CHEMISTRY
A European Journal

Supporting Information

Cross-Metathesis of Terminal Alkynes

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General. All reactions were carried out in flame-dried glassware under Argon unless stated otherwise. The solvents were purified by distillation over the indicated drying agents and were stored and transferred under Argon: THF (Mg-anthracene), diethyl ether (Mg-anthracene), dichloromethane (CaH_2), toluene (Na/K), hexane (Na/K), pyridine (molecular sieves 4 Å), diisopropylamine (CaH_2). Flash chromatography: Merck silica gel 60 (230-400 mesh), unless stated otherwise. Melting points: Büchi melting point apparatus B-540 (corrected). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200, MS (CI): Finnigan MAT 95, MS (ESI) ESQ 3000, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 MHz spectrometer at 298 K (unless otherwise noted) in the indicated solvents; ^{1}H and ^{13}C chemical shifts (δ) are given in parts per million (ppm) relative to TMS, coupling constants (J) in Hertz (Hz). The solvent signals were used as references ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.20 ppm) and the chemical shifts converted to the TMS scale. Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich, Fluka, Strem) were used as received. The powdered molecular sieves were flame dried under vacuum and stored under Ar.

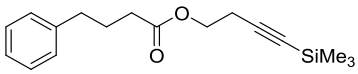
Representative Procedure for the Cross Metathesis of Terminal Alkynes: 4-(Trimethylsilyl)but-3-yn-1-yl 4-methoxybenzoate.[1] A suspension containing but-3-yn-1-yl 4-methoxybenzoate (102 mg, 0.5 mmol), trimethyl(prop-1-yn-1-yl)silane **5** (148 µL, 1 mmol, 2 equiv.), powdered MS 5Å (2 g) and MS 4Å (1 g) in toluene (22 mL) was stirred for 5 min at room temperature before a solution of complex **3** (5.2 mg, 5 µmmol, 1 mol%) in toluene (2 mL) was added. After stirring for 1 h, TLC indicated complete conversion. The mixture was filtered through a pad of Celite and the filtrate was evaporated. Purification of the residue by flash chromatography on neutral alumina (toluene/AcOEt, 100:0 to 95:5) afforded the cross metathesis product as a colorless oil (133 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 4.38 (t, J = 7.0 Hz, 2H), 3.86 (s, 3H), 2.68 (t, J = 7.0 Hz, 2H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1, 163.6, 131.8 (2C), 122.7, 113.7 (2C), 102.5, 86.7, 62.5, 55.6, 20.7, 0.1 (3C); IR (film): $\tilde{\nu}$ = 2960, 2901, 2840, 2179, 1713, 1606, 1511, 1248, 1166, 1100, 1029, 842 cm^{-1}; MS (EI) m/z (%): 276 (8) [M^+], 261 (8), 231 (6), 209 (6), 189 (8), 165 (7), 152 (100), 135 (85), 107 (6), 92 (8), 77 (10); HRMS (ESI): m/z: calcd. for $C_{15}H_{20}O_3Si$+Na: 299.1074; found: 299.1076.

4-(Trimethylsilyl)but-3-yn-1-yl 4-chlorobenzoate.[1] Prepared analogously; the compound was obtained by flash chromatography on neutral alumina (toluene/AcOEt, 100:0 to 95:5) as a yellow liquid (132 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5

[1] P. Persich, J. Llaveria, R. Lhermet, T. de Haro, R. Stade, A. Kondoh, A. Fürstner, *Chem. Eur. J.* **2013**, *19*, 13047-13058.

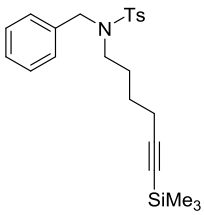
Hz, 2H), 4.41 (t, J = 6.9 Hz, 2H), 2.69 (t, J = 6.9 Hz, 2H), 0.14 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.6, 139.7, 131.2 (2C), 128.9 (2C), 128.7, 102.2, 87.0, 63.0, 20.6, 0.11 (3C); IR (film): $\tilde{\nu}$ = 2961, 2852, 2179, 1722, 1595, 1488, 1402, 1266, 1249, 1103, 1091, 1015, 838 cm^{-1}; MS (EI) *m*/*z* (%): 265 (18), 235 (15), 213 (18), 193 (12), 169 (12), 141 (31), 139 (100), 124 (82), 111 (49), 109 (79), 75 (20); HRMS (ESI): *m*/*z*: calcd. for $C_{14}H_{17}ClO_2Si$+Na: 303.0579; found: 303.0576.

4-(Trimethylsilyl)but-3-yn-1-yl 4-phenylbutanoate. Prepared analogously; the compound



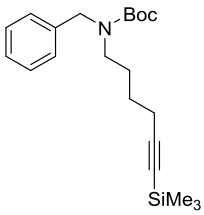
was obtained by flash chromatography on neutral alumina (toluene/AcOEt, 100:0 to 9:1) as a pale orange liquid (97 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 4.15 (t, J = 7.0 Hz, 2H), 2.68-2.61 (m, 2H), 2.54 (t, J = 7.0 Hz, 2H), 2.33 (t, J = 7.5 Hz, 2H), 2.00-1.91 (m, 2H), 0.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.4, 141.5, 128.7 (2C), 128.6 (2C), 126.2, 102.5, 86.7, 62.3, 35.3, 33.7, 26.7, 20.5, 0.2 (3C); IR (film): $\tilde{\nu}$ = 3028, 2959, 2885, 2179, 1736, 1248, 1141, 838, 698 cm^{-1}; MS (EI) *m*/*z* (%): 288 (8) [M$^+$], 273 (6), 221 (6), 184 (100), 147 (34), 125 (27), 117 (17), 104 (22), 91 (43), 73 (50); HRMS (EI): *m*/*z*: calcd. for $C_{17}H_{24}O_2Si$: 288.1546; found: 288.1546.

***N*-Benzyl-4-methyl-*N*-(6-(trimethylsilyl)hex-5-yn-1-yl)benzenesulfonamide.**[1] Prepared



analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 9:1) as a colorless oil (188 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 8.1 Hz, 2H), 7.33-7.23 (m, 7H), 4.30 (s, 2H), 3.08 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.04 (t, J = 6.9 Hz, 2H), 1.48-1.37 (m, 2H), 1.36-1.26 (m, 2H), 0.11 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.3, 137.2, 136.6, 129.8 (2C), 128.7 (2C), 128.4 (2C), 127.9, 127.3 (2C), 106.9, 84.9, 52.0, 47.6, 27.2, 25.7, 21.6, 19.4, 0.3 (3C); IR (film): $\tilde{\nu}$ = 3031, 2956, 2866, 2172, 1599, 1495, 1455, 1338, 1248, 1156, 1089, 1023, 840, 758 cm^{-1}; MS (EI) *m*/*z* (%): 398 (11), 322 (2), 300 (35), 274 (14), 258 (27), 184 (5), 149 (3), 91 (100), 73 (9); HRMS (ESI): *m*/*z*: calcd. for $C_{23}H_{31}NO_2SSi$+Na: 436.1737; found: 436.1741.

***tert*-Butyl benzyl(6-(trimethylsilyl)hex-5-yn-1-yl)carbamate**.[1] Prepared analogously; the



compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 9:1) as a colorless oil (167 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.27 (m, 2H), 7.26-7.18 (m, 3H), 4.43 (bs, 2H), 3.21 and 3.13 (bs, 2H, rotamers), 2.20 (t, J = 6.9 Hz, 2H), 1.66-1.37 (m, 13H), 0.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.1 and 155.7 (1C, rotamers), 138.5, 128.5 (2C), 127.8, 127.2 (2C), 107.1, 84.8, 79.7, 50.4 and 49.8 (1C, rotamers), 45.9, 28.5 (3C), 27.2, 25.9, 19.7, 0.3 (3C); IR (film): $\tilde{\nu}$ = 2960, 2932, 2861, 2174, 1691, 1454, 1414, 1365, 1248, 1156, 1117, 1028, 834 cm^{-1}; MS (EI) *m*/*z* (%): 359 (2) [M$^+$], 303 (11), 288 (29), 258 (16), 212 (13), 190 (32), 186 (22), 168 (17), 146 (24), 120 (30), 91

(100), 73 (28), 57 (70); HRMS (ESI): *m*/*z*: calcd. for $C_{21}H_{33}NO_2Si$+Na: 382.2173; found: 382.2170.

Trimethyl(4-((tetrahydro-2H-pyran-2-yl)oxy)but-1-yn-1-yl)silane.[1] Prepared analogously; the compound was obtained by flash chromatography on neutral alumina (toluene/AcOEt, 100:0 to 9:1) as a colorless oil (99 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.66 (t, *J* = 3.2 Hz, 1H), 3.92-3.86 (m, 1H), 3.85-3.77 (m, 1H), 3.58-3.47 (m, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.89-1.77 (m, 1H), 1.75-1.66 (m, 1H), 1.64-1.46 (m, 4H); 0.14 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 104.1, 98.7, 85.8, 65.7, 62.2, 30.7, 25.6, 21.5, 19.4, 0.2 (3C); IR (film): $\tilde{\nu}$ = 2942, 2873, 2178, 1441, 1352, 1258, 1200, 1122, 1032, 907, 836, 815, 759 cm^{-1}; MS (EI) *m*/*z* (%): 173 (5), 127 (28), 109 (10), 99 (15), 85 (10), 75 (50), 55 (19); HRMS (ESI): *m*/*z*: calcd. for $C_{12}H_{22}O_2Si$+Na: 249.1281; found: 249.1280.

Representative Procedure for the Cross Metathesis of Internal Alkynes: 4-(Trimethylsilyl)but-3-yn-1-yl 4-methylbenzenesulfonate.[2] A suspension containing hex-3-yne-1,6-diyl bis(4-methylbenzenesulfonate) (106 mg, 0.25 mmol), trimethyl(prop-1-yn-1-yl)silane **5** (148 µL, 1 mmol, 4 equiv.), complex **3** (5.2 mg, 5 µmmol, 2 mol%) and powdered MS 5Å (0.5 g) in toluene (5 mL) was stirred for 2 h at ambient temperature. After filtration of the mixture through a short pad of Celite, the filtrate was evaporated. Purification of the residue by flash chromatography on silica (hexane/AcOEt, 100:0 to 9:1) afforded the title compound as a colorless liquid (141 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.08 (t, *J* = 7.3 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.1, 133.1, 130.0 (2C), 128.1 (2C), 100.5, 87.6, 67.7, 21.8, 20.9, 0.0 (3C); IR (film): $\tilde{\nu}$ = 2960, 2900, 2180, 1598, 1361, 1249, 1175, 976, 839 cm^{-1}; MS (EI) *m*/*z* (%): 281 (46), 229 (100), 165 (10), 149 (16), 109 (13), 91 (38); HRMS (ESI): *m*/*z*: calcd. for $C_{14}H_{20}O_3SSi$+Na: 319.0795; found: 319.0793.

Hex-1-yn-1-yldimethyl(phenyl)silane.[1] Prepared analogously using (dimethylphenyl)(prop-1-yn-1-yl)silane as the reagent; the product was obtained by flash chromatography on silica (pentane) as a colorless oil (154 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.61 (m, 2H), 7.39-7.36 (m, 3H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.60-1.50 (m, 2H), 1.50-1.39 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 133.8 (2C), 129.3, 127.9 (2C), 109.8, 82.3, 30.8, 22.1, 19.8, 13.7, –0.4 (2C); IR (film): $\tilde{\nu}$ = 3069, 2958, 2932, 2873, 2173, 1428, 1248, 1114, 834, 825, 778 cm^{-1}; MS (EI) *m*/*z* (%): 216 (5) [M$^+$], 201 (100), 174 (19), 159 (9), 145 (11), 105 (7), 43 (8); HRMS (ESI): *m*/*z*: calcd. for $C_{14}H_{20}Si$: 216.1334; found: 216.1333.

[2] E. Wenkert, B. C. Bookser, T. S. Arrhenius *J. Am. Chem. Soc.* **1992**, *114*, 644-654.

Bis(4-(dimethyl(phenyl)silyl)but-3-yn-1-yl) adipate.[1] Prepared analogously using (dimethylphenyl)(prop-1-yn-1-yl)silane as the reagent; the reaction was carried out at 60°C. The product was obtained by flash chromatography on silica (pentane/AcOEt, 95:5) as a colorless oil (80 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.58 (m, 4H), 7.41-7.35 (m, 6H), 4.21 (t, *J* = 6.9 Hz, 4H), 2.62 (t, *J* = 6.9 Hz, 4H), 2.35-2.30 (m, 4H), 1.69-1.63 (m, 4H), 0.40 (s, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.1 (2C), 137.2 (2C), 133.8 (4C), 129.5 (2C), 128.0 (4C), 104.3 (2C), 84.6 (2C), 62.2 (2C), 33.8 (2C), 24.4 (2C), 20.6 (2C), –0.7 (4C); IR (film): $\tilde{\nu}$ = 3069, 2959, 2179, 1735, 1428, 1248, 1165, 1115, 902, 836, 820, 779 cm^{-1}; MS (EI) *m*/*z* (%): 518 (3) [M$^+$], 441 (17), 315 (5), 239 (6), 171 (12), 159 (100), 135 (42); HRMS (ESI): *m*/*z*: calcd. for $C_{30}H_{38}O_4Si_2$+Na: 541.2201; found: 541.2199.

Trimethyl(phenylethynyl)silane.[3] Prepared analogously; the compound was obtained by flash chromatography on silica (hexane) as a colorless oil (274 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.45 (m, 2H), 7.32-7.27 (m, 3H), 0.26 (s, 9H), ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.1 (2C), 128.6, 128.3 (2C), 123.3, 105.3, 94.2, 0.1 (3C); MS (EI) *m*/*z* (%): 174 (18) [M$^+$], 159 (100), 143 (5), 129 (7), 115 (4), 105 (8).

((2-Methoxyphenyl)ethynyl)trimethylsilane.[4] Prepared analogously; the compound was obtained by flash chromatography on silica (hexane/AcOEt, 100:0 to 95:5) as a colorless liquid (96 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.28 (ddd, *J* = 8.4, 7.6, 1.7 Hz, 1H), 6.91-6.83 (m, 2H), 3.88 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.5, 134.3, 130.1, 120.5, 112.5, 110.8, 101.4, 98.6, 56.0, 0.2 (3C); IR (film): $\tilde{\nu}$ = 2959, 2889, 2836, 2157, 1595, 1490, 1434, 1249, 1113, 1025, 862, 836, 748 cm^{-1}; MS (EI) *m*/*z* (%): 204 (54) [M$^+$], 189 (100), 161 (32), 159 (31), 135 (8), 115 (31), 89 (4); HRMS (EI): *m*/*z*: calcd. for $C_{12}H_{16}OSi$: 204.0970; found: 204.0968.

Trimethyl((2-(methylthio)phenyl)ethynyl)silane.[5] Prepared analogously; the compound was obtained by flash chromatography on silica (hexane/AcOEt, 100:0 to 95:5) as a pale yellow liquid (100 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.31-7.24 (m, 1H), 7.13 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 2.48 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.1, 132.8, 129.1, 124.2, 124.1, 121.3, 102.3, 101.5, 15.1, 0.1 (3C); IR (film): $\tilde{\nu}$ = 3060, 2959, 2921, 2898, 2155, 1461, 1433, 1248, 858, 837, 747 cm^{-1}; MS (EI) *m*/*z* (%): 220 (81) [M$^+$], 205 (74), 189 (16), 177 (29), 147 (32), 129 (10), 115 (100), 89 (8), 73 (9); HRMS (EI): *m*/*z*: calcd. for $C_{12}H_{16}SSi$: 220.0742; found: 220.0743.

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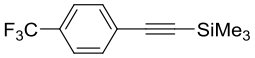
[3] C. Rossy, J. Majimel, M. Tréguer Delapierre, E. Fouquet, F.-X. Felpin, *J. Organomet. Chem.* **2014**, *755*, 78-85.

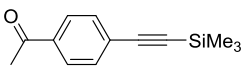
[4] E. González-Cantalapiedra, Ó. de Frutos, C. Atienza, C. Mateo, A. M. Echavarren, *Eur. J. Org. Chem.* **2006**, 1430-1443.

[5] C.-H. Lin, C.-C. Chen, M.-J. Wu. *Chem. Eur. J.* **2013**, *19*, 2578-2581.

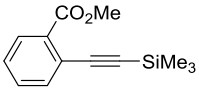
Trimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane.[6] Prepared analogously; the compound was obtained by flash chromatography on silica (hexane/AcOEt, 100:0 to 94:1) as a colorless liquid (235 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 4H), 0.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.3 (2C), 130.3 (d, *J* = 32 Hz), 127.1, 125.3 (d, *J* = 4 Hz, 2C), 124.0 (d, *J* = 273 Hz), 103.6, 97.3, –0.1 (3C); ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.9; IR (film): $\tilde{\nu}$ = 2963, 2163, 1614, 1323, 1252, 1130, 864, 842 cm^{-1}; MS (EI) *m*/*z* (%): 242 (14) [M$^+$], 227 (100), 197 (5), 170 (4), 151 (4); HRMS (EI): *m*/*z*: calcd. for $C_{12}H_{13}F_3Si$: 242.0739; found: 242.0741.



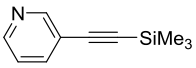
1-(4-((Trimethylsilyl)ethynyl)phenyl)ethan-1-one.[7] Prepared analogously; the compound was obtained by flash chromatography on silica (hexane/AcOEt, 100:0 to 95:5) as a colorless liquid (106 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 2.58 (s, 3H), 0.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.4, 136.5, 132.2 (2C), 128.2 (2C), 128.1, 104.2, 98.2, 26.7, 0.0 (3C); IR (film): $\tilde{\nu}$ = 2960, 2900, 2158, 1684, 1600, 1262, 1249, 859, 836 cm^{-1}; MS (EI) *m*/*z* (%): 216 (23) [M$^+$], 201 (100), 158 (10), 143 (7), 93 (4); HRMS (EI): *m*/*z*: calcd. for $C_{13}H_{16}OSi$: 216.0970; found: 216.0968.



Methyl 2-((trimethylsilyl)ethynyl)benzoate.[8] Prepared analogously; the compound was obtained by flash chromatography on silica (hexane/AcOEt, 100:0 to 95:5) as a colorless liquid (77 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.4 Hz, 1H), 7.36 (td, *J* = 7.6, 1.4 Hz, 1H), 3.92 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.0, 134.6, 132.7, 131.6, 130.4, 128.3, 123.4, 103.4, 99.8, 52.1, 0.0 (3C); IR (film): $\tilde{\nu}$ = 2956, 2900, 2159, 1733, 1718, 1482, 1447, 1296, 1247, 1079, 864, 837, 755 cm^{-1}; MS (EI) *m*/*z* (%): 232 (2) [M$^+$], 217 (25), 201 (5), 187 (100), 158 (7), 143 (9), 129 (5), 115 (5); HRMS (ESI): *m*/*z*: calcd. for $C_{13}H_{16}O_2Si$+Na: 255.0812; found: 255.0815.



3-((Trimethylsilyl)ethynyl)pyridine.[9] Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 4:1) as a colorless liquid (60 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 2.0 Hz, 1H), 8.51 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.72 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.22 (dd, *J* = 7.9, 4.8, 1H), 0.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8, 148.9, 138.9, 123.0, 120.4, 101.6, 98.4, –0.1 (3C); IR (film): $\tilde{\nu}$ = 2956, 2924, 2854, 1730, 1606, 1510, 1463, 1377, 1258, 1120, 1036 cm^{-1}; MS (EI) *m*/*z* (%): 175 (21) [M$^+$], 160 (100), 144 (2), 130 (7), 106 (5); HRMS (EI): *m*/*z*: calcd. for $C_{10}H_{13}NSi$: 175.0817; found: 175.0816.



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6 J.-J. Dai, C. Fang, B. Xiao, J. Yi, J. Xu, Z.-J. Liu, X. Lu, L. Liu, Y. Fu, *J. Am. Chem. Soc.* **2013**, *135*, 8436-8439.

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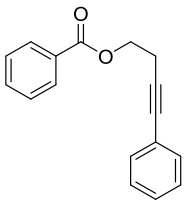
8 I. M. Jones, A. D. Hamilton, *Org. Lett.* **2010**, *12*, 3651-3653.

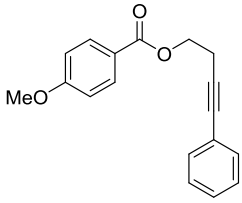
9 N. Sakai, R. Komatsu, N. Uchida, R. Ikeda, T. Konakahara, *Org. Lett.* **2010**, *12*, 1300-1303.

Representative Procedure for the Cross Metathesis of π-Arene Chromium Complexes:



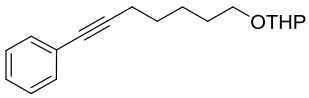
4-Phenylbut-3-ynyl benzoate (9a).[10] A suspension containing the tricarbonyl chromium complex **7** (35.7 mg, 0.15 mmol), pent-3-yn-1-yl benzoate (56.5 mg, 0.3 mmol, 2 equiv.), powdered MS 5Å (600 mg) and MS 4Å (300 mg) in toluene (6.1 mL) was stirred for 5 min at ambient temperature before a solution of complex **3** (3.1 mg, 3 μmol, 2 mol%) in toluene (1 mL) was introduced. After stirring for 1 h, acetic acid (5 mL) was added, followed by MnO_2 (77 mg, 0.75 mmol) after 5 min. The black mixture was stirred for 1 h before it was filtered through a pad of silica. The filtrate was evaporated and the residue purified by flash chromatography on silica (hexane/AcOEt, 100:0 to 96:4) to afford compound **9a** as a white solid (35.5 mg, 95%). mp = 34-36°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-8.07 (m, 2H), 7.60-7.53 (m, 1H), 7.49-7.38 (m, 4H), 7.31-7.26 (m, 3H), 4.52 (t, *J* = 6.9 Hz, 2H), 2.90 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.5, 133.2, 131.8 (2C), 130.2, 129.8 (2C), 128.5 (2C), 128.4 (2C), 128.1, 123.5, 85.6, 82.3, 63.0, 20.2; IR (film): $\tilde{\nu}$ = 3062, 2960, 2908, 1717, 1451, 1267, 1109, 755, 708 cm^{-1}; MS (EI) *m*/*z* (%): 165 (1), 128 (100), 115 (11), 105 (26), 89 (3), 77 (28), 51 (9); HRMS (ESI): *m*/*z*: calcd. for $C_{17}H_{14}O_2$+Na: 273.0886; found: 273.0885.

4-Phenylbut-3-ynyl 4-methoxybenzoate (9b). Prepared analogously as a white solid (38 mg,



90%); mp = 86-88°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.9 Hz, 2H), 7.43-7.37 (m, 2H), 7.30-7.27 (m, 3H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.48 (t, *J* = 6.9 Hz, 2H), 3.87 (s, 3H), 2.88 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.3, 163.6, 131.9 (2C), 131.8 (2C), 128.4 (2C), 128.0, 123.6, 122.6, 113.8 (2C), 85.7, 82.2, 62.7, 55.6, 20.3; IR (film): $\tilde{\nu}$ = 3003, 2962, 2907, 2836, 1721, 1602, 1245, 1105, 1025, 846, 758, 691 cm^{-1}; MS (EI) *m*/*z* (%): 152 (8), 135 (33), 128 (10), 115 (9), 107 (6), 92 (10), 77 (13); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{16}O_3$+Na: 303.0992; found: 303.0991.

2-(7-Phenylhept-6-ynyloxy)tetrahydro-2*H*-pyran (9c). Prepared analogously as a pale



yellow oil (41 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.35 (m, 2H), 7.29-7.23 (m, 3H), 4.57 (dd, *J* = 4.1, 2.9 Hz, 1H), 3.90-3.82 (m, 1H), 3.74 (td, *J* = 9.6, 6.8 Hz, 1H), 3.52-3.45 (m, 1H), 3.39 (td, *J* = 9.6, 6.8 Hz, 1H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.88-1.36 (m, 14H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.7 (2C), 128.3 (2C), 127.6, 124.2, 99.0, 90.5, 80.8, 67.7, 62.5, 30.9, 29.8, 28.9, 28.9, 26.0, 25.7, 19.8, 19.5; IR (film): $\tilde{\nu}$ = 2935, 2858, 1490, 1441, 1119, 1022, 755, 691, 525 cm^{-1}; MS (EI) *m*/*z* (%): 286 (7) [M$^+$], 187 (6), 155 (7), 143 (13), 128 (23), 115 (39), 91 (15), 85 (100), 67 (9), 55 (8), 41 (22); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{26}O_2$+Na: 309.1825; found: 309.1825.

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[10] For the chromium decomplexation procedure, see: P. Ricci, K. Krämer, X. C. Cambeiro, I. Larrosa, *J. Am. Chem. Soc.* **2013**, *135*, 13258-13261.

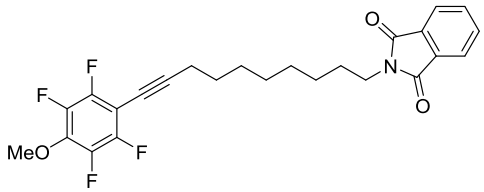
Representative Procedure for Cross Metathesis Reactions of Phenyl Aacetylene Derivatives: 4-(Pentafluorophenyl)but-3-ynyl 4-methoxybenzoate (10a). A suspension containing ethynyl(pentafluoro)benzene (48.0 mg, 0.25 mmol), pent-3-yn-1-yl 4-methoxybenzoate (109 mg, 0.5 mmol, 2 equiv.), powdered MS 5Å (2 g) and MS 4Å (1 g) in toluene (9.5 mL) was stirred for 5 min at room temperature before a solution of complex **3** (5.2 mg, 5 μmmol, 2 mol%) in toluene (1 mL) was introduced. The suspension was stirred for 1 h before it was diluted with EtOAc and filtered through a pad of Celite. The filtrate was evaporated and the residue purified by flash chromatography on silica (eluent: hexane/AcOEt, 100:0 to 95:5) to afford product **10a** as a white solid (74 mg, 80%). Mp = 95-97°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.50 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 2.97 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1, 163.7, 149.0 (m), 146.5 (m), 142.7 (m), 140.1 (m), 139.0 (m), 136.5 (m), 131.9 (2C), 122.3, 113.8 (2C), 100.3 (m), 99.4 (q, *J* = 4 Hz), 66.3 (q, *J* = 4 Hz), 61.9, 55.6, 20.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –136.7 (dd, *J* = 21, 7 Hz, 2F), –153.5 (t, *J* = 21 Hz, 1F), –162.2 (m, 2F); IR (film): $\tilde{\nu}$ = 2968 , 2945, 2910, 2847, 2251, 1706, 1603, 1491, 1261, 1103, 978, 770 cm^{-1}; MS (EI) *m*/*z* (%): 370 (1) [M^{+}], 218 (10), 152 (100), 135 (69), 92 (8), 77 (11); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{11}F_5O_3$+Na: 393.0521; found: 393.0520.

4-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)but-3-ynyl 4-methoxybenzoate (10b). Prepared analogously as a white solid (84 mg, 88%). Mp = 105-107°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.49 (t, *J* = 6.7 Hz, 2H), 4.08 (t, *J* = 1.5 Hz, 3H), 3.87 (s, 3H), 2.96 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 163.7, 149.1 (m), 146.6 (m), 142.1 (m), 139.6 (m), 138.7 (m), 131.9 (2C), 122.4, 113.8 (2C), 98.1 (m), 97.8 (t, *J* = 4 Hz), 67.1 (t, *J* = 4 Hz), 62.3 (t, *J* = 4 Hz), 62.1, 55.6, 20.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –138.6 (dd, *J* = 21, 8 Hz, 2F), –158.3 (dd, *J* = 21, 8 Hz, 2F); IR (film): $\tilde{\nu}$ = 3012, 2965, 2842, 2245, 1704, 1602, 1488, 1254, 1106, 978, 770 cm^{-1}; MS (EI) *m*/*z* (%): 230 (100), 215 (16), 174 (3), 152 (13), 135 (43), 92 (11), 77 (13); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{14}F_4O_4$+Na: 405.0720; found: 405.0720.

Cyclopentyl 10-(2,3,5,6-tetrafluoro-4-methoxyphenyl)dec-9-ynoate (10c). Prepared analogously; the compound was obtained by flash chromatography on neutral alumina (hexane/toluene, 4:1 to 1:1) as a colorless oil (101 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.15 (tt, *J* = 5.7, 2.7 Hz, 1H), 4.08 (t, *J* = 1.4 Hz, 3H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.26 (t, *J* = 7.5 Hz, 2H), 1.90-1.80 (m, 2H), 1.76-1.53 (m, 10H), 1.50-1.40 (m, 2H), 1.38-1.30 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.8, 148.9 (m), 146.4 (m), 142.1 (m), 139,6 (m), 138.2 (m), 102.6 (t, *J* = 4 Hz), 98.7 (t, *J* = 18

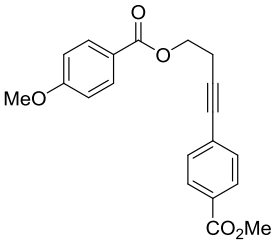
Hz), 76.9, 65.7 (t, J = 4 Hz), 62.3 (t, J = 4 Hz), 34.7, 32.8 (2C), 29.1, 28.8 (2C), 28.7, 28.3, 25.1, 23.9, 19.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –139.0 (dd, J = 21, 8 Hz, 2F), –158.6 (dd, J = 21, 8 Hz, 2F); IR (film): $\tilde{\nu}$ = 2935, 2859, 2245, 1728, 1504, 1489, 1428, 1162, 1074, 986 cm^{-1}; MS (EI) m/z (%): 346 (6), 311 (4), 287 (3), 245 (11), 232 (100), 219 (14), 193 (30), 153 (5), 135 (3), 93 (2), 81 (4), 69 (5); HRMS (ESI): m/z: calcd. for $C_{22}H_{26}F_4O_3$+Na: 437.1710; found: 437.1710.

2-(10-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)dec-9-yn-1-yl)isoindoline-1,3-dione (10d).



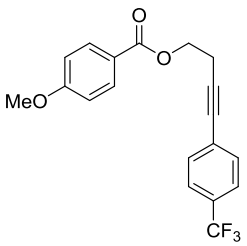
Prepared analogously; the compound was obtained by flash chromatography on neutral alumina (hexane/toluene, 3:7 to 1:4) as a white solid (112 mg, 97%). mp = 73-75°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86-7.81 (m, 2H), 7.73-7.68 (m, 2H), 4.07 (t, J = 1.4 Hz, 3H), 3.70-3.65 (m, 2H), 2.46 (t, J = 7.0 Hz, 2H), 1.73-1.55 (m, 4H), 1.49-1.40 (m, 2H), 1.38-1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.6 (2C), 148.9 (m), 146.4 (m), 142.1 (m), 139.6 (m), 138.2 (m), 133.9 (2C), 132.3 (2C), 123.2 (2C), 102.6 (t, J = 4 Hz), 98.7 (t, J = 18 Hz), 65.6 (t, J = 4 Hz), 62.3 (t, J = 4 Hz), 38.1, 29.1, 29.0, 28.7, 28.7, 28.3, 26.9, 19.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –139.0 (dd, J = 21, 8 Hz, 2F), –158.6 (dd, J = 21, 8 Hz, 2F); IR (film): $\tilde{\nu}$ = 2934, 2920, 2240, 1719, 1491, 1395, 1059, 991, 720, 530 cm^{-1}; MS (EI) m/z (%): 361 (1), 314 (1), 268 (4), 232 (100), 217 (11), 193 (11), 160 (29), 121 (10); HRMS (ESI): m/z: calcd. for $C_{25}H_{23}F_4NO_3$+Na: 484.1506; found: 484.1506.

4-(4-(Methoxycarbonyl)phenyl)but-3-ynyl 4-methoxybenzoate (10e). Prepared



analogously; the compound was obtained by flash chromatography on silica (15-40 µm) (hexane/AcOEt, 100:0 to 4:1) as a white solid (60 mg, 71%). mp = 101-103°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 9.0 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 4.48 (t, J = 6.9 Hz, 2H), 3.91 (s, 3H), 3.87 (s, 3H), 2.90 (t, J = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.7, 166.2, 163.6, 131.8 (2C), 131.7 (2C), 129.5 (2C), 129.3, 128.3, 122.4, 113.8 (2C), 89.1, 81.6, 62.4, 55.5, 52.3, 20.3; IR (film): $\tilde{\nu}$ = 2971, 2951, 2839, 1713, 1604, 1273, 1099, 1020, 847, 766 cm^{-1}; MS (EI) m/z (%): 307 (2), 186 (100), 155 (31), 152 (20), 135 (32), 107 (3), 92 (4), 77 (5); HRMS (ESI): m/z: calcd. for $C_{20}H_{18}O_5$+Na: 361.1046; found: 361.1045.

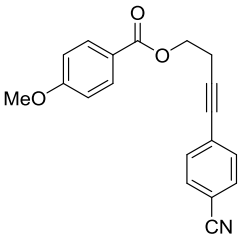
4-(4-(Trifluoromethyl)phenyl)but-3-ynyl 4-methoxybenzoate (10f). Prepared analogously;



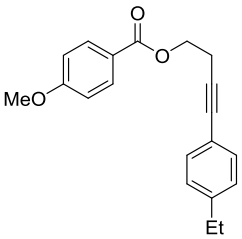
the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 98:2) as a white solid (76 mg, 87%). Mp = 94-96°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.9 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 4.49 (t, J = 6.8 Hz, 2H), 3.87 (s, 3H), 2.90 (t, J = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 163.6, 132.0 (2C), 131.8 (2C), 129.7 (q, J = 32

Hz), 127.3, 125.2 (q, J = 4 Hz, 2C), 124.0 (q, J = 271 Hz), 122.4, 113.7 (2C), 88.6, 81.0, 62.3, 55.5, 20.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.8; IR (film): $\tilde{\nu}$ = 3022, 2960, 2923, 2848, 1708, 1603, 1319, 1254, 1101, 1025, 843, 770 cm^{-1}; MS (EI) *m*/*z* (%): 348 (1) [M$^+$], 196 (41), 177 (10), 152 (100), 135 (63), 107 (9), 92 (12), 77 (14); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{15}F_3O_3$+Na: 371.0866; found: 371.0865.

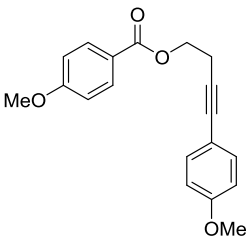
4-(4-Cyanophenyl)but-3-ynyl 4-methoxybenzoate (10g). Prepared analogously; the compound was obtained by flash chromatography on silica (15-40 µm) (hexane/AcOEt, 100:0 to 85:15) as a white solid (68 mg, 89%). mp = 115-117°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 4.48 (t, J = 6.8 Hz, 2H), 3.86 (s, 3H), 2.90 (t, J = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1, 163.7, 132.3 (2C), 132.0 (2C), 131.8 (2C), 128.5, 122.4, 118.6, 113.8 (2C), 111.4, 90.8, 80.9, 62.2, 55.5, 20.3; IR (film): $\tilde{\nu}$ = 2966, 2937, 2843, 2226, 1710, 1603, 1250, 1101, 1024, 839, 766 cm^{-1}; MS (EI) *m*/*z* (%): 305 (1) [M$^+$], 152 (100), 140 (10), 135 (67), 107 (5), 92 (17), 77 (20); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{15}NO_3$+Na: 328.0944; found: 328.0944.



4-(4-Ethylphenyl)but-3-ynyl 4-methoxybenzoate (10h). Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 98.5:1.5) as a white solid (51 mg, 66%). mp = 79-81°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.47 (t, J = 7.0 Hz, 2H), 3.86 (s, 3H), 2.87 (t, J = 7.0 Hz, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ =166.2, 163.6, 144.3, 131.8 (2C), 131.7 (2C), 127.9 (2C), 122.6, 120.7, 113.7 (2C), 84.9, 82.2, 62.8, 55.5, 28.9, 20.2, 15.5; IR (film): $\tilde{\nu}$ = 3006, 2964, 2920, 2839, 1704, 1603, 1509, 1253, 1166, 1103, 1027, 832, 767 cm^{-1}; MS (EI) *m*/*z* (%): 156 (100), 141 (40), 135 (24), 128 (5), 107 (4), 92 (5), 77 (9); HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{20}O_3$+Na: 331.1305; found: 331.1305.

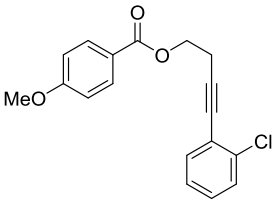


4-(4-Methoxyphenyl)but-3-ynyl 4-methoxybenzoate (10i). Prepared analogously; the compound was obtained by flash chromatography on silica (15-40 µm) (hexane/AcOEt, 100:0 to 9:1), followed by a second flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 9:1) as a white solid (52 mg, 67%). mp = 94-96°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 4.46 (t, J = 7.0 Hz, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 2.86 (t, J = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2, 163.6, 159.5, 133.1 (2C), 131.8 (2C), 122.7, 115.7, 114.0 (2C), 113.8 (2C), 84.1, 82.0, 62.8, 55.5, 55.4, 20.3; IR (film): $\tilde{\nu}$ = 2960, 2935, 2906, 2839, 1707, 1603, 1508, 1244, 1165, 1104, 1025, 834,

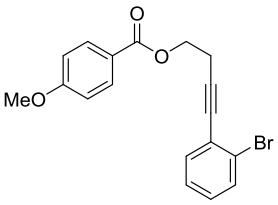


767 cm^{-1}; MS (EI) *m*/*z* (%): 158 (100), 143 (8), 135 (14), 115 (3), 107 (2), 92 (3), 77 (4); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{18}O_4$+Na: 333.1097; found: 333.1097.

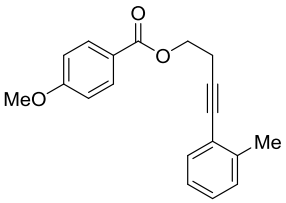
4-(2-Chlorophenyl)but-3-ynyl 4-methoxybenzoate (10j). Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 98.5:1.5) as an orange oil (64 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 9.0 Hz, 2H), 7.45-7.41 (m, 1H), 7.39-7.35 (m, 1H), 7.25-7.14 (m, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.51 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 2.94 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2, 163.6, 136.0, 133.5, 131.9 (2C), 129.3, 129.0, 126.5, 123.4, 122.6, 113.8 (2C), 91.4, 79.0, 62.5, 55.5, 20.5; IR (film): $\tilde{\nu}$ = 3067, 2961, 2935, 2908, 2839, 1709, 1605, 1251, 1166, 1099, 846, 752 cm^{-1}; MS (EI) *m*/*z* (%): 164 (31), 162 (100), 152 (20), 135 (50), 127 (10), 107 (7), 92 (9), 77 (13); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{15}ClO_3$+Na: 337.0602; found: 337.0602.



4-(2-Bromophenyl)but-3-ynyl 4-methoxybenzoate (10k). Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 98.5:1.5) as a colorless oil (76 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.9 Hz, 2H), 7.55 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.23 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.13 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.51 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 2.94 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 163.6, 133.5, 132.4, 131.9 (2C), 129.2, 127.1, 125.7, 125.6, 122.6, 113.8 (2C), 90.9, 80.8, 62.5, 55.6, 20.5; IR (film): $\tilde{\nu}$ = 3066, 2960, 2934, 2839, 1709, 1604, 1250, 1166, 1099, 1025, 846, 752 cm^{-1}; MS (EI) *m*/*z* (%): 208 (98), 206 (100), 195 (6), 193 (6), 152 (36), 135 (90), 127 (27), 107 (12), 92 (19), 77 (24); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{15}BrO_3$+Na: 381.0097; found: 381.0097.



4-o-Tolylbut-3-ynyl 4-methoxybenzoate (10l). Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 98.5:1.5) as a colorless oil (55 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.22-7.17 (m, 2H), 7.13-7,06 (m, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.49 (t, *J* = 6.9 Hz, 2H), 3.86 (s, 3H), 2.92 (t, *J* = 6.9 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 163.6, 140.2, 132.0, 131.8 (2C), 129.4, 128.0, 125.6, 123.3, 122.5, 113.7 (2C), 89.7, 81.0, 62.8, 55.5, 20.8, 20.4; IR (film): $\tilde{\nu}$ = 3063, 2959, 2917, 2840, 1710, 1605, 1510, 1251, 1166, 1099, 1027, 846, 755 cm^{-1}; MS (EI) *m*/*z* (%): 142 (100), 141 (26), 135 (23), 128 (4), 115 (4), 107 (4), 92 (4), 77 (6); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{18}O_3$+Na: 317.1148; found: 317.1148.

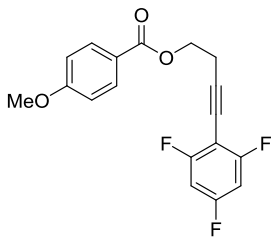


4-(2-(Hydroxymethyl)phenyl)but-3-ynyl 4-methoxybenzoate (10m). Prepared analogously; the compound was obtained by flash chromatography on silica (hexane/AcOEt, 100:0 to 7:3) as a colorless oil (63 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 9.0 Hz, 2H), 7.43-7.38 (m, 2H), 7.30 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.22 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.77 (s, 2H), 4.51 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 2.93 (t, *J* = 6.6 Hz, 2H), 2.10 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.3, 163.7, 142.7, 132.4, 131.9 (2C), 128.5, 127.5, 127.5, 122.4, 121.7, 113.8 (2C), 90.8, 79.8, 64.2, 62.6, 55.6, 20.5; IR (film): $\tilde{\nu}$ = 3436, 3065, 2960, 2840, 1708, 1604, 1510, 1251, 1166, 1101, 1025, 846, 758 cm^{-1}; MS (EI) *m*/*z* (%): 293 (1), 158 (100), 135 (67), 129 (45), 115 (32), 107 (9), 92 (11), 77 (17); HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{18}O_4$+Na: 333.1097; found: 333.1097.

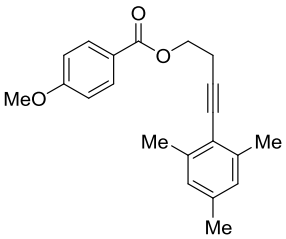
4-(3,5-Difluorophenyl)but-3-ynyl 4-methoxybenzoate (10n). Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 94:1) as a white solid (58 mg, 73%). mp = 78-80°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.9 Hz, 2H), 6.97-6.85 (m, 4H), 6.75 (tt, *J* = 9.0, 2.3 Hz, 1H), 4.47 (t, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.87 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 163.6, 162.8 (dd, *J* = 248, 14 Hz), 131.8 (2C), 126.2 (t, *J* = 11 Hz), 122.4, 114.7 (dd, *J* = 19, 7 Hz, 2C), 113.8 (2C), 104.3 (t, *J* = 25 Hz,), 88.2 (d, *J* = 4 Hz), 80.2, 62.3, 55.5, 20.2; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.0; IR (film): $\tilde{\nu}$ = 3065, 2967, 2914, 2842, 2247, 1704, 1585, 1259, 1101, 989, 843, 767 cm^{-1}; MS (EI) *m*/*z* (%): 316 (1) [M^{+}], 164 (47), 152 (100), 135 (49), 107 (8), 92 (12), 77 (13); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{14}F_2O_3$+Na: 339.0803; found: 339.0802.

4-(3,5-Bis(trifluoromethyl)phenyl)but-3-ynyl 4-methoxybenzoate (10o). Prepared analogously; the compound was obtained by flash chromatography on silica (hexane/AcOEt, 100:0 to 9:1) as a colorless oil (91 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 9.0 Hz, 2H), 7.81 (s, 2H), 7.76 (s, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.50 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 2.91 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 163.8, 131.9 (q, *J* = 34 Hz, 2C), 131.9 (2C), 131.7 (q, *J* = 4 Hz, 2C), 125.9, 123.1 (q, *J* = 274 Hz, 2C), 122.4, 121.5 (sept, *J* = 4 Hz), 113.9 (2C), 90.0, 79.7, 62.1, 55.6, 20.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –63.2; IR (film): $\tilde{\nu}$ = 3083, 2963, 2843, 2237, 1714, 1606, 1384, 1512, 1275, 1166, 1128, 1029, 896, 846, 768 cm^{-1}; MS (EI) *m*/*z* (%): 416 (5) [M^{+}], 397 (8), 264 (15), 245 (6), 152 (100), 135 (77), 92 (8), 77 (11); HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{14}F_6O_3$+Na: 439.0739; found: 439.0738.

4-(2,4,6-Trifluorophenyl)but-3-ynyl 4-methoxybenzoate (10p). Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to

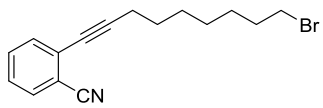


94:1) as a white solid (69 mg, 83%). mp = 89-91°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.66 (dd, *J* = 8.7, 7.1 Hz, 2H), 4.49 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 2.94 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.2, 164.9 (m), 163.6, 163.3 (m), 162.4 (m), 160.8 (m), 131.9 (2C), 122.5, 113.8 (2C), 100.5 (m), 99.1(m), 96.1 (m), 68.1, 62.2, 55.5, 20.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –105.1 (d, *J* = 7 Hz, 2F), –105.9 (t, *J* = 7 Hz, 1F); IR (film): $\tilde{\nu}$ = 3101, 3078, 2961, 2928, 2846, 1703, 1603, 1442, 1258, 1101, 845, 767 cm^{-1}; MS (EI) *m*/*z* (%): 182 (100), 152 (72), 135 (67), 107 (13), 92 (16), 77 (27); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{13}F_3O_3$+Na: 357.0709; found: 357.0708.

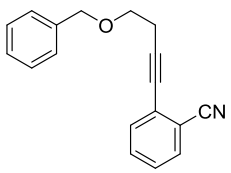


(4-Mesityl)but-3-ynyl 4-methoxybenzoate (10q). Prepared analogously; the compound was obtained by flash chromatography on basic alumina (toluene/AcOEt, 100:0 to 98.5:1.5) as a pale orange solid (50 mg, 62%). mp = 67-69°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.83 (s, 2H), 4.50 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3, 163.6, 140.2 (2C), 137.3, 131.8 (2C), 127.6 (2C), 122.7, 120.3, 113.7 (2C), 93.3, 79.8, 63.1, 55.5, 21.4, 21.1 (2C), 20.6; IR (film): $\tilde{\nu}$ = 3000, 2968, 2942, 2913, 2841, 1706, 1605, 1510, 1254, 1164, 1104, 1027, 846, 765 cm^{-1}; MS (EI) *m*/*z* (%): 170 (10), 155 (16), 135 (12), 107 (2), 92 (2), 77 (3); HRMS (ESI): *m*/*z*: calcd. for $C_{21}H_{22}O_3$+Na: 345.1461; found: 345.1461.

2-(9-Bromonon-1-yn-1-yl)benzonitrile (10r). Prepared analogously; the compound was obtained by flash chromatography on neutral alumina (hexane/toluene, 100:0 to 4:1, then hexane/AcOEt, 9:1) as a colorless oil (434 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63-7.59 (m, 1H), 7.53-7.47 (m, 2H), 7.34 (m, 1H), 3.41 (t, *J* = 7.0 Hz, 2H), 2.49 (t, *J* = 7.00 Hz, 2H), 1.92-1.83 (m, 2H), 1.70-1.61 (m, 2H), 1.56-1.42 (m, 4H), 1.42-1.34 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.6, 132.4, 132.3, 128.1, 127.7, 117.9, 115.4, 97.8, 77.4, 34.1, 32.8, 28.7, 28.3, 28.3, 28.1, 19.6; IR (film): $\tilde{\nu}$ = 2932, 2857, 2229, 1593, 1481, 1444, 1249, 760, 561, 510 cm^{-1}; MS (EI) *m*/*z* (%): 305 (6) [M^{+}], 303 (7) [M^{+}], 182 (73), 168 (100), 155 (35), 140 (45), 127 (28), 115 (28), 95 (4), 81 (17), 67 (8), 55 (23), 41 (7); HRMS (ESI): *m*/*z*: calcd. for $C_{16}H_{18}BrN$+Na: 326.0515; found: 326.0516.

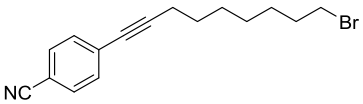


2-(4-(Benzyloxy)but-1-ynyl)benzonitrile (10s). Prepared analogously; the compound was obtained by flash chromatography on silica (15-40 µm) (toluene/AcOEt, 100:0 to 94:1) as a colorless oil (61 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (td, *J* = 7.8, 1.0 Hz, 1H), 7.52-7.49 (m, 2H), 7.41-7.26 (m, 6H), 4.61 (s, 2H), 3.75 (t, *J* = 6.9 Hz, 2H), 2.82 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 132.6, 132.5, 132.3, 128.5 (2C), 127.9, 127.8 (2C),

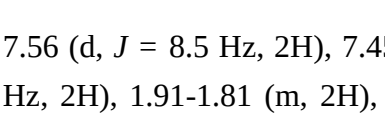


127.8, 127.7, 117.8, 115.5, 94.5, 78.2, 73.2, 68.2, 21.2; IR (film): $\tilde{\nu}$ = 3065, 3031, 2931, 2863, 2229, 1482, 1097, 761, 735, 685 cm^{-1}; MS (EI) *m*/*z* (%): 261 (4) [M^+], 230 (41), 205 (6), 156 (9), 140 (8), 127 (12), 105 (13), 91 (100); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{15}NO$+Na: 284. 1046; found: 284.1046.

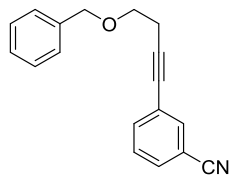
4-(9-Bromo-non-1-yn-1-yl)benzonitrile (10t). Prepared analogously; the compound was obtained by flash chromatography on neutral alumina (hexane/toluene, 100:0 to 4:1, then hexane/AcOEt, 9:1) as a colorless oil (68 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.91-1.81 (m, 2H), 1.66-1.56 (m, 2H), 1.50-1.41 (m, 4H), 1.40-1.32 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.2 (2C), 132.0 (2C), 129.2, 118.8, 110.9, 95.5, 79.6, 34.1, 32.8, 28.8, 28.4, 28.3, 28.1, 19.6; IR (film): $\tilde{\nu}$ = 2932, 2856, 2226, 1604, 1500, 837, 554 cm^{-1}; MS (EI) *m*/*z* (%): 305 (17) [M^+], 303 (19) [M^+], 182 (64), 168 (100), 154 (53), 140 (79), 127 (28), 116 (33), 95 (11), 81 (34), 67 (10), 55 (28), 41 (31); HRMS (ESI): *m*/*z*: calcd. for $C_{16}H_{18}BrN$+Na: 326.0515; found: 326.0515.

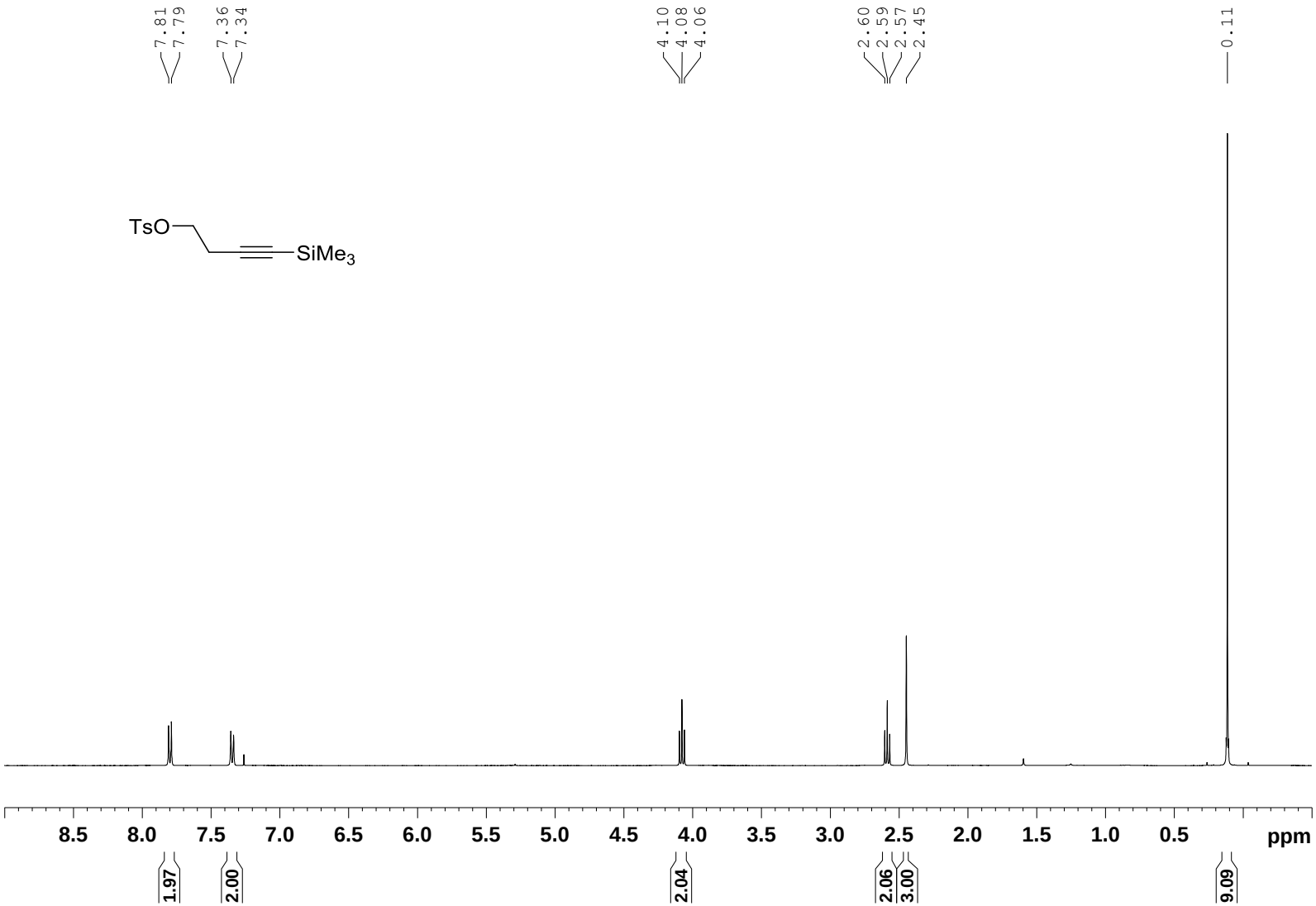


4-(7-(Dodecylthio)hept-1-yn-1-yl)benzonitrile (10u). Prepared analogously; the compound was obtained by flash chromatography on neutral alumina (hexane/toluene, 100:0 to 4:1, then hexane/AcOEt, 9:1) as a white solid (92 mg, 93%). mp = 45-47°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 2.55-2.47 (m, 4H), 2.43 (t, *J* = 6.9 Hz, 2H), 1.68-1.51 (m, 8H), 1.40-1.31 (m, 2H), 1.30-1.21 (m, 16H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.2 (2C), 130.0 (2C), 129.1, 118.8, 110.9, 95.4, 79.7, 32.3, 32.1, 32.0, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 29.3, 29.1, 28.3, 28.2, 22.8, 19.5, 14.3; IR (film): $\tilde{\nu}$ = 2955, 2916, 2846, 2225, 1605, 1468, 837, 719, 553 cm^{-1}; MS (EI) *m*/*z* (%): 397 (4) [M^+], 281 (4), 229 (100), 195 (19), 180 (14), 166 (11), 154 (13), 140 (12), 116 (11), 87 (11), 69 (15), 55 (30), 43 (35); HRMS (ESI): *m*/*z*: calcd. for $C_{26}H_{39}NS$+Na: 420.2695; found: 420.2697.



3-(4-(Benzyloxy)but-1-ynyl)benzonitrile (10v). Prepared analogously; the compound was obtained by flash chromatography on silica (15-40 µm) (hexane/AcOEt, 100:0 to 9:1) as a colorless oil (58 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (t, *J* = 1.4 Hz, 1H), 7.62-7.53 (m, 2H), 7.43-7.27 (m, 6H), 4.60 (s, 2H), 3.68 (t, *J* = 6.9 Hz, 2H), 2.73 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.1, 135.8, 135.1, 131.1, 129.2, 128.6 (2C), 127.9, 127.8 (2C), 125.4, 118.3, 112.8, 90.1, 79.5, 73.2, 68.2, 21.0; IR (film): $\tilde{\nu}$ = 3065, 3031, 2929, 2862, 2231, 1478, 1096, 797, 682 cm^{-1}; MS (EI) *m*/*z* (%): 261 (8) [M^+], 233 (15), 232 (14), 154 (4), 140 (6), 127 (9), 105 (12), 91 (100); HRMS (ESI): *m*/*z*: calcd. for $C_{18}H_{15}NO$+Na: 284.1046; found: 284.1046.

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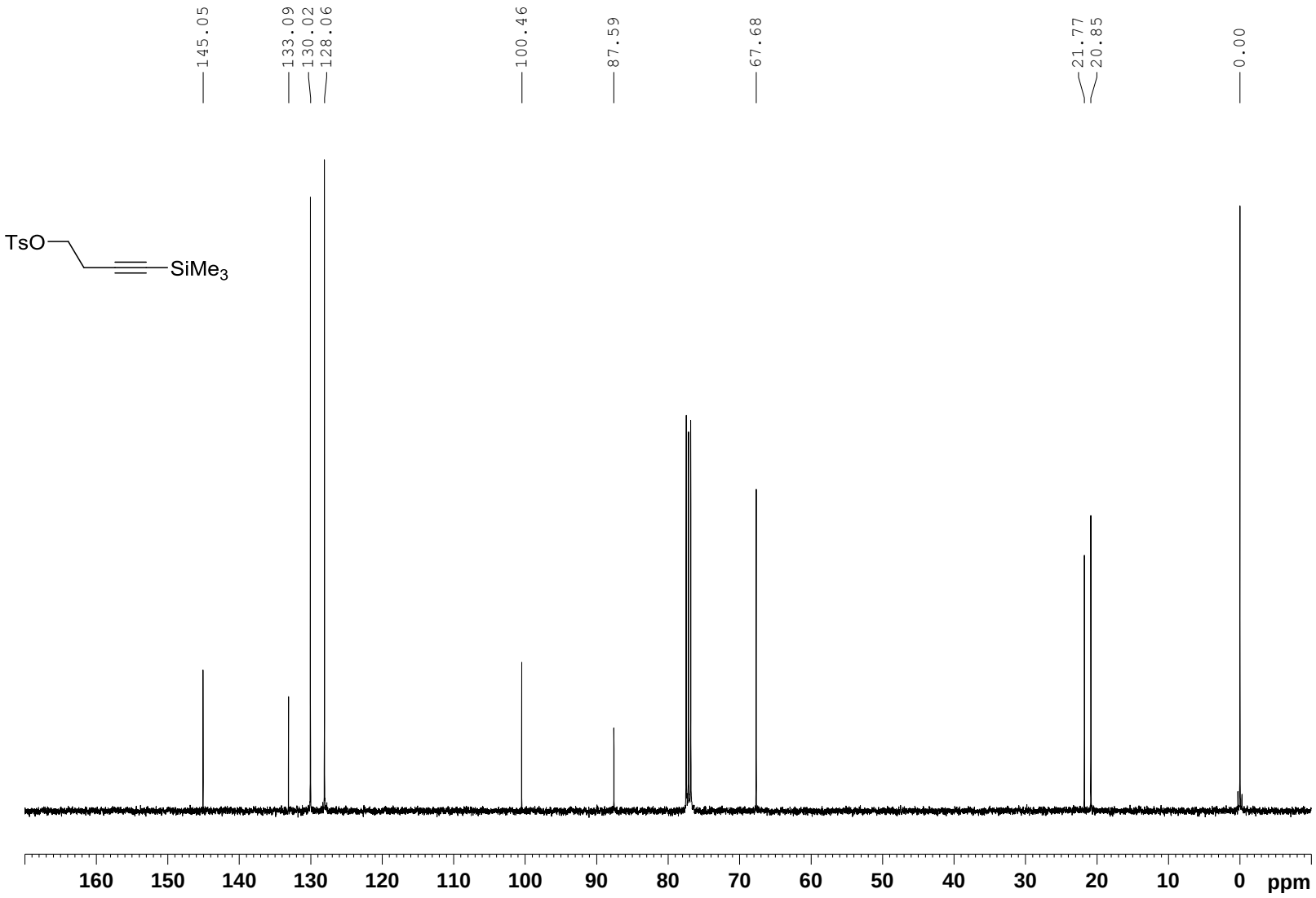
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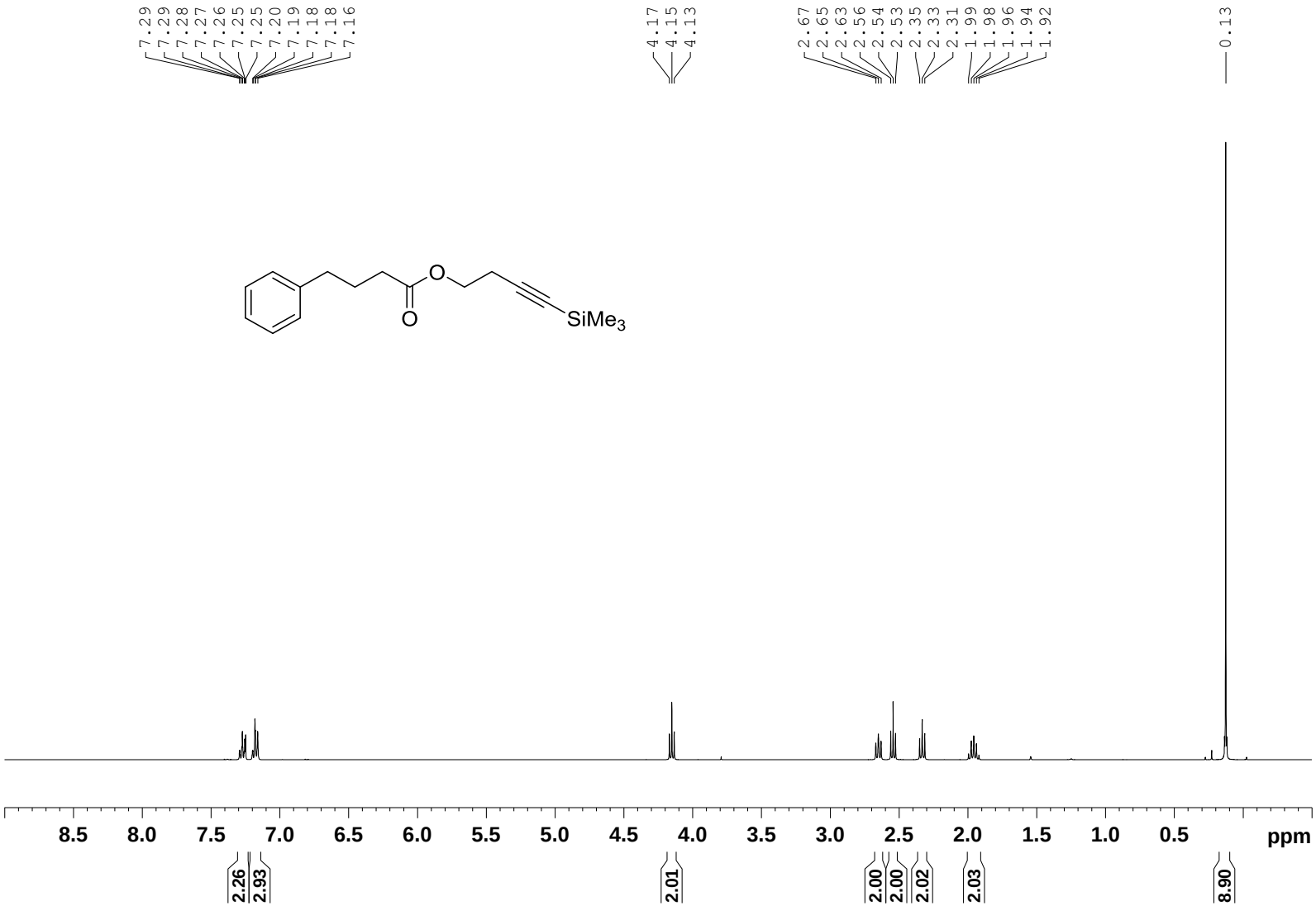
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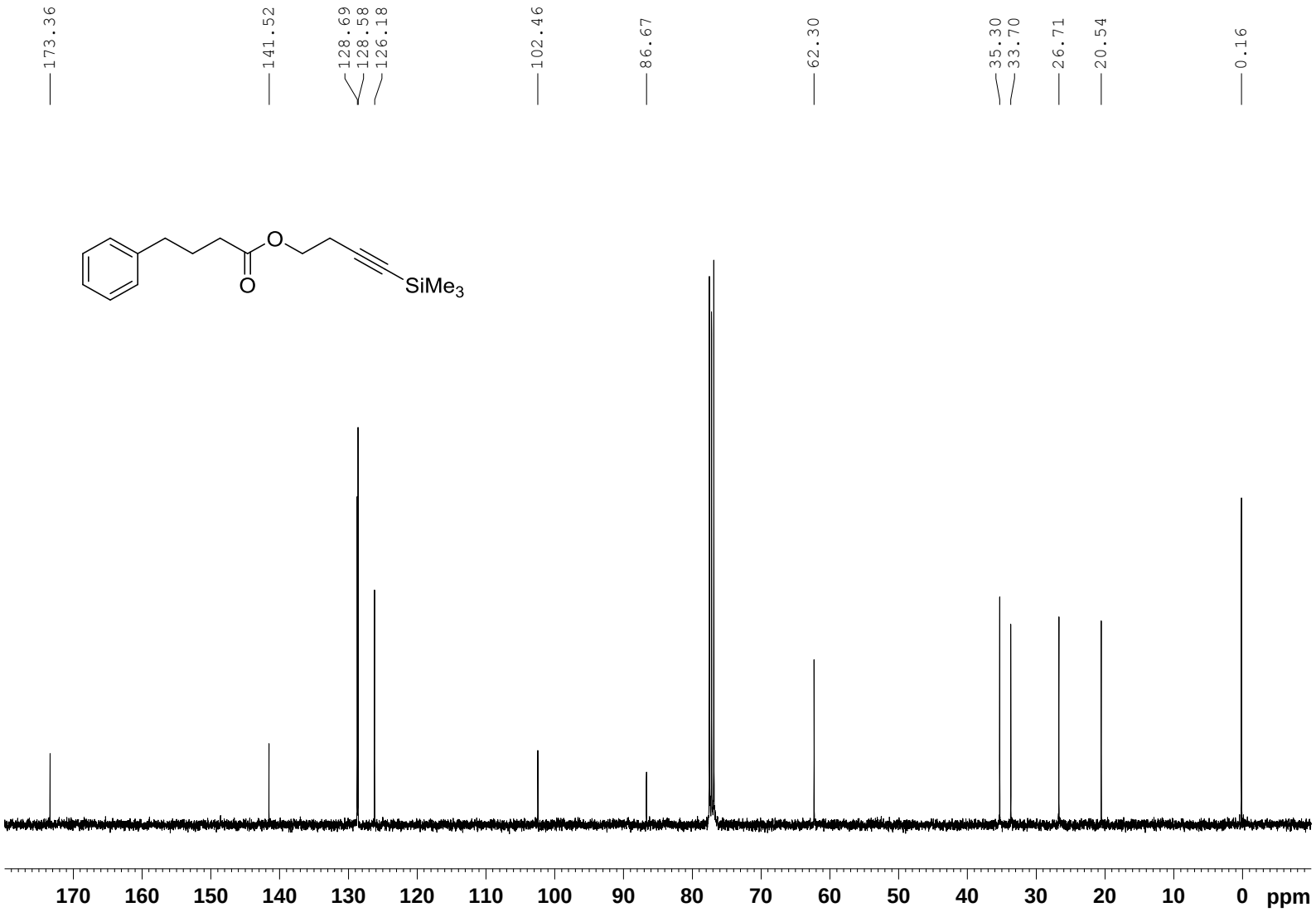
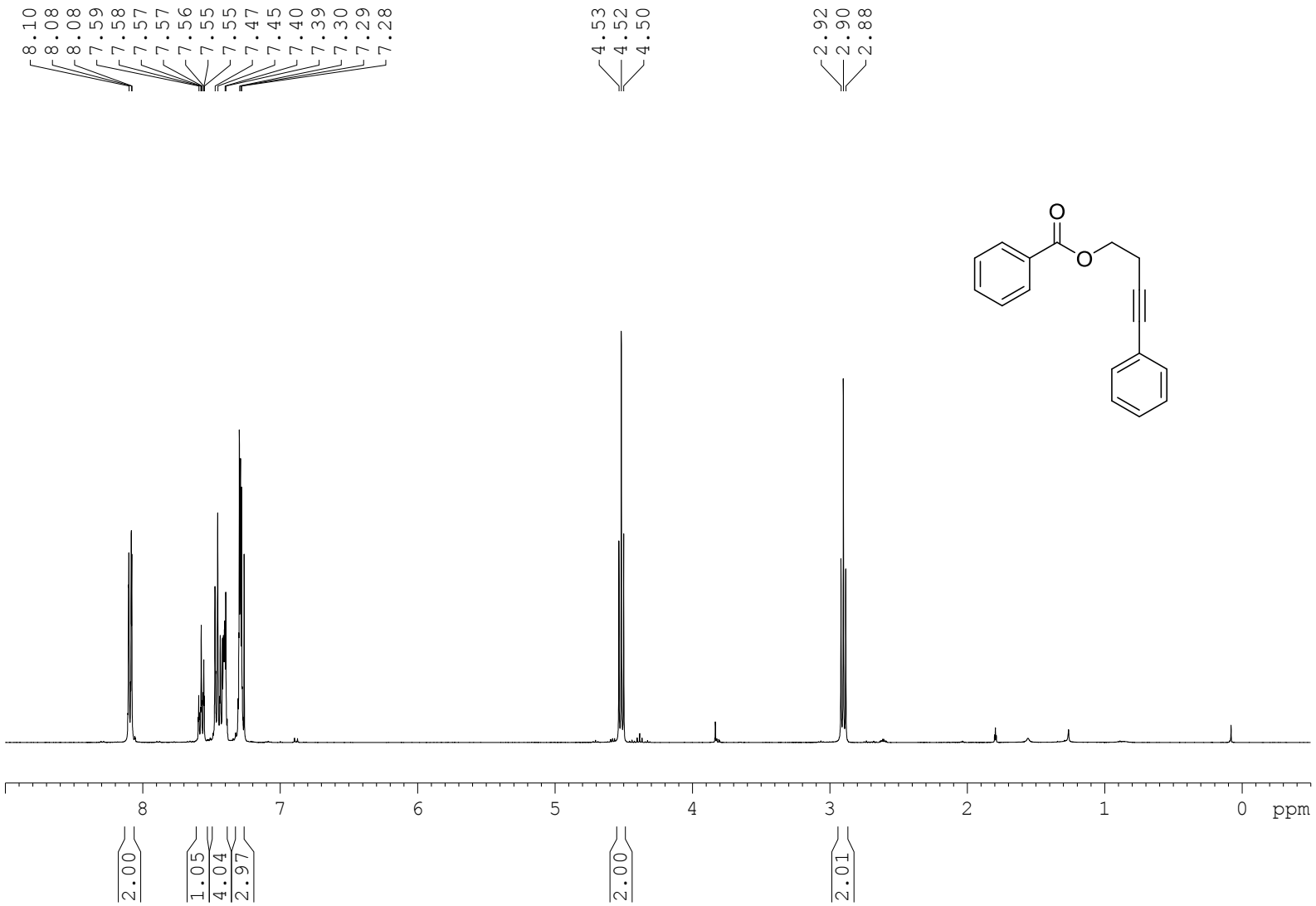
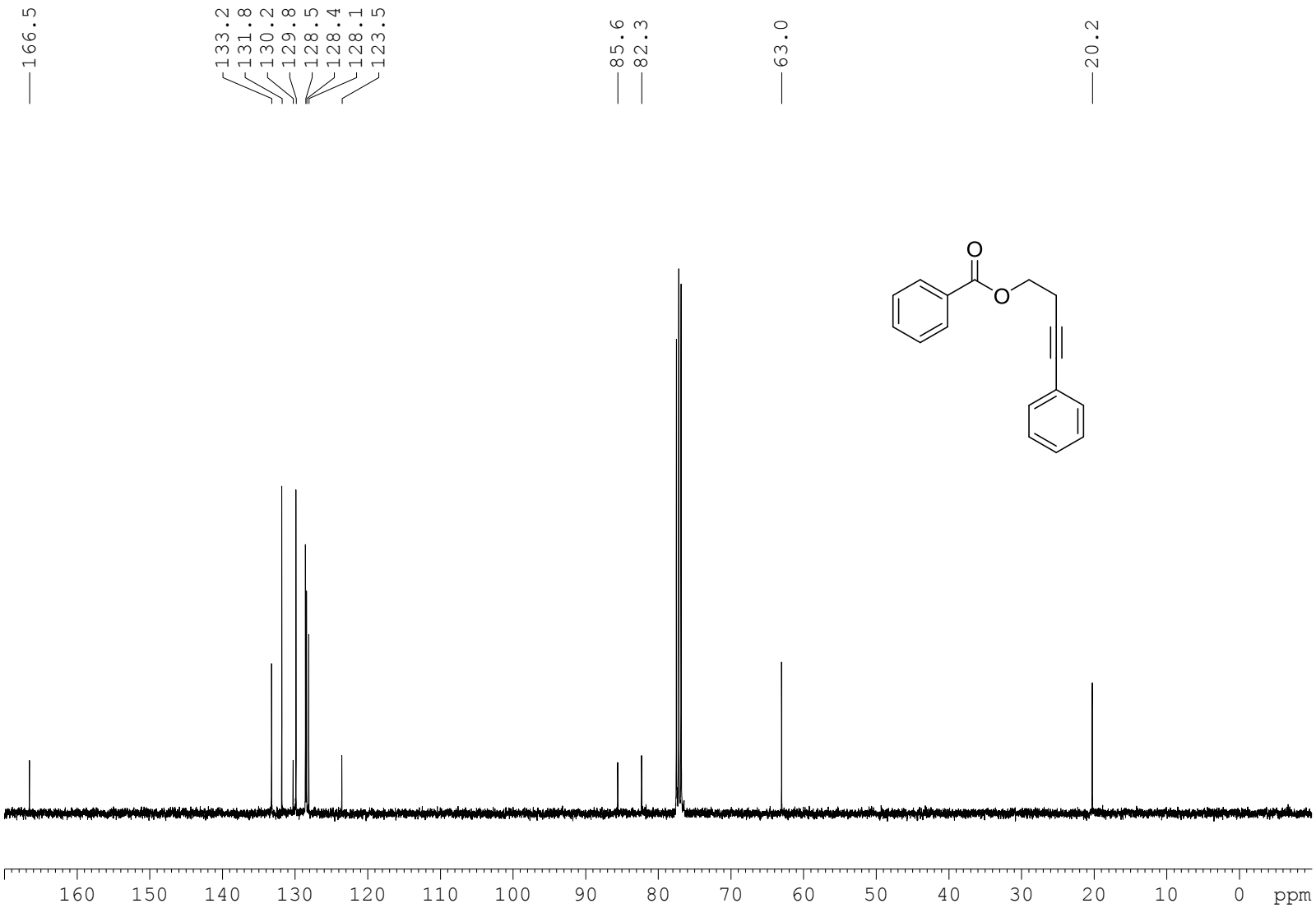
2.0
1.5
1.0
0.5
ppm
2.26
2.93
2.01
2.00
2.00
2.02
2.03
8.90


173.36
141.52
128.69
128.58
126.18
102.46
86.67
62.30
35.30
33.70
26.71
20.54
0.16
O
O
SiMe3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

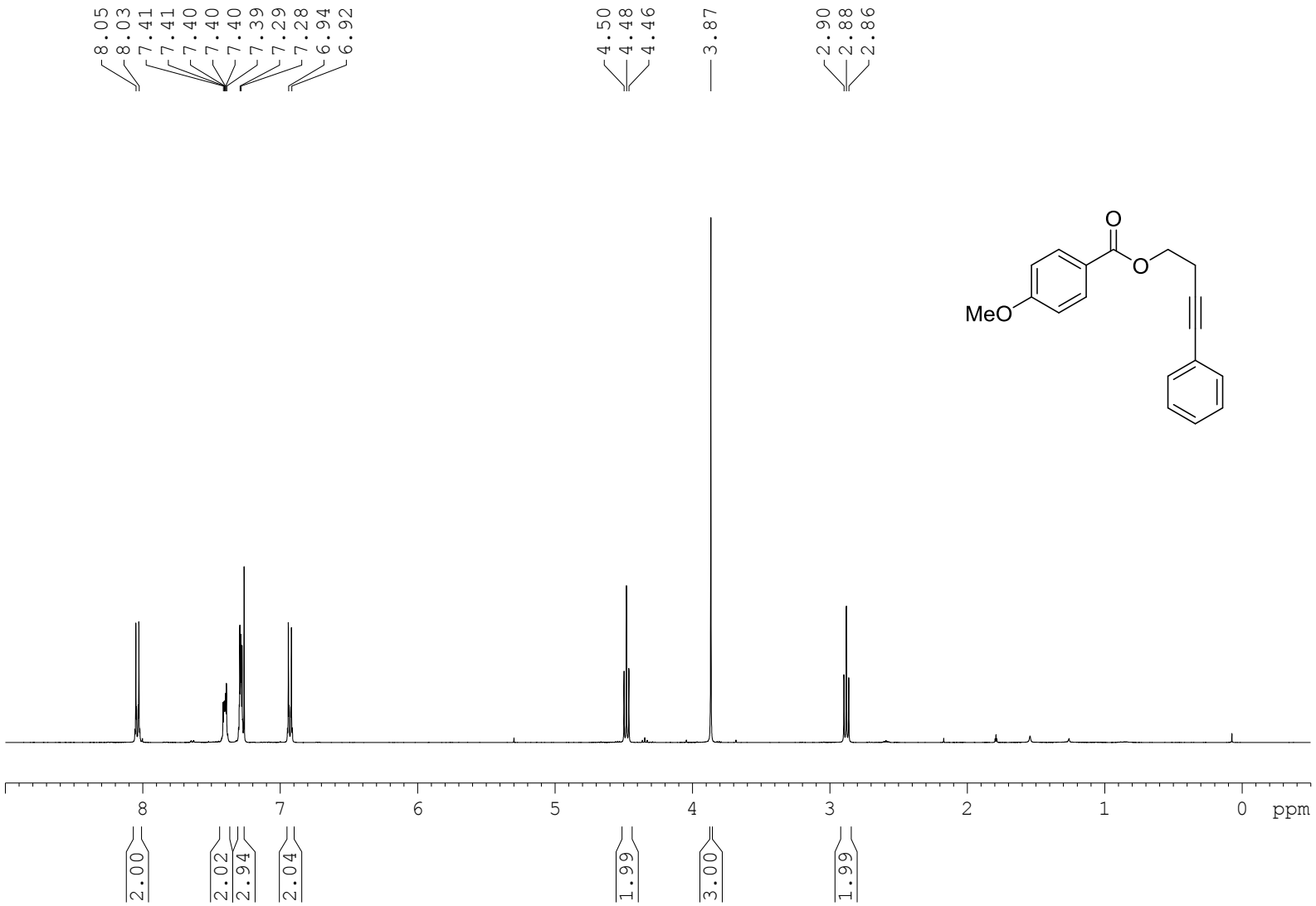
^{1}H NMR (400 MHz, $CDCl_3$) Compound 9a



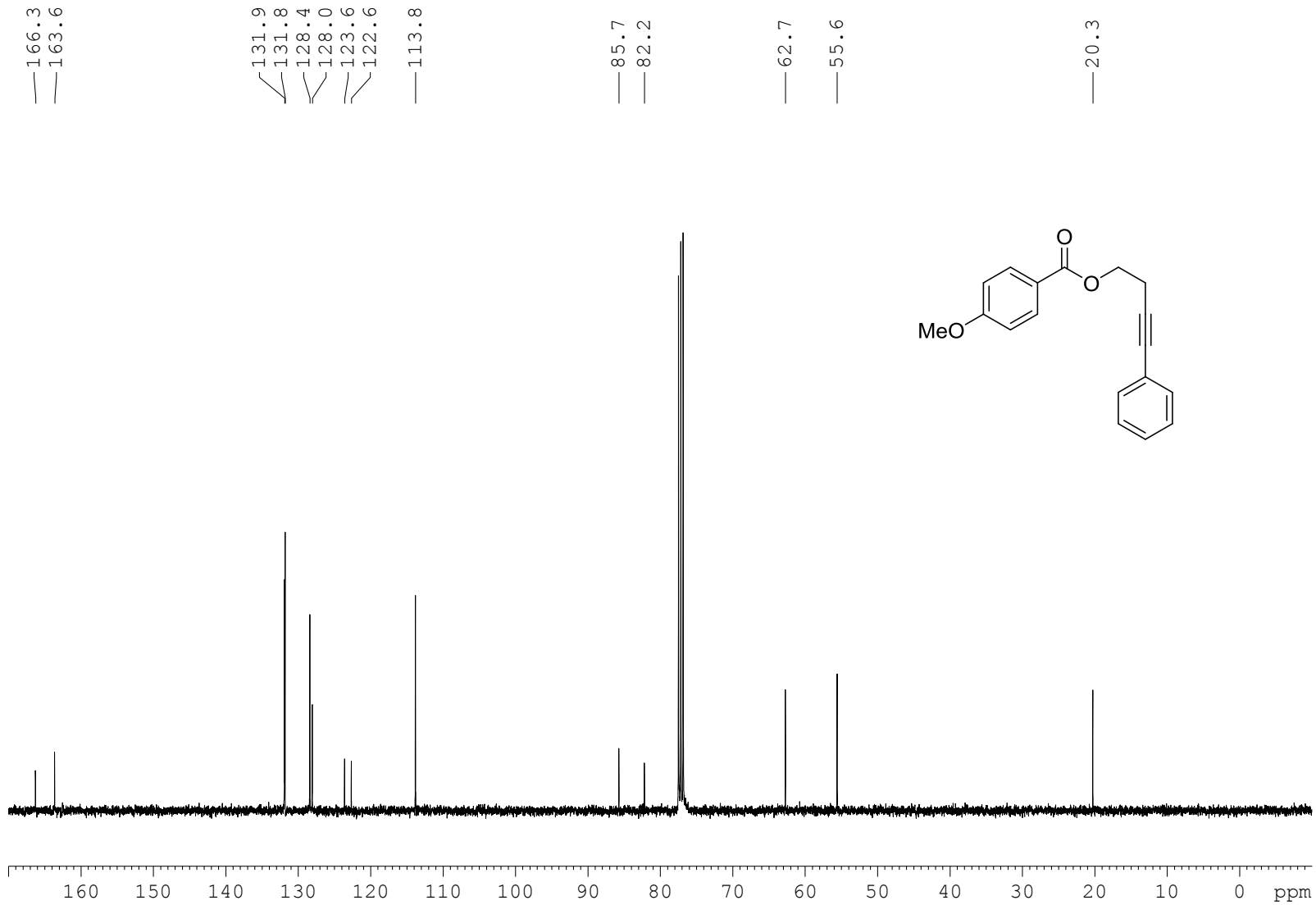
^{13}C NMR (101 MHz, $CDCl_3$) Compound 9a



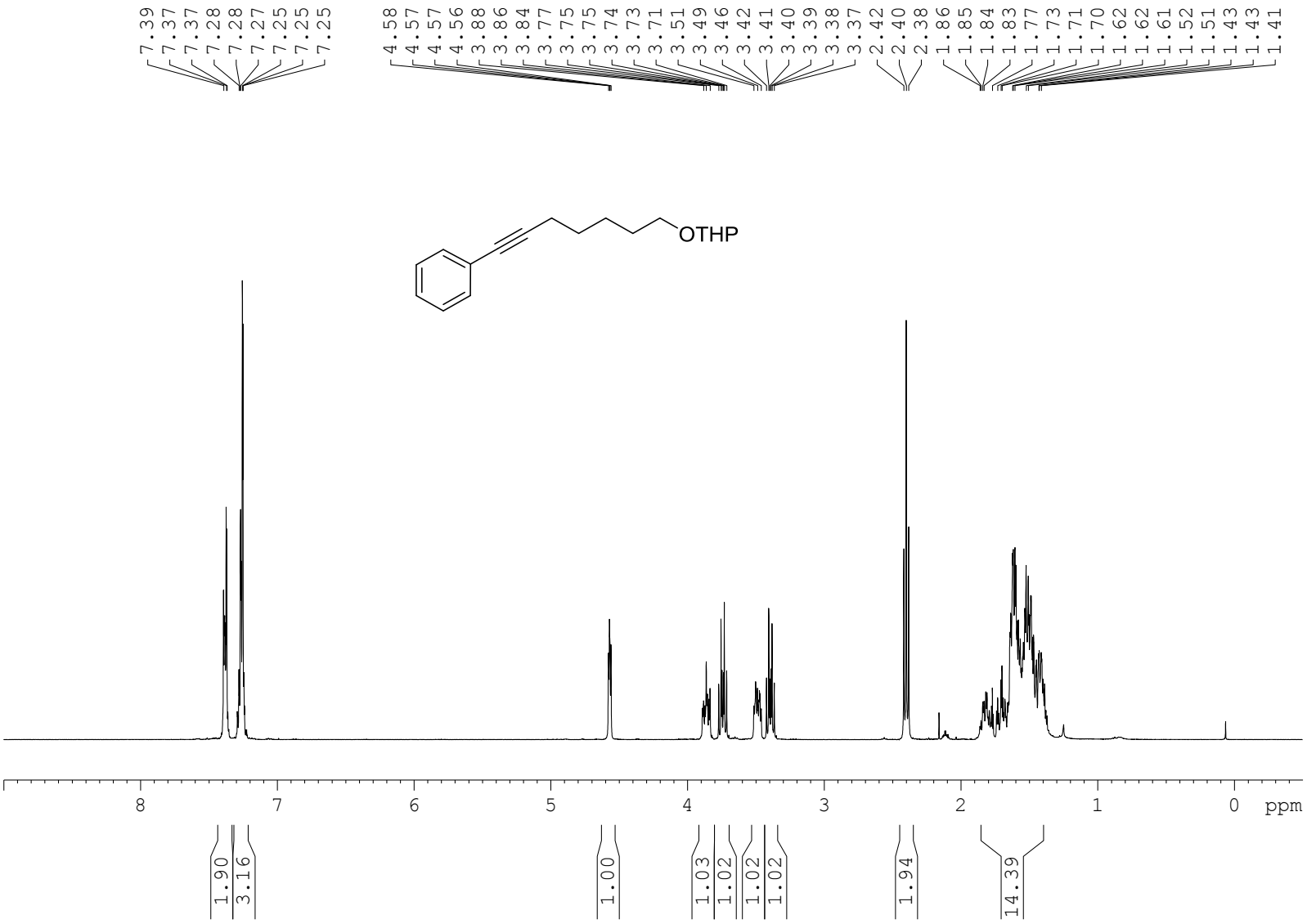
^{1}H NMR (400 MHz, $CDCl_3$) Compound 9b



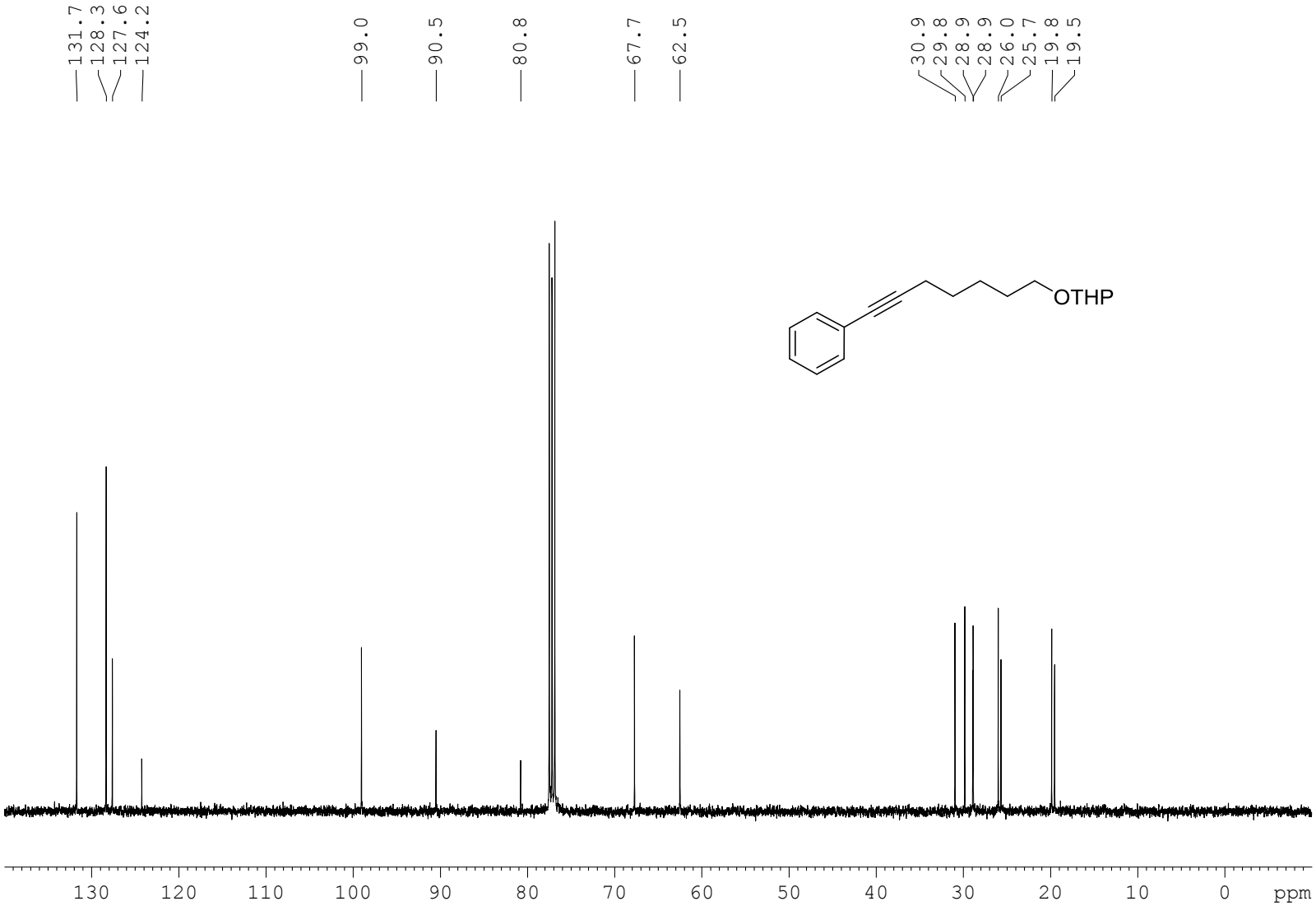
^{13}C NMR (101 MHz, $CDCl_3$) Compound 9b



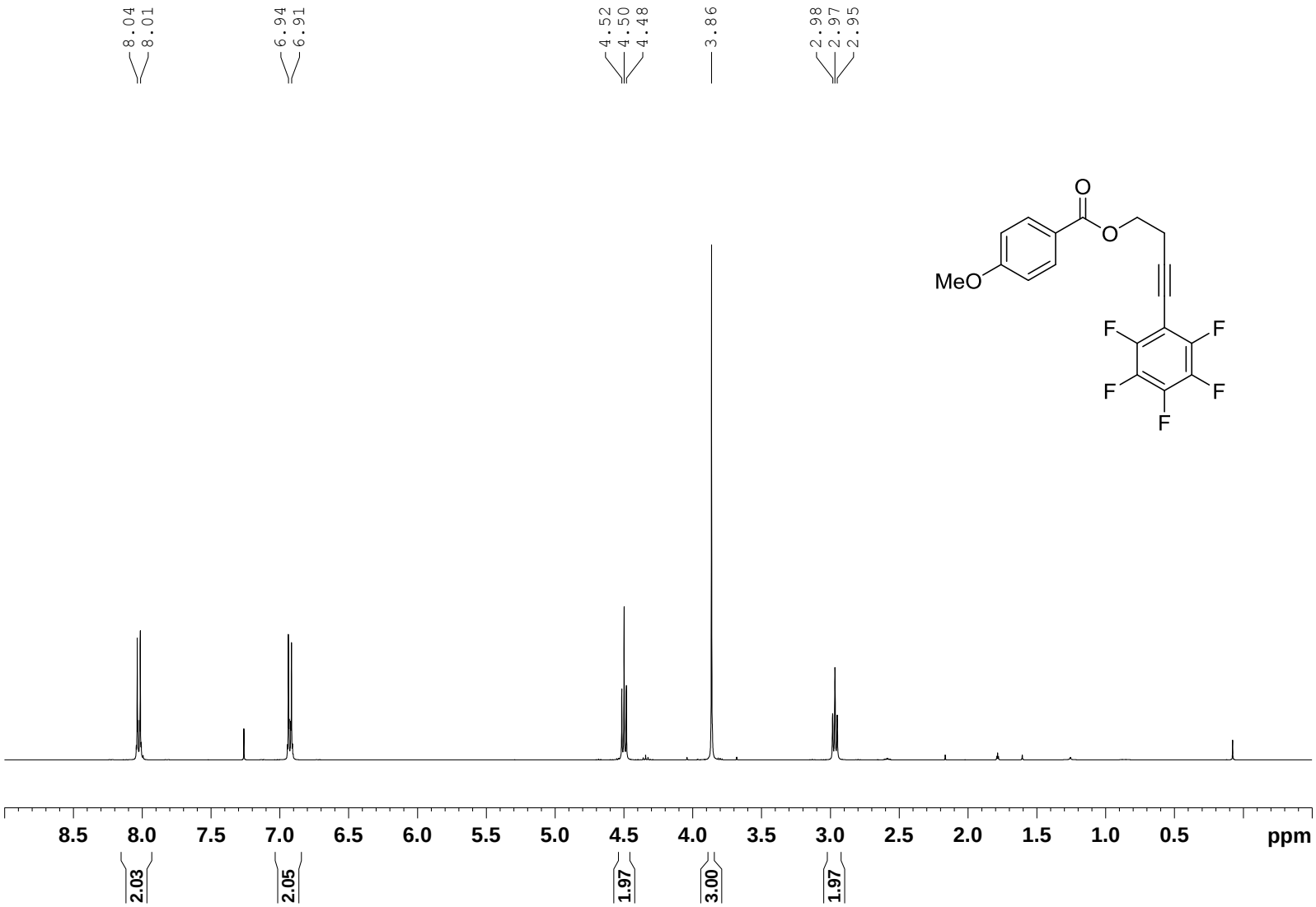
^{1}H NMR (400 MHz, $CDCl_3$) Compound 9c



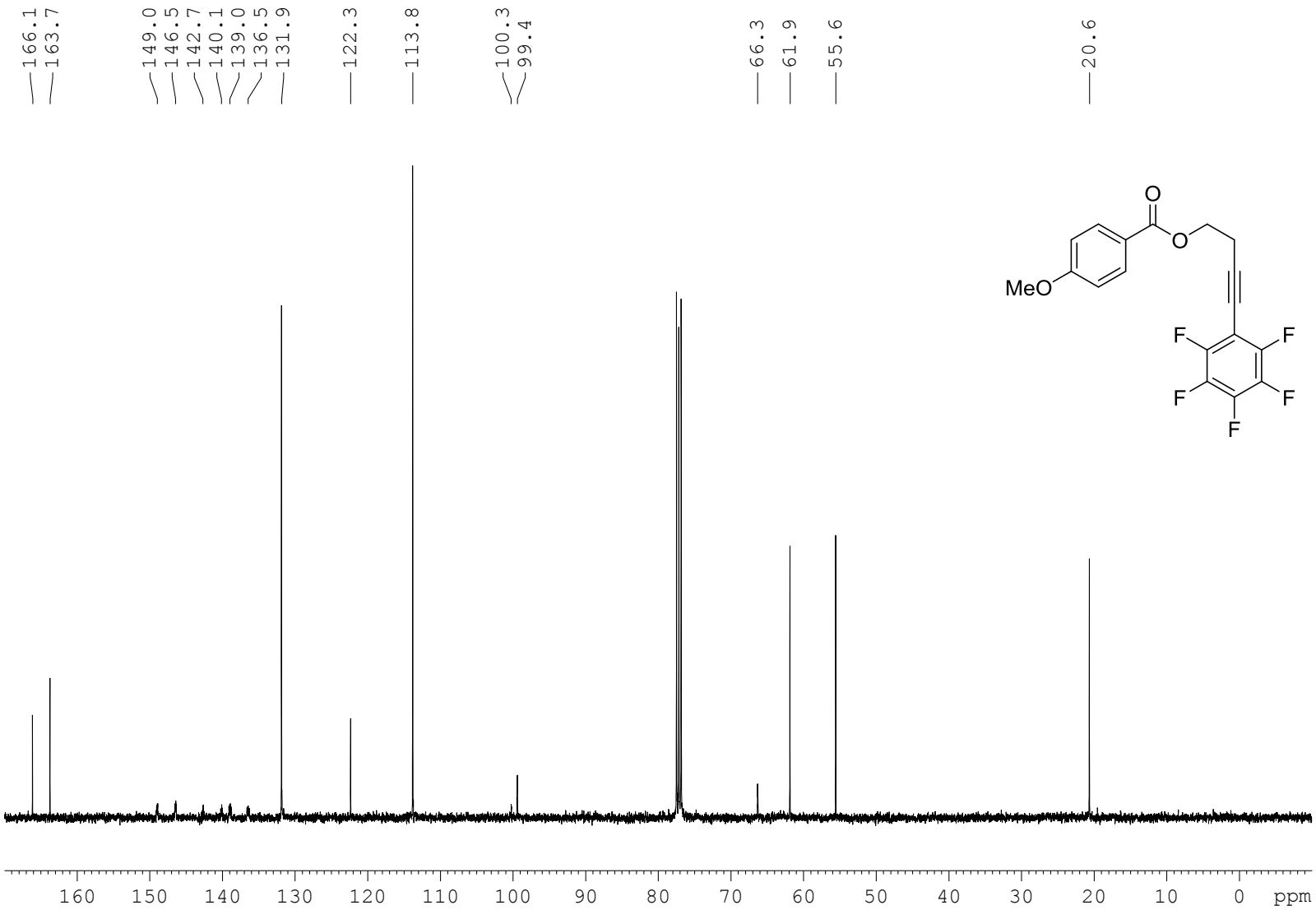
^{13}C NMR (101 MHz, $CDCl_3$) Compound 9c



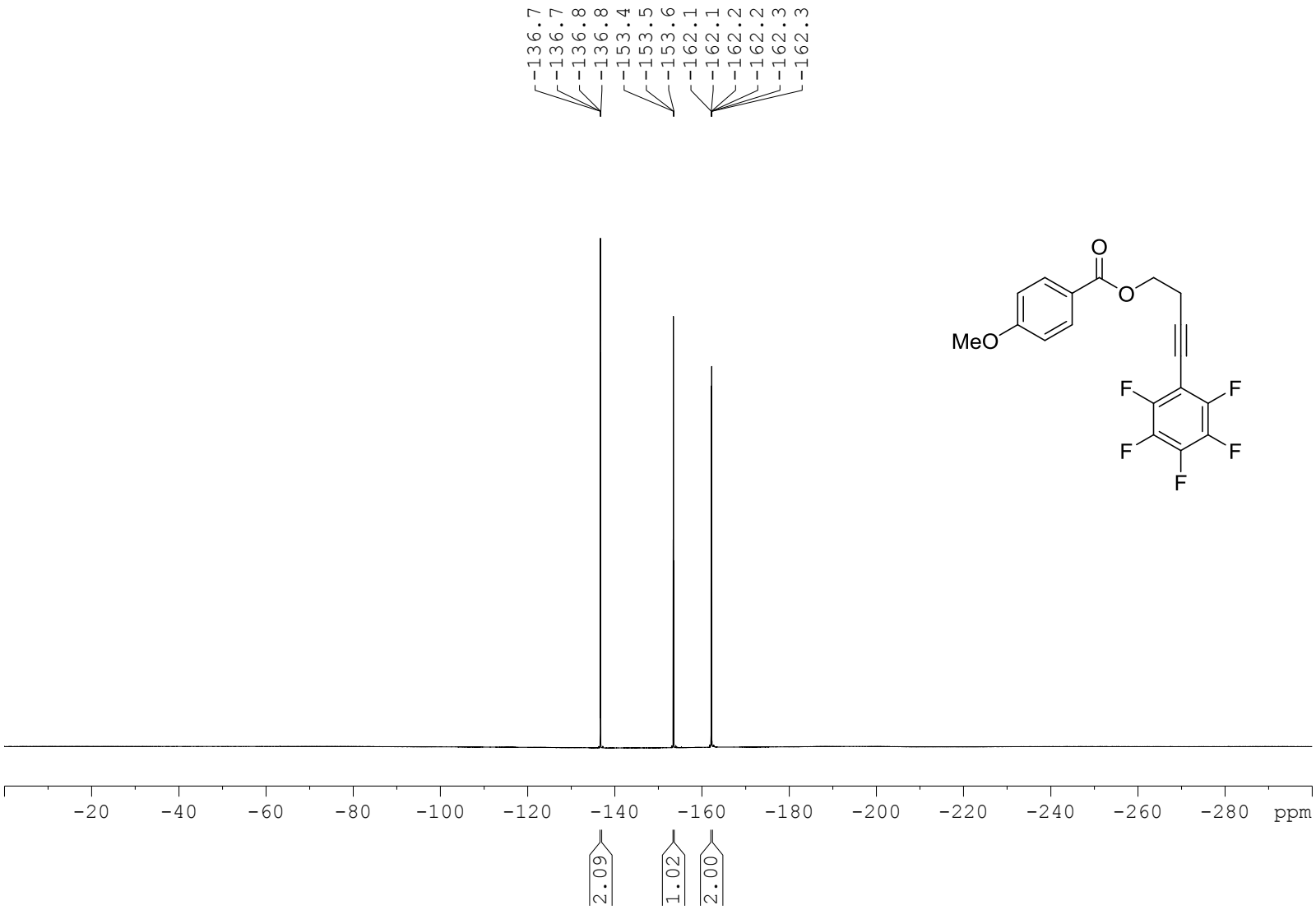
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10a



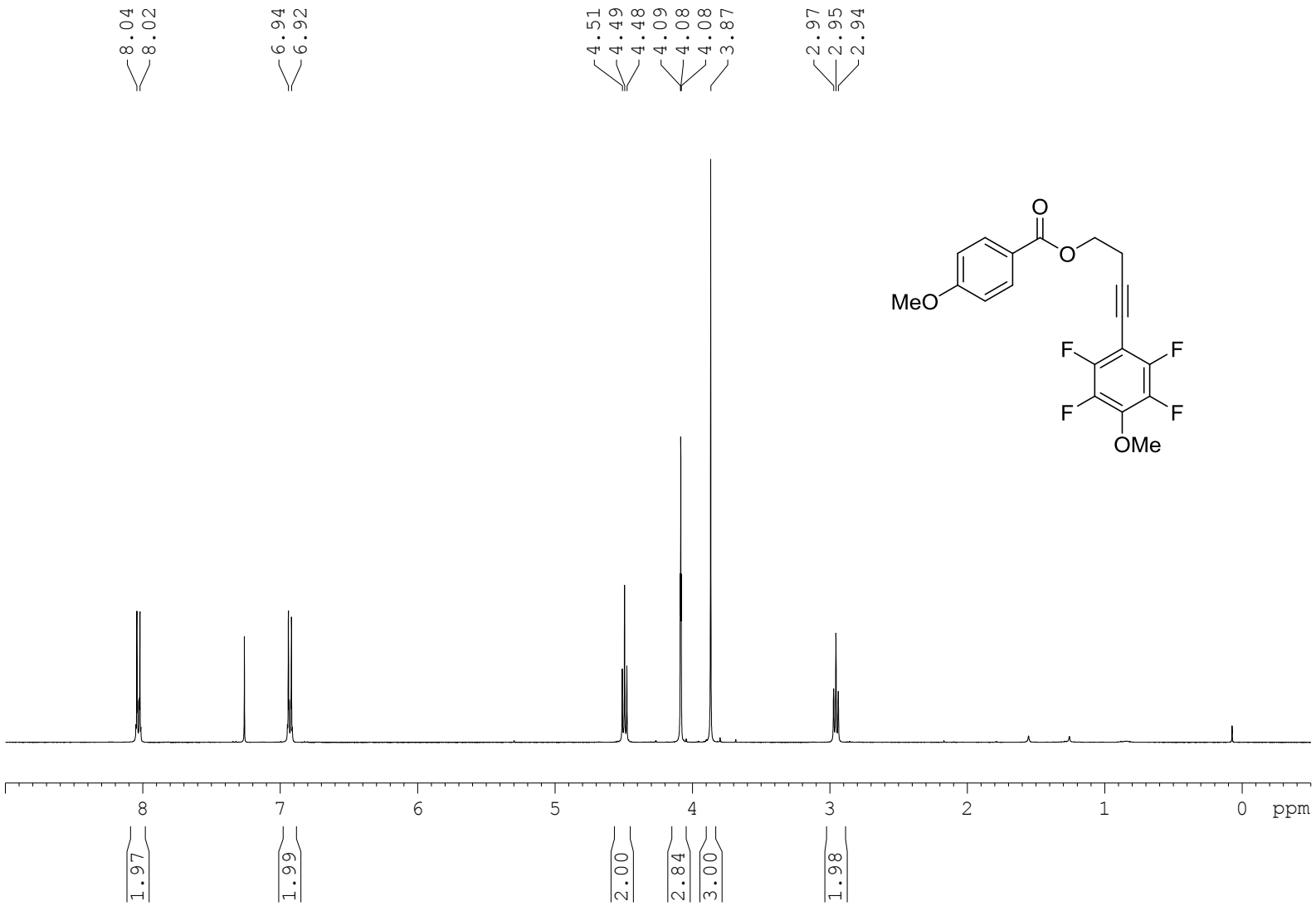
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10a



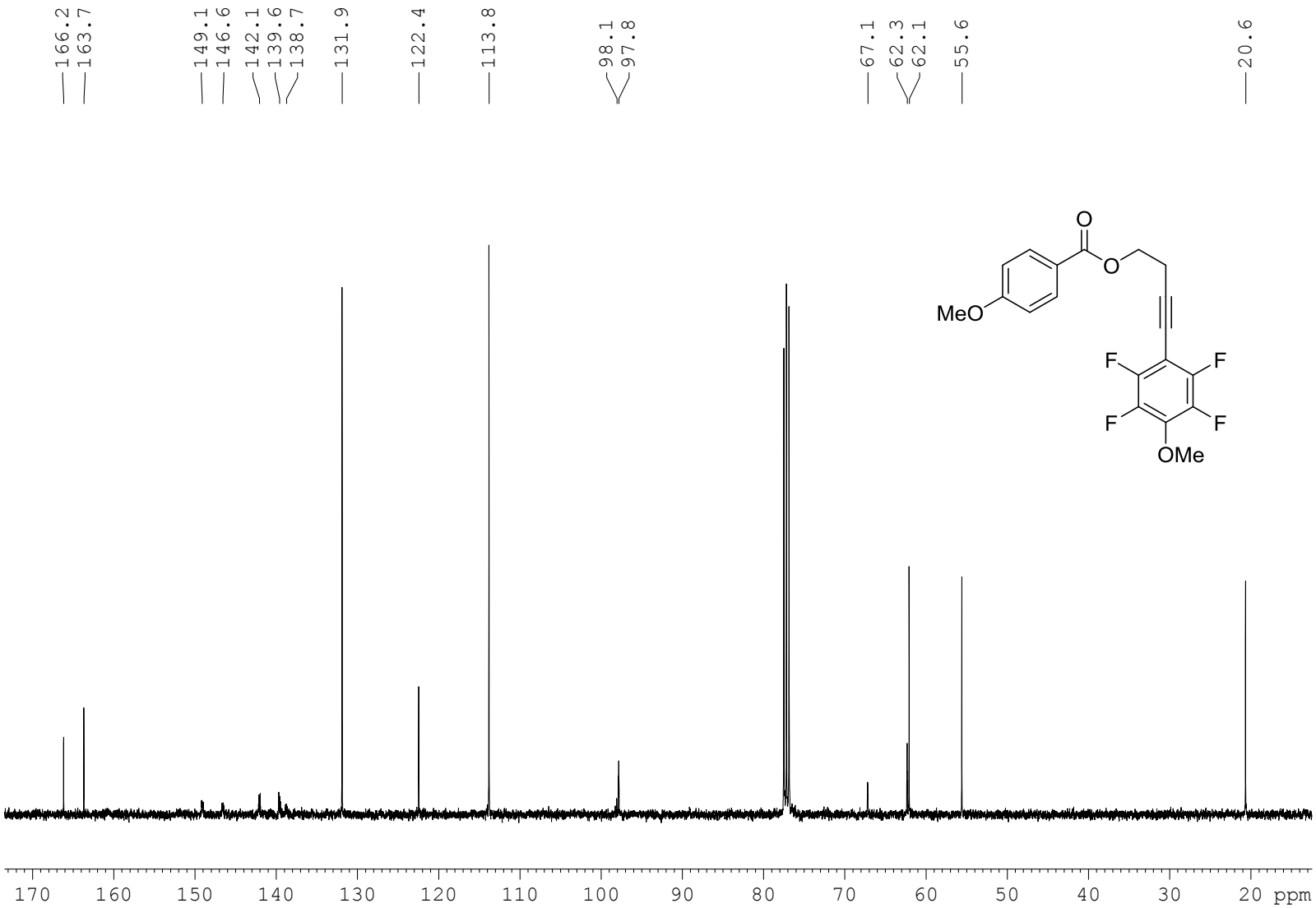
^{19}F NMR (282 MHz, $CDCl_3$) Compound 10a



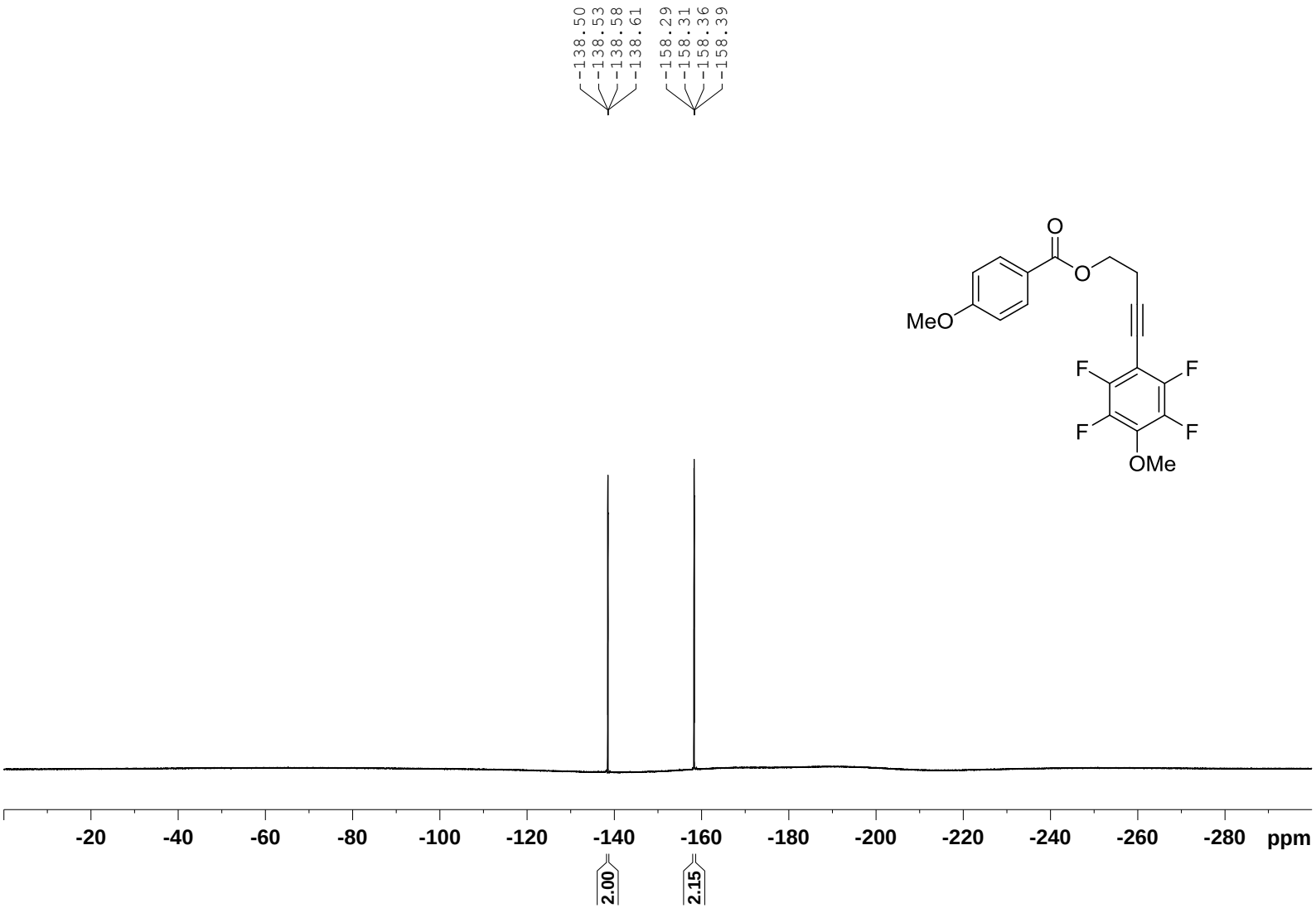
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10b



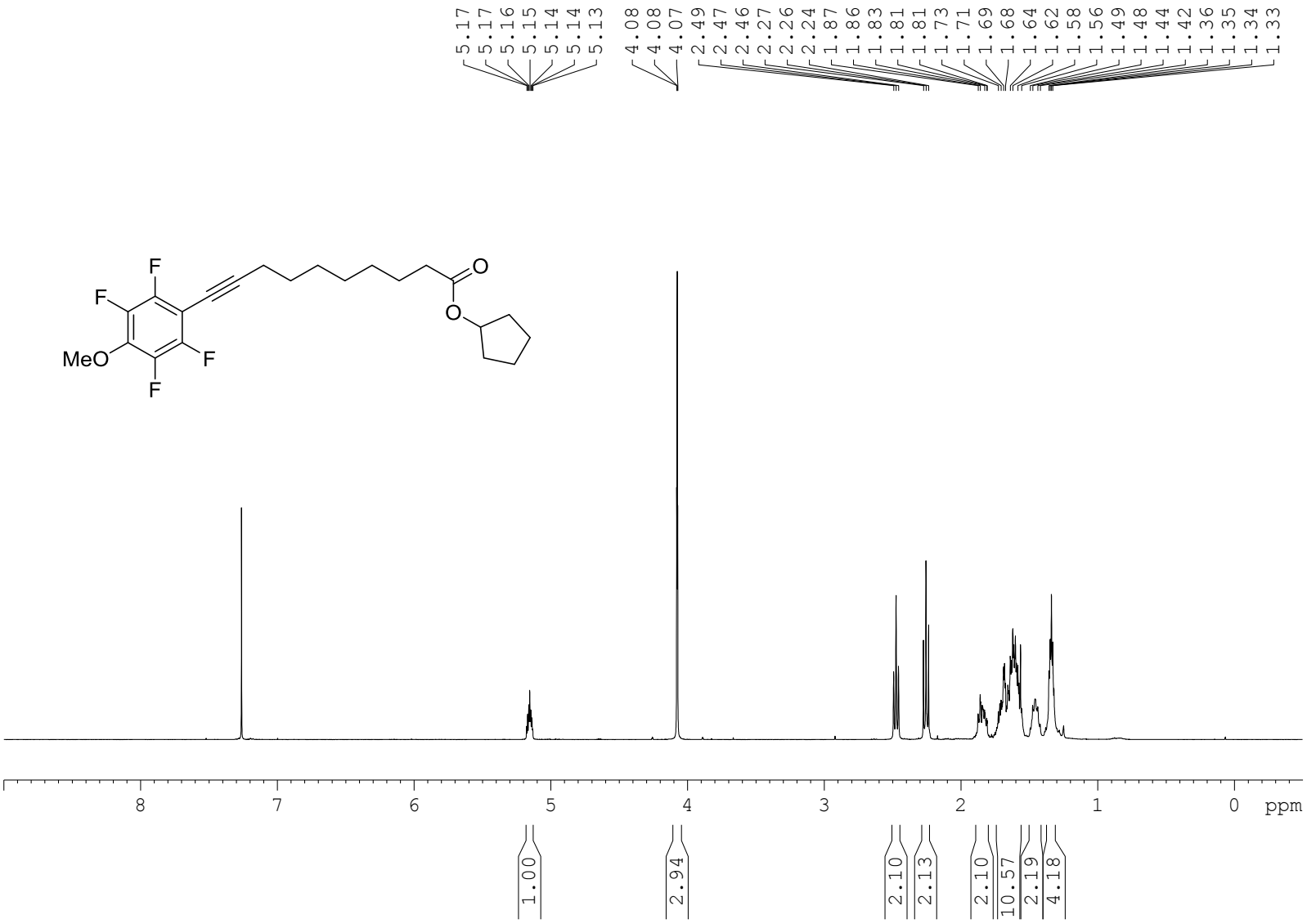
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10b



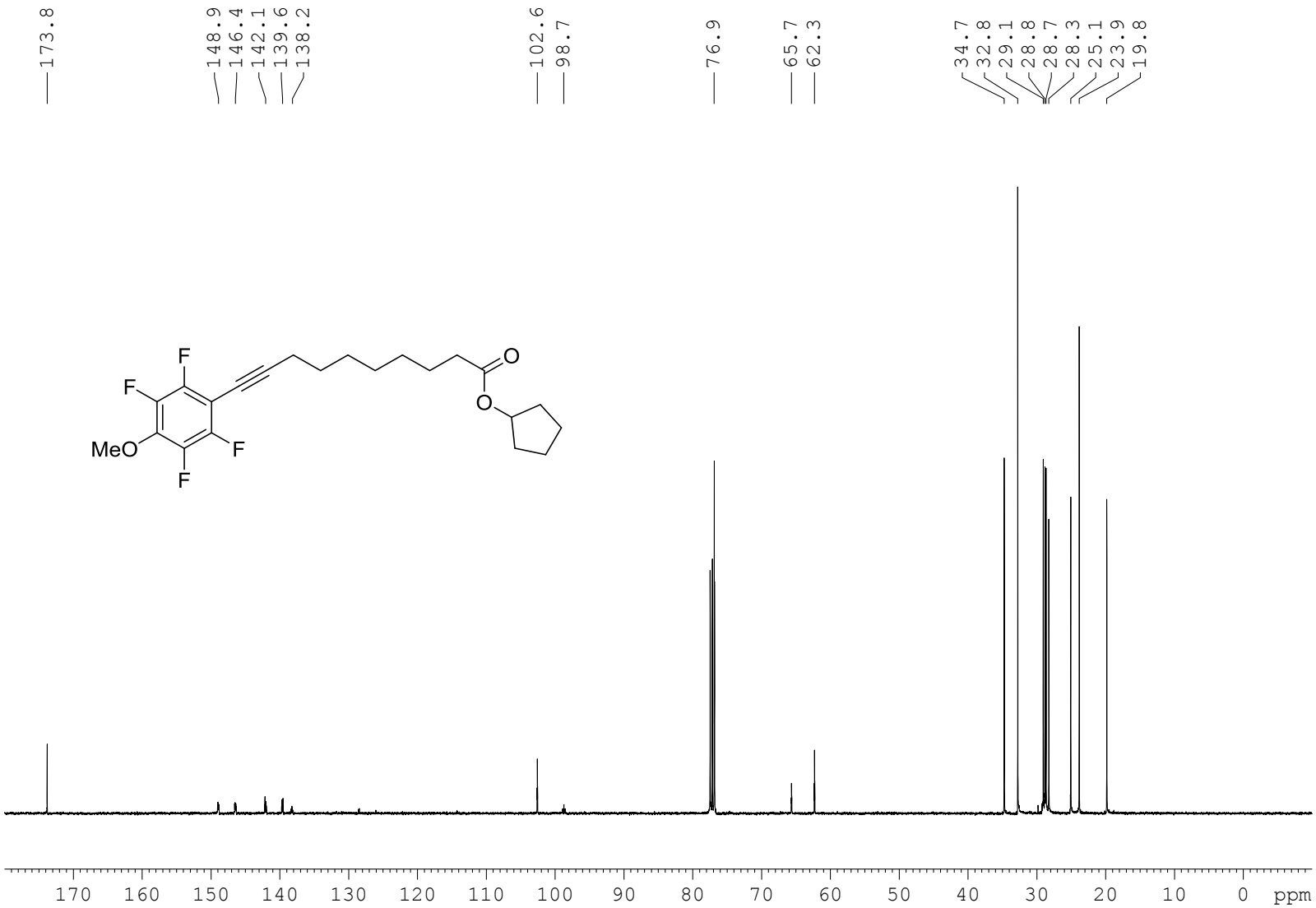
^{19}F NMR (282 MHz, $CDCl_3$) Compound 10b



^{1}H NMR (400 MHz, $CDCl_3$) Compound 10c

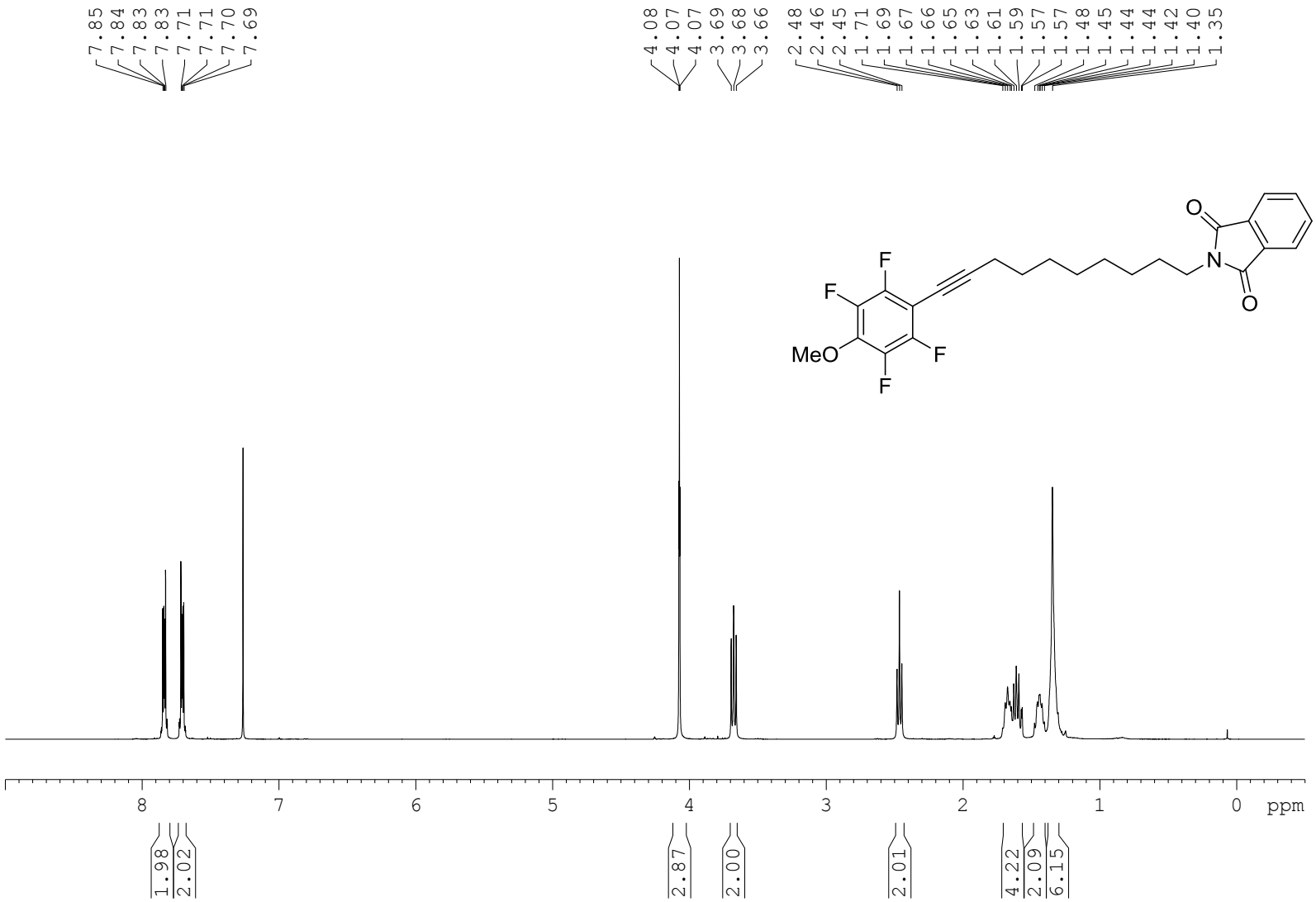


^{13}C NMR (101 MHz, $CDCl_3$) Compound 10c

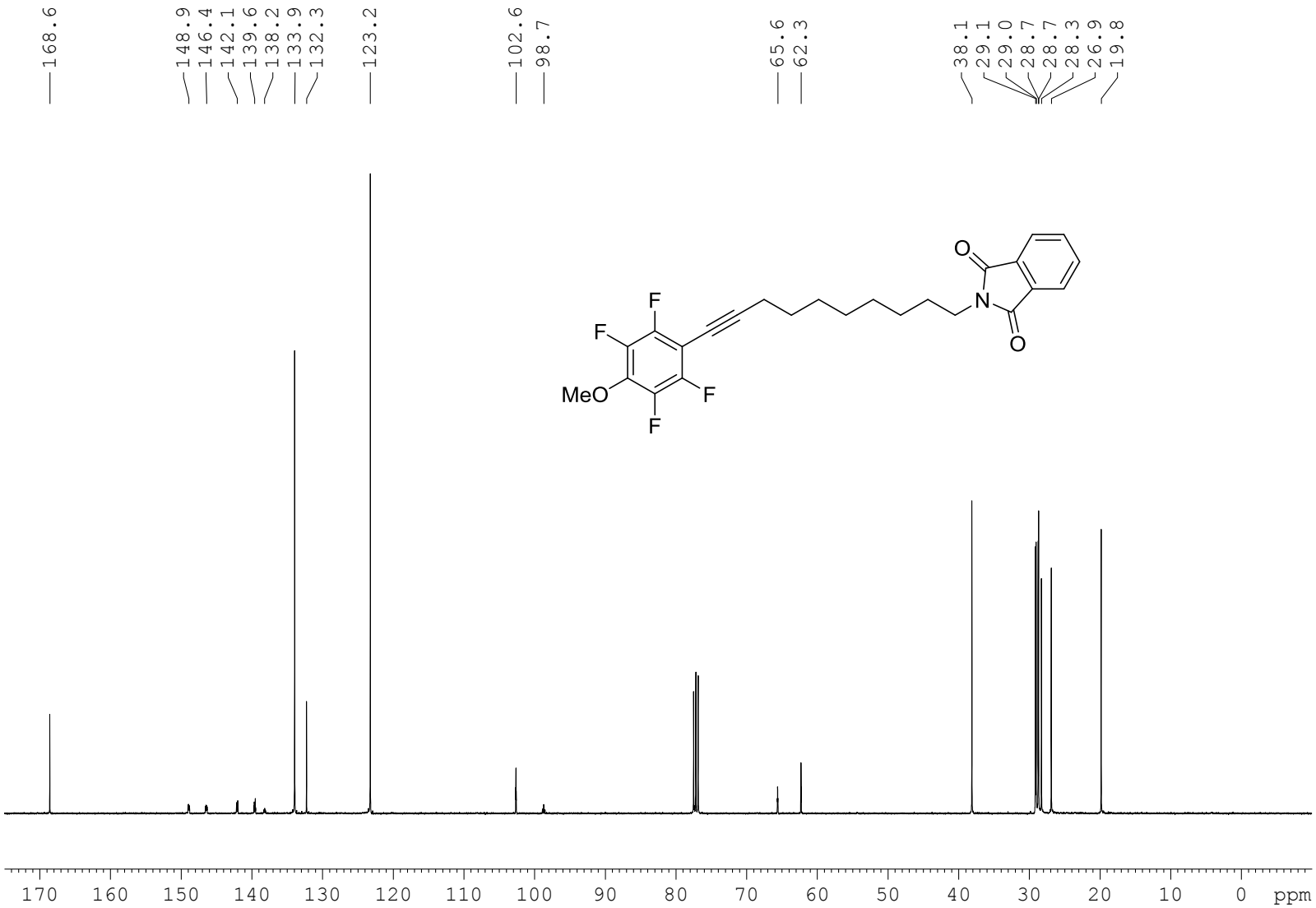


^{19}F NMR (282 MHz, $CDCl_3$) Compound 10c

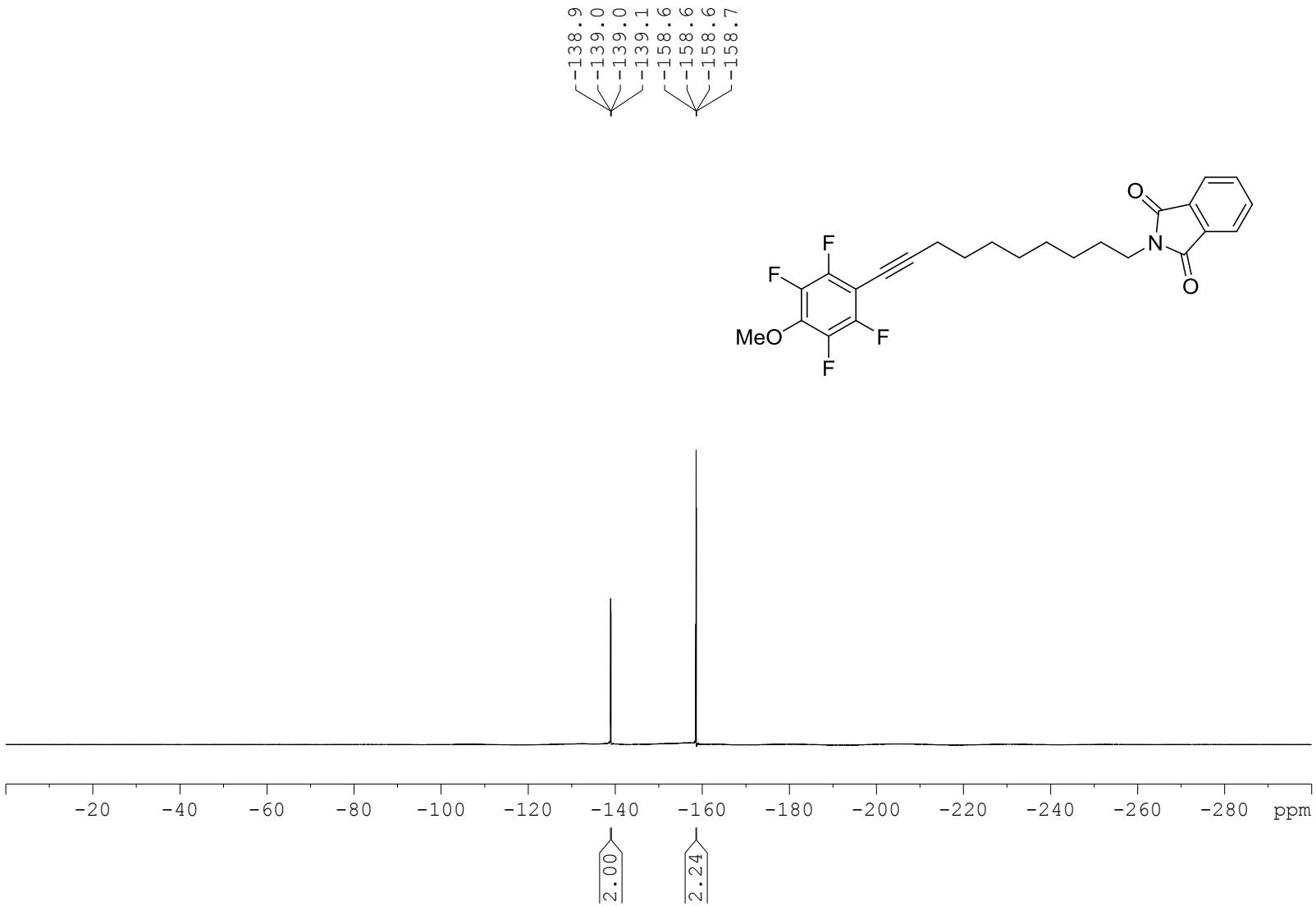
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10d



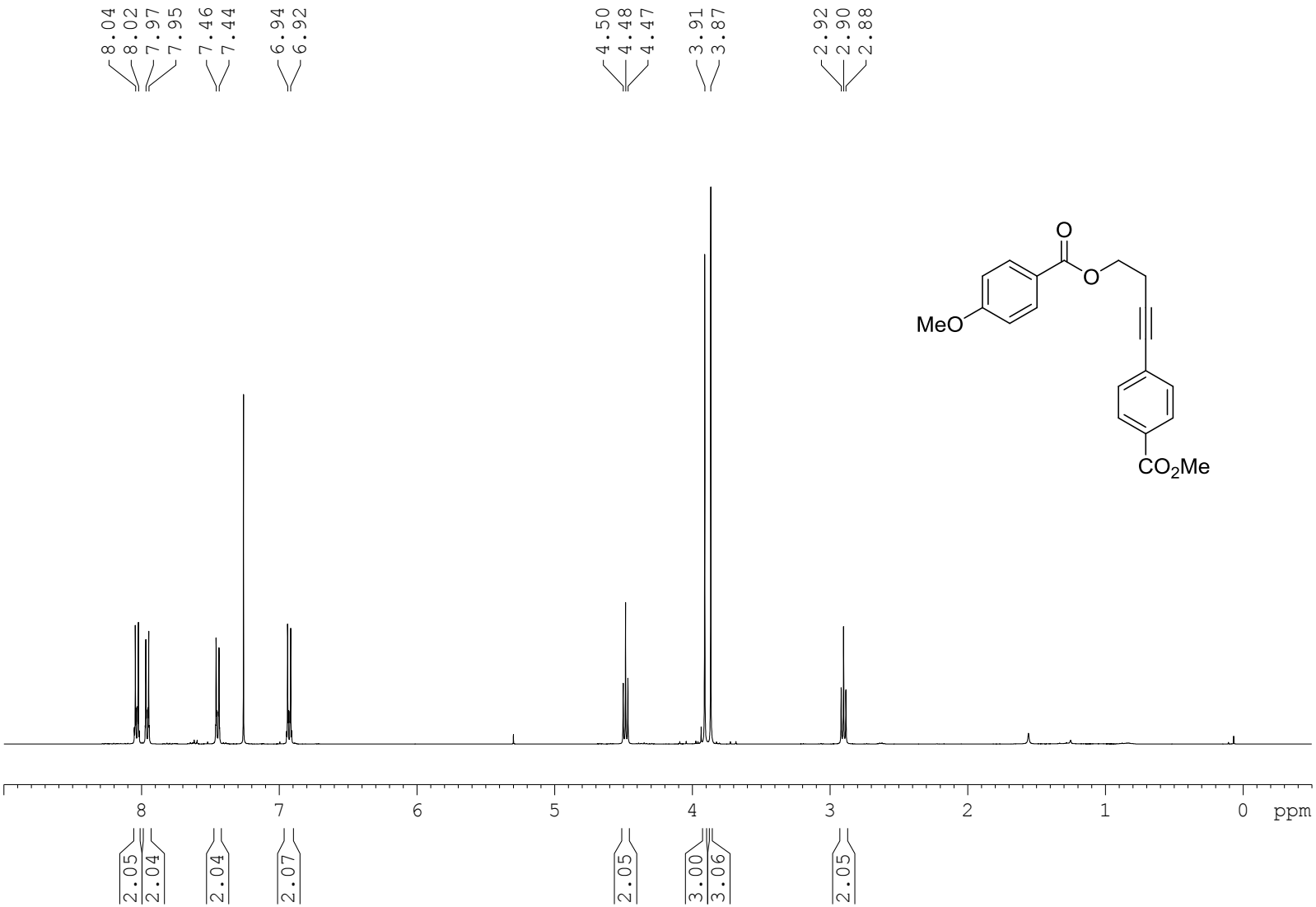
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10d



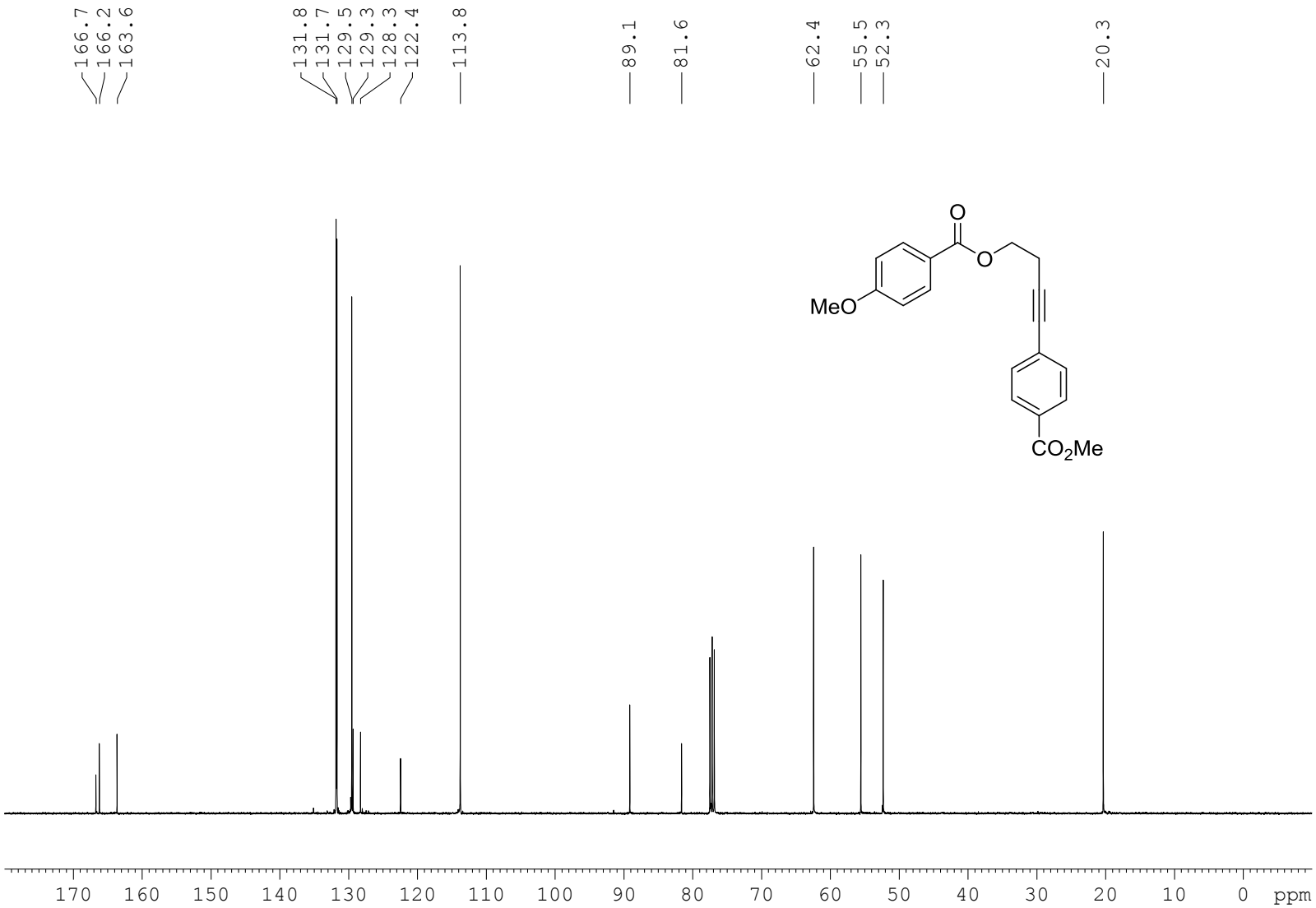
^{19}F NMR (282 MHz, $CDCl_3$) Compound 10d



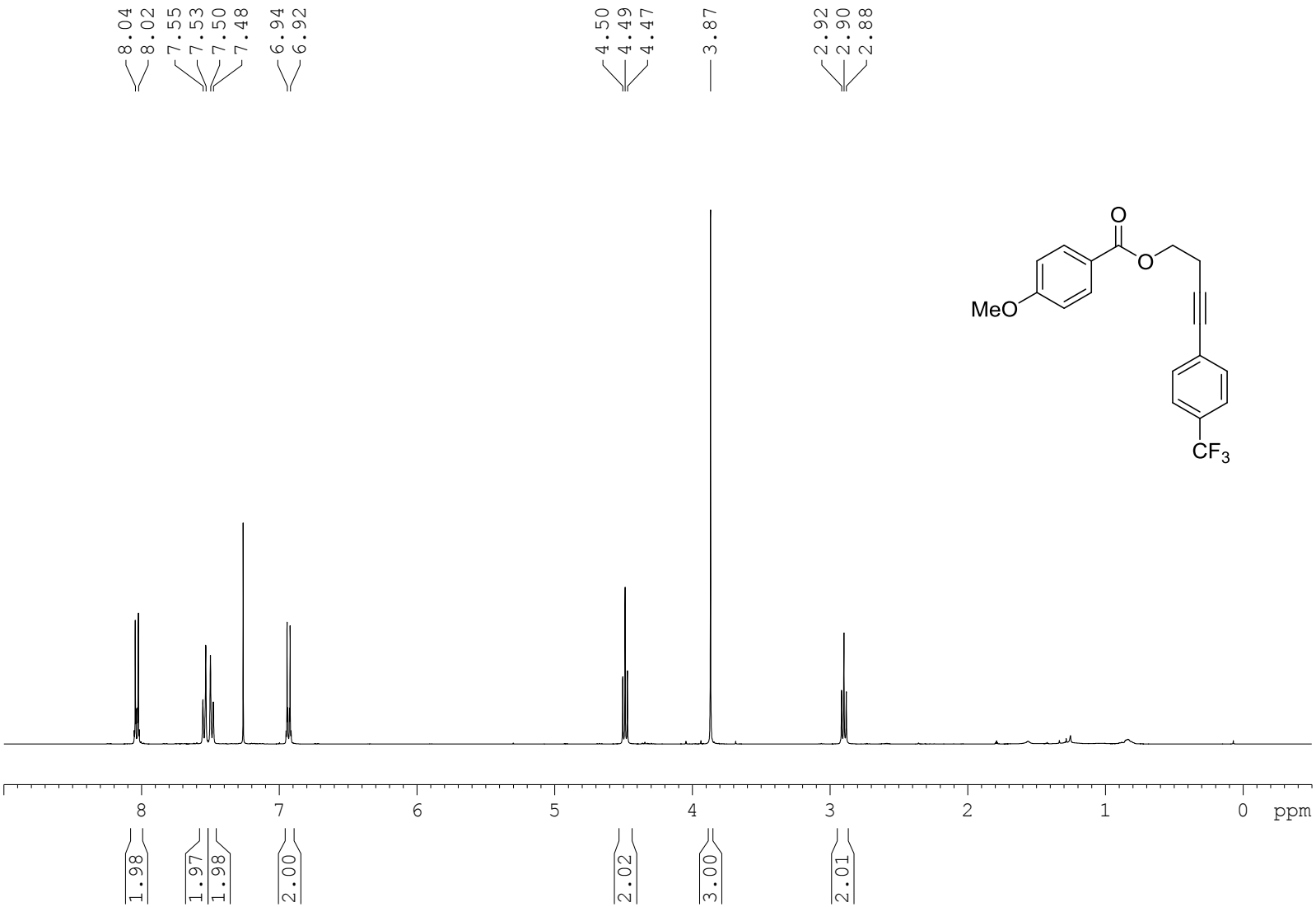
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10e



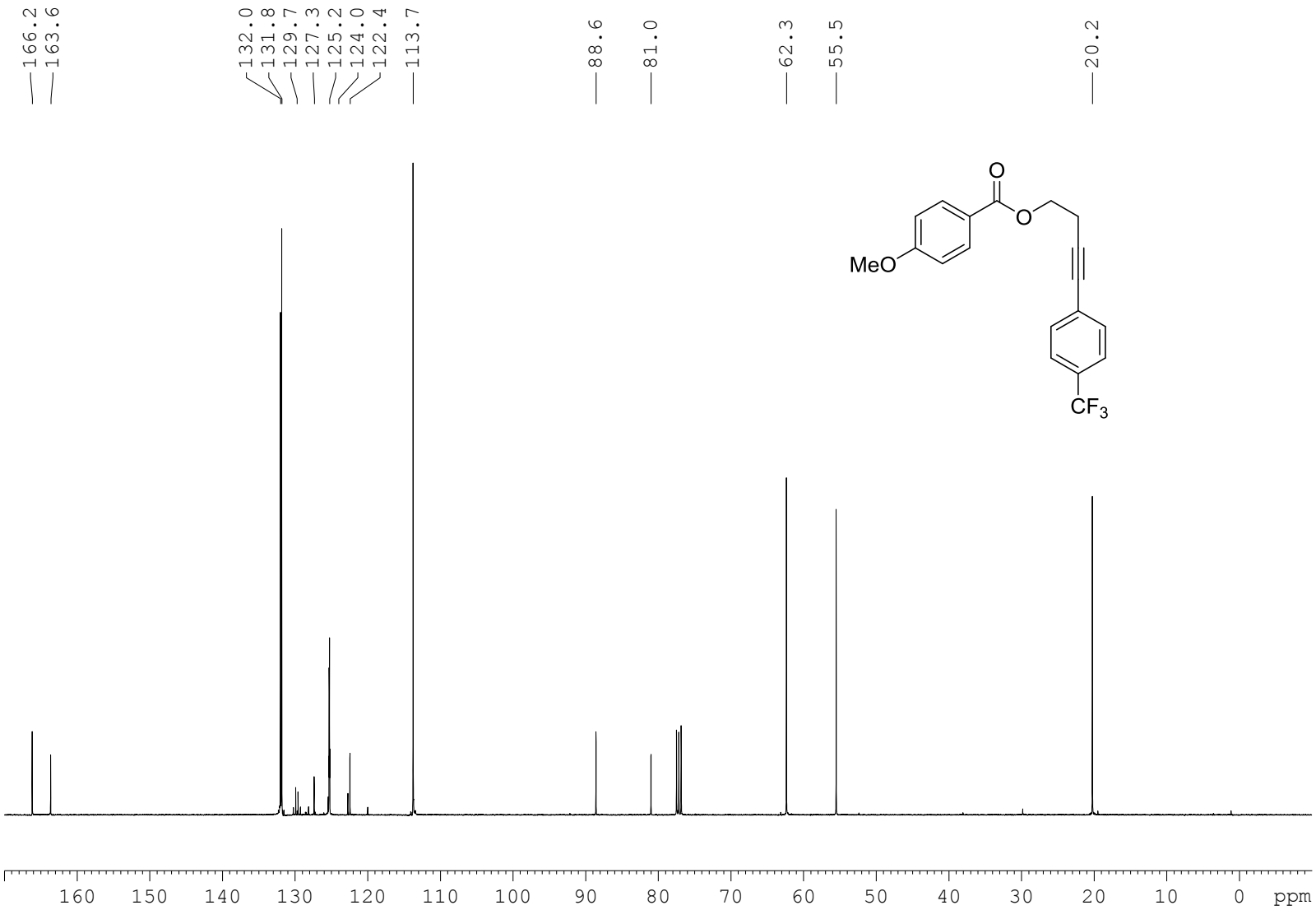
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10e



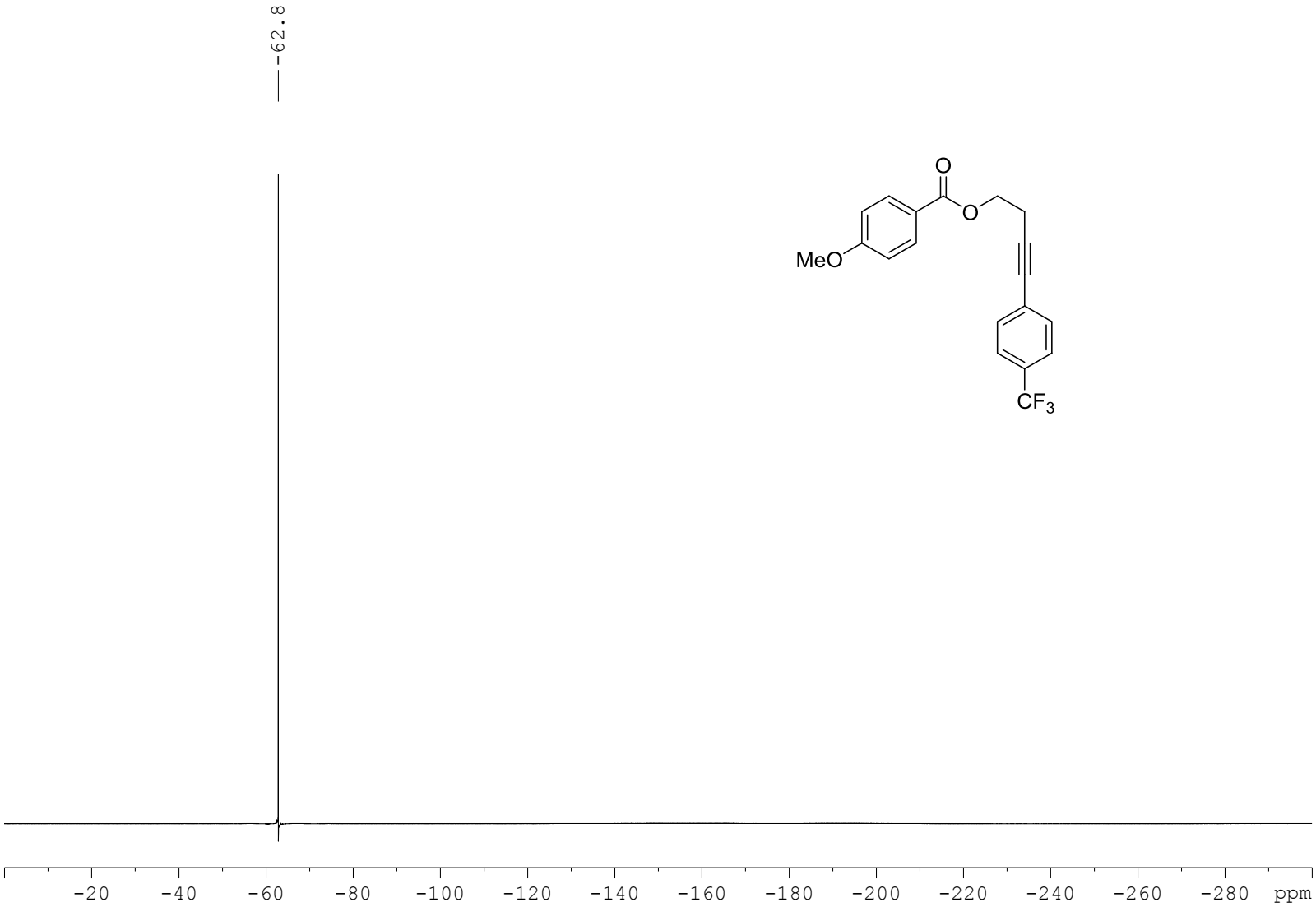
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10f



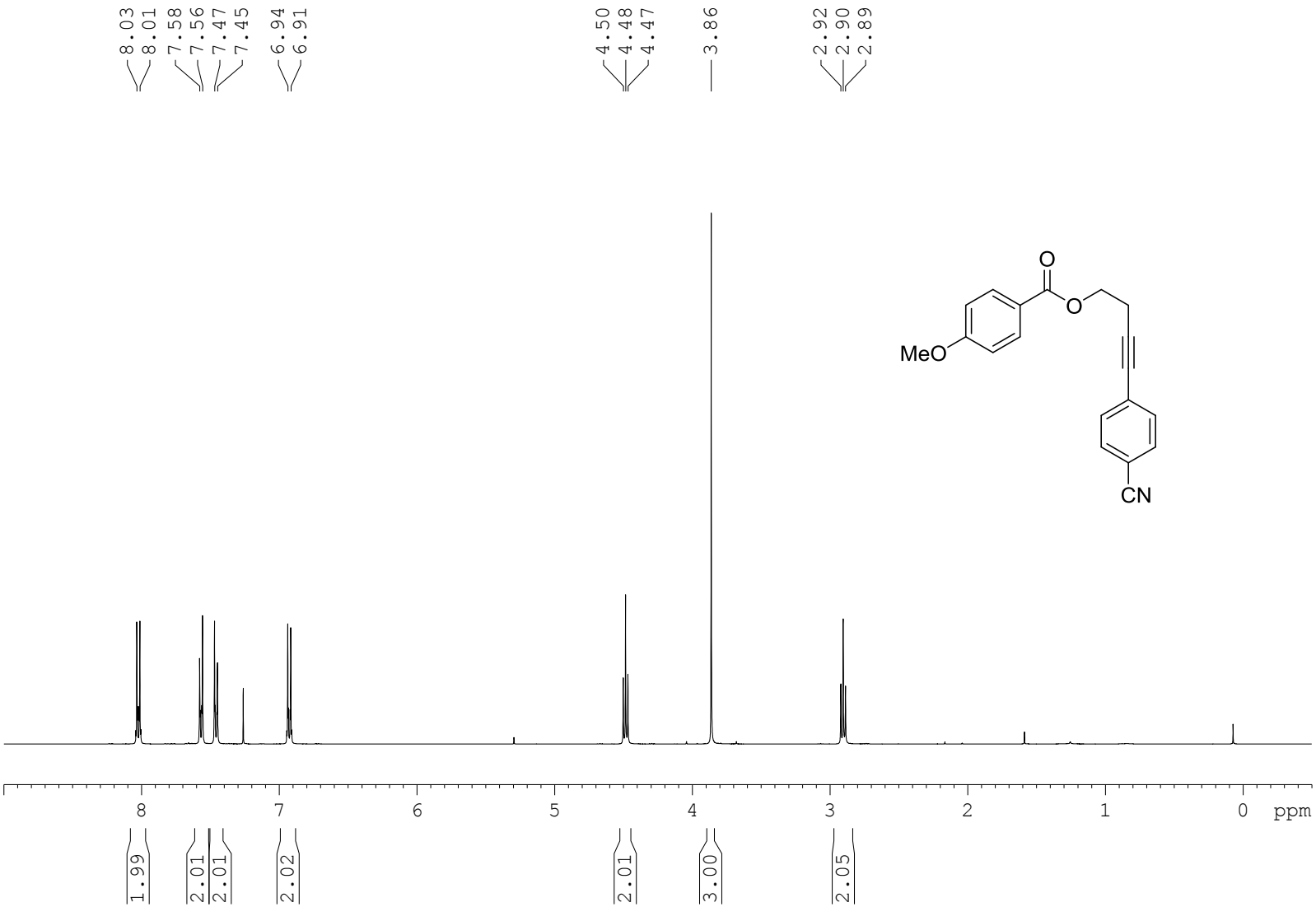
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10f



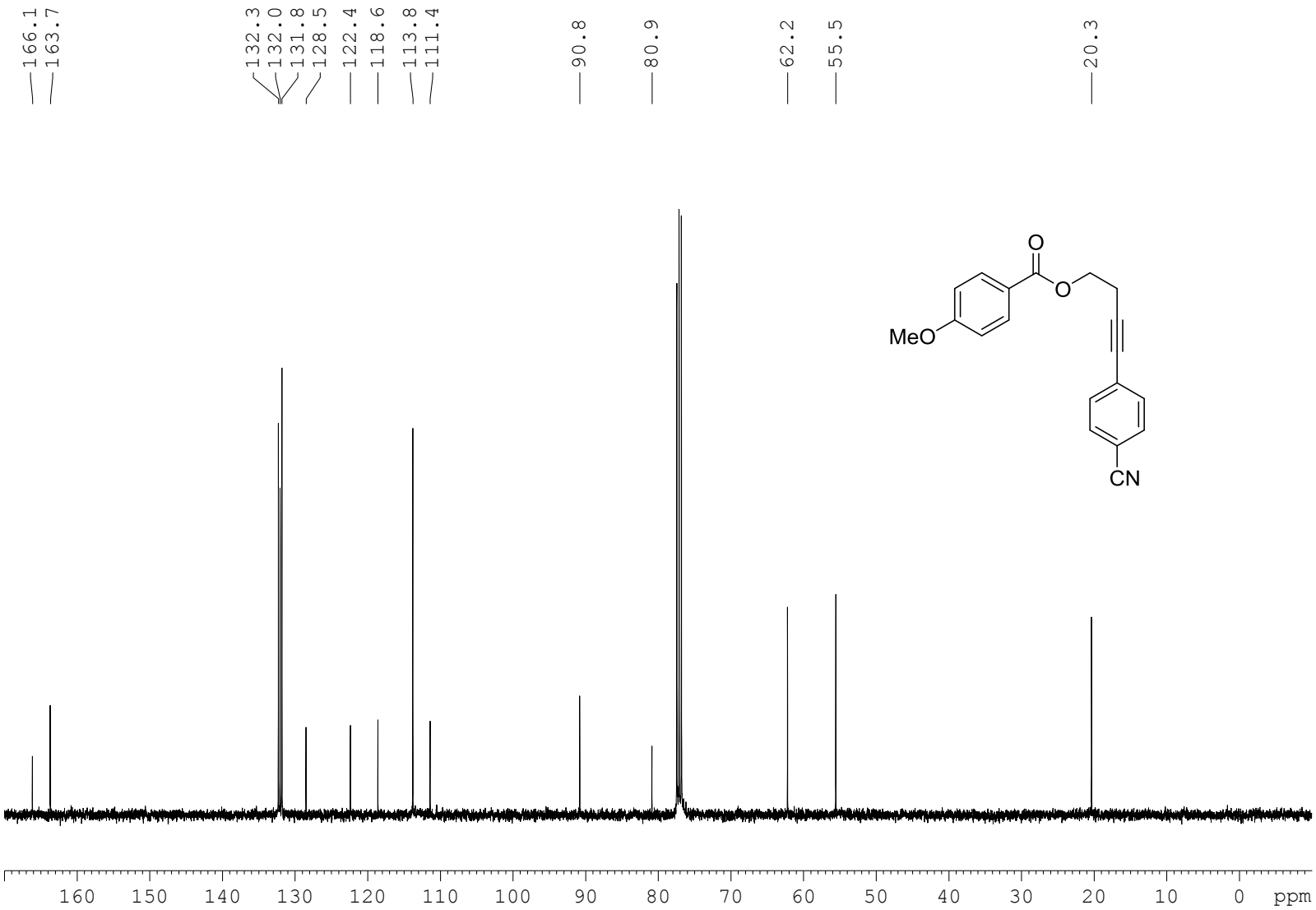
^{19}F NMR (282 MHz, $CDCl_3$) Compound 10f



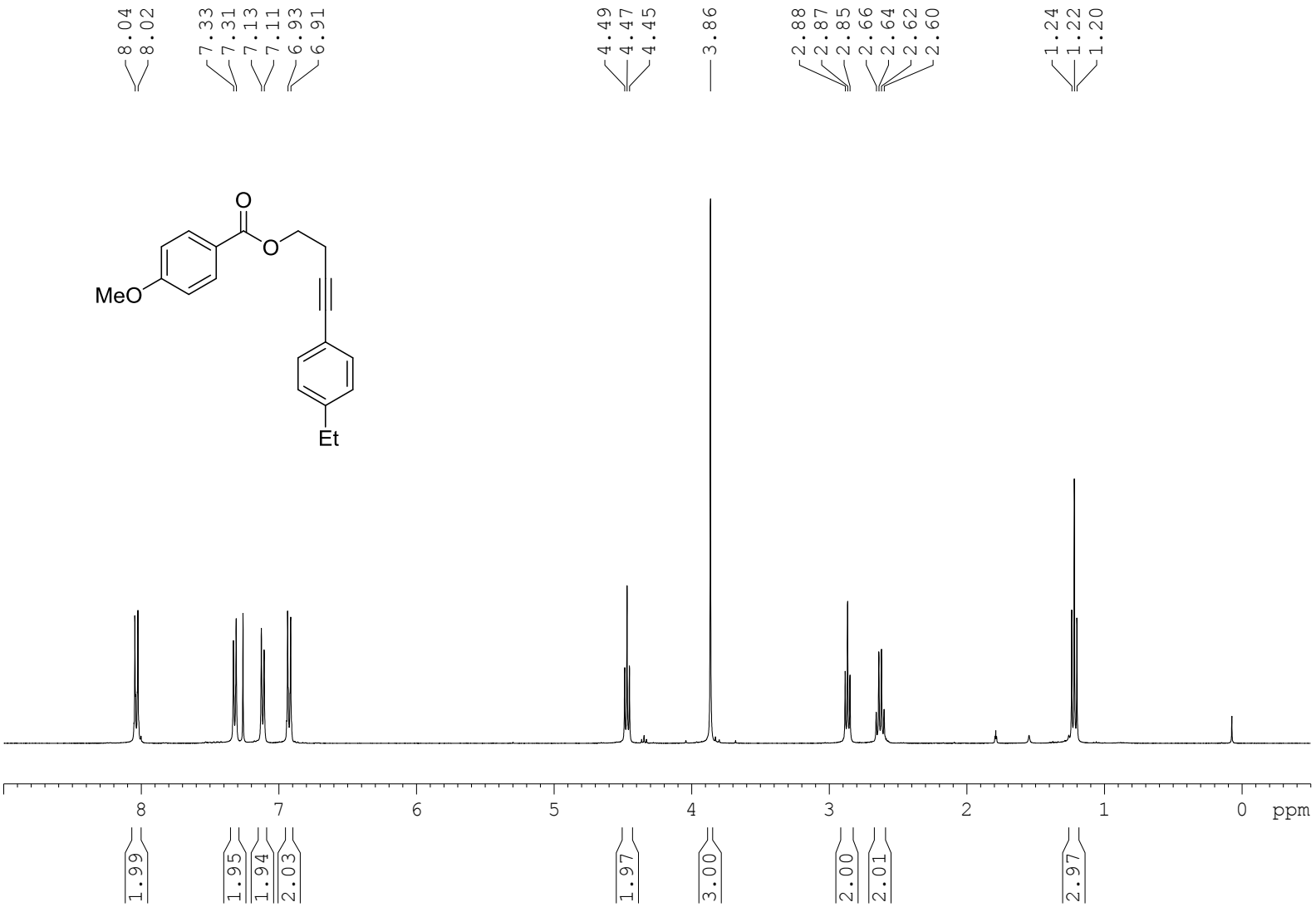
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10g



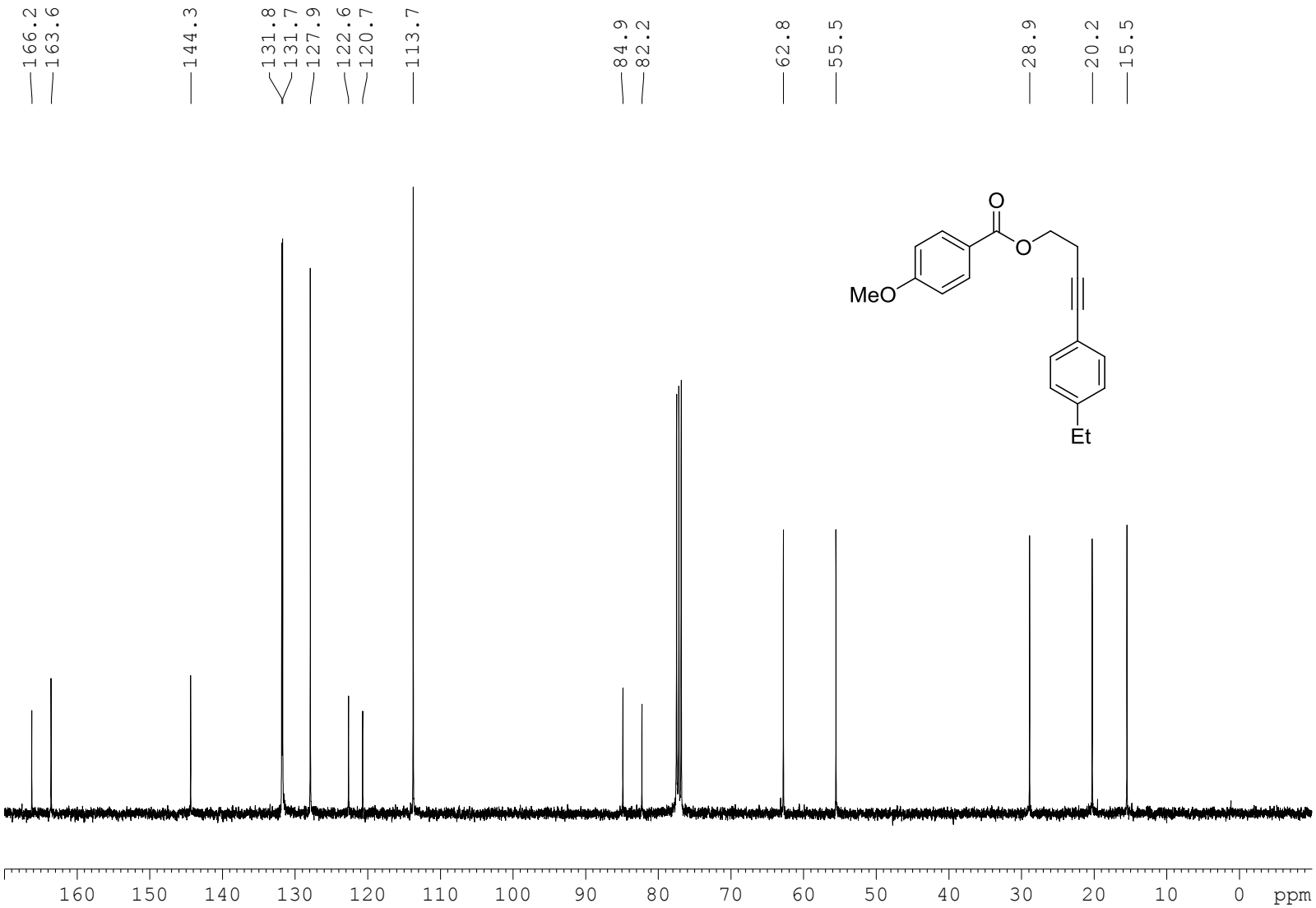
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10g



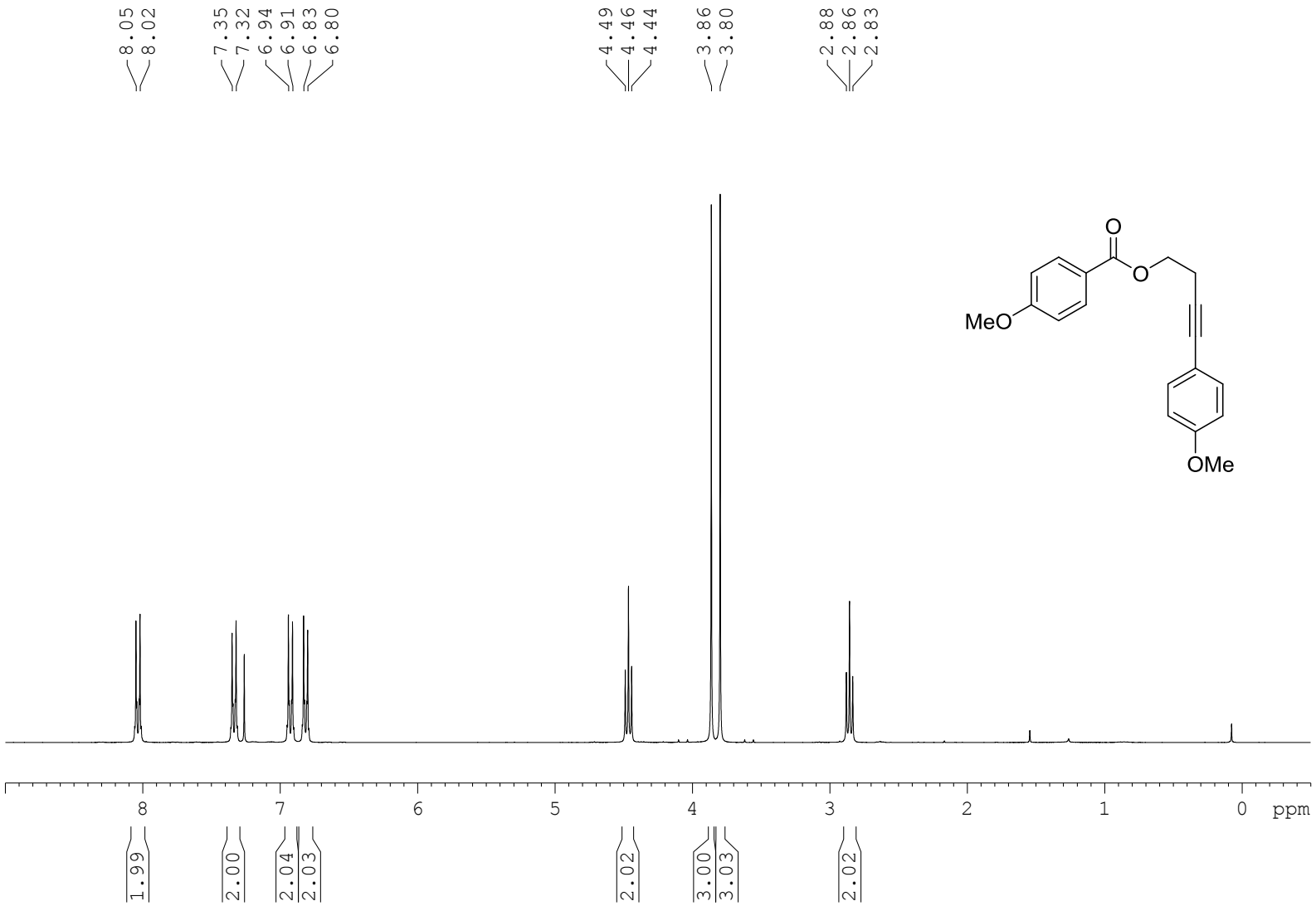
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10h



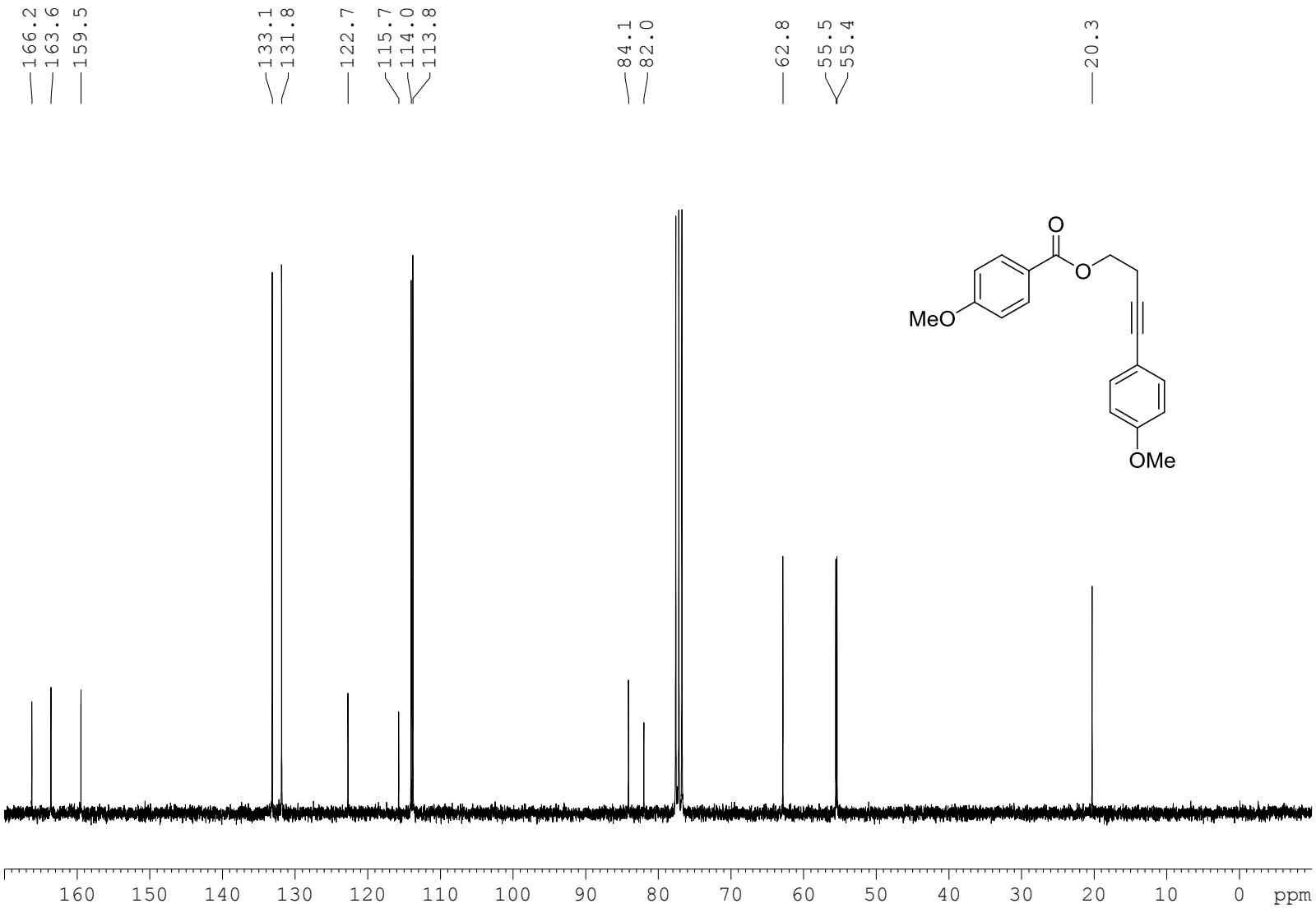
^{13}C NMR (400 MHz, $CDCl_3$) Compound 10h



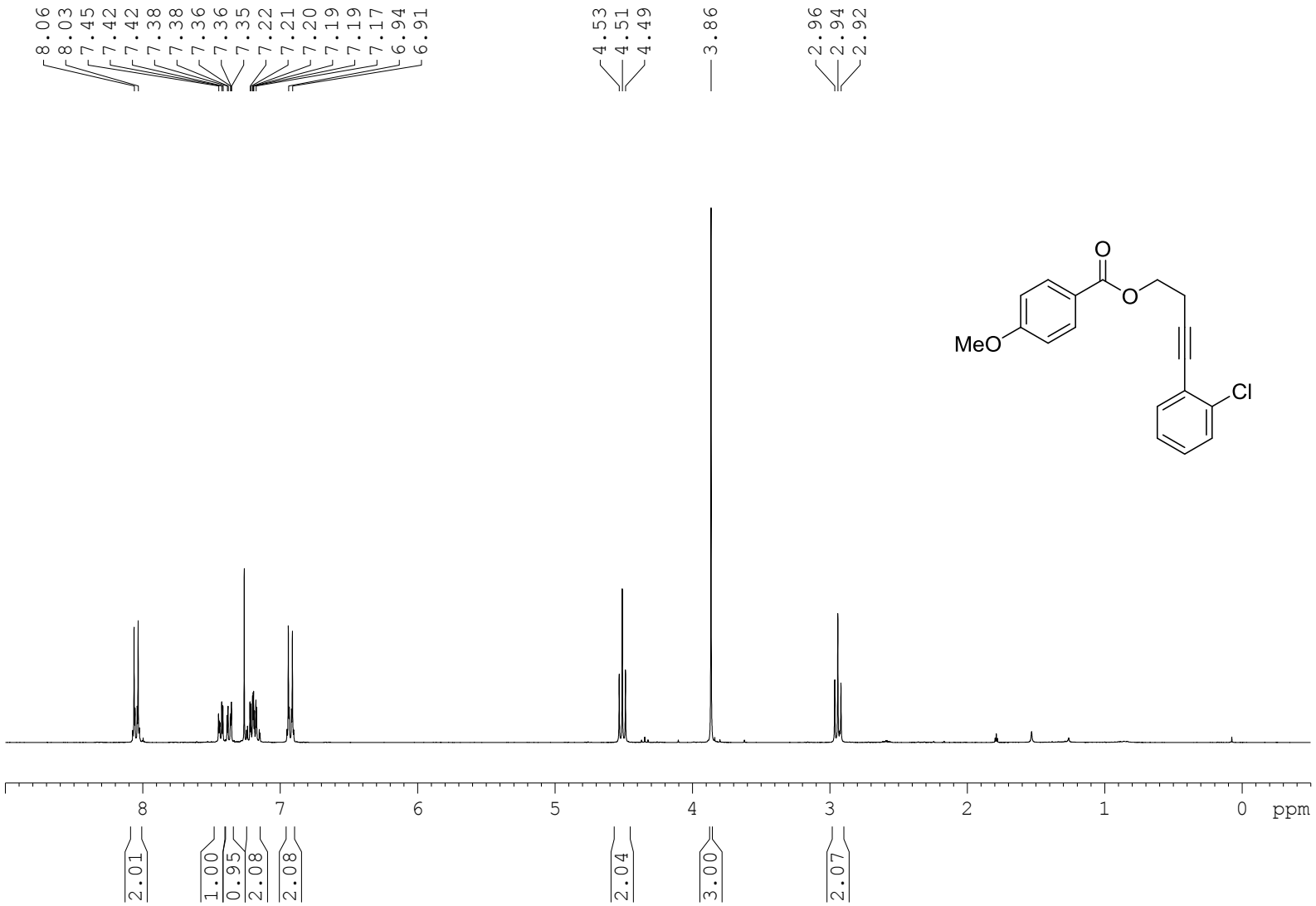
^{1}H NMR (300 MHz, $CDCl_3$) Compound 10i



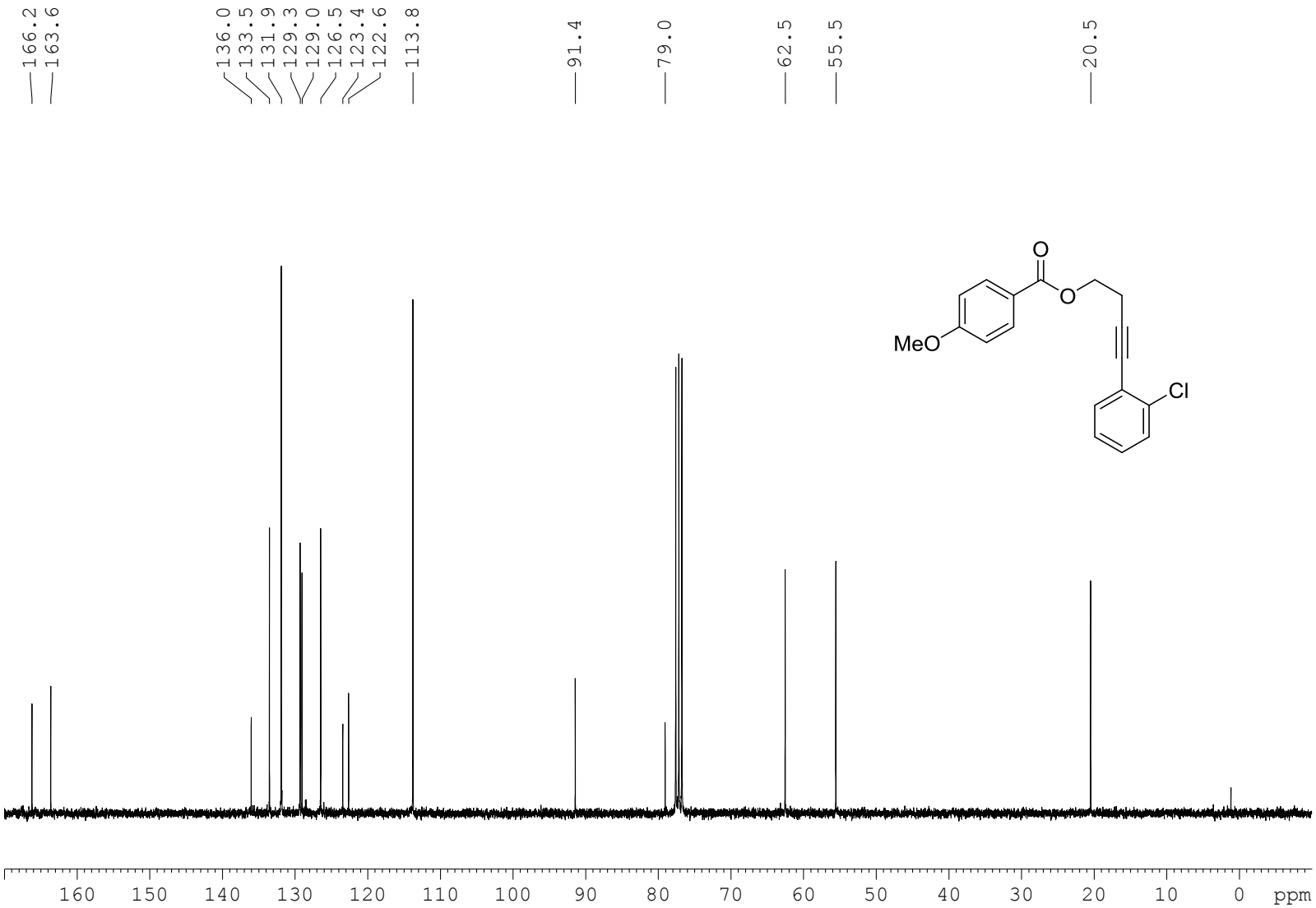
^{13}C NMR (75 MHz, $CDCl_3$) Compound 10i



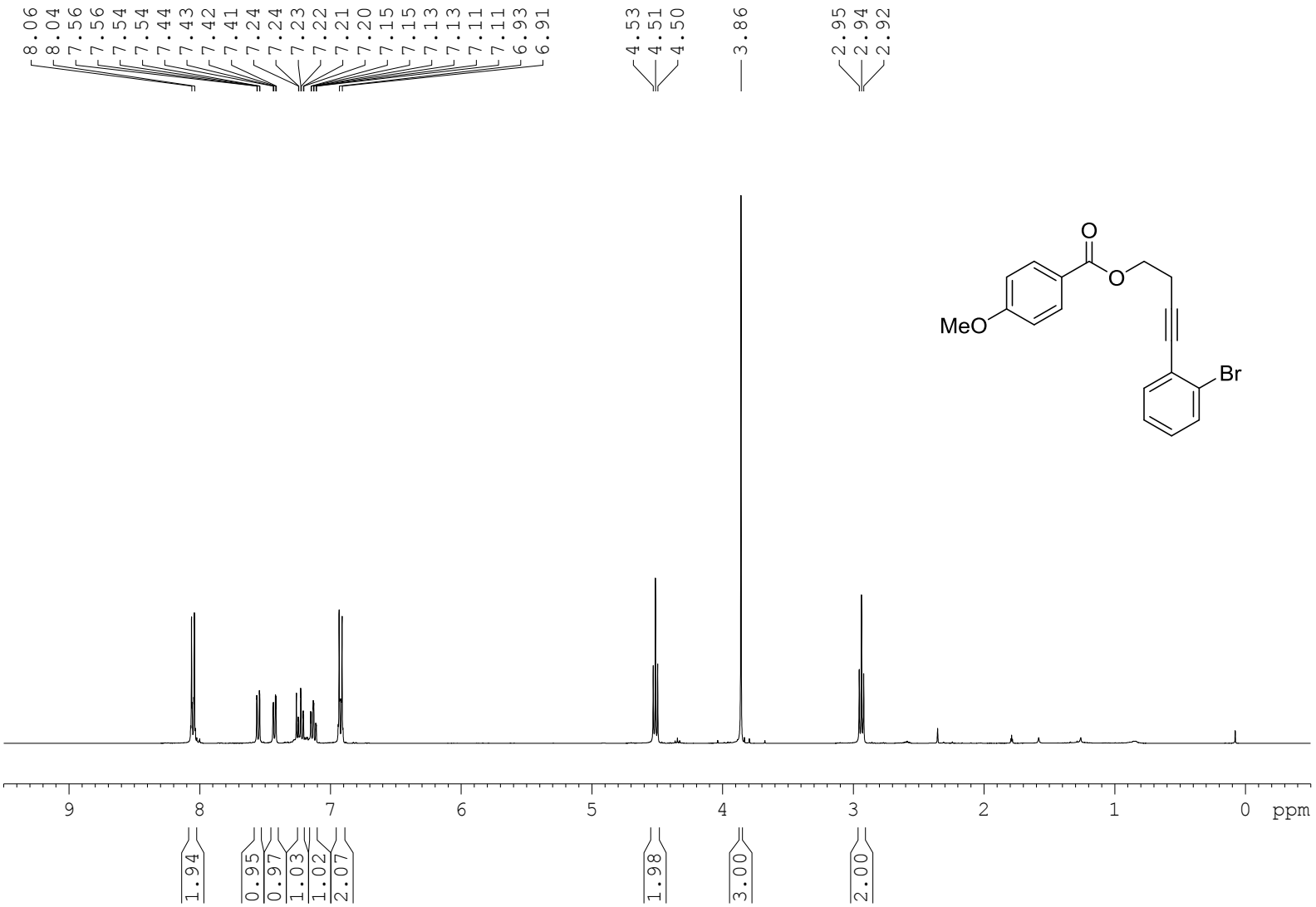
^{1}H NMR (300 MHz, $CDCl_3$) Compound 10j



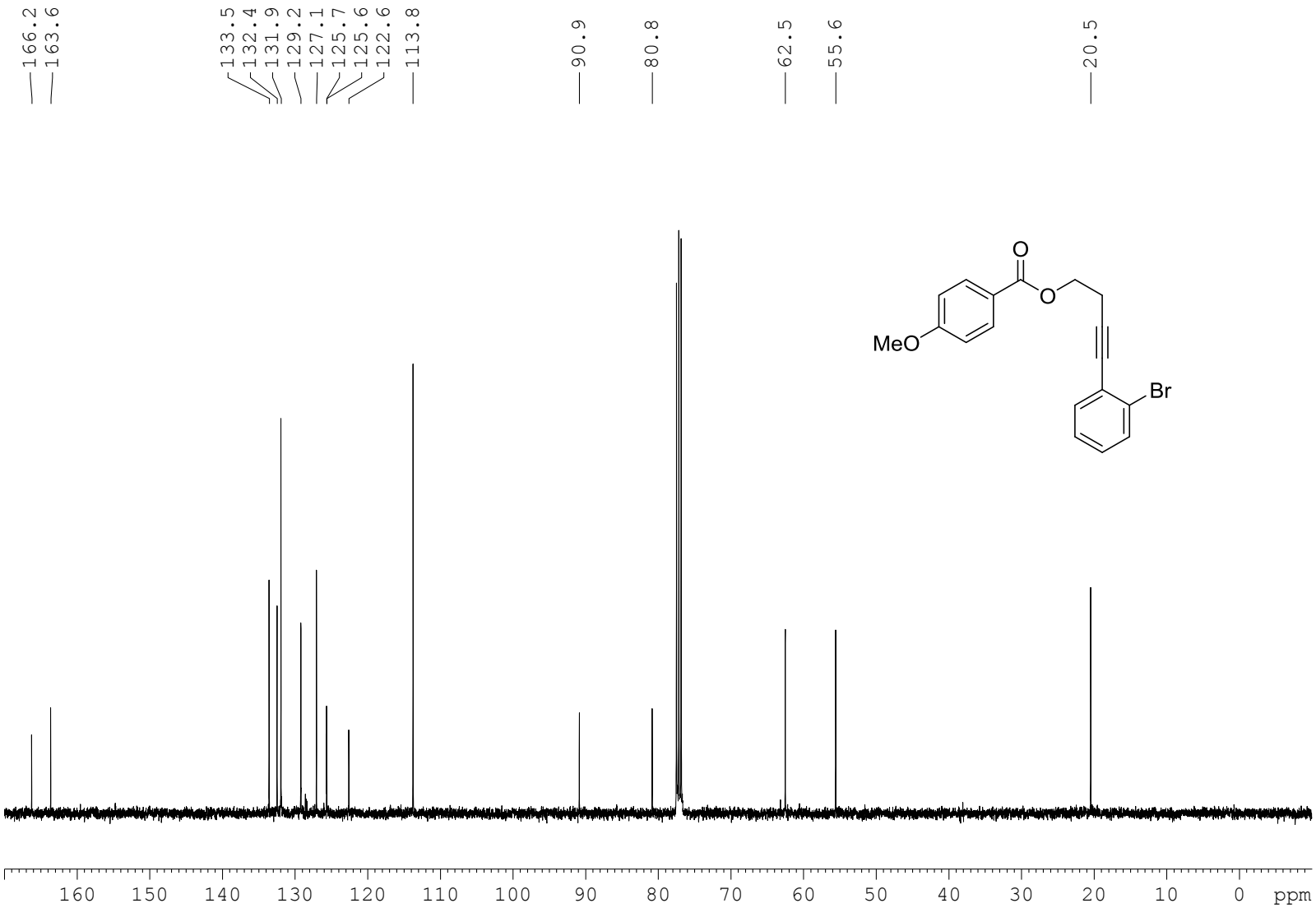
^{13}C NMR (75 MHz, $CDCl_3$) Compound 10j



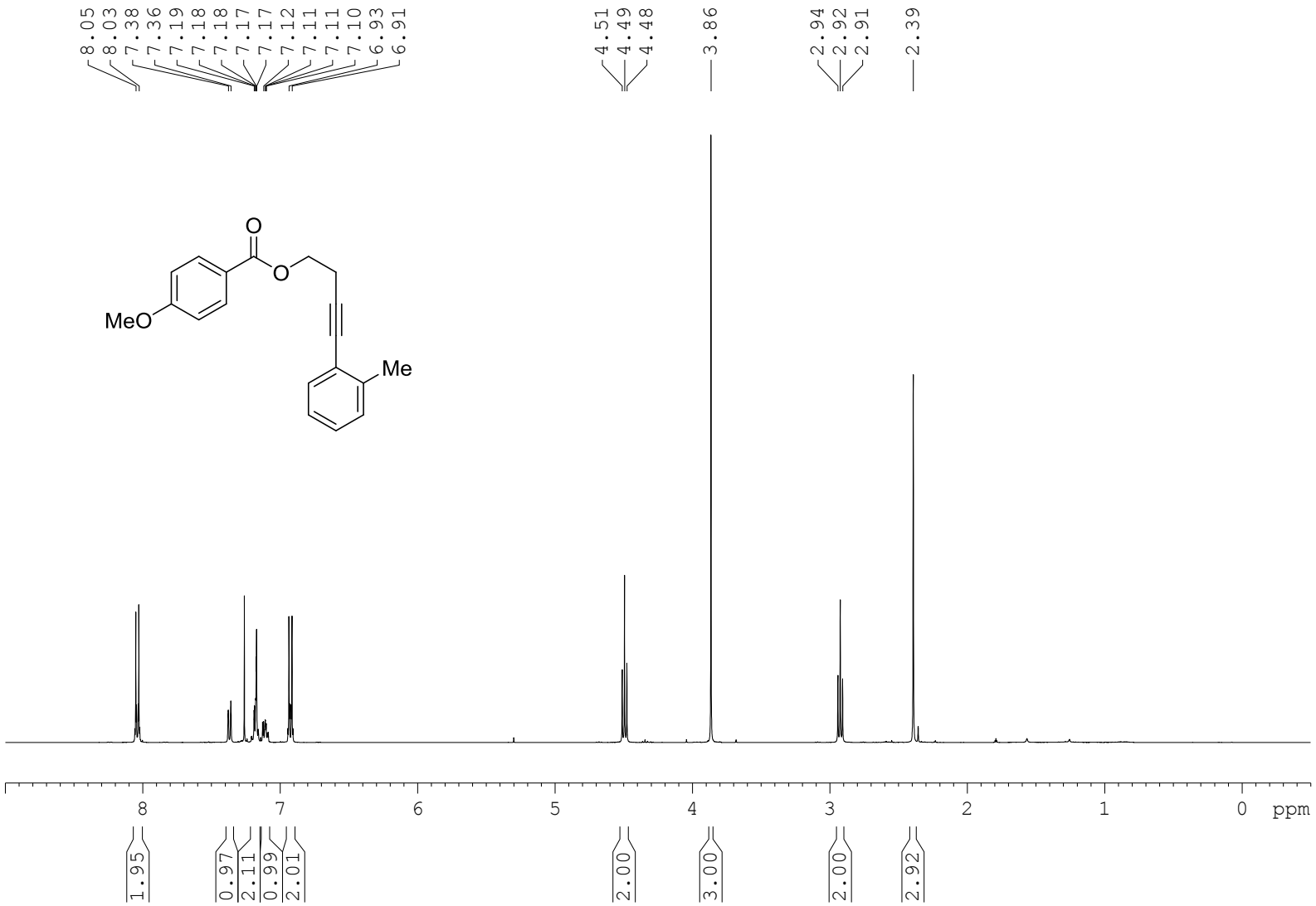
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10k



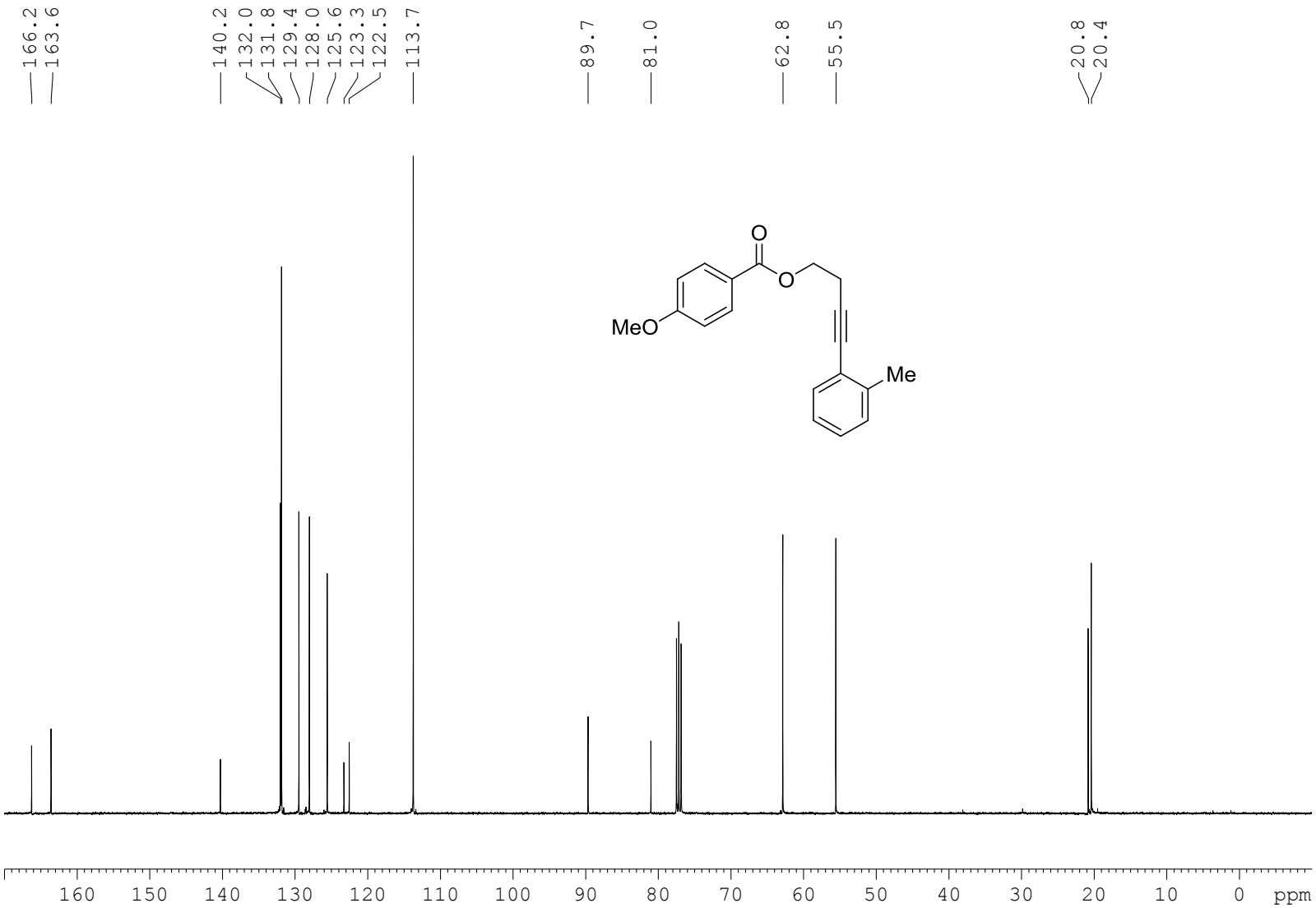
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10k



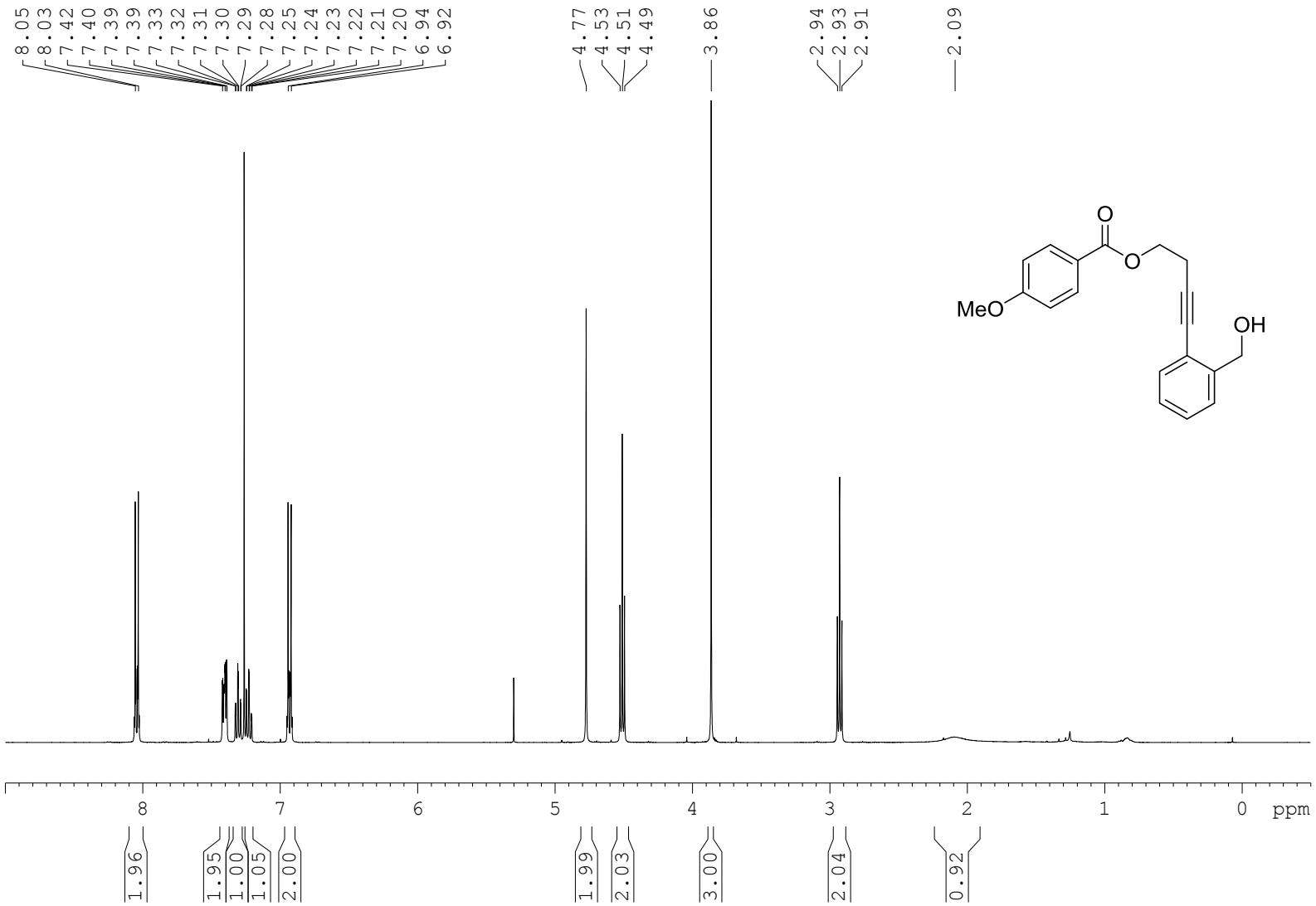
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10l



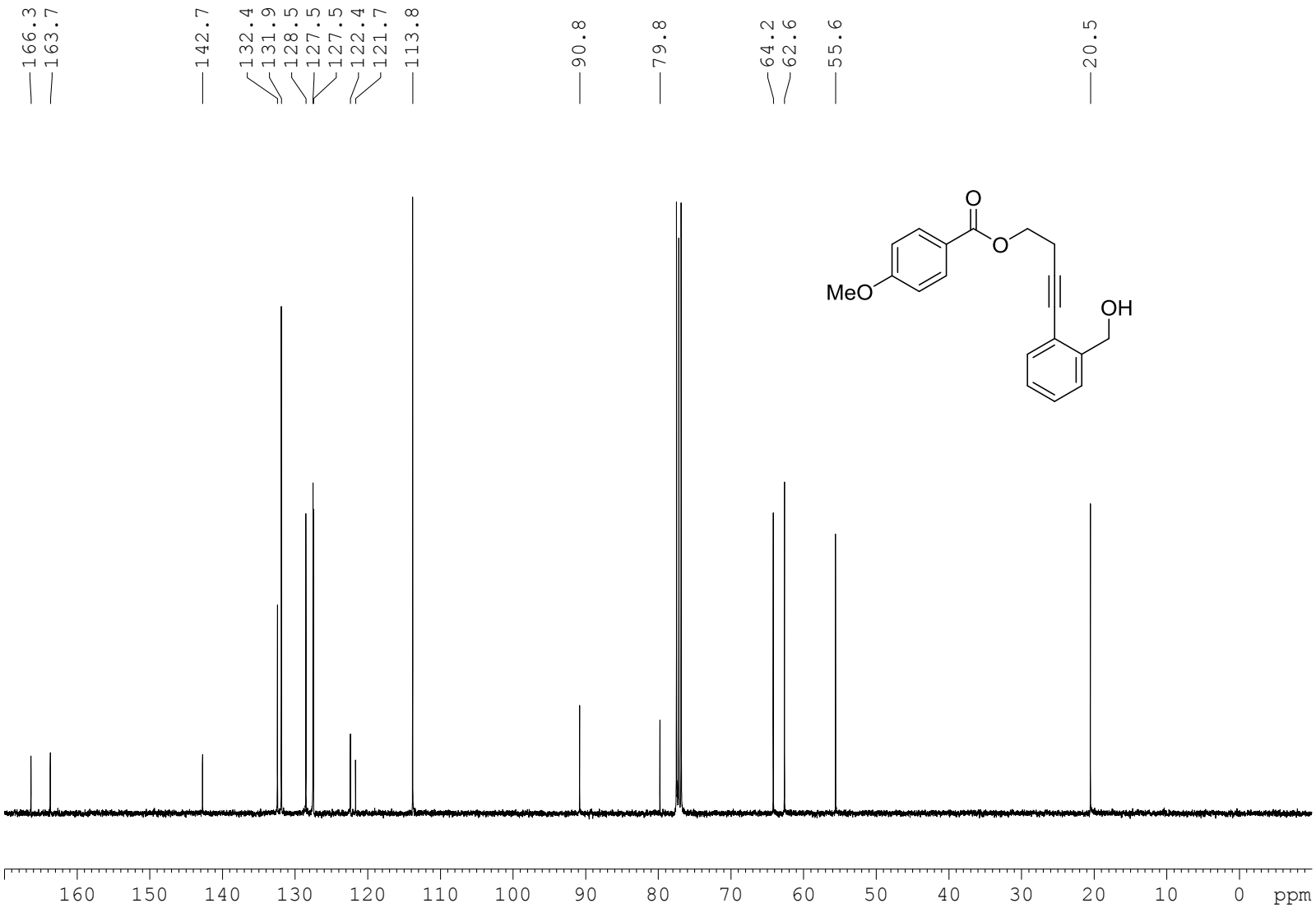
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10l



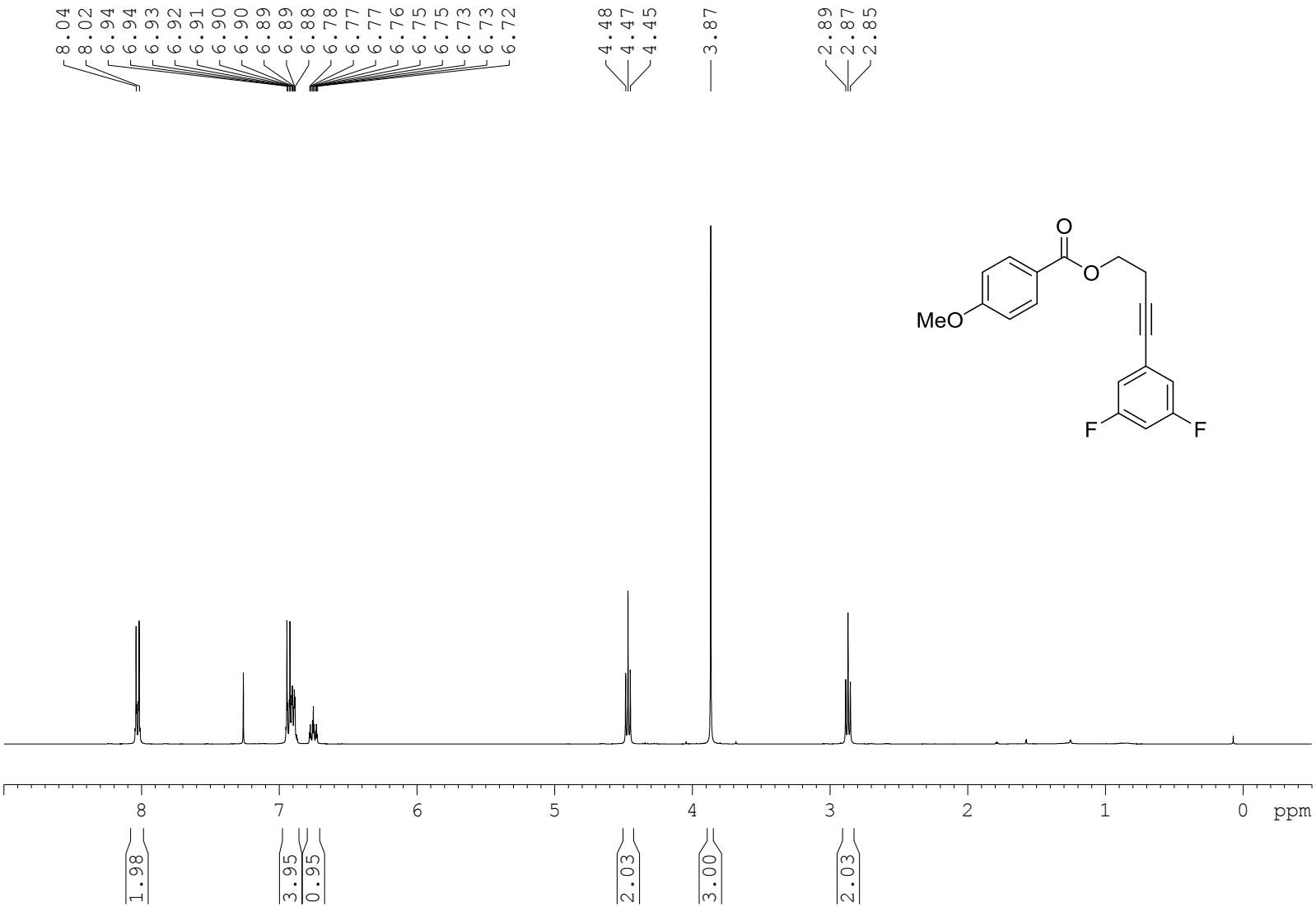
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10m



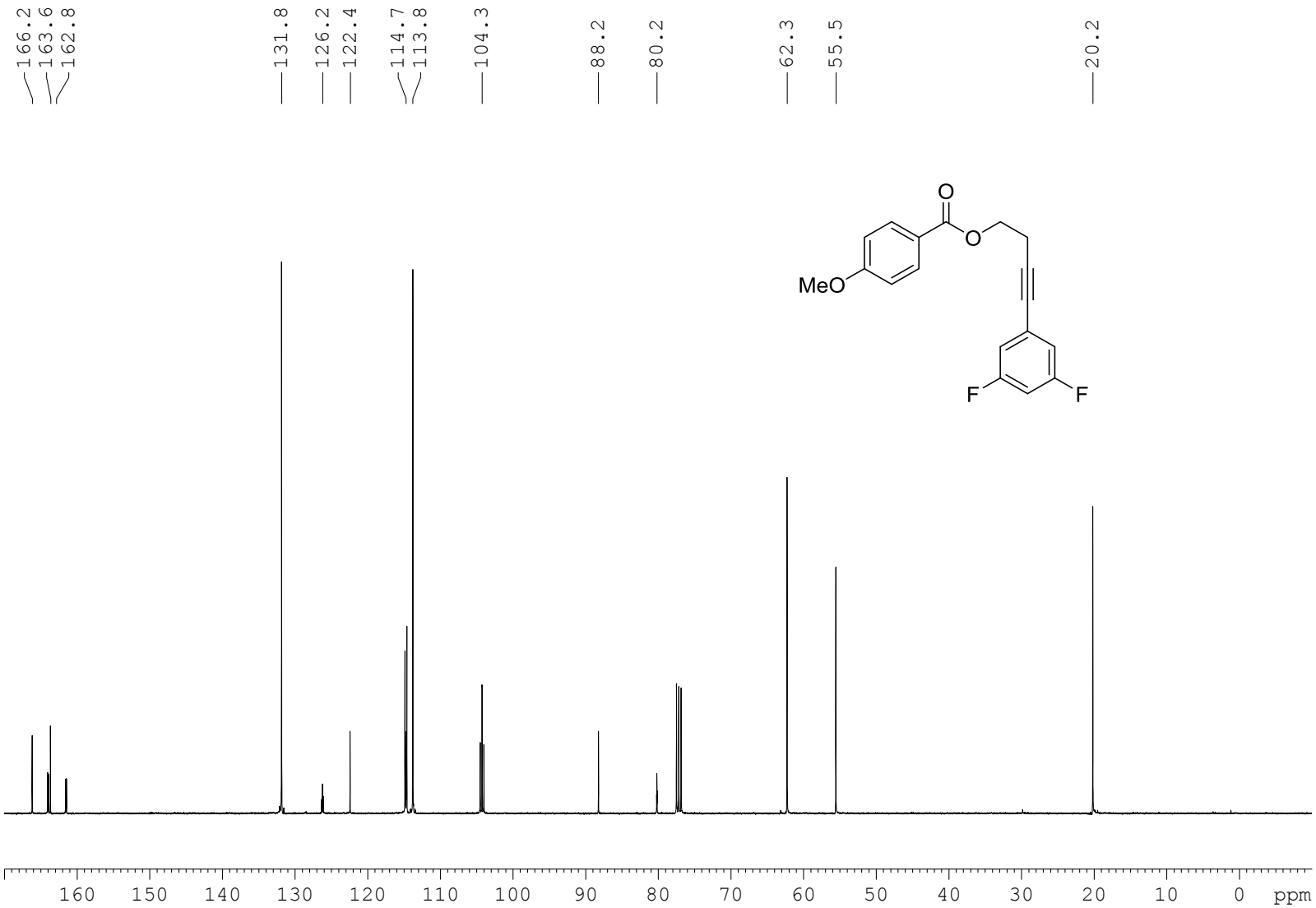
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10m



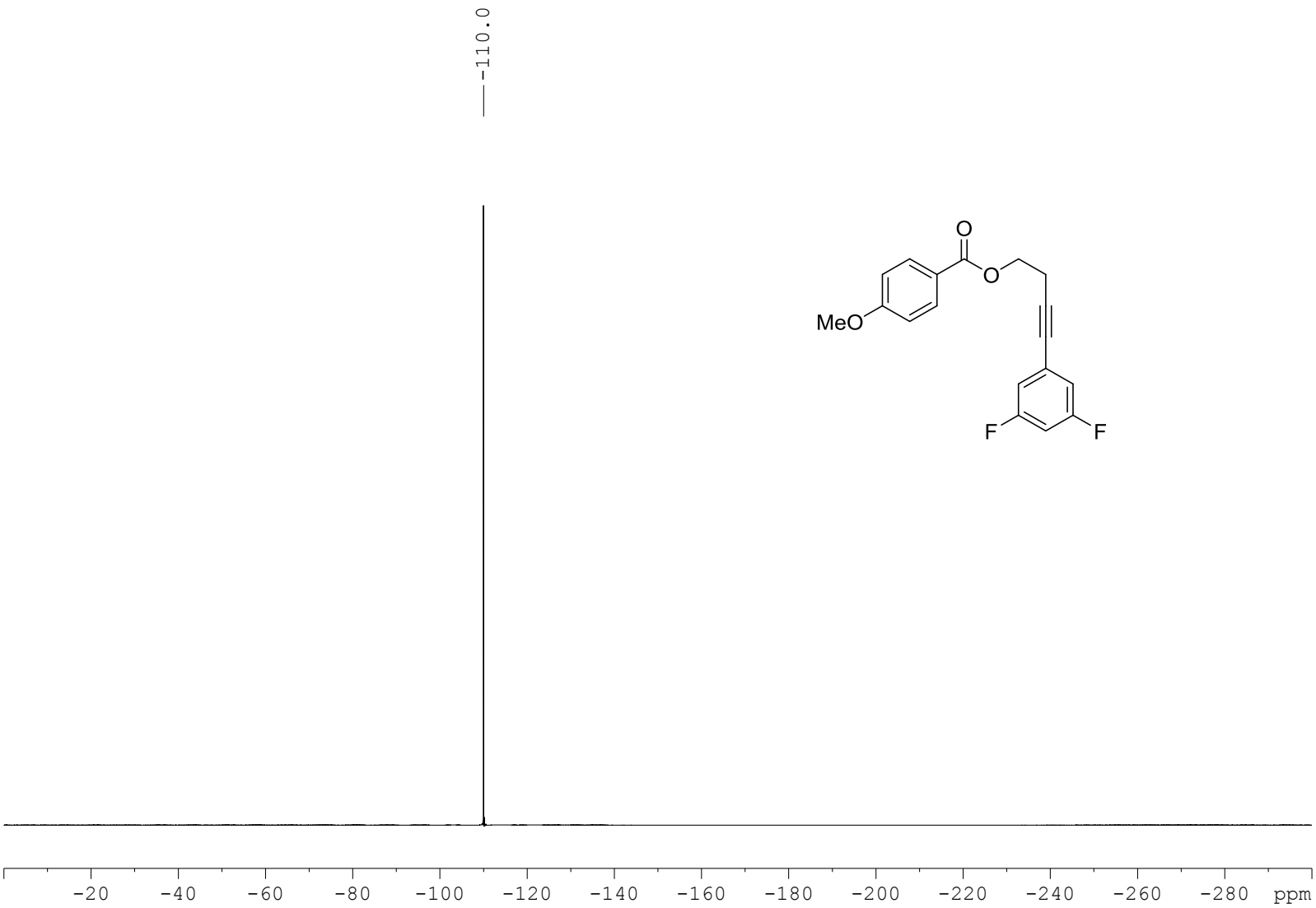
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10n



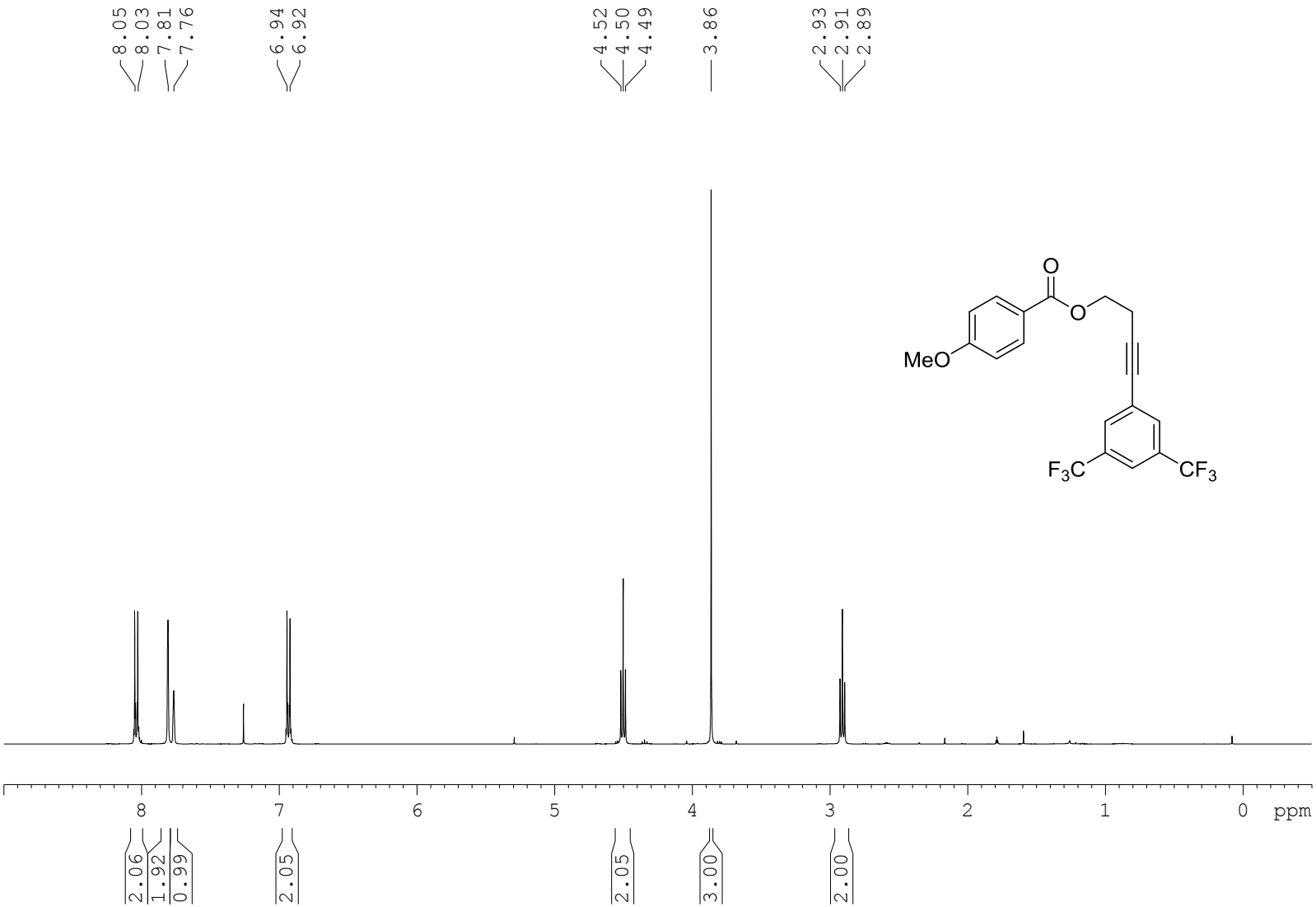
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10n



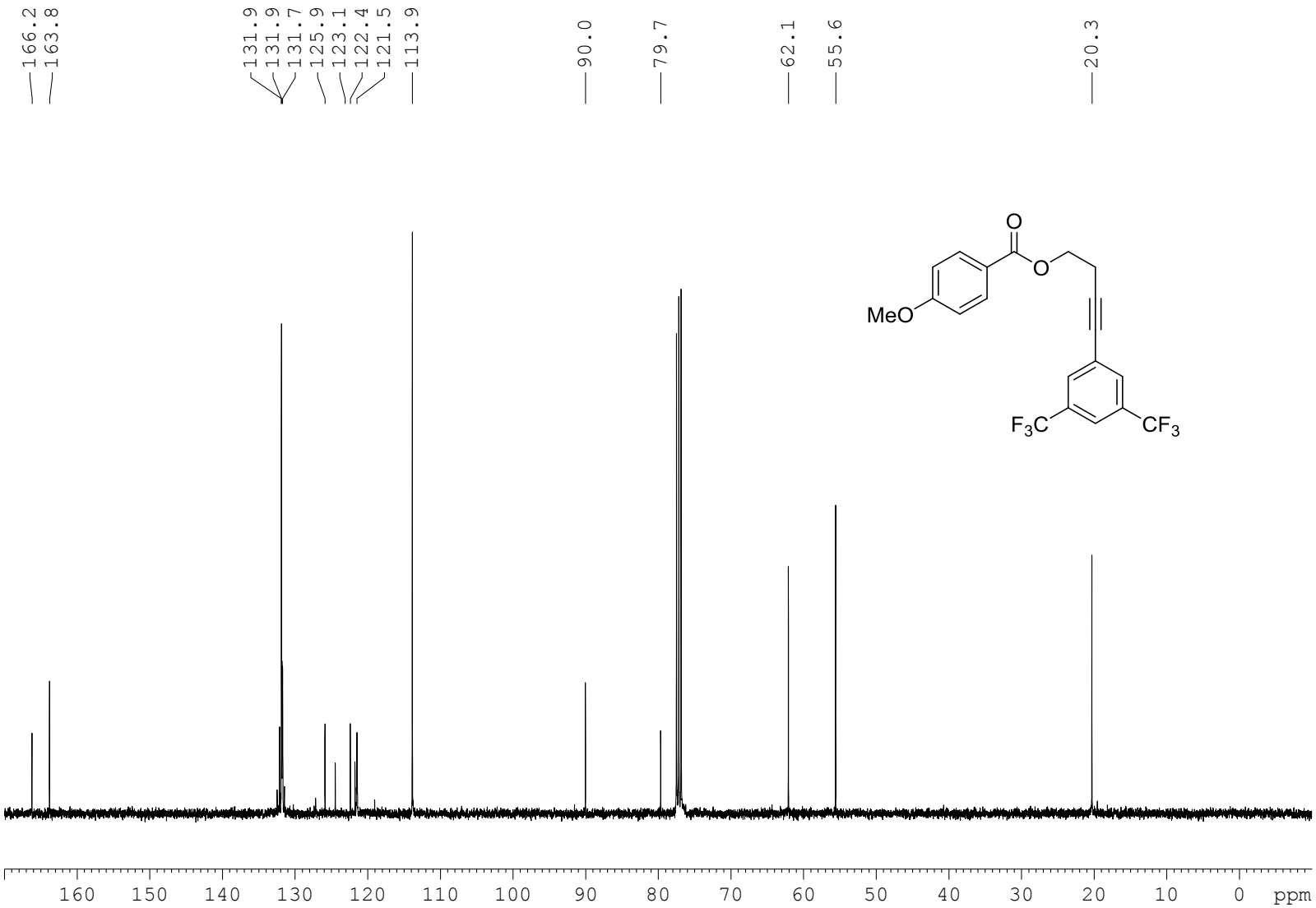
^{19}F NMR (282 MHz, $CDCl_3$) Compound 10n



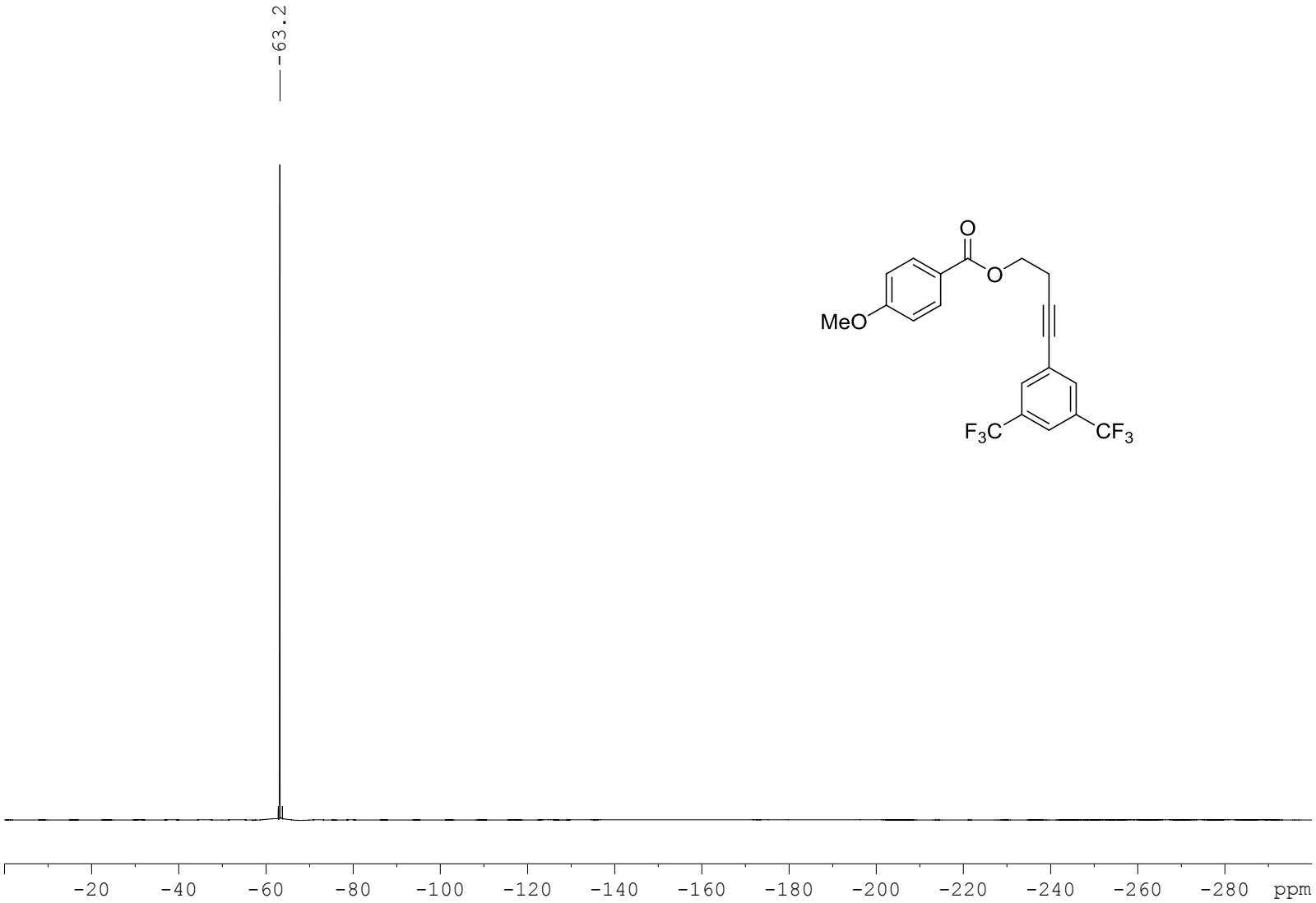
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10o



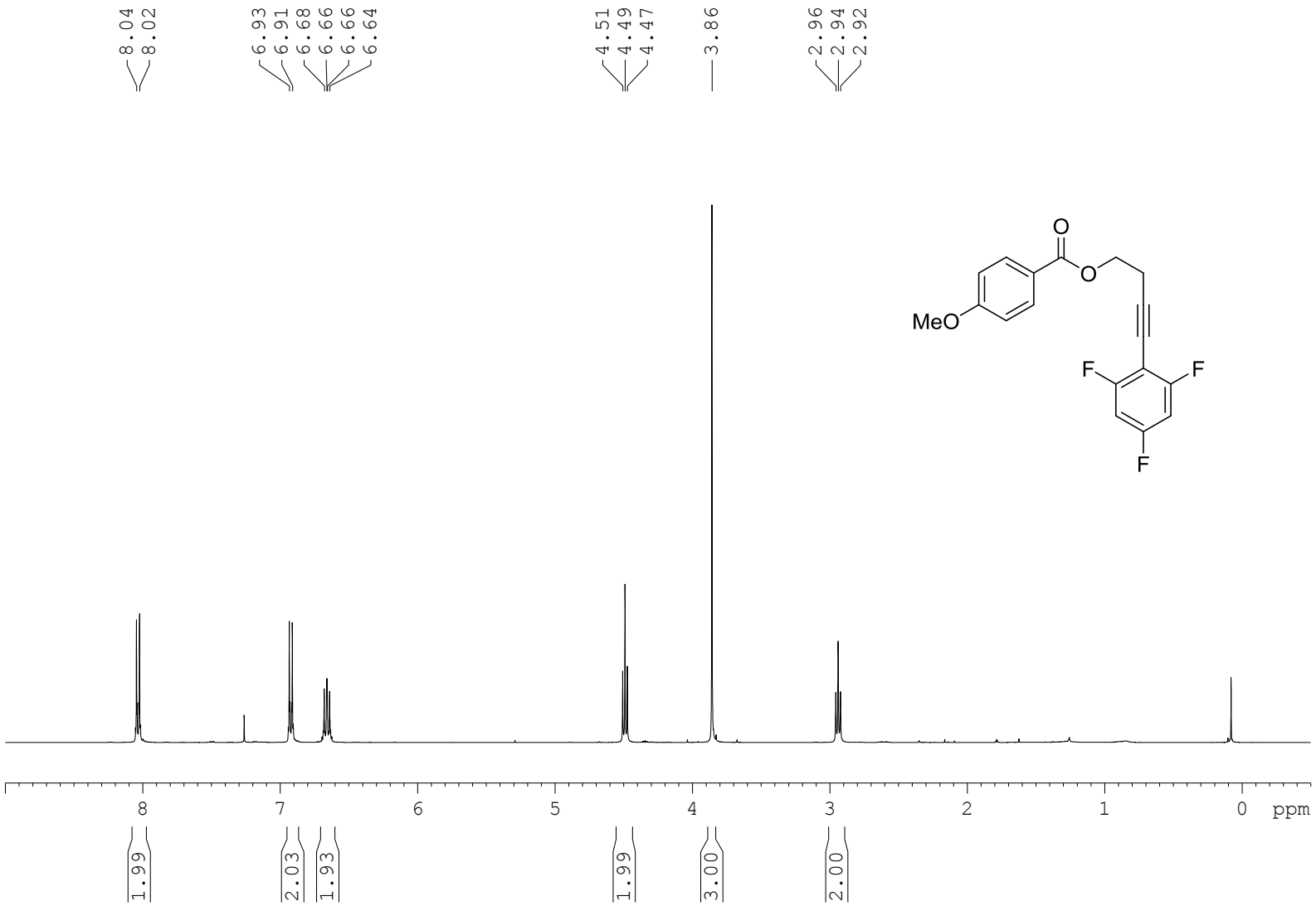
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10o



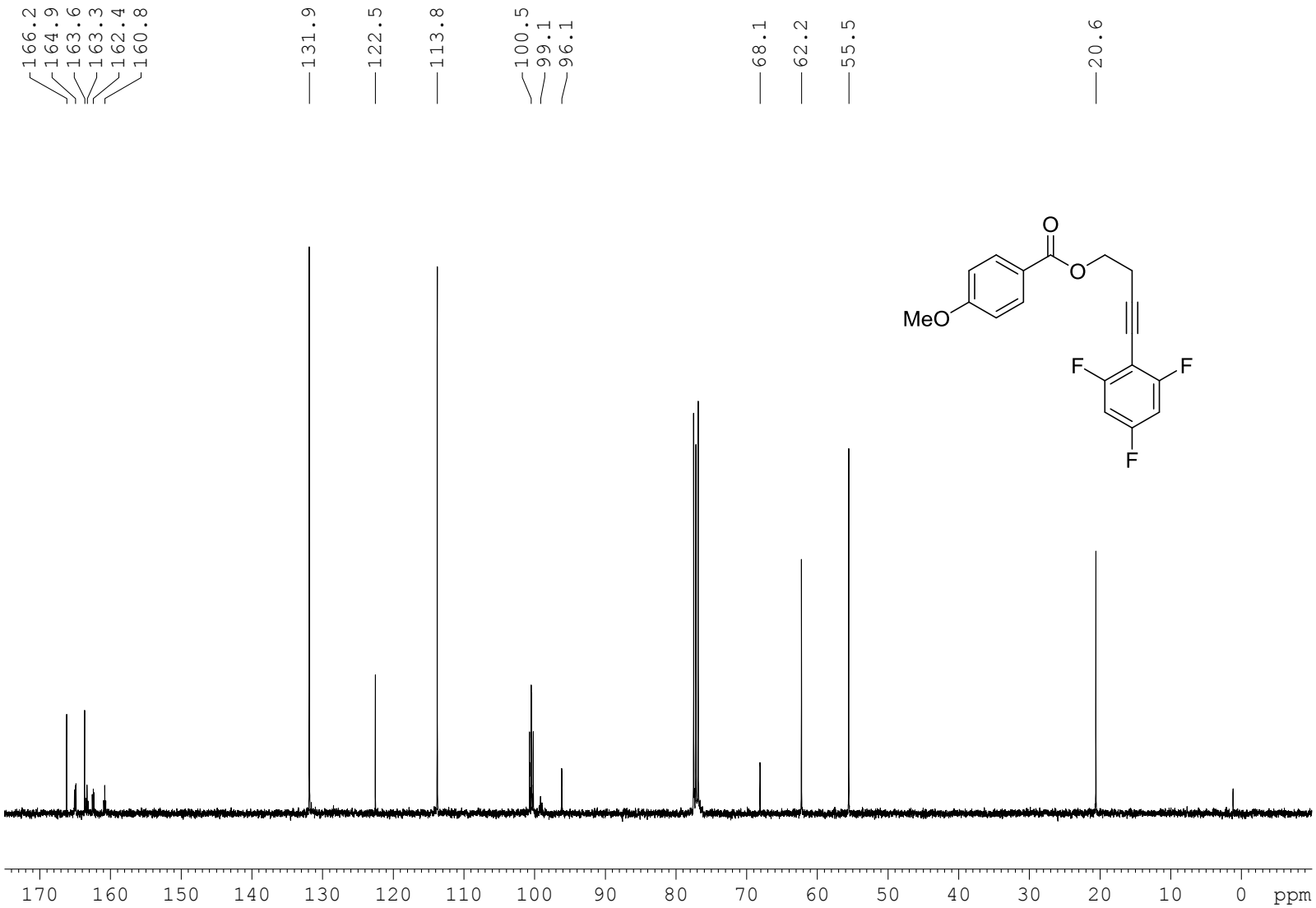
^{19}F NMR (282 MHz, $CDCl_3$) Compound 10o



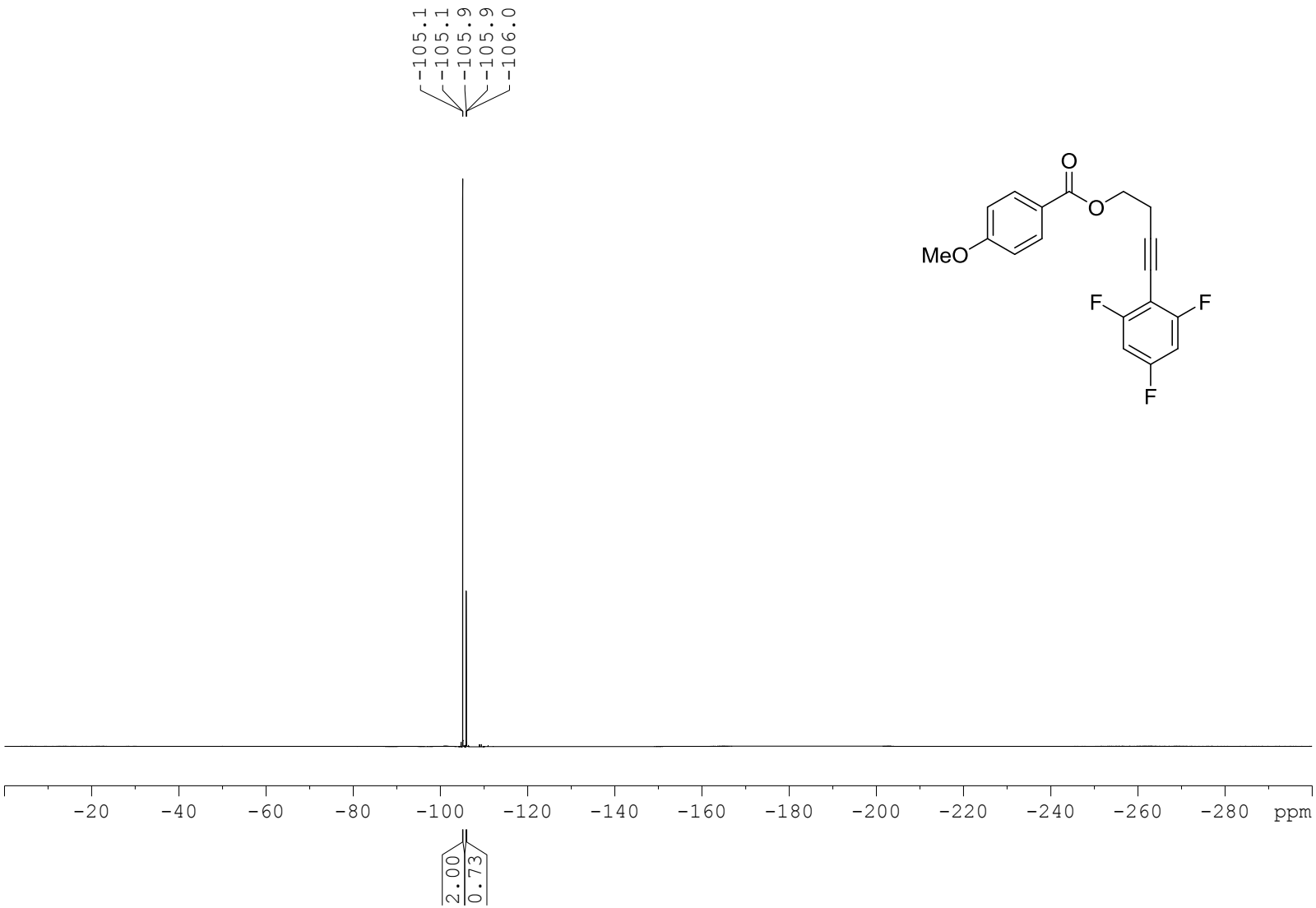
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10p



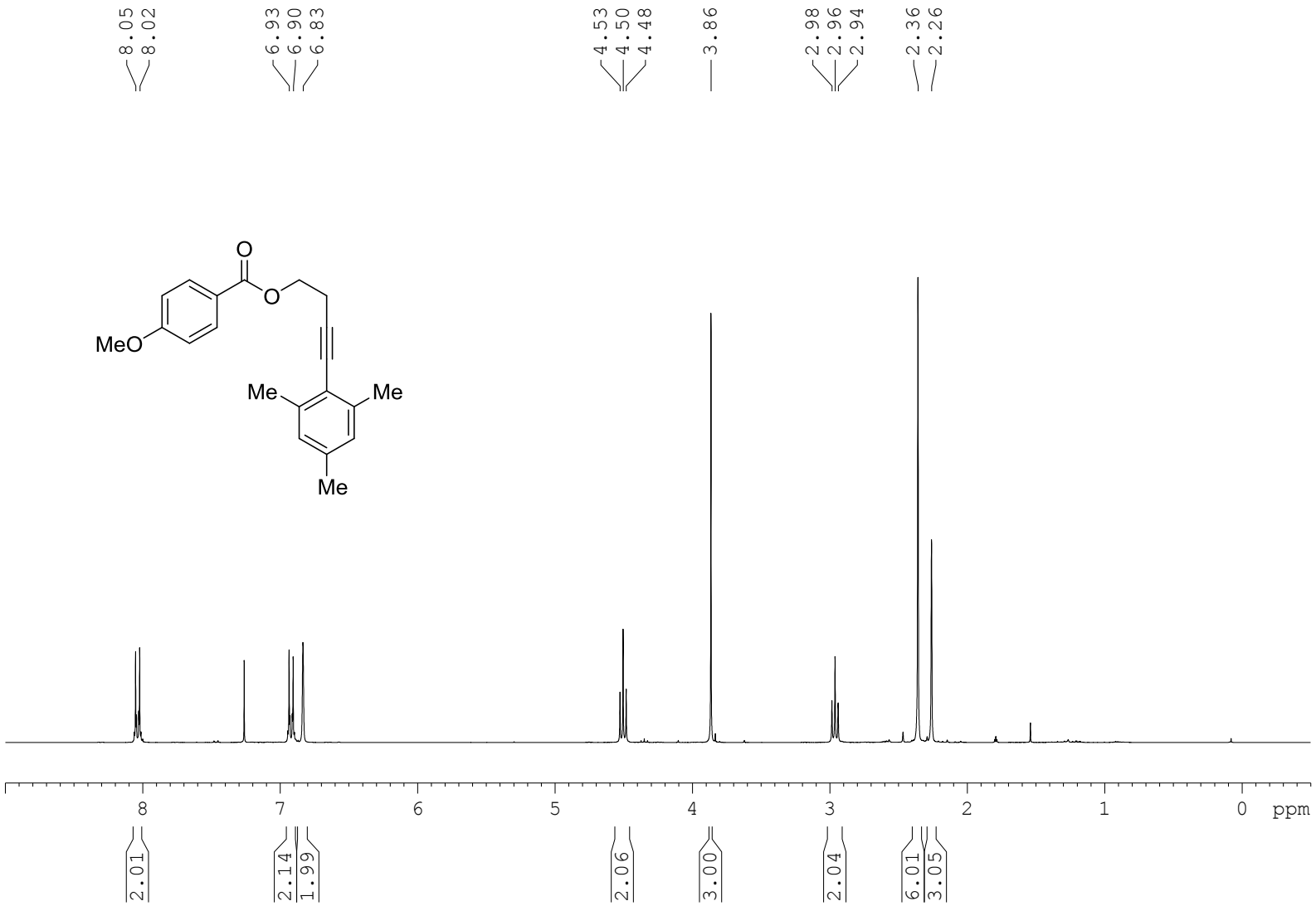
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10p



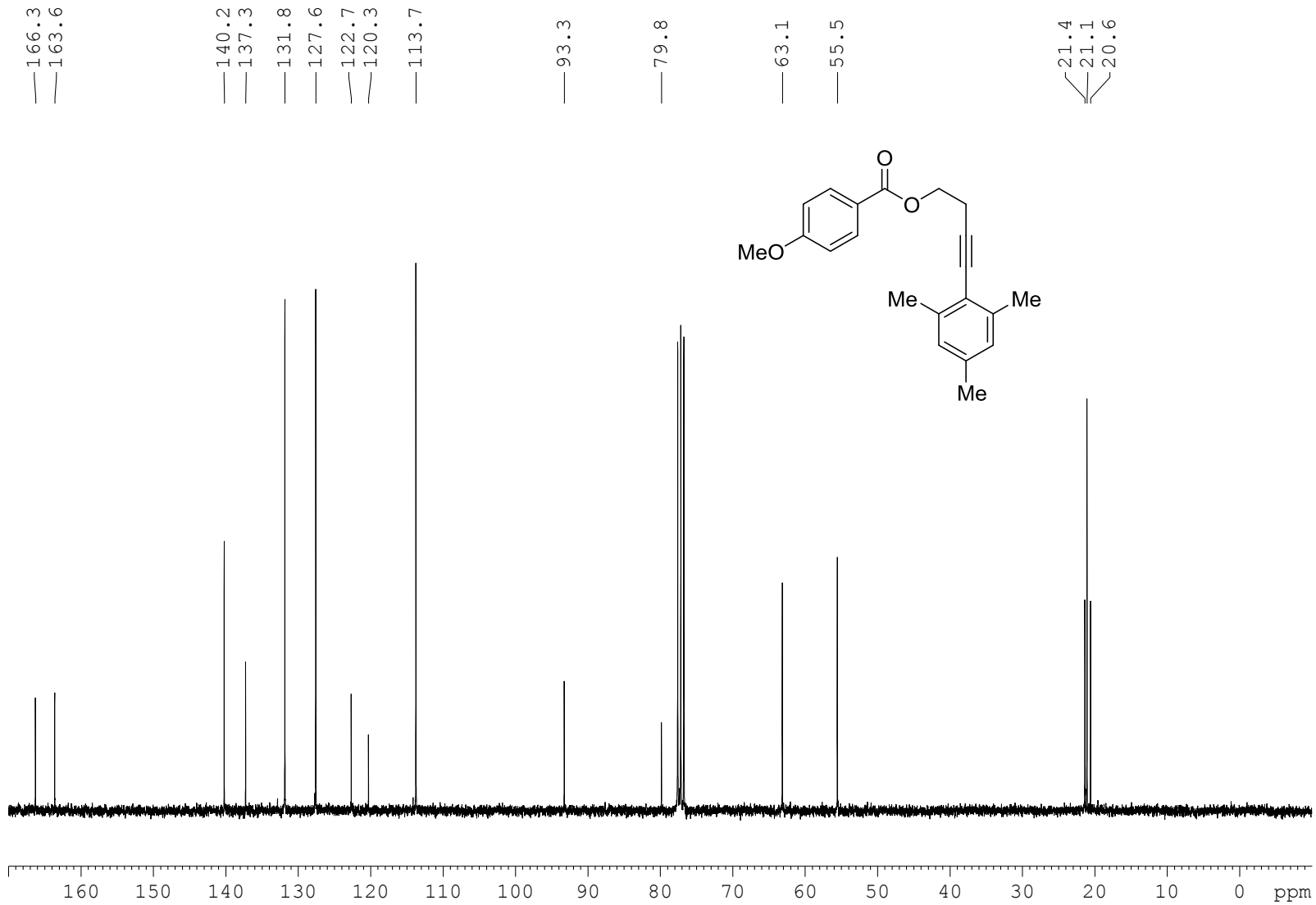
^{19}F NMR (282 MHz, $CDCl_3$) Compound 10p



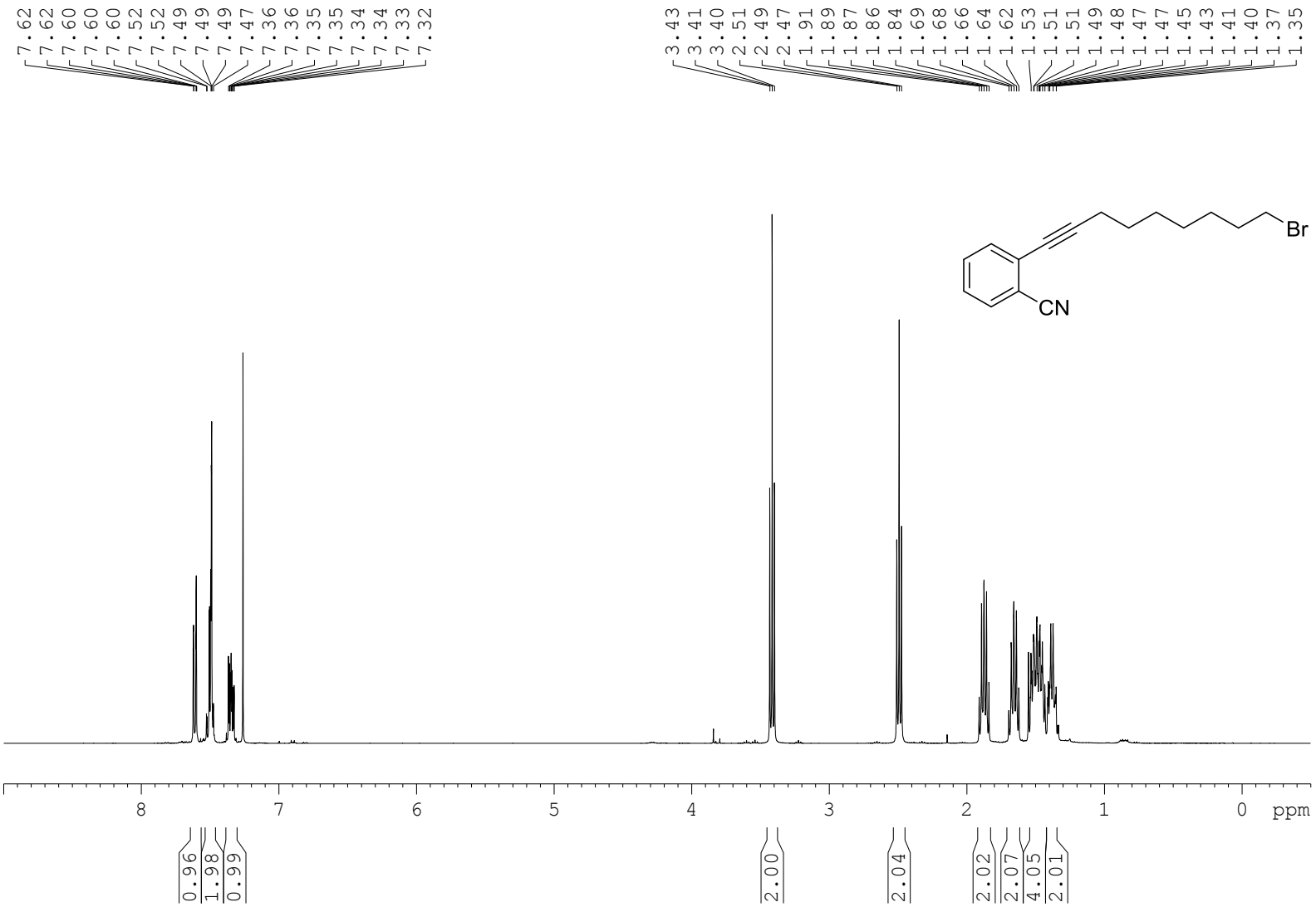
^{1}H NMR (300 MHz, $CDCl_3$) Compound 10q



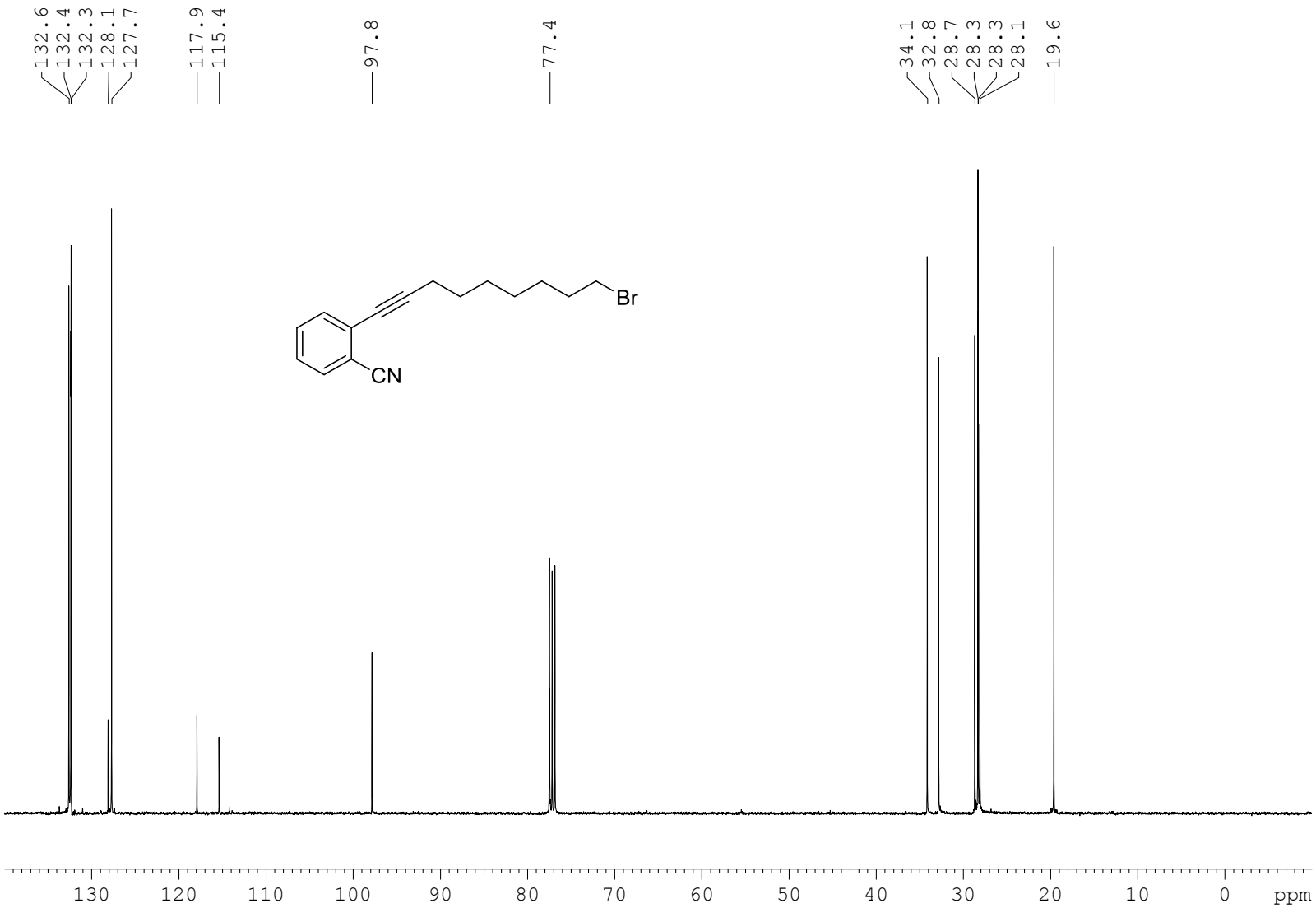
^{13}C NMR (75 MHz, $CDCl_3$) Compound 10q



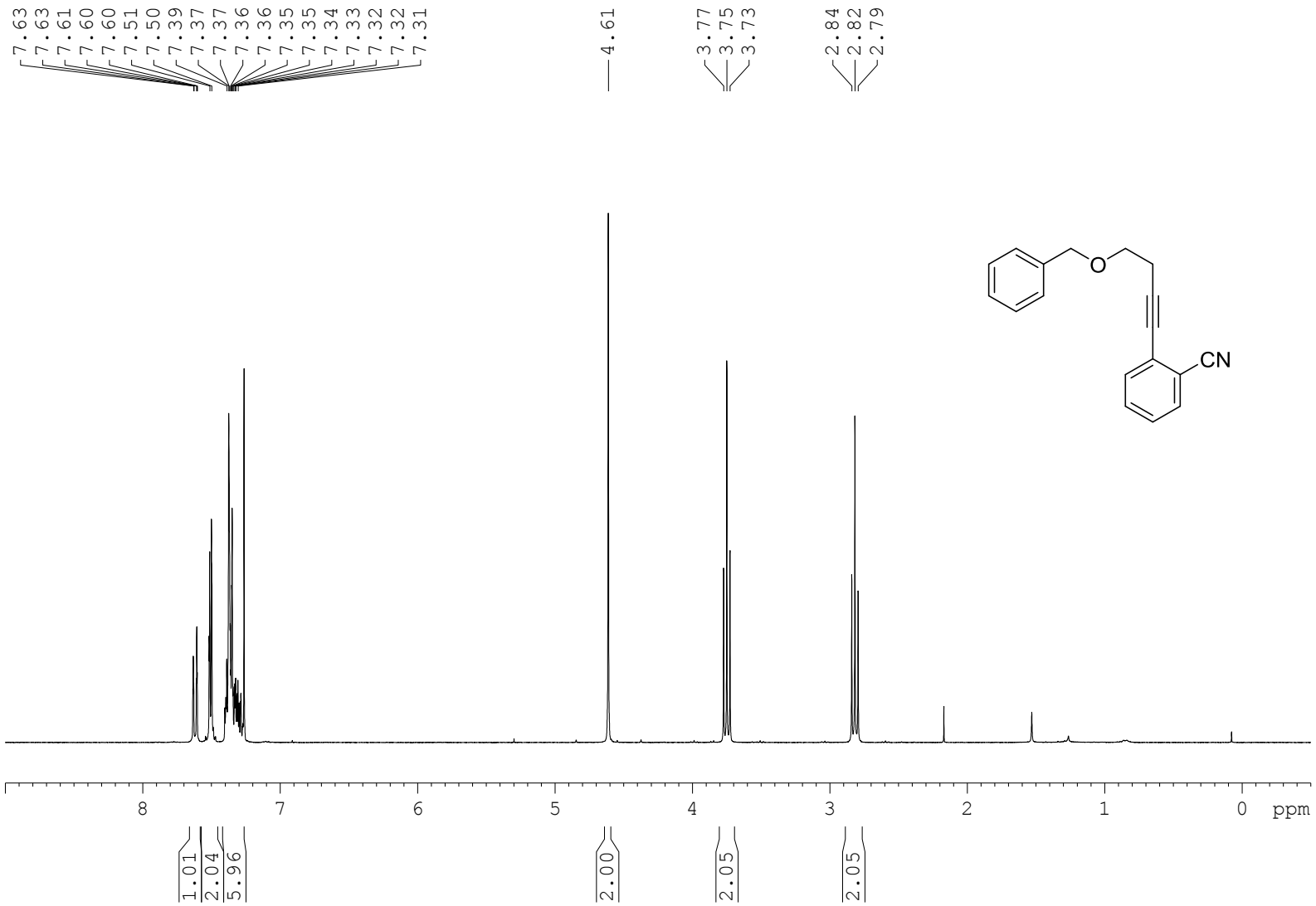
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10r



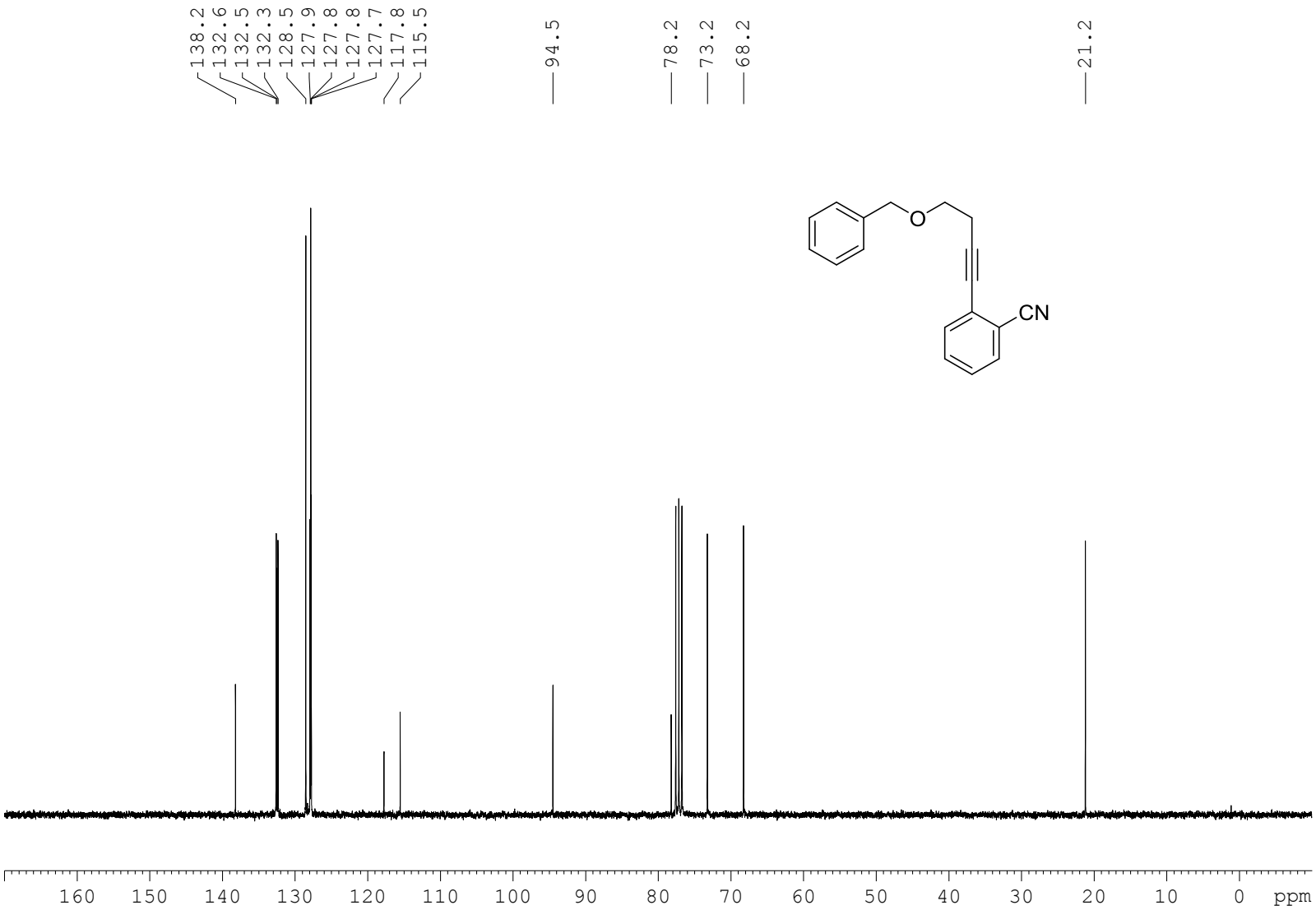
^{13}C NMR (101 MHz, $CDCl_3$) Compound 10r



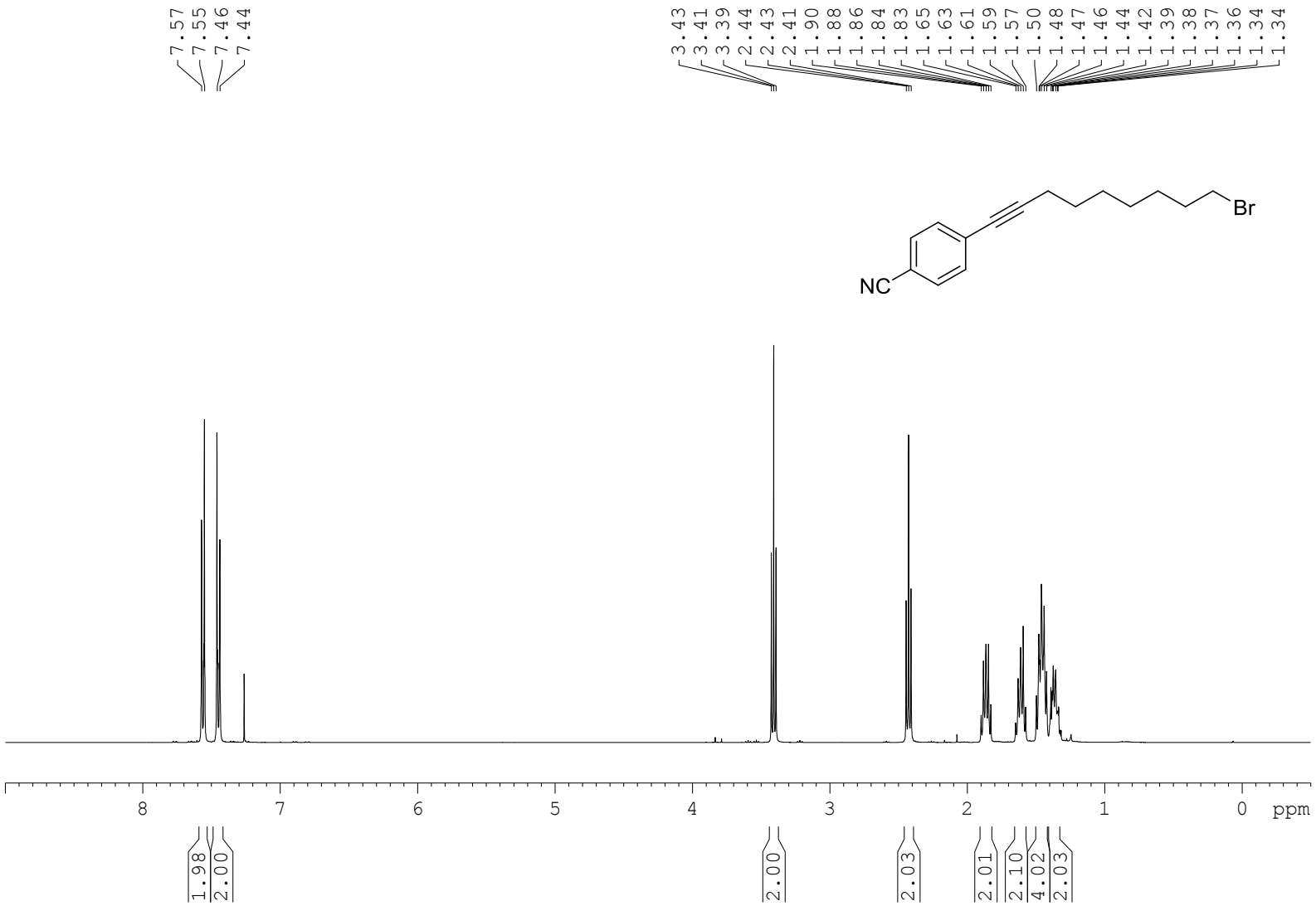
^{1}H NMR (300 MHz, $CDCl_3$) Compound 10s



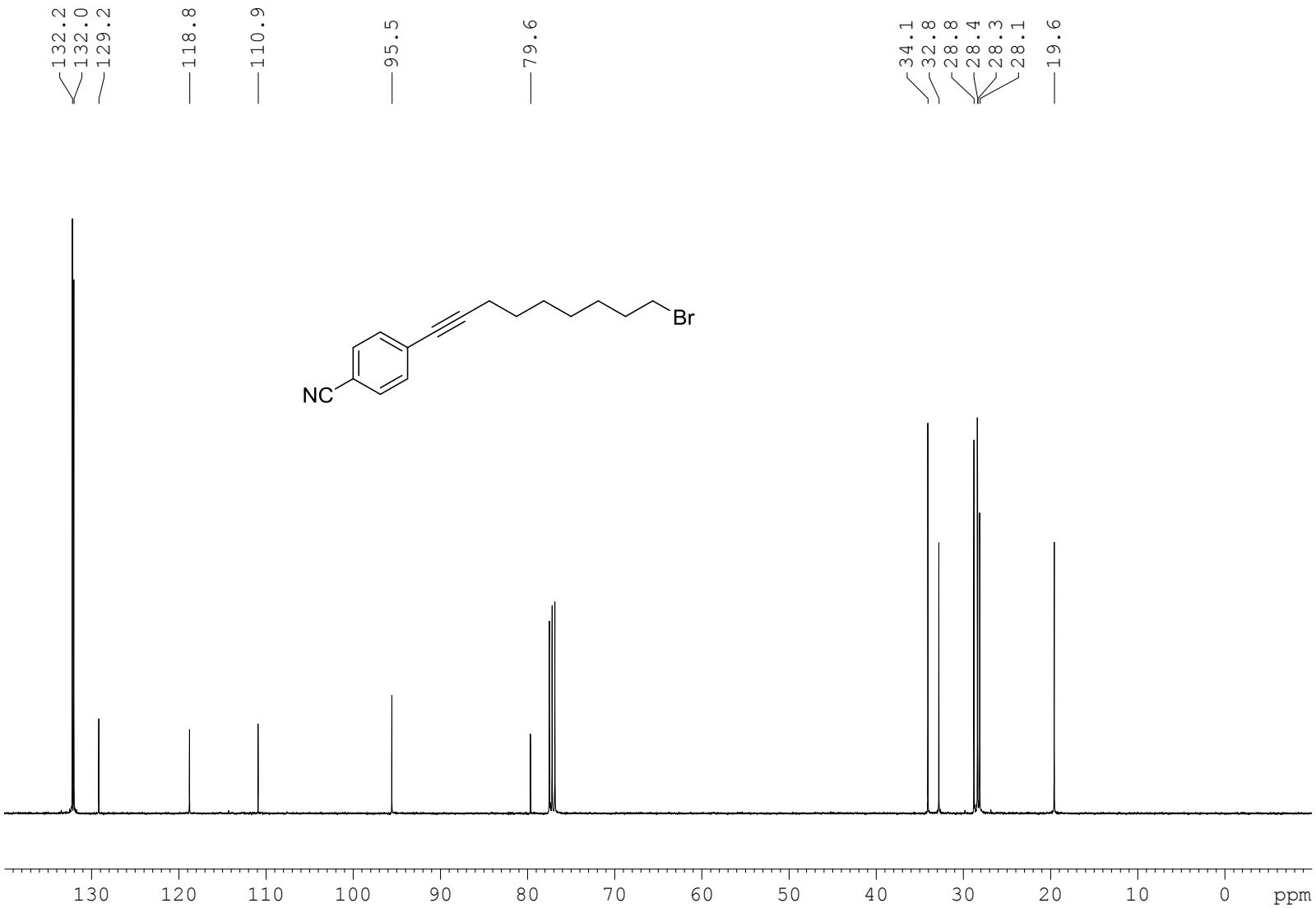
^{13}C NMR (75 MHz, $CDCl_3$) Compound 10s



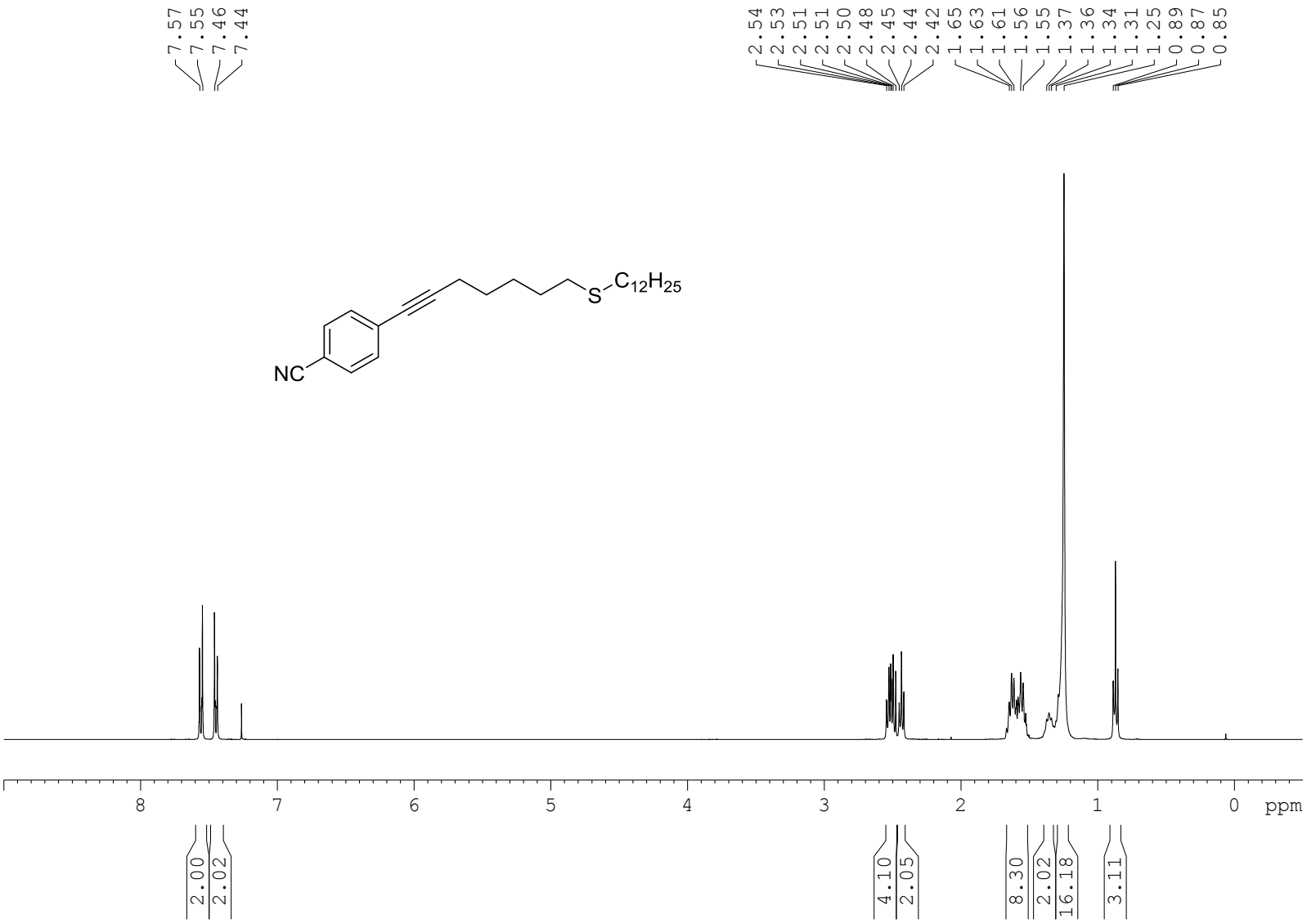
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10t



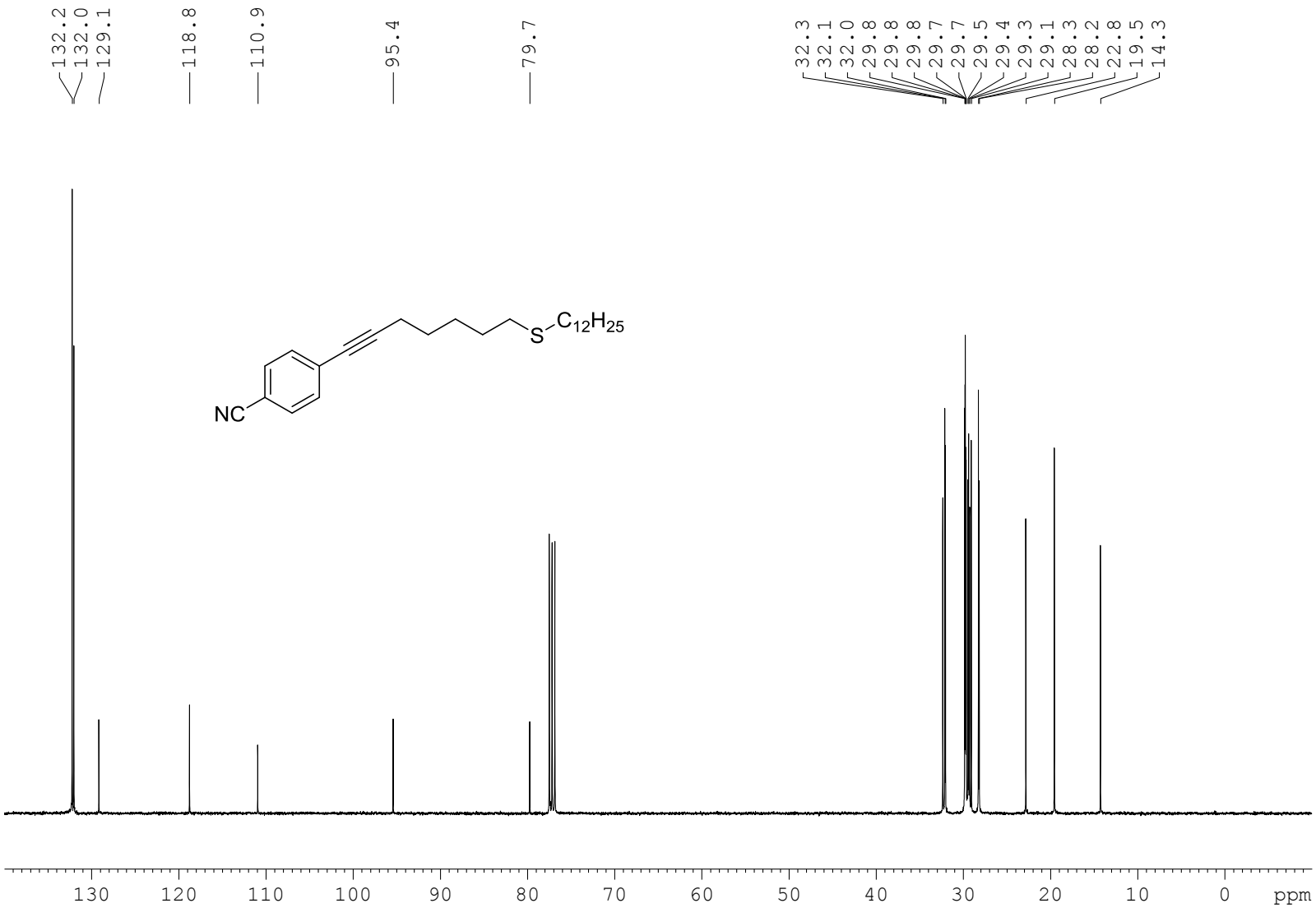
^{19}F NMR (101 MHz, $CDCl_3$) Compound 10t



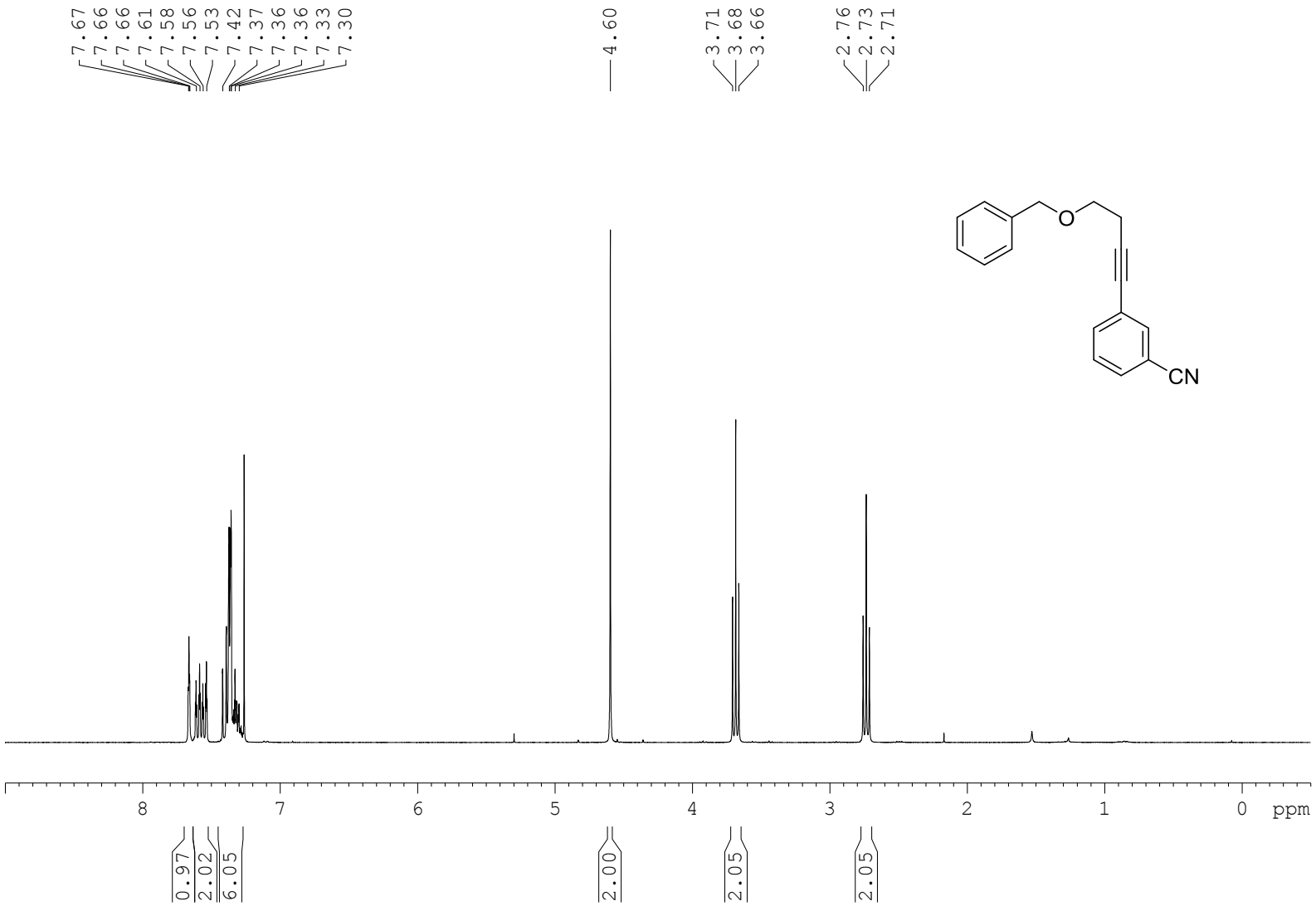
^{1}H NMR (400 MHz, $CDCl_3$) Compound 10u



^{13}C NMR (101 MHz, $CDCl_3$) Compound 10u



^{1}H NMR (300 MHz, $CDCl_3$) Compound 10v



^{13}C NMR (75 MHz, $CDCl_3$) Compound 10v