# A Triple Photoredox/Cobalt/Brønsted Acid Catalysis Enabling Markovnikov Hydroalkoxylation of Unactivated Alkenes

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## 1. Instrumentation and Chemicals

NMR spectra were recorded on a Bruker AVANCE NEO 400N spectrometer, operating at 400 MHz for $^{1}$H NMR, 100.6 MHz for $^{13}$C NMR. Chemical shift values for $^{1}$H and $^{13}$C are referenced to $Me_4Si$ and the residual solvent resonances, respectively. Chemical shifts were reported in $\delta$ ppm. Mass spectra were obtained with JMS-T100TD (DART). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60$F_{254}$. Silica gel (Wakosil® 60, 64~210 μm) was used for column chromatography. Biotage Selekt was used for purification. IR spectra were measured with a Thermo Scientific iD7 ATR Accessory for the Thermo Scientific Nicolet iS5 FT-IR Spectrometer. Melting points were measured on a Stanford Research Systems MPA100. CV measurements were recorded with a Hokuto Denko HZ-7000 potentiostat. UV-Vis absorption spectra were recorded on a Shimadzu UV-1900. Fluorescence spectra were recorded on a Shimadzu RF-6000. Kessil A160W Tuna Blue (highest blue and intensity setting) was used as a light source. TEKNOS MG9 was used as a fan.

All reactions were carried out under nitrogen or argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Dichloromethane and acetonitrile were purchased from FUJIFILM Wako Pure Chemical Co., stored under nitrogen, and used as received. $Ir(ppy)_3$ was purchased from Aldrich Chemical Co., stored under nitrogen, and used as received. LiOTf was was purchased from Tokyo Chemical Industry Co., stored under nitrogen, and used as received. Na dispersion was was purchased from Tokyo Chemical Industry Co., stored under nitrogen, and used as received. Cobalt catalysts **Co-1**–**3** were prepared by the reported procedure.[1] **PTH-2** and **PTH-3** were prepared by the reported procedure.[2] **HX-2** was prepared by the reported procedure.[3] The redox active ester **10a** was prepared by the reported procedure.[4]

## 2. Synthesis and Characterizationof Organophotoredox Catalyst PTH-1

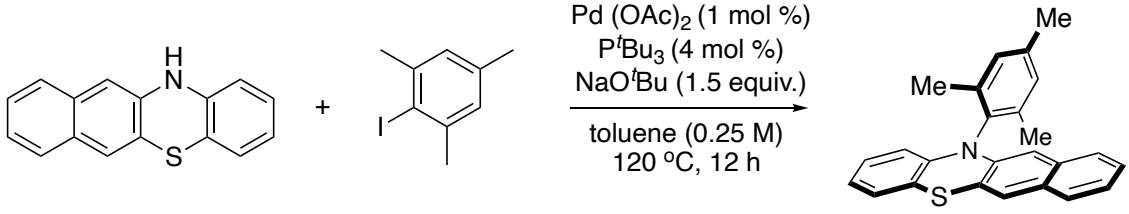
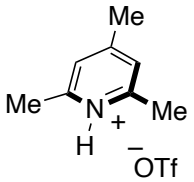



**Figure S1.** Synthesis of **PTH-1**.

In a glovebox, to an oven-dried vial with a stirring bar was added palladium acetate (4.5 mg, 0.02 mmol), tri-*tert*-butyl phosphine (16.2 mg, 0.08 mmol) and toluene (8 mL). After stirring at room temperature for 10 min, benzo[*b*]phenoxazine (498.7 mg, 2.0 mmol), mesityl iodide (639.8 mg, 2.6 mmol) and sodium *tert*-butoxide (288.3 mg, 3.0 mmol) were sequentially added to the reaction solution. After sealing the vial with a cap and removed from the glove box, the reaction was stirred at 120 °C overnight and quenched with $NH_4Cl$ aq. The resultant reaction solution was extracted with ethyl acetate three times and the combined organic layer was dried over $Na_2SO_4$ and filtered. After volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (Biotage Selekt, 0:100–4:96, dichloromethane/hexane) gave the coupling product **PTH-1** (173.0 mg, 0.47 mmol, 23% isolated yield). White solid. **M.p.** 240–242 °C. **IR** (neat) 743, 907, 1247, 1314, 1336, 1448, 1478, 1572, 2917, 3052 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.48 (m, 1H), 7.35 (s, 1H), 7.27 (m, 1H), 7.19–7.12 (m, 2H), 7.11 (s, 2H), 6.96 (dd, $J$ =7.6, 1.6 Hz, 1H), 6.79 (dd, $J$ = 7.2, 1.6 Hz, 1H), 6.73 (td, $J$ = 7.6, 1.6 Hz, 1H), 6.11 (s, 1H), 5.93 (dd, $J$ = 7.2, 1.6 Hz, 1H), 2.41 (s, 3H), 2.15 (s, 6H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 140.1, 138.6, 138.3, 137.8 (×2C), 134.9, 133.7, 130.4, 130.1, 127.1, 126.6, 126.1, 126.1, 125.8, 123.9, 121.5, 121.2, 117.9, 114.4, 108.7, 21.1, 17.8. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{22}NS$, 368.1467; found, 368.1469.

## 3. Synthesis and Characterization of Brønsted Acid Catalysts HX-1 and 3

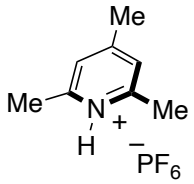
**Synthesis of HX-1.** To a 30 ml round bottom flask with a stirring bar was added collidine (1.05 mL, 8.0 mmol) and TfOH (1.20 g, 8.0 mmol) at 0 ℃. After stirring at 0 ℃ for 10 min, the obtained white solid was washed with ether and dried under reduced pressure to afford collidine·HOTf (**HX-1**, 1.37 g, 5.1 mmol, 63% isolated yield).




White solid. **M.p.** 79–81 °C. **IR** (neat) 515, 638, 1029, 1155, 1224, 1242, 1286, 1639, 2974, 3080 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 14.53 (brs, 1H), 7.30 (s, 2H), 2.80 (s, 6H), 2.57 (s, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 159.3, 153.0, 125.3, 120.3 (q, $J_{C\text{-}F}$ = 318.6 Hz), 22.1, 19.4. **$^{19}$F NMR** (376.5 MHz, $CDCl_3$) $\delta$ –78.4. **HRMS–DART** (*m/z*): $[M–OTf]^+$ calcd for $C_8H_{12}N$; 122.0964, found 122.0959.

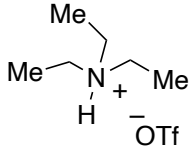
**Synthesis of HX-3.** To a 30 ml round bottom flask with a stirring bar was added collidine (0.66 mL, 5.0 mmol) and $HPF_6$ solution (20 wt%, 3.65 g) at 0 ℃. After stirring at 0 ℃ for 10 min, the obtained

white solid was washed with ether and dried under reduced pressure to afford collidine·$HPF_6$ (**HX-3**, 0.53 g, 2.0 mmol, 40% isolated yield).




White solid. **M.p.** 230–233 °C. **IR** (neat) 516, 712, 765, 990, 1011, 1039, 1073, 1637, 2996, 3191 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 13.35 (brs, 1H), 7.32 (s, 2H), 2.80 (s, 6H), 2.58 (s, 3H). **$^{13}$C NMR** (100.6 MHz, $D_2O$) $\delta$ 160.1, 151.6, 125.1, 21.1, 18.3. **$^{19}$F NMR** (376.5 MHz, $CDCl_3$) $\delta$ –149.7, –149.8. **HRMS–DART** (*m/z*): $[M–PF_6]^+$ calcd for $C_8H_{12}N$; 122.0964, found 122.0966.

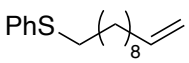
**Synthesis of HX-4.** To a 30 ml round bottom flask with a stirring bar was added $Et_3N$ (1.25 mL, 9.0 mmol) in DCM (0.5 M, 6.0 mL) and TfOH (0.45 g, 3.0 mmol) at 0 ℃. After stirring at 0 ℃ for 30 min, the organic layer was dried over $Na_2SO_4$ and filtered. the obtained colirless oil was washed with ether and dried under reduced pressure to afford and dried under reduced pressure to afford $Et_3N$·HOTf (**HX-3**, 0.46 g, 1.8 mmol, 62% isolated yield).




A colorless gel. **IR** (neat) 518, 638, 1028, 1158, 1224, 1239, 1279, 1477, 2821, 3059 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.87 (brs, 1H), 3.18 (q, $J$ = 7.2 Hz, 6H), 1.38 (t, $J$ = 7.2 Hz, 9H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 120.2 (q, $J_{C\text{-}F}$ = 319.1 Hz), 46.9, 8.6. **$^{19}$F NMR** (376.5 MHz, $CDCl_3$) $\delta$ –78.4. **HRMS–DART** (*m/z*): $[M–OTf]^+$ calcd for $C_6H_6N$; 102.1277, found 102.1279.

## 4. Synthesis and Characterization of Alkenes

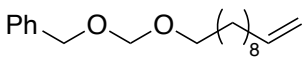
Alkene **2e** was synthesized according to the modified procedure.[5] To a solution of thiophenol (0.31 ml, 330 mg, 3.0 mmol) in DMF (6.5 ml) was added $K_2CO_3$ (539 mg, 3.9 mmol), followed by the 11-Bromo-1-undecene (0.65 ml, 700 mg, 3 mmol). The reaction was stirred at room temperature overnight and then diluted with water. The combined hexane extracts were dried with $Na_2SO_4$ and the solvent was removed under reduced pressure. The oily residue was purified by flash chromatography on silica gel (Biotage Selekt, 100:0, hexane/EtOAc). The oily precipitate was dried in vacuo to afford the desired **2e** (780 mg, 3.0 mmol, 99 %) as a colorless oil.




**IR** (neat) 690, 736, 909, 1025, 1438, 1465, 1480, 2852, 2924, 3074 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33–7.25 (m, 4H), 7.16 (t, $J$ = 7.2 Hz, 1H), 5.81 (m, 1H), 5.01–4.92 (m, 2H), 2.91 (t, $J$ = 7.2 Hz, 2H), 2.04 (q, $J$ = 7.2 Hz, 2H), 1.64 (quintet, $J$ = 7.2 Hz, 2H), 1.43–1.27 (m, 12H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 139.2, 137.0, 128.8, 128.8, 125.6, 114.1, 33.8, 33.6, 29.4, 29.4, 29.1 (× 2C), 29.1, 28.9, 28.8. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{27}S$, 263.1828; found, 263.1825.

**{[(Undec-10-en-1-yloxy)methoxy]methyl}benzene (2i)**

Alkene **2i** was synthesized according to the modified procedure.[6] A flask was placed under $N_2$ atmosphere by three cycles of evacuating and $N_2$ backfilling and charged with undec-10-en-1-ol (801 µL, 4.0 mmol, 1.0 equiv.). Dry $CH_2Cl_2$ (10 mL) and DIPEA (1.40 mL, 8.0 mmol, 2.0 equiv.) were added and the solution was cooled to 0 °C. BOMCl (1.04 mL, 1.90 mmol, 1.9 equiv.) was added dropwise. After stirring for 15 min, the ice bath was removed and the reaction mixture was stirred for 16 h at room temperature. The solution was diluted with $CH_2Cl_2$, washed with sat. aq. $NaHCO_3$, dried over $Na_2SO_4$ and the solvent was removed under reduced pressure. The oily residue was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–93:7, hexane/EtOAc) to afford the desired product **2i** (577 mg, 2.0 mmol, 50%) as a colorless oil.

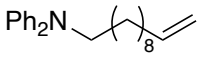



**IR** (neat) 697, 734, 908, 994, 1028, 1046, 1113, 1455, 2854, 2925 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36–7.26 (m, 5H), 5.81 (m, 1H), 5.01–4.92 (m, 2H), 4.76 (s, 2H), 4.60 (s, 2H), 3.58 (t, $J$ = 6.8 Hz, 2H), 2.04 (dt, $J$ = 7.2, 6.8 Hz, 2H), 1.63–1.56 (m, 2H), 1.37–1.29 (m, 12H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 139.2, 138.0, 128.4, 127.9, 127.6, 114.1, 94.6, 69.2, 68.1, 33.8, 29.7, 29.5, 29.4 (×2C), 29.1, 28.9, 26.2. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{19}H_{34}NO_2$,308.2584; found, 308.2584.

***N*-Phenyl-*N*-(undec-10-en-1-yl)aniline (2j)**

Alkene **2j** was synthesized according to the modified procedure.[7] The undec-10-en-1-ol (3.41 g, 20 mmol, 1.0 equiv.) and trimethylamine (4.16 ml, 30 mmol, 1.5 equiv.) were added to a round-bottom flask containing dry DCM (6.7 mL). The flask was sealed with a rubber septum and purged with nitrogen. The mixture was cooled to 0 °C, and methanesulfonylchloride (2.63 g, 34 mmol, 1.48 equiv.) was added to the mixture while being stirred vigorously. After 1h, the mixture was washed with HCl 2mol/L, saturated $NaHCO_3$ and brine, dried over $Na_2SO_4$ and concentrated under reduced pressure, afforded brown liquid. The mesylated product (5.68 g, >20 mmol, >99% yield) was used in the next step without further purification.

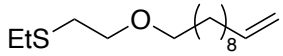
Diphenylamine (1.33 g, 7.8 mmol, 1.12 equiv.) was dissolved in anhydrous THF (42 mL) and the solution was cooled to –78 °C. A 13.6 mL portion of *n*-bulithium (7.91 mmol, 1.13 equiv.) was added dropwise. The mixture was stirred at –78 °C for 30 min then kept at room temperature for 2 h. The suspension was cooled to –20 °C and transferred into a second flask containing a cold (–78 °C) solution of the mesylated product (7.0 mmol, 1.0 equiv.) in anhydrous THF (12 mL). The reaction mixture was stirred at –78 °C for 30 min and then at room temperature overnight. The precipitate was filtered off and the solvents were removed in vacuo. The resulting oil was hydrolyzed with deionized water. The aqueous layer was washed dichloromethane. The organic fractions were combined, dried over magnesium sulfate, and the solvent was evaporated off. The oily residue was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–95:5, hexane/EtOAc) to afford the desired **2j** (960 mg, 3.0 mmol, 43 %) as a colorless oil.



**IR** (neat) 692, 745, 908, 1244, 1363, 1494, 1574, 1588, 2852, 2923 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.27–7.23 (m, 4H), 6.99–6.97 (m, 4H), 6.93 (t, $J$ = 7.2 Hz, 2H), 5.81 (m, 1H), 5.01–4.91 (m, 2H), 3.67 (t, $J$ = 7.6 Hz, 2H), 2.03 (dt, $J$ = 7.2, 6.8 Hz, 2H),1.69–1.61 (m, 2H), 1.38–1.26 (m, 12H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 148.1, 139.2, 129.2, 121.0, 120.9, 114.1, 52.3, 33.8, 29.5, 29.4, 29.4, 29.1, 28.9, 27.4, 27.1. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{32}N$, 322.2529; found, 322.2529.

**Ethyl[2-(undec-10-en-1-yloxy)ethyl]sulfane (2l)**

A flask was placed under $N_2$ atmosphere by three cycles of evacuating and $N_2$ backfilling and charged with NaH (0.48 g, 60 wt.% dispersion in oil, 12.0 mmol, 1.5 equiv.) in dry DMF (40 mL). 2-(Ethylthio)ethan-1-ol (0.83 mL, 8.0 mmol, 1.0 equiv.) was added and stirred for 1 h. 11-Bromoundec-1-ene (1.73 mL, 8.0 mmol, 1.0 equiv.) was added dropwise at 0 ℃. The reaction was stirred at room temperature overnight and then diluted with water. The water layer was extracted with $Et_2O$ three times. The combined $Et_2O$ layer was dried with $Na_2SO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–96:4, hexane/EtOAc) to afford the desired product **2l** (1.00 g, 3.9 mmol, 48 %) as a colorless oil.




**IR** (neat) 637, 909, 993, 1107, 1265, 1358, 1456, 1640, 2853, 2924 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 5.81 (m, 1H), 5.02–4.91 (m, 2H), 3.58 (t, $J$ = 7.2 Hz, 2H), 3.44 (t, $J$ = 6.8 Hz, 2H), 2.71 (t, $J$ = 7.2 Hz, 2H), 2.59 (q, $J$ = 7.2 Hz, 2H), 2.04 (dt, $J$ = 7.6, 6.8 Hz, 2H),1.60–1.53 (m, 2H), 1.42–1.25 (m, 15H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 139.2, 114.1, 71.2, 70.5, 33.8, 31.1, 29.7, 29.5, 29.4, 29.4, 29.1, 28.9, 26.4, 26.1, 14.9. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{15}H_{34}NOS$, 276.2356; found, 276.2364.

## 5. Procedures for Hydroalkoxylation of Alkenes by A Triple Catalysis

**The reaction in Table 1, entry 1 is representative (limiting reagent: alkene).** In a glovebox, to an oven-dried vial with a stirring bar was added photoredox catalyst **PTH-1** (3.7 mg, 0.01 mmol), **Co-1** (1.2 mg, 0.002 mmol), **HX-1** (5.4 mg, 0.02 mmol) and DCM (500 μL). Then, cyclopentanol **1a** (54.4 μL, 0.6 mmol) and 4-phenyl-1-butene **2a** (30.0 μL, 0.2 mmol) were added to the reaction mixture. After sealing the vial with a cap and removal from the glove box, the reaction was stirred and irradiated with a 34W blue LED (0.5 cm away) with a cooling fan to keep the temperature around 40 °C (Figure S2). After 24 h, the reaction was quenched with a short plug of silica gel using diethyl ether. After volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) gave the **3aa** (32.3 mg, 0.15 mmol, 74% isolated yield) as a pale yellow oil.

**The reaction in Table 1, entry 13 is representative (limiting reagent: alcohol).** In a glovebox, to an oven-dried vial with a stirring bar was added photoredox catalyst **PTH-1** (3.7 mg, 0.01 mmol), **Co-1** (1.2 mg, 0.002 mmol), **HX-1** (5.4 mg, 0.02 mmol) and DCM (500 μL). Then, cyclopentanol **1a** (18.1 μL, 0.2 mmol) and 4-phenyl-1-butene **2a** (60.1 μL, 0.4 mmol) were added to the reaction mixture. After sealing the vial with a cap and removal from the glove box, the reaction was stirred and irradiated with a 34W blue LED (0.5 cm away) with a cooling fan to keep the temperature around 40 °C (Figure S2). After 24 h, the reaction was quenched with a short plug of silica gel using diethyl ether. After volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) gave the **3aa** (37.6 mg, 0.17 mmol, 86% isolated yield.) as a pale yellow oil.

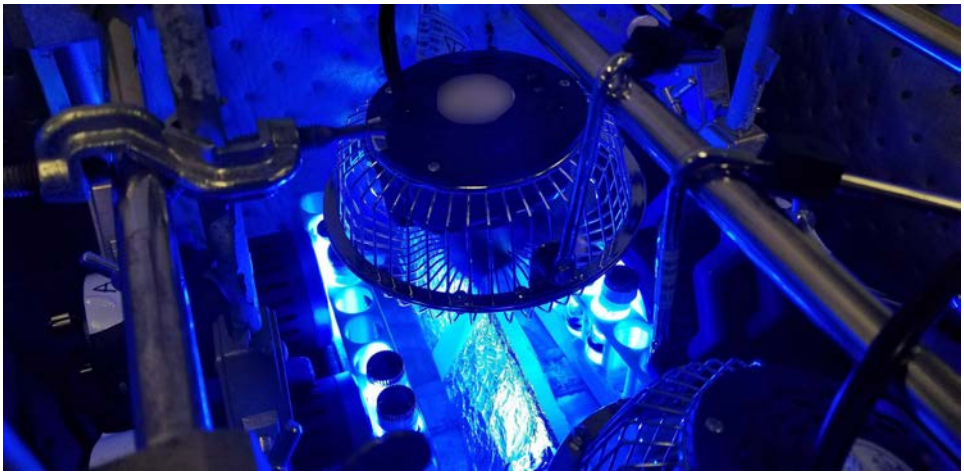
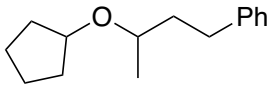


**Figure S2.** Light set up

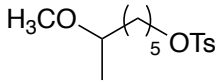
## 6. Characterization Data for Coupling Products

**[3-(Cyclopentyloxy)butyl]benzene (3aa)**



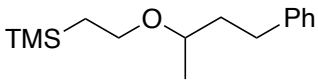

The product **3aa** was purified by flash chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) (Table 1, entry 1; 32.3 mg, 0.15 mmol, 74% isolated yield. Table 1, entry 13; 37.6 mg, 0.17 mmol, 86% isolated yield.). Pale yellow oil. **IR** (neat) 698, 745, 1091, 1132, 1337, 1371, 1453, 1495, 2869, 2961 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.27 (t, $J$ = 8.0 Hz, 2H), 7.20–7.15 (m, 3H), 3.98 (quintet, $J$ = 5.2 Hz, 1H), 3.38 (m, 1H), 2.75 (m, 1H), 2.61 (m, 1H), 1.86–1.49 (m, 10H), 1.16 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.6, 128.4, 128.3, 125.6, 78.8, 72.6, 38.8, 33.2, 32.5, 32.1, 23.4, 23.3, 20.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{23}O$; 219.1743, found 219.1746.

**2-Methoxypropyl-4-methylbenzenesulfonate (3bb)**



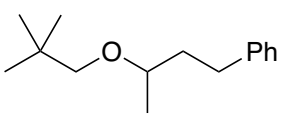

The product **3bb** was purified by flash chromatography on silica gel (Biotage Selekt, 98:2–88:12, hexane/EtOAc) (Figure 1; 27.6 mg, 0.09 mmol, 46% isolated yield). Pale yellow oil. **IR** (neat) 555, 664, 815, 940, 1096, 1176, 1188, 1359, 2861, 2932 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 4.02 (t, $J$ = 6.4 Hz, 2H), 3.29 (s, 3H), 3.24 (m, 1H), 2.45 (s, 3H), 1.68–1.61 (m, 2H), 1.46 (m, 1H), 1.37–1.21 (m, 5H), 1.09 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 144.6, 133.2, 129.8, 127.8, 76.5, 70.6, 55.9, 36.1, 28.8, 25.4, 24.7, 21.6, 18.9. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{25}O_4S$; 301.1468, found 301.1461.

**Trimethyl{2-[(4-phenylbutan-2-yl)oxy]ethyl}silane (3ca)**




The product **3ca** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–97:3, hexane/EtOAc) (Figure 1; 27.0 mg, 0.11 mmol, 54% isolated yield). Pale yellow oil. **IR** (neat) 835, 858, 1091, 1134, 1247, 1454, 1496, 2860, 2925, 2952 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.30–7.26 (m, 2H), 7.20–7.16 (m, 3H), 3.58 (m, 1H), 3.43–3.36 (m, 2H), 2.76–2.61 (m, 2H), 1.84 (m, 1H), 1.70 (m, 1H), 1.16 (d, $J$ = 6.0 Hz, 3H), 0.96–0.91 (m, 2H), 0.02 (s, 9H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.5, 128.4, 128.3, 125.6, 74.0, 65.3, 38.5, 31.9, 19.7, 18.6, –1.3. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{15}H_{30}NOSi$; 268.2091, found 268.2096.

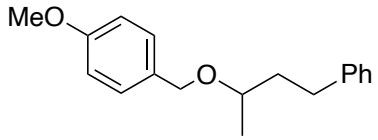
**[3-(Neopentyloxy)butyl]benzene (3da)**




The product **3da** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 24.2 mg, 0.11 mmol, 55% isolated yield). Colorless oil. **IR** (neat) 698, 744, 1092, 1137, 1362, 1455, 1479, 1604, 2865, 2952 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28 (t, $J$ = 7.2 Hz, 2H),

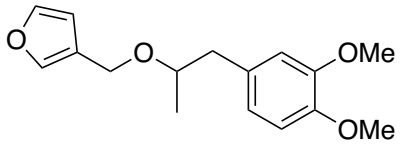
7.20–7.15 (m, 3H), 3.35 (sixtet, $J$ = 6.4 Hz, 1H), 3.16 (d, $J$ = 8.8 Hz, 1H), 2.96 (d, $J$ = 8.8 Hz, 1H), 2.76 (ddd, $J$ = 13.6, 9.2, 6.4 Hz, 1H), 2.65 (ddd, $J$ = 13.6, 9.6, 6.4 Hz, 1H), 1.84 (m, 1H), 1.69 (m, 1H), 1.13 (d, $J$ = 6.4 Hz, 3H), 0.92 (s, 9H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.7, 128.4, 128.3, 125.6, 78.9, 74.8, 38.7, 32.1, 31.9, 26.8, 19.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{25}O$; 221.1900, found 221.1903.

**1-Methoxy-4-{[(4-phenylbutan-2-yl)oxy]methyl}benzene (3ea)**



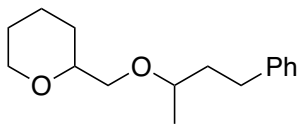

The product **3ea** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 40.6 mg, 0.15 mmol, 75% isolated yield). Colorless oil. The spectrum data of product **3ea** was consistent with the literature.[8]

**3-({[1-(3,4-Dimethoxyphenyl)propan-2-yl]oxy}methyl)furan (3fc)**




The reaction conditions were modified. The reaction was carried out with **1f** (17.2 μL, 0.2 mmol), **2c** (34.3 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3fc** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 53.1 mg, 0.19 mmol, 96% isolated yield). Colorless oil. **IR** (neat) 874, 1029, 1090, 1141, 1157, 1237, 1262, 1515, 2835, 2933 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36 (s, 1H), 7.33 (s, 1H), 6.80 (d, $J$ = 8.4 Hz, 1H), 6.74–6.73 (m, 2H), 6.30 (s, 1H), 4.42 (d, $J$ = 12.0 Hz, 1H), 4.29 (d, $J$ = 12.0 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.68 (m, 1H), 2.84 (dd, $J$ = 13.6, 6.0 Hz, 1H), 2.62 (dd, $J$ = 13.6, 6.0 Hz, 1H), 1.18 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 148.6, 147.4, 143.2, 140.2, 131.7, 122.8, 121.3, 112.7, 112.0, 110.3, 76.0, 62.1, 55.9, 55.8, 42.8, 19.6. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{16}H_{24}NO_4$; 294.1699, found 294.1696.

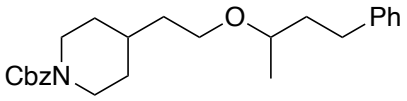
**2-{[(4-Phenylbutan-2-yl)oxy]methyl}tetrahydro-2H-pyran (3ga)**




The product **3ga** was purified by flash chromatography on silica gel (Biotage Selekt, 99:1–95:5, hexane/EtOAc) (Figure 1; 33.3 mg, 0.13 mmol, 67% isolated yield). Colorless oil. **IR** (neat) 699, 746, 1047, 1094, 1136, 1205, 1374, 1496, 2847, 2931 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by $^1$H NMR analysis. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.25 (m, 2H), 7.20–7.15 (m, 3H), 4.01 (m, 1H), 3.55–3.36 (m, 4H + 0.5 × 1H), 3.24 (m, 0.5 × 1H), 2.78–2.61 (m, 2H), 1.95–1.84 (m, 2H), 1.74–1.26 (m, 6H), 1.18–1.17 (m, 3H). Signals for two diastereomers were given: **$^{13}$C NMR**

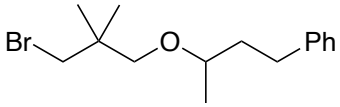
(100.6 MHz, $CDCl_3$) $\delta$ 142.5 (×2C) , 128.4 (×2C), 128.3 (×2C), 125.6, 125.6, 77.2 (×2C), 75.3 (×2C), 72.4, 72.1, 68.5, 68.5, 38.2, 38.2, 31.9 (×2C), 28.7, 28.6, 26.1, 26.0, 23.2, 23.1, 19.6 (×2C). **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{25}O_2$; 249.1849, found 249.1849.

**Benzyl 4-{2-[(4-Phenylbutan-2-yl)oxy]ethyl}piperidine-1-carboxylate (3ha)**



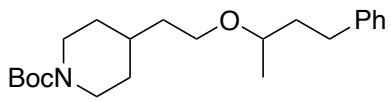

The product **3ha** was purified by flash chromatography on silica gel (99:1–85:15, hexane/EtOAc) (Figure 1; 30.1 mg, 0.08 mmol, 38% isolated yield). Colorless oil. **IR** (neat) 1087, 1135, 1208, 1238, 1276, 1364, 1429, 1696, 2856, 2924 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36–7.25 (m, 7H), 7.19–7.17 (m, 3H), 5.12 (s, 2H), 4.16 (brs, 2H), 3.53 (m, 1H), 3.39–3.33 (m, 2H), 2.78–2.59 (m, 4H), 1.84 (m, 1H), 1.74–1.57 (m, 4H), 1.51 (quintet, $J$ = 6.0 Hz, 2H), 1.16–1.13 (m, 5H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 155.2, 142.3, 136.9, 128.4, 128.3, 128.3, 127.9, 127.8, 125.7, 74.6, 66.9, 65.5, 44.2, 38.3, 36.6, 32.8, 32.0, 31.8, 19.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{34}NO_3$; 396.2533, found 396.2540.

**[3-(3-Bromo-2,2-dimethylpropoxy)butyl]benzene (3ia)**




The reaction conditions were modified. The reaction was carried out with **1i** (73.7 μL, 0.6 mmol), **2a** (30.0 μL, 0.2 mmol), **Ir(ppy)$_3$** (1.3 mg, 0.002 mmol, 1 mol %) or **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3ia** was purified by flash chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) (Figure 1; **Ir(ppy)$_3$**: 31.0 mg, 0.10 mmol, 52% isolated yield, **PTH-1**: 23.9 mg, 0.08 mmol, 40 % isolated yield). Pale yellow oil. **IR** (neat) 698, 744, 1089, 1135, 1377, 1454, 1474, 2863, 2928, 2964. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28 (t, $J$ = 7.6 Hz, 2H), 7.21–7.16 (m, 3H), 3.45–3.35 (m, 3H), 3.29 (d, $J$ = 8.8 Hz, 1H), 3.14 (d, $J$ = 8.8 Hz, 1H), 2.75 (m, 1H), 2.64 (m, 1H), 1.83 (m, 1H), 1.70 (m, 1H), 1.14 (d, $J$ = 6.0 Hz, 3H), 1.03 (s, 6H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.6, 128.4, 128.3, 125.6, 74.8, 74.3, 43.9, 38.6, 36.2, 31.8, 23.5, 19.5. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{24}BrO$; 299.1005, found 299.1003.

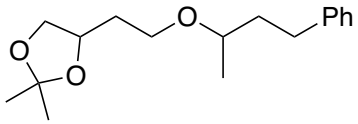
***tert*-Butyl 4-{2-[(4-Phenylbutan-2-yl)oxy]ethyl}piperidine-1-carboxylate (3ja)**




The product **3ja** was purified by flash chromatography on silica gel (Biotage Selekt, 98:2–85:15, hexane/EtOAc) (Figure 1; 41.9 mg, 0.12 mmol, 58% isolated yield). Colorless oil. **IR** (neat) 1138, 1171, 1245, 1277, 1365, 1421, 1693, 2856, 2926, 2970 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.26 (m, 2H), 7.19–7.16 (m, 3H), 4.06 (brs, 2H), 3.54 (dt, $J$ = 9.2, 6.4 Hz, 1H), 3.41–3.34 (m, 2H),

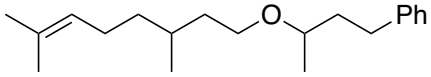
2.76–2.60 (m, 4H), 1.85 (m, 1H), 1.75–1.65 (m, 3H), 1.61–1.49 (m, 3H), 1.45(s, 9H), 1.18–1.10 (m, 5H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 154.9, 142.3, 128.3, 128.3, 125.7, 79.1, 74.6, 65.6, 44.0 (×2C), 38.3, 36.7, 32.9, 32.2, 32.0, 31.8, 28.4, 19.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{36}NO_3$; 362.2690, found 362.2695.

**2,2-Dimethyl-4-{2-[(4-phenylbutan-2-yl)oxy]ethyl}-1,3-dioxolane (3ka)**



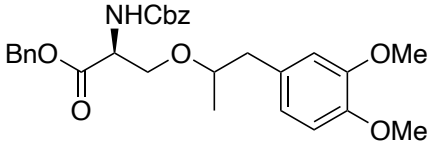

The product **3ka** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–90:10, hexane/EtOAc) (Figure 1; 22.8 mg, 0.08 mmol, 41% isolated yield). Pale yellow oil. **IR** (neat) 859, 1055, 1088, 1214, 1369, 1454, 1496, 2853, 2930, 2983 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by $^1$H NMR analysis. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.27 (t, $J$ = 7.6 Hz, 2H), 7.20–7.16 (m, 3H), 4.25 (m, 0.5 × 1H), 4.20 (m, 0.5 × 1H), 4.08 (m, 1H), 3.66–3.54 (m, 2H), 3.48–3.35 (m, 2H), 2.76–2.59 (m, 2H), 1.94–1.77 (m, 3H), 1.68 (m, 1H), 1.41 (s, 3H), 1.36 (s, 3H), 1.16 (d, $J$ = 6.0 Hz, 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.3, 142.3, 128.4, 128.4, 128.3 (×2C), 125.7 (×2C), 108.5, 108.4, 74.7, 74.7, 74.1, 73.8, 69.7, 69.7, 64.9, 64.9, 38.4, 38.3, 34.2, 34.2, 31.8, 31.7, 26.9, 25.8, 19.5, 19.5. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{27}O_3$; 279.1955, found 279.1954.

**{3-[(3,7-Dimethyloct-6-en-1-yl)oxy]butyl}benzene (3la)**




The product **3la** was purified by flash chromatography on silica gel (100:0–95:5, hexane/$Et_2O$) (Figure 1; 42.7mg, 0.15 mmol, 74% isolated yield). Colorless oil. **IR** (neat) 698, 1094, 1136, 1339, 1375, 1454, 1496, 2859, 2924, 2964 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by $^1$H-NMR analysis. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.25 (m, 2H), 7.20–7.15 (m, 3H), 5.11 (m, 1H), 3.52 (m, 1H), 3.41–3.31 (m, 2H), 2.73 (m, 1H), 2.34 (m, 1H), 2.07–1.90 (m, 2H), 1.84 (m, 1H), 1.75–1.56 (m, 9H), 1.45–1.31 (m, 2H), 1.18–1.15 (m, 4H), 0.90 (d, $J$ = 6.0 Hz, 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.5 (×2C), 131.1 (×2C), 128.4 (×4C), 128.3 (×4C), 125.6 (×2C), 124.9 (×2C), 74.5, 74.5, 66.6 (×2C), 38.5 (×2C), 37.3, 37.2, 37.2, 37.2, 31.9, 31.9, 29.6, 29.6, 25.7 (×2C), 25.5 (×2C), 19.7, 19.7 (×2C), 19.5, 17.6 (×2C). **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{33}O$; 289.2526, found 289.2524.

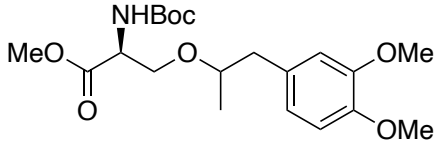
**Benzyl *N*-[(Benzyloxy)carbonyl]-*O*-[1-(3,4-dimethoxyphenyl)propan-2-yl]-L-serinate (3mc)**




The reaction conditions were modified. The reaction was carried out with **1m** (65.9 mg, 0.2 mmol), **2c** (34.3 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), and **HX-1** (5.4 mg, 0.02 mmol, 10

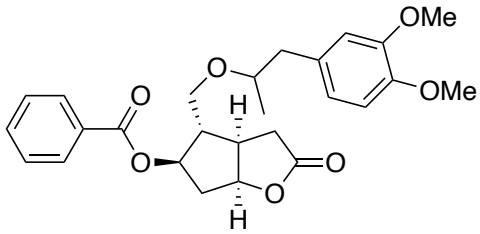
mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3mc** was purified by flash chromatography on silica gel (Biotage Selekt, 98:2–80:20, hexane/AcOEt) (Figure 1; 61.2mg, 0.12 mmol, 60% isolated yield). Pale yellow oil. **IR** (neat) 1029, 1158, 1237, 1262, 1338, 1455, 1516, 1725, 2933, 3345 $cm^{-1}$. The ratio (50:50) of the diastereomers was determined by $^1H$ NMR analysis. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.37–7.25 (m, 10H), 6.73–6.63 (m, 3H), 5.59 (d, $J$ = 8.8 Hz, 0.5 × 1H), 5.39 (d, $J$ = 8.8 Hz, 0.5 × 1H), 5.26–4.99 (m, 4H), 4.47 (m, 1H), 4.00 (dd, $J$ = 8.8, 2.4 Hz, 0.5 × 1H), 3.84–3.73 (m, 7H), 3.55–3.44 (m, 1H + 0.5 × 1H), 2.67 (m, 1H), 2.52 (m, 1H), 1.08 (d, $J$ = 6.0 Hz, 0.5 × 3H), 1.03 (d, $J$ = 6.0 Hz, 0.5 × 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 170.1, 170.1, 155.9, 155.9, 148.5, 148.4, 147.3, 147.2, 136.2, 136.0, 135.3, 135.2, 131.1, 131.0, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 121.1, 121.0, 112.6, 112.3, 110.8, 110.8, 77.6, 77.3, 68.6, 68.1, 66.9, 66.9, 66.9, 66.7, 55.6, 55.6, 55.5, 54.5, 54.4, 42.5, 42.4, 19.0, 18.9 (Only observed peaks). **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{29}H_{34}NO_7$; 508.2330, found 508.2340.

**Methyl *N*-(*tert*-Butoxycarbonyl)-*O*-[1-(3,4-dimethoxyphenyl)propan-2-yl]-L-serinate (3nc)**



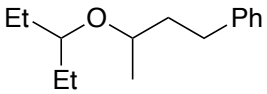

The reaction conditions were modified. The reaction was carried out with **1n** (43.8 mg, 0.2 mmol), **2c** (34.3 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h.The product **3nc** was purified by flash chromatography on silica gel (Biotage Selekt, 97:3–75:25, hexane/AcOEt) (Figure 1; 36.5mg, 0.09 mmol, 46% isolated yield). Pale yellow oil. **IR** (neat) 1030, 1160, 1238, 1262, 1516, 1716, 1752, 2934, 2973, 3407 $cm^{-1}$. The ratio (59:41) of the diastereomers was determined by $^1H$ NMR analysis. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.79 (m, 1H), 6.71–6.67 (m, 2H), 5.30 (d, $J$ = 8.4 Hz, 0.41 × 1H), 5.17 (d, $J$ = 8.4 Hz, 0.59 × 1H), 4.35 (m, 1H), 3.95–3.85 (m, 6H + 0.59 × 1H), 3.74–3.70 (m, 0.59 × 3H + 0.41 × 2H), 3.63 (s, 0.41 × 3H), 3.55 (m, 1H), 3.49 (dd, $J$ = 9.2, 3.2 Hz, 0.59 × 1H), 2.73 (m, 1H), 2.57 (m, 1H), 1.45 (s, 0.41 × 9H), 1.44 (s, 0.59 × 9H), 1.12 (d, $J$ = 6.0 Hz, 0.41 × 3H), 1.10 (d, $J$ = 6.0 Hz, 0.59 × 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 171.2, 171.2, 155.5, 148.7, 148.6, 147.5, 147.4, 131.4, 131.3, 121.3, 121.2, 112.8, 112.7, 111.0, 79.9, 79.8, 77.7, 77.4, 68.7, 68.5, 55.9, 55.8, 55.8, 54.2, 54.1, 52.3, 52.2, 42.6, 42.5, 28.3, 28.3, 19.2, 19.1 (Only observed peaks). **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{32}NO_7$; 398.2173, found 398.2168.

**(3aR,4S,5R,6aS)-4-({[1-(3,4-Dimethoxyphenyl)propan-2-yl]oxy}methyl)-2-oxohexahydro-2H-cyclopenta[b]furan-5-yl Benzoate (3oc)**



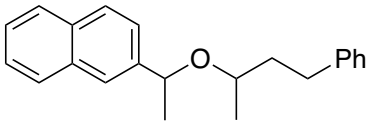
The reaction conditions were modified. The reaction was carried out with **1o** (27.6 mg, 0.1 mmol), **2c** (17.1 μL, 0.1 mmol), **PTH-1** (1.8 mg, 0.005 mmol, 5 mol %), and **HX-1** (2.7 mg, 0.01 mmol, 10 mol %) in DCM (250 μL) under blue LED irradiation for 24 h. The product **3oc** was purified by flash chromatography on silica gel (Biotage Selekt, 90:10–50:50, hexane/AcOEt) (Figure 1; 36.6 mg, 0.08 mmol, 81% isolated yield). Pale yellow oil. **IR** (neat) 714, 1027, 1108, 1263, 1273, 1451, 1516, 1714, 1771, 2965 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by $^{1}$H NMR analysis. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.98 (d, $J$ = 7.2 Hz, 2H), 7.55 (d, $J$ = 7.2 Hz, 1H), 7.44 (t, $J$ = 7.2 Hz, 2H), 6.78 (m, 1H), 6.72–6.70 (m, 2H), 5.33 (dt, $J$ = 6.0, 2.8 Hz, 0.5 × 1H), 5.25 (dt, $J$ = 6.0, 2.8 Hz, 0.5 × 1H), 5.01 (t, $J$ = 5.6 Hz, 0.5 × 1H), 4.95 (t, $J$ = 6.0 Hz, 0.5 × 1H), 3.89–3.83 (m, 6H), 3.63–3.56 (m, 2H), 3.33 (m, 1H), 2.88–2.24 (m, 8H), 1.16 (d, $J$ = 6.4 Hz, 0.5 × 3H), 1.14 (d, $J$ = 6.4 Hz, 0.5 × 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 176.8, 176.8, 166.0, 166.0, 148.7, 147.5, 133.2, 131.5, 131.4, 129.7, 129.6, 128.4, 121.3, 121.3, 112.6, 112.6, 111.1, 85.3, 85.2, 78.9, 78.7, 77.5, 77.4, 69.0, 55.9, 55.9, 53.5, 53.4, 42.9, 42.8, 40.9, 40.8, 38.8, 38.7, 36.2, 36.2, 19.4, 19.3 (Only observed peaks). **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{31}O_7$; 455.2064, found 455.2060.

**[3-(Pentan-3-yloxy)butyl]benzene (3pa)**



The product **3pa** was purified by flash chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) (Figure 1; 24.2 mg, 0.11 mmol, 55% isolated yield). Colorless oil. The spectrum data of product **3pa** was consistent with the literature.[9]

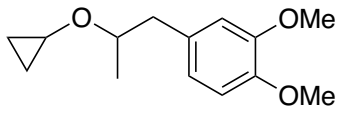
**2-{1-[(4-Phenylbutan-2-yl)oxy]ethyl}naphthalene (3qa)**



The product **3qa** was purified by flash chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) (Figure 1; 30.4 mg, 0.10 mmol, 50% isolated yield). Pale yellow oil. **IR** (neat) 747, 820, 1086, 1126, 1319, 1372, 1454, 2927, 2971, 3057 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by $^{1}$H NMR analysis. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.86–7.80 (m, 3H), 7.72 (s, 0.5 × 1H), 7.69 (s, 0.5 × 1H), 7.55–7.43 (m, 3H), 7.31–7.27 (m, 1H), 7.22–7.18 (m, 0.5 × 1H + 1H), 7.13–7.05 (m, 0.5 × 1H + 1H), 6.96 (m, 1H), 4.69 (q, $J$ = 6.4 Hz, 0.5 × 1H), 4.65 (q, $J$ = 6.4 Hz, 0.5 × 1H), 3.49 (sixtet, $J$ = 6.0 Hz, 0.5 × 1H), 3.38 (m, 0.5 × 1H), 2.74–2.67 (m, 0.5 × 1H + 1H), 2.40 (m, 0.5 × 1H), 1.97–1.76

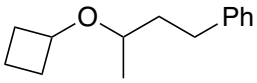
(m, 0.5 × 1H + 1H), 1.61 (m, 0.5 × 1H), 1.53 (d, $J$ = 6.4 Hz, 0.5 × 3H), 1.50 (d, $J$ = 6.4 Hz, 0.5 × 3H), 1.20 (d, $J$ = 6.4 Hz, 0.5 × 3H), 1.08 (d, $J$ = 6.4 Hz, 0.5 × 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) *d* 142.4, 142.4, 142.3, 141.7, 133.2, 133.2, 133.0, 132.9, 128.4 (×2C), 128.3, 128.3, 128.2, 128.1, 127.8, 127.8, 127.7, 127.7, 126.0, 126.0, 125.7, 125.7, 125.6, 125.5, 124.9 (×2C), 124.6, 124.4, 75.8, 74.8, 72.6, 71.6, 39.2, 37.8, 32.1, 31.6, 24.5, 24.0, 20.8, 19.4 (Only observed peaks). **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{22}H_{28}NO$; 322.2165, found 322.2172.

**4-(2-Cyclopropoxypropyl)-1,2-dimethoxybenzene (3rc)**



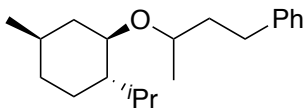

The reaction conditions were modified. The reaction was carried out with **1r** (11.7 μL, 0.2 mmol), **2c** (34.3 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3rc** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 19.2 mg, 0.08 mmol, 41% isolated yield). Colorless oil. **IR** (neat) 1030, 1141, 1157, 1210, 1238, 1262, 1516, 2833, 2932, 2968 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.79 (m, 1H), 6.73–6.72 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.72 (sixtet, $J$ = 6.4 Hz, 1H), 3.30 (m, 1H), 2.83 (dd, $J$ = 14.4, 6.4 Hz, 1H), 2.55 (dd, $J$ = 14.4, 6.4 Hz, 1H), 1.18 (d, $J$ = 6.4 Hz, 3H), 0.54 (m, 1H), 0.47 (m, 1H), 0.43–0.32 (m, 2H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 148.5, 147.3, 131.8, 121.3, 112.7, 110.9, 77.2, 55.8, 55.8, 51.2, 42.8, 19.8, 6.0, 5.5. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{14}H_{24}NO_3$; 254.1751, found 254.1755.

**(3-Cyclobutoxybutyl)benzene (3sa)**




The product **3sa** was purified by flash chromatography on silica gel (100:0–97.5:2.5, hexane/$Et_2O$) (Figure 1; 29.4 mg, 0.14 mmol, 72% isolated yield). Pale yellow oil. **IR** (neat) 698, 747, 1113, 1145, 1238, 1333, 1372, 1496, 2871, 2969 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) 7.29 (t, $J$ = 12.0 Hz, 2H), 7.20–7.15 (m, 3H), 3.97 (quintet, $J$ = 7.6 Hz, 1H), 3.40 (sixtet, $J$ = 6.4Hz, 1H), 2.74 (ddd, $J$ = 14.0, 9.2, 5.6 Hz, 1H), 2.63 (ddd, $J$ = 14.0, 9.2, 4.8 Hz, 1H), 2.23–2.16 (m, 2H), 2.01–1.87 (m, 2H), 1.80 (m, 1H), 1.72–1.63 (m, 2H), 1.46 (m, 1H), 1.14 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.4, 128.4, 128.3, 125.6, 72.7, 71.4, 38.6, 31.9, 31.8, 31.3, 20.4, 12.7. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{21}O$; 205.1587, found 205.1586.

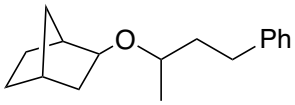
**(3-{[(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl]oxy}butyl)benzene (3ta)**




The product **3ta** was purified by flash chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) (Figure 1; 28.8 mg, 0.10 mmol, 50% isolated yield). Pale yellow oil. **IR** (neat) 698, 745, 1050, 1085, 1131, 1371, 1454, 2868, 2921, 2953 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by

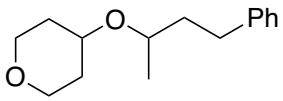
$^1$H NMR analysis. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31–7.25 (m, 2H), 7.21–7.15 (m, 3H), 3.53 (m, 1H), 3.09 (dd, $J$ = 10.8, 4.0 Hz, 0.5 × 1H), 3.04 (dd, $J$ = 10.8, 4.0 Hz, 0.5 × 1H), 2.77–2.58 (m, 2H), 2.28 (m, 1H), 2.01 (m, 1H), 1.81 (m, 1H), 1.72 (m, 1H), 1.67–1.60 (m, 2H), 1.39–1.12 (m, 5H), 1.01–0.82 (m, 9H), 0.80–0.74 (m, 3H). Signals for two diastereomers were given:**$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.6, 142.5, 128.4, 128.3, 128.3, 128.2, 125.6, 125.6, 77.8, 76.2, 73.3, 71.9, 48.8, 48.5, 42.5, 41.7, 39.2, 38.6, 34.5, 34.5, 32.1, 31.7, 31.6, 31.6, 24.9, 23.1, 23.0, 22.4, 21.6, 21.3, 21.3, 20.1, 16.0, 16.0. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{33}O$; 289.2526, found 289.2528.

**2-[(4-Phenylbutan-2-yl)oxy]bicyclo[2.2.1]heptane (3ua)**



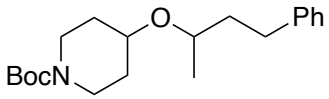

The product **3ua** was purified by flash chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) (Figure 1; 35.8 mg, 0.15 mmol, 73% isolated yield). Colorless oil. **IR** (neat) 698, 1058, 1086, 1132, 1339, 1371, 1453, 1496, 2869, 2953 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by $^1$H NMR analysis. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.25 (m, 2H), 7.20–7.15 (m, 3H), 3.51–3.40 (m, 2H), 2.74 (m, 1H), 2.60 (m, 1H), 2.23 (s, 2H), 1.80 (m, 1H), 1.68 (m, 1H), 1.57 (m, 1H), 1.52–1.43 (m, 2H), 1.42–1.34 (m, 2H), 1.16 (d, $J$ = 6.0 Hz, 0.5 × 3H), 1.13 (d, $J$ = 6.0 Hz, 0.5 × 3H), 1.11–0.91 (m, 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.6, 142.5, 128.4 (×2C), 128.3, 128.3, 125.6 (×2C), 80.0, 79.5, 72.1, 71.8, 41.8, 40.5, 40.3, 39.9, 38.9, 38.8, 35.2, 35.1, 34.9, 34.8, 32.2, 32.1, 28.6 (×2C), 24.8, 24.7, 20.6, 20.3. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{17}H_{28}NO$; 262.2165, found 262.2162.

**4-[(4-Phenylbutan-2-yl)oxy]tetrahydro-2H-pyran (3va)**



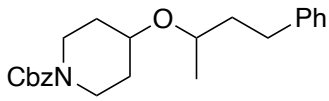

The product **3va** was purified by flash chromatography on silica gel (100:0–85:15, hexane/EtOAc) (Figure 1; 19.7 mg, 0.08 mmol, 42% isolated yield). The reaction was also carried out with **1v** (19.1 μL, 0.2 mmol), **2a** (60.1 μL, 0.4 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3va** was purified by flash chromatography on silica gel (100:0–85:15, hexane/EtOAc) (Figure 1; 16.9 mg, 0.07 mmol, 36% isolated yield). Yellow oil. **IR** (neat) 699, 746, 871, 1002, 1088, 1130, 1372, 1454, 2853, 2925 cm $^{-1}$. **$^1$H NMR** $\delta$ 7.28 (t, $J$ = 8.0 Hz, 2H), 7.20–7.16 (m, 3H), 3.95 (dt, $J$ = 12.0, 4.4 Hz, 2H), 3.58–3.50 (m, 2H), 3.47–3.40 (m, 2H), 2.76 (ddd, $J$ = 12.0, 10.0, 6.4 Hz, 1H), 2.74 (ddd, $J$ = 12.0, 10.0, 5.6 Hz, 1H), 1.88–1.79 (m, 3H), 1.72 (m, 1H), 1.65–1.52 (m, 2H), 1.17 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.3, 128.3, 128.3, 125.7, 71.8, 71.6, 65.9, 65.9, 38.8, 33.8, 32.8, 32.0, 20.7. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{15}H_{26}NO_2$; 252.1958, found 252.1958.

***tert*-Butyl 4-[(4-Phenylbutan-2-yl)oxy]piperidine-1-carboxylate (3wa)**



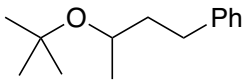

The product **3wa** was purified by flash chromatography on silica gel (100:0–85:15, hexane/EtOAc) (Figure 1; 28.0 mg, 0.08 mmol, 42% isolated yield). Colorless oil. **IR** (neat) 1037, 1089, 1132, 1172, 1236, 1365, 1422, 1693, 2861, 2928 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.26 (m, 2H), 7.19–7.16 (m, 3H), 3.80–3.77 (m, 2H), 3.56–3.46 (m, 2H), 3.10–3.03 (m, 2H), 2.75 (m, 1H), 2.61 (m, 1H), 1.87–1.68 (m, 4H), 1.55–1.44 (m, 11H), 1.16 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 154.9, 142.3, 128.3 (×2C), 125.7, 79.4, 72.2, 72.0, 41.5 (×2C), 38.9, 32.4, 32.0, 31.4, 28.4, 20.7. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{32}NO_3$; 334.2377, found 334.2381.

**Benzyl 4-[(4-Phenylbutan-2-yl)oxy]piperidine-1-carboxylate (3xa)**



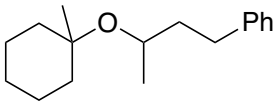

The product **3xa** was purified by flash chromatography on silica gel (100:0–83:17, hexane/EtOAc) (Figure 1; 31.6 mg, 0.09 mmol, 43% isolated yield). Colorless oil. **IR** (neat) 698, 748, 1036, 1084, 1130, 1226, 1429, 1696, 2861, 2927 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.37–7.25 (m, 7H), 7.19–7.16 (m, 3H), 5.13 (s, 2H), 3.82 (brs, 2H), 3.57–3.49 (m, 2H), 3.23–3.16 (m, 2H), 2.74 (m, 1H), 2.65 (m, 1H), 1.87–1.69 (m, 4H), 1.53 (brs, 2H), 1.16 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 155.3, 142.2, 136.9, 128.5, 128.3, 128.3, 127.9, 127.8, 125.7, 72.0, 71.8, 67.0, 41.5, 41.5, 38.8, 32.3, 32.0, 31.2, 20.6. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{30}NO_3$; 368.2220, found 368.2221.

**[3-(*tert*-Butoxy)butyl]benzene (3ya)**




The reaction conditions were modified. The reaction was carried out with **1y** (191.3 μL, 2.0 mmol), **2a** (30.0 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3ya** was purified by flash chromatography on silica gel (100:0–97:3, hexane/$Et_2O$) (Figure 1; 27.6 mg, 0.13 mmol, 67% isolated yield). Pale yellow oil. The spectrum data of product **3ya** was consistent with the literature.[10]

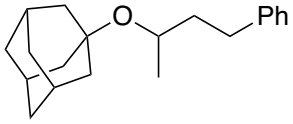
**{3-[(1-Methylcyclohexyl)oxy]butyl}benzene (3za)**




The product **3za** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–90:10, hexane/DCM) (Figure 1; **1a** (10 equiv.) : 28.1 mg, 0.11 mmol, 57% isolated yield. **1a** (3 equiv.) : 22.7 mg, 0.09 mmol, 46% isolated yield). Pale yellow oil. **IR** (neat) 698, 745, 1054, 1122, 1167, 1374, 1448, 2858, 2929, 2966 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.24 (m, 2H), 7.20–7.15 (m, 3H),

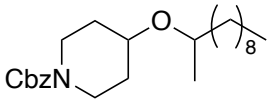
3.69 (sixtet, $J$ = 6.0 Hz, 1H), 2.65 (t, $J$ = 8.4 Hz, 2H), 1.86–1.68 (m, 2H), 1.63–1.56 (m, 4H), 1.43–1.37 (m, 6H), 1.18 (d, $J$ = 6.0 Hz, 3H), 1.13 (s, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.7, 128.3, 128.3, 125.6, 74.6, 65.9, 40.6, 37.8, 37.4, 32.1, 25.9, 25.2, 22.9, 22.9, 22.9. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{27}O$; 247.2056, found 247.2058.

**1-[(4-Phenylbutan-2-yl)oxy]adamantane (3Aa)**



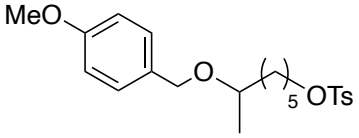

The product **3Aa** was purified by flash chromatography on silica gel (100:0–98:2, hexane/EtOAc) (Figure 1; 27.3 mg, 0.10 mmol, 48% isolated yield). Pale yellow oil. **IR** (neat) 698, 746, 984, 1084, 1115, 1354, 1371, 1453, 2850, 2904 cm $^{-1}$. **$^1$H NMR** $\delta$ 7.27 (t, $J$ = 7.2 Hz, 2H), 7.20–7.15 (m, 3H), 3.80 (sixtet, $J$ = 6.0 Hz, 1H), 2.72 (ddd, $J$ = 13.6, 10.0, 5.2 Hz, 1H), 2.58 (ddd, $J$ = 13.6, 10.0, 5.2 Hz, 1H), 2.13 (s, 3H), 1.82–1.57 (m, 14H), 1.16 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 142.7, 128.3, 128.2, 125.6, 72.5, 65.0, 42.8, 40.6, 36.4, 32.6, 30.6, 23.5. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{29}O$; 285.2213, found 285.2210.

**Benzyl 4-(Undecan-2-yloxy)piperidine-1-carboxylate (3xd)**




The product **3xd** was purified by flash chromatography on silica gel (Biotage Selekt, 99:1–84:16, hexane/EtOAc) (Figure 1; 33.5 mg, 0.09 mmol, 43% isolated yield). Pale yellow oil. **IR** (neat) 1039, 1088, 1126, 1225, 1273, 1363, 1429, 1701, 2854, 2924 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36–7.27 (m, 5H), 5.12 (s, 2H), 3.82 (brs, 2H), 3.54–3.45 (m, 2H), 3.24–3.16 (m, 2H), 1.78 (brs, 2H), 1.49–1.44 (m, 2H), 1.37–1.18 (m, 16H), 1.11 (d, $J$ = 6.0 Hz, 3H), 0.88 (t, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 155.3, 136.9, 128.4, 127.9, 127.8, 72.7, 71.6, 67.0, 41.5, 41.5, 37.3, 31.9, 29.7, 29.6, 29.6, 29.3, 25.8, 22.7, 20.6, 14.1. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{40}NO_3$; 390.3006, found 390.3003.

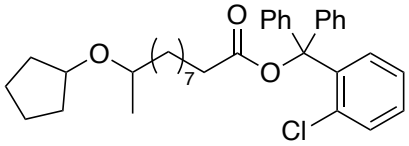
**6-[(4-Methoxybenzyl)oxy]heptyl 4-Methylbenzenesulfonate (3eb)**




The product **3eb** was purified by flash chromatography on silica gel (99:1–90:10, hexane/EtOAc) (Figure 1; 45.5 mg, 0.11 mmol, 56% isolated yield). Colorless oil. **IR** (neat) 576, 814, 937, 1173, 1245, 1356, 1512, 1612, 2860, 2933 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H), 7.33 (d, $J$ = 8.4 Hz, 2H), 7.24 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 2H), 4.48 (d, $J$ = 11.2 Hz, 1H), 4.34 (d, $J$ = 11.2 Hz, 1H), 4.01 (t, $J$ = 6.8 Hz, 2H), 3.80 (s, 3H), 3.44 (sixtet, $J$ = 6.0 Hz, 1H), 2.44 (s, 3H), 1.66–1.59 (m, 2H), 1.50 (m, 1H), 1.43–1.21 (m, 5H), 1.14 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 159.0, 144.6, 133.2, 131.0, 129.8, 129.2, 127.9, 113.7, 74.2, 70.6, 69.9, 55.3, 36.4,

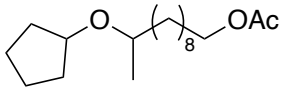
28.8, 25.4, 24.9, 21.6, 19.6. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{22}H_{34}NO_5S$; 424.2152, found 424.2146.

**(2-Chlorophenyl)diphenylmethyl 9-(Cyclopentyloxy)decanoate (3ae)**



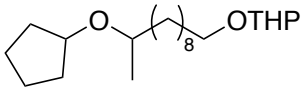

The product **3ae** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–96:4, hexane/EtOAc) (Figure 1; 17.1 mg, 0.03 mmol, 16% isolated yield). Paleyellow oil. **IR** (neat) 700, 755, 1044, 1149, 1337, 1370, 1447, 1742, 2855, 2928 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35–7.16 (m, 14H), 3.96 (m, 1H), 3.38 (m, 1H), 2.54 (t, $J$ = 7.6 Hz, 2H), 1.77–1.62 (m, 6H), 1.60–1.41 (m, 4H), 1.39–1.26 (m, 12H), 1.10 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 172.0, 142.8, 139.9, 133.7, 131.7, 131.5, 129.1, 128.0, 127.8, 127.3, 125.8, 89.5, 78.6, 73.1, 37.2, 35.0, 33.1, 32.5, 29.7, 29.5, 29.3, 29.2, 25.8, 24.8, 23.4, 23.3, 20.4. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{35}H_{47}ClNO_3$; 564.3239, found 564.3236.

**10-(Cyclopentyloxy)undecyl acetate (3af)**



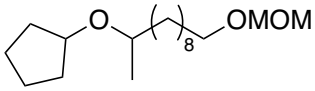

The product **3af** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–98:2, hexane/EtOAc) (Figure 1; 37.6 mg, 0.13 mmol, 63% isolated yield). Pale yellow oil. **IR** (neat) 1042, 1117, 1132, 1236, 1366, 1437, 1458, 1741, 1458, 1741, 2855, 2927 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 4.05 (d, $J$ = 6.4 Hz, 2H), 3.97 (quintet, $J$ = 4.4 Hz, 1H), 3.38 (sixtet, $J$ = 5.2 Hz, 1H), 2.05 (s, 3H), 1.76–1.42 (m, 11H), 1.35–1.28 (m, 13H), 1.10 (d, $J$ = 5.2 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 171.3, 78.6, 73.2, 64.7, 37.2, 33.1, 32.5, 29.7, 29.5, 29.5, 29.2, 28.6, 25.9, 25.8, 23.4, 23.3, 21.0, 20.4. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{18}H_{38}NO_3$; 316.2846, found 316.2846.

**2-{[10-(Cyclopentyloxy)undecyl]oxy}tetrahydro-2H-pyran (3ag)**



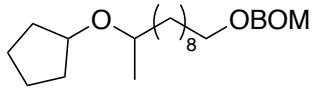

The product **3ag** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 34.6 mg, 0.10 mmol, 51% isolated yield). Pale yellow oil. **IR** (neat) 869, 1034, 1079, 1121, 1201, 1340, 1370, 1454, 2855, 2928 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 4.58 (m, 1H), 3.96 (m, 1H), 3.87 (m, 1H), 3.73 (m, 1H), 3.50 (m, 1H), 3.41–3.35 (m, 2H), 1.84 (m, 1H), 1.75–1.64 (m, 5H), 1.61–1.50 (m, 11H), 1.35–1.28 (13H), 1.10 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 98.8, 78.6, 73.2, 67.7, 62.3, 37.2, 33.1, 32.5, 30.8, 29.7, 29.7, 29.6, 29.6, 29.5, 26.2, 25.8, 25.5, 23.4, 23.3, 20.4, 19.7. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{21}H_{44}NO_3$; 358.3316, found 358.3312.

**{[11-(Methoxymethoxy)undecan-2-yl]oxy}cyclopentane (3ah)**



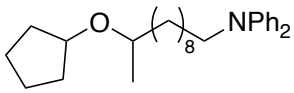

The product **3ah** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–95:5, hexane/EtOAc) (Figure 1; 34.2 mg, 0.11 mmol, 57% isolated yield). Paleyellow oil. **IR** (neat) 920, 1045, 1087, 1111, 1149, 1337, 1371, 1465, 2854, 2926 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 4.62 (s, 2H), 4.00 (quintet, $J$ = 4.4 Hz, 1H), 3.52 (t, $J$ = 6.8 Hz, 2H), 3.40–3.36 (m, 4H), 1.78–1.66 (m, 4H), 1.62–1.54 (m, 4H), 1.54–1.43 (m, 2H), 1.40–1.28 (m, 14H), 1.10 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 96.4, 78.6, 73.2, 67.9, 55.1, 37.2, 33.1, 32.5, 29.7, 29.7, 29.6, 29.6, 29.4, 26.2, 25.8, 23.4, 23.3, 20.4. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{18}H_{40}NO_3$;318.3003, found 318.2990.

**[({[10-(Cyclopentyloxy)undecyl]oxy}methoxy)methyl]benzene (3ai)**



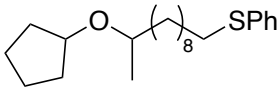

The product **3ai** was purified by flash chromatography on silica gel (100:0–90:10, hexane/EtOAc) (Figure 1; 45.5 mg, 0.12 mmol, 60% isolated yield). Paleyellow oil. **IR** (neat) 697, 734, 1028, 1046, 1114, 1165, 1372, 1454, 2855, 2927 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36–7.27 (m, 5H), 4.76 (s, 2H), 4.60 (s, 2H), 3.96 (m, 1H), 3.59 (t, $J$ = 6.8 Hz, 2H), 3.38 (m, 1H), 1.78–1.65 (m, 4H), 1.64–1.42 (m, 6H), 1.40–1.28 (m, 14H) 1.10 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 137.9, 128.3, 127.8, 127.6, 94.5, 78.6, 73.1, 69.2, 68.1, 37.2, 33.1, 32.4, 29.7 (×2C), 29.6, 29.5, 29.4, 26.2, 25.8, 23.3, 23.3, 20.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{41}O_3$; 377.3050, found 377.3051.

***N*-[10-(Cyclopentyloxy)undecyl]-*N*-phenylaniline (3aj)**




The product **3aj** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–97:3, hexane/EtOAc) (Figure 1; 55.0 mg, 0.13 mmol, 67% isolated yield). Paleyellow oil. **IR** (neat) 695, 748, 1046, 1240, 1371, 1496, 1589, 1741, 2854, 2928 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.28–7.23 (m, 4H), 6.99–6.97 (m, 4H), 6.93 (t, $J$ = 7.2 Hz, 2H), 3,96 (quintet, $J$ = 4.4 Hz, 1H), 3,68 (d, $J$ = 7.6 Hz, 1H), 3,66 (d, $J$ = 7.6 Hz, 1H), 3.38 (m, 1H), 1.78–1.63 (m, 6H), 1.61–1.54 (m, 2H), 1.52–1.43 (m, 3H), 1.34–1.25 (m, 13H), 1.10 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 148.1, 129.2, 121.0, 120.9, 78.6, 73.2, 52.3, 37.2, 33.1, 32.5, 29.7, 29.6, 29.6, 29.4, 27.4, 27.1, 25.8, 23.4, 23.3, 20.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{42}NO$; 408.3266, found 408.3268.

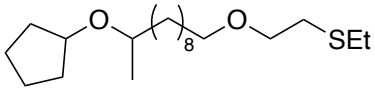
**[10-(Cyclopentyloxy)undecyl](phenyl)sulfane (3ak)**




The product **3ak** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 36.7 mg, 0.11 mmol, 53% isolated yield). Pale yellow oil. **IR** (neat) 690, 736, 1025, 1044, 1092, 1130, 1438, 1480, 2853, 2925 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33–7.25 (m, 4H), 7.16

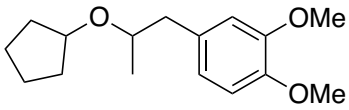
(t, $J$ = 7.2 Hz, 1H), 3.96 (m, 1H), 3.38 (m, 1H), 2.91 (t, $J$ = 7.2 Hz, 2H), 1.78–1.54 (m, 7H), 1.52–1.49 (m, 6H), 1.46–1.27 (m, 11H), 1.10 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 137.0, 128.8 (×2C), 125.6, 78.6, 73.2, 37.2, 33.5, 33.1, 32.5, 29.7, 29.5, 29.4, 29.1 (×2C), 28.8, 25.8, 23.4, 23.3, 20.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{22}H_{37}OS$; 349.2560, found 349.2559.

**(2-{[10-(Cyclopentyloxy)undecyl]oxy}ethyl)(ethyl)sulfane (3al)**



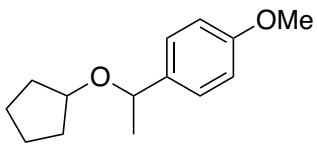

The product **3al** was purified by flash chromatography on silica gel (100:0–95:5, hexane/AcOEt) (Figure 1; 18.8 mg, 0.05 mmol, 27 % isolated yield). Colorless oil. **IR** (neat) 909, 993, 1110, 1265, 1358, 1456, 1641, 2854, 2925, 3075 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 3.96 (m, 1H), 3.58 (t, $J$ = 6.8 Hz, 2H), 3.44 (t, $J$ = 6.8 Hz, 2H), 3.38 (m, 1H), 2.71 (t, $J$ = 6.8 Hz, 2H), 2.59 (q, $J$ = 7.2 Hz, 2H), 1.78–1.64 (m, 4H), 1.63–1.42 (m, 7H), 1.34–1.25 (m, 16H), 1.10 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 78.6, 73.2, 71.2, 70.5, 37.2, 33.1, 32.5, 31.1, 29.7, 29.7, 29.6, 29.5, 29.4, 26.4, 26.1, 25.8, 23.4, 23.3, 20.4, 14.9. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{41}O_2S$; 345.2822, found 345.2829.

**4-[2-(Cyclopentyloxy)propyl]-1,2-dimethoxybenzene (3ac)**




The reaction conditions were modified. The reaction was carried out with **1a** (18.1 μL, 0.2 mmol), **2c** (34.3 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3ac** was purified by flash chromatography on silica gel (Biotage Selekt, 99:1–90:10, hexane/EtOAc) (Figure 1; 52.9 mg, 0.20 mmol, 99% isolated yield). Pale yellow oil. **IR** (neat) 1030, 1157, 1237, 1261, 1333, 1464, 1515, 2833, 2869, 2957 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.80–6.72 (m, 3H), 3.91 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.58 (sixtet, $J$ = 6.4 Hz, 1H), 2.75 (dd, $J$ = 13.6, 6.4 Hz, 1H), 2.56 (dd, $J$ = 13.6, 6.4 Hz, 1H), 1.73–1.41 (m, 8H), 1.13 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 148.4, 147.2, 132.2, 121.3, 112.9, 110.9, 79.1, 74.7, 55.9, 55.8, 43.2, 33.1, 32.4, 23.4, 23.2, 20.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{25}O_3$; 265.1798, found 265.1804.

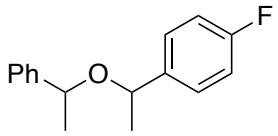
**1-[1-(Cyclopentyloxy)ethyl]-4-methoxybenzene (3am)**




The reaction conditions were modified. The reaction was carried out with **1a** (18.1 μl , 0.2 mmol), **2m** (26.8 μl, 0.2 mmol) , **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3am** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–95:5, hexane/EtOAc) (Figure 1; 38.3 mg,

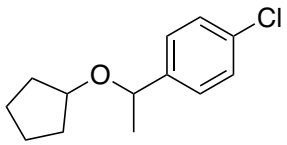
0.17 mmol, 87% isolated yield). Pale yellow oil. **IR** (neat) 831, 1038, 1091, 1171, 1243, 1441, 1511, 1611, 2869, 2955 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.24 (d, $J$ = 8.8 Hz, 2H), 6.87 (d, $J$ = 8.8 Hz, 2H), 4.41 (q, $J$ = 6.4 Hz, 1H), 3.82–3.76 (m, 4H), 1.76–1.40 (m, 8H), 1.38 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 158.7, 136.7, 127.3, 113.6, 78.3, 74.9, 55.2, 33.0, 31.8, 24.6, 23.5, 23.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{21}O_2$; 221.1536, found 221.1542.

**1-Fluoro-4-[1-(1-phenylethoxy)ethyl]benzene (3Bn)**



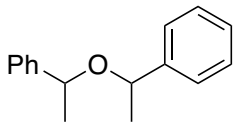

The reaction conditions were modified. The reaction was carried out with **1B** (24.2 μL, 0.2 mmol), **2n** (23.9 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3Bn** was purified by flash chromatography on silica gel (100:0–97.5:2.5, hexane/$Et_2O$) (Figure 1; 46.4 mg, 0.19 mmol, 95% isolated yield). Pale yellow oil. **IR** (neat) 701, 761, 835, 1029, 1089, 1222, 1509, 1604, 2928, 2975 cm $^{-1}$. The ratio (53:47) of the diastereomers was determined by $^{1}$H NMR analysis. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36 (m, 1H), 7.31–7.20 (m, 6H), 7.03 (m, 1H), 6.95 (m, 1H), 4.51 (m, 1H), 4.21 (m, 1H), 1.45 (m, 3H), 1.36 (m, 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 162.1 (d, $J_{C\text{-}F}$ = 244.8 Hz), 161.9 (d, $J_{C\text{-}F}$ = 244.8 Hz), 144.0, 143.9, 140.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 139.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.5, 128.3, 127.8 (d, $J_{C\text{-}F}$ = 7.7 Hz), 127.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 127.4, 127.2, 126.3, 126.2, 115.3 (d, $J_{C\text{-}F}$ = 21.2 Hz), 115.0 (d, $J_{C\text{-}F}$ = 21.3 Hz), 74.7, 74.6, 73.9, 73.8, 24.7, 24.6, 23.1, 22.9. Signals for two diastereomers (53:47) were given: **$^{19}$F NMR** (376.5 MHz, $CDCl_3$) $\delta$ –115.4, –115.9. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{16}H_{21}FNO$; 262.1602, found 262.1606.

**1-Chloro-4-[1-(cyclopentyloxy)ethyl]benzene (3ao)**



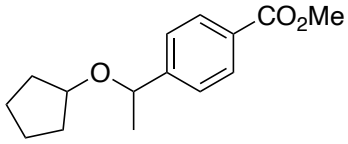

The reaction conditions were modified. The reaction was carried out with **1a** (18.1 μL, 0.2 mmol), **2o** (25.4 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h or 12h. The product **3ao** was purified by flash chromatography on silica gel (100:0–98:2, hexane/$Et_2O$) (Figure 1; 39.6 mg, 0.18 mmol, 88% isolated yield, 12 h : 90% NMR yield). Pale yellow oil. **IR** (neat) 546, 781, 826, 1014, 1088, 1336, 1367, 1488, 2869, 2958 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.30 (d, $J$ = 8.4 Hz, 2H), 7.25 (d, $J$ = 8.4 Hz, 2H), 4.43 (q, $J$ = 6.4 Hz, 1H), 3.78 (quintet, $J$ = 4.8 Hz, 1H), 1.78–1.40 (m, 8H), 1.37 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 143.3, 132.7, 128.4, 127.6, 78.8, 74.8, 33.0, 31.9, 24.6, 23.5, 23.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{18}ClO$; 225.1041, found 225.1040.

**[Oxybis(ethane-1,1-diyl)]dibenzene (3Bp)**



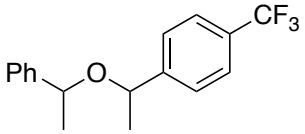

The reaction conditions were modified. The reaction was carried out with **1B** (24.2 μL, 0.2 mmol), **2p** (20.8 μL, 0.2 mmol) , **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h.The product **3Bp** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 42.4 mg, 0.19 mmol, 94% isolated yield). Colorless oil. The ratio (51:49) of the diastereomers was determined by $^{1}$H NMR analysis. The spectrum data of product **3Bp** was consistent with the literature.[11]

**Methyl 4-[1-(Cyclopentyloxy)ethyl]benzoate (3aq)**




The reaction conditions were modified. The reaction was carried out with **1a** (18.1 μL, 0.2 mmol), **2q** (32.4 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3aq** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–95:5, hexane/EtOAc) (Figure 1; 36.8 mg, 0.15 mmol, 74% isolated yield). Pale yellow oil. **IR** (neat) 773, 857, 1092, 1110, 1275, 1435, 1611, 1721, 2870, 2952 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 8.4 Hz, 2H), 7.39 (d, $J$ = 8.4 Hz, 2H), 4.51 (q, $J$ = 6.4 Hz, 1H), 3.91 (s, 3H), 3.79 (quintet, $J$ = 4.4 Hz, 1H), 1.76–1.42 (m, 8H), 1.40 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 167.0, 150.3, 129.7, 129.0, 126.1, 79.1, 75.2, 52.0, 33.0, 31.9, 24.5, 23.5, 23.4. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{15}H_{24}NO_3$; 266.1751, found 266.1752.

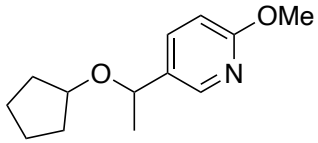
**1-[1-(1-Phenylethoxy)ethyl]-4-(trifluoromethyl)benzene (3Br)**




The reaction conditions were modified. The reaction was carried out with **1B** (24.2 μL, 0.2 mmol), **2r** (34.2 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3Br** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–95:5, hexane/EtOAc) (Figure 1; 34.1 mg, 0.12 mmol, 58% isolated yield). Colorless oil. **IR** (neat) 700, 761, 841, 1018, 1066, 1088, 1122, 1163, 1323, 2976 cm $^{-1}$. The ratio (50:50) of the diastereomers was determined by $^{1}$H NMR analysis. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.62 (d, $J$ = 8.0 Hz, 0.5 × 2H), 7.52 (d, $J$ = 8.0 Hz, 0.5 × 2H), 7.41–7.33 (m, 3H), 7.32–7.20 (m, 4H), 4.54 (m, 1H), 4.31 (q, $J$ = 6.4 Hz, 0.5 × 1H), 4.20 (q, $J$ = 6.4 Hz, 0.5 × 1H), 1.47 (m, 3H), 1.39 (m, 3H). Signals for two diastereomers were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 148.4, 148.4, 143.7, 143.6, 129.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 129.6 (q, $J_{C\text{-}F}$ = 33.0 Hz), 128.5, 128.3,

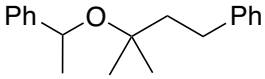
127.6, 127.3, 126.5 (×2C), 126.4 (×2C), 126.2, 126.2, 125.5 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.2 (q, $J_{C\text{-}F}$ = 3.9 Hz), 75.1 (×2C), 74.1, 74.0, 24.6, 24.6, 23.3, 22.9. Signals for two diastereomers were given: **$^{19}$F NMR** (376.5 MHz, $CDCl_3$) $\delta$ –62.4, –62.4. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{17}H_{21}F_3NO$; 312.1570, found 312.1568.

**5-[1-(Cyclopentyloxy)ethyl]-2-methoxypyridine (3as)**



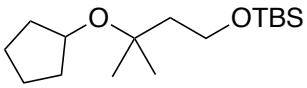

The reaction conditions were modified. The reaction was carried out with **1a** (18.1 μL, 0.2 mmol), **2s** (27.0 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol % or 10.8 mg, 0.04 mmol, 20 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3as** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–97:3, hexane/EtOAc) (Figure 1; 21.6 mg, 0.10 mmol, 49% isolated yield, 20 mol % Collidine HOTf : 54% isolated yield). Pale yellow oil. **IR** (neat) 1028, 1093, 1252, 1282, 1323, 1397, 1492, 1608, 2871, 2955 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 2.4 Hz, 1H), 7.58 (dd, $J$ = 8.4, 2.4 Hz, 1H), 6.74 (d, $J$ = 8.4 Hz, 1H), 4.43 (q, $J$ = 6.4 Hz, 1H), 3.93 (s, 3H), 3.78 (m, 1H), 1.74–1.42 (m, 8H), 1.40 (d, $J$ = 6.4 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 163.7, 144.8, 136.9, 132.5, 110.9, 78.5, 72.7, 53.4, 33.0, 31.9, 24.2, 23.4, 23.4. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{13}H_{20}NO_2$; 222.1489, found 222.1482.

**[3-Methyl-3-(1-phenylethoxy)butyl]benzene (3Bt)**



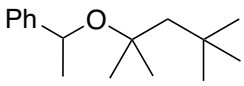

The reaction conditions were modified. The reaction was carried out with **1B** (72.6 μL, 0.6 mmol), **2t** (29.2 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 48 h. The product **3Bt** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 36.1 mg, 0.13 mmol, 67% isolated yield). Colorless oil. The spectrum data of product **3Bt** was consistent with the literature.[12]

***tert*-Butyl[3-(cyclopentyloxy)-3-methylbutoxy]dimethylsilane (3au)**



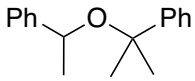

The product **3au** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 45.6 mg, 0.16 mmol, 80% isolated yield). Red oil. **IR** (neat) 774, 836, 1045, 1091, 1152, 1255, 1362, 1472, 2857, 2956 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 3.99 (m, 1H), 3.71 (t, $J$ = 7.2 Hz, 2H), 1.81–1.64 (m, 6H), 1.49–1.42 (m, 4H), 1.15 (s, 6H), 0.89 (s, 9H), 0.05 (s, 6H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 73.9, 73.1, 59.7, 43.8, 34.9, 27.1, 26.0, 23.6, 18.3, –5.3. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{35}O_2Si$; 287.2401, found 287.2403.

**{1-[(2,4,4-Trimethylpentan-2-yl)oxy]ethyl}benzene (3Bv)**



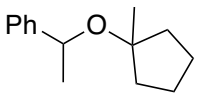
The reaction conditions were modified. The reaction was carried out with **1B** (72.6 μL, 0.6 mmol), **2v** (31.2 μL, 0.2 mmol), **Ir(ppy)$_3$** (1.3 mg, 0.002 mmol, 1 mol %) or **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3Bv** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; **Ir(ppy)$_3$**: 42.5 mg, 0.18 mmol, 91% isolated yield, **PTH-1**: 23.4 mg, 0.10 mmol, 50% isolated yield). Colorless oil. **IR** (neat) 700, 759, 1020, 1028, 1081, 1125, 1213, 1365, 1383, 2952 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35–7.26 (m, 4H), 7.19 (t, $J$ = 7.2 Hz, 1H), 4.65 (q, $J$ = 6.4 Hz, 1H), 1.52 (s, 2H), 1.34 (d, $J$ = 6.4 Hz, 3H), 1.22 (s, 3H), 1.05 (s, 3H), 1.02 (s, 9H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 147.9, 128.0, 126.4, 125.7, 69.6, 54.9, 31.8, 31.3, 28.7, 27.2, 26.8. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{16}H_{30}NO$; 252.2322, found 252.2324.

**[2-(1-Phenylethoxy)propan-2-yl]benzene (3Bw)**



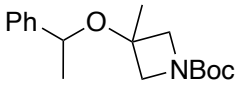
The reaction conditions were modified. The reaction was carried out with **1B** (24.2 μL, 0.2 mmol), **2w** (26.0 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3Bw** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 40.6 mg, 0.17 mmol, 84% isolated yield). Colorless oil. The spectrum data of product **3Bw** was consistent with the literature.[13]

**{1-[(1-Methylcyclopentyl)oxy]ethyl}benzene (3Bx)**



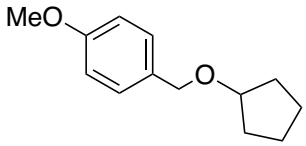
The reaction conditions were modified. The reaction was carried out with **1B** (72.6 μL, 0.6 mmol), **2x** (21.1 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 48 h. The product **3Bx** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 20.0 mg, 0.10 mmol, 49% isolated yield). Pale yellow oil. **IR** (neat) 700, 759, 954, 1028, 1082, 1203, 1374, 1448, 2870, 2966 cm $^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.36–7.28 (m, 4H), 7.20 (tt, $J$ = 7.2, 1.6 Hz, 1H), 4.58 (q, $J$ = 6.8 Hz, 1H), 1.89 (m, 1H), 1.82–1.70 (m, 2H), 1.62–1.41 (m, 4H), 1.37–1.36 (m, 4H), 1.20 (s, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 147.4, 128.1, 126.4, 125.5, 85.6, 70.9, 39.0, 38.4, 26.7, 24.9, 23.9, 23.7. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{14}H_{24}NO$; 222.1852, found 222.1850.

***tert*-Butyl 3-Methyl-3-(1-phenylethoxy)azetidine-1-carboxylate (3By)**



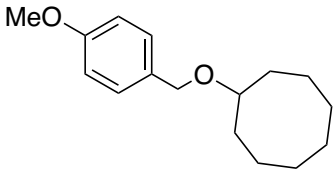

The product **3By** was purified by flash chromatography on silica gel (100:0–70:30, hexane/EtOAc) (Figure 1; 30.4 mg, 0.10 mmol, 52% isolated yield). Yellow oil. **IR** (neat) 701, 1081, 1106, 1149, 1366, 1399, 1702, 2882, 2929, 2974 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33–7.32 (m, 4H), 7.25 (m, 1H), 4.56 (q, $J$ = 6.4 Hz, 1H), 3.93 (d, $J$ = 8.8 Hz, 1H), 3.81 (d, $J$ = 8.8 Hz, 1H), 3.66 (d, $J$ = 8.8 Hz, 1H), 3.54 (d, $J$ = 8.8 Hz, 1H), 1.43–1.42 (m, 15H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 156.5, 145.1, 128.4, 127.3, 125.7, 79.5, 72.6, 72.5, 60.8, 28.4, 25.6, 24.2. **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{26}NO_3$; 292.1907, found 292.1905.

**1-[(Cyclopentyloxy)methyl]-4-methoxybenzene (3ez)**



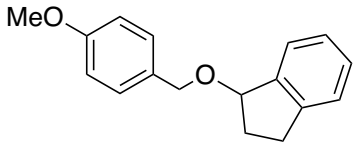

The reaction conditions were modified. The reaction was carried out with **1e** (83.0 mg, 0.6 mmol), **2z** (17.7 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol%), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol%) in DCM (500 μL) under blue LED irradiation for 48 h.The product **3ez** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 21.8 mg, 0.11 mmol, 53% isolated yield). Paleyellow oil. The spectrum data of product **3ez** was consistent with the literature.[14]

**[(4-Methoxybenzyl)oxy]cyclooctane (3eA)**



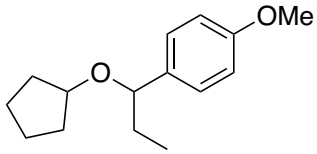

The reaction conditions were modified. The reaction was carried out with **1e** (83.0 mg, 0.6 mmol), **2A** (25.9 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol%), and **HX-1** (5.4 mg, 0.02 mmol, 10 mol%) in DCM (500 μL) under blue LED irradiation for 48 h. The product **3eA** was purified by flash chromatography on silica gel (100:0–95:5, hexane/AcOEt) (Figure 1; 33.5 mg, 0.13 mmol, 67% isolated yield). Pale yellow oil. **IR** (neat) 820, 1037, 1071, 1171, 1246, 1465, 1512, 1613, 2852, 2921. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.26 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 2H), 4.43 (s, 2H), 3.80 (s, 3H), 3.50 (m, 1H), 1.89–1.82 (m, 2H), 1.77–1.67 (m, 4H), 1.62–1.49 (m, 5H), 1.46–1.39 (m, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 158.9, 131.4, 129.0, 113.7, 78.4, 69.6, 55.2, 31.4, 27.3, 25.4, 23.1. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{16}H_{28}NO$; 266.2115, found 266.2111.

**1-[(4-Methoxybenzyl)oxy]-2,3-dihydro-1H-indene (3eB)**



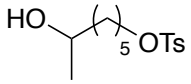

The product **3eB** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–93:7, hexane/EtOAc) (Figure 1; 50.9 mg, 0.2 mmol, 99% isolated yield). Colorless oil. **IR** (neat) 756, 1034, 1074, 1246, 1301, 1460, 1512, 1611, 2850, 2934 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 (d, $J$ = 6.8 Hz, 1H), 7.31 (dt, $J$ = 8.4, 2.0 Hz, 2H), 7.25–7.19 (m, 3H), 6.88 (d, $J$ = 6.8 Hz, 2H), 5.00 (dd, $J$ = 6.4, 4.4 Hz, 1H), 4.59 (d, $J$ = 11.6 Hz, 1H), 4.55 (d, $J$ = 11.6 Hz, 1H), 3.80 (s, 3H), 3.09 (m, 1H), 2.81 (m, 1H), 2.34 (m, 1H), 2.13 (m, 1H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 159.1, 144.0, 142.9, 130.9, 129.3, 128.3, 126.3, 125.1, 124.8, 113.8, 82.3, 70.2, 55.3, 32.4, 30.2. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{17}H_{22}NO_2$; 272.1645, found 272.1648.

**1-[1-(Cyclopentyloxy)propyl]-4-methoxybenzene (3aC)**



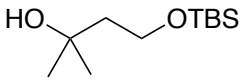

The reaction conditions were modified. The reaction was carried out with **1a** (18.1 μL, 0.2 mmol), **2C** (29.9 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL) under blue LED irradiation for 24 h. The product **3aC** was purified by flash chromatography on silica gel (Biotage Selekt, 100:0–90:10, hexane/EtOAc) (Figure 1; 46.9 mg, 0.2 mmol, 99% isolated yield). Pale yellow oil. **IR** (neat) 1039, 1055, 1100, 1171, 1247, 1302, 1511, 1611, 2871, 2958 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.21 (d, $J$ = 8.4 Hz, 2H), 6.87 (d, $J$ = 8.4 Hz, 2H), 4.10 (dd, $J$ = 7.2, 6.0 Hz, 1H), 3.80 (s, 3H), 3.76 (m, 1H), 1.78–1.39 (m, 10H), 0.88 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 158.7, 135.7, 127.8, 113.5, 80.8, 78.4, 55.2, 33.1, 31.6, 23.4, 10.6. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{15}H_{26}NO_2$; 252.1958, found 255.1961.

**6-Hydroxyheptyl 4-Methylbenzenesulfonate (5ab)**



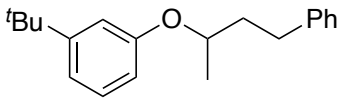

The reaction conditions were modified. The reaction was carried out with **4a** (10.8 μL, 0.2 mmol), **2b** (40.1 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in acetone (500 μL) under blue LED irradiation for 24 h. The product **5ab** was purified by flash chromatography on silica gel (100:0–65:35, hexane/EtOAc) (Figure 1; 42.2 mg, 0.15 mmol, 74% isolated yield). Pale yellow oil. **IR** (neat) 555, 664, 815, 938, 1175, 1189, 1356, 2862, 2933, 3400 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 4.03 (t, $J$ = 6.4 Hz, 2H), 3.74 (m, 1H), 2.45 (s, 3H), 1.69–1.62 (m, 2H), 1.43–1.26 (m, 6H), 1.17 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 144.7, 133.2, 129.8, 127.9, 70.5, 67.9, 39.0, 28.8, 25.3, 25.1, 23.6, 21.6. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{14}H_{26}NO_4S$; 304.1577, found 304.1578.

**4-[(*tert*-Butyldimethylsilyl)oxy]-2-methylbutan-2-ol (5au)**



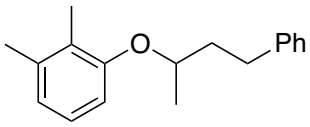

The reaction conditions were modified. The reaction was carried out with **4a** (10.8 μL, 0.2 mmol), **2u** (48.1 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in acetone (500 μL) under blue LED irradiation for 24 h. The product **5au** was purified by flash chromatography on silica gel (100:0–90:10, hexane/EtOAc) (Figure 1; 29.2 mg, 0.13 mmol, 67% isolated yield). Pale yellow oil. The spectrum data of product **5au** was consistent with the literature.[15]

**1-(*tert*-Butyl)-3-[(4-phenylbutan-2-yl)oxy]benzene (7aa)**



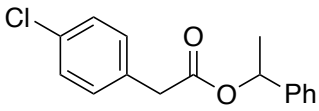

The product **7aa** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 35.5 mg, 0.13 mmol, 63% isolated yield). Pale yellow oil. **IR** (neat) 698, 1222, 1273, 1289, 1486, 1579, 1604, 2866, 2963, 3026 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.25 (m, 2H), 7.21–7.17 (m, 4H), 6.97 (m, 1H), 6.91 (t, $J$ = 2.4 Hz, 1H), 6.67 (dd, $J$ = 8.0, 2.4 Hz, 1H), 4.37 (m, 1H), 2.85–2.70 (m, 2H), 2.08 (m, 1H), 1.88 (m, 1H), 1.33 (d, $J$ = 6.0 Hz, 3H), 1.30 (s, 9H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 157.9, 153.0, 141.9, 128.9, 128.5, 128.4, 125.8, 117.7, 113.9, 112.0, 72.6, 38.3, 34.7, 31.9, 31.3, 19.8. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{20}H_{30}NO$; 300.2322, found 300.2322.

**1,2-Dimethyl-3-[(4-phenylbutan-2-yl)oxy]benzene (7ba)**



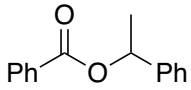

The product **7ba** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 22.0 mg, 0.09 mmol, 43% isolated yield). Colorless oil. **IR** (neat) 699, 768, 1100, 1256, 1454, 1470, 1584, 2928, 2971, 3026 cm $^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.29–7.25 (m, 2H), 7.20–7.17 (m, 3H), 7.01 (m, 1H), 6.75 (d, $J$ = 8.0 Hz, 1H), 6.65 (d, $J$ = 8.0 Hz, 1H), 4.34 (m, 1H), 2.84–2.71 (m, 2H), 2.27 (s, 3H), 2.22 (s, 3H), 2.08 (m, 1H), 1.91 (m, 1H), 1.31 (d, $J$ = 6.0 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 155.9, 142.0, 138.0, 128.5, 128.3, 126.2, 125.8, 125.6, 122.0, 110.7, 73.1, 38.5, 31.9, 20.2, 19.9, 11.9. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{18}H_{26}NO$; 272.2009, found 272.2006.

**1-Phenylethyl 2-(4-Chlorophenyl)acetate (9ap)**



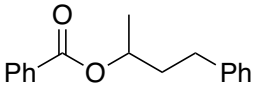
The reaction conditions were modified. The reaction was carried out with **8a** (102.4 mg, 0.6 mmol), **2p** (20.8 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in $PhCF_3$ (500 μL) under blue LED irradiation for 24 h. The product **9ap** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 52.4 mg, 0.19 mmol, 95% isolated yield). Yellow oil. **IR** (neat) 699, 1063, 1092, 1159, 1251, 1492, 1732, 2359, 2980, 3032 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35–7.27 (m, 7H), 7.19 (d, $J$ = 8.4 Hz, 2H), 5.88 (q, $J$ = 6.8 Hz, 1H), 3.60 (s, 2H), 1.52 (d, $J$ = 6.8 Hz, 3H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 170.3, 141.3, 133.0, 132.4, 130.6, 128.6, 128.5, 127.9, 126.0, 73.0, 40.9, 22.1. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{16}H_{19}ClNO_2$; 292.1099, found 292.1091.

**1-Phenylethyl Benzoate (9bp)**



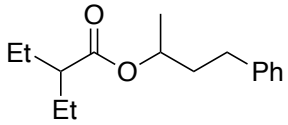
The reaction conditions were modified. The reaction was carried out with **8b** (73.3 mg, 0.6 mmol), **2p** (20.8 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in $PhCF_3$ (500 μL) under blue LED irradiation for 24 h. The product **9bp** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 45.0 mg, 0.20 mmol, 99% isolated yield). Colorless oil. The spectrum data of product **9bp** was consistent with the literature.[16]

**4-Phenylbutan-2-yl Benzoate (9ba)**



The reaction conditions were modified. The reaction was carried out with **8b** (73.3 mg, 0.6 mmol), **2a** (30.0 μL, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in $PhCF_3$ (500 μL) under blue LED irradiation for 24 h. The product **9ba** was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) (Figure 1; 13.2 mg, 0.05 mmol, 26% isolated yield). Yellow oil. The spectrum data of product **9ba** was consistent with the literature.[17]

**4-Phenylbutan-2-yl 2-Ethylbutanoate (9ca)**



The product **9ca** was purified by flash chromatography on silica gel (100:0–97:3, hexane/EtOAc) (Figure 1; 12.9 mg, 0.05 mmol, 26% isolated yield). Pale yellow oil. **IR** (neat) 699, 1130, 1150, 1181, 1728, 2360, 2876, 2934, 2964, 3027 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.30–7.26 (m, 2H), 7.20–7.17 (m, 3H), 4.99 (m, 1H), 2.69 (ddd, $J$ = 14.0, 10.4, 5.2 Hz, 1H), 2.60 (ddd, $J$ = 14.0, 10.4, 5.2 Hz, 1H), 2.19 (m, 1H), 1.93 (m, 1H), 1.81 (m, 1H), 1.68–1.49 (m, 4H), 1.25 (d, $J$ = 5.2 Hz, 3H), 0.94–

0.90 (m, 6H). **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 175.9, 141.6, 128.4, 128.3, 125.9, 70.0, 49.3, 37.8, 31.8, 25.2, 25.1, 20.1, 11.9, 11.9. **HRMS–DART** (*m/z*): $[M+NH_4]^+$ calcd for $C_{16}H_{28}NO_2$; 266.2115, found 266.2113.

## 7. Labelling Experiments

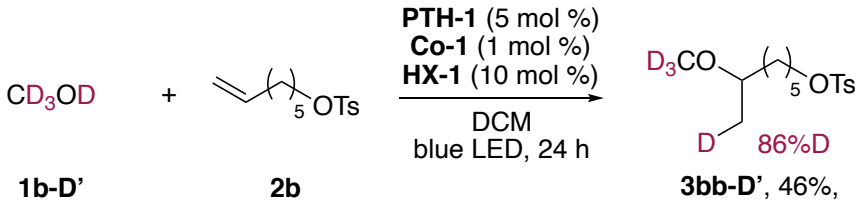



**Figure S3.**

**The reaction with 1b-D (Figure 2A, top)**. In a glovebox, to an oven-dried vial equipped with a stirring bar was added **1b-D** (24.2 µL, 0.6 mmol), **2b** (53.7 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), **Co-1** (1.2 mg, 0.002mmol, 1 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 µL). After sealing the vial with a cap and removal from the glove box, the reaction was stirred and irradiated with a 34W blue LED (0.5 cm away), with a cooling fan to keep the temperature at around 40 °C (Figure S2). After 24 h, the reaction was quenched with a short plug of silica gel using AcOEt. After volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (Biotage Selekt, 92:8–82:18, hexane/EtOAc) gave the coupling product **3bb-D** (Figure 2A; 23.5 mg, 0.08 mmol, 39% isolated yield: mixture of deuterated and nondeuterated compounds, 81:19) as a pale yellow oil. The ratio (81%D) of deuterium incorporation was determined by $^1$H NMR analysis: **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 4.02 (t, $J$ = 6.4 Hz, 2H), 3.29 (s, 3H), 3.23 (m, 1H), 2.45 (s, 3H), 1.68–1.61 (m, 2H), 1.45 (m, 1H), 1.38–1.22 (m, 5H), 1.10–1.06 (m, 2H + 0.19× 1H). Signals for deuterated and nondeuterated compounds were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 144.6, 133.3, 129.8, 127.9, 76.5, 76.5, 70.6, 55.9, 36.1, 36.1, 28.8, 25.5, 24.7, 21.6, 18.9, 18.7 (t, $J_{C\text{-}D}$ = 19.1 Hz). **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{24}DO_4S$; 302.1531, found 302.1524.

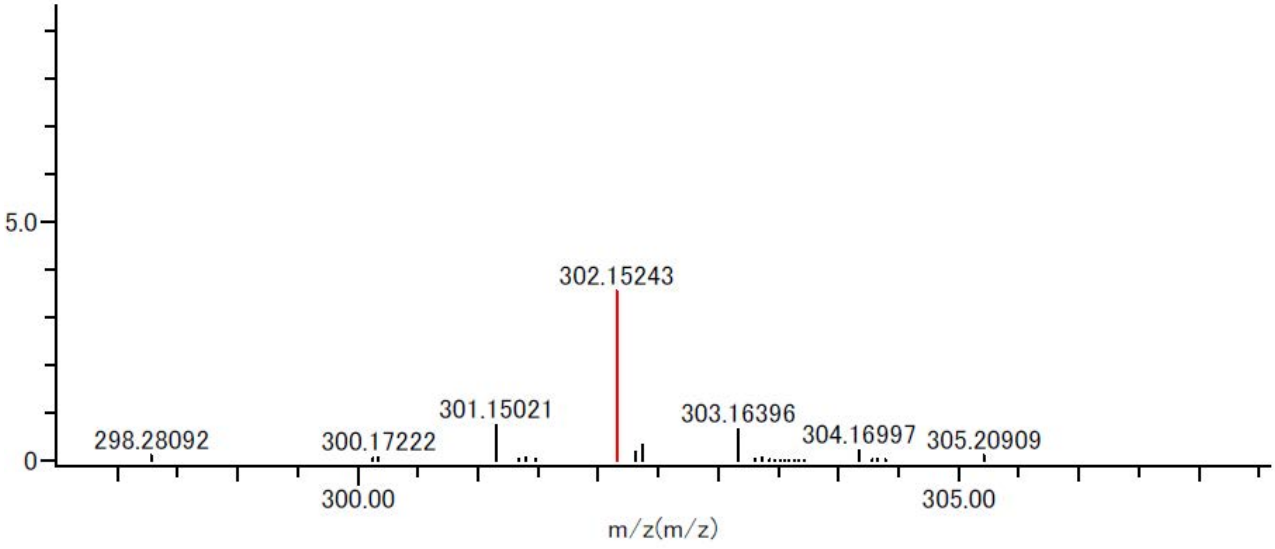



**Figure S4**. HRMS spectrum of **3bb-D**

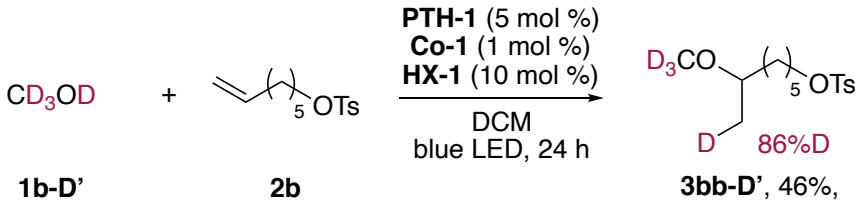



**Figure S5**.

**The reaction with 1b-D (Figure 2A, top)**. In a glovebox, to an oven-dried vial equipped with a stirring bar was added **1b-D'** (24.3 μL, 0.6 mmol), **2b** (53.7 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), **Co-1** (1.2 mg, 0.002mmol, 1 mol %) and **HX-1** (5.4 mg, 0.02 mmol, 10 mol %) in DCM (500 μL). After sealing the vial with a cap and removal from the glove box, the reaction was stirred and irradiated with a 34W blue LED (0.5 cm away), with a cooling fan to keep the temperature at around 40 °C. After 24 h, the reaction was quenched with a short plug of silica gel using AcOEt. After volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (Biotage Selekt, 98:2–88:12, hexane/EtOAc) gave the coupling product **3bb-D'** (Figure 2A; 28.0 mg, 0.09 mmol, 46% isolated yield: mixture of deuterated and nondeuterated compounds, 86:14) as a pale yellow oil. The ratio (86%D) of deuterium incorporation was determined by $^1$H NMR analysis: **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.79 (d, $J$ = 8.0 Hz, 2H), 7.34 (d, $J$ = 8.0 Hz, 2H), 4.02 (t, $J$ = 6.4 Hz, 2H), 3.23 (m, 1H), 2.45 (s, 3H), 1.68–1.61 (m, 2H), 1.45 (m, 1H), 1.38–1.22 (m, 5H), 1.10–1.06 (m, 0.86 × 2H + 0.14× 3H). Signals for deuterated and nondeuterated compounds were given: **$^{13}$C NMR** (100.6 MHz, $CDCl_3$) $\delta$ 144.6, 133.1, 129.8, 127.8, 76.4, 76.3, 70.5, 55.0 (quintet, $J_{C\text{-}D}$ = 21.7 Hz), 36.0, 36.0, 28.7, 25.4, 24.7, 21.6, 18.9, 18.6 (t, $J_{C\text{-}D}$ = 19.2 Hz). **HRMS–DART** (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{21}D_4O_4S$; 305.1719, found 305.1718.

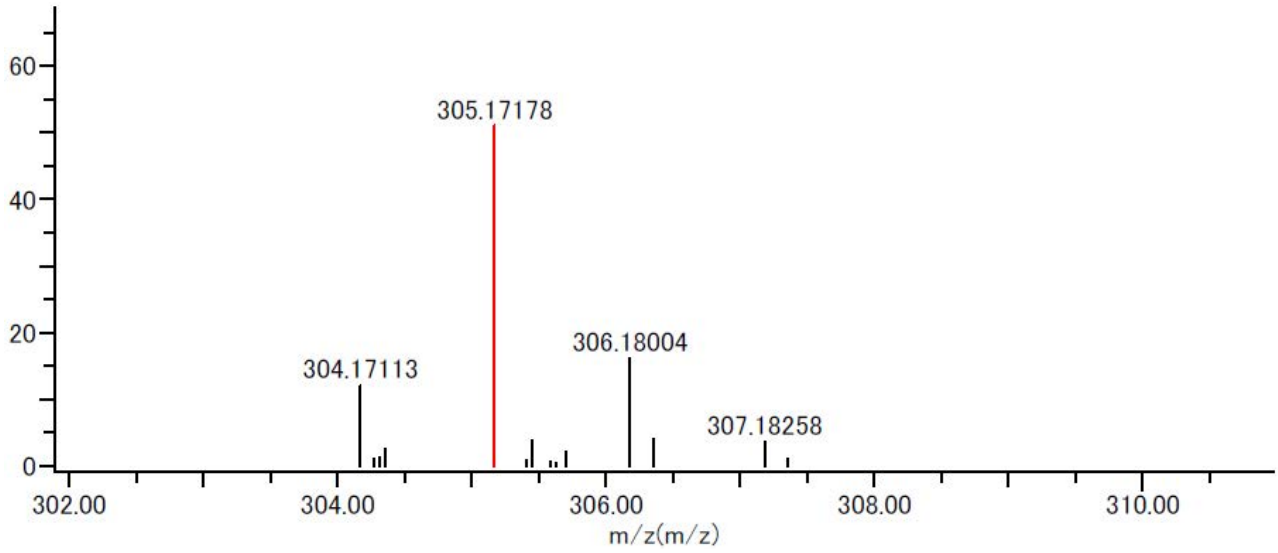



**Figure S6**. HRMS spectrum of **3bb-D'**

**Decarboxylative Cross-Coupling of Secondary Alipahtic Aliphatic Redox Active Ester**

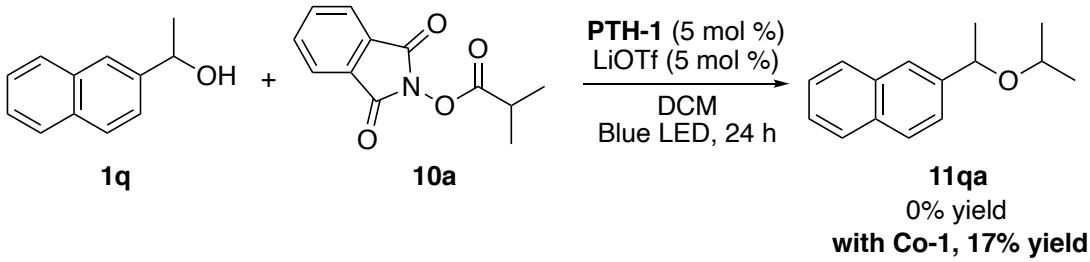



**Figure S7**.

**Figure 2B.** In a glovebox, to an oven-dried vial equipped with a stirring bar was added **1q** (103.3 mg, 0.6 mmol), **10a** (46.6 mg, 0.2 mmol), **PTH-1** (3.7 mg, 0.01 mmol, 5 mol %), lithium triflate (1.6 mg, 0.01 mmol), **Co-1** (1.2 mg, 0.01 mmol, 1 mol %) in DCM (500 μL). After sealing the vial with a cap and removal from the glove box, the reaction was stirred and irradiated with a 34W blue LED (0.5 cm away), with a cooling fan to keep the temperature at around 40 °C. After 24 h, the reaction was quenched with a short plug of silica gel using AcOEt. After volatiles were removed under reduced pressure, purification by flash column chromatography on silica gel (100:0–95:5, hexane/EtOAc) gave the coupling product **11qa** (Figure 2B; 7.3 mg, 0.03 mmol, 17% isolated yield) as a pale yellow oil. The spectrum data of product **11qa** was consistent with the literature.[18]

## 8. Stern-Volmer Luminescence Quenching Analysis

Several Stern-Volmer luminescence quenching experiments were carried out.

1. Quencher **Co-1** with or without colldinium salt **HX-1** (**Figure S8**)

The cobalt complex **Co-1** has a broad absorption in visible light region (Figure S17). To consider the inner filter effect of **Co-1**, the quenching ratio $I_0/I$, based on the measured steady-state emission intensity (I at 432 nm) of the excited state of **PTH-1** has been corrected followingly.[19]

$$(I_0/I)_{corr} = (I_0/I)\,\frac{\text{Abs (PTH-1)}}{\text{Abs (PTH-1) + Abs (Co-1)}}\,\frac{1-10^{-[\text{Abs(PTH-1)+Abs(Co-1)}]}}{1-10^{-\text{Abs(PTH-1)}}}$$

**Procedure without HX-1:** In a glovebox, to a screw-top 1.0 cm quartz cuvette was added 40 μM solution of **PTH-1** in degassed DCE and cobalt-salen complex **Co-1** (quencher) of appropriate concentration in degassed DCE (quencher concentration = 20 μM, 40 μM, 60 μM, 80 μM). The fluorescence intensity was measured at λ = 430 nm after excitation at λ = 362 nm in the quartz cuvette.
**Procedure with HX-1:** In a glovebox, to a screw-top 1.0 cm quartz cuvette was added 40 μM solution of PTH in degassed DCE, collidinium salt **HX-1** of appropriate concentration in degassed DCE (concentration = 40 μM), and cobalt-salen complex (quencher) of appropriate concentration in degassed DCE (quencher concentration = 20 μM, 40 μM, 60 μM, 80 μM). The fluorescence intensity was measured at λ = 430 nm after excitation at λ = 362 nm in the quartz cuvette.

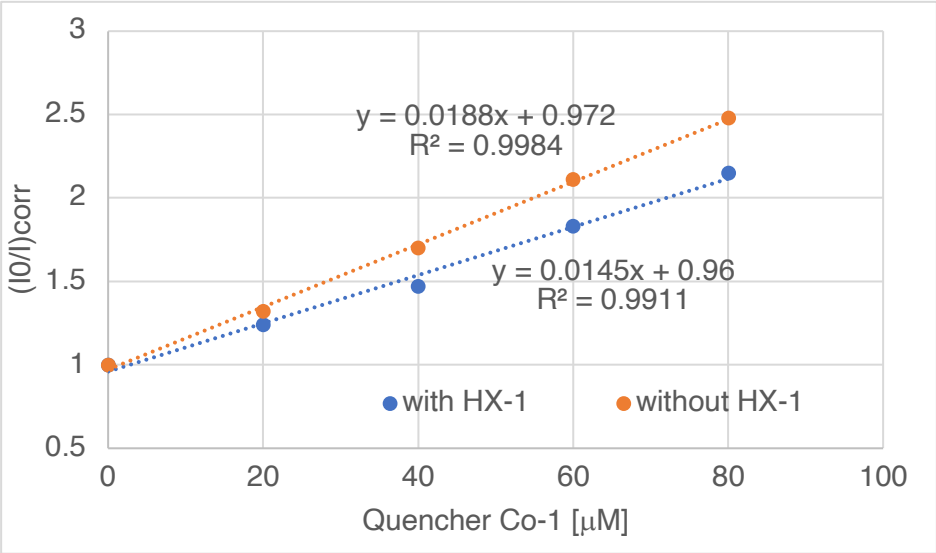



**Figure S8.**

**2.** Quencher: colldinium salt **HX-1** (**Figure S9**)

**Procedure:** In a glovebox, to a screw-top 1.0 cm quartz cuvette was added 40 μM solution of PTH in degassed DCE and collidinium salt (quencher) of appropriate concentration in degassed DCE (quencher concentration = 20 μM, 40 μM, 60 μM, 80 μM). The fluorescence intensity was measured at λ = 430 nm after excitation at λ = 362 nm in the quartz cuvette.

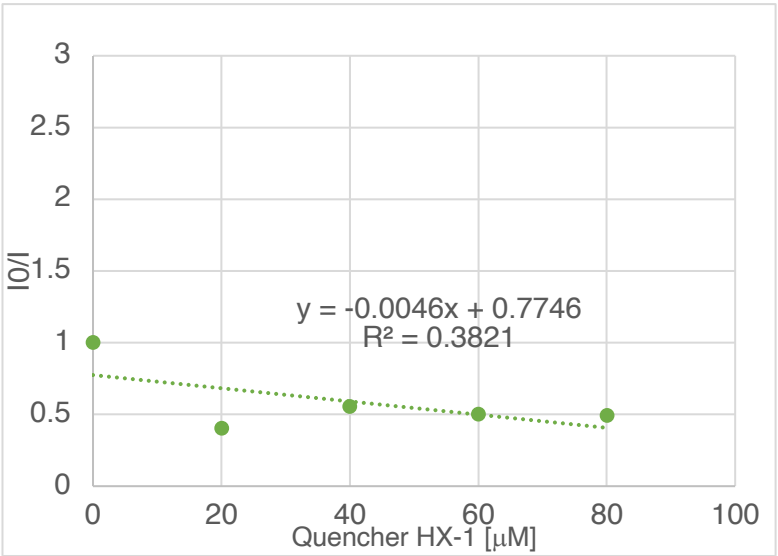



**Figure S9.**

The Stern-Volmer experiments revealed that the fluorescence of **PTH-1** is quenched by **Co-1**, but not by **HX-1 (**Figure S8 and S9**)**.

## 9. Cyclic Voltammetry Experiments

CV measurements were carried out under nitrogen atmosphere in organic solutions with 0.1 M of tetrabutylammonium perchlorate ($^{n}Bu_4NClO_4$) as a supporting electrolyte. Measurements were made with a glassy carbon electrode (area = 0.07 $cm^2$), an $Ag/AgNO_3$ reference electrode, and a Pt wire counter electrode. The sample solution preparad with appropriate concentration and the sweep rates were set to 100 mV/s. Ferrocene was used as an internal standard.

While the $E_{1/2}$ of **Co-1** did not change with or without **HX-1** (Figure S14 vs. Figure S11), the cathodic current corresponding to Co(I) to Co(II) with **HX-1** (Figure S14) became weaker than one in Figure S11. This result implied that Co(III)–H species was generated through single electron reduction of Co(II) to Co(I) by excited state of **PTH-1** followed by fast protonation of Co(I) by **HX-1**. The concerted mechanism involving Brønsted acidic activation of Co(II) by **HX-1** under the single electron transfer would not be feasible.

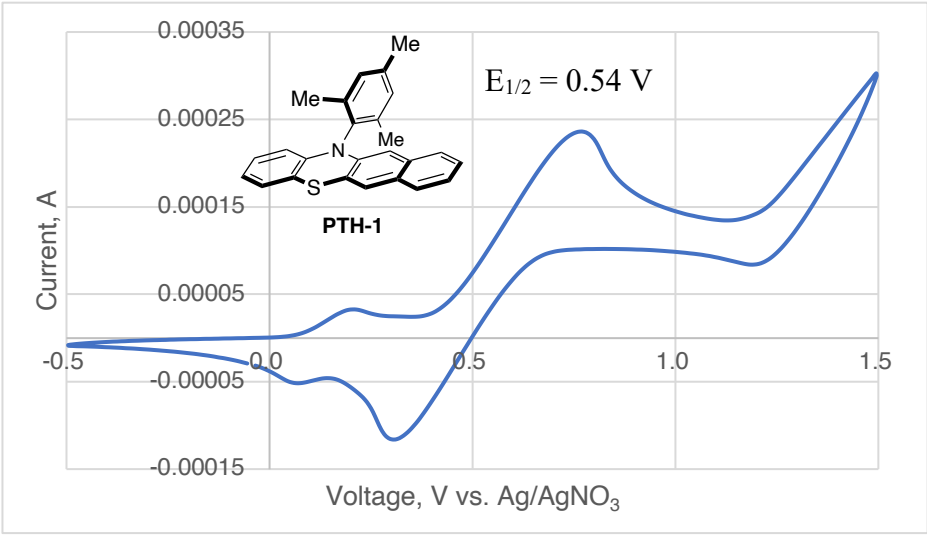



**Figure S10.** Cyclic voltammogram of **PTH-1** in DCM (10 mM).

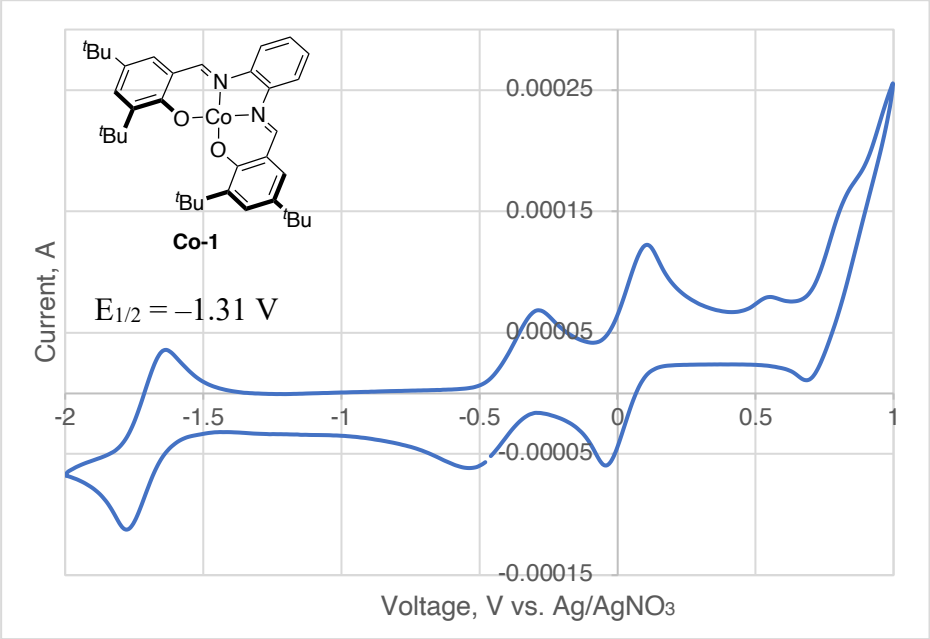



**Figure S11.** Cyclic voltammogram of **Co-1** in DMF (10 mM).

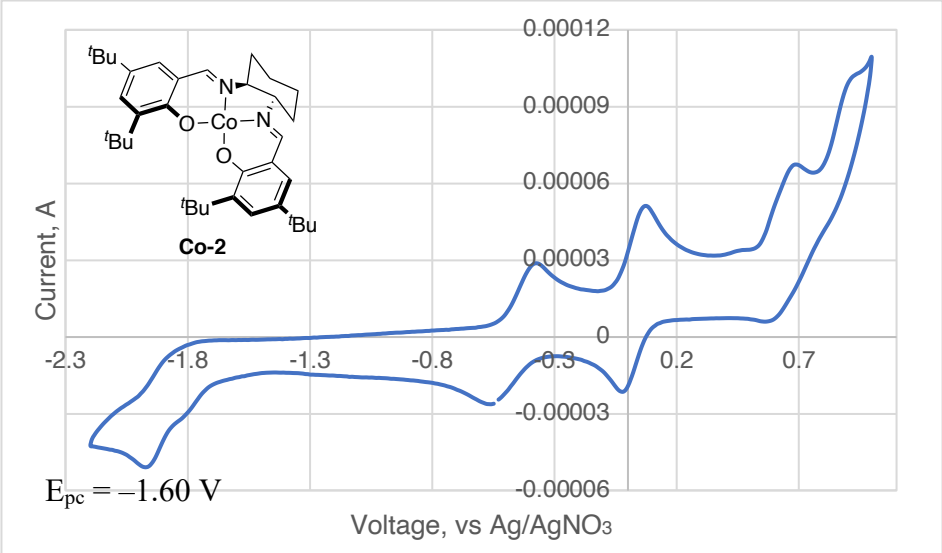



**Figure S12.** Cyclic voltammogram of **Co-2** in DMF (3 mM).

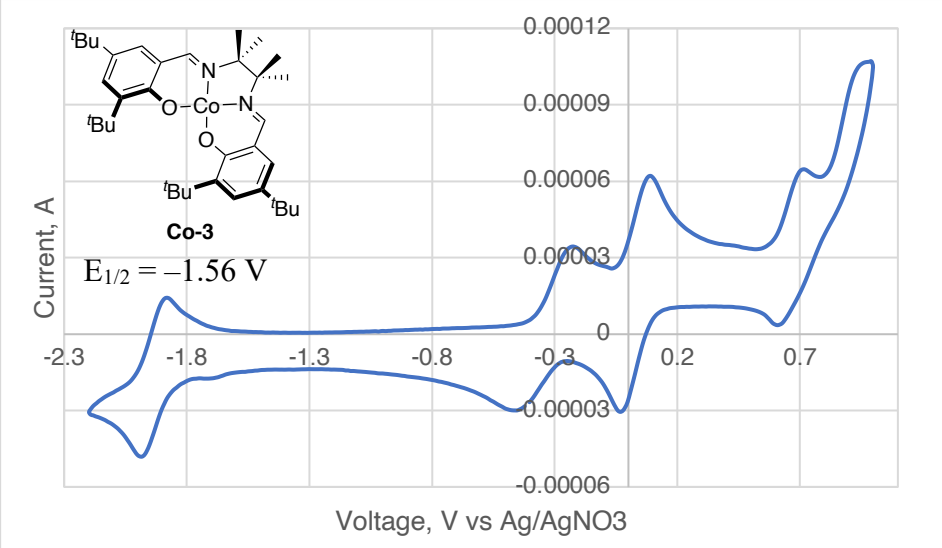



**Figure S13.** Cyclic voltammogram of **Co-3** in DMF (3 mM).

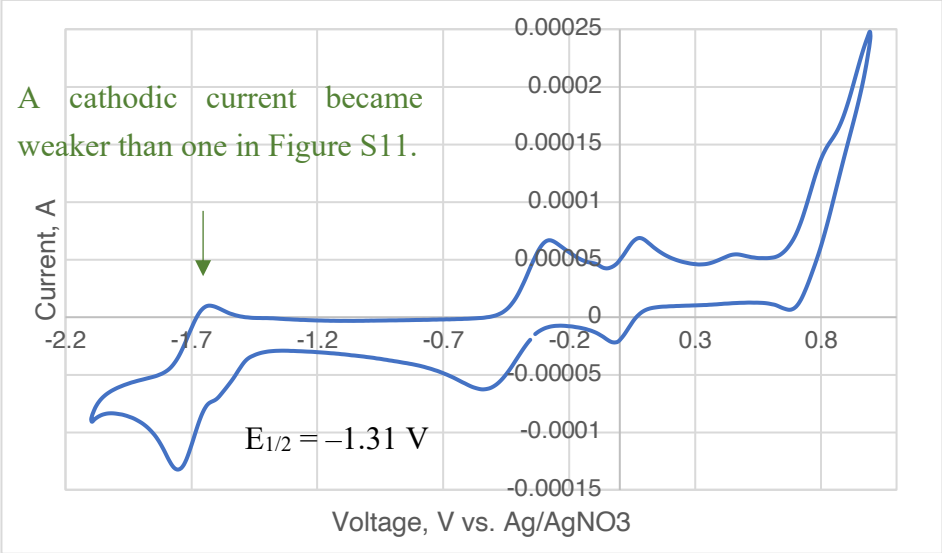



**Figure S14.** Cyclic voltammogram of **Co-1** (0.1 M) and **HX-1** (0.1 M) in DMF (10 mM).

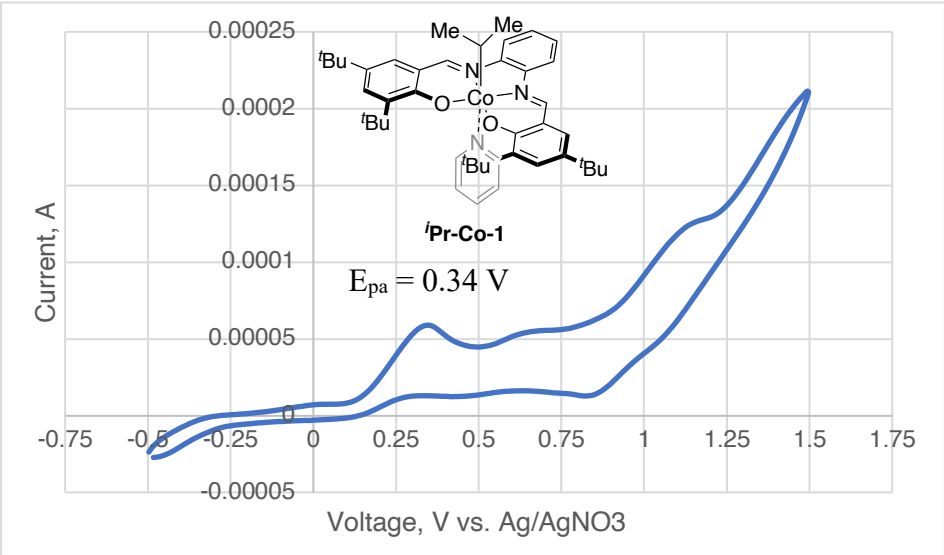



**Figure S15.** Cyclic voltammogram of **$^{i}$Pr-Co-1** in DCM (3 mM).

## 10. UV-Vis Adsorption Spectra Experiments

UV-Vis adsorption spectrum of organophotocatalyst **PTH-1** was measured with 40 μM acetonitrile solution.

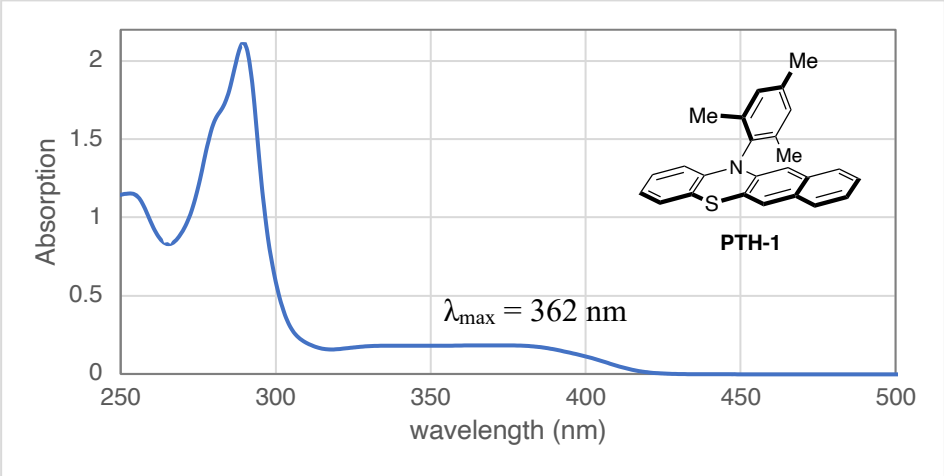



**Figure S16.** UV-Vis spectrum of **PTH-1**.

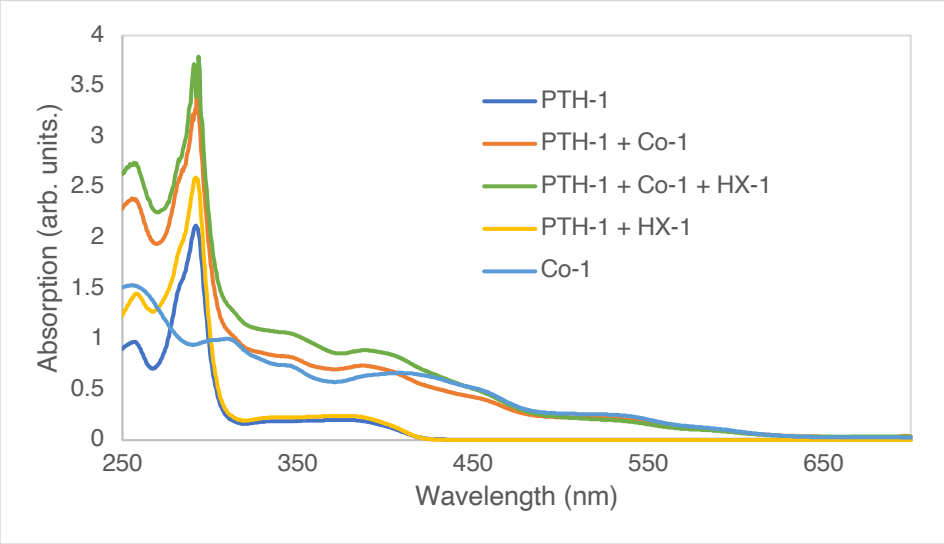



**Figure S17.** UV-Vis spectra of **PTH-1**, **Co-1** and **HX-1** (40 μM)

## 11. Fluorescence spectra of PTH-1

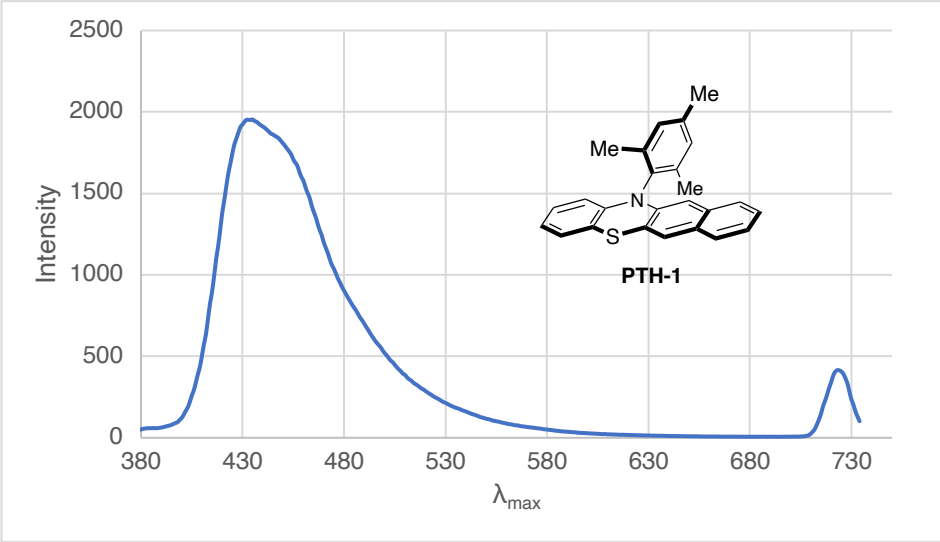



**Figure S18.** Fluorescence spectrum of **PTH-1** was scanned from 372 to 734 nm after excitation at 362 nm.

## 12. Summary of Redox Properties of Organophotocatalysts

| | PTH1 | PTH2[a] | PTH3[b] |
|---|---|---|---|
| $E_{1/2}$ ($^2PC^{\bullet+}/^1PC$) (V vs $Ag/AgNO_3$)[c] | 0.54 | – | – |
| $E_{1/2}$ ($^2PC^{\bullet+}/^1PC$) (V vs SCE)[d] | 0.92 | (0.85) | 0.68 |
| $\lambda_{max,em}$ (nm) | 435 | 439 | – |
| $E_{S1,\ exp}$ (eV)[e] | 2.85 | 2.82 | 2.80 |
| $E^{0*}_{S1,\ exp}$ ($^2PC^{\bullet+}/^1PC^*$) (V vs SCE)[f] | –1.94 | (–1.97) | –2.1 |

[a] ref 2a. [b] ref 20. [c] Determined by CV experiments. [d] $E_{1/2}$ ($Ag/AgNO_3$) (V vs SCE) = 0.38 V. [e] Singlet energies were calculated using the maximum wavelength of emission. [f] Singlet excited state reduction potentials were calculated using the singlet energies and the $E_{1/2}$.

## 13. Proposed Mechanism for Formation of 3aa'

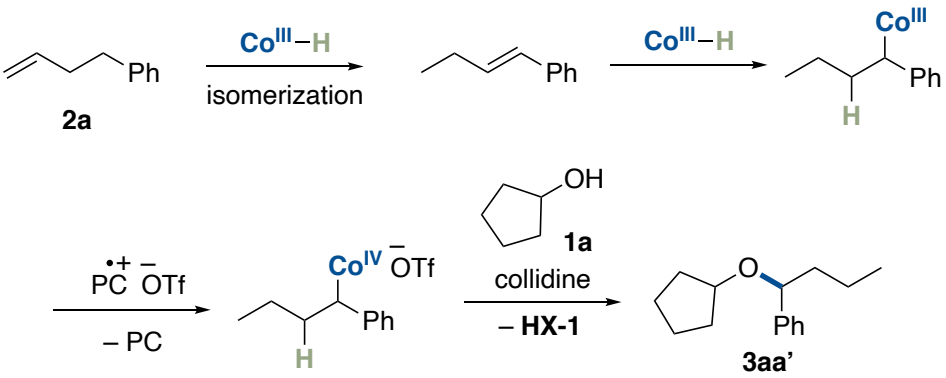



**Figure S19.** Mechanism for formation of 3aa'

## 14. Reactions with Other Nucleophiles

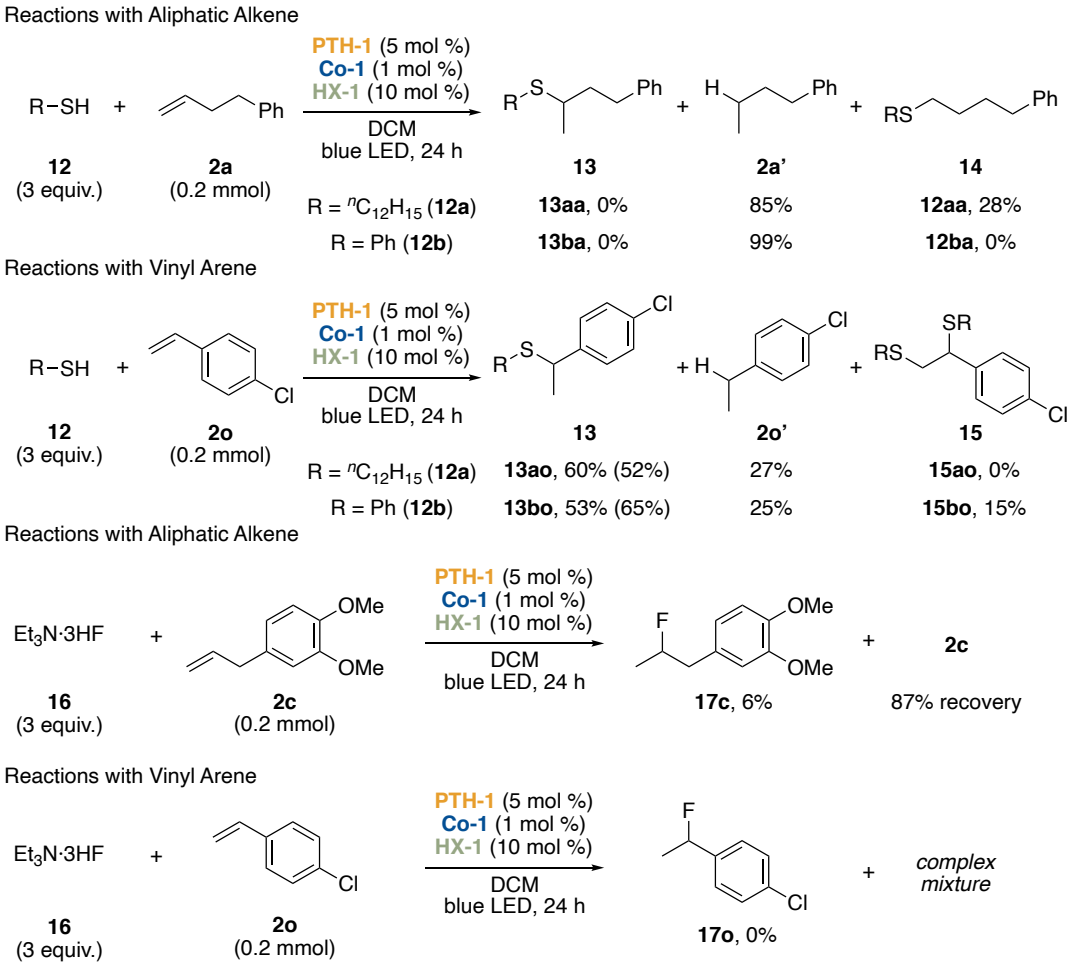
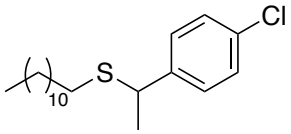


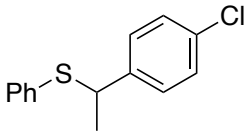

**Figure S20.** Reactions with other nucleophiles

### [1-(4-Chlorophenyl)ethyl](dodecyl)sulfane (13ao)



The product **13ao** was purified by flash chromatography on silica gel (100:0–99:1, hexane/EtOAc) (Figure S20, 35.6 mg, 0.10 mmol, 52% isolated yield). Paleyellow oil. The spectrum data of product **13ao** was consistent with the literature.[21]

### [1-(4-Chlorophenyl)ethyl](phenyl)sulfane (13bo)



The product **13bo** was purified by flash chromatography on silica gel (98:2–95:5, hexane/EtOAc) (Figure S20; 32.5 mg, 0.13 mmol, 65% isolated yield). Pale yellow oil. The spectrum data of product **13bo** was consistent with the literature.[22]

## 15. Intramolecular Hydroalkoxylation of Alkenol

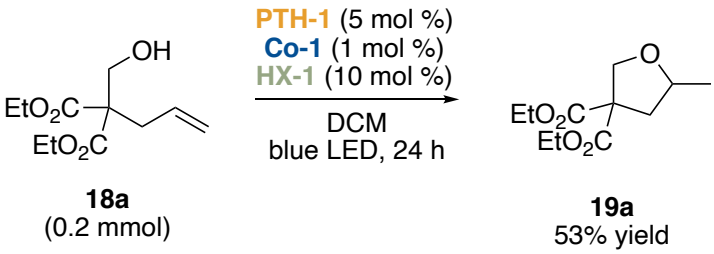
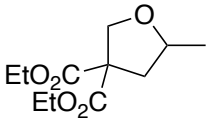


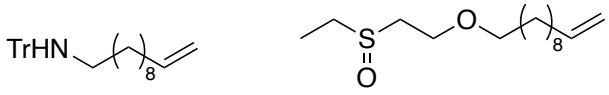

**Figure S21.** Intramolecular reaction

**Diethyl 5-Methyldihydrofuran-3,3(*2H*)-dicarboxylate (19a)**



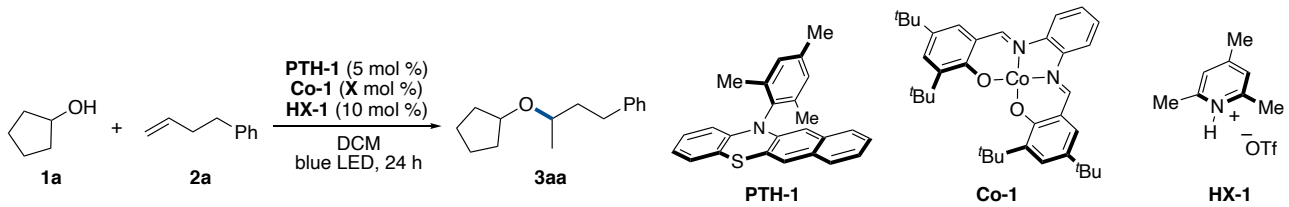

The product **19a** was purified by flash chromatography on silica gel (100:0–93:7, hexane/EtOAc) (Figure S21. 24.3 mg, 0.11 mmol, 53% isolated yield). Yellow oil. The spectrum data of product **19a** was consistent with the literature.[23]

## 16. Unsuccessful Substrates




*starting materials were fully recovered.*

## 17. Kinetic Study




In a glovebox, to an oven-dried vial with a stirring bar was added photoredox catalyst **PTH-1** (3.7 mg, 0.01 mmol), **Co-1** (2 μmol for 1 mol %; 1.6 μmol for 0.8 mol %; 1.2 μmol for 0.6 mol %; 0.8 μmol for 0.4 mol %; 0.4 μmol for 0.2 mol %), **HX-1** (5.4 mg, 0.02 mmol) and DCM (500 μL). Then, cyclopentanol **1a** (54.4 μL, 0.6 mmol), 4-phenyl-1-butene **2a** (30.0 μL, 0.2 mmol) and mesitylene (27.6 μL, 0.2 mmol, internal standard) were added to the reaction mixture. After sealing the vial with a cap and removal from the glove box, the reaction was stirred and irradiated with a 34W blue LED (0.5 cm away) with a cooling fan to keep the temperature around 40 °C (Figure S2). An aliquot (10 μL) was taken out at the indicated times (1, 2, 3, 4 and 5 h). The aliquot was directly subjected to a NMR tube filled with $CDCl_3$ and the yield of **3aa** was determined by $^1$H-NMR analysis.

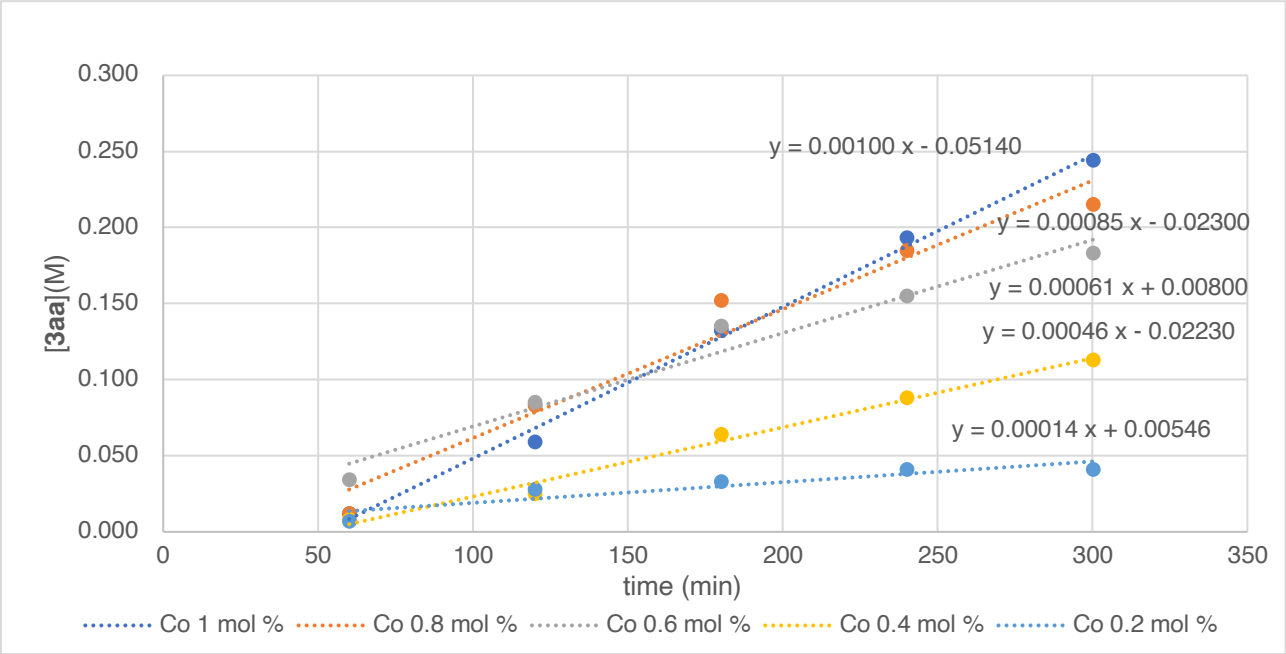



**Figure S22**. Steady state kinetics at different [Co]

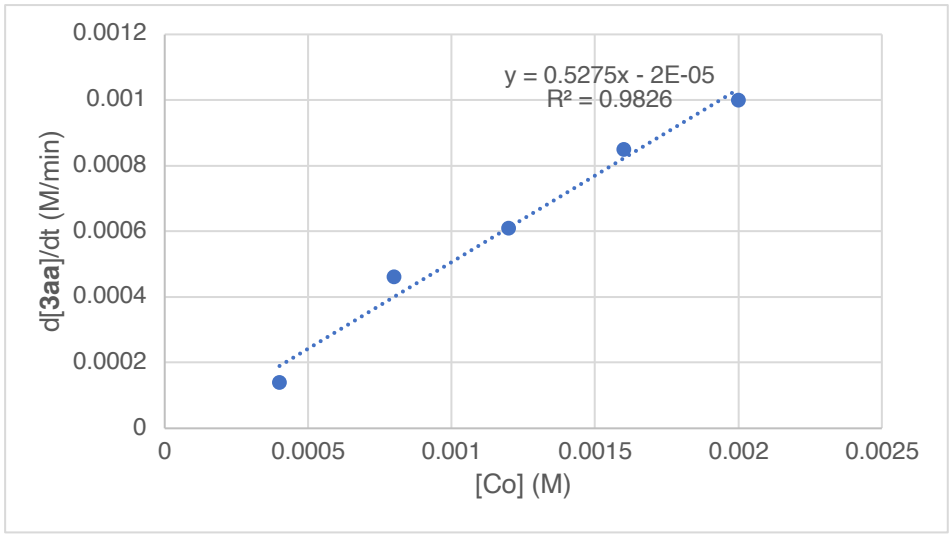



**Figure S23**. Steady state rate of **3aa** formation as a function of [Co]

Zhu and co-workers reported the bimetallic pathway on Co-catalyzed hydrofunctionalization of alkenes,[24] since the reaction rate was proportional to the square of the cobalt concentration. In contrast, the reaction rate was found to be proportional to [Co] in our reaction (Figure S23. Therefore, we assumed that the reaction would involve single cobalt complex and the radical cation form of photoredox catalyst would oxidize the alkyl-Co(III) complex.

## 18. Isolation of N-Phenyl Benzo[*b*]phenothiazine Radical Cation

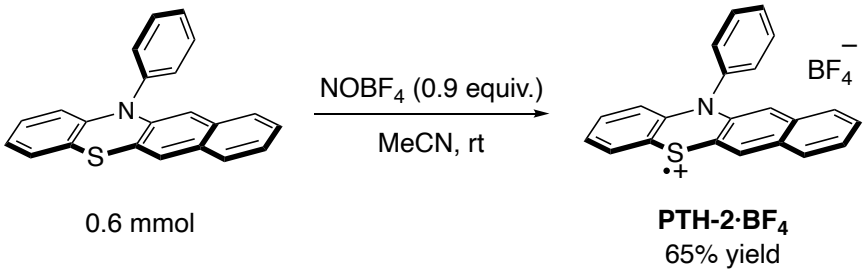



**Figure S24.** Preparation of **PTH-2·BF$_4$**

**Figure S24. PTH-2·BF$_4$** was prepared according to the reported procedure.[25] In a Schlenk tube, **PTH-2** (195.3 mg, 0.6 mmol, 1.0 equiv.) was dissolved in 2 mL anhydrous MeCN. Then the mixture was cooled to 0 ℃ and nitrosonium tetrafluoroborate (63.1 mg, 0.54 mmol, 0.90 equiv) was slowly added to the mixture. The mixture turned deep purple immediately and was stirred for a further 20 min. The mixture was freeze-pump-thawed for three cycles to remove the generated NO. Then the mixture was warmed to room temperature and the solvent removed. The solid was then dissolved in DCM (1.5 mL). A purple solid precipitated upon addition of hexanes. The purple solid was washed with hexanes three times to remove excess **PTH-2** then dried under reduced pressure. The obtained **PTH-2·BF$_4$** (150 mg, 0.39 mmol, 65%) was characterized by its absorption spectrum.

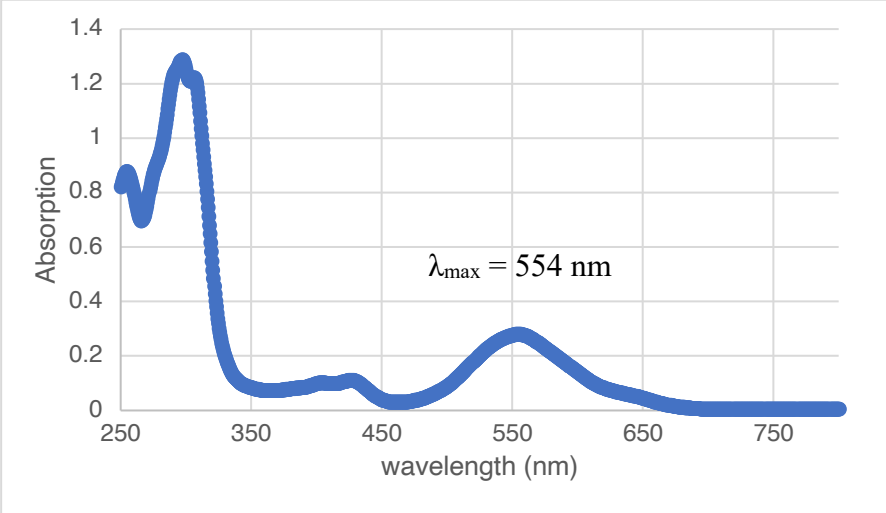



**Figure S25.** UV-Vis absorption spectrum of **PTH-2·BF$_4$**

## 19. Stoichiometric Reaction

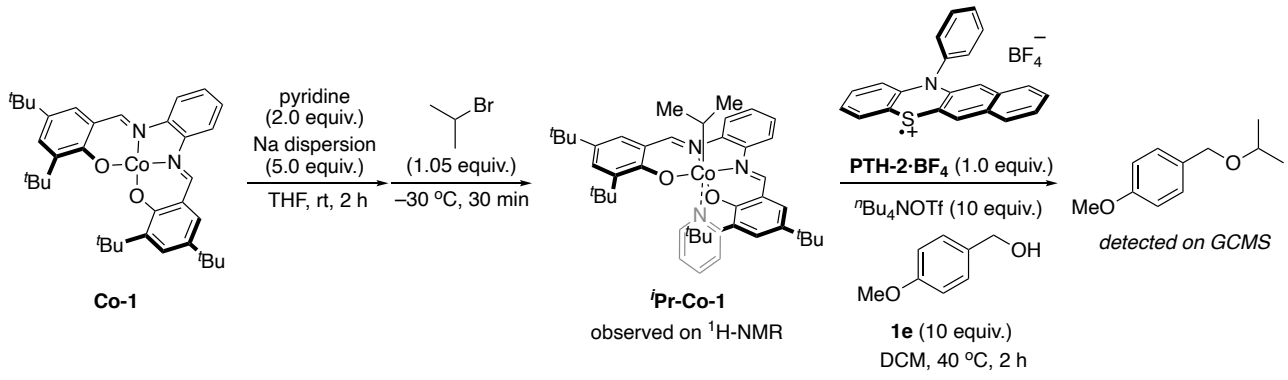



**Figure S26.** Stoichiometric Reaction

**$^{i}$Pr-Co-1** was prepared according to the literature procedure.[26] In a glove box, an oven-dried 4 mL vial equipped with a Teflon-coated magnetic stir bar was charged with **Co-1** (59.8 mg, 0.10 mmol) and anhydrous THF (1.0 mL). Pyridine (16.1 µL, 0.20 mmol) and Na dispersion (27.6 mg, 0.3 mmol, 25%wt) were sequentially added via syringe. The resulting red suspension was stirred at ambient temperature for 2 hours until a dark green solution was formed. After the vial was wrapped aluminum foil to avoid light and cooled at –30 °C, 2-bromopropane (9.9 µL, 0.11 mmol, 1.05 equiv.) was added. After stirring for 30 min at –30 °C, the solution was passed through a short pad of silica gel (3 mm hight) with small amount of DCM (50 µL) to remove unreacted Na. Then, methyl benzoate (7.0 mg, 0.051 mmol) was added to the reaction mixture and the aliquot (10 µL) was used to determine the yield of **$^{i}$Pr-Co-1** (0.031 mmol, 31% yield, Figure S26) on $^{1}$H-NMR (benzene-$d_6$) analysis (we have already confirmed that **$^{i}$Pr-Co-1** was not decomposed by silica gel). The resulting mixture was kept in the refrigerator in the glovebox and used as a stock solution ([**$^{i}$Pr-Co-1**] = 0.031 mol/L). Although we could not fully characterize the **$^{i}$Pr-Co-1** on $^{1}$H-NMR, the signals $\delta$ –0.41 and 4.35 were consistent with ones of reported *i*Pr-Co(III) complex.[27,27]

In a glovebox, an aliquot of **$^{i}$Pr-Co-1** solution (160 µL, 5 µmol), tetrabutylammonium triflate (19.6 mg, 50 µmol) and **PTH-2·BF$_4$** (2.1 mg, 50 µmol) were added to an oven-dried 4 mL vial equipped with a Teflon-coated magnetic stir bar. To the reaction mixture, DCM solution (130 µL) of *p*-methoxy benzylalcohol **1e** (6.9 mg, 50 µmol) was added. After sealing the vial with a cap, the reaction mixture was stirred at 40 °C for 2 h. Then, the solution was passed through a short pad of silica gel and evaculated. The residue was purified by flash chromatography on silica gel (100:0–95:5, hexane/EtOAc) and a trace amount of desired product was detected on GCMS.

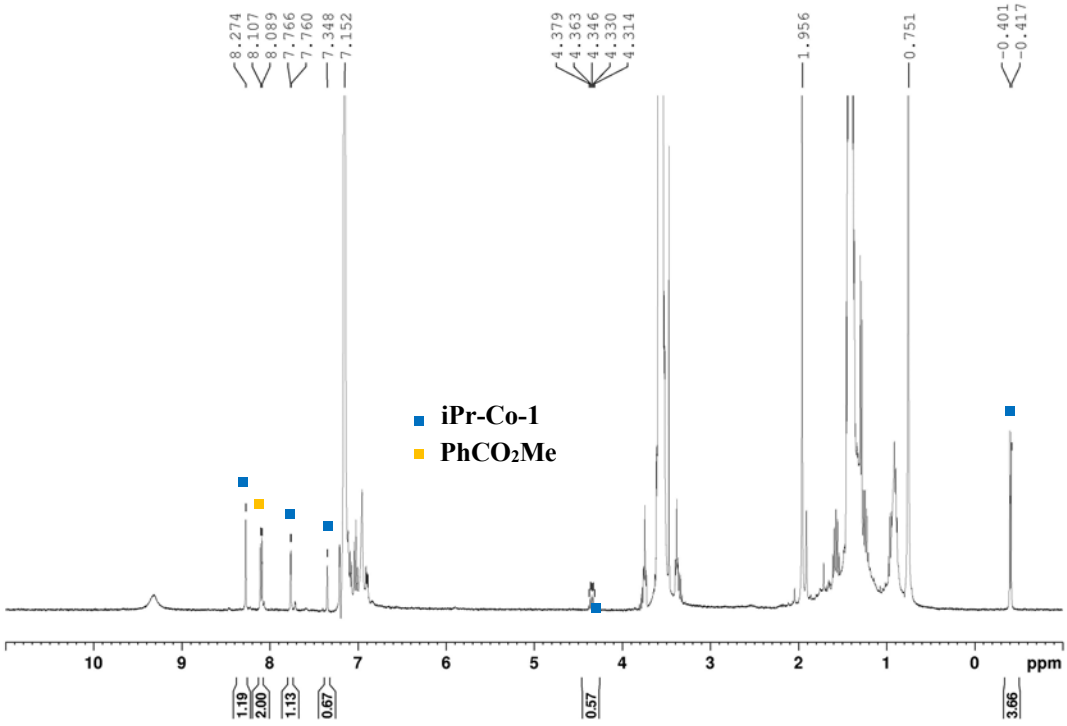



**Figure S27.** $^{1}$H-NMR of **$^{i}$Pr-Co-1**

## 20. Computational Studies

To gain the deep mechanistic insight into the C–O bond formation step, the computational studies were carried out based on the Shigehisa's report[28]. All the restricted and unrestricted density functional theory (DFT) calculations were performed with the Gaussian 16 package.[29] The method (U)B3LYP functional with the 6-31G(d) basis set was used for the geometry optimization and normal vibrational mode analysis. The dispertion-corrected method (U)BP86[30]-D3[31] functional with the 6-311+G(d,p) basis set was used to calculate single-point energies with SMD[32] model (dichloromethane). The IRC calculations were performed for each transitions state to confirm the transition state connecting the reaction pathway between the starting materials and the products.

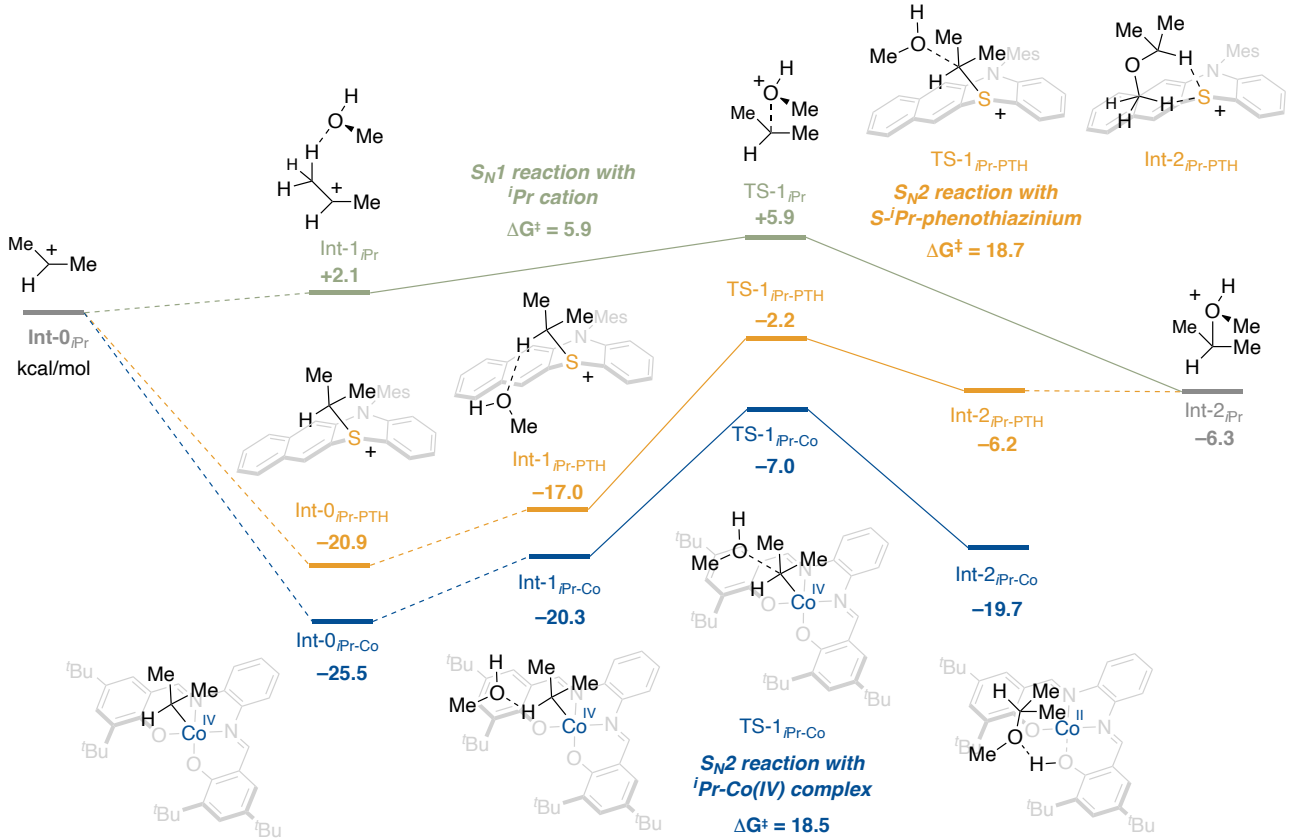



**Figure S28.** Substitution with *i*Pr cation intermediates

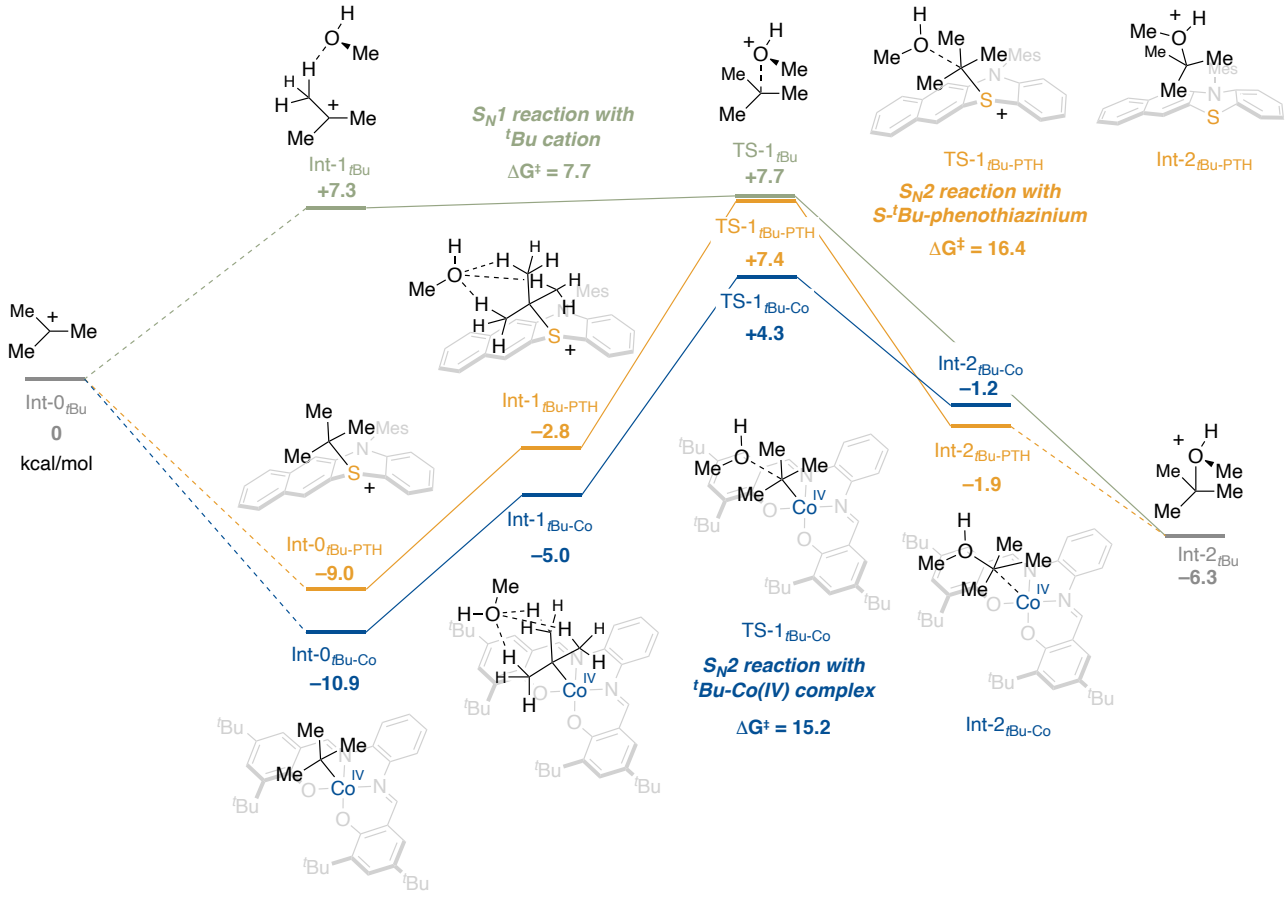



**Figure S29.** Substitution with *t*Bu cation intermediates

| UBP86D3/6-311+G(d,p)/SMD(DCM)//UB3LYP/6-31G(d) | | | |
|---|---|---|---|
| | E (hartree) | Gcorr (hartree) | Gibbs (hartree) |
| Int-0$_{i\text{Pr}}$ | -118.336941 | 0.062504 | -118.274437 |
| MeOH | -115.7679644 | 0.028753 | -115.7392114 |
| Int-1$_{i\text{Pr}}$ | -234.1183786 | 0.108025 | -234.0103536 |
| TS-1$_{i\text{Pr}}$ | -234.1140125 | 0.109751 | -234.0042615 |
| Int-2$_{i\text{Pr}}$ | -234.1499687 | 0.118913 | -234.0310557 |
| PTH | -1418.654214 | 0.335958 | -1418.318256 |
| Int-0$_{i\text{Pr-PTH}}$ | -1537.053353 | 0.427292 | -1536.626061 |
| Int-1$_{i\text{Pr-PTH}}$ | -1652.828775 | 0.470963 | -1652.357812 |
| TS-1$_{i\text{Pr-PTH}}$ | -1652.802725 | 0.46849 | -1652.334235 |
| Int-2$_{i\text{Pr-PTH}}$ | -1652.813559 | 0.473001 | -1652.340558 |
| Co | -3043.153839 | 0.674948 | -3042.478891 |
| Int-0$_{i\text{Pr-Co}}$ | -3161.56029 | 0.766366 | -3160.793924 |
| Int-1$_{i\text{Pr-Co}}$ | -3277.332933 | 0.028753 | -3277.30418 |
| TS-1$_{i\text{Pr-Co}}$ | -3277.312633 | 0.809229 | -3276.503404 |
| Int-2$_{i\text{Pr-Co}}$ | -3277.336382 | 0.813738 | -3276.522644 |
| | | | |

| | | | |
|---|---|---|---|
| Int-0$_{t\text{Bu}}$ | -157.6848997 | 0.086758 | -157.5981417 |
| MeOH | -115.7679644 | 0.028753 | -115.7392114 |
| Int-1$_{t\text{Bu}}$ | -273.4597303 | 0.134047 | -273.3256833 |
| TS-1$_{t\text{Bu}}$ | -273.4601082 | 0.134958 | -273.3251502 |
| Int-2$_{t\text{Bu}}$ | -273.4824609 | 0.144939 | -273.3375219 |
| PTH | -1418.654214 | 0.335958 | -1418.318256 |
| Int-0$_{t\text{Bu-PTH}}$ | -1576.38501 | 0.454277 | -1575.930733 |
| Int-1$_{i\text{Bu-PTH}}$ | -1692.157088 | 0.497077 | -1691.660011 |
| TS-1$_{t\text{Bu-PTH}}$ | -1692.132939 | 0.489161 | -1691.643778 |
| Int-2$_{t\text{Bu-PTH}}$ | -1692.148695 | 0.496103 | -1691.652592 |
| Co | -3043.153839 | 0.674948 | -3042.478891 |
| Int-0$_{t\text{Bu-Co}}$ | -3200.719945 | 0.79321 | -3199.926735 |
| Int-1$_{t\text{Bu-Co}}$ | -3316.486361 | 0.835332 | -3315.651029 |
| TS-1$_{t\text{Bu-Co}}$ | -3316.47229 | 0.828175 | -3315.644115 |
| Int-2$_{t\text{Bu-Co}}$ | -3316.488592 | 0.837911 | -3315.650681 |

**Figure S30.** Total electronic energy and free energy in DCM

**Int-0$_{i\text{Pr}}$**

1 1

| | | | |
|---|---|---|---|
| C | -0.63011458 | 0.09001637 | 0.00000000 |
| C | 0.65592442 | -0.56330863 | 0.01762200 |
| H | 0.62893642 | -1.64299563 | 0.17278500 |
| H | 1.07010342 | -0.35724463 | -0.99943600 |
| H | 1.37275142 | -0.04468863 | 0.67214600 |
| C | -1.91620058 | -0.56327263 | -0.01759900 |
| H | -2.63326158 | -0.04477663 | -0.67189300 |
| H | -1.88928958 | -1.64301563 | -0.17241500 |
| H | -2.32995558 | -0.35720663 | 0.99967100 |
| H | -0.63010858 | 1.18445037 | 0.00020800 |

**MeOH**

0 1

| | | | |
|---|---|---|---|
| O | -0.74468087 | 0.07364975 | 0.00000000 |
| C | -2.15602887 | -0.06838625 | 0.00001600 |
| H | -2.53065387 | -0.59300125 | -0.89289200 |
| H | -2.53031587 | -0.59231225 | 0.89346300 |
| H | -2.57354587 | 0.94219575 | -0.00025200 |
| H | -0.35964987 | -0.81523225 | 0.00007000 |

**Int-1*i*Pr**

1 1

| | | | |
|---|---|---|---|
| C | -1.72667762 | -0.43371521 | 0.00000000 |
| C | -2.58087462 | 0.32246779 | -0.80528700 |
| H | -2.35319262 | 0.37434279 | -1.87226200 |
| H | -3.54640662 | -0.45073421 | -0.74619000 |
| H | -3.00287562 | 1.23133279 | -0.37016000 |
| C | -0.77316562 | -1.44470421 | -0.46842300 |
| H | -0.92551362 | -2.39724021 | 0.05895300 |
| H | -0.77452762 | -1.58748721 | -1.55054500 |
| H | 0.23108138 | -1.11241821 | -0.14870200 |
| O | -4.79746662 | -1.31419321 | -0.74792800 |
| C | -5.99967162 | -0.76608321 | -0.14484500 |
| H | -6.38615562 | 0.07624979 | -0.72600500 |
| H | -6.75256162 | -1.55434921 | -0.06885400 |
| H | -5.72023662 | -0.43662121 | 0.85615000 |
| H | -5.00875762 | -1.63520921 | -1.64218200 |
| H | -1.81441562 | -0.31573221 | 1.08270400 |

**TS-1*i*Pr**

1 1

| | | | |
|---|---|---|---|
| C | -0.18821604 | -0.18821604 | 0.00000000 |
| C | -0.42093942 | 1.06086316 | -0.64402372 |
| H | 0.18961750 | 1.27553341 | -1.52278132 |
| H | -1.47235215 | 0.77331429 | -1.00113188 |
| H | -0.58241116 | 1.91292550 | 0.02220029 |
| C | 0.54555886 | -1.31224007 | -0.56260118 |
| H | 0.03498272 | -2.26510041 | -0.37466039 |
| H | 0.82721788 | -1.18782602 | -1.60979791 |
| H | 1.47326931 | -1.37548332 | 0.04494562 |
| O | -2.83380582 | -0.55019103 | -0.92998515 |
| C | -4.07852838 | -0.41526264 | -0.20877492 |
| H | -4.81612752 | 0.13810839 | -0.79877243 |
| H | -4.47943356 | -1.39799879 | 0.05989992 |
| H | -3.85664882 | 0.14365578 | 0.70205228 |
| H | -3.02725800 | -1.01635330 | -1.76054931 |
| H | -0.62411913 | -0.33244744 | 0.99062031 |

**Int-2*i*Pr**

1 1

| | | | |
|---|---|---|---|
| C | 1.54664488 | 0.56464811 | 0.00000000 |

| | | | |
|---|---|---|---|
| C | 0.44308488 | -0.40016989 | -0.36806200 |
| H | 0.23631088 | -0.39436989 | -1.44464800 |
| H | 0.66977288 | -1.41764889 | -0.03977200 |
| H | -0.47248012 | -0.07713989 | 0.13940400 |
| C | 1.39173088 | 1.98499211 | -0.49311100 |
| H | 2.23529488 | 2.62469311 | -0.21955500 |
| H | 1.23281488 | 2.02570211 | -1.57658100 |
| H | 0.49991888 | 2.40848711 | -0.01746300 |
| O | 2.84578988 | -0.06648889 | -0.61796300 |
| C | 4.17939788 | 0.46704011 | -0.24439700 |
| H | 4.90493688 | -0.21605389 | -0.68449800 |
| H | 4.29227488 | 1.48457611 | -0.61805100 |
| H | 4.21698088 | 0.42341211 | 0.84247400 |
| H | 2.75327888 | -0.14017289 | -1.59029100 |
| H | 1.80040288 | 0.50981711 | 1.06044200 |

**PTH**

0 1

| | | | |
|---|---|---|---|
| C | 0.20458266 | 0.18821604 | 0.00000000 |
| C | 1.53412766 | 0.24910604 | 0.41457400 |
| C | 2.25506566 | -0.91518096 | 0.68700600 |
| C | 1.67201666 | -2.18513896 | 0.49849300 |
| C | 0.32867666 | -2.22818696 | 0.08253500 |
| C | -0.39485034 | -1.05962696 | -0.15253000 |
| C | 3.81012366 | -3.45016496 | 0.71791600 |
| C | 4.61009066 | -2.27698096 | 0.91099200 |
| C | 5.98334766 | -2.33916896 | 0.84451800 |
| H | 6.56213066 | -1.42829296 | 0.97743300 |
| C | 6.66764166 | -3.56589396 | 0.64638800 |
| C | 5.88382166 | -4.75205096 | 0.50511400 |
| C | 4.46798766 | -4.65672996 | 0.53286300 |
| H | 2.02288166 | 1.21011404 | 0.55099300 |
| H | -0.15727634 | -3.18737396 | -0.04674900 |
| H | 3.89438266 | -5.56770996 | 0.40820800 |
| N | 2.39674566 | -3.37982596 | 0.72926900 |
| S | 3.86770866 | -0.74408896 | 1.41250000 |
| H | -1.43220534 | -1.13694396 | -0.46612900 |
| H | -0.34909134 | 1.10167404 | -0.19488100 |
| C | 6.55177366 | -5.99185196 | 0.32242900 |
| C | 7.92823666 | -6.05165996 | 0.27804800 |
| H | 8.42535666 | -7.00767596 | 0.13658100 |
| C | 8.70201766 | -4.87453396 | 0.41576200 |
| H | 9.78626266 | -4.93461396 | 0.37844200 |
| C | 8.08201066 | -3.65677496 | 0.59725800 |
| H | 8.67018466 | -2.74841796 | 0.70632200 |
| H | 5.95782366 | -6.89667396 | 0.21581600 |
| C | 1.66242166 | -4.62440996 | 0.74156500 |
| C | 1.23976066 | -5.13367096 | 1.98159300 |
| C | 1.38921366 | -5.30495796 | -0.46025400 |
| C | 0.53274466 | -6.34034996 | 1.99837200 |
| C | 0.67879566 | -6.50821696 | -0.39128200 |
| C | 0.23896266 | -7.04102996 | 0.82483000 |
| H | 0.20525366 | -6.74221396 | 2.95502200 |
| H | 0.46553066 | -7.04268596 | -1.31484100 |
| C | 1.54512366 | -4.40067696 | 3.26562000 |
| H | 2.62501766 | -4.28588596 | 3.41331900 |
| H | 1.11616566 | -3.39216496 | 3.26313600 |

| | | | |
|---|---|---|---|
| H | 1.13947066 | -4.94098996 | 4.12615800 |
| C | 1.84660566 | -4.76240496 | -1.79437600 |
| H | 1.55473566 | -5.43631896 | -2.60532300 |
| H | 1.41040266 | -3.77793596 | -1.99903600 |
| H | 2.93520366 | -4.64220296 | -1.82774800 |
| C | -0.55416134 | -8.32651696 | 0.86636800 |
| H | -0.38955734 | -8.86904096 | 1.80327200 |
| H | -1.63197434 | -8.13001696 | 0.78976400 |
| H | -0.28605334 | -8.99036996 | 0.03769800 |

**Int-0$_{i\text{Pr-PTH}}$**

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| | | | |
|---|---|---|---|
| C | 0.35188217 | 0.20442496 | -0.00803188 |
| C | 1.59217617 | -0.39461004 | 0.14162112 |
| C | 1.68937517 | -1.71883404 | 0.60200712 |
| C | 0.54702317 | -2.51159604 | 0.86604512 |
| C | -0.70111383 | -1.86144604 | 0.72342412 |
| C | -0.79053783 | -0.54122404 | 0.30581512 |
| C | 1.77706617 | -4.63688704 | 1.17275212 |
| C | 3.06851317 | -4.07032504 | 0.92975212 |
| C | 4.20454717 | -4.84863904 | 0.78553512 |
| H | 5.15967417 | -4.37529204 | 0.56969812 |
| C | 4.14969317 | -6.24943404 | 0.92593812 |
| C | 2.87711817 | -6.83797204 | 1.22529512 |
| C | 1.72966317 | -6.01809304 | 1.33100412 |
| H | 2.49941917 | 0.15372796 | -0.09523188 |
| H | -1.60622083 | -2.41645204 | 0.93261112 |
| H | 0.77631317 | -6.49450304 | 1.52384712 |
| N | 0.59988517 | -3.86362404 | 1.21755712 |
| S | 3.33082817 | -2.32080004 | 0.86436412 |
| H | -1.77407183 | -0.09162404 | 0.20782712 |
| H | 0.27363617 | 1.22685996 | -0.36081288 |
| C | 3.82735817 | -1.82830704 | 2.63982612 |
| C | 2.80858817 | -2.24672704 | 3.68623112 |
| H | 2.62354017 | -3.32366704 | 3.67431412 |
| H | 3.20194617 | -1.98692804 | 4.67570912 |
| H | 1.86069517 | -1.71591504 | 3.55467912 |
| C | 4.14002517 | -0.33375004 | 2.62982812 |
| H | 4.56525817 | -0.06300604 | 3.60227512 |
| H | 4.87143017 | -0.06529804 | 1.86077812 |
| H | 3.23477617 | 0.26498396 | 2.48731112 |

| | | | |
|---|---|---|---|
| C | 2.80393717 | -8.24893504 | 1.38806212 |
| C | 3.93212517 | -9.02507504 | 1.25742112 |
| H | 3.86432317 | -10.10157904 | 1.38336212 |
| C | 5.18962717 | -8.43831404 | 0.95718212 |
| H | 6.06568217 | -9.07137104 | 0.85622012 |
| C | 5.29764617 | -7.07797504 | 0.79444012 |
| H | 6.25648517 | -6.62091904 | 0.56452112 |
| H | 1.84380017 | -8.70423104 | 1.61430012 |
| C | -0.66150683 | -4.57400704 | 1.38240112 |
| C | -1.20261383 | -4.71616504 | 2.67075212 |
| C | -1.29985083 | -5.10612904 | 0.24569212 |
| C | -2.41159383 | -5.40777704 | 2.80198912 |
| C | -2.50524783 | -5.78847004 | 0.43343712 |
| C | -3.08077083 | -5.94843904 | 1.69941812 |
| H | -2.83959683 | -5.52654604 | 3.79443112 |
| H | -3.00772183 | -6.20700404 | -0.43537188 |
| C | -0.51246383 | -4.15084704 | 3.88899912 |
| H | 0.48054217 | -4.59351104 | 4.03227412 |
| H | -0.37893583 | -3.06535104 | 3.81253912 |
| H | -1.09721583 | -4.35047904 | 4.79067412 |
| C | -0.71637383 | -4.95428604 | -1.13965188 |
| H | -1.34548483 | -5.45771104 | -1.87816388 |
| H | -0.63788983 | -3.90094004 | -1.43421588 |
| H | 0.28873017 | -5.38634304 | -1.20799888 |
| C | -4.39931183 | -6.66467204 | 1.86498112 |
| H | -4.50168483 | -7.09105904 | 2.86746912 |
| H | -5.24010883 | -5.97505004 | 1.71528612 |
| H | -4.51032783 | -7.47361204 | 1.13597012 |
| H | 4.75143017 | -2.41134104 | 2.73725412 |

**Int-1*i*Pr-PTH**

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| | | | |
|---|---|---|---|
| C | -0.16930023 | 0.19187359 | 0.00000000 |
| C | -1.21321223 | 1.08615259 | 0.17649900 |
| C | -0.96304623 | 2.39299059 | 0.62769700 |
| C | 0.34968877 | 2.87050559 | 0.85069400 |
| C | 1.38971577 | 1.92652959 | 0.68287700 |
| C | 1.13236177 | 0.62487659 | 0.27682400 |
| C | -0.29649123 | 5.23965459 | 1.15907400 |
| C | -1.69822523 | 5.01808959 | 0.96853800 |
| C | -2.60638223 | 6.05629059 | 0.85629600 |

| | | | |
|---|---|---|---|
| H | -3.66162823 | 5.83191959 | 0.71624900 |
| C | -2.18686523 | 7.39819859 | 0.96779700 |
| C | -0.79695823 | 7.64836859 | 1.20768500 |
| C | 0.10716177 | 6.56395159 | 1.29084800 |
| H | -2.23559323 | 0.78340359 | -0.03055000 |
| H | 2.41092677 | 2.23613759 | 0.86251400 |
| H | 1.15643577 | 6.78346059 | 1.44484700 |
| N | 0.64891577 | 4.19434759 | 1.18524900 |
| S | -2.39736723 | 3.38778859 | 0.92247600 |
| H | 1.96767477 | -0.05871941 | 0.15798100 |
| H | -0.36205823 | -0.81806641 | -0.34487300 |
| C | -2.96286723 | 3.03200559 | 2.70722100 |
| C | -1.88703323 | 3.30463059 | 3.74412800 |
| H | -1.51966523 | 4.33304359 | 3.69728100 |
| H | -2.31879723 | 3.15087659 | 4.73995400 |
| H | -1.04310823 | 2.61577059 | 3.63842000 |
| C | -3.51668023 | 1.60967059 | 2.73940000 |
| H | -3.97831323 | 1.44358159 | 3.71891200 |
| H | -4.28793223 | 1.44921559 | 1.97922900 |
| H | -2.72760123 | 0.86150159 | 2.61449700 |
| O | -5.57640423 | 4.71105159 | 1.43533500 |
| C | -6.59170023 | 4.12702659 | 0.61001800 |
| H | -7.30847023 | 3.54149459 | 1.19965300 |
| H | -7.13486423 | 4.88650259 | 0.03406500 |
| H | -6.08247923 | 3.45969459 | -0.08859900 |
| H | -6.01100923 | 5.32438059 | 2.04816000 |
| H | -3.78709423 | 3.75096959 | 2.76546900 |
| C | -0.36179523 | 8.99599559 | 1.33964200 |
| C | -1.26046023 | 10.03240259 | 1.23526800 |
| H | -0.91663223 | 11.05759059 | 1.33654500 |
| C | -2.63651123 | 9.78106459 | 0.99398600 |
| H | -3.32695623 | 10.61484959 | 0.91160500 |
| C | -3.09103123 | 8.49035359 | 0.86358100 |
| H | -4.14226223 | 8.28786159 | 0.67609900 |
| H | 0.69090577 | 9.19462259 | 1.52110500 |
| C | 2.05180477 | 4.56244159 | 1.31573600 |
| C | 2.64095277 | 4.56648859 | 2.59063700 |
| C | 2.77866377 | 4.91169359 | 0.16141600 |
| C | 3.98837977 | 4.92977259 | 2.69050900 |
| C | 4.12145177 | 5.26694659 | 0.31737300 |
| C | 4.74726577 | 5.28006859 | 1.56951300 |

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|---|---|---|---|
| H | 4.45489677 | 4.93917359 | 3.67264100 |
| H | 4.69368077 | 5.54182959 | -0.56558800 |
| C | 1.85822077 | 4.19438559 | 3.82705900 |
| H | 0.99506777 | 4.85428259 | 3.97297300 |
| H | 1.47834077 | 3.16720359 | 3.77120300 |
| H | 2.48730577 | 4.26702059 | 4.71809000 |
| C | 2.14378277 | 4.90829459 | -1.20948200 |
| H | 2.86378377 | 5.22921859 | -1.96669900 |
| H | 1.78984277 | 3.90916259 | -1.49029700 |
| H | 1.28215677 | 5.58398659 | -1.26024800 |
| C | 6.20750677 | 5.64042159 | 1.70042700 |
| H | 6.44171077 | 6.00971959 | 2.70343000 |
| H | 6.84445377 | 4.76555259 | 1.51647000 |
| H | 6.49697677 | 6.40910259 | 0.97670800 |

**TS-1*i*Pr-PTH**

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| | | | |
|---|---|---|---|
| C | -1.90671036 | 0.89198035 | 0.00000000 |
| C | -2.70347936 | 2.02963835 | -0.03106900 |
| C | -2.29485436 | 3.21455435 | 0.59729100 |
| C | -1.04526036 | 3.29928535 | 1.25382500 |
| C | -0.25978236 | 2.12539235 | 1.28048700 |
| C | -0.68330736 | 0.95004735 | 0.67093400 |
| C | -1.18194936 | 5.74568635 | 1.72437800 |
| C | -2.45781436 | 5.91995735 | 1.09299800 |
| C | -3.00607936 | 7.17684635 | 0.92348200 |
| H | -3.96221336 | 7.27511935 | 0.41399500 |
| C | -2.35791436 | 8.34370835 | 1.39001700 |
| C | -1.10328236 | 8.18454035 | 2.05812600 |
| C | -0.55000636 | 6.88840735 | 2.20082700 |
| H | -3.65618936 | 2.01563335 | -0.55458500 |
| H | 0.70048264 | 2.14733635 | 1.77934100 |
| H | 0.41348364 | 6.79782335 | 2.68732300 |
| N | -0.56894436 | 4.47937635 | 1.85351700 |
| S | -3.45923436 | 4.54954035 | 0.58172300 |
| H | -0.04105236 | 0.07558535 | 0.71449200 |
| H | -2.23149436 | -0.01813565 | -0.49344000 |
| C | -4.92631636 | 3.98387335 | 3.25049100 |
| C | -4.42802136 | 5.20042835 | 3.93944600 |
| H | -5.17066536 | 6.00256235 | 3.94572500 |
| H | -4.11278836 | 4.97605235 | 4.96198000 |

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|---|---|---|---|
| H | -3.55278236 | 5.58810435 | 3.39482900 |
| C | -4.26710536 | 2.66466735 | 3.43710800 |
| H | -4.03154836 | 2.48807435 | 4.49169400 |
| H | -4.86321036 | 1.83969535 | 3.03571500 |
| H | -3.31243936 | 2.65482835 | 2.88791300 |
| O | -6.52800836 | 3.64269935 | 4.48148100 |
| C | -7.76149736 | 4.34846535 | 4.20706900 |
| H | -8.15630836 | 4.09575235 | 3.21760300 |
| H | -8.49377436 | 4.10401235 | 4.98113400 |
| H | -7.52835636 | 5.41204635 | 4.25795700 |
| H | -6.70423436 | 2.68563235 | 4.47435100 |
| H | -5.58063336 | 4.11198535 | 2.39715800 |
| C | -0.43996036 | 9.34204035 | 2.54772100 |
| C | -0.99445136 | 10.59078135 | 2.37724300 |
| H | -0.47699236 | 11.46876035 | 2.75276500 |
| C | -2.23612936 | 10.74528435 | 1.71076200 |
| H | -2.65560436 | 11.73843935 | 1.58103700 |
| C | -2.90510136 | 9.64380535 | 1.22720000 |
| H | -3.85582536 | 9.75589635 | 0.71187100 |
| H | 0.51456064 | 9.22709335 | 3.05462000 |
| C | 0.73923364 | 4.43520235 | 2.48126800 |
| C | 0.82387064 | 4.18187035 | 3.85980700 |
| C | 1.88938964 | 4.65389135 | 1.69984500 |
| C | 2.09098164 | 4.14880435 | 4.45095600 |
| C | 3.13267864 | 4.61034535 | 2.33774200 |
| C | 3.25775764 | 4.35710635 | 3.70874100 |
| H | 2.16670864 | 3.95623435 | 5.51865600 |
| H | 4.02870964 | 4.78036135 | 1.74519300 |
| C | -0.41590536 | 3.95197135 | 4.69119500 |
| H | -1.09514936 | 4.81196035 | 4.64373700 |
| H | -0.97230936 | 3.07176435 | 4.34527500 |
| H | -0.15385336 | 3.78943935 | 5.74035300 |
| C | 1.79640464 | 4.92877635 | 0.21763900 |
| H | 2.79112764 | 5.08361135 | -0.20854600 |
| H | 1.32854164 | 4.09519235 | -0.31926300 |
| H | 1.19865664 | 5.82355035 | 0.00909900 |
| C | 4.61787964 | 4.28889235 | 4.36110300 |
| H | 4.55711364 | 4.47603535 | 5.43754000 |
| H | 5.06893664 | 3.29735335 | 4.22546500 |
| H | 5.30768164 | 5.01949035 | 3.92617100 |

**Int-2$_{i\text{Pr-PTH}}$**

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| | | | |
|---|---|---|---|
| C | 0.19939805 | -0.10910459 | 0.00000000 |
| C | -1.12457495 | 0.32345741 | 0.00493500 |
| C | -1.45635695 | 1.59112941 | 0.48641200 |
| C | -0.46665595 | 2.48784841 | 0.93388700 |
| C | 0.86477605 | 2.03163941 | 0.91908200 |
| C | 1.18823205 | 0.75280741 | 0.46981100 |
| C | -1.97104995 | 4.47506641 | 1.07207000 |
| C | -3.11497295 | 3.77618441 | 0.56259300 |
| C | -4.24555395 | 4.45364341 | 0.16000800 |
| H | -5.06937995 | 3.89636641 | -0.28181400 |
| C | -4.36823495 | 5.85974941 | 0.30909500 |
| C | -3.26693095 | 6.56207441 | 0.89181200 |
| C | -2.09144995 | 5.84840541 | 1.24429900 |
| H | -1.91564595 | -0.32664359 | -0.35882200 |
| H | 1.65457205 | 2.68624141 | 1.26508000 |
| H | -1.25592695 | 6.41071241 | 1.64429700 |
| N | -0.77480995 | 3.79594341 | 1.39192900 |
| S | -3.18416995 | 2.00020841 | 0.60881400 |
| H | 2.22825905 | 0.44061541 | 0.47897500 |
| H | 0.44938305 | -1.09935559 | -0.36680200 |
| C | -4.65760495 | 3.18494641 | 4.06592900 |
| C | -5.06958695 | 4.63440241 | 4.00100500 |
| H | -5.45618795 | 4.92154241 | 3.02014000 |
| H | -5.79531295 | 4.88101441 | 4.78140100 |
| H | -4.16854795 | 5.23645141 | 4.16243000 |
| C | -4.14614695 | 2.70422341 | 5.40512600 |
| H | -4.85173195 | 2.92686341 | 6.21162900 |
| H | -3.90950695 | 1.63310041 | 5.40076600 |
| H | -3.21021095 | 3.23072041 | 5.61785500 |
| O | -5.96829795 | 2.33484341 | 3.82650400 |
| C | -6.51426795 | 2.23549641 | 2.44884200 |
| H | -5.76780495 | 1.77176841 | 1.80306100 |
| H | -7.42518395 | 1.64400941 | 2.53439700 |
| H | -6.74050895 | 3.25358741 | 2.14397700 |
| H | -5.82255795 | 1.43798141 | 4.18929300 |
| H | -4.01411695 | 2.88429041 | 3.23447400 |
| C | -3.37731695 | 7.96675041 | 1.07541100 |
| C | -4.51858795 | 8.63879941 | 0.69450100 |
| H | -4.58659795 | 9.71366341 | 0.83523700 |

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|---|---|---|---|
| C | -5.60408695 | 7.94136541 | 0.11086900 |
| H | -6.49235095 | 8.48662941 | -0.19422400 |
| C | -5.52955795 | 6.57814541 | -0.07772000 |
| H | -6.35540495 | 6.03926041 | -0.53716900 |
| H | -2.54157995 | 8.50680541 | 1.51324900 |
| C | 0.31364105 | 4.58398741 | 1.93609900 |
| C | 0.50987305 | 4.58364041 | 3.32640700 |
| C | 1.15139005 | 5.32495341 | 1.07957500 |
| C | 1.55832705 | 5.34320041 | 3.85477600 |
| C | 2.18571405 | 6.06954141 | 1.65543100 |
| C | 2.40992705 | 6.09174841 | 3.03678500 |
| H | 1.71444405 | 5.34773341 | 4.93123000 |
| H | 2.83715205 | 6.64669241 | 1.00304000 |
| C | -0.38904995 | 3.78112841 | 4.23664400 |
| H | -1.43297295 | 4.10984741 | 4.14469500 |
| H | -0.36162895 | 2.71314841 | 3.99075000 |
| H | -0.08630895 | 3.89741741 | 5.28147800 |
| C | 0.95473105 | 5.32380341 | -0.41834400 |
| H | 1.72560005 | 5.92506141 | -0.90785200 |
| H | 1.00652905 | 4.31000441 | -0.83115700 |
| H | -0.02135995 | 5.73584041 | -0.69907100 |
| C | 3.55648905 | 6.88180041 | 3.62136000 |
| H | 3.38416605 | 7.12052041 | 4.67539500 |
| H | 4.49442405 | 6.31449641 | 3.56294200 |
| H | 3.71314105 | 7.82072041 | 3.08025300 |

**Int-0$_{i\text{Pr-Co}}$**

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| | | | |
|---|---|---|---|
| Co | -0.45008184 | -0.25368248 | 0.00000000 |
| N | 0.79267116 | 1.09764252 | -0.34745000 |
| N | -1.73167584 | 1.11525952 | -0.26032100 |
| C | -3.01377684 | 0.93651452 | -0.47719400 |
| H | -3.61828984 | 1.81773452 | -0.68576000 |
| C | 2.06516916 | 0.90977452 | -0.65423300 |
| H | 2.62653116 | 1.77938152 | -0.99162600 |
| C | -3.69904084 | -0.30101648 | -0.46903000 |
| C | -5.11068184 | -0.26991248 | -0.61057000 |
| C | -2.99401684 | -1.54190348 | -0.35460300 |
| C | -5.85186884 | -1.43114948 | -0.61531800 |
| H | -5.58925784 | 0.69908152 | -0.70490500 |
| C | -3.74679784 | -2.76279948 | -0.38215400 |

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| C | -5.12687584 | -2.64730448 | -0.49875600 |
| C | 2.77990416 | -0.29693748 | -0.56882300 |
| C | 4.17072116 | -0.25676848 | -0.87261400 |
| C | 2.14371516 | -1.51804148 | -0.14883900 |
| C | 4.95982016 | -1.37181048 | -0.73739400 |
| H | 4.58789116 | 0.68901252 | -1.20178200 |
| C | 2.97037116 | -2.68431948 | 0.03700100 |
| C | 4.31574916 | -2.55434048 | -0.26786900 |
| O | -1.67644584 | -1.56747948 | -0.27948800 |
| O | 0.84951816 | -1.57681248 | 0.03241700 |
| C | -1.16287784 | 2.41584852 | -0.26870400 |
| C | -1.85405984 | 3.62986252 | -0.19731000 |
| C | -1.13814984 | 4.82502652 | -0.19185000 |
| C | 0.25920916 | 4.81330852 | -0.23399200 |
| C | 0.95407416 | 3.60658952 | -0.28267400 |
| C | 0.23970916 | 2.40430552 | -0.31661400 |
| C | -0.55876284 | -0.31679648 | 2.07496700 |
| C | 0.66742616 | 0.35961852 | 2.64022400 |
| H | 1.60170816 | -0.03361848 | 2.23428400 |
| H | 0.64124616 | 1.44617652 | 2.51030000 |
| C | -1.86835984 | 0.20508752 | 2.60833400 |
| H | -1.94609884 | 1.29445552 | 2.54214800 |
| H | -2.74080784 | -0.25344048 | 2.13745300 |
| H | 0.67862716 | 0.16540752 | 3.72474000 |
| H | -5.70404484 | -3.56238748 | -0.51252100 |
| H | 4.94086616 | -3.42855148 | -0.14276700 |
| H | -2.93582784 | 3.65806352 | -0.12619300 |
| H | -1.67254384 | 5.76778052 | -0.13367100 |
| H | 0.81157916 | 5.74715952 | -0.20862600 |
| H | 2.03836516 | 3.61516652 | -0.27295600 |
| H | -1.91025284 | -0.05977848 | 3.67698500 |
| C | 2.39523016 | -4.02711848 | 0.53060700 |
| C | 1.71918816 | -3.83973348 | 1.91024100 |
| C | 1.37767916 | -4.56170748 | -0.50319800 |
| C | 3.48868416 | -5.10152748 | 0.70482500 |
| H | 2.44118216 | -3.48028948 | 2.65306400 |
| H | 0.88999416 | -3.13253048 | 1.86102700 |
| H | 1.32477516 | -4.79858448 | 2.26501700 |
| H | 1.86503616 | -4.74156848 | -1.46853700 |
| H | 0.95922216 | -5.51417948 | -0.15721800 |
| H | 0.55652216 | -3.86192048 | -0.65619500 |

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| H | 3.02447116 | -6.02260048 | 1.07193300 |
| H | 3.98698016 | -5.34627848 | -0.23990900 |
| H | 4.25084916 | -4.80677648 | 1.43546100 |
| C | -3.06625184 | -4.14430048 | -0.32800200 |
| C | -2.19571284 | -4.32089948 | -1.59661500 |
| C | -2.20726984 | -4.27194448 | 0.95268600 |
| C | -4.08970784 | -5.29861948 | -0.30537600 |
| H | -2.82030584 | -4.29900248 | -2.49712000 |
| H | -1.44067084 | -3.53756248 | -1.68418800 |
| H | -1.68344284 | -5.28926448 | -1.56813100 |
| H | -2.82784184 | -4.15194548 | 1.84902000 |
| H | -1.75197284 | -5.26777748 | 0.99540400 |
| H | -1.40610684 | -3.53304448 | 0.97897100 |
| H | -3.54962784 | -6.24966048 | -0.25656000 |
| H | -4.74926884 | -5.25261948 | 0.56903500 |
| H | -4.70916484 | -5.32640748 | -1.20876100 |
| C | 6.46366816 | -1.39785748 | -1.04843900 |
| C | 7.24848016 | -1.77679348 | 0.23088100 |
| C | 6.73915616 | -2.44714048 | -2.15288000 |
| C | 6.97275316 | -0.03083448 | -1.54215500 |
| H | 7.08002316 | -1.04486748 | 1.02890200 |
| H | 6.96526916 | -2.76316348 | 0.61336000 |
| H | 8.32287816 | -1.80369048 | 0.01736000 |
| H | 6.20445316 | -2.19801748 | -3.07628000 |
| H | 7.81065816 | -2.47991848 | -2.37982200 |
| H | 6.43654316 | -3.45525448 | -1.85026400 |
| H | 8.04398516 | -0.09393248 | -1.75875400 |
| H | 6.47063316 | 0.28401452 | -2.46435300 |
| H | 6.83815916 | 0.75329052 | -0.78782500 |
| C | -7.38242984 | -1.46445148 | -0.74513000 |
| C | -7.77315184 | -2.26545948 | -2.01093900 |
| C | -7.98779684 | -2.14735948 | 0.50519500 |
| C | -7.98175284 | -0.05065648 | -0.86313600 |
| H | -7.36425984 | -1.80006148 | -2.91474300 |
| H | -7.41439884 | -3.29946248 | -1.97299900 |
| H | -8.86378484 | -2.29939748 | -2.11090000 |
| H | -7.73727484 | -1.59457348 | 1.41769000 |
| H | -9.07964184 | -2.18409948 | 0.42073700 |
| H | -7.63266484 | -3.17622648 | 0.62659900 |
| H | -9.07063584 | -0.11975448 | -0.95215800 |
| H | -7.76464484 | 0.56156852 | 0.02005600 |

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| H | -7.61468584 | 0.47721752 | -1.75106000 |
| H | -0.49642984 | -1.40362148 | 2.12584400 |

**Int-1$_{i\text{Pr-Co}}$**

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|---|---|---|---|
| Co | -0.43941412 | 1.39147801 | 0.00000000 |
| N | 0.80357188 | 2.77408901 | -0.20173400 |
| N | -1.72149612 | 2.78162501 | -0.10361200 |
| C | -3.00372812 | 2.62733101 | -0.33577200 |
| H | -3.60942612 | 3.52581001 | -0.44259200 |
| C | 2.07664888 | 2.61821401 | -0.52157000 |
| H | 2.64096488 | 3.51819201 | -0.76013800 |
| C | -3.68850312 | 1.39602201 | -0.46590000 |
| C | -5.10083012 | 1.44217701 | -0.59981200 |
| C | -2.98298812 | 0.15134501 | -0.49545400 |
| C | -5.84182712 | 0.28930801 | -0.73678900 |
| H | -5.57958012 | 2.41555201 | -0.58121800 |
| C | -3.73583712 | -1.05825799 | -0.66131100 |
| C | -5.11619412 | -0.93167099 | -0.76218900 |
| C | 2.79064288 | 1.40835401 | -0.56452100 |
| C | 4.18228888 | 1.48226801 | -0.86138500 |
| C | 2.15531888 | 0.14938401 | -0.27798100 |
| C | 4.97330988 | 0.36112901 | -0.84786000 |
| H | 4.59782788 | 2.45881901 | -1.08651500 |
| C | 2.98491988 | -1.02872599 | -0.22206300 |
| C | 4.33016188 | -0.86591299 | -0.51098600 |
| O | -1.66499912 | 0.11640701 | -0.42552400 |
| O | 0.86239888 | 0.06839001 | -0.09788400 |
| C | -1.15194812 | 4.07545401 | 0.02435200 |
| C | -1.84260612 | 5.27516201 | 0.22592000 |
| C | -1.12703512 | 6.46341701 | 0.35459900 |
| C | 0.27012988 | 6.45681301 | 0.30529800 |
| C | 0.96456488 | 5.26229901 | 0.12664100 |
| C | 0.25047888 | 4.06957401 | -0.03033500 |
| C | -0.55602112 | 1.10360501 | 2.07157500 |
| H | -0.49890712 | 0.01995601 | 2.00254200 |
| C | 0.67225688 | 1.71037501 | 2.69826300 |
| H | 1.60278488 | 1.39359501 | 2.22229700 |
| H | 0.63200088 | 2.80358101 | 2.73402000 |
| C | -1.86201112 | 1.56698001 | 2.65481600 |
| H | -1.93517512 | 2.65635801 | 2.72565100 |

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|---|---|---|---|
| H | -2.73596412 | 1.17101201 | 2.13260800 |
| H | 0.69423088 | 1.33475501 | 3.73316500 |
| C | -0.78084612 | -1.84276499 | 5.24276600 |
| H | -1.00533812 | -2.85428899 | 4.87779100 |
| H | -0.24619612 | -1.91935299 | 6.19917500 |
| O | -0.05572812 | -1.07390799 | 4.28320400 |
| H | 0.78425788 | -1.52668899 | 4.11438400 |
| H | -5.69267112 | -1.83973899 | -0.88056600 |
| H | 4.95608788 | -1.74810799 | -0.48313100 |
| H | -2.92407812 | 5.29507101 | 0.30413600 |
| H | -1.66127112 | 7.39446201 | 0.51440900 |
| H | 0.82269988 | 7.38302401 | 0.42650700 |
| H | 2.04888088 | 5.27056101 | 0.13223500 |
| H | -1.72485612 | -1.32083099 | 5.41705500 |
| H | -1.89341212 | 1.16329601 | 3.67899200 |
| C | 2.41164288 | -2.41881699 | 0.12030000 |
| C | 1.74591088 | -2.38918899 | 1.51801800 |
| C | 1.38318888 | -2.83311499 | -0.95688300 |
| C | 3.50362188 | -3.50781299 | 0.16244100 |
| H | 2.48423388 | -2.12242099 | 2.28599700 |
| H | 0.92070888 | -1.67762099 | 1.55970600 |
| H | 1.35079588 | -3.38236799 | 1.76139400 |
| H | 1.86205488 | -2.90172899 | -1.94054500 |
| H | 0.96721688 | -3.81904099 | -0.71793700 |
| H | 0.56175488 | -2.12037299 | -1.02187800 |
| H | 3.04034888 | -4.46491099 | 0.42369200 |
| H | 3.99468088 | -3.64190099 | -0.80775400 |
| H | 4.27223588 | -3.30015599 | 0.91601700 |
| C | -3.05358812 | -2.43613699 | -0.76608800 |
| C | -2.18105412 | -2.46551899 | -2.04519000 |
| C | -2.19574112 | -2.70864199 | 0.49256800 |
| C | -4.07558612 | -3.58649599 | -0.87759900 |
| H | -2.80432312 | -2.34029199 | -2.93816900 |
| H | -1.42661912 | -1.67677399 | -2.04054600 |
| H | -1.66825312 | -3.43062599 | -2.12774500 |
| H | -2.81790012 | -2.69454899 | 1.39563200 |
| H | -1.73737412 | -3.70157899 | 0.41981800 |
| H | -1.39817612 | -1.97445399 | 0.60700400 |
| H | -3.53464612 | -4.53645499 | -0.93832200 |
| H | -4.73615212 | -3.64188199 | -0.00445200 |
| H | -4.69443312 | -3.51032499 | -1.77863100 |

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| C | 6.47772288 | 0.37093201 | -1.15853000 |
| C | 7.26215588 | -0.14628199 | 0.07153200 |
| C | 6.75599588 | -0.54911799 | -2.37195100 |
| C | 6.98582888 | 1.78470001 | -1.49713700 |
| H | 7.09286088 | 0.49339801 | 0.94513000 |
| H | 6.97864088 | -1.16883899 | 0.34294200 |
| H | 8.33684688 | -0.14961899 | -0.14249500 |
| H | 6.22186988 | -0.19977499 | -3.26262500 |
| H | 7.82778088 | -0.55586699 | -2.60013500 |
| H | 6.45377288 | -1.58479199 | -2.18324900 |
| H | 8.05758988 | 1.74739201 | -1.71728700 |
| H | 6.48473888 | 2.19889201 | -2.37974700 |
| H | 6.84829188 | 2.48044801 | -0.66108400 |
| C | -7.37284812 | 0.27090801 | -0.86719400 |
| C | -7.76625112 | -0.37820199 | -2.21629200 |
| C | -7.97706712 | -0.55147399 | 0.29659400 |
| C | -7.97212612 | 1.68886101 | -0.82003400 |
| H | -7.35835812 | 0.18834701 | -3.06087300 |
| H | -7.40766412 | -1.40966799 | -2.29859900 |
| H | -8.85708512 | -0.40018599 | -2.31807200 |
| H | -7.72450012 | -0.10794499 | 1.26640200 |
| H | -9.06914812 | -0.57775799 | 0.21047300 |
| H | -7.62232112 | -1.58760599 | 0.29768200 |
| H | -9.06125512 | 1.63086101 | -0.91451700 |
| H | -7.75298412 | 2.19490401 | 0.12753300 |
| H | -7.60620812 | 2.31570001 | -1.64157900 |

**TS-1*i*Pr-Co**

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|---|---|---|---|
| Co | -0.20458266 | -0.02454992 | 0.00000000 |
| N | 1.06673134 | 1.35176208 | -0.03780600 |
| N | -1.47632566 | 1.35302508 | 0.02638600 |
| C | -2.77950966 | 1.19555008 | -0.08074000 |
| H | -3.40180766 | 2.08854208 | -0.08727300 |
| C | 2.35833034 | 1.19122508 | -0.24186600 |
| H | 2.96362334 | 2.08533008 | -0.38170600 |
| C | -3.47175366 | -0.03235592 | -0.19931900 |
| C | -4.89393466 | 0.02667408 | -0.26160600 |
| C | -2.77886866 | -1.28561592 | -0.29262100 |
| C | -5.65284366 | -1.10868292 | -0.40820600 |
| H | -5.35967966 | 1.00431808 | -0.19036200 |

| | | | |
|---|---|---|---|
| C | -3.56242966 | -2.47939292 | -0.47725800 |
| C | -4.94105366 | -2.33688992 | -0.51682500 |
| C | 3.05756534 | -0.03519292 | -0.27976100 |
| C | 4.46533834 | 0.03172108 | -0.48225100 |
| C | 2.39500134 | -1.29024792 | -0.07464700 |
| C | 5.24740634 | -1.09738892 | -0.46926300 |
| H | 4.90284434 | 1.01172508 | -0.64321400 |
| C | 3.20794934 | -2.47753092 | -0.03340000 |
| C | 4.57300834 | -2.32643292 | -0.23307700 |
| O | -1.46949566 | -1.34933592 | -0.22507700 |
| O | 1.08886434 | -1.35951992 | 0.06724200 |
| C | -0.90304866 | 2.65059708 | 0.13177800 |
| C | -1.59499766 | 3.85932808 | 0.27629000 |
| C | -0.88662366 | 5.05291008 | 0.38397900 |
| C | 0.51113534 | 5.04845608 | 0.36199700 |
| C | 1.20773134 | 3.85069808 | 0.22881100 |
| C | 0.50320134 | 2.64735108 | 0.09958700 |
| C | -0.50534766 | -0.77908192 | 2.66835000 |
| H | -0.13535666 | -1.49447192 | 1.95039200 |
| C | 0.38741334 | 0.28566508 | 3.19222200 |
| H | 1.39072334 | 0.23580308 | 2.76708900 |
| H | -0.03887266 | 1.27751308 | 2.99306800 |
| C | -1.94114566 | -0.80571692 | 3.02327000 |
| H | -2.50276166 | -0.19671392 | 2.29925300 |
| H | -2.35693166 | -1.81350792 | 2.95592000 |
| H | 0.44608934 | 0.18872708 | 4.28416000 |
| C | -0.60920166 | -3.38517692 | 4.63572100 |
| H | -0.99444766 | -3.99533792 | 3.81092000 |
| H | -0.04402066 | -4.01665692 | 5.32941300 |
| O | 0.22395634 | -2.31236392 | 4.16071700 |
| H | 0.98297434 | -2.70595392 | 3.69549600 |
| H | -5.53339966 | -3.23249992 | -0.65282600 |
| H | 5.18357834 | -3.21981492 | -0.21546300 |
| H | -2.67813466 | 3.88706308 | 0.31526000 |
| H | -1.42703066 | 5.98741708 | 0.49678100 |
| H | 1.06065334 | 5.97935208 | 0.45987500 |
| H | 2.29176534 | 3.86706008 | 0.24014900 |
| H | -1.43915566 | -2.92576792 | 5.17403200 |
| H | -2.11843566 | -0.37570792 | 4.01403500 |
| C | 2.59869534 | -3.87709492 | 0.19125300 |
| C | 1.87569834 | -3.92787792 | 1.56033200 |

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| C | 1.60297934 | -4.20098392 | -0.94620800 |
| C | 3.66468834 | -4.99199892 | 0.20797300 |
| H | 2.58400534 | -3.70942892 | 2.37261900 |
| H | 1.05245234 | -3.21139392 | 1.58544000 |
| H | 1.46329834 | -4.92865392 | 1.73390000 |
| H | 2.12085734 | -4.21950492 | -1.91177800 |
| H | 1.15626434 | -5.19001492 | -0.78775200 |
| H | 0.80254234 | -3.46326492 | -0.99832400 |
| H | 3.17173534 | -5.95543492 | 0.37614700 |
| H | 4.19871634 | -5.06509292 | -0.74542800 |
| H | 4.40135334 | -4.85603892 | 1.00834100 |
| C | -2.90050866 | -3.85851192 | -0.67395500 |
| C | -2.04356766 | -3.82840992 | -1.96320500 |
| C | -2.02343666 | -4.21624892 | 0.54983700 |
| C | -3.93729366 | -4.98927492 | -0.83505400 |
| H | -2.67673466 | -3.64379592 | -2.83854500 |
| H | -1.27913566 | -3.05079992 | -1.92226800 |
| H | -1.54570166 | -4.79431692 | -2.10816100 |
| H | -2.63311066 | -4.25019392 | 1.46283400 |
| H | -1.57723066 | -5.20819892 | 0.41284500 |
| H | -1.21654666 | -3.49500092 | 0.68327000 |
| H | -3.41015466 | -5.93959592 | -0.97006100 |
| H | -4.58061766 | -5.09413492 | 0.04660200 |
| H | -4.57481166 | -4.84604592 | -1.71437900 |
| C | 6.76901034 | -1.08935392 | -0.68757900 |
| C | 7.47423134 | -1.67076492 | 0.56118000 |
| C | 7.11627534 | -1.95347892 | -1.92364800 |
| C | 7.30786034 | 0.33334608 | -0.92728500 |
| H | 7.25690334 | -1.07014692 | 1.45189700 |
| H | 7.16525334 | -2.70135892 | 0.76689100 |
| H | 8.56021734 | -1.67679792 | 0.41365800 |
| H | 6.63903234 | -1.55793392 | -2.82722200 |
| H | 8.19995534 | -1.96042892 | -2.08743200 |
| H | 6.79545134 | -2.99376792 | -1.80274300 |
| H | 8.39129334 | 0.29618908 | -1.08124800 |
| H | 6.86591334 | 0.79272108 | -1.81903300 |
| H | 7.12170334 | 0.99121208 | -0.07019100 |
| C | -7.18845366 | -1.10900392 | -0.47455100 |
| C | -7.64640366 | -1.69562192 | -1.83167700 |
| C | -7.75361566 | -1.97490292 | 0.67696700 |
| C | -7.77104166 | 0.31040308 | -0.34174200 |

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| H | -7.26816966 | -1.09628192 | -2.66733600 |
| H | -7.30126066 | -2.72525792 | -1.97388100 |
| H | -8.74086166 | -1.70478492 | -1.88862500 |
| H | -7.45909366 | -1.57324292 | 1.65343200 |
| H | -8.84861466 | -1.99160992 | 0.63465500 |
| H | -7.40674566 | -3.01235892 | 0.62129300 |
| H | -8.86401066 | 0.26616308 | -0.38961500 |
| H | -7.50372666 | 0.77466508 | 0.61488500 |
| H | -7.43475066 | 0.96782208 | -1.15183800 |

**Int-2*i*Pr-Co**

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| | | | |
|---|---|---|---|
| Co | 0.14647137 | 0.67243674 | 0.00000000 |
| N | 1.46009237 | 2.04275274 | -0.13441200 |
| N | -1.09915463 | 2.04242474 | -0.07905600 |
| C | -2.40443163 | 1.86826174 | -0.07658600 |
| H | -3.03585963 | 2.75424674 | -0.06979600 |
| C | 2.73880237 | 1.86514174 | -0.29483700 |
| H | 3.36546737 | 2.74015874 | -0.46168600 |
| C | -3.08778063 | 0.63087974 | -0.10475800 |
| C | -4.51078363 | 0.68275374 | -0.10078300 |
| C | -2.39539263 | -0.62049526 | -0.18781000 |
| C | -5.27118863 | -0.45828726 | -0.19080500 |
| H | -4.97755063 | 1.65975674 | -0.02804700 |
| C | -3.17608363 | -1.81570326 | -0.33719000 |
| C | -4.55841063 | -1.68076126 | -0.31881800 |
| C | 3.45172537 | 0.60994274 | -0.31071000 |
| C | 4.81058037 | 0.68260174 | -0.68523900 |
| C | 2.88792437 | -0.63981226 | 0.02301600 |
| C | 5.60780237 | -0.45122026 | -0.74904700 |
| H | 5.21820237 | 1.65742374 | -0.92900500 |
| C | 3.64274537 | -1.82564226 | -0.06027500 |
| C | 4.98752637 | -1.67323026 | -0.43786200 |
| O | -1.07685663 | -0.67731426 | -0.13383100 |
| O | 1.54459737 | -0.66246526 | 0.42734100 |
| C | -0.52347963 | 3.33904474 | -0.10663100 |
| C | -1.21513663 | 4.55754474 | -0.12016600 |
| C | -0.50857563 | 5.75612074 | -0.11675100 |
| C | 0.89015137 | 5.75841674 | -0.09552800 |
| C | 1.58771637 | 4.55557474 | -0.09055400 |
| C | 0.88488237 | 3.34508274 | -0.11170700 |

| | | | |
|---|---|---|---|
| C | 1.76635437 | 0.04209574 | 4.11658900 |
| H | 1.11117537 | 0.66372274 | 4.74348200 |
| C | 2.87243737 | 0.91118974 | 3.53420100 |
| H | 2.45321137 | 1.73710274 | 2.95064700 |
| H | 3.47665937 | 1.33616074 | 4.34177700 |
| C | 2.30647037 | -1.12293126 | 4.94294900 |
| H | 2.89634637 | -0.73810026 | 5.78157800 |
| H | 1.50478437 | -1.73792026 | 5.36255100 |
| H | 3.53813337 | 0.32355374 | 2.89162600 |
| C | -0.32375163 | -0.95710426 | 3.37415500 |
| H | -0.85166963 | -0.25894426 | 4.03524100 |
| H | -0.88993163 | -1.08324826 | 2.45114200 |
| O | 0.94999537 | -0.41499426 | 3.00276900 |
| H | 1.45809037 | -0.73914926 | 1.42858000 |
| H | -5.14990363 | -2.58182126 | -0.41681800 |
| H | 5.59155237 | -2.56734726 | -0.50523300 |
| H | -2.29839263 | 4.58822074 | -0.12903000 |
| H | -1.05286063 | 6.69528974 | -0.12201400 |
| H | 1.43486737 | 6.69680674 | -0.07882300 |
| H | 2.67161337 | 4.57513874 | -0.05799900 |
| H | -0.22075363 | -1.92593926 | 3.87425200 |
| H | 2.95377737 | -1.76390626 | 4.33518100 |
| C | 3.05695137 | -3.23778126 | 0.17852400 |
| C | 2.56555837 | -3.39970726 | 1.63595500 |
| C | 1.89668937 | -3.47503926 | -0.81609100 |
| C | 4.10259237 | -4.34787626 | -0.06321700 |
| H | 3.38504537 | -3.23470926 | 2.34536500 |
| H | 1.74999537 | -2.72128326 | 1.89189700 |
| H | 2.19605237 | -4.41984326 | 1.78761100 |
| H | 2.25612837 | -3.41669326 | -1.84981700 |
| H | 1.47773437 | -4.47609326 | -0.66426700 |
| H | 1.09269037 | -2.75010026 | -0.68985100 |
| H | 3.62517537 | -5.32011426 | 0.09445200 |
| H | 4.48816537 | -4.33948826 | -1.08841600 |
| H | 4.94905537 | -4.28637226 | 0.63022900 |
| C | -2.51947063 | -3.19672926 | -0.54489700 |
| C | -1.68948063 | -3.16999926 | -1.85166500 |
| C | -1.62435663 | -3.55687826 | 0.66404000 |
| C | -3.56043763 | -4.32644626 | -0.68842200 |
| H | -2.34023563 | -2.99016426 | -2.71512600 |
| H | -0.92606463 | -2.39021026 | -1.83155000 |

| | | | |
|---|---|---|---|
| H | -1.19240763 | -4.13550026 | -2.00353000 |
| H | -2.21713463 | -3.59151326 | 1.58633000 |
| H | -1.17875163 | -4.54808026 | 0.51843400 |
| H | -0.81774563 | -2.83498926 | 0.79433100 |
| H | -3.03655263 | -5.27558226 | -0.84366200 |
| H | -4.17945663 | -4.43894126 | 0.20920300 |
| H | -4.22112263 | -4.17644526 | -1.54951400 |
| C | 7.09306637 | -0.41893926 | -1.14941500 |
| C | 7.94627337 | -0.99668426 | 0.00525000 |
| C | 7.29882537 | -1.27443626 | -2.42269200 |
| C | 7.58120437 | 1.01217774 | -1.44326500 |
| H | 7.82781837 | -0.40463126 | 0.91986200 |
| H | 7.67860337 | -2.03297426 | 0.23742500 |
| H | 9.00663937 | -0.98462326 | -0.27000700 |
| H | 6.70840737 | -0.88605726 | -3.26006800 |
| H | 8.35404237 | -1.26010126 | -2.71711700 |
| H | 7.01482637 | -2.32059526 | -2.26701800 |
| H | 8.64070737 | 0.98835174 | -1.71718200 |
| H | 7.03913037 | 1.46756874 | -2.28023400 |
| H | 7.48535737 | 1.66659674 | -0.56883100 |
| C | -6.80845563 | -0.46675226 | -0.17832600 |
| C | -7.33392563 | -1.07605726 | -1.50029300 |
| C | -7.30801363 | -1.31691726 | 1.01435000 |
| C | -7.39051463 | 0.95204374 | -0.03659800 |
| H | -7.00266463 | -0.48825026 | -2.36377600 |
| H | -6.99124163 | -2.10630226 | -1.64444800 |
| H | -8.42987663 | -1.09105026 | -1.50027100 |
| H | -6.96363363 | -0.89935026 | 1.96738000 |
| H | -8.40371563 | -1.33938626 | 1.03036900 |
| H | -6.95846563 | -2.35334026 | 0.95599800 |
| H | -8.48431263 | 0.90243874 | -0.02535300 |
| H | -7.07453363 | 1.43213074 | 0.89701300 |
| H | -7.10120863 | 1.59823274 | -0.87359800 |

**Int-0$_{t\mathrm{Bu}}$**

1 1

| | | | |
|---|---|---|---|
| C | -0.58101474 | 0.43371521 | 0.00000000 |
| C | -1.48496274 | -0.72103379 | -0.00352100 |
| H | -2.05917374 | -0.69696479 | 0.94089800 |
| H | -2.25652774 | -0.58798179 | -0.77863600 |
| H | -0.98801674 | -1.68603379 | -0.10916300 |

| | | | |
|---|---|---|---|
| C | -1.13108774 | 1.79206821 | 0.01186900 |
| H | -0.90171374 | 2.22627921 | -0.98147700 |
| H | -2.20819174 | 1.84333021 | 0.17821600 |
| H | -0.58021974 | 2.43387121 | 0.71405500 |
| C | 0.87058226 | 0.23029321 | -0.00441100 |
| H | 1.12828226 | -0.28996279 | 0.93789900 |
| H | 1.15126226 | -0.49208779 | -0.78586000 |
| H | 1.45617726 | 1.14727521 | -0.08197000 |

**Int-1$_{t\mathrm{Bu}}$**

1 1

| | | | |
|---|---|---|---|
| C | -0.38448362 | -0.40098199 | -0.01006806 |
| C | 0.19989238 | -0.44580999 | 1.31328694 |
| H | 0.04815738 | -1.39308499 | 1.83911694 |
| H | 1.30089138 | -0.43832999 | 1.04373994 |
| H | -0.00531262 | 0.42608501 | 1.93720094 |
| C | -0.40333562 | -1.60948399 | -0.84718506 |
| H | 0.62758138 | -1.65755399 | -1.25334706 |
| H | -0.55142562 | -2.52952699 | -0.27506906 |
| H | -1.08835762 | -1.54245099 | -1.69559706 |
| C | -0.86426162 | 0.87078001 | -0.56931806 |
| H | -1.95092662 | 0.87918601 | -0.34809206 |
| H | -0.43943862 | 1.75031401 | -0.07897506 |
| H | -0.77798362 | 0.92244001 | -1.65882806 |
| O | 2.85232338 | -0.83779199 | -0.05030506 |
| C | 3.82836638 | 0.14865401 | -0.43843706 |
| H | 4.46424338 | 0.43764501 | 0.40551594 |
| H | 4.45121938 | -0.22096899 | -1.26009506 |
| H | 3.27352038 | 1.02371001 | -0.78237006 |
| H | 3.33354938 | -1.61890999 | 0.26684794 |

**TS-1$_{t\mathrm{Bu}}$**

1 1

| | | | |
|---|---|---|---|
| C | -0.35188217 | 0.18821604 | 0.00000000 |
| C | -0.27557917 | -0.24453496 | 1.38984400 |
| H | -0.89623117 | -1.11362096 | 1.62054000 |
| H | 0.78885383 | -0.57142096 | 1.44480600 |
| H | -0.39338717 | 0.56490904 | 2.11527500 |
| C | -0.67952017 | -0.76061096 | -1.07496200 |
| H | 0.23299383 | -0.87036596 | -1.68228100 |
| H | -1.00892117 | -1.73812796 | -0.72153600 |

| | | | |
|---|---|---|---|
| H | -1.42280517 | -0.32080896 | -1.75554300 |
| C | -0.10767917 | 1.59728504 | -0.33819300 |
| H | -1.08428717 | 2.09875804 | -0.18953300 |
| H | 0.58382583 | 2.08001704 | 0.35869200 |
| H | 0.18497783 | 1.75427504 | -1.37855700 |
| O | 2.39649483 | -0.49185696 | -0.09300000 |
| C | 3.55378383 | 0.36479404 | -0.10822900 |
| H | 4.29569883 | 0.04419004 | 0.63131700 |
| H | 4.01531283 | 0.39551104 | -1.10161900 |
| H | 3.21014383 | 1.36793404 | 0.15335700 |
| H | 2.70119983 | -1.38836796 | -0.30717600 |

**Int-2$_{t\mathrm{Bu}}$**

1 1

| | | | |
|---|---|---|---|
| C | -0.31908867 | -0.38455511 | -0.00921171 |
| C | 0.67028433 | -1.36533511 | -0.61155571 |
| H | 0.58235933 | -2.36596211 | -0.17156171 |
| H | 0.56575033 | -1.42926011 | -1.69802571 |
| H | 1.68207133 | -1.00963011 | -0.39043671 |
| C | -0.33263367 | -0.36132711 | 1.50628329 |
| H | -1.09840067 | 0.30760089 | 1.90862129 |
| H | -0.45398067 | -1.36158511 | 1.93528429 |
| H | 0.63739733 | 0.02012689 | 1.84437629 |
| C | -0.30591667 | 0.97913989 | -0.66849671 |
| H | 0.68017433 | 1.42284589 | -0.49290971 |
| H | -0.45181967 | 0.90509589 | -1.74946371 |
| H | -1.04400267 | 1.66226289 | -0.23914371 |
| O | -1.73437967 | -1.03721911 | -0.48583171 |
| C | -3.04068667 | -0.47433611 | -0.08040771 |
| H | -3.79316367 | -1.06980711 | -0.59707071 |
| H | -3.15402267 | -0.52751611 | 1.00250129 |
| H | -3.05507367 | 0.55059989 | -0.44192071 |
| H | -1.70885667 | -1.99726511 | -0.30104371 |

**Int-0$_{t\mathrm{Bu\text{-}PTH}}$**

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| | | | |
|---|---|---|---|
| C | -0.05728314 | 0.45008183 | 0.00000000 |
| C | -1.13323814 | 1.30658283 | 0.16912500 |
| C | -0.94337614 | 2.58788483 | 0.71435500 |
| C | 0.34265786 | 3.08164883 | 1.04005900 |
| C | 1.41405186 | 2.17208783 | 0.88198200 |

| | | | |
|---|---|---|---|
| C | 1.21415486 | 0.89273683 | 0.38320500 |
| C | -0.37462014 | 5.41947283 | 1.40012600 |
| C | -1.75151714 | 5.17179283 | 1.09315200 |
| C | -2.65691014 | 6.20094483 | 0.89079300 |
| H | -3.68182814 | 5.96892383 | 0.61373300 |
| C | -2.27830614 | 7.54871883 | 1.05153200 |
| C | -0.92445314 | 7.81785983 | 1.43782300 |
| C | -0.01141814 | 6.74858783 | 1.58985700 |
| H | -2.13379114 | 0.99374383 | -0.11473500 |
| H | 2.41461586 | 2.49244783 | 1.14138000 |
| H | 1.01634886 | 6.98476183 | 1.83662700 |
| N | 0.58791686 | 4.39183083 | 1.46452400 |
| S | -2.41135014 | 3.53195083 | 1.00131000 |
| H | 2.07183886 | 0.23563083 | 0.27511200 |
| H | -0.20276614 | -0.53995617 | -0.41798000 |
| C | -3.04693914 | 3.06985883 | 2.79497900 |
| C | -0.52983414 | 9.17059483 | 1.62984000 |
| C | -1.43127514 | 10.19283883 | 1.44304900 |
| H | -1.11862914 | 11.22216783 | 1.59167600 |
| C | -2.76976314 | 9.92220583 | 1.05463400 |
| H | -3.46242114 | 10.74543183 | 0.90979900 |
| C | -3.18616714 | 8.62665483 | 0.86249400 |
| H | -4.20923314 | 8.41077783 | 0.56592300 |
| H | 0.49443886 | 9.38438183 | 1.92230500 |
| C | 1.97364286 | 4.78707683 | 1.68401700 |
| C | 2.49464586 | 4.75994083 | 2.98783900 |
| C | 2.75195386 | 5.19434983 | 0.58256800 |
| C | 3.82569986 | 5.15056183 | 3.17178000 |
| C | 4.07526886 | 5.57432583 | 0.82258200 |
| C | 4.63396386 | 5.55749383 | 2.10615100 |
| H | 4.23918486 | 5.13591683 | 4.17726400 |
| H | 4.68619386 | 5.89319983 | -0.01864300 |
| C | 1.66032586 | 4.32758683 | 4.16960500 |
| H | 0.77361586 | 4.96034083 | 4.29234300 |
| H | 1.31222186 | 3.29336783 | 4.06265400 |
| H | 2.24137586 | 4.38708883 | 5.09356500 |
| C | 2.19351786 | 5.22582683 | -0.82104300 |
| H | 2.94567086 | 5.59195683 | -1.52450800 |
| H | 1.88258286 | 4.22956583 | -1.15727300 |
| H | 1.31878286 | 5.88193883 | -0.89709200 |
| C | 6.07566686 | 5.94702083 | 2.32683500 |

| | | | |
|---|---|---|---|
| H | 6.25346586 | 6.26078683 | 3.35977100 |
| H | 6.74503486 | 5.10185283 | 2.12076700 |
| H | 6.37532286 | 6.76545483 | 1.66430900 |
| C | -1.94321214 | 3.27506283 | 3.82244000 |
| H | -1.07693214 | 2.63835983 | 3.62278900 |
| H | -1.62053514 | 4.31875283 | 3.87166200 |
| H | -2.33482914 | 3.00191283 | 4.80977500 |
| C | -4.24373814 | 3.99457083 | 3.02574600 |
| H | -5.01207814 | 3.87787983 | 2.25379100 |
| H | -4.69911314 | 3.72636283 | 3.98606100 |
| H | -3.94913014 | 5.04603483 | 3.08450600 |
| C | -3.47753414 | 1.60599783 | 2.67973900 |
| H | -3.92395014 | 1.30803483 | 3.63546600 |
| H | -4.23529514 | 1.45702883 | 1.90287500 |
| H | -2.63195114 | 0.93919083 | 2.48986600 |

**Int-1**$_{t\text{Bu-PTH}}$

1 1

| | | | |
|---|---|---|---|
| C | -0.98360655 | -0.15648286 | 0.00000000 |
| C | -1.66556455 | 1.04867214 | 0.06055100 |
| C | -1.14772955 | 2.12298914 | 0.80269200 |
| C | 0.10778145 | 2.04895914 | 1.45123400 |
| C | 0.76426945 | 0.79799314 | 1.39245100 |
| C | 0.22690245 | -0.27297686 | 0.69208500 |
| C | 0.25492545 | 4.46053214 | 1.97909900 |
| C | -0.99449655 | 4.79445014 | 1.36397800 |
| C | -1.36990255 | 6.10663014 | 1.12931500 |
| H | -2.30711455 | 6.31425214 | 0.62002500 |
| C | -0.56626255 | 7.18425614 | 1.55349000 |
| C | 0.65202745 | 6.87484914 | 2.24141700 |
| C | 1.03165845 | 5.52473114 | 2.42451100 |
| H | -2.60984055 | 1.17178514 | -0.46151300 |
| H | 1.71662145 | 0.68256614 | 1.89323000 |
| H | 1.97937045 | 5.32121814 | 2.90762000 |
| N | 0.71454045 | 3.13307114 | 2.09605400 |
| S | -2.17815455 | 3.55813414 | 0.90888300 |
| H | 0.77430945 | -1.21060786 | 0.67291600 |
| H | -1.38468955 | -0.98727086 | -0.57012900 |
| C | -3.36967355 | 3.30298314 | 2.44677400 |
| C | -4.14512255 | 4.61568114 | 2.55586800 |
| H | -4.67676855 | 4.85901314 | 1.62906700 |

| | | | |
|---|---|---|---|
| H | -4.89180055 | 4.48074214 | 3.34737200 |
| H | -3.50108855 | 5.45561614 | 2.83205400 |
| C | -2.56467155 | 2.99795814 | 3.70094100 |
| H | -1.89597455 | 3.82073814 | 3.96932100 |
| H | -3.27418855 | 2.85936414 | 4.52485300 |
| H | -1.98367355 | 2.07680114 | 3.60087400 |
| O | -6.27385055 | 2.99296214 | 4.67919100 |
| C | -7.68111155 | 3.11086514 | 4.45235300 |
| H | -8.21190555 | 2.17636814 | 4.67649600 |
| H | -8.12404055 | 3.92517914 | 5.04057700 |
| H | -7.81071655 | 3.33812214 | 3.39184700 |
| H | -6.14512155 | 2.79052414 | 5.61836000 |
| C | 1.46469545 | 7.94874514 | 2.69849900 |
| C | 1.08577845 | 9.25276814 | 2.47816800 |
| H | 1.71484445 | 10.06476514 | 2.83084500 |
| C | -0.11929155 | 9.55485514 | 1.79137800 |
| H | -0.39650855 | 10.59136714 | 1.62603900 |
| C | -0.92983555 | 8.54168014 | 1.33784200 |
| H | -1.85459355 | 8.76410114 | 0.81187600 |
| H | 2.39058745 | 7.72364714 | 3.22056400 |
| C | 2.04667745 | 2.93405314 | 2.65139400 |
| C | 2.18119345 | 2.64030414 | 4.01816000 |
| C | 3.16649745 | 3.05009814 | 1.80476600 |
| C | 3.47164145 | 2.46045014 | 4.52820500 |
| C | 4.43265545 | 2.86090014 | 2.36571000 |
| C | 4.60925045 | 2.56250014 | 3.72185900 |
| H | 3.58785145 | 2.23518914 | 5.58559700 |
| H | 5.30553445 | 2.95040014 | 1.72331400 |
| C | 0.98150245 | 2.52052114 | 4.92694700 |
| H | 0.39849745 | 3.44850814 | 4.95161300 |
| H | 0.30662945 | 1.71965214 | 4.60262300 |
| H | 1.29440645 | 2.29660814 | 5.95017600 |
| C | 3.02495845 | 3.36788614 | 0.33447200 |
| H | 4.00775945 | 3.43907214 | -0.13859100 |
| H | 2.45699445 | 2.59407914 | -0.19550100 |
| H | 2.50660545 | 4.31980714 | 0.17165600 |
| C | 5.98904345 | 2.33481414 | 4.29065500 |
| H | 6.01844745 | 2.53583414 | 5.36584300 |
| H | 6.30614445 | 1.29429214 | 4.14329300 |
| H | 6.73369945 | 2.97206714 | 3.80304400 |
| C | -4.27734855 | 2.14198714 | 2.03967500 |

| | | | |
|---|---|---|---|
| H | -4.81115155 | 2.34385414 | 1.10422500 |
| H | -3.72854655 | 1.20064714 | 1.94402200 |
| H | -5.02303955 | 2.02580214 | 2.83502300 |

**TS-1$_{t\text{Bu-PTH}}$**

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| | | | |
|---|---|---|---|
| C | -1.05555617 | 1.62847788 | -0.01381799 |
| C | -1.68670917 | 2.80132088 | -0.41056199 |
| C | -1.19038017 | 4.05754388 | -0.02686999 |
| C | -0.03483417 | 4.16416888 | 0.78321501 |
| C | 0.58176783 | 2.95749388 | 1.18005501 |
| C | 0.08612483 | 1.71983088 | 0.78498301 |
| C | -0.12875817 | 6.64696688 | 1.01383701 |
| C | -1.31174317 | 6.79981288 | 0.21698201 |
| C | -1.91547517 | 8.03694188 | 0.07229001 |
| H | -2.79811517 | 8.12582588 | -0.55820699 |
| C | -1.38915617 | 9.20418688 | 0.67600201 |
| C | -0.20669417 | 9.06646388 | 1.46737601 |
| C | 0.38425983 | 7.78655088 | 1.61811301 |
| H | -2.56452517 | 2.75885388 | -1.05108399 |
| H | 1.47338983 | 3.00073588 | 1.79223901 |
| H | 1.28172383 | 7.70909688 | 2.21975701 |
| N | 0.50903583 | 5.39692588 | 1.17885801 |
| S | -2.01363417 | 5.46715488 | -0.71625499 |
| H | 0.60270383 | 0.82043388 | 1.10636301 |
| H | -1.44201717 | 0.66496088 | -0.32953999 |
| C | -4.42096917 | 5.06838888 | 2.12416901 |
| C | -4.11624817 | 6.47156688 | 2.45484701 |
| H | -4.92830917 | 7.15681488 | 2.20098601 |
| H | -3.83816517 | 6.57645988 | 3.50773201 |
| H | -3.22617817 | 6.77974388 | 1.86910401 |
| C | -3.51599217 | 4.00389788 | 2.58378101 |
| H | -3.01034417 | 4.25610088 | 3.51844601 |
| H | -4.01612217 | 3.03412088 | 2.65669801 |
| H | -2.72873817 | 3.87677788 | 1.80885301 |
| O | -5.78694917 | 4.80085188 | 4.15947101 |
| C | -6.95421417 | 5.57060788 | 4.48246801 |
| H | -7.82846117 | 5.25521888 | 3.89916201 |
| H | -7.18544417 | 5.49927088 | 5.55122101 |
| H | -6.72073217 | 6.61100488 | 4.24713001 |
| H | -5.95746817 | 3.87758788 | 4.40544501 |

| | | | |
|---|---|---|---|
| C | 0.34059083 | 10.22380788 | 2.08236801 |
| C | -0.25651617 | 11.45407488 | 1.91578701 |
| H | 0.17305883 | 12.33276188 | 2.38798901 |
| C | -1.42654517 | 11.58753588 | 1.12787501 |
| H | -1.88085017 | 12.56583188 | 1.00245301 |
| C | -1.98260917 | 10.48399088 | 0.52005001 |
| H | -2.87643517 | 10.58132788 | -0.09139699 |
| H | 1.24081483 | 10.12499388 | 2.68330201 |
| C | 1.79296083 | 5.38570288 | 1.85435201 |
| C | 1.84341983 | 5.25903188 | 3.25349601 |
| C | 2.96044983 | 5.51159888 | 1.08131801 |
| C | 3.09841183 | 5.25823788 | 3.87037801 |
| C | 4.19062883 | 5.50565388 | 1.74603101 |
| C | 4.28360583 | 5.37709188 | 3.13619601 |
| H | 3.15020783 | 5.16344488 | 4.95262701 |
| H | 5.10105883 | 5.60543488 | 1.15958201 |
| C | 0.58323283 | 5.12708388 | 4.07688201 |
| H | -0.08386917 | 5.98529688 | 3.93083801 |
| H | 0.02094983 | 4.22401188 | 3.80760001 |
| H | 0.82235783 | 5.06540688 | 5.14208601 |
| C | 2.89625383 | 5.65337188 | -0.42060599 |
| H | 3.90054883 | 5.74140588 | -0.84337899 |
| H | 2.41051983 | 4.78845688 | -0.88747799 |
| H | 2.32749283 | 6.54225888 | -0.71755199 |
| C | 5.62855483 | 5.34416188 | 3.82198101 |
| H | 5.55617383 | 5.66958288 | 4.86436501 |
| H | 6.04290783 | 4.32758788 | 3.82449701 |
| H | 6.35349583 | 5.98753488 | 3.31309501 |
| C | -5.50927617 | 4.76451188 | 1.15847701 |
| H | -5.24812917 | 5.20395588 | 0.18589501 |
| H | -5.67682017 | 3.69406988 | 1.02571001 |
| H | -6.44008017 | 5.25201088 | 1.46971301 |

**Int-2$_{t\text{Bu-PTH}}$**

1 1

| | | | |
|---|---|---|---|
| C | 0.05961252 | 0.29061102 | 0.00000000 |
| C | -0.67276148 | 1.28285402 | -0.65003900 |
| C | -0.35256748 | 2.63462002 | -0.48580900 |
| C | 0.69095152 | 3.03151902 | 0.37828400 |
| C | 1.42228252 | 2.01422802 | 1.02123100 |
| C | 1.11697652 | 0.66832502 | 0.82626300 |

| | | | |
|---|---|---|---|
| C | 0.08021552 | 5.43981402 | 0.37213700 |
| C | -1.03378048 | 5.27377602 | -0.51570400 |
| C | -1.94811748 | 6.28895802 | -0.70451100 |
| H | -2.77347748 | 6.13797102 | -1.39733600 |
| C | -1.80909848 | 7.54976202 | -0.06893500 |
| C | -0.68599548 | 7.74004602 | 0.79513600 |
| C | 0.22375952 | 6.66974002 | 1.00003000 |
| H | -1.47951848 | 1.01339502 | -1.32720300 |
| H | 2.25273352 | 2.28368402 | 1.66200100 |
| H | 1.07096752 | 6.83819802 | 1.65464200 |
| N | 1.00558552 | 4.39325902 | 0.58904100 |
| S | -1.17546748 | 3.81946502 | -1.52997000 |
| H | 1.71532352 | -0.08516698 | 1.33001900 |
| H | -0.18199348 | -0.75641698 | -0.15385700 |
| C | -3.79468248 | 3.59648802 | 2.17938300 |
| C | -3.18473548 | 4.89892202 | 2.64103900 |
| H | -3.84941948 | 5.75377102 | 2.48968400 |
| H | -2.87225748 | 4.84699802 | 3.68740300 |
| H | -2.29635848 | 5.08181802 | 2.02593800 |
| C | -2.92945648 | 2.37914502 | 2.42884800 |
| H | -2.56491548 | 2.34577802 | 3.45898600 |
| H | -3.45133348 | 1.44463802 | 2.18922800 |
| H | -2.06369048 | 2.43321502 | 1.75835500 |
| O | -5.01318648 | 3.33172802 | 3.27550200 |
| C | -6.18690248 | 4.21790002 | 3.36243200 |
| H | -6.75005548 | 4.19522402 | 2.42891800 |
| H | -6.78070948 | 3.85351402 | 4.20085300 |
| H | -5.80203248 | 5.21185502 | 3.57621500 |
| H | -5.30066148 | 2.40240302 | 3.18108200 |
| C | -0.52267748 | 8.99866302 | 1.43353700 |
| C | -1.42901748 | 10.01552902 | 1.22528500 |
| H | -1.28950548 | 10.97470602 | 1.71562500 |
| C | -2.53980148 | 9.82448802 | 0.36777600 |
| H | -3.24054648 | 10.63845302 | 0.20609800 |
| C | -2.72500148 | 8.61545102 | -0.26704500 |
| H | -3.56829448 | 8.46788002 | -0.93799700 |
| H | 0.33348452 | 9.14970302 | 2.08623600 |
| C | 2.26091452 | 4.71627202 | 1.23618200 |
| C | 2.35931052 | 4.73920802 | 2.63958500 |
| C | 3.36851352 | 5.00882302 | 0.41970400 |
| C | 3.59511152 | 5.06072402 | 3.21154600 |

| | | | |
|---|---|---|---|
| C | 4.58099752 | 5.32466902 | 1.03963300 |
| C | 4.71825052 | 5.35351202 | 2.43155600 |
| H | 3.68055652 | 5.08272802 | 4.29571400 |
| H | 5.44186752 | 5.55487202 | 0.41596400 |
| C | 1.17243352 | 4.42874702 | 3.52365100 |
| H | 0.34445252 | 5.12531602 | 3.34446000 |
| H | 0.79151552 | 3.41560102 | 3.34675200 |
| H | 1.44952552 | 4.50222702 | 4.57920400 |
| C | 3.25723452 | 4.98858202 | -1.08592400 |
| H | 4.21850452 | 5.23043802 | -1.54743400 |
| H | 2.94382152 | 4.00495902 | -1.45396500 |
| H | 2.51862152 | 5.71461602 | -1.44490300 |
| C | 6.04925652 | 5.67098502 | 3.07062300 |
| H | 5.93009552 | 5.98979302 | 4.11067900 |
| H | 6.70595752 | 4.79138302 | 3.06951300 |
| H | 6.57379452 | 6.46521102 | 2.52898900 |
| C | -4.44801948 | 3.63386502 | 0.81620000 |
| H | -3.64902648 | 3.73578502 | 0.07098100 |
| H | -4.98698248 | 2.70735702 | 0.59054500 |
| H | -5.11698348 | 4.49043902 | 0.69589700 |

**Int-0$_{t\text{Bu-Co}}$**

1 2

| | | | |
|---|---|---|---|
| Co | -0.00632900 | 0.78458800 | 0.09777200 |
| N | 1.24656600 | 2.12511500 | -0.28105800 |
| N | -1.29167200 | 2.13325500 | -0.23560900 |
| C | -2.59290800 | 1.94974200 | -0.30762600 |
| H | -3.21792800 | 2.82563000 | -0.46894200 |
| C | 2.53645400 | 1.92848700 | -0.48882500 |
| H | 3.12478400 | 2.78659600 | -0.80678000 |
| C | -3.27486100 | 0.71651000 | -0.23762800 |
| C | -4.69585300 | 0.74917400 | -0.26563700 |
| C | -2.55756800 | -0.52420800 | -0.24998900 |
| C | -5.43247000 | -0.41140400 | -0.30306900 |
| H | -5.18012700 | 1.72003400 | -0.25525400 |
| C | -3.31245900 | -1.74236200 | -0.36443000 |
| C | -4.69603900 | -1.62708300 | -0.36398600 |
| C | 3.24187600 | 0.71978900 | -0.35032300 |
| C | 4.65158600 | 0.76502700 | -0.54755200 |
| C | 2.56953000 | -0.51448600 | -0.04895400 |
| C | 5.42264300 | -0.36461500 | -0.43110600 |

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|---|---|---|---|
| H | 5.09731300 | 1.72554900 | -0.78370500 |
| C | 3.36758900 | -1.70902400 | 0.06681200 |
| C | 4.73441100 | -1.57303300 | -0.12119200 |
| O | -1.24331600 | -0.54317900 | -0.19766200 |
| O | 1.26713000 | -0.55698800 | 0.08834000 |
| C | -0.72508000 | 3.42232500 | -0.42500600 |
| C | -1.42087000 | 4.62881900 | -0.56820700 |
| C | -0.71363600 | 5.81948500 | -0.70834100 |
| C | 0.68430800 | 5.81805000 | -0.69077500 |
| C | 1.38387500 | 4.62357300 | -0.54383500 |
| C | 0.67910500 | 3.41914800 | -0.42978400 |
| C | -0.05998000 | 1.08109000 | 2.31934500 |
| C | 1.34194900 | 0.73243100 | 2.77082800 |
| H | 1.59612100 | -0.31247900 | 2.60017000 |
| H | 2.10928300 | 1.37042700 | 2.32514700 |
| C | -0.43080900 | 2.51357100 | 2.62910300 |
| H | -1.44513700 | 2.77195000 | 2.32077600 |
| H | -0.38820300 | 2.62202600 | 3.72441500 |
| H | 1.37858300 | 0.90862900 | 3.85812500 |
| H | -5.27139600 | -2.54132300 | -0.42660500 |
| H | 5.33986600 | -2.46520100 | -0.03235400 |
| H | -2.50437500 | 4.66045100 | -0.56693100 |
| H | -1.25591200 | 6.75291200 | -0.81985200 |
| H | 1.23155600 | 6.75054900 | -0.78425800 |
| H | 2.46714500 | 4.64740900 | -0.50907500 |
| H | 0.27110400 | 3.24100400 | 2.21535200 |
| C | 2.74600100 | -3.09062600 | 0.35604300 |
| C | 1.98576600 | -3.06727300 | 1.70301000 |
| C | 1.79099100 | -3.46758900 | -0.80028700 |
| C | 3.81121000 | -4.20226800 | 0.45777900 |
| H | 2.66276700 | -2.81415100 | 2.52796200 |
| H | 1.16485100 | -2.34920700 | 1.68951500 |
| H | 1.56391700 | -4.05697000 | 1.91144700 |
| H | 2.33938400 | -3.53592700 | -1.74701000 |
| H | 1.33615100 | -4.44593200 | -0.60607300 |
| H | 0.99179400 | -2.73555000 | -0.91594600 |
| H | 3.31075900 | -5.15335300 | 0.66672200 |
| H | 4.37057700 | -4.33035100 | -0.47566700 |
| H | 4.52467300 | -4.02440900 | 1.27079000 |
| C | -2.63233200 | -3.11633300 | -0.52060800 |
| C | -1.80761000 | -3.11648500 | -1.83141800 |

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|---|---|---|---|
| C | -1.72693200 | -3.41078500 | 0.69723000 |
| C | -3.65426700 | -4.26778800 | -0.61938700 |
| H | -2.46341600 | -2.97459800 | -2.69822700 |
| H | -1.05452500 | -2.32634200 | -1.83774800 |
| H | -1.29600400 | -4.07800500 | -1.95280700 |
| H | -2.31285800 | -3.41431700 | 1.62441000 |
| H | -1.26899800 | -4.40069100 | 0.58995700 |
| H | -0.92762600 | -2.67592400 | 0.78851500 |
| H | -3.11282300 | -5.21205200 | -0.73718000 |
| H | -4.27049600 | -4.35668900 | 0.28287000 |
| H | -4.31701400 | -4.16500800 | -1.48596900 |
| C | 6.94712800 | -0.38321400 | -0.61865700 |
| C | 7.61933400 | -0.87726900 | 0.68517000 |
| C | 7.31015700 | -1.33927500 | -1.78077500 |
| C | 7.50286900 | 1.01417100 | -0.95051300 |
| H | 7.38958800 | -0.21141800 | 1.52472600 |
| H | 7.29755800 | -1.88769200 | 0.95905200 |
| H | 8.70770900 | -0.90171500 | 0.56043400 |
| H | 6.85485900 | -1.00843400 | -2.72093900 |
| H | 8.39671100 | -1.36413400 | -1.92052700 |
| H | 6.98012800 | -2.36599600 | -1.59016000 |
| H | 8.58887600 | 0.95755600 | -1.07642400 |
| H | 7.08592400 | 1.40937100 | -1.88417900 |
| H | 7.30413600 | 1.73484400 | -0.14855400 |
| C | -6.96833700 | -0.44858500 | -0.30707000 |
| C | -7.46485600 | -1.13147100 | -1.60448500 |
| C | -7.46341400 | -1.25116700 | 0.92041000 |
| C | -7.57832400 | 0.96394100 | -0.24003200 |
| H | -7.13437700 | -0.58030400 | -2.49200500 |
| H | -7.10349500 | -2.16134700 | -1.69415300 |
| H | -8.56005500 | -1.16558000 | -1.61493400 |
| H | -7.13853800 | -0.78227300 | 1.85616200 |
| H | -8.55838600 | -1.29284800 | 0.92505100 |
| H | -7.09510900 | -2.28256400 | 0.91516600 |
| H | -8.67075400 | 0.89284200 | -0.23626700 |
| H | -7.28189000 | 1.49499400 | 0.67215800 |
| H | -7.29436000 | 1.57424200 | -1.10532900 |
| C | -1.10828900 | 0.07784700 | 2.74150800 |
| H | -2.10201100 | 0.30722100 | 2.34862400 |
| H | -0.84364700 | -0.94760000 | 2.48067800 |
| H | -1.17985500 | 0.13399100 | 3.84059800 |

**Int-1$_{t\text{Bu-Co}}$**

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| | | | |
|---|---|---|---|
| Co | -0.03959700 | 0.61027300 | -0.35487300 |
| N | 1.22210700 | 1.82900600 | -1.01419400 |
| N | -1.31552600 | 1.88454600 | -0.92748900 |
| C | -2.61991000 | 1.71135800 | -0.93525600 |
| H | -3.23840300 | 2.54642400 | -1.25796100 |
| C | 2.50609800 | 1.57603200 | -1.19310700 |
| H | 3.10079200 | 2.34377700 | -1.68372000 |
| C | -3.31514600 | 0.52907000 | -0.60291200 |
| C | -4.73640500 | 0.57879800 | -0.61238400 |
| C | -2.61422200 | -0.69911900 | -0.37193700 |
| C | -5.48872100 | -0.55177000 | -0.39860200 |
| H | -5.20738900 | 1.53945600 | -0.79312500 |
| C | -3.38801200 | -1.90156800 | -0.21977900 |
| C | -4.76951000 | -1.76618900 | -0.22032700 |
| C | 3.19894000 | 0.40938500 | -0.82235200 |
| C | 4.60577500 | 0.39218300 | -1.04561800 |
| C | 2.51781200 | -0.72721400 | -0.26621400 |
| C | 5.36587100 | -0.70134300 | -0.71425400 |
| H | 5.05796200 | 1.27806000 | -1.47916400 |
| C | 3.30506900 | -1.88472300 | 0.07809900 |
| C | 4.66962100 | -1.81107000 | -0.15431400 |
| O | -1.29995300 | -0.73085600 | -0.33799000 |
| O | 1.21822200 | -0.72309300 | -0.10200100 |
| C | -0.73782300 | 3.09906000 | -1.38485000 |
| C | -1.42239300 | 4.26135900 | -1.75996000 |
| C | -0.70525300 | 5.38732300 | -2.15410100 |
| C | 0.69253900 | 5.36780800 | -2.16276900 |
| C | 1.38126700 | 4.21796700 | -1.78694600 |
| C | 0.66610600 | 3.07340200 | -1.41419300 |
| C | -0.04262000 | 1.37386500 | 1.79264100 |
| C | 1.36552300 | 1.11167500 | 2.26715000 |
| H | 1.61577300 | 0.05225600 | 2.29721100 |
| H | 2.12166300 | 1.64959000 | 1.68951900 |
| C | -0.40667700 | 2.83644500 | 1.80025500 |
| H | -1.42480000 | 3.03004800 | 1.45817400 |
| H | -0.34211500 | 3.14818700 | 2.85555500 |
| H | 1.40563400 | 1.50326700 | 3.29739800 |
| C | 1.25883000 | 3.88395800 | 5.64769700 |

| | | | |
|---|---|---|---|
| H | 0.63175100 | 4.62616400 | 6.15909600 |
| H | 2.02283800 | 3.51783200 | 6.34614900 |
| O | 0.48239300 | 2.81724800 | 5.09786100 |
| H | 0.03078300 | 2.37318500 | 5.83158600 |
| H | -5.35780700 | -2.66412300 | -0.08407800 |
| H | 5.26612900 | -2.67565800 | 0.10521700 |
| H | -2.50523600 | 4.30877900 | -1.74574800 |
| H | -1.23938200 | 6.28624300 | -2.44483400 |
| H | 1.24833500 | 6.25256400 | -2.45634200 |
| H | 2.46525900 | 4.23127200 | -1.77925300 |
| H | 1.76026300 | 4.37205200 | 4.80896600 |
| H | 0.29303000 | 3.45864700 | 1.23746700 |
| C | 2.67185100 | -3.16801800 | 0.65334900 |
| C | 1.94007300 | -2.85745400 | 1.98027700 |
| C | 1.68792500 | -3.75669900 | -0.38423500 |
| C | 3.72401000 | -4.25377000 | 0.96082000 |
| H | 2.63850500 | -2.45693100 | 2.72512900 |
| H | 1.13243900 | -2.13897200 | 1.83508500 |
| H | 1.50539000 | -3.77559100 | 2.39167200 |
| H | 2.21537900 | -4.02504000 | -1.30704800 |
| H | 1.22520300 | -4.66760300 | 0.01334200 |
| H | 0.89578200 | -3.05026900 | -0.63186100 |
| H | 3.21555900 | -5.13397700 | 1.36769100 |
| H | 4.26250700 | -4.57817100 | 0.06334800 |
| H | 4.45642000 | -3.92639600 | 1.70791300 |
| C | -2.72824900 | -3.28924900 | -0.10049100 |
| C | -1.92992400 | -3.57351400 | -1.39667000 |
| C | -1.80187600 | -3.34115900 | 1.13595900 |
| C | -3.76605800 | -4.41960900 | 0.05811800 |
| H | -2.60126500 | -3.60276000 | -2.26275900 |
| H | -1.16764700 | -2.81375400 | -1.57855200 |
| H | -1.43263100 | -4.54759400 | -1.32566900 |
| H | -2.36932100 | -3.14506200 | 2.05395800 |
| H | -1.35731100 | -4.33887400 | 1.22673500 |
| H | -0.99316600 | -2.61498800 | 1.05991800 |
| H | -3.23895700 | -5.37664600 | 0.12919000 |
| H | -4.36562300 | -4.30986600 | 0.96931700 |
| H | -4.44455200 | -4.48705700 | -0.79972200 |
| C | 6.88654600 | -0.78057000 | -0.91797100 |
| C | 7.57732100 | -1.00766400 | 0.44836200 |
| C | 7.21802800 | -1.95877600 | -1.86559600 |

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|---|---|---|---|
| C | 7.45205200 | 0.51109600 | -1.53729000 |
| H | 7.37075000 | -0.18063700 | 1.13715900 |
| H | 7.24808100 | -1.93535900 | 0.92843500 |
| H | 8.66295700 | -1.07405300 | 0.31458600 |
| H | 6.74930700 | -1.81998900 | -2.84626600 |
| H | 8.30154900 | -2.02811000 | -2.01426600 |
| H | 6.87944100 | -2.91985000 | -1.46423300 |
| H | 8.53492300 | 0.41402500 | -1.66621400 |
| H | 7.02203900 | 0.71332600 | -2.52516900 |
| H | 7.27597200 | 1.38330300 | -0.89677200 |
| C | -7.02491400 | -0.56377200 | -0.36949200 |
| C | -7.55581300 | -1.49013900 | -1.49019700 |
| C | -7.50652000 | -1.08904100 | 1.00452700 |
| C | -7.61577000 | 0.84211800 | -0.58410900 |
| H | -7.23634300 | -1.13798300 | -2.47743100 |
| H | -7.20815400 | -2.52196200 | -1.37271200 |
| H | -8.65141900 | -1.50869200 | -1.47495100 |
| H | -7.15756200 | -0.44322300 | 1.81834500 |
| H | -8.60170400 | -1.11154400 | 1.03594800 |
| H | -7.15069700 | -2.10517800 | 1.20548000 |
| H | -8.70881800 | 0.79132300 | -0.54805300 |
| H | -7.29468700 | 1.54409600 | 0.19443100 |
| H | -7.34046000 | 1.25713300 | -1.56070600 |
| C | -1.08499700 | 0.47955500 | 2.41742300 |
| H | -2.08482000 | 0.63146100 | 2.00325500 |
| H | -0.82565300 | -0.57850700 | 2.36538700 |
| H | -1.13141200 | 0.76315300 | 3.48185200 |

**TS-1*t*Bu-Co**

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|---|---|---|---|
| Co | -0.01493700 | 0.76128900 | -0.65971000 |
| N | 1.25087100 | 2.12650500 | -0.83714400 |
| N | -1.29254400 | 2.13517900 | -0.72856500 |
| C | -2.59333400 | 1.97793600 | -0.60057700 |
| H | -3.21749900 | 2.87025800 | -0.59533000 |
| C | 2.55703400 | 1.96873000 | -0.80765800 |
| H | 3.18149400 | 2.85545100 | -0.89996000 |
| C | -3.28995600 | 0.74939400 | -0.50138700 |
| C | -4.70918600 | 0.81995500 | -0.41463700 |
| C | -2.61555700 | -0.51315400 | -0.56043200 |
| C | -5.48598200 | -0.31430600 | -0.41354000 |

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|---|---|---|---|
| H | -5.16098200 | 1.80557300 | -0.36293600 |
| C | -3.41963400 | -1.70276300 | -0.64571100 |
| C | -4.79659300 | -1.54964800 | -0.54992200 |
| C | 3.25536300 | 0.74531900 | -0.66982500 |
| C | 4.67571100 | 0.80606100 | -0.71791800 |
| C | 2.57137000 | -0.50226200 | -0.48907200 |
| C | 5.44853000 | -0.32629400 | -0.61260100 |
| H | 5.13202400 | 1.78166900 | -0.85217500 |
| C | 3.37033000 | -1.69828300 | -0.39560600 |
| C | 4.74952300 | -1.55394900 | -0.45908600 |
| O | -1.29946100 | -0.58640000 | -0.53007500 |
| O | 1.26004400 | -0.55332500 | -0.39284600 |
| C | -0.72777400 | 3.42416400 | -0.93009800 |
| C | -1.42889300 | 4.62581400 | -1.08884300 |
| C | -0.73202000 | 5.81417100 | -1.28964000 |
| C | 0.66426100 | 5.81112100 | -1.34507800 |
| C | 1.36952200 | 4.61955000 | -1.20030600 |
| C | 0.67796000 | 3.42046800 | -0.98881500 |
| C | 0.12621900 | 0.45585000 | 2.76583600 |
| C | 1.57845400 | 0.30214200 | 2.96237700 |
| H | 2.00275500 | -0.22066200 | 2.09168700 |
| H | 2.09816600 | 1.25043100 | 3.10707100 |
| C | -0.48630700 | 1.79115200 | 2.80687300 |
| H | -1.47324200 | 1.83015600 | 2.34227800 |
| H | -0.61258500 | 1.96293200 | 3.89520600 |
| H | 1.74834700 | -0.36179400 | 3.81999700 |
| C | 0.62557300 | 0.77774600 | 6.76003500 |
| H | 0.15096600 | 1.44967300 | 7.48560500 |
| H | 0.95145800 | -0.13574300 | 7.27290700 |
| O | -0.24559800 | 0.48659600 | 5.65902700 |
| H | -1.03123000 | 0.04672200 | 6.01914700 |
| H | -5.40420500 | -2.44406400 | -0.59644100 |
| H | 5.35018300 | -2.45194100 | -0.39510600 |
| H | -2.51266500 | 4.65037000 | -1.07441300 |
| H | -1.28102800 | 6.74211400 | -1.41534500 |
| H | 1.20578200 | 6.73662400 | -1.51369700 |
| H | 2.45121400 | 4.64063400 | -1.26912400 |
| H | 1.50314200 | 1.27866700 | 6.34492200 |
| H | 0.16963400 | 2.57798800 | 2.42587200 |
| C | 2.73150500 | -3.09679400 | -0.26496300 |
| C | 1.94384800 | -3.19194800 | 1.06225700 |

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|---|---|---|---|
| C | 1.79056300 | -3.35308600 | -1.46589200 |
| C | 3.78128200 | -4.22699600 | -0.25301500 |
| H | 2.61245300 | -3.04812900 | 1.92090500 |
| H | 1.15120000 | -2.44355200 | 1.09687300 |
| H | 1.48276800 | -4.18159900 | 1.16092700 |
| H | 2.35228800 | -3.32449800 | -2.40674000 |
| H | 1.33471700 | -4.34660400 | -1.37924800 |
| H | 0.99318000 | -2.61145900 | -1.51598800 |
| H | 3.26600700 | -5.18994000 | -0.17159700 |
| H | 4.37267900 | -4.25183200 | -1.17499300 |
| H | 4.46830700 | -4.15298300 | 0.59811200 |
| C | -2.79605700 | -3.09347000 | -0.89184300 |
| C | -2.02977000 | -3.06836100 | -2.23724000 |
| C | -1.83809500 | -3.47938900 | 0.25780800 |
| C | -3.86205300 | -4.20448200 | -0.98976500 |
| H | -2.71481700 | -2.85902600 | -3.06685500 |
| H | -1.24408000 | -2.31076100 | -2.23888800 |
| H | -1.56549300 | -4.04384700 | -2.42407600 |
| H | -2.36393700 | -3.47784900 | 1.22140200 |
| H | -1.44794500 | -4.49108700 | 0.09553700 |
| H | -0.99074100 | -2.79684200 | 0.31132000 |
| H | -3.36307100 | -5.15934700 | -1.18576700 |
| H | -4.43177300 | -4.31957000 | -0.06004700 |
| H | -4.56764700 | -4.03306000 | -1.81023300 |
| C | 6.98480500 | -0.32263200 | -0.66702300 |
| C | 7.54949300 | -0.91906000 | 0.64463800 |
| C | 7.46088600 | -1.17709000 | -1.86645100 |
| C | 7.55230200 | 1.09942700 | -0.83318900 |
| H | 7.24181900 | -0.32397300 | 1.51237400 |
| H | 7.21356900 | -1.94888000 | 0.80698200 |
| H | 8.64505500 | -0.93120700 | 0.61427900 |
| H | 7.08404800 | -0.77175300 | -2.81212700 |
| H | 8.55594800 | -1.18642300 | -1.91331400 |
| H | 7.12565300 | -2.21693500 | -1.79020200 |
| H | 8.64616700 | 1.05906500 | -0.86269200 |
| H | 7.21684800 | 1.56673200 | -1.76622400 |
| H | 7.27077200 | 1.75240500 | 0.00143400 |
| C | -7.01977500 | -0.30179000 | -0.30958800 |
| C | -7.63183100 | -0.93984700 | -1.57981500 |
| C | -7.45702600 | -1.11263700 | 0.93386600 |
| C | -7.57643900 | 1.12769300 | -0.17291700 |

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|---|---|---|---|
| H | -7.34482700 | -0.38121900 | -2.47770600 |
| H | -7.31165600 | -1.97845000 | -1.71459100 |
| H | -8.72598800 | -0.93848400 | -1.51431600 |
| H | -7.05393500 | -0.67178700 | 1.85310800 |
| H | -8.55007500 | -1.12291400 | 1.01474100 |
| H | -7.12055600 | -2.15384000 | 0.88501300 |
| H | -8.66775800 | 1.09253900 | -0.09006200 |
| H | -7.19520000 | 1.63096200 | 0.72355500 |
| H | -7.33472800 | 1.74570000 | -1.04538300 |
| C | -0.71607400 | -0.71871700 | 2.57154200 |
| H | -0.82115400 | -0.80702700 | 1.46226500 |
| H | -0.27315600 | -1.64743500 | 2.93410100 |
| H | -1.73459400 | -0.57013300 | 2.94458100 |

**Int-2$_{t\text{Bu-Co}}$**

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|---|---|---|---|
| Co | 0.06034483 | -0.32758620 | 0.00000000 |
| N | 1.32894083 | 1.04874380 | -0.03121400 |
| N | -1.21664217 | 1.04482880 | 0.00891400 |
| C | -2.52308317 | 0.87519080 | 0.07484400 |
| H | -3.15067917 | 1.76326680 | 0.13310500 |
| C | 2.63415983 | 0.88453080 | -0.08225900 |
| H | 3.25899183 | 1.77220280 | -0.16404400 |
| C | -3.21314317 | -0.35709220 | 0.05419500 |
| C | -4.63599217 | -0.30553820 | 0.12471800 |
| C | -2.52465317 | -1.60756720 | -0.09192200 |
| C | -5.40183017 | -1.44145520 | 0.03514300 |
| H | -5.09647617 | 0.67087280 | 0.23981300 |
| C | -3.32223317 | -2.79958520 | -0.24396700 |
| C | -4.69893417 | -2.66422520 | -0.16083600 |
| C | 3.33004383 | -0.34719620 | -0.03895400 |
| C | 4.74911683 | -0.29017020 | -0.13574700 |
| C | 2.64724683 | -1.59841320 | 0.10884600 |
| C | 5.52001783 | -1.42699220 | -0.09411400 |
| H | 5.20452883 | 0.68856480 | -0.24984800 |
| C | 3.44520383 | -2.79660220 | 0.15525800 |
| C | 4.82177283 | -2.65652920 | 0.05192100 |
| O | -1.21618117 | -1.67308420 | -0.09188500 |
| O | 1.33728683 | -1.65468920 | 0.21638600 |
| C | -0.65070717 | 2.34660580 | -0.05484800 |
| C | -1.35029117 | 3.55839880 | -0.11793400 |

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|---|---|---|---|
| C | -0.65223317 | 4.76217780 | -0.15958600 |
| C | 0.74508683 | 4.76687880 | -0.14246500 |
| C | 1.44968283 | 3.56716180 | -0.09346600 |
| C | 0.75711183 | 2.35038980 | -0.05877900 |
| C | 0.06165583 | -0.85070020 | 3.96760700 |
| C | 1.54731783 | -1.02621620 | 3.76977400 |
| H | 1.74129883 | -0.85240420 | 2.70534600 |
| H | 2.12502083 | -0.30587120 | 4.35505500 |
| C | -0.42047817 | 0.57112780 | 3.77579500 |
| H | -1.48573117 | 0.68445980 | 4.00957200 |
| H | 0.16742383 | 1.28411880 | 4.35994700 |
| H | 1.88437183 | -2.04419520 | 3.98097100 |
| C | 0.14844683 | -2.29567120 | 6.29432600 |
| H | -0.04503217 | -2.12779620 | 7.35396400 |
| H | -0.47678817 | -3.09301520 | 5.89129400 |
| O | -0.14322717 | -1.02194520 | 5.61545400 |
| H | -1.05522817 | -0.73871620 | 5.82260800 |
| H | -5.29819117 | -3.55986820 | -0.26470400 |
| H | 5.42103283 | -3.55773620 | 0.07659000 |
| H | -2.43383917 | 3.57964780 | -0.14833400 |
| H | -1.20052717 | 5.69772480 | -0.21119900 |
| H | 1.28838383 | 5.70611780 | -0.17581900 |
| H | 2.53342783 | 3.59684380 | -0.08870100 |
| H | 1.20478583 | -2.49269620 | 6.13015000 |
| H | -0.30018717 | 0.81221980 | 2.71270000 |
| C | 2.80181583 | -4.19251920 | 0.28537700 |
| C | 2.02079183 | -4.28875020 | 1.61772200 |
| C | 1.85278983 | -4.43959520 | -0.91079000 |
| C | 3.84605483 | -5.32767320 | 0.28824900 |
| H | 2.70148383 | -4.16362720 | 2.47070000 |
| H | 1.24183883 | -3.52654620 | 1.66718900 |
| H | 1.54757283 | -5.27376620 | 1.70911000 |
| H | 2.41128483 | -4.41317220 | -1.85363400 |
| H | 1.38852083 | -5.42953220 | -0.82492800 |
| H | 1.06262983 | -3.69016320 | -0.95551000 |
| H | 3.32832283 | -6.28851020 | 0.38120300 |
| H | 4.42439683 | -5.35967720 | -0.64171200 |
| H | 4.54627983 | -5.25098720 | 1.12854300 |
| C | -2.67511717 | -4.17086020 | -0.52673300 |
| C | -1.88793617 | -4.09693020 | -1.85806500 |
| C | -1.73161017 | -4.56862620 | 0.63205900 |

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|---|---|---|---|
| C | -3.72069217 | -5.29541120 | -0.67250600 |
| H | -2.56453317 | -3.87589020 | -2.69171600 |
| H | -1.11630317 | -3.32617720 | -1.82696300 |
| H | -1.40513517 | -5.05951820 | -2.06459300 |
| H | -2.28781517 | -4.63361420 | 1.57680300 |
| H | -1.29237217 | -5.55435120 | 0.43738100 |
| H | -0.92079417 | -3.84908820 | 0.74340600 |
| H | -3.20361317 | -6.23780320 | -0.88254400 |
| H | -4.30684017 | -5.44155320 | 0.24269700 |
| H | -4.41349817 | -5.11363120 | -1.50172500 |
| C | 7.05364483 | -1.42697520 | -0.20355100 |
| C | 7.66398583 | -2.05852420 | 1.07054100 |
| C | 7.48354983 | -2.25107420 | -1.44087000 |
| C | 7.62091083 | -0.00300520 | -0.35346000 |
| H | 7.38965083 | -1.48501220 | 1.96369300 |
| H | 7.32957083 | -3.09107020 | 1.21842400 |
| H | 8.75787583 | -2.07344220 | 1.00068100 |
| H | 7.07485083 | -1.81944220 | -2.36134900 |
| H | 8.57631883 | -2.26388120 | -1.52750400 |
| H | 7.14547483 | -3.29106620 | -1.38009200 |
| H | 8.71279983 | -0.04590820 | -0.42625400 |
| H | 7.25106383 | 0.49020180 | -1.25973500 |
| H | 7.37403283 | 0.62827980 | 0.50837300 |
| C | -6.93750217 | -1.44797420 | 0.10857400 |
| C | -7.51851717 | -2.01464220 | -1.20915900 |
| C | -7.39373217 | -2.33412520 | 1.29233800 |
| C | -7.51103617 | -0.03399520 | 0.31735400 |
| H | -7.21898417 | -1.40080720 | -2.06593000 |
| H | -7.18427517 | -3.04007220 | -1.39911900 |
| H | -8.61390417 | -2.02741720 | -1.16659700 |
| H | -7.01395417 | -1.94421420 | 2.24418500 |
| H | -8.48819817 | -2.35895820 | 1.34956500 |
| H | -7.04552917 | -3.36756820 | 1.19005000 |
| H | -8.60377617 | -0.08224720 | 0.37215600 |
| H | -7.15475217 | 0.41773080 | 1.25085700 |
| H | -7.25387817 | 0.63692180 | -0.51033600 |
| C | -0.80036717 | -1.89834120 | 3.31107000 |
| H | -0.70024117 | -1.76266120 | 2.22519600 |
| H | -0.47153917 | -2.91674220 | 3.53282500 |
| H | -1.86100117 | -1.78282320 | 3.55878600 |

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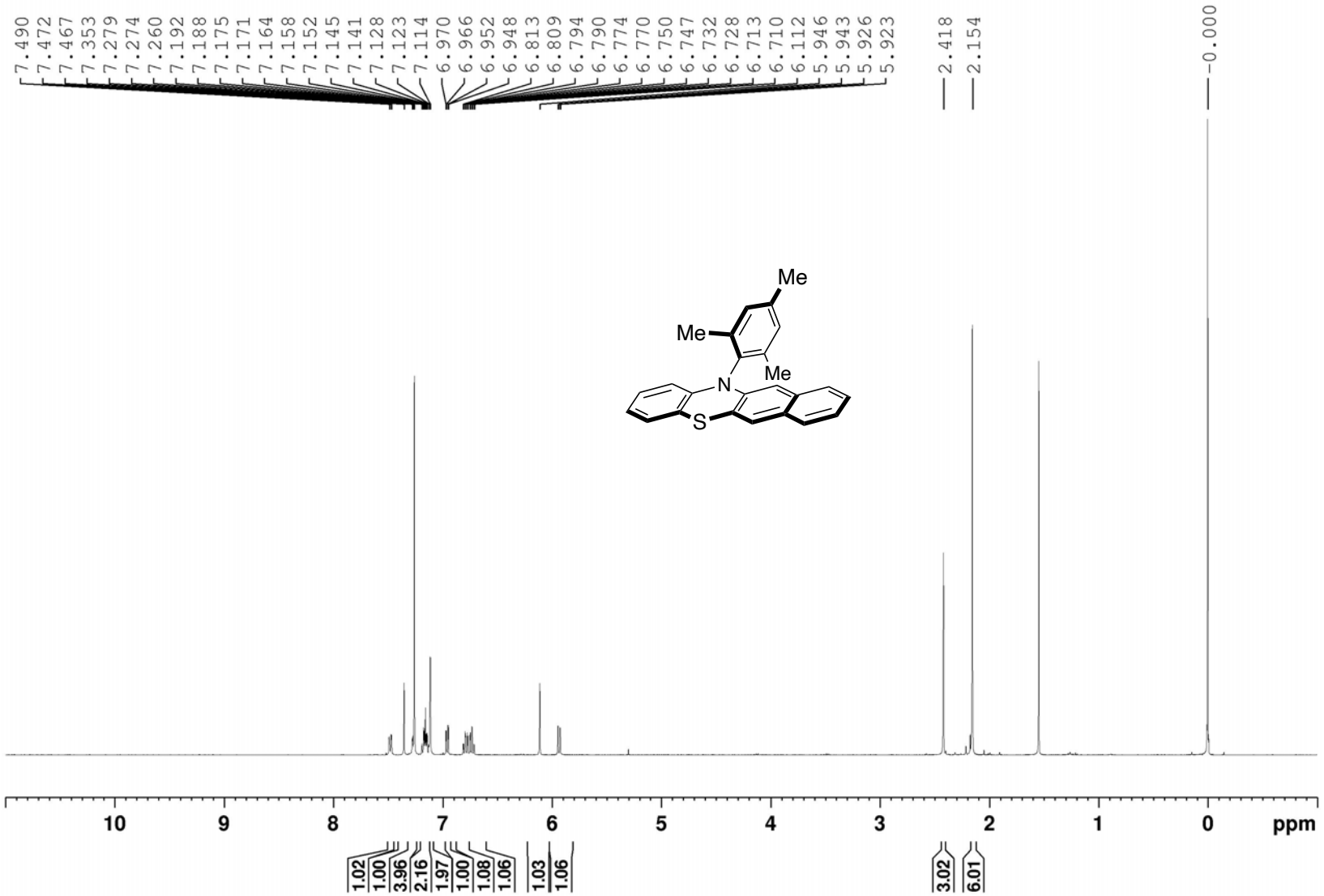
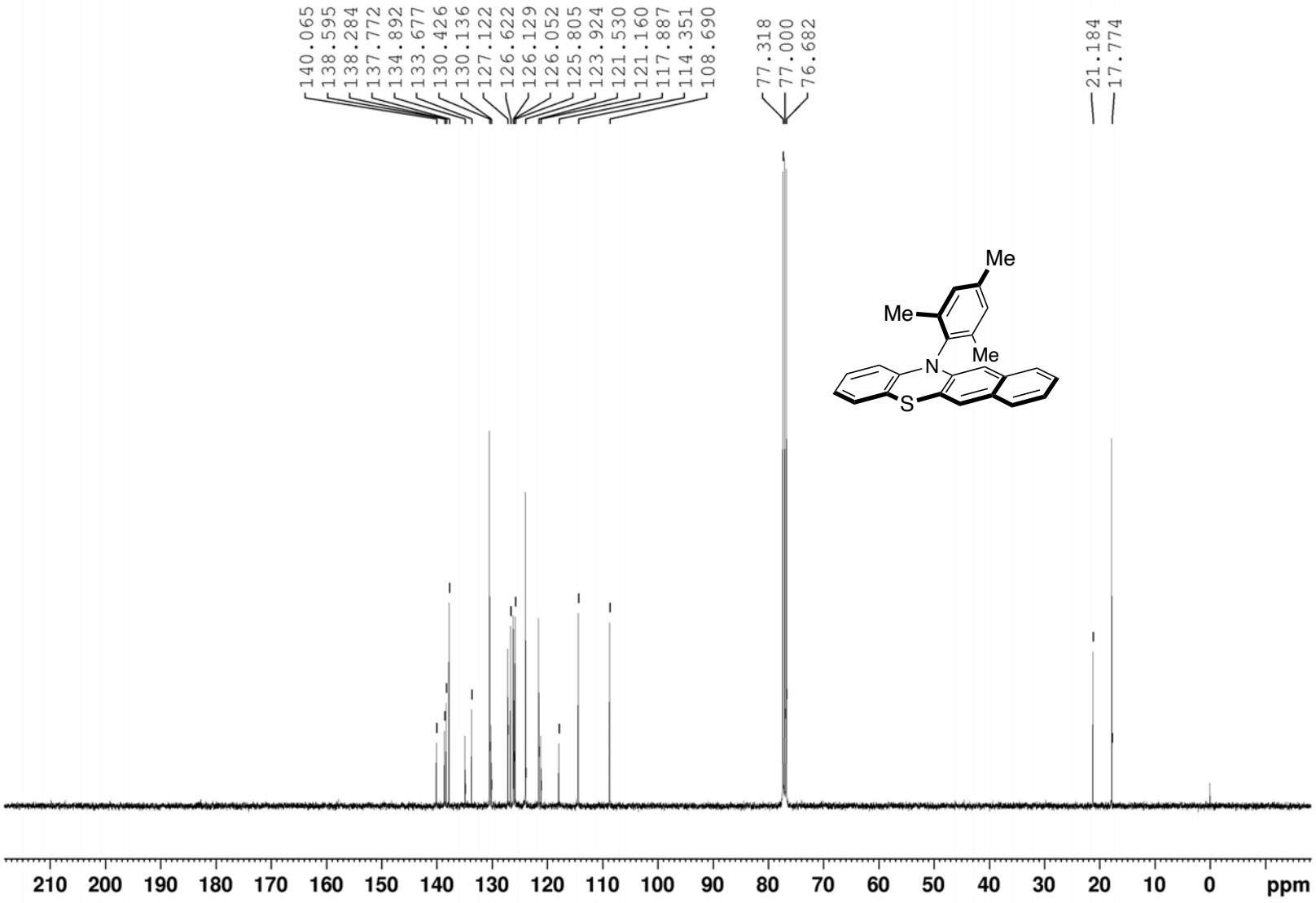
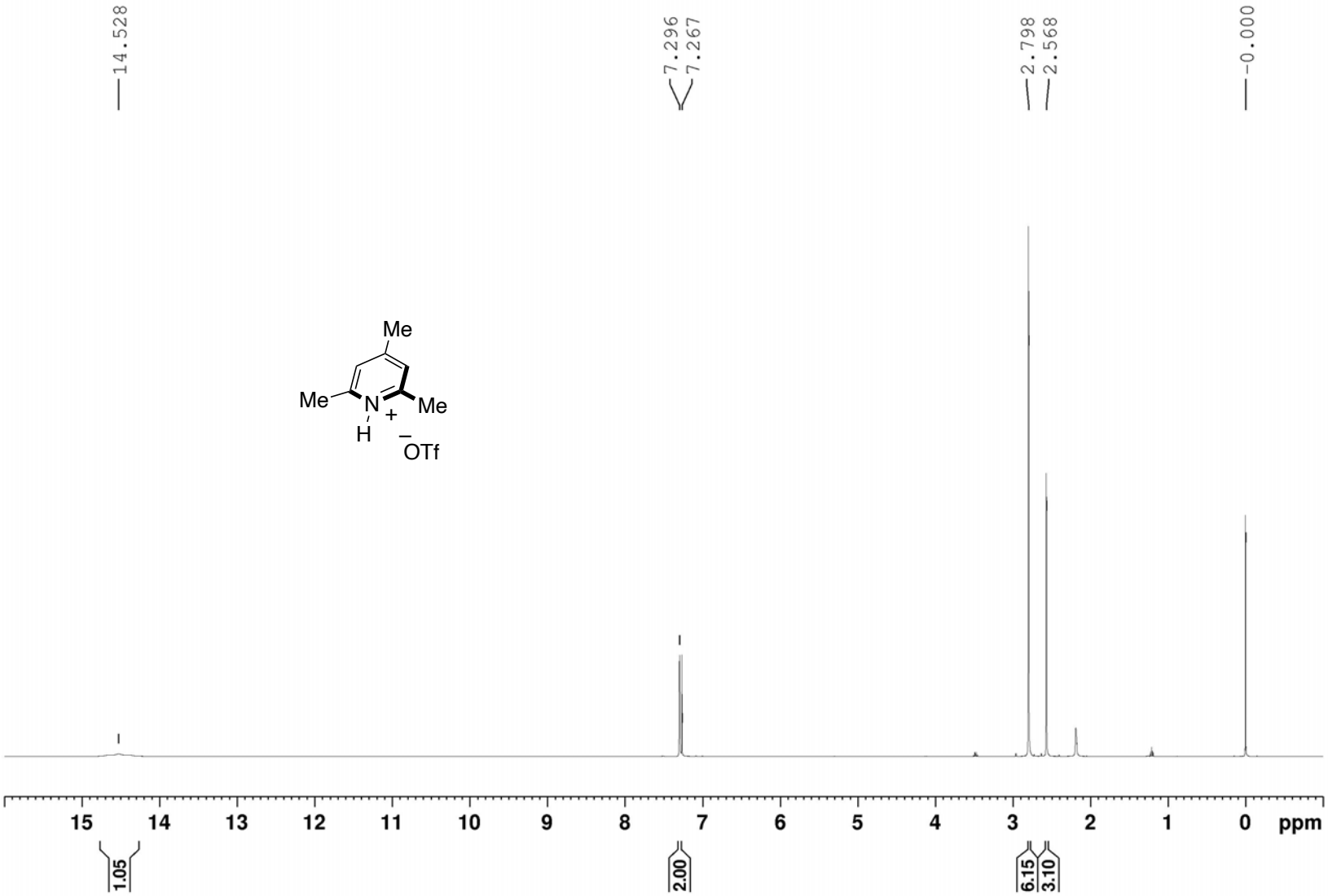


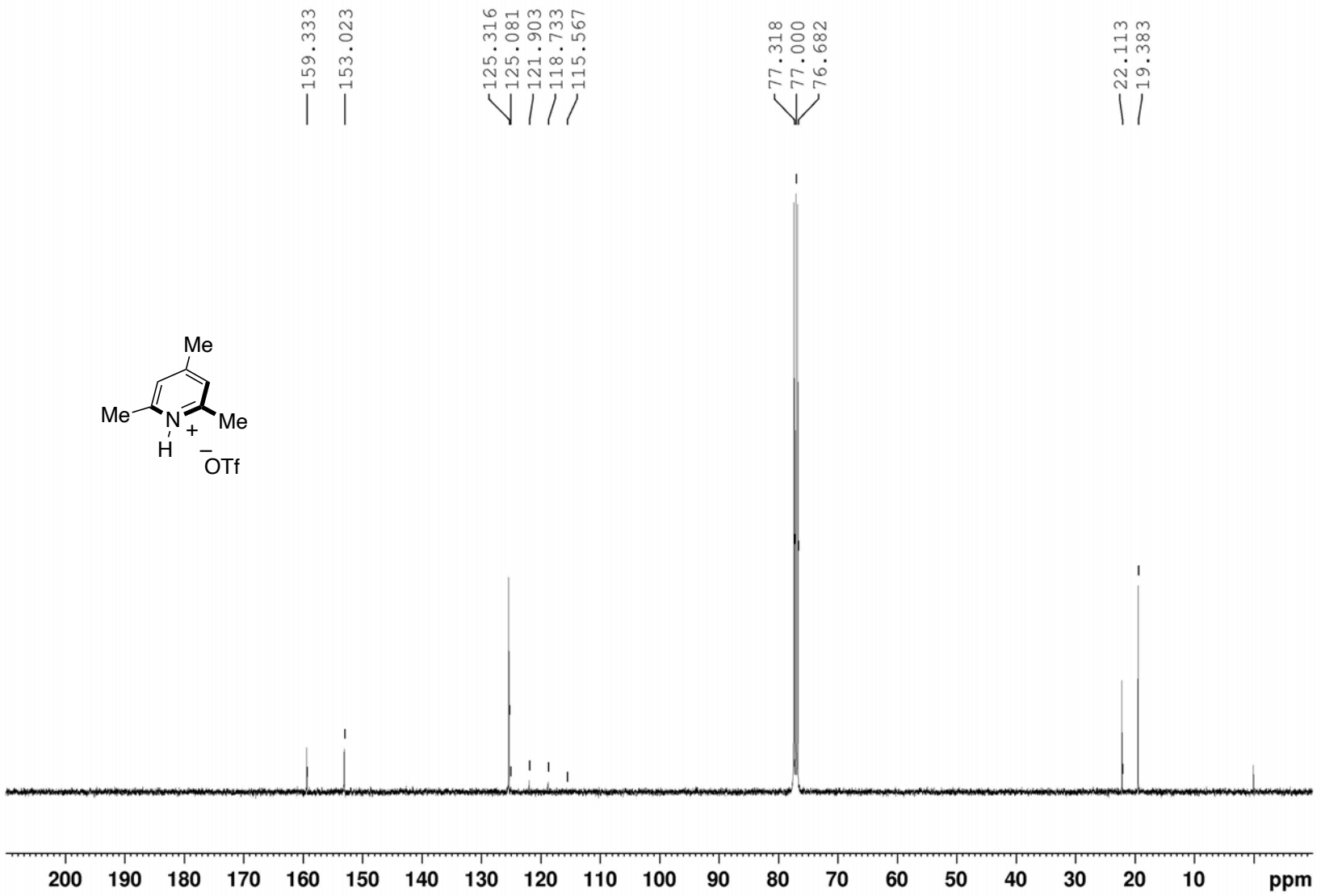

$^{1}$H NMR spectrum of **PTH-1**



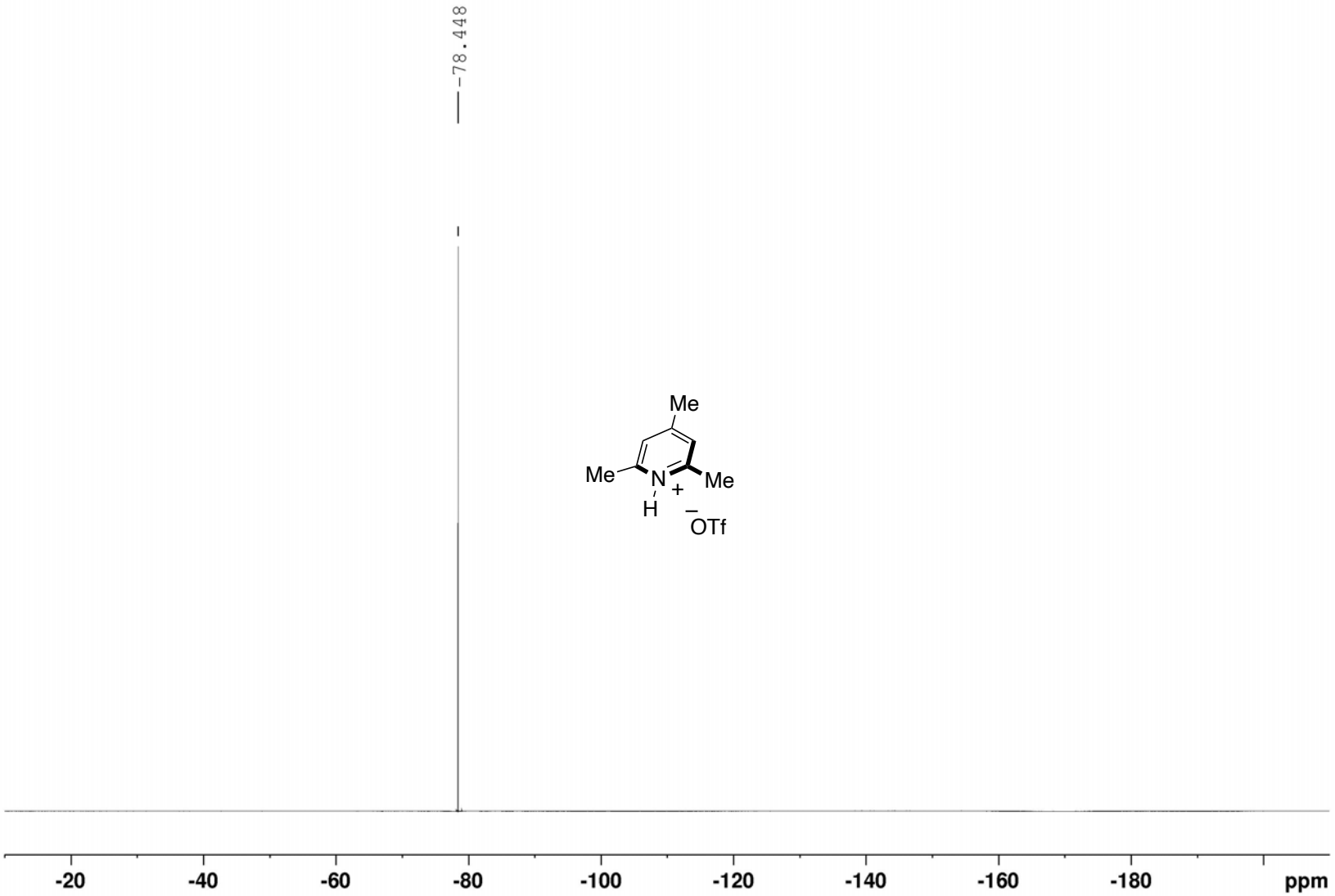

$^{13}$C NMR spectrum of **PTH-1**



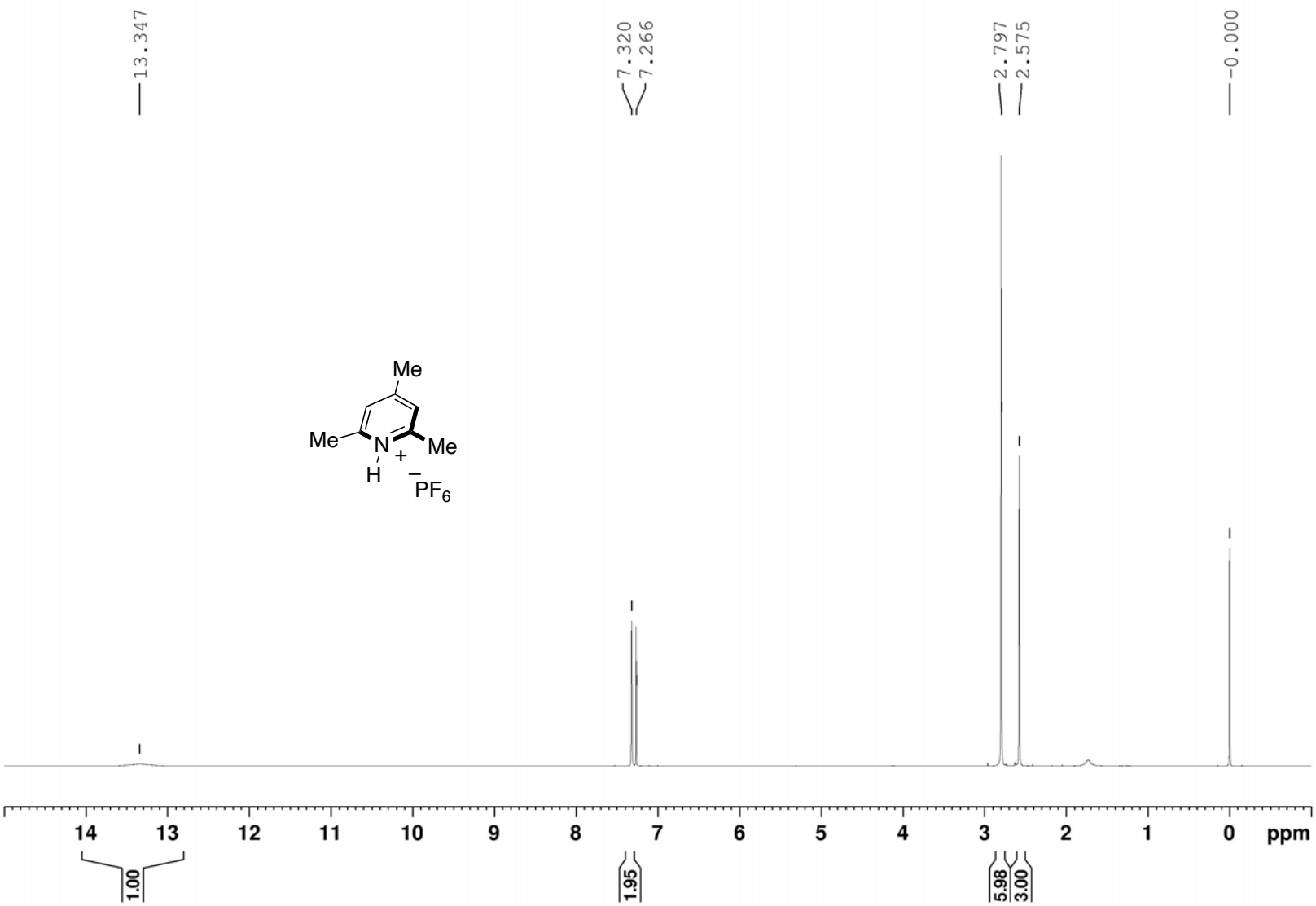

$^{1}$H NMR spectrum of **HX-1**



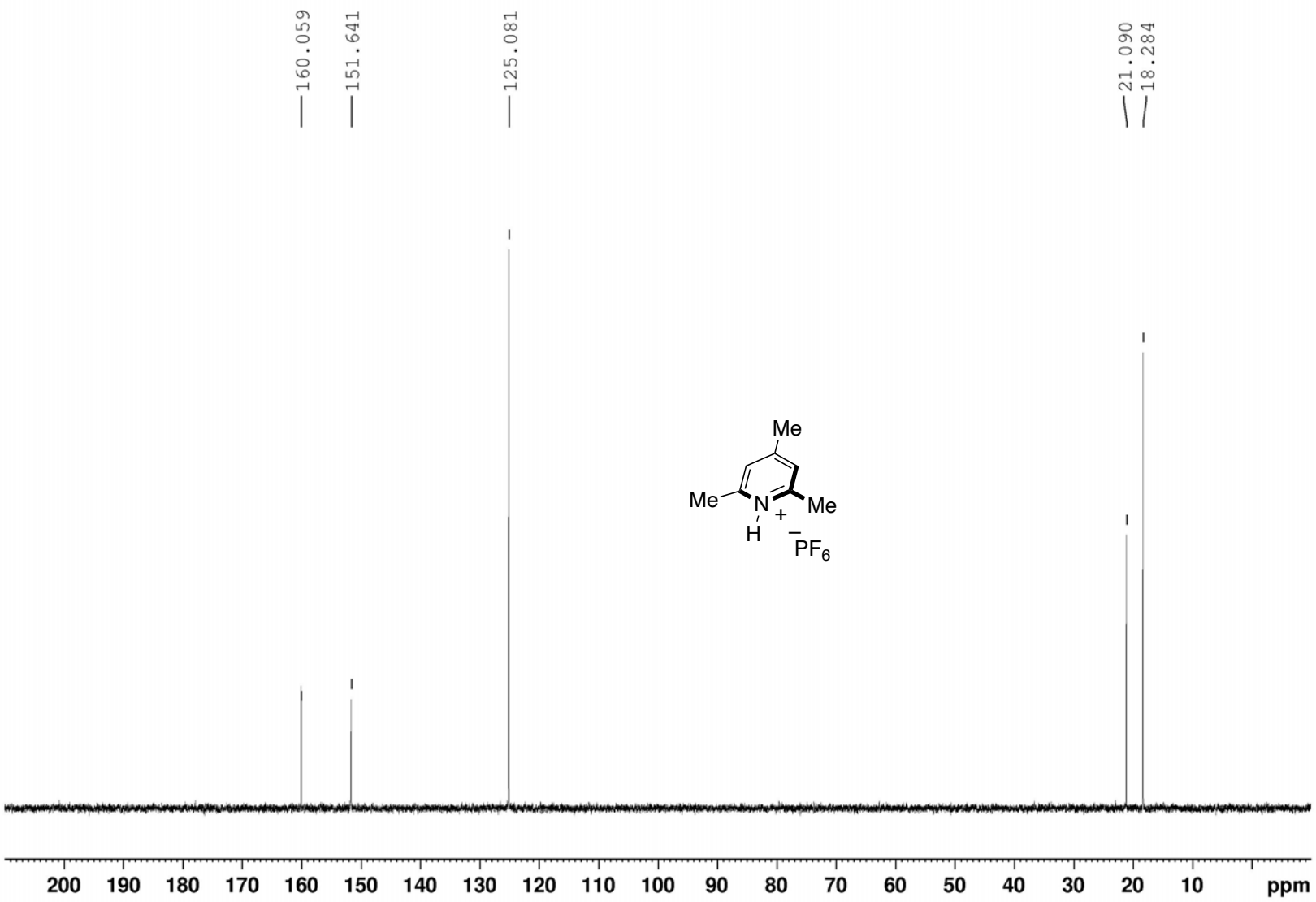

$^{13}$C NMR spectrum of **HX-1**



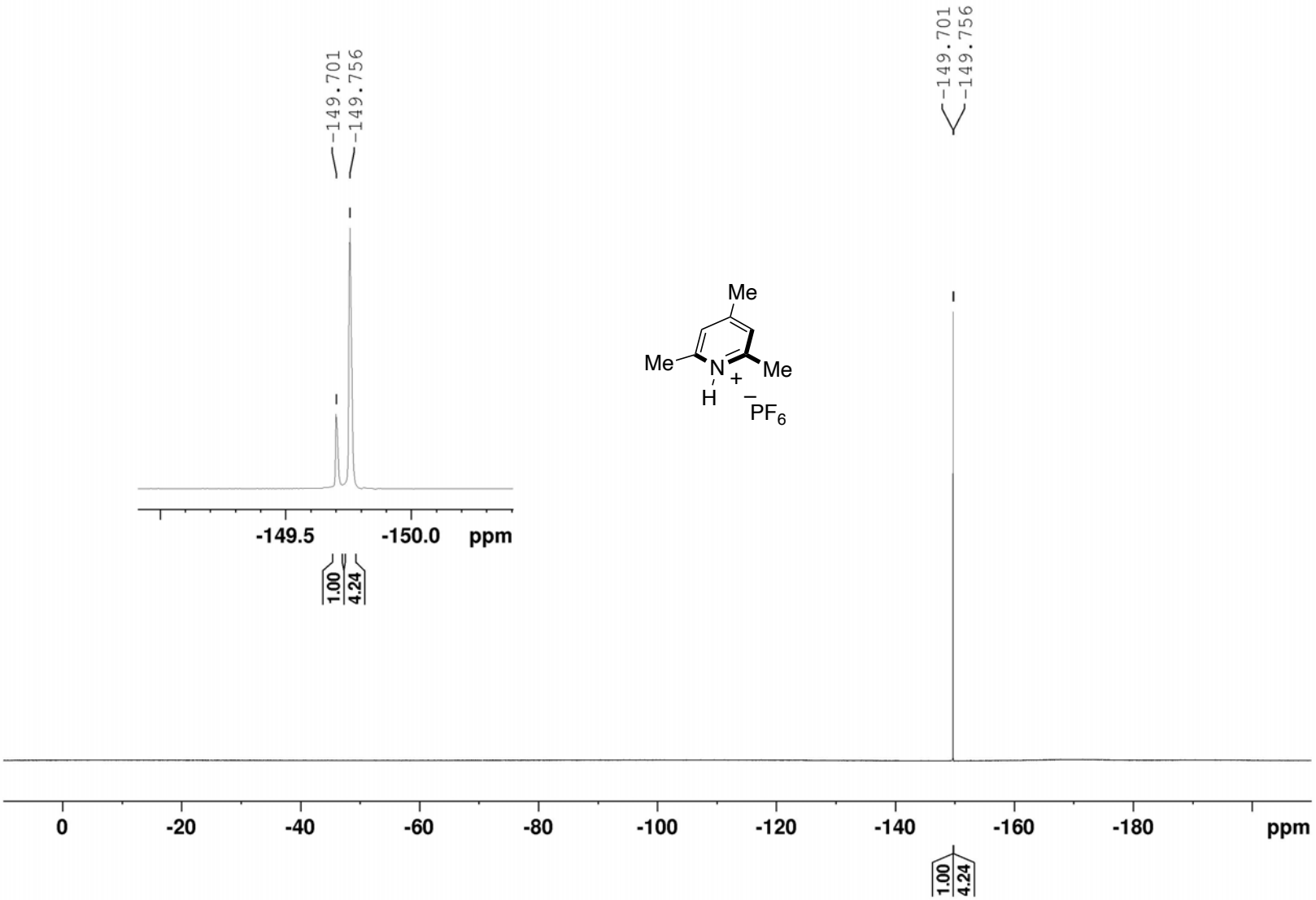

$^{19}$F NMR spectrum of **HX-1**



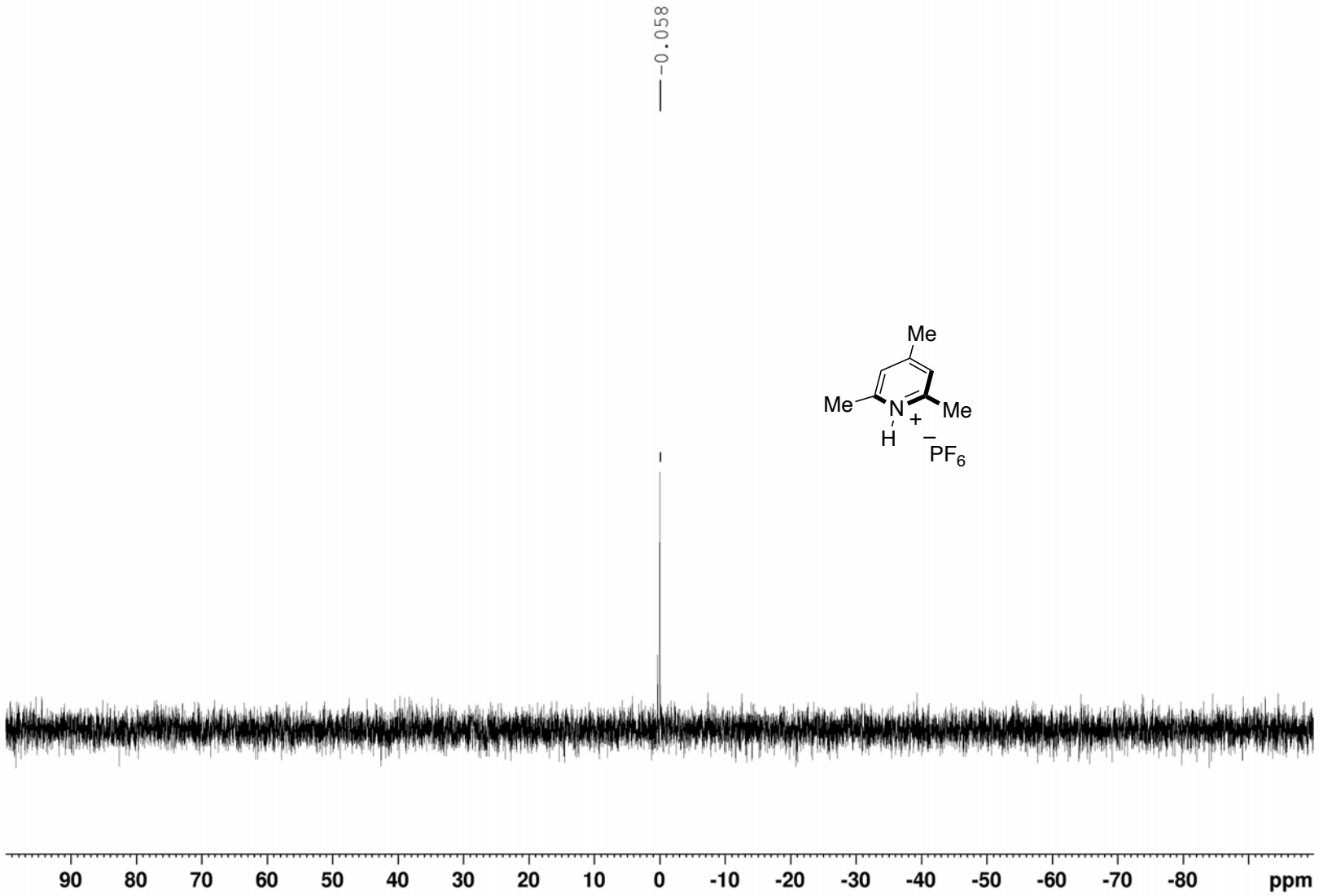

$^{1}$H NMR spectrum of **HX-3**



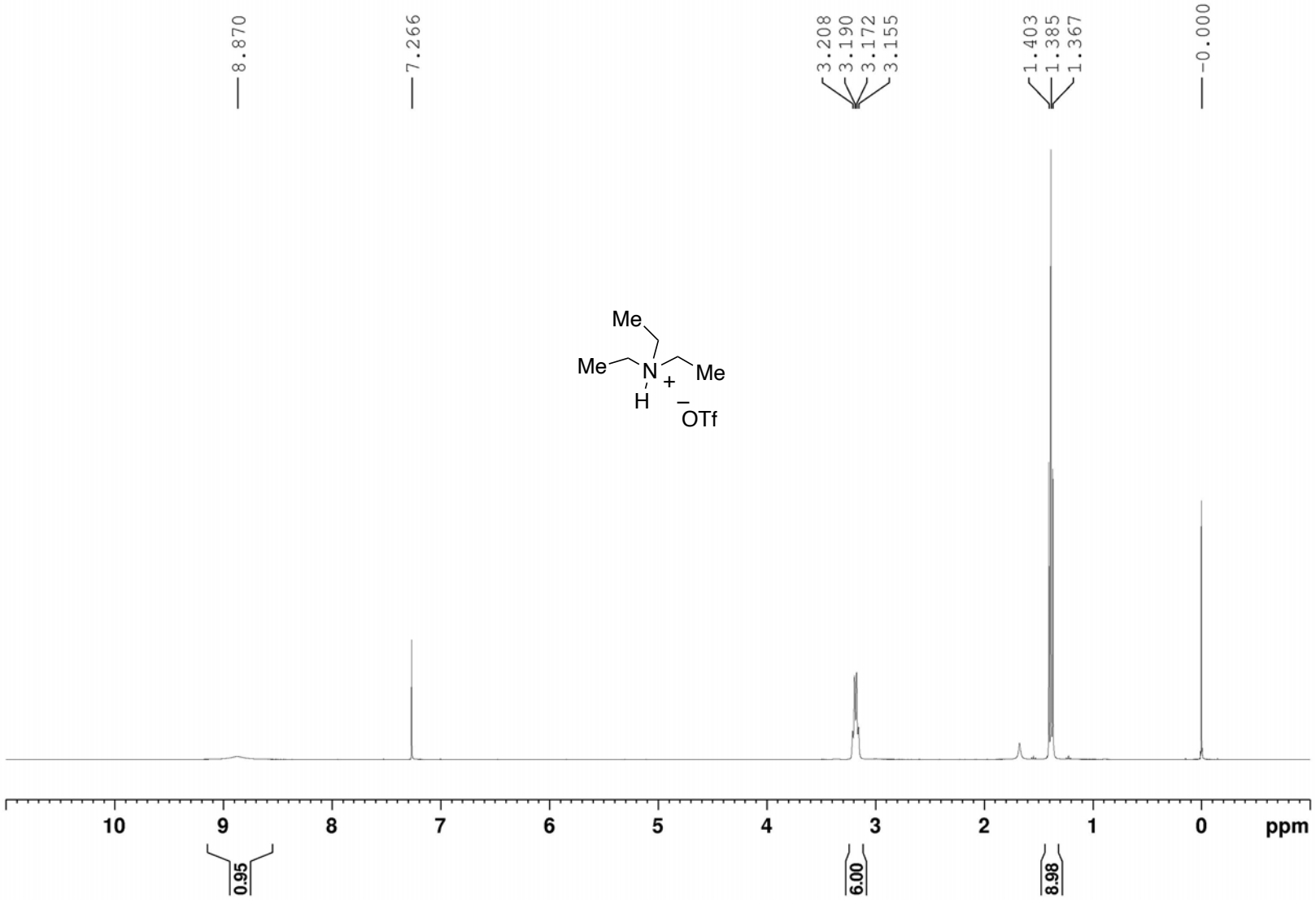

$^{13}$C NMR spectrum of **HX-3**



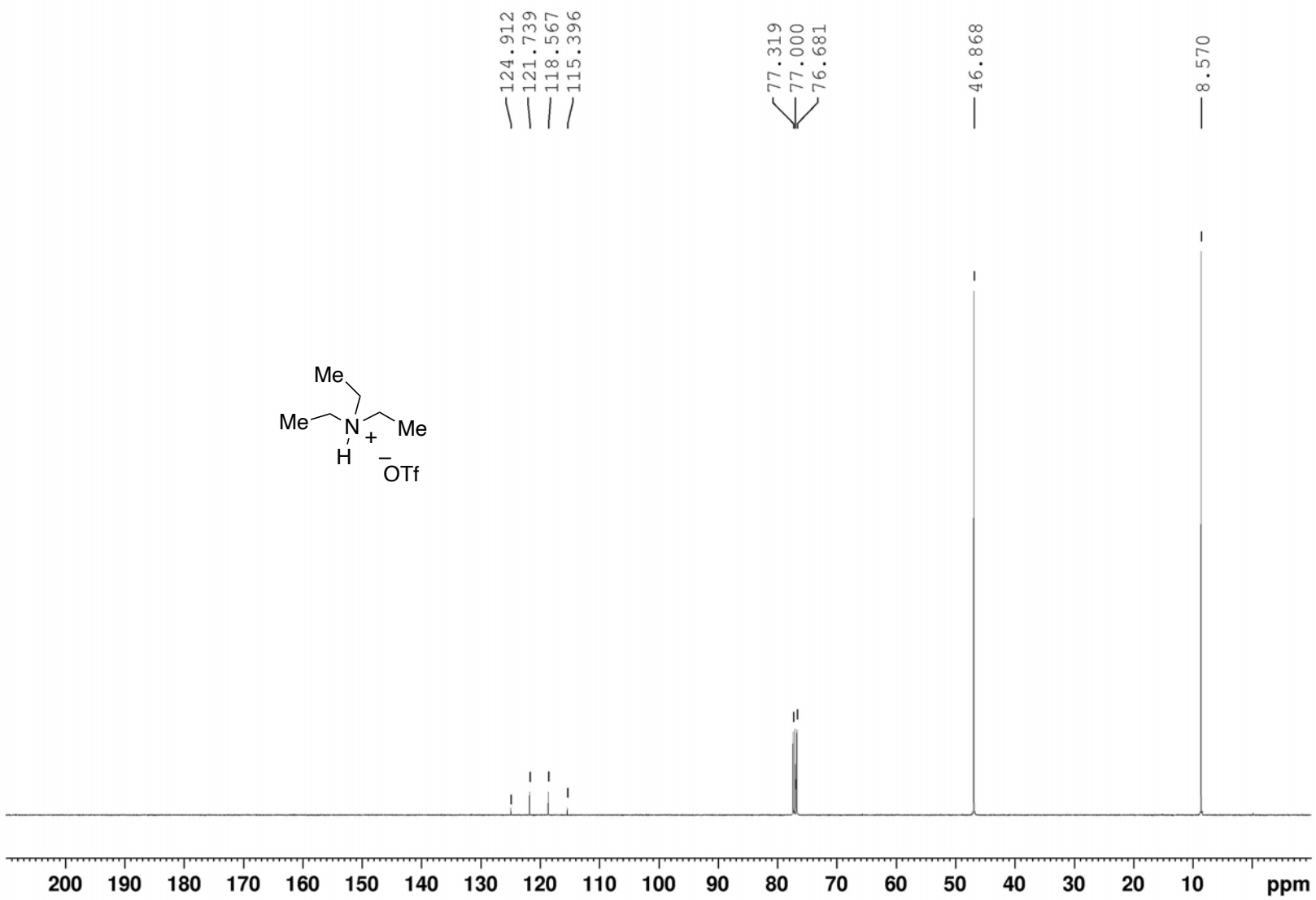

$^{19}$F NMR spectrum of **HX-3**



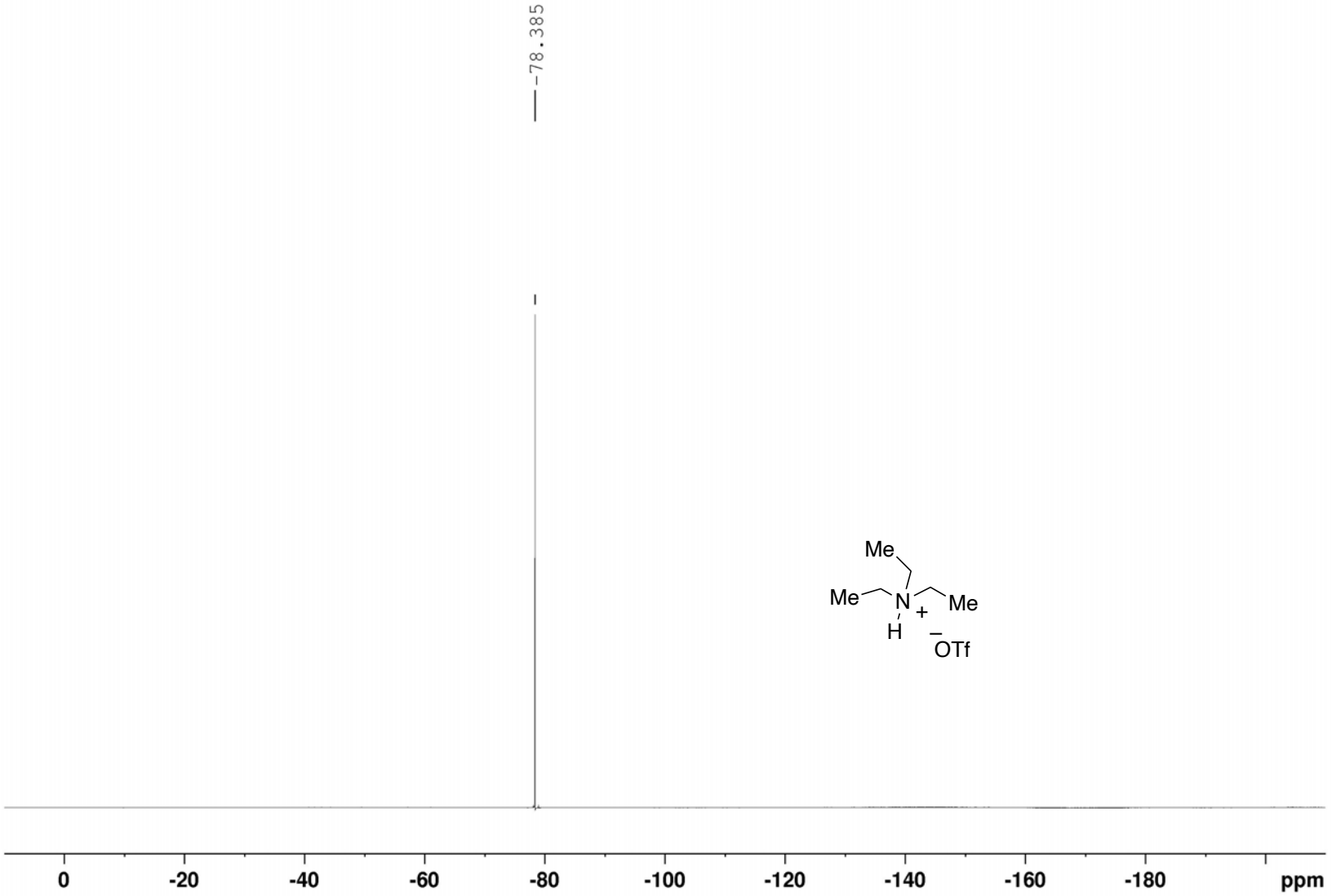

$^{31}$P NMR spectrum of **HX-3**



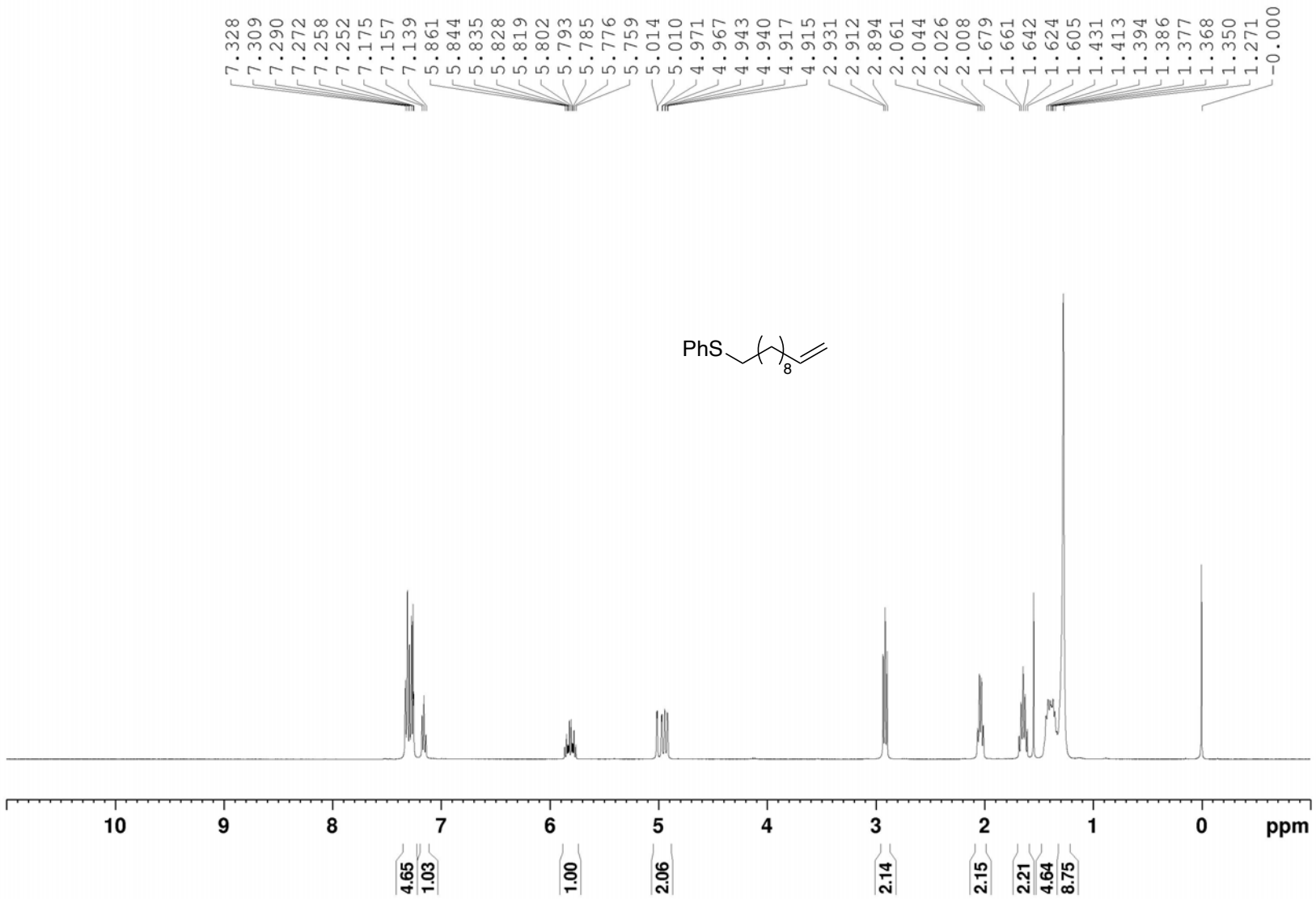

$^{1}$H NMR spectrum of **HX-4**



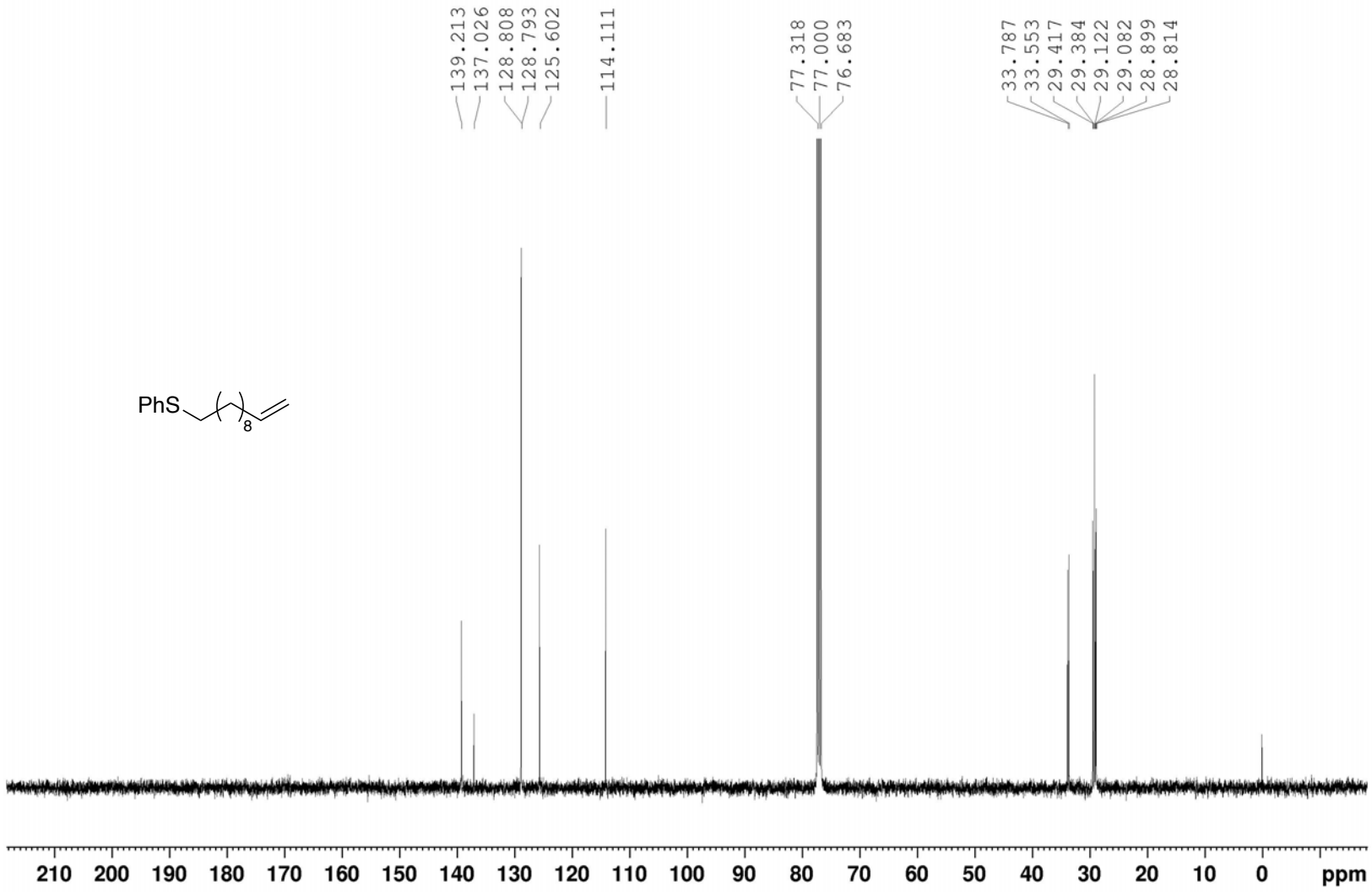

$^{13}$C NMR spectrum of **HX-4**



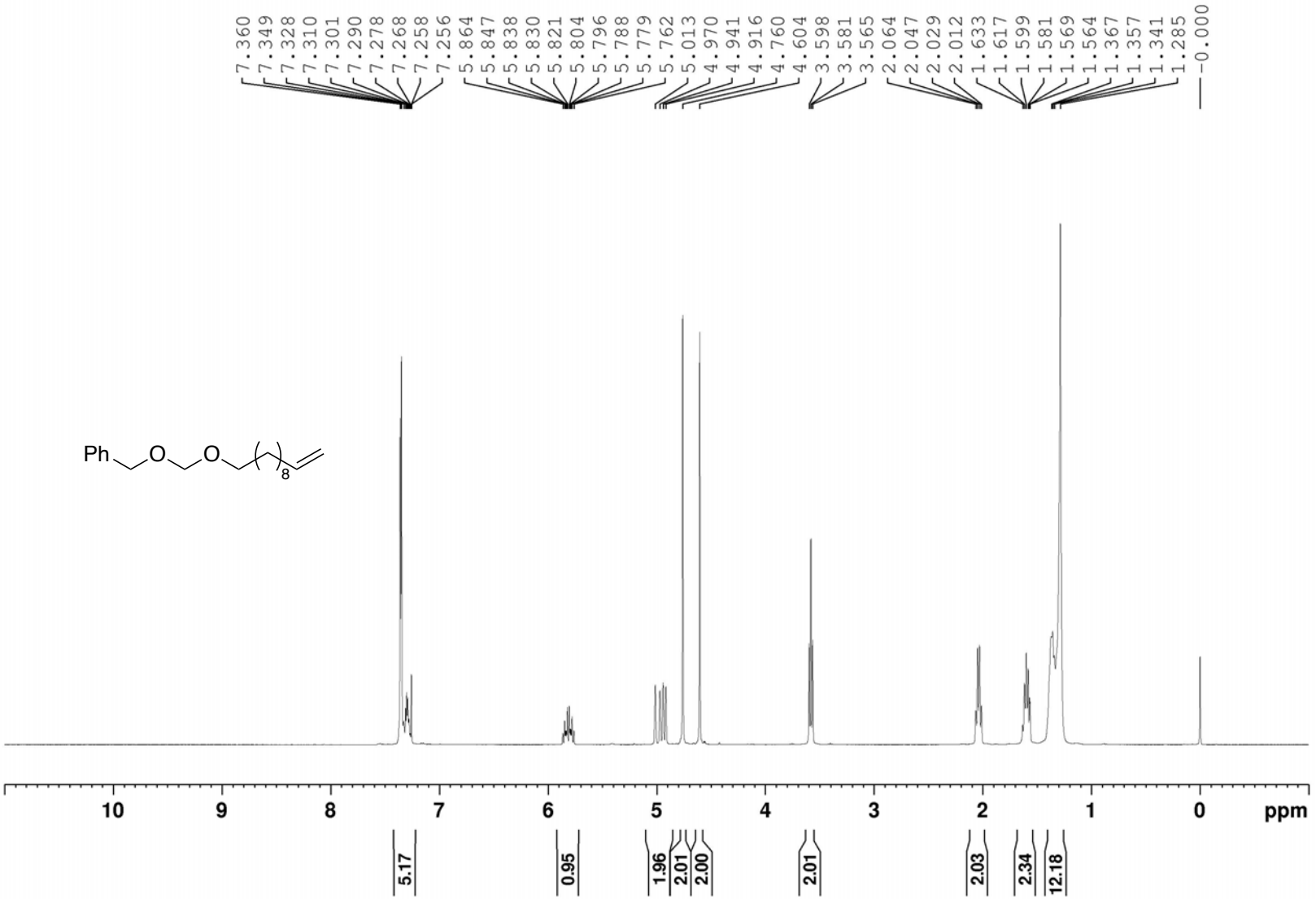

$^{19}$F NMR spectrum of **HX-4**



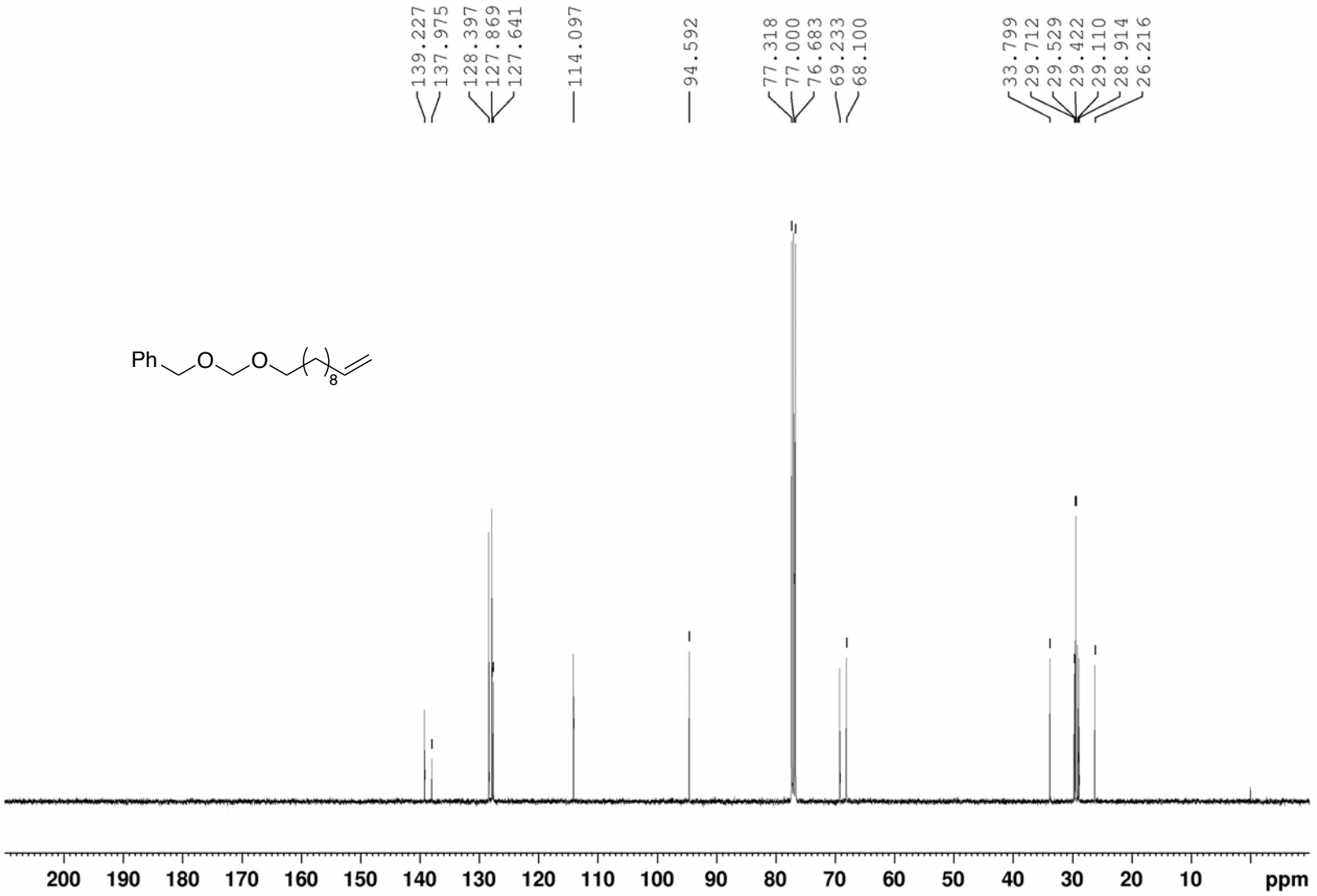

$^{1}$H NMR spectrum of **2e**



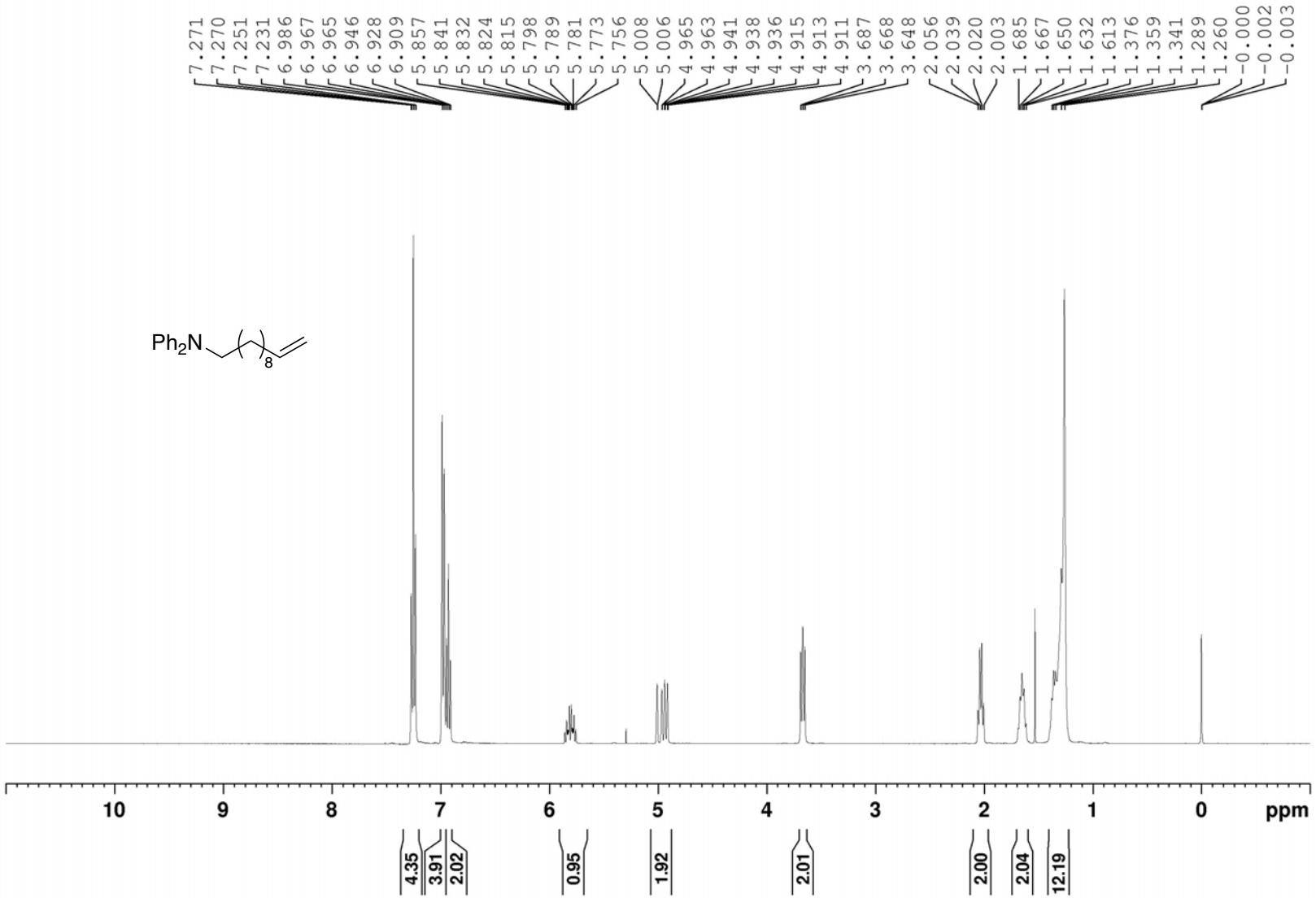

$^{13}$C NMR spectrum of **2e**



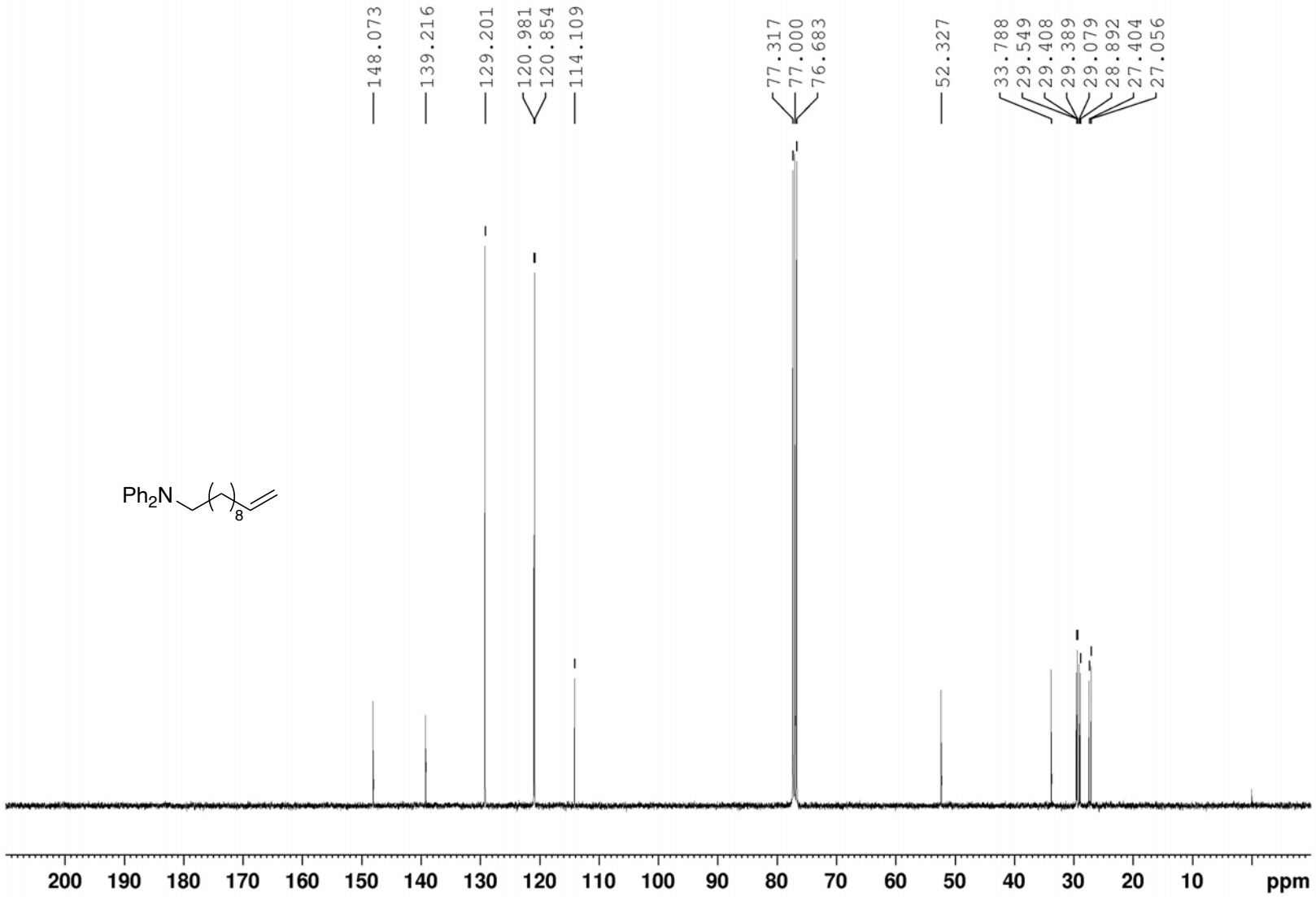

$^{1}$H NMR spectrum of **2i**




$^{13}$C NMR spectrum of **2i**




$^{1}$H NMR spectrum of **2j**

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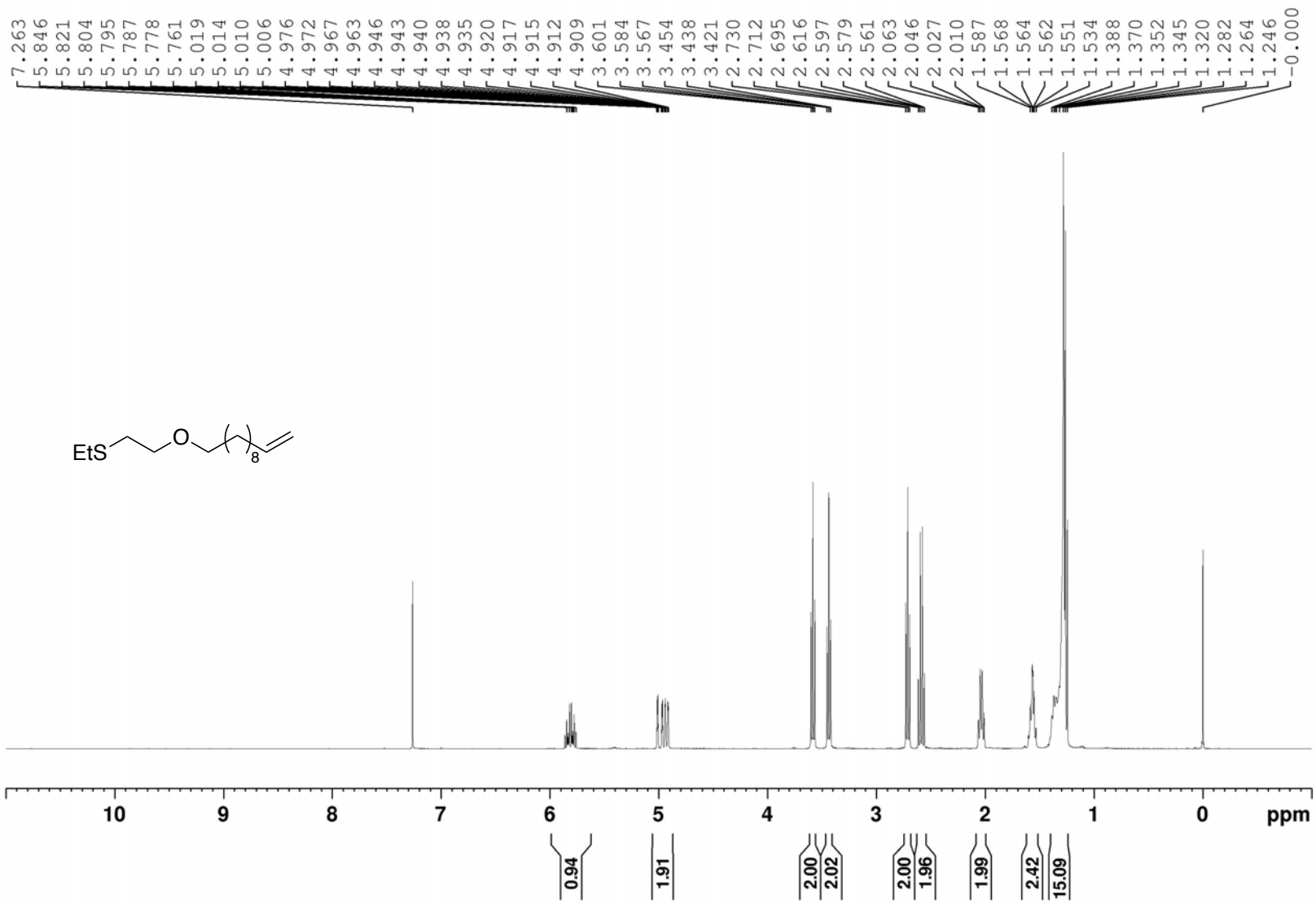
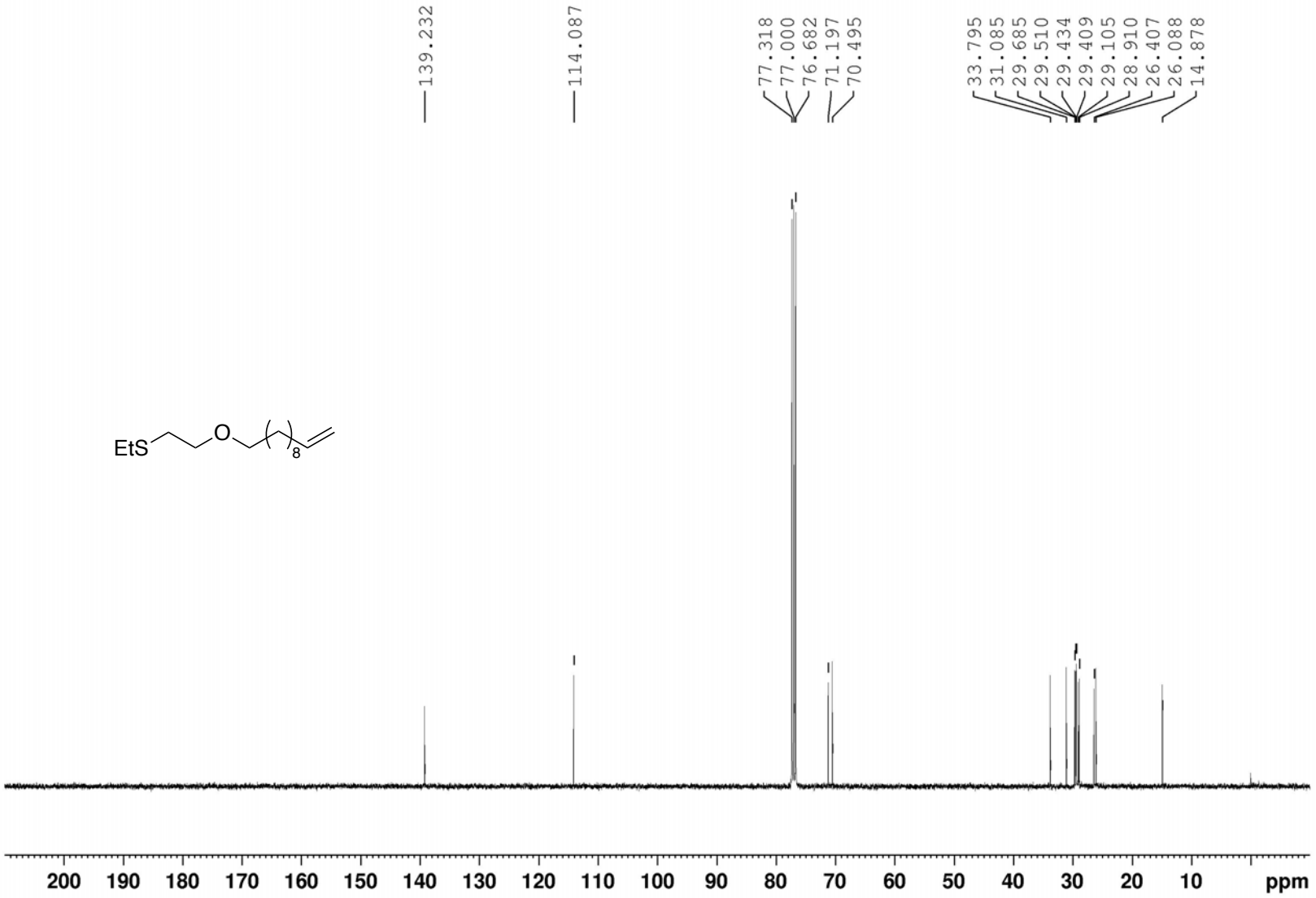
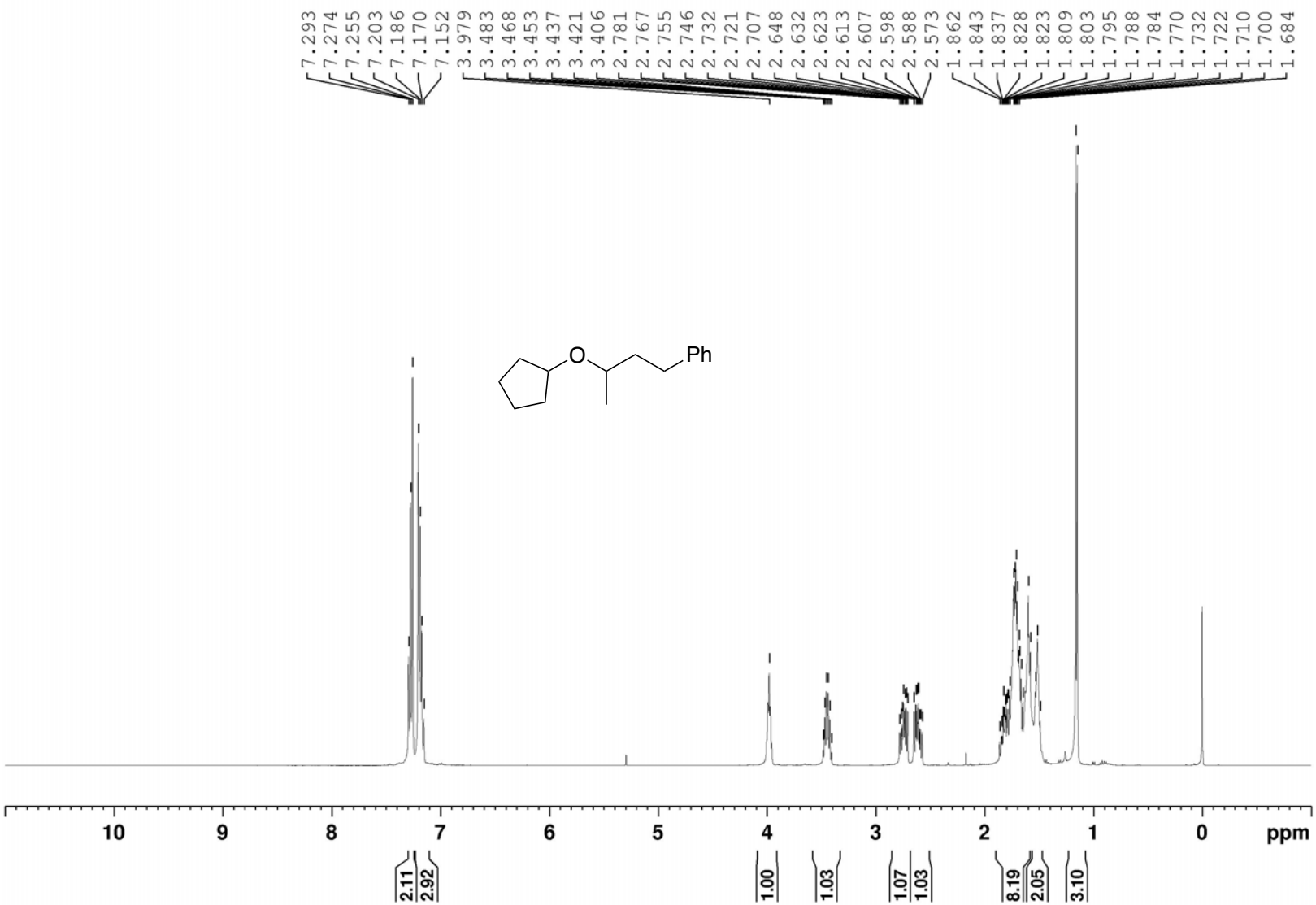


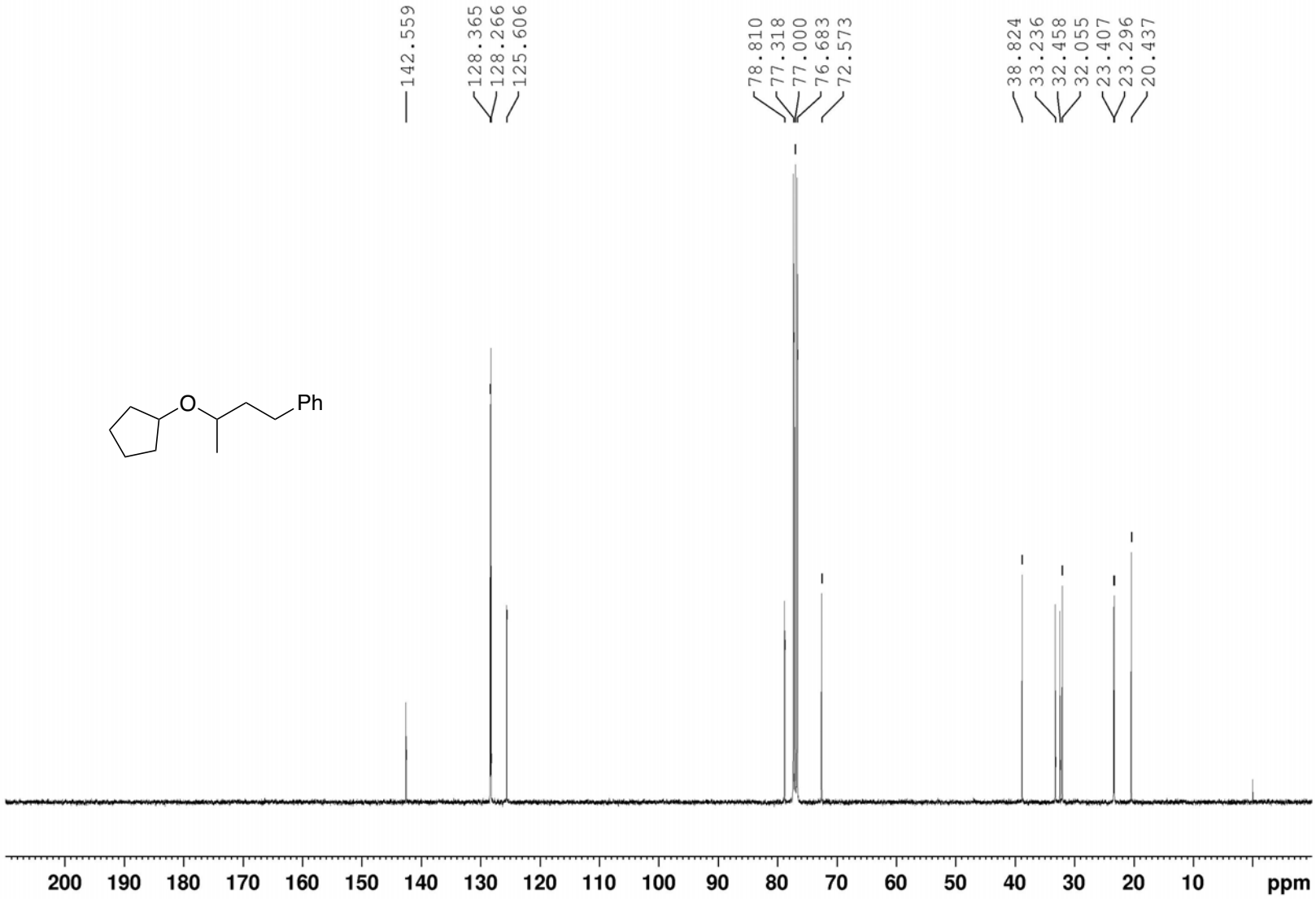

$^{1}$H NMR spectrum of **2l**



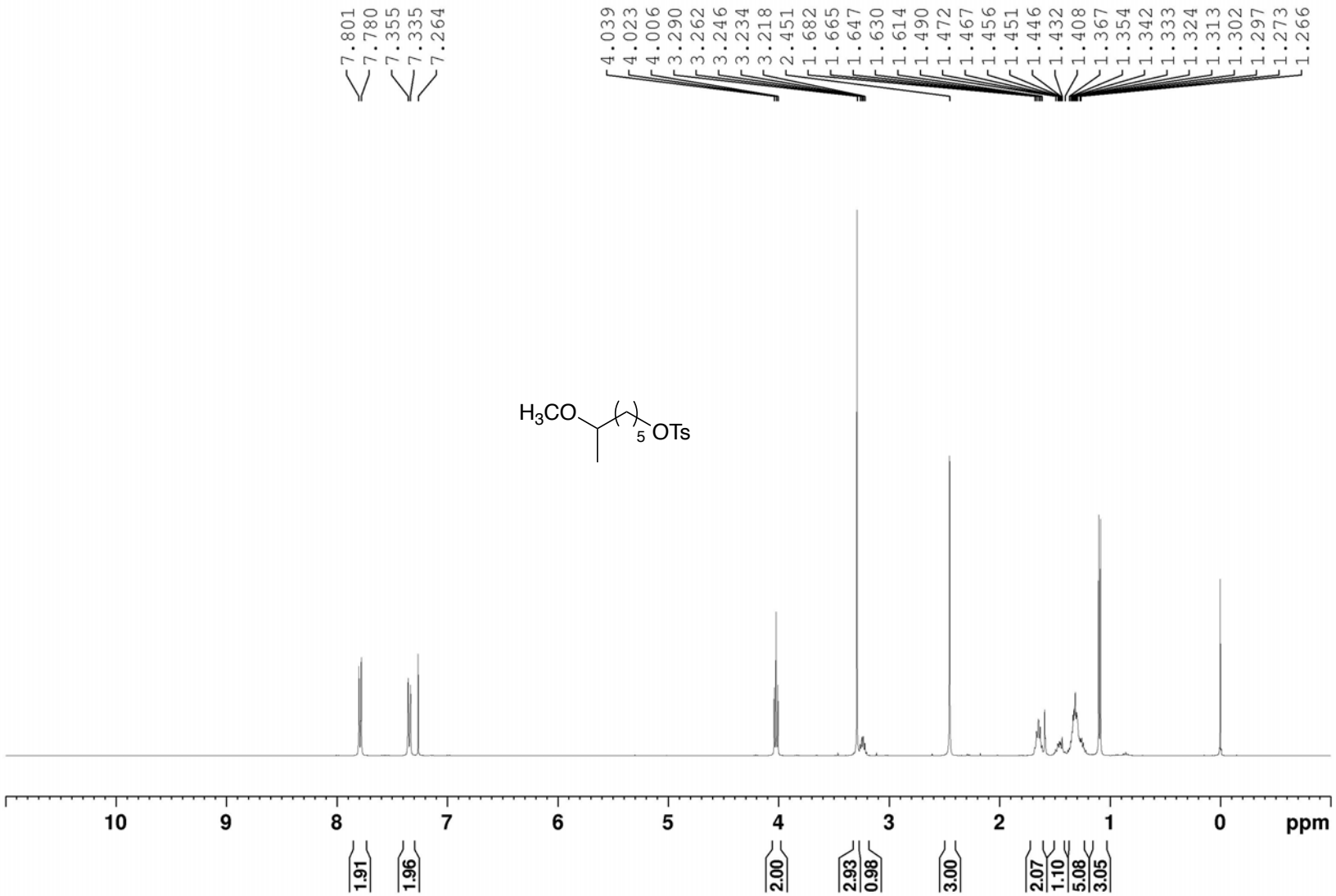

$^{13}$C NMR spectrum of **2l**



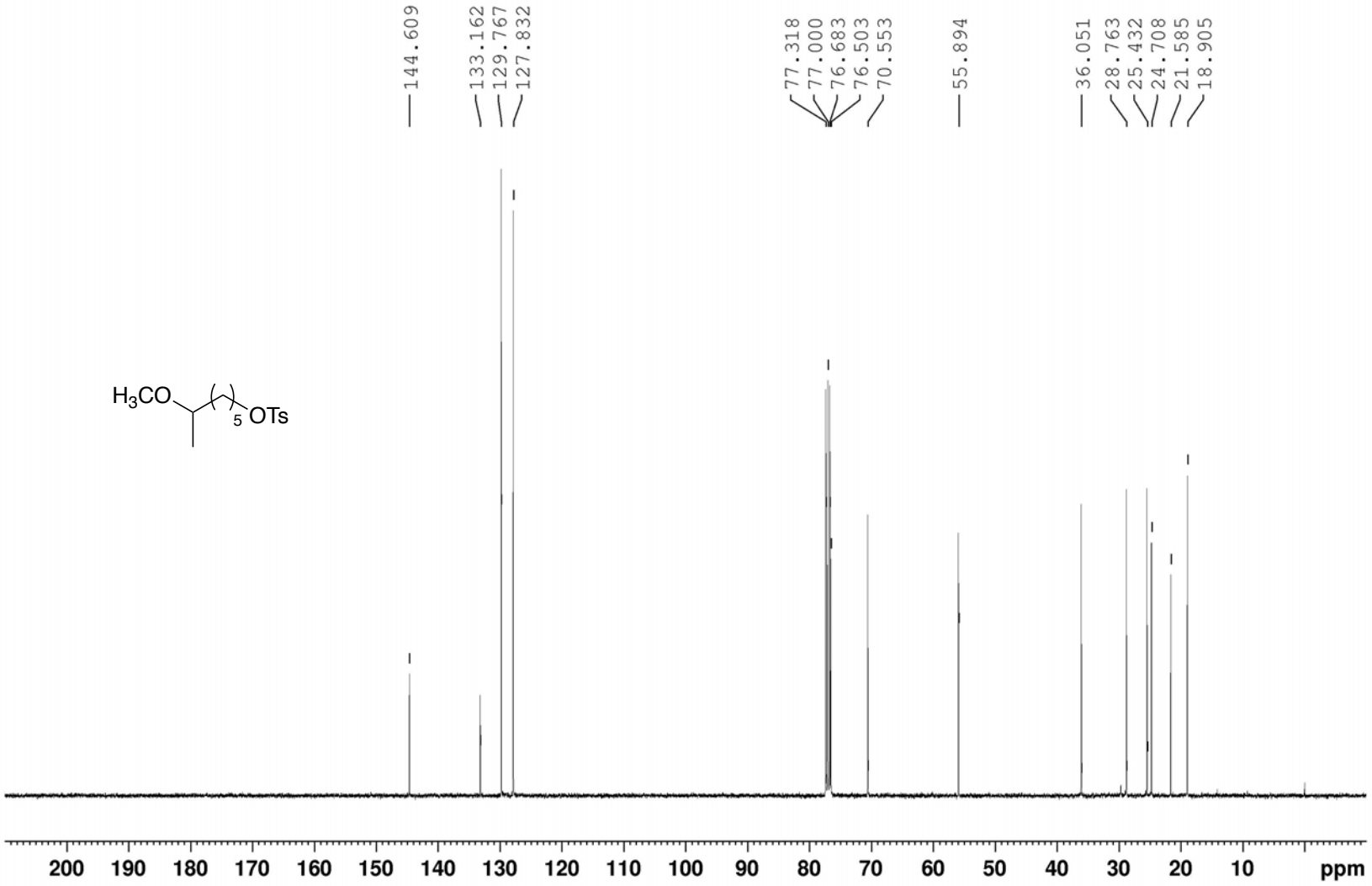

$^{1}$H NMR spectrum of **3aa**



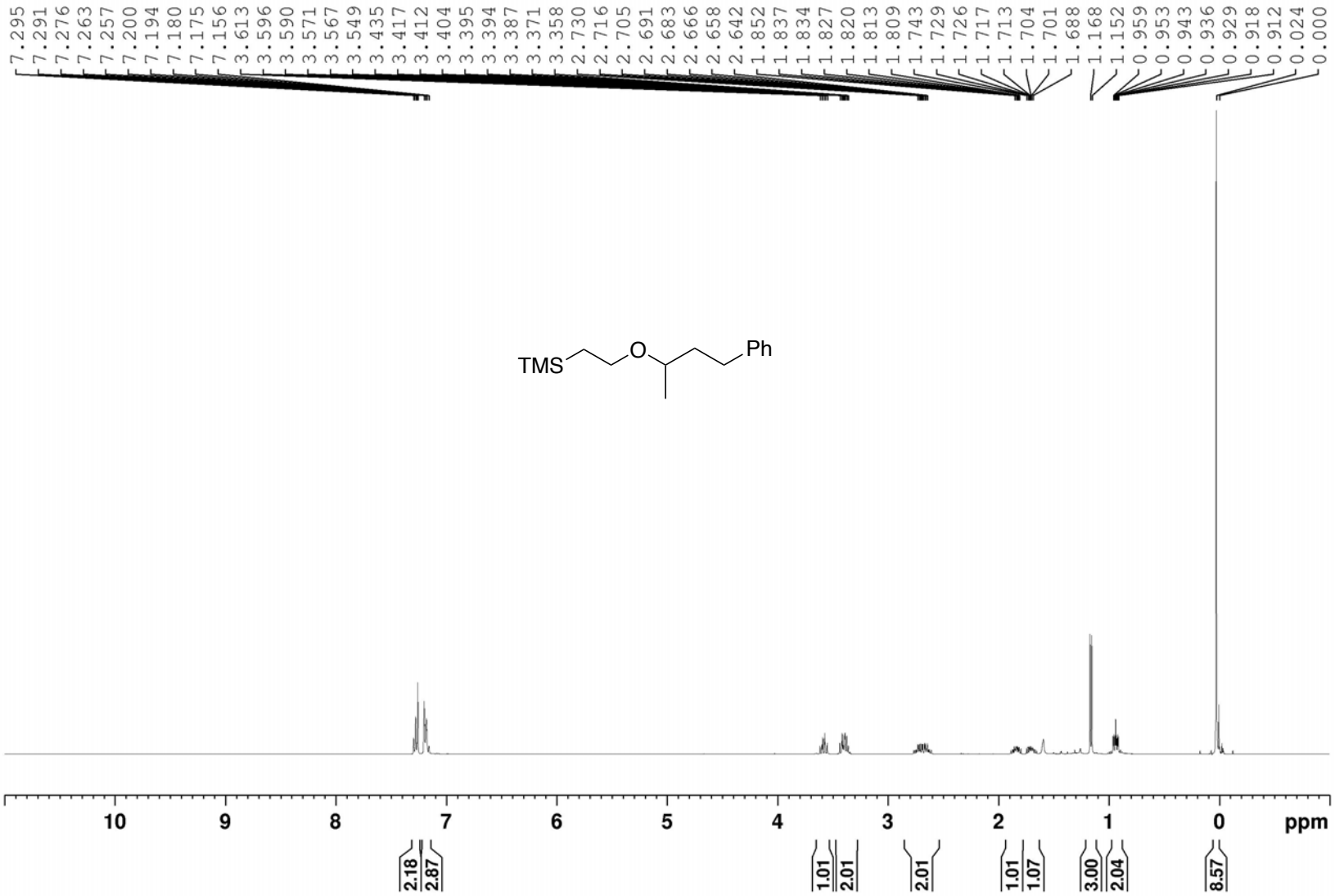

$^{13}$C NMR spectrum of **3aa**




$^{1}$H NMR spectrum of **3bb**




$^{13}$C NMR spectrum of **3bb**

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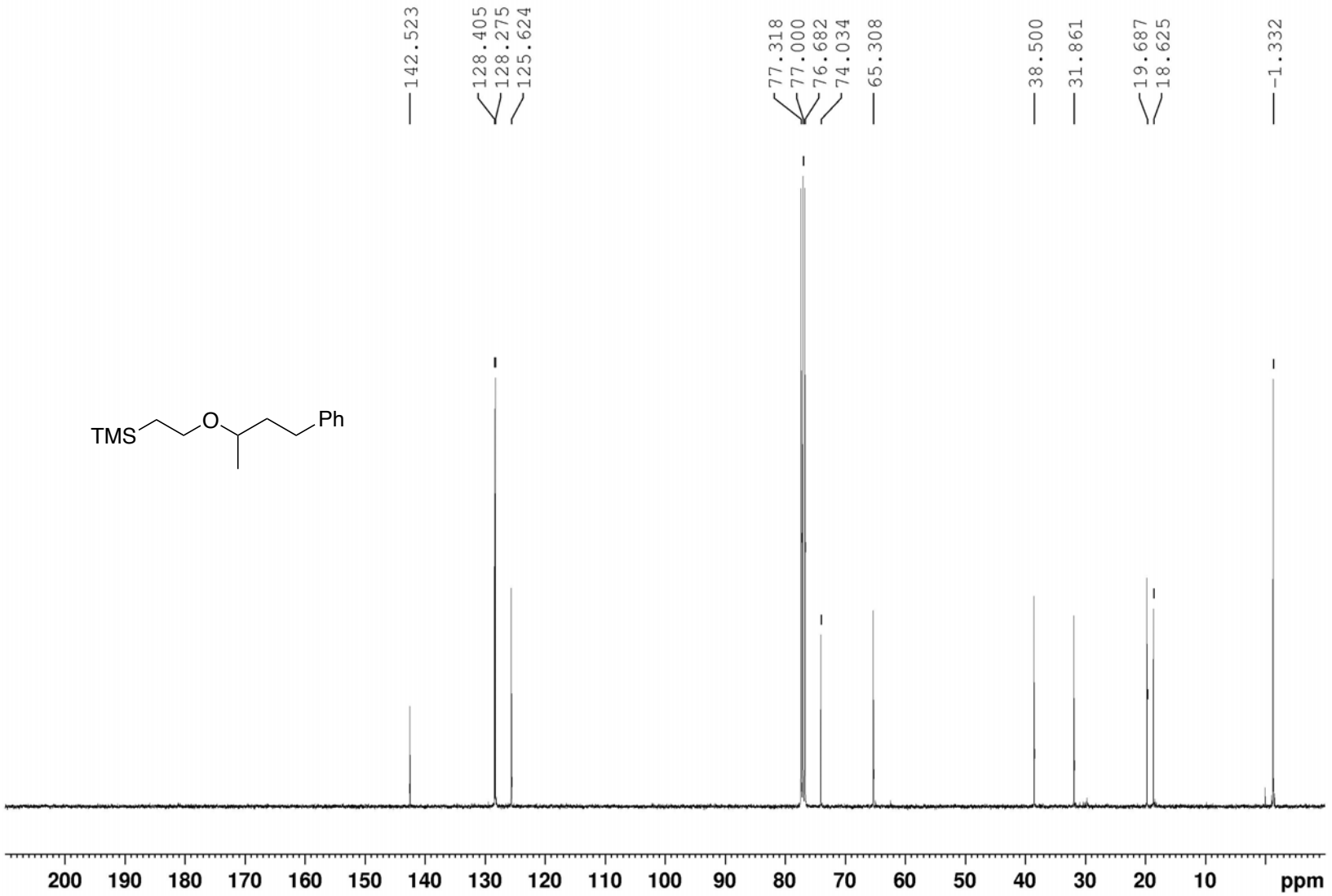
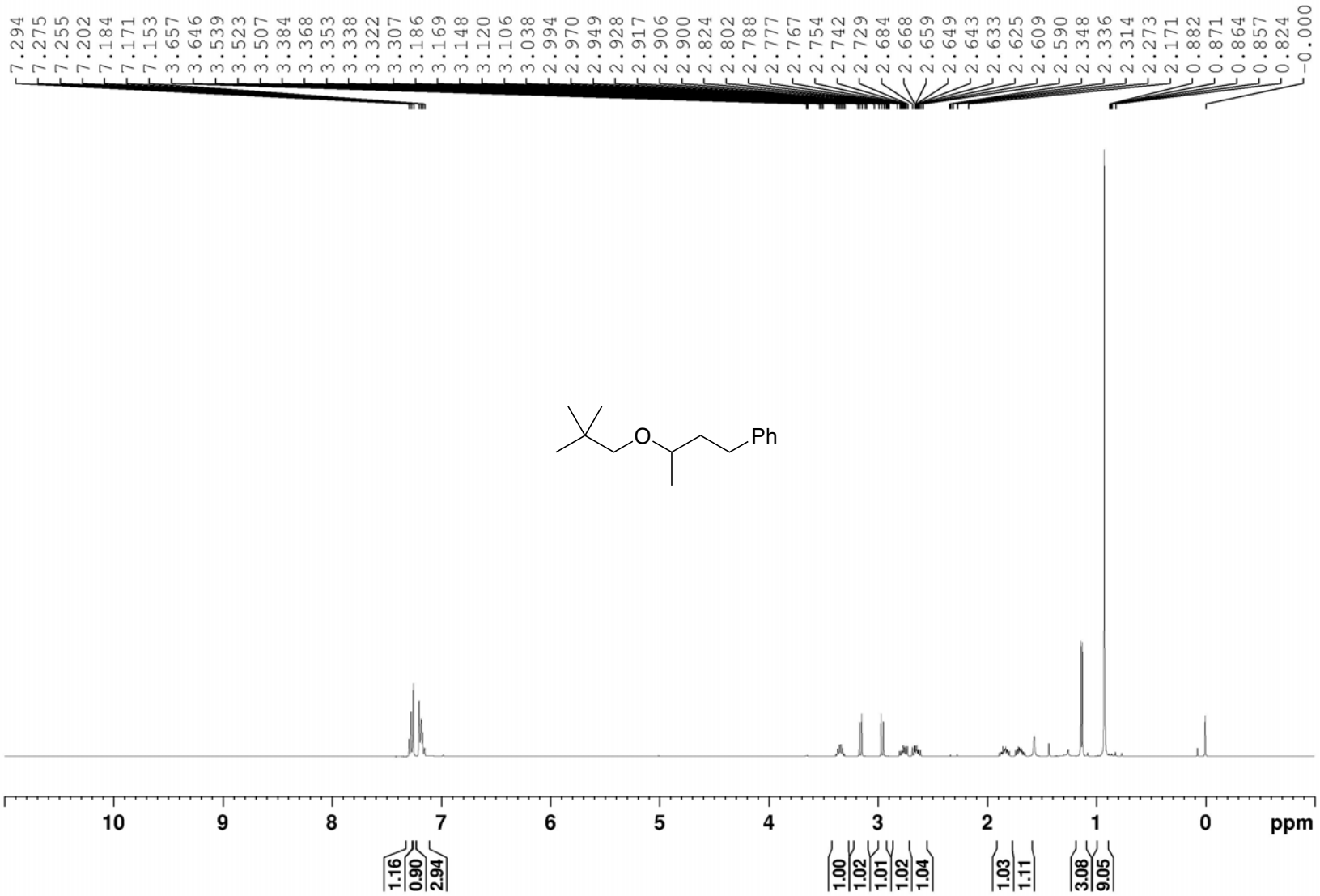



$^{13}$C NMR spectrum of **3ca**

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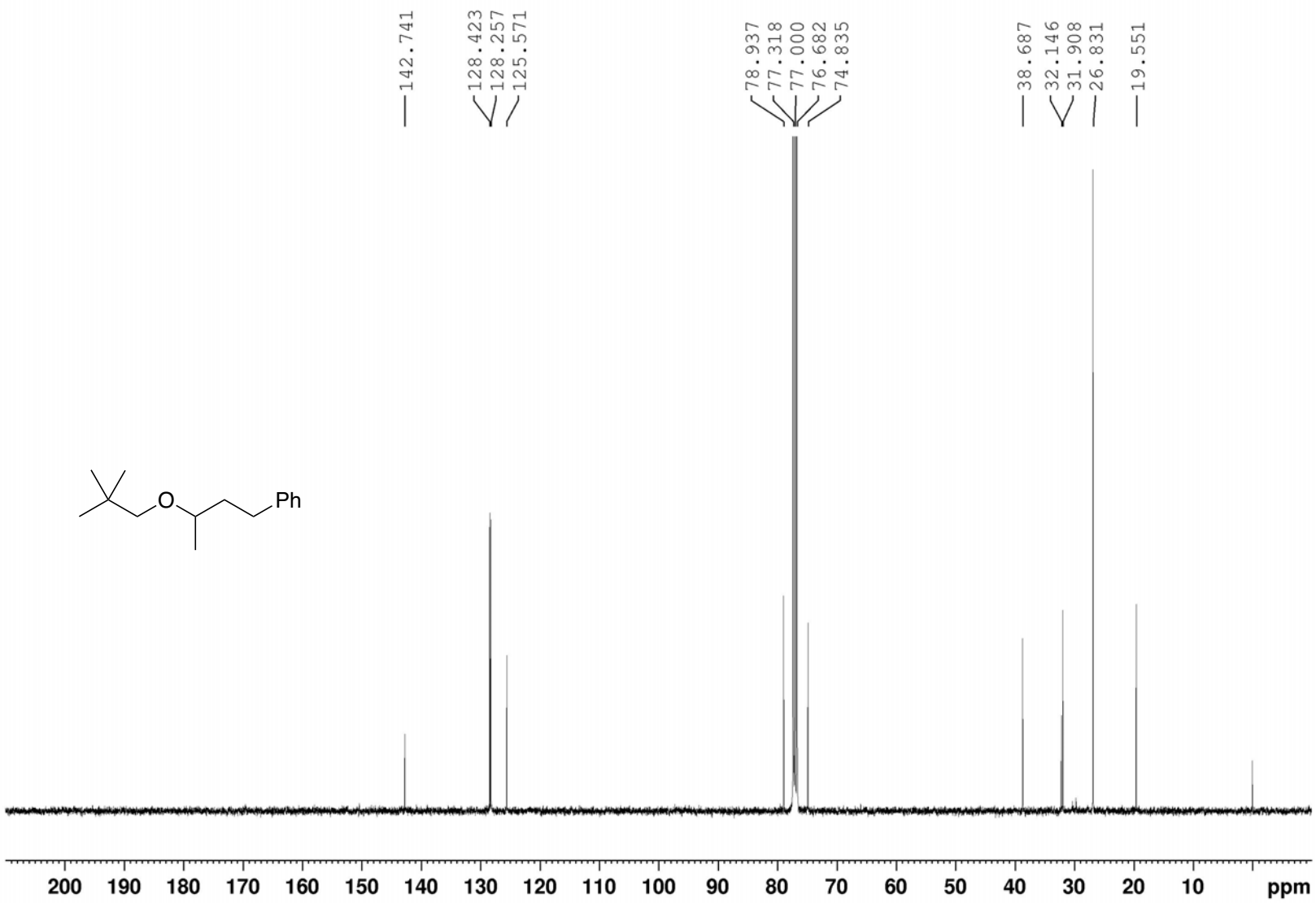
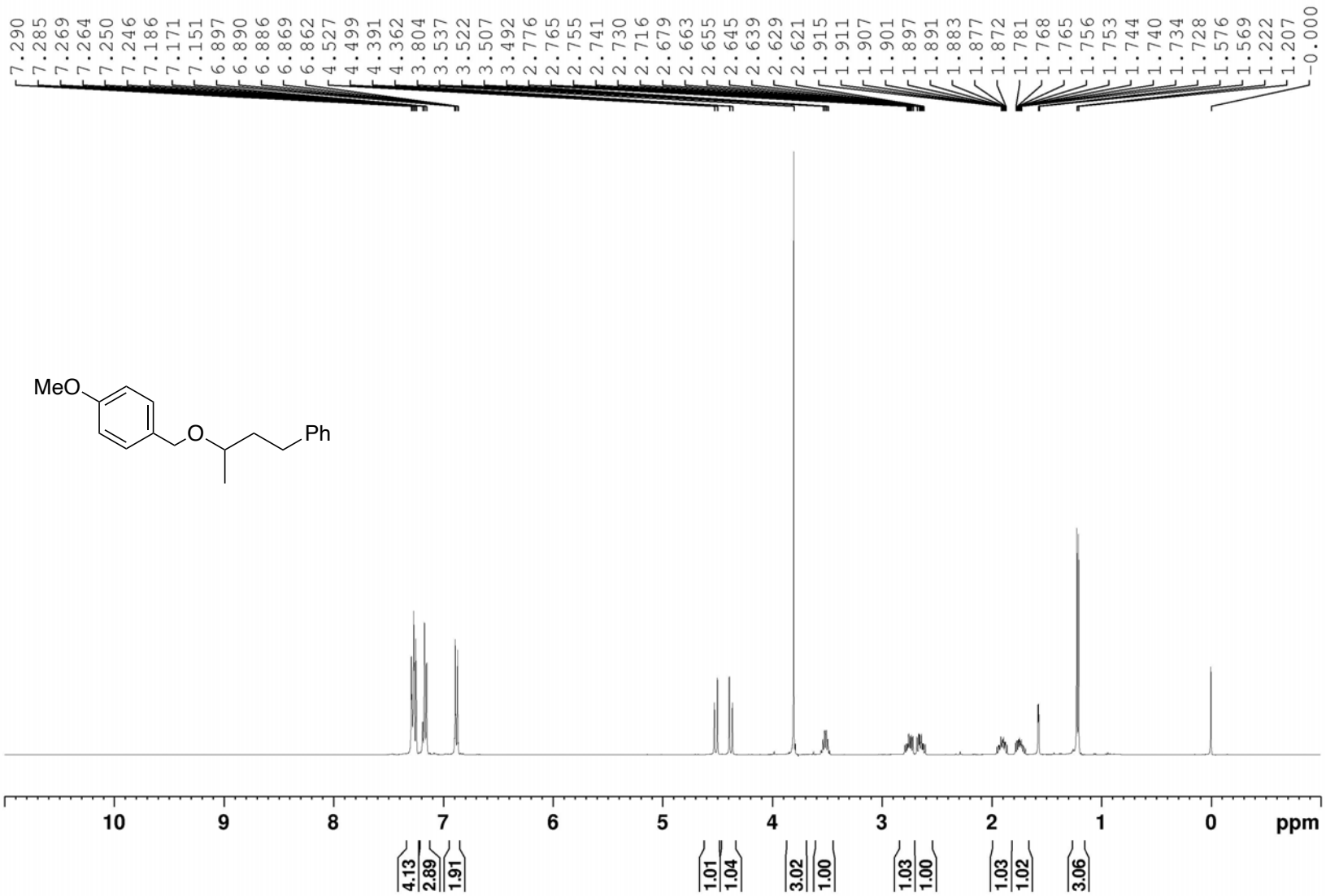



$^{13}$C NMR spectrum of **3da**

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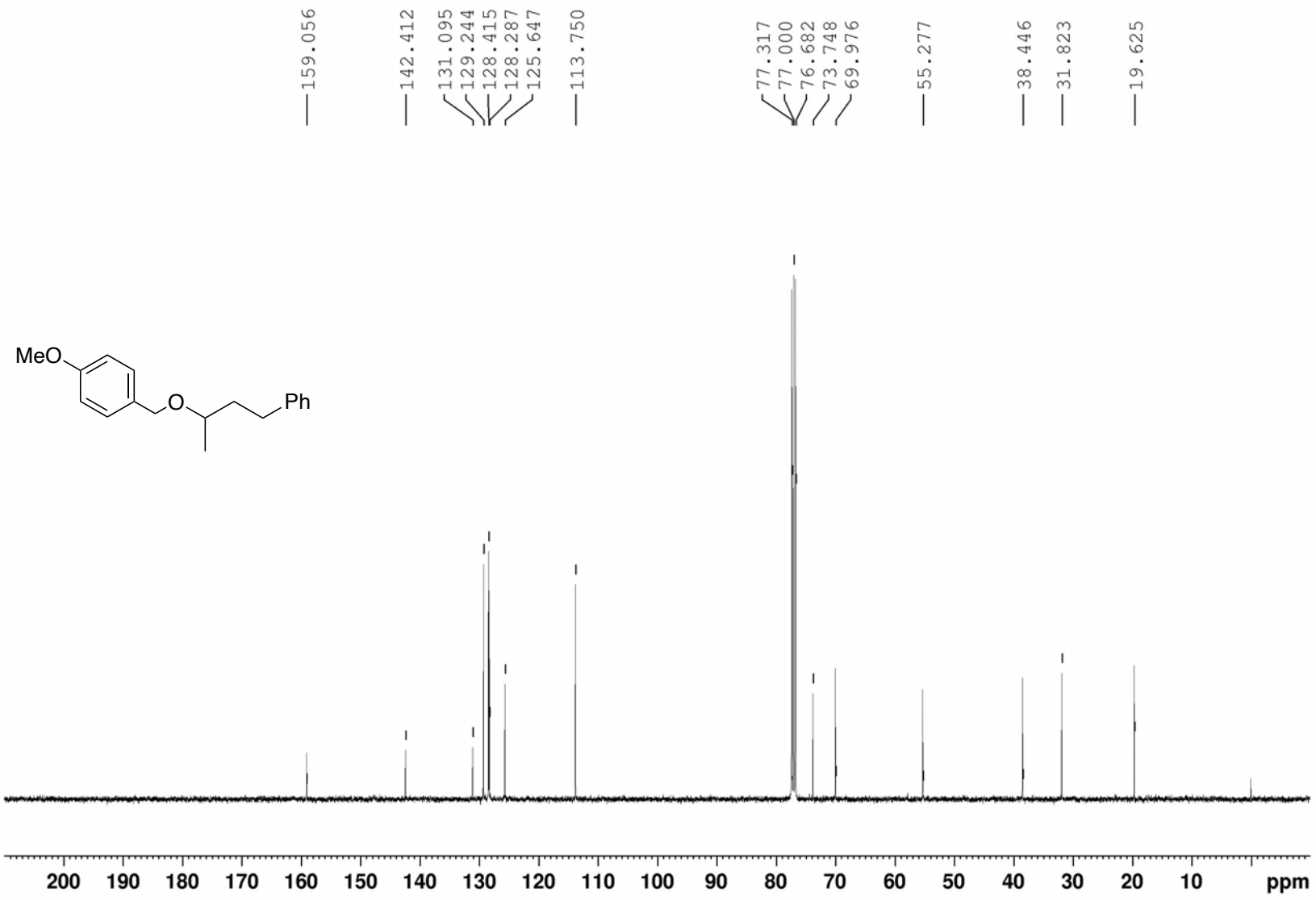


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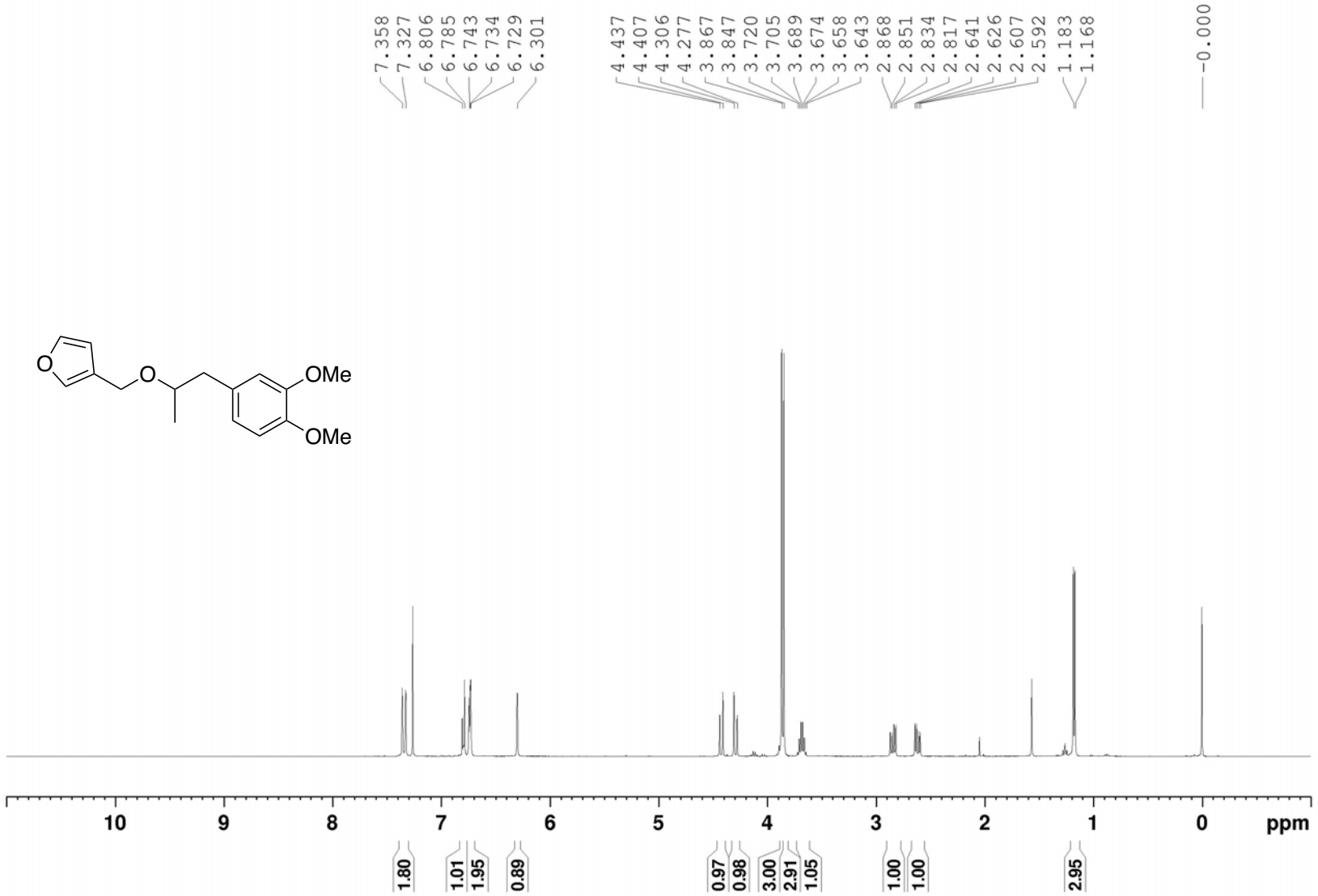


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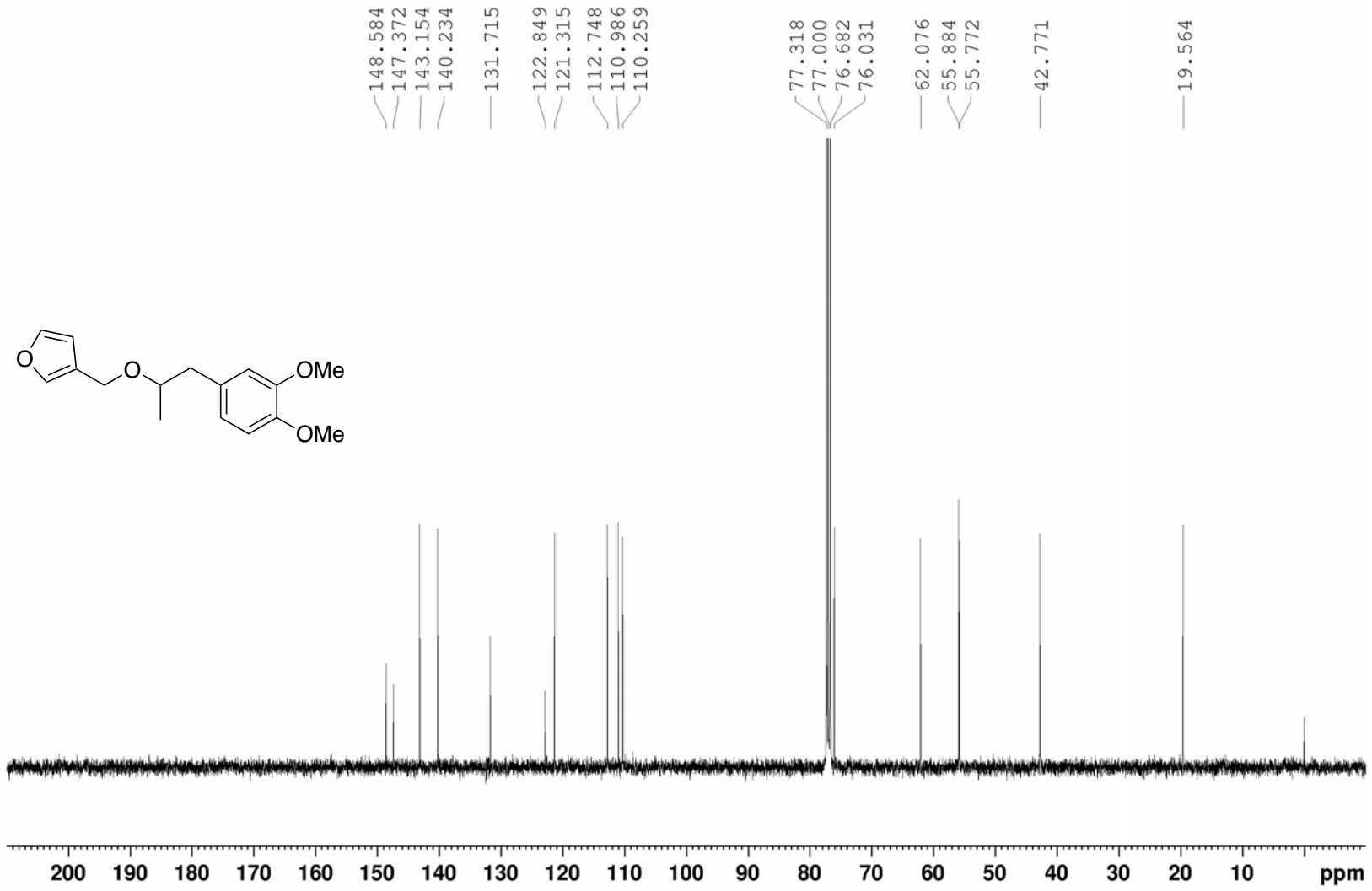
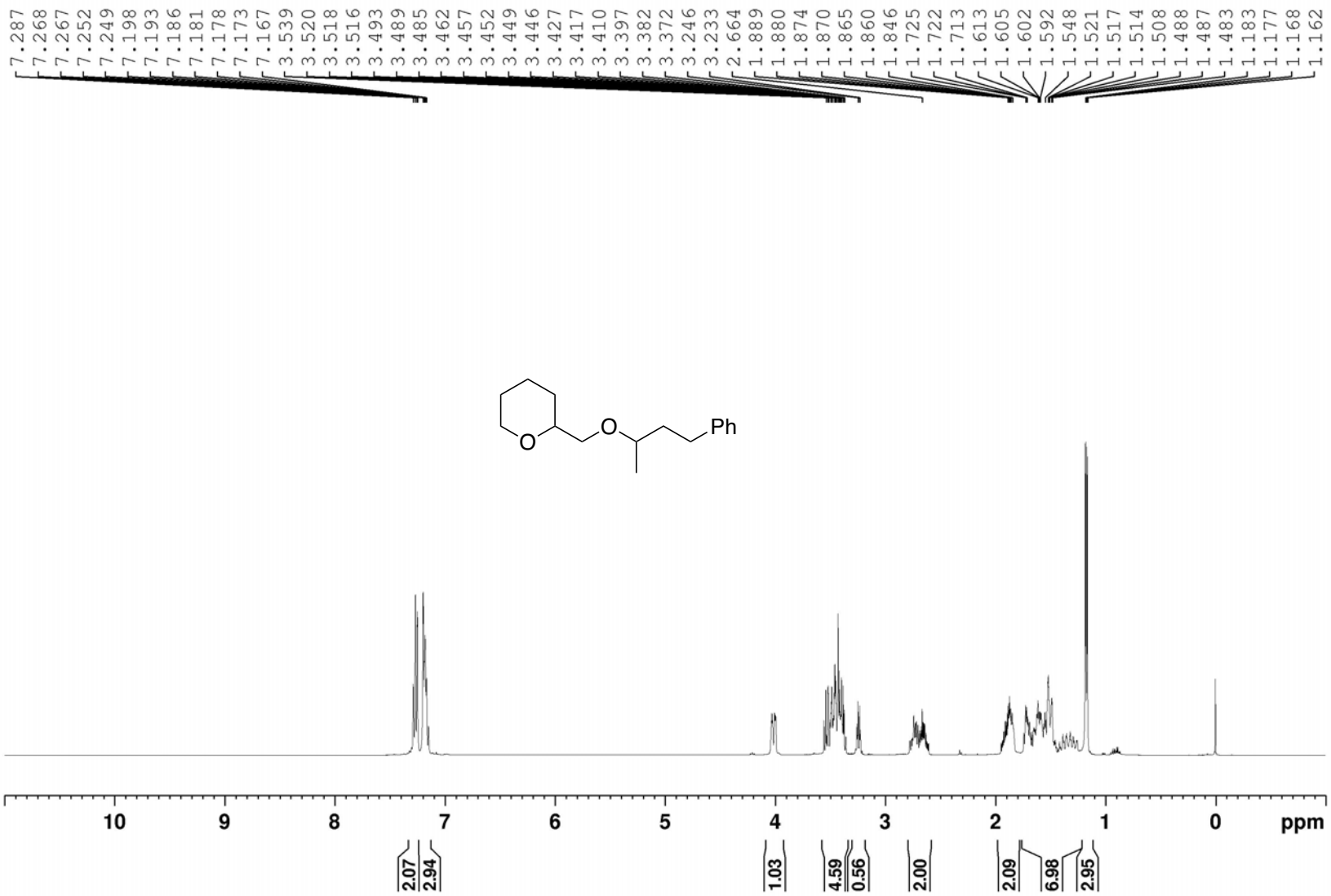



$^{13}$C NMR spectrum of **3fc**

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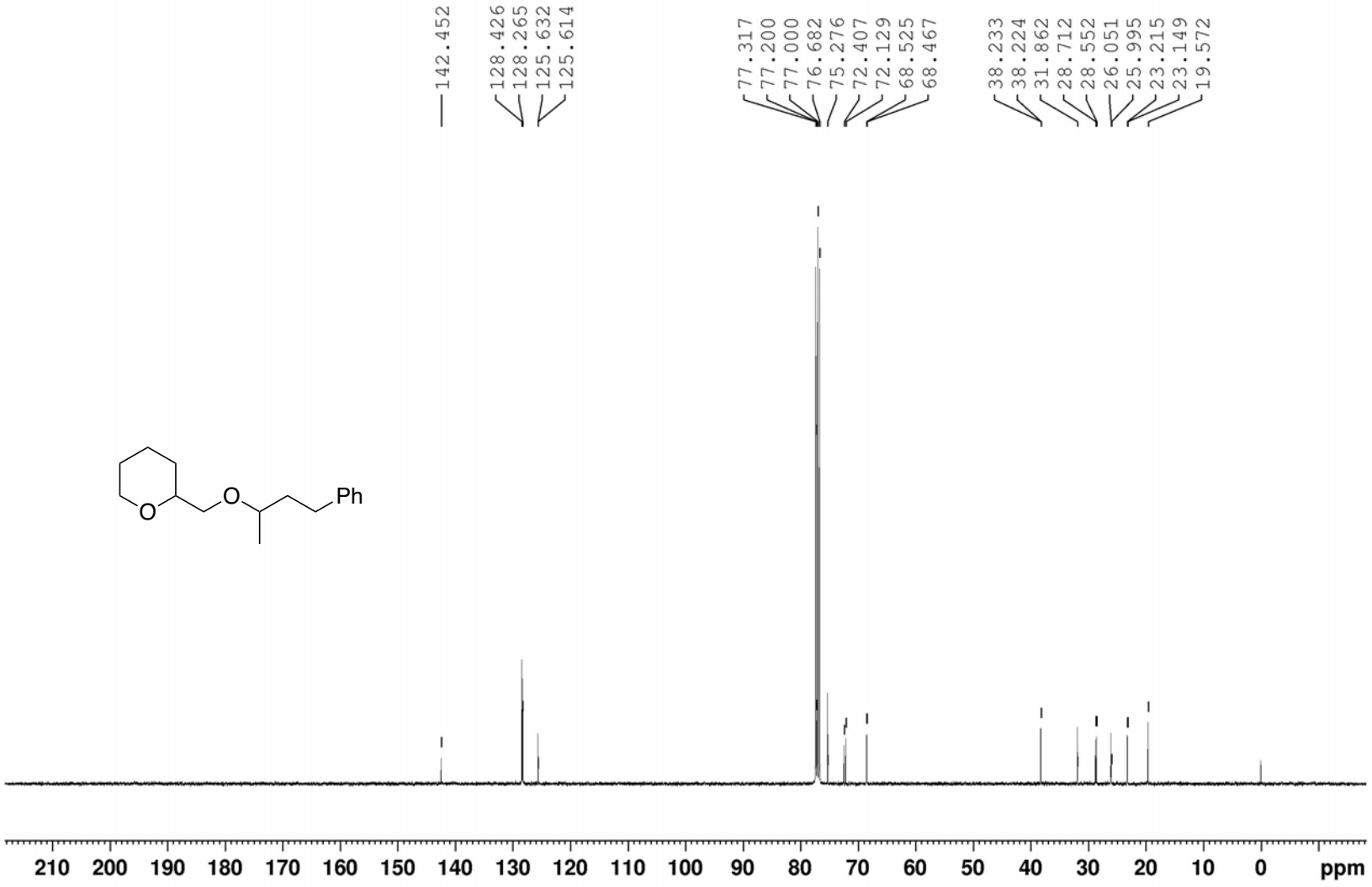
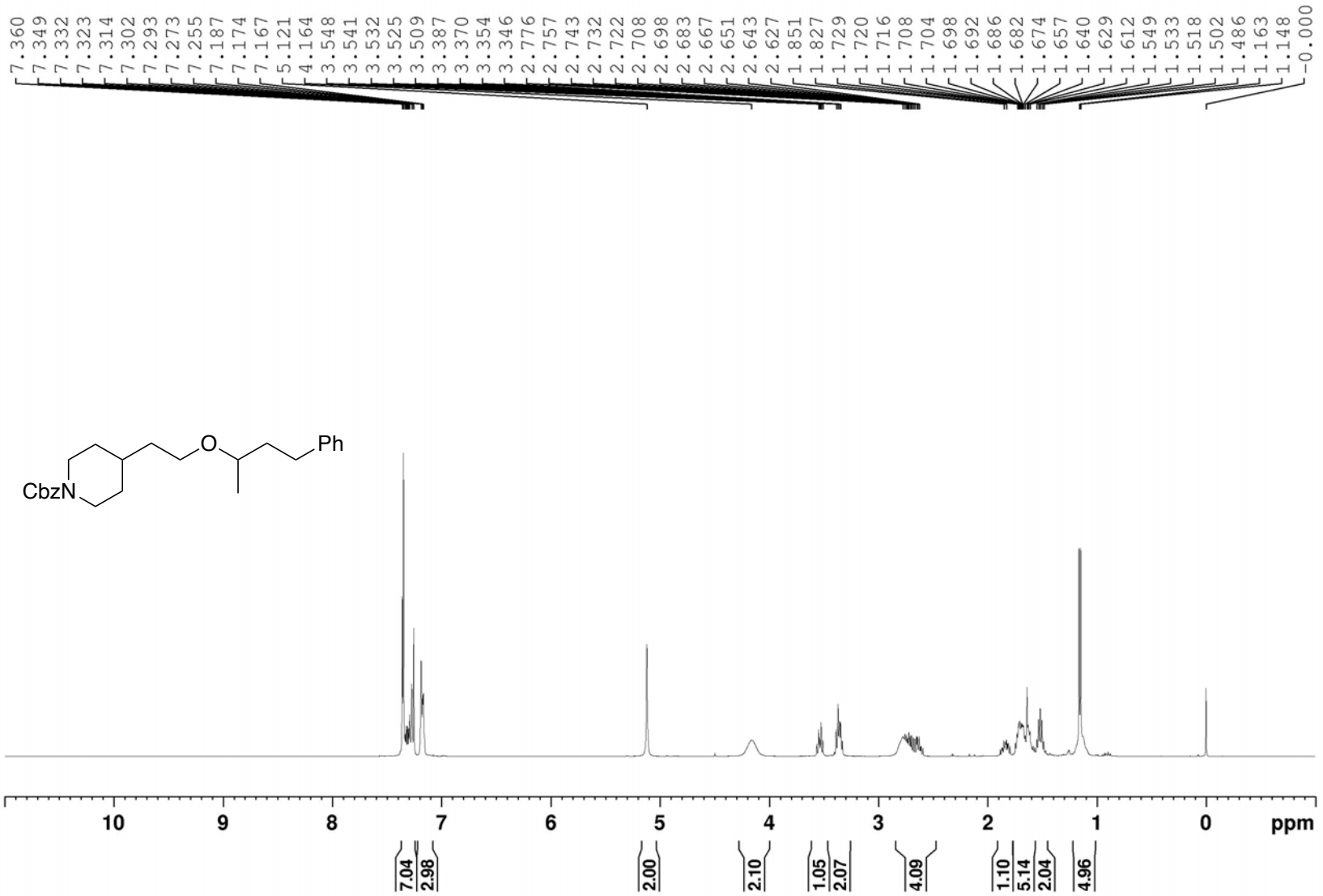
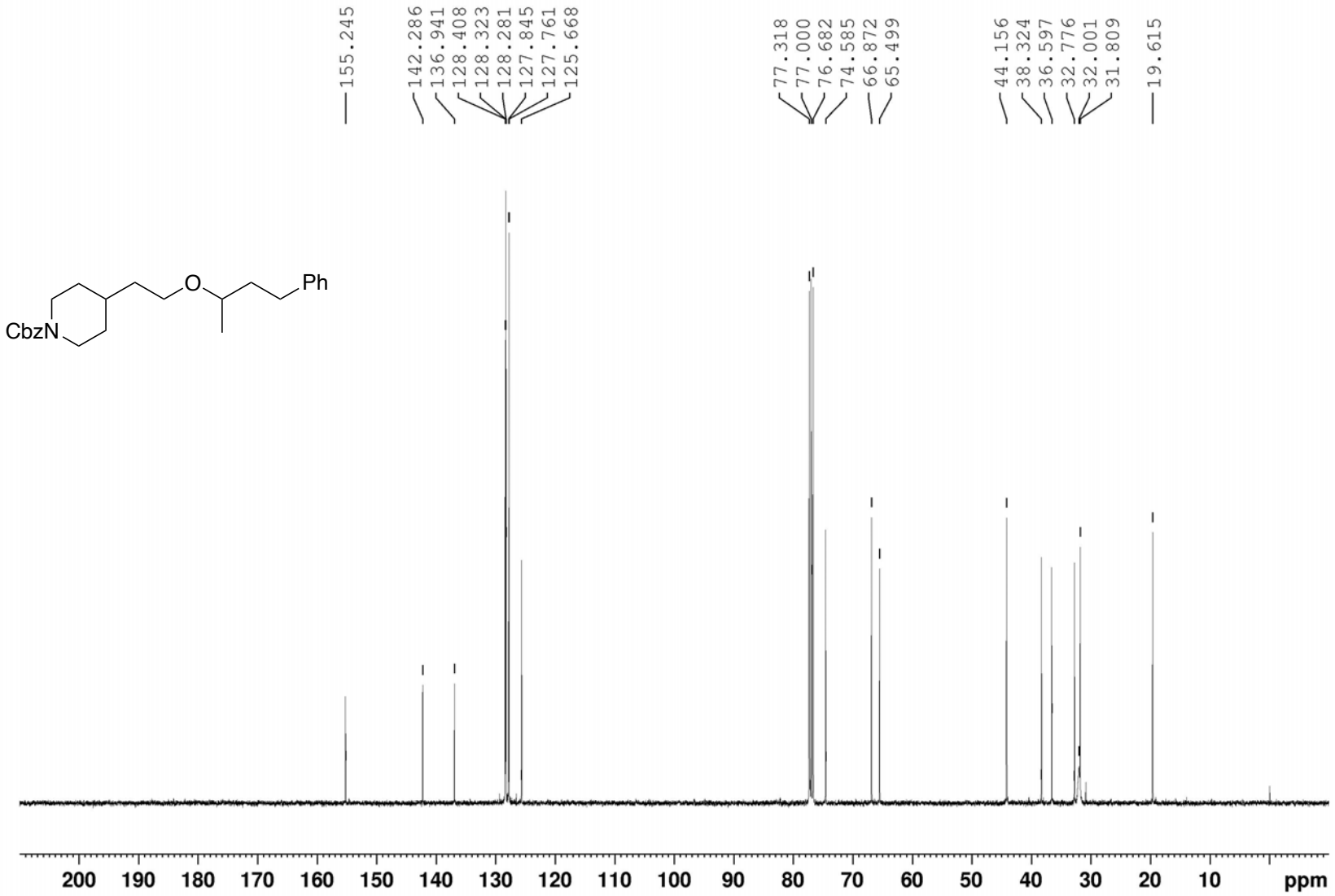


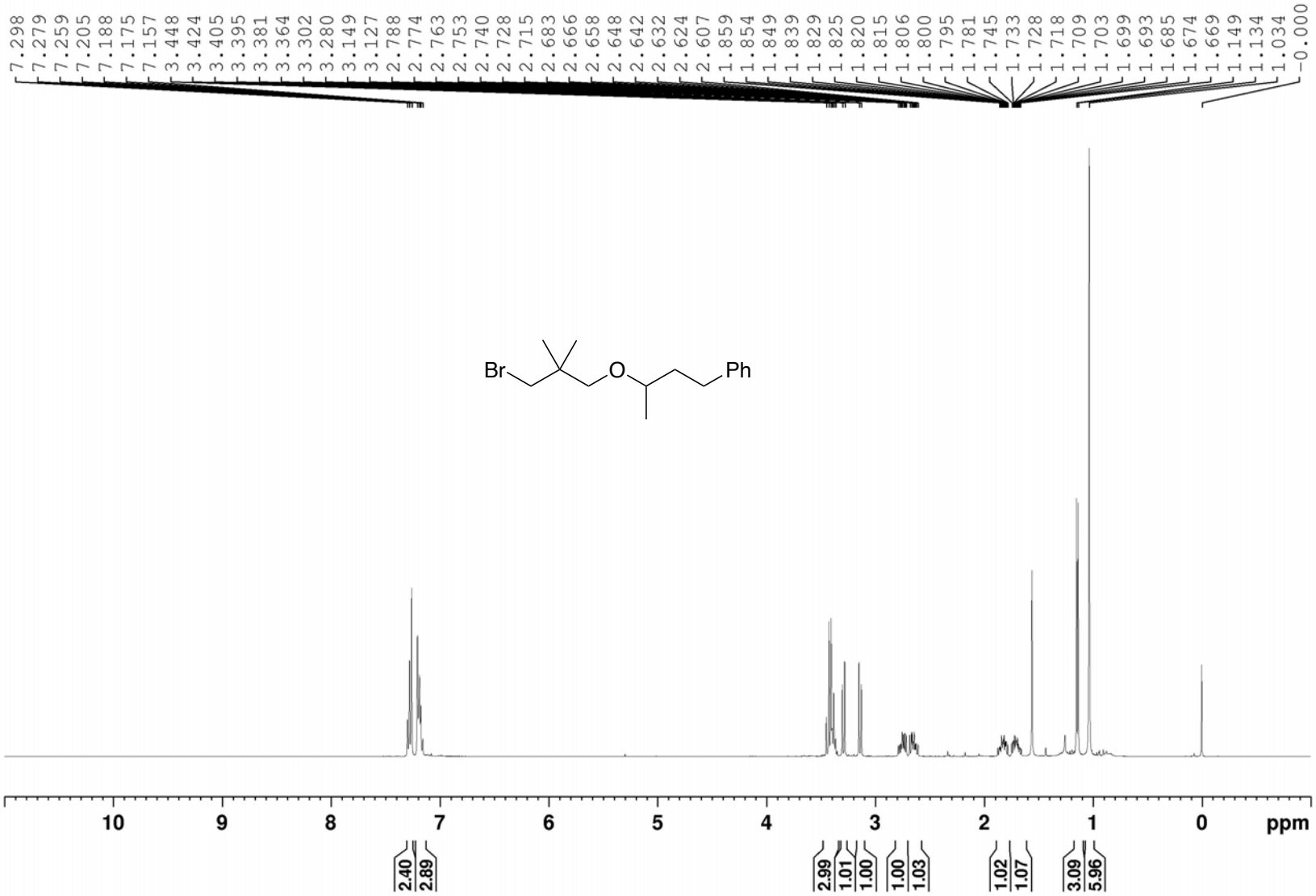

$^{13}$C NMR spectrum of **3ga**



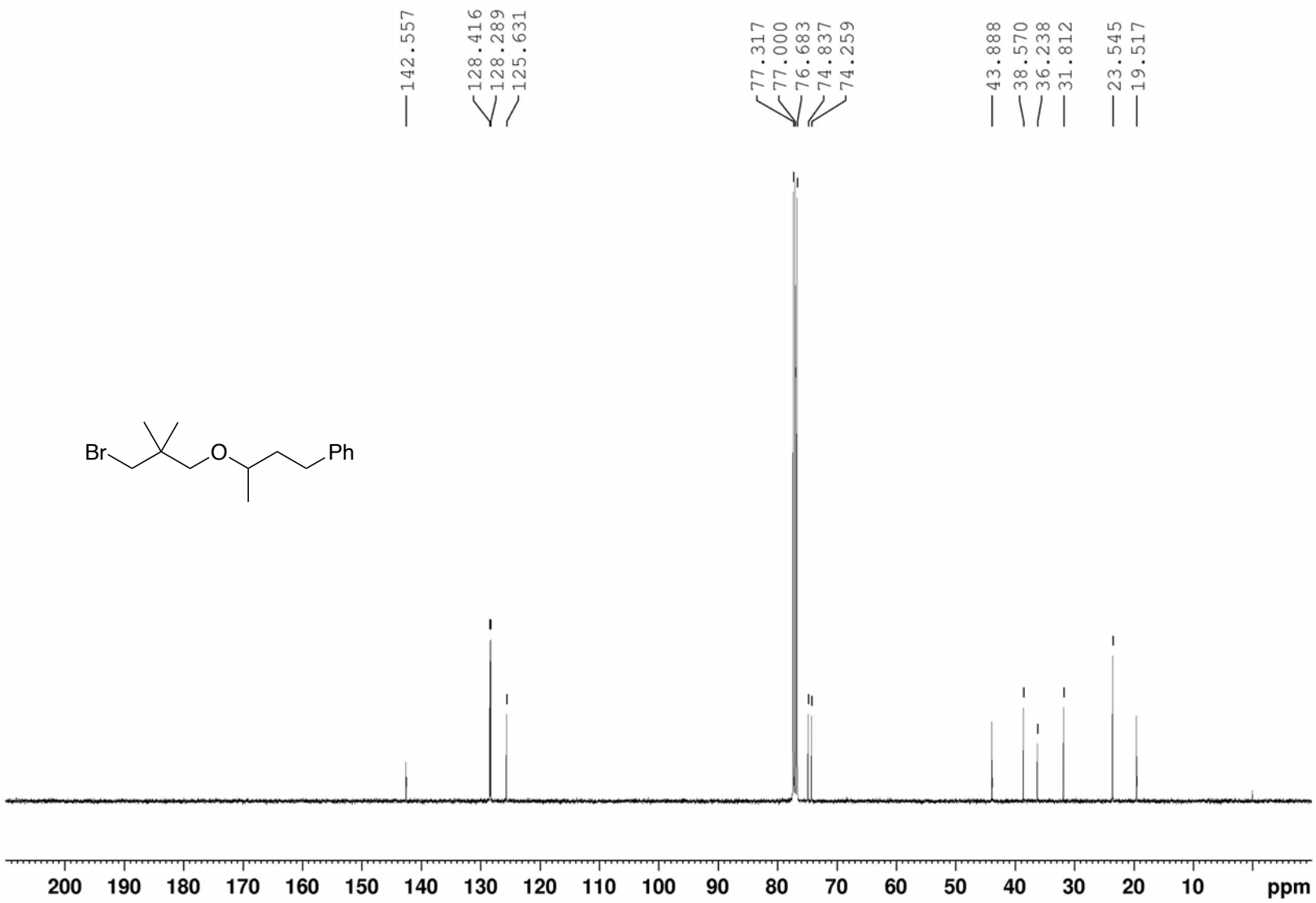

$^{1}$H NMR spectrum of **3ha**



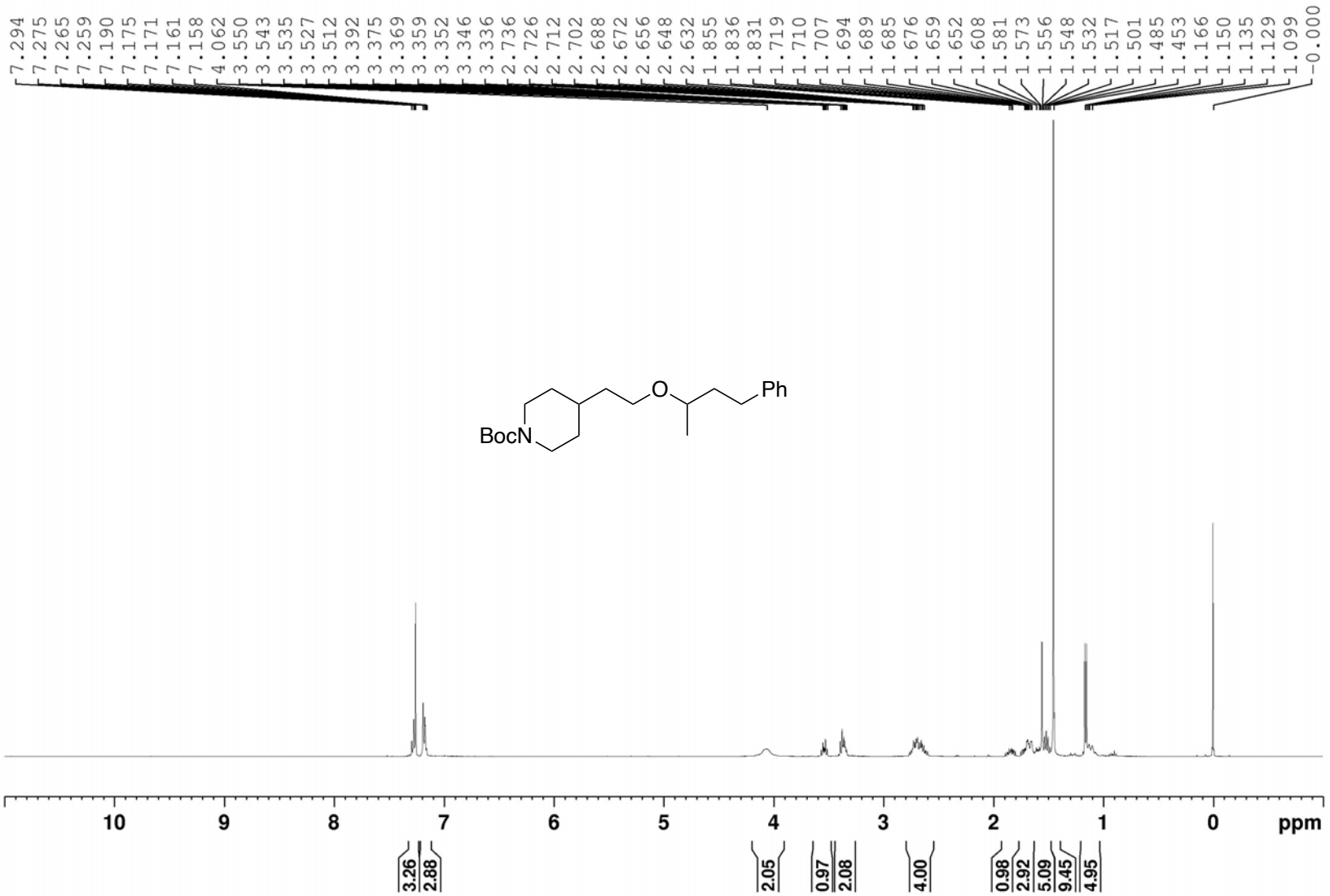

$^{13}$C NMR spectrum of **3ha**




$^{1}$H NMR spectrum of **3ia**




$^{13}$C NMR spectrum of **3ia**

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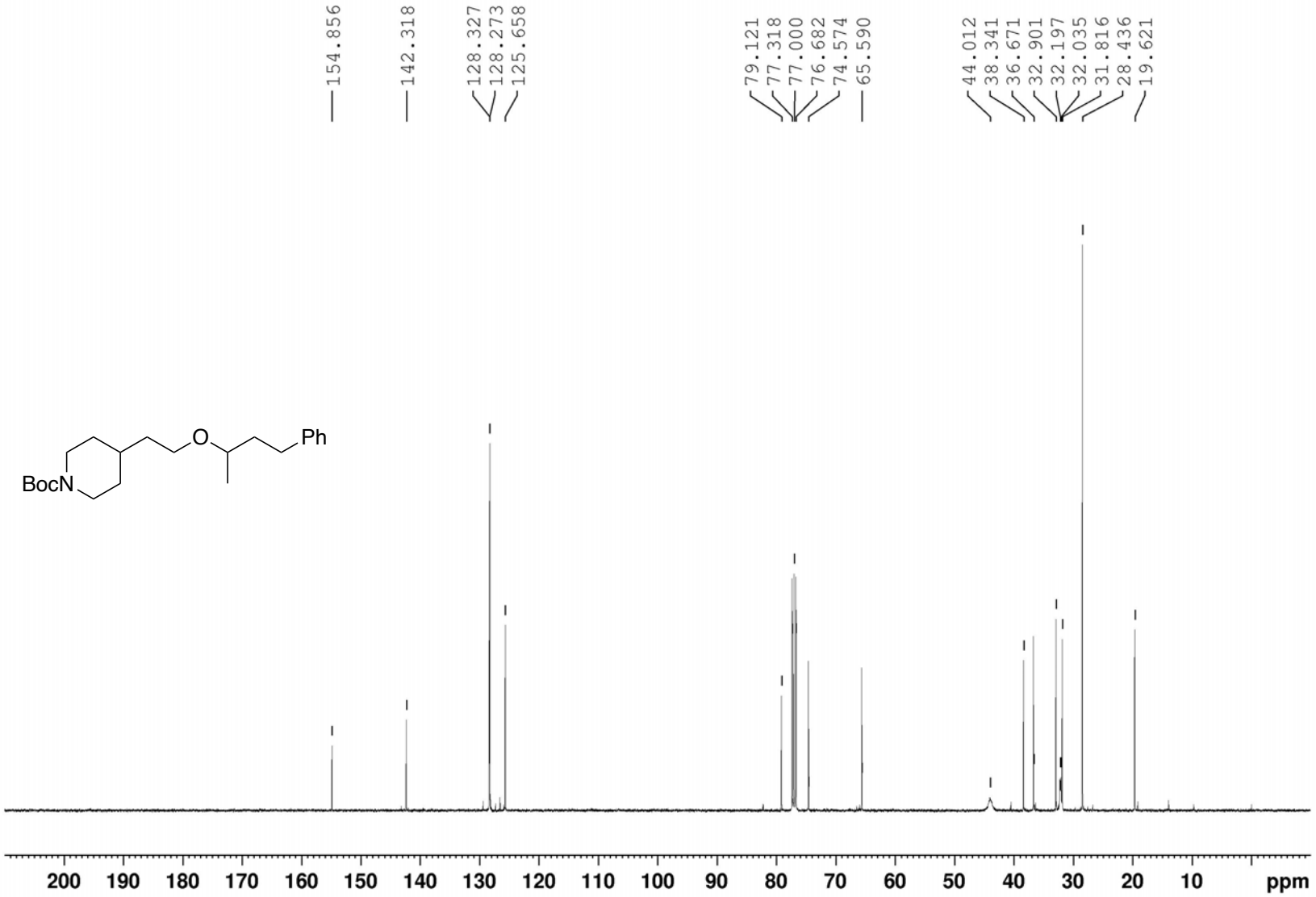
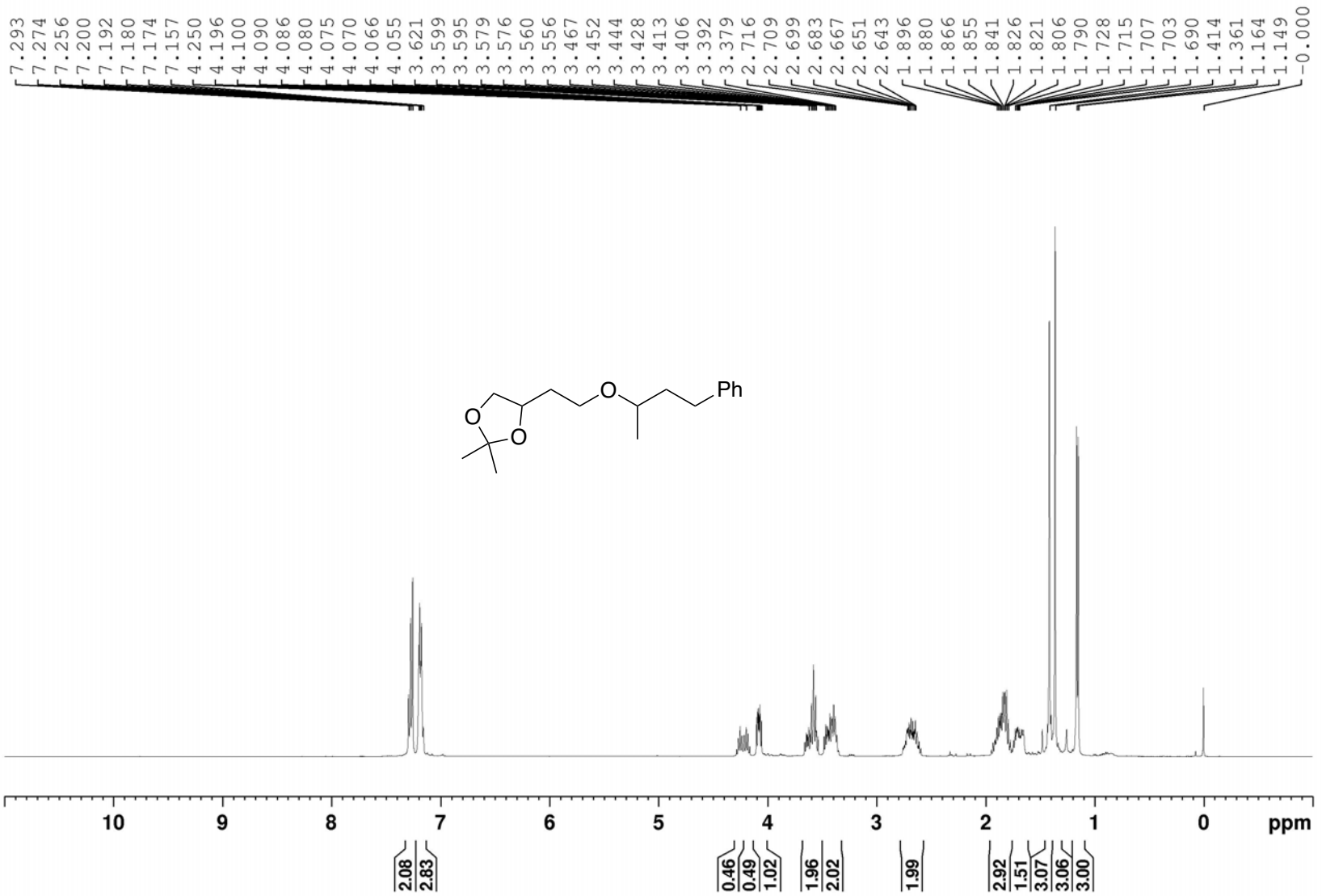



$^{13}$C NMR spectrum of **3ja**

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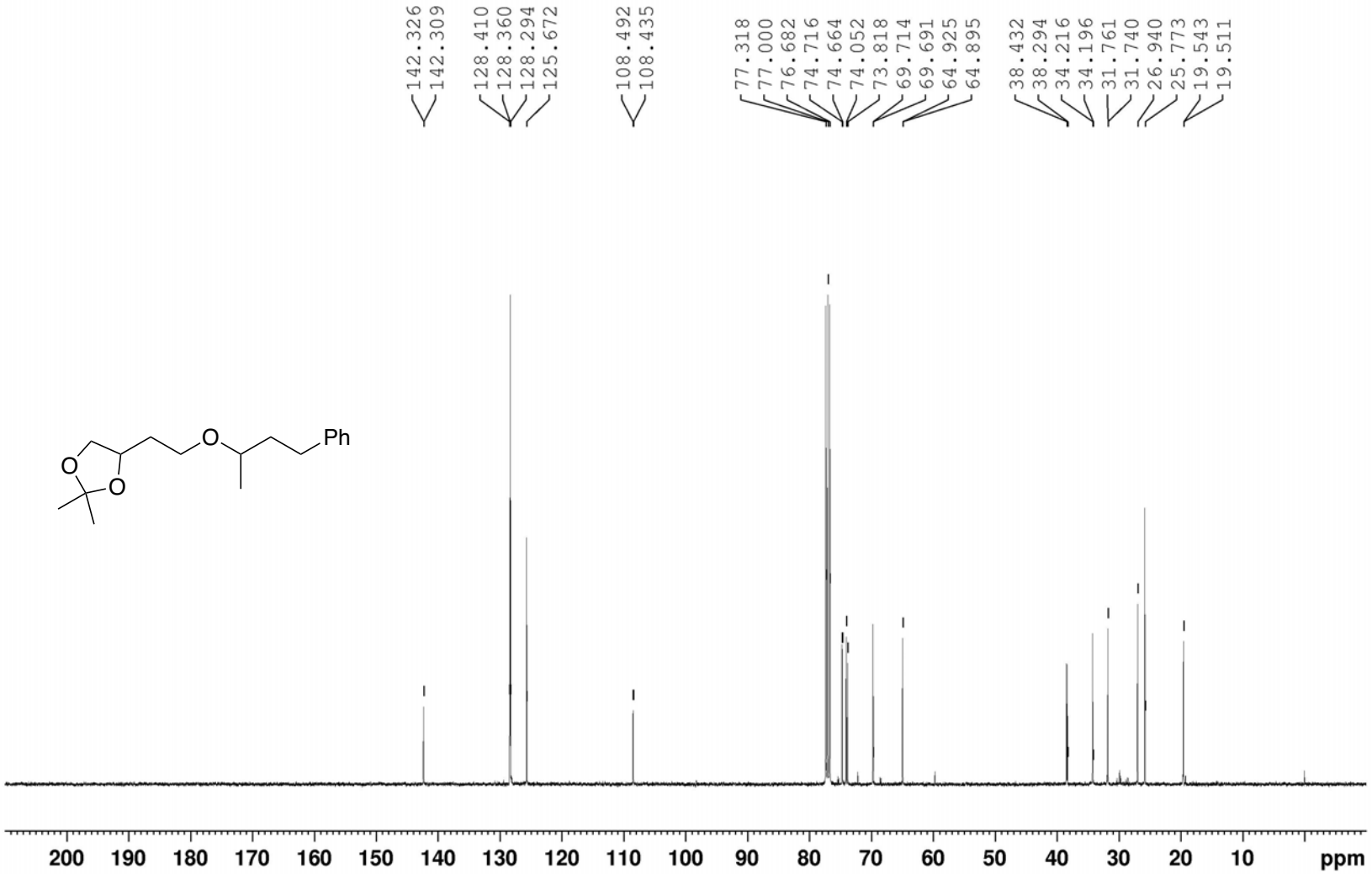


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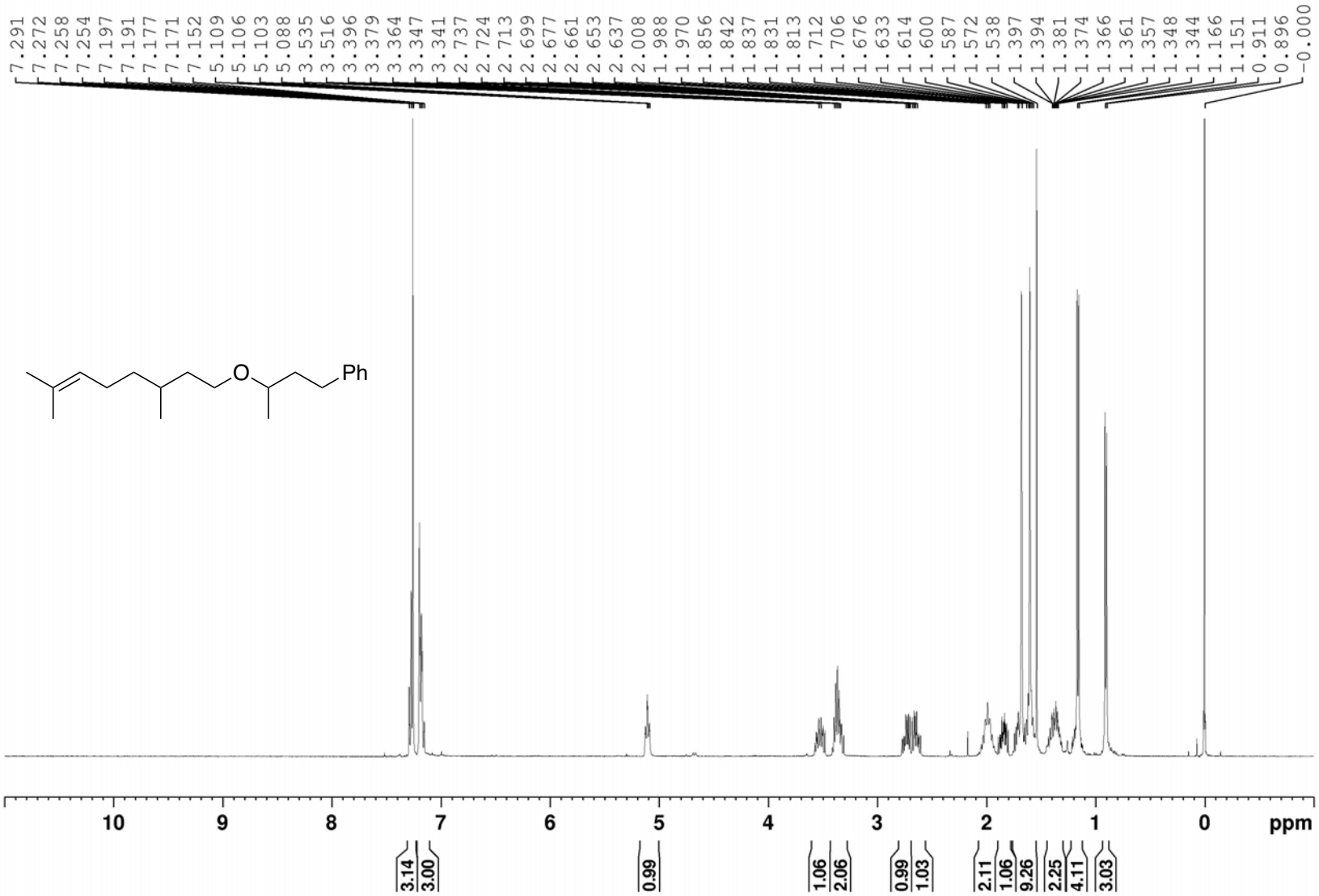
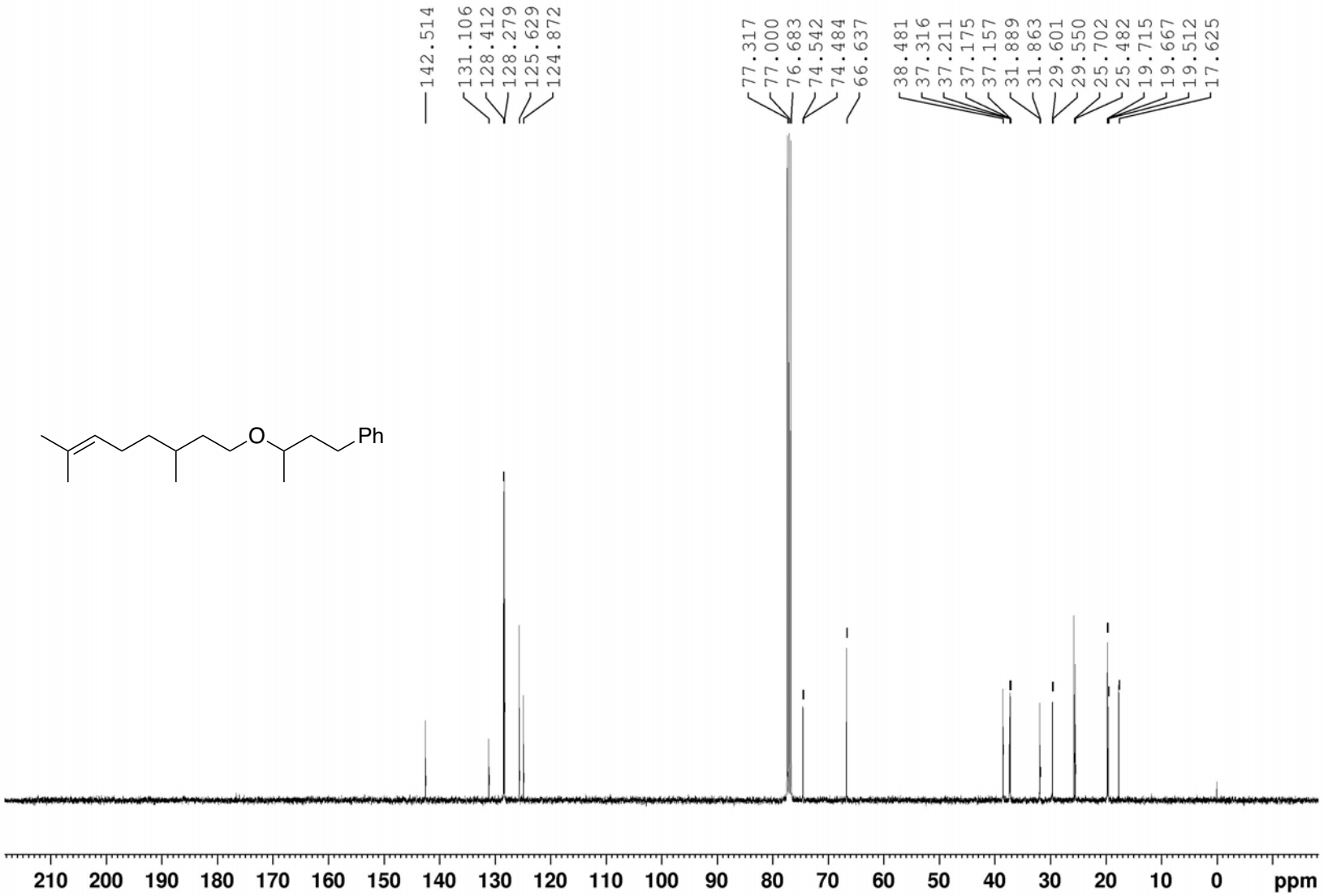
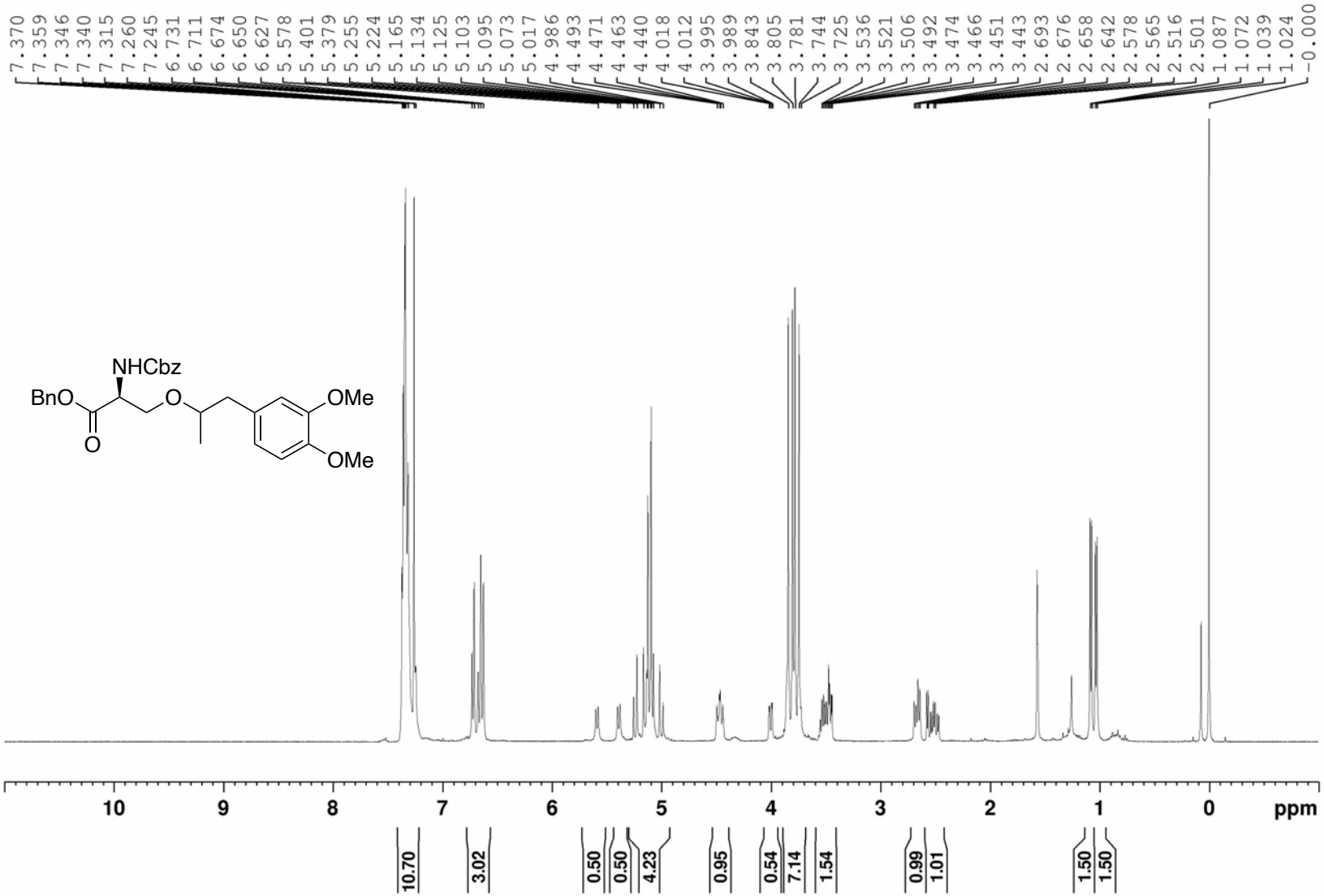


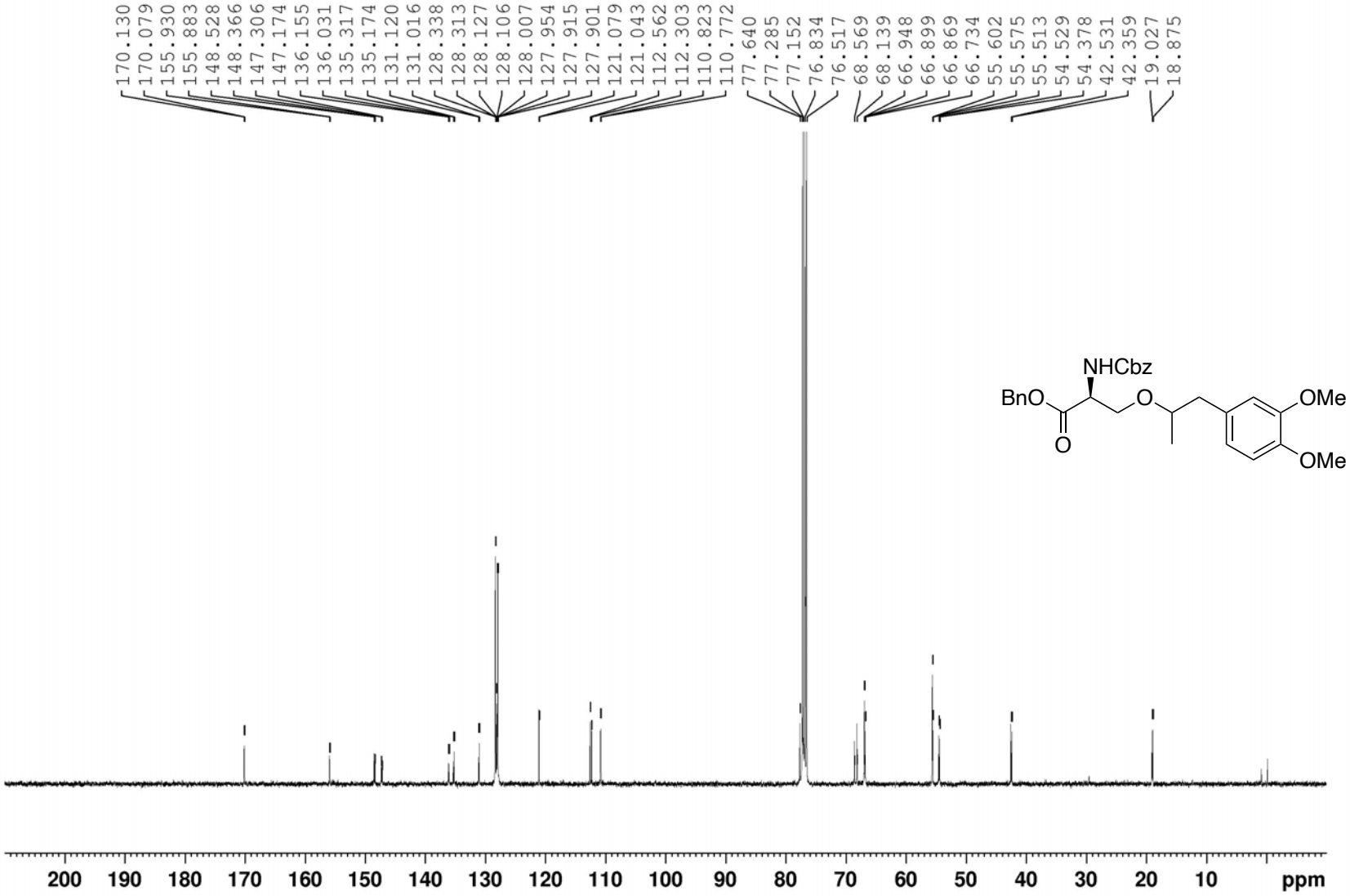

$^{1}$H NMR spectrum of **3la**



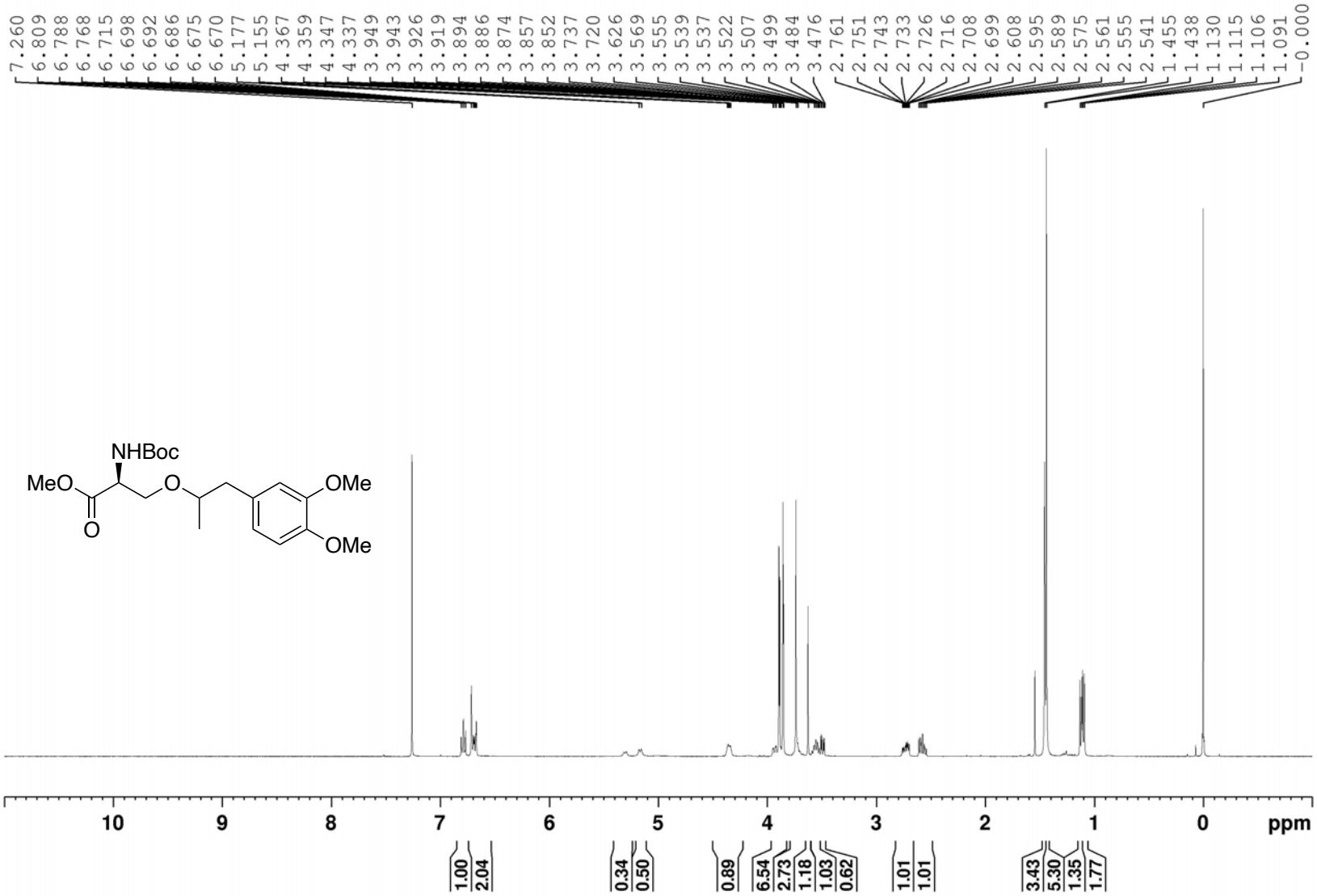

$^{13}$C NMR spectrum of **3la**




$^{1}$H NMR spectrum of **3mc**




$^{13}$C NMR spectrum of **3mc**

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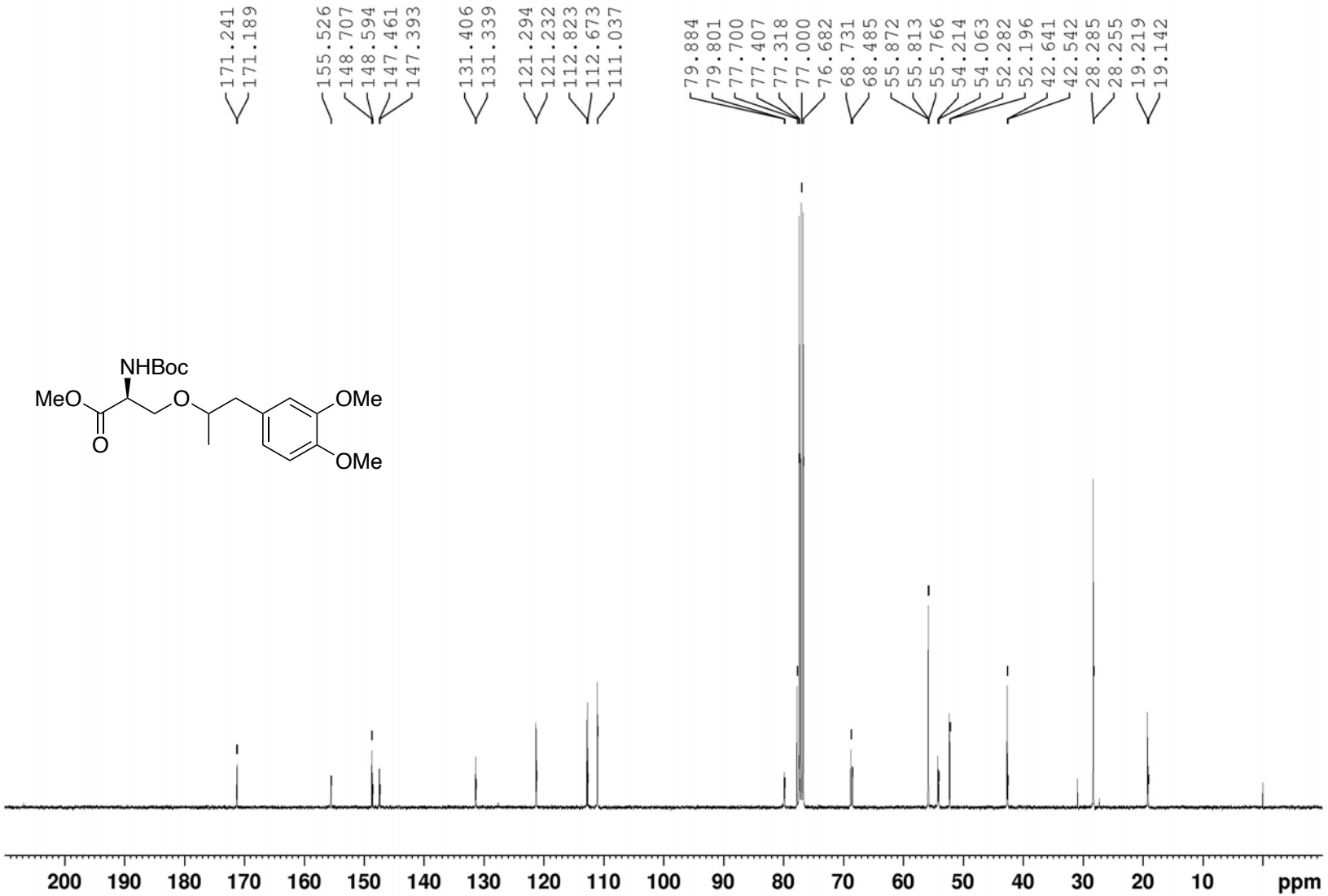


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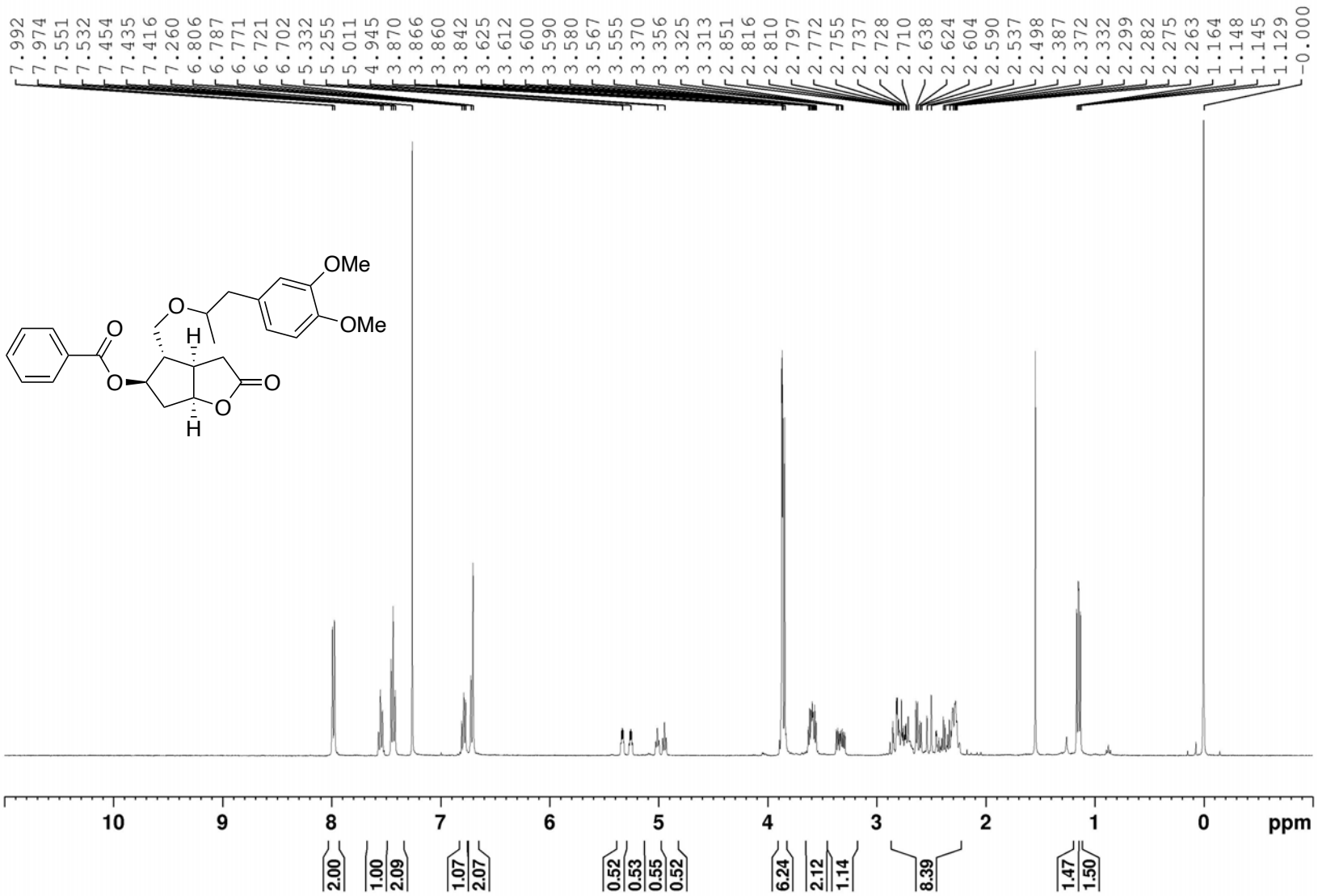


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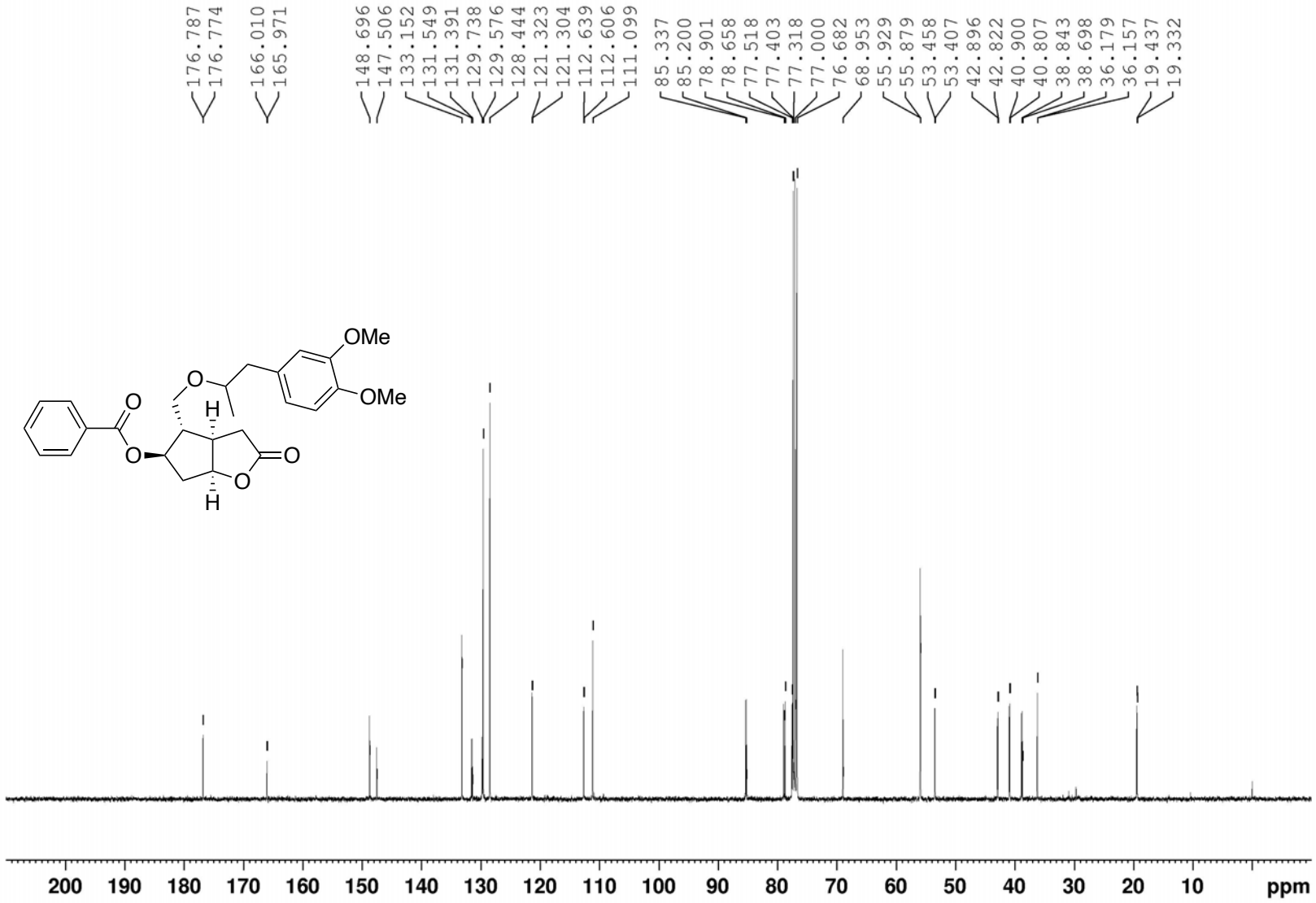
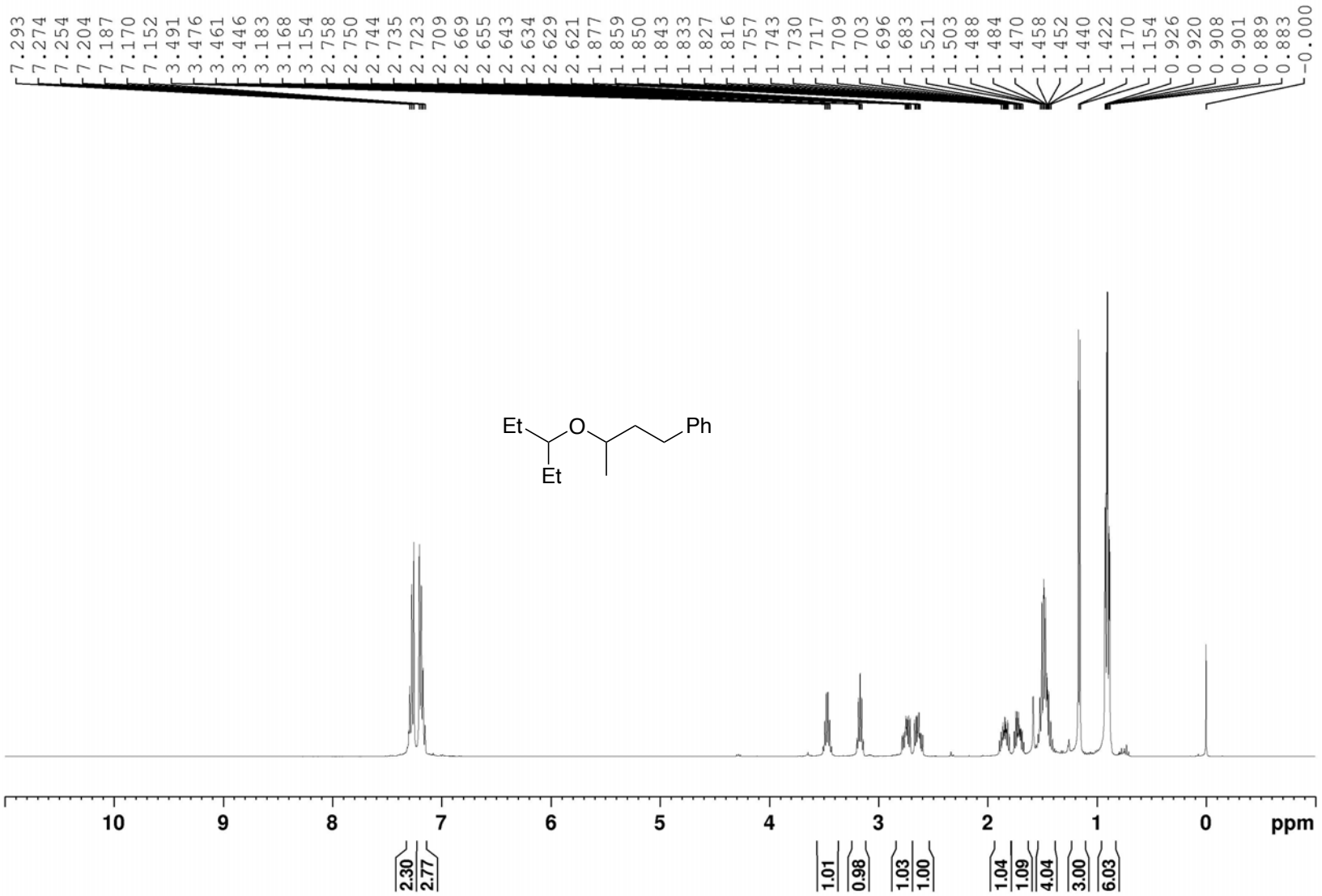
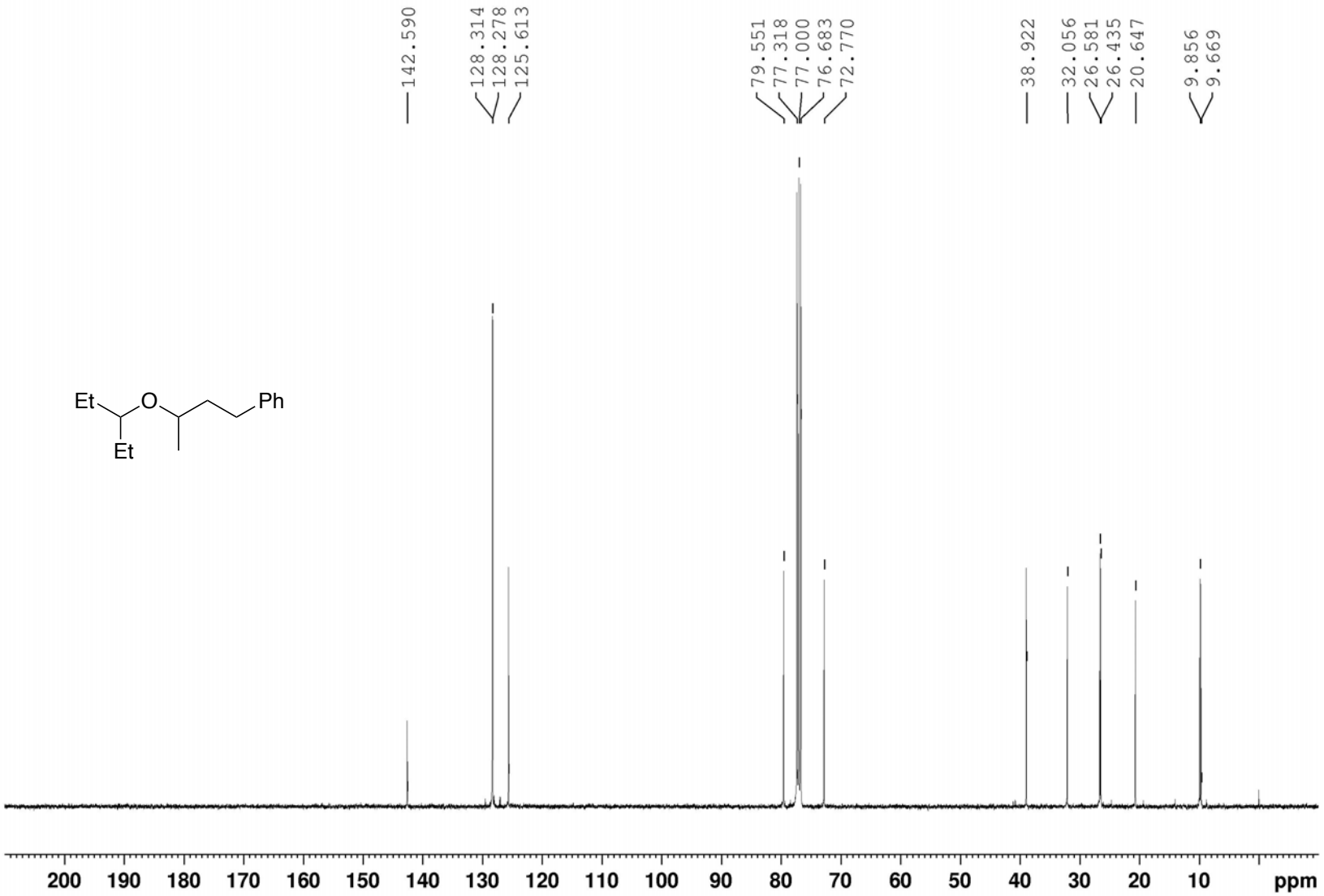


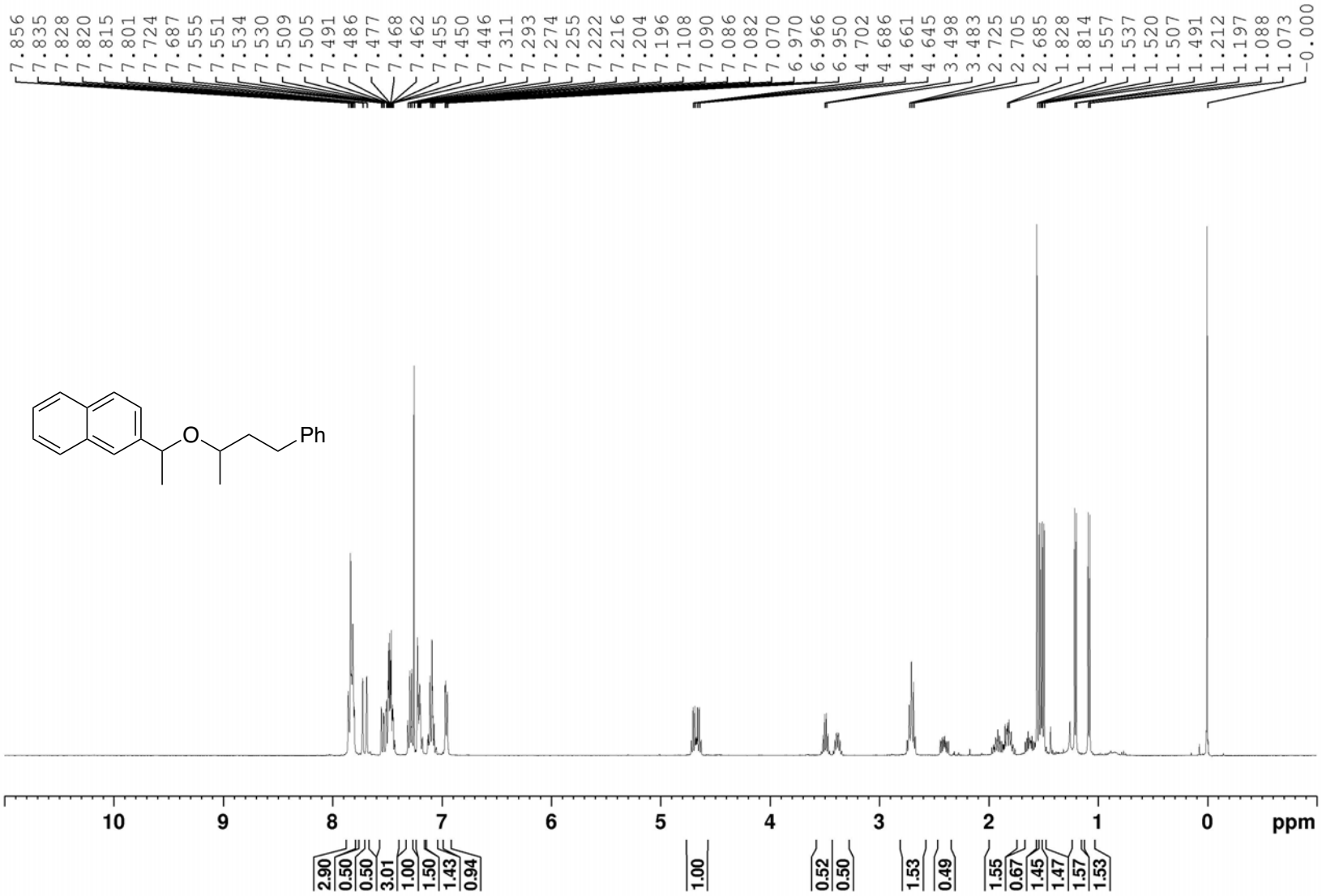

$^{13}$C NMR spectrum of **3oc**



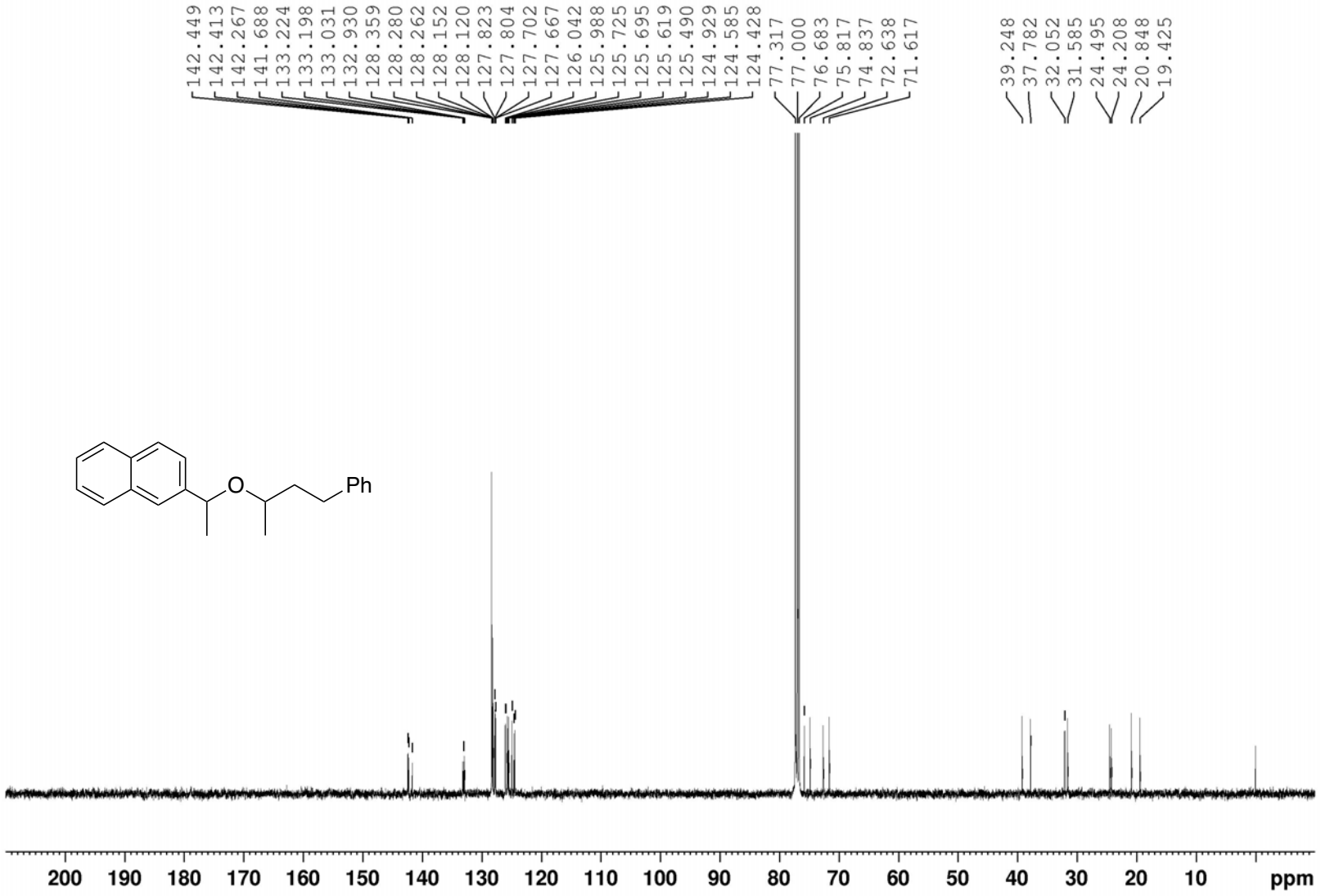

$^{1}$H NMR spectrum of **3pa**



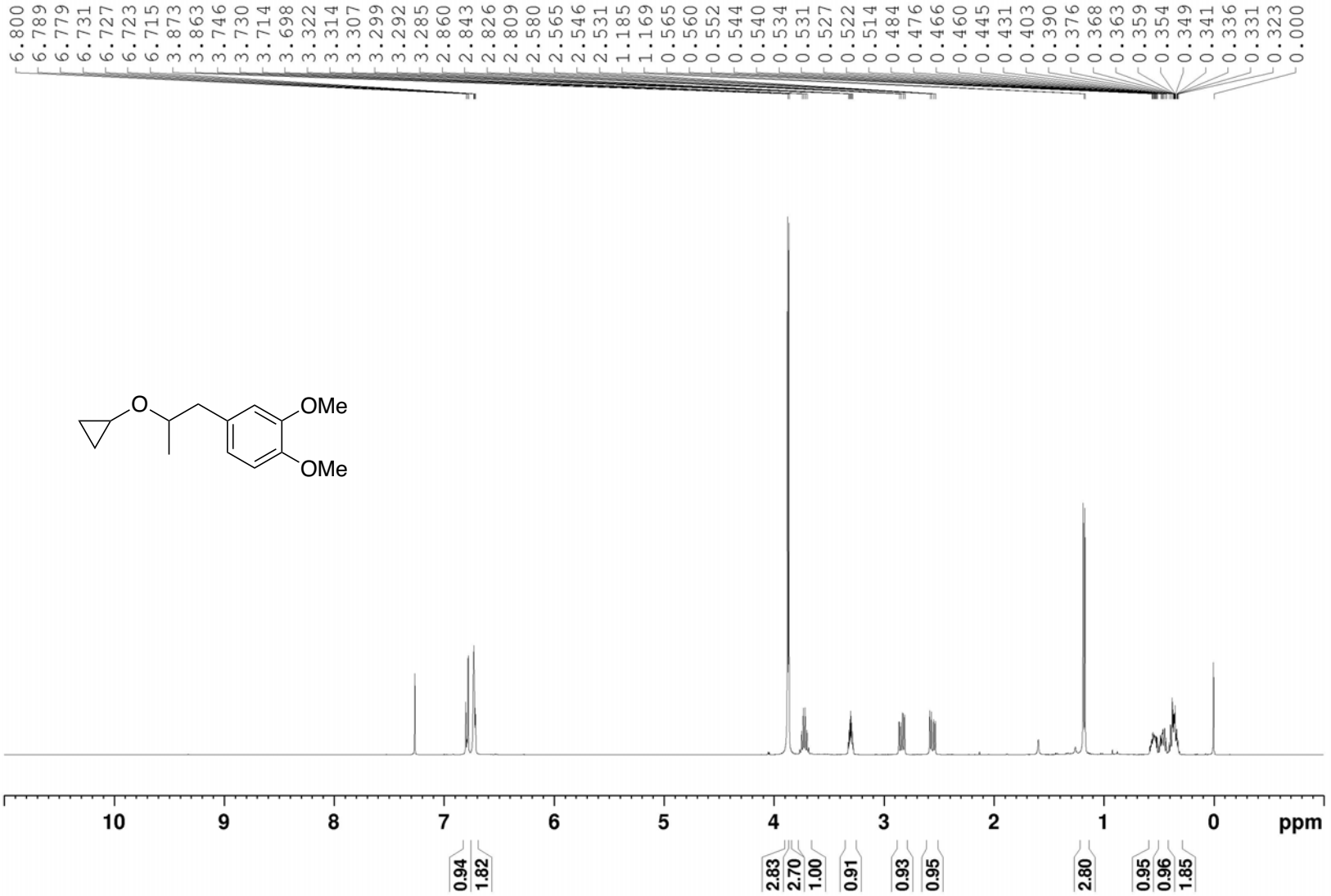

$^{13}$C NMR spectrum of **3pa**



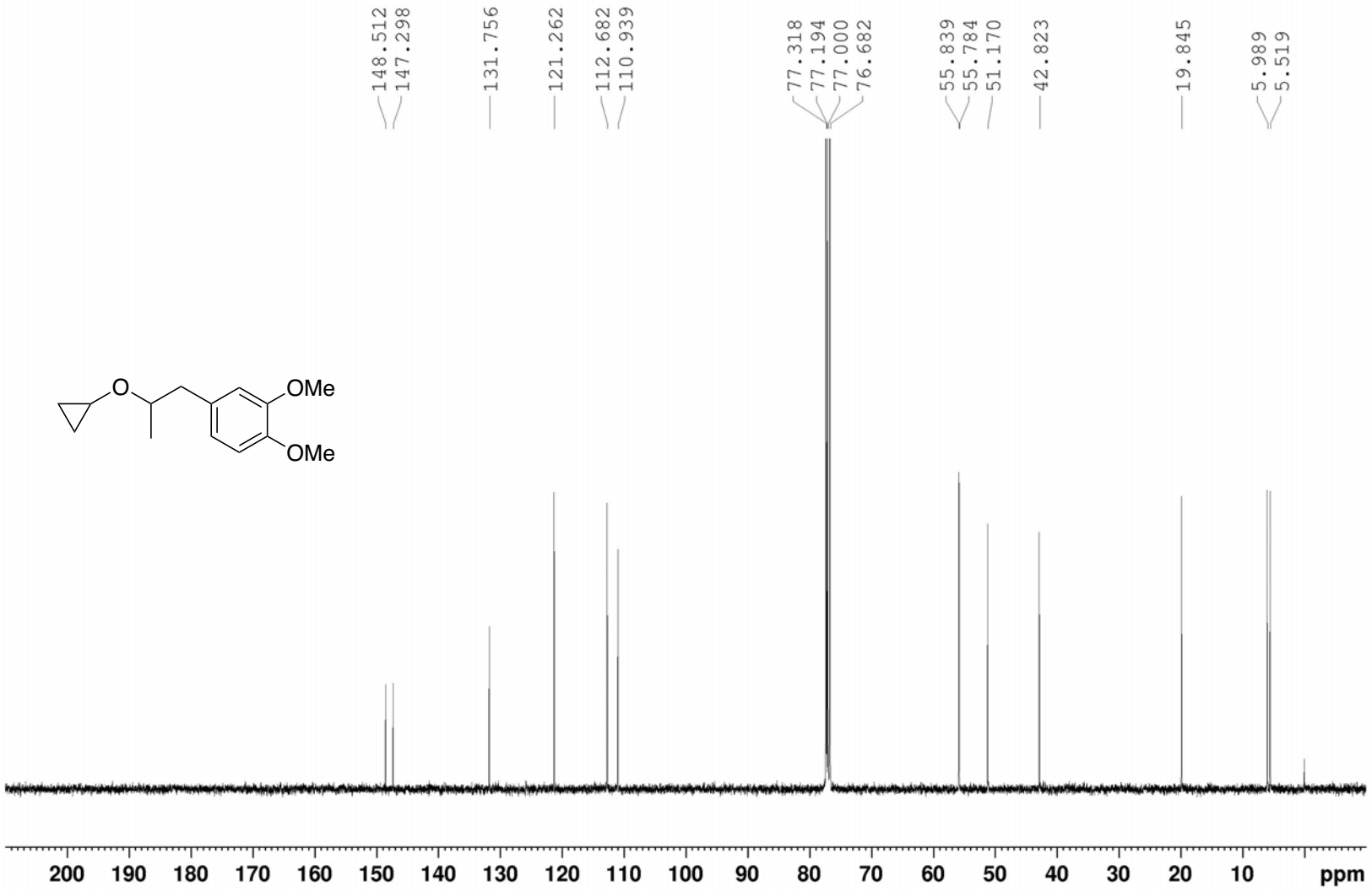

$^{1}$H NMR spectrum of **3qa**



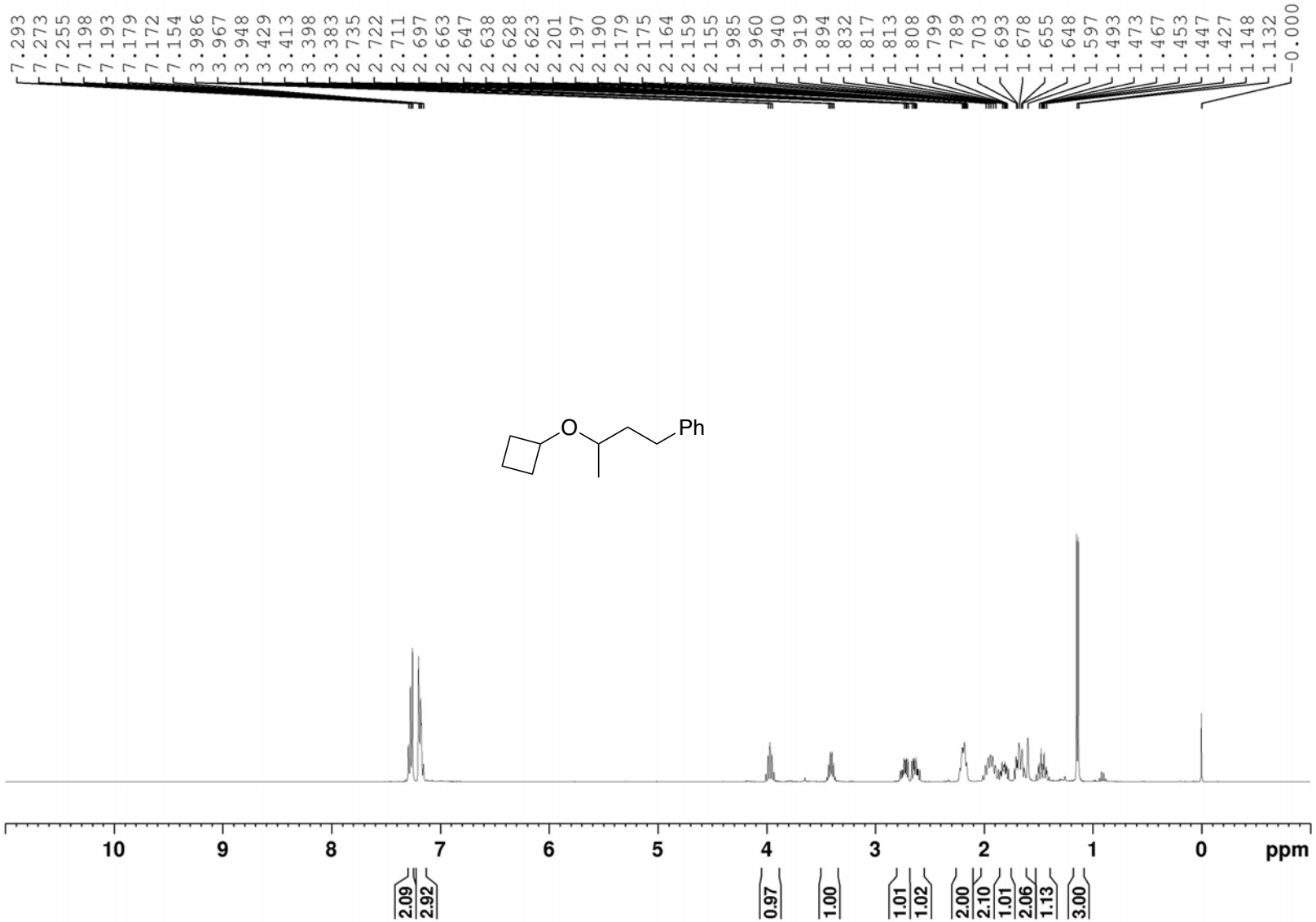

$^{13}$C NMR spectrum of **3qa**



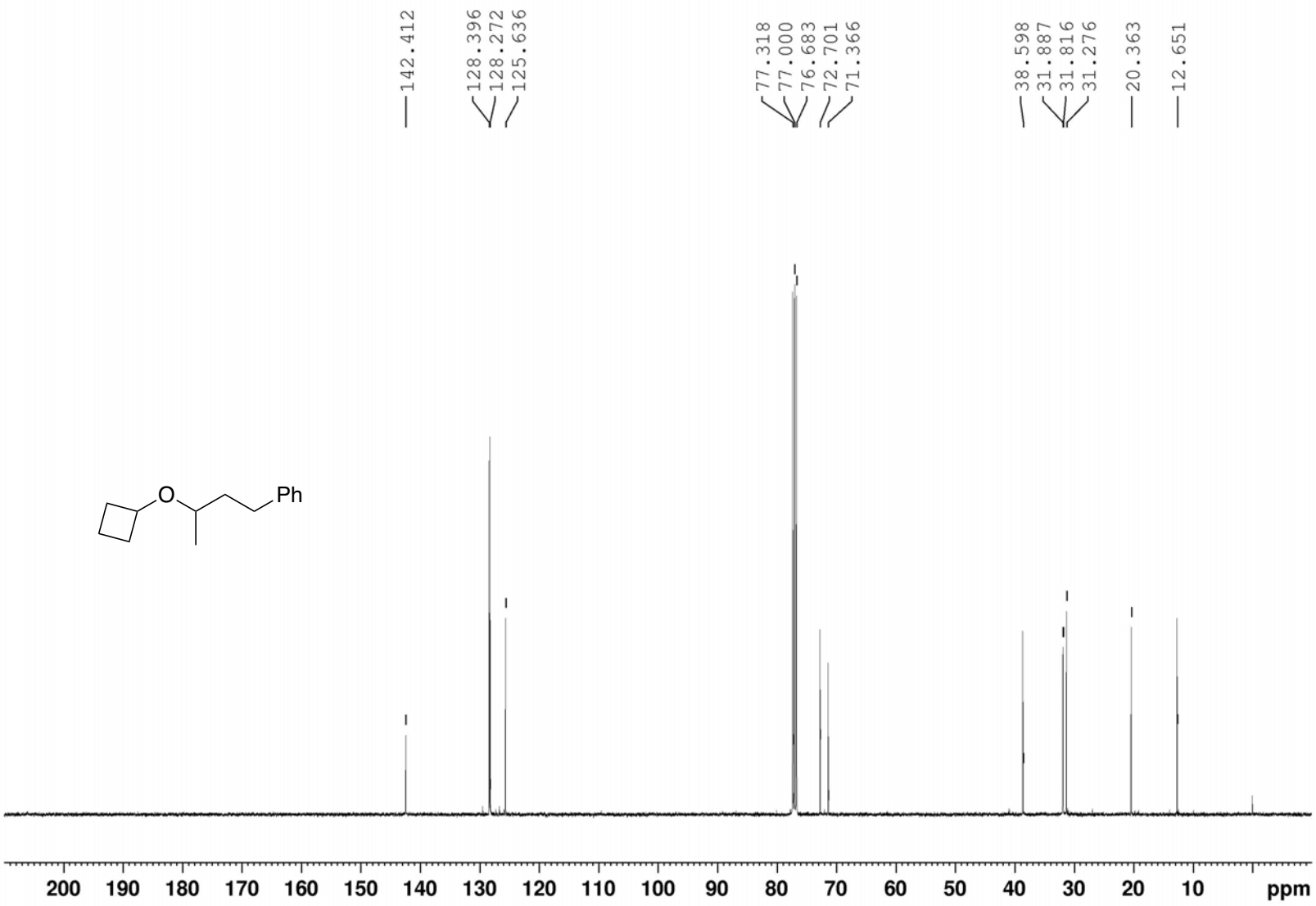

$^{1}$H NMR spectrum of **3rc**



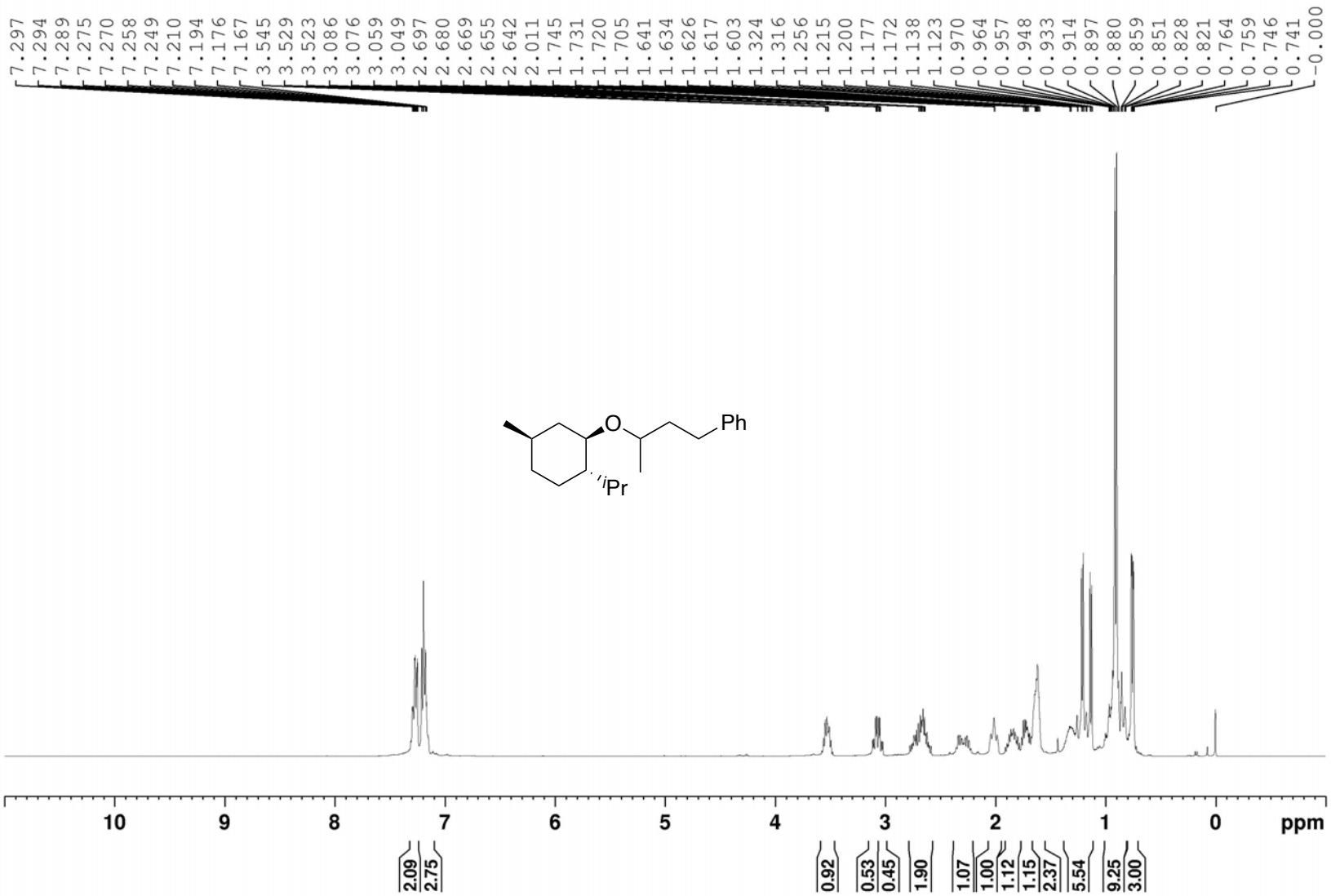

$^{13}$C NMR spectrum of **3rc**



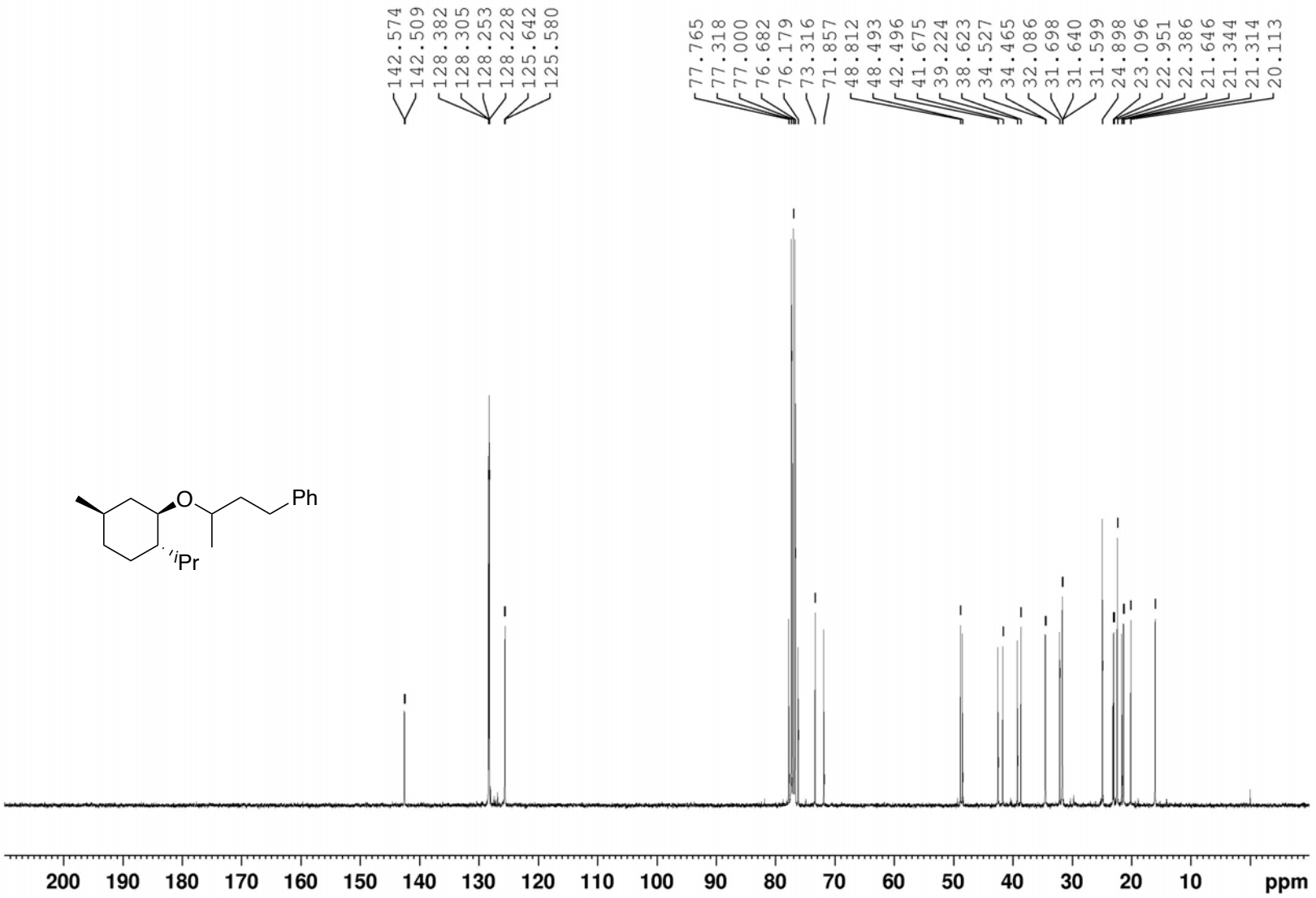

$^{1}$H NMR spectrum of **3sa**



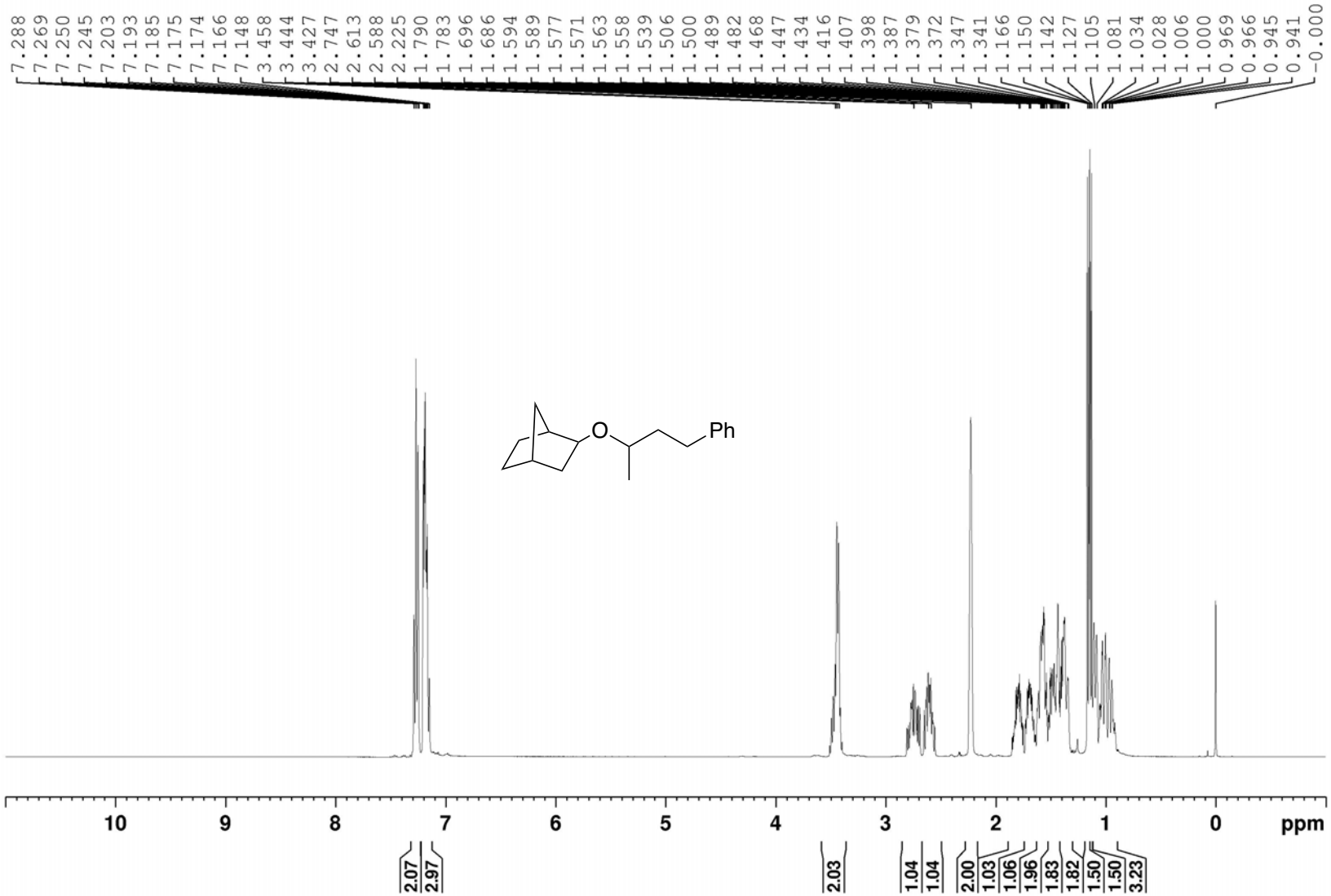

$^{13}$C NMR spectrum of **3sa**



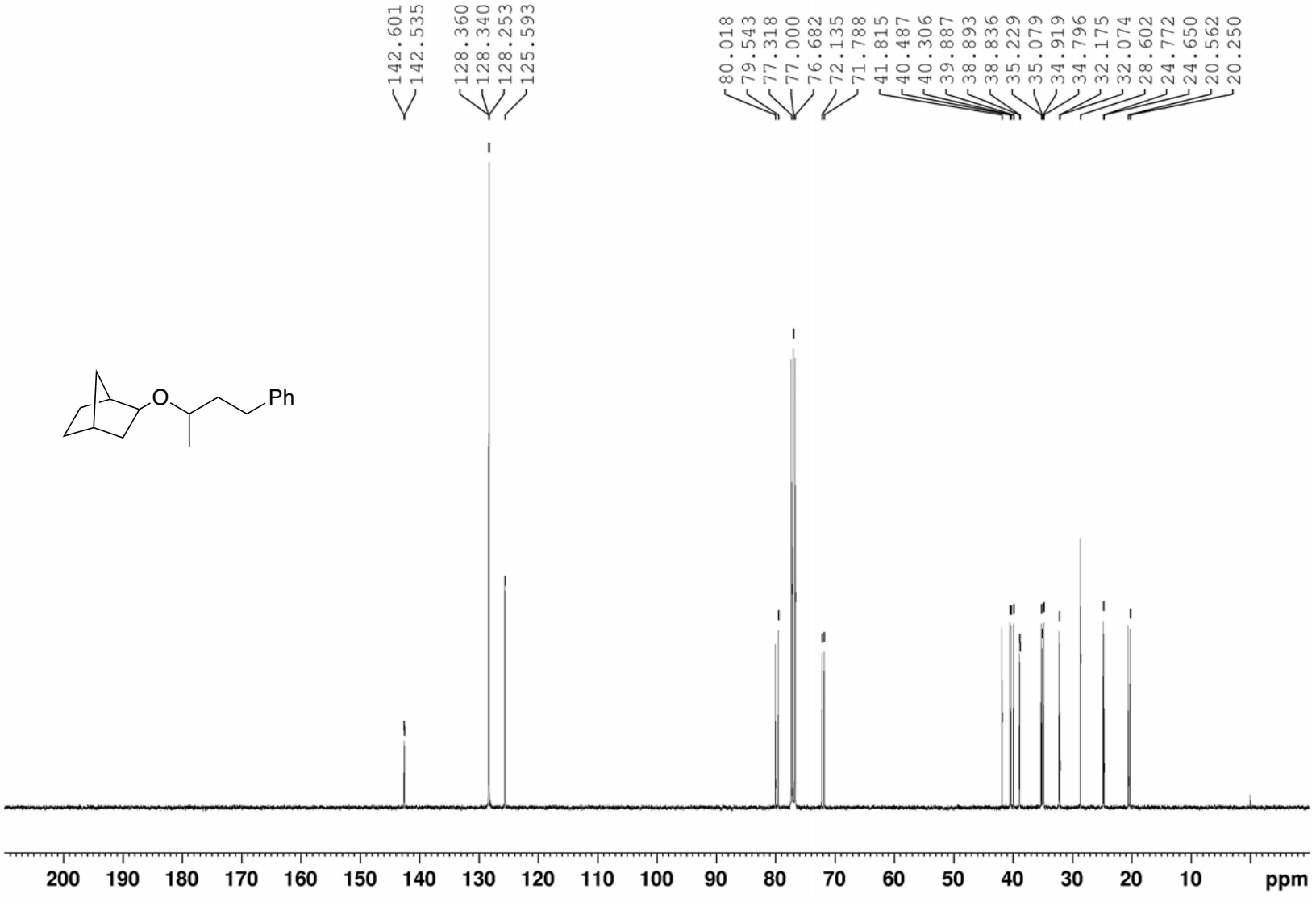

$^{1}$H NMR spectrum of **3ta**



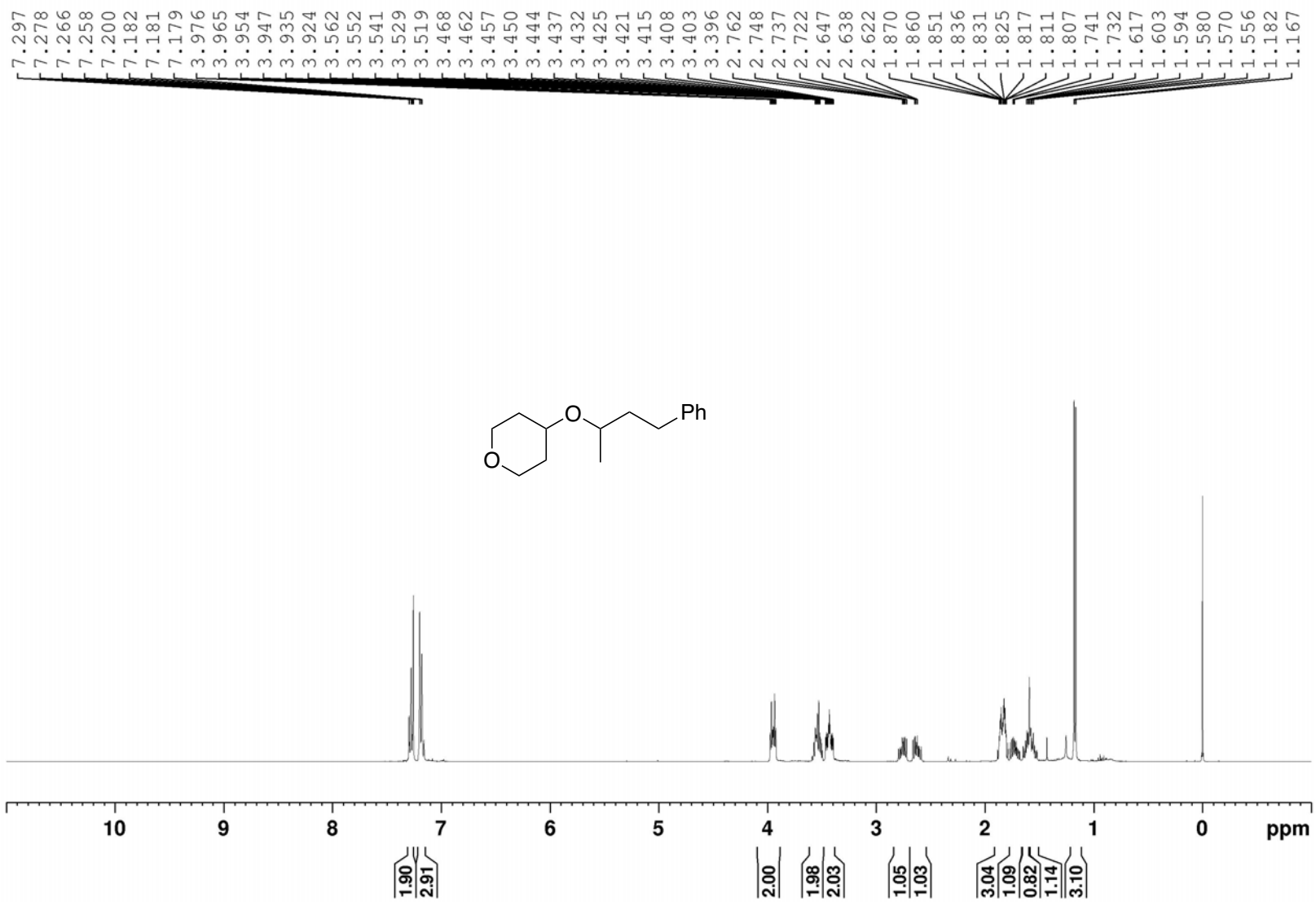

$^{13}$C NMR spectrum of **3ta**



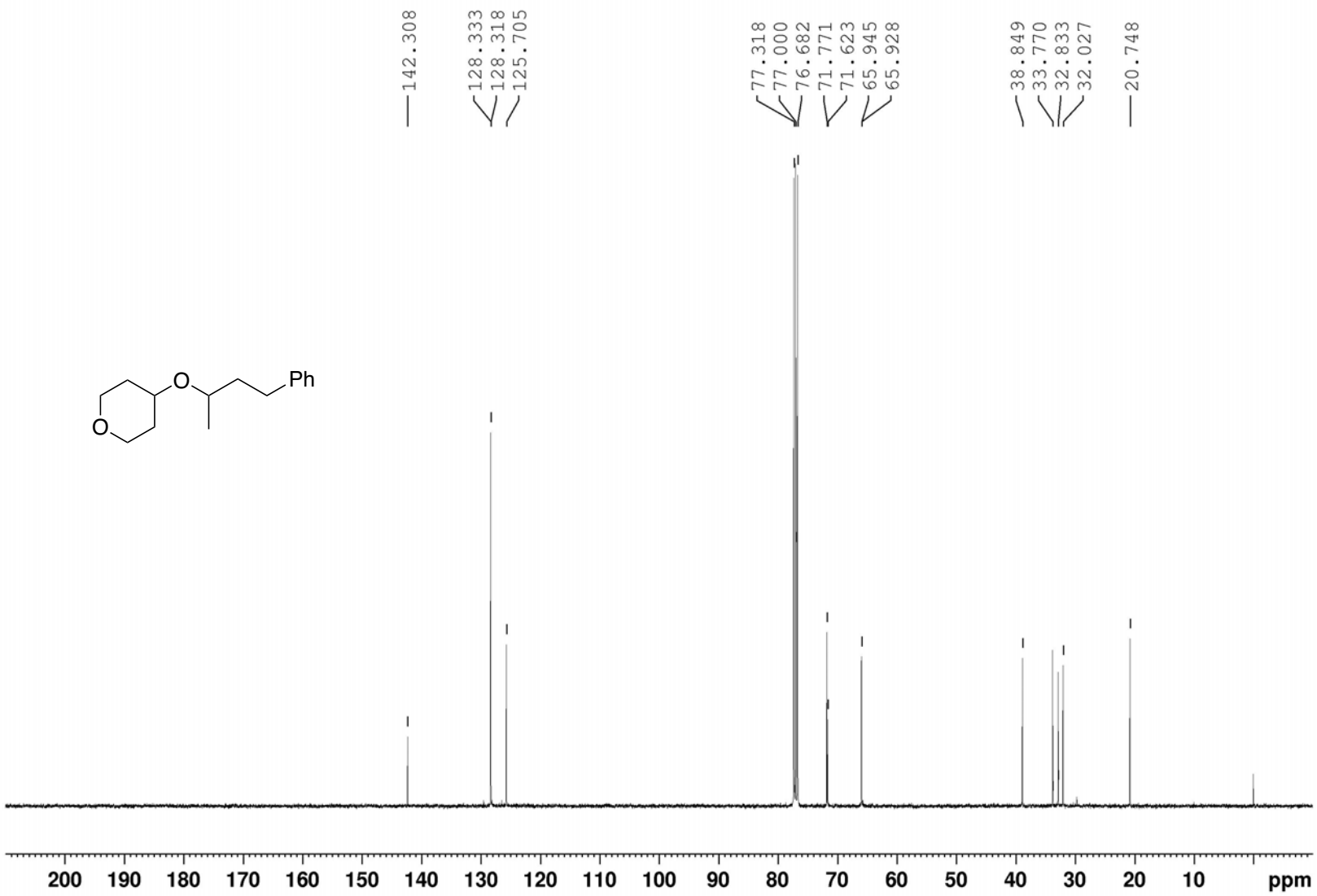

$^{1}$H NMR spectrum of **3ua**



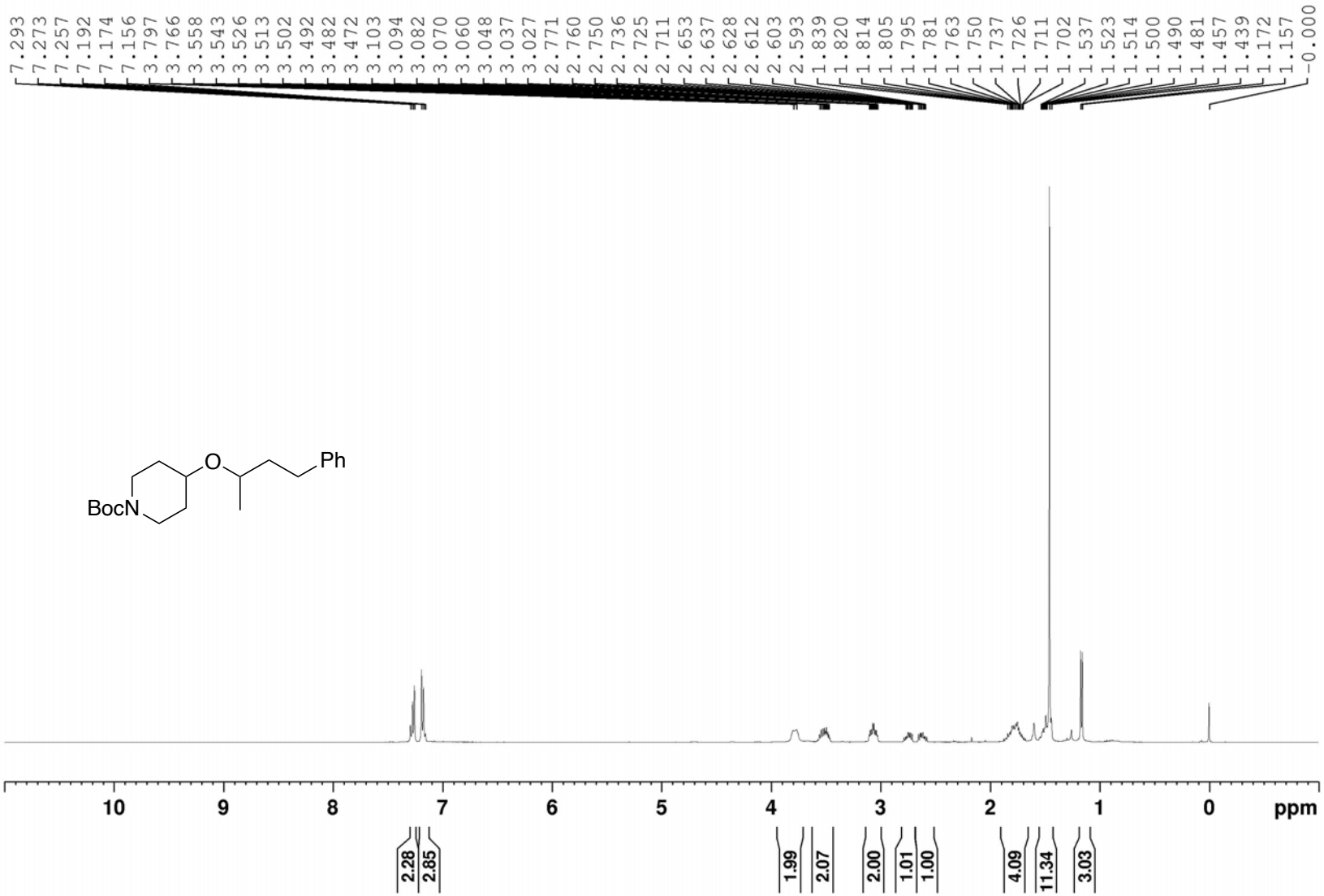

$^{13}$C NMR spectrum of **3ua**



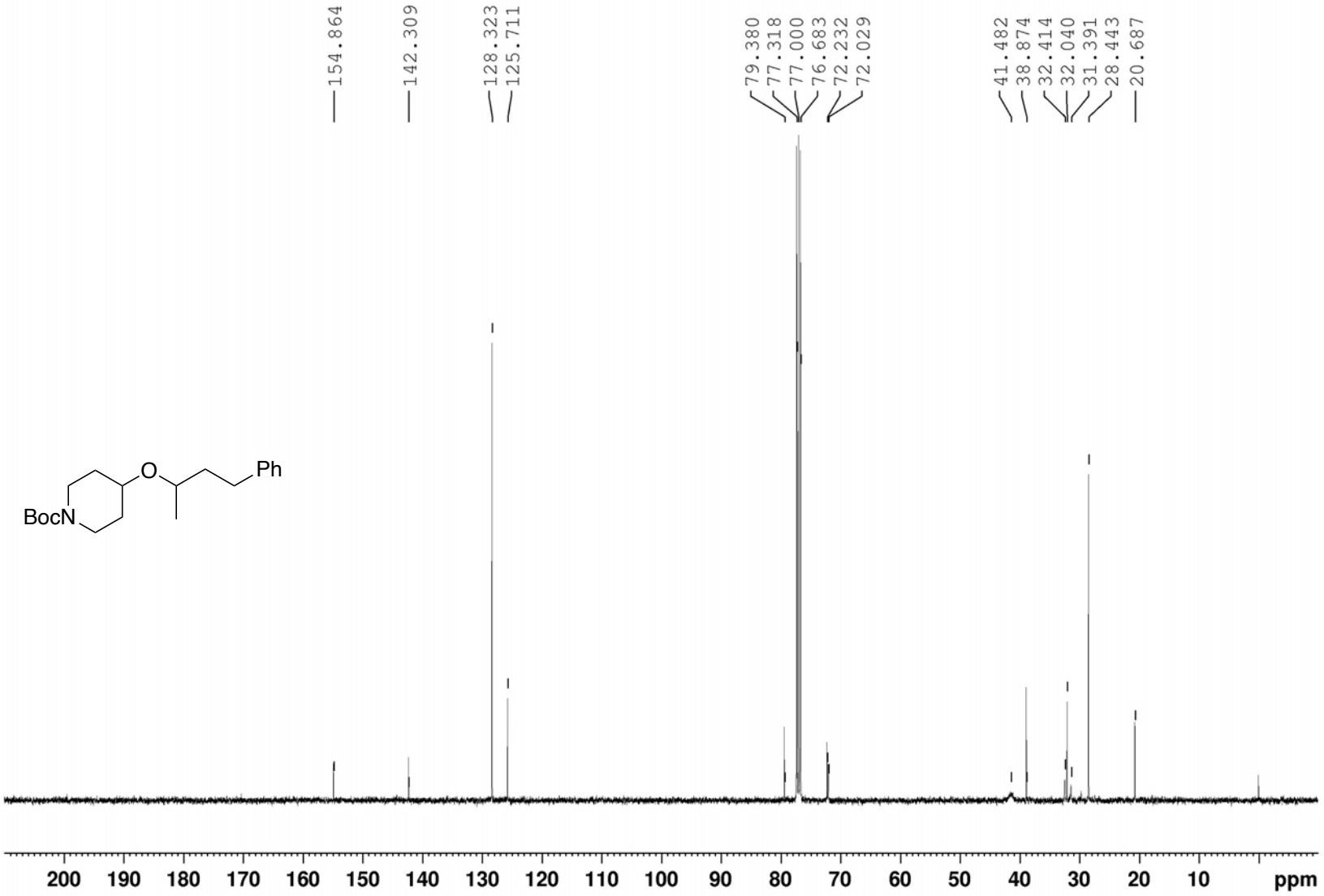

$^{1}$H NMR spectrum of **3va**



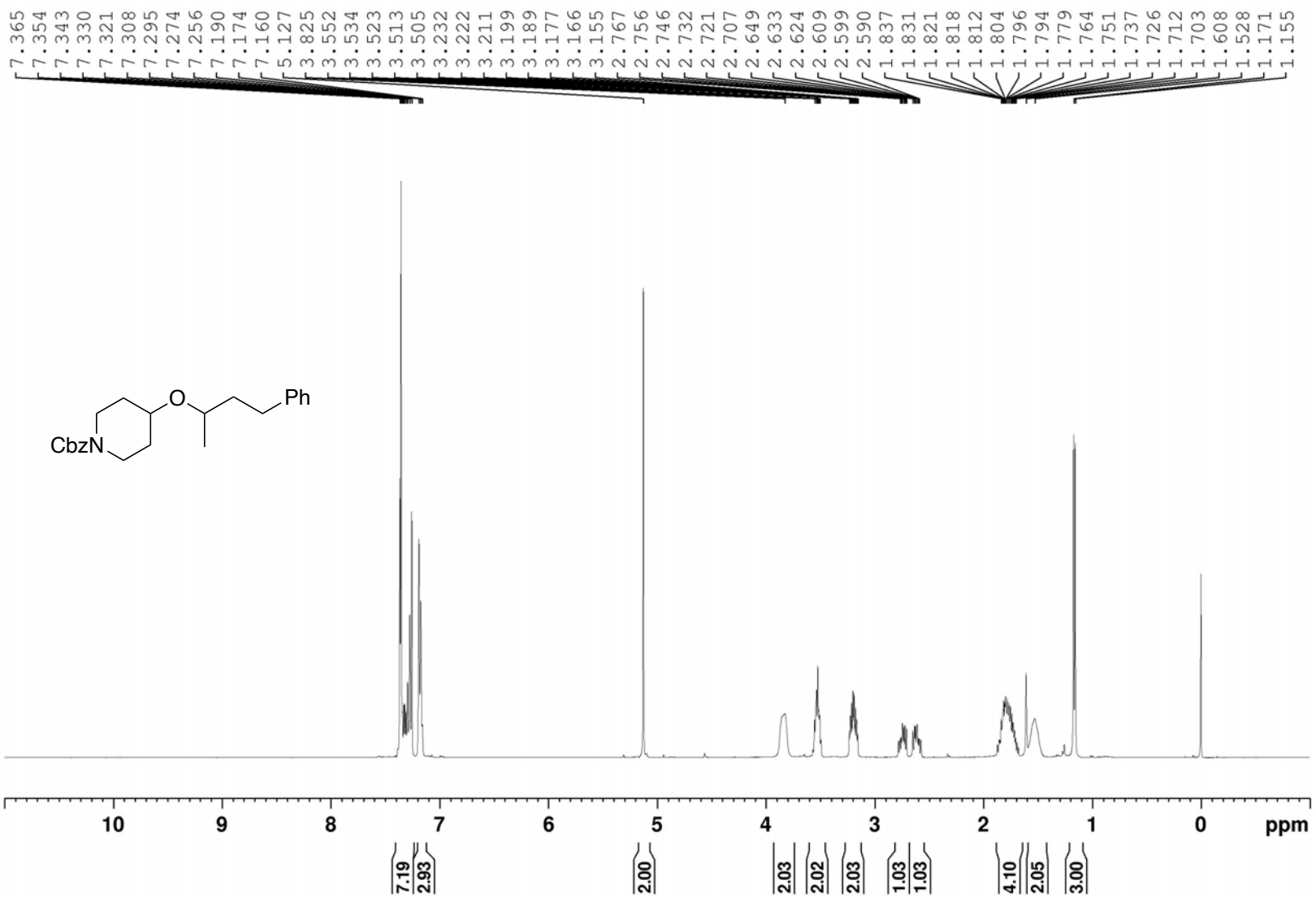

$^{13}$C NMR spectrum of **3va**



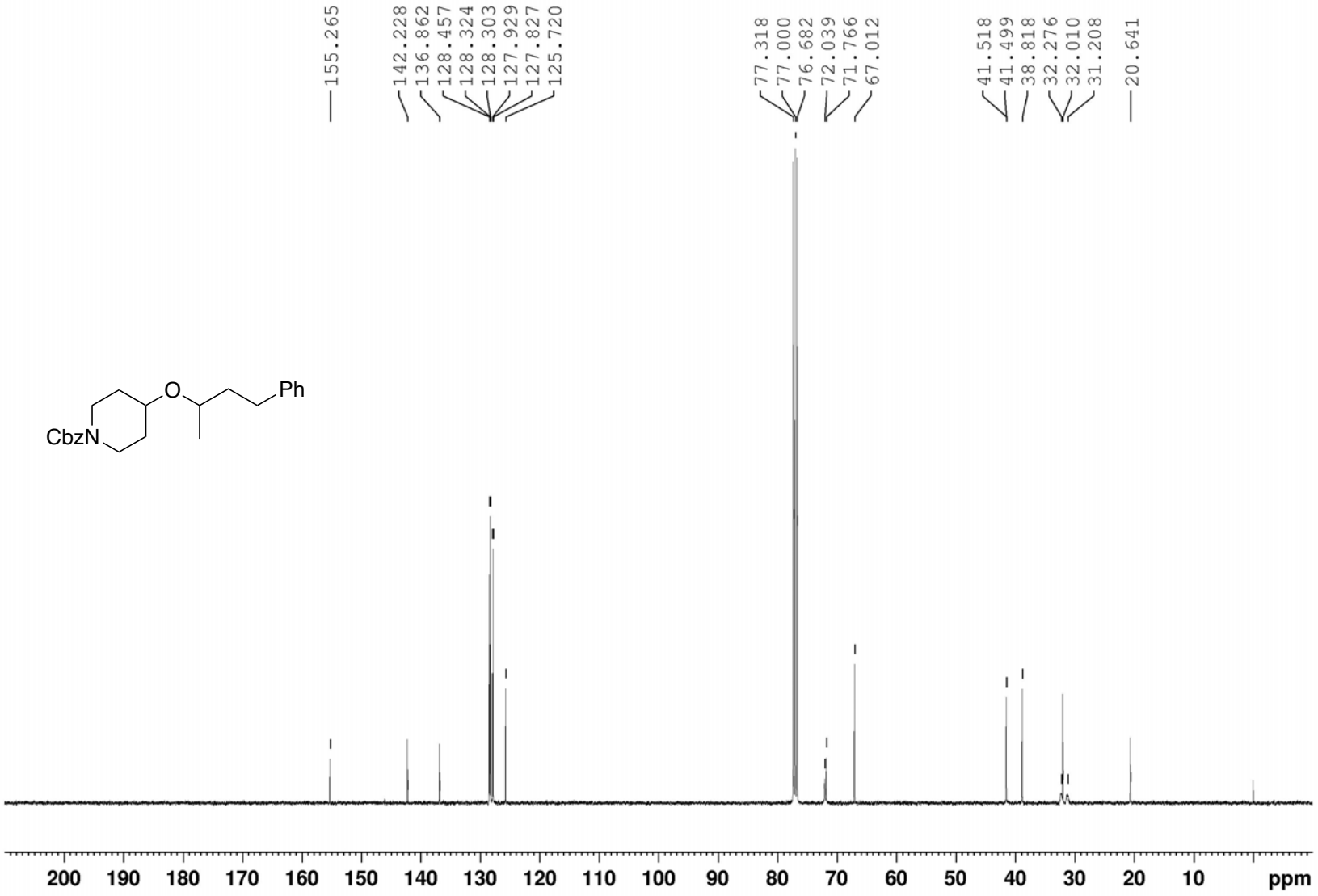

$^{1}$H NMR spectrum of **3wa**



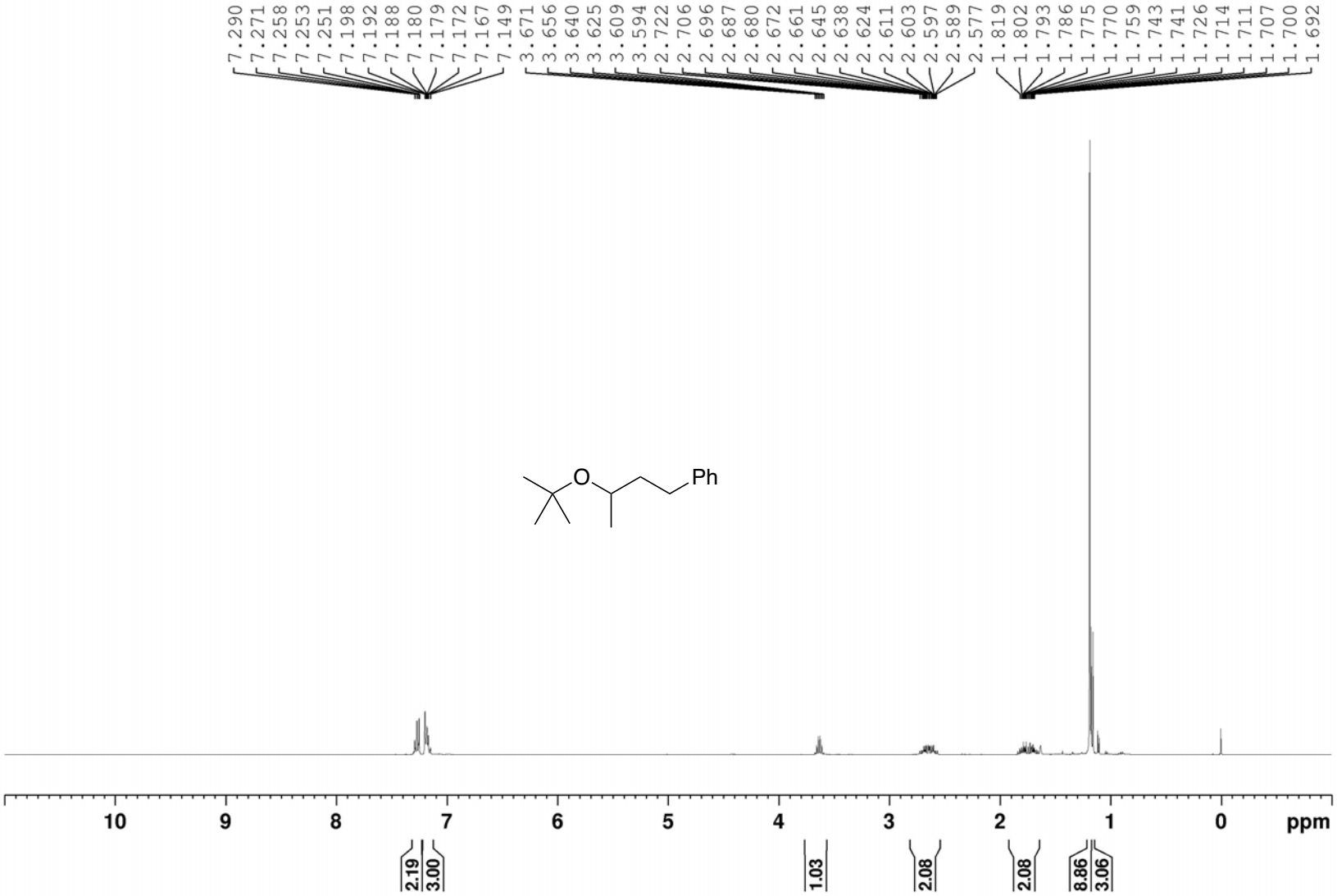

$^{13}$C NMR spectrum of **3wa**



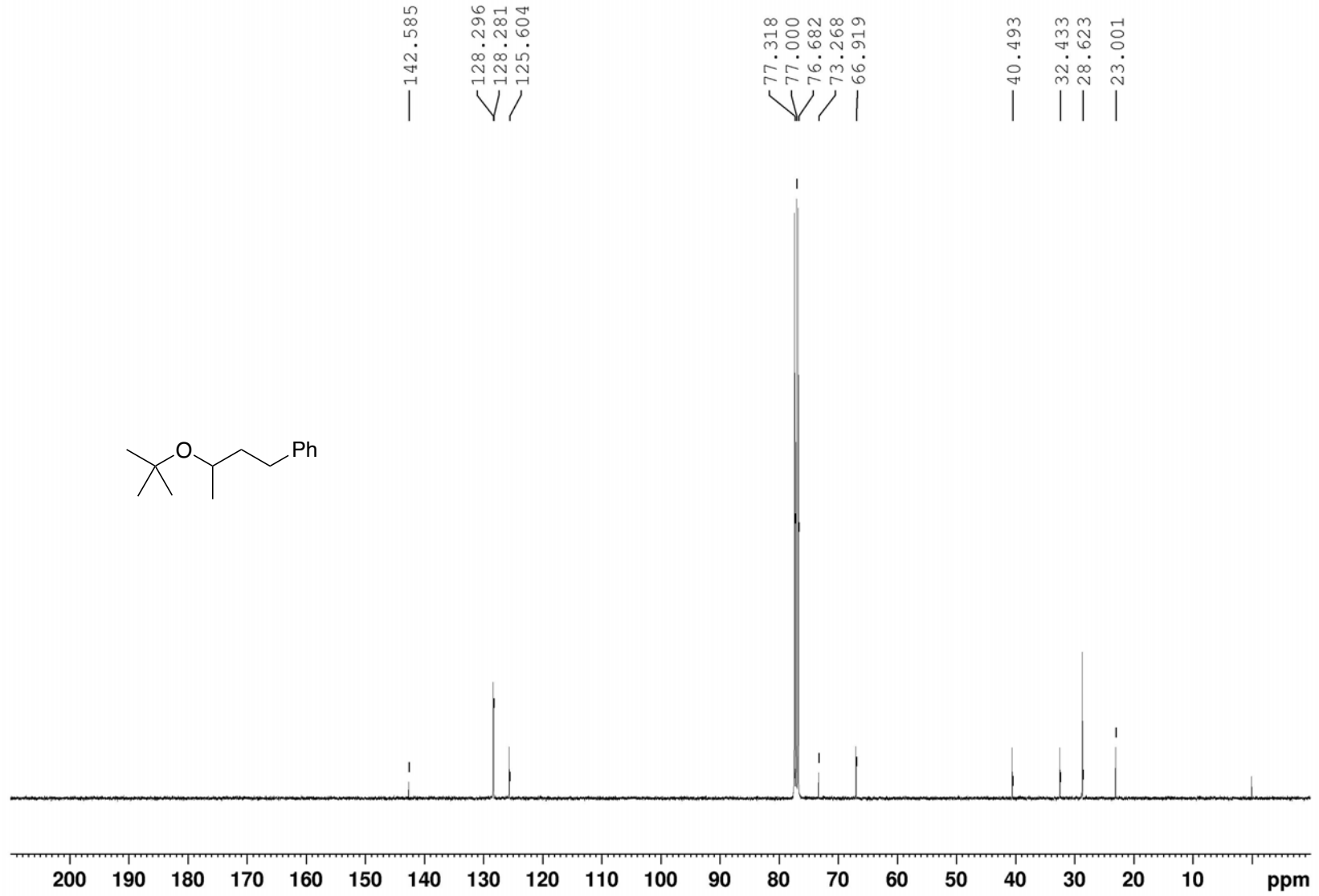

$^{1}$H NMR spectrum of **3xa**



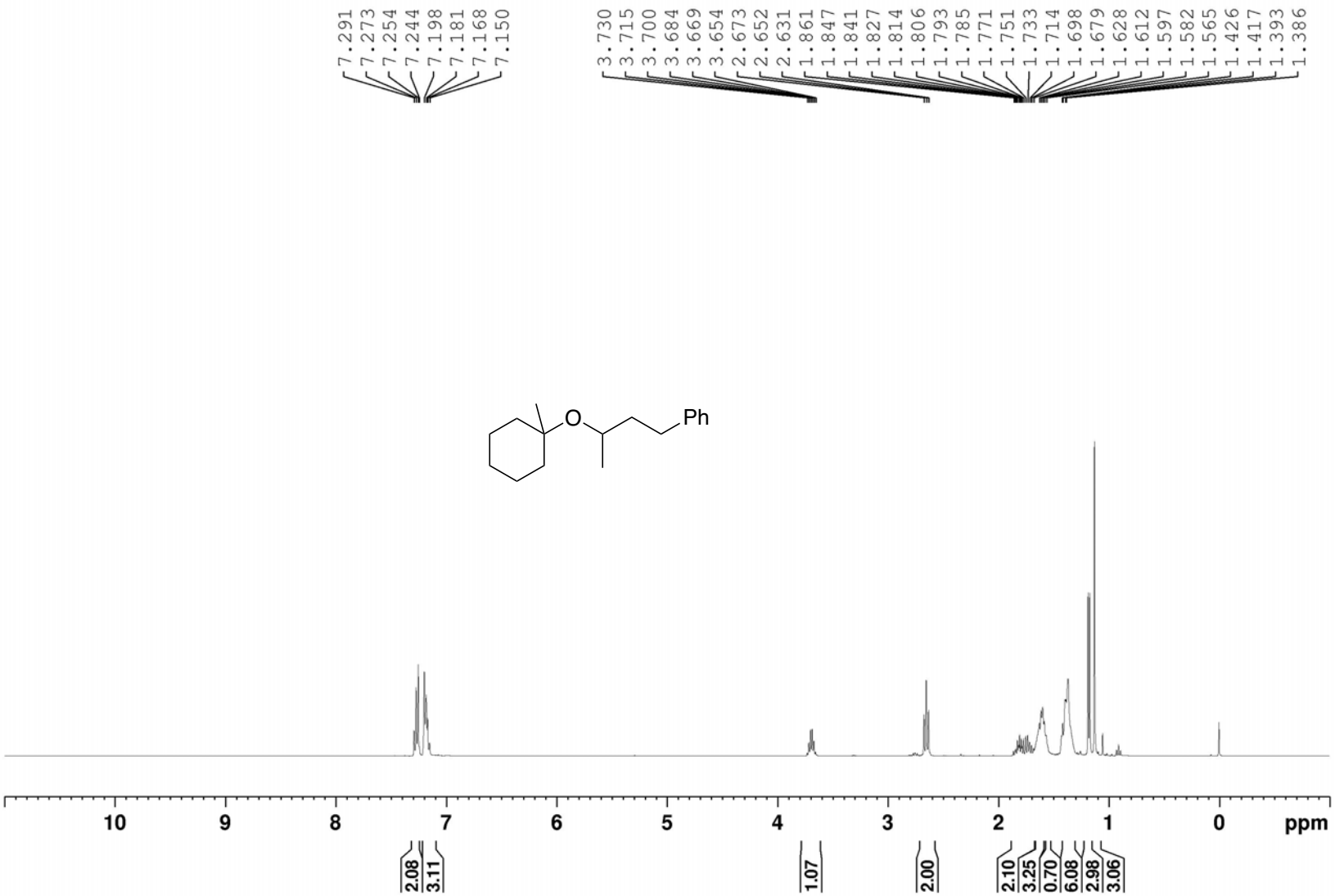

$^{13}$C NMR spectrum of **3xa**



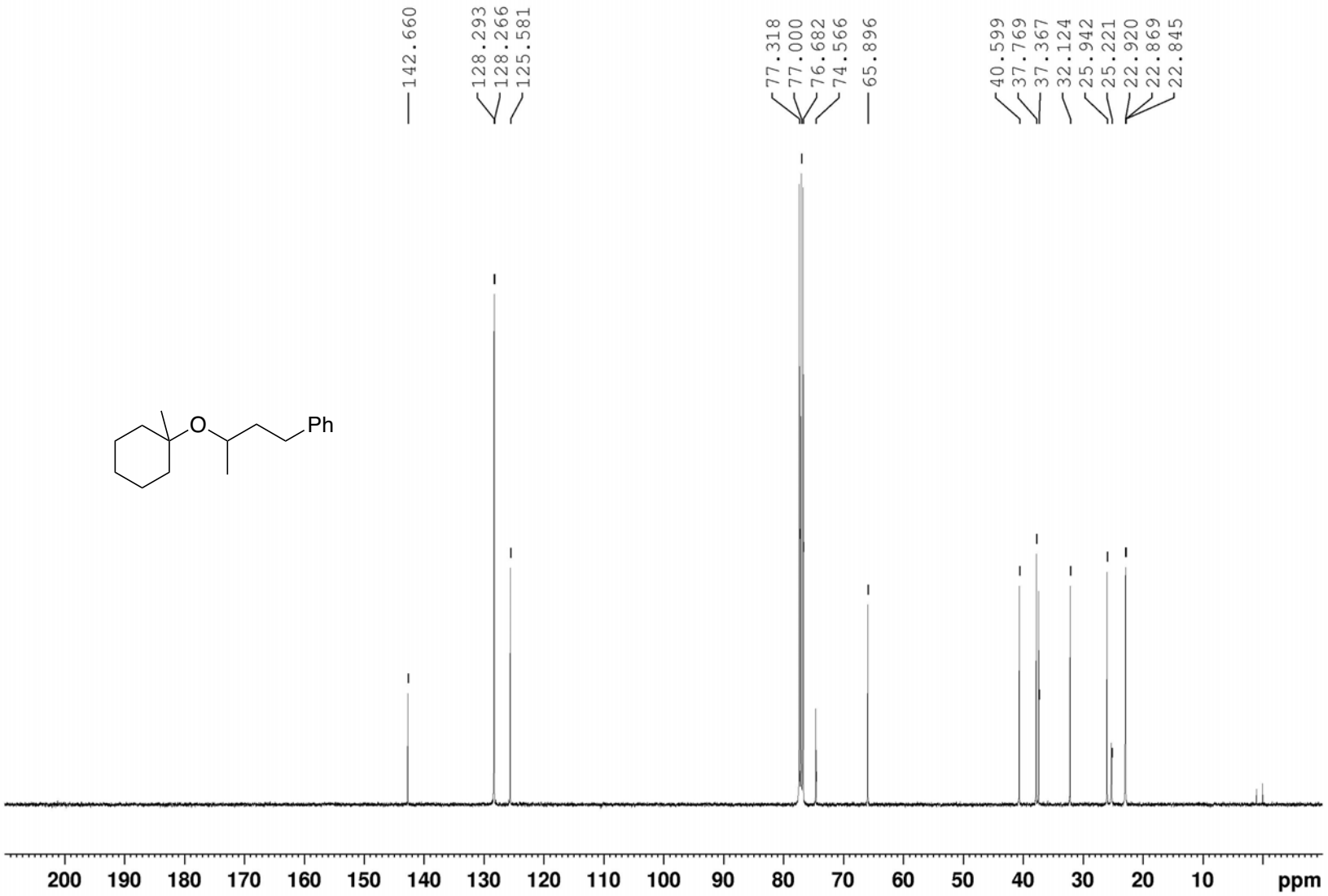

$^{1}$H NMR spectrum of **3ya**



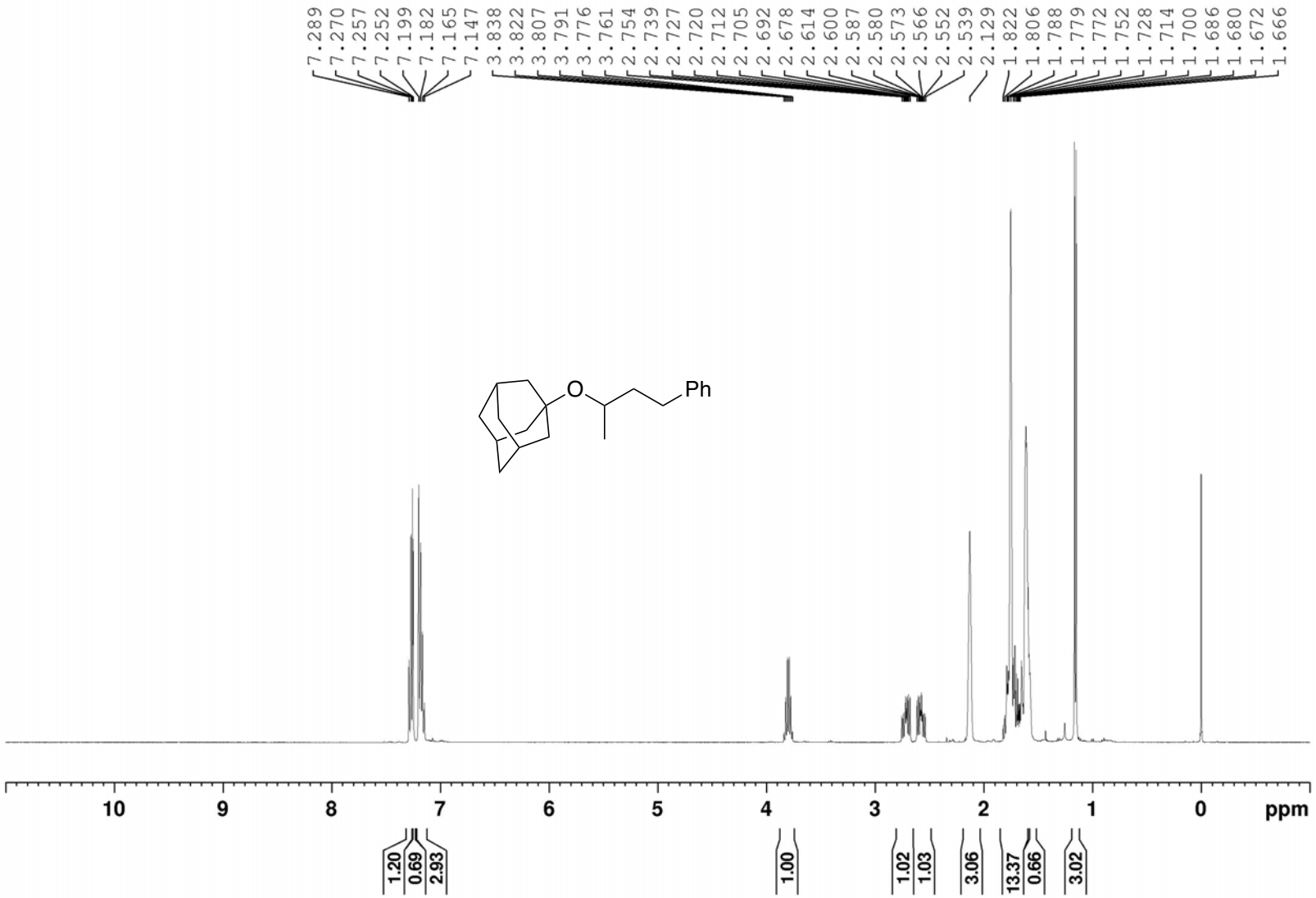

$^{13}$C NMR spectrum of **3ya**



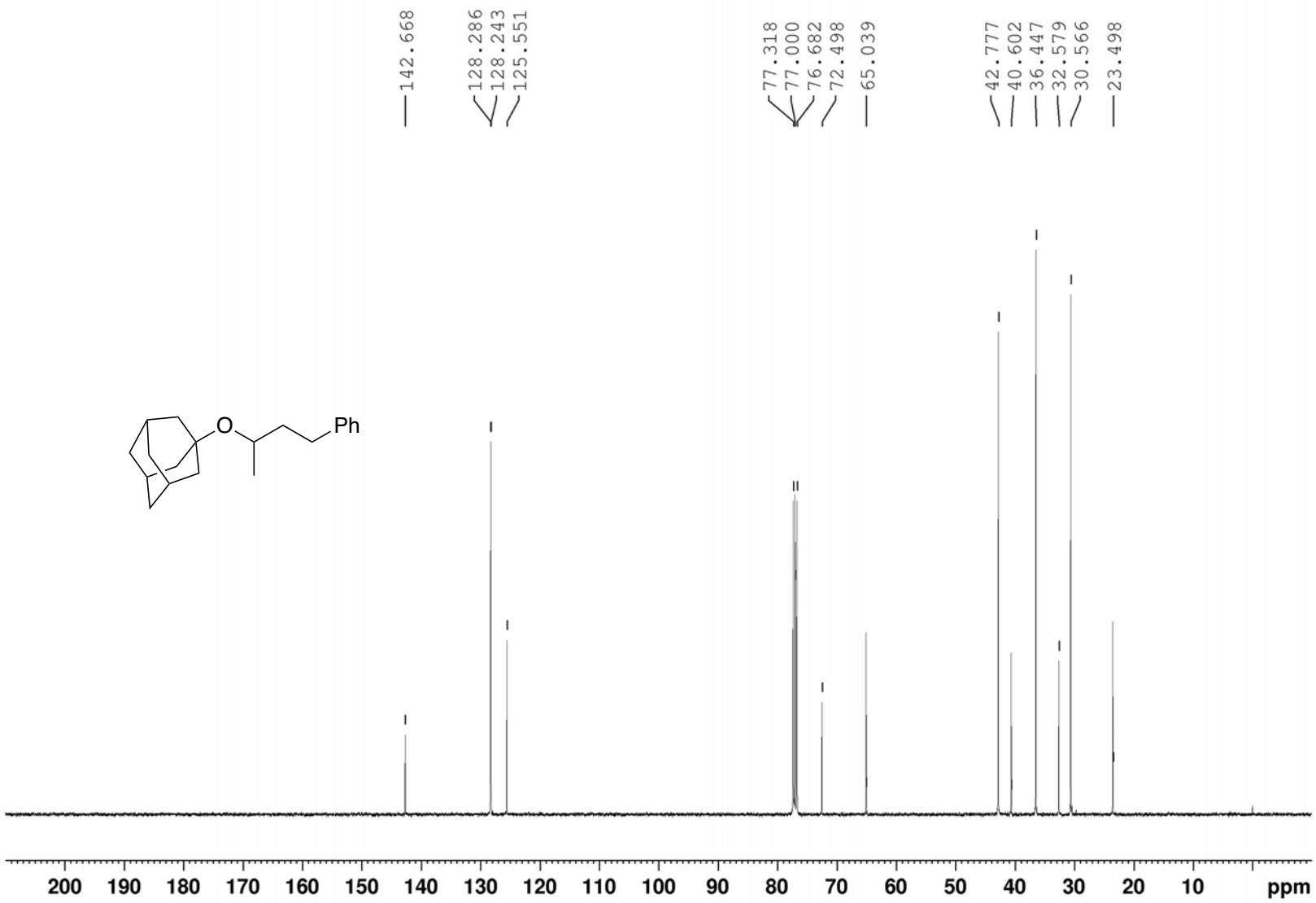

$^{1}$H NMR spectrum of **3za**



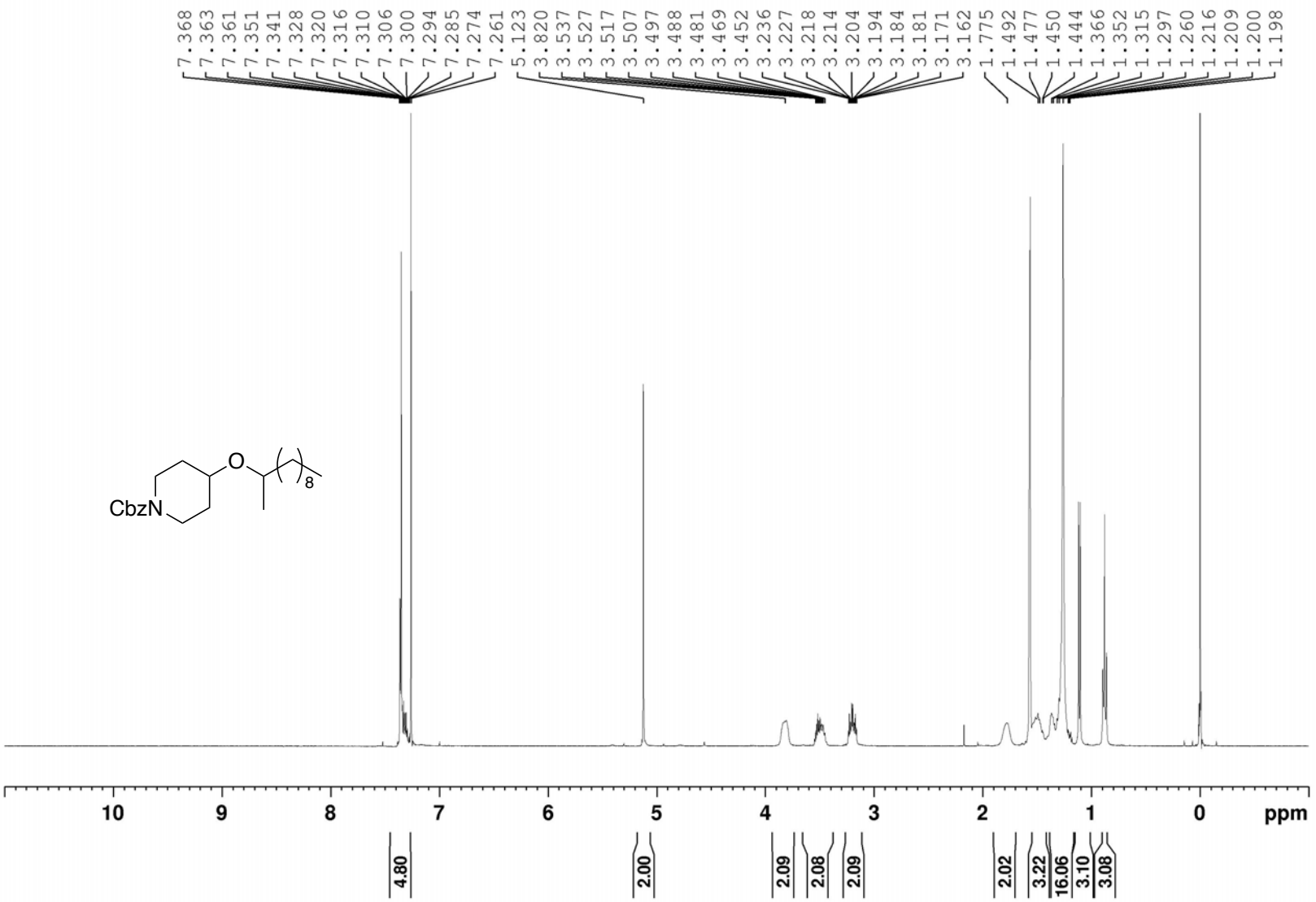

$^{13}$C NMR spectrum of **3za**



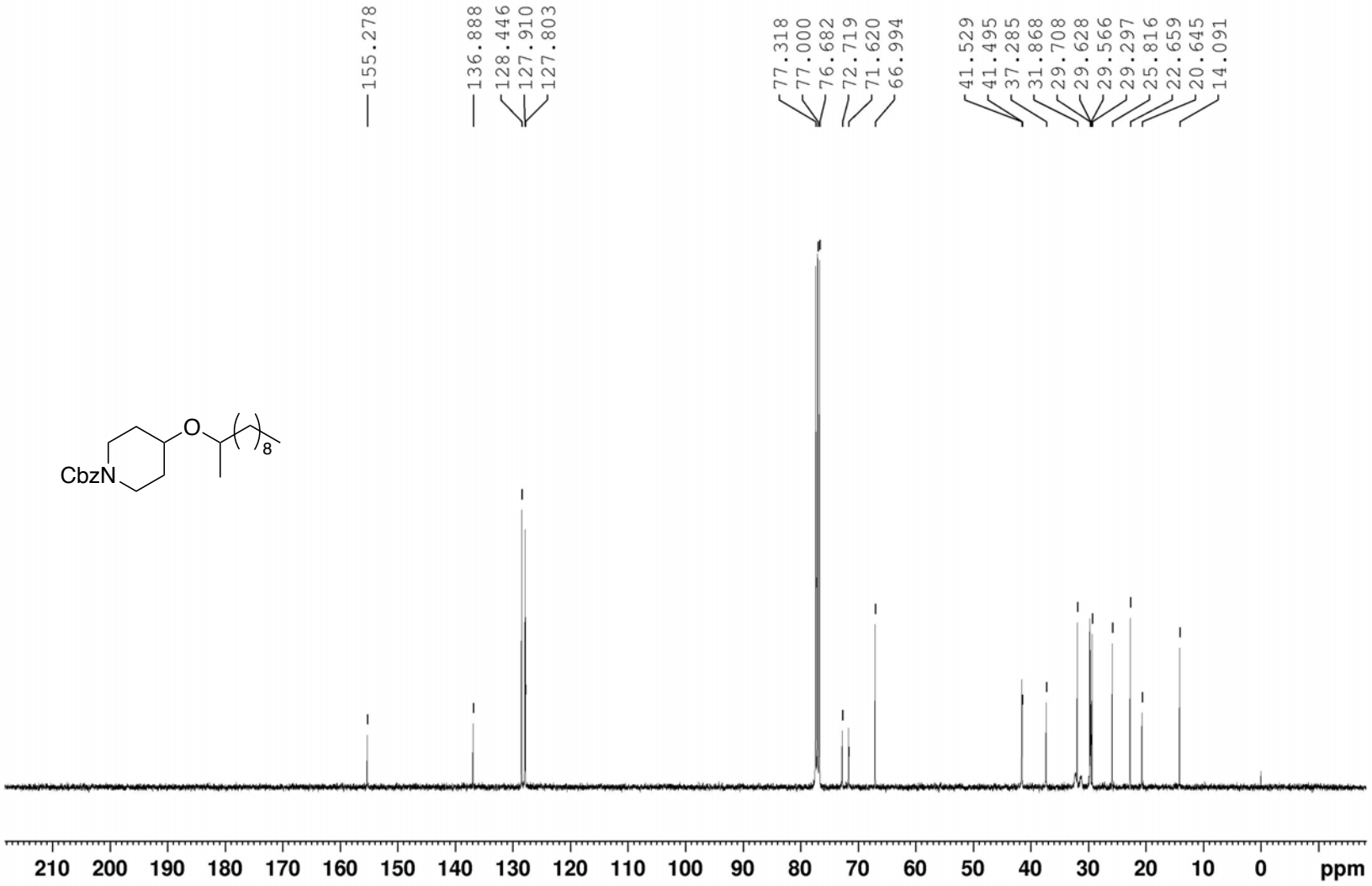

$^{1}$H NMR spectrum of **3Aa**



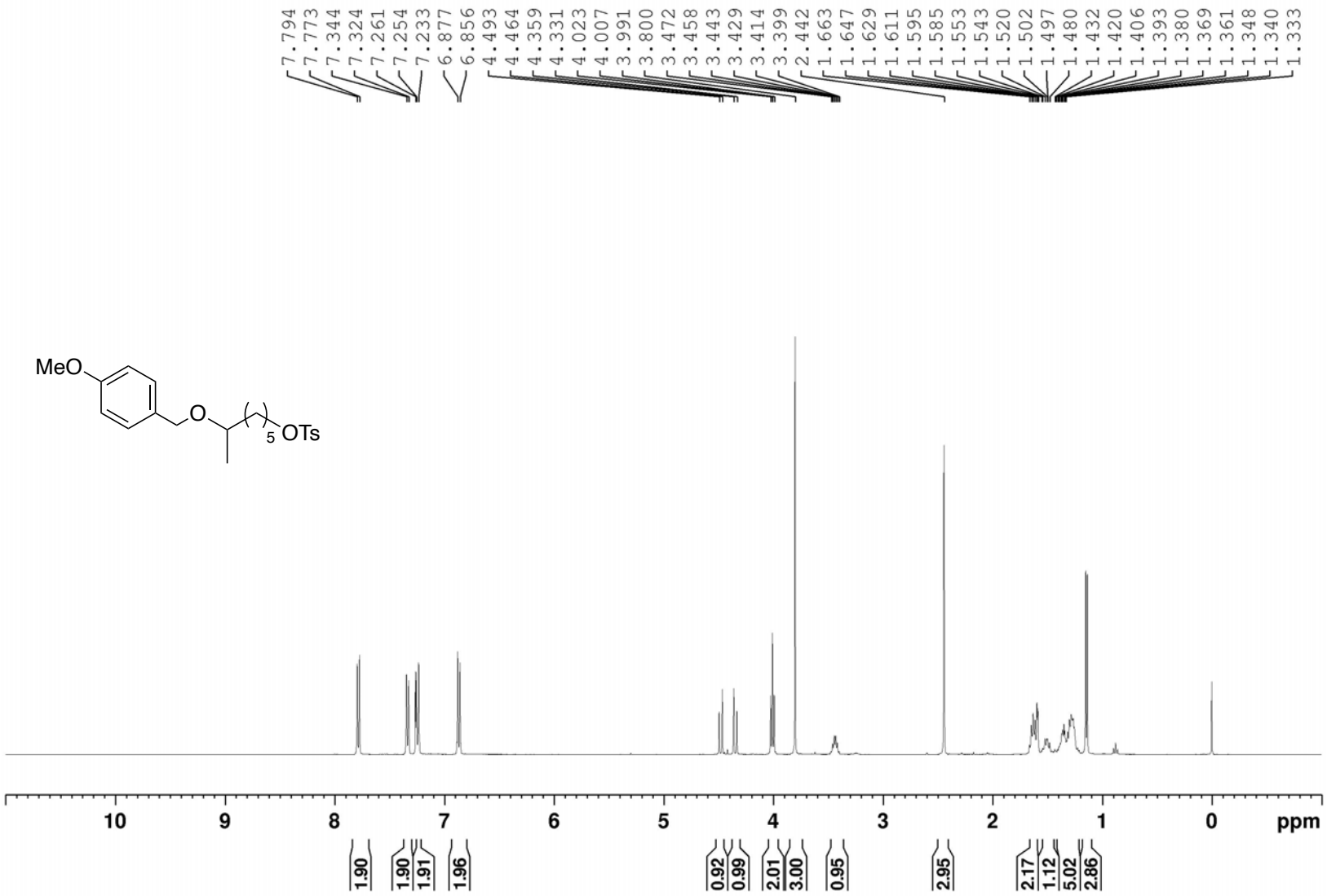

$^{13}$C NMR spectrum of **3Aa**



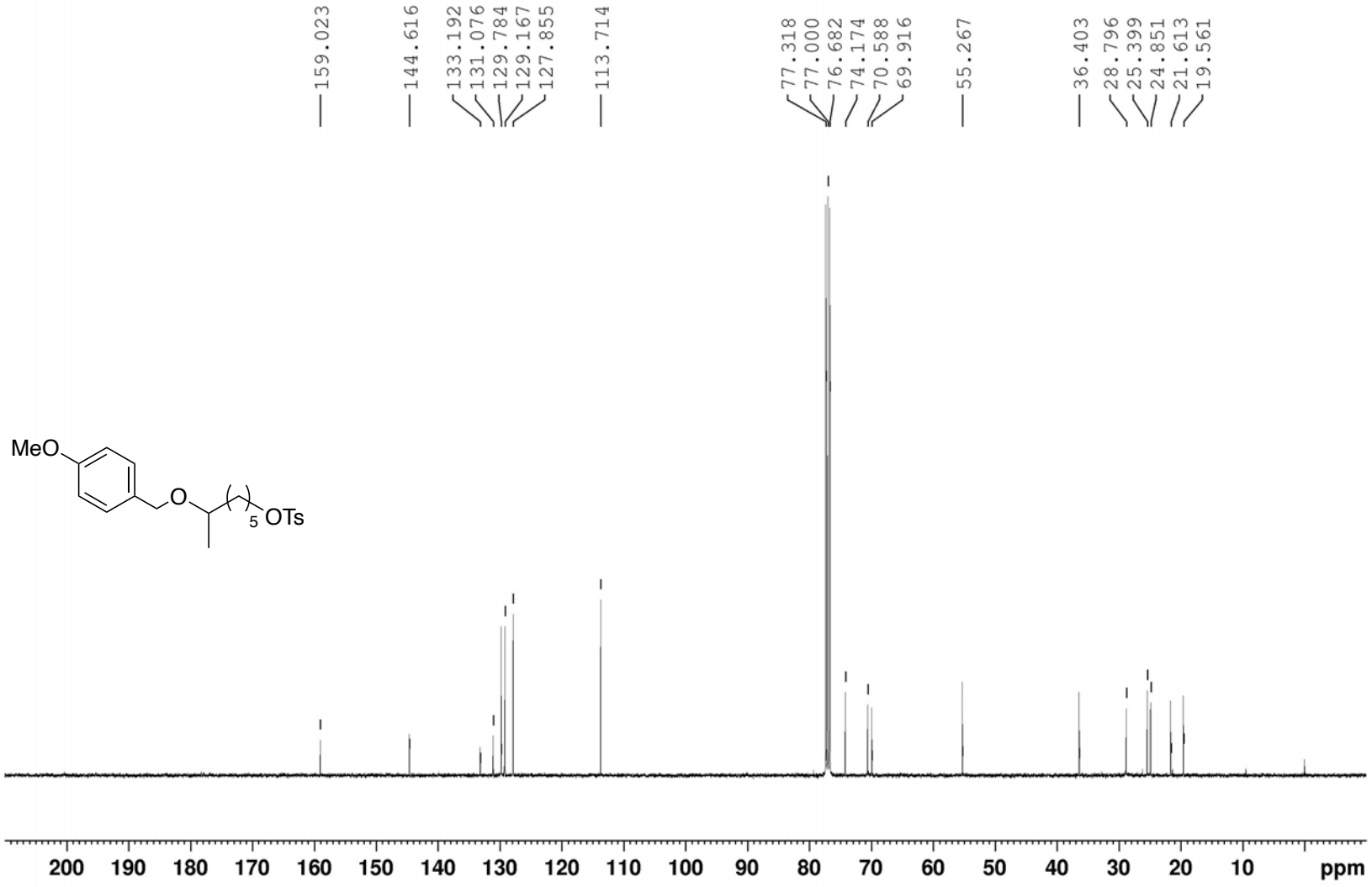

$^{1}$H NMR spectrum of **3xd**



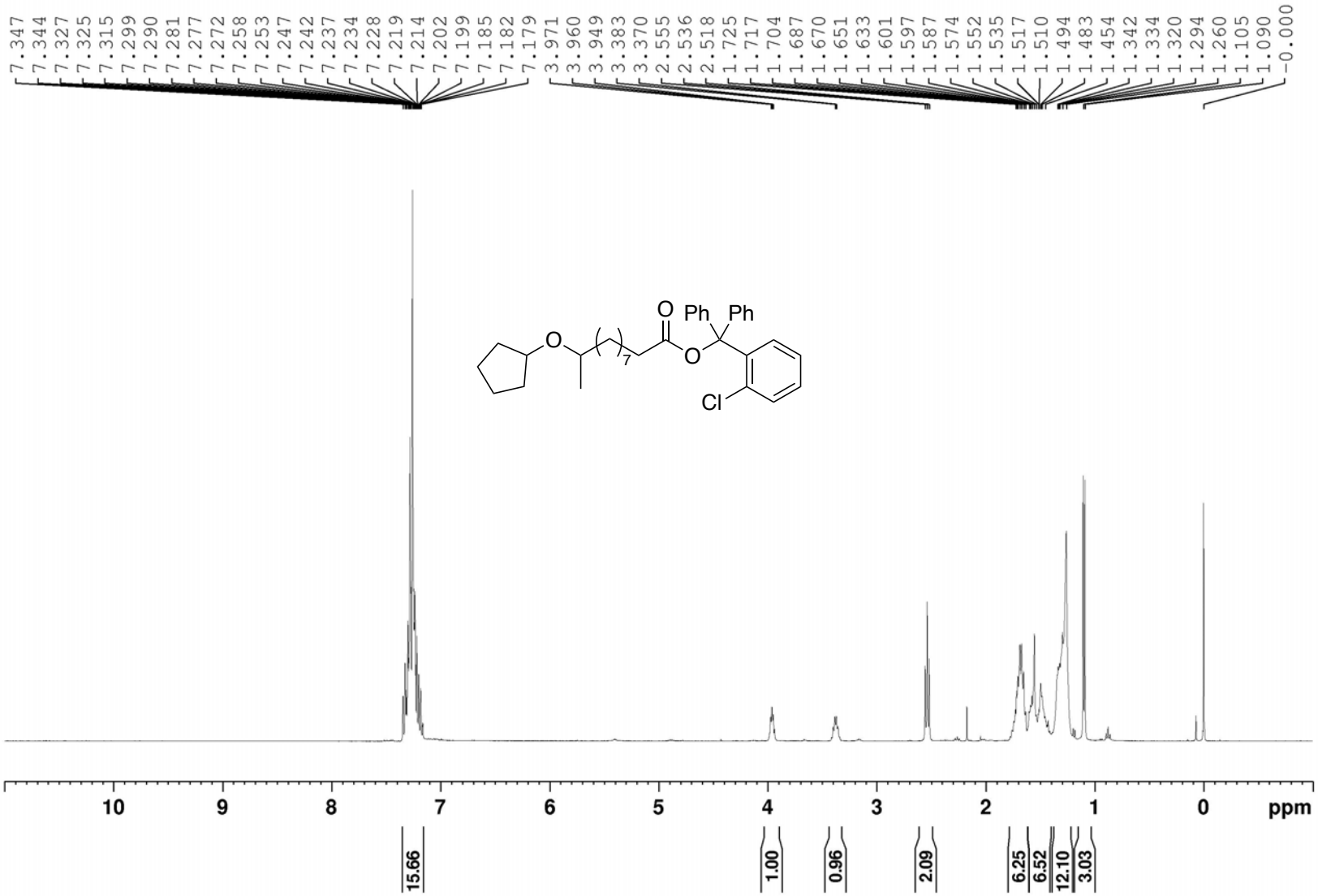

$^{13}$C NMR spectrum of **3xd**



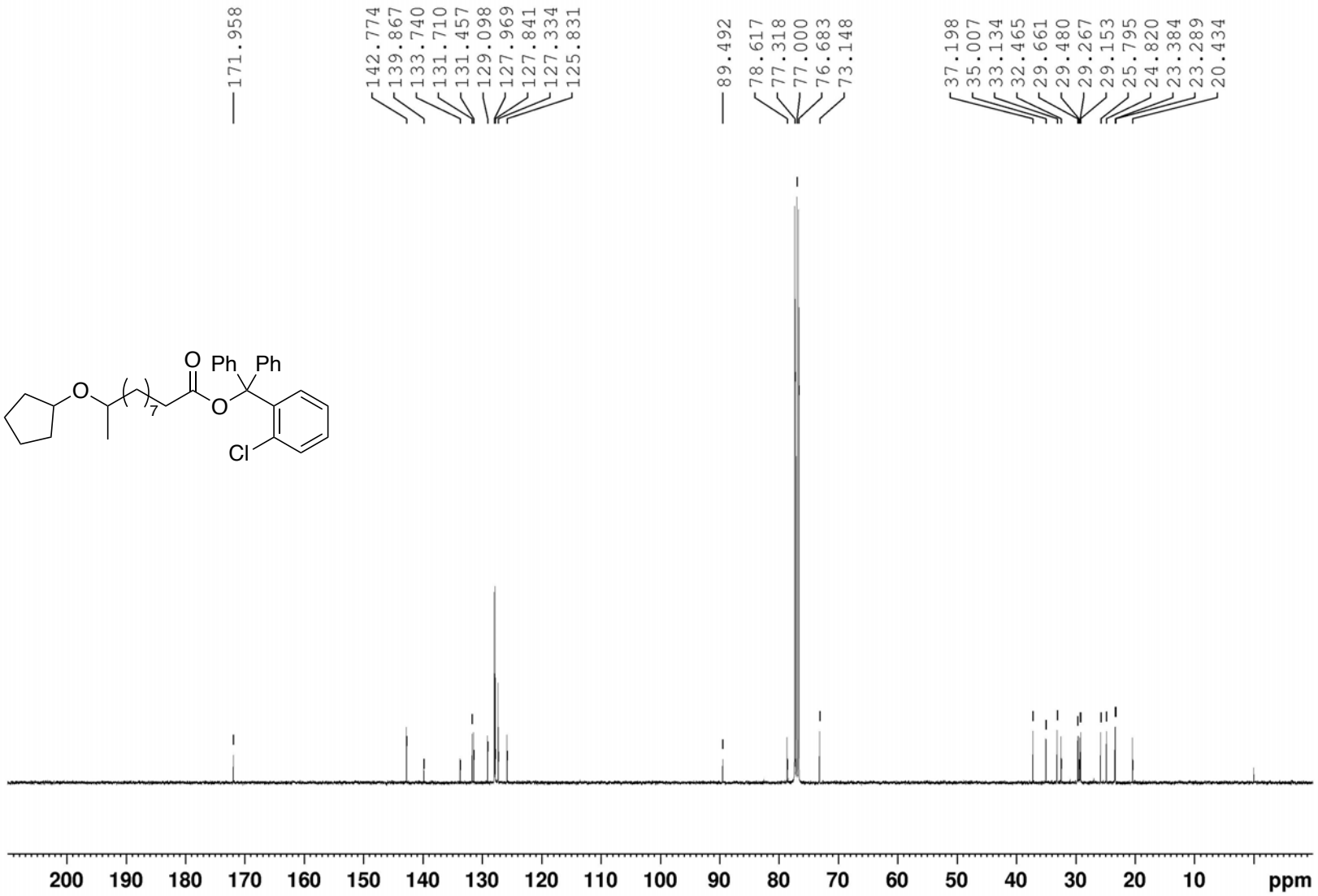

$^{1}$H NMR spectrum of **3eb**



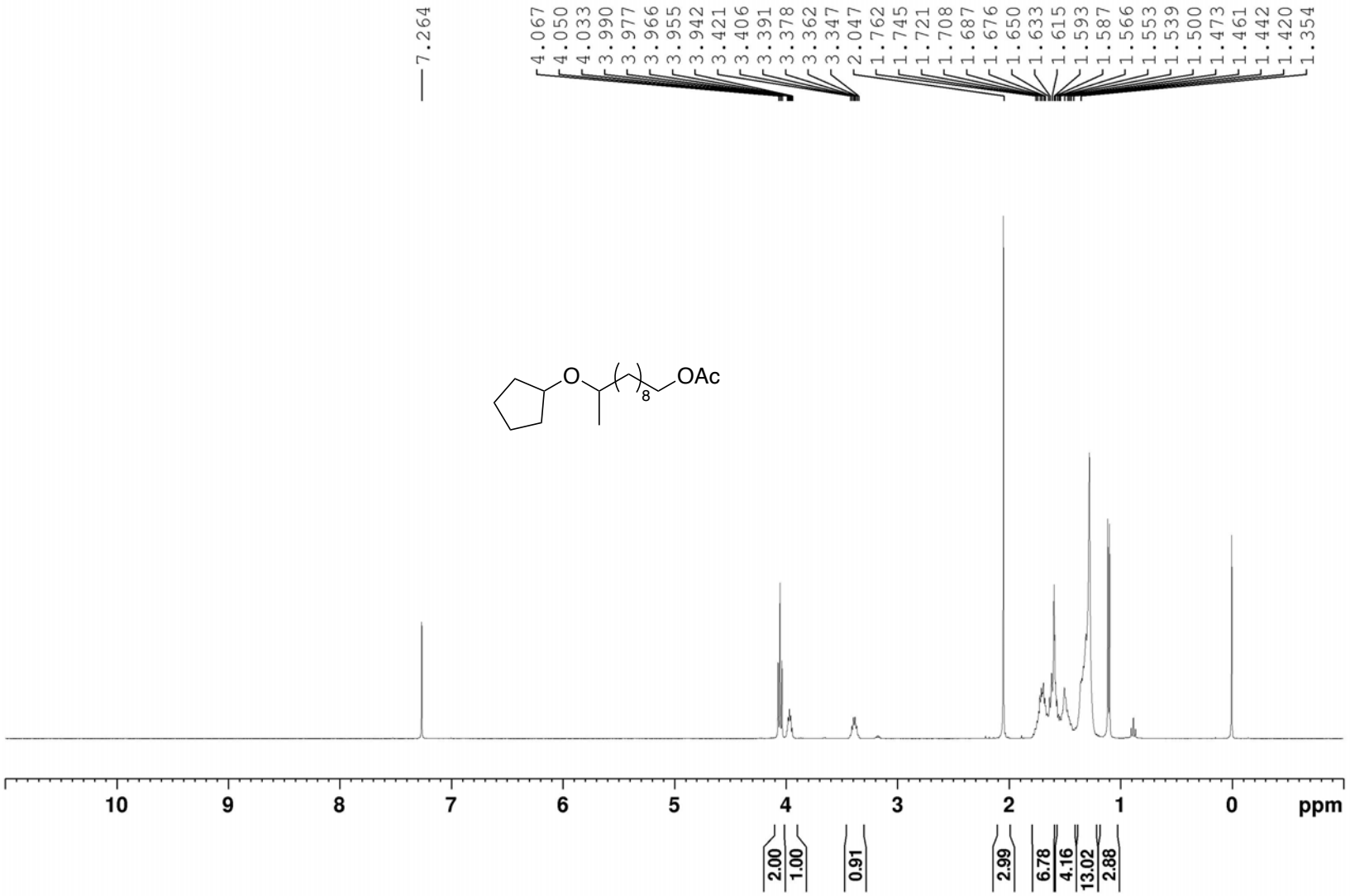

$^{13}$C NMR spectrum of **3eb**



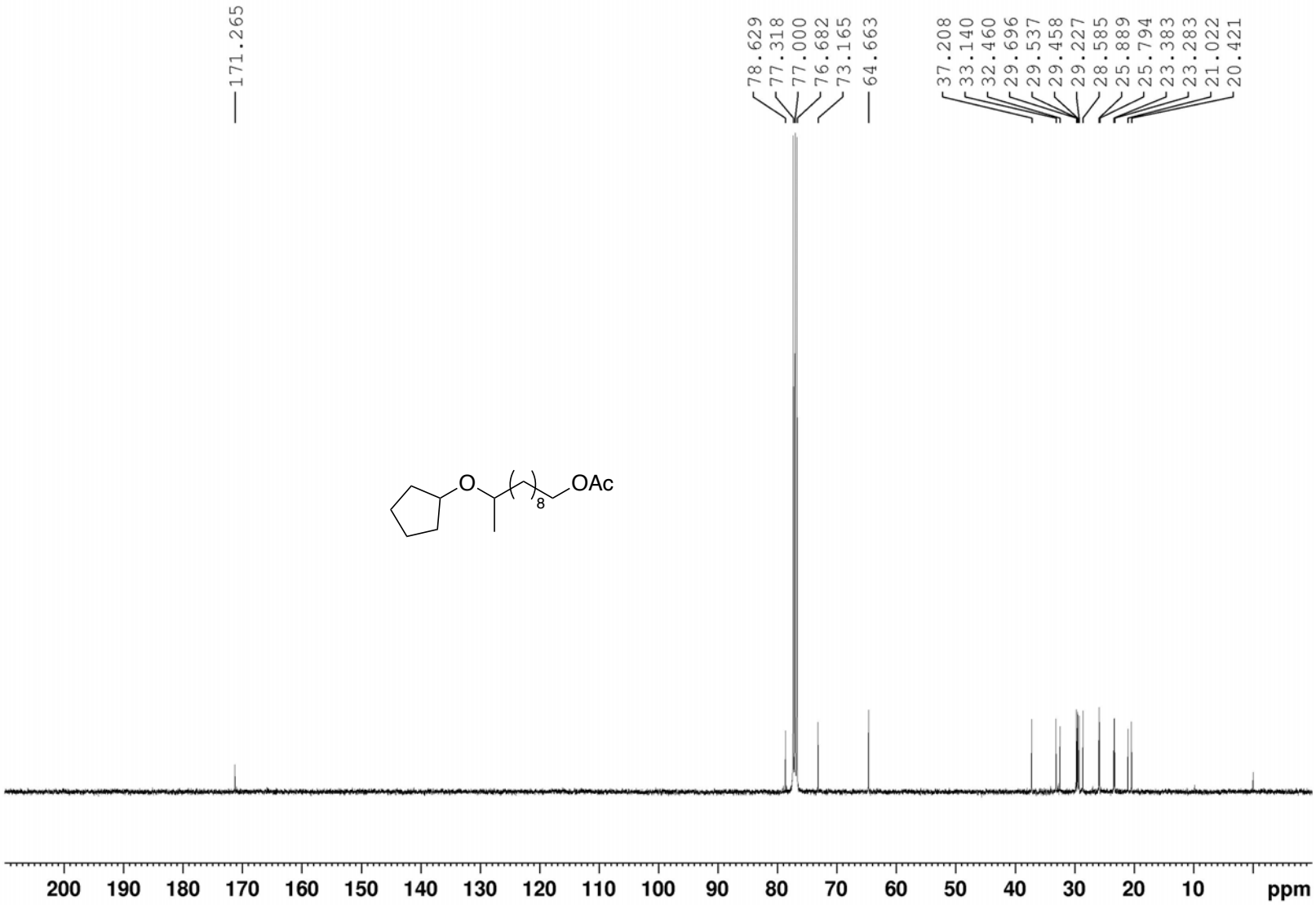

$^{1}$H NMR spectrum of **3ae**



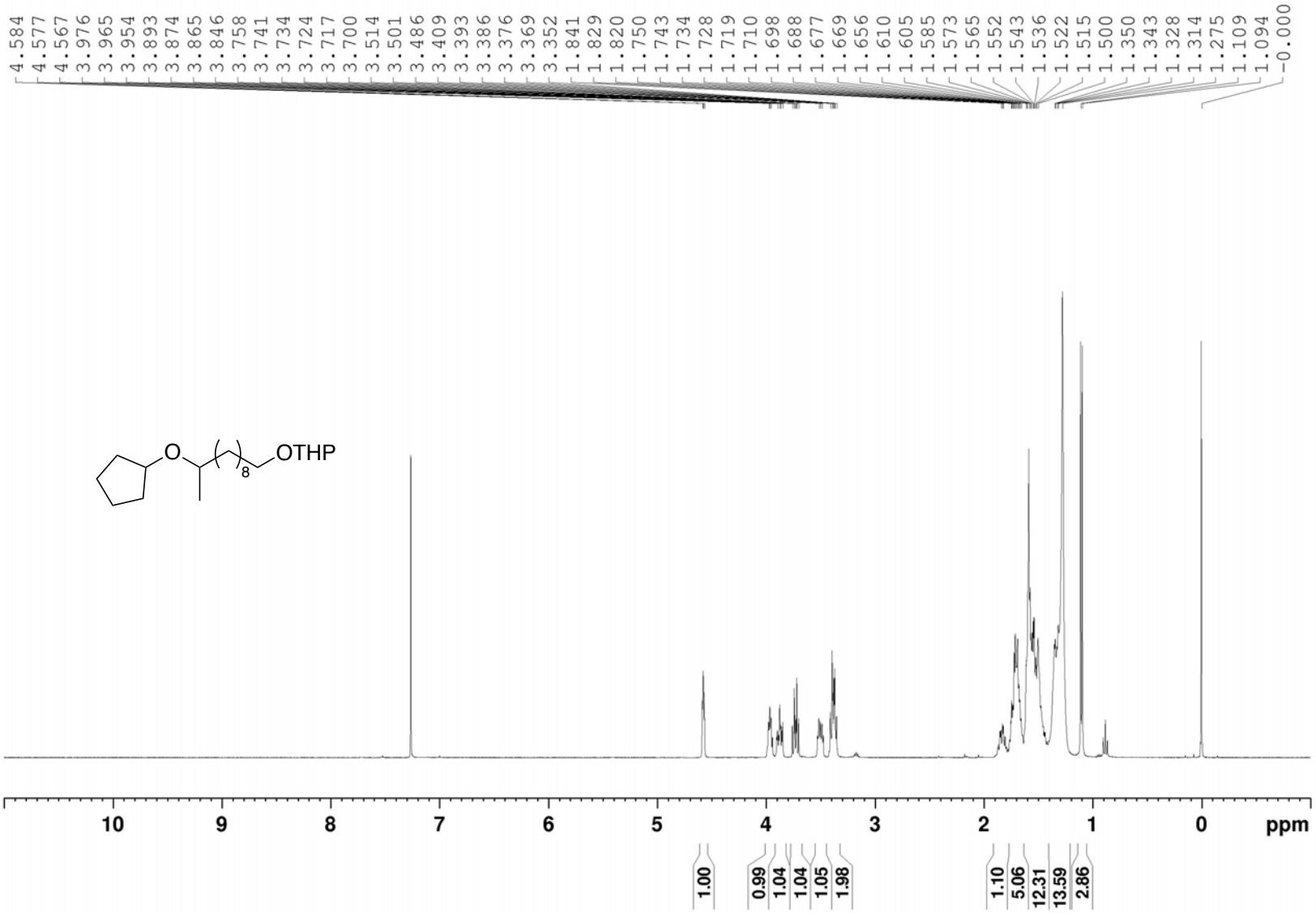

$^{13}$C NMR spectrum of **3ae**



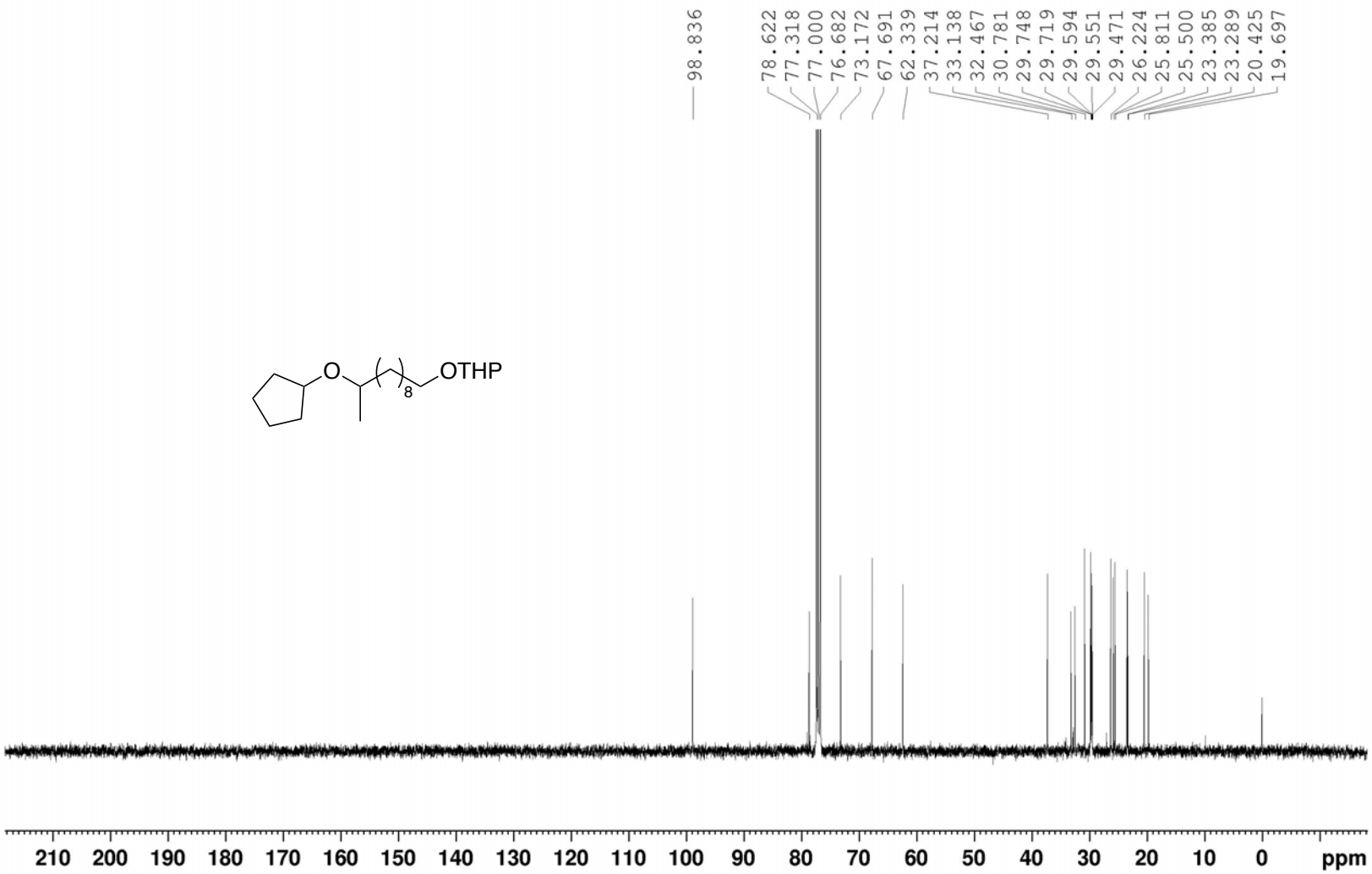

$^{1}$H NMR spectrum of **3af**



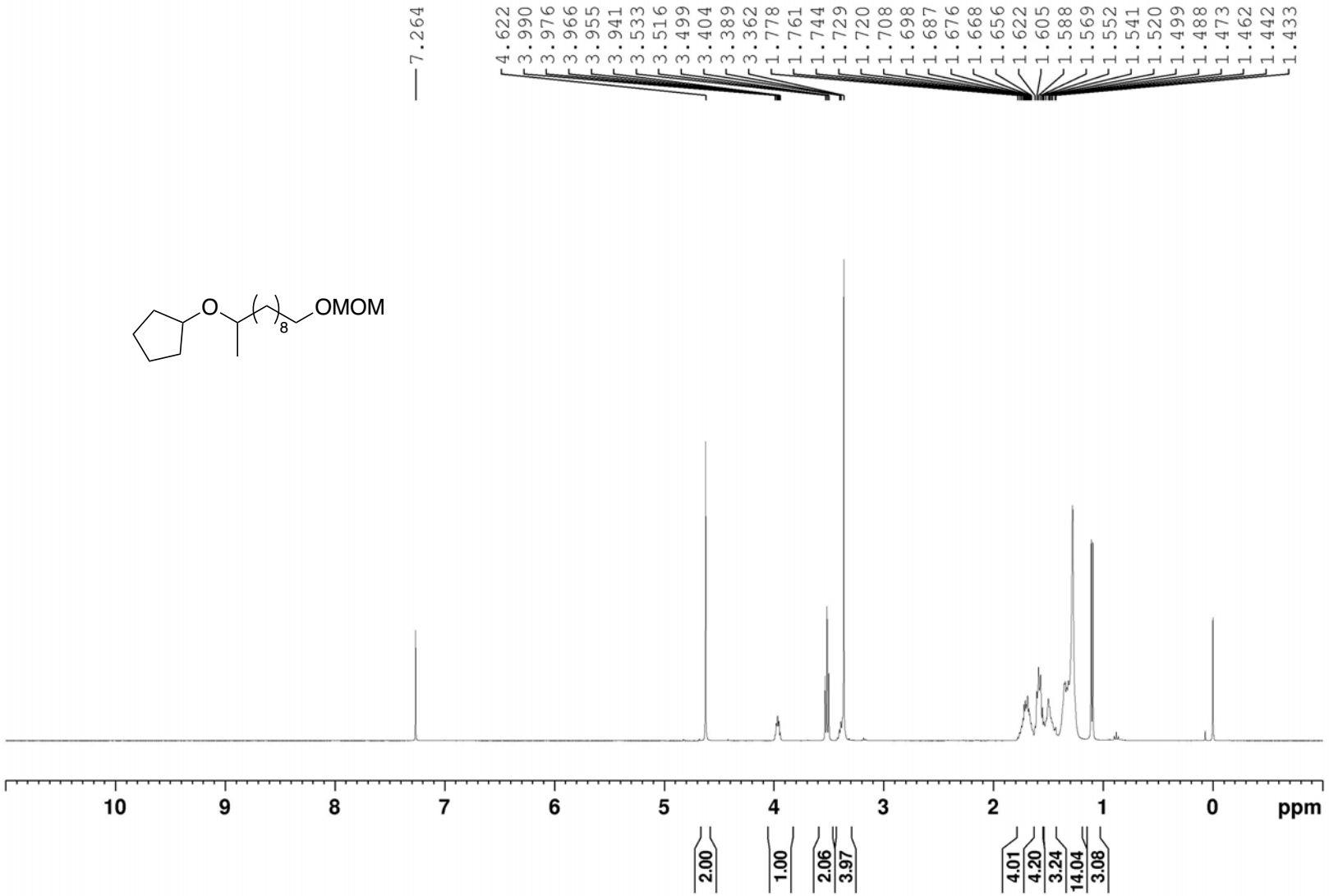

$^{13}$C NMR spectrum of **3af**



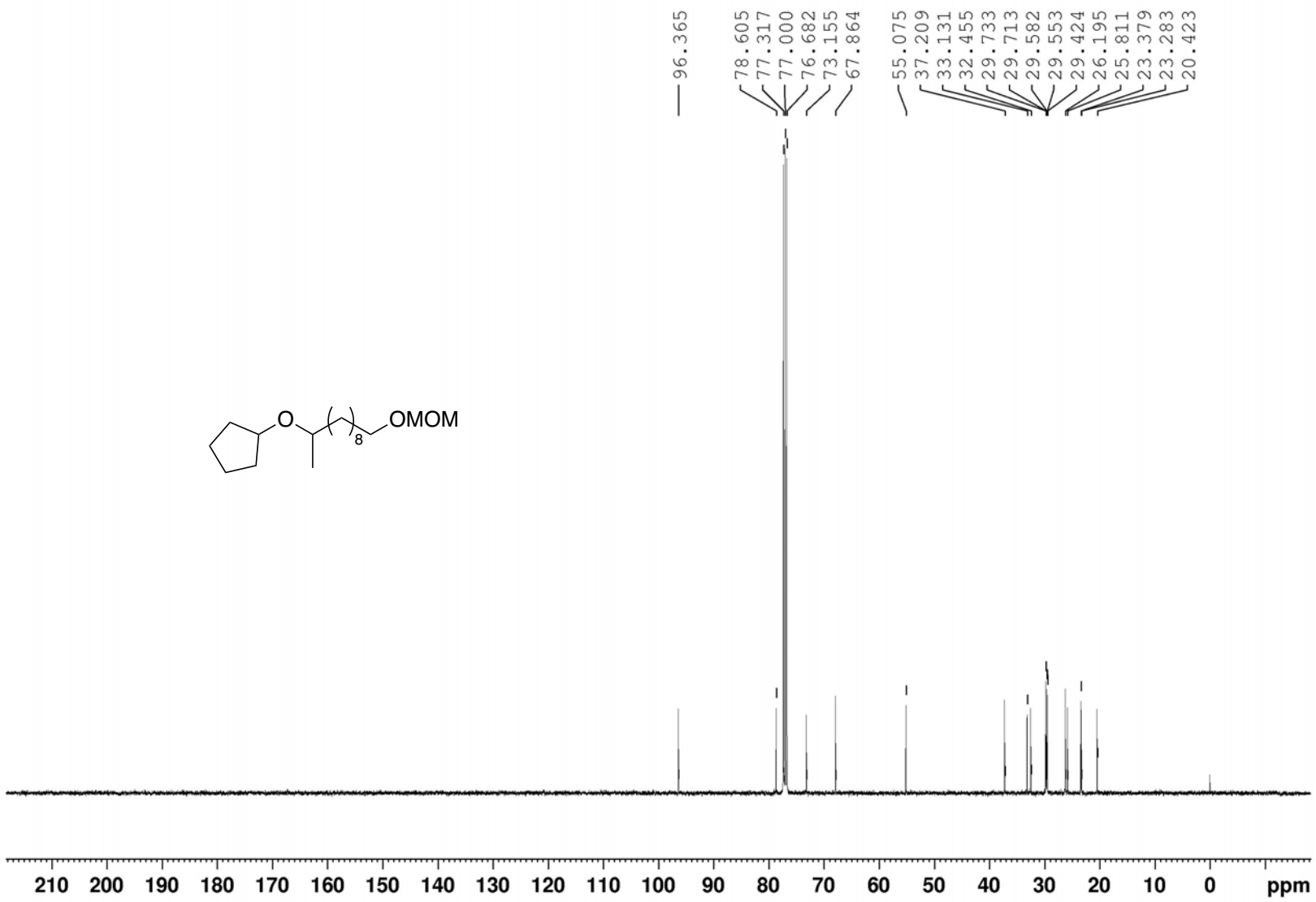

$^{1}$H NMR spectrum of **3ag**



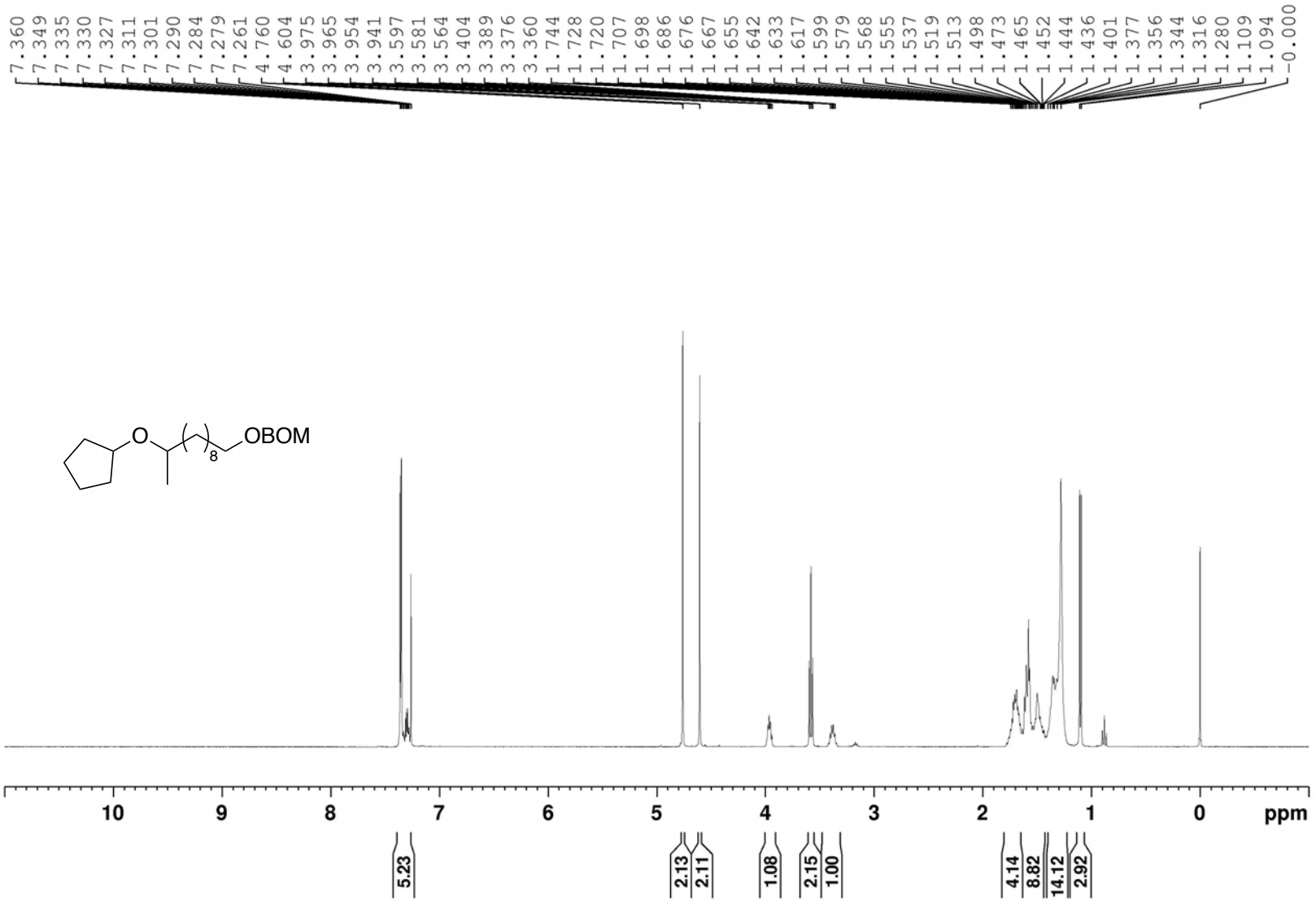

$^{13}$C NMR spectrum of **3ag**



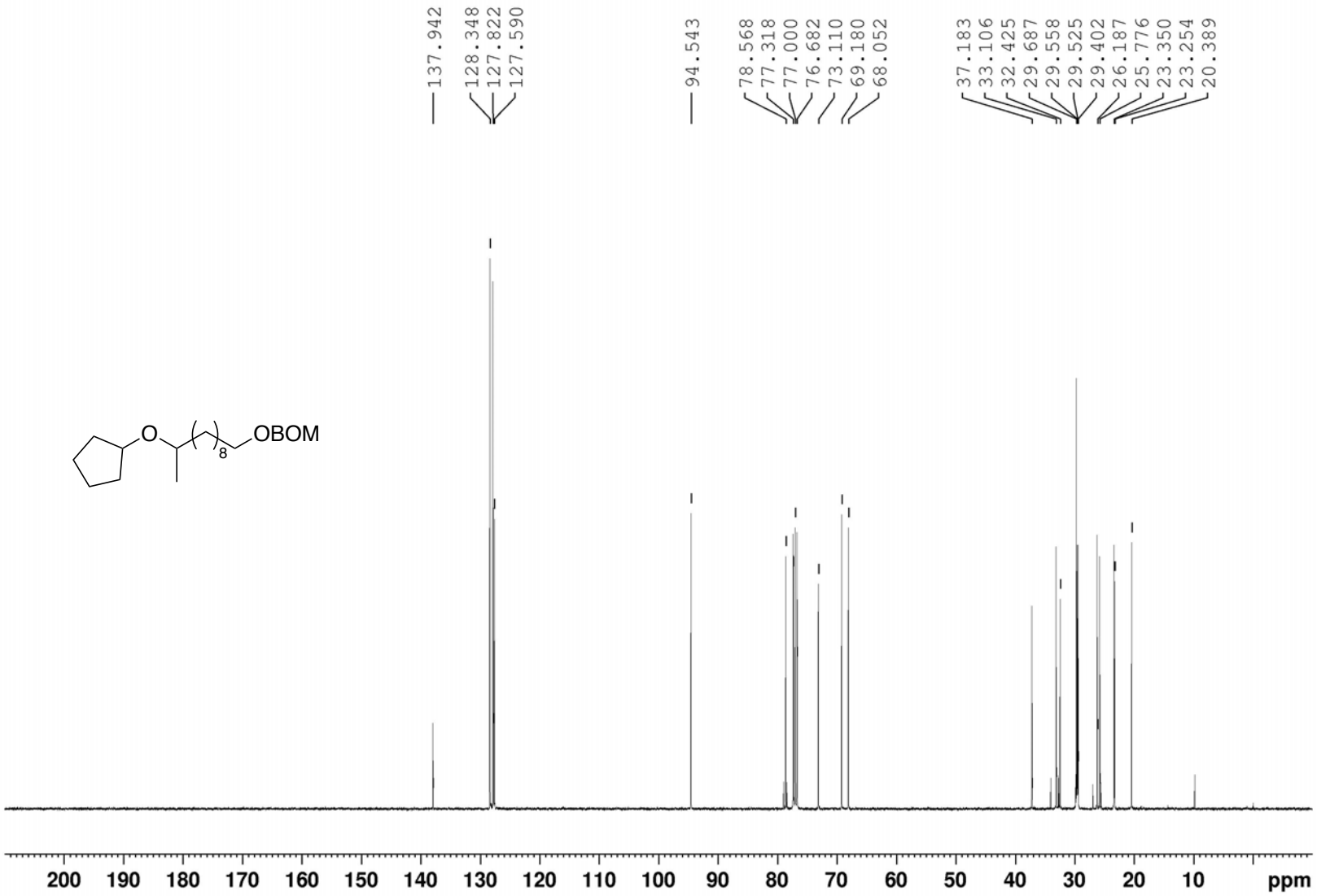

$^{1}$H NMR spectrum of **3ah**



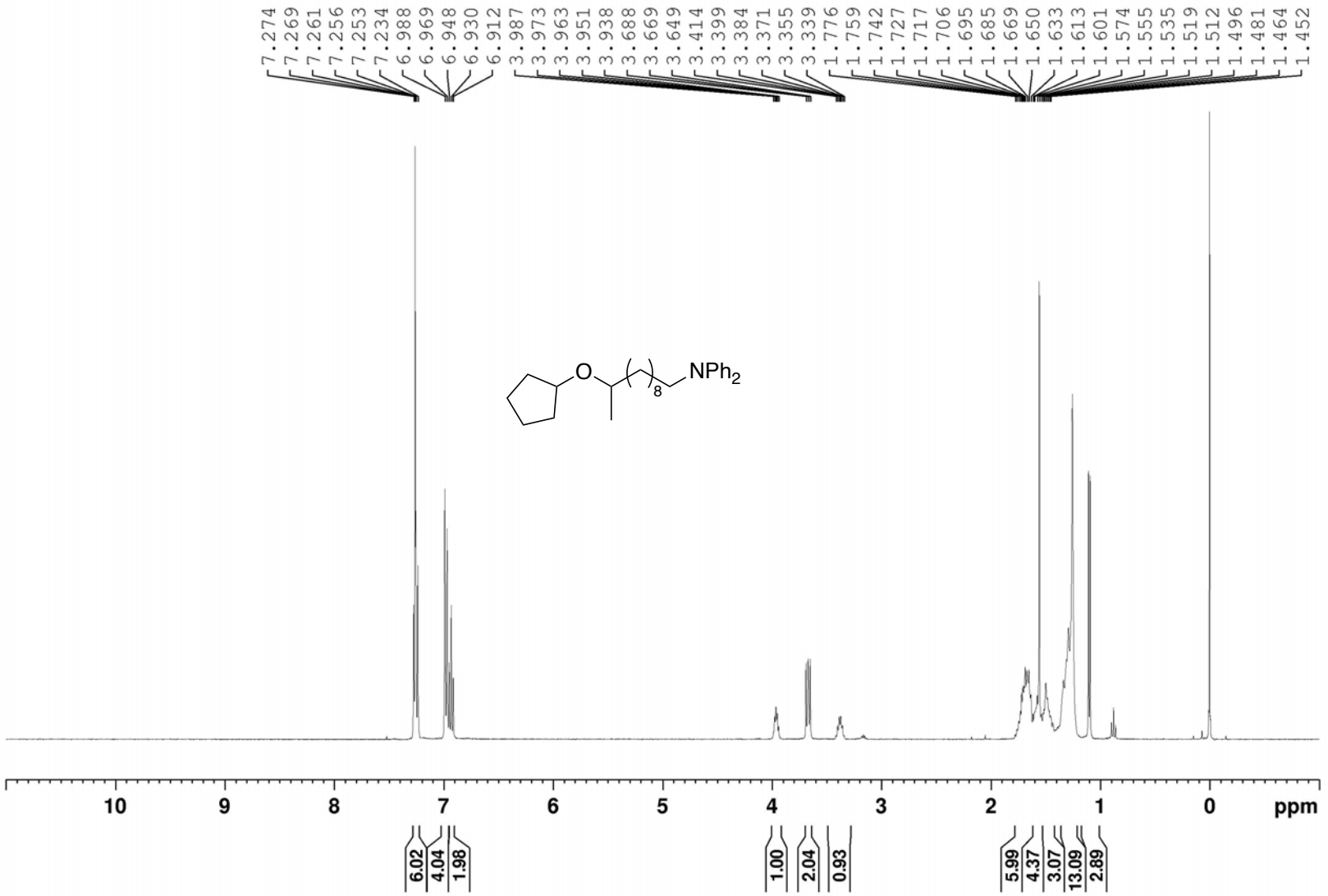

$^{13}$C NMR spectrum of **3ah**



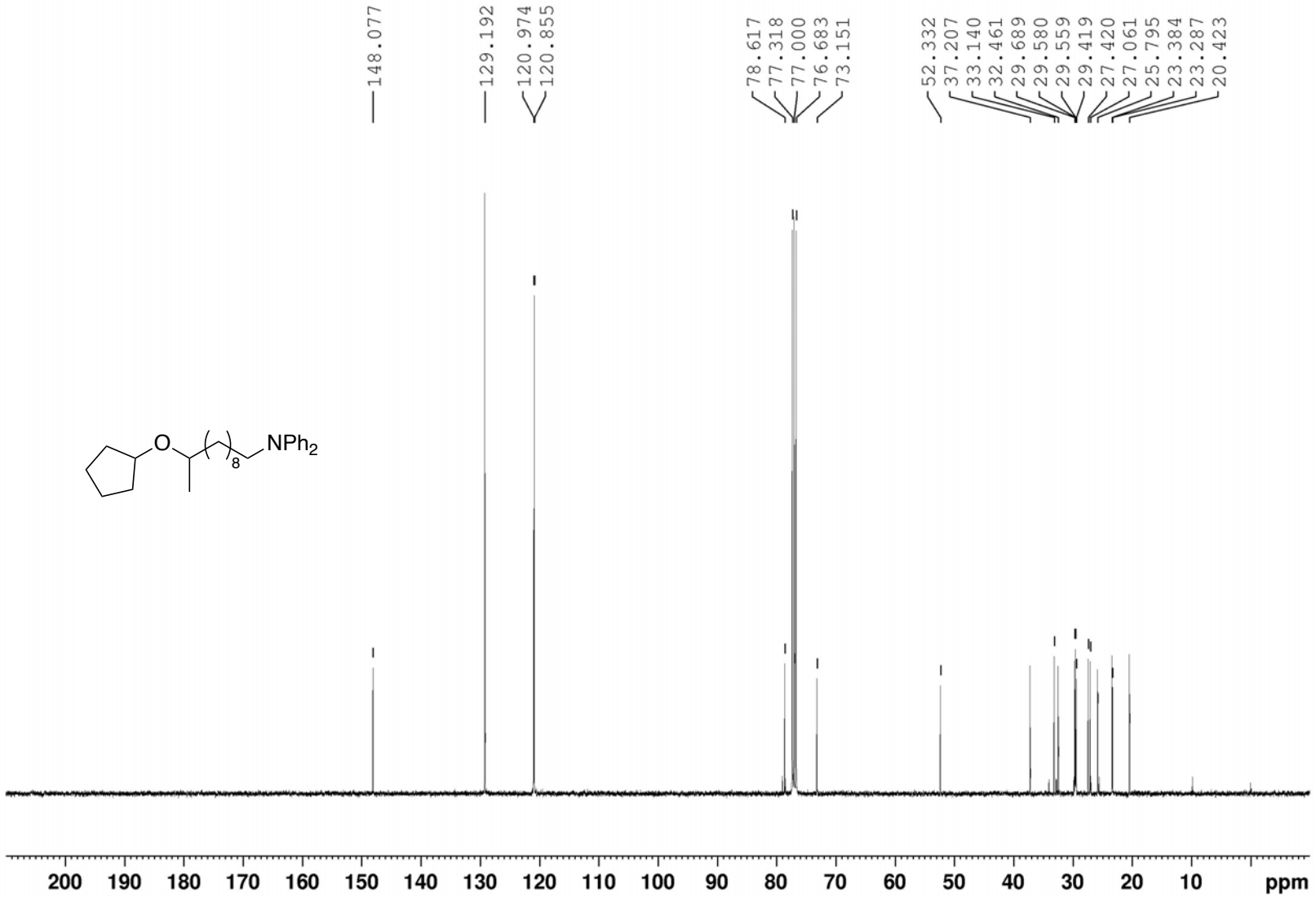

$^{1}$H NMR spectrum of **3ai**



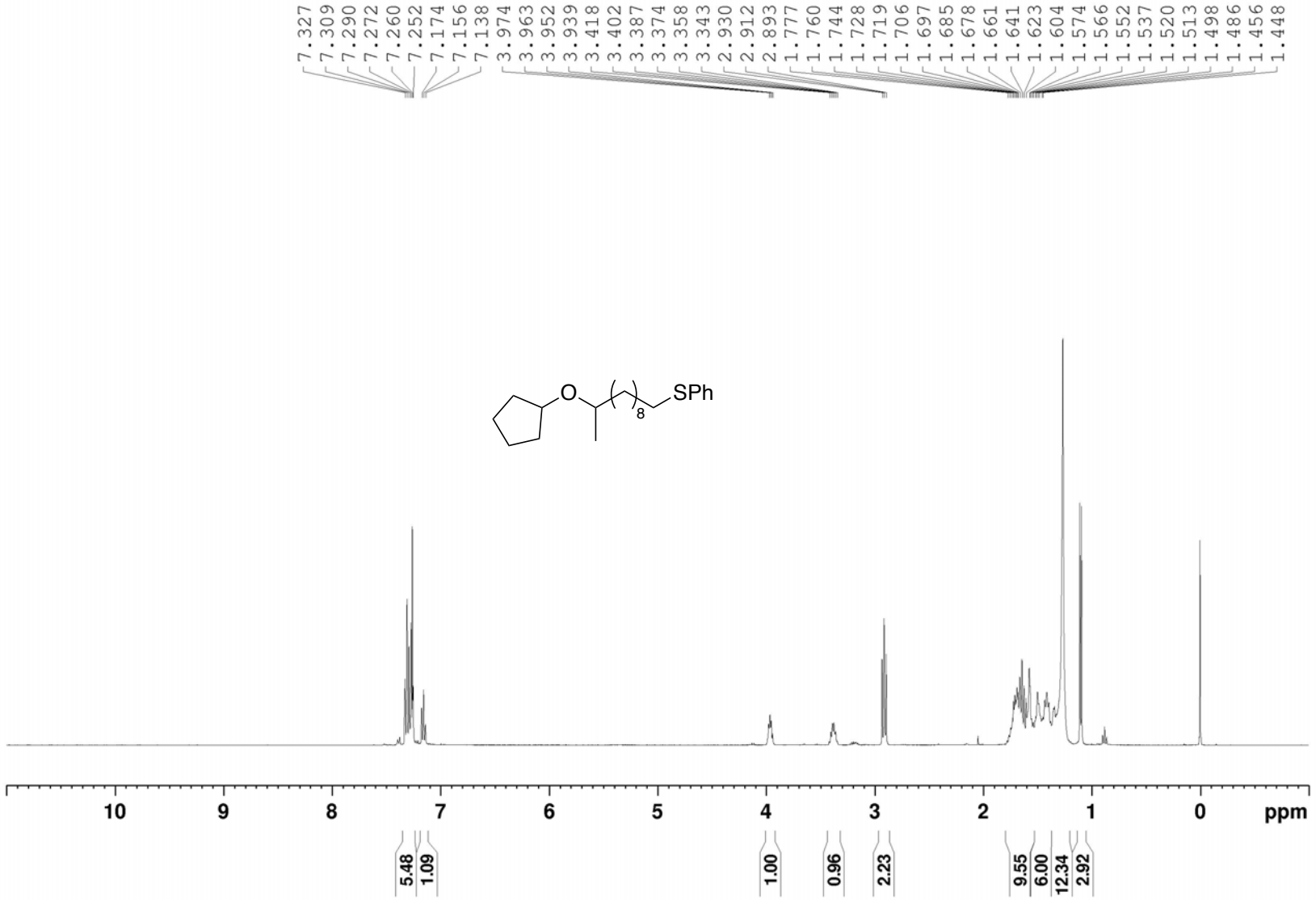

$^{13}$C NMR spectrum of **3ai**



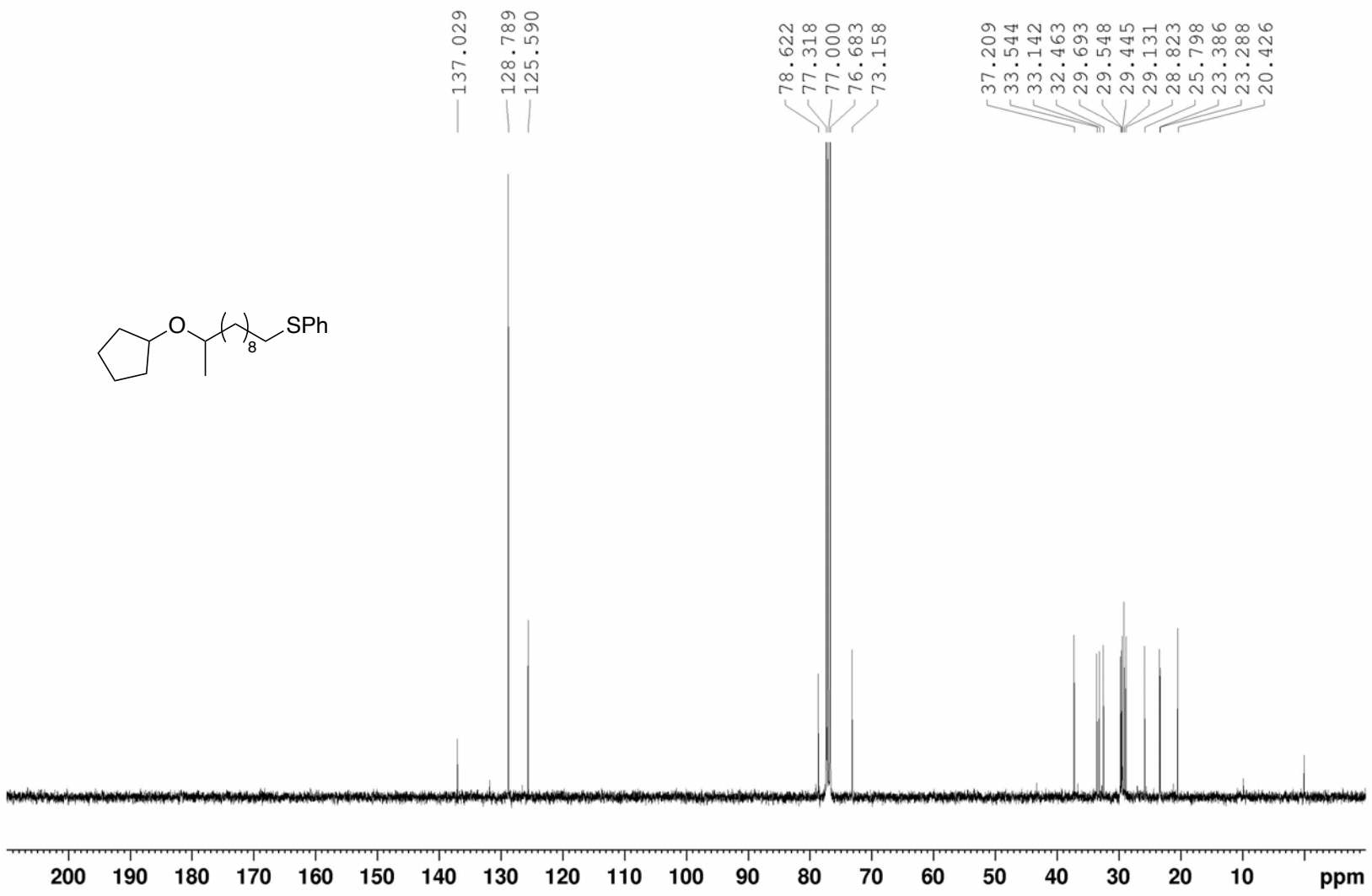

$^{1}$H NMR spectrum of **3aj**



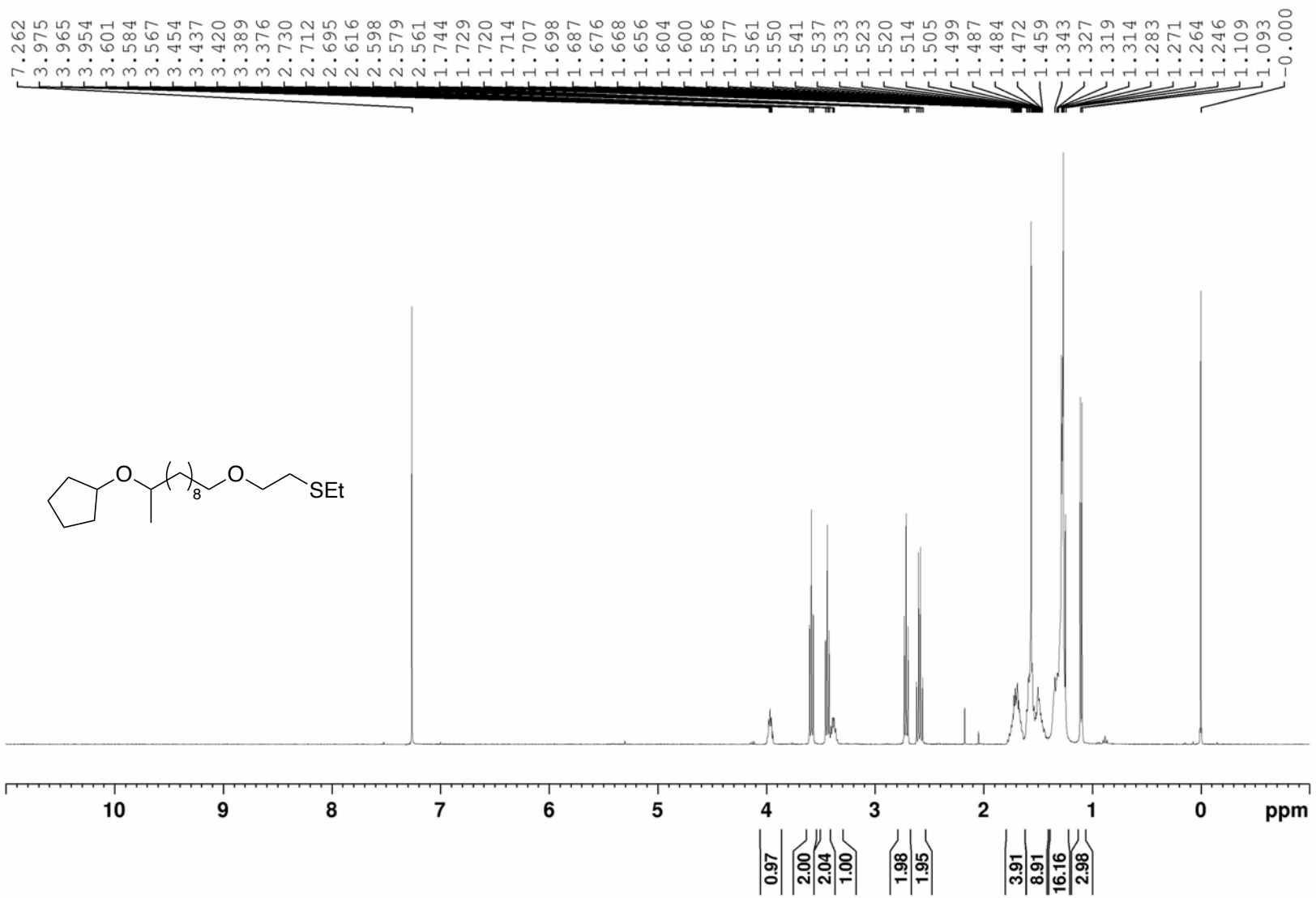

$^{13}$C NMR spectrum of **3aj**



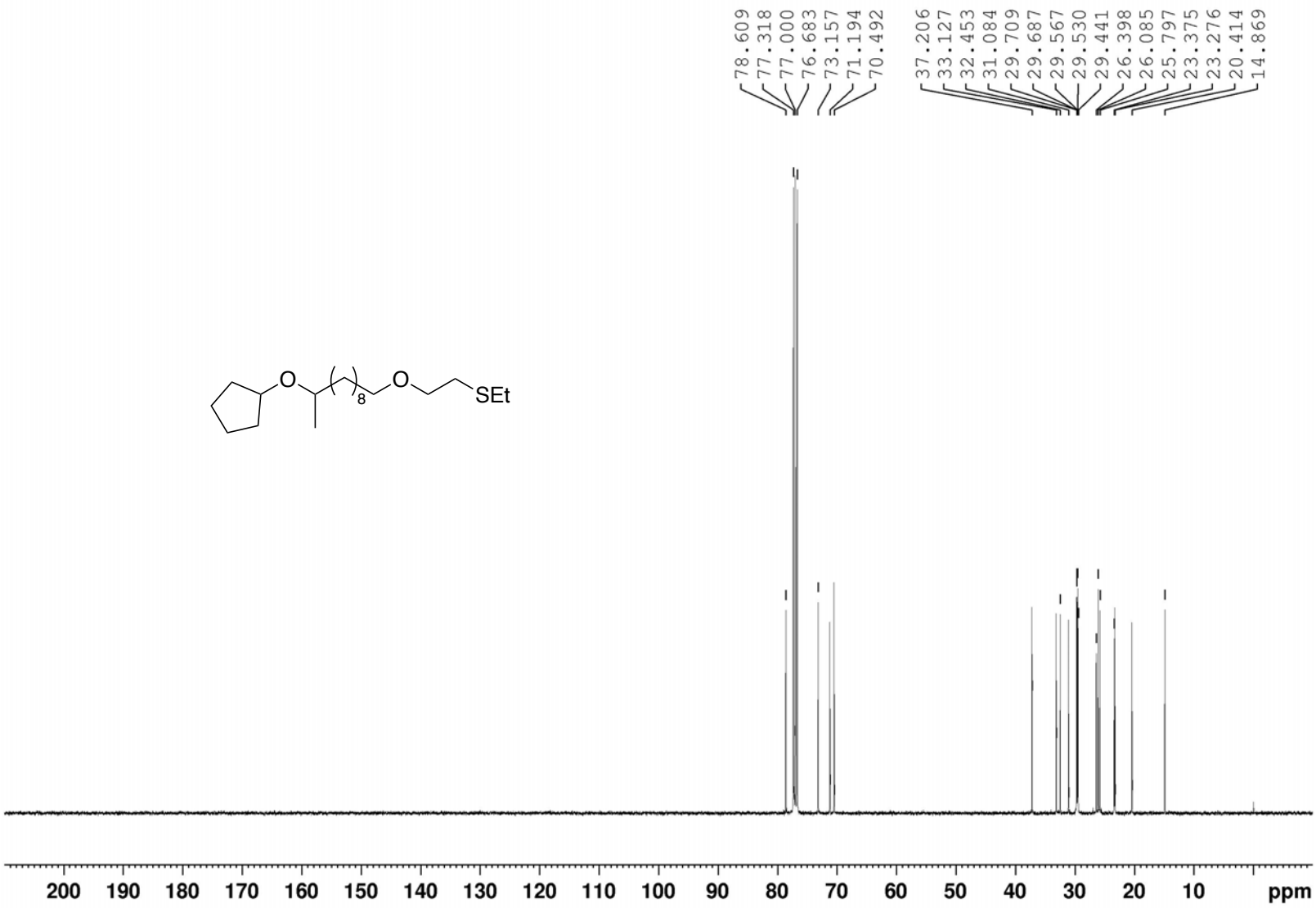

$^{1}$H NMR spectrum of **3ak**



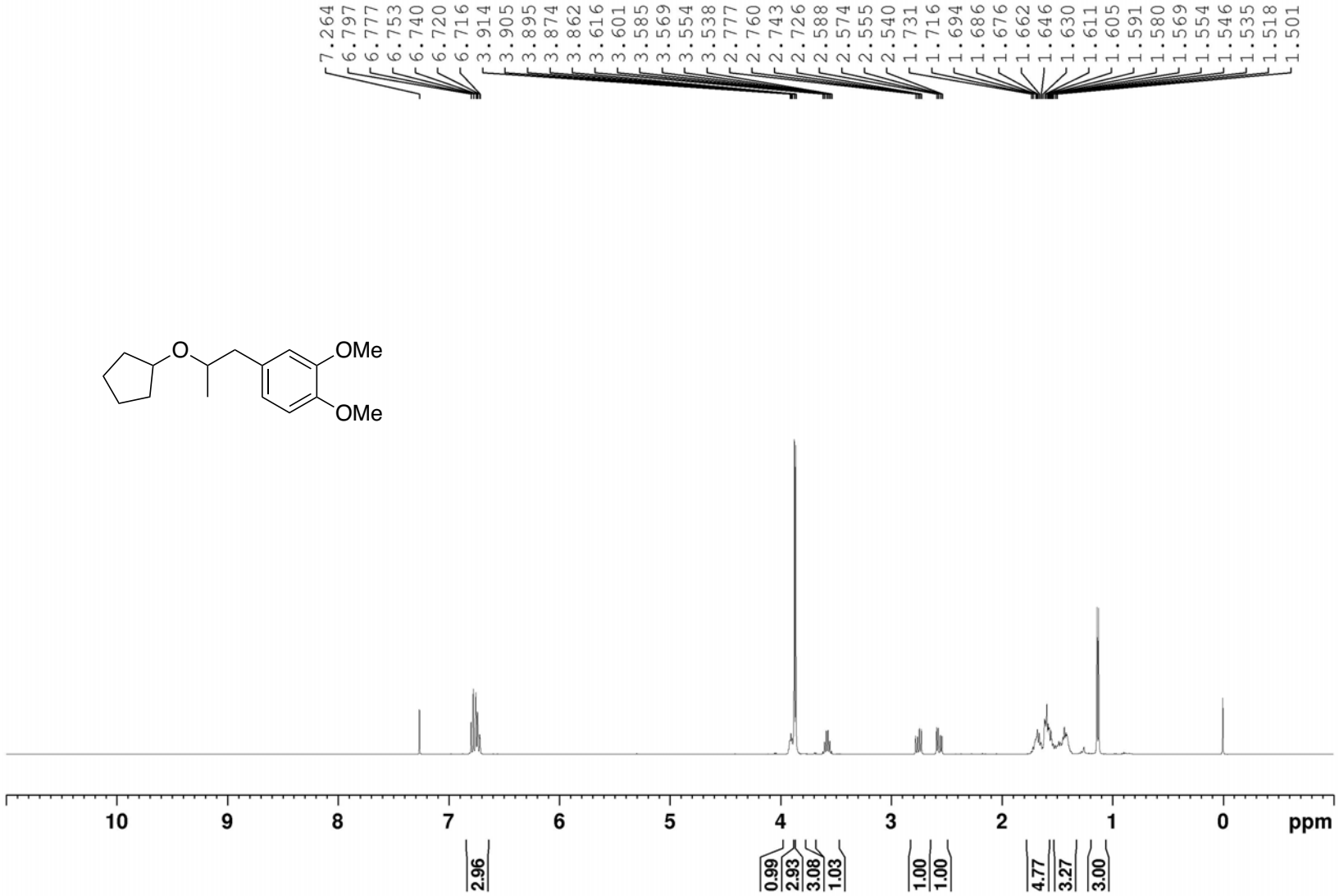

$^{13}$C NMR spectrum of **3ak**



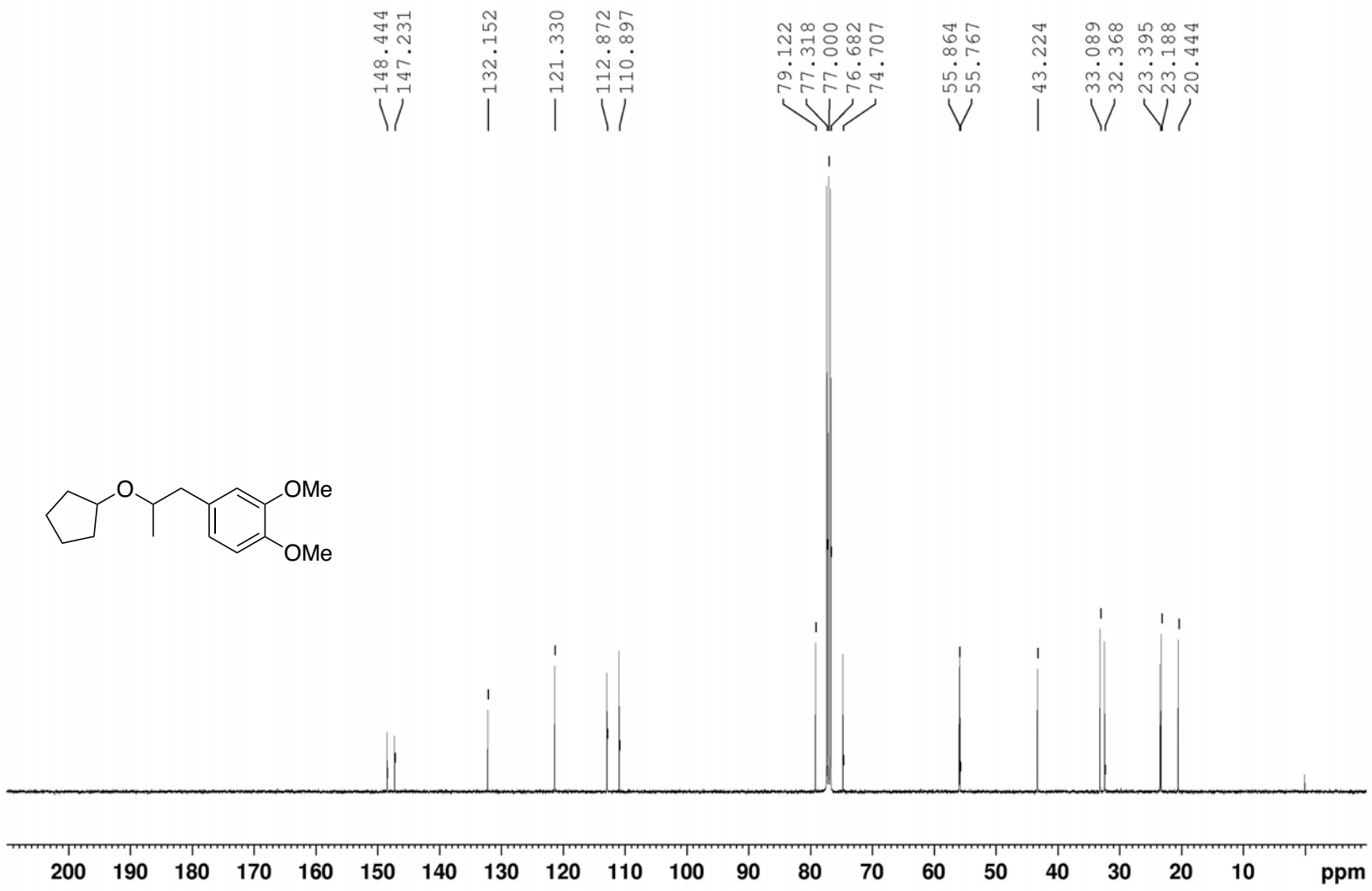

$^{1}$H NMR spectrum of **3al**



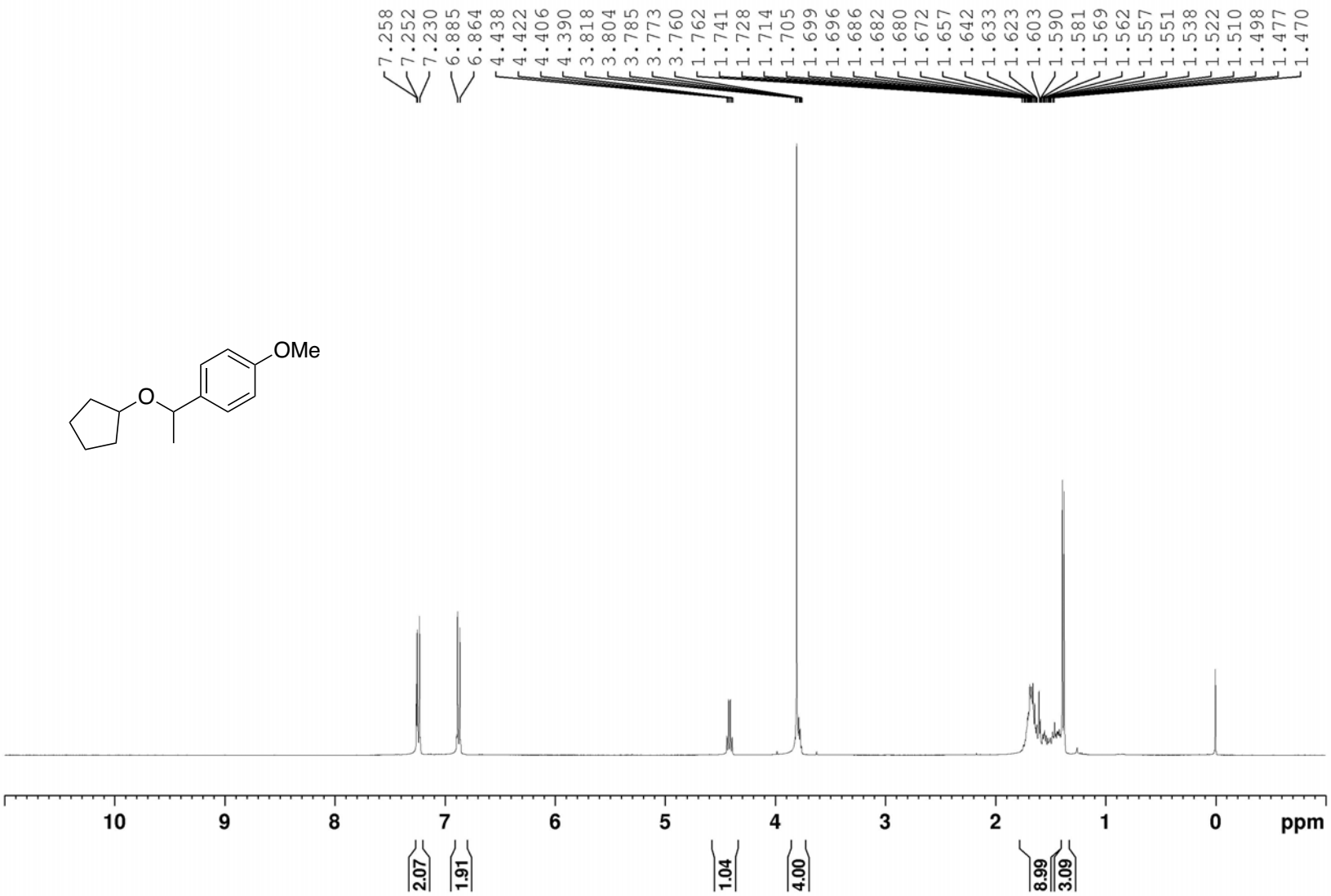

$^{13}$C NMR spectrum of **3al**



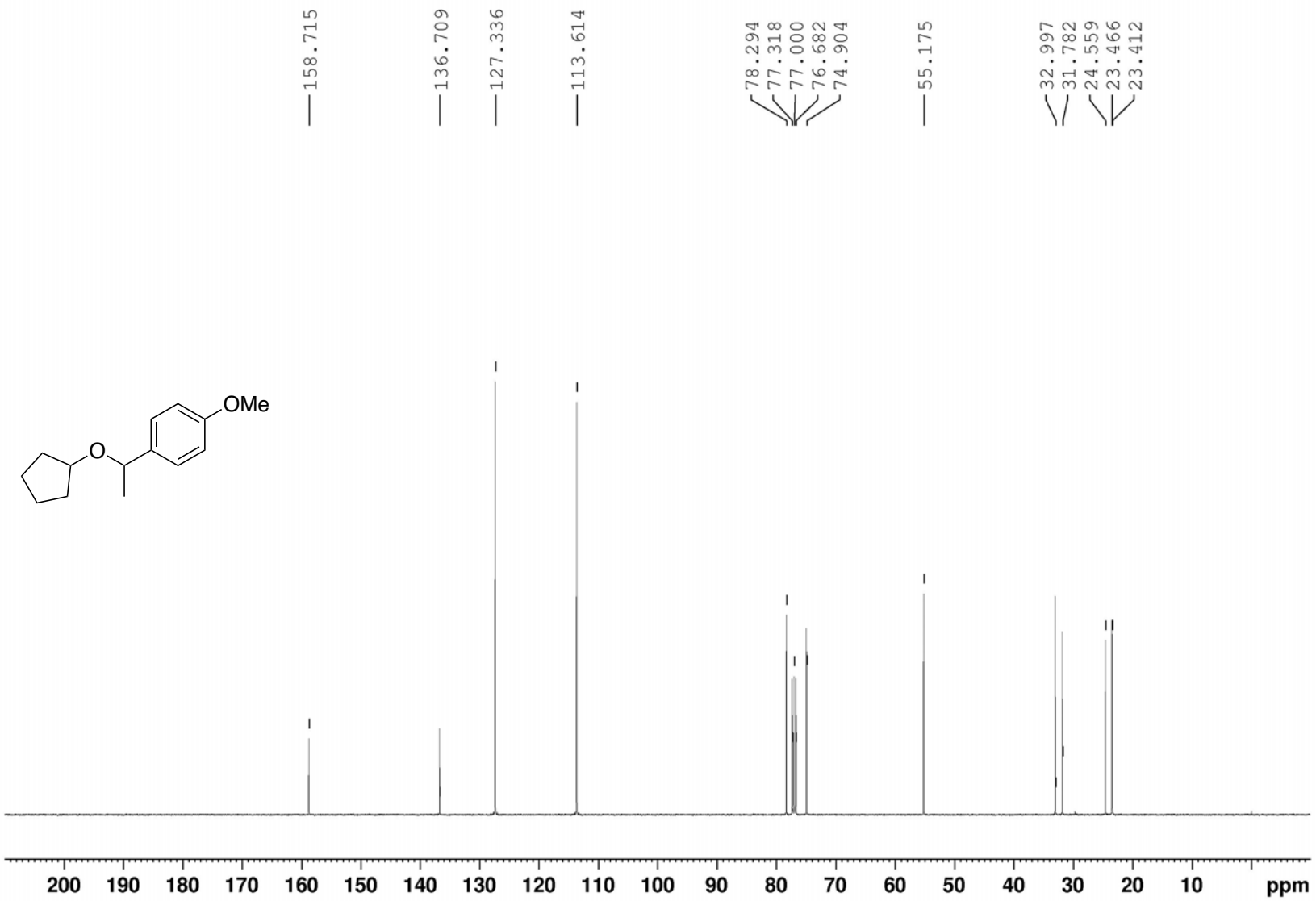

$^{1}$H NMR spectrum of **3ac**



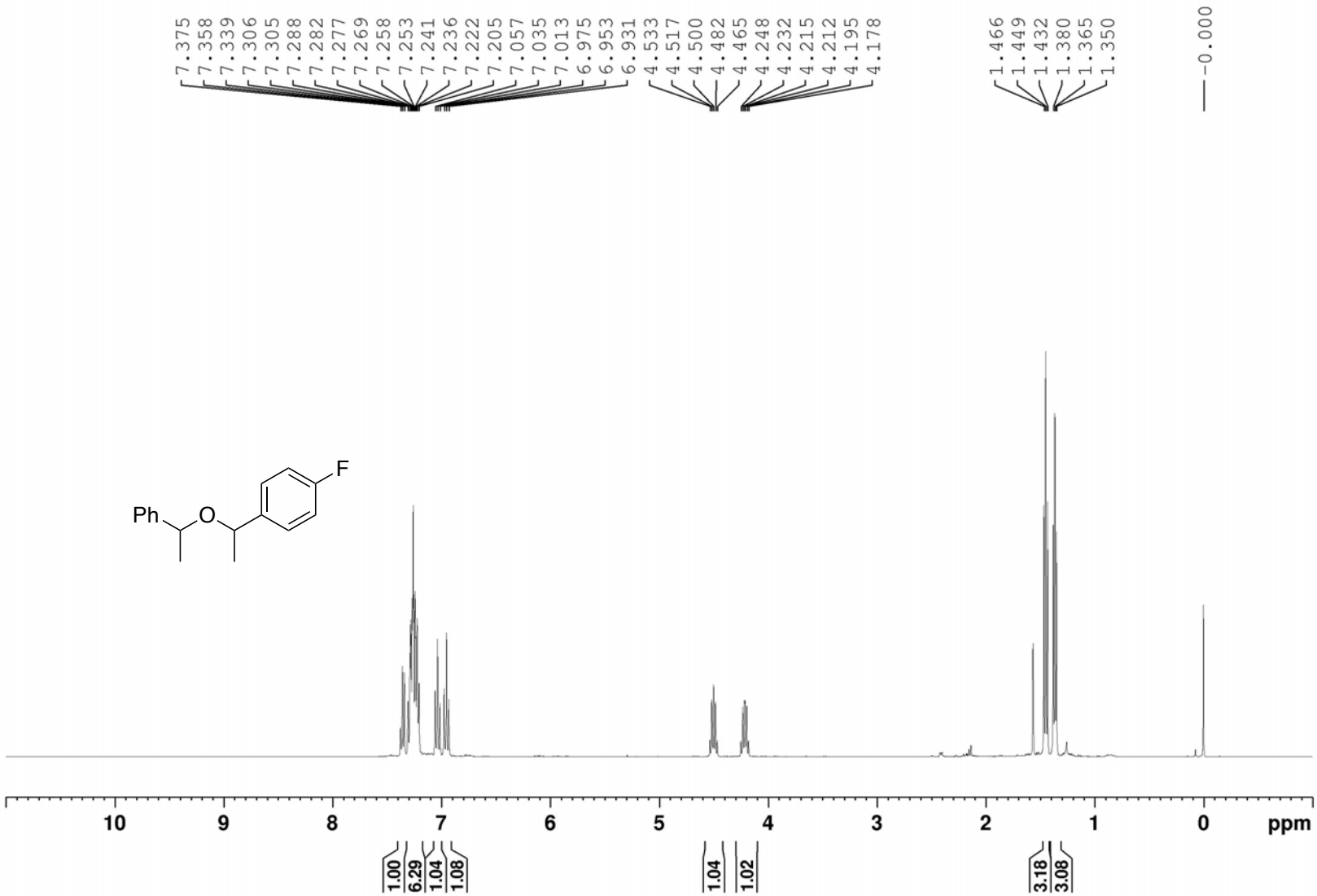

$^{13}$C NMR spectrum of **3ac**



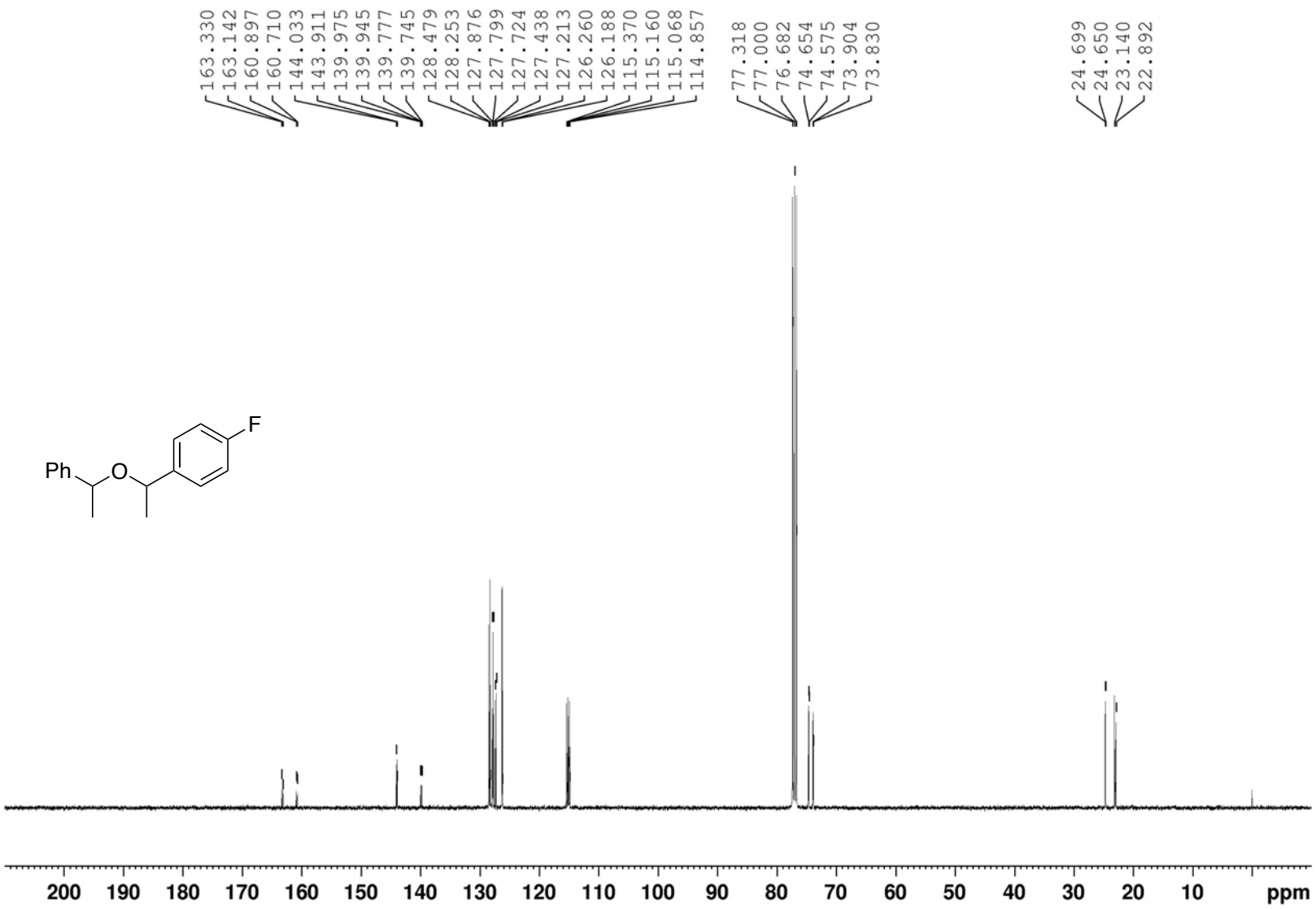

$^{1}$H NMR spectrum of **3am**



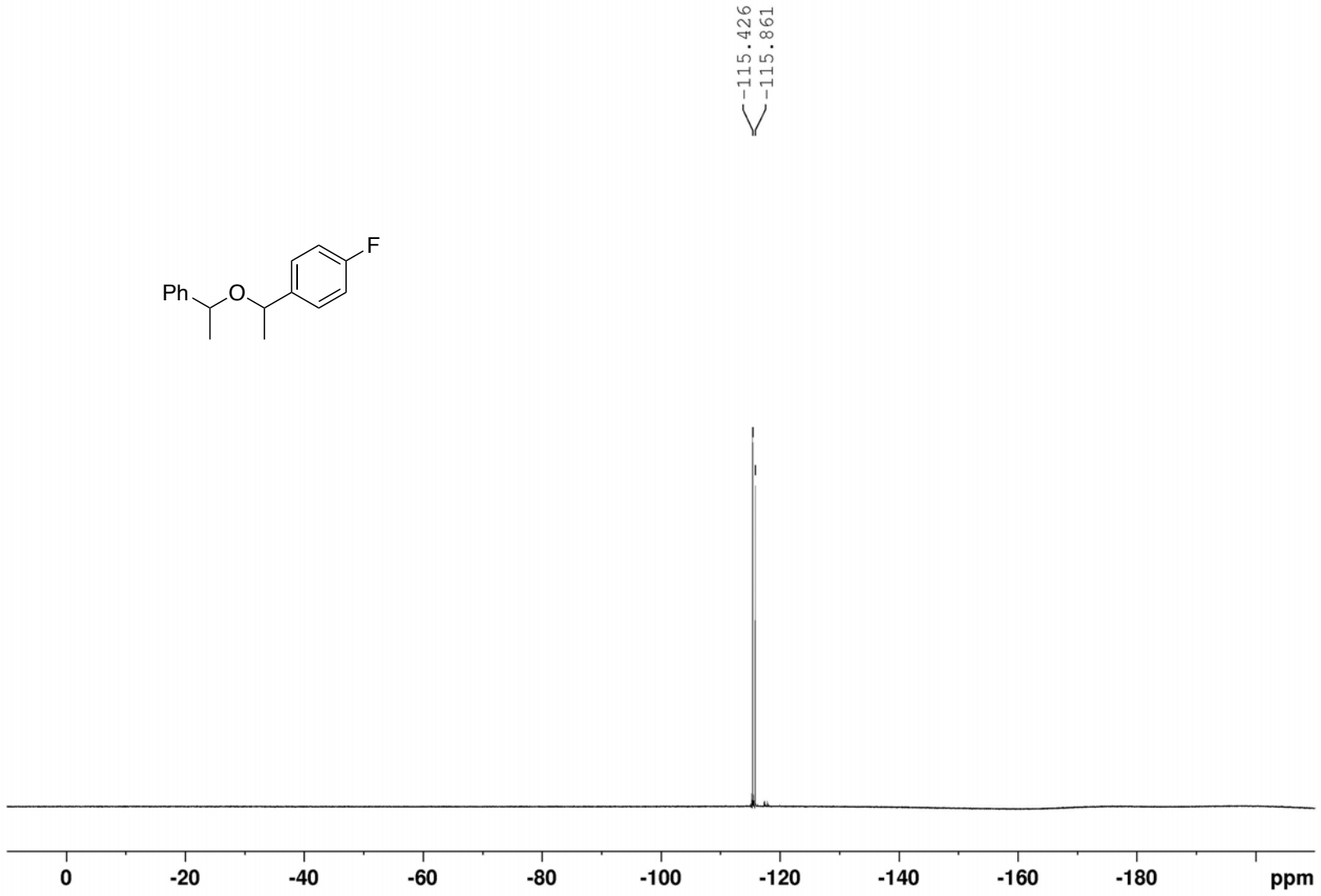

$^{13}$C NMR spectrum of **3am**



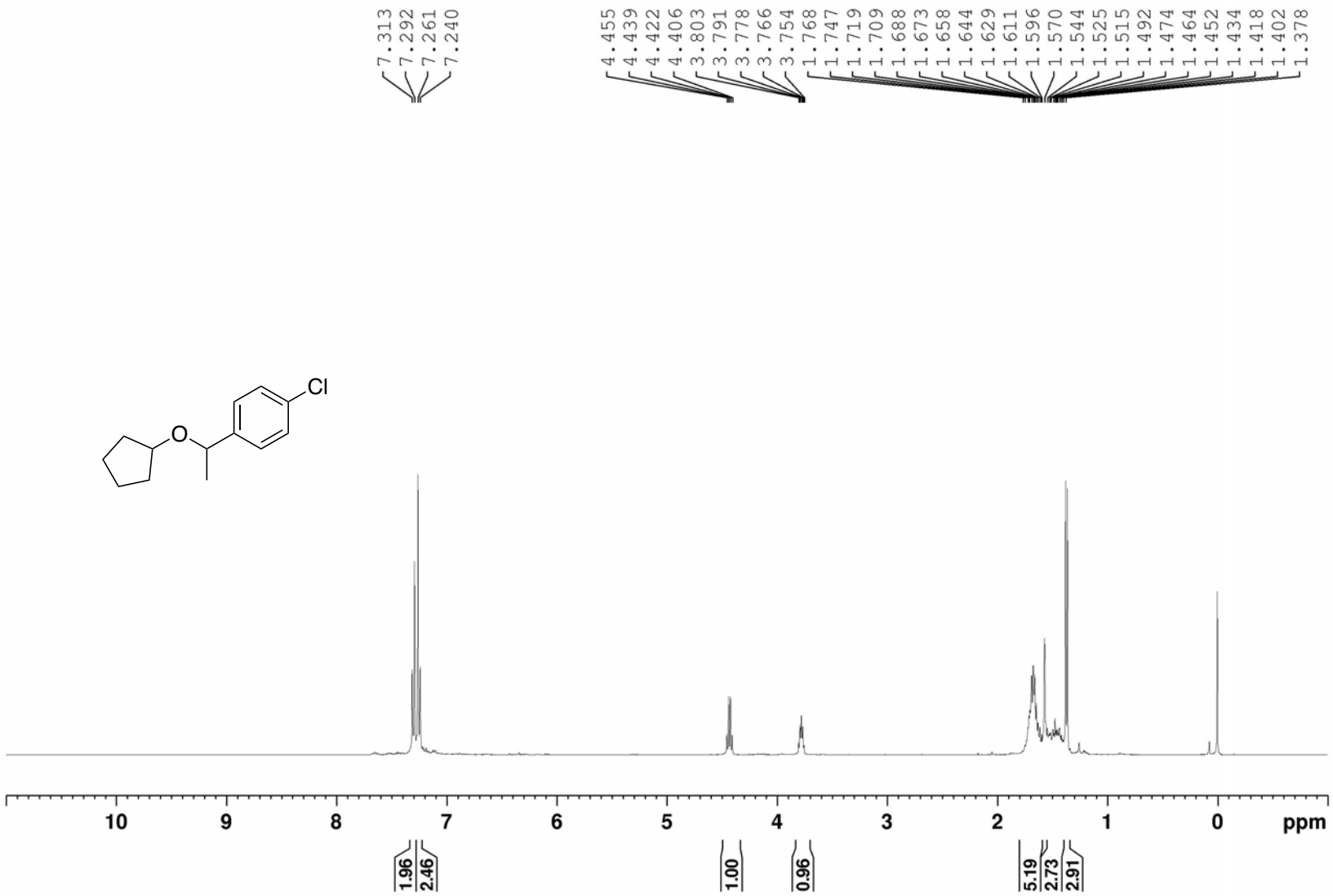

$^{1}$H NMR spectrum of **3Bn**



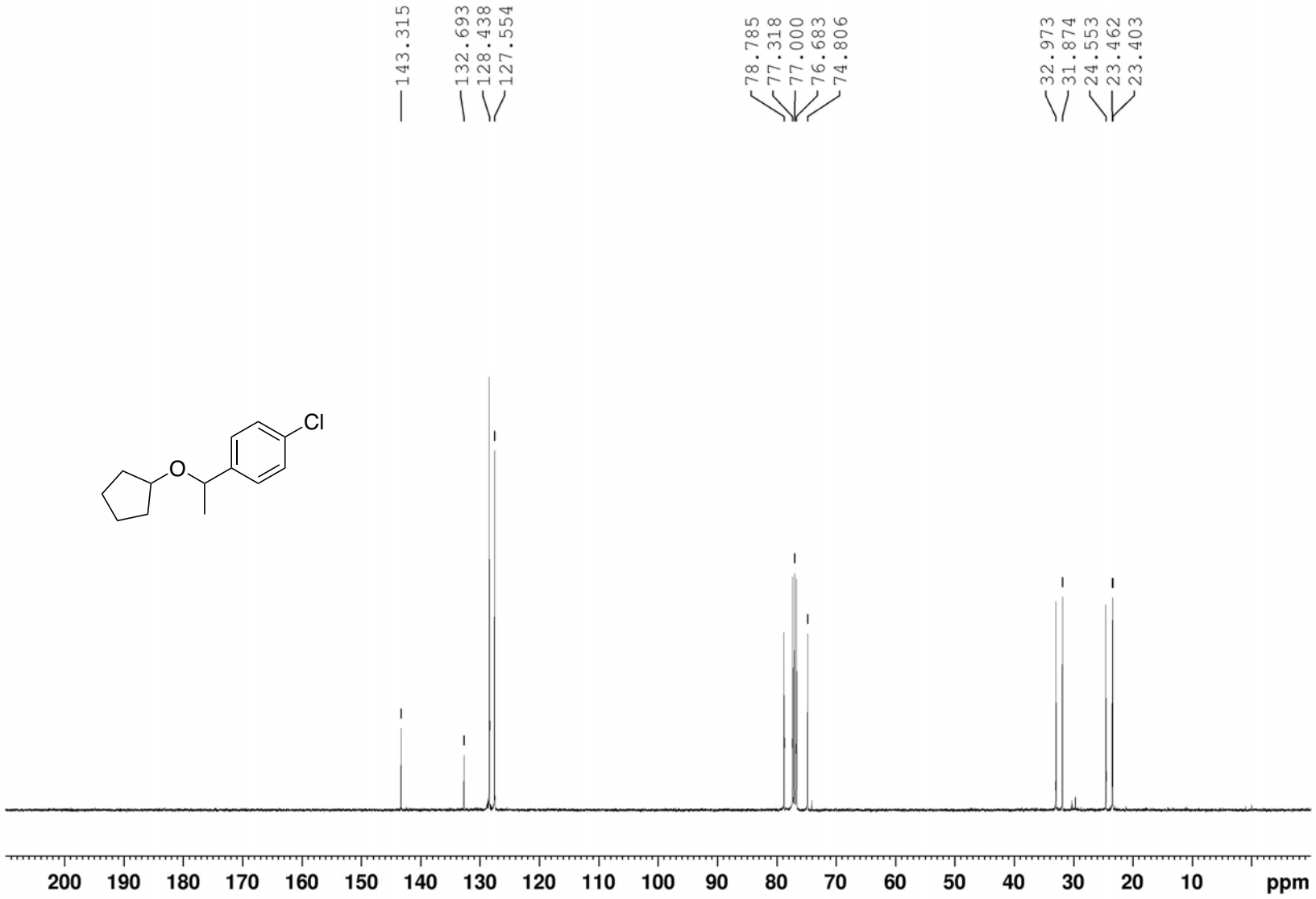

$^{13}$C NMR spectrum of **3Bn**



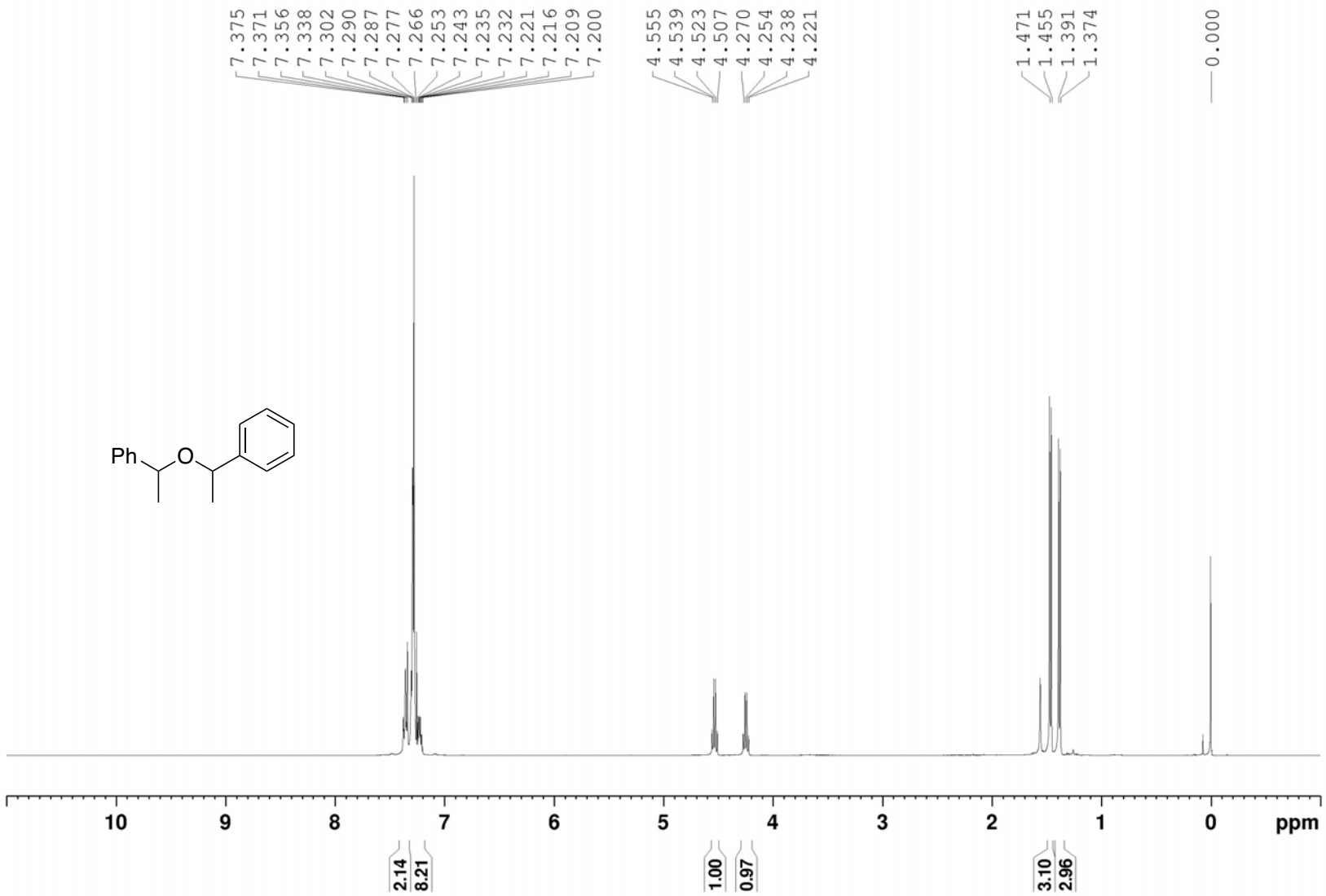

$^{19}$F NMR spectrum of **3Bn**



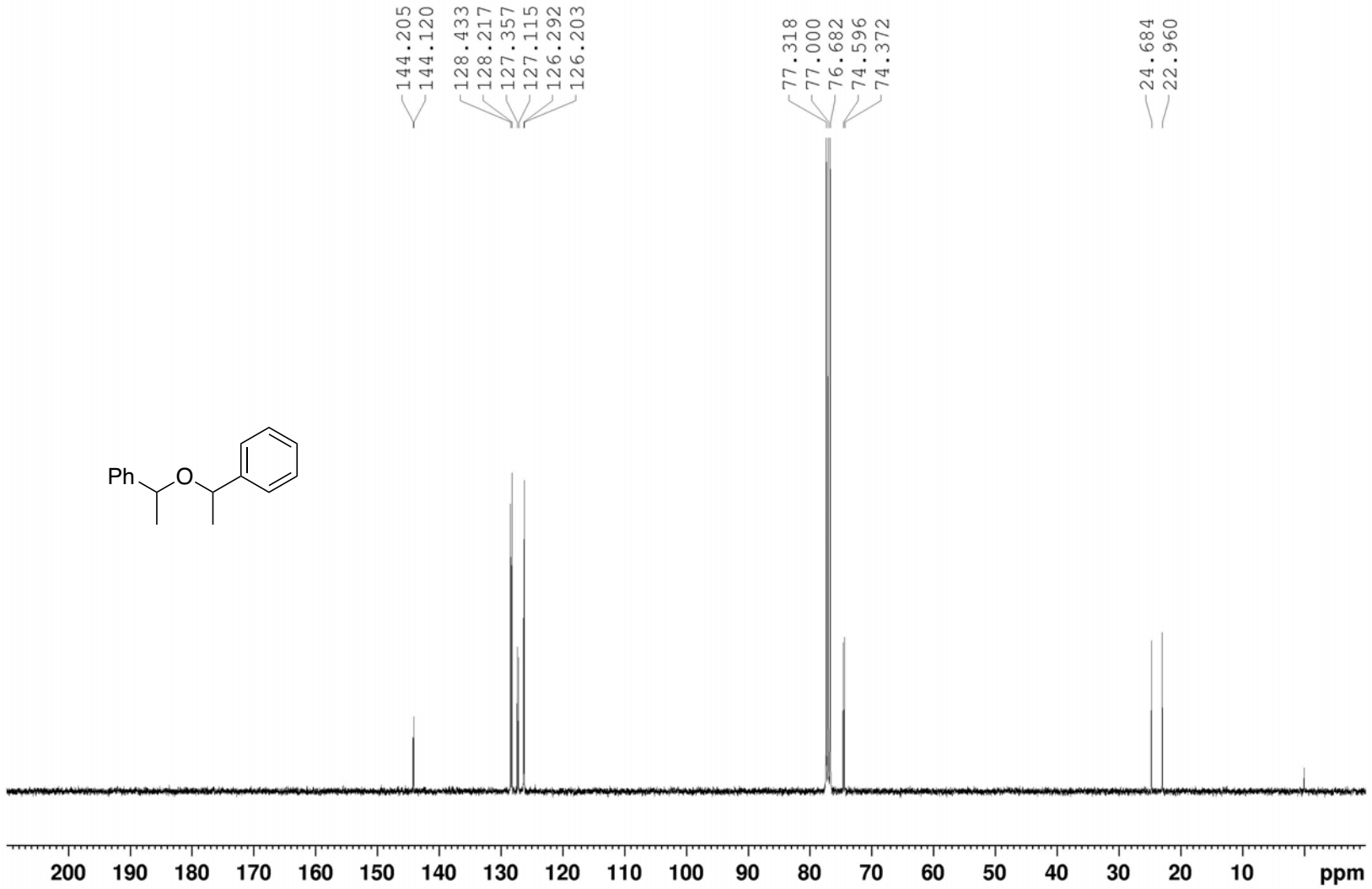

$^{1}$H NMR spectrum of **3ao**



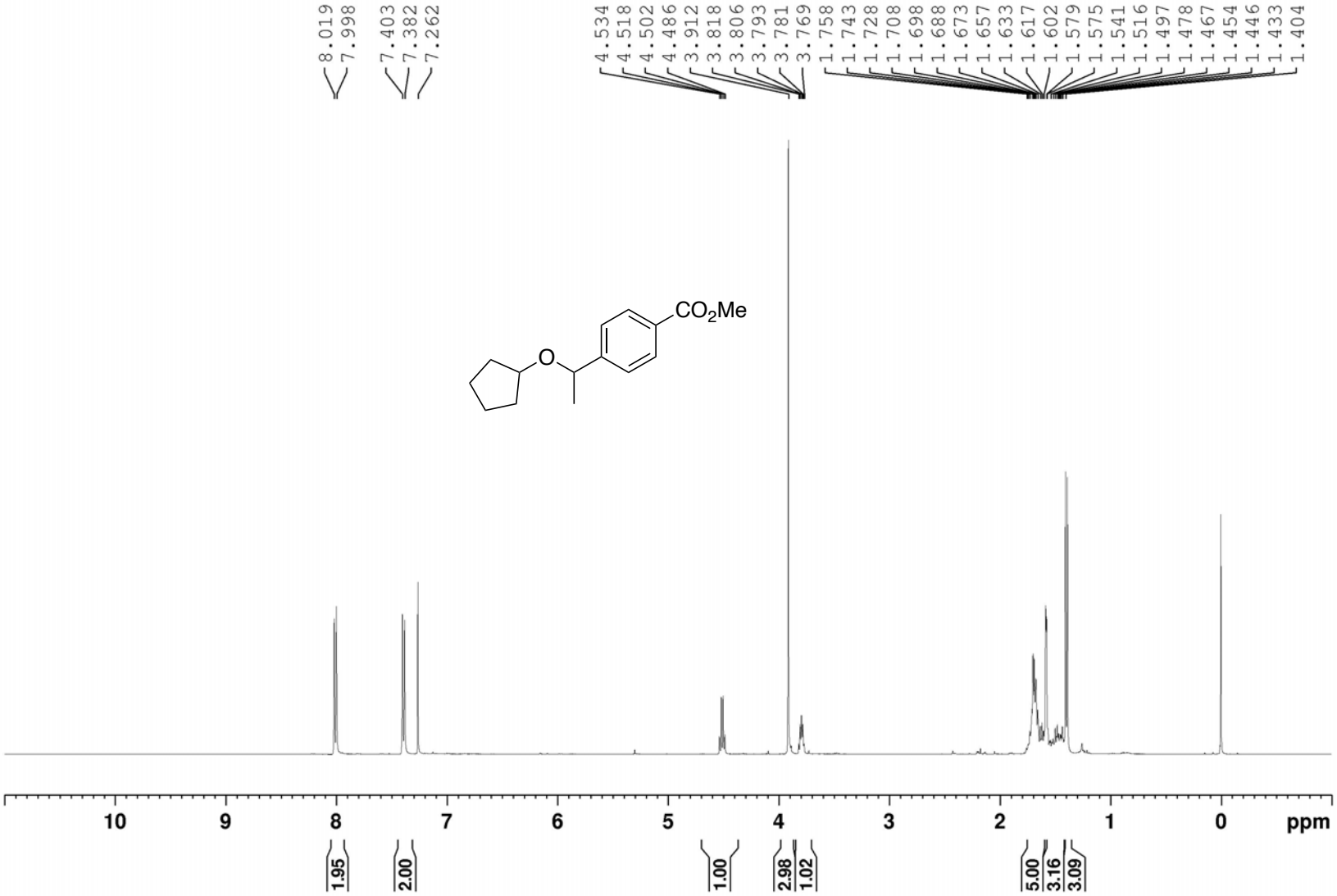

$^{13}$C NMR spectrum of **3ao**



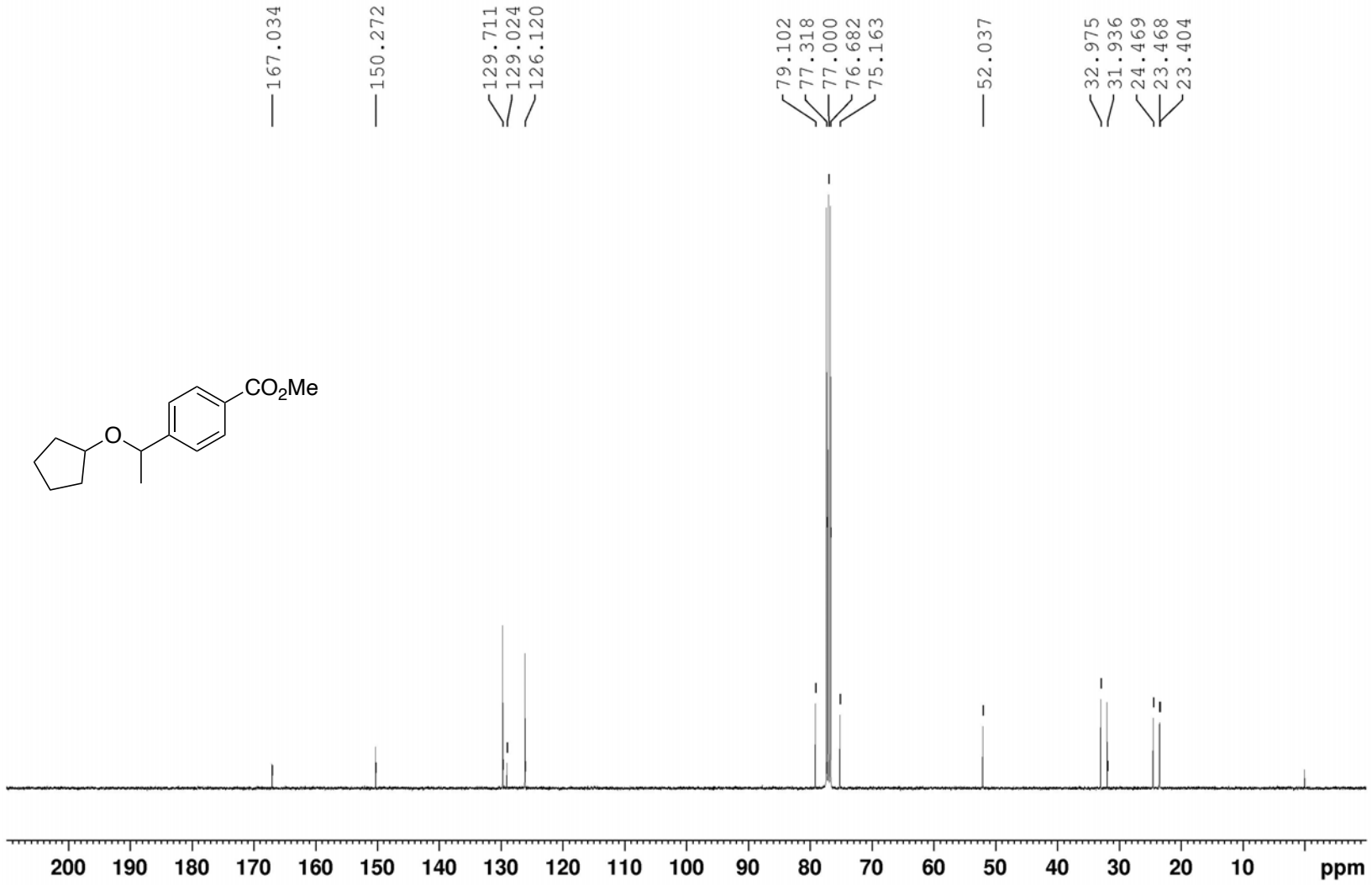

$^{1}$H NMR spectrum of **3Bp**



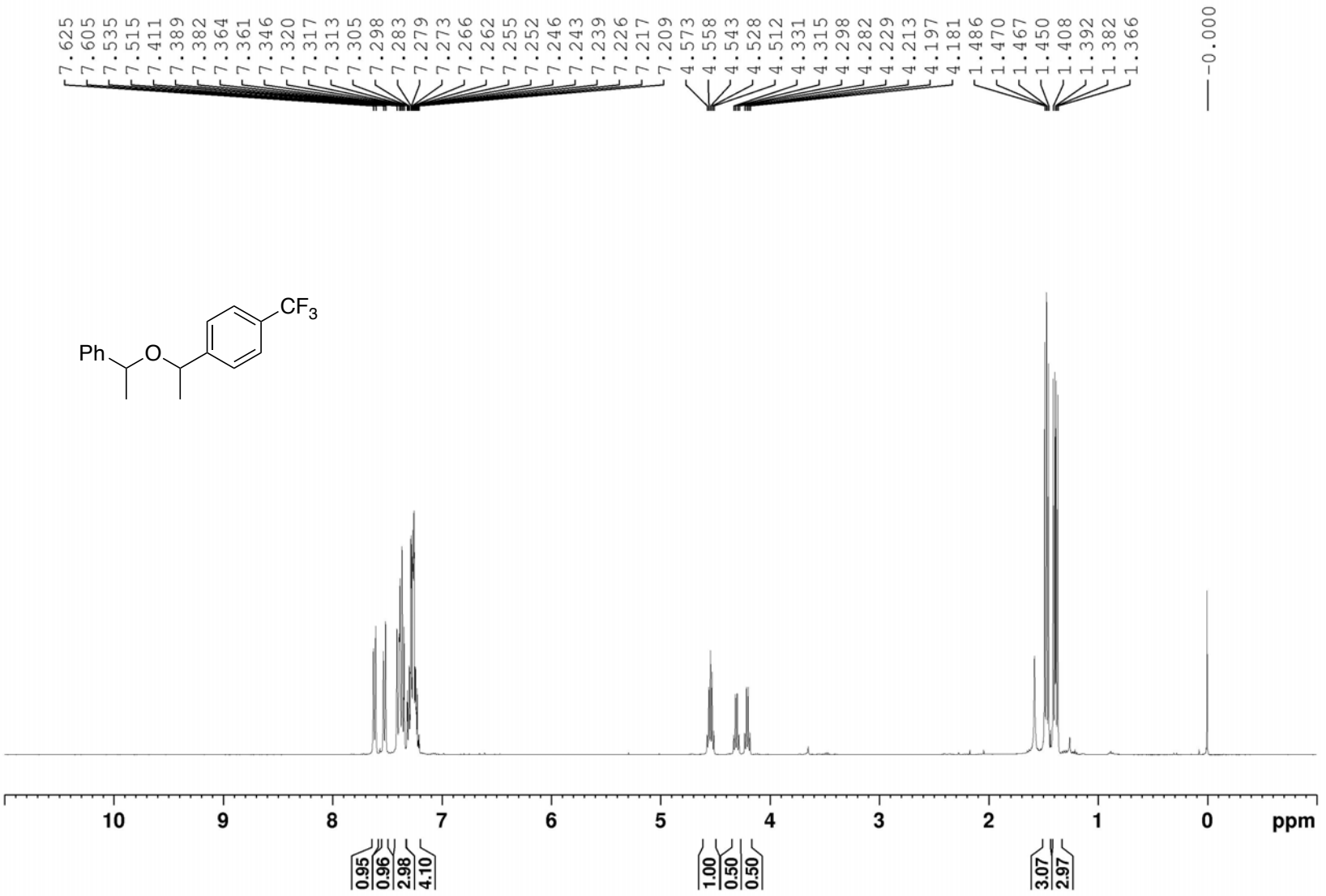

$^{13}$C NMR spectrum of **3Bp**



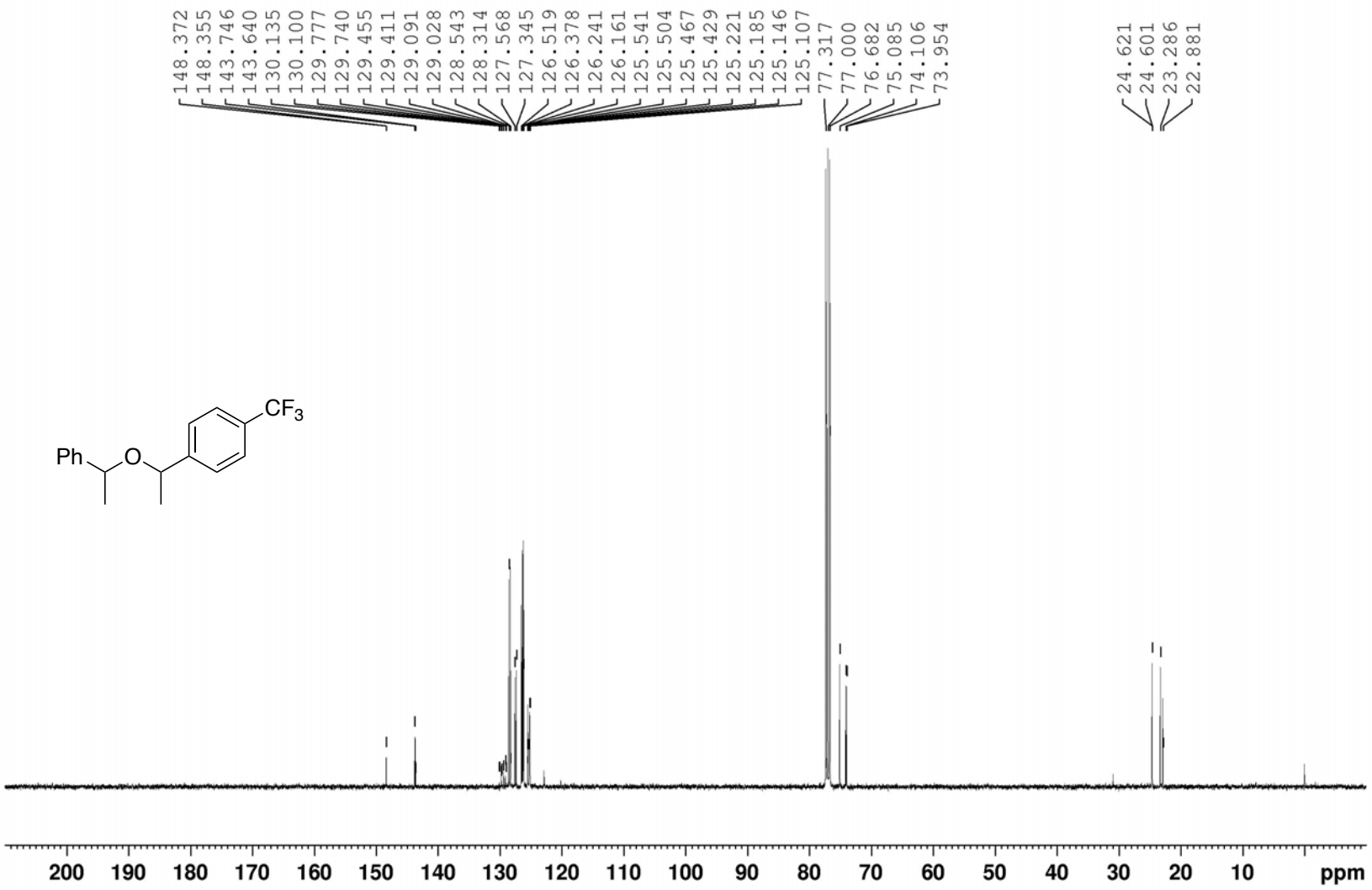

$^{1}$H NMR spectrum of **3aq**



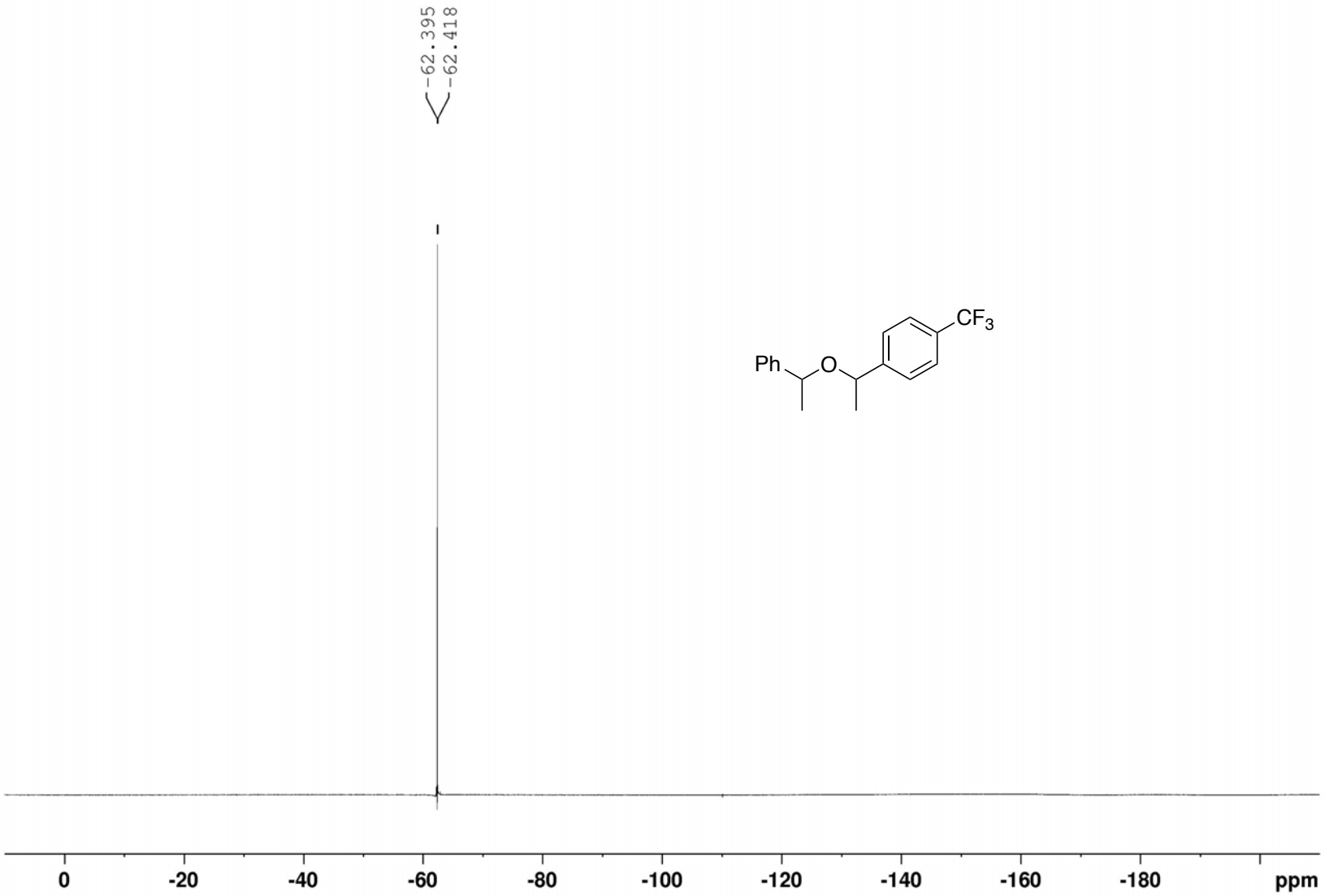

$^{13}$C NMR spectrum of **3aq**



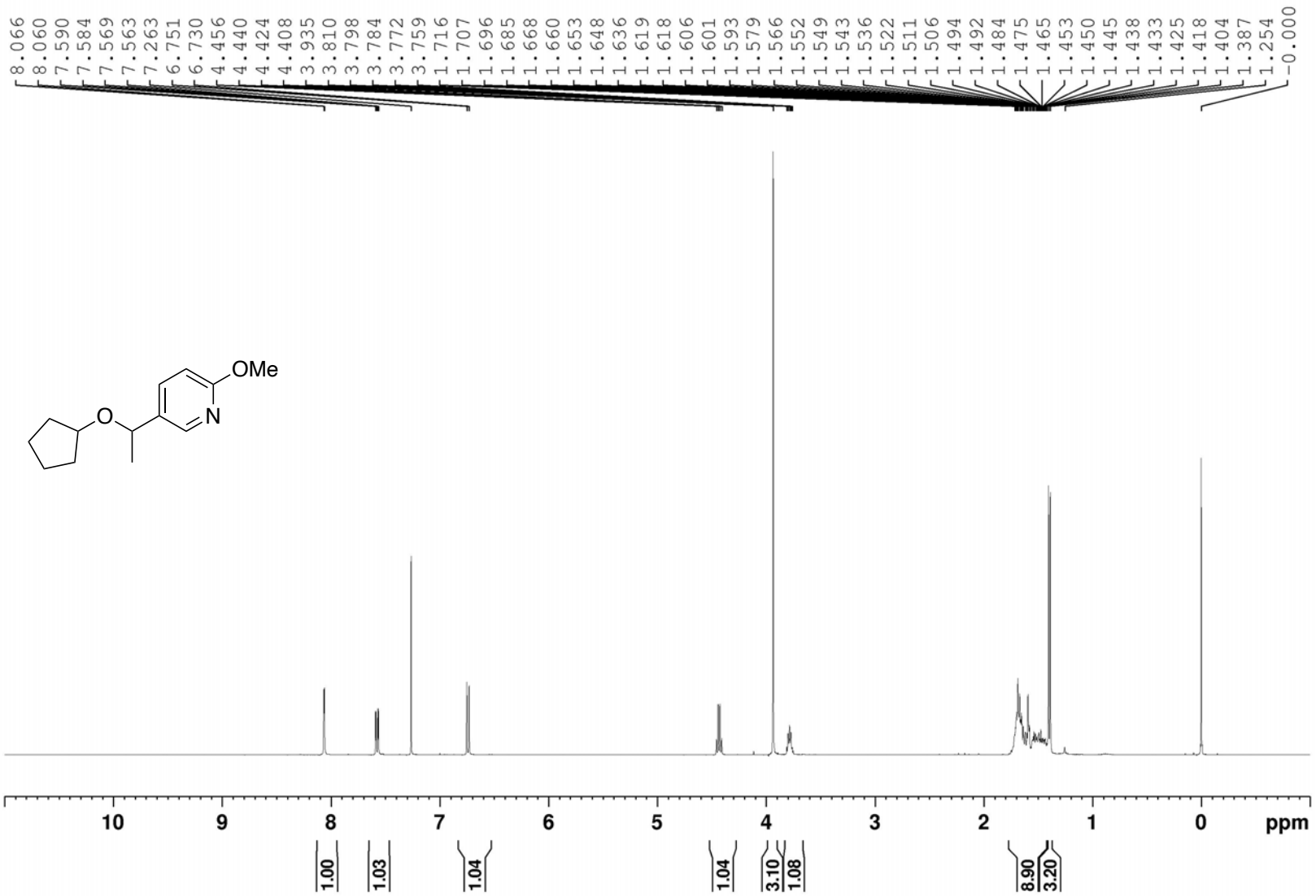

$^{1}$H NMR spectrum of **3Br**



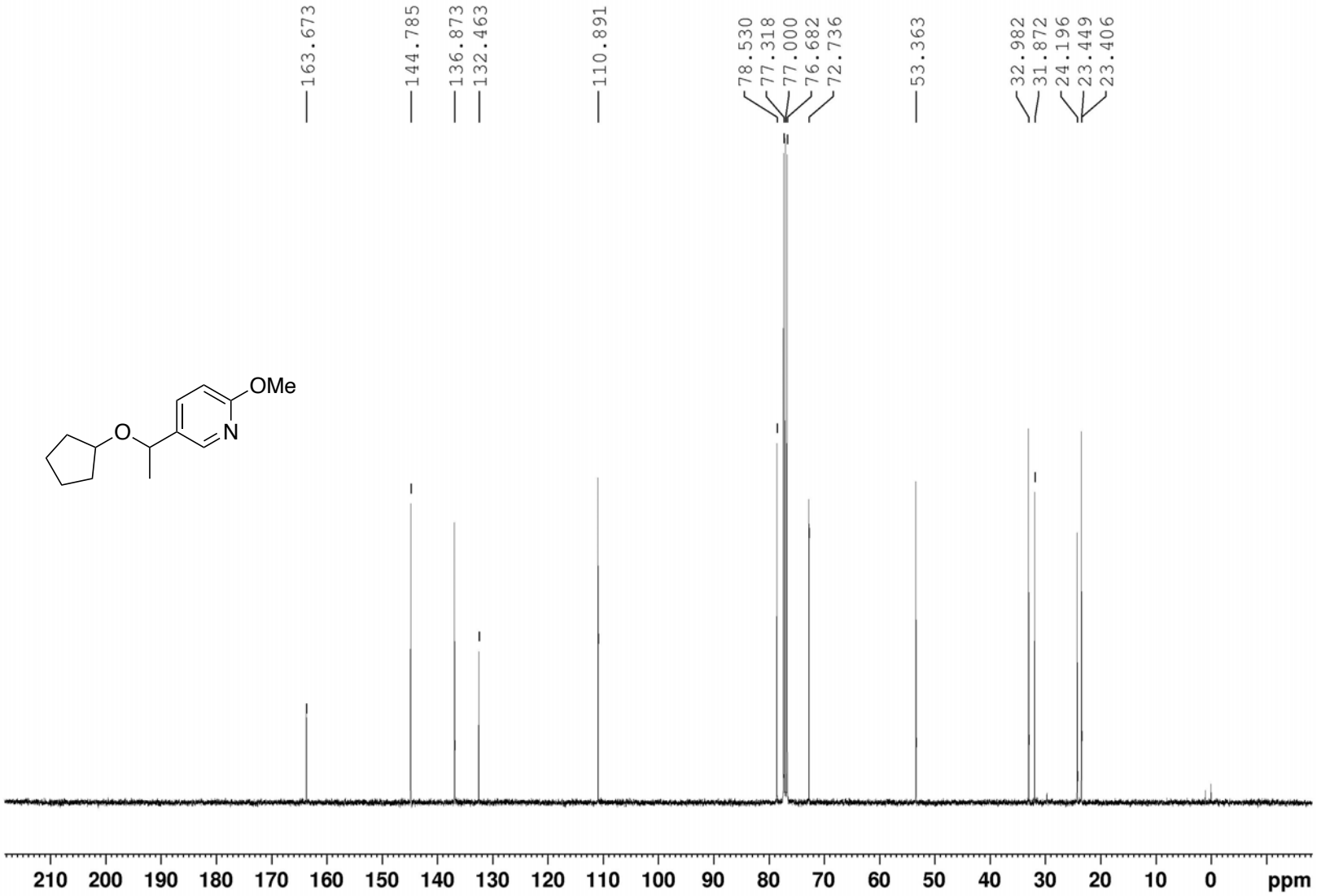

$^{13}$C NMR spectrum of **3Br**



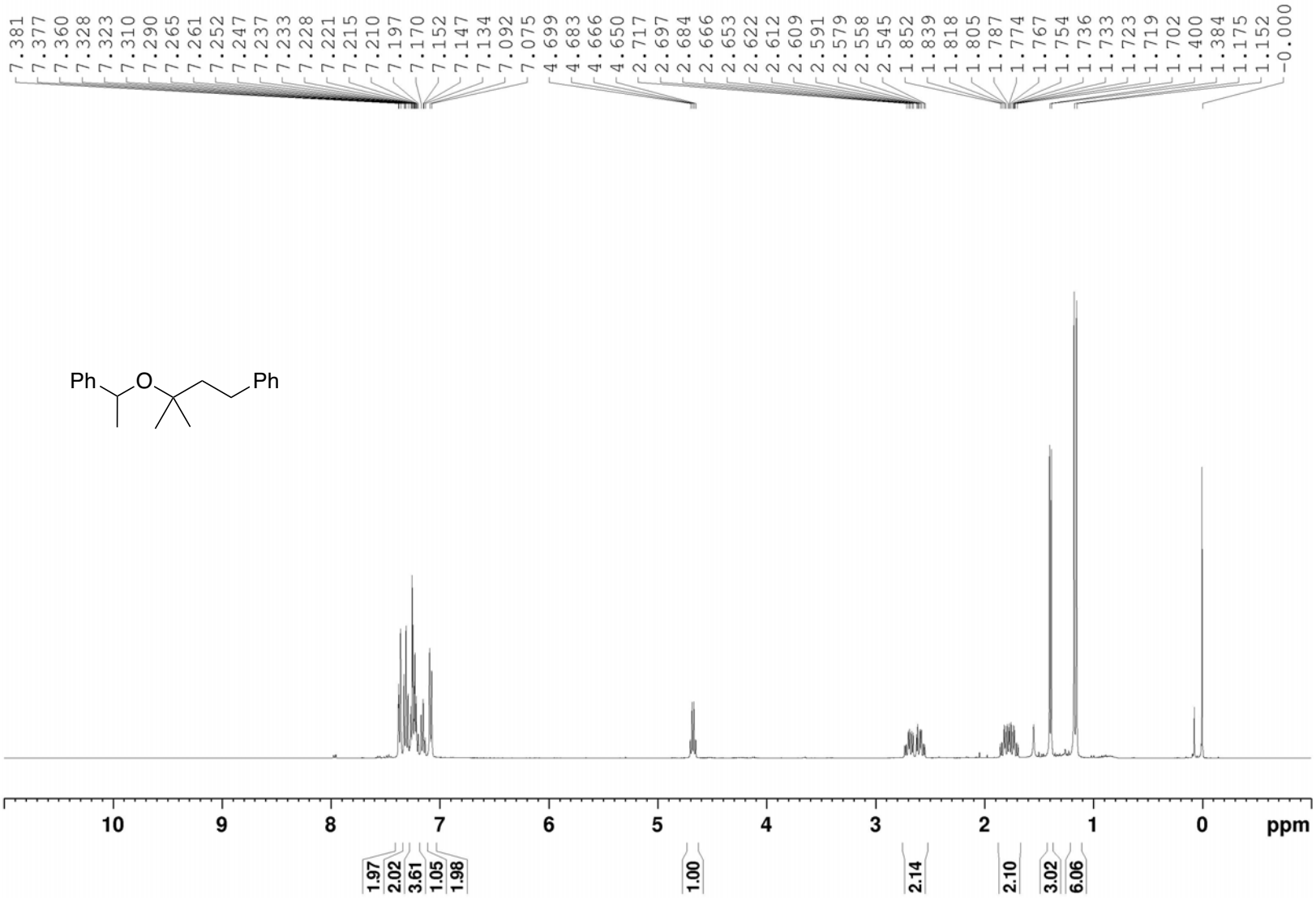

$^{19}$F NMR spectrum of **3Br**



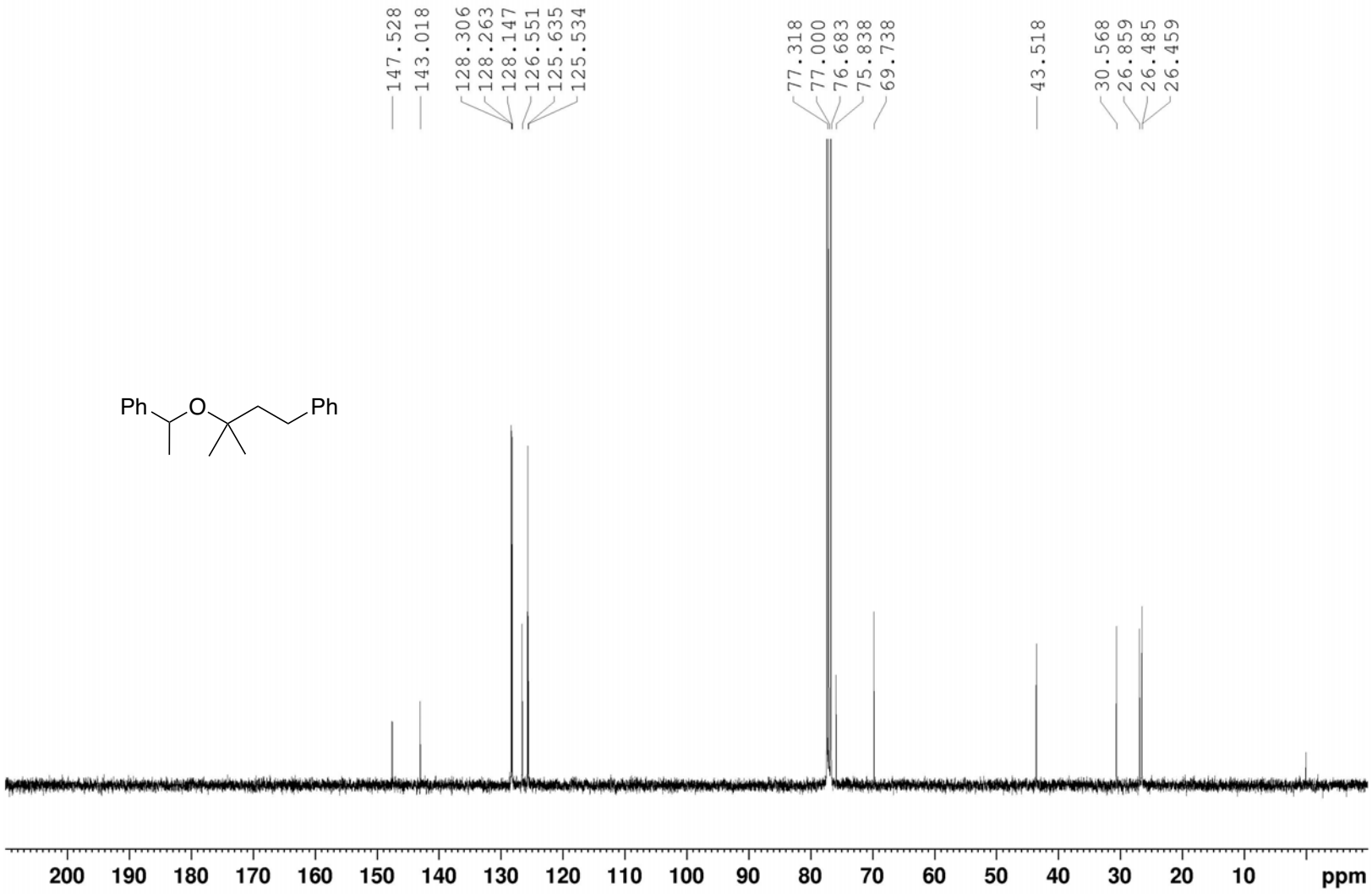

$^{1}$H NMR spectrum of **3as**



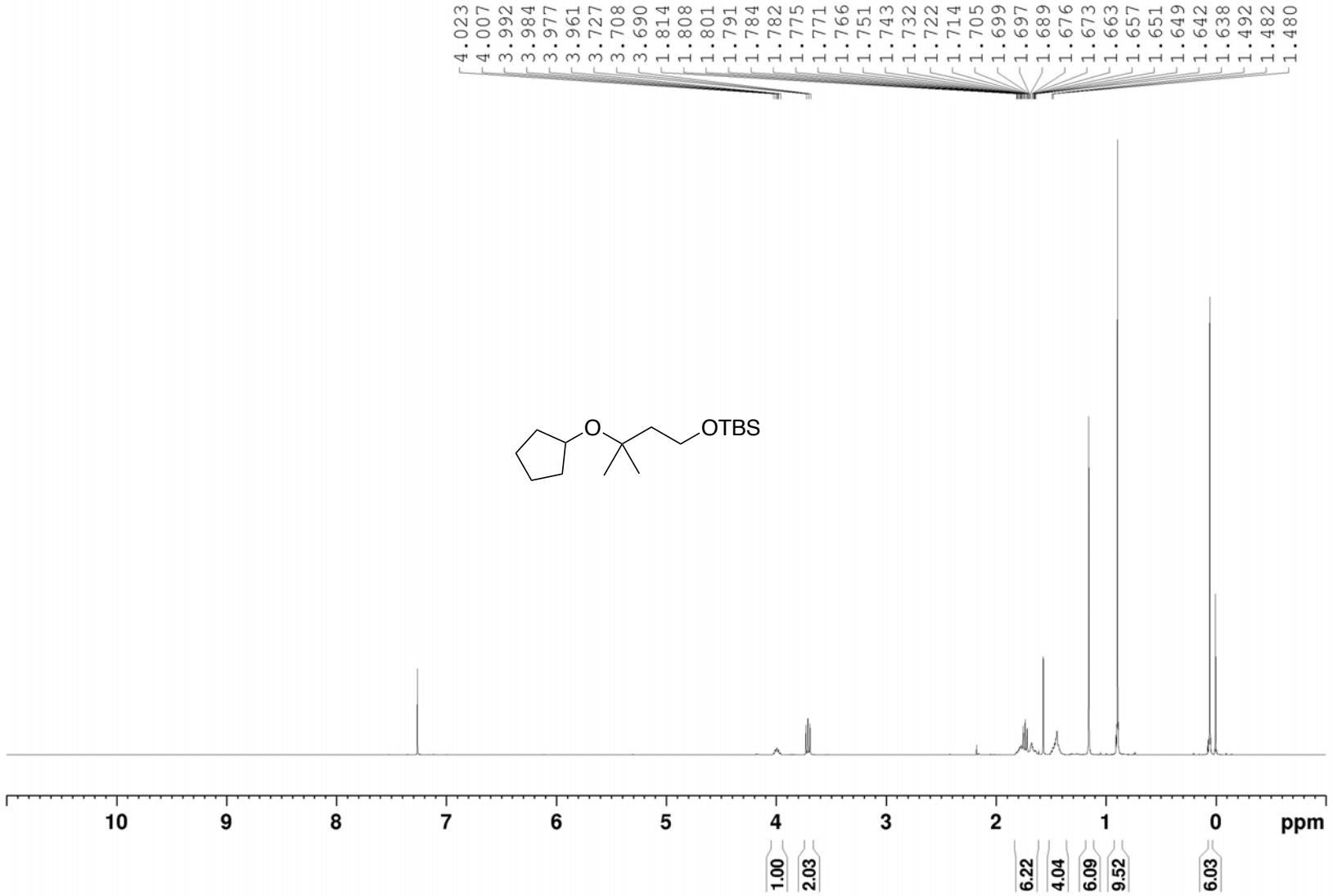

$^{13}$C NMR spectrum of **3as**



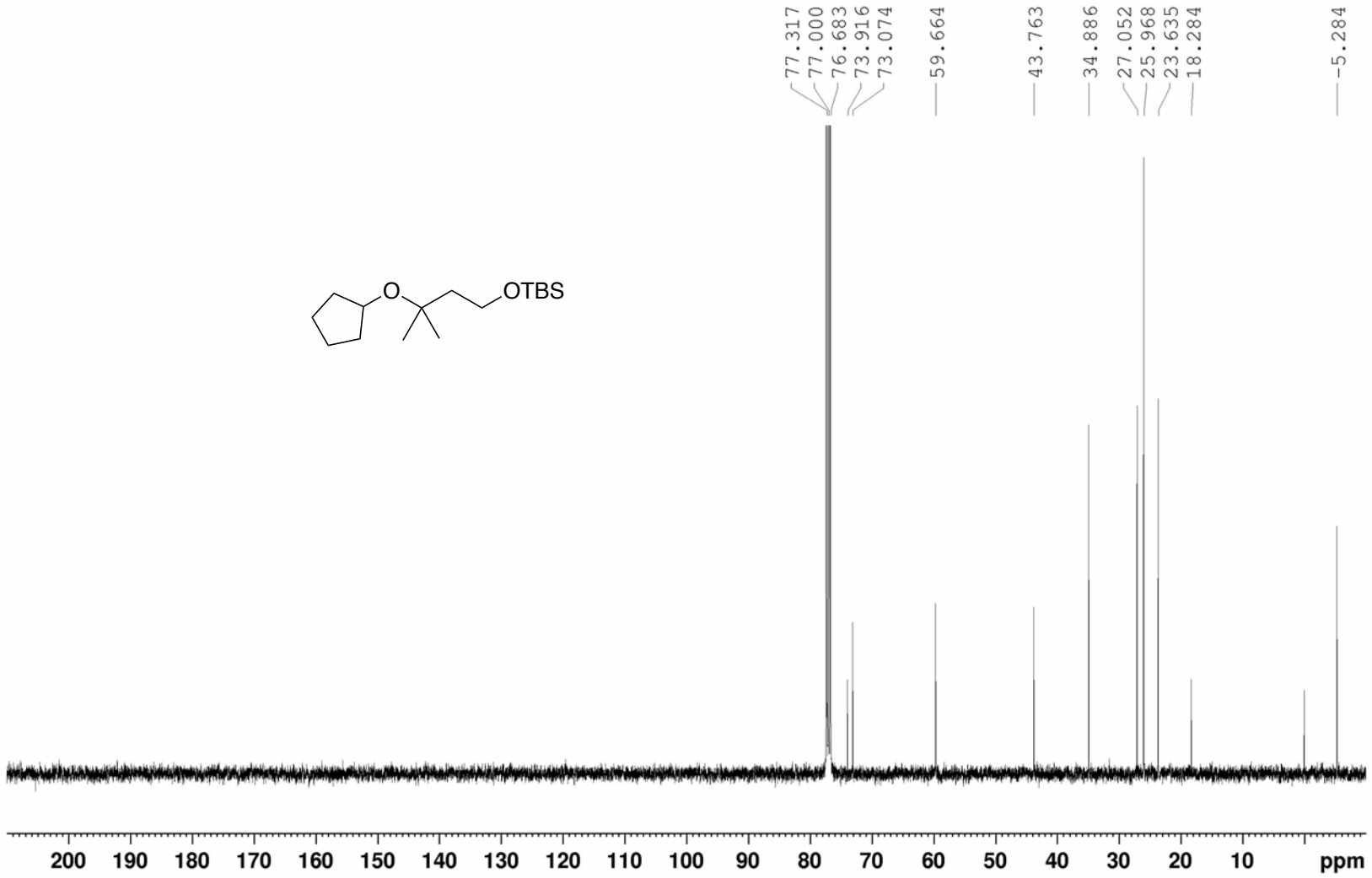

$^{1}$H NMR spectrum of **3Bt**



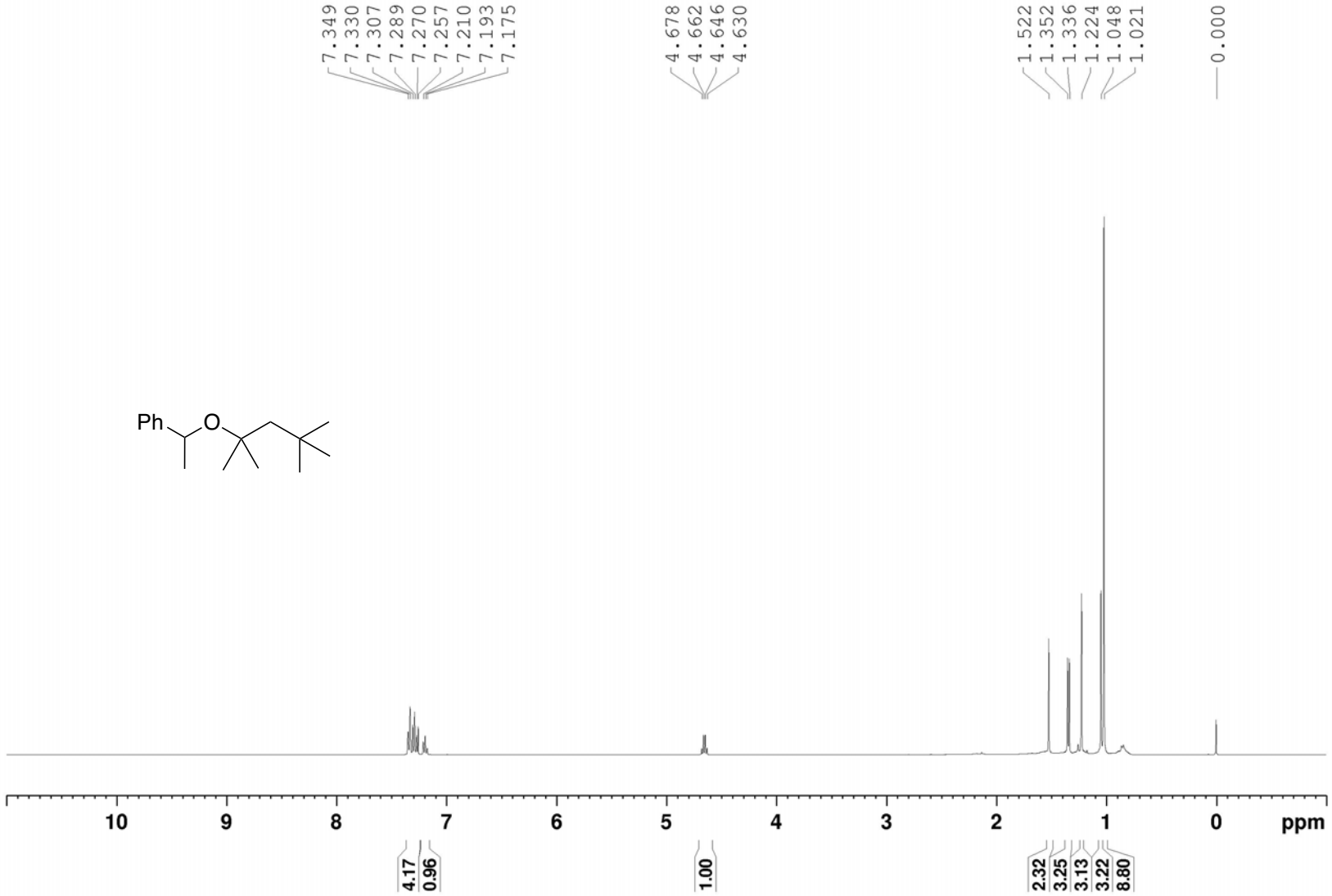

$^{13}$C NMR spectrum of **3Bt**



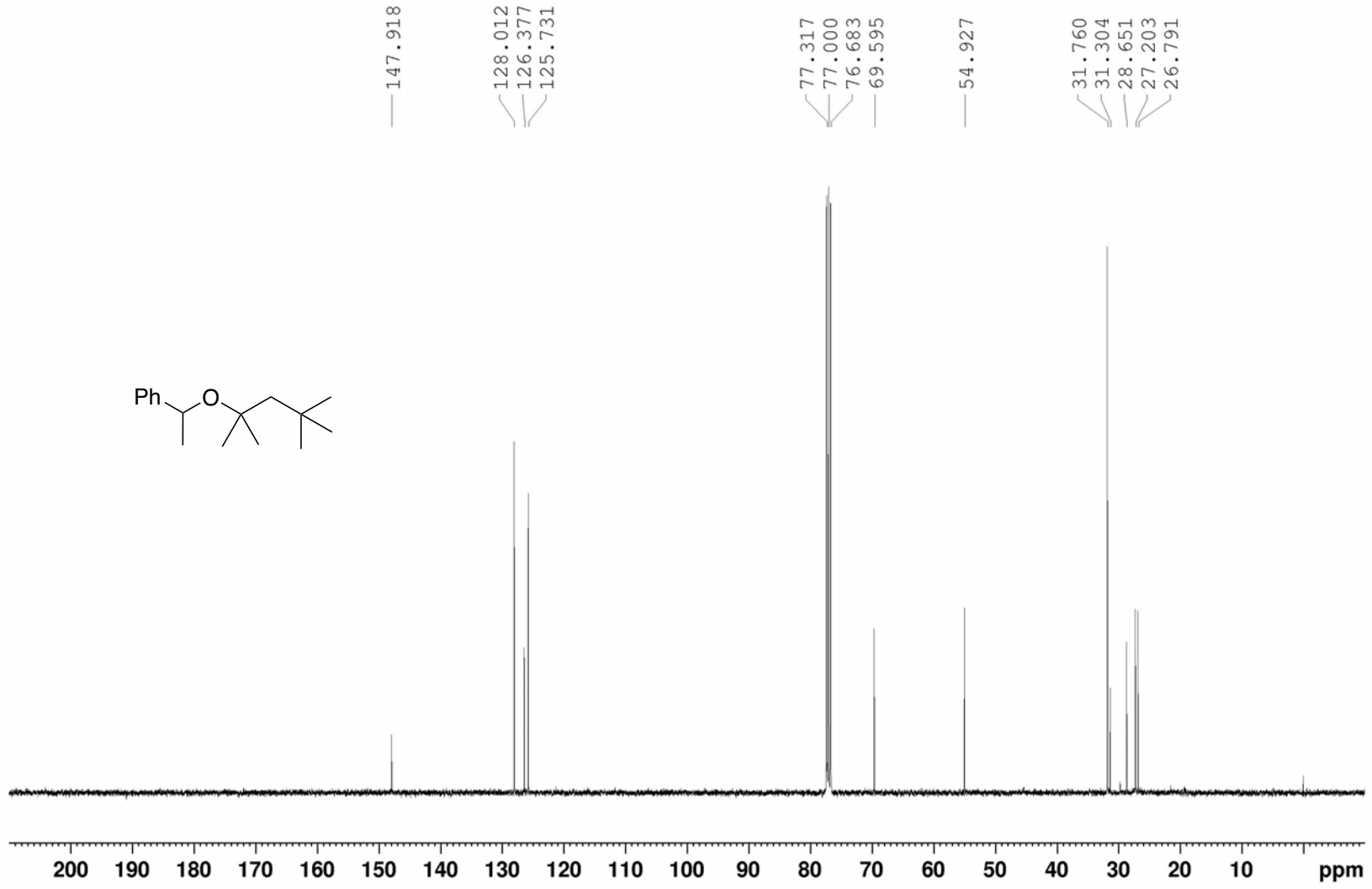

$^{1}$H NMR spectrum of **3au**



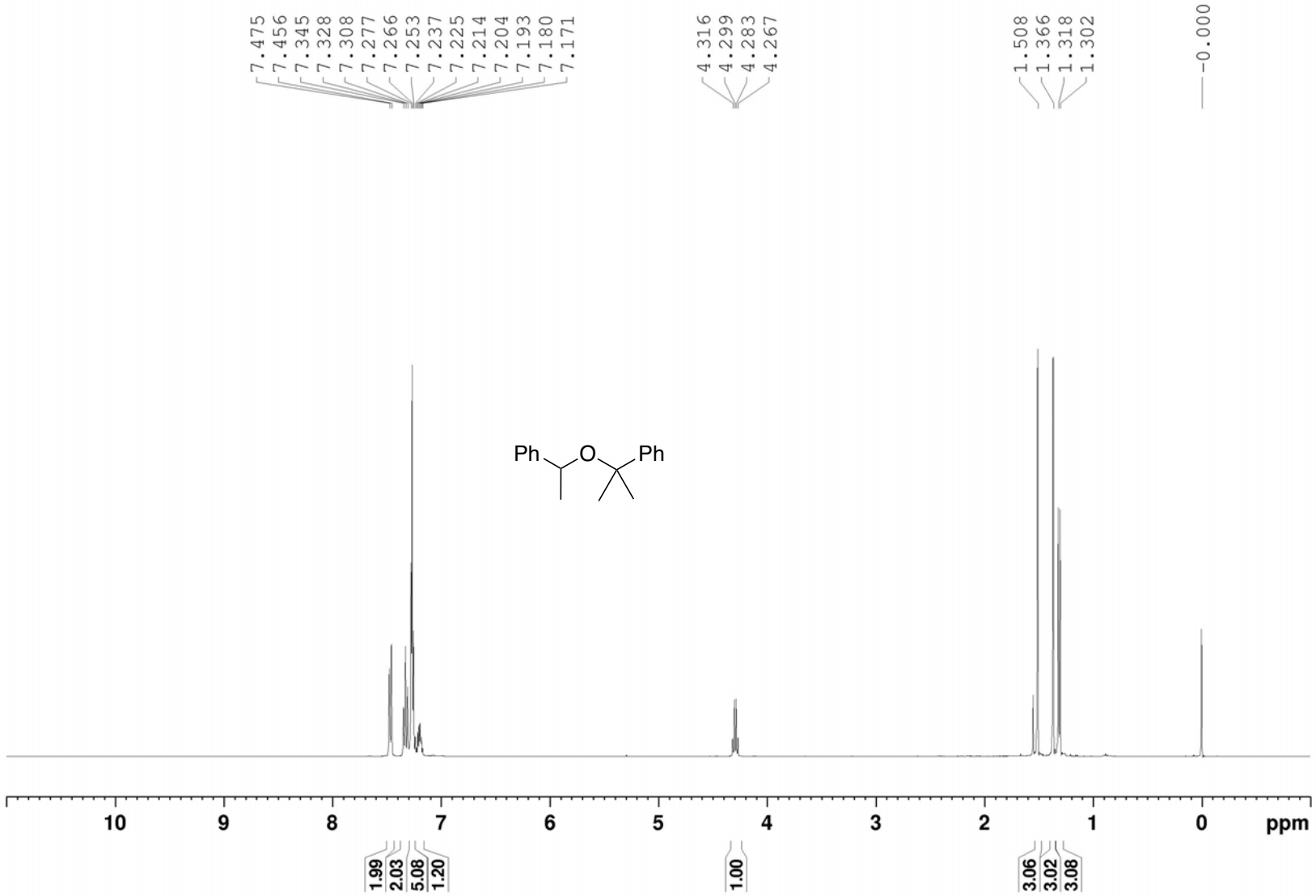

$^{13}$C NMR spectrum of **3au**



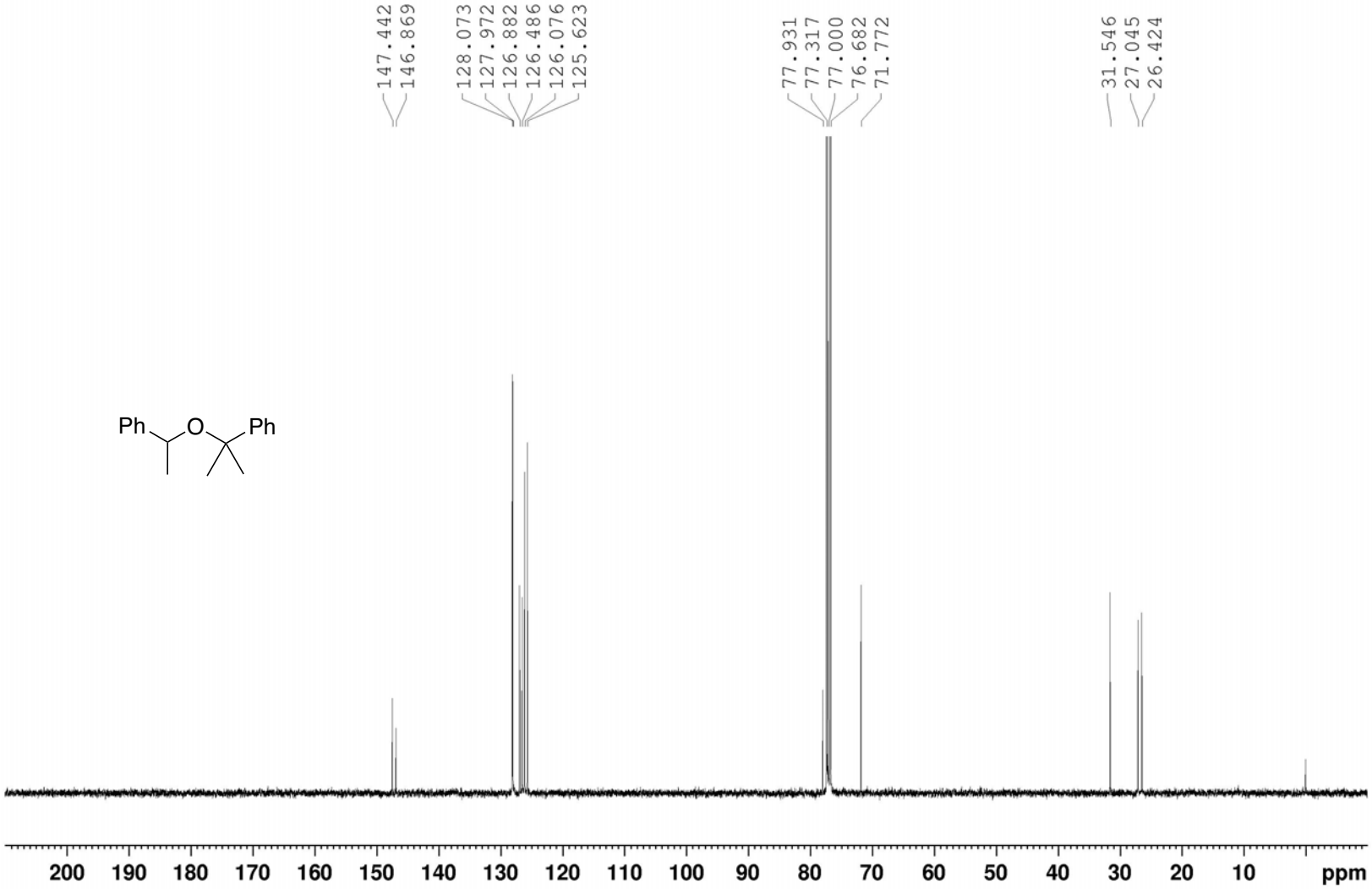

$^{1}$H NMR spectrum of **3Bv**



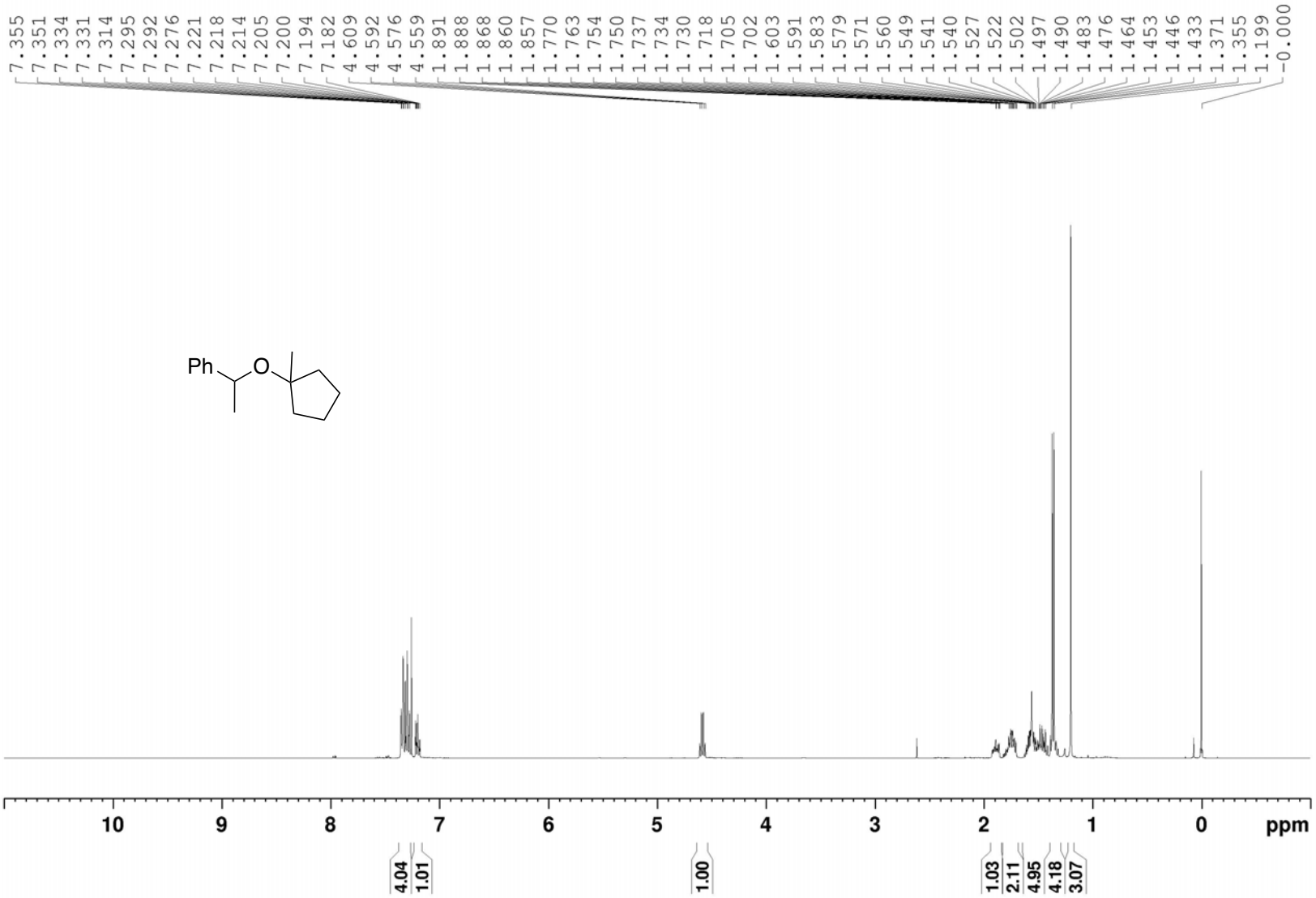

$^{13}$C NMR spectrum of **3Bv**



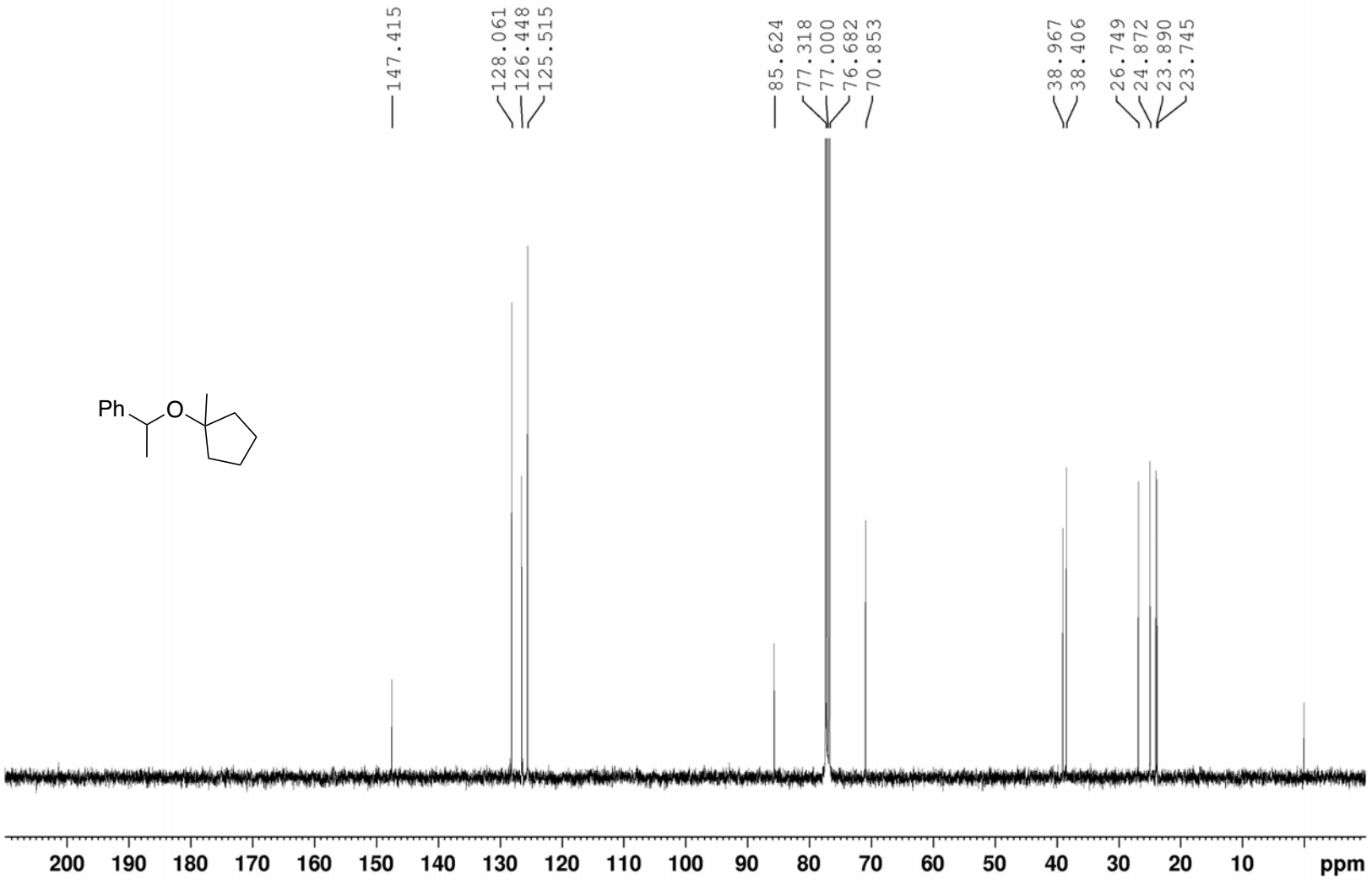

$^{1}$H NMR spectrum of **3Bw**



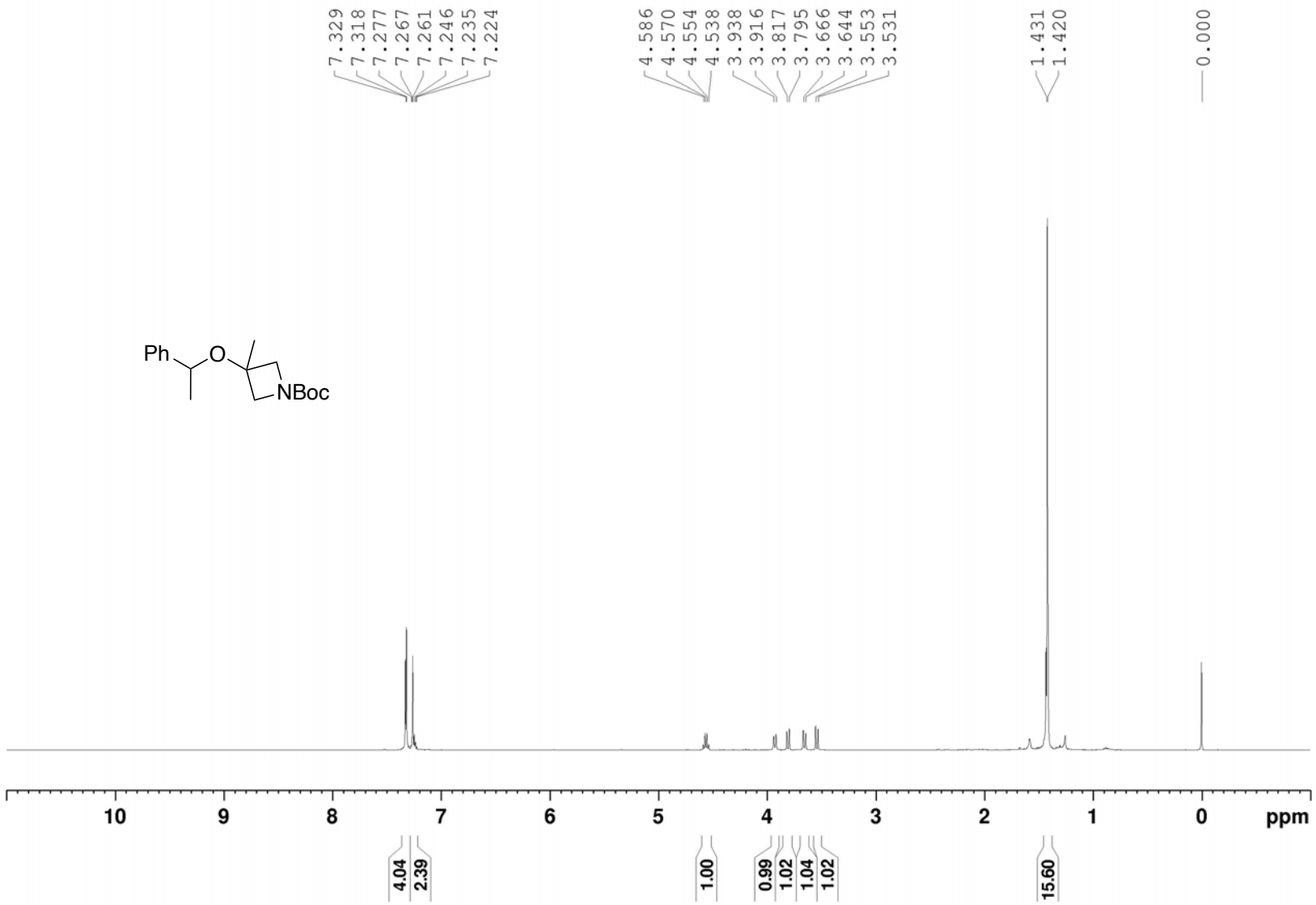

$^{13}$C NMR spectrum of **3Bw**



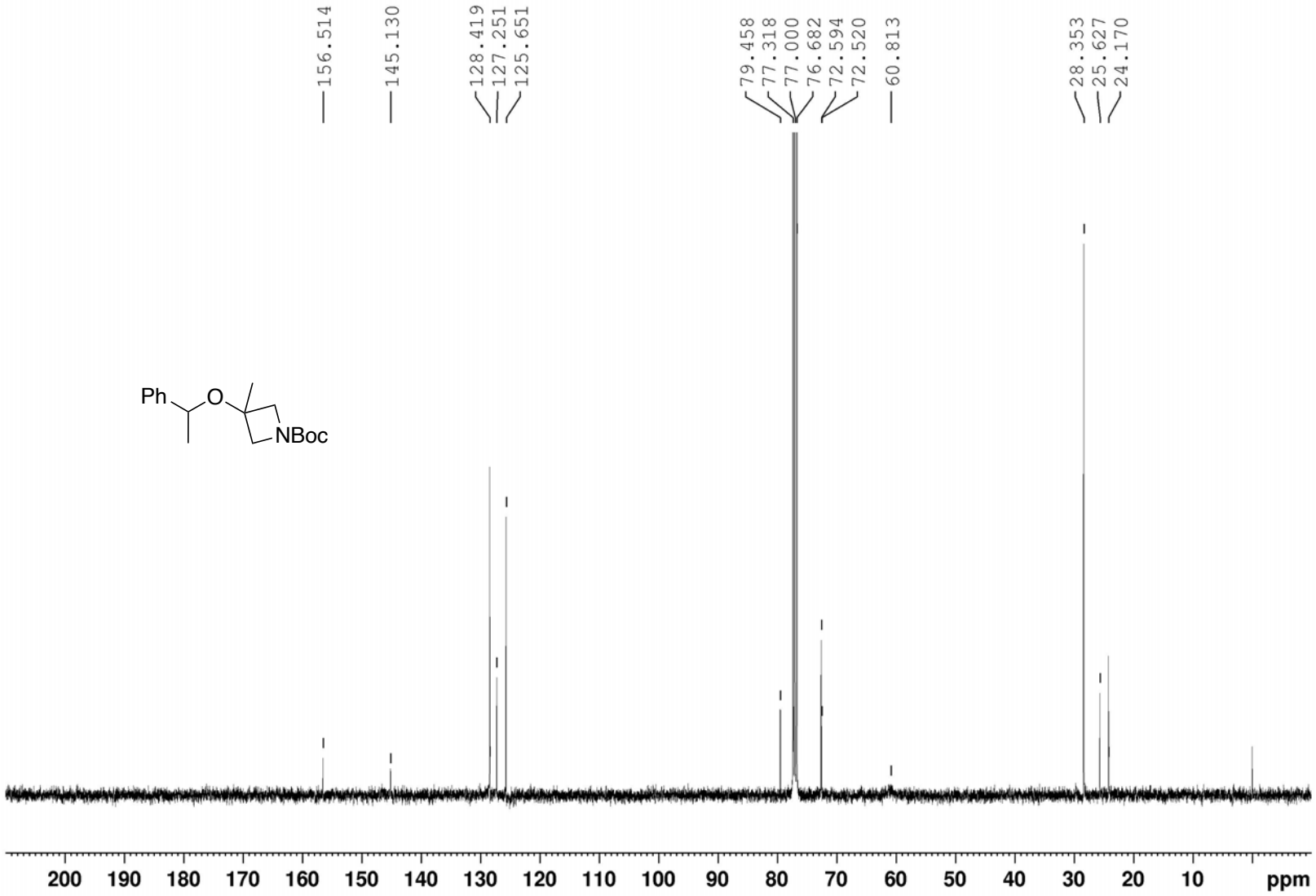

$^{1}$H NMR spectrum of **3Bx**



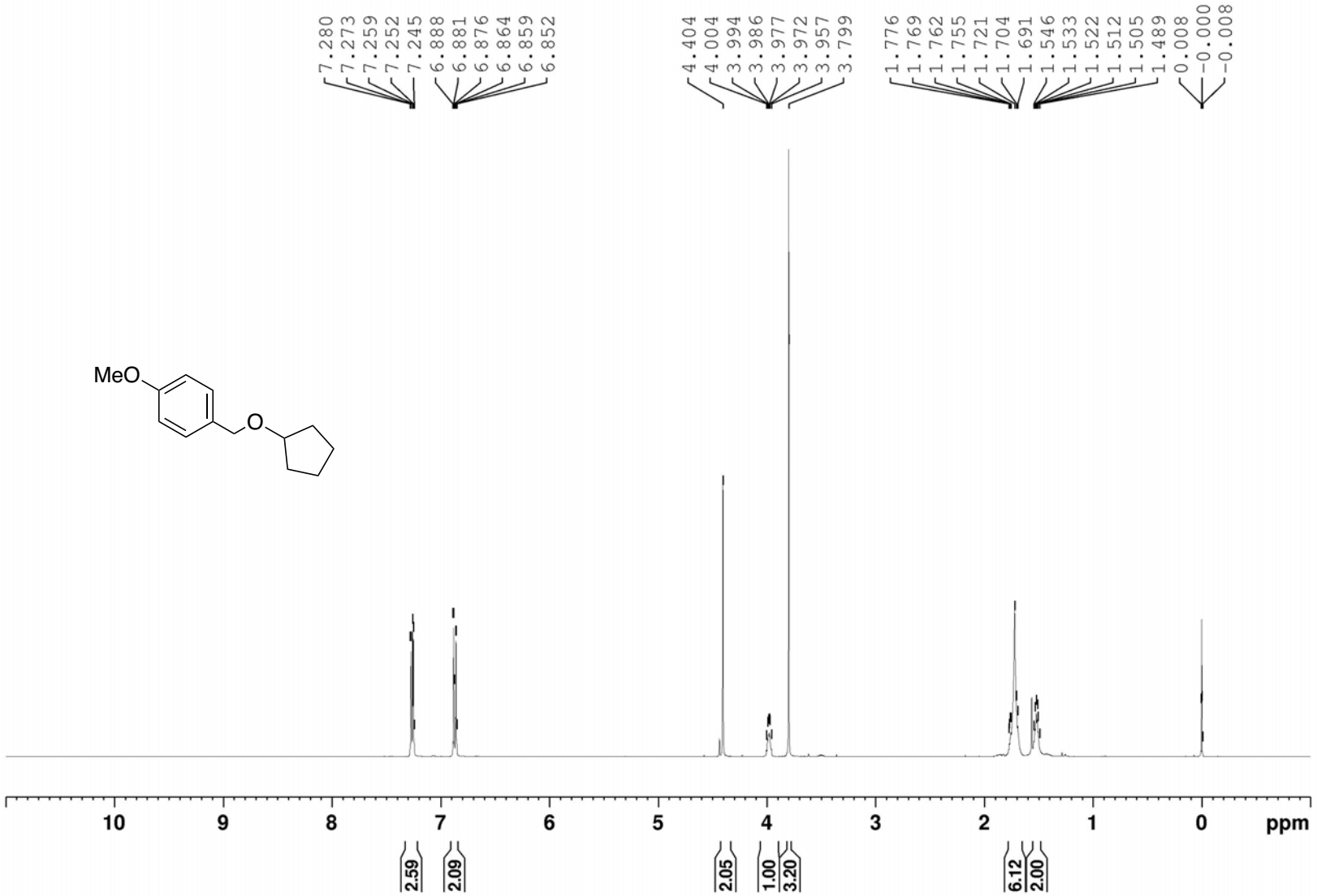

$^{13}$C NMR spectrum of **3Bx**



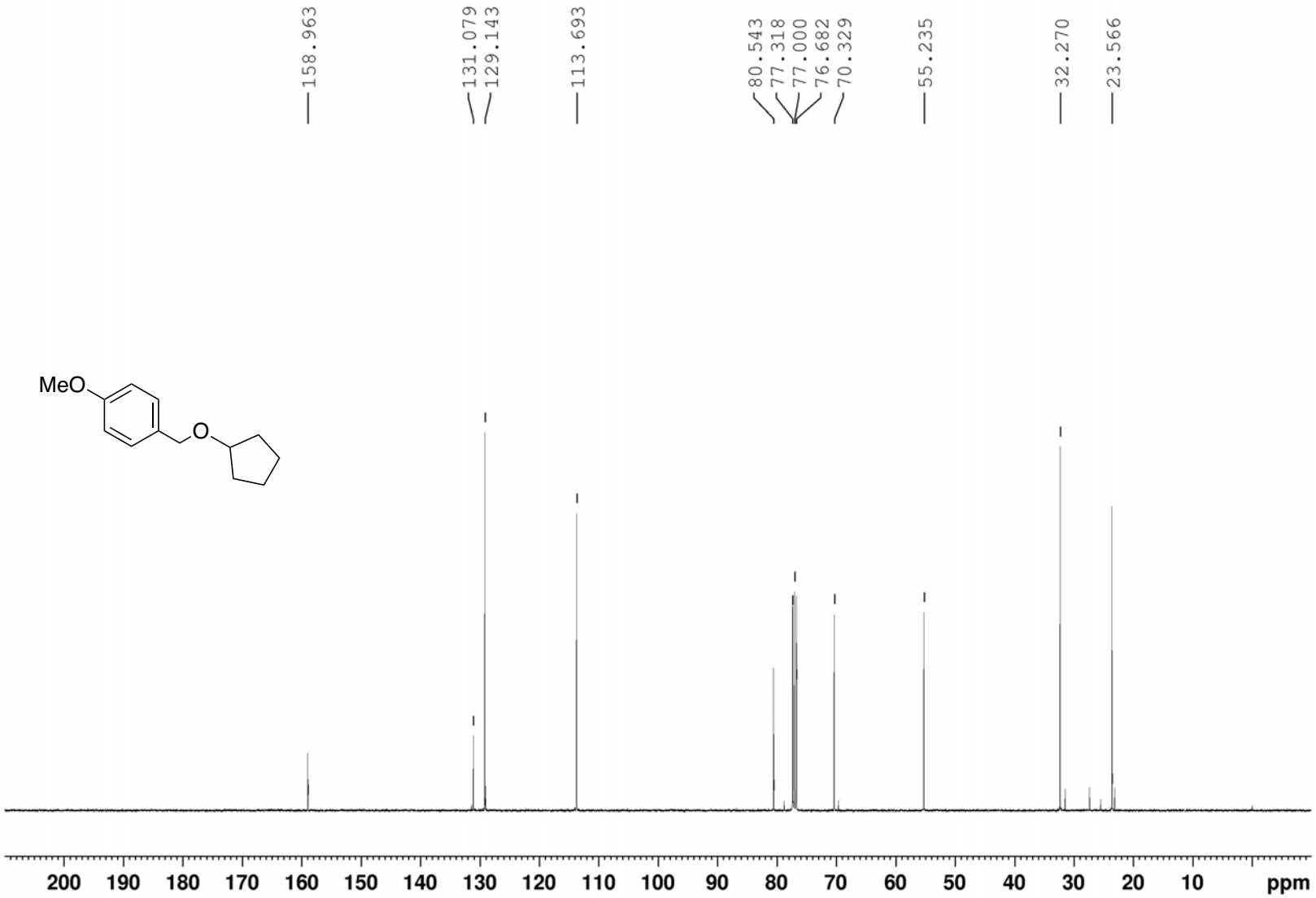

$^{1}$H NMR spectrum of **3By**



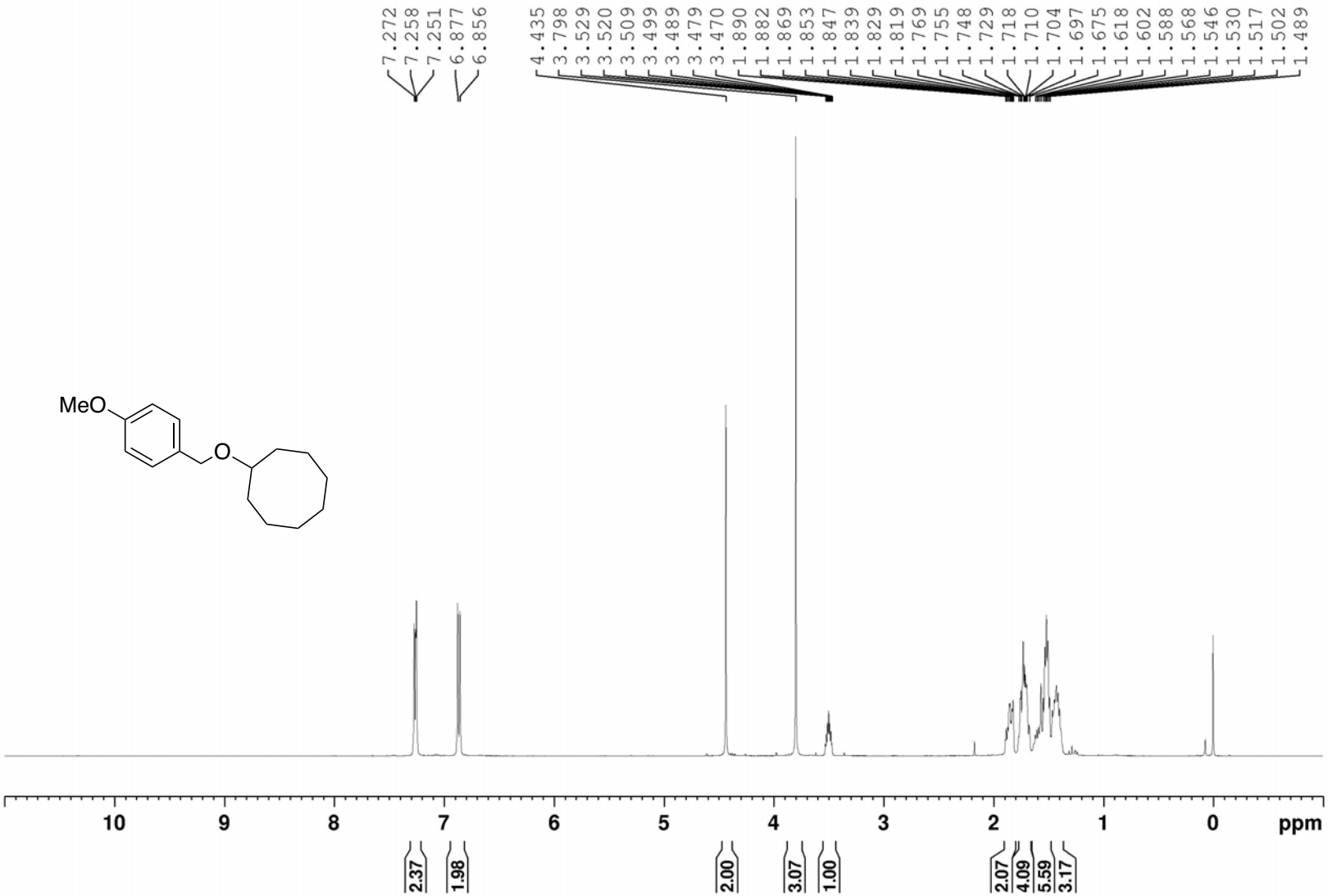

$^{13}$C NMR spectrum of **3By**



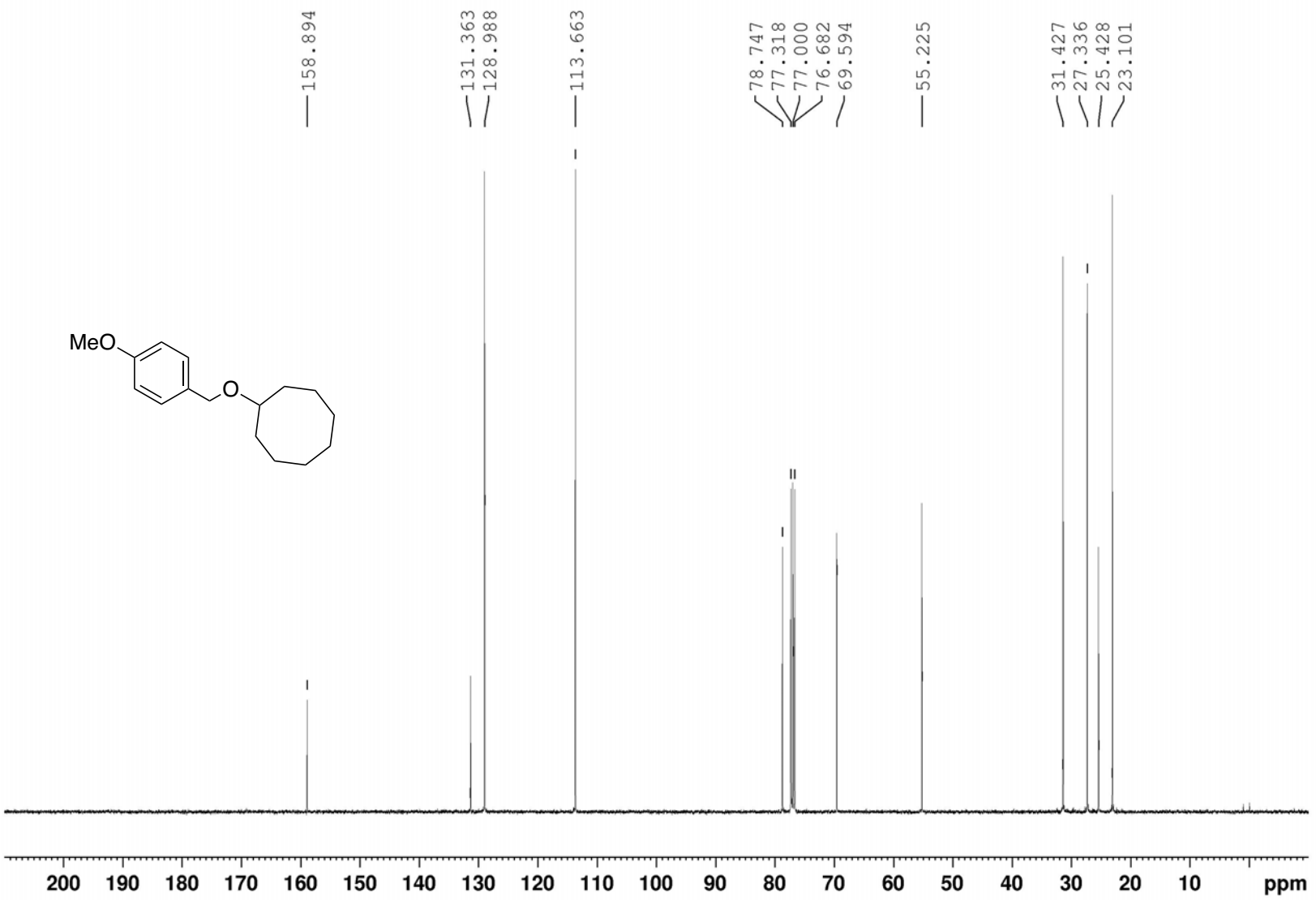

$^{1}$H NMR spectrum of **3ez**



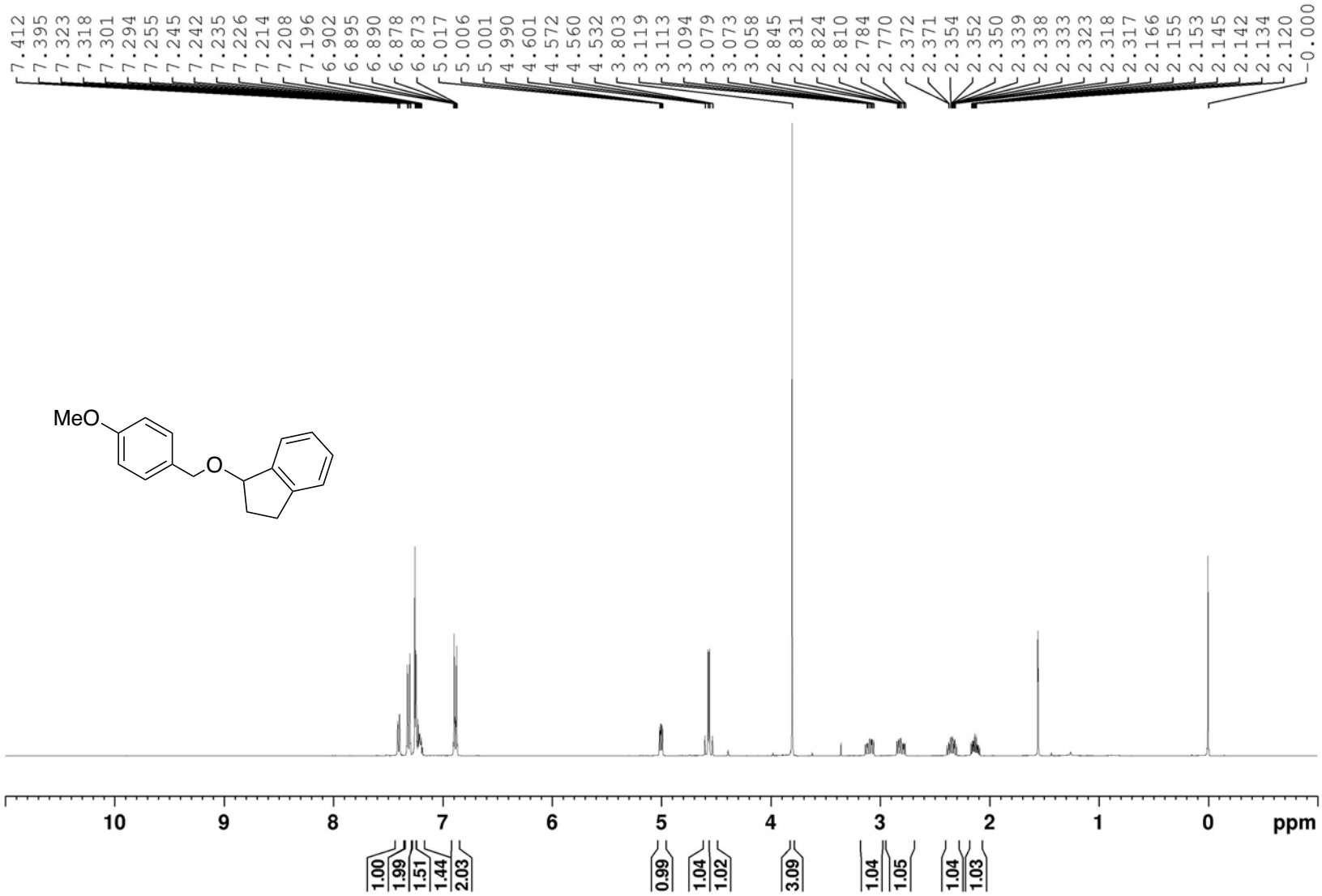

$^{13}$C NMR spectrum of **3ez**



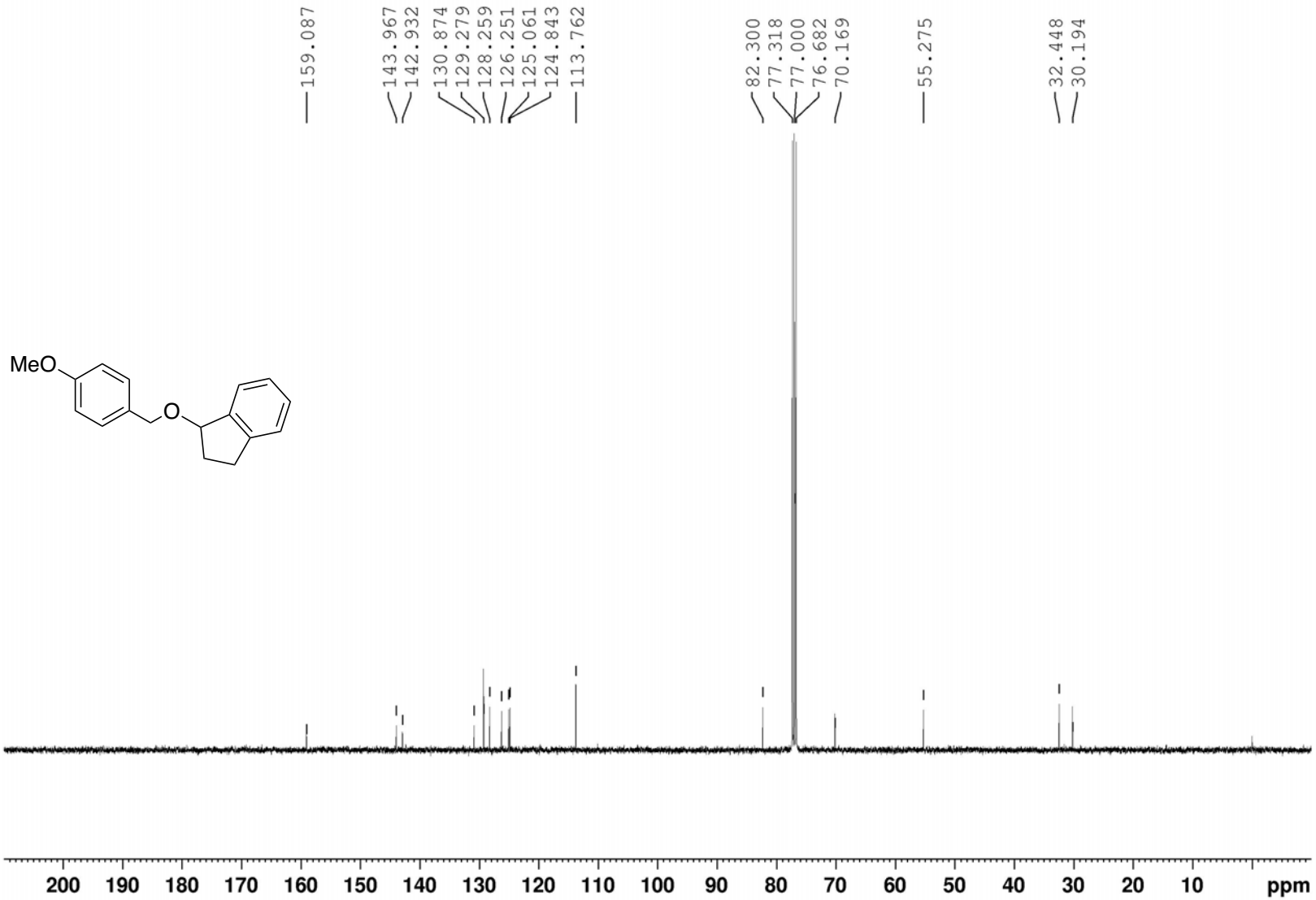

$^{1}$H NMR spectrum of **3eA**



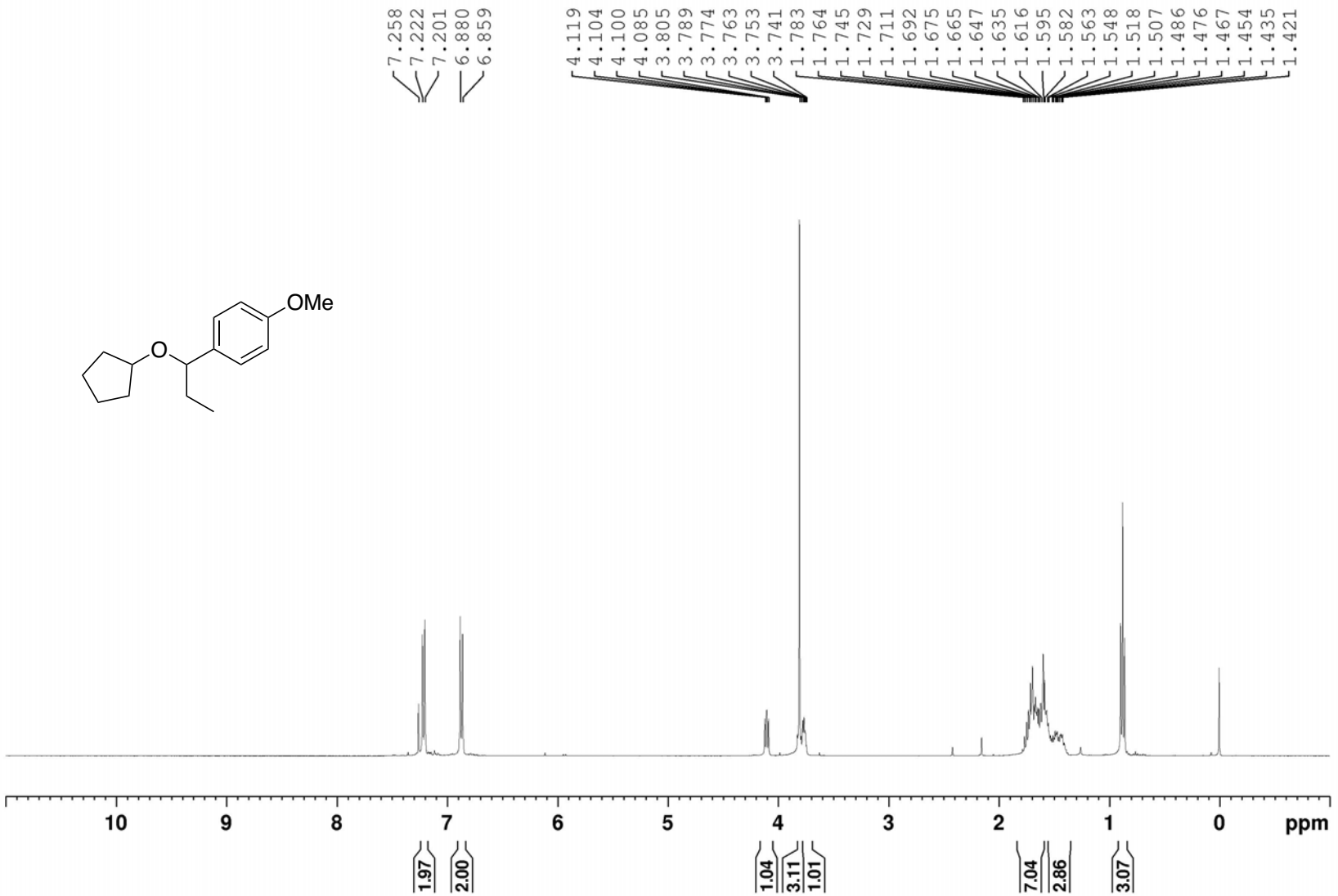

$^{13}$C NMR spectrum of **3eA**



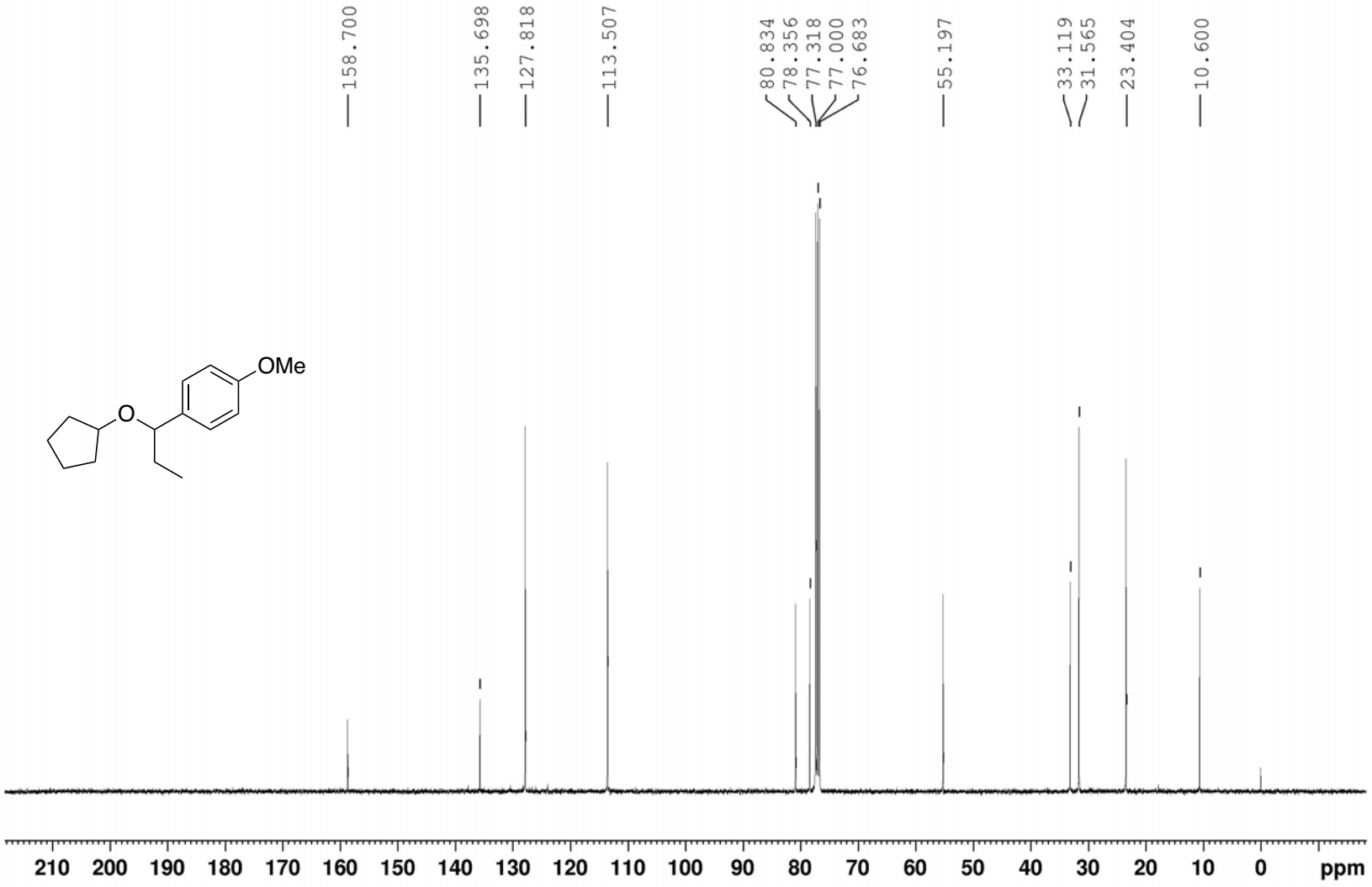

$^{1}$H NMR spectrum of **3eB**



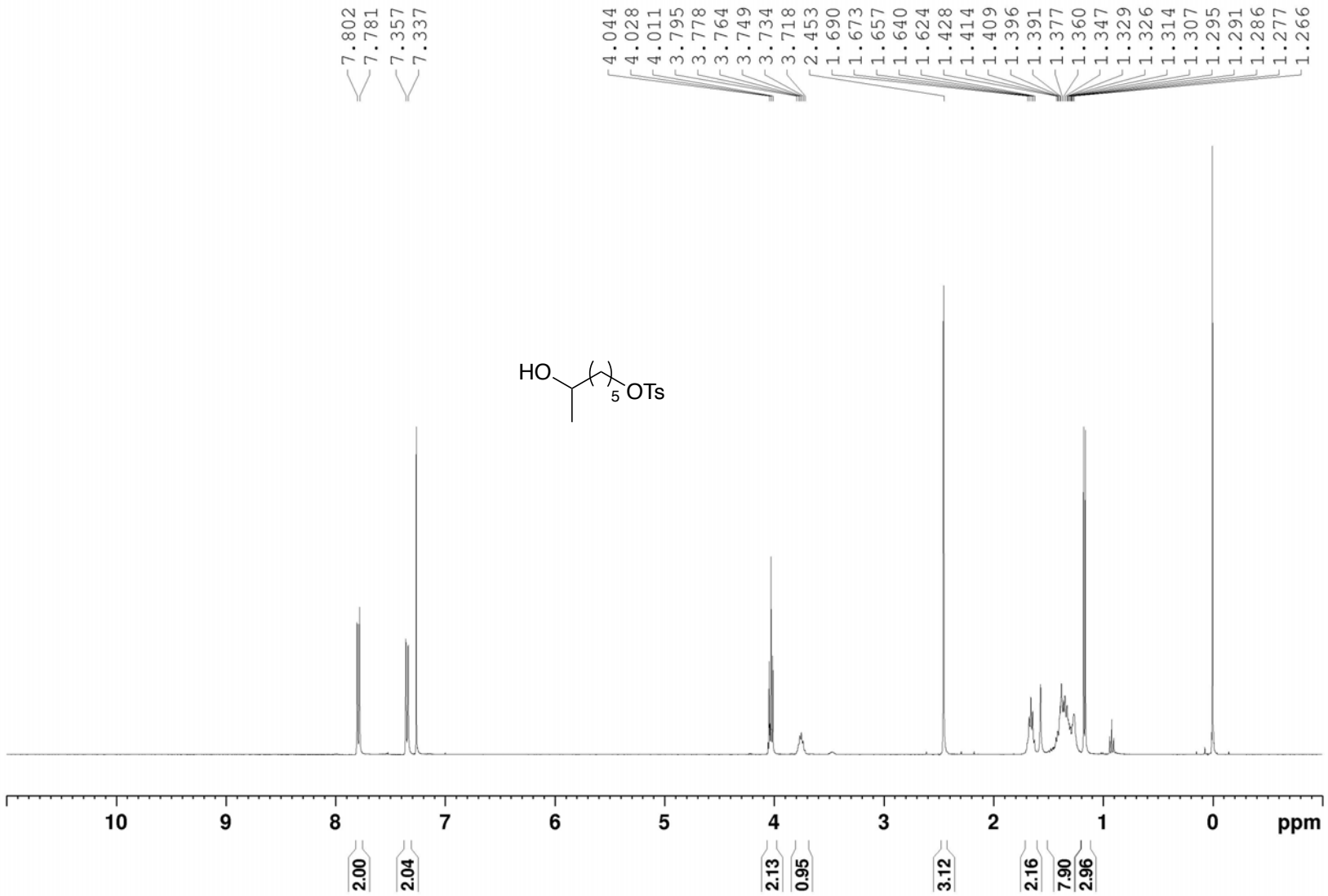

$^{13}$C NMR spectrum of **3eB**



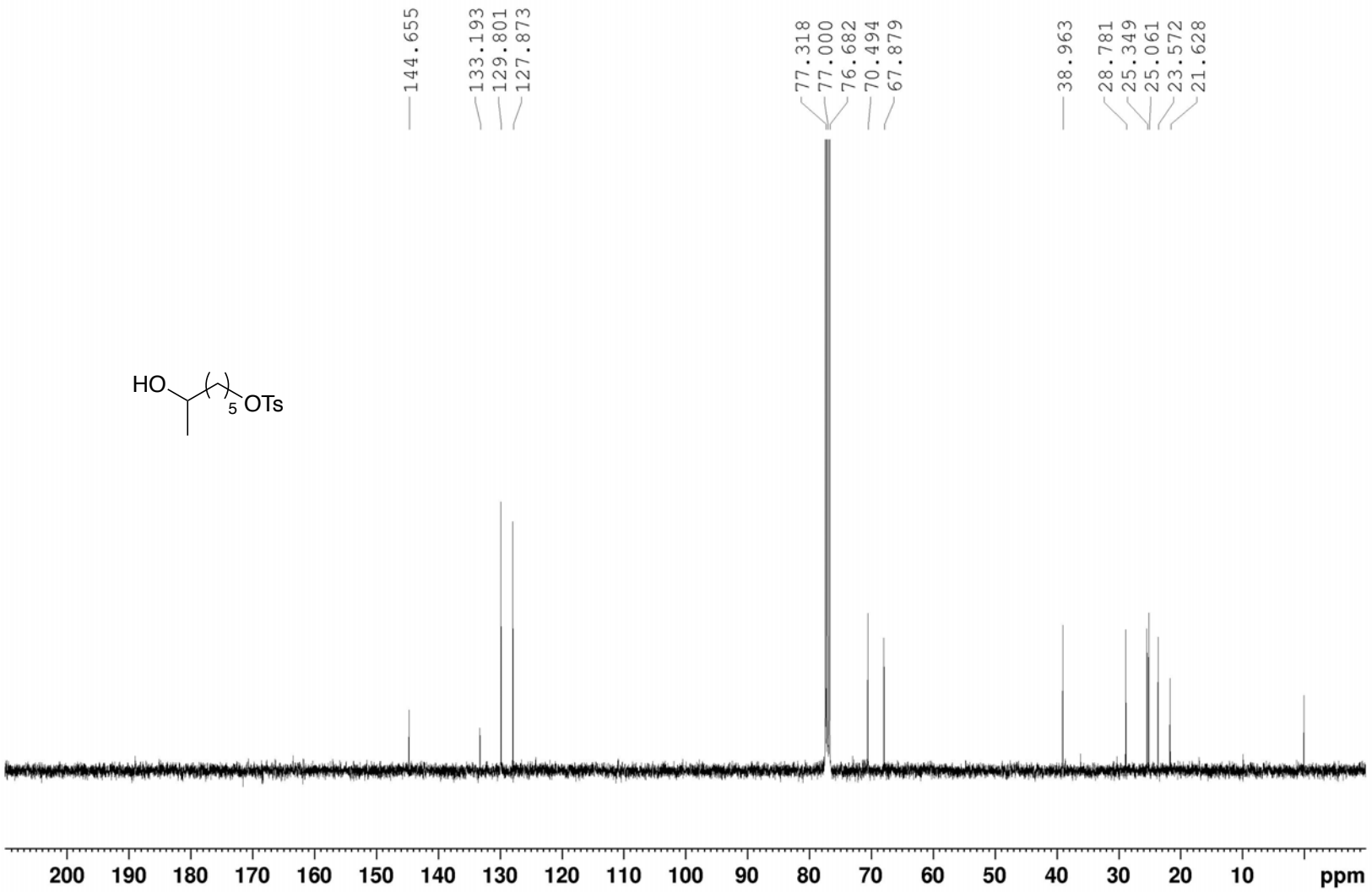

$^{1}$H NMR spectrum of **3aC**



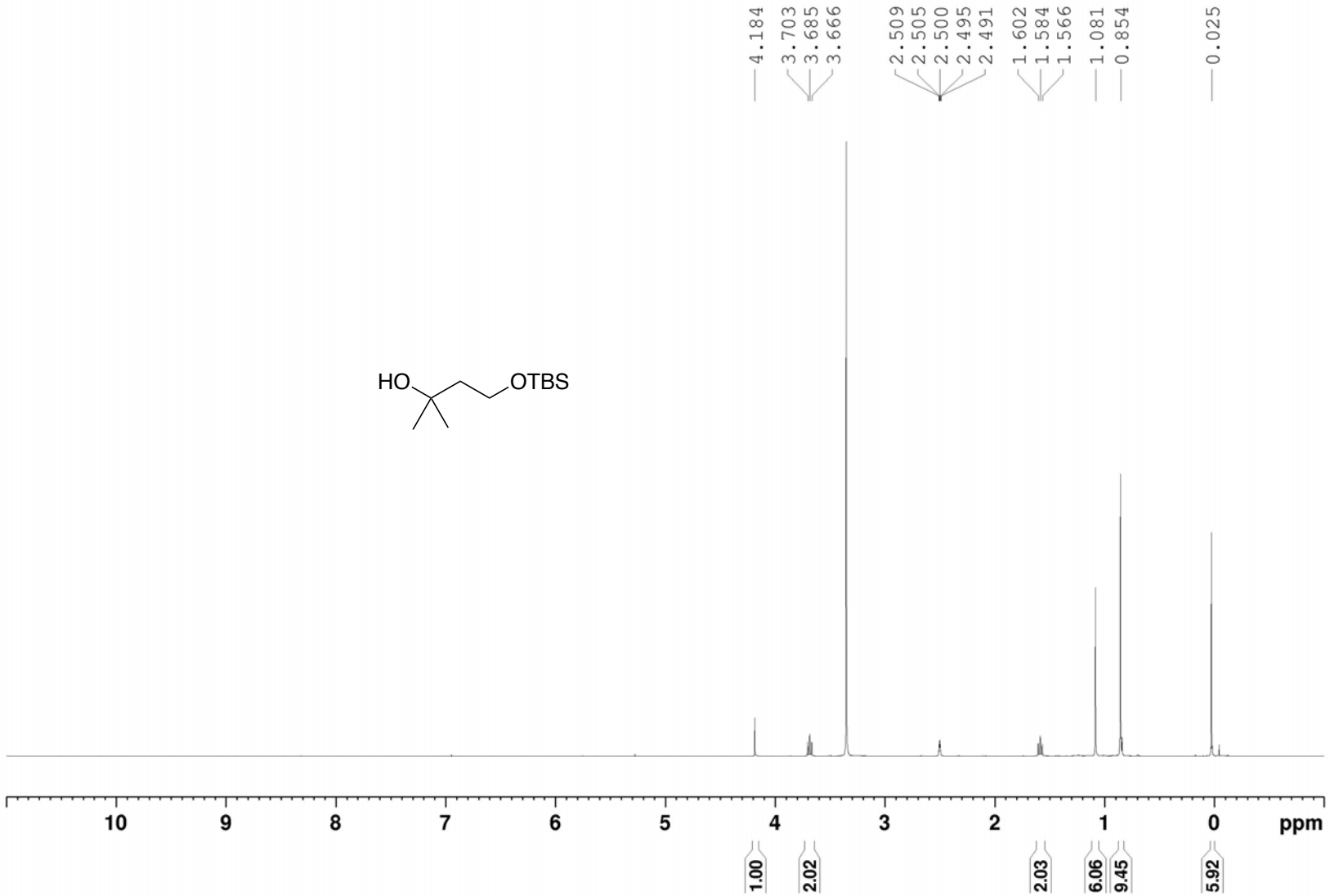

$^{13}$C NMR spectrum of **3aC**



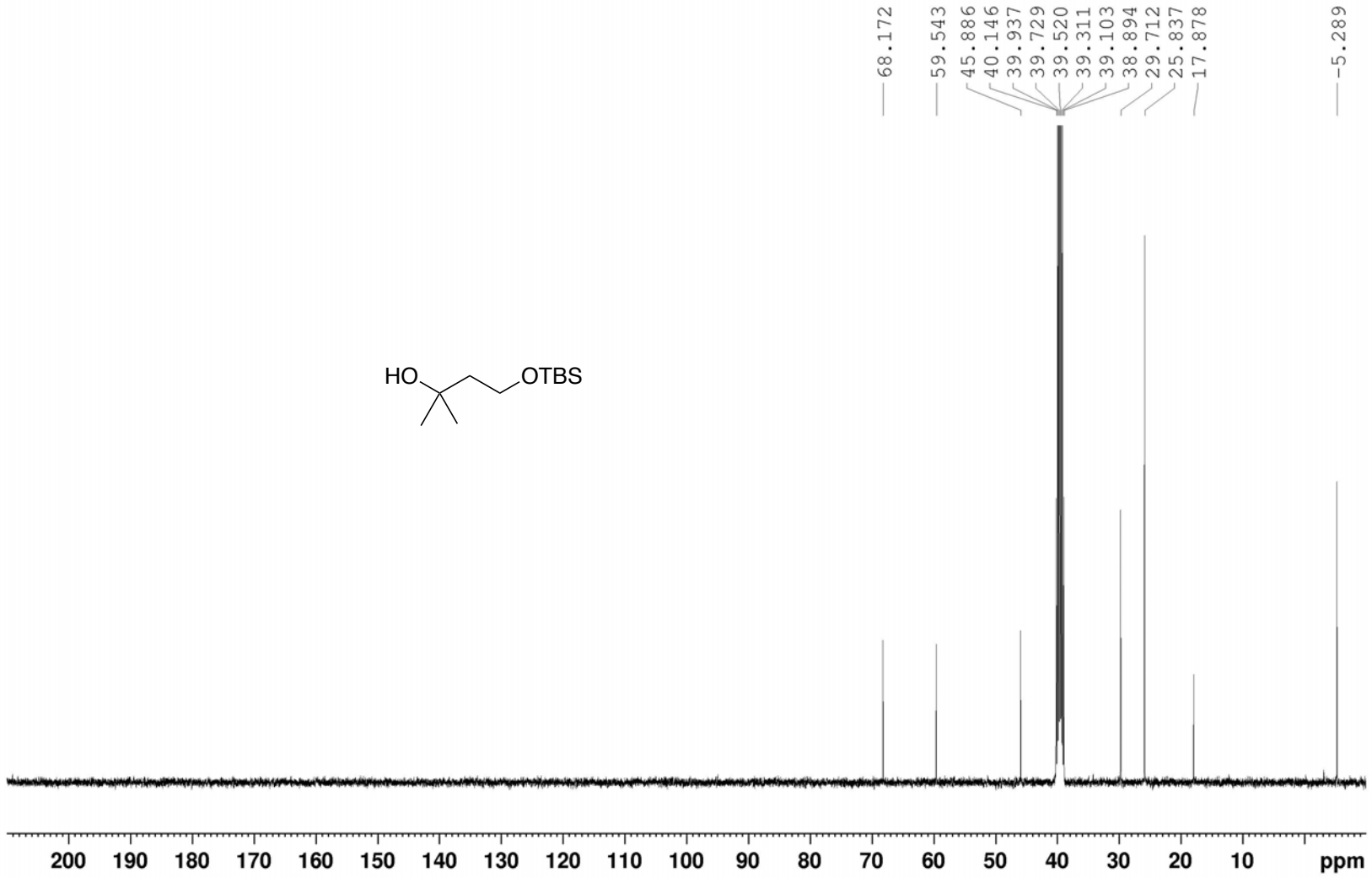

$^{1}$H NMR spectrum of **5ab**



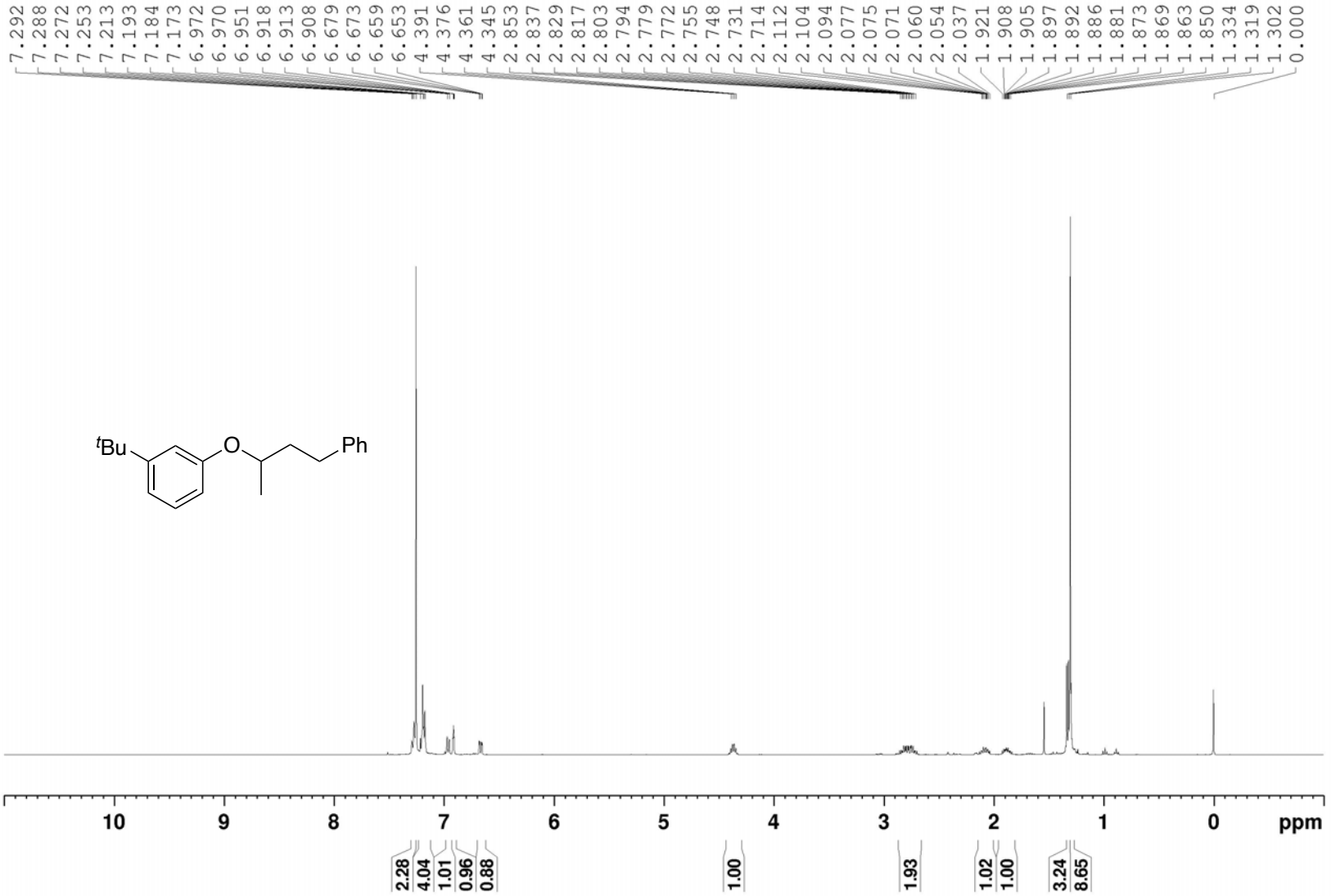

$^{13}$C NMR spectrum of **5ab**



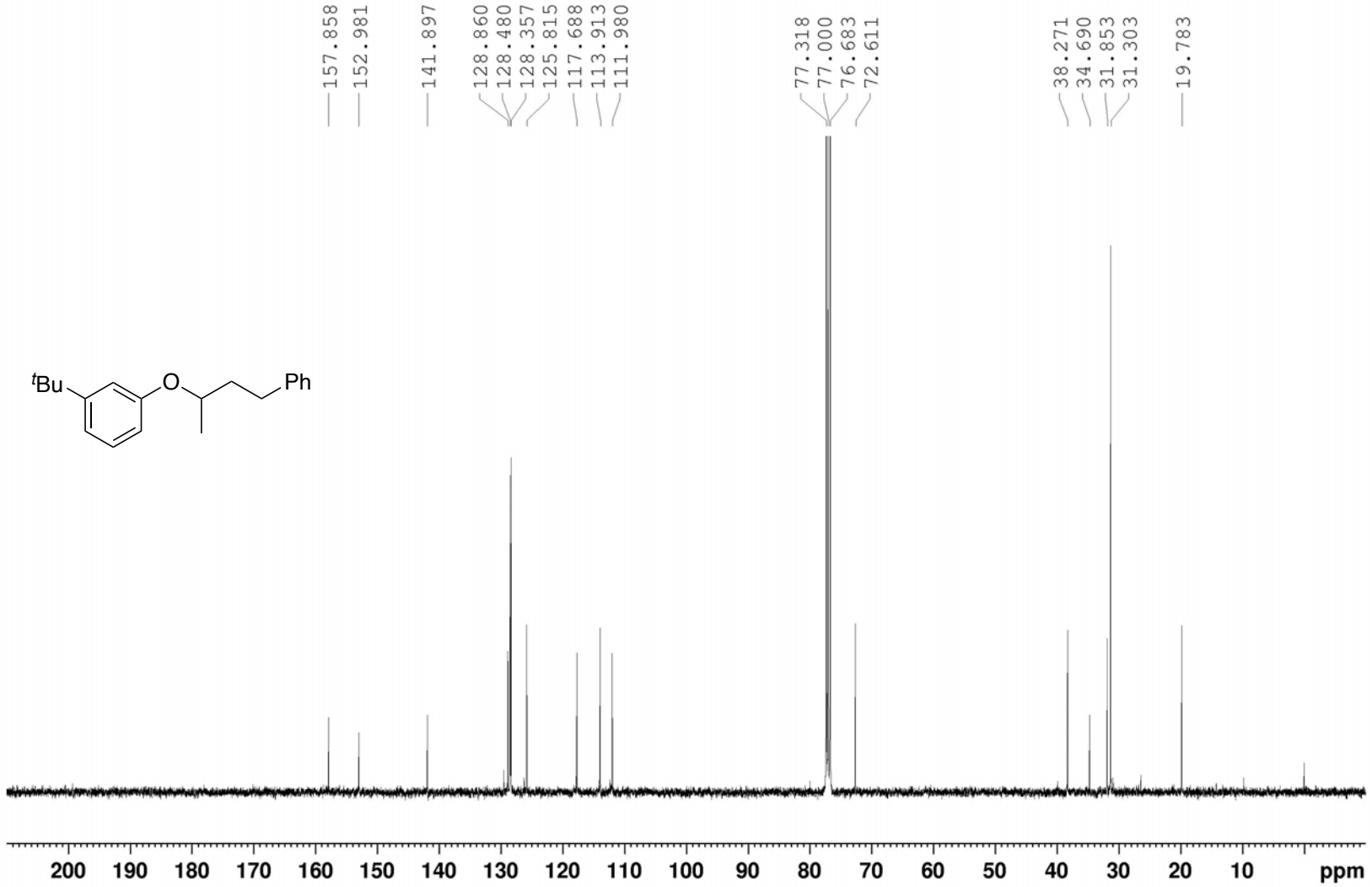

$^{1}$H NMR spectrum of **5au**



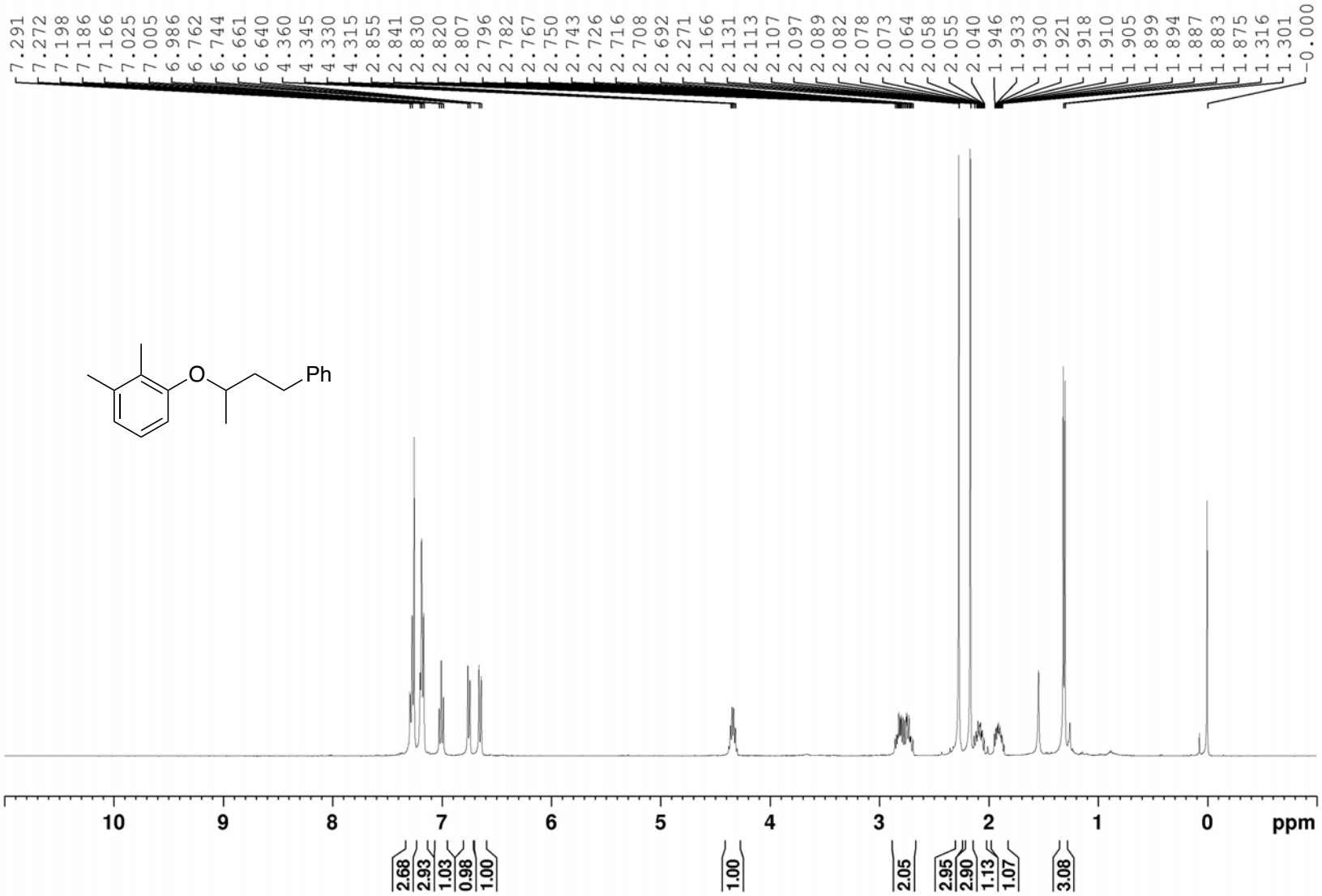

$^{13}$C NMR spectrum of **5au**



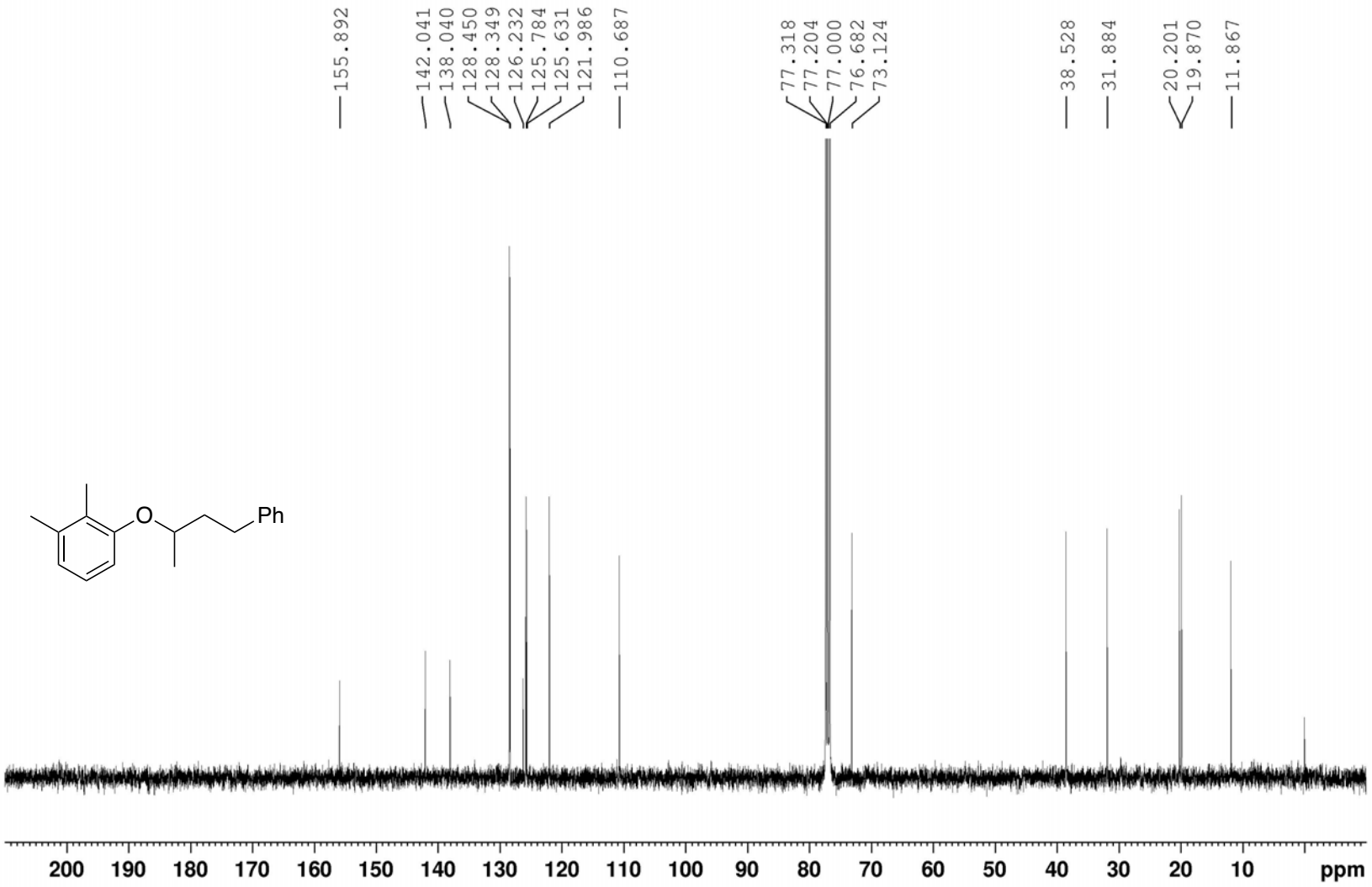

$^{1}$H NMR spectrum of **7aa**



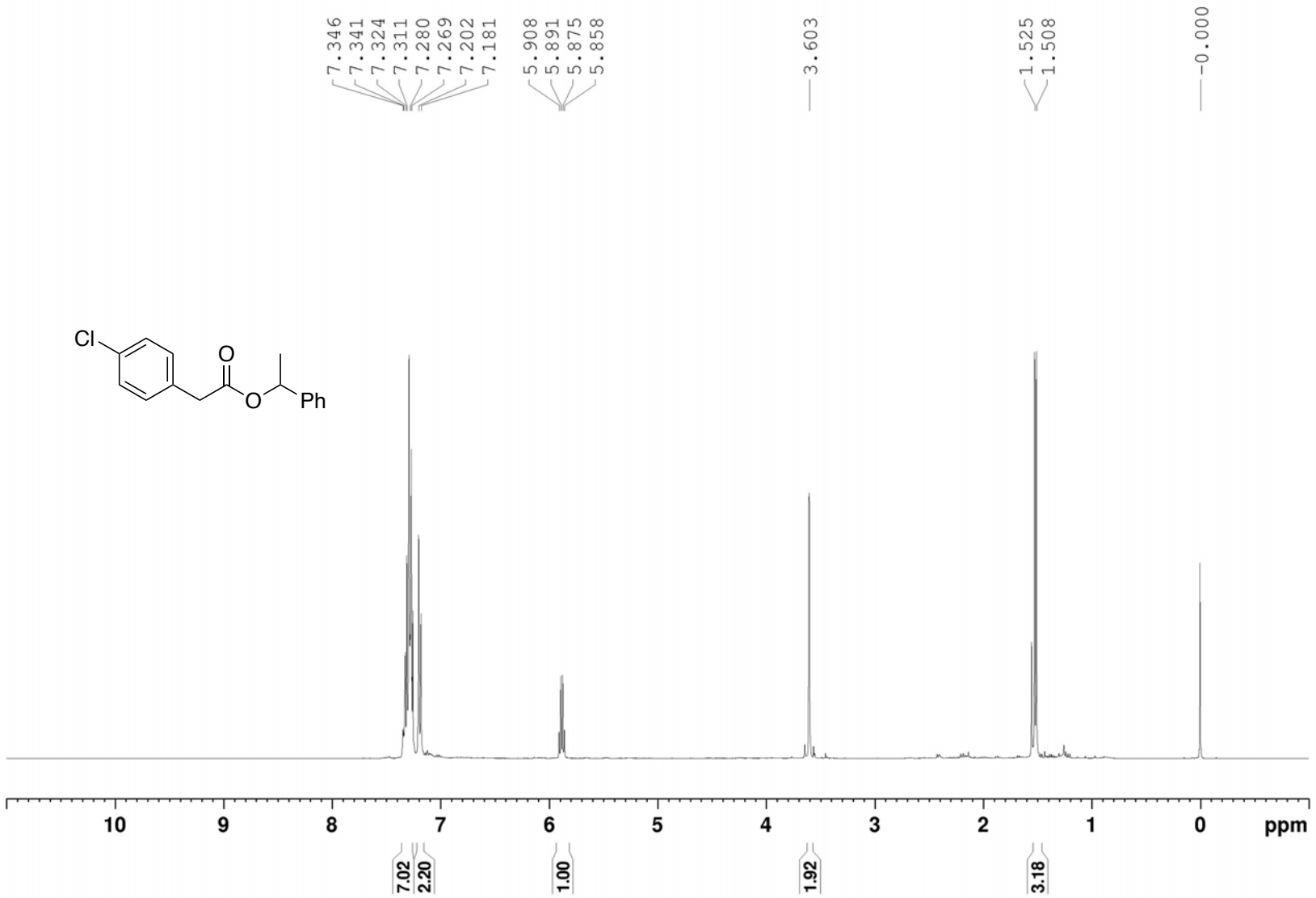

$^{13}$C NMR spectrum of **7aa**



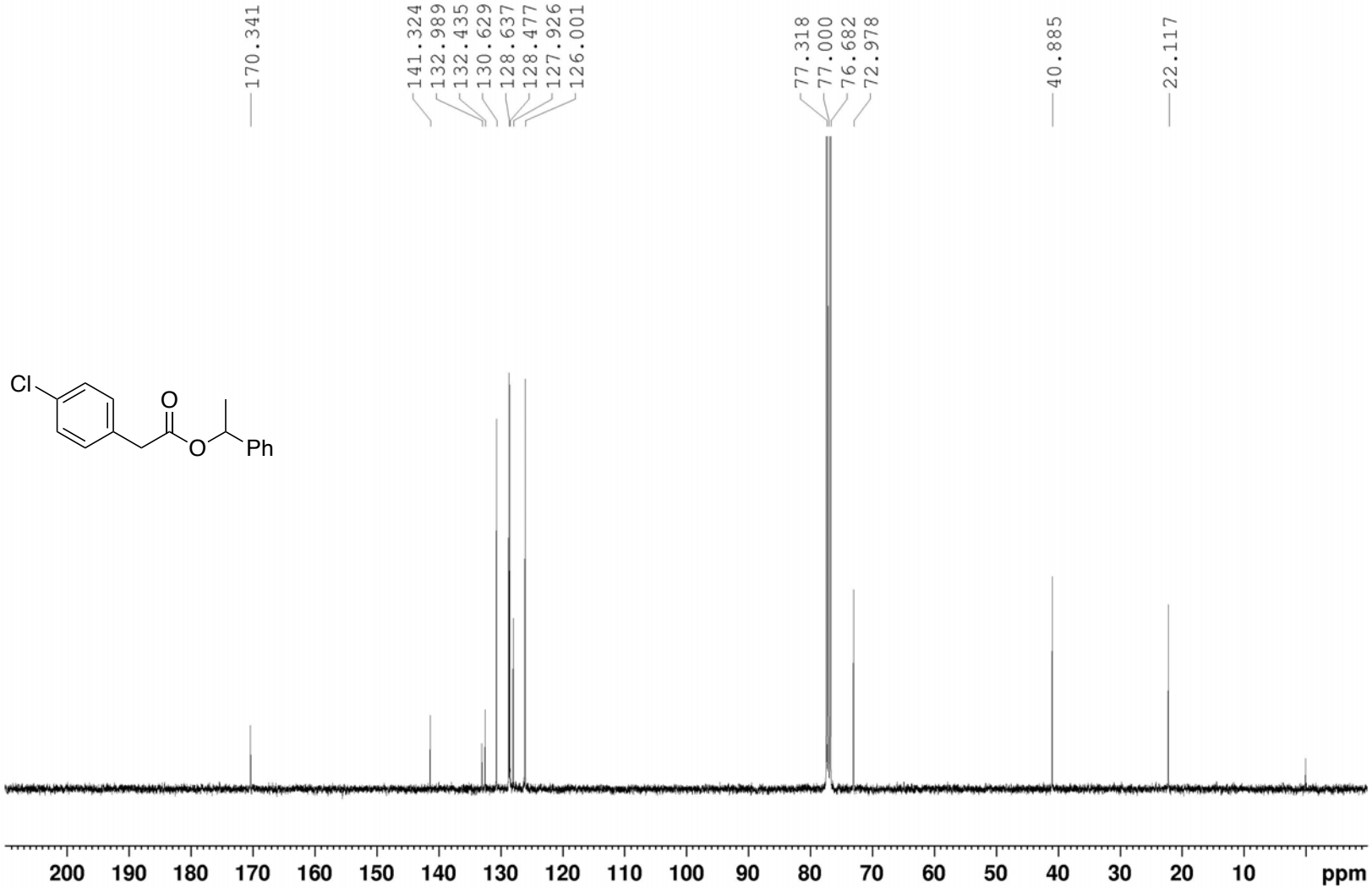

$^{1}$H NMR spectrum of **7ba**



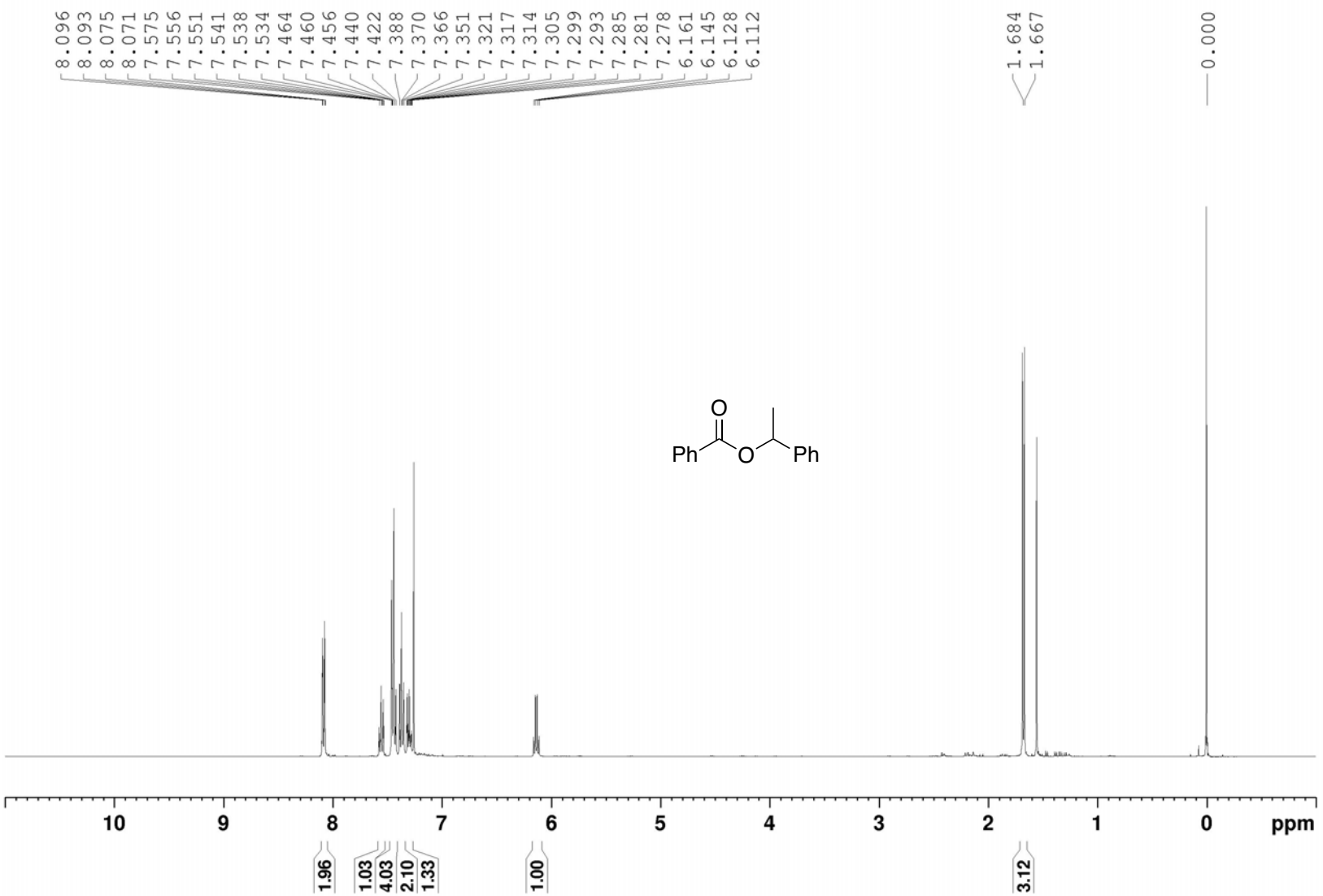

$^{13}$C NMR spectrum of **7ba**



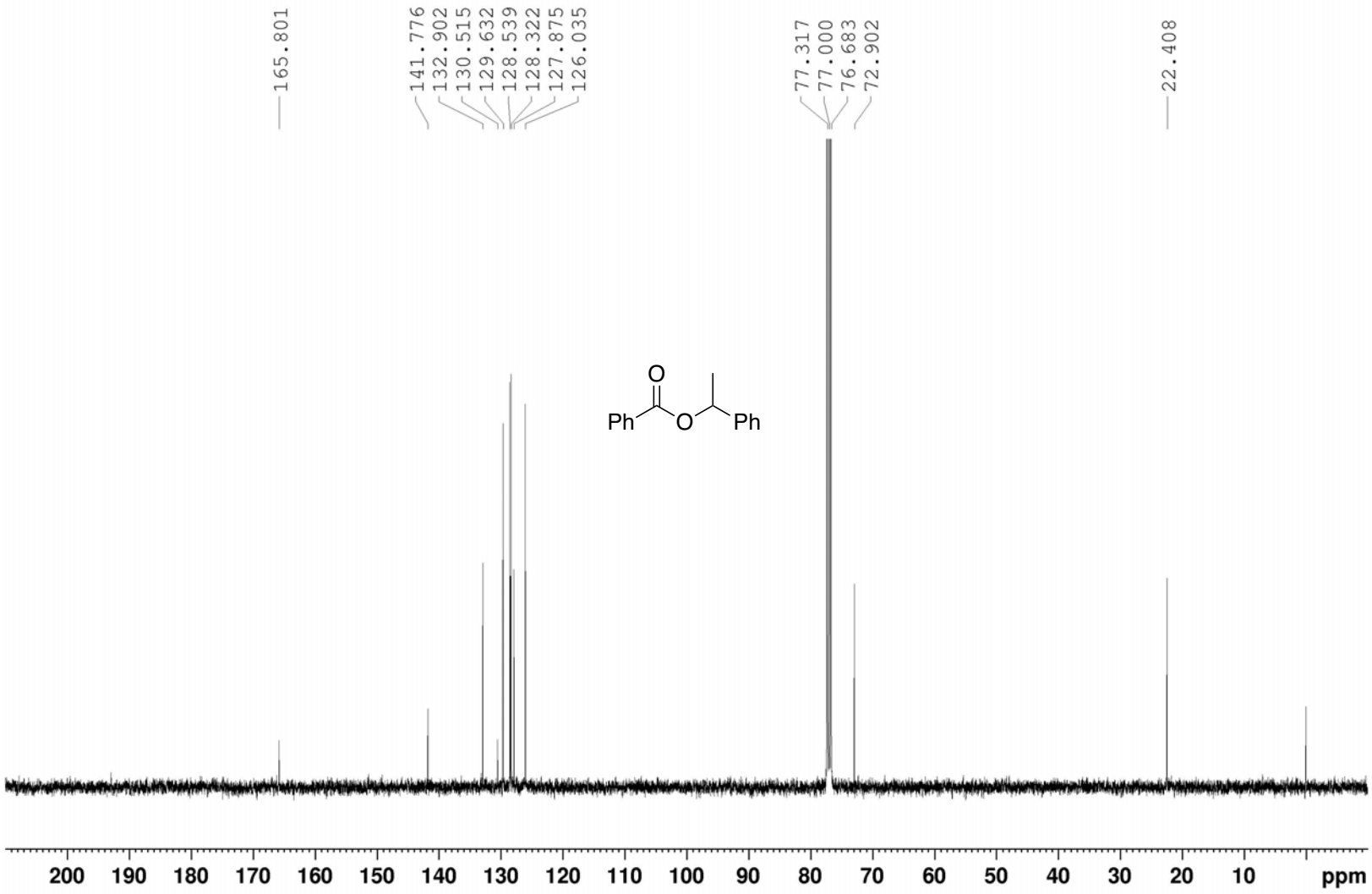

$^{1}$H NMR spectrum of **9ap**



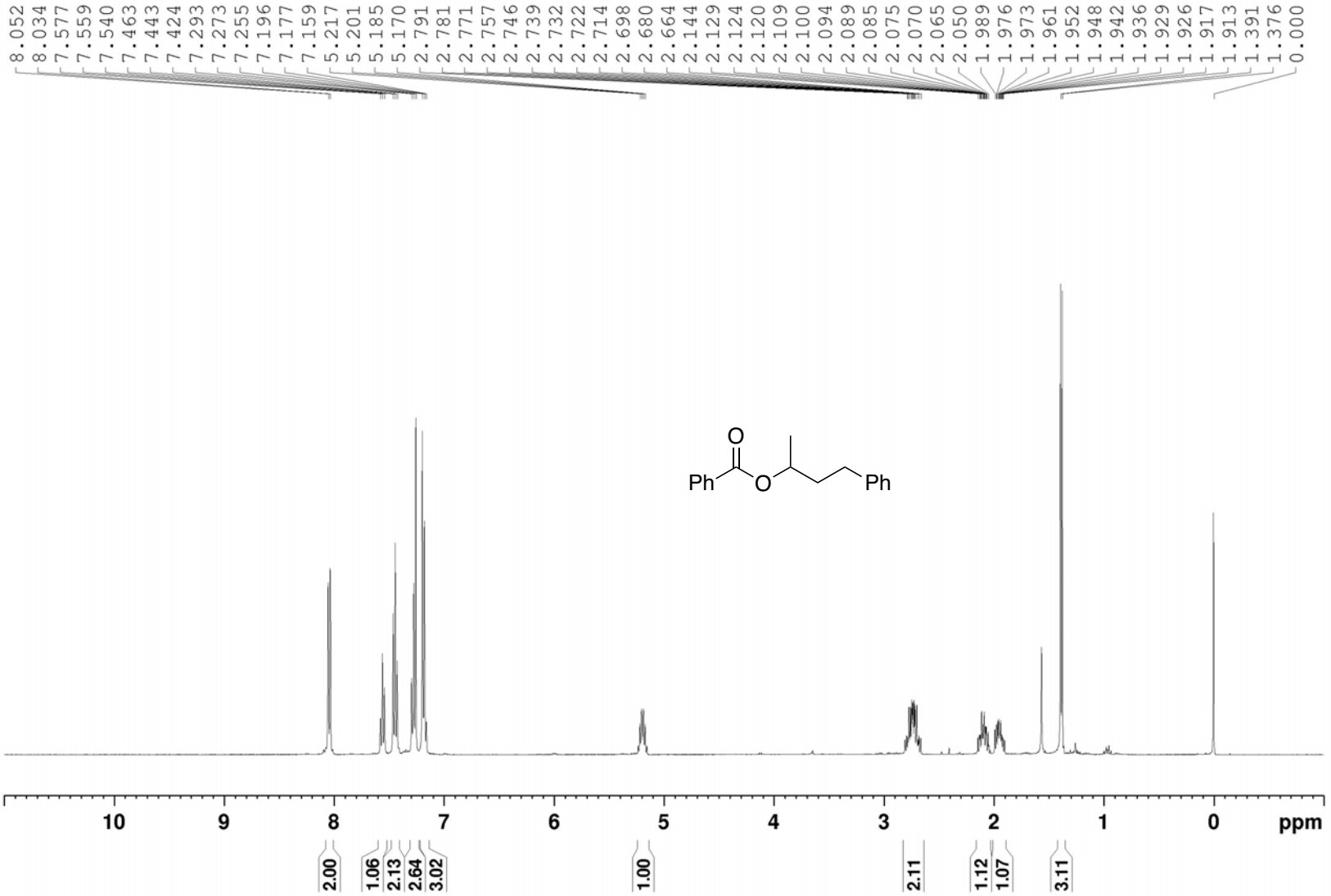

$^{13}$C NMR spectrum of **9ap**



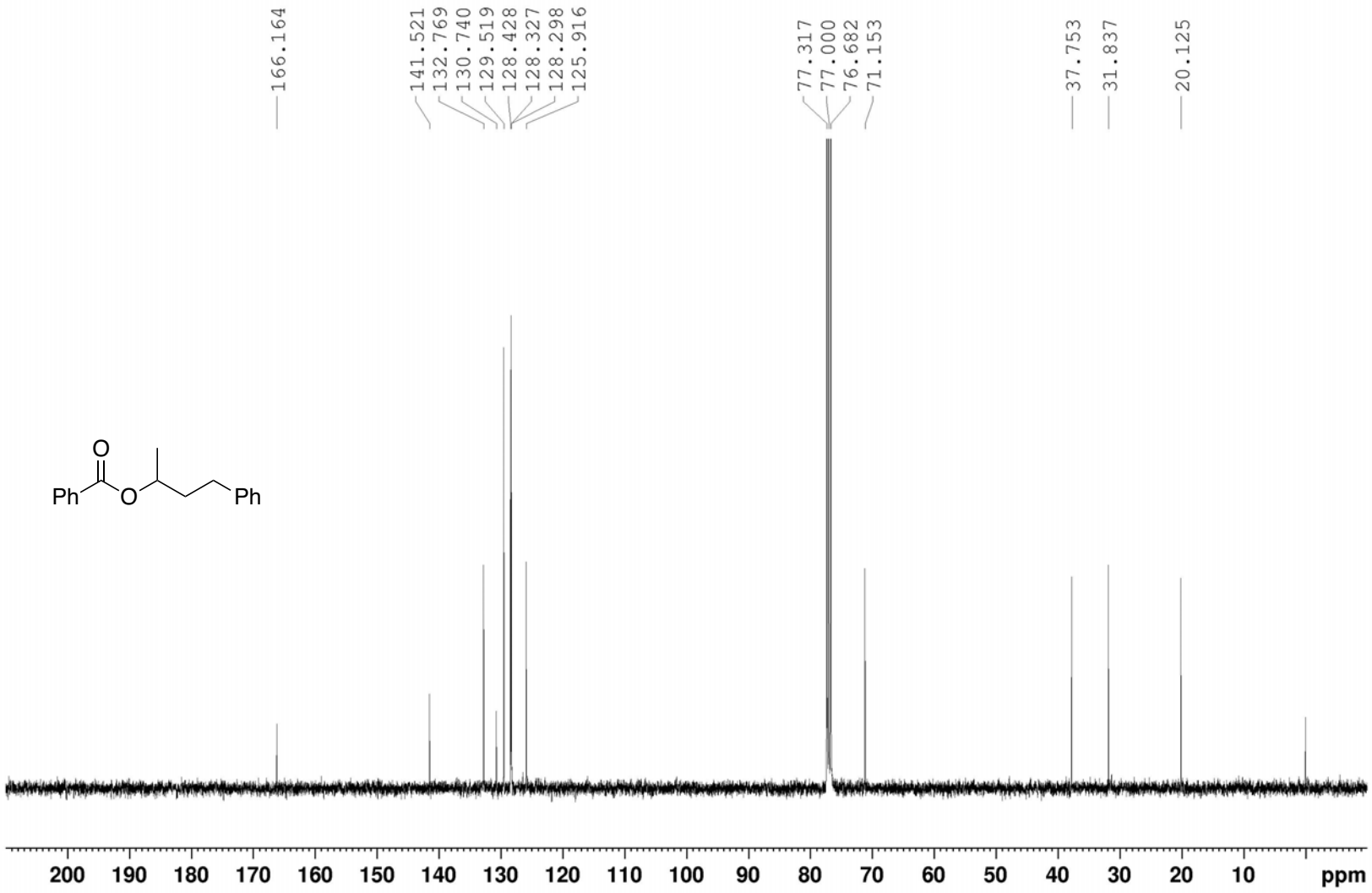

$^{1}$H NMR spectrum of **9bp**



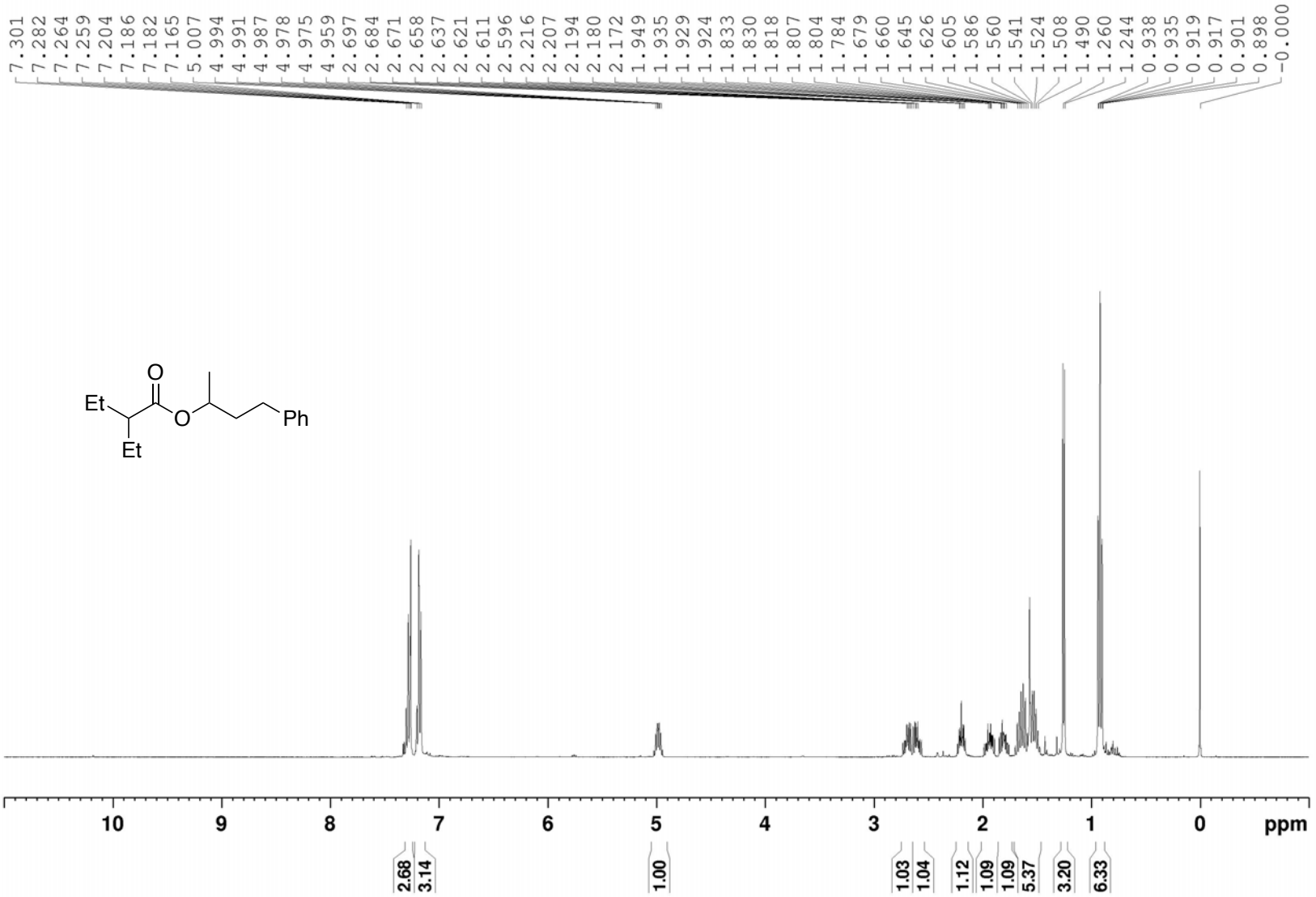

$^{13}$C NMR spectrum of **9bp**



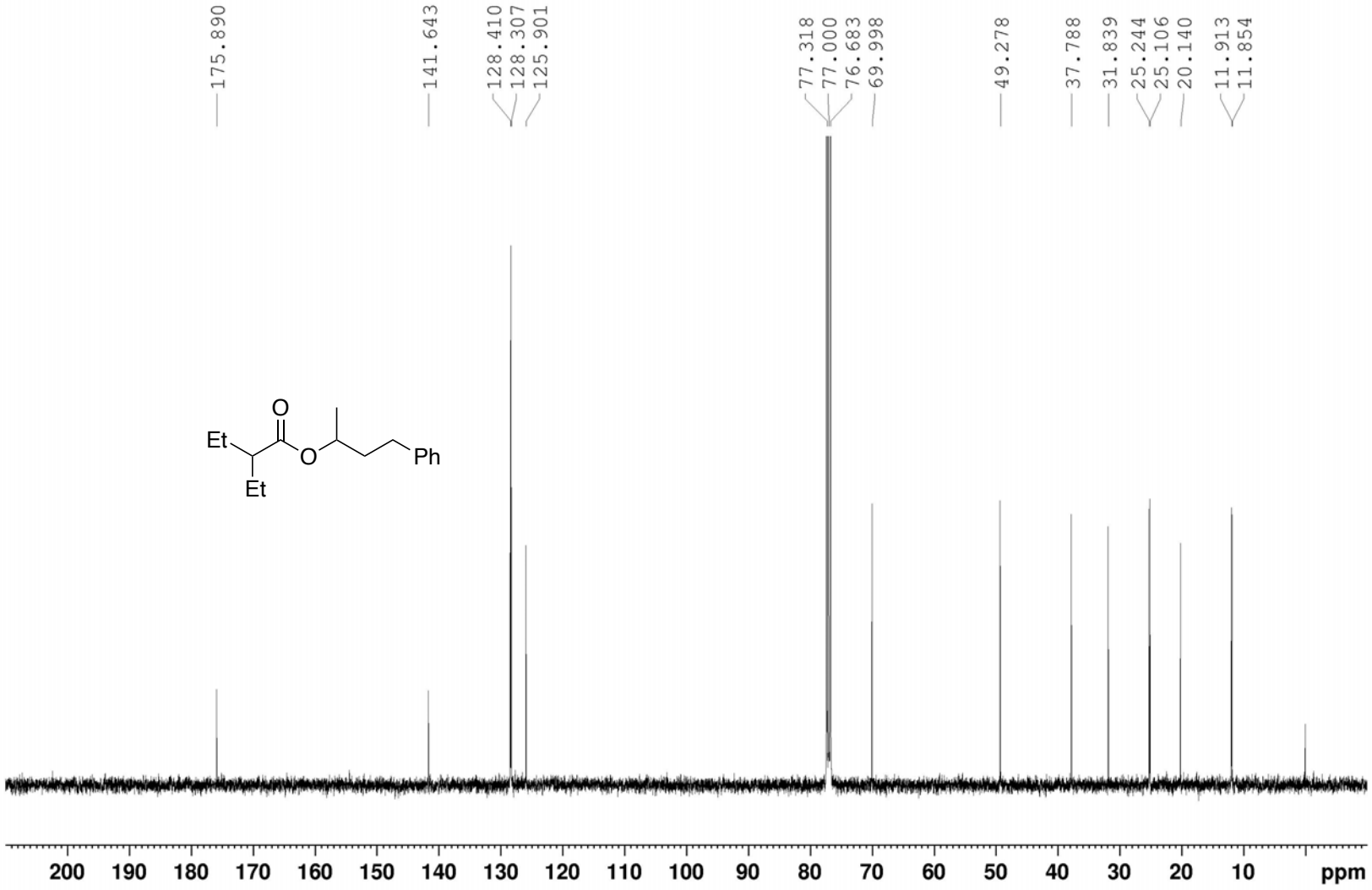

$^{1}$H NMR spectrum of **9ba**



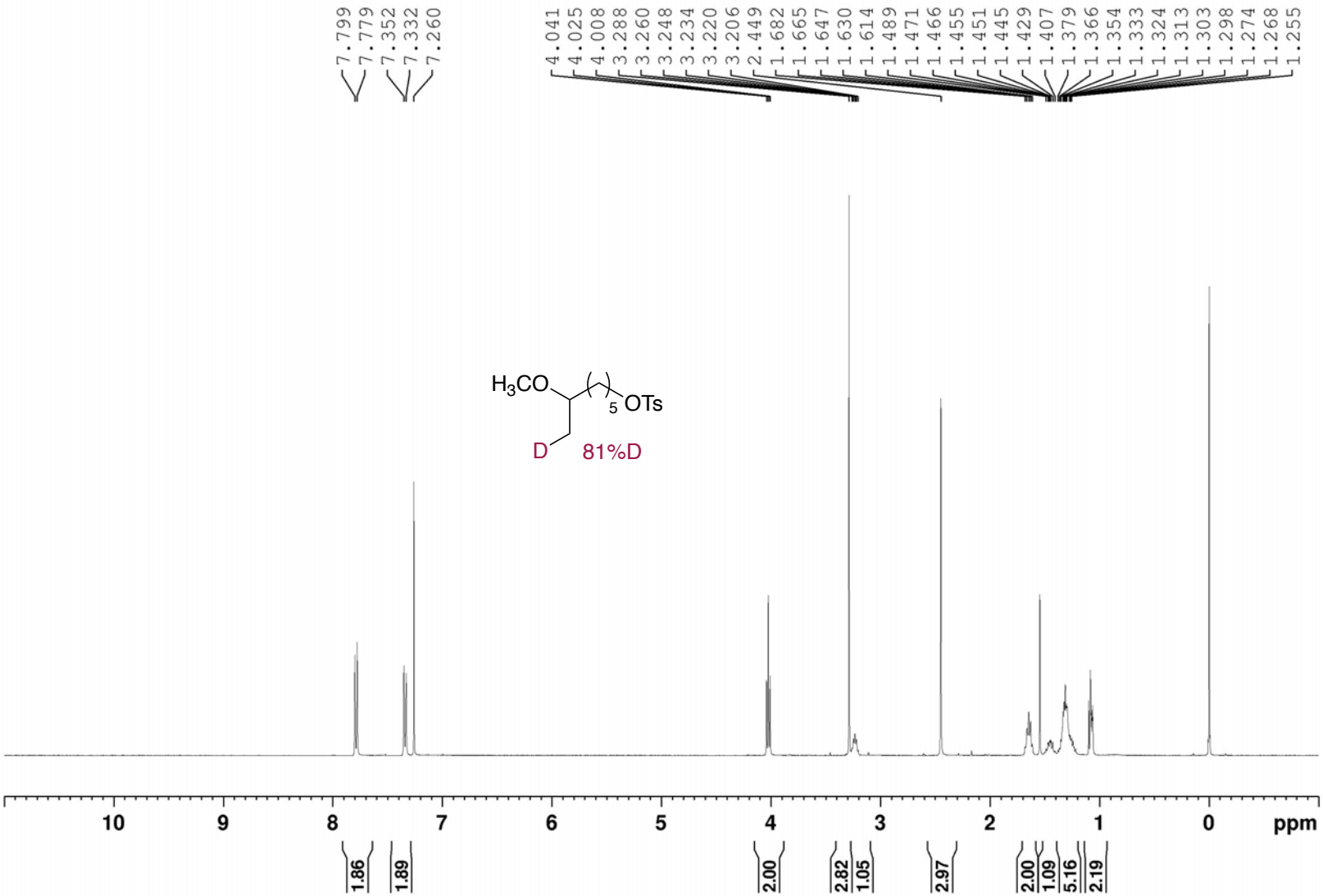

$^{13}$C NMR spectrum of **9ba**



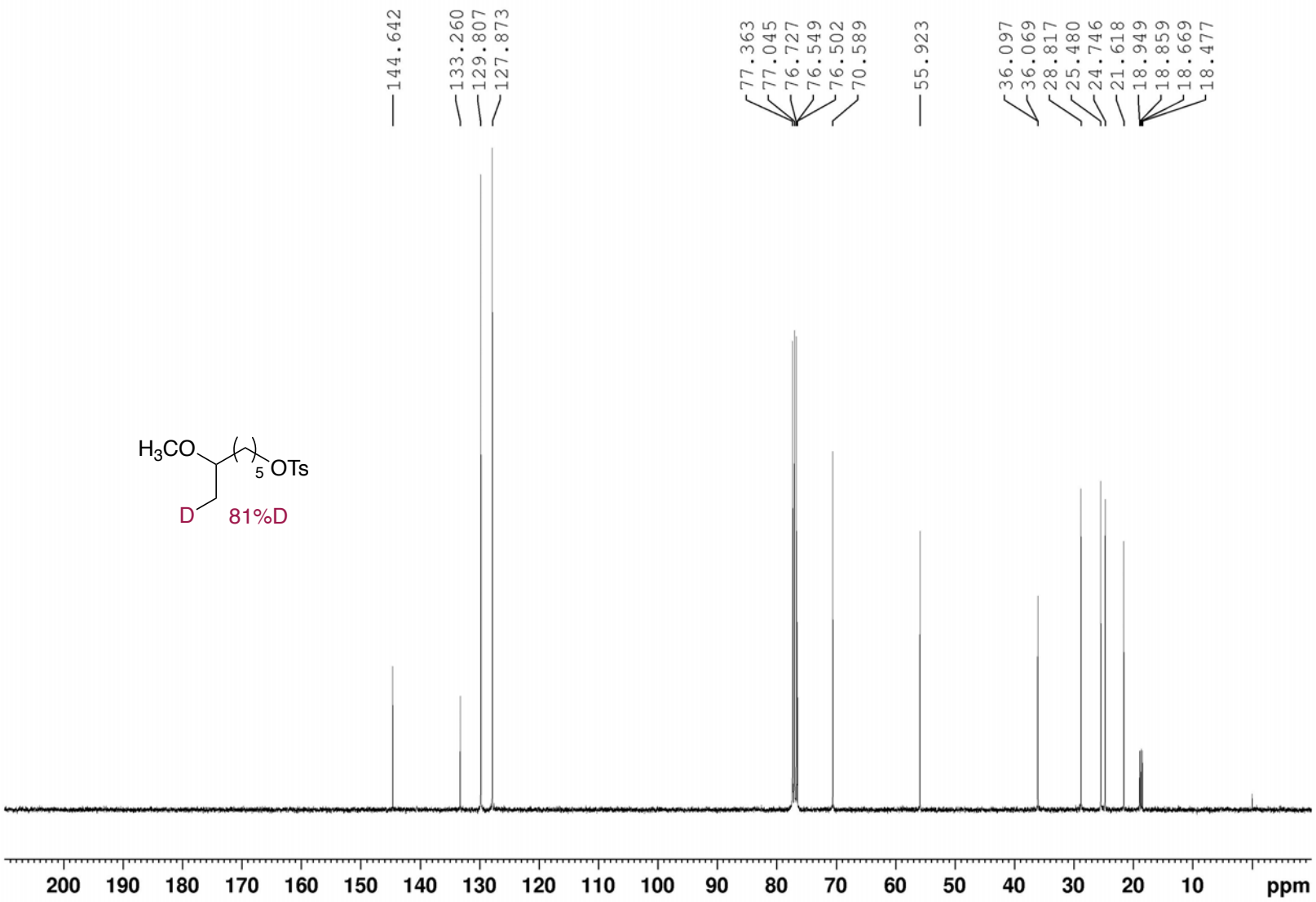

$^{1}$H NMR spectrum of **9ca**



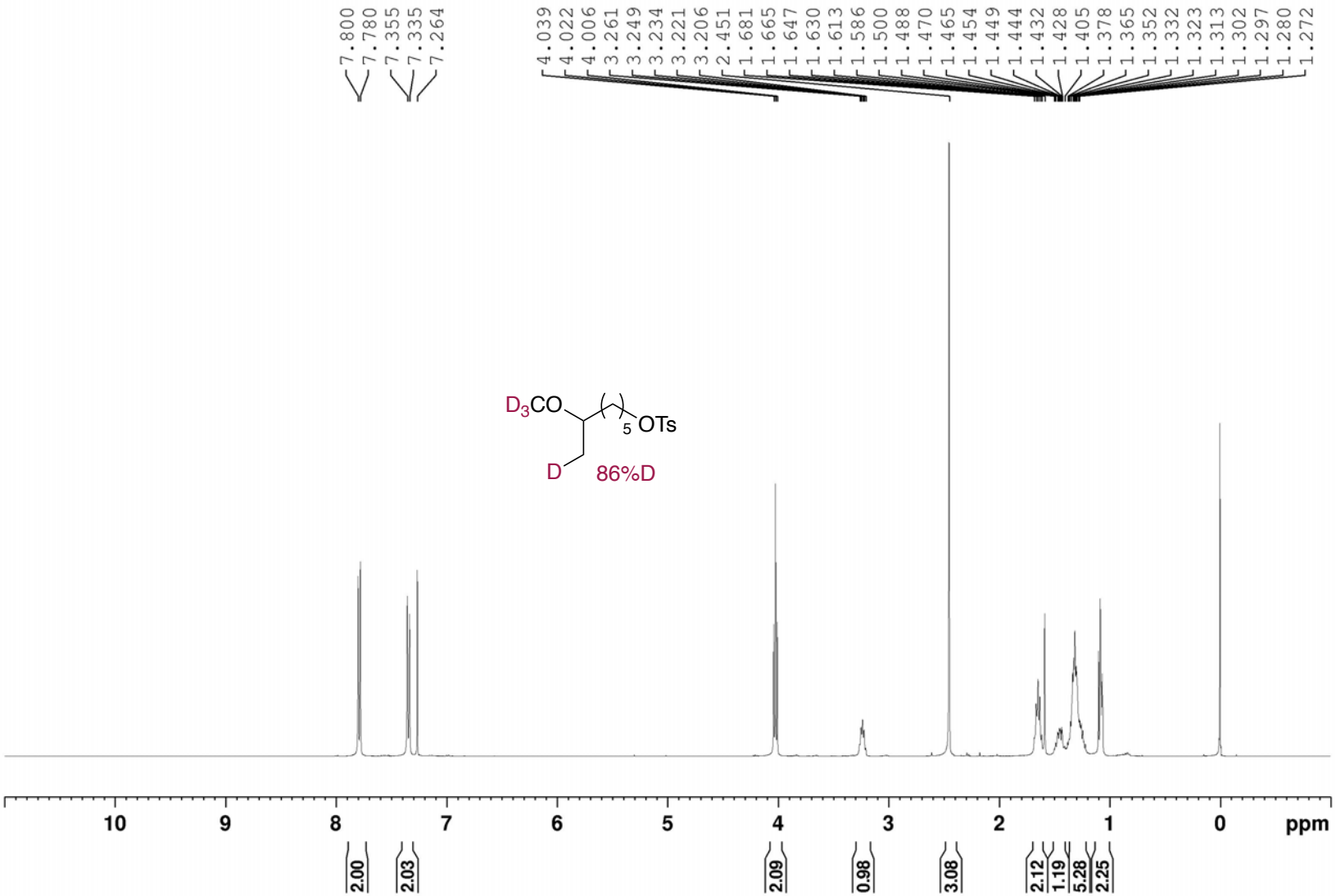

$^{13}$C NMR spectrum of **9ca**



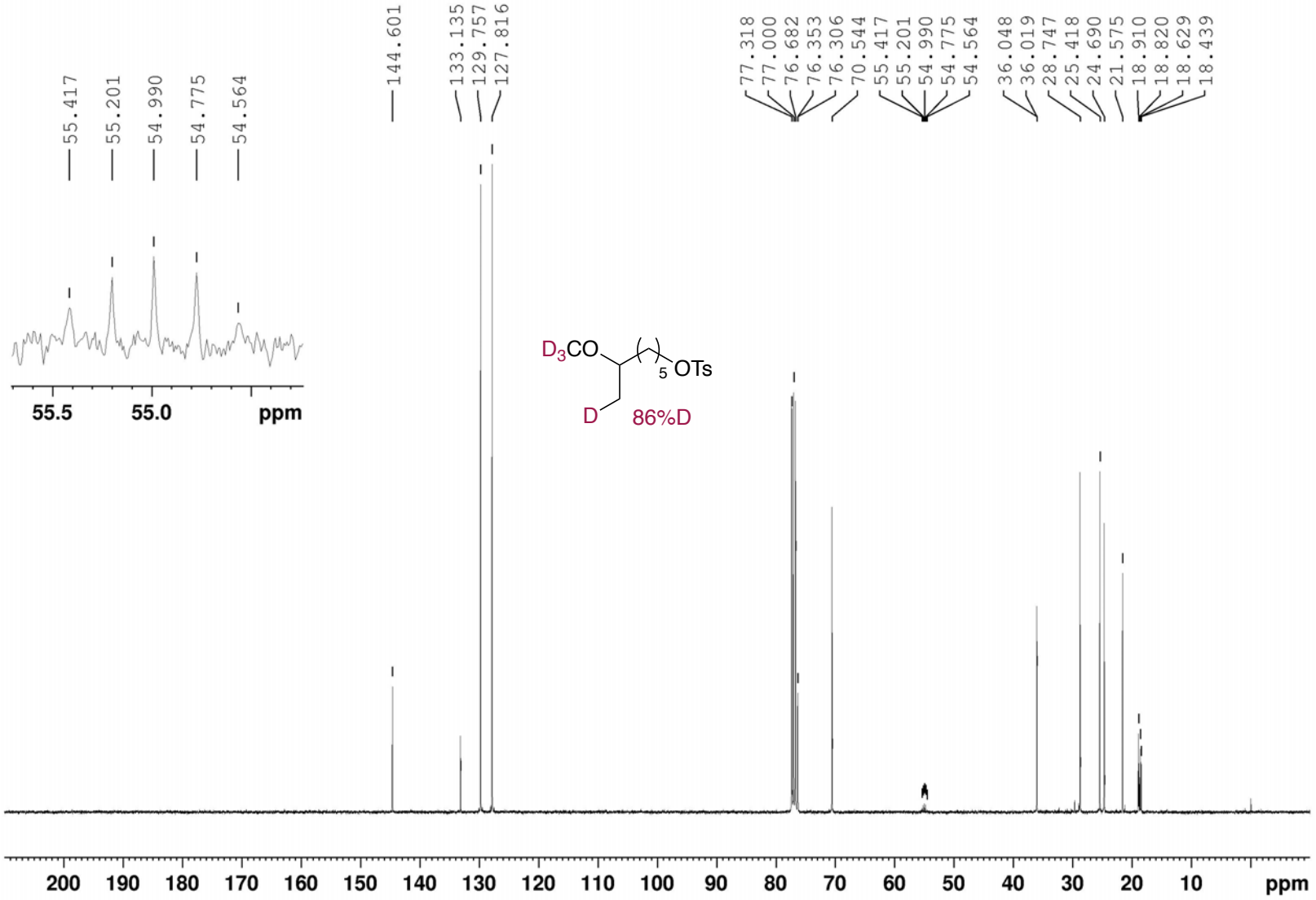

$^{1}$H NMR spectrum of **3bb-D**



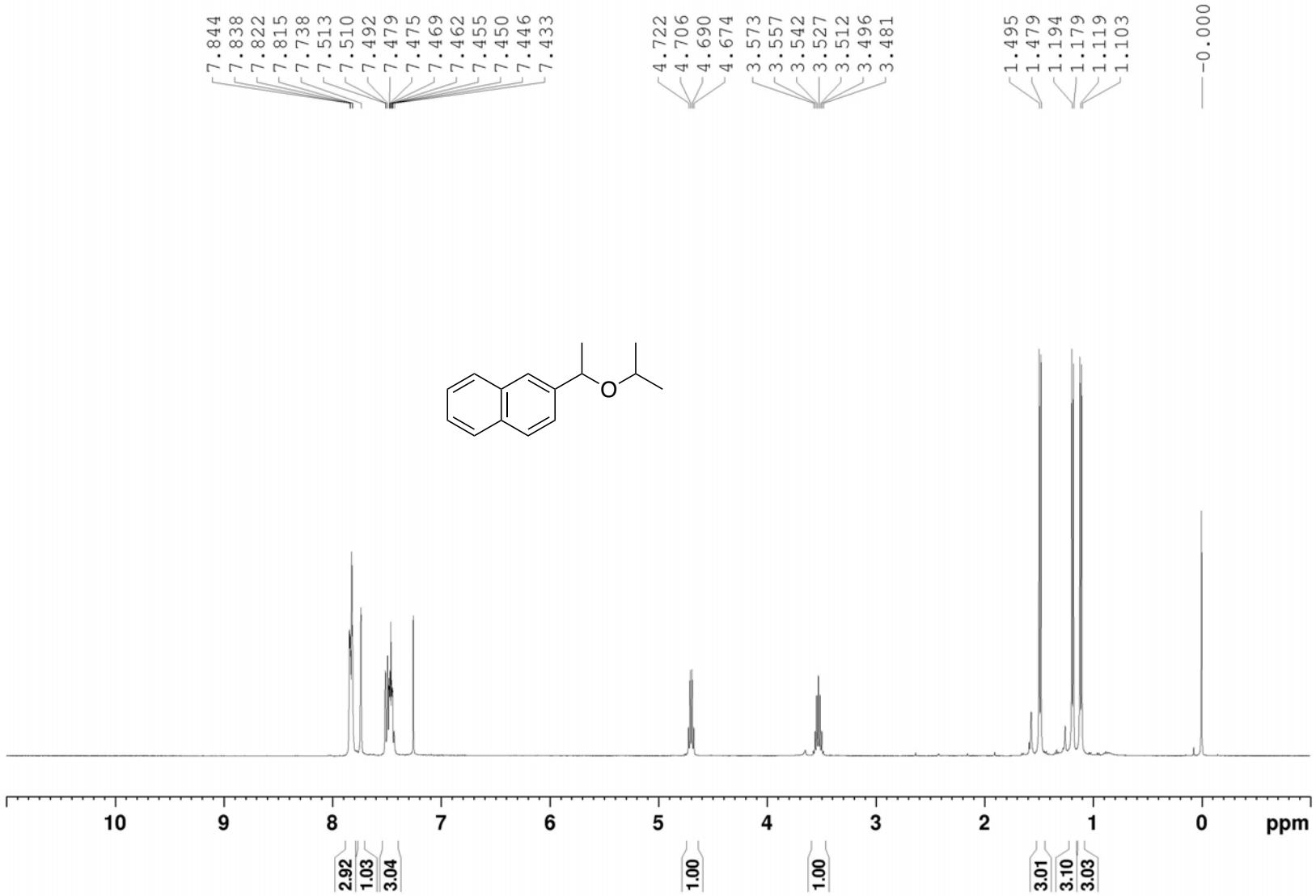

$^{13}$C NMR spectrum of **3bb-D**



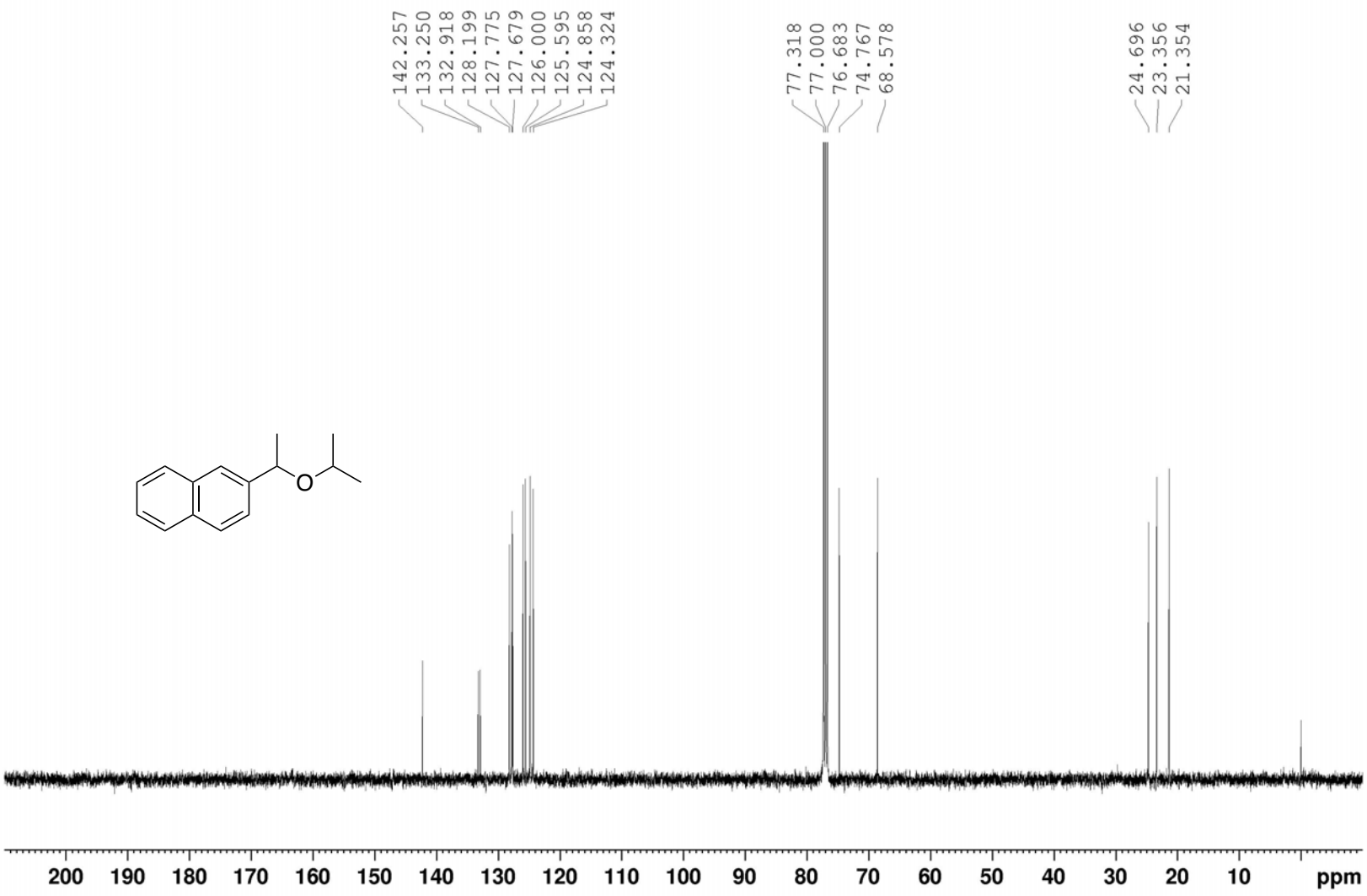

$^{1}$H NMR spectrum of **3bb-D'**



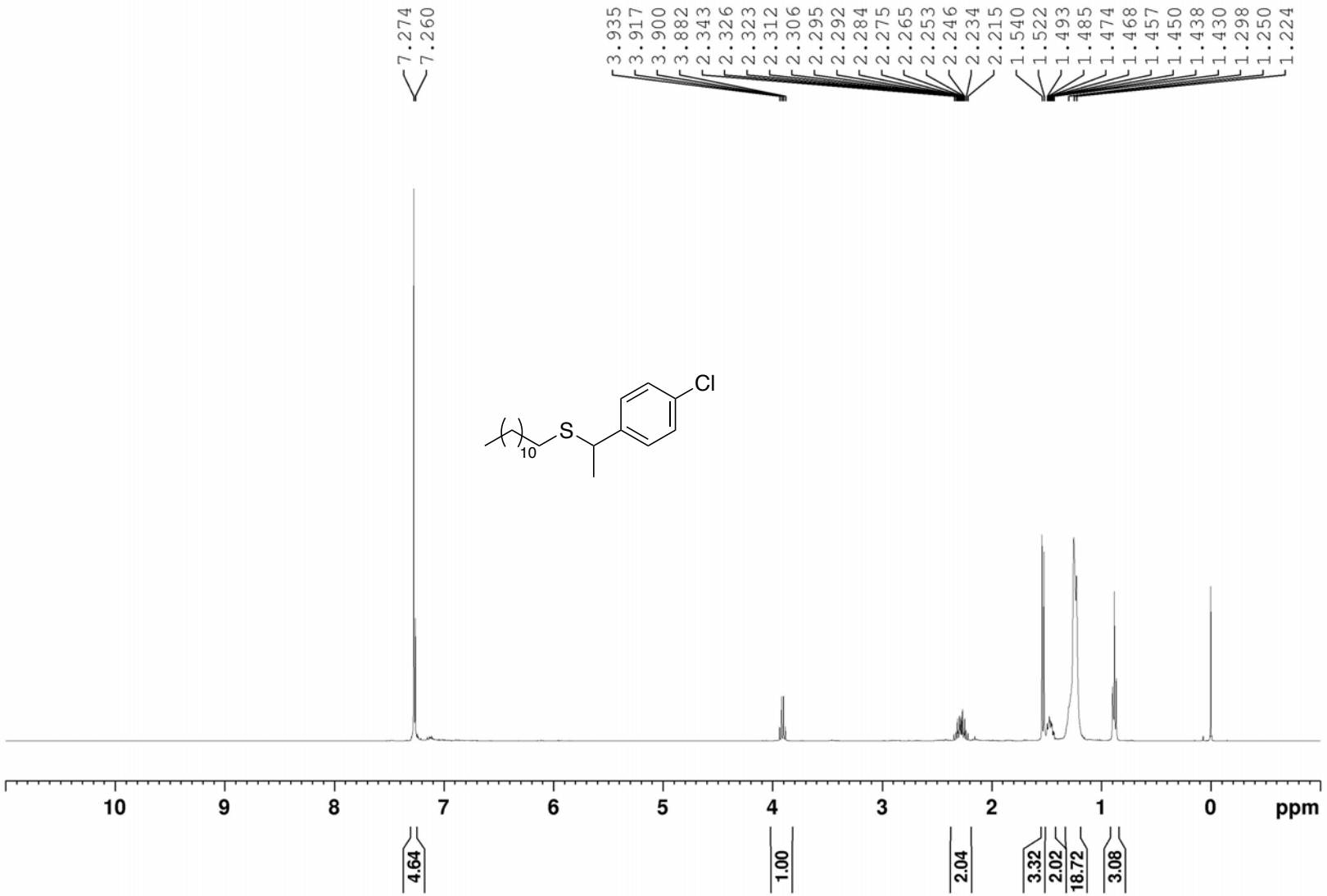

$^{13}$C NMR spectrum of **3bb-D'**



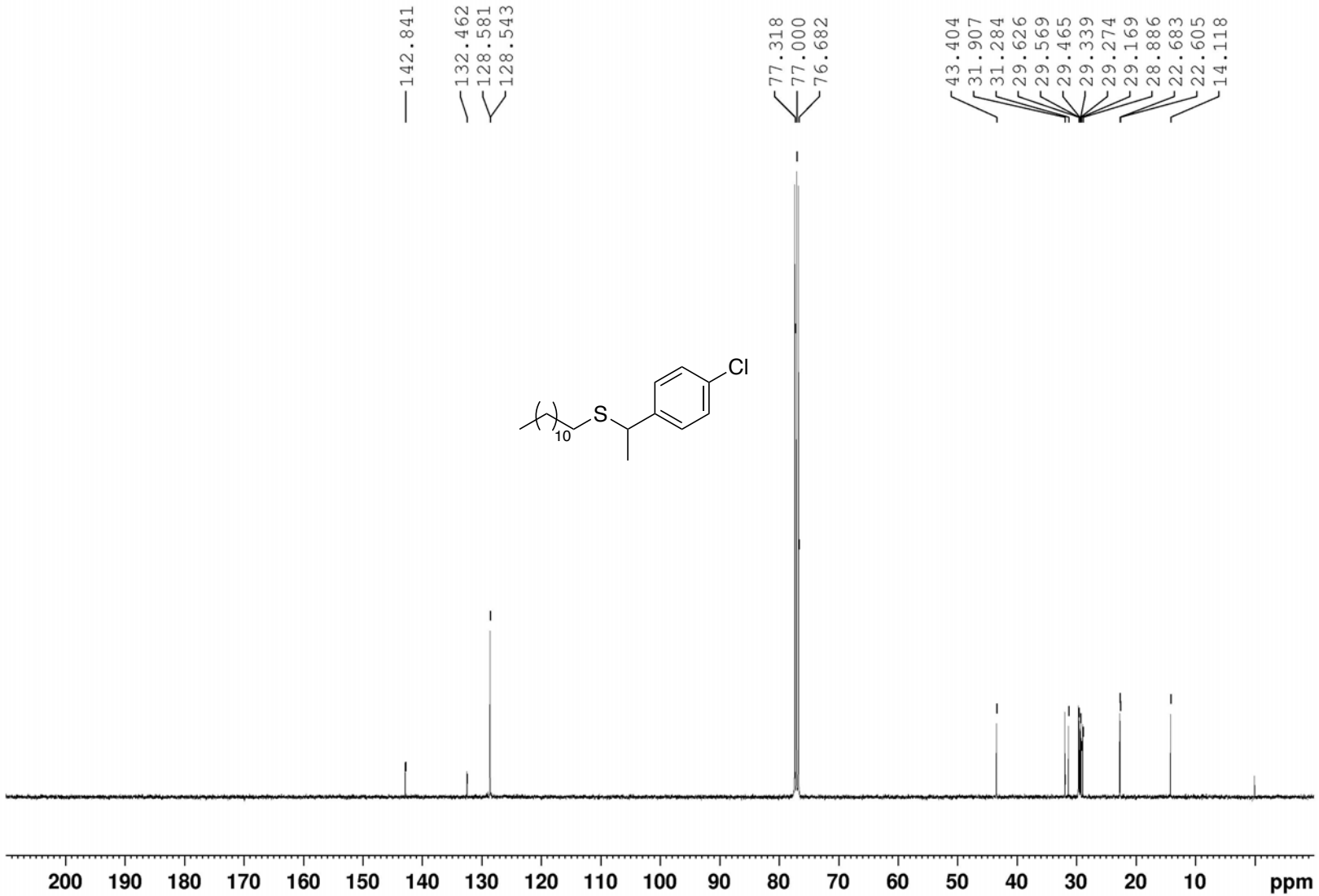

$^{1}$H NMR spectrum of **11qa**



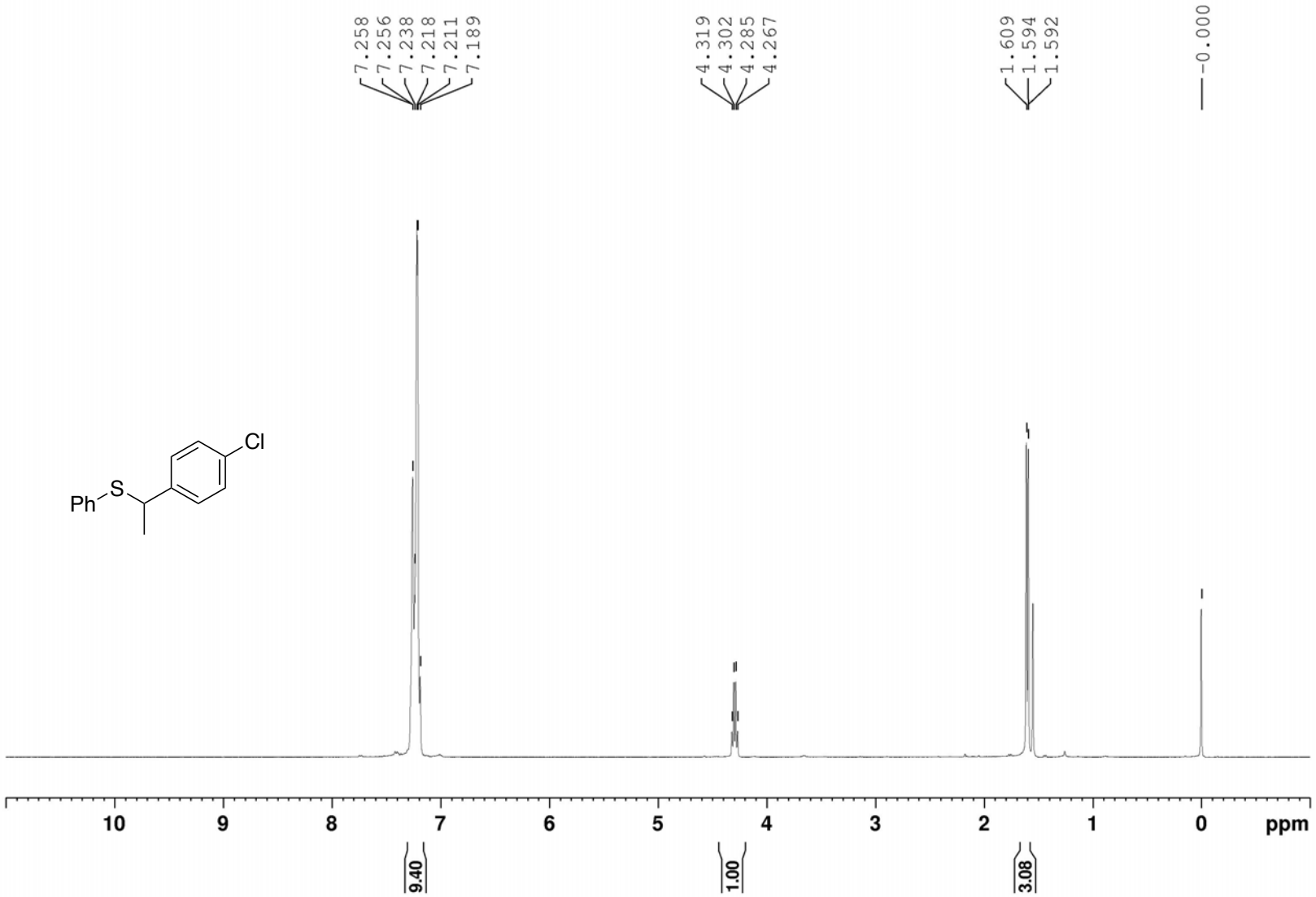

$^{13}$C NMR spectrum of **11qa**



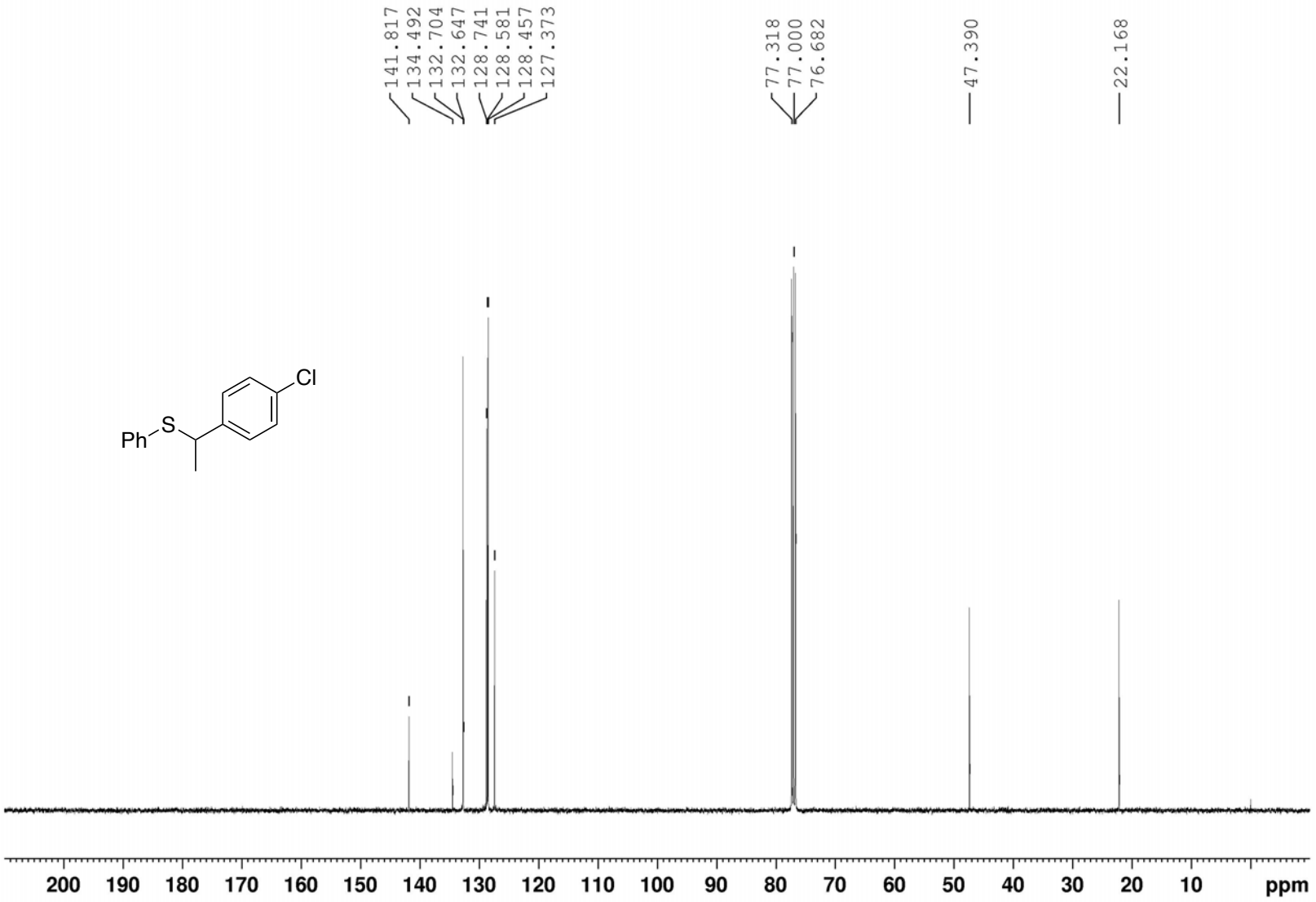

$^{1}$H NMR spectrum of **13ao**



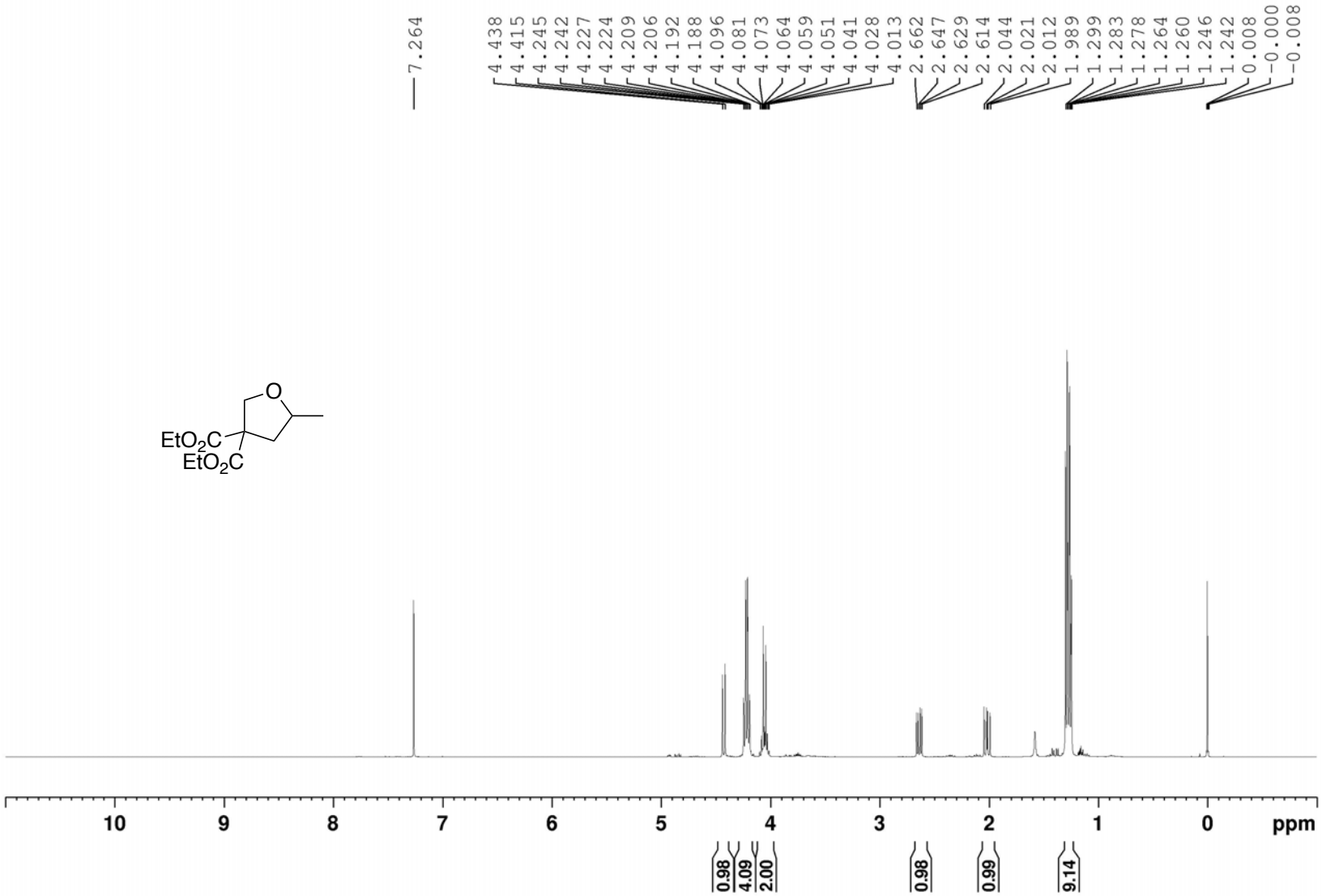

$^{13}$C NMR spectrum of **13ao**



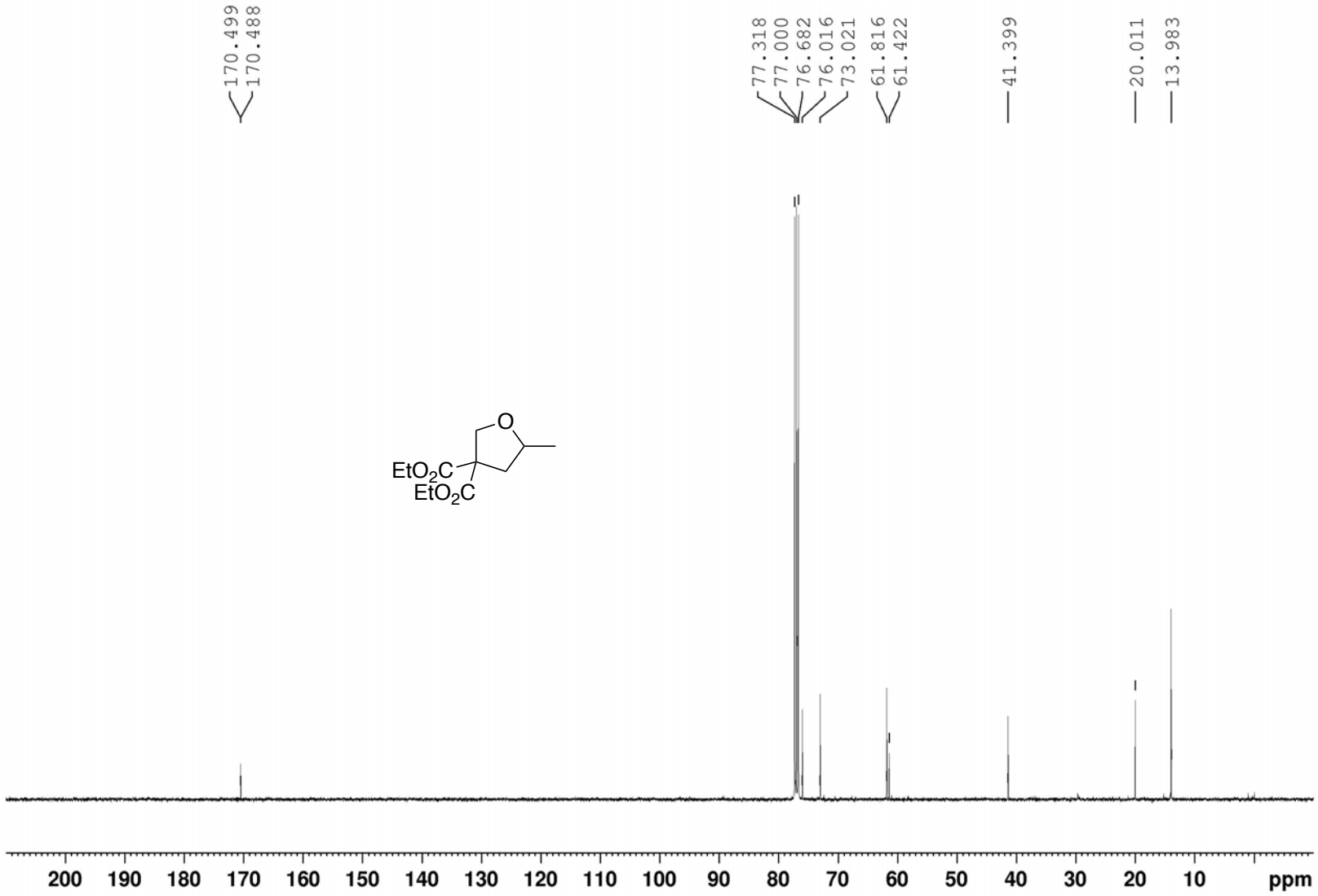

$^{1}$H NMR spectrum of **13bo**




$^{13}$C NMR spectrum of **13bo**




$^{1}$H NMR spectrum of **19a**




$^{13}$C NMR spectrum of **19a**