Recursive Anionic γ'-Spiro-annulation of Cyclic Vinylogous Esters with 2-Vinylbenzoates

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Supporting Information

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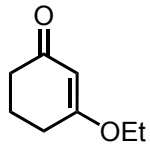
General Information

All air-sensitive reactions were carried out with flame-dried glassware under inert atmosphere with Schlenk line technique. Acetonitrile, 1,4-dioxane, diethyl ether, tetrahydrofuran, toluene and dichloromethane were purified via a commercial solvent purification system. Hexamethylphosphoramide (HMPA) and dimethyl sulfoxide (DMSO) were dried by 4 Å molecular sieves and stored under N_2 atmosphere. Dimethylformamide (DMF) was bought from Acros and used as received. Chemicals were purchased from various sources (Acros, Alfa, Merk, Nova, and Sigma-Aldrich) as reagent grade and used without further purification. Potassium *tert*-butoxide (KO*t*Bu) was stored and weighed in a Glove box. Previously reported compounds were synthesized from commercially available starting materials according to literature procedure. Reactions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 Å F254 plate, which was monitored by UV light (254 nm), $KMnO_4$ or vanillin staining solution as chromogenic agents. Reaction residues were purified via flash column chromatography with silica gel (230-400 mash). All yields refer to isolated products, unless otherwise noted.

NMR spectra were measured on Agilent 400-MR DD2 (400 MHz for ^{1}H NMR spectra; 100 MHz for ^{13}C NMR spectra) or JEOL JNM-ECZ400S/L1(400 MHz for ^{1}H NMR spectra; 100 MHz for ^{13}C NMR spectra) or Varian VNMRS-600 NMR spectrometer (600 MHz for ^{1}H NMR spectra; 150 MHz for ^{13}C NMR spectra) and calibrated from residual solvent signals such as chloroform-d1 (δ_H = 7.26 ppm; δ_C = 77.00 ppm). Chemical shifts were denoted in ppm (δ), and the following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, br = broad, dd = doublet of doublet, dt = doublet of triplet, etc. Coupling constant (J) is reported in Hertz (Hz). Infrared (IR) spectra, reported in wavenumber (cm^{-1}), were measured on Thermo Nicolet iS5 FT-IR spectrometer with ATR sampling technique. High-resolution mass spectroscopy (HRMS) was performed on a TOF instrument with EI and ESI in positive ionization mode. X-ray diffraction was measured on Bruker D8 Venture IuS 3.0 Dual source.

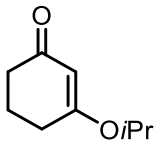
Synthesis and Characterization Data

3-Ethoxycyclohex-2-en-1-one (1a)[1]



A magnetically stirred solution of 1,3-cyclohexanedione (89 mmol, 10 g), ethanol (19.8 mL, 3.8 equiv,), and *p*-toluenesulfonic acid monohydrate (1.78 mmol, 338 mg) in toluene (150 mL) was heated to reflux in an oil bath for 16 h using a Dean–Stark apparatus. After completion of the reaction, the mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford **1a** as a colorless oil (7.6 g, 95%). *Rf*: 0.4 (hexane/EtOAc=3/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 3.90 (q, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 6.3 Hz, 2H), 2.34 (t, *J* = 6.5 Hz, 2H), 1.97 (m, 2H), 1.36 (t, *J* = 7.0 Hz, 3H).

3-Isopropoxycyclohex-2-en-1-one (1b)[2]



A round-bottom flask charged with 1,3-cyclohexanedione (89 mmol, 10 g) in toluene (150 mL) was fitted with a Dean–Stark apparatus. Isopropanol (340 mmol, 20 g) and *p*-toluenesulfonic acid monohydrate (1.78 mmol, 338 mg) were added, and the reaction mixture was heated at 120 °C in an oil bath and stirred for 16 h. After complete consumption of the cyclohexanedione (as monitored by TLC), the reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford **1b** as a yellow oil (13 g, 95%). R*f*: 0.4 (hexane /EtOAc = 3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ5.35 (s, 1H), 4.43 (septet, *J* = 6.1 Hz, 1H), 2.37-2.33 (m, 4H), 1.97 (p, *J* = 6.5 Hz, 2H), 1.29 (d, *J* = 6.1 Hz, 6H).

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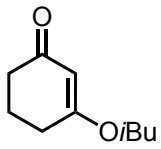
[1] M. Zhou, T.-L. Liu, M. Cao, Z. Xue, H. Lv and X. Zhang, *Org. Lett.*, 2014, **16**, 3484.

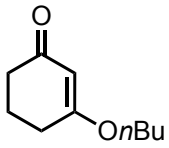
[2] N. Mohanta, M. B. Chaudhari, N. K. Digrawal and B. Gnanaprakasam, *Org. Process Res. Dev.*, 2019, **23**, 1034.

3-Isobutoxycyclohex-2-en-1-one (1c)[3]



A magnetically stirred solution of 1,3-cyclohexanedione (89 mmol, 10 g), iso-butanol (0.43 mol, 40 mL), and *p*-toluenesulfonic acid monohydrate (1.78 mmol, 338 mg) in toluene (150 mL) was heated to reflux in an oil bath for 16 h using a Dean–Stark apparatus. After completion of the reaction, the mixture was cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford compound **1c** as a colorless oil (14.7 g, 79%). R_f: 0.40 (hexane/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1H), 3.55 (d, J = 6.5 Hz, 2H), 2.38 (t, J = 6.2 Hz, 2H), 2.31 (t, J = 6.6 Hz, 2H), 2.11-1.81 (m, 3H), 0.94 (d, J = 6.8 Hz, 6H).

3-Butoxycyclohex-2-en-1-one (1d)[2]



A round-bottom flask charged with 1,3-cyclohexanedione (89 mmol, 10 g) in toluene (150 mL) was fitted with a Dean–Stark apparatus. 1-Butanol (340 mmol, 25.2 g) and *p*-toluenesulfonic acid monohydrate (1.78 mmol, 338 mg) were added, and the reaction mixture was heated at 120 °C in an oil bath and stirred for 16 h. After complete consumption of the cyclohexanedione (as monitored by TLC), the reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford **1d** as a yellow oil (14.2 g, 95%). R$_f$: 0.4 (hexane/ EtOAc = 3/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ5.34 (s, 1H), 3.82 (t, J = 6.5 Hz, 2H), 2.39 (t, J = 6.3 Hz, 2H), 2.33 (t, J = 6.5 Hz, 2H), 1.97 (p, J = 6.3 Hz, 2H), 1.69 (p, J = 6.7 Hz, 2H), 1.42 (sextet, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H).

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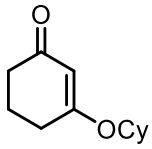
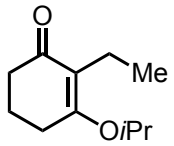
[3] R. Hara, T. Furukawa, H. Kashima, H. Kusama, Y. Horiguchi and I. Kuwajima, *J. Am. Chem. Soc.*, **1999**, *121*, 3072.

3-(Cyclohexyloxy)cyclohex-2-en-1-one (1e)[4]



A round-bottom flask containing 1, 3-cyclohexanedione (8.9 mmol, 1 equiv.) in toluene (15 mL) was added cyclohexanol (36 mmol, 3.6 g) and *p*-toluenesulfonic acid monohydrate (0.18 mmol, 33.8 mg) in Dean-Stark apparatus at 120 °C in an oil bath. The resulting mixture was stirred for 16 h. After the cyclohexanedione was consumed as indicated by TLC analysis, the reaction mixture was allowed to cool down to room temperature and the solvent was removed in vacuo. The crude residue thus obtained was purified by flash column chromatography (hexane/ EtOAc = 3/1) to afford **1e** (1.4 g, 81%) as yellow oil. R_f: 0.5 (hexane/ EtOAc = 1/1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ5.37 (s, 1H), 4.16 (m, 1H), 2.38 (t, *J* = 6.4 Hz, 2H), 2.34 (t, *J* = 6.4 Hz, 2H), 1.99-1.91 (m, 4H), 1.76-1.74 (m, 2H), 1.56-1.54 (m, 1H), 1.50-1.43 (m, 2H), 1.37-1.25 (m, 3H).

2-Ethyl-3-isopropoxycyclohex-2-en-1-one (1f)



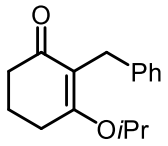
A round-bottom flask charged with 2-ethylcyclohexane-1,3-dione **S1**[5] (89 mmol, 10 g) in toluene (150 mL) was fitted with a Dean–Stark apparatus. 1-Butanol (340 mmol, 25.2 g) and *p*-toluenesulfonic acid monohydrate (1.78 mmol, 338 mg) were added, and the reaction mixture was heated at 120 °C in an oil bath and stirred for 16 h. After complete consumption of the cyclohexanedione (as monitored by TLC), the reaction mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford **1d** as a yellow oil (14.2 g, 95%). R_f: 0.52 (hexane/EtOAc = 1:1). **IR** (film) 2976, 2933, 2871, 1642, 1602, 1452, 1370, 1264, 1228, 1195, 1095, 1060 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.53 (septet, *J* = 6.1 Hz, 1H), 2.51 (t, *J* = 6.1 Hz, 2H), 2.33 (t, *J* = 6.9 Hz, 2H), 2.27 (q, *J* = 7.4 Hz, 2H), 1.96 (p, *J* =

[4] M. Curini, F. Epifano and S. Genovese, *Tetrahedron Lett.*, 2006, **47**, 4697.

[5] Y. Wu, I. Arenas, L. M. Broomfield, E. Martin and A. Shafir, *Chem. Eur. J.*, 2015, **21**, 18779.

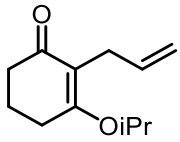
6.0 Hz, 2H), 1.28 (d, *J* = 6.0 Hz, 6H), 0.90 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.41, 170.41, 122.74, 69.95, 36.68, 25.65, 22.99, 21.26, 15.52, 13.31; **HRMS** (ESI, $[M+H]^+$) for $C_{11}H_{19}O_2$ calcd. 183.1380, found: 183.1377.

2-Benzyl-3-isopropoxycyclohex-2-en-1-one (1g)



A round-bottom flask was charged with 2-benzylcyclohexane-1,3-dione **S2**[5] (340 mg, 1.68 mmol) and toluene (8 mL). Isopropanol (1.2 g, 20.9 mmol, 12.4 equiv.) and *p*-toluenesulfonic acid monohydrate (6.4 mg, 0.0336 mmol, 2 mol%) were added, and the flask was fitted with a Dean–Stark apparatus. The reaction mixture was heated at 120 °C (oil bath) and stirred until complete consumption of **S2** (as monitored by TLC). After cooling to room temperature, the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography to afford the corresponding product. (hexane/ EtOAc = 2/1) to afford **1g** (87.1 mg, 22%) as yellow solid (m.p. 55-56 °C). R*f*: 0.37 (hexane/ EtOAc = 2/1). **IR** (cast) 2970, 2916, 2863, 1729, 1629, 1600, 1489, 1450, 1368, 1254, 1236, 1176, 1135, 1099, 1076, 1016 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26-7.24 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.54 (septet, *J* = 6.1 Hz, 1H), 3.61 (s, 2H), 2.54 (t, *J* = 6.1 Hz, 2H), 2.37 (t, *J* = 6.5 Hz, 2H), 1.98 (p, *J* = 6.5 Hz, 2H), 1.24 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 197.89, 171.29, 142.12, 128.86, 127.81, 125.21, 120.39, 70.42, 36.59, 28.02, 25.58, 22.99, 21.12; **HRMS** (ESI, $[M+H]^+$) for $C_{16}H_{21}O_2$ calcd. 245.1536, found: 245.1536.

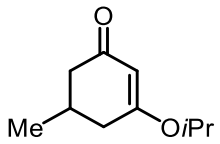
2-Allyl-3-isopropoxycyclohex-2-en-1-one (1h)



A round-bottom flask containing 2-allylcyclohexane-1,3-dione **S3**[5] (3.3 mmol, 500 mg) in toluene (7 mL) was added isopropanol (26.3 mmol, 1.58 g, 8.0 equiv.) and *p*-toluenesulfonic acid monohydrate (0.065 mmol, 13 mg, 2 mol%) in Dean-Stark apparatus at 120 °C in an oil bath. The resulting mixture was stirred for 16 h. After the

cyclohexanedione was consumed as indicated by TLC analysis, the reaction mixture was allowed to cool down to room temperature, and the solvent was removed in vacuo. The crude residue thus obtained was purified by flash column chromatography (hexane/ EtOAc = 8/1 to 4/1) to afford **1h** (261 mg, 41%) as colorless oil. R_f: 0.38 (hexane/ EtOAc = 2/1). **IR** (film) 3074, 2978, 2933, 2866, 1643, 1599, 1452, 1424, 1364, 1235, 1190, 1094 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.77-5.73 (m, 1H), 4.98 (m, 1H), 4.87 (m, 1H), 4.54 (septet, *J* = 6.1 Hz, 1H), 3.02 (d, *J* = 6.5 Hz, 2H), 2.54 (t, *J* = 6.1 Hz, 2H), 2.35 (t, *J* = 6.5 Hz, 2H), 1.99 (p, *J* = 6.5 Hz, 2H), 1.28 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 197.87, 171.28, 136.63, 118.62, 113.84, 70.32, 36.55, 26.60, 25.68, 23.04, 21.19; **HRMS** (ESI, $[M+H]^+$) for $C_{12}H_{19}O_2$ calcd. 195.1380, found: 195.1378.

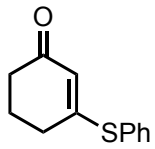
3-Isopropoxy-5-methylcyclohex-2-en-1-one (1i)



A round-bottom flask was charged with 5-methylcyclohexane-1,3-dione **S4**[6] (500 mg, 3.97 mmol) and toluene (2.5 mL). Isopropanol (1.9 g, 31.7 mmol, 8.0 equiv.) and *p*-toluenesulfonic acid monohydrate (15 mg, 0.08 mmol, 2 mol%) were added, and the flask was fitted with a Dean–Stark apparatus. The reaction mixture was heated at 120 °C (oil bath) and stirred for 16 h. After complete consumption of **S4** (as monitored by TLC), the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexane/ EtOAc = 4/1 to 2/1) to afford **1i** (625 mg, 47%) as yellow solid (m.p. 43-45 °C). R_f: 0.5 (hexane/ EtOAc = 1/1). **IR** (cast) 2981, 2962, 2939, 2874, 1643, 1591, 1452, 1424, 1375, 1326, 1272, 1210, 1158, 1135, 1103 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ5.33 (s, 1H), 4.42 (septet, *J* = 6.06 Hz, 1H), 2.43-2.34 (m, 2H), 2.22-2.19 (m, 1H), 2.14-2.09 (m, 1H), 2.05-2.00 (m, 1H), 1.29 (dd, *J* = 9.5, 6.1 Hz, 6H), 1.07 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.88, 176.26, 102.56, 70.94, 45.04, 37.72, 28.77, 21.53, 21.36, 20.89; **HRMS** (ESI, $[M+H]^+$) for $C_{10}H_{17}O_2$ calcd. 169.1223, found:169.1224.

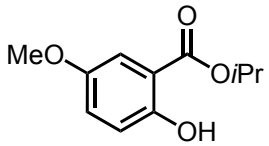
[6] **S4** was obtained from a commercial source.

3-(Phenylthio)cyclohex-2-en-1-one (1j)[7]



Methanesulfonyl chloride (732 μL, 1.08 g, 9.45 mmol) was added to a solution of cyclohexane-1,3-dione (1.00 g, 8.92 mmol) and triethylamine (1.39 mL, 1.01 g, 9.99 mmol) in acetonitrile (10 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 14 h. The reaction was quenched with saturated aqueous sodium carbonate (30 mL), and the mixture was extracted with DCM (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexanes/EtOAc = 10:1 to 8:1) to afford compound **1j** (1.54 g, 85%) as a yellow oil. *Rf*: 0.48 (hexanes/EtOAc = 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.31 (m, 5H), 5.46 (s, 1H), 2.50 (t, *J* = 6.1 Hz, 2H), 2.35 (t, *J* = 6.5 Hz, 2H), 2.02 (m, *J* = 6.3 Hz, 2H).

Isopropyl 2-hydroxy-5-methoxybenzoate (S5)

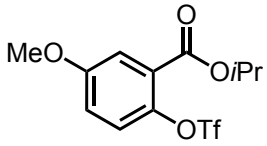


A round-bottom flask was charged with 2-hydroxy-5-methoxybenzoic acid (1.00 g, 5.95 mmol), evacuated, and backfilled with N_2. Isopropanol (11.4 mL, 148.8 mmol, 25 equiv) and conc. $H_2SO_{4(aq)}$ (1.11 mL, 20.8 mmol, 3.5 equiv.) were added, and the reaction mixture was heated at reflux for 16 h. After completion (TLC), the mixture was cooled to room temperature and carefully quenched with saturated $NaHCO_{3(aq)}$. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (1% EtOAc in hexanes) afforded isopropyl 2-hydroxy-5-methoxybenzoate **S5** (638.3 mg, 51%) as a colorless oil. **IR** (film) 3196, 2981, 2945, 2835, 1670, 1616, 1487, 1366, 1323, 1280, 1213, 1180, 1103, 1077, 1036 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 7.30 (d, J = 3.1

[7] B. M. Trost, R. N. Bream and J. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 3109.

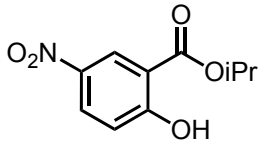
Hz, 1H), 7.06 (dd, J = 9.0, 3.1 Hz, 1H), 6.90 (d, J = 9.0 Hz, 1H), 5.29 (septet, J = 6.3 Hz, 1H), 3.79 (s, 3H), 1.39 (d, J = 6.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.44, 156.09, 151.89, 123.36, 118.39, 112.52, 112.39, 69.28, 55.92, 21.84; **HRMS** (ESI, $[M+H]^+$) for $C_{11}H_{15}O_4$ calcd. 211.0965, found: 211.0962.

Isopropyl 5-methoxy-2-(((trifluoromethyl)sulfonyl)oxy)benzoate (S6)



A round-bottom flask containing isopropyl 2-hydroxy-5-methoxybenzoate **S5** (2.67 mmol, 560 mg) was vacuumed for 2 minutes. The whole system was backfilled with N_2, and then DCM (0.6 M), trifluoromethanesulfonic anhydride (3.2 mmol, 900 mg) and pyridine (9.6 mmol, 760 mg) was added to the flask under ice bath and stirred at 0 ˚C for 3 h. After 3 h, the mixture was concentrated under reduced pressure, quenched with $NaCl_{(aq.)}$ and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/ EtOAc = 20/1) to afford **S6** (910 mg, 99%) as colorless oil. R_f: 0.31 (hexanes/EtOAc = 10/1). **IR** (film): 2981, 1719, 1591, 1491, 1421, 1290, 1246, 1201, 1158, 1137, 1106, 1068, 1032 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 3.2 Hz, 1H), 7.19 (d, *J* = 9.1 Hz, 1H), 7.07 (dd, *J* = 9.1, 3.2 Hz, 1H), 5.32 (septet, *J* = 6.3 Hz, 1H), 3.87 (s, 3H), 1.40 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.27, 158.64, 141.60, 126.17, 123.62, 119.22, 118.73 (q), 116.77, 70.41, 55.94, 21.63; **HRMS** (ESI, $[M+Na]^+$) for $C_{12}H_{13}F_3O_6S$ calcd. 365.0277, found: 365.0280.

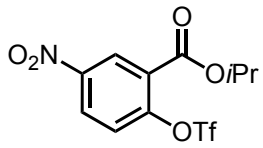
Isopropyl 2-hydroxy-5-nitrobenzoate (S7)



A round-bottom flask containing 2-hydroxy-5-nitrobenzoic acid (11 mmol, 2.0 g) was vacuumed for 2 minutes. The whole system was backfilled with N_2, and then isopropanol (275 mmol, 16.5 g) and conc. $H_2SO_{4(aq)}$ (3.5 equiv., 3.85 mmol, 214 µL)

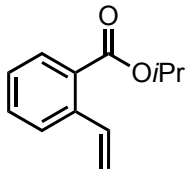
were added to the flask. The resulting mixture was reflux and stirred for 16 h. After the benzoic acid was consumed as indicated by TLC analysis, the reaction mixture was cool down to room temperature, quenched with $NaHCO_{3(aq.)}$ and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude thus obtained was purified by flash column chromatography (1% EtOAc in hexanes) to afford **S7** (1357 mg, 56%) as white solid (m.p. 67-69 °C). R_f: 0.8 (hexanes/EtOAc = 2/1). **IR** (cast) 2927, 2846, 2113, 1667, 1624, 1582, 1526, 1478, 1449, 1373, 1338, 1294, 1253, 1213, 1139, 1099, 1072, 1044 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 8.76 (d, *J* = 2.8 Hz, 1H), 8.32 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.07 (d, *J* = 9.2 Hz, 1H), 5.35 (septet, *J* = 6.3 Hz, 1H), 1.44 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 168.52, 166.46, 139.92, 130.34, 126.60, 118.56, 112.69, 70.94, 21.77; **HRMS** (ESI, $[M+H]^+$) for $C_{10}H_{11}NO_5$ calcd. 226.0710 found: 226.0705.

Isopropyl 5-nitro-2-(((trifluoromethyl)sulfonyl)oxy)benzoate (S8)



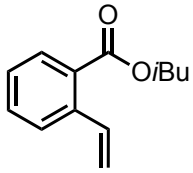
A round-bottom flask containing isopropyl 2-hydroxy-5-nitrobenzoate **S7** (1.33 mmol, 300 mg) was vacuumed for 2 minutes. The whole system was backfilled with N_2, and then DCM (0.6 M, 2.2 mL), Trifluoromethanesulfonic anhydride (1.6 mmol, 450 mg) and pyridine (4.8 mmol, 380 mg) was added to the flask under ice bath and stirred at 0 ˚C for 1 h. After 1 h, the mixture was concentrated under reduced pressure, quenched with $NaCl_{(aq.)}$ and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes/EtOAc = 10/1) to afford **S8** (385 mg, 82%) as white solid (m.p. 74-76 °C). R_f: 0.29 (hexanes/ EtOAc = 10/1). **IR** (film): 2987, 2358, 2340, 1725, 1624, 1538, 1472, 1430, 1350, 1275, 1209, 1175, 1135, 1101, 1066 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.90 (d, *J* = 2.9 Hz, 1H), 8.47 (dd, *J* = 8.9, 2.9 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 5.37 (septet, *J* = 6.3 Hz, 1H), 1.43 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.34, 151.59, 146.68, 128.51, 128.05, 126.85, 124.18, 118.64 (q), 71.61, 21.61; **HRMS** (ESI, $[M+Na]^+$) for $C_{11}H_{10}F_3NO_7S$ calcd. 380.0022, found: 380.0024.

Isopropyl 2-vinylbenzoate (2b)



A round-bottom flask charged with 2-vinylbenzoic acid (1.35 mmol, 200 mg) and isopropanol (2 equiv. 2.7 mmol, 162 mg) was evacuated for 2 min and backfilled with N_2. CH_2Cl_2 (0.5 M, 2.7 mL) was added, and the mixture was stirred until a clear solution was obtained. DCC (1.1 equiv., 1.485 mmol, 306 mg) and DMAP (0.27 mmol, 33 mg, 0.2 equiv.) were then added sequentially, and the reaction mixture was stirred at room temperature for 16 h. After consumption of the acid (as monitored by TLC), the mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1% EtOAc in hexane) to afford **2b** (182 mg, 71%) as colorless oil. R_f: 0.26 (hexane). **IR** (film) 2984, 2928, 2857, 2366, 2338, 2114, 1712, 1483, 1449, 1287, 1251, 1136, 1106, 1070, 1044, 1022 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.58-7.56 (m, 1H), 7.48-7.42 (m, 2H), 7.31 (td, *J* = 7.8, 1.1 Hz, 1H), 5.65 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.34 (dd, *J* = 11.0, 1.3 Hz, 1H), 5.25 (septet, *J* = 6.3 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.01, 139.29, 135.88, 131.77, 130.07, 129.47, 127.31, 127.09, 116.18, 68.54, 21.91; **HRMS** (ESI, $[M+Na]^+$) for $C_{12}H_{14}O_2$ calcd. 213.0886, found: 213.0884.

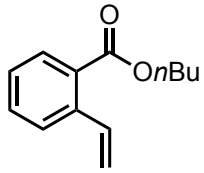
Isobutyl 2-vinylbenzoate (2c)



A round-bottom flask charged with 2-vinylbenzoic acid (2.03 mmol, 300 mg) was evacuated for 2 min and backfilled with N_2. The flask was cooled in an ice bath, and CH_2Cl_2 (0.5 M, 5.1 mL), DMF (0.06 equiv., 0.12 mmol, 10 μL), and thionyl chloride (1.2 equiv., 2.43 mmol, 176 μL) were added sequentially under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 2 h, then

concentrated under reduced pressure to afford the crude acid chloride, which was used in the next step without further purification. The reaction mixture was evacuated and backfilled with N_2 again, then cooled in an ice bath. Isobutanol (2 equiv., 4.05 mmol, 300 mg), DMAP (0.05 equiv., 0.10 mmol, 12.4 mg), and triethylamine (2.0 equiv., 4.05 mmol, 565 µL) were added, followed by CH_2Cl_2 (0.2 M, 10.1 mL), under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. After completion (as monitored by TLC), the mixture was concentrated under reduced pressure, diluted with CH_2Cl_2, and washed with water. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1% EtOAc in hexane) to afford **2c** (209 mg, 51%) as colorless oil. R_f: 0.23 (hexane). **IR** (film) 2959, 2871, 2358, 2340, 1713, 1596, 1565, 1469, 1376, 1283, 1244, 1199, 1129, 1071 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.59-7.57 (m, 1H), 7.49-7.45 (m, 2H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 5.65 (dd, *J* = 17.5, 1.2 Hz, 1H), 5.35 (dd, *J* = 11.0, 1.4 Hz, 1H), 4.10 (d, *J* = 6.7 Hz, 2H), 2.08 (septet, *J* = 6.7 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.47, 139.54, 136.02, 131.96, 130.22, 129.00, 127.35, 127.21, 116.29, 71.21, 27.86, 19.26; **HRMS** (ESI, $[M+Na]^+$) for $C_{13}H_{16}O_2$ calcd. 227.1043, found: 227.1034.

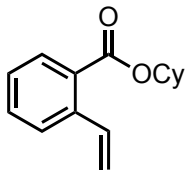
Butyl 2-vinylbenzoate (2d)



A round-bottom flask charged with 2-vinylbenzoic acid (1.36 mmol, 200 mg) was evacuated for 2 min and backfilled with N_2. The flask was cooled in an ice bath, and CH_2Cl_2 (0.5 M, 2.7 mL), DMF (0.06 equiv., 0.082 mmol, 7 µL), and thionyl chloride (1.2 equiv., 1.63 mmol, 118 µL) were added sequentially under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 2 h, then concentrated under reduced pressure to afford the crude acid chloride, which was used in the next step without further purification. The reaction mixture was evacuated and backfilled with N_2 again, then cooled in an ice bath. Butanol (2 equiv., 2.72 mmol, 200 mg), DMAP (0.05 equiv., 0.07 mmol, 8.3 mg), and triethylamine (2.0 equiv., 2.72 mmol,

379 μL) were added, followed by CH_2Cl_2 (0.2 M, 6.8 mL), under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. After completion (as monitored by TLC), the mixture was concentrated under reduced pressure, diluted with CH_2Cl_2, and washed with water. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1% EtOAc in hexane) to afford **2d** (176 mg, 64%) as colorless oil. R_f: 0.34 (hexane). **IR** (film) 2956, 2928, 2868, 2363, 2338, 1712, 1574, 1480, 1285, 1246, 1199, 1130, 1073 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.58-7.57 (m, 1H), 7.49-7.45 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 5.66 (dd, *J* = 17.5, 0.8 Hz, 1H), 5.35 (dd, *J* = 11.0, 0.8 Hz, 1H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.75 (p, *J* = 6.7 Hz, 2H), 1.48 (sextet, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.46, 139.46, 135.92, 131.91, 130.18, 128.99, 127.32, 127.14, 116.25, 64.89, 30.71, 19.28, 13.71; **HRMS** (ESI, $[M+Na]^+$) for $C_{13}H_{16}O_2$ calcd. 227.1043, found: 227.1040.

Cyclohexyl 2-vinylbenzoate (2e)

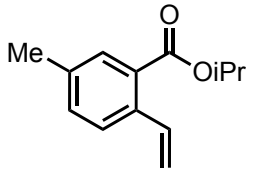


A round-bottom flask was charged with 2-vinylbenzoic acid (3.38 mmol, 500 mg) and cyclohexanol (2.0 equiv., 6.76 mmol, 677 mg). The flask was evacuated for 2 min and backfilled with N_2. CH_2Cl_2 (6.76 mL, 0.5 M) was added, and the reaction mixture was stirred until a clear solution was obtained. DCC (3.72 mmol, 768 mg, 1.1 equiv.) and DMAP (0.676 mmol, 83 mg, 0.2 equiv.) were then added sequentially, and the mixture was stirred at room temperature for 16 h.

After complete consumption of the acid (as monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane) to afford **2e** (497 mg, 64%) as a colorless oil. R_f: 0.27 (hexane). **IR** (film) 2933, 2857, 2361, 2335, 1709, 1568, 1483, 1448, 1285, 1246, 1199, 1131, 1070, 1036, 1012 cm^{-1}; **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.58-7.56 (m, 1H), 7.49-7.42 (m, 2H), 7.32 (td, *J* = 7.8, 1.1 Hz, 1H), 5.63 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.34 (dd, *J* = 11.0, 1.3 Hz, 1H), 5.03 (septet, *J* = 2.0 Hz, 1H), 1.98-1.94 (m, 2H), 1.81-1.76 (m, 2H) 1.61-1.55 (m, 3H), 1.55-1.32 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.92, 139.33, 135.99, 131.77, 130.15, 129.54, 127.32, 127.11, 116.14, 73.36, 31.62, 25.44, 23.69; HRMS (ESI, $[M+Na]^+$) for $C_{15}H_{18}O_2$ calcd. 253.1199, found: 253.1194.

Isopropyl 5-methyl-2-vinylbenzoate (2f)



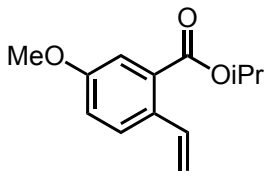
A round-bottom flask was charged with 5-methyl-2-hydroxybenzoic acid (3.00 g, 19.7 mmol, 1.0 equiv.), evacuated for 2 min, and backfilled with N_2. Isopropanol (37.7 mL, 492.5 mmol, 25 equiv.) and conc. H_2SO_4 (3.68 mL, 69.0 mmol, 3.5 equiv.) were added sequentially, and the reaction mixture was heated at reflux with stirring for 16 h. After complete consumption of the acid (as monitored by TLC), the reaction mixture was cooled to room temperature and quenched with saturated $NaHCO_3$. The mixture was extracted with EtOAc, and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford isopropyl 5-methyl-2-hydroxybenzoate, which was used directly in the next step without further purification.

The obtained isopropyl 5-methyl-2-hydroxybenzoate (3.06 mmol) was transferred to a round-bottom flask, evacuated for 2 min, and backfilled with N_2. DCM (6.1 mL, 0.5 M) was added, and the solution was cooled to 0 °C in an ice bath. Trifluoromethanesulfonic anhydride (0.62 mL, 3.67 mmol, 1.2 equiv.) and pyridine (0.88 mL, 11.0 mmol, 3.6 equiv.) were added sequentially, and the reaction mixture was stirred at 0 °C for 1 h. Upon completion, the reaction mixture was concentrated under reduced pressure, quenched with saturated $NaCl_{(aq)}$, and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. Purification by flash column chromatography (hexane/EtOAc = 10:1) afforded isopropyl 5-methyl-2-(((trifluoromethyl)sulfonyl)oxy)benzoate.

A round-bottom flask was charged with isopropyl 5-methyl-2-(((trifluoromethyl)sulfonyl)oxy)benzoate (3.06 mmol, 1000 mg) and evacuated for 2

min, then backfilled with N_2. Potassium vinyltrifluoroborate (3.37 mmol, 1.1 equiv., 451 mg), triethylamine (3.06 mmol, 1.0 equiv., 309 mg, 0.43 mL), $Pd(dppf)Cl_2$, CH_2Cl_2 (0.06 mmol, 2 mol%, 50 mg), and 1-propanol (15.3 mL, 0.2 M) were then added sequentially. The resulting reaction mixture was heated to reflux and stirred for 5 h. After complete consumption of the starting benzoate (as monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water, and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1% EtOAc in hexane) to afford **2f** (180 mg, 29%) as a colorless oil. R_f: 0.5 (hexane/ EtOAc = 10/1). **IR** (film) 2984, 1710, 1616, 1557, 1493, 1372, 1293, 1253, 1196, 1144, 1107, 1070, 1033 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.27 (m, 1H), 5.60 (d, *J* = 17.5 Hz, 1H), 5.30-5.19 (m, 2H), 2.37 (s, 3H), 1.38 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ167.20, 137.22, 136.40, 135.64, 132.55, 130.41, 129.36, 126.95, 115.34, 68.47, 21.93, 20.98; **HRMS** (ESI, $[M+Na]^+$) for $C_{13}H_{16}O_2$ calcd. 227.1043, found: 227.1040.

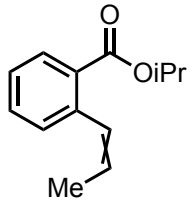
Isopropyl 5-methoxy-2-vinylbenzoate (2g)



A round-bottom flask was charged with isopropyl 5-methoxy-2-(((trifluoromethyl)sulfonyl)oxy)benzoate **S6** (0.88 mmol, 300 mg) and evacuated for 2 min, then backfilled with N_2. Potassium vinyltrifluoroborate (0.97 mmol, 1.1 equiv., 130 mg), triethylamine (0.88 mmol, 1.0 equiv., 90 mg, 0.12 mL), $Pd(dppf)Cl_2.CH_2Cl_2$ (0.018 mmol, 2 mol%, 15 mg), and 1-propanol (4.4 mL, 0.2 M) were added sequentially. The resulting reaction mixture was heated to reflux and stirred for 5 h. After complete consumption of the starting benzoate (as monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water, and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (3% EtOAc in hexane) to afford **2g** (157 mg, 82%) as a colorless oil. R_f: 0.35 (hexane/ EtOAc = 20/1). **IR** (film) 2981, 2837, 1710, 1604, 1492, 1461, 1373,

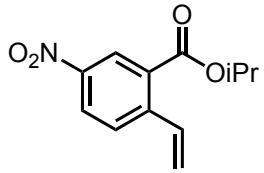
1285, 1253, 1216, 1180, 1143, 1106, 1066, 1044, 1024 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.01 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.54 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.26-5.22 (m, 2H), 3.84 (s, 3H), 1.37 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.87, 158.69, 135.19, 131.83, 130.53, 128.30, 117.92, 114.65, 114.49, 68.72, 55.46, 21.90; **HRMS** (ESI, $[M+Na]^+$) for $C_{13}H_{16}O_3$ calcd. 243.0992, found: 243.0990.

Isopropyl 2-(prop-1-en-1-yl)benzoate (2h)



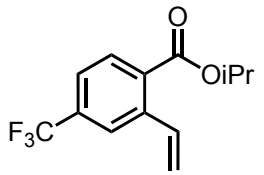
A round-bottom flask was charged with 2-(prop-1-en-1-yl)benzoic acid (1.85 mmol, 300 mg), and isopropanol (3.70 mmol, 222 mg, 0.28 mL, 2.0 equiv.). The flask was evacuated for 2 min and backfilled with N_2. CH_2Cl_2 (3.7 mL, 0.5 M) was then added, and the reaction mixture was stirred until a clear solution was obtained. DCC (2.04 mmol, 421 mg, 1.1 equiv.) and DMAP (0.37 mmol, 45 mg, 0.2 equiv.) were added sequentially, and the resulting mixture was stirred at room temperature for 16 h. After complete consumption of the acid (as monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford **2h (**185 mg, 49%) as colourless oil. R_f: 0.43 (hexane/ EtOAc = 20/1). **IR** (film) 2981, 2939, 2458, 2340, 1710, 1605, 1574, 1486, 1452, 1372, 1278, 1242, 1180, 1135, 1095, 1068, 1044 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.53-7.51 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 15.7 Hz, 1H), 6.18-6.12 (m, 1H), 5.30-5.21 (m, 1H), 1.93 (dd, *J* = 6.6, 1.2 Hz, 3H), 1.39 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.23, 139.31, 131.58, 130.00, 129.73, 128.92, 128.20, 127.03, 126.36, 68.32, 21.91, 18.71; **HRMS** (ESI, $[M+Na]^+$) for $C_{13}H_{16}O_2$ calcd. 227.1043, found: 227.1038.

Isopropyl 5-nitro-2-vinylbenzoate (2i)



A round-bottom flask was charged with isopropyl 5-nitro-2-(((trifluoromethyl)sulfonyl)oxy)benzoate **S8** (0.84 mmol, 300 mg), evacuated for 2 min, and backfilled with N_2. Potassium vinyltrifluoroborate (0.93 mmol, 125 mg, 1.1 equiv.), triethylamine (0.84 mmol, 0.12 mL, 1.0 equiv.), $Pd(dppf)Cl_2.CH_2Cl_2$ (0.0168 mmol, 14 mg, 2 mol%), and 1-propanol (4.2 mL, 0.2 M) were added sequentially. The resulting mixture was heated to reflux and stirred for 3 h. After complete consumption of the starting benzoate (as monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water, and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1% EtOAc in hexane) to afford **2i** (79 mg, 40%) as a white solid (m.p. 55–56 °C). R_f: 0.57 (hexane/ EtOAc = 10/1). **IR** (film) 3097, 2987, 2936, 2358, 2340, 1713, 1605, 1582, 1518, 1475, 1342, 1307, 1245, 1197, 1126, 1101, 1063 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.3 Hz, 1H), 8.30 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.81 (d, *J* = 17.5 Hz, 1H), 5.56 (d, *J* = 11.0 Hz, 1H), 5.28 (septet, *J* = 6.3 Hz, 1H), 1.41 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.87, 146.69, 145.44, 134.29, 130.29, 128.25, 126.17, 125.59, 120.20, 69.81, 21.85. **HRMS** (ESI, $[M+Na]^+$) for $C_{12}H_{13}NO_4$ calcd. 258.0737, found: 258.0729.

Isopropyl 4-(trifluoromethyl)-2-vinylbenzoate (2j)

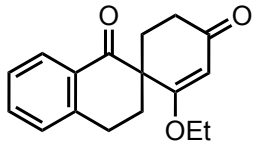


A round-bottom flask was charged with 2-hydroxy-4-(trifluoromethyl)benzoic acid (2.00 g, 9.7 mmol, 1.0 equiv.), evacuated, and backfilled with N_2. Isopropanol (242 mmol, 14.6 mL, 25 equiv.) and concentrated $H_2SO_{4(aq)}$ (34 mmol, 1.9 mL, 3.5 equiv.) were added, and the mixture was heated at reflux for 16 h. After complete consumption of the starting benzoate (as monitored by TLC), the reaction was cooled to room

temperature and carefully quenched with saturated $NaHCO_{3(aq)}$. The mixture was extracted with EtOAc, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by flash column chromatography (1% EtOAc in hexanes) afforded isopropyl 2-hydroxy-4-(trifluoromethyl)benzoate. The obtained isopropyl 2-hydroxy-4-(trifluoromethyl)benzoate (500 mg, 1.84 mmol, 1.0 equiv.) was dissolved in dry DCM (3.1 mL, 0.6 M) under N_2 and cooled to 0 °C. Trifluoromethanesulfonic anhydride (2.21 mmol, 0.37 mL, 1.2 equiv.) was added dropwise, followed by pyridine (0.53 mL, 6.62 mmol, 3.6 equiv.). The reaction mixture was stirred at 0 °C for 1 h, then concentrated under reduced pressure. The residue was quenched with saturated $NaCl_{(aq)}$ and extracted with EtOAc. Purification by flash column chromatography afforded isopropyl 4-(trifluoromethyl)-2-(((trifluoromethyl)sulfonyl)oxy)benzoate.

A round-bottom flask was charged with isopropyl 4-(trifluoromethyl)-2-(((trifluoromethyl)sulfonyl)oxy)benzoate (1.84 mmol, 700 mg), evacuated for 2 min, and backfilled with N_2. Potassium vinyltrifluoroborate (2.02 mmol, 270 mg, 1.1 equiv.), triethylamine (1.84 mmol, 186 mg, 0.26 mL, 1.0 equiv.), $Pd(dppf)Cl_2.CH_2Cl_2$ complex (0.037 mmol, 30 mg, 2 mol%), and 1-propanol (9.2 mL, 0.2 M) were added sequentially. The resulting mixture was heated to reflux and stirred for 5 h. After complete consumption of the starting benzoate (as monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water, and extracted with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (1% EtOAc in hexanes) to afford **2j** (324.7 mg, 69%) as a colorless oil. R_f: 0.62 (hexanes/ EtOAc = 10/1). **IR** (film) 2987, 2358, 2340, 1717, 1326, 1299, 1279, 1251, 1168, 1126, 1089, 1068, 1041 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.80 (s, 1H), 7.55 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.41 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.72 (dd, *J* = 17.5, 0.8 Hz, 1H), 5.45 (dd, *J* = 11.0, 0.8 Hz, 1H), 5.26 (septet, *J* = 6.3 Hz, 1H), 1.38 (d, *J* = 6.3 Hz, 6H); **^{13}C{^{1}H}{^{19}F} NMR** (125 MHz, $CDCl_3$) δ165.96, 139.82, 134.64, 133.41, 132.58, 130.59, 123.95, 123.84, 123.59, 117.90, 69.27, 21.79 **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.14; **HRMS** (ESI, $[M+H]^+$) for $C_{13}H_{14}F_3O_2$ calcd. 259.0940, found: 259.0940.

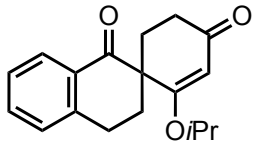
2-Ethoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3a)



A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-ethoxycyclohex-2-en-1-one (**1a**) (0.29 mmol, 41 mg, 1.0 equiv.), and ethyl 2-vinylbenzoate (**2a**)[8] (0.58 mmol, 102 mg, 2.0 equiv.) were then added under a nitrogen atmosphere. The reaction mixture was heated at 150 °C and stirred for 3 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was cooled to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford the desired product **3a** (31 mg, 40%). R_f: 0.14 (hexane/ EtOAc = 2/1). **IR** (film) 2936, 2361, 2335, 1679, 1650, 1595, 1458, 1376, 1354, 1295, 1216, 1194, 1024 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.50 (td, *J* = 7.6, 1.1 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 5.53 (s, 1H), 3.93-3.87 (m, 2H), 3.18-3.09 (m, 1H), 3.03-2.96 (m, 1H), 2.86-2.78 (m, 1H), 2.43-2.35 (m, 3H), 2.08-2.01 (m, 2H), 1.25 (t, *J* = 7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.50, 196.13, 176.95, 142.72, 133.72, 131.20, 128.67, 128.19, 126.94, 104.75, 64.77, 50.99, 32.57, 31.29, 28.47, 24.78, 13.82; **HRMS** (ESI, $[M+H]^+$) for $C_{17}H_{19}O_3$ calcd. 271.1329, found: 271.1334.

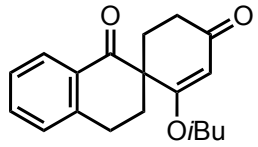
[8] S. Kawashima, K. Aikawa and K. Mikami, *Eur. J. Org. Chem.*, 2016, 3166. **2a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.51-7.42 (m, 2H), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H), 5.65 (dd, *J* = 17.5, 1.3 Hz, 1H), 5.35 (dd, *J* = 11.0, 1.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 4H).

2-Isopropoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3b)



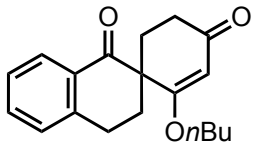
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-isopropoxycyclohex-2-en-1-one (**1b**) (0.29 mmol, 45 mg, 1.0 equiv.), and isopropyl 2-vinylbenzoate (**2b**) (0.58 mmol, 110 mg, 2.0 equiv.) were then added under a nitrogen atmosphere.The resulting reaction mixture was heated at 150 °C and stirred for 2 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EtOAc = 8/1 to 2/1) to afford **3b** (48 mg, 58%) as yellow oil. R*f*: 0.17 (hexane/ EtOAc = 2/1). **IR** (film) 2981, 2936, 2363, 2332, 1680, 1650, 1591, 1454, 1362, 1323, 1295, 1216, 1195, 1101 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 5.51 (s, 1H), 4.44 (septet, *J* = 6.1 Hz, 1H), 3.15-3.09 (m, 1H), 3.01-2.97 (m, 1H), 2.82-2.76 (m, 1H), 2.42-2.35 (m, 3H), 2.06-2.01 (m, 2H), 1.22 (dd, *J* = 6.1, 2.9 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.42, 196.14, 175.94, 142.67, 133.61, 131.33, 128.63, 128.11, 126.88, 104.97, 71.44, 51.02, 32.50, 31.35, 28.42, 24.82, 21.29, 20.89; **HRMS** (ESI, $[M+H]^+$) for $C_{18}H_{21}O_3$ calcd. 285.1485, found: 285.1486.

2-Isobutoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3c)



A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 32.5 mg, 1.0 equiv.), copper(I) bromide (0.10 equiv., 0.029 mmol, 4 mg,), and triphenylphosphine (0.20 equiv., 0.058 mmol, 15 mg,) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-isobutoxycyclohex-2-en-1-one (**1c**) (0.29 mmol, 49 mg, 1.0 equiv.), and isobutyl 2-vinylbenzoate (**2c**) (0.58 mmol, 119 mg, 2.0 equiv.) were then added under a nitrogen atmosphere. The resulting mixture was heated at 150 °C and stirred for 1 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 8:1 to 4:1) to afford **3c** (35 mg, 40%) as a yellow oil. R_f: 0.4 (hexane/ EtOAc = 2/1). **IR** (film) 2959, 2925, 2871, 2363, 2341, 1680, 1651, 1595, 1453, 1350, 1295, 1215, 1194 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.25-7.23 (m, 1H), 5.49 (s, 1H), 3.63-3.54 (m, 2H), 3.14-3.08 (m, 1H), 3.02-2.98 (m, 1H), 2.81-2.76 (m, 1H), 2.51-2.46 (m, 1H), 2.40-2.37 (m, 2H), 2.09-1.99 (m, 2H), 1.91-1.86 (m, 1H), 0.80 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.27, 196.08, 177.31, 142.77, 133.60, 131.43, 128.61, 128.03, 126.85, 104.38, 75.04, 50.91, 32.52, 31.49, 28.64, 27.53, 24.92, 18.80, 18.73; **HRMS** (ESI, $[M+H]^+$) for $C_{19}H_{23}O_3$ calcd.299.1642, found: 299.1643.

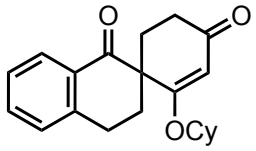
2-Butoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3d)



A round-bottom flask was charged with potassium *tert*-butoxide (1.0 equiv., 0.29 mmol, 32.5 mg,), copper(I) bromide (0.10 equiv., 0.029 mmol, 4 mg), and triphenylphosphine (0.20 equiv., 0.058 mmol, 15 mg,) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-butoxycyclohex-2-en-1-one (**1d**) (0.29 mmol, 49 mg), and butyl 2-vinylbenzoate (**2d**) (2.0 equiv., 0.58 mmol, 118.4 mg) were then added under a nitrogen atmosphere.

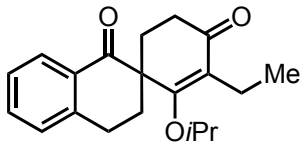
The resulting mixture was heated at 150 °C and stirred for 1 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EtOAc = 8/1 to 2/1) to afford **3d** (36 mg, 42 %) as yellow oil. R_f: 0.28 (hexane/ EtOAc = 2/1). **IR** (film) 2956, 2928, 2874, 1680, 1650, 1595, 1454, 1349, 1295, 1216, 1193, 1122, 1018 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 6.6 Hz, 1H), 7.31 (t, *J* = 6.6 Hz, 1H), 7.25-7.23 (m, 1H), 5.50 (s, 1H), 3.82-3.79 (m, 2H), 3.13-3.08 (m, 1H), 2.99-2.96 (m, 1H), 2.80-2.75 (m, 1H), 2.44-2.35 (m, 3H), 2.05-2.00 (m, 2H), 1.57-1.55 (m, 2H), 1.25-1.22 (m, 2H), 0.82-0.79 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.26, 196.02, 177.11, 142.69, 133.58, 131.27, 128.59, 128.04, 126.82, 104.48, 68.67, 50.92, 32.52, 31.33, 30.19, 28.50, 24.80, 18.89, 13.45; **HRMS** (ESI, $[M+H]^+$) for $C_{19}H_{23}O_3$ calcd. 299.1642, found: 299.1640.

2-(Cyclohexyloxy)-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3e)



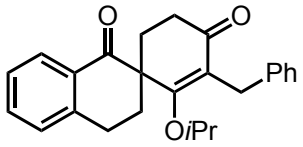
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 32.5 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-(cyclohexyloxy)cyclohex-2-en-1-one (**1e**) (0.29 mmol, 57 mg, 1.0 equiv.), and cyclohexyl 2-vinylbenzoate (**2e**) (0.58 mmol, 134 mg, 2.0 equiv.) were then added under a nitrogen atmosphere. The resulting mixture was heated at 150 °C and stirred for 4 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexanes/EtOAc = 8:1 to 4:1) to afford **3e** (42 mg, 45%) as a yellow oil. R_f: 0.36 (hexanes/ EtOAc = 2/1). **IR** (film) 3007, 2942, 2851, 1681, 1643, 1592, 1453, 1352, 1295, 1215, 1196, 1122, 1014 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.25-7.23 (m, 1H), 5.50 (s, 1H), 4.20 (s, 1H), 3.13-3.09 (m, 2H), 2.08-2.07 (m, 1H), 2.45-2.42 (m, 3H), 2.05-2.02 (m, 2H), 1.77 (s, 2H), 1.52 (s, 2H), 1.43-1.41 (m, 3H), 1.28-1.22 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.43, 196.21, 176.09, 142.73, 133.54, 131.45, 128.59, 128.01, 126.81, 104.69, 76.16, 50.98, 32.45, 31.48, 30.67, 30.14, 28.53, 25.16, 24.89, 22.90, 22.82; **HRMS** (ESI, $[M+H]^+$) for $C_{21}H_{25}O_3$ calcd. 325.1798, found:325.1796.

3-Ethyl-4-isopropoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-3-ene-1',2-dione (3f)



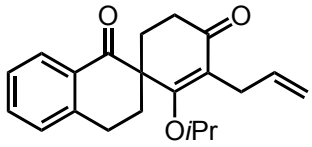
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 32.5 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 2-ethyl-3-isopropoxycyclohex-2-en-1-one (**1f**) (0.29 mmol, 53 mg, 1.0 equiv.), and isopropyl 2-vinylbenzoate **2b** (0.58 mmol, 110 mg, 2.0 equiv.) were added under a nitrogen atmosphere. The resulting mixture was heated at 150 °C and stirred for 3 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 16:1 to 4:1) to afford **3f** (33 mg, 37%) as a yellow oil. R_f: 0.46 (hexane/ EtOAc = 4/1). **IR** (film) 2978, 2930, 2877, 1659, 1598, 1454, 1369, 1356, 1325, 1296, 1257, 1220, 1188, 1101, 1080 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 4.06 (septet, *J* = 6.0 Hz, 1H), 3.19-3.14 (m, 1H), 3.01-2.96 (m, 1H), 2.71-2.65 (m, 1H), 2.49-2.42 (m, 2H), 2.38-2.31 (m, 3H), 2.05-1.99 (m, 2H), 1.20 (d, *J* = 6.0 Hz, 3H), 1.18 (d, *J* = 6.0 Hz, 3H), 1.01 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.80, 195.62, 169.32, 142.60, 133.78, 130.69, 128.93, 128.77, 128.41, 127.04, 74.02, 51.26, 32.52, 32.37, 29.09, 24.80, 22.66, 21.92, 17.27, 13.40; **HRMS** (ESI, $[M+Na]^+$) for $C_{20}H_{24}O_3$ calcd. 335.1618, found: 335.1614.

3-Benzyl-4-isopropoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-3-ene-1',2-dione (3g)



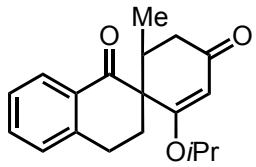
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 2-benzyl-3-isopropoxycyclohex-2-en-1-one (**1g**) (0.29 mmol, 71 mg), and isopropyl 2-vinylbenzoate (**2b**) (0.58 mmol, 110 mg, 2.0 equiv.) were added under a nitrogen atmosphere. The resulting mixture was heated at 150 °C and stirred for 2 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was cooled to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 16:1 to 4:1) to afford **3g** (48 mg, 45%) as a yellow oil. R_f: 0.37 (hexane/ EtOAc = 4/1). **IR** (film): 3021, 2981, 2928, 1659, 1598, 1452, 1348, 1296, 1281, 1238, 1219, 1191, 1099, 1078, 1011 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53 (td, *J* = 7.5, 1.2 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.25-7.22 (m, 4H), 7.15-7.11 (m, 1H), 4.07 (septet, *J* = 6.1 Hz, 1H), 3.77 (q, *J* = 16.4 Hz, 2H), 3.21-3.16 (m, 1H), 3.01-2.96 (m, 1H), 2.73-2.68 (m, 1H), 2.55-2.48 (m, 1H), 2.39-2.35 (m, 2H), 2.09-2.04 (m, 2H), 1.17 (d, *J* = 6.1 Hz, 3H), 1.01 (d, *J* = 6.1 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.22, 195.40, 170.56, 142.52, 140.94, 133.90, 130.55, 128.83, 128.47, 128.35, 128.10, 127.13, 125.98, 125.48, 74.32, 51.44, 32.31, 32.30, 29.54, 29.03, 24.78, 22.69, 21.88; **HRMS** (ESI, $[M+Na]^+$) for $C_{25}H_{26}O_3$ calcd. 397.1774, found: 397.1778.

3-Allyl-4-isopropoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-3-ene-1',2-dione (3h)



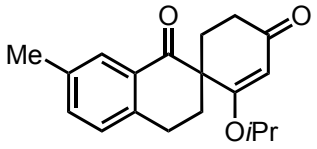
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 2-allyl-3-isopropoxycyclohex-2-en-1-one (**1h**) (0.29 mmol, 57 mg, 1.0 equiv.), and isopropyl 2-vinylbenzoate (**2b**) (0.58 mmol, 110 mg, 2.0 equiv.) were added under a nitrogen atmosphere. The resulting mixture was heated at 150 °C and stirred for 2 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EtOAc = 16/1 to 4/1) to afford **3h** (25 mg, 27 %) as yellow oil. R_f: 0.49 (hexane/ EtOAc = 4/1). **IR** (film): 2984, 2930, 1659, 1598, 1453, 1355, 1296, 1261, 1220, 1193, 1098, 1080, 1018 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.53 (td, *J* = 7.5, 1.1 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 5.90-5.84 (m, 1H), 5.07-4.97 (m, 2H), 4.18 (septet, *J* = 6.0 Hz, 1H), 3.19-3.12 (m, 3H), 3.01-2.97 (m, 1H), 2.75-2.70 (m, 1H), 2.51-2.46 (m, 1H), 2.38-2.34 (m, 2H), 2.06-2.01 (m, 2H), 1.17 (d, *J* = 6.0 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.27, 195.62, 170.81, 142.61, 136.13, 133.81, 130.76, 128.78, 128.41, 127.07, 123.87, 114.63, 74.46, 51.73, 32.44, 32.34, 28.87, 28.15, 24.82, 22.72, 22.29; **HRMS** (ESI, $[M+Na]^+$) for $C_{21}H_{24}O_3$ calcd. 347.1618, found: 347.1617.

2-Isopropoxy-6-methyl-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3i)



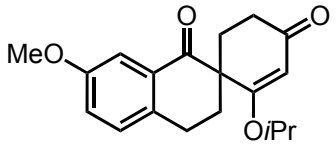
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), with 3-isopropoxy-5-methylcyclohex-2-en-1-one (**1i**) (0.29 mmol, 49 mg) and isopropyl 2-vinylbenzoate (**2b**) (0.58 mmol, 110 mg, 2.0 equiv.) were added under a nitrogen atmosphere. The resulting mixture was heated at 150 °C and stirred for 2 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford the desired product. The crude product was purified by flash column chromatography (hexane/ EtOAc = 8/1 to 2/1) to afford **3i** (33 mg, 48% dr > 6:1) as yellow oil. R*f*: 0.31 (hexane/ EtOAc = 2/1). **IR** (film) 2978, 2936, 2359, 2340, 1681, 1650, 1591, 1455, 1365, 1323, 1291, 1216, 1103 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.48 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 5.44 (s, 1H), 4.39 (septet, *J* = 6.1 Hz, 1H), 3.10-2.97 (m, 2H), 2,91 (br, 1H), 2.45-2.41 (m, 2H), 2.29-2.25 (m, 1H), 2.19 (dd, *J* = 17.2, 9.2 Hz, 1H), 1.16 (d, *J* = 6.1 Hz, 3H), 1.12 (d, *J* = 6.1 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.27, 196.81, 143.37, 133.39, 132.70, 128.44, 127.90, 126.77, 103.67, 71.68, 54.45, 40.82, 32.81, 26.77, 25.13, 21.23, 20.88, 16.56; **HRMS** (ESI, $[M+Na]^+$) for $C_{19}H_{22}O_3$ calcd. 321.1461, found: 321.1457.

2-Isopropoxy-7'-methyl-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3j)



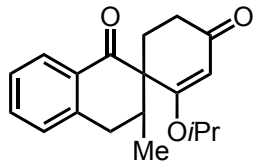
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-isopropoxycyclohex-2-en-1-one (**1b**) (0.29 mmol, 45 mg, 1.0 equiv.), and isopropyl 5-methyl-2-vinylbenzoate (**2f**) (0.58 mmol, 118 mg, 2.0 equiv.) were then added under a nitrogen atmosphere. The resulting reaction mixture was heated at 150 °C and stirred for 2 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford the desired product. The crude product was purified by flash column chromatography (hexane/ EtOAc = 8/1 to 4/1) to afford **3j** (38 mg, 44%) as yellow oil. R_f: 0.21 (hexane/ EtOAc = 2/1). **IR** (film) 2981, 2939, 1717, 1676, 1650, 1591, 1495, 1452, 1362, 1322, 1286, 1243, 1217, 1193, 1165, 1137, 1103 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.32 (dd, J = 7.8, 1.6 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 5.51 (s, 1H), 4.44 (septet, J = 6.1 Hz, 1H), 3.10-3.04 (m, 1H), 2.96-2.93 (m, 1H), 2.79-2.74 (m, 1H), 2.41-2.34 (m, 6H), 2.05-1.99 (m, 2H), 1.22 (d, J = 6.1 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.53, 196.42, 176.11, 139.79, 136.64, 134.65, 131.06, 128.59, 128.20, 105.01, 71.43, 51.10, 32.53, 31.46, 28.42, 24.42, 21.33, 20.93, 20.91; **HRMS** (ESI, $[M+H]^+$) for $C_{19}H_{23}O_3$ calcd. 299.1642, found: 299.1642.

2-Isopropoxy-7'-methoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3k)



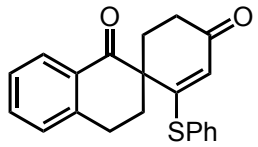
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-isopropoxycyclohex-2-en-1-one (**1b**) (0.29 mmol, 45 mg) and isopropyl 5-methoxy-2-vinylbenzoate (**2g**) (0.58 mmol, 128 mg) were then added under a nitrogen atmosphere. The resulting reaction mixture was heated at 150 °C and stirred for 6 h. After complete consumption of the vinylogous ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EtOAc = 8/1 to 2/1) to afford **3k** (26 mg, 29%) as yellow oil. R_f: 0.17 (hexane/ EtOAc = 2/1). **IR** (film): 2981, 2933, 2358, 2340, 1677, 1645, 1592, 1495, 1449, 1416, 1322, 1284, 1255, 1218, 1170, 1103, 1032 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.8 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.09 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.52 (s, 1H), 4.45 (septet, *J* = 6.1 Hz, 1H), 3.84 (s, 3H), 3.08-3.03 (m, 1H), 2.95-2.90 (m, 1H), 2.80-2.75 (m, 1H), 2.41-2.35 (m, 3H), 2.07-1.99 (m, 2H), 1.22 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.47, 196.17, 176.02, 158.51, 135.26, 132.07, 129.90, 122.18, 109.91, 105.05, 71.46, 55.49, 50.95, 32.55, 31.58, 28.40, 24.08, 21.35, 20.91; **HRMS** (ESI, $[M+Na]^+$) for $C_{19}H_{22}O_4$ calcd. 337.1410, found: 337.1409.

2-Isopropoxy-3'-methyl-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3l)



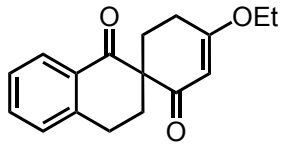
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-isopropoxycyclohex-2-en-1-one (**1b**) (0.29 mmol, 45 mg) and isopropyl 2-(prop-1-en-1-yl)benzoate (**2h**) (0.58 mmol, 119 mg) were then added under a nitrogen atmosphere. The resulting reaction mixture was heated at 150 °C and stirred for 6 h. After complete consumption of the starting material as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Crude product was purified by flash column chromatography (hexane/ EtOAc = 16/1 to 4/1) to afford **3l** (30 mg, 35%) as yellow oil. R_f: 0.29 (hexane/ EtOAc = 2/1). **IR** (film) 2987, 2930, 2358, 2340, 1679, 1651, 1593, 1458, 1362, 1323, 1277, 1222, 1200, 1180, 1105 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 5.66 (s, 1H), 4.51 (septet, *J* = 6.2 Hz, 1H), 3.07-3.03 (m, 1H), 2,91-2.89 (m, 2H), 2.32-2.20 (m, 3H), 1.99-1.96 (m, 1H), 1.28 (dd, *J* = 8.3, 6.2 Hz, 6H), 1.04 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.83, 196.16, 173.96, 142.23, 133.67, 130.34, 128.51, 128.44, 126.98, 107.12, 71.46, 55.36, 33.72, 33.05, 32.35, 21.32, 21.25, 21.12, 15.73; **HRMS** (ESI, $[M+Na]^+$) for $C_{19}H_{22}O_3$ calcd. 321.1461, found: 321.1456.

2-(phenylthio)-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-2-ene-1',4-dione (3m)



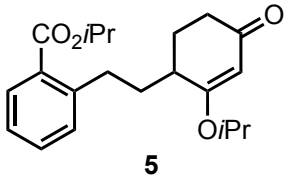
A round-bottom flask was charged with potassium *tert*-butoxide (0.29 mmol, 33 mg, 1.0 equiv.), copper(I) bromide (0.029 mmol, 4 mg, 0.10 equiv.), and triphenylphosphine (0.058 mmol, 15 mg, 0.20 equiv.) inside a glovebox. The flask was removed, evacuated, and backfilled with N_2. DMF (1.0 mL, 0.29 M), 3-(phenylthio)cyclohex-2-en-1-one (**1j**) (0.29 mmol, 59 mg) and isopropyl 2-vinylbenzoate (**2b**) (0.58 mmol, 110 mg) were then added under a nitrogen atmosphere. The resulting reaction mixture was heated at 150 °C and stirred for 1 h. After complete consumption of the ester as monitored by TLC, the reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was separated, and the aqueous phase was further extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ EtOAc = 16/1 to 4/1) to afford **3m** (33 mg, 34%) as white solid (m.p. 107-109 °C). R_f: 0.65 (hexane/ EtOAc = 2/1). **IR** (cast): 2936, 2868, 2358, 2340, 1714, 1599, 1454, 1322, 1290, 1253, 1208, 1134, 1099, 1032, 1006 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* =7.8, 1.2 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.26-7.19 (m, 5H), 7.14 (d, *J* = 7.8 Hz, 1H), 5.69 (s, 1H), 3.35 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.62-2.59 (m, 1H), 2.39-2.32 (m, 1H), 2.09-2.03 (m, 1H), 1.94-1.76 (m, 3H), 1.67-1.60 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.73, 143.89, 140.02, 134.15, 132.90, 131.51, 130.28, 129.17, 128.16, 127.05, 126.88, 125.78, 124.70, 83.58, 39.82, 35.97, 33.01, 32.49, 24.50; **HRMS** (ESI, $[M+H]^+$) for $C_{21}H_{19}O_2S$ calcd. 335.1100, found: 335.1100.

4-Ethoxy-3',4'-dihydro-1'H-spiro[cyclohexane-1,2'-naphthalen]-3-ene-1',2-dione (4a) [See Scheme 2]

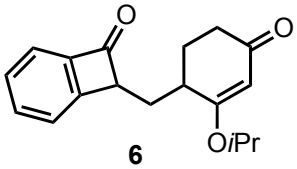


A round-bottom flask containing potassium *tert*-butoxide (0.29 mmol, 33 mg) was removed from the glovebox, evacuated, and backfilled with N_2. DMSO (0.29 M, 1.0mL), 3-ethoxycyclohex-2-en-1-one **1a** (0.29 mmol, 41 mg), and ethyl 2-vinylbenzoate **2a** (0.58 mmol, 102 mg) were then added under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 18 h. Upon complete consumption of the ester as monitored by TLC, the reaction mixture was quenched with water and extracted with ethyl acetate. The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexane/EtOAc = 16:1 to 4:1) to afford **4a** (6 mg, 8%) as a yellow oil along with **3a** (29%). **4a**: R_f: 0.26 (hexane/ EtOAc = 4/1). **IR** (film): 2984, 2933, 2846, 2358, 2340, 1679, 1639, 1599, 1453, 1379, 1346, 1310, 1295, 1238, 1188, 1156, 1034 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 5.41 (s, 1H), 4.01-3.88 (m, 2H), 3.08-2.97 (m, 2H), 2.77-2.60 (m, 2H), 2.50-2.45 (m, 2H), 1.99-1.86 (m, 2H), 1.38 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.68, 197.78, 176.65, 143.31, 133.43, 131.94, 128.58, 127.85, 126.74, 102.32, 64.44, 55.24, 30.49, 28.44, 25.61, 25.13, 14.15; **HRMS** (ESI, $[M+Na]^+$) for $C_{17}H_{18}NaO_3$ calcd. 293.1148, found: 293.1150.

Isopropyl 2-(2-(2-isopropoxy-4-oxocyclohex-2-en-1-yl)ethyl)benzoate (5) and 8-((2-isopropoxy-4-oxocyclohex-2-en-1-yl)methyl)bicyclo[4.2.0]octa-1,3,5-trien-7-one (6) [See Scheme 4a]



5

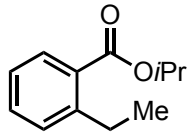


6

A round-bottom flask was charged with potassium *tert*-butoxide (1.16 mmol, 132 mg), copper(I) bromide (0.116 mmol, 16 mg), and triphenylphosphine (0.232 mmol, 60 mg) inside a glovebox. The flask was removed from the glovebox, evacuated, and backfilled with nitrogen. DMF (4.0 mL, 0.29 M), 3-isopropoxycyclohex-2-en-1-one (**1b)** (1.16 mmol, 180 mg), and isopropyl 2-vinylbenzoate (**2b**) (2.32 mmol, 400 mg) were added sequentially. The reaction mixture was stirred at room temperature for 1 h. Upon completion, the reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography (hexanes/EtOAc, gradient from 8:1 to 2:1) to afford compound **5** as a colorless oil (16 mg, 5%, R_f: 0.35, hexane/EtOAc = 2:1) and compound **6** as a green oil (50 mg, 15%, R_f: 0.35, hexane/EtOAc = 2:1) along with **3b** (19%) and **4b** (9%). **5**: **IR** (film) 2981, 2928, 2868, 2358, 2340, 1710, 1650, 1590, 1452, 1372, 1247, 1218, 1140, 1181, 1106, 1091, 1077 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.41 (td, *J* = 7.6, 1.4 Hz, 1H), 7.27-7.24 (m, 2H), 5.30 (s, 1H), 5.24 (septet, *J* = 6.3 Hz, 1H), 4.43 (septet, *J* = 6.0 Hz, 1H), 3.15-3.10 (m, 1H), 2.99-2.94 (m, 1H), 2.53-2.43 (m, 2H), 2.33-2.28 (m, 1H), 2.15-2,09 (m, 1H), 2.04-1.94 (m, 2H), 1.82-1.76 (m, 1H), 1.36 (d, *J* = 6.3 Hz, 6H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.27 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 199.78, 179.40, 167.04, 143.44, 131.78, 130.83, 130.64, 130.25, 126.04, 102.56, 70.82, 68.23, 38.80, 33.76, 33.20, 32.39, 25.64, 21.97, 21.95, 21.57, 21.28; **HRMS** (ESI, $[M+H]^+$) for $C_{21}H_{29}O_4$ calcd. 345.2060, found: 345.2059. **6**: **IR** (film) 2987, 2936, 2358, 2340, 1697, 1645, 1589, 1557, 1456, 1378, 1313, 1194, 1102 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 5.44 (s, 1H), 4.38 (septet, *J* = 6.0 Hz, 1H), 3.43 (d, *J* = 5.8 Hz, 1H), 2.78-2.66 (m, 3H), 2.44-2.37 (m, 1H), 2.34-2.25 (m, 2H), 2.03-1.94 (m, 1H), 1.29 (d, *J* = 6.0 Hz, 3H), 1.19 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 206.37, 193.26, 176.94, 139.33, 137.96, 129.77, 129.17, 126.57, 125.30,

104.01, 71.19, 59.27, 37.04, 31.51, 29.60, 26.09, 21.58, 21.10; **HRMS** (ESI, $[M+Na]^+$) for $C_{18}H_{20}O_3$ calcd. 307.1305, found: 307.1308.

Isopropyl 2-ethylbenzoate (7)[9]

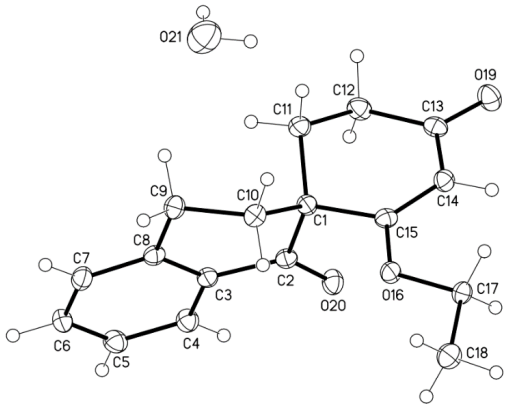


A round-bottom flask containing isopropyl 2-vinylbenzoate **2b** (0.53 mmol, 100 mg) was vacuumed for 2 minutes. The whole system was backfilled with N_2, and then MeOH (0.53 M) and 10% Pd/C (17 mg) was added to the flask under H_2 atmosphere and stirred at rt for 2 h. After 2 h, the mixture was filtered through celite and concentrated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography (hexanes) to afford **9** (85 mg, 84 %) as colorless oil. R_f: 0.34 (hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.30-7.27 (m, 2H), 5.29 (septet, J = 6.1 Hz, 1H), 3.02 (m, 2H), 1.42 (m, 6H), 1.29 (m, 3H).

[9] A. Benazet, O. Duclos, N. Guillo, G. Lassalle, K. Macary and V. Vin, *US Pat. Appl.*, US 20140235616 A1, 2014.

Single Crystal X-ray Diffraction Data

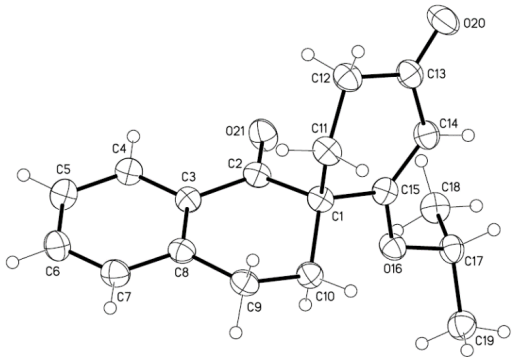
Table S1. Crystal Data and Structure Refinement for compound **3a**



Identification code	**3a (CCDC 2498522)**
Empirical formula	$C_{17}H_{20}O_4$
Formula weight	288.33
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.1310(2)
b/Å	11.62229(19)
c/Å	8.68459(15)
α/°	90
β/°	97.7171(15)
γ/°	90
Volume/Å^3	1413.39(4)
Z	4
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	0.780
F(000)	616.0
Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.312 to 134.144
Index ranges	$-15 \leq h \leq 16$, $-12 \leq k \leq 13$, $-10 \leq l \leq 10$
Reflections collected	7942
Independent reflections	2517 [R_{int} = 0.0218, R_{sigma} = 0.0228]
Data/restraints/parameters	2517/0/194

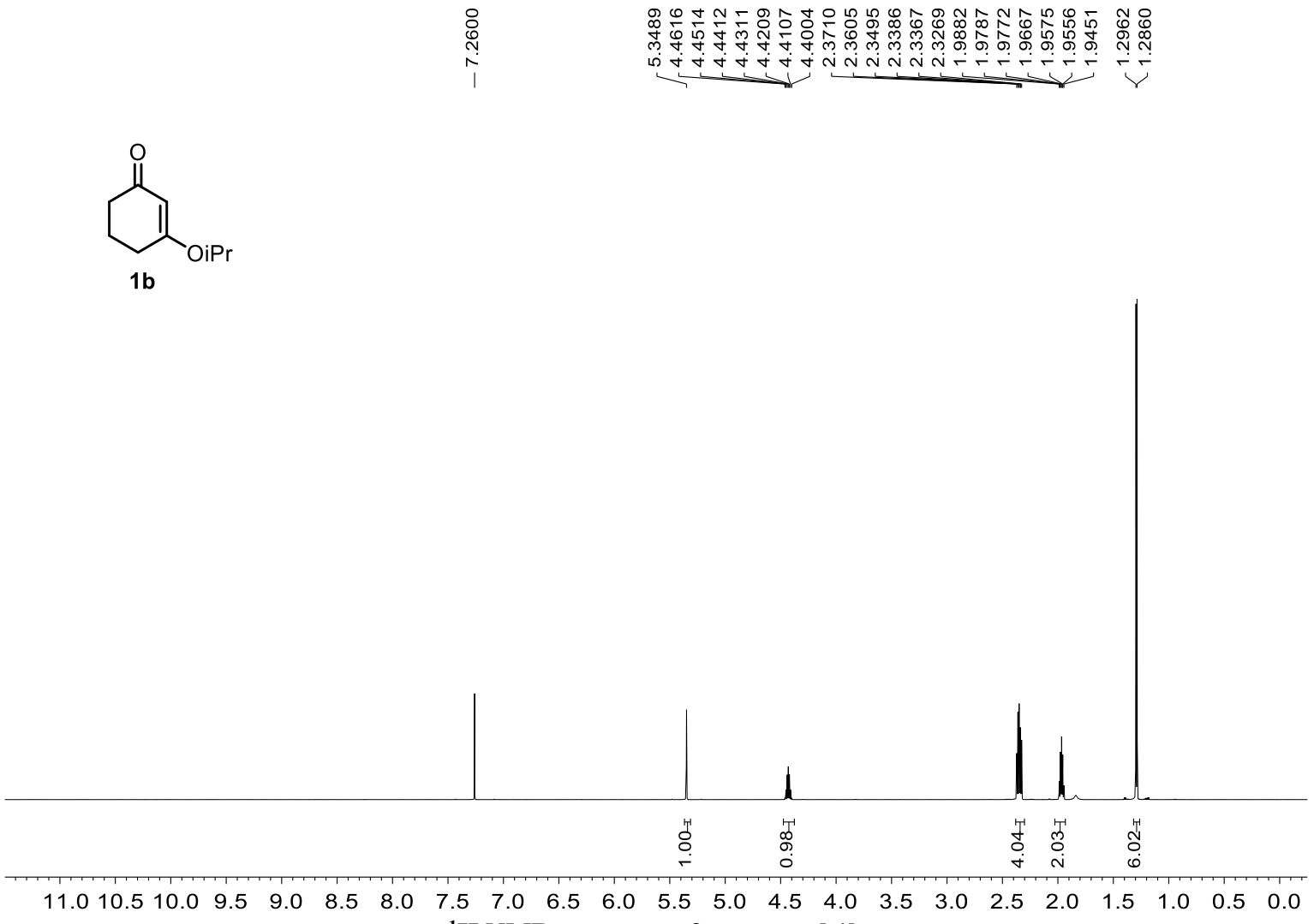
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0412, wR_2 = 0.1174
Final R indexes [all data]	R_1 = 0.0449, wR_2 = 0.1209
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.49

Table S2. Crystal Data and Structure Refinement for compound **3b**

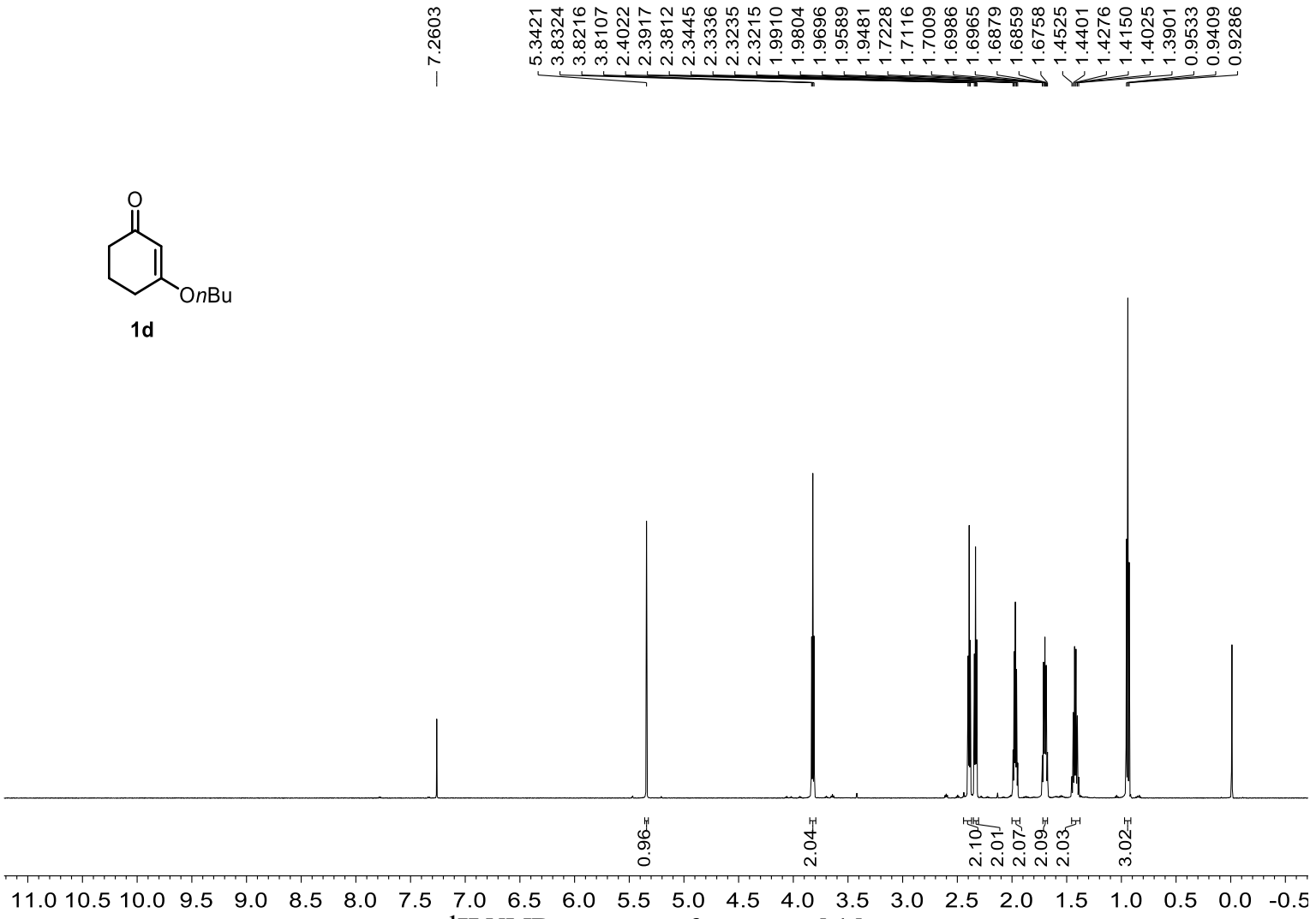


Identification code	**3b (CCDC 2498523)**
Empirical formula	$C_{18}H_{20}O_3$
Formula weight	284.34
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.50120(10)
b/Å	18.0028(3)
c/Å	22.3143(3)
α/°	97.0950(10)
β/°	90.0170(10)
γ/°	90.3820(10)
Volume/$Å^3$	2990.24(8)
Z	8
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	0.680
F(000)	1216.0
Crystal size/mm^3	0.17 × 0.15 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	3.99 to 134.148

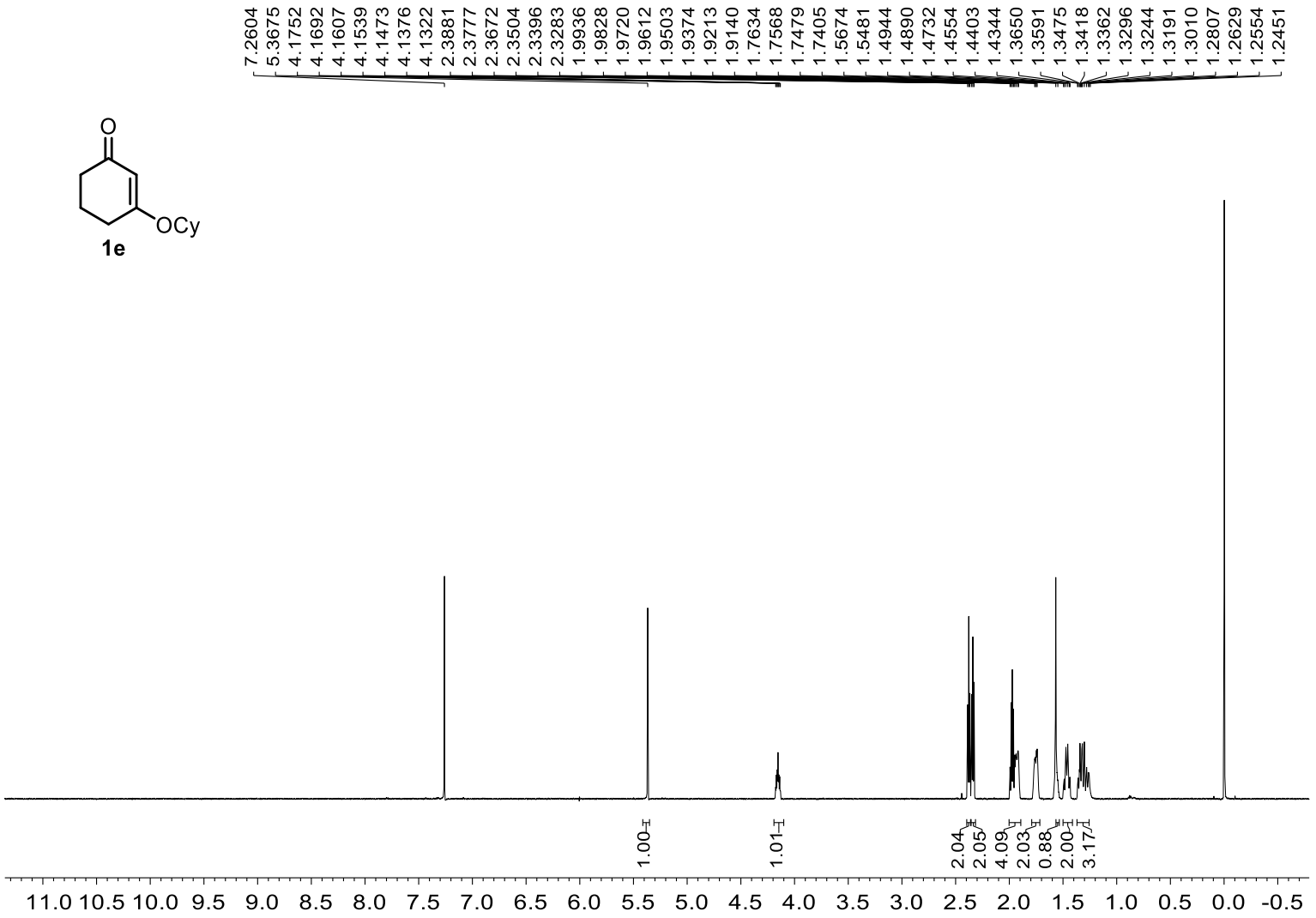
Index ranges	$-8 \leq h \leq 8$, $-21 \leq k \leq 21$, $-24 \leq l \leq 26$
Reflections collected	41043
Independent reflections	10585 [R_{int} = 0.0393, R_{sigma} = 0.0329]
Data/restraints/parameters	10585/0/767
Goodness-of-fit on F^2	1.112
Final R indexes [I>=2σ (I)]	R_1 = 0.0576, wR_2 = 0.1616
Final R indexes [all data]	R_1 = 0.0669, wR_2 = 0.1764
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.28



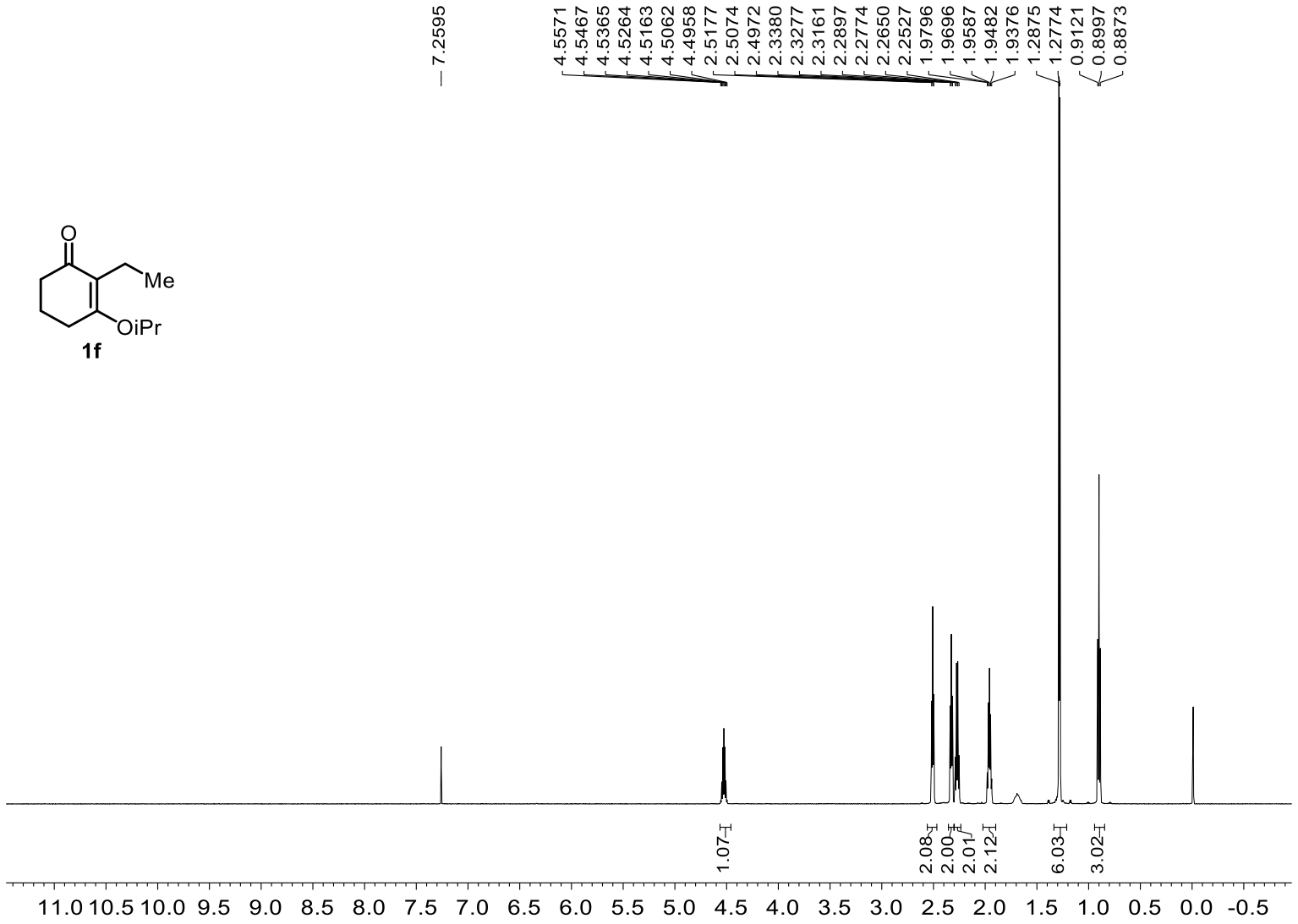
^{1}H NMR spectrum of compound 1b



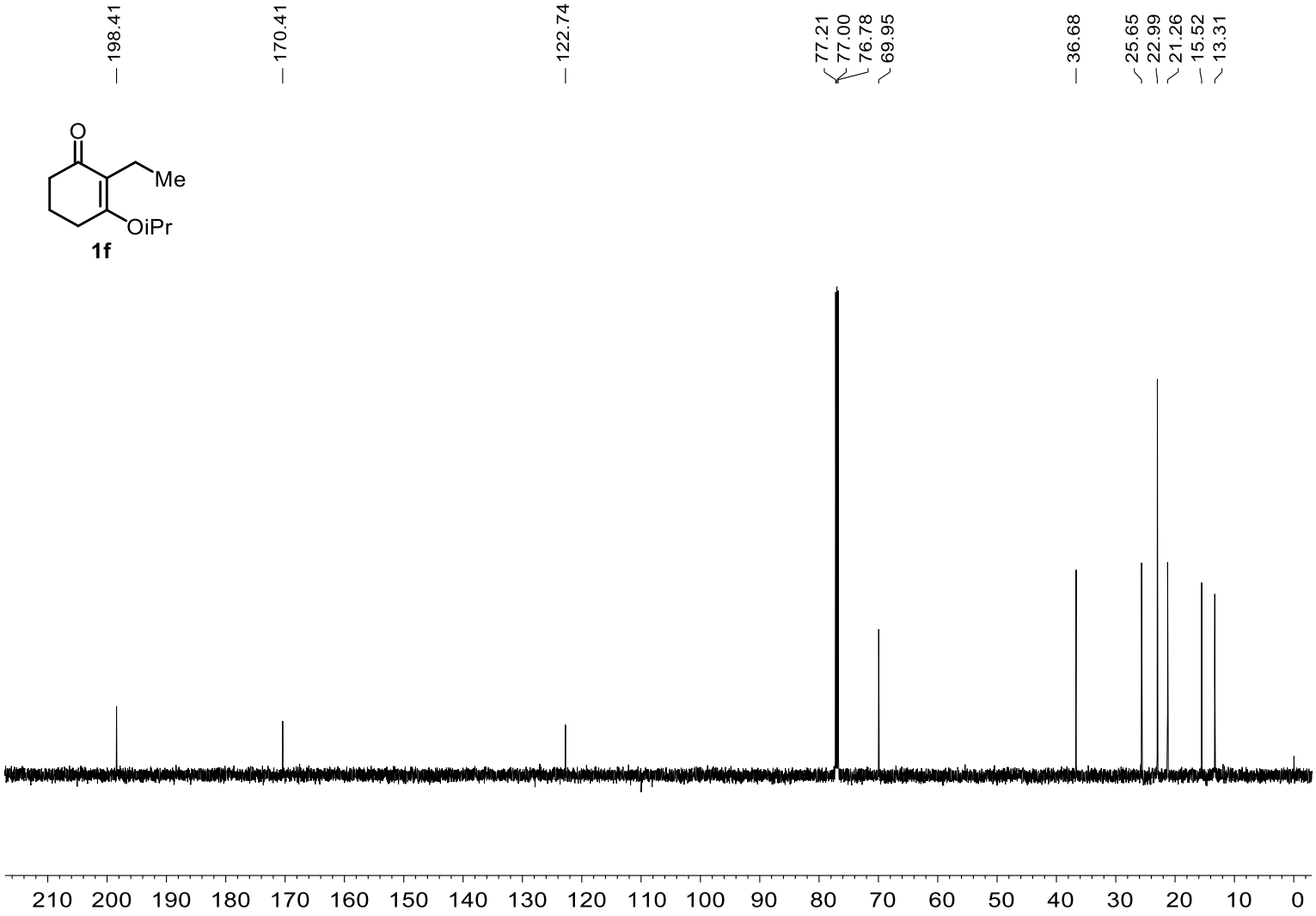
^{1}H NMR spectrum of compound 1d



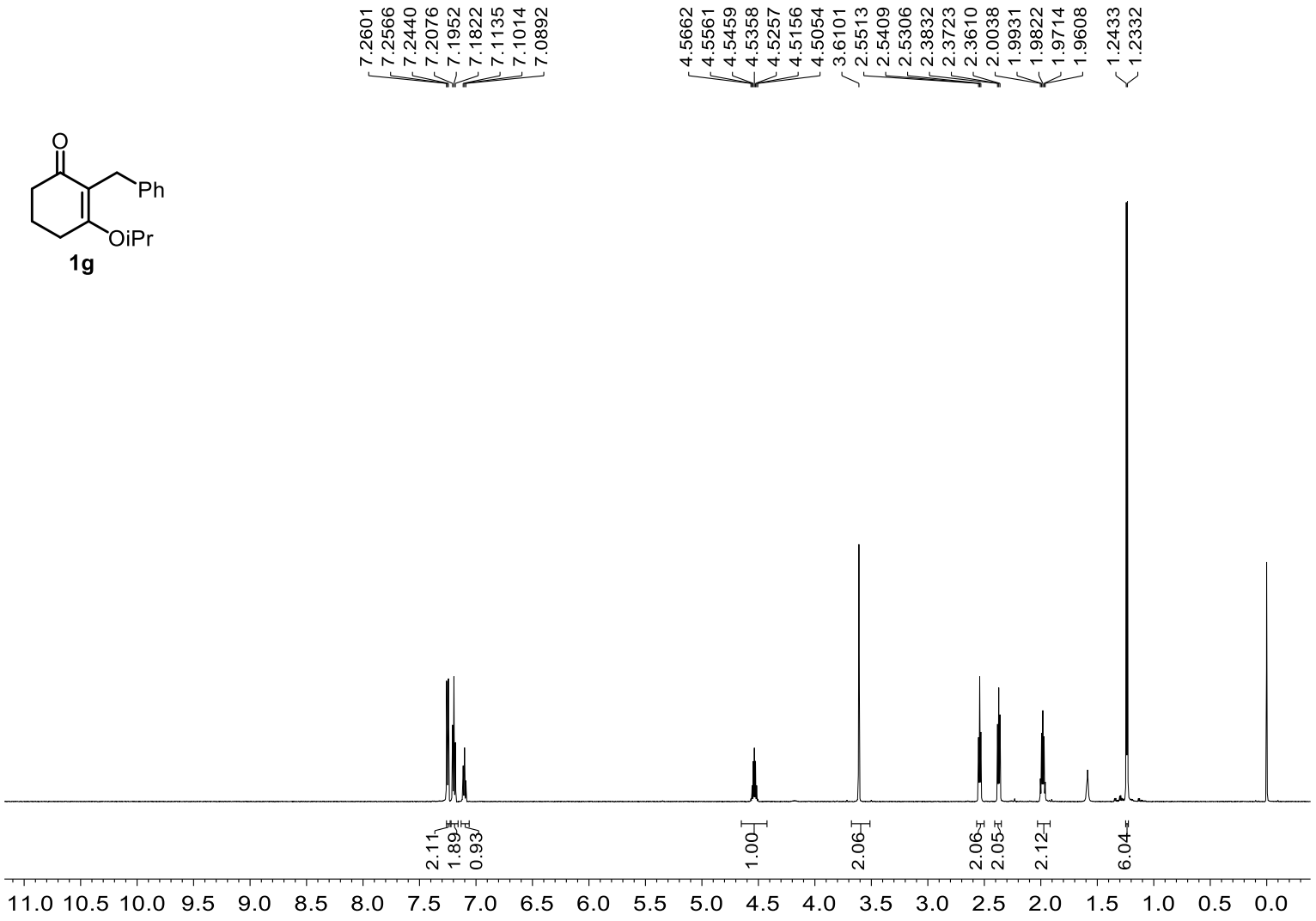
^{1}H NMR spectrum of compound 1e



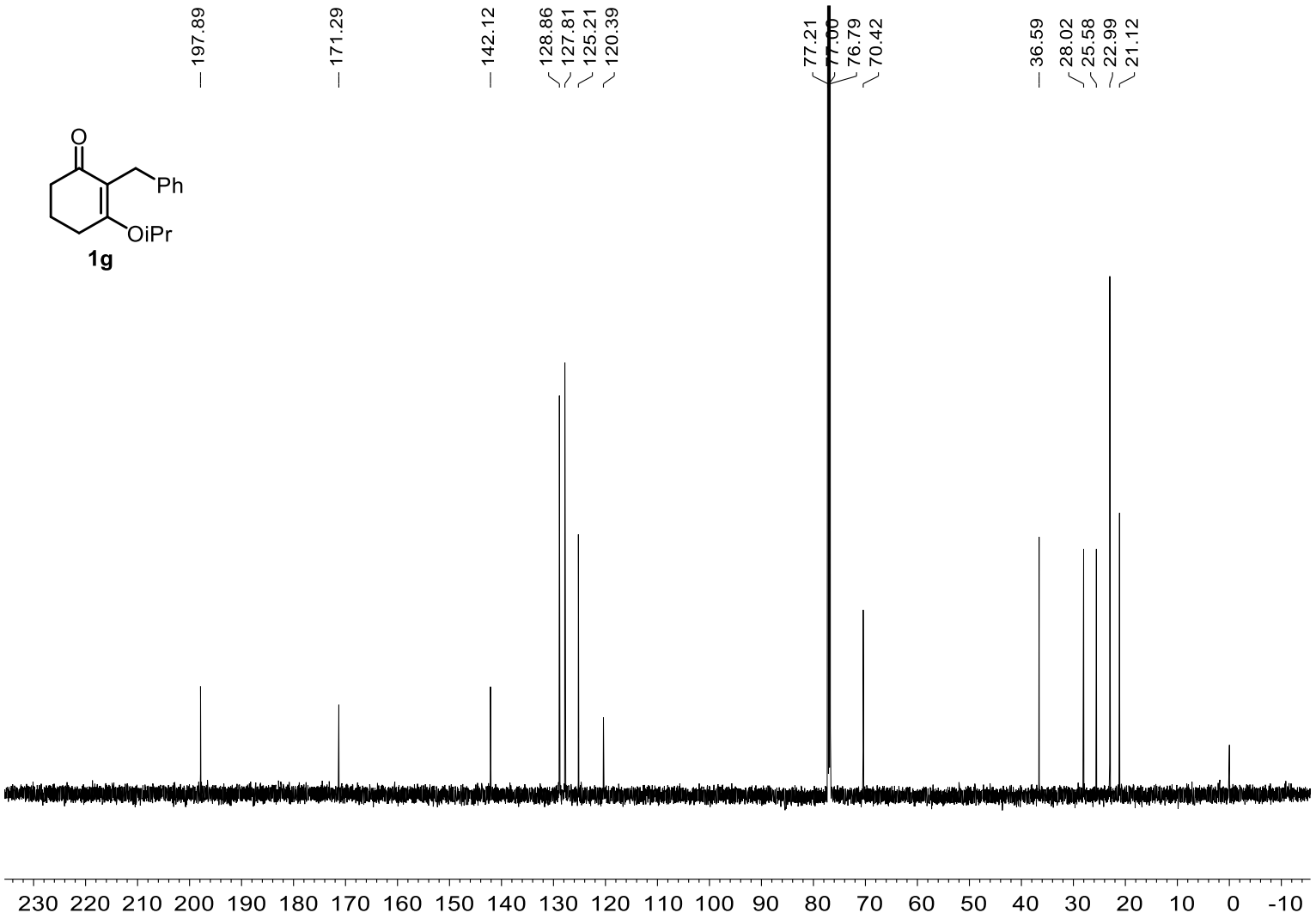
^{1}H NMR spectrum of compound 1f



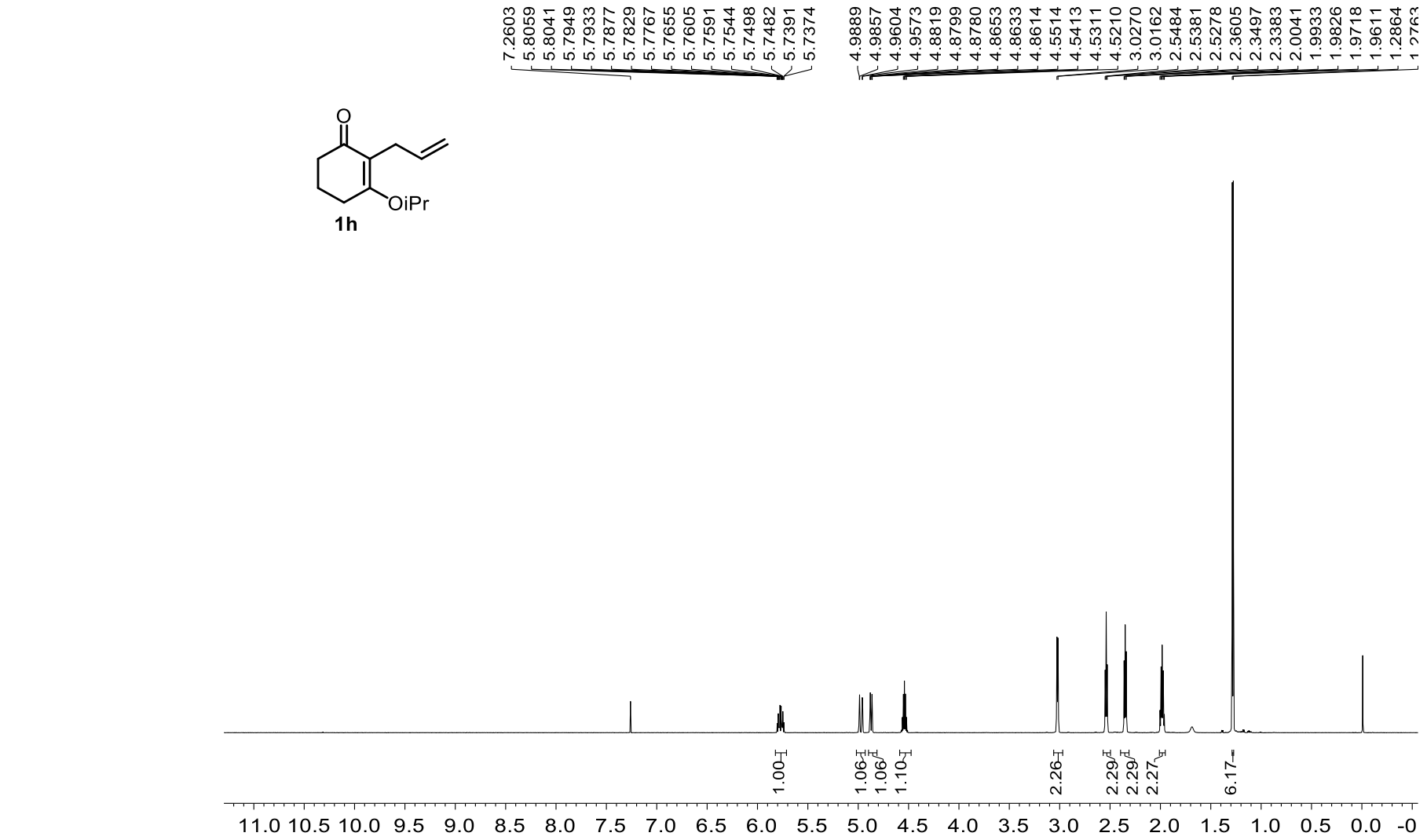
^{13}C NMR spectrum of compound 1f



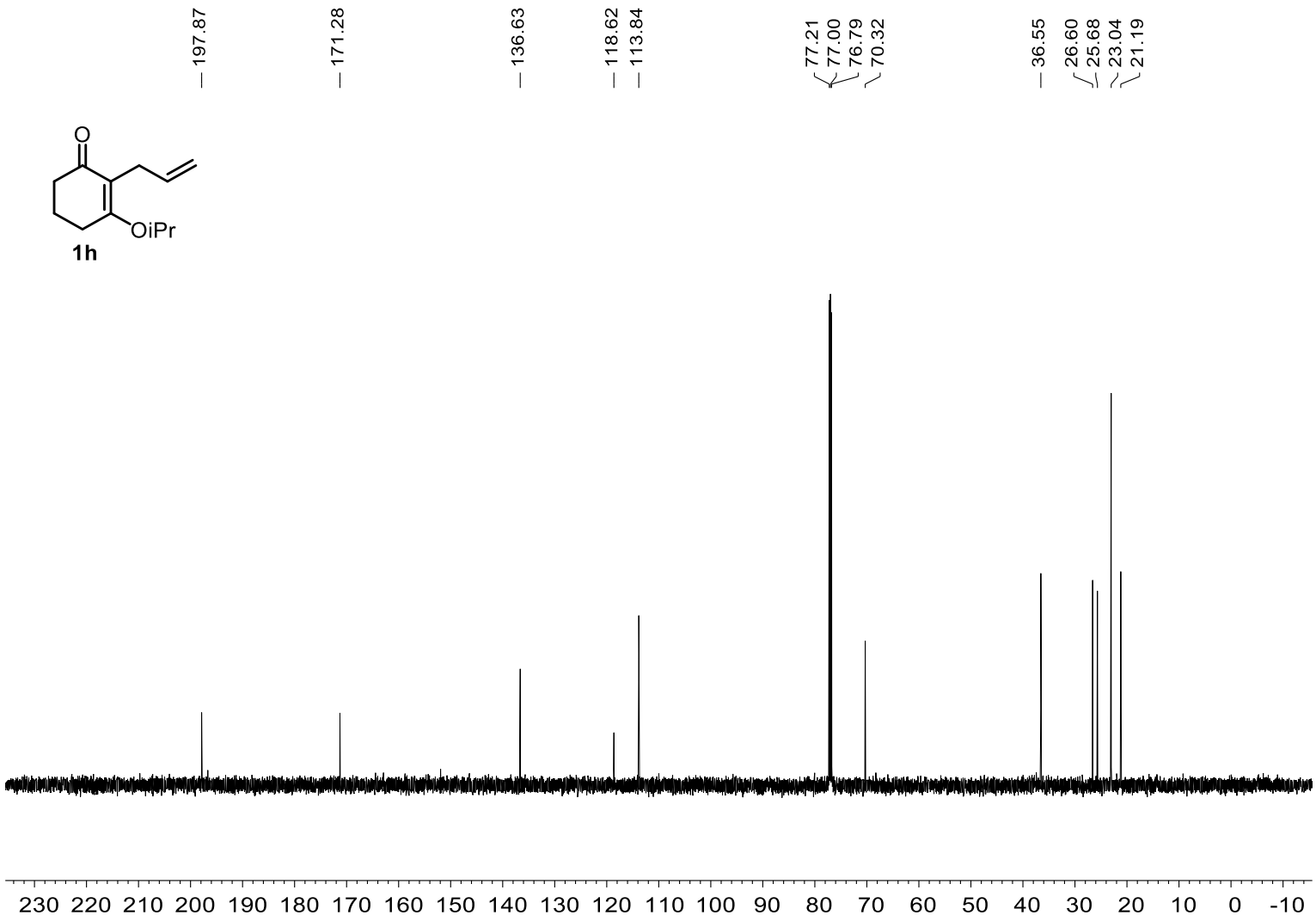
^{1}H NMR spectrum of compound 1g



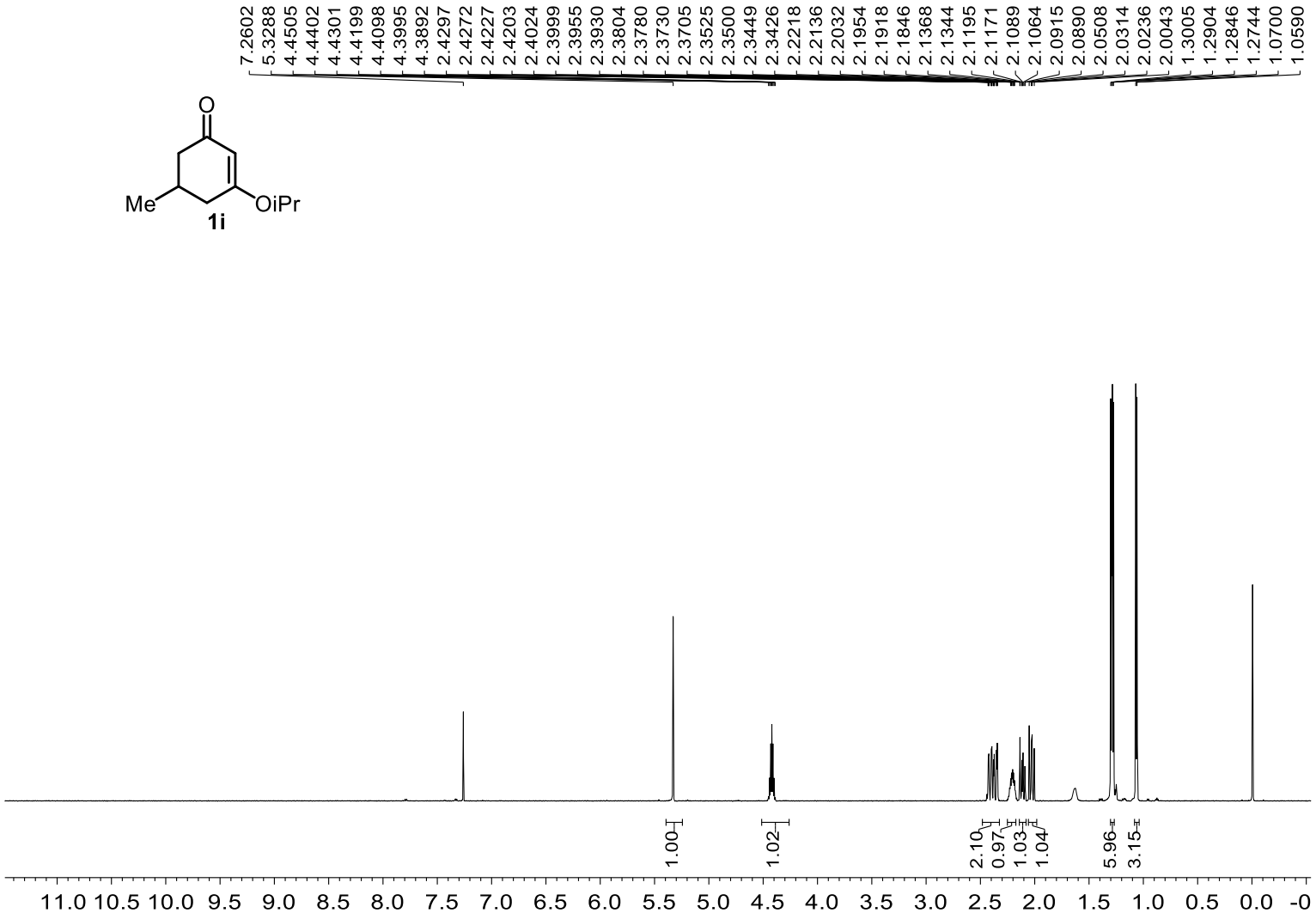
^{13}C NMR spectrum of compound 1g



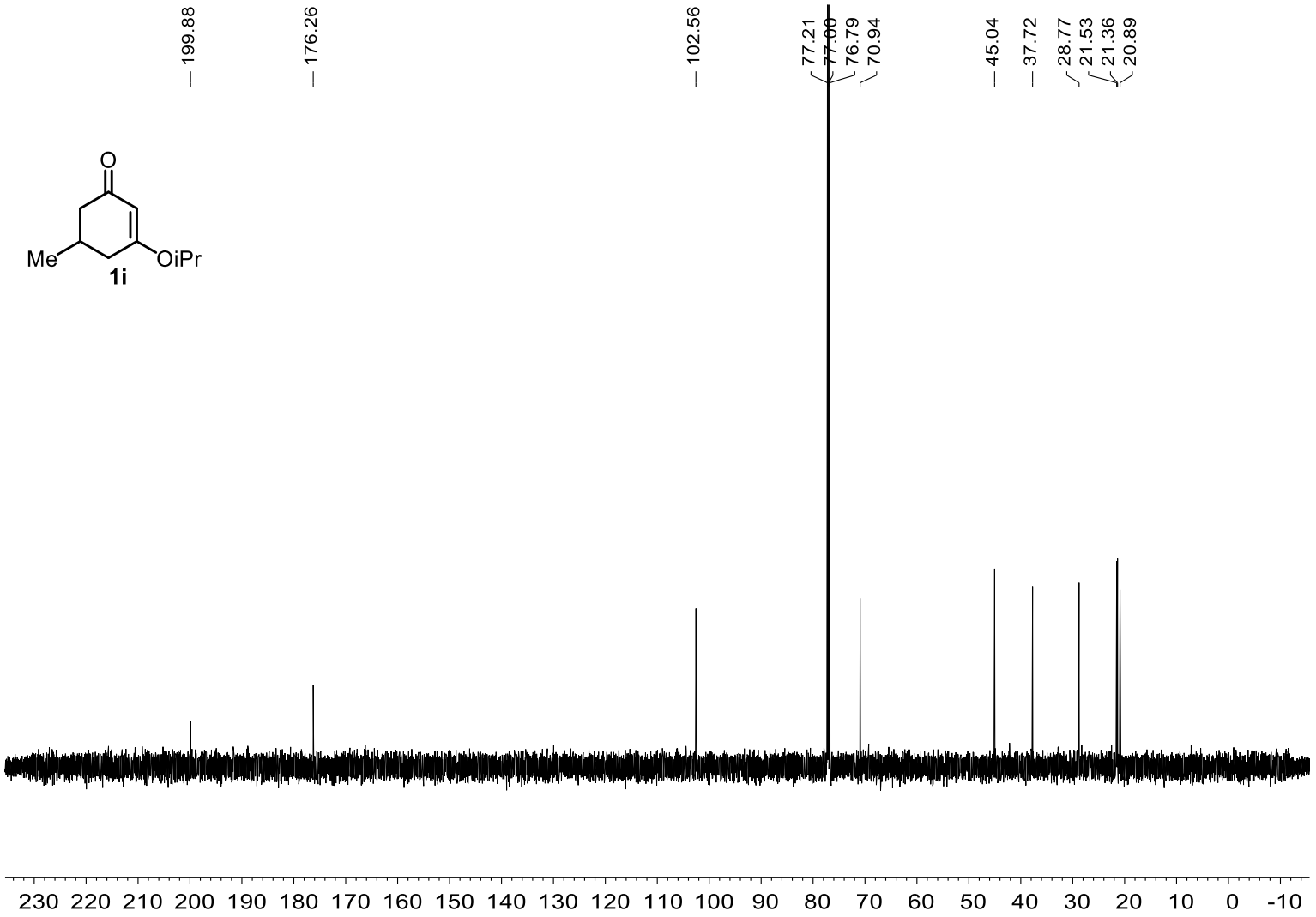
^{1}H NMR spectrum of compound 1h



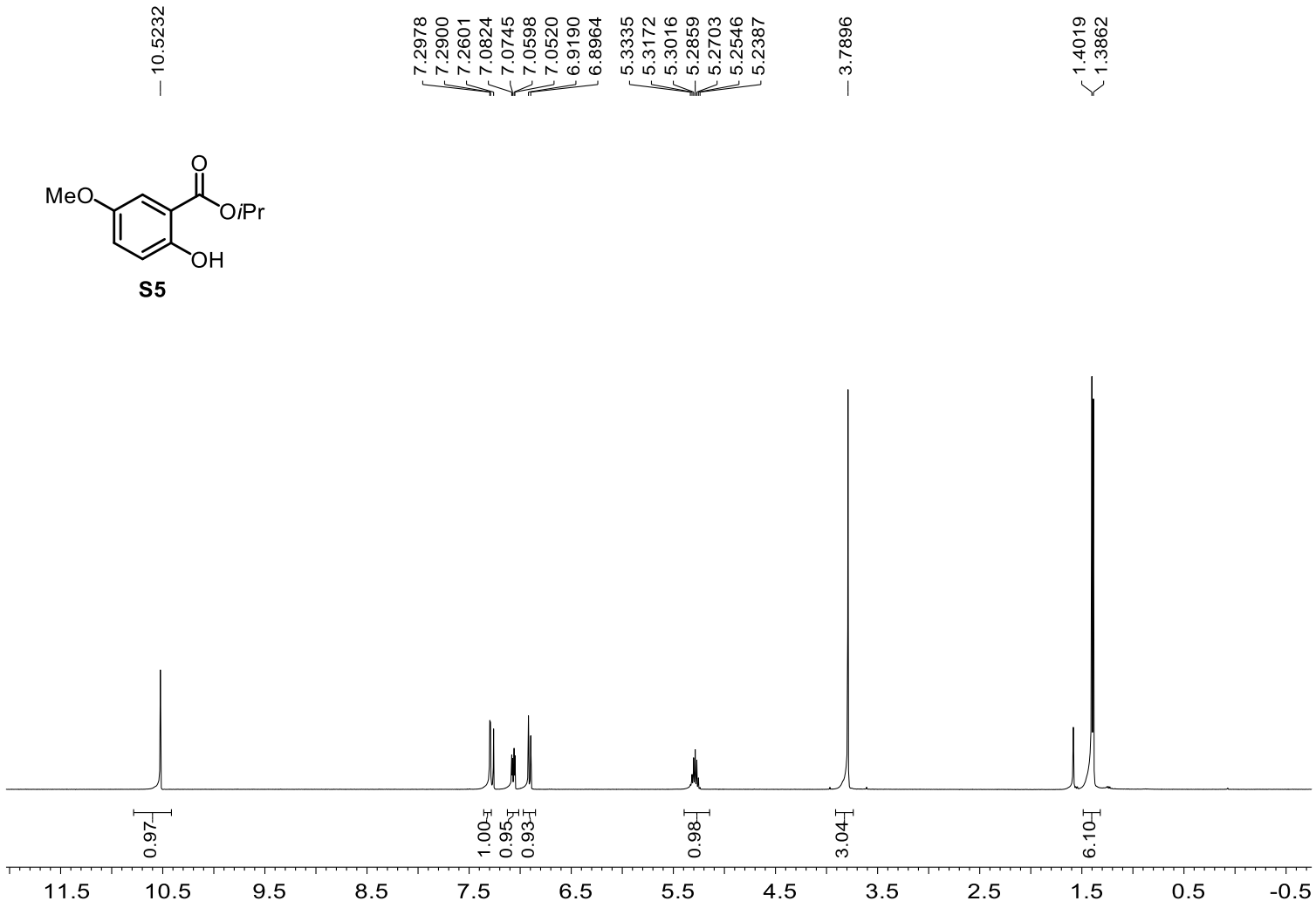
^{13}C NMR spectrum of compound 1h



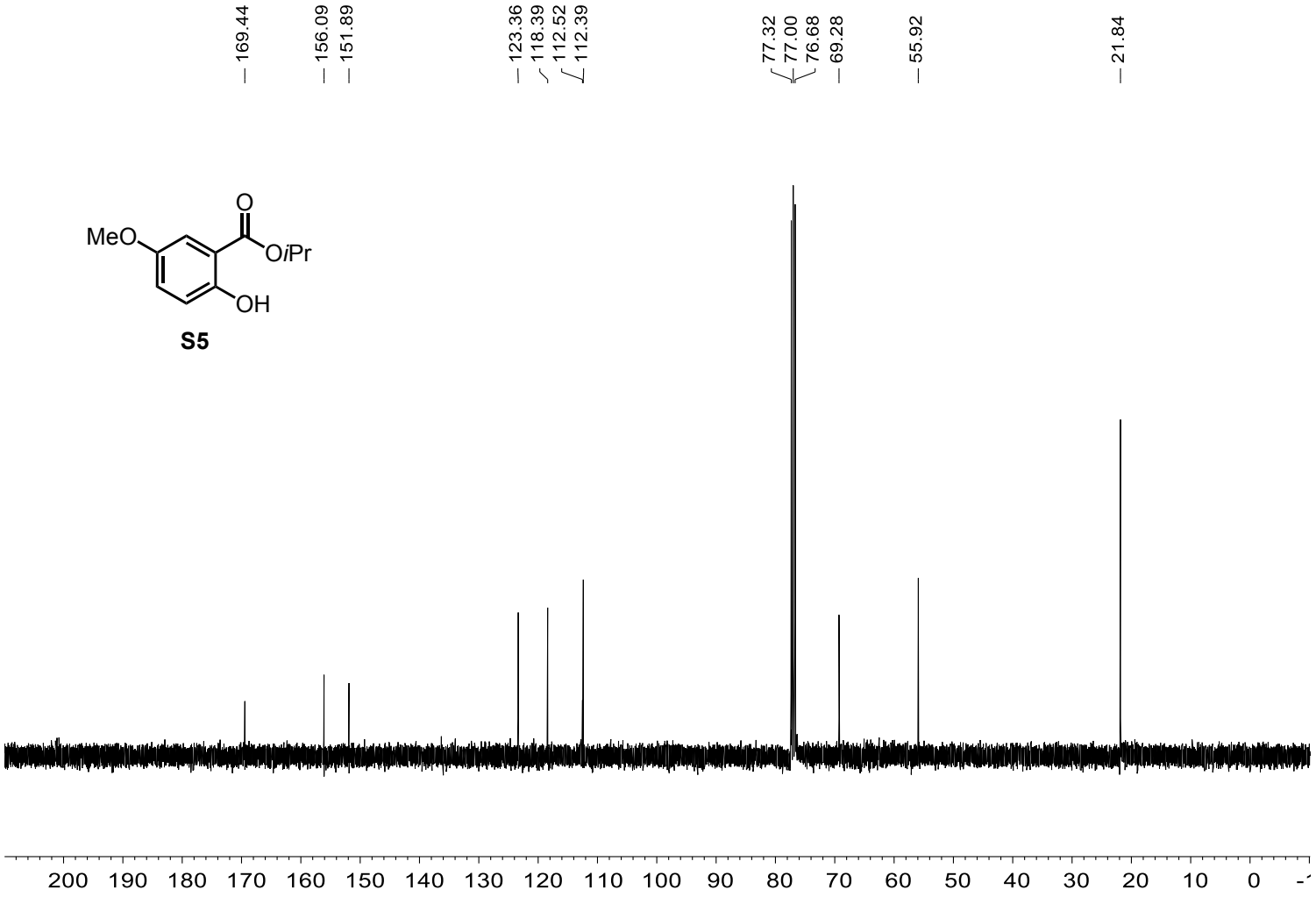
^{1}H NMR spectrum of compound 1i



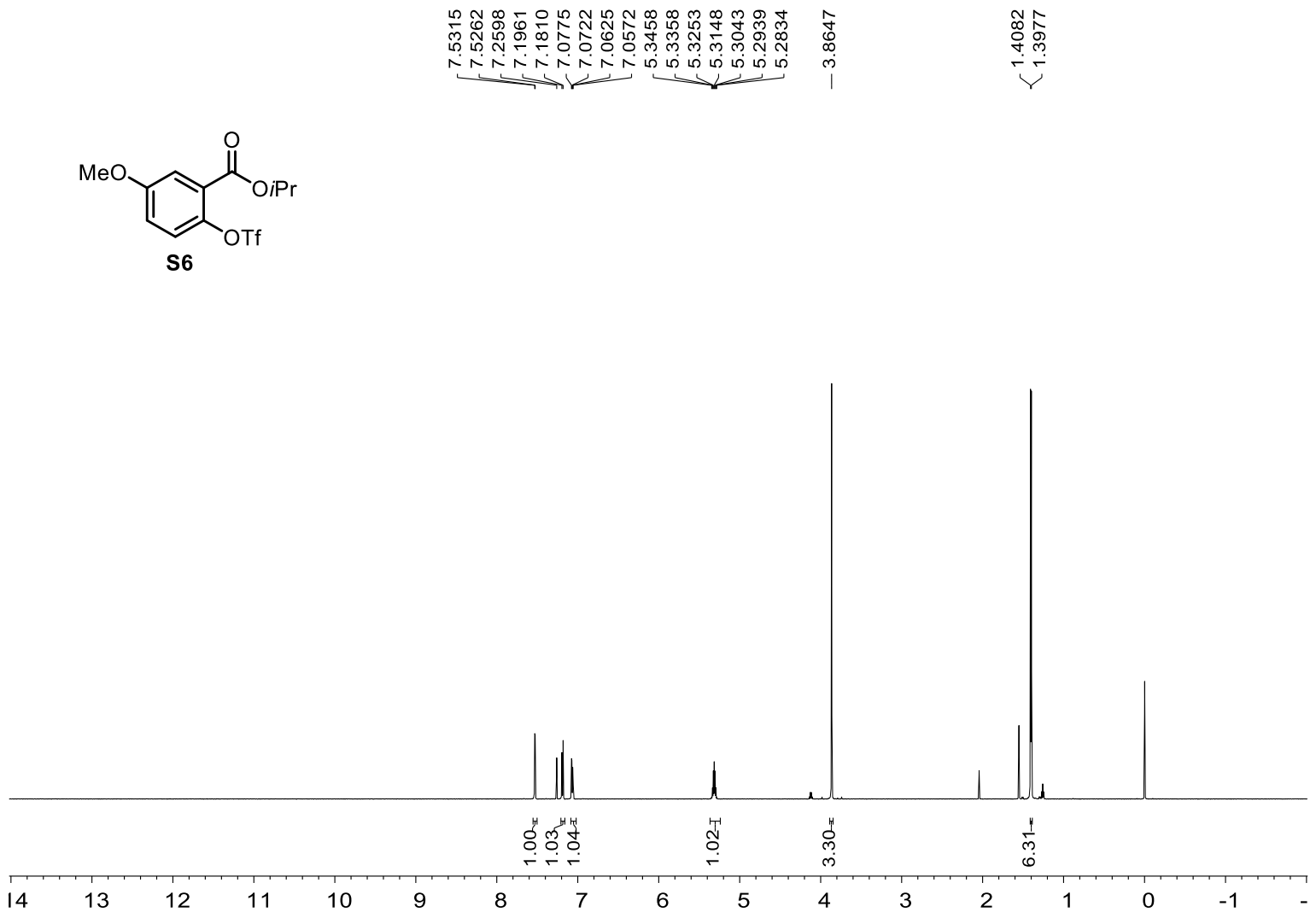
^{13}C NMR spectrum of compound 1i



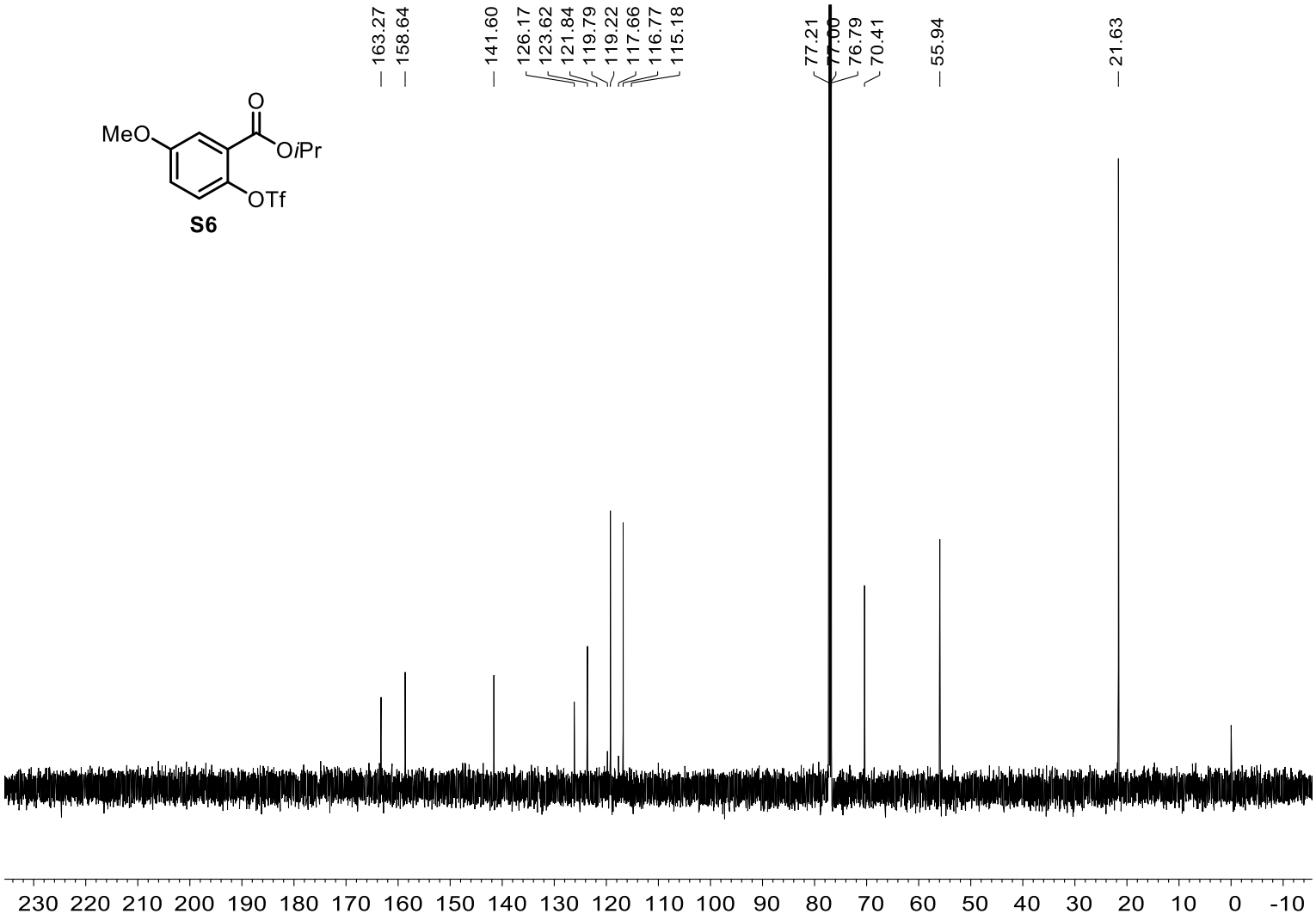
^{1}H NMR spectrum of compound S5



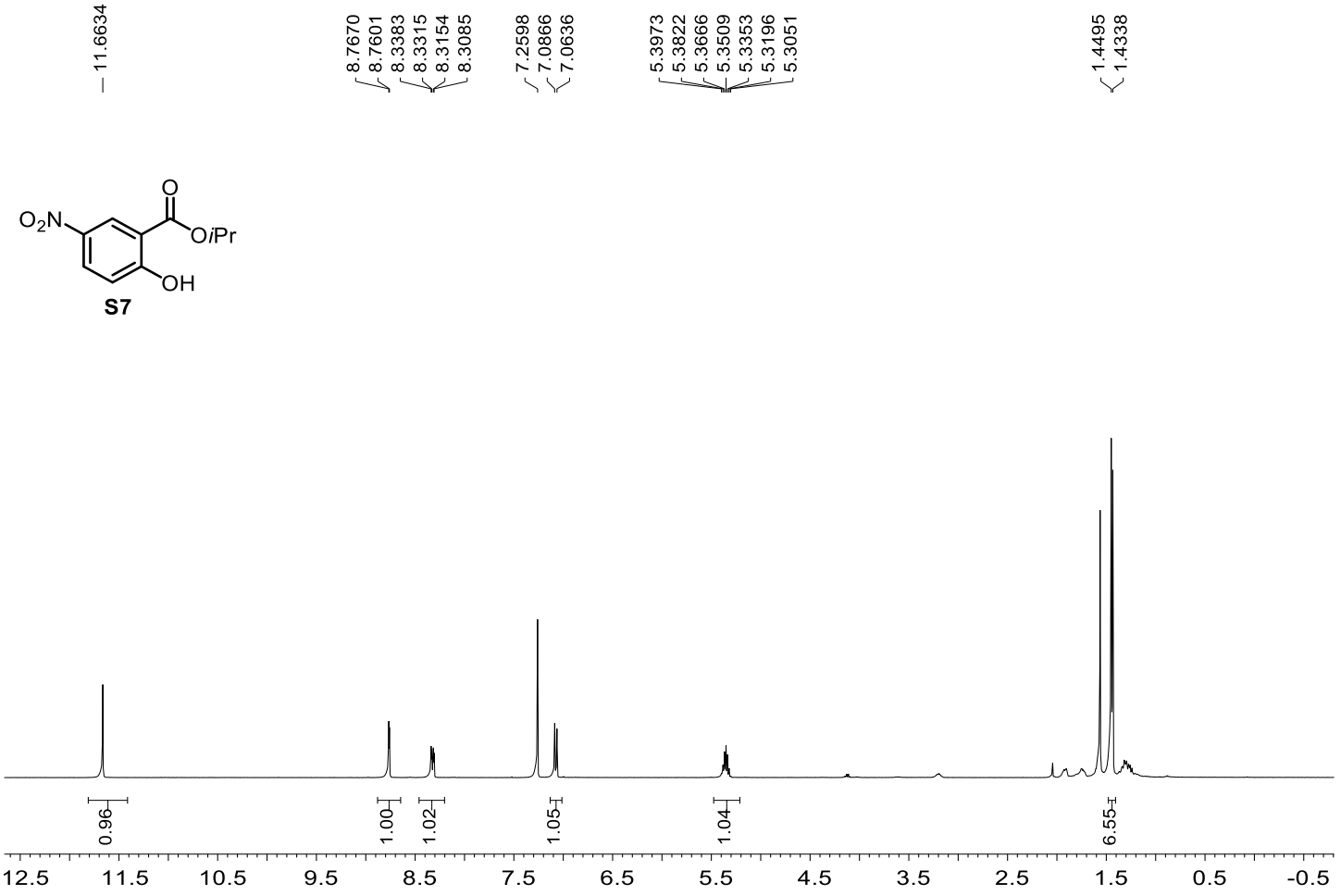
^{13}C NMR spectrum of compound S5



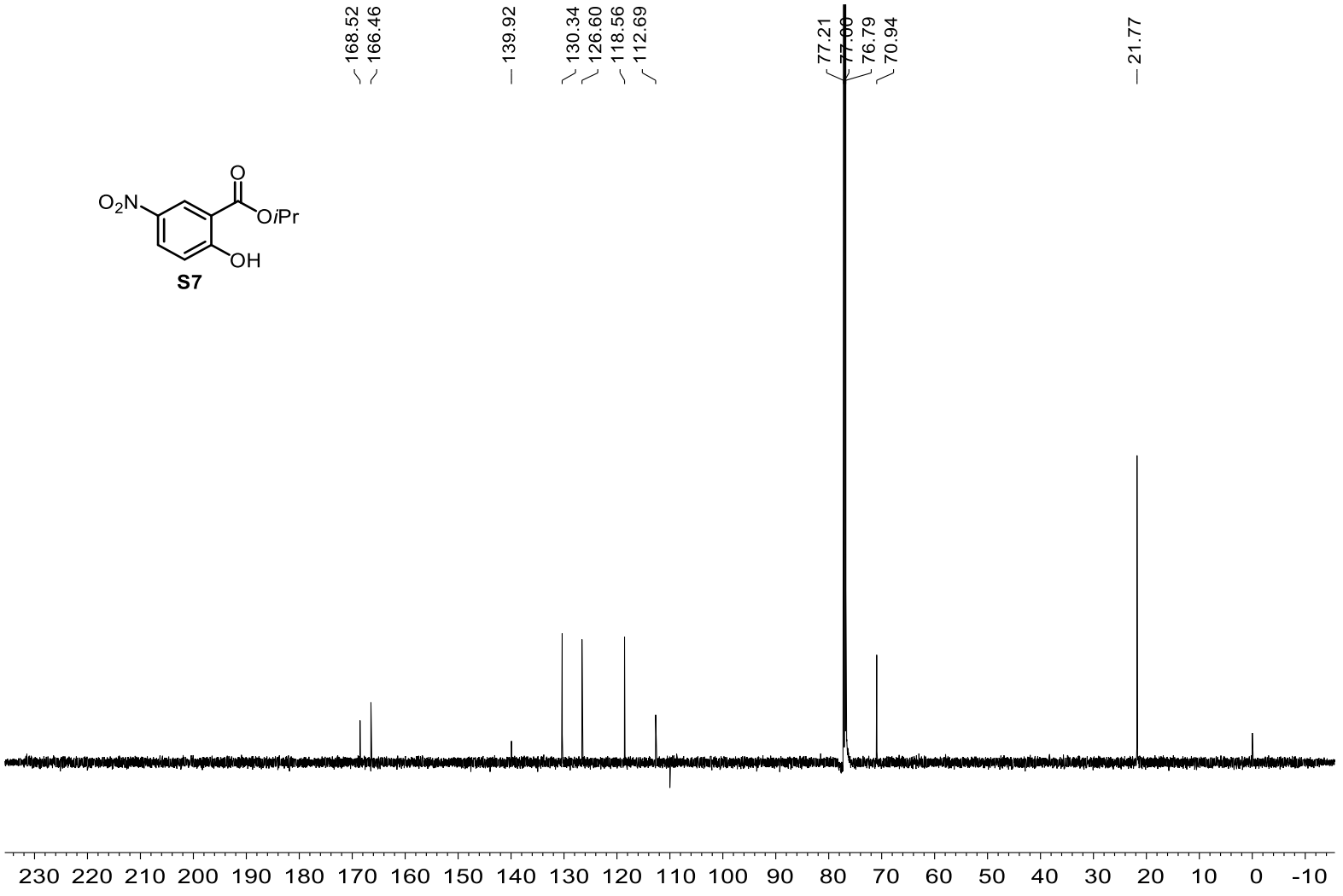
^{1}H NMR spectrum of compound S6



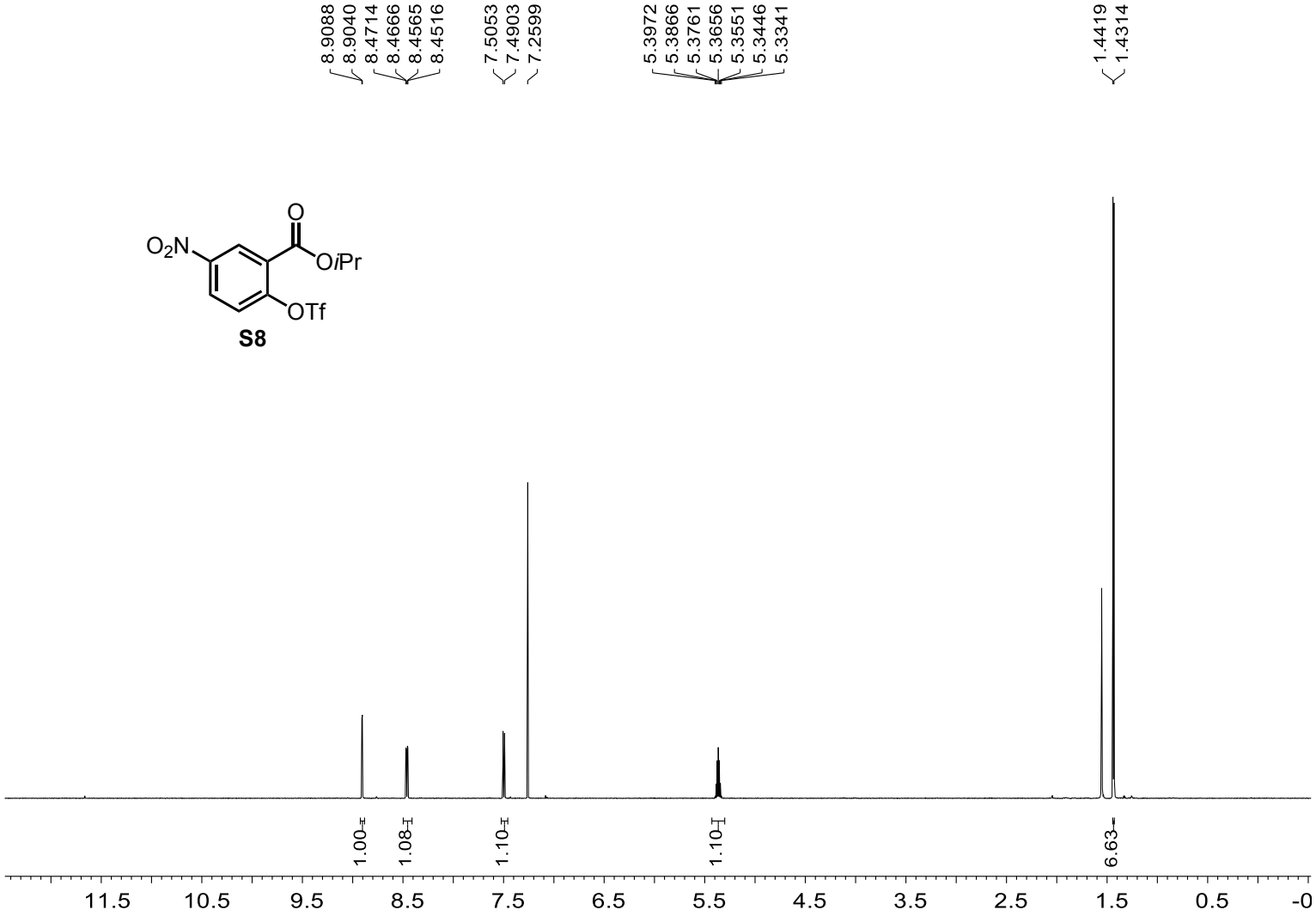
^{13}C NMR spectrum of compound S6



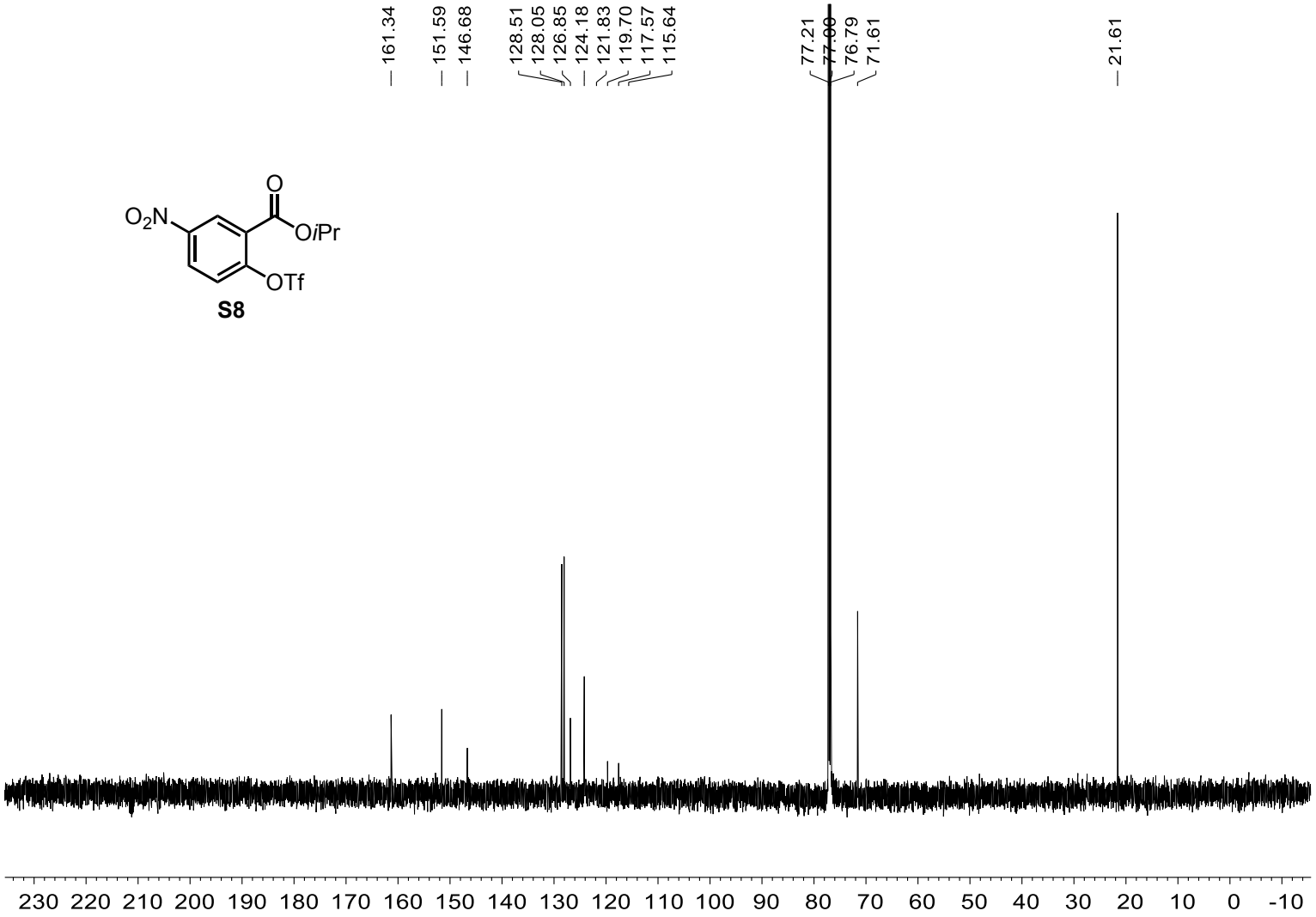
^{1}H NMR spectrum of compound S7



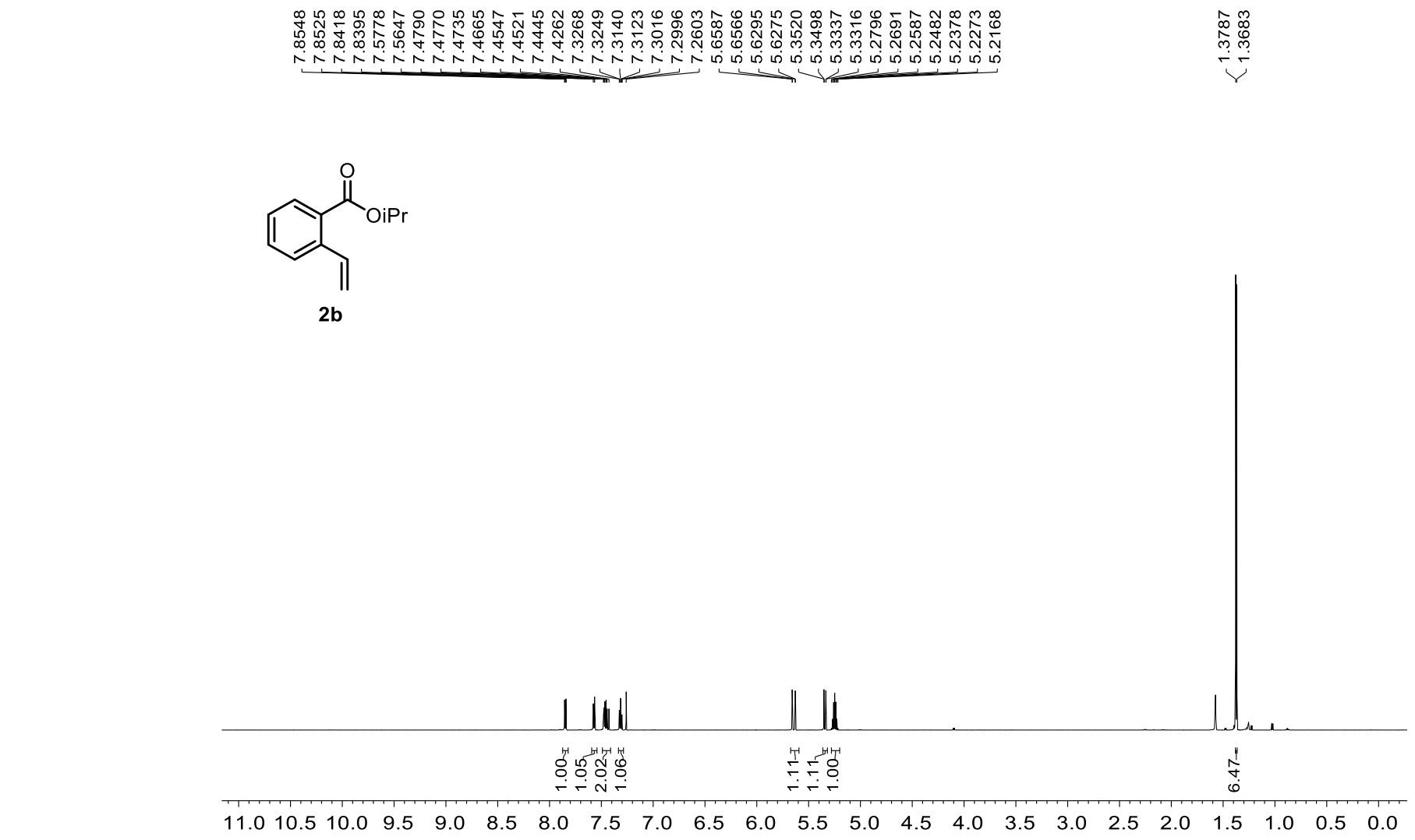
^{13}C NMR spectrum of compound S7



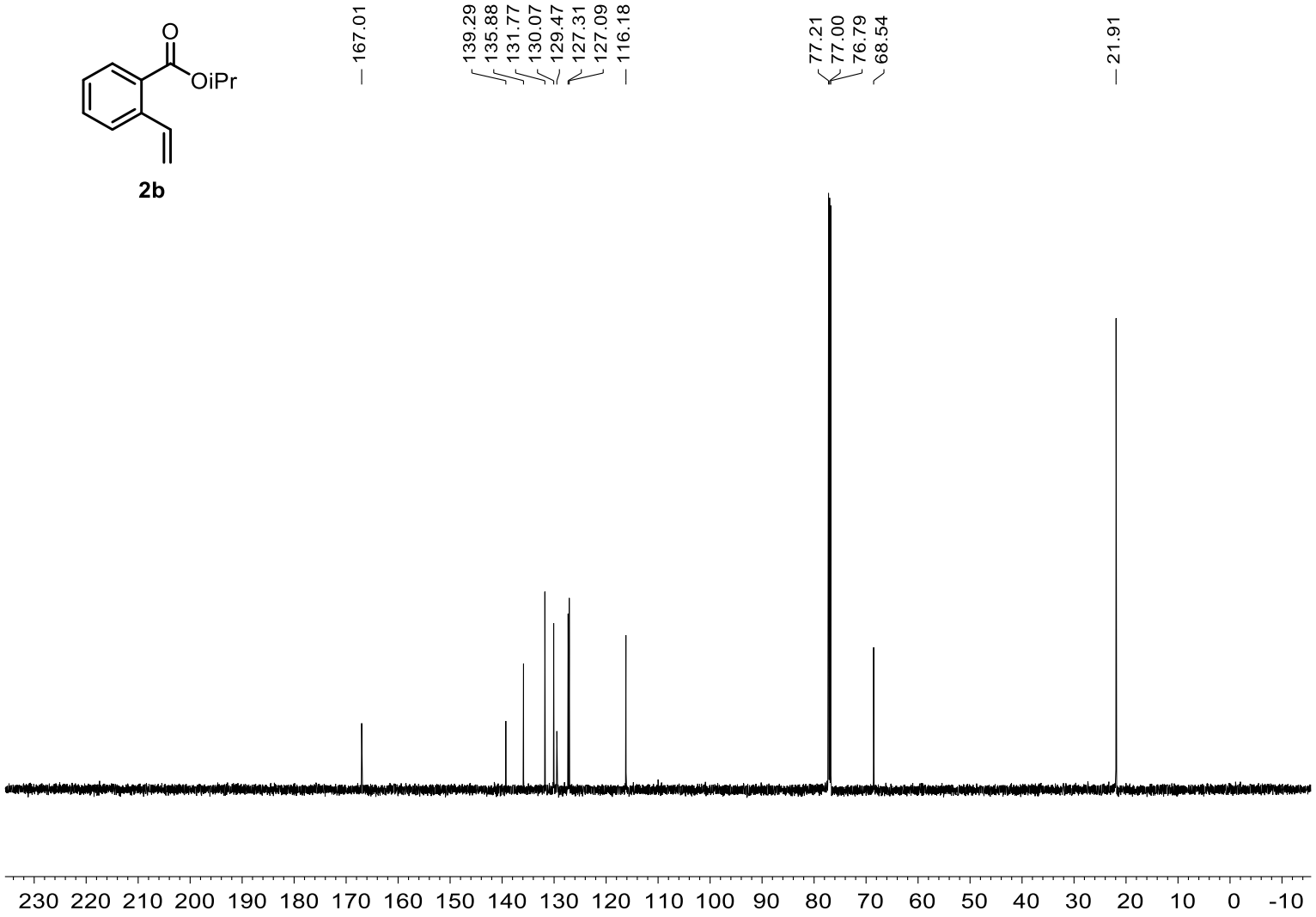
^{1}H NMR spectrum of compound S8



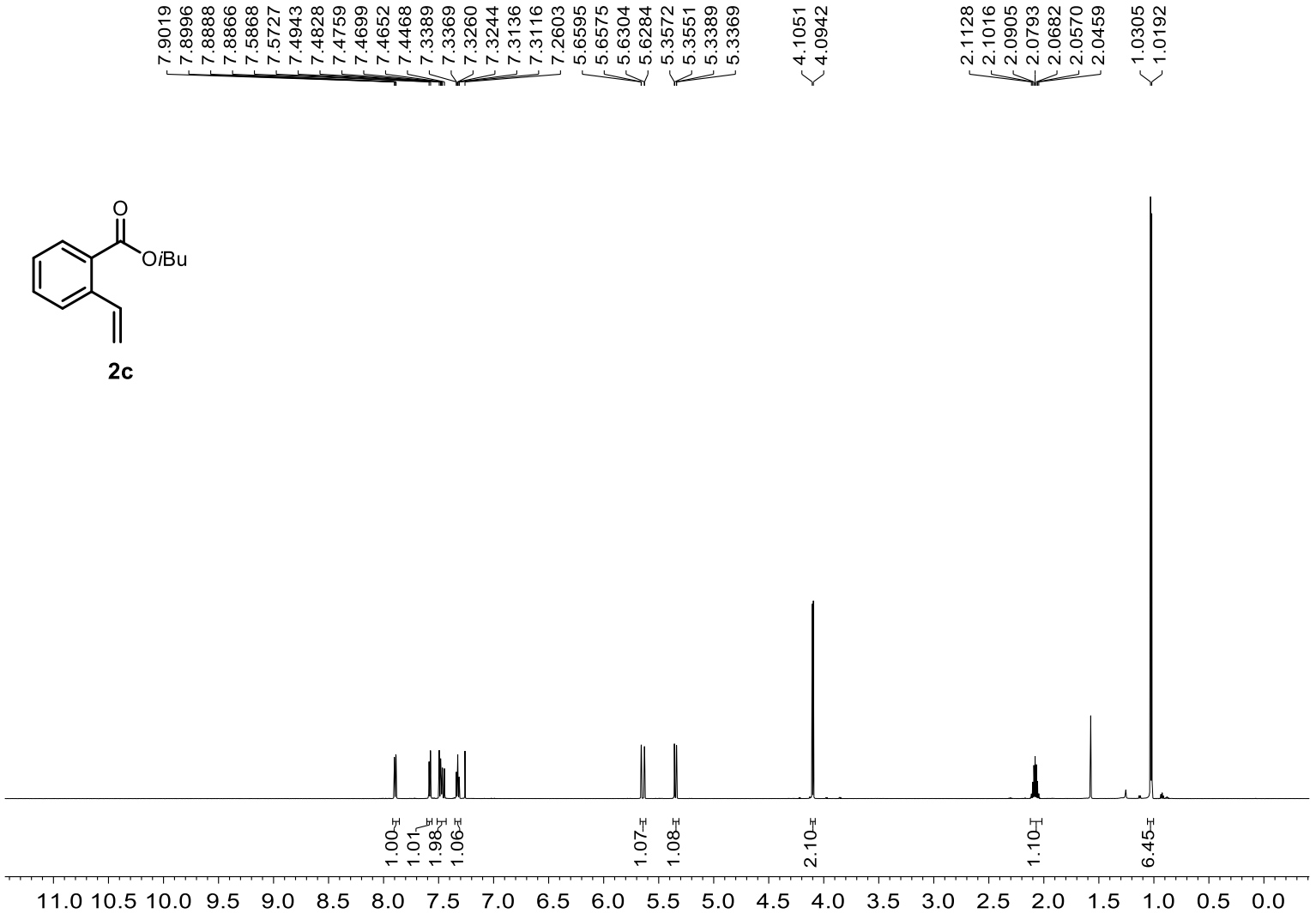
^{13}C NMR spectrum of compound S8



^{1}H NMR spectrum of compound 2b

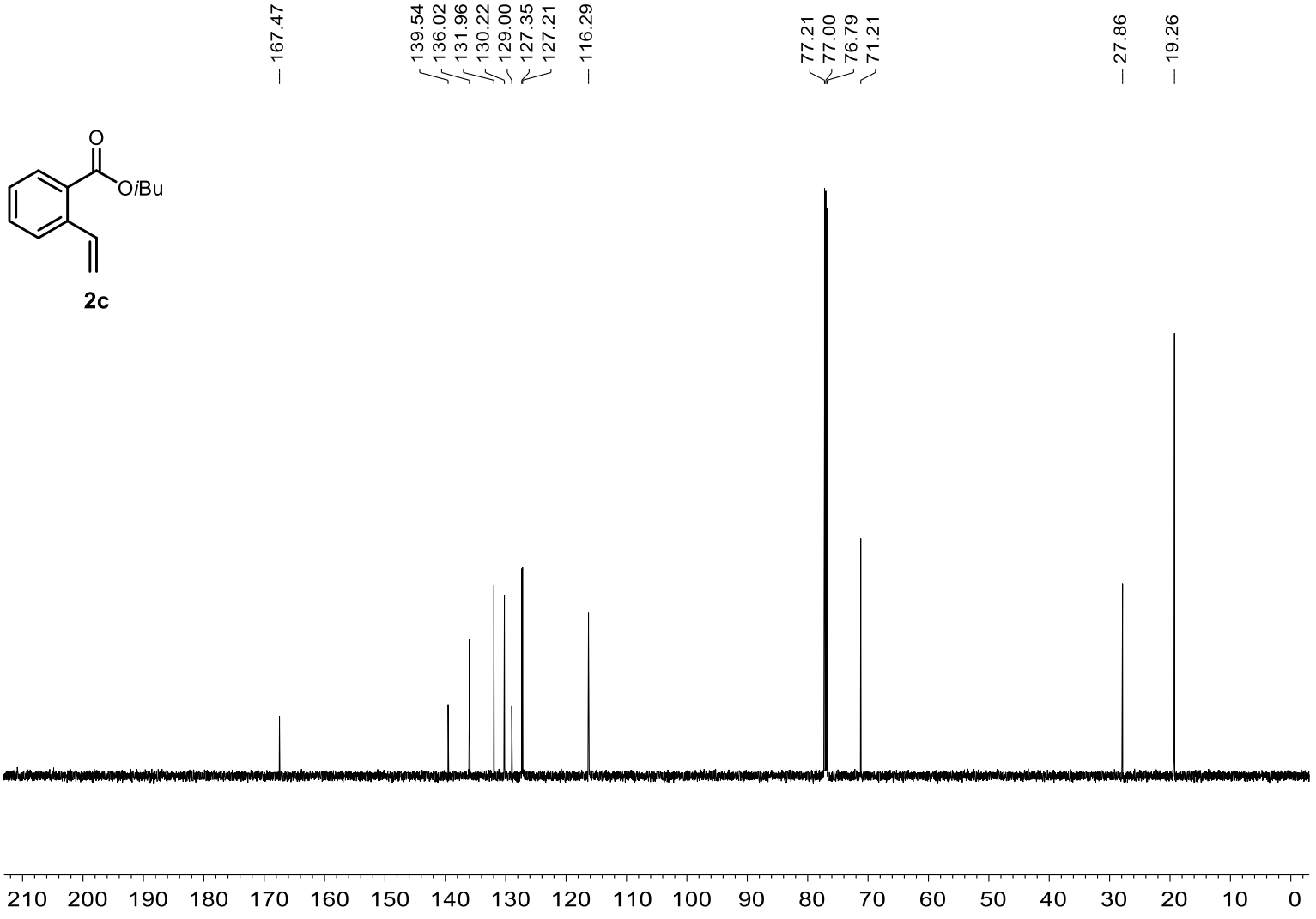


^{13}C NMR spectrum of compound 2b

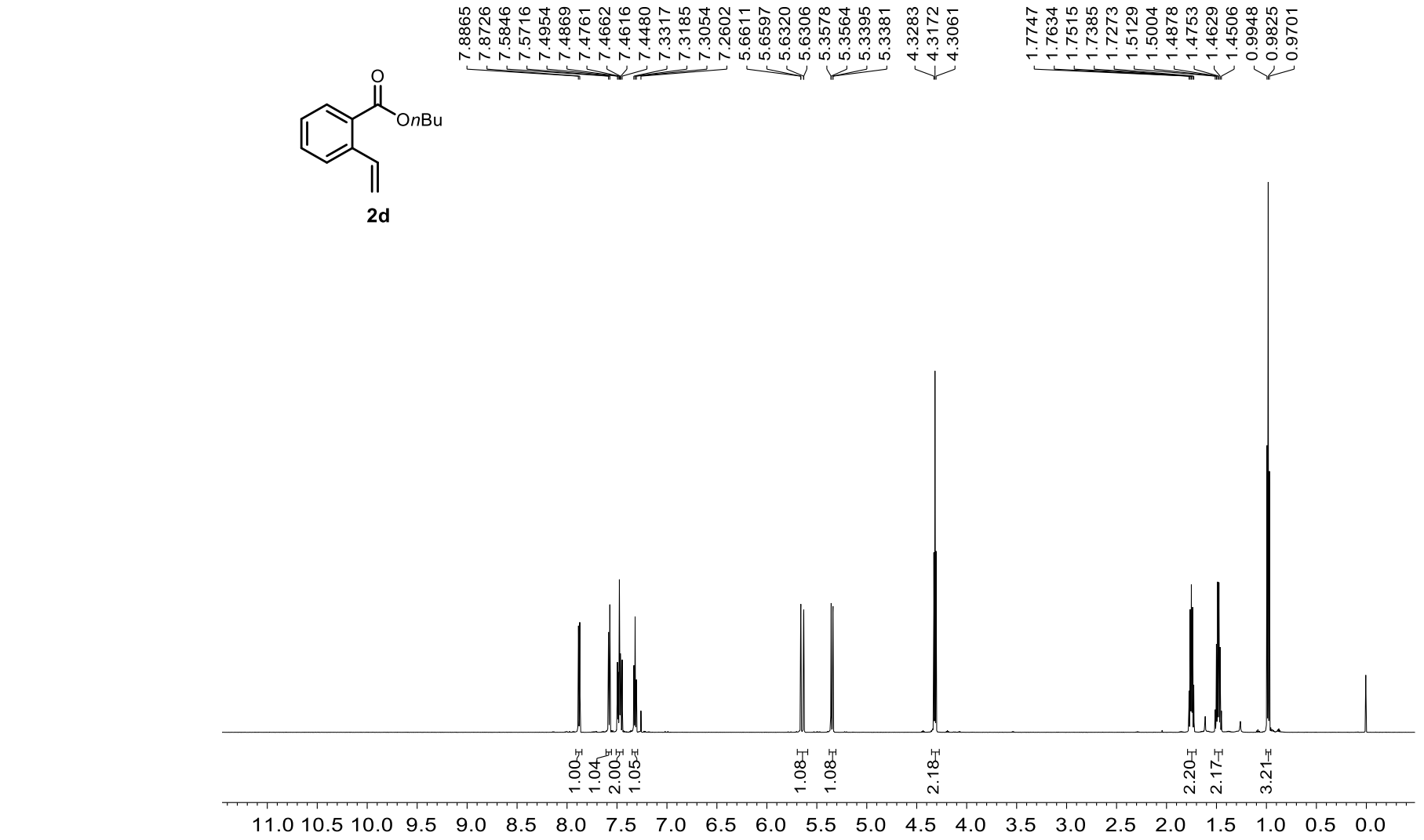


2c

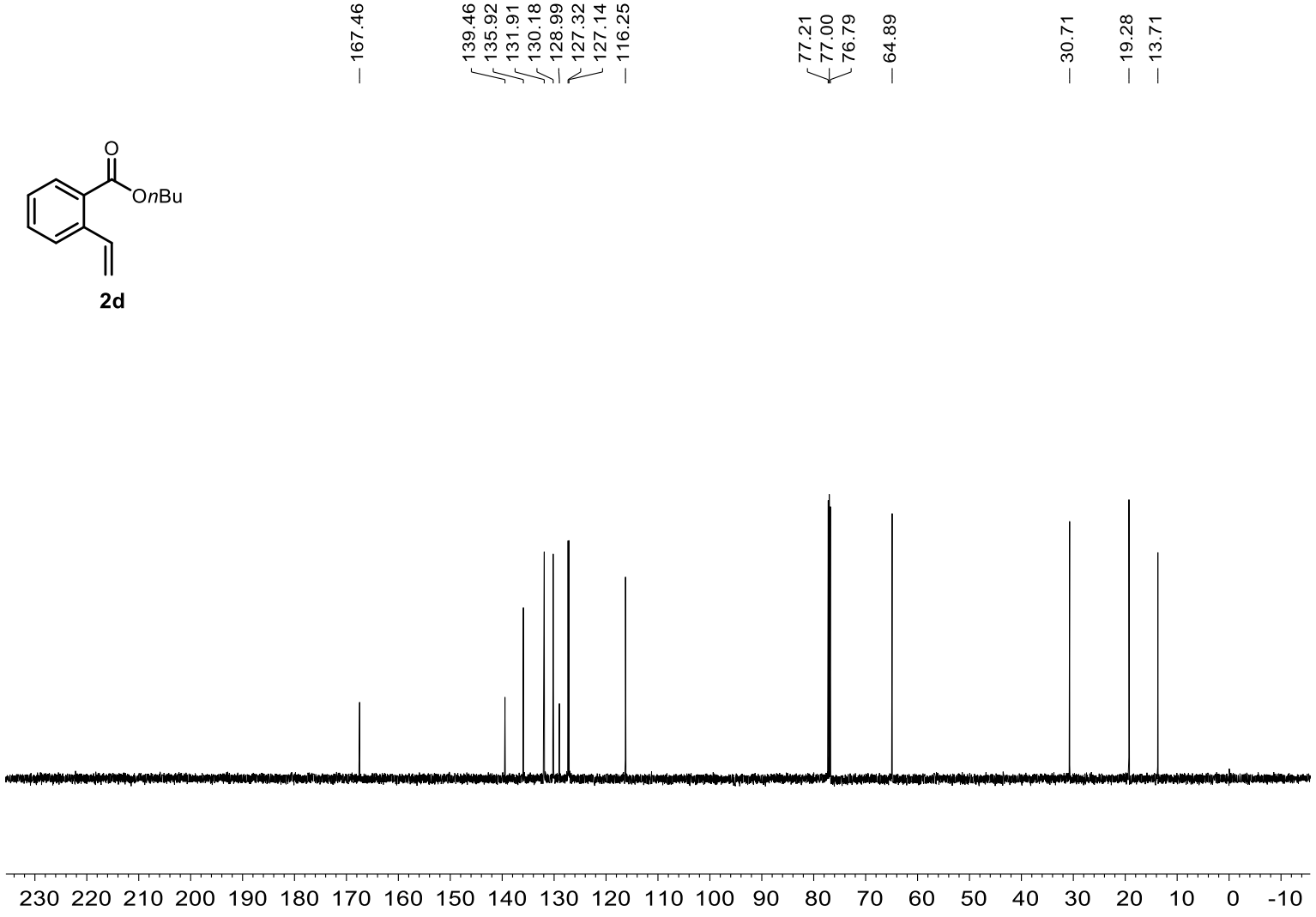
^{1}H NMR spectrum of compound 2c



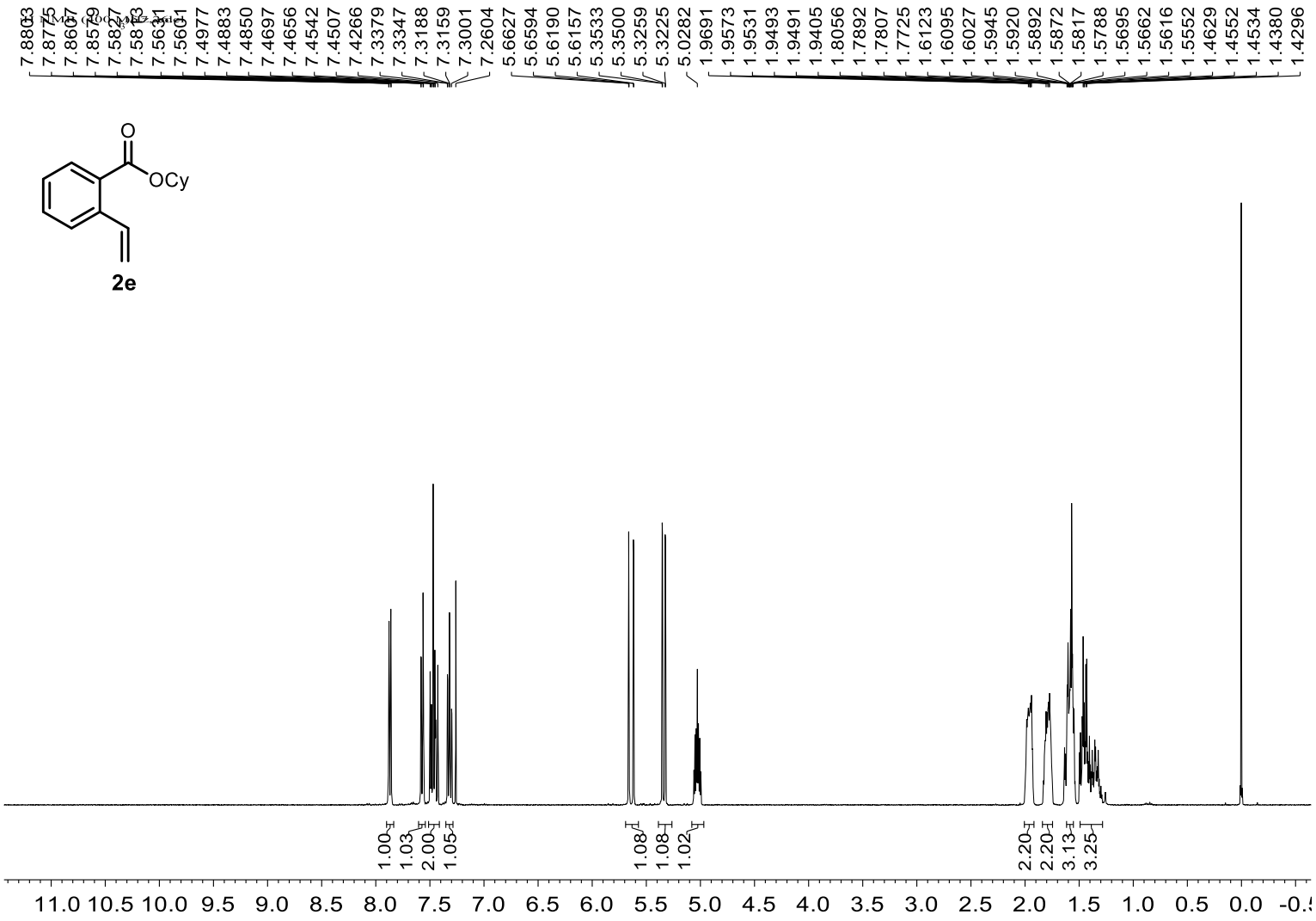
^{13}C NMR spectrum of compound 2c



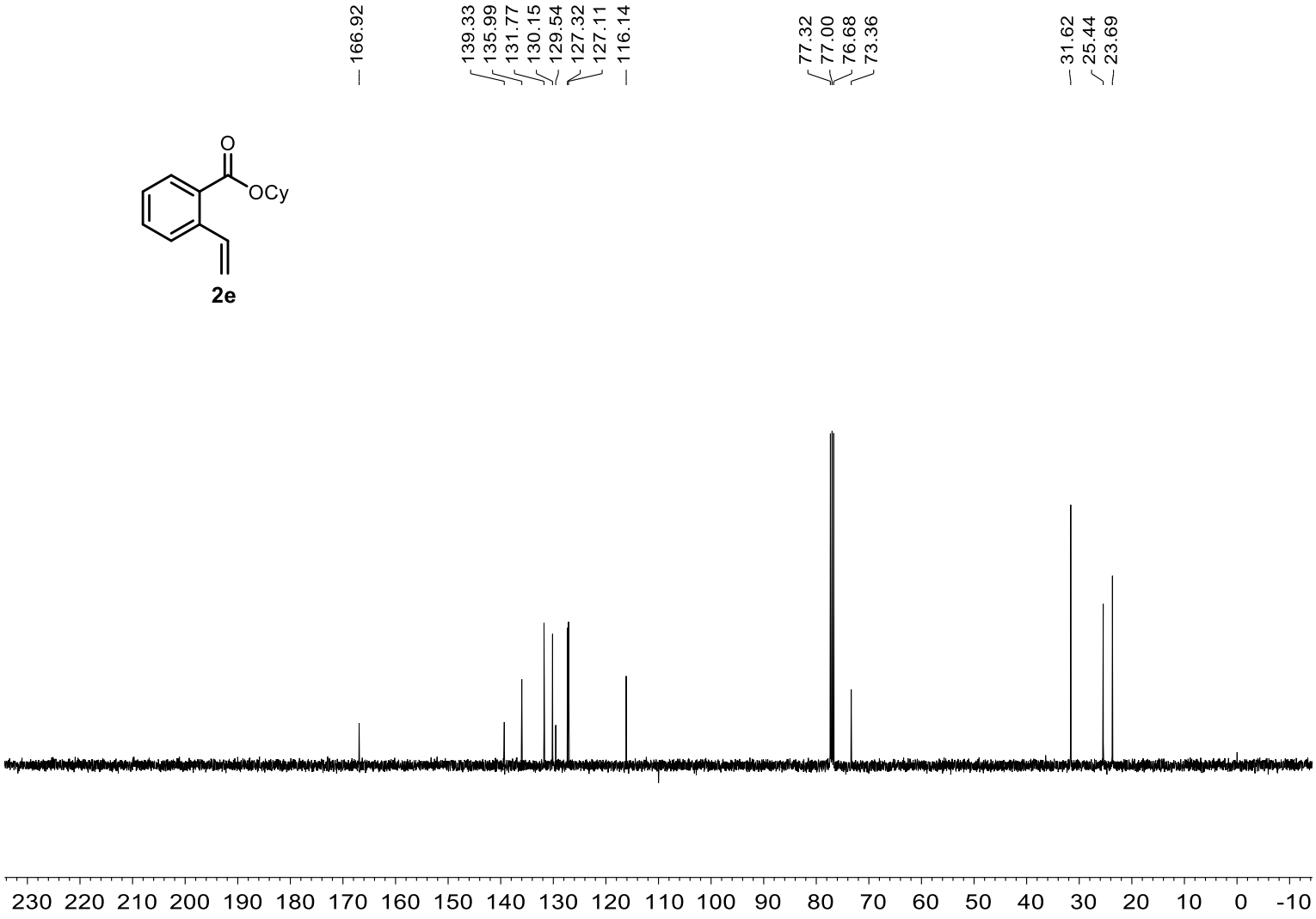
^{1}H NMR spectrum of compound 2d



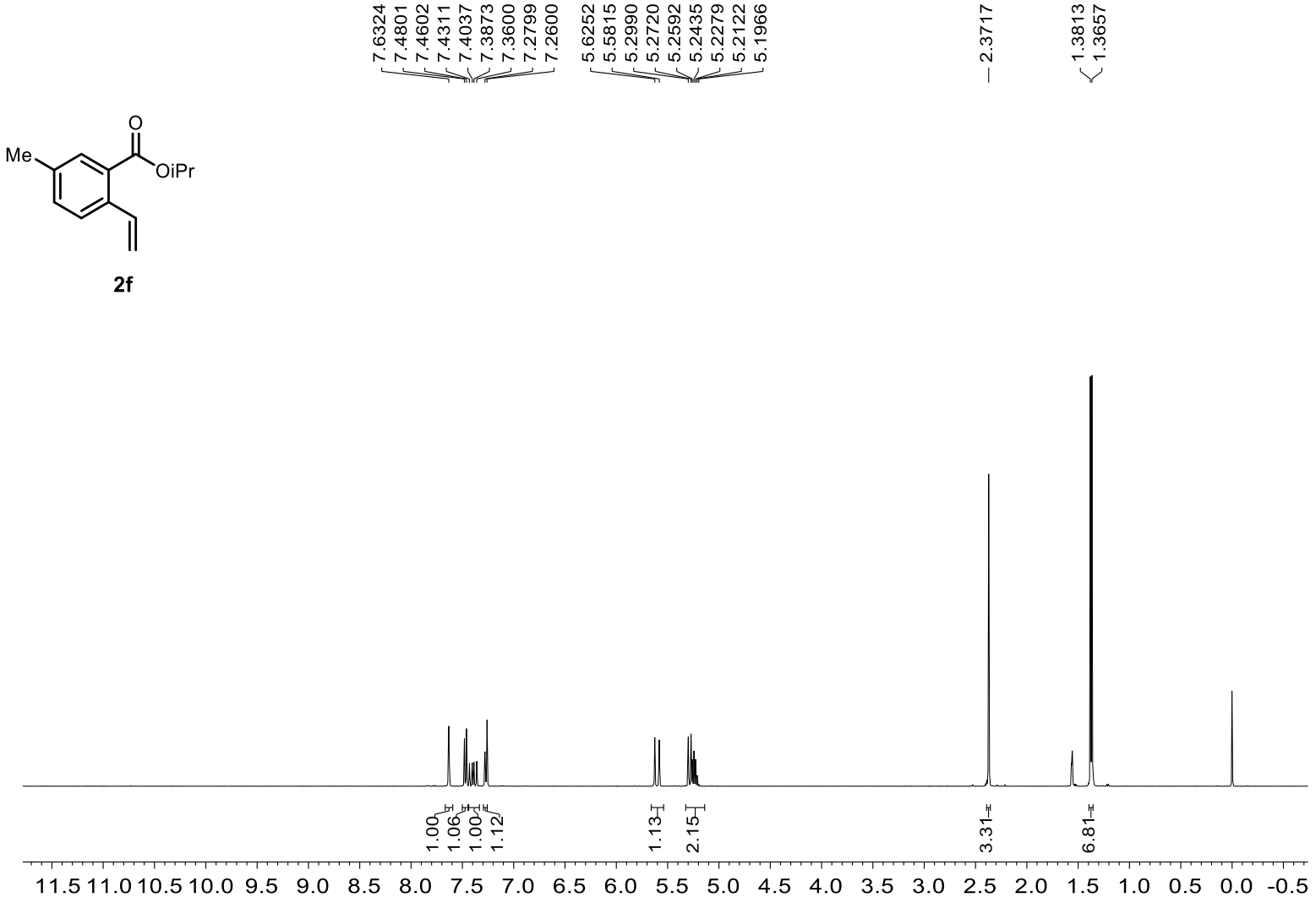
^{13}C NMR spectrum of compound 2d



^{1}H NMR spectrum of compound 2e

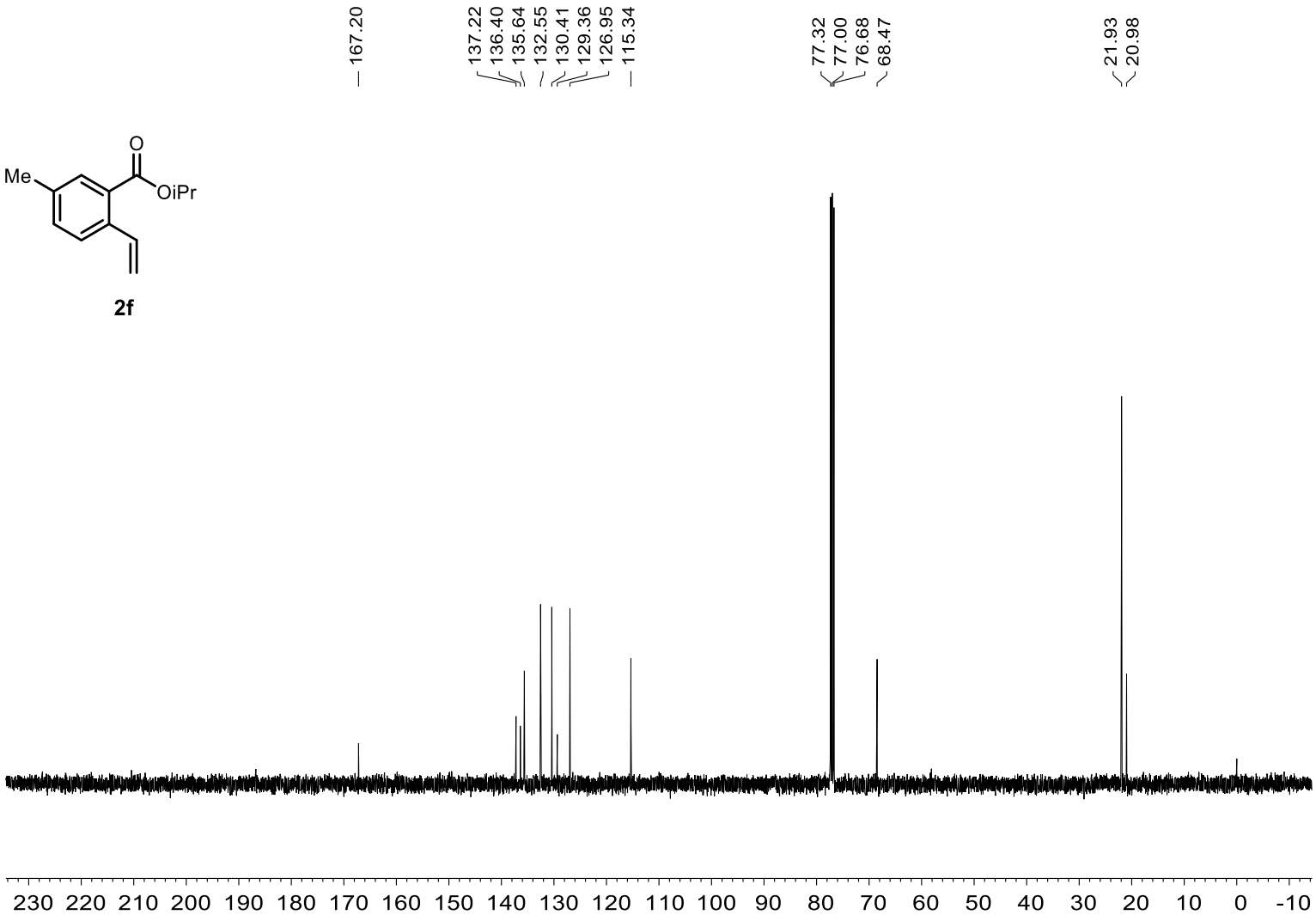


^{13}C NMR spectrum of compound 2e

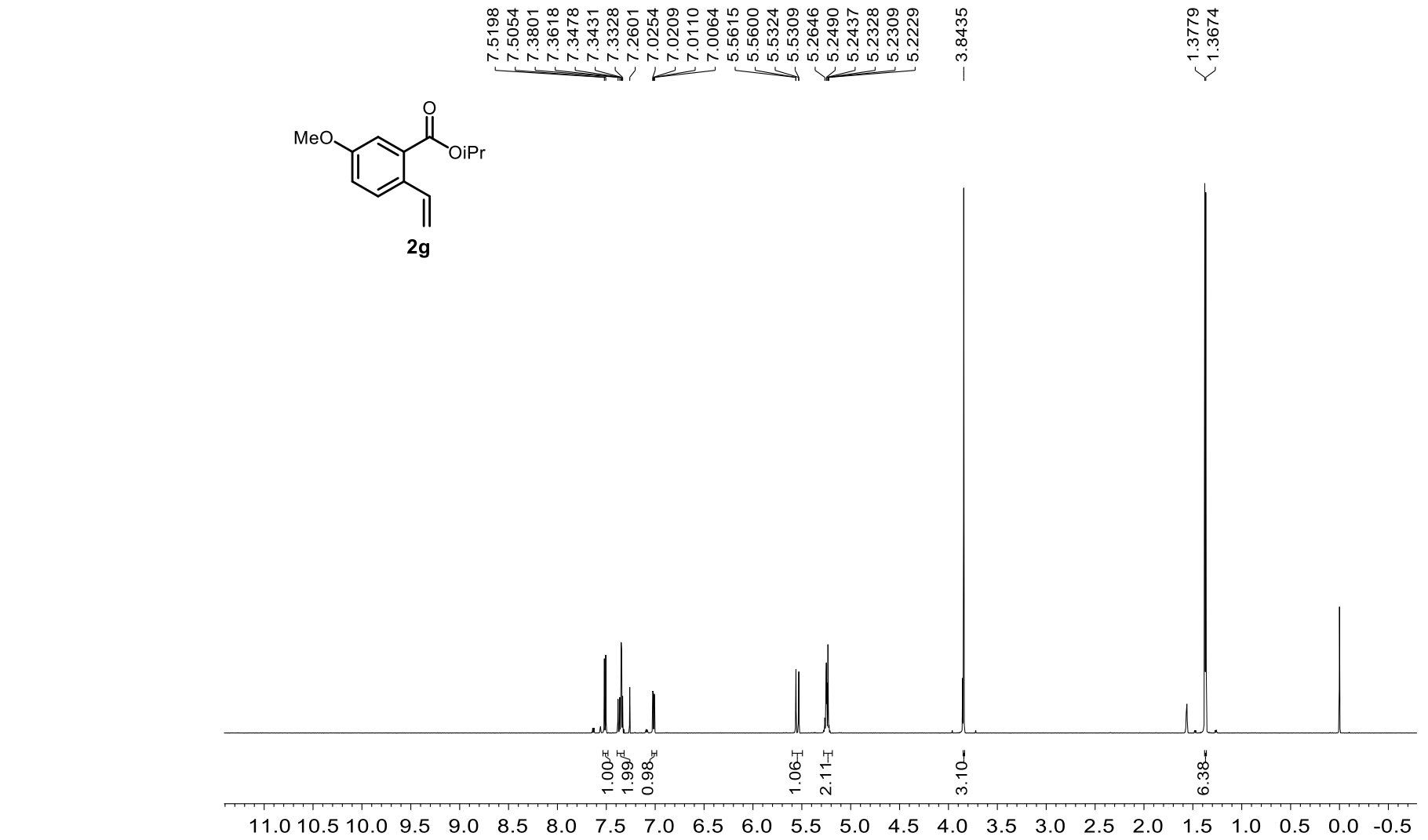


2f

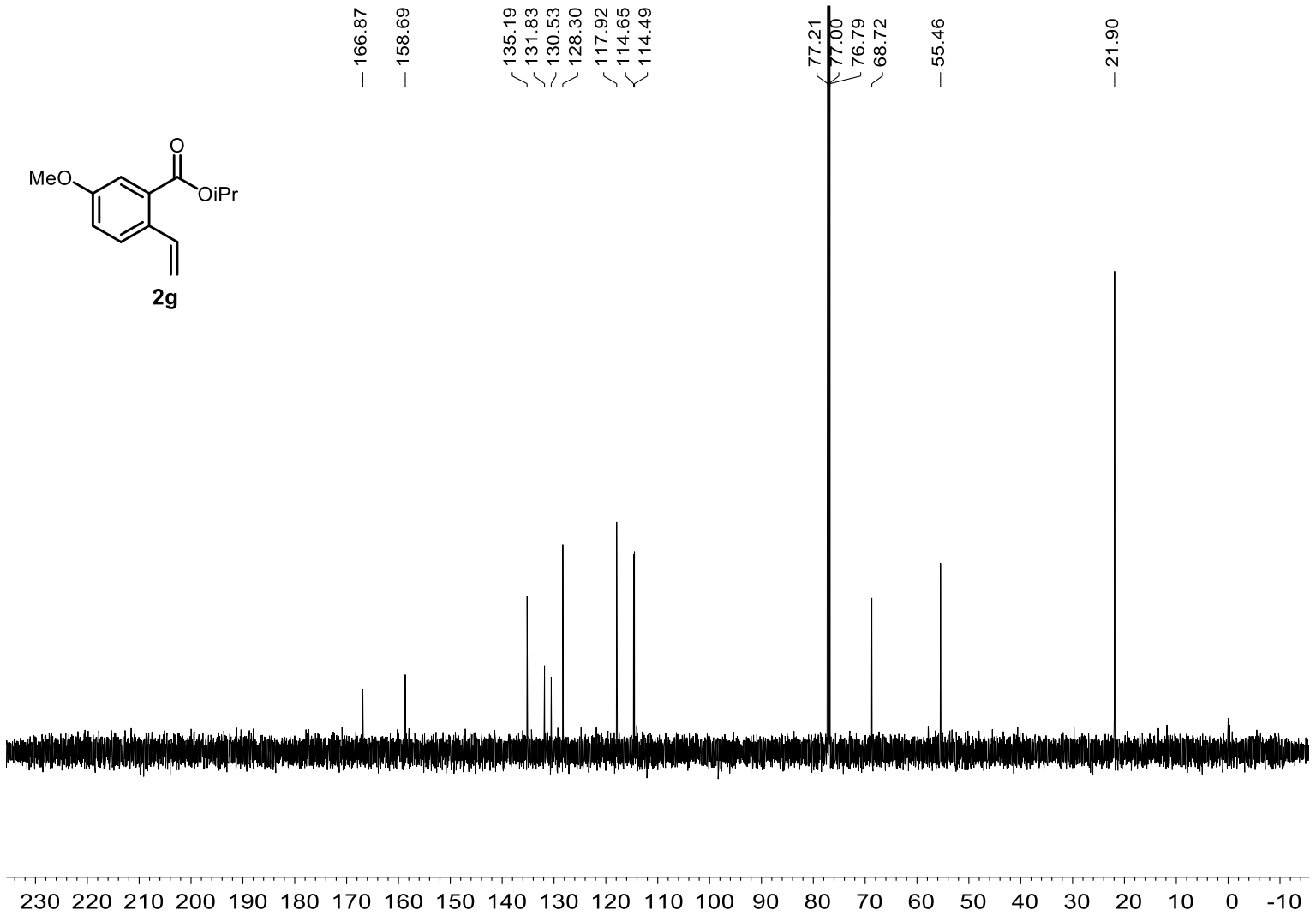
^{1}H NMR spectrum of compound 2f



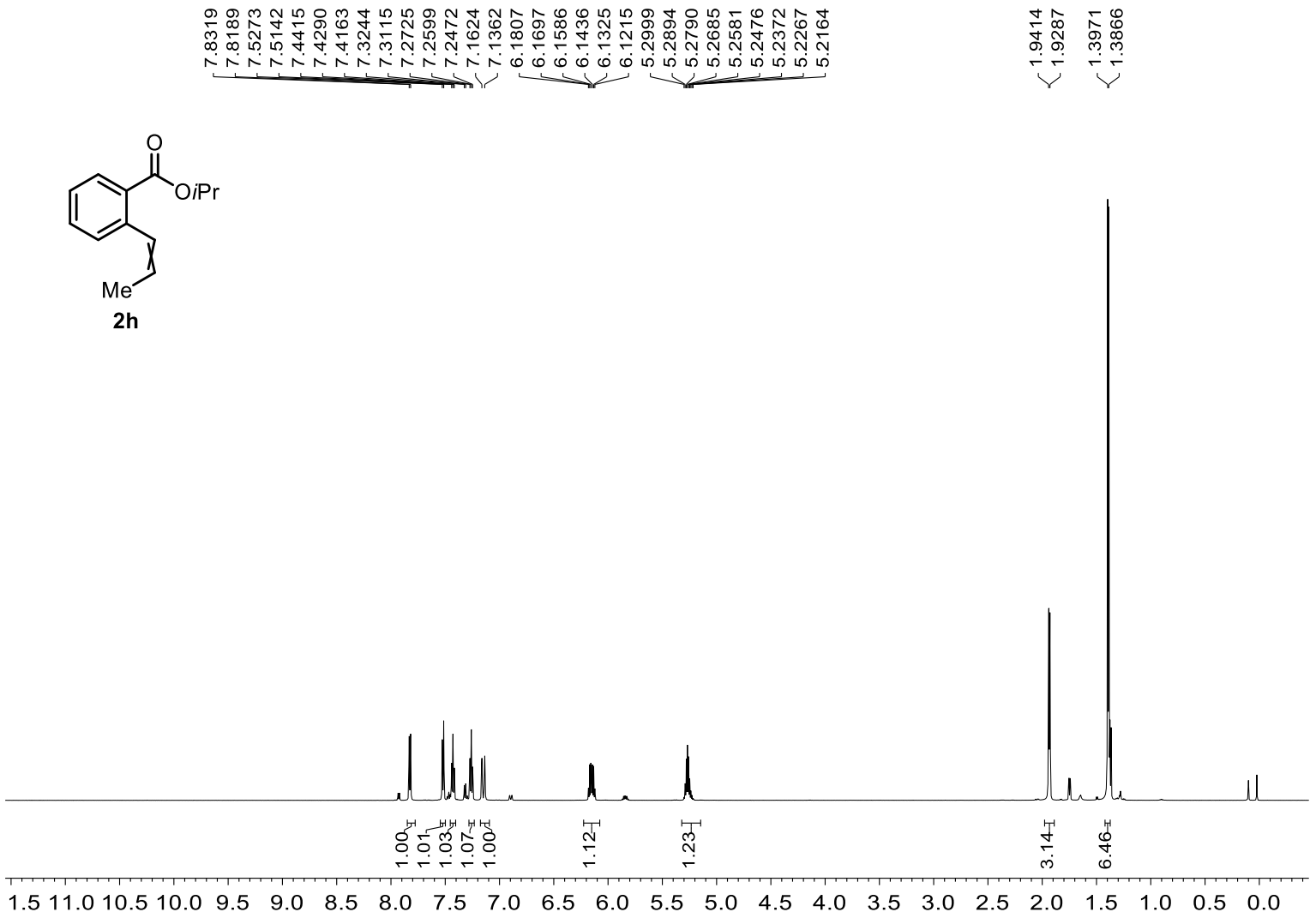
^{13}C NMR spectrum of compound 2f



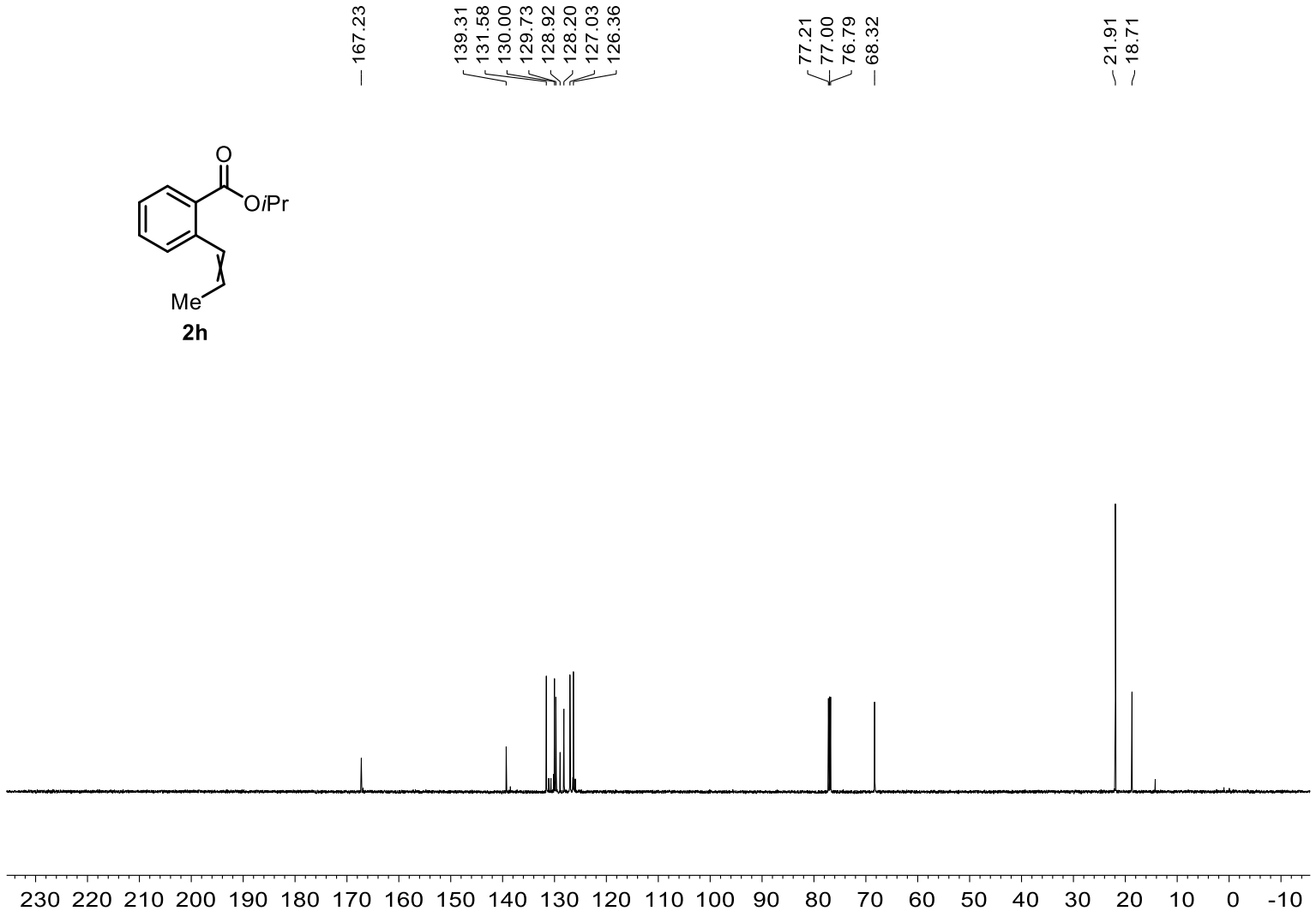
^{1}H NMR spectrum of compound 2g



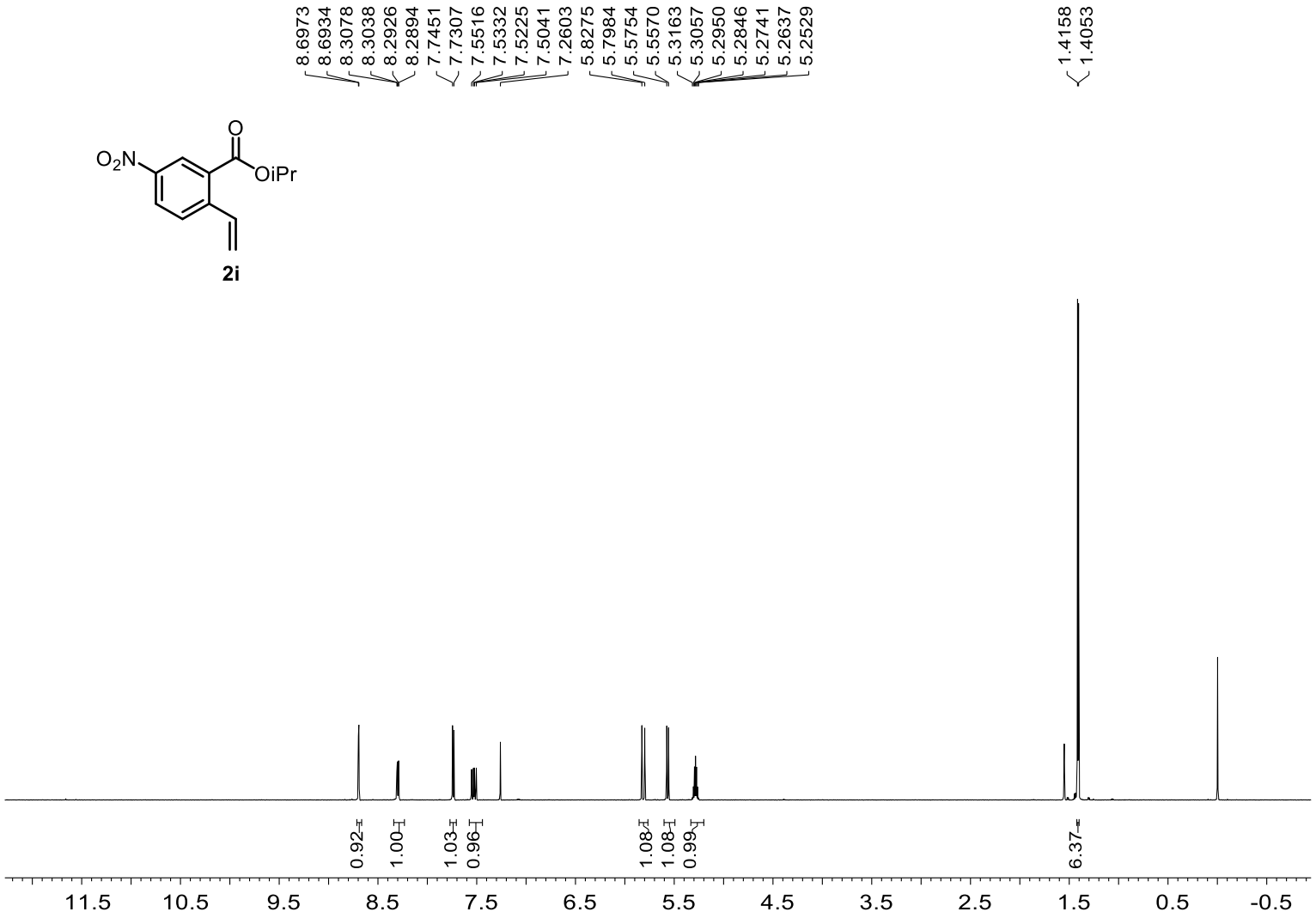
^{13}C NMR spectrum of compound 2g



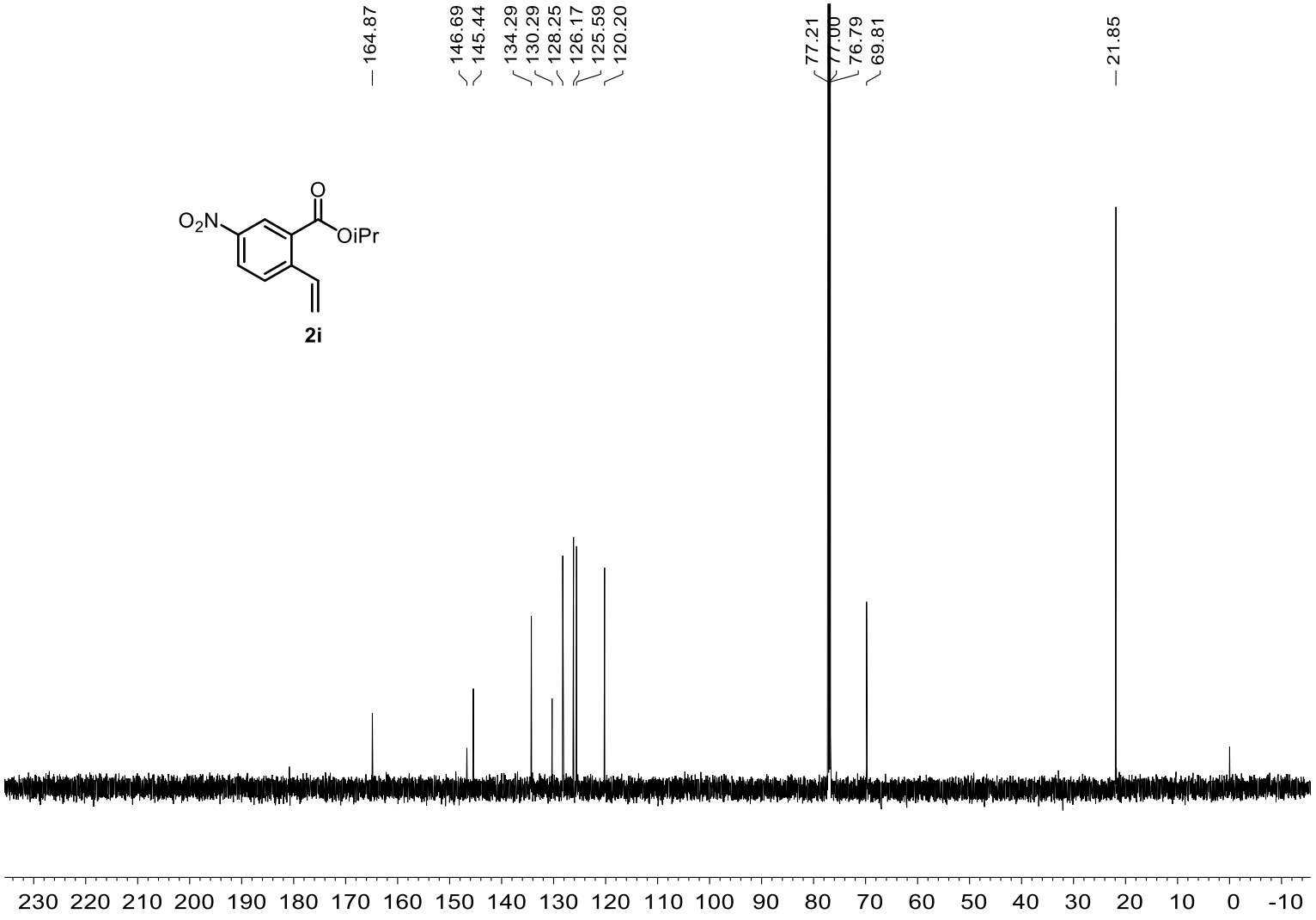
^{1}H NMR spectrum of compound 2h



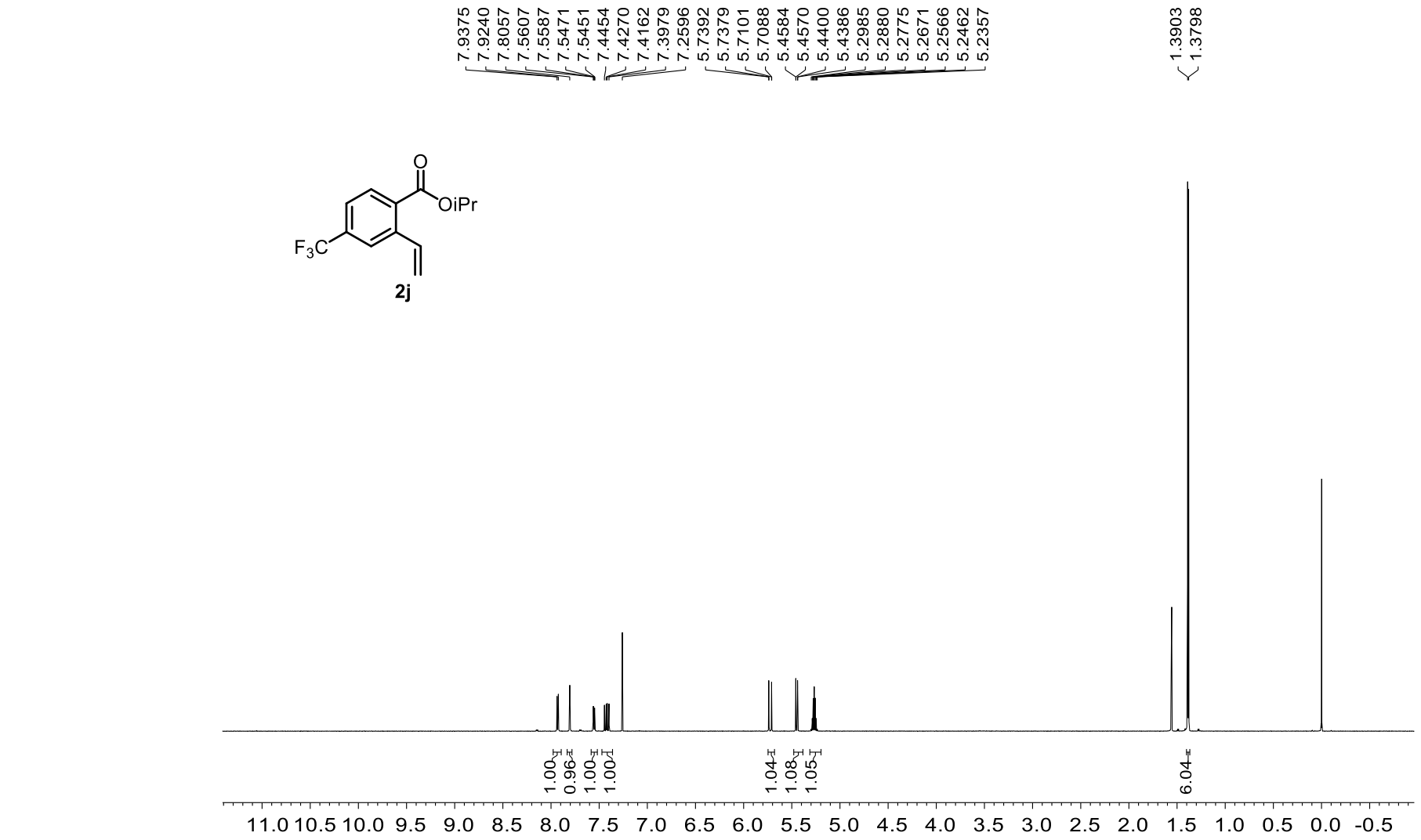
^{13}C NMR spectrum of compound 2h



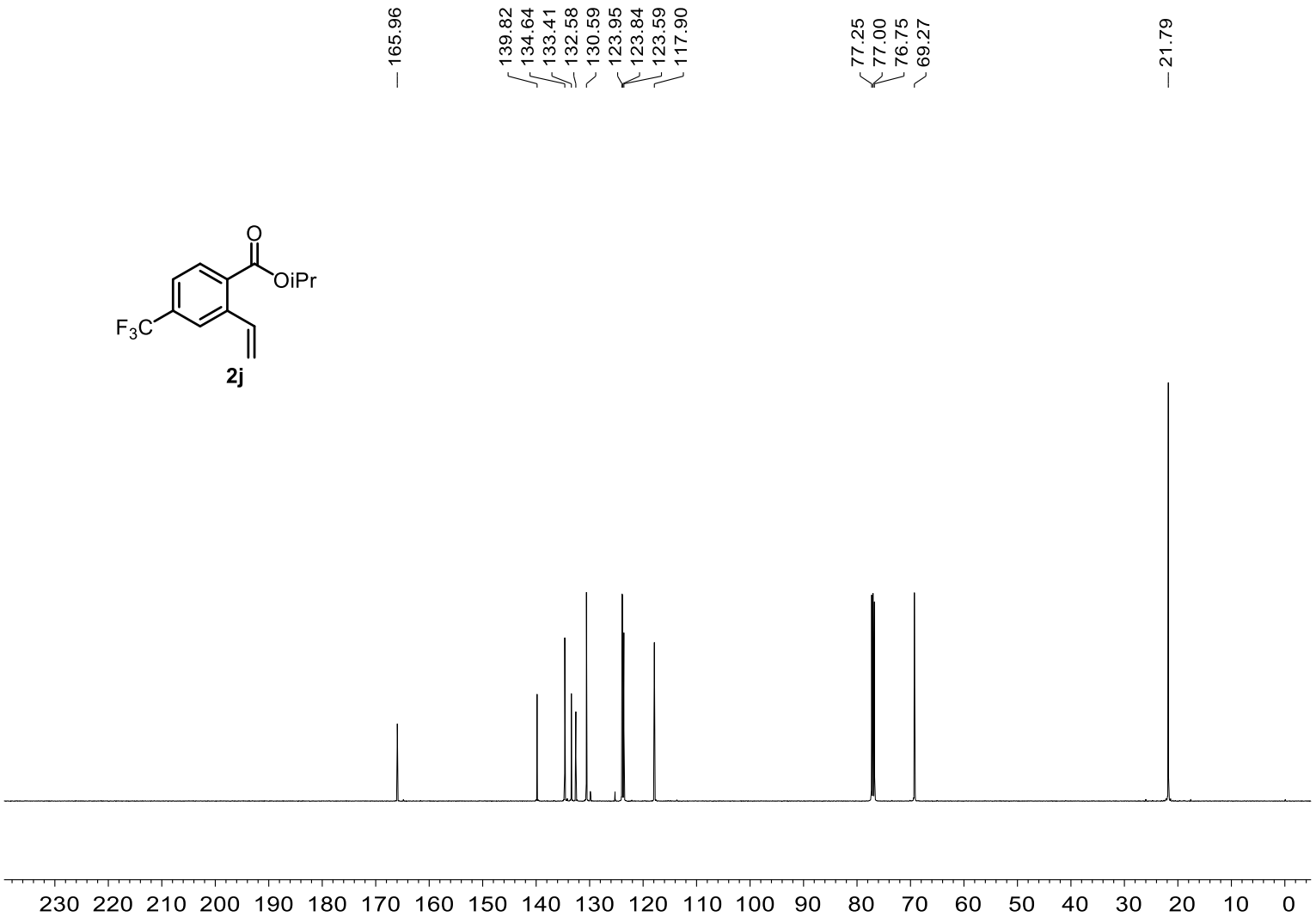
^{1}H NMR spectrum of compound 2i



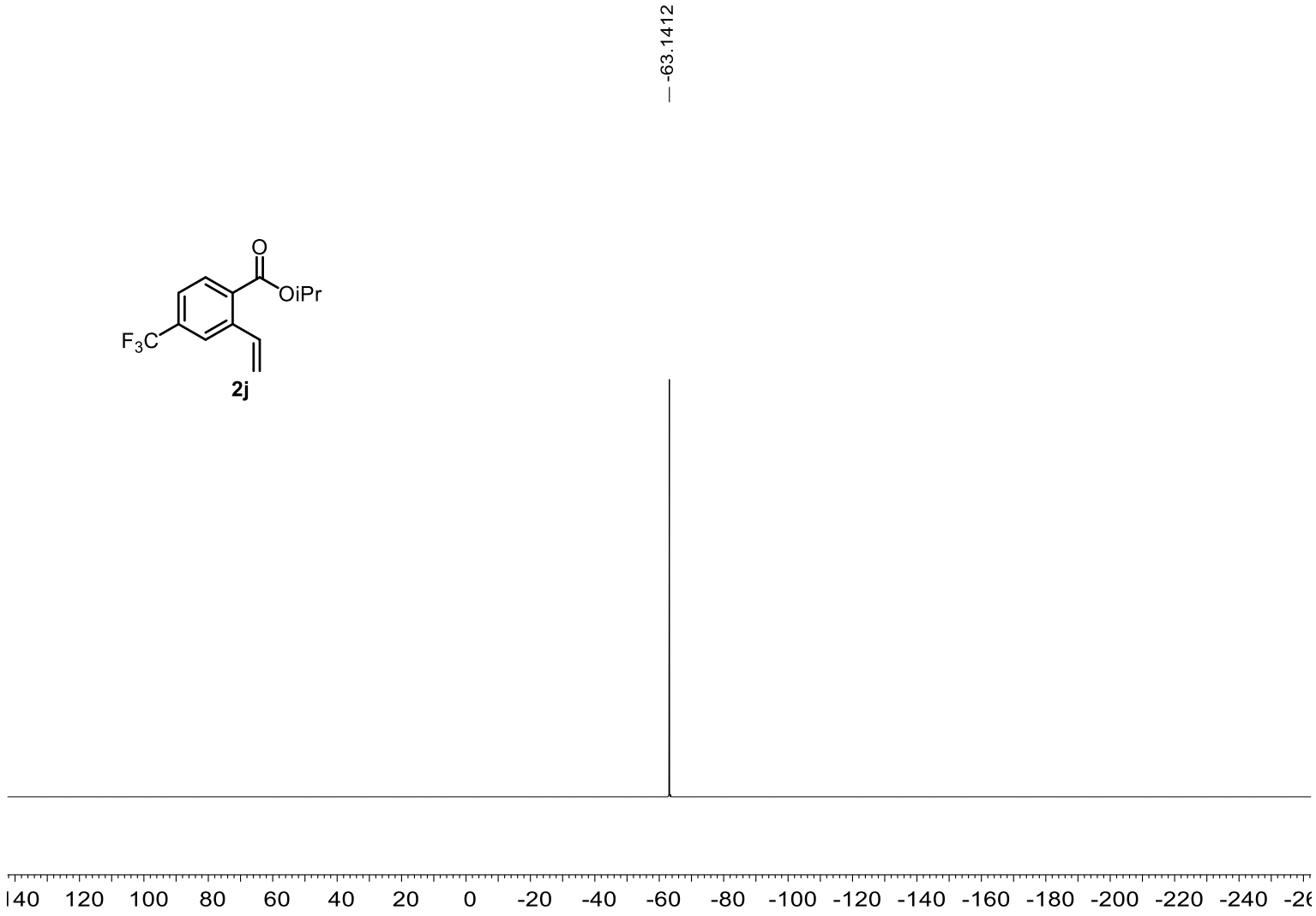
^{13}C NMR spectrum of compound 2i



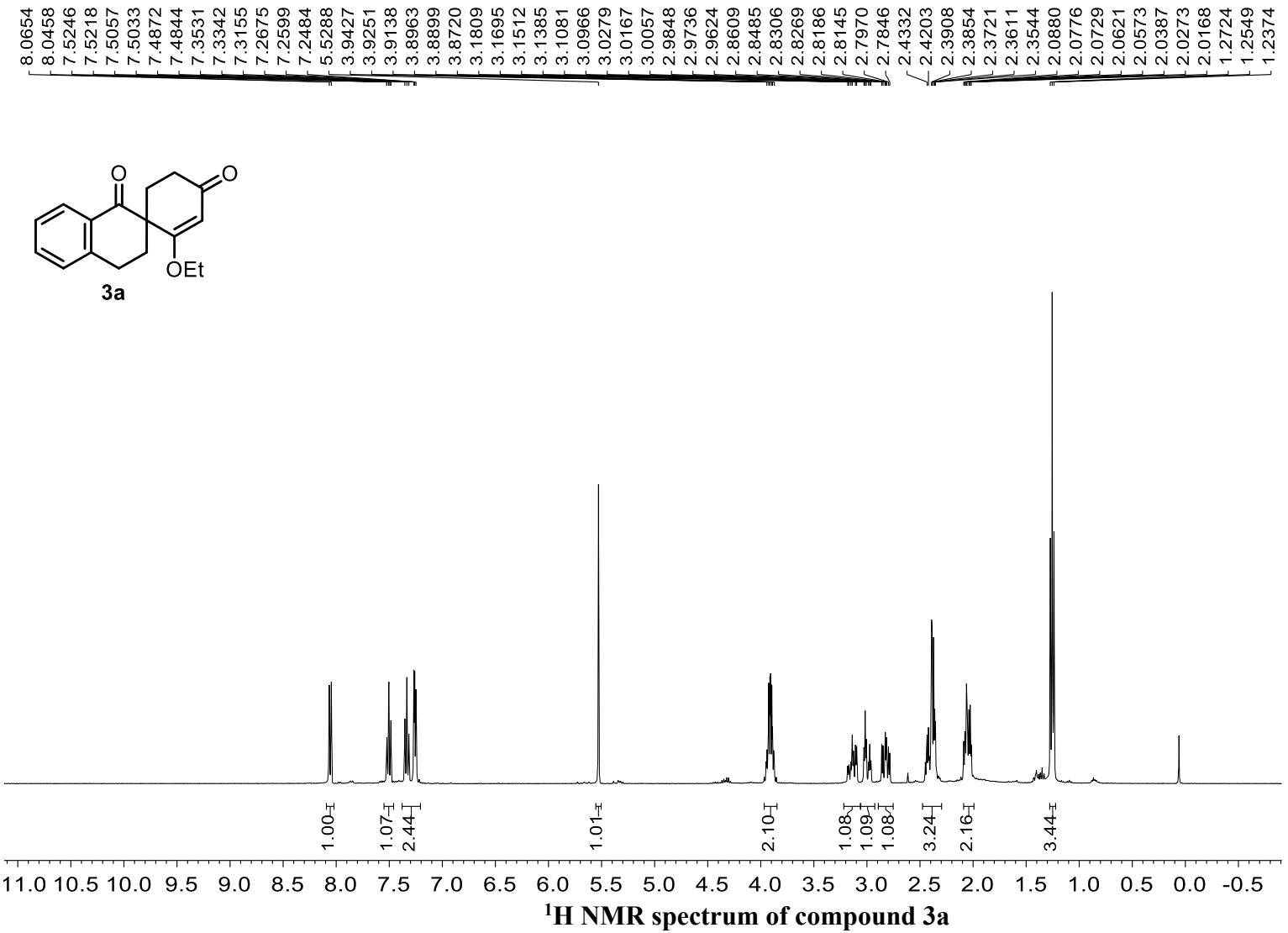
^{1}H NMR spectrum of compound 2j



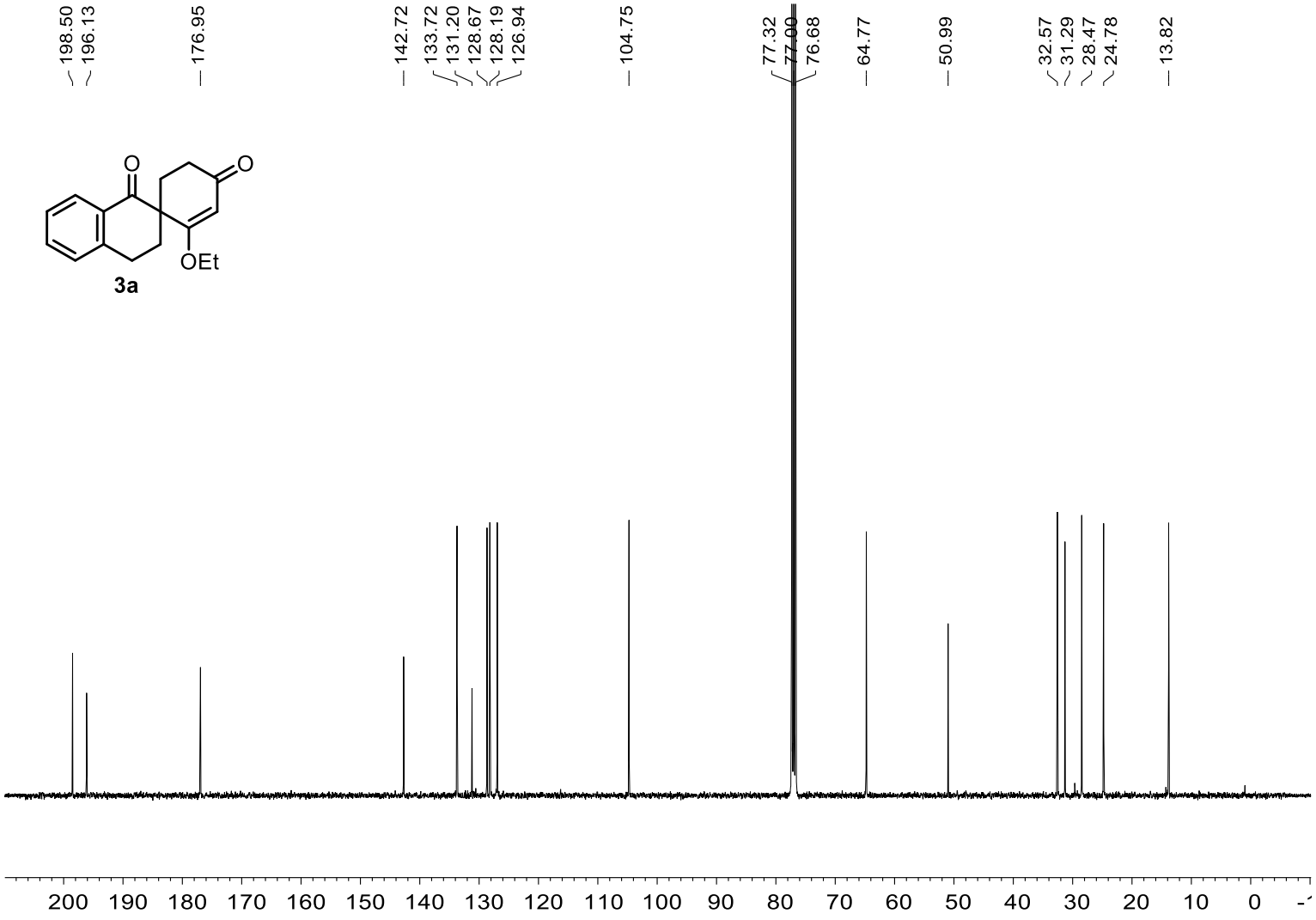
^{13}C NMR spectrum of compound 2j



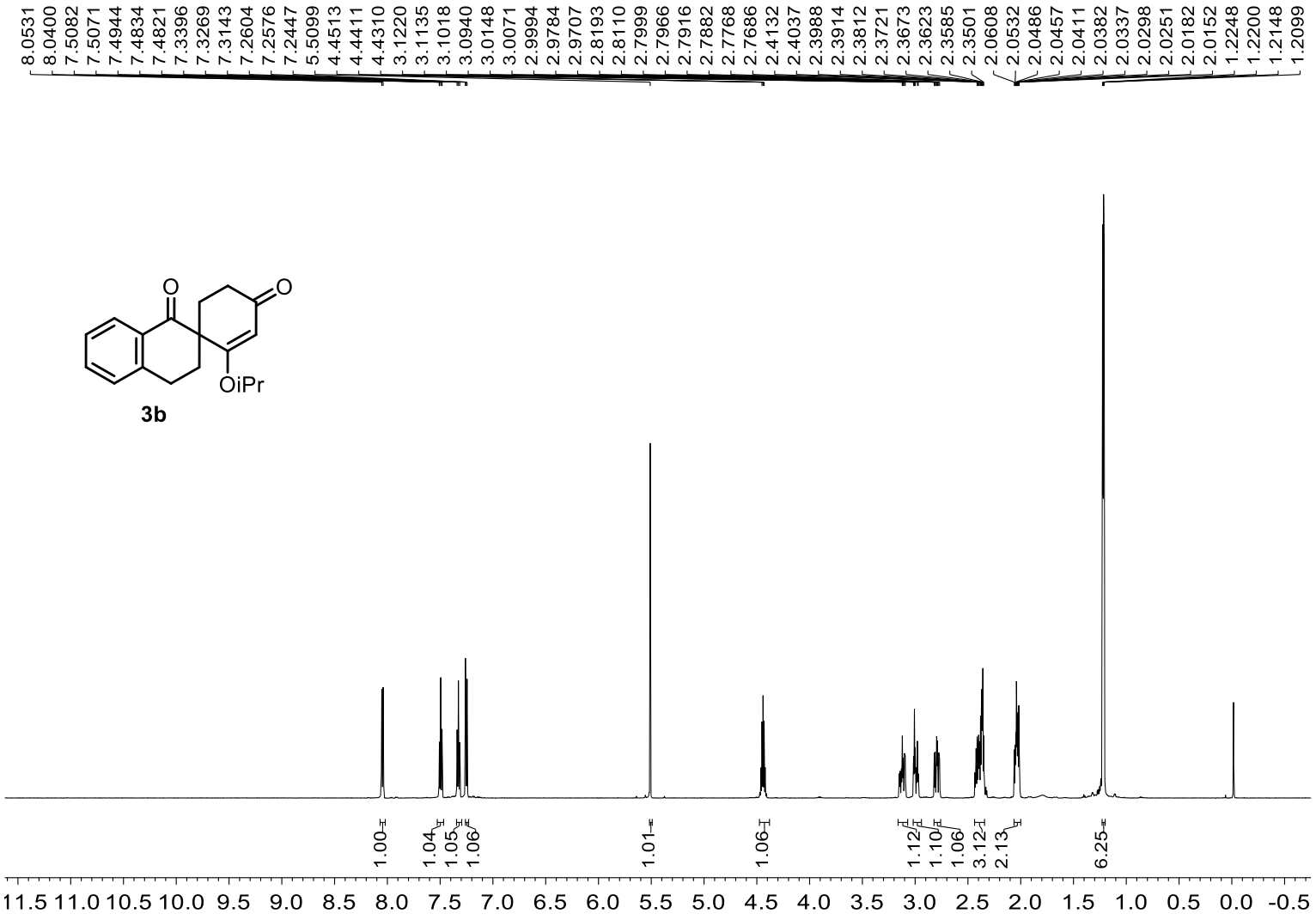
^{19}F NMR spectrum of compound 2j



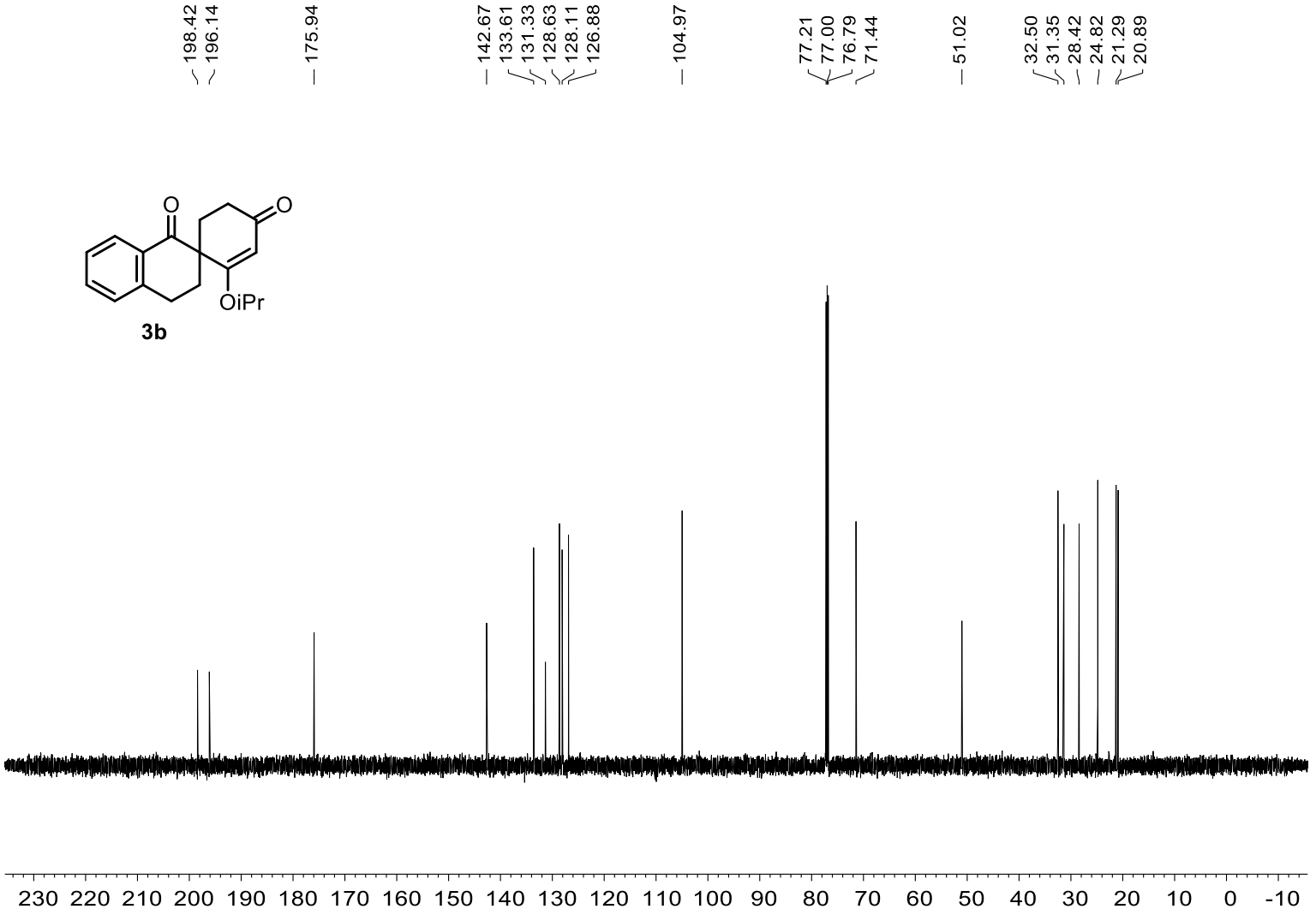
^{1}H NMR spectrum of compound 3a



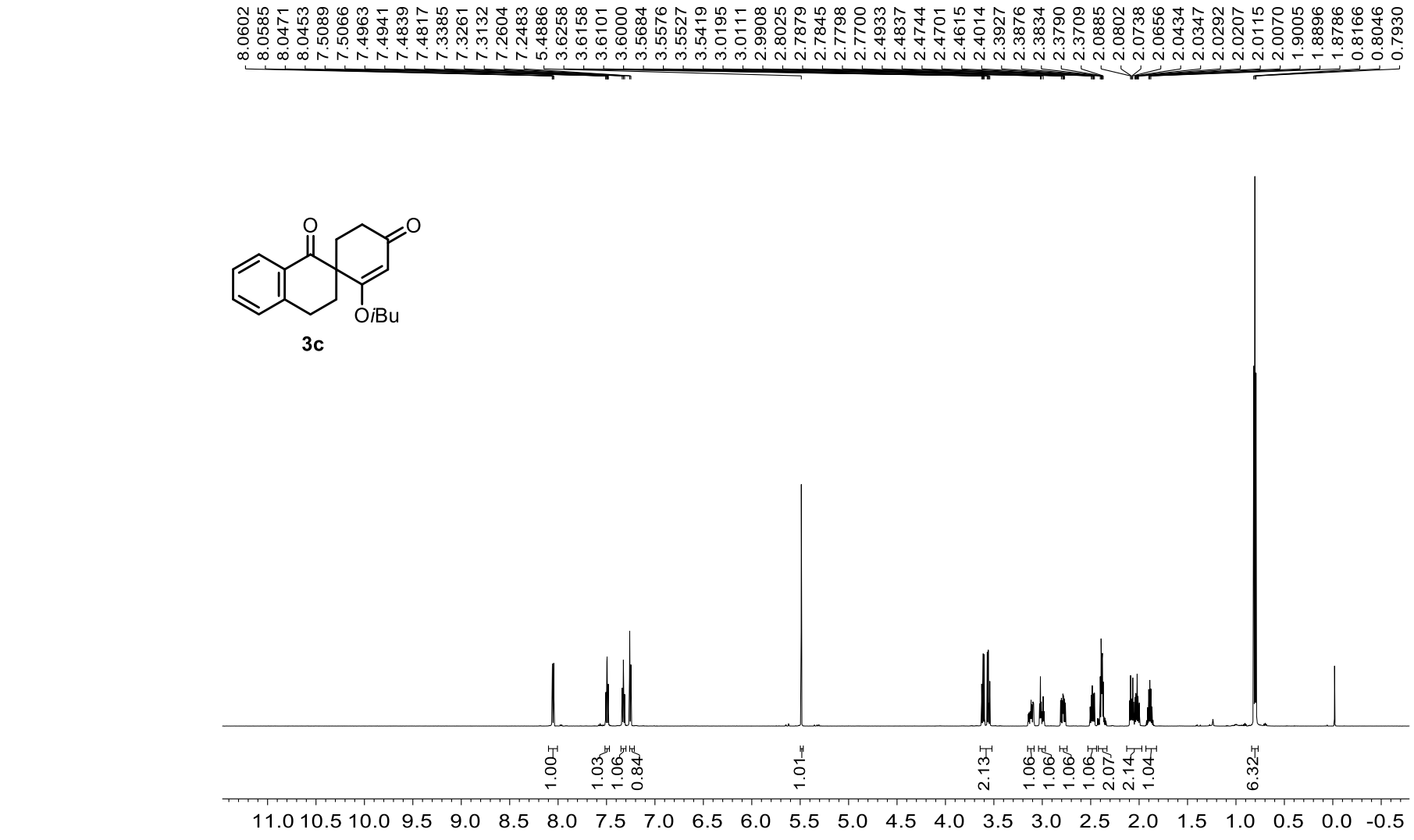
^{13}C NMR spectrum of compound 3a



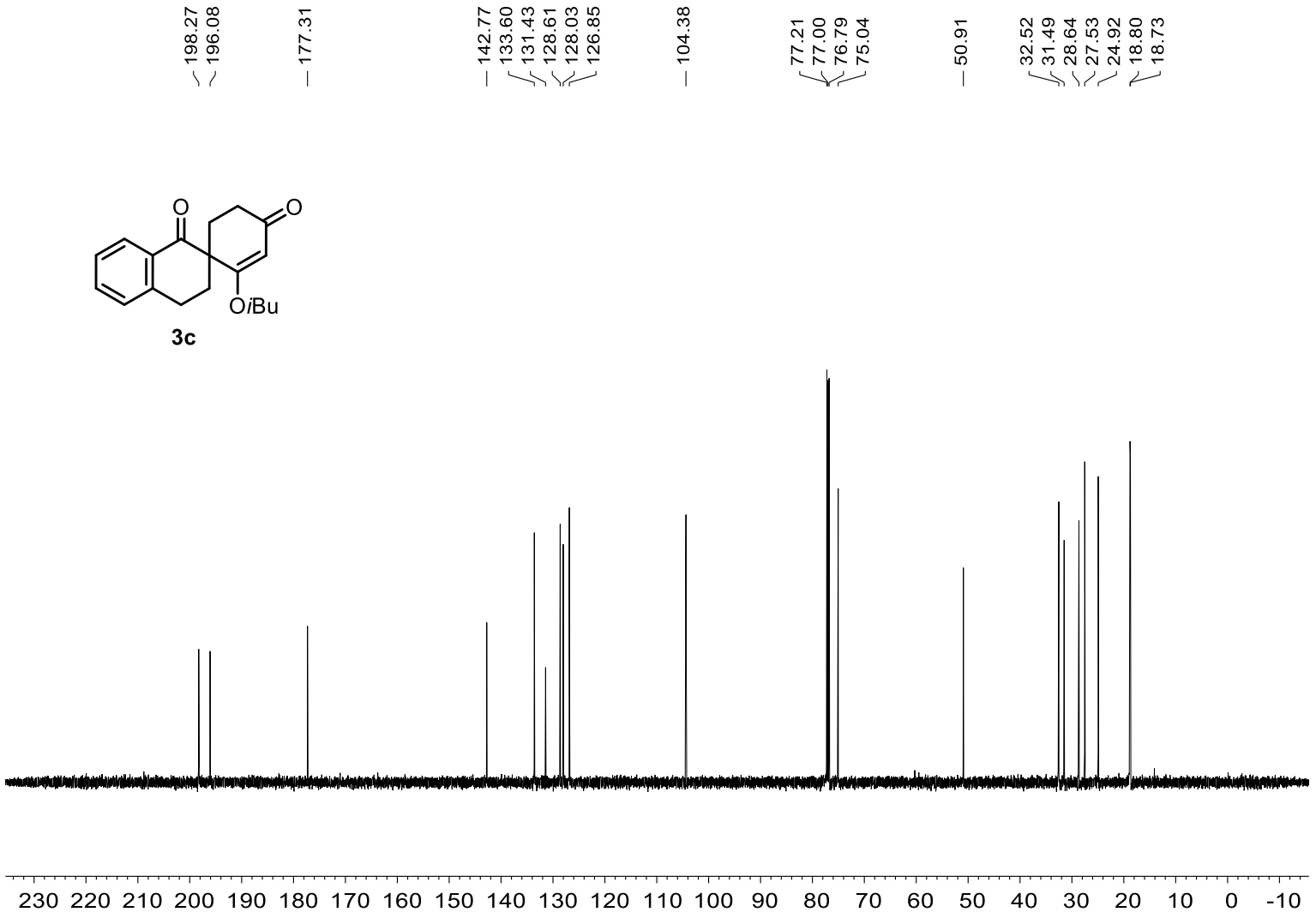
^{1}H NMR spectrum of compound 3b



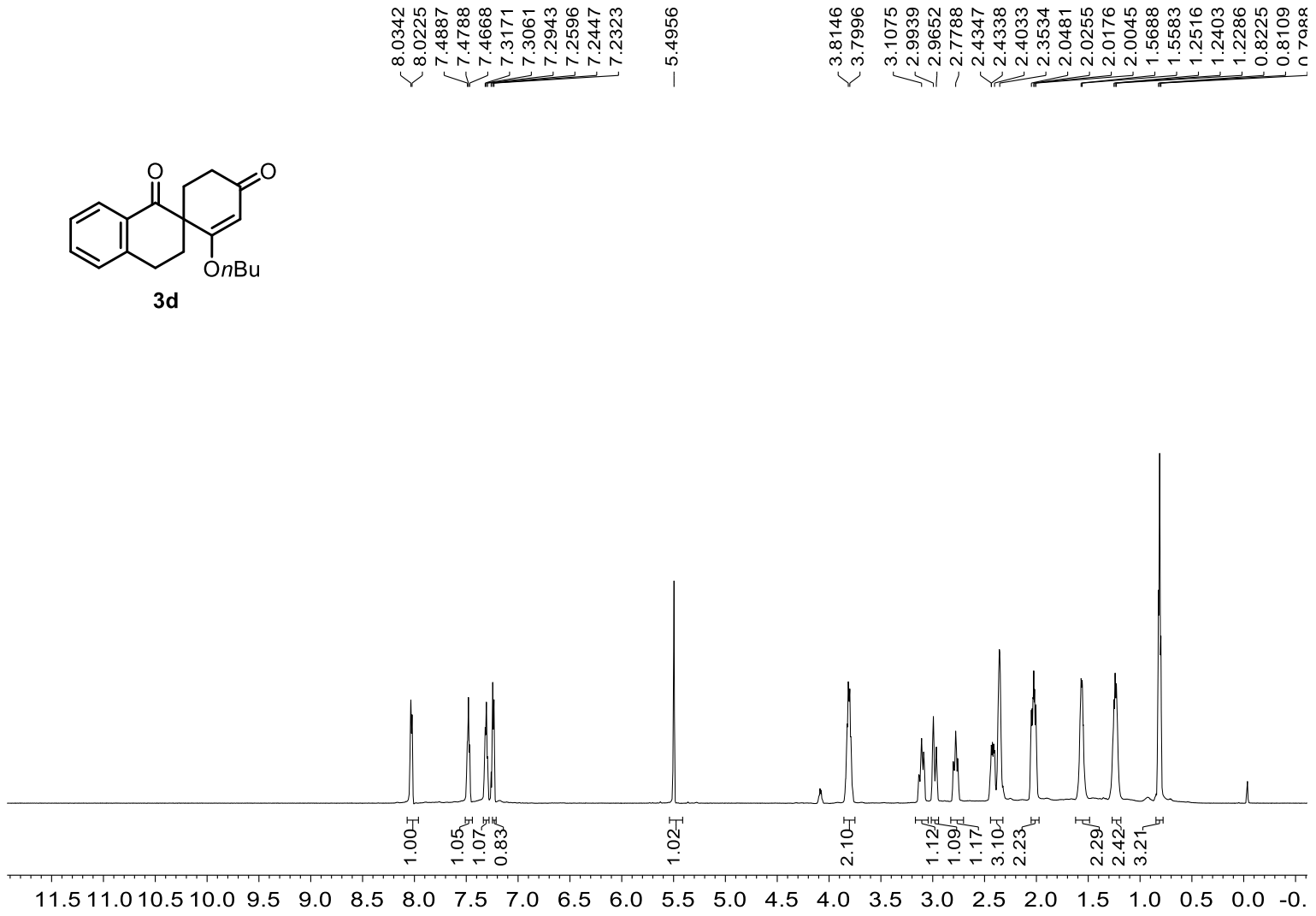
^{13}C NMR spectrum of compound 3b



^{1}H NMR spectrum of compound 3c

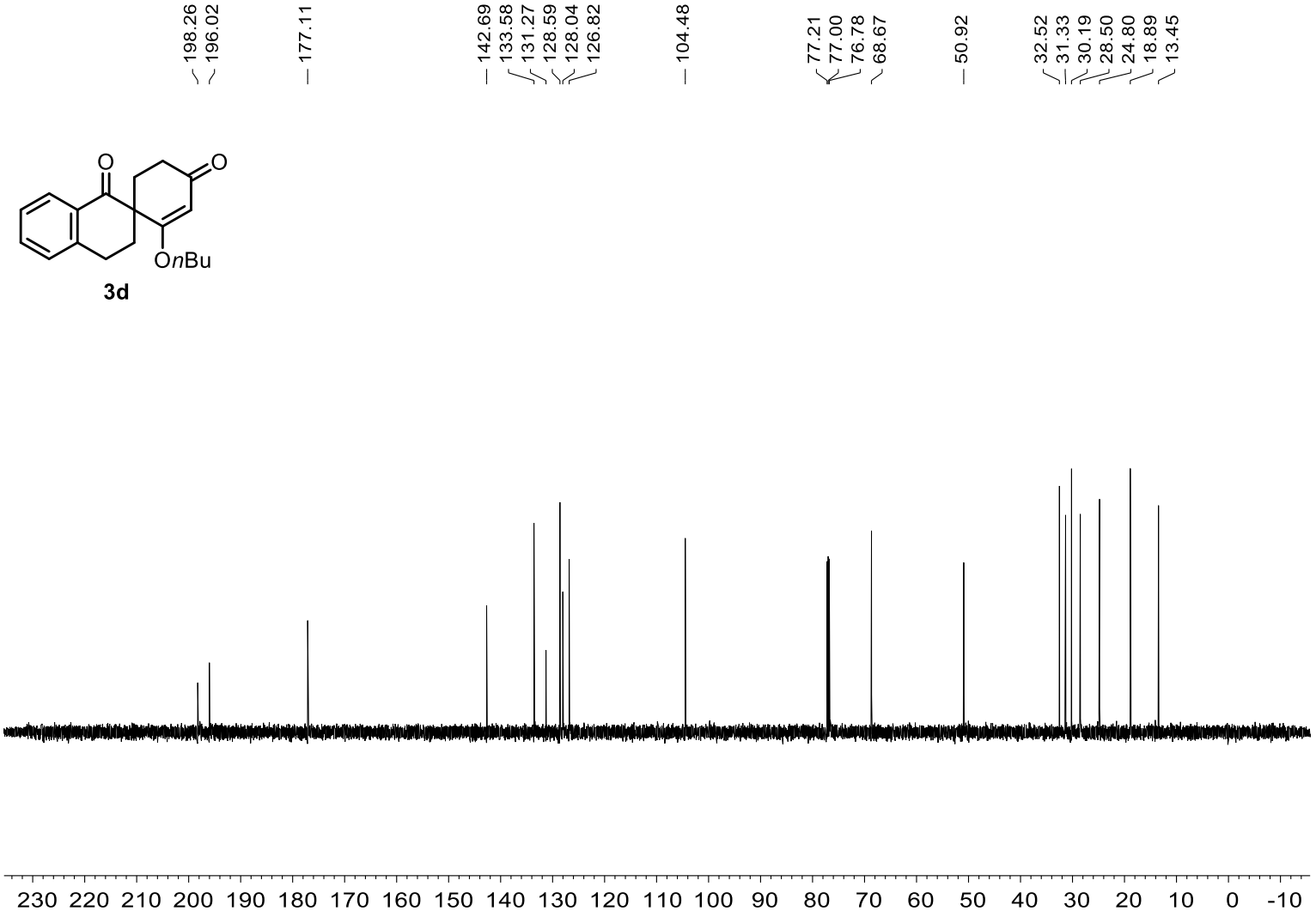


^{13}C NMR spectrum of compound 3c

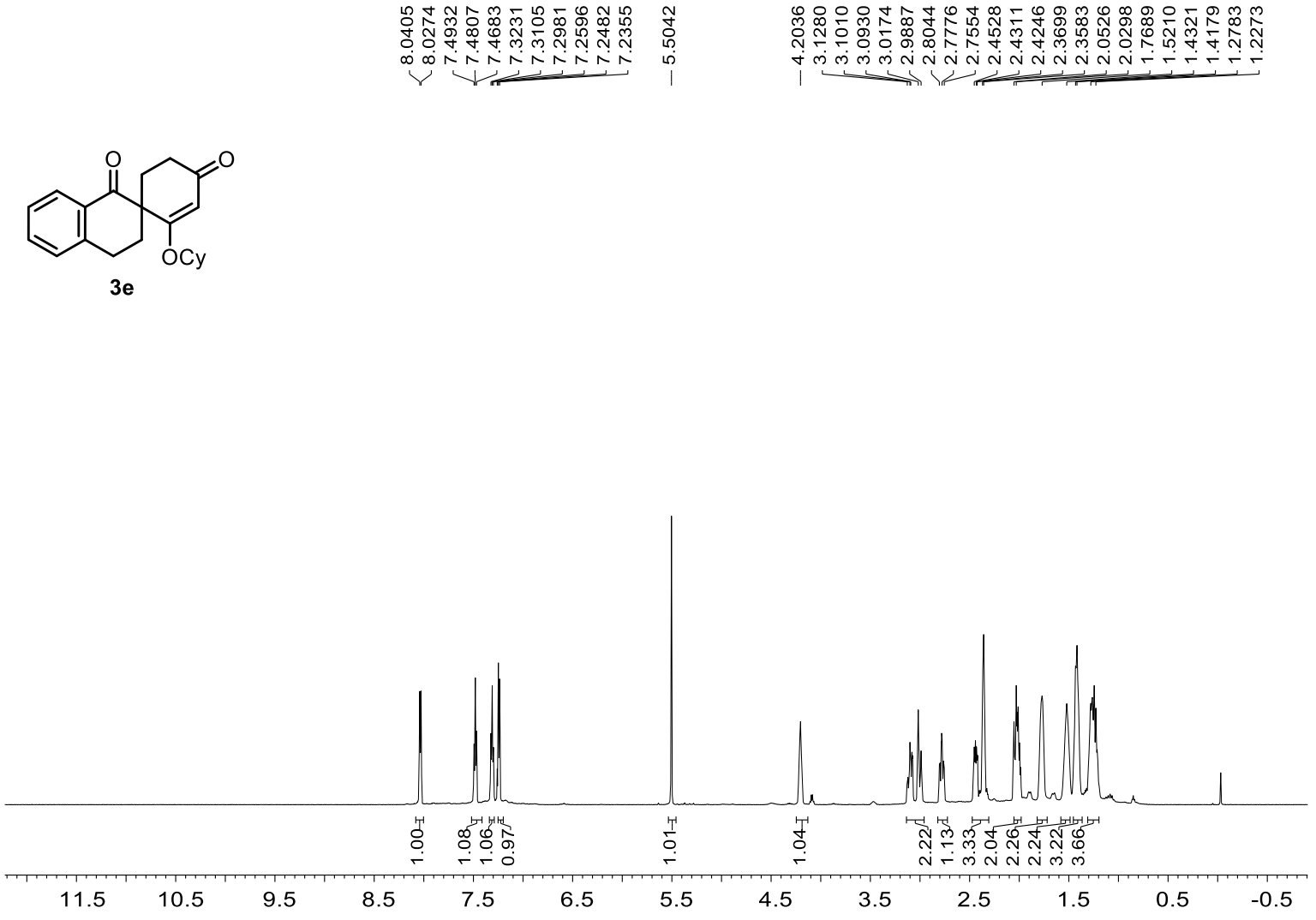


3d

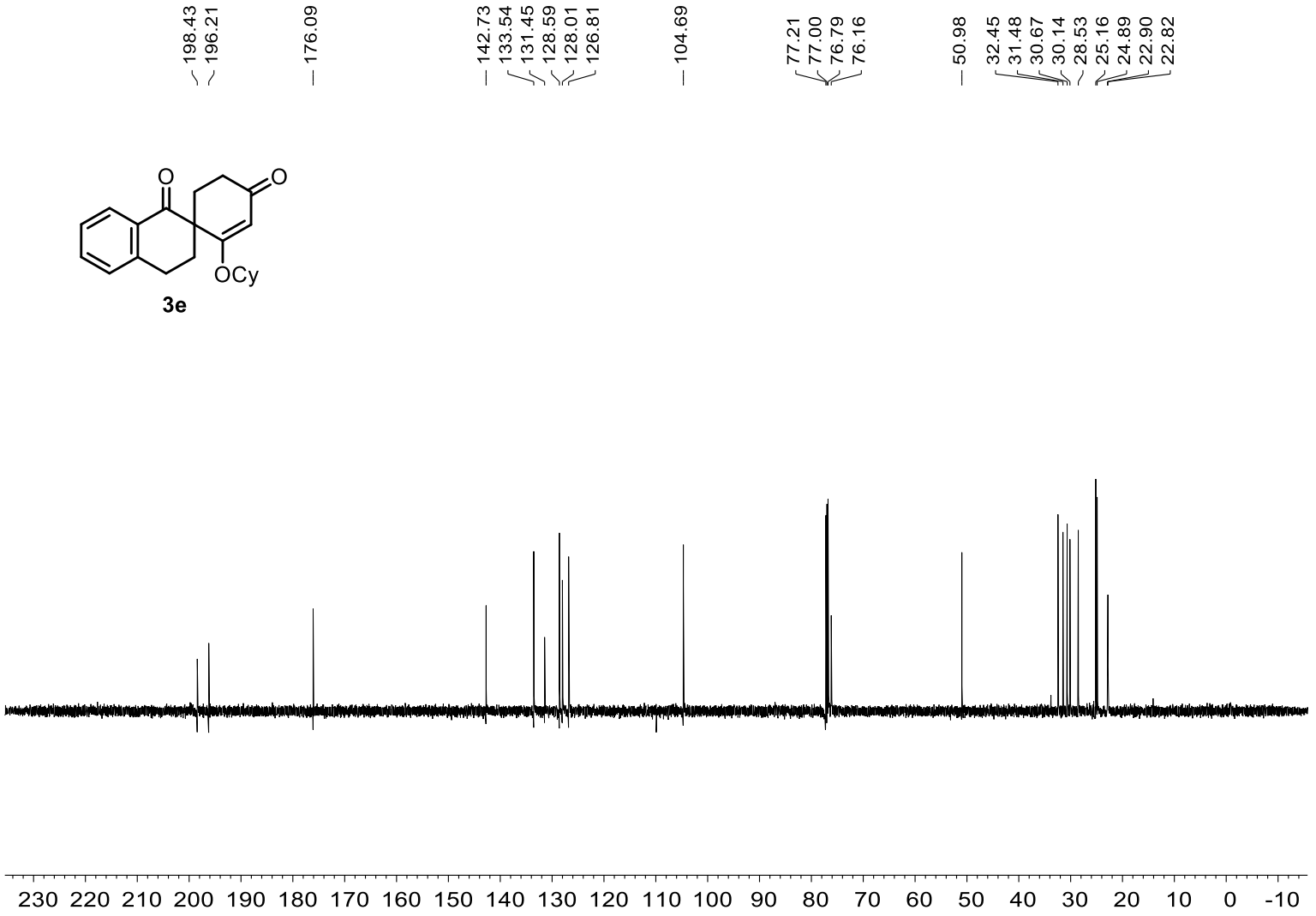
^{1}H NMR spectrum of compound 3d



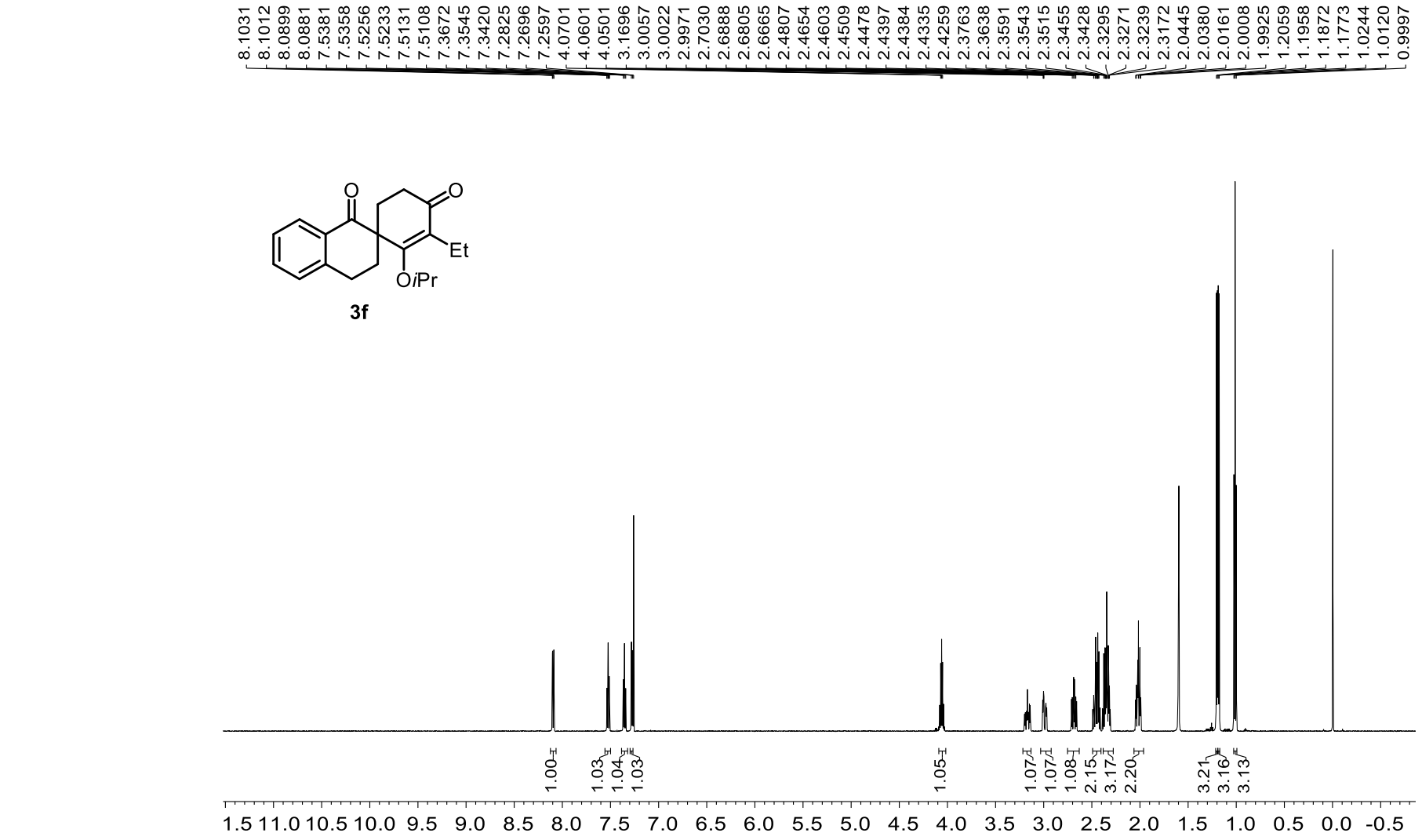
^{13}C NMR spectrum of compound 3d



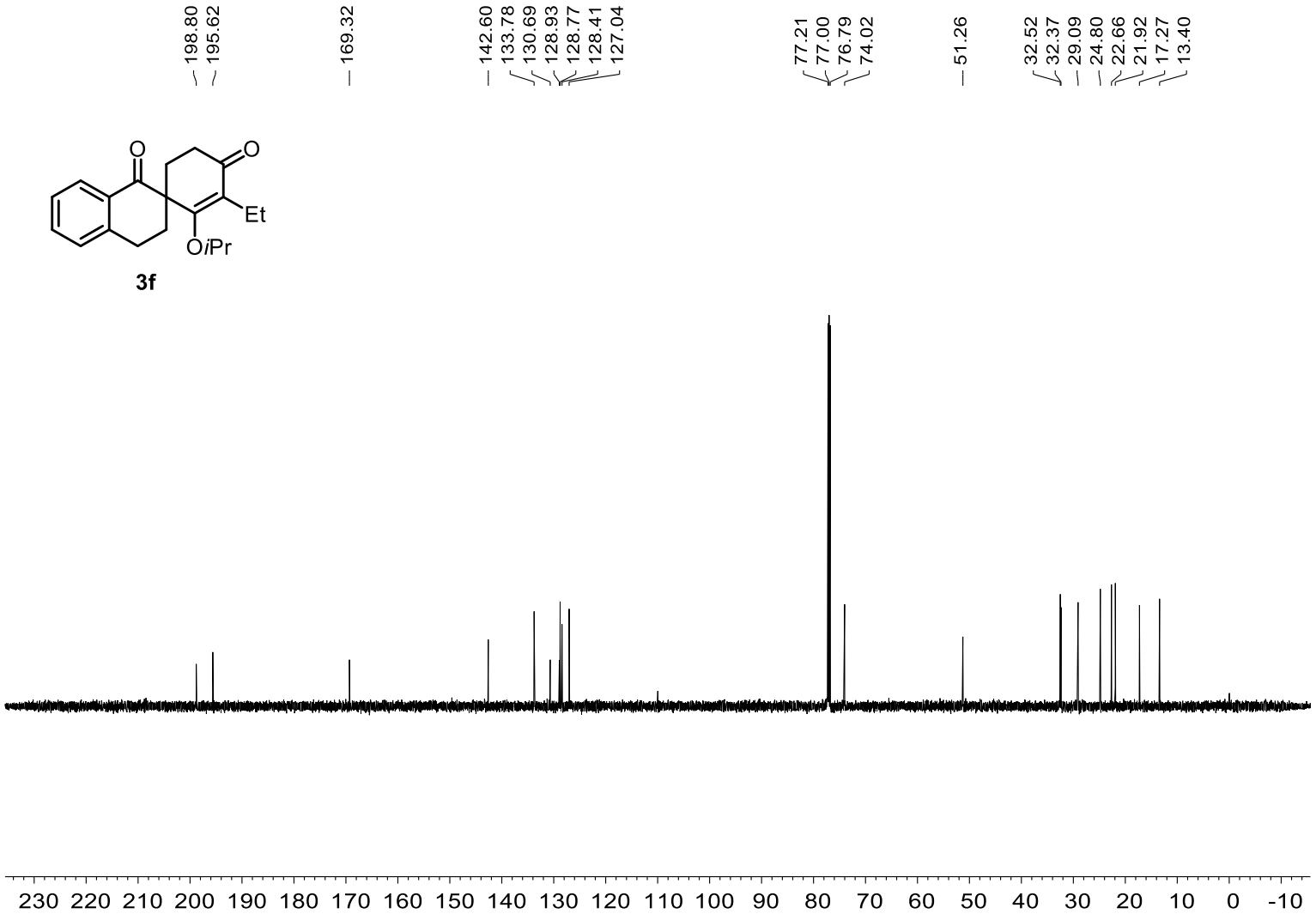
^{1}H NMR spectrum of compound 3e



^{13}C NMR spectrum of compound 3e

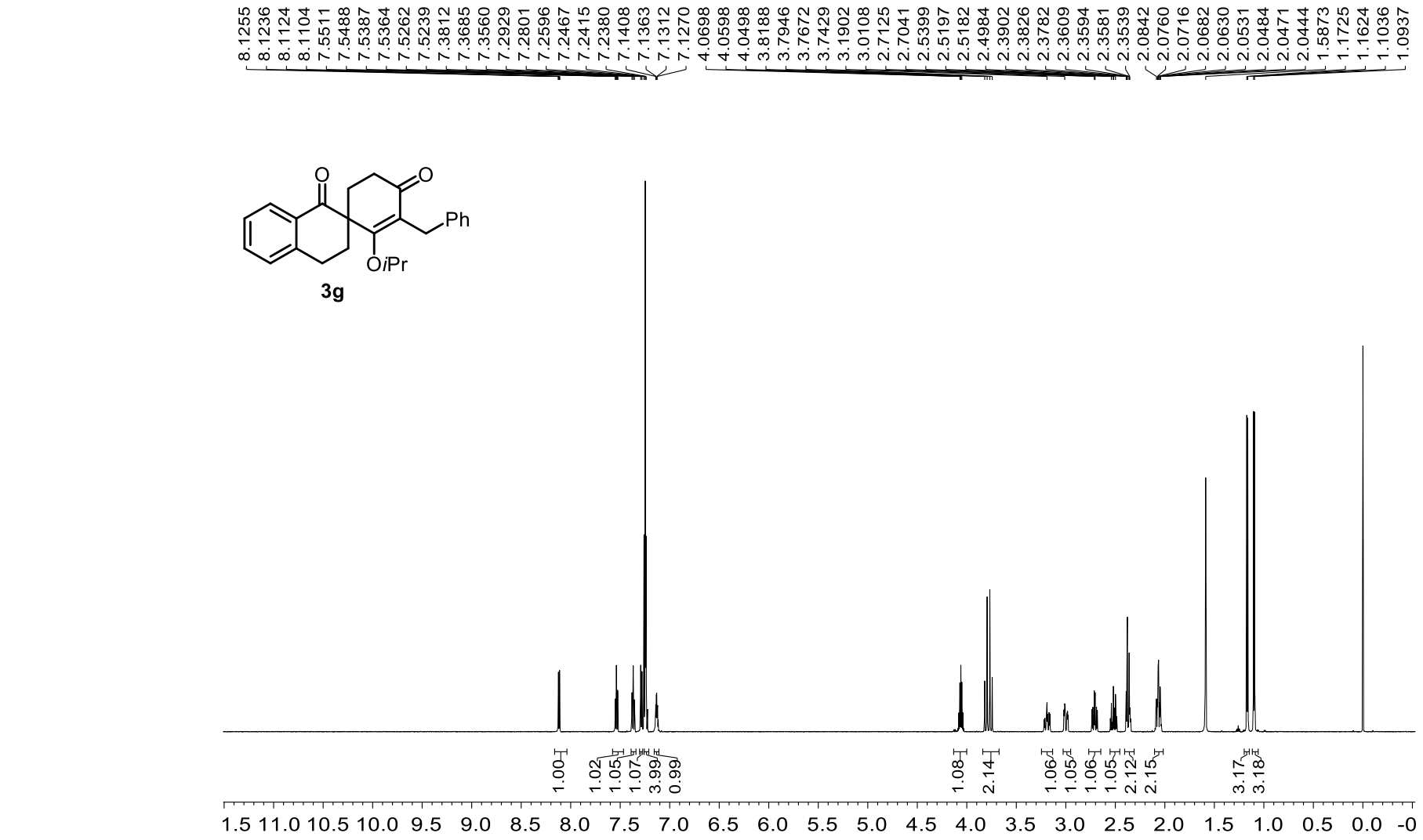


^{1}H NMR spectrum of compound 3f

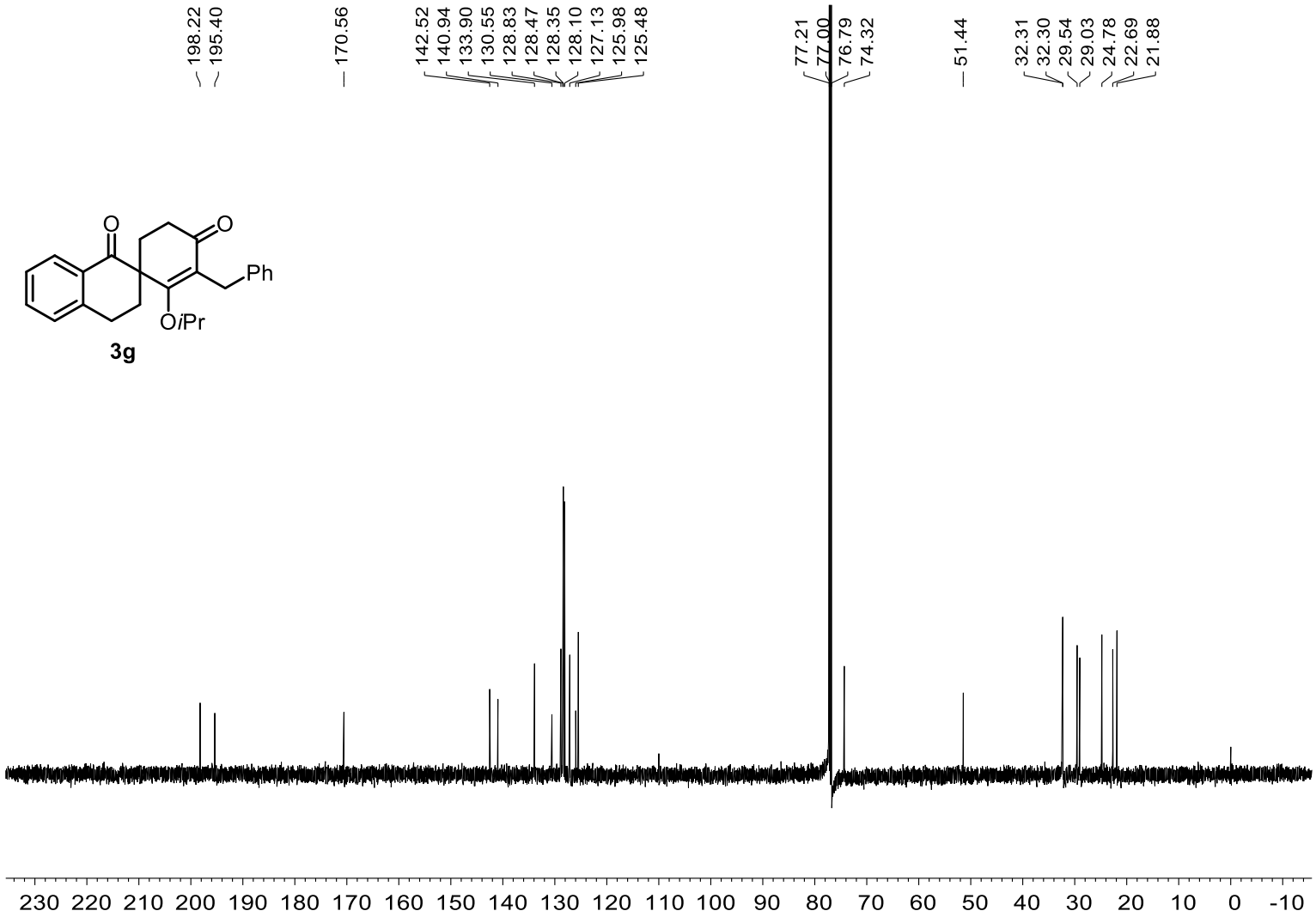


3f

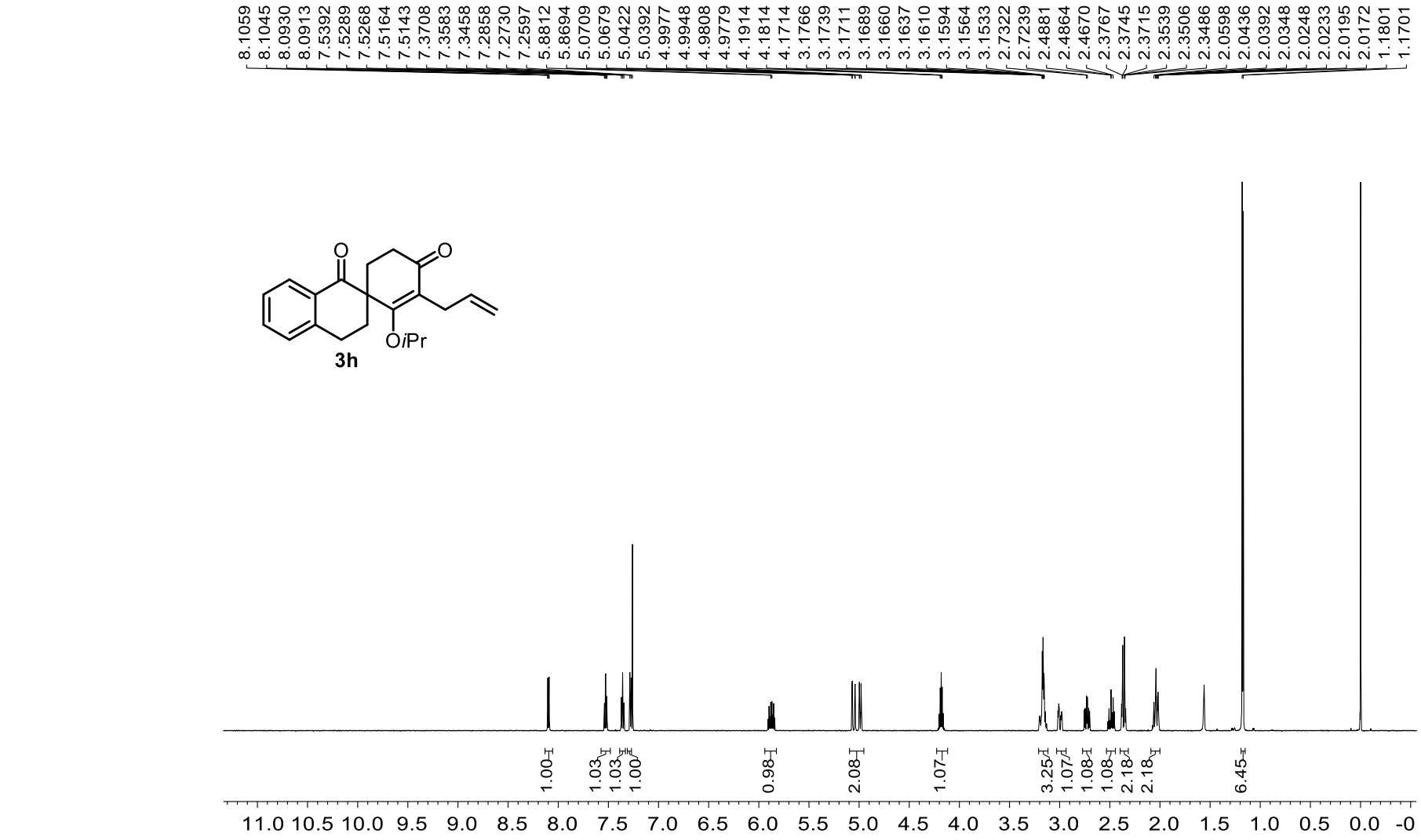
^{13}C NMR spectrum of compound 3f



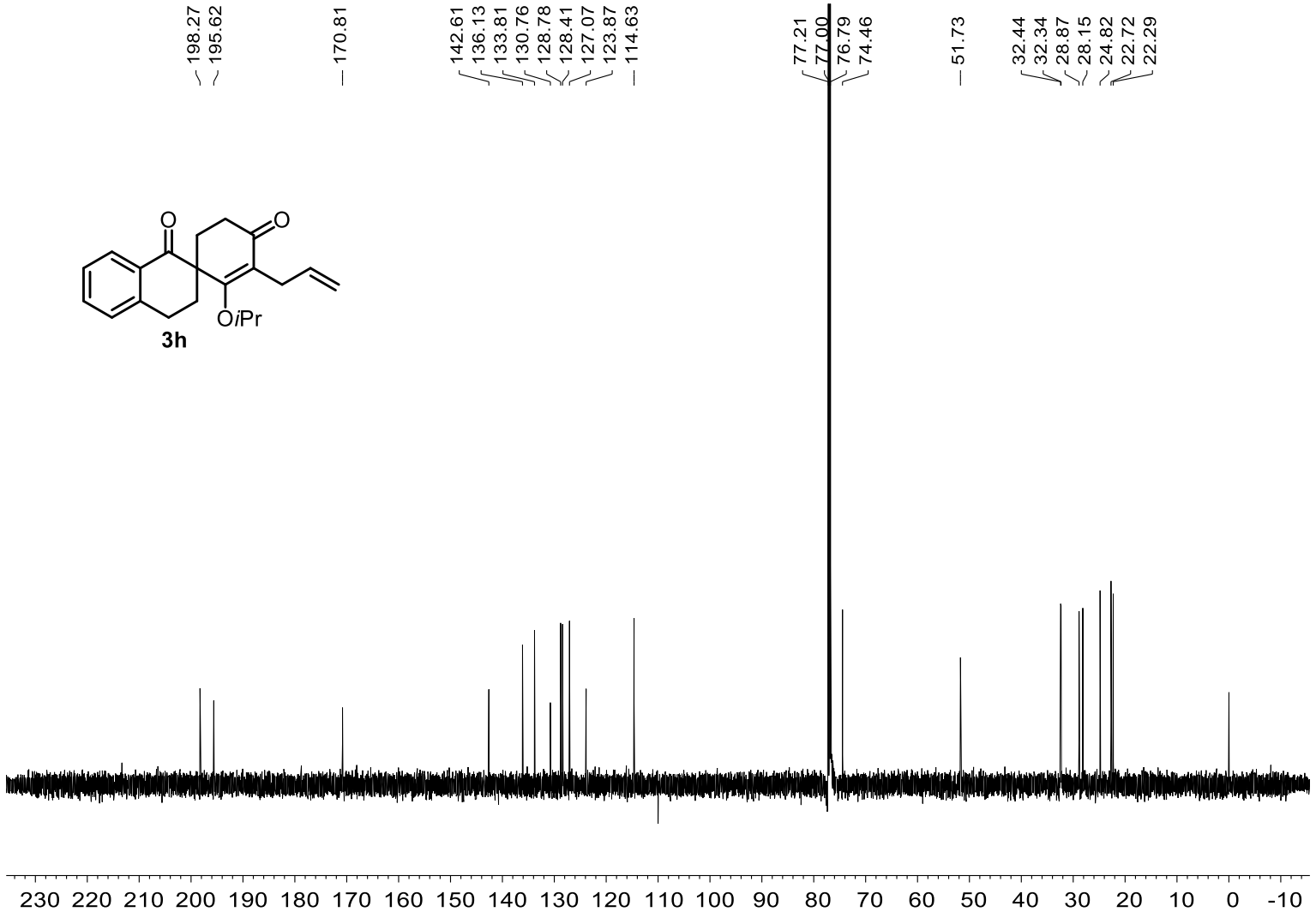
^{1}H NMR spectrum of compound 3g



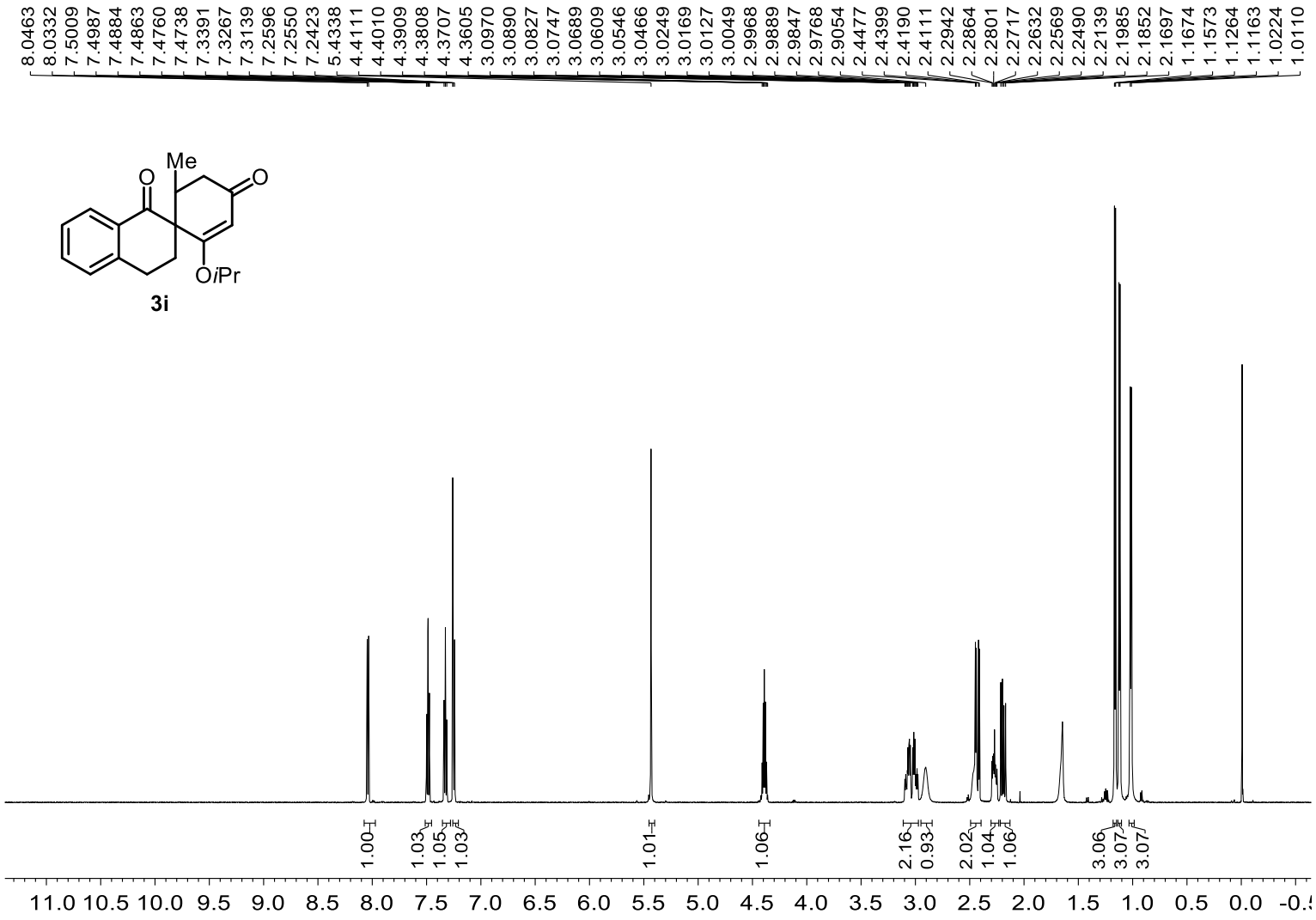
^{13}C NMR spectrum of compound 3g



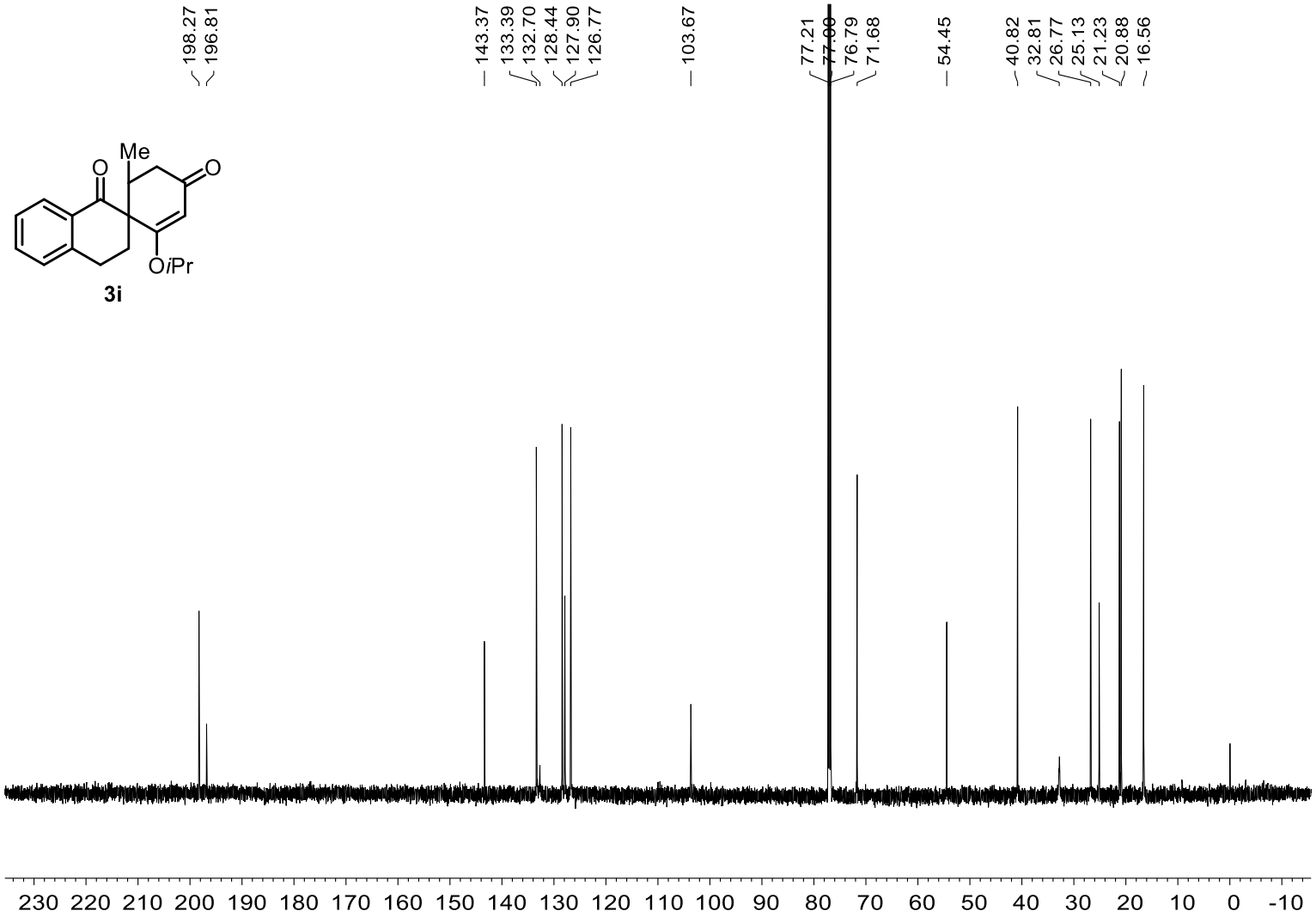
^{1}H NMR spectrum of compound 3h



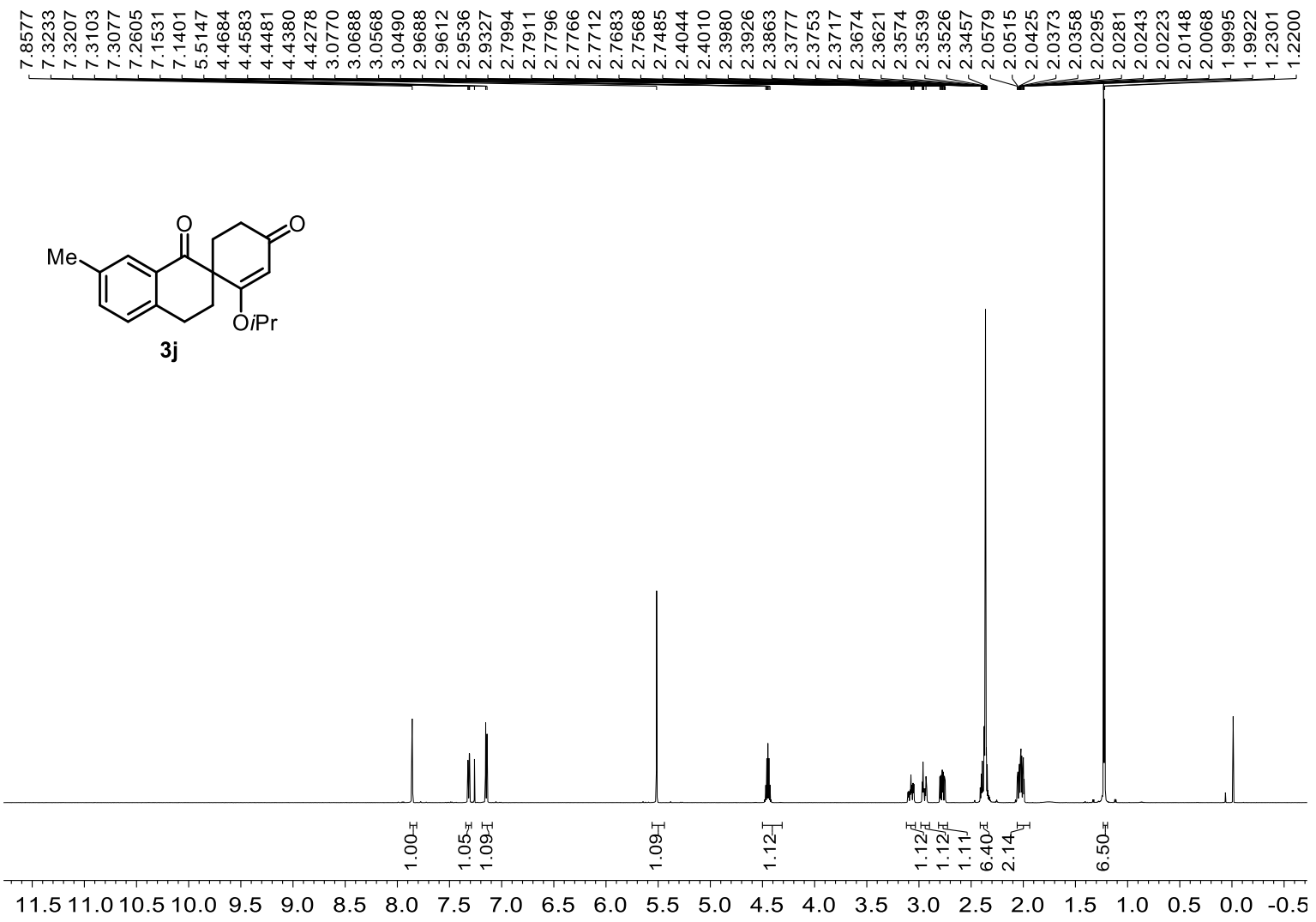
^{13}C NMR spectrum of compound 3h



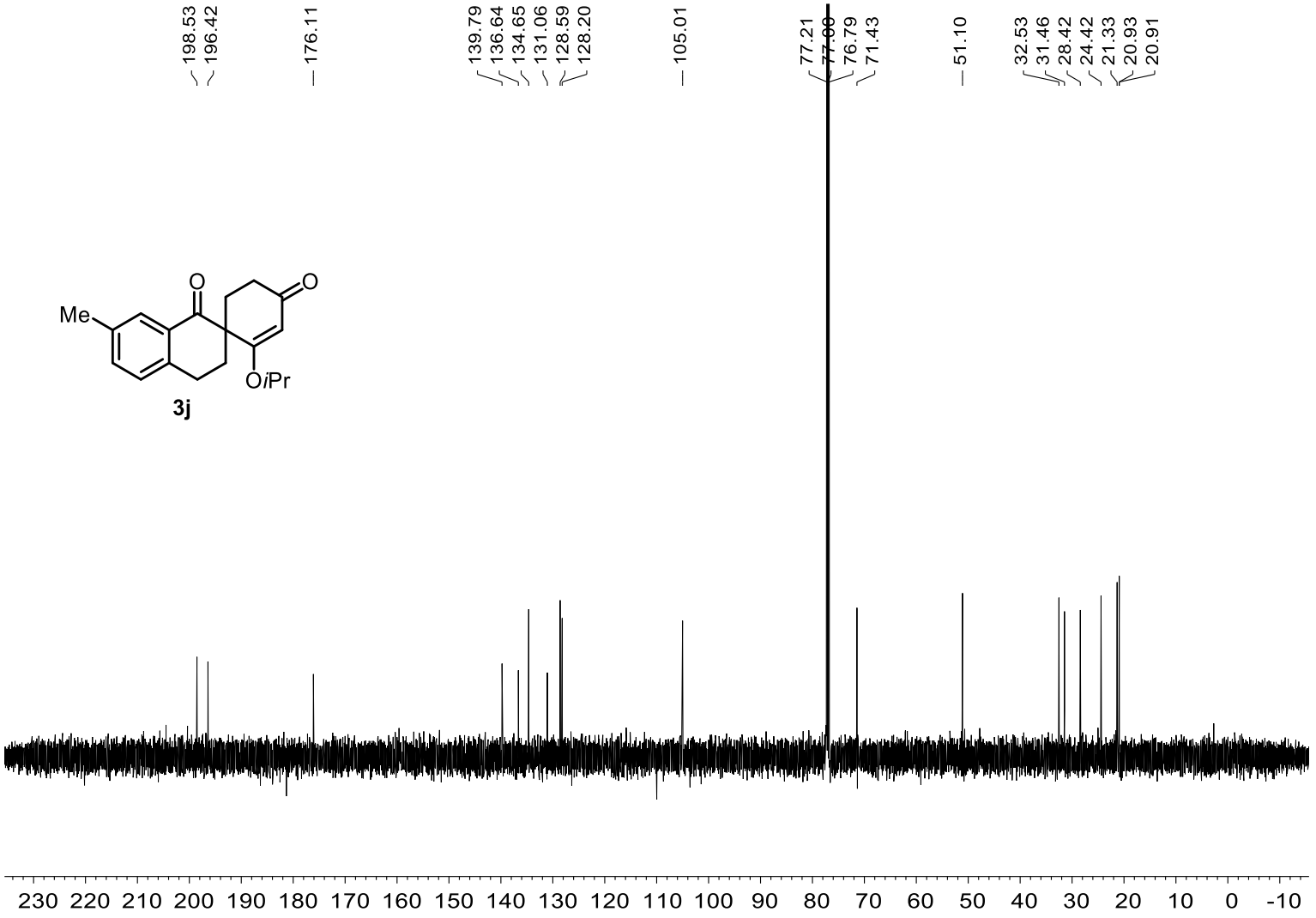
^{1}H NMR spectrum of compound 3i



^{13}C NMR spectrum of compound 3i

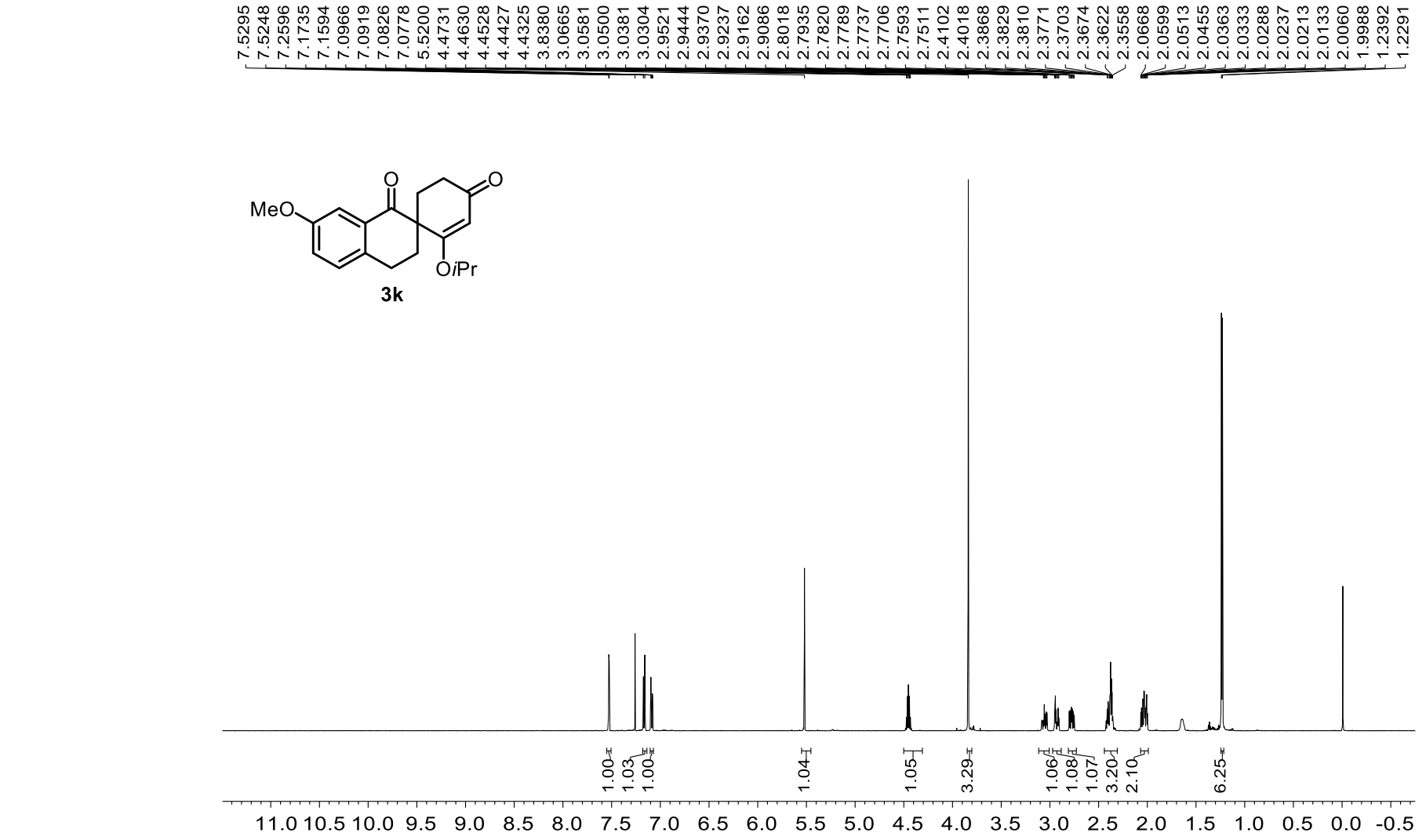


^{1}H NMR spectrum of compound 3j

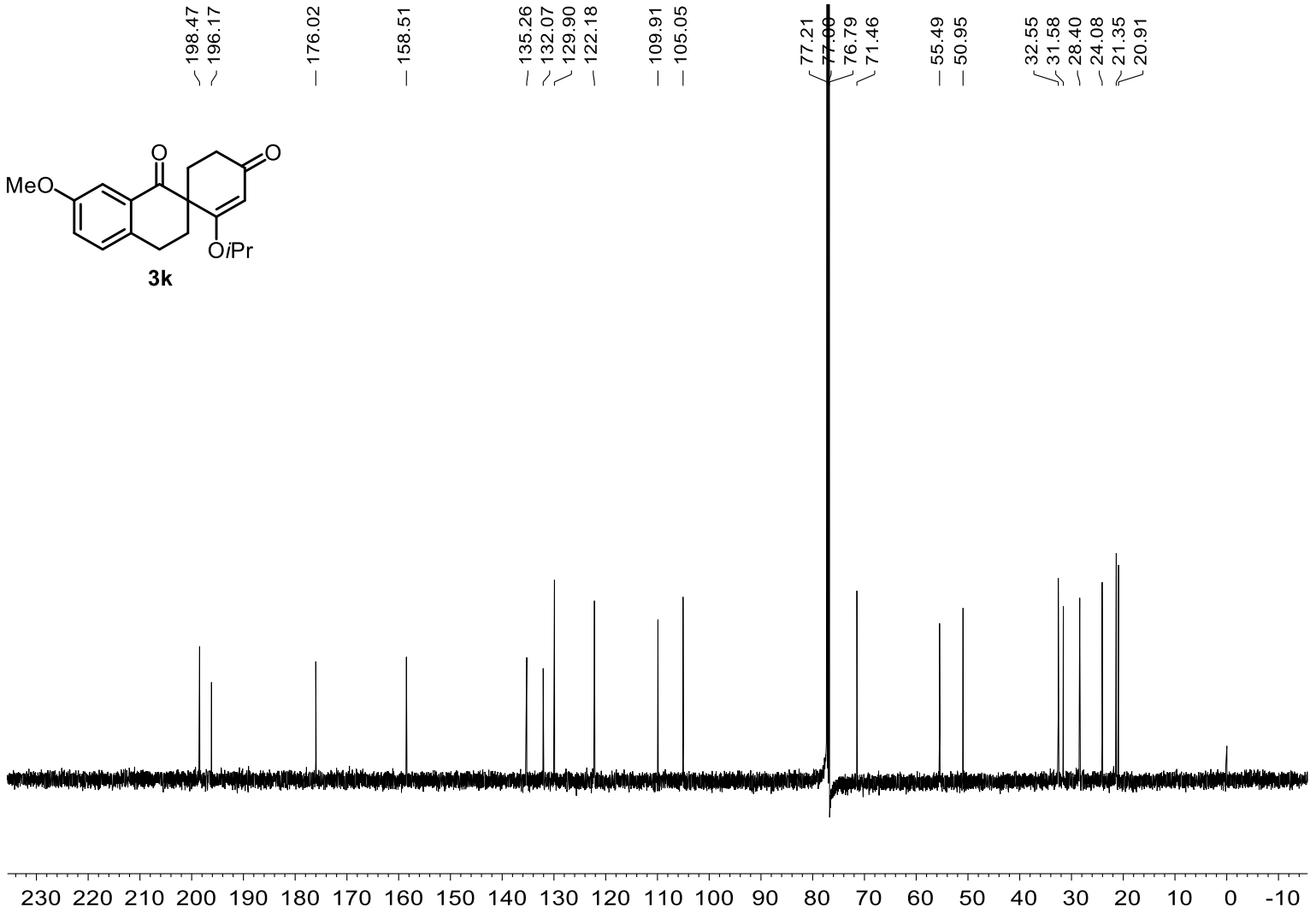


3j

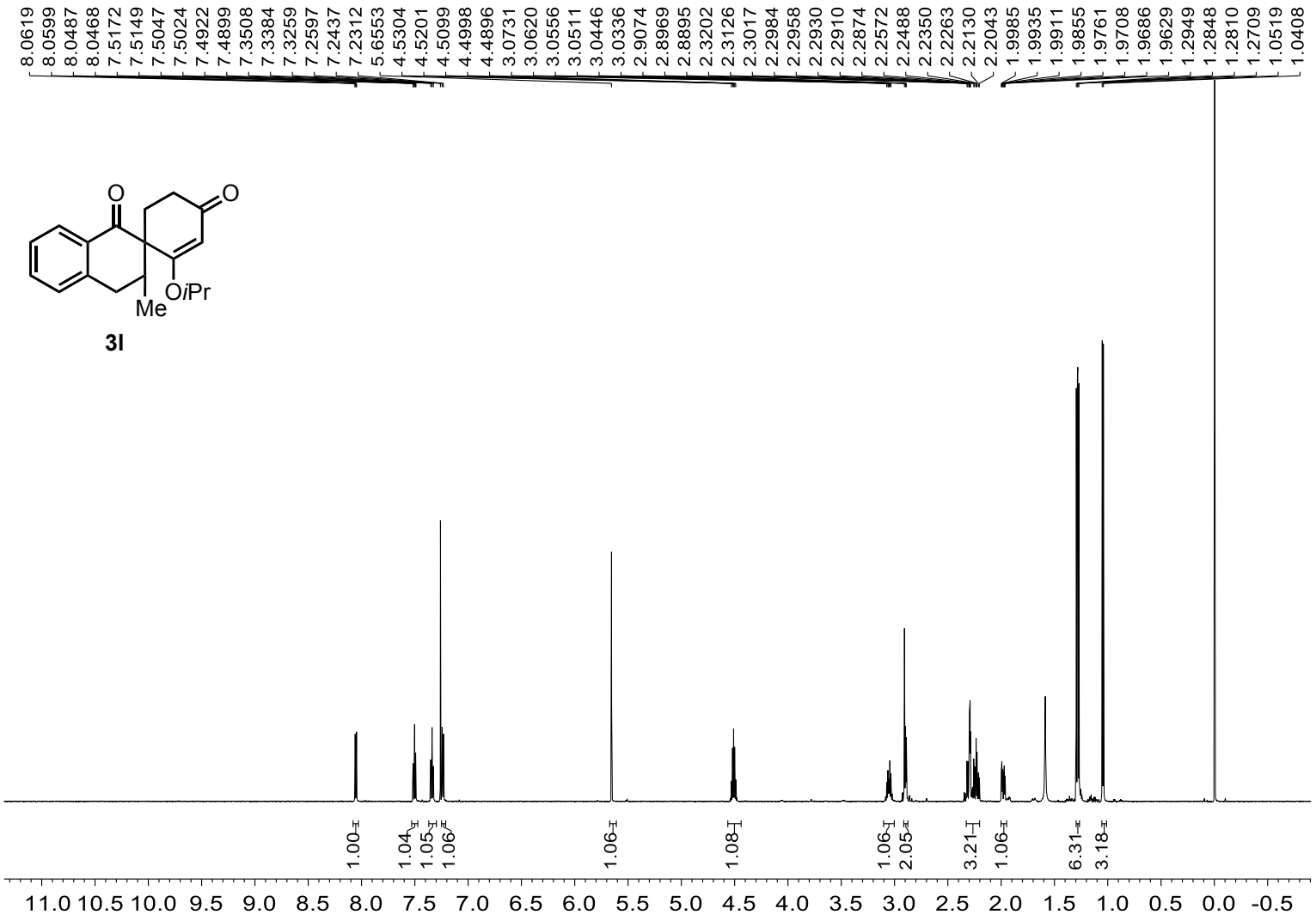
^{13}C NMR spectrum of compound 3j



^{1}H NMR spectrum of compound 3k

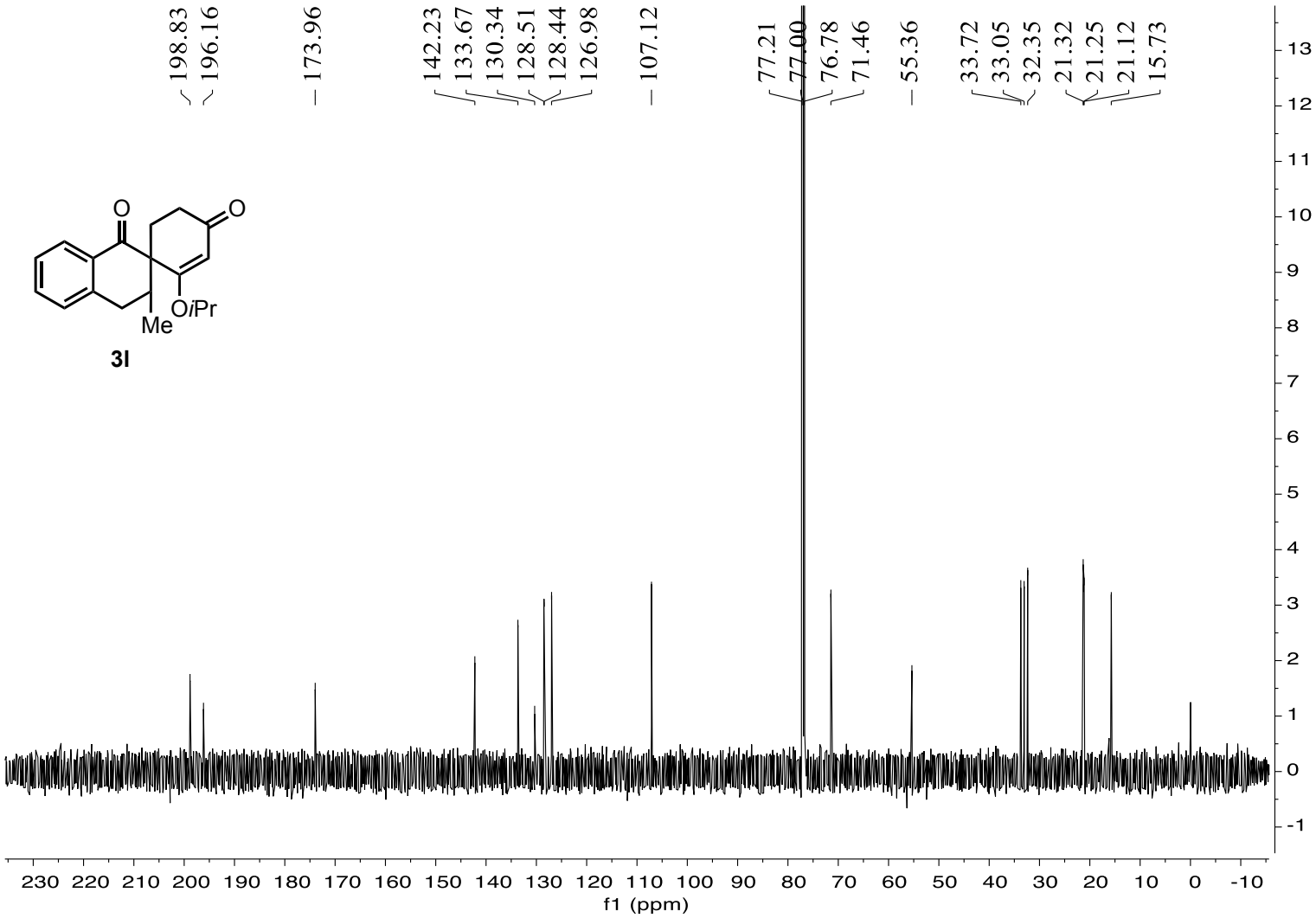


^{13}C NMR spectrum of compound 3k

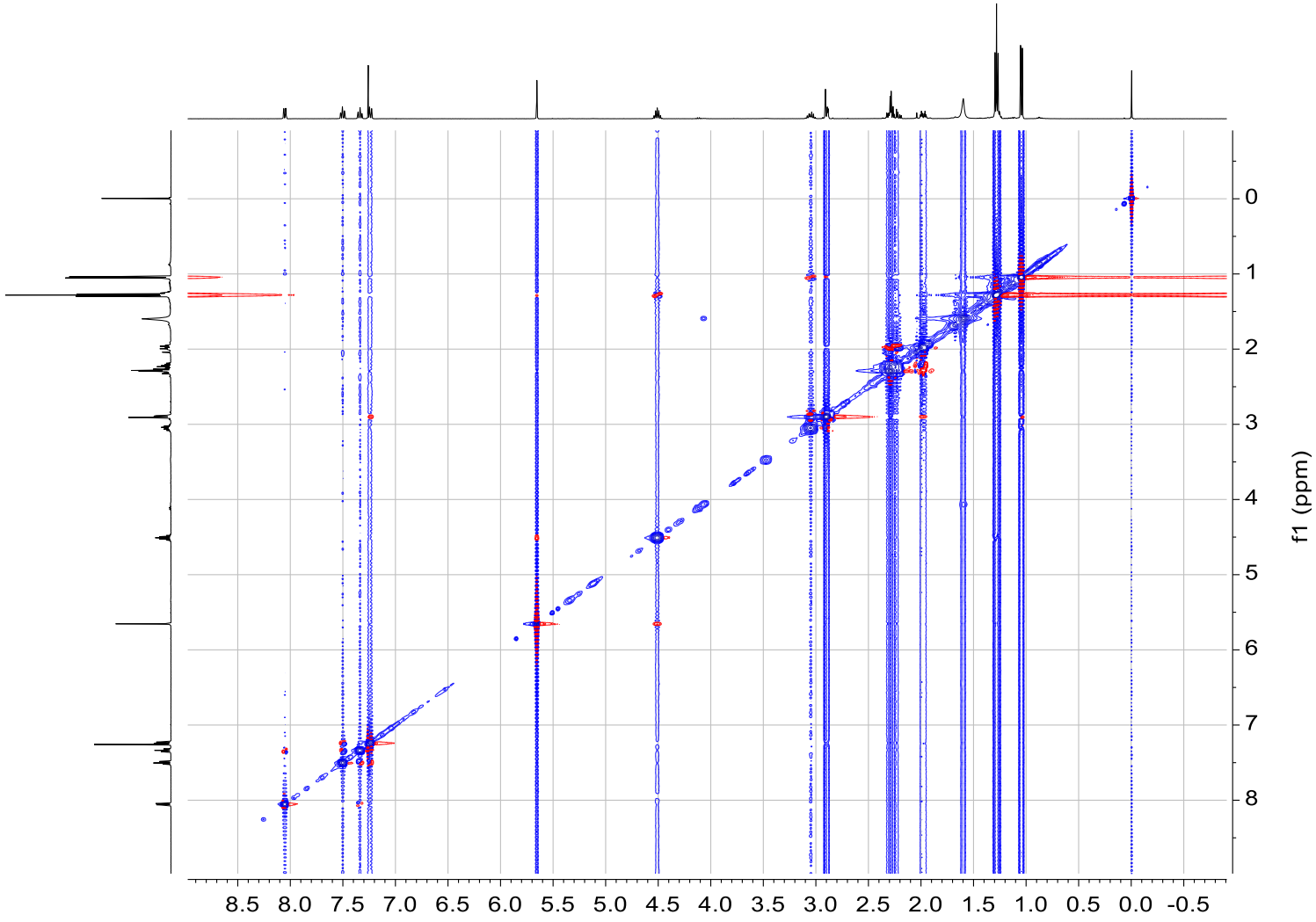


3l

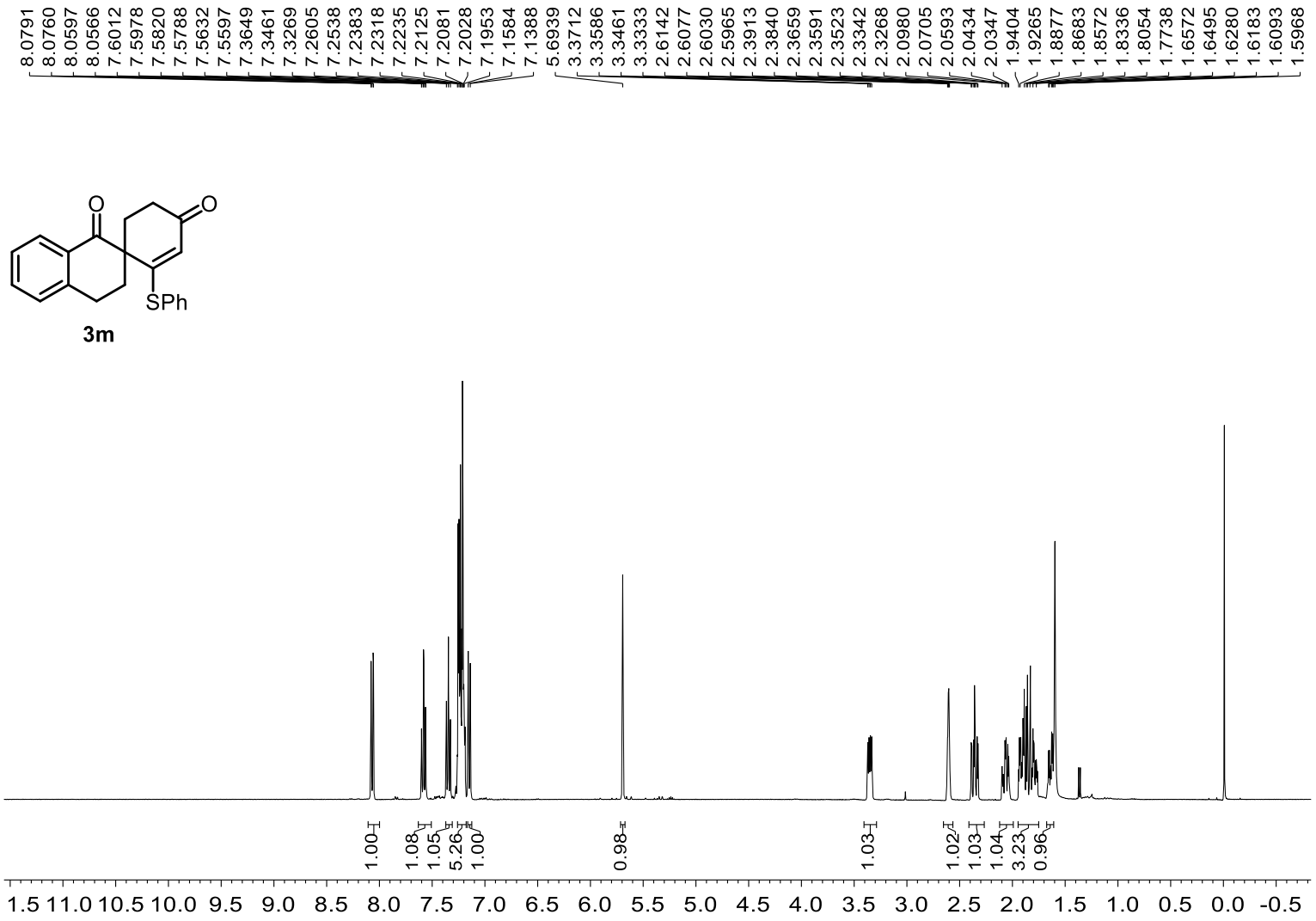
^{1}H NMR spectrum of compound 3l



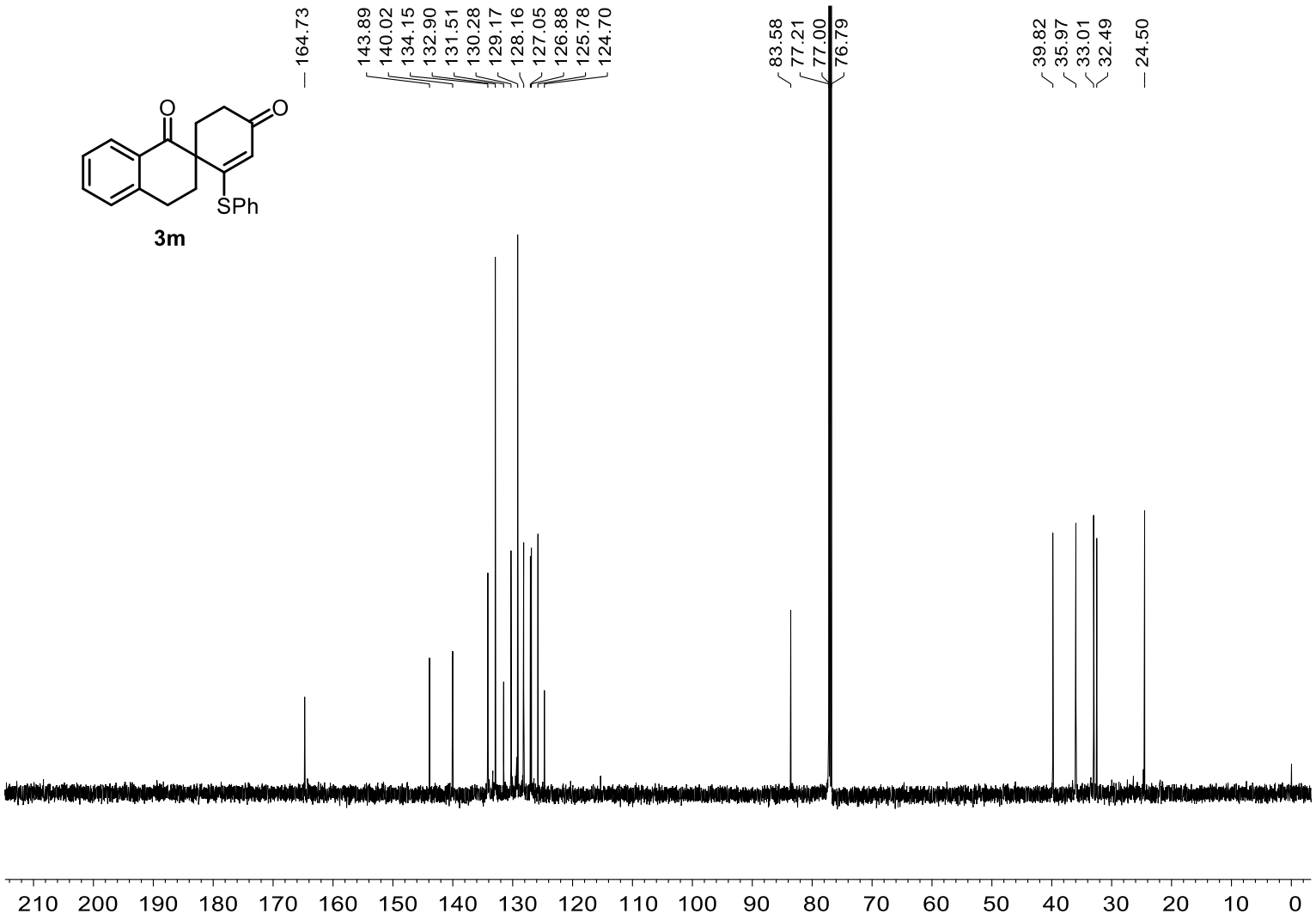
^{13}C NMR spectrum of compound 3l



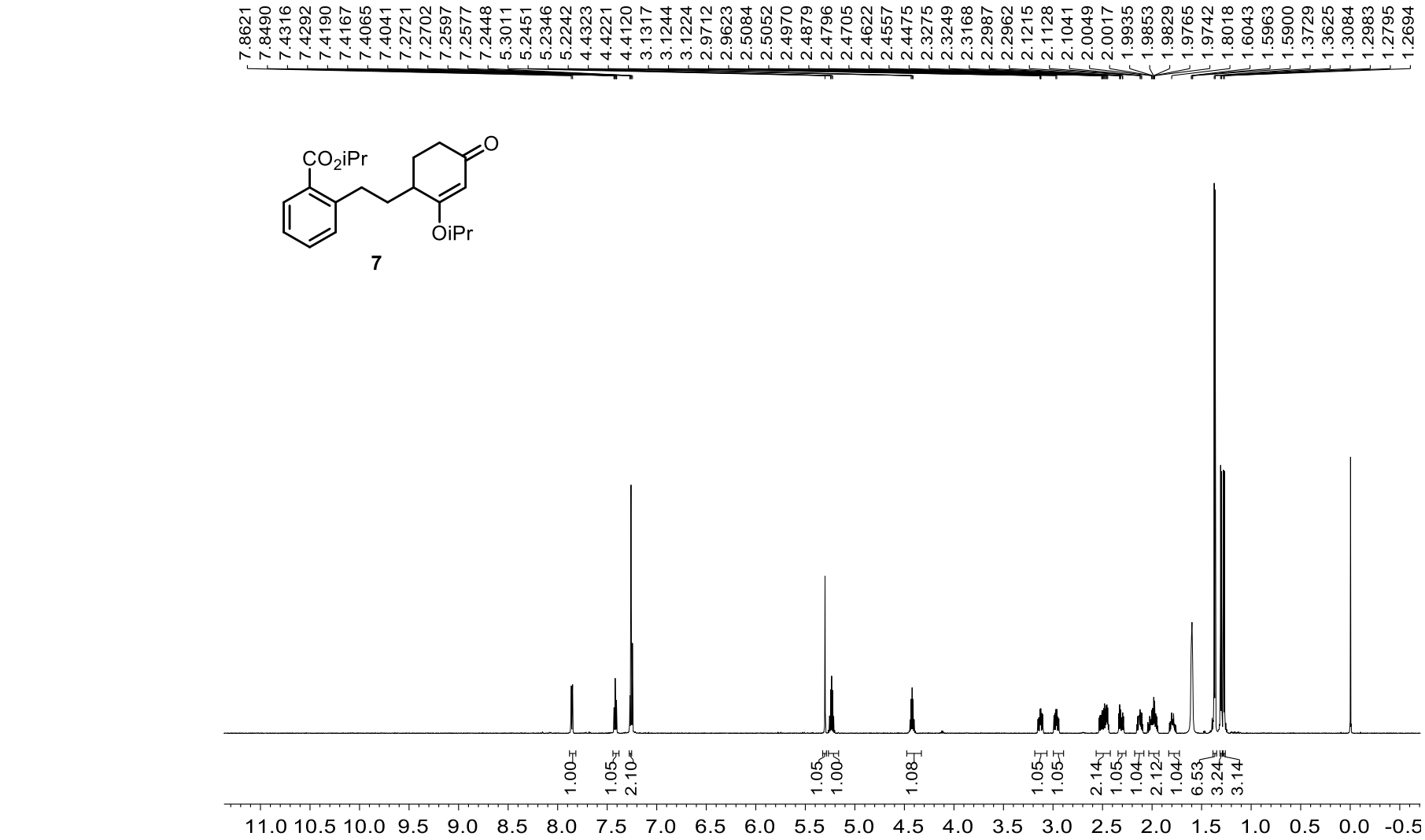
NOESY NMR spectrum of compound 3l



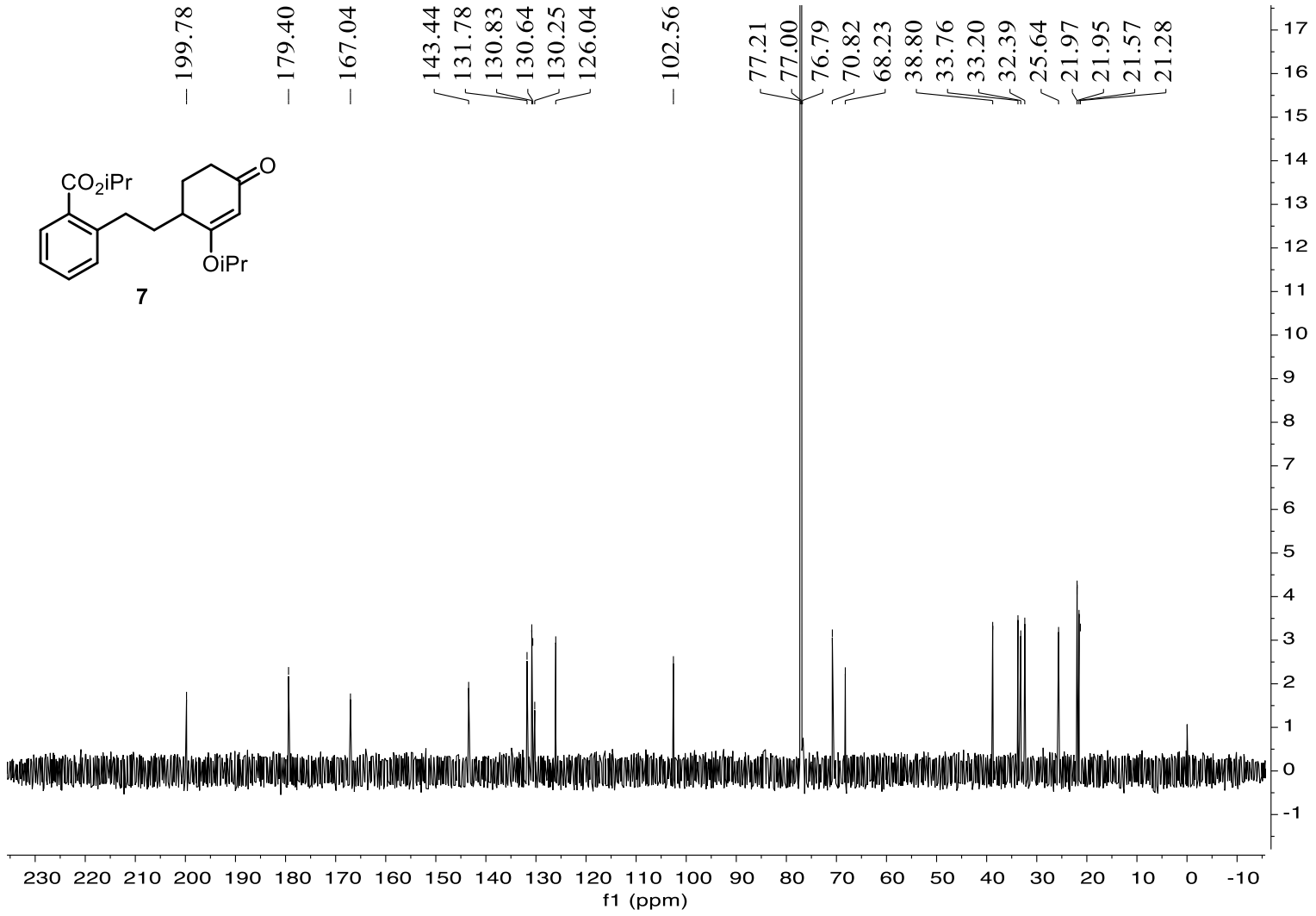
^{1}H NMR spectrum of compound 3m



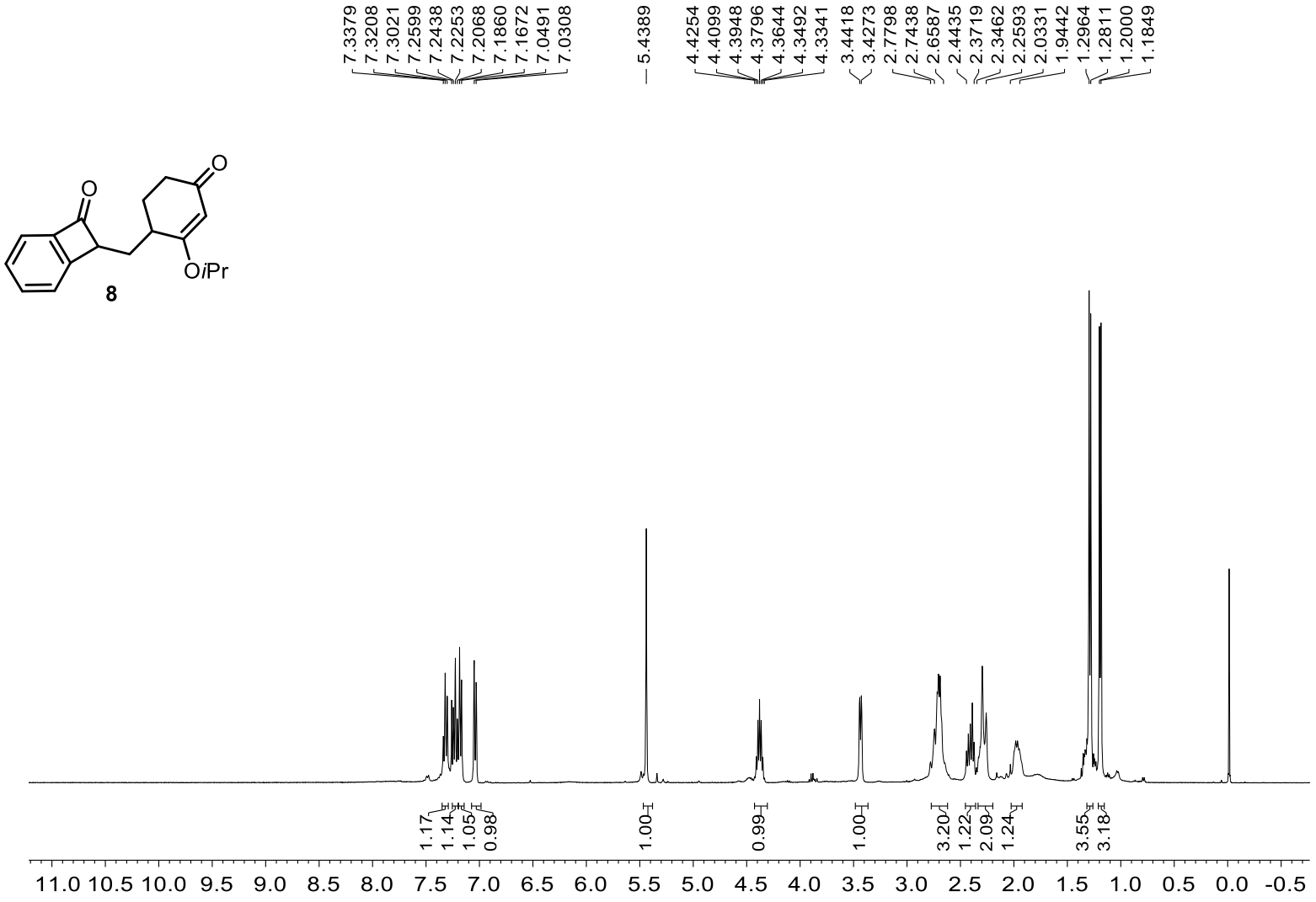
^{13}C NMR spectrum of compound 3m



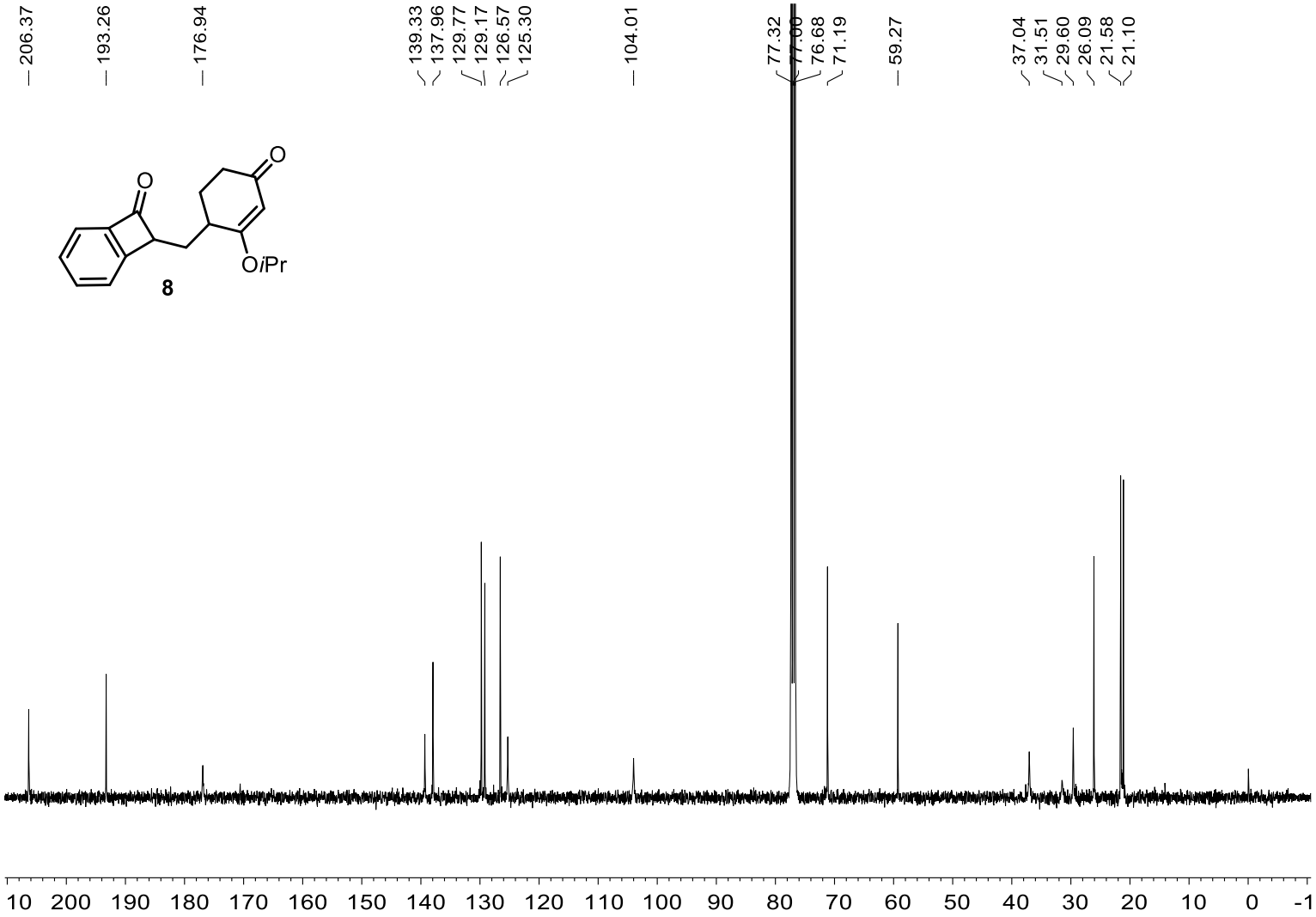
^{1}H NMR spectrum of compound 7



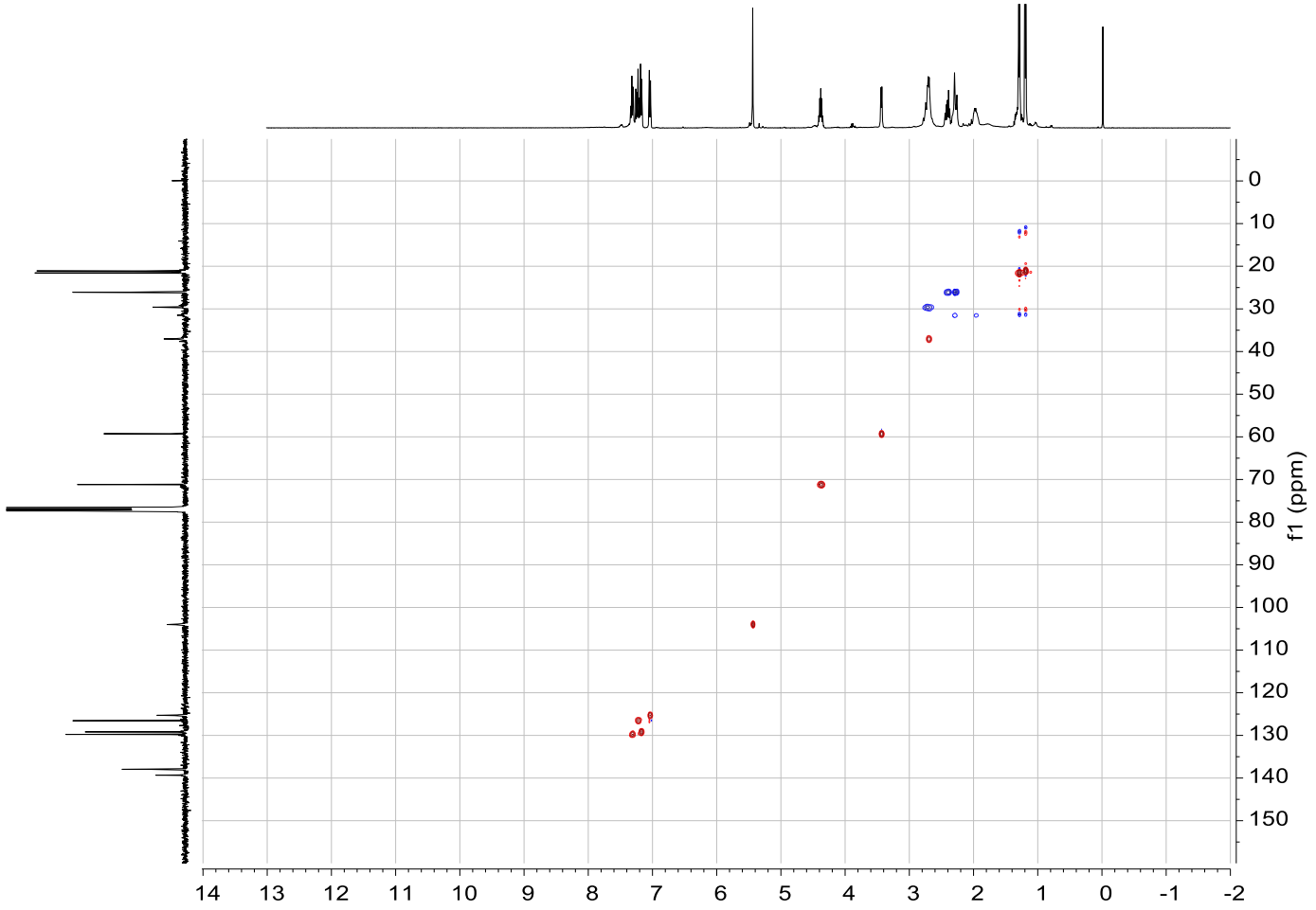
^{13}C NMR spectrum of compound 7



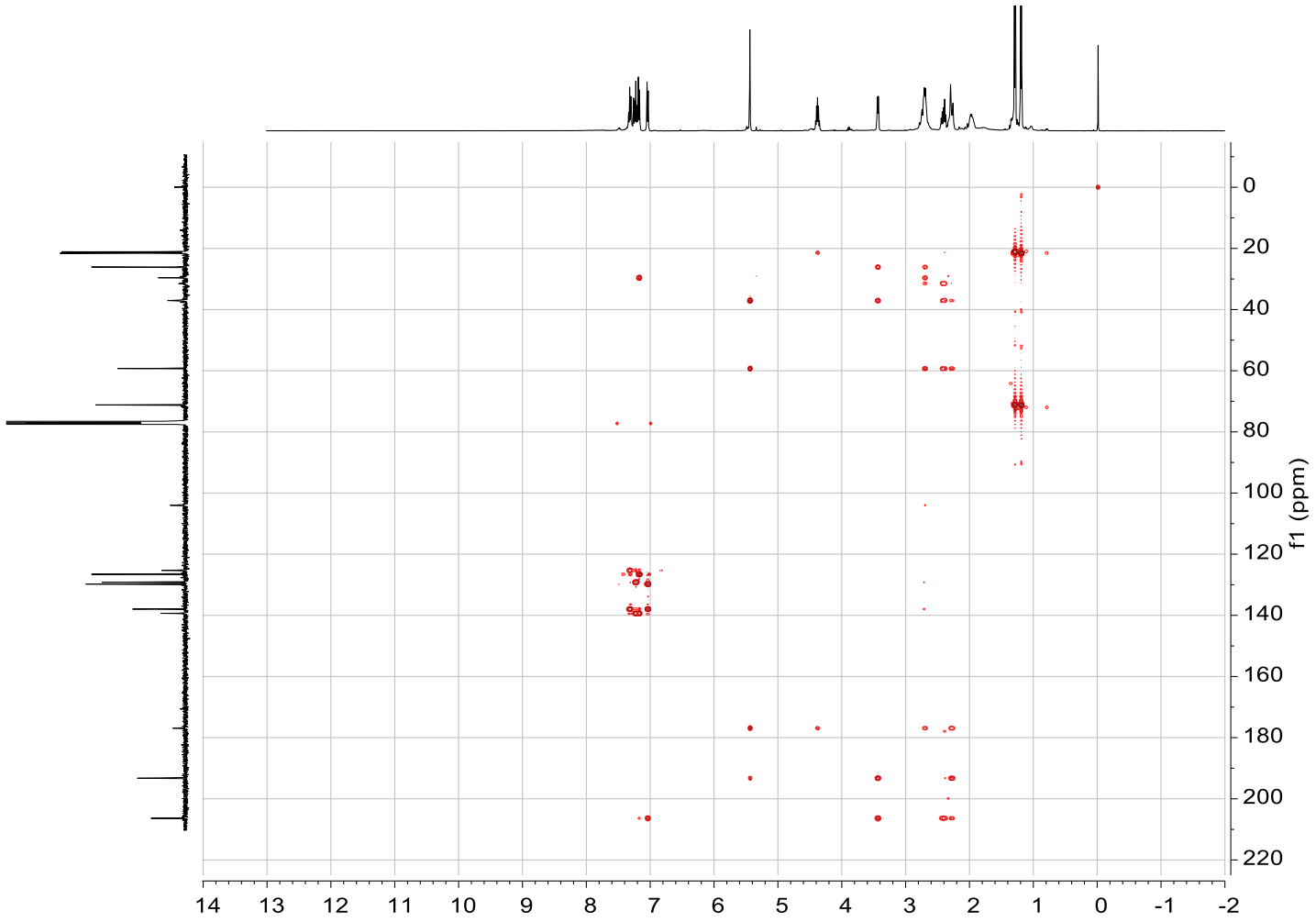
^{1}H NMR spectrum of compound 8



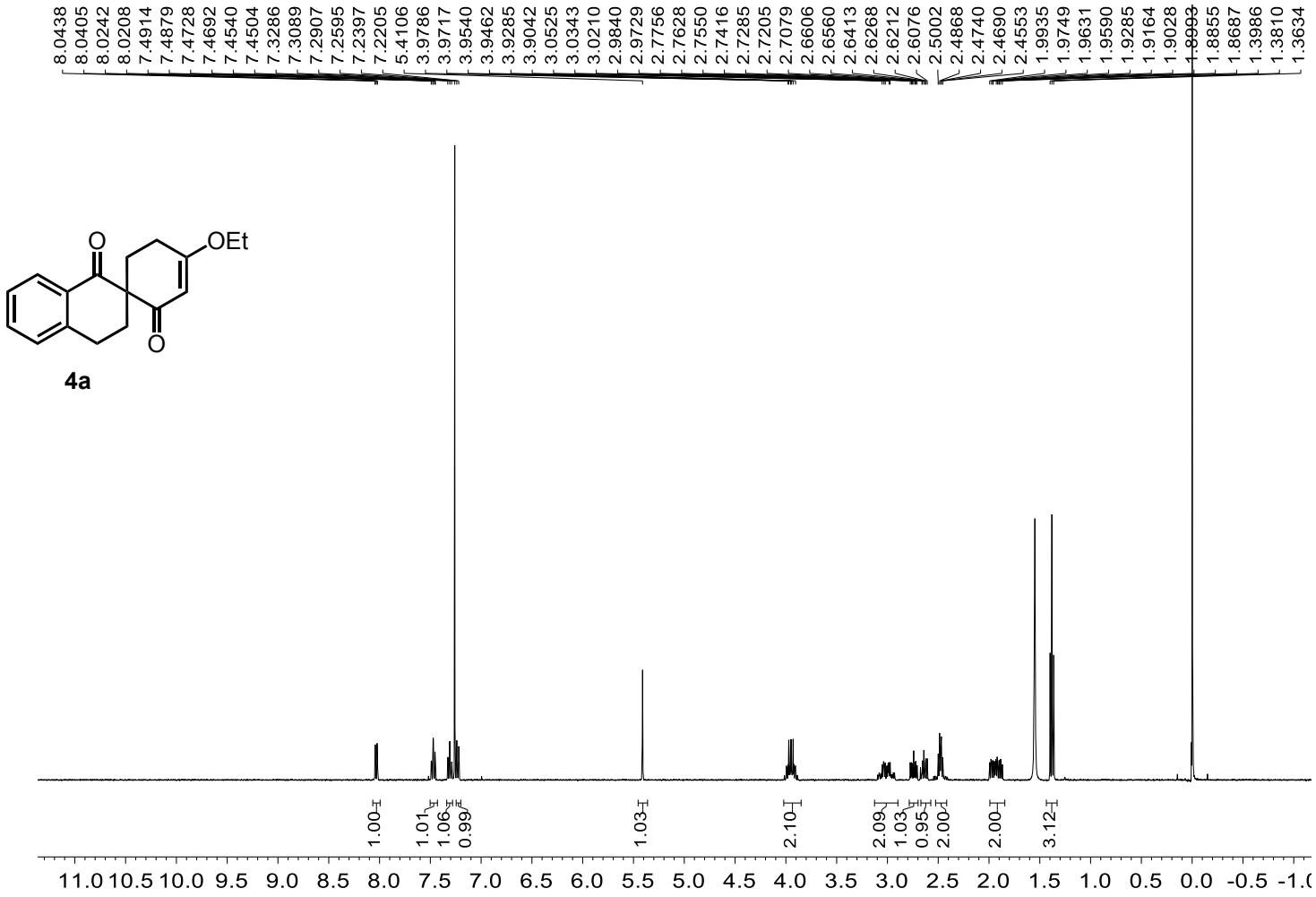
^{13}C NMR spectrum of compound 8



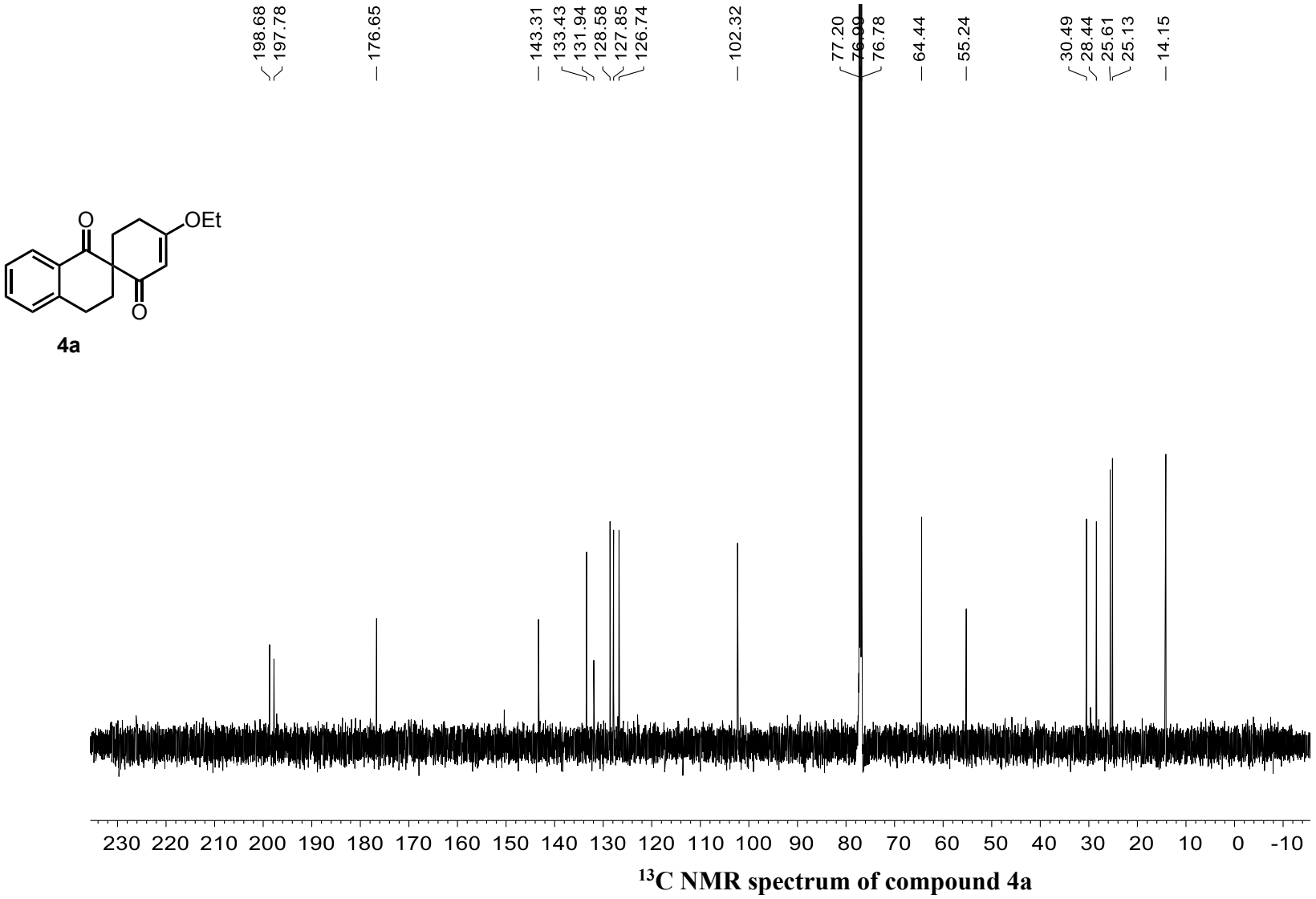
HSQC NMR spectrum of compound 8



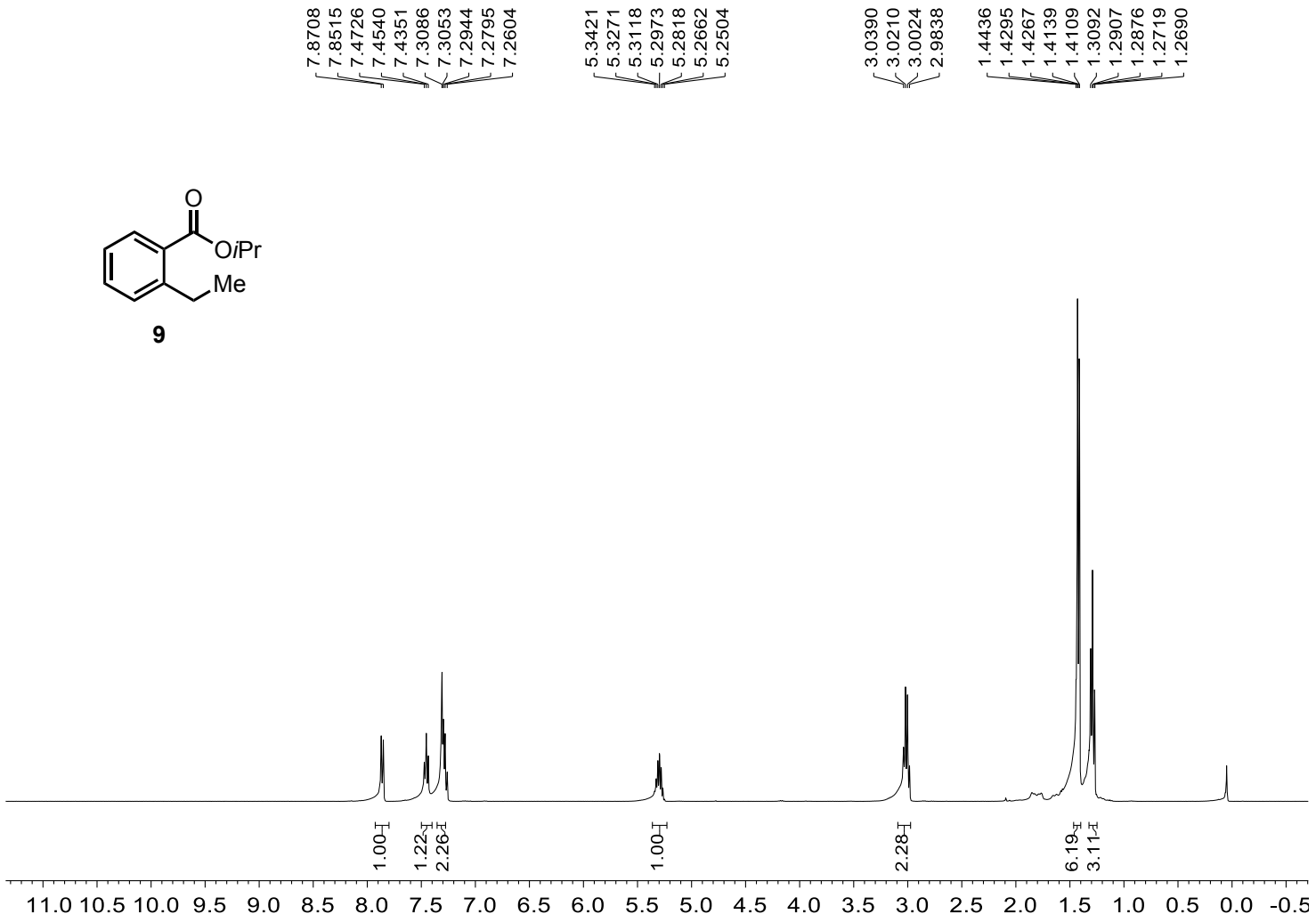
HMBC NMR spectrum of compound 8



^{1}H NMR spectrum of compound 4a



^{13}C NMR spectrum of compound 4a



^{1}H NMR spectrum of compound 9