Supplementary Information for

Enantioselective α-Functionalizations of Ketones via Allylic Substitution of Silyl Enol Ethers

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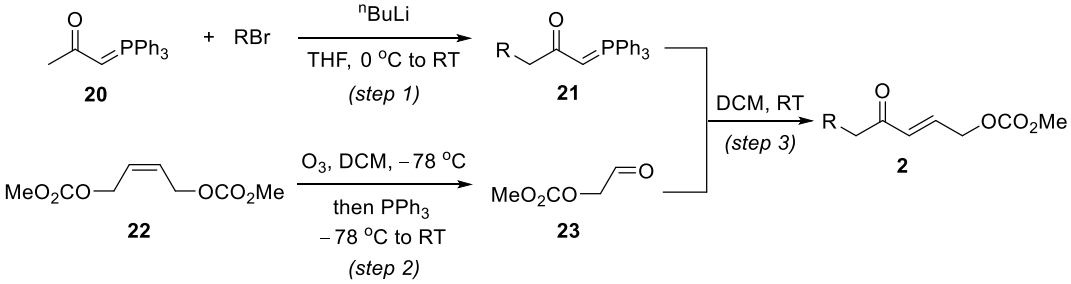
1. General information

All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled glovebox or by using Schlenk techniques. All dry solvents were obtained by passing it through a solvent column composed of activated A-1 alumina and further degassed by the freeze-pump-thaw method. Unless otherwise indicated, all commercially available starting materials were purchased and used directly without further purification. The ^{1}H and ^{13}C NMR spectra were acquired on 400 MHz or 600 MHz Bruker instruments at the University of California, Berkeley. Chemical shifts are reported in δ (ppm) with reference to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.10 ppm for ^{13}C NMR). Coupling constants (*J*) are reported in Hz. Optical rotation values were measured by a Perkin Elmer 241 Automatic Polarimeter.

2. Synthesis of substrates

2.1 General procedures for the synthesis of *α,β*-unsaturated ketone substrates.

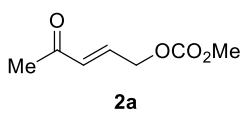


Step 1: To a well stirred solution of **20** (4.77 g, 15.0 mmol) and THF (120 mL) under N_2 atmosphere at -78 °C was added ^{n}BuLi (2.5 M in THF, 9.0 mL) dropwise. The resulting mixture was stirred at -78 °C for an additional 1 h. Then, the alkyl bromide (22.5 mmol) in THF (15 mL) was added to the above solution slowly. After addition was complete, the reaction solution was allowed to gradually warm to room temperature and was stirred for 12 h. The reaction was quenched with water (200 mL) and extracted with ethyl acetate (150 mL × 3). The organic layer was dried by with anhydrous Na_2SO_4 and condensed to afford ylide **21** without further purification.

Step 2: Through a solution of dicarbonate **22** (1.54 g, 7.50 mmol) in DCM (50 mL) at -78 °C in a 100 mL flask was bubbled ozone gas until the solution sustained a blue color. Then, PPh_3 (2.34 g, 22.5 mmol) was added to the reaction mixture in one portion. The reaction was stirred at room temperature for an additional 6 h to afford a solution of aldehyde **23**.

Step 3: To the above solution of **23** was added yide **21** in DCM (10 mL) at room temperature. The resulting mixture was stirred for 12 h. After this time, the reaction solution was condensed, and the residue was purified by flash column chromatography using hexane/ethyl acetate as eluent to afford the pure substrates **2**.

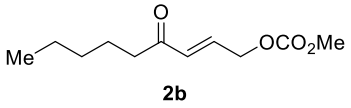
(*E*)-Methyl (4-oxopent-2-en-1-yl) carbonate (2a) [1]



2a

Yellow oil. 2.1 g, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.76 (dt, J = 16.0 Hz, J = 4.8 Hz, 1H), 6.30 (dt, J = 16.0 Hz, J = 2.0 Hz, 1H), 4.82 (dd, J = 4.8 Hz, J = 2.0 Hz, 2H), 3.83 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.52, 155.28, 138.99, 130.98, 65.92, 55.12, 27.44; HRMS (EI): $[M]^{\oplus}$ calcd for $C_7H_{10}O_4^{\oplus}$ 158.0579, found 158.0582.

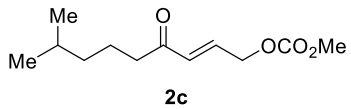
(*E*)-Methyl (4-oxonon-2-en-1-yl) carbonate (2b)



2b

Yellow oil. 1.9 g, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.76 (dt, J = 16.0 Hz, J = 4.8 Hz, 1H), 6.30 (dt, J = 16.0 Hz, J = 2.0 Hz, 1H), 4.79 (dd, J = 4.8 Hz, J = 2.0 Hz, 2H), 3.80 (s, 3H), 2.53 (t, J = 7.6 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.33 – 1.25 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.89, 155.37, 137.87, 130.14, 66.15, 55.19, 40.90, 31.42, 23.66, 22.48, 13.95; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{11}H_{18}O_4Na^{\oplus}$ 237.1097, found 237.1099.

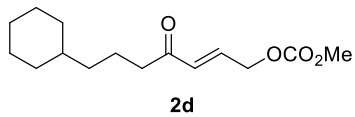
(*E*)-Methyl (8-methyl-4-oxonon-2-en-1-yl) carbonate (2c)



2c

Yellow oil. 2.3 g, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.78 (dt, J = 16.0 Hz, J = 4.8 Hz, 1H), 6.32 (dt, J = 16.0 Hz, J = 2.0 Hz, 1H), 4.81 (dd, J = 4.8 Hz, J = 2.0 Hz, 2H), 3.83 (s, 3H), 2.53 (t, J = 7.2 Hz, 2H), 1.65 – 1.49 (m, 3H), 1.21 – 1.15 (m, 2H), 0.88 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.81, 155.37, 137.82, 130.16, 66.15, 55.19, 41.18, 38.49, 27.89, 22.52, 21.83; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{20}O_4Na^{\oplus}$ 251.1254, found 251.1252.

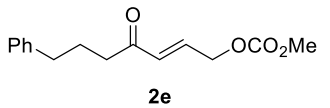
(*E*)-7-Cyclohexyl-4-oxohept-2-en-1-yl methyl carbonate (2d)



2d

Yellow oil. 1.7 g, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.77 (dt, J = 16.0 Hz, J = 4.8 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 4.81 (dd, J = 4.8 Hz, J = 2.0 Hz, 2H), 3.83 (s, 3H), 2.53 (t, J = 7.2 Hz, 2H), 1.70 – 1.58 (m, 7H), 1.26 – 1.11 (m, 6H), 0.91 – 0.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.91, 155.40, 137.83, 130.19, 66.19, 55.22, 41.29, 37.56, 37.05, 33.31, 26.72, 26.41, 21.38; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{24}O_4Na^{\oplus}$ 291.1567, found 291.1567.

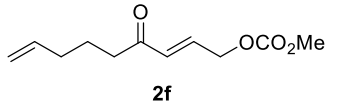
(*E*)-Methyl (4-oxo-7-phenylhept-2-en-1-yl) carbonate (2e)



2e

Yellow oil. 2.2 g, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 (t, J = 7.2 Hz, 2H), 7.21 – 7.16 (m, 3H), 6.74 (dt, J = 16.0 Hz, J = 4.8 Hz, 1H), 6.30 (dt, J = 16.0 Hz, J = 2.0 Hz, 1H), 4.80 (dd, J = 4.8 Hz, J = 2.0 Hz, 2H), 3.82 (s, 3H), 2.64 (t, J = 7.2 Hz, 2H), 2.57 (t, J = 7.2 Hz, 2H), 2.00 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.26, 155.25, 141.47, 137.97, 129.92, 128.44, 128.36, 125.94, 65.98, 55.08, 39.86, 34.97, 25.22; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{18}O_4Na^{\oplus}$ 285.1097, found 285.1106.

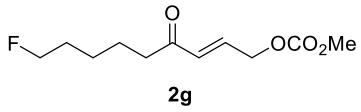
(*E*)-Methyl (4-oxonona-2,8-dien-1-yl) carbonate (2f)



2f

Yellow oil. 1.5 g, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.77 (dt, J = 16.0 Hz, J = 4.8 Hz, 1H), 6.31 (d, J = 16.0 Hz, 1H), 5.81 – 5.71 (m, 1H), 5.03 – 4.96 (m, 2H), 4.81 (dd, J = 4.8 Hz, J = 2.0 Hz, 2H), 3.82 (s, 3H), 2.56 (t, J = 7.2 Hz, 2H), 2.07 (q, J = 7.2 Hz, 2H), 1.75 – 1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.51, 155.32, 137.97, 137.90, 130.06, 115.34, 66.08, 55.15, 39.94, 33.03, 22.86; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{11}H_{16}O_4Na^{\oplus}$ 235.0941, found 235.0941.

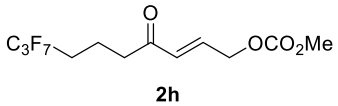
(*E*)-9-Fluoro-4-oxonon-2-en-1-yl methyl carbonate (2g)



2g

Yellow oil. 1.4 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.78 (dt, J = 16.0 Hz, J = 4.4 Hz, 1H), 6.32 (d, J = 16.0 Hz, 1H), 4.81 (dd, J = 4.4 Hz, J = 1.2 Hz, 2H), 4.49 (t, J = 6.0 Hz, 1H), 4.37 (t, J = 6.0 Hz, 1H), 3.82 (s, 3H), 2.58 (t, J = 7.2 Hz, 2H), 1.77 – 1.62 (m, 4H), 1.45 – 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.36, 155.35, 138.09, 130.00, 83.89 (d, J_{CF} =162.9 Hz), 66.09, 55.20, 40.65, 30.24 (d, J_{CF} =19.6 Hz), 24.89 (d, J_{CF} =5.1 Hz), 23.42; ^{19}F NMR (376 MHz, $CDCl_3$) δ -217.39 – -217.77 (m, 1F); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{11}H_{17}O_4FNa^{\oplus}$ 255.1003, found 255.1007.

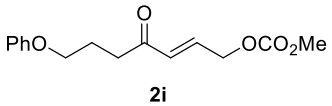
(*E*)-8,8,9,9,10,10,10-Heptafluoro-4-oxodec-2-en-1-yl methyl carbonate (2h)



2h

Yellow oil. 1.9 g, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.81 (dt, J = 16.0 Hz, J = 4.4 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 4.82 (d, J = 2.4 Hz, 2H), 3.82 (s, 3H), 2.69 (t, J = 6.8 Hz, 2H), 2.17 – 2.04 (m, 2H), 1.98 – 1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.74, 155.35, 138.68, 129.60, 65.98, 55.24, 39.42, 29.73 (t, J_{CF} =142.0 Hz), 14.54 (three carbon signals from C_3F_7 unit did not appear); ^{19}F NMR (376 MHz, $CDCl_3$) δ -79.72 – -79.77 (m, 3F), -114.59 – -114.66 (m, 2F), –127.01 (s, 2F); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{13}O_4F_7Na^{\oplus}$ 377.0594, found 377.0608.

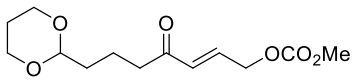
(*E*)-Methyl (4-oxo-7-phenoxyhept-2-en-1-yl) carbonate (2i)



2i

Yellow oil. 2.3 g, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29 – 7.25 (m, 2H), 6.94 (td, J = 7.2 Hz, J = 0.8 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.81 (dt, , J = 16.0 Hz, J = 4.4 Hz, 1H), 6.35 (dt, , J = 16.0 Hz, J = 1.6 Hz, 1H), 4.81 (dd, J = 4.4 Hz, J = 1.6 Hz, 2H), 3.99 (t, J = 6.0 Hz, 2H), 3.82 (s, 3H), 2.80 (t, J = 7.2 Hz, 2H), 2.15 – 2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.87, 158.84, 155.34, 138.25, 130.08, 129.50, 120.76, 114.48, 66.62, 66.05, 55.19, 37.09, 23.49; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{18}O_5Na^{\oplus}$ 301.1046, found 301.1046.

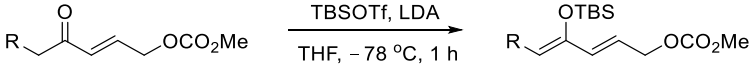
(*E*)-7-(1,3-Dioxan-2-yl)-4-oxohept-2-en-1-yl methyl carbonate (2j)



2j

Yellow oil. 2.6 g, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.77 (dt, J = 16.0 Hz, J = 4.4 Hz, 1H), 6.31 (dt, J = 16.0 Hz, J = 2.0 Hz, 1H), 4.80 (dd, , J = 4.4 Hz, J = 2.0 Hz, 2H), 4.51 (t, , J = 4.8 Hz, 1H), 4.08 (dd, J = 10.4 Hz, J = 4.8 Hz, 2H), 3.82 (s, 3H), 3.74 (td, J = 12.4 Hz, J = 2.4 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2H), 2.12 – 2.00 (m, 1H), 1.77 – 1.68 (m, 2H), 1.63 – 1.58 (m, 2H), 1.34 – 1.31 (m, 1H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.94, 155.06, 137.74, 129.80, 101.77, 66.59, 65.85, 54.88, 40.20, 34.16, 25.58, 18.16; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{20}O_6Na^{\oplus}$ 295.1152, found 295.1142.

2.2 General procedures for the TBS protection of *α,β*-unsaturated ketones.

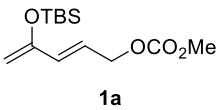


2 **1**

To a well stirred solution of *α,β*-unsaturated ketone **2** (5.0 mmol, 1.0 equiv) and THF (50 mL) under

N_2 atmosphere at -78 °C was added TBSOTf (1.8 g, 7.0 mmol). The mixture was stirred for 10 min at -78 °C, at which time LDA (0.2 M in THF, 30 mL) was added dropwise. The resulting mixture was stirred at -78 °C for 1 h. The reaction was quenched by addition of MeOH (0.5 mL), condensed and purified by flash column chromatography using hexane/ethyl acetate as eluent to afford the pure silyl enolates **1**.

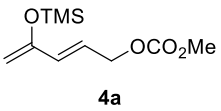
(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)penta-2,4-dien-1-yl methyl carbonate (**1a**)



1a

Silyl enolate **1a** was synthesized by a method that was different from the general procedure: To a well stirred solution of **2a** (1.2 g, 4.2 mmol) and THF (22 mL) under N_2 atmosphere at 0 °C was added Et_3N (2.5 mL, 11 mmol). Then, TBSOTf (2.0 mL, 5.1 mmol) was added dropwise, and the resulting solution was kept at 0 °C for 1 h. At this time, the reaction was quenched by addition of saturated $NaHCO_3$ (aq) (30 mL) and extracted with ethyl acetate (30 mL × 3). The organic layer was condensed and purified by flash column chromatography (hexane/ethyl acetate = 100/1 – 20/1) to afford the pure substrate **1a**. Colorless oil. 0.87 g, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.15 (d, J = 15.2 Hz, 1H), 6.03 (dt, J = 15.2 Hz, J = 6.0 Hz, 1H), 4.70 (d, J = 6.0 Hz, 2H), 4.35 (d, J = 4.4 Hz, 2H), 3.79 (s, 3H), 0.96 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.60, 154.04, 132.08, 123.19, 96.96, 67.55, 54.77, 25.80, 18.26, -4.69; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{24}O_4SiNa^{\oplus}$ 295.1336, found 295.1328.

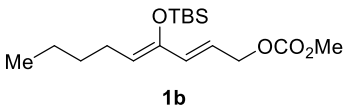
(*E*)-Methyl (4-((trimethylsilyl)oxy)penta-2,4-dien-1-yl) carbonate (**4a**)



4a

4a was prepared by a synthetic procedure that was the same as that used to prepare **1a**, except that TMSOTf was instead of TBSOTf. Colorless oil, 0.28 g, 29% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (d, J = 15.3 Hz, 1H), 6.00 (dt, J = 15.2, 6.0 Hz, 1H), 4.70 (d, J = 6.0 Hz, 2H), 4.37 (s, 2H), 3.80 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.67, 153.87, 131.90, 123.37, 97.24, 67.61, 54.91, 0.07; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{10}H_{19}O_4Si^{\oplus}$ 231.1047, found 231.1040.

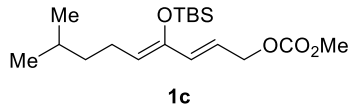
(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)nona-2,4-dien-1-yl methyl carbonate (**1b**)



1b

Colorless oil, 0.82 g, 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.12 (d, J = 15.2 Hz, 1H), 5.80 (dt, J = 15.2 Hz, J = 6.8 Hz, 1H), 4.82 (t, J = 7.2 Hz, 1H), 4.65 (d, J = 6.4 Hz, 2H), 3.77 (s, 3H), 2.08 (dd, J = 14.0 Hz, J = 7.2 Hz, 2H), 1.33 – 1.30 (m, 4H), 0.98 (s, 9H), 0.88 (t, J = 7.2 Hz, 3H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.70, 147.08, 133.93, 120.47, 117.86, 68.12, 54.77, 31.63, 26.00, 25.90, 22.50, 18.44, 13.98, -3.66; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{32}O_4SiNa^{\oplus}$ 351.1962, found 351.1959.

(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-8-methylnona-2,4-dien-1-yl methyl carbonate (**1c**)

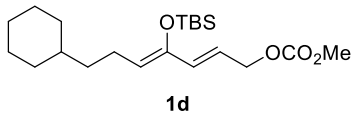


1c

Colorless oil, 0.89 g, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.12 (d, J = 15.2 Hz, 1H), 5.80 (dt, J = 15.2 Hz, J = 6.4 Hz, 1H), 4.81 (t, J = 7.2 Hz, 1H), 4.65 (d, J = 6.4 Hz, 2H), 3.77 (s, 3H), 2.09 (dd, J = 15.6 Hz, J = 7.2 Hz, 2H), 1.60 – 1.50 (m, 1H), 1.22 (dd, J = 15.6 Hz, J = 7.2 Hz, 2H), 0.99 (s, 9H), 0.87 (d, J = 6.8 Hz, 6H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.70, 146.99, 133.93, 120.47, 118.04, 68.13, 54.80, 38.58, 27.89, 26.01,

24.20, 22.55, 18.45, -3.63; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{34}O_4SiNa^{\oplus}$ 365.2119, found 365.2121.

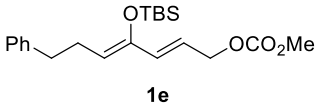
(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-7-cyclohexylhepta-2,4-dien-1-yl methyl carbonate (1d)



1d

Colorless oil, 1.0 g, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.12 (d, J = 15.2 Hz, 1H), 5.80 (dt, J = 15.2 Hz, J = 6.4 Hz, 1H), 4.81 (t, J = 7.2 Hz, 1H), 4.65 (d, J = 6.4 Hz, 2H), 3.77 (s, 3H), 2.09 (dd, J = 14.8 Hz, J = 7.2 Hz, 2H), 1.70 – 1.60 (m, 5H), 1.26 – 1.14 (m, 6H), 0.99 (s, 9H), 0.90 – 0.83 (m, 2H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.70, 146.92, 133.97, 120.41, 118.19, 68.14, 54.79, 37.52, 37.17, 33.32, 26.74, 26.43, 26.02, 23.66, 18.45, -3.61; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{38}O_4SiNa^{\oplus}$ 405.2432, found 405.2427.

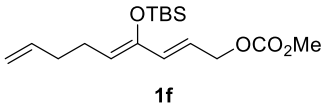
(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-7-phenylhepta-2,4-dien-1-yl methyl carbonate (1e)



1e

Colorless oil, 1.0 g, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29 (t, J = 7.2 Hz, 2H), 7.21 – 7.18 (m, 3H), 6.13 (d, J = 15.2 Hz, 1H), 5.84 (dt, J = 15.2 Hz, J = 6.4 Hz, 1H), 4.87 (t, J = 7.2 Hz, 1H), 4.66 (d, J = 6.4 Hz, 2H), 3.78 (s, 3H), 2.66 (t, J = 7.6 Hz, 2H), 2.43 (dd, J = 15.6 Hz, J = 7.6 Hz, 2H), 1.00 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 155.66, 147.47, 141.84, 133.60, 128.42, 128.39, 125.89, 121.03, 116.33, 67.97, 54.76, 35.59, 27.89, 25.99, 18.42, -3.60; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{32}O_4SiNa^{\oplus}$ 399.1962, found 399.1953.

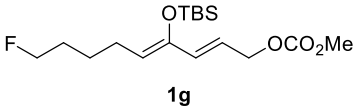
(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)nona-2,4,8-trien-1-yl methyl carbonate (1f)



1f

Colorless oil, 0.93 g, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (d, J = 15.4 Hz, 1H), 5.85 – 5.74 (m, 2H), 5.01 (d, J = 17.2 Hz, 1H), 4.95 (d, J = 10.2 Hz, 1H), 4.84 (t, J = 7.1 Hz, 1H), 4.64 (d, J = 6.5 Hz, 2H), 3.77 (s, 3H), 2.19 (dd, J = 14.5, 7.1 Hz, 2H), 2.08 (dd, J = 14.1, 7.1 Hz, 2H), 0.98 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.67, 147.39, 138.17, 133.67, 120.83, 116.57, 114.87, 68.02, 54.78, 33.46, 25.99, 25.50, 18.44, -3.63; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{30}O_4SiNa^{\oplus}$ 349.1806, found 349.1798.

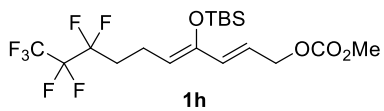
(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-9-fluorononа-2,4-dien-1-yl methyl carbonate (1g)



1g

Colorless oil, 0.69 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (d, J = 15.4 Hz, 1H), 5.81 (dt, J = 15.2, 6.5 Hz, 1H), 4.80 (t, J = 7.3 Hz, 1H), 4.63 (d, J = 6.4 Hz, 2H), 4.46 (t, J = 6.1 Hz, 1H), 4.35 (t, J = 6.0 Hz, 1H), 3.75 (s, 3H), 2.12 (q, J = 7.4 Hz, 2H), 1.74 – 1.60 (m, 2H), 1.49 – 1.40 (m, 2H), 0.97 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.63, 147.57, 133.53, 120.93, 116.67, 83.85 (d, J_{CF} = 164.5 Hz), 67.93, 54.73, 30.03 (d, J_{CF} = 19.5 Hz), 25.93, 25.60, 25.03 (d, J_{CF} = 5.1 Hz), 18.39, -3.69; ^{19}F NMR (376 MHz, $CDCl_3$) δ -217.40 – -217.85 (m, 1F); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{31}FO_4SiNa^{\oplus}$ 369.1868, found 369.1865.

(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-8,8,9,9,10,10,10-heptafluorodeca-2,4-dien-1-yl methyl carbonate (1h)

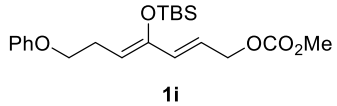


1h

Colorless oil, 0.33 g, 14% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (d, J = 15.5 Hz, 1H), 5.96 – 5.77 (m, 1H), 4.80 (t, J = 7.3 Hz, 1H), 4.66 (d, J = 6.2 Hz, 2H), 3.77 (s, 3H), 2.40 (dd, J = 15.8, 7.6 Hz, 2H), 2.15 –

2.02 (m, 2H), 0.99 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.67, 148.90, 132.71, 122.34, 112.78, 67.73, 54.84, 30.42 (t, J_{CF} = 21.9 Hz), 25.84, 18.39, 17.15, -3.70; ^{19}F NMR (376 MHz, $CDCl_3$) δ -79.92 (t, J = 9.3 Hz, 3F), -114..95 – -115.02 (m, 2F), -127.20 (s, 2F) (three carbon signals from C_3F_7 unit did not appear); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{27}F_7O_4SiNa^{\oplus}$ 491.1459, found 491.1457.

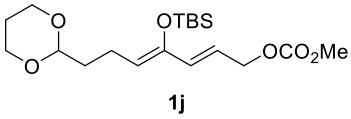
(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-7-phenoxyhepta-2,4-dien-1-yl methyl carbonate (1i)



1i

Colorless oil, 0.31 g, 16% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 6.97 – 6.90 (m, 3H), 6.18 (d, J = 15.2 Hz, 1H), 5.89 (dt, J = 15.2, 6.3 Hz, 1H), 5.00 (t, J = 7.1 Hz, 1H), 4.68 (d, J = 6.3 Hz, 2H), 3.96 (t, J = 6.7 Hz, 2H), 3.80 (s, 3H), 2.61 (q, J = 6.7 Hz, 2H), 1.02 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.97, 155.67, 148.77, 133.29, 129.48, 121.63, 120.73, 114.62, 112.26, 67.90, 67.09, 54.84, 26.48, 26.00, 18.45, -3.57; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{32}O_5SiNa^{\oplus}$ 415.1911, found 415.1907.

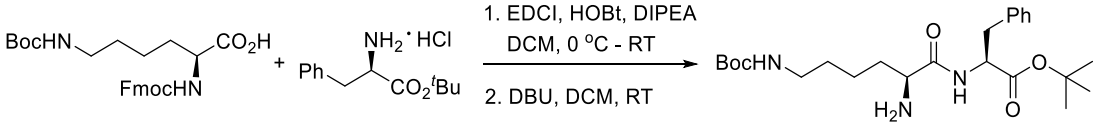
(2*E*,4*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-7-(1,3-dioxan-2-yl)hepta-2,4-dien-1-yl methyl carbonate (1j)



1j

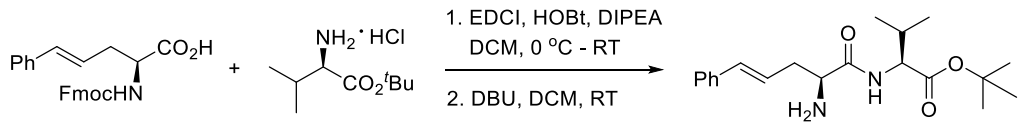
Colorless oil, 0.89 g, 46% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (d, J = 15.4 Hz, 1H), 5.86 – 5.68 (m, 1H), 4.80 (t, J = 7.3 Hz, 1H), 4.62 (d, J = 6.3 Hz, 2H), 4.45 (t, J = 4.9 Hz, 1H), 4.04 (dd, J = 11.1, 4.4 Hz, 2H), 3.79 – 3.65 (m, 5H), 2.16 (dd, J = 14.8, 7.3 Hz, 2H), 2.10 – 1.96 (m, 1H), 1.59 (dd, J = 12.7, 7.1 Hz, 2H), 1.29 (d, J = 13.3 Hz, 1H), 0.95 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.59, 147.43, 133.64, 120.76, 116.49, 101.73, 67.95, 66.83, 54.71, 34.79, 25.94, 25.85, 20.71, 18.37, -3.71; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{34}O_6SiNa^{\oplus}$ 409.2017, found 409.2004.

2.3 Synthesis of peptide substrates



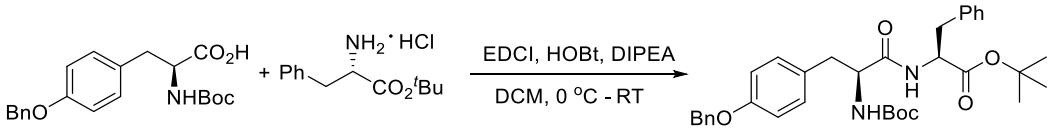
24 **25** **26**

To a well stirred solution of amino ester **25** (2.6 g, 10 mmol) in DCM (50 mL) was added DIPEA (1.8 mL, 11 mmol) dropwise. Then, amino acid **24** (4.7 g, 10 mmol), HOBt (1.5 g, 11 mmol), and EDCI (2.1 g, 11 mmol) were added, and the resulting mixture was stirred at room temperature for 12 h. After this time, the reactsion was washed with sat. aqueous $NaHCO_3$ (50 mL), citric acid (10 wt% aqueous, 50 mL) and brine (50 mL) in sequence and extracted with DCM (50 mL × 3). The organic layers were combined and dried with $NaSO_4$ and condensed. Then, to the condensed mixture above was added DCM (100 mL) and DBU (3.0 g, 20 mmol). The mixture was stirred at room temperature for 2 h, then condensed, and the residue was purified by flash column chromatography (DCM/MeOH = 50/1 – 20/1) to afford the pure substrate **26** (2.3 g) as white solid in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 1H), 7.30 – 7.15 (m, 5H), 4.75 (dt, J = 8.2, 6.5 Hz, 1H), 4.56 (br s, 1H), 3.33 (dd, J = 7.9, 4.5 Hz, 1H), 3.18 – 2.97 (m, 4H), 1.76 – 1.68 (m, 1H), 1.49 – 1.41 (m, 23H), 1.32 – 1.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.48, 170.80, 156.01, 136.38, 129.42, 128.27, 126.82, 82.05, 78.96, 54.94, 53.01, 40.12, 38.28, 34.54, 29.83, 28.40, 27.92, 22.70; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{24}H_{40}O_5N_3^{\oplus}$ 450.2962, found 450.2962.



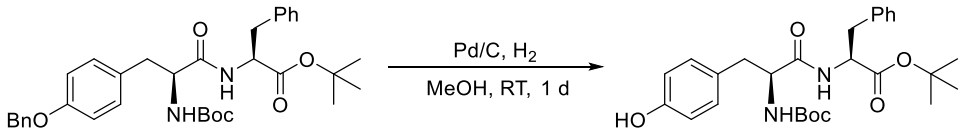
27 **28** **29**

This compound was prepared by a synthetic procedure that was the same as that used to prepare **26**. White solid, 2.1 g, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.1 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (dd, *J* = 14.2, 6.5 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.25 – 6.17 (m, 1H), 4.48 (dd, *J* = 9.2, 4.5 Hz, 1H), 3.57 (dd, *J* = 8.4, 4.0 Hz, 1H), 2.87 – 2.74 (m, 1H), 2.52 (dt, *J* = 14.2, 8.2 Hz, 1H), 2.31 – 2.18 (m, 1H), 1.56 – 1.51 (m, 11H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.22, 170.97, 136.96, 133.69, 128.48, 127.34, 126.16, 125.93, 81.64, 57.09, 54.46, 38.76, 31.22, 28.01, 19.02, 17.60; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{20}H_{31}O_3N_2^{\oplus}$ 347.2329, found 347.2337.



30 **31** **32**

To a well stirred solution of **31** (2.6 g, 10 mmol) in DCM (50 mL) was added DIPEA (1.8 mL, 11 mmol) dropwise. Then, **30** (3.7 g, 10 mmol), HOBt (1.5 g, 11 mmol), and EDCI (2.1 g, 11 mmol) were added, and the resulting mixture was stirred at room temperature for 12 h. After this time, the reaction solution was washed with saturated $NaHCO_3$ (aq) (50 mL), citric acid (10 wt% aqueous, 50 mL) and brine (50 mL) in sequence and extracted with DCM (50 mL). The organic layer was dried with $NaSO_4$, and condensed. The residue was purified by flash column chromatography (hexane/ethyl acetate = 6/1 – 4/1) to afford pure **32** (5.3 g) as a white solid in 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 7.25 – 7.18 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 6.7 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.32 (s, 1H), 5.09 – 4.84 (m, 3H), 4.64 (d, *J* = 5.5 Hz, 1H), 4.31 (d, *J* = 4.9 Hz, 1H), 3.08 – 2.93 (m, 4H), 1.41 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.72, 170.02, 157.78, 155.26, 136.96, 136.01, 130.38, 129.50, 128.75, 128.52, 128.27, 127.89, 127.39, 126.87, 114.90, 82.21, 79.97, 69.89, 55.76, 53.65, 38.12, 37.48, 28.23, 27.84; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{34}H_{42}N_2O_6Na^{\oplus}$ 597.2935, found 597.2931.

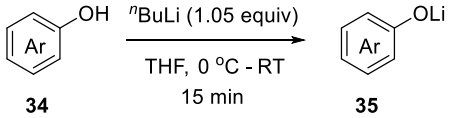


32 **33**

To a well stirred solution of **32** (2.5 g, 4.4 mmol) in MeOH (350 mL) was added Pd/C (5 wt%, 0.93 g, 0.45 mmol). The resulting mixture was stirred under hydrogen atmosphere for one day. The reaction solution was filtered and purified by flash column chromatography (hexane/ethyl acetate = 3/1) to afford the pure substrate **33** (1.7 g) as white solid in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 3H), 7.06 (d, *J* = 7.0 Hz, 2H), 7.01 (d, *J* = 5.9 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.35 (br s, 1H), 5.92 (br s, 1H), 4.99 (br s, 1H), 4.64 (br s, 1H), 4.28 (br s, 1H), 3.10 – 2.84 (m, 4H), 1.41 (s, 9H), 1.36 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.38, 170.08, 155.58, 155.54, 135.87, 130.31, 129.48, 128.32, 127.31, 126.93, 115.68, 82.47, 80.35, 55.93, 53.84, 38.09, 37.44, 28.22, 27.82; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for

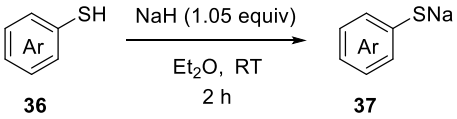
$C_{27}H_{36}N_2O_6Na^{\oplus}$ 507.2466, found 507.2465.

2.4 General procedure for the preparation of lithium phenoxides derivatives



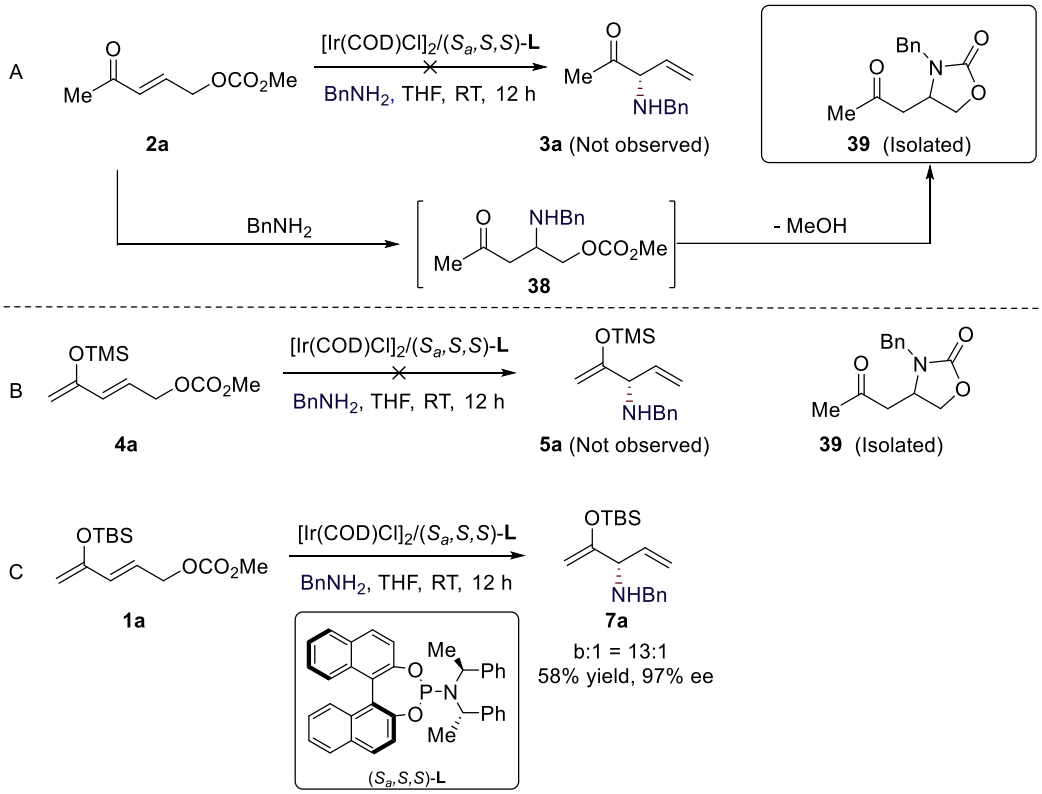
To a well stirred solution of **34** (1.0 equiv) and THF (1.0 M) under N_2 atmosphere at 0 °C was added ^{n}BuLi (2.5 M in THF, 1.05 equiv) dropwise. The reaction was stirred for 15 min at room temperature. After this time, the reaction solution was condensed and dried to afford phenoxide product **35**.

2.5 General procedure for the preparation of sodium arylthiolate derivatives



To a well stirred solution of NaH (60% oil dispersion, 1.05 equiv) and Et_2O (0.25 M) under N_2 atmosphere at room temperature was added **36** (1.0 equiv) dropwise. The reaction was stirred for 2 h at room temperature. After this time, the reaction solution was filtered, washed by Et_2O for three times. The solid was collected and dried to afford thiolate product **37**.

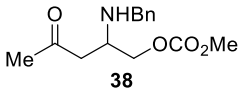
3. Initial trials



These three reactions were conducted following the same procedure as that in "Development of the process for the construction of C-N bonds," except that different electrophiles were used. The reaction

was stirred at room temperature for 12 h. The crude reaction solution was condensed to obtain a ^{1}H NMR spectrum (with CH_2Br_2 as internal standard). For reaction A, we observed intermediate **38** (19% yield) and compound **39** (44% yield); For reaction B, we observed intermediate **38** (33% yield) and compound **39** (29% yield). Compound **38** was identified by ^{1}H NMR spectroscopy. Compound **38** converted to compound **39** at room temperature in the glovebox.

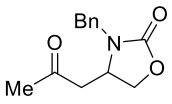
2-(Benzylamino)-4-oxopentyl methyl carbonate (38)



38

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 4.23 (qd, *J* = 10.9, 4.8 Hz, 2H), 3.92 – 3.77 (m, 5H), 3.42 – 3.31 (m, 1H), 2.69 (dd, *J* = 6.2, 2.3 Hz, 2H), 2.17 (s, 3H).

1-(1-Benzylaziridin-2-yl)propan-2-one (39)

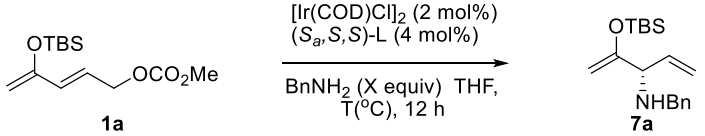


39

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 5H), 4.61 (d, *J* = 15.4 Hz, 1H), 4.53 (t, *J* = 8.8 Hz, 1H), 4.21 (d, *J* = 15.4 Hz, 1H), 4.09 – 3.98 (m, 1H), 3.87 (dd, *J* = 9.1, 6.4 Hz, 1H), 2.90 (dd, *J* = 18.2, 4.1 Hz, 1H), 2.54 (dd, *J* = 18.2, 9.2 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.31, 158.39, 135.98, 128.95, 128.07, 127.91, 68.19, 50.88, 46.65, 46.41, 30.24; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{15}NO_3Na^{\oplus}$ 256.0944, found 256.0945.

4. Development of the process for the construction of C-N bonds[a]

General procedure: To a 4 mL vial containing a magnetic stir bar were added $[Ir(COD)Cl]_2$ (2.6 mg, 0.0040 mmol), (*S*$_a$,*S*,*S*)-L (4.4 mg, 0.0080 mmol) and THF (0.2 mL) in a nitrogen-filled glovebox, and the resulting mixture was stirred at RT for 10 min. Then, *n*-propylamine (0.1 mL) was added to the vial. The vial was sealed with a PTFE lined cap and stirred at 50 °C for 20 min. Next, the volatile materials were evaporated under vacuum. Compound **1a** (54 mg, 0.20 mmol) in THF (0.25 M to 1.0 M) was added, and the reaction was stirred at RT for 10 min. After this time, benzylamine (54 mg, 0.50 mmol) was added to the reaction, and the vial sealed with a PTFE lined cap was removed from the glovebox and stirred at the stated temperature for 12 h. The crude reaction solution was condensed to obtain a ^{1}H NMR spectrum (with CH_2Br_2 as internal standard). For isolation, the reaction was further purified by flash column chromatography using hexane/ethyl acetate as eluent to afford pure **7a**.

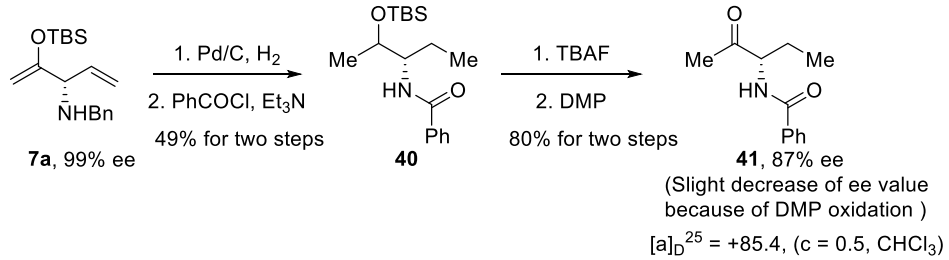


1a **7a**

Entry	X	Concentration	T/ °C	b:l	Yield (%)	ee (%)
1	1.2	0.25 M	RT	13:1	58	/
2	2.0	0.25 M	RT	13:1	68	/
3	2.5	0.25 M	RT	13:1	72	/
4	3.0	0.25 M	RT	13:1	58	/
5	1.2	0.25 M	35	12:1	72	/
6	1.2	0.25 M	50	10:1	55	/
7	2.5	1.0 M	40	12:1	82 (isolated)	99(*S*)

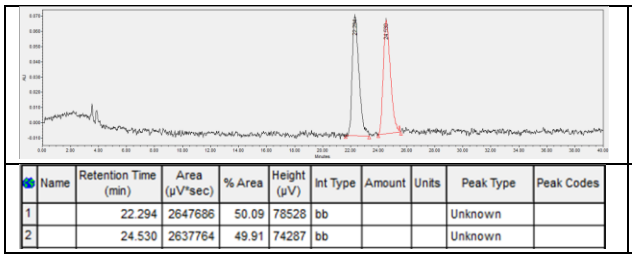
[a]B:l ratios and yields were determined by crude ^{1}H NMR with CH_2Br_2 as internal standard. Ee value was determined by chiral HPLC.

5. Determination of absolute configuration of 7a

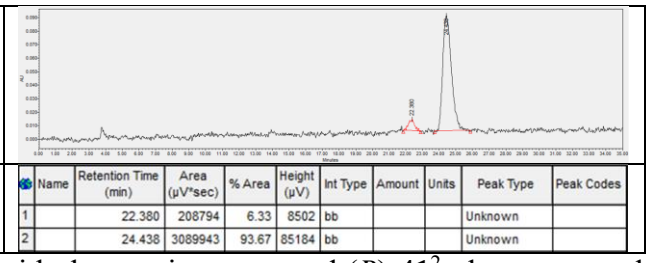


Synthesis of intermediate **40**: To a well stirred solution of **7a** (91 mg, 0.30 mmol) in MeOH (4.0 mL) was added Pd/C (5 wt%, 64 mg, 0.030 mmol of Pd). The resulting mixture was stirred under hydrogen atmosphere for 12 h. Then, it was filtered through Celite, condensed and dissolved in DCM (15 mL) under nitrogen at -78 ºC. Triethylamine (61 mg, 0.60 mmol) was added to the solution. Next, benzoyl chloride (63 mg, 0.45 mmol) was added dropwise. The reaction was allowed to warm to room temperature and was stirred for another 6 h. After this time, it was quenched with sat. aqueous $NaHCO_3$ (15 mL) and extracted by DCM (15 mL × 3). The organic layer was dried with $NaSO_4$, condensed and purified by flash column chromatography (hexane/ethyl acetate = 10/1) to afford **40** (47.0 mg) as a mixture of diastereomers (ratio = 1.5:1) as a colorless oil in 49% yield. As the isomers could not be isolated from each other and it is also unnecessary to isolate them from each other, the given data here is for the mixture of these two isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (br s, 2H, corresponding to 2 Ar-H), 7.51 – 7.34 (m, 3H, corresponding to 3 Ar-H), 6.44 – 6.16 (m, 1H, corresponding to N-H), 4.12 – 3.81 (m, 2H, corresponding to O-CH & N-CH), 1.78 – 1.49 (m, 2H, corresponding to -CH_2-), 1.20 – 1.16 (m, 3H, corresponding to -CH_3), 0.99 – 0.86 (m, 12H, corresponding to Si^{t}Bu & -CH_3), 0.11 – -0.03 (m, 6H, corresponding to $Si(CH_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.28, 167.04, 135.09, 134.99, 131.38, 131.36, 128.68, 128.64, 126.84, 126.80, 70.62, 69.05, 56.37, 56.23, 26.40, 25.97, 25.88, 21.59, 21.03, 20.62, 18.08, 18.05, 10.87, 10.75, -4.07, -4.11, -4.82 (two peaks were overlapped, CH_3) (The amount of carbon signals is doubled because of two isomers); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{31}NSiO_2Na^{\oplus}$ 344.2016, found 344.2017.

Synthesis of known product **41**: To a well stirred solution of **40** (13 mg, 0.040 mmol) in THF (0.5 mL) was added TBAF (1 M in THF, 0.1 mL). The resulting solution was stirred at room temperature for 5 h. After this time, the reaction was quenched by sat. aqueous H_2O (5 mL) and extracted by DCM (5 mL × 3). The organic layer was dried with $NaSO_4$ and condensed. To the residue above in dry DCM (1.5 mL) was added DMP (26 mg, 0.060 mmol) in three portions at 0 ºC. The reaction solution was allowed to warm to room temperature and was stirred for 1.5 h. After this time, the reaction was quenched with sat. aqueous $NaHCO_3$ (15 mL), sat. aqueous $Na_2S_2O_3$ (15 mL) and extracted with DCM (15 mL × 3). The organic layer was dried with $NaSO_4$, condensed and purified by flash column chromatography (hexane/ethyl acetate = 3/1 – 2/1) to afford **41** (6.6 mg) as a yellow oil in 80% yield. $[\alpha]_D^{25}$ +85.4 (*c* 0.50, $CHCl_3$) for 87% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 6.98 (br s, 1H), 4.86 (dd, *J* = 11.6, 6.0 Hz, 1H), 2.28 (s, 3H), 2.21 – 2.13 (m, 1H), 1.86 – 1.75 (m, 1H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.75, 167.07, 134.21, 131.81, 128.71, 127.13, 59.99, 27.26, 24.51, 8.94; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{15}NO_2Na^{\oplus}$ 228.0995, found 228.0993; HPLC: chiral OD-H Column; detected at 220 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 22.4 min (minor), 24.4 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		22.294	2647686	50.09	78528	bb			Unknown	
2		24.530	2637764	49.91	74287	bb			Unknown	

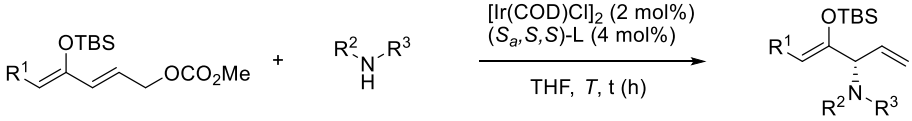


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		22.380	208794	6.33	8502	bb			Unknown	
2		24.438	3089943	93.67	85184	bb			Unknown	

By comparing the rotation data and HPLC data with the previous reported (*R*)-**41**[2], the compound **41** in our report is determined to be *S*.

6. Scope of substrates

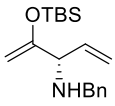
6.1 Scope for the construction of an alpha C-N bond



1 **7 or 8**

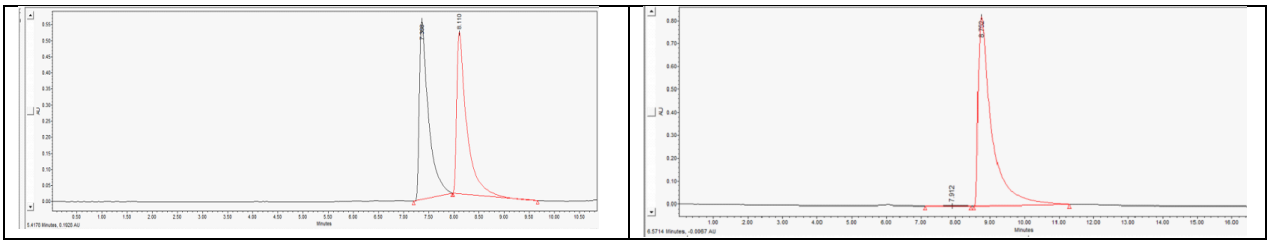
General procedure: To a 4 mL vial containing a magnetic stir bar were added $[Ir(COD)Cl]_2$ (2.6 mg, 0.0040 mmol), (*Sa,S,S*)-L (4.4 mg, 0.0080 mmol) and THF (0.2 mL) in a nitrogen-filled glovebox. The resulting mixture was stirred at RT for 10 min. Then, *n*-propylamine (0.1 mL) was added to the reaction. The vial was sealed with a PTFE-lined cap and stirred at 50 ºC for 20 min. Next, the volatile materials were evaporated under vacuum. Compound **1** (0.20 mmol) in THF (0.2 mL) was added, and the reaction was stirred at RT for 10 min. Then, the amine (0.50 mmol) was added to the reaction. The vial was sealed with a PTFE-lined cap and was removed from the glovebox and stirred at the stated temperature for the stated time. After this time, the crude reaction solution was condensed to obtain a ^{1}H NMR spectrum (with CH_2Br_2 as internal standard). The product was further purified by flash column chromatography using hexane/ethyl acetate as eluent to afford pure product.

(*S*)-*N*-Benzyl-2-((*tert*-butyldimethylsilyl)oxy)penta-1,4-dien-3-amine (7a)



7a

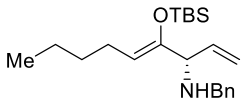
The reaction was run at 40 ºC for 12 h. B:l = 12:1, yellow oil, 50 mg, 82% yield. $[\alpha]_D^{25}$ +5.3 (*c* 1.90, $CHCl_3$) for 99% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 5.81 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.24 (dt, *J* = 17.3, 1.4 Hz, 1H), 5.18 – 5.11 (m, 1H), 4.25 (d, *J* = 1.2 Hz, 1H), 4.18 (d, *J* = 1.3 Hz, 1H), 3.79 – 3.70 (m, 2H), 3.53 (d, *J* = 6.7 Hz, 1H), 1.66 (s, 1H, might be NH), 0.92 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.00, 140.56, 138.47, 128.38, 128.32, 126.88, 116.26, 90.38, 64.85, 51.02, 25.77, 18.18, -4.64, -4.69; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{18}H_{30}NOSi^{\oplus}$ 304.2091, found 304.2105; HPLC: chiral AD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 0.6 mL/min; Retention time: 7.9 min (minor), 8.8 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.368	7104742	50.36	556100	bb			Unknown	
2		8.110	7001771	49.64	506563	bb			Unknown	

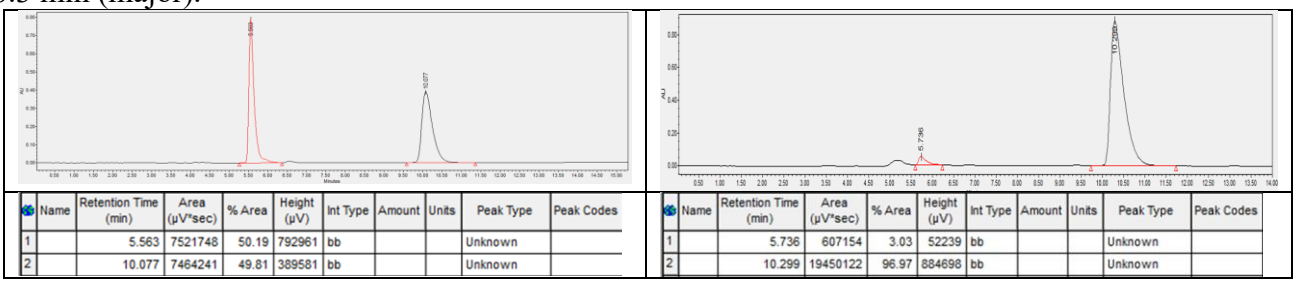
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.912	46088	0.21	1457	bb			Unknown	
2		8.752	22388086	99.79	823945	bb			Unknown	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)nona-1,4-dien-3-amine (7b)



7b

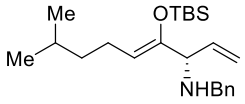
The reaction was run at 55 ºC for 15 h. B:l = 17:1, colorless oil, 65 mg, 90% yield. $[\alpha]_D^{25}$ -4.2 (*c* 3.93, $CHCl_3$) for 94% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 5H), 5.81 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.26 – 5.20 (m, 1H), 5.20 – 5.15 (m, 1H), 4.74 (t, *J* = 7.1 Hz, 1H), 3.83 – 3.66 (m, 2H), 3.51 (d, *J* = 7.0 Hz, 1H), 2.05 (q, *J* = 7.0 Hz, 2H), 1.37 – 1.27 (m, 4H), 0.96 – 0.85 (m, 12H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.68, 140.59, 138.92, 128.40, 128.33, 126.91, 116.37, 109.40, 65.12, 51.36, 32.10, 26.01, 25.14, 22.60, 18.50, 14.09, -3.66, -3.75; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{38}NOSi^{\oplus}$ 360.2717, found 360.2717; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 1.0 mL/min; Retention time: 5.7 min (minor), 10.3 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.563	7521748	50.19	792961	bb			Unknown	
2		10.077	7464241	49.81	389581	bb			Unknown	

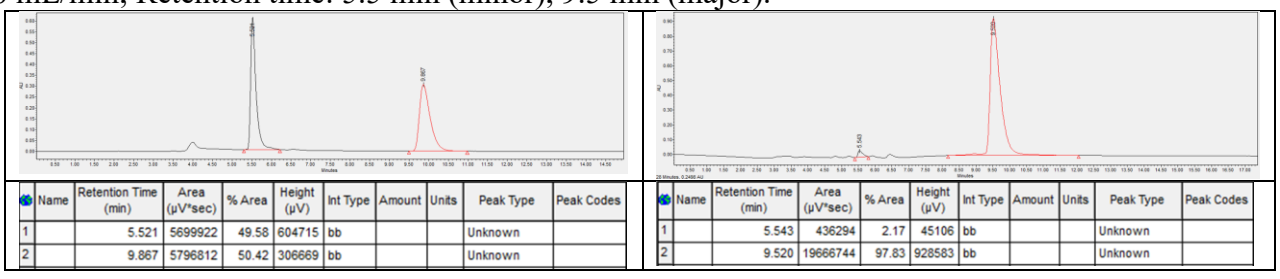
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.736	607154	3.03	52239	bb			Unknown	
2		10.299	19450122	96.97	884698	bb			Unknown	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-8-methylnona-1,4-dien-3-amine (7c)



7c

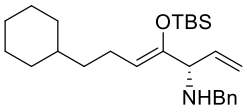
The reaction was run at 50 ºC for 15 h. B:l = 18:1, yellow oil, 72 mg, 96% yield. $[\alpha]_D^{25}$ -4.3 (*c* 3.12, $CHCl_3$) for 96% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 5H), 5.80 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.27 – 5.20 (m, 1H), 5.20 – 5.15 (m, 1H), 4.72 (t, *J* = 7.0 Hz, 1H), 3.80 – 3.67 (m, 2H), 3.50 (d, *J* = 7.0 Hz, 1H), 2.05 (dd, *J* = 15.6, 7.4 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.27 – 1.17 (m, 2H), 0.94 (s, 9H), 0.88 (d, *J* = 6.6 Hz, 6H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.56, 140.60, 138.91, 128.41, 128.33, 126.91, 116.39, 109.56, 65.10, 51.36, 39.07, 27.98, 26.01, 23.41, 22.66, 22.62, 18.50, -3.65, -3.74; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{40}NOSi^{\oplus}$ 374.2874, found 374.2886; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 1.0 mL/min; Retention time: 5.5 min (minor), 9.5 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.521	5699922	49.58	604715	bb			Unknown	
2		9.867	5796812	50.42	306669	bb			Unknown	

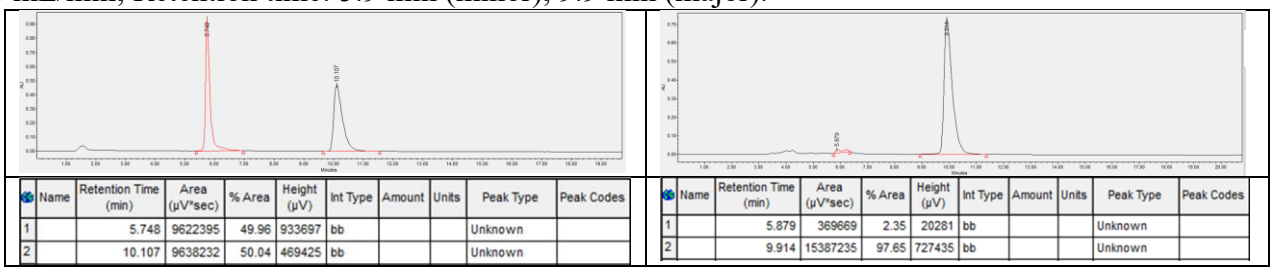
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.543	436294	2.17	45106	bb			Unknown	
2		9.520	19666744	97.83	928583	bb			Unknown	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-7-cyclohexylhepta-1,4-dien-3-amine (7d)



7d

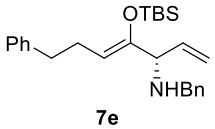
The reaction was run at 50 ºC for 15 h. B:l = 17:1, yellow oil, 79 mg, 96% yield. $[\alpha]_D^{25}$ -2.9 (*c* 4.44, $CHCl_3$) for 96% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 5.80 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 4.72 (t, *J* = 7.0 Hz, 1H), 3.82 – 3.66 (m, 2H), 3.50 (d, *J* = 7.0 Hz, 1H), 2.05 (dd, *J* = 14.9, 7.2 Hz, 2H), 1.76 – 1.59 (m, 5H), 1.27 – 1.08 (m, 6H), 0.98 – 0.83 (m, 11H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.48, 140.60, 138.92, 128.40, 128.33, 126.90, 116.35, 109.68, 65.10, 51.34, 37.61, 33.42, 33.36, 26.80, 26.50, 26.02, 22.86, 18.50, -3.64, -3.72; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{26}H_{44}NOSi^{\oplus}$ 414.3187, found 414.3209; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 1.0 mL/min; Retention time: 5.9 min (minor), 9.9 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.748	9622395	49.96	933697	bb			Unknown	
2		10.107	9638232	50.04	469425	bb			Unknown	

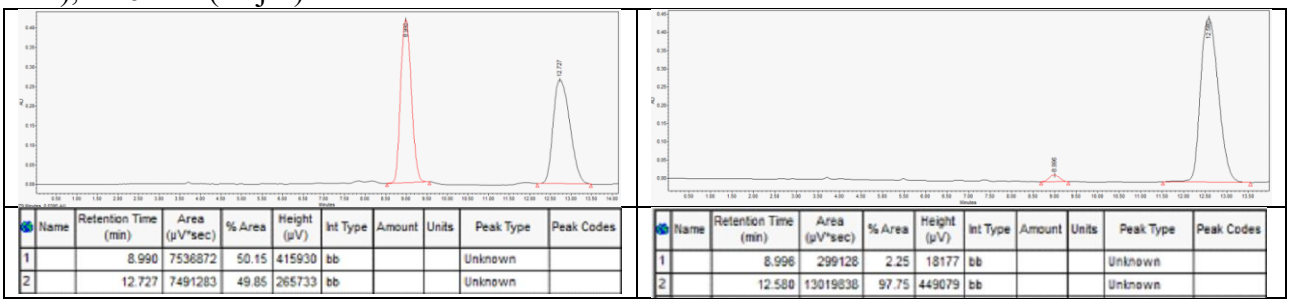
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.879	369669	2.35	20281	bb			Unknown	
2		9.914	15387235	97.65	727435	bb			Unknown	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-7-phenylhepta-1,4-dien-3-amine (7e)



7e

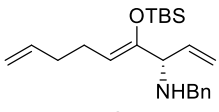
The reaction was run at 50 ºC for 12 h. B:l = 14:1, yellow oil, 59 mg, 73% yield. $[\alpha]_D^{25}$ -2.2 (*c* 1.03, $CHCl_3$) for 95% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 10H), 5.85 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.269 – 5.22 (m, 2H), 4.87 (t, *J* = 7.1 Hz, 1H), 3.81 – 3.72 (m, 2H), 3.56 (d, *J* = 7.0 Hz, 1H), 2.74 – 2.67 (m, 2H), 2.42 (dd, *J* = 15.4, 7.3 Hz, 2H), 0.97 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.28, 142.25, 140.47, 138.73, 128.49, 128.39, 128.31, 128.30, 126.91, 125.75, 116.46, 108.31, 64.99, 51.28, 36.09, 27.14, 26.00, 18.47, -3.62, -3.71; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{26}H_{38}NOSi^{\oplus}$ 408.2717, found 408.2711; HPLC: chiral AD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 99.9/0.1; flow = 1.0 mL/min; Retention time: 9.0 min (minor), 12.6 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.990	7536872	50.15	415930	bb			Unknown	
2		12.727	7491283	49.85	265733	bb			Unknown	

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.996	299128	2.25	18177	bb			Unknown	
2		12.580	13019838	97.75	449079	bb			Unknown	

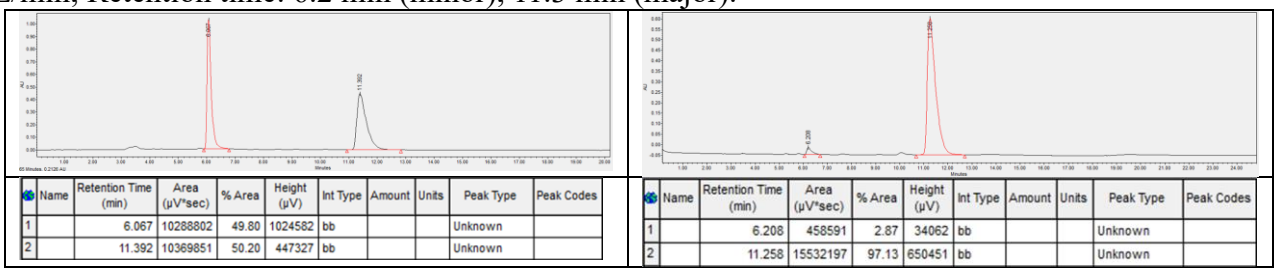
(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)nona-1,4,8-trien-3-amine (7f)



7f

The reaction was run at 55 ºC for 15 h. B:l = 15:1, yellow oil, 62 mg, 87% yield. $[\alpha]_D^{25}$ -2.7 (*c* 3.94, $CHCl_3$) for 94% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 5.90 – 5.71 (m, 2H), 5.23 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.07 – 4.98 (m, 1H), 4.98 – 4.92 (m, 1H), 4.77 (t, *J* = 6.7 Hz, 1H), 3.81 – 3.68 (m, 2H), 3.51 (d, *J* = 7.0 Hz, 1H), 2.24 – 2.01 (m, 4H), 0.94 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.17, 140.55, 138.81, 138.63, 128.41, 128.32, 126.92, 116.46, 114.58, 108.39, 65.05, 51.33, 33.96,

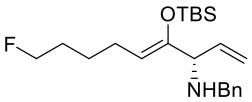
26.00, 24.78, 18.49, -3.63, -3.71; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{36}NOSi^{\oplus}$ 358.2561, found 358.2561; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 1.0 mL/min; Retention time: 6.2 min (minor), 11.3 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.067	10288802	49.80	1024582	bb			Unknown	
2		11.392	10369851	50.20	447327	bb			Unknown	

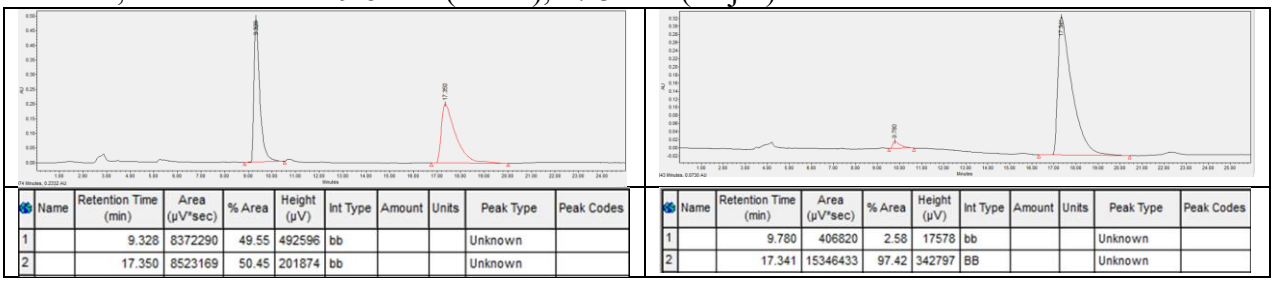
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.208	458591	2.87	34062	bb			Unknown	
2		11.258	15532197	97.13	650451	bb			Unknown	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-9-fluorononona-1,4-dien-3-amine (7g)



7g

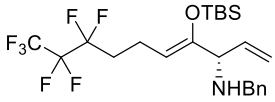
The reaction was run at 55 °C for 18 h. B:l = 16:1, yellow oil, 60 mg, 79% yield. $[\alpha]_D^{25}$ -4.4 (*c* 3.07, $CHCl_3$) for 95% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 5H), 5.79 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.25 – 5.17 (m, 2H), 4.75 (t, *J* = 7.1 Hz, 1H), 4.49 (t, *J* = 6.2 Hz, 1H), 4.38 (t, *J* = 6.2 Hz, 1H), 3.78 – 3.69 (m, 2H), 3.51 (d, *J* = 7.0 Hz, 1H), 2.09 (q, *J* = 7.3 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.49 – 1.41 (m, 2H), 0.93 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.42, 140.50, 138.79, 128.43, 128.31, 126.96, 116.54, 108.51, 84.11 (d, J_{CF} = 164.5 Hz), 65.04, 51.38, 30.18 (d, J_{CF} = 19.4 Hz), 25.98, 25.39 (d, J_{CF} = 5.3 Hz), 24.89, 18.49, -3.65, -3.74; ^{19}F NMR (376 MHz, $CDCl_3$) δ -215.33 – -219.20 (m, 1F); HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{37}FNOSi^{\oplus}$ 378.2623, found 378.2626; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 1.0 mL/min; Retention time: 9.8 min (minor), 17.3 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		9.328	8372290	49.55	492596	bb			Unknown	
2		17.350	8523169	50.45	201874	bb			Unknown	

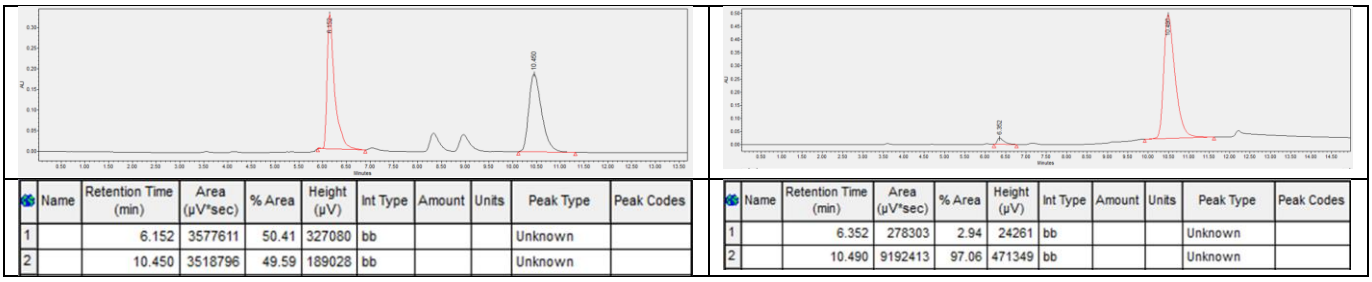
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		9.780	406820	2.58	17578	bb			Unknown	
2		17.341	15346433	97.42	342797	BB			Unknown	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-8,8,9,9,10,10,10-heptafluorodeca-1,4-dien-3-amine (7h)



7h

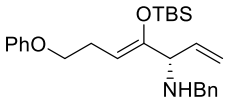
The reaction was run at 55 °C for 24 h. B:l = 15:1, yellow oil, 74 mg, 74% yield. $[\alpha]_D^{25}$ -1.9 (*c* 3.07, $CHCl_3$) for 94% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 5H), 5.77 (ddd, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.25 – 5.20 (m, 2H), 4.77 (t, *J* = 7.1 Hz, 1H), 3.73 (dd, *J* = 35.7, 13.0 Hz, 2H), 3.52 (d, *J* = 7.1 Hz, 1H), 2.40 – 2.30 (m, 2H), 2.14 – 2.01 (m, 2H), 0.93 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.22, 140.34, 138.39, 128.49, 128.30, 127.06, 116.98, 105.49, 64.84, 51.44, 30.80 (t, *J* = 22.6 Hz), 25.85, 18.43, 16.41, -3.72, -3.80 (three carbon signals from C_3F_7 unit did not appear); ^{19}F NMR (376 MHz, $CDCl_3$) δ -79.80 (t, *J* = 9.5 Hz, 3F), -114.83 – -114.94 (m, 2F), -127.12 (s, 2F) ; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{33}F_7NOSi^{\oplus}$ 500.2214, found 500.2222; HPLC: chiral OD-H column (250 mm); detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 1.0 mL/min; Retention time: 6.4 min (minor), 10.5 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.152	3577611	50.41	327080	bb			Unknown	
2		10.450	3518796	49.59	189028	bb			Unknown	

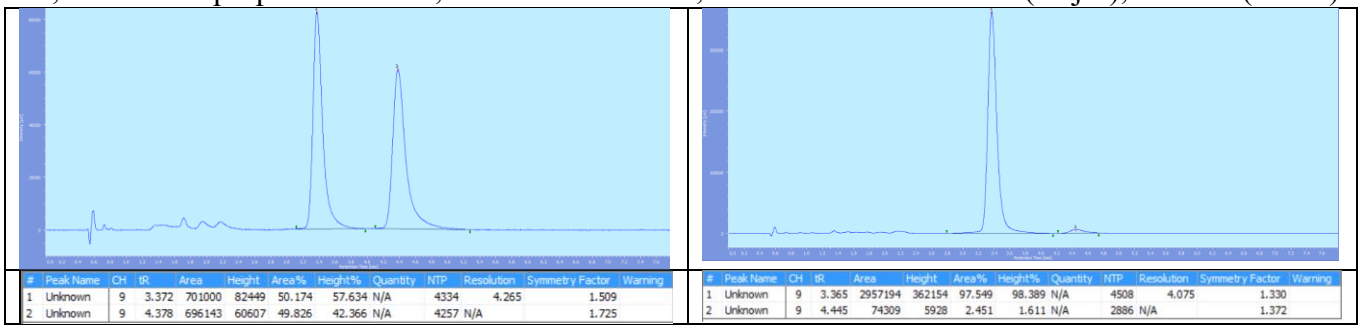
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.352	278303	2.94	24261	bb			Unknown	
2		10.490	9192413	97.06	471349	bb			Unknown	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-7-phenoxyhepta-1,4-dien-3-amine (7i)



7i

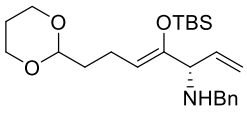
The reaction was run at 55 °C for 16 h. B:l = 10:1, yellow oil, 65 mg, 77% yield. $[\alpha]_D^{25}$ -4.7 (*c* 2.86, $CHCl_3$) for 95% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 7H), 7.02 – 6.92 (m, 3H), 5.86 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.40 – 5.19 (m, 2H), 4.95 (t, *J* = 7.0 Hz, 1H), 3.99 (t, *J* = 6.9 Hz, 2H), 3.80 (dd, *J* = 21.6 Hz, 12.8 Hz, 2H), 3.60 (d, *J* = 7.0 Hz, 1H), 2.61 (q, *J* = 6.9 Hz, 2H), 1.00 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.13, 152.02, 140.44, 138.57, 129.46, 128.44, 128.34, 126.98, 120.59, 116.78, 114.67, 104.33, 67.54, 65.02, 51.38, 25.98, 25.76, 18.49, -3.59, -3.69; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{26}H_{38}NO_2Si^{\oplus}$ 424.2666, found 424.2667; The enantiomeric excess was determined by SFC analysis: chiral OD-H column; detected at 220 nm, 40 °C; *n*-hexane/*i*-propanol = 90/10; flow = 2.5 mL/min; Retention time: 3.4 min (major), 4.4 min (minor).



#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	3.372	701000	82449	50.174	57.634	N/A	4334	4.265	1.509	
2	Unknown	9	4.378	696143	60607	49.826	42.366	N/A	4257	N/A	1.725	

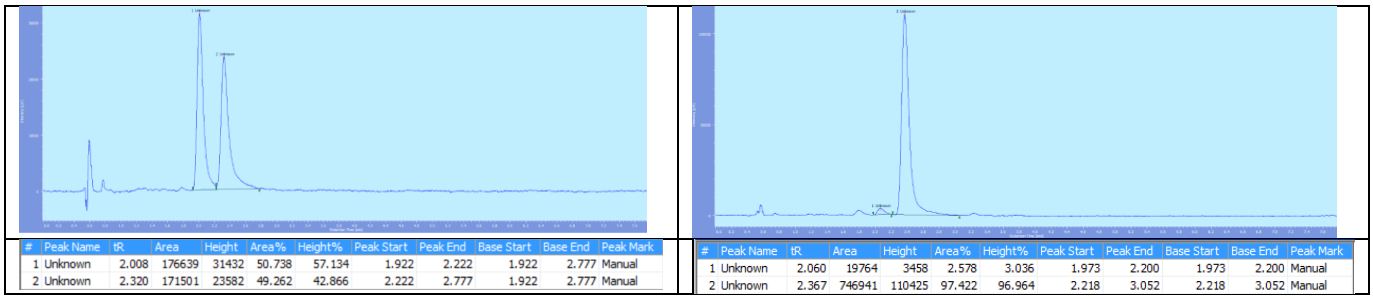
#	Peak Name	CH	tR	Area	Height	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	3.365	2957194	362154	97.549	98.389	N/A	4508	4.075	1.330	
2	Unknown	9	4.445	74309	5928	2.451	1.611	N/A	2886	N/A	1.372	

(*S*,*Z*)-*N*-Benzyl-4-((*tert*-butyldimethylsilyl)oxy)-7-(1,3-dioxan-2-yl)hepta-1,4-dien-3-amine (7j)



7j

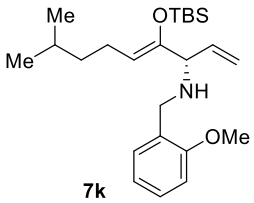
The reaction was run at 55 °C for 22 h. B:l = 19:1, colorless oil, 75 mg, 90% yield. $[\alpha]_D^{25}$ -1.7 (*c* 4.47, $CHCl_3$) for 95% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 5H), 5.80 (ddd, *J* = 17.2, 10.2, 6.9 Hz, 1H), 5.22 (d, *J* = 17.3 Hz, 1H), 5.17 (d, *J* = 10.3 Hz, 1H), 4.74 (t, *J* = 7.1 Hz, 1H), 4.50 (t, *J* = 5.2 Hz, 1H), 4.08 (dd, *J* = 10.8, 4.9 Hz, 2H), 3.79 – 3.66 (m, 4H), 3.50 (d, *J* = 6.9 Hz, 1H), 2.20 – 2.00 (m, 3H), 1.65 – 1.60 (m, 2H), 1.32 (d, *J* = 13.4 Hz, 1H), 0.93 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.24, 140.55, 138.82, 128.42, 128.32, 126.93, 116.42, 108.28, 102.03, 66.93, 65.04, 51.32, 35.33, 26.01, 25.96, 20.04, 18.50, -3.67, -3.74; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{24}H_{40}NO_3Si^{\oplus}$ 418.2772, found 418.2784; The enantiomeric excess was determined by SFC analysis: chiral OD-H column; detected at 220 nm, 40 °C; *n*-hexane/*i*-propanol = 92/8; flow = 2.5 mL/min; Retention time: 2.1 min (minor), 2.4 min (major).



#	Peak Name	tR	Area	Height	Area%	Height%	Peak Start	Peak End	Base Start	Base End	Peak Mark
1	Unknown	2.008	176639	31432	50.738	57.134	1.922	2.222	1.922	2.777	Manual
2	Unknown	2.320	171501	23582	49.262	42.866	2.222	2.777	1.922	2.777	Manual

#	Peak Name	tR	Area	Height	Area%	Height%	Peak Start	Peak End	Base Start	Base End	Peak Mark
1	Unknown	2.060	19764	3458	2.578	3.036	1.973	2.200	1.973	2.200	Manual
2	Unknown	2.367	746941	110425	97.422	96.964	2.218	3.052	2.218	3.052	Manual

(*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-*N*-(2-methoxybenzyl)-8-methylnona-1,4-dien-3-amine (7k)



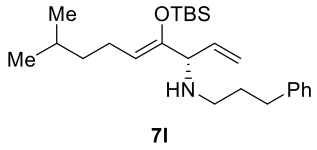
7k

The reaction was run at 55 °C for 20 h. B:l = 16:1, yellow oil, 69 mg, 85% yield. $[\alpha]_D^{25}$ +7.9 (*c* 4.32, $CHCl_3$) for 93% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 2H), 6.98 – 6.85 (m, 2H), 5.83 (ddd, *J* = 17.3, 10.2, 7.3 Hz, 1H), 5.29 – 5.18 (m, 2H), 4.79 (t, *J* = 7.0 Hz, 1H), 3.87 (s, 3H), 3.78 (dd, *J* = 36.6, 13.3 Hz, 2H), 3.50 (d, *J* = 7.3 Hz, 1H), 2.08 (dd, *J* = 15.5, 7.3 Hz, 2H), 1.88 (br s, 1H), 1.60 – 1.58 (m, 1H), 1.29 – 1.23 (m, 2H), 0.96 (s, 9H), 0.91 (d, *J* = 6.6 Hz, 6H), 0.11 (d, *J* = 1.1 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.77, 149.97, 139.22, 130.06, 128.56, 128.13, 120.36, 116.39, 110.23, 109.28, 64.92, 55.17, 46.73, 39.03, 27.95, 25.97, 23.39, 22.66, 22.62, 18.44, -3.76, -3.95; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{24}H_{42}NO_2Si^{\oplus}$ 404.2979, found 404.2980; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 99.8/0.2; flow = 0.5 mL/min; Retention time: 12.8 min (minor), 14.3 min (major).

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.639	25341125	50.35	1338682	bb			Unknown	
2		14.285	24988109	49.65	1309070	bb			Unknown	

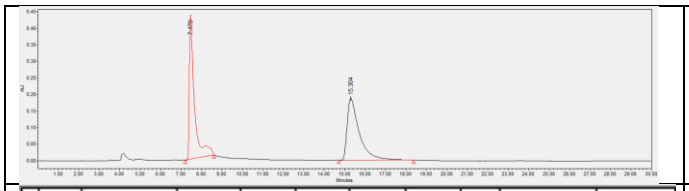
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.769	1675161	3.45	77755	bb			Unknown	
2		14.321	46868893	96.55	2750550	bb			Unknown	

(*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-8-methyl-*N*-(3-phenylpropyl)nona-1,4-dien-3-amine (7l)

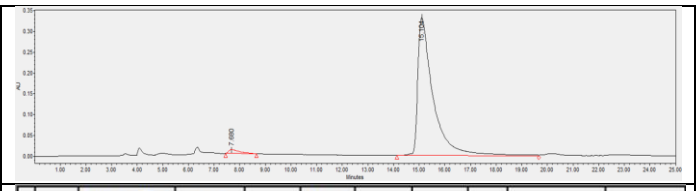


7l

The reaction was run at 55 °C for 18 h. B:l = 11:1, yellow oil, 69 mg, 86% yield. $[\alpha]_D^{25}$ -1.6 (*c* 4.46, $CHCl_3$) for 96% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.22 (m, 2H), 7.20 – 7.03 (m, 3H), 5.71 (ddd, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.19 – 5.03 (m, 2H), 4.61 (t, *J* = 7.0 Hz, 1H), 3.39 (d, *J* = 7.1 Hz, 1H), 2.73 – 2.35 (m, 4H), 1.99 (dd, *J* = 15.5, 7.3 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.57 – 1.46 (m, 1H), 1.20 – 1.14 (m, 2H), 0.92 (s, 9H), 0.84 (d, *J* = 6.6 Hz, 6H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.64, 142.35, 139.03, 128.42, 128.36, 125.78, 116.10, 109.28, 66.02, 47.15, 39.03, 33.85, 32.08, 27.97, 26.02, 23.38, 22.65, 22.62, 18.51, -3.62, -3.71; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{25}H_{44}NOSi^{\oplus}$ 402.3187, found 402.3187; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 1.0 mL/min; Retention time: 7.7 min (minor), 15.1 min (major).

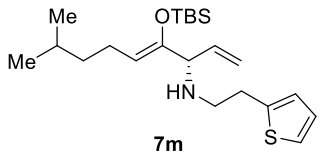


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.470	7541294	49.33	430995	bb			Unknown	
2		15.304	7746060	50.67	187554	bb			Unknown	



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.680	294080	2.09	9592	bb			Unknown	
2		15.104	13786120	97.91	333180	BV			Unknown	

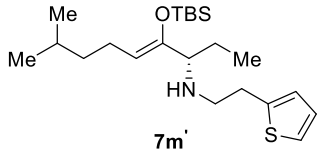
(*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-8-methyl-*N*-(2-(thiophen-2-yl)ethyl)nona-1,4-dien-3-amine (7m)



7m

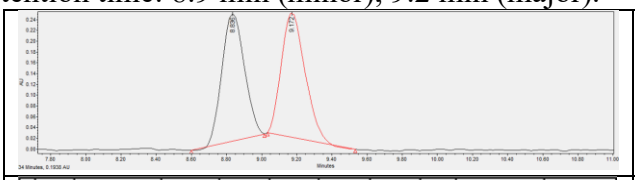
The reaction was run at 55 °C for 20 h. B:l = 18:1, yellow oil, 63 mg, 80% yield. $[\alpha]_D^{25}$ -10.4 (*c* 1.08, $CHCl_3$) for 96% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 4.7 Hz, 1H), 6.92 (dd, *J* = 5.0, 3.4 Hz, 1H), 6.84 (d, *J* = 2.9 Hz, 1H), 5.74 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.19 – 5.13 (m, 2H), 4.63 (t, *J* = 7.0 Hz, 1H), 3.45 (d, *J* = 7.1 Hz, 1H), 3.07 – 2.95 (m, 2H), 2.92 – 2.76 (m, 2H), 2.01 (dd, *J* = 15.9, 7.0 Hz, 2H), 1.61 – 1.50 (m, 1H), 1.43 (s, 1H), 1.22 – 1.18 (m, 2H), 0.92 (s, 9H), 0.87 (d, *J* = 6.7 Hz, 6H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.43, 142.77, 138.75, 126.86, 125.02, 123.52, 116.32, 109.43, 65.79, 48.83, 38.99, 30.74, 27.94, 25.98, 23.34, 22.62, 22.61, 18.46, -3.67, -3.82; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{40}NSOSi^{\oplus}$ 394.2594, found 394.2595; Ee value was determined by **7m'** from the hydrogenation of **7m**.

(*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-8-methyl-*N*-(2-(thiophen-2-yl)ethyl)non-4-en-3-amine (7m')

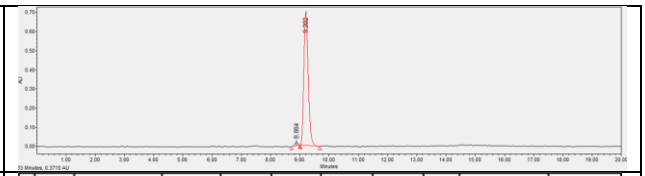


7m'

Procedure: To a well stirred solution of **7m** (38 mg, 0.10 mmol) in MeOH (2.0 mL) was added PtO_2 (5.5 mg, 0.040 mmol). The resulting mixture was stirred under hydrogen atmosphere for 12 h. After this time, it was condensed and purified by flash column chromatography (hexane/ethyl acetate = 20/1) to afford the pure substrate **7m'** (30 mg) as colorless oil in 79% yield. $[\alpha]_D^{25}$ -19.5 (*c* 1.82, $CHCl_3$) for 96% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 5.1 Hz, 1H), 6.92 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 4.51 (t, *J* = 7.0 Hz, 1H), 3.05 – 2.88 (m, 3H), 2.82 – 2.72 (m, 2H), 2.03 (dd, *J* = 15.4, 7.3 Hz, 2H), 1.61 – 1.50 (m, 2H), 1.47 – 1.39 (m, 1H), 1.20 (dd, *J* = 15.3, 7.2 Hz, 2H), 0.93 (s, 9H), 0.88 – 0.83 (m, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.28, 143.00, 126.81, 124.92, 123.48, 108.89, 64.34, 48.72, 39.25, 30.81, 27.87, 26.37, 26.08, 23.30, 22.67, 22.64, 18.60, 10.56, -3.37, -3.75; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{42}NSOSi^{\oplus}$ 396.2751, found 396.2750; HPLC: two chiral OD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 0.5 mL/min; Retention time: 8.9 min (minor), 9.2 min (major).

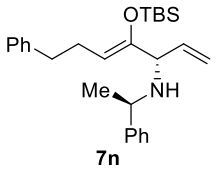


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.836	2118873	49.39	236432	bb			Unknown	
2		9.172	2171051	50.61	230308	bb			Unknown	



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.884	131438	1.92	17711	bb			Unknown	
2		9.202	6701362	98.08	685823	bb			Unknown	

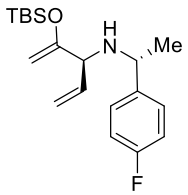
(*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-7-phenyl-*N*-((*R*)-1-phenylethyl)hepta-1,4-dien-3-amine (7n)



7n

The reaction was run with $[Ir(COD)Cl]_2$ (4 mol%) and (*S*$_a$,*S*,*S*)-L (8 mol%) in THF (0.5 M) at 55 °C for 22 h. B:l = 9:1, dr = 96:4, yellow oil, 64 mg, 76% yield. $[\alpha]_D^{25}$ -22.3 (*c* 1.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.22 (m, 10H), 5.92 – 5.71 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.67 (t, *J* = 7.0 Hz, 1H), 3.87 (q, *J* = 6.6 Hz, 1H), 3.35 (d, *J* = 5.9 Hz, 1H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.59 – 2.35 (m, 2H), 1.35 (d, *J* = 6.6 Hz, 3H), 0.97 (s, 9H), 0.14 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.83, 145.86, 142.26, 139.48, 128.56, 128.39, 128.33, 126.80 (two carbon signals are overlapped, CH of Ph), 125.79, 115.28, 107.95, 62.43, 54.83, 36.18, 27.00, 26.03, 25.01, 18.56, -3.56, -3.59; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{27}H_{40}NOSi^{\oplus}$ 422.2874, found 422.2874.

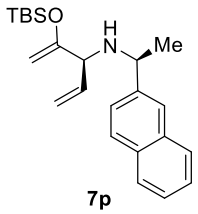
(*S*)-2-((*tert*-Butyldimethylsilyl)oxy)-*N*-((*R*)-1-(4-fluorophenyl)ethyl)penta-1,4-dien-3-amine (7o)



7o

The reaction was run at 40 °C for 16 h. B:l = 8:1, dr = 95:5, colorless oil, 48 mg, 71% yield. $[\alpha]_D^{25}$ +16.3 (*c* 2.53, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.36 – 7.25 (m, 2H), 7.11 – 6.96 (m, 2H), 5.77 (ddd, *J* = 17.5, 10.2, 7.5 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 4.25 (d, *J* = 1.0 Hz, 1H), 4.15 (d, *J* = 1.3 Hz, 1H), 3.85 (q, *J* = 6.6 Hz, 1H), 3.41 (d, *J* = 7.5 Hz, 1H), 1.70 (s, 1H), 1.35 (d, *J* = 6.6 Hz, 3H), 0.93 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.84 (d, J_{CF} = 244.2 Hz), 158.54, 141.51, 138.22, 128.29 (d, J_{CF} = 7.8 Hz), 116.63, 115.16 (d, J_{CF} = 21.1 Hz), 90.05, 62.81, 53.83, 25.76, 24.10, 18.17, -4.60, -4.76; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.60 (s, 1F); HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{19}H_{31}NFOSi^{\oplus}$ 336.2153, found 336.2150.

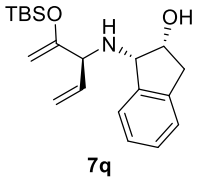
(*S*)-2-((*tert*-Butyldimethylsilyl)oxy)-*N*-((*S*)-1-(naphthalen-2-yl)ethyl)penta-1,4-dien-3-amine (7p)



7p

The reaction was run in THF (0.5 M) at 50 °C for 18 h. B:l = 13:1, dr = 97:3, yellow oil, 57 mg, 77% yield. $[\alpha]_D^{25}$ -23.0 (*c* 2.51, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.88 – 7.73 (m, 4H), 7.55 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.52 – 7.42 (m, 2H), 5.89 – 5.74 (m, 1H), 5.21 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.08 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.18 (d, *J* = 1.1 Hz, 1H), 4.06 – 3.94 (m, 2H), 3.34 (d, *J* = 5.9 Hz, 1H), 1.77 (s, 1H), 1.40 (d, *J* = 6.6 Hz, 3H), 0.97 (s, 9H), 0.27 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.41, 143.13, 138.83, 133.54, 132.93, 128.10, 127.84, 127.70, 125.83, 125.64, 125.44, 125.40, 115.24, 90.60, 62.70, 54.87, 25.77, 25.14, 18.22, -4.64, -4.71; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{34}NOSi^{\oplus}$ 368.2404, found 368.2403.

(1*S*,2*R*)-1-(((*S*)-2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (7q)

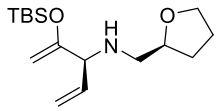


7q

The reaction was run in THF (0.5 M) at 40 °C for 11 h. B:l = 10:1, dr = 95:5, yellow oil, 54 mg, 78% yield. $[\alpha]_D^{25}$ +3.6 (*c* 1.75, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 7.26 – 7.21 (m, 4H), 5.96 – 5.78 (m, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.36 (dd, *J* = 7.8, 4.4 Hz, 1H), 4.31 (d, *J* = 1.3 Hz, 1H), 4.25 (d, *J* = 1.4 Hz, 1H), 4.21 (d, *J* = 5.1 Hz, 1H), 3.74 (d, *J* = 5.9 Hz, 1H), 3.03 (d, *J* = 2.4 Hz, 2H), 2.02 (br s, 1H), 0.95 (s, 9H), 0.22 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.17, 142.39, 141.42, 137.95, 128.03,

126.70, 125.68, 123.61, 116.55, 91.42, 70.57, 64.53, 63.28, 39.76, 25.80, 18.21, -4.44, -4.87; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{20}H_{32}NO_2Si^{\oplus}$ 346.2197, found 346.2195.

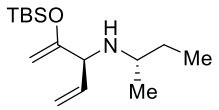
(*S*)-2-((*tert*-Butyldimethylsilyl)oxy)-*N*-(((*S*)-tetrahydrofuran-2-yl)methyl)penta-1,4-dien-3-amine (7r)



7r

The reaction was run at 40 ºC for 19 h. B:l = 8:1, dr = 98:2, yellow oil, 33 mg, 56% yield. $[\alpha]_D^{25}$ +11.0 (*c* 1.77, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.76 (ddd, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.20 (dd, *J* = 17.2, 0.9 Hz, 1H), 5.12 (dd, *J* = 10.3, 0.8 Hz, 1H), 4.24 (s, 1H), 4.12 (s, 1H), 4.00 - 3.96 (m, 1H), 3.83 (dd, *J* = 14.9, 6.8 Hz, 1H), 3.72 (dd, *J* = 14.6, 7.4 Hz, 1H), 3.48 (d, *J* = 6.9 Hz, 1H), 2.69 – 2.56 (m, 2H), 1.97 - 1.92 (m, 1H), 1.90 – 1.82 (m, 2H), 1.61 - 1.55 (m, 2H), 0.91 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.33, 138.59, 116.17, 89.89, 78.59, 68.00, 65.86, 51.52, 29.37, 25.90, 25.73, 18.14, -4.67, -4.71; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{16}H_{32}NO_2Si^{\oplus}$ 298.2197, found 298.2198.

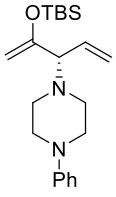
(*S*)-*N*-((*S*)-*sec*-Butyl)-2-((*tert*-butyldimethylsilyl)oxy)penta-1,4-dien-3-amine (7s)



7s

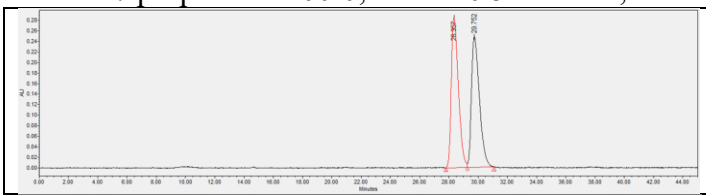
The reaction was run at 40 ºC for 19 h. B:l > 20:1, dr = 95:5, yellow oil, 38 mg, 70% yield. $[\alpha]_D^{25}$ +10.5 (*c* 0.47, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.19 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.11 (dd, *J* = 10.2, 0.8 Hz, 1H), 4.20 (s, 1H), 4.10 (s, 1H), 3.61 (d, *J* = 6.7 Hz, 1H), 2.64 – 2.54 (m, 1H), 1.54 – 1.43 (m, 1H), 1.36 (s, 1H), 1.30 – 1.26 (m, 1H), 1.00 (d, *J* = 6.2 Hz, 3H), 0.92 (s, 9H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.57, 138.96, 115.80, 89.83, 62.93, 50.81, 29.33, 25.76, 20.12, 18.17, 10.25, -4.64, -4.79; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{15}H_{32}NOSi^{\oplus}$ 270.2248, found 270.2245.

(*S*)-1-(2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)-4-phenylpiperazine (7t)

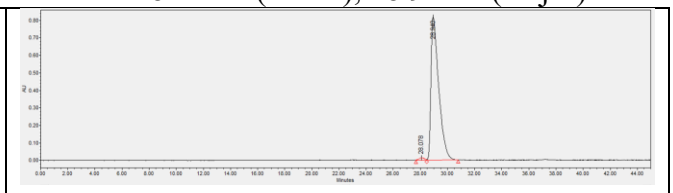


7t

The reaction was run at RT for 11 h. B:l > 20:1, yellow oil, 66 mg, 92% yield. $[\alpha]_D^{25}$ +7.5 (*c* 4.16, $CHCl_3$) for 97% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 5.87 (ddd, *J* = 17.4, 10.1, 8.4 Hz, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.18 (dd, *J* = 10.2, 1.6 Hz, 1H), 4.29 (s, 1H), 4.17 (s, 1H), 3.21 – 3.12 (m, 4H), 3.13 (d, *J* = 8.3 Hz, 1H), 2.70 – 2.63 (m, 4H), 0.94 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.61, 151.54, 137.34, 129.12, 119.45, 117.51, 115.88, 91.49, 74.21, 50.79, 49.39, 25.76, 18.20, -4.56, -4.65; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{21}H_{35}F_7N_2OSi^{\oplus}$ 359.2513, found 359.2514; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 28.1 min (minor), 28.9 min (major).

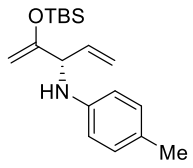


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		28.357	9568789	50.51	285004	BV			Unknown	
2		29.752	9374935	49.49	248368	VB			Unknown	



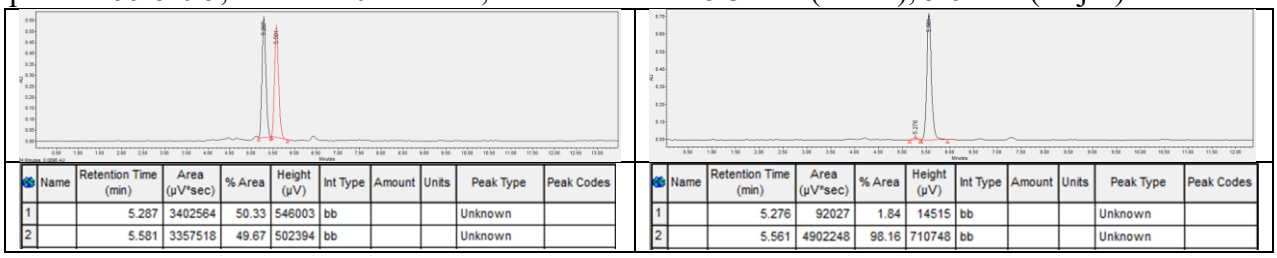
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		28.078	374580	1.14	13488	BV			Unknown	
2		28.940	32571215	98.86	816259	VB			Unknown	

(*S*)-*N*-(2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)-4-methylaniline (7u)



7u

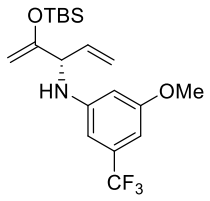
The general procedure was followed, except that DABCO (20 mol%) was added to the reaction along with the amine. The reaction was run at RT for 15 h. B:l > 20:1, yellow oil, 53 mg, 87% yield. $[\alpha]_D^{25}$ -13.8 (*c* 3.28, $CHCl_3$) for 96% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.3 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 5.90 (ddd, *J* = 17.0, 10.3, 5.7 Hz, 1H), 5.32 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 4.32 (d, *J* = 1.4 Hz, 1H), 4.26 (d, *J* = 5.5 Hz, 1H), 4.15 (d, *J* = 1.4 Hz, 1H), 3.87 (br s, 1H), 2.23 (s, 3H), 0.93 (s, 9H), 0.17 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.34, 144.79, 137.53, 129.62, 126.88, 116.18, 114.04, 90.30, 60.95, 25.77, 20.49, 18.18, -4.67, -4.75; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{18}H_{30}NOSi^{\oplus}$ 304.2091, found 304.2087; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 1.0 mL/min; Retention time: 5.3 min (minor), 5.6 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.287	3402564	50.33	546003	bb			Unknown	
2		5.581	3357518	49.67	502394	bb			Unknown	

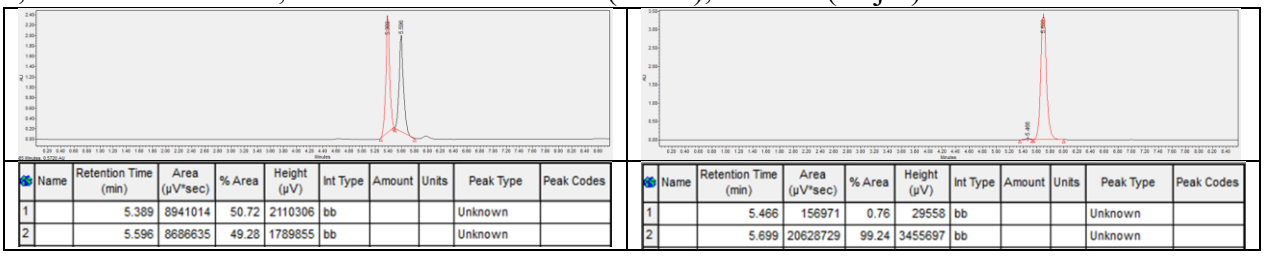
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.276	92027	1.84	14515	bb			Unknown	
2		5.561	4902248	98.16	710748	bb			Unknown	

(*S*)-*N*-(2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)-3-methoxy-5-(trifluoromethyl)aniline (7v)



7v

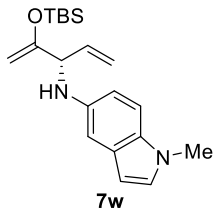
The general procedure was followed, except that DABCO (5 mol%) was added to the reaction along with the amine. The reaction was run at RT for 15 h. B:l > 20:1, yellow oil, 54 mg, 70% yield. $[\alpha]_D^{25}$ -12.3 (*c* 2.87, $CHCl_3$) for 98% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 6.46 (d, *J* = 12.9 Hz, 2H), 6.27 (s, 1H), 5.90 (ddd, *J* = 17.1, 10.3, 5.6 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.33 (d, *J* = 1.4 Hz, 1H), 4.28 (t, *J* = 6.5 Hz, 1H), 4.18 (d, *J* = 1.6 Hz, 2H), 3.78 (s, 3H), 0.92 (s, 9H), 0.18 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.87, 156.55, 148.60, 136.64, 132.28 (q, J_{CF} = 31.8 Hz), 125.61, 116.73, 103.62, 102.36, 99.60, 90.68, 60.59, 55.41, 25.71, 18.17, -4.74, -4.82; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28 (s, 3F); HRMS (EI): $[M]^{\oplus}$ calcd for $C_{19}H_{28}NF_3O_2Si^{\oplus}$ 387.1841, found 387.1849; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 5.5 min (minor), 5.7 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.389	8941014	50.72	2110306	bb			Unknown	
2		5.596	8686635	49.28	1789855	bb			Unknown	

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.466	156971	0.76	29558	bb			Unknown	
2		5.699	20628729	99.24	3455697	bb			Unknown	

(*S*)-*N*-(2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)-1-methyl-1*H*-indol-5-amine (7w)



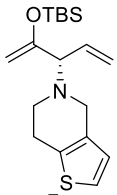
7w

The general procedure was followed, except that DABCO (40 mol%) was added to the reaction along with the amine. The reaction was run at RT for 12 h. B:l > 20:1, yellow oil, 60 mg, 88% yield. $[\alpha]_D^{25}$ -14.4 (*c* 3.77, $CHCl_3$) for 98% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 1H), 6.94 (d, *J* = 3.0 Hz, 1H), 6.85 (d, *J* = 1.9 Hz, 1H), 6.68 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.30 (d, *J* = 2.9 Hz, 1H), 5.96 (ddd, *J* = 16.4, 10.3, 5.8 Hz, 1H), 5.37 (dd, *J* = 17.2, 0.9 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.35 (s, 1H), 4.33 (d, *J* = 5.8 Hz, 1H), 4.16 (s, 1H), 3.82 (s, 0H), 3.72 (s, 3H), 0.96 (s, 3H), 0.20 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.75, 140.73, 138.02, 131.57, 129.23, 128.83, 116.01, 112.56, 109.62, 104.44, 99.79, 90.24, 62.22, 32.88, 25.80, 18.19, -4.67, -4.68; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{30}N_2OSiNa^{\oplus}$ 365.2020, found 365.2022; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 1.0 mL/min; Retention time: 24.0 min (minor), 25.9 min (major).

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		23.559	6378752	50.75	171978	bb			Unknown	
2		25.682	6190700	49.25	153583	bb			Unknown	

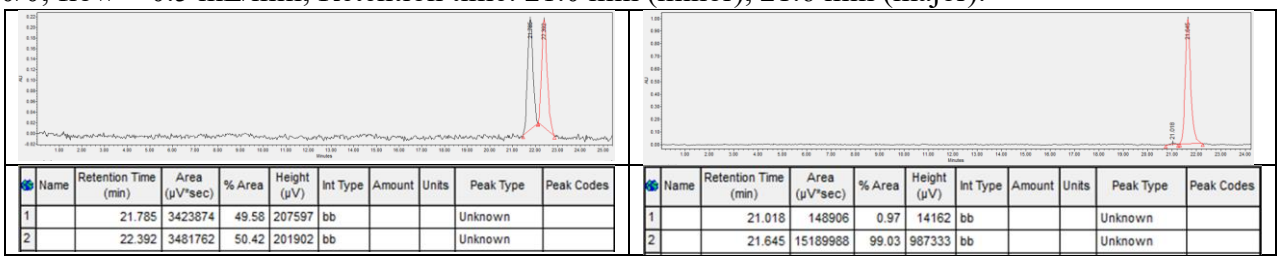
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		23.994	87988	1.13	4091	bb			Unknown	
2		25.896	7712931	98.87	187550	bb			Unknown	

(*S*)-5-(2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridine (7x)



7x

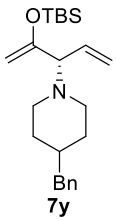
The reaction was run in THF (0.5 M), 50 ºC for 11 h. B:l > 20:1, yellow oil, 57 mg, 85% yield. $[\alpha]_D^{25}$ +28.6 (*c* 2.25, $CHCl_3$) for 98% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 7.05 (d, *J* = 5.1 Hz, 1H), 6.72 (d, *J* = 5.1 Hz, 1H), 5.95 – 5.83 (m, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 5.19 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.34 (s, 1H), 4.20 (s, 1H), 3.69 (d, *J* = 14.5 Hz, 1H), 3.56 (d, *J* = 14.5 Hz, 1H), 3.36 (d, *J* = 8.0 Hz, 1H), 3.06 – 2.99 (m, 1H), 2.90 – 2.80 (m, 2H), 2.74 (ddd, *J* = 11.9, 7.6, 4.7 Hz, 1H), 0.92 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.75, 137.42, 134.52, 133.69, 125.48, 122.46, 117.37, 91.44, 73.09, 50.99, 48.07, 25.98, 25.80, 18.20, -4.57, -4.60; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{18}H_{30}NSOSi^{\oplus}$ 336.1812, found 336.1811; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 21.0 min (minor), 21.6 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		21.785	3423874	49.58	207597	bb			Unknown	
2		22.392	3481762	50.42	201902	bb			Unknown	

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		21.018	148906	0.97	14162	bb			Unknown	
2		21.645	15189988	99.03	987333	bb			Unknown	

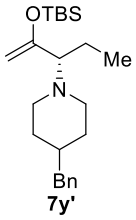
(*S*)-4-Benzyl-1-(2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)piperidine (7y)



7y

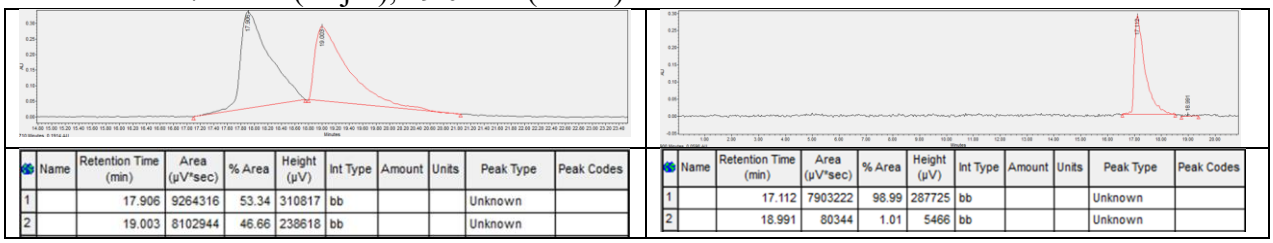
The reaction was run at RT for 18 h. B:l > 20:1, yellow oil, 56 mg, 75% yield. $[\alpha]_D^{25}$ +11.4 (*c* 0.79, $CHCl_3$) for 98% ee; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 0H), 7.14 (d, *J* = 7.1 Hz, 1H), 5.91 – 5.76 (m, 1H), 5.13 (dd, *J* = 23.9, 13.7 Hz, 2H), 4.22 (s, 1H), 4.13 (s, 1H), 3.09 (d, *J* = 8.0 Hz, 1H), 2.94 (dd, *J* = 28.8, 10.7 Hz, 2H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.94 (q, *J* = 12.1 Hz, 2H), 1.60 (d, *J* = 12.7 Hz, 2H), 1.55 – 1.45 (m, 1H), 1.32 – 1.22 (m, 2H), 0.92 (s, 9H), 0.16 (d, *J* = 1.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.06, 141.04, 137.65, 129.20, 128.18, 125.75, 116.81, 91.21, 74.19, 51.33, 51.17, 43.40, 38.26, 32.65, 25.79, 18.19, -4.60; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{38}NOSi^{\oplus}$ 372.2717, found 372.2721; Ee value was determined by **7y**' from the hydrogenation of **7y**.

(*S*)-4-Benzyl-1-(2-((*tert*-butyldimethylsilyl)oxy)pent-1-en-3-yl)piperidine (7y')



7y'

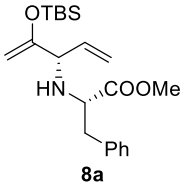
This compound was prepared by a synthetic procedure that was the same as that used to prepare **7m**'. Colorless oil, 46 mg, 62% yield. $[\alpha]_D^{25}$ +13.7 (*c* 1.42, $CHCl_3$) for 98% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.17 (m, 3H), 4.17 (s, 1H), 4.01 (s, 1H), 2.96 (d, *J* = 11.1 Hz, 1H), 2.77 – 2.73 (m, 2H), 2.56 (d, *J* = 7.0 Hz, 2H), 2.32 (dd, *J* = 11.5, 9.9 Hz, 1H), 2.11 (t, *J* = 11.2 Hz, 1H), 1.79 – 1.71 (m, 1H), 1.66 (d, *J* = 11.8 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.43 – 1.32 (m, 1H), 1.28 – 1.17 (m, 1H), 0.95 (s, 9H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.23 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.07, 141.10, 129.24, 128.16, 125.72, 91.80, 71.52, 52.56, 48.18, 43.51, 38.42, 33.28, 32.97, 25.81, 22.75, 18.13, 11.24, -4.25, -4.95; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{40}NOSi^{\oplus}$ 374.2874, found 374.2871; HPLC: chiral OD-H + OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 99/1; flow = 0.5 mL/min; Retention time: 17.1 min (major), 19.0 min (minor).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.906	9264316	53.34	310817	bb			Unknown	
2		19.003	8102944	46.66	238618	bb			Unknown	

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.112	7903222	98.99	287725	bb			Unknown	
2		18.991	80344	1.01	5466	bb			Unknown	

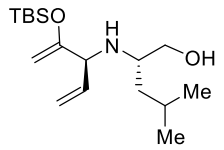
Methyl ((*S*)-2-((*tert*-butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)-L-phenylalaninate (8a)



8a

The reaction was run at RT for 19 h. B:l > 20:1, dr > 99:1, yellow oil, 65 mg, 87% yield. $[\alpha]_D^{25}$ +6.5 (*c* 3.11, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 5H), 5.78 (ddd, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 4.19 (s, 1H), 4.12 (s, 1H), 3.74 – 3.59 (m, 4H), 3.49 (d, *J* = 7.1 Hz, 1H), 3.08 – 2.90 (m, 2H), 1.83 (s, 1H), 0.90 (s, 9H), 0.16 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.00, 157.51, 138.09, 137.33, 129.32, 128.48, 126.76, 116.46, 90.37, 64.51, 60.37, 51.63, 40.07, 25.72, 18.10, -4.71, -4.75; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{33}NO_3NaSi^{\oplus}$ 398.2121, found 398.2122.

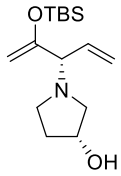
(*S*)-2-(((*S*)-2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)amino)-4-methylpentan-1-ol (8b)



8b

The reaction was run at 40 °C for 19 h. B:l = 5:1, dr = 93:7, yellow oil, 44 mg, 71% yield. $[\alpha]_D^{25}$ +19.5 (*c* 1.57, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 16.9, 10.3, 6.3 Hz, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.19 (d, *J* = 1.1 Hz, 1H), 4.14 (d, *J* = 1.1 Hz, 1H), 3.62 – 3.56 (m, 2H), 3.21 (dd, *J* = 10.6, 4.8 Hz, 1H), 2.81 – 2.71 (m, 1H), 1.66 – 1.57 (m, 1H), 1.34 – 1.27 (m, 2H), 0.92 (s, 9H), 0.88 (t, *J* = 6.3 Hz, 6H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.81, 138.78, 116.09, 90.58, 63.07, 62.93, 53.40, 42.03, 25.75, 24.95, 23.32, 22.72, 18.17, -4.54, -4.98; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{35}NO_2NaSi^{\oplus}$ 336.2329, found 336.2331.

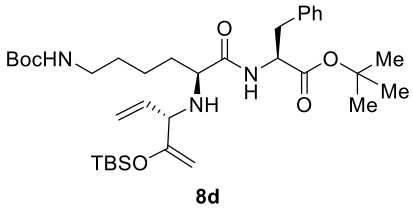
(*R*)-1-((*S*)-2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)pyrrolidin-3-ol (8c)



8c

The reaction was run at RT for 19 h. B:l = 13:1, dr = 95:5, yellow oil, 41 mg, 72% yield. $[\alpha]_D^{25}$ +31.1 (*c* 0.98, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 17.3, 10.0, 8.6 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.09 (dd, *J* = 10.1, 1.5 Hz, 1H), 4.28 – 4.26 (m, 2H), 4.11 (s, 1H), 3.07 (d, *J* = 8.5 Hz, 1H), 2.93 – 2.89 (m, 1H), 2.69 (d, *J* = 10.2 Hz, 1H), 2.51 (dd, *J* = 10.2, 4.9 Hz, 1H), 2.32 – 2.28 (m, 1H), 2.17 – 1.97 (m, 2H), 1.75 – 1.64 (m, 1H), 0.92 (s, 9H), 0.17 (m, 3H), 0.16 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.32, 138.20, 116.70, 90.68, 73.33, 71.18, 60.79, 50.08, 34.72, 25.74, 18.20, -4.54, -4.71; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{29}NO_2NaSi^{\oplus}$ 306.1859, found 306.1859.

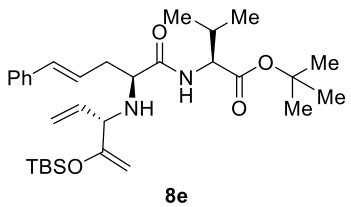
Peptide-1 (8d)



8d

The reaction was run with **1a** (0.2 mmol), peptide **26** (0.1 mmol), $[Ir(COD)Cl]_2$ (4 mol%) and (S_a,*S*,*S*)-L (8 mol%) in THF (0.5 M) at 50 °C for 2 d. B:l = 9:1, dr = 95:5, yellow oil, 43 mg, 67% yield. $[\alpha]_D^{25}$ +0.1 (*c* 2.45, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 1H), 7.25 – 7.24 (m, 2H), 7.21 – 7.18 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 5.79 – 5.66 (m, 1H), 5.18 (d, *J* = 17.3 Hz, 1H), 5.05 (d, *J* = 10.4 Hz, 1H), 4.70 (dd, *J* = 14.4, 7.1 Hz, 1H), 4.47 (br s, 1H), 4.11 (d, *J* = 14.1 Hz, 2H), 3.39 (s, 1H), 3.14 – 2.96 (m, 5H), 1.55 – 1.49 (m, 1H), 1.46 – 1.38 (m, 22H), 1.22 – 1.15 (m, 2H), 0.88 (s, 9H), 0.14 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.82, 170.58, 156.22, 155.94, 137.92, 136.55, 129.48, 128.42, 126.89, 115.96, 91.57, 81.89, 79.09, 64.08, 59.72, 52.99, 40.32, 38.39, 33.74, 30.01, 28.50, 28.03, 25.76, 23.05, 18.16, -4.55, -4.94; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{35}H_{60}N_3O_6Si^{\oplus}$ 646.4246, found 646.4245.

Peptide-2 (8e)

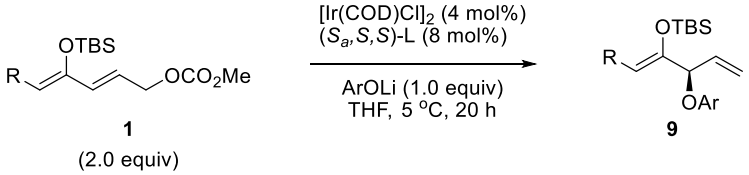


8e

The reaction was run with **1a** (0.2 mmol), peptide **29** (0.1 mmol), $[Ir(COD)Cl]_2$ (4 mol%) and (S_a,*S*,*S*)-L (8 mol%) in THF (0.5 M) at 50 °C for 2 d. B:l = 15:1, dr = 96:4, yellow oil, 42 mg, 77% yield. $[\alpha]_D^{25}$ +45.3 (*c* 3.13, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.5 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.24 – 7.16 (m, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.20 – 6.03 (m, 1H), 5.61 (ddd, *J* = 17.2, 10.1, 8.3

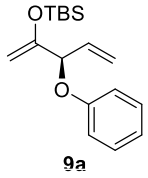
Hz, 1H), 5.18 (d, J = 10.1 Hz, 1H), 5.11 (d, J = 17.1 Hz, 1H), 4.45 (dd, J = 9.6, 4.5 Hz, 1H), 4.26 (d, J = 1.3 Hz, 1H), 4.05 (d, J = 1.4 Hz, 1H), 3.43 – 3.25 (m, 2H), 2.84 – 2.66 (m, 1H), 2.45 (dt, J = 14.1, 8.8 Hz, 1H), 2.31 – 2.15 (m, 1H), 1.79 (d, J = 9.8 Hz, 1H), 1.46 (s, 9H), 0.96 (d, J = 6.9 Hz, 3H), 0.91 (d, J = 6.9 Hz, 3H), 0.80 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.82, 170.88, 158.52, 136.96, 136.89, 133.78, 128.50, 127.40, 126.32, 126.00, 117.52, 89.10, 81.57, 64.63, 58.48, 57.00, 37.37, 31.06, 28.11, 25.60, 19.35, 18.00, 17.45, -4.62, -4.90; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{31}H_{51}N_2O_4Si^{\oplus}$ 543.3613, found 543.3614.

6.2 Scope for the construction of an α C-O bond



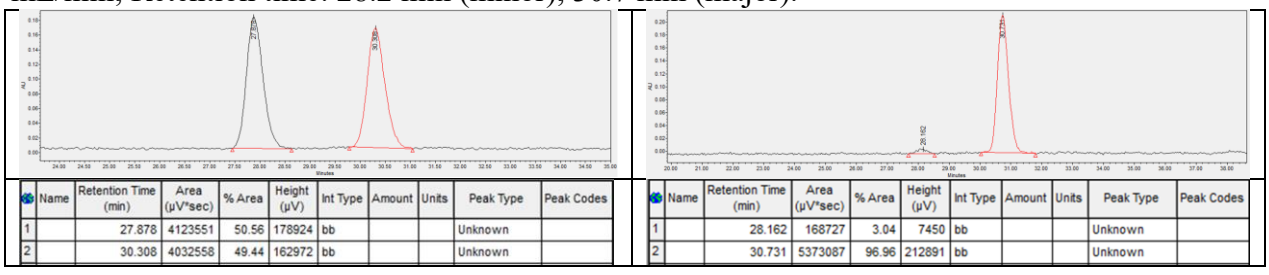
General procedure: To a 4 mL vial containing a magnetic stir bar were added $[Ir(COD)Cl]_2$ (2.6 mg, 0.0040 mmol), (R_a,R,R)-L (4.4 mg, 0.0080 mmol) and THF (0.2 mL) in a nitrogen-filled glovebox. The resulting mixture was stirred at RT for 10 min. After this time, *n*-propylamine (0.1 mL) was added to the reaction. The vial was sealed with a PTFE-lined cap and stirred at 50 °C for 20 min. Next, the volatile materials were evaporated under vacuum. Compound **1** (0.20 mmol) in THF (0.2 mL) was added, and the reaction was stirred at RT for 10 min. After this time, the phenoxide ArOLi (0.1 mmol) was added to the reaction. The vial was sealed with a PTFE lined cap and was removed from the glovebox and stirred at 5 °C for 20 h. After this time, the crude reaction solution was condensed to obtain a ^{1}H NMR spectrum (with CH_2Br_2 as internal standard). The product was further purified by flash column chromatography using hexane/ethyl acetate as eluent to afford pure **9**.

(*R*)-*tert*-Butyldimethyl((3-phenoxypenta-1,4-dien-2-yl)oxy)silane (9a)



9a

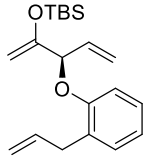
Colorless oil, b:l = 13:1, 21 mg, 71% yield. $[\alpha]_D^{25}$ -7.2 (c 0.87, $CHCl_3$) for 94% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 6.94 – 6.93 (m, 3H), 6.06 – 5.94 (m, 1H), 5.41 (dd, J = 17.3, 1.2 Hz, 1H), 5.27 (dd, J = 10.5, 1.2 Hz, 1H), 4.86 (d, J = 5.7 Hz, 1H), 4.46 (s, 1H), 4.24 (s, 1H), 0.93 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.96, 156.18, 135.55, 129.32, 121.03, 117.40, 116.02, 90.95, 79.96, 25.72, 18.16, -4.48, -4.80; HRMS (EI): $[M]^{\oplus}$ calcd for $C_{17}H_{26}O_2Si^{\oplus}$ 290.1702, found 290.1705; HPLC: two chiral OD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 28.2 min (minor), 30.7 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		27.878	4123551	50.56	178924	bb			Unknown	
2		30.308	4032558	49.44	162972	bb			Unknown	

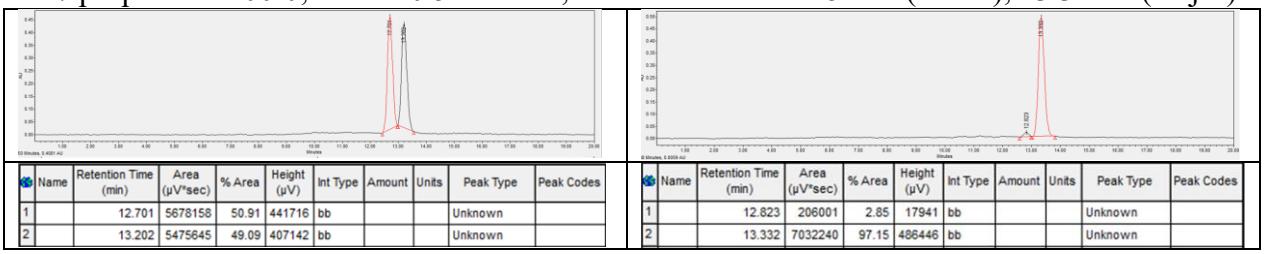
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		28.162	168727	3.04	7450	bb			Unknown	
2		30.731	5373087	96.96	212891	bb			Unknown	

(*R*)-((3-(2-Allylphenoxy)penta-1,4-dien-2-yl)oxy)(*tert*-butyl)dimethylsilane (9b)



9b

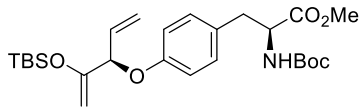
The reaction was run at 50 °C for 2 d. Colorless oil, b:l = 11:1, 20 mg, 61% yield. $[\alpha]_D^{25}$ -8.1 (*c* 0.42, $CHCl_3$) for 94% ee; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.13 (m, 2H), 7.01 – 6.79 (m, 2H), 6.09 – 5.96 (m, 2H), 5.42 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 5.12 – 5.04 (m, 2H), 4.87 (d, *J* = 5.8 Hz, 1H), 4.48 (s, 1H), 4.23 (d, *J* = 1.3 Hz, 1H), 3.47 (d, *J* = 6.1 Hz, 2H), 0.96 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.36, 155.41, 137.14, 135.80, 129.88, 129.34, 127.05, 120.86, 117.02, 115.50, 113.23, 90.10, 79.84, 34.65, 25.72, 18.14, -4.52, -4.76; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{30}O_2NaSi^{\oplus}$ 353.1907, found 353.1910; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 12.8 min (minor), 13.3 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.701	5678158	50.91	441716	bb			Unknown	
2		13.202	5475645	49.09	407142	bb			Unknown	

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.823	206001	2.85	17941	bb			Unknown	
2		13.332	7032240	97.15	486446	bb			Unknown	

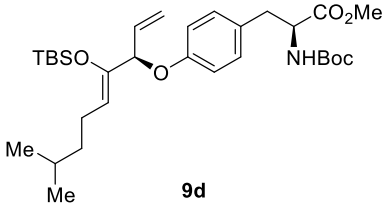
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(((*R*)-2-((*tert*-butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)oxy)phenyl)propanoate (9c)



9c

Yellow oil, b:l = 13:1, dr = 96:4, 40 mg, 81% yield. $[\alpha]_D^{25}$ +25.4 (*c* 2.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 5.97 (ddd, *J* = 16.8, 10.4, 6.0 Hz, 1H), 5.39 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.94 (d, *J* = 7.7 Hz, 1H), 4.81 (d, *J* = 5.9 Hz, 1H), 4.53 (dd, *J* = 13.8, 6.2 Hz, 1H), 4.44 (s, 1H), 4.23 (d, *J* = 1.1 Hz, 1H), 3.70 (s, 3H), 3.10 – 2.92 (m, 2H), 1.42 (s, 9H), 0.92 (s, 9H), 0.18 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.52, 157.06, 156.11, 155.18, 135.49, 130.16, 128.29, 117.39, 116.06, 90.94, 80.05, 79.94, 54.57, 52.22, 37.55, 28.38, 25.70, 18.14, -4.48, -4.82; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{29}H_{45}O_3Si^{\oplus}$ 469.3132, found 469.3123.

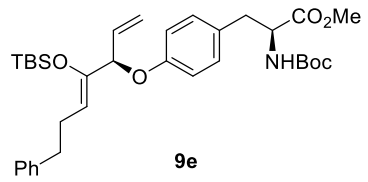
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(((*R*,*Z*)-4-((*tert*-butyldimethylsilyl)oxy)-8-methylnona-1,4-dien-3-yl)oxy)phenyl)propanoate (9d)



9d

Yellow oil, b:l = 11:1, dr = 97:3, 42 mg, 75% yield. $[\alpha]_D^{25}$ +31.1 (*c* 2.97, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.06 – 5.88 (m, 1H), 5.33 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 4.95 (d, *J* = 7.7 Hz, 1H), 4.86 – 4.83 (m, 2H), 4.53 (d, *J* = 6.3 Hz, 1H), 3.69 (s, 3H), 3.06 – 2.94 (m, 2H), 2.06 (dd, *J* = 15.4, 7.4 Hz, 2H), 1.56 – 1.51 (m, 1H), 1.42 (s, 9H), 1.22 (dd, *J* = 15.3, 6.9 Hz, 2H), 0.95 (s, 9H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.16 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.55, 157.19, 155.17, 147.27, 135.45, 130.18, 128.11, 117.43, 115.96, 112.40, 80.79, 79.94, 54.59, 52.22, 38.71, 37.61, 28.39, 27.97, 26.04, 23.32, 22.60, 22.59, 18.63, -3.70, -3.90; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{31}H_{51}NO_6NaSi^{\oplus}$ 584.3377, found 584.3366.

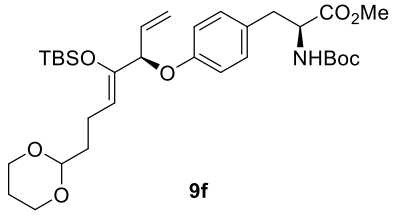
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(((*R*,*Z*)-4-((*tert*-butyldimethylsilyl)oxy)-7-phenylhepta-1,4-dien-3-yl)oxy)phenyl)propanoate (9e)



9e

Yellow oil, b:l = 9:1, dr = 96:4, 51 mg, 85% yield. $[\alpha]_D^{25}$ +25.7 (*c* 2.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.19 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.07 – 5.90 (m, 1H), 5.36 (d, *J* = 18.9 Hz, 1H), 5.31 (d, *J* = 10.5 Hz, 1H), 5.08 – 4.83 (m, 3H), 4.59 (dd, *J* = 13.6, 6.0 Hz, 1H), 3.74 (s, 3H), 3.15 – 2.96 (m, 2H), 2.78 – 2.61 (m, 2H), 2.44 (dd, *J* = 15.4, 7.3 Hz, 2H), 1.46 (s, 9H), 0.99 (s, 9H), 0.20 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.54, 157.12, 155.17, 147.96, 142.02, 135.34, 130.20, 128.50, 128.34, 128.20, 125.82, 117.54, 115.96, 110.99, 80.67, 79.95, 54.58, 52.23, 37.61, 35.76, 28.39, 27.00, 26.03, 18.62, -3.65, -3.87; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{34}H_{49}NO_6NaSi^{\oplus}$ 618.3221, found 618.3211.

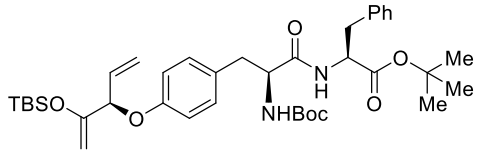
Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(((*R*,*Z*)-4-((*tert*-butyldimethylsilyl)oxy)-7-(1,3-dioxan-2-yl)hepta-1,4-dien-3-yl)oxy)phenyl)propanoate (9f)



9f

Yellow oil, b:l = 16:1, dr = 96:4, 44 mg, 73% yield. $[\alpha]_D^{25}$ +40.4 (*c* 2.37, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.94 (ddd, *J* = 16.4, 10.5, 5.6 Hz, 1H), 5.33 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 4.95 (d, *J* = 8.1 Hz, 1H), 4.87 – 4.83 (m, 2H), 4.52 (dd, *J* = 13.4, 5.7 Hz, 1H), 4.45 (t, *J* = 5.2 Hz, 1H), 4.07 (dd, *J* = 11.5, 4.0 Hz, 2H), 3.75 – 3.67 (m, 5H), 3.05 - 2.94 (m, 2H), 2.16 (dd, *J* = 14.9, 7.4 Hz, 2H), 2.09 – 2.00 (m, 1H), 1.63 – 1.58 (m, 2H), 1.41 (s, 9H), 1.31 (d, *J* = 13.4 Hz, 1H), 0.94 (s, 9H), 0.16 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.52, 157.11, 155.17, 147.94, 135.40, 130.18, 128.17, 117.48, 115.96, 111.01, 101.86, 80.69, 79.93, 66.90, 54.57, 52.22, 37.57, 34.95, 28.37, 26.01, 25.92, 19.90, 18.61, -3.72, -3.96; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{32}H_{51}NO_8NaSi^{\oplus}$ 628.3276, found 618.3246.

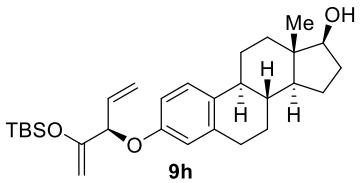
***tert*-Butyl ((*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(((*R*)-2-((*tert*-butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)oxy)phenyl)propanoyl)-*L*-phenylalaninate (9g)**



9g

Yellow oil, b:l = 14:1, dr = 96:4, 57 mg, 83% yield. $[\alpha]_D^{25}$ +21.7 (*c* 3.47, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 3H), 7.11 – 7.03 (m, 4H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.36 (d, *J* = 5.6 Hz, 1H), 5.95 (ddd, *J* = 16.7, 10.4, 6.0 Hz, 1H), 5.38 (d, *J* = 17.3 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 4.93 (br s, 1H), 4.79 (d, *J* = 5.9 Hz, 1H), 4.64 (d, *J* = 5.9 Hz, 1H), 4.43 (s, 1H), 4.29 (br s, 1H), 4.21 (d, *J* = 1.3 Hz, 1H), 3.05 – 2.88 (m, 4H), 1.40 (s, 9H), 1.35 (s, 9H), 0.92 (s, 9H), 0.17 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.77, 170.11, 157.01, 156.10, 155.35, 136.10, 135.49, 130.27, 129.58, 128.79, 128.39, 126.99, 117.35, 116.12, 90.84, 82.37, 80.13, 80.01, 55.79, 53.74, 38.21, 37.47, 28.31, 27.95, 25.69, 18.12, -4.50, -4.82. HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{38}H_{56}N_2O_7NaSi^{\oplus}$ 703.3749, found 703.3770.

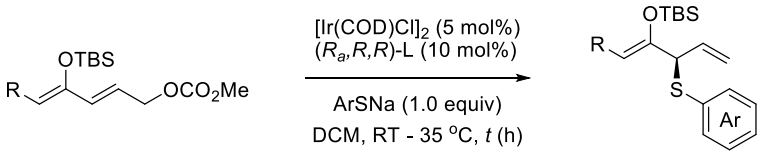
(8*R*,9*S*,13*S*,14*S*,17*S*)-3-(((*R*)-2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)oxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (9h)



9h

Yellow oil, b:l = 12:1, dr = 97:3, 39 mg, 82% yield. $[\alpha]_D^{25}$ +30.6 (*c* 1.66, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 5.97 (ddd, *J* = 16.6, 10.5, 5.9 Hz, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.25 (d, *J* = 10.5 Hz, 1H), 4.79 (d, *J* = 5.9 Hz, 1H), 4.45 (s, 1H), 4.22 (d, *J* = 1.4 Hz, 1H), 3.73 (t, *J* = 8.5 Hz, 1H), 2.85 – 2.78 (m, 2H), 2.33 – 2.27 (m, 1H), 2.20 – 2.09 (m, 2H), 1.94 (dt, *J* = 12.4, 3.2 Hz, 1H), 1.90 – 1.83 (m, 1H), 1.72 – 1.67 (m, 1H), 1.53 – 1.23 (m, 8H), 1.21 – 1.16 (m, 1H), 0.94 (s, 9H), 0.77 (s, 3H), 0.19 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.38, 155.85, 137.83, 135.74, 132.98, 126.17, 117.17, 116.05, 113.22, 90.60, 81.99, 79.92, 50.12, 44.05, 43.33, 38.86, 36.79, 30.67, 29.84, 27.34, 26.33, 25.74, 23.20, 18.16, 11.14, -4.50, -4.69; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{29}H_{45}O_3Si^{\oplus}$ 469.3132, found 469.3123.

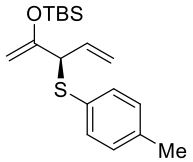
6.3 Scope for the construction of an alpha C-S bond



1 (2.0 equiv) **10**

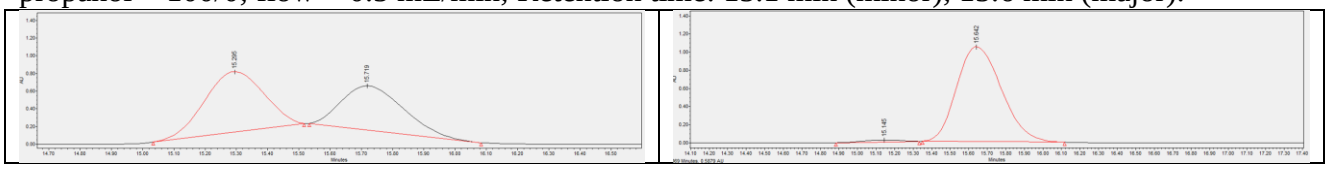
General procedure: To a 4 mL vial containing a magnetic stir bar were added $[Ir(COD)Cl]_2$ (3.2 mg, 0.0050 mmol), (*Ra,R,R*)-L (5.6 mg, 0.010 mmol) and THF (0.4 mL) in a nitrogen-filled glovebox. The resulting mixture was stirred at RT for 10 min. After this time, *n*-propylamine (0.2 mL) was added to the reaction. The vial was sealed with a PTFE-lined cap and stirred at 50 ºC for 20 min. Next, the volatile materials were evaporated under vacuum. Compound **1** (0.20 mmol) in DCM (1.0 mL) was then added, and the reaction was stirred at RT for 10 min. After this time, LiCl (13 mg, 0.30 mmol) and ArSNa (0.10 mmol) were added to the reaction. The vial was sealed with a PTFE-lined cap and was removed from the glovebox and stirred at RT – 35 ºC for 14 – 24 h. After this time, the crude reaction solution was condensed to obtain a ^1H NMR spectrum (with CH_2Br_2 as internal standard). The product was further purified by flash column chromatography eluting with hexane/ethyl acetate to afford pure **10**.

(*R*)-*tert*-Butyldimethyl((3-(*p*-tolylthio)penta-1,4-dien-2-yl)oxy)silane (10a)



10a

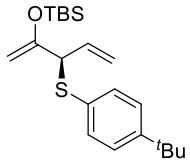
The reaction was run at RT for 14 h. Yellow oil, b:l > 20:1, 23 mg, 73% yield. $[\alpha]_D^{25}$ +32.1 (*c* 0.81, $CHCl_3$) for 97% ee. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.99 – 5.90 (m, 1H), 5.17 – 4.93 (m, 2H), 4.14 (d, *J* = 36.9 Hz, 2H), 4.04 (d, *J* = 8.6 Hz, 1H), 2.33 (s, 3H), 0.98 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.51, 137.40, 135.74, 133.37, 131.46, 129.49, 116.41, 91.17, 58.70, 25.77, 21.22, 18.27, -4.62, -4.74; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{18}H_{29}SOSi^{\oplus}$ 321.1703, found 321.1721; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 15.1 min (minor), 15.6 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		15.295	8995554	56.50	683766	bb			Unknown	
2		15.719	6925300	43.50	500244	bb			Unknown	

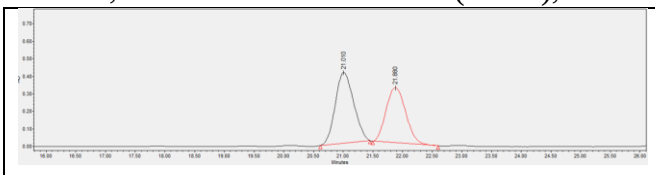
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		15.145	290861	1.63	21316	bb			Unknown	
2		15.642	17534181	98.37	1047225	bb			Unknown	

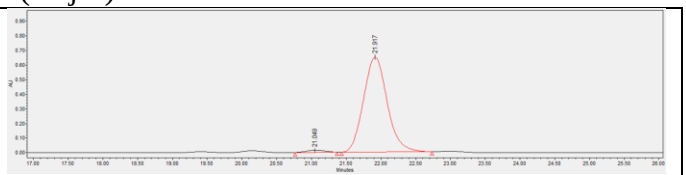
(*R*)-*tert*-Butyl((3-((4-(*tert*-butyl)phenyl)thio)penta-1,4-dien-2-yl)oxy)dimethylsilane (10b)



10b

The reaction was run at RT for 24 h. Yellow oil, b:l > 20:1, 29 mg, 81% yield. $[\alpha]_D^{25}$ +34.1 (*c* 1.7, $CHCl_3$) for 96% ee. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.23 (m, 4H), 6.00 – 5.94 (m, 1H), 5.18 – 4.99 (m, 2H), 4.17 (d, *J* = 45.6 Hz, 2H), 4.07 (d, *J* = 8.5 Hz, 1H), 1.30 (s, 9H), 0.97 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.66, 150.42, 135.87, 132.64, 131.76, 125.72, 116.42, 91.21, 58.33, 34.60, 31.34, 25.78, 18.27, -4.63, -4.76; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{21}H_{35}OSSi^{\oplus}$ 363.2172, found 363.2171; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.3 mL/min; Retention time: 21.0 min (minor), 21.9 min (major).

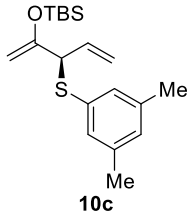




	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		21.010	8687175	54.59	403570	bb			Unknown	
2		21.880	7225408	45.41	313624	bb			Unknown	

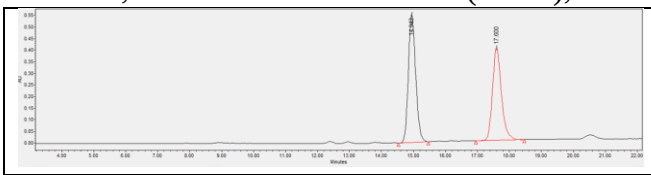
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		21.049	276217	1.77	14179	bb			Unknown	
2		21.917	15372728	98.23	651418	bb			Unknown	

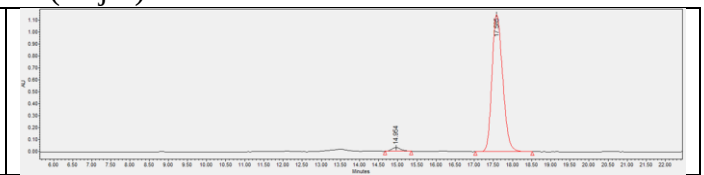
(*R*)-*tert*-Butyl((3-((3,5-dimethylphenyl)thio)penta-1,4-dien-2-yl)oxy)dimethylsilane (10c)



10c

The reaction was run at RT for 24 h. Yellow oil, b:l > 20:1, 27 mg, 81% yield. $[\alpha]_D^{25}$ +37.5 (*c* 0.93, $CHCl_3$) for 96% ee. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.03 (s, 2H), 6.85 (s, 1H), 5.90 – 5.90 (m, 1H), 5.20 – 4.97 (m, 2H), 4.29 – 3.99 (m, 3H), 2.27 (s, 6H), 0.97 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.57, 138.18, 135.76, 134.75, 130.09, 128.97, 116.45, 91.12, 57.92, 25.76, 21.21, 18.27, -4.64, -4.78.; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{19}H_{31}OSSi^{\oplus}$ 335.1859, found 335.1874; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 15.0 min (minor), 17.6 min (major).

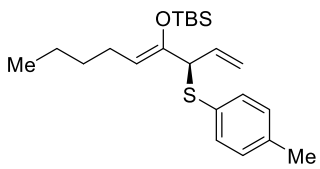




	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		14.943	8796067	53.34	552976	bb			Unknown	
2		17.600	7694619	46.66	399541	bb			Unknown	

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		14.954	514734	2.25	31216	bb			Unknown	
2		17.585	22326627	97.75	1150172	bb			Unknown	

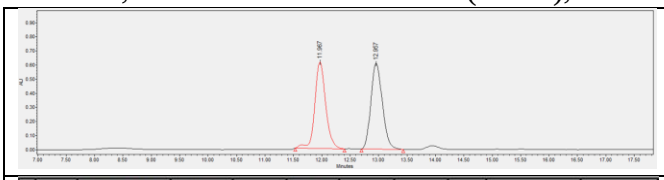
(*R*,*Z*)-*tert*-Butyldimethyl((3-(*p*-tolylthio)nona-1,4-dien-4-yl)oxy)silane (10d)



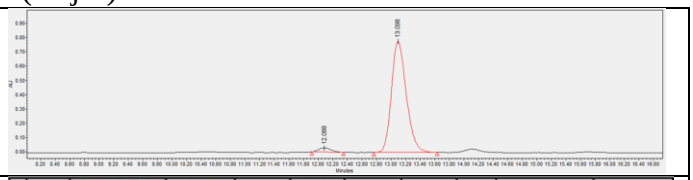
10d

The reaction was run at 35 °C for 18 h. Yellow oil, b:l = 14:1, 23 mg, 61% yield. $[\alpha]_D^{25}$ +41.0 (*c* 1.1, $CHCl_3$) for 94% ee. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 5.88 – 5.82 (m, 1H), 5.05 – 4.94 (m, 2H), 4.67 (t, *J* = 7.0 Hz, 1H), 3.95 (d, *J* = 8.3 Hz, 1H), 2.32 (s, 3H), 2.06 – 1.99 (m, 2H), 1.30

– 1.25 (m, 4H), 0.98 (s, 9H), 0.88 (t, *J* = 6.1 Hz, 3H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.43, 137.35, 136.30, 133.33, 131.36, 129.44, 116.00, 111.70, 57.71, 31.84, 26.01, 25.36, 22.52, 21.21, 18.55, 14.10, -3.60, -3.65; (ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{36}OSNaSi^{\oplus}$ 399.2148, found 399.2141; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 12.1 min (minor), 13.1 min (major).

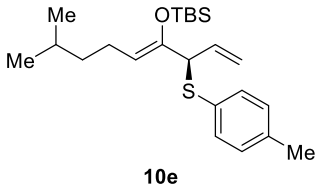


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.967	8128880	48.77	612644	bb			Unknown	
2		12.957	8538137	51.23	609470	bb			Unknown	



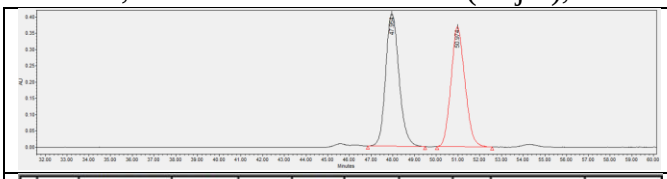
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.088	356204	3.14	29444	bb			Unknown	
2		13.098	10997961	96.86	782001	bb			Unknown	

(*R*,*Z*)-*tert*-Butyldimethyl((8-methyl-3-(*p*-tolylthio)nona-1,4-dien-4-yl)oxy)silane (10e)

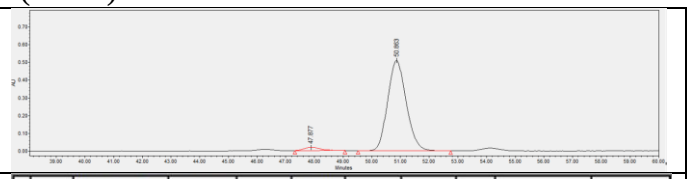


10e

The reaction was run at 35 °C for 16 h. Colorless oil, b:l = 15:1, 26 mg, 66% yield. $[\alpha]_D^{25}$ +37.6 (*c* 1.4, $CHCl_3$) for 94% ee. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 5.88 – 5.82(m, 1H), 5.06 – 4.91 (m, 2H), 4.64 (t, *J* = 7.0 Hz, 1H), 3.95 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 3H), 2.07 – 1.98 (m, 2H), 1.53 – 1.49 (m, 1H), 1.17 (q, *J* = 7.5 Hz, 2H), 0.99 (s, 9H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.20 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.32, 137.35, 136.32, 133.35, 131.37, 129.44, 115.98, 111.84, 57.69, 38.80, 27.88, 26.02, 23.62, 22.65, 22.60, 21.21, 18.55, -3.58, -3.64; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{39}OSSi^{\oplus}$ 391.2485, found 391.2471; HPLC: two chiral OD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.3 mL/min; Retention time: 47.9 min (major), 50.9 min (minor).

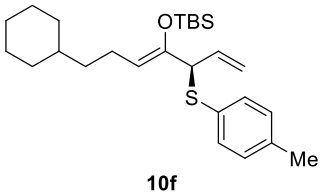


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		47.954	17458573	51.49	406865	bb			Unknown	
2		50.974	16446286	48.51	368160	bb			Unknown	



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		47.877	768664	3.23	18452	bb			Unknown	
2		50.863	23037904	96.77	511014	bb			Unknown	

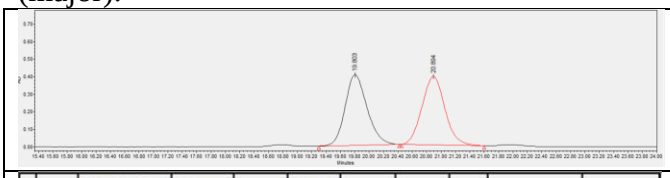
(*R*,*Z*)-*tert*-Butyl((7-cyclohexyl-3-(*p*-tolylthio)hepta-1,4-dien-4-yl)oxy)dimethylsilane (10f)



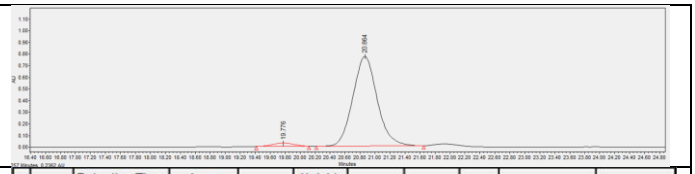
10f

The reaction was run at 35 °C for 16 h. Colorless oil, b:l > 20:1, 27 mg, 62% yield. $[\alpha]_D^{25}$ +33.9 (*c* 1.4, $CHCl_3$) for 94% ee. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 5.88 – 5.82 (m, 1H), 5.03 – 4.94 (m, 2H), 4.65 (t, *J* = 7.0 Hz, 1H), 3.95 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 3H), 2.06 – 1.99 (m, 2H), 1.69 – 1.63 (m, 5H), 1.24 – 1.12 (m, 6H), 0.98 (s, 9H), 0.85 (q, *J* = 10.7, 10.2 Hz, 2H), 0.19 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.26, 137.33, 136.32, 133.31, 131.42, 129.45, 115.98, 111.97, 57.70, 37.56, 37.37, 33.39, 33.36, 26.81, 26.47, 26.03, 23.10, 21.21, 18.55, -3.58, -3.62 (one CH_2 carbon signal was not observed because of overlapping); HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{26}H_{43}OSSi^{\oplus}$ 431.2798, found 431.2795; HPLC: chiral OD-H column; detected at

220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.3 mL/min; Retention time: 19.8 min (minor), 20.9 min (major).

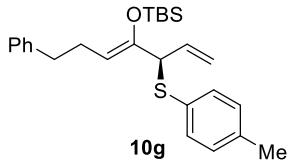


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		19.803	8520371	49.53	403133	bb			Unknown	
2		20.894	8683521	50.47	390696	bb			Unknown	



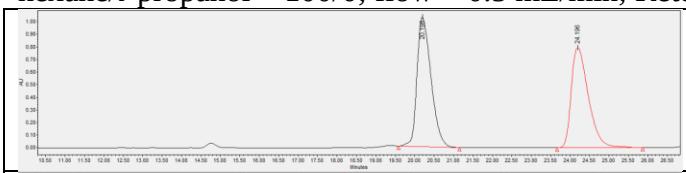
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		19.776	558275	3.09	28043	bb			Unknown	
2		20.864	17493525	96.91	771980	bb			Unknown	

(*R*,*Z*)-*tert*-Butyldimethyl((7-phenyl-3-(p-tolylthio)hepta-1,4-dien-4-yl)oxy)silane (10g)

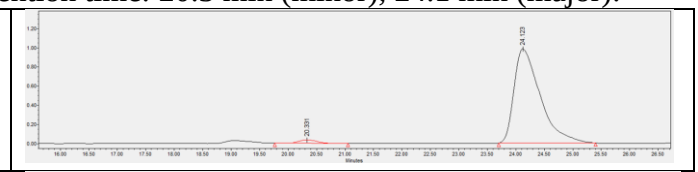


10g

The reaction was run at 35 °C for 20 h. Yellow oil, b:l = 16:1, 29 mg, 69% yield. $[\alpha]_D^{25}$ +25.8 (*c* 1.2, $CHCl_3$) for 95% ee; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 4H), 7.20 – 7.15 (m, 3H), 7.09 (d, *J* = 7.3 Hz, 2H), 5.87 – 5.81 (m, 1H), 5.05 – 4.94 (m, 2H), 4.73 (t, *J* = 6.9 Hz, 1H), 3.96 (d, *J* = 8.3 Hz, 1H), 2.65 – 2.53 (m, 2H), 2.39 – 2.30 (m, 5H), 0.99 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.07, 142.22, 137.45, 136.17, 133.41, 131.25, 129.47, 128.49, 128.34, 125.79, 116.13, 110.60, 57.59, 35.89, 27.47, 26.02, 21.22, 18.54, -3.54, -3.59; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{26}H_{36}OSNaSi^{\oplus}$ 447.2148, found 447.2150; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 20.3 min (minor), 24.1 min (major).

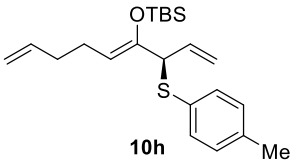


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.198	25740649	51.51	1027545	bb			Unknown	
2		24.196	24231828	48.49	795923	bb			Unknown	



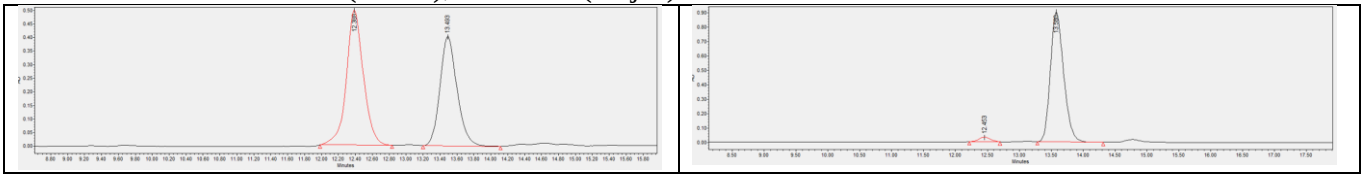
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.331	763315	2.36	34967	bb			Unknown	
2		24.123	31621260	97.64	985861	bb			Unknown	

(*R*,*Z*)-*tert*-Butyldimethyl((3-(*p*-tolylthio)nona-1,4,8-trien-4-yl)oxy)silane (10h)



10h

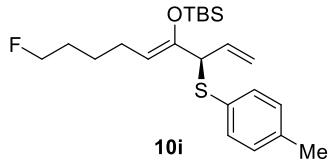
The reaction was run at 35 °C for 14 h. Yellow oil, b:l = 14:1, 30 mg, 81% yield. $[\alpha]_D^{25}$ +26.7 (*c* 1.9, $CHCl_3$) for 94% ee. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 5.91 – 5.73 (m, 2H), 5.01 – 4.94 (m, 4H), 4.69 (t, *J* = 6.8 Hz, 1H), 3.95 (d, *J* = 8.4 Hz, 1H), 2.32 (s, 3H), 2.17 – 2.01 (m, 4H), 0.98 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.96, 138.51, 137.42, 136.21, 133.37, 131.30, 129.46, 116.10, 114.62, 110.65, 57.64, 33.70, 26.00, 25.04, 21.21, 18.54, -3.55, -3.62; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{22}H_{35}OSSi^{\oplus}$ 375.2172, found 375.2187; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 12.5 min (minor), 13.6 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.388	6935012	55.14	496034	bb			Unknown	
2		13.493	5642669	44.86	402276	bb			Unknown	

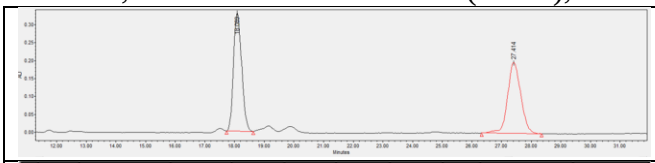
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.453	408262	3.03	32151	bb			Unknown	
2		13.580	13050697	96.97	905360	bb			Unknown	

(*R*,*Z*)-*tert*-Butyl((9-fluoro-3-(*p*-tolylthio)nona-1,4-dien-4-yl)oxy)dimethylsilane (10i)

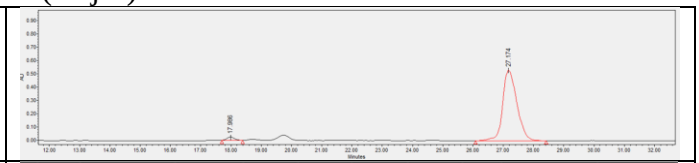


10i

The reaction was run at 35 °C for 14 h. Yellow oil, b:l > 20:1, 32 mg, 80% yield. $[\alpha]_D^{25}$ +26.6 (*c* 1.9, $CHCl_3$) for 95% ee. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 6.9 Hz, 2H), 7.08 (d, *J* = 7.1 Hz, 2H), 5.88 – 5.82 (m, 1H), 5.06 – 4.94 (m, 2H), 4.66 (t, *J* = 6.6 Hz, 1H), 4.45 (t, *J* = 5.6 Hz, 1H), 4.38 (t, *J* = 5.6 Hz, 1H), 3.96 (d, *J* = 8.2 Hz, 1H), 2.32 (s, 3H), 2.12 – 2.03 (m, 2H), 1.68 – 1.60 (m, 2H), 1.43 – 1.39 (m, 2H), 0.99 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.16, 137.44, 136.18, 133.34, 131.24, 129.47, 116.15, 110.80, 84.09 ($J_{C\text{-}F}$ = 164.3 Hz), 57.55, 30.06 ($J_{C\text{-}F}$ = 19.5 Hz), 25.98, 25.16 ($J_{C\text{-}F}$ = 5.3 Hz), 25.07, 21.19, 18.53, -3.56, -3.64; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -217.21 – -217.59 (m, 1F); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{35}FOSNaSi^{\oplus}$ 417.2054, found 417.2050; HPLC: chiral OD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 100/0; flow = 0.5 mL/min; Retention time: 18.0 min (minor), 27.2 min (major).

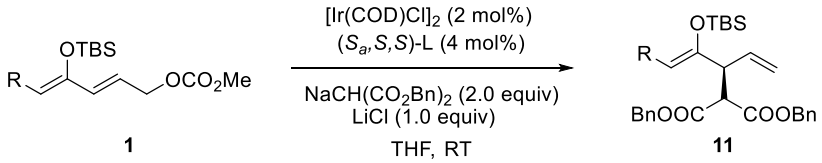


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.089	6297918	50.74	329616	bb			Unknown	
2		27.414	6115290	49.26	197222	bb			Unknown	



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.986	449456	2.55	24629	bb			Unknown	
2		27.174	17199652	97.45	530579	bb			Unknown	

6.4 Scope for the construction of α C-C bond

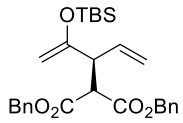


1
(1.0 equiv)

11

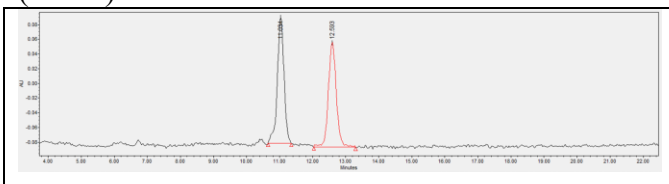
General procedure: To a 4 mL vial containing a magnetic stir bar were added $[Ir(COD)Cl]_2$ (1.3 mg, 0.0020 mmol), (*Ra*,*R*,*R*)-L (2.2 mg, 0.0040 mmol) and THF (0.2 mL) in a nitrogen-filled glovebox. The resulting mixture was stirred at RT for 10 min. After this time, *n*-propylamine (0.1 mL) was added to the reaction. The vial was sealed with a PTFE-lined cap and stirred at 50 °C for 20 min. After this time, the volatile materials were evaporated under vacuum. Compound **1** (0.10 mmol) in THF (0.2 mL) was added, and the reaction was stirred at RT for 10 min. After this time, LiCl (4.2 mg, 0.1 mmol) and $NaCH(CO_2Bn)_2$ (0.20 mmol) were added to the reaction. The vial was sealed with a PTFE-lined cap and was removed from the glovebox and stirred at room temperature for 12 – 20 h. After this time, the crude reaction solution was condensed to obtain a ^{1}H NMR spectrum (with CH_2Br_2 as internal standard). The product was further purified by flash column chromatography using hexane/ethyl acetate eluent to afford pure **11**.

Dibenzyl (*S*)-2-(2-((*tert*-butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)malonate (11a)

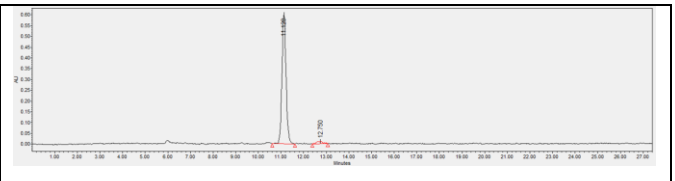


11a

The reaction was run at RT for 20 h. Yellow oil, b:l > 20:1, 42 mg, 87% yield. $[\alpha]_D^{25}$ -8.0 (*c* 2.08, $CHCl_3$) for 94% ee. ^1H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 10H), 5.84 (dt, *J* = 17.3, 9.6 Hz, 1H), 5.14 – 5.07 (m, 5H), 5.02 (d, *J* = 10.2 Hz, 1H), 4.13 (d, *J* = 0.9 Hz, 1H), 4.00 (s, 1H), 3.85 (d, *J* = 10.4 Hz, 1H), 3.52 (t, *J* = 9.6 Hz, 1H), 0.90 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.62 (CO), 167.46 (CO), 156.70 (O-C=), 135.45 (quaternary carbon of Ph), 135.42 (quaternary carbon of Ph), 135.36 (CH=), 128.53 (CH of Ph), 128.51 (CH of Ph), 128.39 (CH of Ph), 128.36 (CH of Ph), 128.34 (CH of Ph), 128.30 (CH of Ph), 117.82 (CH_2=), 90.71 (CH_2=), 67.15 (O-CH_2), 67.13 (O-CH_2), 54.46 (CH), 50.95 (CH), 25.73 ((CH_3)$_3$), 18.17 (Si-C), -4.83 (CH_3), -4.94 (CH_3); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{36}O_5NaSi^{\oplus}$ 503.2224, found 503.2226; HPLC: chiral AD-H column; detected at 220 nm; *n*-hexane/*i*-propanol = 94/6; flow = 1.0 mL/min; Retention time: 11.1 min (major), 12.8 min (minor).

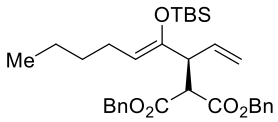


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.034	2404645	50.14	170629	bb			Unknown	
2		12.593	2391019	49.86	142329	bb			Unknown	



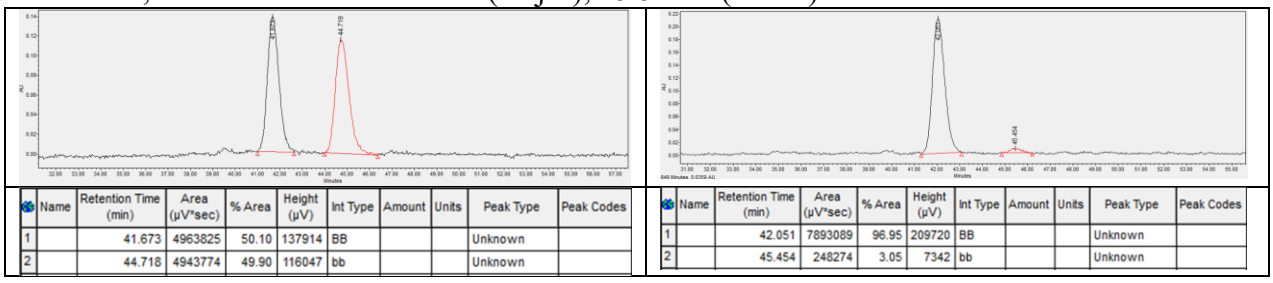
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.128	7664074	97.17	600822	bb			Unknown	
2		12.750	223344	2.83	11480	bb			Unknown	

Dibenzyl (*S,Z*)-2-(4-((*tert*-butyldimethylsilyl)oxy)nona-1,4-dien-3-yl)malonate (11b)



11b

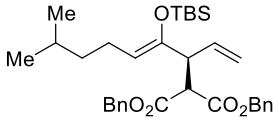
The reaction was run at RT for 14 h. Yellow oil, b:l > 20:1, 50 mg, 93% yield. $[\alpha]_D^{25}$ -25.1 (*c* 3.38, $CHCl_3$) for 94% ee. ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 10H), 5.82 (ddd, *J* = 17.1, 10.1, 8.9 Hz, 1H), 5.19 – 5.00 (m, 6H), 4.46 (t, *J* = 7.0 Hz, 1H), 3.82 (d, *J* = 9.5 Hz, 1H), 3.44 (t, *J* = 9.1 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.28 – 1.17 (m, 4H), 0.93 (s, 9H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.70 (CO), 167.50 (CO), 148.23 (O-C=), 135.80 (CH=), 135.51 (quaternary carbon of Ph), 135.50 (quaternary carbon of Ph), 128.53 (two peaks are overlapped, CH of Ph), 128.30 (CH of Ph), 128.28 (two peaks are overlapped, CH of Ph), 128.22 (CH of Ph), 117.96 (CH_2=), 109.69 (CH=), 67.15, 67.01, 54.92, 50.29, 31.90, 25.95, 25.21, 22.46, 18.44, 14.04, -3.70, -3.87; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{32}H_{44}O_5NaSi^{\oplus}$ 559.2850, found 559.2844; HPLC: two chiral AD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 0.4 mL/min; Retention time: 42.1 min (major), 45.5 min (minor).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		41.673	4963825	50.10	137914	BB			Unknown	
2		44.718	4943774	49.90	116047	bb			Unknown	

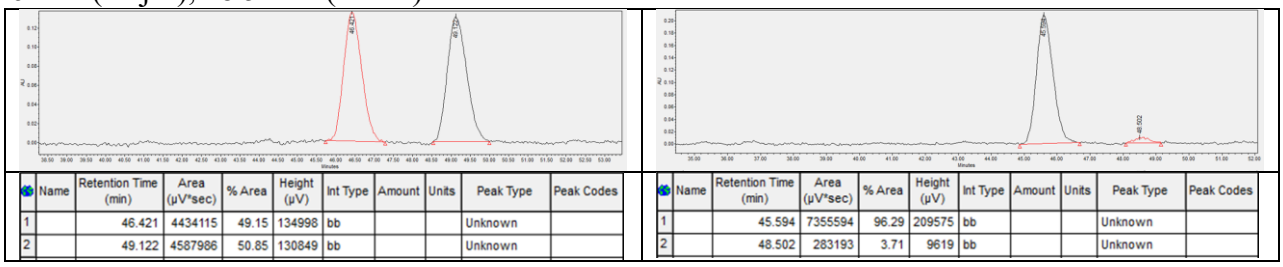
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		42.051	7893089	96.95	209720	BB			Unknown	
2		45.454	248274	3.05	7342	bb			Unknown	

Dibenzyl (*S,Z*)-2-(4-((*tert*-butyldimethylsilyl)oxy)-8-methylnona-1,4-dien-3-yl)malonate (11c)



11c

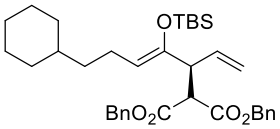
The reaction was run at RT for 20 h. Yellow oil, b:l > 20:1, 49 mg, 88% yield. $[\alpha]_D^{25}$ -26.0 (*c* 3.26, $CHCl_3$) for 93% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 10H), 5.82 (ddd, *J* = 17.1, 10.0, 8.9 Hz, 1H), 5.19 – 4.99 (m, 6H), 4.44 (t, *J* = 7.0 Hz, 1H), 3.82 (d, *J* = 9.5 Hz, 1H), 3.43 (t, *J* = 9.1 Hz, 1H), 1.98 – 1.84 (m, 2H), 1.54 – 1.44 (m, 1H), 1.09 (dd, *J* = 14.9, 7.3 Hz, 2H), 0.93 (s, 9H), 0.83 (d, *J* = 6.6 Hz, 6H), 0.15 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.71 (CO), 167.50 (CO), 148.09 (O-C=), 135.77 (CH=), 135.50, 135.49, 128.54 (two peaks are overlapped, CH of Ph), 128.32 (CH of Ph), 128.28 (two peaks are overlapped, CH of Ph), 128.21 (CH of Ph), 117.99 (CH_2=), 109.82 (CH=), 67.15, 67.01, 54.88, 50.26, 38.85, 27.88, 25.95, 23.50, 22.59, 18.43, -3.70, -3.88; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{33}H_{46}O_5NaSi^{\oplus}$ 573.3006, found 573.3004; HPLC: two chiral AD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 0.4 mL/min; Retention time: 45.6 min (major), 48.5 min (minor).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		46.421	4434115	49.15	134998	bb			Unknown	
2		49.122	4587986	50.85	130849	bb			Unknown	

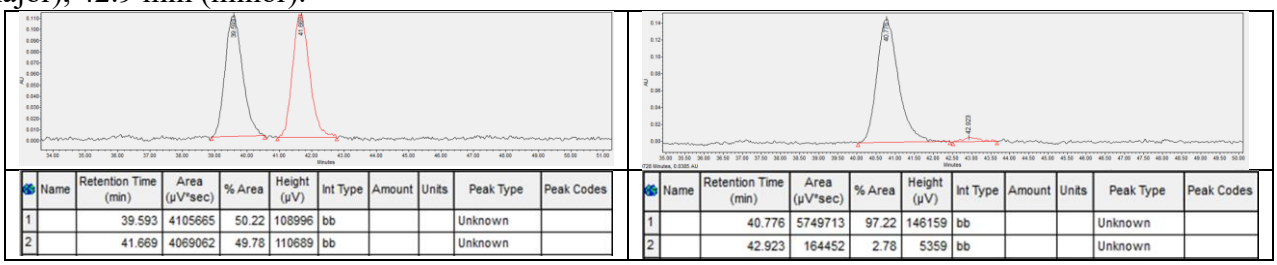
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		45.594	7355594	96.29	209575	bb			Unknown	
2		48.502	283193	3.71	9619	bb			Unknown	

Dibenzyl (*S,Z*)-2-(4-((*tert*-butyldimethylsilyl)oxy)-7-cyclohexylhepta-1,4-dien-3-yl)malonate (11d)



11d

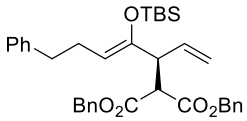
The reaction was run RT for 14 h. Yellow oil, b:l > 20:1, 51 mg, 87% yield. $[\alpha]_D^{25}$ -24.5 (*c* 3.38, $CHCl_3$) for 94% ee. ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 10H), 5.81 (ddd, *J* = 17.1, 10.0, 8.9 Hz, 1H), 5.17 – 5.01 (m, 6H), 4.44 (t, *J* = 7.0 Hz, 1H), 3.82 (d, *J* = 9.6 Hz, 1H), 3.43 (t, *J* = 9.1 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.69 – 1.61 (m, 5H), 1.23 – 1.08 (m, 6H), 0.93 (s, 9H), 0.85 – 0.79 (m, 2H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.69 (CO), 167.51 (CO), 148.03 (O-C=), 135.82 (CH=), 135.51 (two peaks are overlapped, quaternary carbon of Ph), 128.54 (two peaks are overlapped, CH of Ph), 128.31 (CH of Ph), 128.29 (CH of Ph), 128.28 (CH of Ph), 128.22 (CH of Ph), 117.95 (CH_2=), 109.94 (CH=), 67.15, 67.02, 54.91, 50.26, 37.57, 37.46, 33.37, 33.32, 26.78, 26.47, 25.96, 23.00, 18.44, -3.67, -3.86 (one more CH_2 aliphatic carbon signal of the cyclohexyl unit was observed because of the asymmetric environment around the cyclohexyl unit); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{36}H_{50}O_5NaSi^{\oplus}$ 613.3319, found 613.3289; HPLC: two chiral AD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 0.4 mL/min; Retention time: 40.8 min (major), 42.9 min (minor).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		39.593	4105665	50.22	108996	bb			Unknown	
2		41.669	4069062	49.78	110689	bb			Unknown	

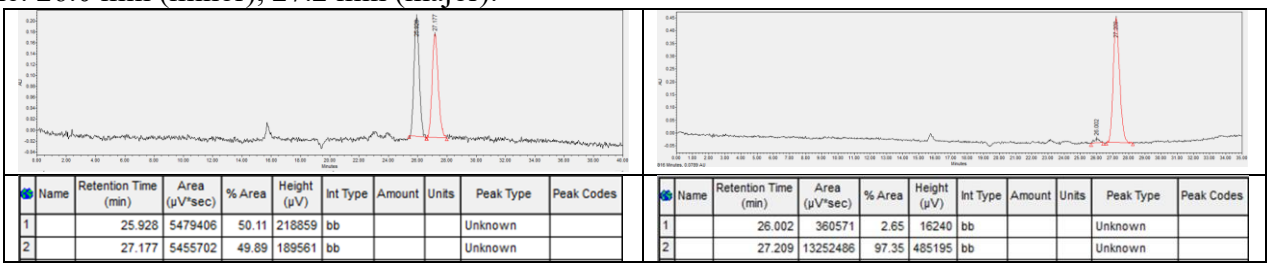
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		40.776	5749713	97.22	146159	bb			Unknown	
2		42.923	164452	2.78	5359	bb			Unknown	

Dibenzyl (*S,Z*)-2-(4-((*tert*-butyldimethylsilyl)oxy)-7-phenylhepta-1,4-dien-3-yl)malonate (11e)



11e

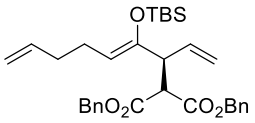
The reaction was run at RT for 14 h. Yellow oil, b:l > 20:1, 54 mg, 92% yield. $[\alpha]_D^{25}$ -28.8 (*c* 3.60, $CHCl_3$) for 95% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 12H), 7.20 – 7.09 (m, 3H), 5.88 – 5.74 (m, 1H), 5.17 – 5.00 (m, 6H), 4.52 (t, *J* = 7.0 Hz, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 3.45 (t, *J* = 9.2 Hz, 1H), 2.50 (t, *J* = 7.9 Hz, 2H), 2.32 – 2.17 (m, 2H), 0.93 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.64 (CO), 167.46 (CO), 148.90 (O-C=), 142.15 (quaternary carbon of terminal Ph), 135.66 (CH=), 135.50 (two peaks are overlapped, quaternary carbon of Bn), 128.57 (CH of Bn), 128.56 (CH of Bn), 128.43 (CH of terminal Ph), 128.35 (CH of Bn), 128.33 (two peaks are overlapped, CH of Bn), 128.32 (CH of Bn), 128.25 (CH of terminal Ph), 125.77 (CH of terminal Ph), 118.11 (CH_2=), 108.63 (CH=), 67.19, 67.06, 54.92, 50.19, 35.91, 27.24, 25.96, 18.44, -3.63, -3.82; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{36}H_{44}O_5NaSi^{\oplus}$ 607.2850, found 607.2846; HPLC: two chiral OD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 94/6; flow = 0.5 mL/min; Retention time: 26.0 min (minor), 27.2 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		25.928	5479406	50.11	218859	bb			Unknown	
2		27.177	5455702	49.89	189561	bb			Unknown	

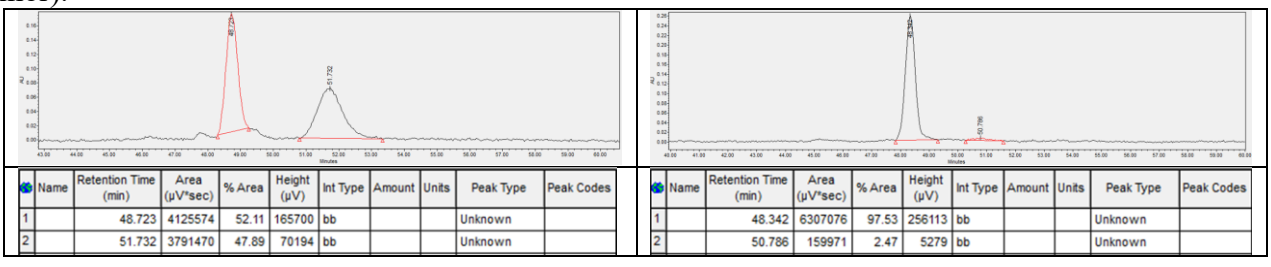
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		26.002	360571	2.65	16240	bb			Unknown	
2		27.209	13252486	97.35	485195	bb			Unknown	

Dibenzyl (*S,Z*)-2-(4-((*tert*-butyldimethylsilyl)oxy)nona-1,4,8-trien-3-yl)malonate (11f)



11f

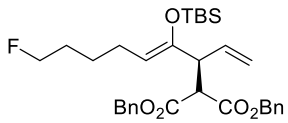
The reaction was run at RT for 20 h. Yellow oil, b:l > 20:1, 48 mg, 90% yield. $[\alpha]_D^{25}$ -28.8 (*c* 2.95, $CHCl_3$) for 95% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 10H), 5.90 – 5.68 (m, 2H), 5.19 – 4.91 (m, 8H), 4.55 – 4.41 (m, 1H), 3.82 (d, *J* = 9.6 Hz, 1H), 3.45 (t, *J* = 9.1 Hz, 1H), 2.42 – 1.67 (m, 4H), 0.94 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.64 (CO), 167.46 (CO), 148.75 (O-C=), 138.44 (CH=), 135.70 (CH=), 135.48 (two peaks are overlapped, quaternary carbon of Ph), 128.54 (two peaks are overlapped, CH of Ph), 128.33 (CH of Ph), 128.31 (two peaks are overlapped, CH of Ph), 128.23 (CH of Ph), 118.07 (CH_2=), 114.57 (CH_2=), 108.66 (CH=), 67.18, 67.05, 54.91, 50.20, 33.73, 25.94, 24.83, 18.42, -3.67, -3.85; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{32}H_{42}O_5NaSi^{\oplus}$ 557.2693, found 557.2694; HPLC: two chiral AD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 99.5/0.5; flow = 0.4 mL/min; Retention time: 48.3 min (major), 50.8 min (minor).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		48.723	4125574	52.11	165700	bb			Unknown	
2		51.732	3791470	47.89	70194	bb			Unknown	

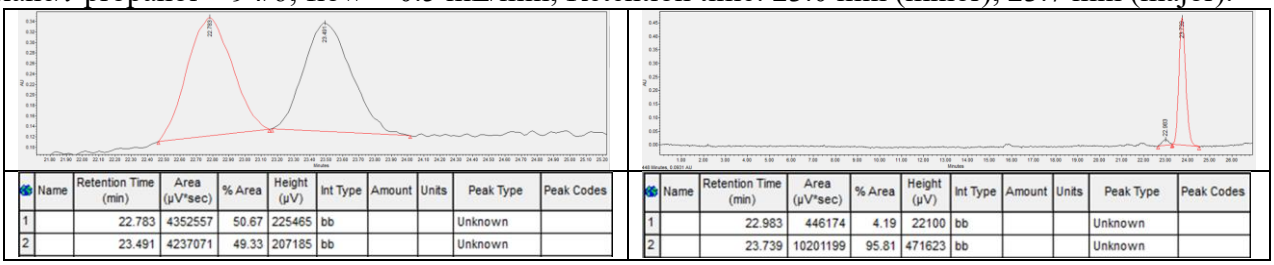
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		48.342	6307076	97.53	256113	bb			Unknown	
2		50.786	159971	2.47	5279	bb			Unknown	

Dibenzyl (*S,Z*)-2-(4-((tert-butyldimethylsilyl)oxy)-9-fluorononа-1,4-dien-3-yl)malonate (11g)



11g

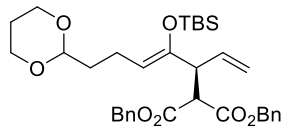
The reaction was run at RT for 20 h. Yellow oil, b:l > 20:1, 45 mg, 82% yield. $[\alpha]_D^{25}$ -24.8 (*c* 2.97, $CHCl_3$) for 92% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 10H), 5.91 – 5.74 (m, 1H), 5.18 – 5.02 (m, 6H), 4.52 – 4.39 (m, 2H), 4.32 (t, *J* = 6.2 Hz, 1H), 3.82 (d, *J* = 9.4 Hz, 1H), 3.44 (t, *J* = 9.0 Hz, 1H), 2.01 – 1.906 (m, 2H), 1.71 – 1.56 (m, 2H), 1.36 – 1.28 (m, 2H), 0.93 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.67 (CO), 167.44 (CO), 148.92 (O-C=), 135.62 (CH=), 135.47 (quaternary carbon of Ph), 135.46 (quaternary carbon of Ph), 128.54 (two peaks are overlapped, CH of Ph), 128.34 (CH of Ph), 128.31 (two peaks are overlapped, CH of Ph), 128.23 (CH of Ph), 118.13 (CH_2=), 108.92 (CH=), 84.03 (d, J_{CF} = 164.1 Hz), 67.19, 67.05, 54.83, 50.20, 30.00 (d, J_{CF} = 19.6 Hz, 1H), 25.92, 25.20 (d, J_{CF} = 5.4 Hz, 1H), 24.93, 18.42, -3.70, -3.88; ^{19}F NMR (376 MHz, $CDCl_3$) δ -215.05 – -218.63 (m, 1F); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{32}H_{43}O_5NaFSi^{\oplus}$ 577.2756, found 577.2736; HPLC: two chiral OD-H columns were connected to each other; detected at 220 nm; *n*-hexane/*i*-propanol = 94/6; flow = 0.5 mL/min; Retention time: 23.0 min (minor), 23.7 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		22.783	4352557	50.67	225465	bb			Unknown	
2		23.491	4237071	49.33	207185	bb			Unknown	

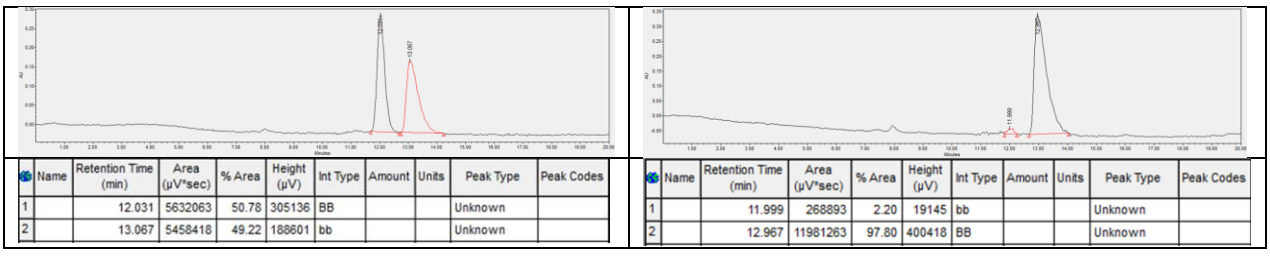
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		22.983	446174	4.19	22100	bb			Unknown	
2		23.739	10201199	95.81	471623	bb			Unknown	

Dibenzyl (*S,Z*)-2-(4-((*tert*-butyldimethylsilyl)oxy)-7-(1,3-dioxan-2-yl)hepta-1,4-dien-3-yl)malonate (11h)



11h

The reaction was run at RT for 14 h. Yellow oil, b:l > 20:1, 47 mg, 79% yield. $[\alpha]_D^{25}$ -24.1 (*c* 3.01, $CHCl_3$) for 96% ee. ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 10H), 5.88 – 5.74 (m, 1H), 5.15 – 5.02 (m, 6H), 4.45 (dt, *J* = 10.4, 6.1 Hz, 2H), 4.06 (dd, *J* = 11.8, 4.3 Hz, 2H), 3.82 (d, *J* = 9.5 Hz, 1H), 3.78 – 3.68 (m, 2H), 3.44 (t, *J* = 9.1 Hz, 1H), 2.13 – 1.98 (m, 3H), 1.53 (dd, *J* = 12.8, 7.5 Hz, 2H), 1.30 (d, *J* = 13.4 Hz, 1H), 0.92 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.62 (CO), 167.45 (CO), 148.86 (O-C=), 135.68 (CH=), 135.46 (two peaks are overlapped, quaternary carbon of Ph), 128.55 (CH of Ph), 128.53 (CH of Ph), 128.30 (two peaks are overlapped, CH of Ph), 128.24 (two peaks are overlapped, CH of Ph), 118.02 (CH_2=), 108.57 (CH=), 101.81 (O-CH-O), 67.15, 67.03, 66.86, 54.88, 50.19, 35.13, 25.95, 25.93, 20.09, 18.42, -3.73, -3.92; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{34}H_{46}O_7NaSi^{\oplus}$ 617.2905, found 617.2903; HPLC: chiral OD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 12.0 min (minor), 13.0 min (major).



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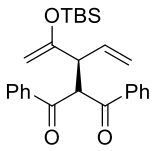
2		13.067	5458418	49.22	188601	bb			Unknown	

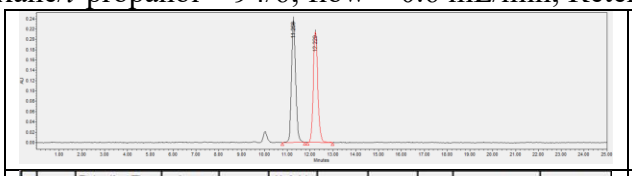
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.999	268893	2.20	19145	bb			Unknown	
2		12.967	11981263	97.80	400418	BB			Unknown	

(*S*)-2-(2-((*tert*-Butyldimethylsilyl)oxy)penta-1,4-dien-3-yl)-1,3-diphenylpropane-1,3-dione (11i)

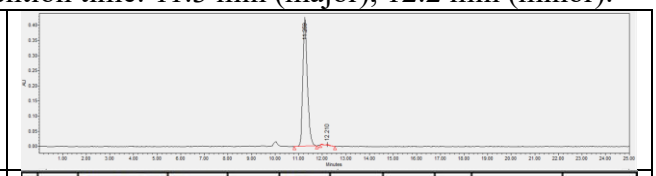


11i

The reaction was run at RT for 12 h. Yellow oil, b:l > 20:1, 40 mg, 95% yield. $[\alpha]_D^{25}$ -13.9 (*c* 2.58, $CHCl_3$) for 98% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.7, 2.5 Hz, 4H), 7.53 (q, *J* = 7.3 Hz, 2H), 7.42 (dt, *J* = 12.1, 7.7 Hz, 4H), 5.93 – 5.79 (m, 2H), 5.09 (d, *J* = 17.1 Hz, 1H), 4.98 (d, *J* = 10.1 Hz, 1H), 4.21 (s, 1H), 4.03 – 3.98 (m, 2H), 0.92 (s, 9H), 0.11 (s, 3H), -0.01 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.20, 193.95, 156.97, 137.40, 137.13, 135.71, 133.39, 133.33, 128.83, 128.78, 128.76, 128.69, 117.87, 91.59, 58.33, 52.32, 25.85, 18.22, -4.77, -5.04; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{26}H_{32}O_3NaSi^{\oplus}$ 443.2012, found 443.2015; HPLC: chiral AD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 94/6; flow = 0.6 mL/min; Retention time: 11.3 min (major), 12.2 min (minor).

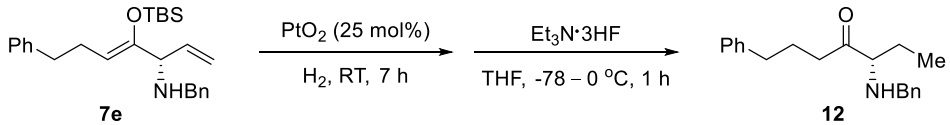


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.268	3039924	50.99	239357	bb			Unknown	
2		12.229	2921962	49.01	213777	bb			Unknown	



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.259	5618867	99.03	419547	bb			Unknown	
2		12.210	54931	0.97	3716	bb			Unknown	

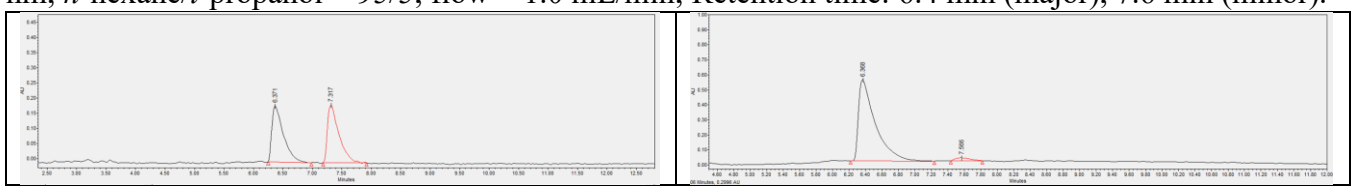
7. Transformations



7e
95% ee

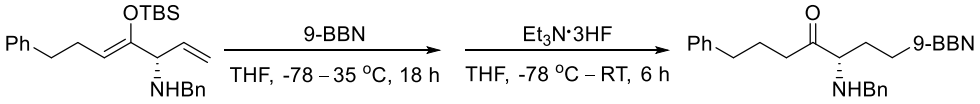
12
85% yield, 94% ee

(*S*)-5-(Benzylamino)-1-phenylheptan-4-one (**12**): To a well stirred solution of **7e** (40 mg, 0.10 mmol) in MeOH (1.0 mL) was added PtO_2 (5.5 mg, 0.025 mmol). The resulting mixture was stirred under 1 atm. of hydrogen for 7 h. After this time, the reaction was filtered through Celite, dried with $NaSO_4$ and condensed. To a well stirred solution of the crude product dissolved in dry THF (0.85 mL) at -78 °C was added $3HF{\cdot}Et_3N$ (11 μL, 0.067 mmol) in dry THF (0.15 mL) dropwise. The resulting solution was stirred at -78 °C for 0.5 h. After this time, the reaction was warmed to 0 °C and was stired for an additional 0.5 h at 0 °C. The reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 8/1 to 6/1) to afford pure product **12** as a yellow oil (25 mg) in 85% yield for two steps. $[\alpha]_D^{25}$ +7.7 (*c* 0.61, $CHCl_3$) for 94% ee. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.16 (m, 10H), 3.76 (d, *J* = 13.1 Hz, 1H), 3.63 (d, *J* = 13.1 Hz, 1H), 3.27 (t, *J* = 6.0 Hz, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 2.61 – 2.50 (m, 1H), 2.47 – 2.37 (m, 1H), 1.99 –1.92 (m, 3H), 1.78 – 1.68 (m, 1H), 1.60 – 1.49 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.77, 141.64, 140.21, 128.52, 128.47, 128.46, 128.26, 127.10, 126.04, 67.78, 52.29, 39.29, 35.23, 25.52, 25.08, 10.14; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{20}H_{26}NO^{\oplus}$ 296.2009, found 296.2005; HPLC: chiral AD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 95/5; flow = 1.0 mL/min; Retention time: 6.4 min (major), 7.6 min (minor).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.371	2531644	49.71	186372	bb			Unknown	
2		7.317	2560883	50.29	190578	bb			Unknown	

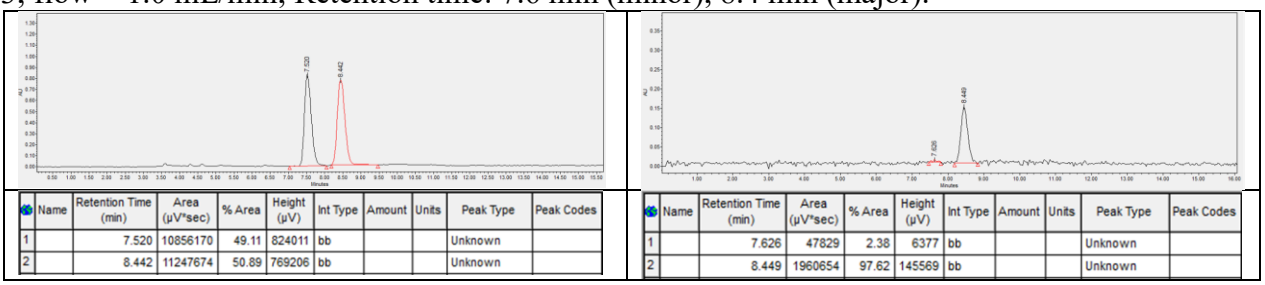
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		6.368	7647697	97.07	540484	bb			Unknown	
2		7.566	230914	2.93	19382	bb			Unknown	



7e
95% ee

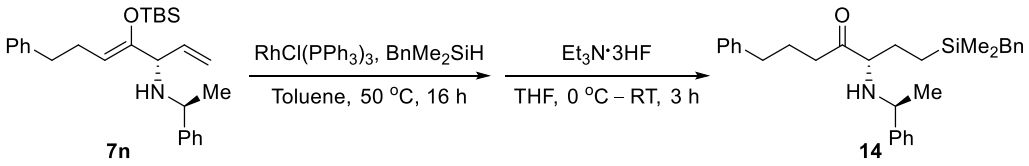
13
93% yield, 95% ee

(*S*)-3-(Benzylamino)-1-((1*S*,5*S*)-9-borabicyclo[3.3.1]nonan-9-yl)-7-phenylheptan-4-one (**13**): To a well stirred solution of **7e** (30 mg, 0.074 mmol) in THF (0.6 mL) under N_2 at – 78 °C was added 9-BBN (0.5 M in THF, 0.18 mL, 0.090 mmol) in THF (0.2 mL) dropwise. The reaction was stirred at 35 °C for 18 h. After this time, the reaction was cooled to – 78 °C. 3HF·Et_3N (18 μL, 0.098 mmol) in dry THF (0.2 mL) was added dropwise. After this addition, the resulting solution was stirred at – 78 °C for 20 min and 0 °C for 2 h in sequence. Next, another batch of 3HF·Et_3N (9.0 μL, 0.049 mmol) in dry THF (0.2 mL) was added to the above reaction solution dropwise. The resulting mixture was stirred at room temperature for 4 h. The reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 50/1) to afford pure **13** as a yellow oil (28 mg) in 93% yield. $[\alpha]_D^{25}$ +31.6 (*c* 1.92, $CHCl_3$) for 95% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.19 (m, 8H), 7.01 (d, *J* = 7.2 Hz, 2H), 5.47 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 14.1 Hz, 1H), 3.53 (td, *J* = 9.7, 2.5 Hz, 1H), 3.49 – 3.39 (m, 1H), 2.44 – 2.27 (m, 3H), 2.27 – 2.14 (m, 1H), 2.08 – 1.98 (m, 2H), 1.93 – 1.61 (m, 13H), 1.52 – 1.47 (m, 1H), 1.04 (dd, *J* = 13.1, 6.1 Hz, 1H), 0.83 (s, 1H), 0.51 – 0.43 (m, 1H), 0.26 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.65, 141.12, 134.54, 129.15, 129.07, 128.64, 128.41, 128.40, 126.06, 71.18, 53.20, 37.08, 34.57, 34.35, 32.33, 31.39, 30.67, 28.07, 24.93, 24.22 (The tertiary carbon connected to boron atom was not observed); HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{28}H_{38}NBONa^{\oplus}$ 438.2939, found 438.2918; HPLC: chiral OD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 97/3; flow = 1.0 mL/min; Retention time: 7.6 min (minor), 8.4 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.520	10856170	49.11	824011	bb			Unknown	
2		8.442	11247674	50.89	769206	bb			Unknown	

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		7.626	47829	2.38	6377	bb			Unknown	
2		8.449	1960654	97.62	145569	bb			Unknown	

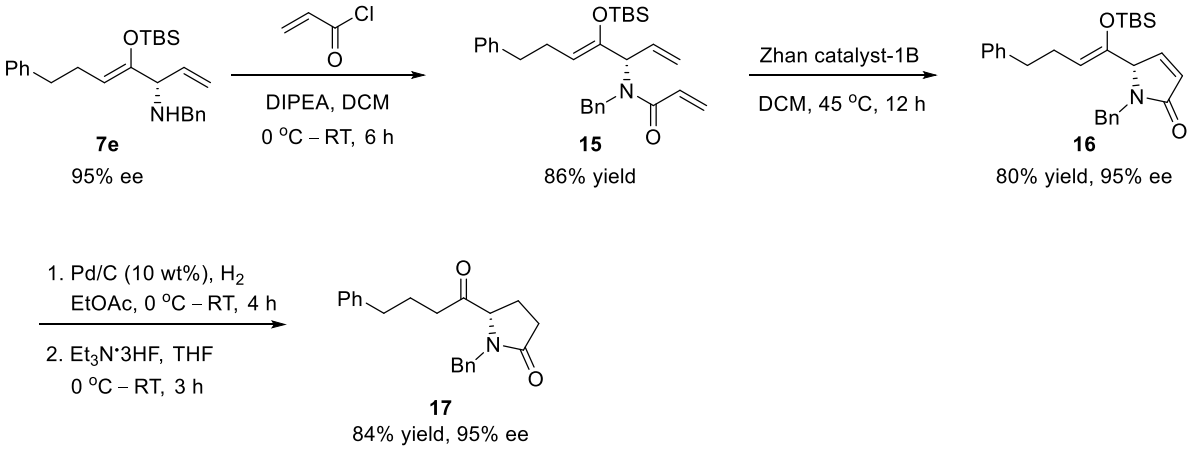


7n

14
54% yield, > 20:1 dr

(*S*)-1-(Benzyldimethylsilyl)-7-phenyl-3-(((*S*)-1-phenylethyl)amino)heptan-4-one (**14**): To a well stirred solution of **7n** (18 mg, 0.043 mmol) in toluene (0.4 mL) under N_2 was added $BnMe_2SiH$ (21 μL, 0.13 mmol) and $RhCl(PPh_3)_3$ (3.9 mg, 0.0043 mmol). The mixture was stirred at 50 °C for 16 h. After this time, the reaction solution was condensed directly to evaporate the volatile materials. To a well stirred solution of the crude silane dissolved in dry THF (0.5 mL) at 0 °C was added 3HF·Et_3N (14 μL,

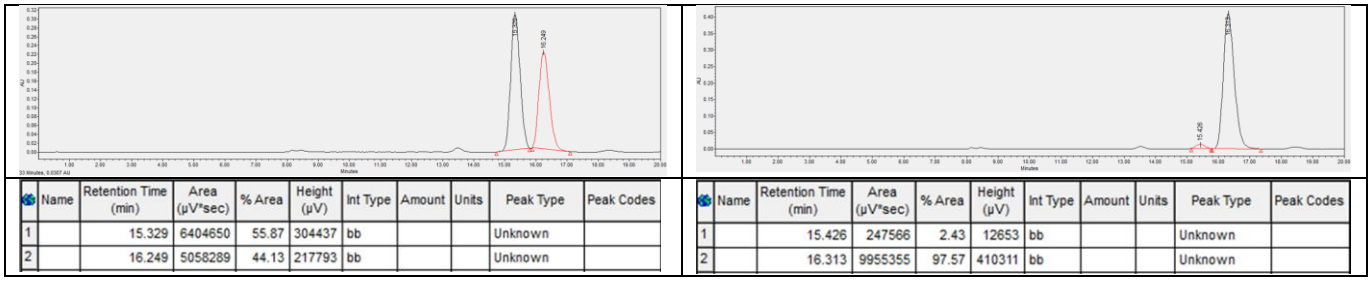
0.086 mmol) in dry THF (0.1 mL) dropwise. After this addition, the reaction was stirred at 0 °C for 1 h and room temperature for 2 h in sequence. This crude reaction solution was condensed to obtain a ^{1}H NMR spectrum for determination of the diastereoselectivity. The product was further purified by flash column chromatography (hexane/ethyl acetate = 20/1 to 12/1) to afford pure **14** as a yellow oil (11 mg) in 54% yield for two steps. $[\alpha]_D^{25}$ -4.1 (*c* 0.71, $CHCl_3$). dr >20:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 7H), 7.19 (t, *J* = 7.6 Hz, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 3.54 (q, *J* = 6.4 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.35 (dt, *J* = 16.9, 7.4 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.03 (s, 2H), 1.91 – 1.83 (m, 3H), 1.46 – 1.40 (m, 1H), 1.30 (d, *J* = 6.5 Hz, 3H), 0.55 (td, *J* = 13.8, 3.8 Hz, 1H), 0.35 (td, *J* = 13.9, 4.5 Hz, 1H), -0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 214.79, 145.56, 141.57, 140.13, 128.51, 128.48 (two peaks were overlapped, CH of Ph), 128.28, 128.11, 127.06, 126.96, 126.06, 124.09, 66.89, 56.85, 40.14, 35.15, 27.35, 25.57, 25.47, 24.96, 10.44, -3.68; HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{30}H_{40}NSiO^{\oplus}$ 458.2874, found 458.2875.



(*S*,*Z*)-*N*-Benzyl-*N*-(4-((*tert*-butyldimethylsilyl)oxy)-7-phenylhepta-1,4-dien-3-yl)acrylamide (**15**): To a well stirred solution of **7e** (34 mg, 0.083 mmol) in DCM (0.5 mL) under N_2 at 0 °C was added DIPEA (27 μL, 0.17 mmol) in DCM (0.2 mL). After this addition, acryloyl chloride (10 μL, 0.13 mmol) in DCM (0.2 mL) was added to the above solution dropwise. The resulting mixture was stirred at room temperature for 12 h. After this time, the reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 15/1) to afford pure product **15** as a colorless oil (33 mg) in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.12 (m, 10H), 6.61 – 4.44 (m, 10H), 2.64 – 2.23 (m, 4H), 0.98 – 0.93 (m, 9H), 0.26 – 0.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.20, 147.53, 141.94, 138.70, 133.43, 128.63, 128.39 (two peaks were overlapped), 128.30, 128.06, 126.98, 126.47, 125.80, 118.14, 112.80, 60.81, 47.49, 35.56, 26.98, 25.89, 18.25, -3.79, -4.01; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{29}H_{39}NSiO_2Na^{\oplus}$ 484.2642, found 484.2635.

(*S*,*Z*)-1-Benzyl-5-(1-((*tert*-butyldimethylsilyl)oxy)-4-phenylbut-1-en-1-yl)-1,5-dihydro-2*H*-pyrrol-2-one (**16**): To a well stirred solution of **15** (17 mg, 0.037 mmol) in DCM (0.4 mL) in a glovebox was added Zhan Catalyst-1B (1.4 mg, 0.0018 mmol). The resulting mixture was stirred at 45 °C for 12 h. After this time, the reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 6/1) to afford pure **16** as colorless oil (13 mg) in 80% yield. $[\alpha]_D^{25}$ -75.6 (*c* 0.71, $CHCl_3$) for 95% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.10 (m, 10H), 6.96 (d, *J* = 5.4 Hz, 1H), 6.17 (d, *J* = 5.1 Hz, 1H), 5.19 (d, *J* = 14.9 Hz, 1H), 4.63 (t, *J* = 7.0 Hz, 1H), 4.18 (s, 1H), 3.84 (d, *J* = 14.9 Hz, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.40 (dd, *J* = 14.6, 7.2 Hz, 2H), 0.88 (s, 9H), 0.06 (s,

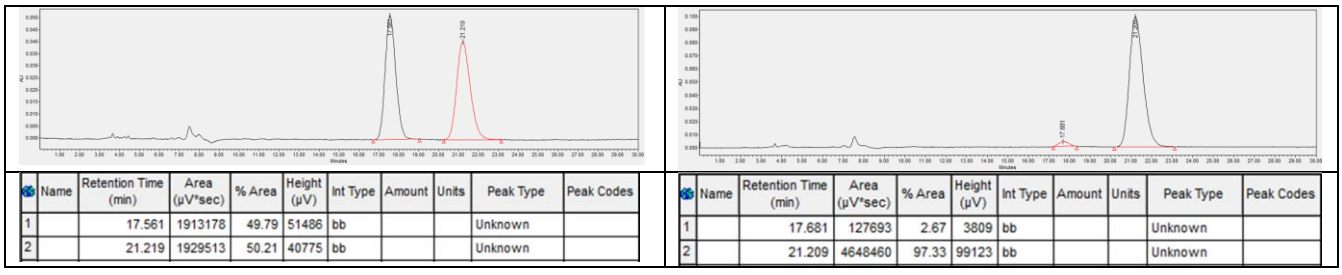
3H), -0.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.69, 146.58, 143.87, 141.56, 137.50, 128.72, 128.49, 128.45, 128.24, 127.54, 127.06, 126.05, 111.30, 66.52, 43.76, 35.71, 27.00, 25.81, 18.35, -3.58, -3.61; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{27}H_{35}NSiO_2Na^{\oplus}$ 456.2329, found 456.2327; HPLC: chiral OD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 90/10; flow = 0.5 mL/min; Retention time: 15.4 min (minor), 16.3 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		15.329	6404650	55.87	304437	bb			Unknown	
2		16.249	5058289	44.13	217793	bb			Unknown	

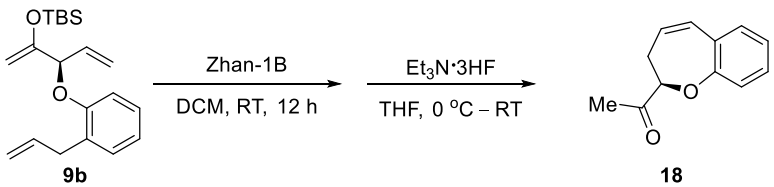
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		15.426	247566	2.43	12653	bb			Unknown	
2		16.313	9955355	97.57	410311	bb			Unknown	

(*S*)-1-Benzyl-5-(4-phenylbutanoyl)pyrrolidin-2-one (**17**): To a well stirred solution of **16** (10 mg, 0.023 mmol) in ethyl acetate (5 mL) under one atm. of hydrogen was added Pd/C (10 wt%, 1.2 mg, 0.0012 mmol). The resulting mixture was stirred at 0 °C for 1 h first, then at room temperature for 3 h. The solution was filtered through Celite, washed with ethyl acetate and condensed to evaporate the volatile materials. To a well stirred solution of the crude hydrogenation product in dry THF (0.3 mL) at 0 °C was added 3HF·Et_3N (4.0 μL, 0.023 mmol) in dry THF (0.1 mL) dropwise. The resulting mixture was stirred at 0 °C for 1 h. After this time, another batch of 3HF·Et_3N (4.0 μL, 0.023 mmol) in dry THF (0.1 mL) was added to the above solution dropwise and the mixtures was stirred for another 2 h at room temperature. This reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 1/1) to afford pure **17** as a yellow oil (6.3 mg) in 84% yield for two steps. $[\alpha]_D^{25}$ +24.0 (*c* 0.42, $CHCl_3$) for 95% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 5H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.13 (dd, *J* = 11.9, 7.8 Hz, 4H), 5.09 (d, *J* = 14.7 Hz, 1H), 3.97 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.84 (d, *J* = 14.7 Hz, 1H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.49 – 2.31 (m, 3H), 2.24 – 2.16 (m, 2H), 1.89 – 1.74 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 208.16, 175.05, 141.08, 135.89, 128.87, 128.65, 128.55, 128.47, 127.91, 126.22, 64.15, 45.64, 38.34, 34.90, 29.57, 24.65, 21.88; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{23}NO_2Na^{\oplus}$ 344.1621, found 344.1618; HPLC: chiral OD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 80/20; flow = 1.0 mL/min; Retention time: 17.7 min (minor), 21.2 min (major).



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.561	1913178	49.79	51486	bb			Unknown	
2		21.219	1929513	50.21	40775	bb			Unknown	

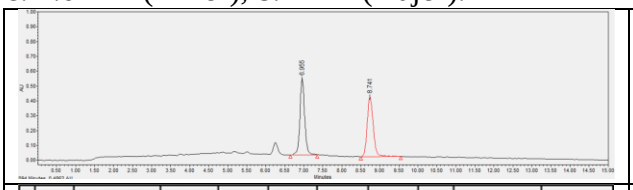
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		17.681	127693	2.67	3809	bb			Unknown	
2		21.209	4648460	97.33	99123	bb			Unknown	



9b
94% ee

18
53% yield, 94% ee

(*R*)-1-(2,3-Dihydrobenzo[b]oxepin-2-yl)ethan-1-one (**18**): To a well stirred solution of **9b** (29 mg, 0.088 mmol) in DCM (1.5 mL) under N_2 was added Zhan Catalyst-1B[3] (3.4 mg, 0.00044 mmol). The mixture was stirred at room temperature for 12 h. After this time, the reaction solution was condensed directly to evaporate the volatile materials. To a well stirred solution of the crude cyclized product dissolved in dry THF (0.6 mL) at 0 °C was added 3HF·Et_3N (29 µL, 0.18 mmol) in dry THF (0.1 mL) dropwise. The resulting solution was stirred at 0 °C for 1 h. Next, another 3HF·Et_3N (14 µL, 0.090 mmol) in dry THF (0.1 mL) was added to the above solution dropwise. The reaction was stirred at room temperature for 11 h. This reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 50/1 to 40/1) to afford pure product **18** as a colorless oil (9 mg) in 53% yield for two steps. $[\alpha]_D^{25}$ +269.0 (*c* 0.40, $CHCl_3$) for 94% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 2H), 7.08 – 7.02 (m, 2H), 6.35 (dd, *J* = 11.8, 2.1 Hz, 1H), 5.96 (ddd, *J* = 11.8, 6.2, 2.7 Hz, 1H), 4.34 (dd, *J* = 10.3, 1.9 Hz, 1H), 2.90 – 2.84 (m, 1H), 2.77 – 2.69 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.71, 157.18, 132.78, 128.63, 128.40, 128.38, 126.97, 123.46, 120.03, 84.50, 35.12, 26.72; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{12}O_2Na^{\oplus}$ 211.0730, found 211.0733; HPLC: chiral OD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 97/3; flow = 1.0 mL/min; Retention time: 7.0 min (minor), 8.7 min (major).



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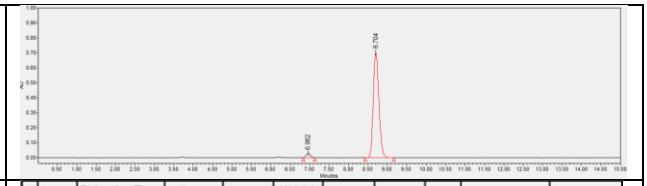

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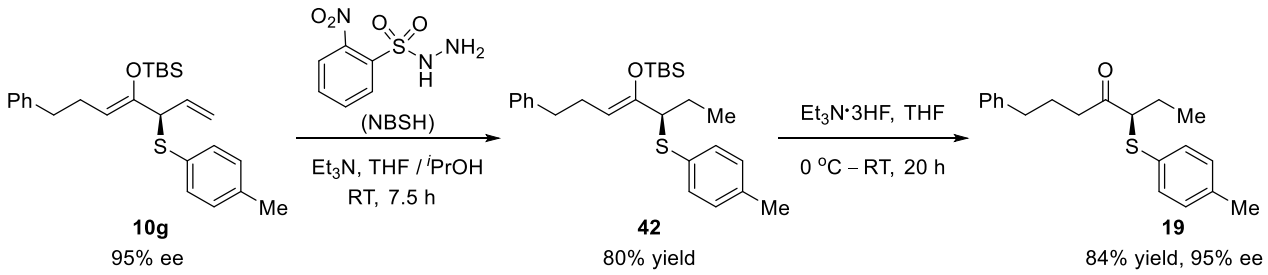

(*R*,*Z*)-*tert*-Butyldimethyl((1-phenyl-5-(*p*-tolylthio)hept-3-en-4-yl)oxy)silane (**42**): To a well stirred solution of **10g** (18 mg, 0.042 mmol) in THF (0.4 mL) under N_2 at room temperature was added freshly prepared NBSH (18 mg, 0.084 mmol) and *iso*-propanol (0.4 mL). The resulting mixture was stirred at room temperature for 7.5 h. After this time, the reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 100/1) to afford pure product **42** as a colorless oil (14 mg) in 80% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.07 (m, 9H), 4.63 – 4.46 (m, 1H), 3.27 (t, *J* = 7.2 Hz, 1H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.33 – 2.30 (m, 5H), 1.73 – 1.63 (m, 2H), 0.98 – 0.95 (m, 12H), 0.19 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.59, 142.28, 137.21, 133.43, 131.62, 129.41, 128.48, 128.30, 125.73, 109.39, 56.41, 36.00, 27.29, 26.30, 26.11, 21.20, 18.65, 12.06, -3.22, -3.59. HRMS (ESI): $[M+H]^{\oplus}$ calcd for $C_{26}H_{39}SiOS^{\oplus}$ 427.2485, found 427.2490.

(*R*)-1-Phenyl-5-(*p*-tolylthio)heptan-4-one (**19**): To a well stirred solution of **42** (14 mg, 0.033 mmol) in dry THF (0.4 mL) at 0 °C was added 3HF·Et_3N (10 µL, 2.0 equiv) in dry THF (0.1 mL) dropwise. The resulting solution was stirred at 0 °C for 1 h. Then, another 3HF·Et_3N (15 µL, 3.0 equiv) in dry THF

(0.1 mL) was added to the above solution dropwise. The reaction was stirred at room temperature for another 1 h. Next, 3HF·Et_3N (15 μL, 3.0 equiv) in dry THF (0.1 mL) was added to the above solution dropwise again and the mixtures was stirred for another 18 h at room temperature. This reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 40/1) to afford pure product **19** as a colorless oil (8.4 mg) in 84% yield. $[\alpha]_D^{25}$ +129.4(*c* 0.48, $CHCl_3$) for 95% ee. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.16 (m, 7H), 7.10 (d, *J* = 7.7 Hz, 2H), 3.46 (t, *J* = 7.4 Hz, 1H), 2.69 – 2.54 (m, 4H), 2.33 (s, 3H), 1.94 – 1.87 (m, 2H), 1.85 – 1.78 (m, 1H), 1.73 – 1.66 (m, 1H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.01, 141.75, 138.34, 133.46, 129.89, 129.15, 128.53, 128.42, 125.97, 59.04, 39.10, 35.21, 25.50, 23.62, 21.22, 12.01; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{24}SONa^{\oplus}$ 335.1440, found 335.1441. HPLC: chiral OD-H column, detected at 220 nm; *n*-hexane/*i*-propanol = 99/1; flow = 1.0 mL/min; Retention time: 17.1 min (major), 19.8 min (minor).

	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
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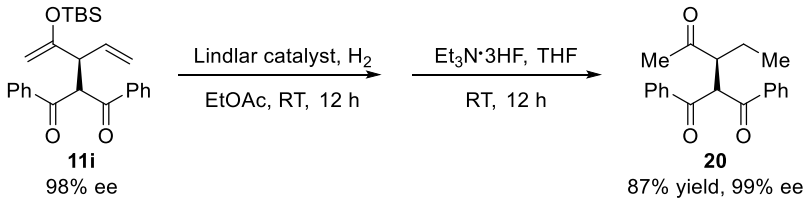
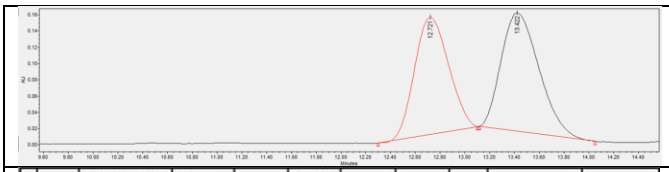
2		19.809	287423	2.65	8571	bb			Unknown	



11i
98% ee

20
87% yield, 99% ee

(*S*)-2-Benzoyl-3-ethyl-1-phenylpentane-1,4-dione (**20**): To a well stirred solution of **11i** (20 mg, 0.048 mmol) in ethyl acetate (2.0 mL) was added Lindlar cat. ($CaCO_3$·Pd, 9.6 mg, 0.048 mmol). The resulting mixture was stirred under 1 atm. of hydrogen for 12 h. Next, another Lindlar cat. ($CaCO_3$·Pd, 20 mg, 0.096 mmol) was added to the above solution. The resulting mixture was stirred under 1 atm. of hydrogen for another 4 h. After this time, the reaction was filtered through Celite, washed by ethyl acetate (10 × 3 mL) and condensed. To a well stirred solution of the crude product above dissolved in dry THF (0.30 mL) at room temperature was added 3HF·Et_3N (8 μL, 1.0 equiv) in dry THF (0.10 mL) dropwise. The resulting solution was stirred for 1 h. Next, another 3HF·Et_3N (23 μL, 3.0 equiv) in dry THF (0.10 mL) was added to the above solution. The resulting mixture was stirred at room temperature for 12 h. After this time, the reaction solution was condensed and further purified by flash column chromatography (hexane/ethyl acetate = 9/1 to 6/1) to afford pure product **20** as a yellow oil (13 mg) in 87% yield for two steps. $[\alpha]_D^{25}$ -261.4 (*c* 0.78, $CHCl_3$) for 99% ee. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.42 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 2H), 5.78 (d, *J* = 10.6 Hz, 1H), 3.89 – 3.78 (m, 1H), 2.37 (s, 3H), 1.61 – 1.51 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 211.35, 195.58, 195.37, 136.80, 136.51, 134.01, 133.45, 129.11, 129.02, 128.76, 128.70, 59.20, 53.74, 31.49, 23.07, 11.32; HRMS (ESI): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{20}NaO_3^{\oplus}$ 331.1305, found 331.1305; HPLC: chiral OD-H column, detected at 254 nm; *n*-hexane/*i*-propanol = 97/3; flow = 1.0 mL/min; Retention time: 12.6 min (major), 13.4 min (minor).



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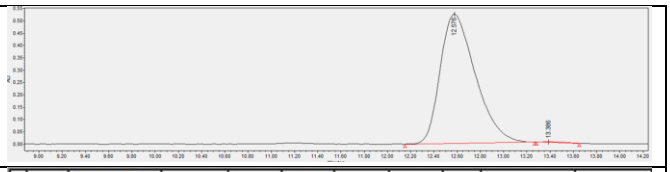

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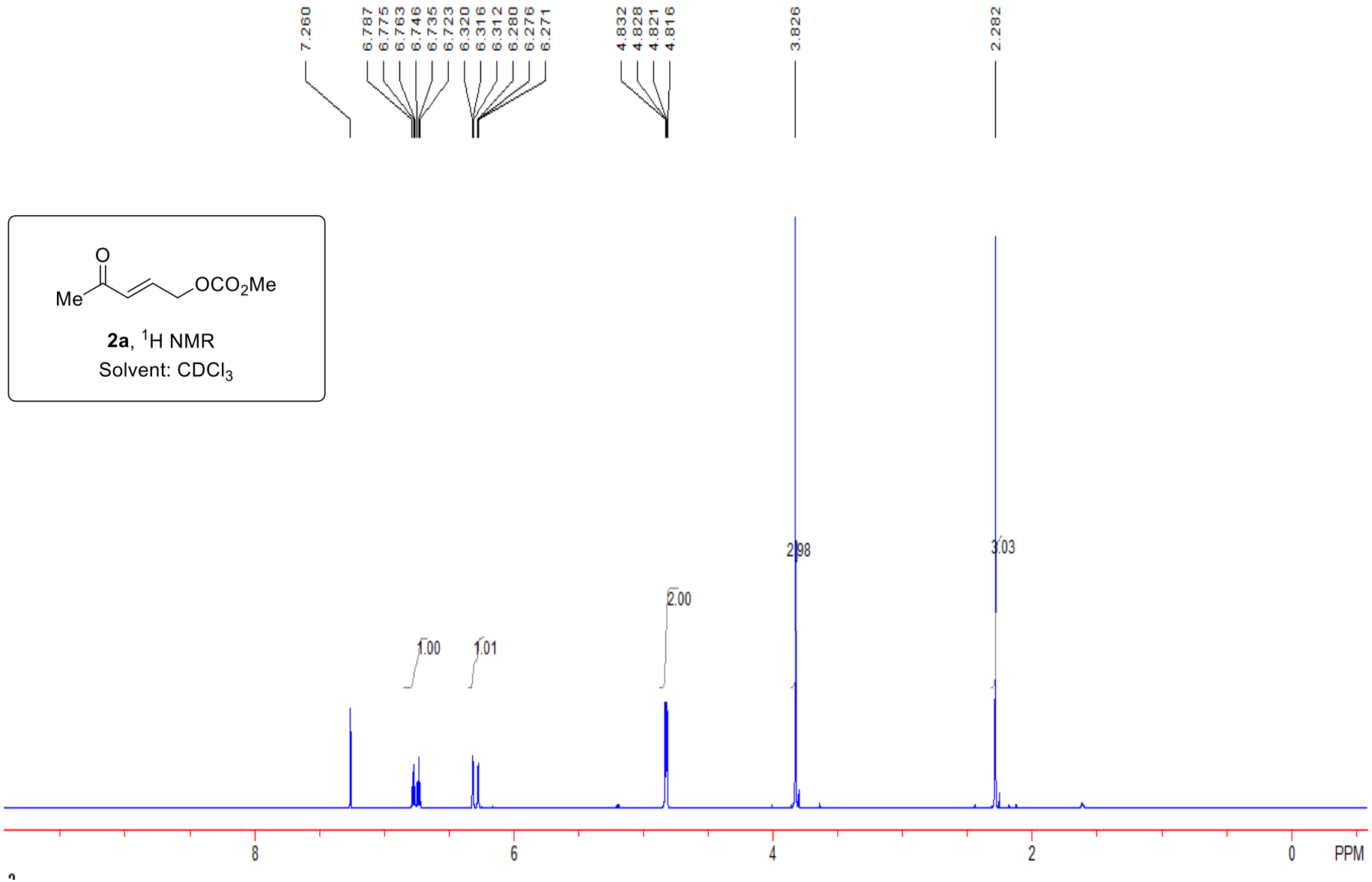
1		12.576	10998554	99.69	523567	bb			Unknown	
2		13.386	34030	0.31	2320	bb			Unknown	

8. Reference

1. Ashfeld, B. L., Miller, K. A., Martin, S. F. Direct, stereoselective substitution in $[Rh(CO)_2Cl]_2$-catalyzed allylic alkylations of unsymmetrical substrates. *Org. Lett.* **6,** 1321−1324 (2004).
2. Gao, W., Wang, Q., Xie, Y., Lv, H., Zhang, X. Rhodium-catalyzed asymmetric hydrogenation of α-dehydroamino ketones: a general approach to chiral α-amino ketones. *Chem. Asian J.* **11**, 231–233 (2016).
3. Zhang, Z.-Y. J. Reccyclable ruthenium catalysts for metathesis reactions. U.S. Patent US 2007/0043180 A1.

9. Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and DEPT spectra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6.312
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6.276
6.271
4.832
4.828
4.821
4.816
3.826
2.282
O
Me
OCO2Me
2a, 1H NMR
Solvent: CDCl3
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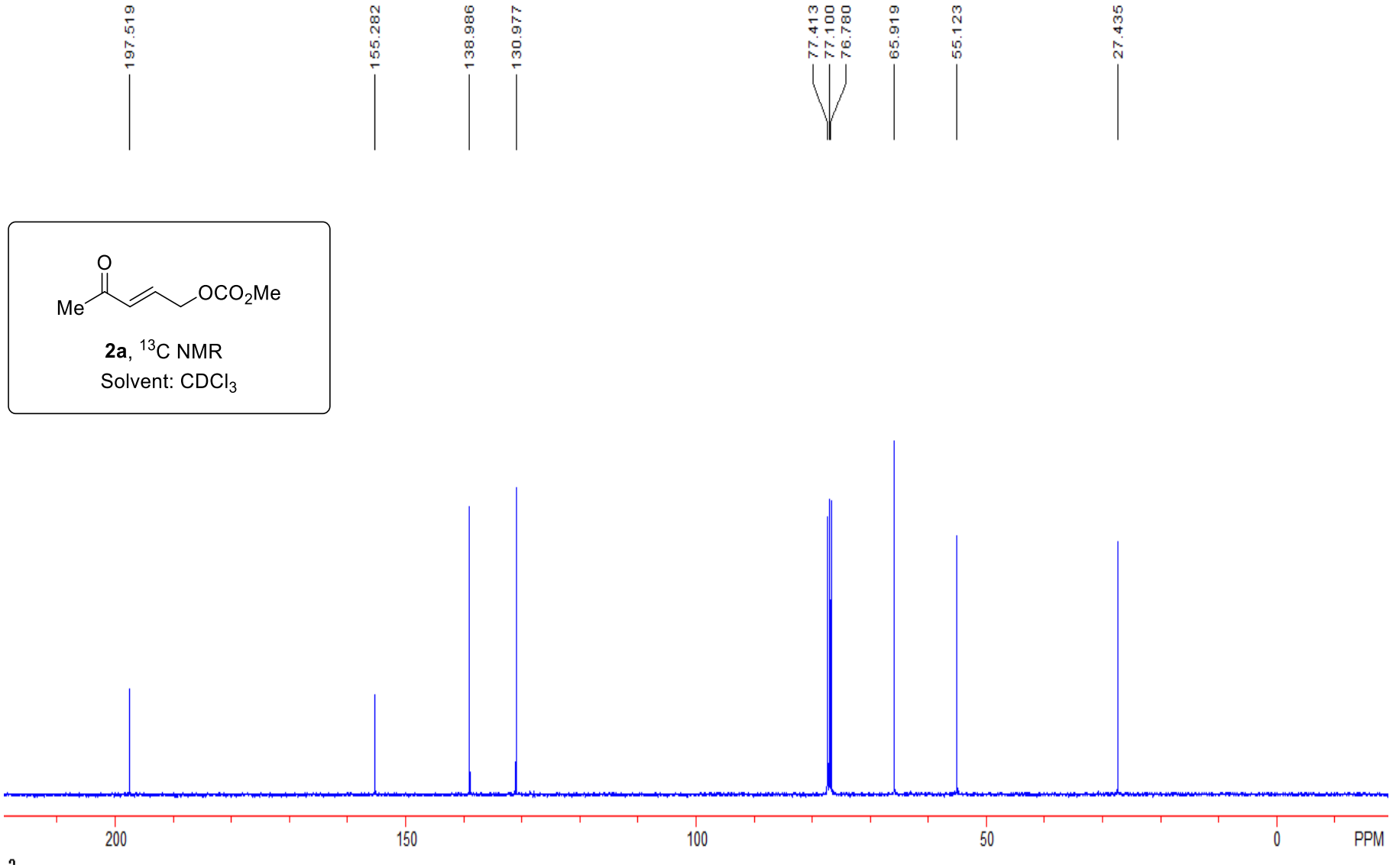
2.00
2.98
3.03
8
6
4
2
0
PPM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Me
OCO2Me
2a, 13C NMR
Solvent: CDCl3
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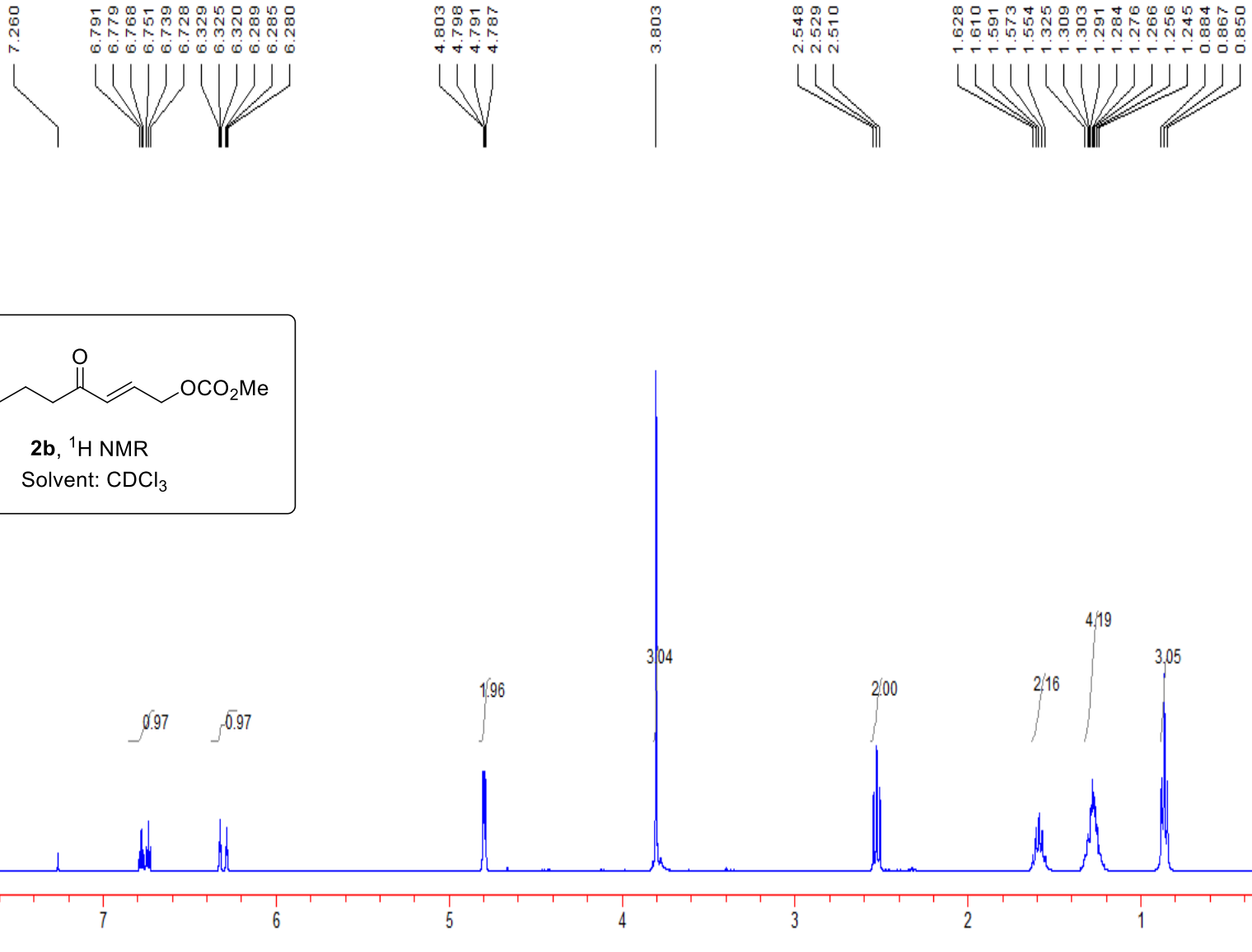
150
100
50
0
PPM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6.329
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6.280
4.803
4.798
4.791
4.787
3.803
2.548
2.529
2.510
1.628
1.610
1.591
1.573
1.554
1.325
1.309
1.303
1.291
1.284
1.276
1.266
1.256
1.245
0.884
0.867
0.850
O
Me
OCO2Me
2b, 1H NMR
Solvent: CDCl3
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0.97
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2.00
2.16
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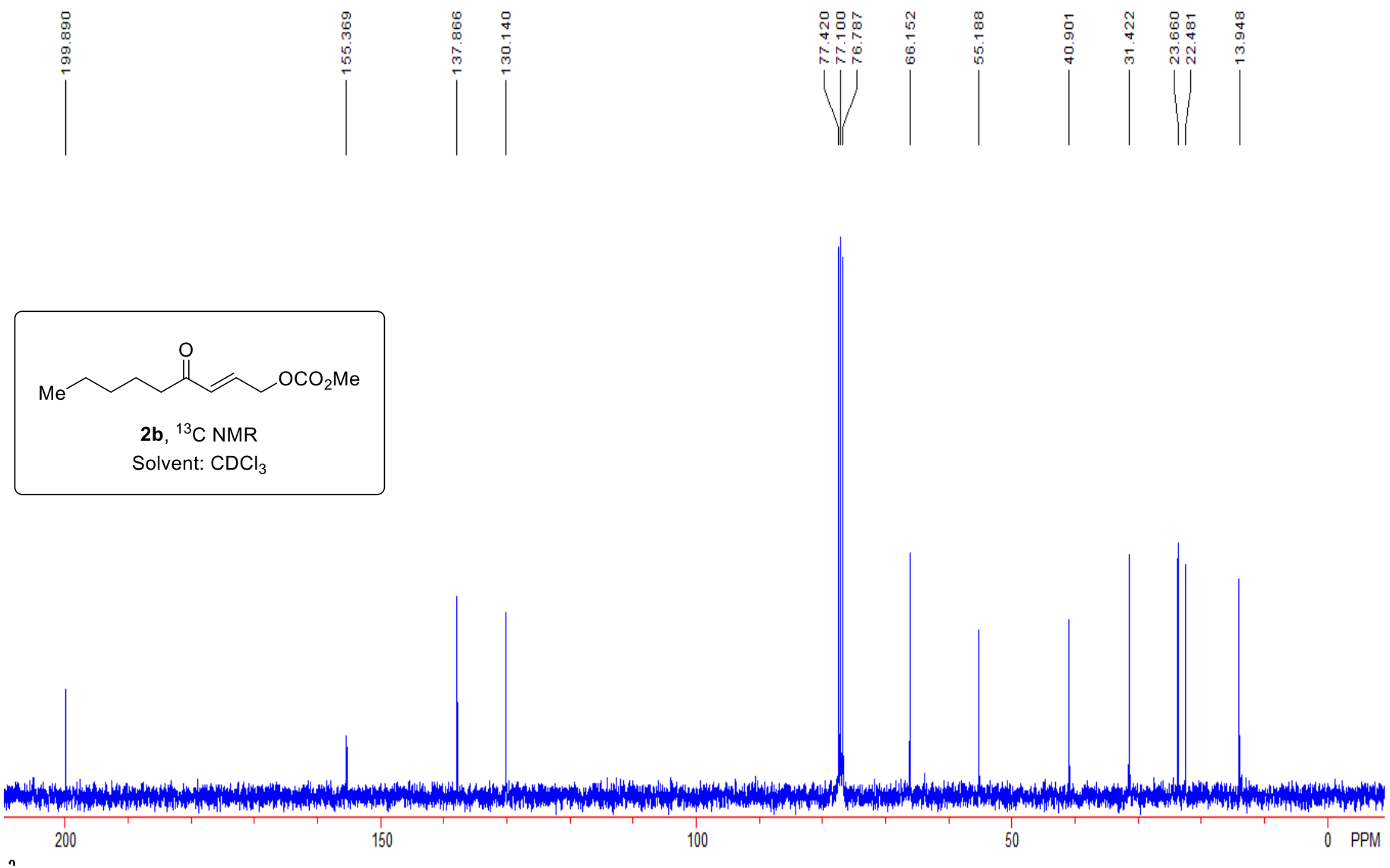
3.05
8
7
6
5
4
3
2
1
0
PPM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O
Me
OCO2Me
2b, 13C NMR
Solvent: CDCl3
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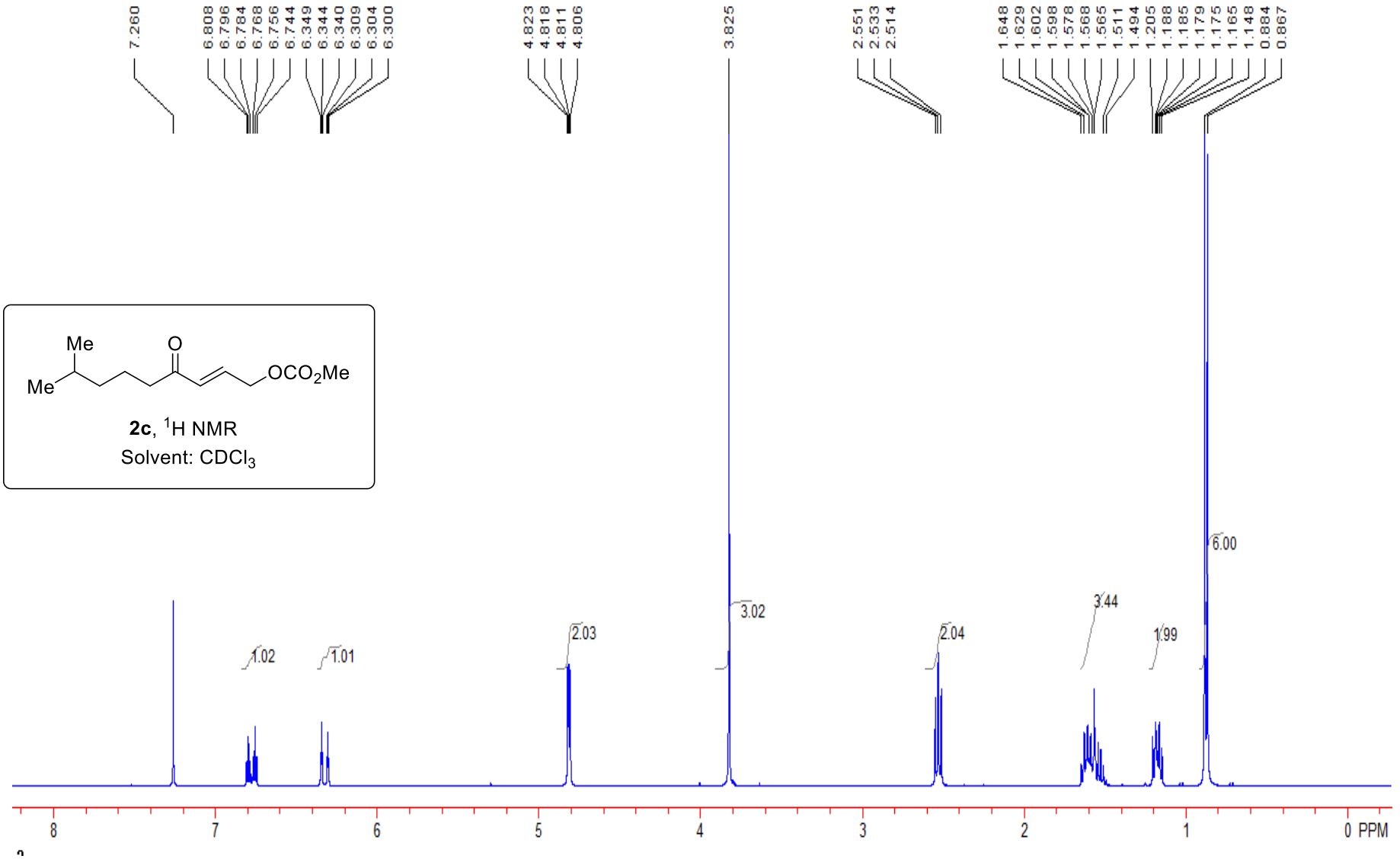
150
100
50
0
PPM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4.811
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2.533
2.514
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1.578
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1.175
1.165
1.148
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0.867
Me
O
Me
OCO2Me
2c, 1H NMR
Solvent: CDCl3
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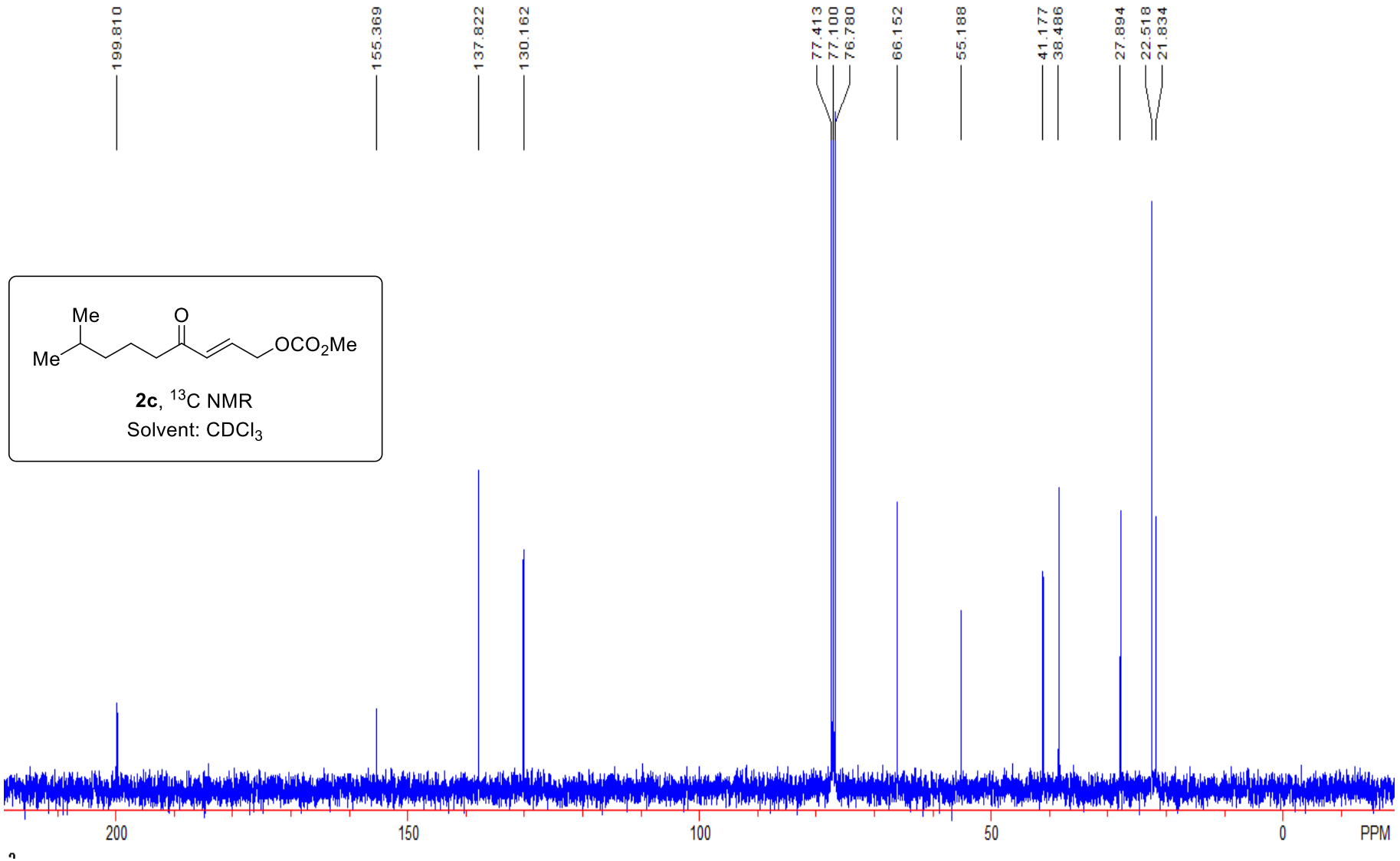
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O
Me
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2c, 13C NMR
Solvent: CDCl3
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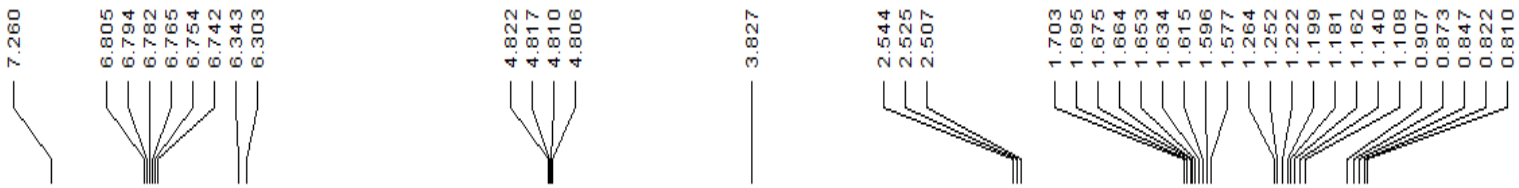
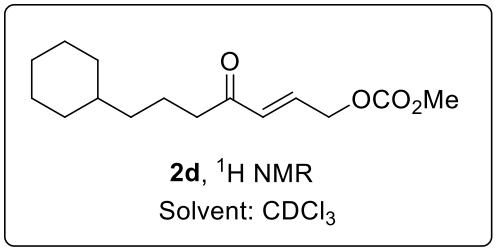
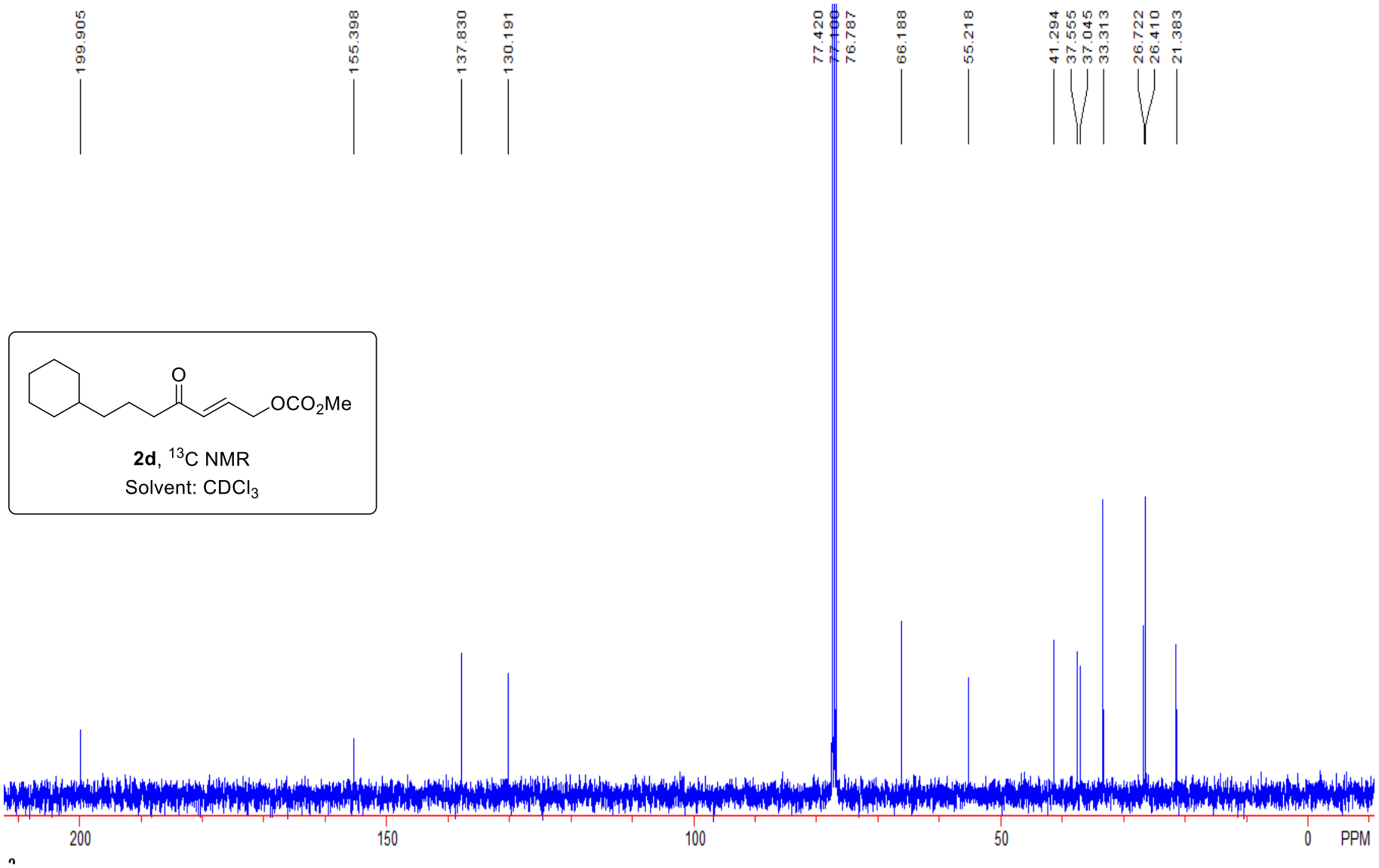
100
50
0
PPM





2d, ^{1}H NMR
Solvent: $CDCl_3$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2d, 13C NMR
Solvent: CDCl3
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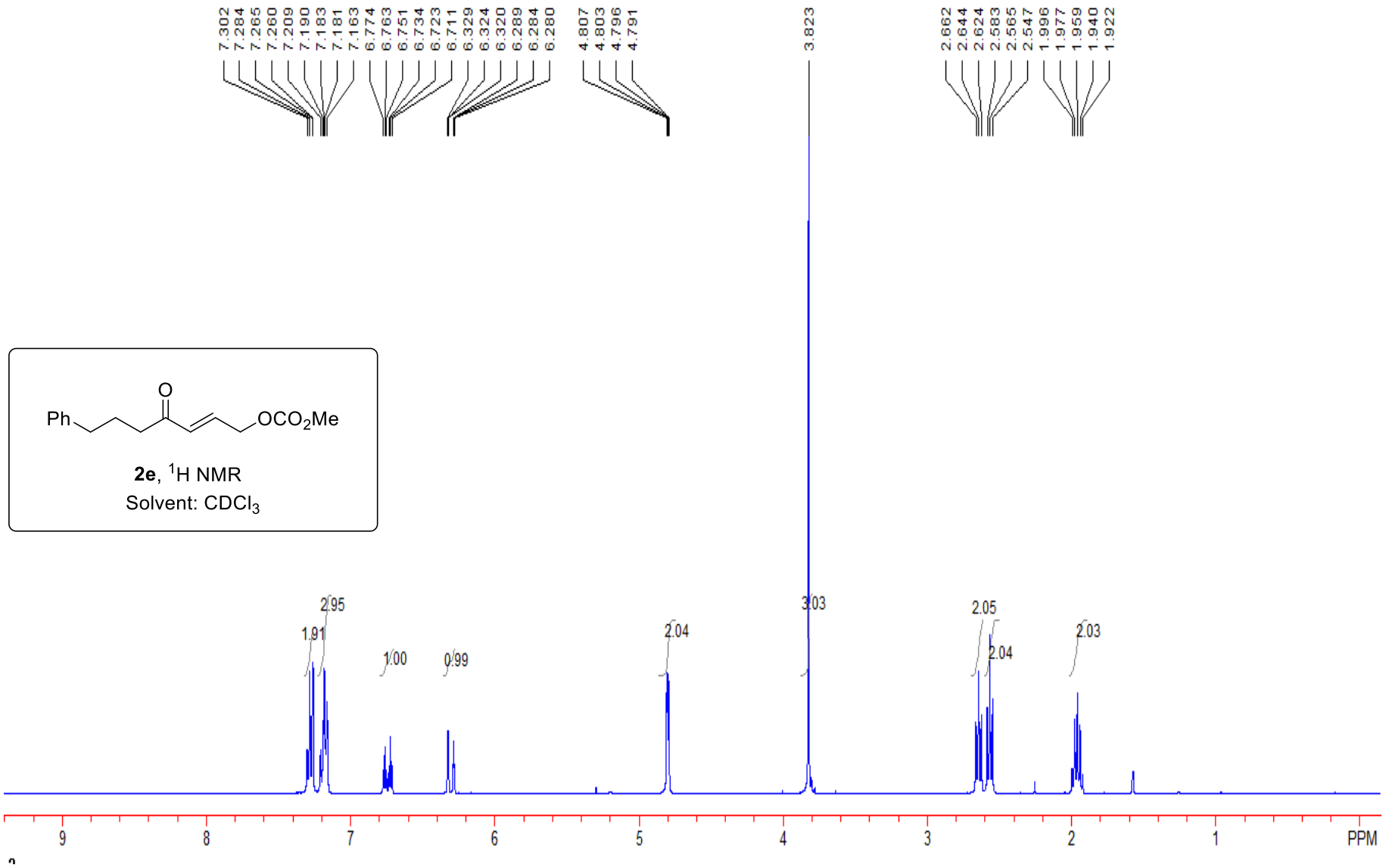
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6.280
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2.624
2.583
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Ph
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2e, 1H NMR
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3
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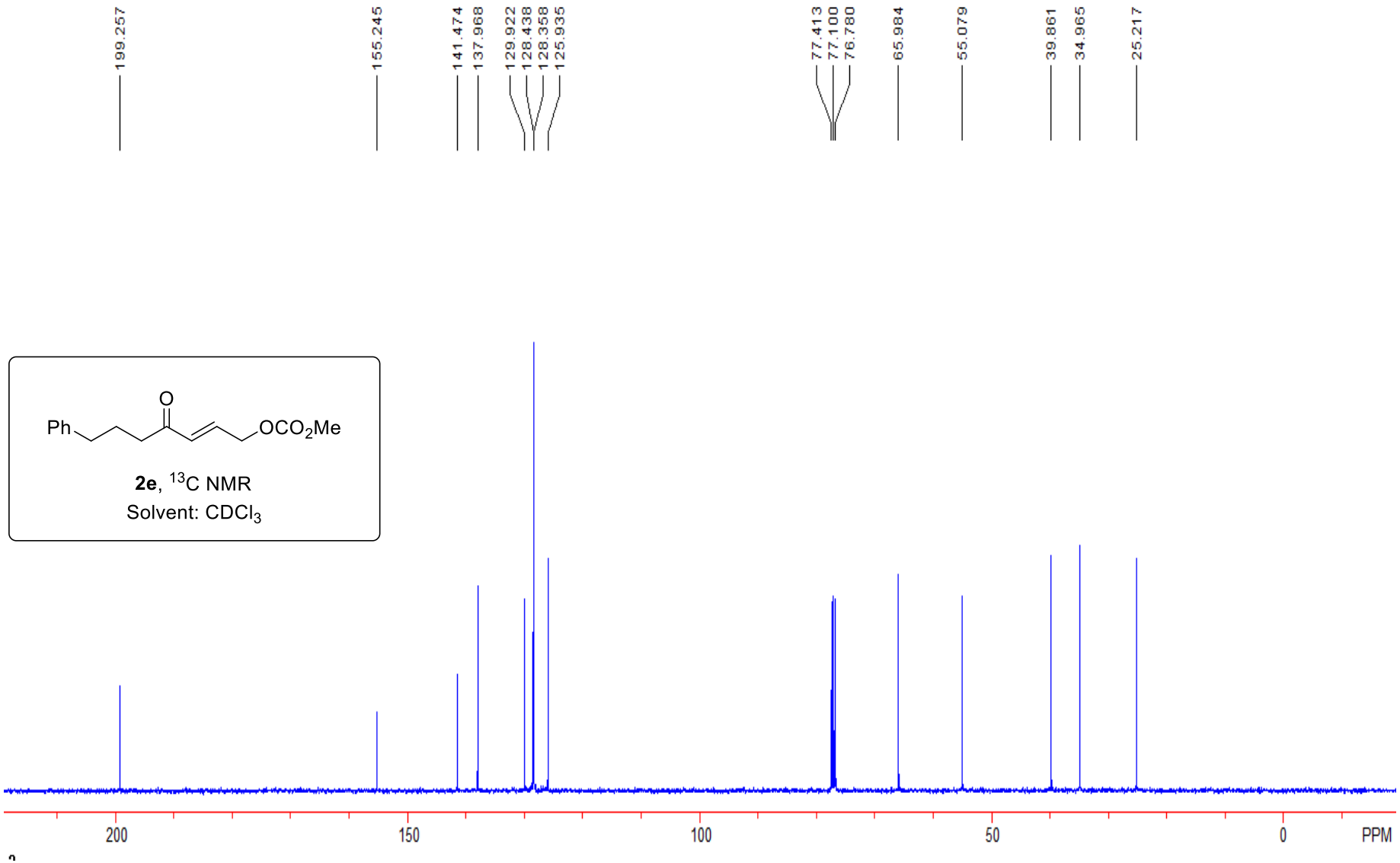
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O
Ph
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2e, 13C NMR
Solvent: CDCl3
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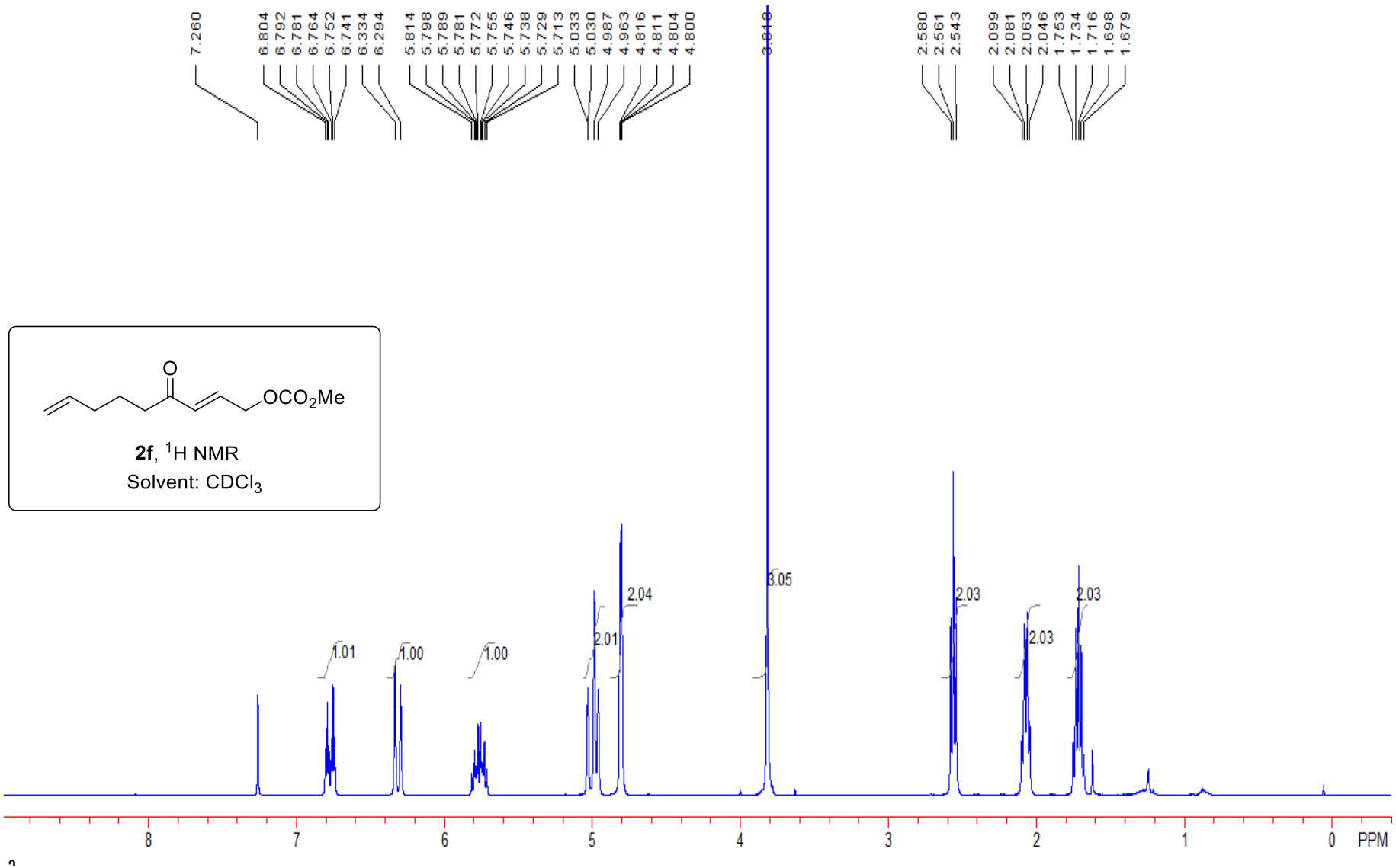
150
100
50
0
PPM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Solvent: CDCl3
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1
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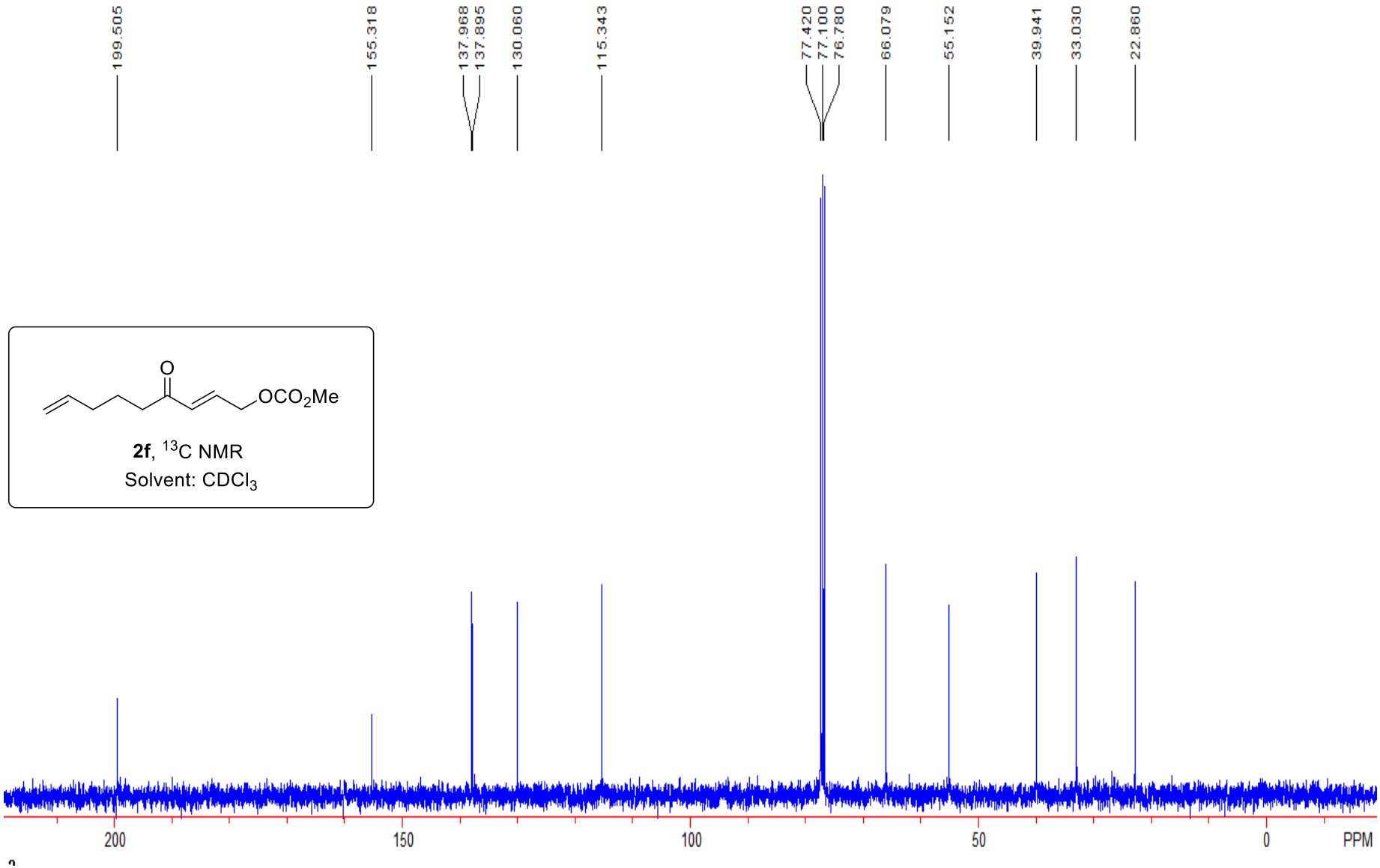
PPM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OCO2Me
2f, 13C NMR
Solvent: CDCl3
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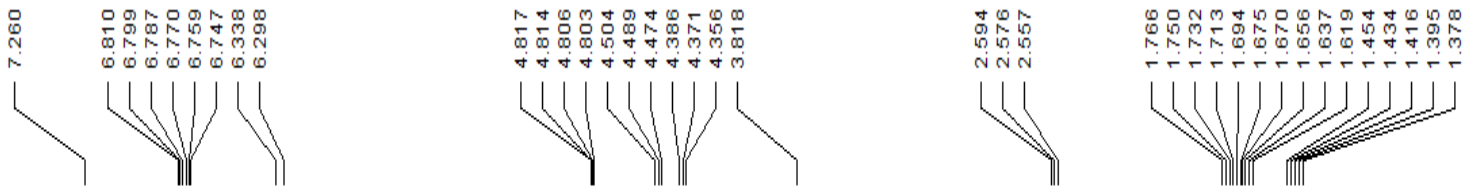
150
100
50
0
PPM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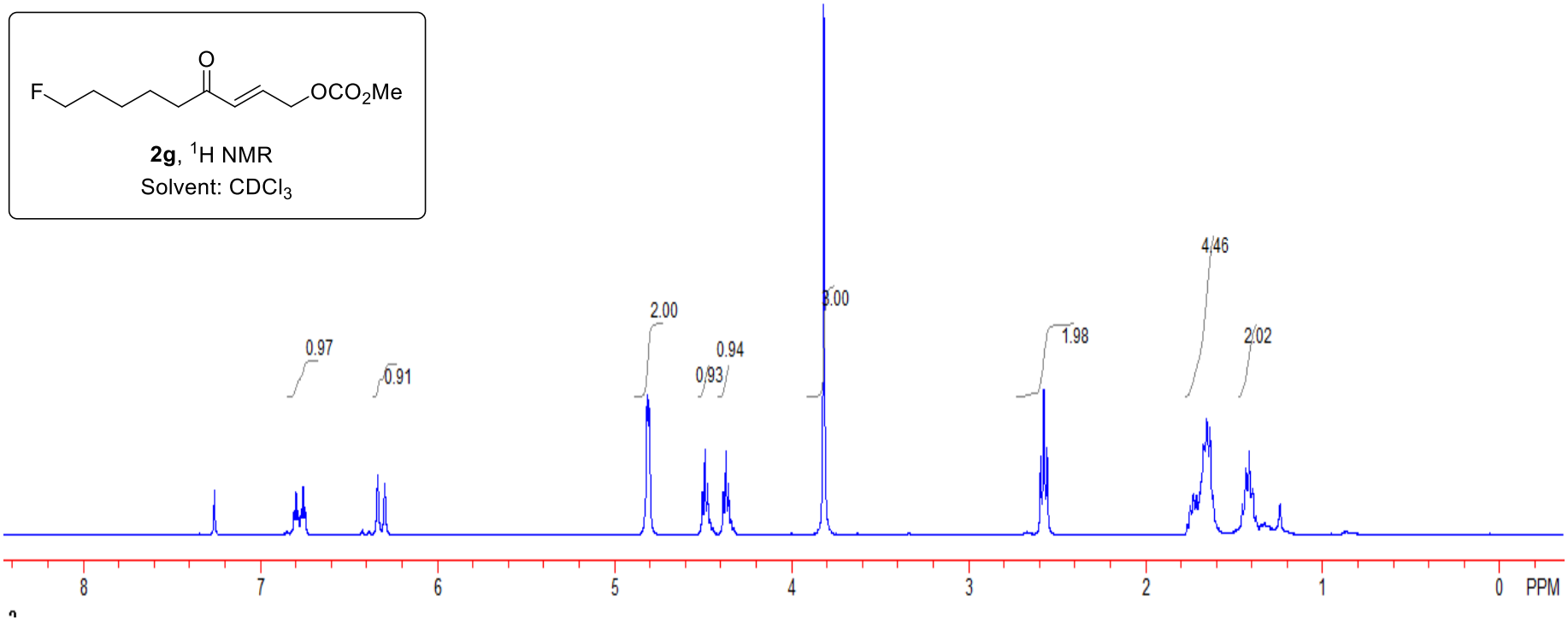
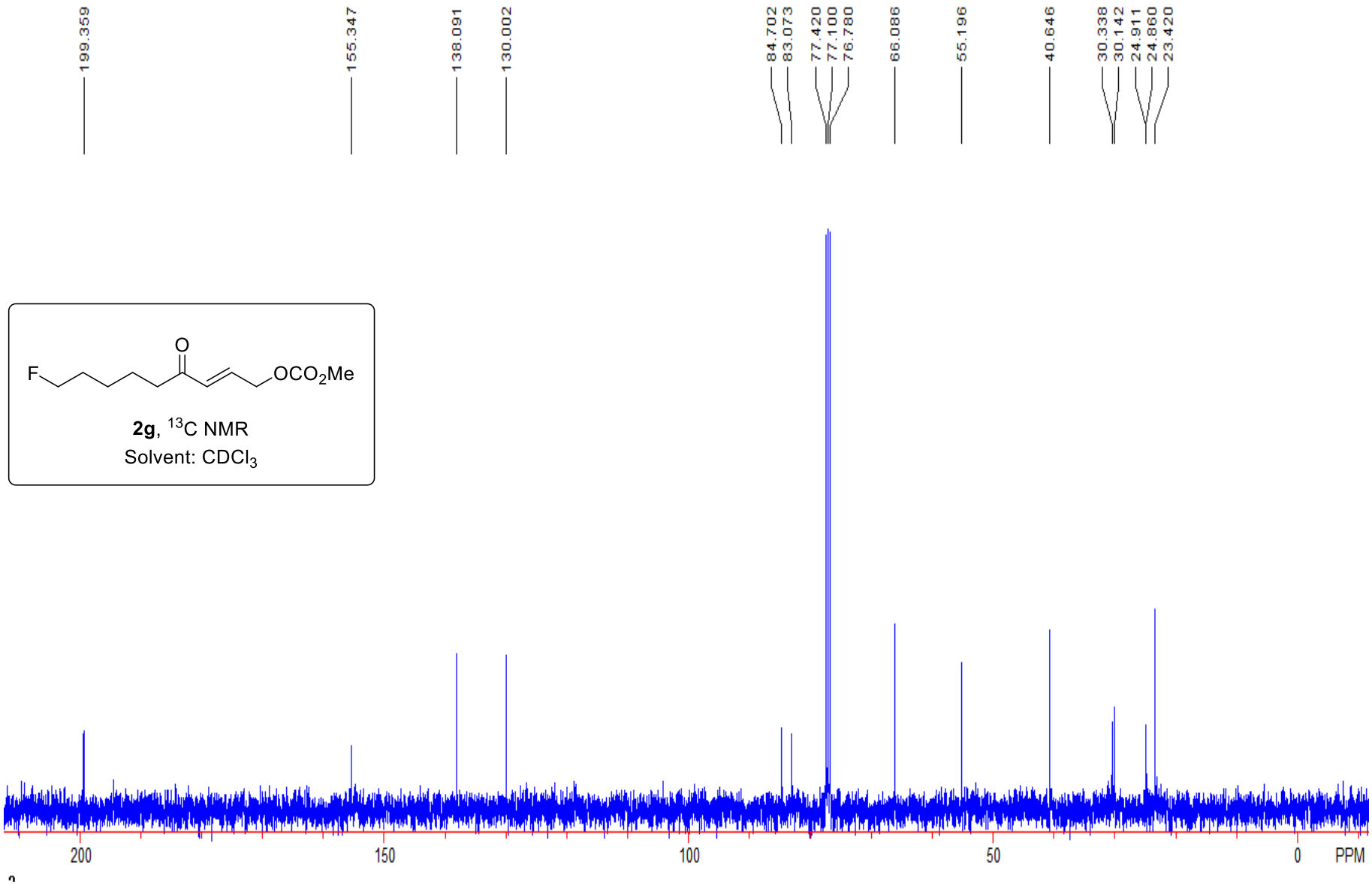
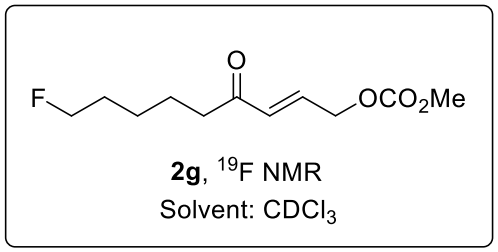
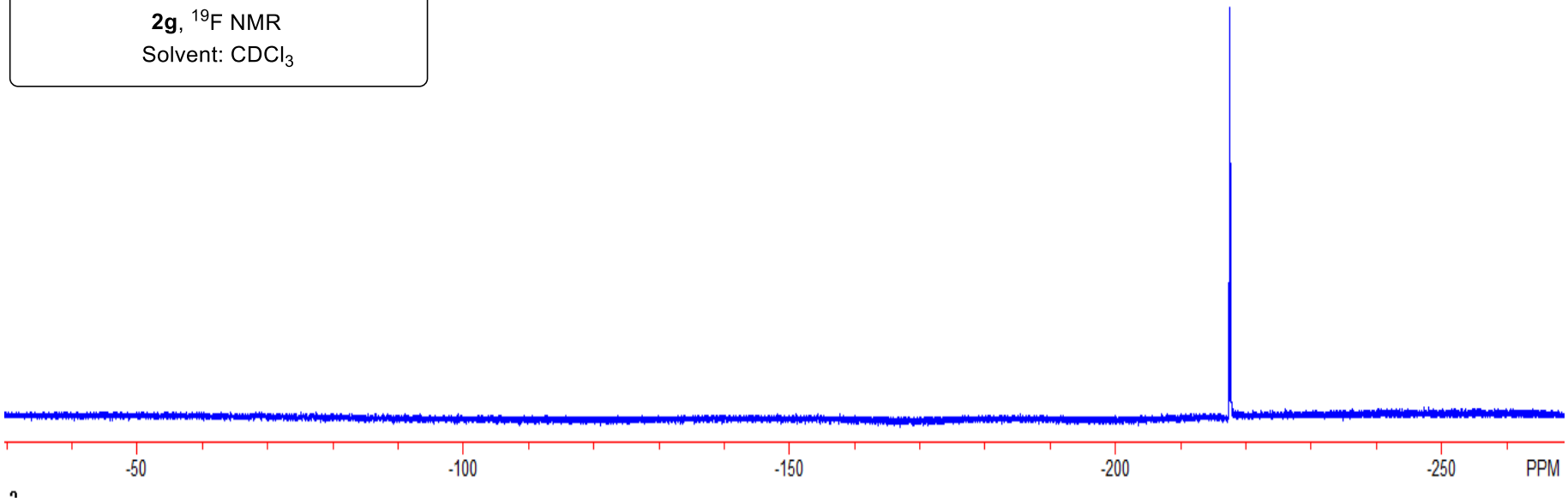
1.378

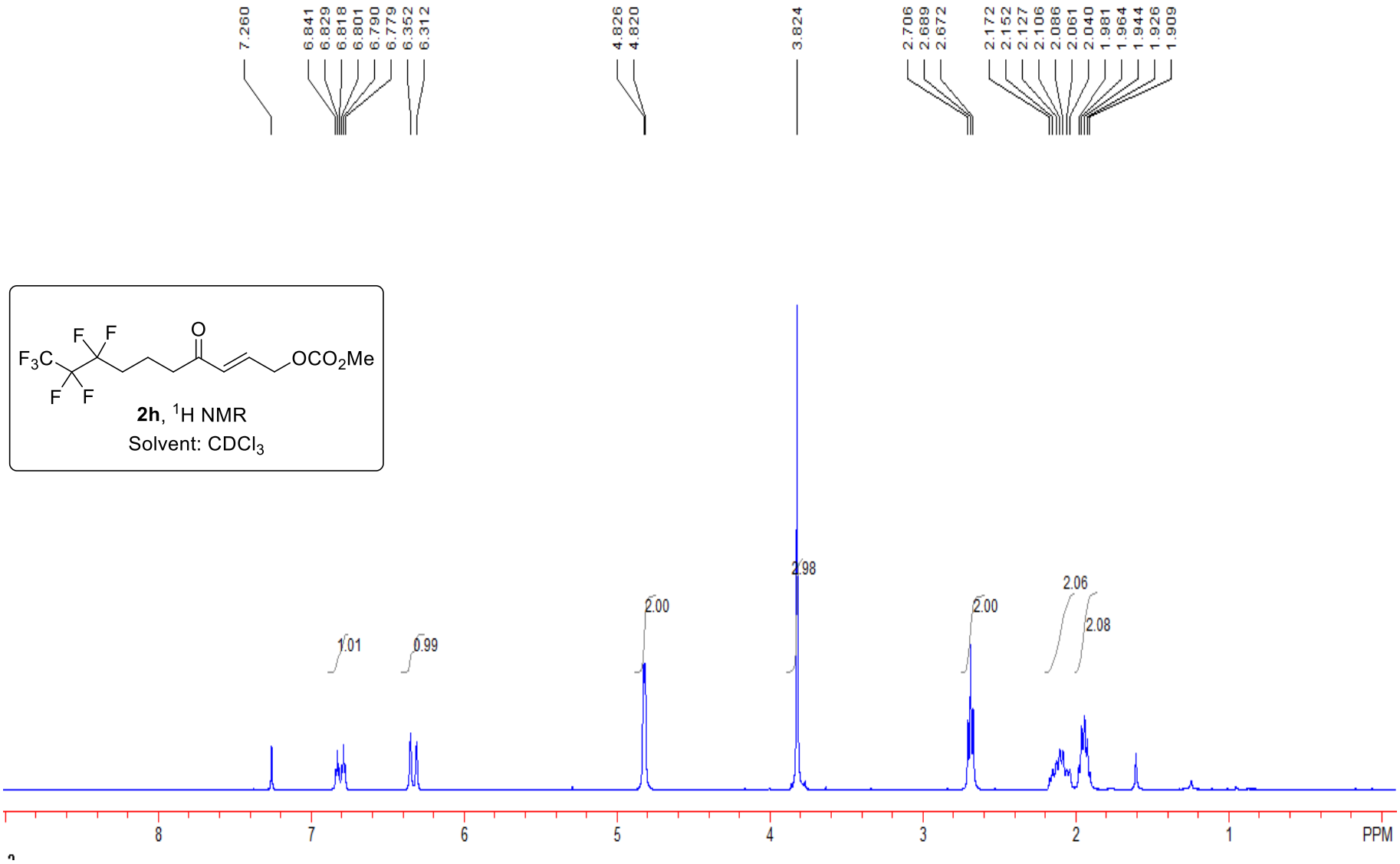

O
F
OCO2Me
2g, 1H NMR
Solvent: CDCl3
0.97
0.91
2.00
0.93
0.94
3.00
1.98
4.46
2.02
8
7
6
5
4
3
2
1
0
PPM


199.359
155.347
138.091
130.002
84.702
83.073
77.420
77.100
76.780
66.086
55.196
40.646
30.338
30.142
24.911
24.860
23.420
F
O
OCO2Me
2g, 13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM



2g, ^{19}F NMR
Solvent: $CDCl_3$

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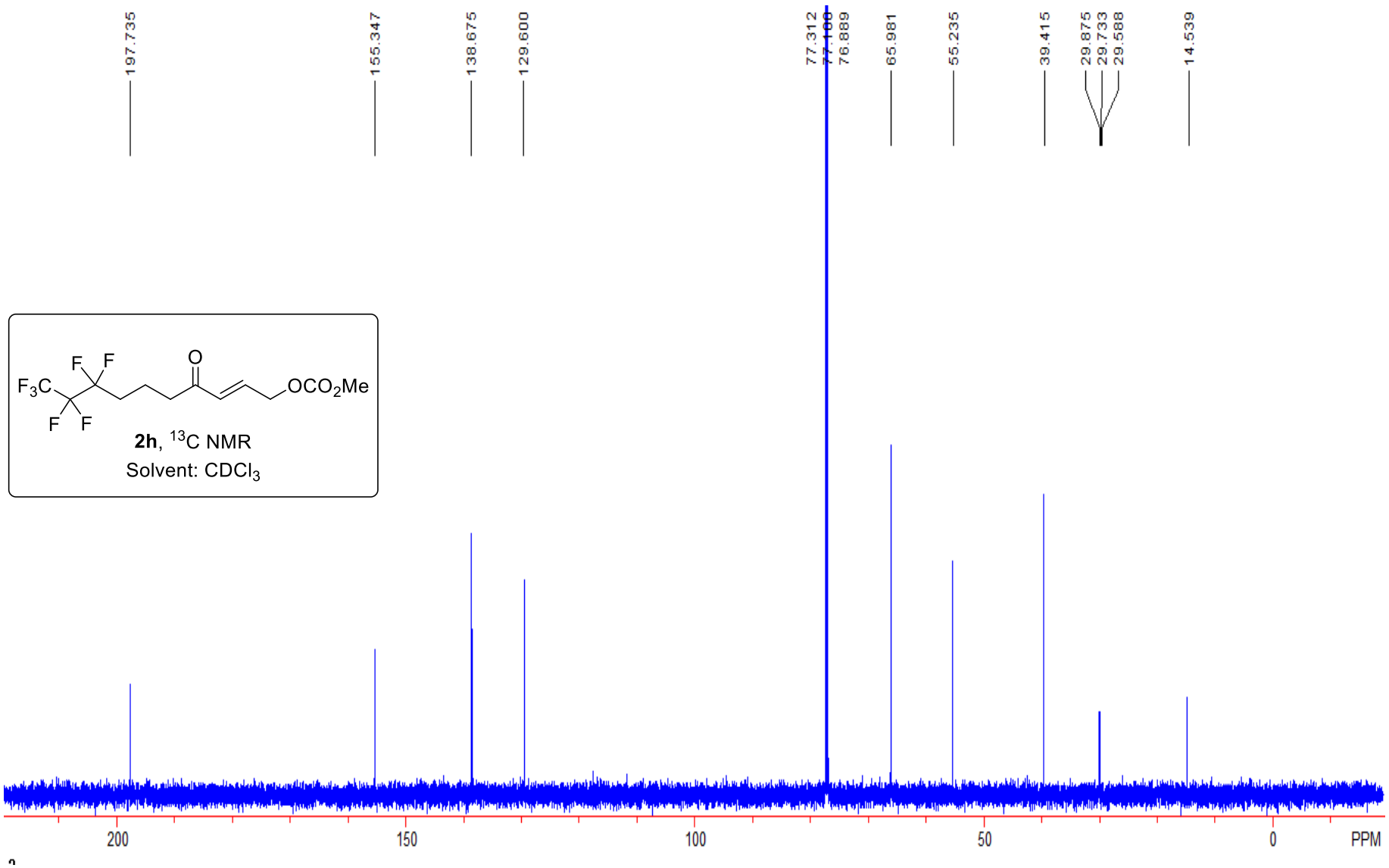
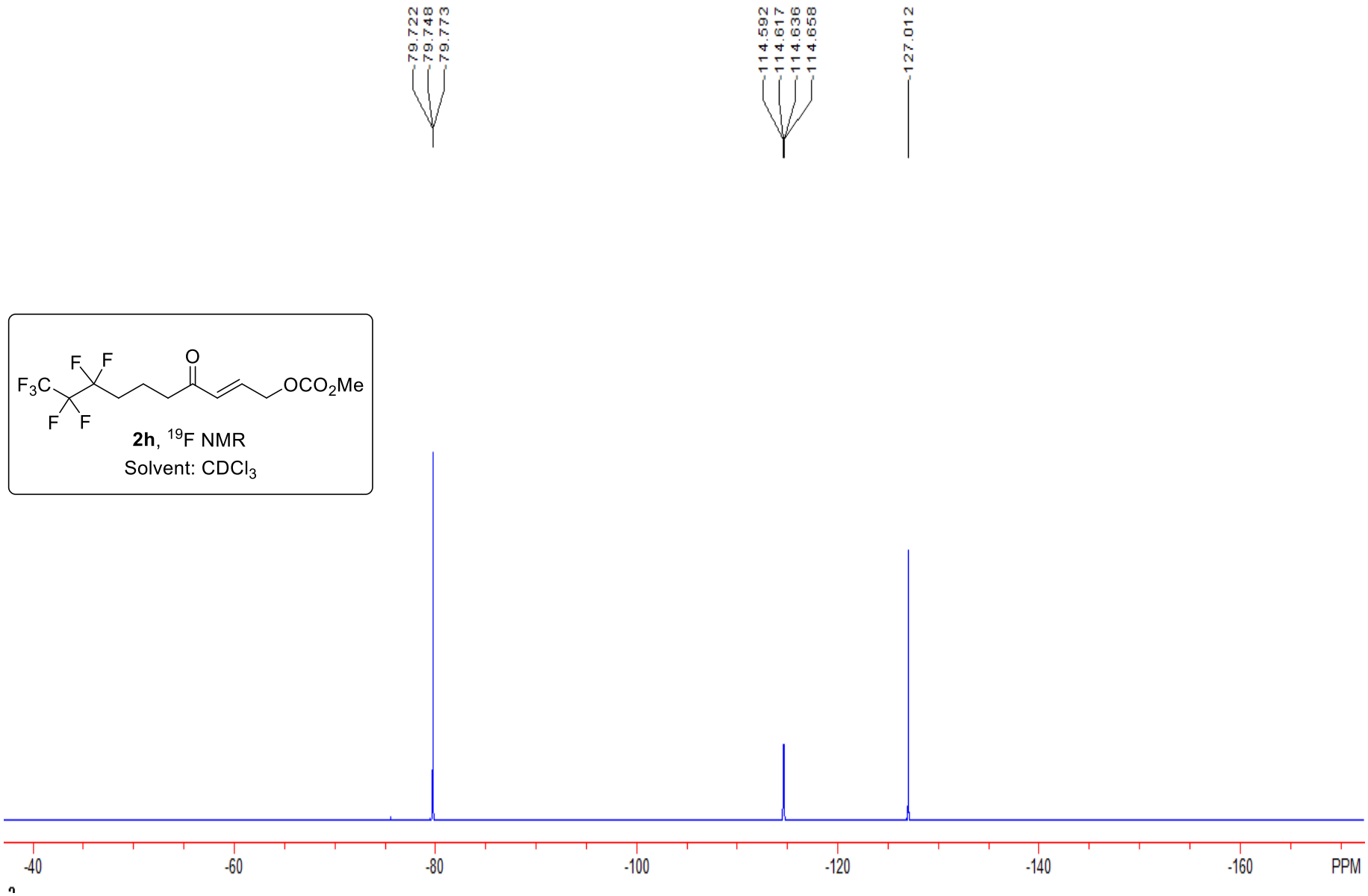
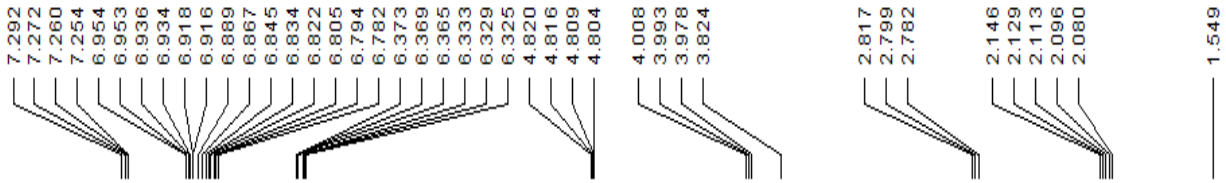
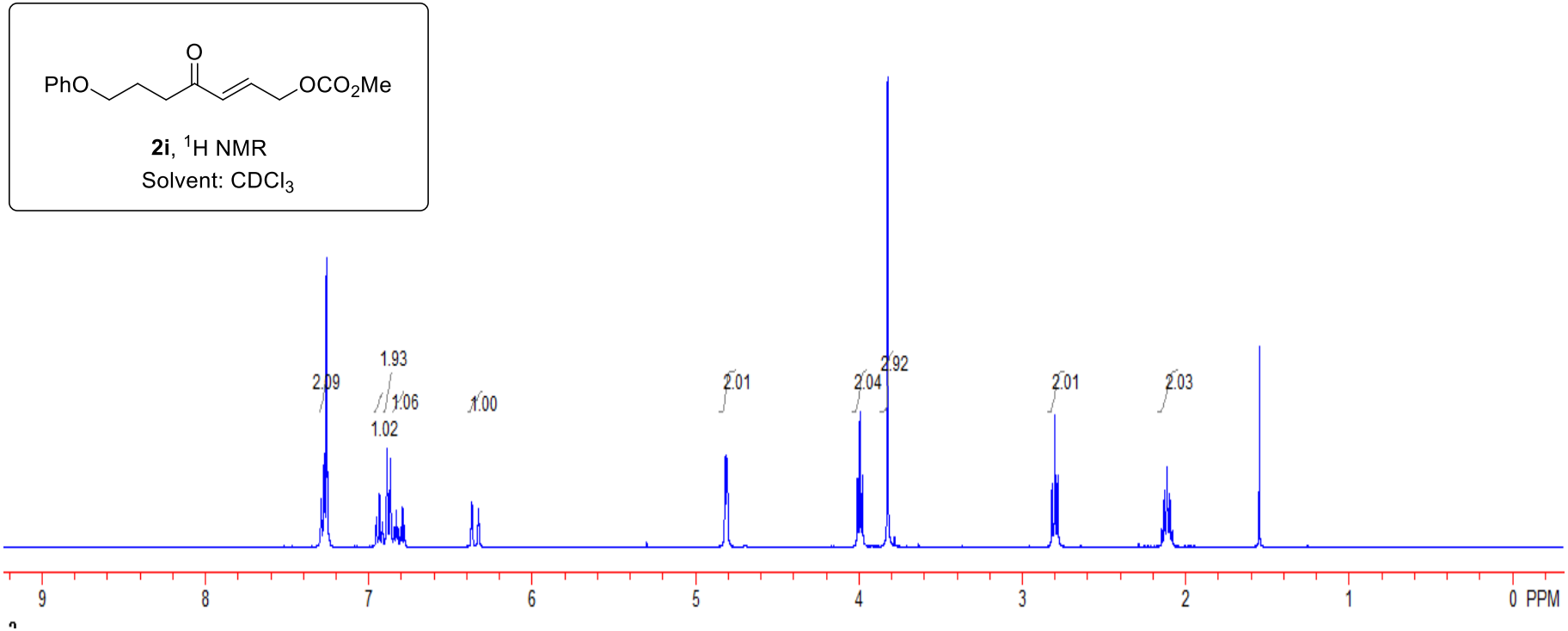
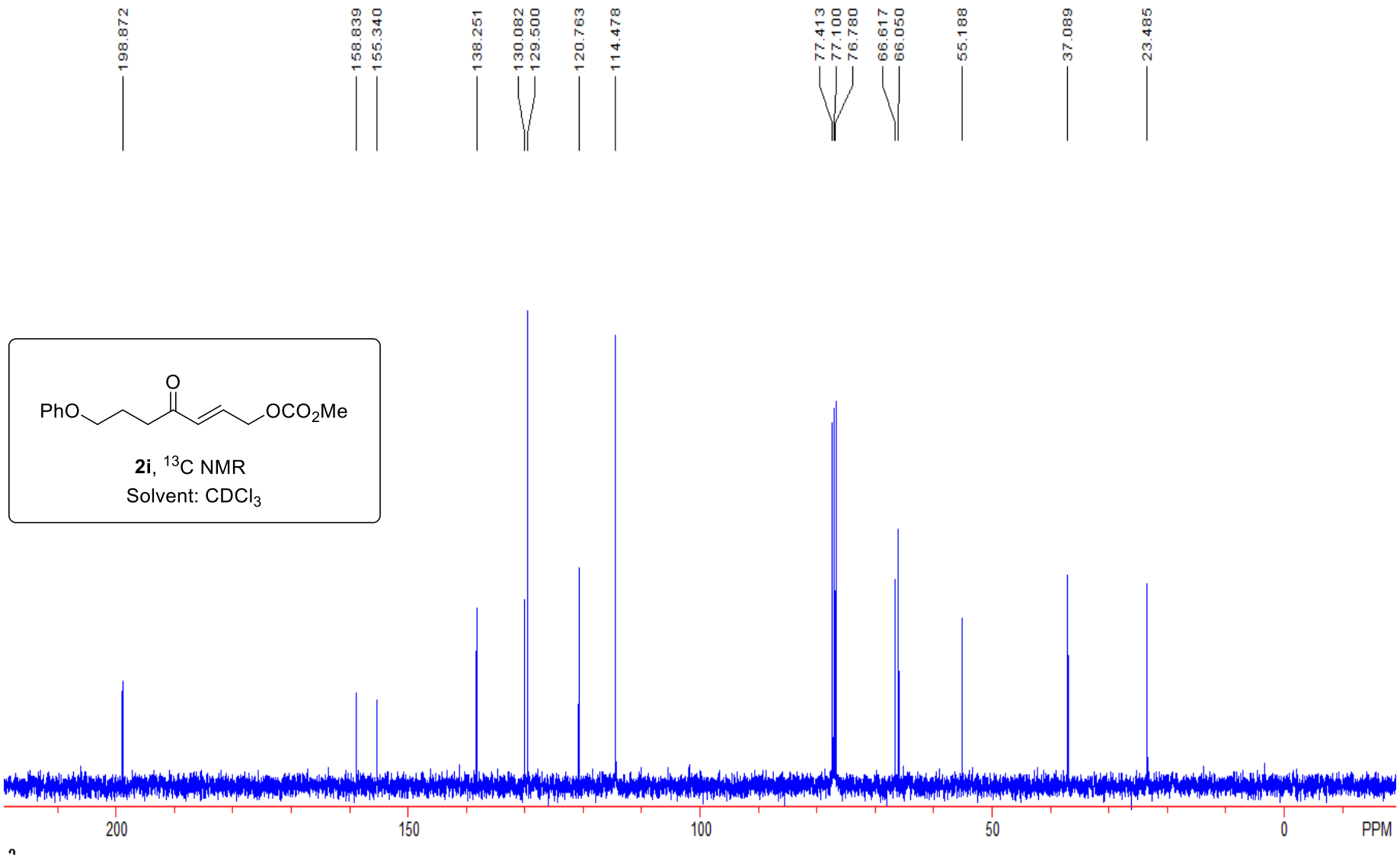
6.841
6.829
6.818
6.801
6.790
6.779
6.352
6.312
4.826
4.820
3.824
2.706
2.689
2.672
2.172
2.152
2.127
2.106
2.086
2.061
2.040
1.981
1.964
1.944
1.926
1.909
F
F
O
F3C
OCO2Me
F
F
2h, 1H NMR
Solvent: CDCl3
1.01
0.99
2.00
2.98
2.00
2.06
2.08
8
7
6
5
4
3
2
1
PPM

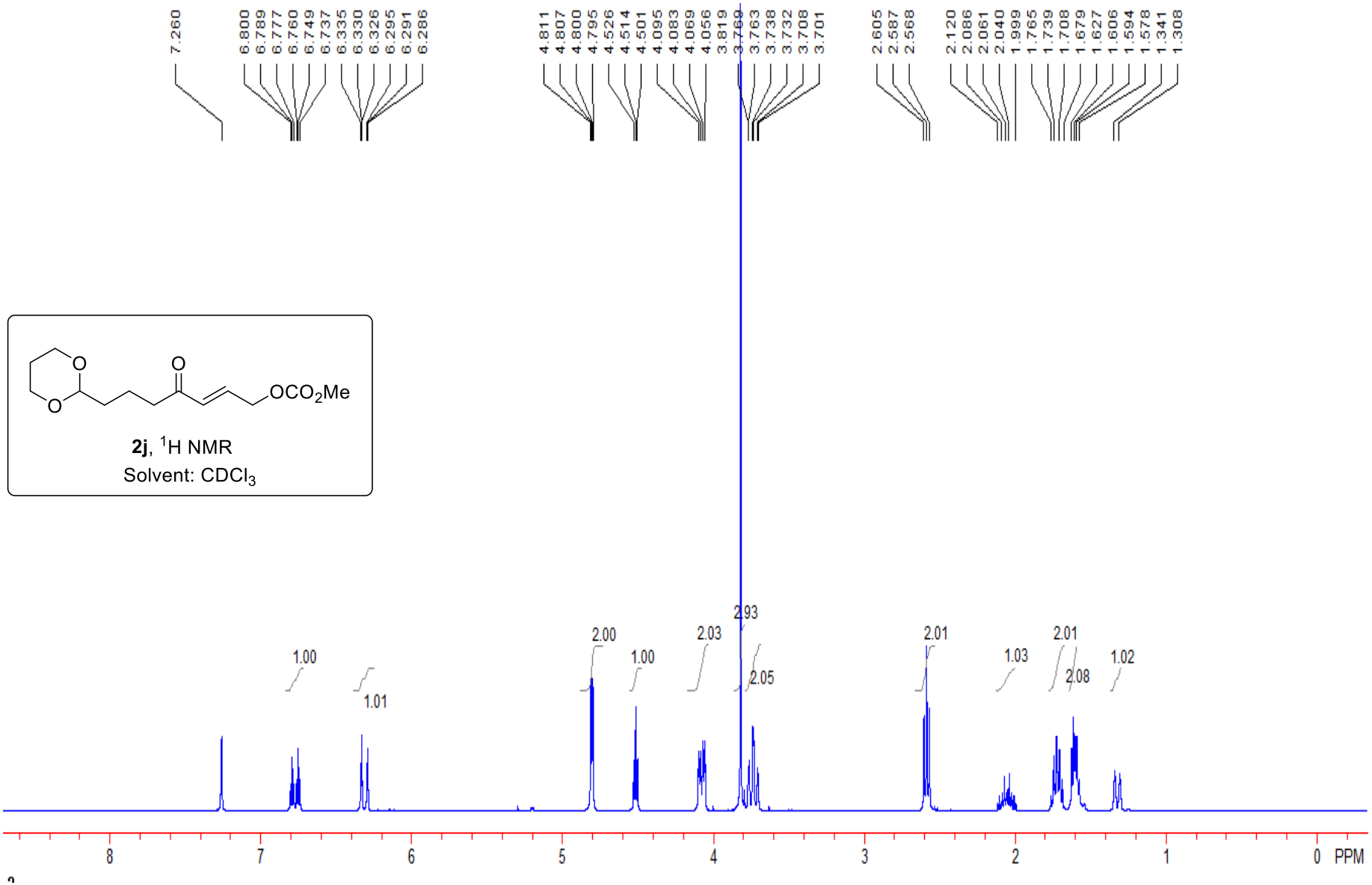

197.735
155.347
138.675
129.600
77.312
77.100
76.889
65.981
55.235
39.415
29.875
29.733
29.588
14.539
F
F
O
F3C
OCO2Me
F
F
2h, 13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM

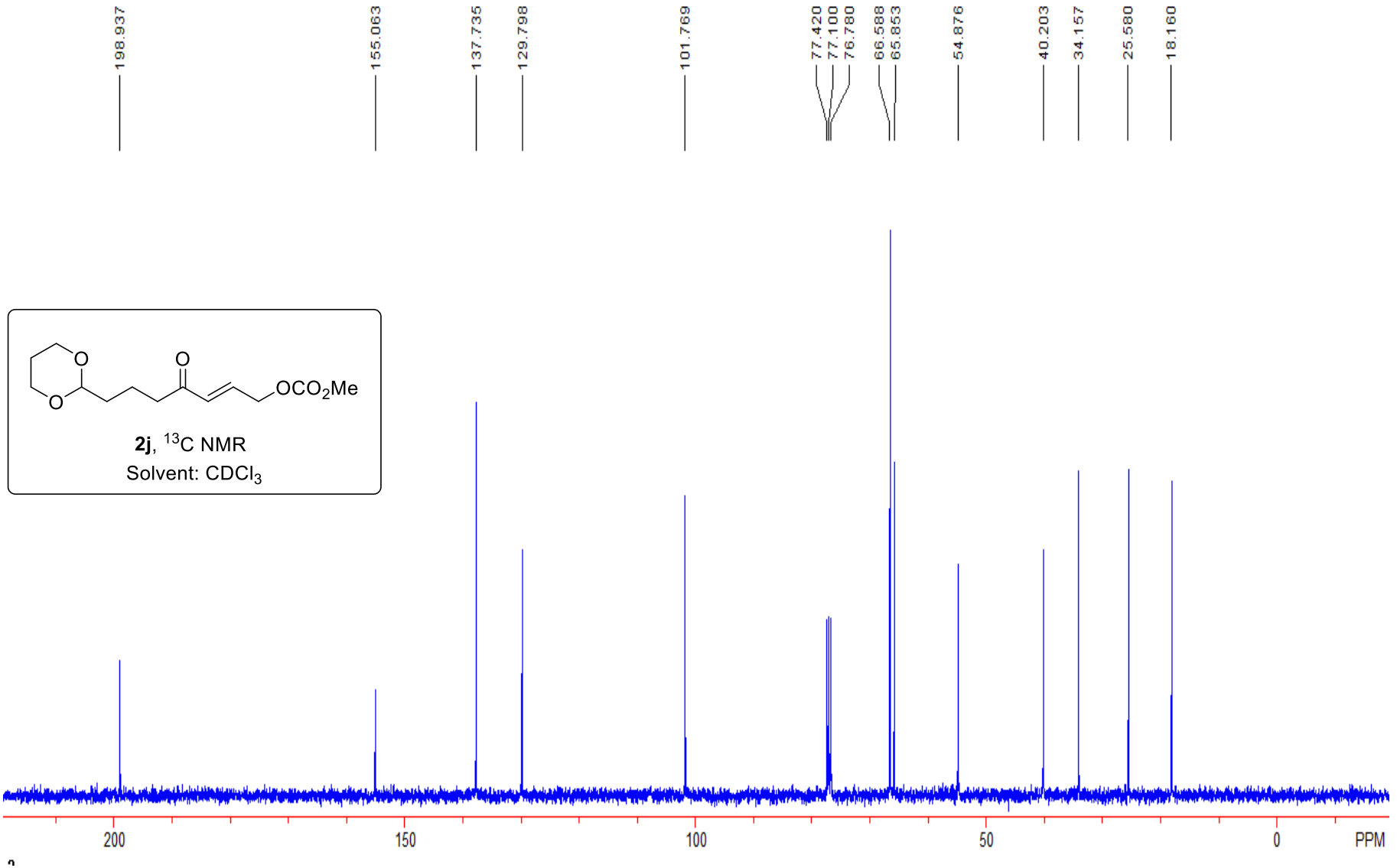

79.722
79.748
79.773
114.592
114.617
114.636
114.658
127.012
F
F
O
F3C
OCO2Me
F
F
2h, 19F NMR
Solvent: CDCl3
-40
-60
-80
-100
-120
-140
-160
PPM


7.292
7.272
7.260
7.254
6.954
6.953
6.936
6.934
6.918
6.916
6.889
6.867
6.845
6.834
6.822
6.805
6.794
6.782
6.373
6.369
6.365
6.333
6.329
6.325
4.820
4.816
4.809
4.804
4.008
3.993
3.978
3.824
2.817
2.799
2.782
2.146
2.129
2.113
2.096
2.080
1.549


PhO
O
OCO2Me
2i, 1H NMR
Solvent: CDCl3
2.09
1.93
1.06
1.02
1.00
2.01
2.04
2.92
2.01
2.03
9
8
7
6
5
4
3
2
1
0 PPM


198.872
158.839
155.340
138.251
130.082
129.500
120.763
114.478
77.413
77.100
76.780
66.617
66.050
55.188
37.089
23.485
PhO
O
OCO2Me
2i, 13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM


7.260
6.800
6.789
6.777
6.760
6.749
6.737
6.335
6.330
6.326
6.295
6.291
6.286
4.811
4.807
4.800
4.795
4.526
4.514
4.501
4.095
4.083
4.069
4.056
3.819
3.769
3.763
3.738
3.732
3.708
3.701
2.605
2.587
2.568
2.120
2.086
2.061
2.040
1.999
1.765
1.739
1.708
1.679
1.627
1.606
1.594
1.578
1.341
1.308
O
O
O
OCO2Me
2j, 1H NMR
Solvent: CDCl3
1.00
1.01
2.00
1.00
2.03
2.93
2.05
2.01
1.03
2.01
2.08
1.02
8
7
6
5
4
3
2
1
0 PPM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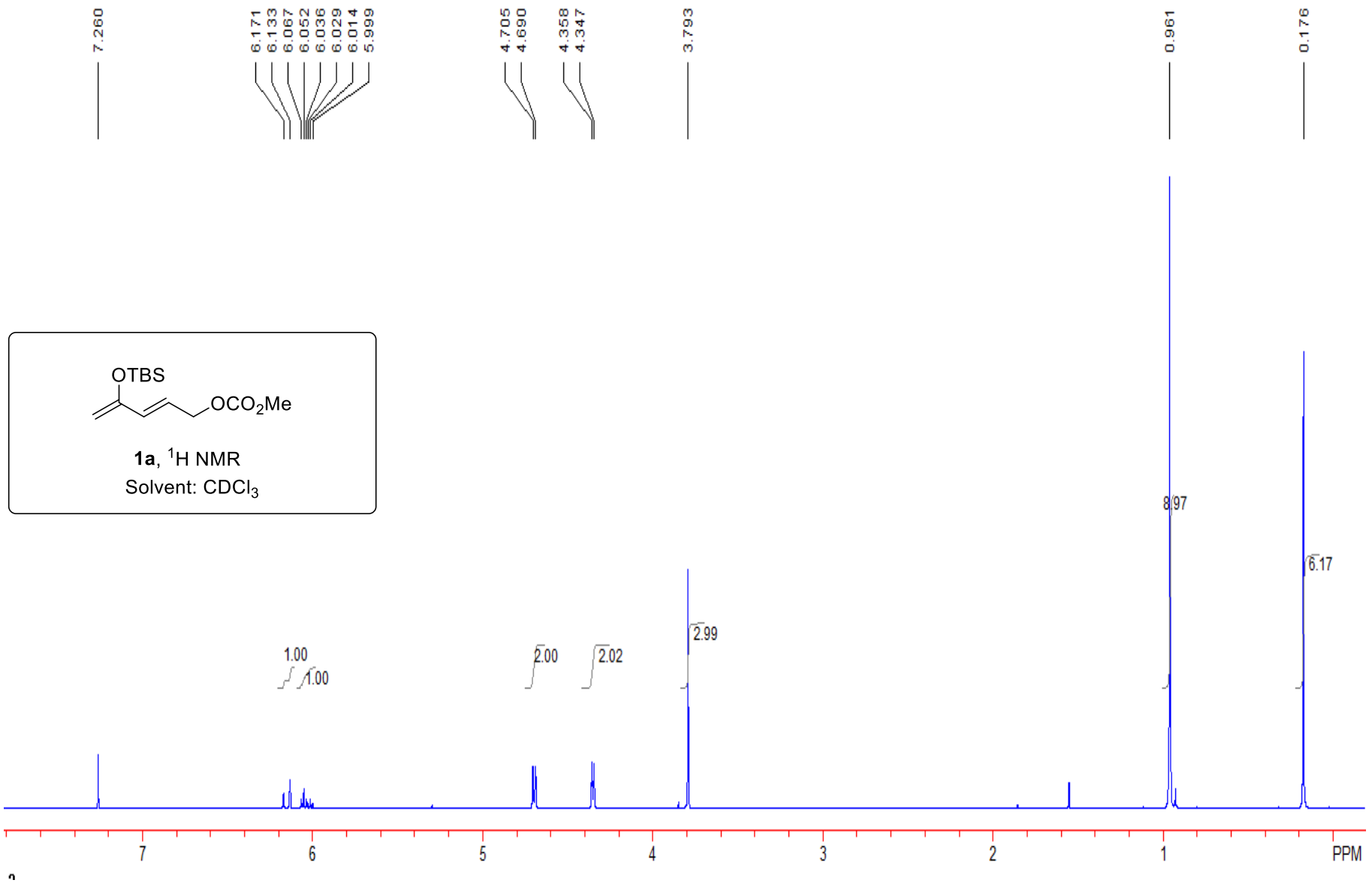
155.063
137.735
129.798
101.769
77.420
77.100
76.780
66.588
65.853
54.876
40.203
34.157
25.580
18.160
O
O
O
OCO2Me
2j, 13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM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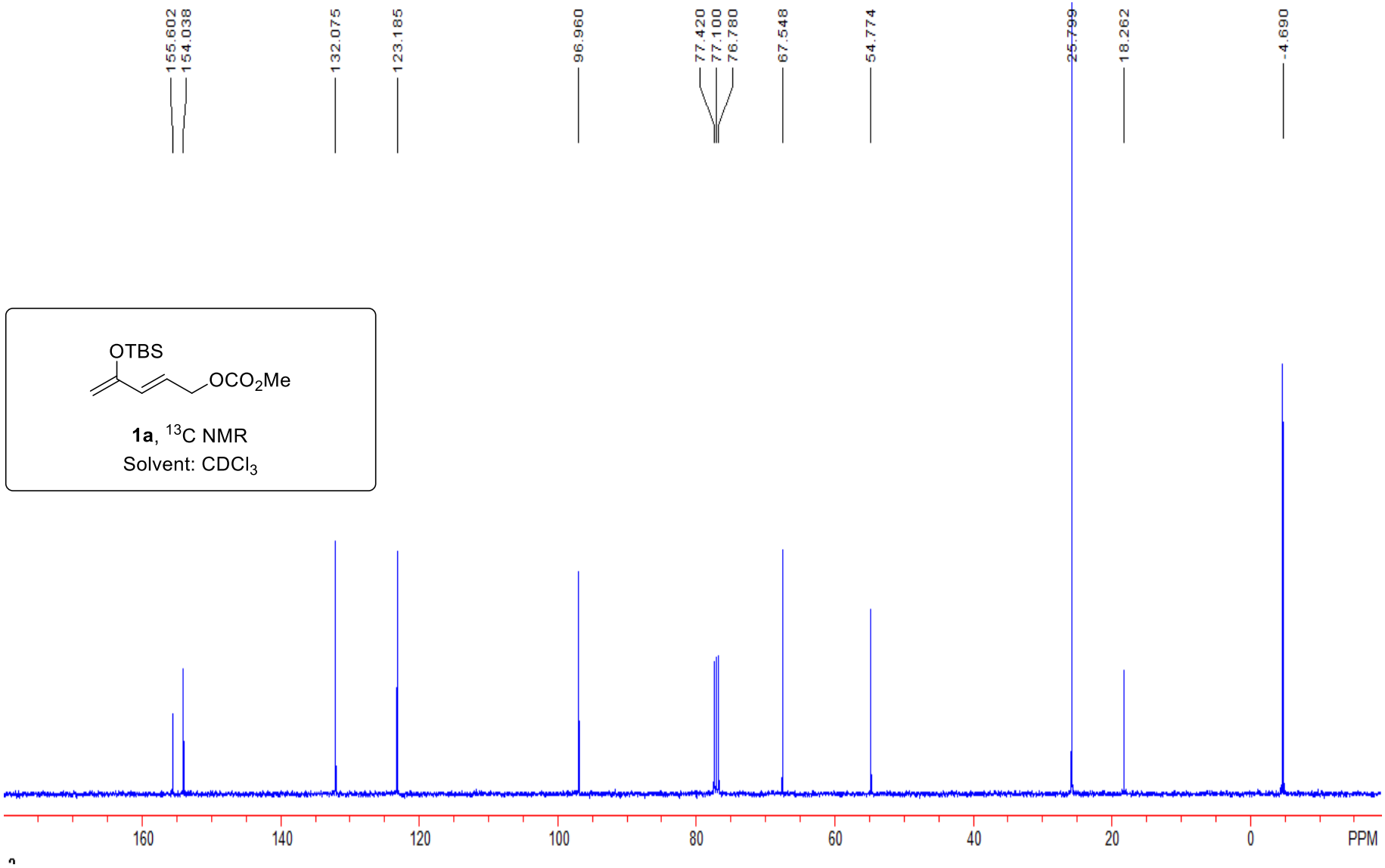
6.171
6.133
6.067
6.052
6.036
6.029
6.014
5.999
4.705
4.690
4.358
4.347
3.793
0.961
0.176
OTBS
OCO2Me
1a, 1H NMR
Solvent: CDCl3
1.00
1.00
2.00
2.02
2.99
8.97
6.17
7
6
5
4
3
2
1
PPM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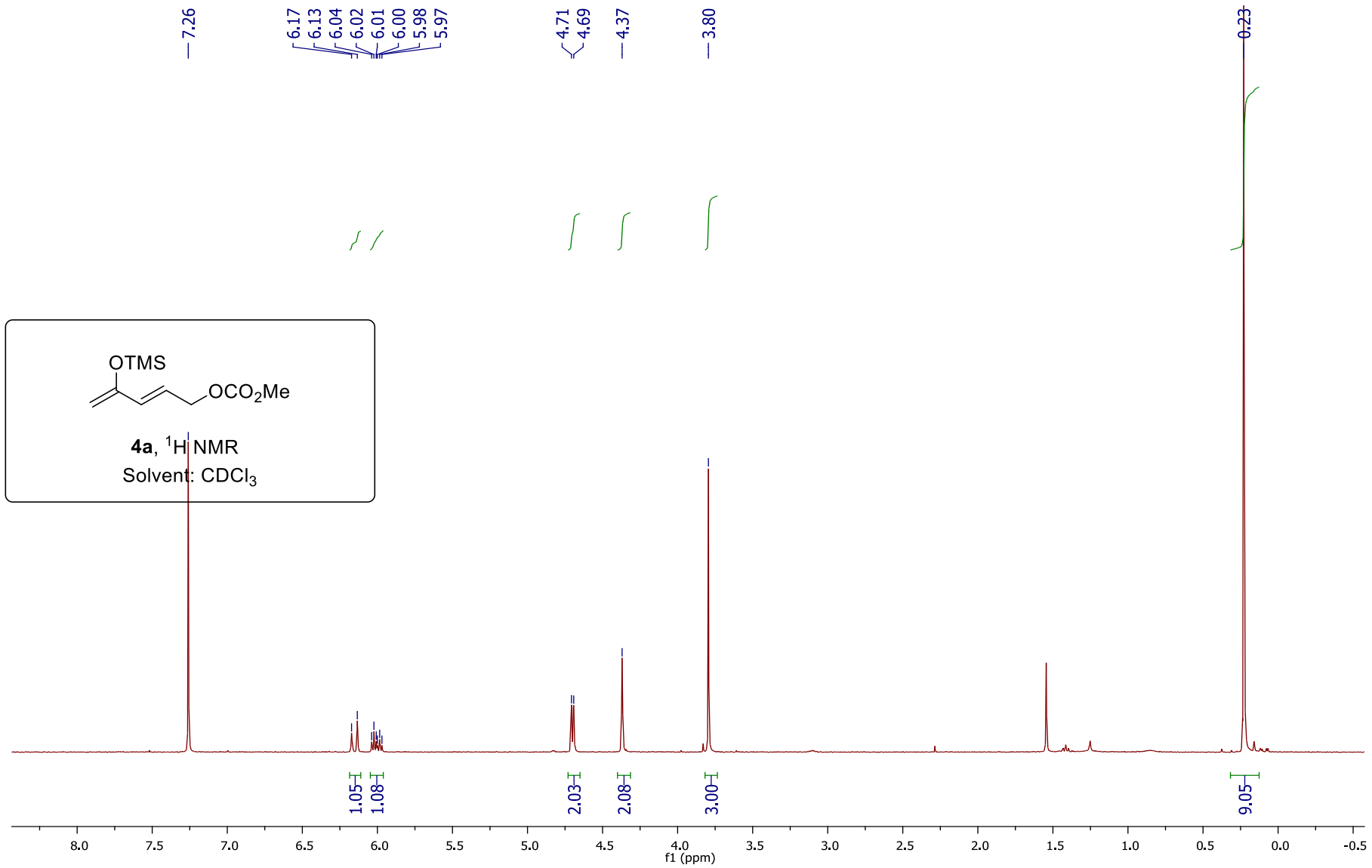
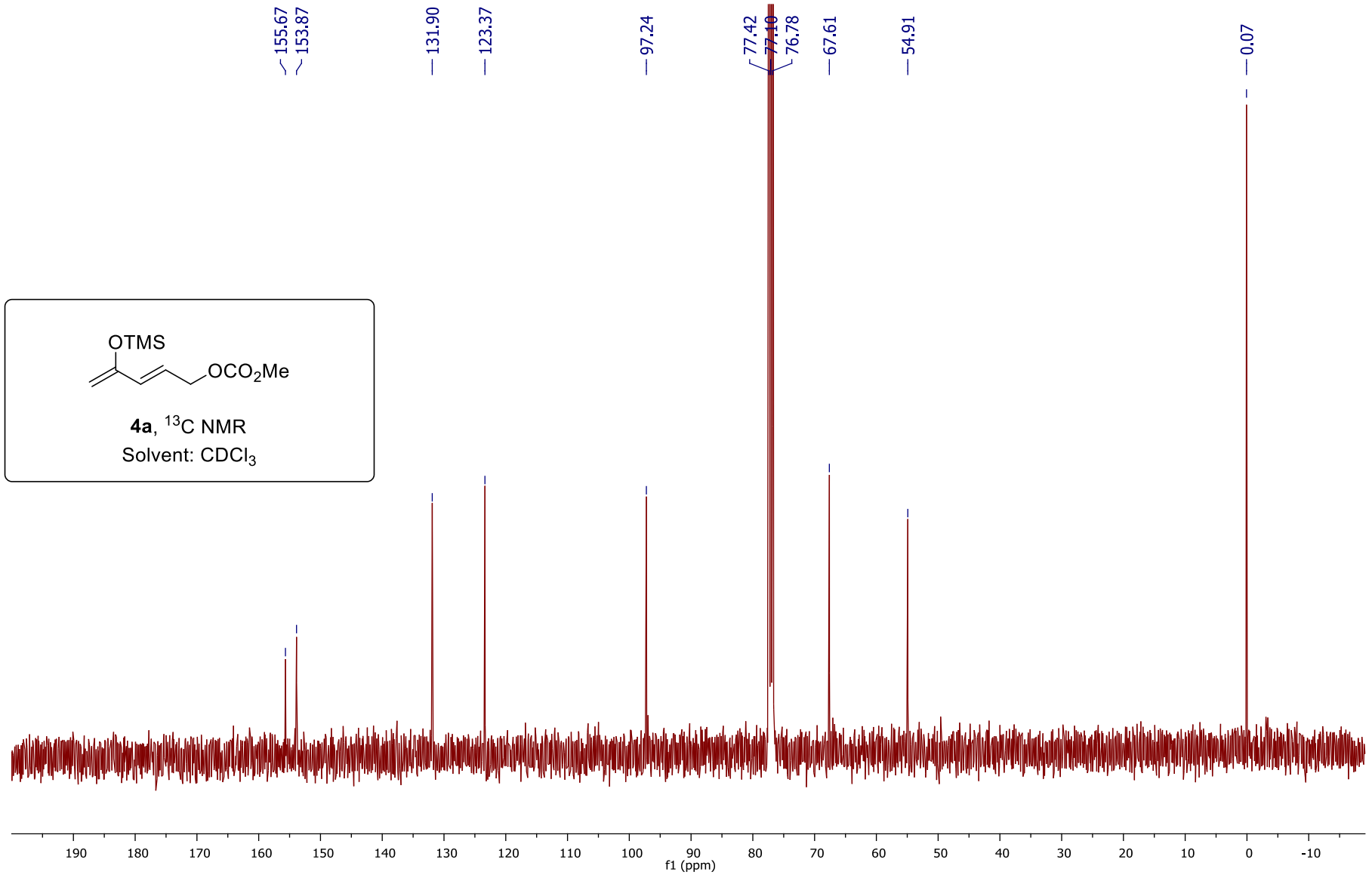
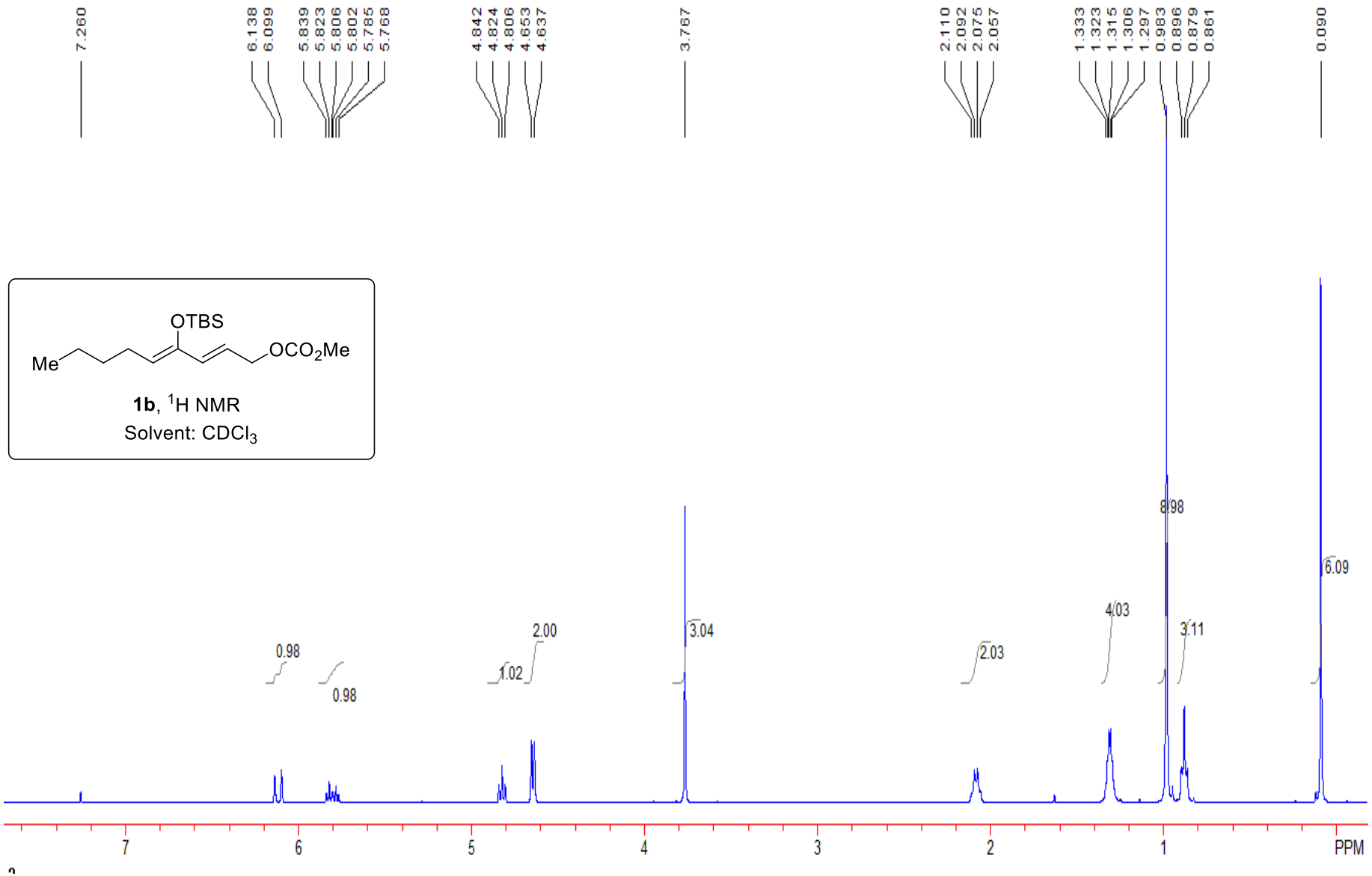
154.038
132.075
123.185
96.960
77.420
77.100
76.780
67.548
54.774
25.799
18.262
-4.690
OTBS
OCO2Me
1a, 13C NMR
Solvent: CDCl3
160
140
120
100
80
60
40
20
0
PPM


7.26
6.17
6.13
6.04
6.02
6.01
6.00
5.98
5.97
4.71
4.69
4.37
3.80
0.23
OTMS
OCO2Me
4a, 1H NMR
Solvent: CDCl3
1.05
1.08
2.03
2.08
3.00
9.05
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)


155.67
153.87
131.90
123.37
97.24
77.42
77.10
76.78
67.61
54.91
0.07
OTMS
OCO2Me
4a, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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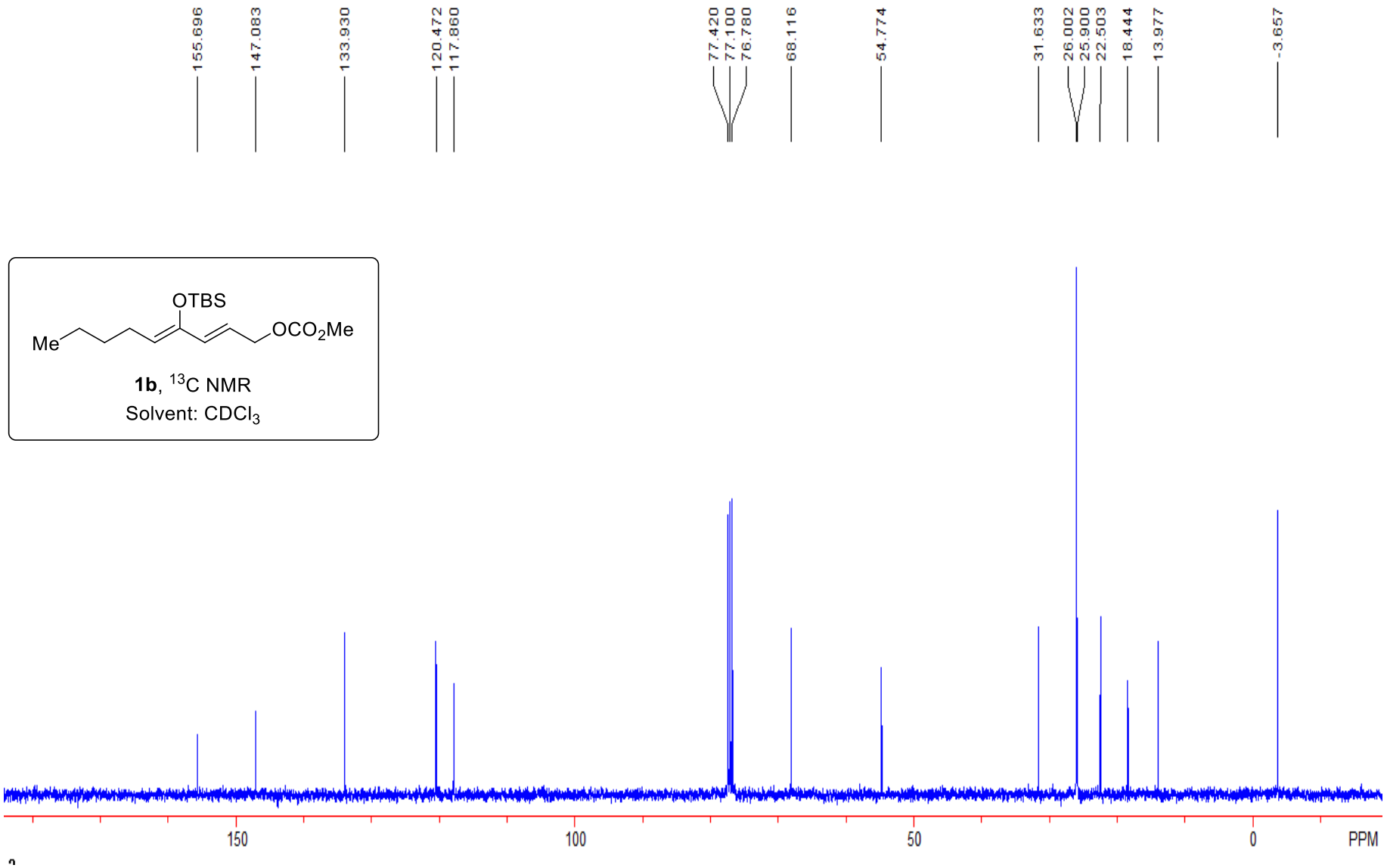
6.138
6.099
5.839
5.823
5.806
5.802
5.785
5.768
4.842
4.824
4.806
4.653
4.637
3.767
2.110
2.092
2.075
2.057
1.333
1.323
1.315
1.306
1.297
0.983
0.896
0.879
0.861
0.090
OTBS
Me
OCO2Me
1b, 1H NMR
Solvent: CDCl3
0.98
0.98
1.02
2.00
3.04
2.03
4.03
8.98
3.11
6.09
7
6
5
4
3
2
1
PPM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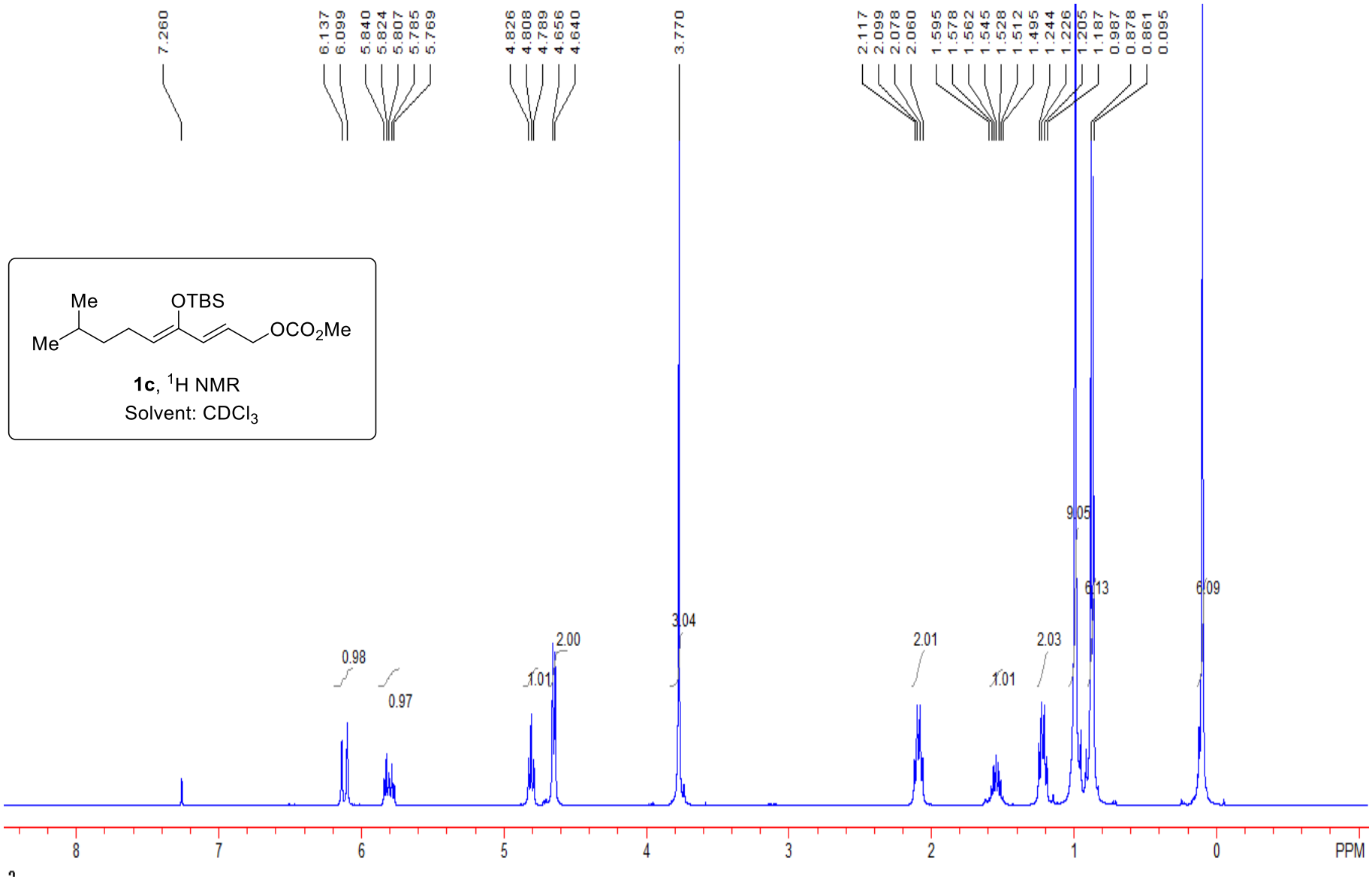
133.930
120.472
117.860
77.420
77.100
76.780
68.116
54.774
31.633
26.002
25.900
22.503
18.444
13.977
-3.657
OTBS
Me
OCO2Me
1b, 13C NMR
Solvent: CDCl3
150
100
50
0
PPM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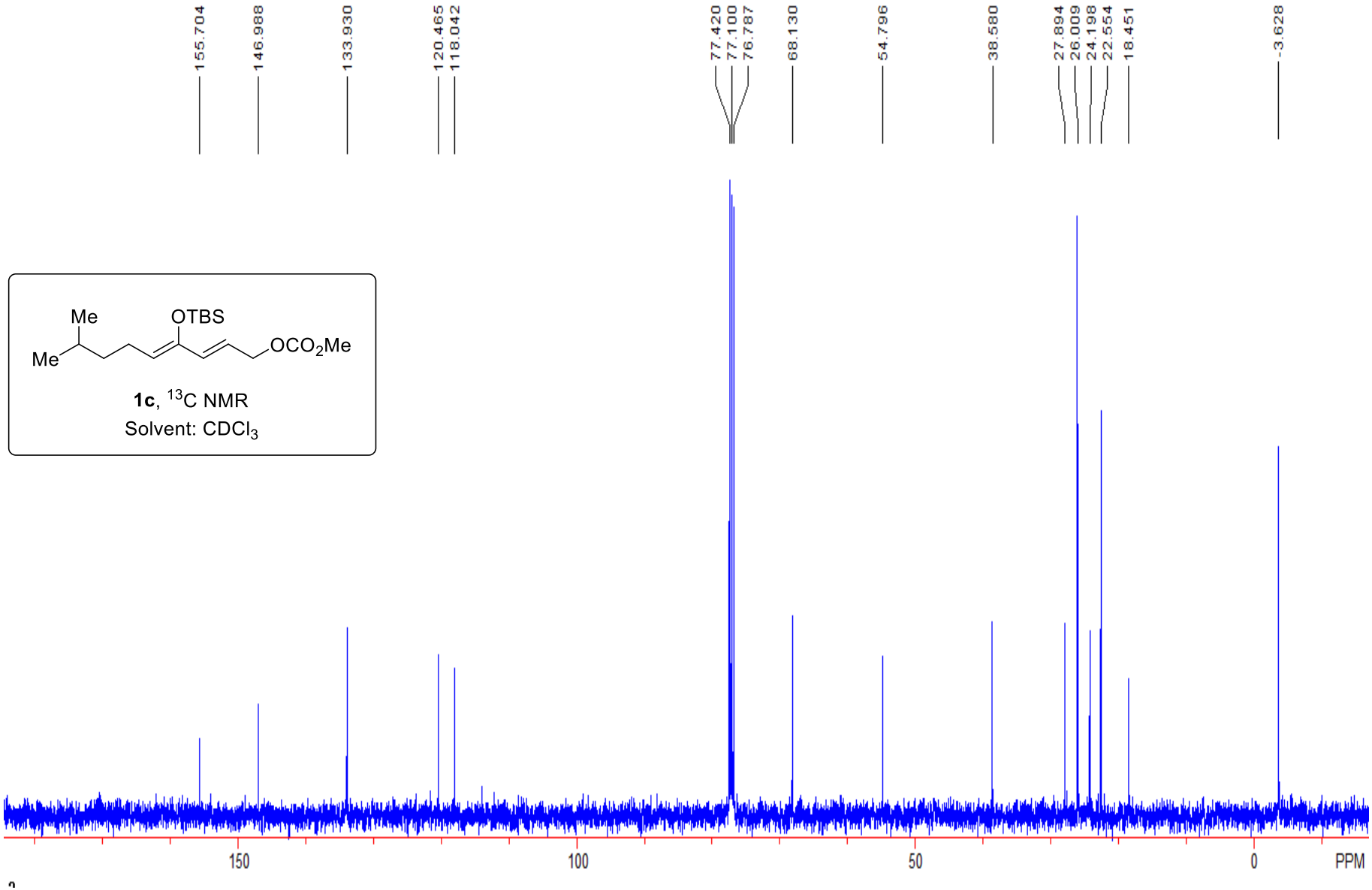
6.137
6.099
5.840
5.824
5.807
5.785
5.769
4.826
4.808
4.789
4.656
4.640
3.770
2.117
2.099
2.078
2.060
1.595
1.578
1.562
1.545
1.528
1.512
1.495
1.244
1.226
1.205
1.187
0.987
0.878
0.861
0.095
Me
OTBS
Me
OCO2Me
1c, 1H NMR
Solvent: CDCl3
0.98
0.97
1.01
2.00
3.04
2.01
1.01
2.03
9.05
6.13
6.09
8
7
6
5
4
3
2
1
0
PPM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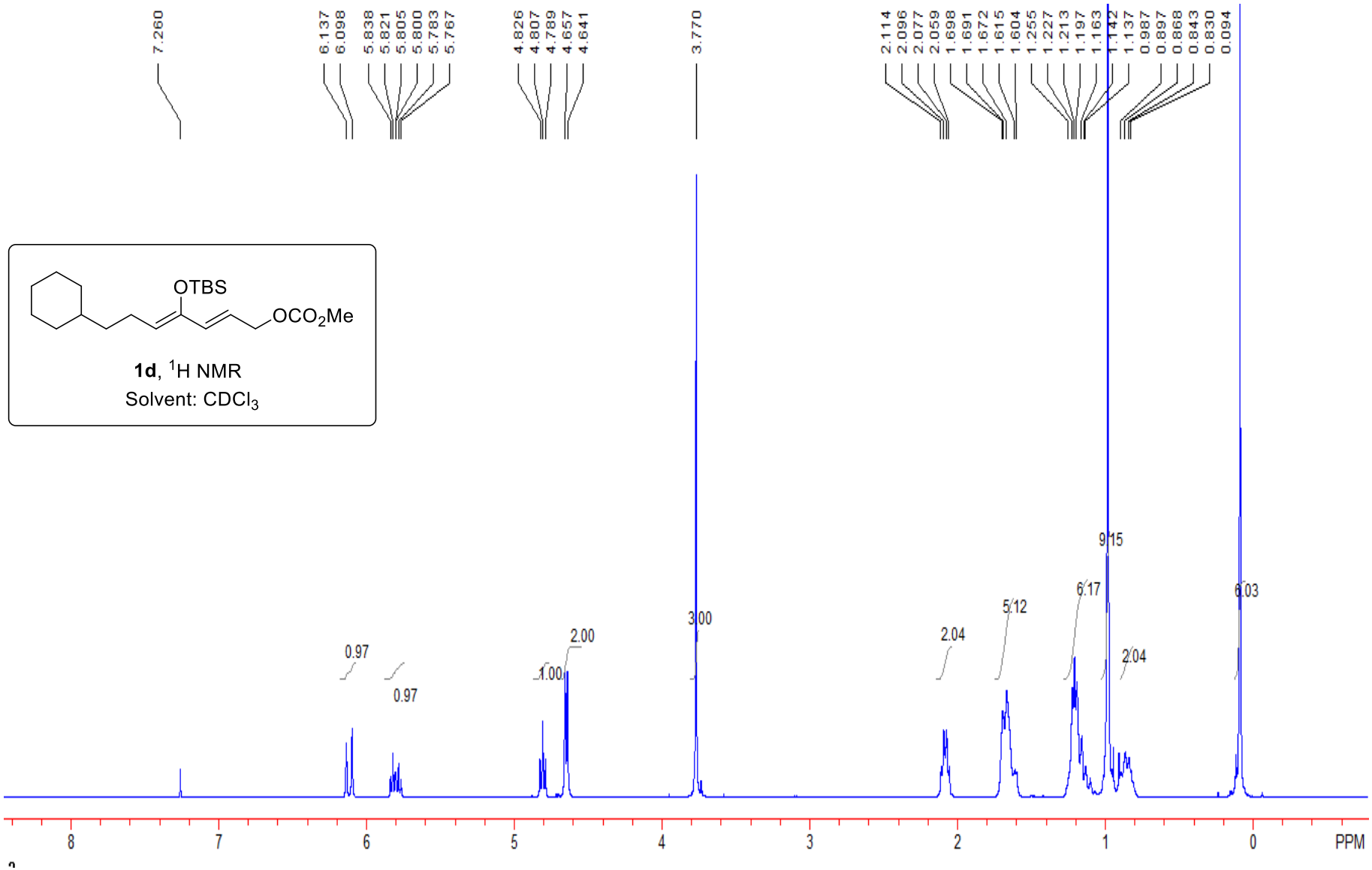
120.465
118.042
77.420
77.100
76.787
68.130
54.796
38.580
27.894
26.009
24.198
22.554
18.451
-3.628
Me
OTBS
Me
OCO2Me
1c, 13C NMR
Solvent: CDCl3
150
100
50
0
PPM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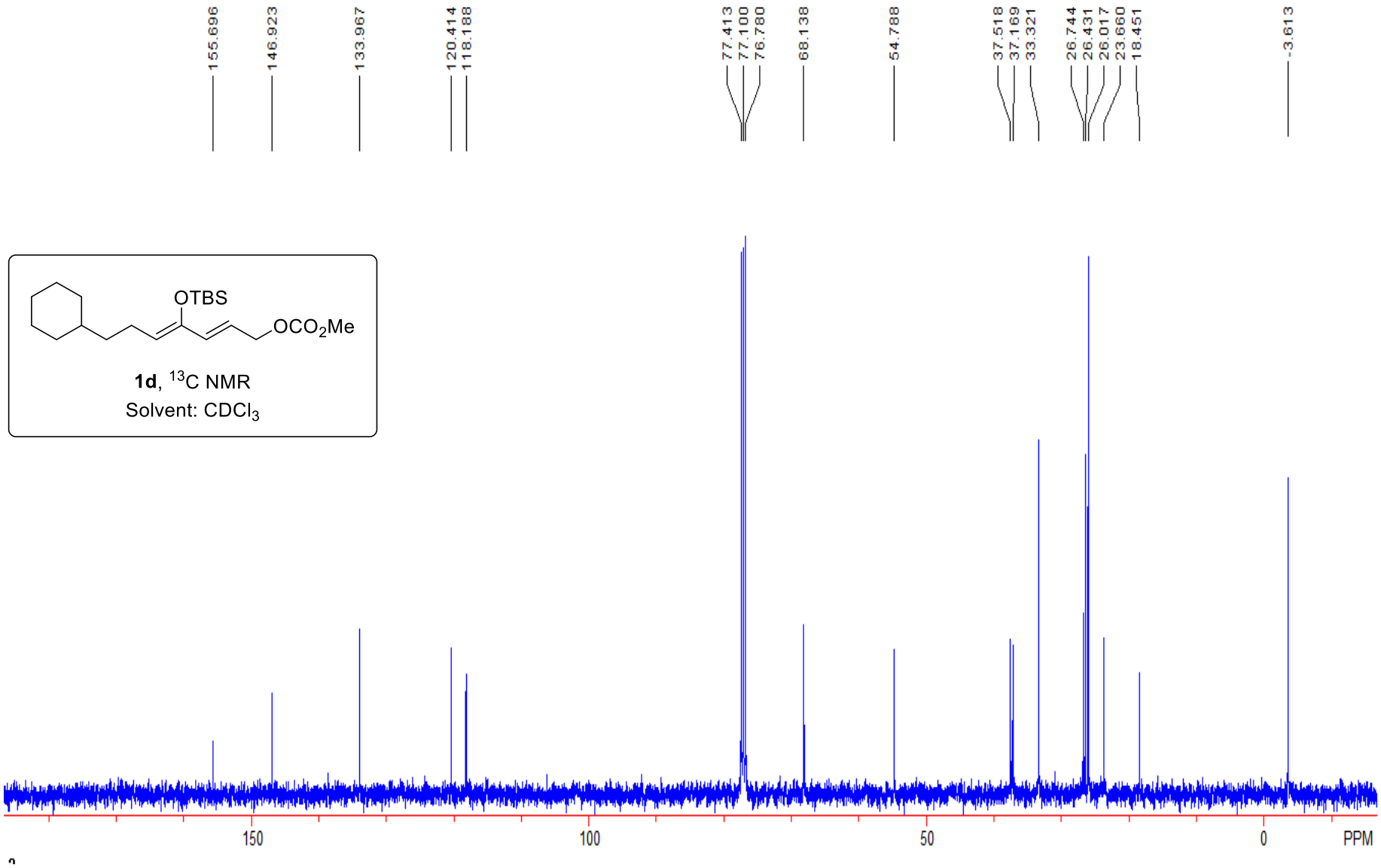
6.137
6.098
5.838
5.821
5.805
5.800
5.783
5.767
4.826
4.807
4.789
4.657
4.641
3.770
2.114
2.096
2.077
2.059
1.698
1.691
1.672
1.615
1.604
1.255
1.227
1.213
1.197
1.163
1.142
1.137
0.987
0.897
0.868
0.843
0.830
0.094
OTBS
OCO2Me
1d, 1H NMR
Solvent: CDCl3
0.97
0.97
1.00
2.00
3.00
2.04
5.12
6.17
9.15
2.04
6.03
8
7
6
5
4
3
2
1
0
PPM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146.923
133.967
120.414
118.188
77.413
77.100
76.780
68.138
54.788
37.518
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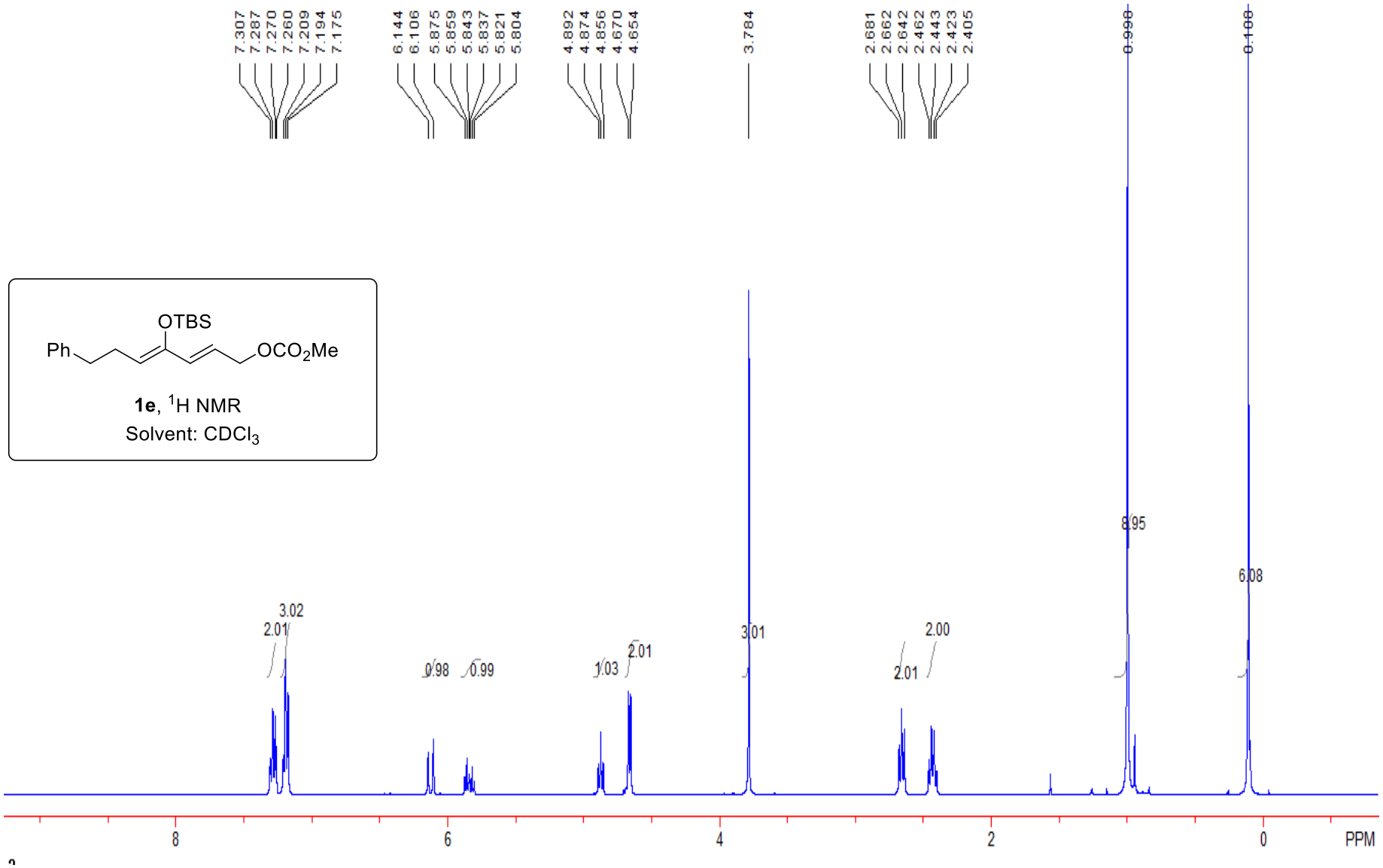
33.321
26.744
26.431
26.017
23.660
18.451
-3.613
OTBS
OCO2Me
1d, 13C NMR
Solvent: CDCl3
150
100
50
0
PPM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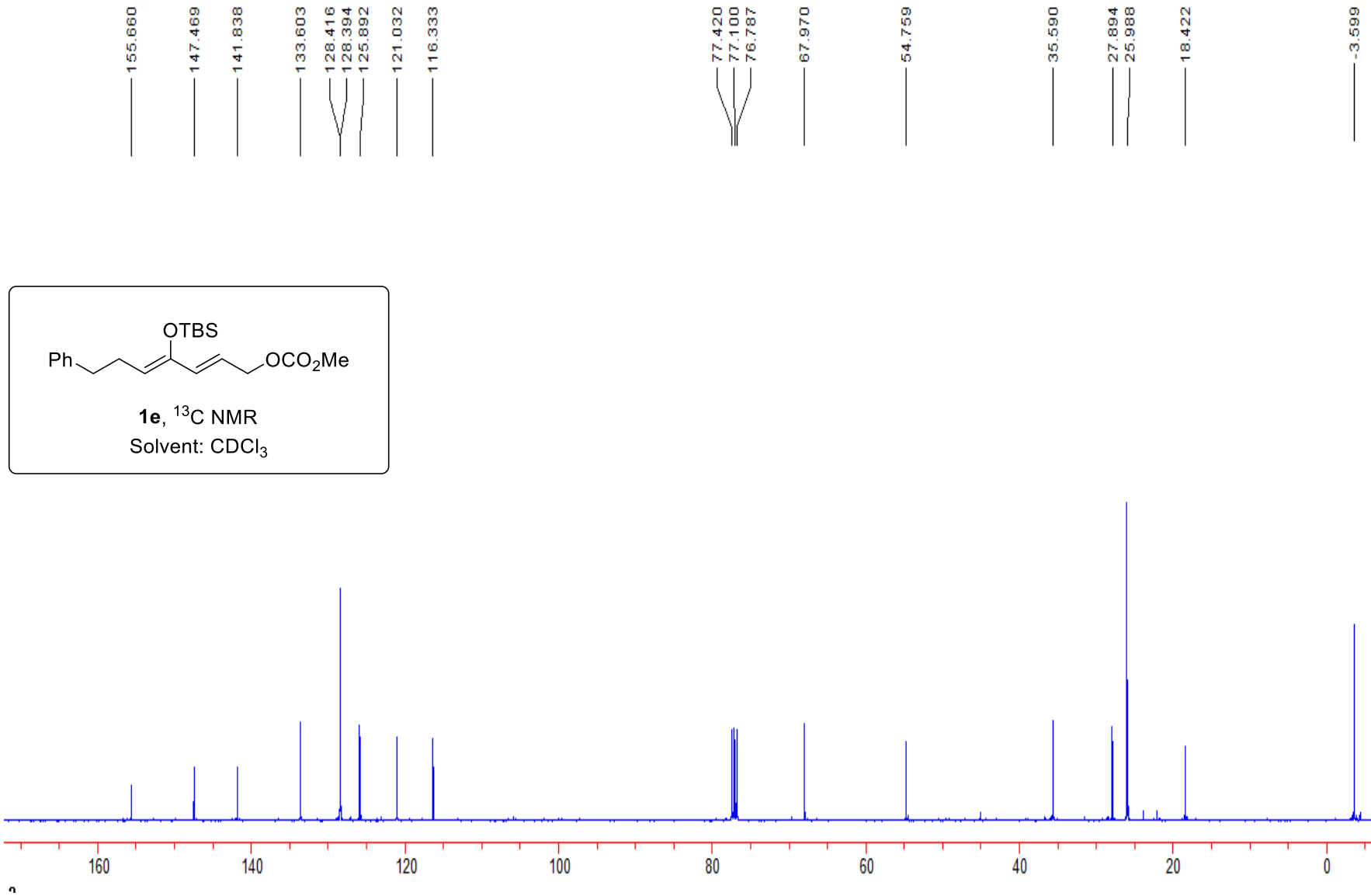
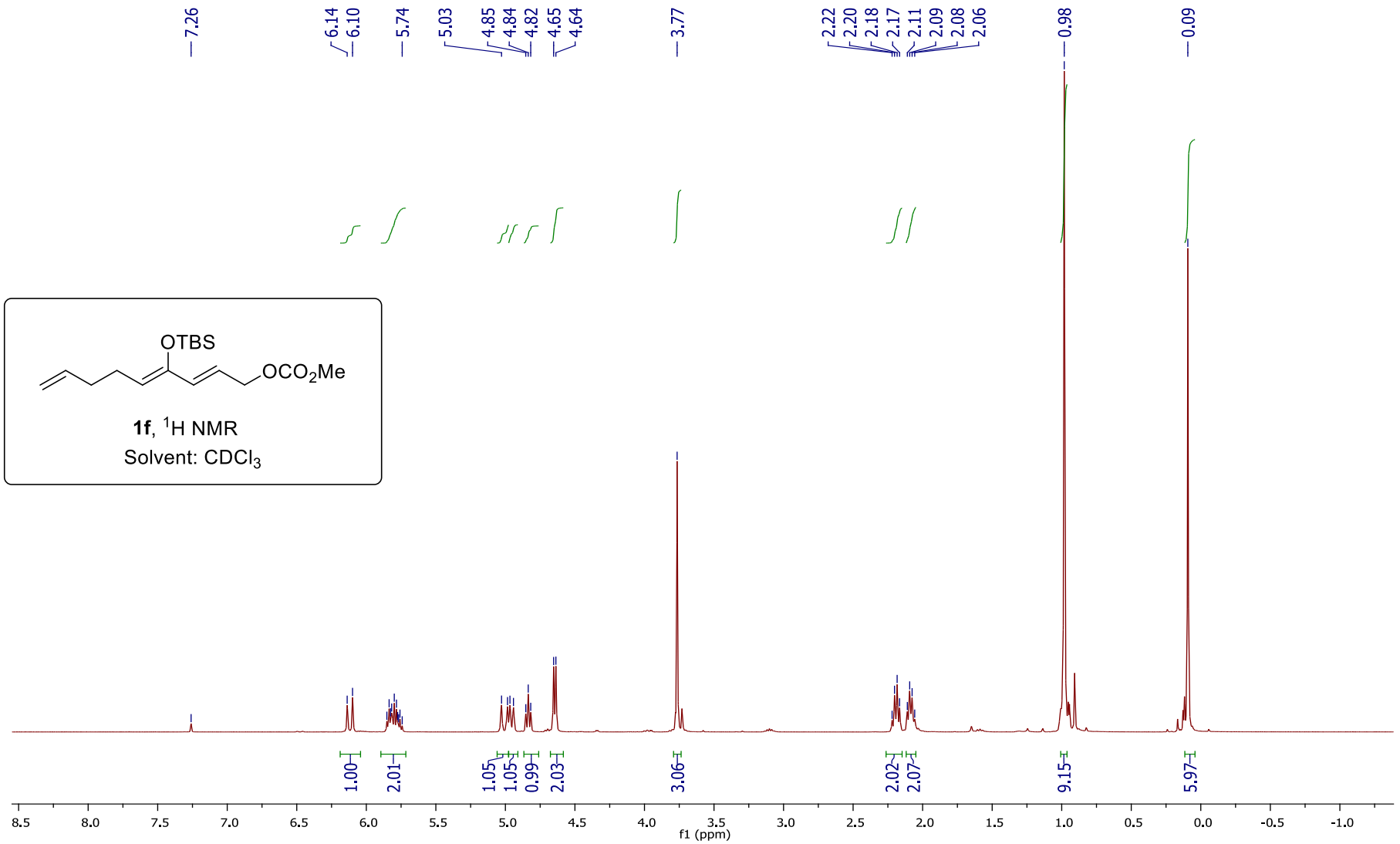
7.287
7.270
7.260
7.209
7.194
7.175
6.144
6.106
5.875
5.859
5.843
5.837
5.821
5.804
4.892
4.874
4.856
4.670
4.654
3.784
2.681
2.662
2.642
2.462
2.443
2.423
2.405
0.998
0.108
OTBS
Ph
OCO2Me
1e, 1H NMR
Solvent: CDCl3
3.02
2.01
0.98
0.99
1.03
2.01
3.01
2.01
2.00
8.95
6.08
8
6
4
2
0
PPM


155.660
147.469
141.838
133.603
128.416
128.394
125.892
121.032
116.333
77.420
77.100
76.787
67.970
54.759
35.590
27.894
25.988
18.422
-3.599
OTBS
Ph
OCO2Me
1e, 13C NMR
Solvent: CDCl3
160
140
120
100
80
60
40
20
0
PPM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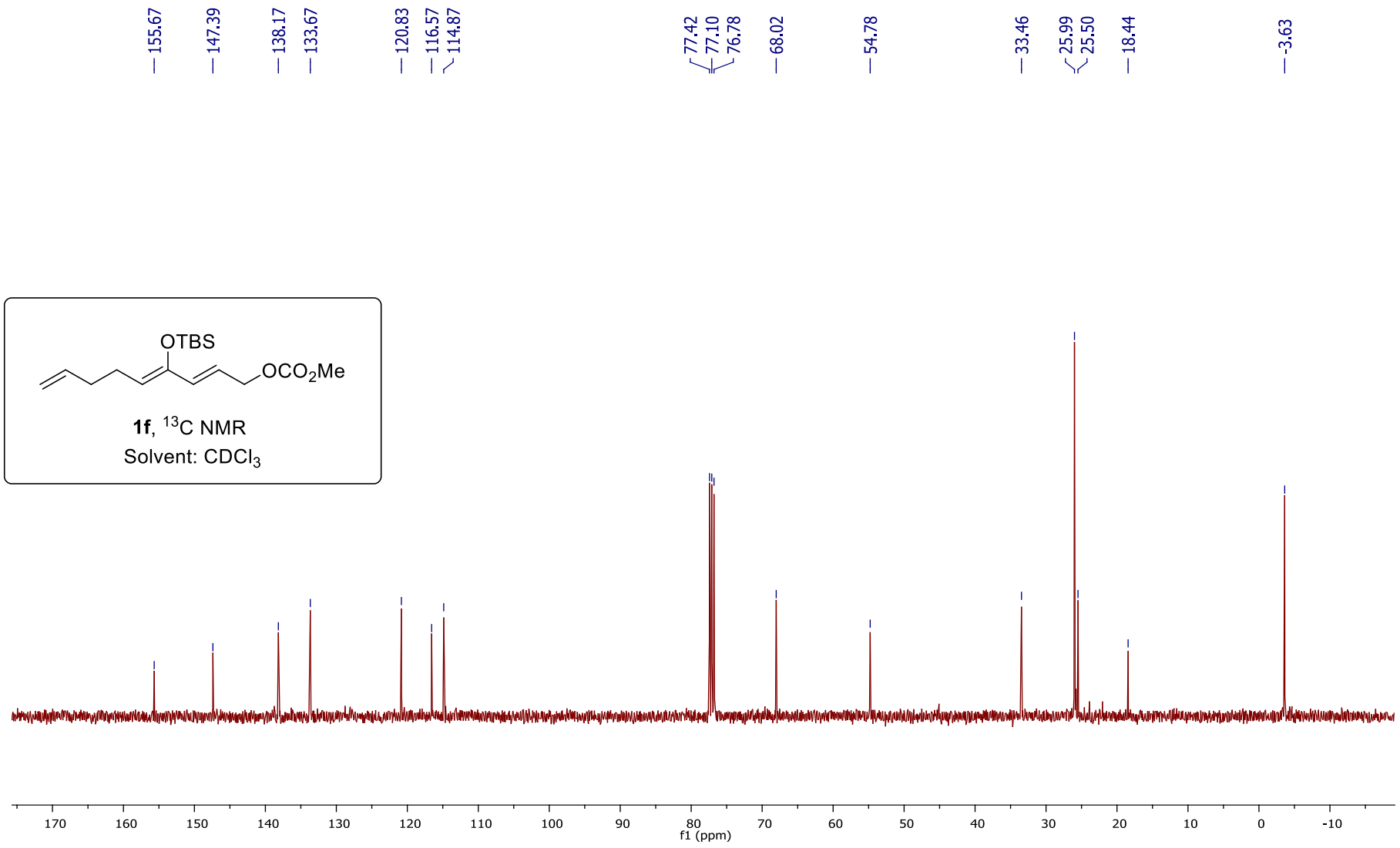
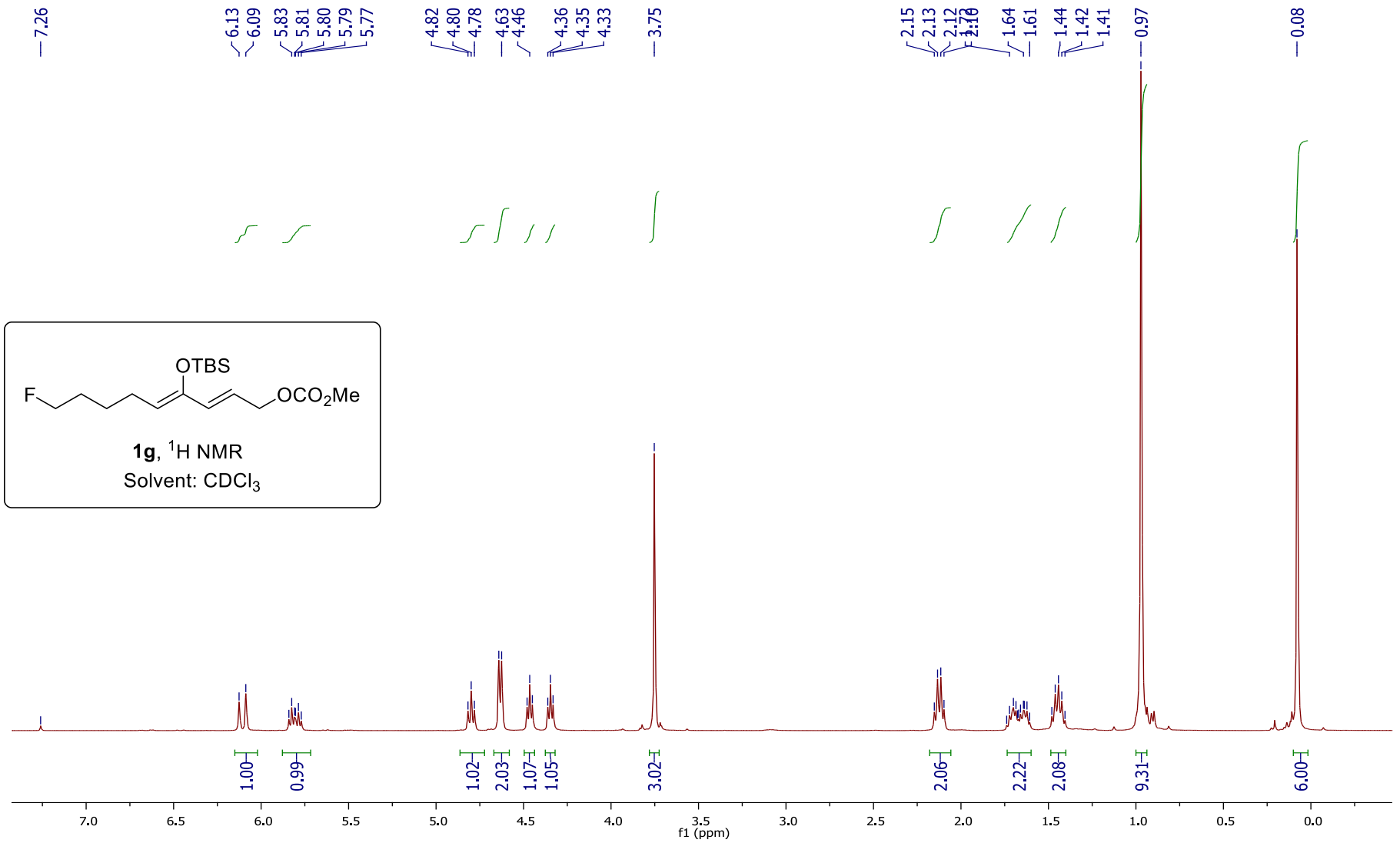
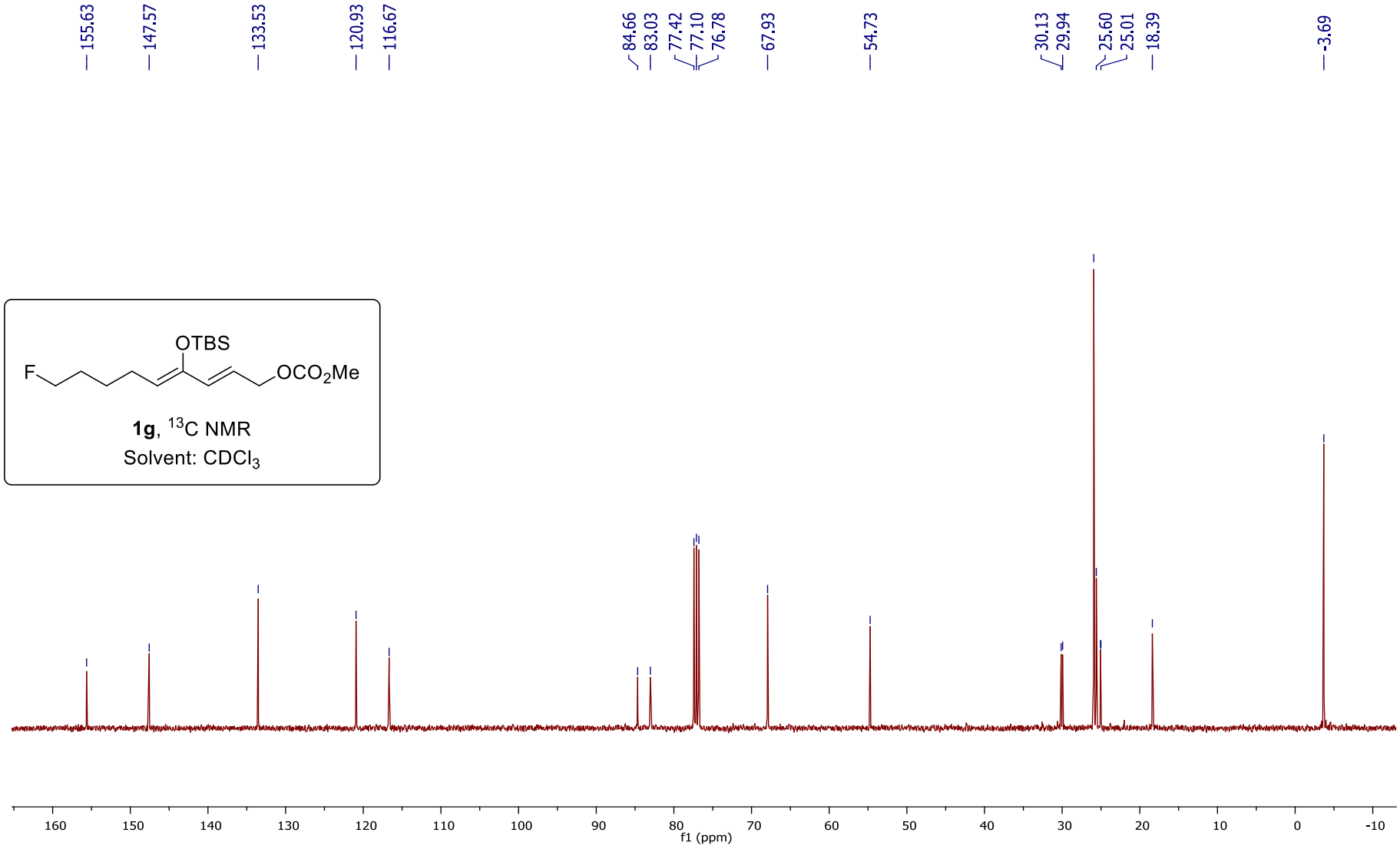
6.14
6.10
5.74
5.03
4.85
4.84
4.82
4.65
4.64
3.77
2.22
2.20
2.18
2.17
2.11
2.09
2.08
2.06
0.98
0.09
OTBS
OCO2Me
1f, 1H NMR
Solvent: CDCl3
1.00
2.01
1.05
1.05
0.99
2.03
3.06
2.02
2.07
9.15
5.97
f1 (ppm)


155.67
147.39
138.17
133.67
120.83
116.57
114.87
77.42
77.10
76.78
68.02
54.78
33.46
25.99
25.50
18.44
-3.63
OTBS
OCO2Me
1f, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
6.13
6.09
5.83
5.81
5.80
5.79
5.77
4.82
4.80
4.78
4.63
4.46
4.36
4.35
4.33
3.75
2.15
2.13
2.12
2.10
1.64
1.61
1.44
1.42
1.41
0.97
0.08
OTBS
F
OCO2Me
1g, 1H NMR
Solvent: CDCl3
1.00
0.99
1.02
2.03
1.07
1.05
3.02
2.06
2.22
2.08
9.31
6.00
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
f1 (ppm)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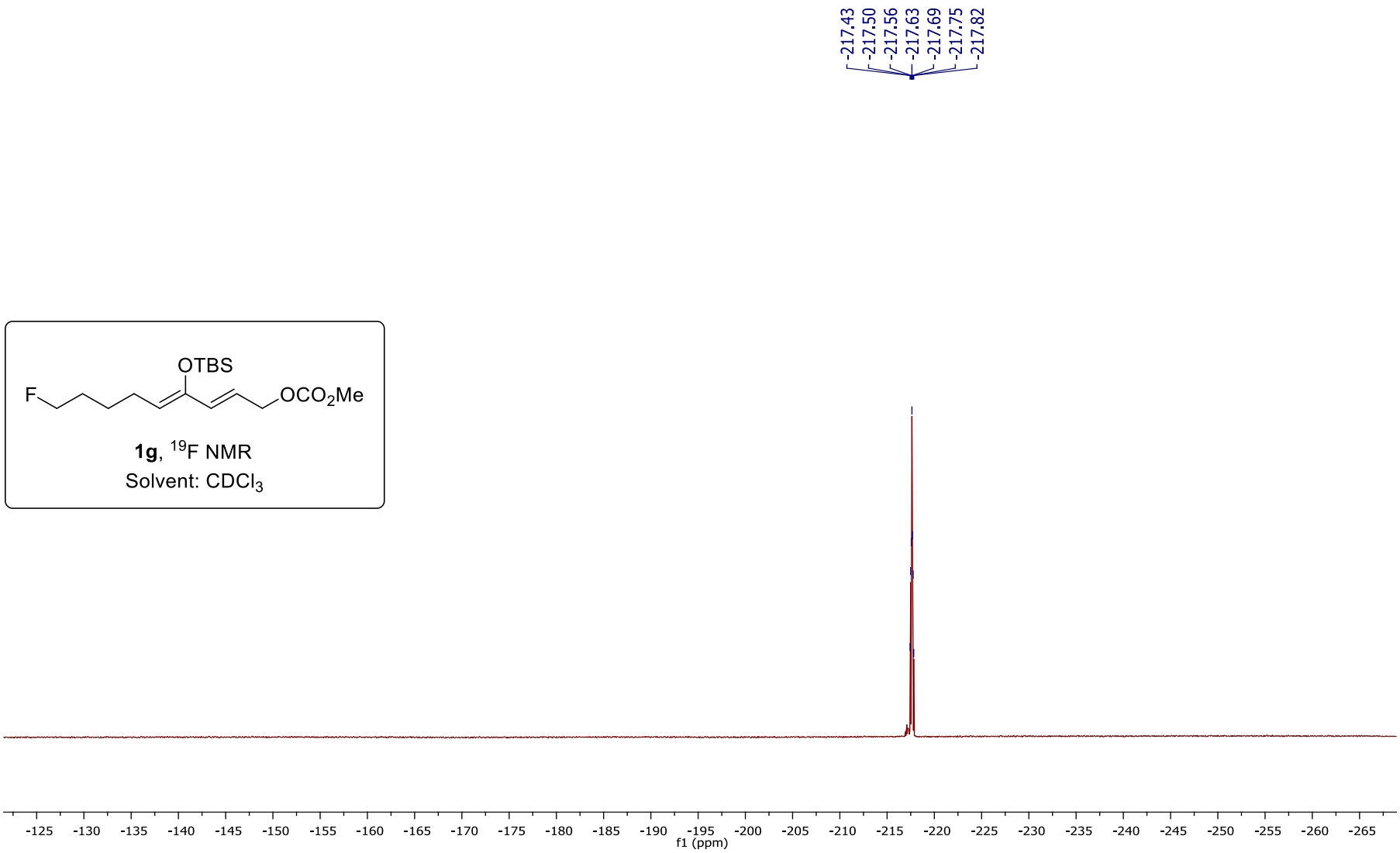
147.57
133.53
120.93
116.67
84.66
83.03
77.42
77.10
76.78
67.93
54.73
30.13
29.94
25.60
25.01
18.39
-3.69
OTBS
F
OCO2Me
1g, 13C NMR
Solvent: CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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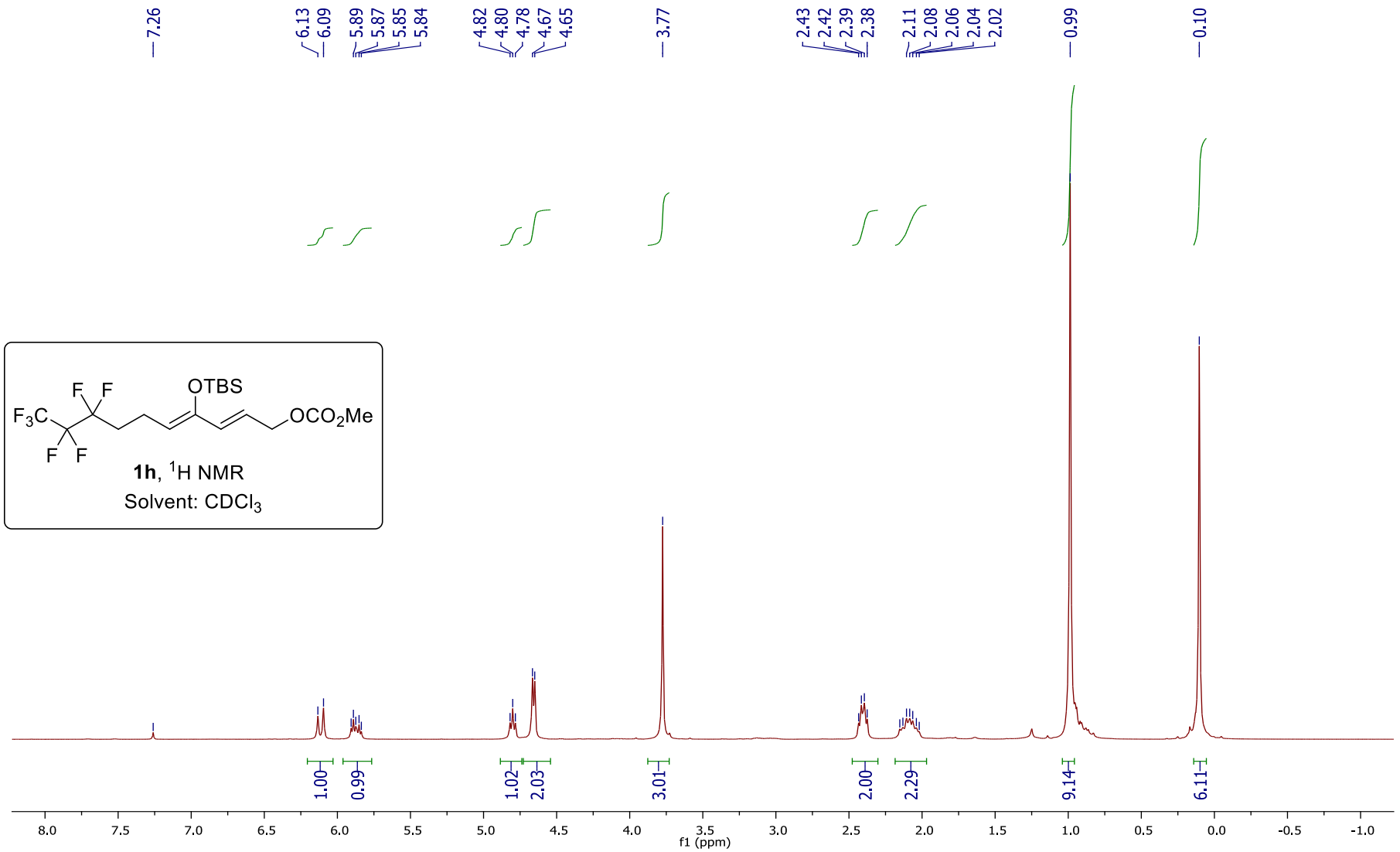
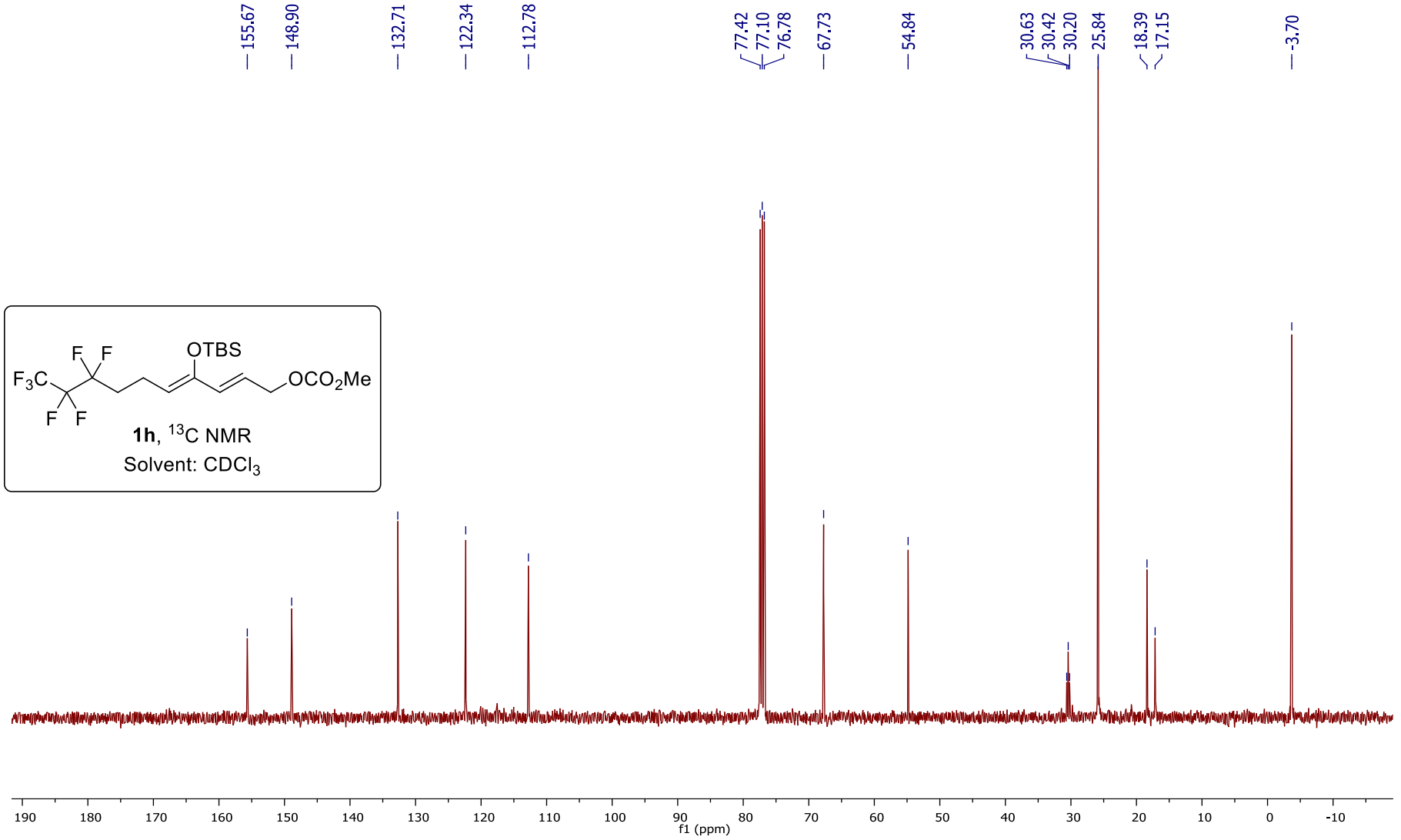
-217.50
-217.56
-217.63
-217.69
-217.75
-217.82
OTBS
F
OCO2Me
1g, 19F NMR
Solvent: CDCl3
-125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 -210 -215 -220 -225 -230 -235 -240 -245 -250 -255 -260 -265
f1 (ppm)


7.26
6.13
6.09
5.89
5.87
5.85
5.84
4.82
4.80
4.78
4.67
4.65
3.77
2.43
2.42
2.39
2.38
2.11
2.08
2.06
2.04
2.02
0.99
0.10
F F
OTBS
F3C
OCO2Me
F F
1h, 1H NMR
Solvent: CDCl3
1.00
0.99
1.02
2.03
3.01
2.00
2.29
9.14
6.11
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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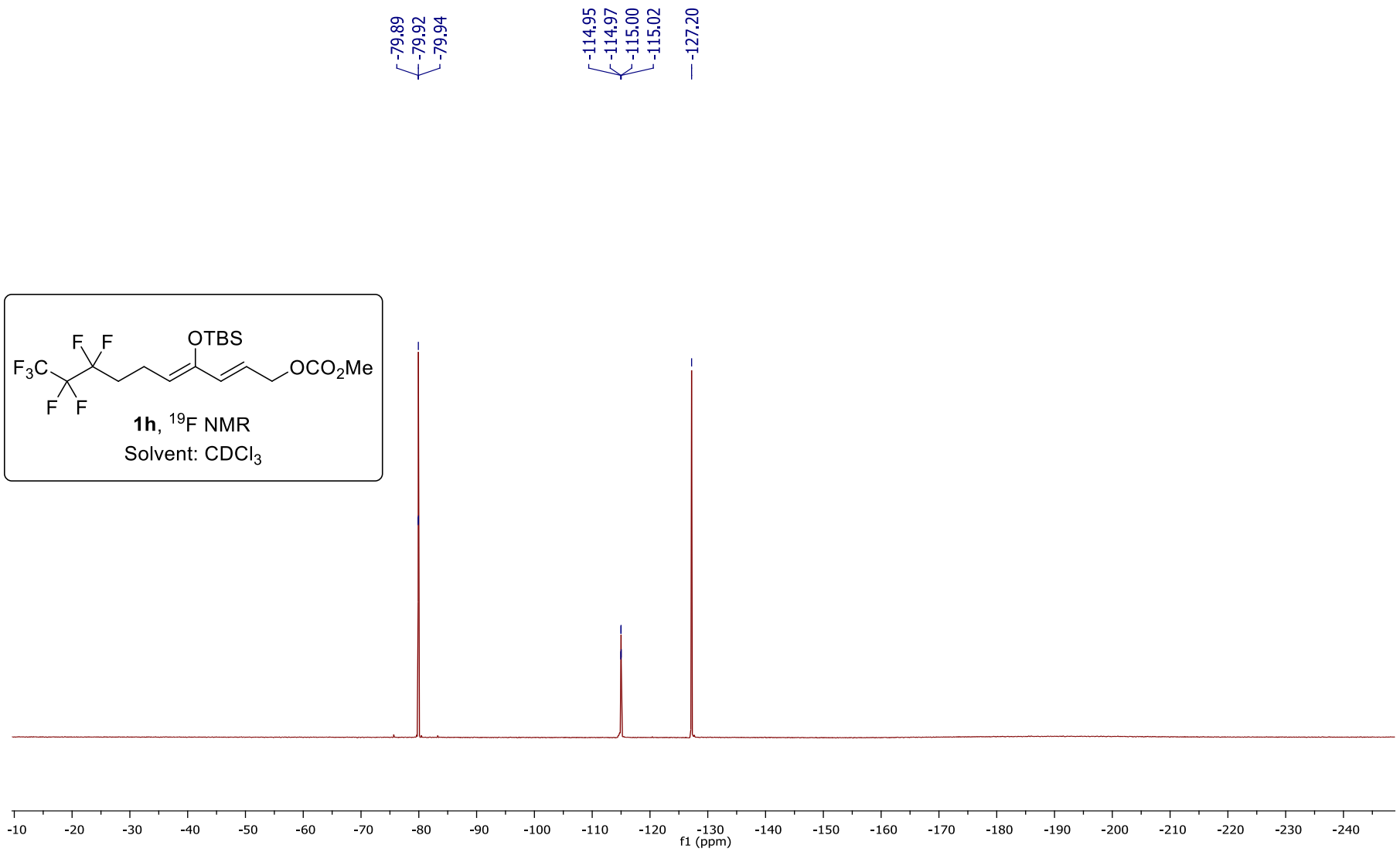
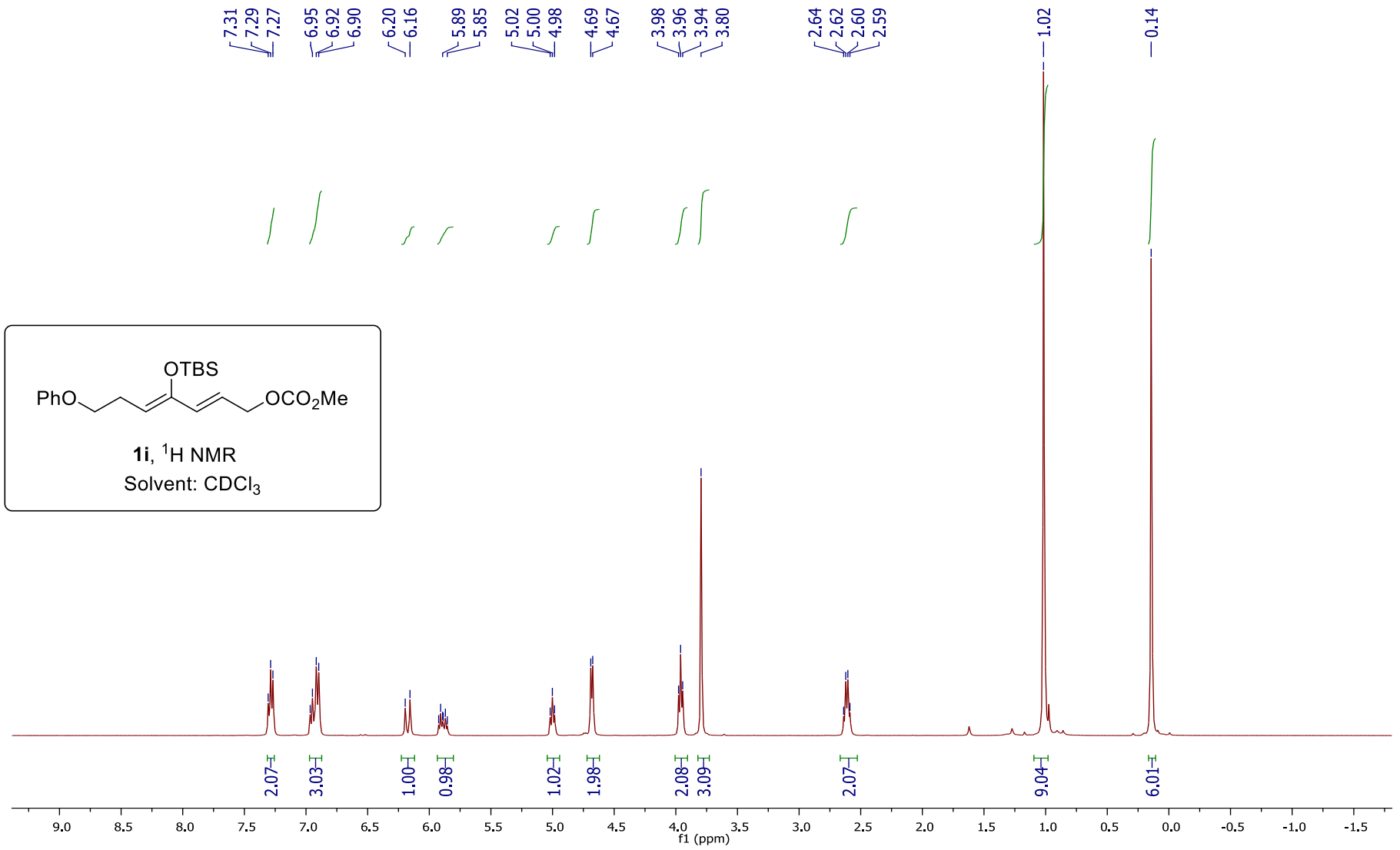
148.90
132.71
122.34
112.78
77.42
77.10
76.78
67.73
54.84
30.63
30.42
30.20
25.84
18.39
17.15
-3.70
OTBS
F F
F3C
OCO2Me
F F
1h, 13C NMR
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-79.89
-79.92
-79.94
-114.95
-114.97
-115.00
-115.02
-127.20
F F
OTBS
F3C
OCO2Me
F F
1h, 19F NMR
Solvent: CDCl3
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)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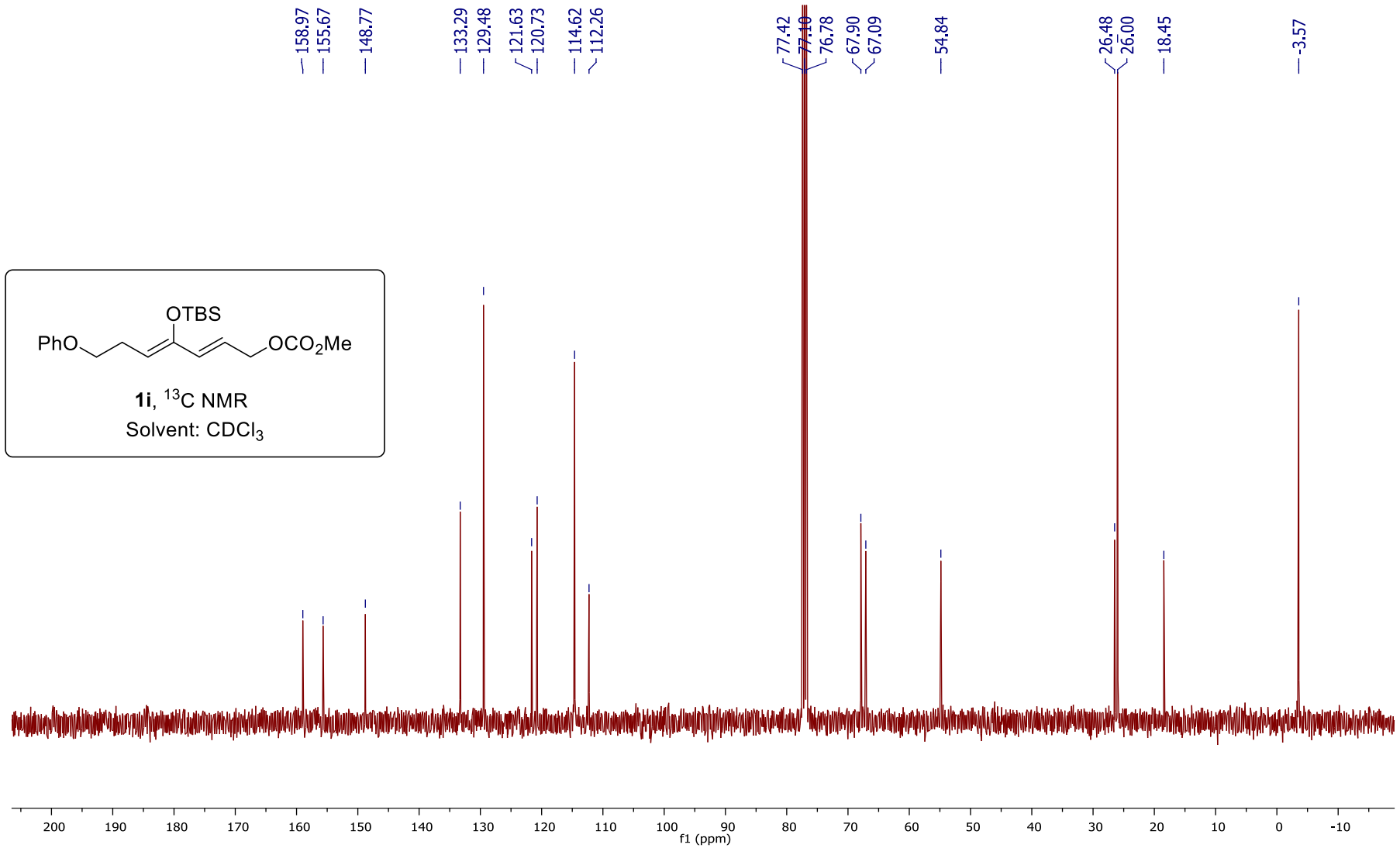
7.29
7.27
6.95
6.92
6.90
6.20
6.16
5.89
5.85
5.02
5.00
4.98
4.69
4.67
3.98
3.96
3.94
3.80
2.64
2.62
2.60
2.59
1.02
0.14
OTBS
PhO
OCO2Me
1i, 1H NMR
Solvent: CDCl3
2.07
3.03
1.00
0.98
1.02
1.98
2.08
3.09
2.07
9.04
6.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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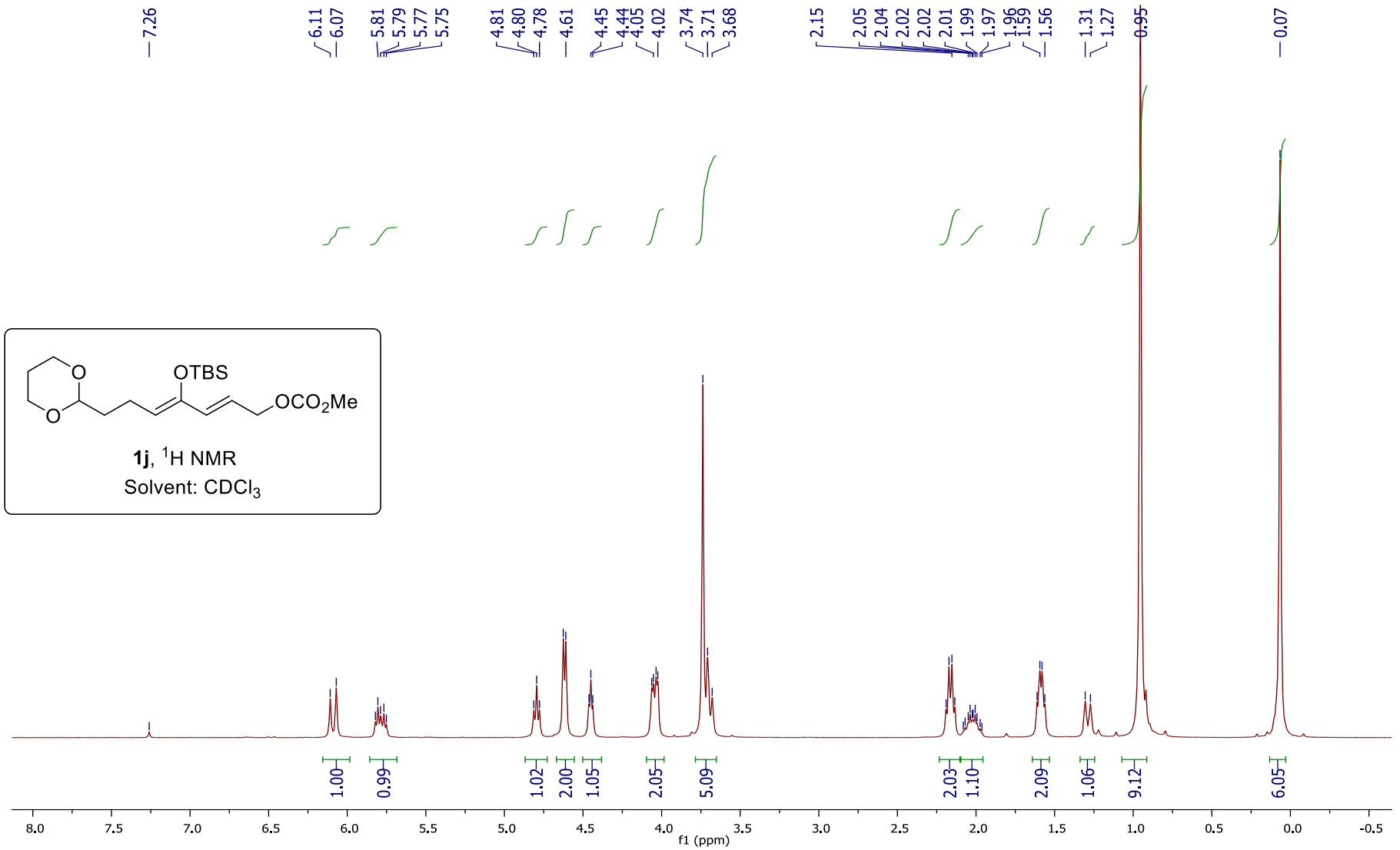
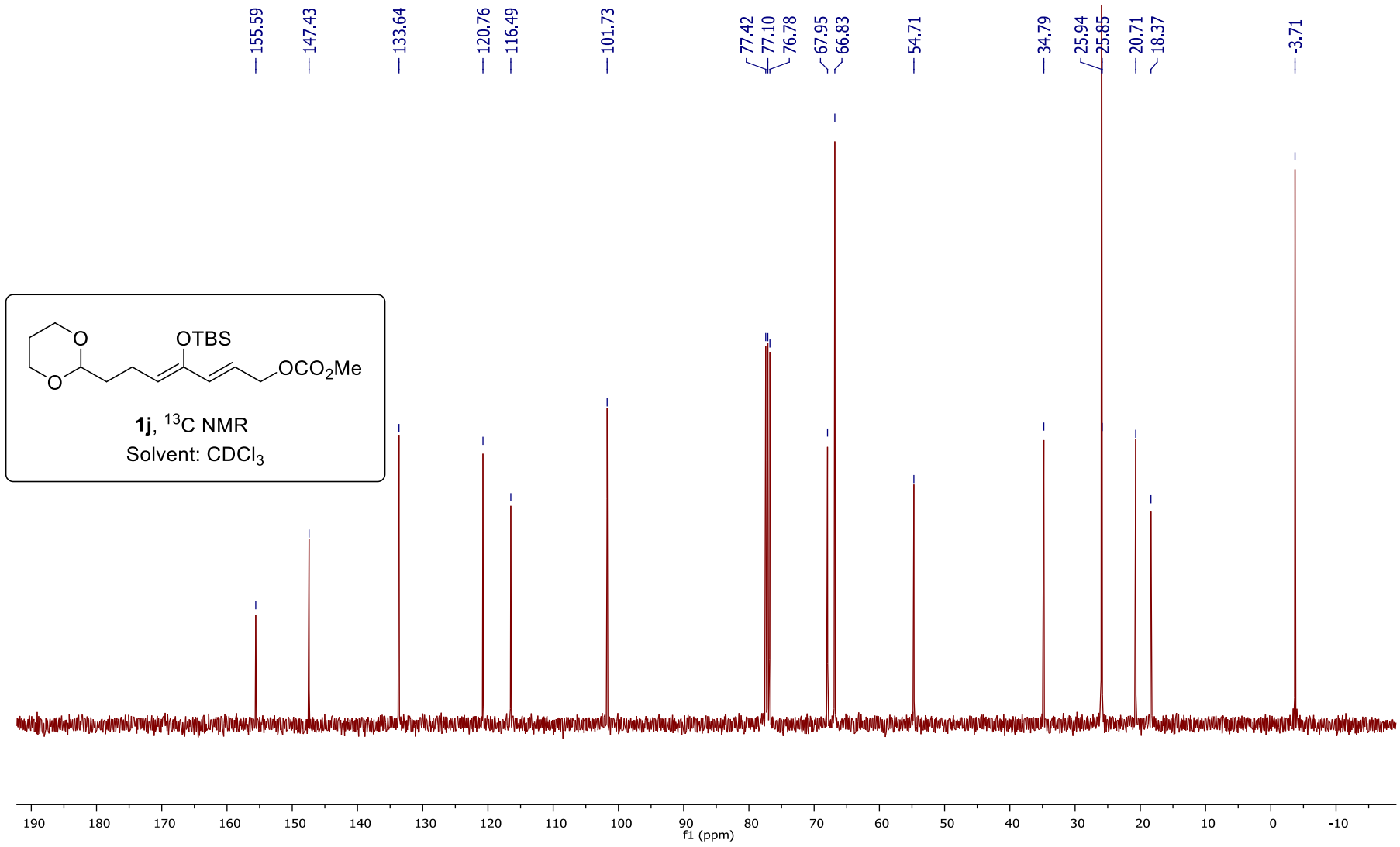
155.67
148.77
133.29
129.48
121.63
120.73
114.62
112.26
77.42
77.10
76.78
67.90
67.09
54.84
26.48
26.00
18.45
-3.57
OTBS
PhO
OCO2Me
1i, 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
6.11
6.07
5.81
5.79
5.77
5.75
4.81
4.80
4.78
4.61
4.45
4.44
4.05
4.02
3.74
3.71
3.68
2.15
2.05
2.04
2.02
2.02
2.01
1.99
1.97
1.96
1.59
1.56
1.31
1.27
0.95
0.07
OTBS
OCO2Me
1j, 1H NMR
Solvent: CDCl3
1.00
0.99
1.02
2.00
1.05
2.05
5.09
2.03
1.10
2.09
1.06
9.12
6.05
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)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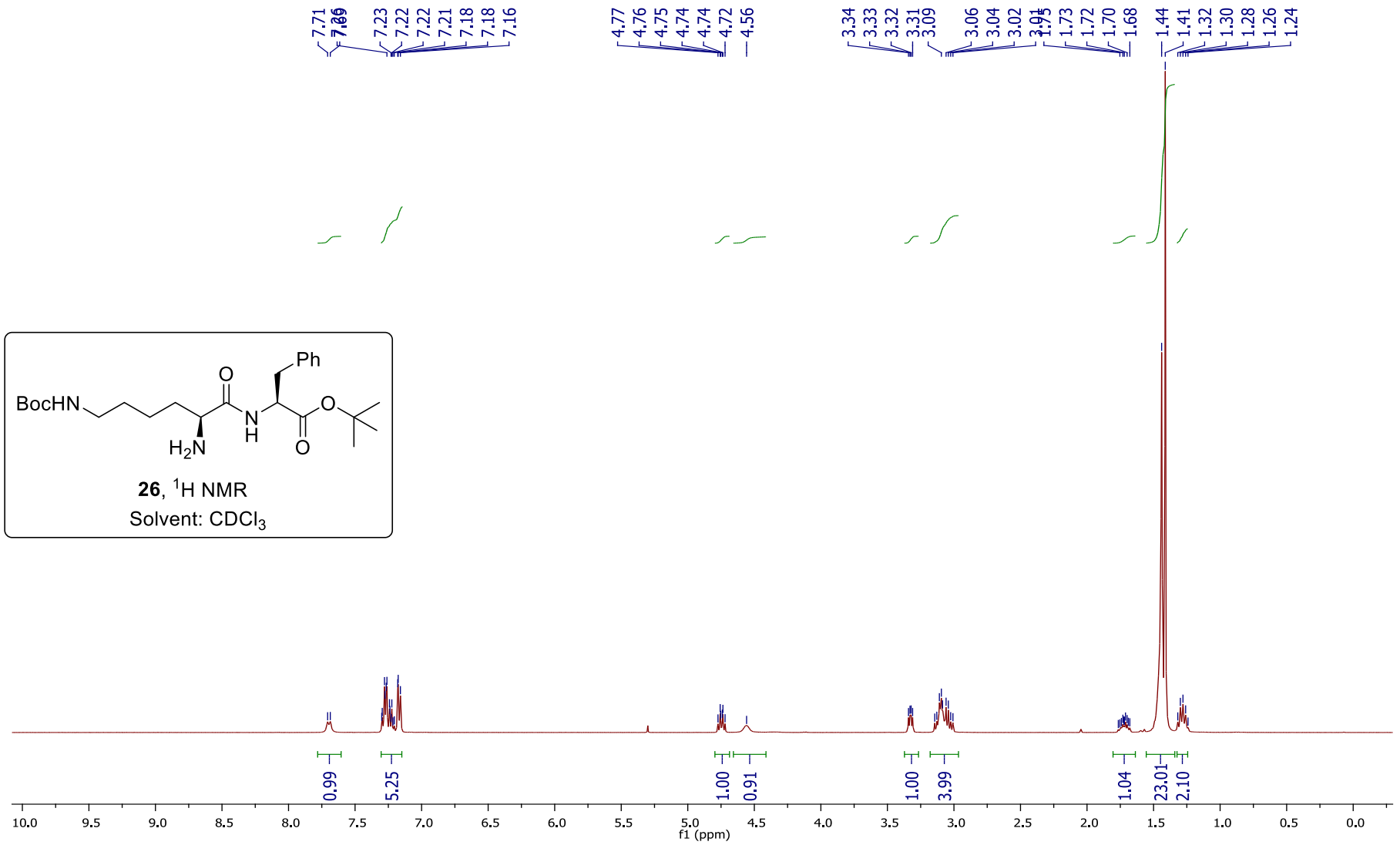
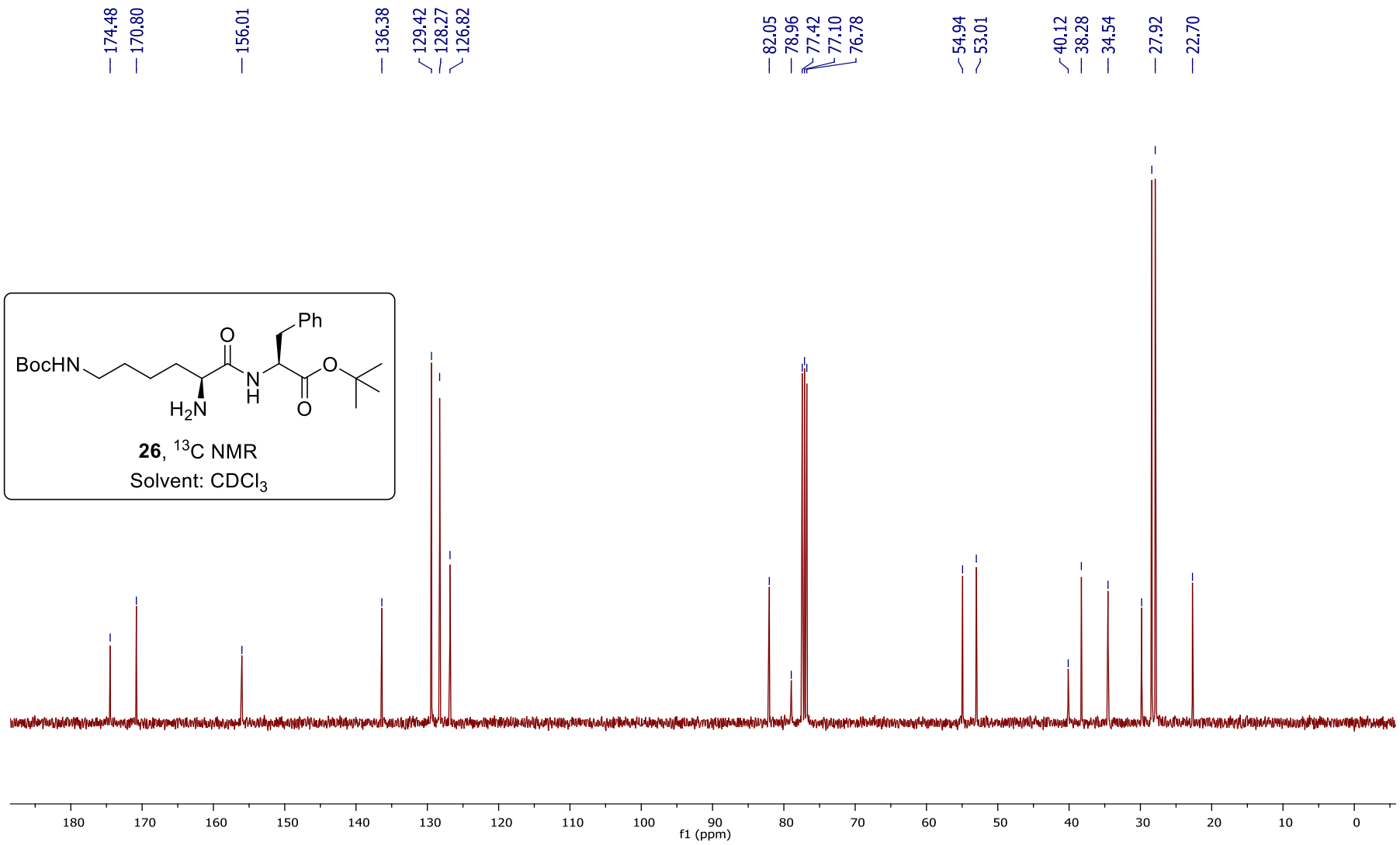
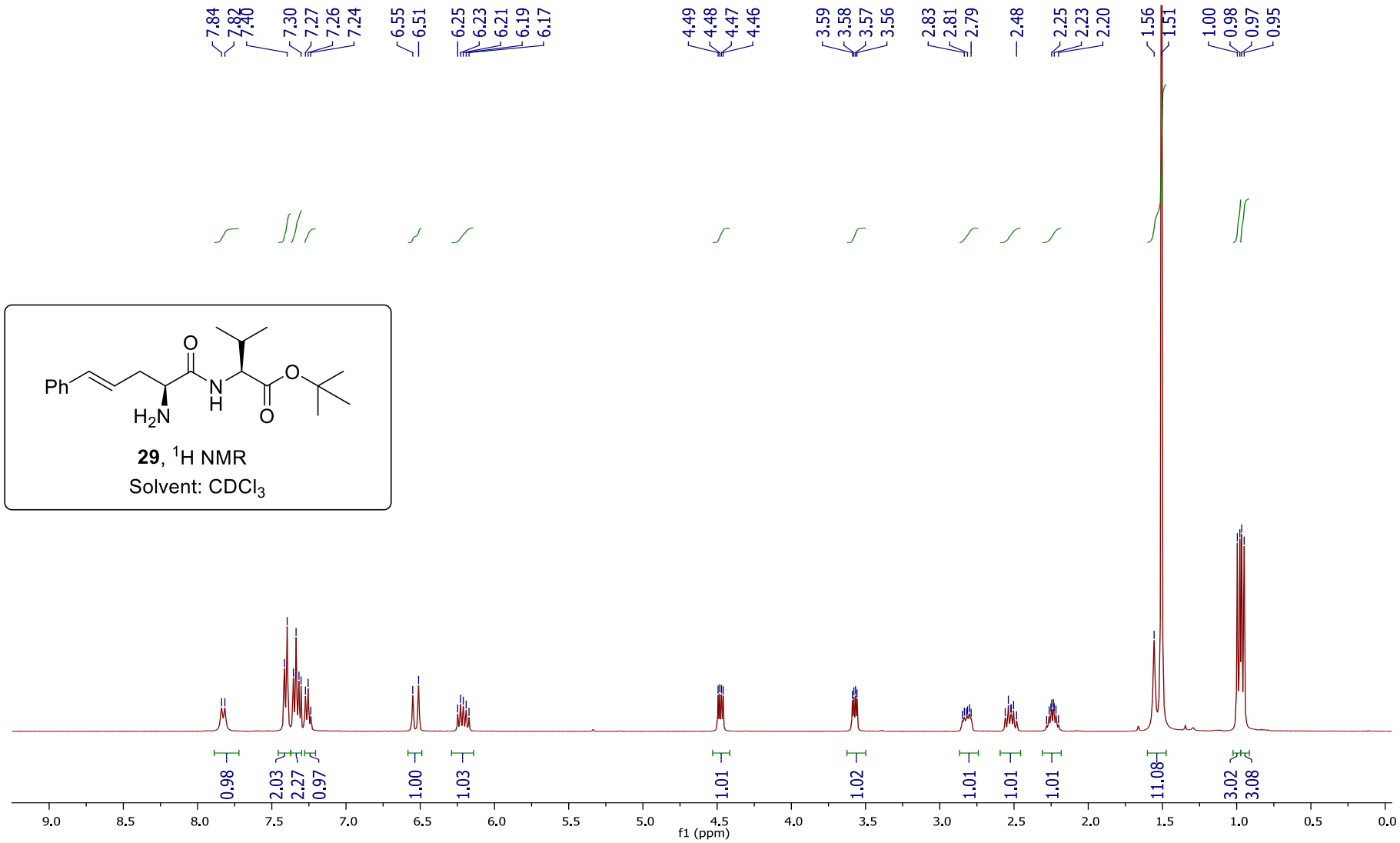
147.43
133.64
120.76
116.49
101.73
77.42
77.10
76.78
67.95
66.83
54.71
34.79
25.94
25.85
20.71
18.37
-3.71
OTBS
OCO2Me
1j, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


BocHN
O
N
H
Ph
O
O
H_2N
26, ^{1}H NMR
Solvent: $CDCl_3$
7.71
7.23
7.22
7.22
7.21
7.18
7.18
7.16
4.77
4.76
4.75
4.74
4.74
4.72
4.56
3.34
3.33
3.32
3.31
3.09
3.06
3.04
3.02
1.73
1.72
1.70
1.68
1.44
1.41
1.32
1.30
1.28
1.26
1.24
0.99
5.25
1.00
0.91
1.00
3.99
1.04
23.01
2.10
f1 (ppm)


174.48
170.80
156.01
136.38
129.42
128.27
126.82
82.05
78.96
77.42
77.10
76.78
54.94
53.01
40.12
38.28
34.54
27.92
22.70
BocHN
O
N
H
Ph
O
O
H2N
26, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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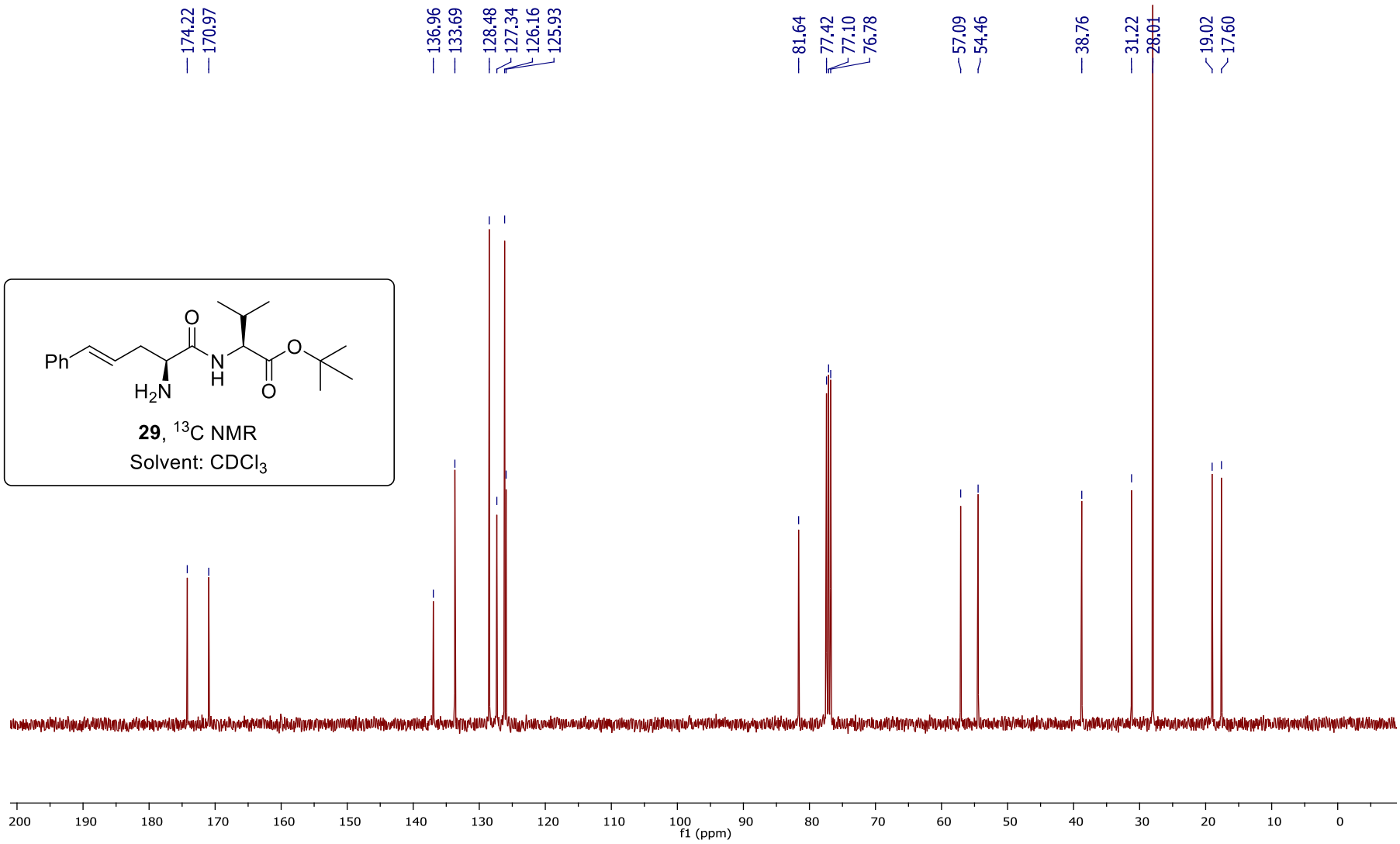
7.82
7.40
7.30
7.27
7.26
7.24
6.55
6.51
6.25
6.23
6.21
6.19
6.17
4.49
4.48
4.47
4.46
3.59
3.58
3.57
3.56
2.83
2.81
2.79
2.48
2.25
2.23
2.20
1.56
1.51
1.00
0.98
0.97
0.95
Ph
O
N
H
O
O
H2N
29, 1H NMR
Solvent: CDCl3
0.98
2.03
2.27
0.97
1.00
1.03
1.01
1.02
1.01
1.01
1.01
11.08
3.02
3.08
9.0
8.5
8.0
7.5
7.0
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
f1 (ppm)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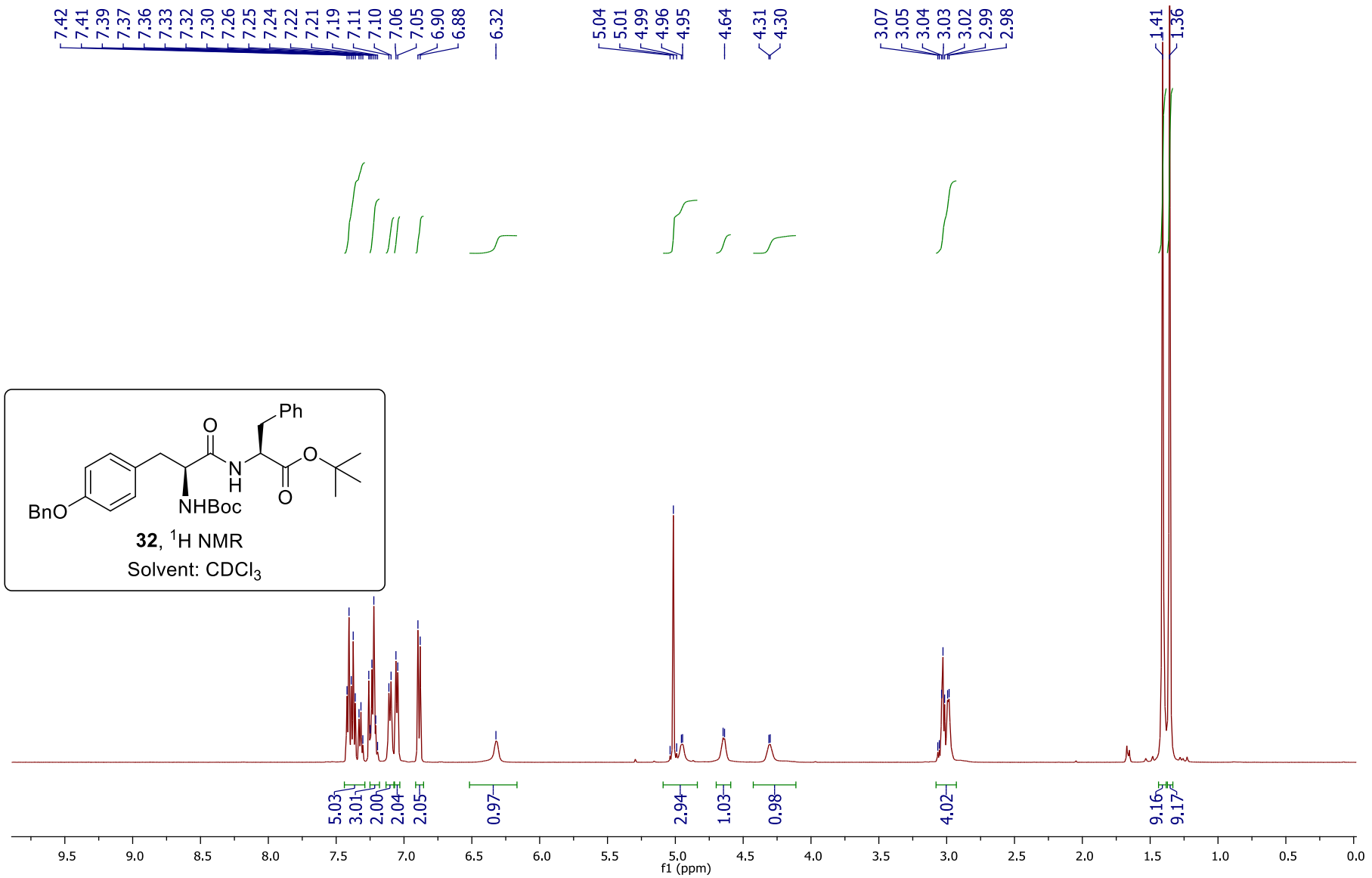
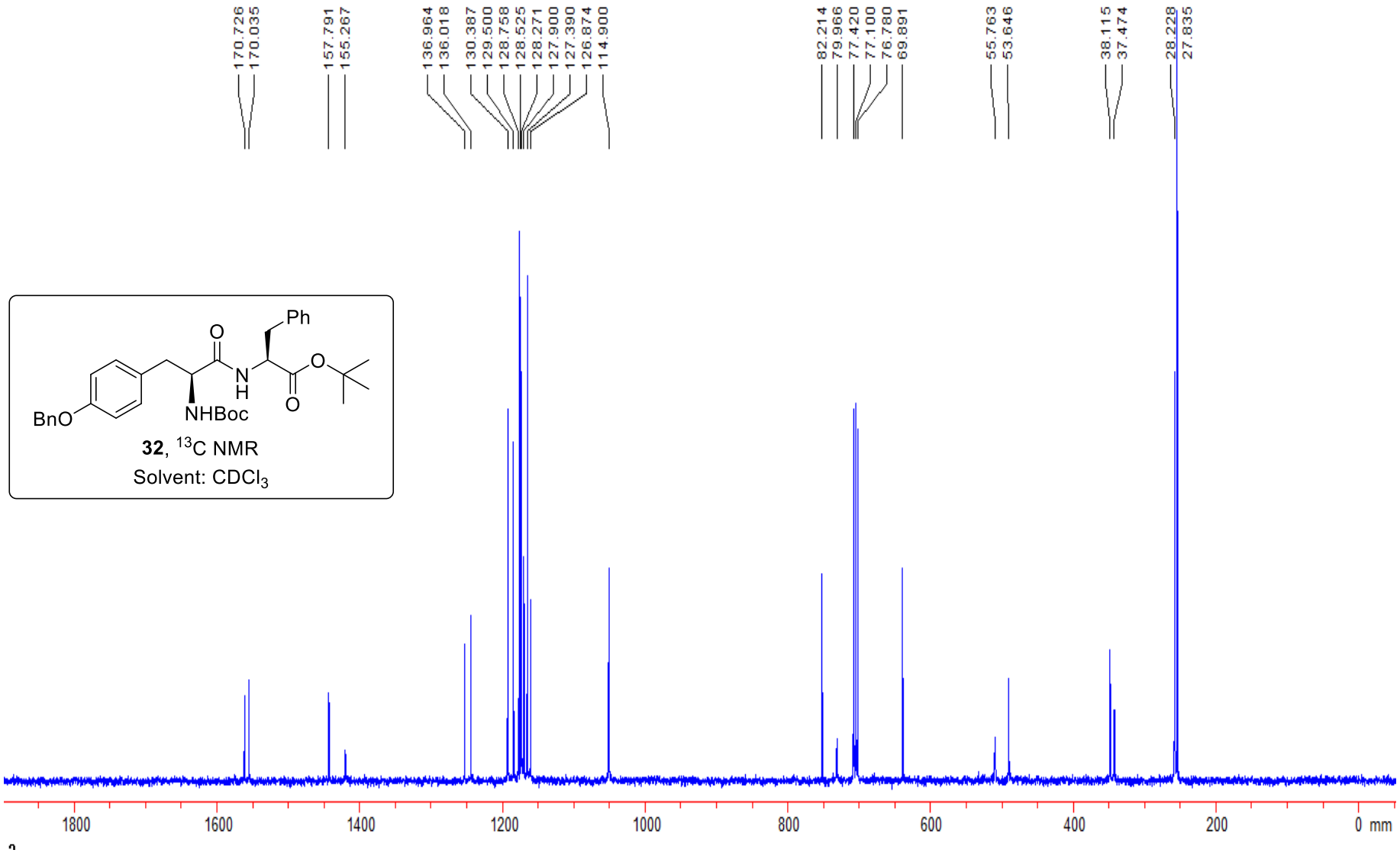
170.97
136.96
133.69
128.48
127.34
126.16
125.93
81.64
77.42
77.10
76.78
57.09
54.46
38.76
31.22
28.01
19.02
17.60
Ph
O
N
H
O
O
H_2N
29, ^{13}C NMR
Solvent: $CDCl_3$
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.42
7.41
7.39
7.37
7.36
7.33
7.32
7.30
7.26
7.25
7.24
7.22
7.21
7.19
7.11
7.10
7.06
7.05
6.90
6.88
6.32
5.04
5.01
4.99
4.96
4.95
4.64
4.31
4.30
3.07
3.05
3.04
3.03
3.02
2.99
2.98
1.41
1.36
Ph
O
N
H
O
O
BnO
NHBoc
32, 1H NMR
Solvent: CDCl3
5.03
3.01
2.00
2.04
2.05
0.97
2.94
1.03
0.98
4.02
9.16
9.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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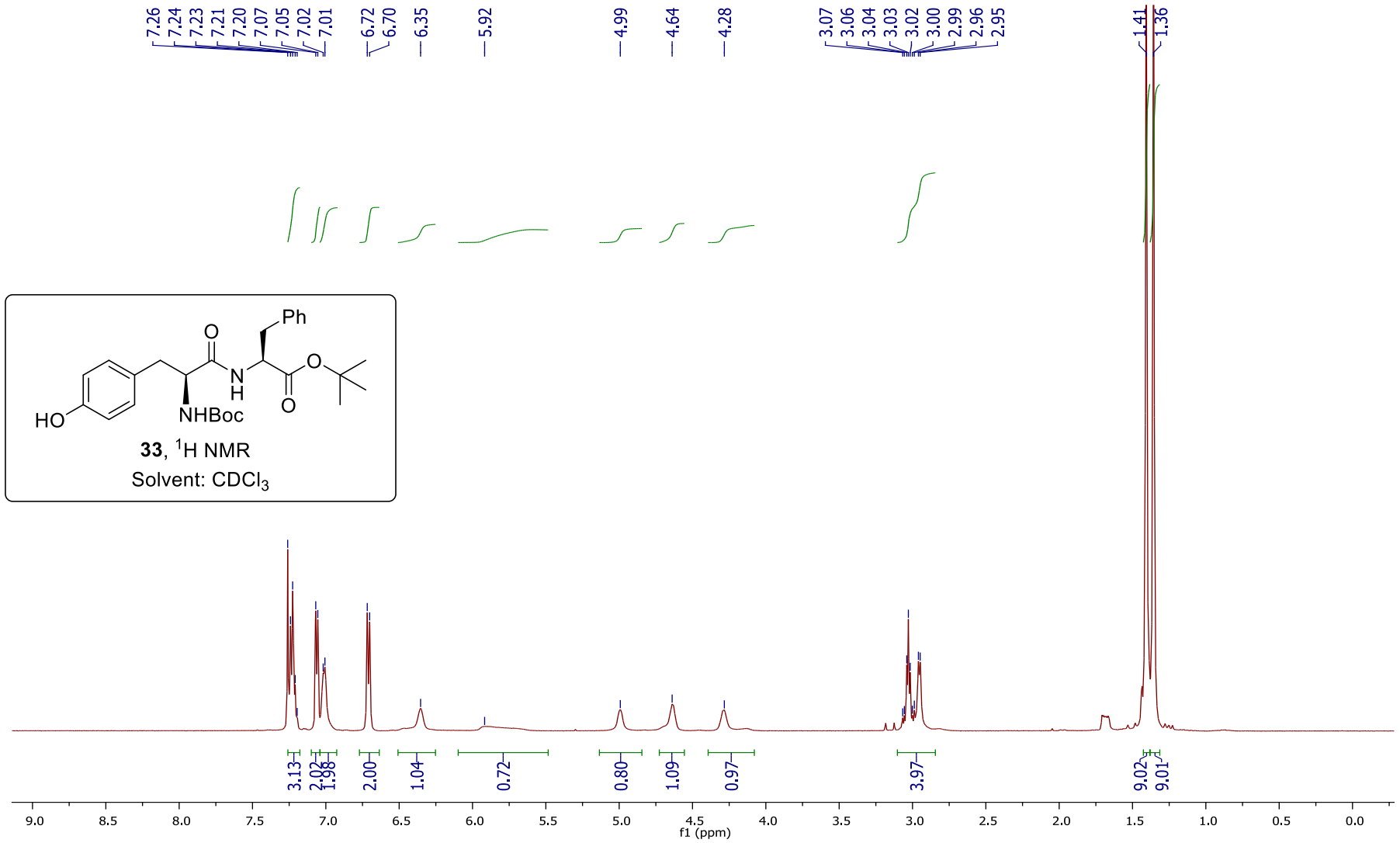
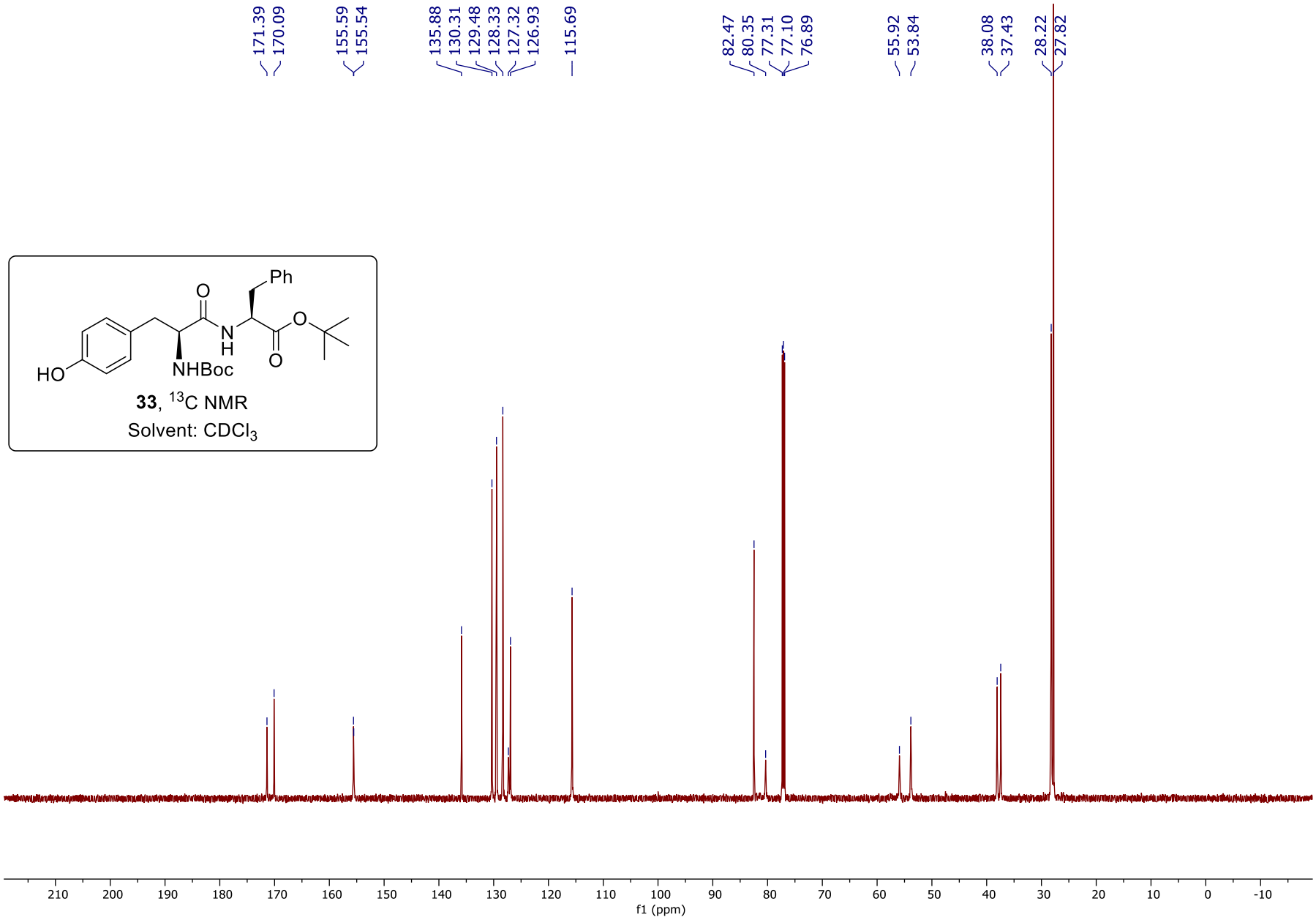
128.271
127.900
127.390
126.874
114.900
82.214
79.966
77.420
77.100
76.780
69.891
55.763
53.646
38.115
37.474
28.228
27.835
Ph
O
N
H
O
O
BnO
NHBoc
32, 13C NMR
Solvent: CDCl3
1800
1600
1400
1200
1000
800
600
400
200
0 mm


7.26
7.24
7.23
7.21
7.20
7.07
7.05
7.02
7.01
6.72
6.70
6.35
5.92
4.99
4.64
4.28
3.07
3.06
3.04
3.03
3.02
3.00
2.99
2.96
2.95
1.41
1.36
Ph
O
N
H
O
O
HO
NHBoc
33, 1H NMR
Solvent: CDCl3
3.13
2.02
1.98
2.00
1.04
0.72
0.80
1.09
0.97
3.97
9.02
9.01
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
f1 (ppm)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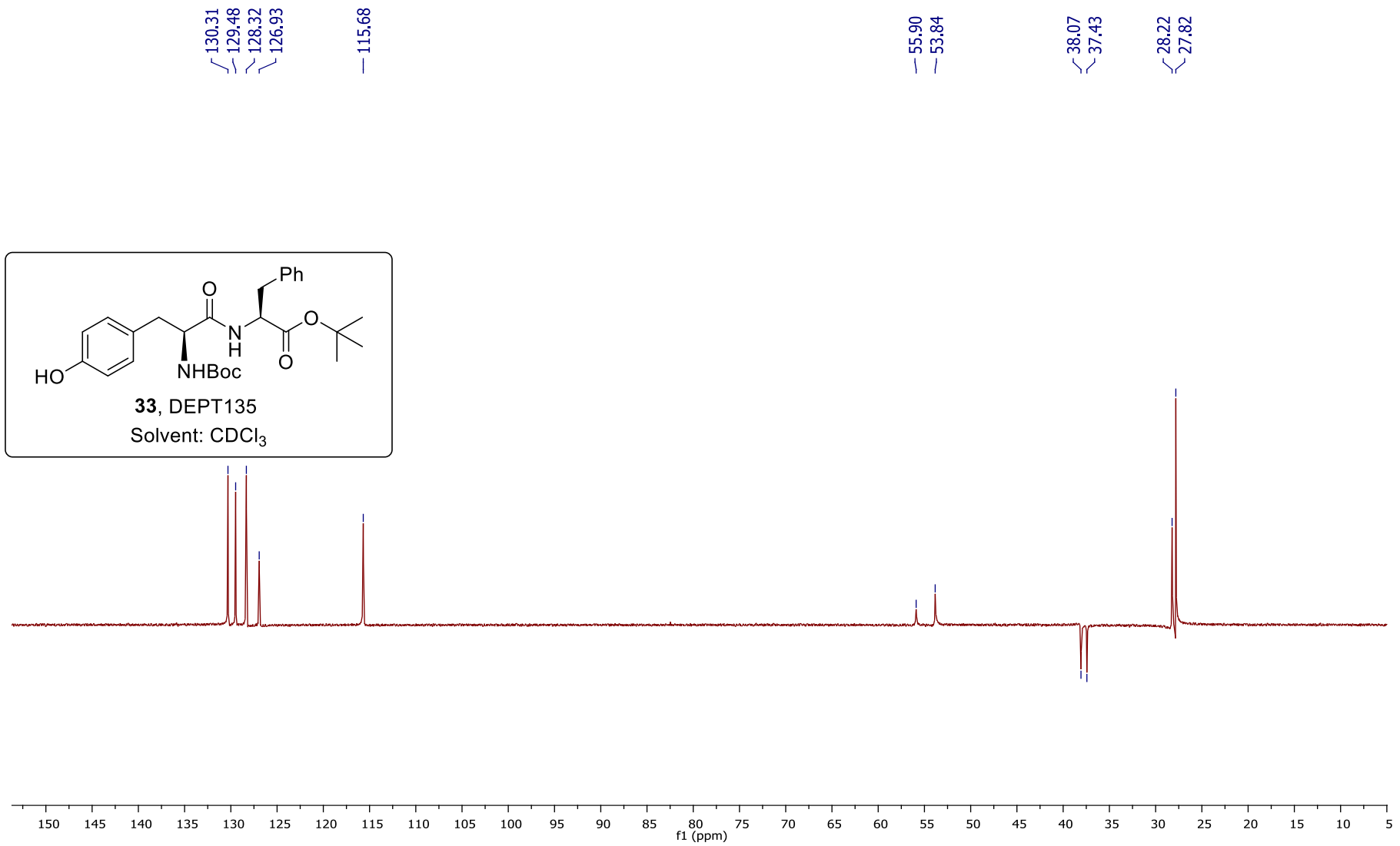
170.09
155.59
155.54
135.88
130.31
129.48
128.33
127.32
126.93
115.69
82.47
80.35
77.31
77.10
76.89
55.92
53.84
38.08
37.43
28.22
27.82
Ph
O
N
H
O
O
HO
NHBoc
33, 13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


130.31
129.48
128.32
126.93
115.68
55.90
53.84
38.07
37.43
28.22
27.82
Ph
O
N
H
O
O
O
HO
NHBoc
33, DEPT135
Solvent: CDCl3
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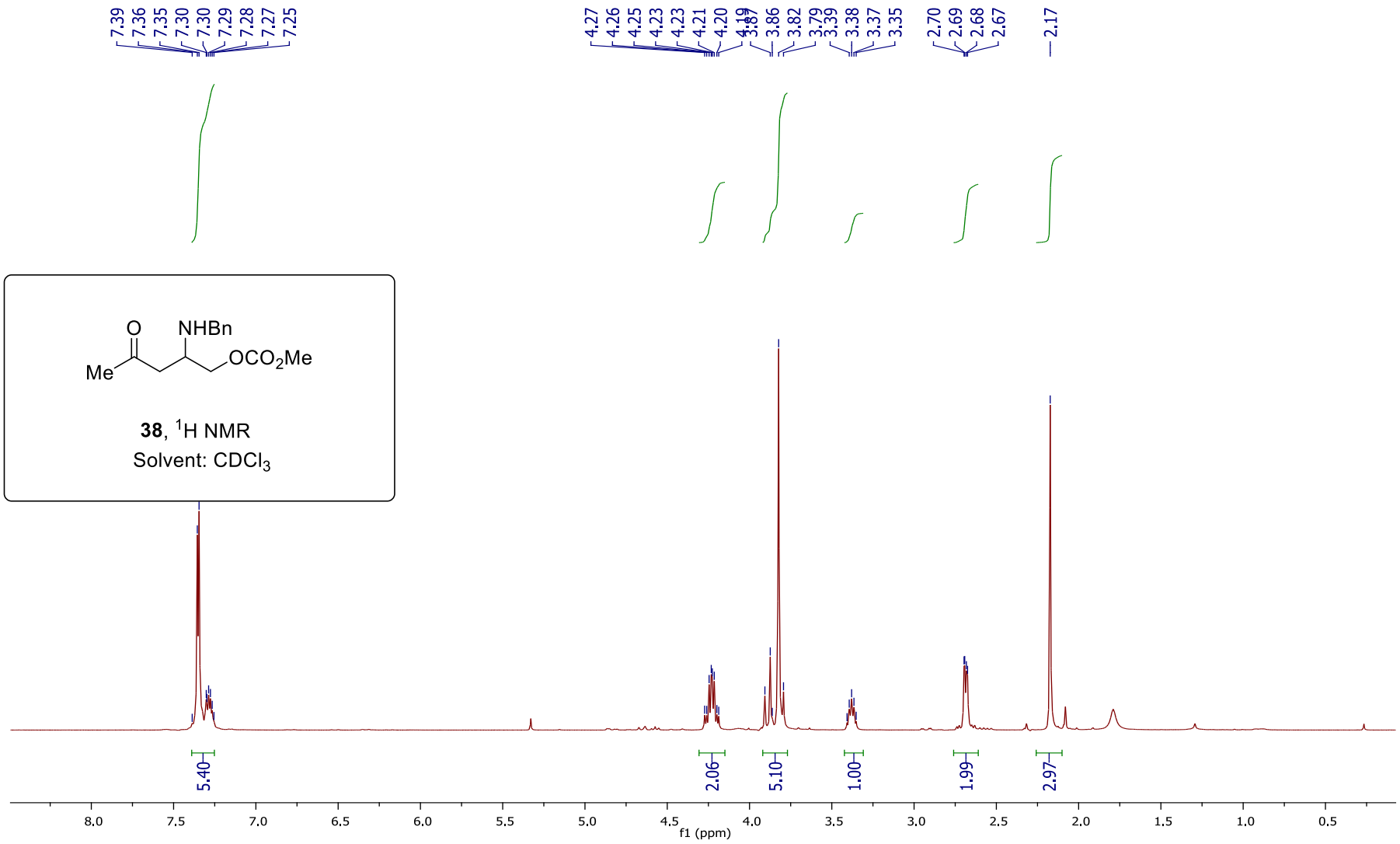
f1 (ppm)


7.39
7.36
7.35
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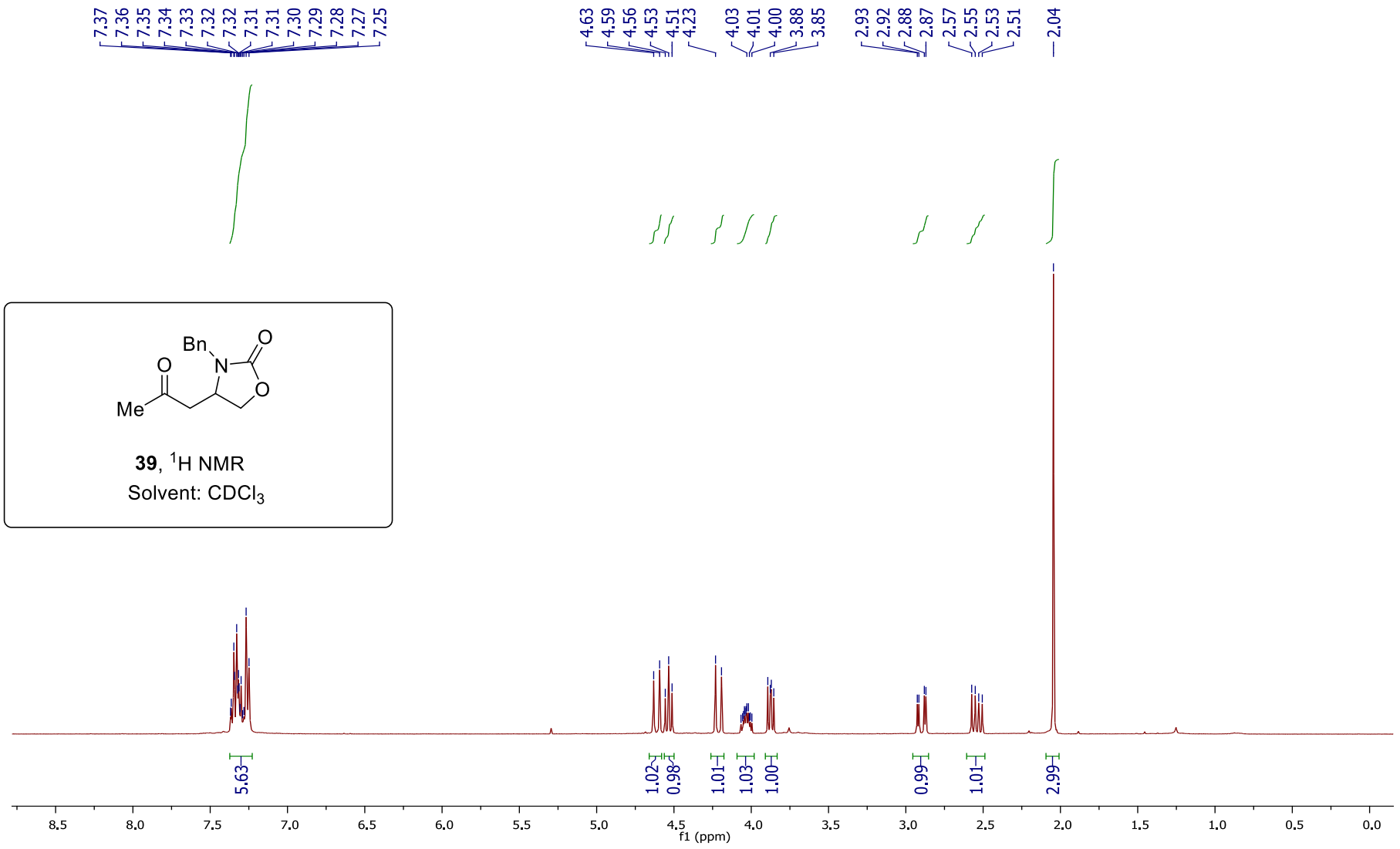
7.30
7.29
7.28
7.27
7.25
4.27
4.26
4.25
4.23
4.23
4.21
4.20
3.87
3.86
3.82
3.79
3.39
3.38
3.37
3.35
2.70
2.69
2.68
2.67
2.17
O
NHBn
Me
OCO2Me
38, 1H NMR
Solvent: CDCl3
5.40
2.06
5.10
1.00
1.99
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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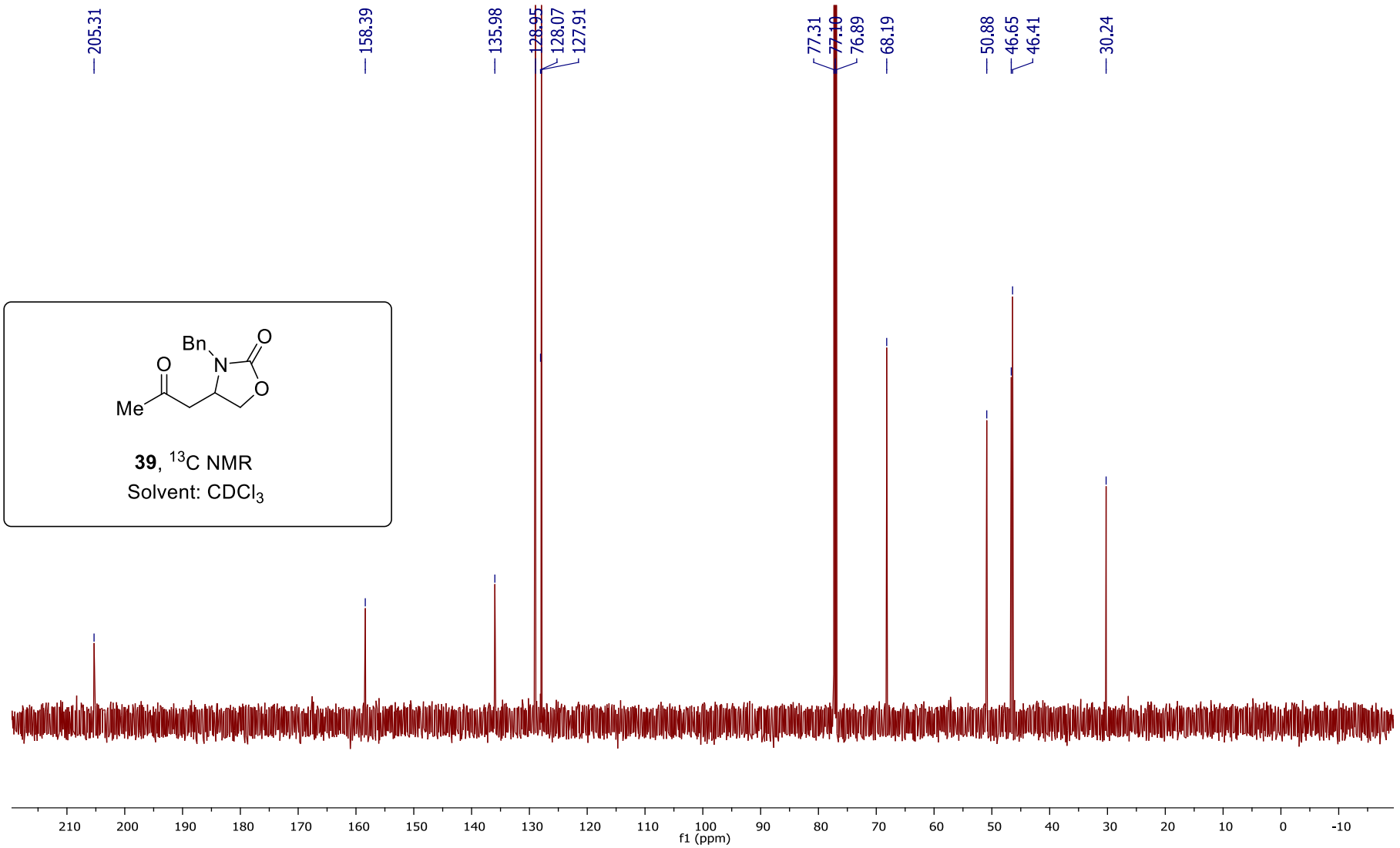
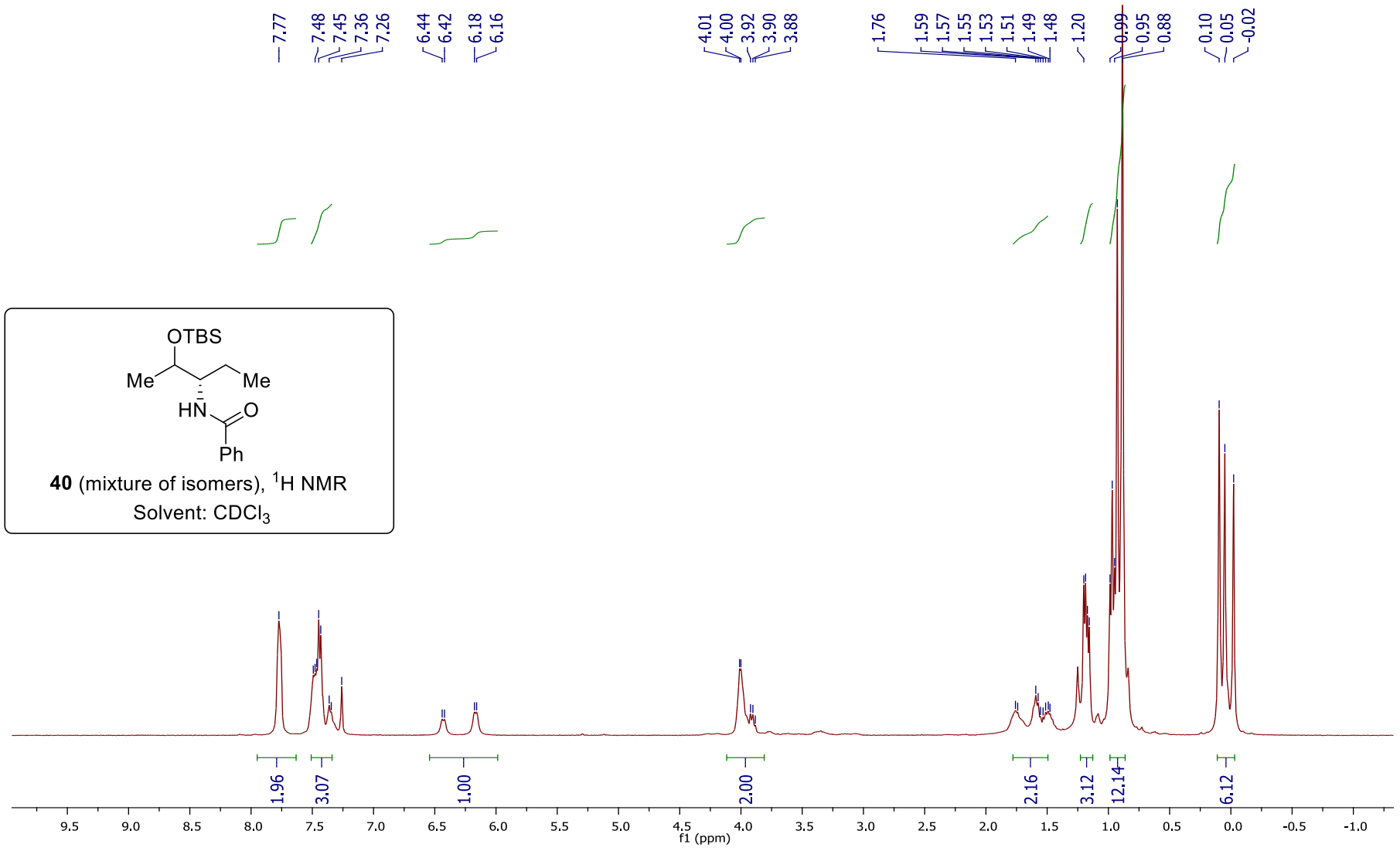
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.25
4.63
4.59
4.56
4.53
4.51
4.23
4.03
4.01
4.00
3.88
3.85
2.93
2.92
2.88
2.87
2.57
2.55
2.53
2.51
2.04
Bn
N
O
O
O
Me
39, 1H NMR
Solvent: CDCl3
5.63
1.02
0.98
1.01
1.03
1.00
0.99
1.01
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


205.31
158.39
135.98
128.95
128.07
127.91
77.31
77.10
76.89
68.19
50.88
46.65
46.41
30.24
Bn
N
O
O
O
Me
39, 13C NMR
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)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7.48
7.45
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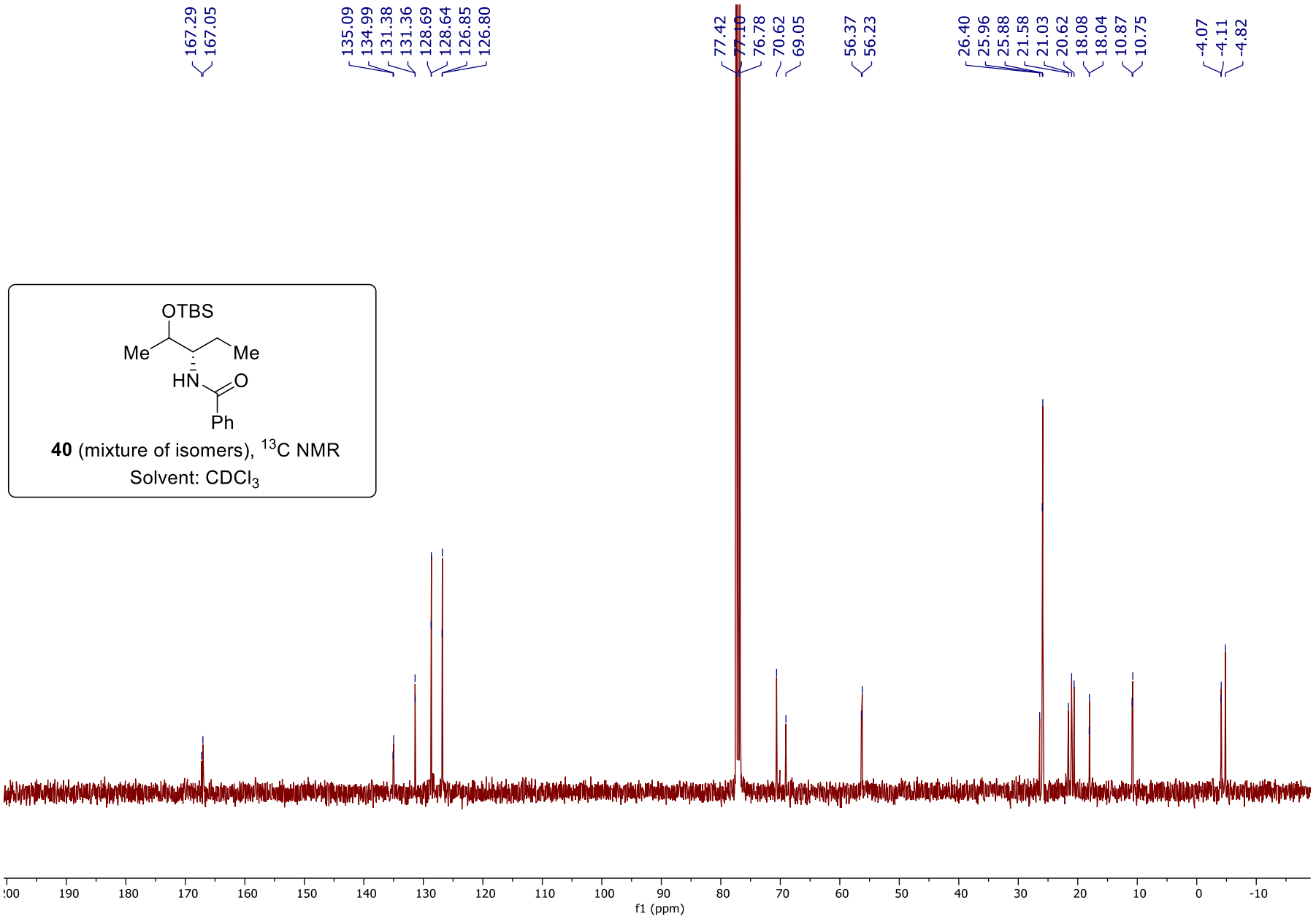
6.18
6.16
4.01
4.00
3.92
3.90
3.88
1.76
1.59
1.57
1.55
1.53
1.51
1.49
1.48
1.20
0.99
0.95
0.88
0.10
0.05
-0.02
OTBS
Me
Me
HN
O
Ph
40 (mixture of isomers), 1H NMR
Solvent: CDCl3
1.96
3.07
1.00
2.00
2.16
3.12
12.14
6.12
f1 (ppm)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167.05
135.09
134.99
131.38
131.36
128.69
128.64
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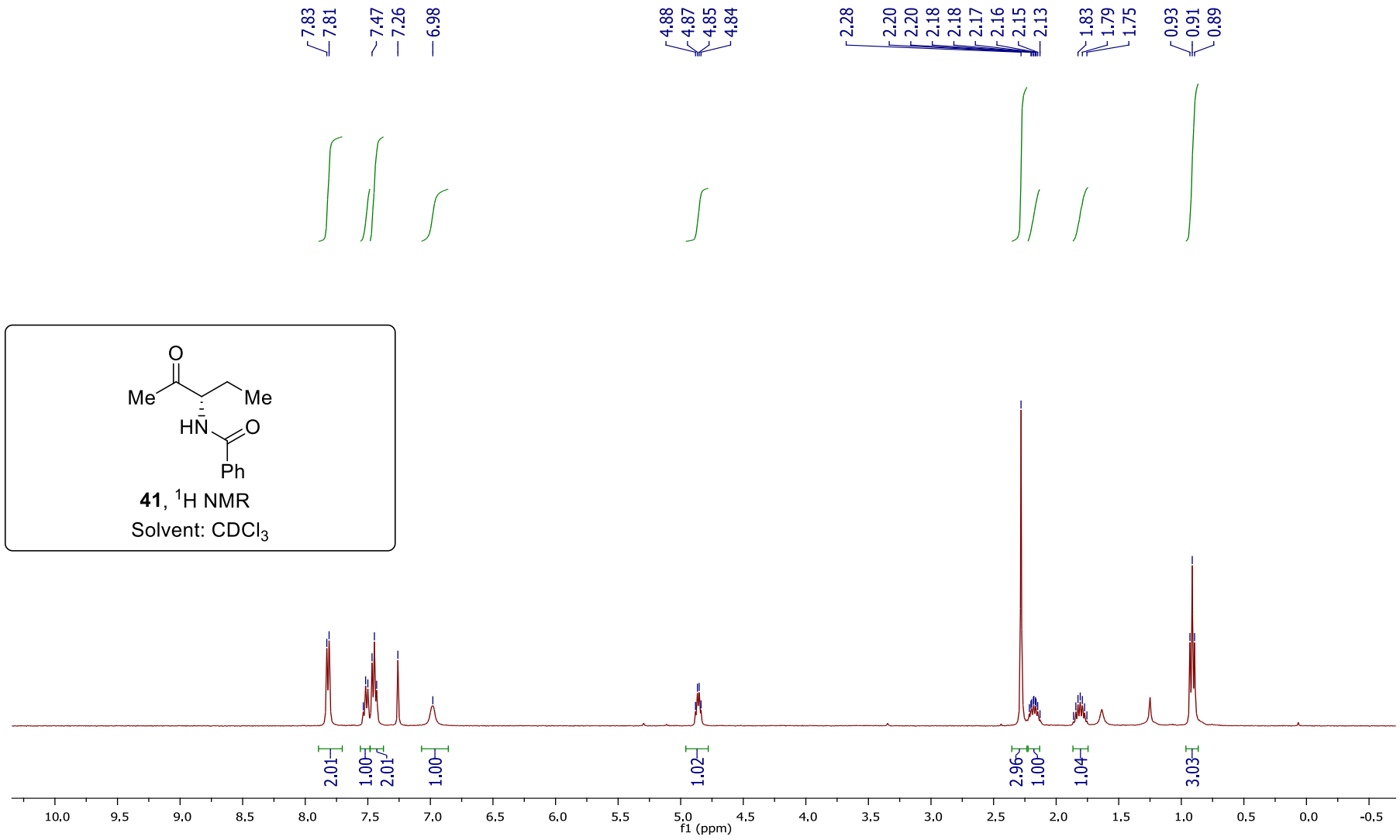
126.80
77.42
77.10
76.78
70.62
69.05
56.37
56.23
26.40
25.96
25.88
21.58
21.03
20.62
18.08
18.04
10.87
10.75
-4.07
-4.11
-4.82
OTBS
Me
Me
HN
O
Ph
40 (mixture of isomers), 13C NMR
Solvent: CDCl3
f1 (ppm)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7.81
7.47
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4.87
4.85
4.84
2.28
2.20
2.20
2.18
2.18
2.17
2.16
2.15
2.13
1.83
1.79
1.75
0.93
0.91
0.89
O
Me
Me
HN
O
Ph
41, 1H NMR
Solvent: CDCl3
2.01
1.00
2.01
1.00
1.02
2.96
1.00
1.04
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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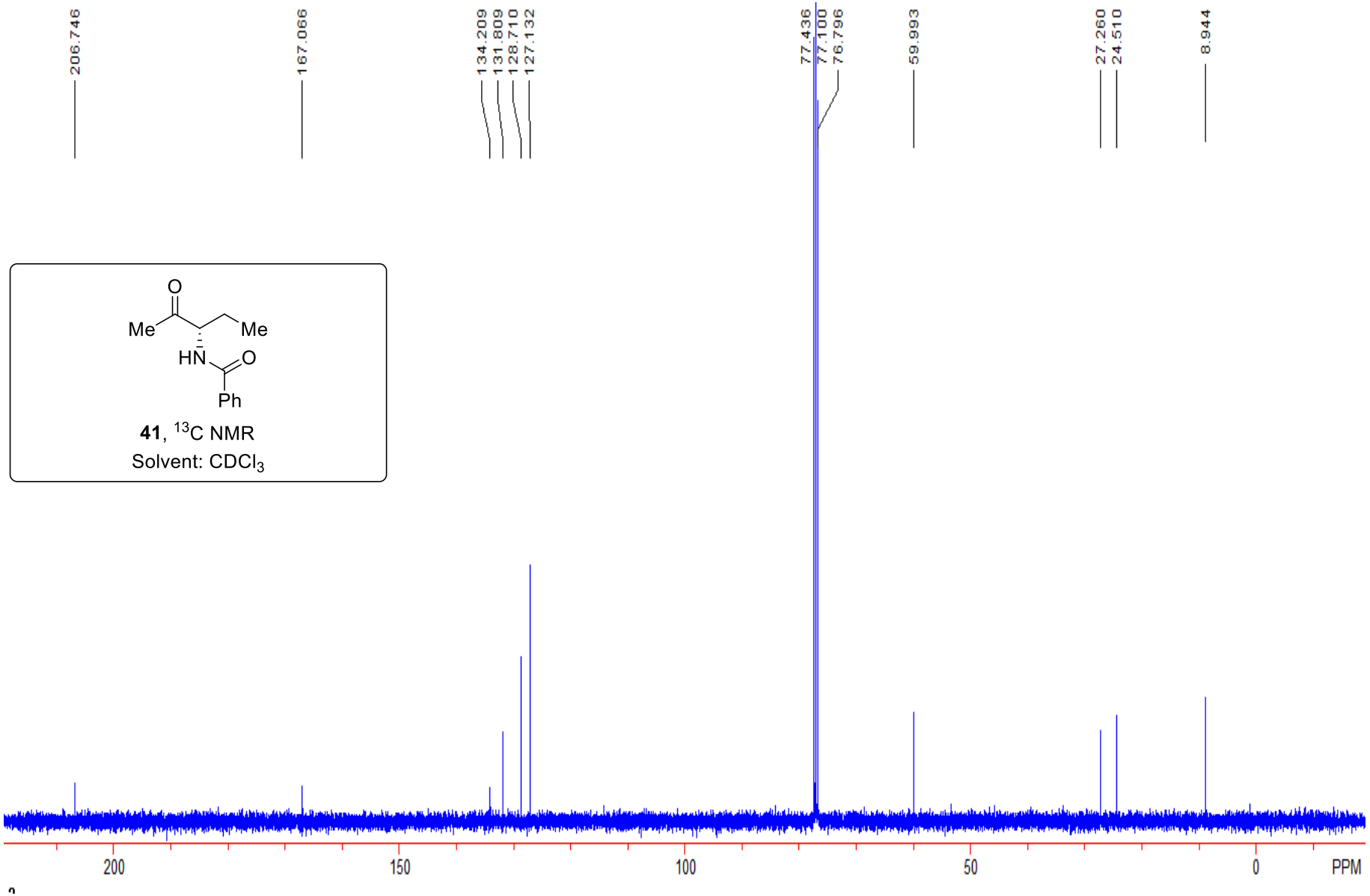
0.5
0.0
-0.5
f1 (ppm)


206.746
167.066
134.209
131.809
128.710
127.132
77.436
77.100
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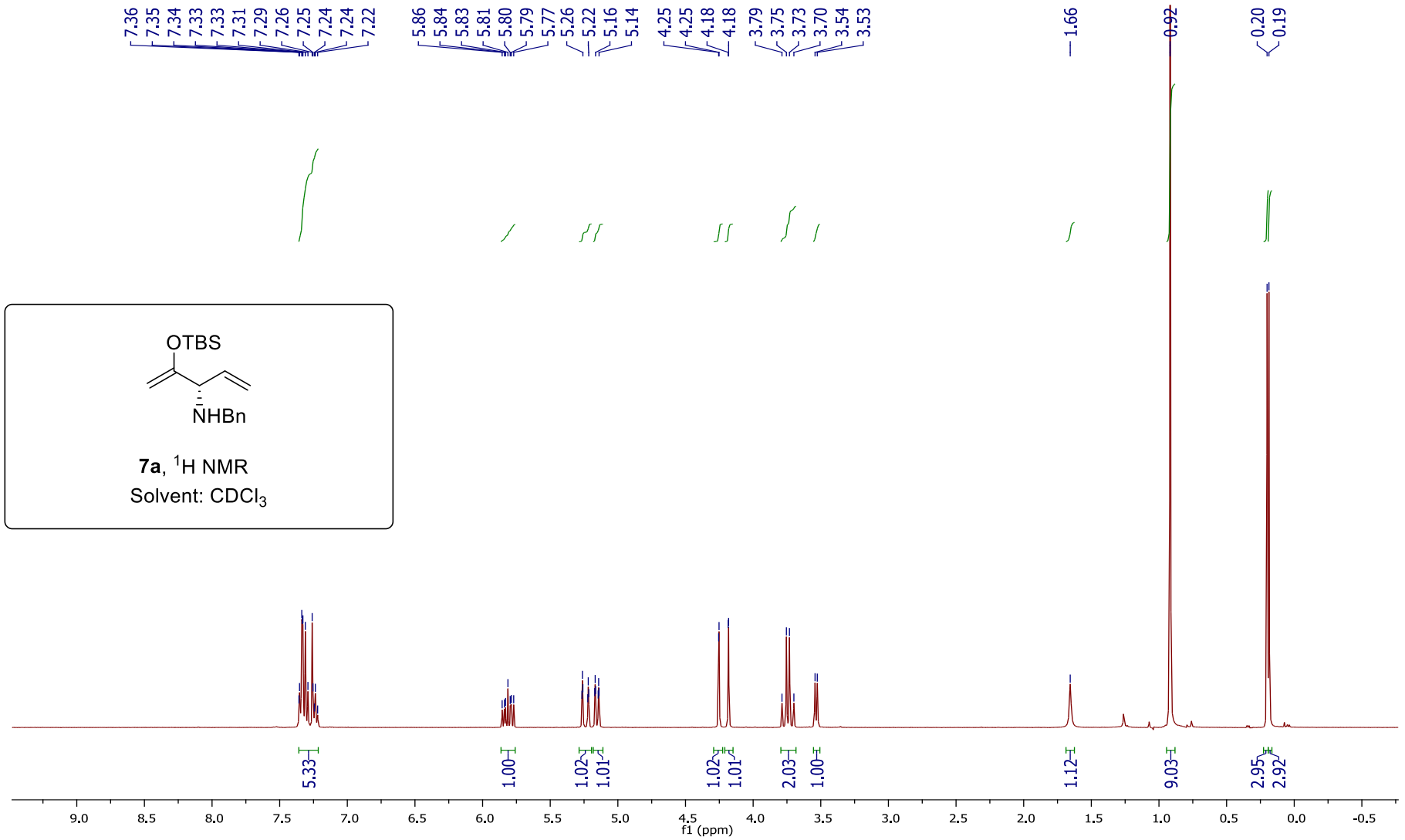
59.993
27.260
24.510
8.944
O
Me
Me
HN
O
Ph
41, 13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM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7.35
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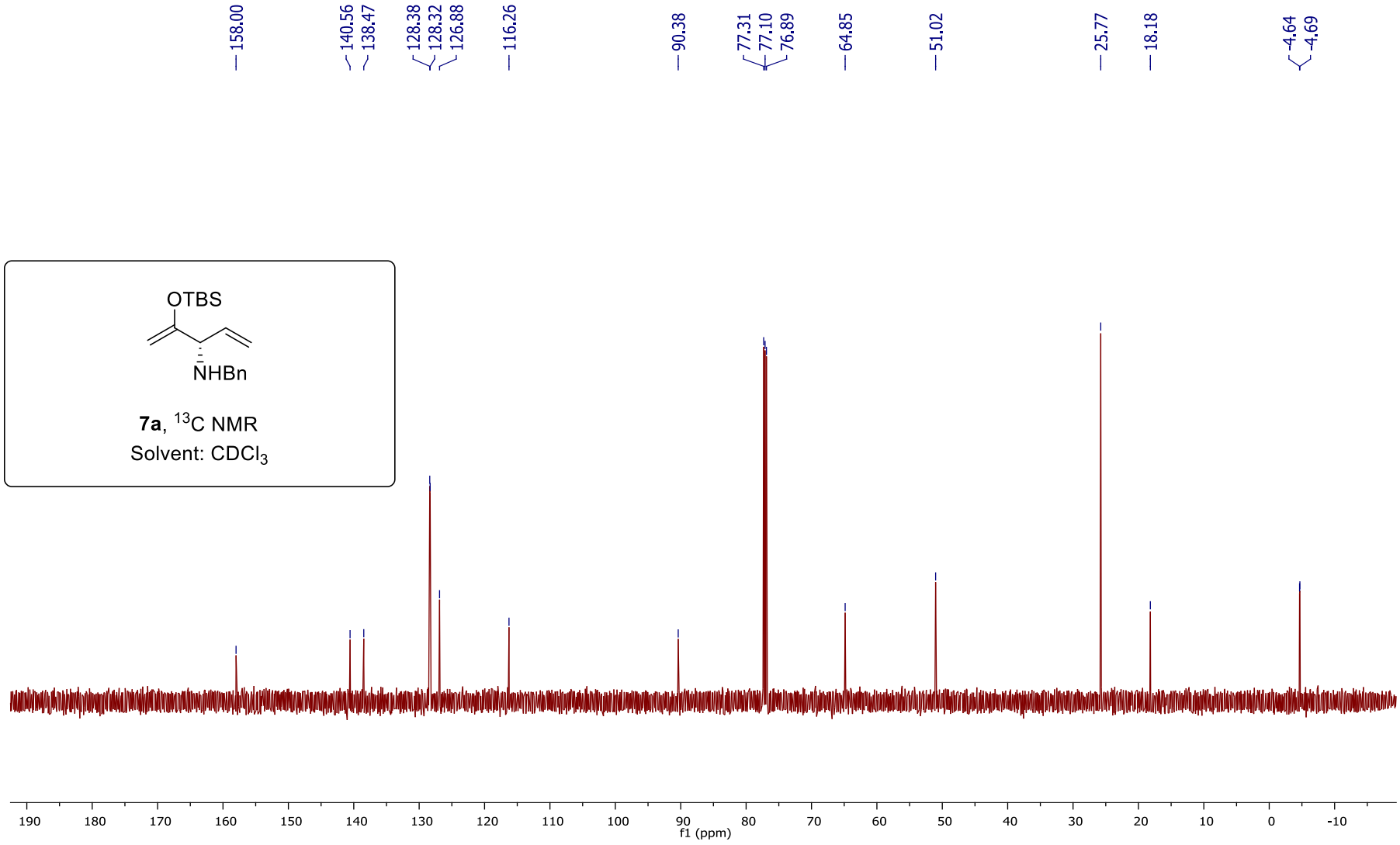
5.86
5.84
5.83
5.81
5.80
5.79
5.77
5.26
5.22
5.16
5.14
4.25
4.25
4.18
4.18
3.79
3.75
3.73
3.70
3.54
3.53
1.66
0.92
0.20
0.19
OTBS
NHBn
7a, 1H NMR
Solvent: CDCl3
5.33
1.00
1.02
1.01
1.02
1.01
2.03
1.00
1.12
9.03
2.95
2.92
f1 (ppm)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140.56
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128.38
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126.88
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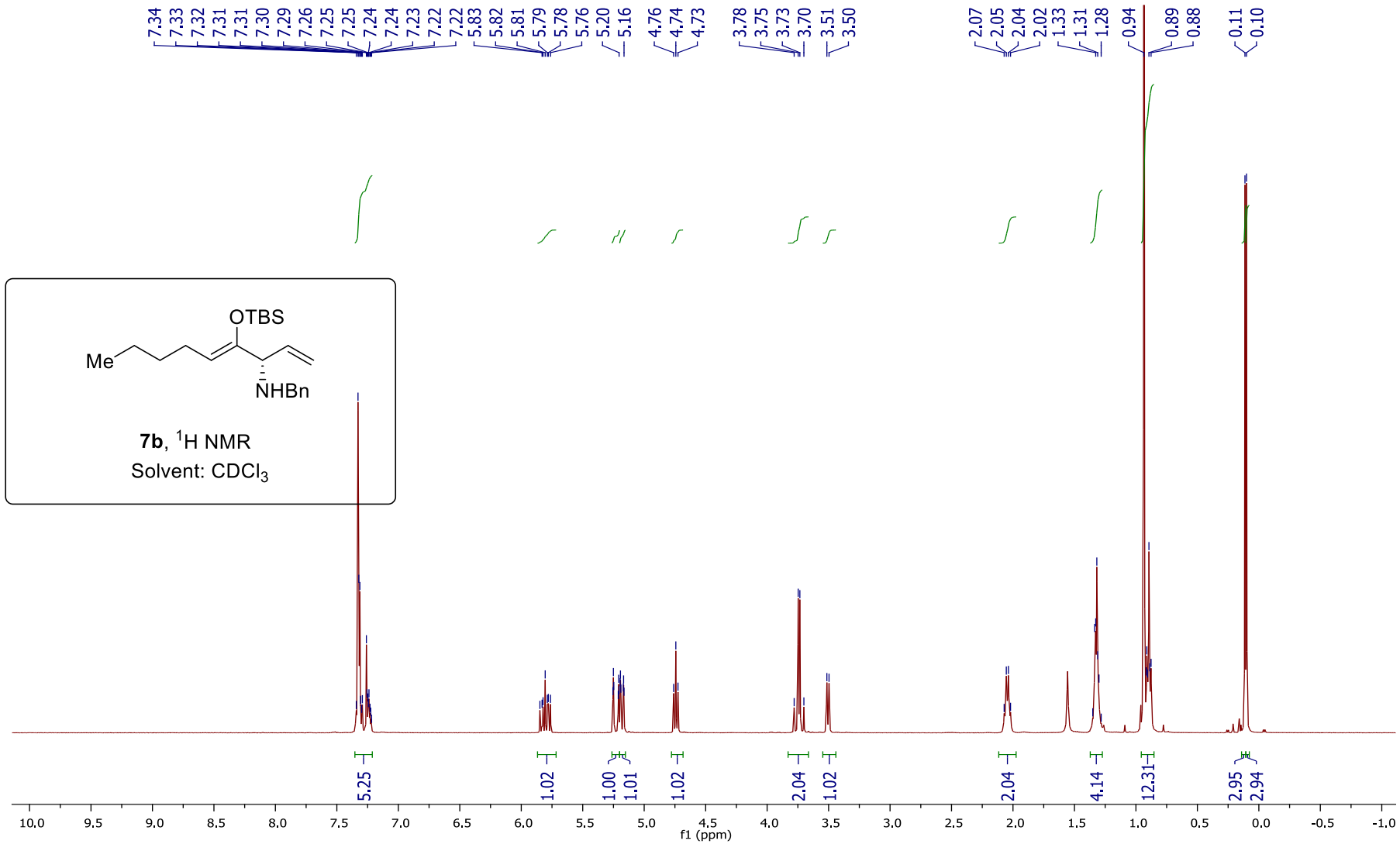
90.38
77.31
77.10
76.89
64.85
51.02
25.77
18.18
-4.64
-4.69
OTBS
NHBn
7a, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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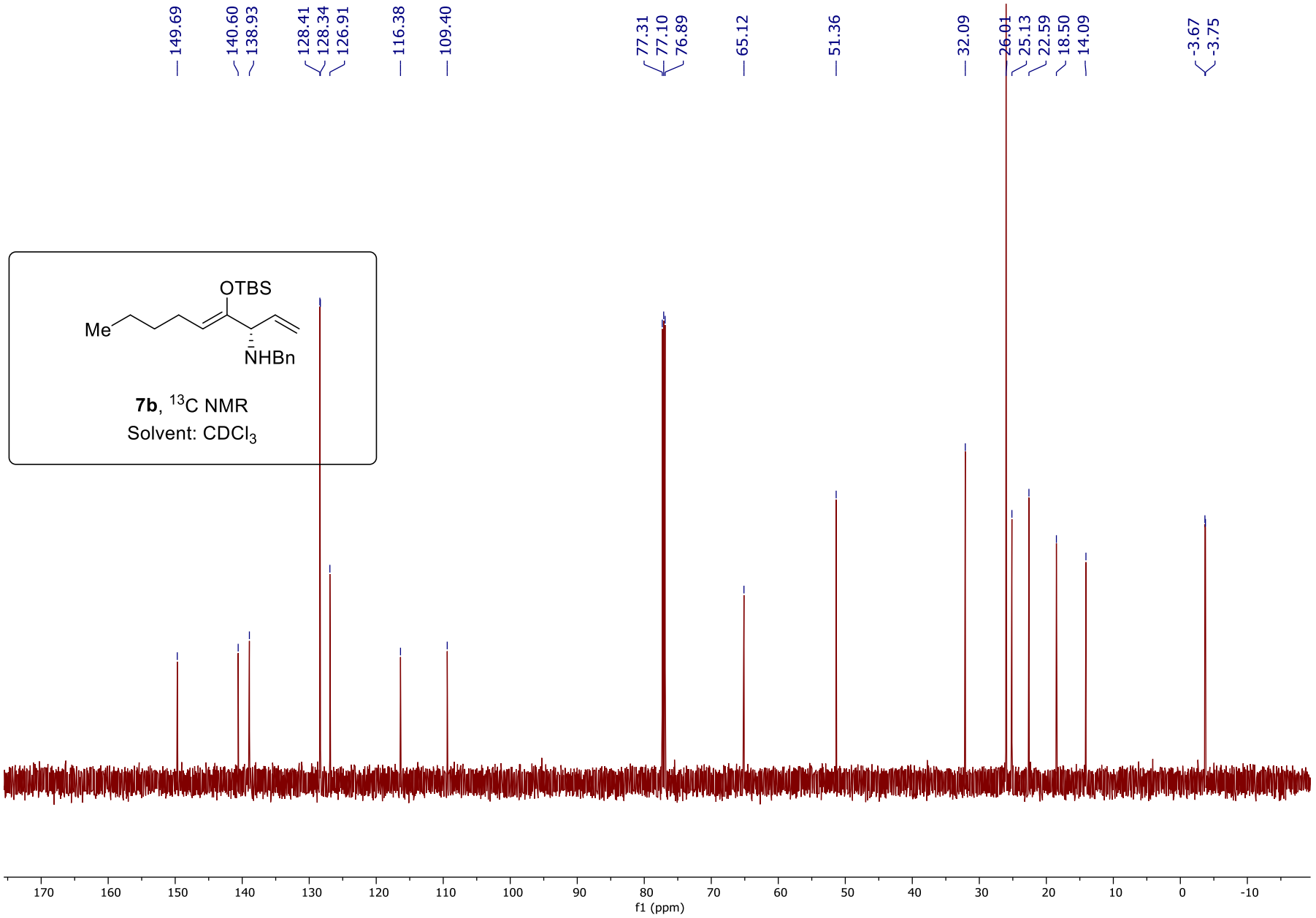
7.33
7.32
7.31
7.31
7.30
7.29
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
5.83
5.82
5.81
5.79
5.78
5.76
5.20
5.16
4.76
4.74
4.73
3.78
3.75
3.73
3.70
3.51
3.50
2.07
2.05
2.04
2.02
1.33
1.31
1.28
0.94
0.89
0.88
0.11
0.10
OTBS
Me
NHBn
7b, 1H NMR
Solvent: CDCl3
5.25
1.02
1.00
1.01
1.02
2.04
1.02
2.04
4.14
12.31
2.95
2.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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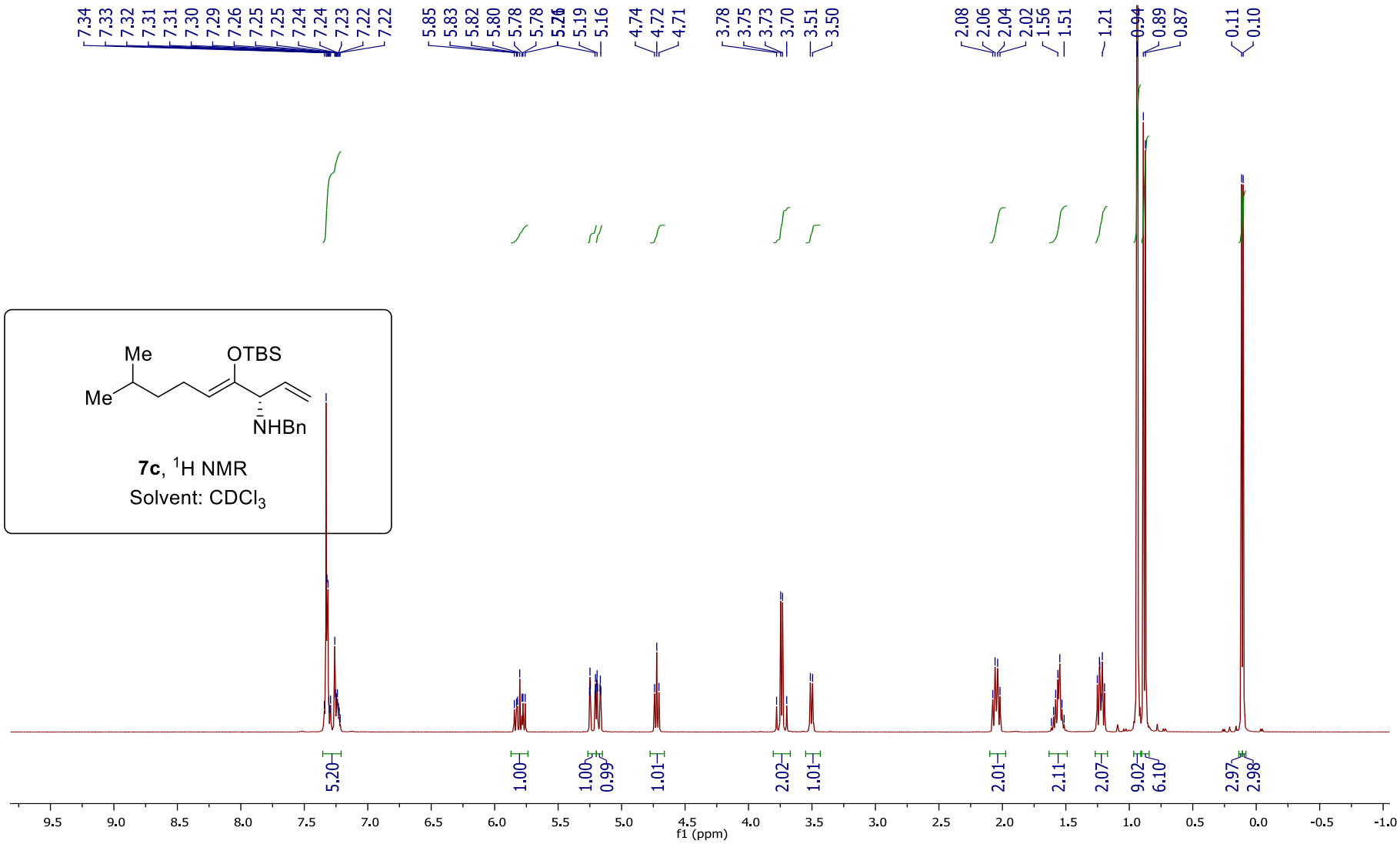
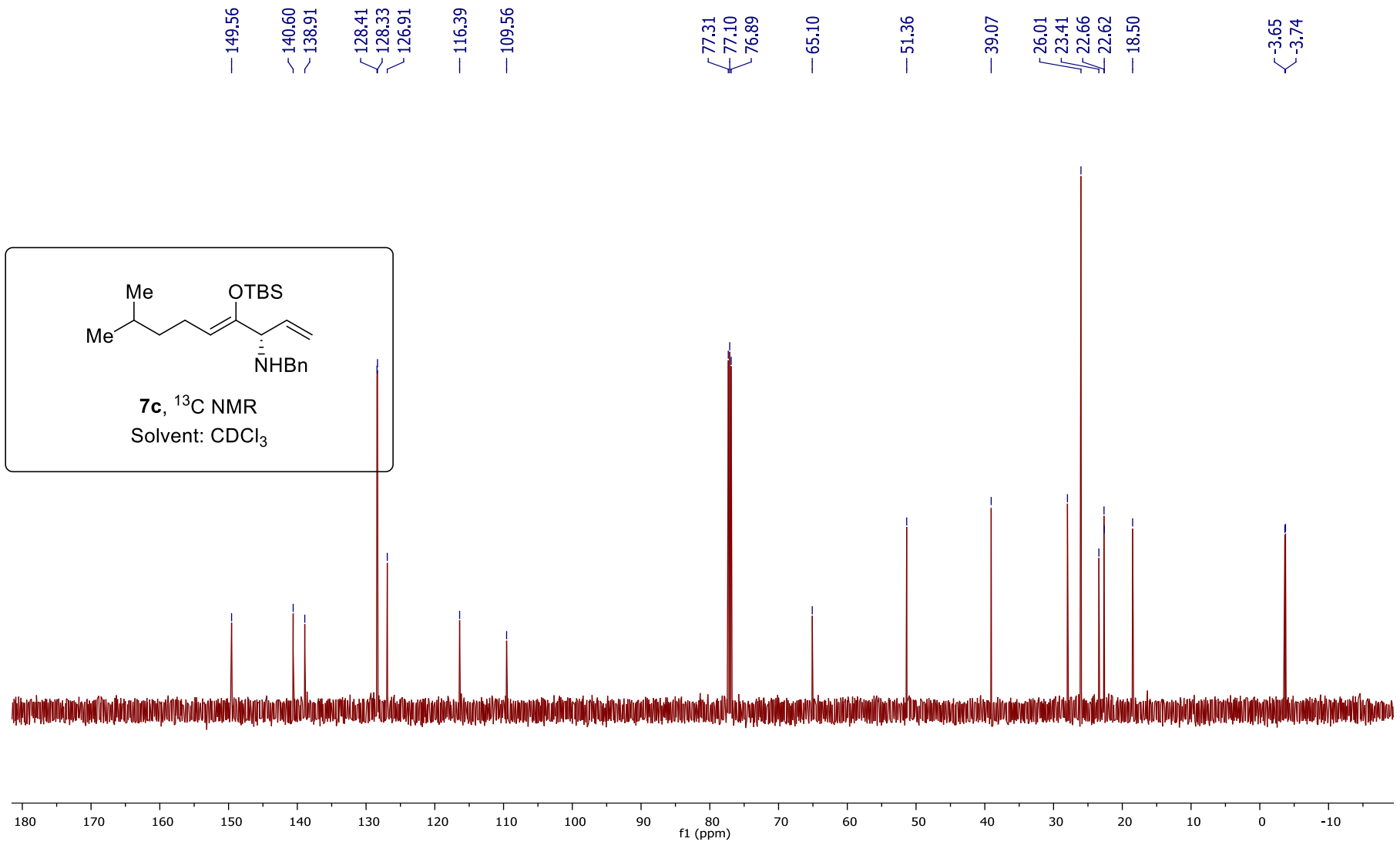
126.91
116.38
109.40
77.31
77.10
76.89
65.12
51.36
32.09
26.01
25.13
22.59
18.50
14.09
-3.67
-3.75
OTBS
Me
NHBn
7b, 13C NMR
Solvent: CDCl3
f1 (ppm)


Me
OTBS
Me
NHBn
7c, 1H NMR
Solvent: CDCl3
f1 (ppm)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140.60
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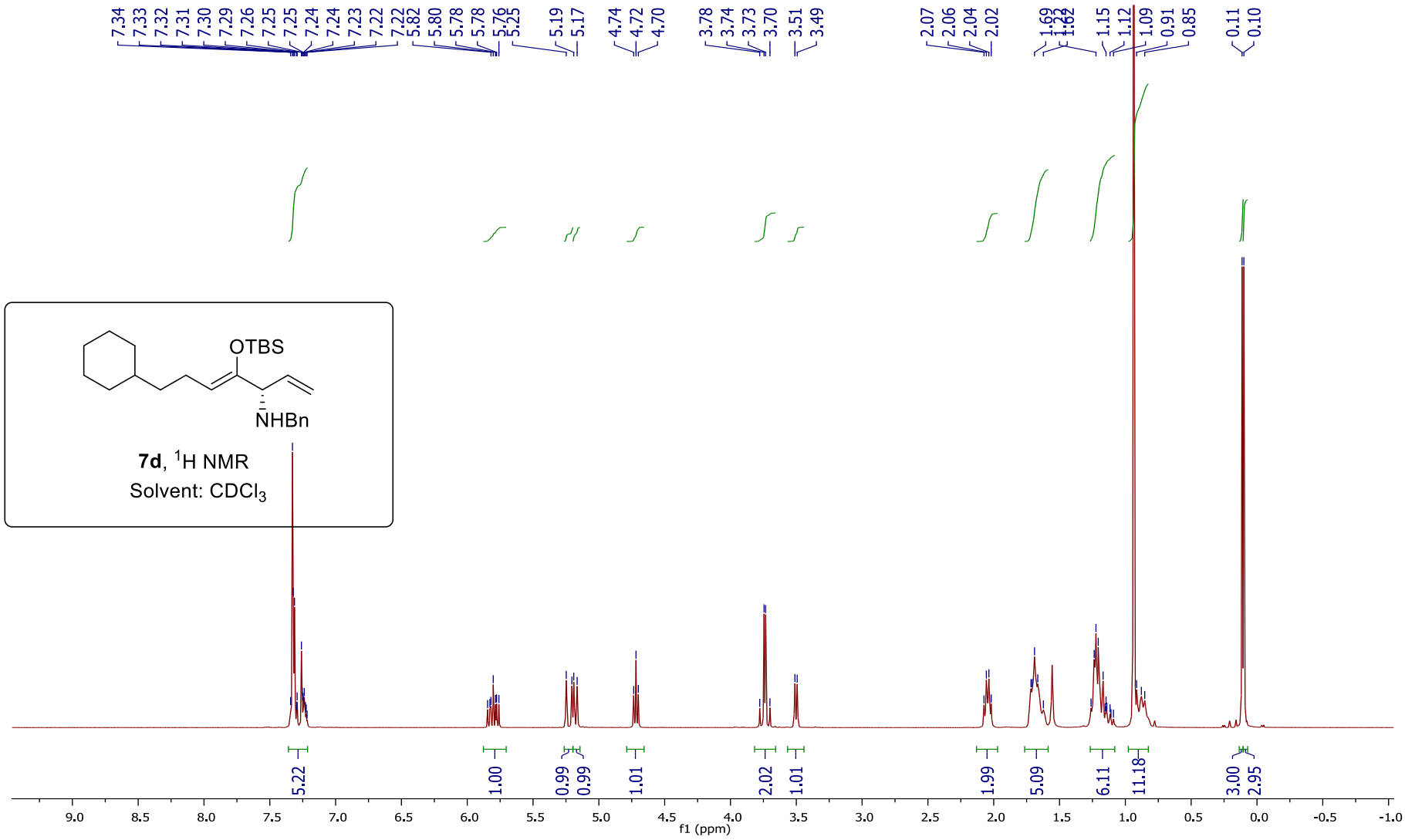
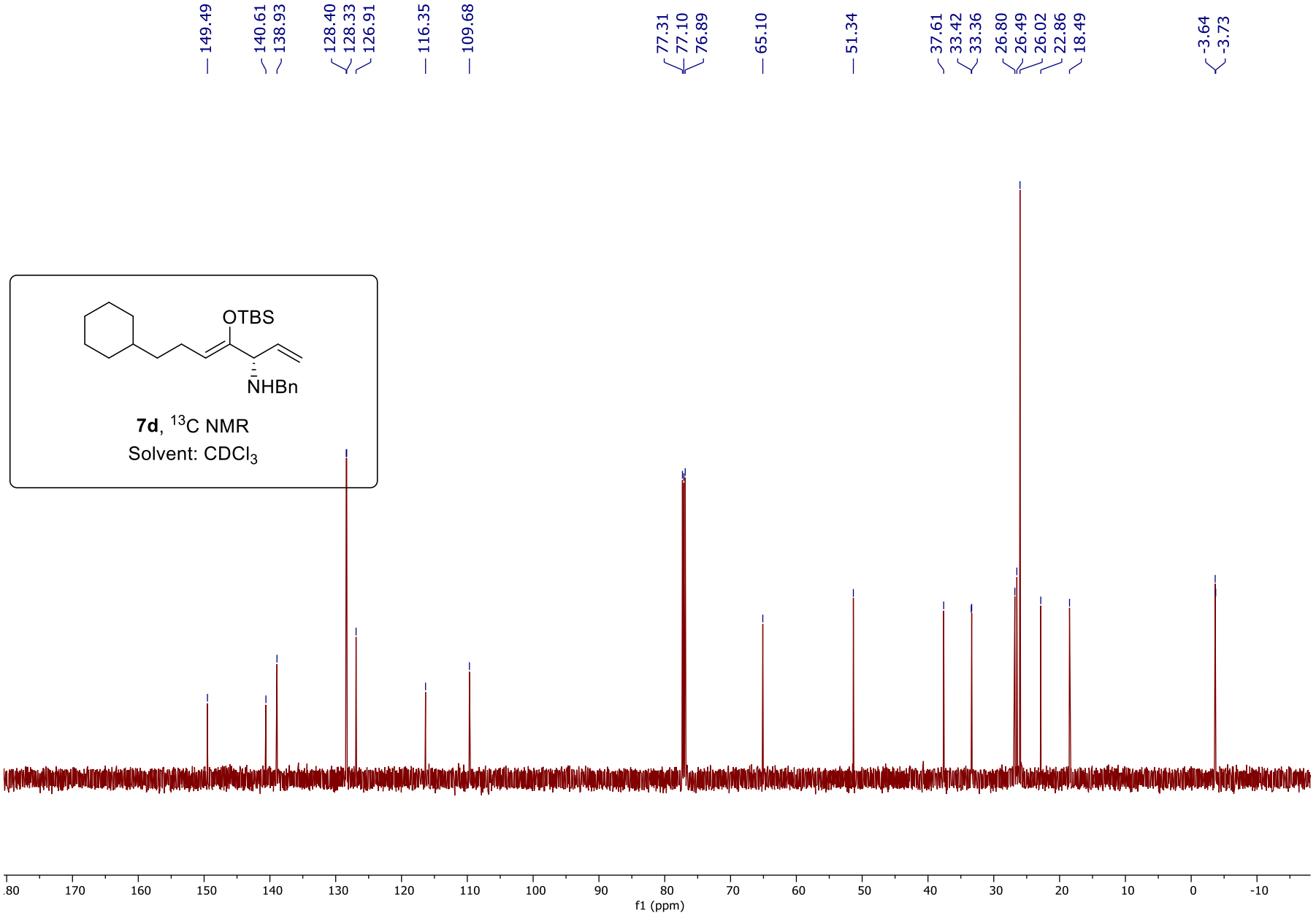
126.91
116.39
109.56
77.31
77.10
76.89
65.10
51.36
39.07
26.01
23.41
22.66
22.62
18.50
-3.65
-3.74
Me
OTBS
Me
NHBn
7c, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
NHBn
7d, 1H NMR
Solvent: CDCl3
f1 (ppm)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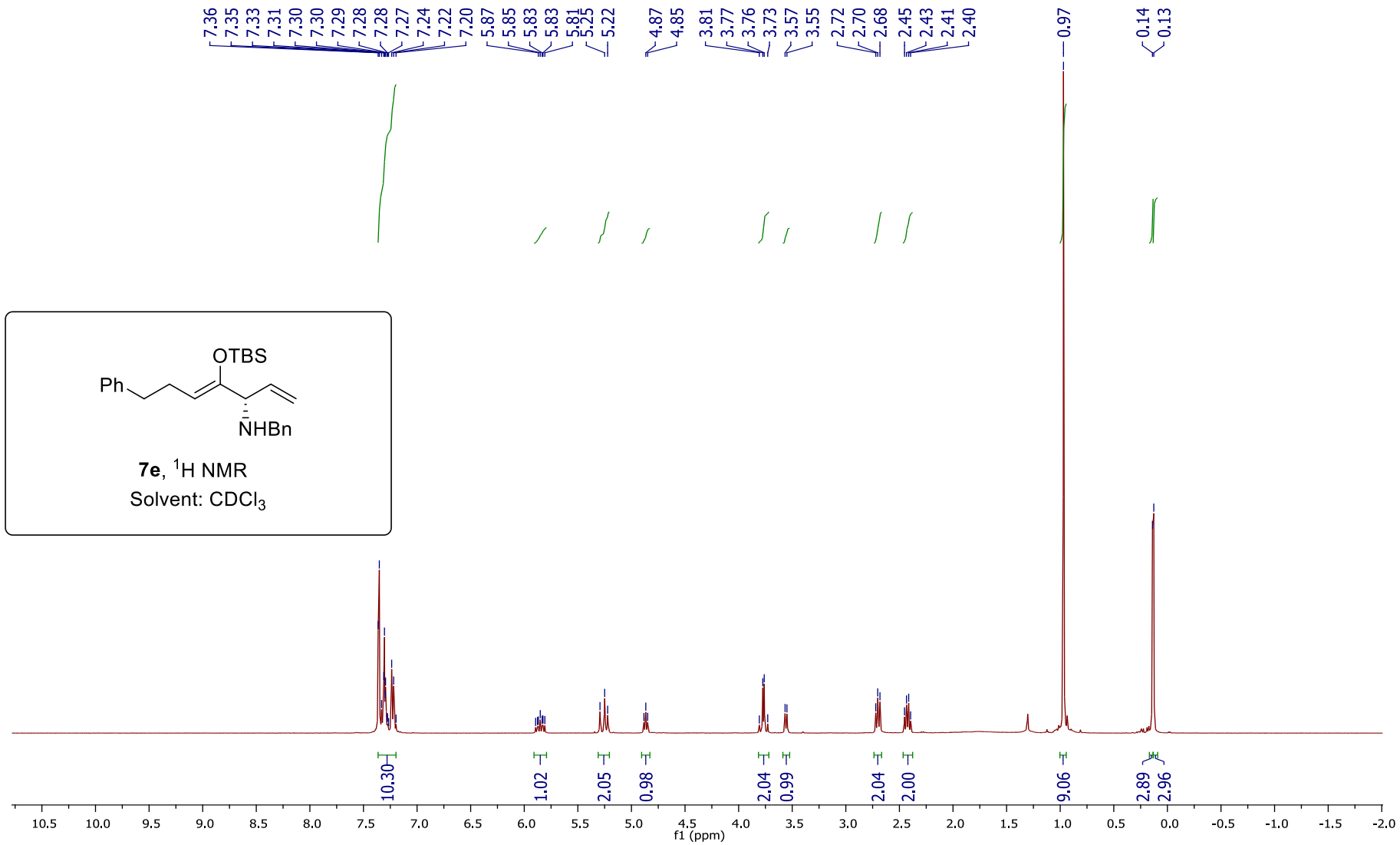
126.91
116.35
109.68
77.31
77.10
76.89
65.10
51.34
37.61
33.42
33.36
26.80
26.49
26.02
22.86
18.49
-3.64
-3.73
OTBS
NHBn
7d, 13C NMR
Solvent: CDCl3
f1 (ppm)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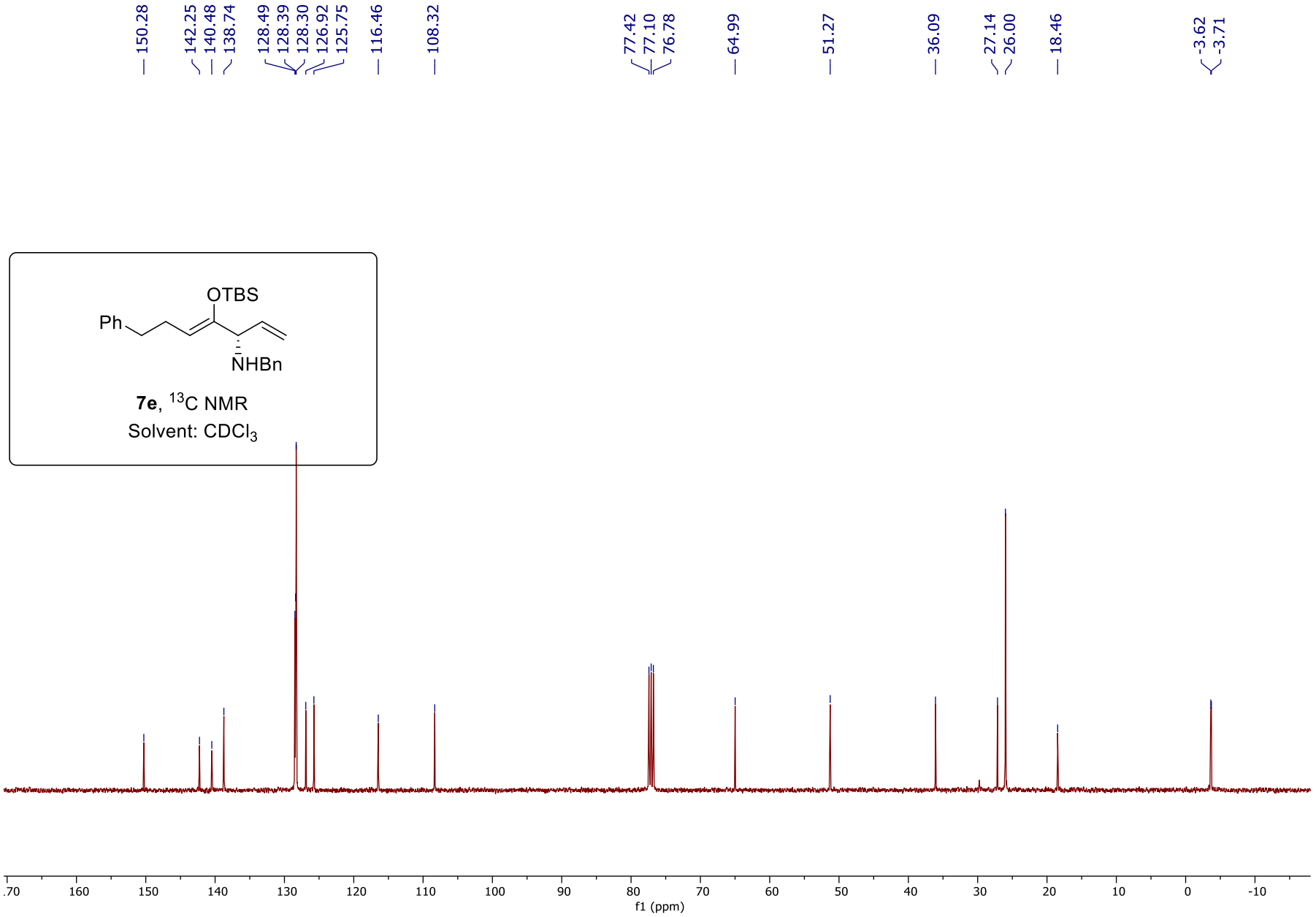
7.33
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.24
7.22
7.20
5.87
5.85
5.83
5.83
5.81
5.25
5.22
4.87
4.85
3.81
3.77
3.76
3.73
3.57
3.55
2.72
2.70
2.68
2.45
2.43
2.41
2.40
0.97
0.14
0.13
OTBS
Ph
NHBn
7e, 1H NMR
Solvent: CDCl3
10.30
1.02
2.05
0.98
2.04
0.99
2.04
2.00
9.06
2.89
2.96
f1 (ppm)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142.25
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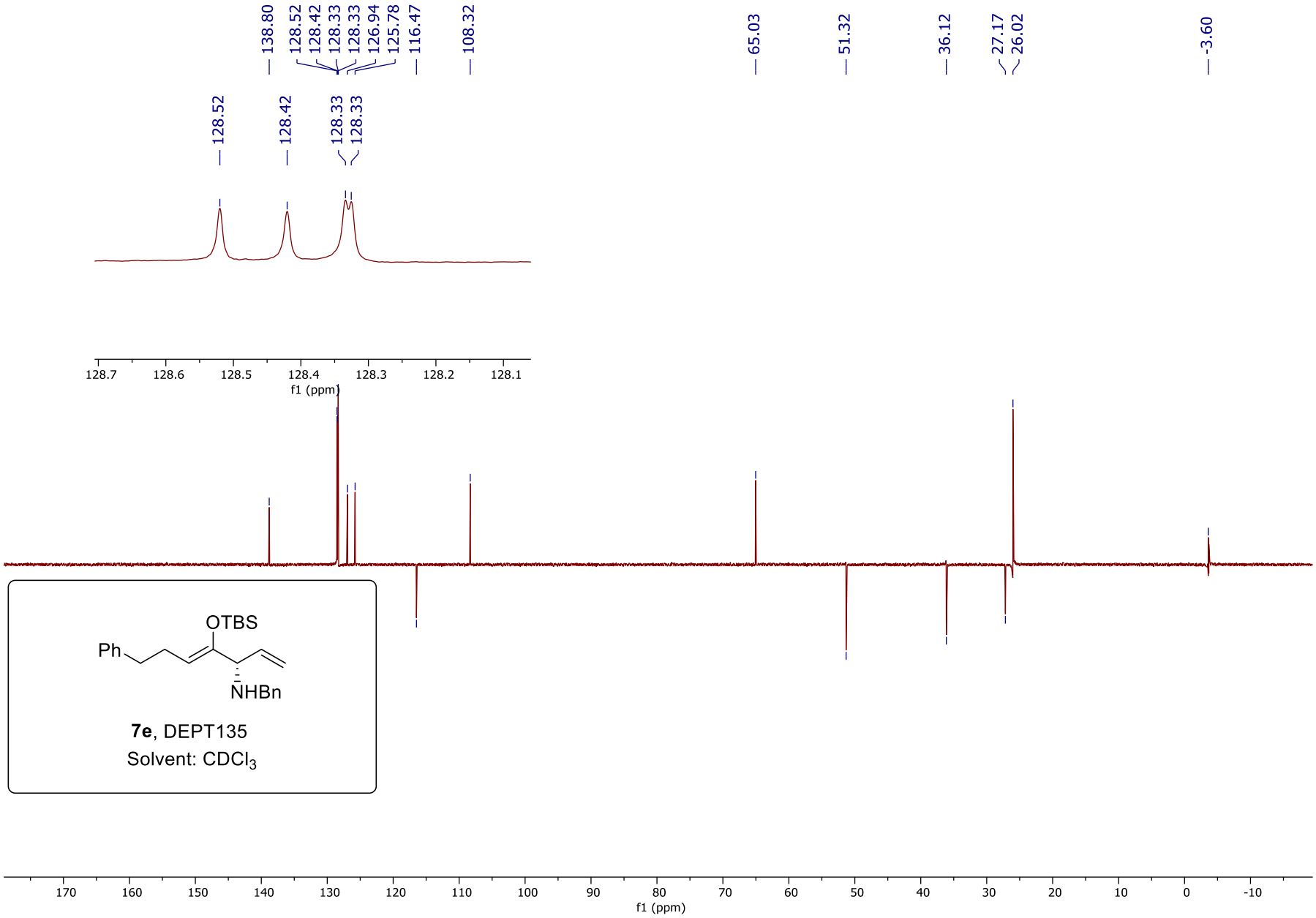
128.39
128.30
126.92
125.75
116.46
108.32
77.42
77.10
76.78
64.99
51.27
36.09
27.14
26.00
18.46
-3.62
-3.71
OTBS
Ph
NHBn
7e, 13C NMR
Solvent: CDCl3
f1 (ppm)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128.52
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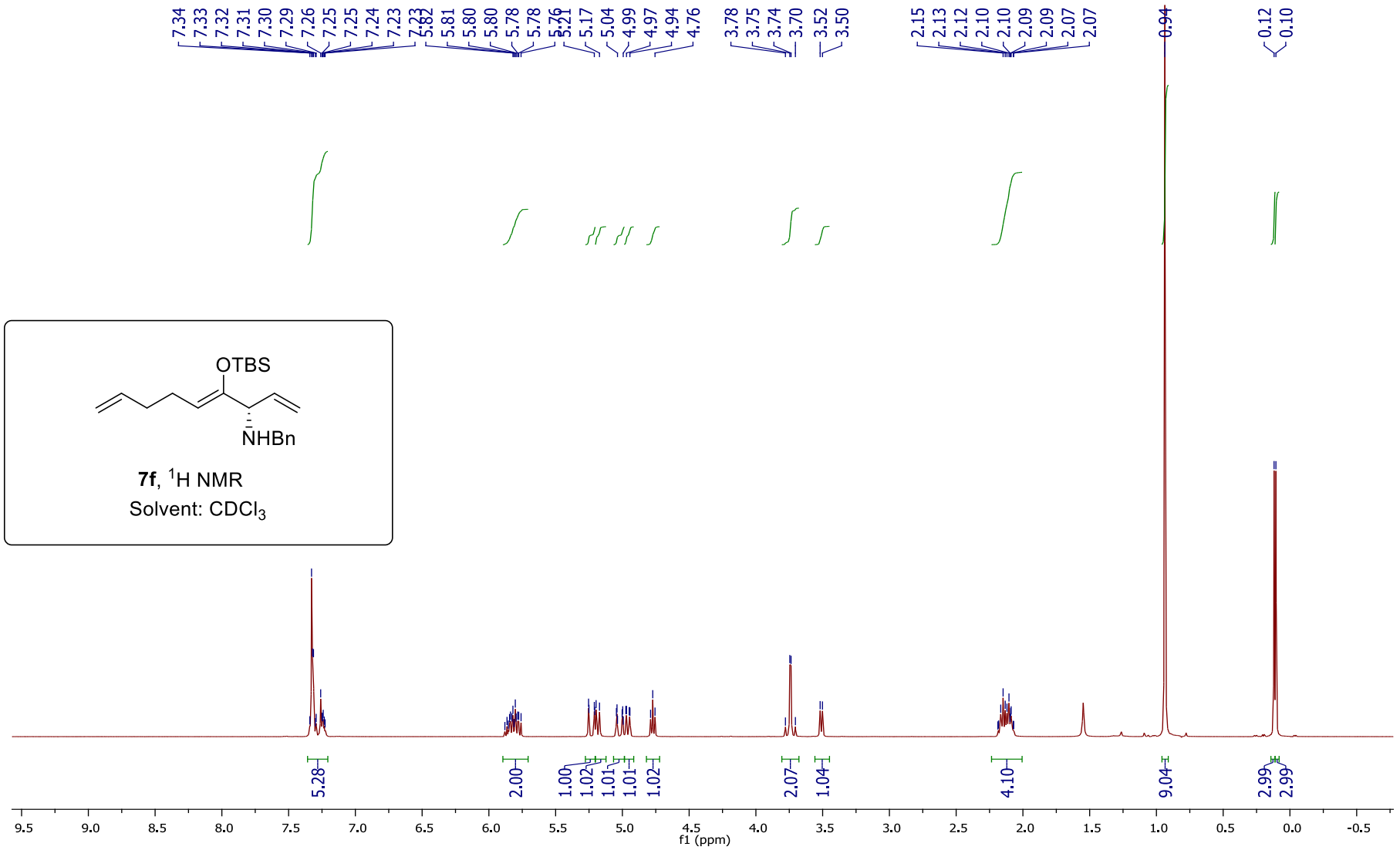
128.33
128.33
126.94
125.78
116.47
108.32
65.03
51.32
36.12
27.17
26.02
-3.60
128.52
128.42
128.33
128.33
128.7
128.6
128.5
128.4
128.3
128.2
128.1
f1 (ppm)
OTBS
Ph
NHBn
7e, DEPT135
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.33
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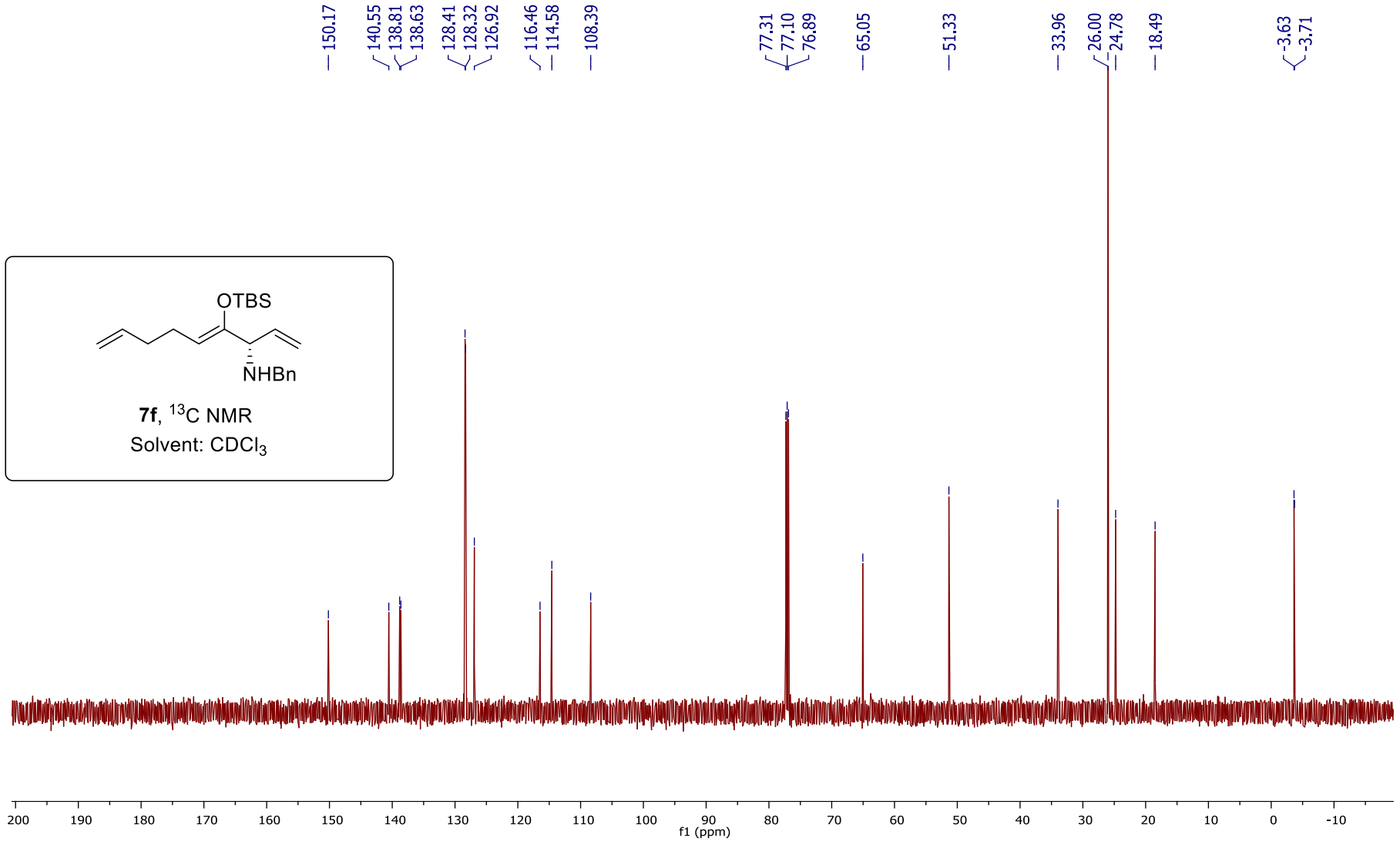
7.29
7.26
7.25
7.25
7.24
7.23
5.82
5.81
5.80
5.80
5.78
5.78
5.21
5.17
5.04
4.99
4.97
4.94
4.76
3.78
3.75
3.74
3.70
3.52
3.50
2.15
2.13
2.12
2.10
2.10
2.09
2.09
2.07
2.07
0.94
0.12
0.10
OTBS
NHBn
7f, 1H NMR
Solvent: CDCl3
5.28
2.00
1.00
1.02
1.01
1.01
1.02
2.07
1.04
4.10
9.04
2.99
2.99
f1 (ppm)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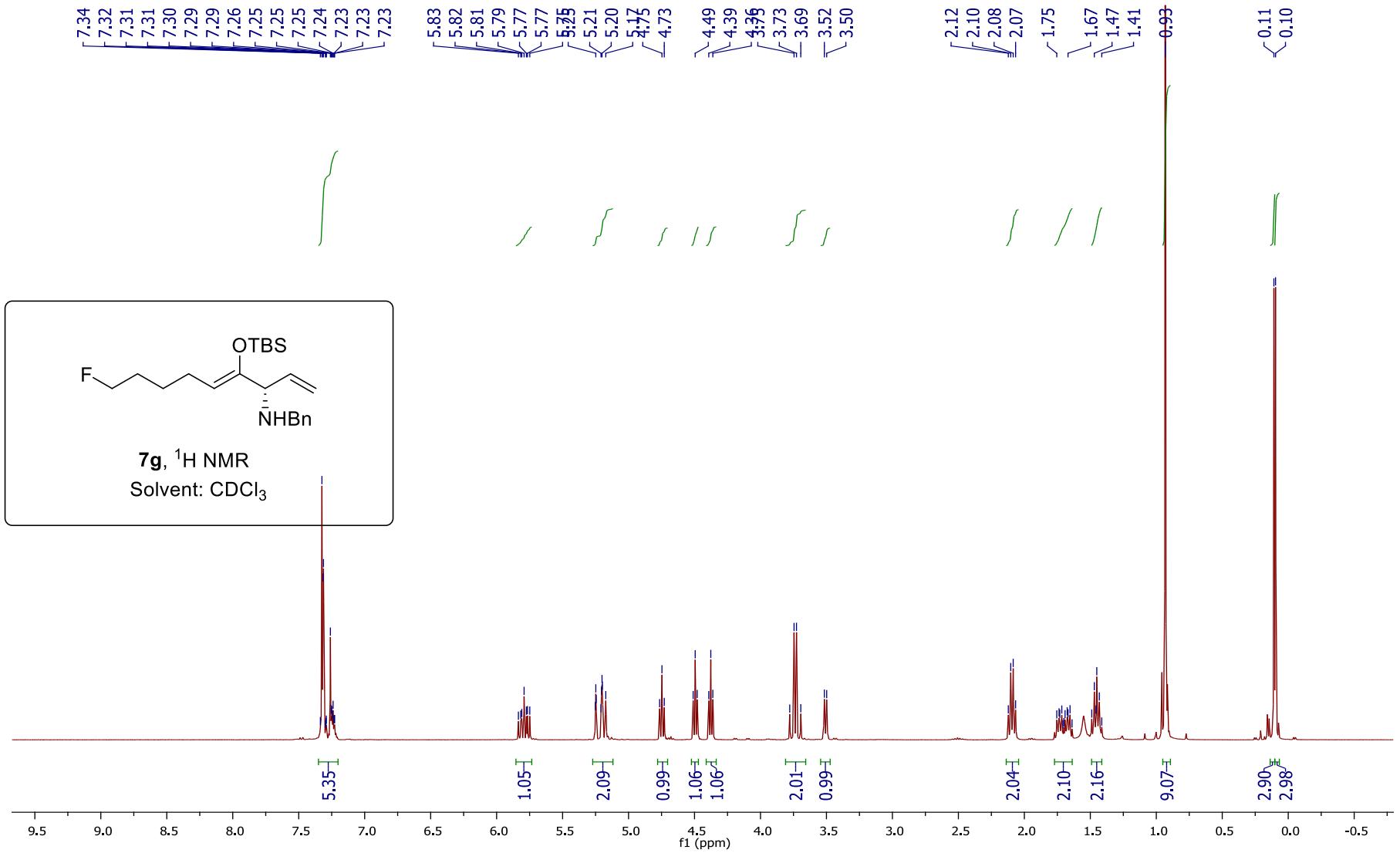
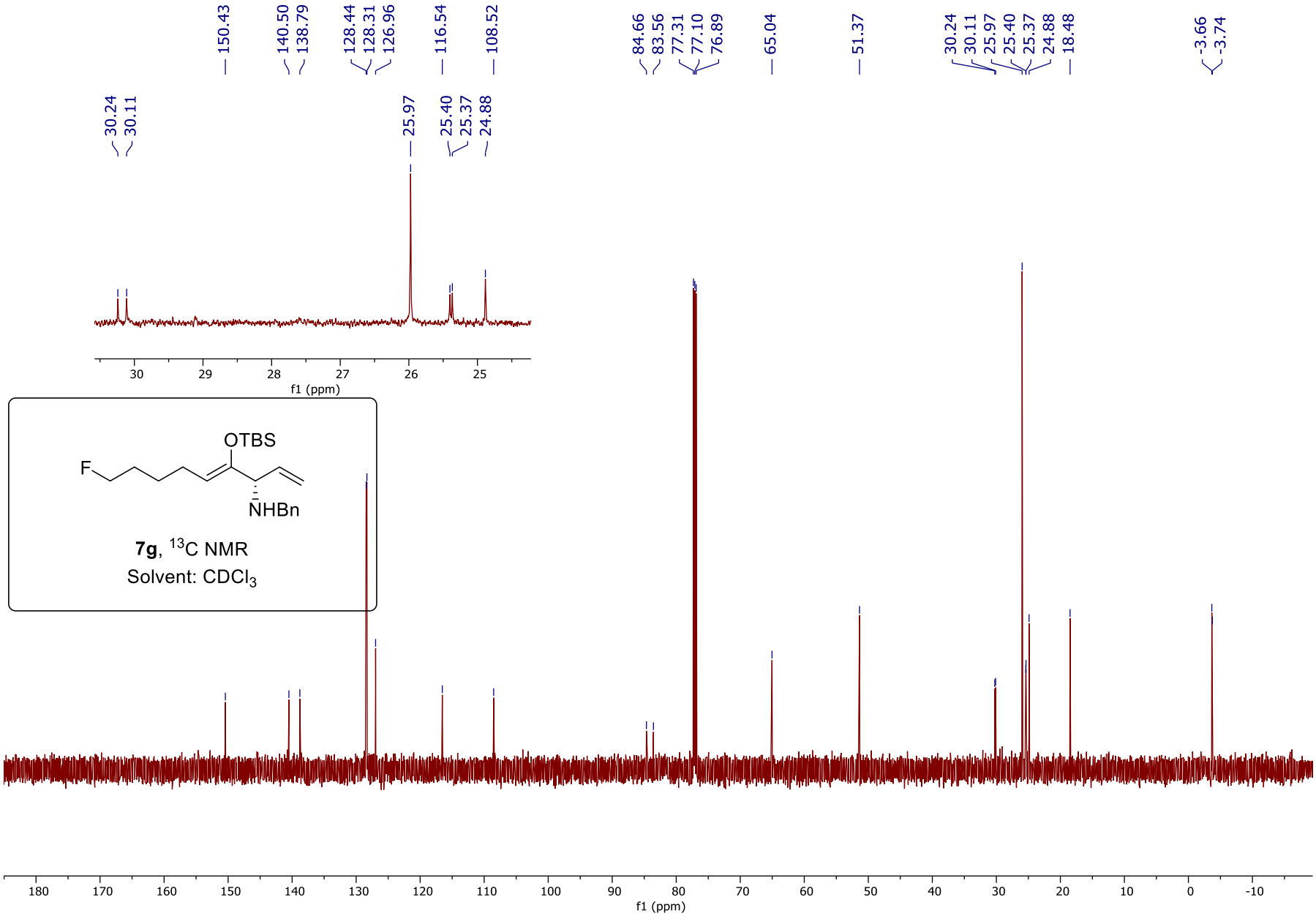
116.46
114.58
108.39
77.31
77.10
76.89
65.05
51.33
33.96
26.00
24.78
18.49
-3.63
-3.71
OTBS
NHBn
7f, 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
F
NHBn
7g, 1H NMR
Solvent: CDCl3
f1 (ppm)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77.10
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65.04
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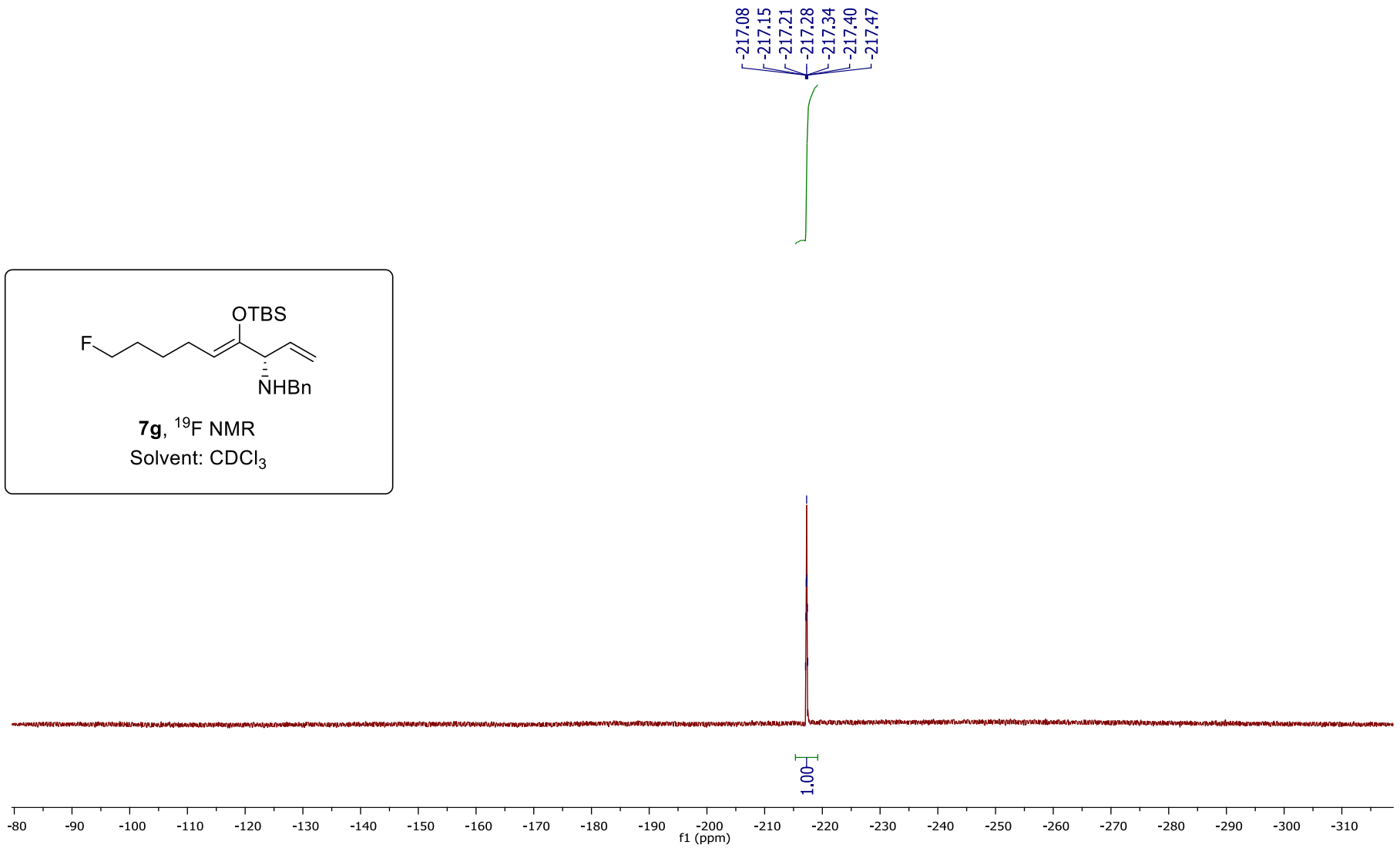
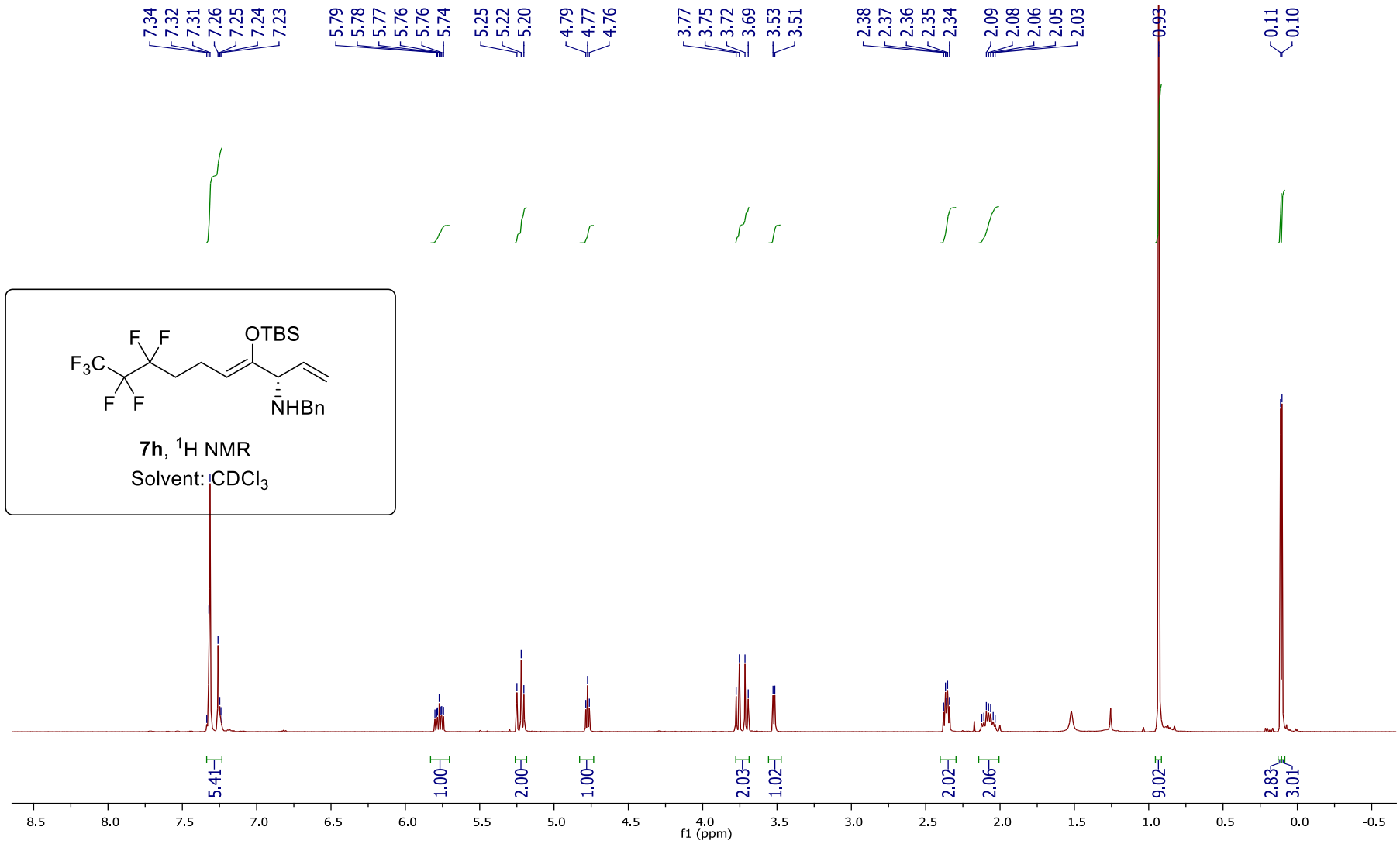
30.24
30.11
25.97
25.40
25.37
24.88
18.48
-3.66
-3.74
f1 (ppm)
OTBS
F
NHBn
7g, 13C NMR
Solvent: CDCl3


-217.08
-217.15
-217.21
-217.28
-217.34
-217.40
-217.47
OTBS
F
NHBn
7g, 19F NMR
Solvent: CDCl3
1.00
-80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290 -300 -310
f1 (ppm)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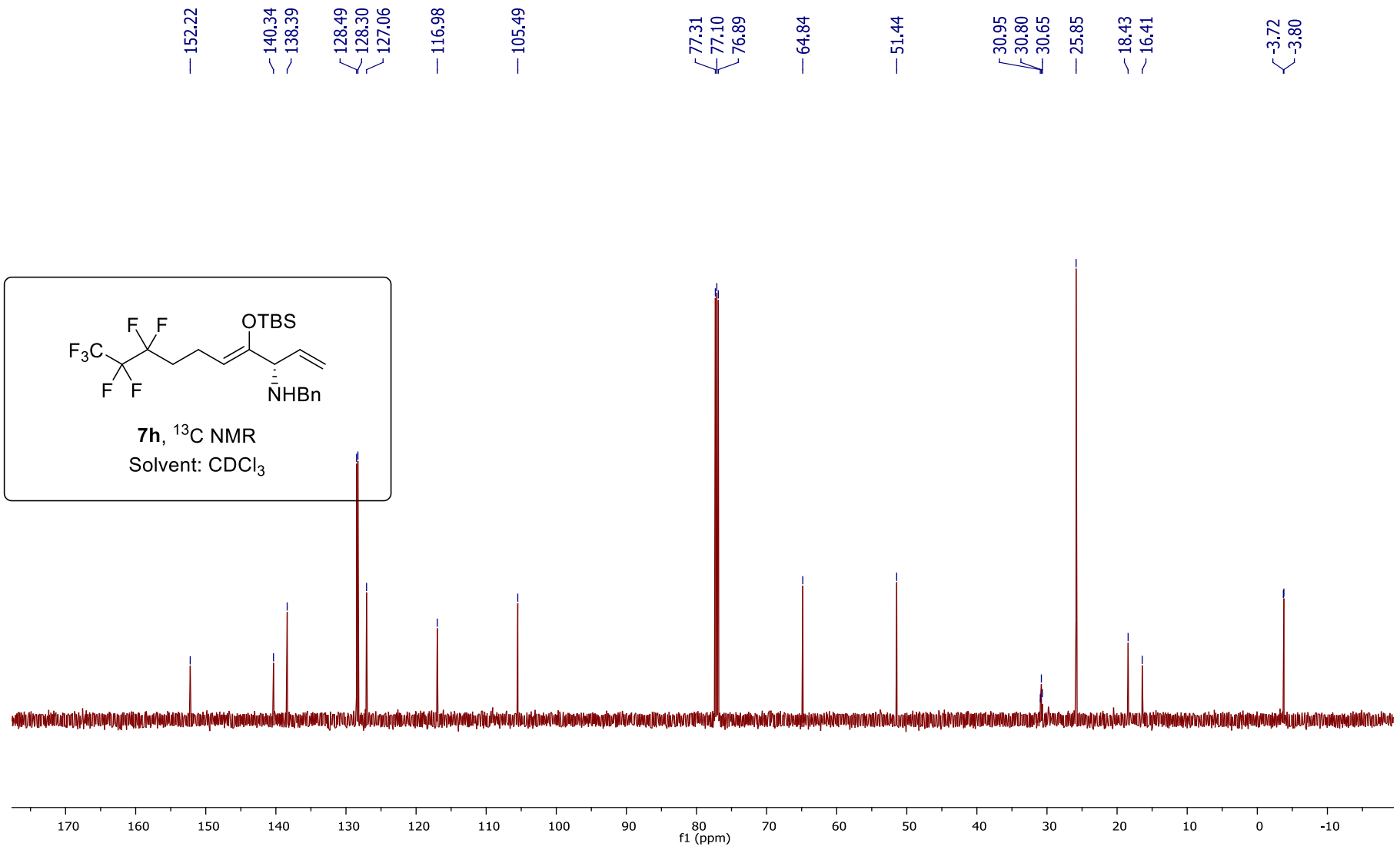
5.79
5.78
5.77
5.76
5.76
5.74
5.25
5.22
5.20
4.79
4.77
4.76
3.77
3.75
3.72
3.69
3.53
3.51
2.38
2.37
2.36
2.35
2.34
2.09
2.08
2.06
2.05
2.03
0.93
0.11
0.10
F
F
OTBS
F3C
F
F
NHBn
7h, 1H NMR
Solvent: CDCl3
5.41
1.00
2.00
1.00
2.03
1.02
2.02
2.06
9.02
2.83
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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140.34
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128.30
127.06
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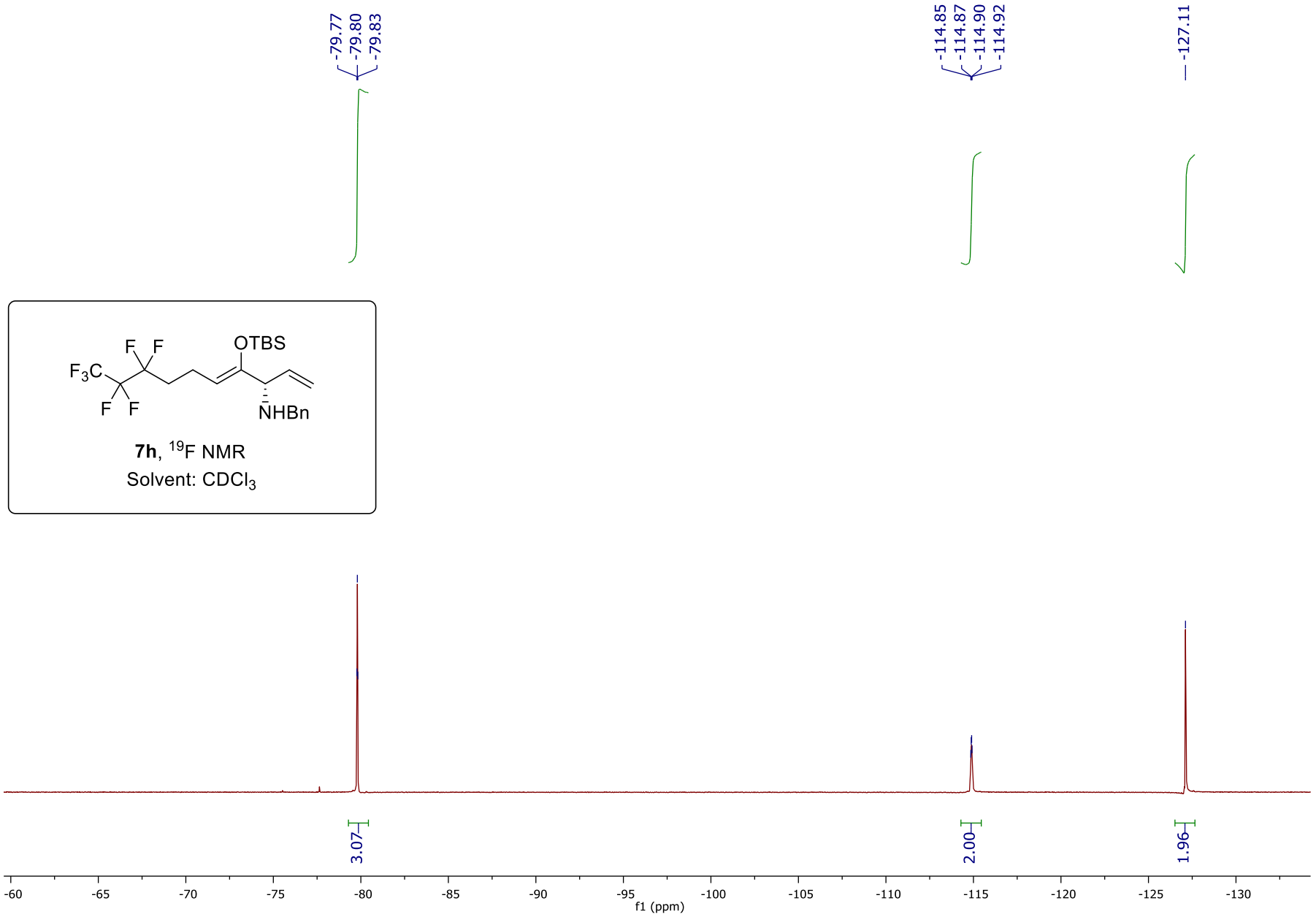
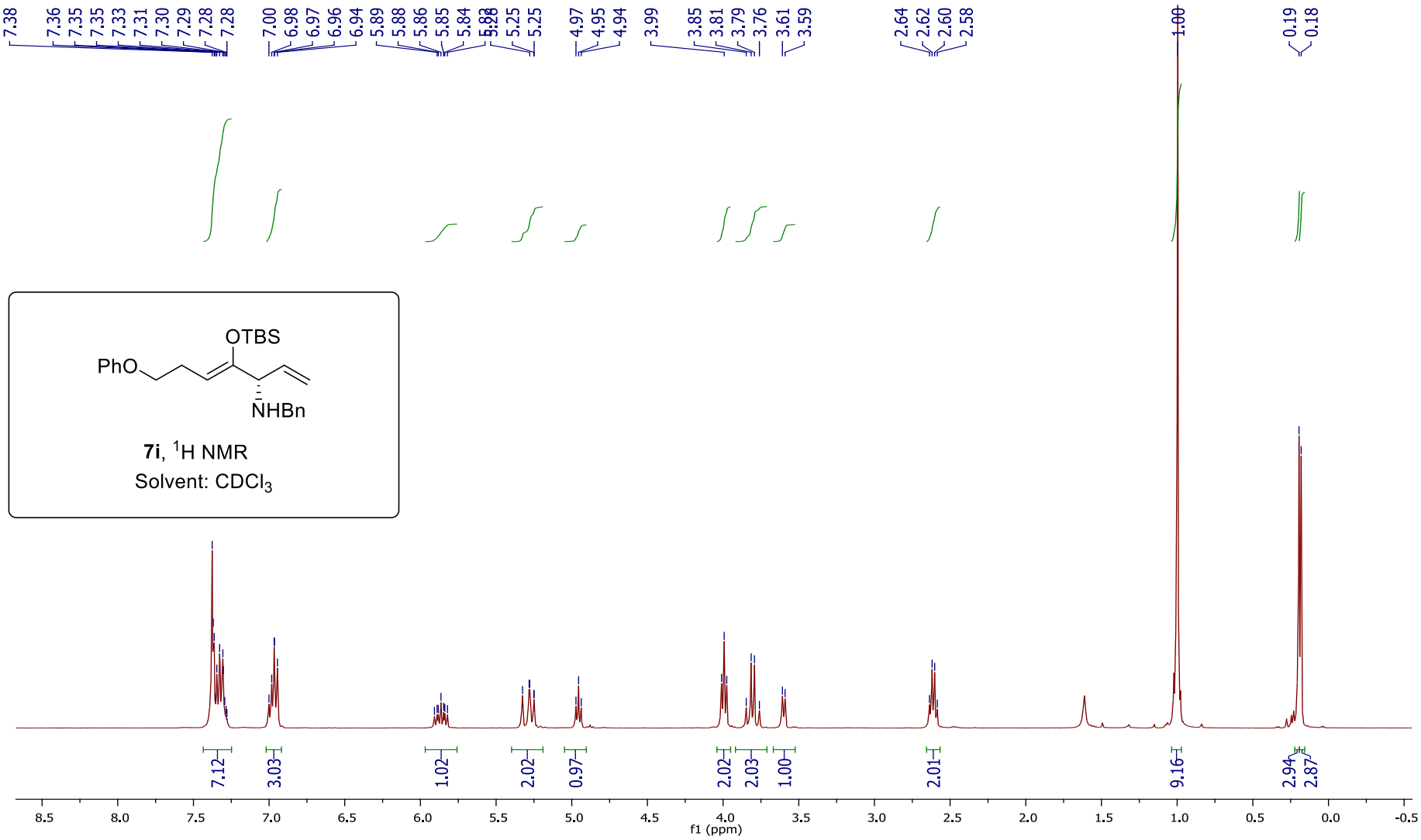
105.49
77.31
77.10
76.89
64.84
51.44
30.95
30.80
30.65
25.85
18.43
16.41
-3.72
-3.80
F
F
OTBS
F3C
F
F
NHBn
7h, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-79.77
-79.80
-79.83
-114.85
-114.87
-114.90
-114.92
-127.11
F
F
OTBS
F3C
F
F
NHBn
7h, 19F NMR
Solvent: CDCl3
3.07
2.00
1.96
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
f1 (ppm)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7.36
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7.35
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7.31
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7.29
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6.97
6.96
6.94
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5.88
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5.84
5.25
5.25
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4.95
4.94
3.99
3.85
3.81
3.79
3.76
3.61
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2.60
2.58
1.00
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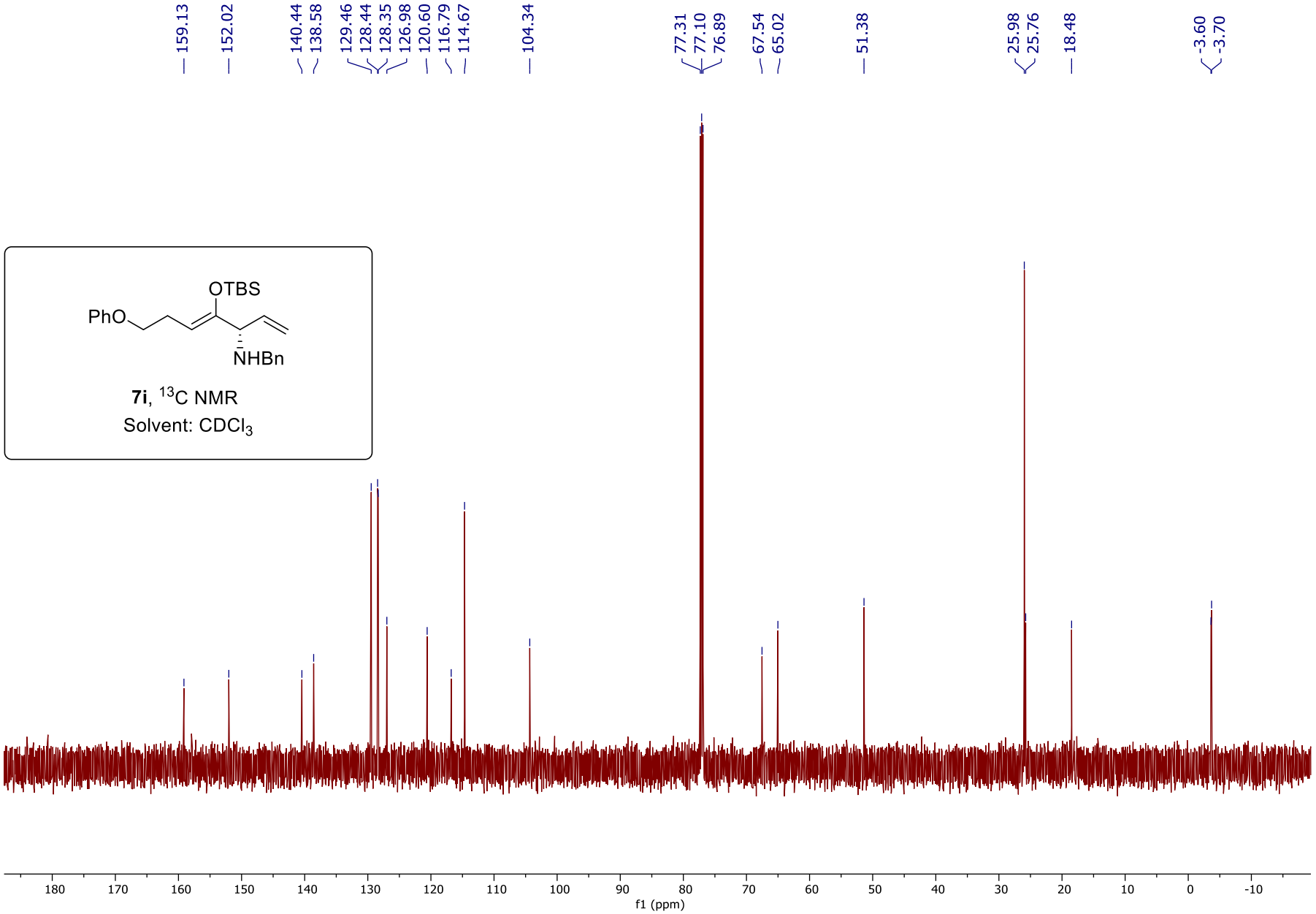
0.18
OTBS
PhO
NHBn
7i, 1H NMR
Solvent: CDCl3
7.12
3.03
1.02
2.02
0.97
2.02
2.03
1.00
2.01
9.16
2.94
2.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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116.79
114.67
104.34
77.31
77.10
76.89
67.54
65.02
51.38
25.98
25.76
18.48
-3.60
-3.70
OTBS
PhO
NHBn
7i, 13C NMR
Solvent: CDCl3
180
170
160
150
140
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120
110
100
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80
70
60
50
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30
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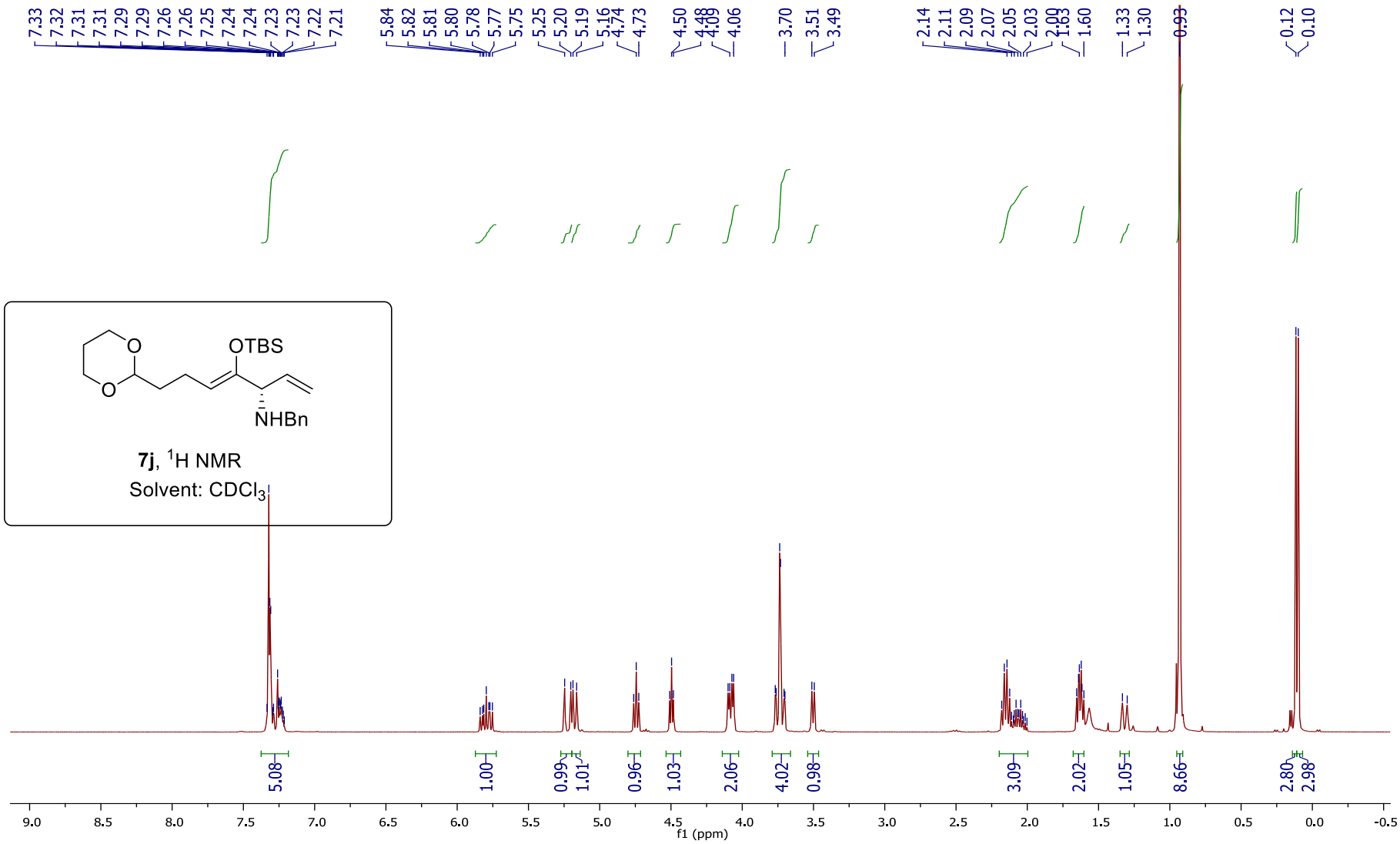
-10
f1 (ppm)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7.23
7.22
7.21
5.84
5.82
5.81
5.80
5.78
5.77
5.75
5.25
5.20
5.19
5.16
4.74
4.73
4.50
4.48
4.09
4.06
3.70
3.51
3.49
2.14
2.11
2.09
2.07
2.05
2.03
2.00
1.83
1.60
1.33
1.30
0.93
0.12
0.10
O
OTBS
O
NHBn
7j, 1H NMR
Solvent: CDCl3
5.08
1.00
0.99
1.01
0.96
1.03
2.06
4.02
0.98
3.09
2.02
1.05
8.66
2.80
2.98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
1.5
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0.5
0.0
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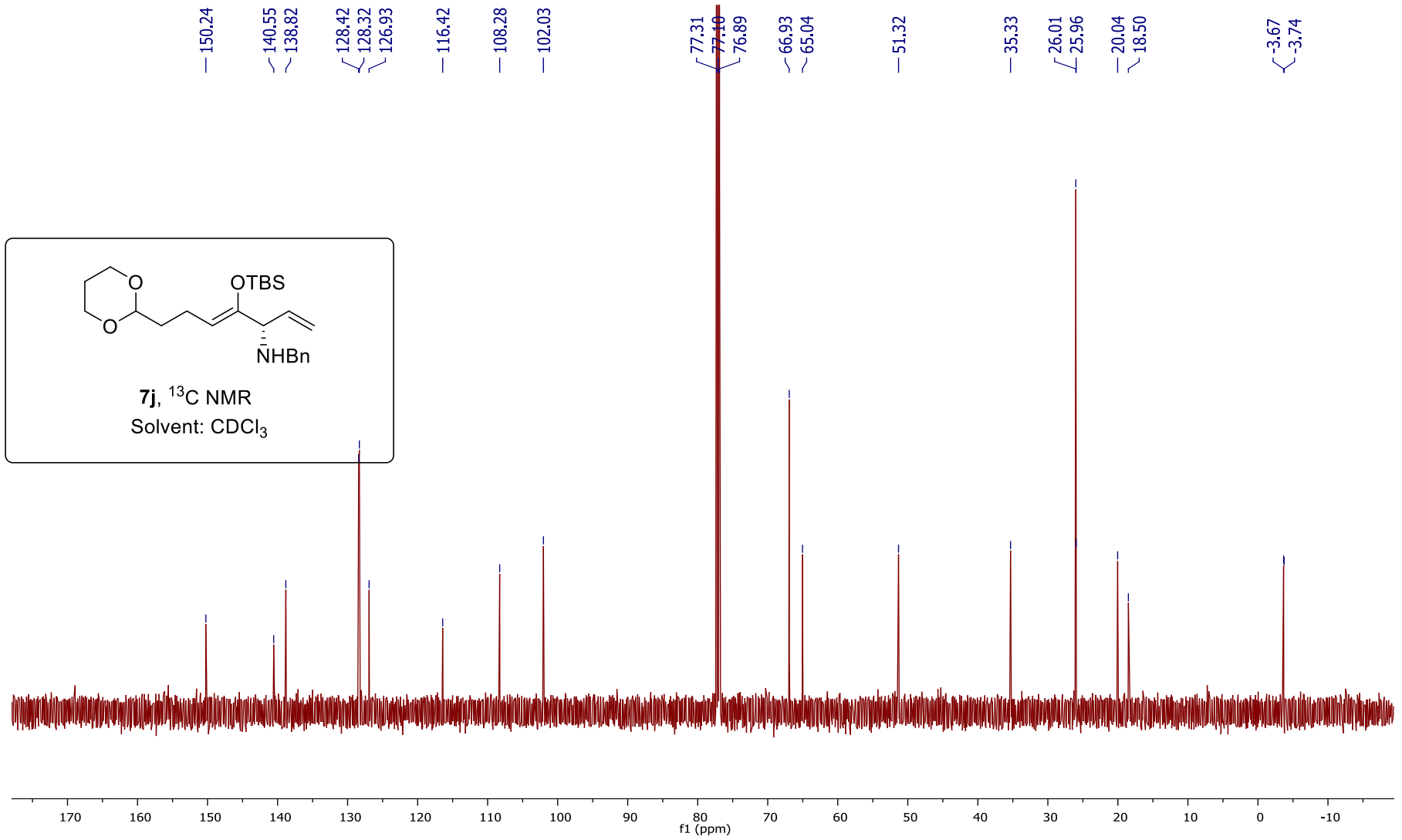
f1 (ppm)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66.93
65.04
51.32
35.33
26.01
25.96
20.04
18.50
-3.67
-3.74
O
O
OTBS
NHBn
7j, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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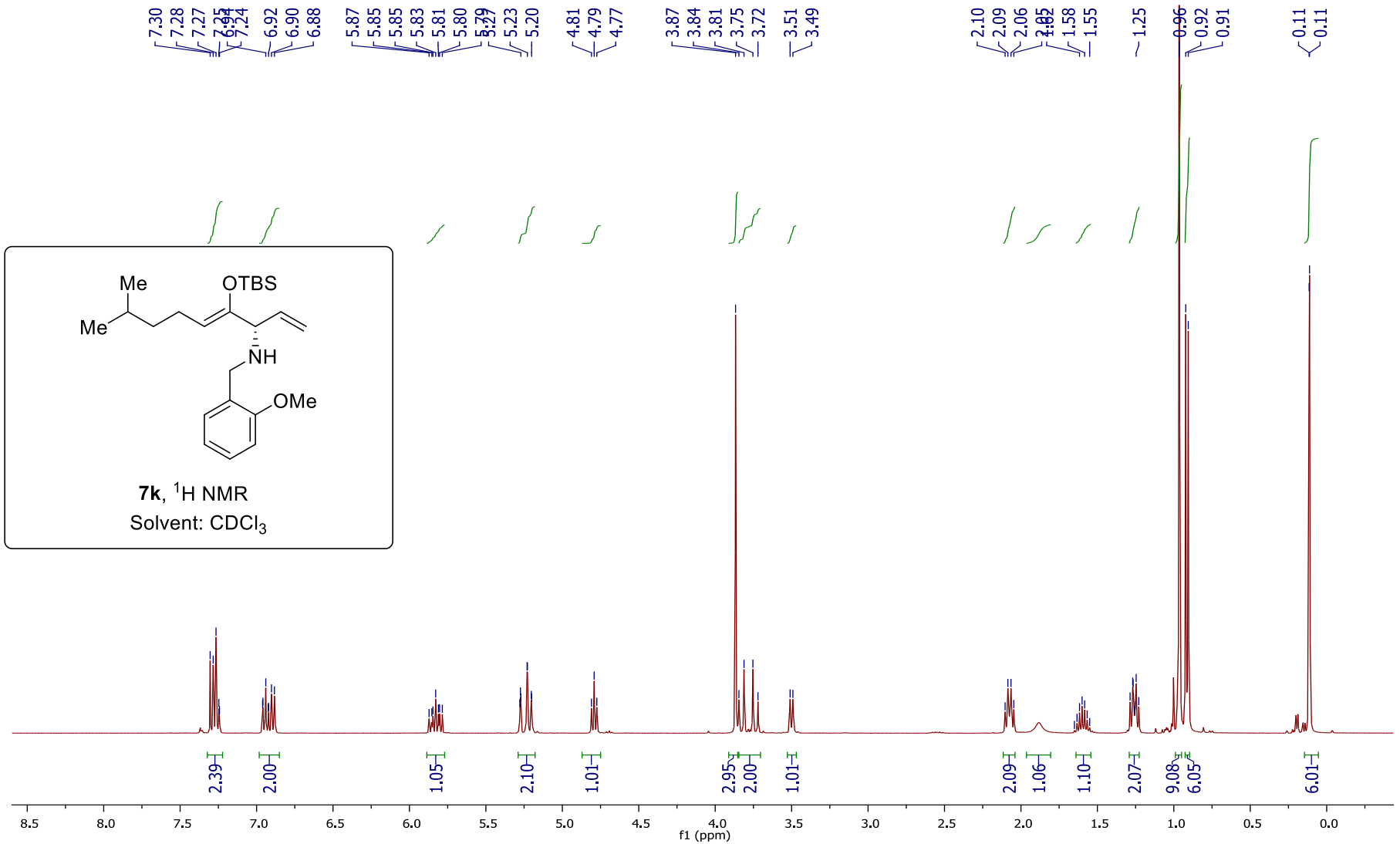
0
-10
f1 (ppm)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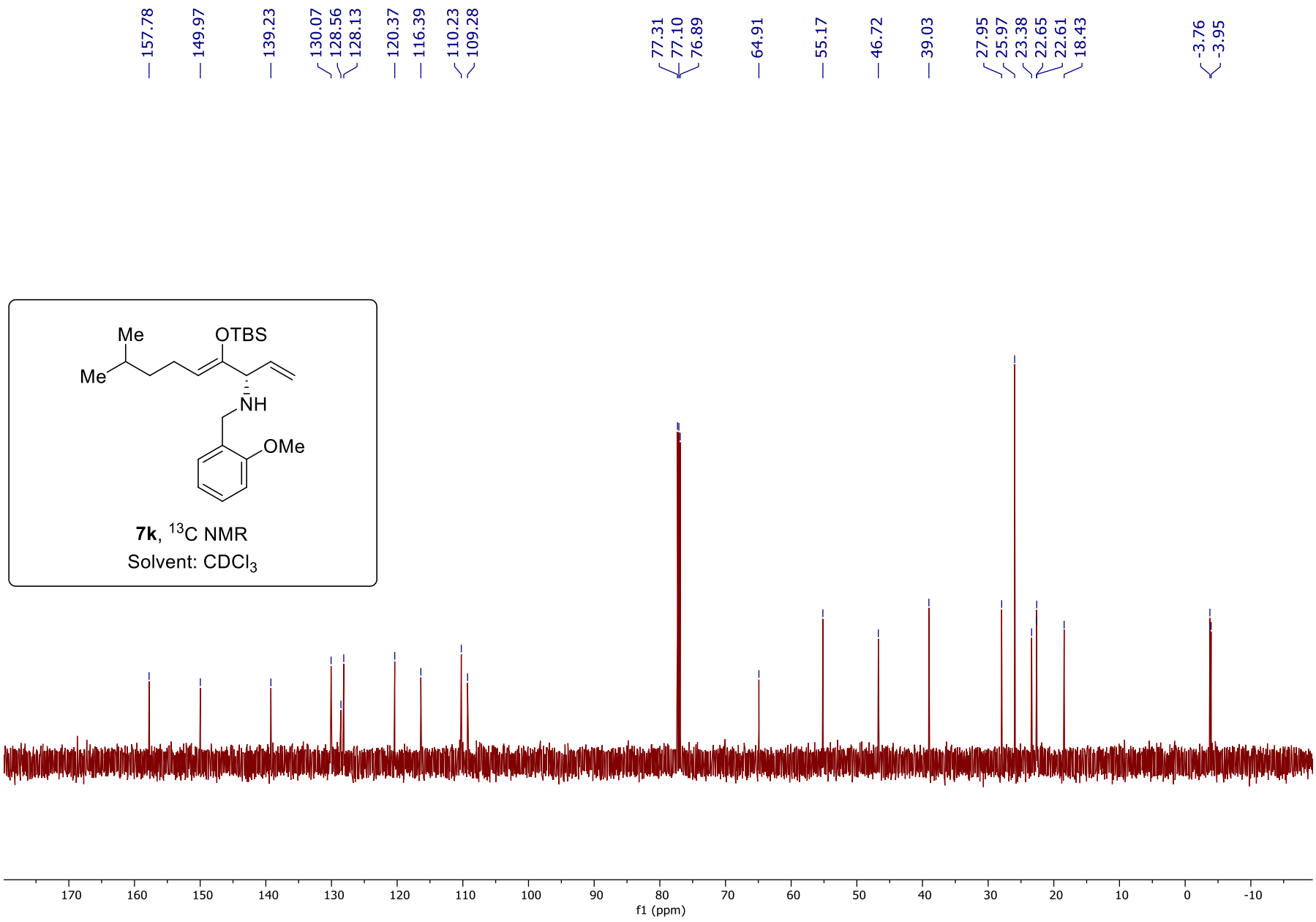
Me
NH
OMe
7k, 1H NMR
Solvent: CDCl3
f1 (ppm)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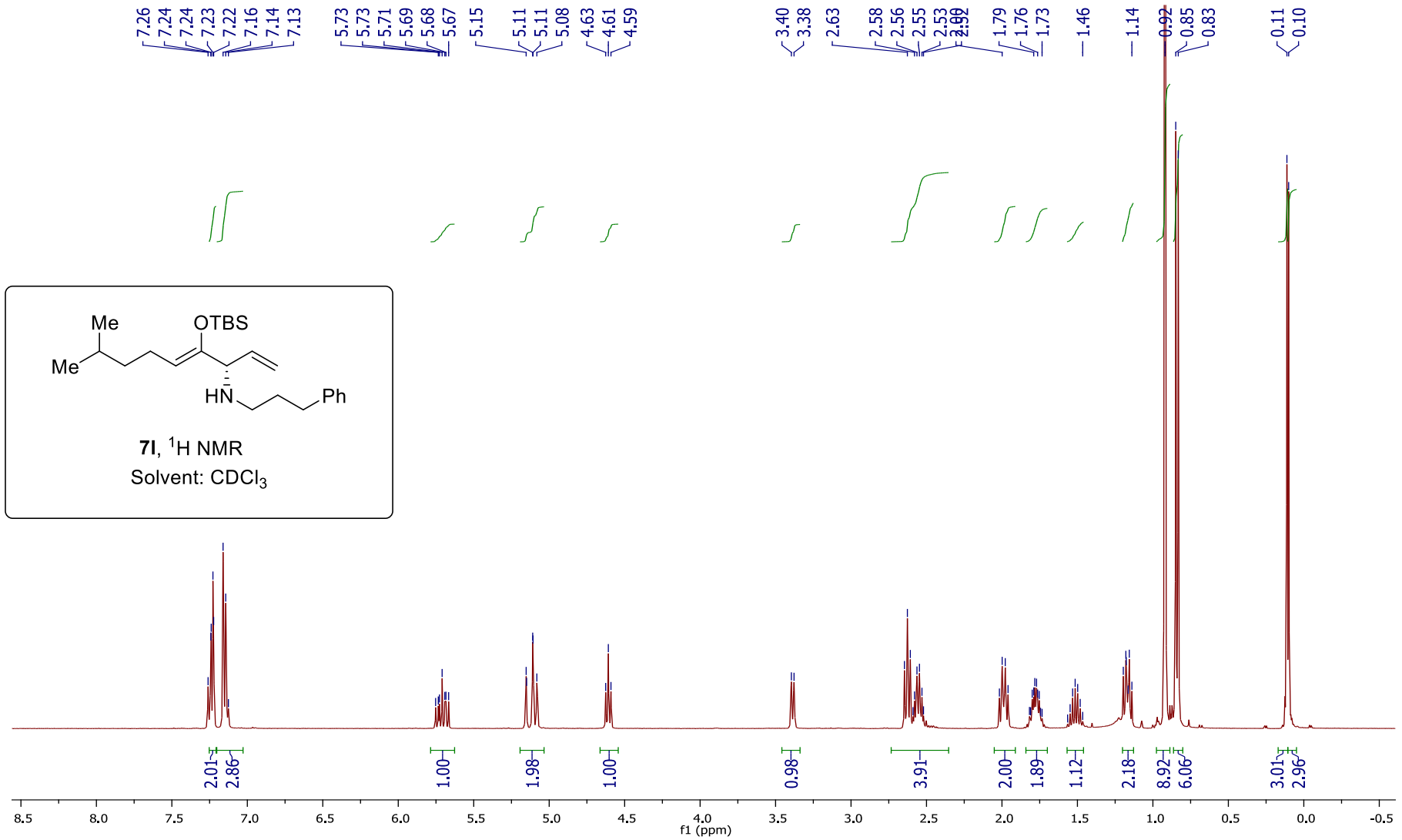
77.31
77.10
76.89
64.91
55.17
46.72
39.03
27.95
25.97
23.38
22.65
22.61
18.43
-3.76
-3.95
Me
OTBS
Me
NH
OMe
7k, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.68
5.67
5.15
5.11
5.11
5.08
4.63
4.61
4.59
3.40
3.38
2.63
2.58
2.56
2.55
2.53
1.79
1.76
1.73
1.46
1.14
0.92
0.85
0.83
0.11
0.10
Me
OTBS
Me
HN
Ph
7I, 1H NMR
Solvent: CDCl3
2.01
2.86
1.00
1.98
1.00
0.98
3.91
2.00
1.89
1.12
2.18
8.92
6.06
3.01
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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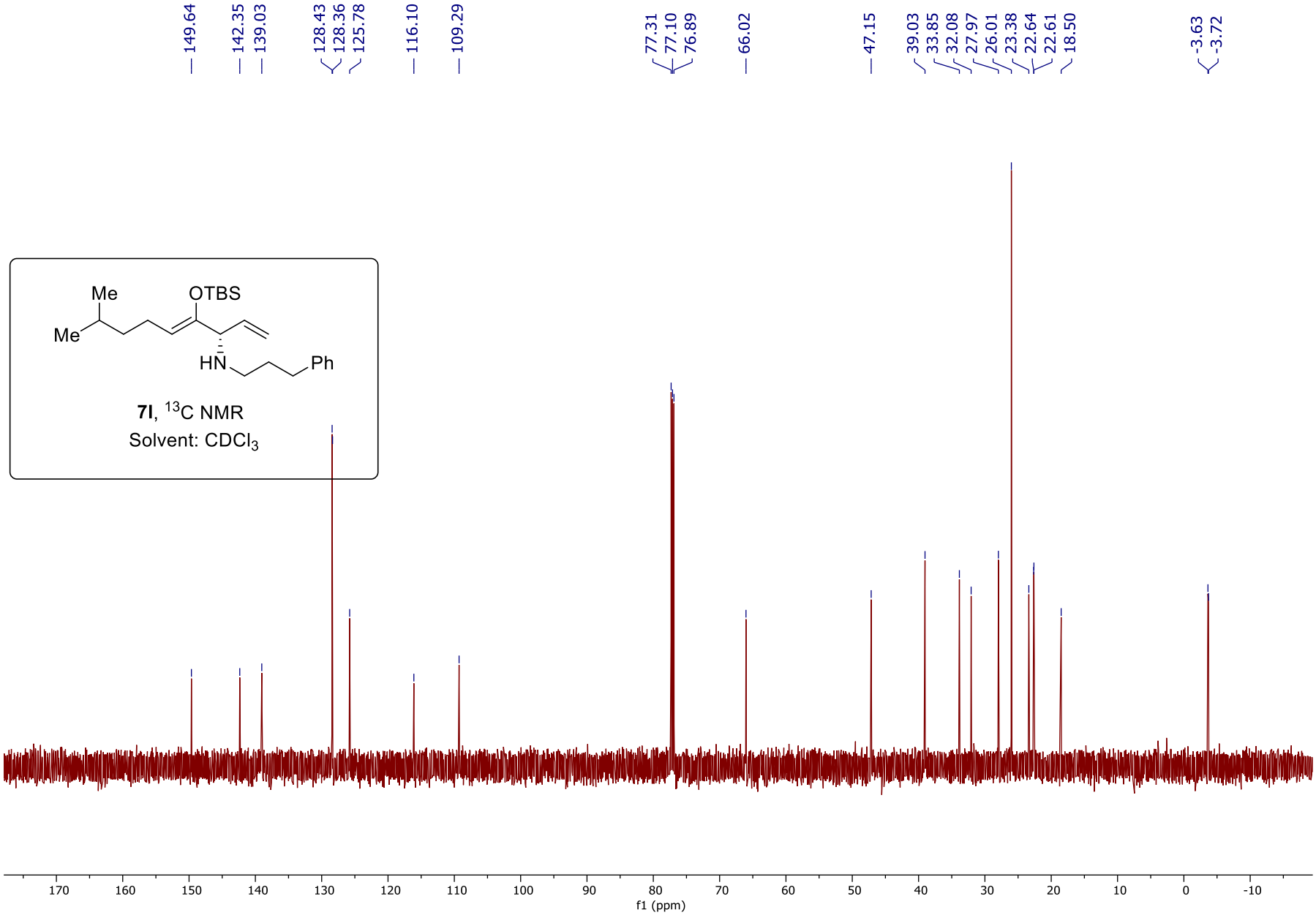
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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116.10
109.29
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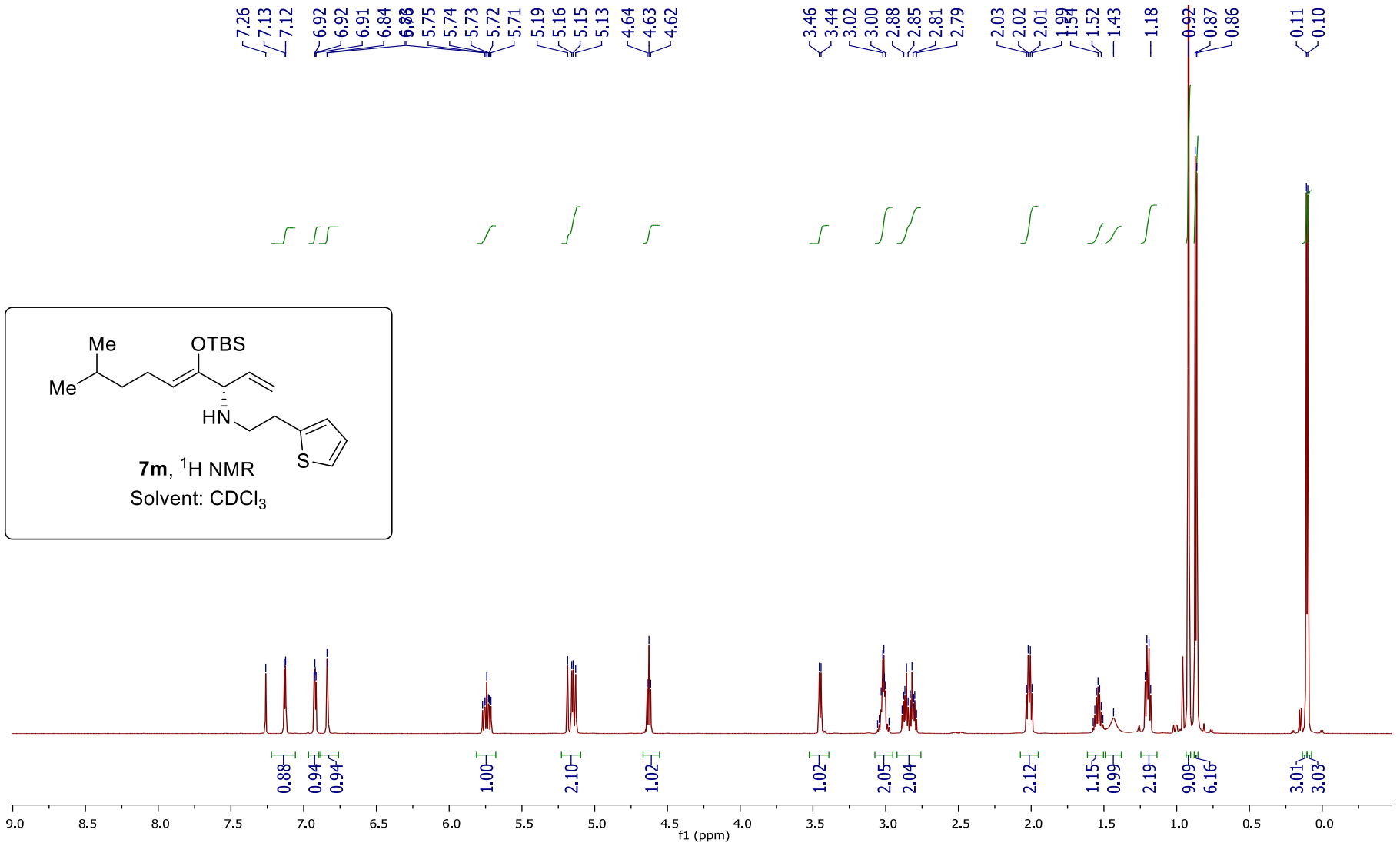
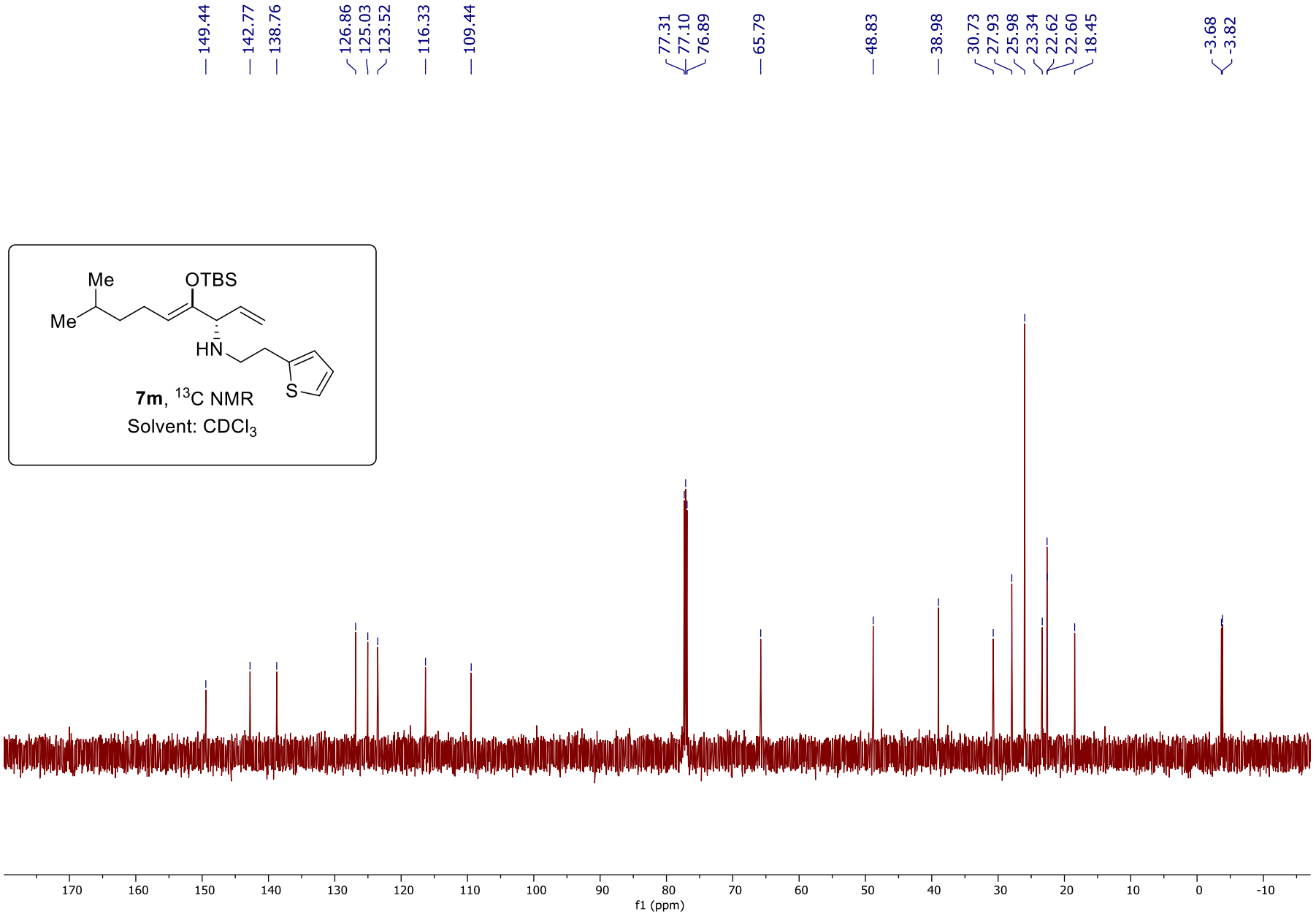
77.10
76.89
66.02
47.15
39.03
33.85
32.08
27.97
26.01
23.38
22.64
22.61
18.50
-3.63
-3.72
Me
OTBS
Me
HN
Ph
7l, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
OTBS
Me
HN
S
7m, 1H NMR
Solvent: CDCl3
f1 (ppm)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123.52
116.33
109.44
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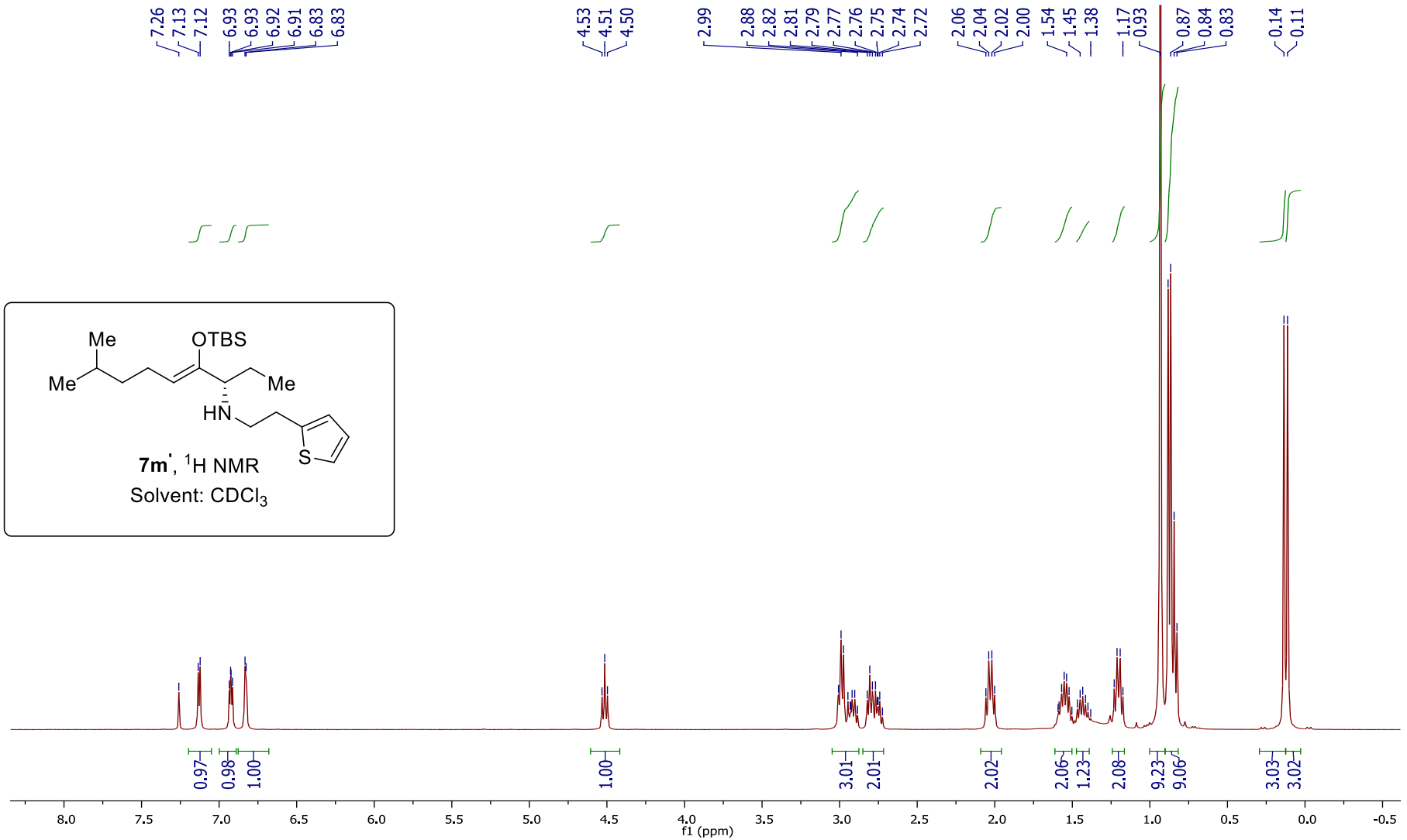
77.10
76.89
65.79
48.83
38.98
30.73
27.93
25.98
23.34
22.62
22.60
18.45
-3.68
-3.82
Me
OTBS
Me
HN
S
7m, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.91
6.83
6.83
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4.51
4.50
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2.88
2.82
2.81
2.79
2.77
2.76
2.75
2.74
2.72
2.06
2.04
2.02
2.00
1.54
1.45
1.38
1.17
0.93
0.87
0.84
0.83
0.14
0.11
Me
OTBS
Me
Me
HN
S
7m', 1H NMR
Solvent: CDCl3
0.97
0.98
1.00
1.00
3.01
2.01
2.02
2.06
1.23
2.08
9.23
9.06
3.03
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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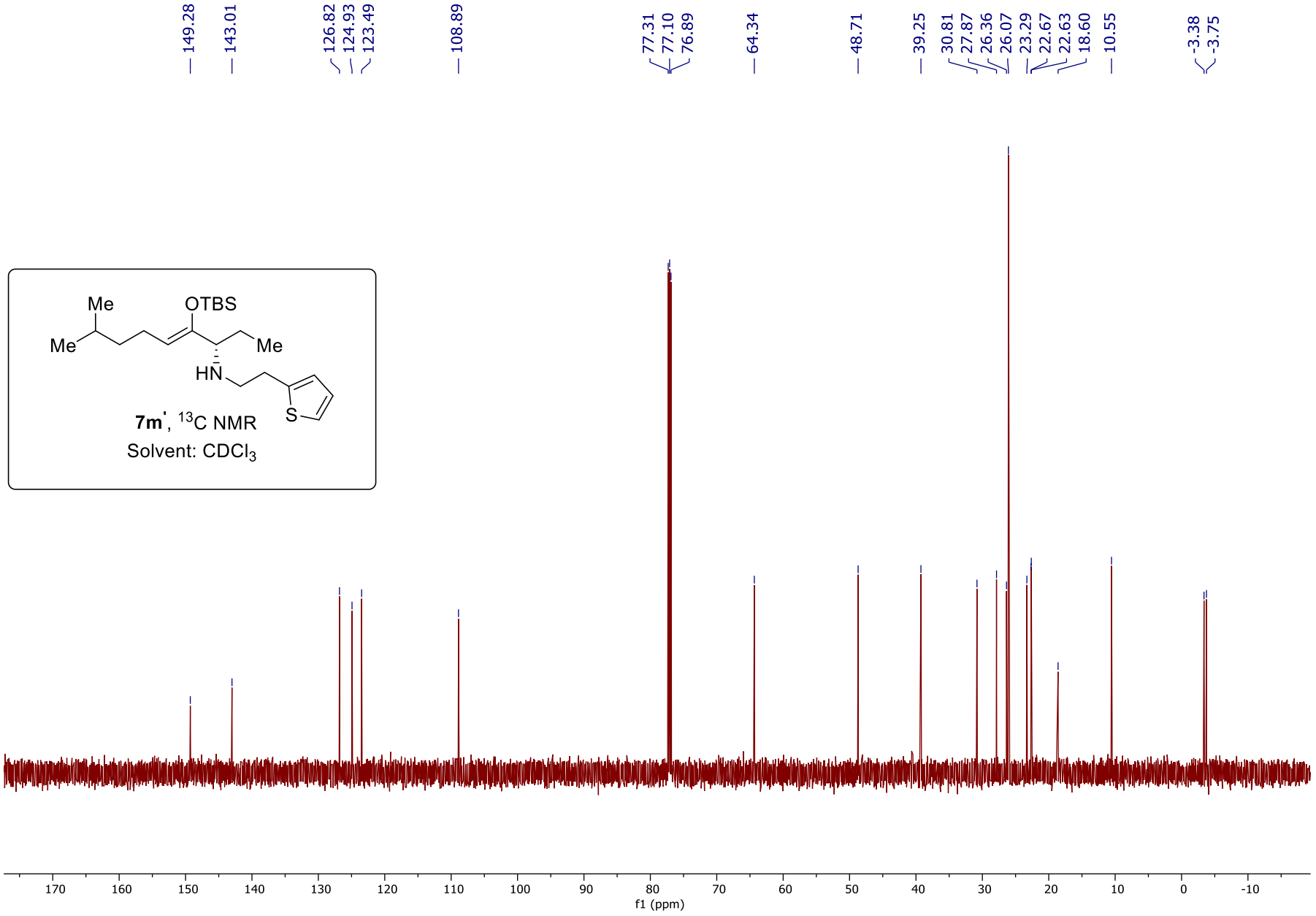
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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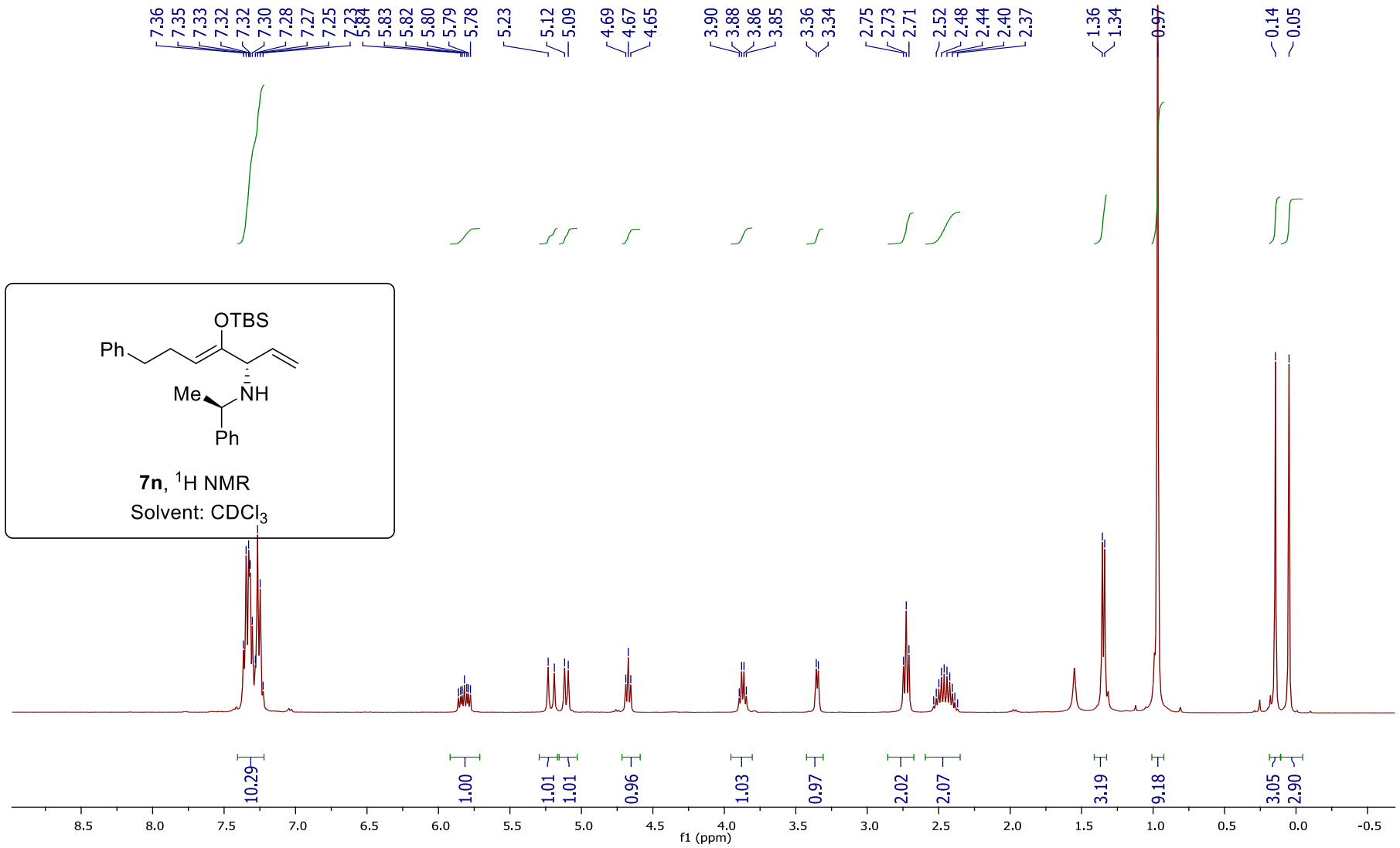
30.81
27.87
26.36
26.07
23.29
22.67
22.63
18.60
10.55
-3.38
-3.75
Me
OTBS
Me
Me
HN
S
7m', 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.23
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5.83
5.82
5.80
5.79
5.78
5.23
5.12
5.09
4.69
4.67
4.65
3.90
3.88
3.86
3.85
3.36
3.34
2.75
2.73
2.71
2.52
2.48
2.44
2.40
2.37
1.36
1.34
0.97
0.14
0.05
OTBS
Ph
Me
NH
Ph
7n, 1H NMR
Solvent: CDCl3
10.29
1.00
1.01
1.01
0.96
1.03
0.97
2.02
2.07
3.19
9.18
3.05
2.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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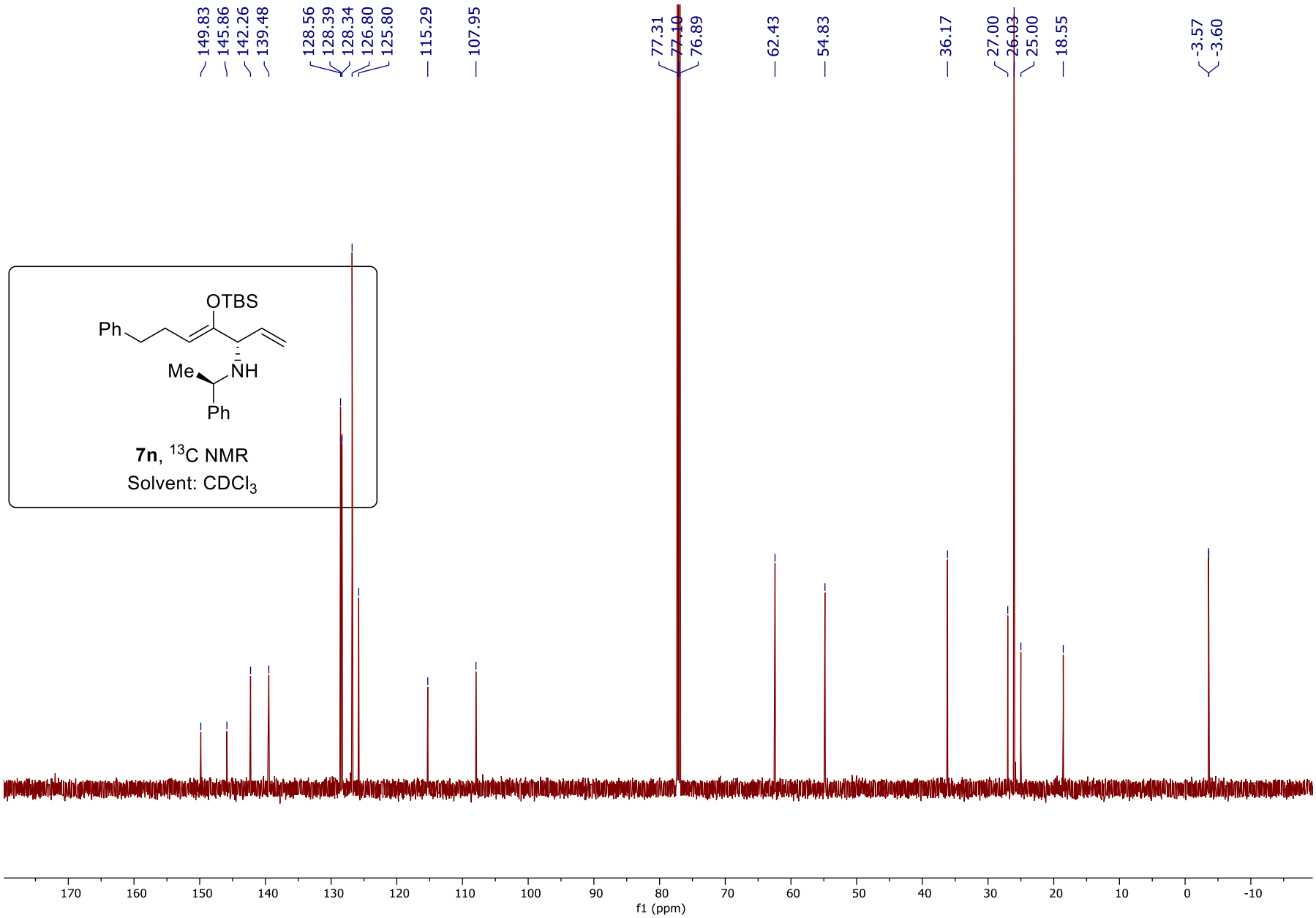
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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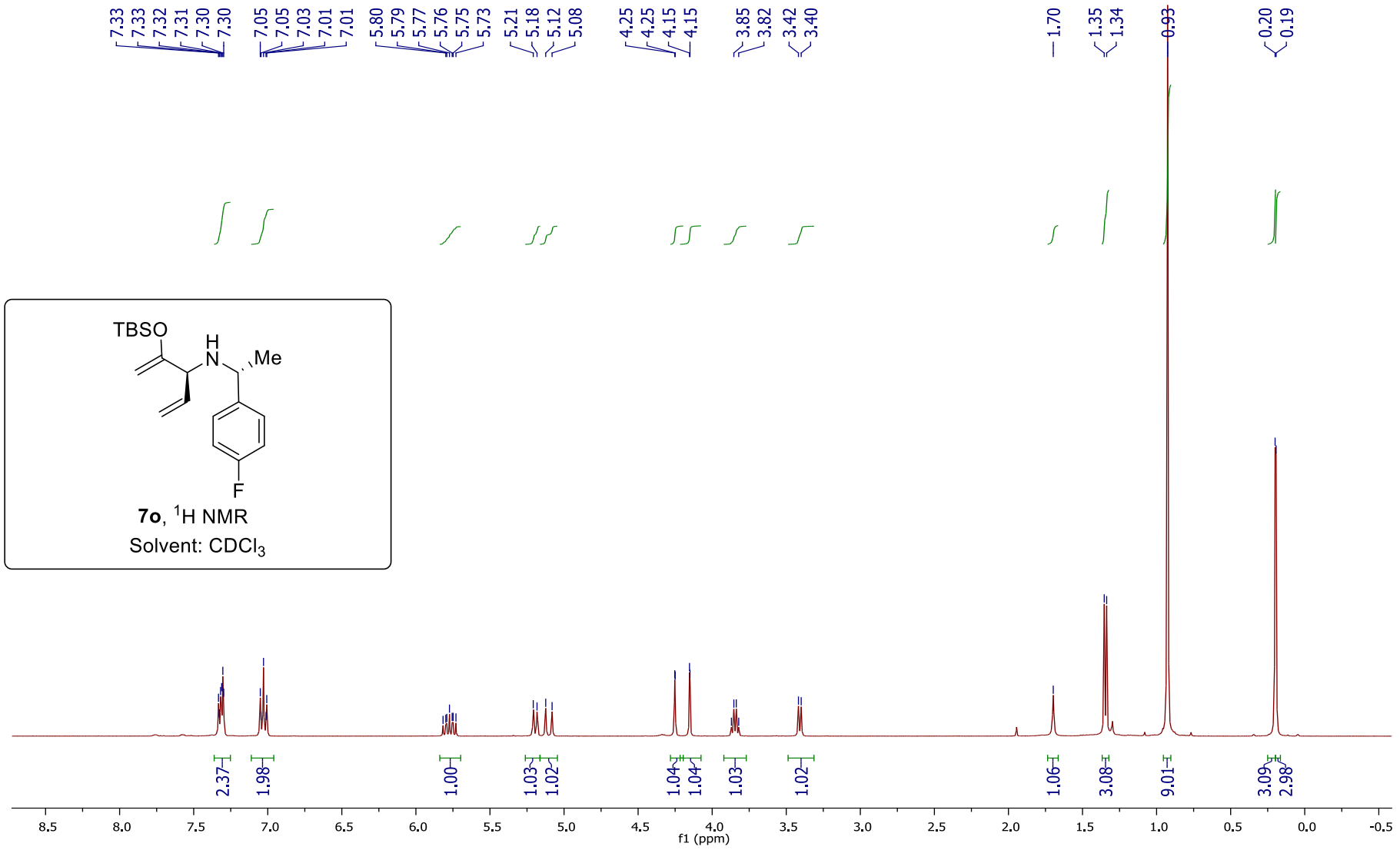
107.95
77.31
77.10
76.89
62.43
54.83
36.17
27.00
26.03
25.00
18.55
-3.57
-3.60
OTBS
Ph
Me
NH
Ph
7n, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
H
N
Me
F
7o, 1H NMR
Solvent: CDCl3
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7.33
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7.30
7.05
7.05
7.03
7.01
7.01
5.80
5.79
5.77
5.76
5.75
5.73
5.21
5.18
5.12
5.08
4.25
4.25
4.15
4.15
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3.42
3.40
1.70
1.35
1.34
0.93
0.20
0.19
2.37
1.98
1.00
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1.02
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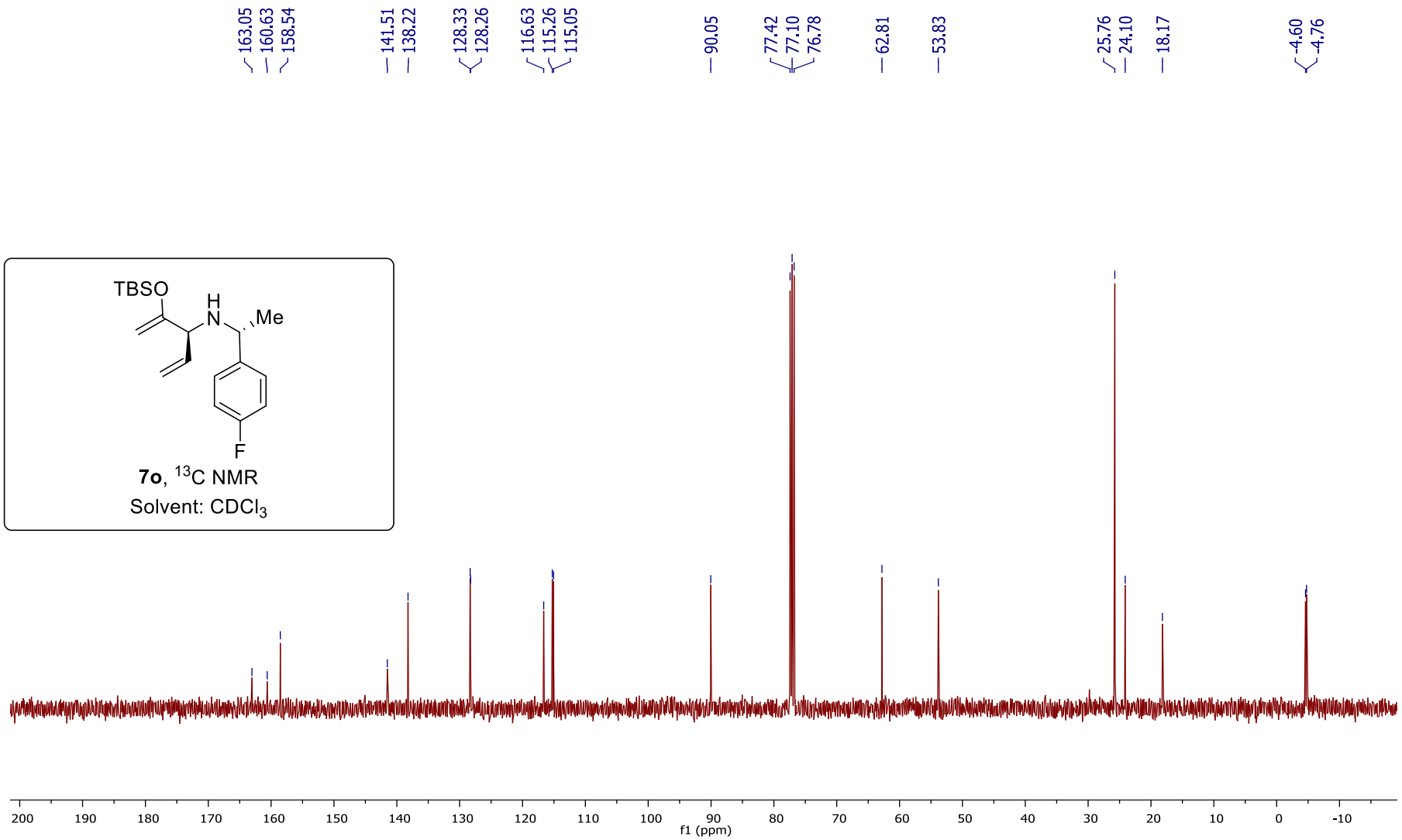
1.04
1.03
1.02
1.06
3.08
9.01
3.09
2.98
f1 (ppm)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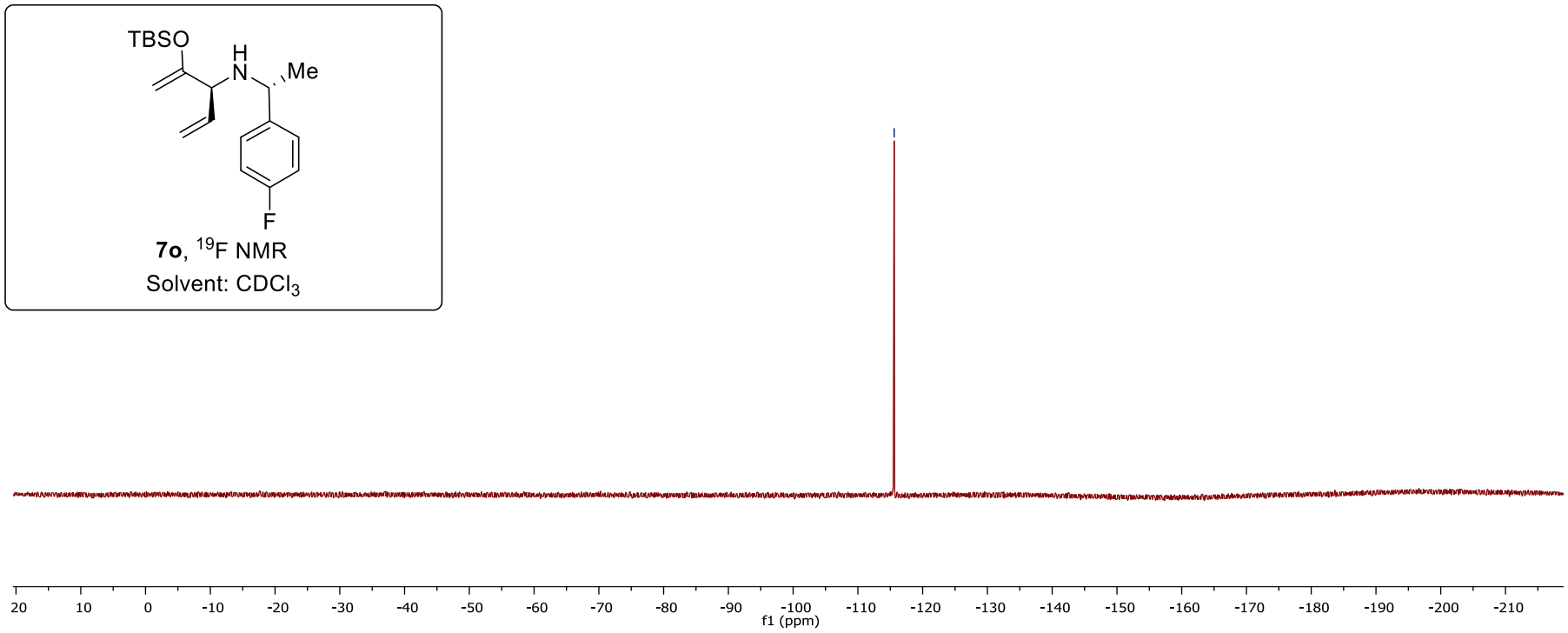
115.26
115.05
90.05
77.42
77.10
76.78
62.81
53.83
25.76
24.10
18.17
-4.60
-4.76
TBSO
H
N
Me
F
7o, 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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F
7o, 19F NMR
Solvent: CDCl3
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20
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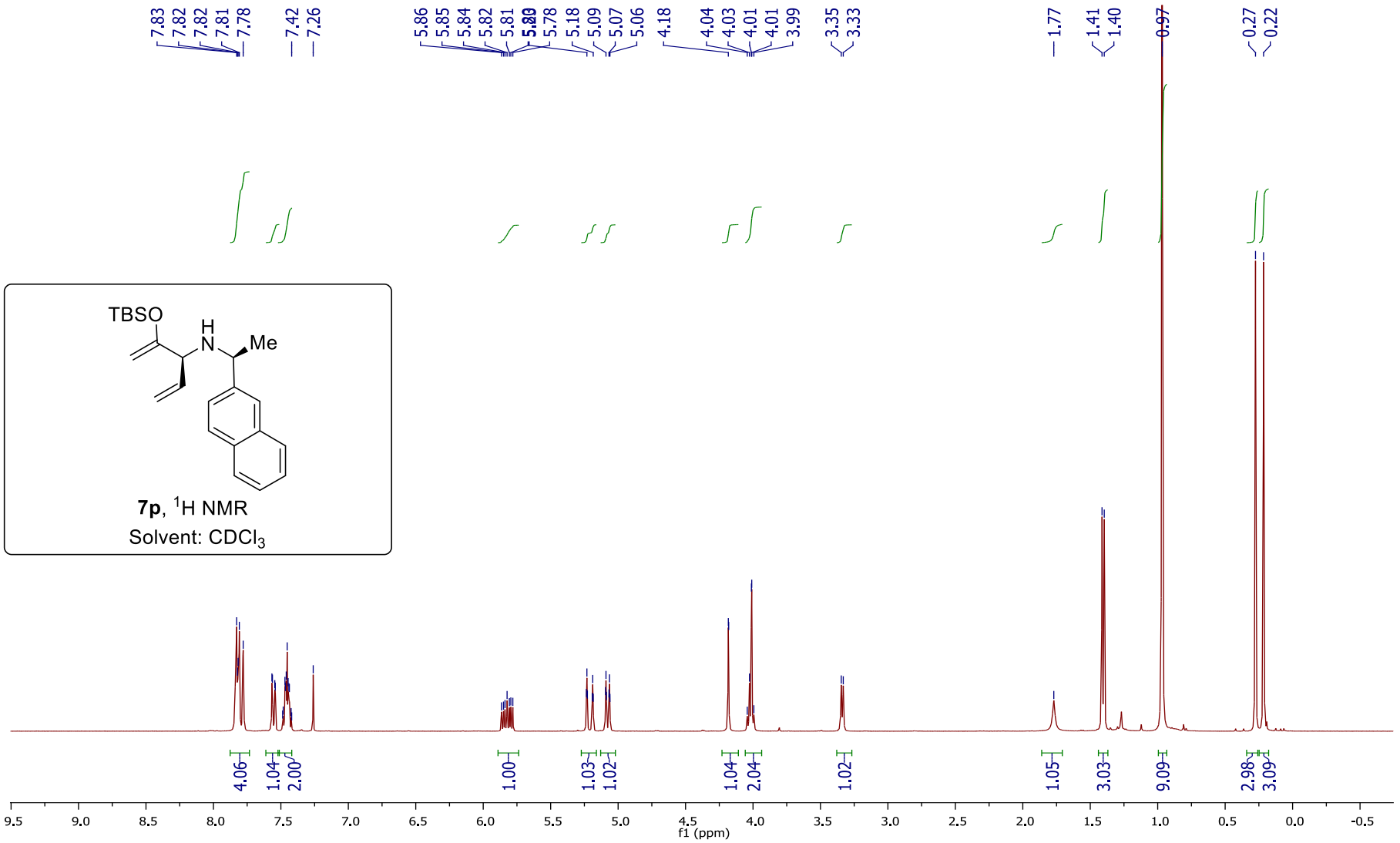
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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5.86
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5.84
5.82
5.81
5.78
5.18
5.09
5.07
5.06
4.18
4.04
4.03
4.01
4.01
3.99
3.35
3.33
1.77
1.41
1.40
0.97
0.27
0.22
TBSO
H
N
Me
7p, 1H NMR
Solvent: CDCl3
4.06
1.04
2.00
1.00
1.03
1.02
1.04
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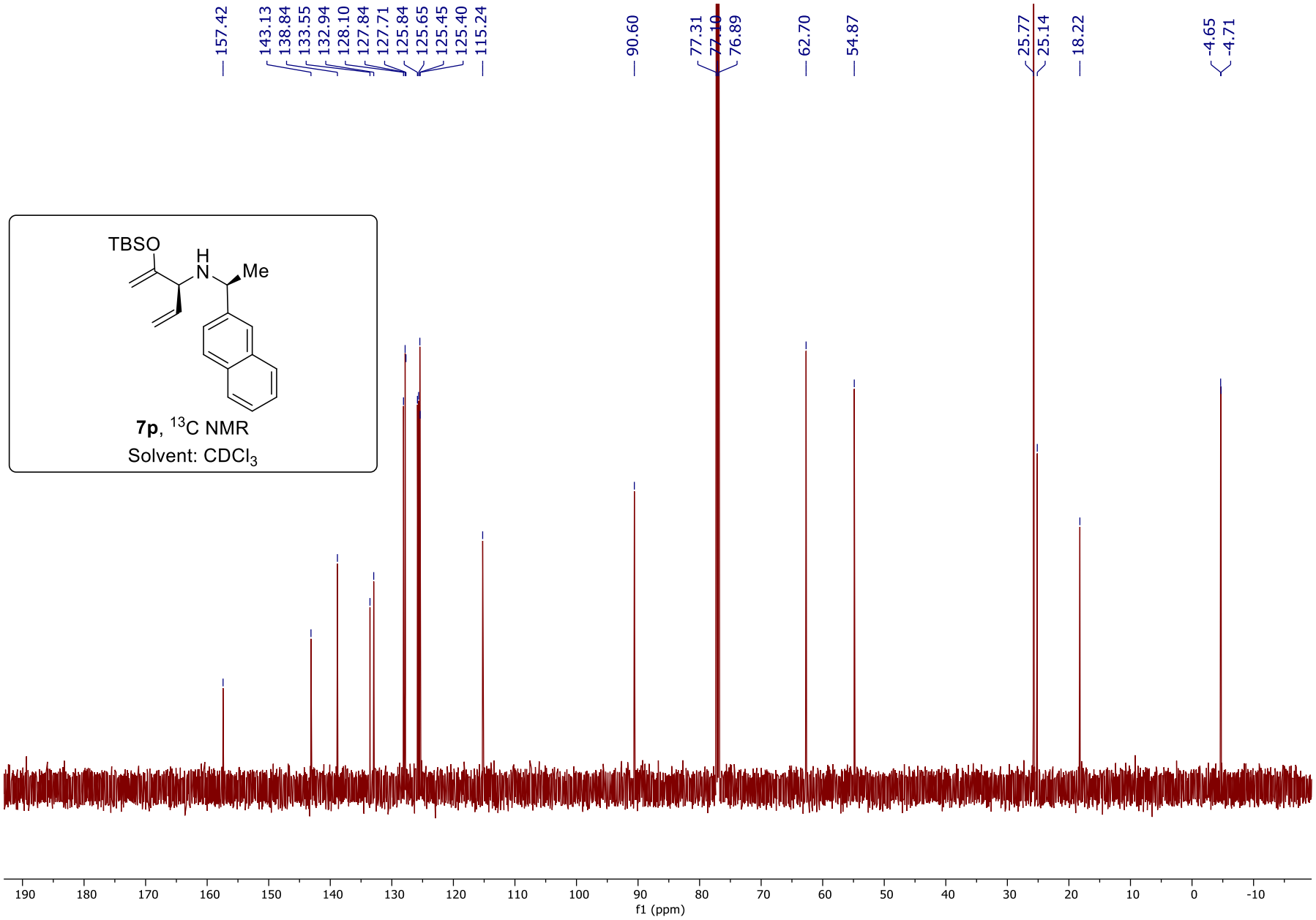
3.03
9.09
2.98
3.09
f1 (ppm)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127.71
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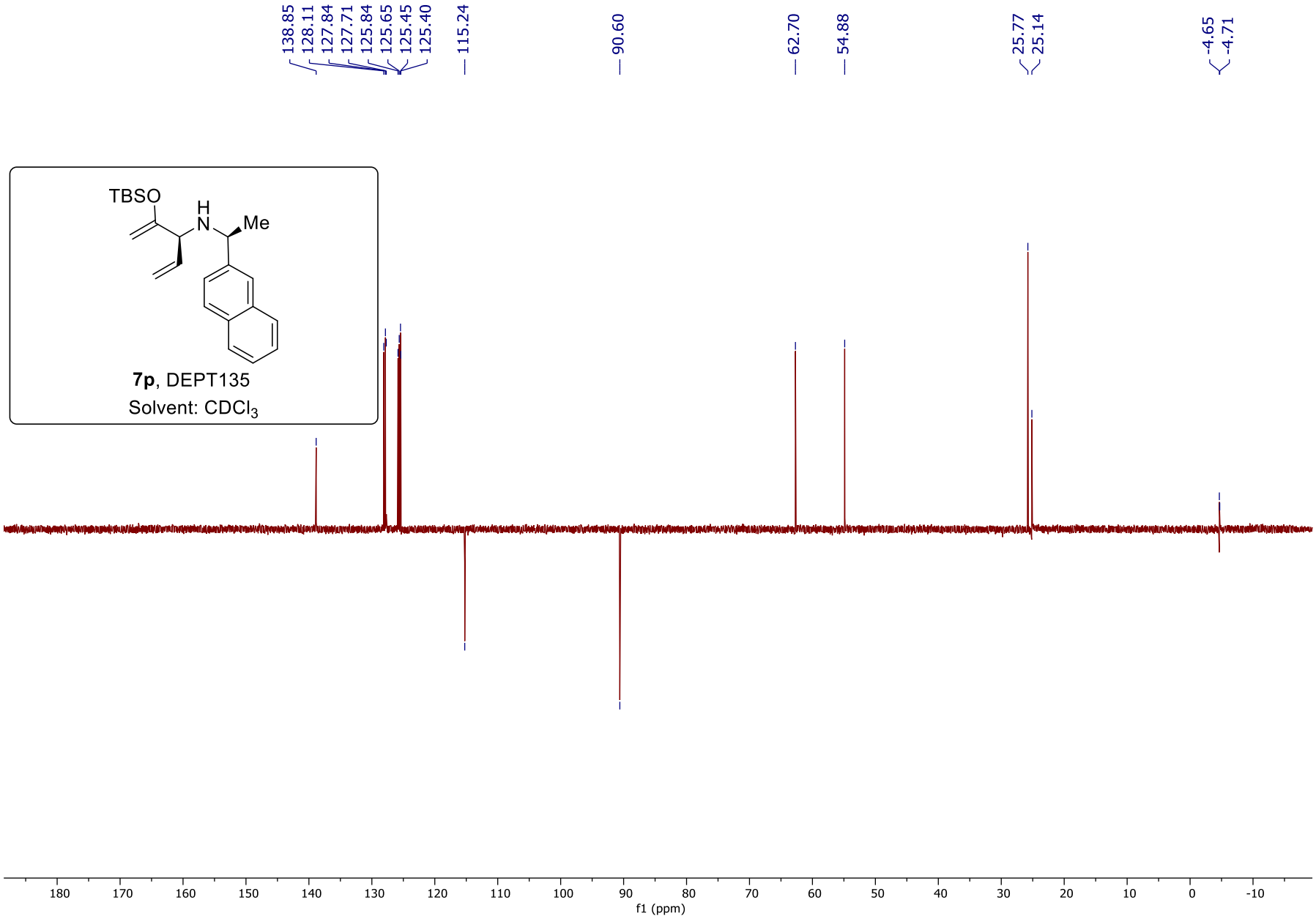
125.65
125.45
125.40
115.24
90.60
77.31
77.10
76.89
62.70
54.87
25.77
25.14
18.22
-4.65
-4.71
TBSO
H
N
Me
7p, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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127.71
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125.65
125.45
125.40
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90.60
62.70
54.88
25.77
25.14
-4.65
-4.71
TBSO
H
N
Me
7p, DEPT135
Solvent: CDCl3
180
170
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100
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80
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40
30
20
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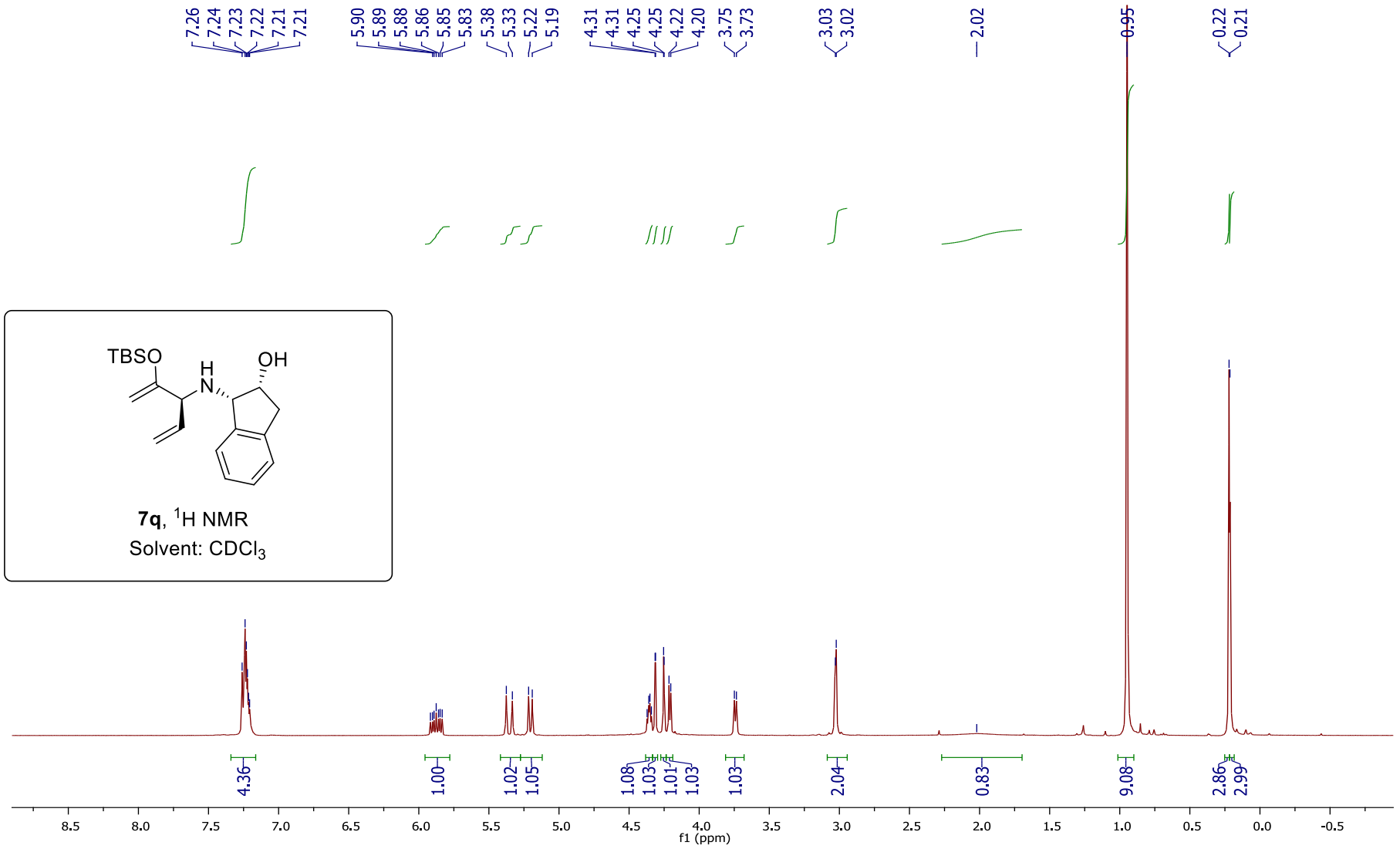
0
-10
f1 (ppm)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5.86
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5.38
5.33
5.22
5.19
4.31
4.31
4.25
4.25
4.22
4.20
3.75
3.73
3.03
3.02
2.02
0.95
0.22
0.21
TBSO
H
N
OH
7q, 1H NMR
Solvent: CDCl3
4.36
1.00
1.02
1.05
1.08
1.03
1.01
1.03
1.03
2.04
0.83
9.08
2.86
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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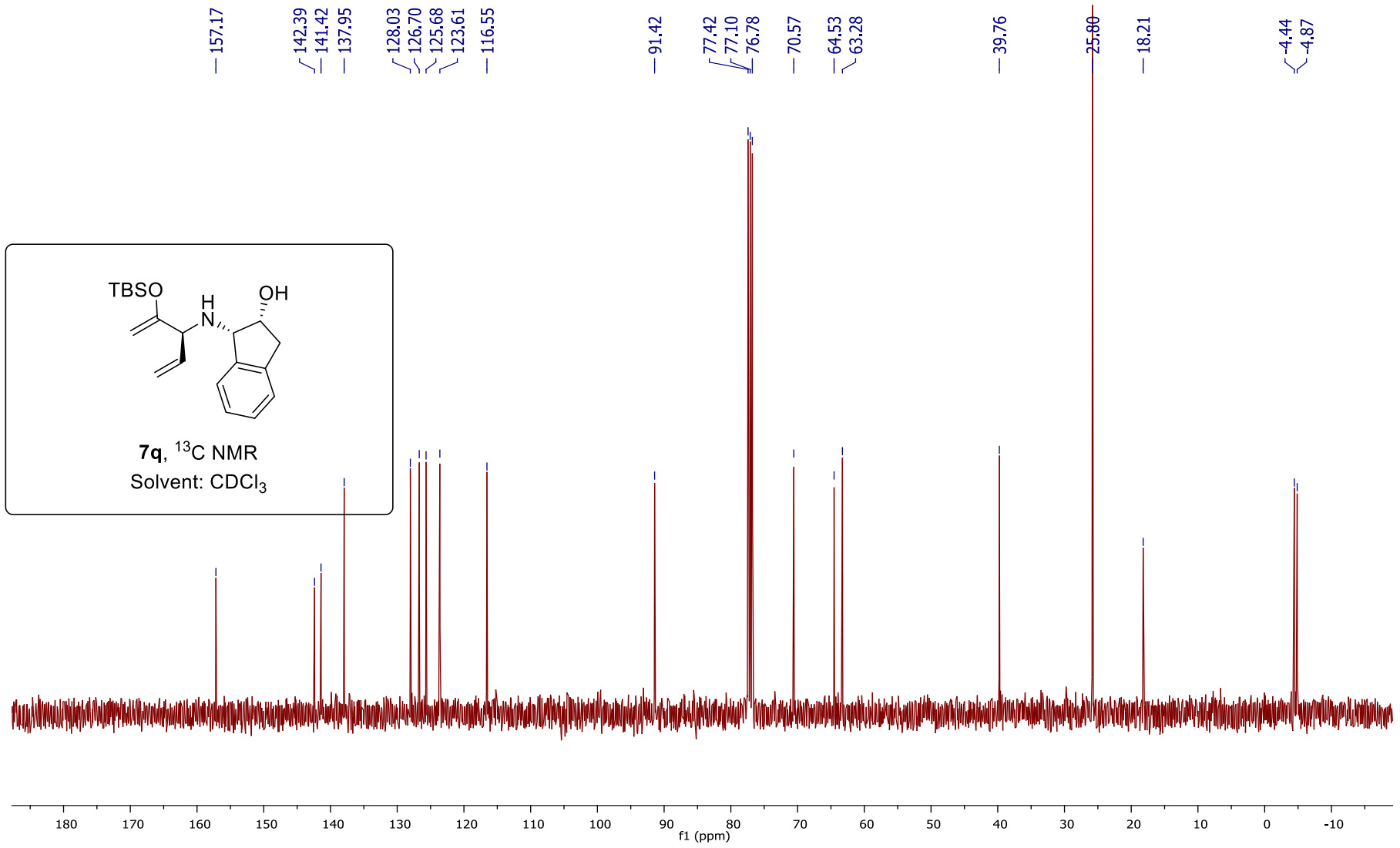
0.5
0.0
-0.5
f1 (ppm)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125.68
123.61
116.55
91.42
77.42
77.10
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70.57
64.53
63.28
39.76
25.80
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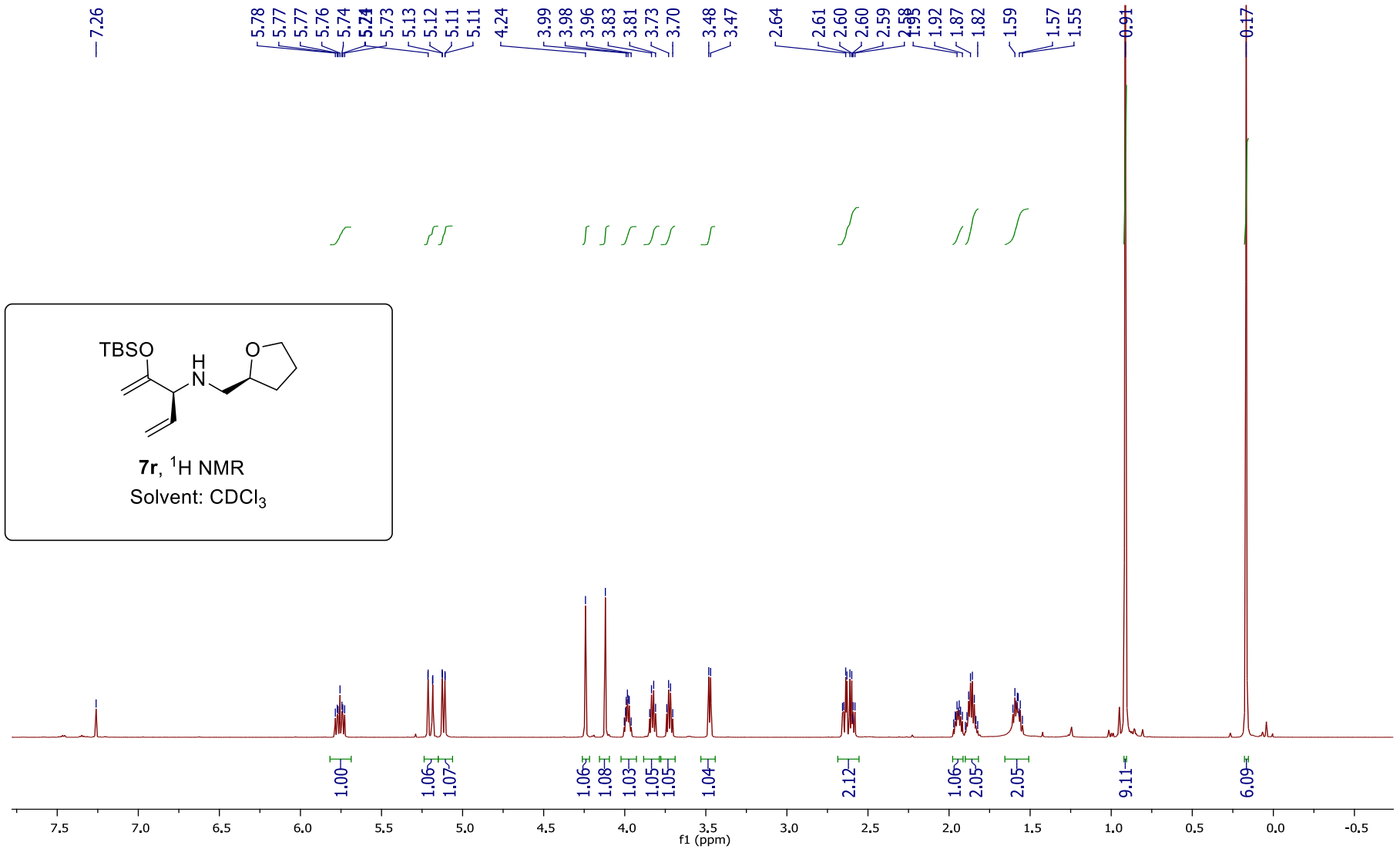
-4.44
-4.87
TBSO
H
N
OH
7q, 13C NMR
Solvent: CDCl3
f1 (ppm)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5.78
5.77
5.77
5.76
5.74
5.73
5.13
5.12
5.11
5.11
4.24
3.99
3.98
3.96
3.83
3.81
3.73
3.70
3.48
3.47
2.64
2.61
2.60
2.60
2.59
1.92
1.87
1.82
1.59
1.57
1.55
0.91
0.17
TBSO
H
N
O
7r, 1H NMR
Solvent: CDCl3
1.00
1.06
1.07
1.06
1.08
1.03
1.05
1.05
1.04
2.12
1.06
2.05
2.05
9.11
6.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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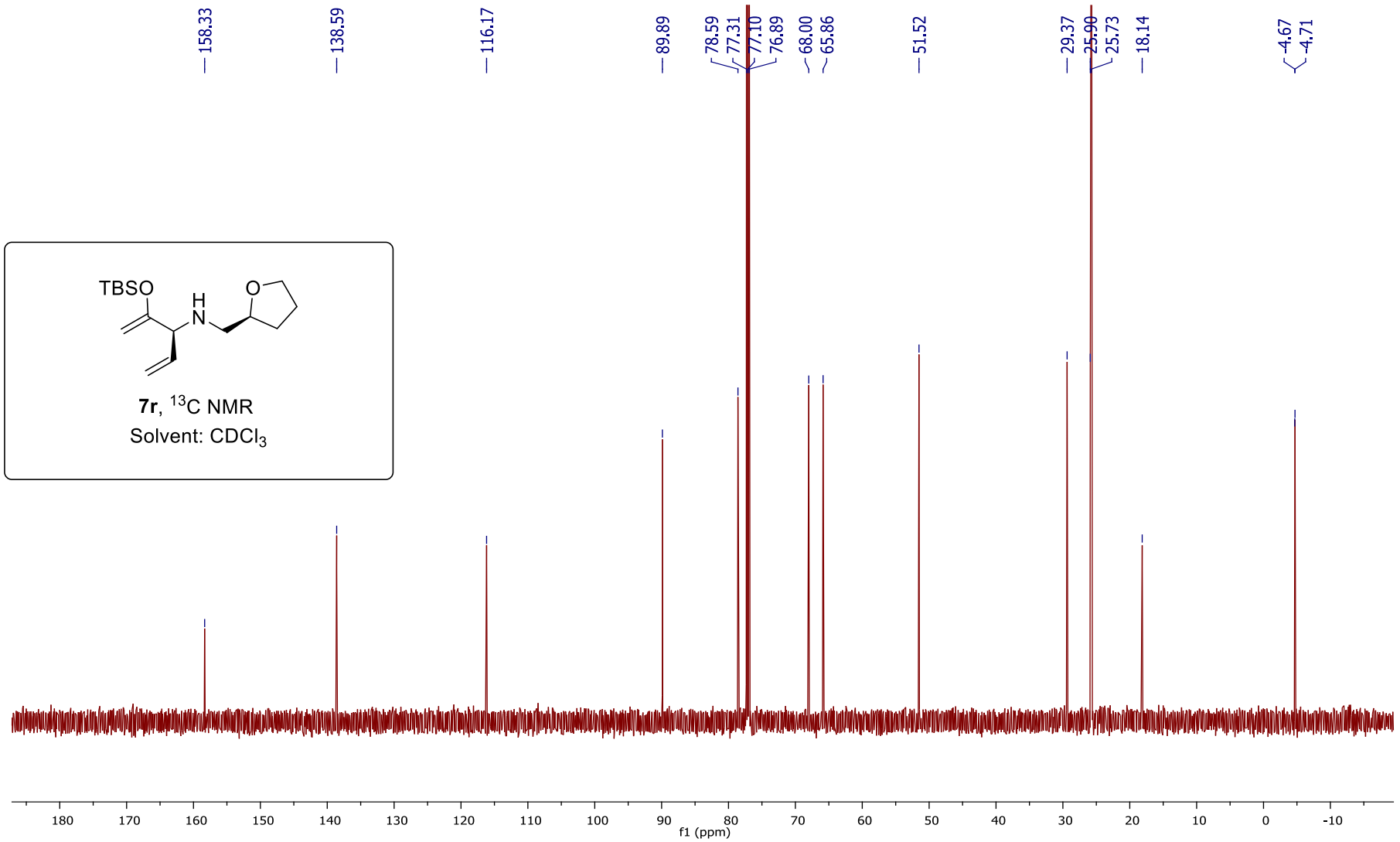
0.5
0.0
-0.5
f1 (ppm)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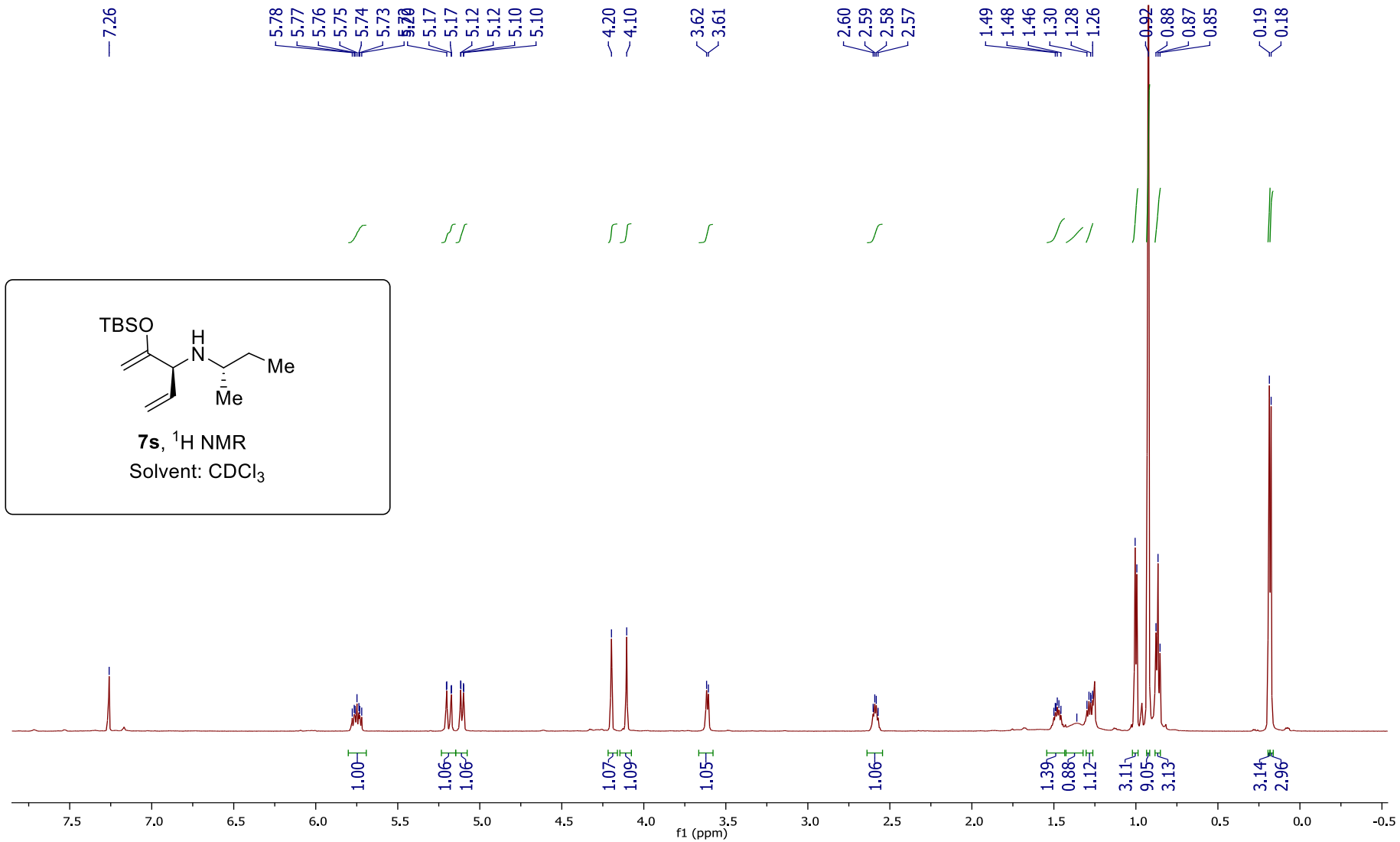
138.59
116.17
89.89
78.59
77.31
77.10
76.89
68.00
65.86
51.52
29.37
25.90
25.73
18.14
-4.67
-4.71
TBSO
H
N
O
7r, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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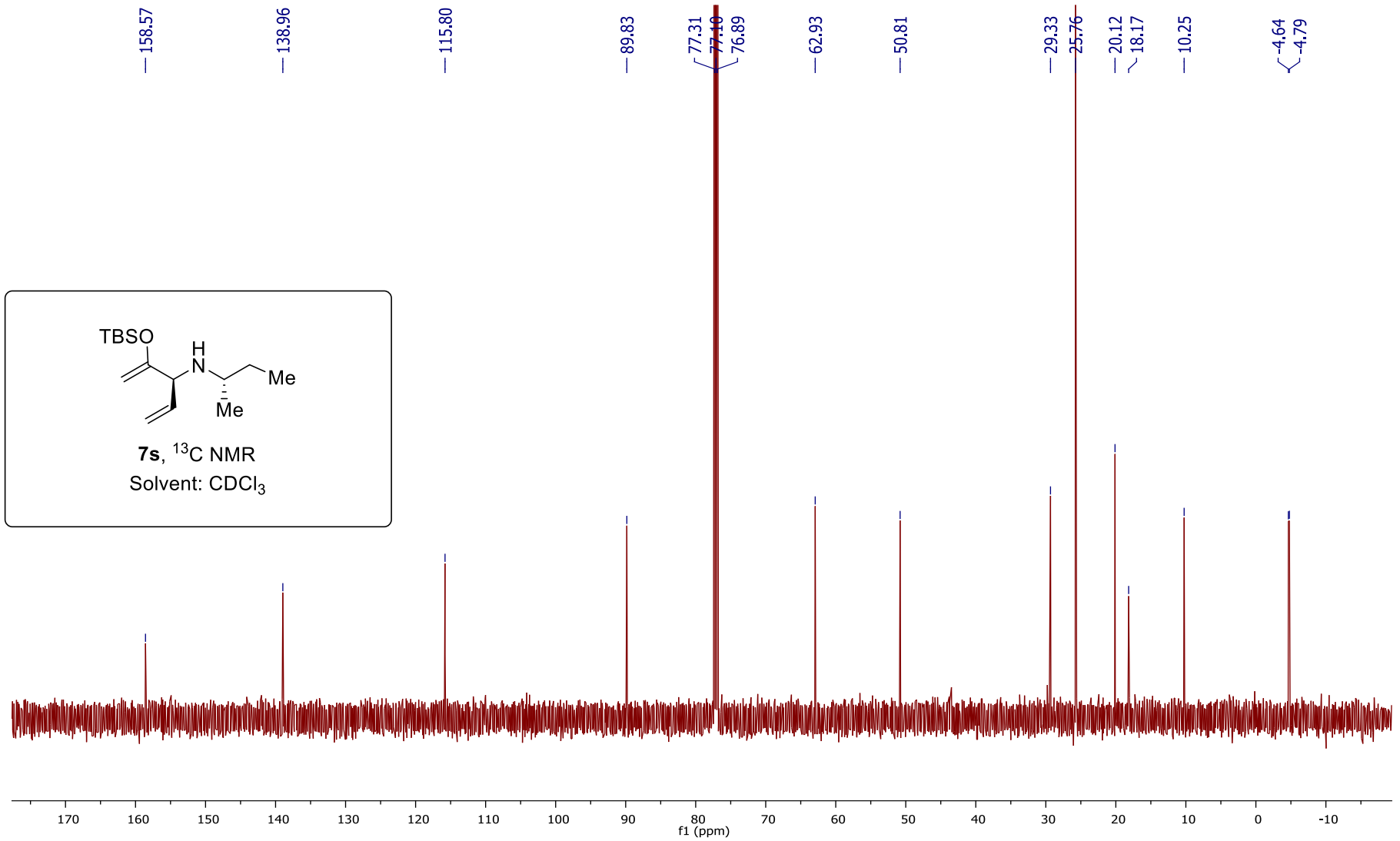
5.78
5.77
5.76
5.75
5.74
5.73
5.17
5.17
5.12
5.12
5.10
5.10
4.20
4.10
3.62
3.61
2.60
2.59
2.58
2.57
1.49
1.48
1.46
1.30
1.28
1.26
0.92
0.88
0.87
0.85
0.19
0.18
TBSO
H
N
Me
Me
7s, 1H NMR
Solvent: CDCl3
1.00
1.06
1.06
1.07
1.09
1.05
1.06
1.39
0.88
1.12
3.11
9.05
3.13
3.14
2.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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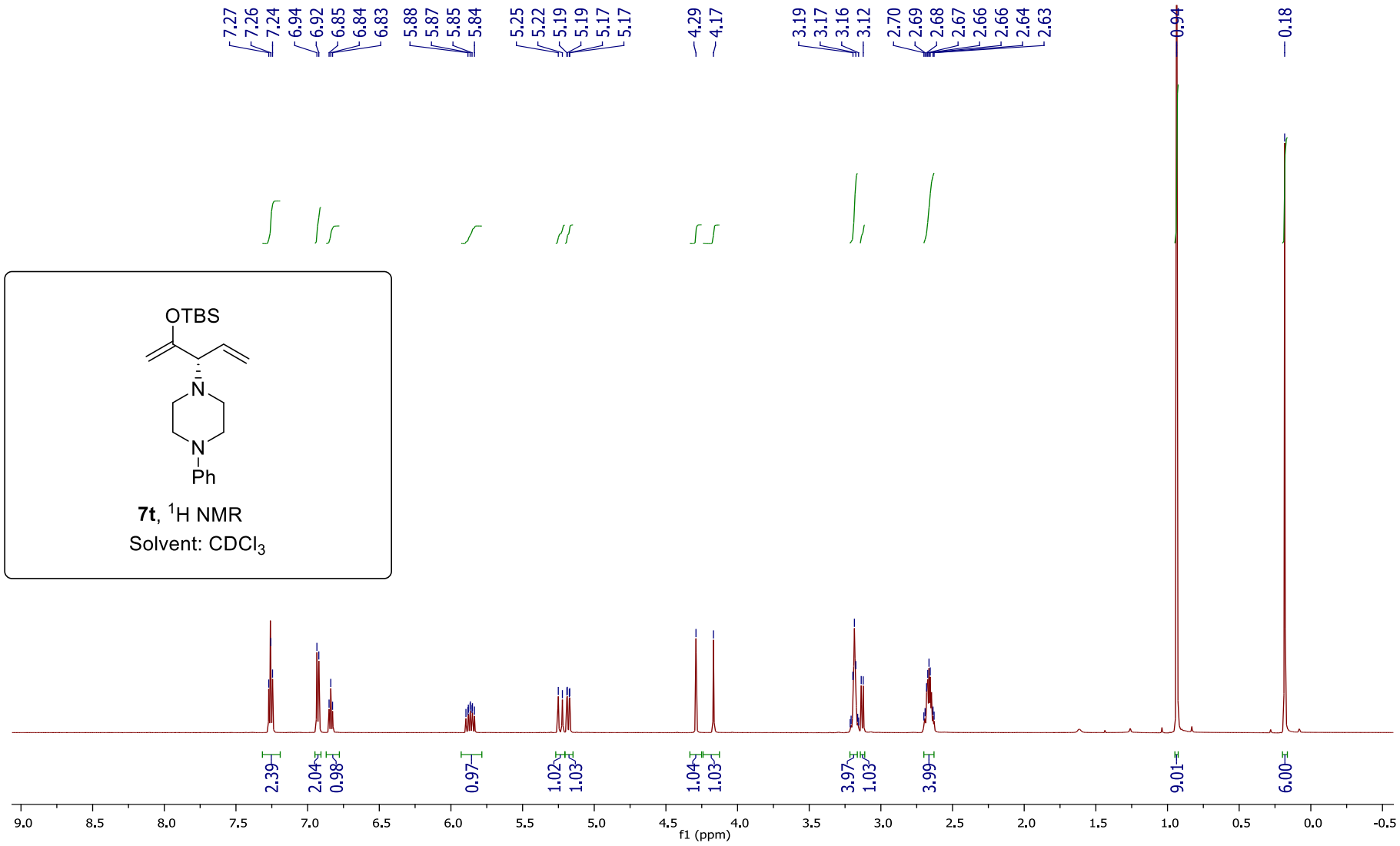
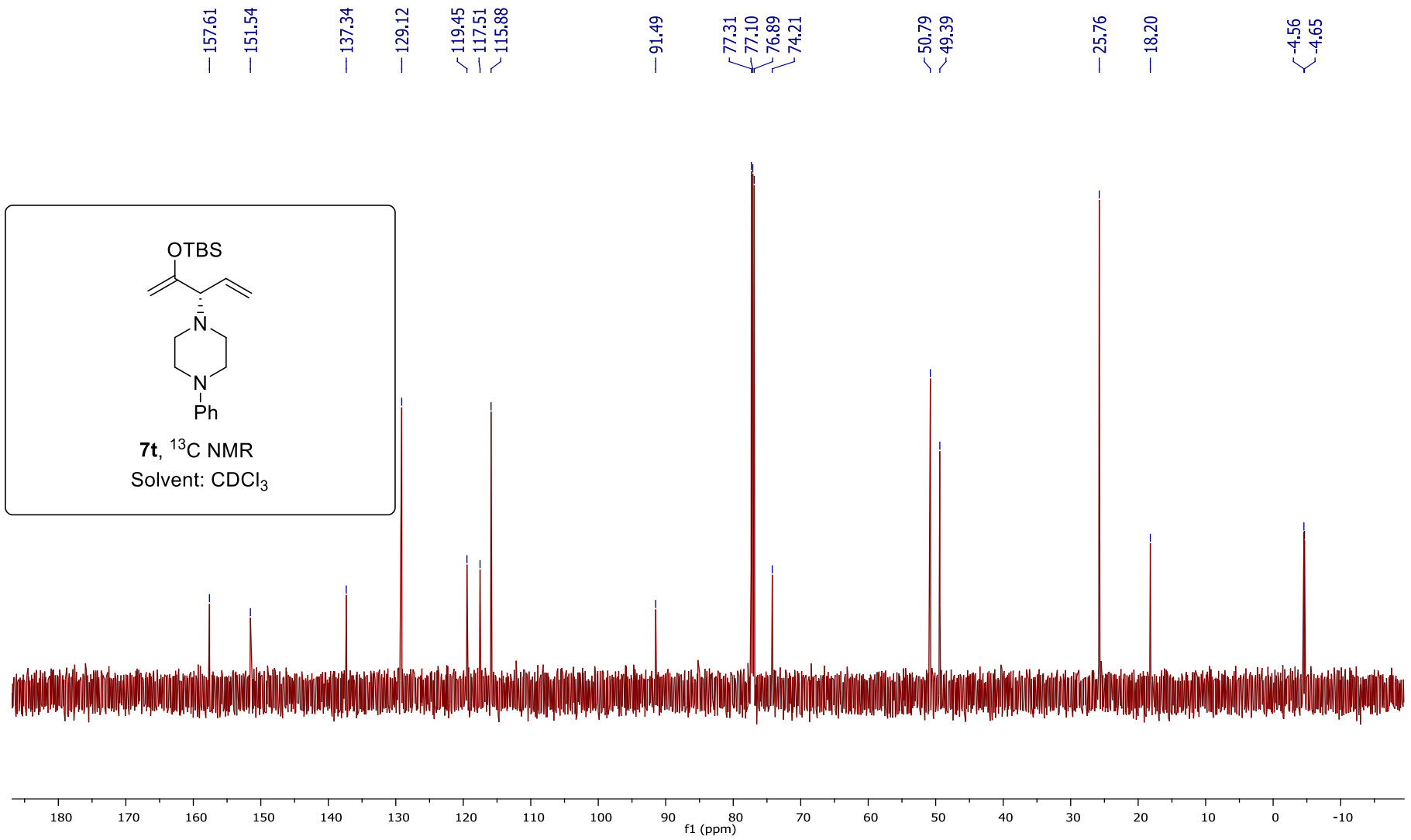
115.80
89.83
77.31
77.10
76.89
62.93
50.81
29.33
25.76
20.12
18.17
10.25
-4.64
-4.79
TBSO
H
N
Me
Me
7s, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.27
7.26
7.24
6.94
6.92
6.85
6.84
6.83
5.88
5.87
5.85
5.84
5.25
5.22
5.19
5.19
5.17
5.17
4.29
4.17
3.19
3.17
3.16
3.12
2.70
2.69
2.68
2.67
2.66
2.66
2.64
2.63
0.94
0.18
OTBS
N
N
Ph
7t, 1H NMR
Solvent: CDCl3
2.39
2.04
0.98
0.97
1.02
1.03
1.04
1.03
3.97
1.03
3.99
9.01
6.00
f1 (ppm)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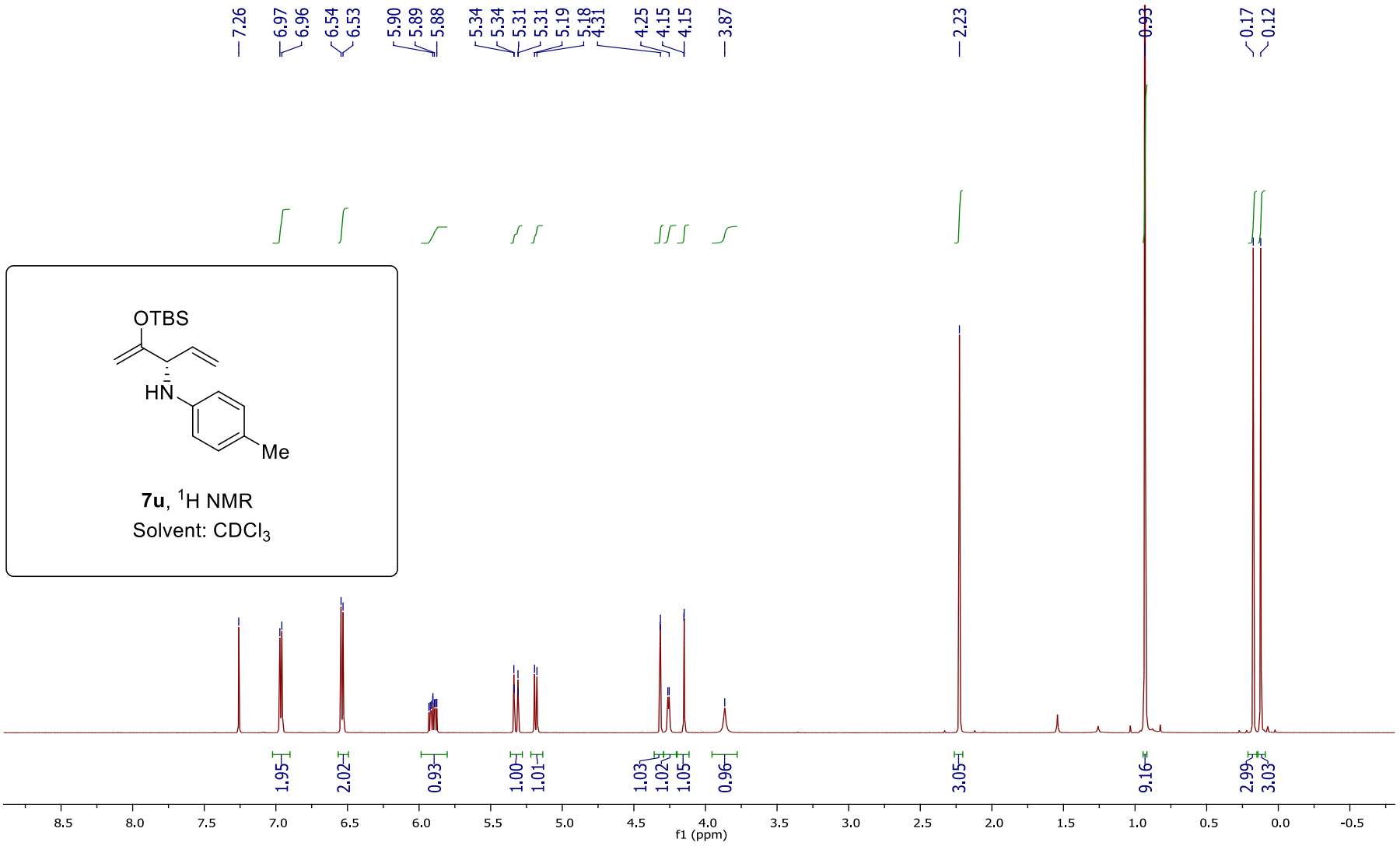
151.54
137.34
129.12
119.45
117.51
115.88
91.49
77.31
77.10
76.89
74.21
50.79
49.39
25.76
18.20
-4.56
-4.65
OTBS
N
N
Ph
7t, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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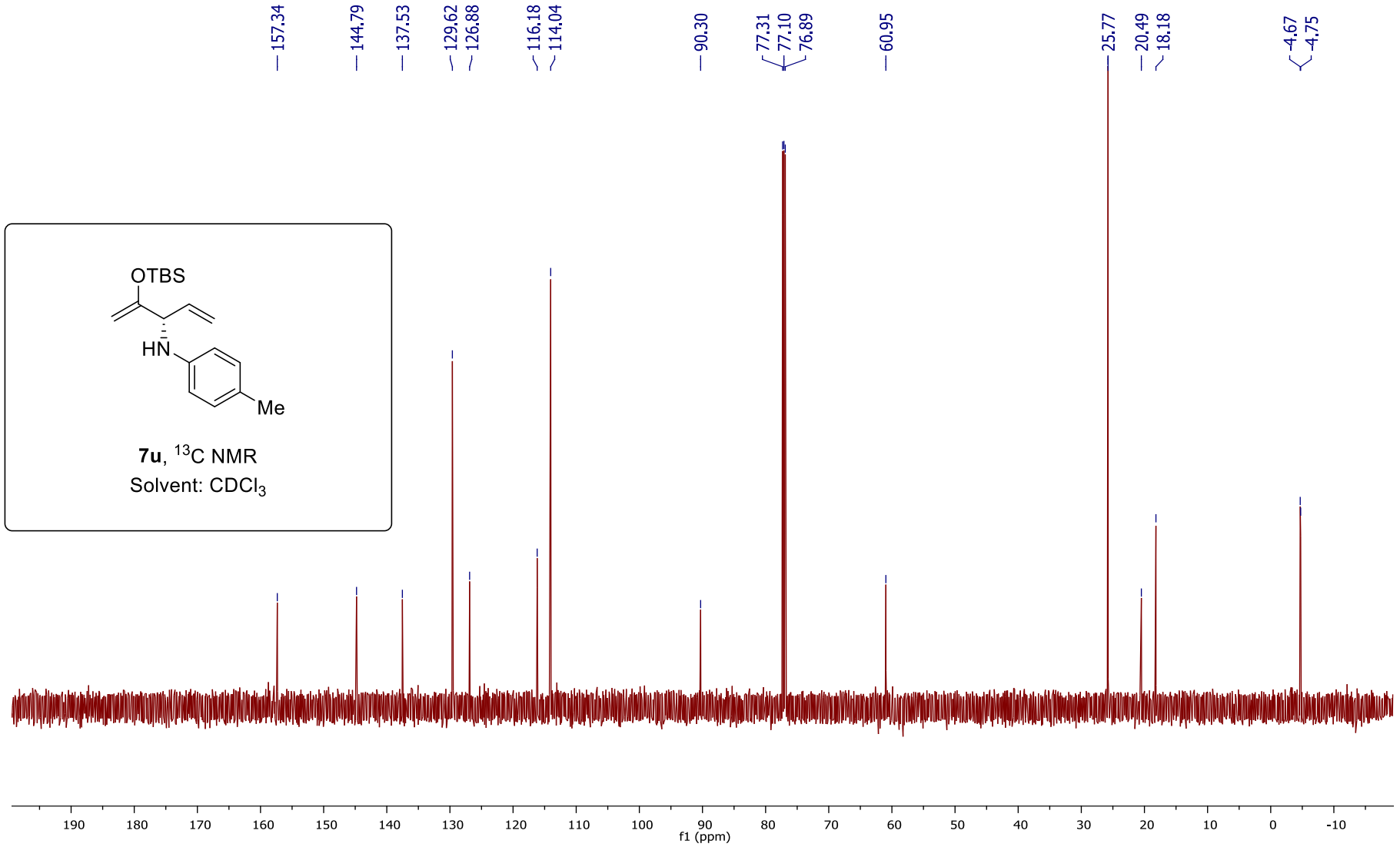
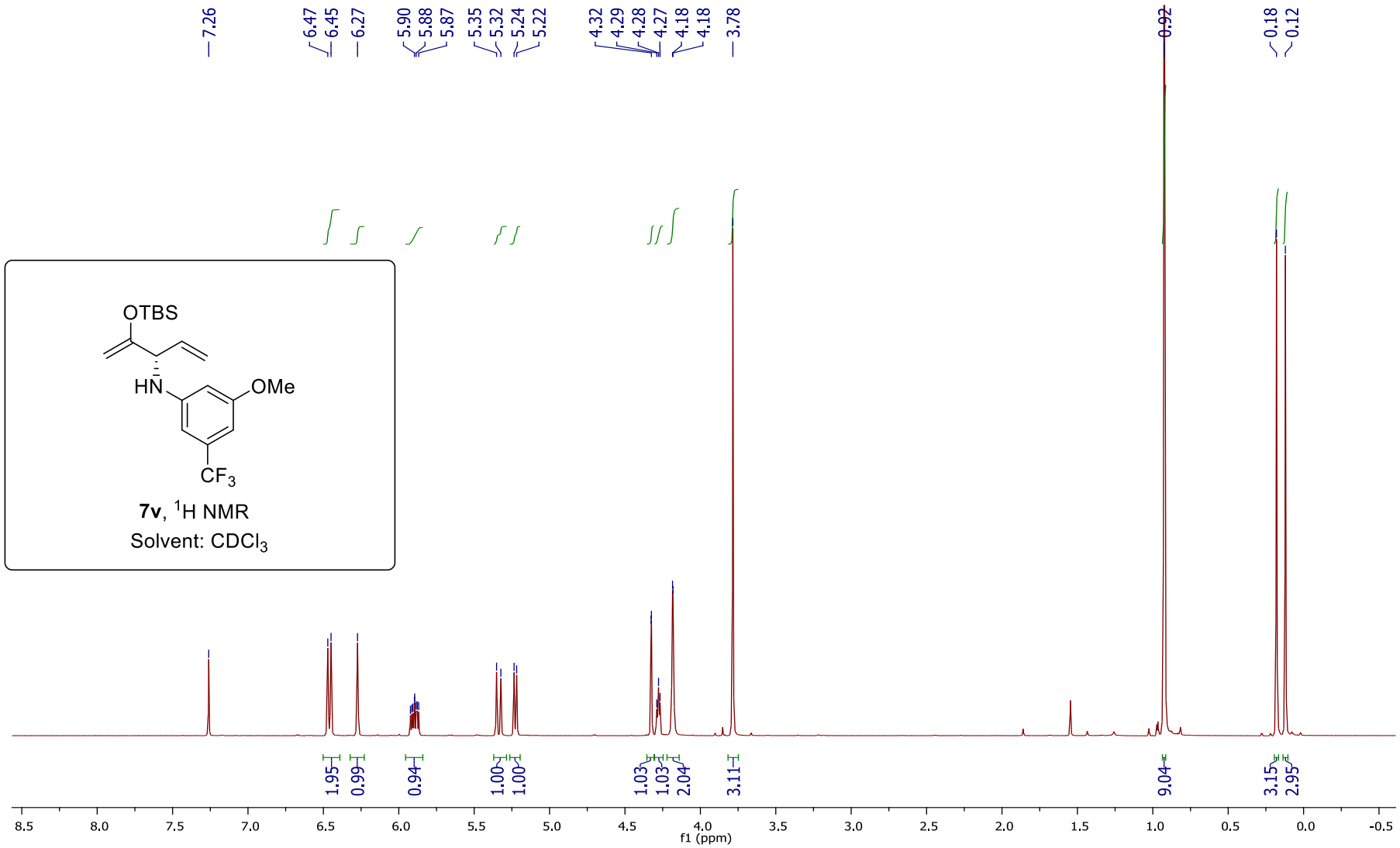
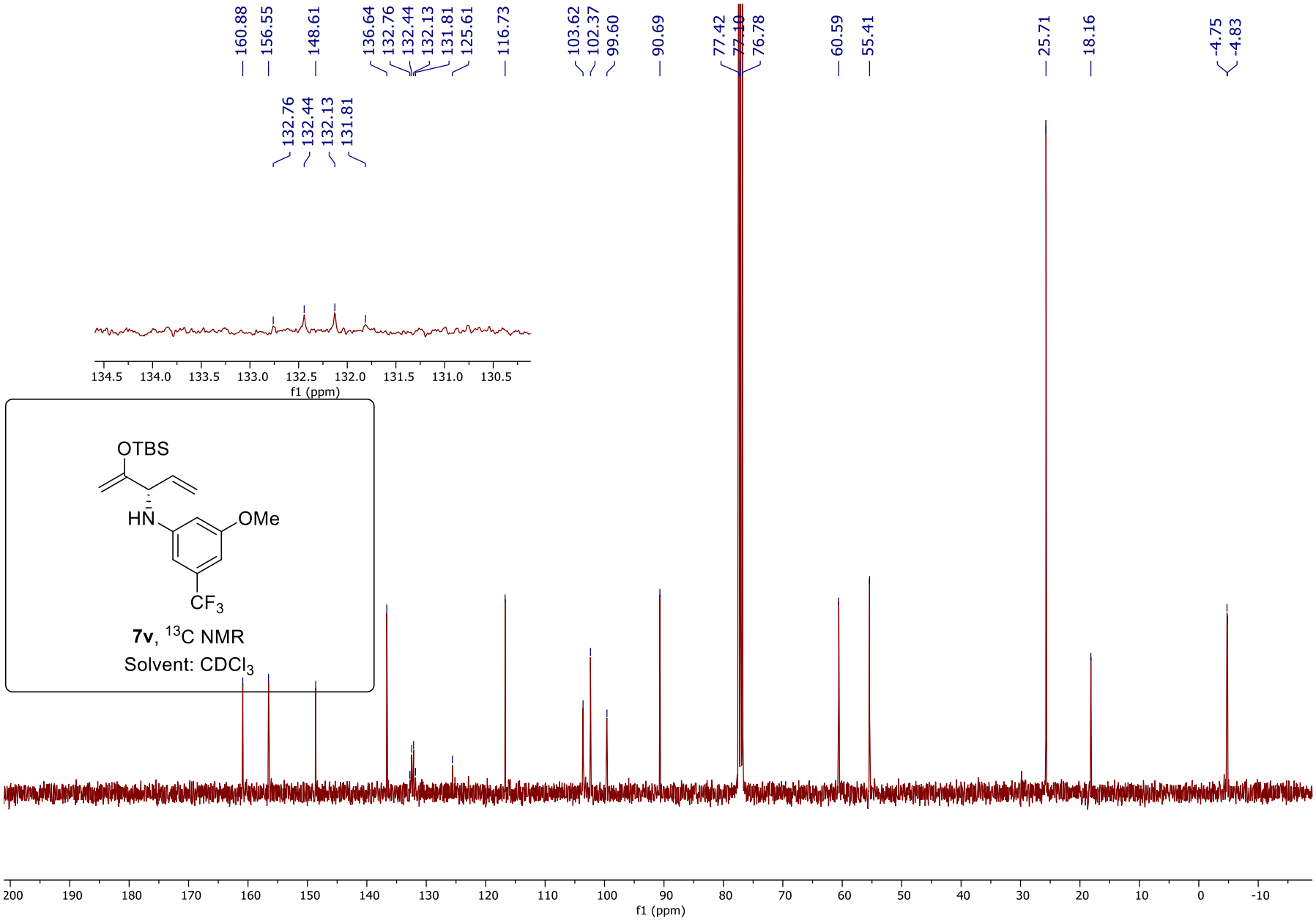
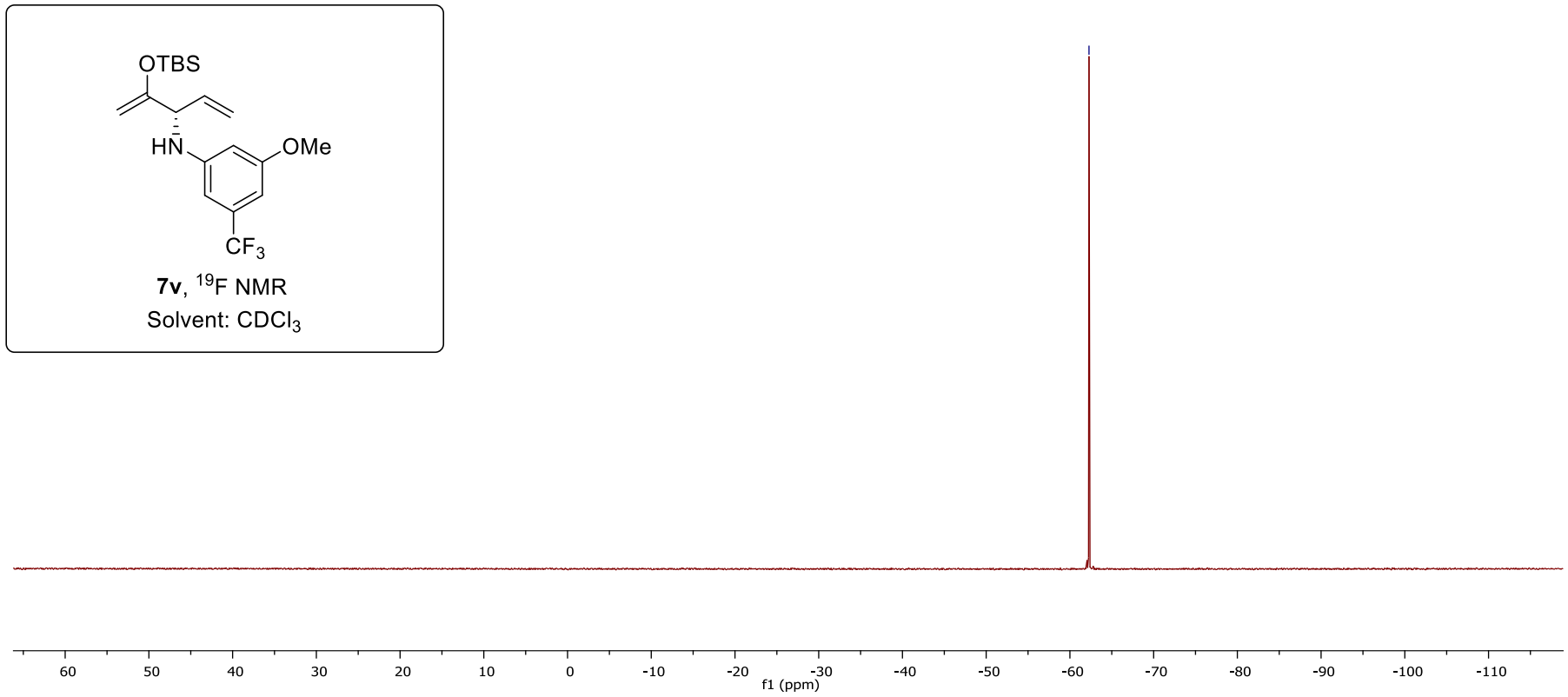
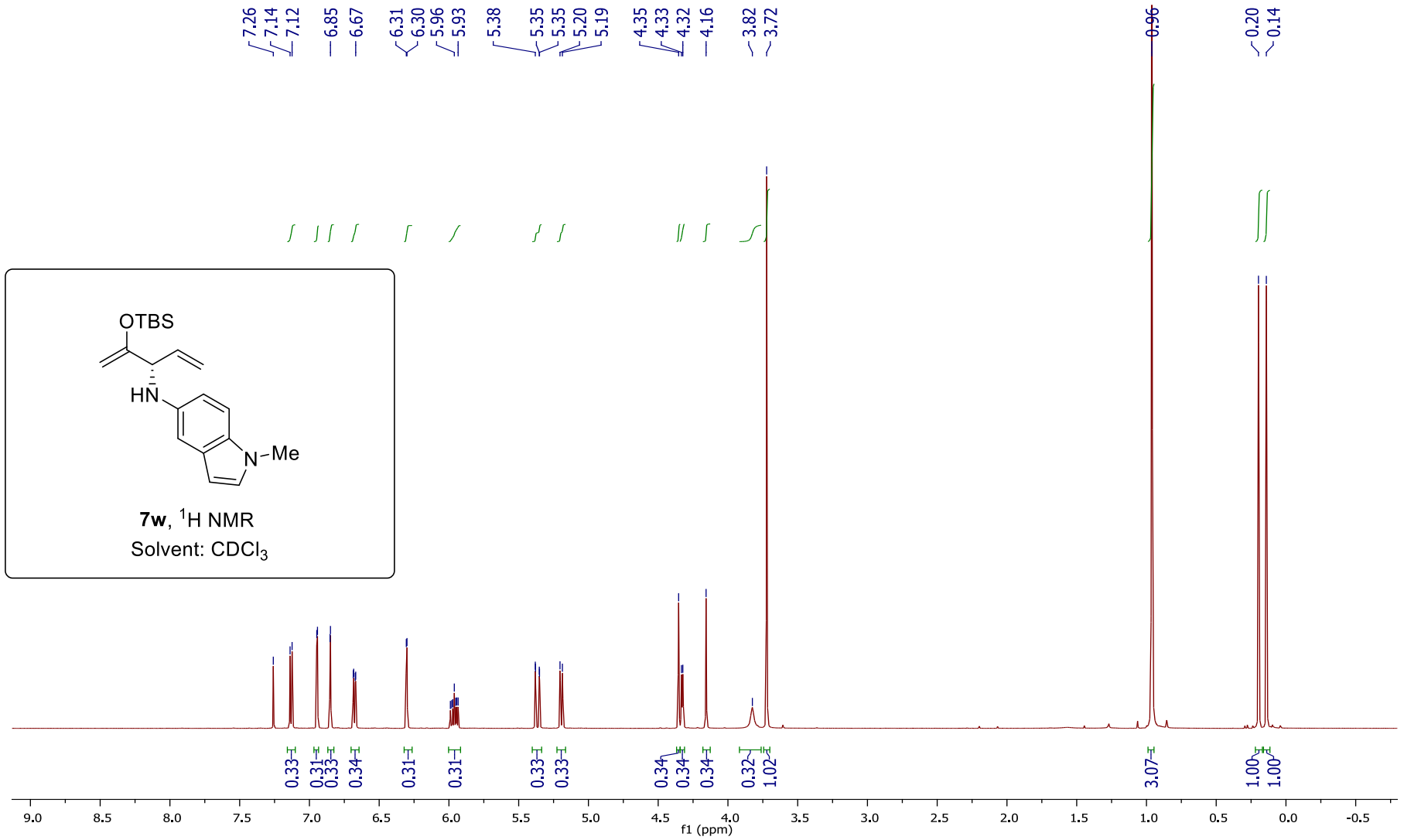
6.97
6.96
6.54
6.53
5.90
5.89
5.88
5.34
5.34
5.31
5.31
5.19
5.18
4.31
4.25
4.15
4.15
3.87
2.23
0.93
0.17
0.12
OTBS
HN
Me
7u, 1H NMR
Solvent: CDCl3
1.95
2.02
0.93
1.00
1.01
1.03
1.02
1.05
0.96
3.05
9.16
2.99
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

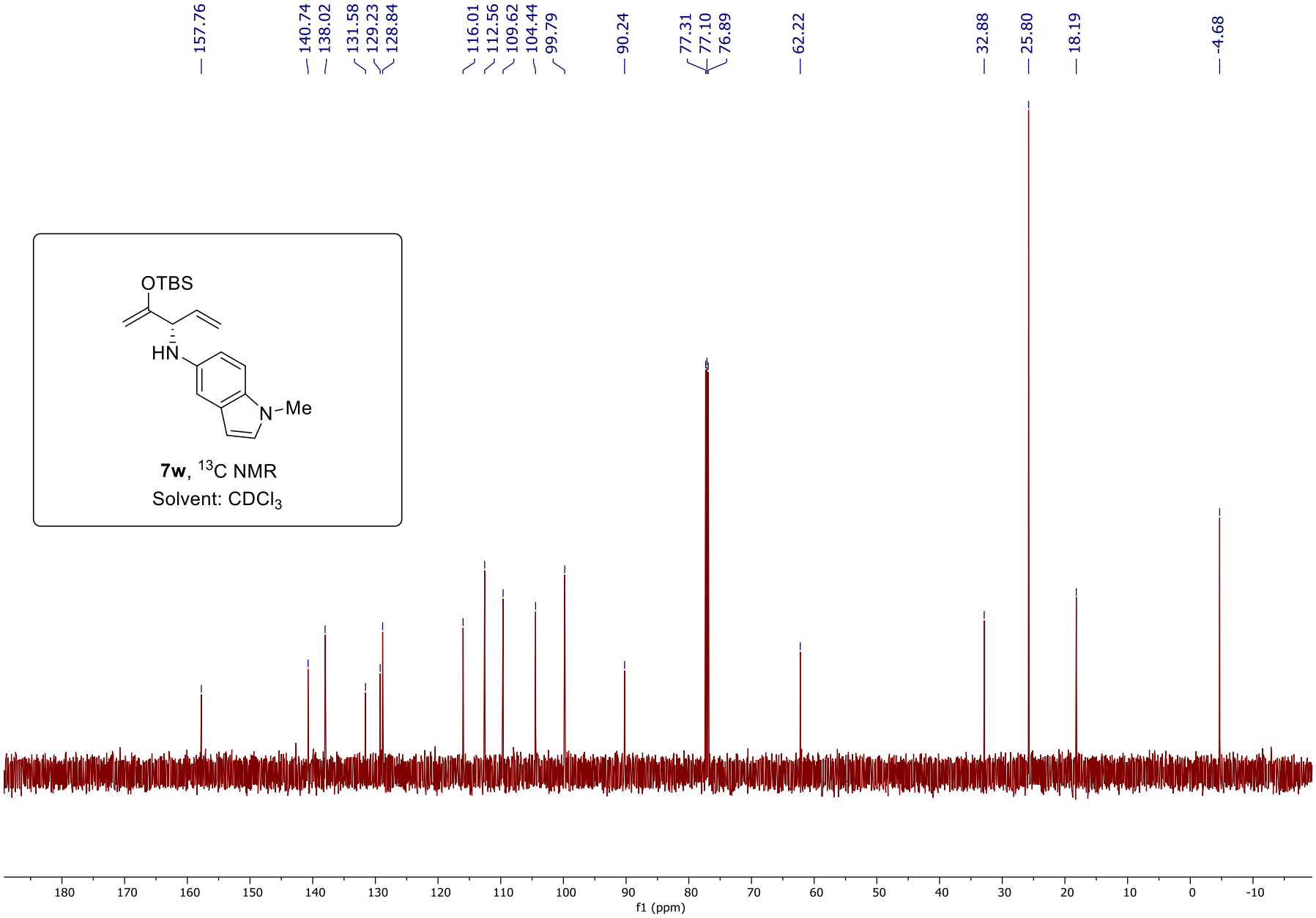

157.34
144.79
137.53
129.62
126.88
116.18
114.04
90.30
77.31
77.10
76.89
60.95
25.77
20.49
18.18
-4.67
-4.75
OTBS
HN
Me
7u, 13C NMR
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

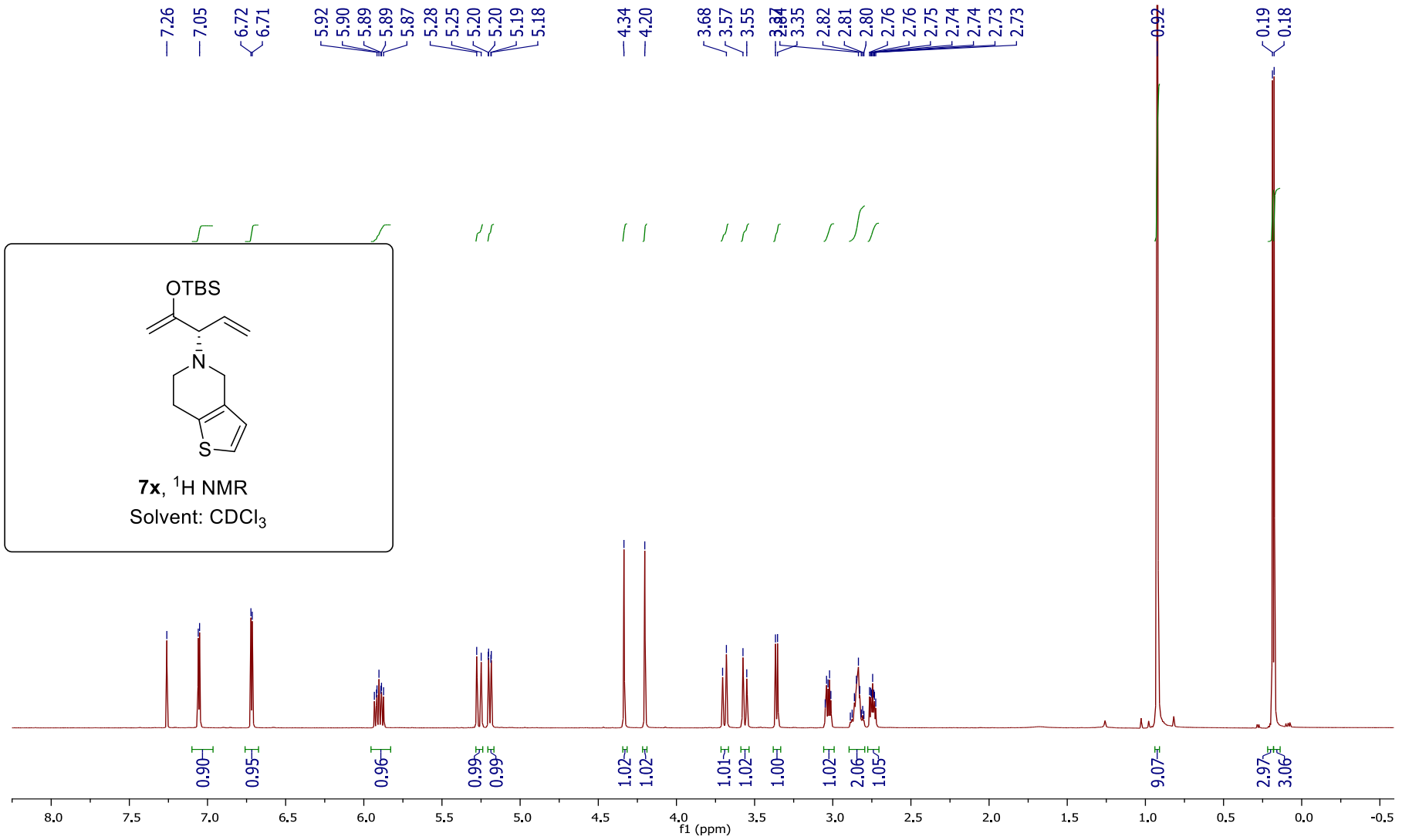

7.26
6.47
6.45
6.27
5.90
5.88
5.87
5.35
5.32
5.24
5.22
4.32
4.29
4.28
4.27
4.18
4.18
3.78
0.92
0.18
0.12
OTBS
HN
OMe
CF3
7v, 1H NMR
Solvent: CDCl3
1.95
0.99
0.94
1.00
1.00
1.03
1.03
2.04
3.11
9.04
3.15
2.95
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

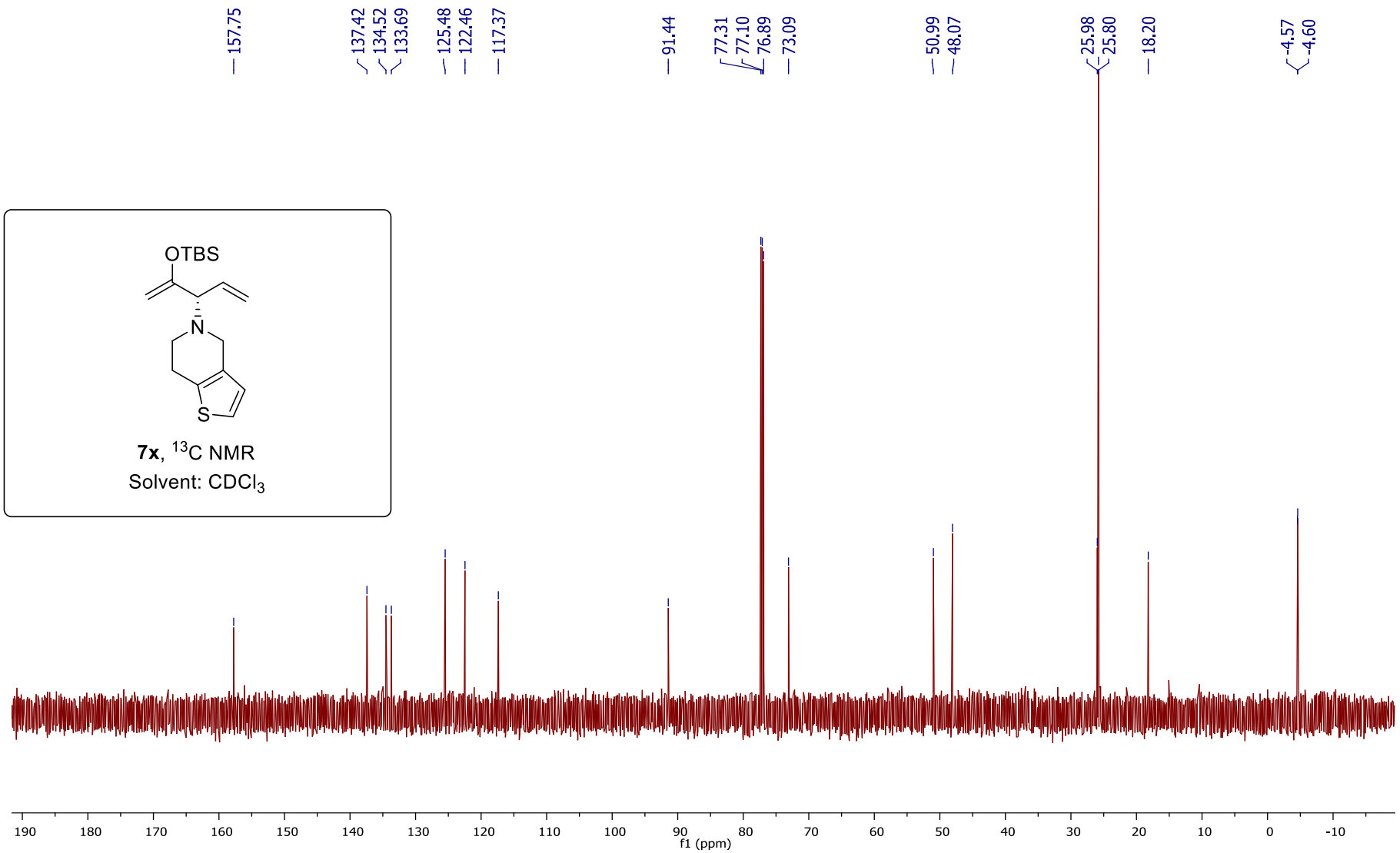

160.88
156.55
148.61
136.64
132.76
132.44
132.13
131.81
125.61
116.73
103.62
102.37
99.60
90.69
77.42
77.10
76.78
60.59
55.41
25.71
18.16
-4.75
-4.83
132.76
132.44
132.13
131.81
134.5 134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5
f1 (ppm)
OTBS
HN
OMe
CF3
7v, 13C NMR
Solvent: CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OTBS
HN
OMe
CF3
7v, 19F NMR
Solvent: CDCl3
-62.28
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)


7.26
7.14
7.12
6.85
6.67
6.31
6.30
5.96
5.93
5.38
5.35
5.35
5.20
5.19
4.35
4.33
4.32
4.16
3.82
3.72
0.96
0.20
0.14
OTBS
HN
N–Me
7w, 1H NMR
Solvent: CDCl3
0.33
0.31
0.33
0.34
0.31
0.31
0.33
0.33
0.34
0.34
0.34
0.32
1.02
3.07
1.00
1.00
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
f1 (ppm)


157.76
140.74
138.02
131.58
129.23
128.84
116.01
112.56
109.62
104.44
99.79
90.24
77.31
77.10
76.89
62.22
32.88
25.80
18.19
-4.68
OTBS
HN
N
Me
7w, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
N
S
7x, 1H NMR
Solvent: CDCl3
7.26
7.05
6.72
6.71
5.92
5.90
5.89
5.89
5.87
5.28
5.25
5.20
5.20
5.19
5.18
4.34
4.20
3.68
3.57
3.55
3.35
2.82
2.81
2.80
2.76
2.76
2.75
2.74
2.74
2.73
2.73
0.92
0.19
0.18
0.90
0.95
0.96
0.99
0.99
1.02
1.02
1.01
1.02
1.00
1.02
2.06
1.05
9.07
2.97
3.06
f1 (ppm)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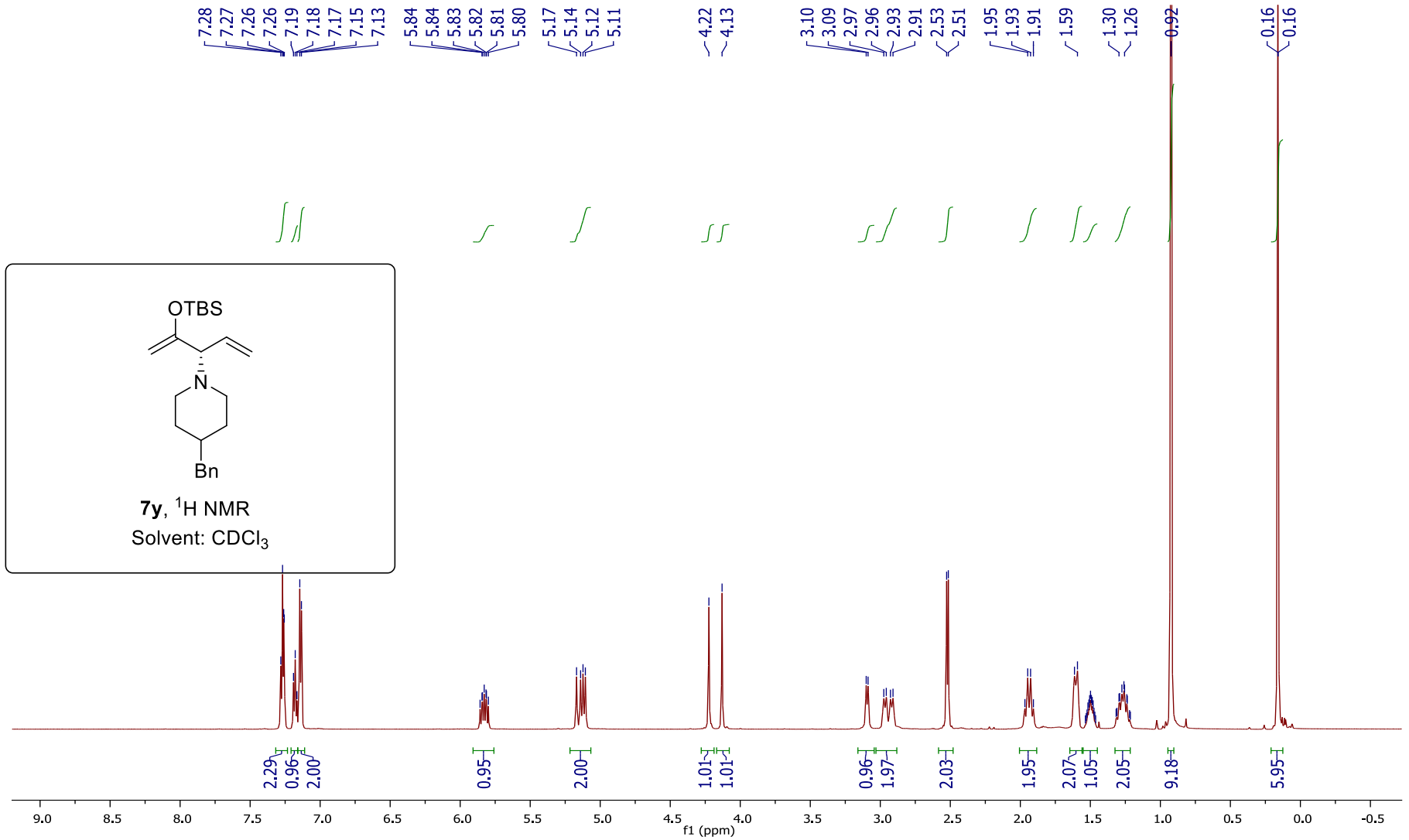
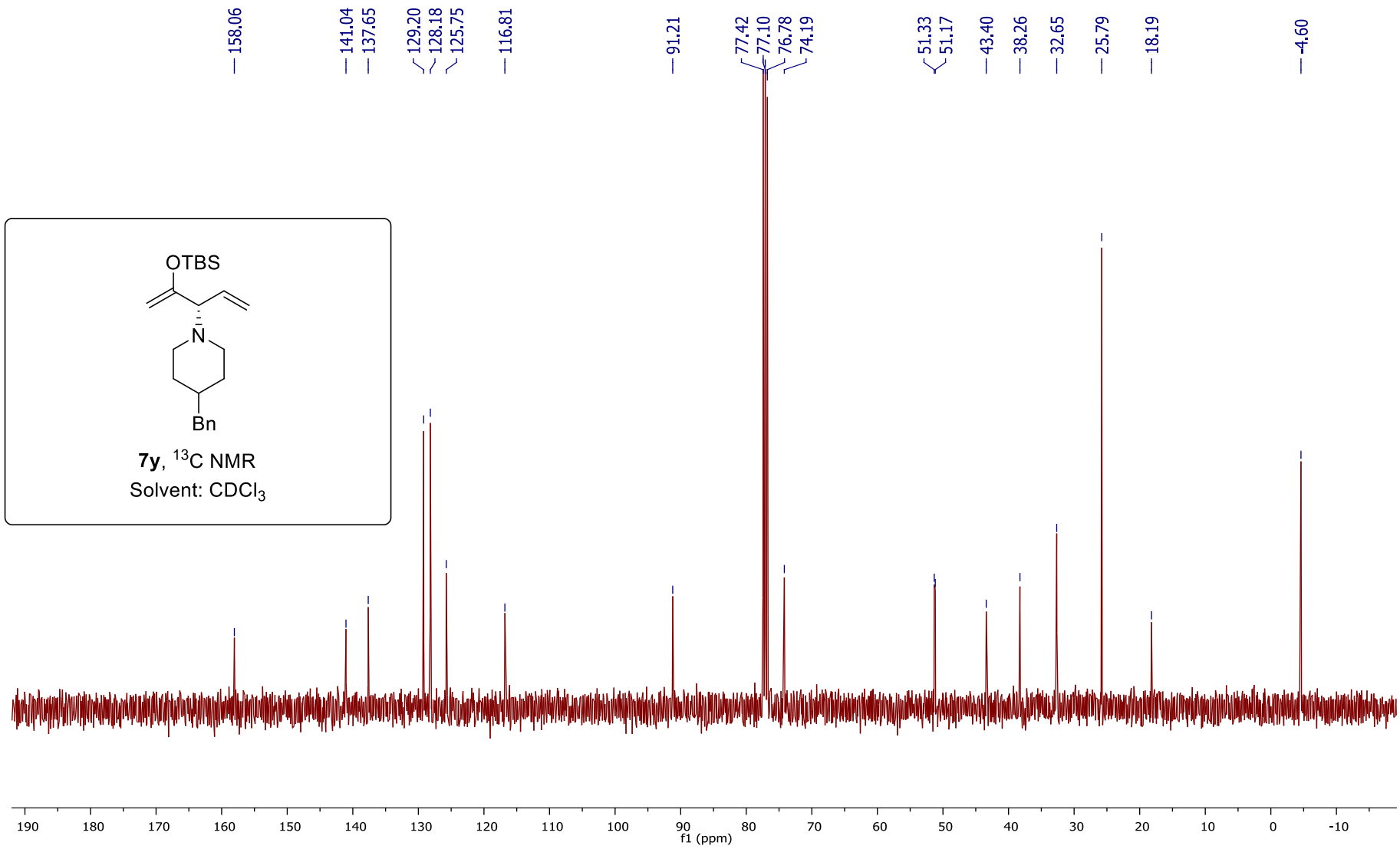
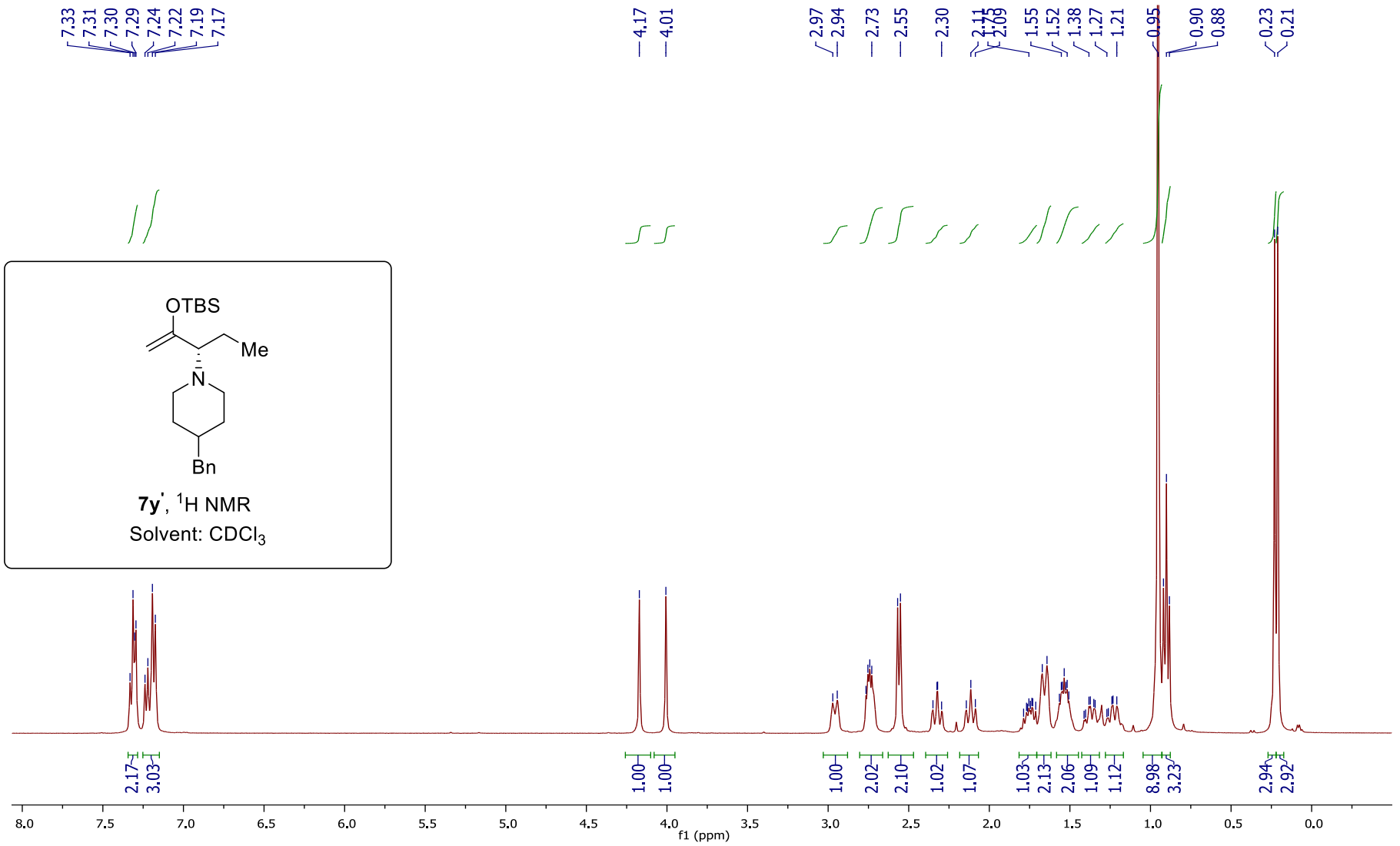
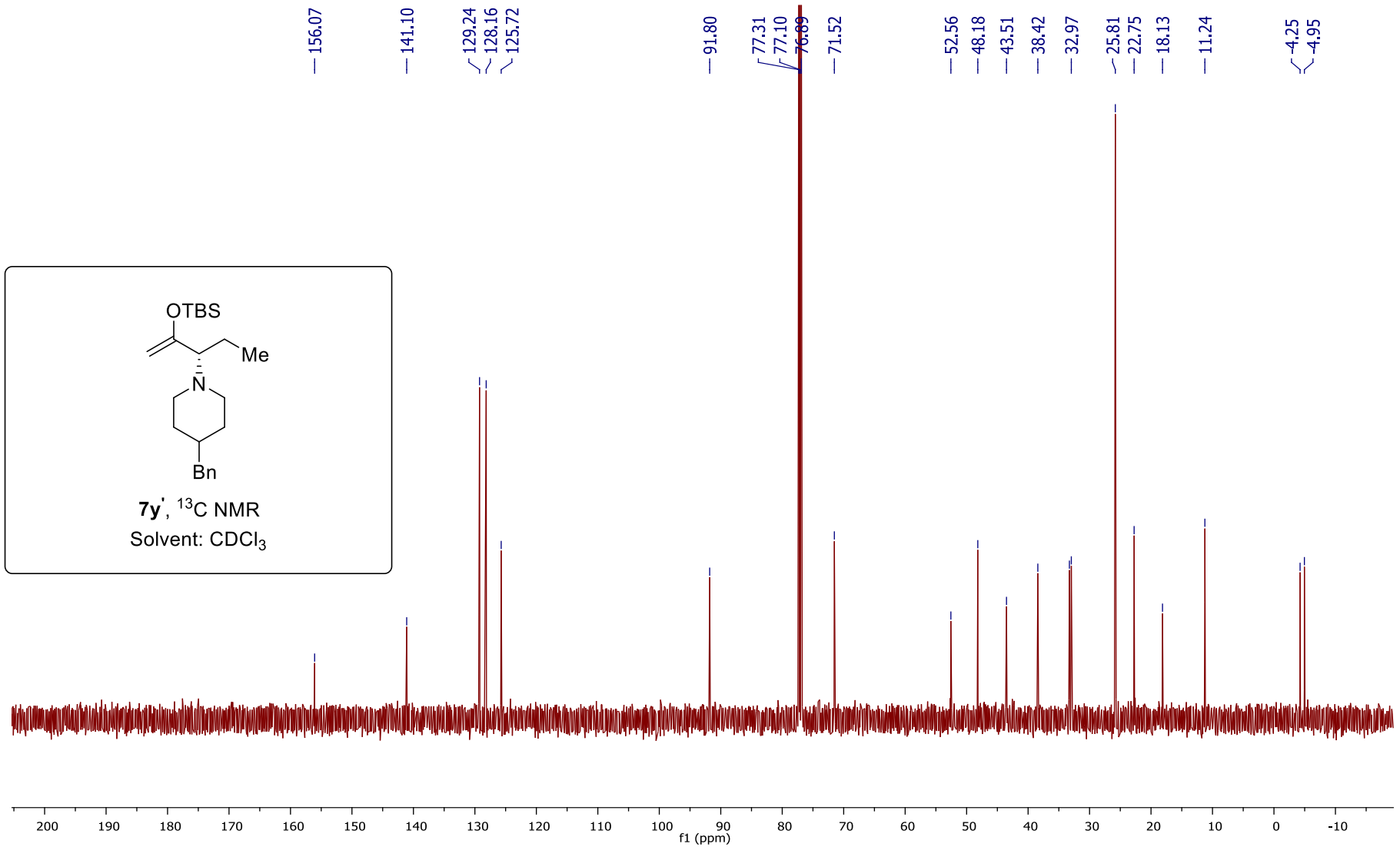
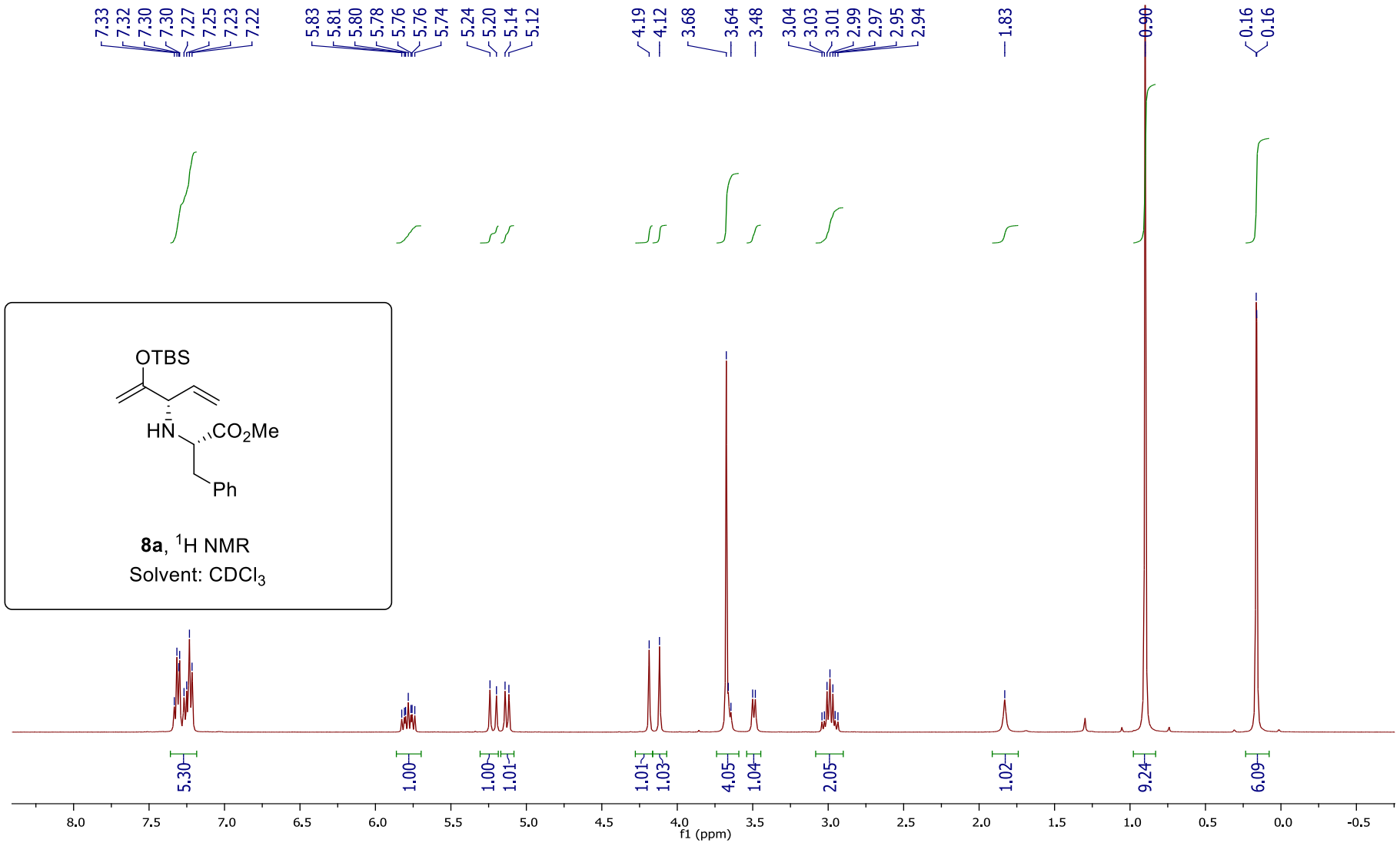
134.52
133.69
125.48
122.46
117.37
91.44
77.31
77.10
76.89
73.09
50.99
48.07
25.98
25.80
18.20
-4.57
-4.60
OTBS
N
S
7x, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

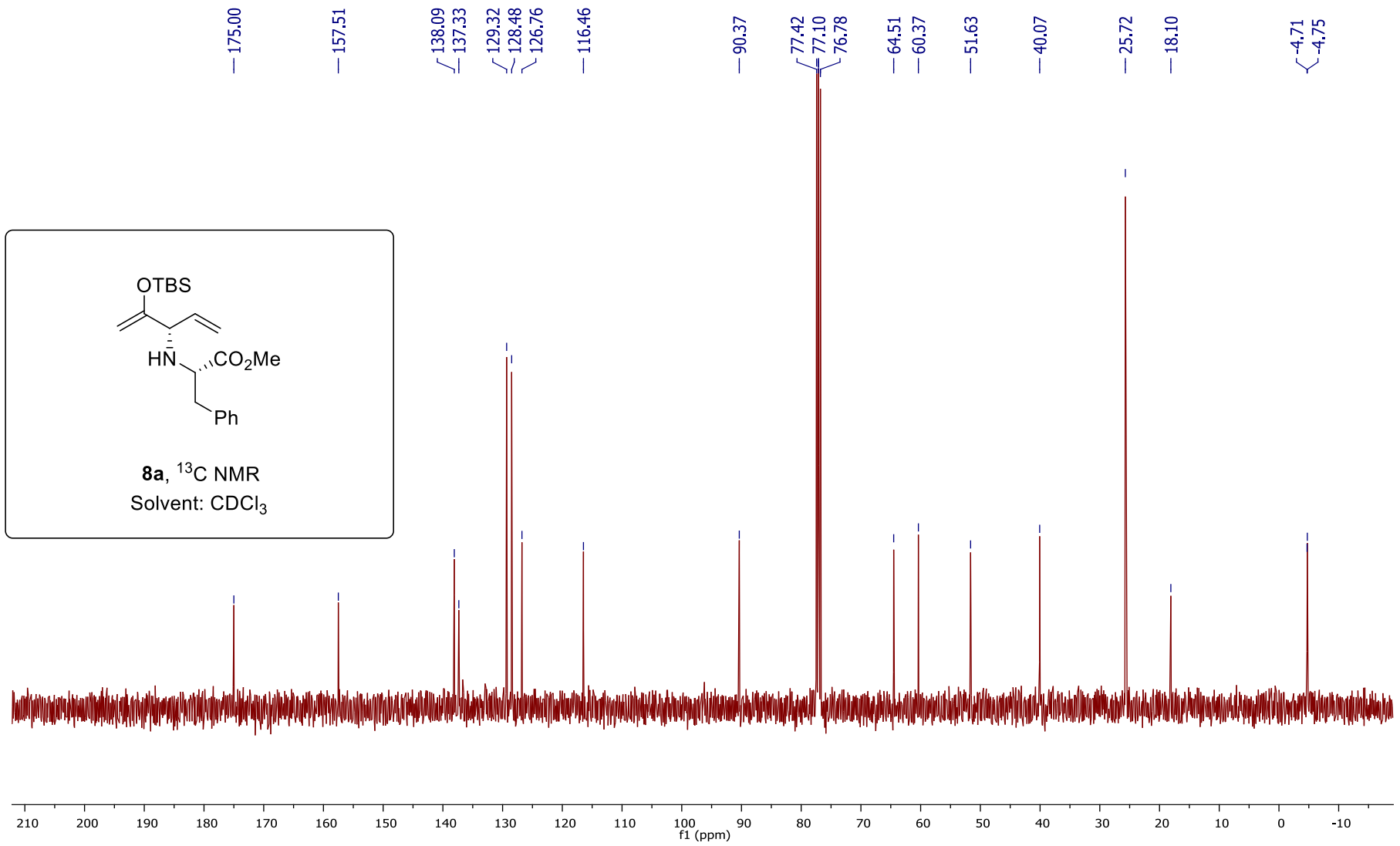

OTBS
N
Bn
7y, 1H NMR
Solvent: CDCl3
7.28 7.27 7.26 7.26 7.19 7.18 7.17 7.15 7.13
5.84 5.84 5.83 5.82 5.81 5.80
5.17 5.14 5.12 5.11
4.22 4.13
3.10 3.09 2.97 2.96 2.93 2.91
2.53 2.51
1.95 1.93 1.91
1.59
1.30 1.26
0.92
0.16 0.16
2.29 0.96 2.00 0.95 2.00 1.01 1.01 0.96 1.97 2.03 1.95 2.07 1.05 2.05 9.18 5.95
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)


158.06
141.04
137.65
129.20
128.18
125.75
116.81
91.21
77.42
77.10
76.78
74.19
51.33
51.17
43.40
38.26
32.65
25.79
18.19
-4.60
OTBS
N
Bn
7y, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
Me
N
Bn
7y', 1H NMR
Solvent: CDCl3
f1 (ppm)


156.07
141.10
129.24
128.16
125.72
91.80
77.31
77.10
76.89
71.52
52.56
48.18
43.51
38.42
32.97
25.81
22.75
18.13
11.24
-4.25
-4.95
OTBS
Me
N
Bn
7y', 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.33
7.32
7.30
7.30
7.27
7.25
7.23
7.22
5.83
5.81
5.80
5.78
5.76
5.76
5.74
5.24
5.20
5.14
5.12
4.19
4.12
3.68
3.64
3.48
3.04
3.03
3.01
2.99
2.97
2.95
2.94
1.83
0.90
0.16
0.16
OTBS
HN
CO2Me
Ph
8a, 1H NMR
Solvent: CDCl3
5.30
1.00
1.00
1.01
1.01
1.03
4.05
1.04
2.05
1.02
9.24
6.09
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)


175.00
157.51
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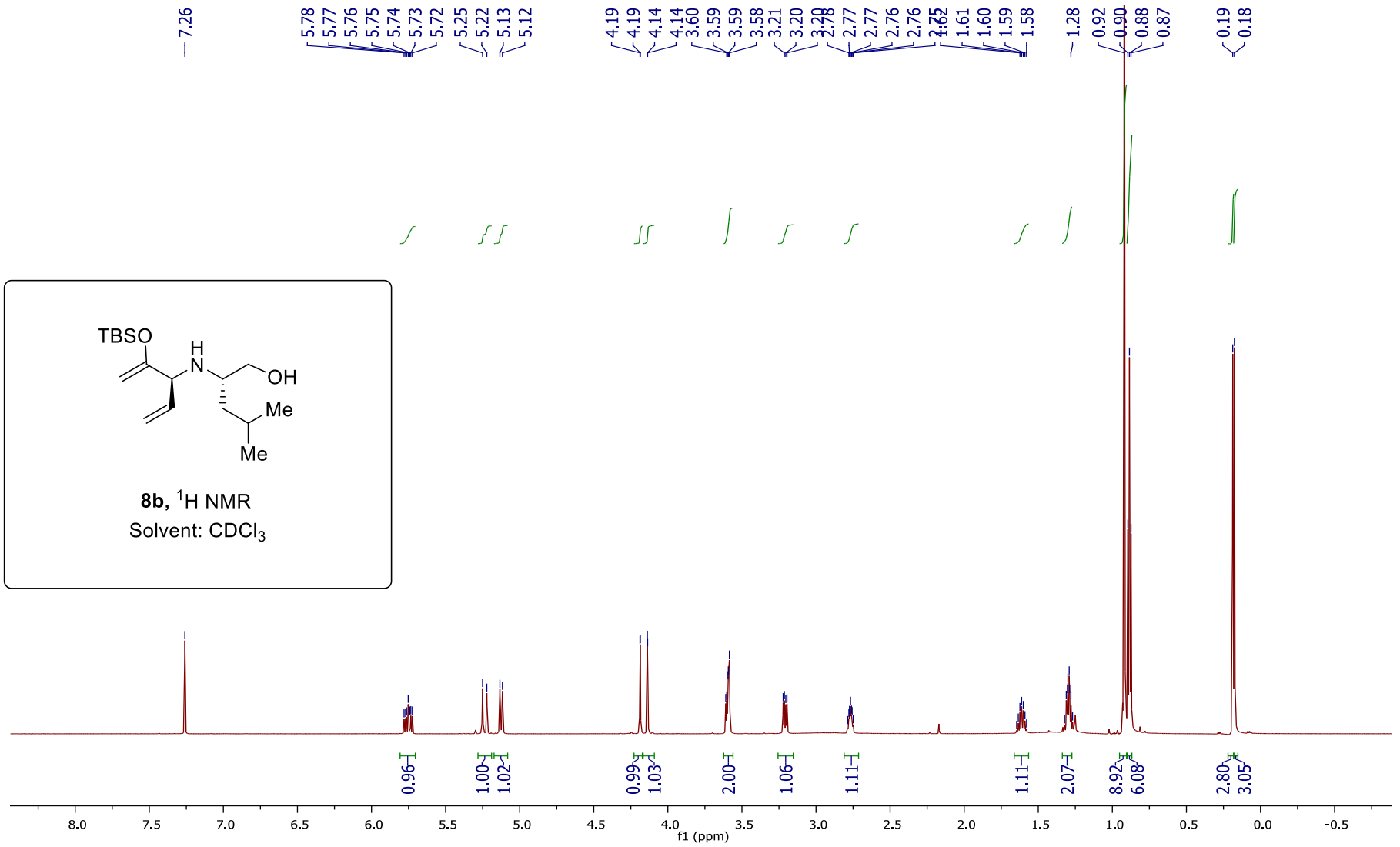
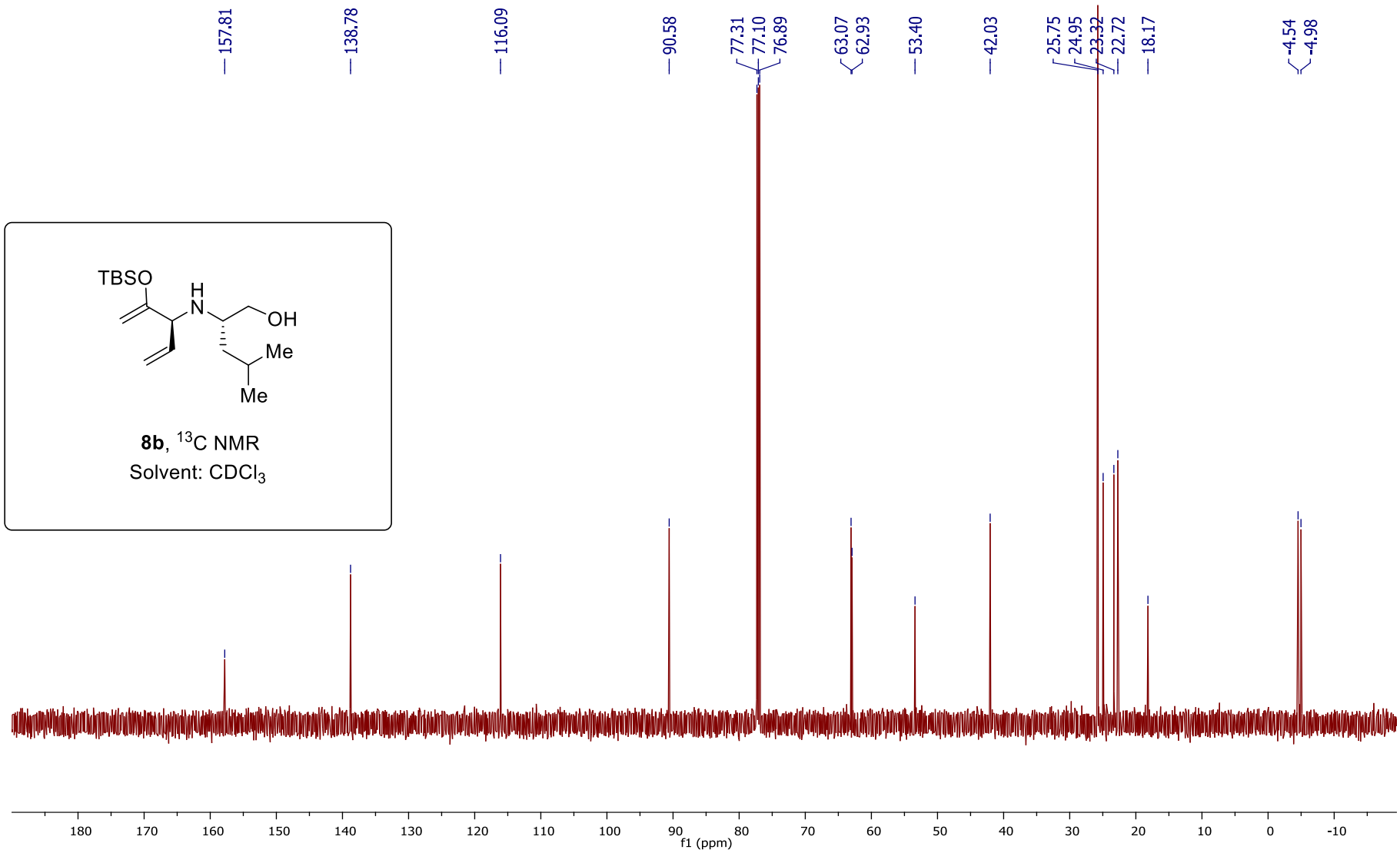
137.33
129.32
128.48
126.76
116.46
90.37
77.42
77.10
76.78
64.51
60.37
51.63
40.07
25.72
18.10
-4.71
-4.75
OTBS
HN
CO2Me
Ph
8a, 13C NMR
Solvent: CDCl3
f1 (ppm)


7.26
5.78
5.77
5.76
5.75
5.74
5.73
5.72
5.25
5.22
5.13
5.12
4.19
4.19
4.14
4.14
3.60
3.59
3.59
3.58
3.21
3.20
3.20
2.78
2.77
2.77
2.76
2.76
1.61
1.60
1.59
1.58
1.28
0.92
0.90
0.88
0.87
0.19
0.18
TBSO
H
N
OH
Me
Me
8b, 1H NMR
Solvent: CDCl3
0.96
1.00
1.02
0.99
1.03
2.00
1.06
1.11
1.11
2.07
8.92
6.08
2.80
3.05
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)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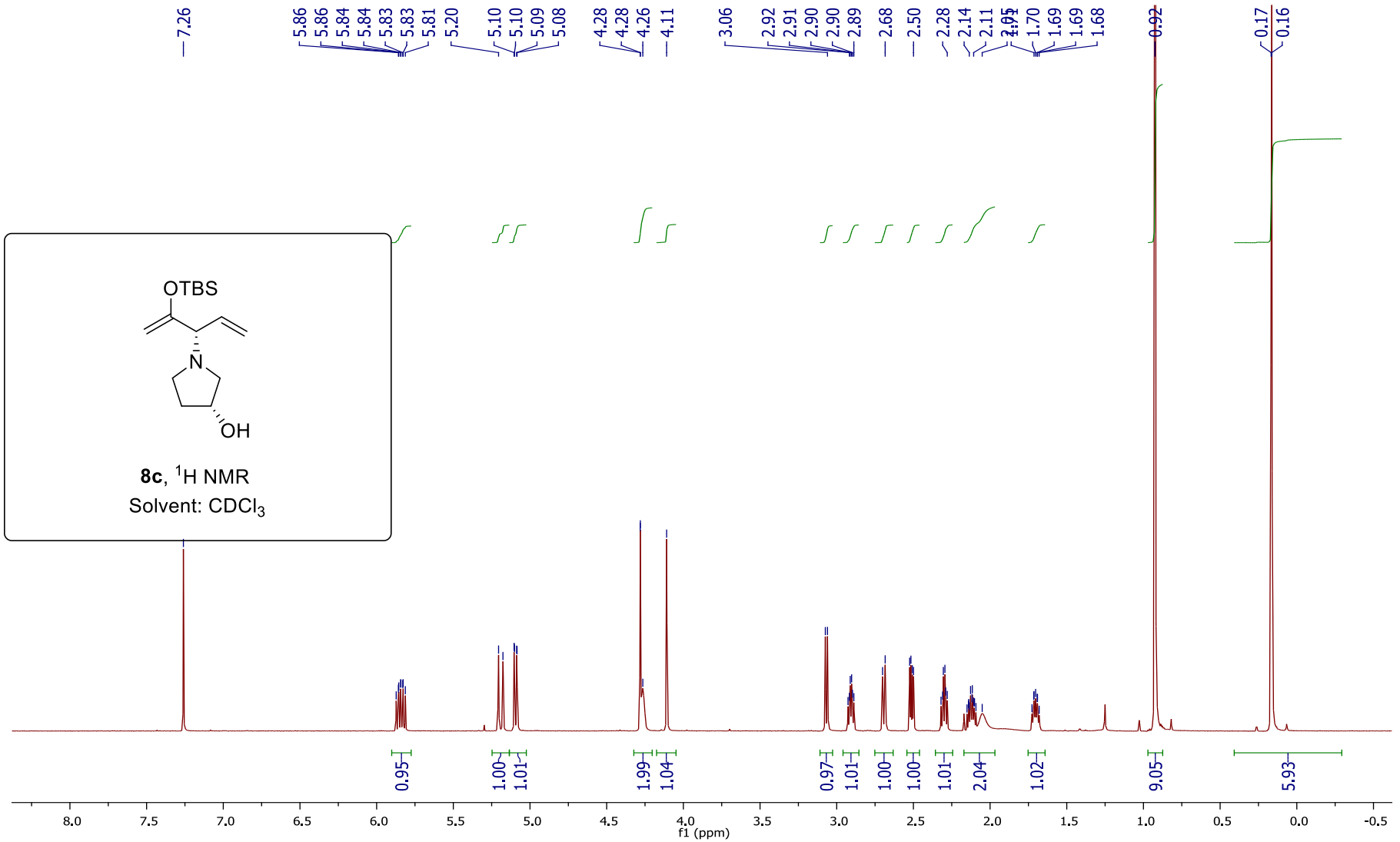
90.58
77.31
77.10
76.89
63.07
62.93
53.40
42.03
25.75
24.95
23.32
22.72
18.17
-4.54
-4.98
TBSO
H
N
OH
Me
Me
8b, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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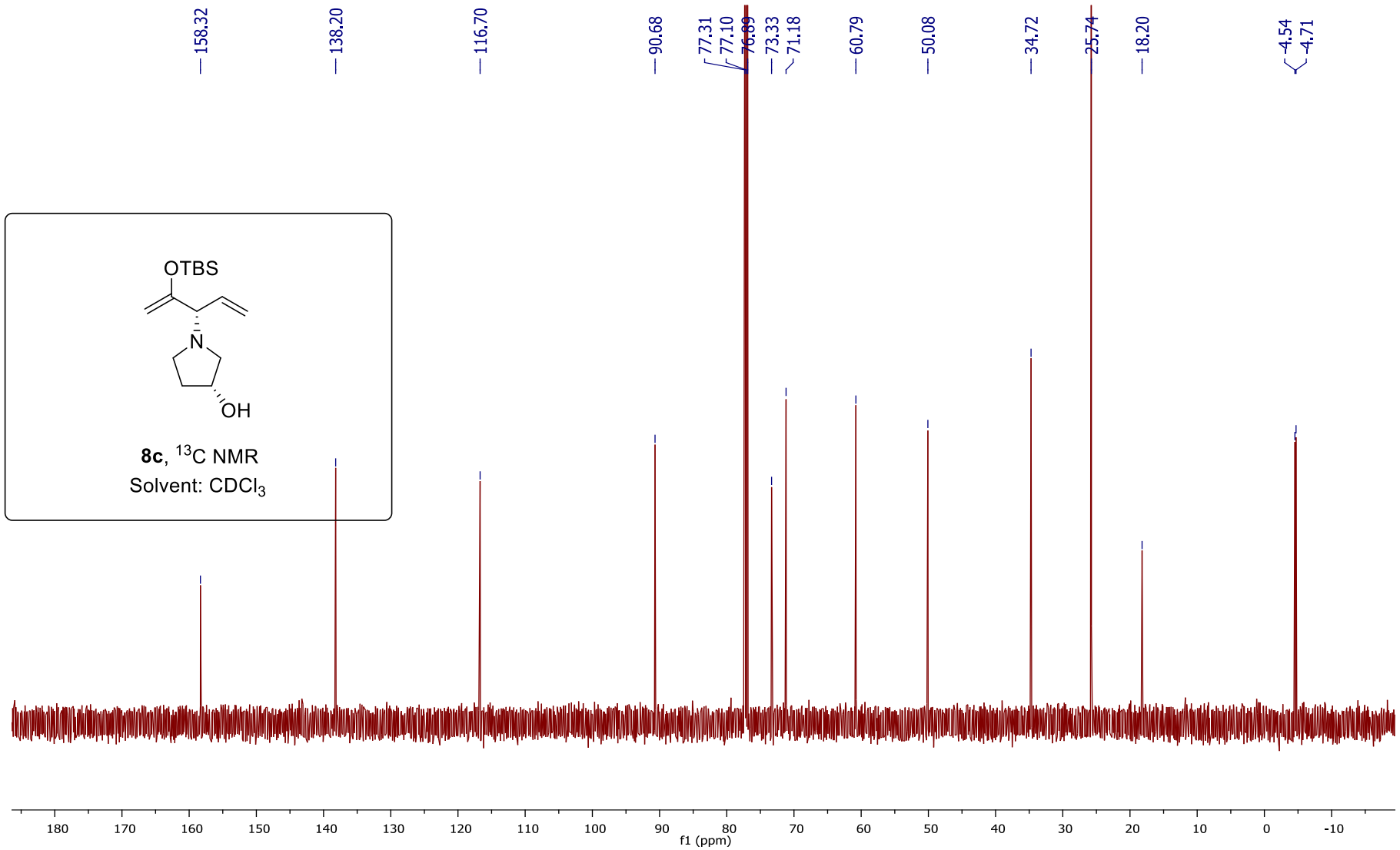
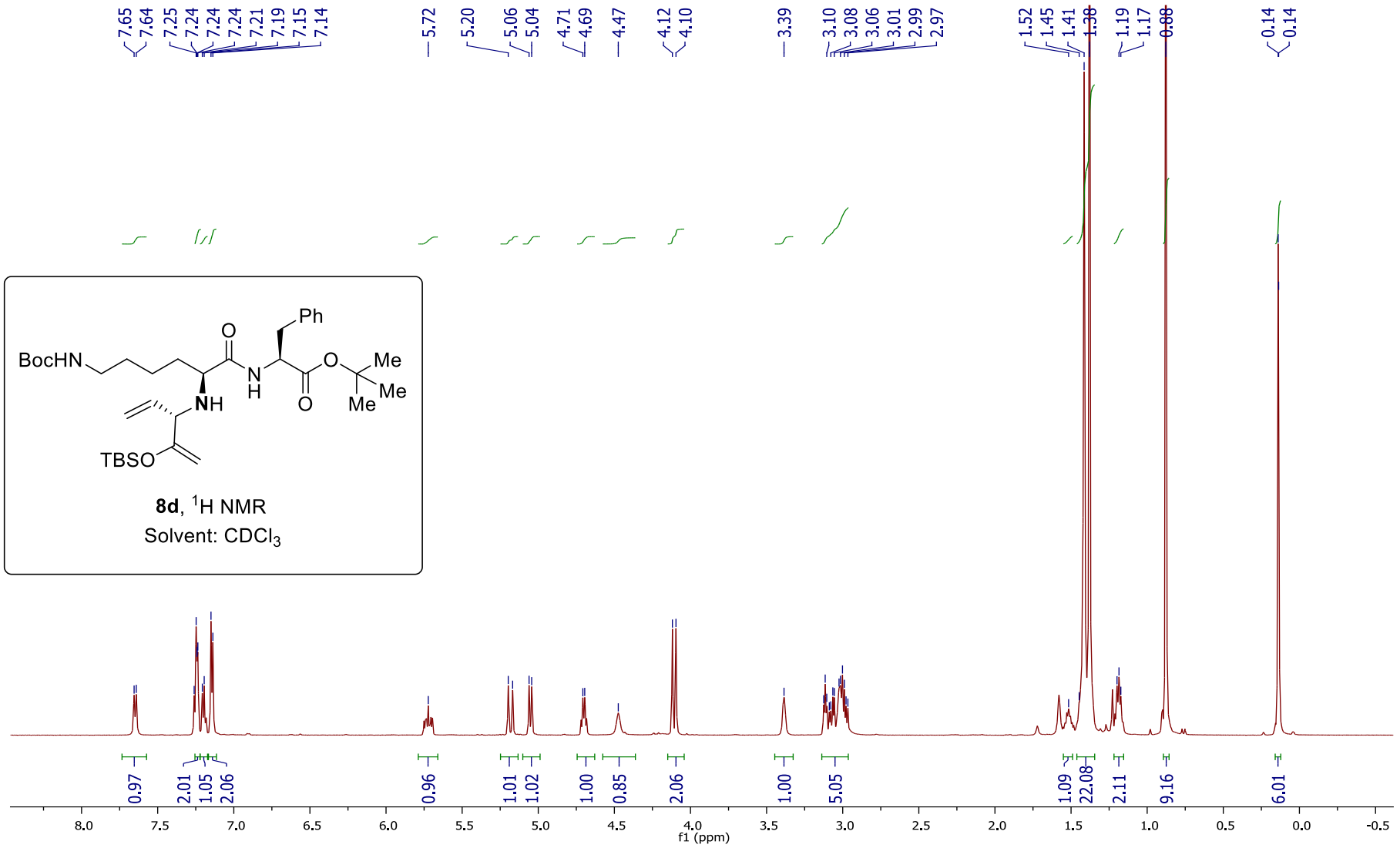
N
OH
8c, 1H NMR
Solvent: CDCl3
7.26
5.86
5.86
5.84
5.84
5.83
5.83
5.81
5.20
5.10
5.10
5.09
5.08
4.28
4.28
4.26
4.11
3.06
2.92
2.91
2.90
2.90
2.89
2.68
2.50
2.28
2.14
2.11
1.70
1.69
1.69
1.68
0.92
0.17
0.16
0.95
1.00
1.01
1.99
1.04
0.97
1.01
1.00
1.00
1.01
2.04
1.02
9.05
5.93
f1 (ppm)


158.32
138.20
116.70
90.68
77.31
77.10
76.89
73.33
71.18
60.79
50.08
34.72
25.74
18.20
-4.54
-4.71
OTBS
N
OH
8c, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.64
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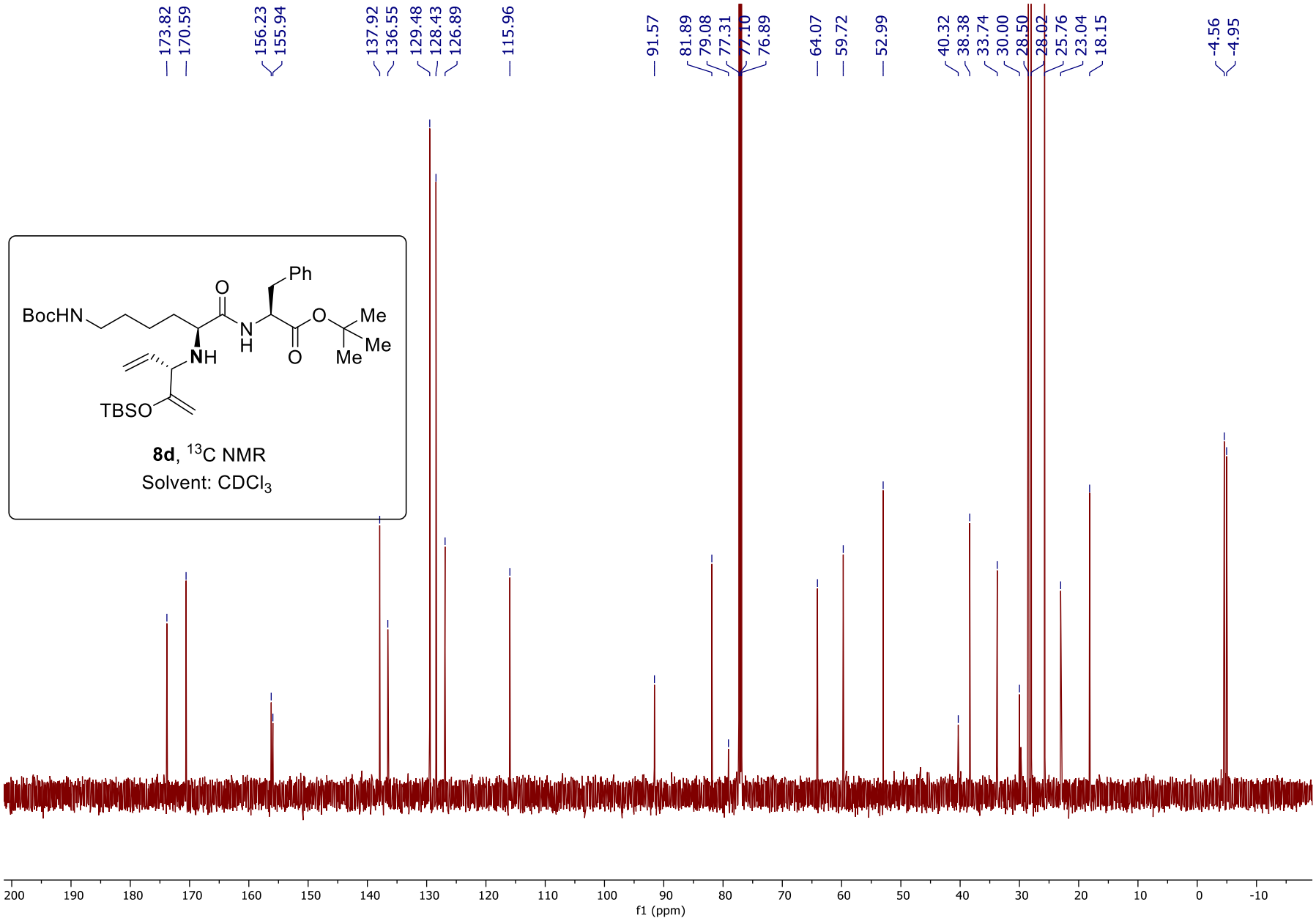
7.24
7.24
7.21
7.19
7.15
7.14
5.72
5.20
5.06
5.04
4.71
4.69
4.47
4.12
4.10
3.39
3.10
3.08
3.06
3.01
2.99
2.97
1.52
1.45
1.41
1.38
1.19
1.17
0.88
0.14
0.14
BocHN
O
N
H
Ph
O
O
Me
Me
Me
NH
TBSO
8d, 1H NMR
Solvent: CDCl3
0.97
2.01
1.05
2.06
0.96
1.01
1.02
1.00
0.85
2.06
1.00
5.05
1.09
22.08
2.11
9.16
6.01
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)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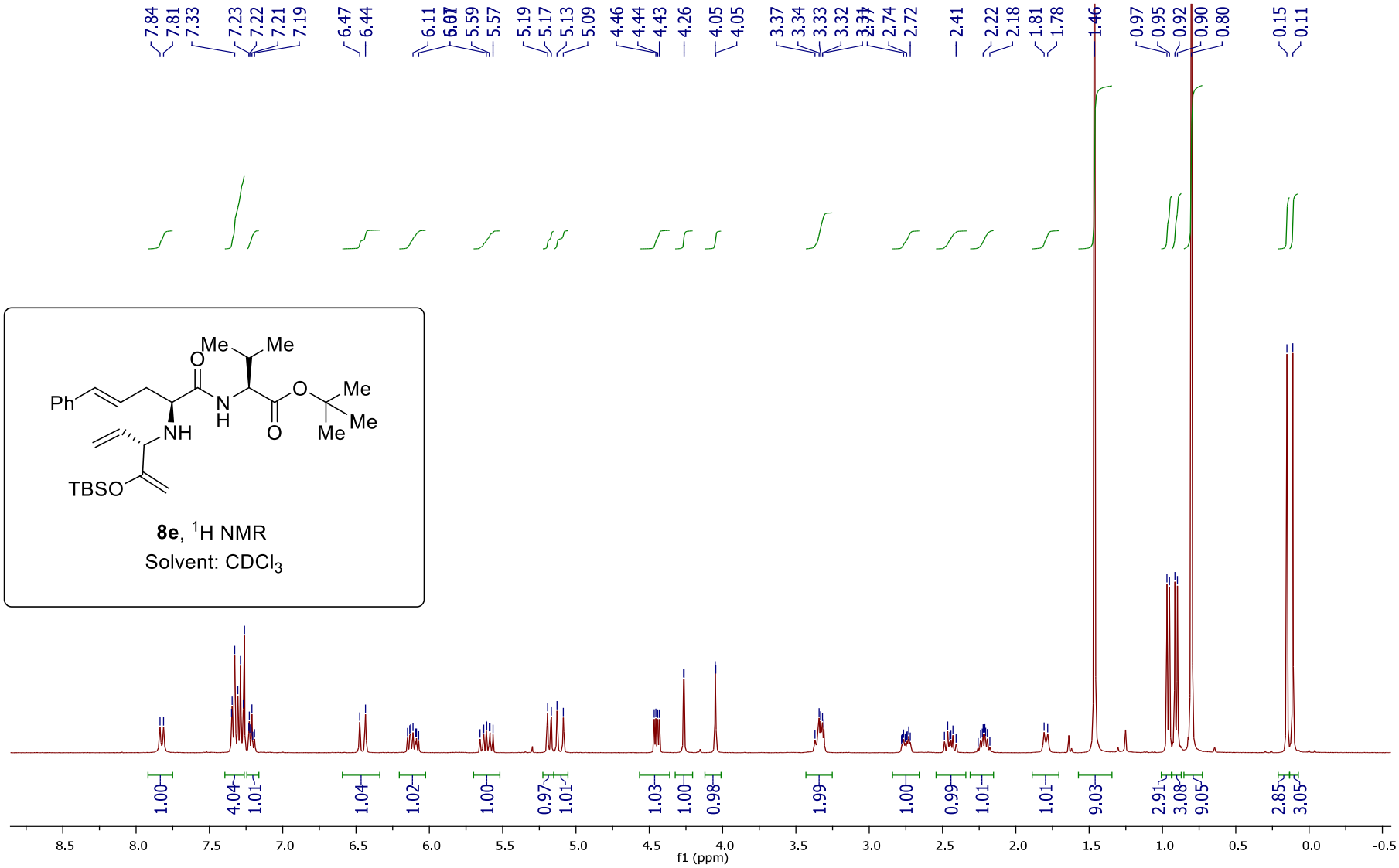
170.59
156.23
155.94
137.92
136.55
129.48
128.43
126.89
115.96
91.57
81.89
79.08
77.31
77.10
76.89
64.07
59.72
52.99
40.32
38.38
33.74
30.00
28.50
28.02
25.76
23.04
18.15
-4.56
-4.95
BocHN
O
N
H
Ph
O
O
Me
Me
Me
NH
TBSO
8d, 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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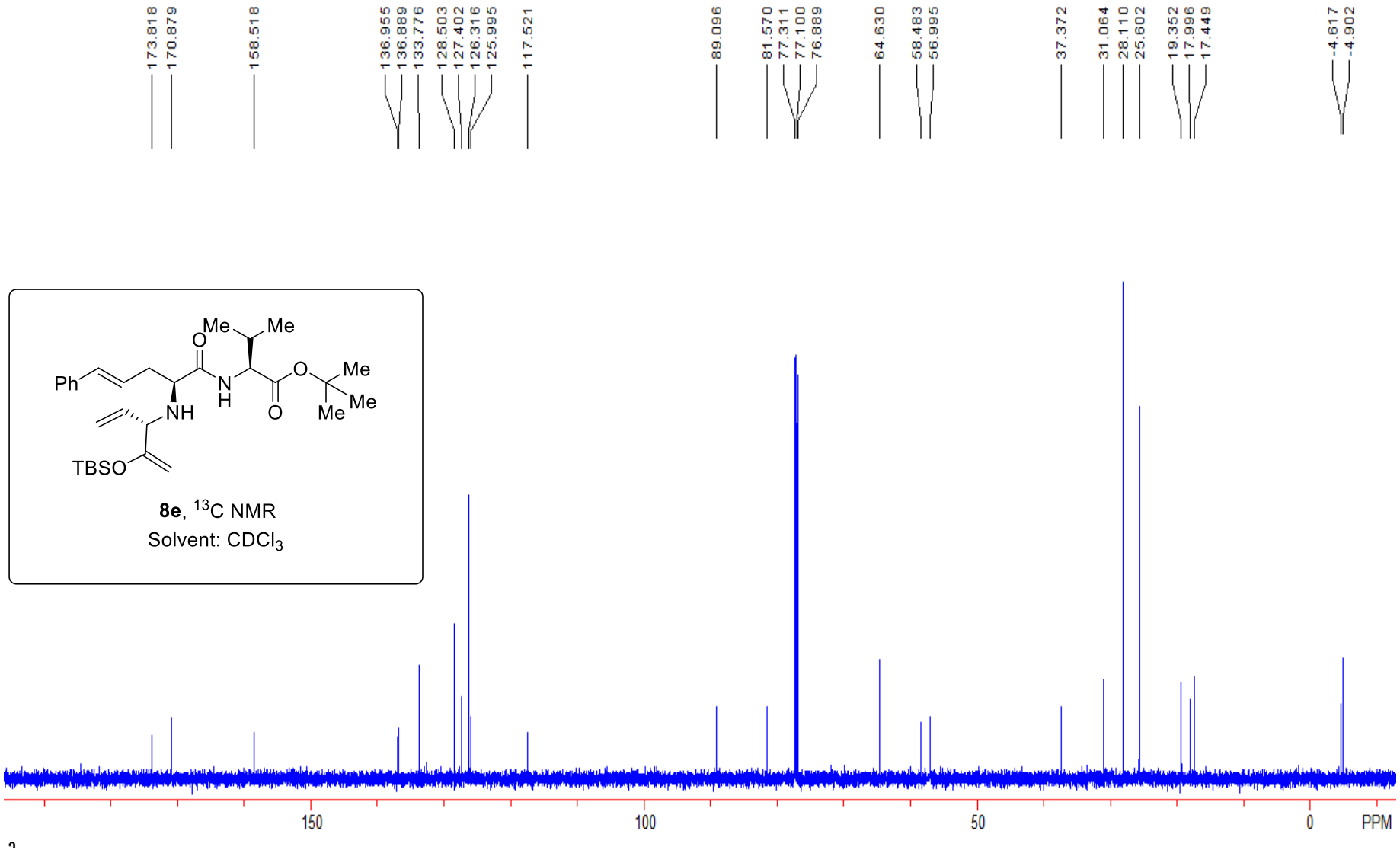
7.81
7.33
7.23
7.22
7.21
7.19
6.47
6.44
6.11
6.07
5.59
5.57
5.19
5.17
5.13
5.09
4.46
4.44
4.43
4.26
4.05
4.05
3.37
3.34
3.33
3.32
2.74
2.72
2.41
2.22
2.18
1.81
1.78
1.46
0.97
0.95
0.92
0.90
0.80
0.15
0.11
Me
Me
O
Ph
N
H
O
Me
Me
NH
O
Me
TBSO
8e, 1H NMR
Solvent: CDCl3
1.00
4.04
1.01
1.04
1.02
1.00
0.97
1.01
1.03
1.00
0.98
1.99
1.00
0.99
1.01
1.01
9.03
2.91
3.08
9.05
2.85
3.05
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)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170.879
158.518
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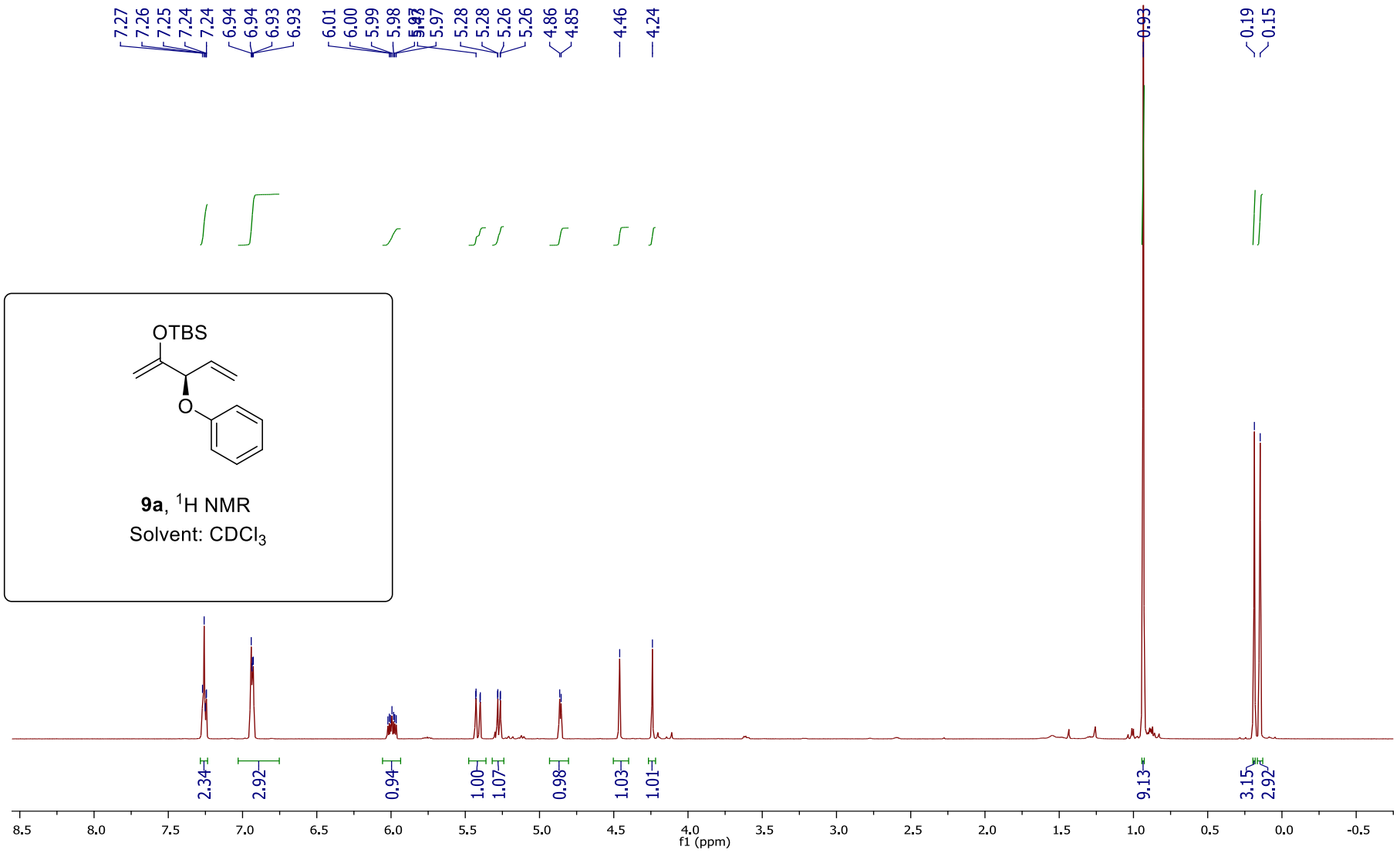
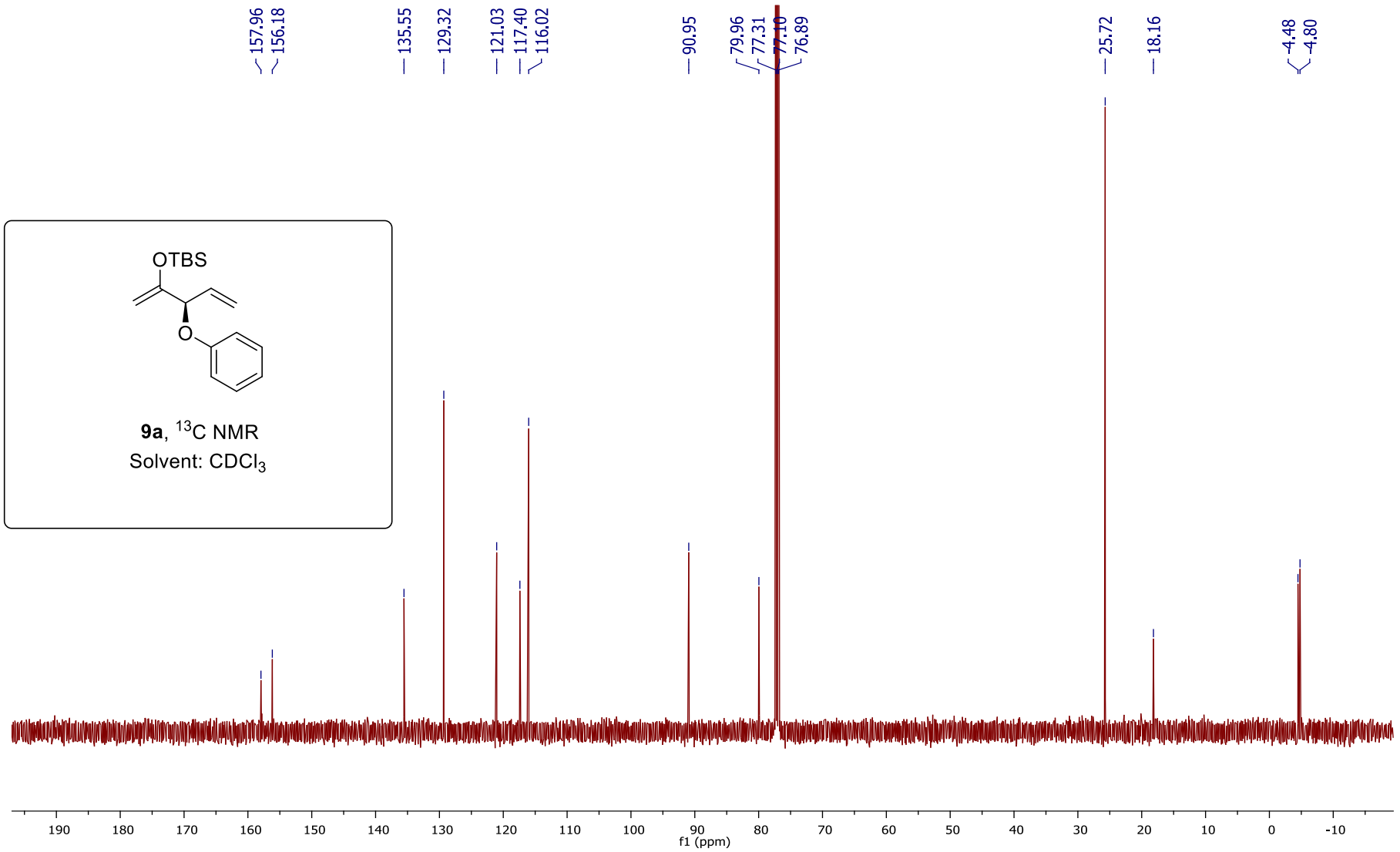
136.889
133.776
128.503
127.402
126.316
125.995
117.521
89.096
81.570
77.311
77.100
76.889
64.630
58.483
56.995
37.372
31.064
28.110
25.602
19.352
17.996
17.449
-4.617
-4.902
Me
Me
O
Ph
N
H
O
Me
Me
Me
NH
TBSO
8e, 13C NMR
Solvent: CDCl3
150
100
50
0
PPM


7.27
7.26
7.25
7.24
7.24
6.94
6.94
6.93
6.93
6.01
6.00
5.99
5.98
5.97
5.28
5.28
5.26
5.26
4.86
4.85
4.46
4.24
0.93
0.19
0.15
OTBS
O
9a, 1H NMR
Solvent: CDCl3
2.34
2.92
0.94
1.00
1.07
0.98
1.03
1.01
9.13
3.15
2.92
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)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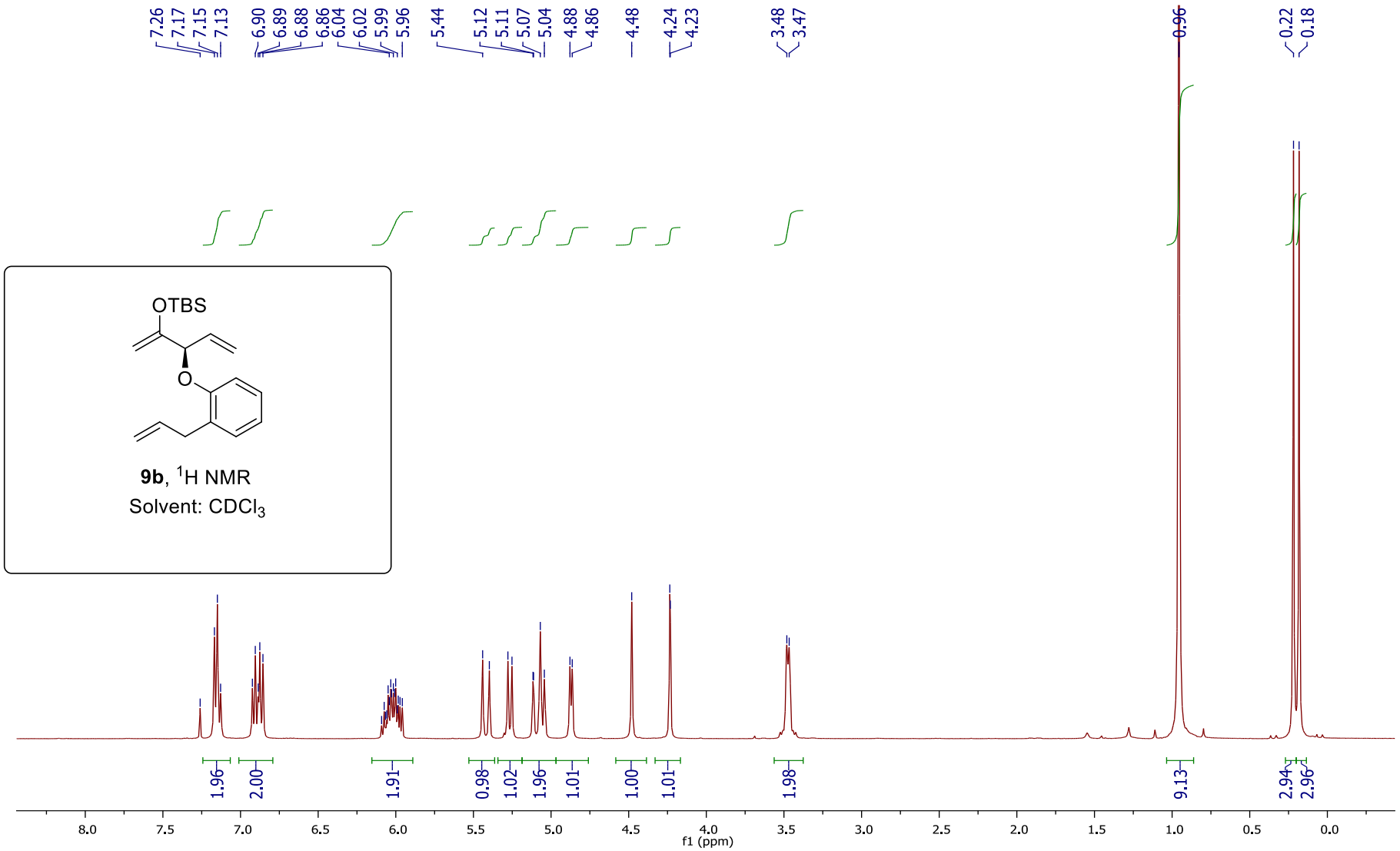
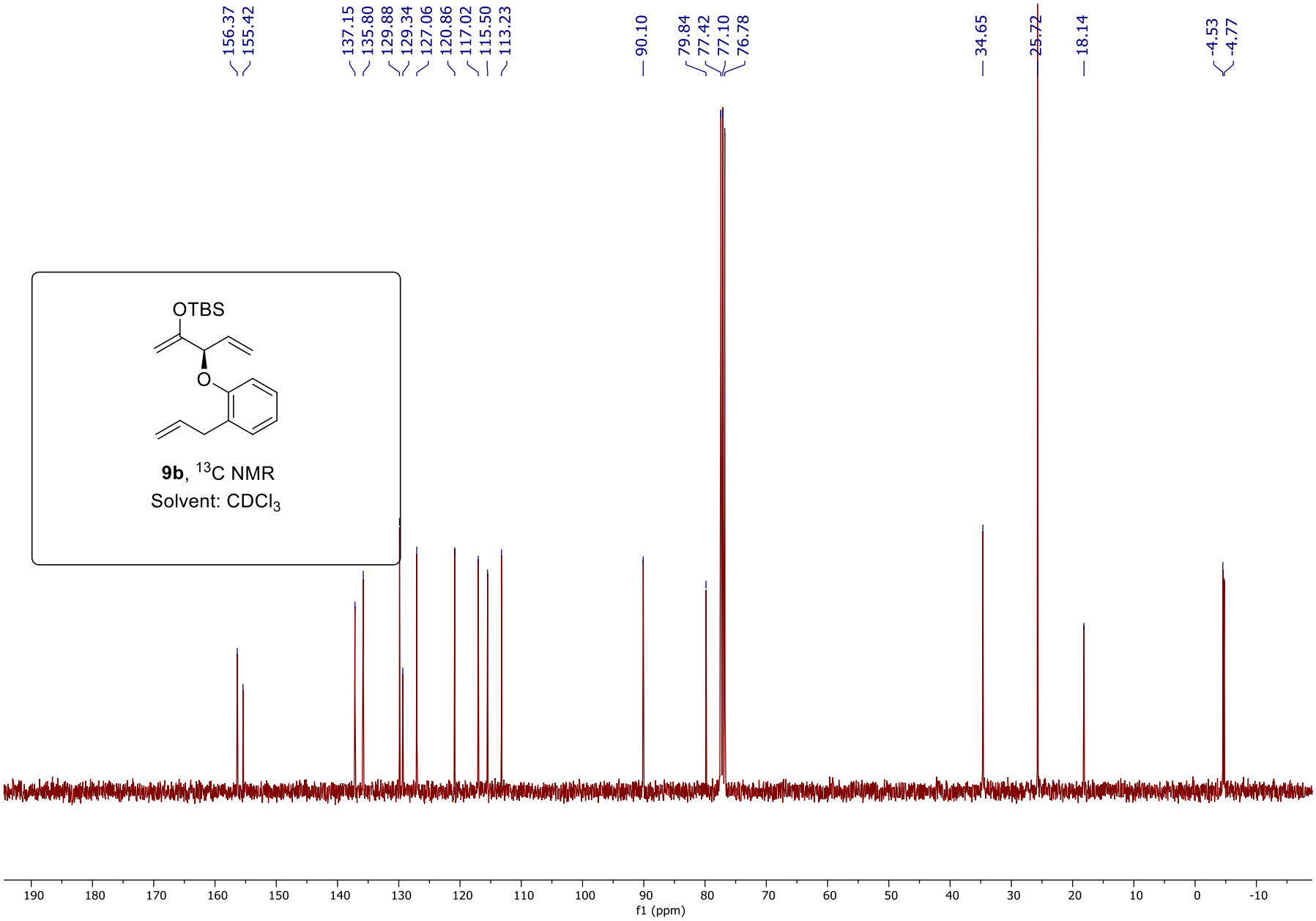
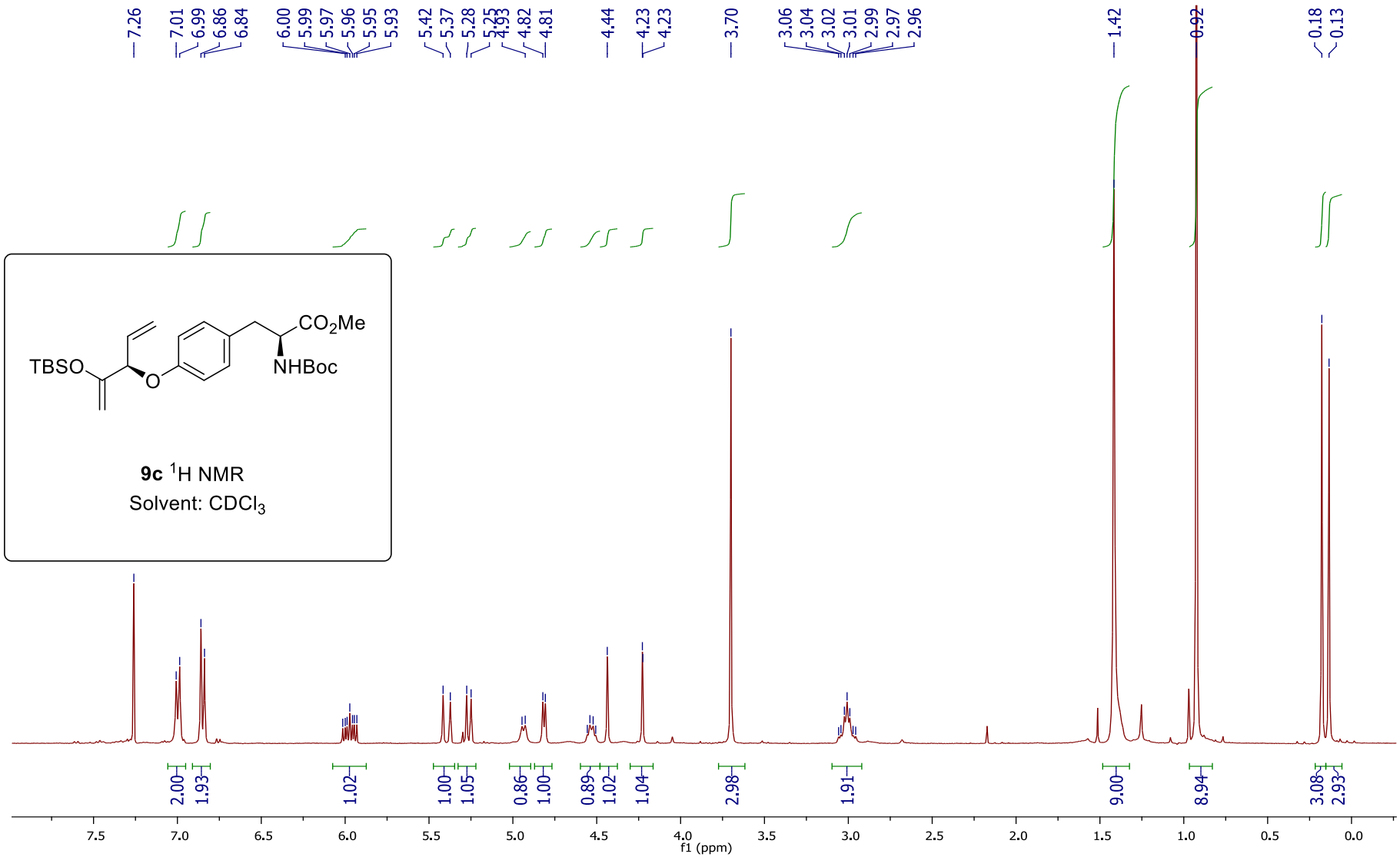
156.18
135.55
129.32
121.03
117.40
116.02
90.95
79.96
77.31
77.10
76.89
25.72
18.16
-4.48
-4.80
OTBS
O
9a, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
7.17
7.15
7.13
6.90
6.89
6.88
6.86
6.04
6.02
5.99
5.96
5.44
5.12
5.11
5.07
5.04
4.88
4.86
4.48
4.24
4.23
3.48
3.47
0.96
0.22
0.18
OTBS
O
9b, 1H NMR
Solvent: CDCl3
1.96
2.00
1.91
0.98
1.02
1.96
1.01
1.00
1.01
1.98
9.13
2.94
2.96
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
f1 (ppm)


156.37
155.42
137.15
135.80
129.88
129.34
127.06
120.86
117.02
115.50
113.23
90.10
79.84
77.42
77.10
76.78
34.65
25.72
18.14
-4.53
-4.77
OTBS
O
9b, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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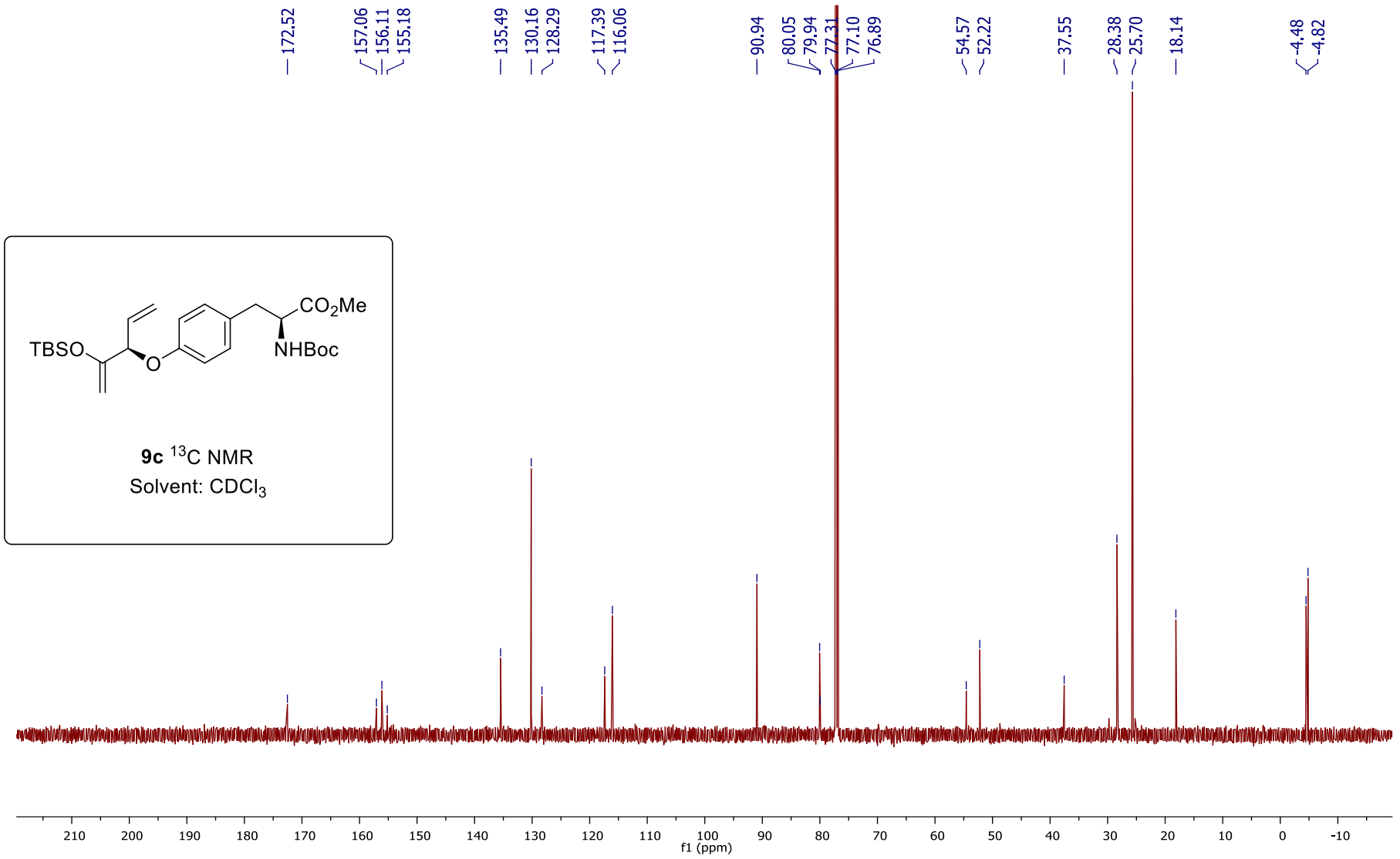
7.01
6.99
6.86
6.84
6.00
5.99
5.97
5.96
5.95
5.93
5.42
5.37
5.28
5.25
4.93
4.82
4.81
4.44
4.23
4.23
3.70
3.06
3.04
3.02
3.01
2.99
2.97
2.96
1.42
0.92
0.18
0.13
TBSO
O
CO2Me
NHBoc
9c 1H NMR
Solvent: CDCl3
2.00
1.93
1.02
1.00
1.05
0.86
1.00
0.89
1.02
1.04
2.98
1.91
9.00
8.94
3.08
2.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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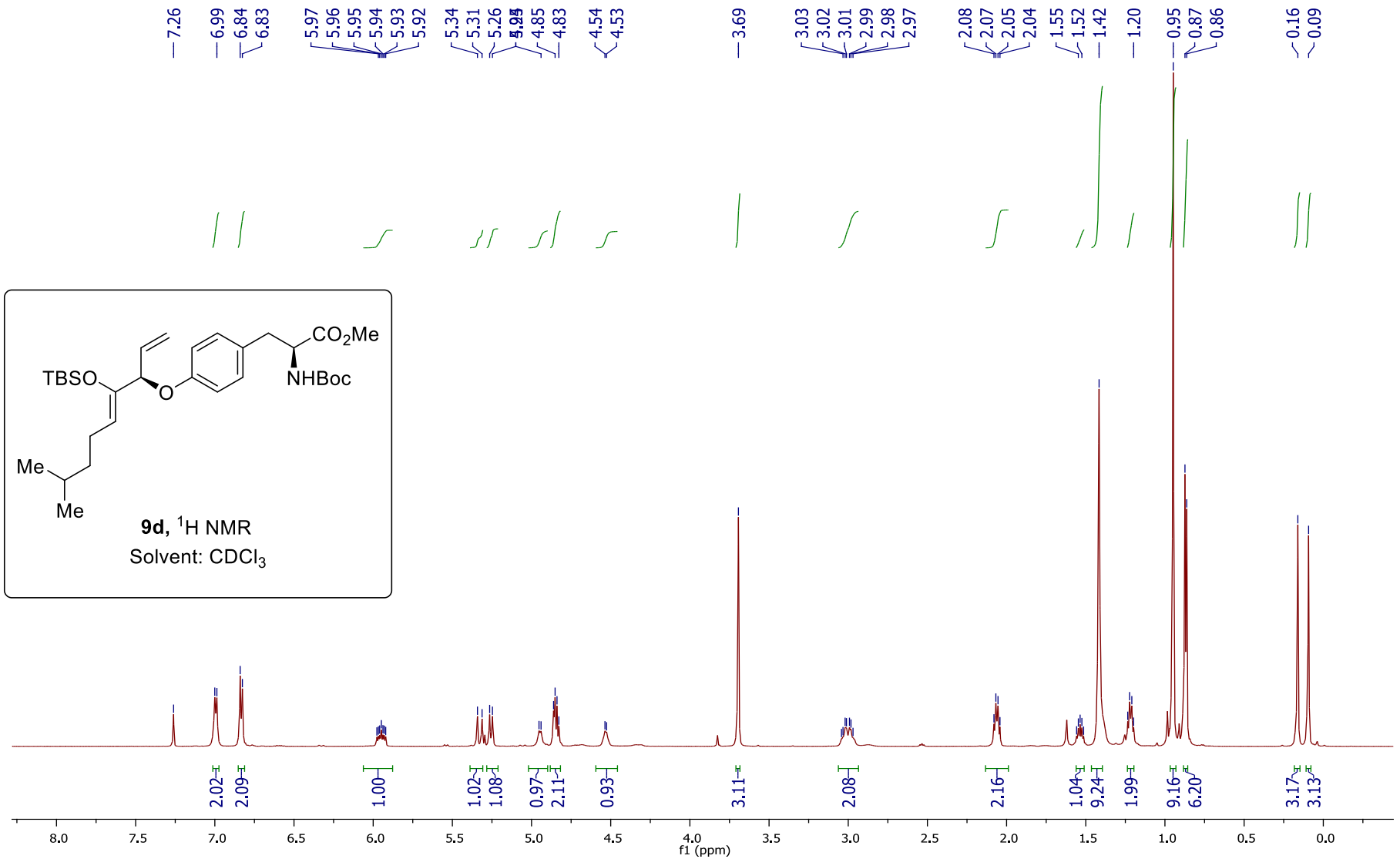
157.06
156.11
155.18
135.49
130.16
128.29
117.39
116.06
90.94
80.05
79.94
77.31
77.10
76.89
54.57
52.22
37.55
28.38
25.70
18.14
-4.48
-4.82
TBSO
O
NHBoc
CO2Me
9c 13C NMR
Solvent: CDCl3
f1 (ppm)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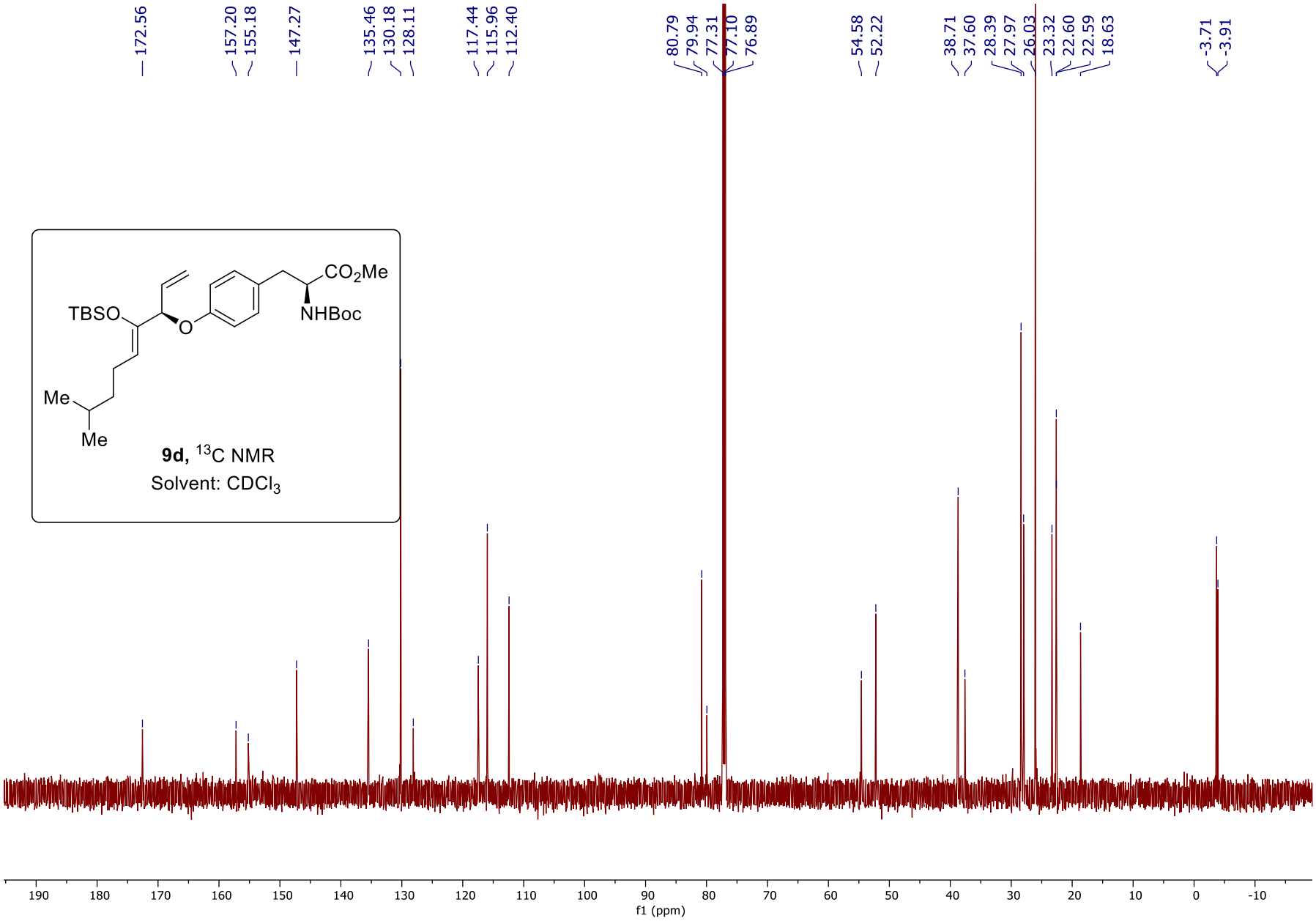
6.99
6.84
6.83
5.97
5.96
5.95
5.94
5.93
5.92
5.34
5.31
5.26
4.85
4.83
4.54
4.53
3.69
3.03
3.02
3.01
2.99
2.98
2.97
2.08
2.07
2.05
2.04
1.55
1.52
1.42
1.20
0.95
0.87
0.86
0.16
0.09
CO2Me
NHBoc
TBSO
O
Me
Me
9d, 1H NMR
Solvent: CDCl3
2.02
2.09
1.00
1.02
1.08
0.97
2.11
0.93
3.11
2.08
2.16
1.04
9.24
1.99
9.16
6.20
3.17
3.13
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
f1 (ppm)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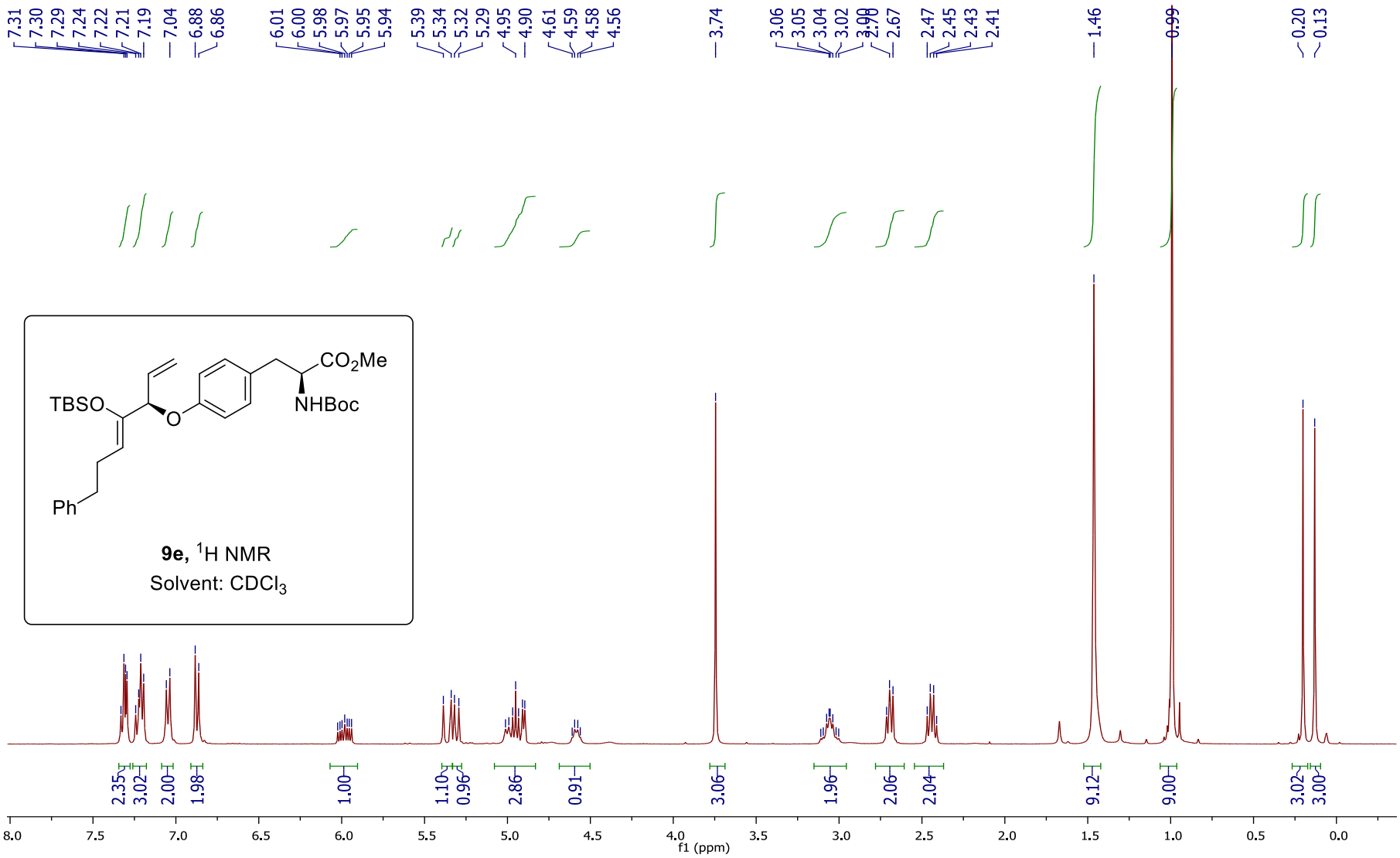
117.44
115.96
112.40
80.79
79.94
77.31
77.10
76.89
54.58
52.22
38.71
37.60
28.39
27.97
26.03
23.32
22.60
22.59
18.63
-3.71
-3.91
TBSO
O
CO2Me
NHBoc
Me
Me
9d, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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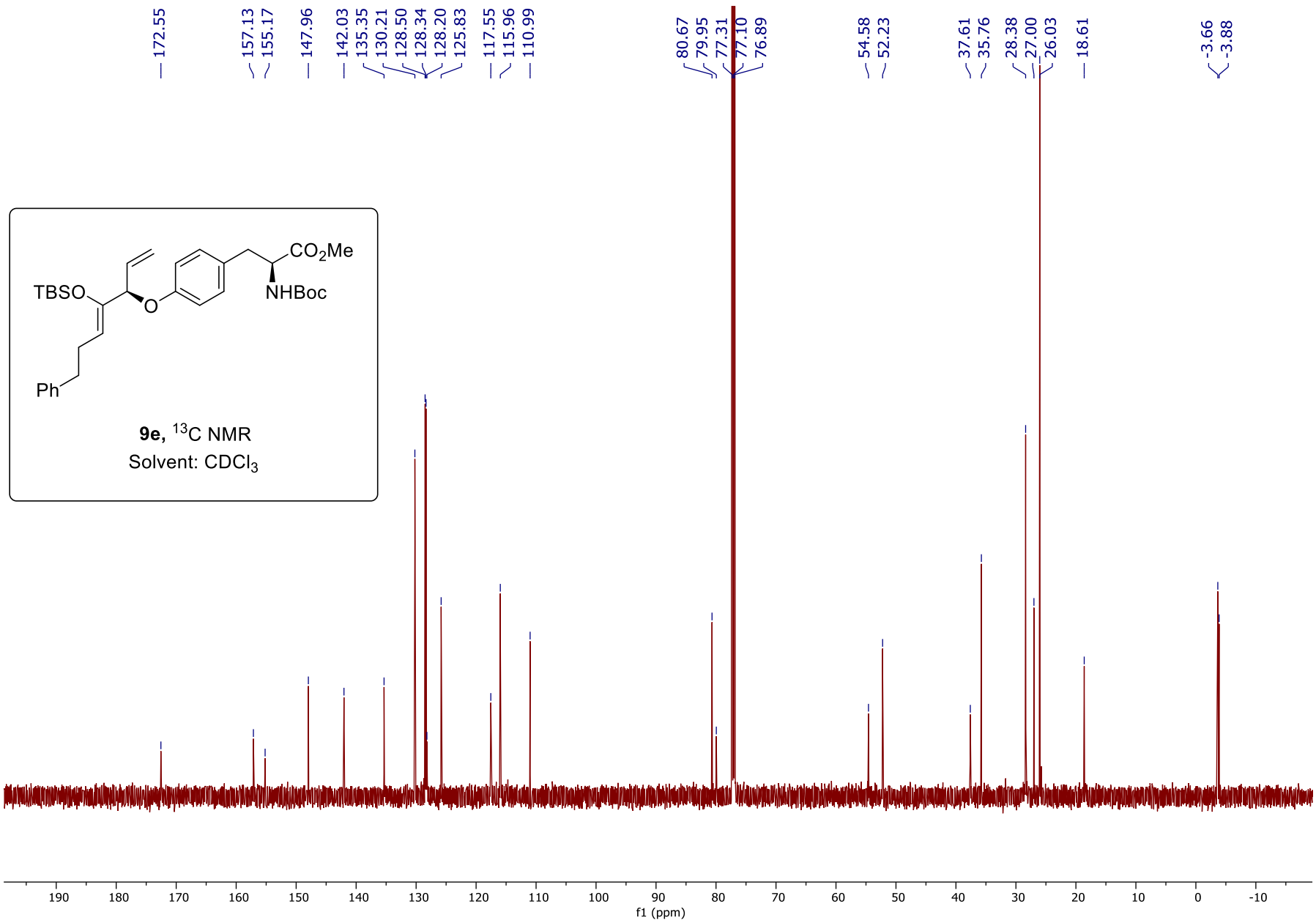
7.30
7.29
7.24
7.22
7.21
7.19
7.04
6.88
6.86
6.01
6.00
5.98
5.97
5.95
5.94
5.39
5.34
5.32
5.29
4.95
4.90
4.61
4.59
4.58
4.56
3.74
3.06
3.05
3.04
3.02
2.67
2.47
2.45
2.43
2.41
1.46
0.99
0.20
0.13
TBSO
O
CO2Me
NHBoc
Ph
9e, 1H NMR
Solvent: CDCl3
2.35
3.02
2.00
1.98
1.00
1.10
0.96
2.86
0.91
3.06
1.96
2.06
2.04
9.12
9.00
3.02
3.00
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
f1 (ppm)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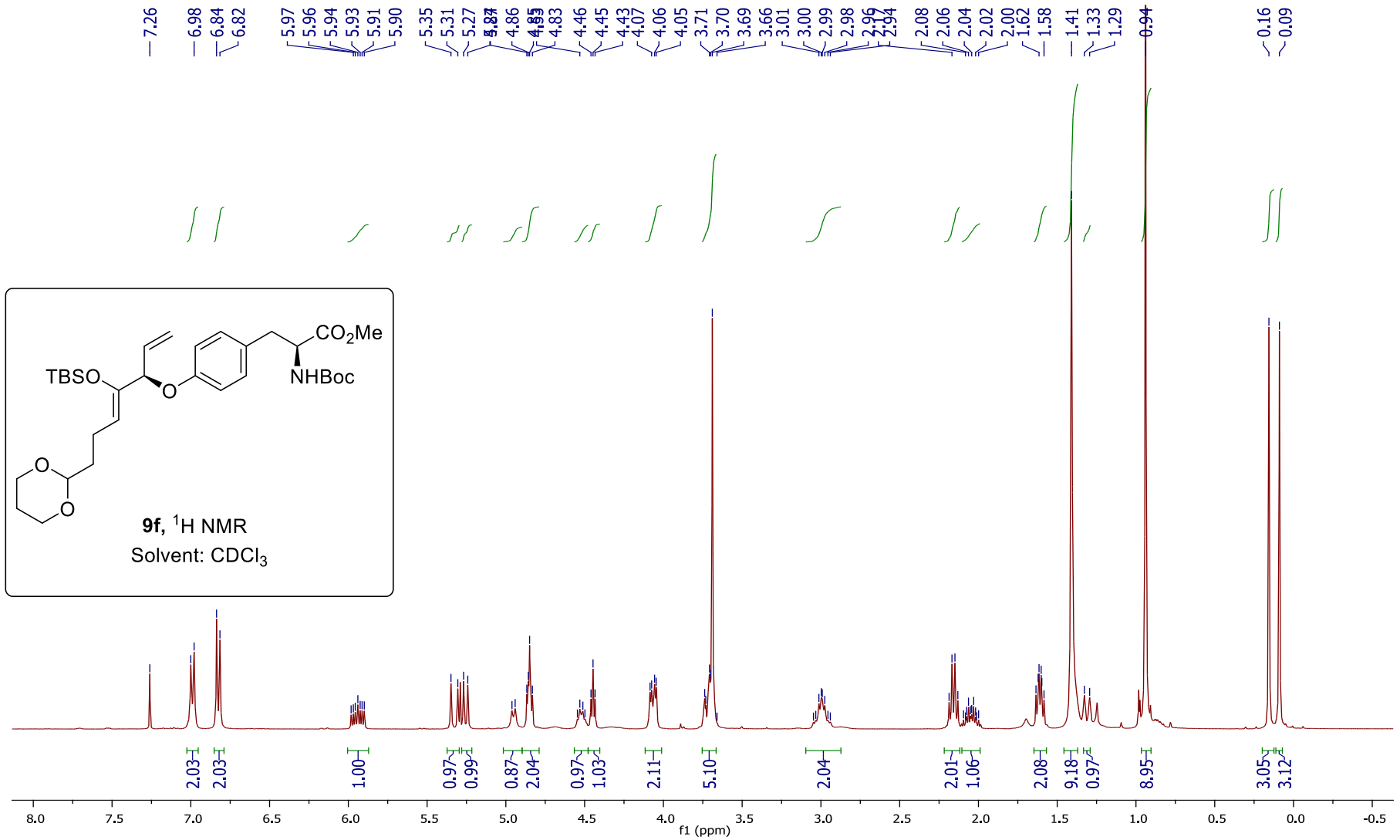
155.17
147.96
142.03
135.35
130.21
128.50
128.34
128.20
125.83
117.55
115.96
110.99
80.67
79.95
77.31
77.10
76.89
54.58
52.23
37.61
35.76
28.38
27.00
26.03
18.61
-3.66
-3.88
TBSO
O
CO2Me
NHBoc
Ph
9e, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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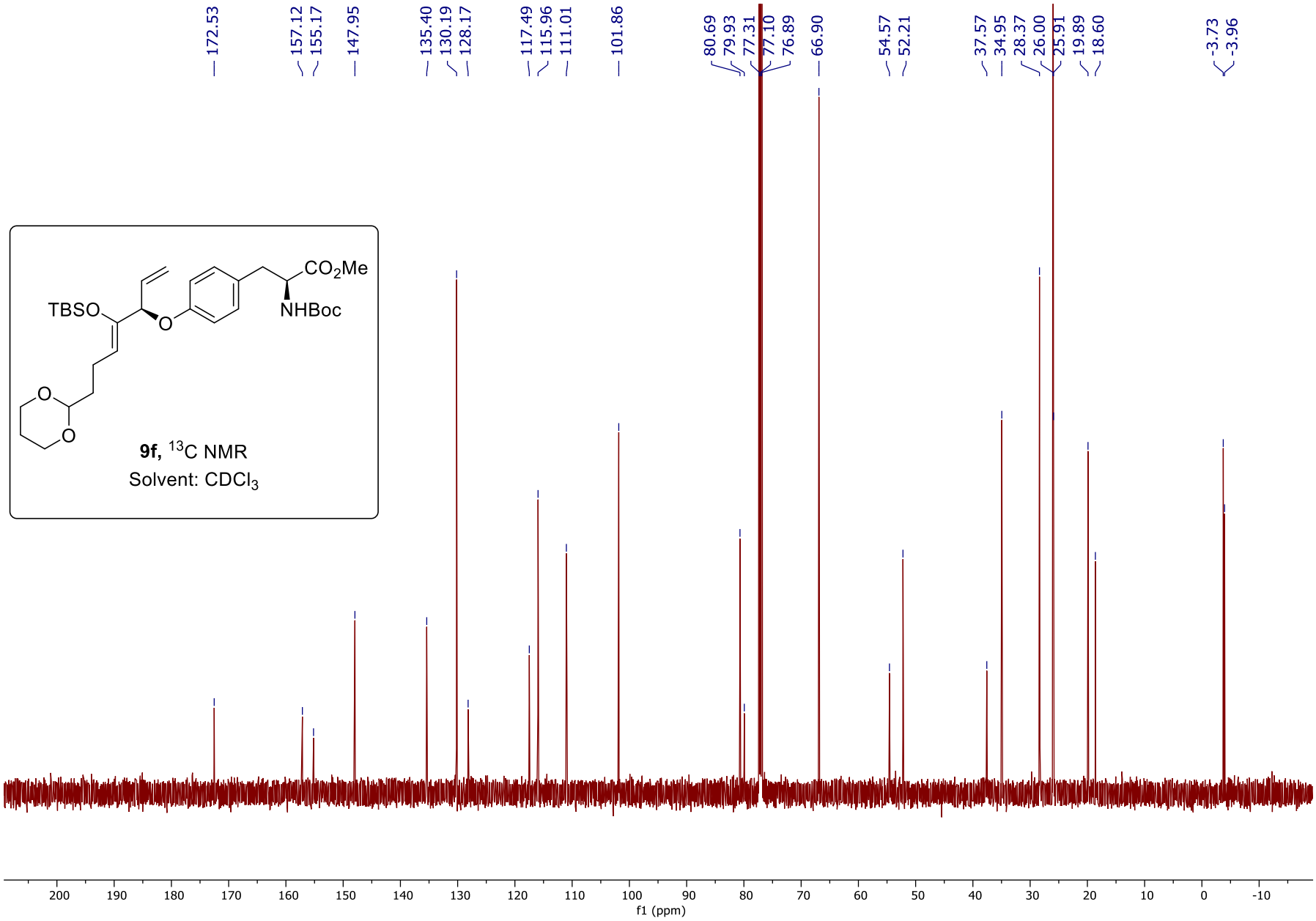
6.98
6.84
6.82
5.97
5.96
5.94
5.93
5.91
5.90
5.35
5.31
5.27
4.86
4.83
4.46
4.45
4.43
4.07
4.06
4.05
3.71
3.70
3.69
3.66
3.01
3.00
2.99
2.98
2.08
2.06
2.04
2.02
2.00
1.62
1.58
1.41
1.33
1.29
0.94
0.16
0.09
TBSO
O
CO2Me
NHBoc
O
O
9f, 1H NMR
Solvent: CDCl3
2.03
2.03
1.00
0.97
0.99
0.87
2.04
0.97
1.03
2.11
5.10
2.04
2.01
1.06
2.08
9.18
0.97
8.95
3.05
3.12
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)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157.12
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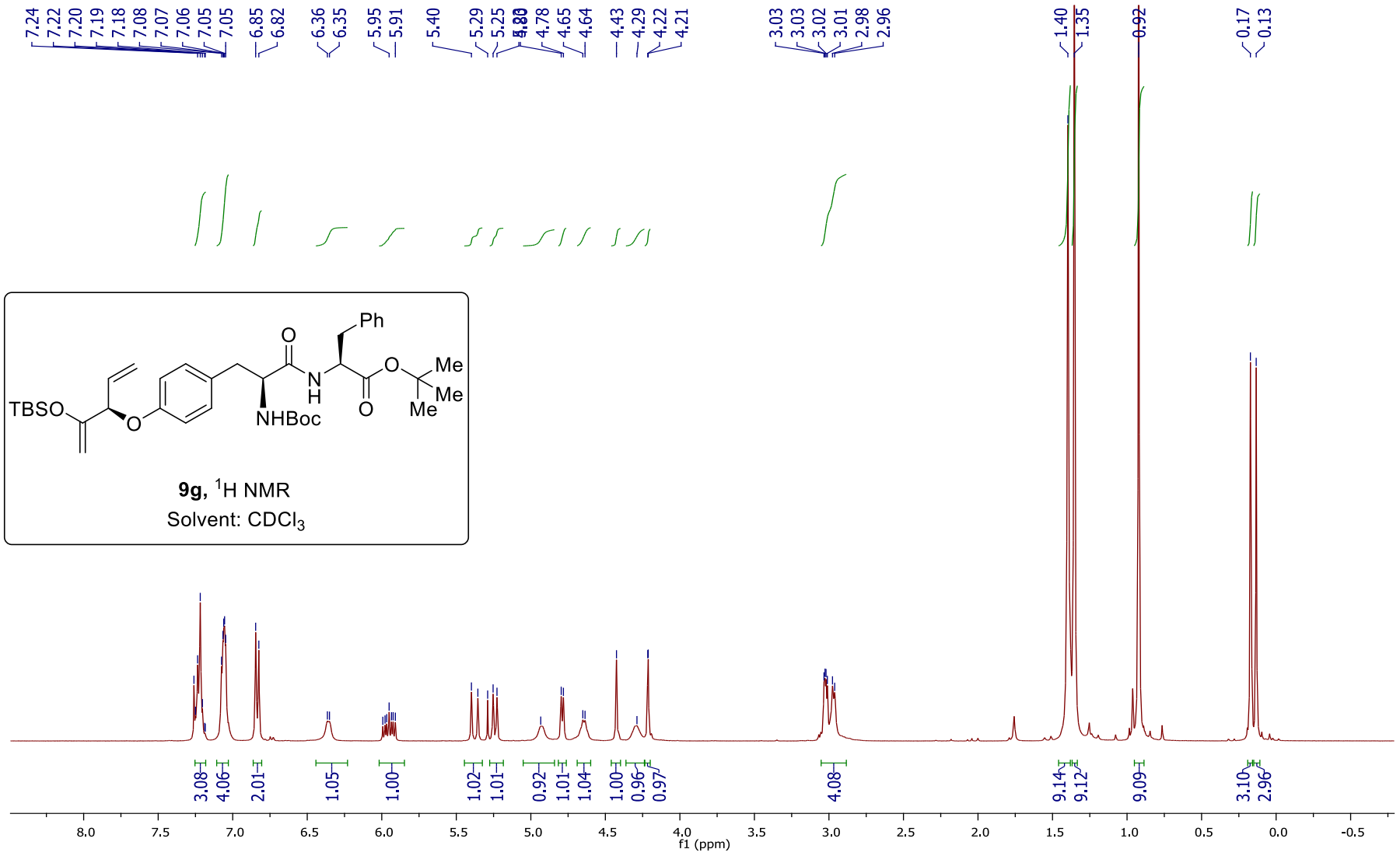
135.40
130.19
128.17
117.49
115.96
111.01
101.86
80.69
79.93
77.31
77.10
76.89
66.90
54.57
52.21
37.57
34.95
28.37
26.00
25.91
19.89
18.60
-3.73
-3.96
CO2Me
NHBoc
TBSO
O
O
O
9f, 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.24
7.22
7.20
7.19
7.18
7.08
7.07
7.06
7.05
7.05
6.85
6.82
6.36
6.35
5.95
5.91
5.40
5.29
5.25
4.78
4.65
4.64
4.43
4.29
4.22
4.21
3.03
3.03
3.02
3.01
2.98
2.96
1.40
1.35
0.92
0.17
0.13
TBSO
O
NHBoc
N
H
O
O
Ph
O
Me
Me
Me
9g, 1H NMR
Solvent: CDCl3
3.08
4.06
2.01
1.05
1.00
1.02
1.01
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1.01
1.04
1.00
0.96
0.97
4.08
9.14
9.12
9.09
3.10
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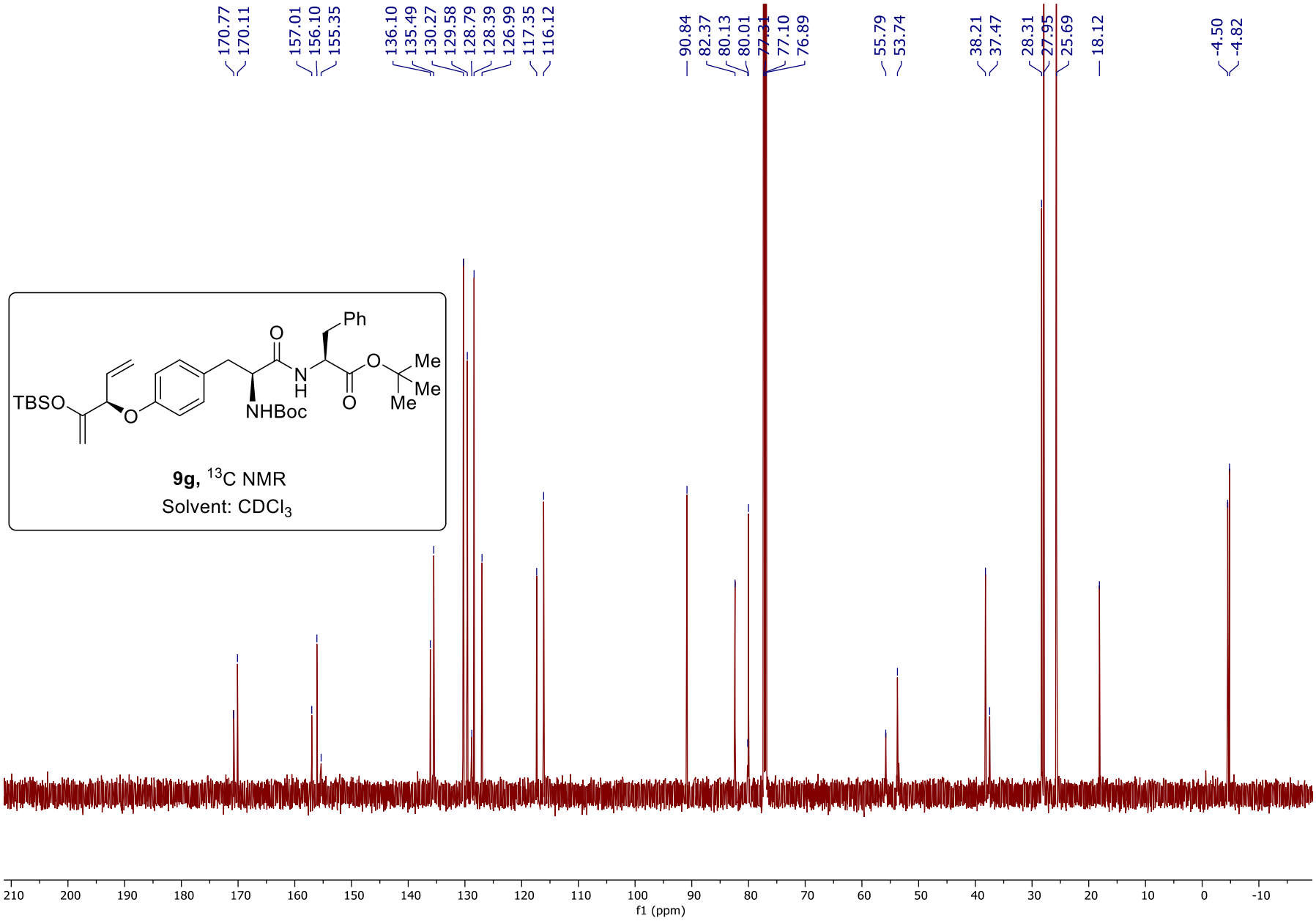
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117.35
116.12
90.84
82.37
80.13
80.01
77.31
77.10
76.89
55.79
53.74
38.21
37.47
28.31
27.95
25.69
18.12
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-4.82
TBSO
O
NHBoc
N
H
O
O
Ph
Me
Me
Me
9g, 13C NMR
Solvent: CDCl3
210
200
190
180
170
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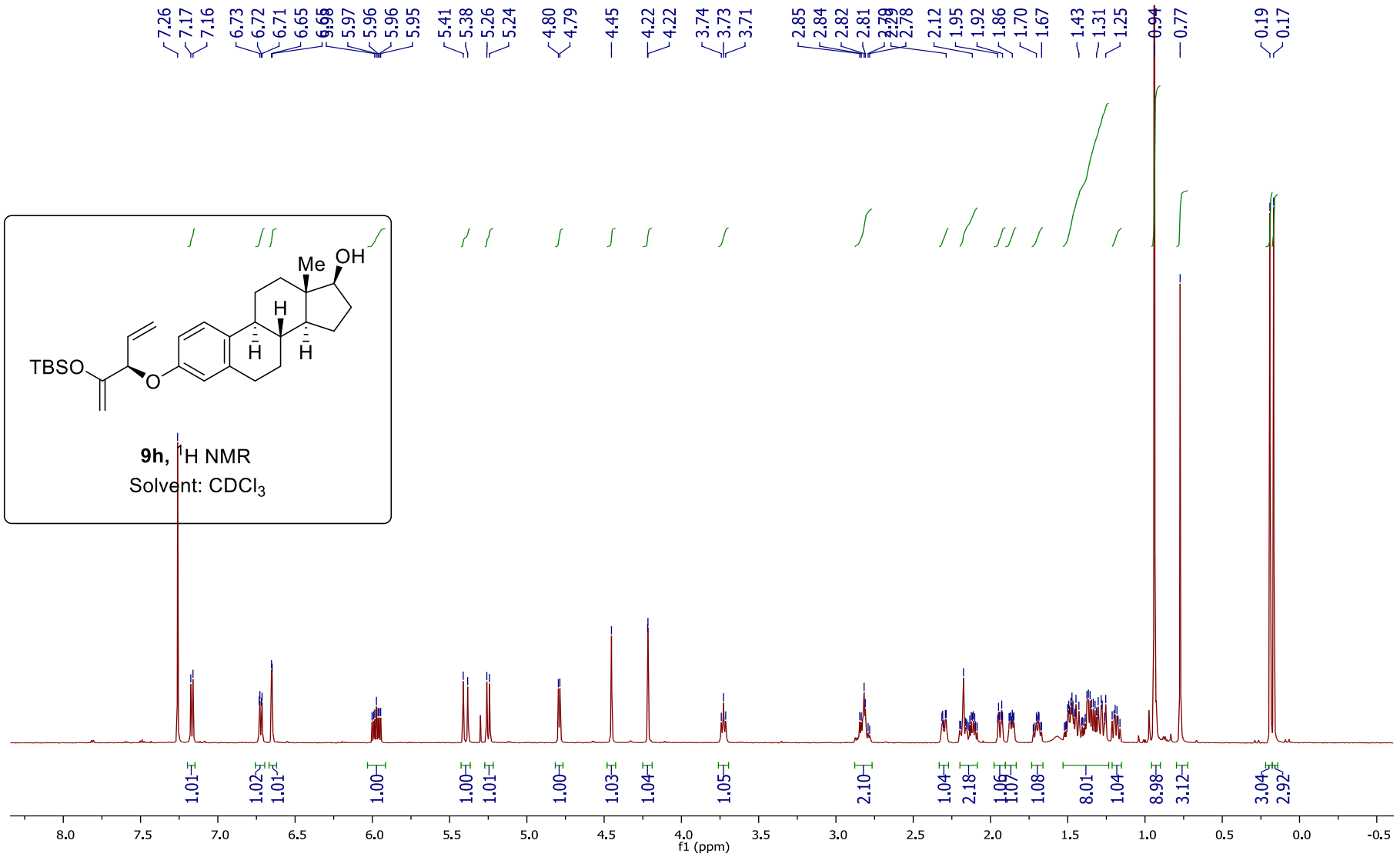
f1 (ppm)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5.38
5.26
5.24
4.80
4.79
4.45
4.22
4.22
3.74
3.73
3.71
2.85
2.84
2.82
2.81
2.78
2.12
1.95
1.92
1.86
1.70
1.67
1.43
1.31
1.25
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0.19
0.17
Me
OH
H
H
H
TBSO
O
9h, 1H NMR
Solvent: CDCl3
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1.02
1.01
1.00
1.00
1.01
1.00
1.03
1.04
1.05
2.10
1.04
2.18
1.06
1.07
1.08
8.01
1.04
8.98
3.12
3.04
2.92
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6.5
6.0
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5.0
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2.5
2.0
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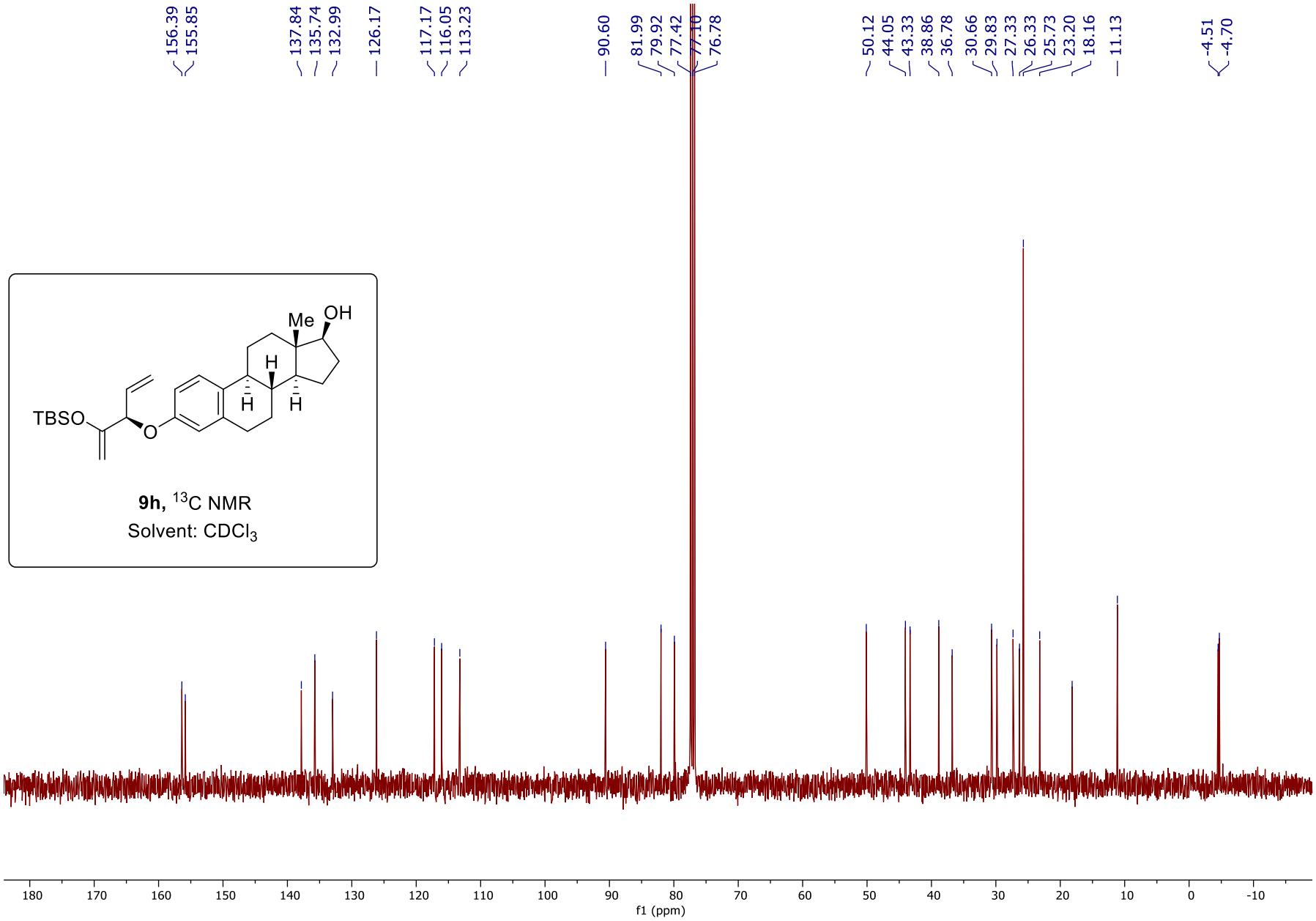
f1 (ppm)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77.42
77.10
76.78
50.12
44.05
43.33
38.86
36.78
30.66
29.83
27.33
26.33
25.73
23.20
18.16
11.13
-4.51
-4.70
Me
OH
H
H
H
TBSO
O
9h, 13C NMR
Solvent: CDCl3
180
170
160
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120
110
100
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80
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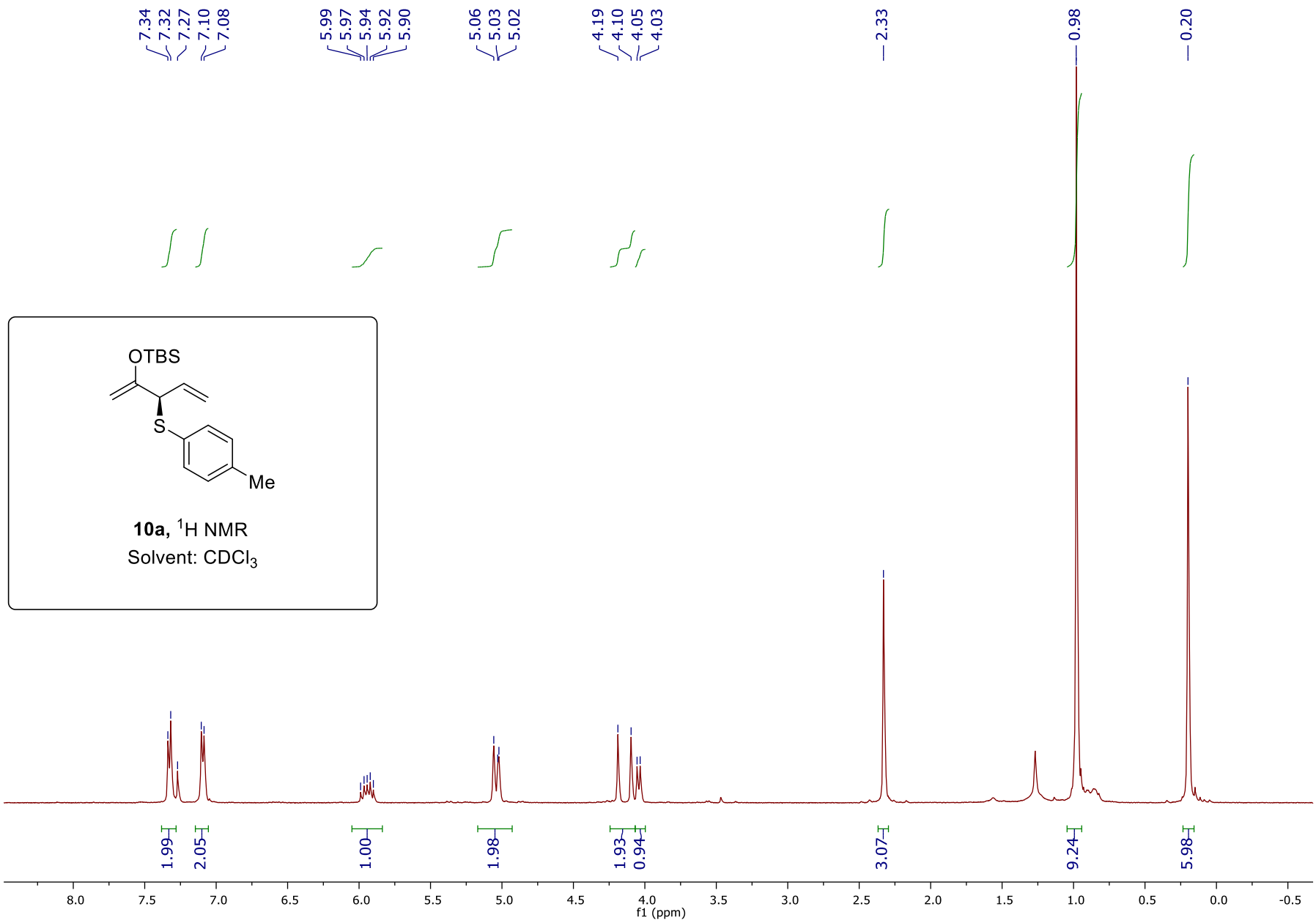
f1 (ppm)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5.06
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5.02
4.19
4.10
4.05
4.03
2.33
0.98
0.20
OTBS
S
Me
10a, 1H NMR
Solvent: CDCl3
1.99
2.05
1.00
1.98
1.93
0.94
3.07
9.24
5.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.5
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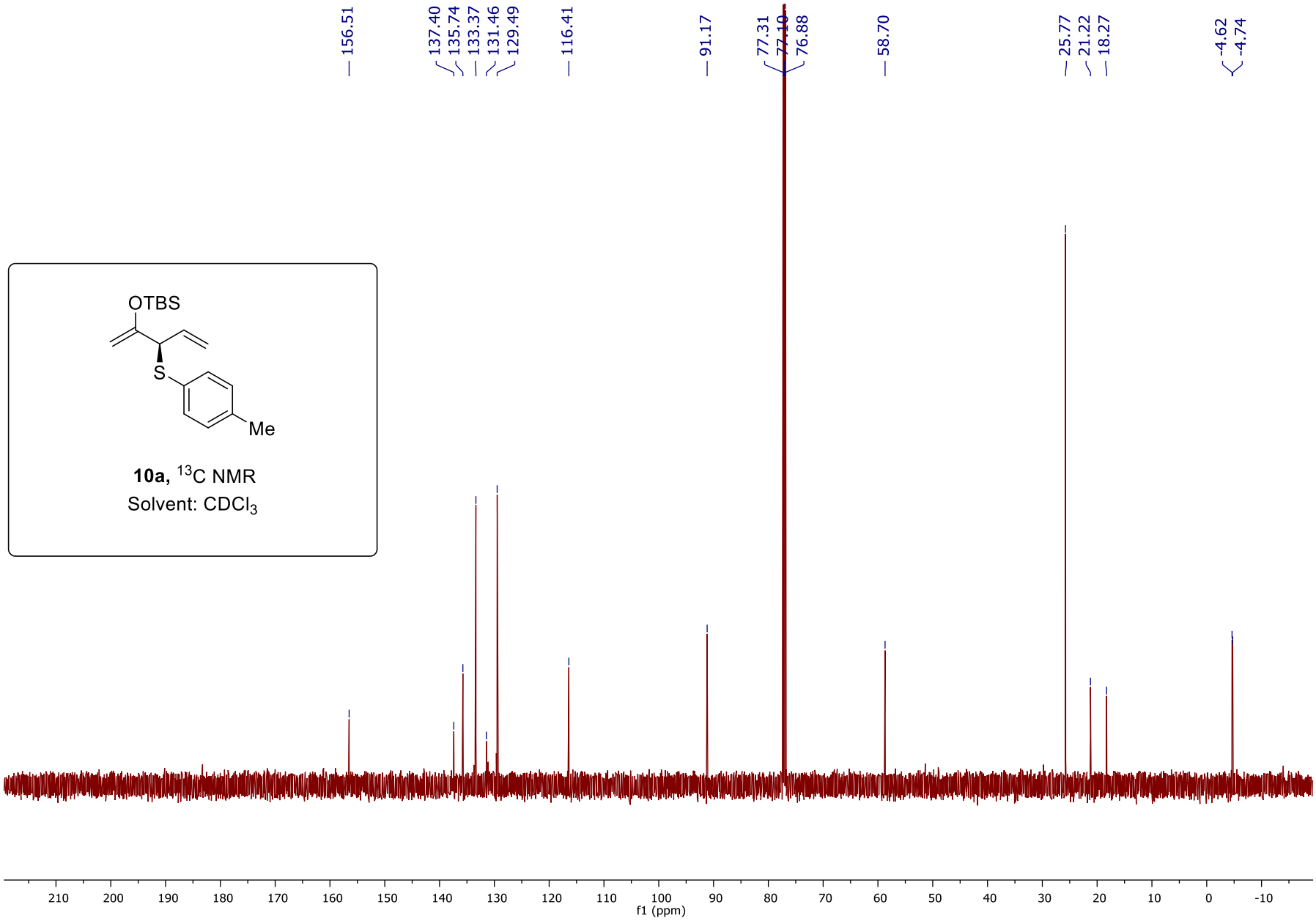
f1 (ppm)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58.70
25.77
21.22
18.27
-4.62
-4.74
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S
Me
10a, 13C NMR
Solvent: CDCl3
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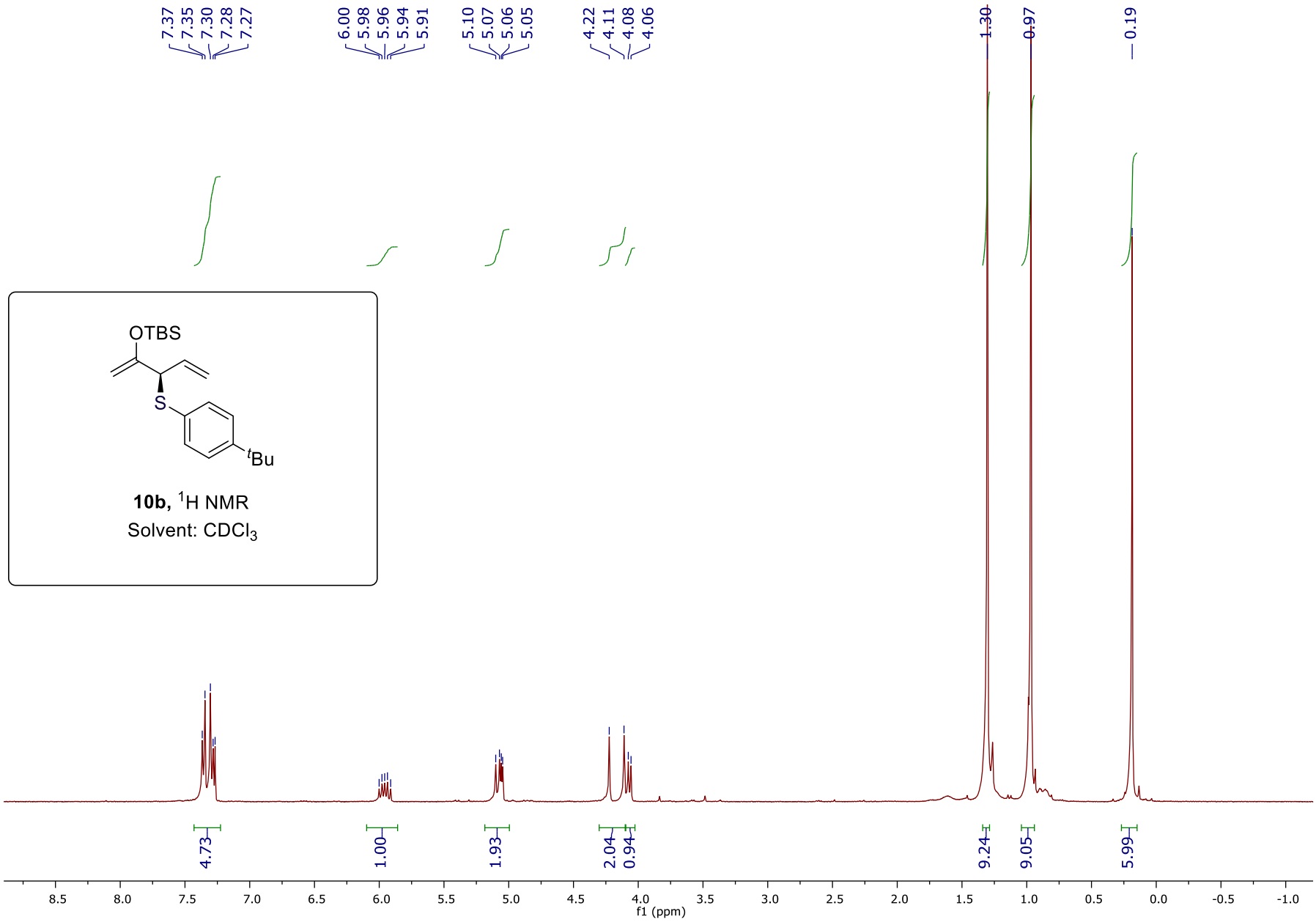
f1 (ppm)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7.28
7.27
6.00
5.98
5.96
5.94
5.91
5.10
5.07
5.06
5.05
4.22
4.11
4.08
4.06
1.30
0.97
0.19
OTBS
S
tBu
10b, 1H NMR
Solvent: CDCl3
4.73
1.00
1.93
2.04
0.94
9.24
9.05
5.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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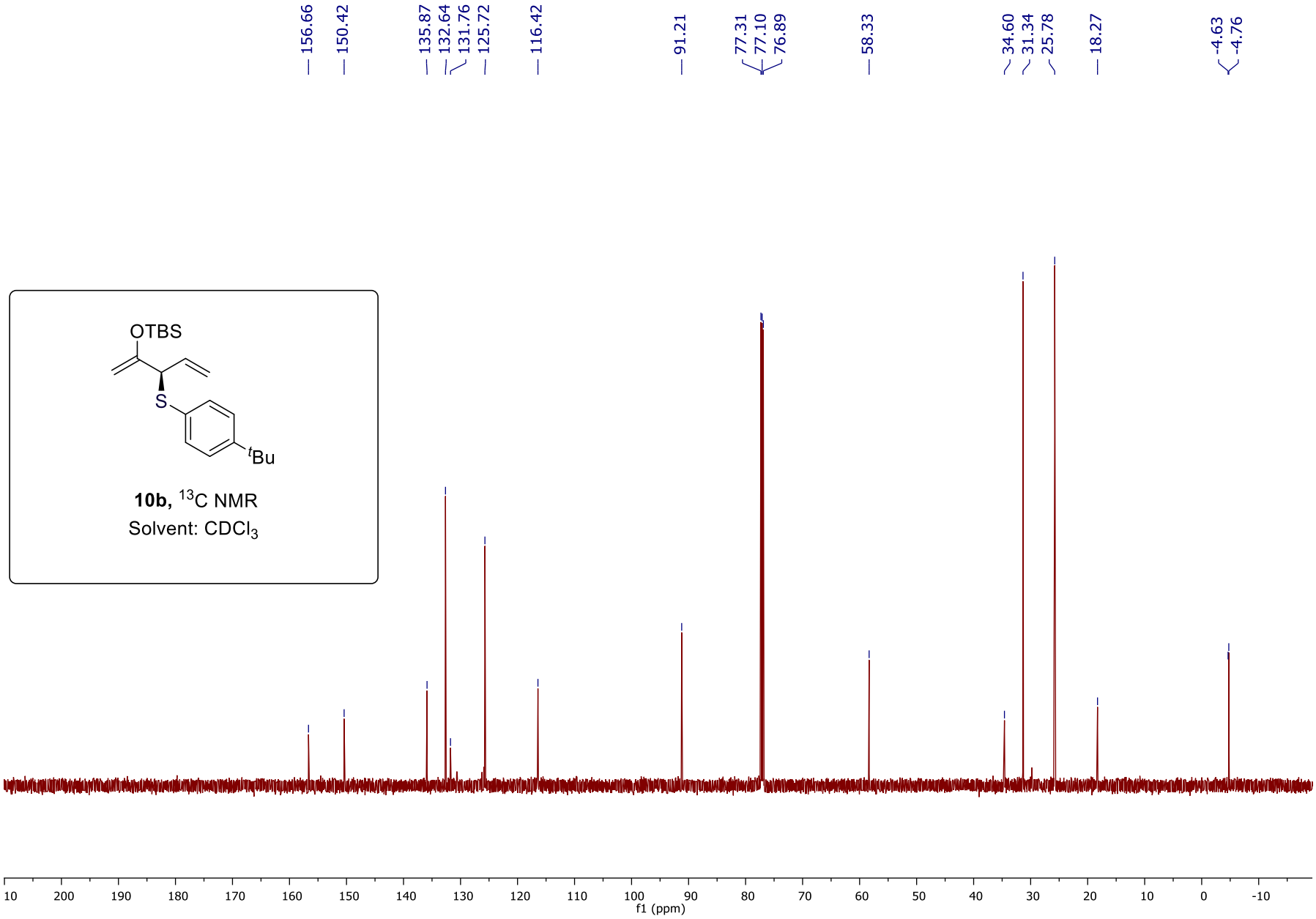
0.0
-0.5
-1.0
f1 (ppm)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76.89
58.33
34.60
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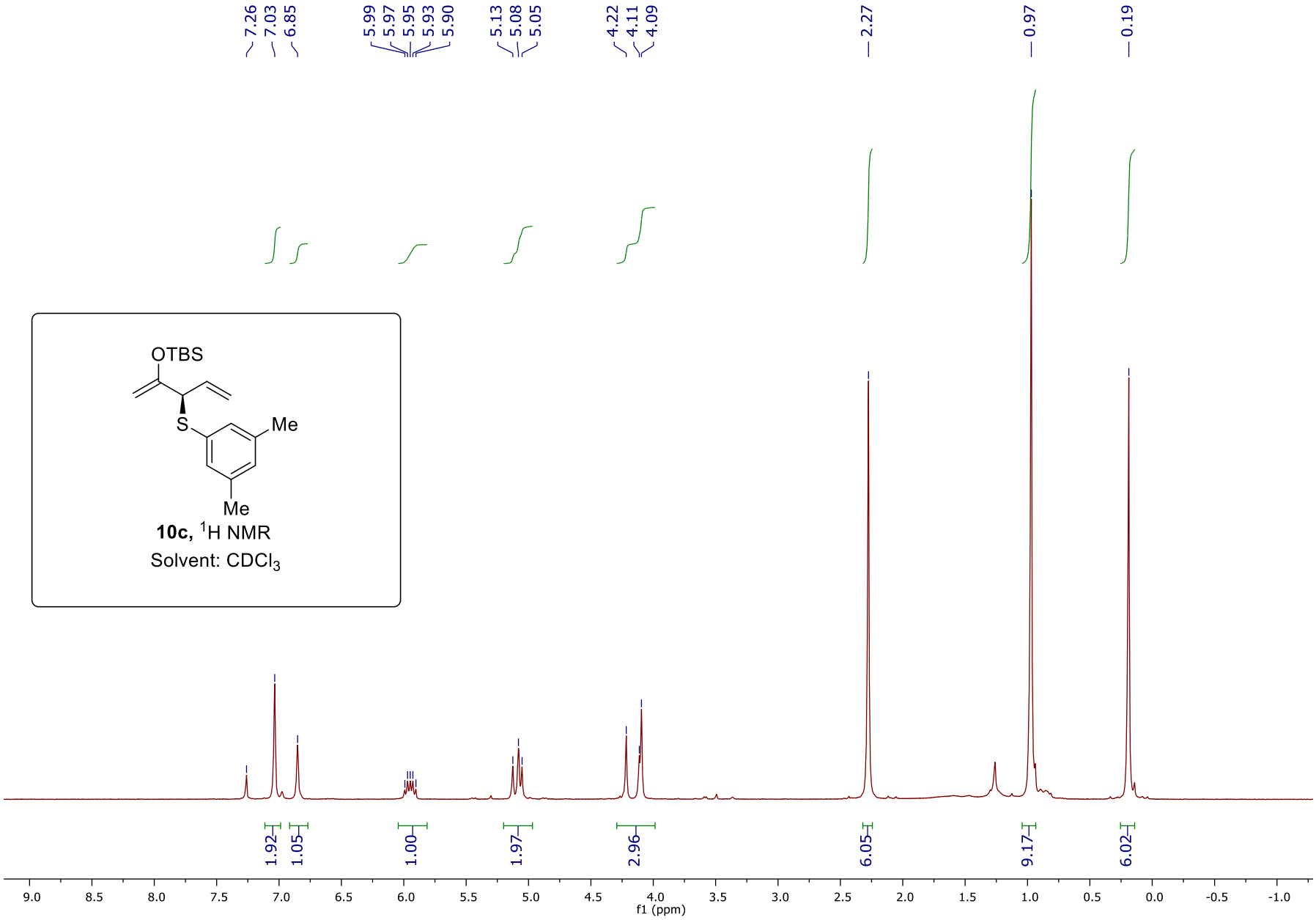
-4.63
-4.76
OTBS
S
tBu
10b, 13C NMR
Solvent: CDCl3
f1 (ppm)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5.95
5.93
5.90
5.13
5.08
5.05
4.22
4.11
4.09
2.27
0.97
0.19
OTBS
S
Me
Me
10c, 1H NMR
Solvent: CDCl3
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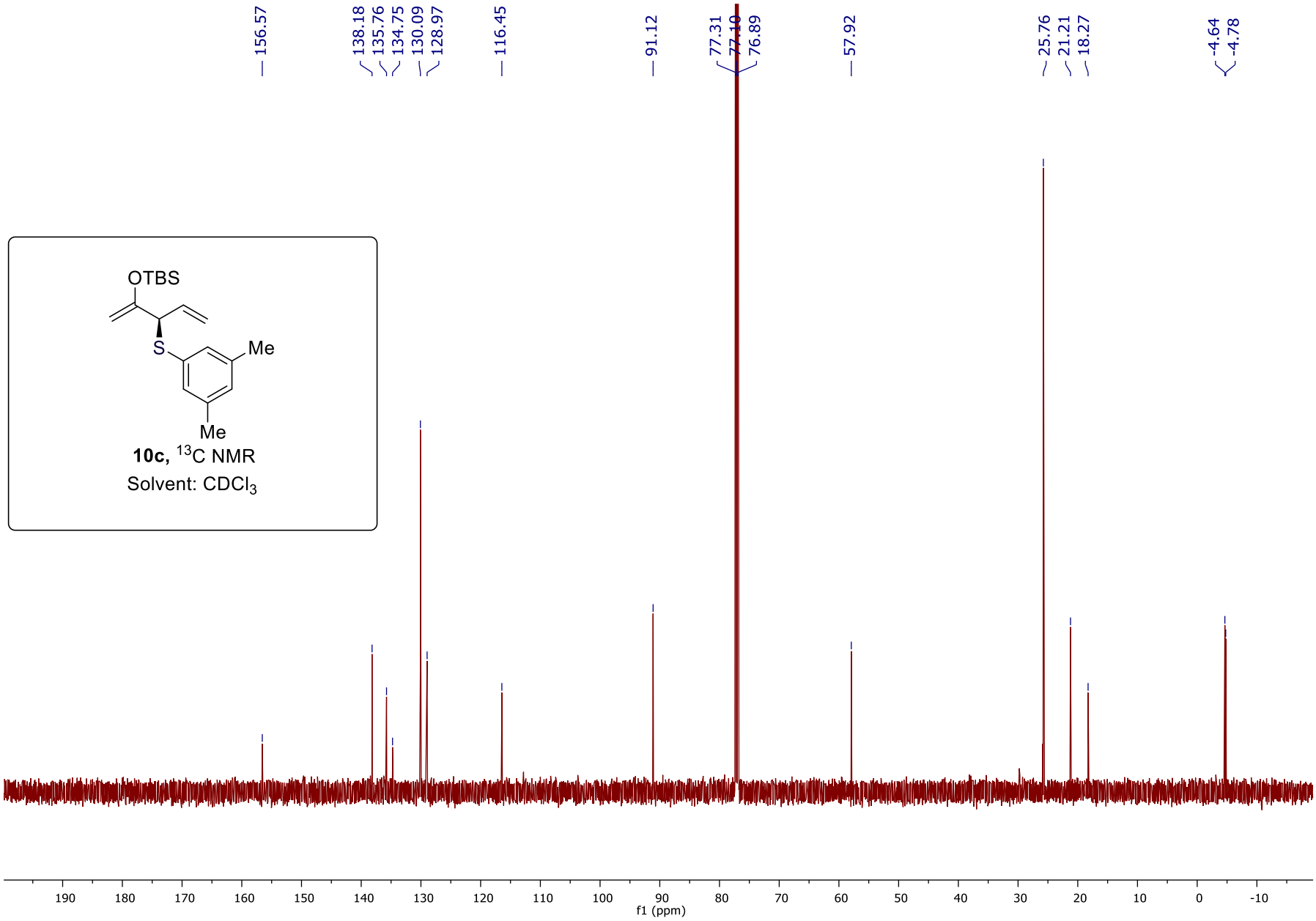
1.05
1.00
1.97
2.96
6.05
9.17
6.02
f1 (ppm)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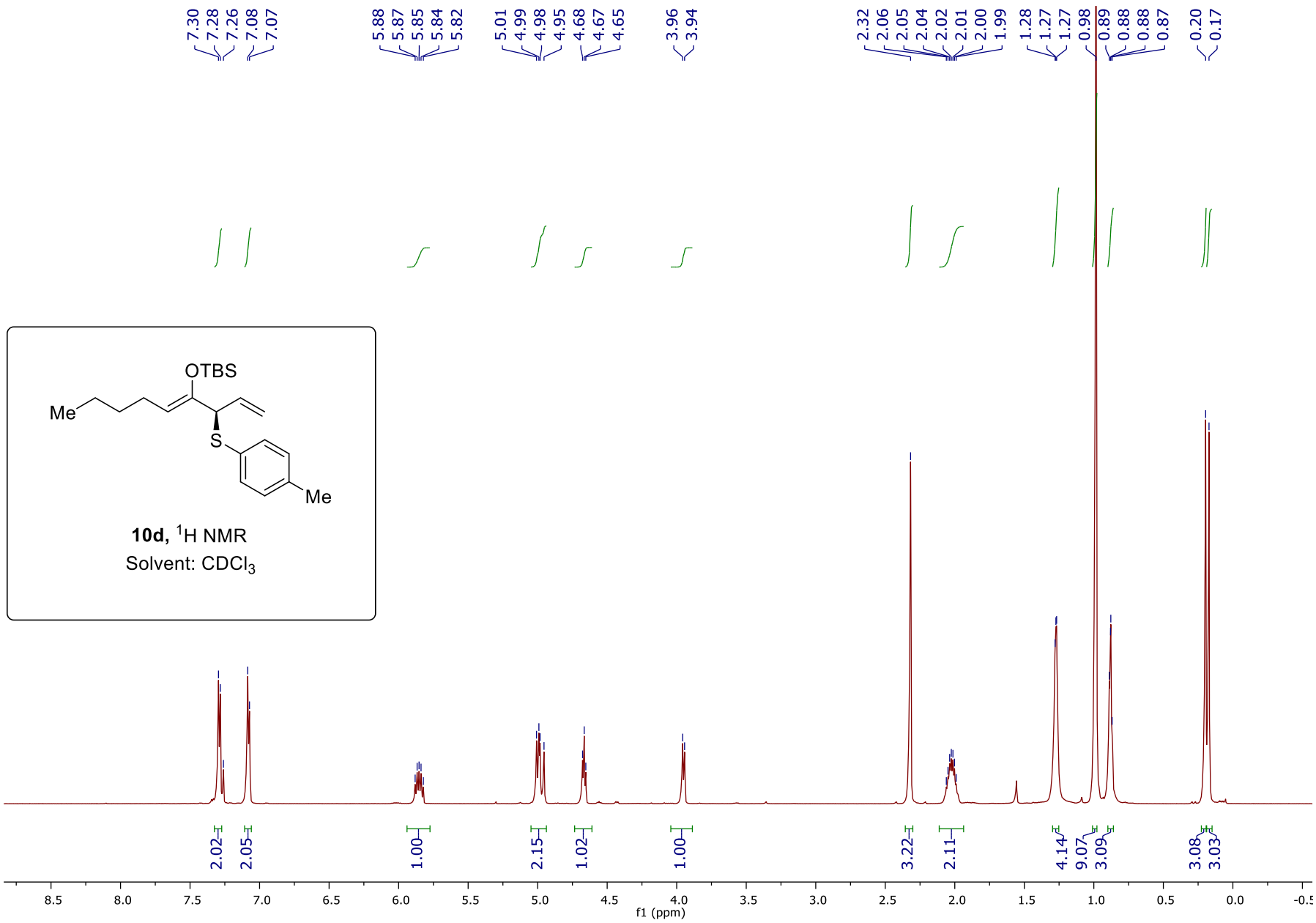
57.92
25.76
21.21
18.27
-4.64
-4.78
OTBS
S
Me
Me
10c, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.82
5.01
4.99
4.98
4.95
4.68
4.67
4.65
3.96
3.94
2.32
2.06
2.05
2.04
2.02
2.01
2.00
1.99
1.28
1.27
1.27
0.98
0.89
0.88
0.88
0.87
0.20
0.17
OTBS
Me
S
Me
10d, 1H NMR
Solvent: CDCl3
2.02
2.05
1.00
2.15
1.02
1.00
3.22
2.11
4.14
9.07
3.09
3.08
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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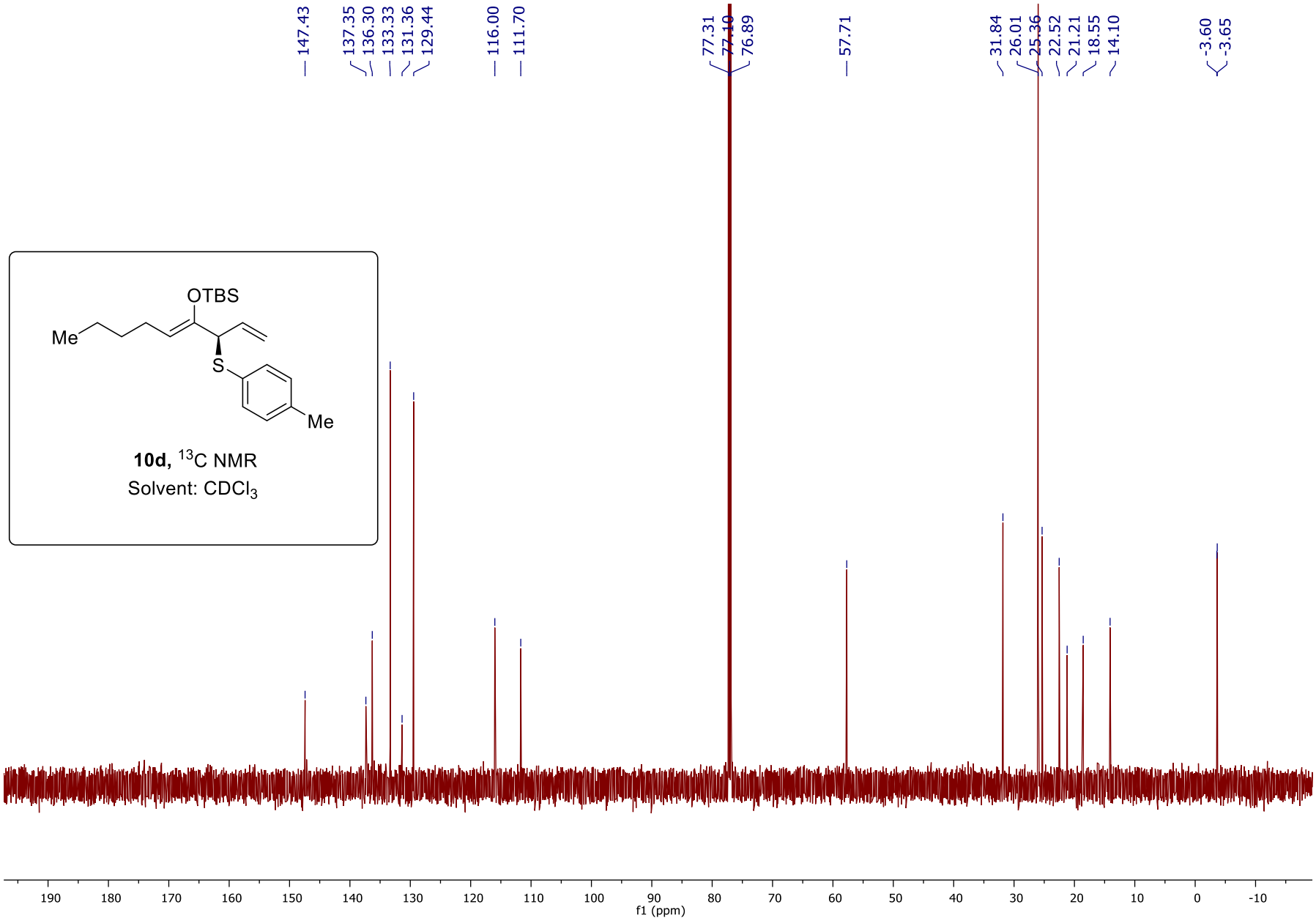
f1 (ppm)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26.01
25.36
22.52
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-3.65
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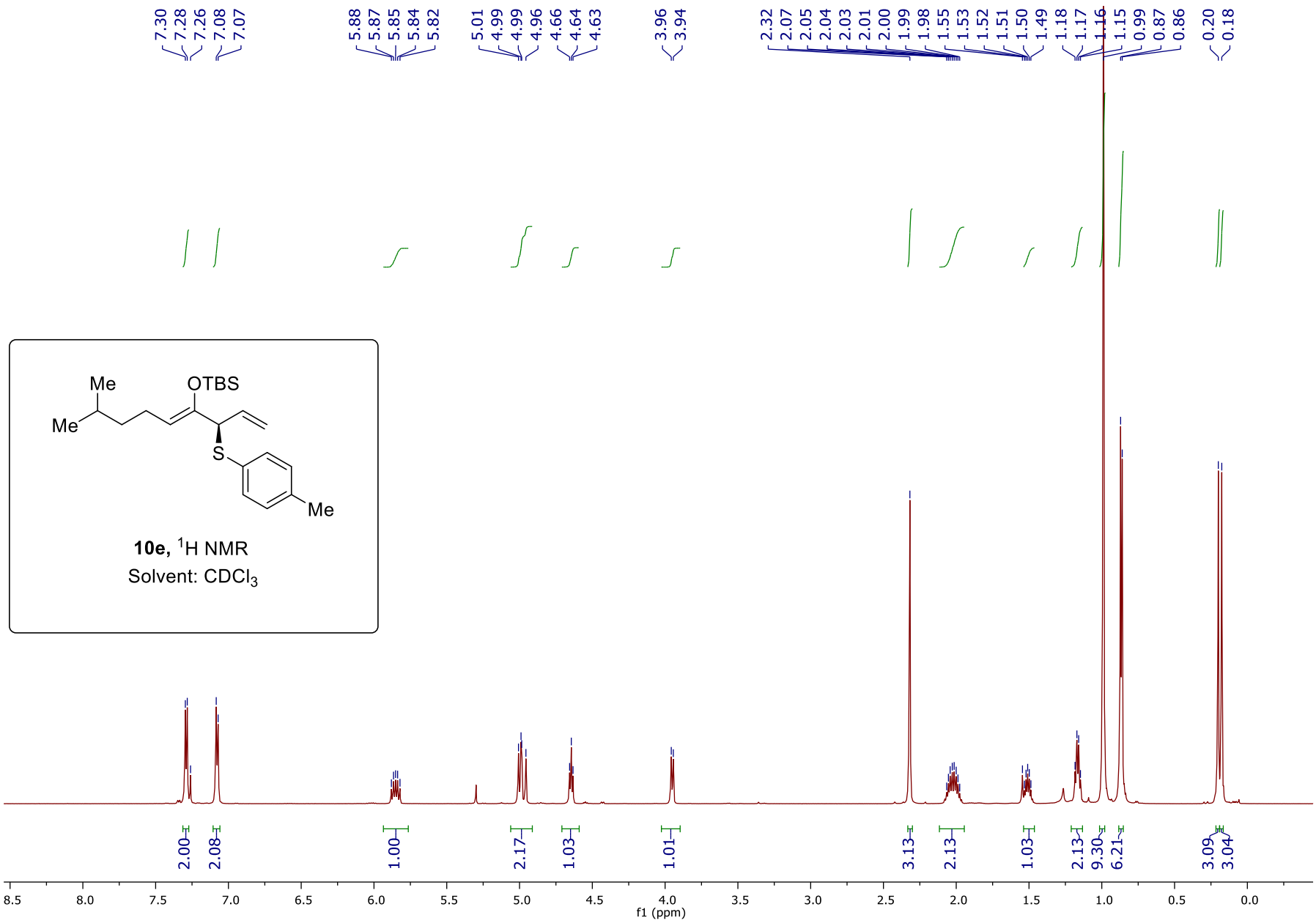
Me
S
Me
10d, 13C NMR
Solvent: CDCl3
f1 (ppm)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5.82
5.01
4.99
4.99
4.96
4.66
4.64
4.63
3.96
3.94
2.32
2.07
2.05
2.04
2.03
2.01
2.00
1.99
1.98
1.55
1.53
1.52
1.51
1.50
1.49
1.18
1.17
1.16
1.15
0.99
0.87
0.86
0.20
0.18
Me
OTBS
Me
S
Me
10e, 1H NMR
Solvent: CDCl3
2.00
2.08
1.00
2.17
1.03
1.01
3.13
2.13
1.03
2.13
9.30
6.21
3.09
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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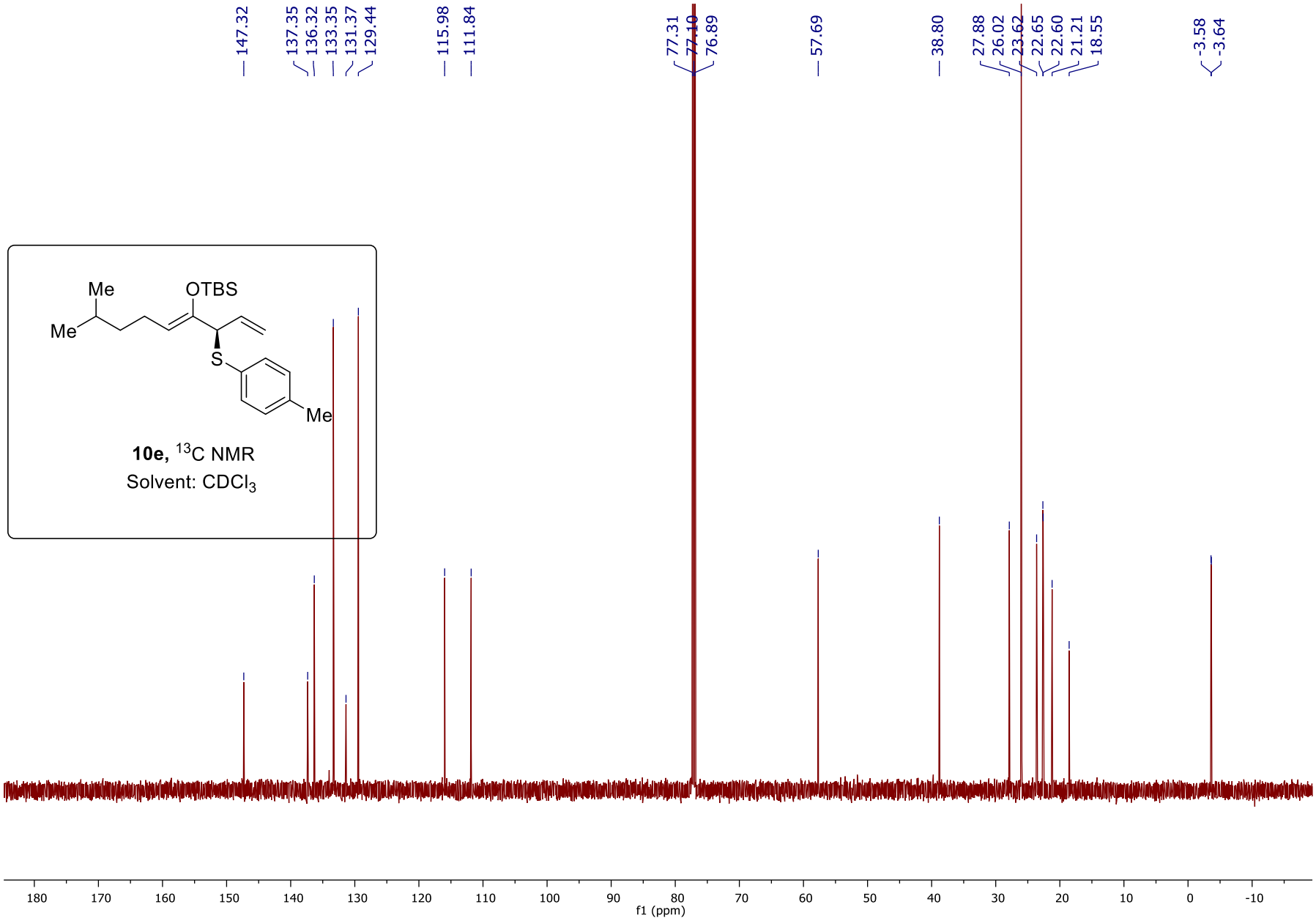
1.5
1.0
0.5
0.0
f1 (ppm)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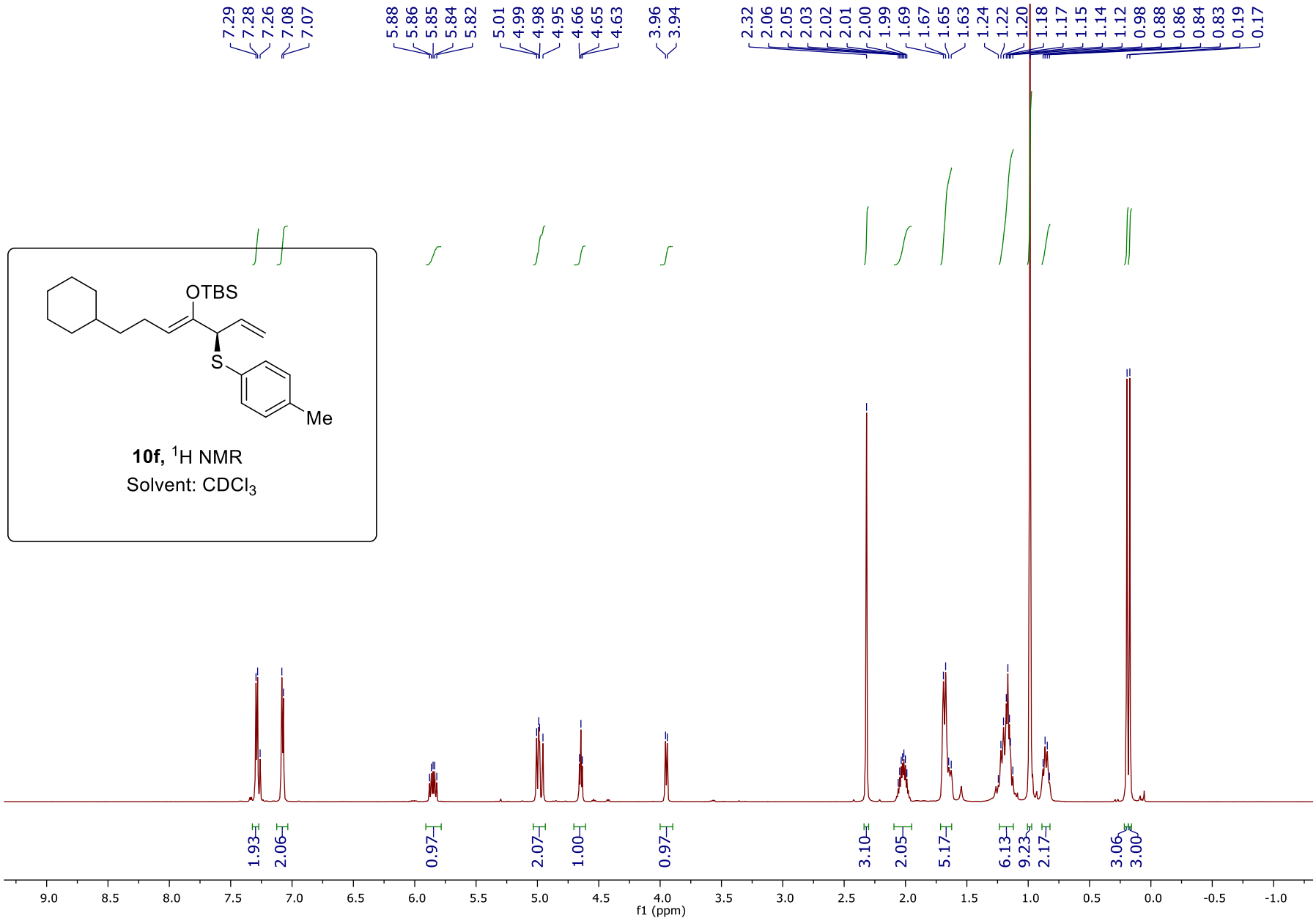
77.31
77.10
76.89
57.69
38.80
27.88
26.02
23.62
22.65
22.60
21.21
18.55
-3.58
-3.64
Me
OTBS
Me
S
Me
10e, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
S
Me
10f, 1H NMR
Solvent: CDCl3
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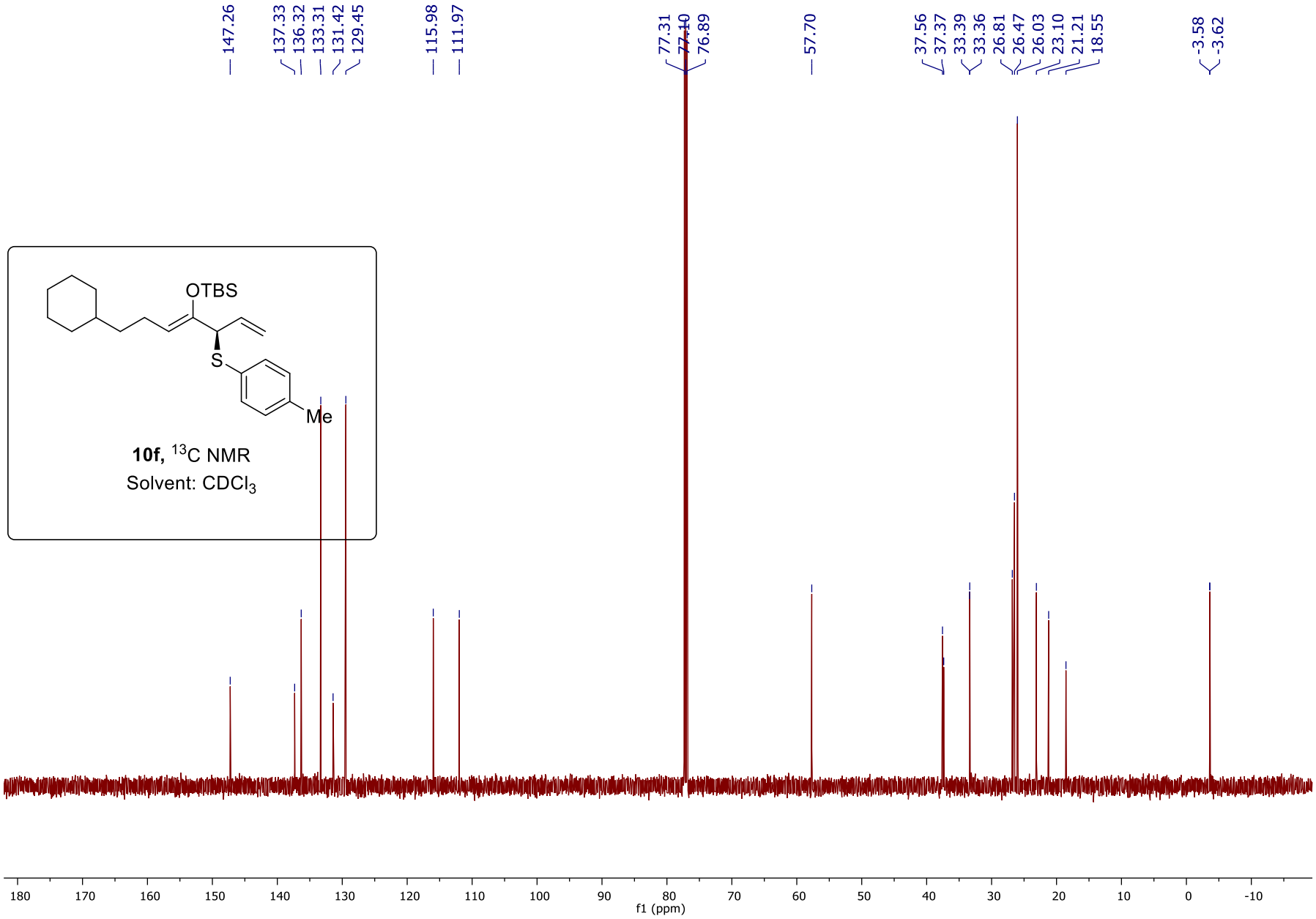
5.88 5.86 5.85 5.84 5.82
5.01 4.99 4.98 4.95 4.66 4.65 4.63
3.96 3.94
2.32 2.06 2.05 2.03 2.02 2.01 2.00 1.99 1.69 1.67 1.65 1.63 1.24 1.22 1.20 1.18 1.17 1.15 1.14 1.12 0.98 0.88 0.86 0.84 0.83 0.19 0.17
1.93 2.06 0.97 2.07 1.00 0.97 3.10 2.05 5.17 6.13 9.23 2.17 3.06 3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 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 -1.0
f1 (ppm)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77.31
77.10
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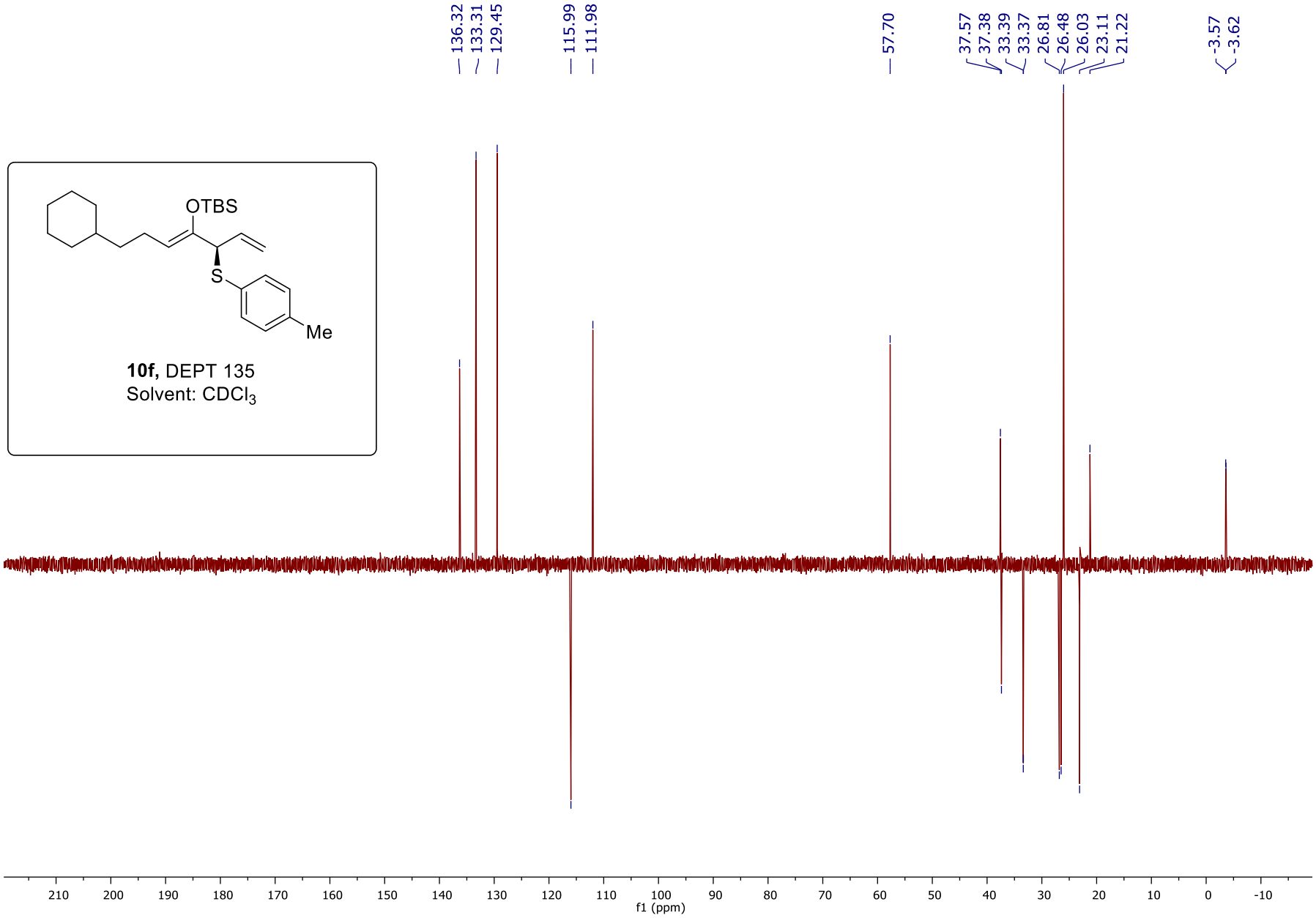
57.70
37.56
37.37
33.39
33.36
26.81
26.47
26.03
23.10
21.21
18.55
-3.58
-3.62
OTBS
S
Me
10f, 13C NMR
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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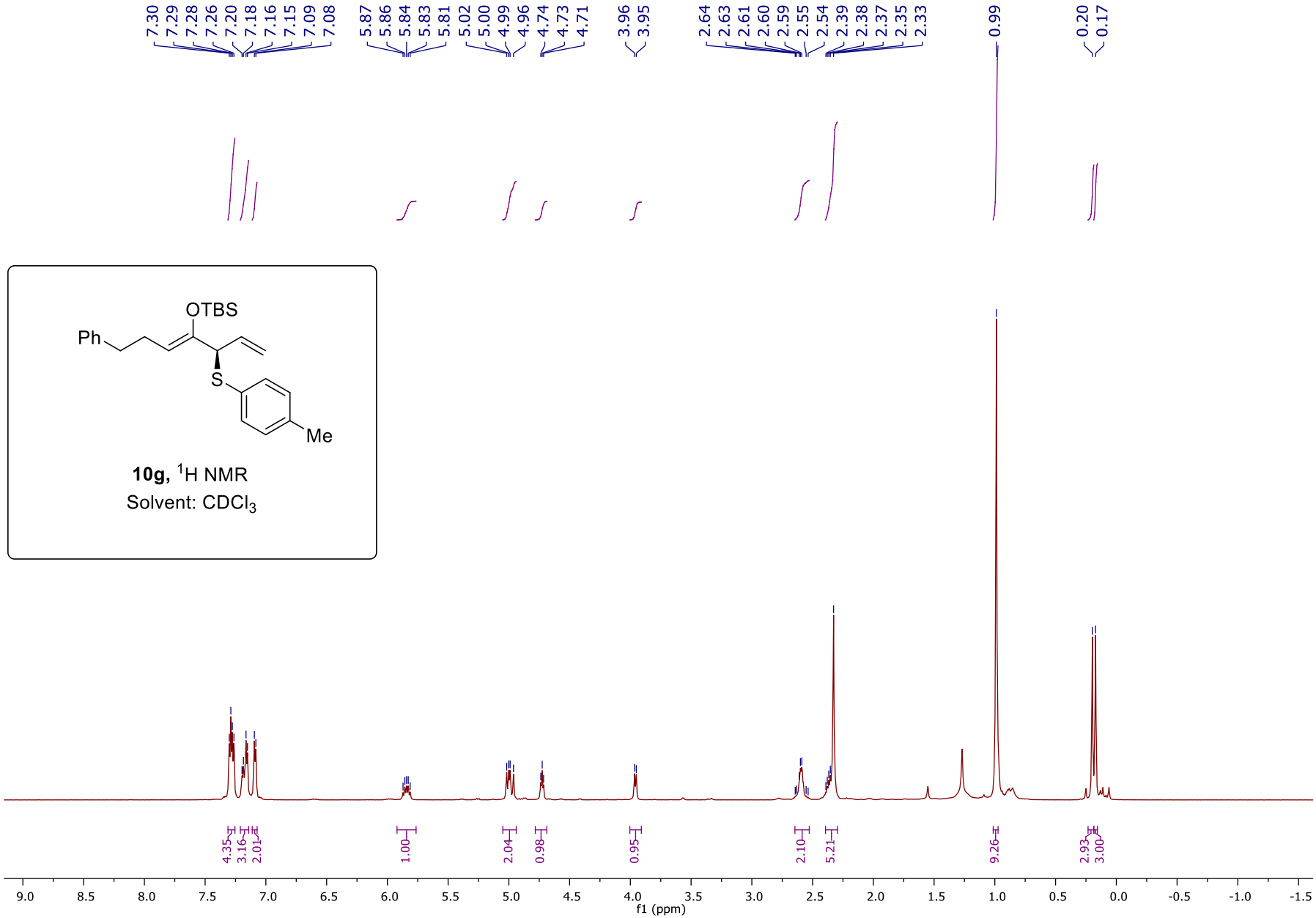
57.70
37.57
37.38
33.39
33.37
26.81
26.48
26.03
23.11
21.22
-3.57
-3.62
OTBS
S
Me
10f, DEPT 135
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.08
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5.86
5.84
5.83
5.81
5.02
5.00
4.99
4.96
4.74
4.73
4.71
3.96
3.95
2.64
2.63
2.61
2.60
2.59
2.55
2.54
2.39
2.38
2.37
2.35
2.33
0.99
0.20
0.17
OTBS
Ph
S
Me
10g, 1H NMR
Solvent: CDCl3
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3.16
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2.04
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0.95
2.10
5.21
9.26
2.93
3.00
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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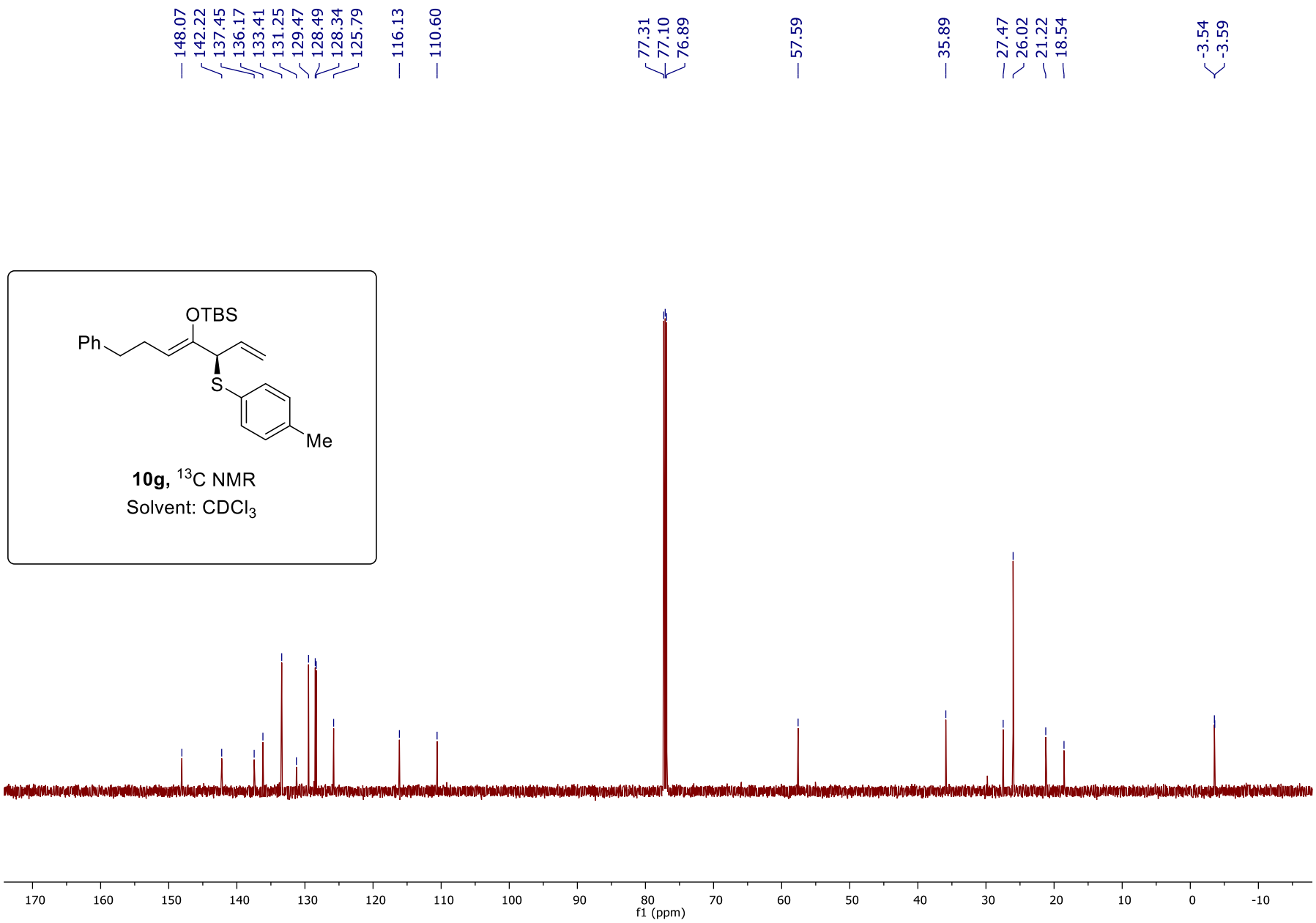
-1.5
f1 (ppm)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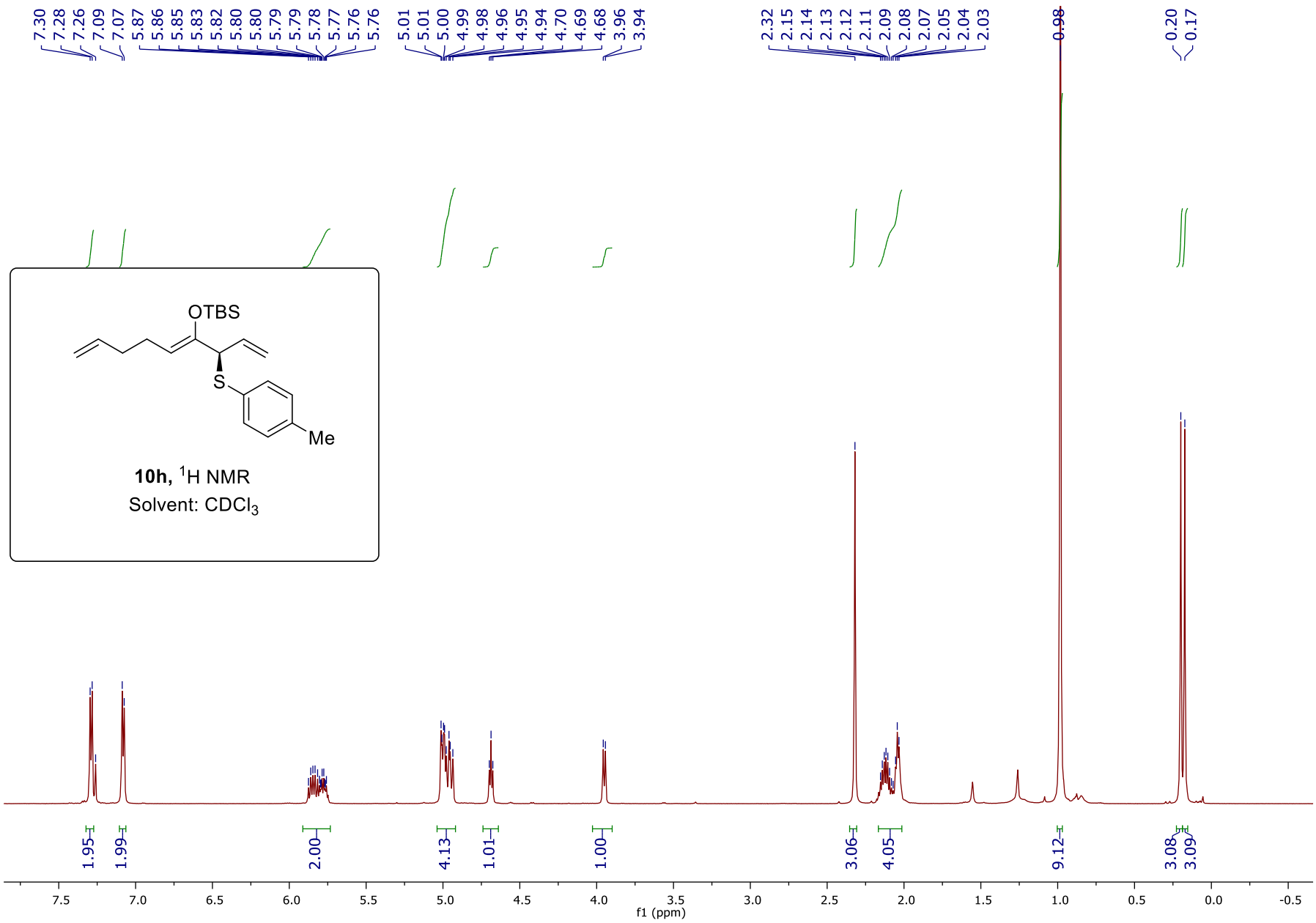
116.13
110.60
77.31
77.10
76.89
57.59
35.89
27.47
26.02
21.22
18.54
-3.54
-3.59
OTBS
Ph
S
Me
10g, 13C NMR
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.28
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7.09
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5.87
5.86
5.85
5.83
5.82
5.80
5.80
5.79
5.79
5.78
5.77
5.76
5.76
5.01
5.01
5.00
4.99
4.98
4.96
4.95
4.94
4.70
4.69
4.68
3.96
3.94
2.32
2.15
2.14
2.13
2.12
2.11
2.09
2.08
2.07
2.05
2.04
2.03
0.98
0.20
0.17
OTBS
S
Me
10h, 1H NMR
Solvent: CDCl3
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1.01
1.00
3.06
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3.09
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7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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2.0
1.5
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0.5
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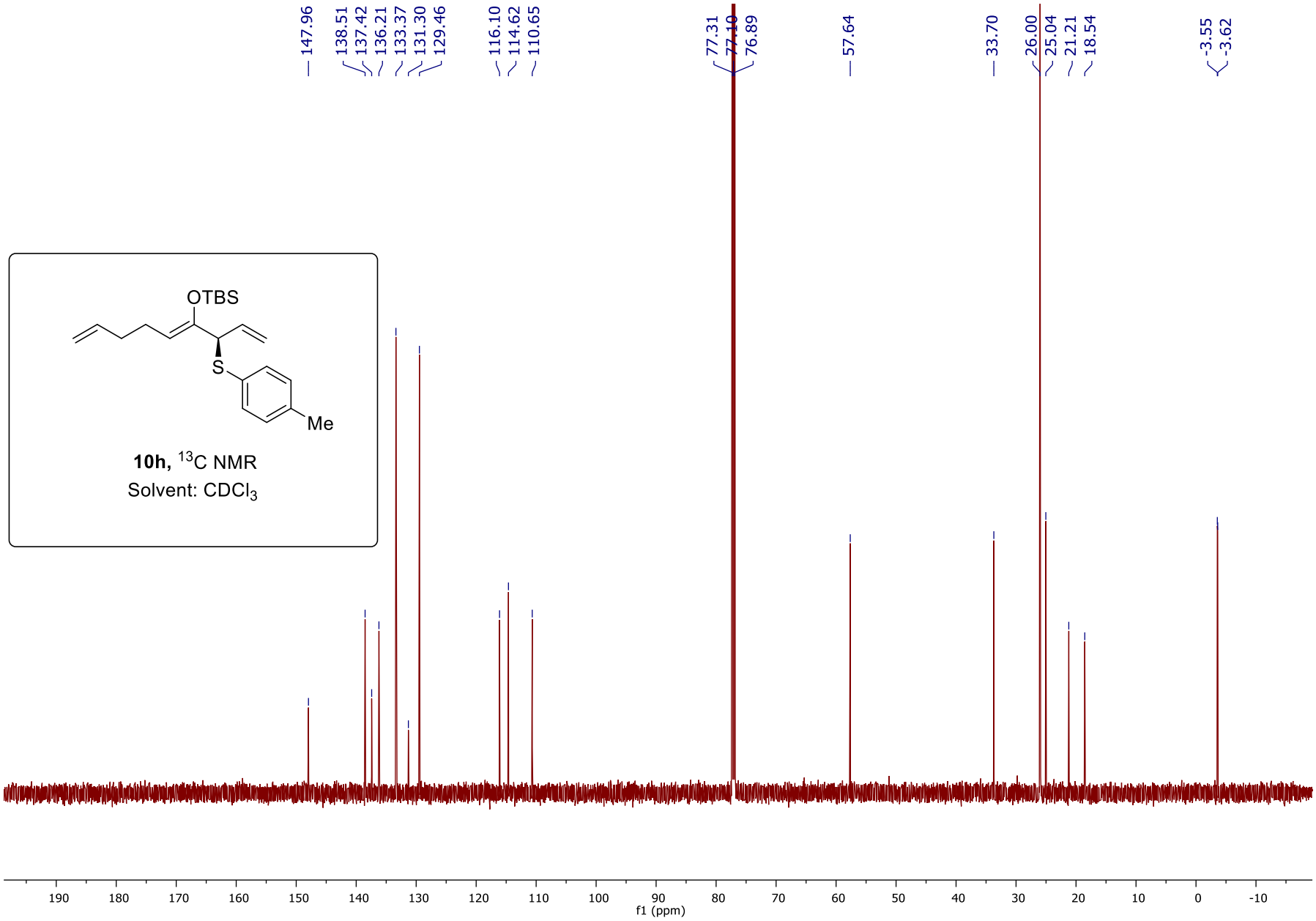
f1 (ppm)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110.65
77.31
77.10
76.89
57.64
33.70
26.00
25.04
21.21
18.54
-3.55
-3.62
OTBS
S
Me
10h, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
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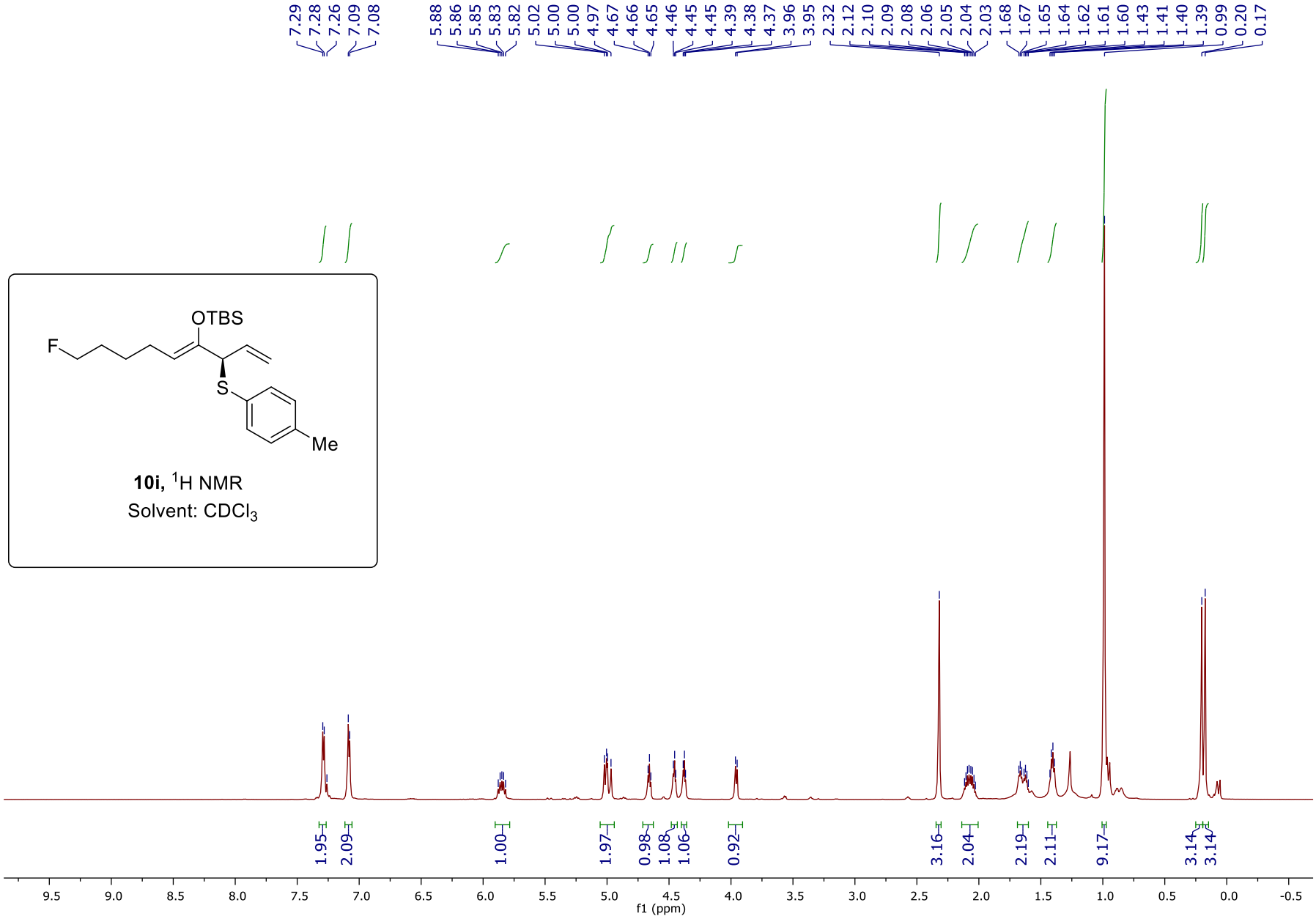
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.28
7.26
7.09
7.08
5.88
5.86
5.85
5.83
5.82
5.02
5.00
5.00
4.97
4.67
4.66
4.65
4.46
4.45
4.45
4.39
4.38
4.37
3.96
3.95
2.32
2.12
2.10
2.09
2.08
2.06
2.05
2.04
2.03
1.68
1.67
1.65
1.64
1.62
1.61
1.60
1.43
1.41
1.40
1.39
0.99
0.20
0.17
OTBS
F
S
Me
10i, 1H NMR
Solvent: CDCl3
1.95
2.09
1.00
1.97
0.98
1.08
1.06
0.92
3.16
2.04
2.19
2.11
9.17
3.14
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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0.5
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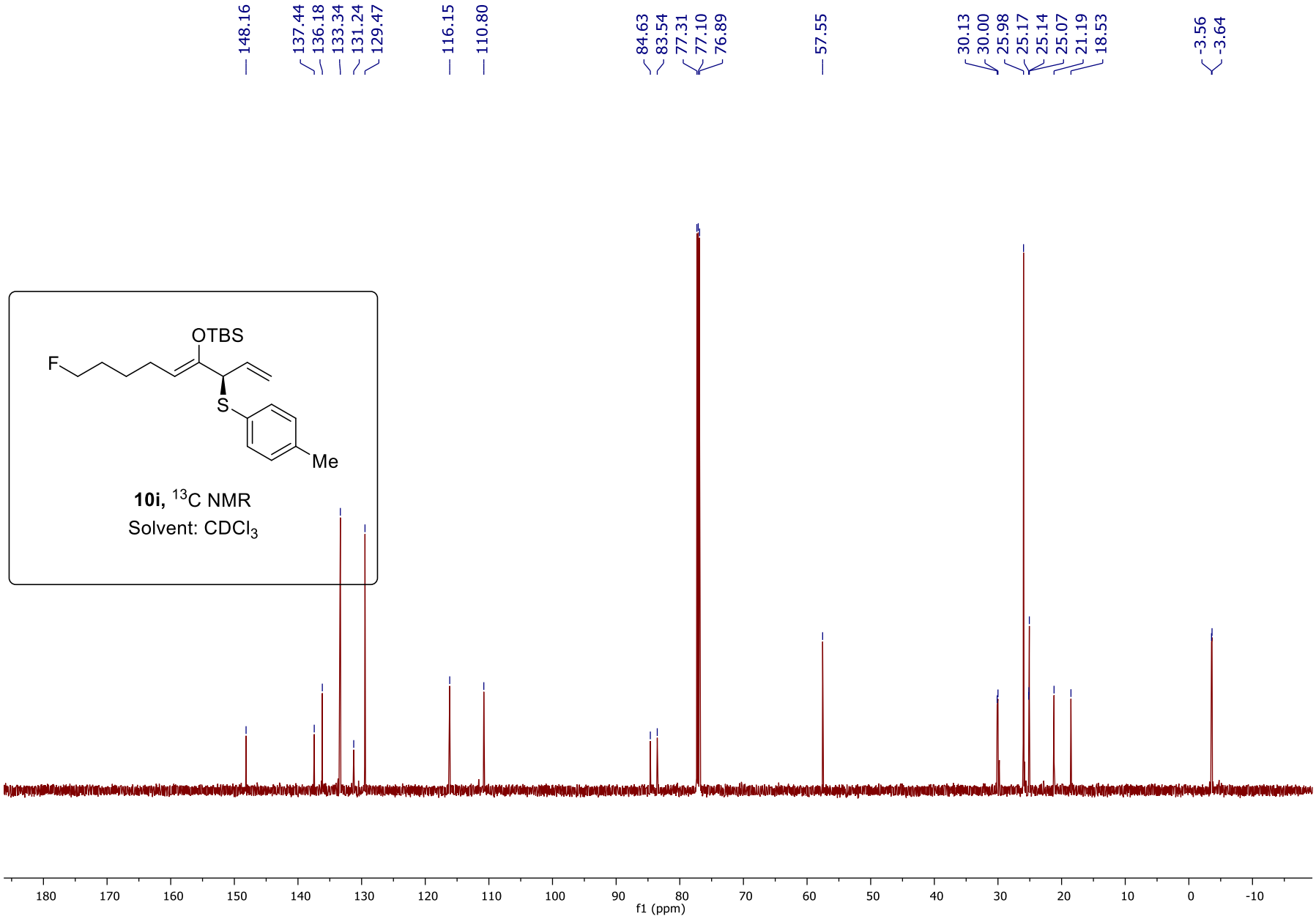
f1 (ppm)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110.80
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83.54
77.31
77.10
76.89
57.55
30.13
30.00
25.98
25.17
25.14
25.07
21.19
18.53
-3.56
-3.64
OTBS
F
S
Me
10i, 13C NMR
Solvent: CDCl3
180
170
160
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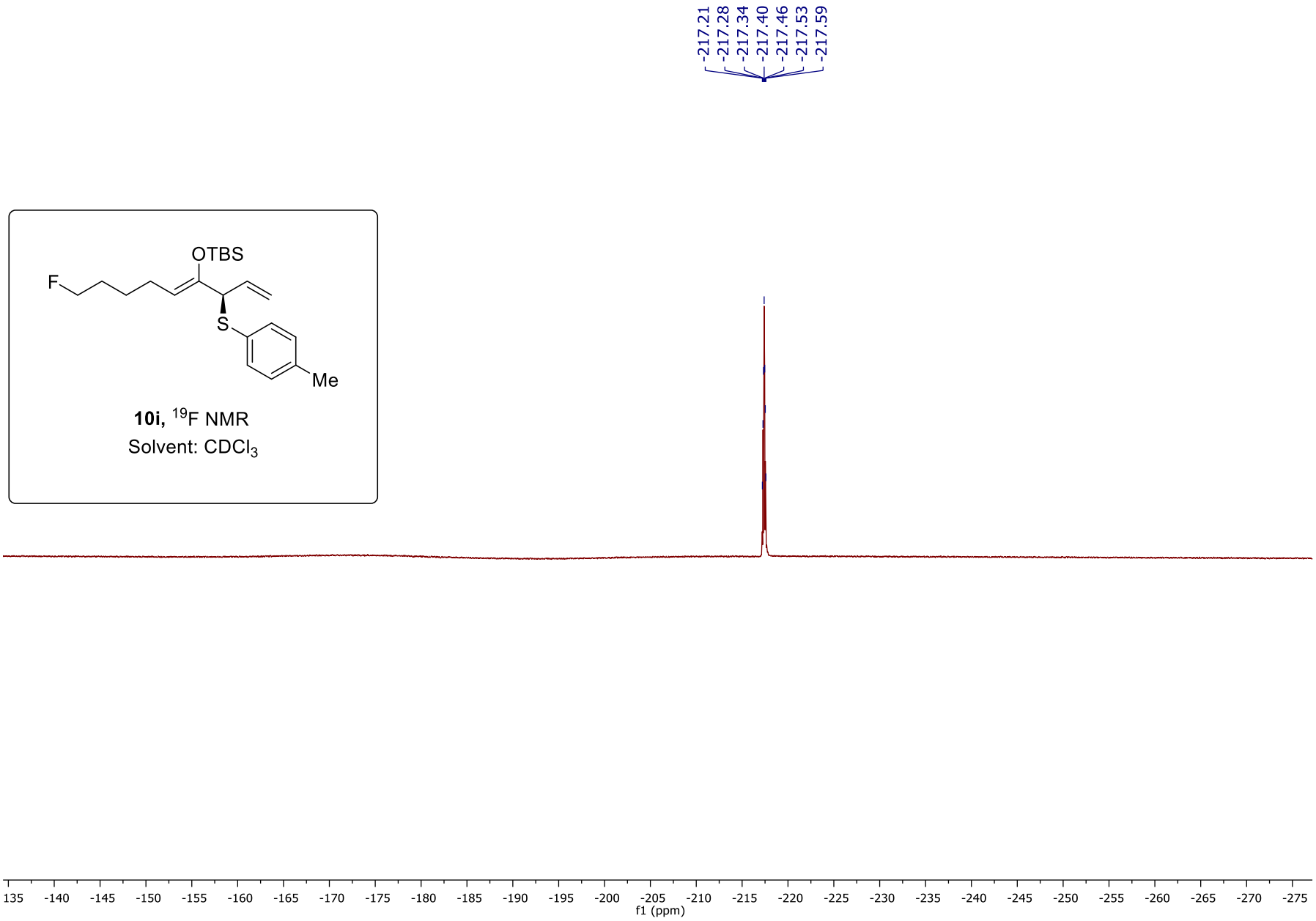
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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-217.46
-217.53
-217.59
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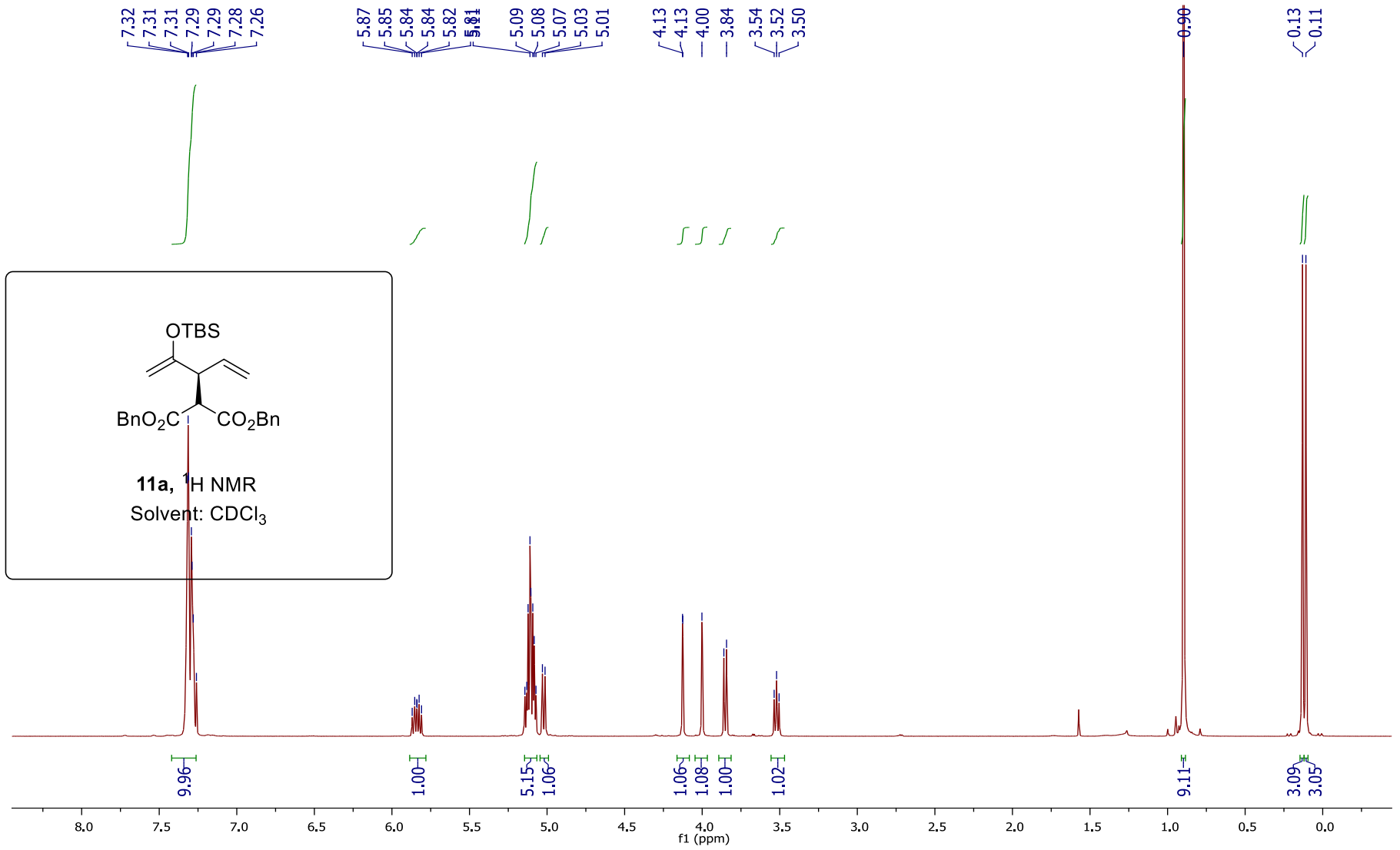
F
S
Me
10i, 19F NMR
Solvent: CDCl3
135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 -210 -215 -220 -225 -230 -235 -240 -245 -250 -255 -260 -265 -270 -275
f1 (ppm)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7.31
7.31
7.29
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7.28
7.26
5.87
5.85
5.84
5.84
5.82
5.09
5.08
5.07
5.03
5.01
4.13
4.13
4.00
3.84
3.54
3.52
3.50
0.90
0.13
0.11
OTBS
BnO2C
CO2Bn
11a, 1H NMR
Solvent: CDCl3
9.96
1.00
5.15
1.06
1.06
1.08
1.00
1.02
9.11
3.09
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
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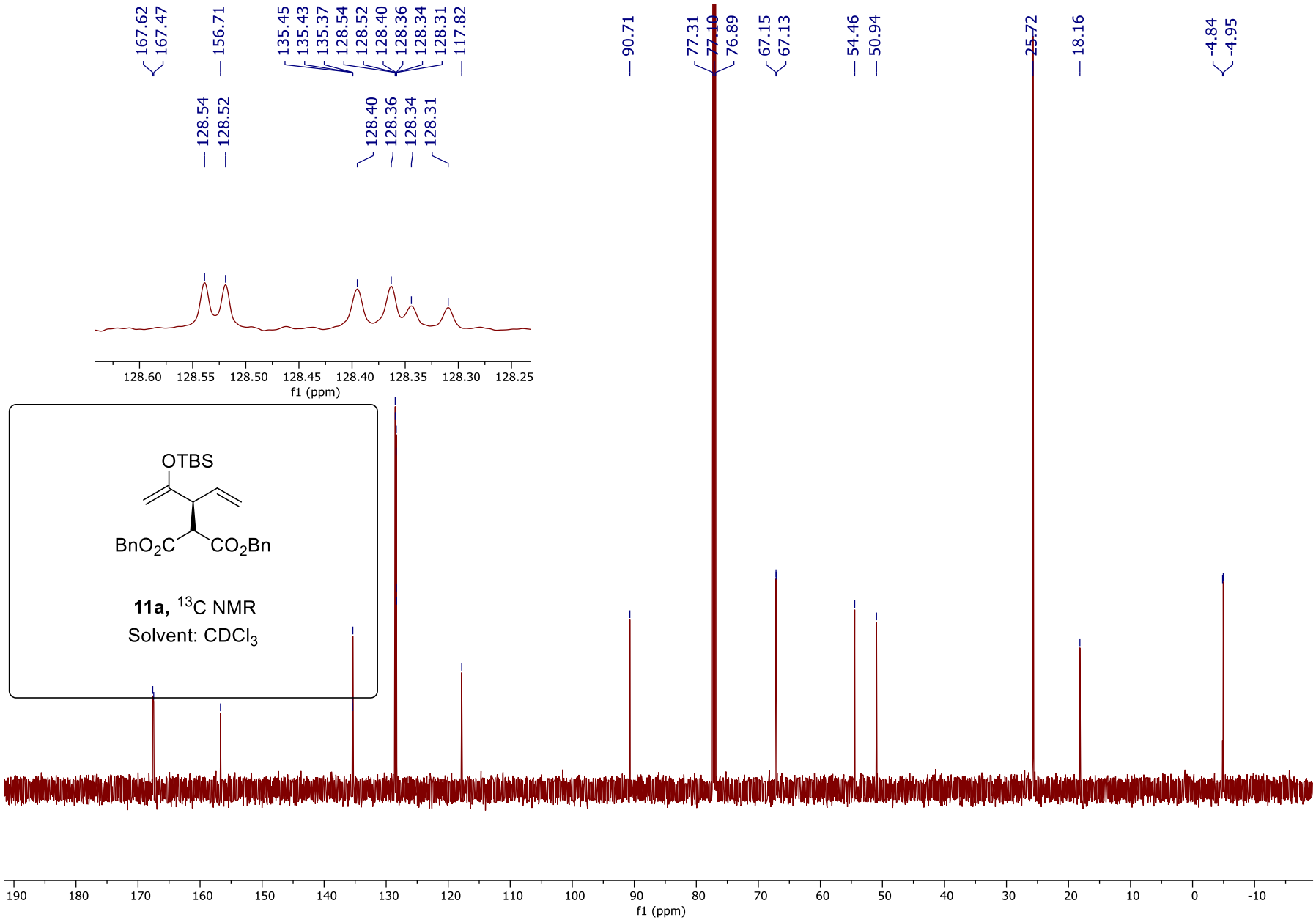
0.0
f1 (ppm)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167.47
156.71
135.45
135.43
135.37
128.54
128.52
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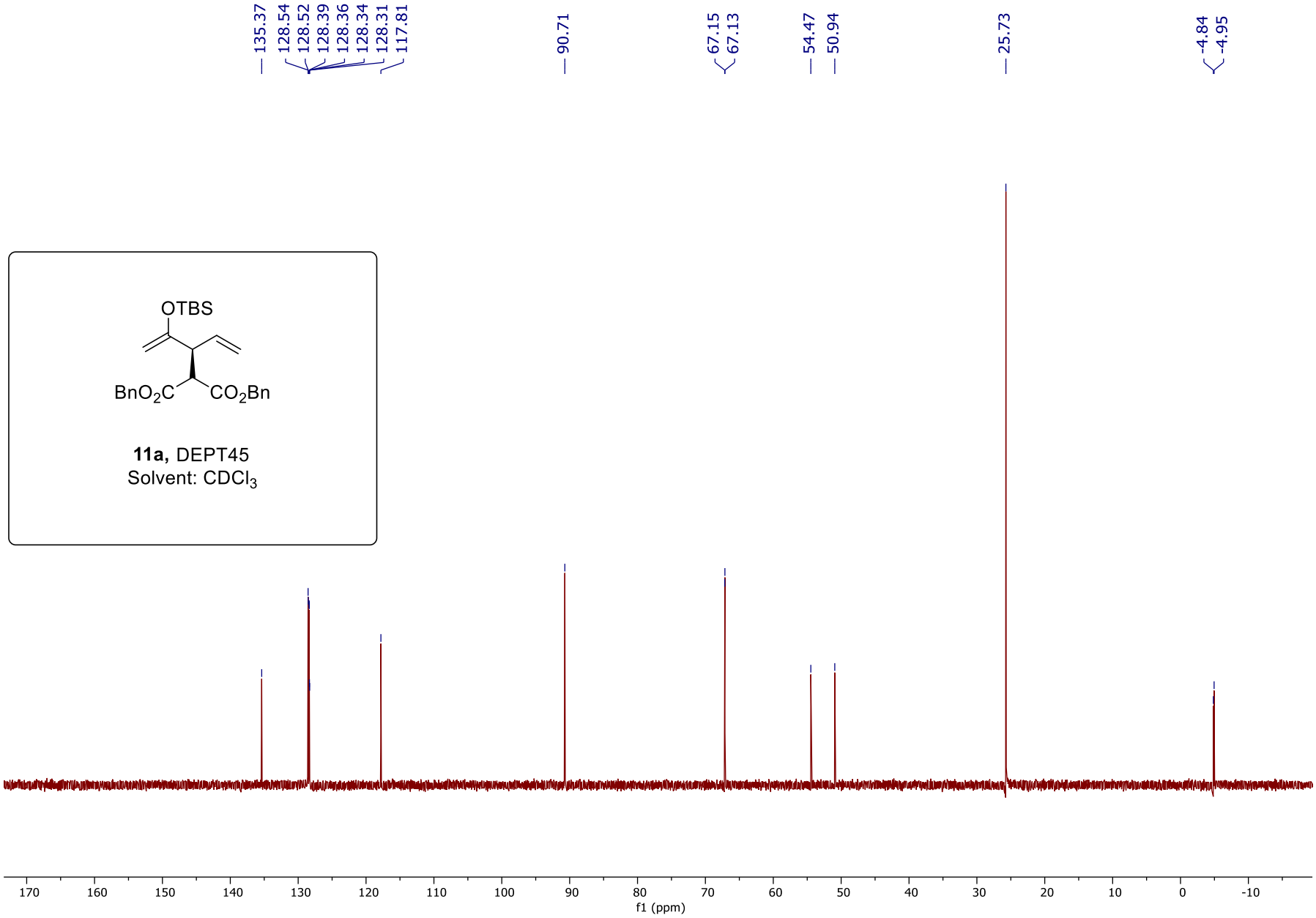
128.36
128.34
128.31
117.82
90.71
77.31
77.10
76.89
67.15
67.13
54.46
50.94
25.72
18.16
-4.84
-4.95
128.54
128.52
128.40
128.36
128.34
128.31
128.60 128.55 128.50 128.45 128.40 128.35 128.30 128.25
f1 (ppm)
OTBS
BnO2C
CO2Bn
11a, 13C NMR
Solvent: CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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128.54
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128.34
128.31
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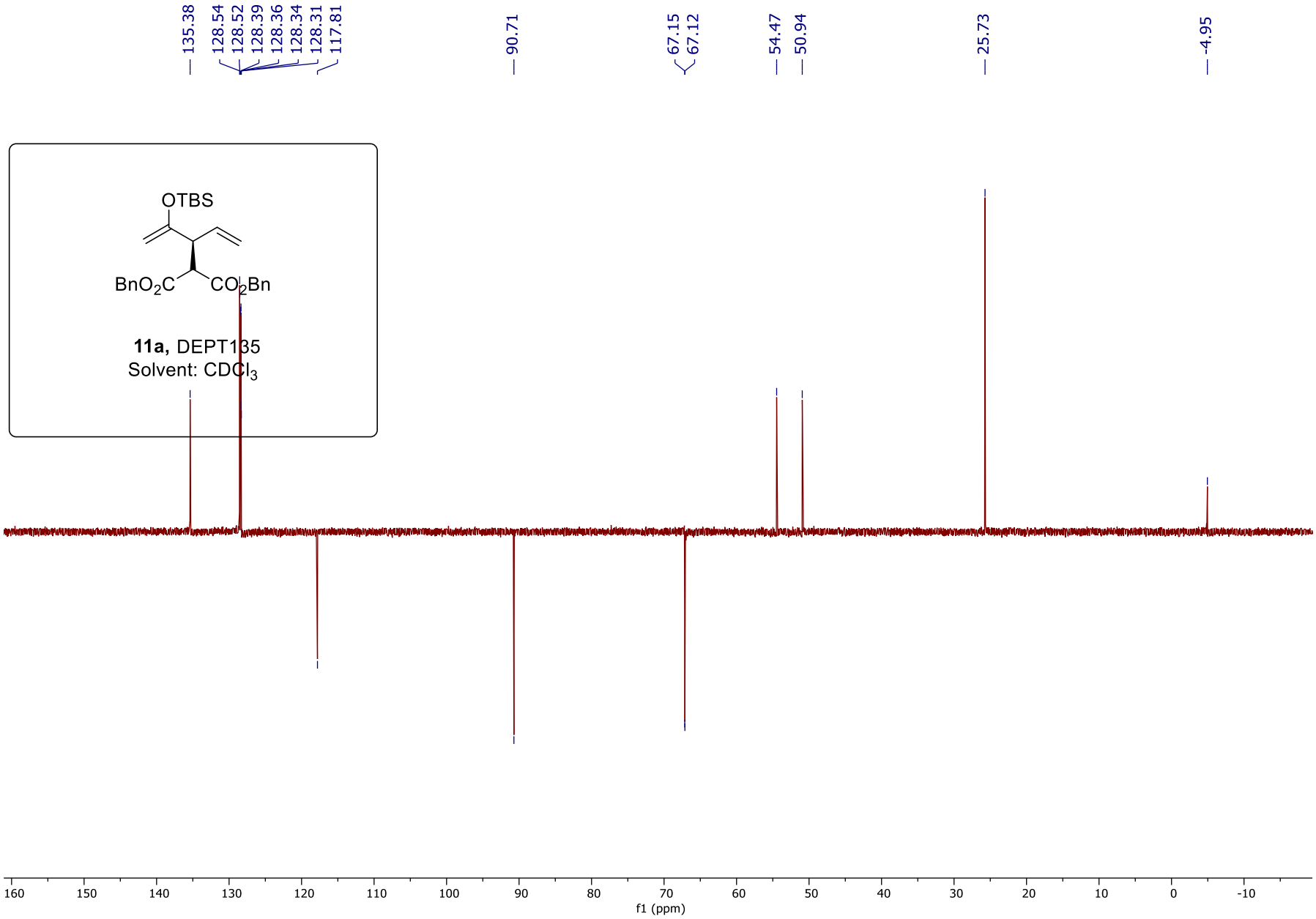
67.15
67.13
54.47
50.94
25.73
-4.84
-4.95
OTBS
BnO2C
CO2Bn
11a, DEPT45
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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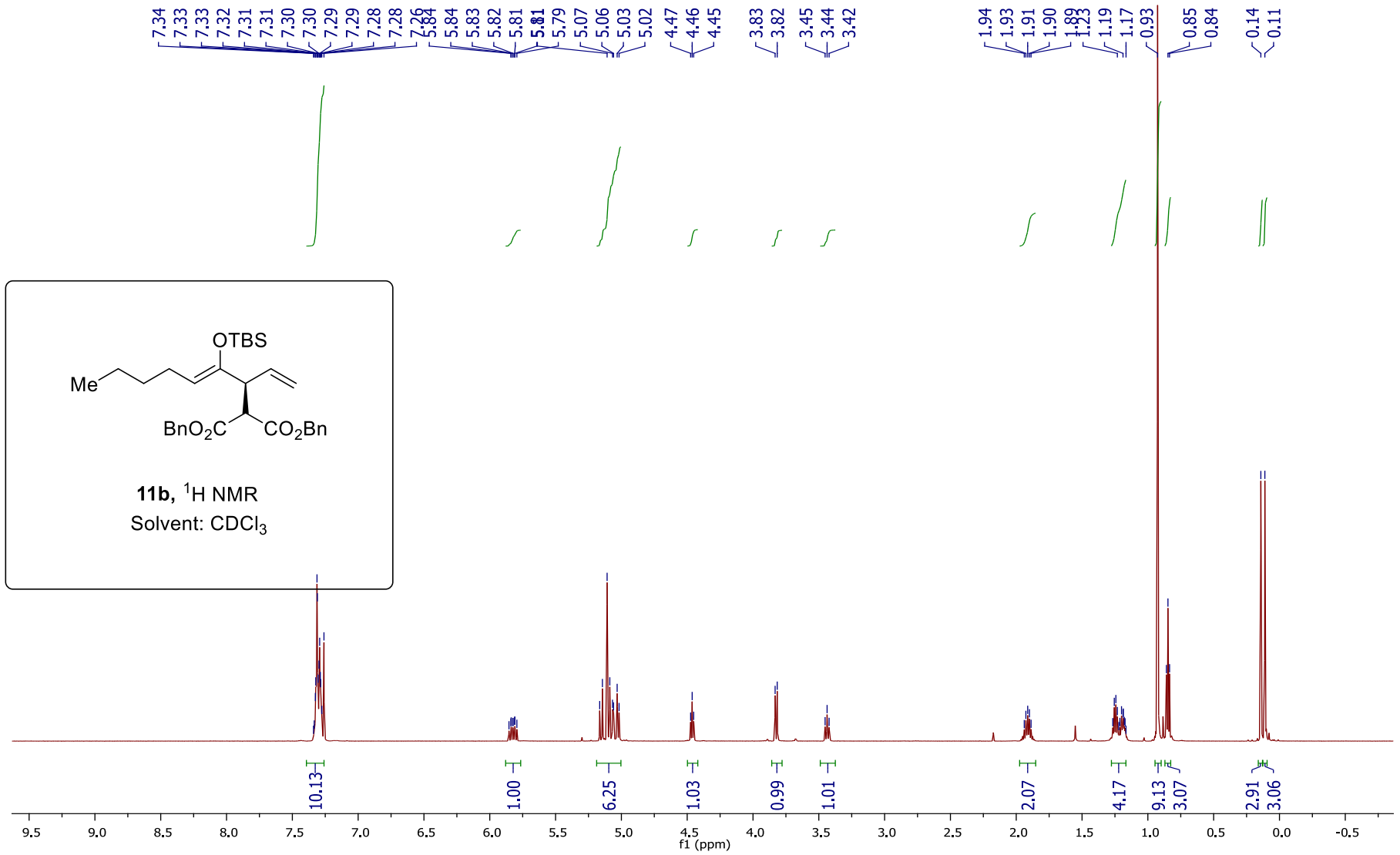
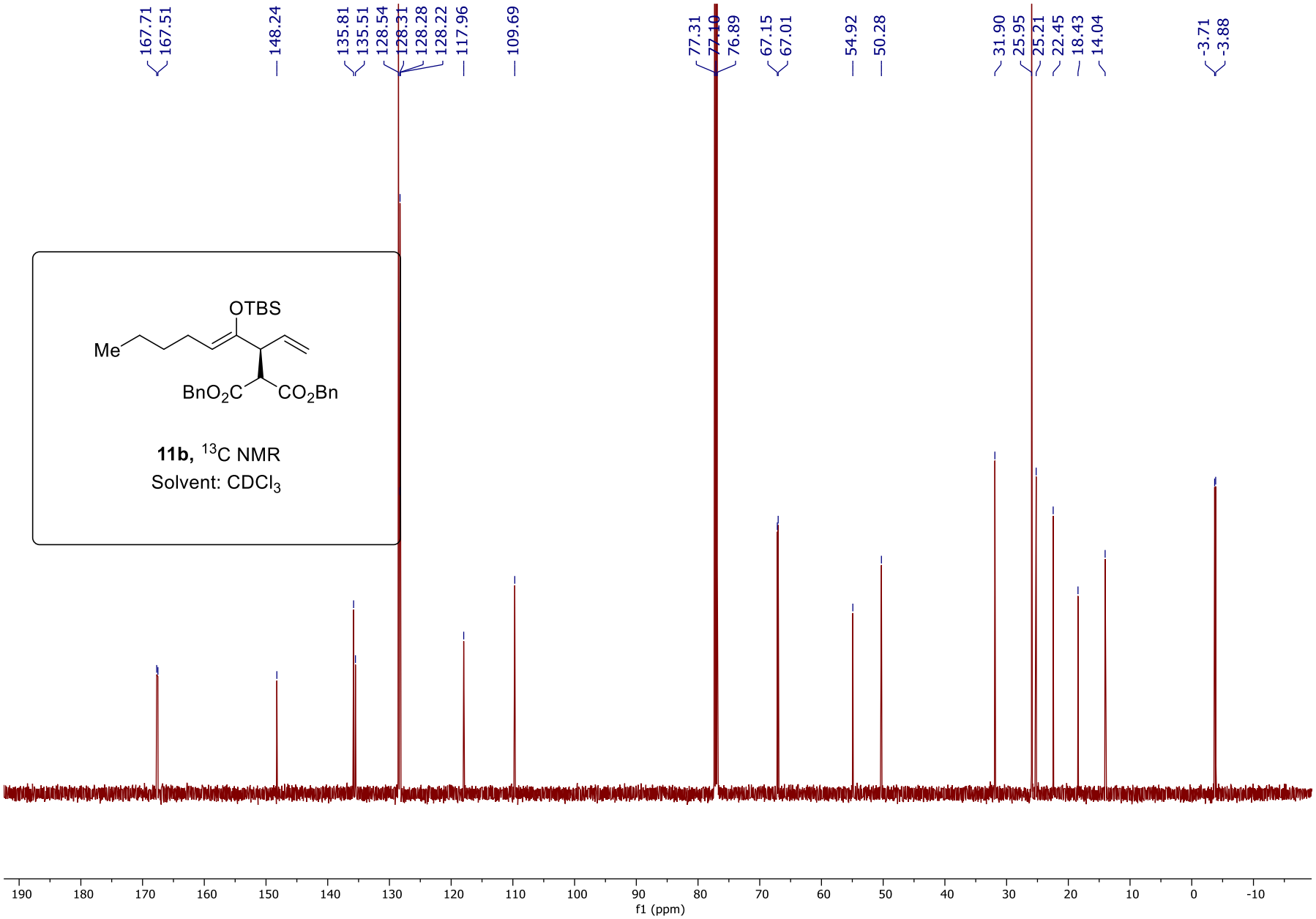
128.39
128.36
128.34
128.31
117.81
90.71
67.15
67.12
54.47
50.94
25.73
-4.95
OTBS
BnO2C
CO2Bn
11a, DEPT135
Solvent: CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
Me
BnO2C
CO2Bn
11b, 1H NMR
Solvent: CDCl3
f1 (ppm)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167.51
148.24
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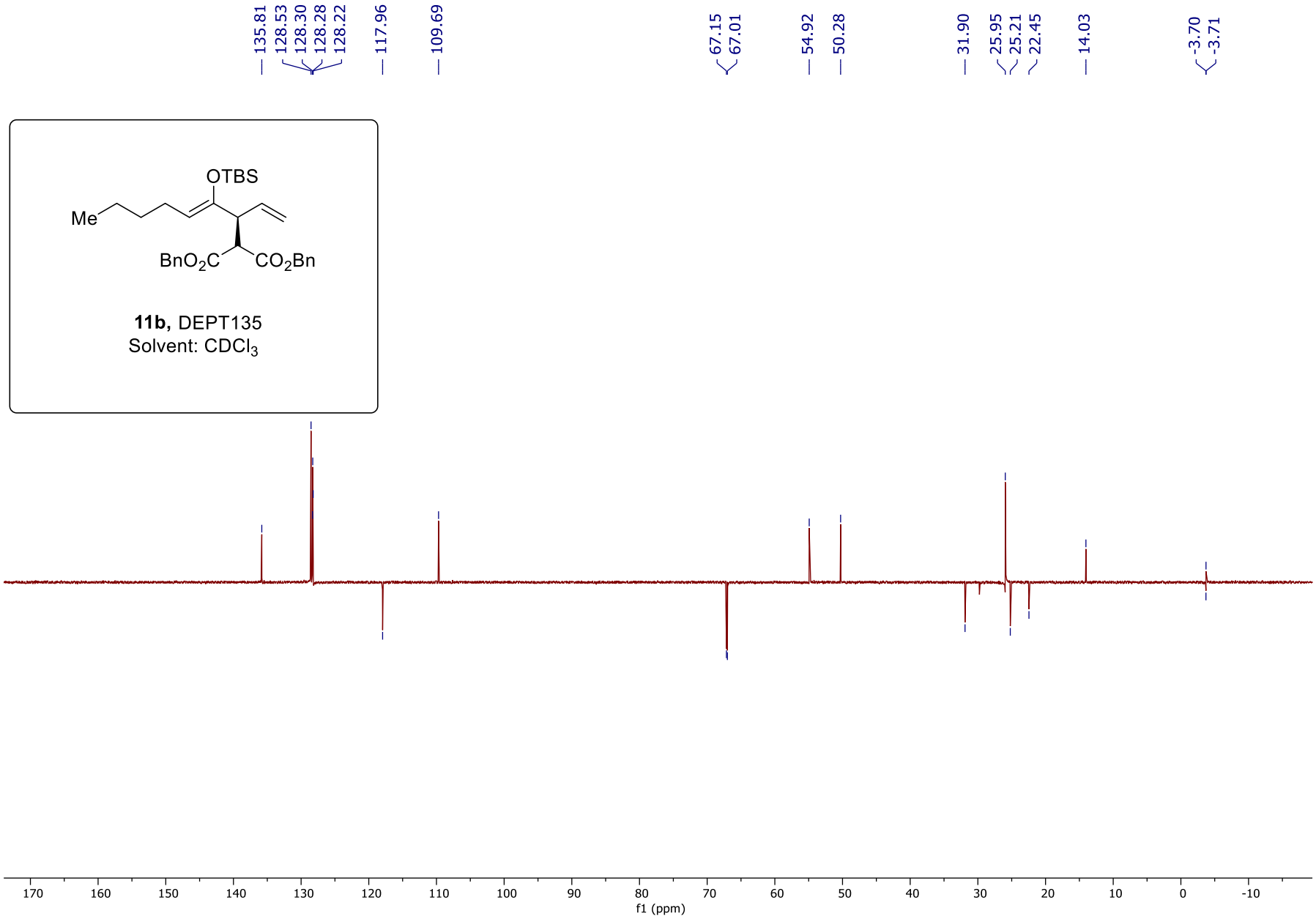
128.54
128.31
128.28
128.22
117.96
109.69
77.31
77.10
76.89
67.15
67.01
54.92
50.28
31.90
25.95
25.21
22.45
18.43
14.04
-3.71
-3.88
OTBS
Me
BnO2C
CO2Bn
11b, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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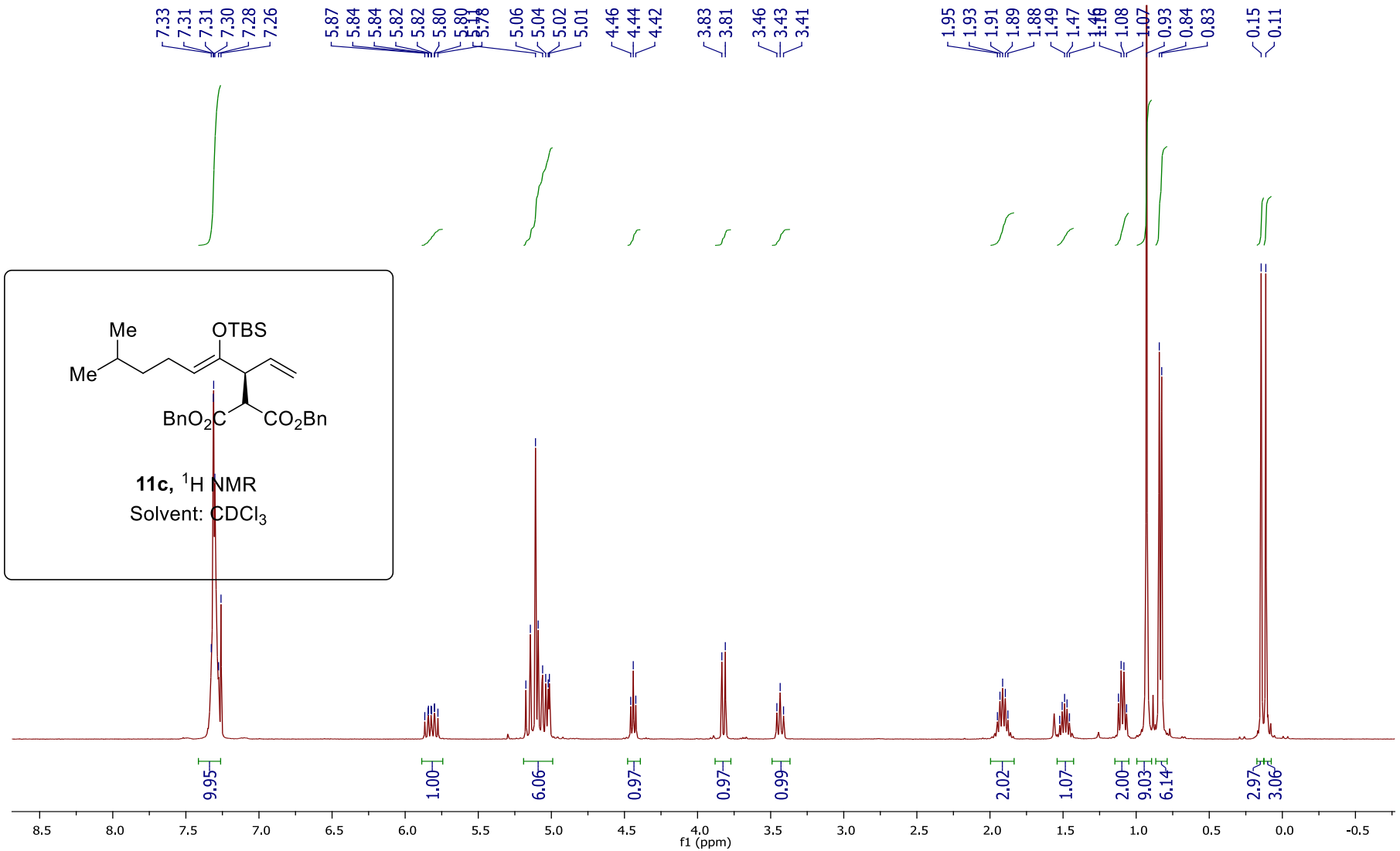
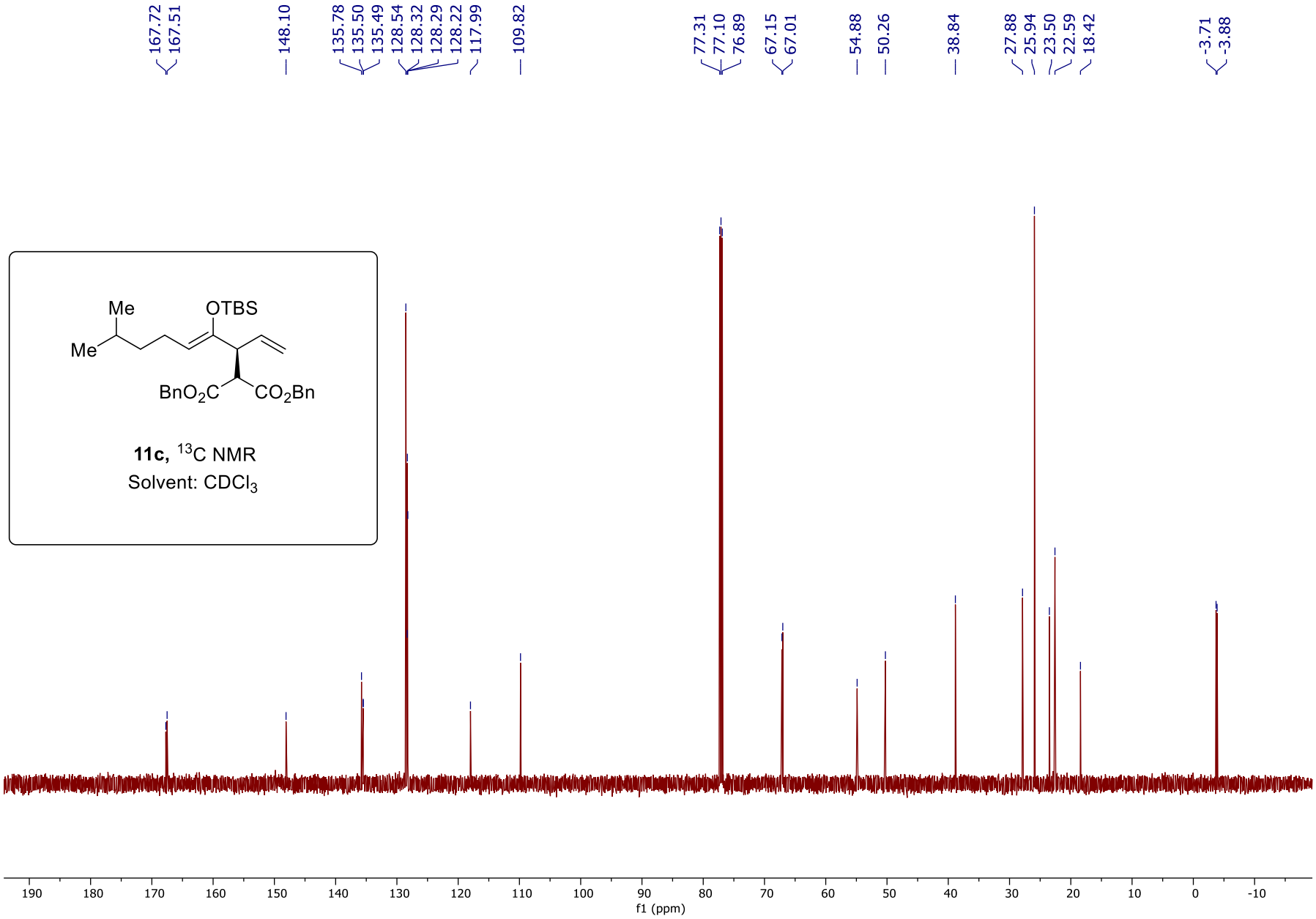
128.53
128.30
128.28
128.22
117.96
109.69
67.15
67.01
54.92
50.28
31.90
25.95
25.21
22.45
14.03
-3.70
-3.71
OTBS
Me
BnO2C
CO2Bn
11b, DEPT135
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
OTBS
Me
BnO2C
CO2Bn
11c, 1H NMR
Solvent: CDCl3
f1 (ppm)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167.51
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135.49
128.54
128.32
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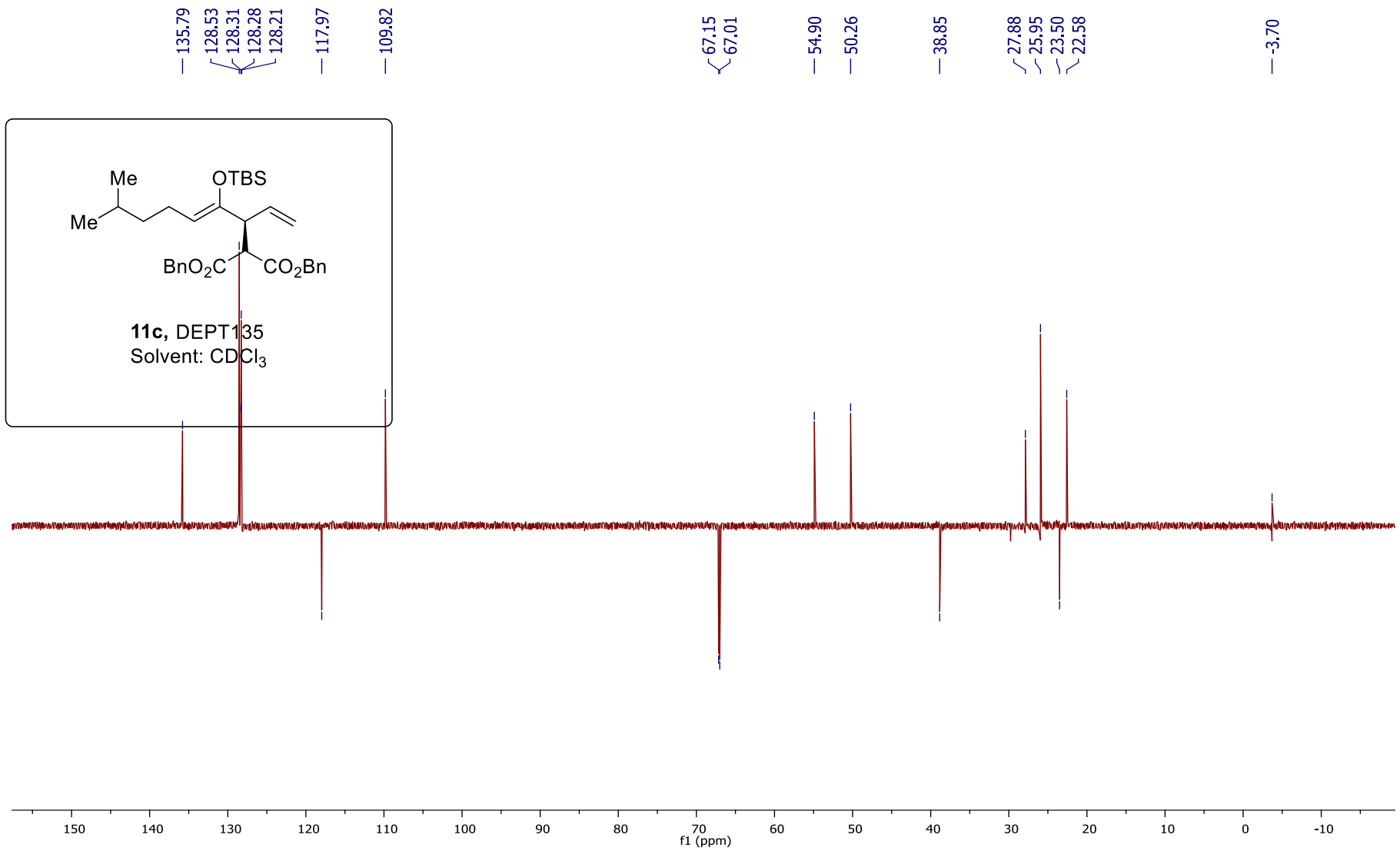
128.22
117.99
109.82
77.31
77.10
76.89
67.15
67.01
54.88
50.26
38.84
27.88
25.94
23.50
22.59
18.42
-3.71
-3.88
Me
OTBS
Me
BnO2C
CO2Bn
11c, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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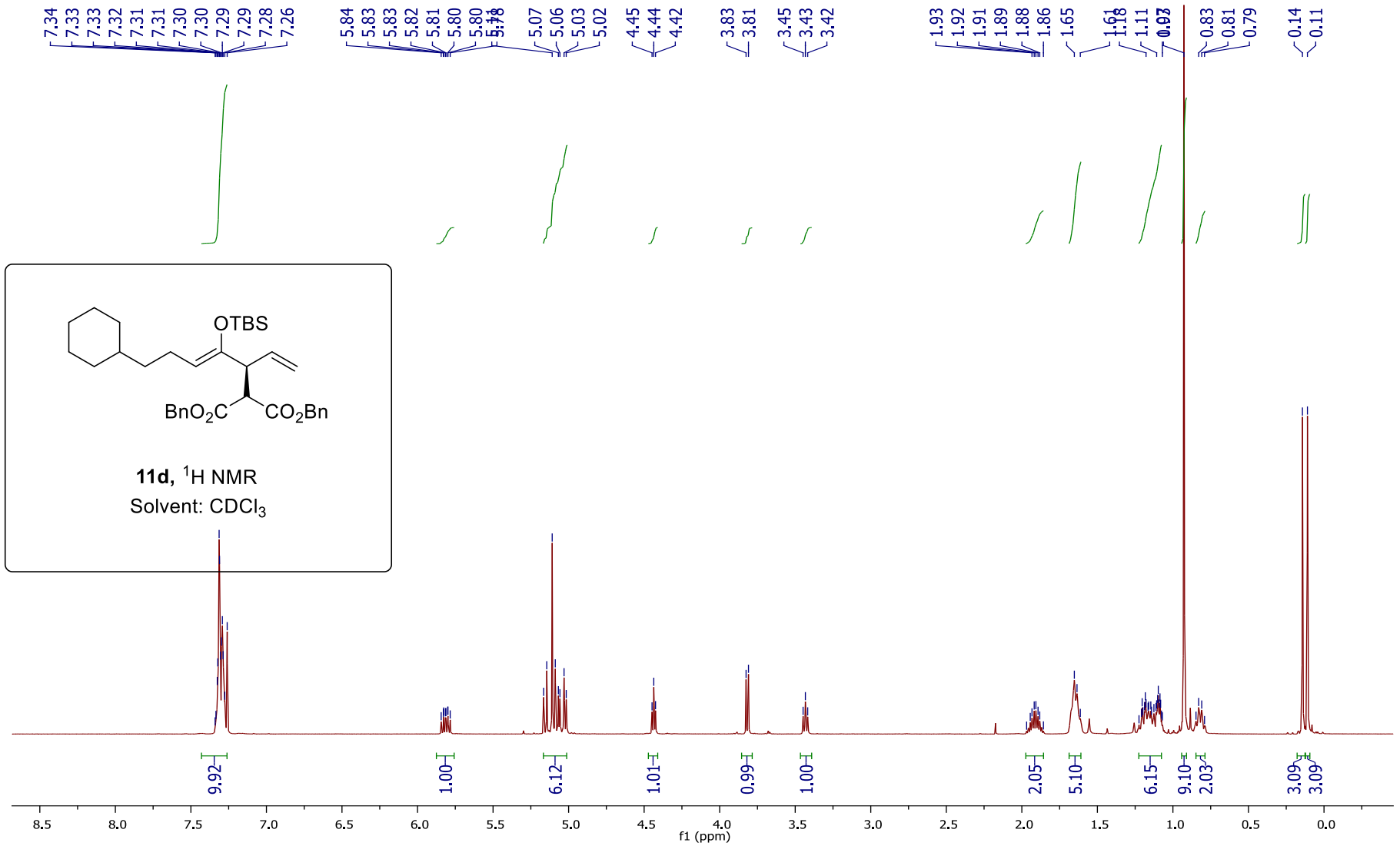
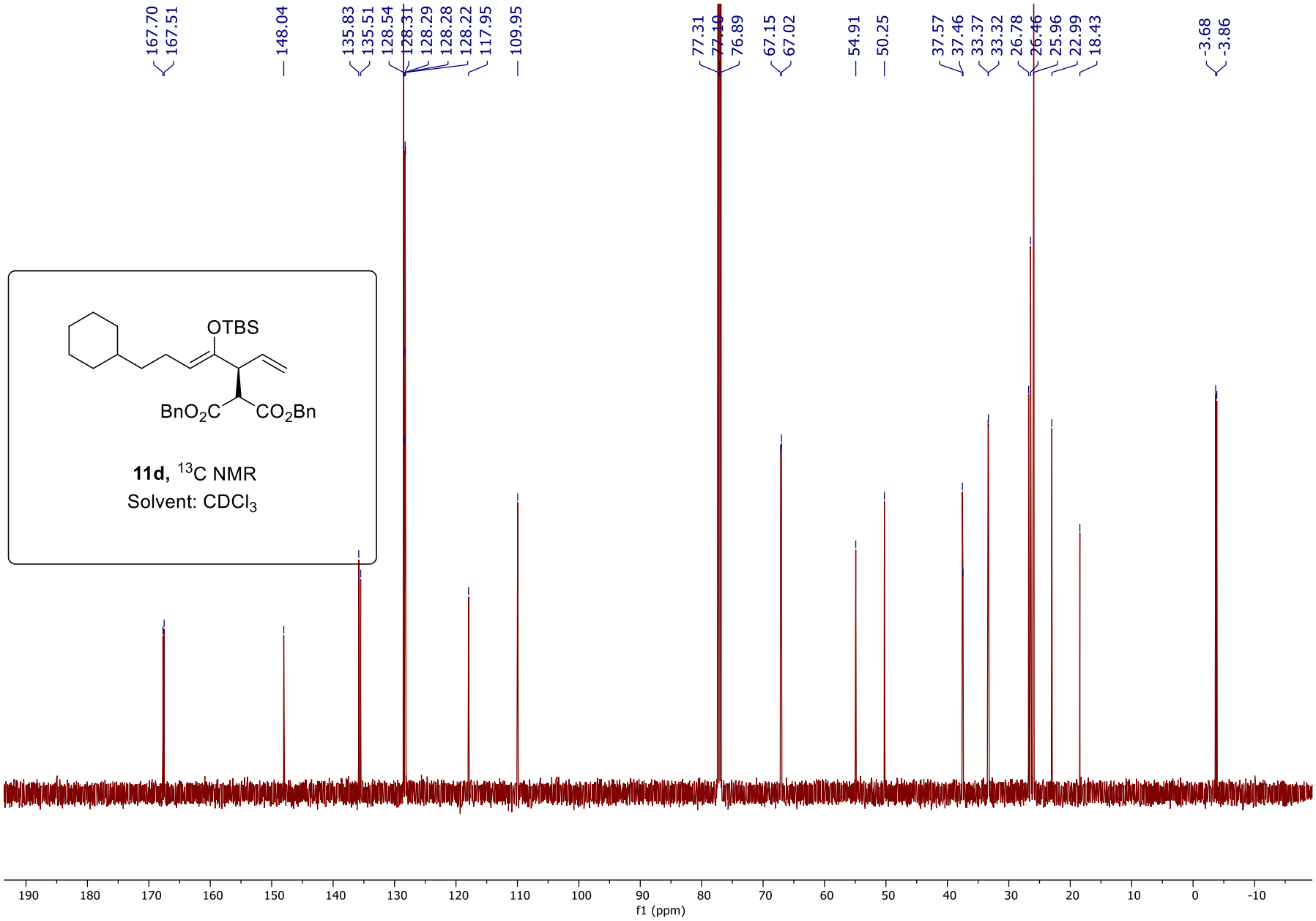
128.28
128.21
117.97
109.82
67.15
67.01
54.90
50.26
38.85
27.88
25.95
23.50
22.58
-3.70
Me
OTBS
Me
BnO2C
CO2Bn
11c, DEPT135
Solvent: CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
BnO2C
CO2Bn
11d, 1H NMR
Solvent: CDCl3
f1 (ppm)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128.29
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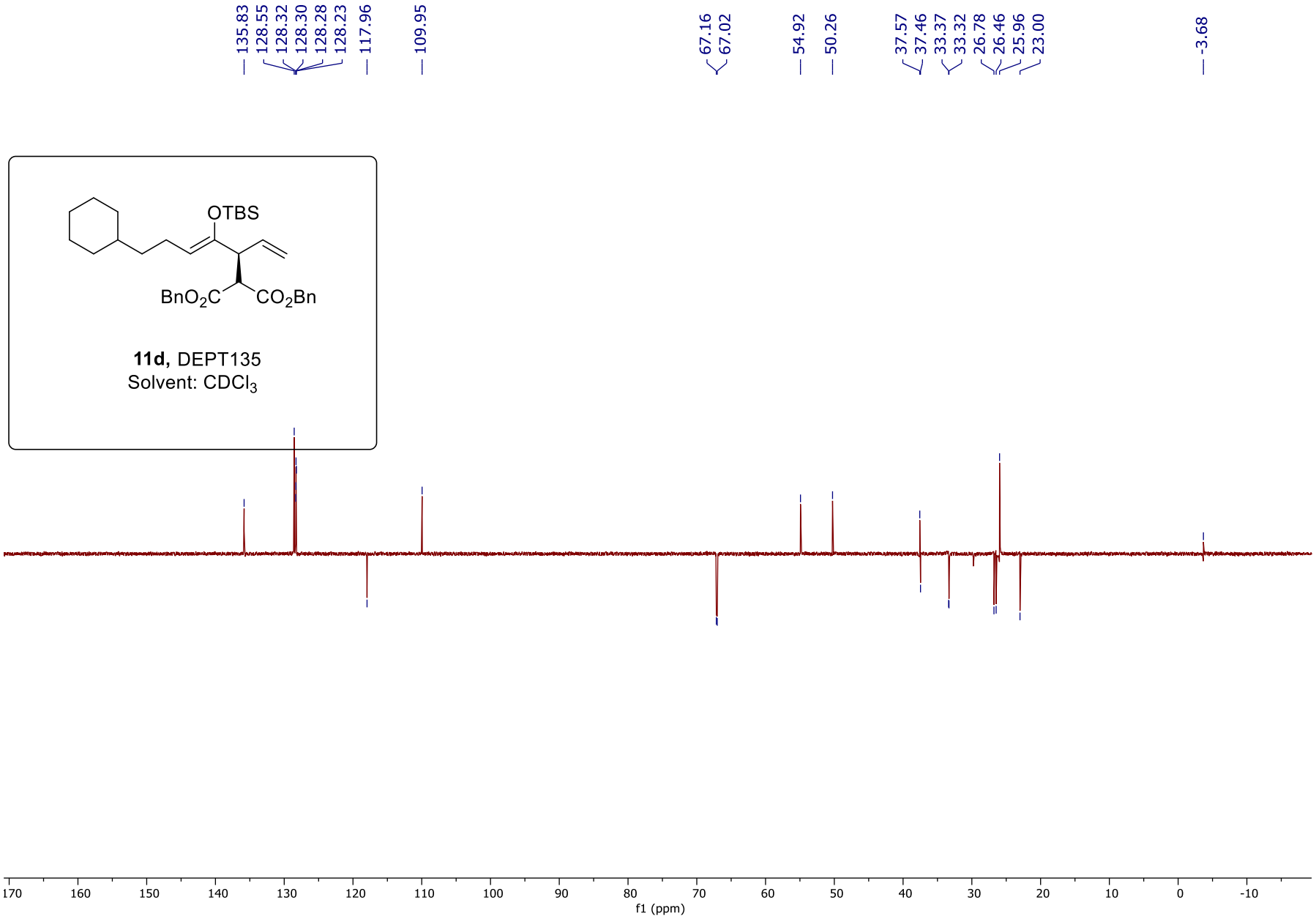
128.22
117.95
109.95
77.31
77.10
76.89
67.15
67.02
54.91
50.25
37.57
37.46
33.37
33.32
26.78
26.46
25.96
22.99
18.43
-3.68
-3.86
OTBS
BnO2C
CO2Bn
11d, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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128.30
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128.23
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109.95
67.16
67.02
54.92
50.26
37.57
37.46
33.37
33.32
26.78
26.46
25.96
23.00
-3.68
OTBS
BnO2C
CO2Bn
11d, DEPT135
Solvent: CDCl3
170
160
150
140
130
120
110
100
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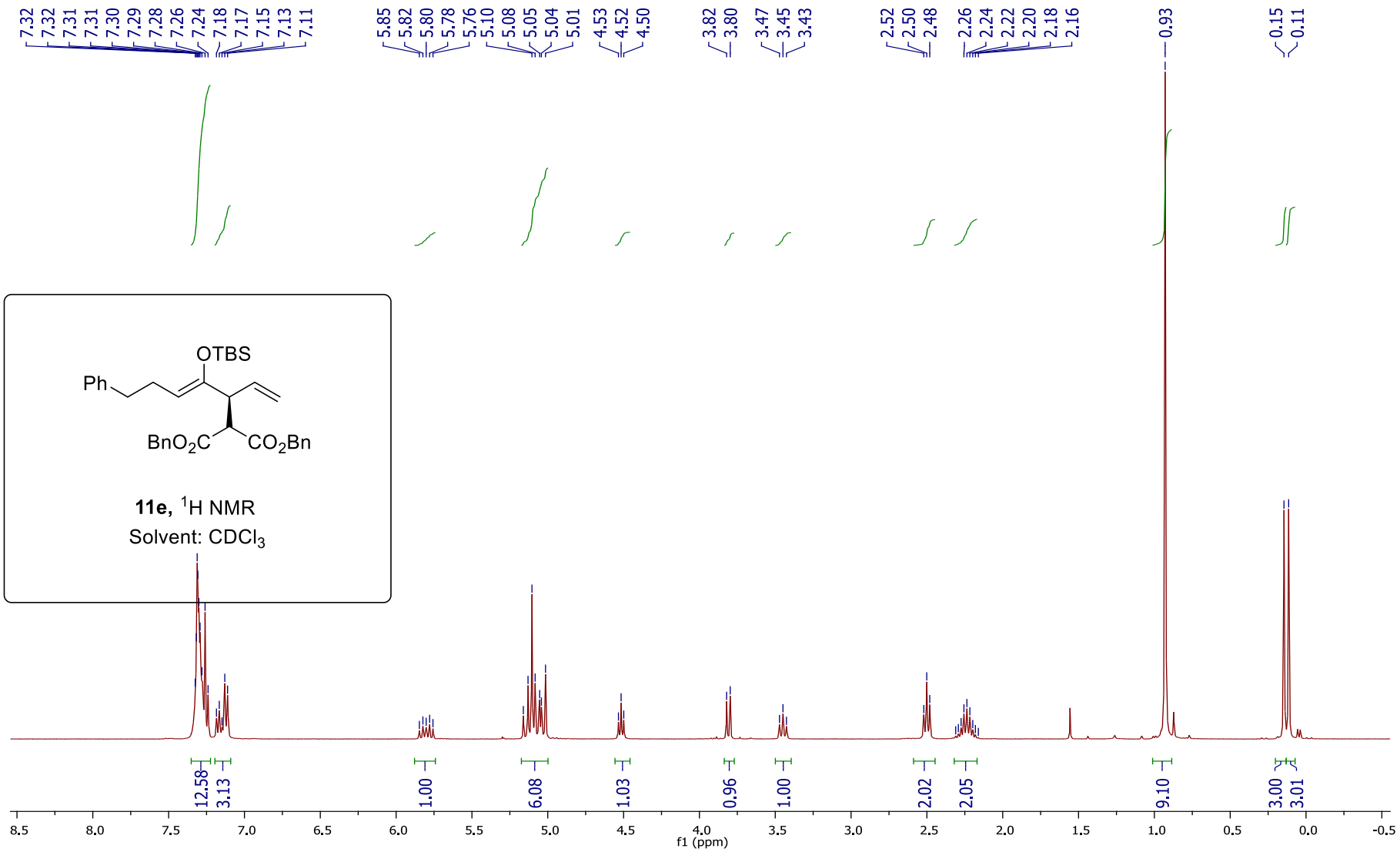
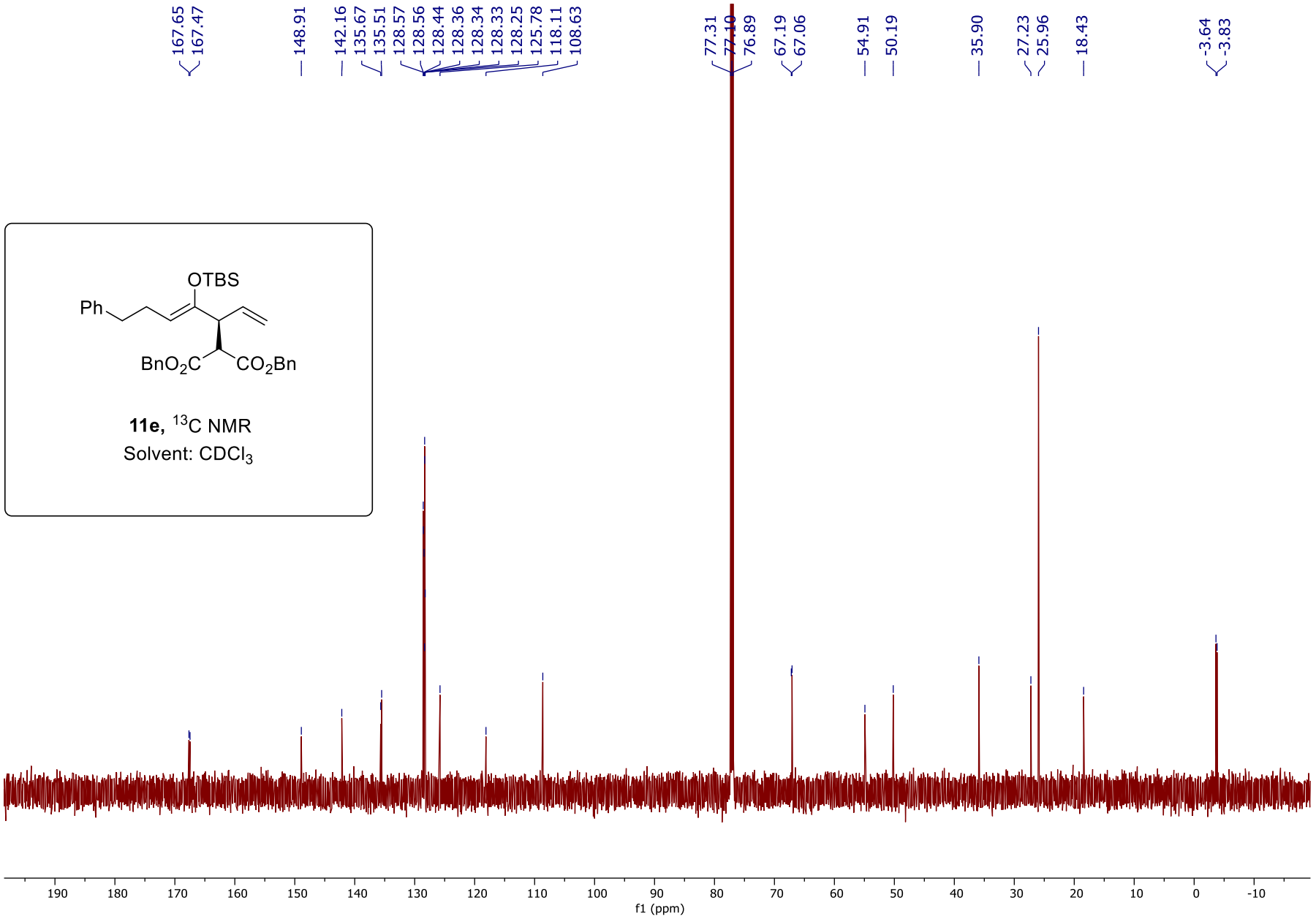
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
Ph
BnO2C
CO2Bn
11e, 1H NMR
Solvent: CDCl3
f1 (ppm)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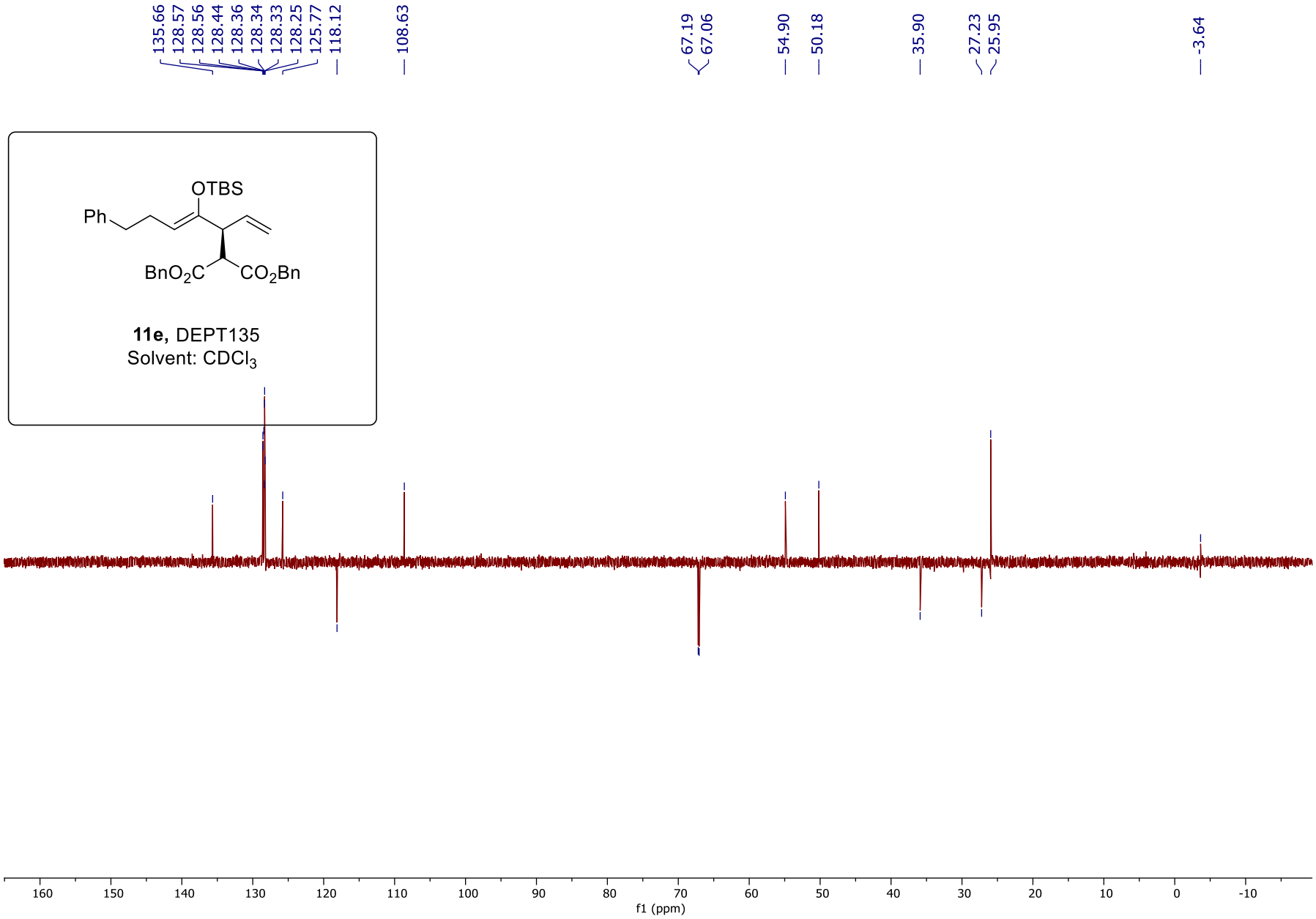
128.25
125.78
118.11
108.63
77.31
77.10
76.89
67.19
67.06
54.91
50.19
35.90
27.23
25.96
18.43
-3.64
-3.83
OTBS
Ph
BnO2C
CO2Bn
11e, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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128.33
128.25
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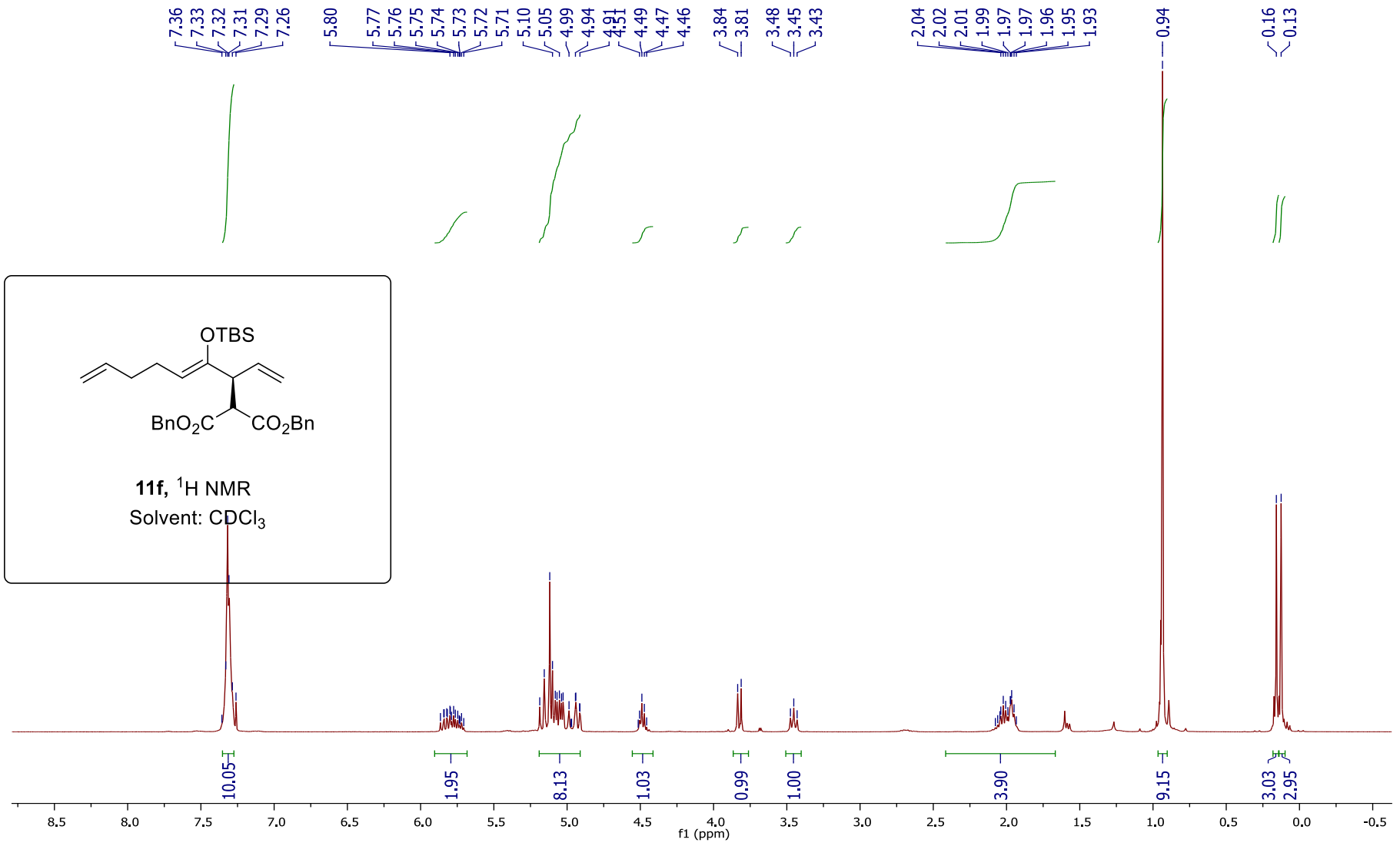
108.63
67.19
67.06
54.90
50.18
35.90
27.23
25.95
-3.64
OTBS
Ph
BnO2C
CO2Bn
11e, DEPT135
Solvent: CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.77
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5.74
5.73
5.72
5.71
5.10
5.05
4.99
4.94
4.91
4.51
4.49
4.47
4.46
3.84
3.81
3.48
3.45
3.43
2.04
2.02
2.01
1.99
1.97
1.97
1.96
1.95
1.93
0.94
0.16
0.13
OTBS
BnO2C
CO2Bn
11f, 1H NMR
Solvent: CDCl3
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8.13
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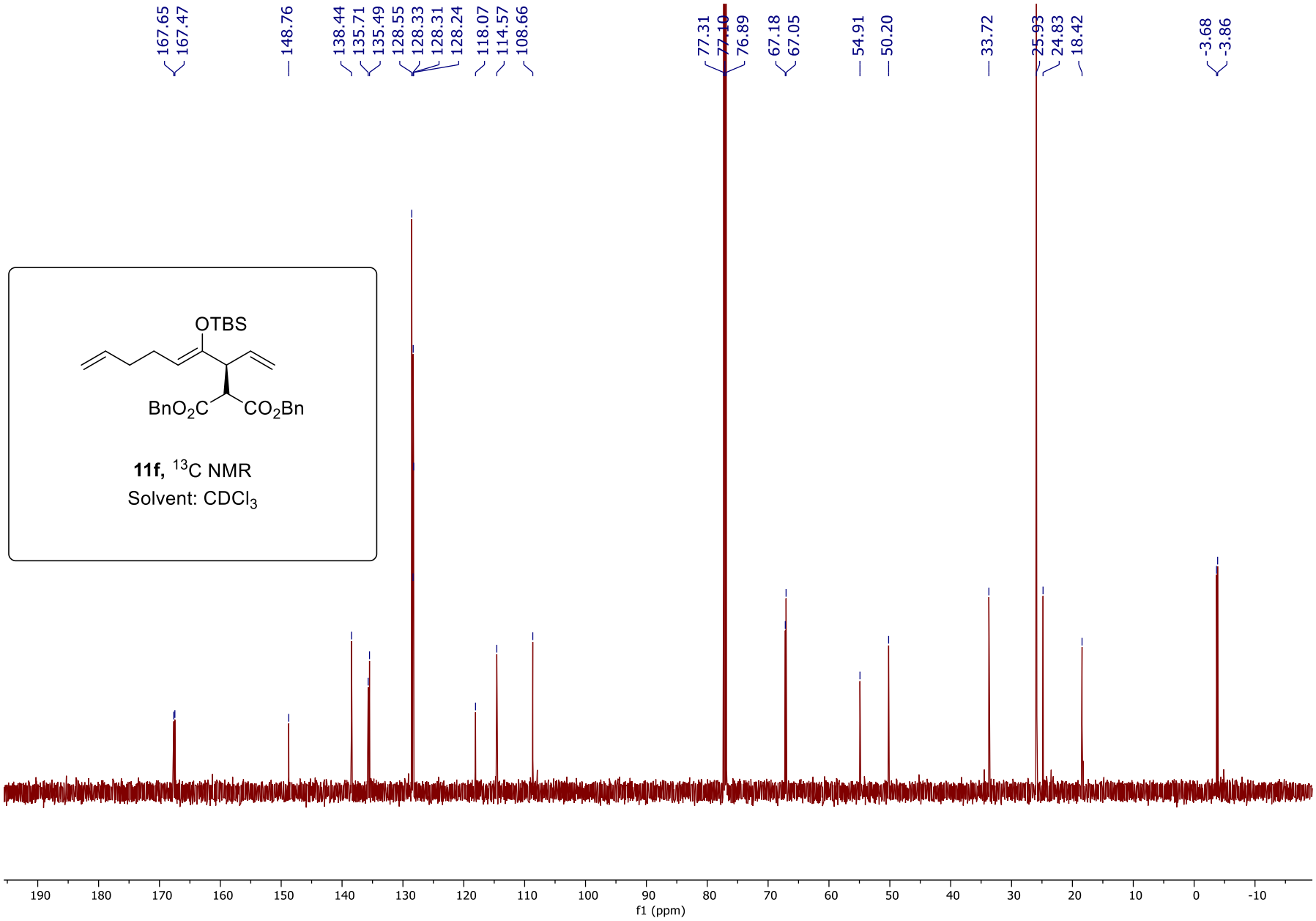
0.99
1.00
3.90
9.15
3.03
2.95
f1 (ppm)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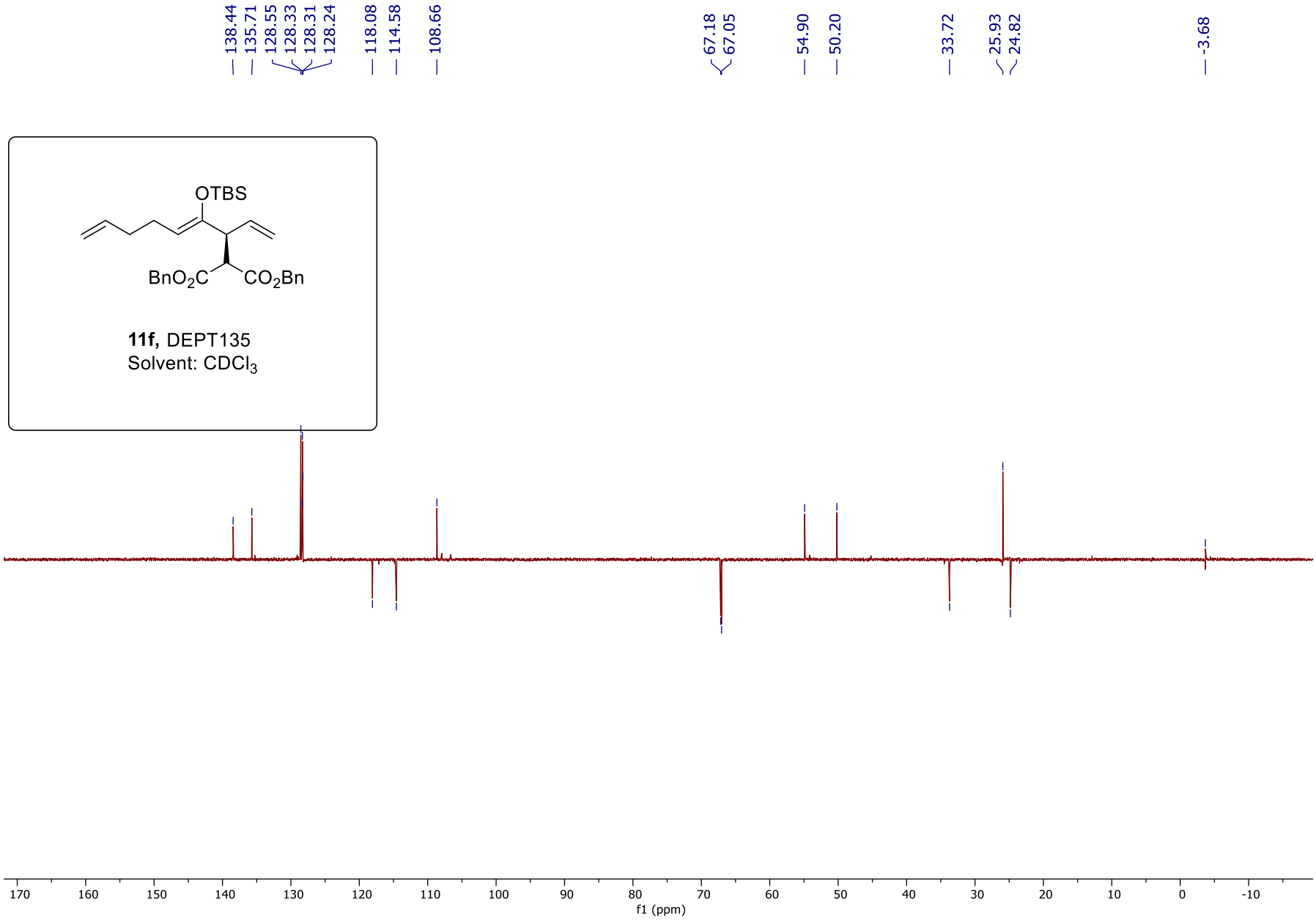
108.66
77.31
77.10
76.89
67.18
67.05
54.91
50.20
33.72
25.93
24.83
18.42
-3.68
-3.86
OTBS
BnO2C
CO2Bn
11f, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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128.33
128.31
128.24
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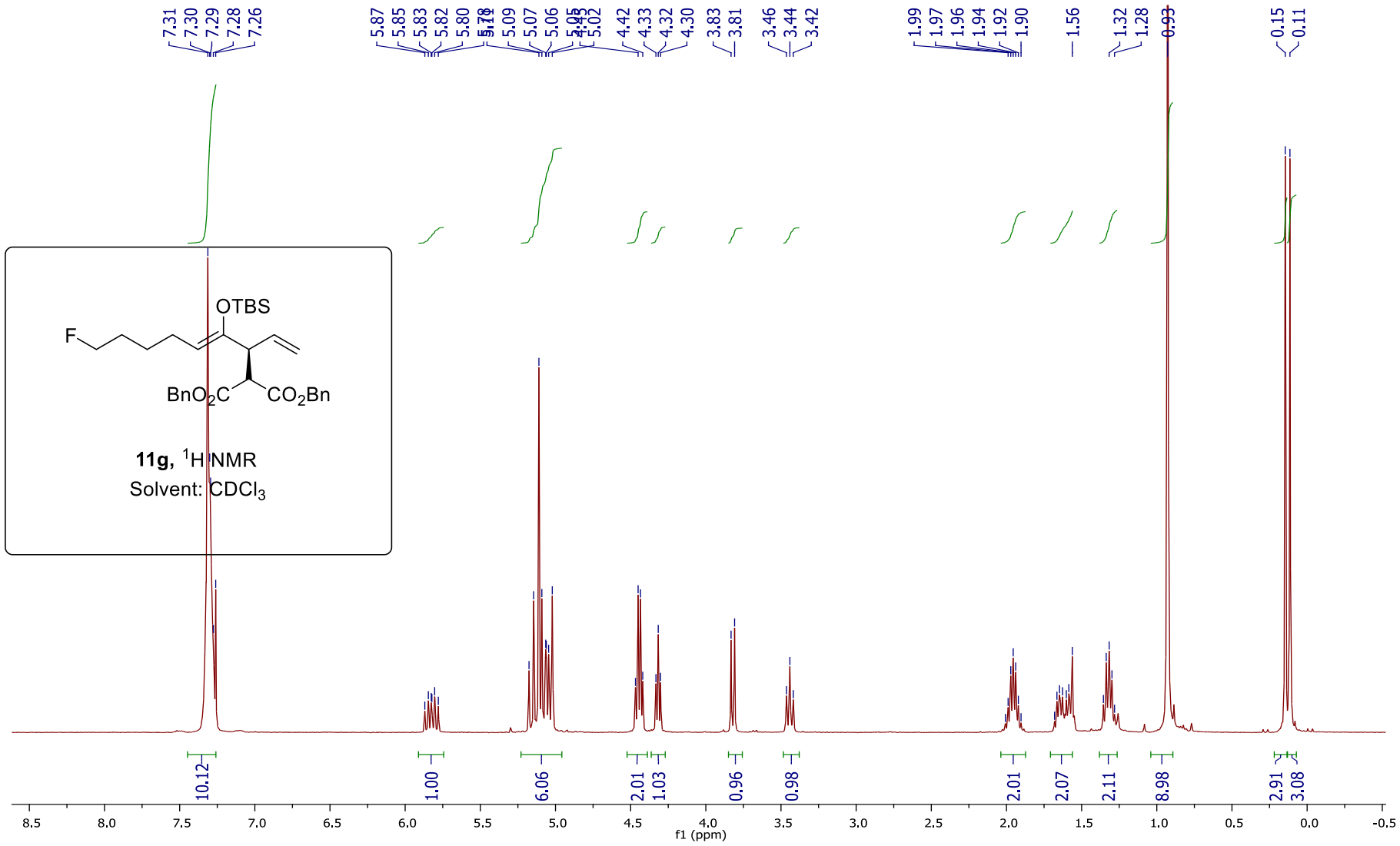
67.18
67.05
54.90
50.20
33.72
25.93
24.82
-3.68
OTBS
BnO2C
CO2Bn
11f, DEPT135
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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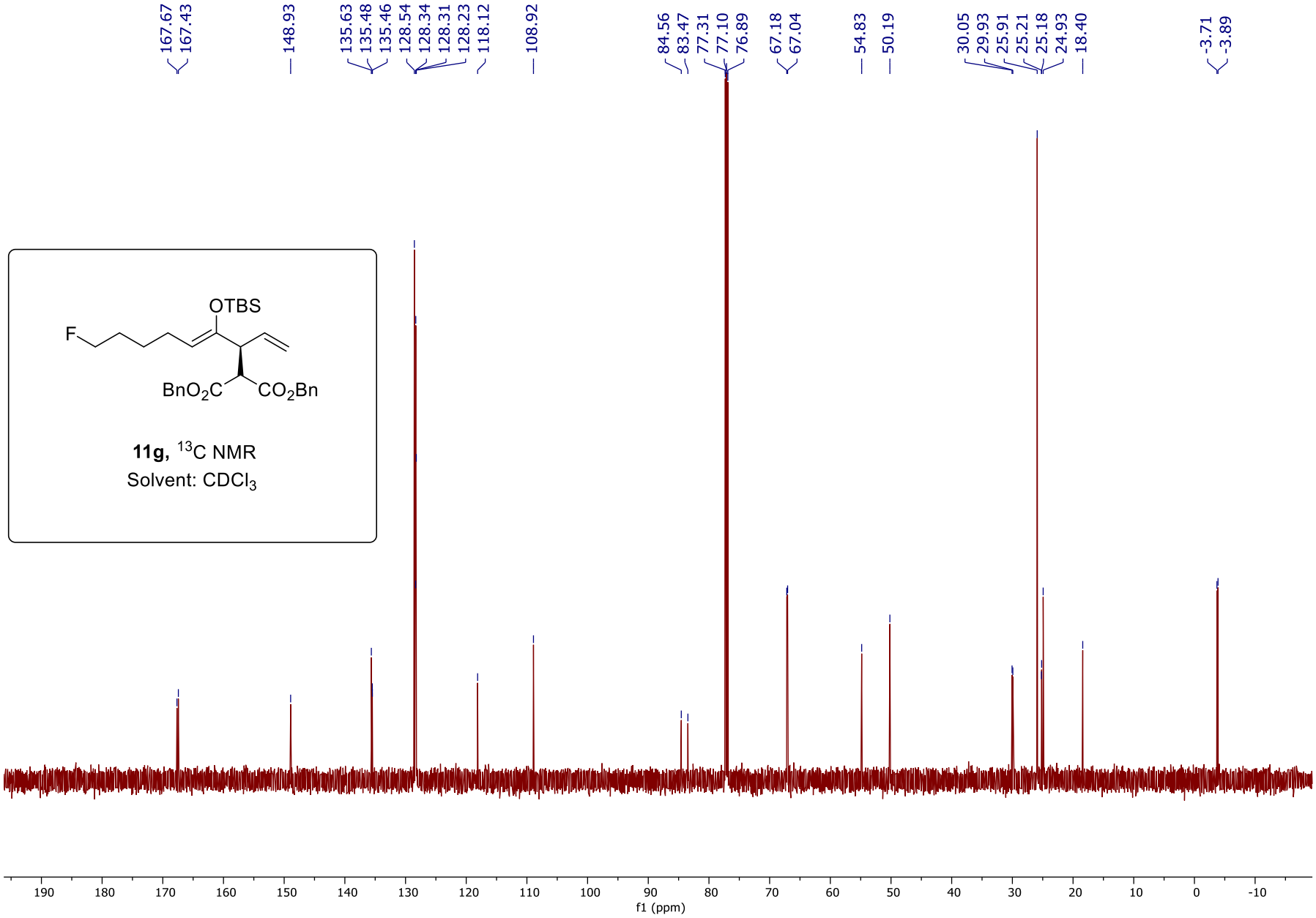
F
BnO2C
CO2Bn
11g, 1H NMR
Solvent: CDCl3
f1 (ppm)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135.46
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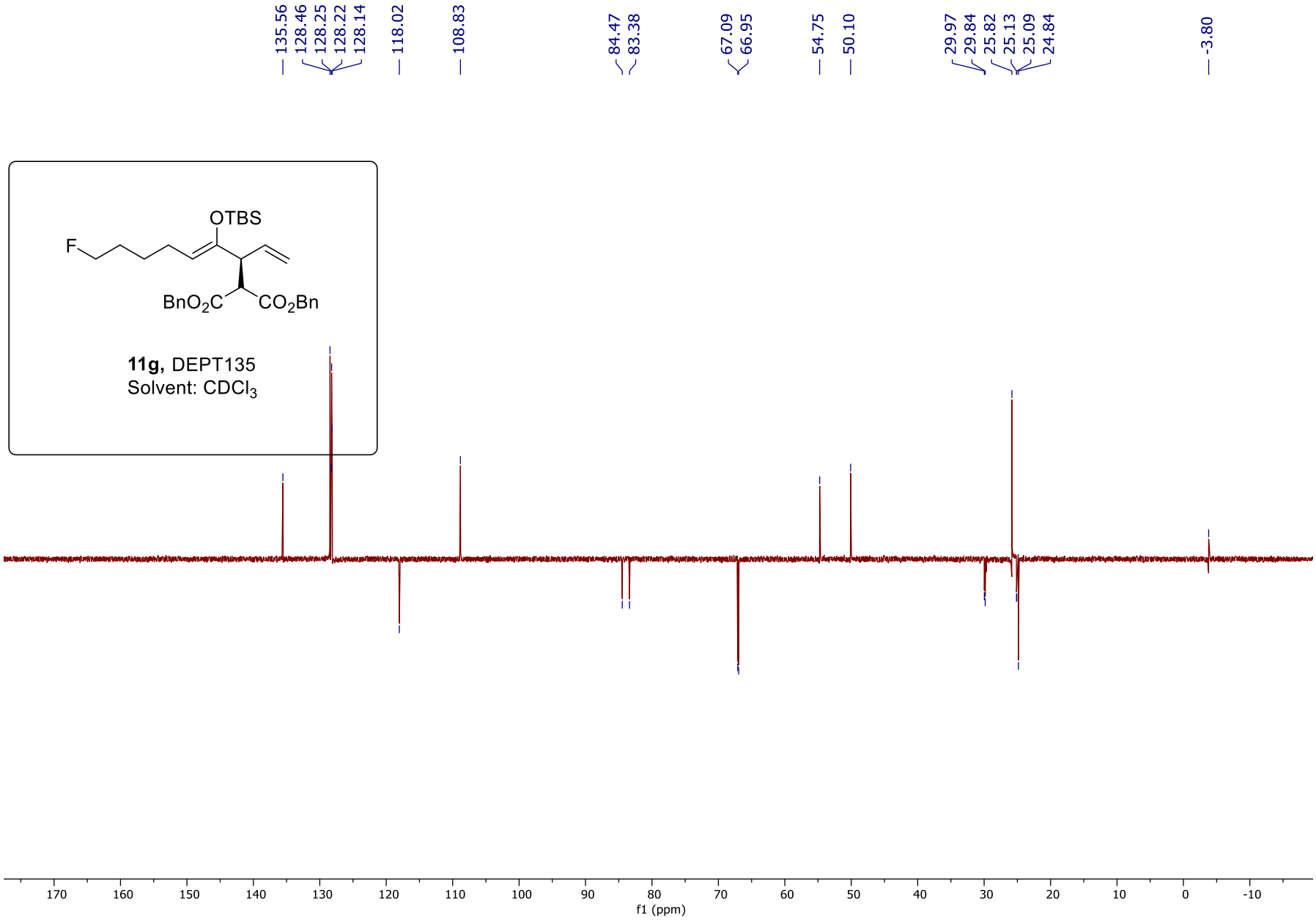
128.34
128.31
128.23
118.12
108.92
84.56
83.47
77.31
77.10
76.89
67.18
67.04
54.83
50.19
30.05
29.93
25.91
25.21
25.18
24.93
18.40
-3.71
-3.89
OTBS
F
BnO2C
CO2Bn
11g, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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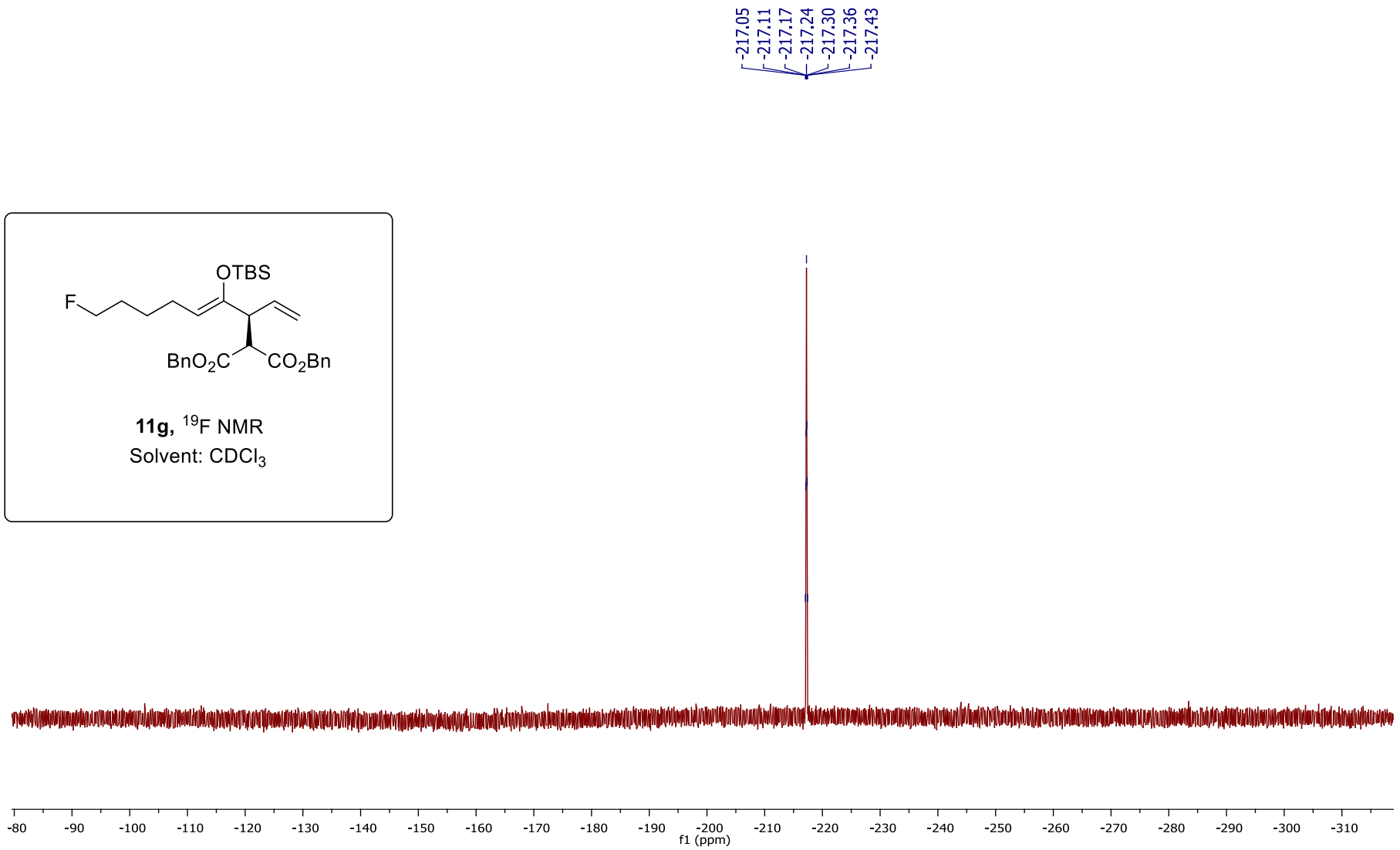
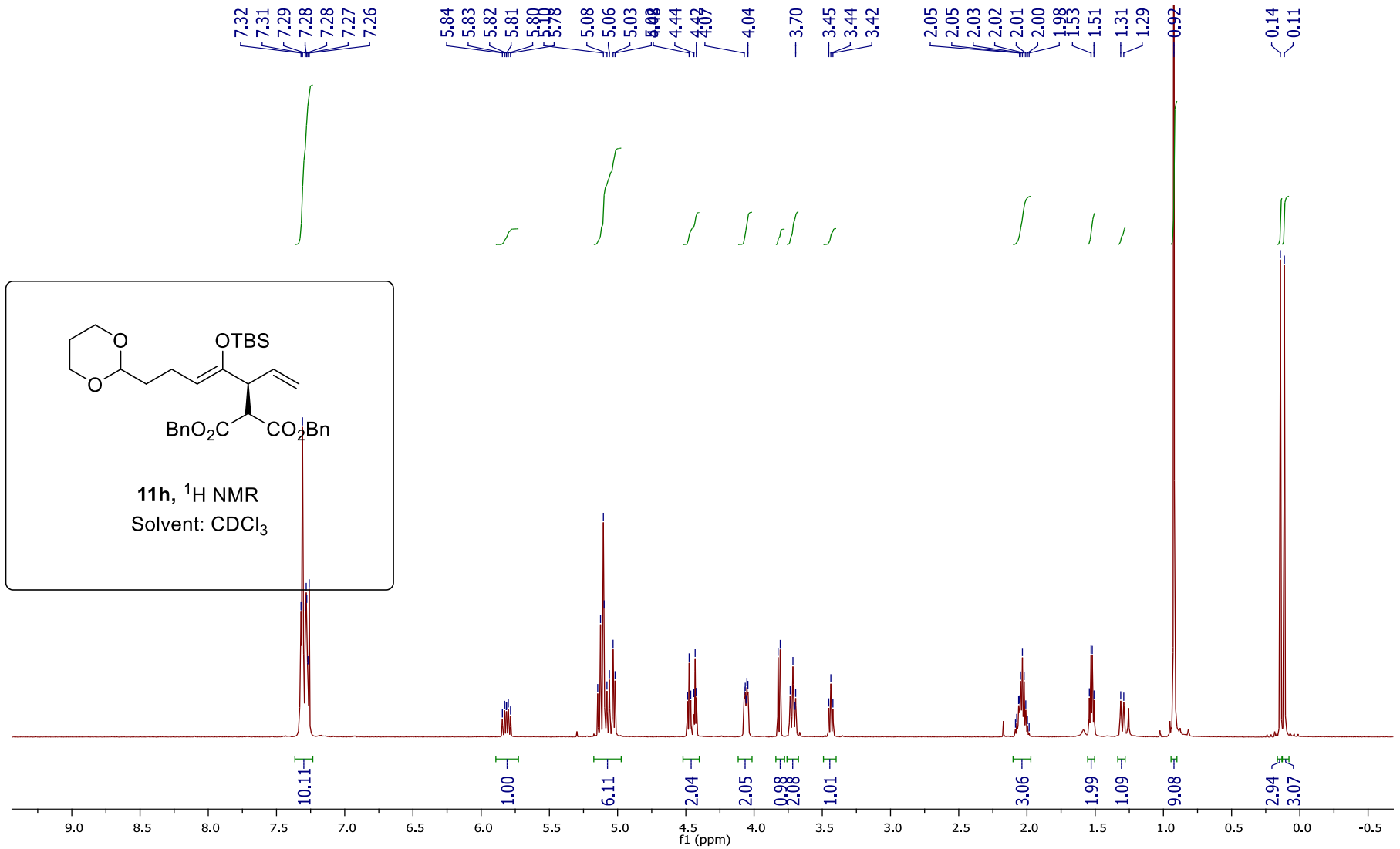
29.97
29.84
25.82
25.13
25.09
24.84
-3.80
OTBS
F
BnO2C
CO2Bn
11g, DEPT135
Solvent: CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-217.05
-217.11
-217.17
-217.24
-217.30
-217.36
-217.43
OTBS
F
BnO2C
CO2Bn
11g, 19F NMR
Solvent: CDCl3
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
-260
-270
-280
-290
-300
-310
f1 (ppm)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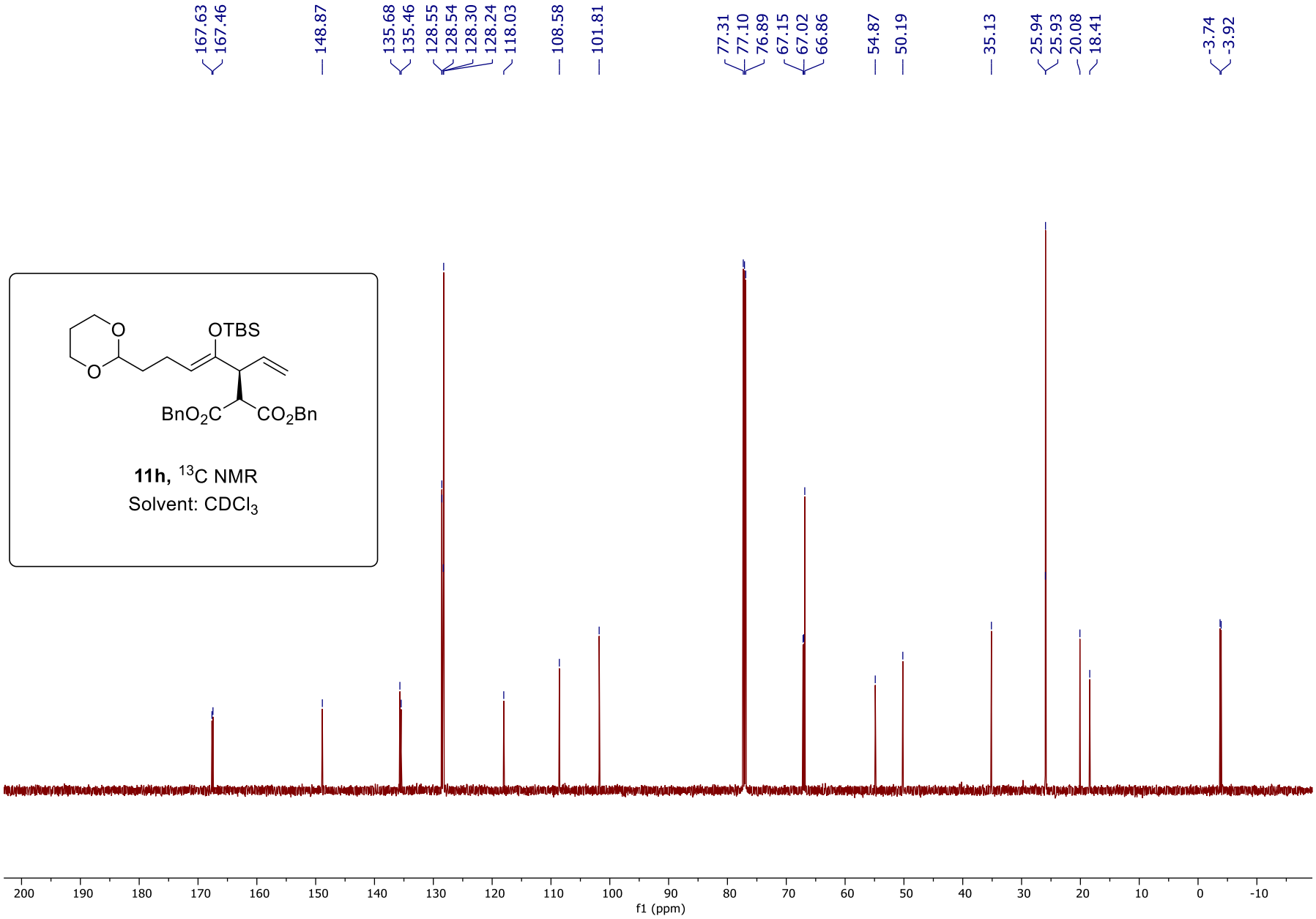
BnO2C
CO2Bn
11h, 1H NMR
Solvent: CDCl3
f1 (ppm)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135.68
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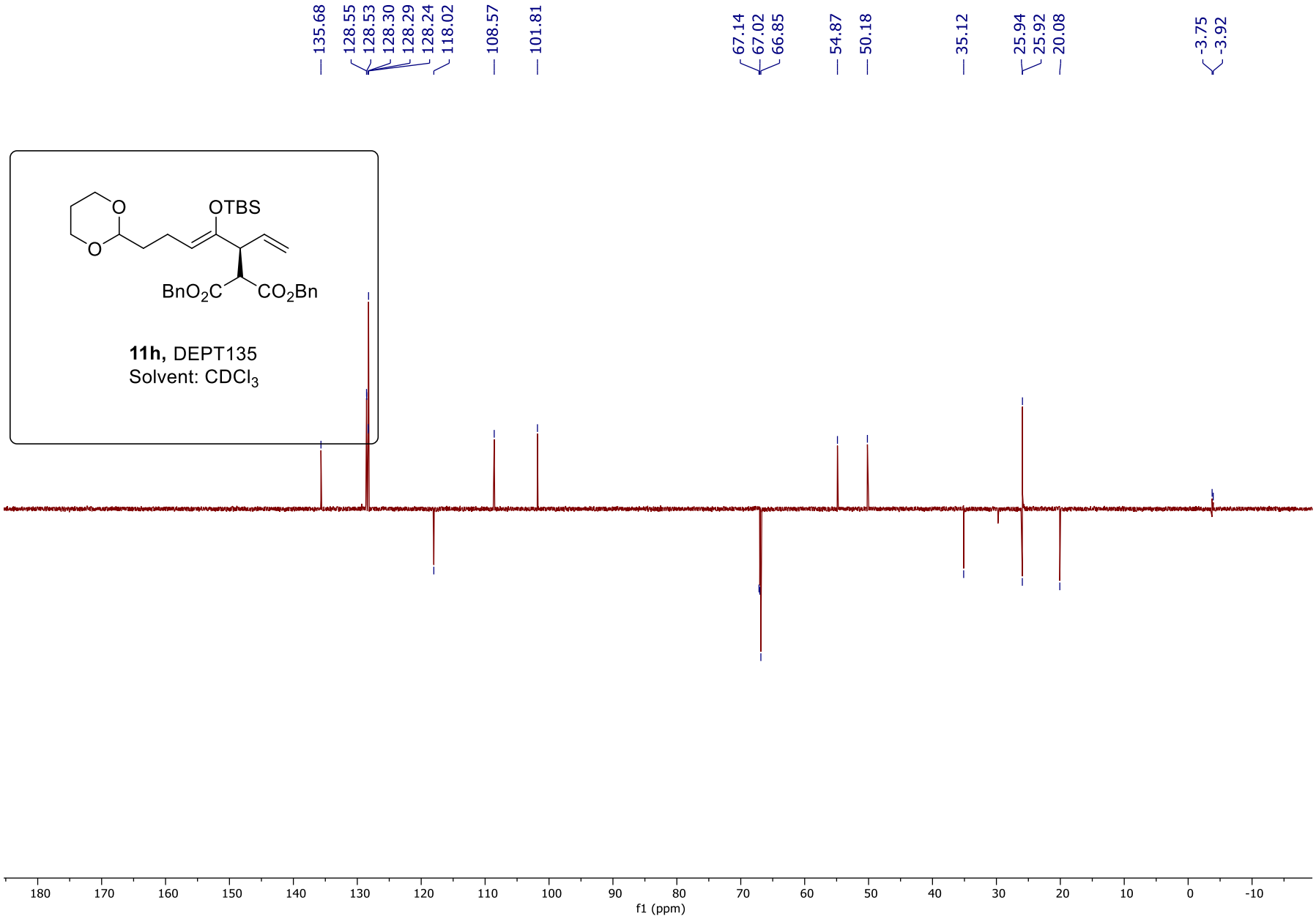
128.55
128.54
128.30
128.24
118.03
108.58
101.81
77.31
77.10
76.89
67.15
67.02
66.86
54.87
50.19
35.13
25.94
25.93
20.08
18.41
-3.74
-3.92
OTBS
O
O
BnO2C
CO2Bn
11h, 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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128.53
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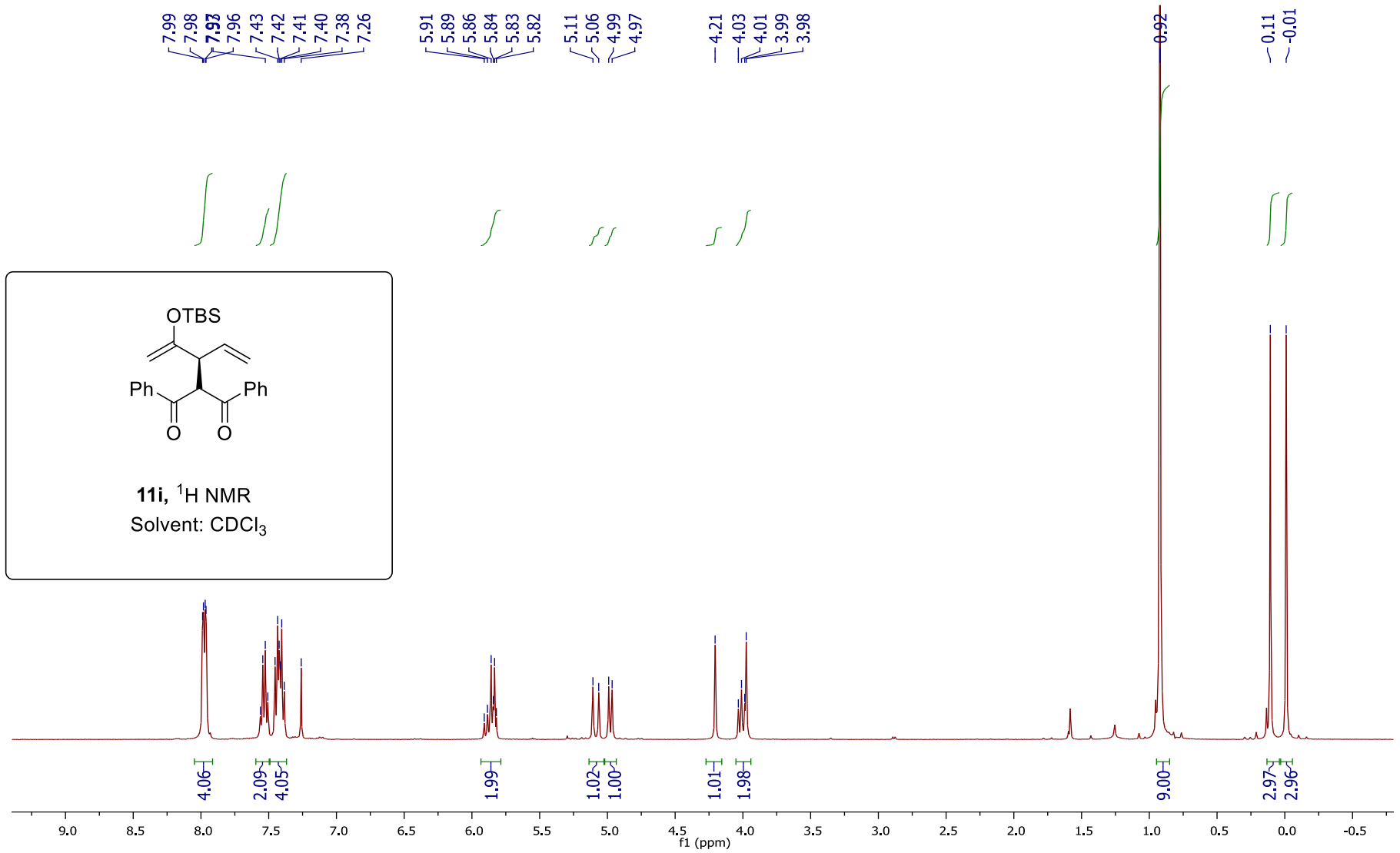
128.24
118.02
108.57
101.81
67.14
67.02
66.85
54.87
50.18
35.12
25.94
25.92
20.08
-3.75
-3.92
OTBS
O
O
BnO2C
CO2Bn
11h, DEPT135
Solvent: CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.98
7.96
7.43
7.42
7.41
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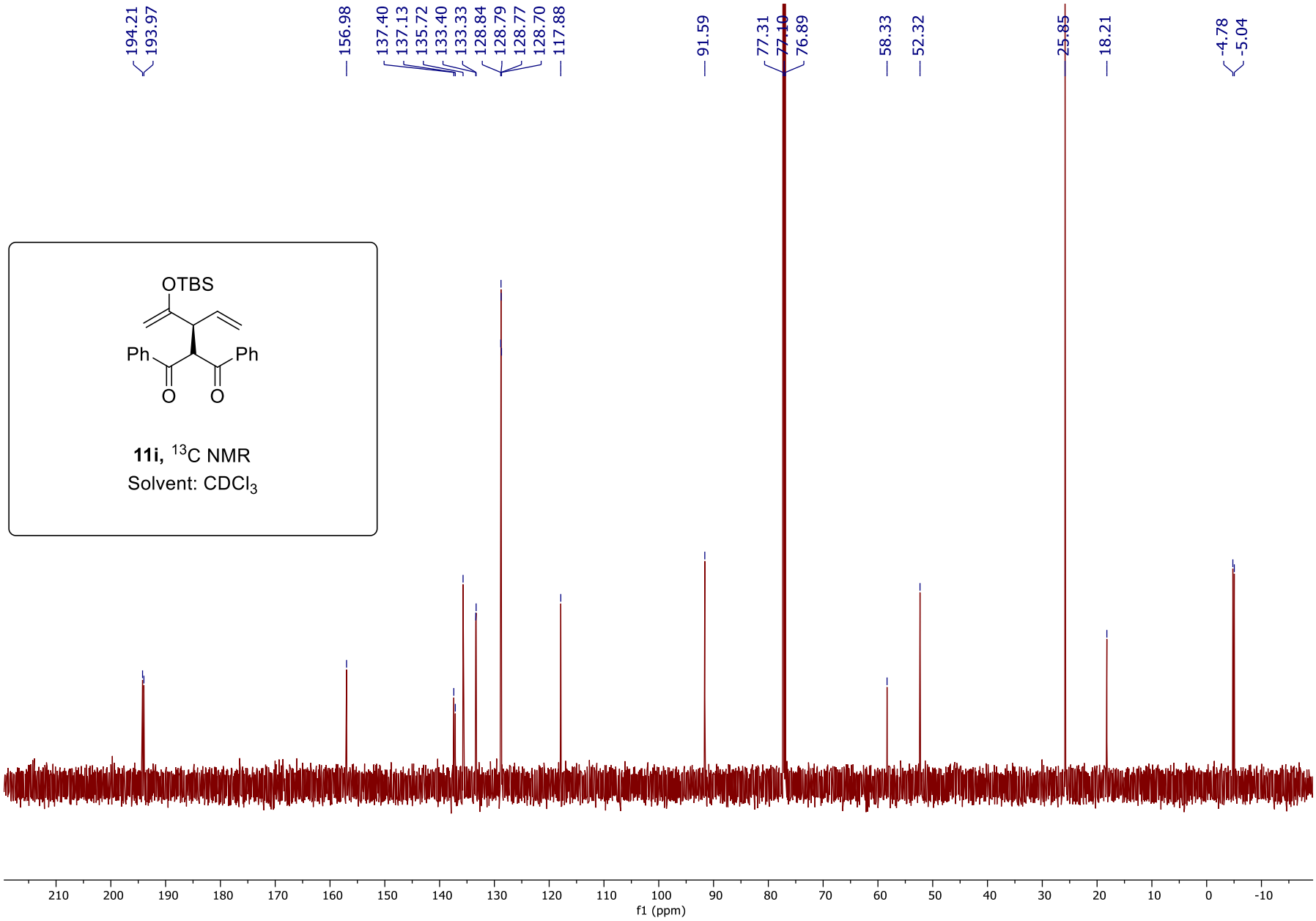
7.38
7.26
5.91
5.89
5.86
5.84
5.83
5.82
5.11
5.06
4.99
4.97
4.21
4.03
4.01
3.99
3.98
0.92
0.11
-0.01
OTBS
Ph
Ph
O
O
11i, 1H NMR
Solvent: CDCl3
4.06
2.09
4.05
1.99
1.02
1.00
1.01
1.98
9.00
2.97
2.96
f1 (ppm)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193.97
156.98
137.40
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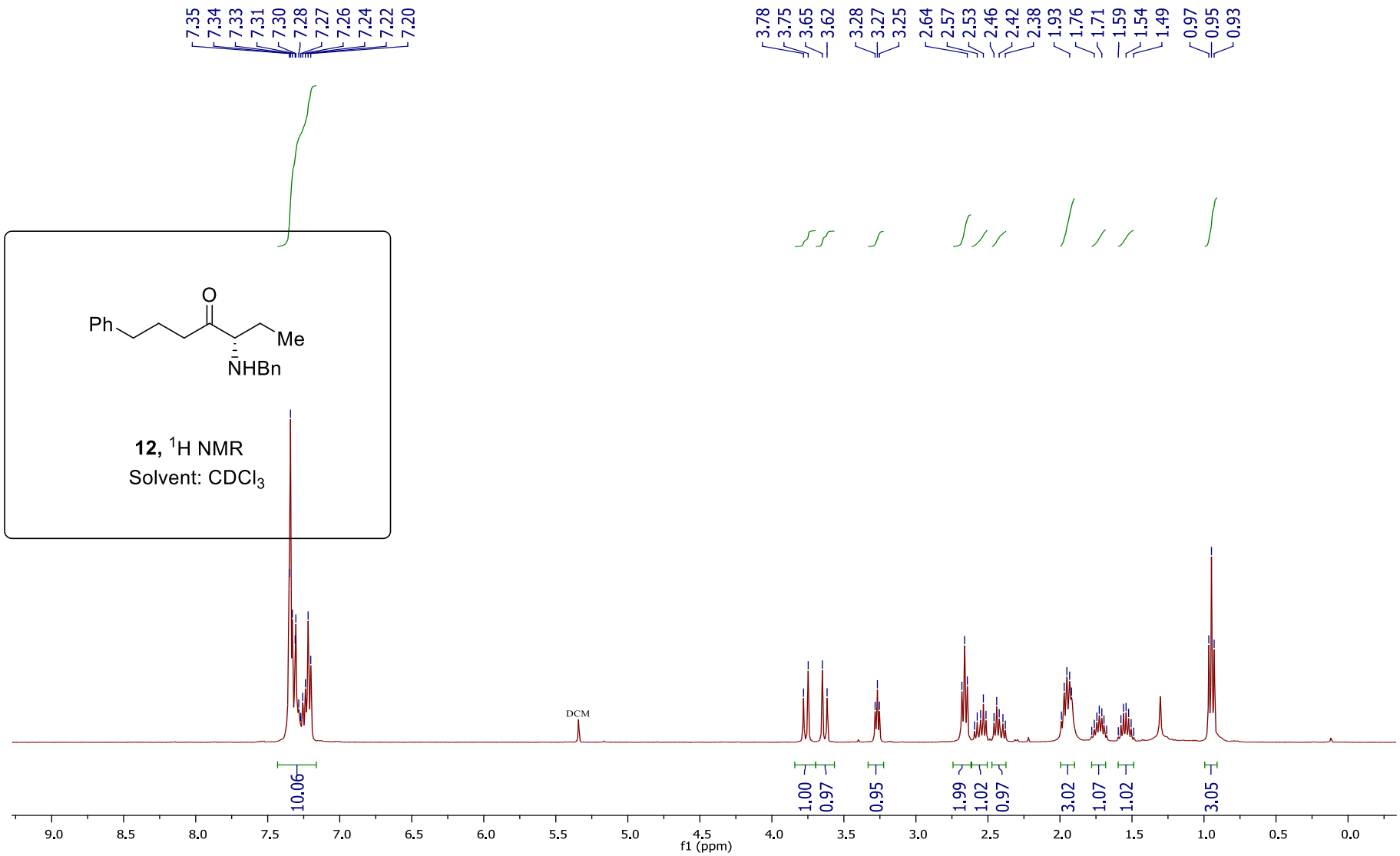
135.72
133.40
133.33
128.84
128.79
128.77
128.70
117.88
91.59
77.31
77.10
76.89
58.33
52.32
25.85
18.21
-4.78
-5.04
OTBS
Ph
Ph
O
O
11i, 13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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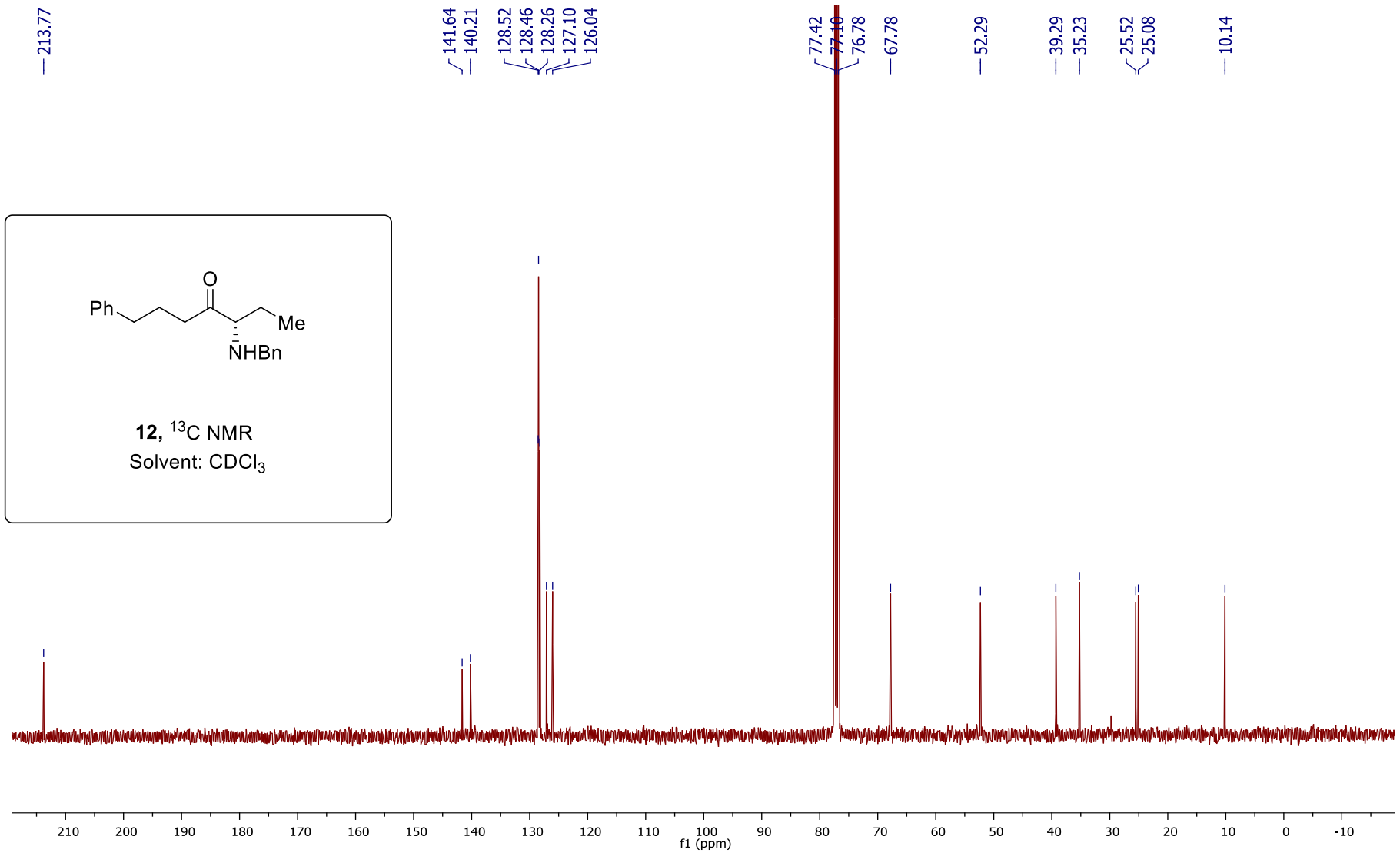
7.34
7.33
7.31
7.30
7.28
7.27
7.26
7.24
7.22
7.20
3.78
3.75
3.65
3.62
3.28
3.27
3.25
2.64
2.57
2.53
2.46
2.42
2.38
1.93
1.76
1.71
1.59
1.54
1.49
0.97
0.95
0.93
O
Ph
Me
NHBn
12, 1H NMR
Solvent: CDCl3
DCM
10.06
1.00
0.97
0.95
1.99
1.02
0.97
3.02
1.07
1.02
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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140.21
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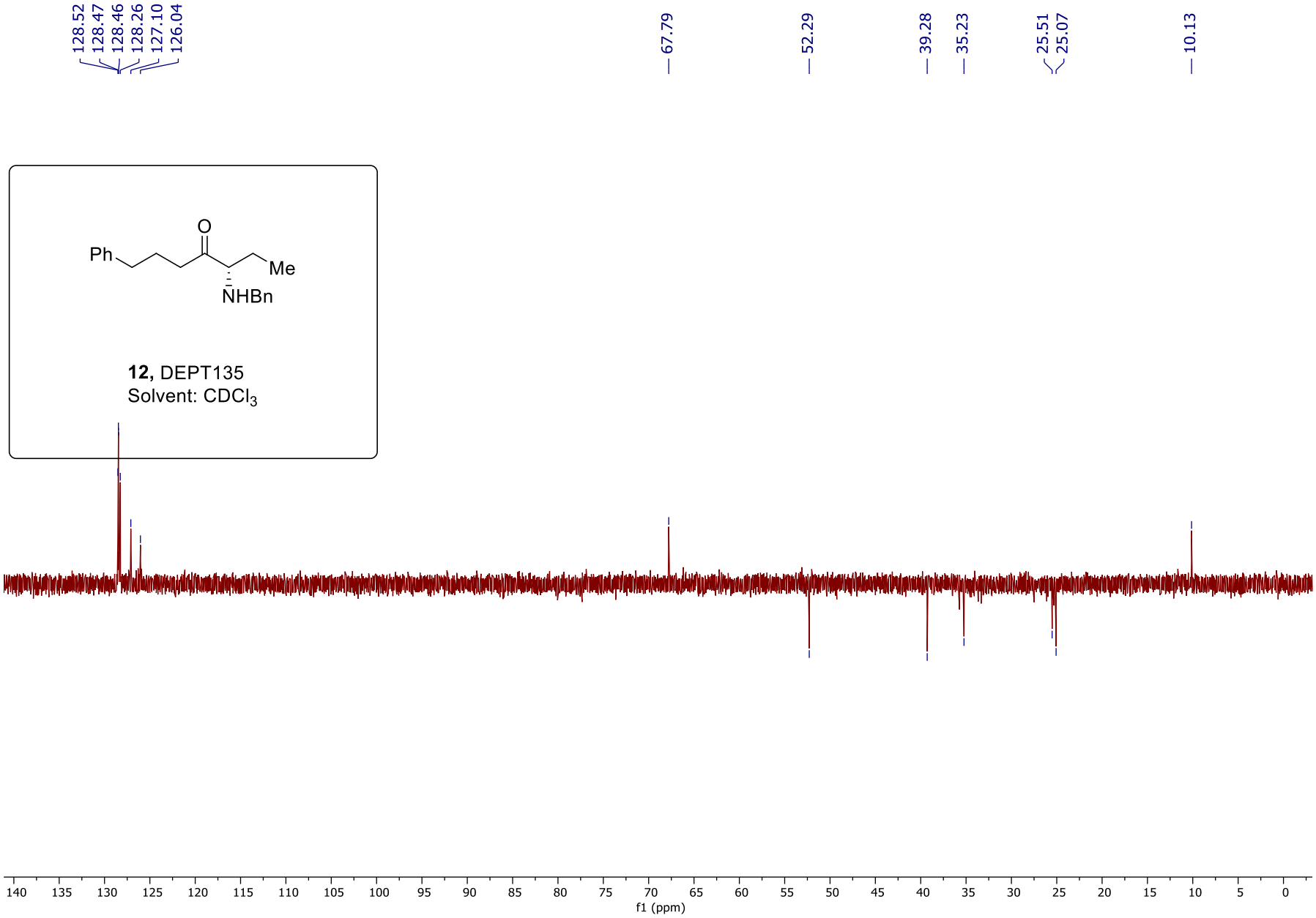
128.26
127.10
126.04
77.42
77.10
76.78
67.78
52.29
39.29
35.23
25.52
25.08
10.14
O
Ph
Me
NHBn
12, 13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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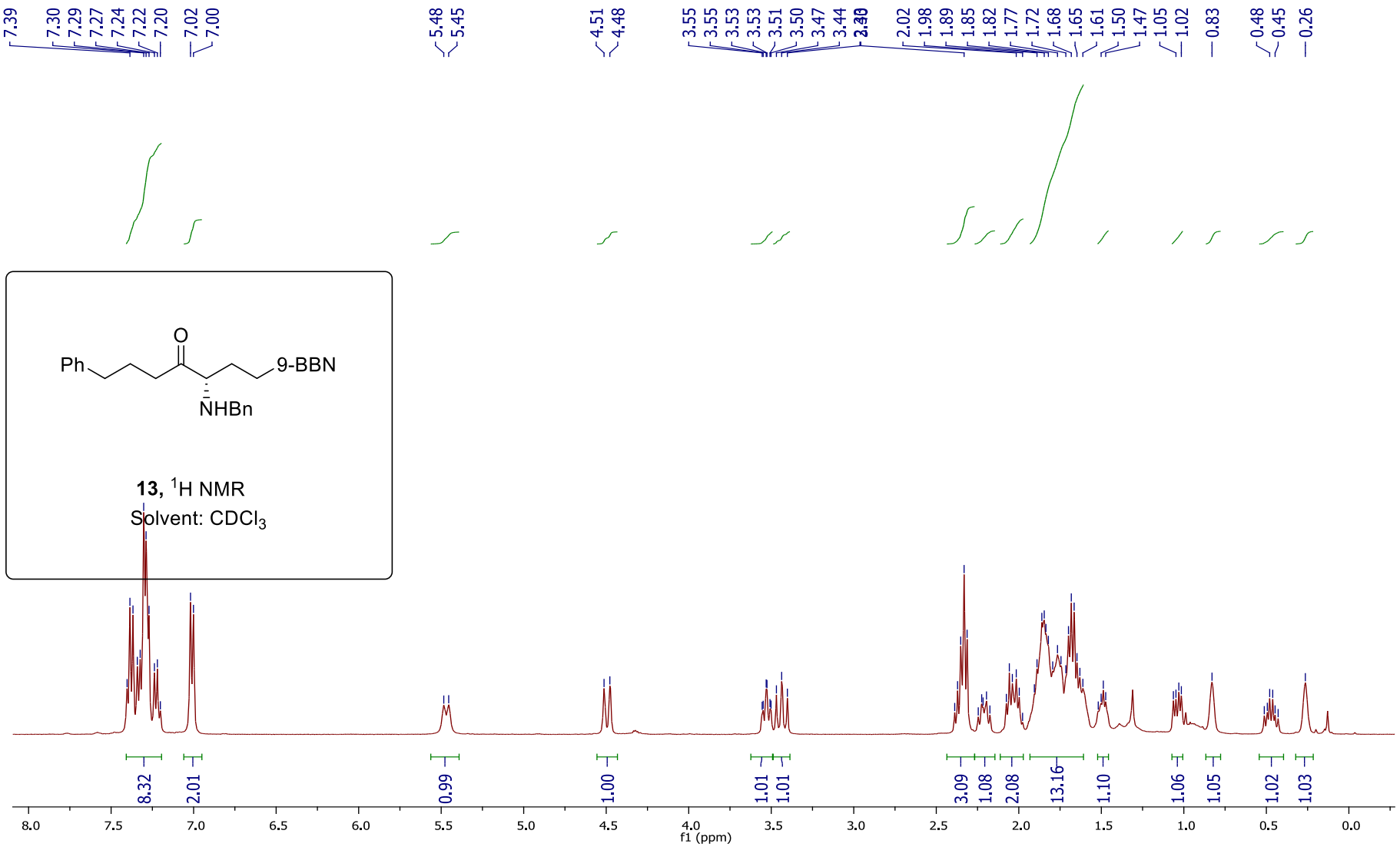
128.47
128.46
128.26
127.10
126.04
67.79
52.29
39.28
35.23
25.51
25.07
10.13
O
Ph
Me
NHBn
12, DEPT135
Solvent: CDCl3
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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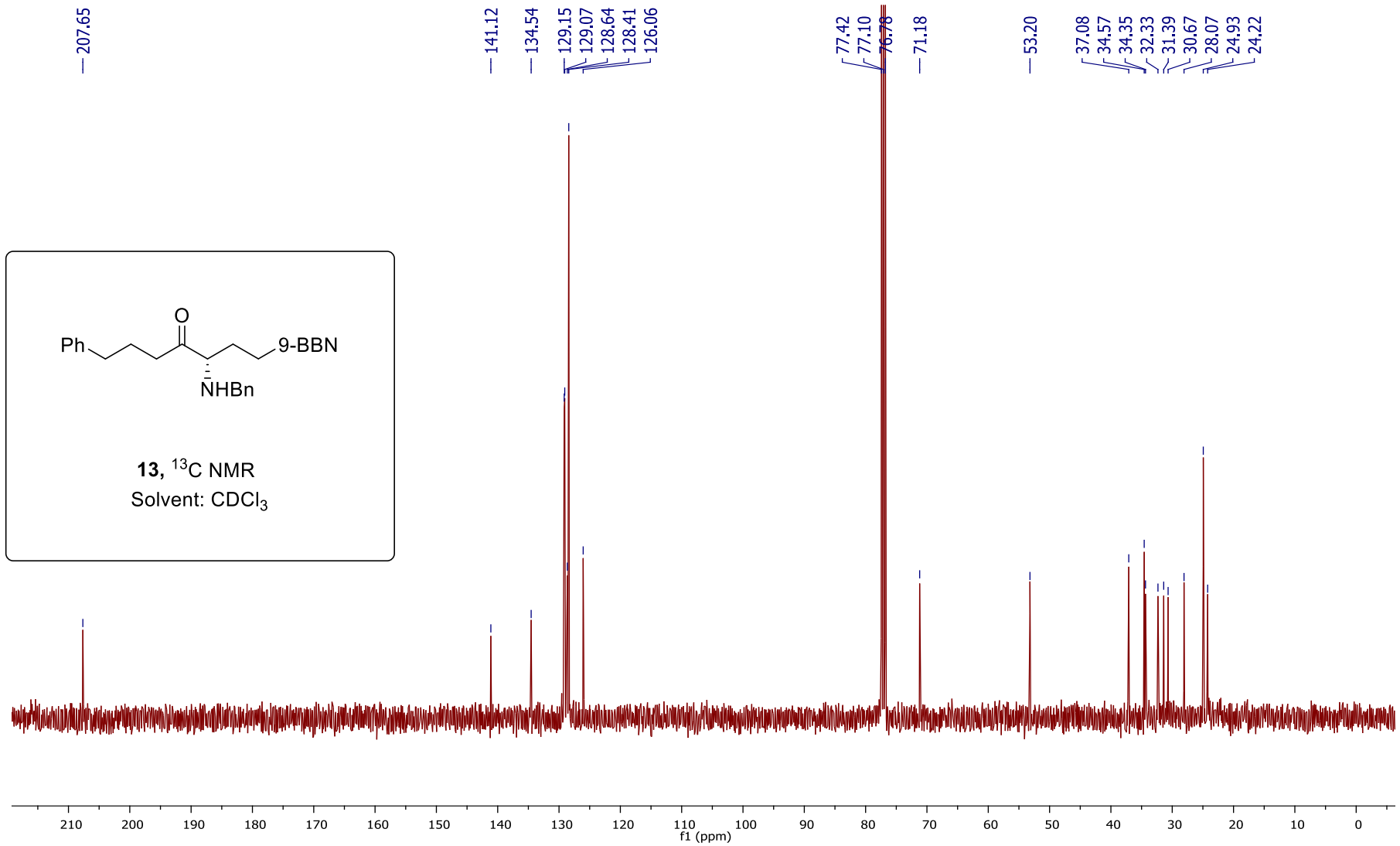
7.30
7.29
7.27
7.24
7.22
7.20
7.02
7.00
5.48
5.45
4.51
4.48
3.55
3.55
3.53
3.53
3.51
3.50
3.47
3.44
2.02
1.98
1.89
1.85
1.82
1.77
1.72
1.68
1.65
1.61
1.50
1.47
1.05
1.02
0.83
0.48
0.45
0.26
O
Ph
9-BBN
NHBn
13, 1H NMR
Solvent: CDCl3
8.32
2.01
0.99
1.00
1.01
1.01
3.09
1.08
2.08
13.16
1.10
1.06
1.05
1.02
1.03
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
f1 (ppm)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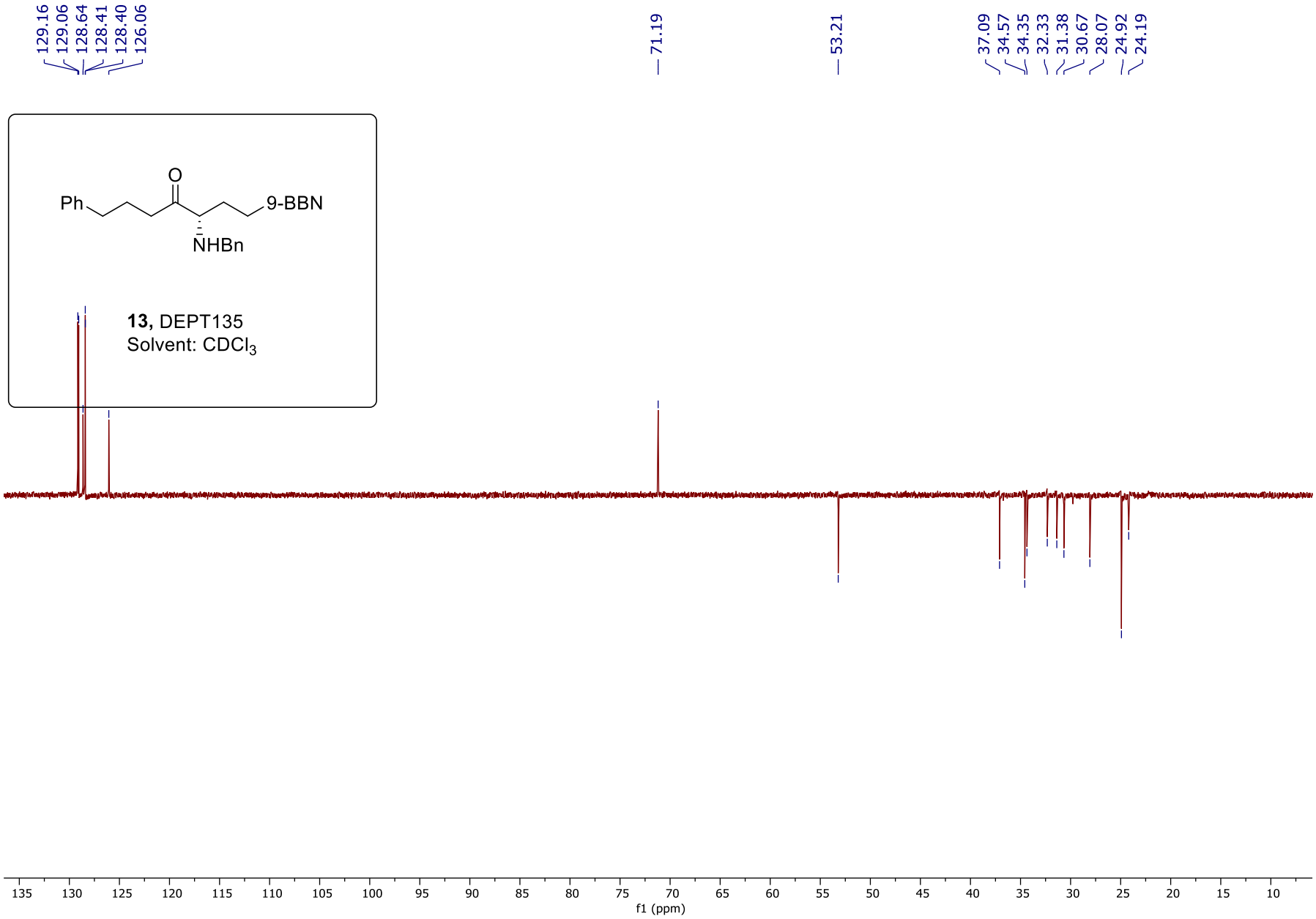
128.41
126.06
77.42
77.10
76.78
71.18
53.20
37.08
34.57
34.35
32.33
31.39
30.67
28.07
24.93
24.22
O
Ph
9-BBN
NHBn
13, 13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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129.06
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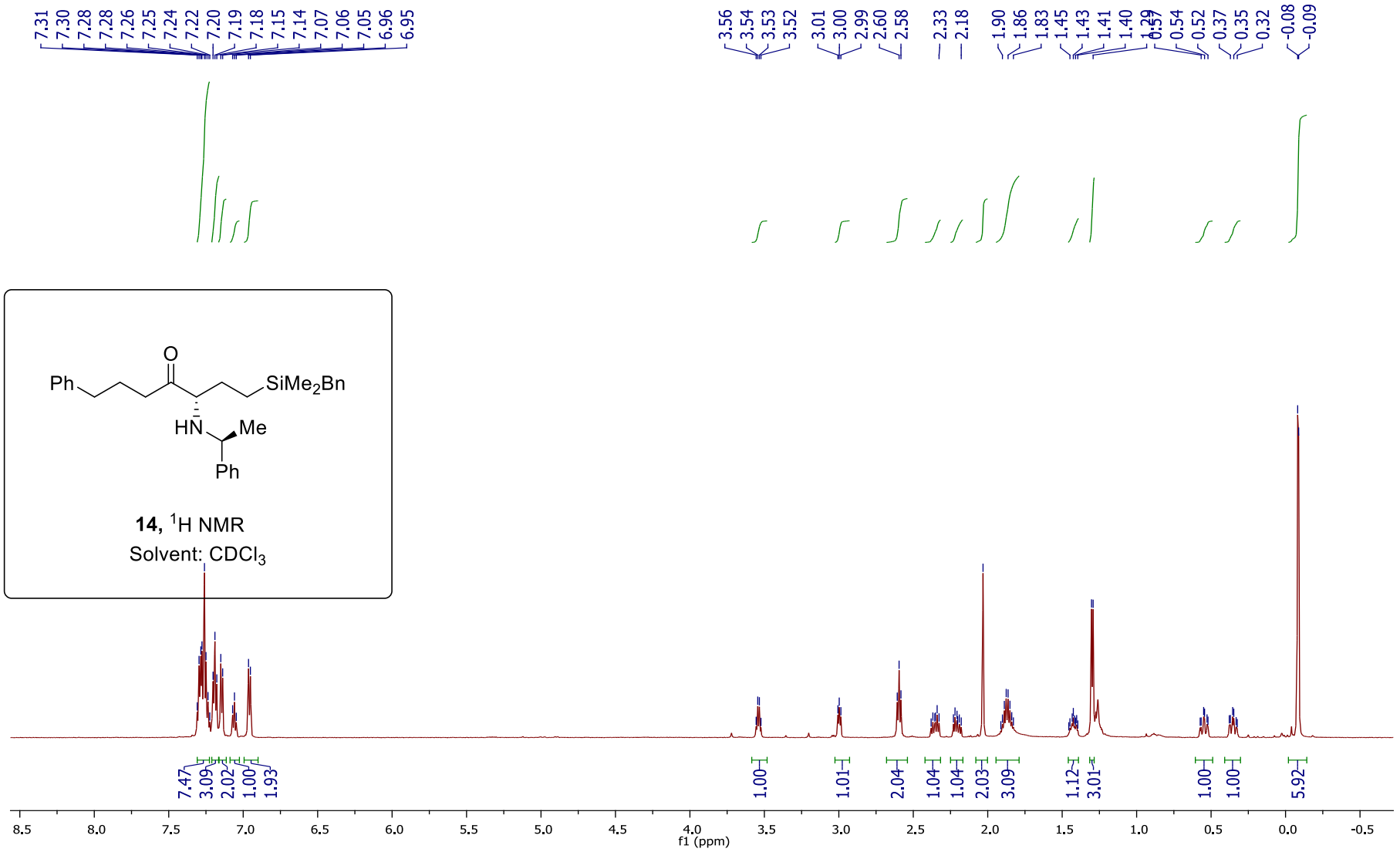
128.41
128.40
126.06
71.19
53.21
37.09
34.57
34.35
32.33
31.38
30.67
28.07
24.92
24.19
O
Ph
9-BBN
NHBn
13, DEPT135
Solvent: CDCl3
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)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7.25
7.24
7.22
7.20
7.19
7.18
7.15
7.14
7.07
7.06
7.05
6.96
6.95
3.56
3.54
3.53
3.52
3.01
3.00
2.99
2.60
2.58
2.33
2.18
1.90
1.86
1.83
1.45
1.43
1.41
1.40
0.54
0.52
0.37
0.35
0.32
-0.08
-0.09
O
Ph
SiMe2Bn
HN
Me
Ph
14, 1H NMR
Solvent: CDCl3
7.47
3.09
2.02
1.00
1.93
1.00
1.01
2.04
1.04
1.04
2.03
3.09
1.12
3.01
1.00
1.00
5.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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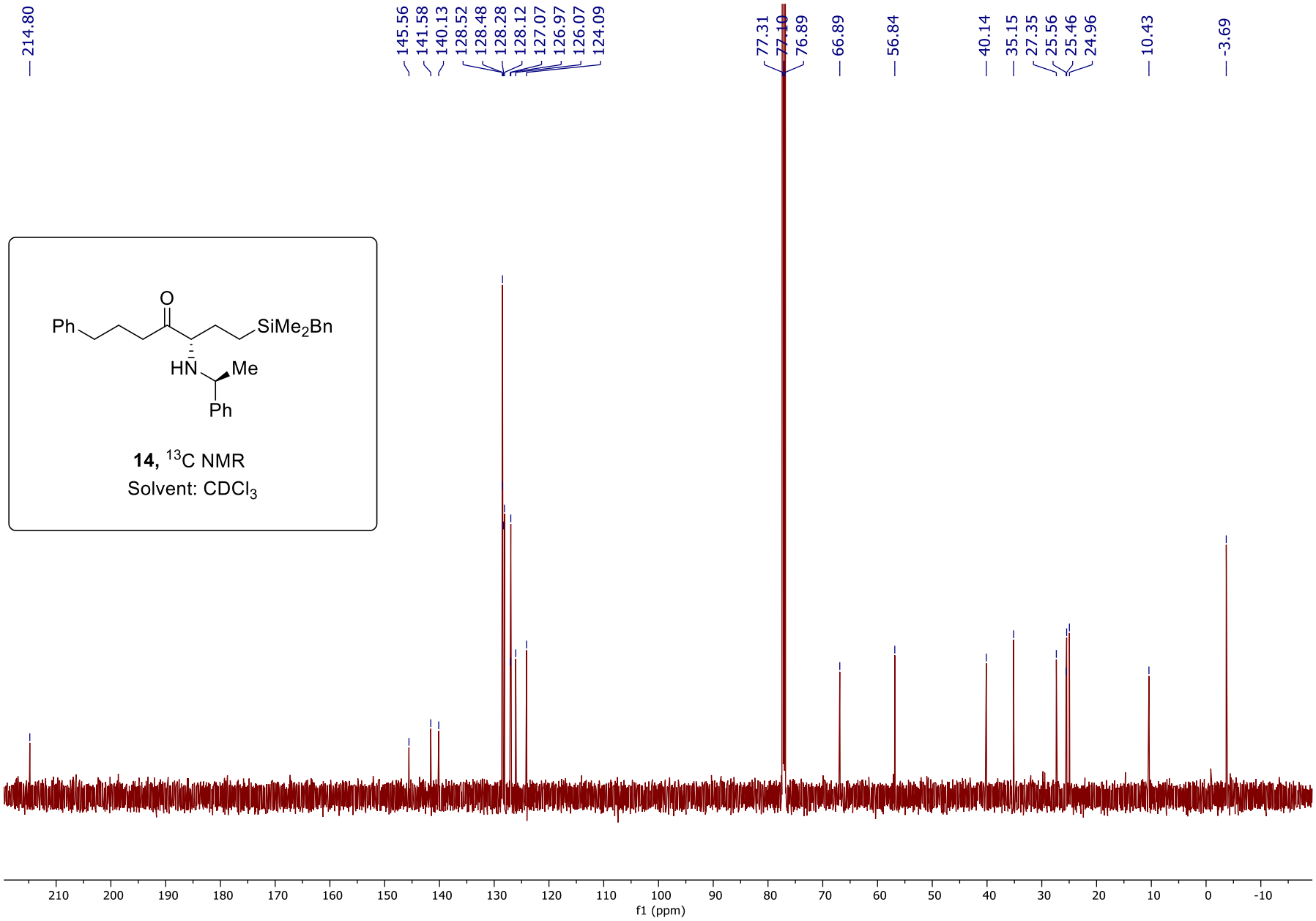
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.12
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126.97
126.07
124.09
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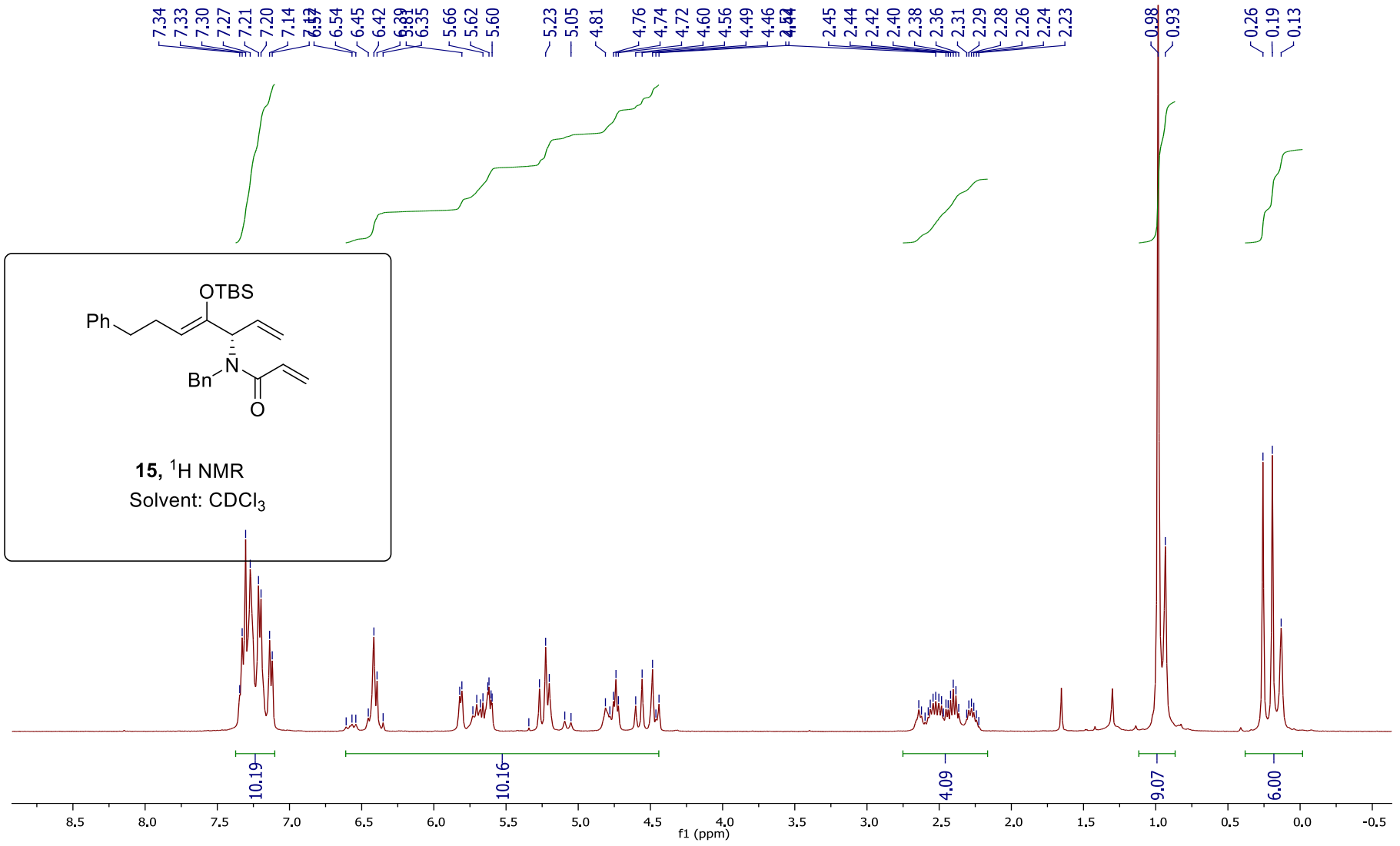
77.10
76.89
66.89
56.84
40.14
35.15
27.35
25.56
25.46
24.96
10.43
-3.69
O
Ph
SiMe2Bn
HN
Me
Ph
14, 13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OTBS
Ph
Bn
N
O
15, 1H NMR
Solvent: CDCl3
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7.33
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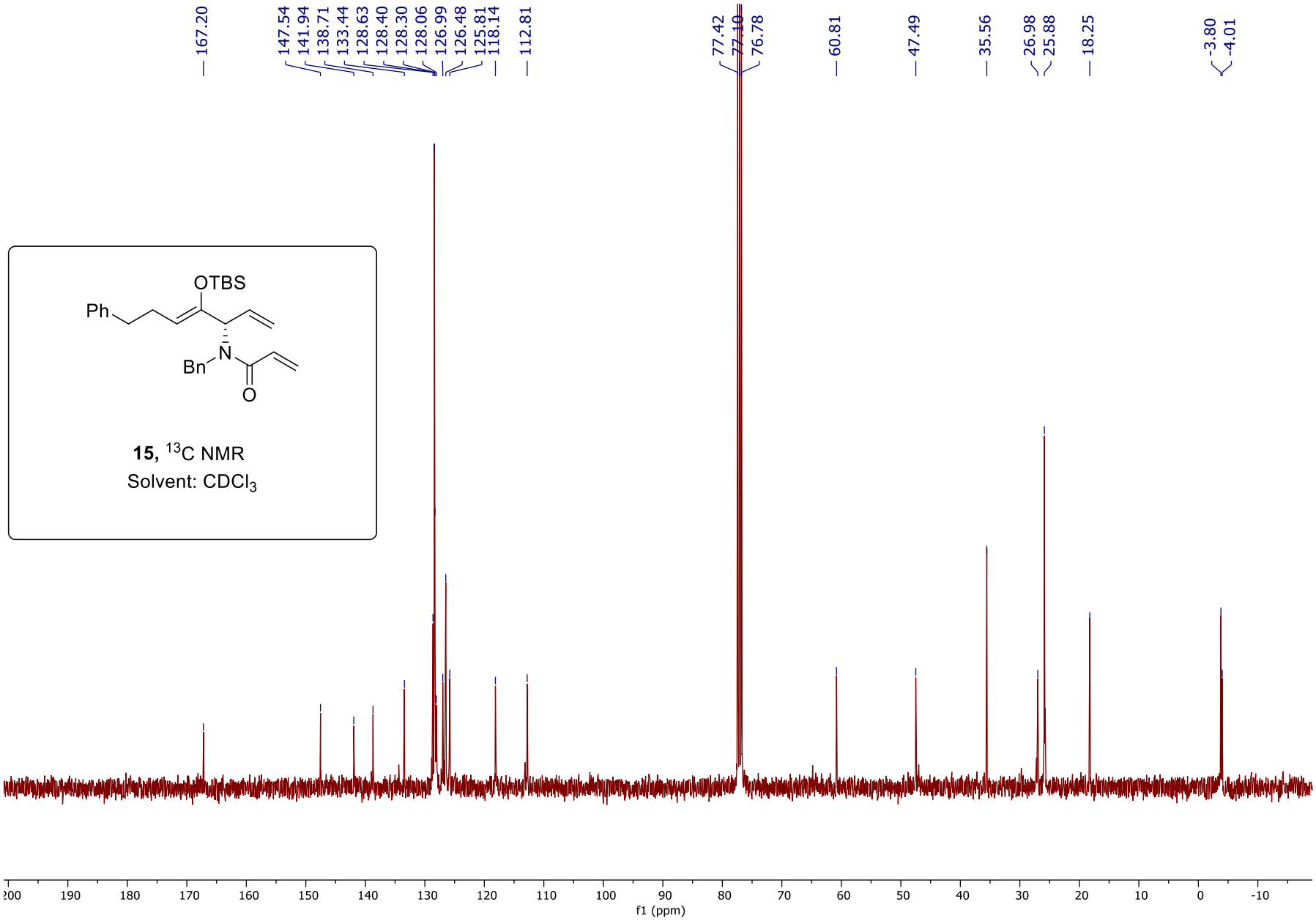
7.14
6.54
6.45
6.42
6.35
5.66
5.62
5.60
5.23
5.05
4.81
4.76
4.74
4.72
4.60
4.56
4.49
4.46
2.45
2.44
2.42
2.40
2.38
2.36
2.31
2.29
2.28
2.26
2.24
2.23
0.98
0.93
0.26
0.19
0.13
10.19
10.16
4.09
9.07
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.30
128.06
126.99
126.48
125.81
118.14
112.81
77.42
77.10
76.78
60.81
47.49
35.56
26.98
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18.25
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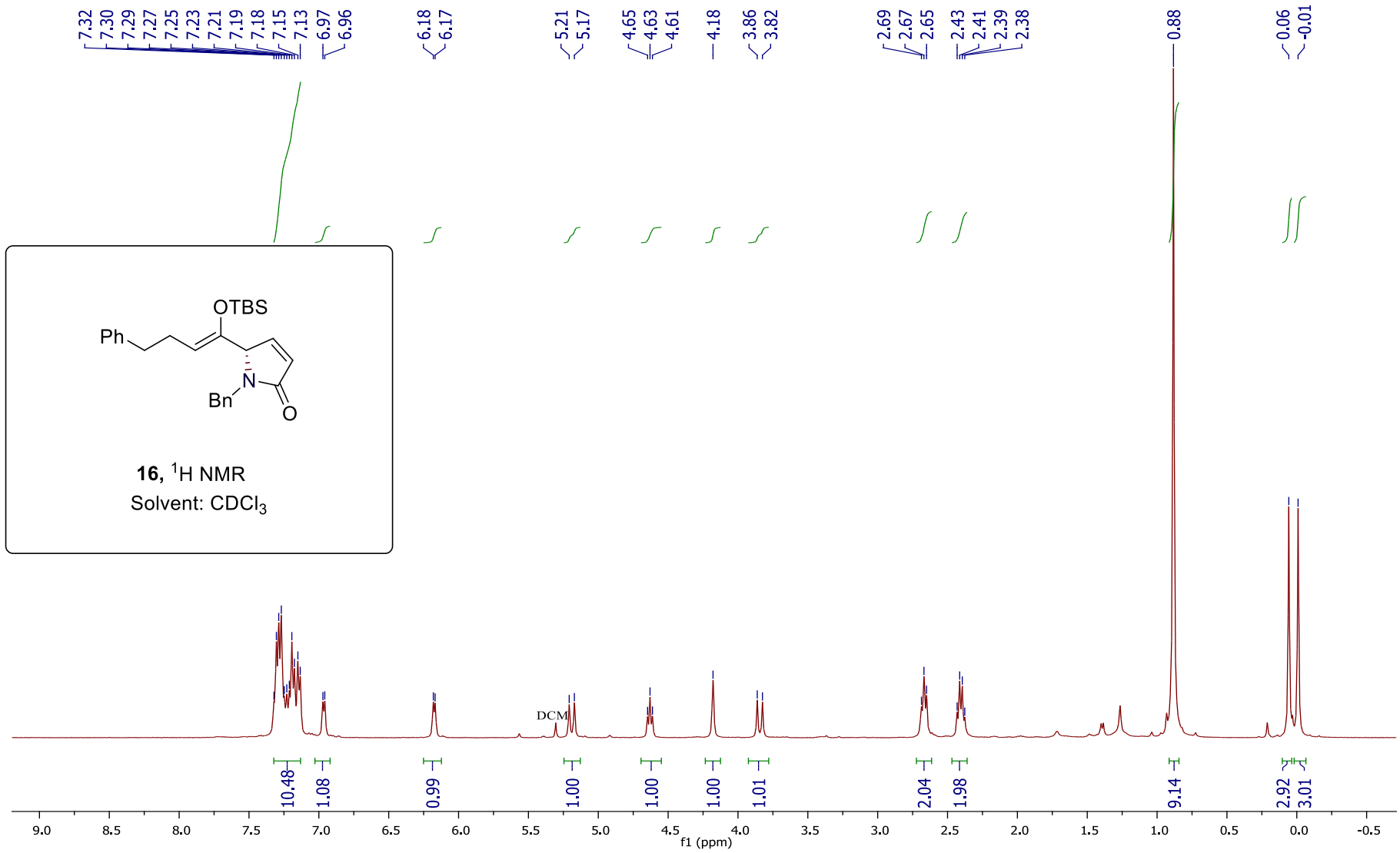
-4.01
OTBS
Ph
N
Bn
O
15, 13C NMR
Solvent: CDCl3
f1 (ppm)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7.21
7.19
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7.15
7.13
6.97
6.96
6.18
6.17
5.21
5.17
4.65
4.63
4.61
4.18
3.86
3.82
2.69
2.67
2.65
2.43
2.41
2.39
2.38
0.88
0.06
-0.01
OTBS
Ph
N
Bn
O
16, 1H NMR
Solvent: CDCl3
DCM
10.48
1.08
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1.00
1.00
1.01
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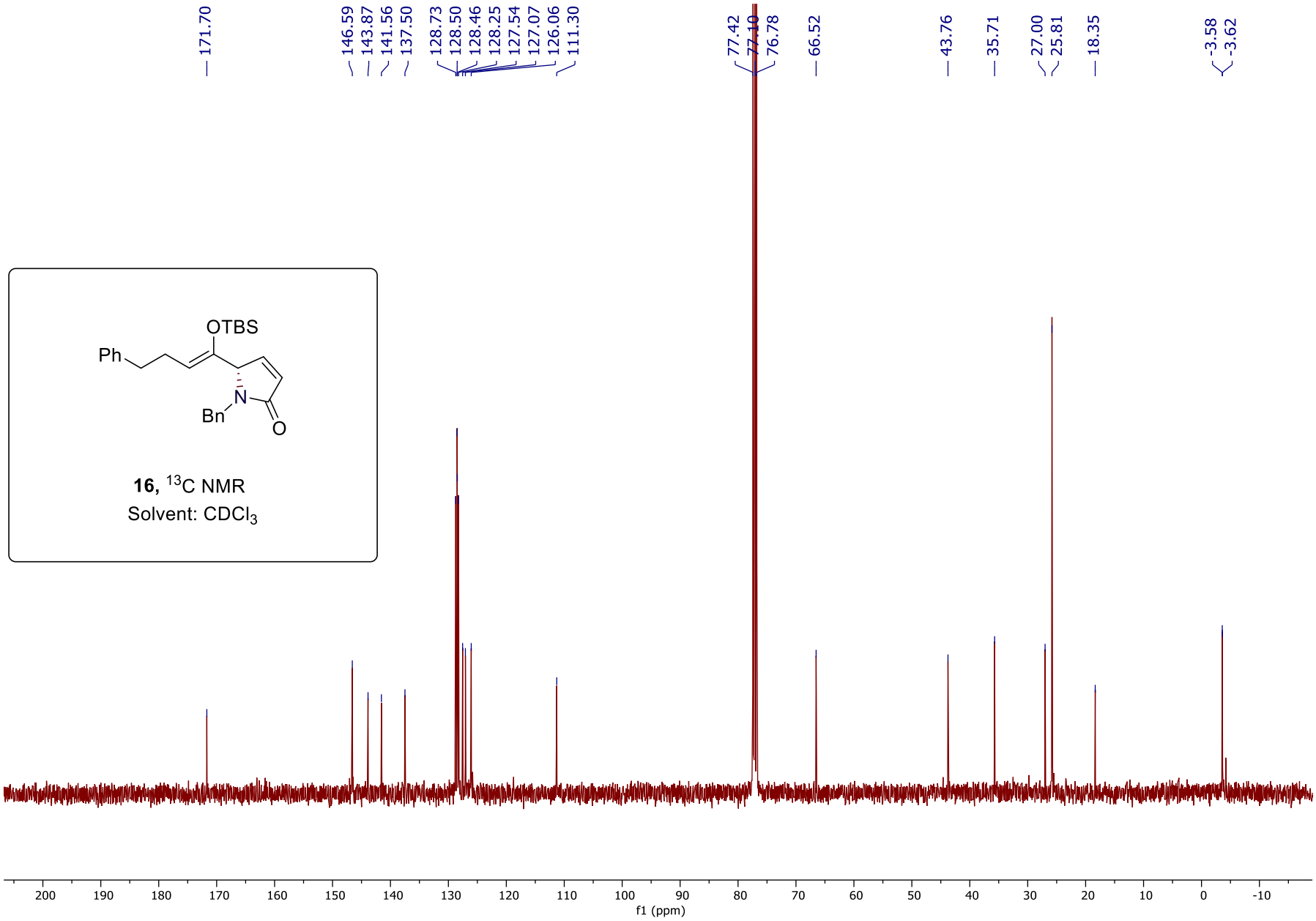
1.98
9.14
2.92
3.01
f1 (ppm)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143.87
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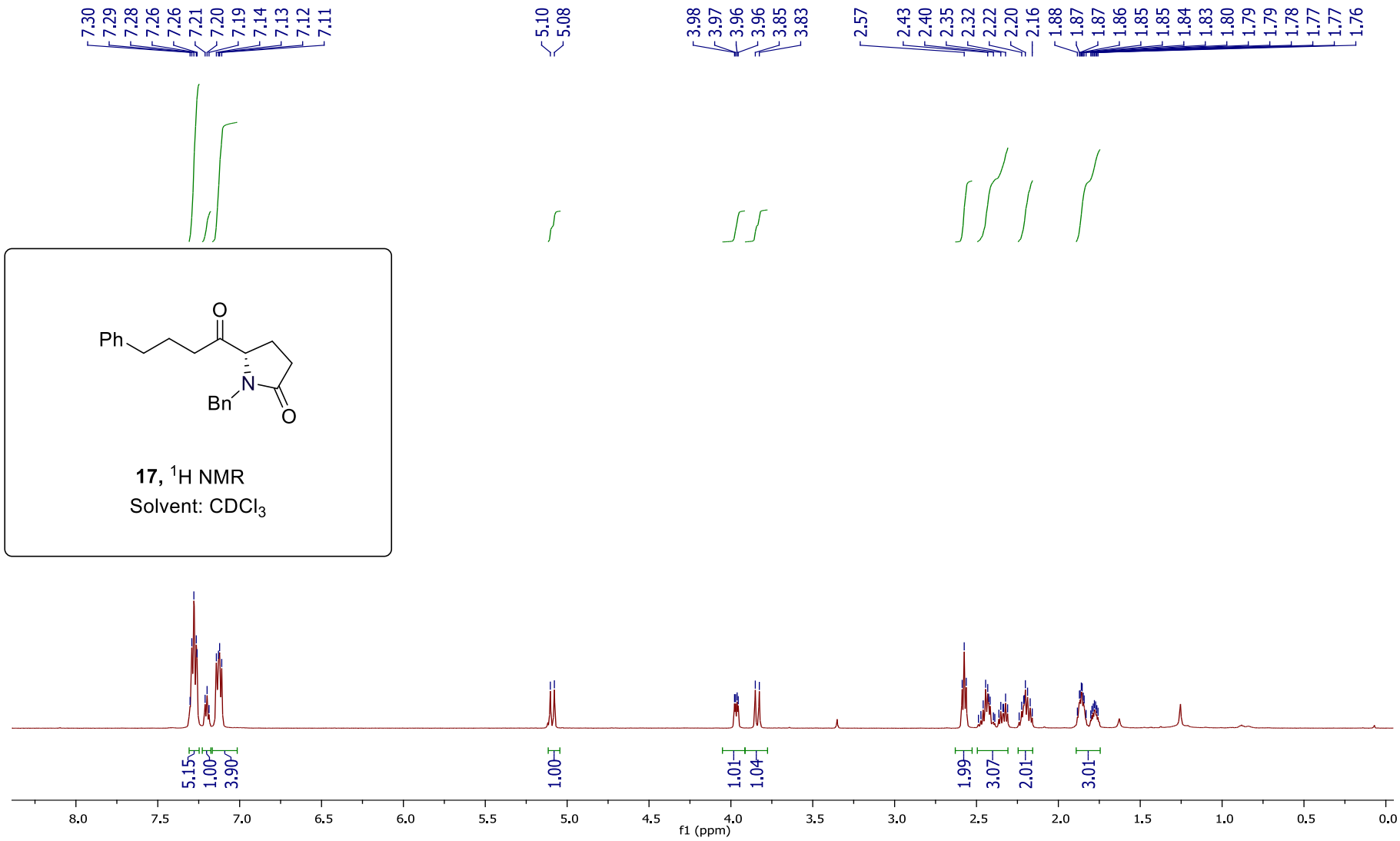
128.50
128.46
128.25
127.54
127.07
126.06
111.30
77.42
77.10
76.78
66.52
43.76
35.71
27.00
25.81
18.35
-3.58
-3.62
OTBS
Ph
N
Bn
O
16, 13C NMR
Solvent: CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.21
7.20
7.19
7.14
7.13
7.12
7.11
5.10
5.08
3.98
3.97
3.96
3.96
3.85
3.83
2.57
2.43
2.40
2.35
2.32
2.22
2.20
2.16
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.83
1.80
1.79
1.79
1.78
1.77
1.77
1.76
O
Ph
N
Bn
O
17, 1H NMR
Solvent: CDCl3
5.15
1.00
3.90
1.00
1.01
1.04
1.99
3.07
2.01
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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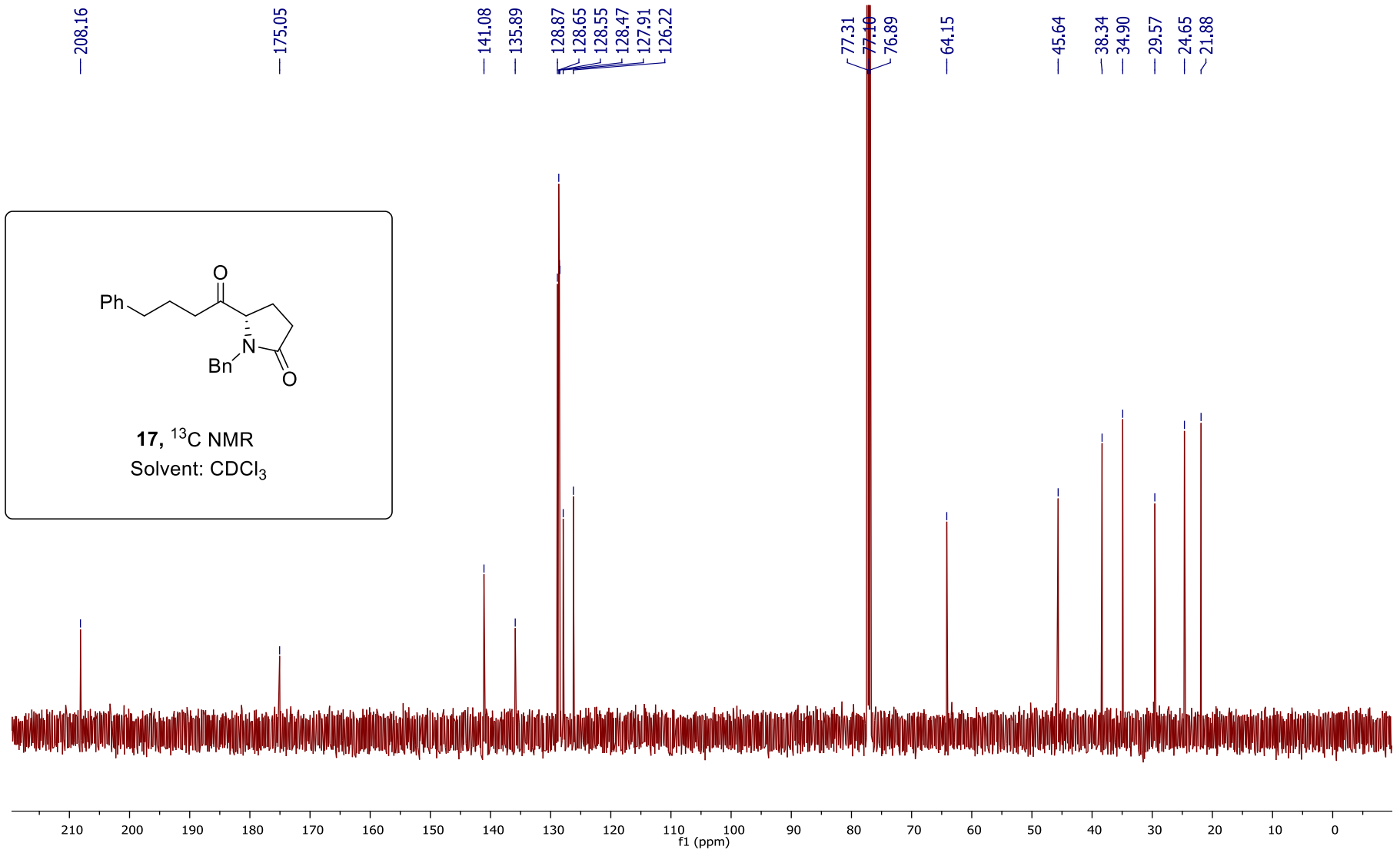
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


208.16
175.05
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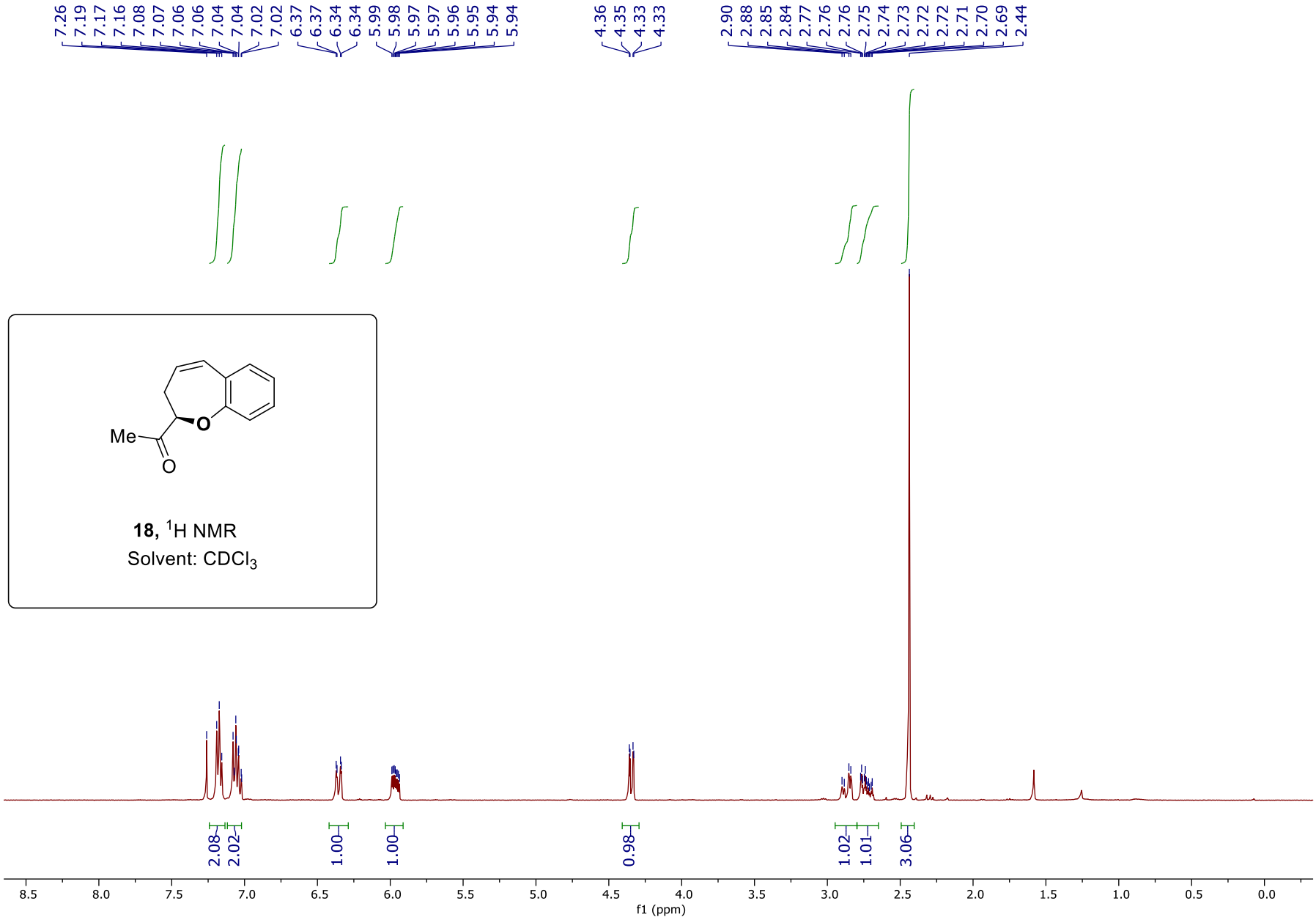
128.47
127.91
126.22
77.31
77.10
76.89
64.15
45.64
38.34
34.90
29.57
24.65
21.88
Ph
O
N
Bn
O
17, 13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.07
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7.06
7.04
7.04
7.02
7.02
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6.37
6.34
6.34
5.99
5.98
5.97
5.97
5.96
5.95
5.94
5.94
4.36
4.35
4.33
4.33
2.90
2.88
2.85
2.84
2.77
2.76
2.76
2.75
2.74
2.73
2.72
2.72
2.71
2.70
2.69
2.44
Me
O
O
18, 1H NMR
Solvent: CDCl3
2.08
2.02
1.00
1.00
0.98
1.02
1.01
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
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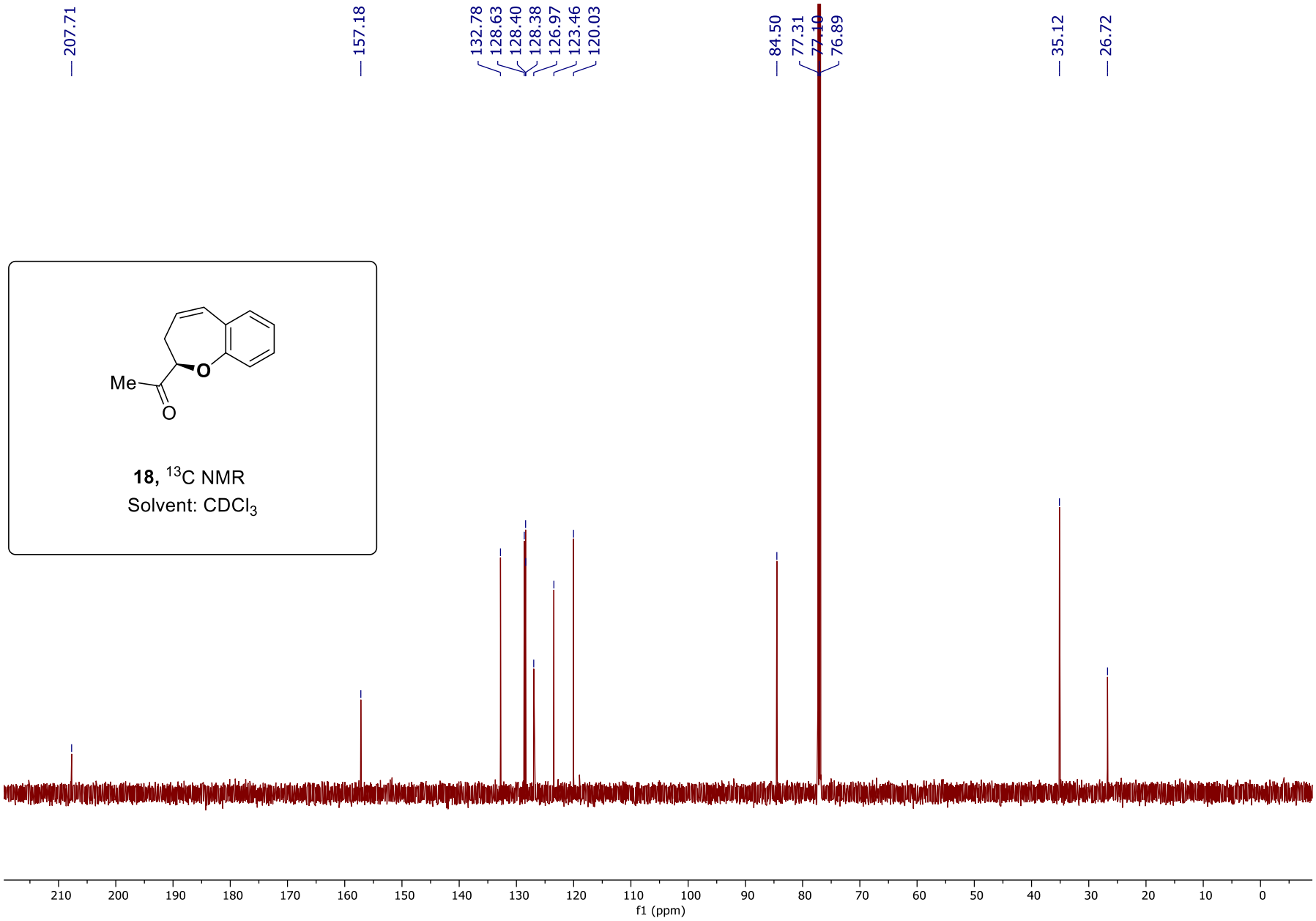
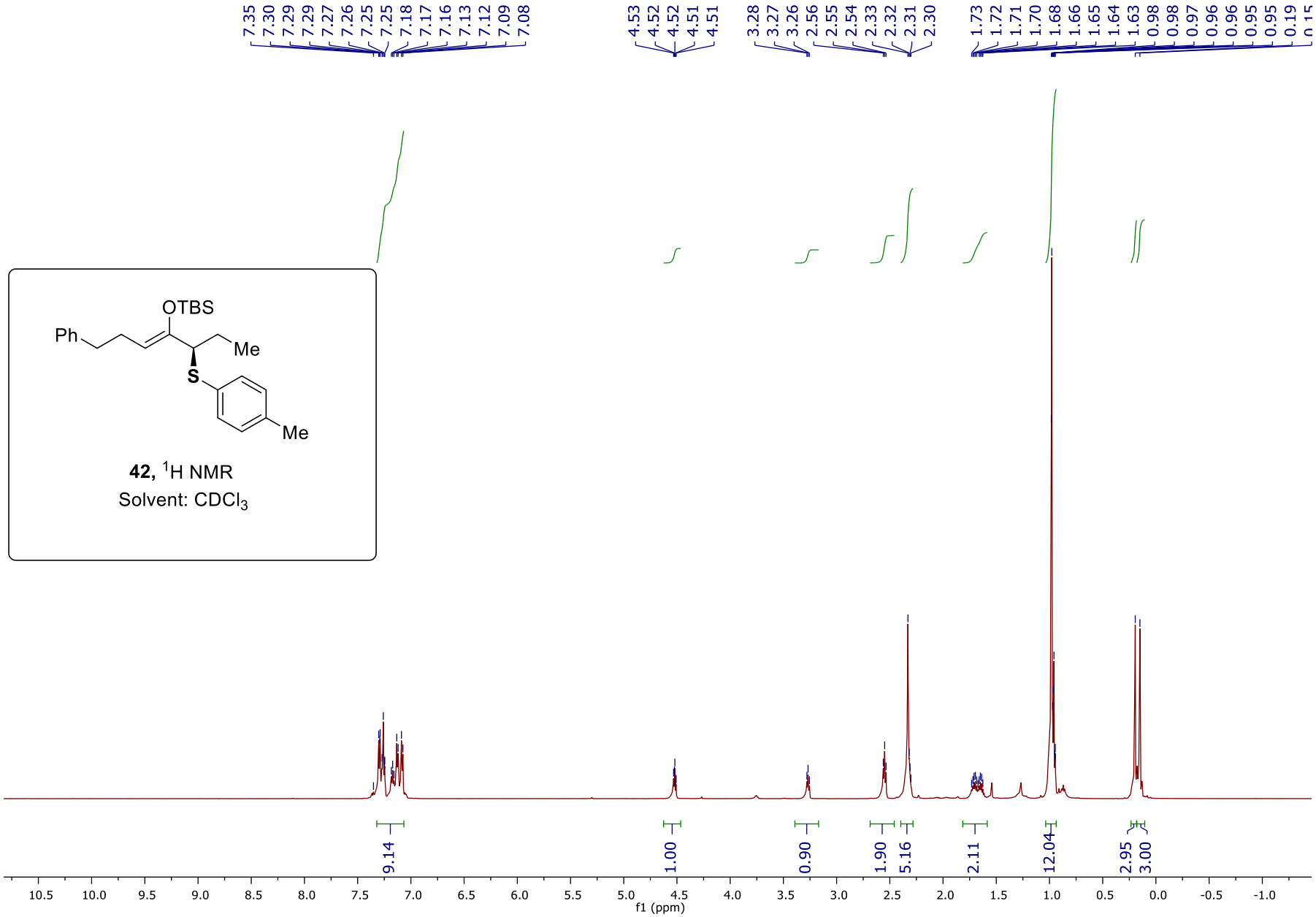
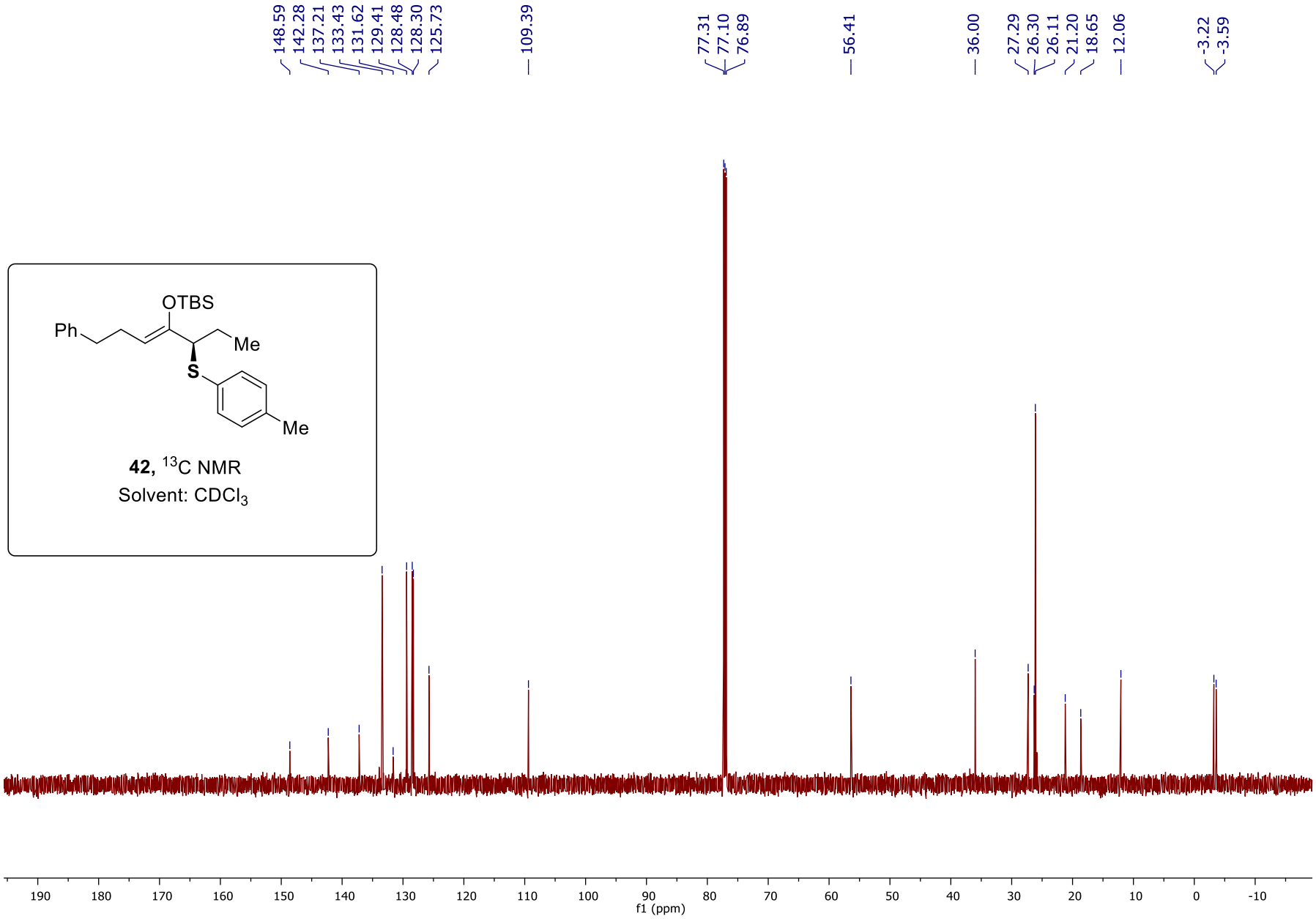
1.5
1.0
0.5
0.0
f1 (ppm)


207.71
157.18
132.78
128.63
128.40
128.38
126.97
123.46
120.03
84.50
77.31
77.10
76.89
35.12
26.72
Me
O
O
18, 13C NMR
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.35 7.30 7.29 7.29 7.27 7.26 7.25 7.25 7.18 7.17 7.16 7.13 7.12 7.09 7.08
4.53 4.52 4.52 4.51 4.51
3.28 3.27 3.26 2.56 2.55 2.54 2.33 2.32 2.31 2.30
1.73 1.72 1.71 1.70 1.68 1.66 1.65 1.64 1.63 0.98 0.98 0.97 0.96 0.96 0.95 0.95 0.19
OTBS
Ph
Me
S
Me
42, 1H NMR
Solvent: CDCl3
9.14
1.00
0.90
1.90
5.16
2.11
12.04
2.95
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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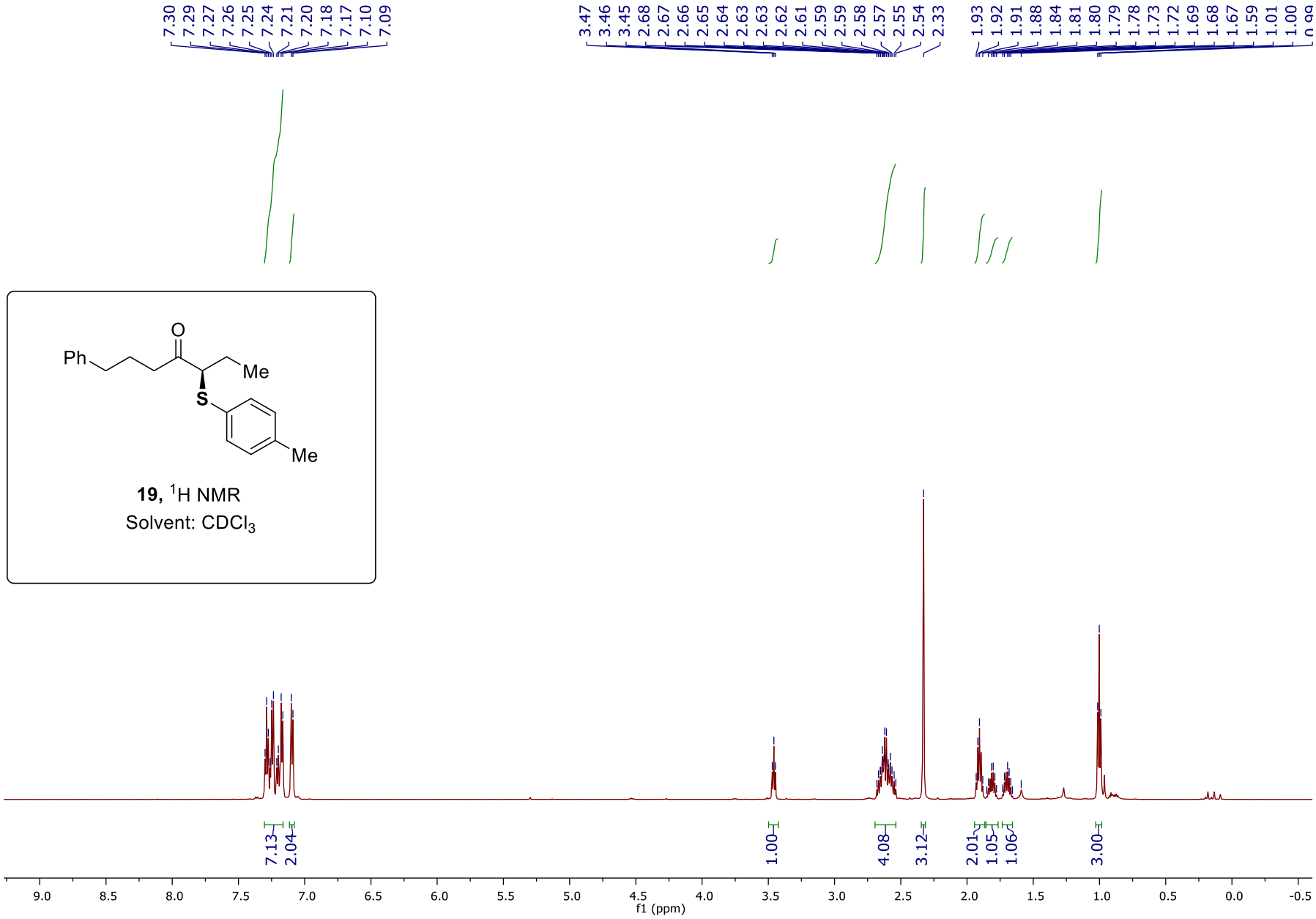
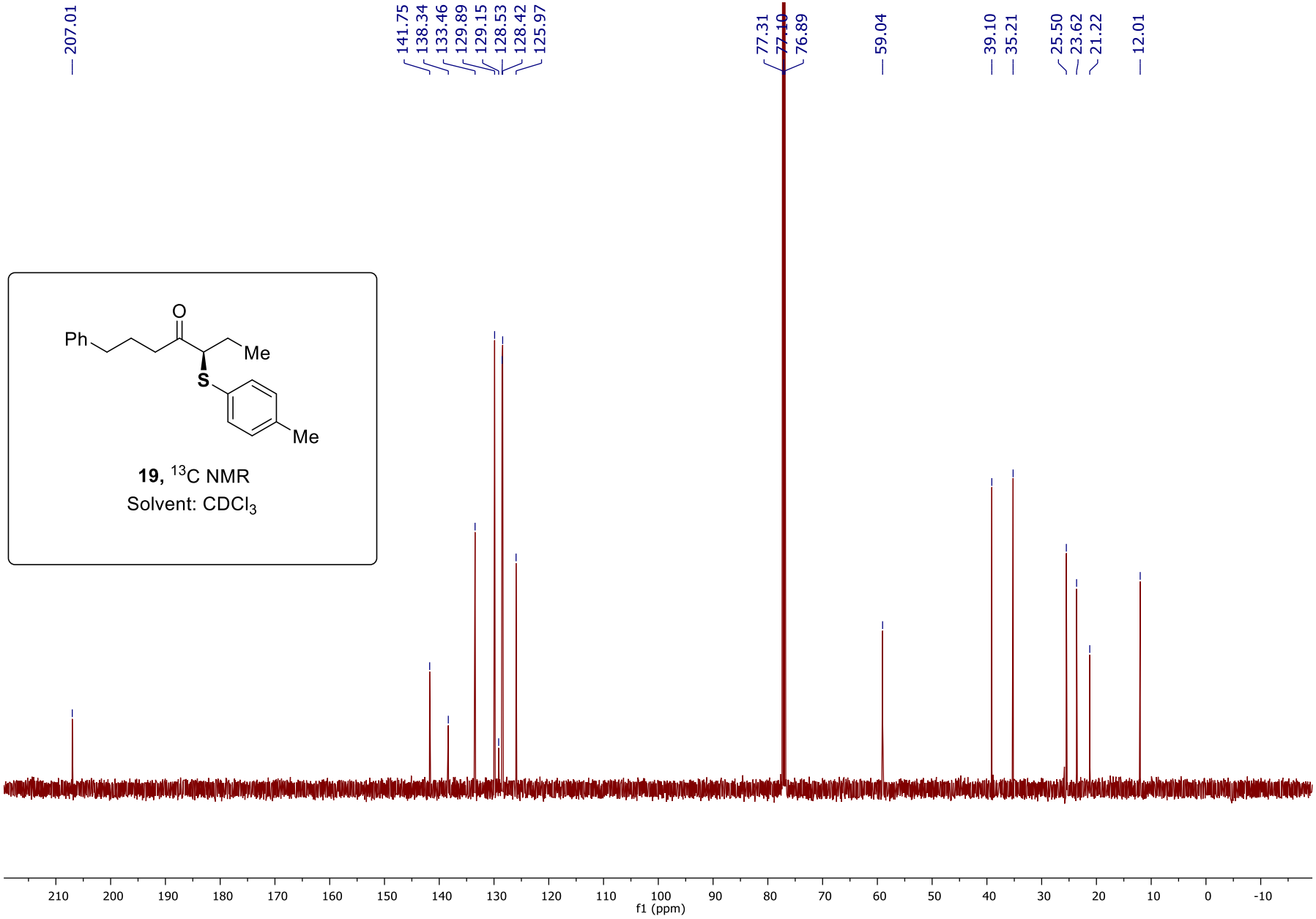
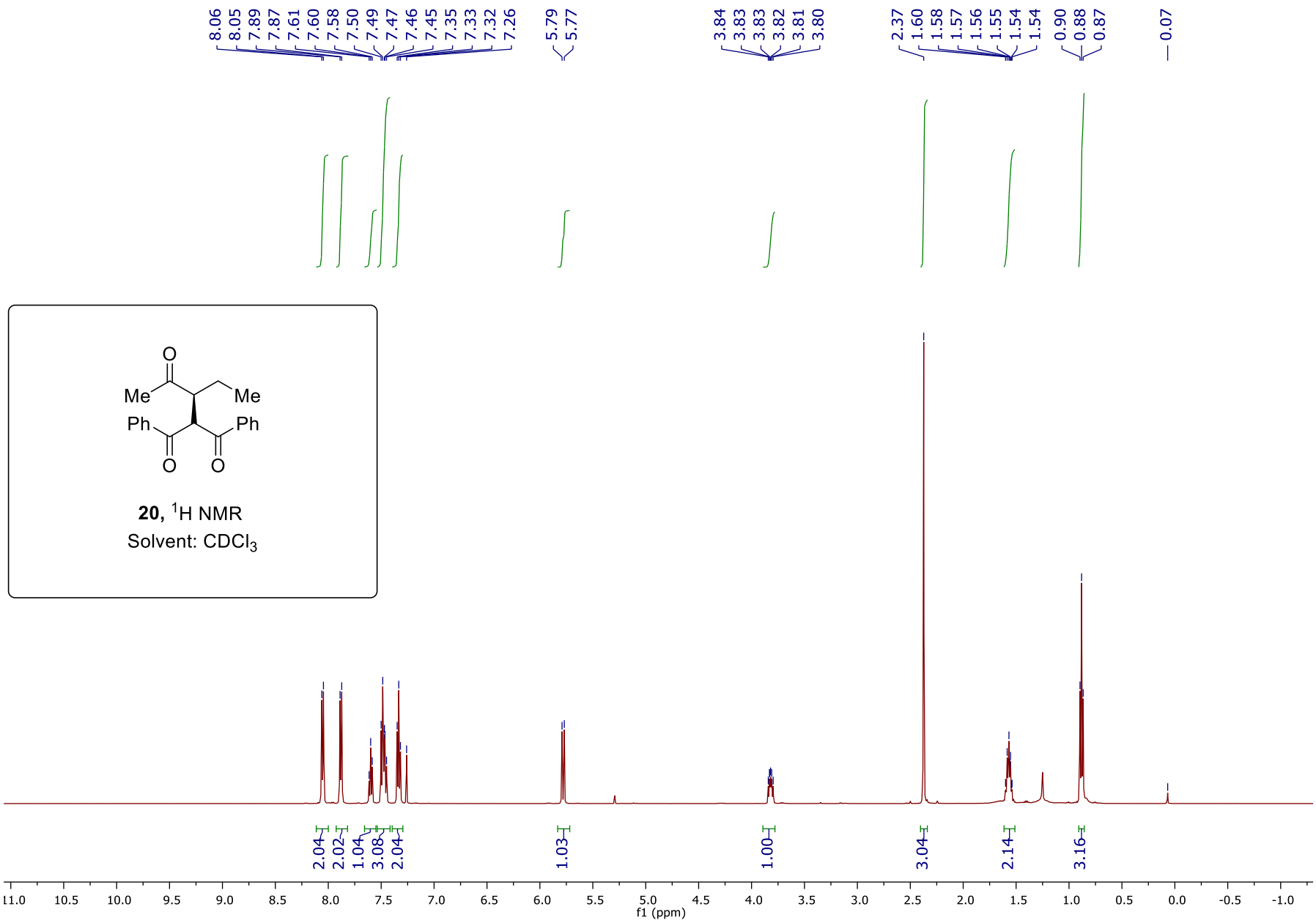
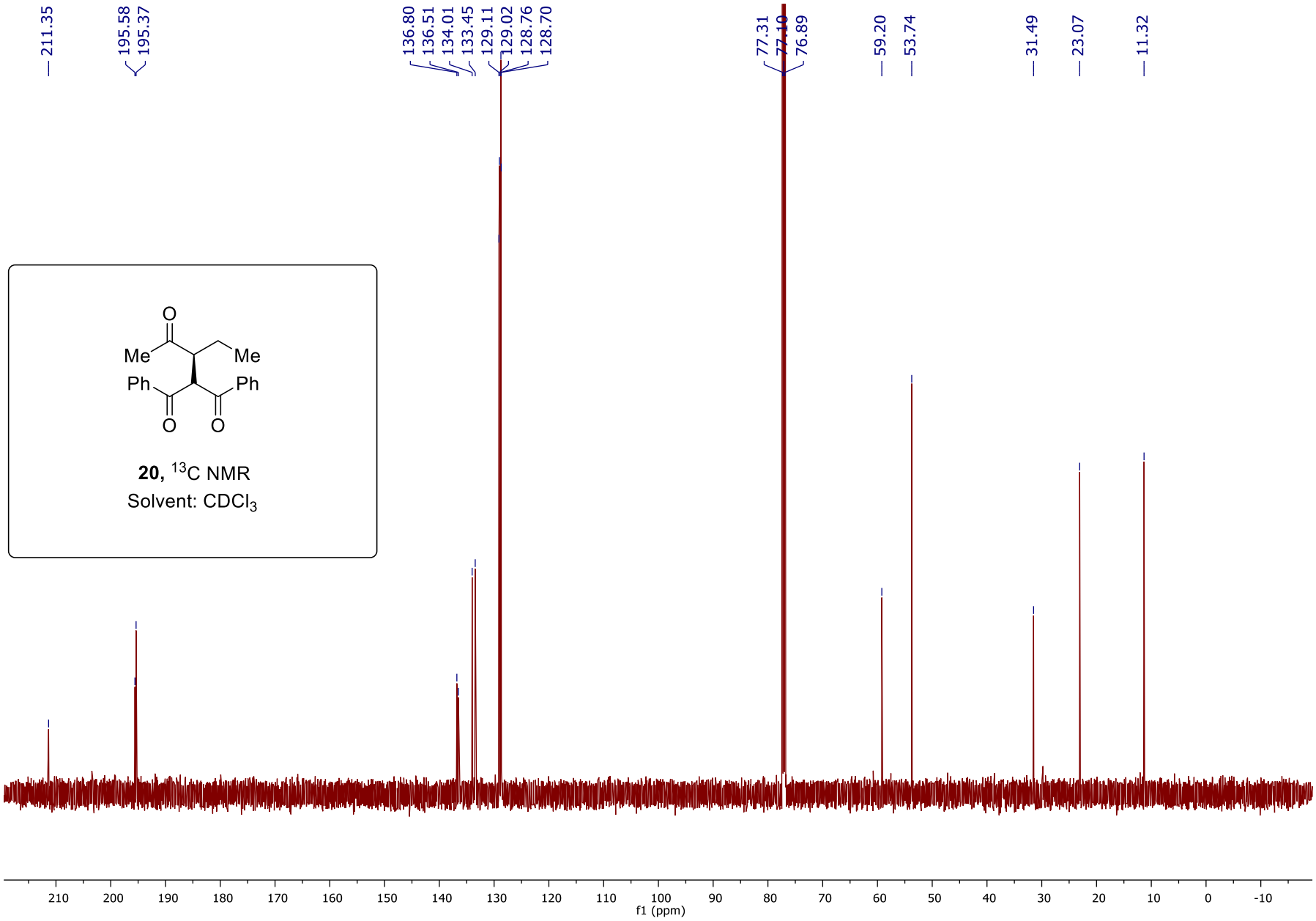
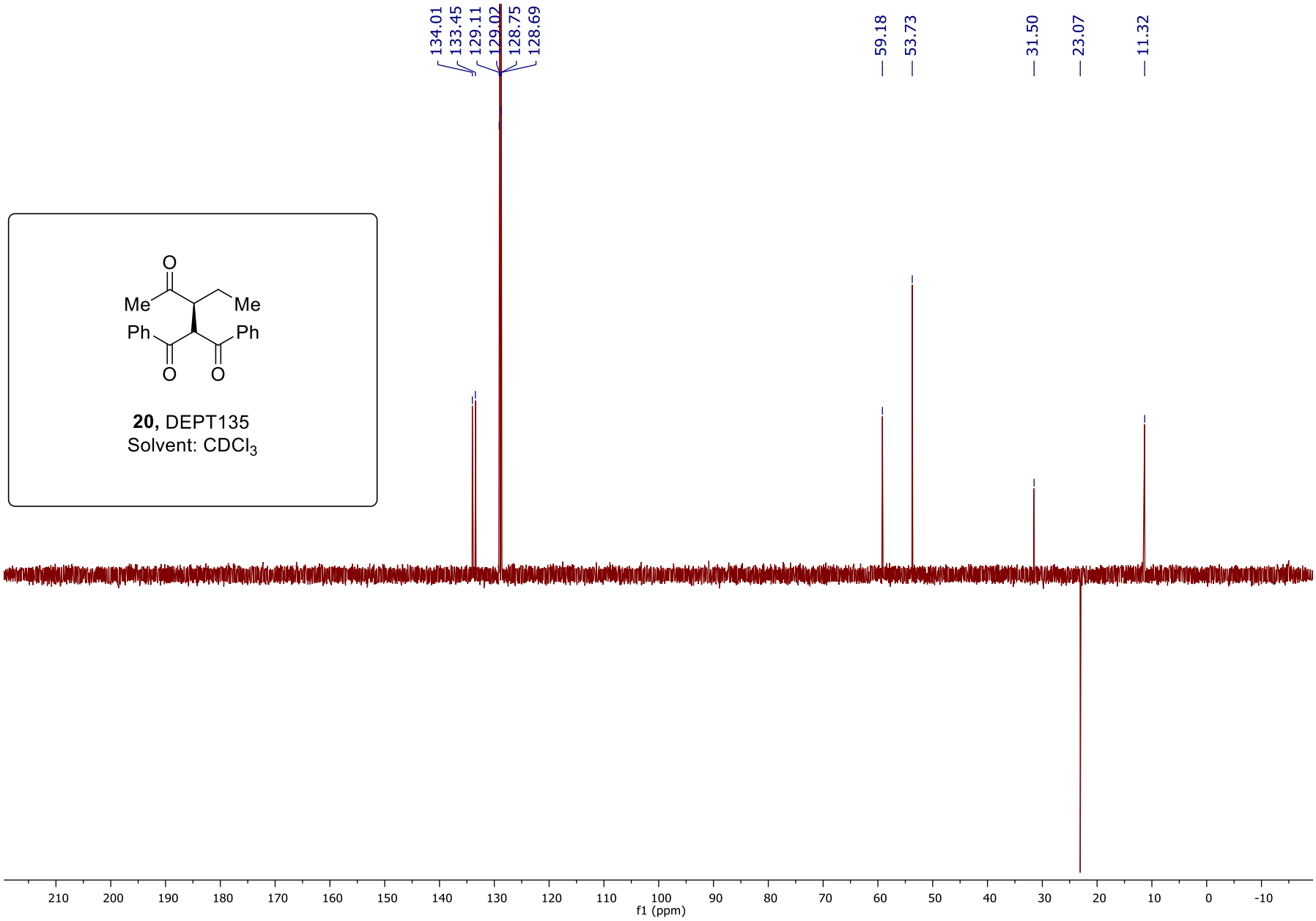
142.28
137.21
133.43
131.62
129.41
128.48
128.30
125.73
109.39
77.31
77.10
76.89
56.41
36.00
27.29
26.30
26.11
21.20
18.65
12.06
-3.22
-3.59
OTBS
Ph
Me
S
Me
42, 13C NMR
Solvent: CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.30
7.29
7.27
7.26
7.25
7.24
7.21
7.20
7.18
7.17
7.10
7.09
3.47
3.46
3.45
2.68
2.67
2.66
2.65
2.64
2.63
2.63
2.62
2.61
2.59
2.59
2.58
2.57
2.55
2.54
2.33
1.93
1.92
1.91
1.88
1.84
1.81
1.80
1.79
1.78
1.73
1.72
1.69
1.68
1.67
1.59
1.01
1.00
O
Ph
Me
S
Me
19, 1H NMR
Solvent: CDCl3
7.13
2.04
1.00
4.08
3.12
2.01
1.05
1.06
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
f1 (ppm)


207.01
141.75
138.34
133.46
129.89
129.15
128.53
128.42
125.97
77.31
77.10
76.89
59.04
39.10
35.21
25.50
23.62
21.22
12.01
O
Ph
Me
S
Me
19, 13C NMR
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)


8.06
8.05
7.89
7.87
7.61
7.60
7.58
7.50
7.49
7.47
7.46
7.45
7.35
7.33
7.32
7.26
5.79
5.77
3.84
3.83
3.83
3.82
3.81
3.80
2.37
1.60
1.58
1.57
1.56
1.55
1.54
1.54
0.90
0.88
0.87
0.07
Me
Me
Ph
Ph
O
O
O
O
20, 1H NMR
Solvent: CDCl3
2.04
2.02
1.04
3.08
2.04
1.03
1.00
3.04
2.14
3.16
f1 (ppm)


211.35
195.58
195.37
136.80
136.51
134.01
133.45
129.11
129.02
128.76
128.70
77.31
77.10
76.89
59.20
53.74
31.49
23.07
11.32
Me
Me
Ph
Ph
O
O
O
O
20, 13C NMR
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)


134.01
133.45
129.11
129.02
128.75
128.69
59.18
53.73
31.50
23.07
11.32
Me
Me
Ph
Ph
O
O
O
O
20, DEPT135
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)