24 3.23 3.13 3.12 3.12 2.45 2.45 2.41 2.41 1.13 1.12 0.00
O
Me
O
O
H
H
Br
11j
1H NMR (500 MHz)
Solvent: CDCl3
1.02 4.48 7.01 1.97 1.01 1.03 1.02 0.99 1.01 1.07 1.02 0.99 1.05 1.00 3.04
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



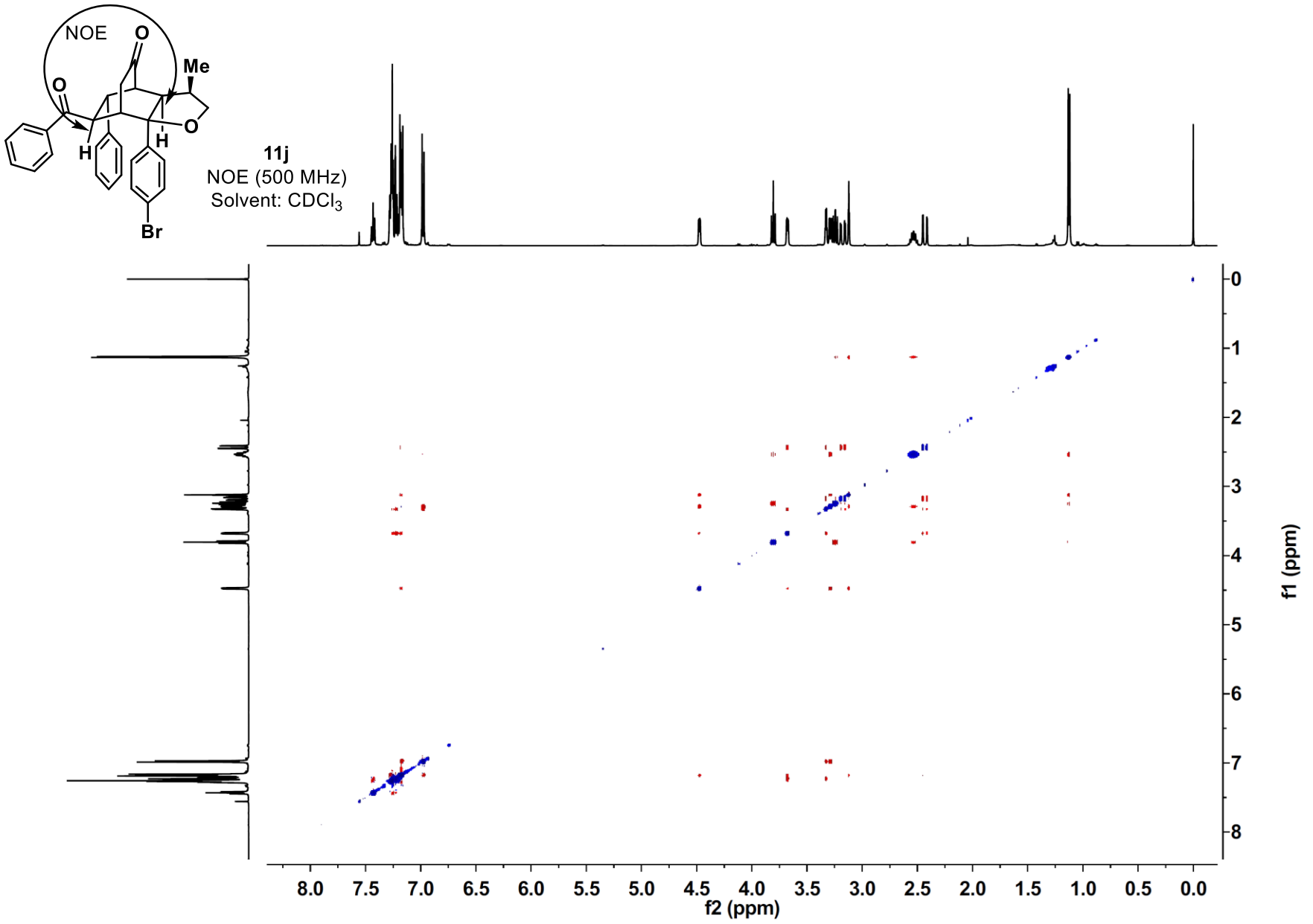
11j

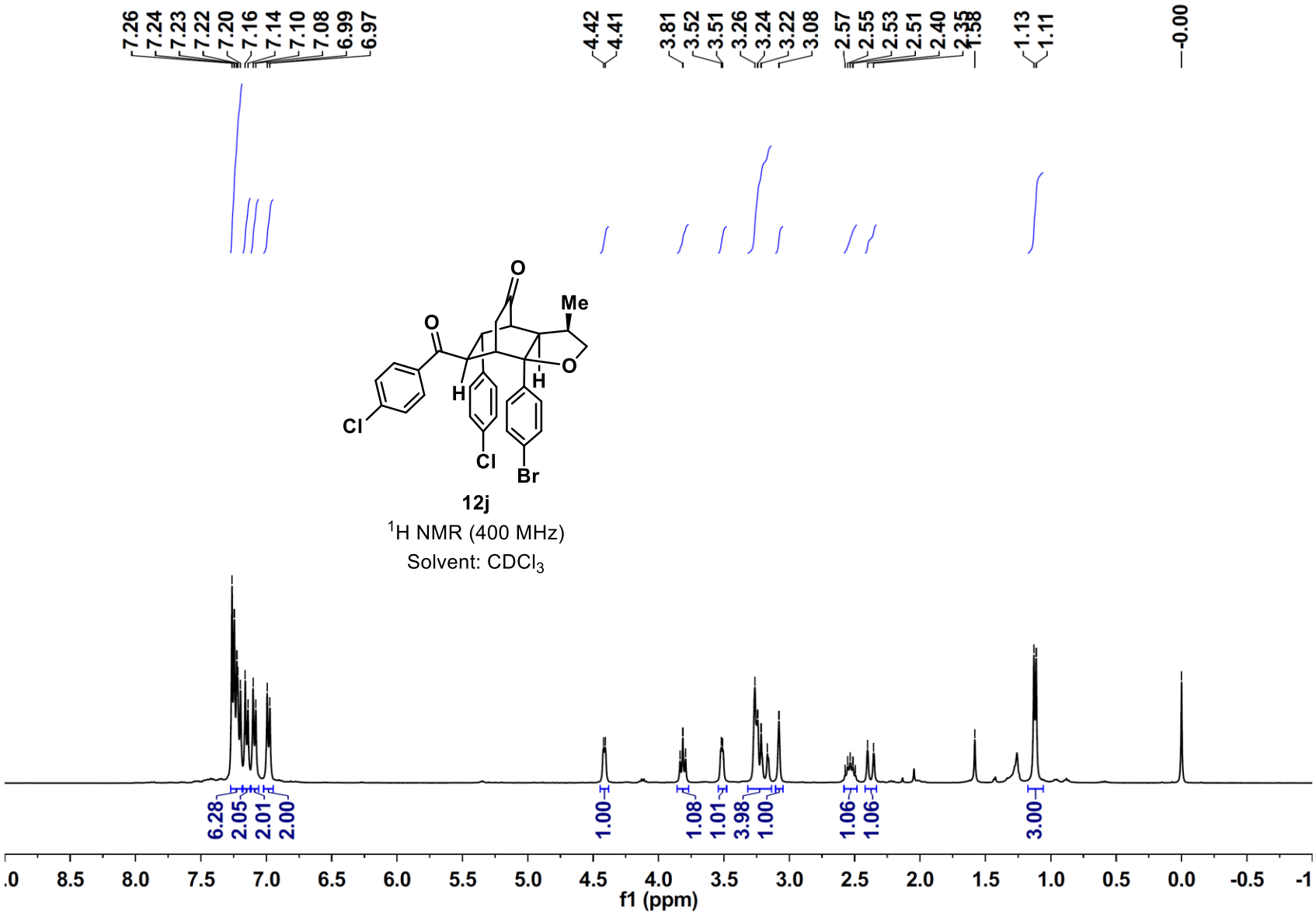
^{13}C NMR (125 MHz)

Solvent: $CDCl_3$



11j
HMQC (500 MHz)
Solvent: $CDCl_3$

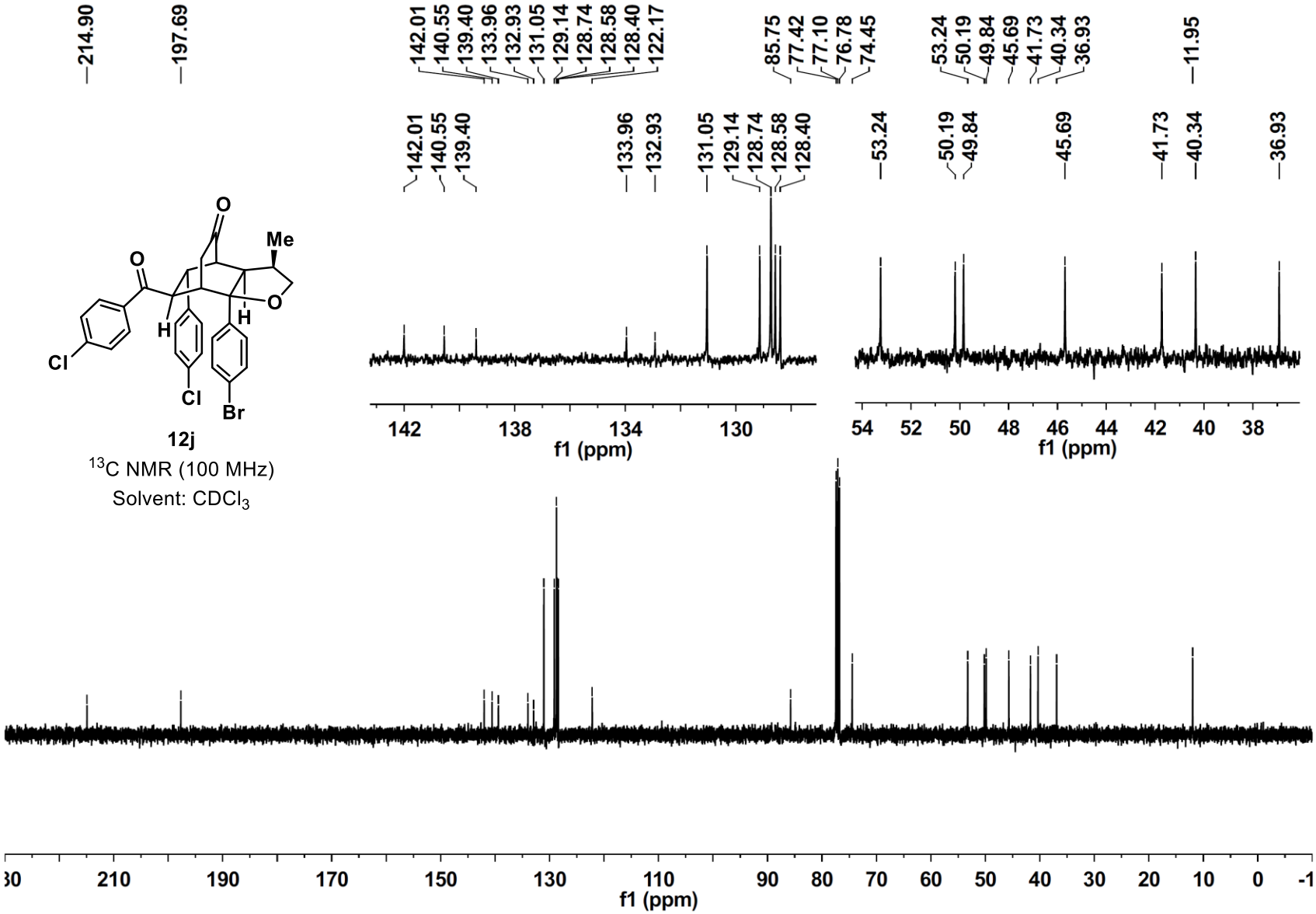

NOE
O
Me
O
O
H
H
Br
11j
NOE (500 MHz)
Solvent: CDCl3
f1 (ppm)
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8



12j

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$


214.90
197.69
142.01
140.55
139.40
133.96
132.93
131.05
129.14
128.74
128.58
128.40
122.17
85.75
77.42
77.10
76.78
74.45
53.24
50.19
49.84
45.69
41.73
40.34
36.93
11.95
O
O
Me
O
H
H
Cl
Cl
Br
12j
13C NMR (100 MHz)
Solvent: CDCl3
f1 (ppm)
f1 (ppm)
f1 (ppm)