Advanced Synthesis & Catalysis

Supporting Information

Iron-Catalyzed Cross Coupling of 1-Alkynylcyclopropyl Tosylates and Related Substrates

Daniel J. Tindall, Helga Krause and Alois Fürstner*

Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany

fax: +49 208 306 2994; phone: +49 208 306 2342; email: fuerstner@kofo.mpg.de

Table of Contents

Crystallographic Information

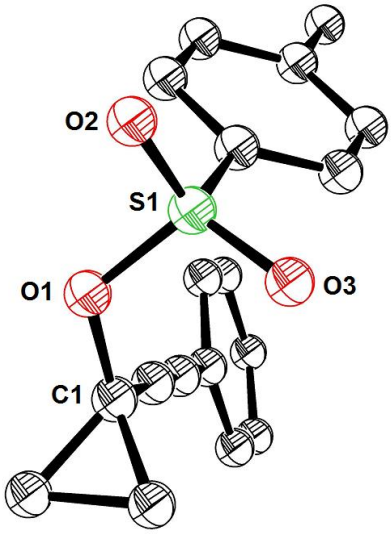


Figure S1. Structure of Compound **1a** in the Solid State

X-ray Crystal Structure Analysis of 9849: C_{18} H_{16} O_3 S, M_r = 312.37 g · mol^{-1}, colorless plate, crystal size 0.341 x 0.173 x 0.010 mm, orthorhombic, space group *Pbca*, a = 7.2040(16) Å, b = 20.271(4) Å, c = 21.103(5) Å, V = 3081.7(12) Å^3, T = 100 K, Z = 8, D_{calc} = 1.347 g·cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.220 mm^{-1}, Empirical absorption correction (T_{min} = 0.95, T_{max} = 1.00), Bruker-AXS Enraf-Nonius KappaCCD diffractometer, 1.930 < θ < 30.616°, 79443 measured reflections, 4735 independent reflections, 3573 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.041 [$I > 2\sigma(I)$], wR_2 = 0.146, 200 parameters, H atoms riding, S = 1.155, residual electron density 0.6 / -0.6 e Å^{-3}. **CCDC 1472161**

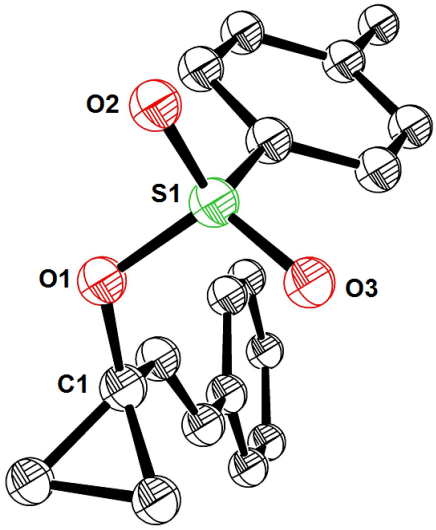


Figure S2. Structure of Compound **16** in the Solid State

X-ray Crystal Structure Analysis of Compound 16: $C_{18}H_{18}O_3S$, M_r = 314.38 g · mol^{-1}, colorless plate, crystal size 0.290 x 0.167 x 0.081 mm, monoclinic, space group $P2_1/c$, a = 21.541(3) Å, b = 7.4591(9) Å, c = 20.595(2) Å, β = 106.055(2)°, V = 3180.1(6) Å^3, T = 200 K, Z = 8, D_{calc} = 1.313 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.213 mm^{-1}, Empirical absorption correction (T_{min} = 0.96, T_{max} = 0.98), Bruker-AXS Enraf-Nonius KappaCCD diffractometer, 2.903 < θ < 31.070°, 91654 measured reflections, 10169 independent reflections, 8602 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.050 [$I > 2\sigma(I)$], wR_2 = 0.145, 399 parameters, H atoms riding, S = 1.059, residual electron density 1.0 / -0.4 e Å^{-3}. **CCDC 1472070**

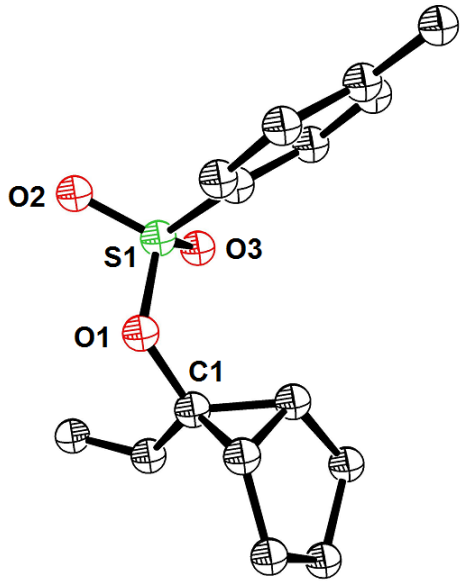


Figure S3. Structure of compound **S11** in the solid state.

X-ray Crystal Structure Analysis of Compound S11: $C_{15}H_{18}O_3S$, M_r = 278.35 g · mol^{-1}, colorless plate, crystal size 0.390 x 0.376 x 0.140 mm, monoclinic, space group $P2_1/c$, a = 6.0865(19) Å, b = 15.313(5) Å, c = 15.003(5) Å, β = 90.171(5)°, V = 1398.3(7) Å^3, T = 100 K, Z = 4, D_{calc} = 1.322 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.233 mm^{-1}, Empirical absorption correction (T_{min} = 0.94, T_{max} = 0.97), Bruker-AXS Enraf-Nonius KappaCCD diffractometer, 3.347 < θ < 36.623°, 54108 measured reflections, 6852 independent reflections, 6046 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.030 [$I > 2\sigma(I)$], wR_2 = 0.092, 173 parameters, H atoms riding, S = 1.051, residual electron density 0.6 / -0.3 e Å^{-3}. **CCDC 1472069**

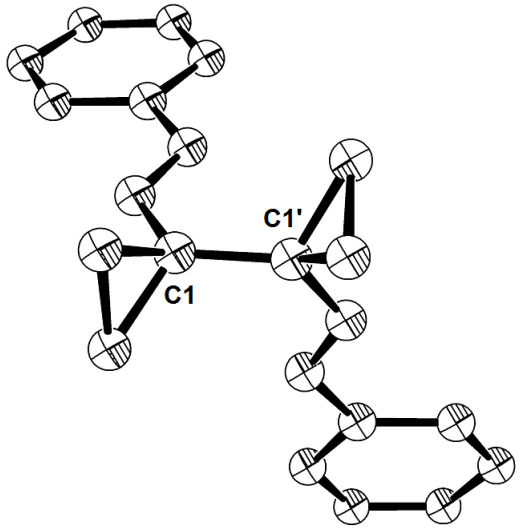


Figure S4. Structure of Compound **20** in the Solid State

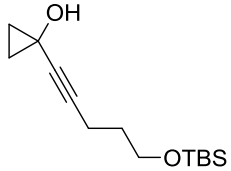
X-ray Crystal Structure Analysis of Compound 20: C_{22} H_{22}, M_r = 286.39 g · mol^{-1}, colorless plate, crystal size 0.180 x 0.100 x 0.030 mm, orthorhombic, space group *Aba2*, a = 11.026(2) Å, b = 21.404(4) Å, c = 7.0746(14) Å, V = 1669.6(6) Å^3, T = 100 K, Z = 4, D_{calc} = 1.139 g·cm^3, λ = 0.71073 Å, μ(*Mo*-K_α) = 0.064 mm^{-1}, Gaussian absorption correction (T_{min} = 0.99, T_{max} = 1.00), Bruker-AXS Smart APEX-II diffractometer, 3.552 < θ < 31.006°, 23686 measured reflections, 2652 independent reflections, 2534 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.033 [$I > 2\sigma(I)$], wR_2 = 0.089, 107 parameters, H atoms riding, S = 1.056, absolute structure parameter = -2.4(10), residual electron density 0.3 / -0.2 e Å^{-3}. **CCDC 1472067**

General

All reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2 (CaH_2), NEt_3 and pyridine were dried by an absorption solvent purification system based on molecular sieves. TMEDA was purified by distillation over CaH_2 and transferred under Ar. **Flash chromatography**: Merck Geduran® Si 60 (40–63 μm) or Merck Silica gel 60 (0.015–0.040 mm). **NMR**: Spectra were recorded on Bruker AV VIII 300, AV 400, or AV 500 spectrometers in the indicated solvents; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 53.84 ppm; residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm); proton and carbon assignments were established using NOESY, HSQC, and HMBC experiments. **IR**: Perkin-Elmer Spectrum One spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. **MS:** EI: Finnigan MAT 8400 (70 eV), ESI: Thermo Scientific LTQ-FT or Thermo Scientific Exactive; GC-EI: Thermo Scientific Trace GC Ultra with a Thermo Scientific ISQ spectrometer; accurate mass determinations: Finnigan MAT 95, Thermo Scientific LTQ FT, or Thermo Scientific Exactive.

Unless stated otherwise, all commercially available compounds (ABCR, Acros, Aldrich) were used as received. $Fe(acac)_3$ was purchased from Aldrich (≥99.9% metals basis). C_2D_5MgBr was prepared according to a literature procedure.[1]

Substrates

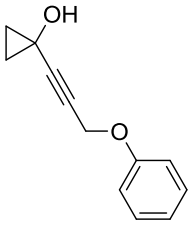
Representative Procedure for the Preparation of 1-Alkynylcyclopropanols. 1-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)cyclopropan-1-ol (S1). 

MeMgCl (2.92 M in THF, 4.2 mL, 12.26 mmol) was added dropwise to a solution of 1-ethoxycyclopropanol (1.24 g, 12.14 mmol)[2] in THF (25 mL) at 0°C. The resulting suspension was stirred at 0 °C for 30 min. In a separate flask, a solution of *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane (2.48 g, 12.50 mmol)[3] in THF (25 mL) was treated at –78 °C with *n*BuLi (1.6 M in hexane, 8.0 mL, 12.80 mmol). The mixture was stirred at –78 °C for 1 h and then transferred via canula into the suspension of the magnesium salt of 1-ethoxycyclopropanol. Stirring was continued at room temperature overnight. The reaction was quenched with sat. aq. NH_4Cl (20 mL) and the aqueous phase extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (20 mL) and brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude material was purified by flash chromatography (silica, hexane/EtOAc, 10:1) to give the title compound as a colorless liquid (2.12 g, 69%). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.67 (t, J = 6.0 Hz, 2 H), 2.29 (t, J = 7.1 Hz, 2 H), 1.73–1.65 (m, 2 H), 1.05–1.00 (m, 2 H), 0.93–0.89 (m, 2 H), 0.89 (s, 9 H), 0.05 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 82.7, 81.8, 61.7, 46.1, 31.8, 26.1, 18.5, 17.3, 15.3, –5.2; IR (film): 3320 (br), 2929, 2953, 2857, 1471, 1234,

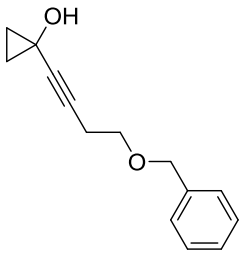
[1] W. M. Czaplik, S. Grupe, M. Mayer, A. Jacobi v. Wangelin, *Chem. Commun.* **2010**, *46*, 6350–6352.
[2] F. Kleinbeck, F. D. Toste, *J. Am. Chem. Soc*. **2009**, *131*, 9178–9179.
[3] E. D. Slack, C. M. Gabriel, B. H. Lipshutz, *Angew. Chem. Int. Ed*. **2014**, *53*, 14051–14054.

1102, 1066, 1007, 962, 831, 774 cm^{-1}; MS (EI): *m*/*z* (%) = 241 (2), 225 (2), 197 (14), 181 (23), 169 (28), 151 (13), 139 (11), 125 (17), 111 (5), 105 (25), 95 (14), 79 (26), 77 (24), 75 (100), 73 (28), 65 (4), 59 (7); HRMS (ESI+): *m*/*z*: calcd. for $C_{14}H_{26}OSiNa$ [M+Na]$^+$: 277.15941; found: 277.15942.

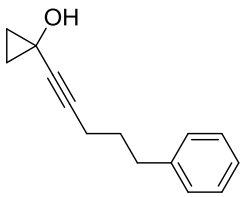
Compound S2. Prepared analogously as a colorless liquid (284 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.24 (m, 2 H), 7.03–6.90 (m, 3 H), 4.71 (s, 2 H), 1.10–1.03 (m, 2 H), 1.02–0.95 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.8, 129.6, 121.6, 115.1, 89.4, 77.6, 56.3, 45.6, 17.5; **IR** (film): $\tilde{\nu}$ = 3366 (br), 1716, 1597, 1493, 1456, 1375, 1302, 1212, 1173, 1054, 1080, 1005, 1028, 989, 970, 751, 690 cm^{-1}; MS (GC-EI, %): *m*/*z* = 188 [M$^+$] (2), 173 (2), 159 (6), 145 (5), 117 (2), 103 (9), 94 (100), 77 (29), 66 (65), 57 (11), 55 (29), 52 (17), 51 (21), 41 (28), 39 (33); HRMS (APPI+): *m*/*z*: calcd. for $C_{12}H_{12}O_2$ [M$^+$]: 188.08318; found: 188.08295.



Compound S3. Prepared analogously as a colorless liquid (593 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.26 (m, 5 H), 4.55 (s, 2 H), 3.57 (t, *J* = 7.0 Hz, 2 H), 2.53 (t, *J* = 7.0 Hz, 2 H), 2.36 (s, 1 H), 1.05–0.98 (m, 2 H), 0.97–0.90 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.2, 128.6, 127.8 (2 C), 82.9, 79.7, 73.1, 68.5, 46.0, 20.4, 17.3; IR (film): $\tilde{\nu}$ = 3379 (br), 2912, 2864, 1354, 1363, 1233, 1096, 1019, 968, 735, 697 cm^{-1}; MS (GC-EI): *m*/*z* (%) = 216 [M$^+$] (<1), 187 (4), 171 (1), 159 (5), 141 (1), 129 (3), 108 (21), 91 (100), 79 (42), 65 (14), 53 (12); HRMS (ESI+): *m*/*z*: calcd. for $C_{14}H_{16}O_2Na$ [M+Na]$^+$: 239.10425; found: 239.10407.



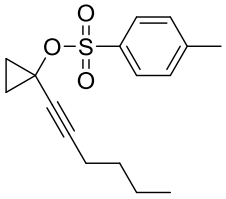
Compound S4. Prepared analogously as a colorless liquid (1.34 g, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.25 (m, 2 H), 7.23–7.15 (m, 3 H), 2.71 (t, *J* = 7.5 Hz, 2 H), 2.29 (s, 1 H), 2.23 (t, *J* = 7.5 Hz, 2 H), 1.83 (q, *J* = 7.5 Hz, 2 H), 1.08–0.99 (m, 2 H), 0.98–0.89 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 141.7, 128.7, 128.5, 126.0, 82.7, 82.4, 46.1, 35.0, 30.4, 18.4, 17.4; IR (film): $\tilde{\nu}$ = 3314 (br), 3026, 2939, 2860, 1496, 1454, 1231, 1019, 968, 744, 698 cm^{-1}; MS (GC-EI): *m*/*z* (%) = 200 [M$^+$] (1), 185 (7), 171 (26), 157 (13), 143 (20), 128 (69), 115 (30), 109 (21), 105 (32), 96 (62), 91 (100), 79 (51), 77 (52), 65 (48), 55 (29); HRMS (ESI+): *m*/*z*: calcd. for $C_{14}H_{16}ONa$ [M+Na]$^+$: 223.10933; found: 223.10943.



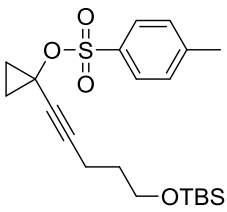
Compound S5. A solution of $LiAlH_4$ (1 M in THF, 3.3 mL, 3.25 mmol) was added dropwise to a solution of compound **S4** (1.04 g, 5.21 mmol) in THF (18.5 mL) and the resulting mixture was stirred at reflux temperature for 1 h. The mixture was cooled in an ice bath and the reaction carefully quenched by slow addition of solid $Na_2SO_4{\cdot}10H_2O$ until gas evolution had ceased. After addition of deionized water (25 mL) the mixture was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by flash chromatography (silica, hexane/*tert*-butyl methyl ether, 10:1⟶1:1) to give the title compound as a colorless oil (903 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.23 (m, 2 H), 7.22–7.14 (m, 3 H), 5.69 (dt, *J* = 15.4 Hz, *J* = 6.8 Hz, 1 H), 5.30 (dt, *J* = 15.4 Hz, *J* = 1.4 Hz, 1 H), 2.64 (t, *J* = 7.7 Hz, 2 H), 2.17–2.06 (m, 2 H), 1.95 (s, 1 H), 1.79–1.67 (m, 2 H), 1.04–0.97 (m, 2 H), 0.72–0.64 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 142.6, 134.3, 128.6, 128.4,

127.0, 125.8, 55.6, 35.5, 31.8, 31.3, 15.9; IR (film): $\tilde{\nu}$ = 3303 (br), 3085, 3025, 2927, 2855, 1496, 1453, 1288, 1214, 1015, 964, 743, 697 cm^{-1}; MS (GC-EI): m/z (%) = 202 [M$^+$] (<1), 155 (2), 145 (5), 130 (25), 111 (13), 107 (17), 105 (13), 98 (30), 91 (100), 83 (63), 79 (12), 77 (17), 65 (18), 55 (21); HRMS (ESI+): m/z: calcd. for $C_{14}H_{18}ONa$ [M+Na]$^+$: 225.12498; found: 225.12507.

Compound 1b. Pyridine (2.7 mL, 33.38 mmol) was added to a solution of 1-(hex-1-yn-1-yl)cyclopropan-1-ol (944 mg, 6.38 mmol)[4] in CH_2Cl_2 (40 mL). After the addition of tosyl chloride (1.52 g, 7.81 mmol) in one portion, the mixture was stirred for 24 h before the reaction was quenched with sat. aq. NH_4Cl. The aqueous phase was extracted with EtOAc, and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 50:1) to give the title compound as a colorless liquid (1.25 g, 63%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.85–7.78 (m, 2 H), 7.40–7.32 (m, 2 H), 2.45 (s, 3 H), 1.98–1.89 (m, 2 H), 1.49–1.43 (m, 2 H), 1.32–1.20 (m, 4 H), 1.10–1.01 (m, 2 H), 0.90–0.80 (m, 3 H); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 145.3, 135.1, 129.9, 128.7, 87.2, 77.1, 55.2, 30.7, 22.3, 21.8, 18.7, 16.5, 13.7; IR (film): $\tilde{\nu}$ = 2299, 3528, 2872, 1365, 1207, 1172, 1095, 1029, 936, 849, 876, 813, 781, 736, 666, 557, 582 cm^{-1}; MS (EI): m/z (%) = 292 [M$^+$] (<1), 250 (13), 237 (12), 199 (3), 186 (6), 171 (4), 155 (64), 139 (24), 137 (10), 119 (8), 109 (74), 91 (100), 81 (12), 79 (24), 77 (8), 67 (17), 65 (16), 53 (9), 41 (12); HRMS (CI): m/z: calcd. for $C_{16}H_{21}O_3S$ [M$^+$]: 293.12114; found: 293.12089.

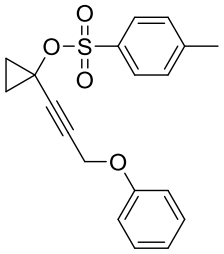


Compound 1c. DMAP (3.80 g, 31.10 mmol) and tosyl chloride (1.90 g, 9.97 mmol) were successively added to a solution of compound **S1** (1.57 g, 6.17 mmol) in CH_2Cl_2 (60 mL). The resulting mixture was stirred at ambient temperature overnight. Sat. aq. NH_4Cl was added and the mixture extracted with EtOAc. The combined extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 20:1) to give the title compound as a colorless liquid (1.91 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.81 (m, 2 H), 7.35–7.29 (m, 2 H), 3.53 (t, J = 6.0 Hz, 2 H), 2.43 (s, 3 H), 2.01 (t, J = 7.2 Hz, 2 H), 1.50–1.42 (m, 4 H), 1.09–1.04 (m, 2 H), 0.87 (s, 9 H), 0.02 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 144.7, 134.9, 129.5, 128.6, 86.5, 77.0, 61.6, 54.9, 31.3, 26.1, 21.8, 18.5, 16.4, 15.3, −5.2; IR (film): $\tilde{\nu}$ = 2922, 9954, 2857, 1366, 1253, 1208, 1173, 1096, 1063, 938, 834, 813, 776, 741, 666, 558, 583 cm^{-1}; MS (EI): m/z (%) = 351 (34), 333 (10), 307 (29), 253 (7), 229 (96), 213 (8), 195 (41), 181 (15), 169 (20), 155 (50), 149 (24), 139 (17), 125 (18), 122 (17), 111 (12), 105 (28), 93 (16), 91 (100), 79 (20), 77 (22), 75 (52), 73 (66), 65 (25); **HRMS** (ESI+): m/z: calcd. for $C_{21}H_{32}O_{24}SSiNa$ [M+Na]$^+$: 431.16828; found: 431.16848.

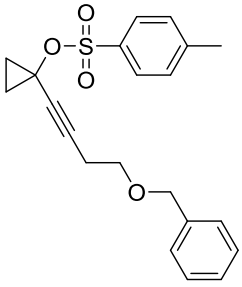


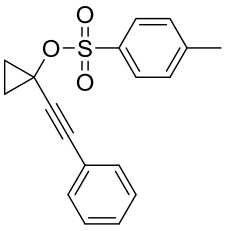
[4] J. Ollivier, P. Dorizon, P. P. Pirasa, A. de Meijere, J. Salaün, *Inorg. Chim. Acta* **1994**, *222*, 37–49.

Compound 1d. Prepared analogously as a colorless liquid (316 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86–7.77 (m, 2 H), 7.32–7.21 (m, 4 H), 7.01–6.92 (m, 1 H), 6.85–6.77 (m, 2 H), 4.42 (s, 2 H), 2.38 (s, 3 H), 1.54–1.44 (m, 2 H), 1.18–1.08 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.8, 145.1, 134.5, 129.6 (2 C), 128.7, 121.7, 115.0, 84.5, 81.0, 56.0, 53.8, 21.8, 16.7; IR (film): $\tilde{\nu}$ = 2921, 1598, 1494, 1365, 1212, 1171, 941, 874, 734, 688, 556 cm^{-1}; MS (GC-EI): m/z (%) = 342 [M$^+$] (1), 248 (6), 187 (19), 170 (73), 155 (100), 145 (6), 139 (45), 131 (9), 115 (3), 103 (13), 91 (86), 77 (11), 65 (13), 52 (3); HRMS (ESI+): m/z: calcd. for $C_{19}H_{18}O_4SNa$ [M+Na]$^+$: 365.08180; found: 365.08175.

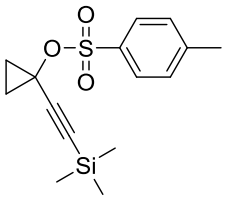


Compound 1e. Et_3N (0.47 mL, 3.27 mmol) was added dropwise to a solution of compound **S3** (590 mg, 2.73 mmol) in CH_2Cl_2 (9 mL), followed by addition of DMAP (333 mg, 2.73 mmol). After stirring for half an hour, tosyl chloride (690 mg, 3.55 mmol) was added in one portion and stirring continued overnight. The yellow suspension was concentrated in vacuo to a volume of approximately 3 mL before it was diluted with deionized water (8 mL) and extracted with Et_2O (8 mL). The aqueous layer was diluted with a sat. aq. NH_4Cl (5 mL) and extracted with Et_2O (6 × 5 mL). The combined organic layers were washed with deionized water (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/*tert*-butyl methyl ether, 5:1) to give the title compound as a colorless oil (735 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.81 (m, 2 H), 7.39–7.24 (m, 7 H), 4.49 (s, 2 H), 3.36 (t, J = 7.2 Hz, 2 H), 2.41 (s, 3 H), 2.26 (t, J = 7.2 Hz, 2 H), 1.50–1.44 (m, 2 H), 1.12–1.06 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 144.7, 138.1, 134.9, 129.5, 128.6 (2 C), 127.9, 127.8, 83.4, 78.1, 73.1, 68.0, 54.7, 21.8, 20.3, 16.4; IR (film): $\tilde{\nu}$ = 3064, 2864, 1365, 1174, 1096, 937, 741, 559 cm^{-1}; MS (EI): m/z (%) = 215 (9), 197 (5), 183 (5), 170 (3), 155 (12), 143 (3), 139 (5), 129 (4), 109 (4), 105 (4), 91 (100), 65 (5), 55 (1); HRMS (ESI+): m/z: calcd. for $C_{21}H_{22}O_4SNa$ [M+Na]$^+$: 393.11310; found: 393.11307.





Compound 1a. Prepared analogously; the spectral data matched those previously reported in the literature.[5] Crystals suitable for X-ray diffraction were grown by slow evaporation from a solution in *tert*-butyl methyl ether. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.88–7.83 (m, 2 H), 7.34–7.23 (m, 5 H), 7.14–7.08 (m, 2 H), 2.31 (s, 3 H), 1.64–1.57 (m, 2 H), 1.28–1.22 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 145.7, 134.7, 131.9, 130.0, 129.0, 128.8, 128.5, 122.2, 86.1, 85.7, 54.9, 21.7, 17.0.

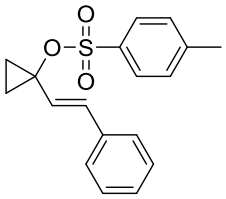


Compound 1f. Prepared analogously as a colorless oil (893 mg, 91%).[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.83 (m, 2 H), 7.36–7.30 (m, 2 H), 2.45 (s, 3 H), 1.59–1.54 (m, 2 H), 1.21–1.16 (m, 2 H), 0.00 (s, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 144.9, 134.6, 129.7, 128.6, 101.4, 90.8, 54.6, 21.9, 17.1, −0.3; IR (film): $\tilde{\nu}$ = 2961, 2173, 1599, 1368, 1300, 1250, 1205, 1171, 1095, 932, 841, 809, 760, 716, 659, 593, 558, 533 cm^{-1}; MS (GC-EI): m/z (%) = 293 (4), 253 (3), 229 (15), 197 (2), 173 (4), 165 (2), 155 (27), 153 (15), 149 (19), 139 (10), 138 (15), 125 (53), 123 (92), 97 (49),

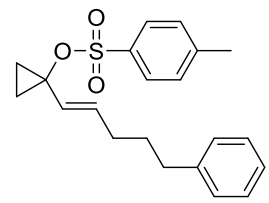
[5] J. Salaün, *J. Org. Chem.* **1976**, *41*, 1237–1240.
[6] S. Bräse, S. Schömenauer, G. McGaffin, A. Stolle, A. de Meijere, *Chem. Eur. J.* **1996**, *2*, 545–555.

95 (15), 91 (75), 83 (18), 75 (33), 73 (100), 67 (13), 65 (19), 59 (33), 53 (10), 45 (14), 43 (15); HRMS (ESI+): *m*/*z*: calcd. for $C_{15}H_{20}O_3SSiNa$ [M+Na]$^+$: 331.07947; found: 331.07952.

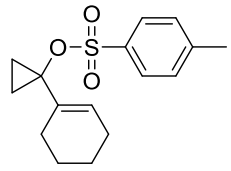
Compound 16. Prepared analogously; the data matched those previously reported in the literature.[7] Crystals suitable for X-ray diffraction were grown by slow evaporation from a solution in *tert*-butyl methyl ether. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.79–7.73 (m, 2 H), 7.32–7.16 (m, 7 H), 6.33 (d, *J* = 16.0 Hz, 1 H), 6.15 (d, *J* = 16.0 Hz, 1 H), 2.35 (s, 3 H), 1.46–1.40 (m, 2 H), 1.06–1.00 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 145.5, 136.4, 135.2, 130.1, 129.6, 128.9, 128.4, 128.2, 127.6, 126.7, 65.9, 21.7, 14.2.



Compound S6. Prepared analogously as a colorless oil (1.25 g, 3.50 mmol, 80%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.76–7.69 (m, 2 H), 7.35–7.23 (m, 4 H), 7.22–7.12 (m, 3 H), 5.58–5.53 (m, 2 H), 2.55 (t, *J* = 7.7 Hz, 2 H), 2.40 (s, 3 H), 1.99–1.90 (m, 2 H), 1.64–1.52 (m, 2 H), 1.32–1.24 (m, 2 H), 0.90–0.81 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 145.2, 142.9, 135.8, 132.0, 130.1, 128.8, 128.7, 128.3 (2 C), 126.1, 66.0, 35.7, 31.8, 31.0, 21.7, 13.6; IR (film): $\tilde{\nu}$ = 3026, 2928, 2857, 1361, 1194, 1171, 1094, 909, 812, 699, 553 cm^{-1}; MS (EI): *m*/*z* (%) = 237 (12), 201 [M−Ts]$^+$ (28), 183 (15), 169 (6), 155 (51), 143 (19), 131 (12), 117 (9), 105 (12), 91 (100), 79 (7), 65 (7); HRMS (ESI+): *m*/*z*: calcd. for $C_{21}H_{24}O_3SNa$ [M+Na]$^+$: 379.13384; found: 379.13414.

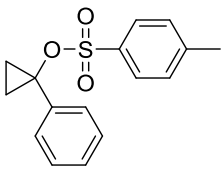


Compound S7. Prepared analogously from 1-phenethylcyclopropan-1-ol (335 mg, 2.06 mmol)[8] in CH_2Cl_2 (6.6 mL), as a colorless oil (561 mg, 86%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.84–7.77 (m, 2 H), 7.40–7.34 (m, 2 H), 7.28–7.21 (m, 2 H), 7.20–7.13 (m, 1 H), 7.11–7.05 (m, 2 H), 2.80–2.71 (m, 2 H), 2.46 (s, 3 H), 2.03–1.95 (m, 2 H), 1.12–1.05 (m, 2 H), 0.62–0.55 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 145.4, 141.9, 136.0, 130.3, 128.8, 128.7, 128.0, 126.3, 67.2, 38.5, 32.2, 21.8, 12.1; IR (film): $\tilde{\nu}$ = 3031, 2951, 2861, 1595, 1359, 1170, 1093, 1032, 838, 807, 710, 697, 553 cm^{-1}; **MS** (EI): *m*/*z* (%) = 316 [M$^+$] (<1), 252 (1), 161 (32), 155 (24), 144 (16), 133 (18), 105 (60), 91 (100), 77 (7), 65 (10), 55 (7), 39 (3); HRMS (ESI+): *m*/*z*: calcd. for $C_{18}H_{20}O_3SNa$ [M+Na]$^+$: 339.10254; found: 339.10242.



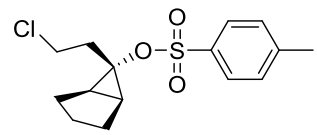
Compound S8. Prepared according to a literature procedure.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 2 H), 7.32–7.27 (m, 2 H), 5.72–5.67 (m, 1 H), 2.43 (s, 3 H), 1.86–1.77 (m, 4 H), 1.32–1.18 (m, 6 H), 0.85–0.78 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 144.3, 135.4, 133.3, 129.4, 128.5, 127.9, 69.9, 25.5, 24.9, 22.0, 21.8 (2 C), 11.7.

[7] A. Stolle, J. Ollivier, P. P. Piras, J. Salaün, A. de Meijere, *J. Am. Chem. Soc*. **1992**, *114*, 4051–4067.
[8] a) D. Rosa, A. Orellana, *Chem. Commun*. **2013**, *49*, 5420–5422; b) S. Ren, C. Feng, T.-P. Loh, *Org. Biomol. Chem*. **2015**, *13*, 5105–5109.
[9] L. G. Quan, H. G. Lee, J. K. Cha, *Org. Lett*. **2007**, *9*, 4439–4442.



Compound S9. Prepared according to a literature procedure.[10] ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.52–7.46 (m, 2 H), 7.31–7.25 (m, 2 H), 7.24–7.18 (m, 3 H), 7.18–7.13 (m, 2 H), 2.37 (s, 3 H), 1.58–1.52 (m ,2 H), 1.17–1.11 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 144.9, 138.3, 135.3, 129.8, 128.5, 128.3, 128.1, 127.9, 67.3, 21.7, 13.9.

Compound S10. Et_3N (0.23 mL, 1.64 mmol) was added dropwise to a solution of *exo*-6-(2-chloroethyl)bicyclo[3.1.0]hexan-6-ol (220 mg, 1.37 mmol)[11] in CH_2Cl_2 (4.4 mL), followed by addition of DMAP (167 mg, 1.37 mmol). After stirring for half an hour at ambient temperature, tosyl chloride (346 mg, 1.78 mmol) was added in one portion and the mixture was stirred overnight. The brown mixture was concentrated in vacuo and the residue was purified by flash chromatography (silica, hexane/*tert*-butyl methyl ether, 10:1) to give the title compound as a colorless liquid (398 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.72 (m, 2 H), 7.37–7.29 (m, 2 H), 3.68 (t, J = 7.5 Hz, 2 H), 2.45 (s, 3 H), 2.25 (t, J = 7.5 Hz, 2 H), 2.08–1.88 (m, 4 H), 1.83–1.70 (m, 3 H), 1.51–1.35 (m, 1 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 144.8, 135.7, 130.0, 127.5, 72.1, 40.8, 31.8, 30.4, 26.4, 25.9, 21.8; IR (film): $\tilde{\nu}$ = 2960, 2873, 1343, 1189, 1169, 1092, 851, 684, 662, 577 cm^{-1}; MS (EI): m/z (%) = 198 (6), 159 (22), 142 (10), 139 (11), 119 (9), 108 (3), 93 (30), 91 (100), 79 (4), 67 (11), 65 (14), 63 (26), 40 (10); HRMS (ESI+): m/z: calcd. for $C_{15}H_{19}ClO_3SNa$ $[M+Na]^+$: 337.06357; found: 337.06330.

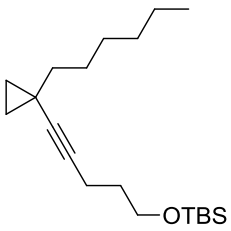


Compound S11. KO*t*Bu (184 mg, 1.91 mmol) were added to a solution of compound **S10** (400 mg, 1.27 mmol) in THF (5 mL) and the resulting yellow suspension was stirred at reflux temperature for 1.5 h. The mixture was concentrated in vacuo to a volume of approximately 2 mL, before it was diluted with deionized water (4 mL), and extracted with *tert*-butyl methyl ether (3 × 5 mL). The aqueous layer was diluted with sat. aq. NH_4Cl (2.5 mL) and extracted with *tert*-butyl methyl ether (3 × 5 mL). The combined extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/*tert*-butyl methyl ether, 10:1) to give the title compound as a colorless solid (226 mg, 64%).[12] Crystals suitable for X-ray diffraction analysis were grown by slow evaporation from a solution in hexane/*tert*-butyl methyl ether (10:1). m.p. = 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.72 (m, 2 H), 7.33–7.27 (m, 2 H), 5.81 (dd, J = 17.4 Hz, J = 10.6 Hz, 1 H), 5.51 (dd, J = 17.4 Hz, J = 1.5 Hz, 1 H), 5.34 (dd, J = 10.6 Hz, J = 1.4 Hz, 1 H), 2.43 (s, 3 H), 2.08–2.02 (m, 2 H), 1.96–1.85 (m, 2 H), 1.83–1.73 (m, 2 H), 1.68–1.56 (m, 1 H), 1.31–1.17 (m, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 144.4, 136.0, 130.0, 129.7, 127.8, 121.7, 70.6, 31.7, 26.4, 23.7, 21.8; IR (solid): $\tilde{\nu}$ = 3055, 2924, 2873, 1357, 1170, 1095, 996, 861, 813, 633, 553 cm^{-1}; MS (EI): m/z (%) = 214 (1), 162 (6), 155 (10), 139 (4), 123 (27), 106 (7), 95 (19), 91 (32), 67 (9), 55 (100), 41 (4); HRMS (ESI+): m/z: calcd. for $C_{15}H_{18}O_3SNa$ $[M+Na]^+$: 301.08689; found: 301.08703.

[10] J. Salaün, *J. Org. Chem*. **1978**, *43*, 2809–2815.
[11] F. Lecornué, J. Ollivier, *Chem. Commun*. **2003**, 584–585.
[12] F. Lecornué, F. Charnay-Pouget, J. Ollivier, *Synlett* **2006**, 1407–1409.

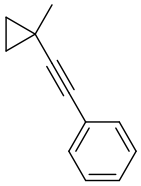
Iron Catalyzed Cross-Coupling Reactions

Representative Procedure for the Iron Catalyzed Cross-Coupling Reactions. *tert*-butyl((5-(1-hexylcyclopropyl)pent-4-yn-1-yl)oxy)-dimethylsilane (2j) (Table 1, entry 11). Method A. Hexylmagnesium bromide (2 M in THF, 0.24 mL, 0.480 mmol) was added dropwise over the course of 5 min to an orange solution of tosylate **1c** (152 mg, 0.372 mmol) and $Fe(acac)_3$ (7 mg, 5 mol%, 0.020 mmol) in THF (4 mL) at −20 °C. After stirring for 10 min at this temperature, the brown mixture was diluted with sat. aq. NH_4Cl (5 mL) and the aqueous phase extracted with EtOAc (3 × 5 mL). The combined extracts were dried over Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (silica, hexane) to give the title compound as a colorless liquid (96 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68 (t, J = 6.2 Hz, 2 H), 2.21 (t, J = 7.0 Hz, 2 H), 1.70–1.62 (m, 2 H), 1.57–1.47 (m, 2 H), 1.35–1.23 (m, 8 H), 0.89 (s, 9 H), 0.88 (t, J = 7.0 Hz, 3 H), 0.79–0.75 (m, 2 H), 0.52–0.47 (m, 2 H), 0.05 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 85.4, 76.0, 61.9, 38.7, 32.3, 32.1, 29.3, 28.0, 26.1, 22.8, 18.5, 15.3, 15.2, 14.3, 12.1, −5.2; IR (film): $\tilde{\nu}$ = 2954, 2927, 2856, 1470, 1463, 1254, 1103, 833, 774 cm^{-1}; MS (EI): m/z (%) = 307 (<1), 265 (100), 235 (1), 191 (14), 189 (38), 161 (6), 151 (5), 139 (3), 133 (4), 119 (26), 105 (16), 101 (18), 93 (11), 91 (19), 79 (13), 75 (96), 59 (15), 43 (11); HRMS (ESI+): m/z: calcd. for $C_{20}H_{38}OSiNa$ $[M+Na]^+$: 345.25841; found: 345.25853.



(*E*)-(2-(1-Methylcyclopropyl)vinyl)benzene (17). Method B. A solution of tosylate **16** (60 mg, 0.191 mmol) and $Fe(acac)_3$ (3.4 mg, 5 mol%, 0.010 mmol) in THF (1.9 mL) was cooled in an ice bath. A premixed solution of MeMgCl (0.5 M in THF, 0.46 mL, 0.229 mmol) and TMEDA (34 µL, 0.229 mmol) was added *via* syringe pump over the course of 30 min. The resulting brown-red solution was stirred at 0°C for 2.5 h. The reaction was quenched with sat. aq. NH_4Cl (3 mL) and deionized water (1.5 mL), and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 4 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (silica, pentane/Et_2O, 100:1) to give compound **17** as a colorless liquid (24 mg, 79%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.36–7.23 (m, 2 H), 7.20–7.12 (m, 3 H), 6.34 (d, J = 16.0 Hz, 1 H), 5.86 (d, J = 16.0 Hz, 1 H), 1.29 (s, 3 H), 0.75–0.65 (m, 4 H); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ = 139.2, 138.5, 128.9, 126.9, 126.0, 125.7, 21.6, 18.1, 15.9; IR (film): $\tilde{\nu}$ = 3077, 3024, 2956, 1648, 1602, 1492, 1447, 1425, 1385, 1073, 1014, 935, 960, 846, 804, 743, 690, 591, 523, 411 cm^{-1}; MS (GC-EI): m/z (%) = 158 [M+] (16), 143 (100), 128 (74), 115 (25), 102 (5), 91 (13), 77 (13), 65 (7), 51 (7); HRMS (EI): m/z: calcd. for $C_{12}H_{14}$ $[M^+]$: 158.10955; found: 158.10938.

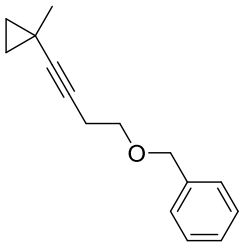
The following compounds were prepared analogously:



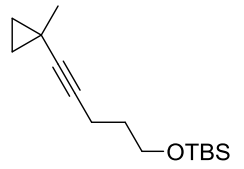
Compound 2a. Colorless liquid (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.34 (m, 2 H), 7.30–7.22 (m, 3 H), 3.17 (s, 3 H), 1.04–0.98 (m, 2 H), 0.71–0.66 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 131.8, 128.3, 127.5, 124.1, 96.4, 75.9, 24.4, 16.8, 7.4. The spectral data matched those previously reported in the literature.[13]

[13] S. Ma, Q. He, *Tetrahedron* **2006**, *62*, 2769–2778.

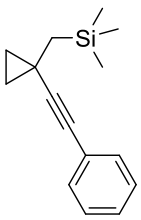
Compound 2b. Colorless liquid (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.25 (m, 5 H), 4.55 (s, 2 H), 3.55 (t, J = 7.2 Hz, 2 H), 2.45 (t, J = 7.2 Hz, 2 H), 1.24 (s, 3 H), 0.85–0.78 (m, 2 H), 0.55–0.49 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.4, 128.5, 127.8 (2 C), 87.5, 73.0, 72.1, 69.1, 24.7, 20.3, 16.2, 6.9; IR (film): $\tilde{\nu}$ = 2961, 2930, 2908, 2860, 1454, 1362, 1100, 1020, 734, 696 cm^{-1}; MS (GC-EI): m/z (%) = 214 [M$^+$] (<1), 213 (4), 199 (14), 185 (5), 172 (6), 159 (10), 141 (4), 129 (3), 105 (8), 93 (17), 91 (100), 77 (19), 65 (17), 51 (5); HRMS (APPI+): m/z: calcd. for $C_{15}H_{18}O$ [M$^+$]: 214.13522; found: 214.13489.



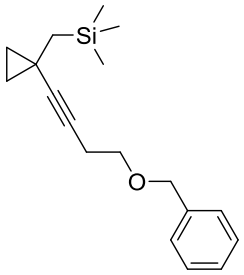
Compound 2c. Colorless liquid (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67 (t, J = 6.2 Hz, 2 H), 2.20 (t, J = 7.0 Hz, 2 H), 1.70–1.61 (m, 2 H), 1.23 (s, 3 H), 0.89 (s, 9 H), 0.82–0.77 (m, 2 H), 0.53–0.48 (m, 2 H), 0.05 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 86.5, 75.2, 61.9, 32.2, 26.1, 24.8, 18.5, 16.2, 15.3, 6.9, −5.2; IR (film): $\tilde{\nu}$ = 3006, 2954, 2857, 1472, 1463, 1254, 1103, 1068, 833, 774 cm^{-1}; MS (GC-EI): m/z (%) = 195 (17), 177 (2), 167 (4), 165 (4), 163 (3), 151 (4), 137 (7), 121 (13), 119 (55), 101 (13), 93 (15), 91 (20), 89 (14), 75 (100), 59 (17); HRMS (ESI+): m/z: calcd. for $C_{15}H_{28}OSiNa$ [M+Na]$^+$: 275.18016; found: 275.18027.



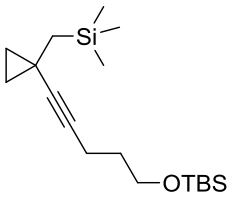
Compound 2d. Colorless liquid (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.23 (m, 2 H), 7.21–7.12 (m, 3 H), 0.96–0.61 (m, 2 H), 0.73 (s, 2 H), 0.58–0.53 (m, 2 H), 0.07 (s, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 131.5, 128.3, 127.4, 124.3, 97.0, 76.1, 26.6, 18.0, 9.0, −0.4; IR (film): $\tilde{\nu}$ = 2956, 2930, 2886, 2857, 2022, 1598, 1494, 1247, 854, 844, 833, 752, 689 cm^{-1}; MS (GC-EI): m/z (%) = 228 [M$^+$] (8), 213 (15), 197 (9), 185 (7), 169 (4), 159 (19), 154 (7), 135 (7), 115 (4), 105 (3), 73 (100), 59 (7), 45 (7); HRMS (EI): m/z: calcd. for $C_{15}H_{20}Si$ [M$^+$]: 228.13343; found: 228.13337.



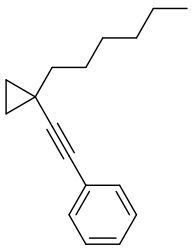
Compound 2e. Colorless liquid (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 5 H), 4.53 (s, 2 H), 3.54 (t, J = 7.2 Hz, 2 H), 2.44 (t, J = 7.2 Hz, 2 H), 0.85–0.80 (m, 2 H), 0.69 (s, 2 H), 0.50–0.46 (m, 2 H), 0.09 (s, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.4, 128.5, 127.8, 127.7, 87.9, 73.0, 72.3, 69.1, 26.8, 20.3, 17.4, 8.4, −0.4; IR (film): $\tilde{\nu}$ = 2952, 2898, 2868, 1246, 1101, 857, 832, 734, 695, 607 cm^{-1}; MS (GC-EI): m/z (%) = 285 [M−H]$^+$ (<1), 213 (1), 199 (3), 195 (3), 181 (5), 167 (4), 155 (3), 141 (3), 135 (3), 105 (8), 103 (7), 91 (66), 75 (11), 73 (100), 65 (7), 59 (6), 45 (7); HRMS (APPI+): m/z: calcd. for $C_{18}H_{26}OSi$ [M$^+$]: 286.17474; found: 286.17464.



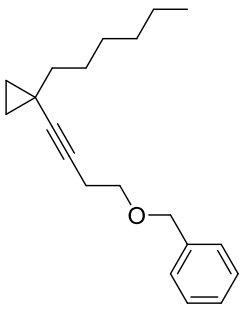
Compound 2f. Colorless liquid (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (t, J = 6.2 Hz, 2 H), 2.18 (t, J = 7.1 Hz, 2 H), 1.70–1.61 (m, 2 H), 0.89 (s, 9 H), 0.83–0.78 (m, 2 H), 0.69 (s, 2 H), 0.50–0.45 (m, 2 H), 0.09 (s, 9 H), 0.05 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 86.9, 75.4, 62.0, 32.2, 27.0, 26.1, 18.5, 17.4, 15.3, 8.5, −0.4, −5.2; IR (film): $\tilde{\nu}$ = 2952, 2929, 2898, 2858, 1248, 1103, 855, 830, 774 cm^{-1}; MS (EI): m/z (%) = 324 [M$^+$] (<1), 267 (32), 239 (2), 193 (3), 179 (17), 166 (8), 161 (2), 151 (23), 149 (10), 147 (56), 133 (9), 123 (5), 99 (3), 91 (2), 73 (100), 59 (8), 45 (5); HRMS (ESI+): m/z: calcd. for $C_{18}H_{36}OSi_2Na$ [M+Na]$^+$: 347.21969; found: 347.21981.



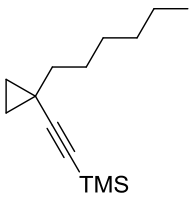
Compound 2g. Colorless liquid (86%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.38–7.32 (m, 2 H), 7.30–7.22 (m, 3 H), 1.67–1.56 (m, 2 H), 1.44–1.38 (m, 2 H), 1.38–1.25 (m, 6 H), 0.98–0.93 (m, 2 H), 0.90 (t, J = 6.9 Hz, 3 H), 0.70–0.65 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 130.8, 127.6, 126.7, 123.6, 94.8, 75.9, 37.6, 31.3, 28.6, 27.3, 22.1, 14.8, 13.3, 11.8; IR (film): $\tilde{\nu}$ = 2955, 2926, 2855, 2223, 1598, 1491, 1022, 753, 689 cm^{-1}; MS (GC-EI): m/z (%) = 226 [M$^+$] (9), 197 (3), 183 (4), 169 (14), 156 (100), 141 (86), 128 (30), 115 (47), 102 (5), 91 (37), 77 (15), 67 (4), 63 (4), 55 (4); HRMS (EI): m/z: calcd. for $C_{17}H_{22}$ [M$^+$]: 226.17215; found: 226.17216.



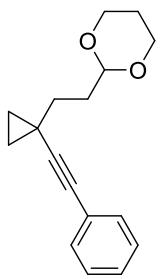
Compound 2h. Colorless liquid (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (t, J = 6.9 Hz, 2 H), 1.58–1.48 (m, 2 H), 1.48–1.35 (m, 4 H), 1.35–1.23 (m, 8 H), 0.90 (t, J = 7.2 Hz, 3 H), 0.89 (t, J = 6.8 Hz, 3 H), 0.80–0.74 (m, 2 H), 0.52–0.46 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 85.2, 76.6, 38.8, 32.1, 31.5, 29.3, 27.9, 22.8, 22.1, 18.6, 15.2, 14.3, 13.8, 12.1; IR (film): $\tilde{\nu}$ = 3005, 2957, 2927, 2857, 1459, 1020, 725 cm^{-1}; MS (EI): m/z (%) = 206 [M$^+$] (2), 177 (3), 163 (3), 149 (5), 136 (24), 122 (18), 121 (32), 108 (11), 107 (77), 105 (13), 95 (12), 94 (18), 93 (69), 91 (47), 81 (17), 80 (19), 79 (100), 78 (12), 77 (35), 67 (19), 65 (14), 55 (19), 43 (20), 41 (24); HRMS (EI): m/z: calcd. for $C_{15}H_{26}$ [M$^+$]: 206.20345; found: 206.20321.



Compound 2i. Colorless liquid (74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.26 (m, 5 H), 4.55 (s, 2 H), 3.55 (t, J = 7.2 Hz, 2 H), 2.46 (t, J = 7.2 Hz, 2 H), 1.57–1.47 (m, 2 H), 1.35–1.22 (m, 8 H), 0.88 (t, J = 7.0 Hz, 3 H), 0.81–0.77 (m, 2 H), 0.52–0.49 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.5, 128.5, 127.8, 127.7, 86.4, 73.0 (2 C), 69.2, 38.6, 32.0, 29.3, 27.9, 22.8, 20.4, 15.2, 14.3, 12.1; IR (film): $\tilde{\nu}$ = 2955, 2926, 2855, 1454, 1362, 1101, 733, 696 cm^{-1}; MS (EI): m/z (%) = 284 [M$^+$] (1), 255 (2), 241 (2), 213 (7), 199 (54), 185 (4), 178 (4), 169 (6), 159 (23), 146 (6), 121 (6), 107 (12), 105 (16), 93 (19), 91 (100), 79 (15), 65 (6), 55 (6); HRMS (ESI+): m/z: calcd. for $C_{20}H_{28}ONa$ [M+Na]$^+$: 307.20323; found: 307.20328.



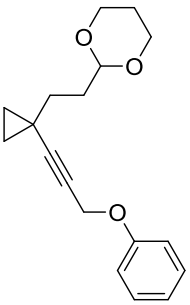
Compound 2k. Colorless liquid (78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61–1.45 (m, 2 H), 1.39–1.22 (m, 8 H), 0.94–0.83 (m, 5 H), 0.59–0.52 (m, 2 H), 0.13 (s, 9 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 112.6, 80.4, 38.1, 32.0, 29.2, 27.8, 22.8, 15.9, 14.3, 12.8, 0.5; IR (film): $\tilde{\nu}$ = 2958, 2928, 2857, 2161, 1459, 1249, 837, 758, 632 cm^{-1}; MS (GC-EI): m/z (%) = 222 [M$^+$] (<1), 207 (25), 193 (2), 179 (4, 165 (4), 152 (14), 148 (15), 137 (70), 133 (7), 123 (10), 119 (12), 109 (10), 105 (10), 99 (10), 97 (13), 95 (7), 93 (5), 91 (6), 85 (8), 83 (10), 73 (100), 69 (5), 59 (33), 55 (4); HRMS (EI): m/z: calcd. for $C_{14}H_{26}Si$ [M$^+$]: 222.18038; found: 222.18049.



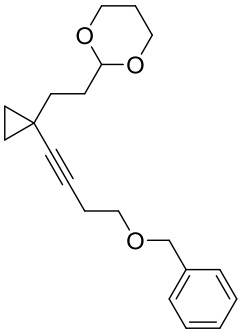
Compound 2l. Colorless liquid (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.35 (m, 2 H), 7.31–7.23 (m, 3 H), 4.67 (t, J = 5.3 Hz, 1 H), 4.19–4.06 (m, 2 H), 3.84–3.74 (m, 2 H), 2.18–2.03 (m, 1 H), 2.01–1.92 (m, 2 H), 1.59–1.51 (m, 2 H), 1.40–1.33 (m, 1 H), 1.04–0.98 (m, 2 H), 0.74–0.68 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 131.8, 128.2, 127.5, 124.0, 101.9, 94.7, 77.3, 67.0, 33.6, 32.6, 26.0, 15.8, 12.1; IR (film): $\tilde{\nu}$ = 2957, 2927, 2850, 1143, 1132, 1005, 891, 883, 754, 636 cm^{-1}; MS (GC-EI): m/z (%) = 256 [M$^+$] (11), 197 (13), 182 (19), 181 (15), 180 (18), 169 (23), 168 (11), 167 (30),

165 (17), 156 (20), 155 (35), 154 (80), 153 (55), 152 (19), 142 (13), 141 (42), 129 (18), 128 (27), 127 (21), 126 (16), 115 (41), 113 (100), 100 (86), 91 (30), 87 (9), 85 (13), 77 (13), 59 (14), 55 (15); HRMS (ESI+): *m*/*z*: calcd. for $C_{17}H_{20}O_2Na$ $[M+Na]^+$: 279.13555; found: 279.13568.

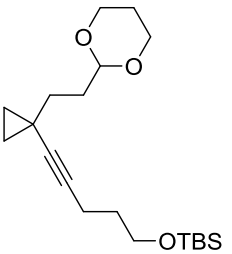
Compound 2m. Colorless liquid (76%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.22 (m, 2 H), 6.99–6.90 (m, 3 H), 4.64 (s, 2 H), 4.58 (t, *J* = 5.2 Hz, 1 H), 4.21–4.05 (m, 2 H), 3.78–3.69 (m, 2 H), 2.13–2.00 (m, 1 H), 1.88–1.80 (m, 2 H), 1.46–1.40 (m, 2 H), 1.36–1.29 (m, 1 H), 0.90–0.85 (m, 2 H), 0.62–0.56 (m, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 158.0, 129.8, 129.5, 121.3, 115.1, 101.8, 92.6, 71.7, 67.0, 56.7, 33.4, 32.2, 26.0, 15.5, 11.5; IR (film): $\tilde{\nu}$ = 2958, 2927, 2854, 1598, 1494, 1377, 1236, 1214, 1144, 1134, 891, 878, 752, 690 cm^{-1}; MS (GC-EI): *m*/*z* (%) = 385 $[M-H]^+$ (<1), 193 (7), 151 (1), 135 (34), 119 (19), 117 (21), 115 (11), 107 (35), 105 (20), 91 (100), 87 (34), 79 (60), 77 (43), 65 (29), 59 (19), 55 (19); HRMS (ESI+): *m*/*z*: calcd. for $C_{18}H_{22}O_3Na$ $[M+Na]^+$: 309.14611; found: 309.14623.



Compound 2n. Colorless liquid (73%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.25 (m, 5 H), 4.59 (t, *J* = 5.3 Hz, 1 H), 4.53 (s, 2 H), 4.13–4.05 (m, 2 H), 3.80–3.70 (m, 2 H), 3.53 (t, *J* = 7.3 Hz, 2 H), 2.44 (t, *J* = 7.3 Hz, 2 H), 2.14–2.00 (m, 1 H), 1.90–1.81 (m, 2 H), 1.44–1.36 (m, 2 H), 1.36–1.28 (m, 1 H), 0.83–0.77 (m, 2 H), 0.56–0.50 (m, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 138.4, 128.5, 127.8, 127.7, 102.0, 85.7, 73.4, 73.0, 69.1, 67.0, 33.5, 32.7, 26.0, 20.3, 15.2, 11.6; IR (film): $\tilde{\nu}$ = 2957, 2927, 2852, 1454, 1378, 1239, 1145, 1135, 1090, 1046, 1004, 892, 736, 697 cm^{-1}; MS (GC-EI): *m*/*z* (%) = 237 (2), 223 (3), 211 (3), 179 (3), 165 (3), 147 (6), 117 (11), 113 (26), 105 (21), 100 (35), 91 (100), 87 (40), 79 (16), 77 (19), 65 (10), 59 (8); HRMS (ESI+): *m*/*z*: calcd. for $C_{20}H_{26}O_3Na$ $[M+Na]^+$: 337.17741; found: 337.17757.



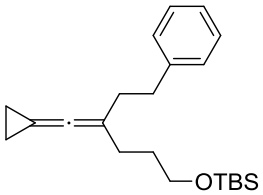
Compound 2o. Colorless liquid (57%). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.59 (t, *J* = 5.3 Hz, 1 H), 4.13–4.05 (m, 2 H), 3.80–3.71 (m, 2 H), 3.65 (t, *J* = 6.1 Hz, 2 H), 2.18 (t, *J* = 7.1 Hz, 2 H), 2.14–2.00 (m, 1 H), 1.89–1.81 (m, 2 H), 1.69–1.61 (m, 2 H), 1.42–1.36 (m, 2 H), 1.36–1.30 (m, 1 H), 0.89 (s, 9 H), 0.80–0.76 (m, 2 H), 0.52–0.50 (m, 2 H), 0.05 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 102.0, 84.6, 76.6, 67.0, 61.9, 33.5, 32.9, 32.3, 26.1, 26.0, 18.5, 15.3, 15.2, 11.6, −5.2; IR (film): $\tilde{\nu}$ = 2953, 2928, 2854, 1471, 1379, 1287, 1146, 1137, 1103, 1006, 834, 774 cm^{-1}; MS (EI): *m*/*z* (%) = 352 $[M^+]$ (4), 351 (7), 296 (23), 295 (100), 237 (23), 221 (11), 219 (45), 193 (12), 164 (11), 163 (84), 145 (48), 143 (11), 135 (14), 133 (51), 131 (36), 129 (11), 121 (14), 119 (33), 117 (37), 115 (11), 113 (50), 105 (59), 101 (25), 100 (20), 93 (15), 91 (43), 89 (13), 87 (33), 79 (18), 77 (12), 75 (96), 73 (31), 67 (11), 59 (23); HRMS (ESI+): *m*/*z*: calcd. for $C_{20}H_{36}O_3SiNa$ $[M+Na]^+$: 375.23259; found: 375.23265.



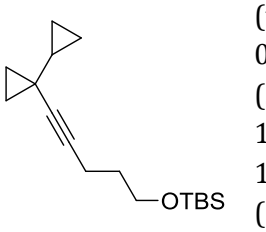
Compound 2p. Isolated as a 4:1 mixture with the corresponding allene. An analytical pure sample was obtained by preparative HPLC as a colorless liquid (49%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.24 (m, 2 H), 7.23–7.14 (m, 3 H), 3.71 (t, *J* = 6.2 Hz, 2 H), 2.90–2.82 (m, 2 H), 2.26 (t, *J* = 7.0 Hz, 2 H), 1.75–1.66 (m, 2 H), 1.64–1.55 (m, 2 H), 0.90 (s, 9 H), 0.82–0.77 (m, 2 H), 0.51–0.46 (m,

2 H), 0.07 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.5, 128.6, 128.4, 125.8, 84.9, 76.8, 61.9, 40.9, 34.4, 32.3, 26.1, 18.5, 15.3, 15.2, 12.1, −5.1; IR (film): $\tilde{\nu}$ = 2951, 2928, 2857, 1254, 1105, 835, 776, 669 cm^{-1}; MS (GC-EI): *m*/*z* (%) = 327 (<1), 285 (55), 267 (2), 257 (2), 239 (2), 209 (26), 181 (26), 167 (19), 155 (9), 141 (13), 131 (16), 117 (15), 109 (39), 101 (20), 91 (100), 75 (99), 73 (22), 59 (17); HRMS (ESI+): *m*/*z*: calcd. for $C_{22}H_{34}OSiNa$ $[M+Na]^+$: 365.22711; found: 365.22722.

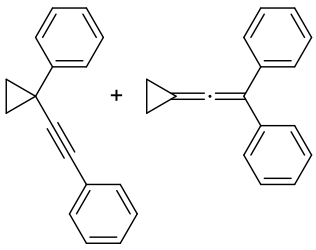
Compound 3p. An analytical pure sample was obtained by preparative HPLC as a colorless liquid (12%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 2 H), 7.21–7.14 (m, 3 H), 3.63 (t, *J* = 6.5 Hz, 2 H), 2.76–2.70 (m, 2 H), 2.36–2.30 (m, 2 H), 2.09 (t, *J* = 7.5 Hz, 2 H), 1.70–1.63 (m, 2 H), 1.44–1.39 (m, 4 H), 0.89 (s, 9 H), 0.51–0.46 (m, 2 H), 0.04 (s, 6 H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 186.4, 142.6, 128.5, 128.4, 125.8, 107.3, 79.4, 63.0, 35.3, 34.4, 31.1, 29.8, 26.1, 18.5, 6.7, −5.1; IR (film): $\tilde{\nu}$ = 2952, 2930, 2857, 1255, 1101, 835, 776, 698 cm^{-1}; MS (GC-EI): *m*/*z* (%) = 342 $[M^+]$ (<1), 285 (6), 267 (2), 223 (6), 209 (10), 195 (10), 181 (29), 169 (31), 167 (40), 155 (10), 141 (22), 129 (11), 119 (15), 117 (17), 115 (12), 105 (15), 93 (16), 91 (100), 89 (14), 77 (11), 75 (65), 73 (49), 59 (16); HRMS (APPI+): *m*/*z*: calcd. for $C_{22}H_{35}OSi$ $[M+H]^+$: 343.24517; found: 343.24521.



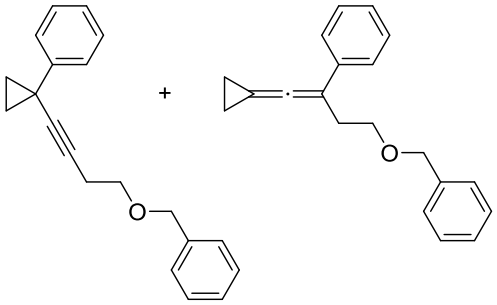
Compound 2q. Colorless liquid (59%). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.67 (t, *J* = 6.2 Hz, 2 H), 2.20 (t, *J* = 7.0 Hz, 2 H), 1.70–1.61 (m, 2 H), 0.89 (s, 9 H), 0.84–0.73 (m, 1 H), 0.77–0.74 (m, 2 H), 0.56–0.52 (m, 2 H), 0.40–0.34 (m, 2 H), 0.28–0.23 (m, 2 H), 0.05 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 84.4, 76.2, 61.9, 32.3, 26.1, 18.5, 16.4, 15.3, 14.1, 13.0, 2.8, −5.2; IR (film): $\tilde{\nu}$ = 2952, 2929, 2857, 1471, 1254, 1103, 1069, 1017, 833, 774 cm^{-1}; MS (GC-EI): *m*/*z* (%) = 221 (20), 193 (6), 175 (5), 163 (7), 149 (5), 145 (18), 135 (6), 119 (12), 117 (22), 115 (11), 105 (17), 101 (16), 91 (27), 89 (17), 79 (11), 77 (11), 75 (100), 73 (21), 59 (21); HRMS (CI): *m*/*z*: calcd. for $C_{17}H_{31}OSi$ $[M+H]^+$: 279.21442; found: 279.21414.



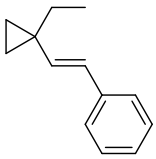
Compound 2r and 3r. Colorless liquid (73% combined yield, alkyne:allene ≈ 7.3:1); distinct signals of the alkyne are marked * and of the allene **: ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.19 (m, 10 H), 1.75** (s, 4 H), 1.60–1.53* (2 H), 1.39–1.33* (m, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 190.4**, 142.0*, 137.9**, 131.9, 128.6, 128.5, 128.4, 128.3, 127.8, 127.0, 126.2, 125.6, 123.8*, 111.9**, 93.9*, 79.2**, 78.5*, 20.7*, 16.4*, 9.1**; IR (film): $\tilde{\nu}$ = 3082, 3058, 3024, 2234, 2215, 2001, 1597, 1490, 1442, 1000, 954, 751, 689, 556 cm^{-1}; MS* (GC-EI): *m*/*z* (%) = 218 $[M^+]$ (100), 217 (78), 215 (36), 203 (53), 202 (82), 190 (13), 189 (37), 165 (5), 163 (7), 141 (9), 139 (9), 129 (5), 115 (25), 108 (13), 107 (10), 101 (12), 95 (20), 94 (11), 91 (11), 77 (6), 63 (6); MS** (GC-EI): *m*/*z* (%) = 218 $[M^+]$ (100), 217 (89), 215 (34), 203 (45), 202 (68), 192 (13), 191 (12), 189 (20), 178 (11), 165 (15), 141 (7), 139 (7), 129 (4), 115 (18), 108 (8), 107 (16), 101 (23), 95 (15), 94 (10), 91 (6), 77 (5), 63 (5); HRMS (APPI+): *m*/*z*: calcd. for $C_{17}H_{14}$ $[M^+]$: 218.10900; found: 218.10861.



Compounds 2s and 3s. Colorless liquid (63% combined yield, alkyne:allene ≈ 1.3:1); distinct signals of the alkyne are marked * and of the allene **: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 9 H), 7.21–7.15 (m, 1 H), 4.57* (s, 2 H), 4.54** (s, 2 H), 3.72* (t, J = 7.2 Hz, 2 H), 3.62** (t, J = 7.1 Hz, 2 H), 2.86** (t, J = 7.1 Hz, 2 H), 2.56* (t, J = 7.2 Hz, 2 H), 1.71–1.65** (m, 2 H), 1.65–1.59** (m, 2 H), 1.41–1.35* (2 H), 1.23–1.18* (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 188.9**, 142.5*, 138.6**, 138.3*, 137.8**, 128.6, 128.5 (2 C), 128.4, 127.8 (3 C), 127.7, 126.4, 126.0, 125.9, 125.6, 104.9**, 85.1*, 80.1**, 75.1*, 73.2**, 73.1*, 69.4**, 69.0*, 30.8**, 20.5*, 20.2*, 15.8*, 8.3**; IR (film): $\tilde{\nu}$ = 3060, 3028, 3008, 2912, 2858, 2006, 1600, 1496, 1453, 1272, 1100, 1027, 752, 734, 694 cm^{-1}; MS* (GC-EI): m/z (%) = 276 [M$^+$] (0.97), 247 (1.75), 231 (1.13), 215 (1.38), 185 (2.54), 170 (8.74), 155 (18.39), 153 (12.25), 143 (13.23), 141 (13.00), 129 (15.55), 128 (15.68), 117 (14.86), 115 (21.73), 106 (18.46), 105 (24.21), 92 (33.99), 91 (100.00), 79 (11.29), 78 (12.03), 77 (36.46), 65 (15.70), 51 (14.46); MS** (GC-EI): m/z (%) = 276 [M$^+$] (2), 243 (1), 231 (1), 215 (2), 185 (11), 170 (8), 155 (20), 153 (12), 143 (13), 141 (16), 129 (20), 128 (16), 117 (18), 115 (26), 106 (17), 105 (22), 92 (32), 91 (100), 79 (12), 78 (15), 77 (38), 65 (17), 51 (15); HRMS (APPI+): m/z: calcd. for $C_{20}H_{20}O$ [M$^+$]: 276.15087; found: 276.15041.

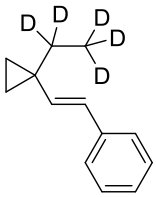


Compound 18. Colorless liquid (17%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 4 H), 7.20–7.14 (m, 1 H), 6.29 (dd, J = 16.1 Hz, J = 3.0 Hz, 1 H), 5.99 (dd, J = 16.1 Hz, J = 3.0 Hz, 1 H), 1.54 (q, J = 7.4 Hz, 2 H), 0.98 (t, J = 7.4 Hz, 3 H), 0.71–0.60 (m, 4 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.1, 136.4, 128.6, 126.7, 126.3, 125.8, 29.2, 23.6, 14.5, 11.4; IR (film): $\tilde{\nu}$ = 3078, 3025, 2999, 2963, 2930, 2874, 1645, 1602, 1494, 1448, 1376, 1046, 1015, 963, 939, 818, 746, 692, 538 cm^{-1}; MS (GC-EI): m/z (%) = 171 [M$^+$] (2), 143 (100), 128 (48), 115 (13), 102 (2), 91 (5); HRMS (APPI+): m/z: calcd. for $C_{13}H_{16}$ [M$^+$]: 172.12465; found: 172.12436.



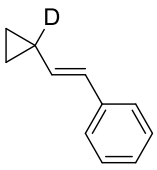
The spectral data for (*E*)-(2-cyclopropylvinyl)benzene (**19**) matched the previously reported values.[14]

Compound [D_5]-18. Colorless liquid (16%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 4 H), 7.22–7.15 (m, 1 H), 6.30 (d, J = 16.1 Hz, 1 H), 5.98 (d, J = 16.1 Hz, 1 H), 0.71–0.61 (m, 4 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.1, 136.5, 128.6, 126.7, 126.3, 125.8, 23.4, 14.4; IR (film): $\tilde{\nu}$ = 3077, 3026, 3000, 2220, 1646, 1601, 1493, 1448, 1056, 1016, 962, 941, 744, 692, 531 cm^{-1}; MS (GC-EI): m/z (%) = 177 [M$^+$] (4), 143 (100), 128 (44), 115 (13), 102 (3), 91 (8), 77 (5), 65 (5), 51 (4); HRMS (EI): m/z: calcd. for $C_{13}H_{11}D_5$ [M$^+$]: 177.15604; found: 177.15583.

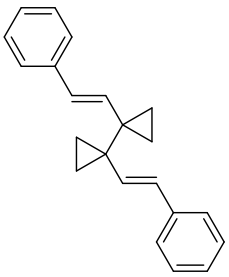


[14] C. Vila, M. Giannerini, V. Hornillos, M. Fañanás-Mastral, B. L. Feringa, *Chem. Sci.* **2014**, *5*, 1361–1367.

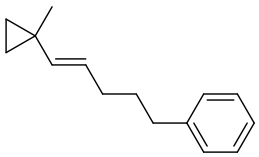
Compound [D]-19. Colorless liquid (20%). Isolated as a 2:1 mixture with compound **[D_5]-18.;** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.25 (m, 4 H), 7.21–7.14 (m, 1 H), 6.47 (d, J = 15.8 Hz, 1 H), 5.73 (dt, J = 15.8 Hz, J = 4.5 Hz, 1 H), 0.85–0.79 (m, 2 H), 0.54–0.48 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 137.9, 135.0, 128.6, 127.5, 126.7, 125.7, 7.3; IR (film): $\tilde{\nu}$ = 3077, 3026, 3000, 2220, 1646, 1601, 1493, 1448, 1056, 1016, 962, 941, 744, 692, 531cm^{-1}; MS (GC-EI): m/z (%)= 145 [M]$^+$ (49), 144 (43), 143 (12), 130 (100), 129 (96), 128 (50), 116 (26), 115 (25), 102 (7), 91 (13), 89 (8), 77 (12), 71 (12), 67 (10), 66 (11), 65 (12), 63 (12), 51 (14), 39 (12); HRMS (APPI+): m/z: calculated for $C_{11}H_{11}D$ [M]$^+$: 145.09963, found: 145.09947.



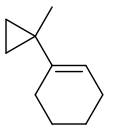
Compound 20. Colorless solid (26%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a solution in hexane. m.p. **=** 65.0-65.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.23 (m, 4 H), 7.18–7.13 (m, 1 H), 6.46 (d, J = 16.2 Hz, 1 H), 6.07 (d, J = 16.2 Hz, 1 H), 0.83–0.75 (m, 4 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 138.1, 136.5, 128.6, 127.1, 126.7, 125.9, 25.1, 13.9; IR (solid): $\tilde{\nu}$ = 3077, 3019, 2997, 1643, 1493, 1053, 965, 948, 749, 690, 538 cm^{-1}; MS (GC-EI): m/z (%) = 286 [M$^+$] (23), 258 (8), 243 (6), 228 (9), 215 (7), 195 (92), 182 (62), 167 (100), 154 (44), 141 (44), 128 (66), 115 (62), 103 (11), 91 (96), 77 (20), 65 (14); HRMS (EI): m/z: calcd. for $C_{22}H_{22}$ [M$^+$]: 286.17215; found: 286.17201.



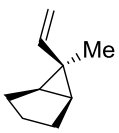
Compound 21. Colorless liquid (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.24 (m, 2 H), 7.22–7.14 (m, 3 H), 5.37 (dt, J = 15.4 Hz, J = 6.8 Hz, 1 H), 5.08 (d, J = 15.4 Hz, 1 H), 2.62 (t, J = 7.5 Hz, 2 H), 2.05 (q, J = 7.5 Hz, 2 H), 1.69 (quint., J = 7.5 Hz, 2 H), 1.15 (s, 3 H), 0.55–0.48 (m, 4 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 142.8, 138.3, 128.6, 128.4, 125.7, 125.6, 35.5, 32.3, 31.6, 21.8, 17.0, 15.0; IR (film): $\tilde{\nu}$ = 3075, 3026, 2929, 2856, 1604, 1496, 1453, 1384, 1084, 1013, 965, 932, 742, 697, 575, 487 cm^{-1}; MS (GC-EI): m/z (%) = 200 [M$^+$] (3), 185 (1), 171 (3), 143 (5), 130 (19), 117 (12), 109 (12), 104 (58), 91 (52), 81 (100), 67 (35), 55 (12), 41 (12); HRMS (EI): m/z: calcd. for $C_{15}H_{20}$ [M$^+$]: 200.15650; found: 200.15665.



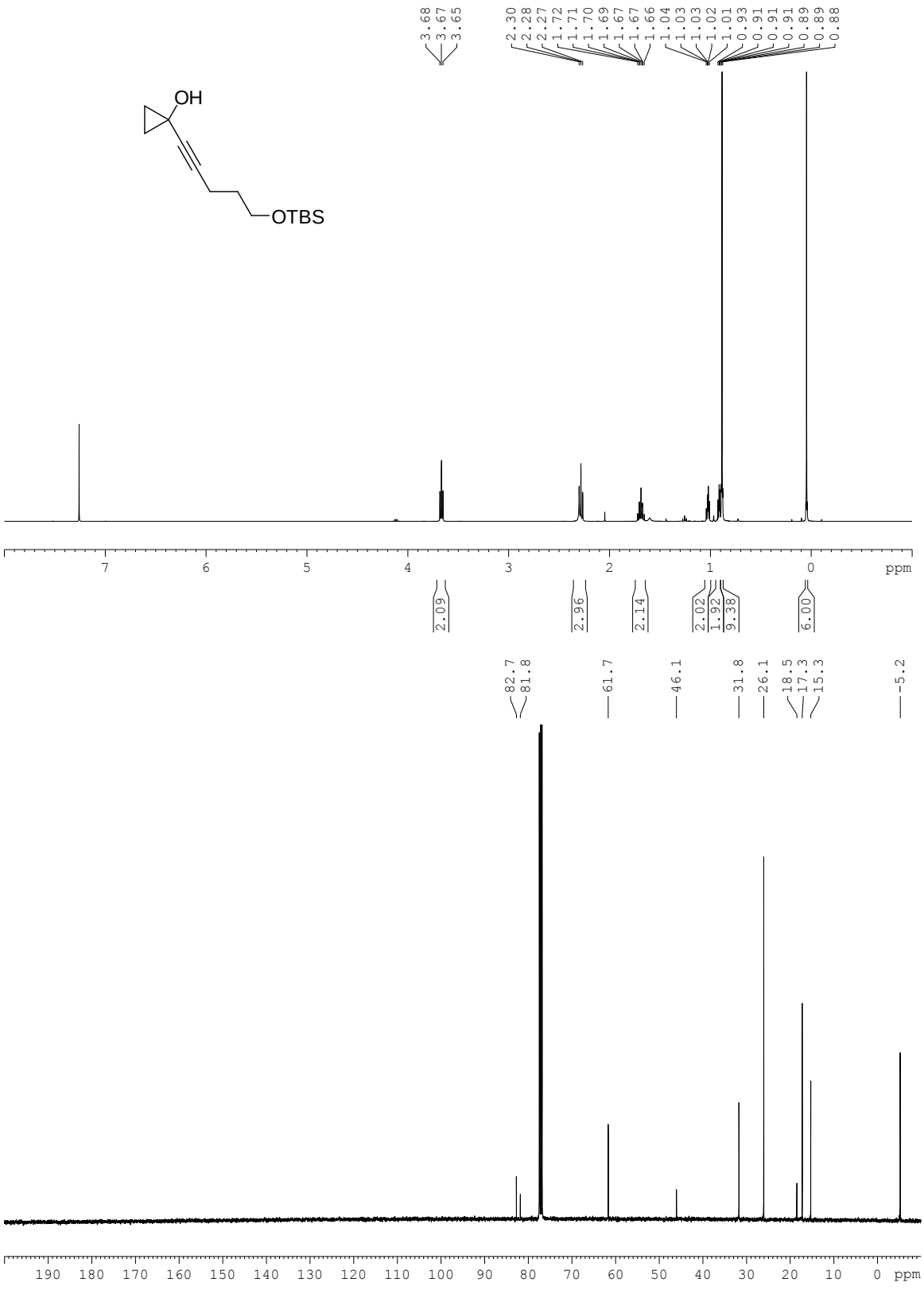
Compound 22. Colorless liquid (48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.51–5.46 (m, 1 H), 2.02–1.95 (m, 2 H), 1.94–1.88 (m, 2 H), 1.63–1.48 (m, 4 H), 1.12 (s, 3 H), 0.59–0.54 (m, 2 H), 0.34–0.30 (m, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 141.3, 120.2, 26.0, 25.4, 24.0, 23.3, 22.8, 21.5, 12.6; IR (film): $\tilde{\nu}$ = 3076, 3001, 2924, 2858, 2837, 1448, 1424, 1376, 1313, 1264, 1136, 1082, 1039, 1010, 932, 919, 862, 840, 795, 735, 545, 463, 434 cm^{-1}; MS (GC-EI): m/z (%) = 136 [M$^+$] (5), 121 (66), 107 (34), 105 (7), 93 (73), 79 (100), 67 (38), 55 (17), 41 (20); HRMS (EI): m/z: calcd. for $C_{10}H_{16}$ [M$^+$]: 136.12520; found: 136.12534.



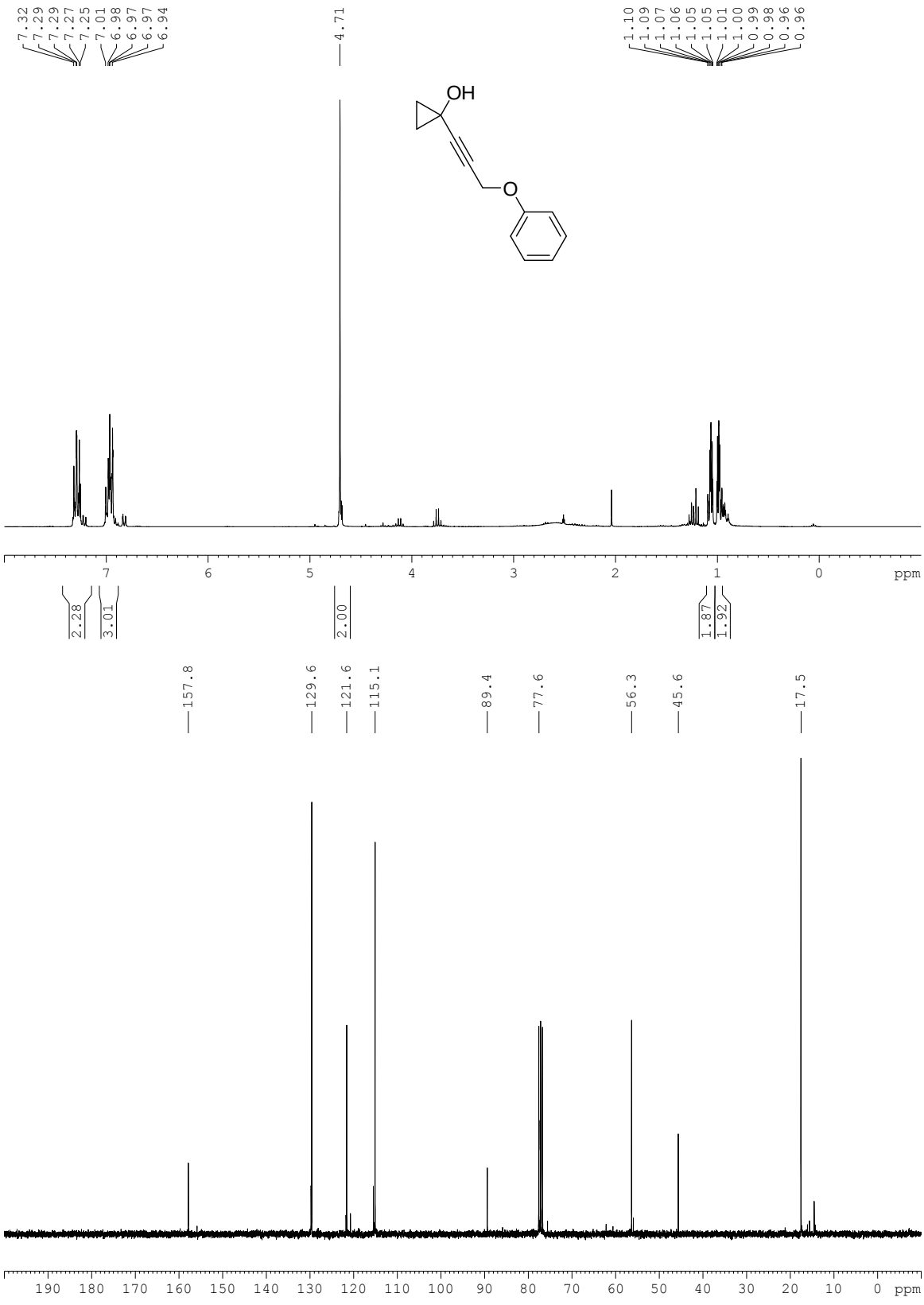
Compound 23. Colorless liquid (39%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.78 (dd, J = 17.4 Hz, J = 10.7 Hz, 1 H), 5.15 (dd, J = 17.4 Hz, J = 2.0 Hz, 1 H), 5.11 (dd, J = 10.7 Hz, J = 2.0 Hz, 1 H), 1.92–1.79 (m, 2 H), 1.81–1.71 (m, 1 H), 1.71–1.64 (m, 2 H), 1.45–1.35 (m, 1 H), 1.35–1.33 (m, 2 H), 1.08 (s, 3 H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 138.6, 114.7, 34.3, 26.1, 25.9 (2 C), 24.2; IR (film): $\tilde{\nu}$ = 3007, 2926, 2860, 1446, 914 cm^{-1}; MS (GC-EI): m/z (%) = 122 [M$^+$] (16), 107 (44), 93 (37), 91 (28), 81 (31), 79 (100), 77 (29), 67 (27), 65 (14), 53 (24); HRMS (EI): m/z: calcd. for C_9H_{14} [M$^+$]: 122.10955; found: 122.10942.



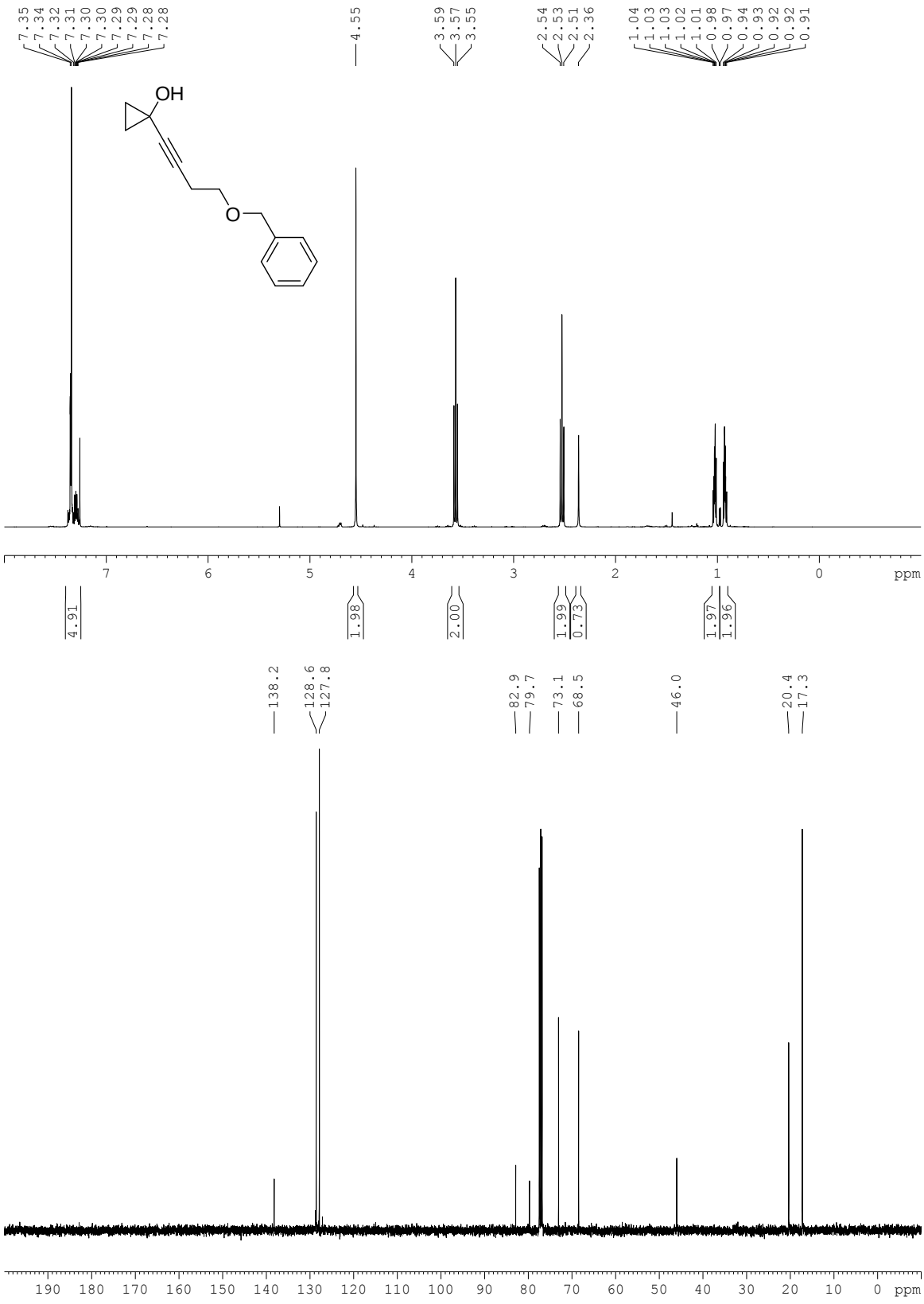
Compound S1


OH
OTBS
3.68
3.67
3.65
2.30
2.28
2.27
1.72
1.71
1.70
1.69
1.67
1.67
1.66
1.04
1.03
1.03
1.02
1.01
0.93
0.91
0.91
0.91
0.89
0.89
0.88
ppm
2.09
2.96
2.14
2.02
1.92
9.38
6.00
82.7
81.8
61.7
46.1
31.8
26.1
18.5
17.3
15.3
-5.2
ppm

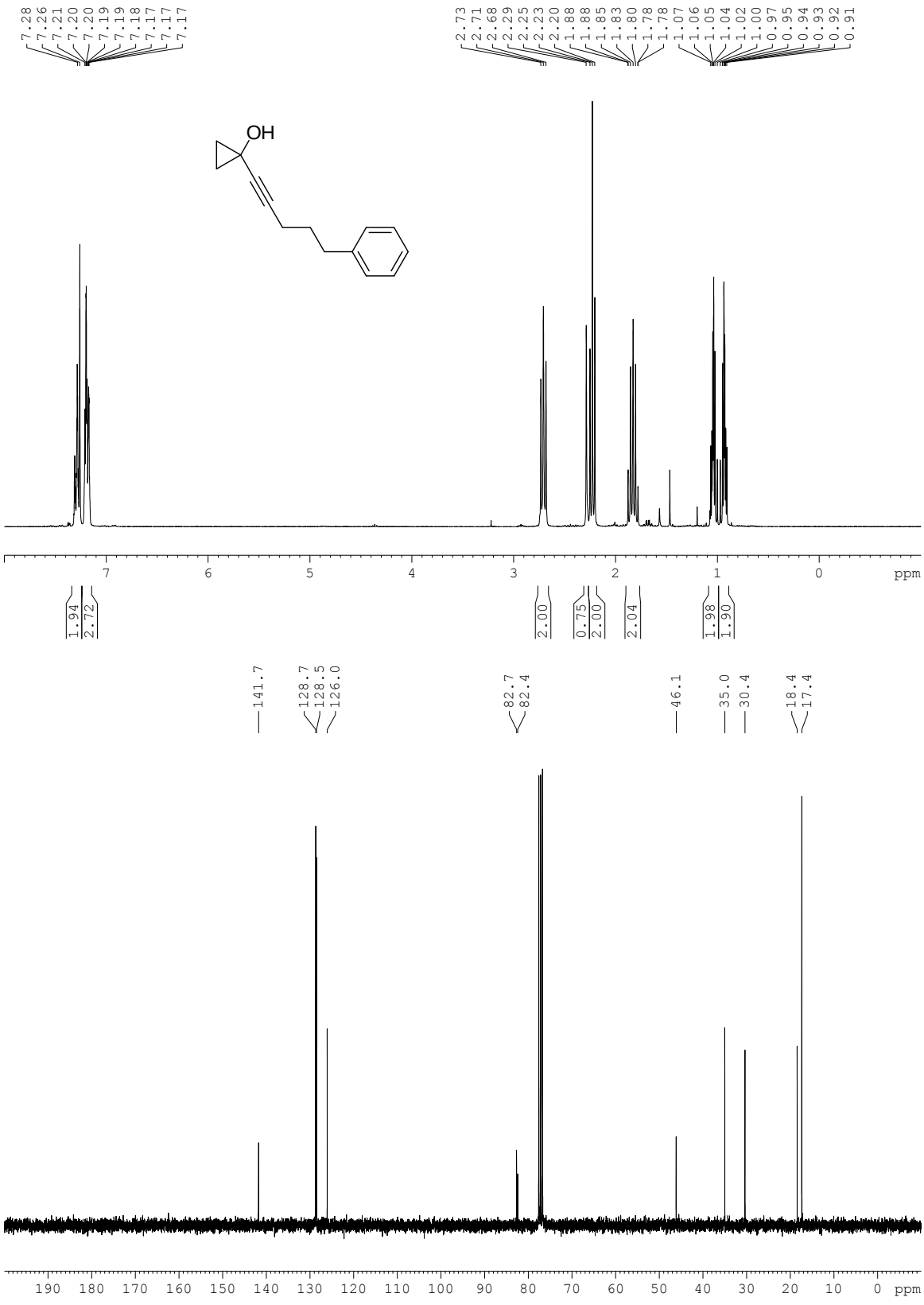
Compound S2


7.32
7.29
7.29
7.27
7.25
7.01
6.98
6.97
6.97
6.94
4.71
1.10
1.09
1.07
1.06
1.05
1.05
1.01
1.00
0.99
0.98
0.96
0.96
OH
O
ppm
2.28
3.01
2.00
1.87
1.92
157.8
129.6
121.6
115.1
89.4
77.6
56.3
45.6
17.5
ppm

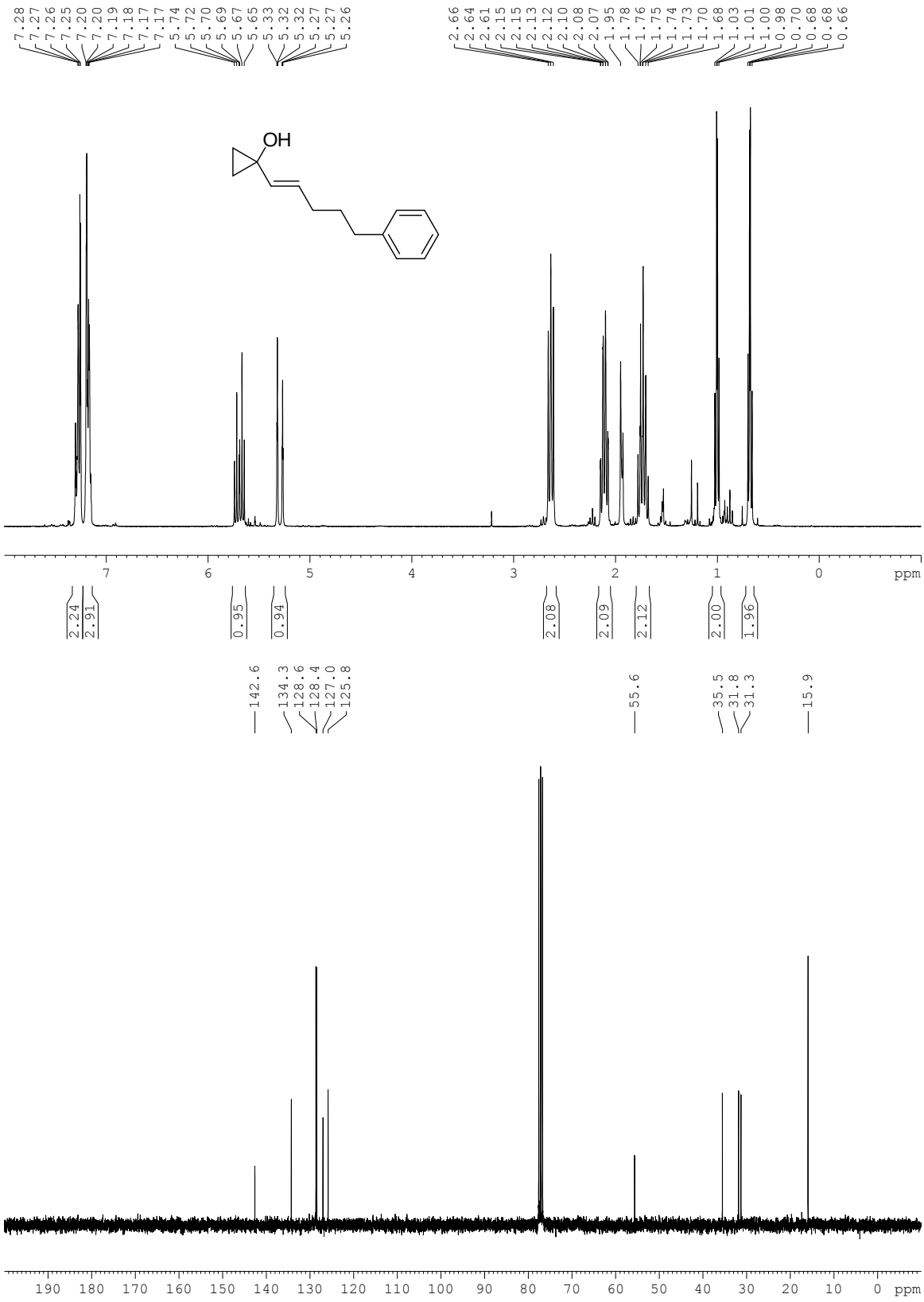
Compound S3


7.35
7.34
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
4.55
3.59
3.57
3.55
2.54
2.53
2.51
2.36
1.04
1.03
1.03
1.02
1.01
0.98
0.97
0.94
0.93
0.92
0.92
0.91
OH
O
ppm
4.91
1.98
2.00
1.99
0.73
1.97
1.96
138.2
128.6
127.8
82.9
79.7
73.1
68.5
46.0
20.4
17.3
ppm

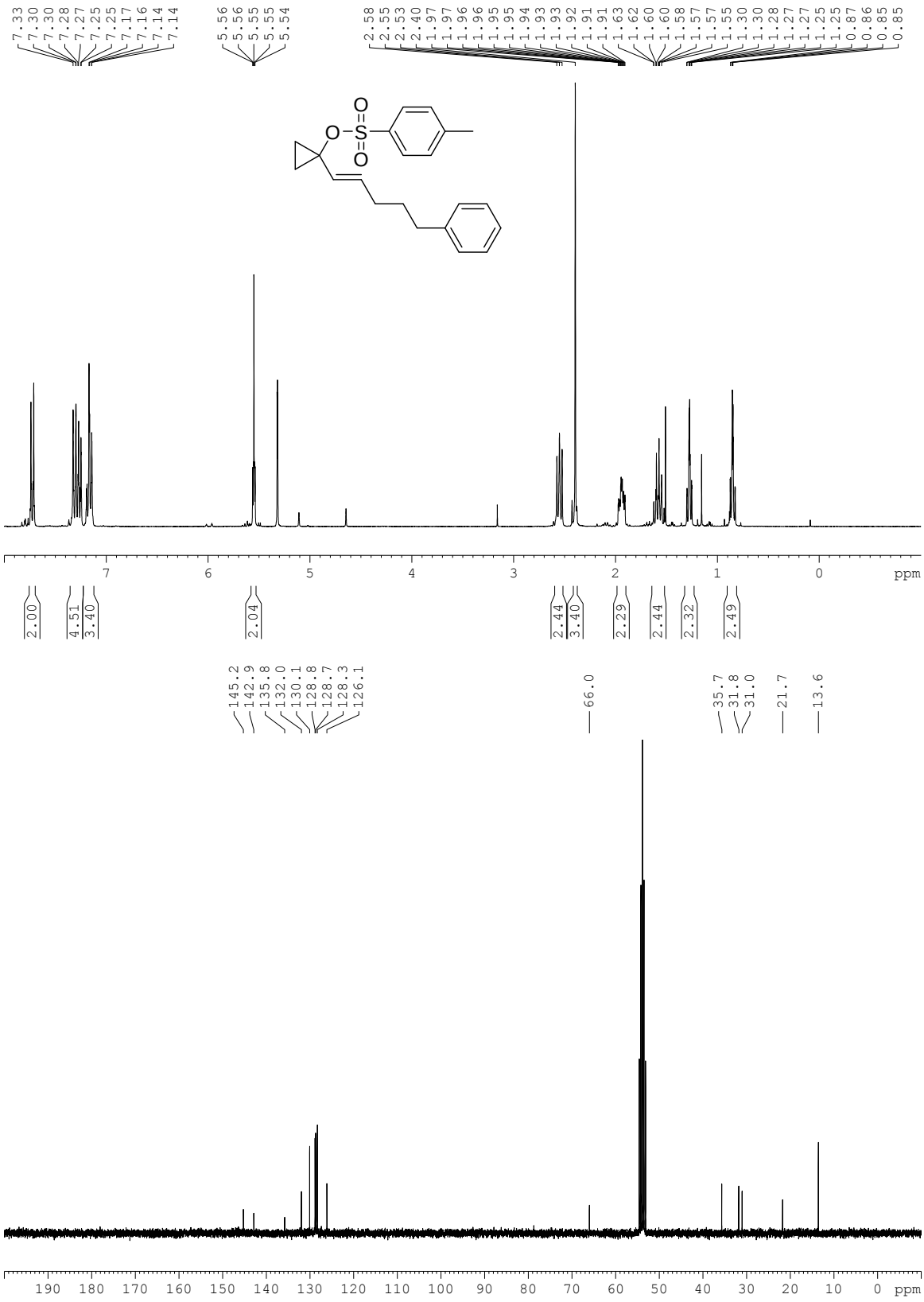
Compound S4


7.28
7.26
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.17
2.73
2.71
2.68
2.29
2.25
2.23
2.20
1.88
1.85
1.83
1.80
1.78
1.78
1.07
1.06
1.05
1.04
1.02
1.00
0.97
0.95
0.94
0.93
0.92
0.91
OH
ppm
1.94
2.72
2.00
0.75
2.00
2.04
1.98
1.90
141.7
128.7
128.5
126.0
82.7
82.4
46.1
35.0
30.4
18.4
17.4
ppm

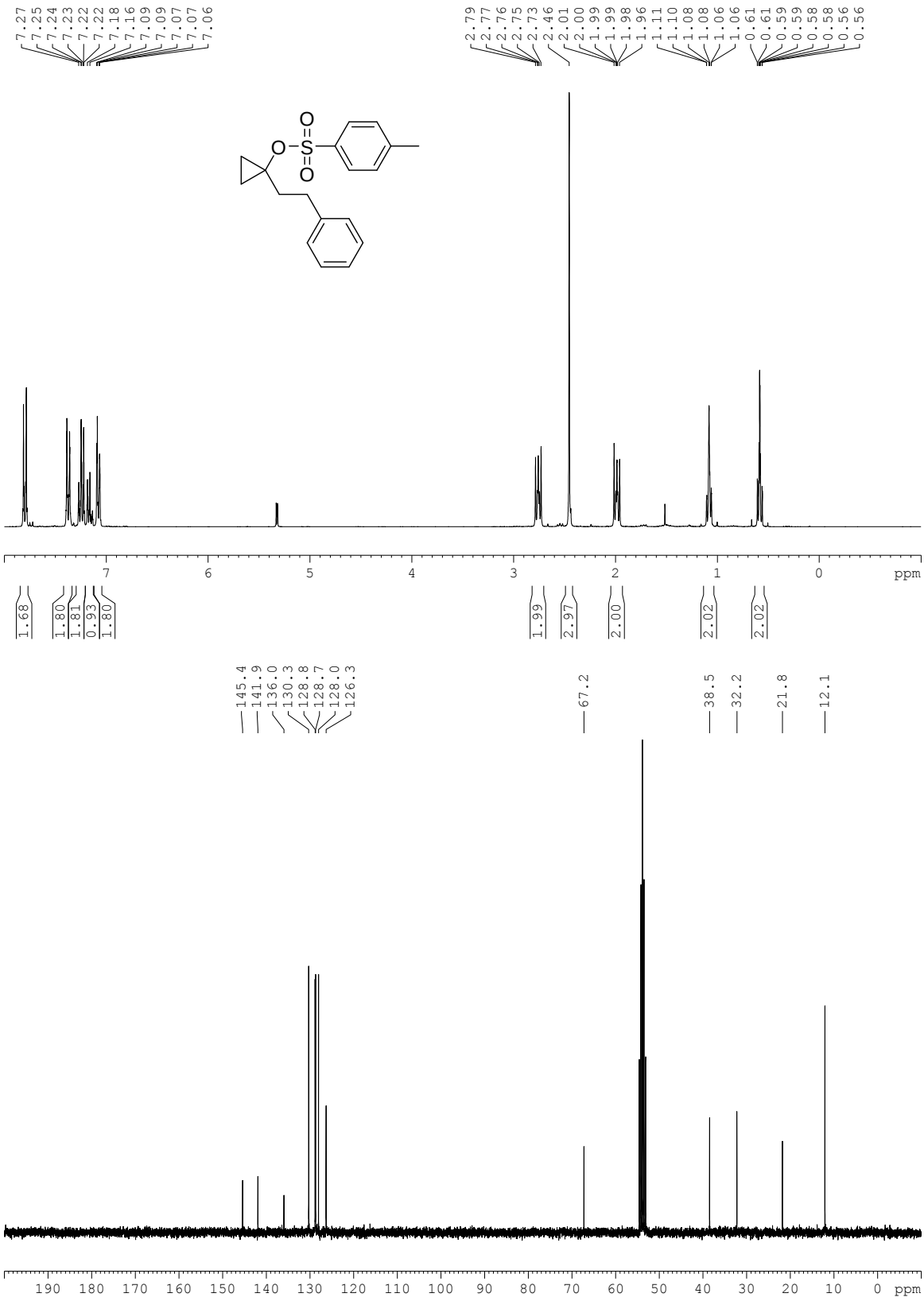
Compound S5


7.28
7.27
7.26
7.25
7.20
7.20
7.19
7.18
7.17
7.17
5.74
5.72
5.70
5.69
5.67
5.65
5.33
5.32
5.32
5.27
5.27
5.26
2.66
2.64
2.61
2.15
2.15
2.13
2.12
2.10
2.08
2.07
1.95
1.78
1.76
1.75
1.74
1.73
1.70
1.68
1.03
1.01
1.00
0.98
0.70
0.68
0.68
0.66
OH
ppm
2.24
2.91
0.95
0.94
2.08
2.09
2.12
2.00
1.96
142.6
134.3
128.6
128.4
127.0
125.8
55.6
35.5
31.8
31.3
15.9
ppm

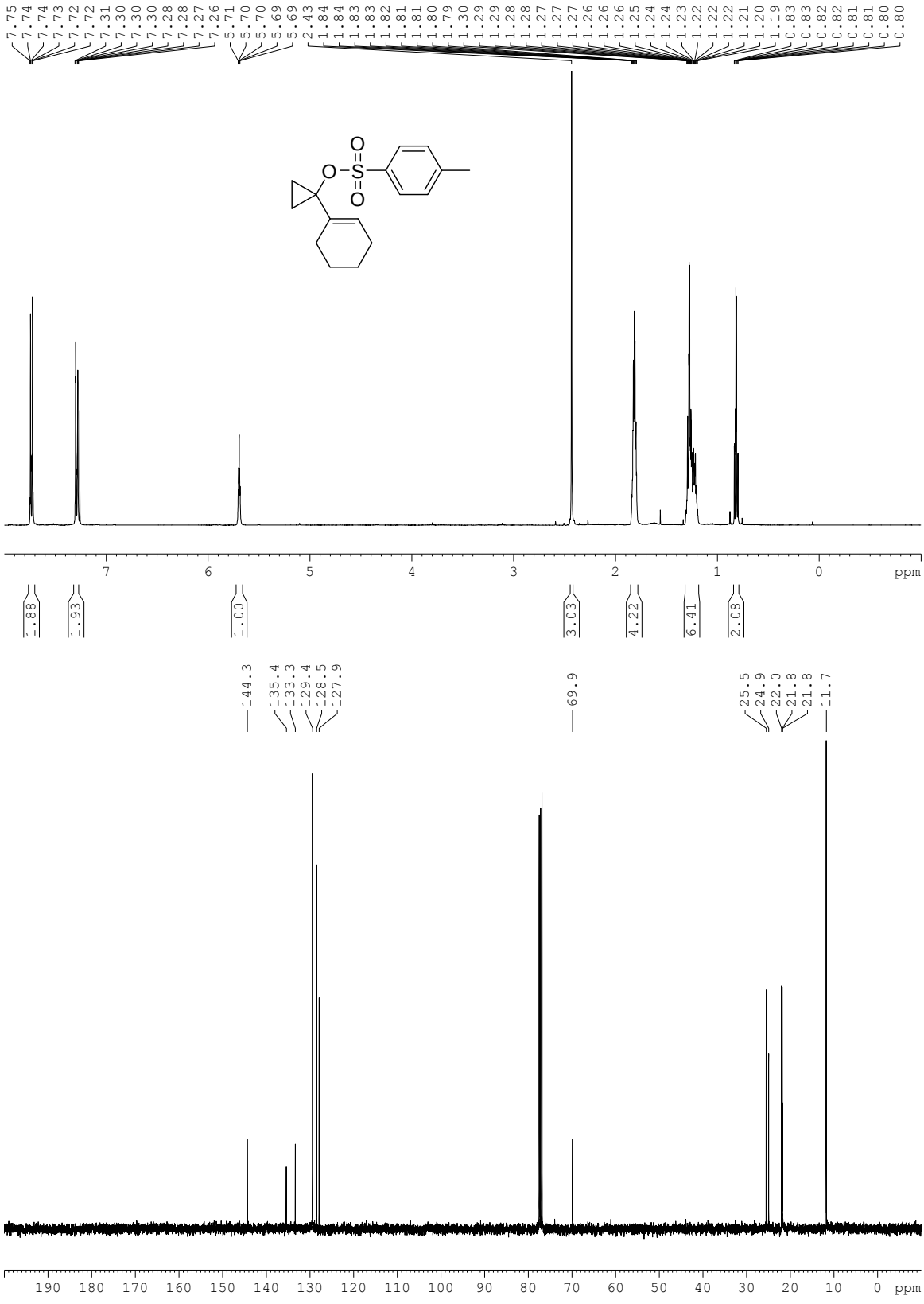
Compound S6


7.33
7.30
7.30
7.28
7.27
7.25
7.25
7.17
7.16
7.14
7.14
5.56
5.56
5.55
5.55
5.54
2.58
2.55
2.53
2.40
1.97
1.97
1.96
1.96
1.95
1.95
1.94
1.93
1.93
1.92
1.91
1.91
1.63
1.62
1.60
1.60
1.58
1.57
1.57
1.55
1.30
1.30
1.28
1.27
1.27
1.25
1.25
0.87
0.86
0.85
0.85
O
O
S
O
O
7
6
5
4
3
2
1
0
ppm
2.00
4.51
3.40
2.04
2.44
3.40
2.29
2.44
2.32
2.49
145.2
142.9
135.8
132.0
130.1
128.8
128.7
128.3
126.1
66.0
35.7
31.8
31.0
21.7
13.6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

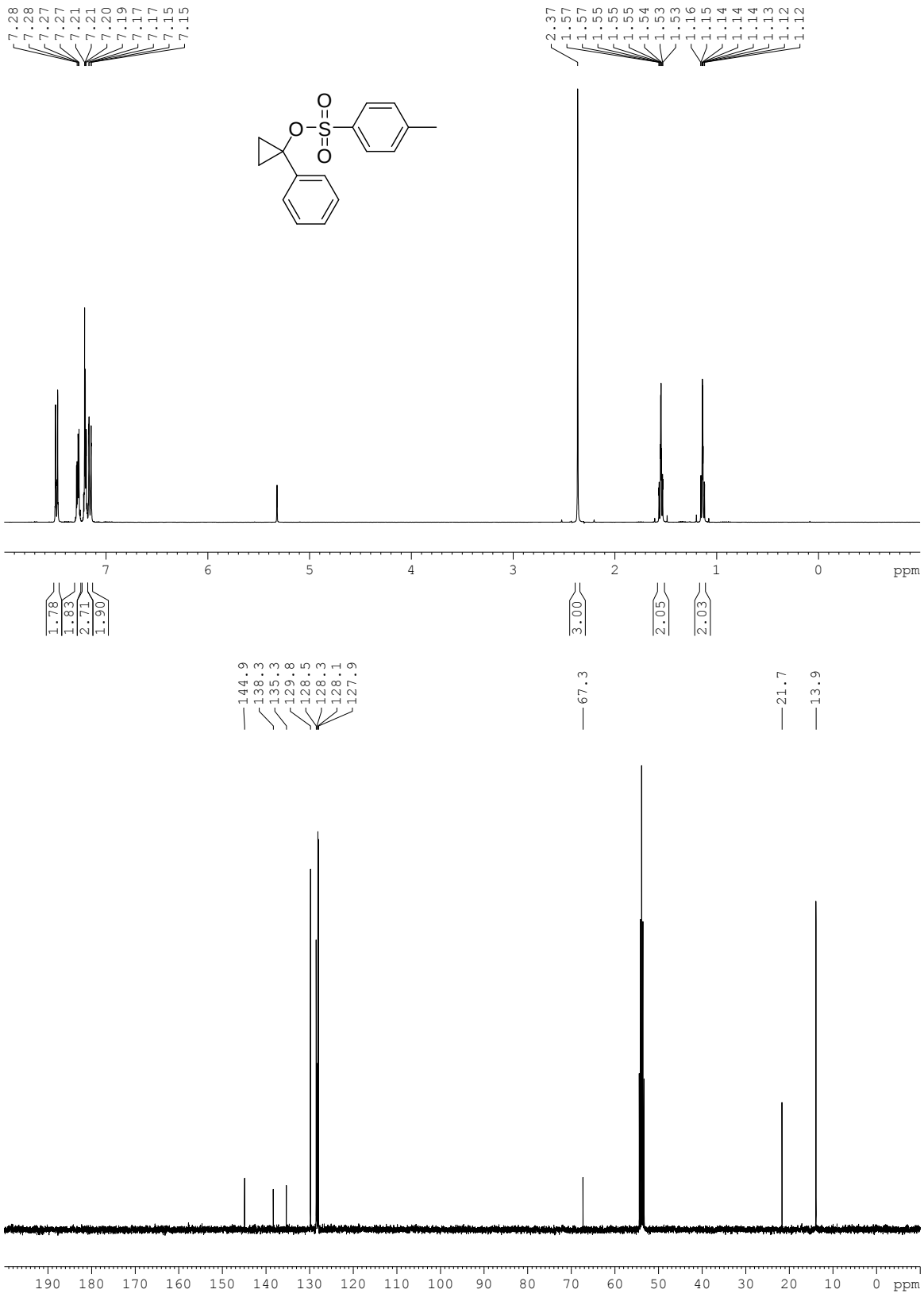
Compound S7


7.27
7.25
7.24
7.23
7.22
7.22
7.18
7.16
7.09
7.09
7.07
7.07
7.06
2.79
2.77
2.76
2.75
2.73
2.46
2.01
2.00
1.99
1.99
1.98
1.96
1.11
1.10
1.08
1.08
1.06
1.06
0.61
0.59
0.59
0.58
0.58
0.56
0.56
O
O
S
O
O
7
6
5
4
3
2
1
0
ppm
1.68
1.80
1.81
0.93
1.80
1.99
2.97
2.00
2.02
2.02
145.4
141.9
136.0
130.3
128.8
128.7
128.0
126.3
67.2
38.5
32.2
21.8
12.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

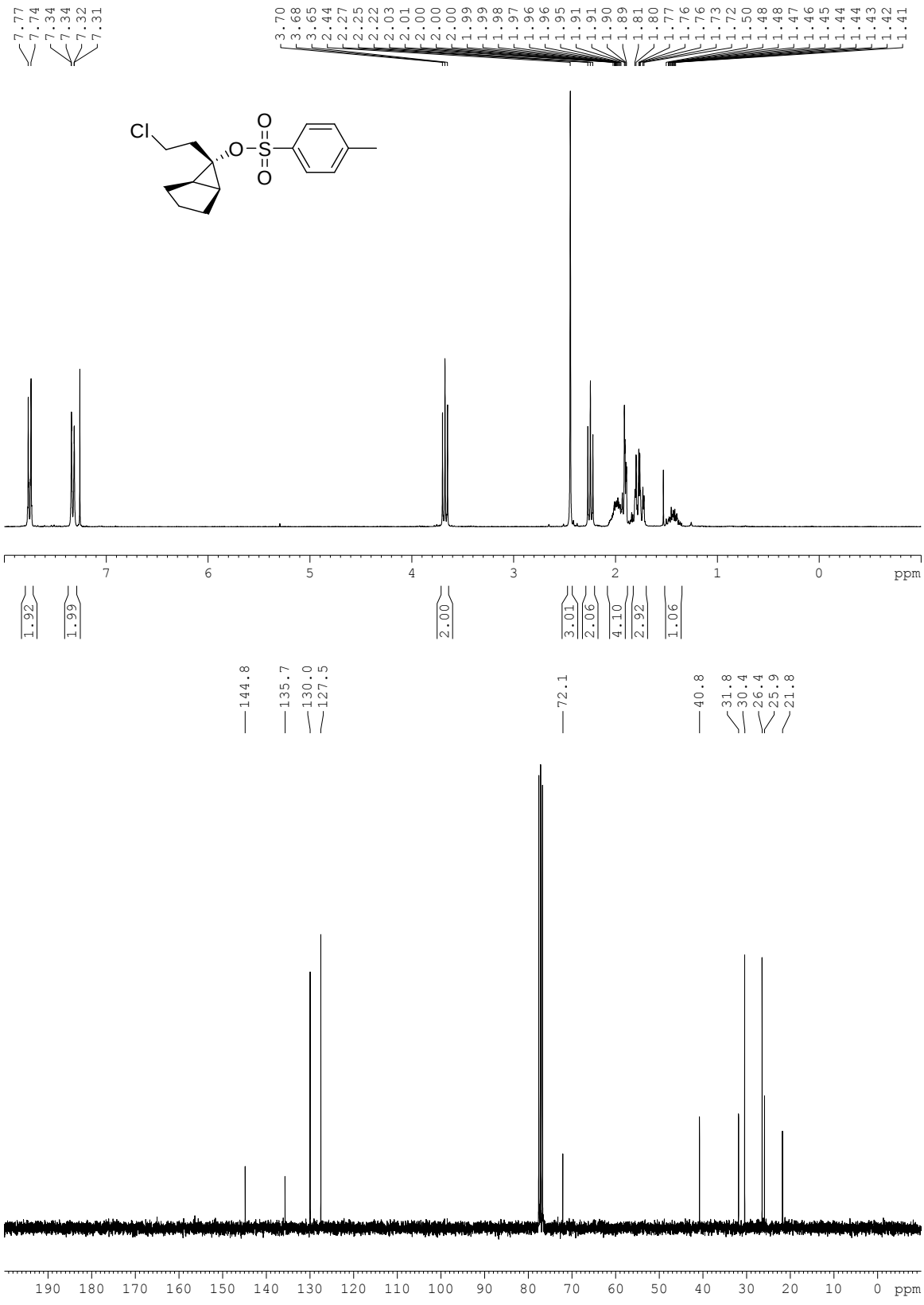
Compound S8


7.75 7.74 7.74 7.73 7.72 7.72 7.31 7.30 7.30 7.30 7.28 7.28 7.27 7.26
5.71 5.70 5.70 5.69 5.69
2.43 1.84 1.84 1.83 1.83 1.82 1.81 1.81 1.80 1.79 1.30 1.29 1.29 1.28 1.28 1.27 1.27 1.27 1.26 1.26 1.26 1.25 1.24 1.24 1.23 1.22 1.22 1.22 1.21 1.20 1.19 0.83 0.83 0.82 0.82 0.81 0.81 0.80 0.80
O
O
S
O
O
7 6 5 4 3 2 1 0 ppm
1.88 1.93 1.00 3.03 4.22 6.41 2.08
144.3 135.4 133.3 129.4 128.5 127.9 69.9 25.5 24.9 22.0 21.8 21.8 11.7
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

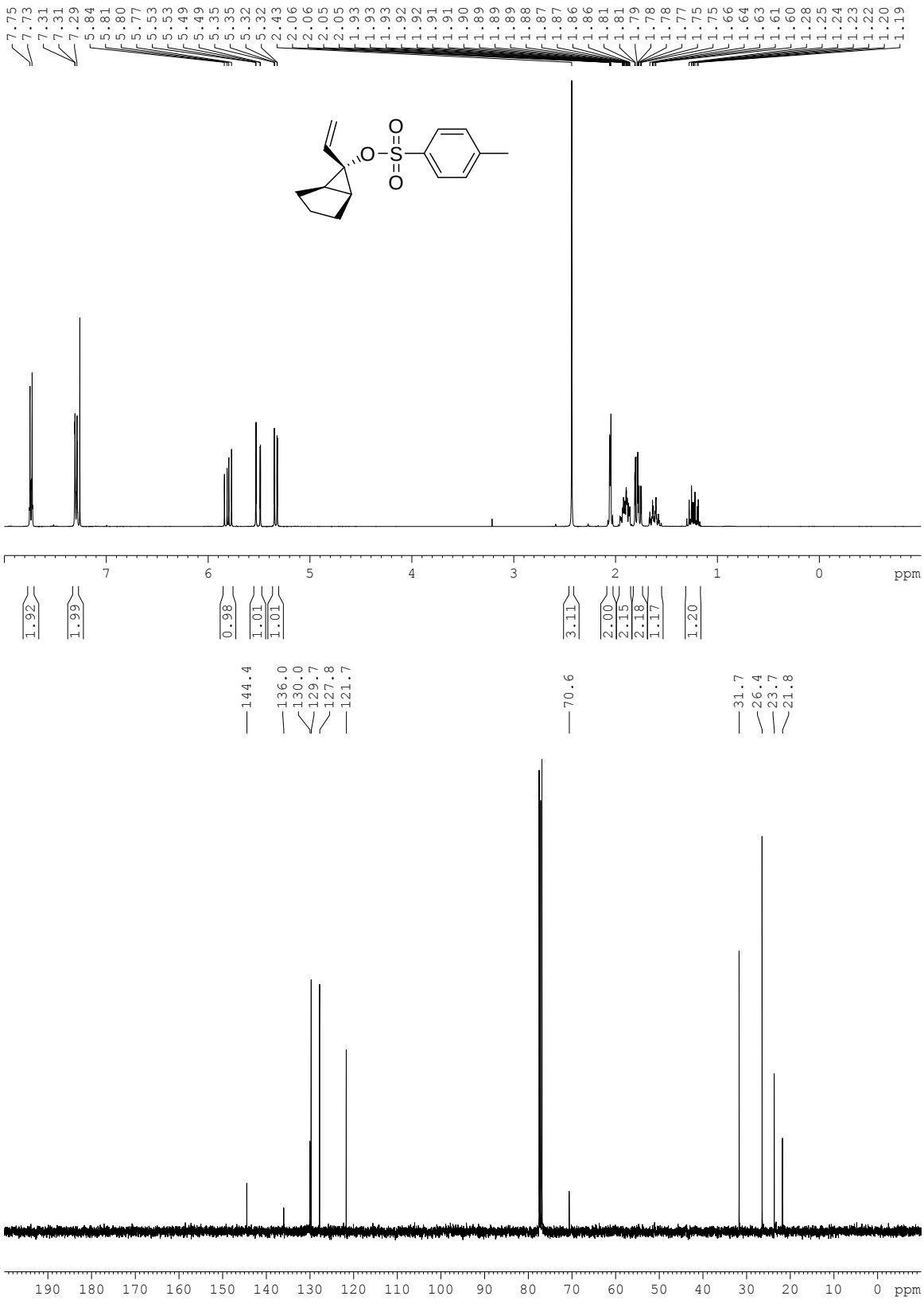
Compound S9


7.28
7.28
7.27
7.27
7.21
7.21
7.20
7.19
7.17
7.17
7.15
7.15
2.37
1.57
1.57
1.55
1.55
1.55
1.54
1.53
1.53
1.16
1.15
1.14
1.14
1.14
1.13
1.12
1.12
O
O
S
O
O
7
6
5
4
3
2
1
0
ppm
1.78
1.83
2.71
1.90
3.00
2.05
2.03
144.9
138.3
135.3
129.8
128.5
128.3
128.1
127.9
67.3
21.7
13.9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

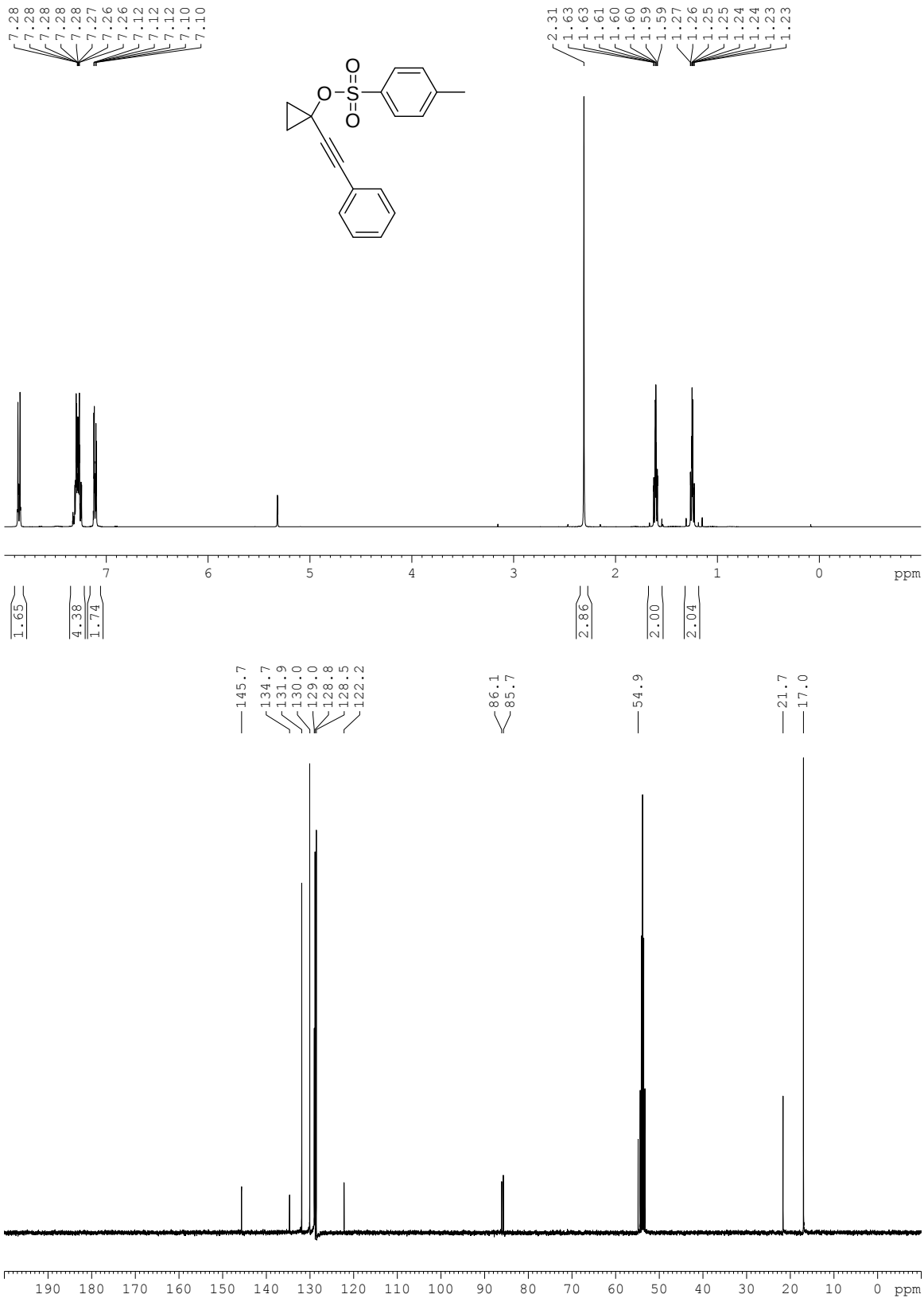
Compound S10



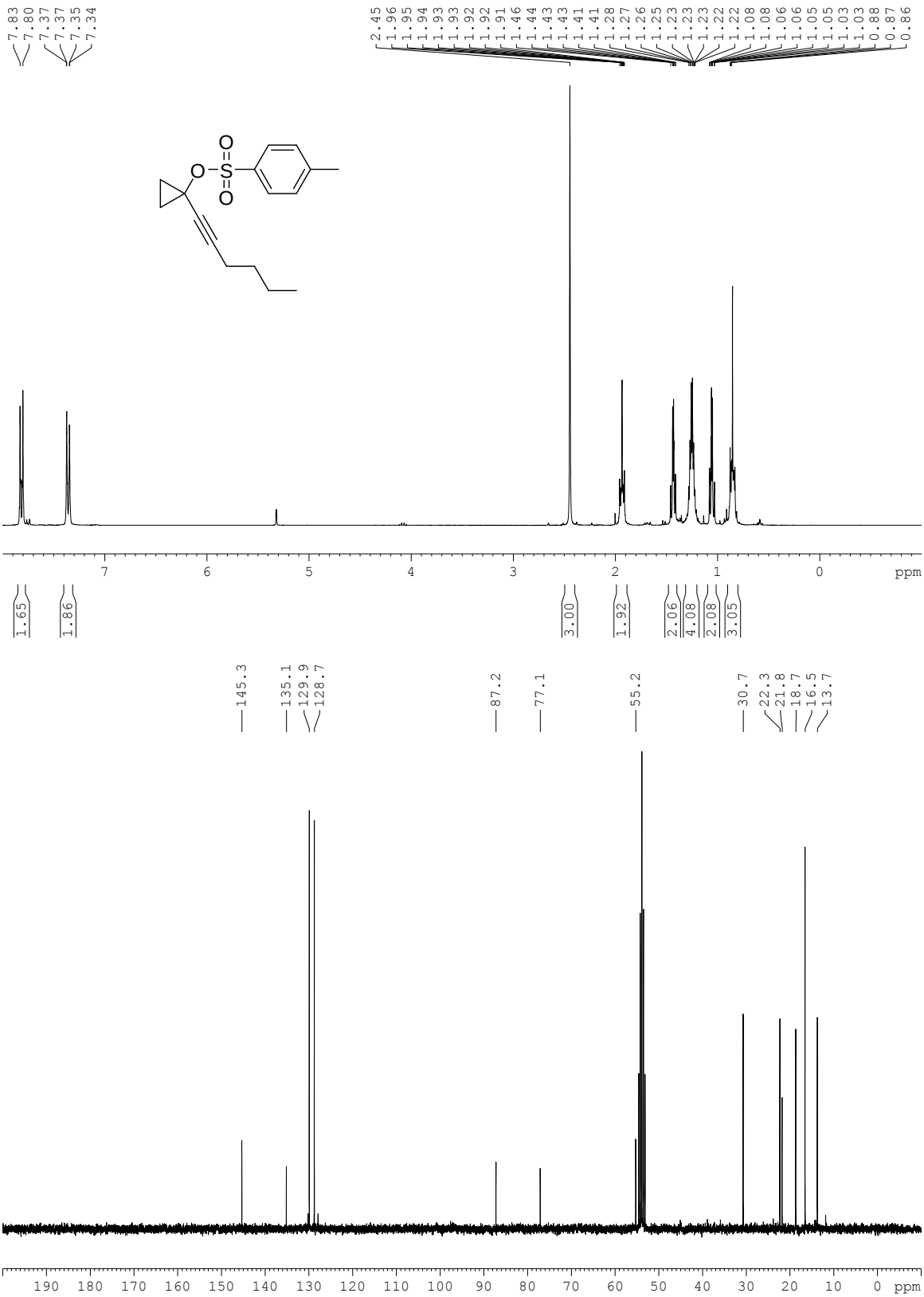
Compound S11



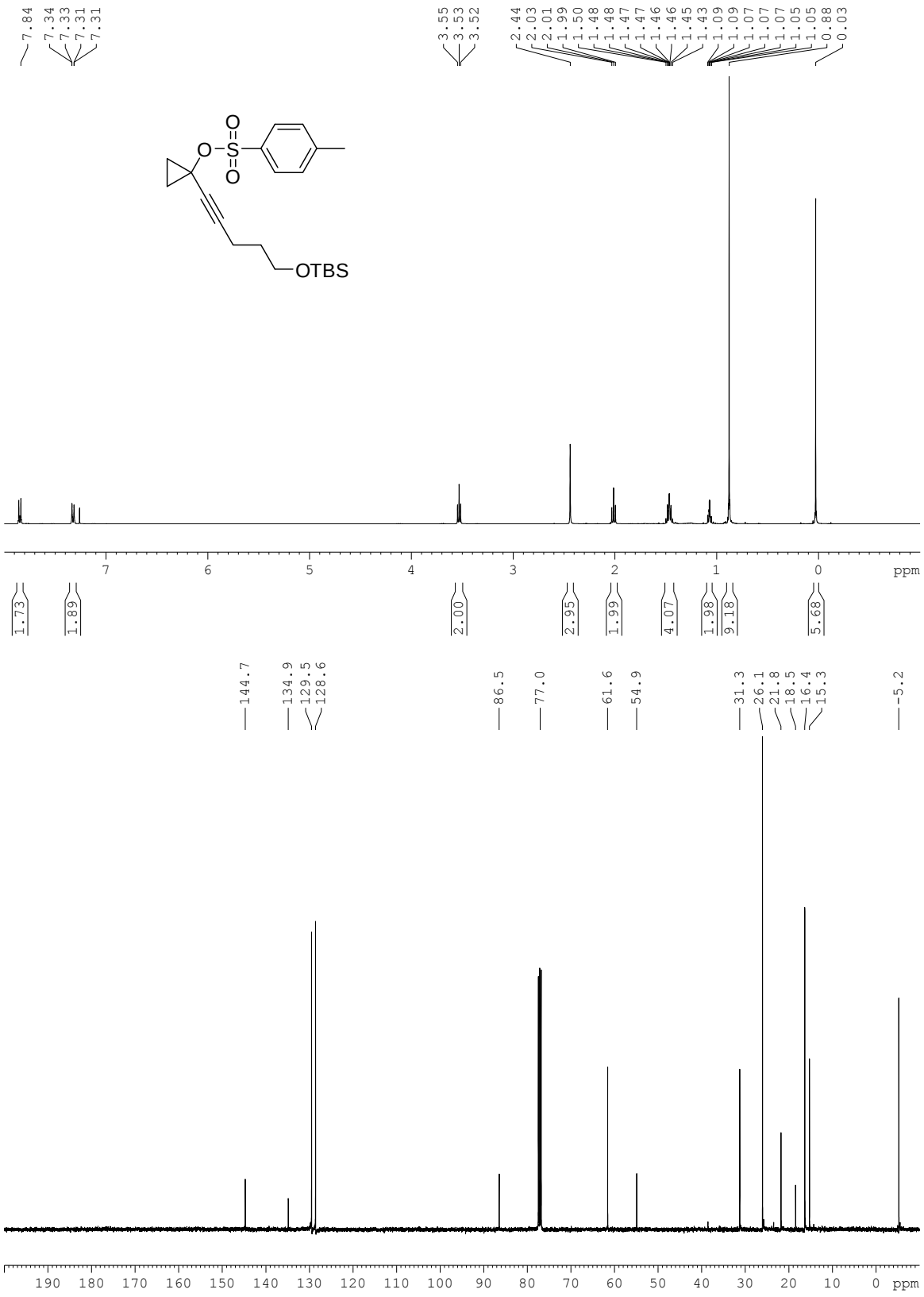
Compound 1a


7.28
7.28
7.28
7.28
7.28
7.27
7.26
7.26
7.12
7.12
7.12
7.10
7.10
2.31
1.63
1.63
1.61
1.60
1.60
1.59
1.59
1.27
1.26
1.25
1.25
1.24
1.24
1.23
1.23
O
O=S=O
ppm
1.65
4.38
1.74
2.86
2.00
2.04
145.7
134.7
131.9
130.0
129.0
128.8
128.5
122.2
86.1
85.7
54.9
21.7
17.0
ppm

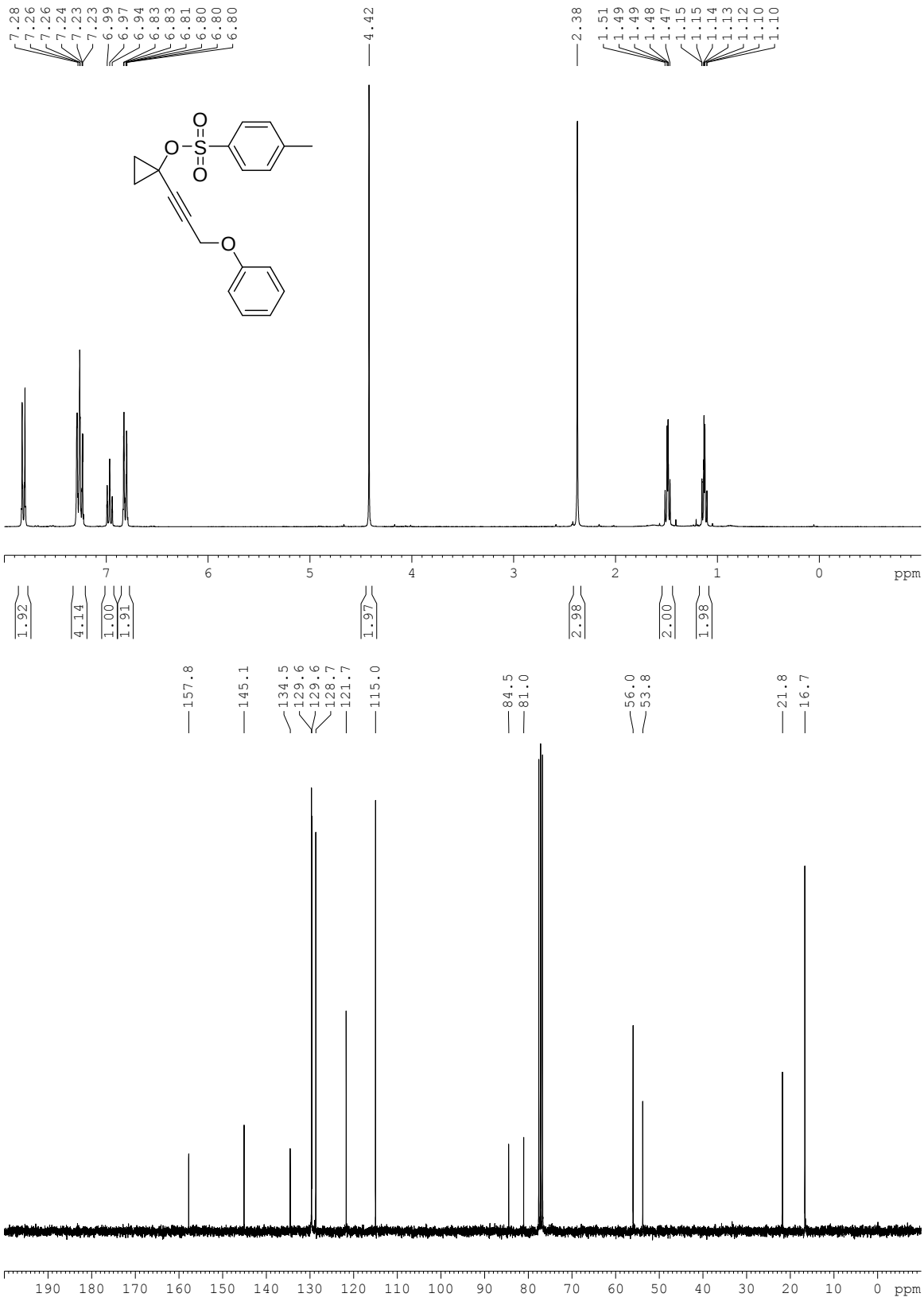
Compound 1b


7.83
7.80
7.37
7.37
7.35
7.34
2.45
1.96
1.95
1.94
1.93
1.93
1.92
1.92
1.91
1.46
1.44
1.43
1.43
1.41
1.41
1.28
1.27
1.26
1.25
1.23
1.23
1.23
1.22
1.22
1.08
1.08
1.06
1.06
1.05
1.05
1.03
0.88
0.87
0.86
O
O
O
S
O
7
6
5
4
3
2
1
0
ppm
1.65
1.86
3.00
1.92
2.06
4.08
2.08
3.05
145.3
135.1
129.9
128.7
87.2
77.1
55.2
30.7
22.3
21.8
18.7
16.5
13.7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

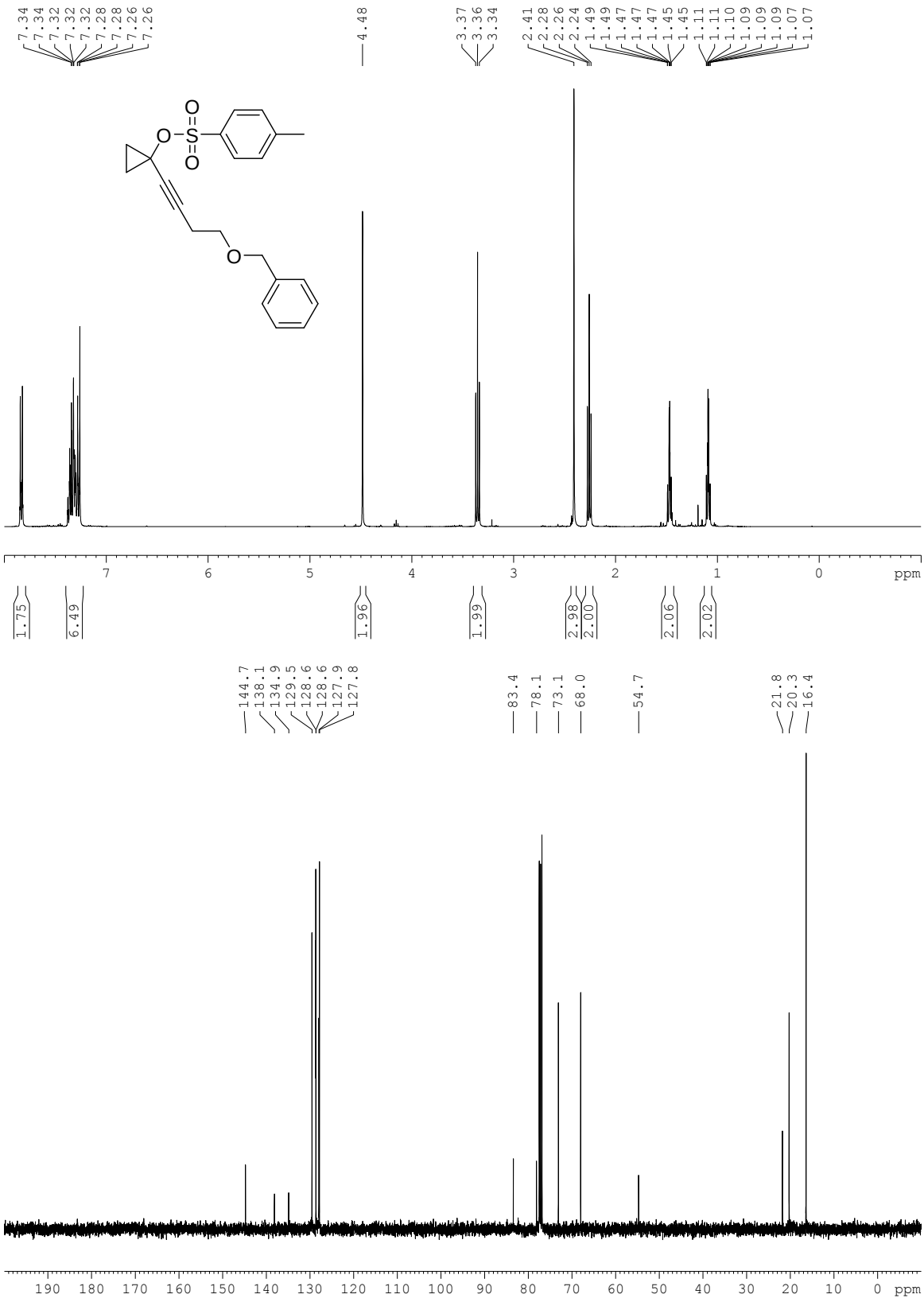
Compound 1c


7.84
7.34
7.33
7.31
7.31
3.55
3.53
3.52
2.44
2.03
2.01
1.99
1.50
1.48
1.48
1.47
1.47
1.46
1.46
1.45
1.43
1.09
1.09
1.07
1.07
1.07
1.05
1.05
0.88
0.03
O
O
S
O
O
OTBS
ppm
1.73
1.89
2.00
2.95
1.99
4.07
1.98
9.18
5.68
144.7
134.9
129.5
128.6
86.5
77.0
61.6
54.9
31.3
26.1
21.8
18.5
16.4
15.3
-5.2
ppm

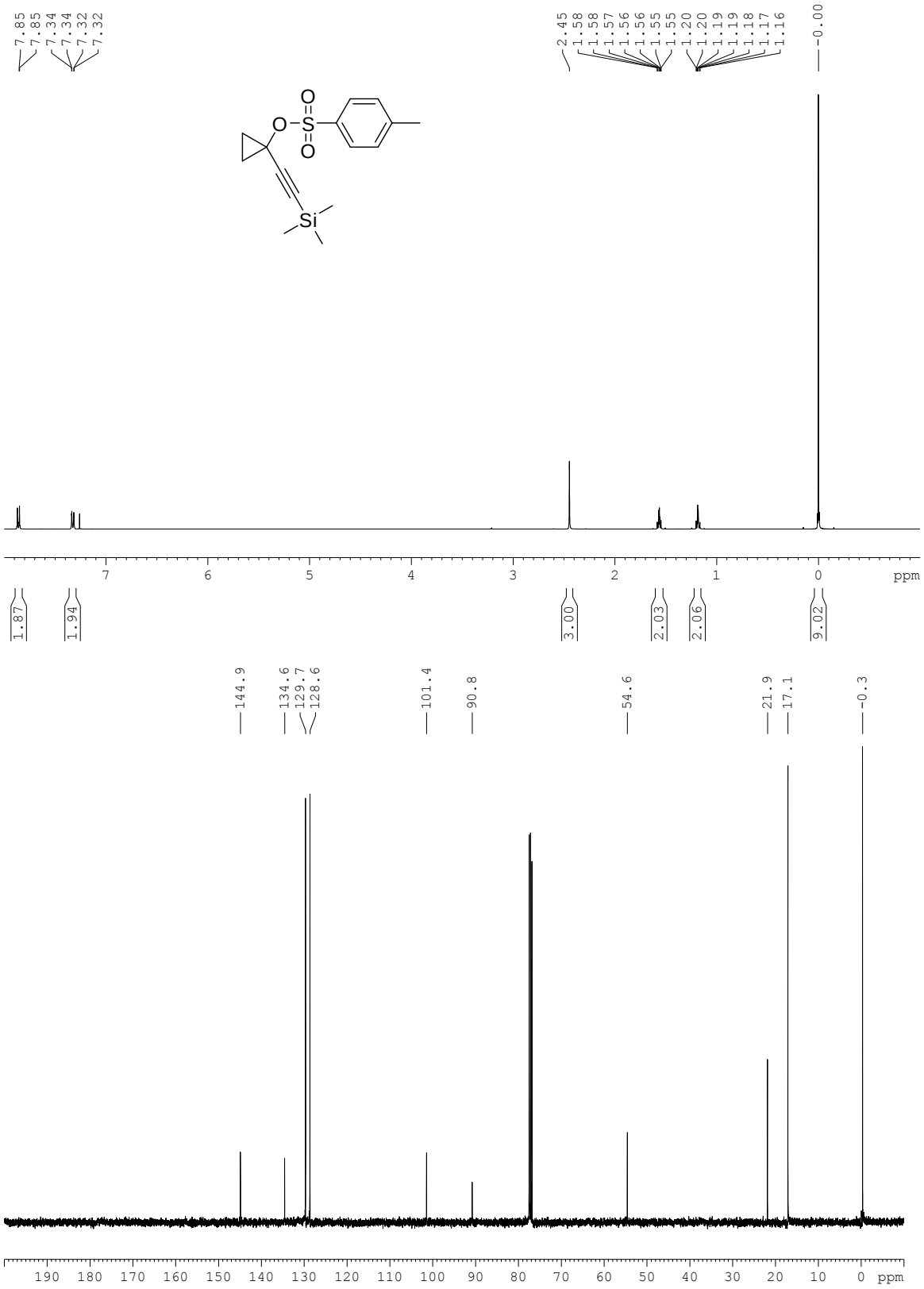
Compound 1d


7.28
7.26
7.26
7.24
7.23
7.23
6.99
6.97
6.94
6.83
6.83
6.81
6.80
6.80
6.80
4.42
2.38
1.51
1.49
1.49
1.48
1.47
1.15
1.15
1.14
1.13
1.12
1.10
1.10
O
O=S
O
O
O
7
6
5
4
3
2
1
0
ppm
1.92
4.14
1.00
1.91
1.97
2.98
2.00
1.98
157.8
145.1
134.5
129.6
129.6
128.7
121.7
115.0
84.5
81.0
56.0
53.8
21.8
16.7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

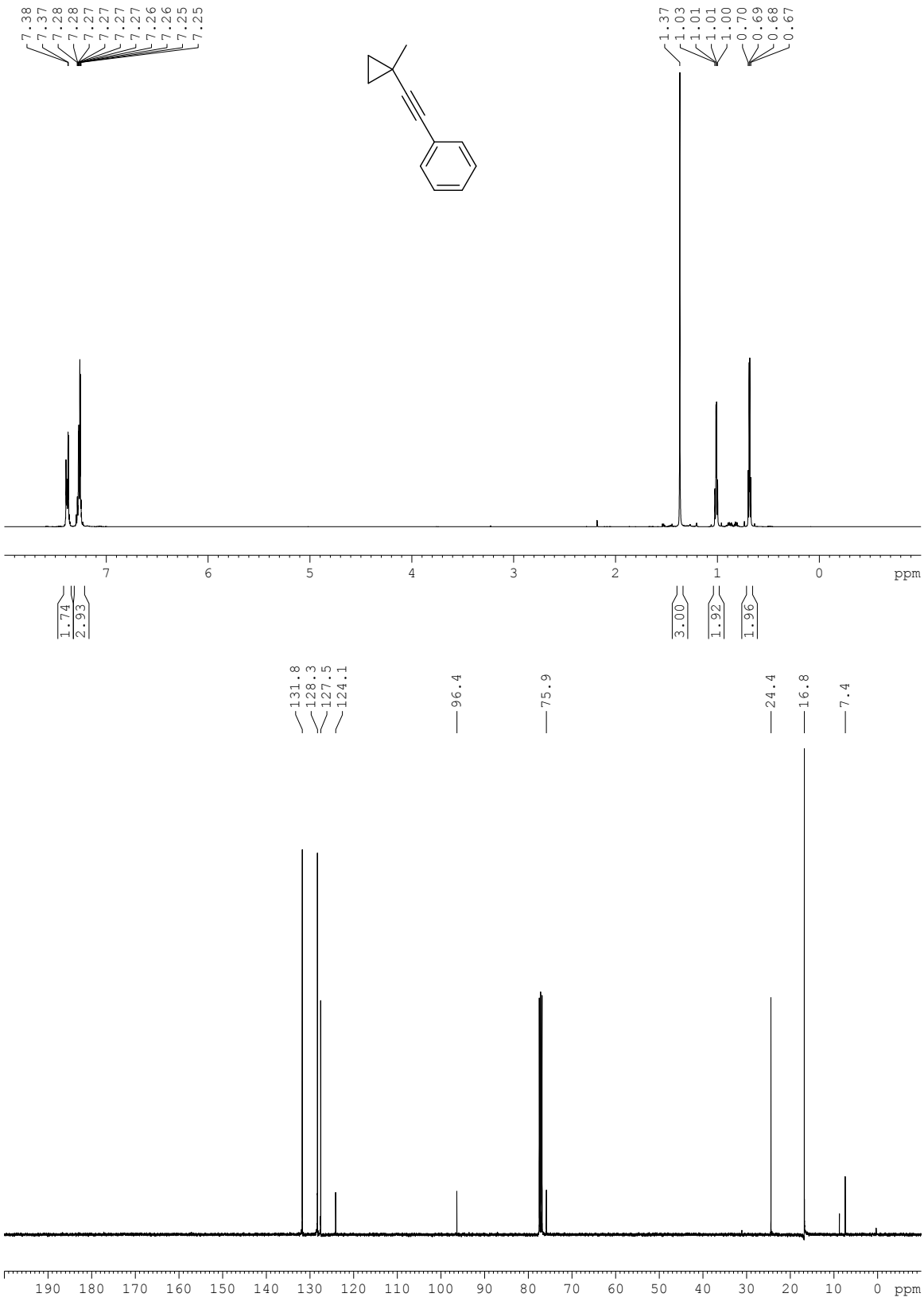
Compound 1e


7.34
7.34
7.32
7.32
7.32
7.28
7.28
7.26
7.26
4.48
3.37
3.36
3.34
2.41
2.28
2.26
2.24
1.49
1.49
1.47
1.47
1.47
1.45
1.45
1.11
1.11
1.10
1.09
1.09
1.09
1.07
1.07
O
O
S
O
O
ppm
1.75
6.49
1.96
1.99
2.98
2.00
2.06
2.02
144.7
138.1
134.9
129.5
128.6
128.6
127.9
127.8
83.4
78.1
73.1
68.0
54.7
21.8
20.3
16.4
ppm

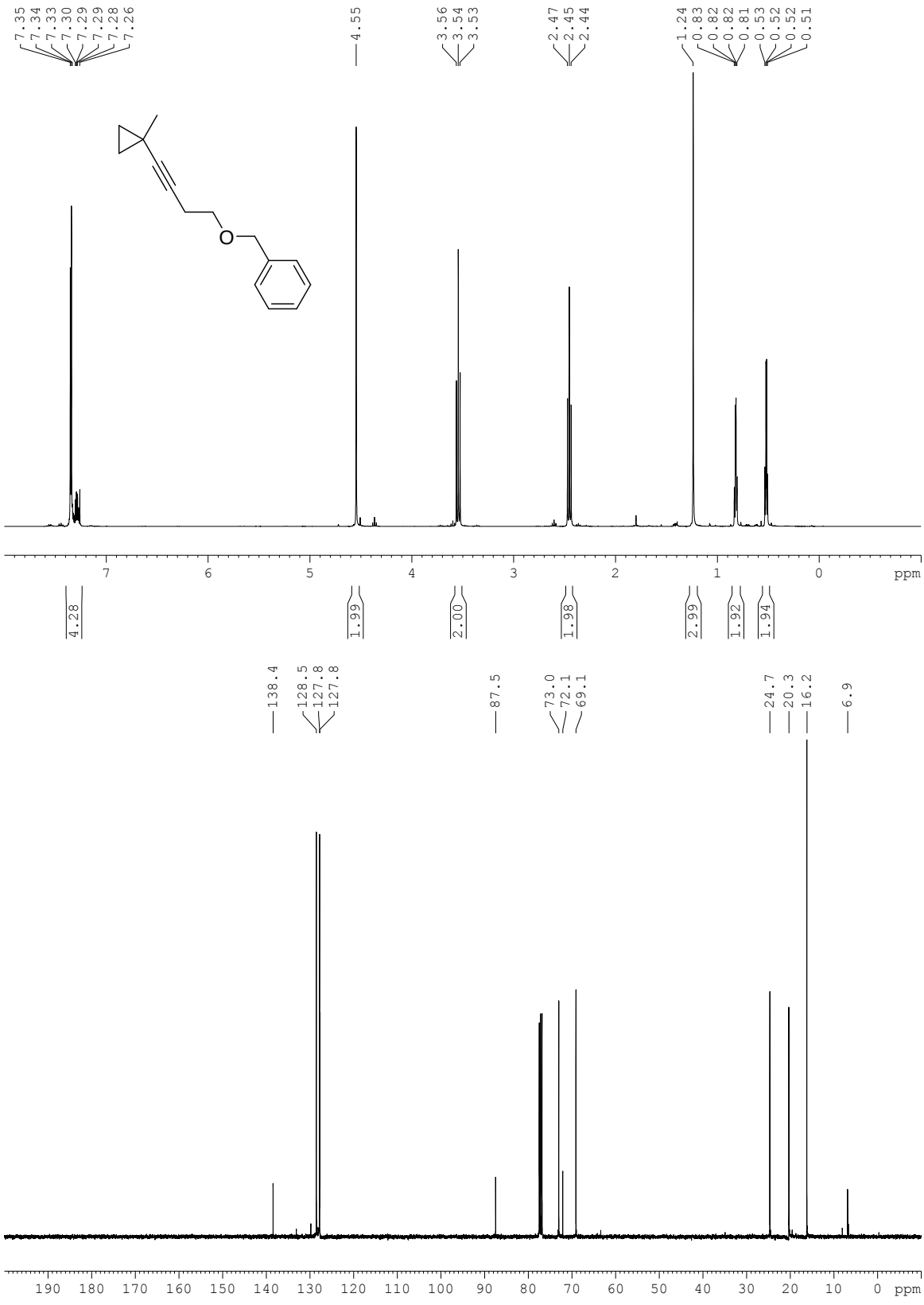
Compound 1f


7.85
7.85
7.34
7.34
7.32
7.32
2.45
1.58
1.58
1.57
1.56
1.56
1.55
1.55
1.20
1.20
1.19
1.19
1.18
1.17
1.16
0.00
O
O
S
O
O
Si
7
6
5
4
3
2
1
0
ppm
1.87
1.94
3.00
2.03
2.06
9.02
144.9
134.6
129.7
128.6
101.4
90.8
54.6
21.9
17.1
-0.3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

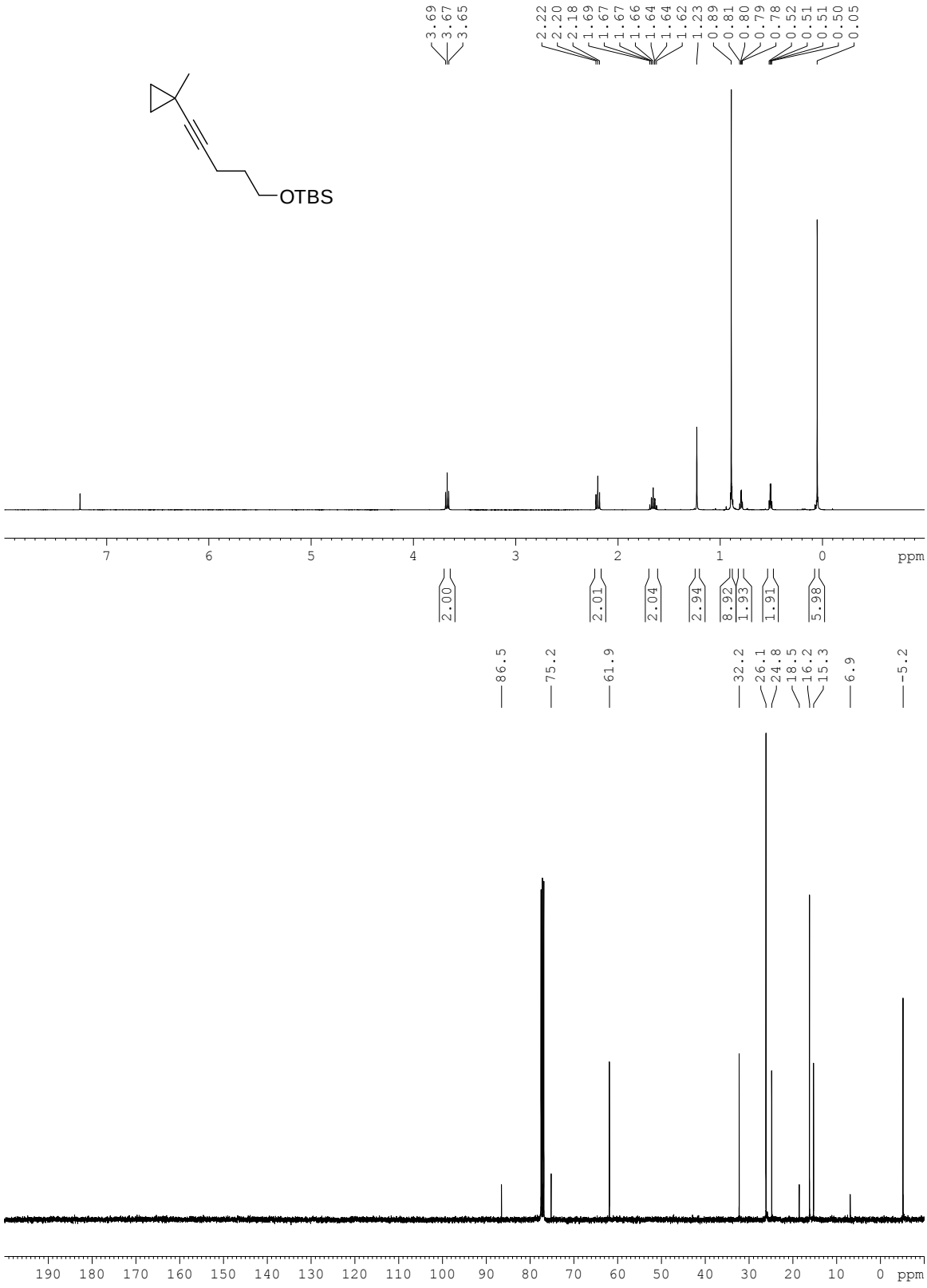
Compound 2a


7.38
7.37
7.28
7.28
7.27
7.27
7.27
7.27
7.26
7.26
7.25
7.25
1.37
1.03
1.01
1.01
1.00
0.70
0.69
0.68
0.67
ppm
1.74
2.93
3.00
1.92
1.96
131.8
128.3
127.5
124.1
96.4
75.9
24.4
16.8
7.4
ppm

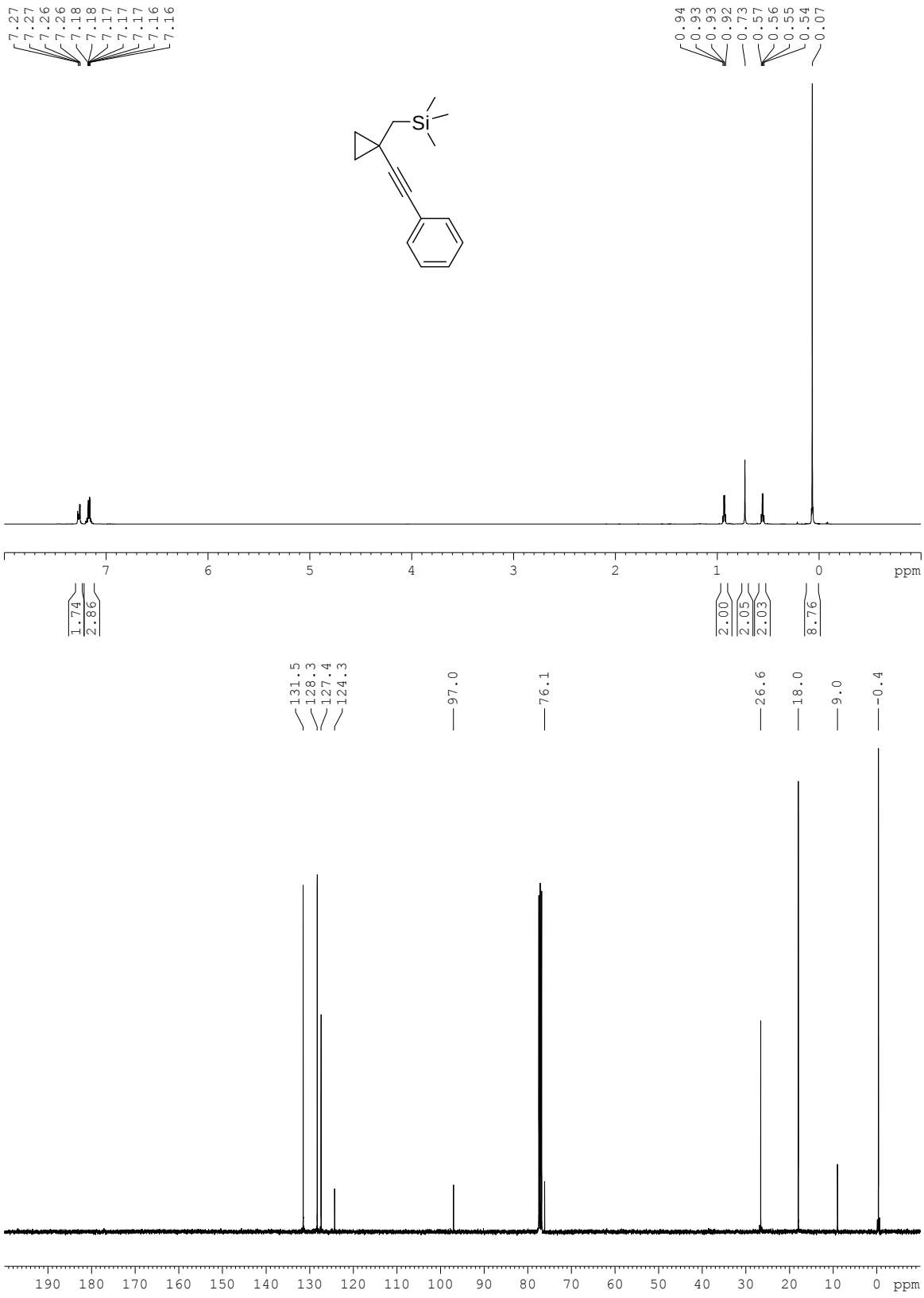
Compound 2b


7.35
7.34
7.33
7.30
7.29
7.29
7.28
7.26
4.55
3.56
3.54
3.53
2.47
2.45
2.44
1.24
0.83
0.82
0.82
0.81
0.53
0.52
0.52
0.51
O
ppm
4.28
1.99
2.00
1.98
2.99
1.92
1.94
138.4
128.5
127.8
127.8
87.5
73.0
72.1
69.1
24.7
20.3
16.2
6.9
ppm

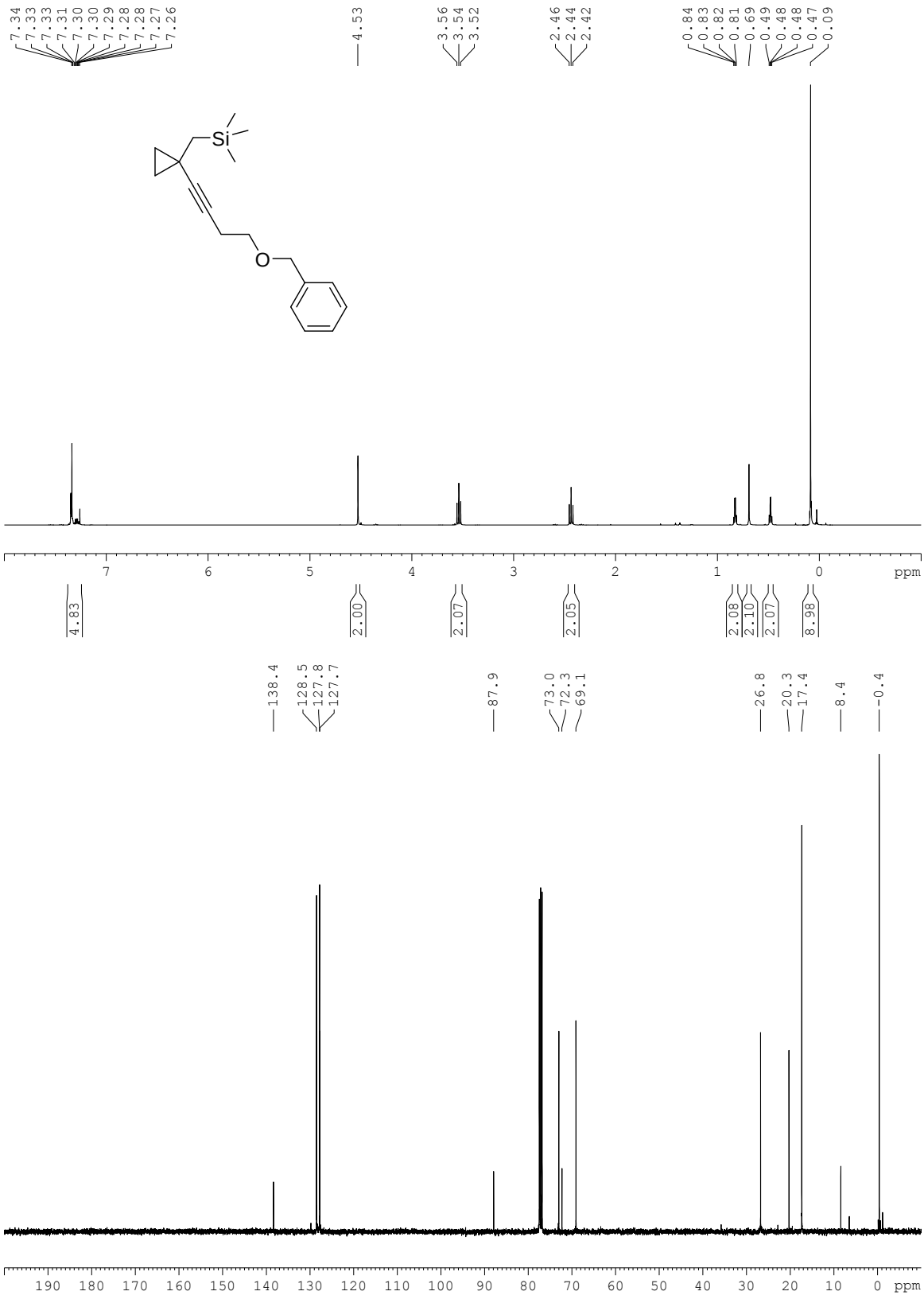
Compound 2c


3.69
3.67
3.65
2.22
2.20
2.18
1.69
1.67
1.67
1.66
1.64
1.64
1.62
1.23
0.89
0.81
0.80
0.79
0.78
0.52
0.51
0.51
0.50
0.05
OTBS
ppm
2.00
2.01
2.04
2.94
8.92
1.93
1.91
5.98
86.5
75.2
61.9
32.2
26.1
24.8
18.5
16.2
15.3
6.9
-5.2
ppm

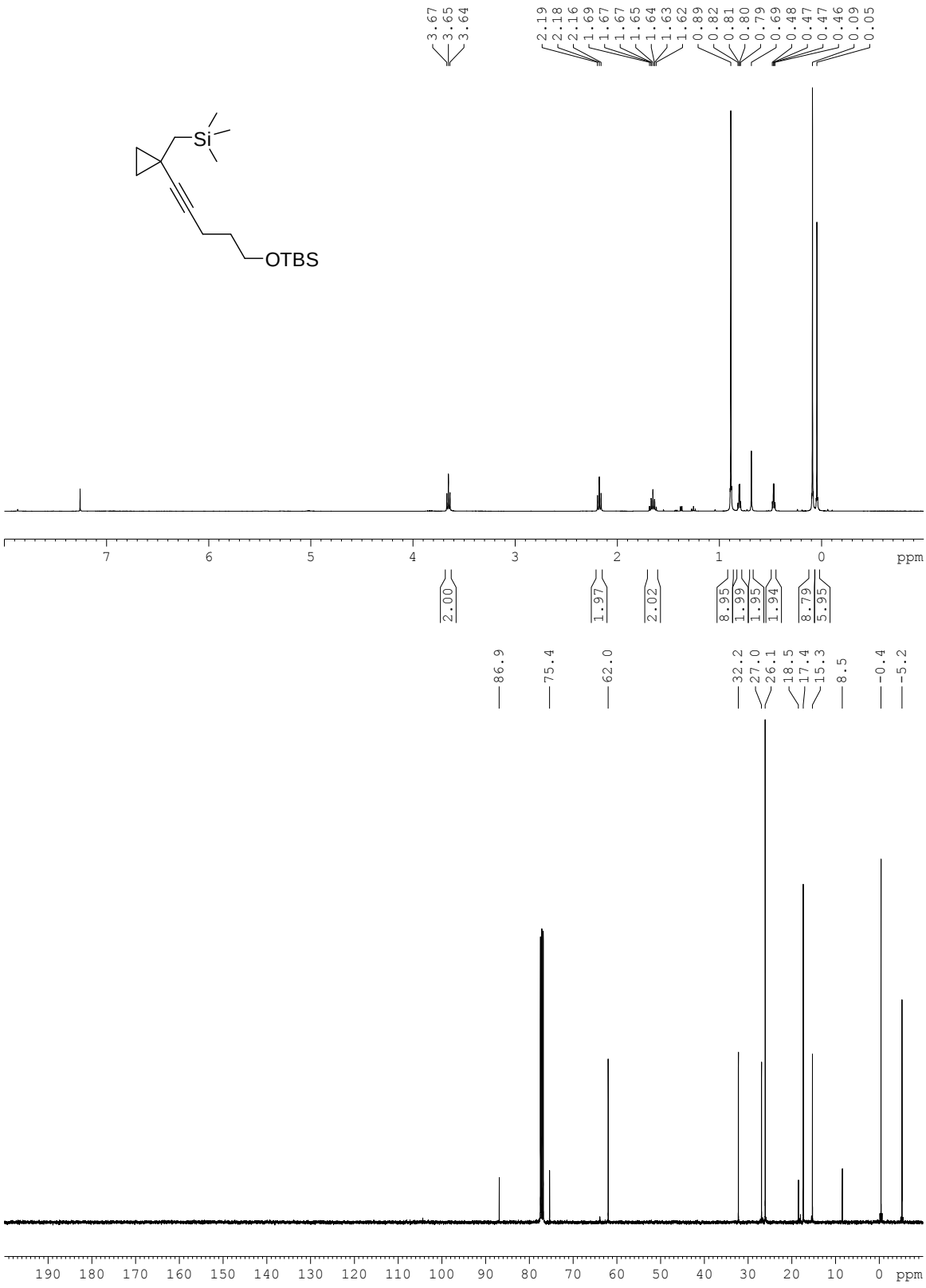
Compound 2d


7.27
7.27
7.26
7.26
7.18
7.18
7.17
7.17
7.17
7.16
7.16
0.94
0.93
0.93
0.92
0.73
0.57
0.56
0.55
0.54
0.07
Si
ppm
1.74
2.86
2.00
2.05
2.03
8.76
131.5
128.3
127.4
124.3
97.0
76.1
26.6
18.0
9.0
-0.4
ppm

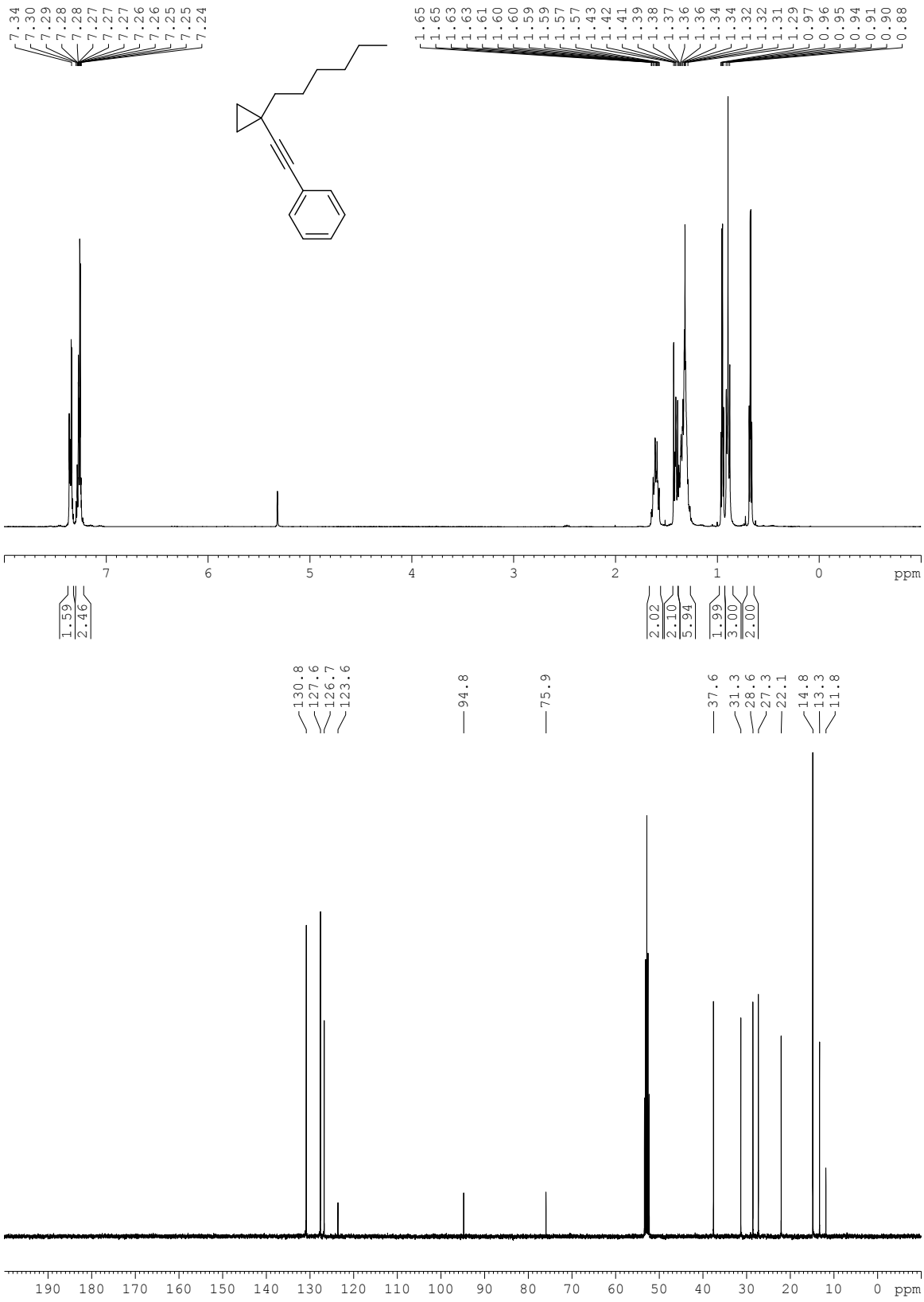
Compound 2e


7.34
7.33
7.33
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
4.53
3.56
3.54
3.52
2.46
2.44
2.42
0.84
0.83
0.82
0.81
0.69
0.49
0.48
0.48
0.47
0.09
Si
O
ppm
4.83
2.00
2.07
2.05
2.08
2.10
2.07
8.98
138.4
128.5
127.8
127.7
87.9
73.0
72.3
69.1
26.8
20.3
17.4
8.4
0.4
ppm

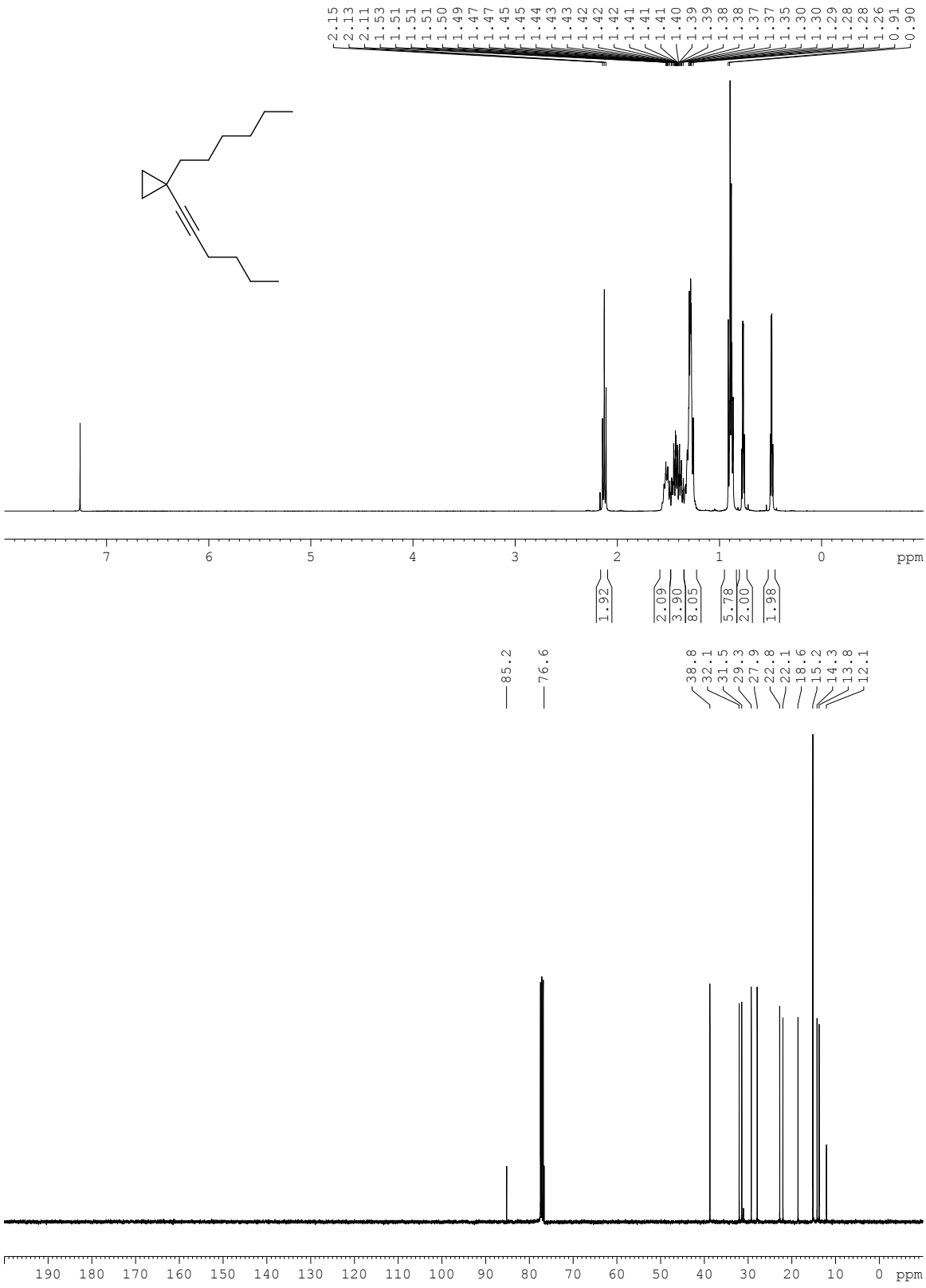
Compound 2f


3.67
3.65
3.64
2.19
2.18
2.16
1.69
1.67
1.67
1.65
1.64
1.63
1.62
0.89
0.82
0.81
0.80
0.79
0.69
0.48
0.47
0.47
0.46
0.09
0.05
Si
OTBS
ppm
2.00
1.97
2.02
8.95
1.99
1.95
1.94
8.79
5.95
86.9
75.4
62.0
32.2
27.0
26.1
18.5
17.4
15.3
8.5
-0.4
-5.2
ppm

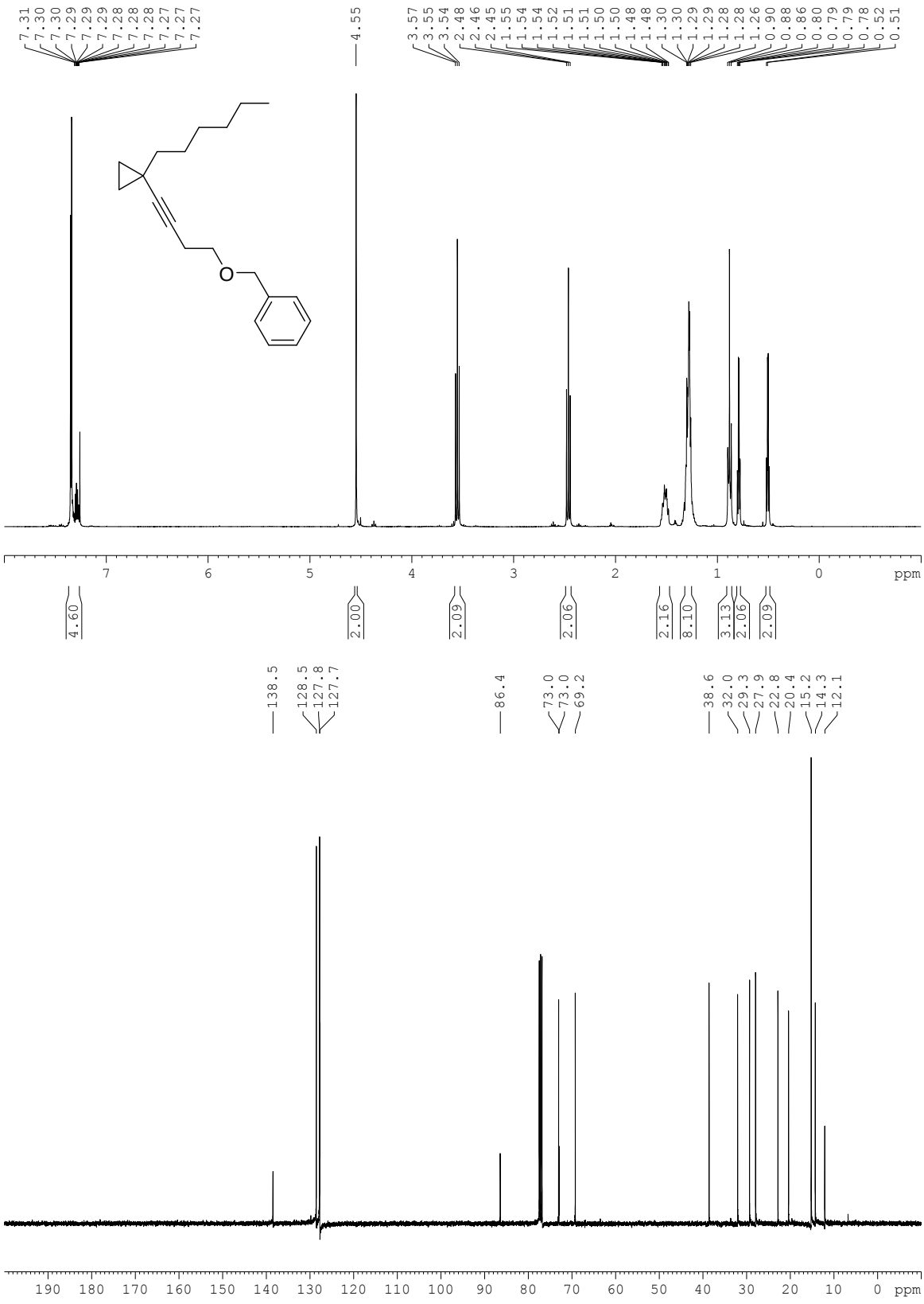
Compound 2g


7.34
7.30
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
1.65
1.65
1.63
1.63
1.61
1.60
1.60
1.59
1.59
1.57
1.57
1.43
1.42
1.41
1.39
1.38
1.37
1.36
1.36
1.34
1.34
1.32
1.32
1.31
1.29
0.97
0.96
0.95
0.94
0.91
0.90
0.88
ppm
1.59
2.46
2.02
2.10
5.94
1.99
3.00
2.00
130.8
127.6
126.7
123.6
94.8
75.9
37.6
31.3
28.6
27.3
22.1
14.8
13.3
11.8
ppm

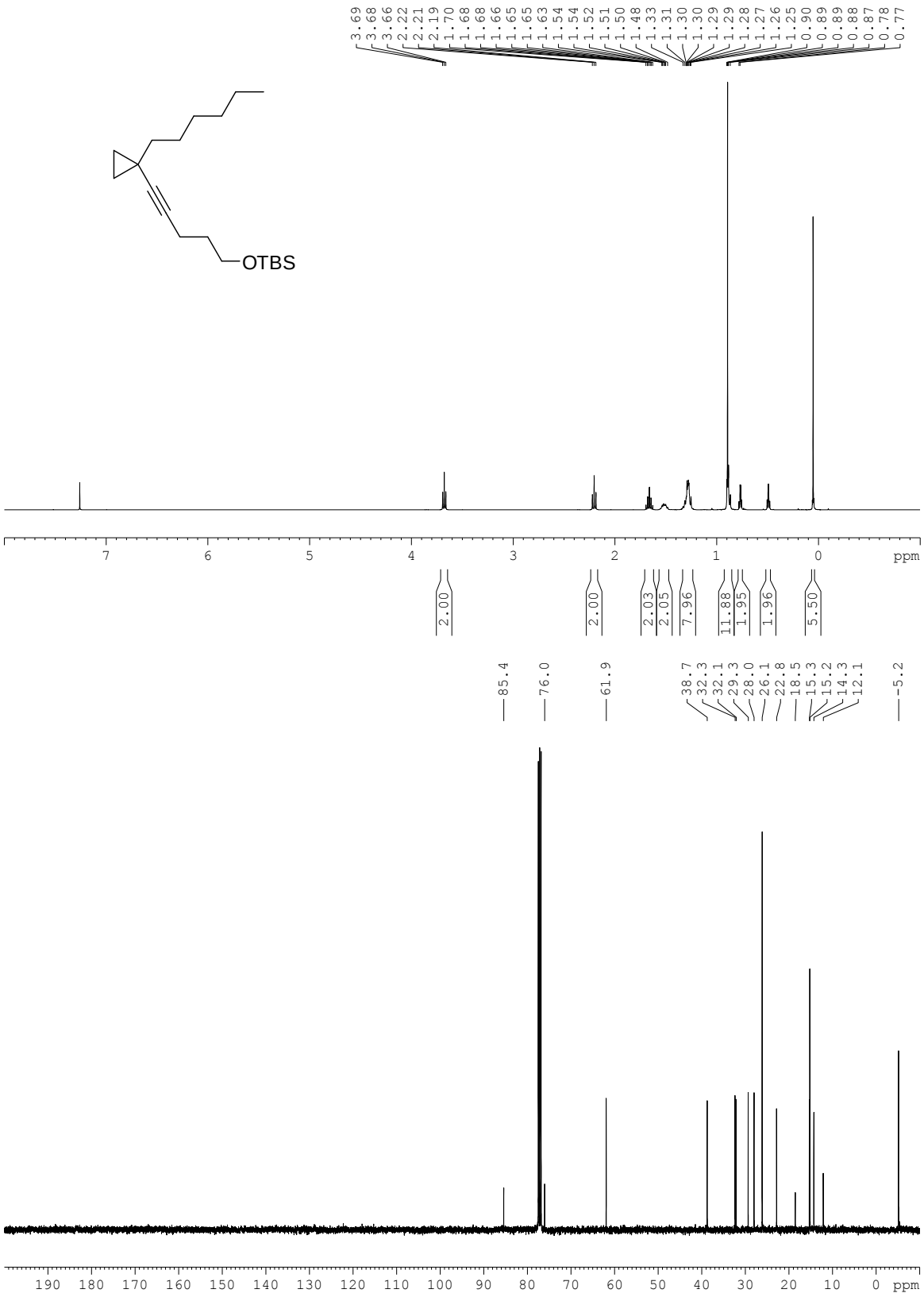
Compound 2h


2.15
2.13
2.11
1.53
1.51
1.51
1.51
1.50
1.49
1.47
1.47
1.45
1.45
1.44
1.43
1.43
1.42
1.42
1.42
1.41
1.41
1.41
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.35
1.30
1.30
1.29
1.28
1.26
0.91
0.90
7
6
5
4
3
2
1
0
ppm
1.92
2.09
3.90
8.05
5.78
2.00
1.98
85.2
76.6
38.8
32.1
31.5
29.3
27.9
22.8
22.1
18.6
15.2
14.3
13.8
12.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

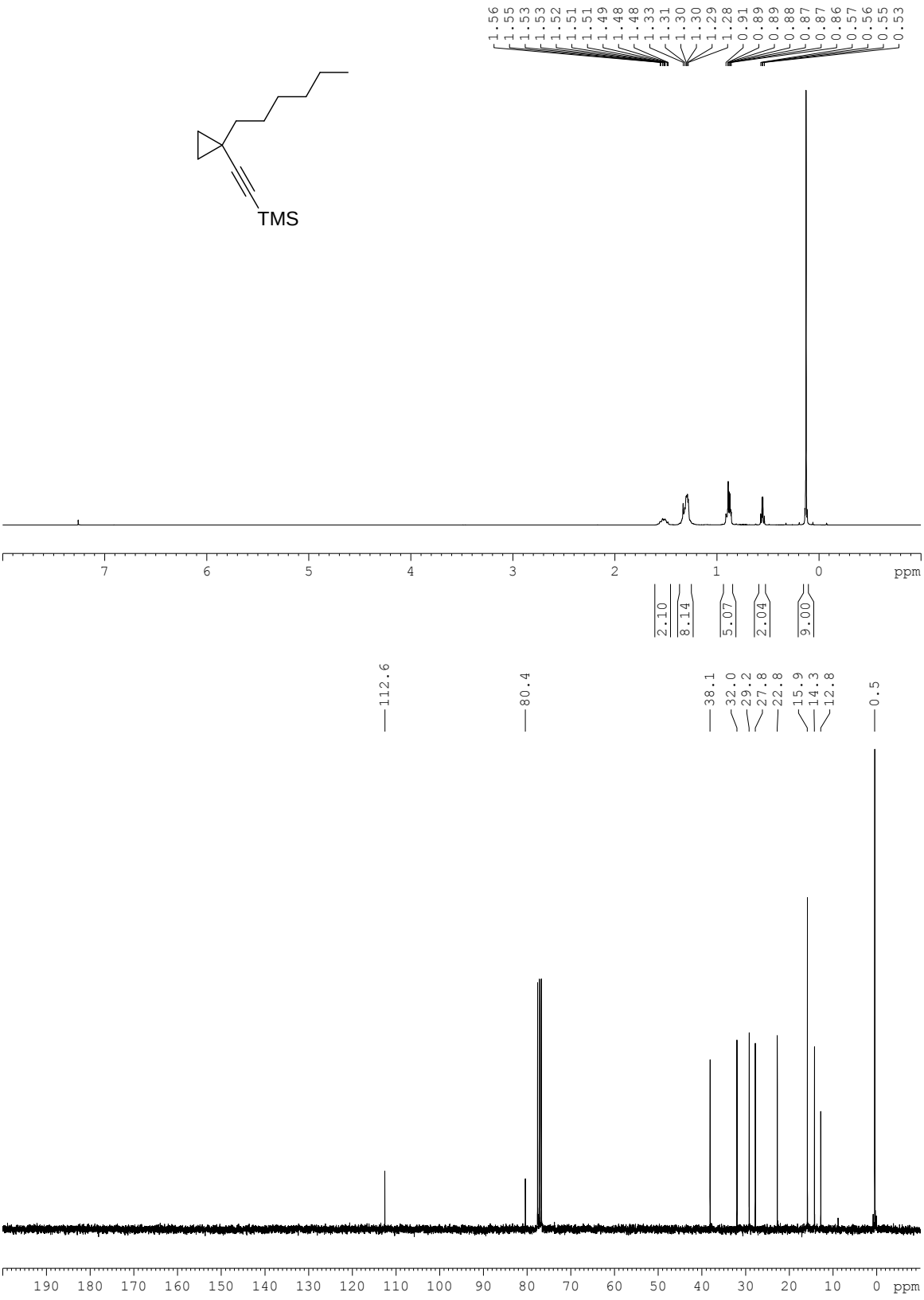
Compound 2i


7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.27
4.55
3.57
3.55
3.54
2.48
2.46
2.45
1.55
1.54
1.54
1.52
1.51
1.51
1.50
1.50
1.48
1.48
1.30
1.30
1.29
1.29
1.28
1.28
1.26
0.90
0.88
0.86
0.80
0.79
0.79
0.78
0.52
0.51
O
7
6
5
4
3
2
1
0
ppm
4.60
2.00
2.09
2.06
2.16
8.10
3.13
2.06
2.09
138.5
128.5
127.8
127.7
86.4
73.0
73.0
69.2
38.6
32.0
29.3
27.9
22.8
20.4
15.2
14.3
12.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

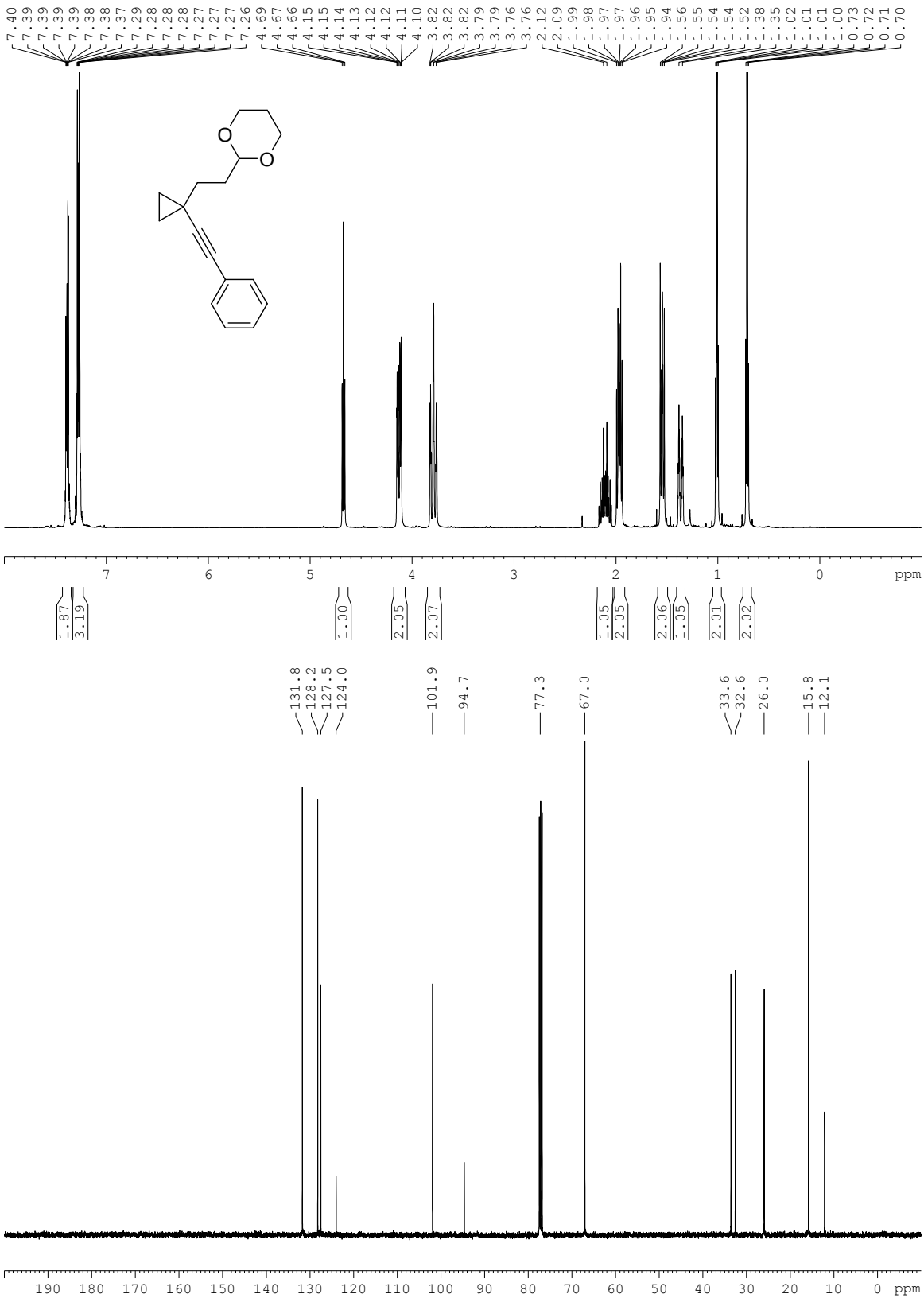
Compound 2j


3.69
3.68
3.66
2.22
2.21
2.19
1.70
1.68
1.68
1.66
1.65
1.65
1.63
1.54
1.54
1.52
1.51
1.50
1.48
1.33
1.31
1.30
1.30
1.29
1.29
1.28
1.27
1.26
1.25
0.90
0.89
0.89
0.88
0.87
0.78
0.77
OTBS
ppm
2.00
2.00
2.03
2.05
7.96
11.88
1.95
1.96
5.50
85.4
76.0
61.9
38.7
32.3
32.1
29.3
28.0
26.1
22.8
18.5
15.3
15.2
14.3
12.1
-5.2
ppm

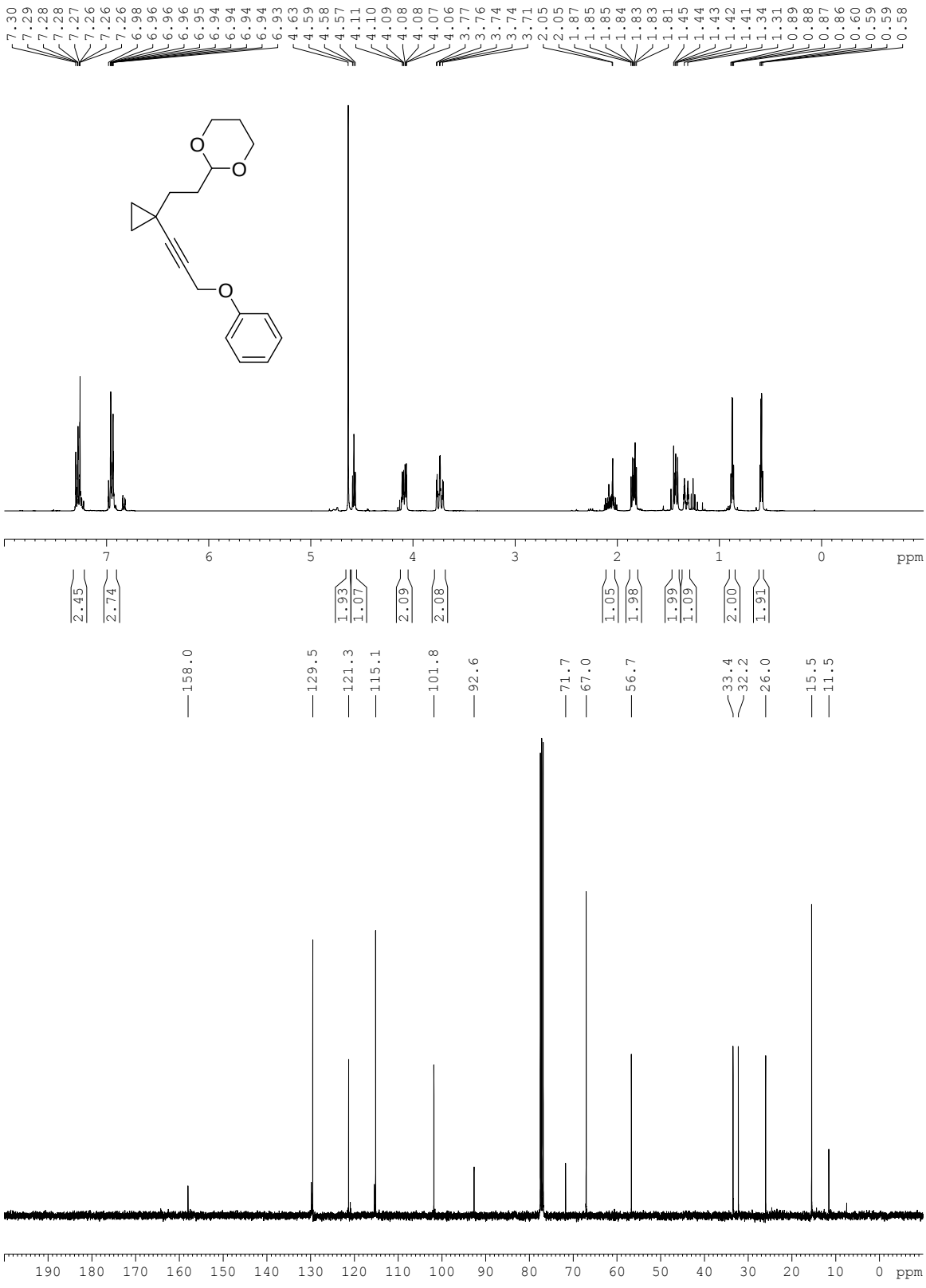
Compound 2k


1.56
1.55
1.53
1.53
1.52
1.51
1.51
1.49
1.48
1.48
1.33
1.31
1.30
1.30
1.29
1.28
0.91
0.89
0.89
0.88
0.87
0.87
0.86
0.57
0.56
0.55
0.53
TMS
7
6
5
4
3
2
1
0
ppm
2.10
8.14
5.07
2.04
9.00
112.6
80.4
38.1
32.0
29.2
27.8
22.8
15.9
14.3
12.8
0.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

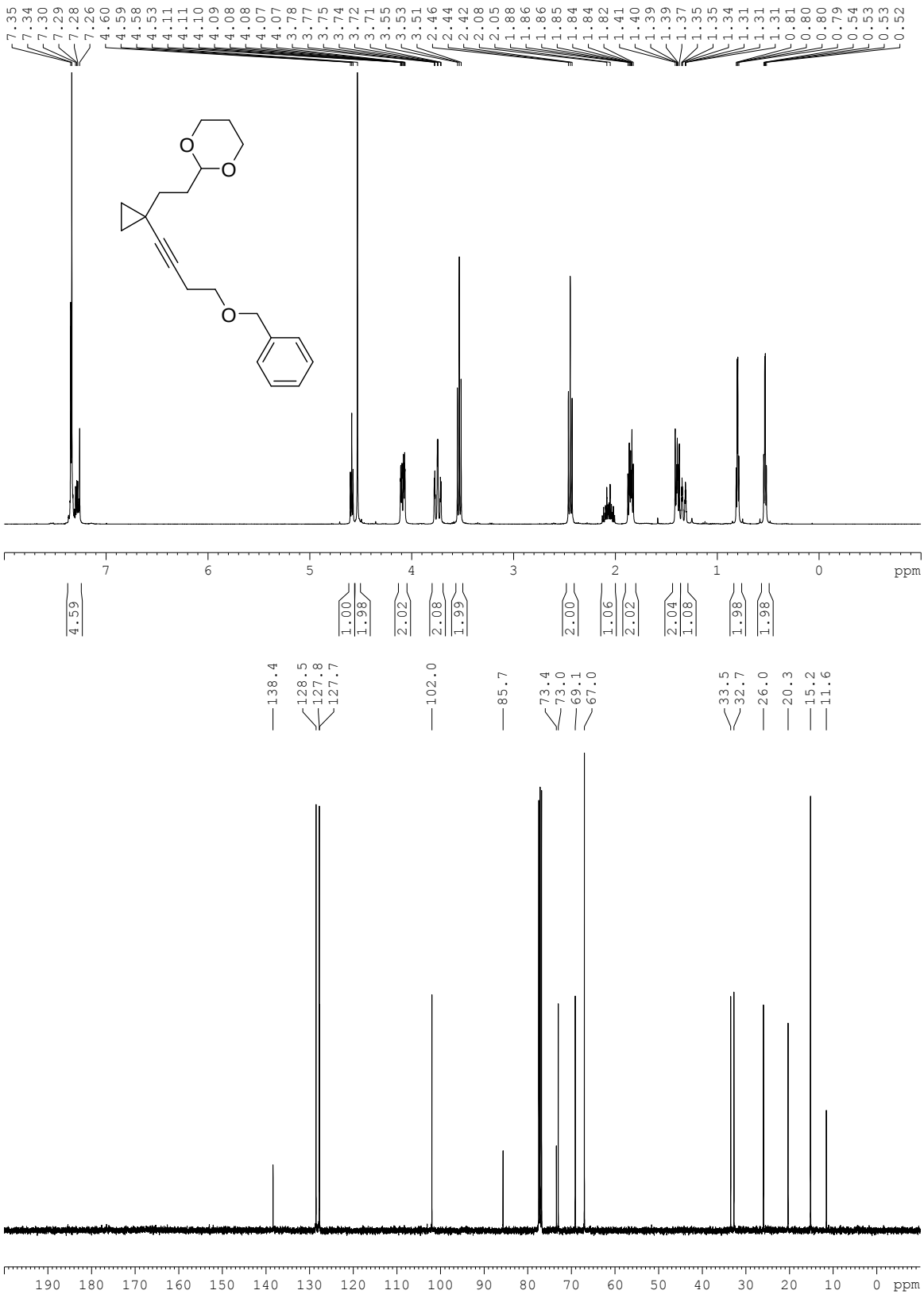
Compound 2l


7.40 7.39 7.39 7.39 7.39 7.38 7.38 7.37 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26
4.69 4.67 4.66 4.15 4.14 4.13 4.12 4.12 4.11 4.10
3.82 3.82 3.79 3.79 3.76 3.76
2.12 2.09 1.99 1.98 1.97 1.97 1.96 1.95 1.94 1.56 1.55 1.54 1.54 1.52 1.38 1.35 1.02 1.01 1.01 1.00 0.73 0.72 0.71 0.70
O
O
7 6 5 4 3 2 1 0 ppm
1.87 3.19 1.00 2.05 2.07 1.05 2.05 2.06 1.05 2.01 2.02
131.8 128.2 127.5 124.0 101.9 94.7 77.3 67.0 33.6 32.6 26.0 15.8 12.1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

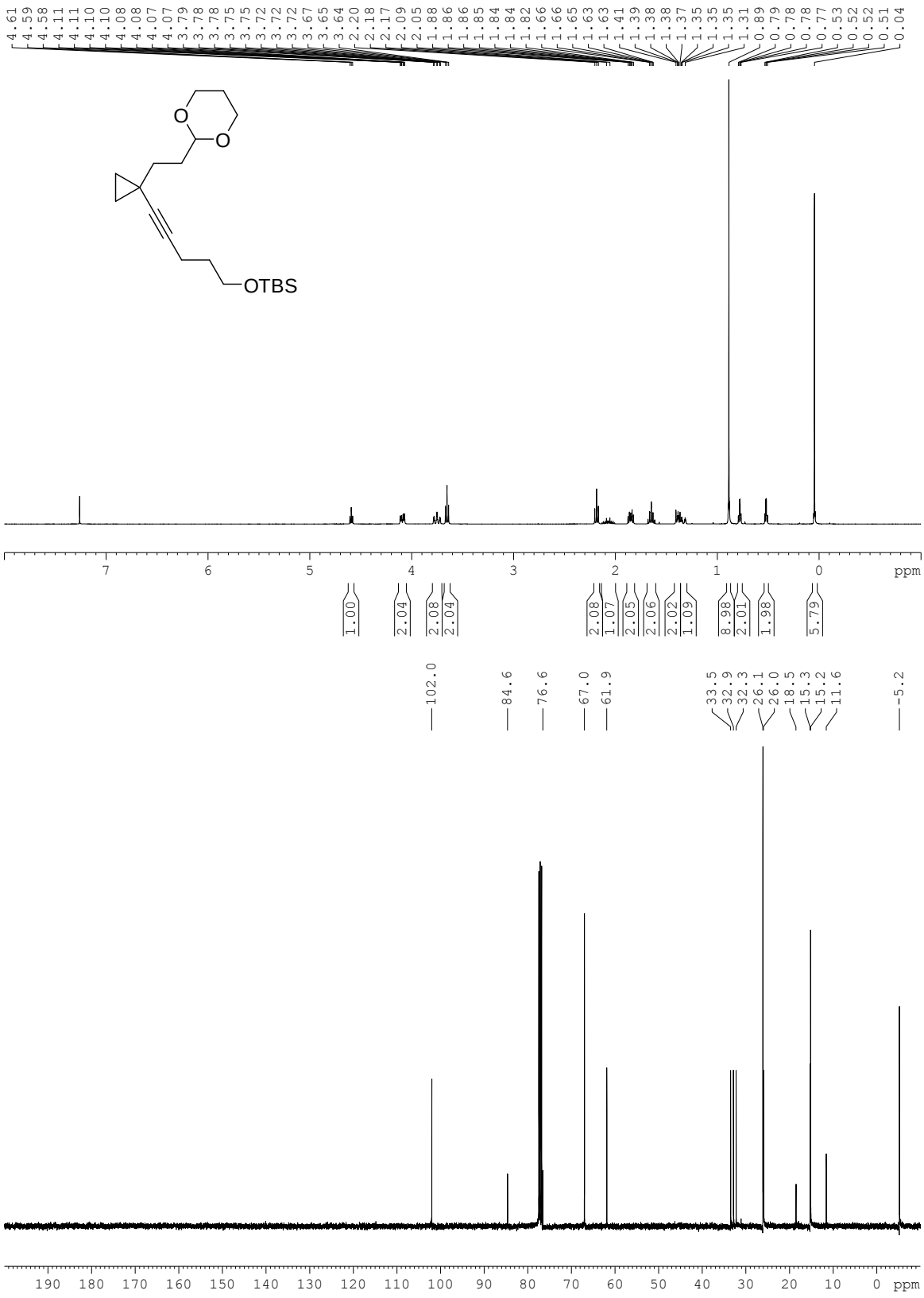
Compound 2m


7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.26 6.98 6.96 6.96 6.96 6.95 6.94 6.94 6.94 6.94 6.93
4.63 4.59 4.58 4.57 4.11 4.10 4.09 4.08 4.08 4.07 4.06 3.77 3.76 3.74 3.74 3.71
2.05 2.05 1.87 1.85 1.85 1.84 1.83 1.83 1.81 1.45 1.44 1.43 1.42 1.41 1.34 1.31 0.89 0.88 0.87 0.86 0.60 0.59 0.59 0.58
O
O
O
7 6 5 4 3 2 1 0 ppm
2.45 2.74 1.93 1.07 2.09 2.08 1.05 1.98 1.99 1.09 2.00 1.91
158.0 129.5 121.3 115.1 101.8 92.6 71.7 67.0 56.7 33.4 32.2 26.0 15.5 11.5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

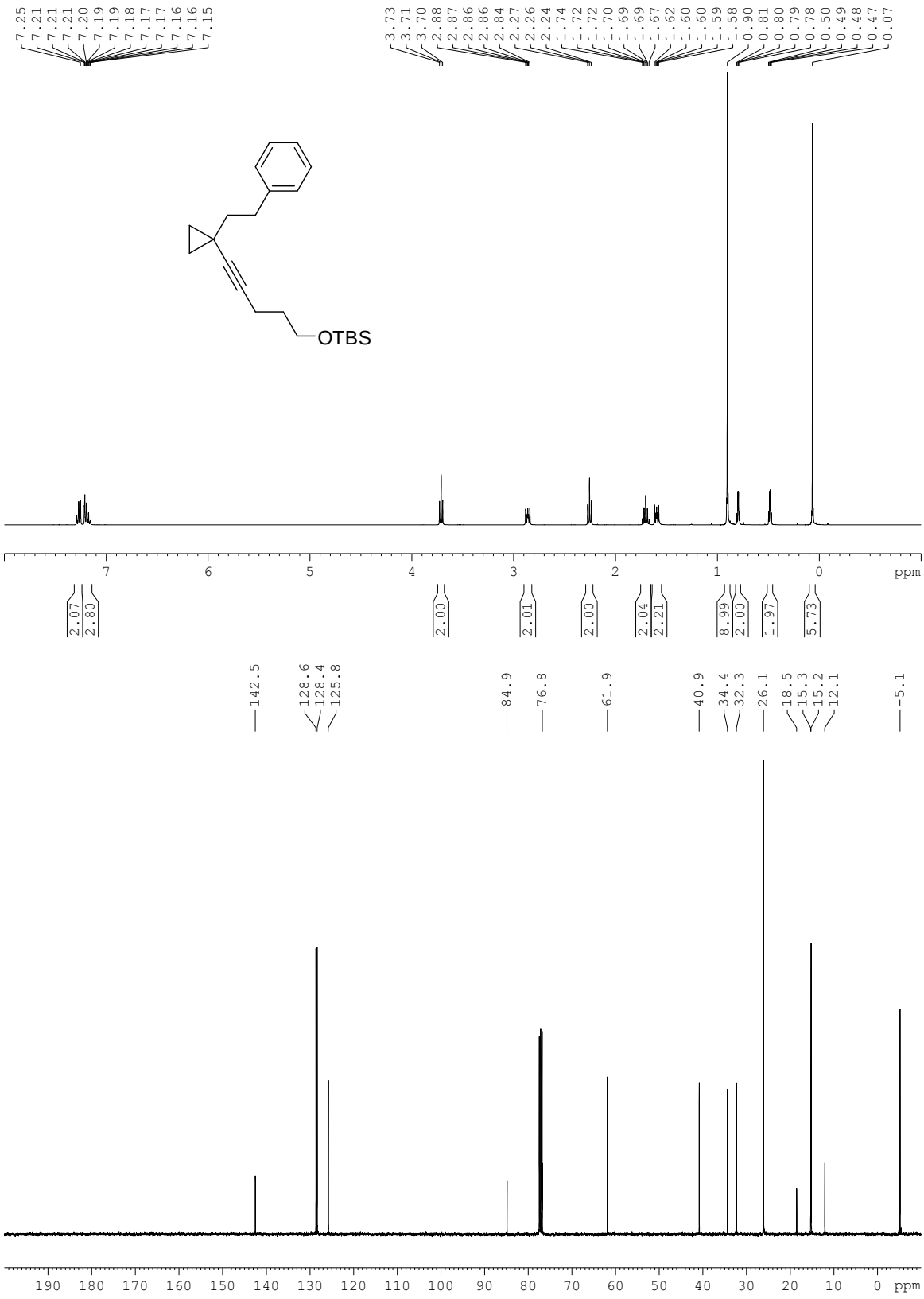
Compound 2n


7.35 7.34 7.30 7.29 7.28 7.26 4.60 4.59 4.58 4.53 4.11 4.11 4.10 4.09 4.08 4.08 4.07 4.07 3.78 3.77 3.75 3.74 3.72 3.71 3.55 3.53 3.51 2.46 2.44 2.42 2.08 2.05 1.88 1.86 1.86 1.85 1.84 1.84 1.82 1.41 1.40 1.39 1.39 1.37 1.35 1.35 1.34 1.31 1.31 1.31 0.81 0.80 0.80 0.79 0.54 0.53 0.53 0.52
O
O
O
7 6 5 4 3 2 1 0 ppm
4.59 1.00 1.98 2.02 2.08 1.99 2.00 1.06 2.02 2.04 1.08 1.98 1.98
138.4 128.5 127.8 127.7 102.0 85.7 73.4 73.0 69.1 67.0 33.5 32.7 26.0 20.3 15.2 11.6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

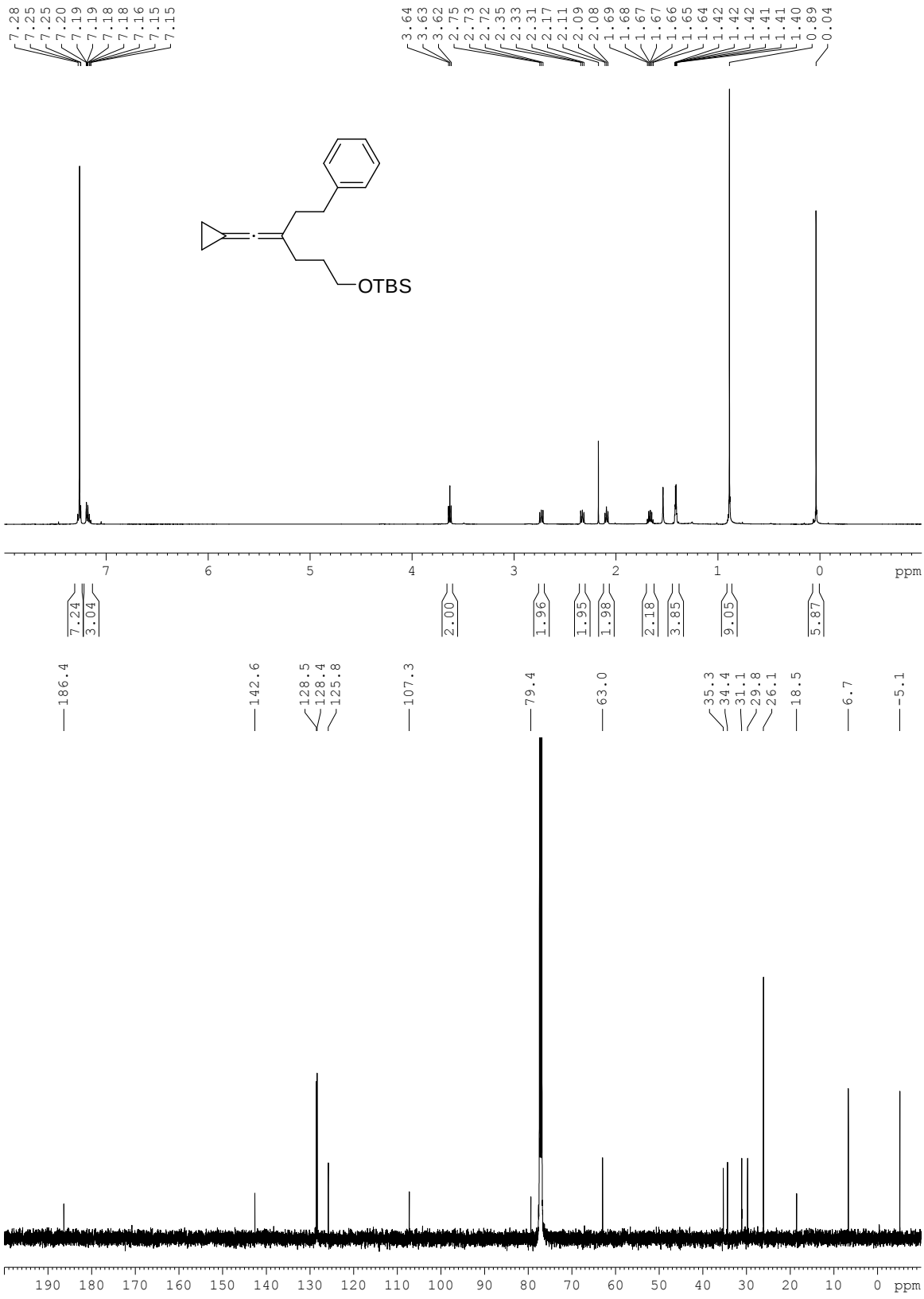
Compound 2o


4.61 4.59 4.58 4.11 4.11 4.10 4.10 4.08 4.08 4.07 4.07 3.79 3.78 3.78 3.75 3.75 3.72 3.72 3.72 3.67 3.65 3.64 2.20 2.18 2.17 2.09 2.05 1.88 1.86 1.86 1.85 1.84 1.84 1.82 1.66 1.66 1.65 1.63 1.63 1.41 1.39 1.38 1.38 1.37 1.35 1.35 1.35 1.31 0.89 0.79 0.78 0.78 0.77 0.53 0.52 0.52 0.51 0.04
O
O
OTBS
7 6 5 4 3 2 1 0 ppm
1.00 2.04 2.08 2.04 2.08 1.07 2.05 2.06 2.02 1.09 8.98 2.01 1.98 5.79
102.0 84.6 76.6 67.0 61.9 33.5 32.9 32.3 26.1 26.0 18.5 15.3 15.2 11.6 -5.2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

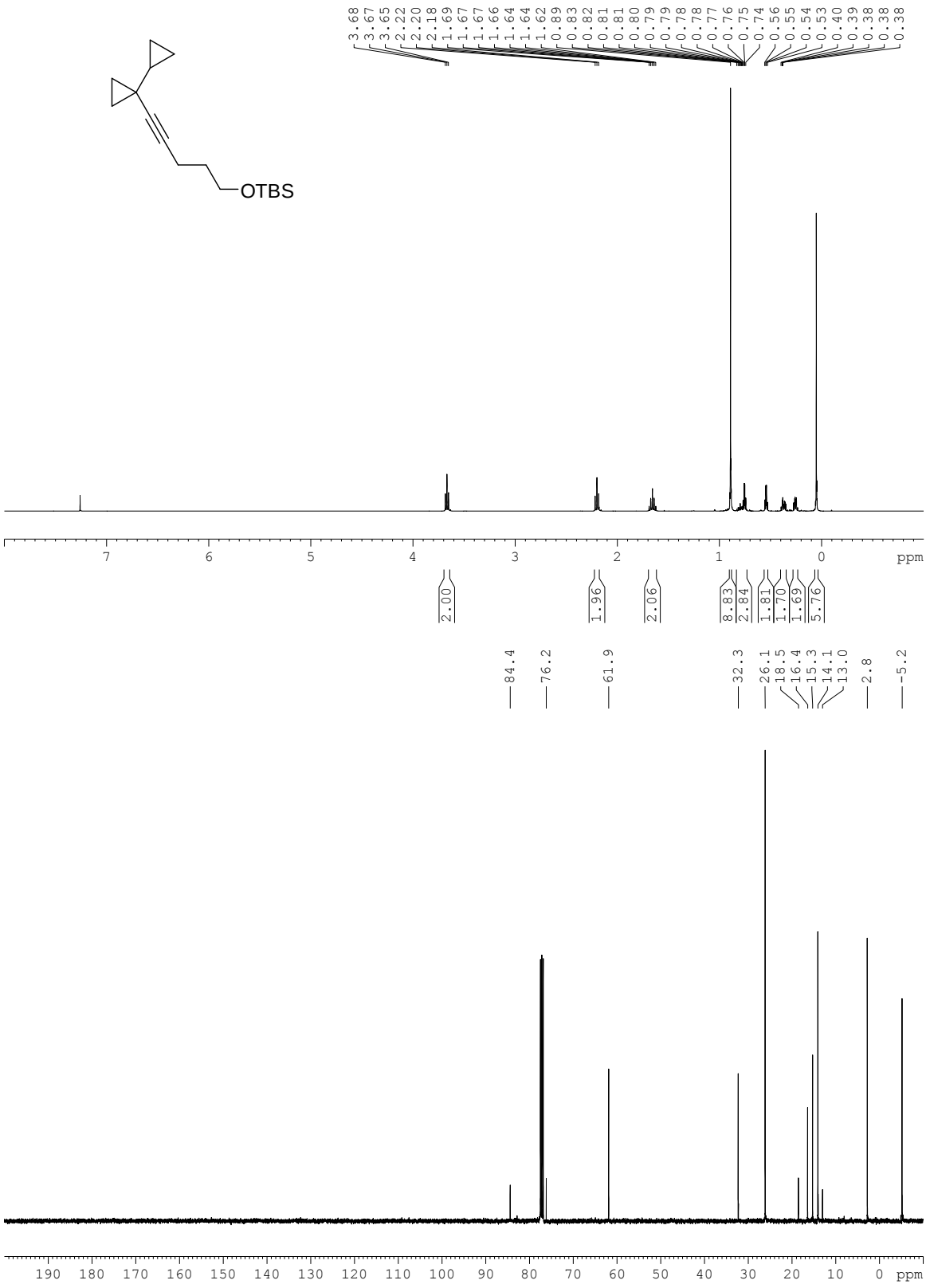
Compound 2p


7.25
7.21
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
3.73
3.71
3.70
2.88
2.87
2.86
2.86
2.84
2.27
2.26
2.24
1.74
1.72
1.72
1.70
1.69
1.69
1.67
1.62
1.60
1.60
1.59
1.58
0.90
0.81
0.80
0.79
0.78
0.50
0.49
0.48
0.47
0.07
OTBS
ppm
2.07
2.80
2.00
2.01
2.00
2.04
2.21
8.99
2.00
1.97
5.73
142.5
128.6
128.4
125.8
84.9
76.8
61.9
40.9
34.4
32.3
26.1
18.5
15.3
15.2
12.1
5.1
ppm

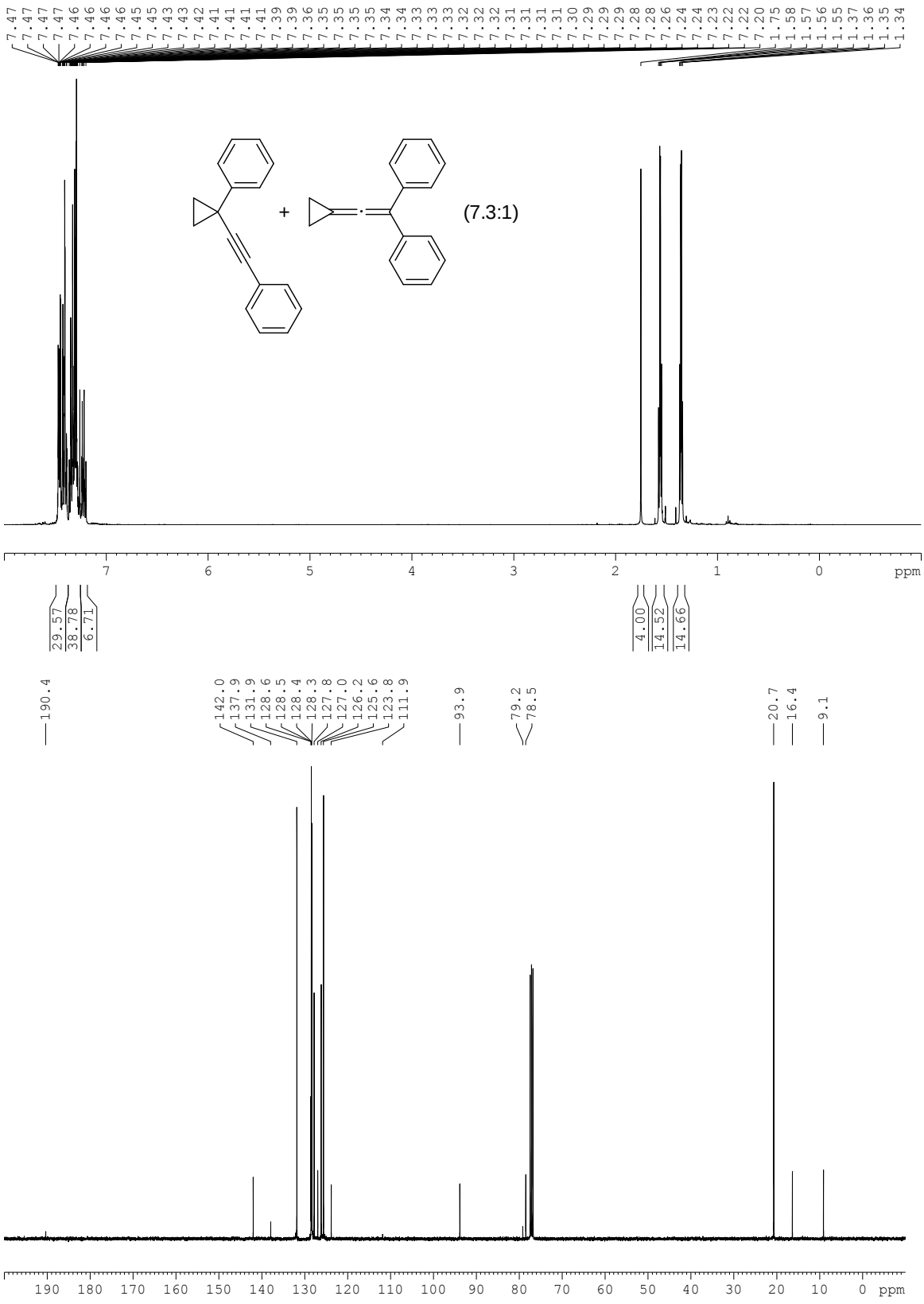
Compound 3p


7.28
7.25
7.25
7.20
7.19
7.19
7.18
7.18
7.16
7.15
7.15
3.64
3.63
3.62
2.75
2.73
2.72
2.35
2.33
2.31
2.17
2.11
2.09
2.08
1.69
1.68
1.67
1.67
1.66
1.65
1.64
1.42
1.42
1.42
1.41
1.41
1.40
0.89
0.04
OTBS
ppm
7.24
3.04
2.00
1.96
1.95
1.98
2.18
3.85
9.05
5.87
186.4
142.6
128.5
128.4
125.8
107.3
79.4
63.0
35.3
34.4
31.1
29.8
26.1
18.5
6.7
-5.1
ppm

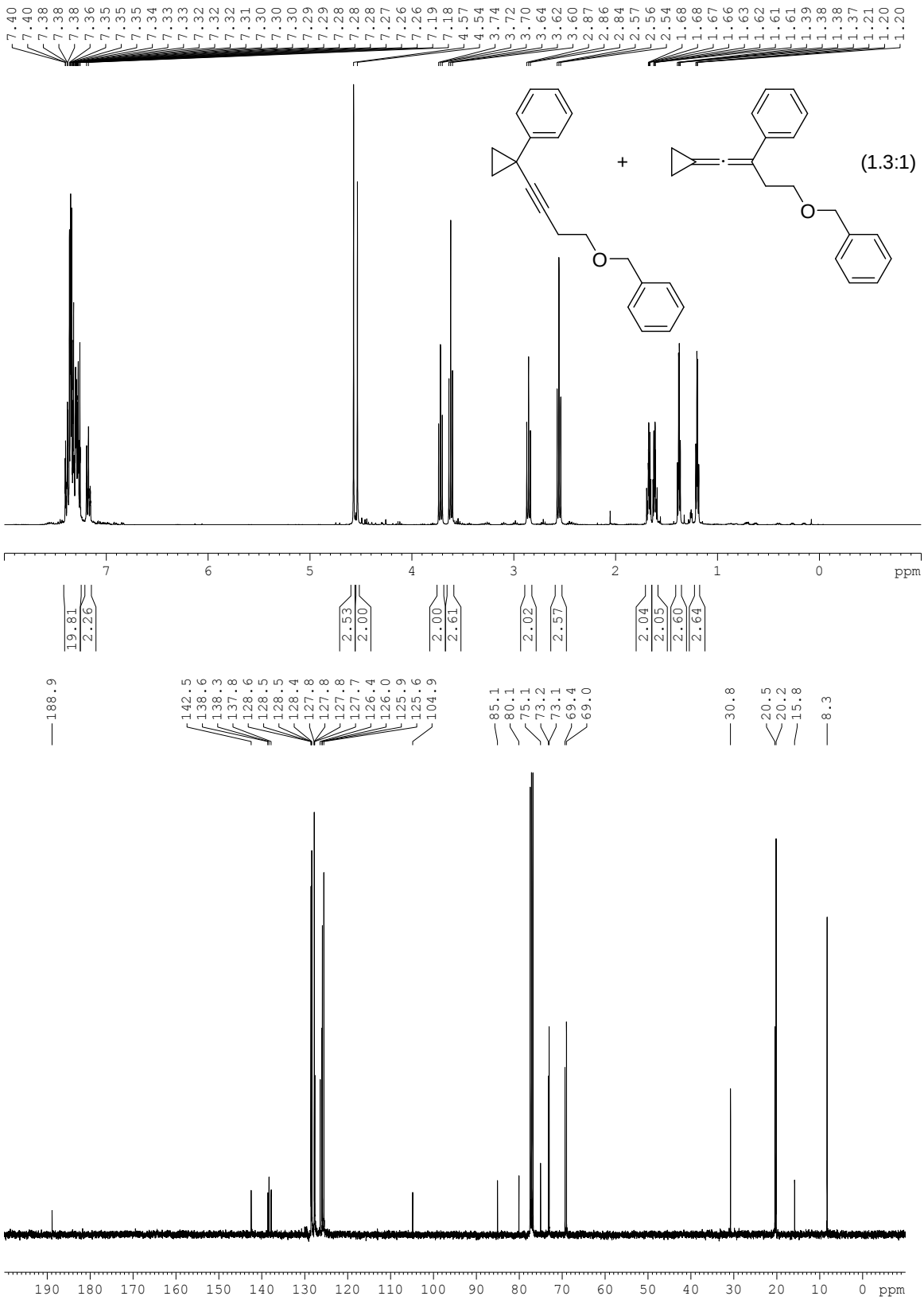
Compound 2q


3.68
3.67
3.65
2.22
2.20
2.18
1.69
1.67
1.67
1.66
1.64
1.64
1.62
0.89
0.83
0.82
0.81
0.81
0.80
0.79
0.79
0.78
0.78
0.77
0.76
0.75
0.74
0.56
0.55
0.54
0.53
0.40
0.39
0.38
0.38
0.38
OTBS
7
6
5
4
3
2
1
0
ppm
2.00
1.96
2.06
8.83
2.84
1.81
1.70
1.69
5.76
84.4
76.2
61.9
32.3
26.1
18.5
16.4
15.3
14.1
13.0
2.8
-5.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

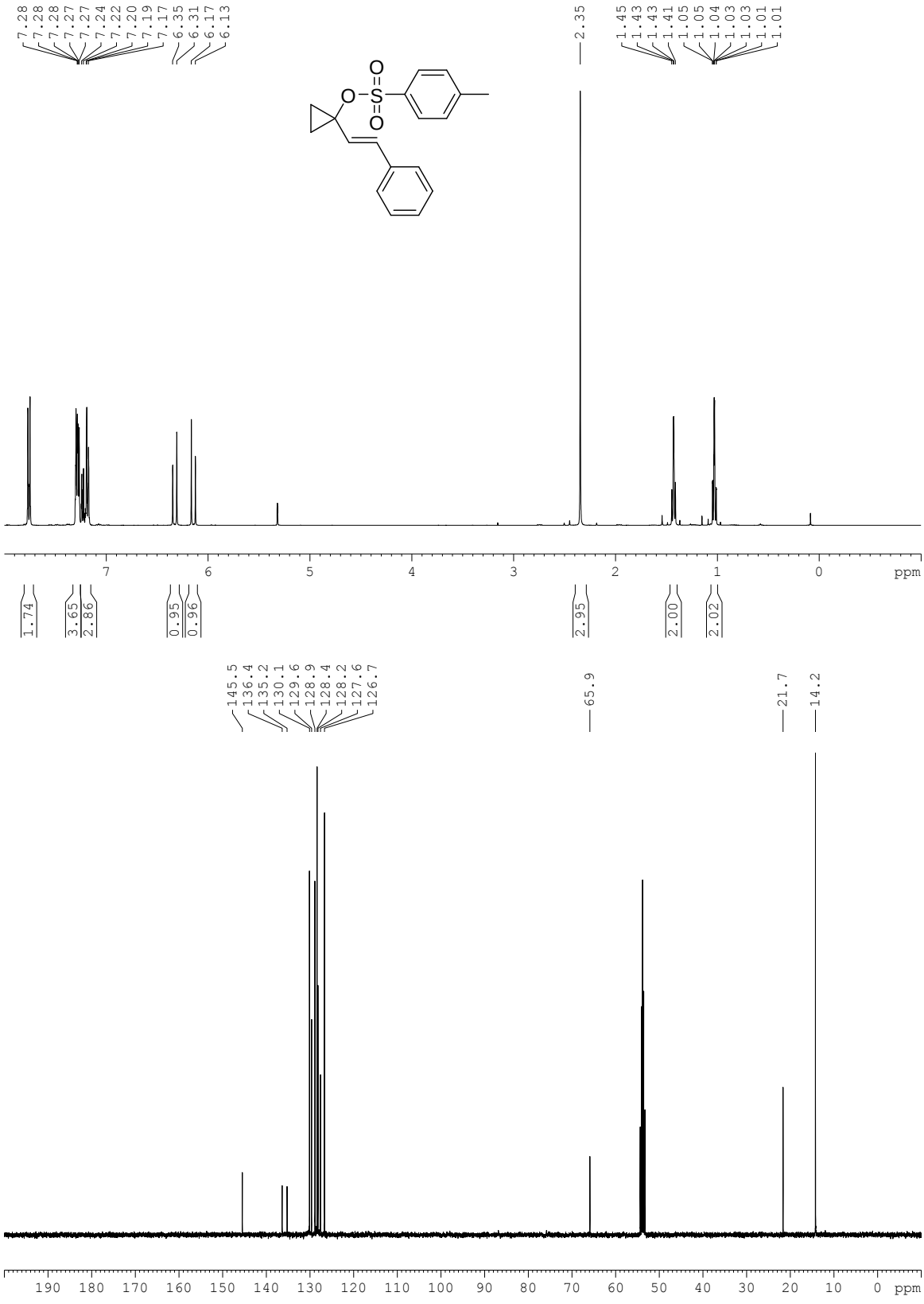
Compounds 2r and 3r



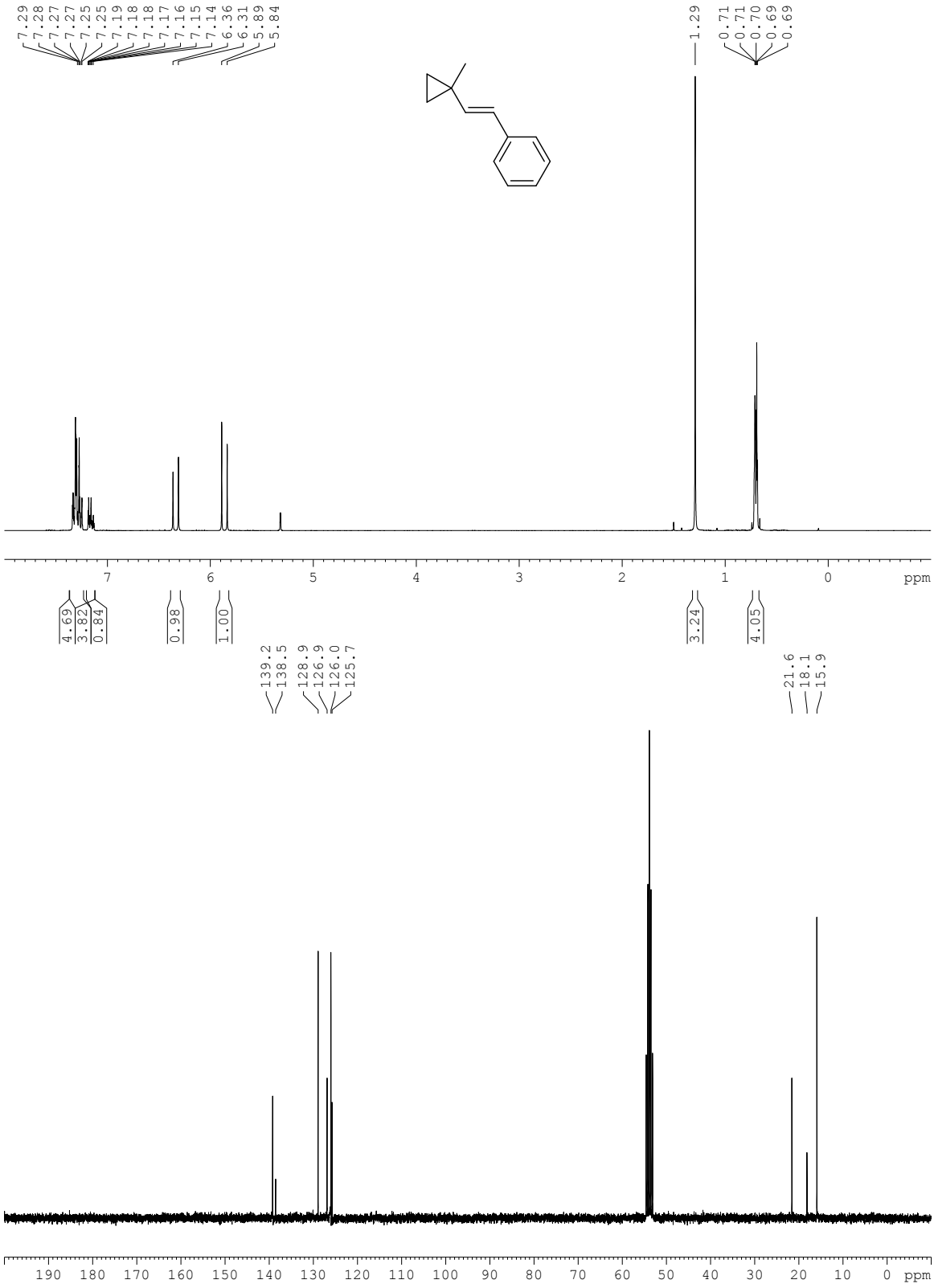
Compounds 2s and 3s



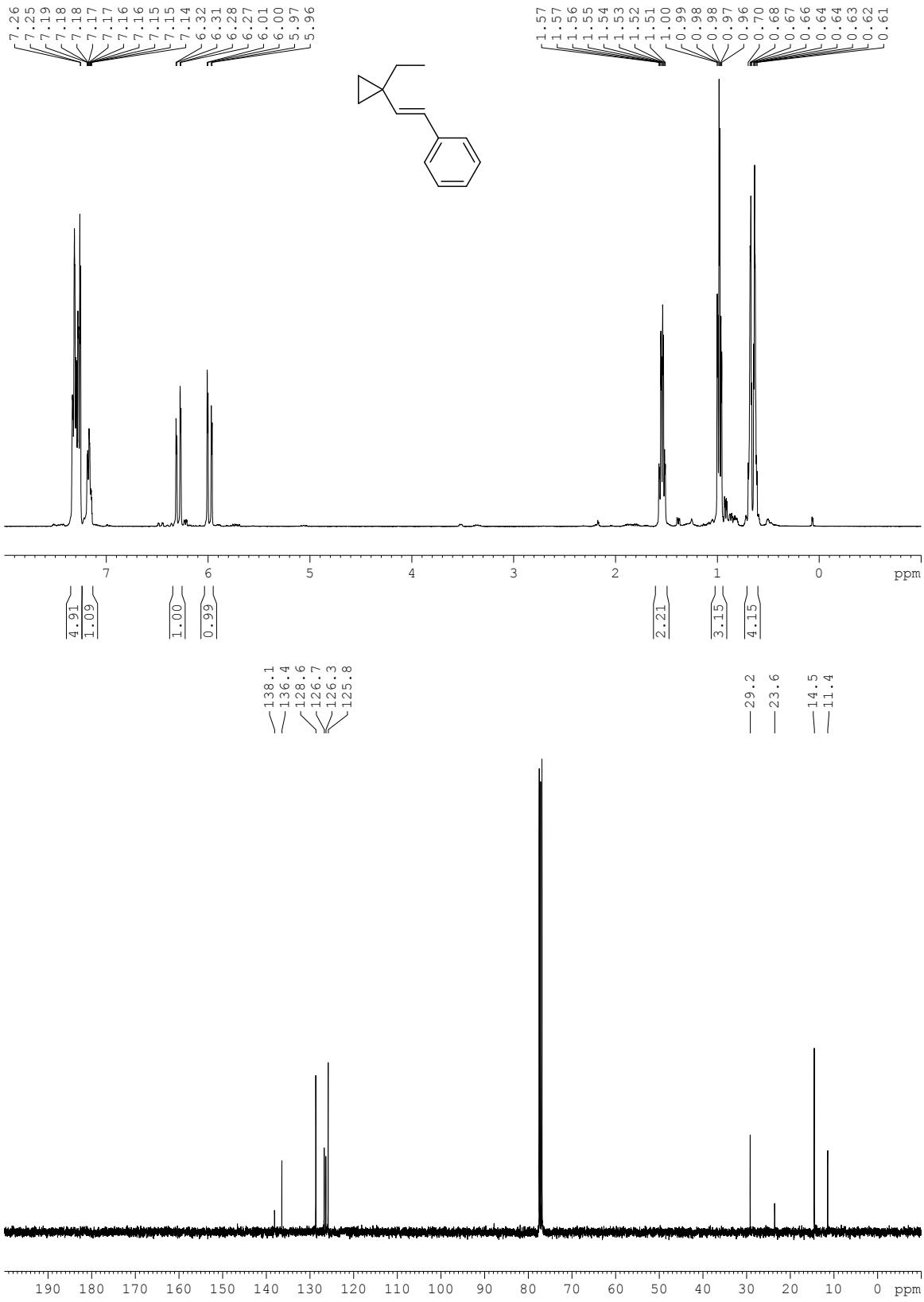
Compound 16


7.28
7.28
7.28
7.27
7.27
7.24
7.22
7.20
7.19
7.17
6.35
6.31
6.17
6.13
2.35
1.45
1.43
1.43
1.41
1.05
1.05
1.04
1.03
1.03
1.01
1.01
O
O
S
O
O
7
6
5
4
3
2
1
0
ppm
1.74
3.65
2.86
0.95
0.96
2.95
2.00
2.02
145.5
136.4
135.2
130.1
129.6
128.9
128.4
128.2
127.6
126.7
65.9
21.7
14.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

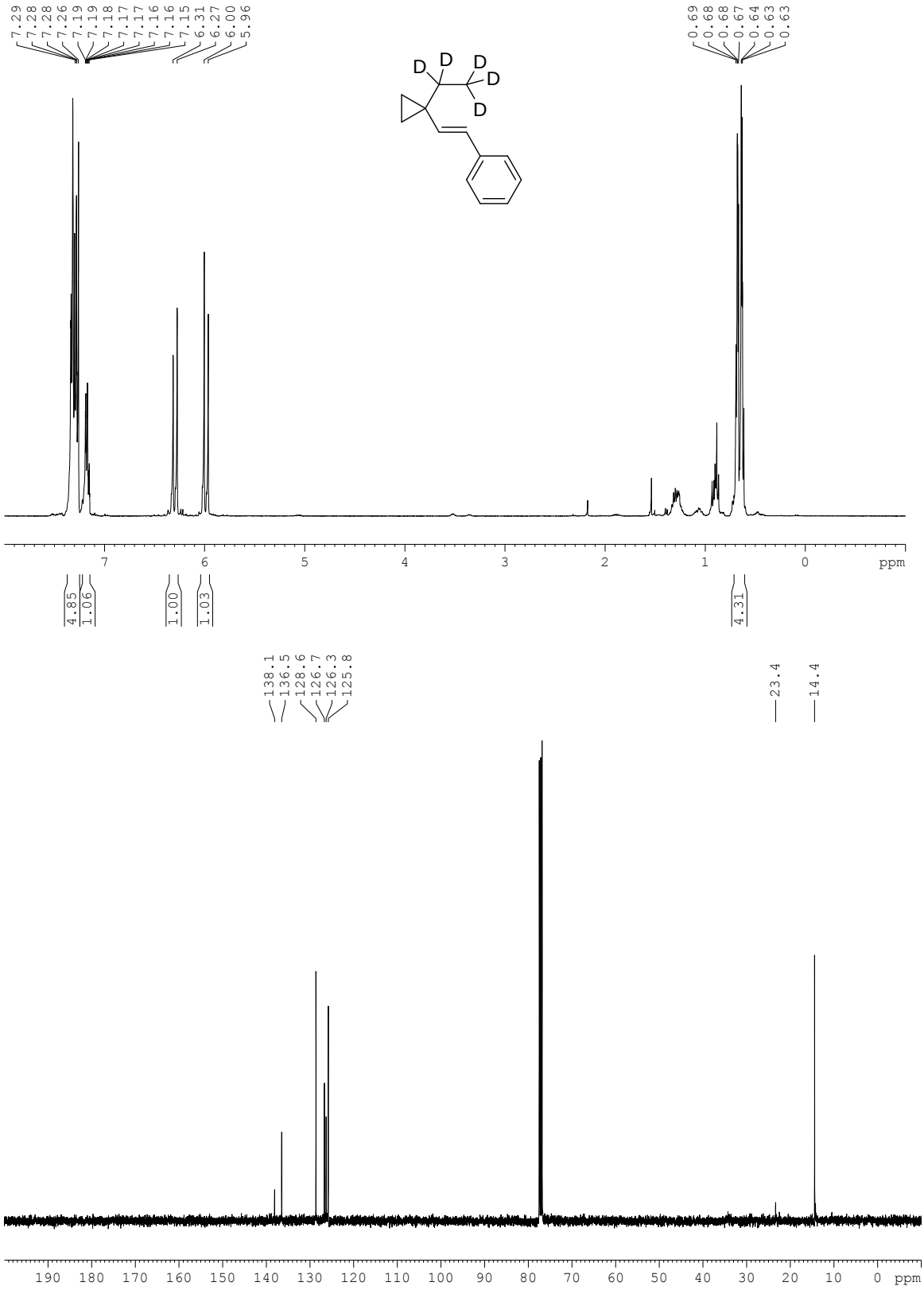
Compound 17


7.29
7.28
7.27
7.27
7.25
7.19
7.18
7.17
7.16
7.15
7.14
6.36
6.31
5.89
5.84
1.29
0.71
0.71
0.70
0.69
0.69
4.69
3.82
0.84
0.98
1.00
3.24
4.05
139.2
138.5
128.9
126.9
126.0
125.7
21.6
18.1
15.9
ppm
ppm

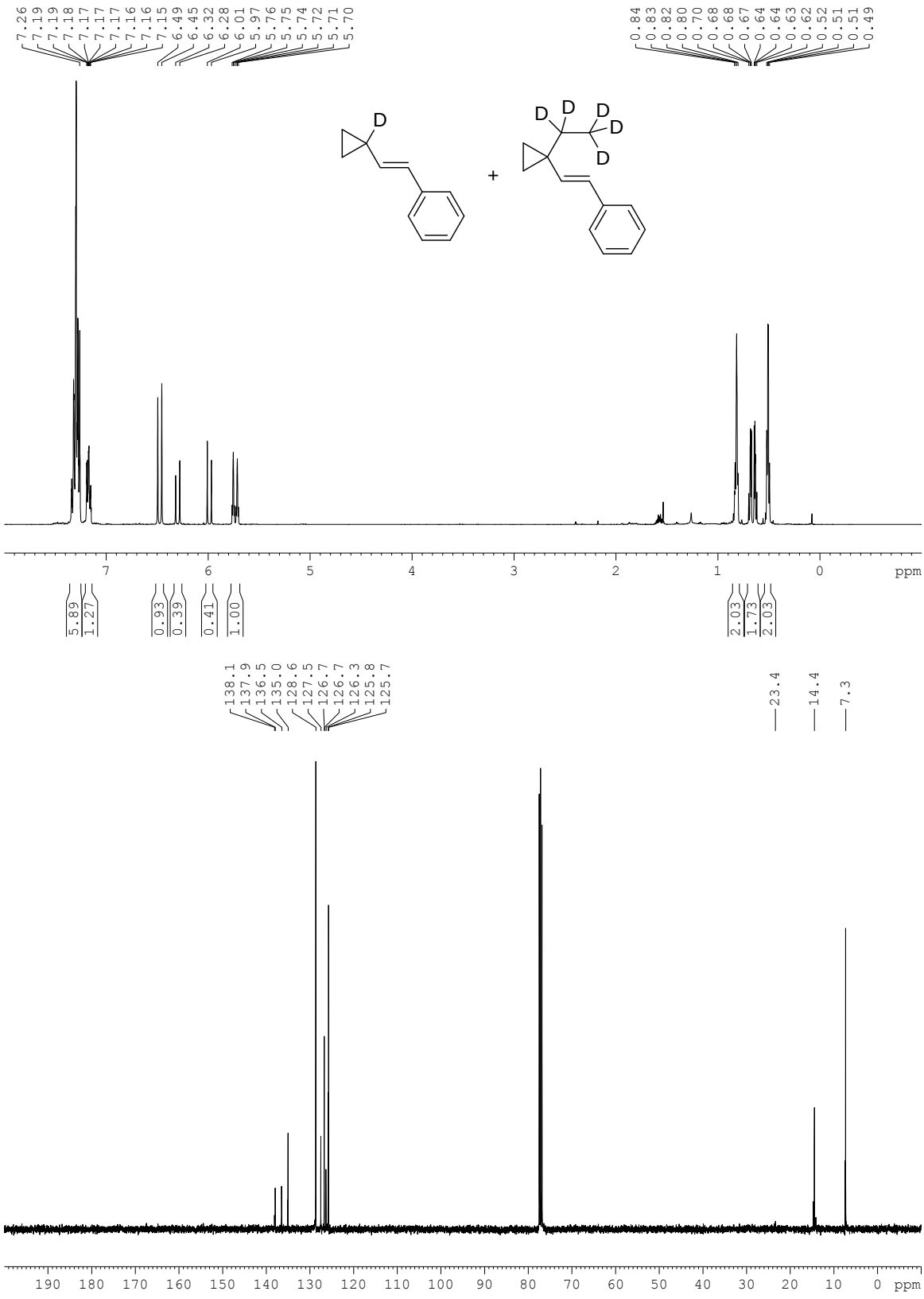
Compound 18


7.26
7.25
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
6.32
6.31
6.28
6.27
6.01
6.00
5.97
5.96
1.57
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.00
0.99
0.98
0.98
0.97
0.96
0.70
0.68
0.67
0.66
0.64
0.64
0.63
0.62
0.61
ppm
4.91
1.09
1.00
0.99
2.21
3.15
4.15
138.1
136.4
128.6
126.7
126.3
125.8
29.2
23.6
14.5
11.4
ppm

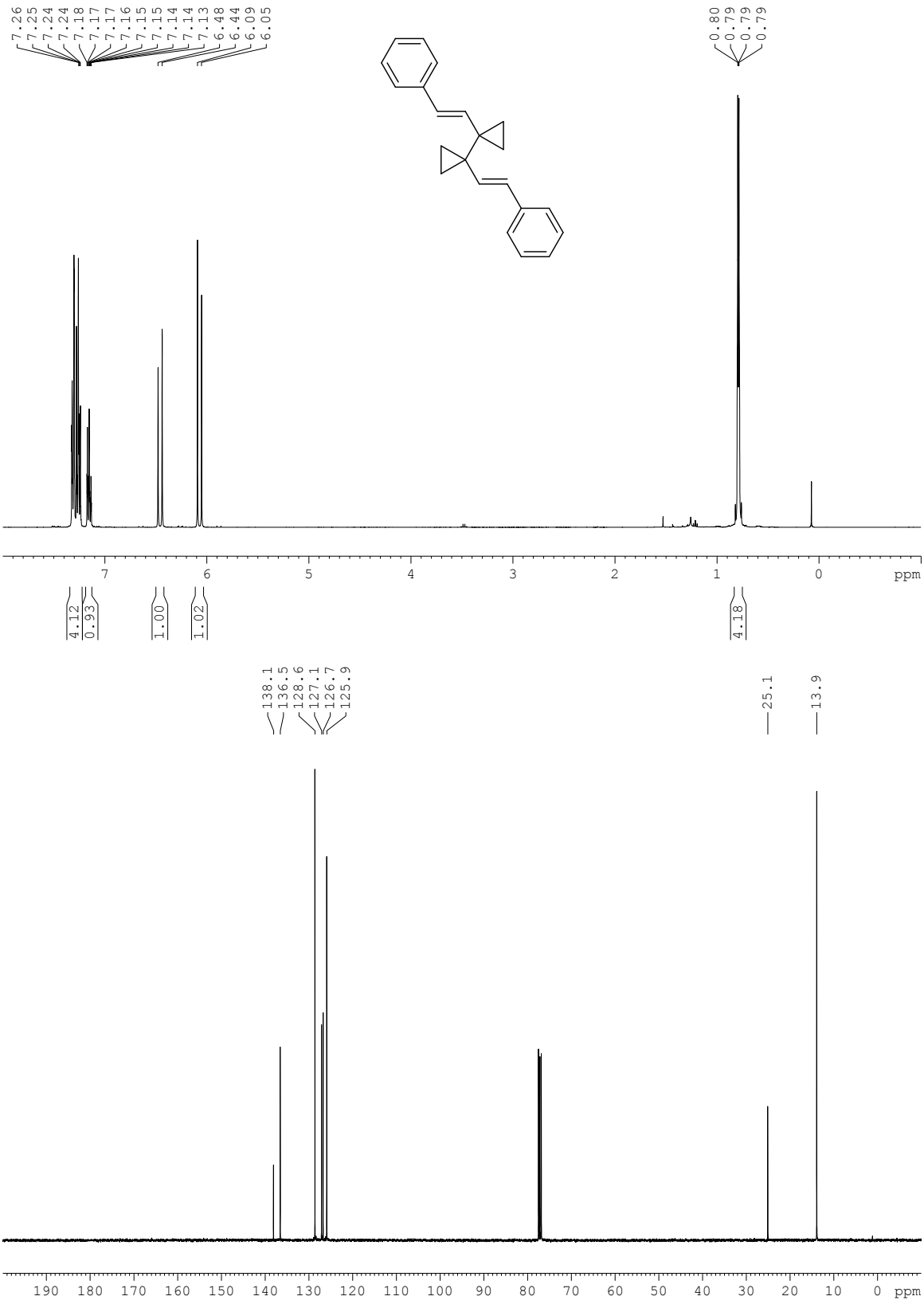
Compound [D_5]-18



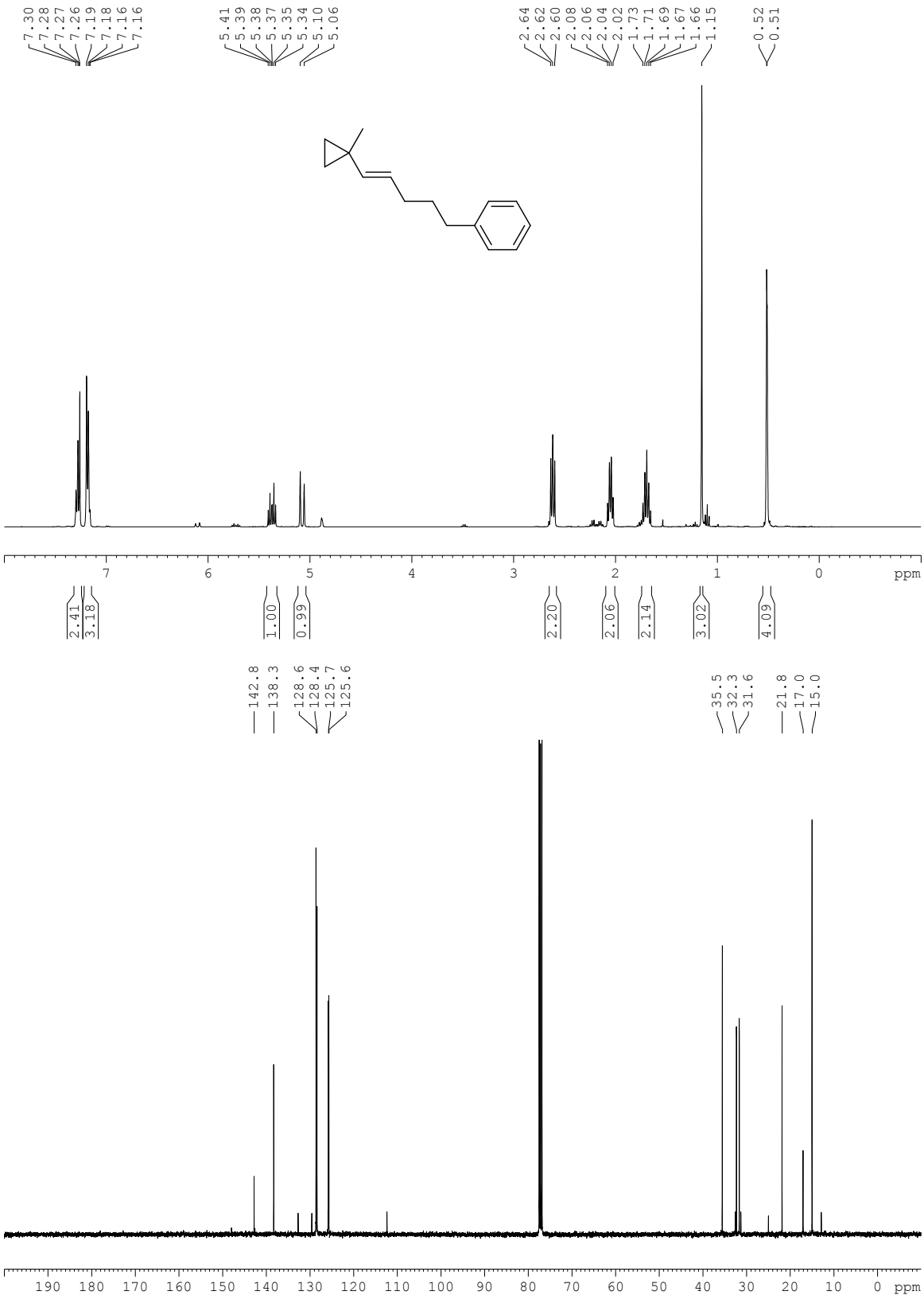
Compounds [D]-19 and [D_5]-18



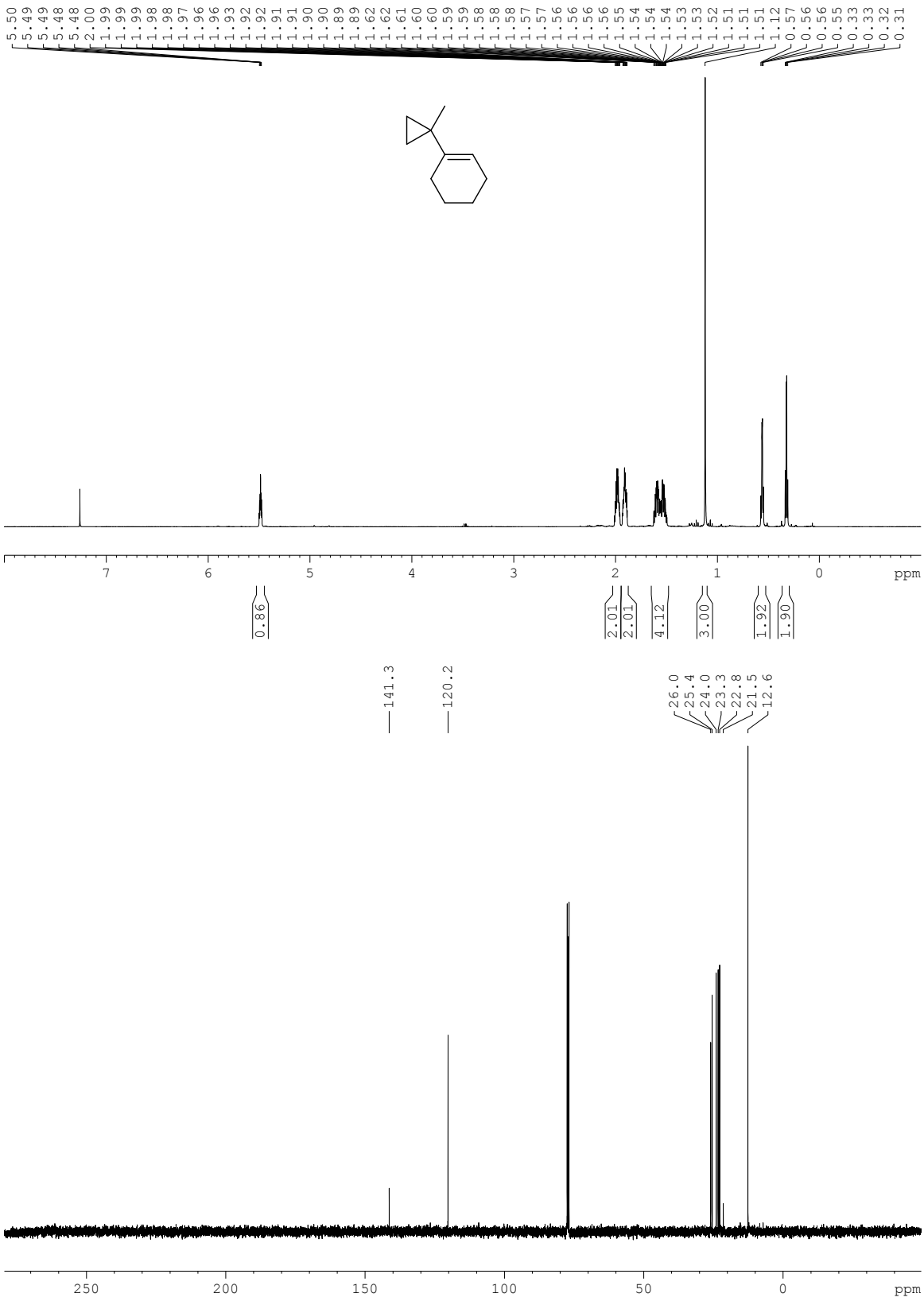
Compound 20


7.26
7.25
7.24
7.24
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.13
6.48
6.44
6.09
6.05
0.80
0.79
0.79
0.79
ppm
4.12
0.93
1.00
1.02
4.18
138.1
136.5
128.6
127.1
126.7
125.9
25.1
13.9
ppm

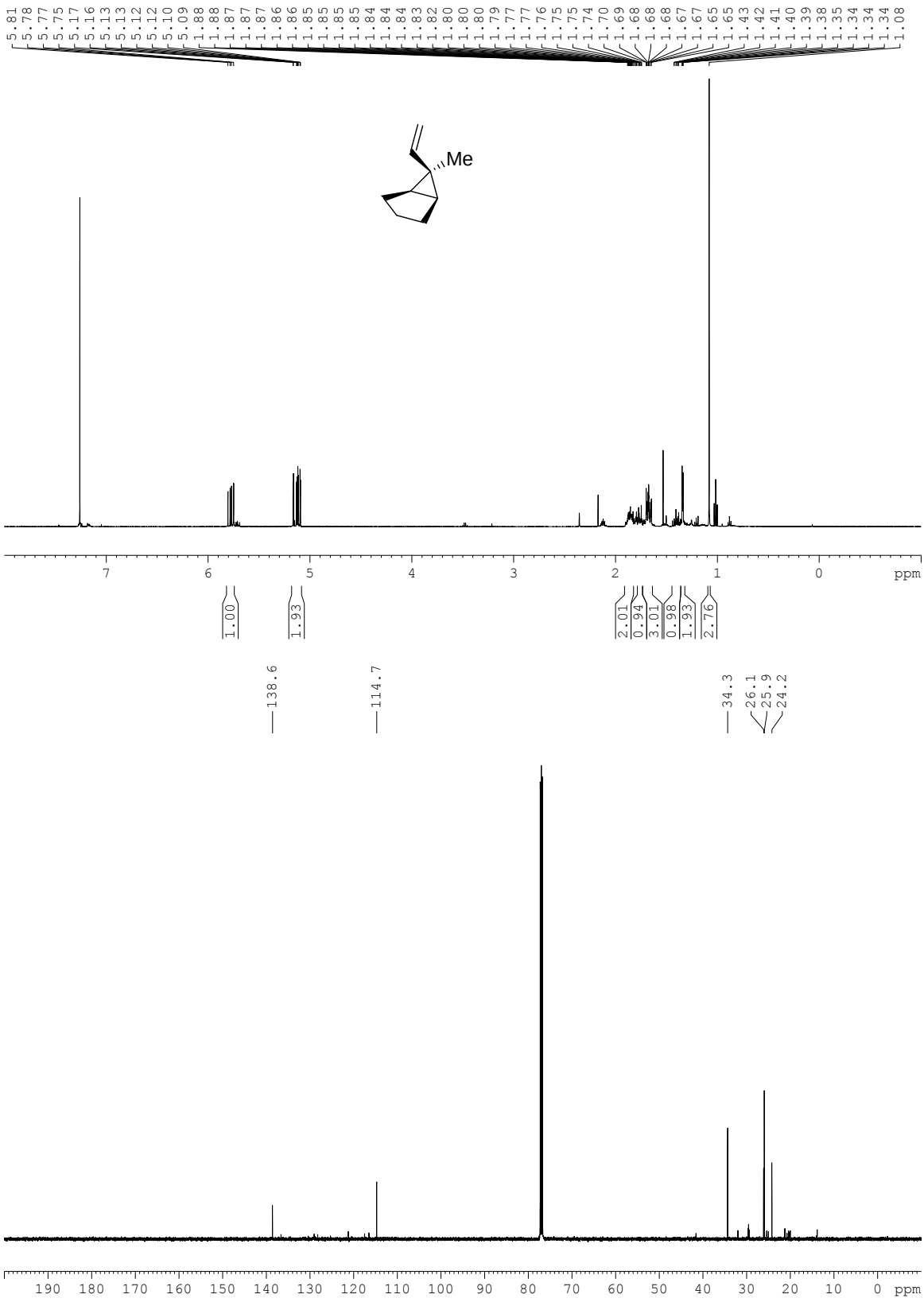
Compound 21


7.30
7.28
7.27
7.26
7.19
7.18
7.16
7.16
5.41
5.39
5.38
5.37
5.35
5.34
5.10
5.06
2.64
2.62
2.60
2.08
2.06
2.04
2.02
1.73
1.71
1.69
1.67
1.66
1.15
0.52
0.51
ppm
2.41
3.18
1.00
0.99
2.20
2.06
2.14
3.02
4.09
142.8
138.3
128.6
128.4
125.7
125.6
35.5
32.3
31.6
21.8
17.0
15.0
ppm

Compound 22


5.50 5.49 5.49 5.48 5.48 2.00 1.99 1.99 1.99 1.98 1.98 1.97 1.96 1.96 1.93 1.92 1.92 1.91 1.91 1.90 1.90 1.89 1.89 1.62 1.61 1.60 1.60 1.59 1.59 1.58 1.58 1.58 1.57 1.57 1.56 1.56 1.56 1.56 1.55 1.54 1.54 1.54 1.53 1.53 1.52 1.51 1.51 1.51 1.12 0.57 0.56 0.56 0.55 0.33 0.33 0.32 0.31
7 6 5 4 3 2 1 0 ppm
0.86 2.01 2.01 4.12 3.00 1.92 1.90
141.3 120.2 26.0 25.4 24.0 23.3 22.8 21.5 12.6
250 200 150 100 50 0 ppm

Compound 23


5.81 5.78 5.77 5.75 5.17 5.16 5.13 5.13 5.12 5.12 5.10 5.09 1.88 1.88 1.87 1.87 1.87 1.86 1.86 1.85 1.85 1.85 1.85 1.84 1.84 1.84 1.83 1.82 1.80 1.80 1.80 1.79 1.77 1.77 1.76 1.75 1.75 1.74 1.70 1.69 1.68 1.68 1.68 1.67 1.67 1.65 1.65 1.43 1.42 1.41 1.40 1.39 1.38 1.35 1.34 1.34 1.34 1.08
Me
7 6 5 4 3 2 1 0 ppm
1.00 1.93 2.01 0.94 3.01 0.98 1.93 2.76
138.6 114.7 34.3 26.1 25.9 24.2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm