Supporting information for

Gold(I)-catalyzed Nicholas Reaction with Aromatic Molecules Utilizing a Bifunctional Propargyl Dicobalt Hexacarbonyl Complex

Toshitaka Okamura,[†] Shogo Fujiki,[†] Yoshiharu Iwabuchi,[†] and Naoki Kanoh[*,†,‡]

† Graduate School of Pharmaceutical Sciences, Tohoku University, 6-3 Aza-aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan

‡ Institute of Medicinal Chemistry, Hoshi University, 2-4-41 Ebara, Shinagawa-ku, Tokyo 142-8501, Japan

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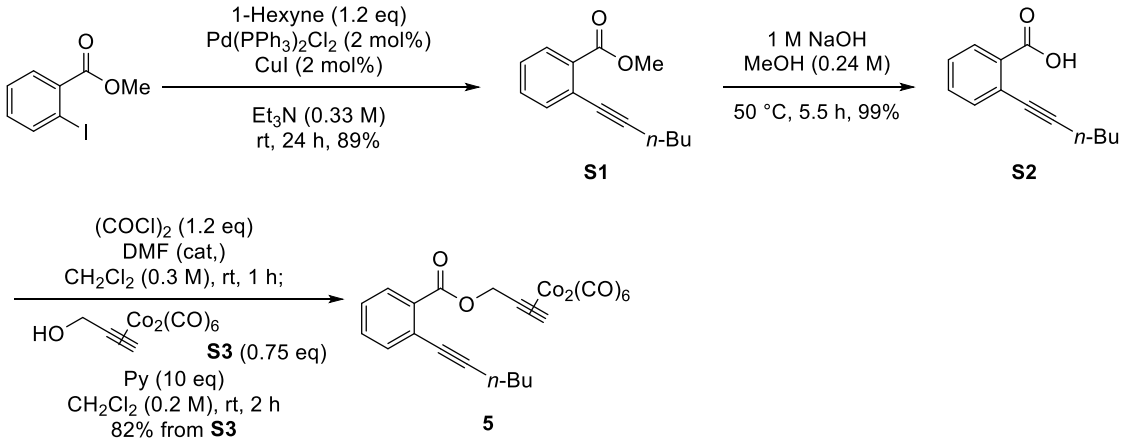
1. General procedure

All reactions were carried out under an argon atmosphere with dehydrated solvents under anhydrous conditions, unless otherwise noted. Dehydrated THF and CH_2Cl_2 were purchased from Kanto Chemical Co., Inc. Other solvents were dehydrated and distilled according to standard protocols. Reagents were obtained from commercial suppliers, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on Silica gel plates (Merck Kieselgel 60 F_{254}) or Silica gel plates (Fuji Silysia Chemical Co., Ltd.). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 μm). Flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μm). Fluorous column chromatography was performed on FluoroFlash® Silica Gel 40 μm (SIGMA-ALDRICH, Co.). All melting points were determined with Yazawa Micro Melting Point BY-2 and are uncorrected. IR spectra were recorded on a JASCO *FT/IR*-410 Fourier Transform Infrared Spectrophotometer. ^{1}H-NMR (400 and 600 MHz) and ^{13}C-NMR spectra (100 and 150 MHz) were recorded on JEOL JNM-AL-400, JEOL JNM-ECA-600 spectrometers, respectively. ^{19}F-NMR spectra (560 MHz) are recorded on JEOL JNM-ECA-600 spectrometers. For ^{1}H-NMR spectra, chemical shifts (δ) are given from TMS (0.00 ppm) or $CHCl_3$ (7.26 ppm) in $CDCl_3$ as an internal standard. For ^{13}C-NMR spectra, chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm) as an internal standard. For ^{19}F-NMR spectra, chemical shifts (δ) are given from C_6F_6 (164.9 ppm) as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, m = multiplet, br = broad. EI mass spectra were recorded on JEOL JMS-DX303, JEOL JMS-700 and JEOL JMS-T 100 GC. FAB mass spectra were recorded on JEOL JMS-700. ESI mass spectra were recorded on Thermo Scientific Exactive Mass Spectrometer.

2. Synthesis of Nicholas complex precursors

2-1. Synthesis of reagent 5



Methyl 2-(hex-1-yn-1-yl)benzoate (S1)

To a solution of methyl 2-iodobenzoate (524 mg, 2.00 mmol) and 1-hexyne (0.28 mL, 2.44 mmol) in Et_3N (6.0 mL) was added $Pd(PPh_3)_2Cl_2$ (28.0 mg, 39.9 μmol) and CuI (8.97 mg, 47.0 μmol) at room temperature. The reaction mixture was stirred at the same temperature for 24 h, then concentrated under vacuo. CH_2Cl_2 (30 mL) was added to the residue, and the organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20) to give alkyne **S1** (385 mg, 1.78 mmol, 89%). Characterization data were in agreement with previously reported values.[1]

2-(Hex-1-yn-1-yl)benzoic acid (S2)

To a solution of benzoate **S1** (1.27 g, 5.89 mmol) in MeOH (25 mL) was added 1 M NaOH (25 mL) at room temperature. The reaction mixture was stirred at the same temperature for 5.5 h. The mixture was poured into 1 M HCl (30 mL), and extracted with Et_2O (40 mL × 2). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 1) to give benzoic acid **S2** (1.18 g,

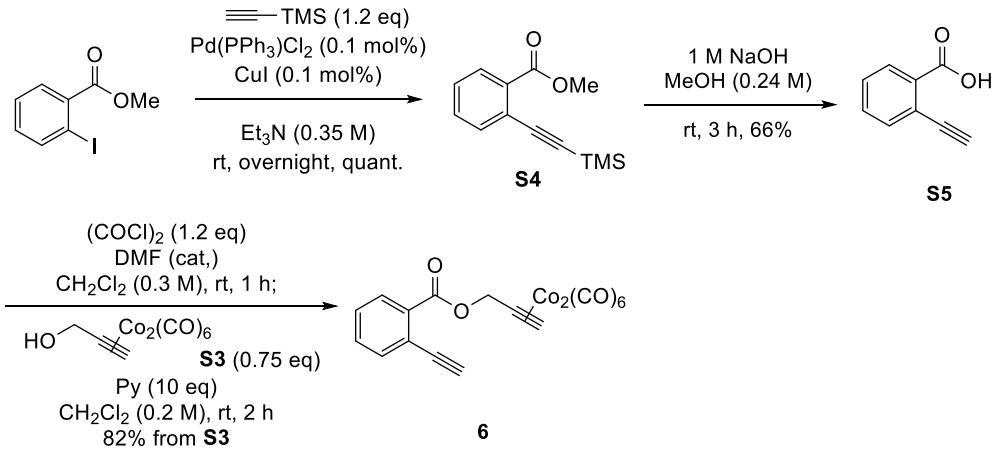
mmol, 99%). Characterization data were in agreement with previously reported values.[1]

Reagent 5

To a solution of benzoic acid **S2** (296 mg, 1.46 mmol) in CH_2Cl_2 (4.8 mL) was added $(COCl)_2$ (150 μL, 1.75 mmol) and DMF (10 μL, 0.13 μmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated under vacuo. To the residue was added CH_2Cl_2 (7.3 mL), pyridine (1.2 mL), and alkyne cobalt complex **S3**[2] (370 mg, 1.10 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (4 mL) and extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified with silica gel column chromatography (AcOEt : Hexane = 1 : 20) to give complex **5** (471 mg, 0.90 mmol, 82% from **S3**).

5: red oil; IR (neat): 2022 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.43 (td, *J* = 7.6, 1.0 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.12 (s, 1H), 5.52 (s, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.69-1.58 (m, 2H), 1.58-1.45 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.1, 165.6, 134.5, 131.8, 131.0, 130.1, 127.1, 125.2, 96.5, 88.7, 79.3, 72.2, 65.4, 30.8, 22.1, 19.6, 13.7; HRMS (ESI): calcd for $C_{22}H_{16}O_8Co_2Na$ ($[M+Na]^+$): 548.9401, found 548.9393.

2-2. Synthesis of reagent 6



Methyl 2-((trimethylsilyl)ethynyl)benzoate (S4)

To a solution of methyl 2-iodobenzoate (5.24 g, 20.0 mmol) and TMS acetylene (3.39 mL, 24.0 mmol) in Et_3N (60 mL) was added $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol) and CuI (3.8 mg, 0.02 mmol) at room temperature. The reaction mixture was stirred at the same temperature overnight and concentrated under vacuo. To the residue was added CH_2Cl_2 (30 mL) and the organic layer was washed with sat. aq.NH_4Cl (30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under vacuo and purified by column chromatography on silica gel (AcOEt : hexane = 1 : 30) to give alkyne **S4** (5.14 g, quant.). Characterization data were in agreement with previously reported values.[3]

2-Ethynylbenzoic acid (S5)

To a solution of benzoate **S4** (996 mg, 4.29 mmol) in MeOH (18 mL) was added 1 M NaOH (18 mL) at room temperature. The reaction mixture was stirred at the same temperature for 3 h. The mixture was poured into conc. HCl (4 mL), and extracted with Et_2O (30 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated under vacuo and purified by column chromatography on silica gel (AcOEt : hexane = 4 : 1 to 1 : 1) to give benzoic acid **S5** (412 mg, 2.82 mmol, 66%). Characterization data were in agreement with previously

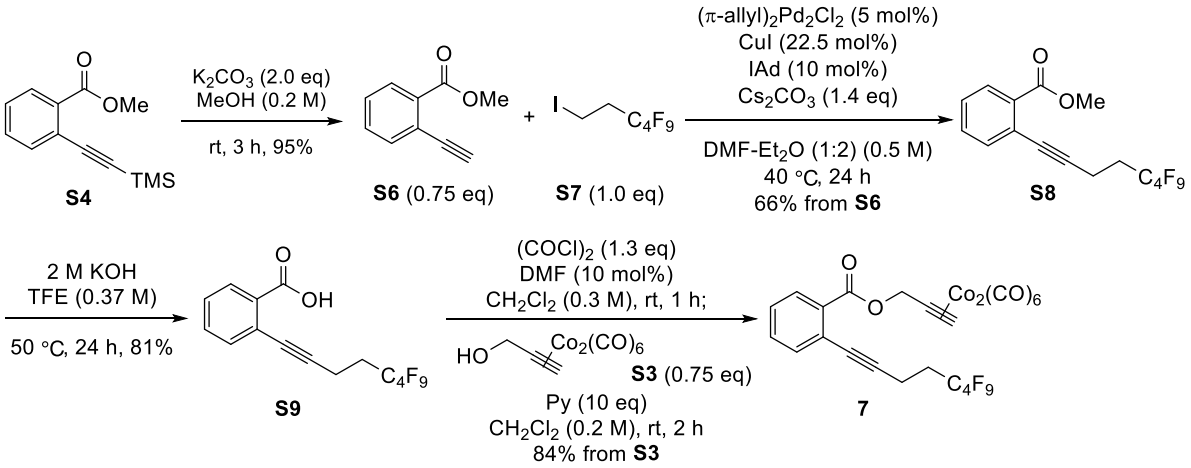
reported values.[4]

Reagent 6

To a solution of benzoic acid **S5** (295 mg, 2.02 mmol) in CH_2Cl_2 (6.8 mL) was added $(COCl)_2$ (0.21 mL, 2.42 mmol) and DMF (10 μL, 0.13 μmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated in vacuo. To the residue was added CH_2Cl_2 (10 mL), pyridine (1.6 mL) and alkyne cobalt complex **S3** (345 mg, 1.01 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (10 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 20) to give complex **6** (395 mg, 0.830 mmol, 82% from **S3**).

6: red oil; IR (neat): 2036 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 7.4 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 6.13 (s, 1H), 5.54 (s, 2H), 3.44 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.1, 165.3, 135.2, 132.0, 131.7, 130.2, 128.5, 123.1, 88.3, 82.6, 82.0, 72.3, 65.6; HRMS (ESI): calcd for $C_{18}H_8O_8Co_2Na$ ($[M+Na]^+$): 492.8775, found 492.8754.

2-3. Synthesis of reagent 7



Methyl 2-ethynylbenzoate (S6)

To a solution of alkyne **S4** (2.0 g, 8.6 mmol) in MeOH (45 mL) was added K_2CO_3 (2.3 g, 17.0 mmol) at room temperature. The mixture was stirred at the same temperature for 3 h. To the mixture was added sat. NH_4Cl aq. (30 mL), and the resulting mixture was extracted with Et_2O (30 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under vacuo, and purified by column chromatography on silica gel (AcOEt : hexane = 1: 8) to give terminal alkyne **S6** (1.3 g, 8.2 mmol, 95%). Characterization data were in agreement with previously reported values.[3]

Methyl 2-(5,5,6,6,7,7,8,8,8-nonafluorooct-1-yn-1-yl)benzoate (S8)

To a solution of $(\pi\text{-allyl})_2Pd_2Cl_2$ (92 mg, 0.25 mmol), 1,3-di(1-adamantyl)imidazolium hydrochloride (IAd) (198 mg, 0.5 mmol), CuI (216 mg, 1.12 mmol), and Cs_2CO_3 (2.28 g, 7.0 mmol) in DMF-Et_2O (1:2) (10 mL) was added alkyne **S6** (0.92 mL, 3.75 mmol) and 2-(nonafluorobutyl)ethyl iodide (**S7)** (0.86 mL, 5.0 mmol) at room temperature. The reaction mixture was stirred at 40 °C for 24 h, the reaction mixture was concentrated under vacuo and purified by column chromatography on silica gel (CH_2Cl_2 : Hexane = 1 : 30 to 1 : 8) to give alkyne **S8** (1.08 g, 2.70 mmol, 53% from **S6**).

S8: yellow oil; IR (neat): 2955, 1734 cm^{-1}; 1H-NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.37 (t, *J* = 7.6 Hz, 2H), 2.56-2.41 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 195.8, 193.3, 167.3, 138.2, 133.4, 131.5, 129.5, 129.2, 129.1, 52.9, 27.9, 24.8 (t, $^1J_{CF}$ = 23.1 Hz); ^{19}F-NMR (562 MHz, $CDCl_3$): δ 84.1 (s, 3F), 117.5 (s, 2F), 127.5 (s, 2F), 129.2 (s, 2F); HRMS (ESI): calcd for $C_{11}H_{11}O_2F_9Na$ ($[M+Na]^+$): 429.0508, found 429.0505.

2-(5,5,6,6,7,7,8,8,8-Nonafluorooct-1-yn-1-yl)benzoic acid (S9)

To a solution of benzoate **S8** (274 mg, 0.67 mmol) in 2,2,2-trifluoroethanol (TFE) (1.8 mL) was added 2 M KOH (1.8 mL) at room temperature. The reaction mixture was and stirred at 50 °C for 16 h. To the mixture was added 1 M HCl (5 mL), and the resulting mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20) to give benzoic acid **S9** (244 mg, 0.62 mmol, 92%).

S9: white solid; mp. 82-84 °C; IR (neat): 1705 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.7, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.64-2.38 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.8, 134.3, 132.6, 131.2, 130.8, 127.9, 124.2, 92.7, 80.2, 30.3 (t, $^1J_{CF}$ = 21.3 Hz), 11.9 (t, $^2J_{CF}$ = 4.9 Hz) ; ^{19}F-NMR (562 MHz, $CDCl_3$): δ 84.1 (s, 3F), 118.5 (s, 2F) 127.6 (s, 2F), 129.1 (s, 2F); HRMS (EI): calcd for $C_{15}H_9O_2F_9$ (M^+): 392.0459, found 392.0440.

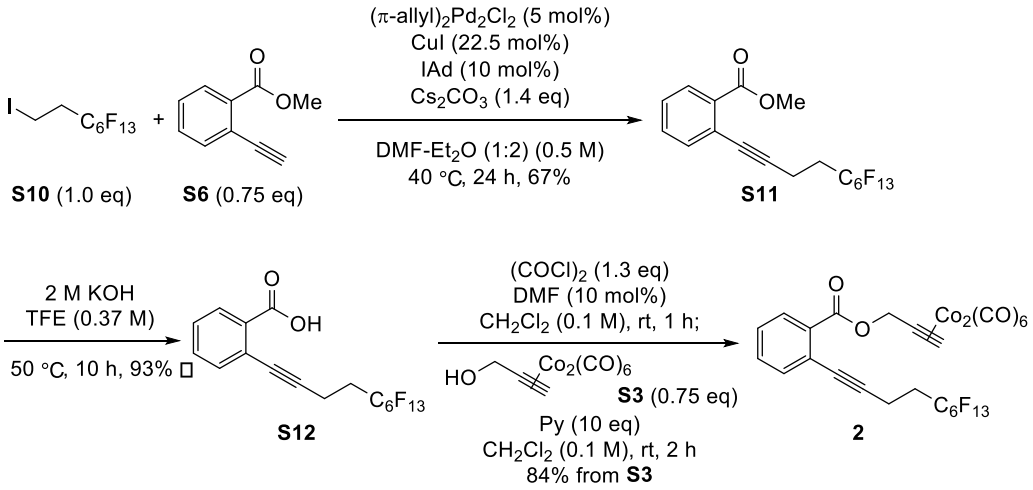
Reagent 7

To a solution of benzoic acid **S9** (196 mg, 0.50 mmol) in CH_2Cl_2 (1.7 mL) was added $(COCl)_2$ (58 μL, 0.65 mmol) and DMF (4.0 μL, 0.05 μmol) at room temperature. The

reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated under vacuo. To the residue was added CH_2Cl_2 (2.5 mL), pyridine (0.38 mL, 5.0 mmol) and then alkyne cobalt complex **S3** (128 mg, 0.38 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (5 mL), extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified with silica gel column chromatography (AcOEt : Hexane = 1 : 100) to give reagent **7** (231 mg, 0.32 mmol, 84% from **S3**).

7: red oil; IR (neat): 2030, 1732 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 6.13 (s, 1H), 5.53 (s, 2H), 2.82 (t, J = 6.8 Hz, 2H), 2.56-2.43 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 199.0, 165.2, 134.4, 132.0, 131.1, 130.2, 127.7, 124.3, 92.0, 88.6, 80.4, 72.1, 65.4, 30.4 (t, $^1J_{CF}$ = 21.5 Hz), 11.9 (t, $^2J_{CF}$ = 5.7 Hz) ; ^{19}F-NMR (562 MHz, $CDCl_3$): δ 84.1 (s, 3F), 118.6 (s, 2F), 127.7 (s, 2F), 129.9 (s, 2F); HRMS (EI): calcd for $C_{21}H_{11}F_9O_5Co_2$ ([M-3CO]$^+$): 631.9127, found: 631.9111.

2-4. Synthesis of reagent 2



Methyl 2-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodec-1-yn-1-yl)benzoate (S11)

To a solution of $(\pi\text{-allyl})_2Pd_2Cl_2$ (46 mg, 0.13 mmol), IAd (99 mg, 0.25 mmol), CuI (108 mg, 0.56 mmol), and Cs_2CO_3 (1.14 g, 3.5 mmol) in DMF-Et_2O (1:2) (5 mL) was added alkyne **S6** (0.46 mL, 1.88 mmol), and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (**S10**) (0.60 mL, 2.5 mmol) at room temperature. The reaction mixture was stirred at 40 °C for 24 h and concentrated under vacuo and purified by column chromatography on silica gel (CH_2Cl_2 : Hexane = 1 : 30 to 1 : 8) to give alkyne **S11** (629 mg, 1.24 mmol, 67% from **S6**).

S11: yellow oil; IR (neat): 1733 cm^{-1}; 1H-NMR (600 MHz, $CDCl_3$): δ 7.91 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 3.92 (s, 3H), 2.82 (t, J = 7.6 Hz, 2H), 2.56-2.42 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 166.6, 134.2, 132.0, 131.6, 130.3, 127.7, 123.6, 91.5, 80.4, 52.0, 30.6 (t, $^1J_{CF}$ = 21.7 Hz), 11.9 (t, $^2J_{CF}$ = 5.8 Hz); ^{19}F-NMR (562 MHz, $CDCl_3$): δ 83.9 (s, 3F), 118.3 (s, 2F), 125.1 (s, 2F), 126.0 (s, 2F), 126.7 (s, 2F), 129.3 (s, 2F); HRMS (EI): calcd for $C_{18}H_{11}O_2F_{13}$ (M^+): 506.0551, found 506.0543.

2-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodec-1-yn-1-yl)benzoic acid (S12)

To a solution of benzoate **S11** (1.37 g, 2.71 mmol) in TFE (7.3 mL) was added 2 M KOH (7.3 mL) at room temperature. The reaction mixture was stirred at 50 °C for 10 h. The mixture was added 1 M HCl (15 mL), and the mixture was extracted with Et_2O (20 mL × 3), and concentrated under vacuo. The crude mixture was dissolved in CH_2Cl_2 (10 mL) and extracted with 1 M NaOH (15 mL × 2), and neutralized with 1 M HCl (30 mL), and the mixture was extracted with Et_2O (30 mL × 3). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuo to give carboxylic acid **S12** (1.24 g, 2.5 mmol, 93%).

S12: white solid; mp. 78-80 °C; IR (neat): 1698 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.56-2.44 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 170.5, 134.3, 132.5, 131.2, 130.7, 127.9, 124.1, 92.7, 80.2, 30.4 (t, $^{1}J_{CF}$ = 21.7 Hz), 11.9 (t, $^{2}J_{CF}$ = 5.8 Hz); ^{19}F-NMR (562 MHz, $CDCl_3$): δ 83.9 (s, 3F), 118.3 (s, 2F), 125.1 (s, 2F), 126.0 (s, 2F), 126.7 (s, 2F), 129.3 (s, 2F); HRMS (EI): calcd for $C_{17}H_9O_2F_{13}$ (M^+): 492.0395, found 492.0373.

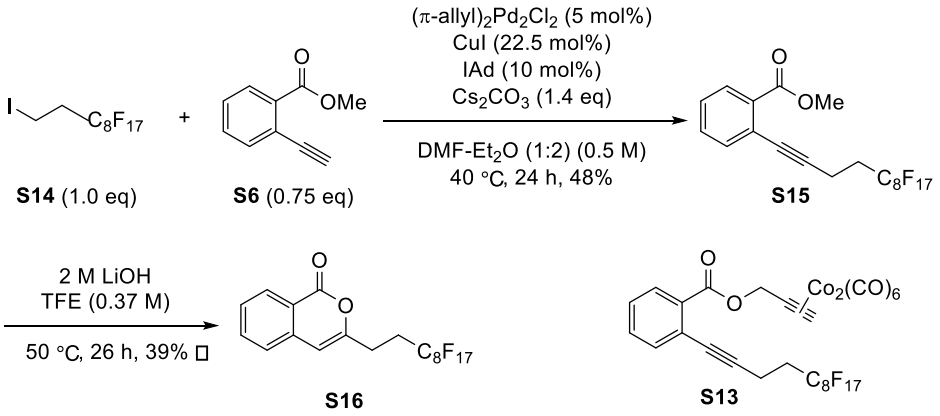
Reagent 2

To a solution of benzoic acid **S12** (248 mg, 0.50 mmol) in CH_2Cl_2 (5.0 mL) was added $(COCl)_2$ (56 μL, 0.65 mmol) and DMF (10 μL, 0.13 μmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated under vacuo. To the residue was added CH_2Cl_2 (5.0 mL), pyridine (0.38 mL, 5.0 mmol) and then alkyne cobalt complex **S3** (128 mg, 0.38 mmol). The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (10 mL), extracted with CH_2Cl_2 (15 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 100) to give reagent **2** (257 mg, 0.31 mmol, 84% from **S3**).

2: red solid; IR (neat): 2029, 1733 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 6.13 (s, 1H), 5.52 (s, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.61-2.45 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 199.1, 165.2, 134.4, 132.0, 131.1, 130.2, 127.7, 124.3, 92.0, 88.6, 80.4, 72.1, 65.4, 30.5 (t, $^{1}J_{CF}$ = 23.1 Hz), 11.9 (t, $^{2}J_{CF}$ = 5.8 Hz); ^{19}F-NMR (562 MHz, $CDCl_3$): δ 83.9 (s, 3F), 118.3 (s, 2F), 125.0 (s, 2F), 125.9 (s, 2F), 126.6 (s, 2F), 129.2 (s, 2F); HRMS

(ESI): calcd for $C_{26}H_{11}O_8Co_2F_{13}Na$ ([M+Na]$^+$): 838.8803, found 838.8793.

2-5. Attempted synthesis of reagent S13



2-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododec-1-yn-1-yl)benzoate (S15)

To a solution of (π-allyl)$_2$Pd$_2$Cl$_2$ (28 mg, 75 μmol), IAd (56 mg, 0.15 mmol), CuI (65 mg, 0.34 mmol), Cs_2CO_3 (684 mg, 2.1 mmol) in DMF-Et_2O (1:2) (3 mL) was added alkyne **S6** (0.16 mL, 1.1 mmol), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (**S14**) (861 mg, 1.5 mmol) at room temperature. The reaction mixture was stirred at 40 °C for 24 h and concentrated under vacuo and purified by column chromatography on silica gel (CH_2Cl_2 : Hexane = 1 : 30 to 1 : 8) to give alkyne **S15** (327 mg, 0.54 mmol, 48% from **S6**).

S15: yellow oil; IR (neat): 2926, 1735 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.57-2.44 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 166.6, 134.2, 132.0, 131.6, 130.3, 127.7, 123.6, 91.5, 80.4, 52.1, 30.6 (t, $^1J_{CF}$ = 21.7 Hz), 11.9 (t, $^2J_{CF}$ = 5.8 Hz); ^{19}F-NMR (562 MHz, $CDCl_3$): δ 83.9 (s, 3F), 117.8 (s, 2F), 1118.3 (s, 2F), 124.8 (s, 2F), 125.0 (s, 2F), 125.8 (s, 2F), 126.6 (s, 2F), 129.2 (s, 2F);

HRMS (EI): calcd for $C_{20}H_{11}O_2F_{17}$ (M^+): 606.0488, found 606.0482.

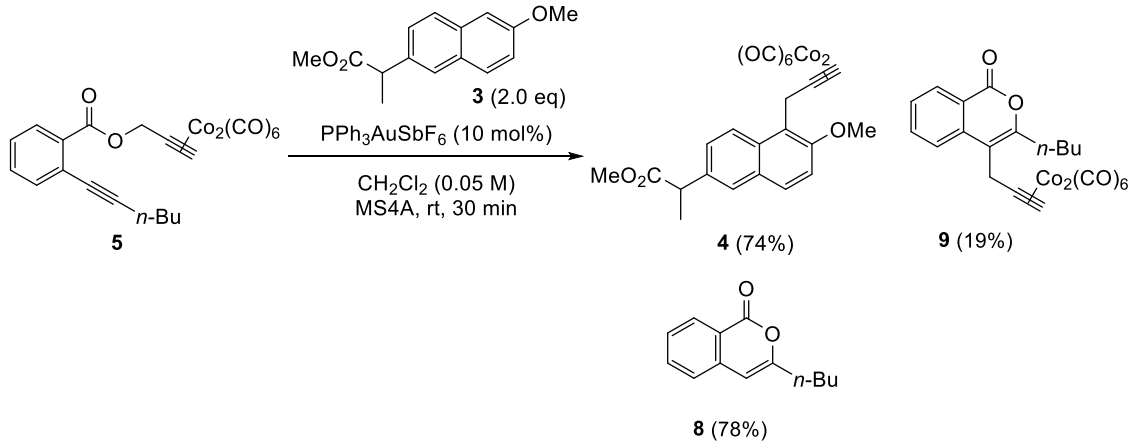
3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1*H*-isochromen-1-one (S16)

To a solution of benzoate **S15** (327 mg, 0.54 mmol) in TFE (1.5 mL) was added 2 M KOH (1.5 mL) at room temperature. The reaction mixture was stirred at the same temperature for 26 h. The mixture was added 1 M HCl (5 mL), and the mixture was extracted with Et_2O (15 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20) to give isocoumalin **S16** (124 mg, 0.21 mmol, 39%). Carboxylic acid was not obtained.

S16: white solid; mp. 74-76 °C; IR (neat): 1718 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.27 (d, J = 7.5 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 2.86 (t, J = 7.5 Hz, 2H), 2.62-2.49 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 162.4, 154.2, 136.9, 135.0, 129.7, 128.3, 125.3, 120.3, 104.2, 28.7 (t, $^1J_{CF}$ = 22.9 Hz), 25.0 (t, $^2J_{CF}$ = 4.3 Hz); ^{19}F-NMR (562 MHz, $CDCl_3$): δ 83.9 (s, 3F), 117.5 (s, 2F), 117.9 (s, 2F), 124.8 (s, 2F), 125.0 (s, 2F), 125.8 (s, 2F), 126.5 (s, 2F), 129.2 (s, 2F); HRMS (EI): calcd for $C_{19}H_9O_2F_{17}$ (M^+): 592.0331, found 592.0310.

3. Reagent screening

3-1. Reaction of reagent 5 with substrate 3



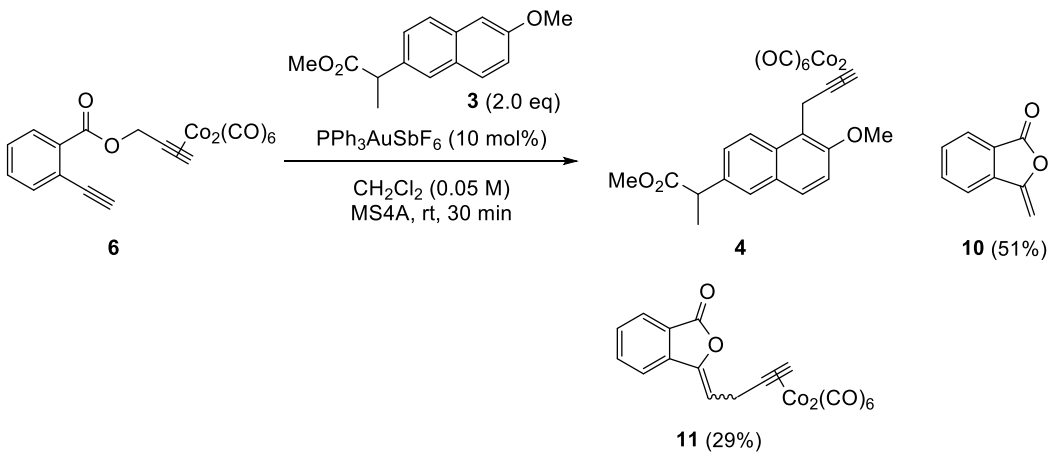
To a solution of **5** (0.1 mmol), naproxen methyl ester **3** (0.2 mmol) and MS4A (50 mg) in CH_2Cl_2 (1.6 mL) was added a solution of 2.5 mM PPh_3AuSbF_6 in CH_2Cl_2 (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), extracted with CH_2Cl_2 (4 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo to give a crude mixture of **4** and **8** and **9**. The ratio was determined by ^{1}H-NMR used toluene as the internal standard.

The analytical samples were obtained by extensive PTLC (AcOEt : hexane = 1 : 8).

8: Characterization data were in agreement with previously reported values.[5]

9: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 7.6 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.6, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 5.93 (s, 1H), 4.19 (s, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.77 (quint, *J* = 7.5 Hz, 2H), 1.45 (sext, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.3, 162.2, 155.6, 137.0, 134.5, 130.2, 127.7, 122.8, 120.8, 111.5, 93.1, 73.8, 30.9, 29.8, 22.5, 13.8; HRMS (EI): calcd for $C_{19}H_{16}O_5Co_2$ ([M-3CO]$^+$): 441.9662, found 441.9668.

3-2. Reaction of reagent 6 with substrate 3



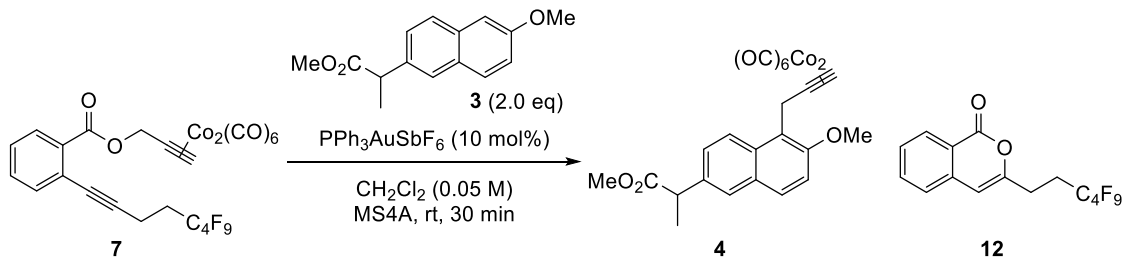
To a solution of **6** (0.1 mmol), naproxen methyl ester **3** (0.2 mmol) and MS4A (50 mg) in CH_2Cl_2 (1.6 mL) was added a solution of 2.5 mM PPh_3AuSbF_6 in CH_2Cl_2 (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), extracted with CH_2Cl_2 (4 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo to give crude mixture of **4** and **10** and **11**. The ratio was determined by ^{1}H-NMR used toluene as the internal standard.

The analytical samples were obtained by PTLC (AcOEt : Hexane 1 : 8).

10: Characterization data were in agreement with previously reported values.[6]

11: red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.75 (t, J = 7.8 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 6.09 (s, 1H), 6.01 (t, J = 8.3 Hz, 1H), 4.11 (d, J = 8.3 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.3, 166.5, 146.8, 137.6, 134.5, 130.3, 126.4, 125.9, 122.9, 110.8, 93.2, 72.8, 30.5; HRMS (ESI): calcd for $C_{18}H_8O_8Co_2Na$ ([M+Na]$^+$): 492.8775, found 492.8765.

3-3. Reaction of reagent 7 with substrate 3

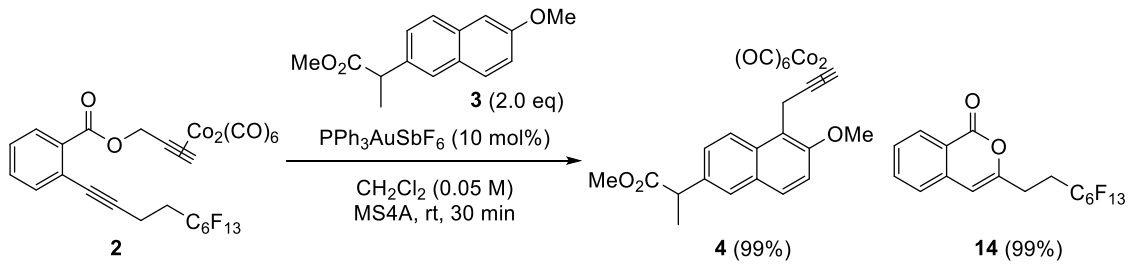


To a solution of **7** (71.6 mg, 0.1 mmol), naproxen methyl ester **3** (60.6 mg, 0.2 mmol) and MS4A (50 mg) in CH_2Cl_2 (1.6 mL) was added a solution of 2.5 mM PPh_3AuSbF_6 in CH_2Cl_2 (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. aq. $NaHCO_3$ (2 mL), extracted with CH_2Cl_2 (7 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo to give crude mixture of **3** and **4** and **12**. The ratio was determined by ^{1}H-NMR used toluene as the internal standard.

The analytical samples were obtained by PTLC (AcOEt : Hexane 1 : 8).

12: white solid; mp. 50-52 °C; IR (neat): 1734 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.27 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 6.37 (s, 1H), 2.86 (t, J = 7.6 Hz, 2H), 2.65-2.47 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 162.3, 154.2, 136.9, 135.0, 129.7, 128.3, 125.3, 120.3, 104.3, 28.6 (t, $^1J_{CF}$ = 21.7 Hz), 25.0 (t, $^2J_{CF}$ = 4.3 Hz); HRMS (EI): calcd for $C_{15}H_9F_9O_2$ (M^+): 392.0459, found 392.0477.

3-4. Reaction of reagent 2 with substrate 3

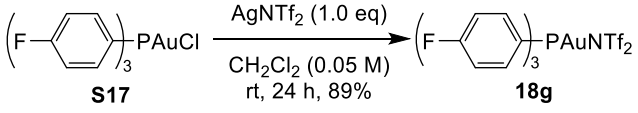


To a solution of **2** (81.6 mg, 0.1 mmol), naproxen methyl ester **3** (60.6 mg, 0.2 mmol) and MS4A (50 mg) in CH_2Cl_2 (1.6 mL) was added a solution of 2.5 mM PPh_3AuSbF_6 in CH_2Cl_2 (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. aq. $NaHCO_3$ (2 mL), extracted with CH_2Cl_2 (7 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo to give crude mixture of **3** and **4** and **14**. The ratio was determined by ^{1}H-NMR used toluene as the internal standard.

The analytical samples were obtained by PTLC (AcOEt : Hexane 1 : 8).

14: white solid; mp. 54-56 °C; IR (neat): 1736 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.28 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 6.38 (s, 1H), 2.87 (t, J = 8.2 Hz, 2H), 2.61-2.48 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 162.3, 154.2, 136.9, 135.0, 129.7, 128.3, 125.3, 120.3, 104.2, 28.7 (t, $^1J_{CF}$ = 22.9 Hz), 25.0 (t, $^2J_{CF}$ = 4.3 Hz); ^{19}F-NMR (562 MHz, $CDCl_3$): δ 83.9 (s, 3F), 117.9 (s, 2F), 125.0 (s, 2F), 126.0 (s, 2F), 126.5 (s, 2F), 129.2 (s, 2F) ; HRMS (EI): calcd for $C_{17}H_9F_{13}O_2$ (M^+): 492.0395, found: 492.0366.

4. Synthesis of gold catalyst 18g

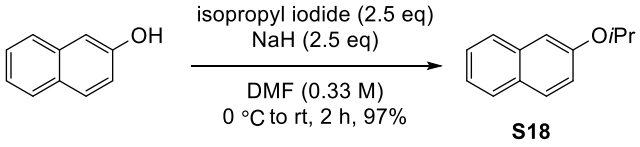


To CH_2Cl_2 (5.2 mL) was added gold catalyst **S17** (164 mg, 0.3 mmol), $AgNTf_2$ (116 mg, 0.3 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 24 h. AgCl was removed by filtration through Celite and concentrated under vacuo to give gold catalyst **18g** (211 mg, 0.27 mmol, 89%).

18g: white crystal; IR (neat): 1590, 1496 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55-7.44 (m, 2H), 7.30-7.19 (m, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.5 (dd, $^1J_{CF}$ = 257.2 Hz, $^1J_{CP}$ = 3.3 Hz), 136.3 (dd, $^2J_{CP}$ = 15.6 Hz, $^2J_{CF}$ = 9.0 Hz), 122.7 (dd, $^3J_{CP}$ = 69.6 Hz, $^3J_{CF}$ = 3.3 Hz), 119.4 (q, $^5J_{CF}$ = 322.8 Hz), 117.5 (dd, $^4J_{CF}$ = 22.1 Hz, $^4J_{CP}$ = 13.9 Hz); HRMS (EI): calcd for $C_{20}H_{12}F_9NO_4PS_2Au$ (M^+): 792.9467, found: 792.9479.

5. Synthesis of substrates

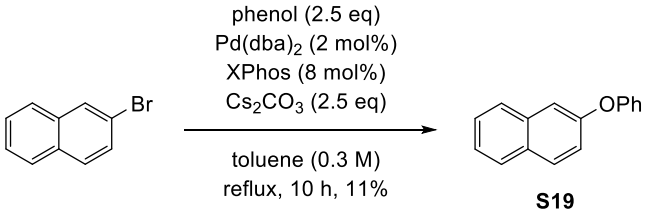
2-Isopropoxynaphthalene (S18)



S18

To a solution of 2-naphthol (446 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added isopropyl iodide (0.50 mL, 5.0 mmol). The reaction mixture was allowed to room temperature and stirred for 2 h. The solution was quenched with sat. NH_4Cl aq. (10 mL) at 0 °C and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give isoproxyether **S18** (362 mg, 1.88 mmol, 97%). Characterization data were in agreement with previously reported values.[7]

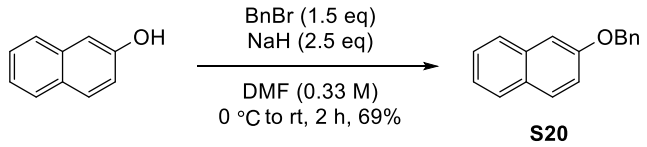
2-Phenoxynaphthalene (S19)



S19

To solution of 2-bromonaphthalene (414 mg, 2.0 mmol) in toluene (6.7 mL) was added Cs_2CO_3 (3.26 g, 5.0 mmol), XPhos (76 mg, 0.16 mmol), $Pd(dba)_2$ (18 mg, 40 μmol), and phenol (471 mg, 5.0 mmol) at room temperature. The reaction mixture was heated to reflux and stirred for 10 h. The solution was quenched with H_2O (10 mL) at room temperature and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (Hexane) to give phenyl ether **S19** (48.7 mg, 0.22 mmol, 11%). Characterization data were in agreement with previously reported values.[8]

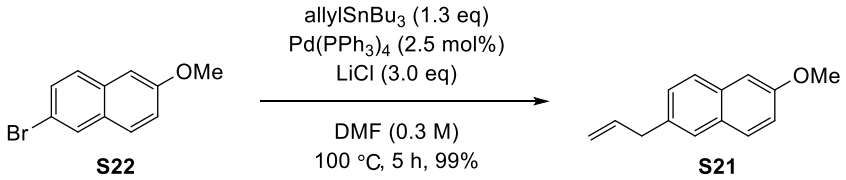
2-(Benzyloxy)naphthalene (20)



S20

To a solution of 2-naphthol (446 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added BnBr (0.36 mL, 3.0 mmol). The reaction mixture was allowed to room temperature and stirred for 2 h. The solution was quenched with MeOH (5.0 mL) and sat. NH_4Cl aq. (10 mL) at 0 °C and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give benzyl ether **S20** (322 mg, 1.37 mmol, 69%). Characterization data were in agreement with previously reported values.[9]

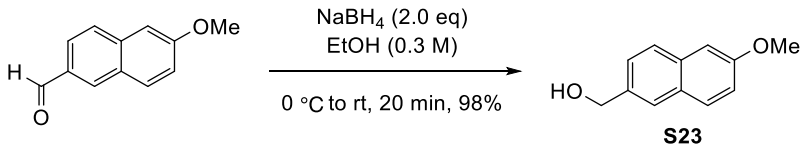
2-Allyl-6-methoxynaphthalene (S21)



S22 **S21**

To a solution of bromide (**S22**) (120 mg, 0.5 mmol) in DMF (1.7 mL) was added LiCl (64 mg, 1.0 mmol), $Pd(PPh_3)_4$ (15 mg, 13 μmol), and allyltributyltin (0.2 mL, 0.65 mmol) at room temperature. The reaction mixture was heated to 100 °C and stirred for 5 h. The solution was quenched with sat.$NaHCO_3$ aq. (2 mL) at room temperature and extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel including 10% K_2CO_3 (AcOEt : Hexane = 1 : 50) to give alkene **S21** (98.7 mg, 0.49 mmol, 99%). Characterization data were in agreement with previously reported values.[10]

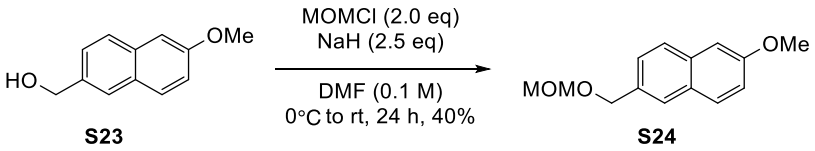
2-(1-Hydroxymethyl)-6-methoxynaphthalene (S23)



S23

To a solution of 6-methoxy-2-naphthaldehyde (376 mg, 2.0 mmol) in EtOH (6.7 mL) added $NaBH_4$ (151 mg, 4.0 mmol) at 0 °C. The reaction mixture was allowed to room temperature and stirred for 20 min. The solution was added sat. NH_4Cl aq. (10 mL) slowly at 0 °C and extracted with Et_2O (15 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1: 4) to give alcohol **S23** (370 mg, 1.96 mmol, 98%). Characterization data were in agreement with previously reported values.[11]

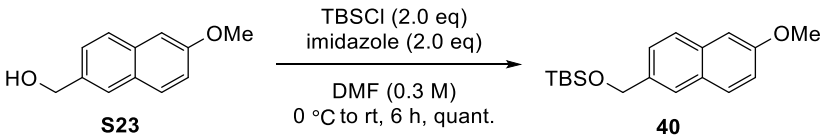
2-Methoxy-6-((methoxymethoxy)methyl)naphthalene (S24)



S23 **S24**

To a solution of alcohol **S23** (94 mg, 0.5 mmol) in DMF (5.0 mL) was added 60% NaH (50 mg, 1.3 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MOMCl (76 μL, 1.0 mmol). The reaction mixture was allowed to room temperature and stirred for 24 h. The solution was quenched with sat. NH_4Cl aq. (5 mL) at 0 °C and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 10) to give ether **S24** (94 mg, 0.34 mmol, 40%). Characterization data were in agreement with previously reported values.[12]

***Tert*-butyl((6-methoxynaphthalen-2-yl)methoxy)dimethylsilane (40)**



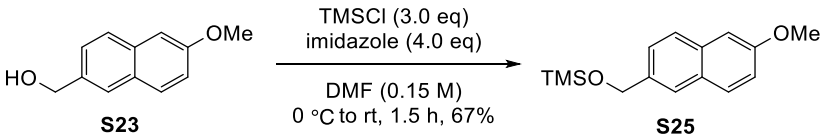
S23 **40**

To a solution of alcohol **S23** (94 mg, 0.5 mmol) and imidazole (64 mg, 1.0 mmol) in DMF (1.7 mL) was added TBSCl (150 mg, 1.0 mmol) at 0 °C. The reaction mixture was stirred for 6 h at room temperature. The solution was quenched with sat. NH_4Cl aq. (2 mL) at 0 °C and extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was concentrated under vacuo and purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give TBS ether **40** (153 mg, quant.).

40: white solid; IR (neat): 1606 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76-7.67 (m, 3H), 7.45 (d, J = 8.7 Hz, 1H), 7.13 (dd, J = 7.2 Hz, J = 2.4 Hz, 1H), 7.12 (s, 1H), 4.86 (s, 2H),

3.92 (s, 3H), 0.96 (s, 9H), 0.12 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.4, 136.8, 133.8, 129.3, 128.8, 126.7, 125.3, 124.4, 118.7, 105.8, 65.2, 55.3, 26.0, 18.5, -5.2; HRMS (EI): calcd for $C_{18}H_{26}O_2Si$ (M^+): 302.1702, found: 302.1703.

((6-Methoxynaphthalen-2-yl)methoxy)trimethylsilane (S25)

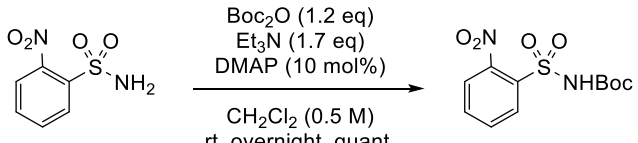


S23 **S25**

To a solution of alcohol **S23** (94 mg, 0.5 mmol) and imidazole (136 mg, 2.0 mmol) in DMF (3.3 mL) was dropwised TMSCl (0.19 mL, 1.5 mmol) at 0 °C. The reaction mixture was stirred for 1.5 h at room temperature. The solution was quenched with H_2O (2 mL) at 0 °C and extracted with Hexane (5 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 100) to give TMS ether **S25** (87.7 mg, 0.34 mmol, 67%).

S25: white solid; IR (neat): 1609 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84-7.64 (m, 3H), 7.40 (dd, J = 8.5 Hz, J = 1.4 Hz, 1H), 7.18-7.08 (m, 2H), 4.82 (s, 2H), 3.92 (s, 3H), 0.17 (s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.5, 136.2, 133.9, 129.3, 128.8, 126.9, 125.7, 125.0, 118.7, 105.7, 64.8, 55.3, -0.3; HRMS (EI): calcd for $C_{15}H_{20}O_2Si$ (M^+): 260.1233, found: 260.1233.

***Tert*-butyl ((4-nitrophenyl)sulfonyl)carbamate (S26)**

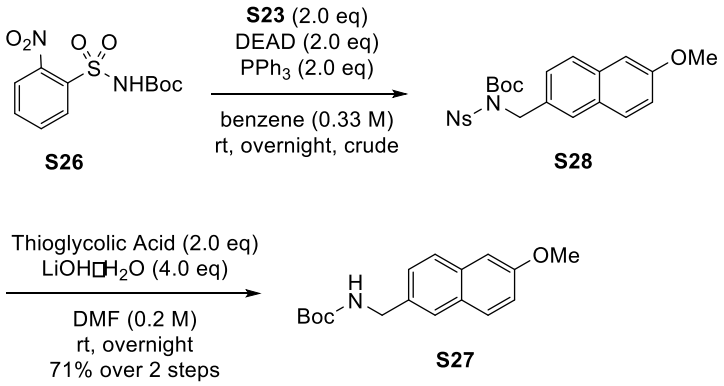


S26

To a solution of nosylamide (1.04 g, 5.2 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (1.1

mL, 8.7 mmol), DMAP (63 mg, 0.52 mmol), and Boc_2O (1.35 g, 6.2 mmol) at room temperature. The reaction mixture was stirred at the same temperature overnight. The solution was quenched with sat. 1 M HCl (10 mL) at 0 °C and filtered, and washed with Hexane : Et_2O = 1 : 2 (10 mL) to carbamate **S26** (1.40 g, quant.). Characterization data were in agreement with previously reported values.[13]

***Tert*-butyl ((6-methoxynaphthalen-2-yl)methyl)carbamate (S27)**



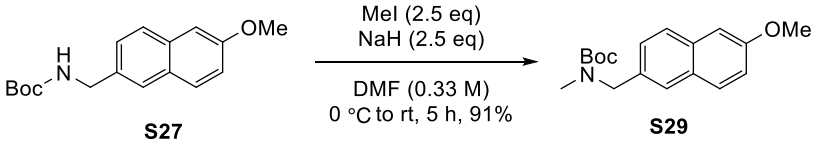
To a solution of alcohol **S23** (263 mg, 1.38 mmol), carbamate **S26** (235 mg, 0.77 mmol), and PPh_3 (367 mg, 1.54 mmol) in benzene (4.5 mL) was dropwised ca. 2.2 M DEAD in toluene (0.71 mL, 1.56 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. The solution was quenched with H_2O (5 mL) at 0 °C and extracted with CH_2Cl_2 (7 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel ($CHCl_3$) to give carbamate **S28** (crude).

To a solution of carbamate **S28** (crude) in DMF (4.0 mL) was added $LiOH•H_2O$ (130 mg, 3.08 mmol), and thioglycol acid (0.11 mL, 1.54 mmol) at room temperature. The reaction mixture was stirred overnight. The solution was quenched with sat. $NaHCO_3$ aq. (5 mL) and extracted with Et_2O (8 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 5) to give carbamate **S27** (156 mg,

0.54 mmol, 71% over 2 steps).

S27: white solid; IR (neat): 3350 (br), 1697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.7, 1H), 7.70 (d, *J* = 8.7, 1H), 7.64 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.20-7.08 (m, 2H), 4.87 (brs, 1H), 4.44 (d, *J* = 5.3 Hz, 2H), 3.92 (s, 3H), 1.48 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.5, 155.9, 134.0, 133.7, 129.0, 128.7, 127.0, 126.2, 125.7, 118.8, 105.6, 79.2, 55.1, 44.6, 28.3; HRMS (EI): calcd for $C_{17}H_{21}NO_3$ (M^+): 287.1521, found: 287.1504.

***Tert*-butyl ((6-methoxynaphthalen-2-yl)methyl)(methyl)carbamate (S29)**



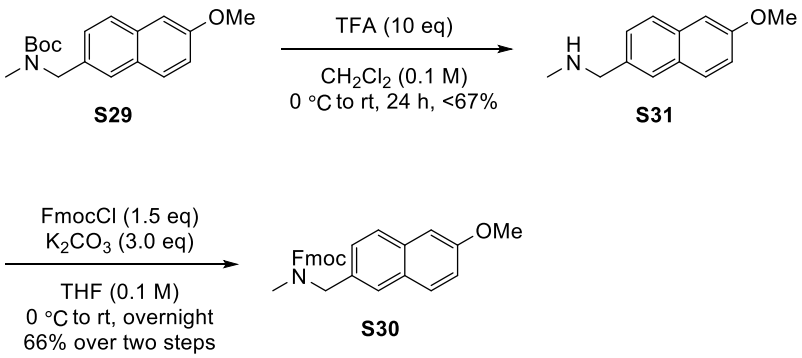
S27 **S29**

To a solution of carbamate **S27** (156 mg, 0.54 mmol) in DMF (1.8 mL) was added 60% NaH (82 mg, 1.4 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MeI (86 μL, 1.0 mmol). The reaction mixture was allowed to room temperature and stirred for 5 h. The solution was quenched with sat. NH_4Cl aq. (2 mL) at 0 °C and extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 10) to give carbamate **S29** (149 mg, 0.49 mmol, 91%).

S29 (a mixture of two rotamers): yellowish oil; IR (neat): 1692 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.3, 1H), 7.68 (d, *J* = 8.9, 1H), 7.56 (s, 1H), 7.32 (brs, 1H), 7.19-7.05 (m, 2H), 4.52 (s, 2H), 3.88 (s, 3H), 2.86 (brs, 1.5H), 2.79 (brs, 1.5H), 1.50 (s, 9H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 157.6, 156.2, 155.9, 133.8, 133.2, 129.1, 128.8, 127.2, 126.6, 126.3, 126.0, 125.8, 118.9, 105.7, 79.7, 55.2, 52.7, 52.0, 33.8, 28.5; HRMS

(EI): calcd for $C_{18}H_{23}NO_3$ (M^+): 301.1678, found: 301.1702.

(9*H*-Fluoren-9-yl)methyl ((6-methoxynaphthalen-2-yl)methyl)(methyl)carbamate (S30)



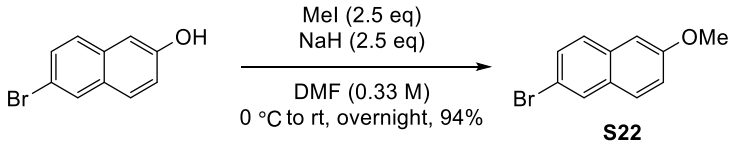
To a solution of carbamate **S29** (160 mg, 0.53 mmol) in CH_2Cl_2 (5.3 mL) was dropwised TFA (0.41 mL, 5.3 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. The solution was quenched with sat. 1 M NaOH (10 mL) at 0 °C and extracted with CH_2Cl_2 (15 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo to give amine **S31** (73.8 mg, <0.36 mmol, <67%).

To solution of crude in THF (3.6 mL) was added K_2CO_3 (150 mg, 1.09 mmol) and FmocCl (140 mg, 0.54 mmol) at 0 °C. The reaction mixture was stirred at the same temperature overnight. The solution was quenched with sat. NH_4Cl aq. (5 mL) at 0 °C and extracted with Et_2O (8 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (toluene : Hexane = 1 : 8) to give carbamate **S30** (149 mg, 0.35 mmol, 66% over 2 steps).

S30 (a mixture of two rotamers): amorphous; IR (neat): 1699 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.85-7.56 (m, 5H), 7.55-7.22 (m, 5H), 7.21-7.07 (m, 4H), 4.63 (s, 1H), 4.51 (s, 3H), 4.30 (brs, 0.5H), 4.25 (brs, 0.5H), 3.93 (s, 3H), 2.92 (brs, 1.5H), 2.87 (brs, 1.5H) ; ^{13}C-NMR (150 MHz, $CDCl_3$): δ 157.6, 156.7, 156.3, 144.03, 143.96, 141.3, 133.9,

132.5, 132.3, 129.2, 128.7, 127.6, 127.3, 127.0, 126.5, 125.8, 125.7, 125.0, 124.8, 119.9, 118.9, 105.7, 67.4, 55.2, 52.6, 52.2, 47.4, 47.3, 34.4, 33.4; HRMS (EI): calcd for $C_{28}H_{25}NO_3$ (M^+): 423.1834, found: 423.1815.

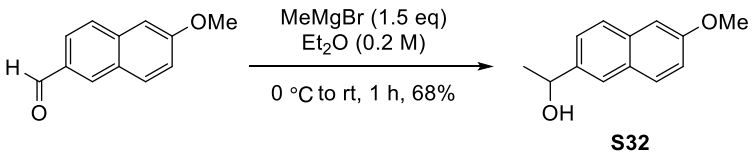
2-Bromo-6-methoxynaphthalene (S22)



S22

To a solution of 6-bromo-2-naphthol (446 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MeI (0.31 mL, 5.0 mmol). The reaction mixture was allowed to room temperature and stirred overnight. The solution was quenched with sat. NH_4Cl aq. (10 mL) at 0 °C and extracted with CH_2Cl_2 (10mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give methyl ether **S22** (446 mg, 1.88 mmol, 94%). Characterization data were in agreement with previously reported values.[14]

2-(1-Hydroxyethyl)-6-methoxynaphthalene (S32)

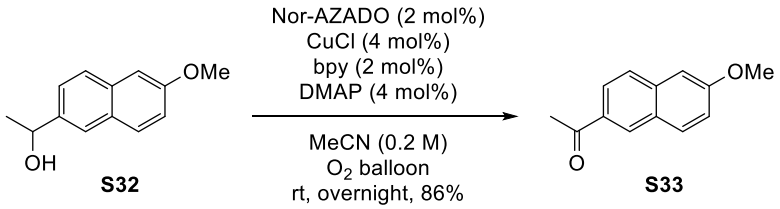


S32

To a solution of 6-methoxy-2-naphthaldehyde (376 mg, 3.0 mmol) in Et_2O (10 mL) was added ca. 3 M MeMgBr in Et_2O (1.0 mL, 3.0 mmol) over 3 min at 0 °C. The reaction mixture was allowed to room temperature and stirred for 1 h. The solution was quenched with 1 M HCl (10 mL) at 0 °C and extracted with Et_2O (15 mL × 3). The combined

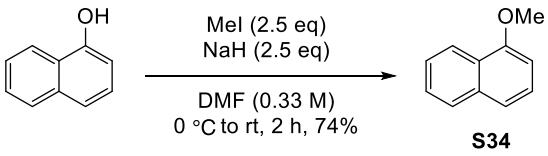
organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 8) to give alcohol **S32** (276 mg, 1.37 mmol, 68%). Characterization data were in agreement with previously reported values.[15]

2-Acetyl-6-methoxynaphthalene (S33)



To a solution of alcohol **S32** (101 mg, 0.50 mmol), DMAP (2.44 mg, 0.02 mmol), bpy (1.56 mg, 0.01 mmol) and Nor-AZADO (1.52 mg, 0.01 mmol) in MeCN (2.5 mL) was added CuCl (3.64 mg, 0.0368 mmol) at room temperature. The mixture was stirred at the same temperature under O_2 atomosphere overnight. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (5 mL), extracted with CH_2Cl_2 (7 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1: 20) to give ketone **S33** (87 mg, 0.43 mmol, 86%). Characterization data were in agreement with previously reported values.[16]

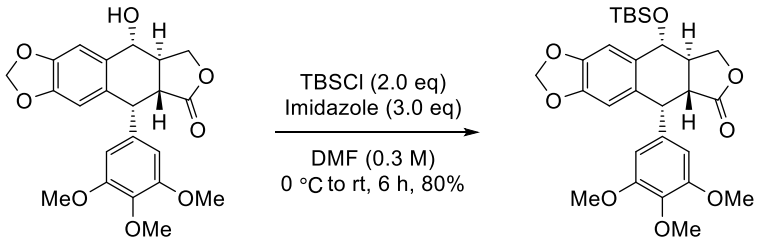
1-Methoxynaphthalene (S34)



To a solution of 1-naphthol (288 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MeI (0.31 mL, 5.0 mmol).

The reaction mixture was allowed to room temperature and stirred for 2 h. The solution was quenched with sat. NH_4Cl aq. (10 mL) at 0 °C and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 100) to give methyl ether **S34** (235 mg, 1.49 mmol, 74%). Characterization data were in agreement with previously reported values.[17]

(5*R*,5*aR*,8*aR*,9*R*)-9-((*Tert*-butyldimethylsilyl)oxy)-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-*d*][1,3]dioxol-6(5a*H*)-one (37).



37

To a solution of podophyllotoxin (207 mg, 0.5 mmol) and imidazole (102 mg, 1.5 mmol) in DMF (1.7 mL) was added TBSCl (150 mg, 1.0 mmol) at 0 °C. The reaction mixture was stirred for 6 h at room temperature. The solution was quenched with sat. NH_4Cl aq. (2 mL) at 0 °C and extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 2) to give TBS ether **37** (211 mg, 0.40 mmol, 80%). Characterization data were in agreement with previously reported values.[18]

6. Functionalization

Procedure A

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 μmol), reagent **2** (50 mg, 60 μmol), and DCE (1.0 mL) at room temperature. To the reaction mixture was added gold catalyst **18g** (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography to give a desired product.

Procedure B

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 μmol), reagent **2** (50 mg, 60 μmol), DCE (1.0 mL), and HFIP (0.1 mL) at room temperature. To the reaction mixture was added gold catalyst **18g** (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography to give a desired product.

Procedure C

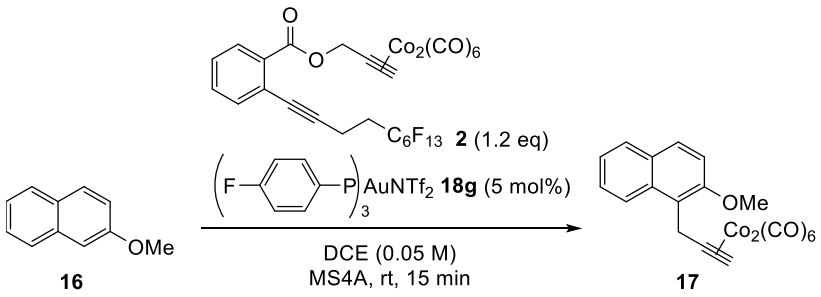
Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 μmol), reagent **2** (61 mg, 75 μmol), DCE (1.0 mL), and HFIP

(0.1 mL) at room temperature. To the reaction mixture was added gold catalyst **18g** (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography to give a desired product.

Procedure D

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 μmol), reagent **2** (50 mg, 60 μmol), and DCE (1.0 mL) at room temperature. To the reaction mixture was added gold catalyst **18g** (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (2 mL), and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography. After concentrated under vacuo, the residue was purified fluorous silica gel chromatography (H_2O : MeOH = 1 : 4). Fraction was extracted with CH_2Cl_2 (3 mL × 3) and then dried over $MgSO_4$, filtered, and concentrated under vacuo to give a desired product.

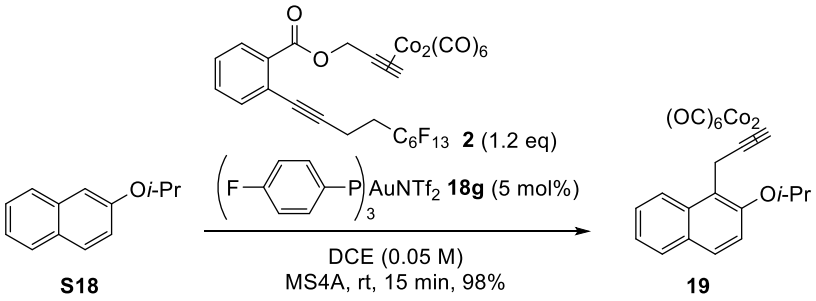
Functionalization of 2-methoxynaphthalene (16)



Procedure A was followed and used gold catalyst **18g** (1.98 mg, 2.5 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **17** (23.8 mg, 49.3 μmol, 99%).

17: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.7 Hz, 1H), 7.82-7.74 (m, 2H), 7.52 (brt, J = 7.2 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 8.7 Hz, 1H), 5.93 (s, 1H), 4.63 (s, 2H), 3.97 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 154.1, 132.7, 129.2, 128.9, 128.7, 126.5, 123.3, 123.2, 121.3, 112.4, 96.4, 73.6, 55.6, 29.0 ; HRMS (EI): calcd for $C_{19}H_{12}O_6Co_2$ ($[M-CO]^+$): 453.9298, found: 453.9312.

Functionalization of 2-isopropoxynaphthalene (S18)

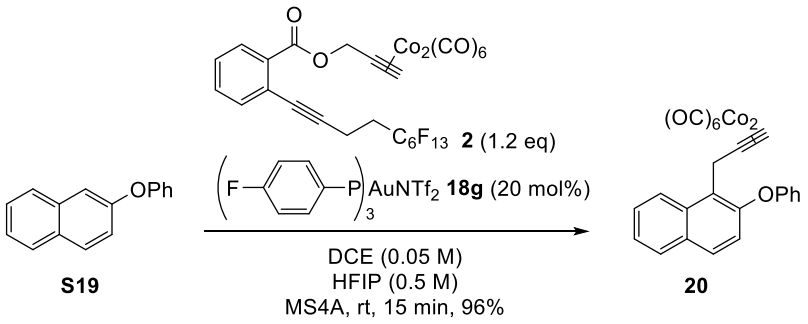


Procedure A was followed and used gold catalyst **18g** (1.98 mg, 2.5 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **19** (30.0 mg, 48.9 μmol, 98%).

19: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.2 Hz, 1H),

7.77 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 9.2 Hz, 1H), 7.52 (t, J = 8.2 Hz, 1H), 7.35 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 9.2 Hz, 1H), 5.91 (s, 1H), 4.72 (quint, J = 6.3 Hz, 1H), 4.63 (s, 2H), 1.42 (d, J = 6.3 Hz, 6H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.9, 152.7, 132.8, 129.2, 128.7, 128.6, 126.4, 123.41, 123.36, 122.6, 115.4, 96.4, 73.9, 71.3, 29.6, 22.4; HRMS (EI): calcd for $C_{19}H_{18}O_4Co_2$ ([M-5CO]$^+$): 369.9814, found: 369.9786.

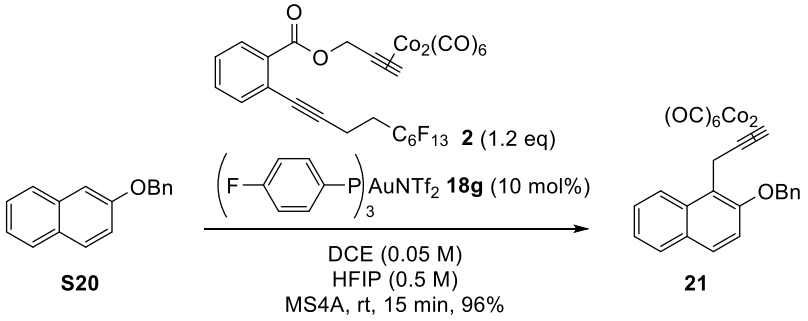
Functionalization of 2-phenoxynaphthalene (S19)



Procedure B was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **20** (26.2 mg, 48.2 μmol, 96%).

20: red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.60 (dt, J = 7.7 Hz, J = 1.0 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 7.7 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.7 Hz, 2H), 5.91 (s, 1H), 4.63 (s, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.6, 157.8, 151.0, 132.7, 131.1, 129.8, 129.2, 128.8, 126.7, 125.9, 124.9, 123.9, 122.8, 119.9, 117.6, 95.5, 73.7, 29.8; HRMS (EI): calcd for $C_{22}H_{14}O_4Co_2$ ([M-3CO]$^+$): 459.9556, found: 459.9544.

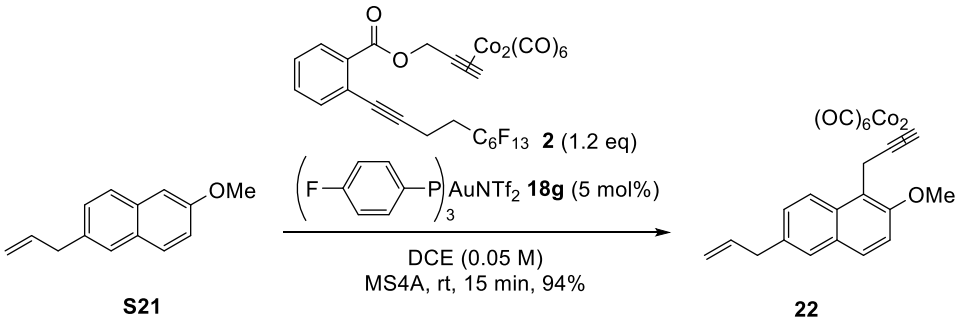
Functionalization of 2-(benzyloxy)naphthalene (S20)



Procedure B was followed and used gold catalyst **18g** (3.96 mg, 5.0 μmol). The crude mixture was purified by silica gel column chromatography (Hexane to CH_2Cl_2 : Hexane = 1 : 50) to give **21** (26.7 mg, 47.8 μmol, 96%).

21: red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.53 (dt, *J* = 8.2 Hz, *J* = 1.2 Hz, 1H), 7.51-7.45 (m, 2H), 7.43-7.32 (m, 4H), 7.30 (d, *J* = 9.2 Hz, 1H), 5.90 (s, 1H), 5.26 (s, 2H), 4.68 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 153.4, 137.1, 132.7, 129.4, 128.9, 128.64, 128.59, 127.9, 127.3, 126.6, 123.6, 123.4, 122.1, 114.2, 96.1, 73.9, 70.9, 29.5; HRMS (EI): calcd for $C_{23}H_{16}O_4Co_2$ ([M-3CO]$^+$): 473.9713, found: 473.9738.

Functionalization of 2-allyl-6-methoxynaphthalene (S21)

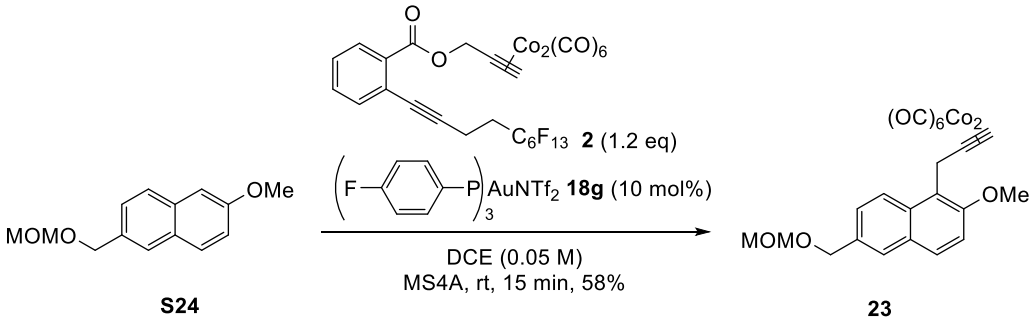


Procedure A was followed and used gold catalyst **18g** (1.98 mg, 2.5 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **22** (24.5 mg,

46.8 μmol, 94%).

22: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.57 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 6.13-5.98 (m, 1H), 5.92 (s, 1H), 5.14 (d, *J* = 5.8 Hz, 1H), 5.10 (s, 1H), 4.61 (s, 2H), 3.96 (s, 3H), 3.52 (d, *J* = 6.3 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 153.7, 137.4, 134.8, 131.3, 129.3, 128.4, 128.1, 127.4, 123.3, 121.1, 116.0, 112.5, 96.4, 73.6, 55.6, 40.0, 29.0; HRMS (EI): calcd for $C_{18}H_{16}O_2Co_2$ ($[M-5CO]^+$): 381.9814, found: 381.9833.

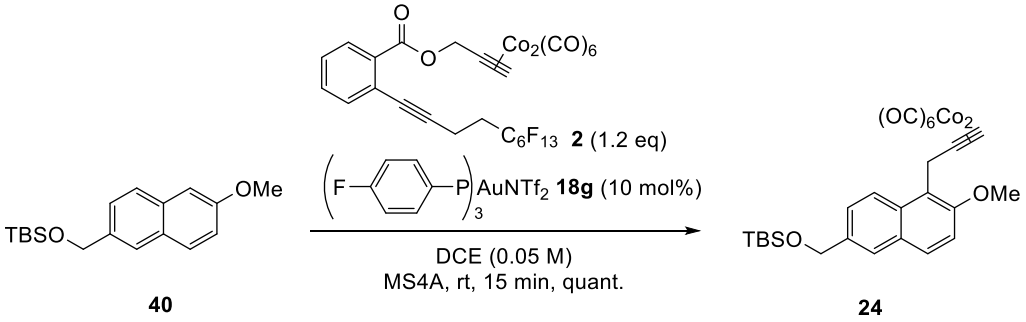
Functionalization of 2-methoxy-6-((methoxymethoxy)methyl)naphthalene (S24)



Procedure D was followed and used gold catalyst **18g** (3.96 mg, 5.0 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50) and then fluorous silica gel column chromatography to give **23** (16.1 mg, 29 μmol, 58%).

23: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.76 (s, 1H), 7.52 (dd, *J* = 9.2 Hz, *J* = 1.9 Hz, 1H), 7.25 (d, *J* = 9.2 Hz, 1H), 5.92 (s, 1H), 4.75 (s, 2H), 4.74 (s, 2H), 4.62 (s, 2H), 3.97 (s, 3H), 3.45 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 154.2, 132.6, 132.2, 128.92, 128.88, 127.6, 126.7, 123.6, 121.2, 112.6, 96.2, 73.5, 69.2, 55.6, 55.4, 29.0; HRMS (EI): calcd for $C_{20}H_{18}O_6Co_2$ ($[M-3CO]^+$): 471.9767, found: 471.9776.

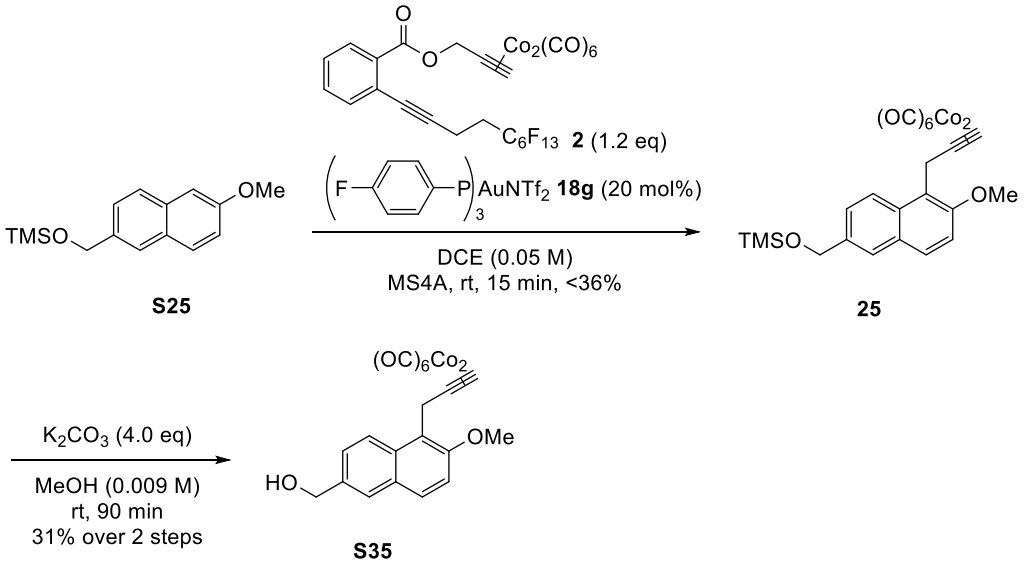
Functionalization of *tert*-butyl((6-methoxynaphthalen-2-yl)methoxy) dimethylsilane (40)



Procedure A was followed and used gold catalyst **18g** (3.96 mg, 5.0 μmol). The crude mixture was purified by silica gel column chromatography ($CHCl_3$: Hexane = 1 : 20 to $CHCl_3$: Hexane = 1 : 15) to give **24** (29.0 mg, quant.).

24: red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.71 (s, 1H), 7.48 (dd, J = 8.7 Hz, J = 1.0 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 5.92 (s, 1H), 4.88 (s, 2H), 4.62 (s, 2H), 3.96 (s, 3H), 0.97 (s, 9H), 0.13 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 153.9, 136.3, 131.9, 129.0, 128.8, 125.5, 125.3, 123.2, 121.2, 112.4, 96.4, 73.5, 65.1, 55.6, 29.1, 26.0, 18.5, -5.2; HRMS (EI): calcd for $C_{25}H_{28}O_6SiCo_2$ ($[M-2CO]^+$): 570.0319, found: 570.0313.

Functionalization of ((6-methoxynaphthalen-2-yl)methoxy)trimethylsilane (S25)



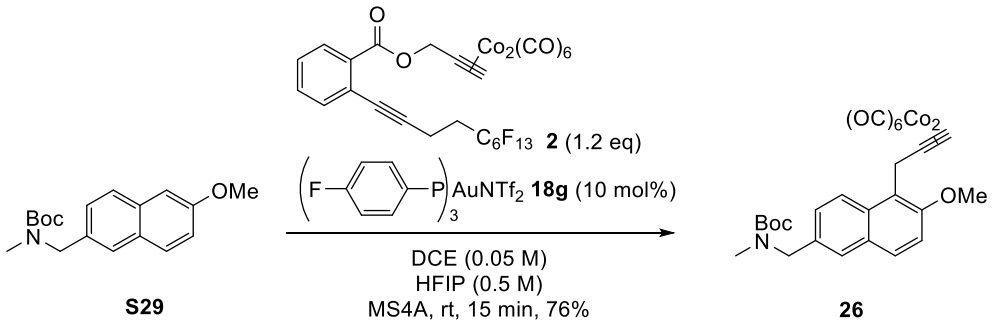
Procedure A was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography ($CHCl_3$: Hexane = 1 : 20 to $CHCl_3$: Hexane = 1 : 15) to give **25** (<10.46 mg, <17.9 μmol, <36%).

To a solution of **25** (<10.46 mg, <17.9 μmol, <36%) in MeOH (2.0 mL) was added K_2CO_3 (10 mg, 7.23 μmol) at room temperature. The reaction mixture was stirred for 90 min at the same temperature. The solution was quenched with sat. NH_4Cl aq. (1 mL) and extracted with CH_2Cl_2 (3 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30 to AcOEt : Hexane = 1 : 4) to give **S35** (7.86 mg, 15.3 μmol, 31% over 2 steps)

S35: red oil; IR (neat): 3321 (br), 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.76 (s, 1H), 7.53 (d, J = 8.7 Hz, 1H), 7.25 (d, J = 8.7 Hz, 1H), 5.92 (s, 1H), 4.84 (s, 2H), 4.62 (s, 2H), 3.97 (s, 3H), 1.70 (brs, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 154.2, 135.7, 132.2, 129.0, 128.9, 126.4, 126.0, 123.7,

121.3, 112.7, 96.3, 73.5, 65.4, 55.6, 29.0; HRMS (EI): calcd for $C_{16}H_{14}O_3Co_2$ ([M-5CO]$^+$): 371.9607, found: 371.9633.

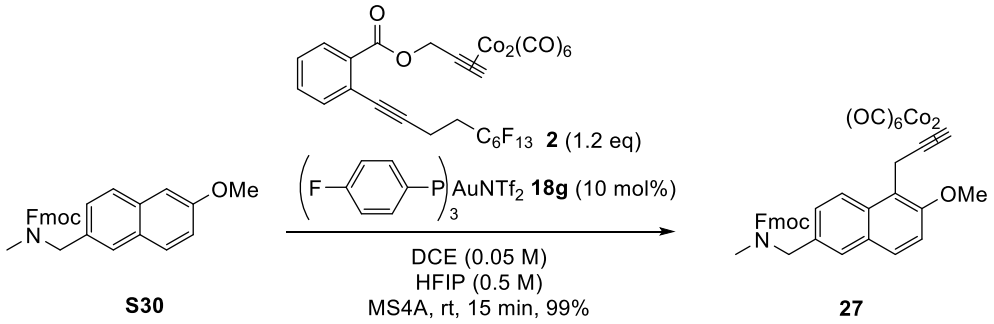
Functionalization of *tert*-butyl ((6-methoxynaphthalen-2-yl)methyl)(methyl) carbamate (S29)



Procedure B was followed and used gold catalyst **18g** (3.96 mg, 5.0 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to 1 : 20) to give **26** (23.8 mg, 38.0 μmol, 76%).

26 (a mixture of two rotamers): red oil; IR (neat): 2019, 1694 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.58 (brs, 1H), 7.41 (brs, 1H), 7.27-7.23 (m, 1H), 5.93 (s, 1H), 4.62 (s, 2H), 4.55 (brs, 2H), 3.97 (s, 3H), 2.88 (brs, 1.5H), 2.80 (brs, 1.5H), 1.49 (s, 9H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 199.8, 156.3, 155.9, 154.1, 133.0, 131.9, 129.0, 128.6, 127.5, 127.4, 127.3, 126.7, 126.2, 123.7, 121.3, 112.7, 96.3, 79.8, 73.5, 55.6, 52.6, 51.8, 33.9, 33.8, 29.0, 28.5; HRMS (FAB): calcd for $C_{22}H_{25}NO_4Co_2$ ([M-5CO]$^+$): 485.0448, found: 485.0455.

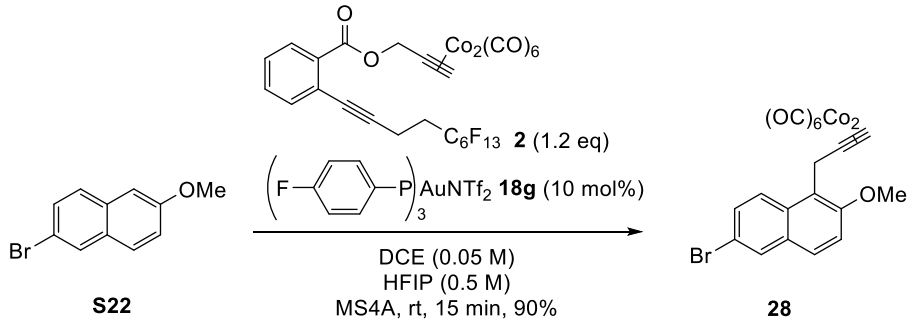
Functionalization of (9*H*-fluoren-9-yl)methyl ((6-methoxynaphthalen-2-yl) methyl)(methyl)carbamate (S30)



Procedure B was followed and used gold catalyst **18g** (3.96 mg, 5.0 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 30 to 1 : 10) to give **27** (35.4 mg, 49.9 μmol, 99%).

27 (a mixture of two rotamers): red oil; IR (neat): 2019, 1702 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.9 Hz, 0.5H), 7.87 (d, *J* = 8.2 Hz, 0.5H), 7.82-7.68 (m, 3H), 7.63 (brs, 1.5H), 7.51 (brd, *J* = 8.2 Hz, 1.5H), 7.41 (t, *J* = 6.8 Hz, 1.5H), 7.38-7.29 (m, 2H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.18 (brd, *J* = 6.8 Hz, 1.5H), 5.92 (s, 1H), 4.69-4.59 (m, 3H), 4.57-4.46 (m, 3H), 4.31 (brs, 0.5H), 4.25 (brs, 0.5H), 3.97 (s, 3H), 2.92 (brs, 1.5H), 2.88 (brs, 1.5H) ; ^{13}C-NMR (150 MHz, $CDCl_3$): δ 199.8, 156.8, 156.4, 154.2, 144.0, 141.4, 132.2, 132.0, 128.9, 128.7, 127.7, 127.6, 127.4, 127.0, 126.7, 126.1, 125.0, 124.9, 123.9, 121.3, 120.0, 112.7, 96.2, 73.5, 67.5, 55.6, 52.5, 52.2, 47.4, 34.4, 33.4, 29.7, 29.0; HRMS (FAB): calcd for $C_{34}H_{27}NO_6Co_2$ ([M-3CO]$^+$): 663.0502, found: 663.0504.

Functionalization of 2-bromo-6-methoxynaphthalene (S22)

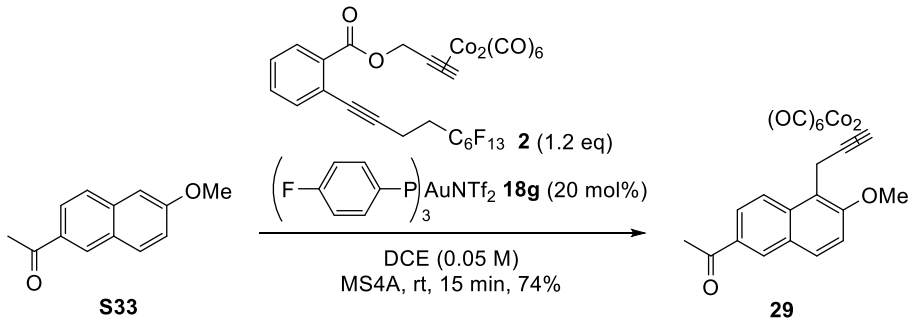


S22 28

Procedure B was followed and used gold catalyst **18g** (3.96 mg, 5.0 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **28** (25.2 mg, 44.9 μmol, 90%).

28: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 1.4 Hz, 1H), 7.82 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 1H), 7.58 (dd, *J* = 9.2 Hz, *J* = 1.4 Hz, 1H), 7.28 (s, 1H), 5.92 (s, 1H), 4.59 (s, 2H), 3.97 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 154.3, 131.1, 130.5, 130.2, 129.8, 128.0, 125.0, 121.5, 117.0, 113.4, 95.7, 73.4, 55.6, 28.8; HRMS (EI): calcd for $C_{16}H_{11}{}^{79}BrO_3Co_2$ ($[M-4CO]^+$): 447.8556, found: 447.8568.

Functionalization of 2-acetyl-6-methoxynaphthalene (S33)



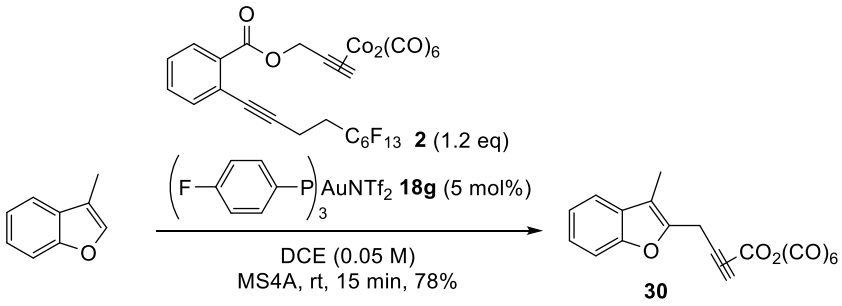
S33 29

Procedure A was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to

1 : 20) to give **29** (19.5 mg, 37.2 μmol, 74%).

29: red oil; IR (neat): 2017, 1677 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.08 (dd, *J* = 9.2 Hz, 1.9 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.33 (d, *J* = 9.2 Hz, 1H), 5.93 (s, 1H), 4.63 (s, 2H), 4.00 (s, 3H), 2.71 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 197.7, 156.3, 135.0, 132.3, 131.2, 130.9, 127.9, 124.6, 123.6, 121.6, 113.1, 95.6, 73.5, 55.6, 28.8, 26.5; HRMS (EI): calcd for $C_{17}H_{14}O_3Co_2$ ([M-5CO]$^+$): 383.9607, found: 383.9607.

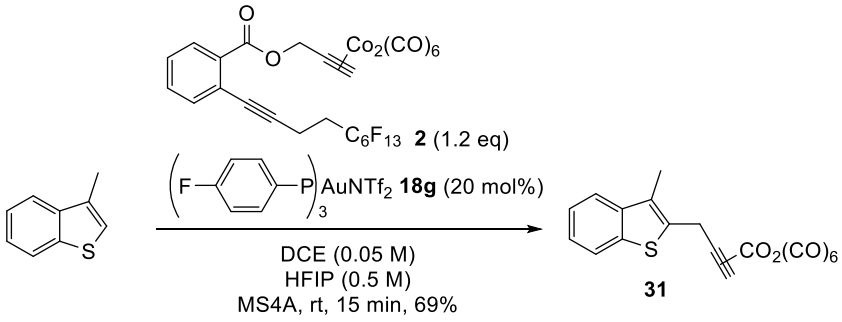
Functionalization of 3-methylbenzofuran



Procedure A was followed and used gold catalyst **18g** (1.98 mg, 2.5 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **30** (17.8 mg, 39.0 μmol, 78%).

30: red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 6.8 Hz, 1.4 Hz, 1H), 7.38 (dd, *J* = 6.8 Hz, 1.4 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1.9 Hz, 1H), 7.20 (dt, *J* = 7.2 Hz, 1.4 Hz, 1H), 6.09 (s, 1H), 4.23 (s, 2H), 2.23 (s, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.4, 153.9, 150.9, 129.8, 123.9, 122.2, 119.1, 111.1, 110.9, 93.3, 73.1, 30.4, 7.9; HRMS (EI): calcd for $C_{17}H_{10}O_7Co_2$ ([M-5CO]$^+$): 427.9141, found: 427.9161.

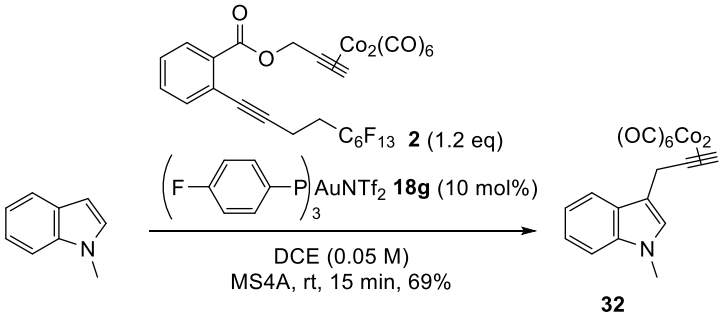
Functionalization of 3-metylbenzothiophene



Procedure B was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **31** (16.2 mg, 34.2 μmol, 68%).

31: red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 6.10 (s, 1H), 4.37 (s, 2H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.4, 140.3, 138.3, 136.5, 128.1, 124.2, 124.0, 122.2, 121.7, 95.1, 73.6, 32.7, 11.7; HRMS (EI): calcd for $C_{17}H_{10}O_5SCo_2$ ($[M\text{-}CO]^+$): 443.8913, found: 443.8926.

Functionalization of 1-methylindole

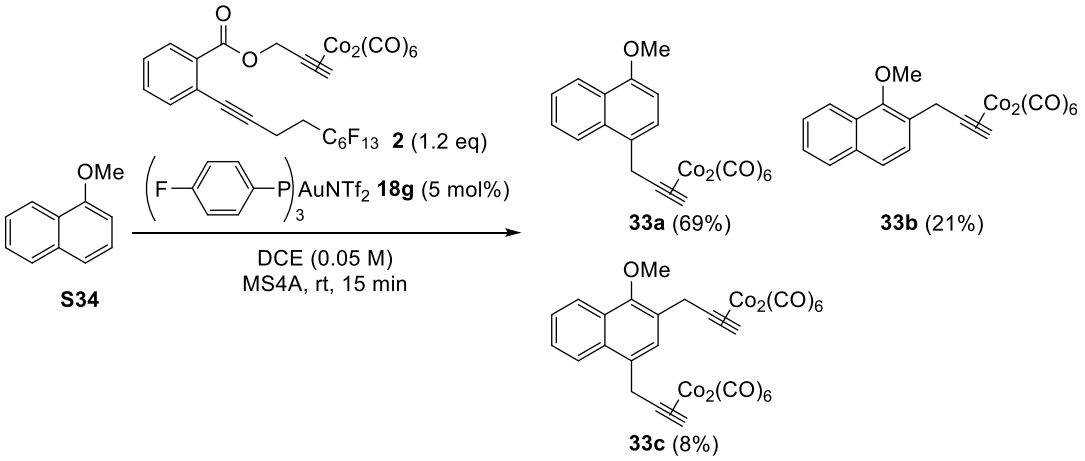


Procedure A was followed and used gold catalyst **18g** (3.96 mg, 5.0 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **32** (15.7 mg,

34.4 μmol, 69%).

32: red oil; IR (neat): 2015 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 6.05 (s, 1H), 4.27 (s, 2H), 3.75 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 137.0, 127.3, 126.9, 121.8, 119.0, 118.7, 114.1, 109.3, 98.9, 73.6, 32.6, 30.1; HRMS (EI): calcd for $C_{16}H_{11}NO_4Co_2$ ([M-2CO]$^+$): 398.9352, found: 398.9341.

Functionalization of 1-methoxynaphthalene (S34)



Procedure A was followed and used gold catalyst **18g** (1.98 mg, 2.5 μmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give **33a** (16.6 mg, 34.7 μmol, 69%), **33b** (5.17 mg, 10.7 μmol, 21%), **33c** (3.22 mg, 4.2 μmol, 8%).

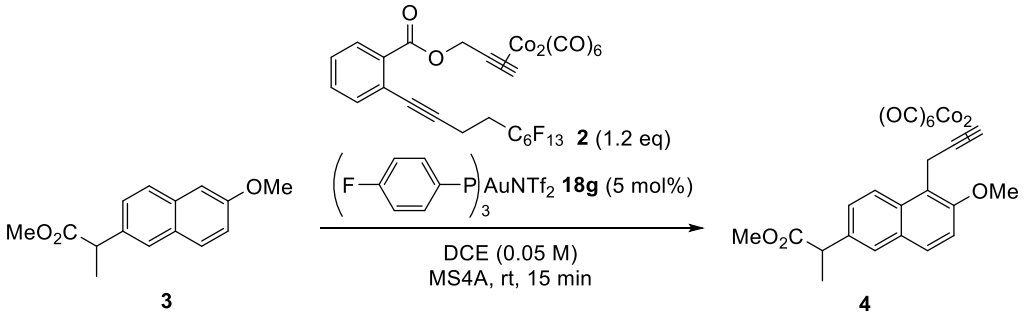
33a: red oil; IR (neat): 2016 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 5.94 (s, 1H), 4.49 (s, 2H), 3.98 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.6, 155.2, 132.2, 128.8, 126.9, 126.5, 126.1, 125.1, 123.7, 122.8, 103.3, 97.4, 73.7, 55.5, 37.5; HRMS (EI): calcd for $C_{15}H_{12}O_2Co_2$ ([M-5CO]$^+$): 341.9501,

found: 341.9494.

33b: red oil; IR (neat): 2020 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.54-7.43 (m, 2H), 7.46 (dt, *J* = 8.2 Hz, *J* = 1.5 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 6.07 (s, 1H), 4.30 (s, 2H), 3.99 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 153.7, 134.4, 128.4, 128.2, 128.1, 126.0, 125.7, 125.6, 124.3, 122.3, 96.6, 73.6, 62.2, 34.3; HRMS (EI): calcd for $C_{15}H_{12}O_2Co_2$ ([M-5CO]$^+$): 341.9501, found: 341.9510.

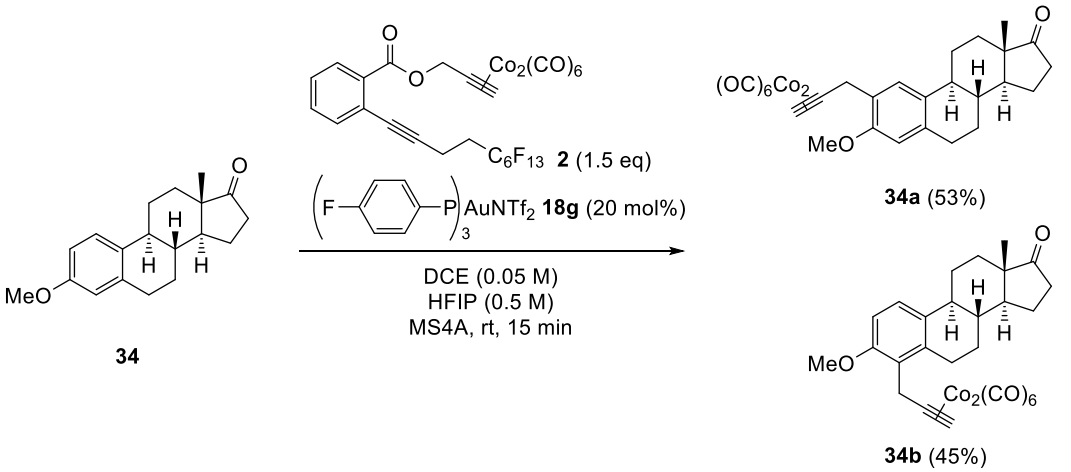
33c: red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.15-8.10 (m, 1H), 8.06-8.01 (m, 1H), 7.58-7.50 (m, 2H), 7.30 (s, 1H), 6.05 (s, 1H), 5.97 (s, 1H), 4.51 (s, 2H), 4.28 (s, 2H), 3.90 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 153.5, 133.1, 132.0, 129.2, 128.7, 127.9, 126.02, 125.99, 124.3, 123.1, 96.8, 96.2, 73.8, 73.5, 62.2, 37.3, 34.3; HRMS (EI): calcd for $C_{28}H_{14}O_{12}Co_4$ ([M-CO]$^+$): 777.7813, found: 777.7826.

Functionalization of naproxen methyl ester (3)



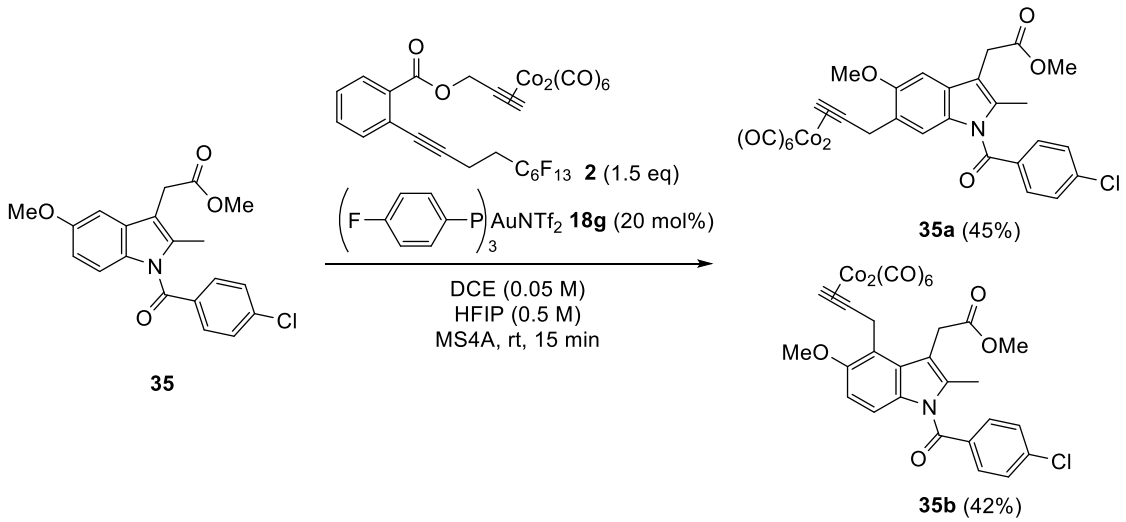
Procedure D was followed and used gold catalyst **18g** (1.98 mg, 2.5 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 30), and then fluorous silica gel column chromatography to give **4** (27.5 mg, 48.4 μmol, 97%). Characterization data were in agreement with previously reported values.[19]

Functionalization of estrone methyl ether (34)



Procedure C was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 20) to give a mixture of **34a** and **34b** (62.02 mg). Characterization data were in agreement with previously reported values.[19]

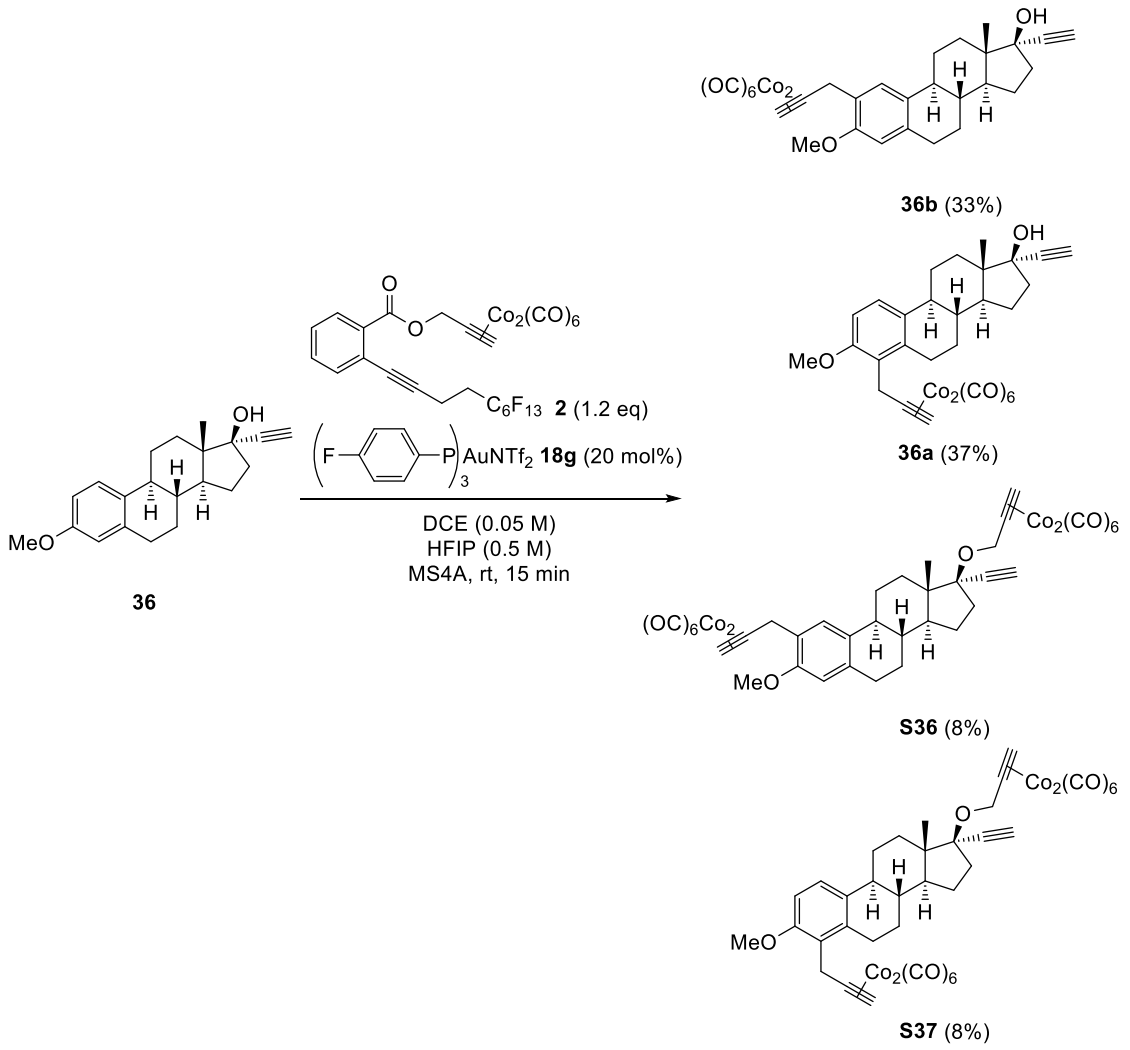
Functionalization of indometacin methyl ester (35)



Procedure C was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to AcOEt : Hexane = 1 : 20) to give **35a** (15.6 mg, 22.5 μmol, 45%) and **35b** (14.52 mg, 20.9 μmol, 42%). Characterization data were in agreement with previously reported

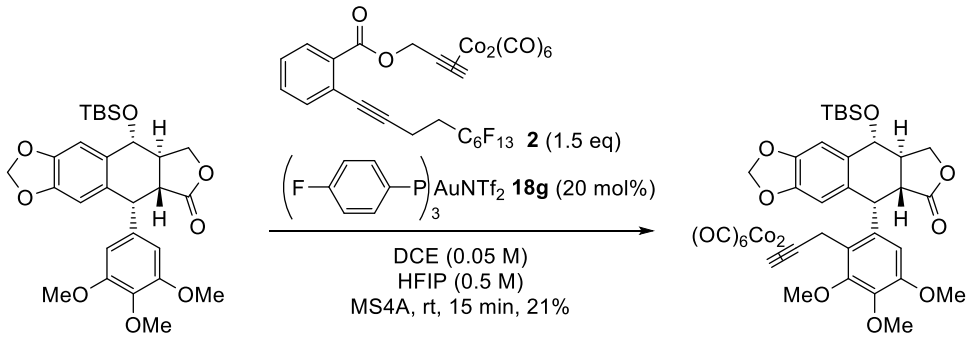
values.[19]

Functionalization of mestranol (36)



Procedure B was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (Pentane) to give a mixture of **36a** and **36b** (12.56 mg) and a mixture of **S36** and **S37** (21.98 mg). Characterization data were in agreement with previously reported values.[19]

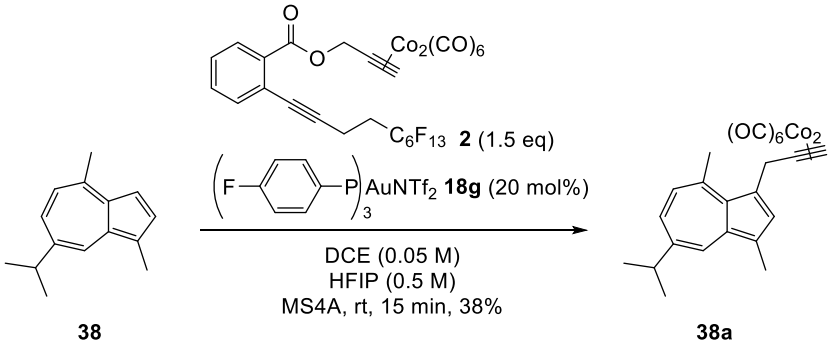
Functionalization of (*5R,5aR,8aR,9R*)-9-((*tert*-butyldimethylsilyl)oxy)-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-*d*][1,3]dioxol-6(5a*H*)-one (37).



Procedure C was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to 1 : 4) to give **37a** (9.58 mg, 11.2 μmol, brsm 99%).

37a: red oil; IR (neat): 2019, 1782 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 6.96 (s, 1H), 6.39 (s, 1H), 6.061 (s, 1H), 6.055 (s, 1H), 5.98 (s, 1H), 5.97 (s, 1H), 4.93 (d, *J* = 9.6 Hz, 1H), 4.91 (s, 1H), 4.81 (d, *J* = 9.6 Hz, 1H), 4.55 (t, *J* = 7.5 Hz, 1H), 4.43 (d, *J* = 15.7 Hz, 1H), 4.00 (dt, *J* = 11.1 Hz, *J* = 8.6 Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H), 3.11-3.01 (m, 1H), 2.98-2.89 (m, 1H), 0.97 (s, 9H), 0.30 (s, 1H), 0.14 (s, 3H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 173.7, 151.9, 151.8, 147.5, 147.3, 141.4, 133.64, 133.60, 132.1, 127.8, 110.8, 109.0, 106.6, 101.4, 96.8, 72.7, 72.3, 71.5, 60.5, 60.4, 55.8, 44.9, 40.9, 39.5, 31.5, 25.8, 18.0, -3.8, -4.1; HRMS (FAB): calcd for $C_{32}H_{38}O_9Co_2$ ($[M-5CO]^+$): 712.0949, found: 712.0972.

Functionalization of guaiazulene (38)

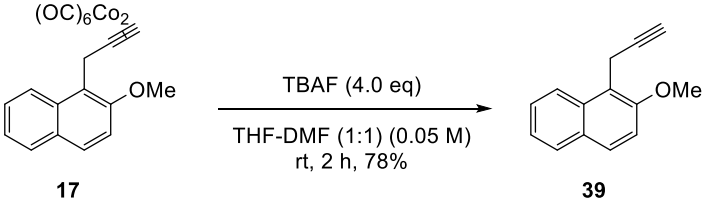


Procedure C was followed and used gold catalyst **18g** (7.92 mg, 10 μmol). The crude mixture was purified by silica gel column chromatography (Pentane) to give **38a** (9.05 mg, 19.2 μmol, 38%).

38a: black oil; IR (neat): 2021 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 2.0 Hz, 1H), 7.48 (s, 1H), 7.30 (d, *J* = 11.0 Hz, 1H), 6.90 (d, *J* = 11.0 Hz, 1H), 5.99 (s, 1H), 4.71 (s, 2H), 3.09-2.96 (m, 4H), 2.58 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 6H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 199.8, 144.6, 140.5, 139.6, 138.2, 134.6, 133.7, 131.8, 126.7, 126.0, 124.5, 99.6, 73.9, 37.7, 36.2, 26.5, 24.5, 12.7; HRMS (EI): calcd for $C_{24}H_{20}O_6Co_2$ ($[M]^+$): 521.9924, found: 521.9934.

7. Decomplexation of dicobalt hexacarbonyl complexes

Decomplexation of 17



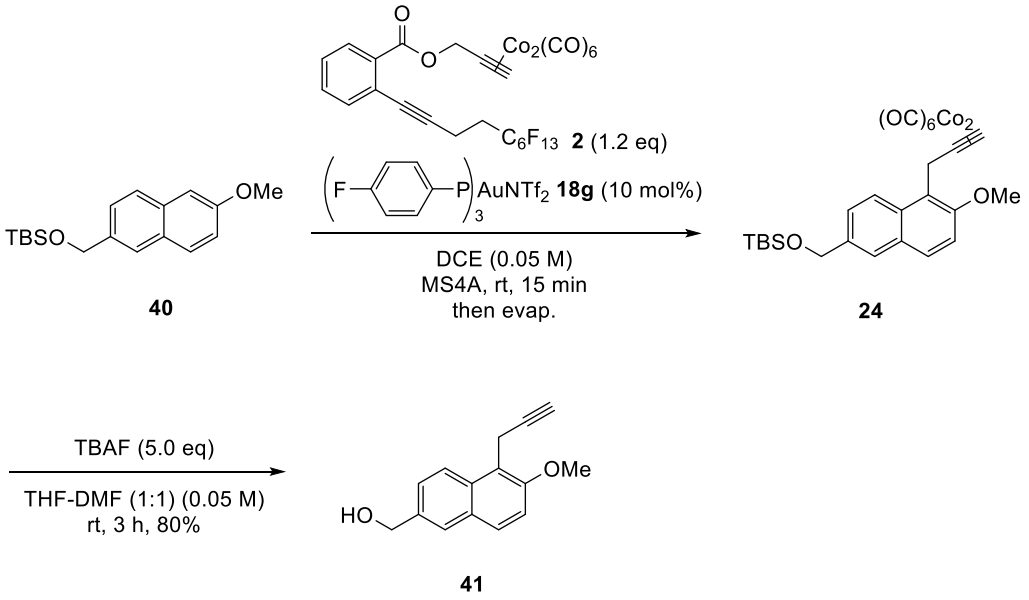
To solution of functionalized compound **17** (5.32 mg, 35 μmol) in THF (0.35 mL) and DMF (0.35 mL) was dropwised 1 M TBAF in THF (0.14 mL, 0.14 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The solution was quenched with sat. NH_4Cl aq. (1 mL) at room temperature and extracted

with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (Hexane) to **39** (5.32 mg, 27.1 μmol, 78%).

39: white solid; IR (neat): 3291 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.88-7.72 (m, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 4.00 (d, *J* = 2.9 Hz, 2H), 3.98 (s, 3H), 1.97 (t, *J* = 2.9 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.0, 132.6, 129.3, 129.0, 128.5, 126.8, 123.6, 123.3, 117.7, 113.6, 82.9, 67.9, 56.9, 14.4; HRMS (EI): calcd for $C_{14}H_{12}O$ ($[M]^+$): 196.0888, found: 196.0895.

8. 1-Pot propargylation

1-Pot propargylation of 40

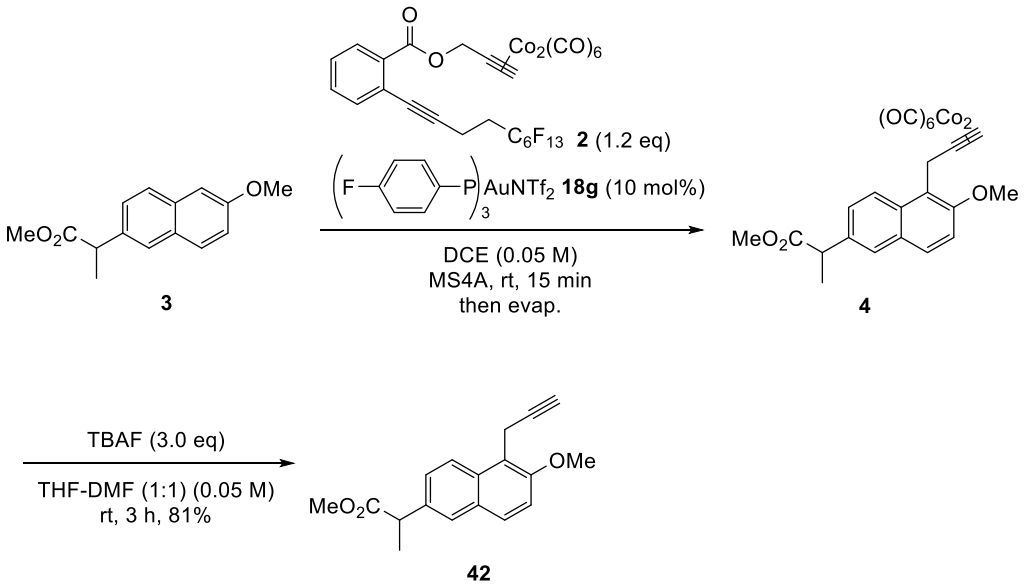


A solution of reagent **2** (50 mg, 60 μmol), **40** (50 μmol) and MS4A (50 mg) in DCE (1.0 mL) was added gold catalyst **18g** (3.96 mg, 5.0 μmol) at room temperature. The reaction mixture was stirred at the same temperature for 15 min. The reaction mixture was concentrated in vacuo. The residue was dissolved in THF (0.5 mL) and DMF (0.5 mL) and dropwised 1 M TBAF in THF (0.25 mL, 0.25 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 3 h. The solution was quenched

with sat. NH_4Cl aq. (2 mL) at room temperature and extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20 to 1 : 4) to **41** (9.10 mg, 40.2 μmol, 80%).

41: white solid; IR (neat): 3407 (br), 3288 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.7 Hz, 1H), 7.83-7.75 (m, 2H), 7.55 (dd, *J* = 9.2 Hz, *J* = 1.4 Hz, 1H), 7.34 (d, *J* = 9.2 Hz, 1H), 4.84 (s, 2H), 4.03-3.95 (m, 5H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.70 (brs, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.1, 136.0, 132.2, 129.2, 128.9, 126.2, 123.9, 120.3, 117.7, 113.9, 82.8, 67.9, 65.4, 56.8, 14.4; HRMS (EI): calcd for $C_{15}H_{14}O_2$ ([M]$^+$): 226.0994, found: 226.0991.

1-Pot propargylation of 3



A solution of reagent **2** (50 mg, 60 μmol), **3** (50 μmol) and MS4A (50 mg) in DCE (1.0 mL) was added gold catalyst **18g** (3.96 mg, 5.0 μmol) at room temperature. The reaction mixture was stirred at the same temperature for 15 min. The reaction mixture was concentrated in vacuo. The residue was dissolved in THF (0.5 mL) and DMF (0.5 mL)

and dropwised 1 M TBAF in THF (0.15 mL, 0.15 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 3 h. The solution was quenched with sat. NH_4Cl aq. (2 mL) at room temperature and extracted with Et_2O (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 50 to 1 : 30) and then fluorous silica gel column chromatography to give **42** (11.4 mg, 40.5 μmol, 81%). Characterization data were in agreement with previously reported values.[19]

9. References

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10. NMR spectra

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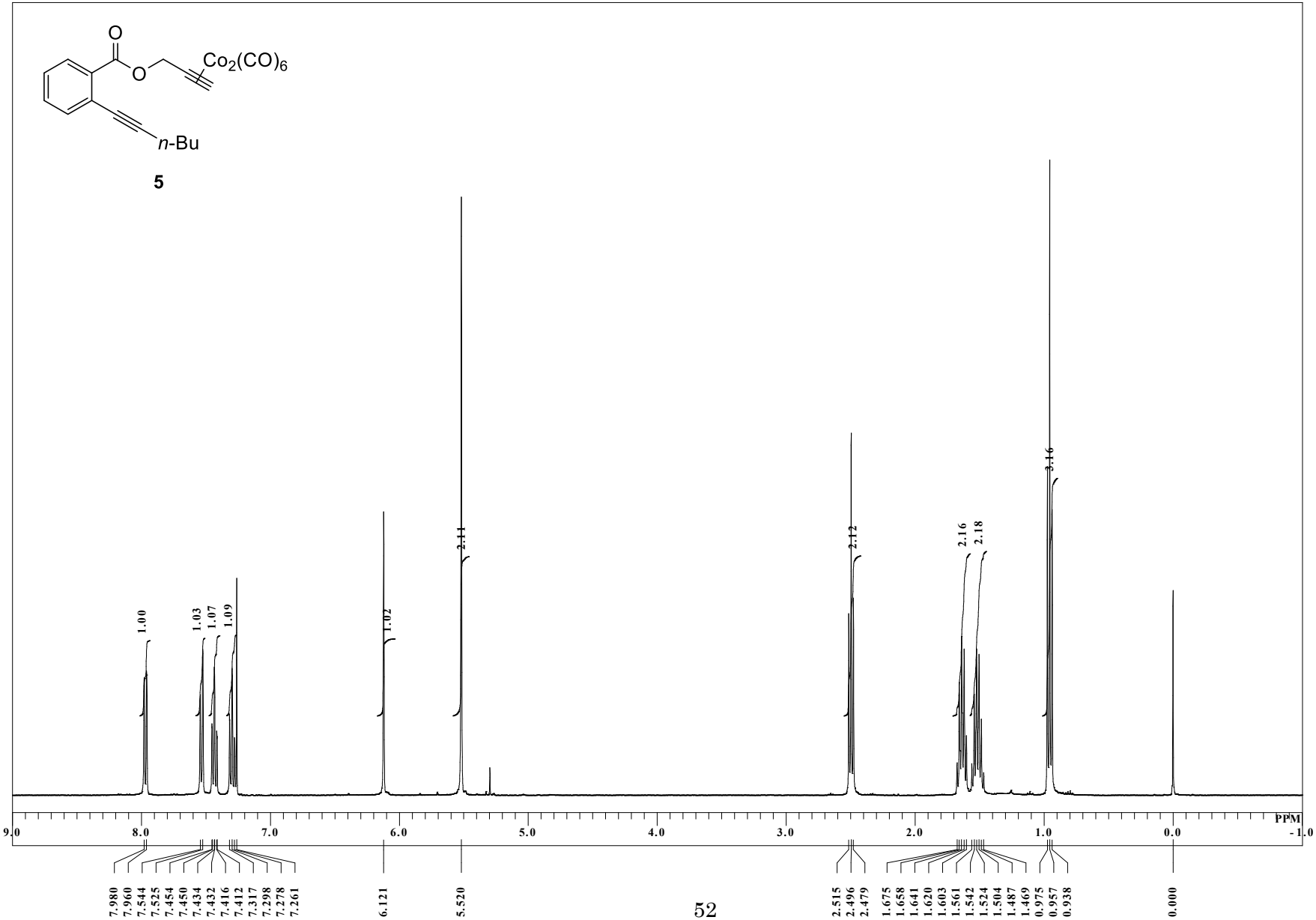

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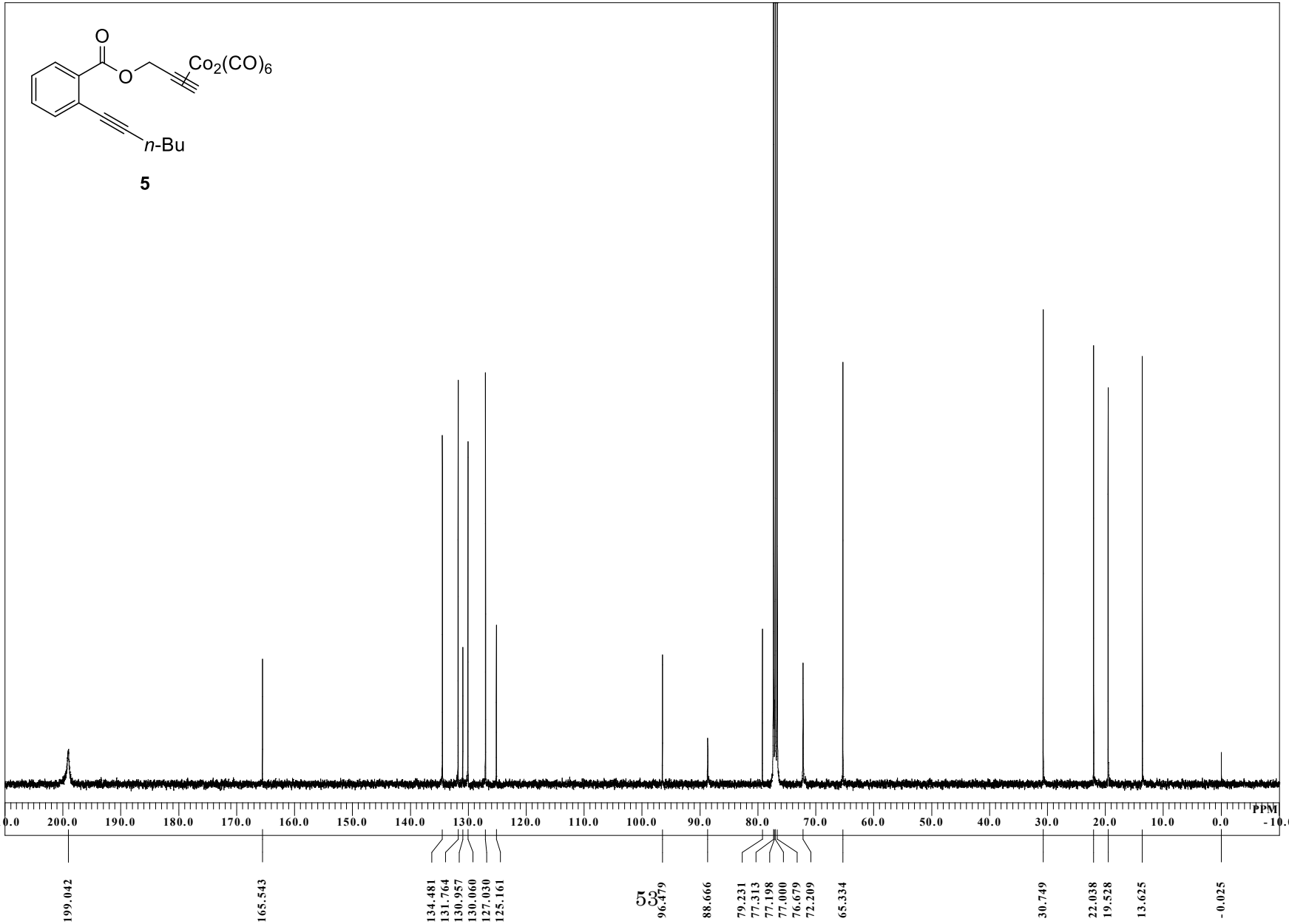
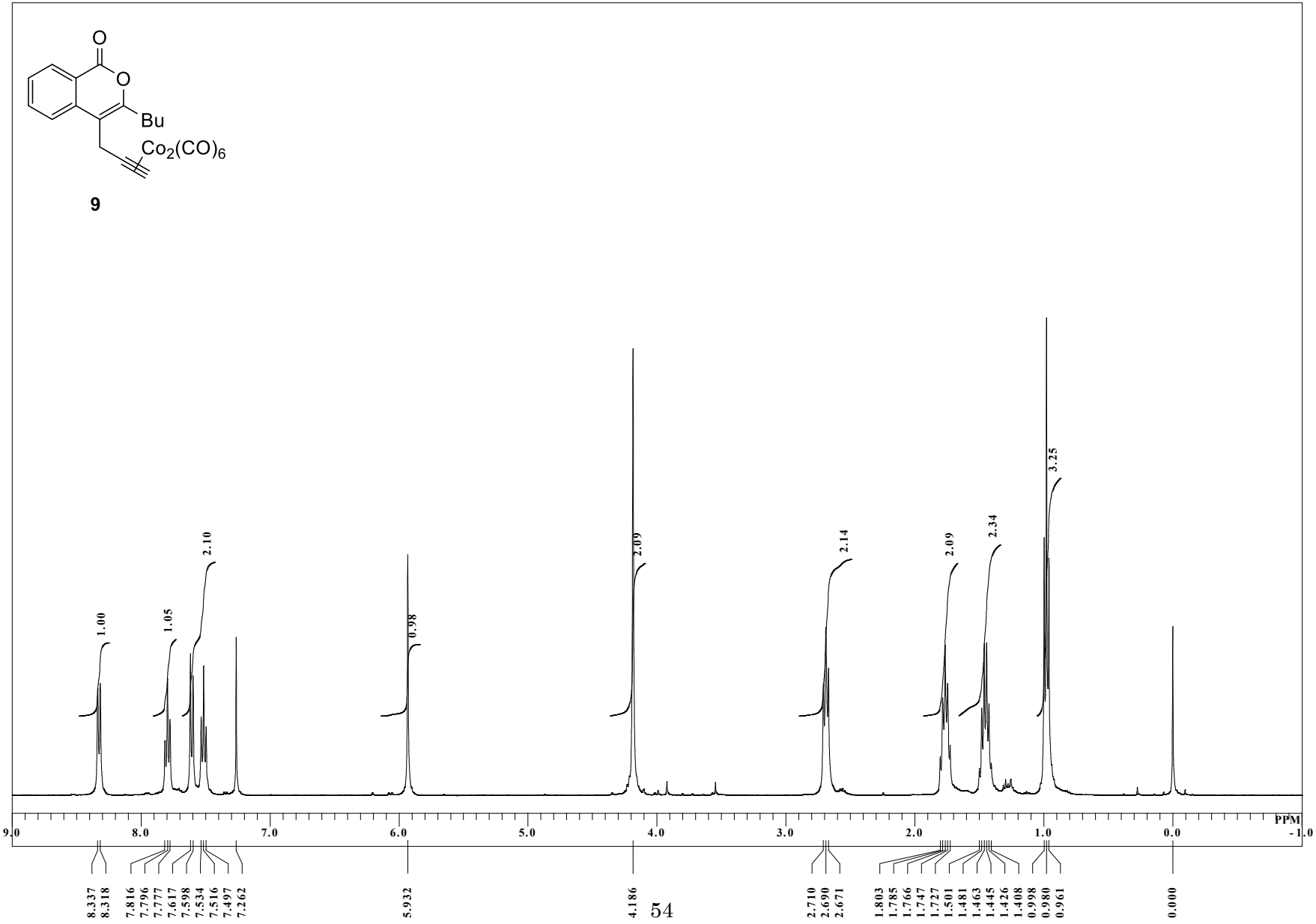


Bu seb- isocoumalin 1H



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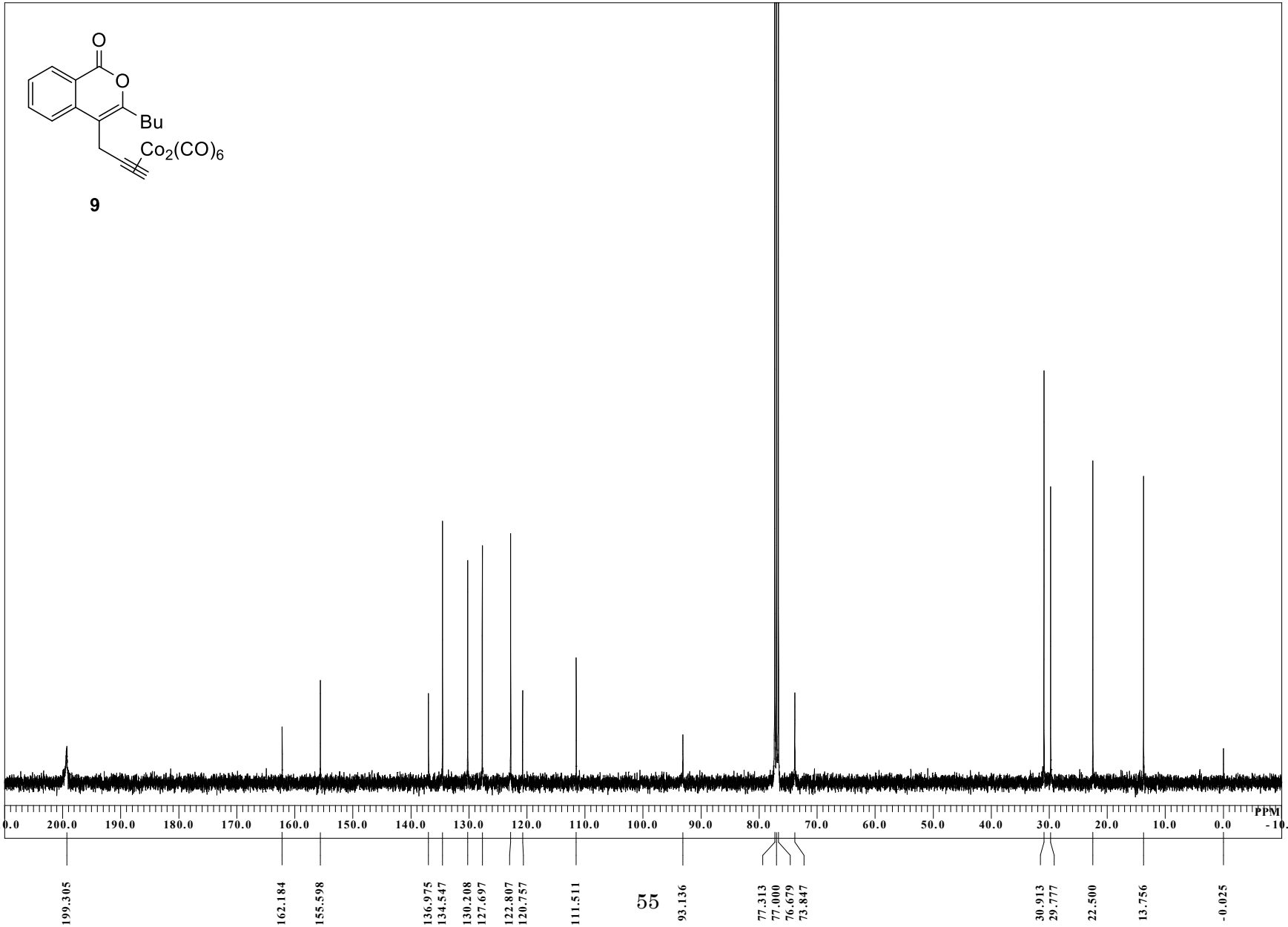

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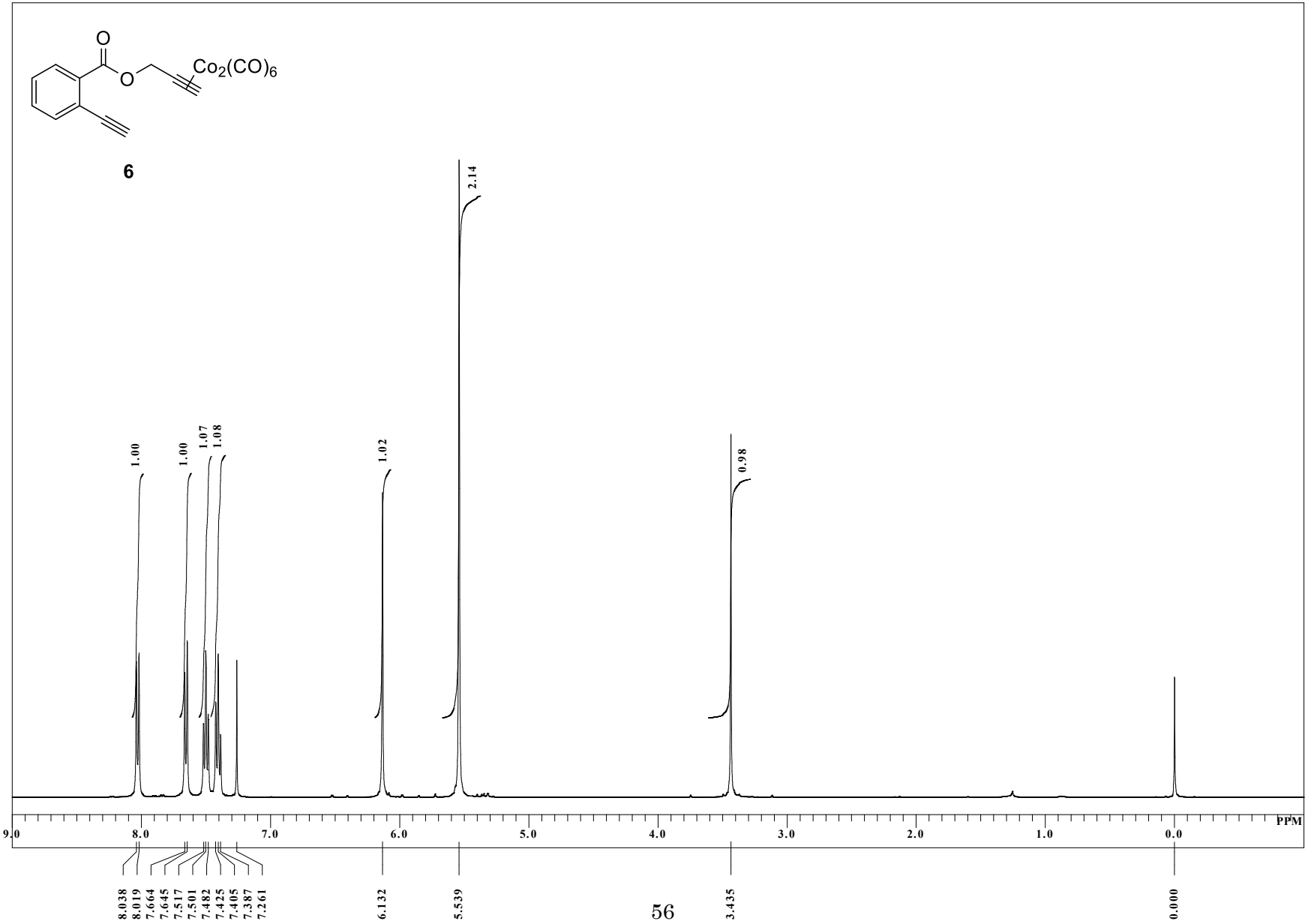

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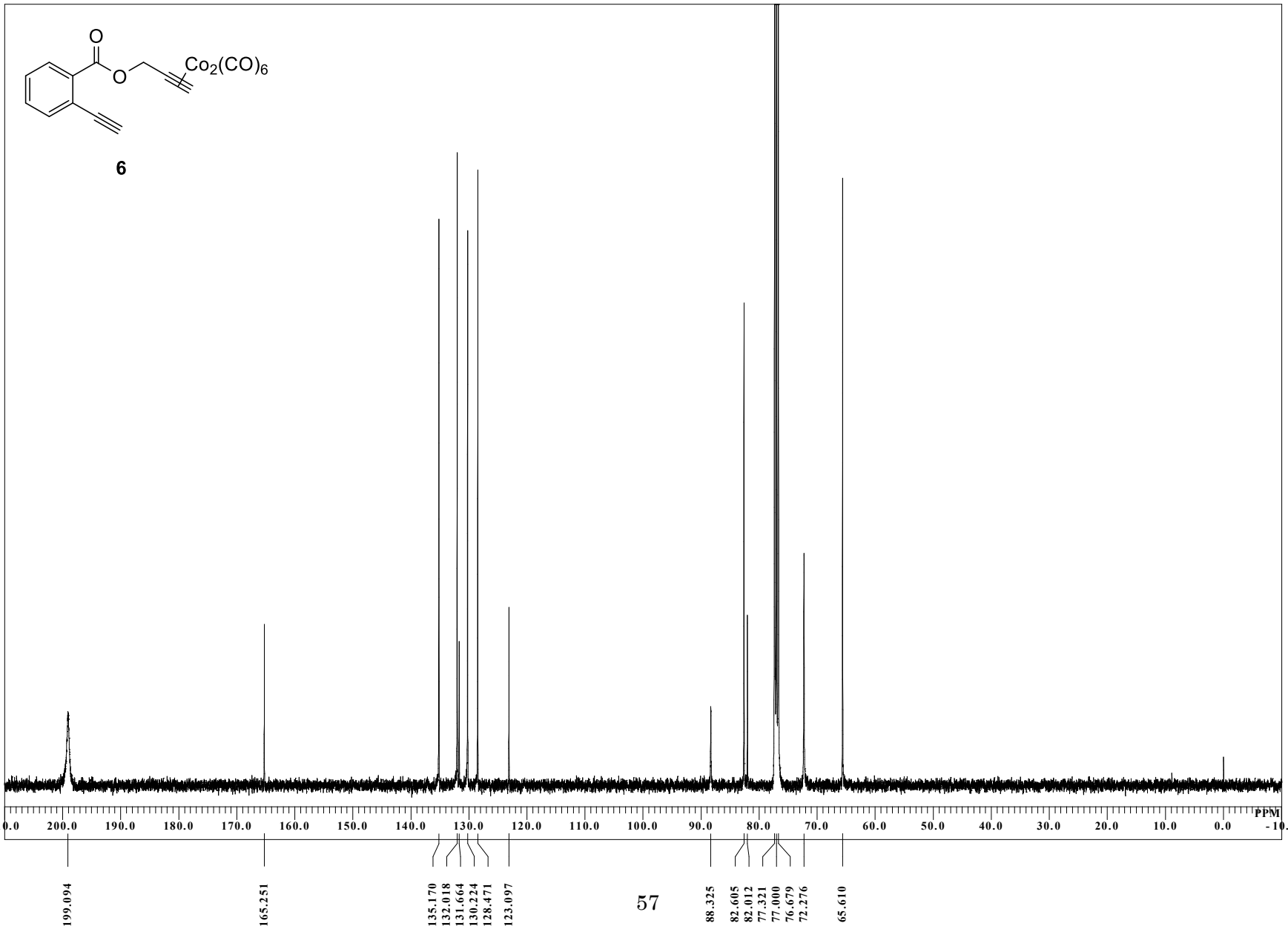

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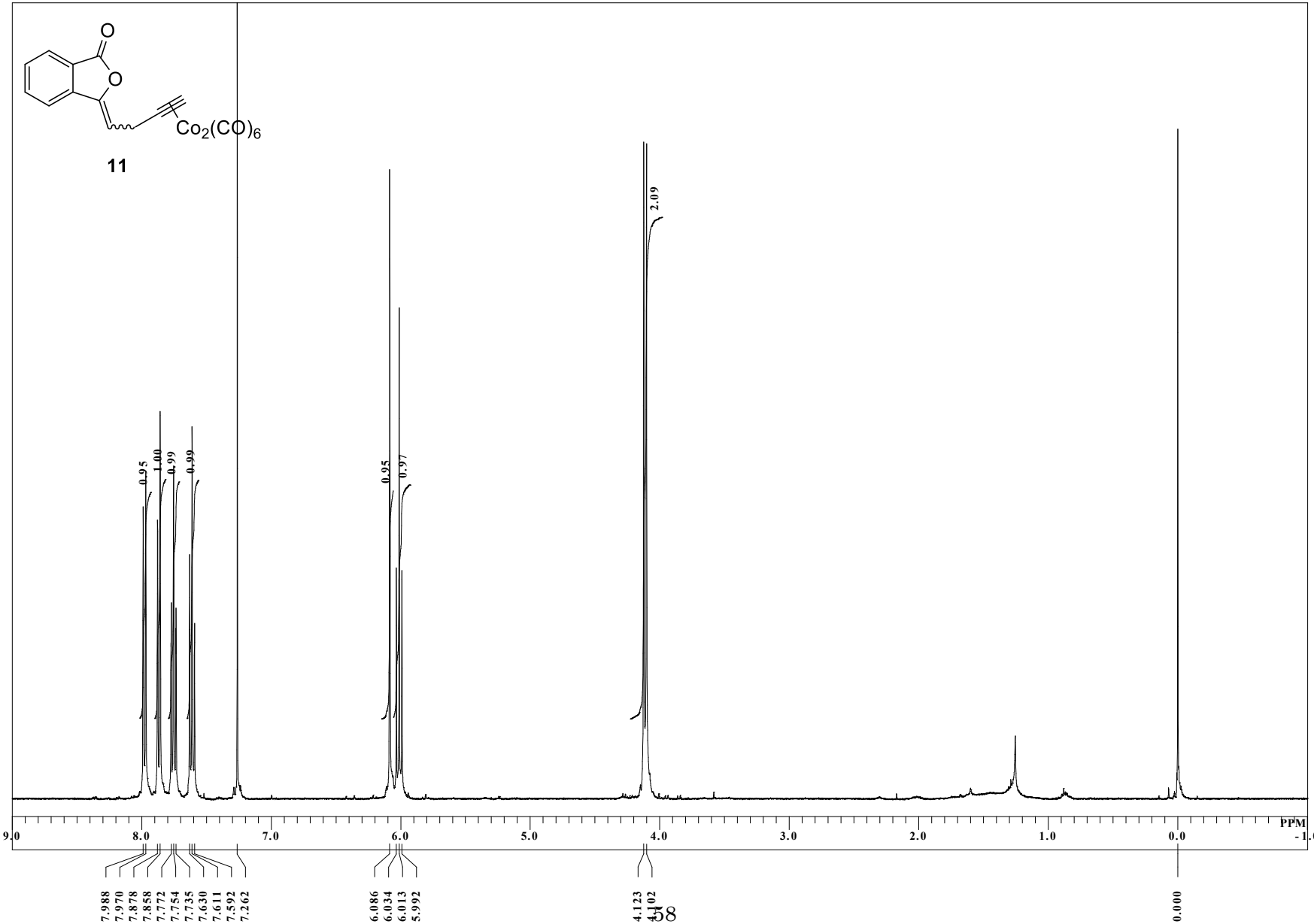
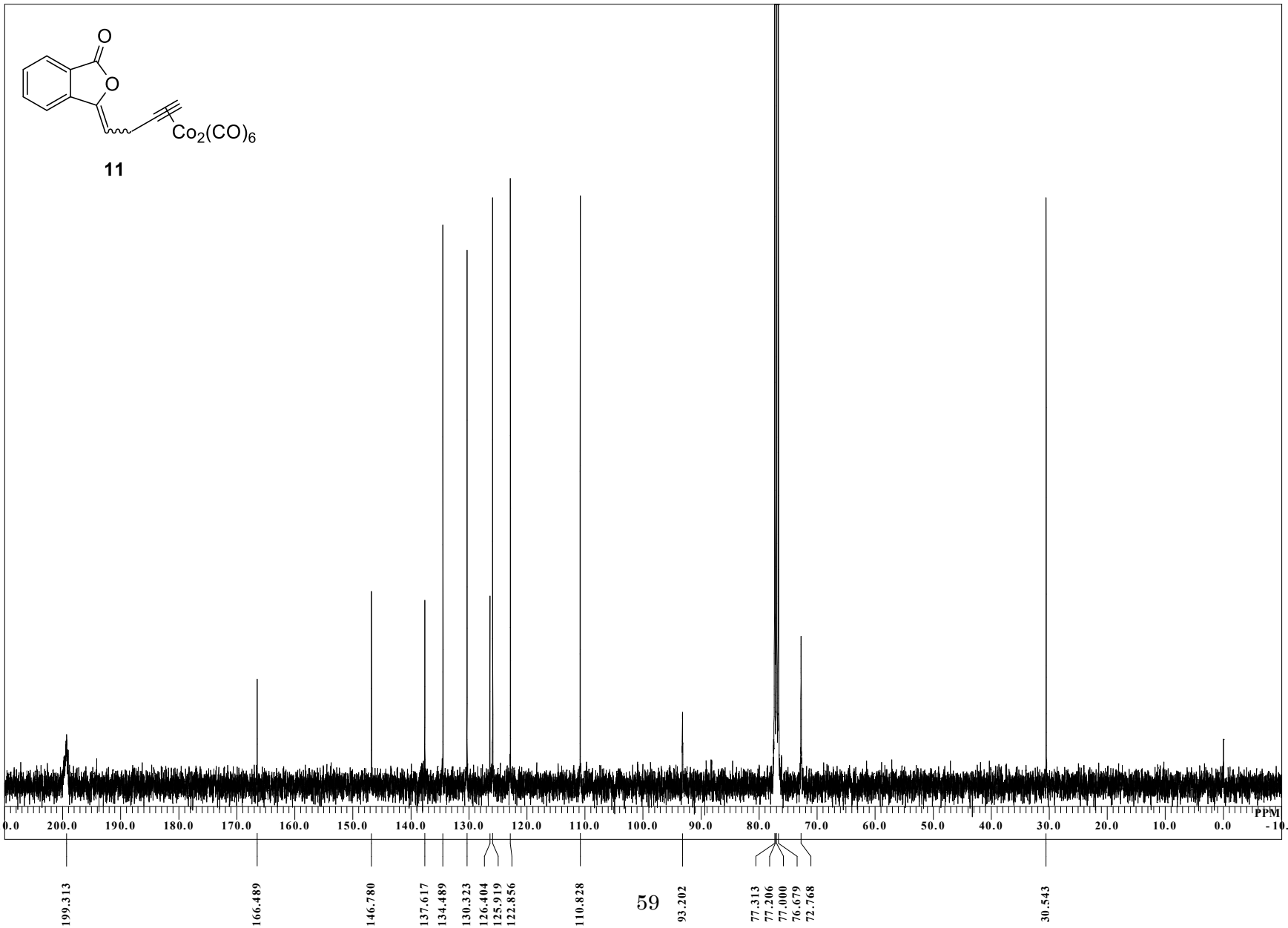
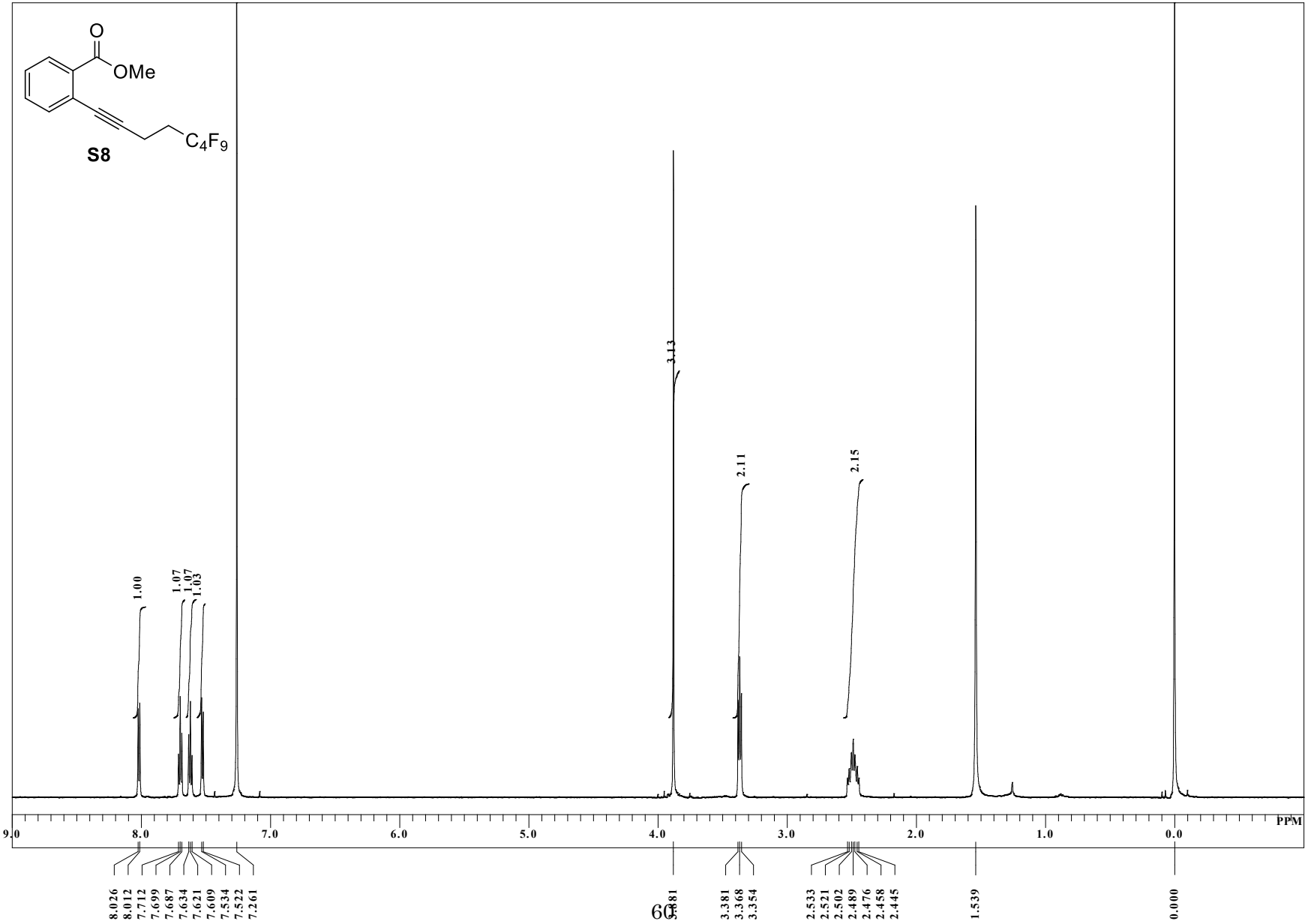


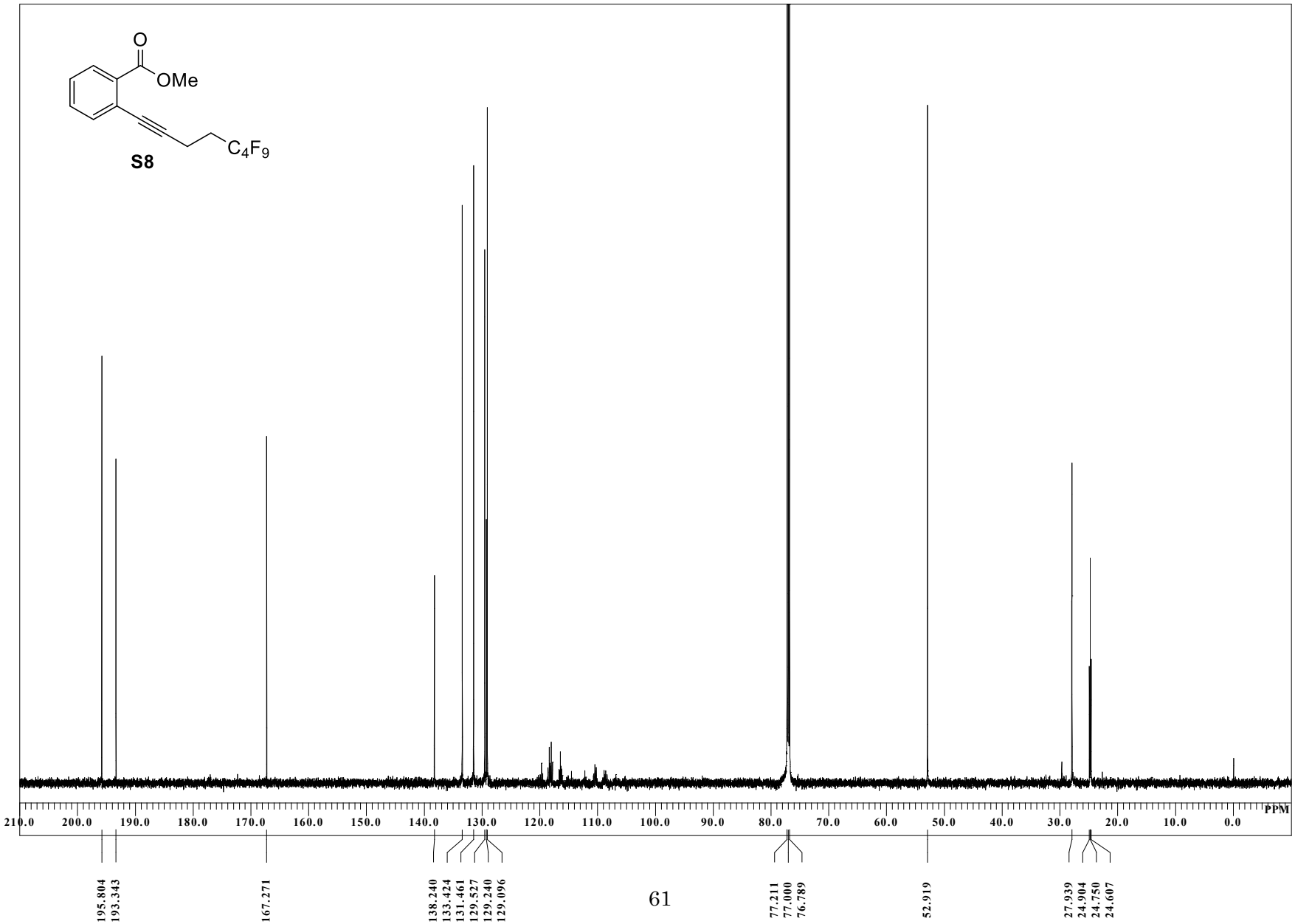
alkyne seb-cycle 13C



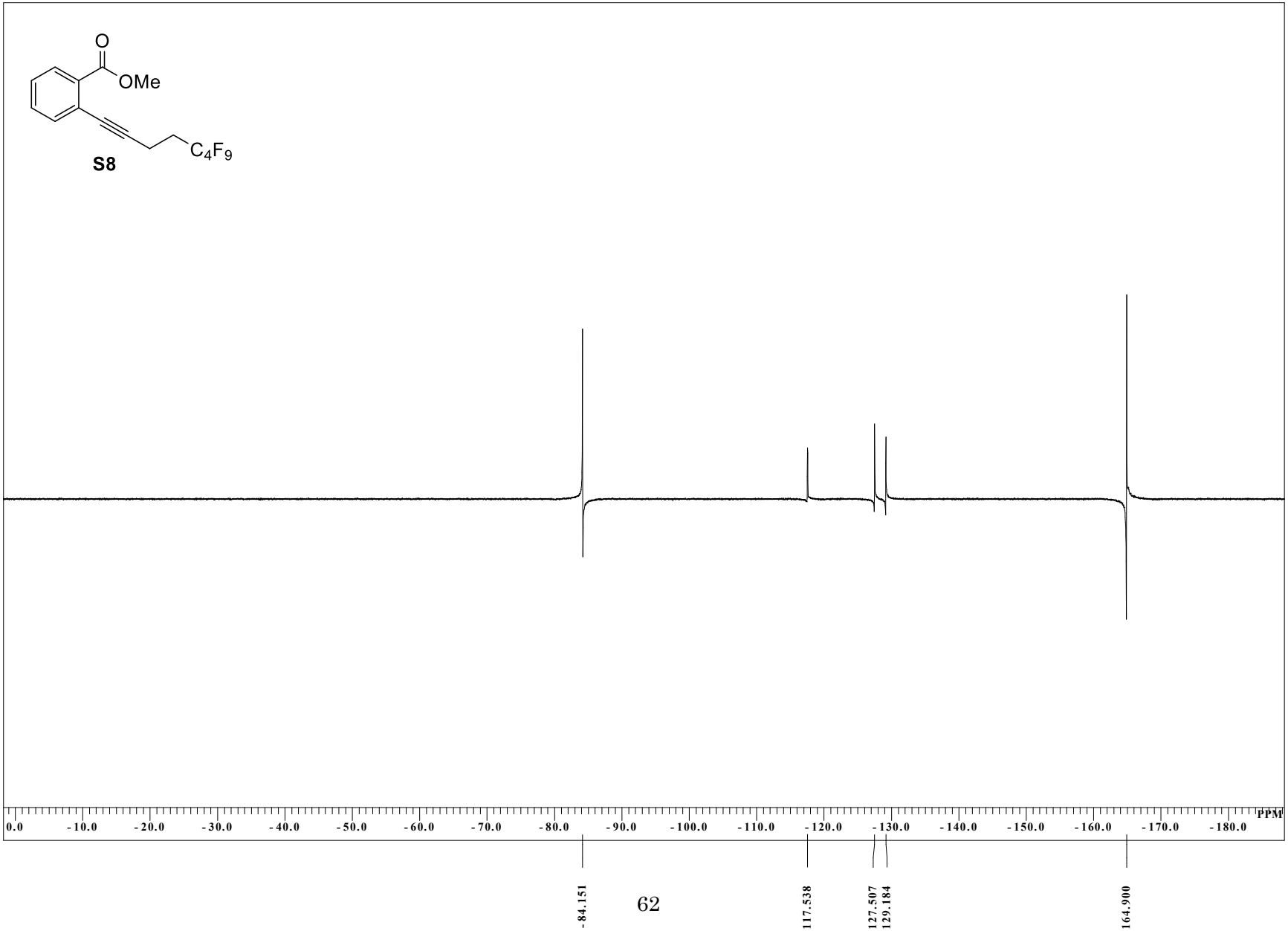
C4F9 Me ester 1H



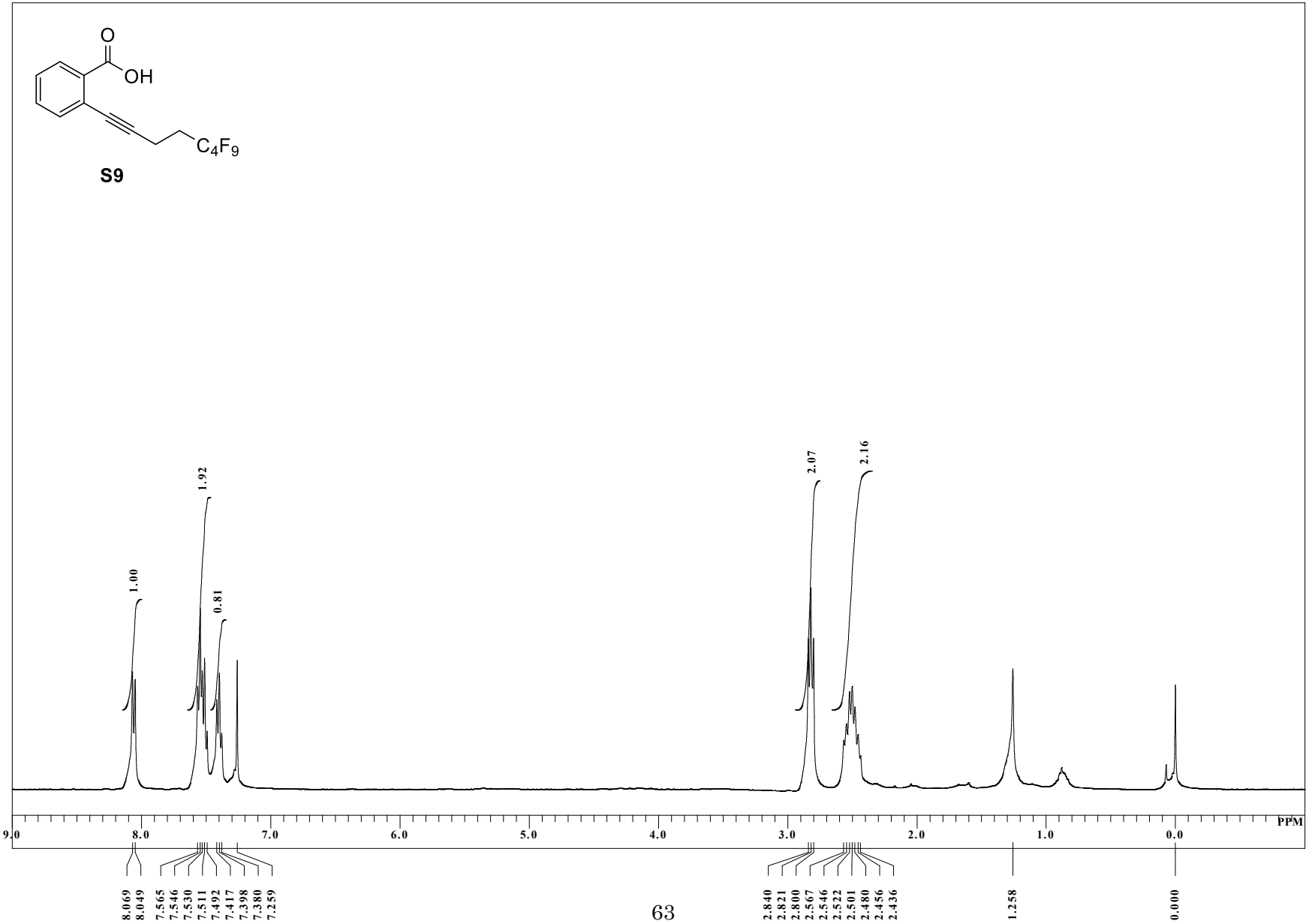
C4F9metylester 13C



C4F9metylester 19F



C4F9 COOH 1H


O
OH
C_4F_9
S9
1.00
1.92
0.81
2.07
2.16
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
8.069
8.049
7.565
7.546
7.530
7.511
7.492
7.417
7.398
7.380
7.259
2.840
2.821
2.800
2.567
2.546
2.522
2.501
2.480
2.456
2.436
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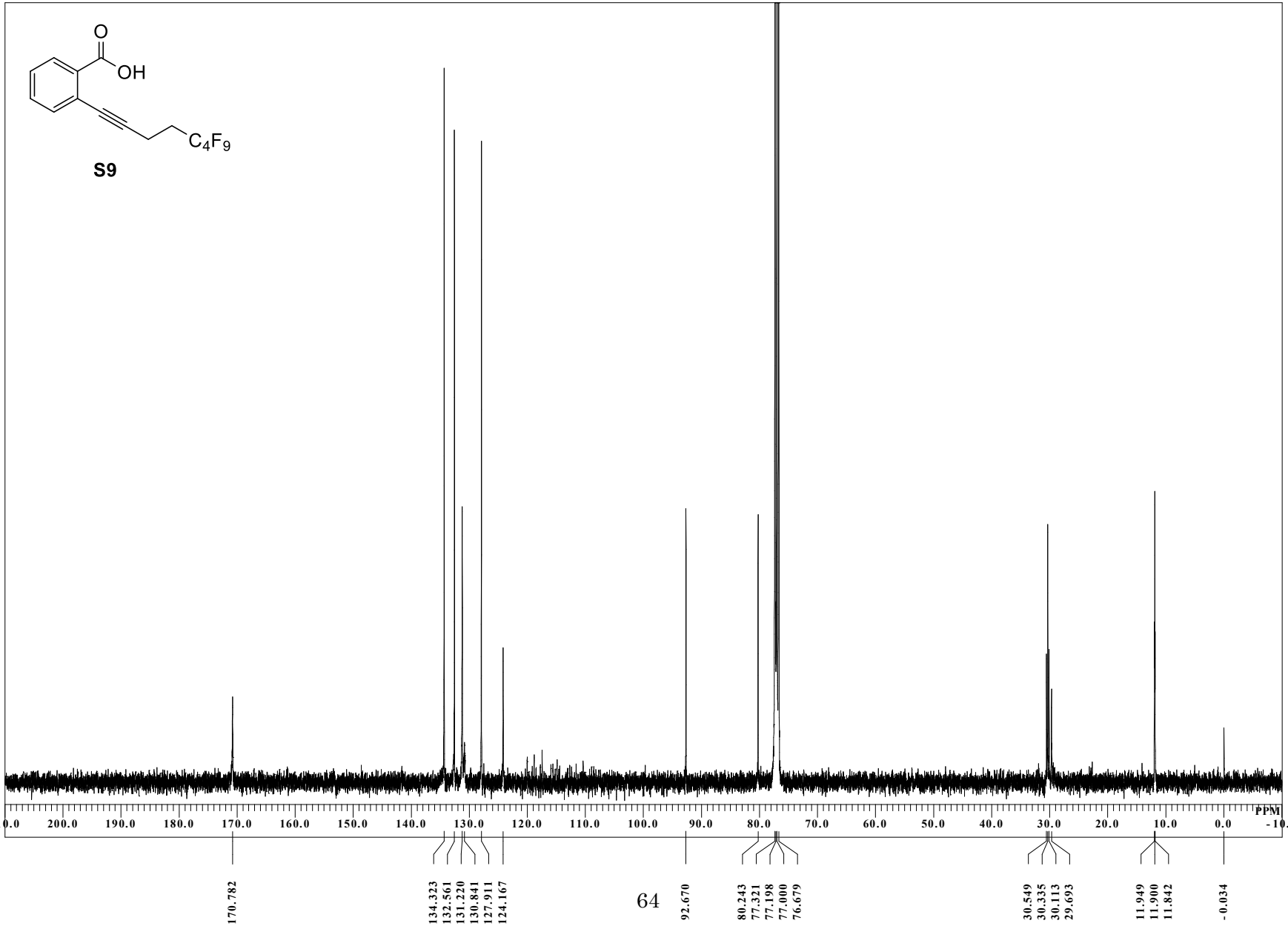
0.000

C4F9carboxylic acid 13C



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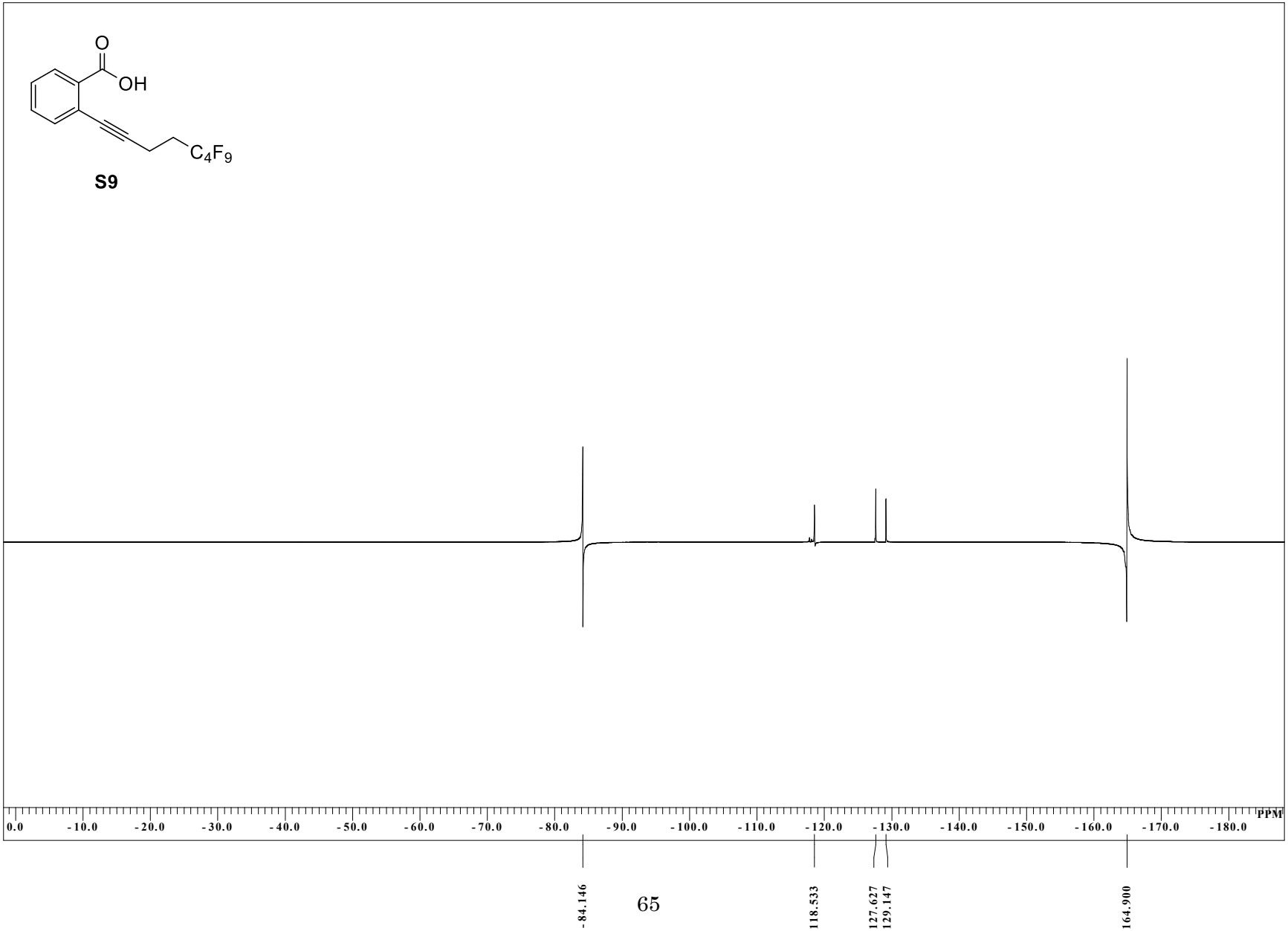

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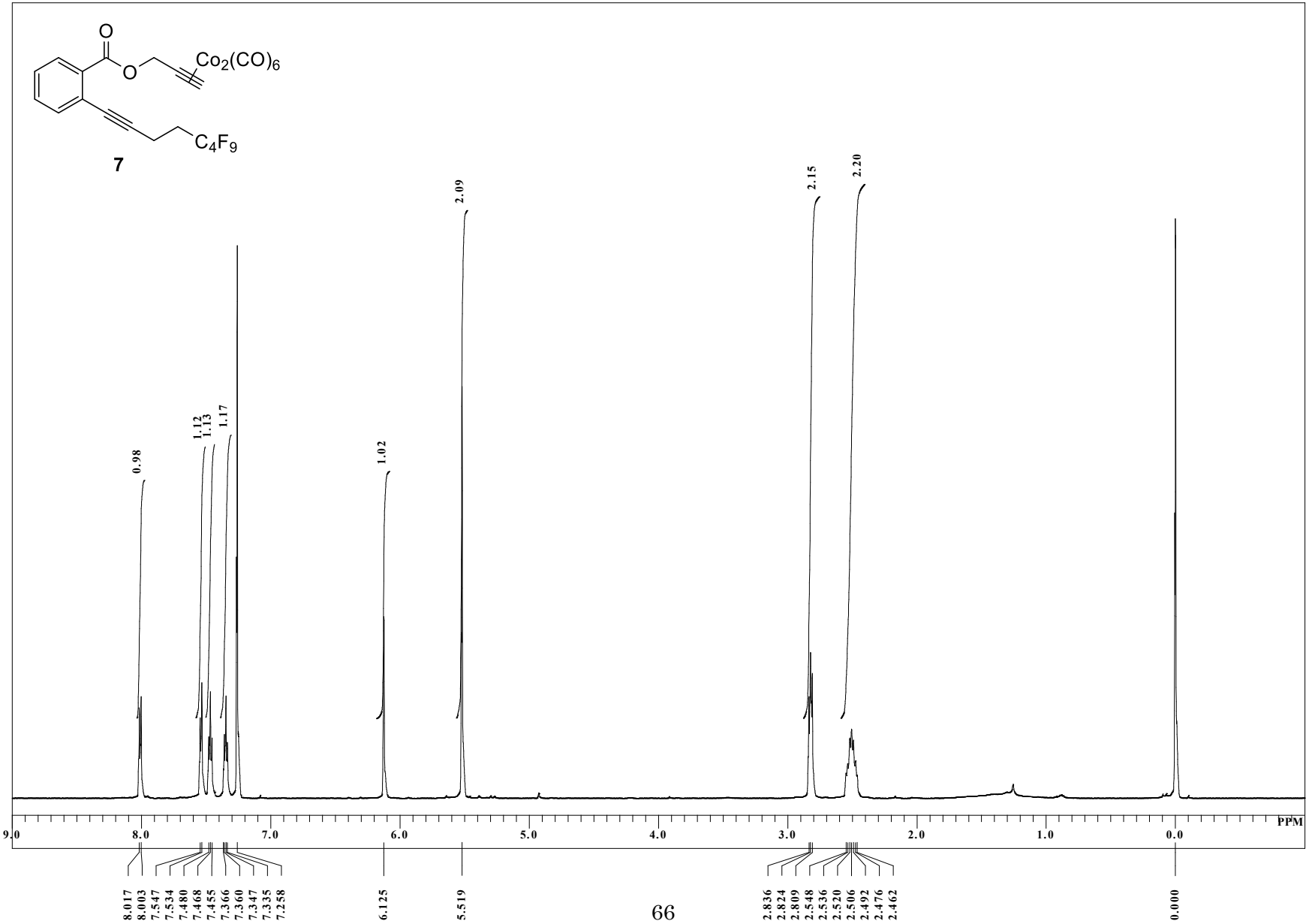

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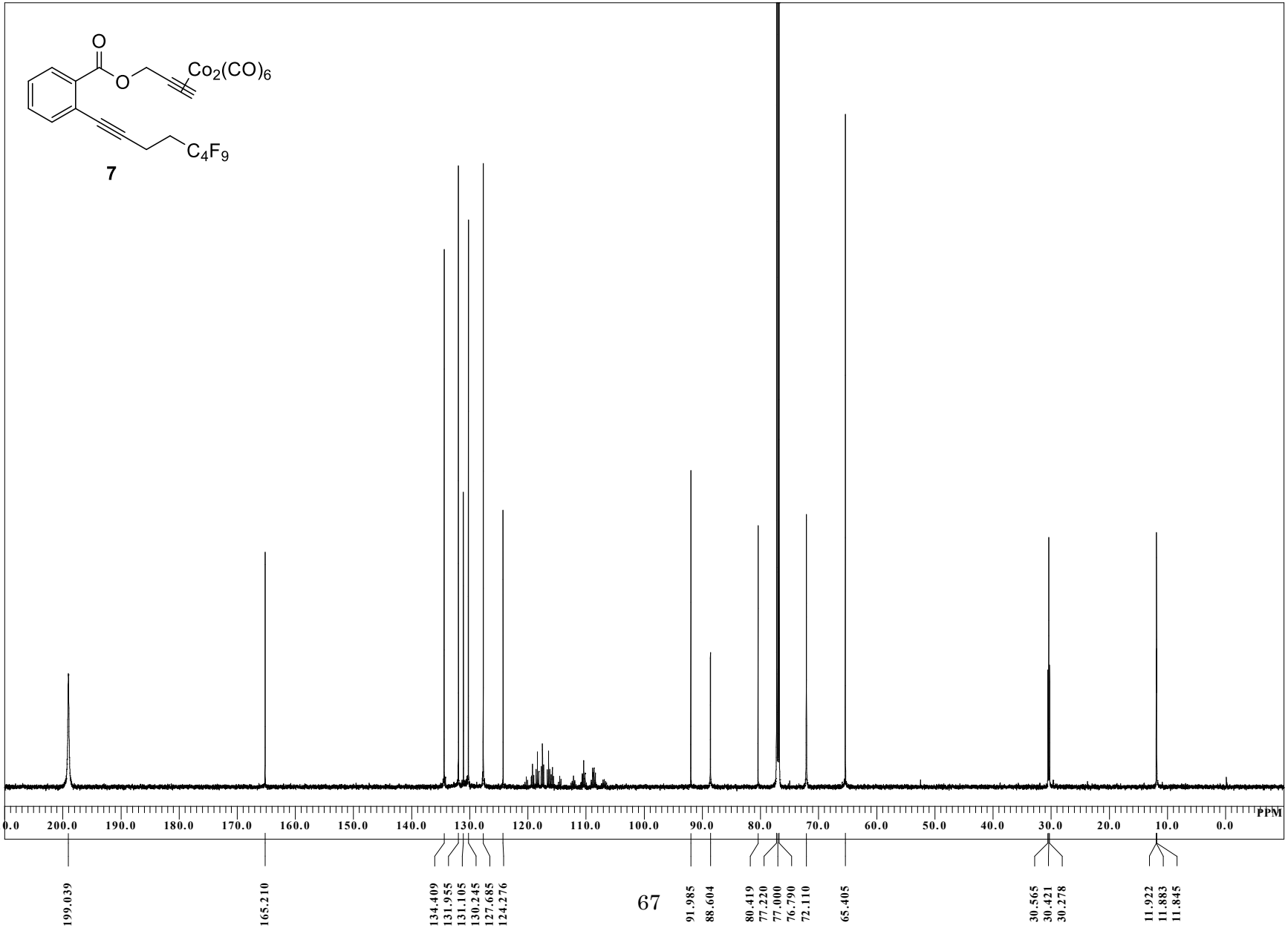

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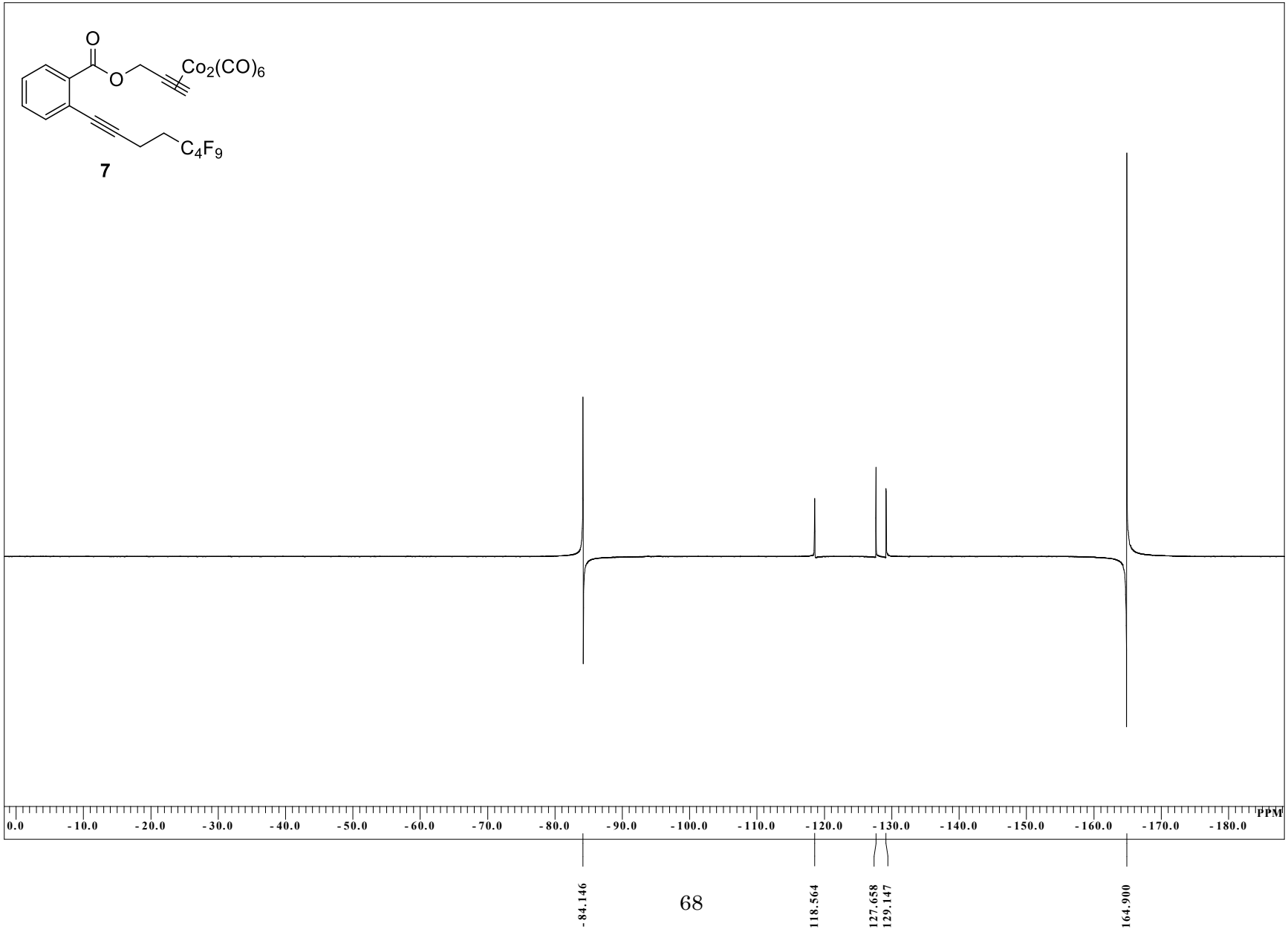
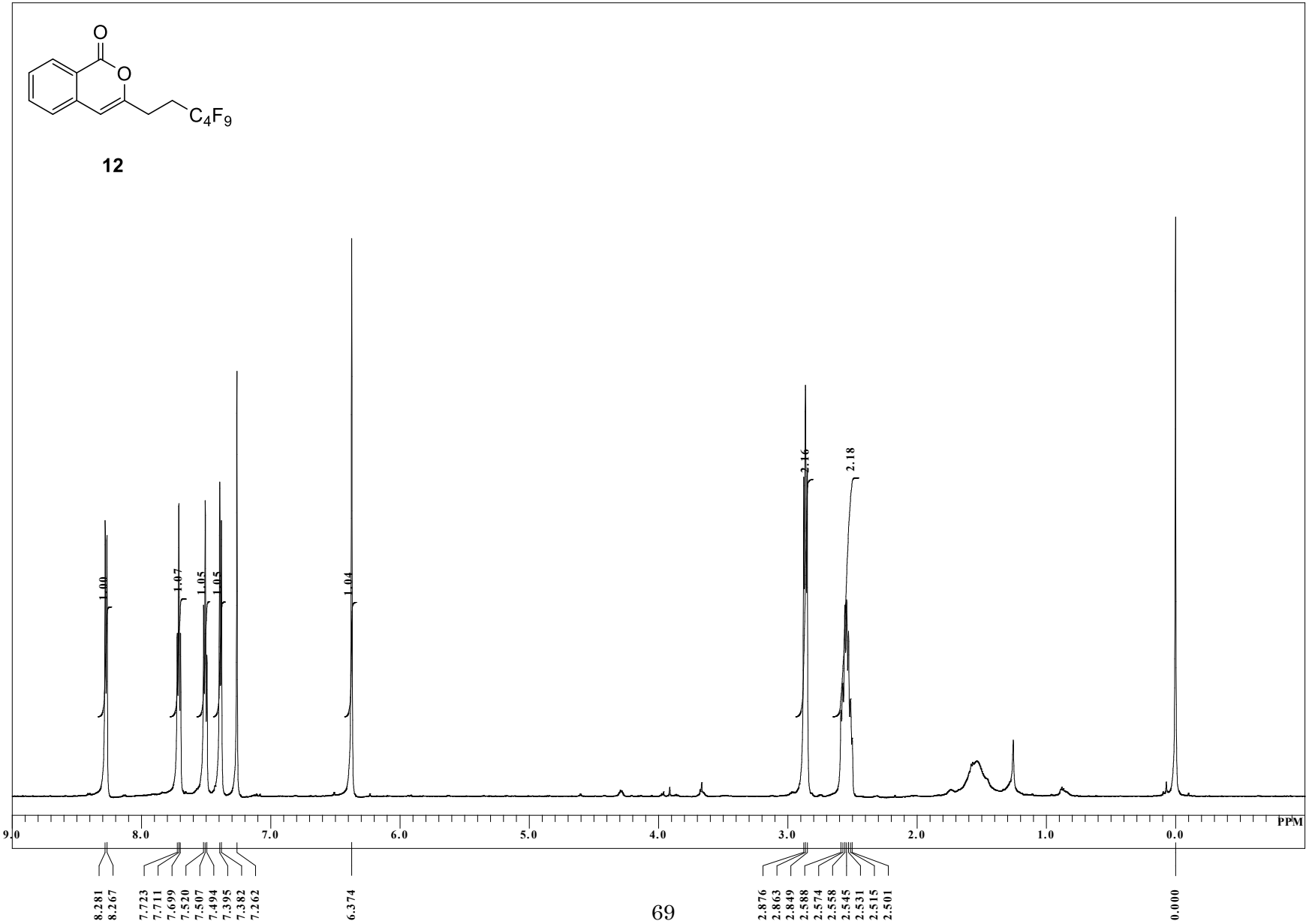
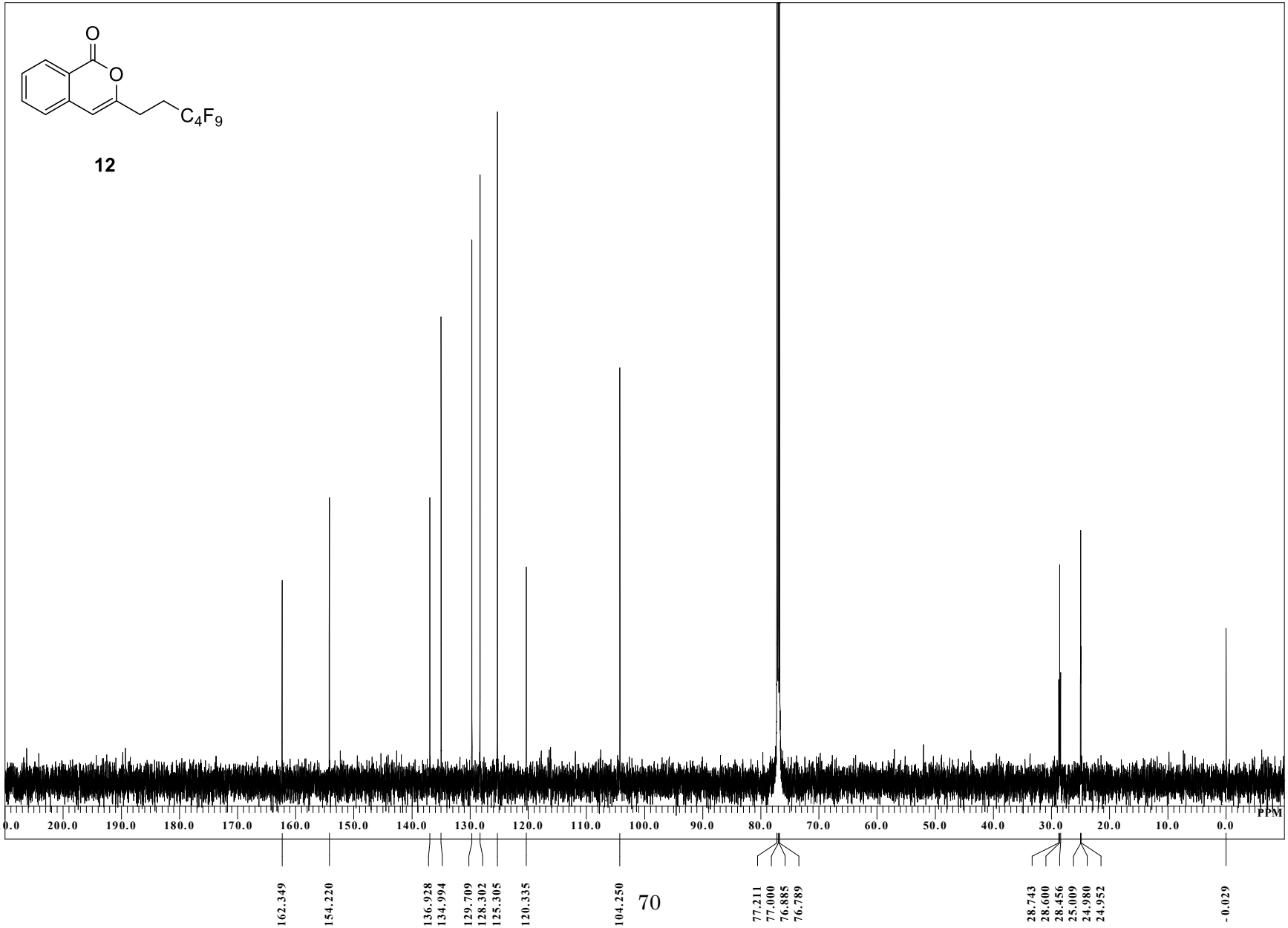


C4F9 isocoumalin 1H



C4F9isocoumalin 13C



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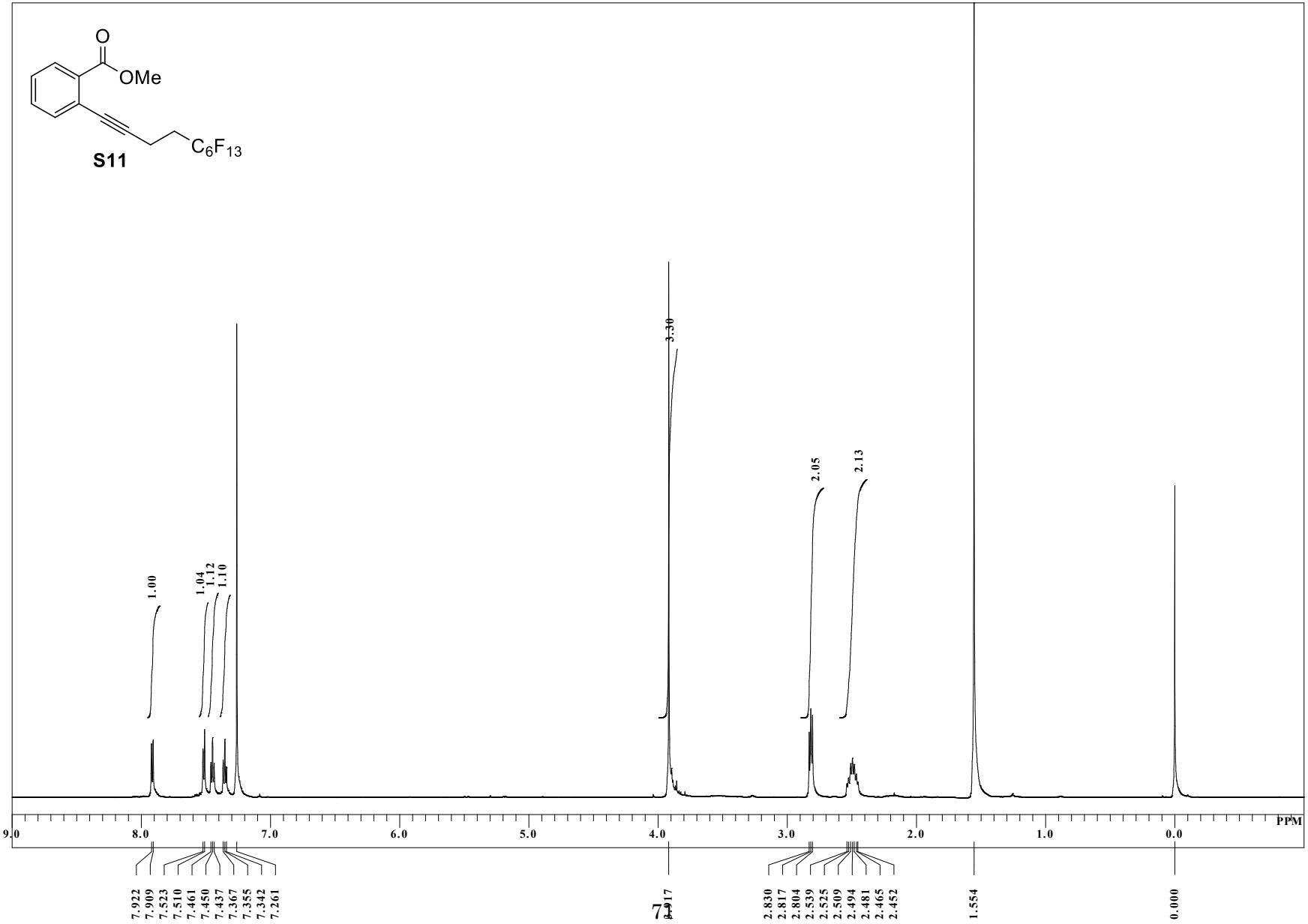
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.922
7.909
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7.355
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2.830
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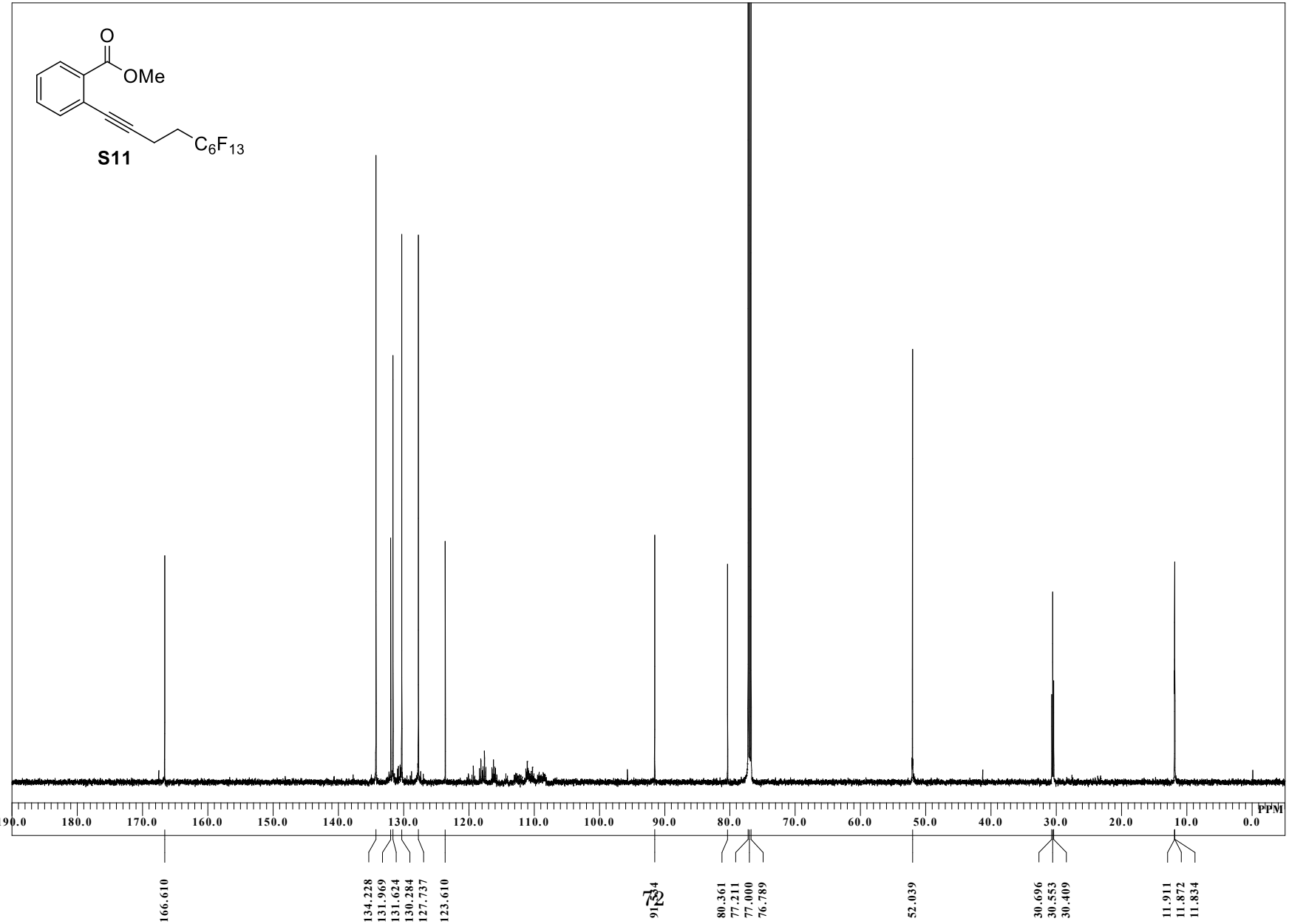
2.465
2.452
1.554
0.000

Me ester 13C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OMe
C_6F_{13}
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160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PPM
166.610
134.228
131.969
131.624
130.284
127.737
123.610
91.734
80.361
77.211
77.000
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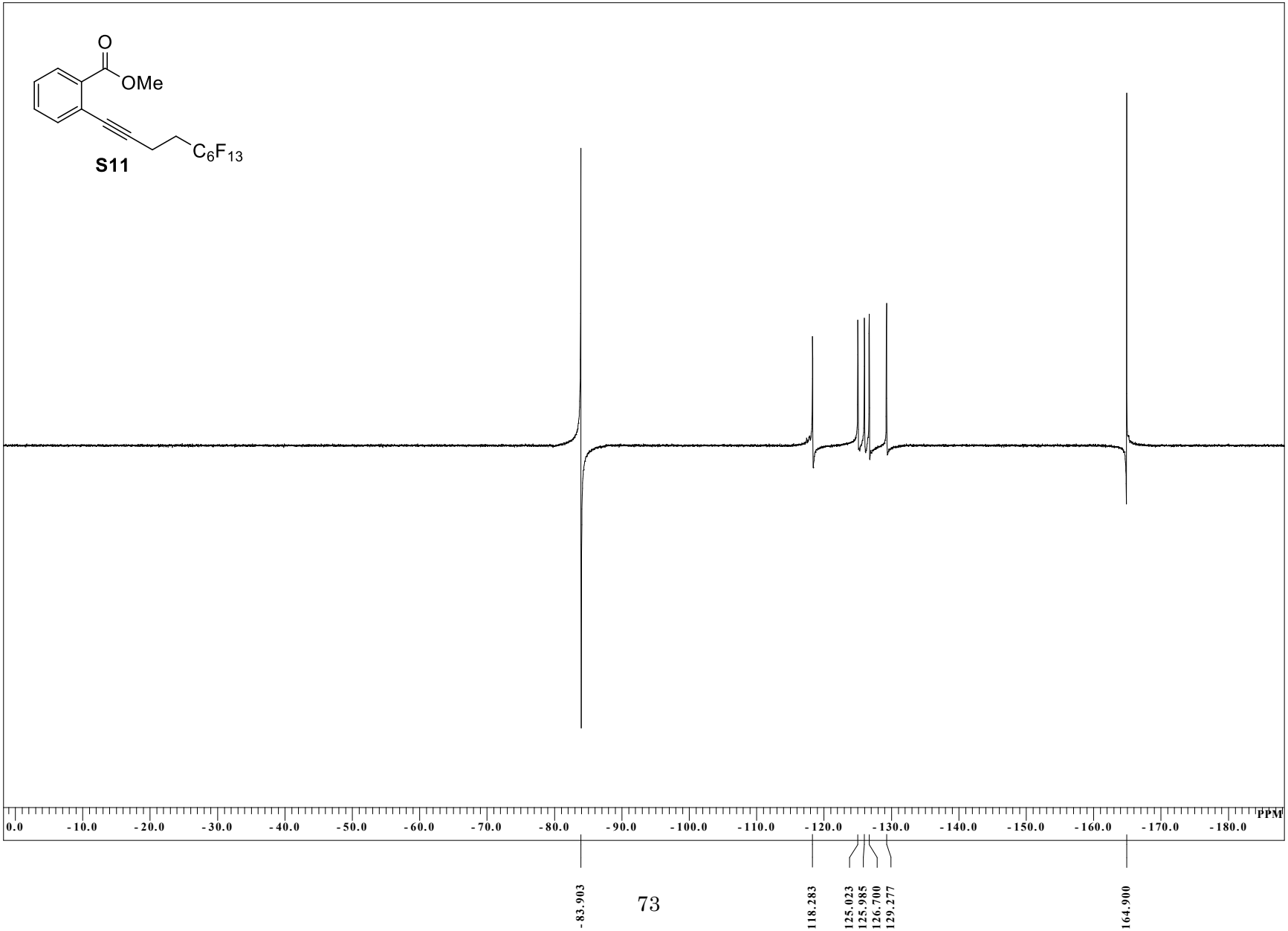
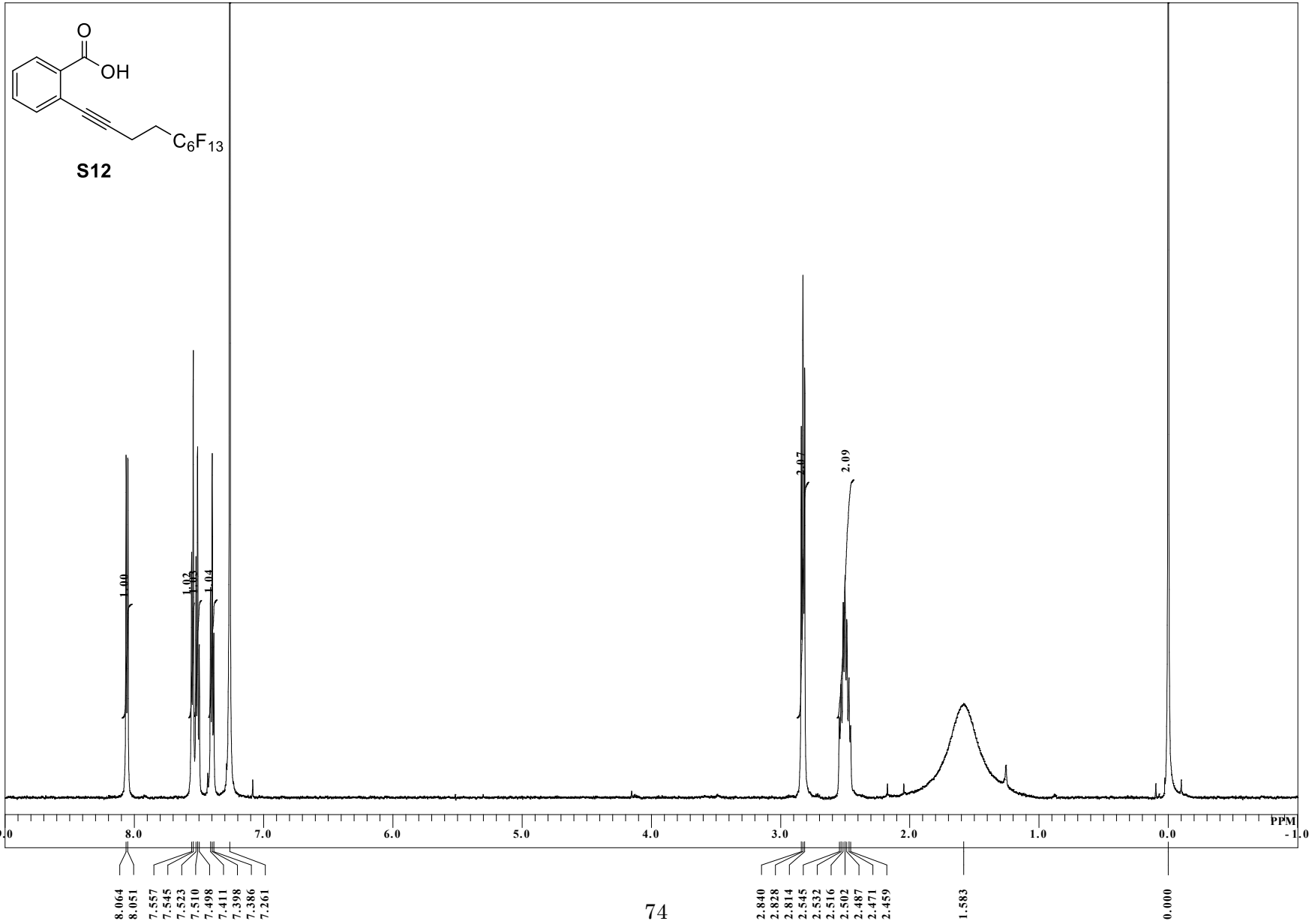
30.409
11.911
11.872
11.834

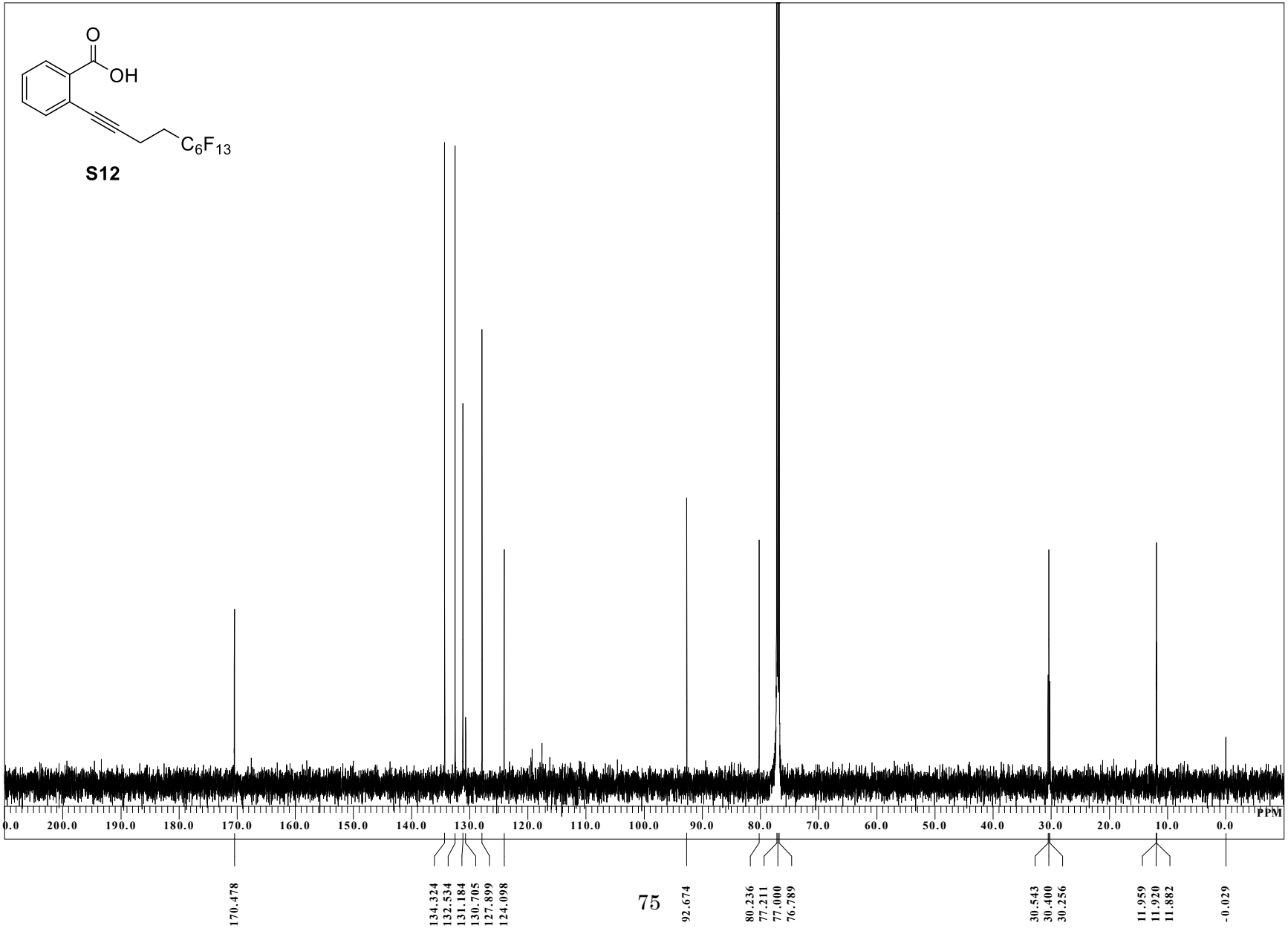
C6F13methylester-19F



C6F13carboxylic acid 1H



COOH 13C


O
OH
C_6F_{13}
S12
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
PPM
170.478
134.324
132.534
131.184
130.705
127.899
124.098
92.674
80.236
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76.789
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11.920
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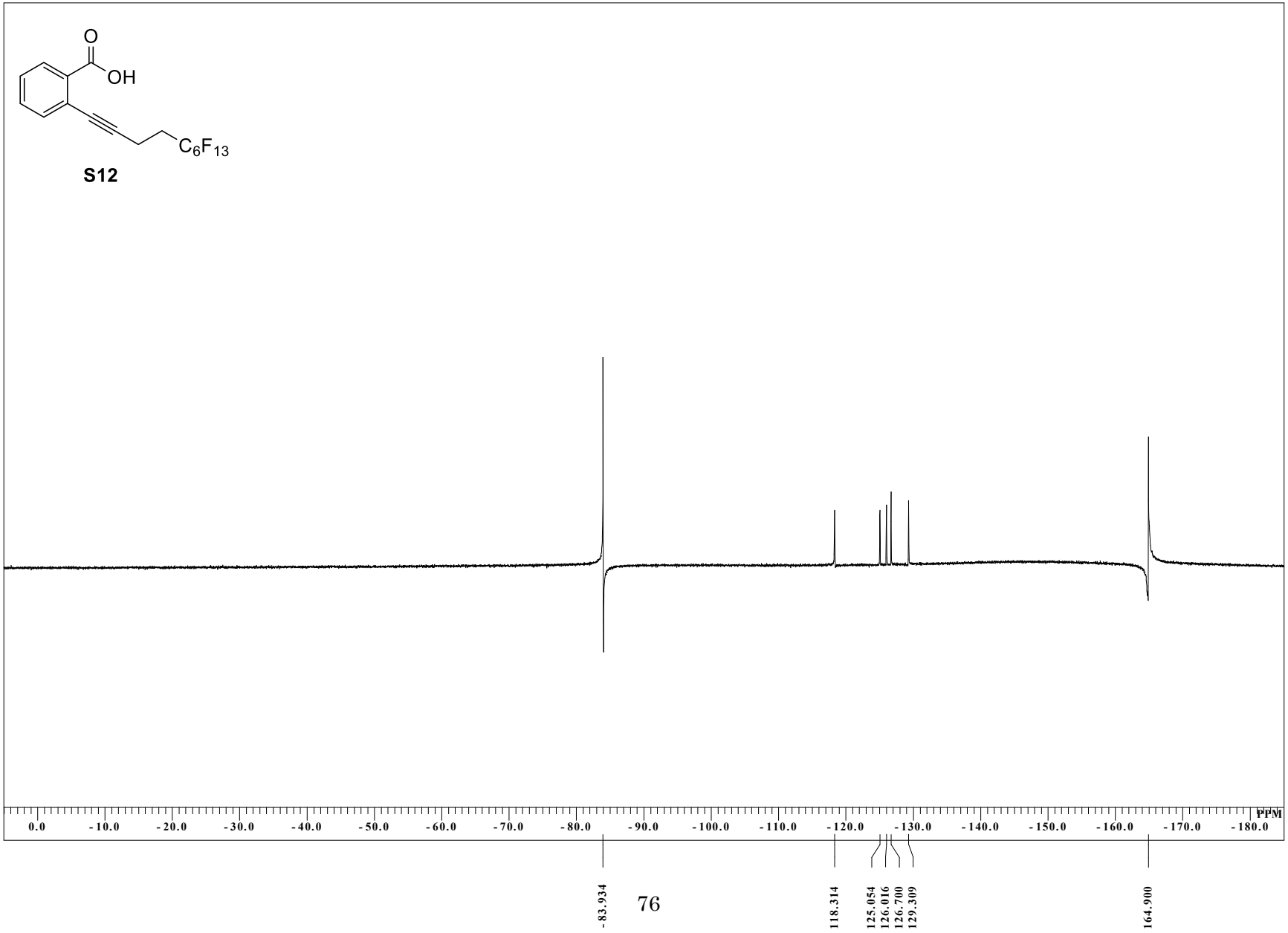
COOH 19F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OH
C_6F_{13}
S12
0.0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
-70.0
-80.0
-90.0
-100.0
-110.0
-120.0
-130.0
-140.0
-150.0
-160.0
-170.0
-180.0
PPM
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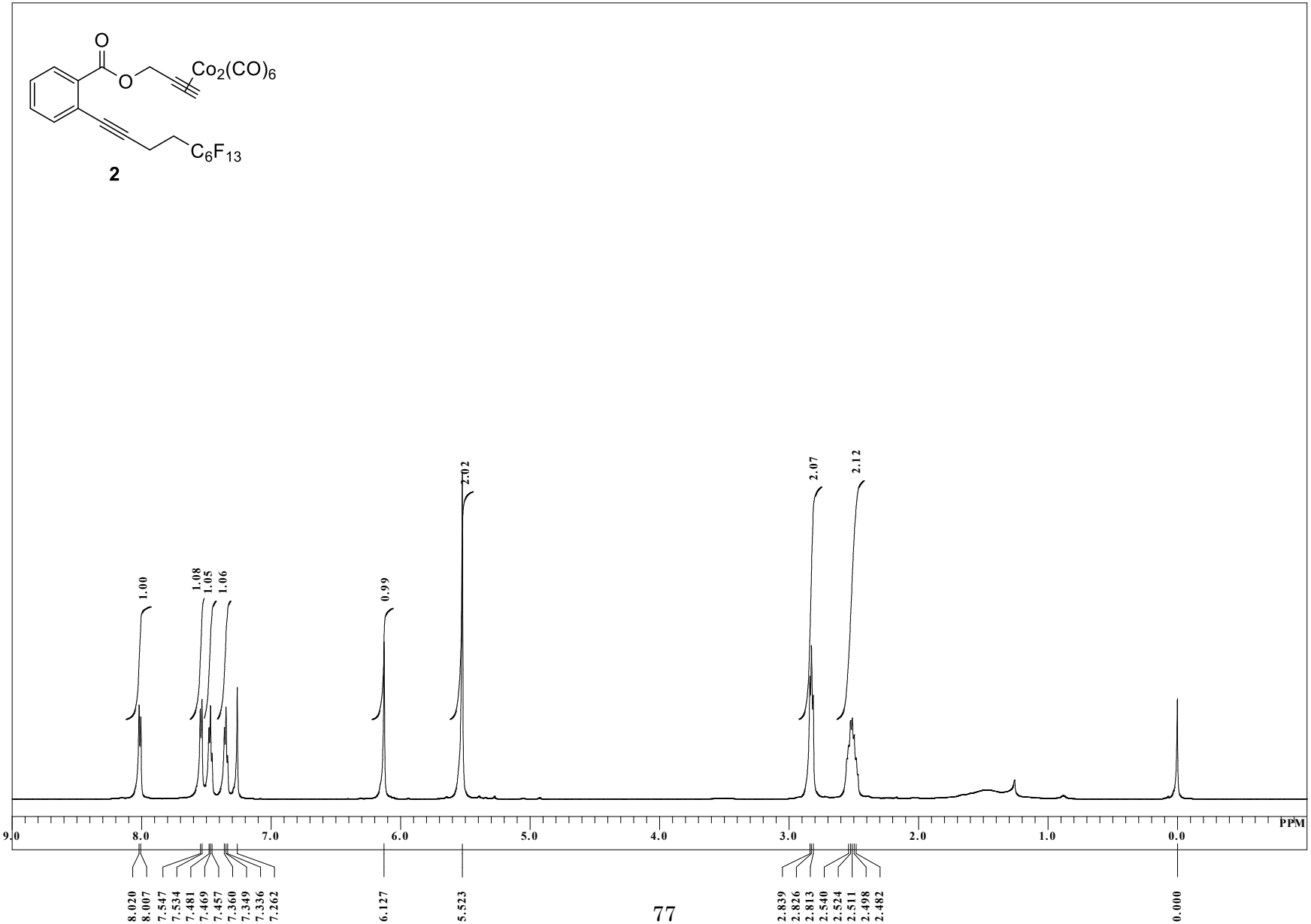
126.016
126.700
129.309
164.900

reagent 1H


O
O
$Co_2(CO)_6$
C_6F_{13}
2
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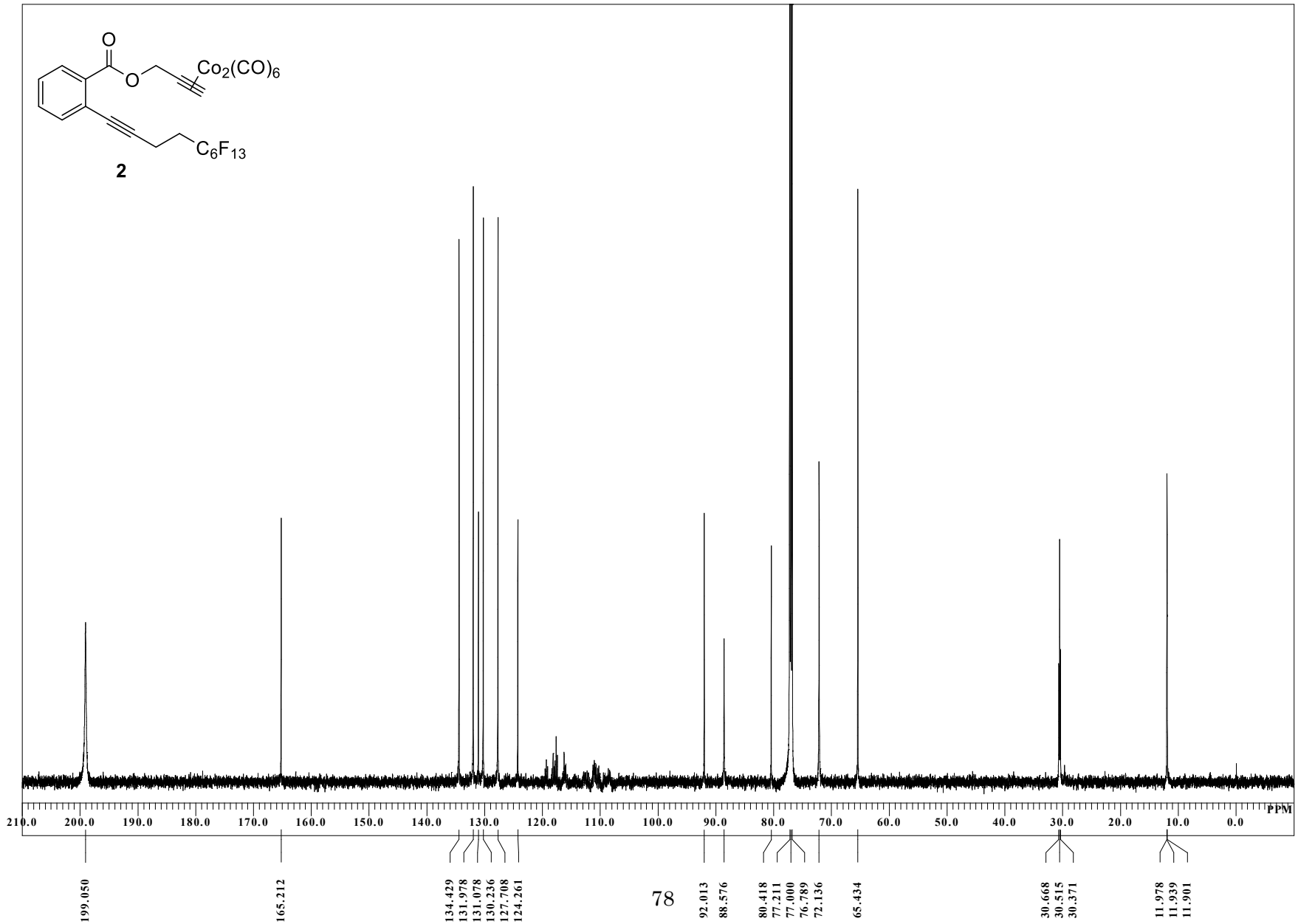
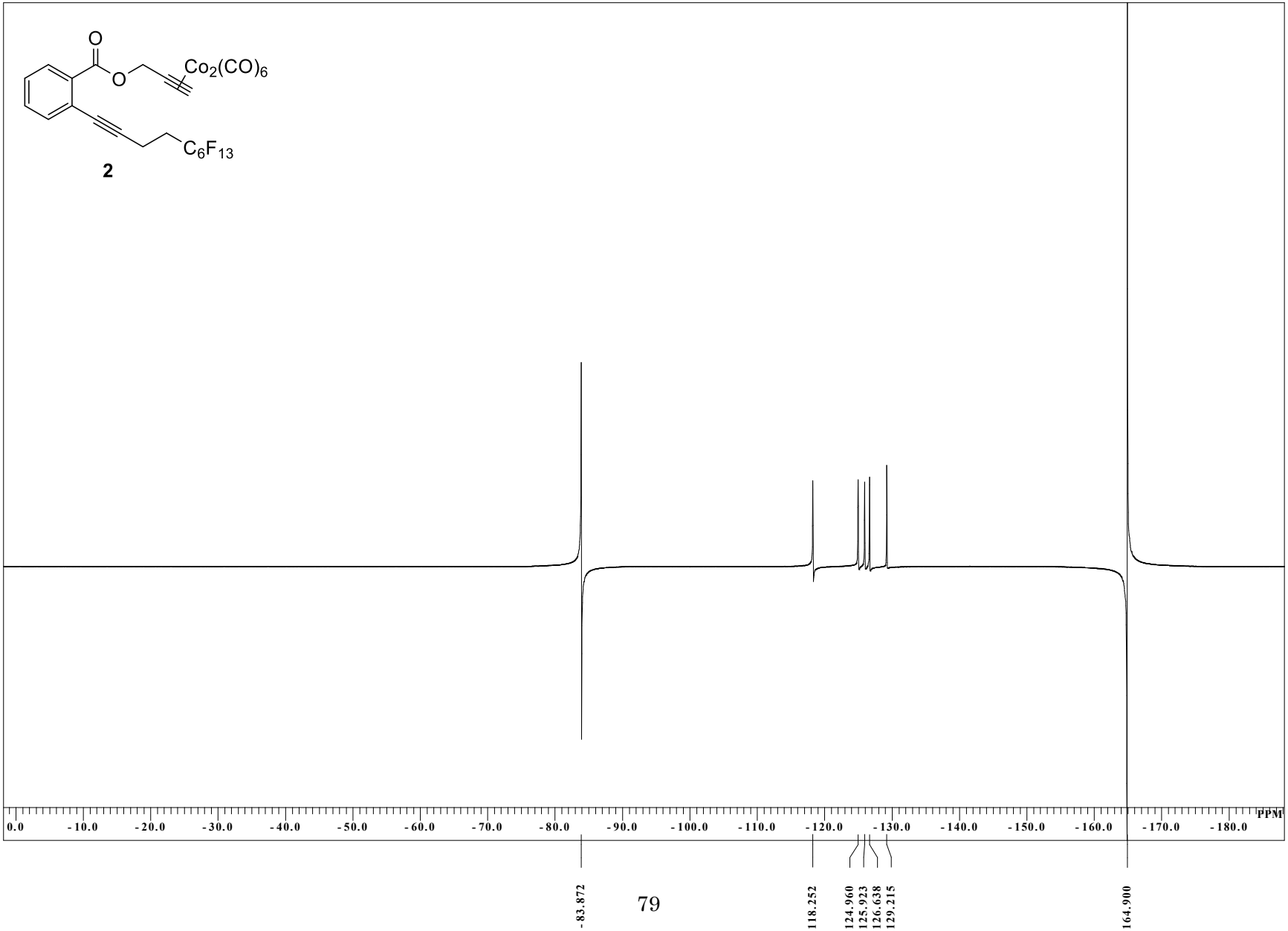
1.08
1.05
1.06
0.99
2.02
2.07
2.12
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
8.020
8.007
7.547
7.534
7.481
7.469
7.457
7.360
7.349
7.336
7.262
6.127
5.523
2.839
2.826
2.813
2.540
2.524
2.511
2.498
2.482
0.000

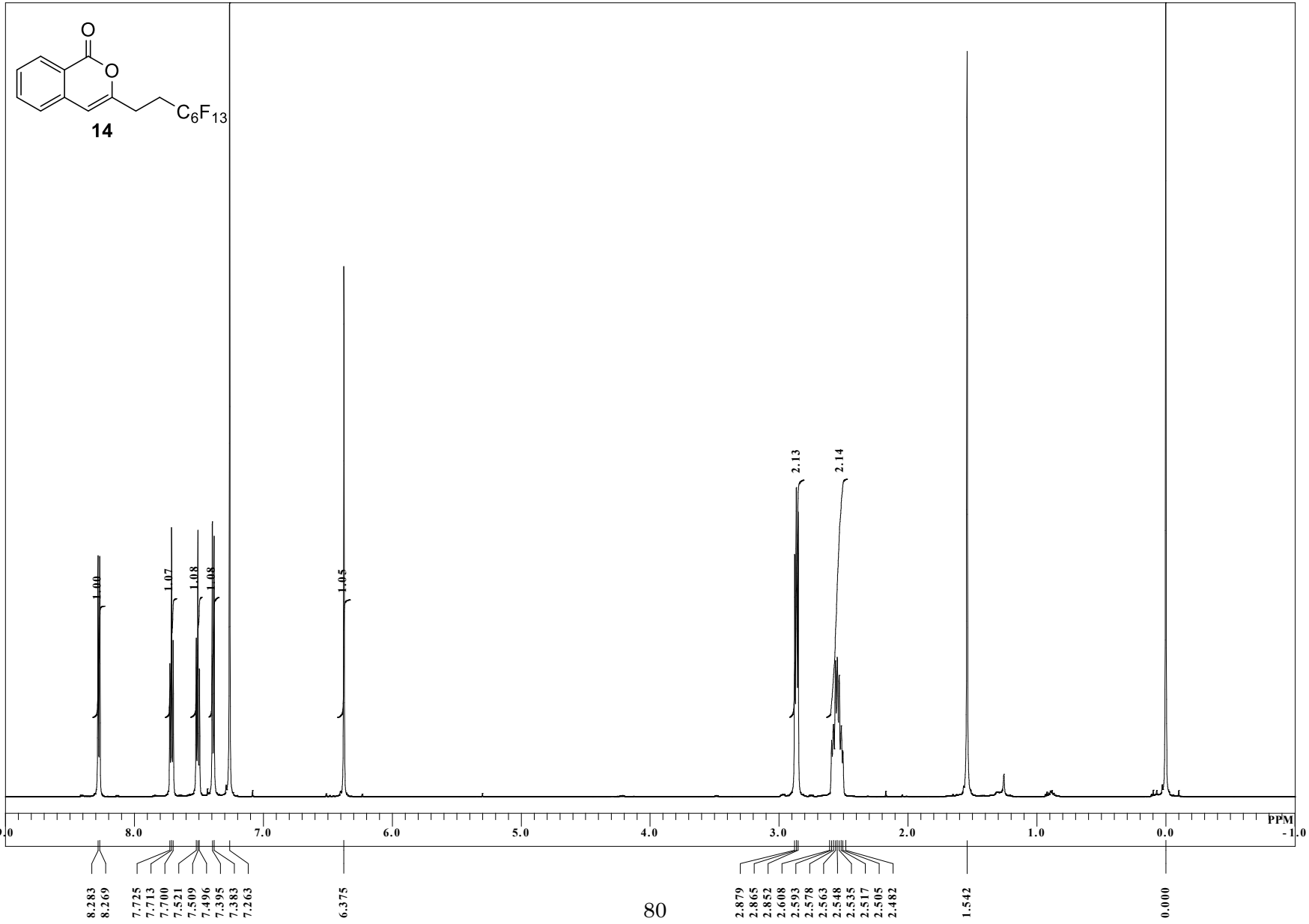
reagent 13C


O
O
$Co_2(CO)_6$
C_6F_{13}
2
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
PPM
199.050
165.212
134.429
131.978
131.078
130.236
127.708
124.261
92.013
88.576
80.418
77.211
77.000
76.789
72.136
65.434
30.668
30.515
30.371
11.978
11.939
11.901

C6F13reagent 19F



isocoumalin 1H



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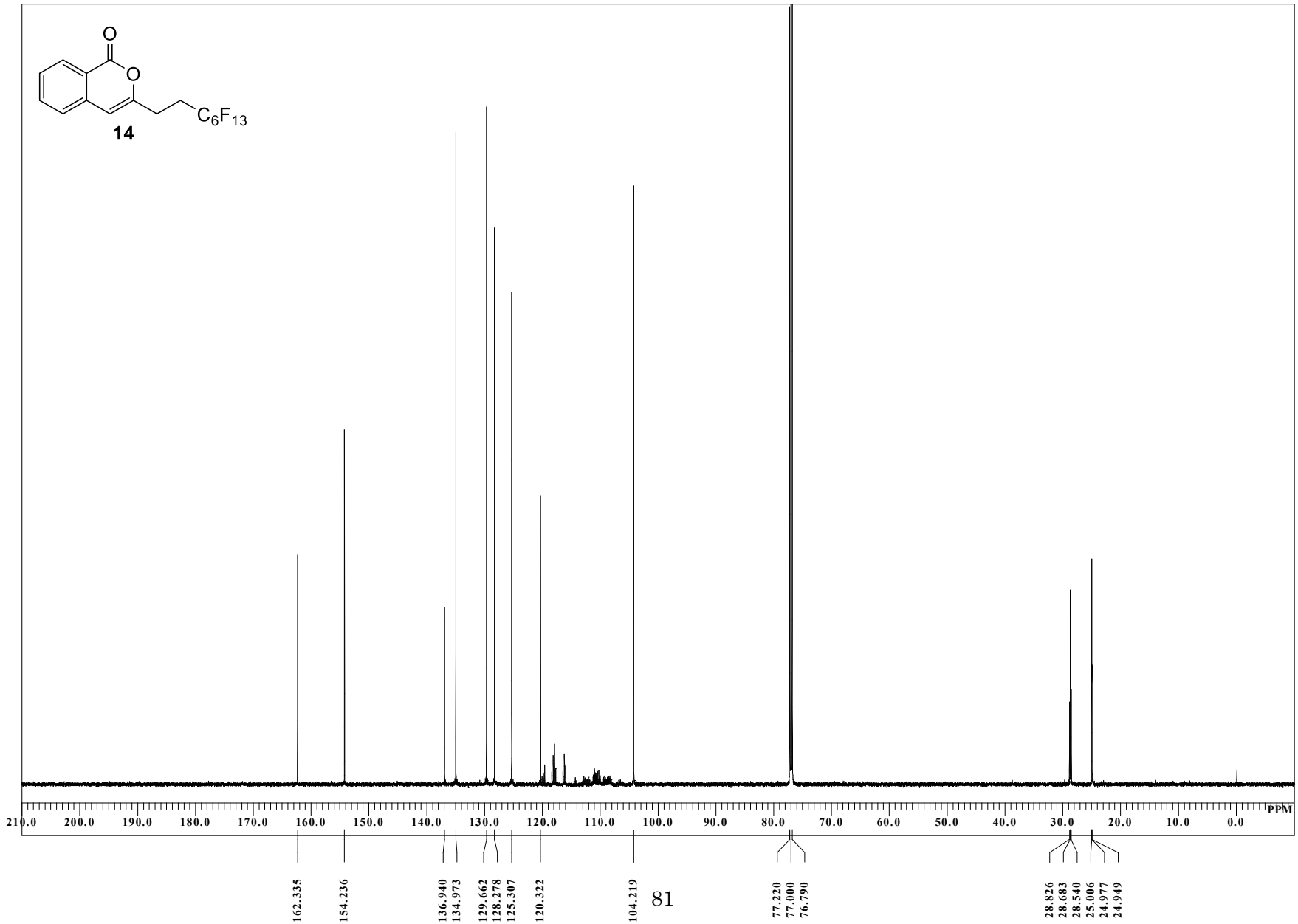

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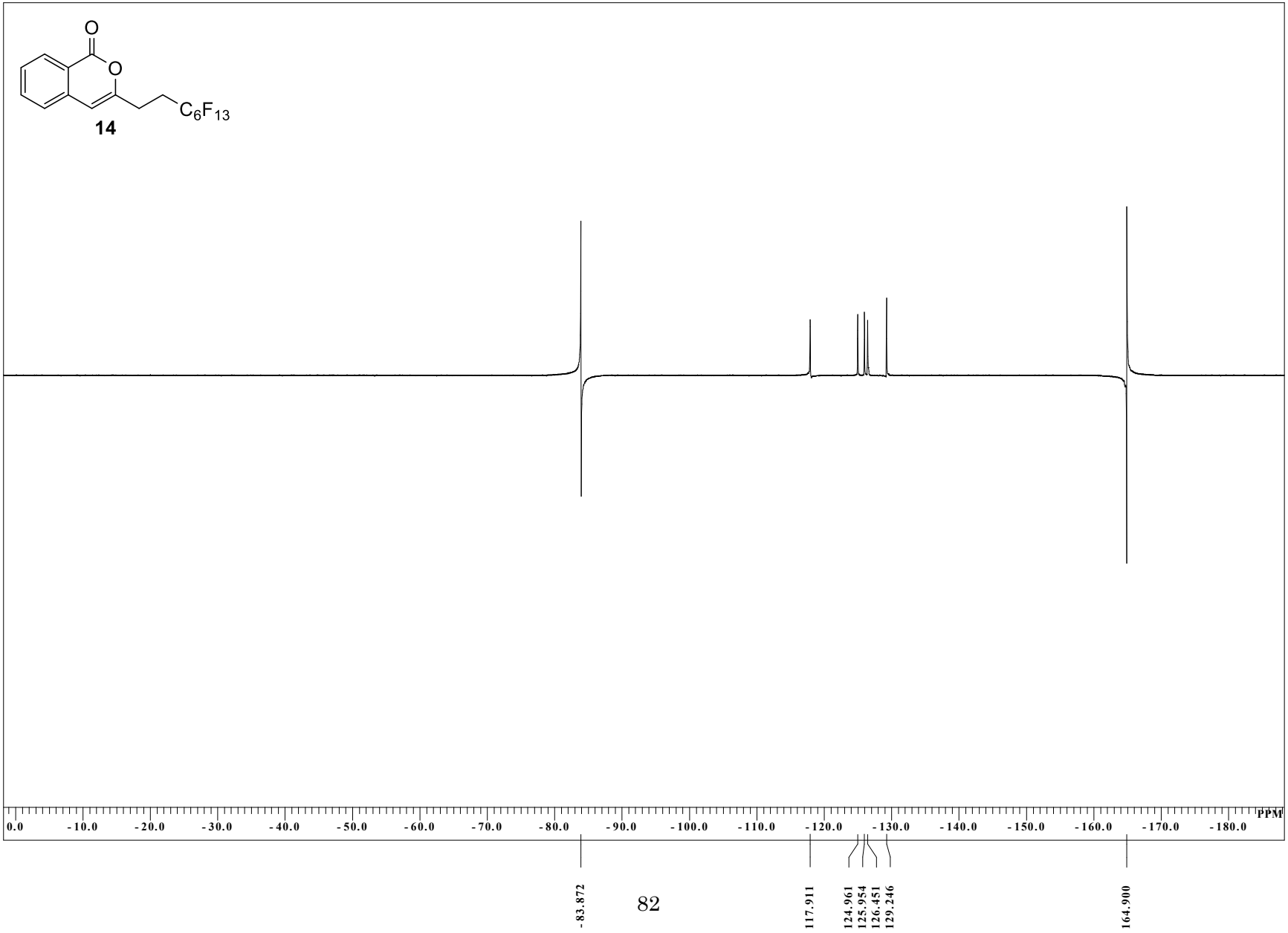
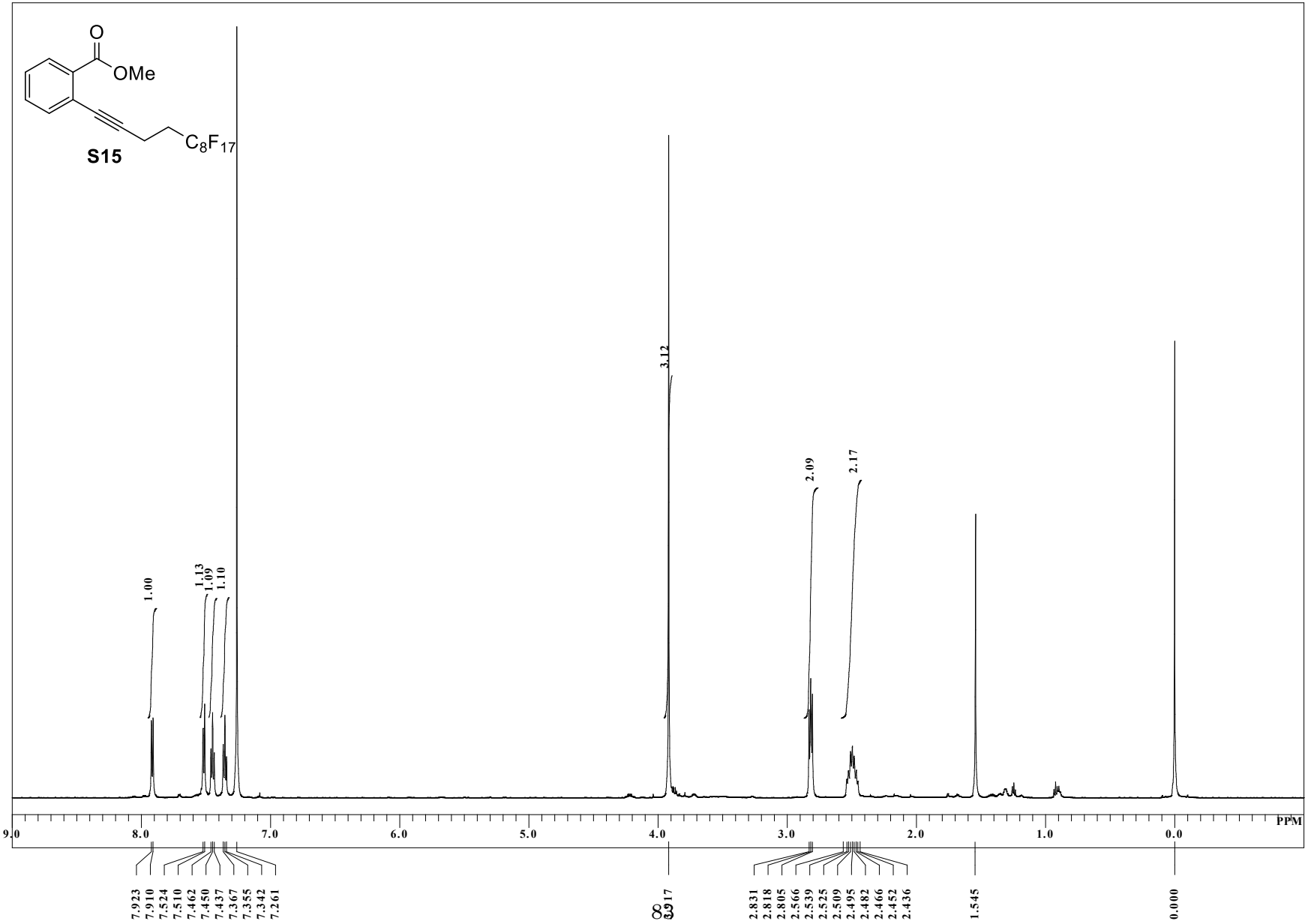


C8F17 Me ester 1H



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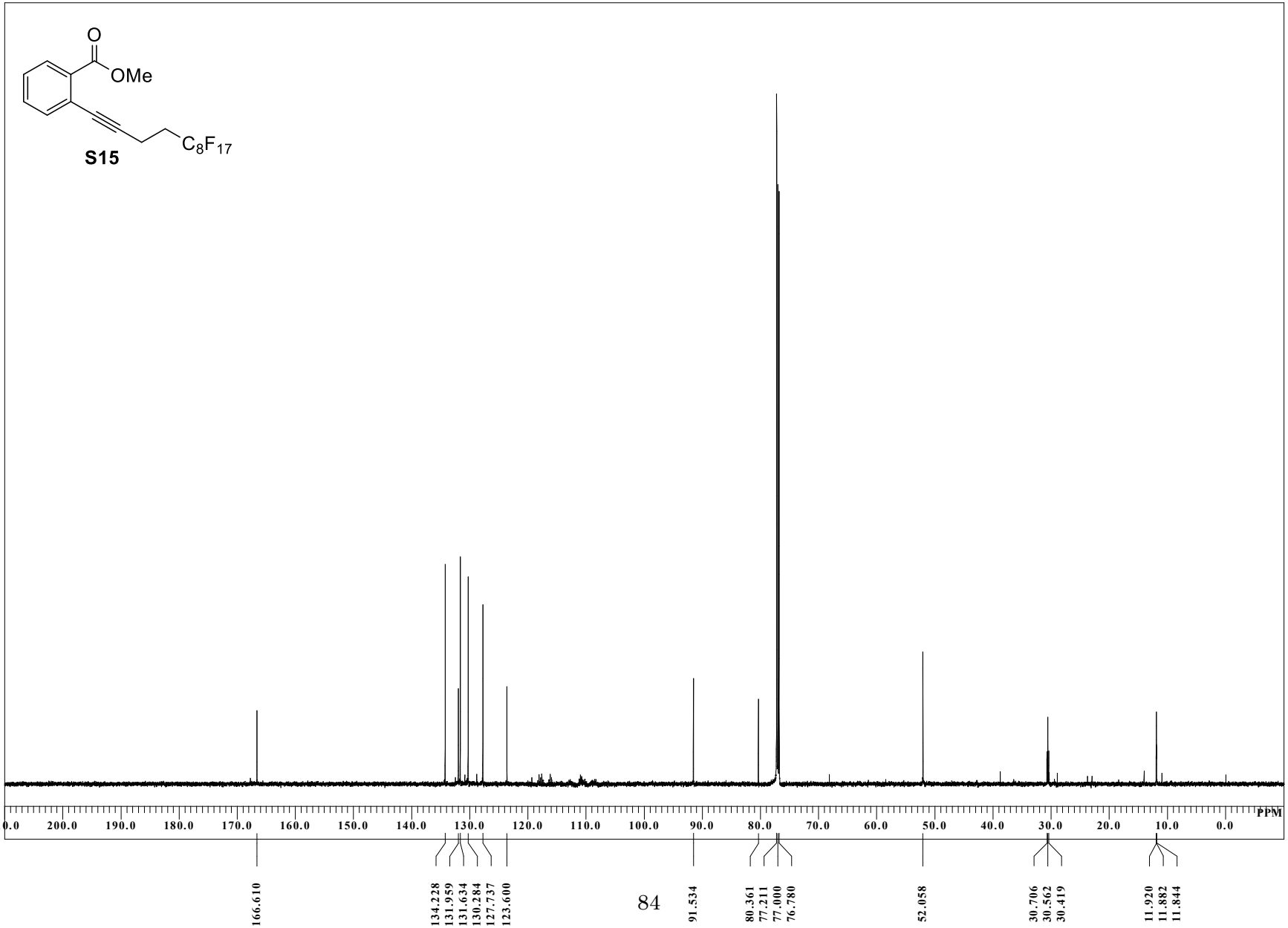

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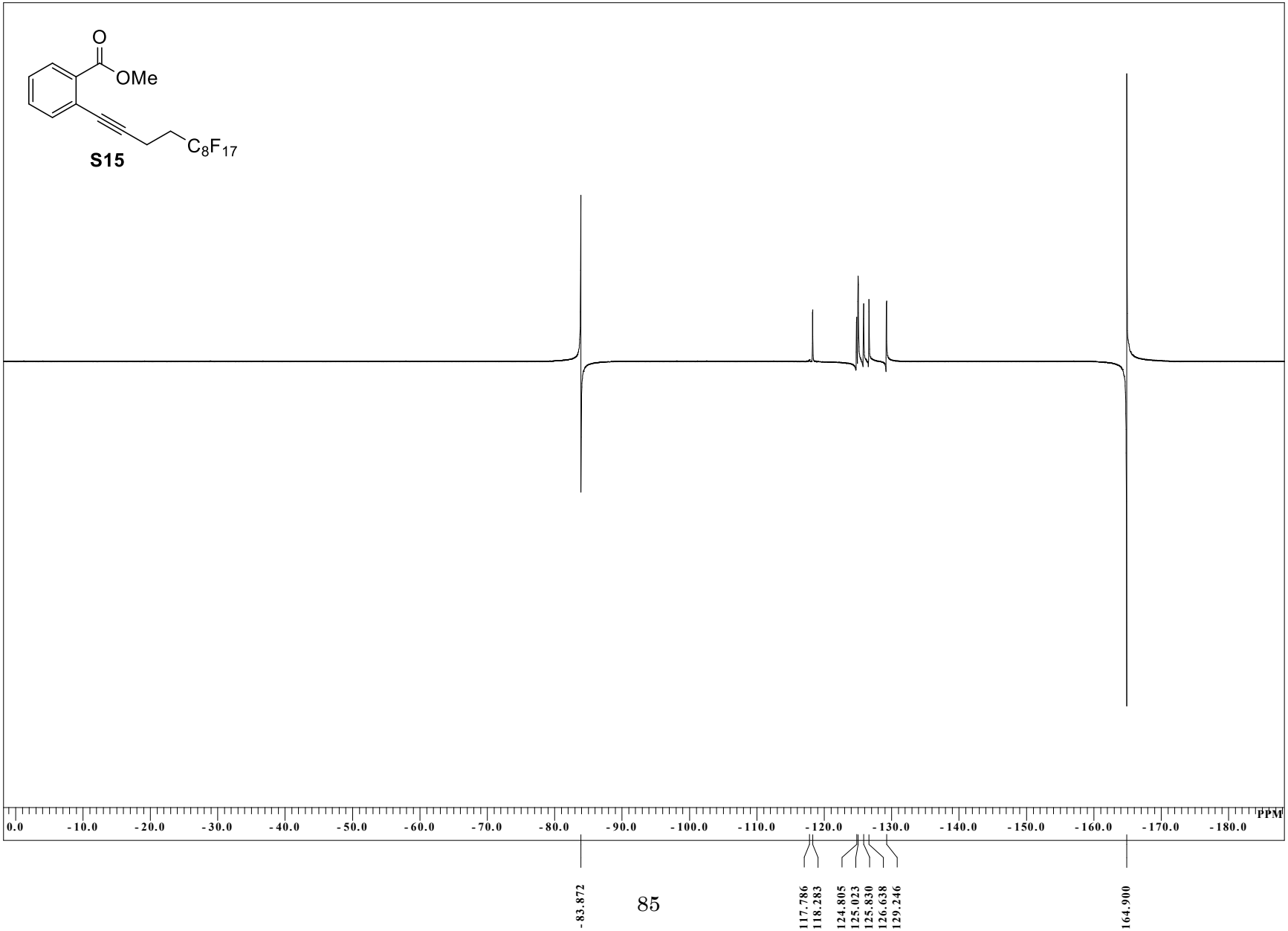

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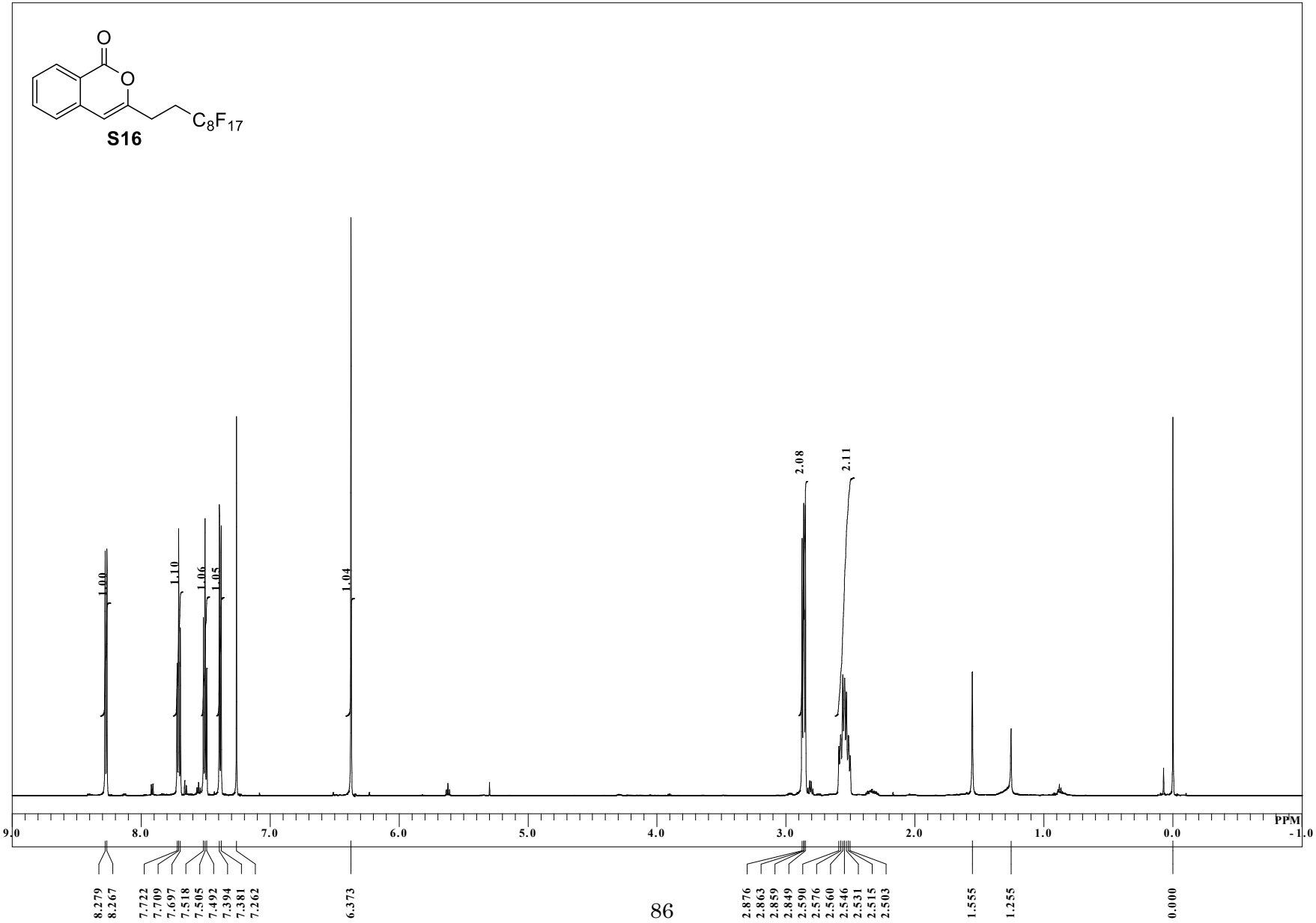

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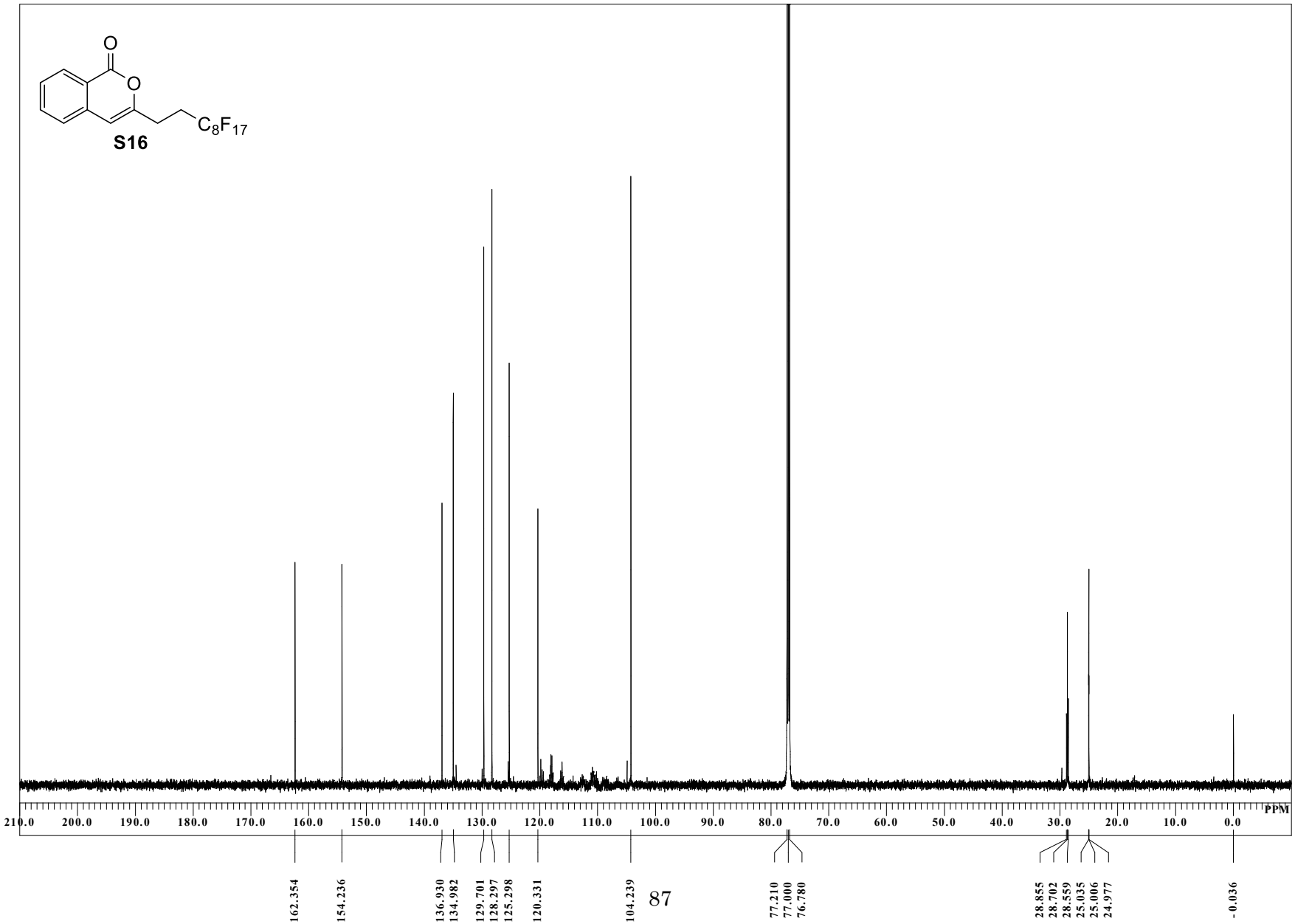

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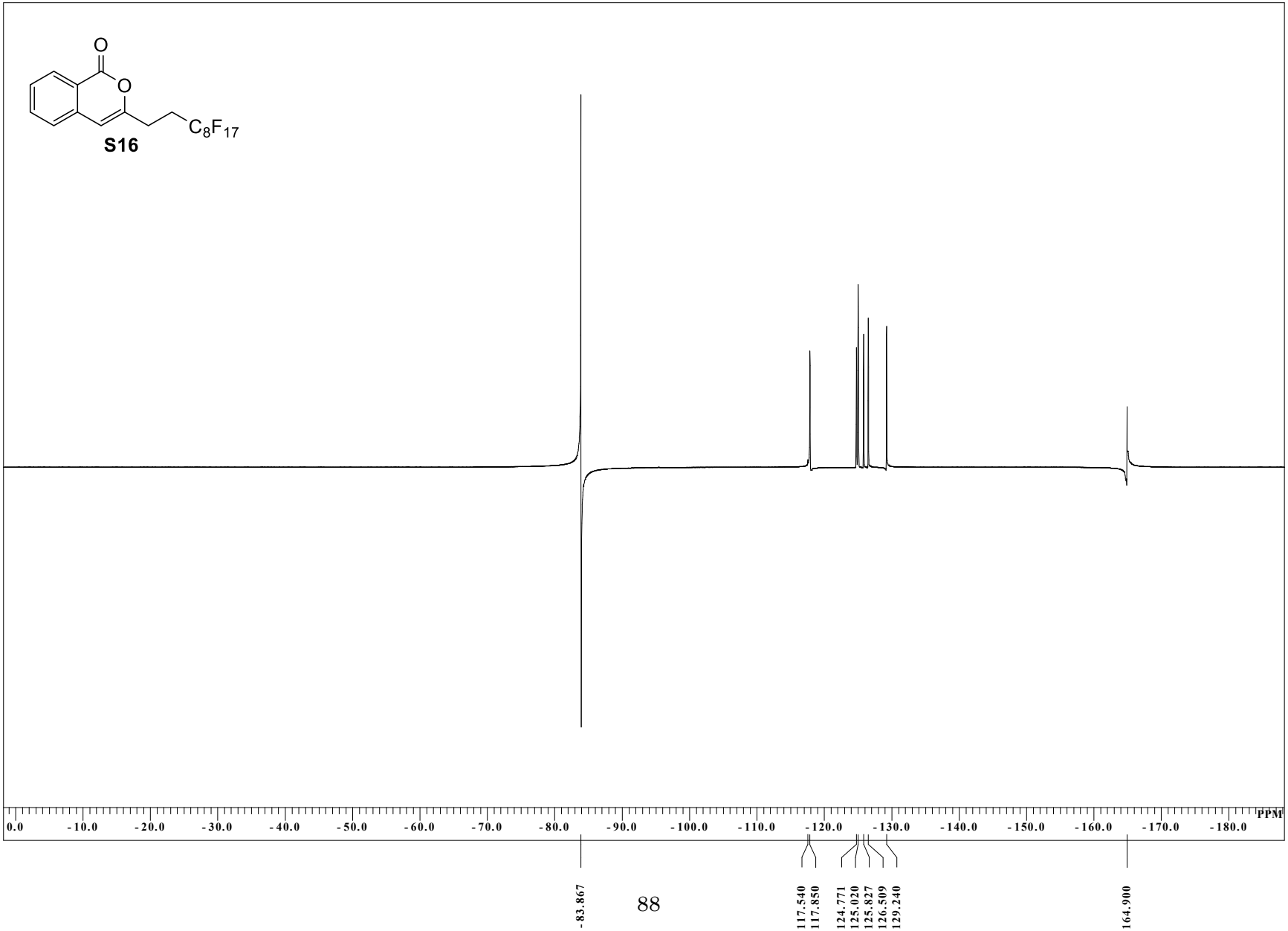
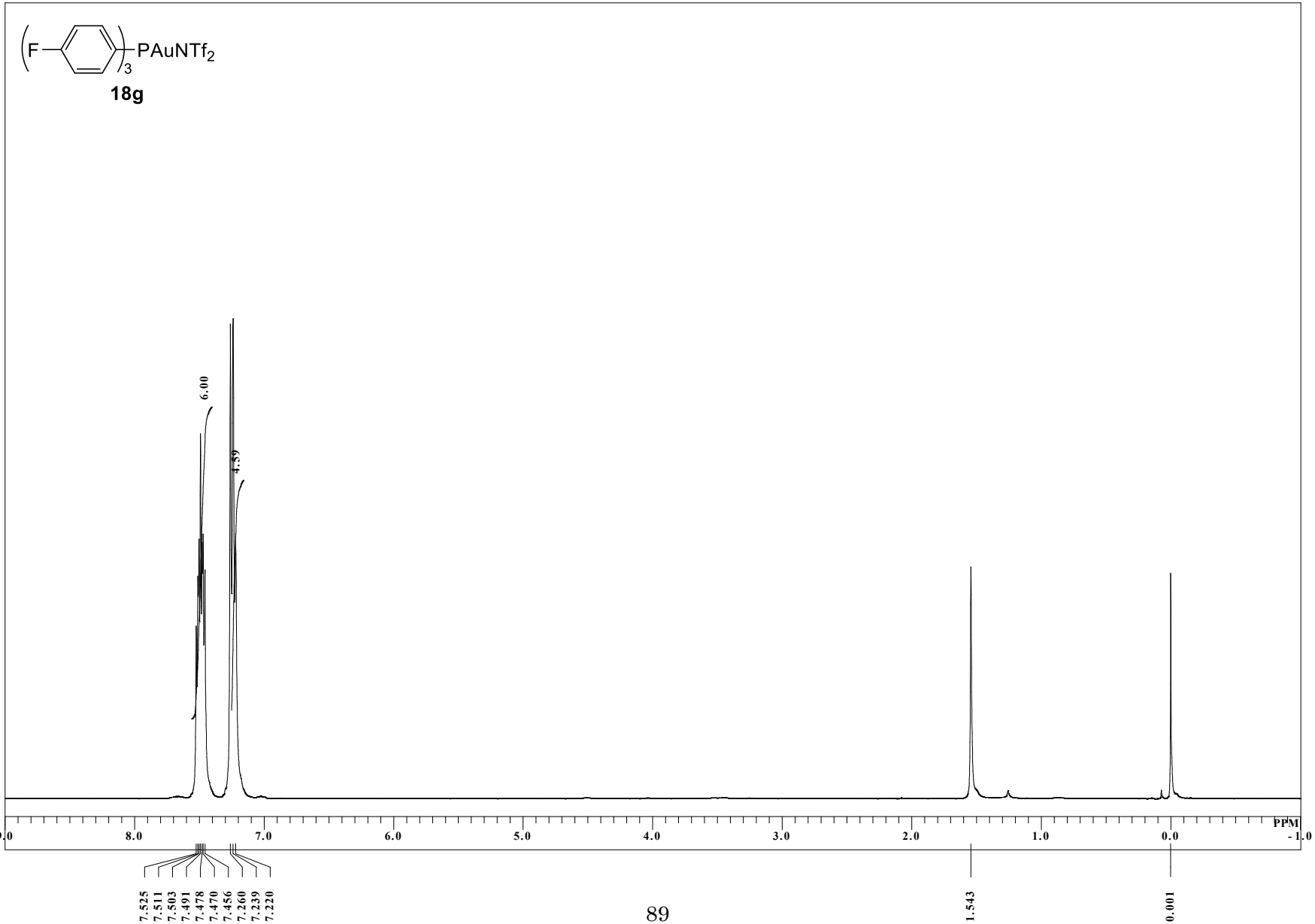
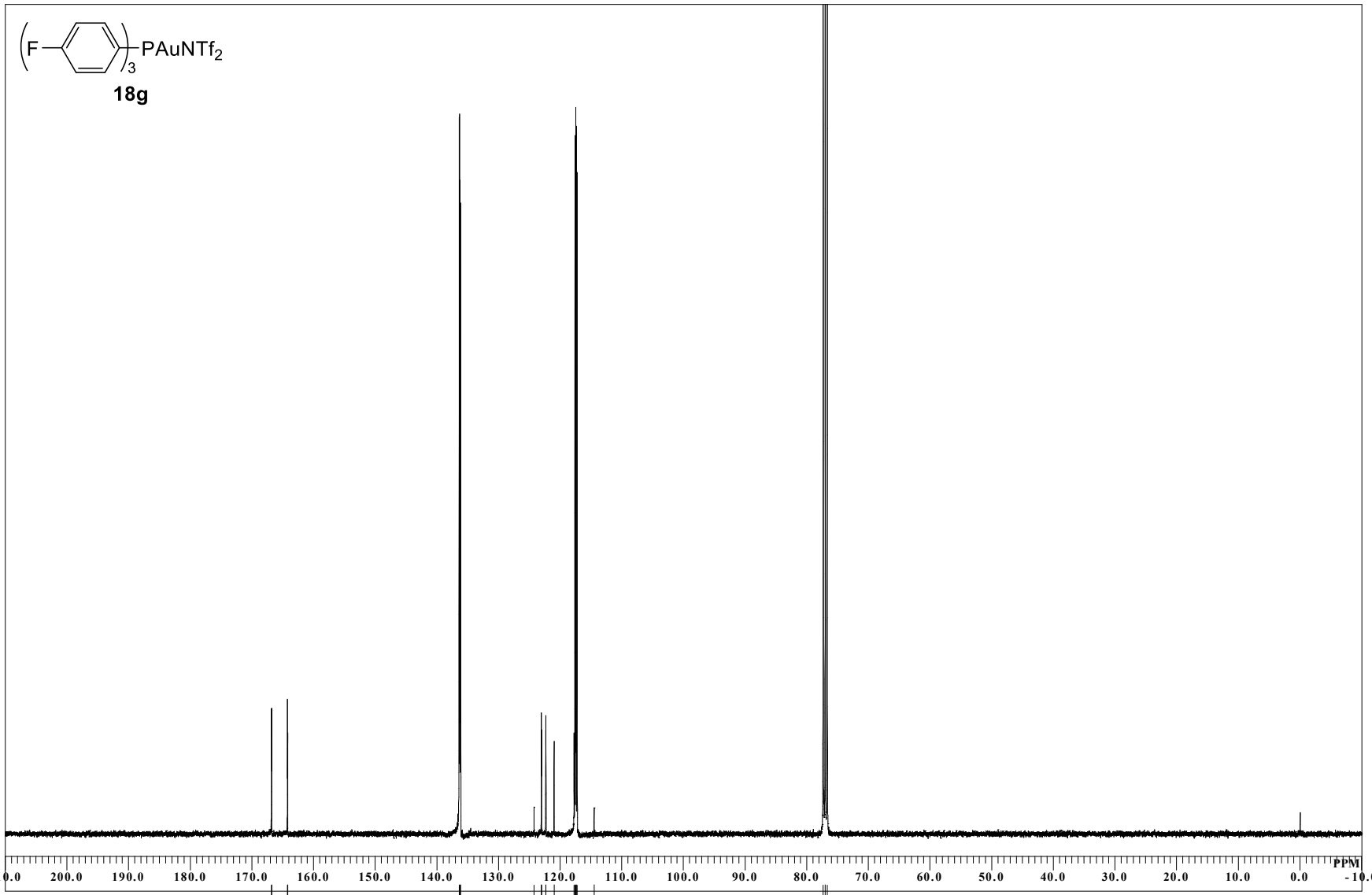


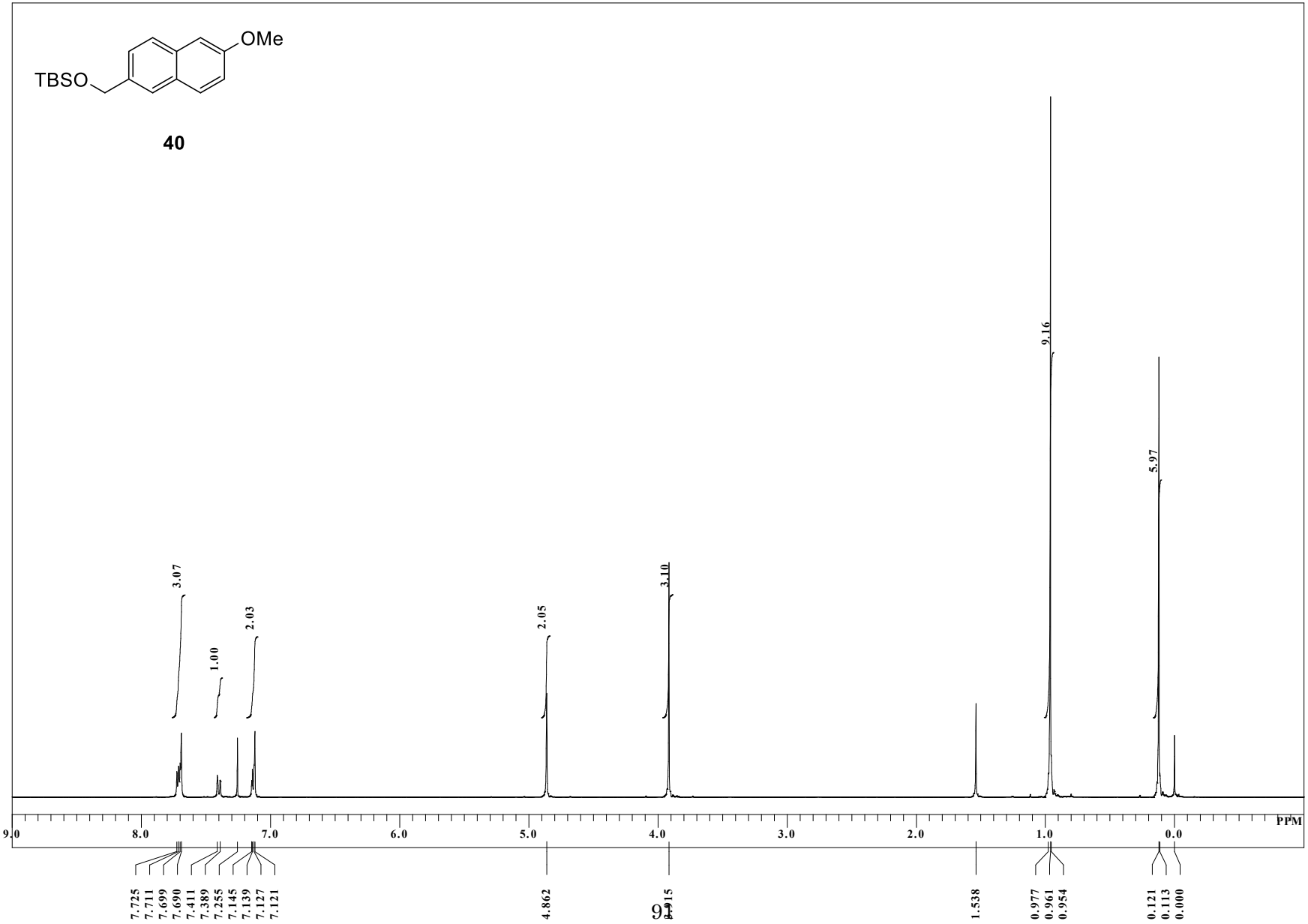
F- AuNTf2 1H


F
PAuNTf2
3
18g
6.00
4.59
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
- 1.0
PPM
7.525
7.511
7.503
7.491
7.478
7.470
7.456
7.260
7.239
7.220
1.543
0.001

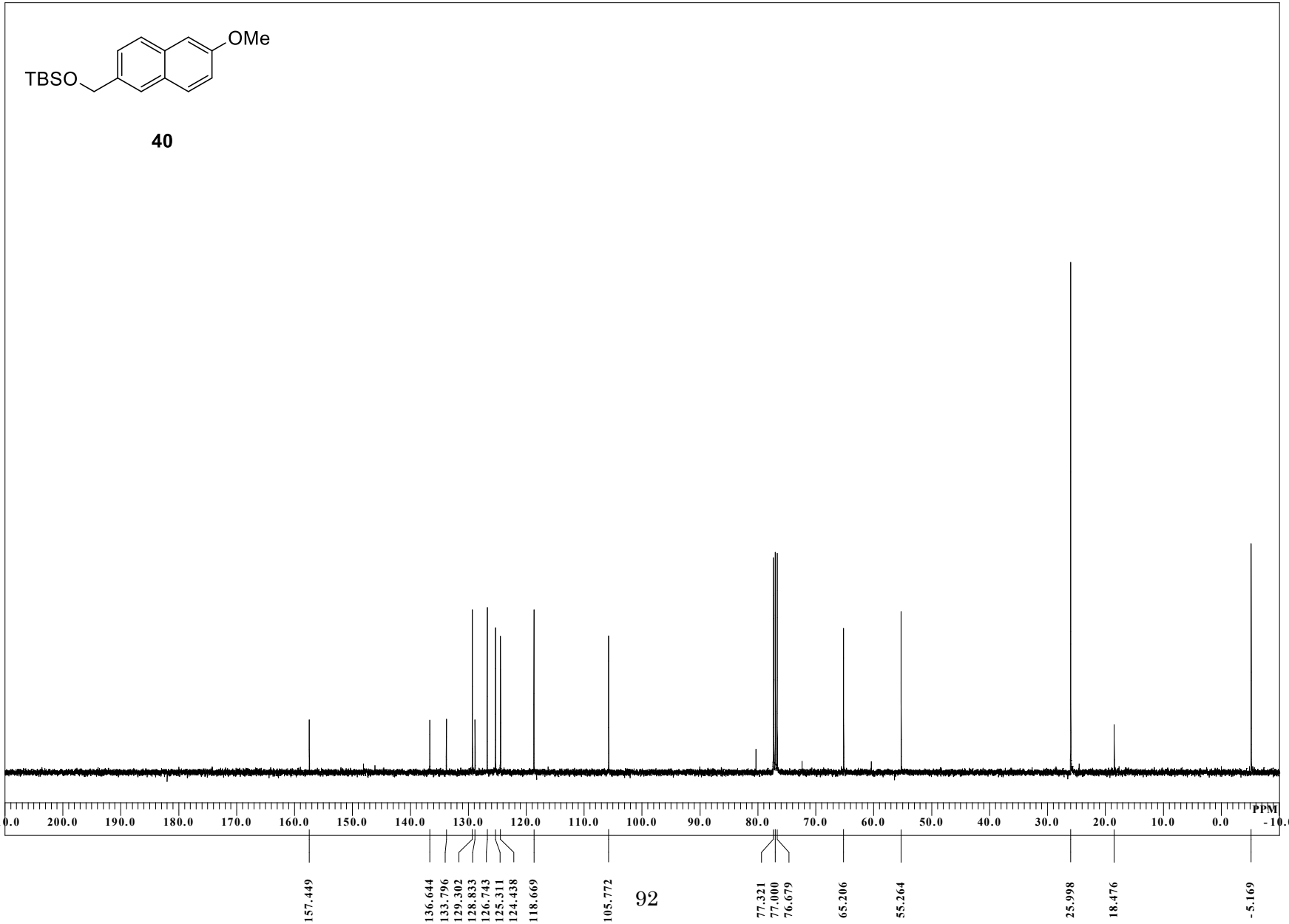
F- AuNTf2 13C


F
PAuNTf2
3
18g
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
PPM
166.815
166.782
164.231
164.198
136.380
136.290
136.224
136.133
124.224
123.031
122.998
122.331
122.299
120.982
117.739
117.599
117.459
117.377
117.237
114.488
77.321
77.000
76.679

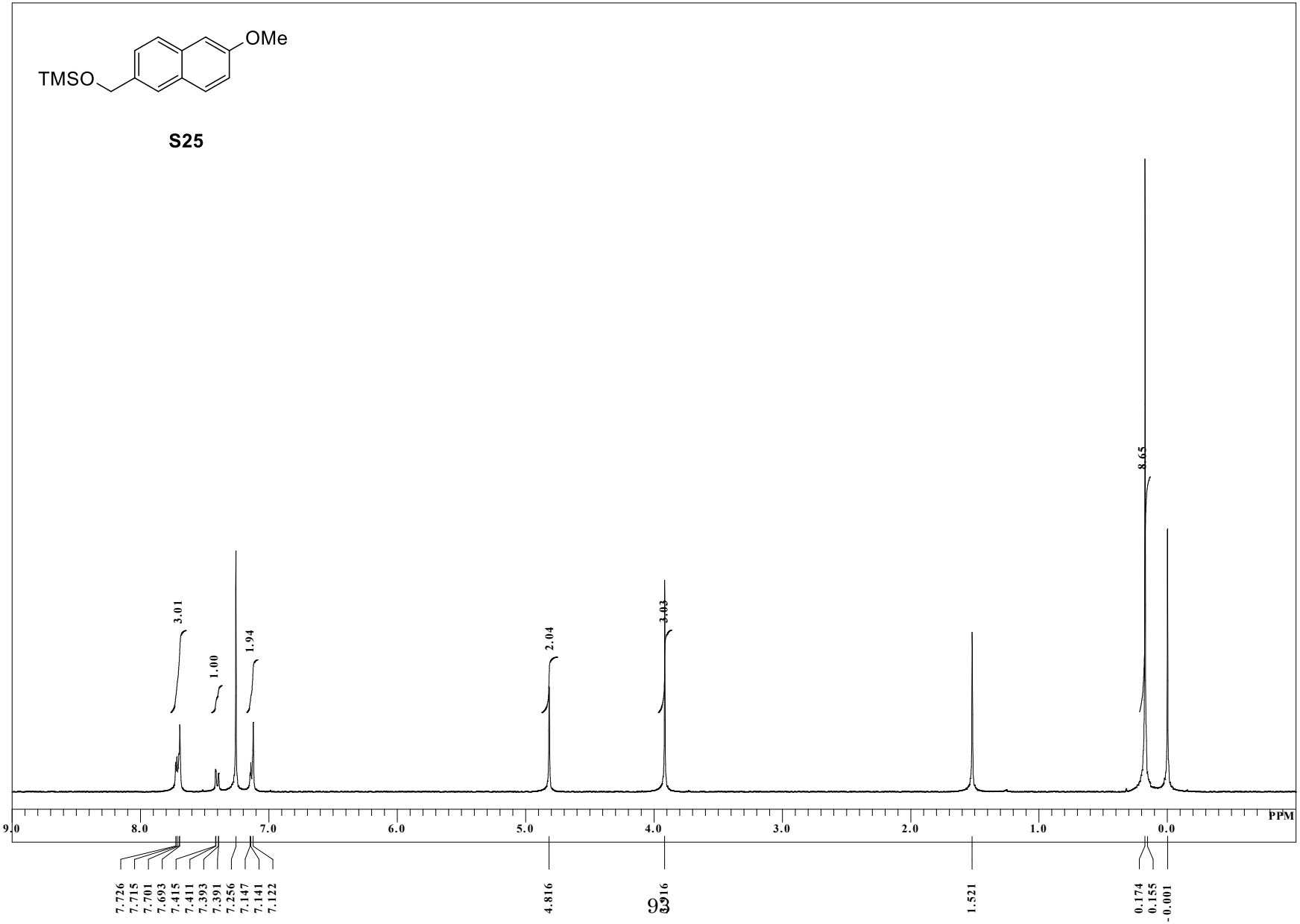
TBS 1H


OMe
TBSO
40
3.07
1.00
2.03
2.05
3.10
9.16
5.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.725
7.711
7.699
7.690
7.411
7.389
7.255
7.145
7.139
7.127
7.121
4.862
4.915
1.538
0.977
0.961
0.954
0.121
0.113
0.000

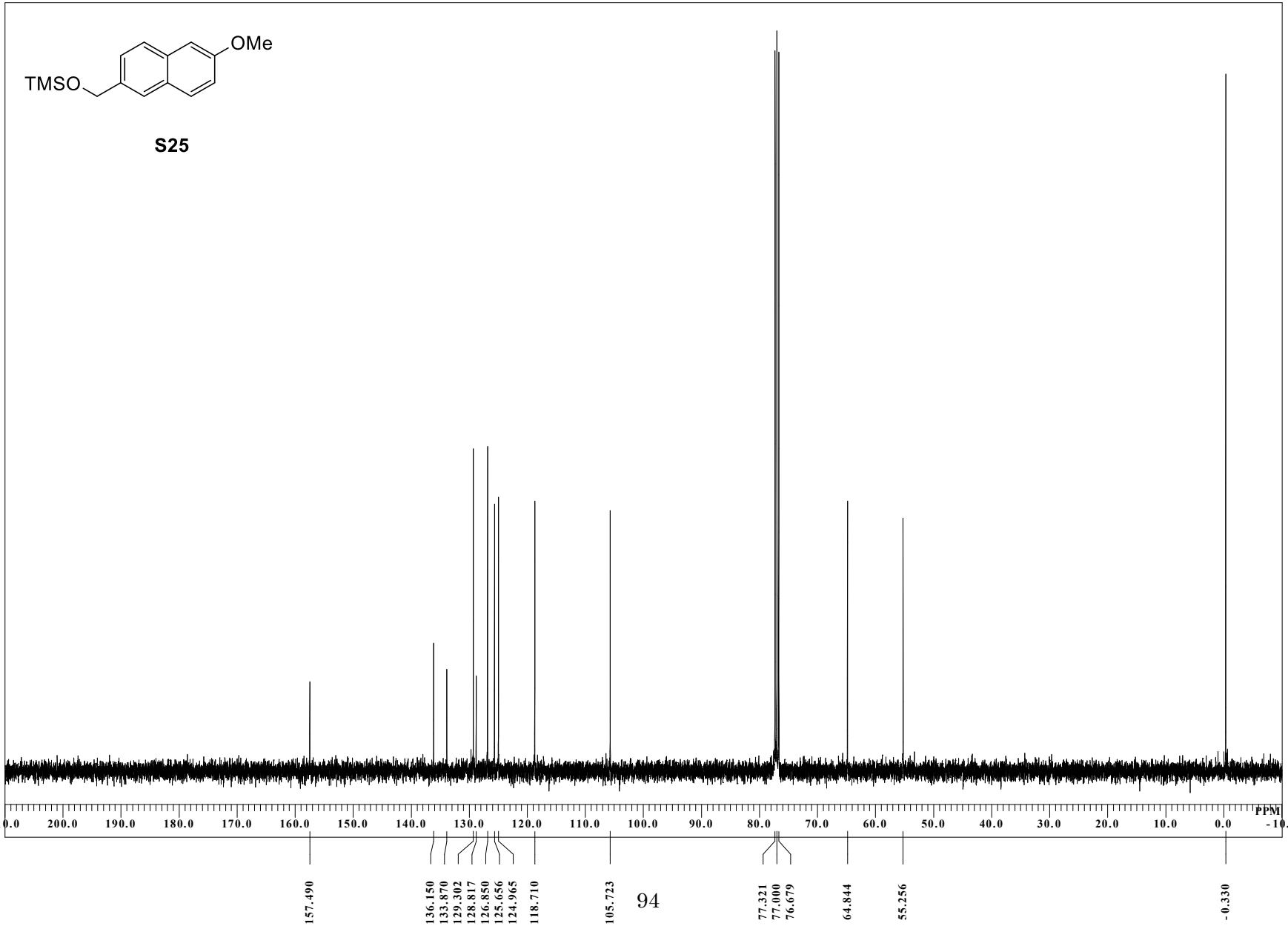
OTBS 13C


OMe
TBSO
40
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
PPM
157.449
136.644
133.796
129.302
128.833
126.743
125.311
124.438
118.669
105.772
77.321
77.000
76.679
65.206
55.264
25.998
18.476
-5.169

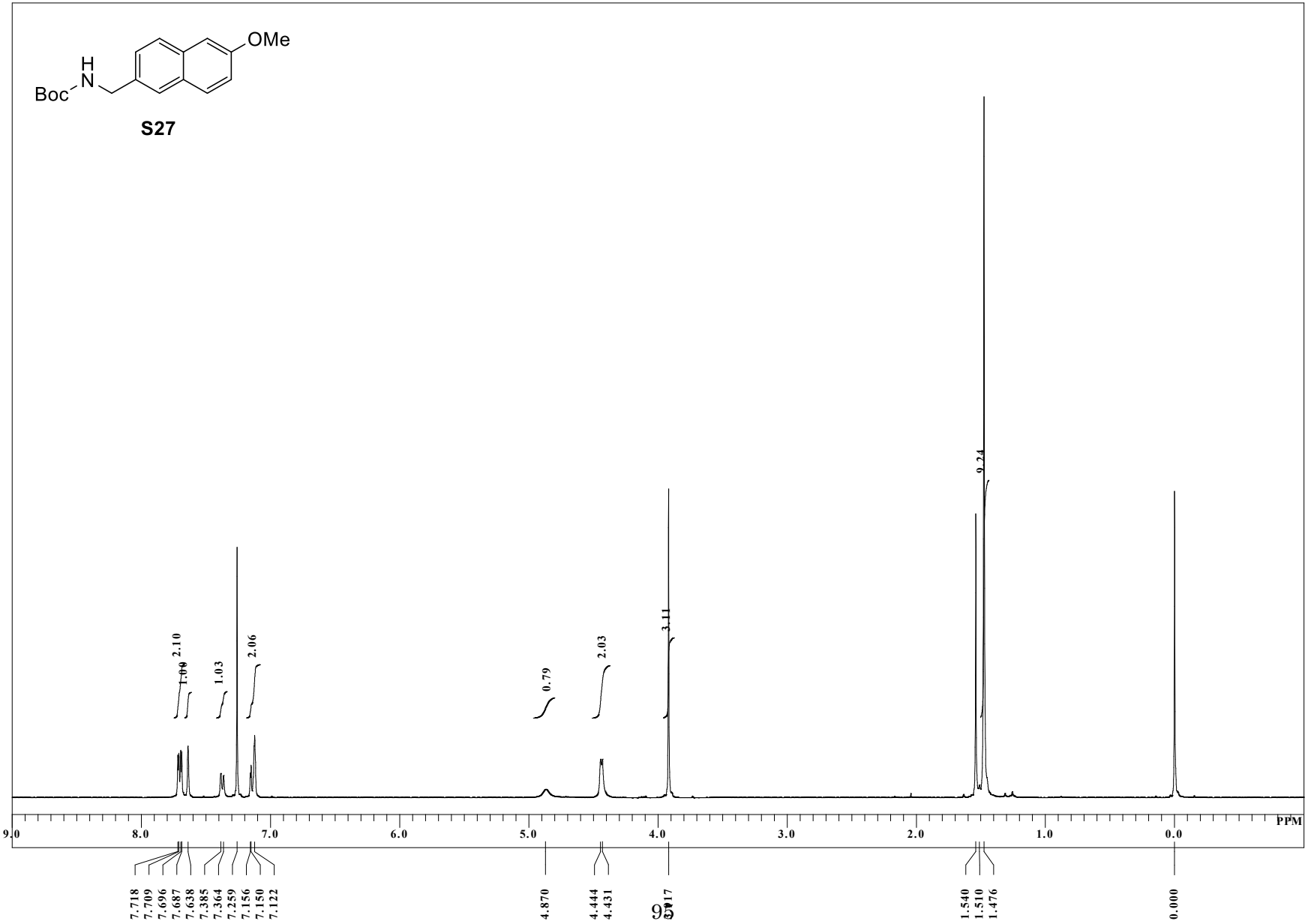
TMS 1H


OMe
TMSO
S25
3.01
1.00
1.94
2.04
3.03
8.65
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.726
7.715
7.701
7.693
7.415
7.411
7.393
7.391
7.256
7.147
7.141
7.122
4.816
3.916
1.521
0.174
0.155
-0.001

TMS 13C


OMe
TMSO
S25
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0
PPM
157.490
136.150
133.870
129.302
128.817
126.850
125.656
124.965
118.710
105.723
77.321
77.000
76.679
64.844
55.256
-0.330

NHBoc 1H


OMe
H
N
Boc
S27
2.10
1.00
1.03
2.06
0.79
2.03
3.11
9.24
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
7.718
7.709
7.696
7.687
7.638
7.385
7.364
7.259
7.156
7.150
7.122
4.870
4.444
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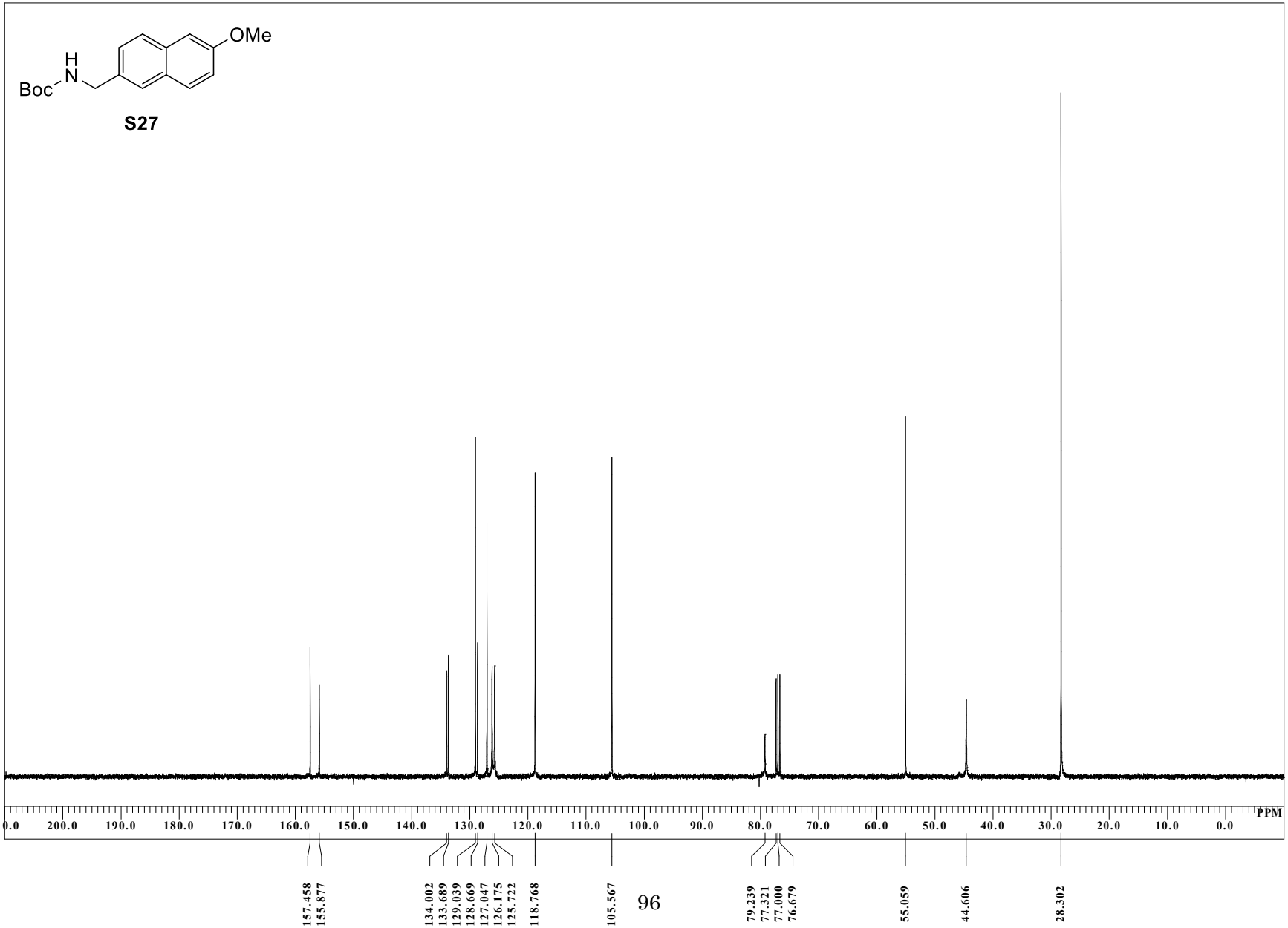
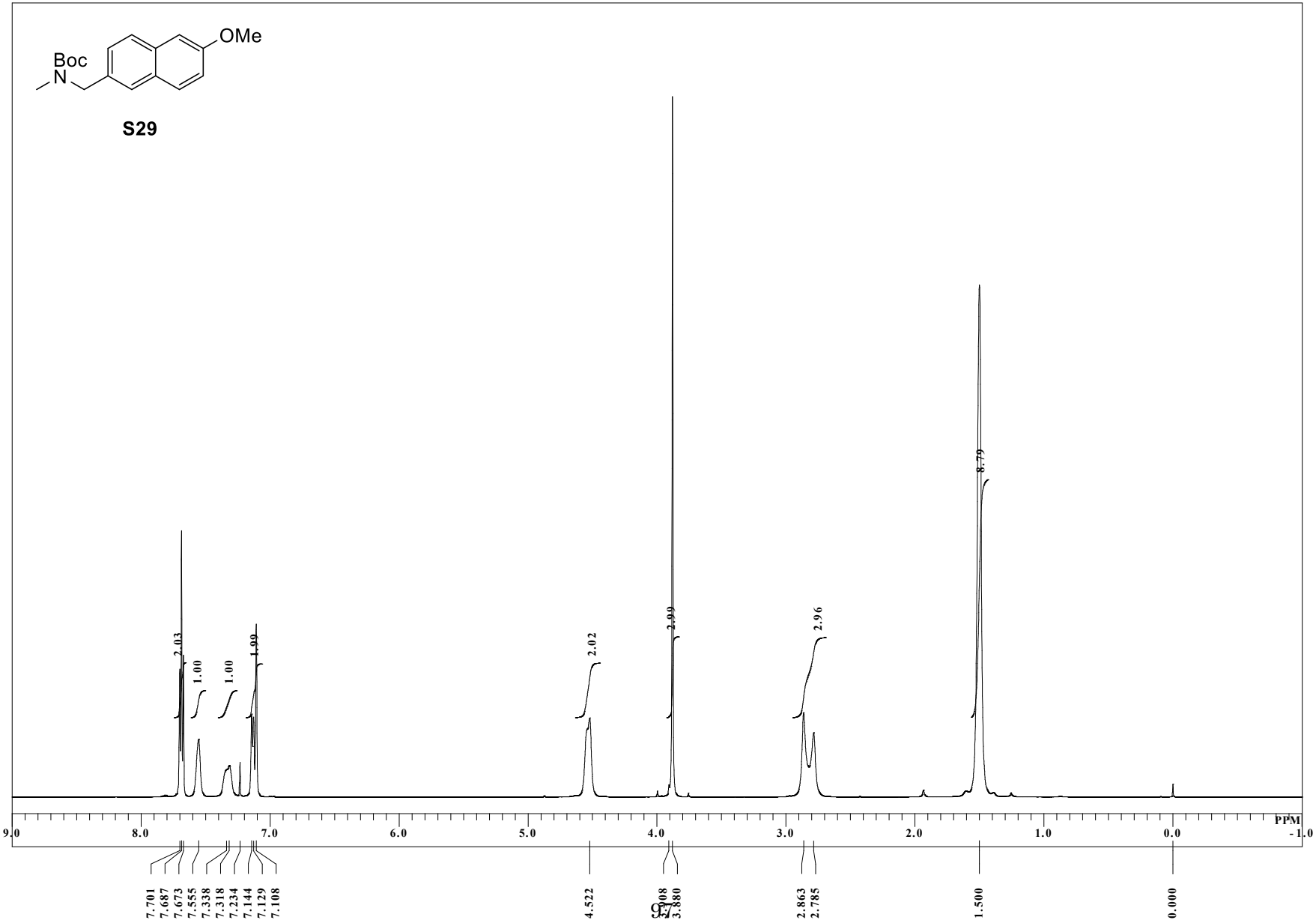
1.540
1.510
1.476
0.000

NHBoc 13C


OMe
H
N
Boc
S27
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PPM
157.458
155.877
134.002
133.689
129.039
128.669
127.047
126.175
125.722
118.768
105.567
79.239
77.321
77.000
76.679
55.059
44.606
28.302

Boc 1H


Boc
N
OMe
S29
2.03
1.00
1.00
1.99
2.02
2.99
2.96
8.79
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
PPM
7.701
7.687
7.673
7.555
7.338
7.318
7.234
7.144
7.129
7.108
4.522
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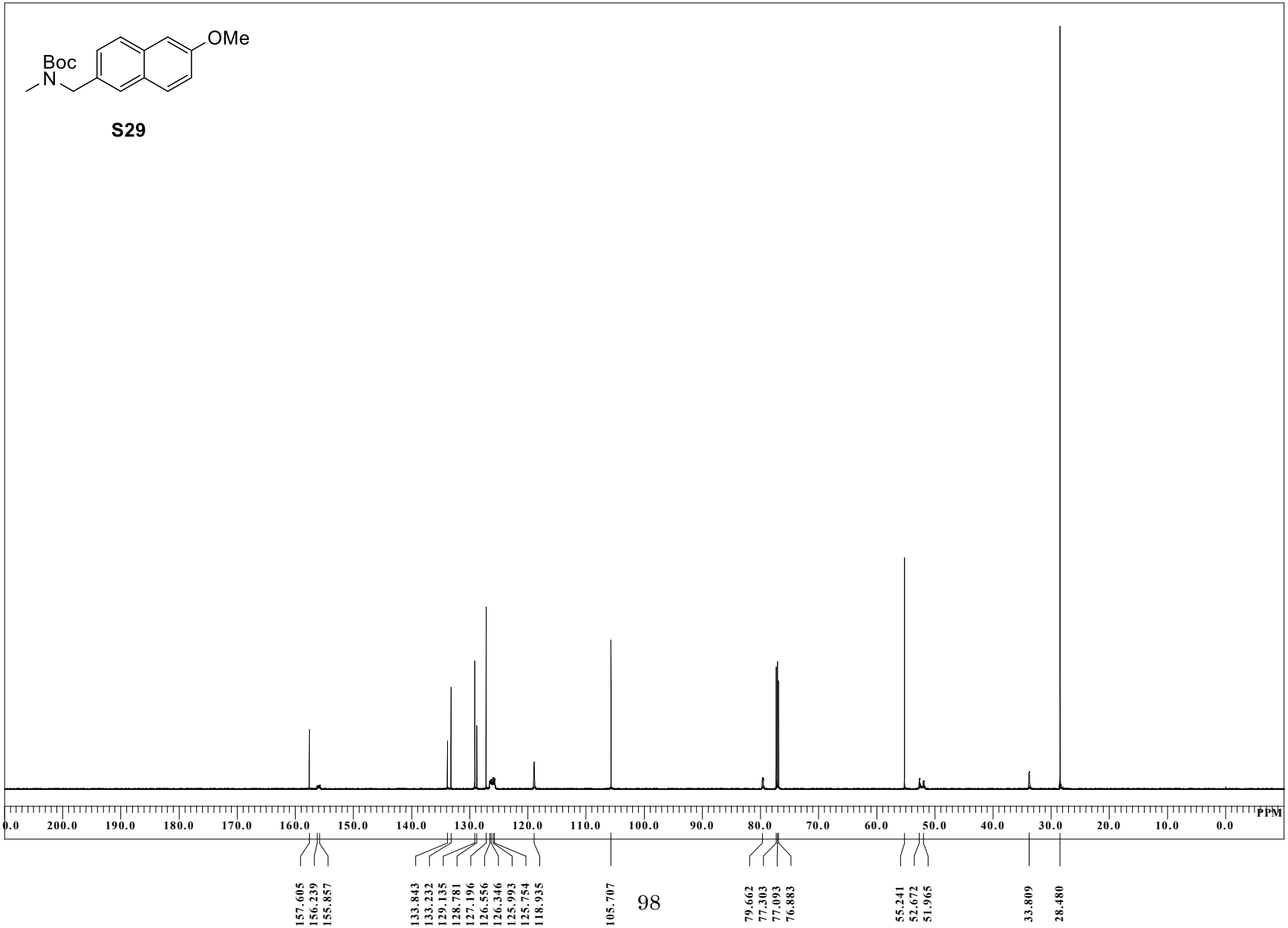
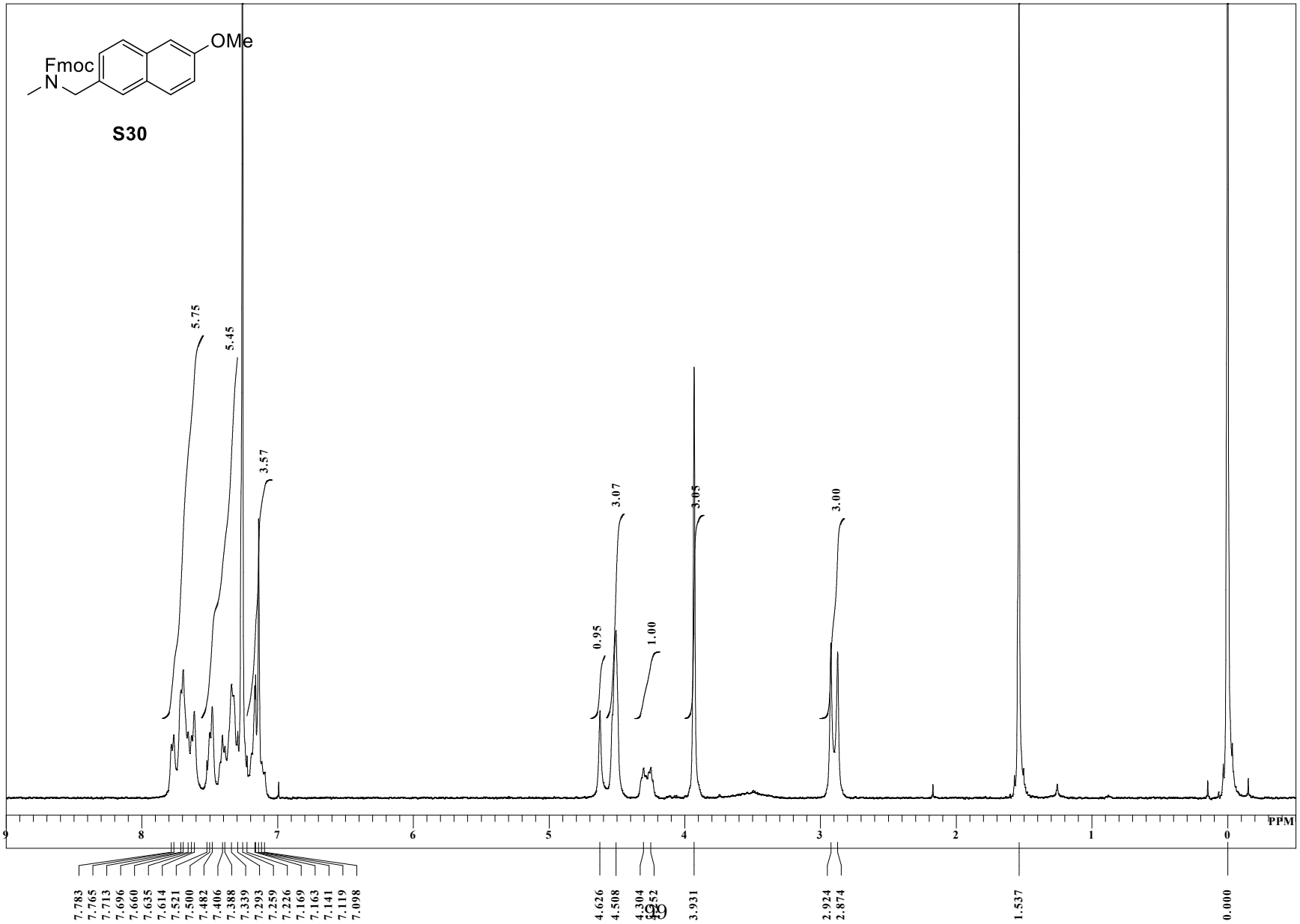
2.863
2.785
1.500
0.000

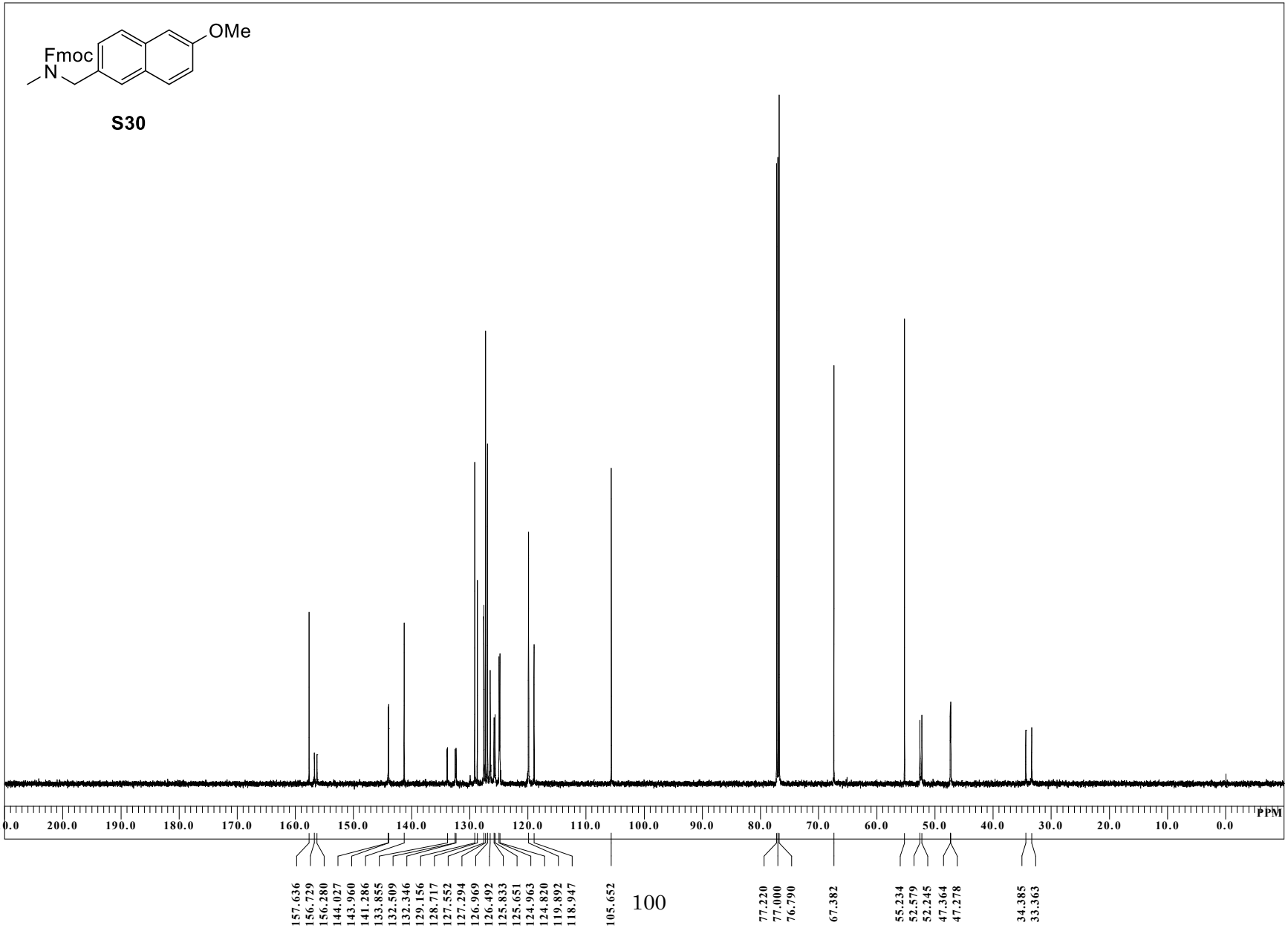
Boc 13C


Boc
N
OMe
S29
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
PPM
157.605
156.239
155.857
133.843
133.232
129.135
128.781
127.196
126.556
126.346
125.993
125.754
118.935
105.707
79.662
77.303
77.093
76.883
55.241
52.672
51.965
33.809
28.480

Fmoc 1H


Fmoc
N
OMe
S30
5.75
5.45
3.57
3.07
3.05
3.00
0.95
1.00
PPM
9
8
7
6
5
4
3
2
1
0
7.783
7.765
7.713
7.696
7.660
7.635
7.614
7.521
7.500
7.482
7.406
7.388
7.339
7.293
7.259
7.226
7.169
7.163
7.141
7.119
7.098
4.626
4.508
4.304
3.931
2.924
2.874
1.537
0.000

Fmoc 13C


Fmoc
N
OMe
S30
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
PPM
157.636
156.729
156.280
144.027
143.960
141.286
133.855
132.509
132.346
129.156
128.717
127.552
127.294
126.969
126.492
125.833
125.651
124.963
124.820
119.892
118.947
105.652
77.220
77.000
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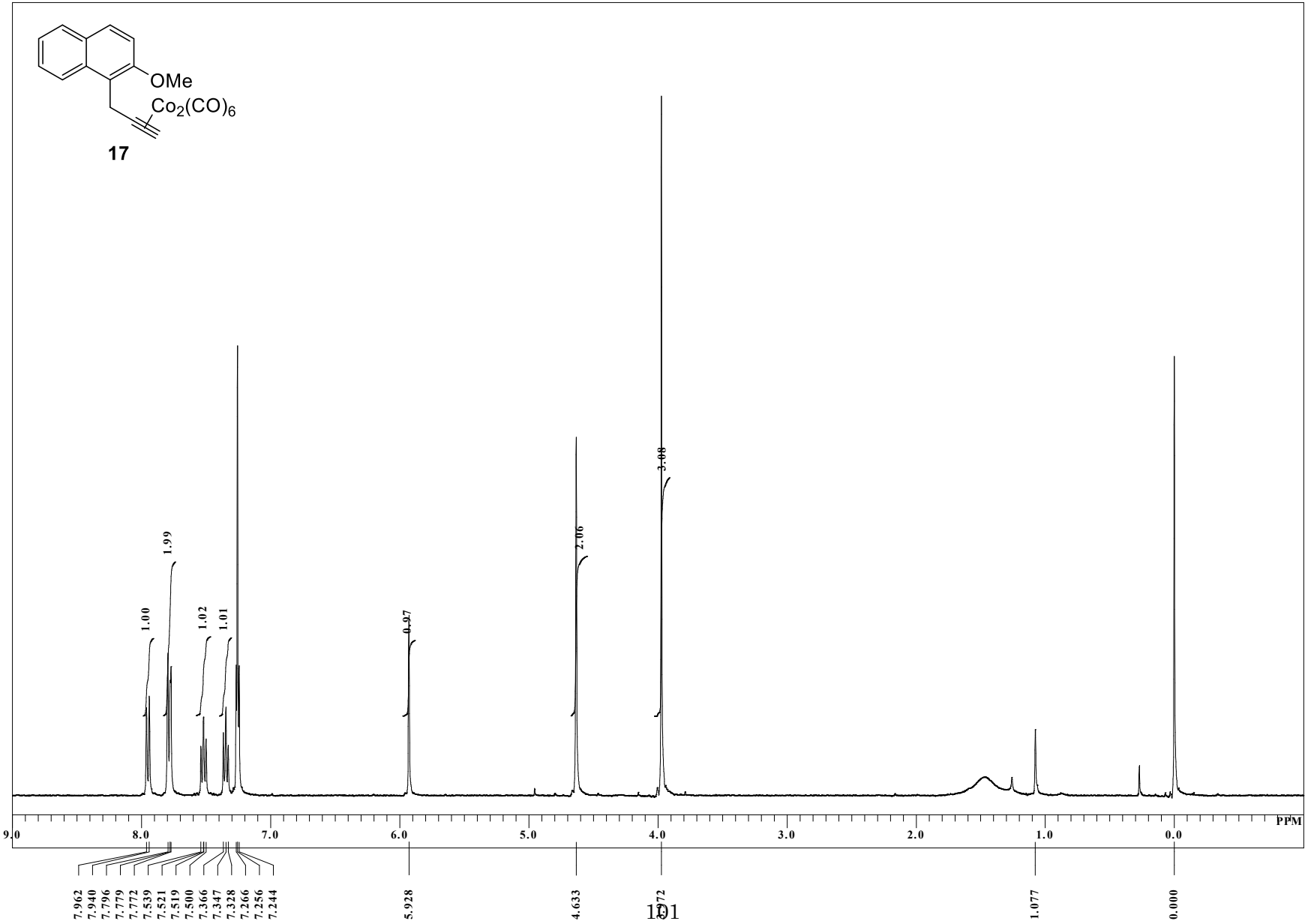
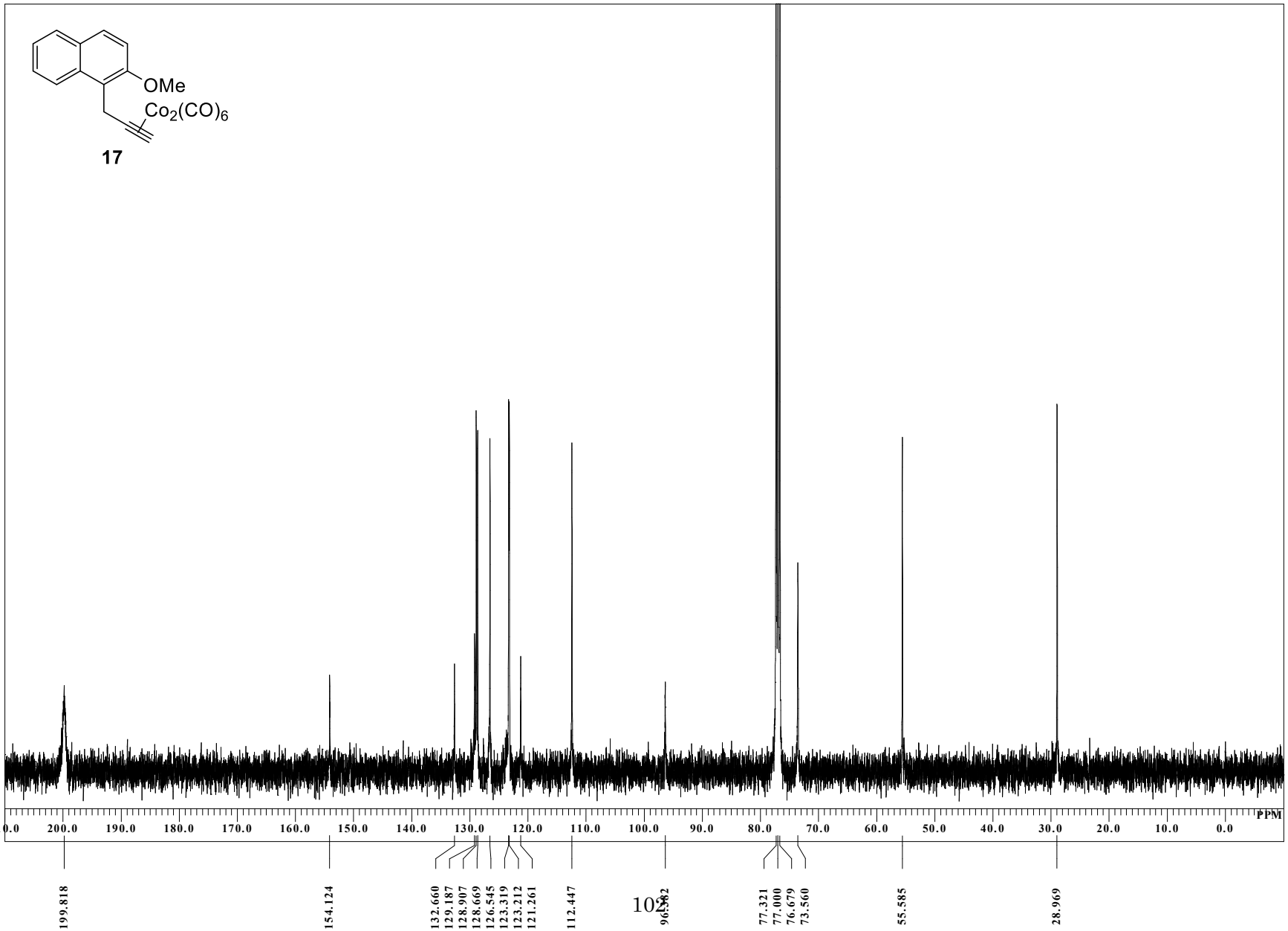
67.382
55.234
52.579
52.245
47.364
47.278
34.385
33.363

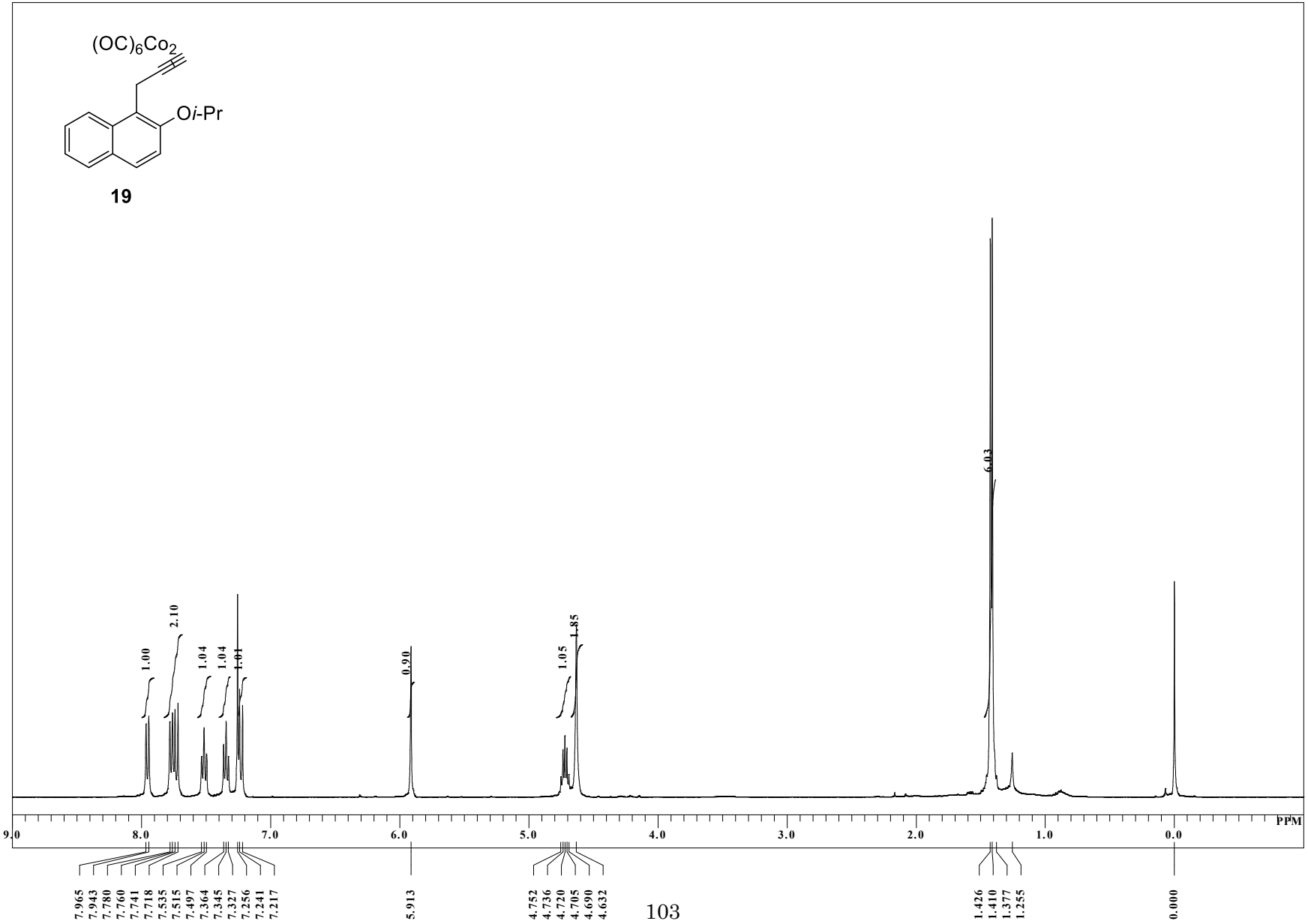
functionalization Me ether 1H



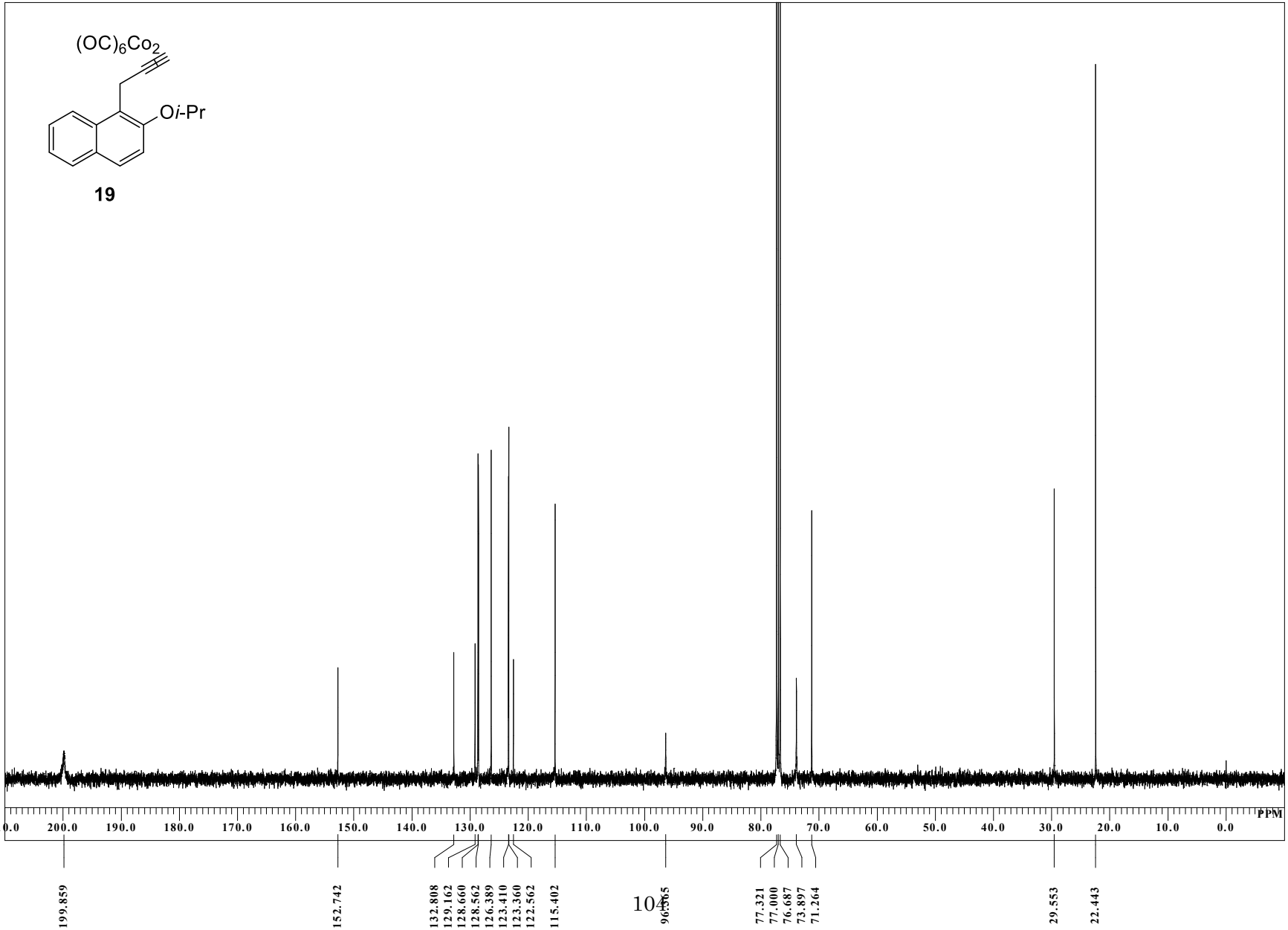
functionalization Me ether 13C



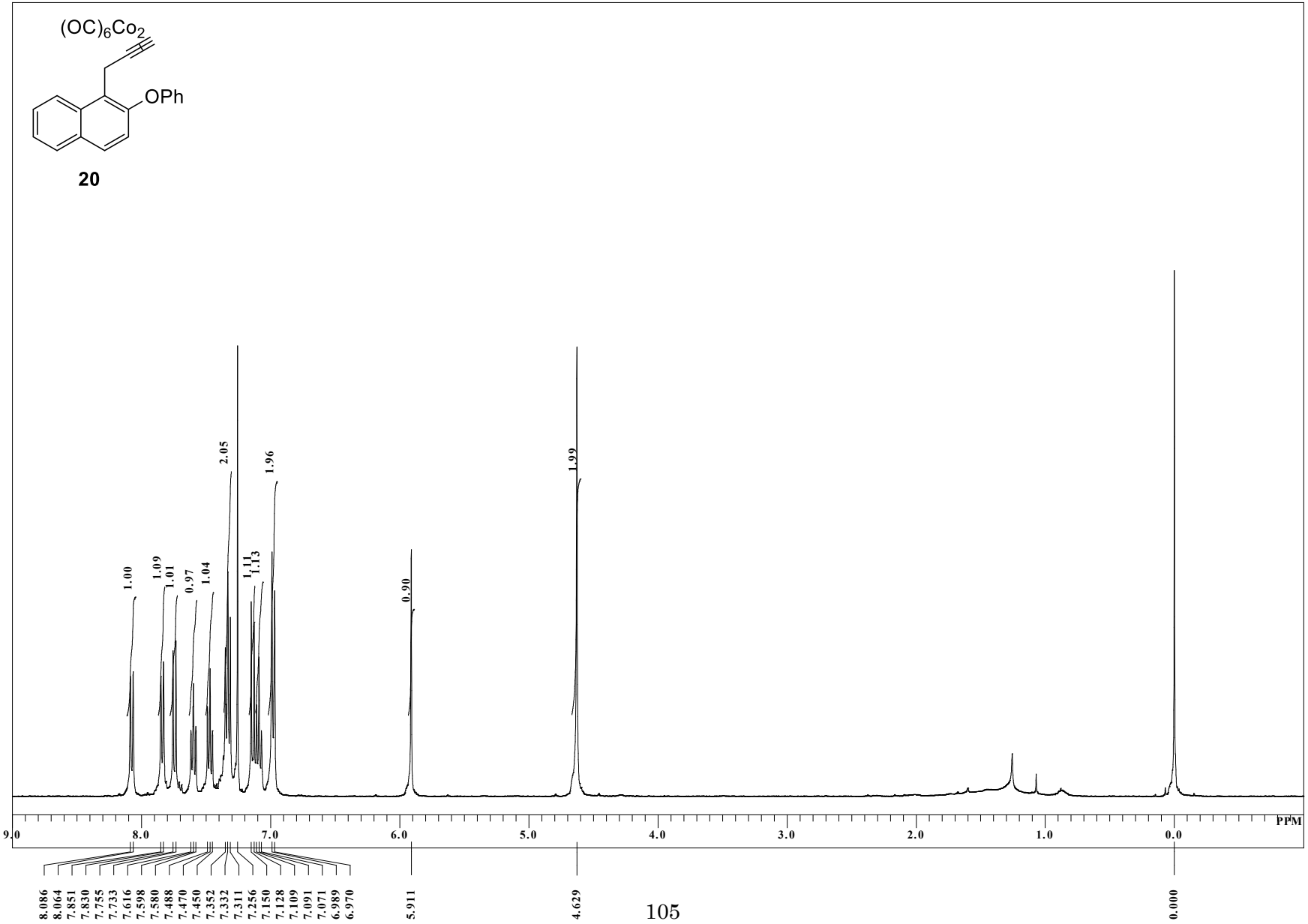
functionalization iPr ether 1H



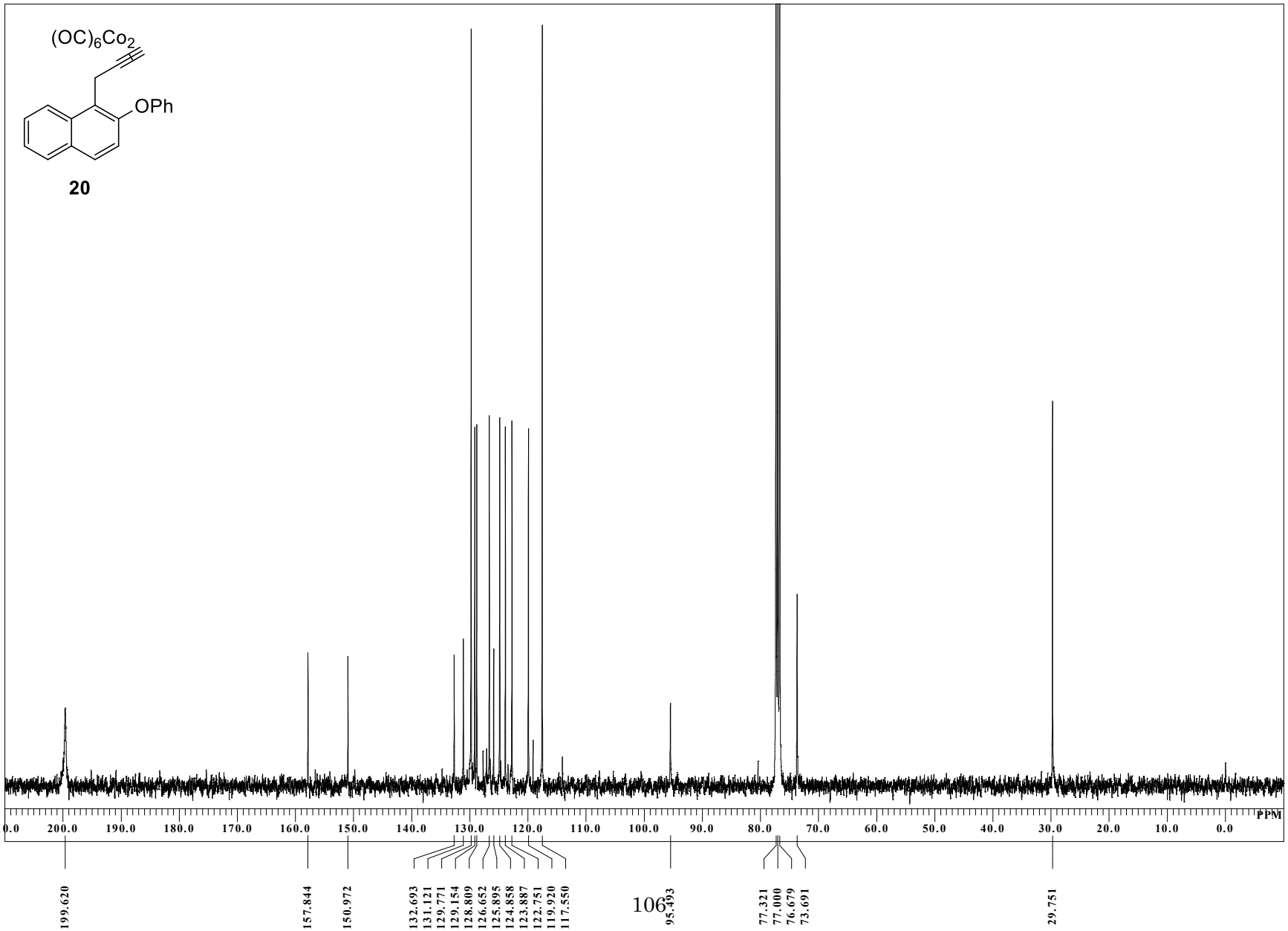
functionalization of iPr ether 13C



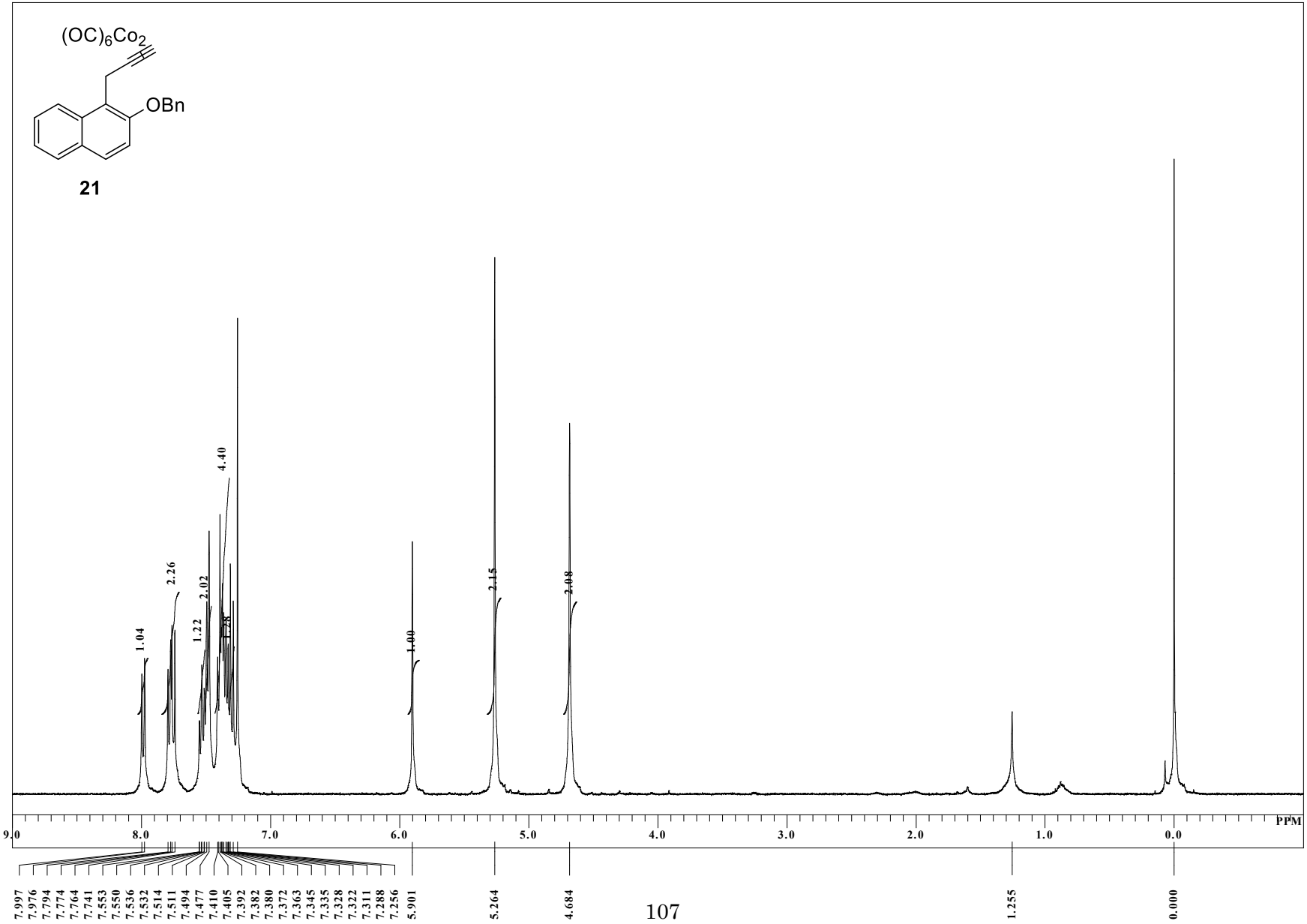
functionalization of Ph ether 1H



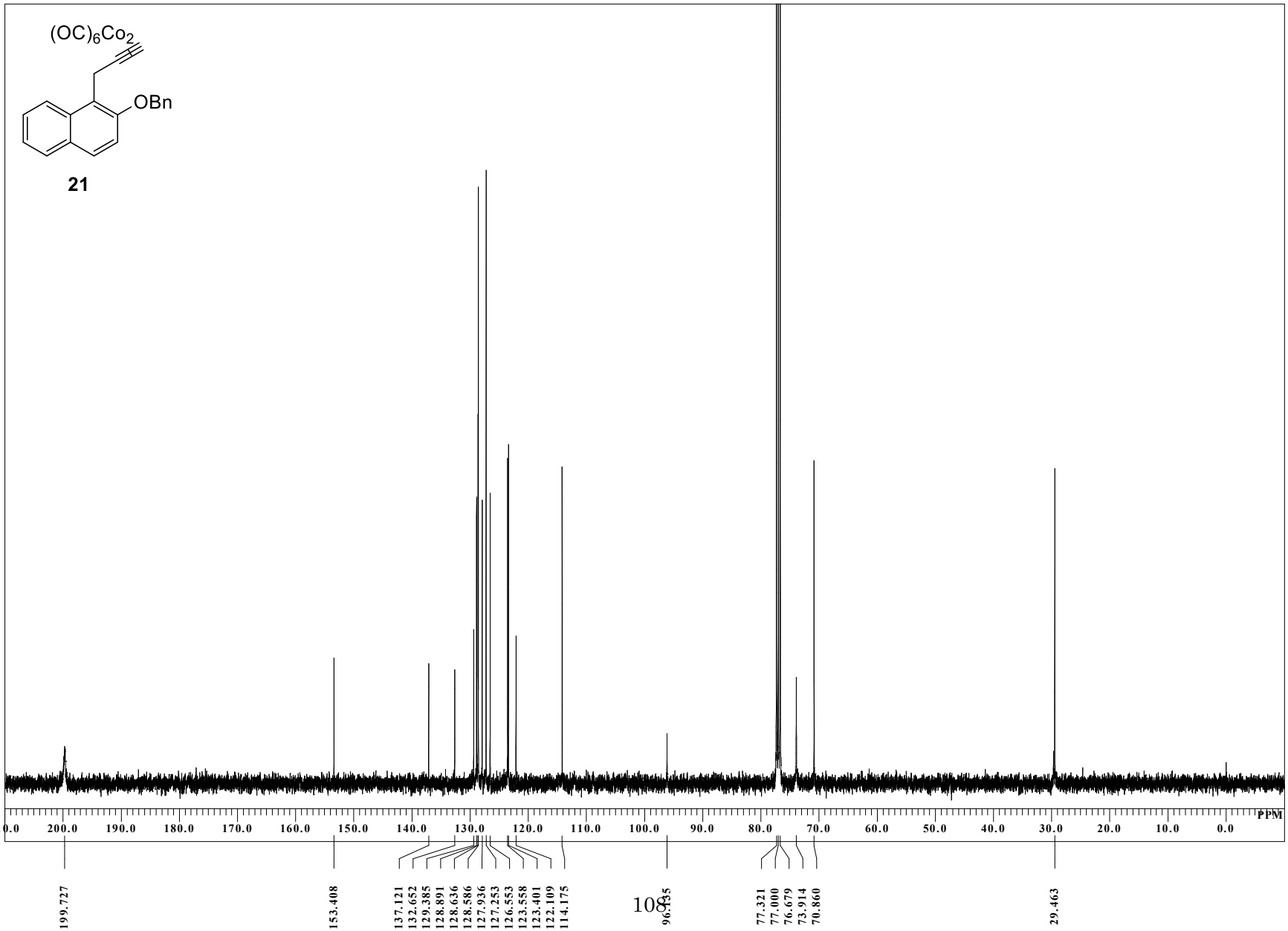
functionalization of Ph ether 13C



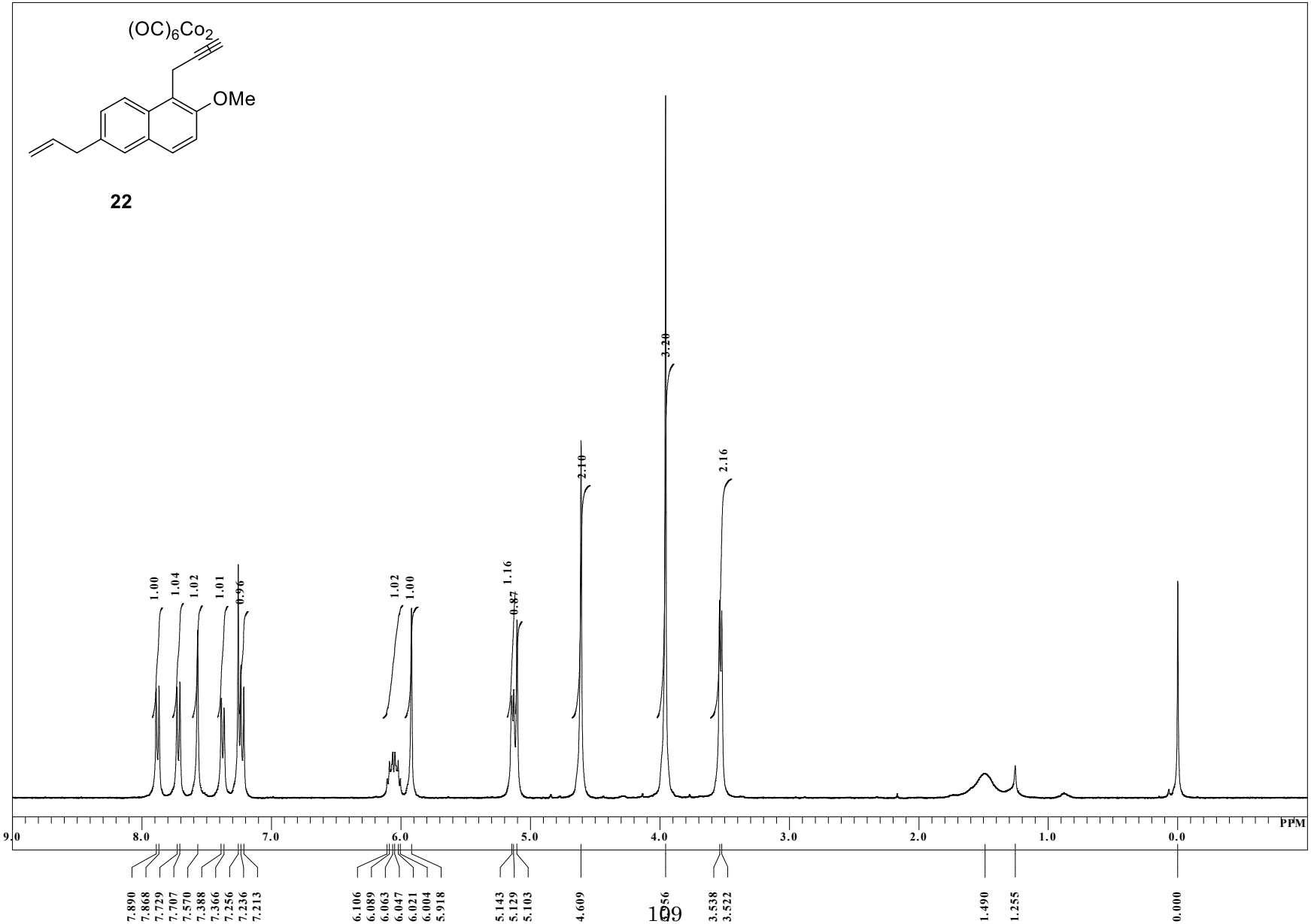
functionalization Bn ether 1H



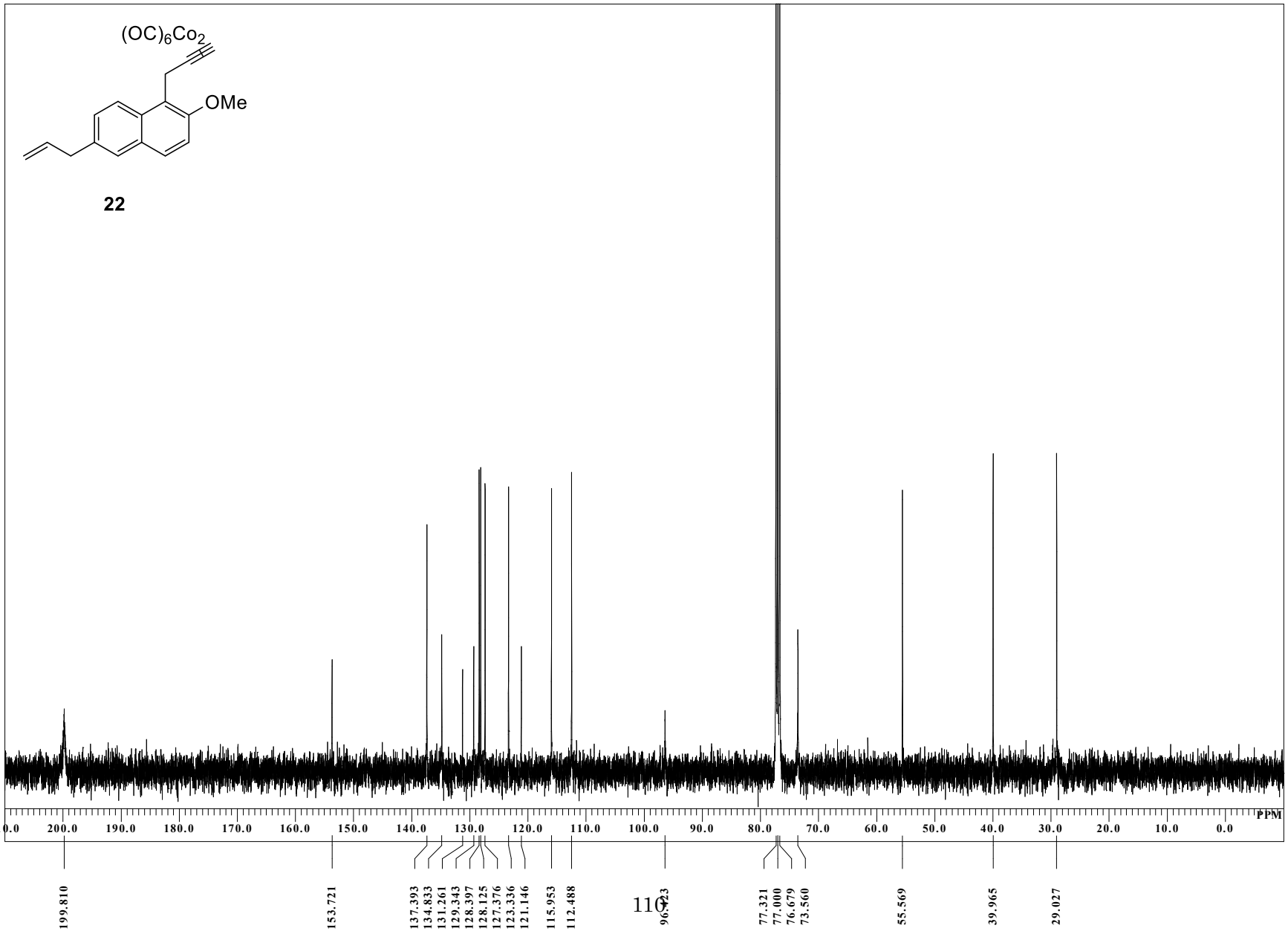
functionalization Bn ether 13C



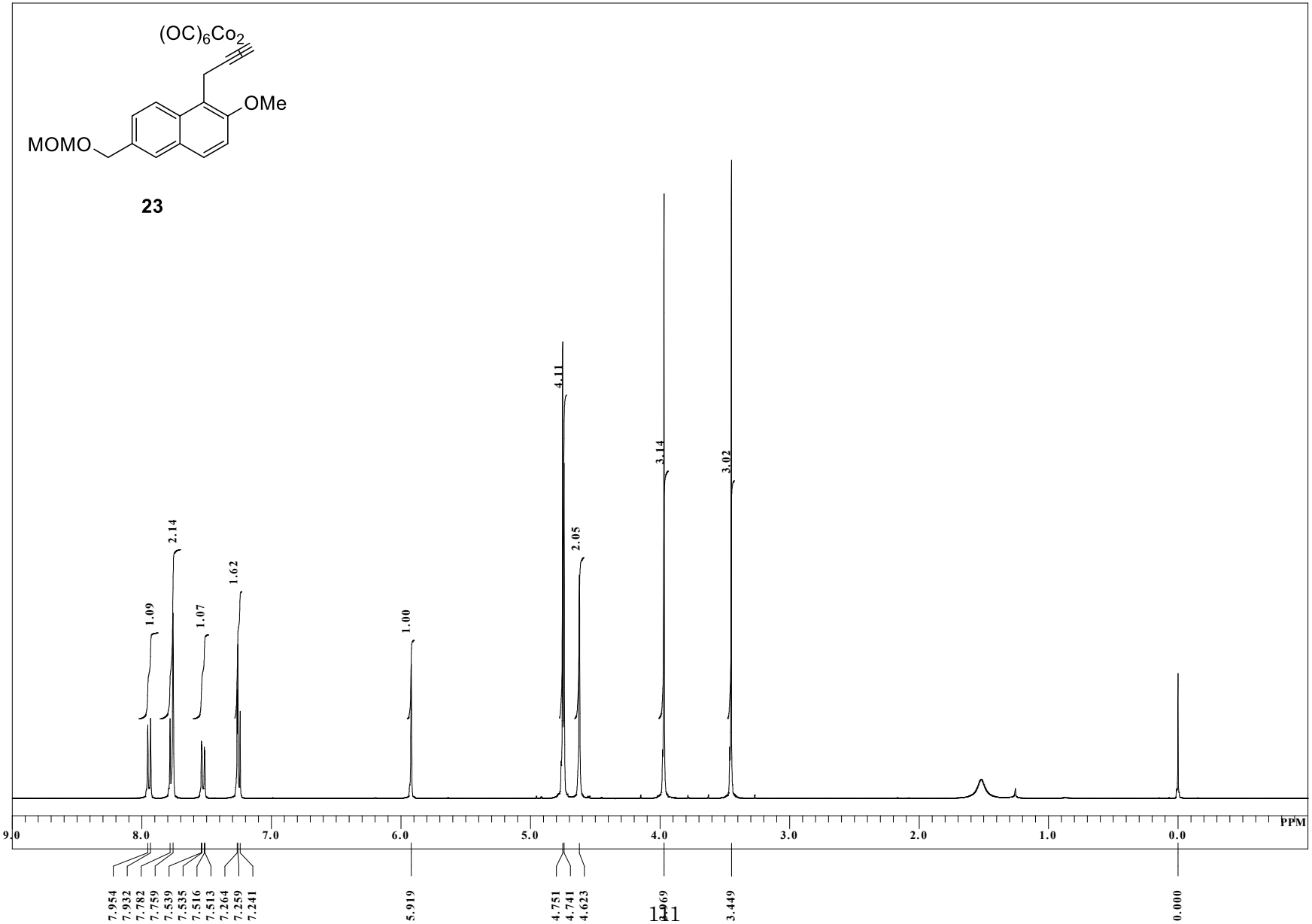
functionalization allyl 1H



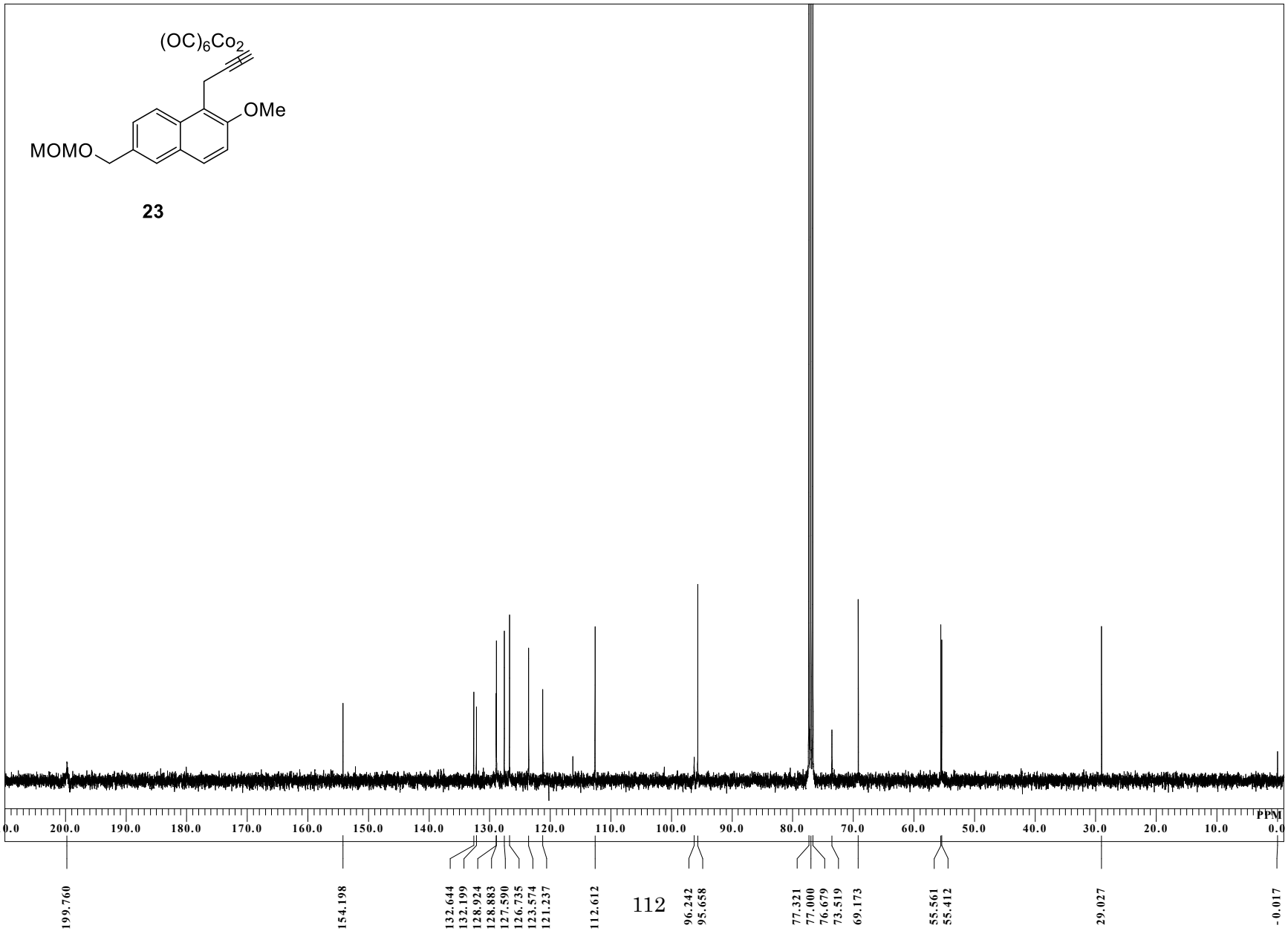
functionalization allyl 13C



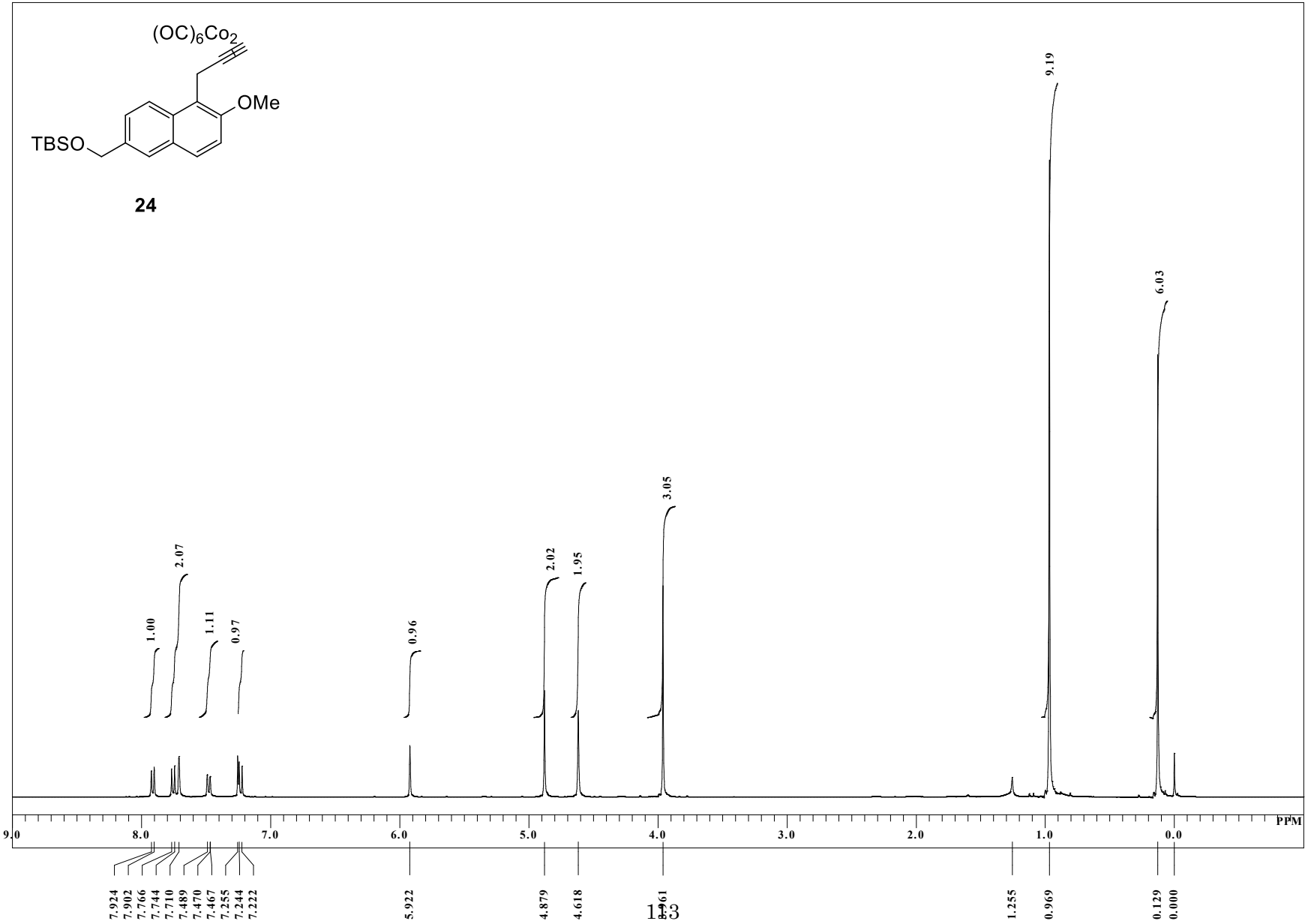
functionalization of MOM 1H



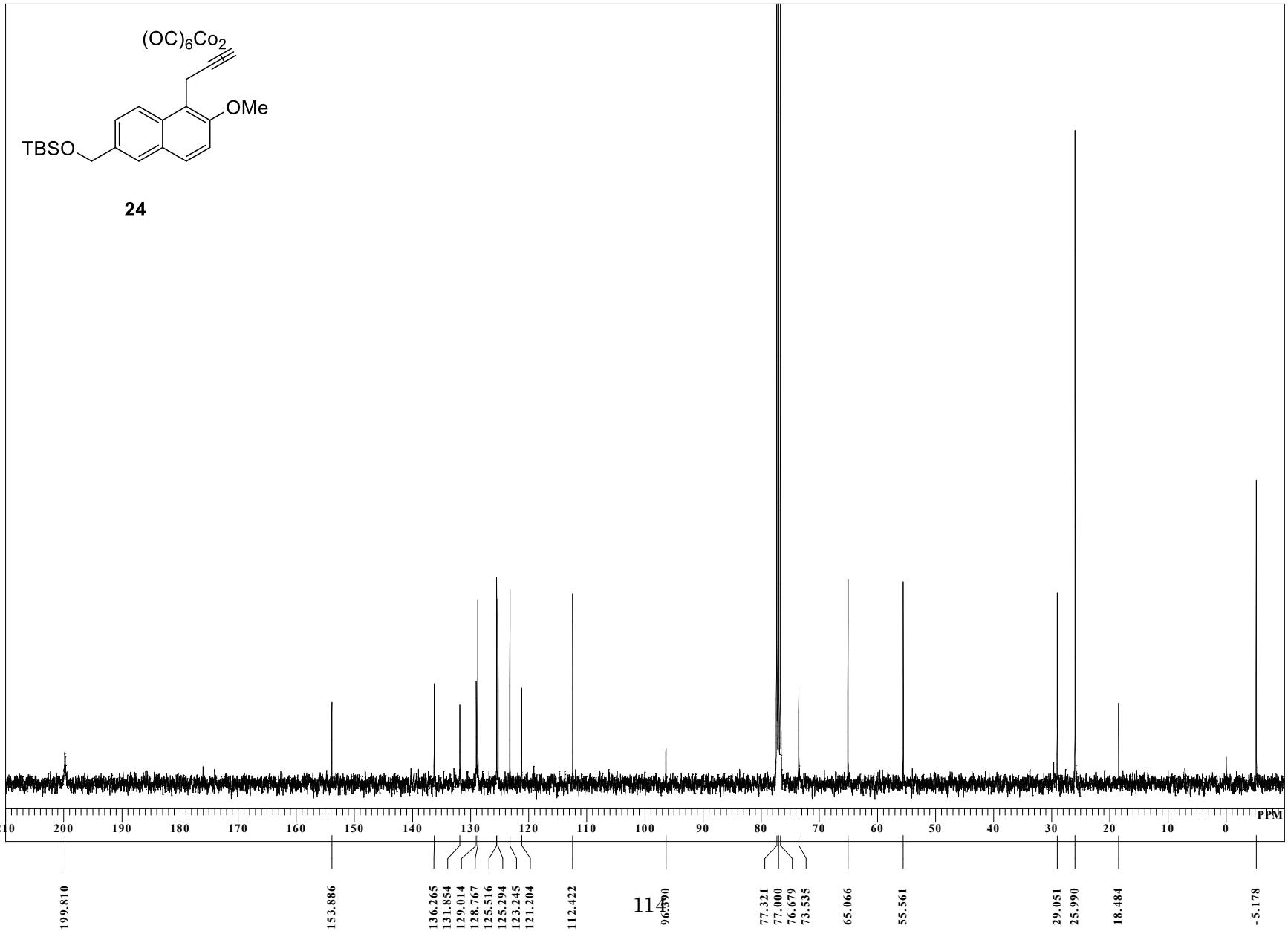
functionalization of MOM 13C



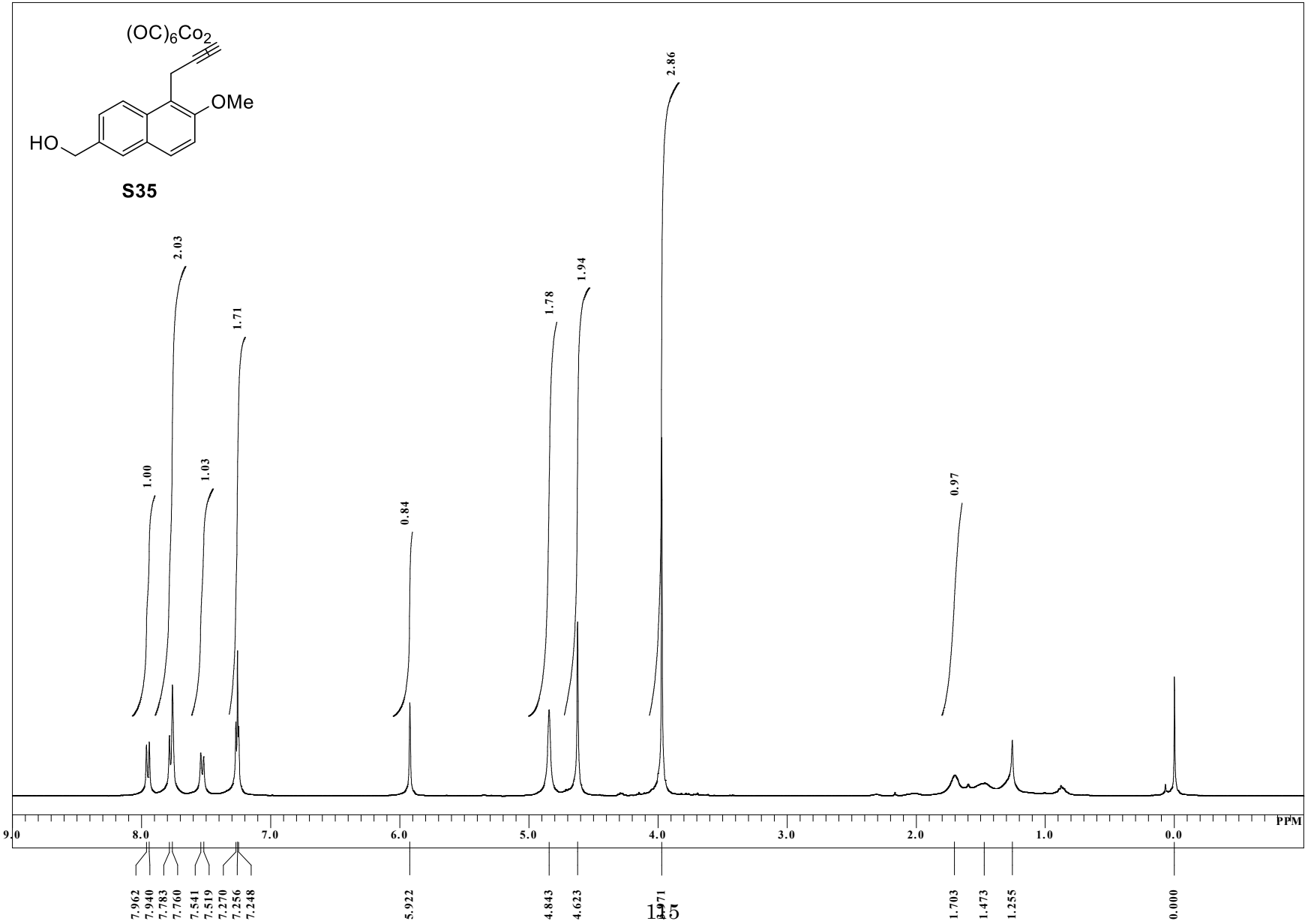
functionalization TBS 1H



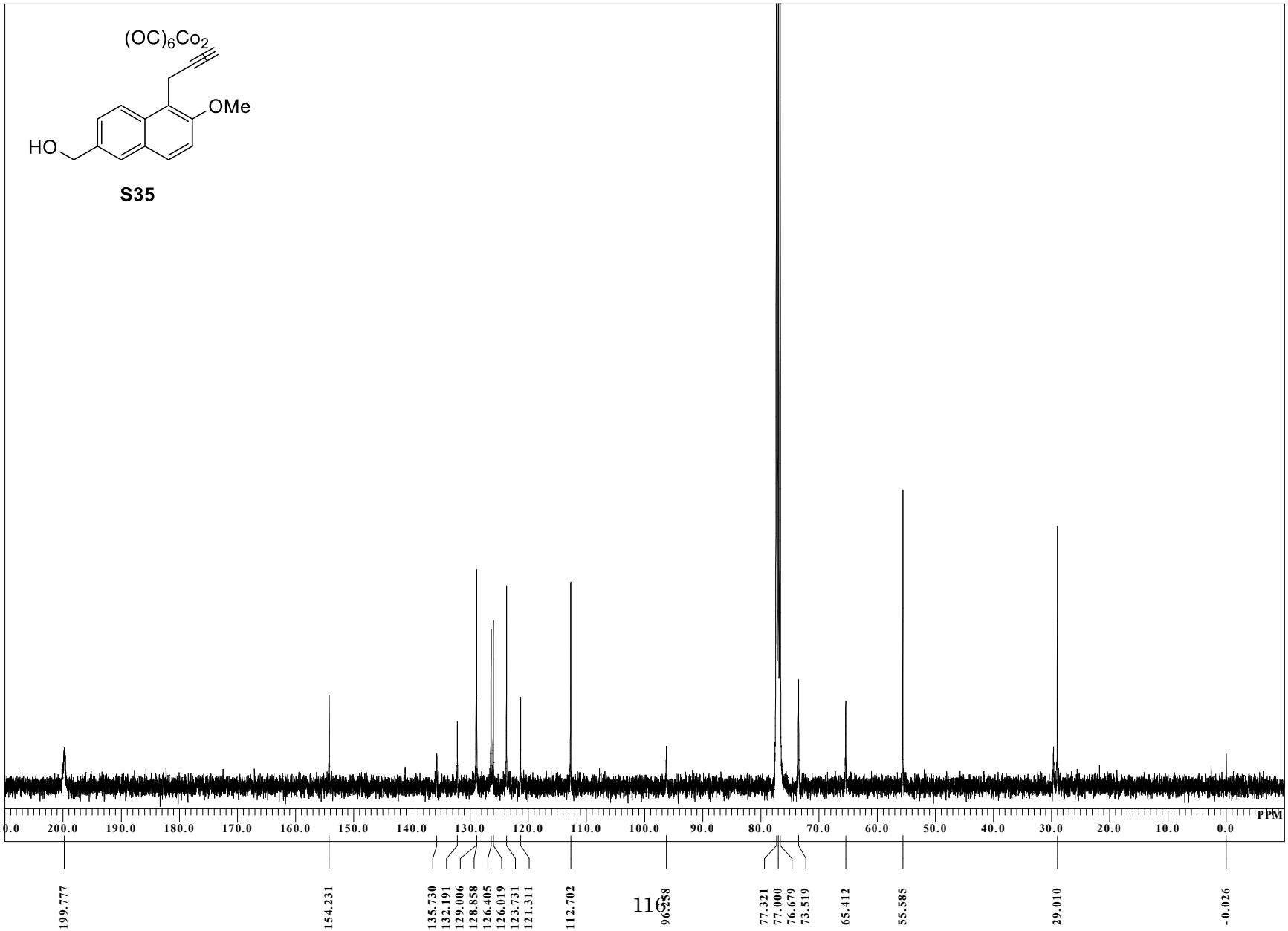
functionalization TBS 13C



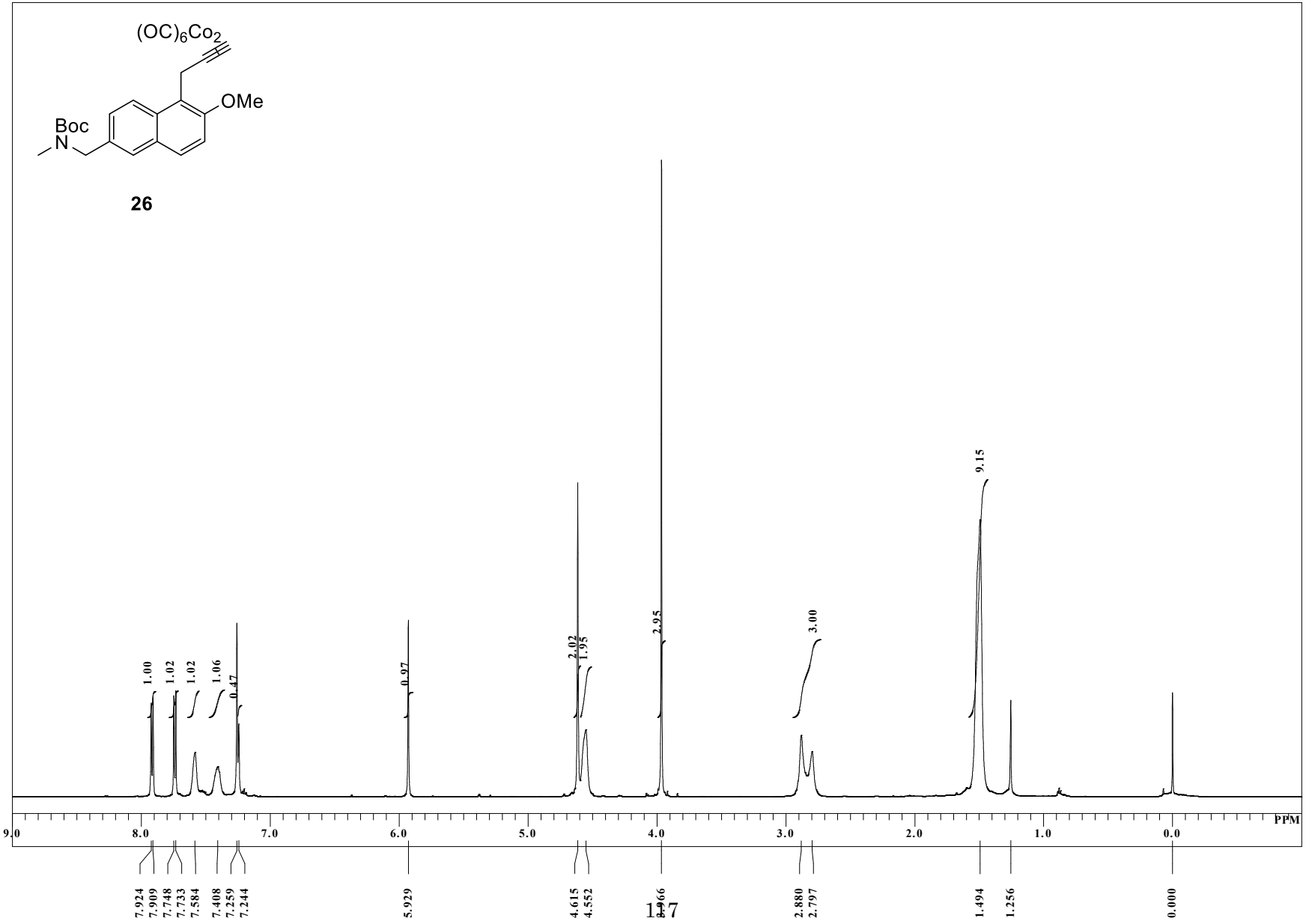
functionalization TMS 1H



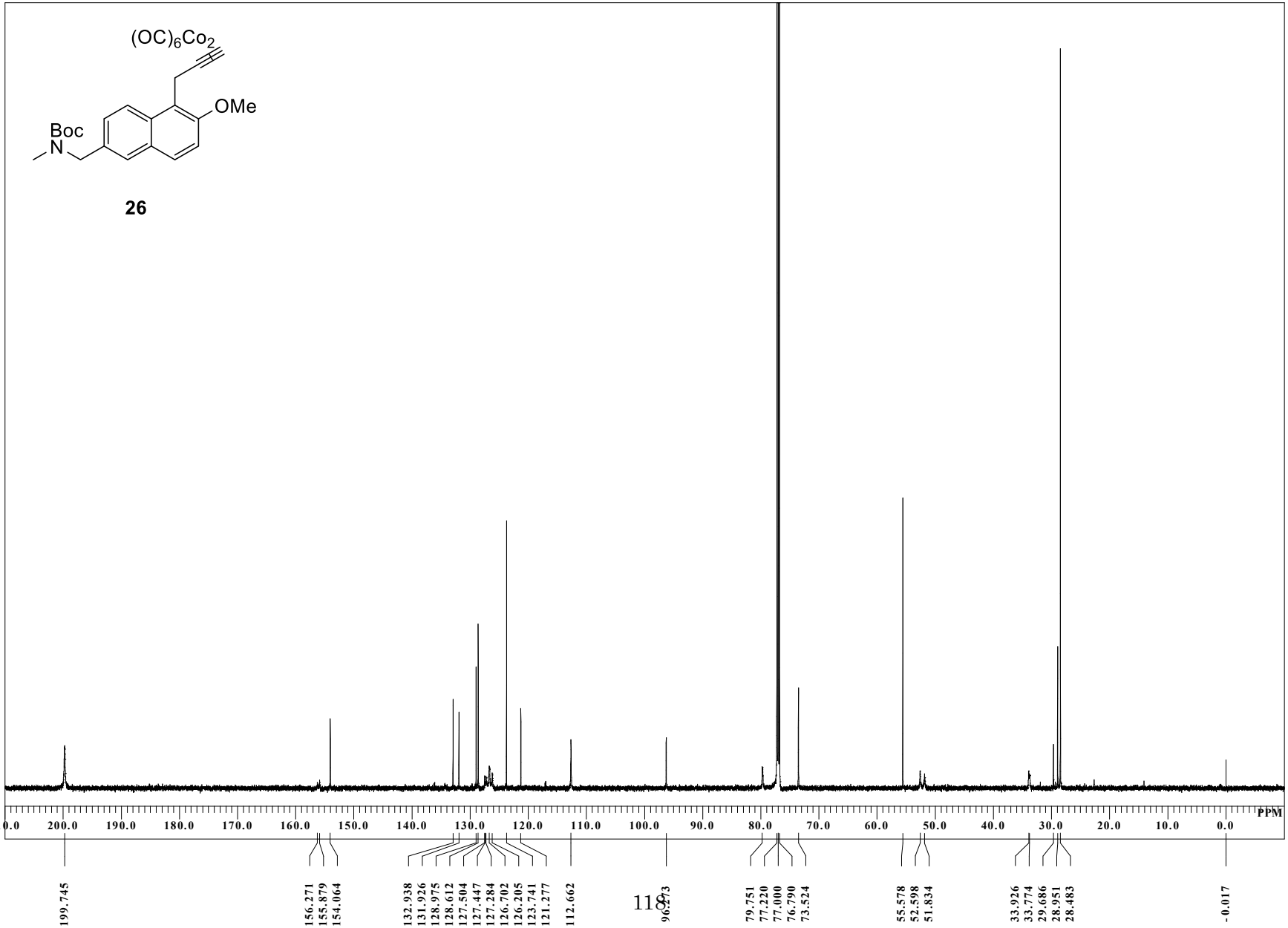
functionalization TMS 13C



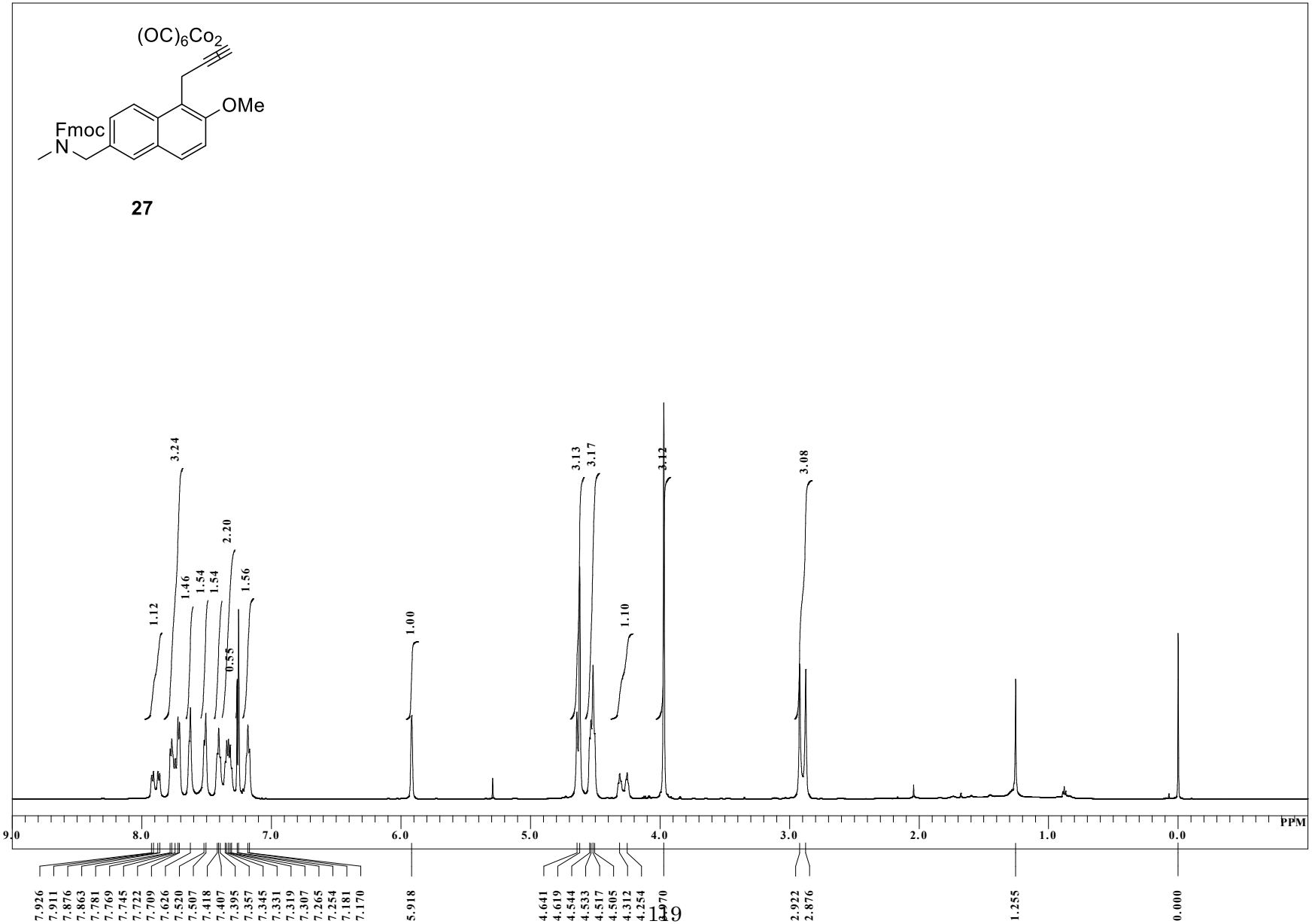
functionalization Boc 1H



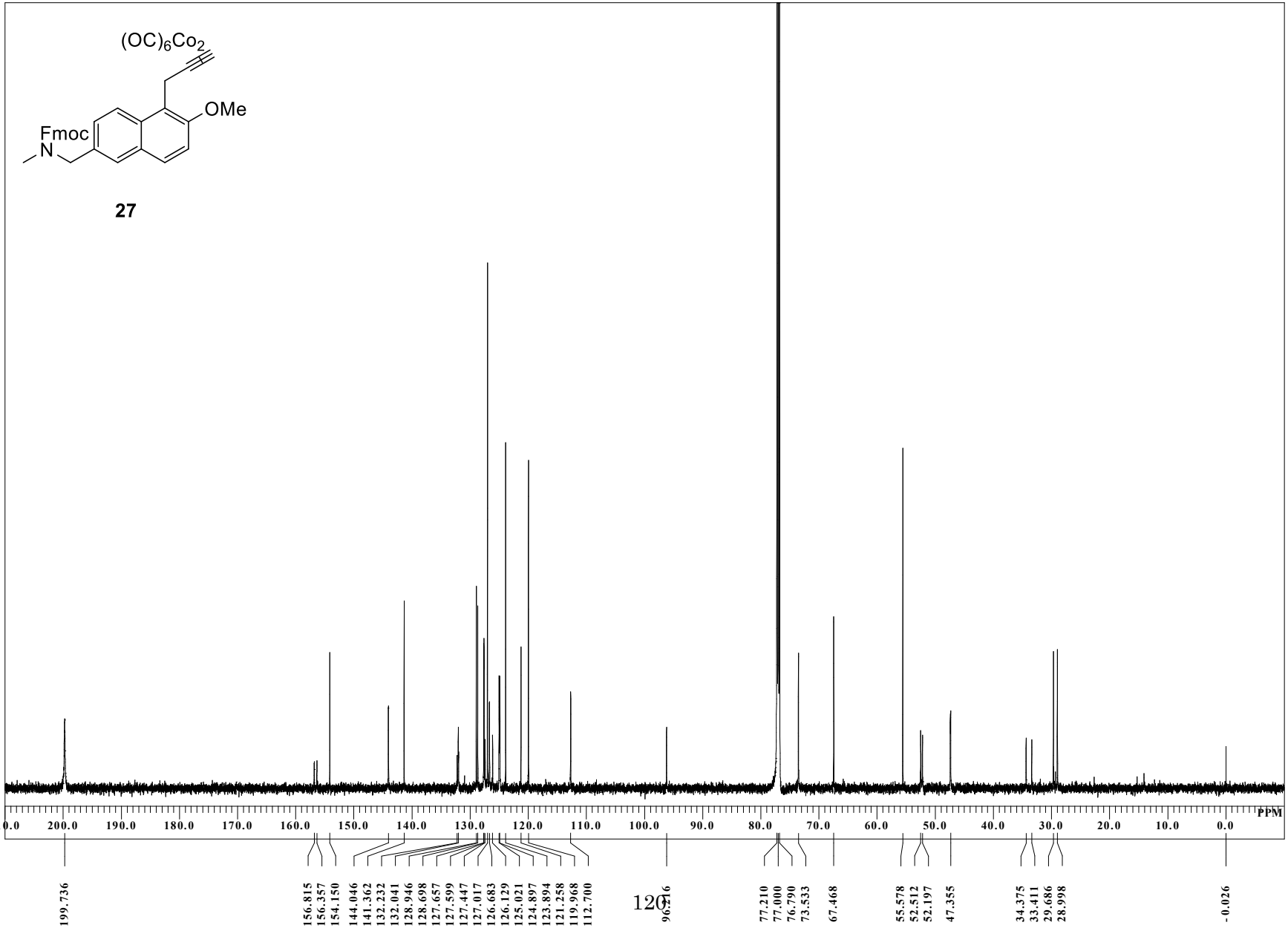
Boc functionalization



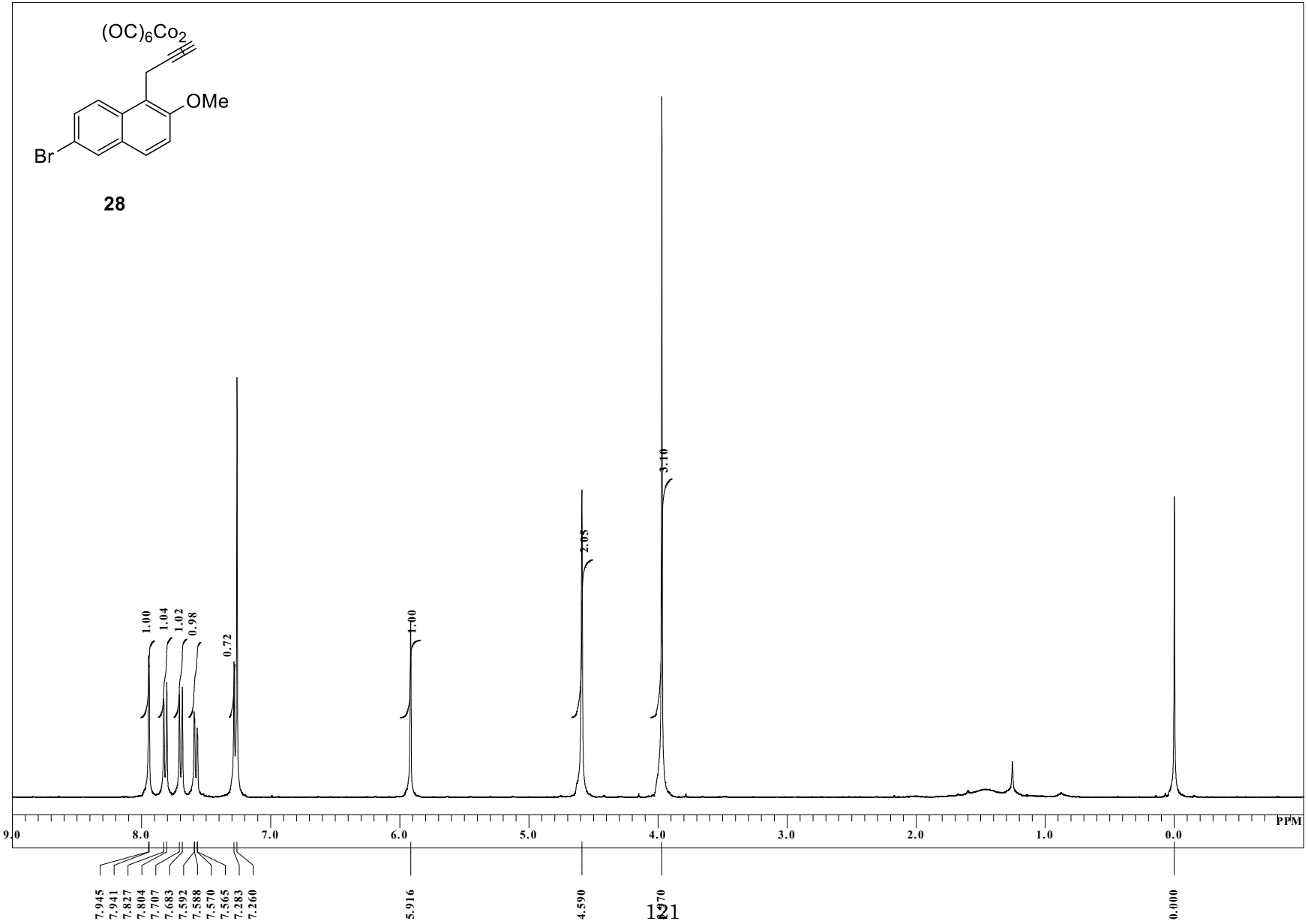
functionalization of Fmoc 1H



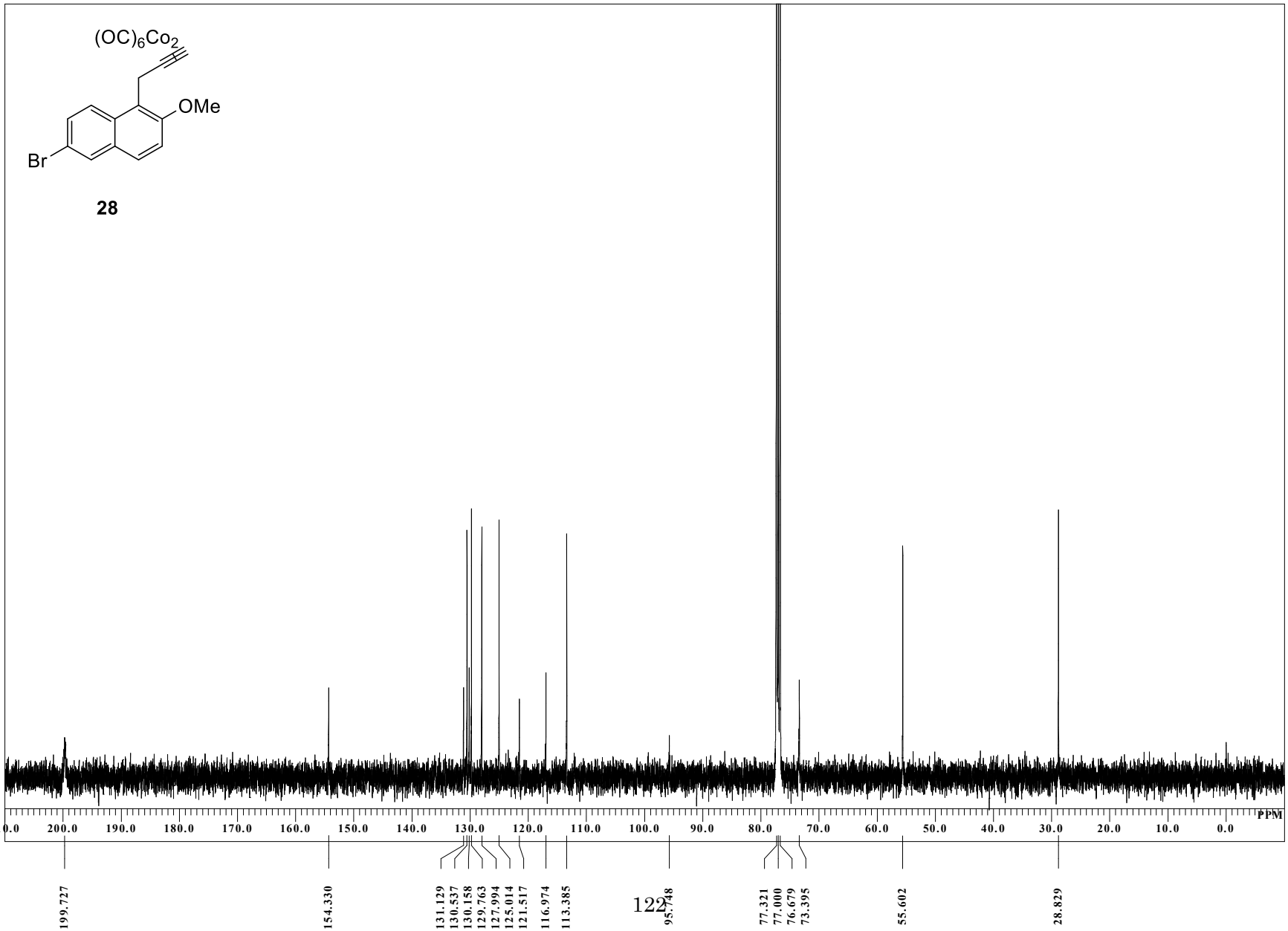
Fmoc functionalization 13C



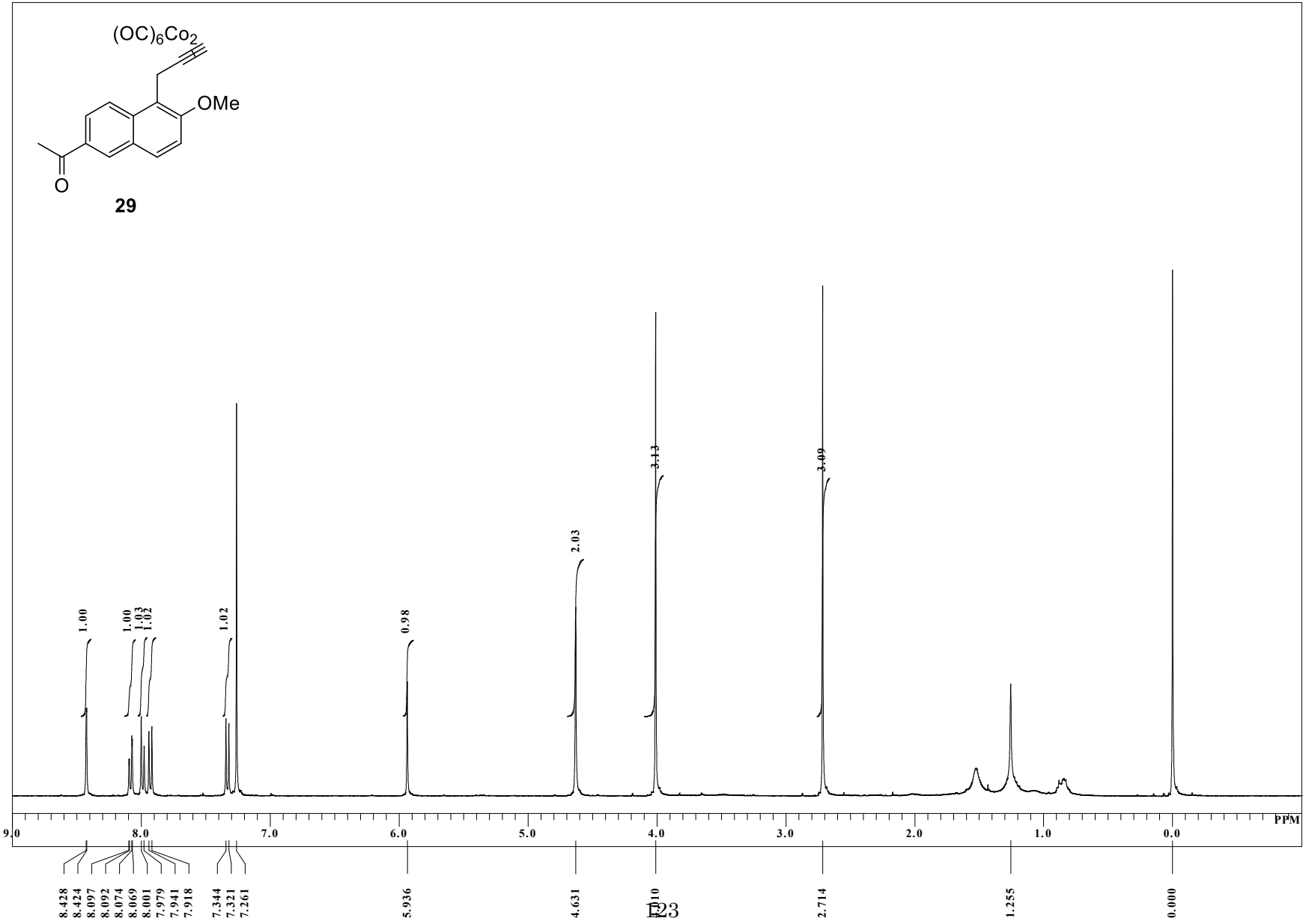
functionalization Br 1H



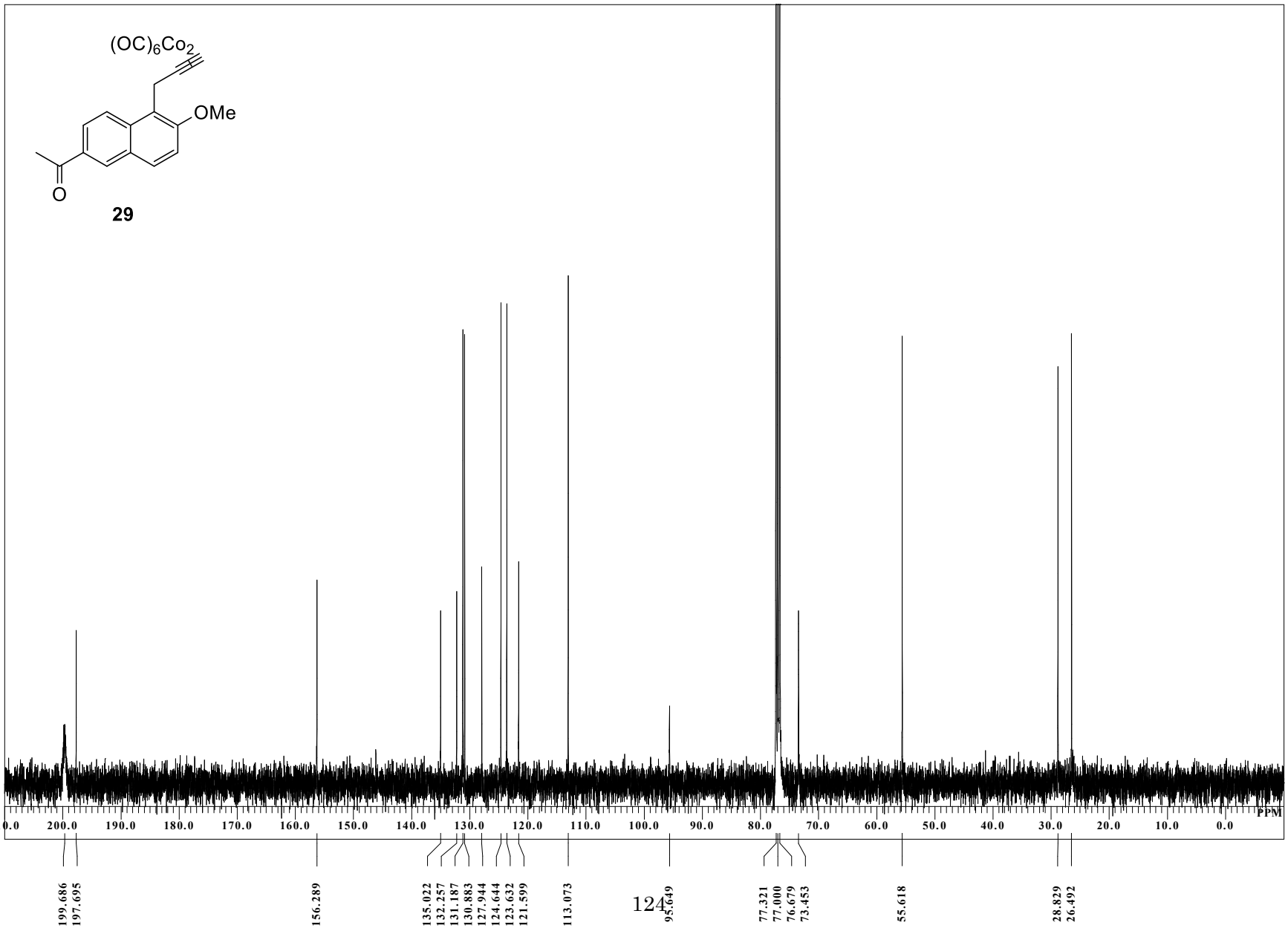
functionalization Br 13C



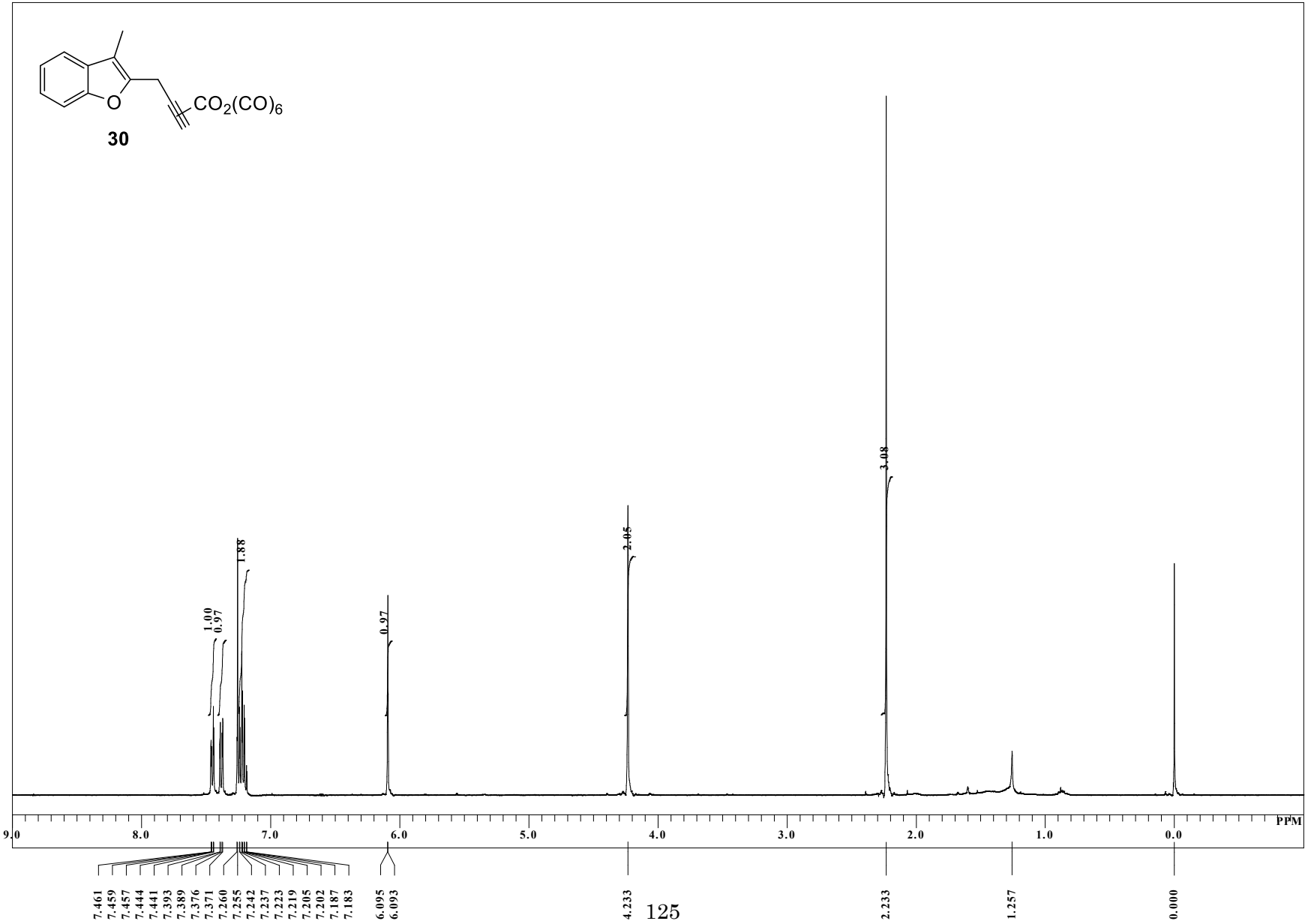
functionalization Ac 1H



functionalization of Ac 13C



functionalization furan 1H



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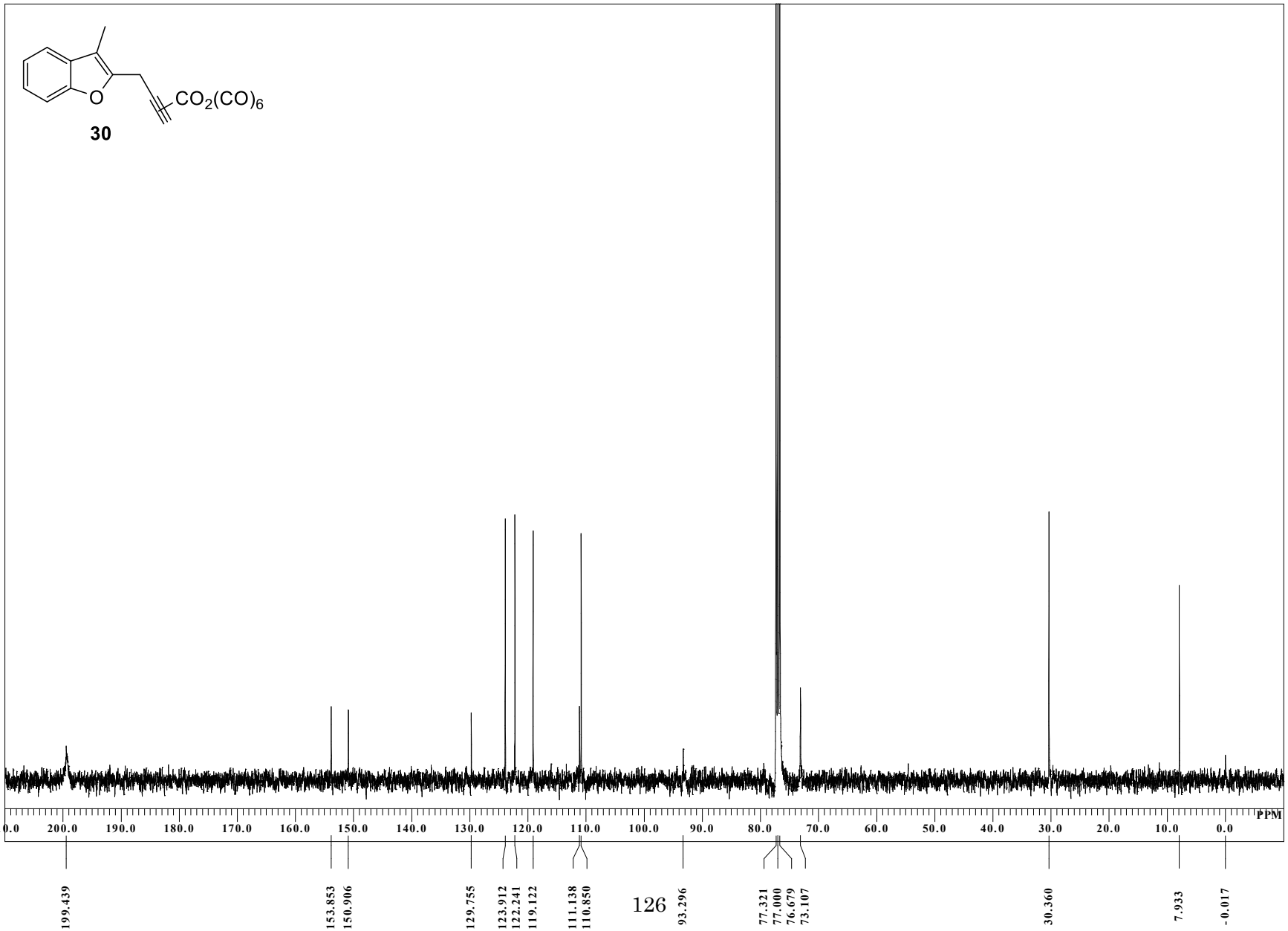
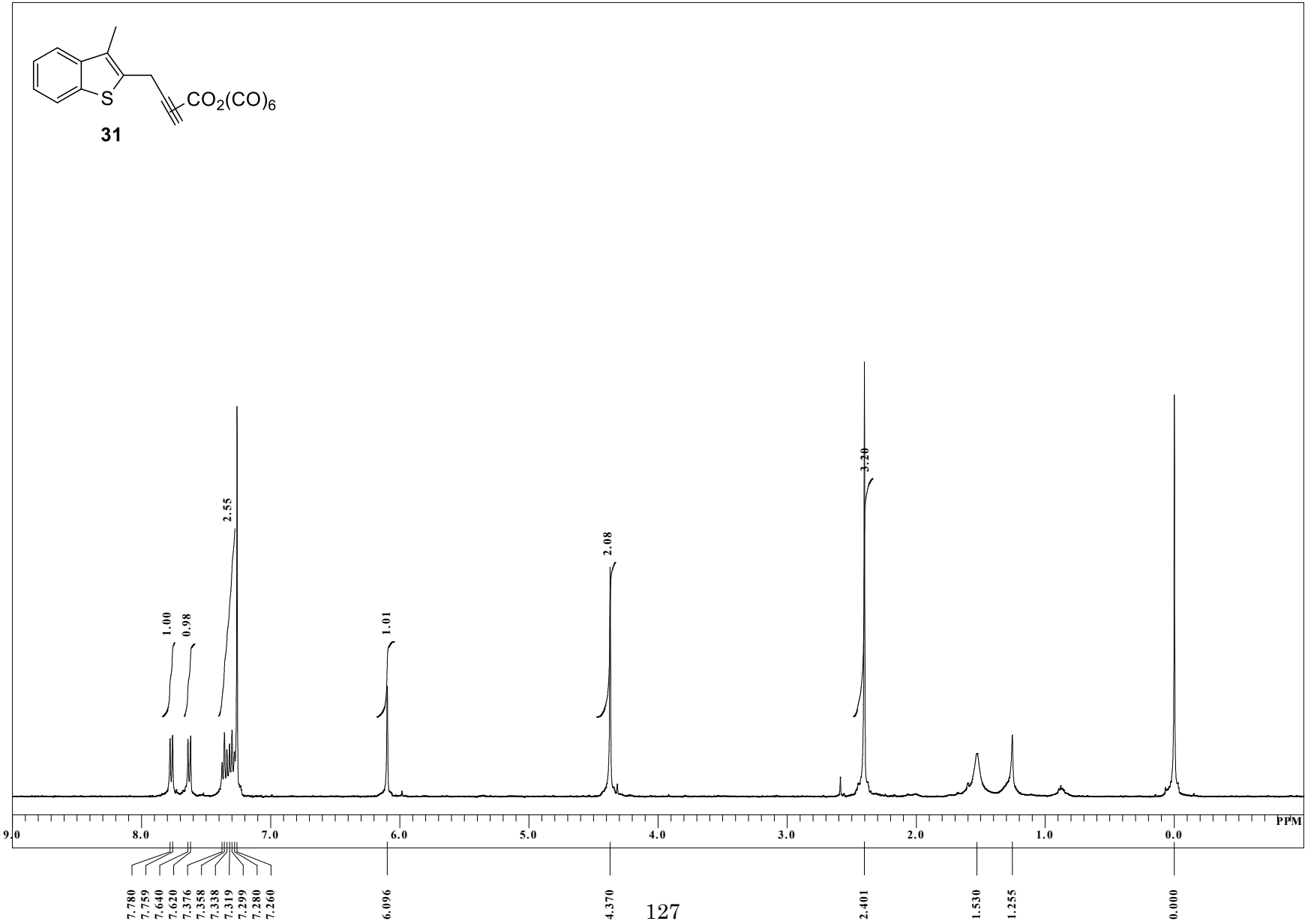


functionalization thiophene 1H



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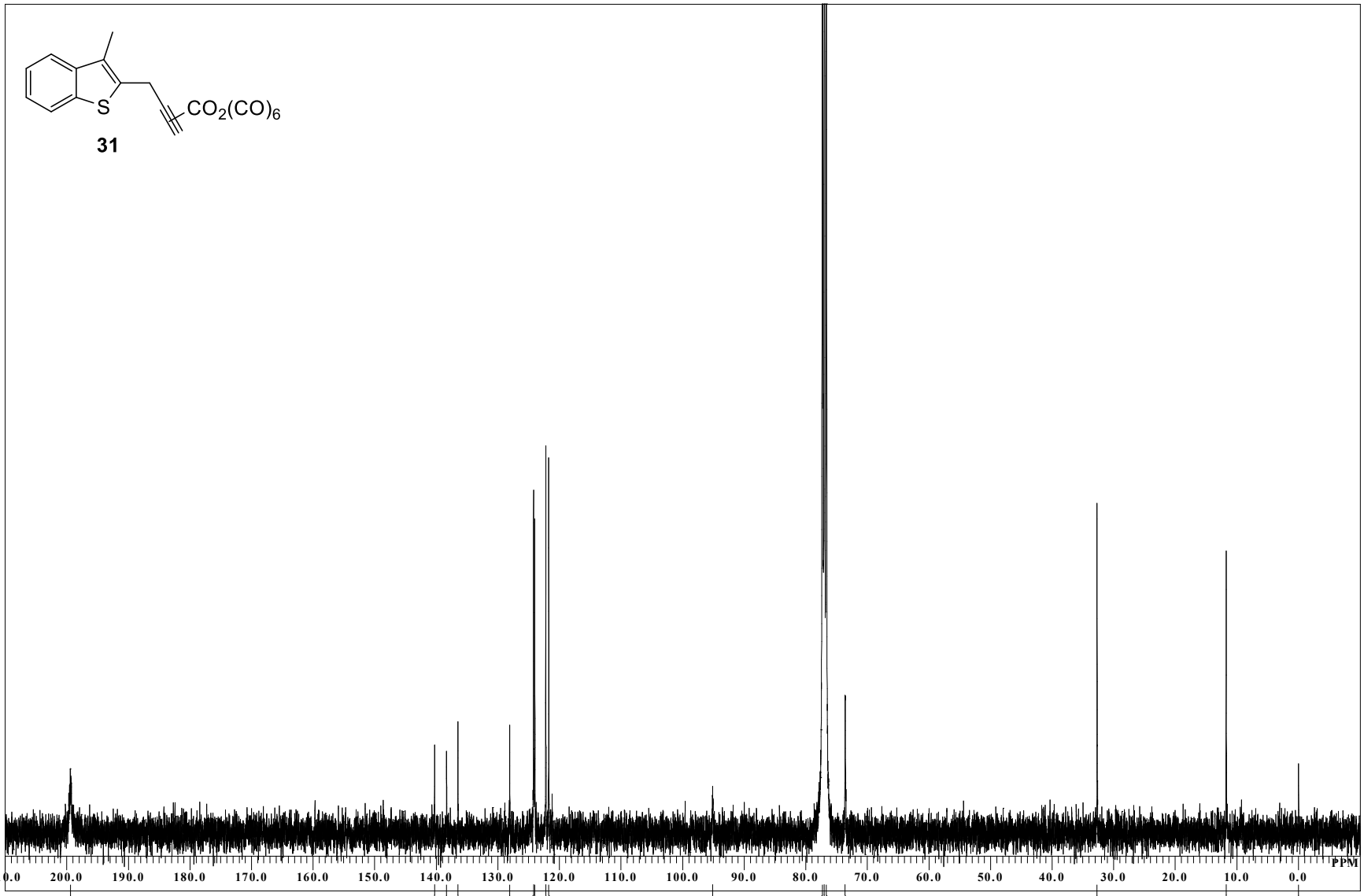
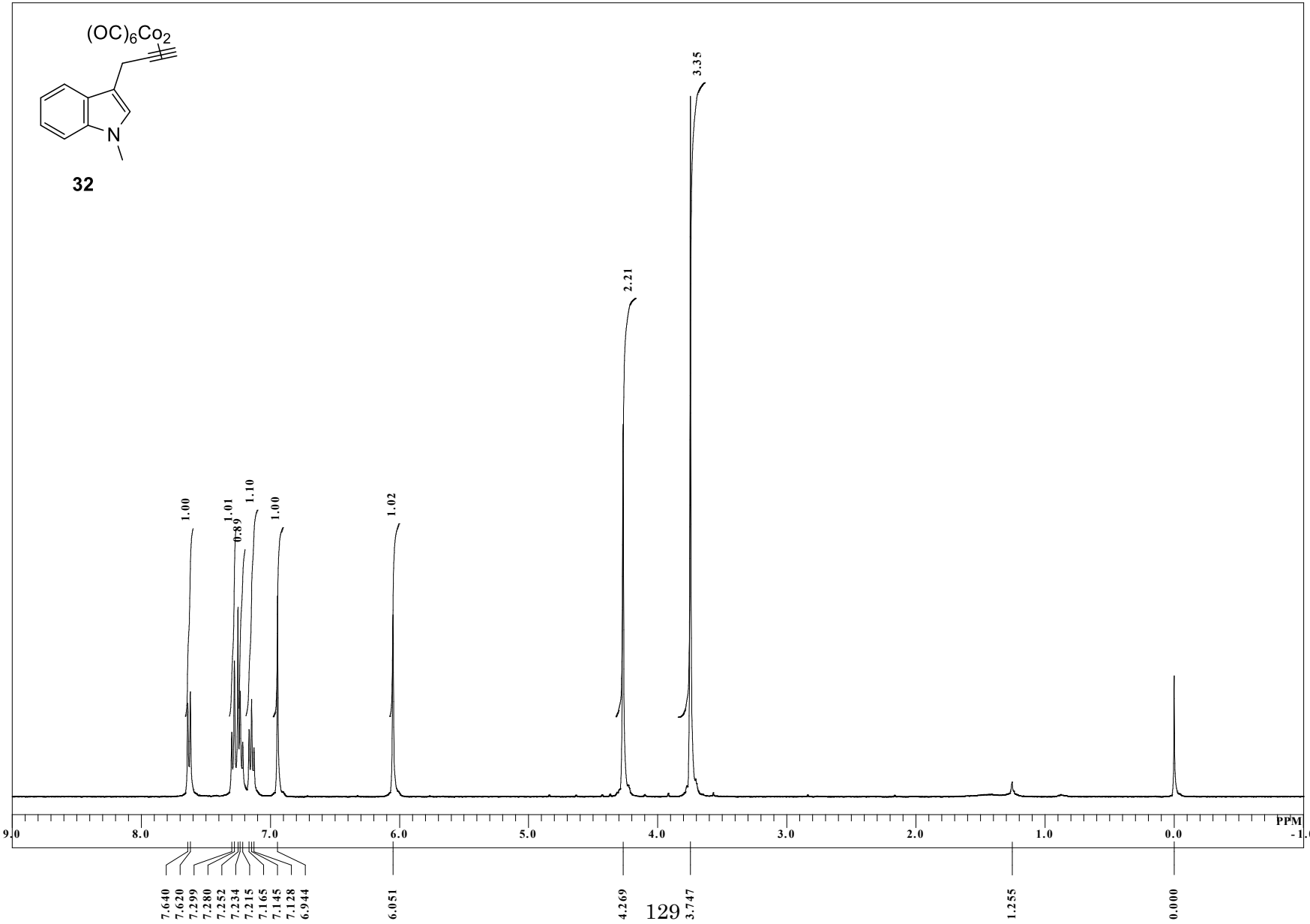
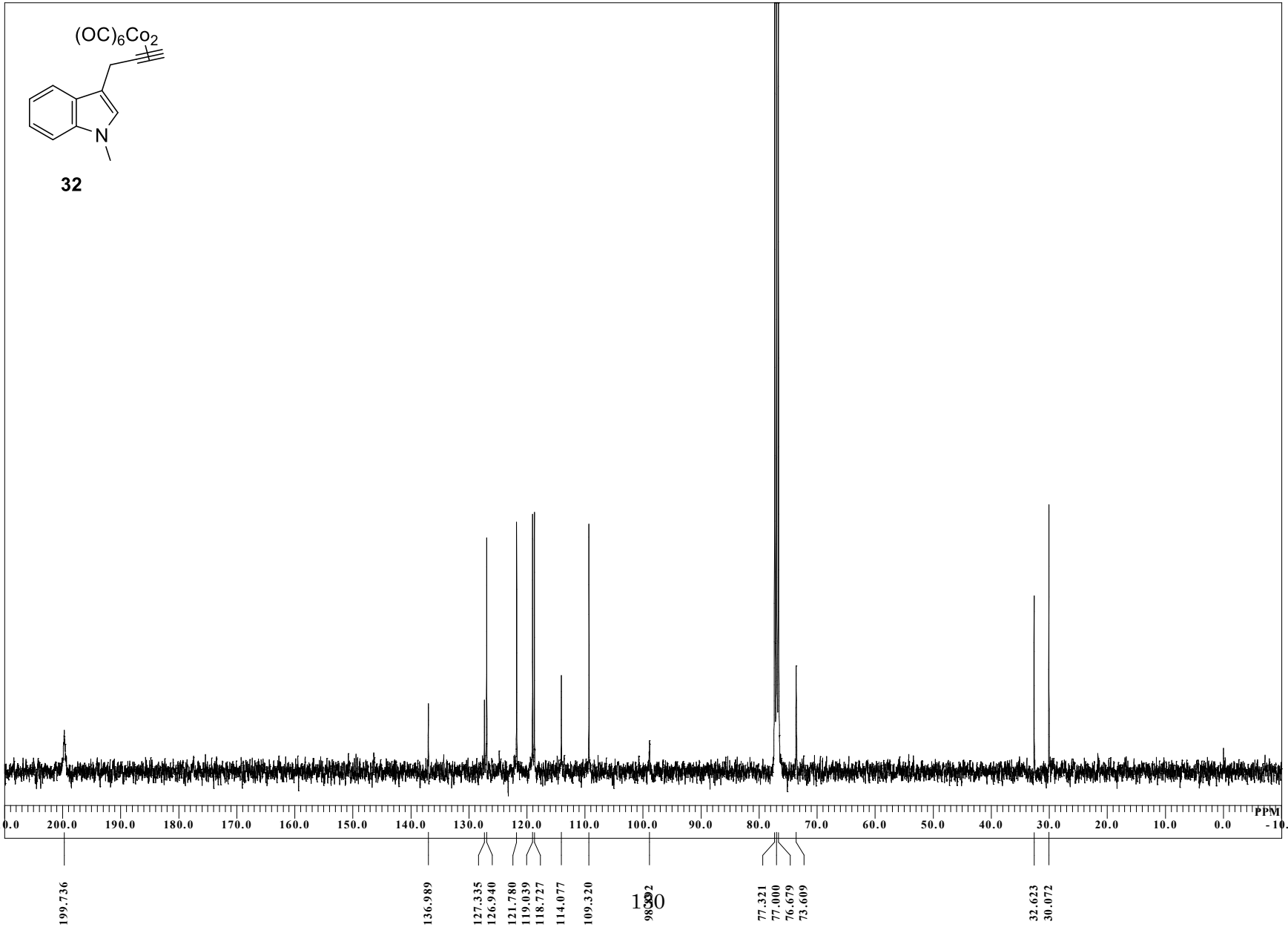


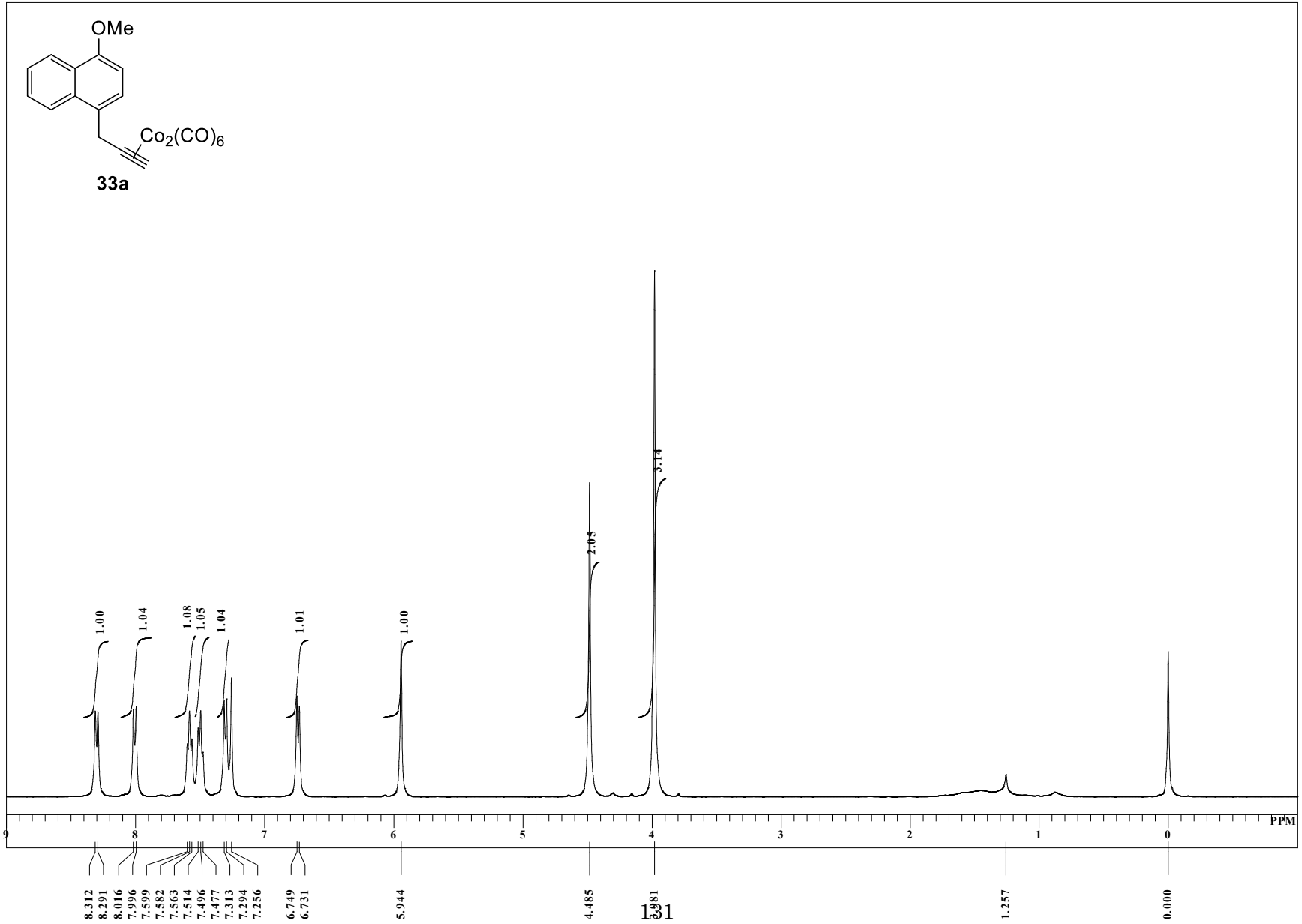
functionalozation of indole 1H



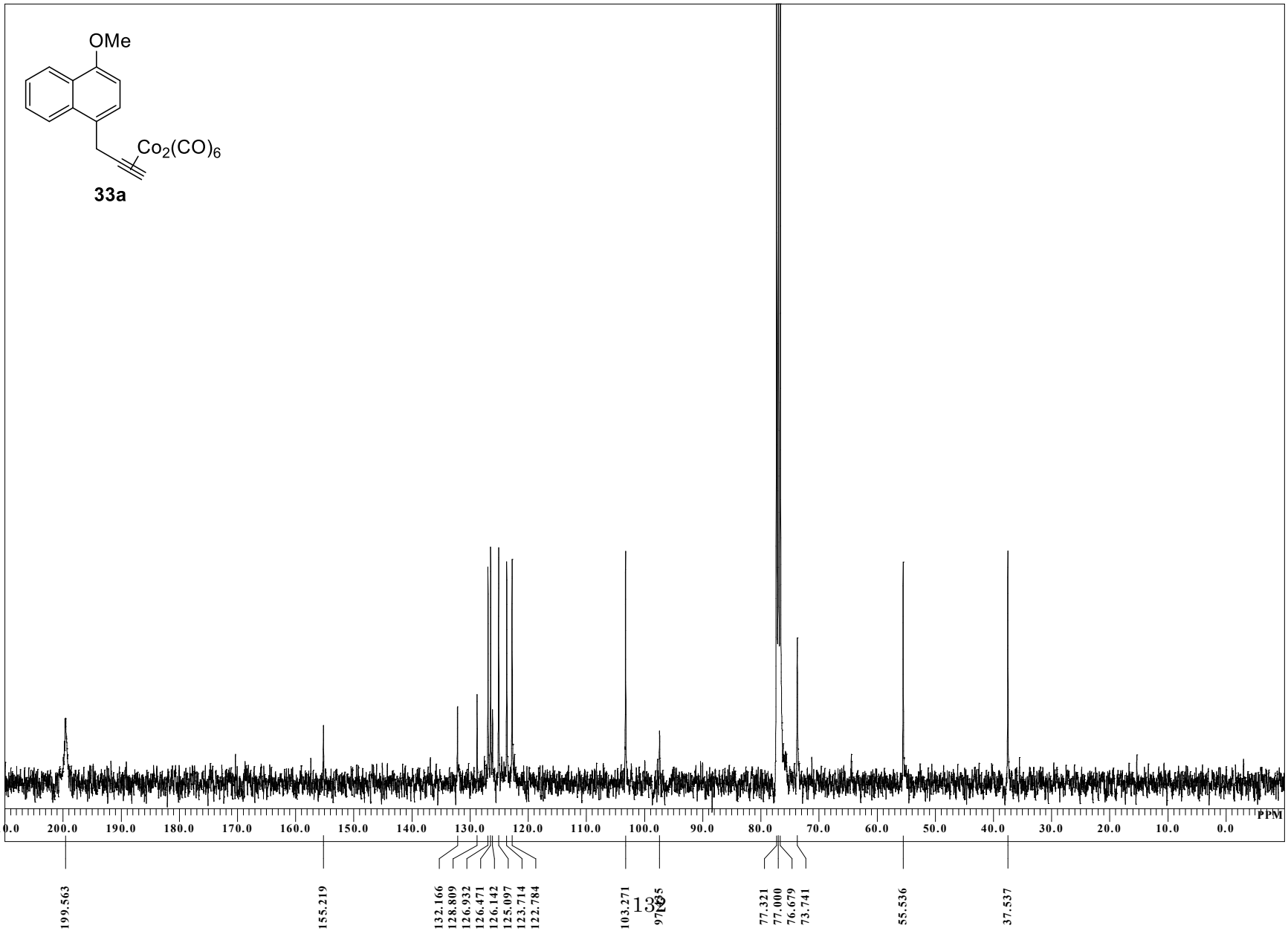
functionalozation of indole 13C

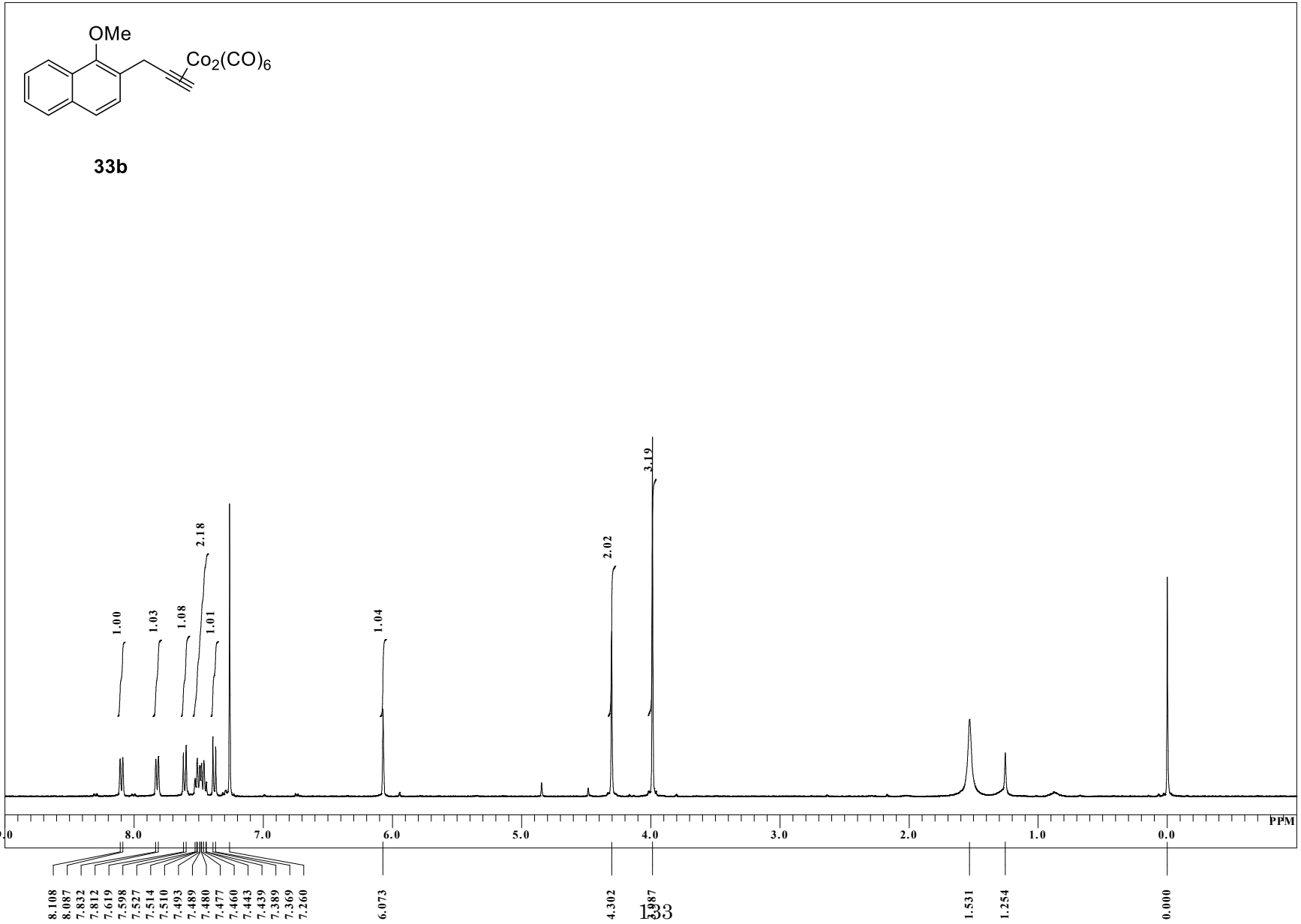


functionalization of 1-OMe-4 1H



functionalization of 1-OMe-4 13C




OMe
$Co_2(CO)_6$
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1.03
1.08
2.18
1.01
1.04
2.02
3.19
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
8.108
8.087
7.832
7.812
7.619
7.598
7.527
7.514
7.510
7.493
7.489
7.480
7.477
7.460
7.443
7.439
7.389
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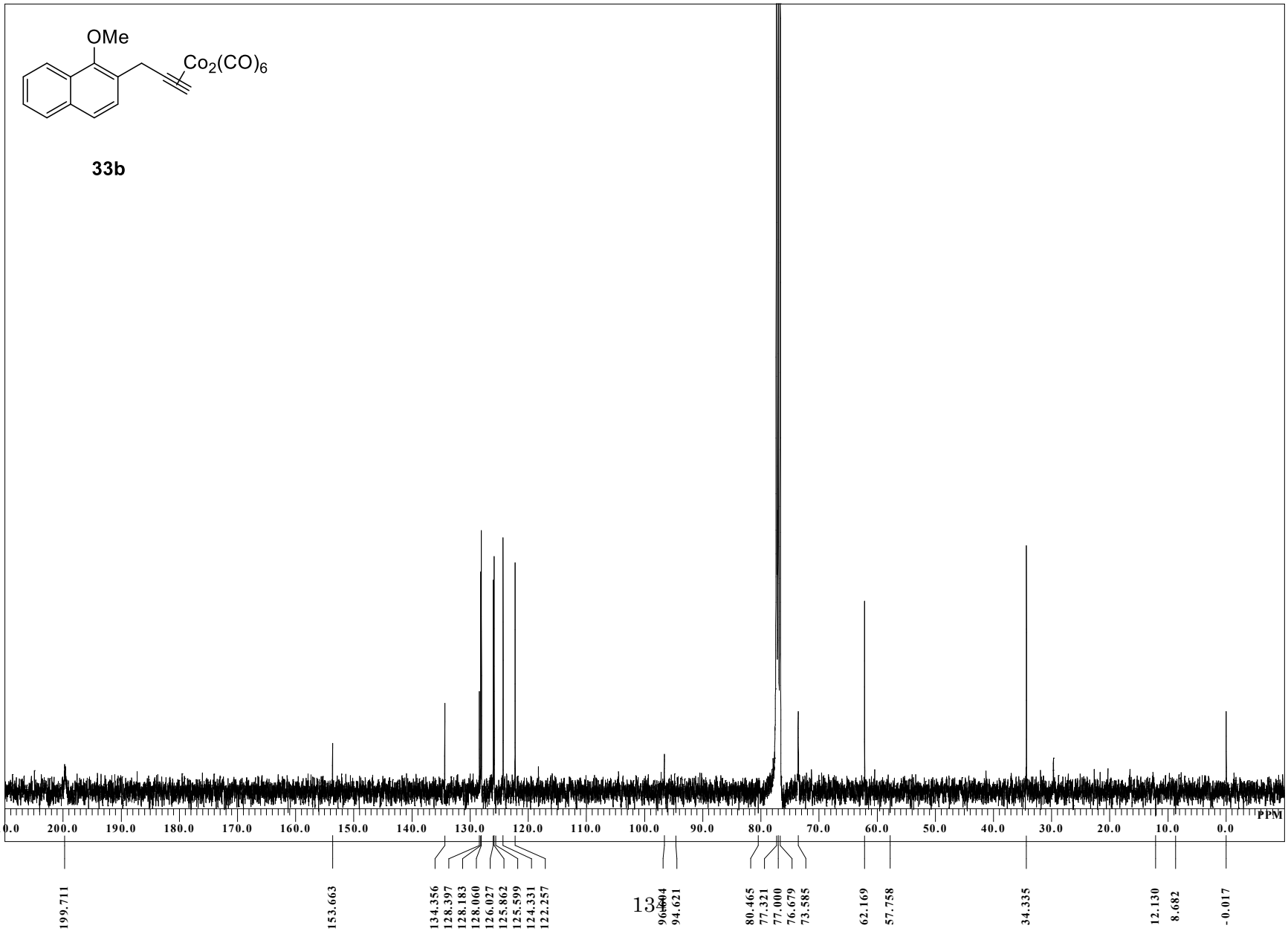
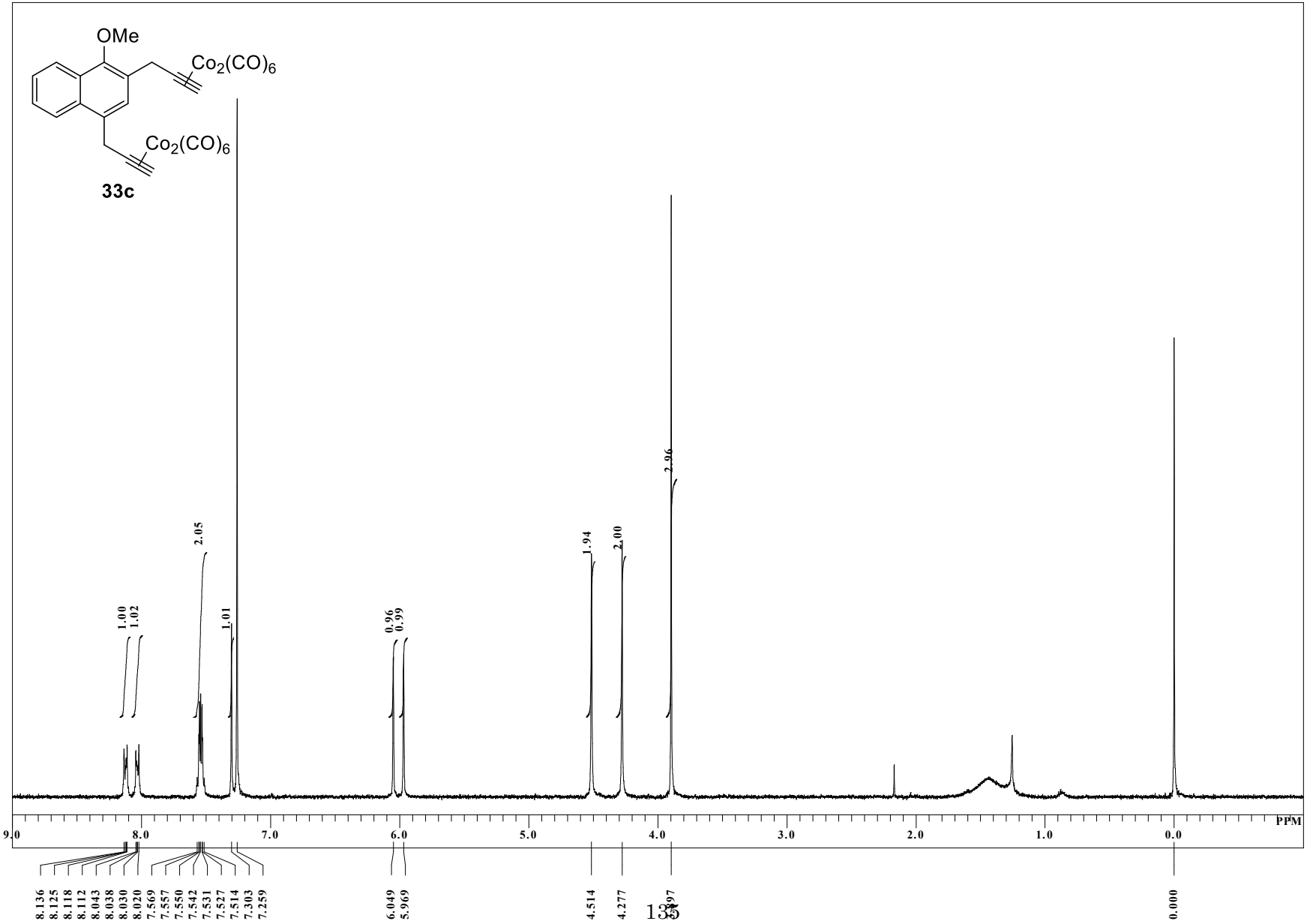
7.260
6.073
4.302
4.287
1.531
1.254
0.000

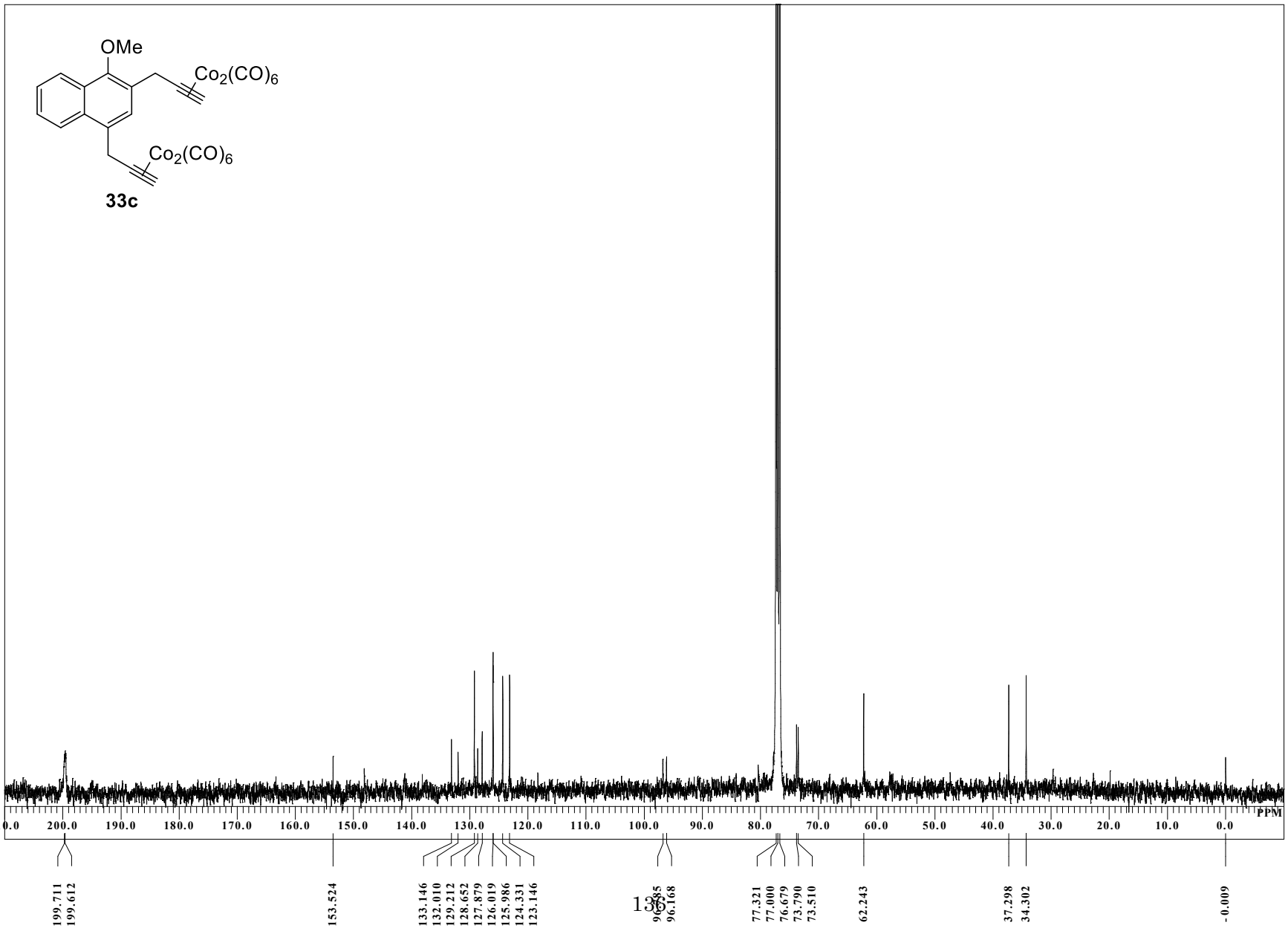
functionalization of 1-OMe-2 13C



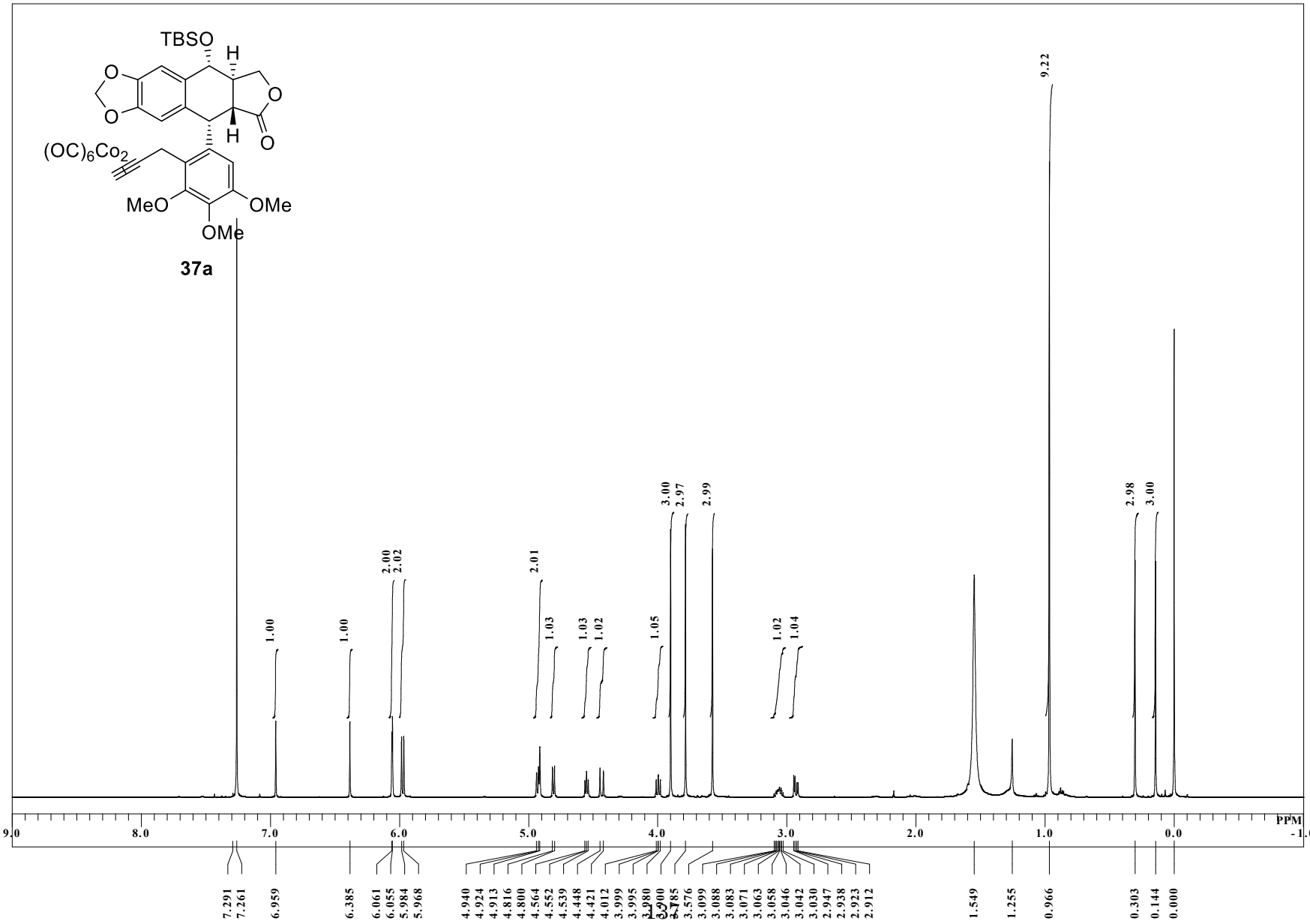
functionalization of 1- OMe- 2,4 1H



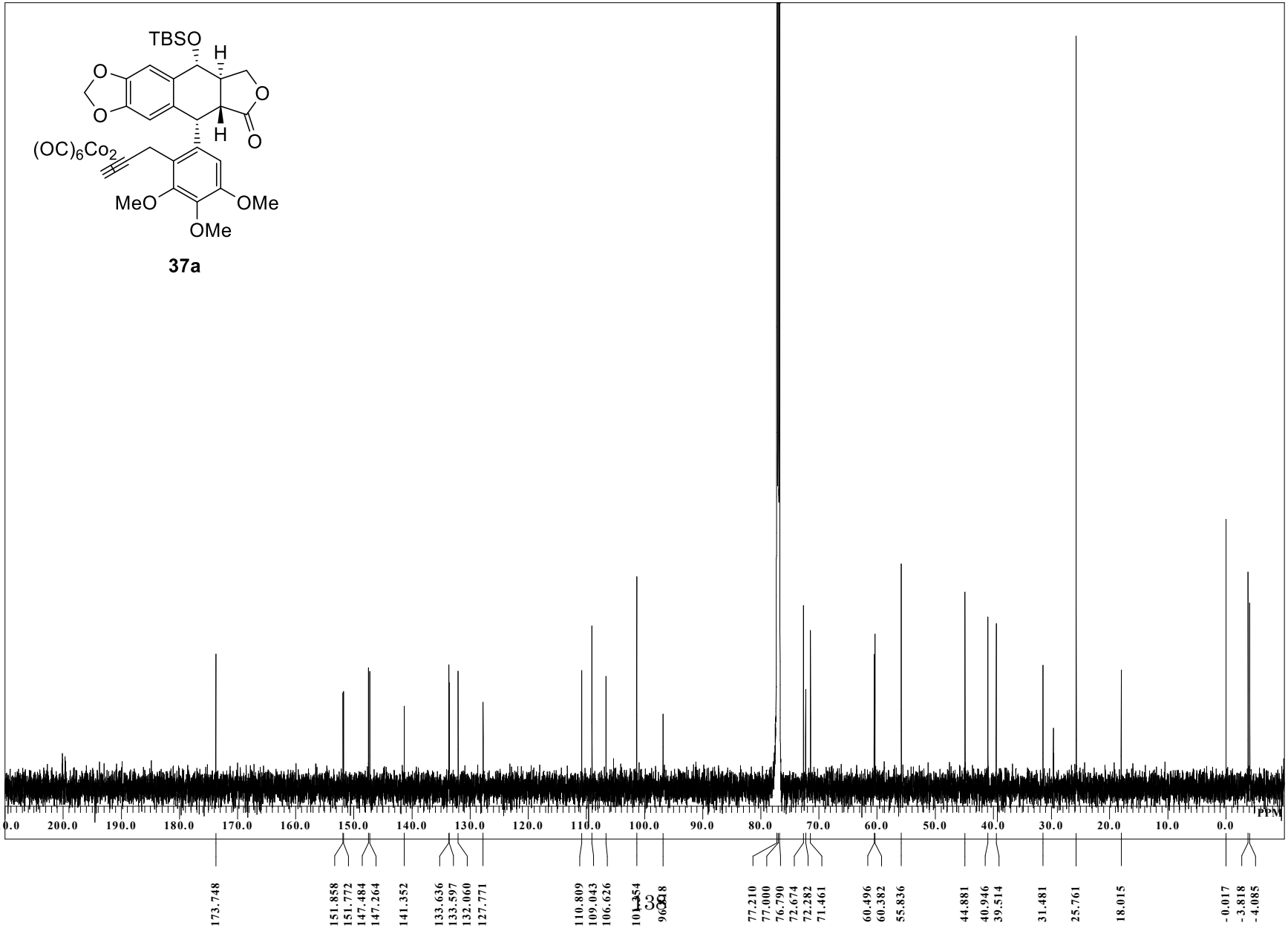
functionalization of 1-OMe-2,4 13C

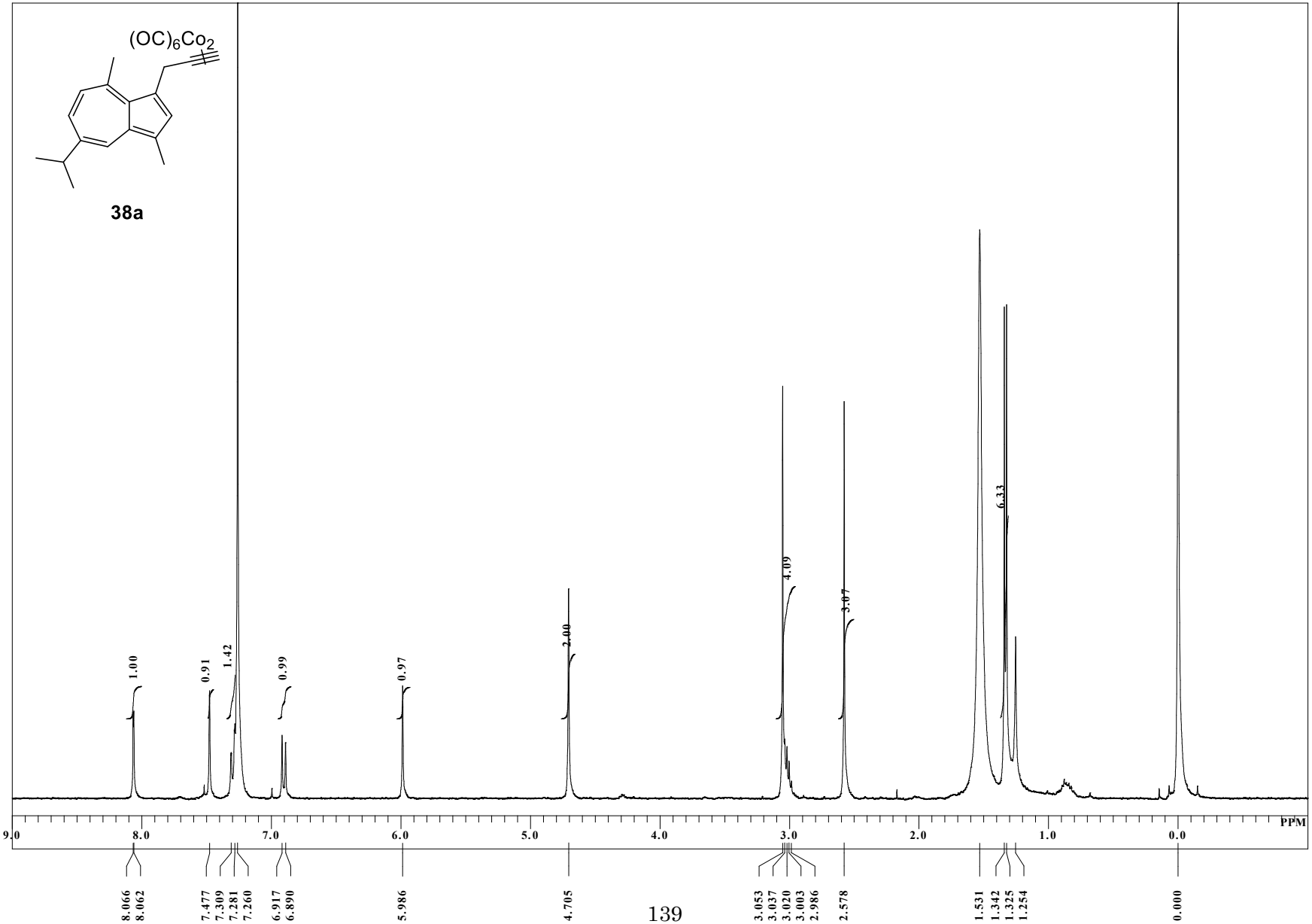


functionalization of podophillotoxin 1H



pod functionalization 13C




(OC)6Co2
38a
1.00
0.91
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0.99
0.97
2.00
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3.07
6.33
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
8.066
8.062
7.477
7.309
7.281
7.260
6.917
6.890
5.986
4.705
3.053
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2.986
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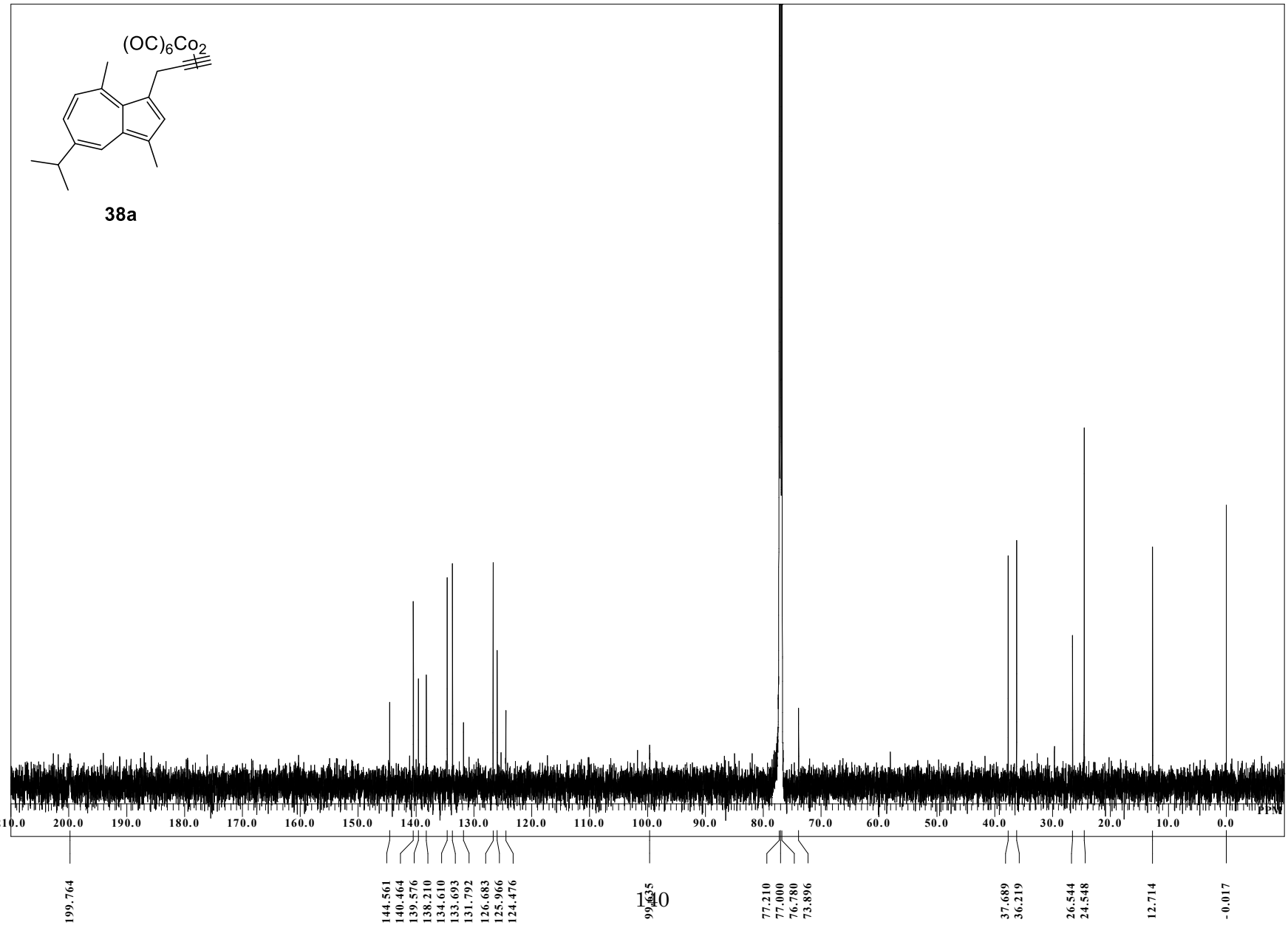
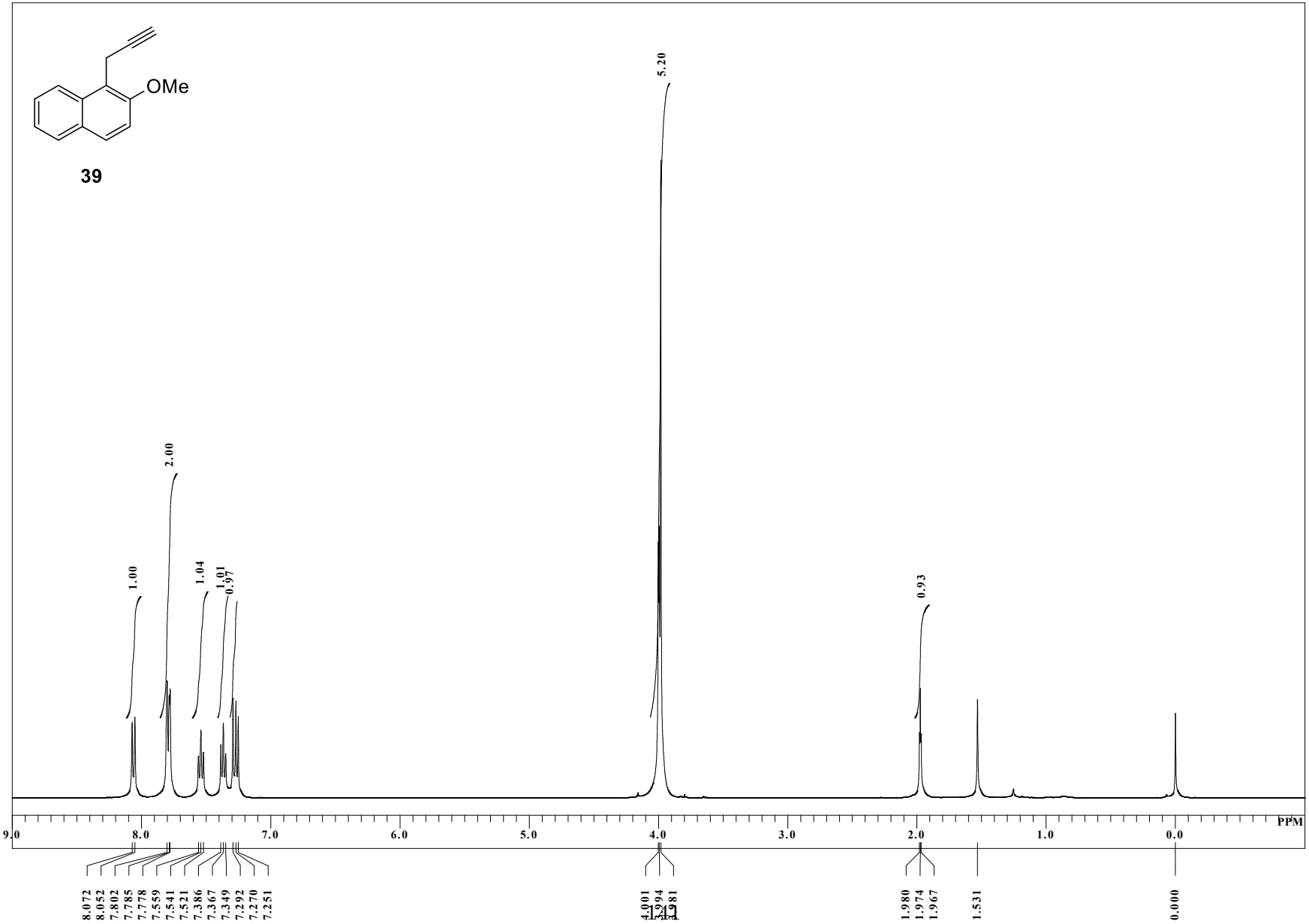
1.531
1.342
1.325
1.254
0.000

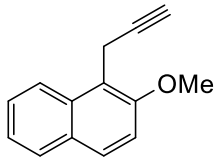
guaiazulene 13C



decomplexation of Me ether 1H



decomplexation of Me ether 13C



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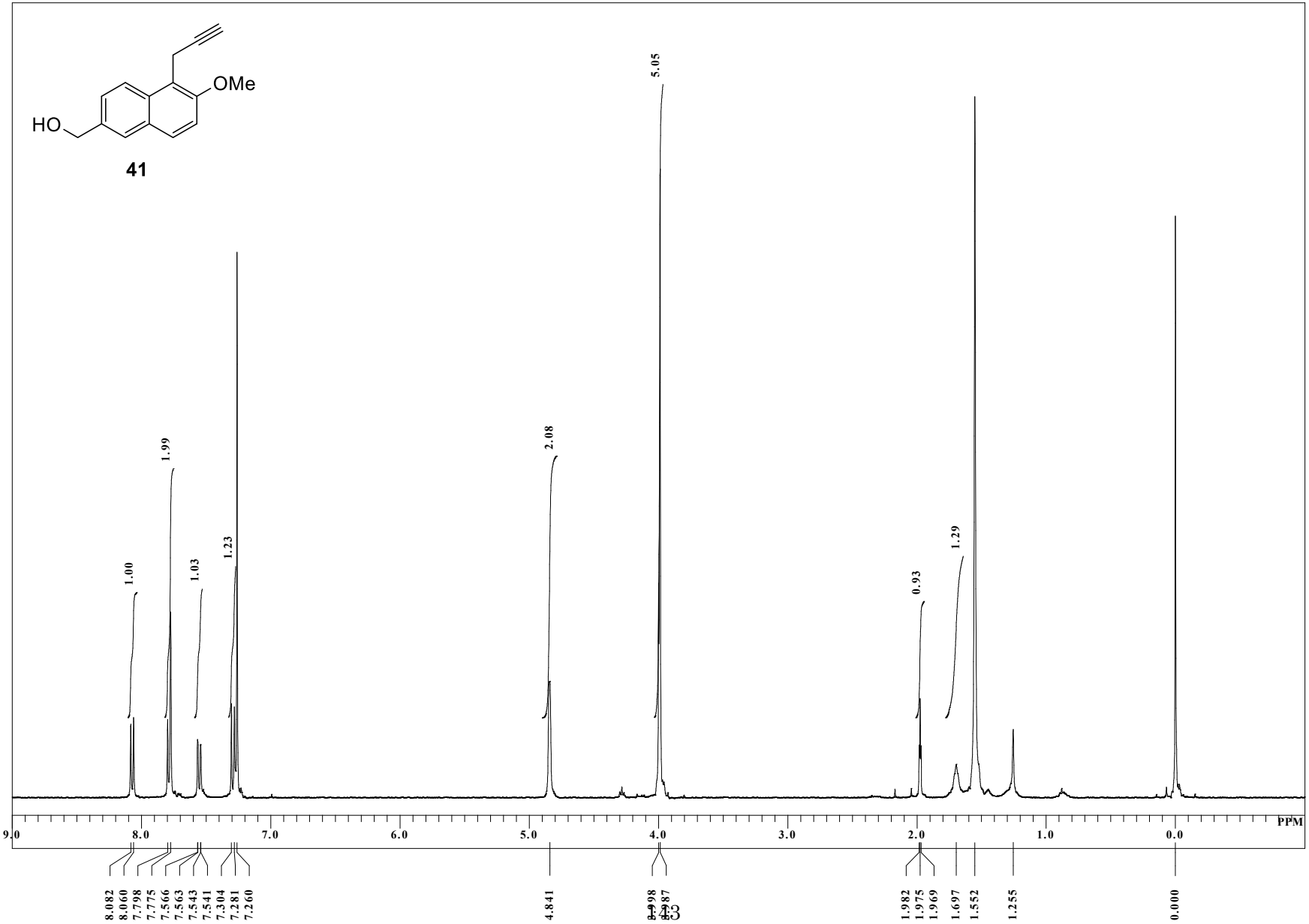
decomplexation of TBS 1H



decomplexation of TBS 13C