Electronic Supplementary Information

Base-Promated Direct and Highly Selective Alkynylation of Electron-Deficient Octafluorotoluene

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Experimental Section:

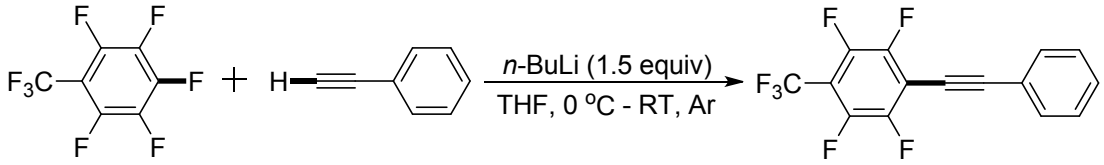
General information:

^{1}H, ^{13}C, ^{19}F NMR were recorded on Varian Mercury Plus 400 instruments at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external CCl_3F, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). HRMS were recorded on an Agilent Q-TOF spectrometer using the ESI method and Waters TOF spectrometer using the EI method. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer.

Materials:

Tetrahydrofuran (THF), diethyl ether and toluene were distilled from sodium /benzophenone prior to use; dichloromethane was distilled from CaH_2. All purchased reagents were used without further purification. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography. Standard reagents and solvents were purified according to known procedures.

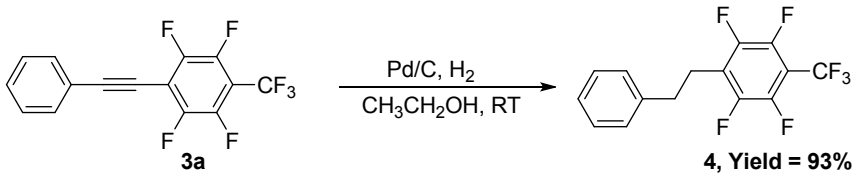
General procedure for alkynylation of electron-deficient octafluorotoluene with terminal alkynes



1a **2a** **3a**

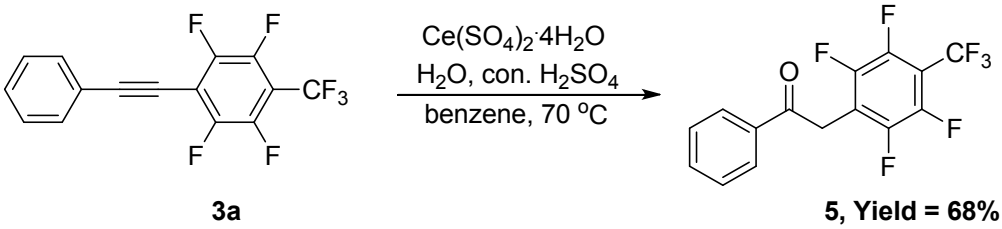
A solution of phenylacetylene **2a** (0.20 mmol, 20.4 mg) in THF (2.0 mL) was added dropwise with *n*-BuLi (2.50 mol/L, 120 µL, 0.30 mmol, 1.5 equiv.) over 5 min at 0 °C under Ar atmosphere. The resulting suspension was stirred at this temperature for 30 min, and octafluorotoluene **1a** (98%, 0.26 mmol, 72.2 mg, 1.5 equiv.) was added. After stirring at this temperature for 1 h, the reaction mixture was allowed to slowly warm to room temperature and stirred for 36 h. The reaction was quenched with saturated ammonium chloride solution and the organic layers were separated. The aqueous layer was washed twice with diethyl ether and the combined organic layer was washed with brine, dried over $MgSO_4$, filtered, concentrated in vacuo. The residue was purified on silica gel using hexane as solvent to afford the product **3a** (52.8 mg, 83% yield).

General procedure for the reduction of the product 3a



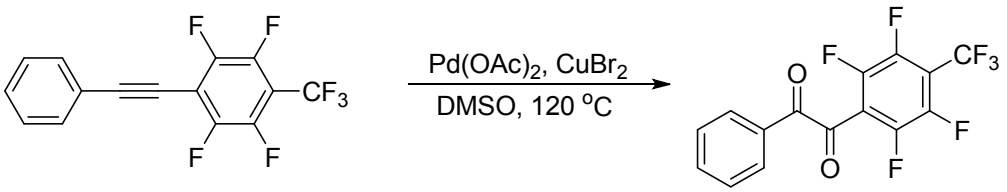
To a solution of **3a** (63.6 mg, 0.2 mmol) in Ethanol (15 mL) was added Pd/C 10% (20 mg). The reaction mixture was stirred under H_2 (1 atm) overnight at room temperature. After the reaction was complete by TLC, the mixture was filtered through a silica gel pad, washed with CH_2Cl_2, and the filtrate was concentrated. The residue was purified using chromatography on silica gel to give the hydrogenated product **4** (60.0 mg, 93% yield).

General procedure for the oxidation of the product 3a



A mixture of **3a** (63.6 mg, 0.2 mmol) and $Ce(SO_4)_2{\cdot}4H_2O$ (80%, 0.02 mmol, 10 mg) were weighed into a 25-mL one-necked round bottom flask covered with aluminum foil. Then benzene (1.0 mL), H_2O (4.0 μL) and concentrated H_2SO_4 (98%, 12 μL) were added to the mixture in order. The reaction flask was immersed in a 70 °C oil bath with stirring under Ar atmosphere for 24 hours. The reaction mixture was extracted with ethyl acetate, dried with anhydrous magnesium sulfate and then concentrated in vacuo. The residue was purified on silica gel to afford the product **5** (45.7 mg, 68% yield).

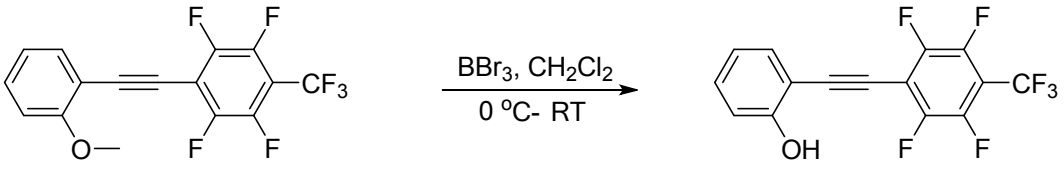
The procedure for the synthesis of 1,2-diketone



3a **6, Yield = 43%**

3a (63.6 mg, 0.2 mmol), $Pd(OAc)_2$ (47%, 9.6 mg, 0.02 mmol), and $CuBr_2$ (4.5 mg, 0.02mmol) were weighed into a 25-mL flask, then DMSO (2.0 mL) was added under air atmosphere. The reaction mixture was heated in an oil bath at 120 °C for 20 h. After the reaction was complete, 10 mL water was added and the mixture was extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography to afford the pure product **6** (30.1 mg, 43% yield).

The procedure for the demethylation of 3l

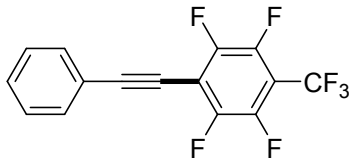


3l **7, Yield = 65%**

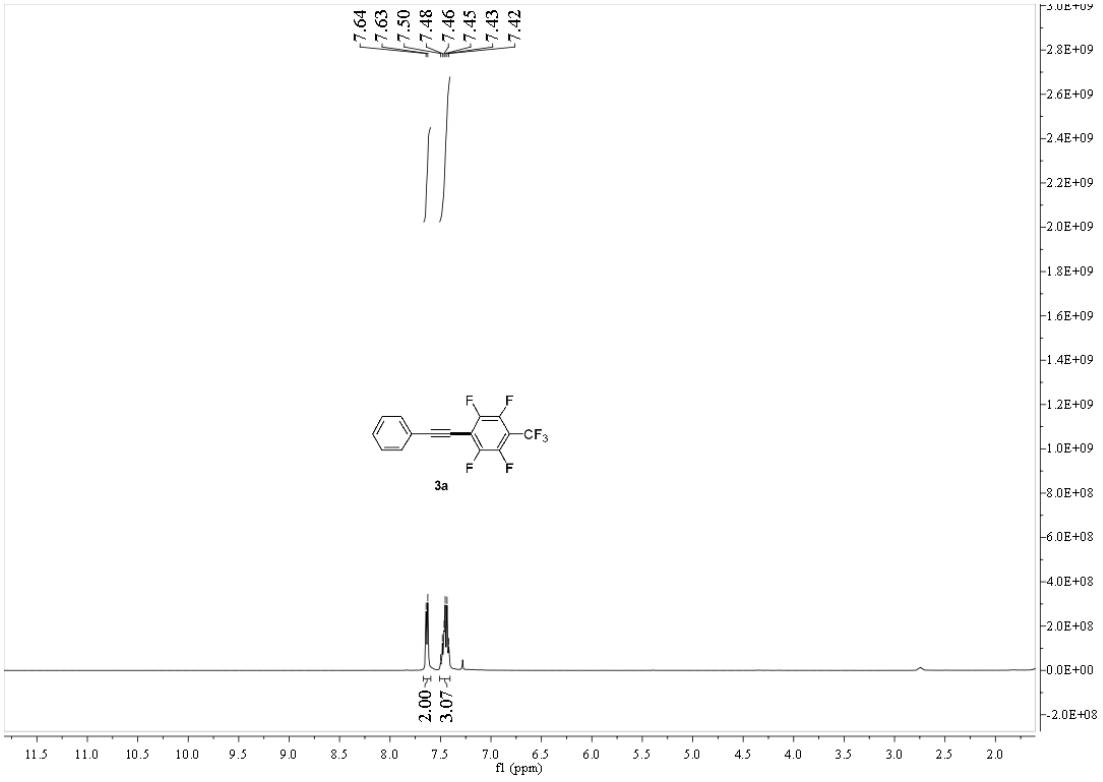
3l (69.6 mg, 0.2 mmol) was weighed into an oven-dried 25-mL flask, then anhydrous CH_2Cl_2 (5.0 mL) was added under Ar. The flask was cooled in an ice bath at 0 °C for 0.5 h and then BBr_3 (99%, 75.9 mg, 0.3 mmol) was added in dropwise via syringe. After the addition of BBr_3 was finished, the reaction mixture was allowed to slowly warm to room temperature and stirred for 24 h, 10 mL water was added and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure. The residue was purified by column chromatography to afford the pure product **7** (43.4 mg, 65% yield).

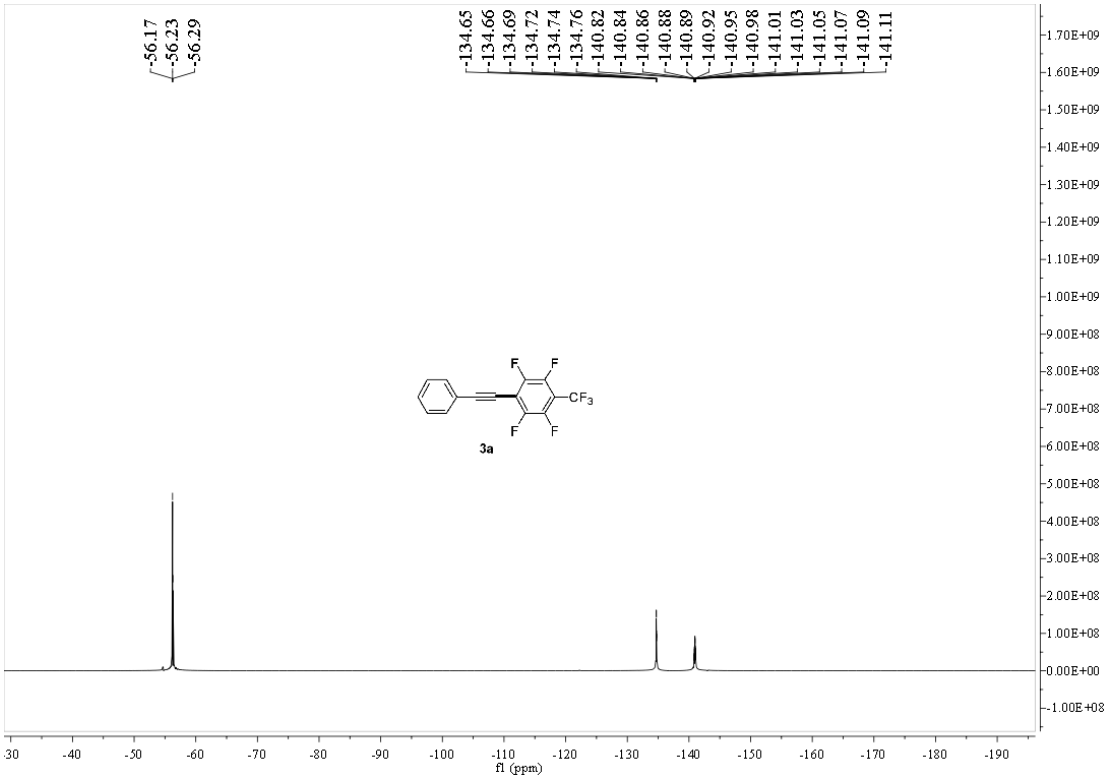
NMR, IR, and HRMS data

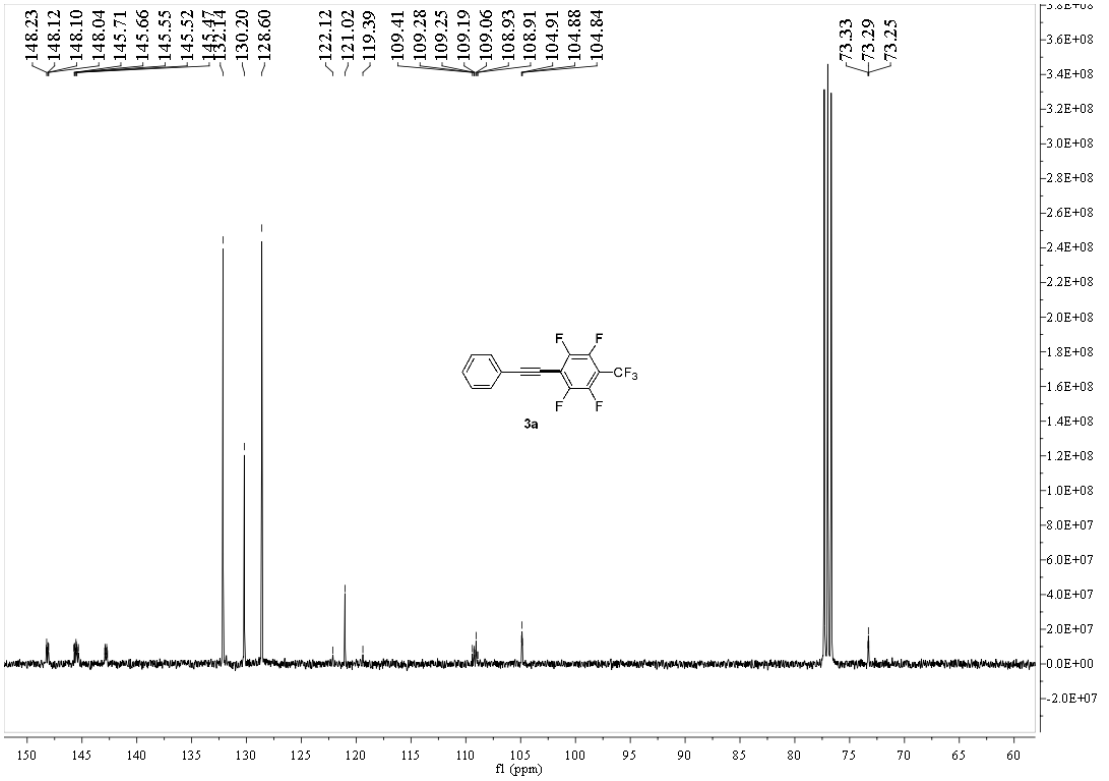
1,2,4,5-tetrafluoro-3-(phenylethynyl)-6-(trifluoromethyl)benzene



3a



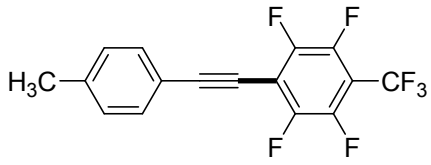




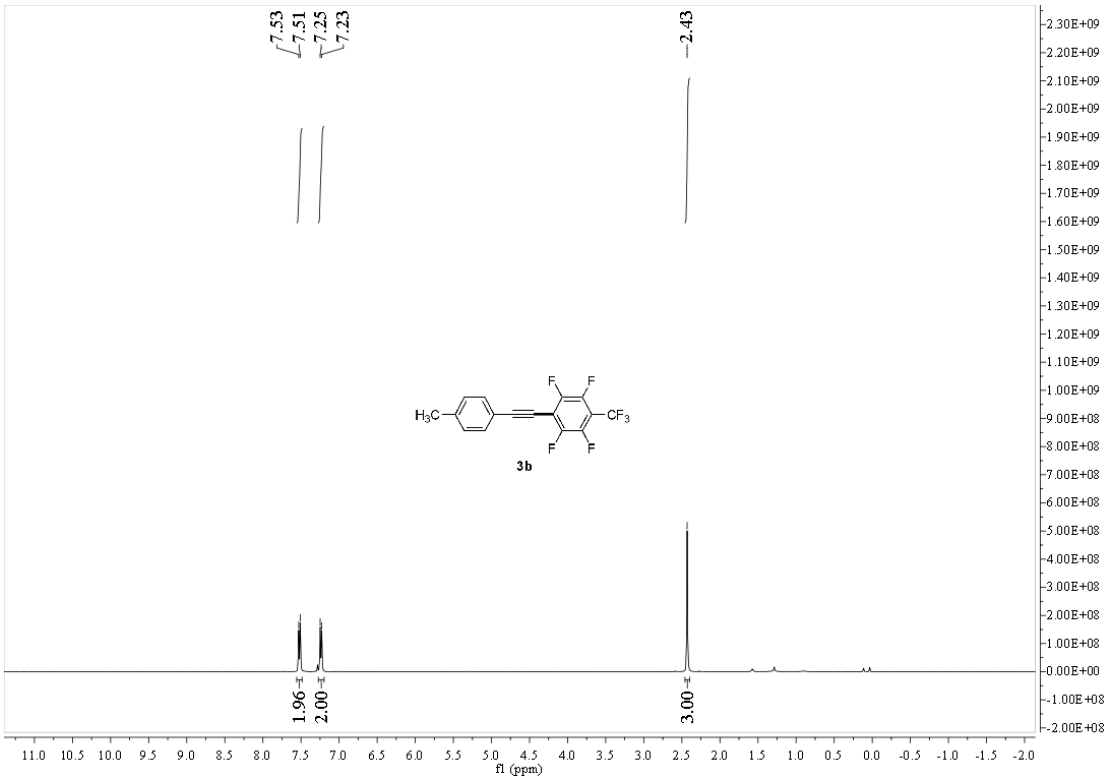
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.63 (d, J = 6.9 Hz, 2H), 7.51 – 7.41 (m, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.6 to -134.7 (m, 2F), -140.9 to -141.0 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 73.3 (t, J = 4.0 Hz), 104.9 (t, J = 3.5 Hz), 108.9 – 109.4 (m), 120.8 (q, $^{1}J_{CF}$ = 274.0 Hz), 121.0, 128.6,

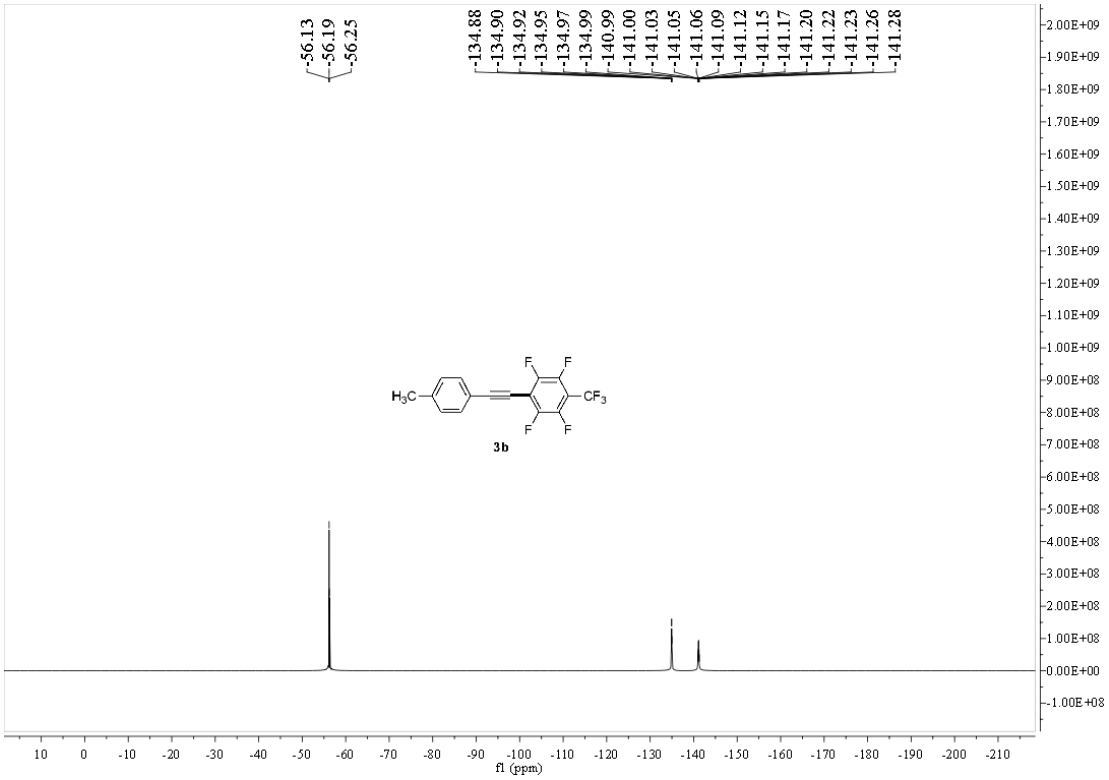
130.2, 132.1, 142.7 – 142.9 (m), 145.3 – 145.7 (m), 148.0 – 148.3 (m); **IR** (KBr) ν (cm^{-1}): 2221, 1484, 1401, 1346, 1271, 1174, 1136, 1072, 981, 873, 760, 690, 529; **HRMS** (EI) found: m/z 318.0269 [M]; calcd. for $C_{15}H_5F_7$ 318.0279.

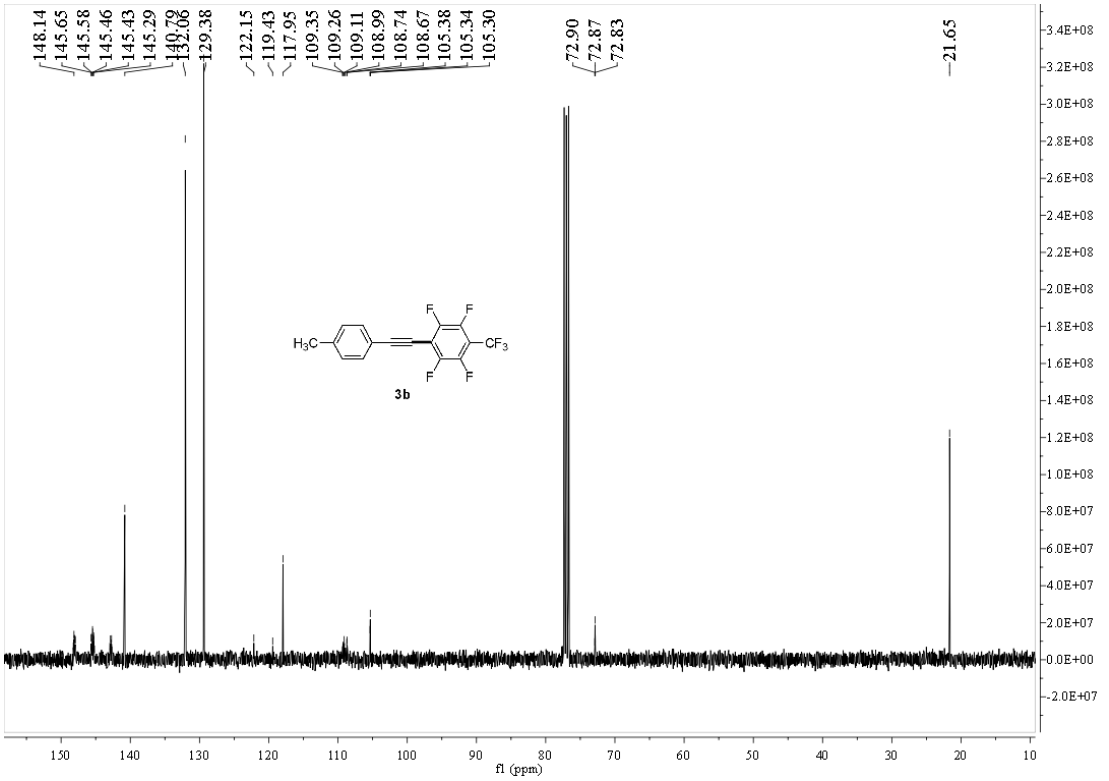
1,2,4,5-tetrafluoro-3-(p-tolylethynyl)-6-(trifluoromethyl)benzene



3b



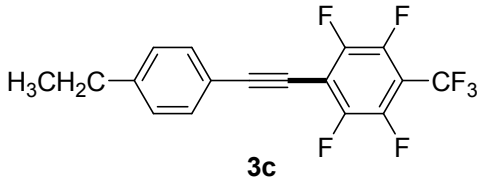




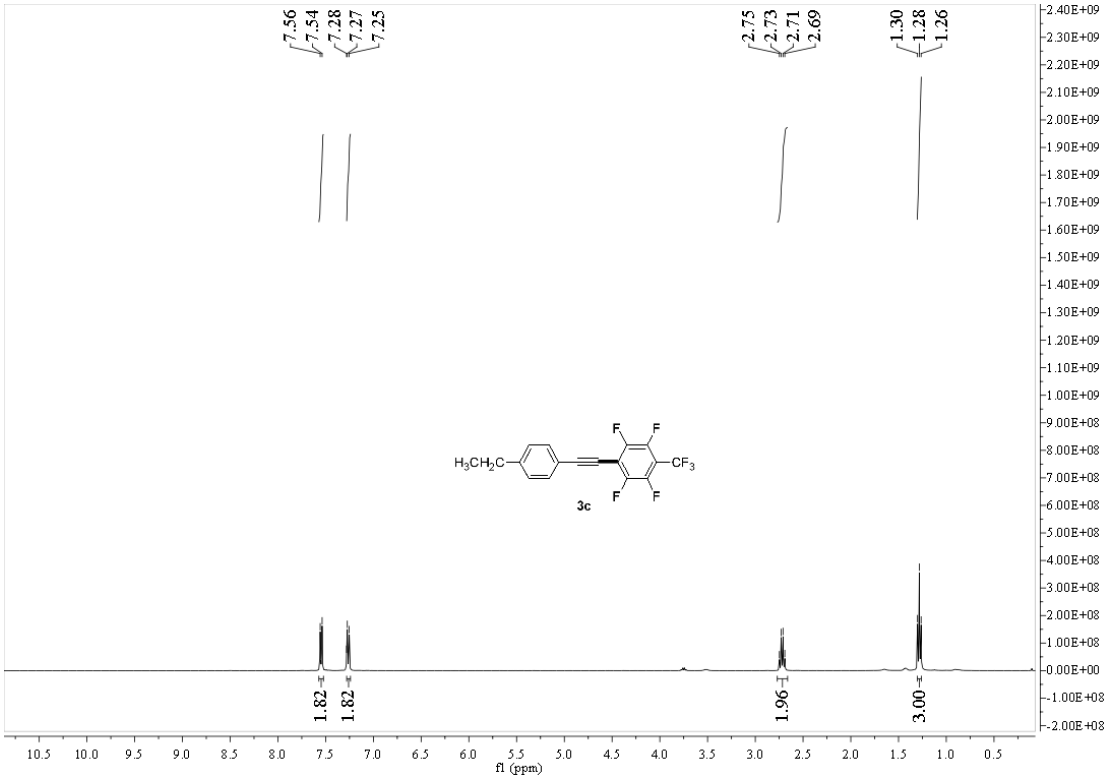
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.52 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.9 to -135.0 (m, 2F), -141.0 to -141.3 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 21.7, 72.9 (t, J = 3.5 Hz), 105.3 (t, J = 4.0 Hz), 108.7 – 109.4 (m), 118.0, 120.8 (q,

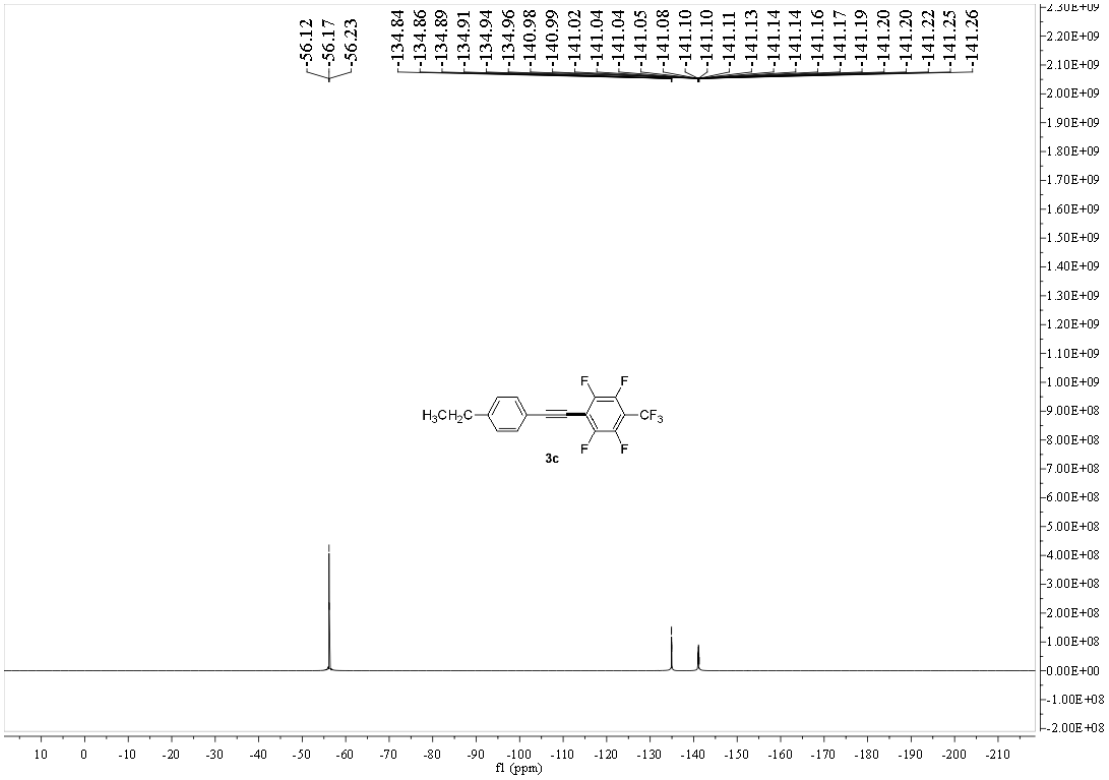
$^1J_{CF}$ = 272.0 Hz), 129.4, 132.1, 140.8, 142.7 – 143.0 (m), 145.2 – 145.7 (m), 148.0 – 148.3 (m); **IR** (KBr) ν (cm^{-1}): 2925, 2221, 1650, 1594, 1486, 1341, 1272, 1190, 1141, 984, 872, 819, 709, 530; **HRMS** (EI) found: m/z 332.0432 [M]; calcd. for $C_{16}H_7F_7$ 332.0436.

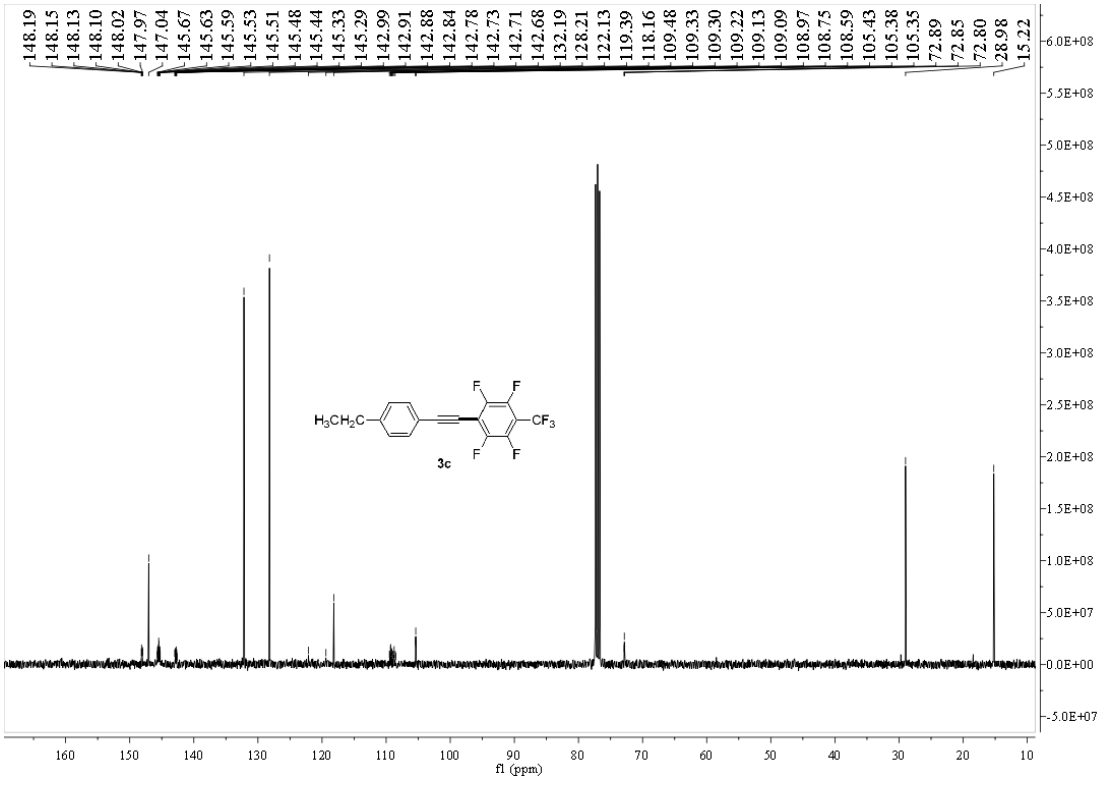
1-((4-ethylphenyl)ethynyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene



3c



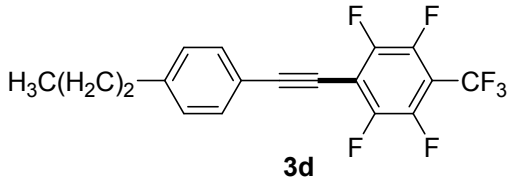




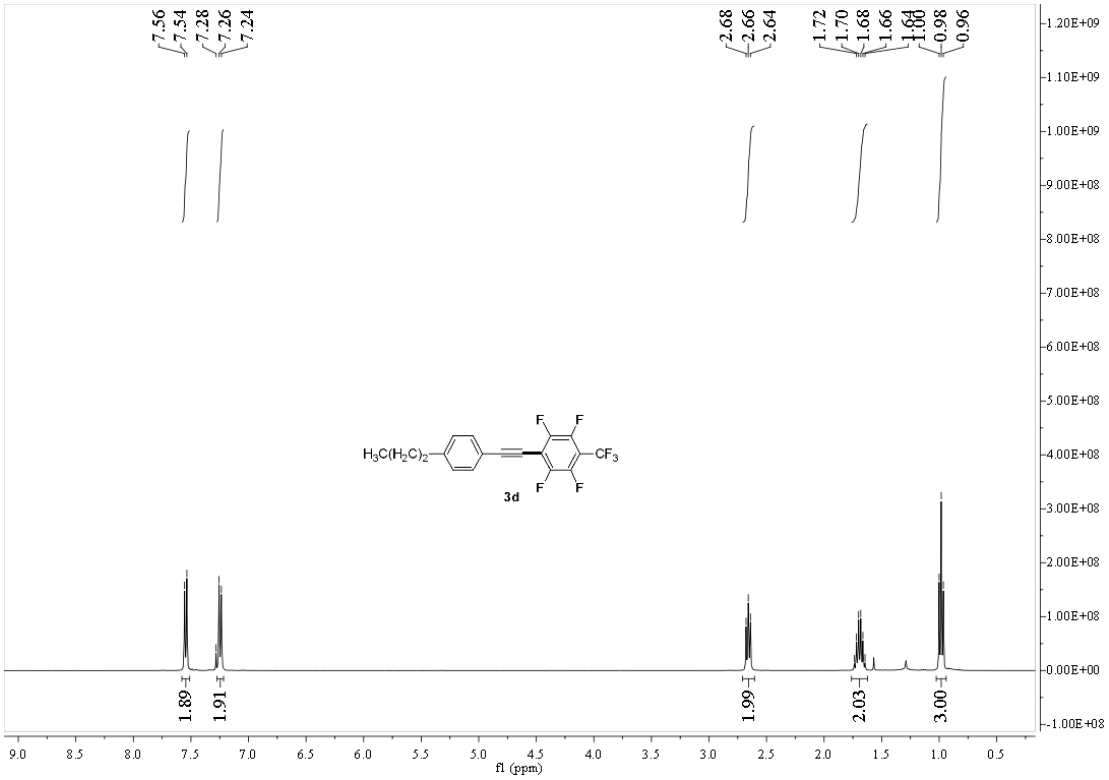
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.55 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 1.28 (t, J = 7.6 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.9 to -135.0 (m, 2F), -141.0 to -141.3 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 15.2, 29.0, 72.9 (t, J = 4.5 Hz), 105.4 (t, J = 4.0 Hz),

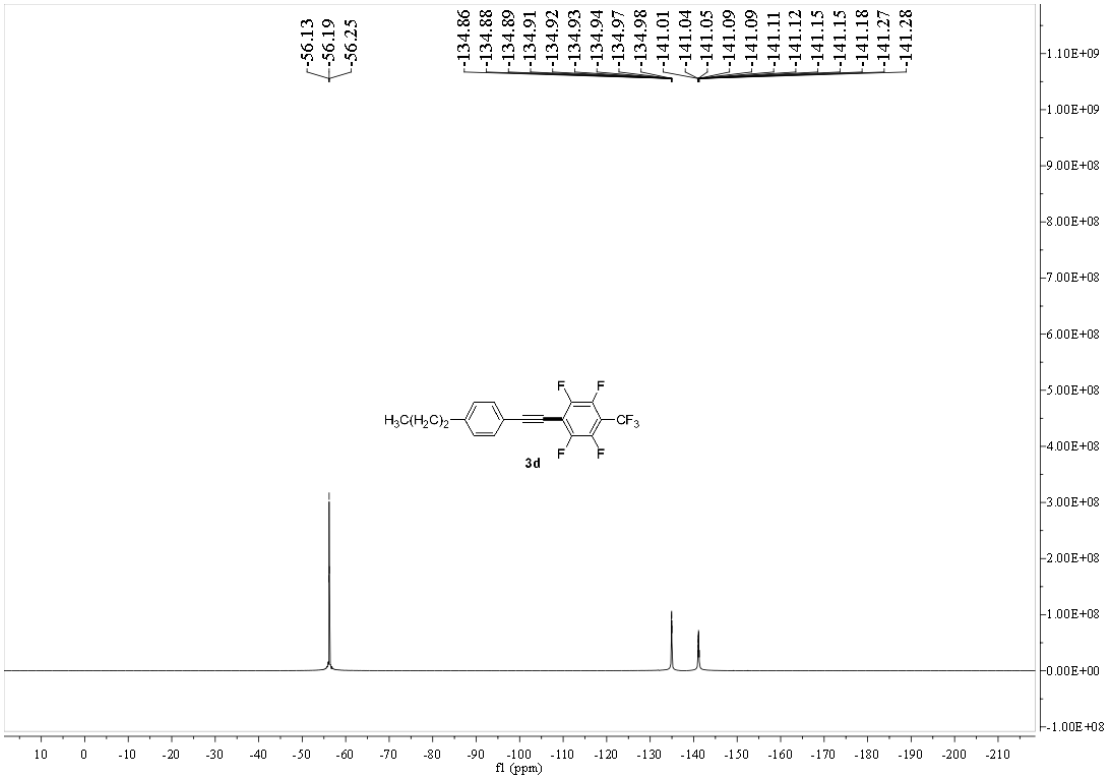
108.5 – 109.5 (m), 118.2, 128.2, 120.8 (q, $^{1}J_{CF}$ = 274.0 Hz), 132.2, 142.6 – 143.0 (m), 145.2 – 145.7 (m), 147.0, 148.0 – 148.2 (m); **IR** (KBr) v (cm^{-1}): 2972, 2936, 2876, 2226, 1648, 1603, 1491, 1341, 1271, 1147, 988, 873, 837, 712, 687, 561, 528; **HRMS** (EI) found: m/z 346.0589 [M]; calcd. for $C_{17}H_9F_7$ 346.0592.

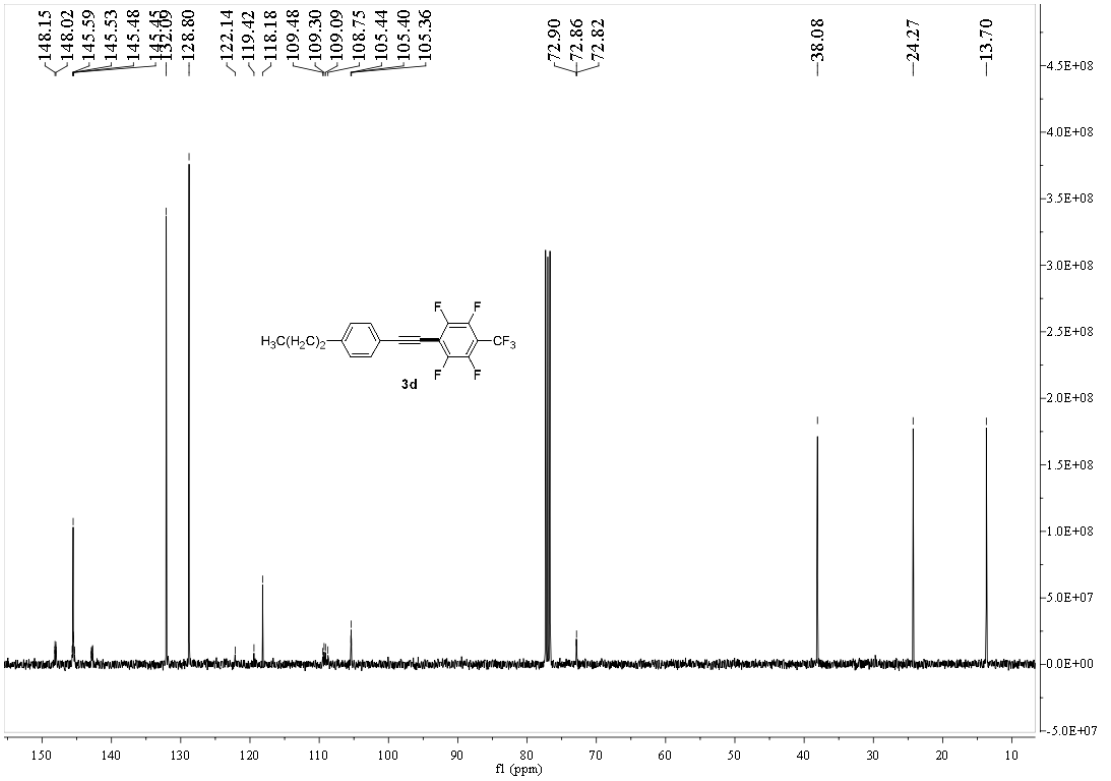
1,2,4,5-tetrafluoro-3-((4-propylphenyl)ethynyl)-6-(trifluoromethyl)benzene



3d



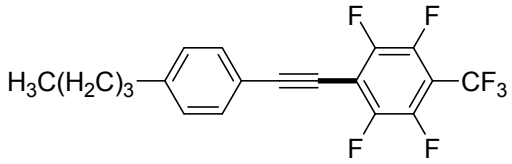




^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.55 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 2.71 – 2.60 (m, 2H), 1.76 – 1.62 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.9 to -135.0 (m, 2F), -141.0 to -141.3 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 13.7, 24.3, 38.1, 72.9 (t, J = 4.0

Hz), 105.4 (t, J = 4.0 Hz), 108.5 – 109.5 (m), 118.2, 120.8 (q, $^1J_{CF}$ = 272.0 Hz), 128.8, 132.1, 142.7 – 142.9 (m), 145.5, 145.3 – 145.7 (m), 148.0 – 148.2 (m); **IR** (KBr) v (cm^{-1}): 2964, 2931, 2870, 2218, 1650, 1595, 1490, 1341, 1273, 1180, 1150, 1025, 987, 873, 812, 712, 570, 535; **HRMS** (EI) found: m/z 360.0742 [M]; calcd. for $C_{18}H_{11}F_7$ 360.0749.

1-((4-butylphenyl)ethynyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene



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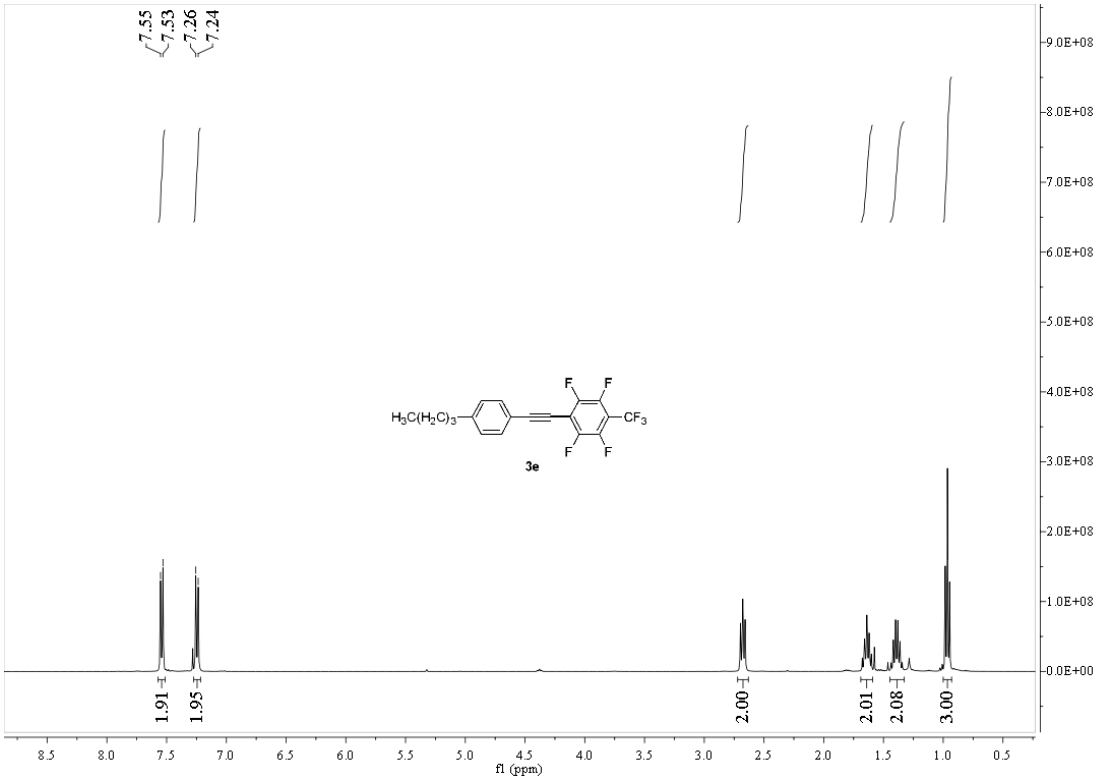
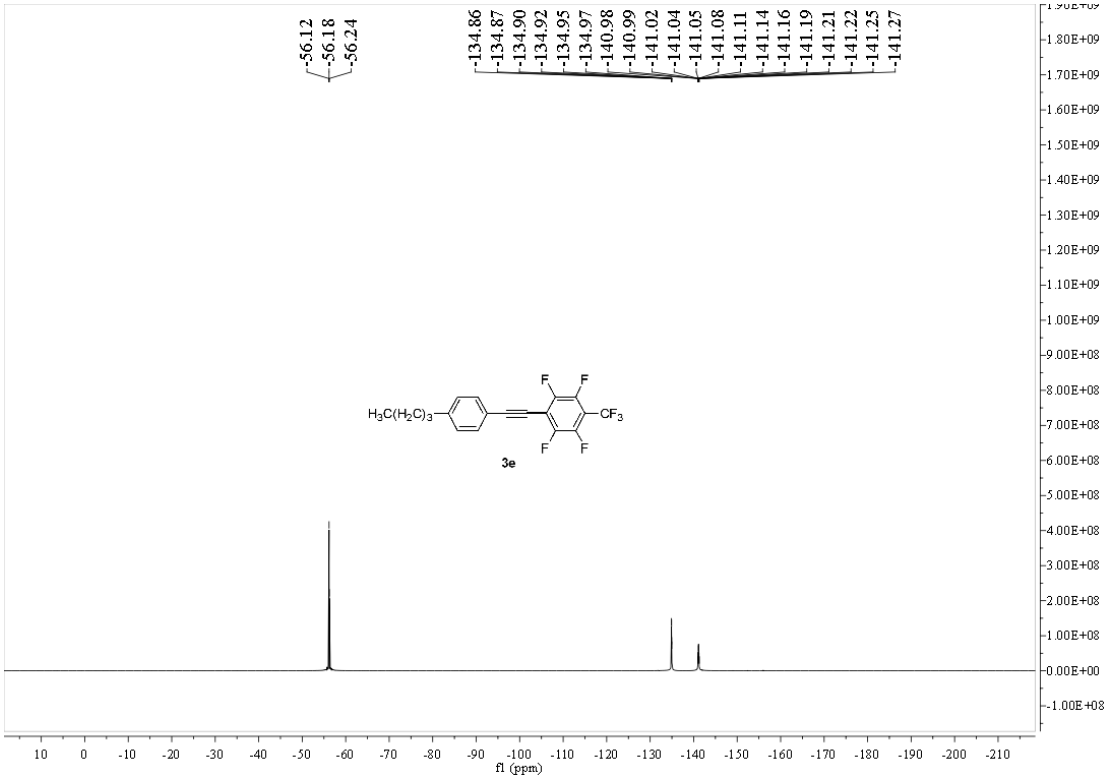
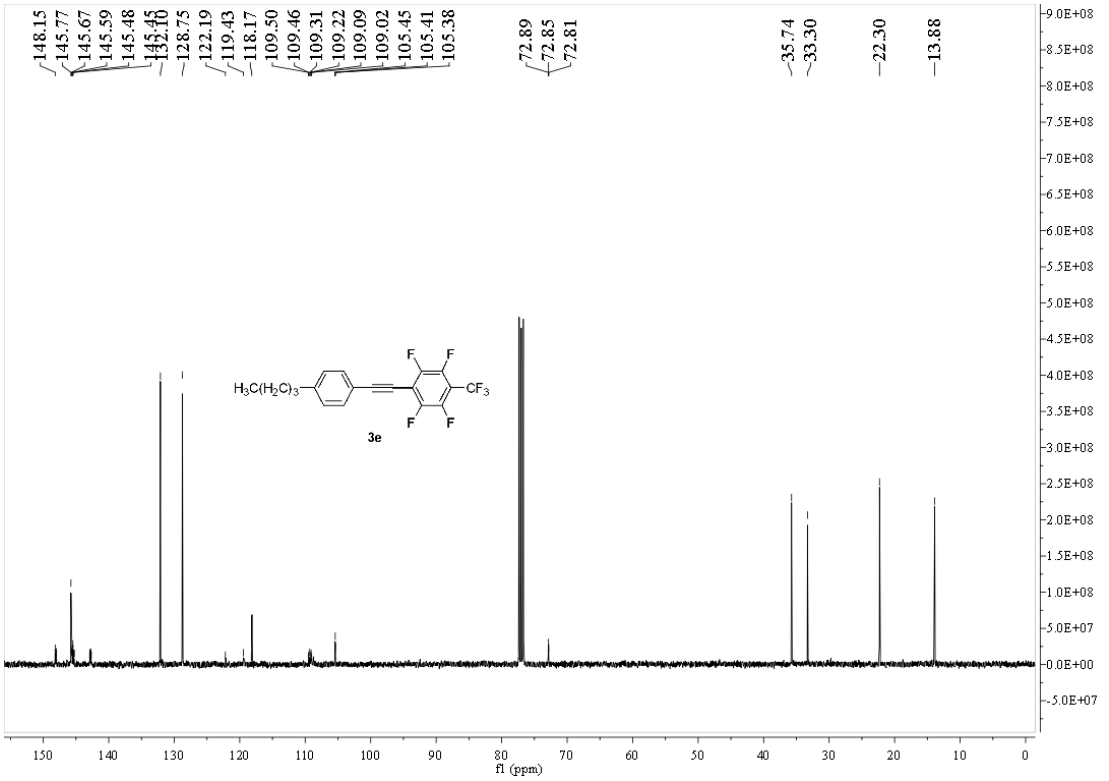


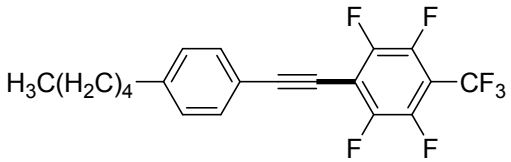




^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.54 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 2.72 – 2.63 (m, 2H), 1.69 – 1.59 (m, 2H), 1.45 – 1.33 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.9 to -135.0 (m, 2F), -141.0 to -141.3 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 13.9, 22.3,

33.3, 35.7, 72.9 (t, J = 4.0 Hz), 105.4 (t, J = 3.5 Hz), 109.0 – 109.5 (m), 118.2, 120.8 (q, $^1J_{CF}$ = 276.0 Hz), 128.8, 132.1, 142.7 – 142.9 (m), 145.3 – 145.7 (m), 145.8, 148.0 – 148.2 (m); **IR** (KBr) v (cm^{-1}): 2963, 2934, 2865, 2222, 1654, 1601, 1490, 1345, 1274, 1230, 1159, 988, 876, 832, 744, 713, 570, 536; **HRMS** (EI) found: m/z 374.0895 [M]; calcd. for $C_{19}H_{13}F_7$ 374.0905.

1,2,4,5-tetrafluoro-3-((4-pentylphenyl)ethynyl)-6-(trifluoromethyl)benzene



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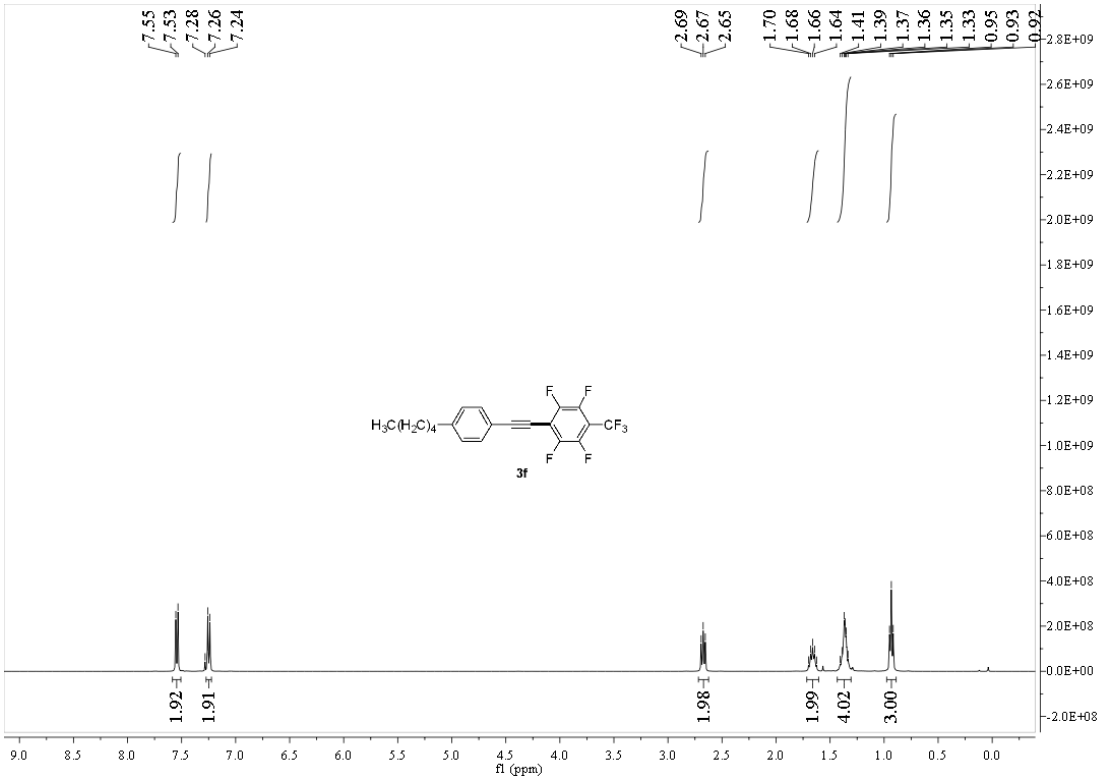
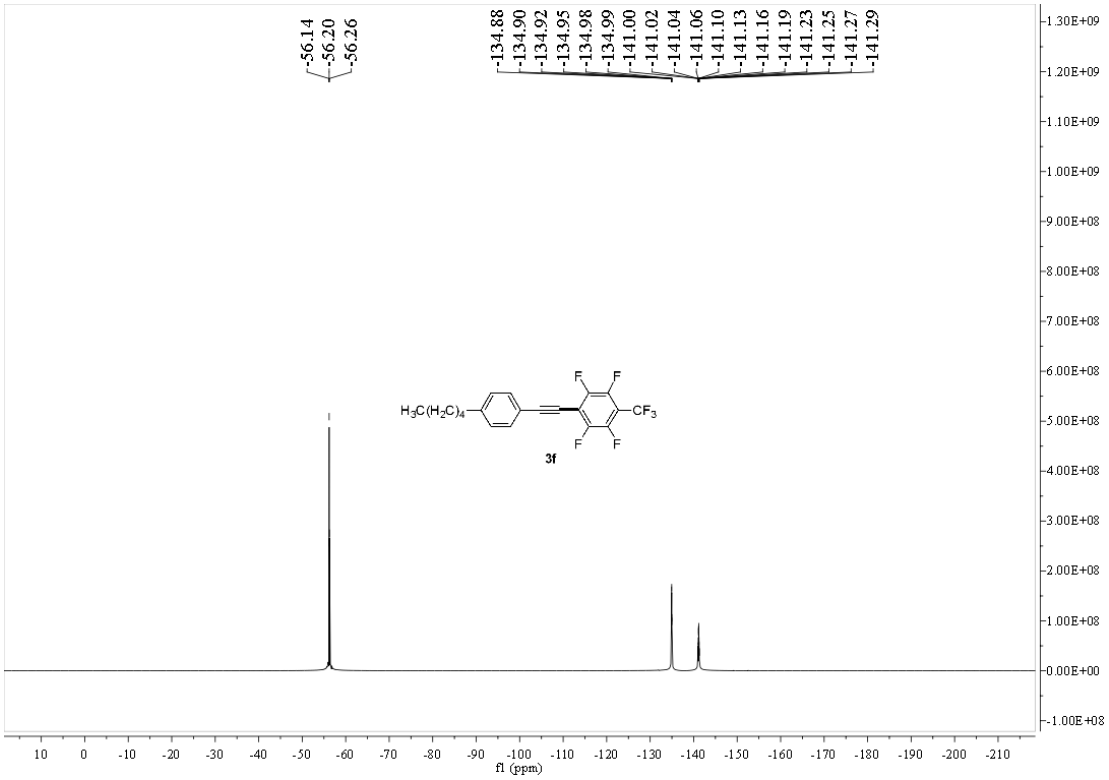
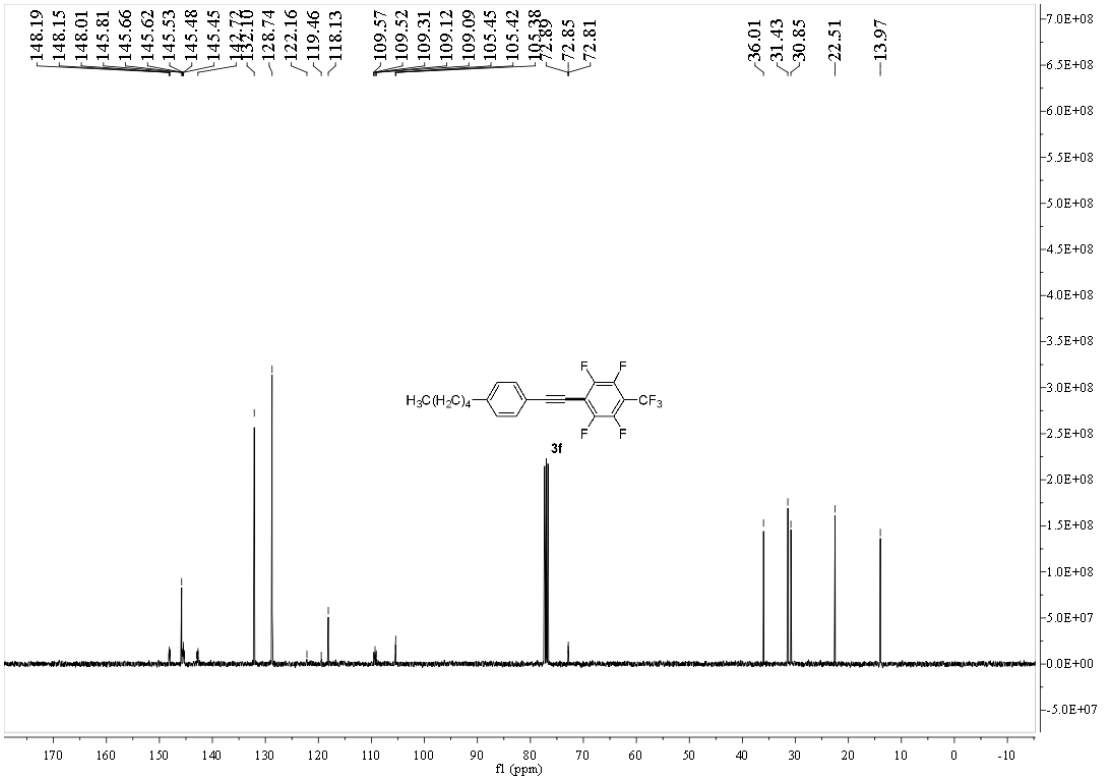


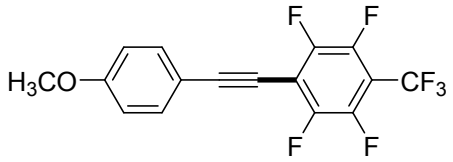




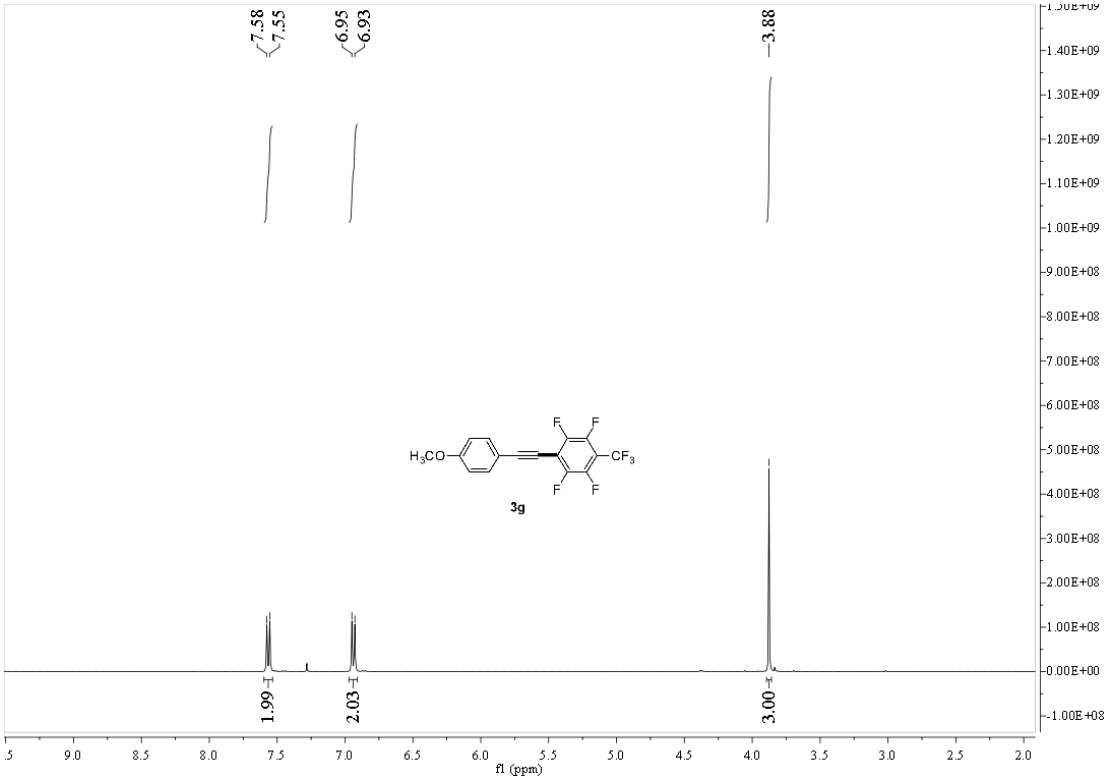
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.54 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 2.72 – 2.62 (m, 2H), 1.72 – 1.61 (m, 2H), 1.43 – 1.31 (m, 4H), 0.93 (t, J = 6.8 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.9 to -135.0 (m, 2F), -141.0 to -141.3 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 14.0, 22.5,

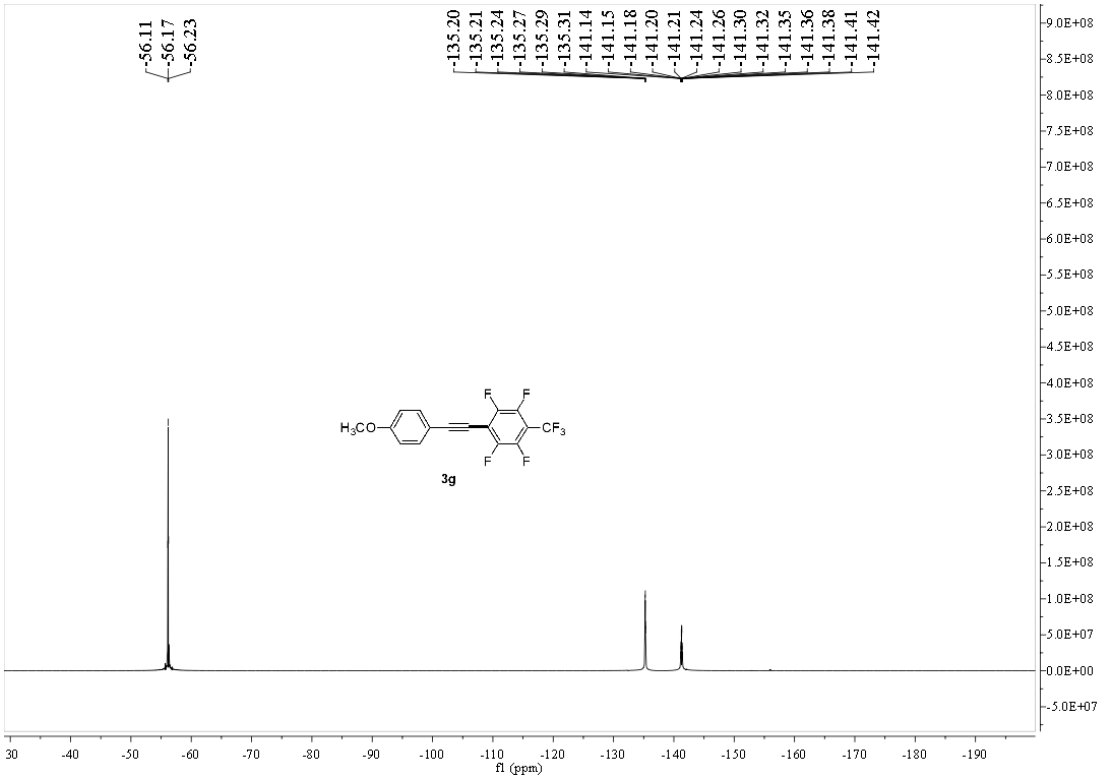
30.9, 31.4, 36.0, 72.9 (t, J = 4.0 Hz), 105.4 (t, J = 3.5 Hz), 109.1 – 109.6 (m), 118.1, 120.8 (q, $^1J_{CF}$ = 270.0 Hz), 128.7, 132.1, 142.7 – 142.9 (m), 145.3 – 145.7 (m), 145.8, 148.0 – 148.2 (m); **IR** (KBr) v (cm^{-1}): 2931, 2860, 2224, 1654, 1600, 1489, 1344, 1274, 1179, 1146, 985, 872, 853, 812, 741, 711, 569, 531; **HRMS** (EI) found: m/z 388.1068 [M]; calcd. for $C_{20}H_{15}F_7$ 388.1062.

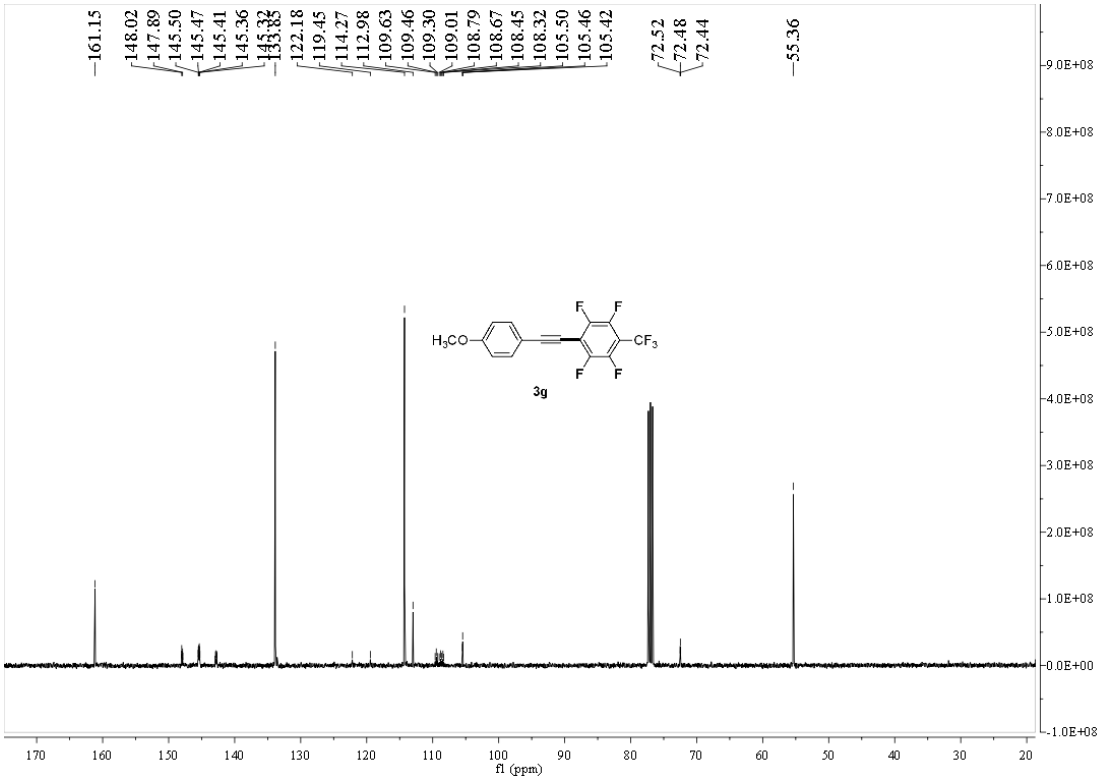
1,2,4,5-tetrafluoro-3-((4-methoxyphenyl)ethynyl)-6-(trifluoromethyl)benzene



3g



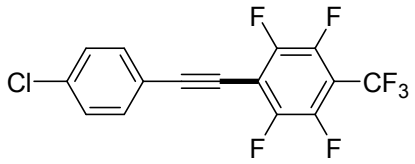




^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.57 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -135.2 to -135.3 (m, 2F), -141.1 to -141.4 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 55.4, 72.5 (t, J = 4.0 Hz), 105.5 (t, J = 4.0 Hz), 108.3 – 109.6 (m), 113.0, 114.3,

120.8 (q, $^1J_{CF}$ = 273.0 Hz), 133.9, 142.7 – 143.0 (m), 145.3 – 145.5 (m), 147.8 – 148.1 (m), 161.2; **IR** (KBr) v (cm^{-1}): 2959, 2847, 2219, 1654, 1602, 1486, 1345, 1264, 1152, 1106, 1028, 984, 874, 830, 741, 536; **HRMS** (EI) found: m/z 348.0378 [M]; calcd. for $C_{16}H_7F_7O$ 348.0385.

1-((4-chlorophenyl)ethynyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene



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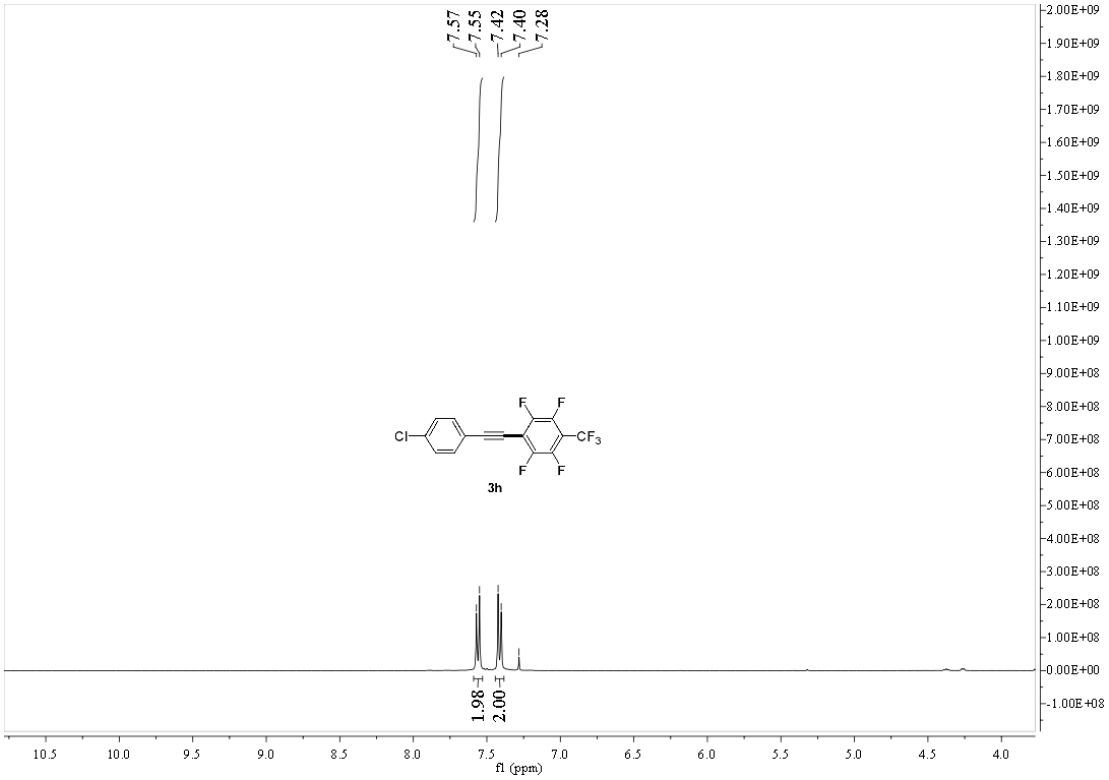
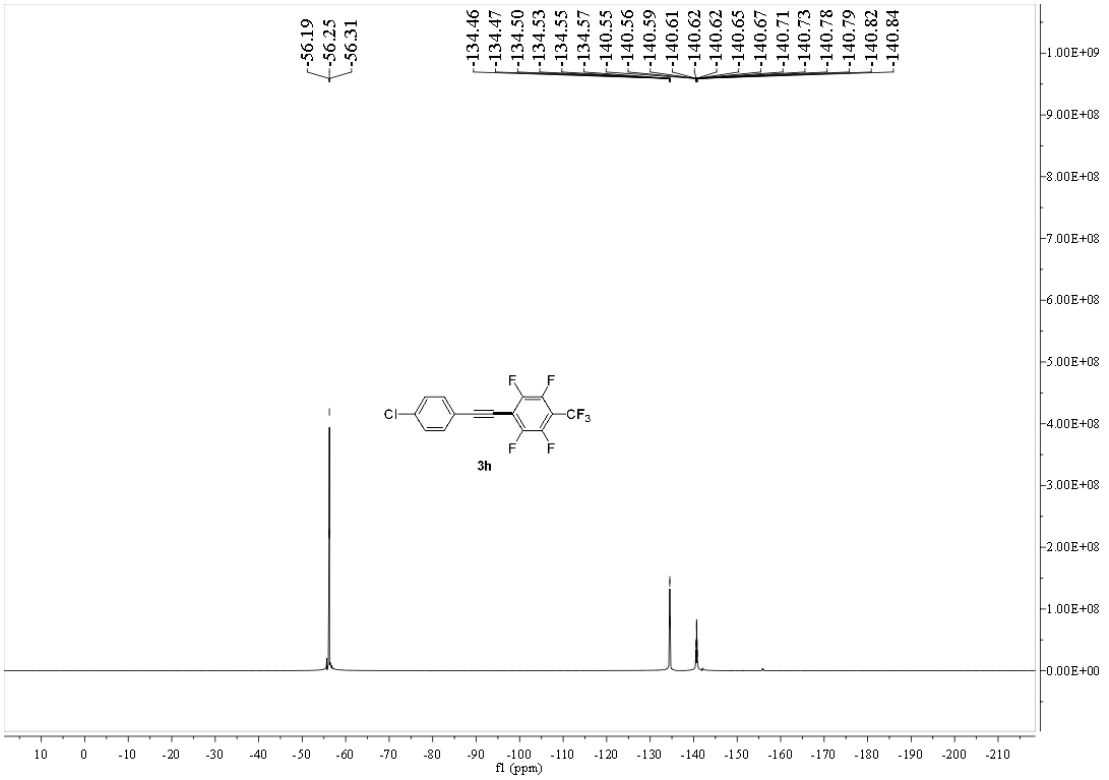
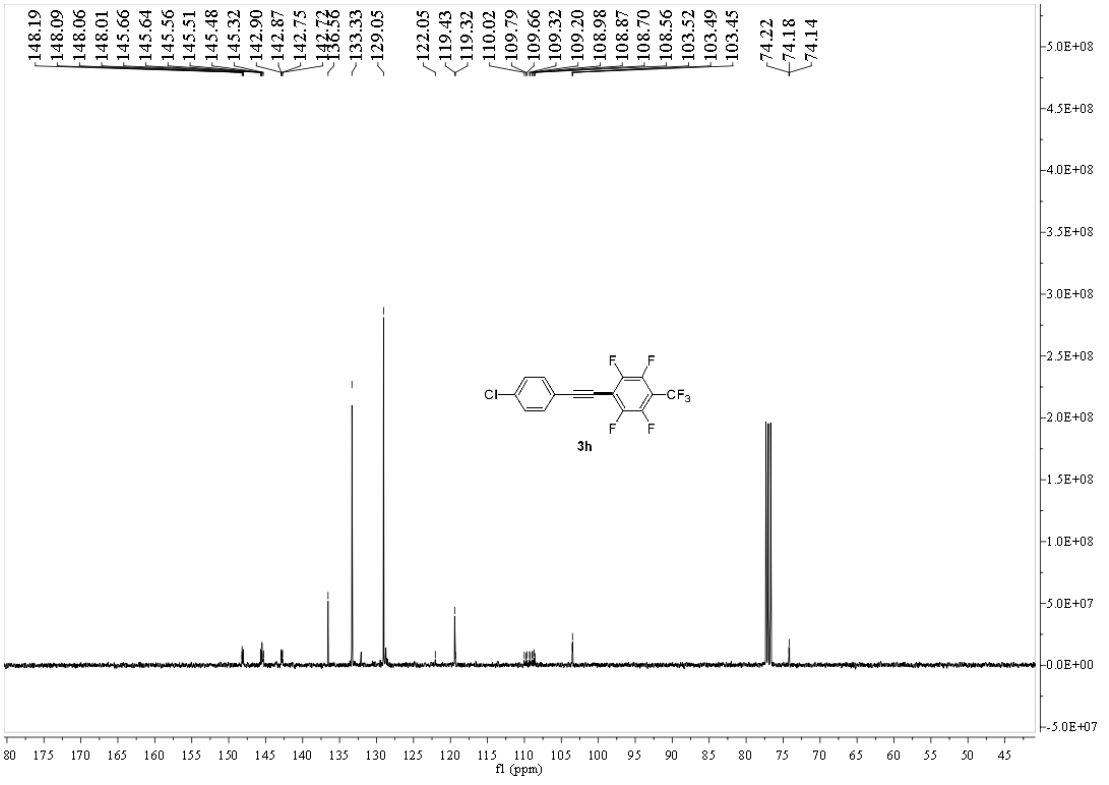


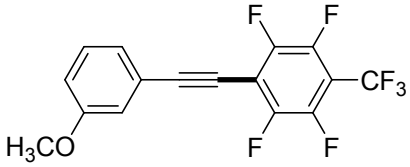




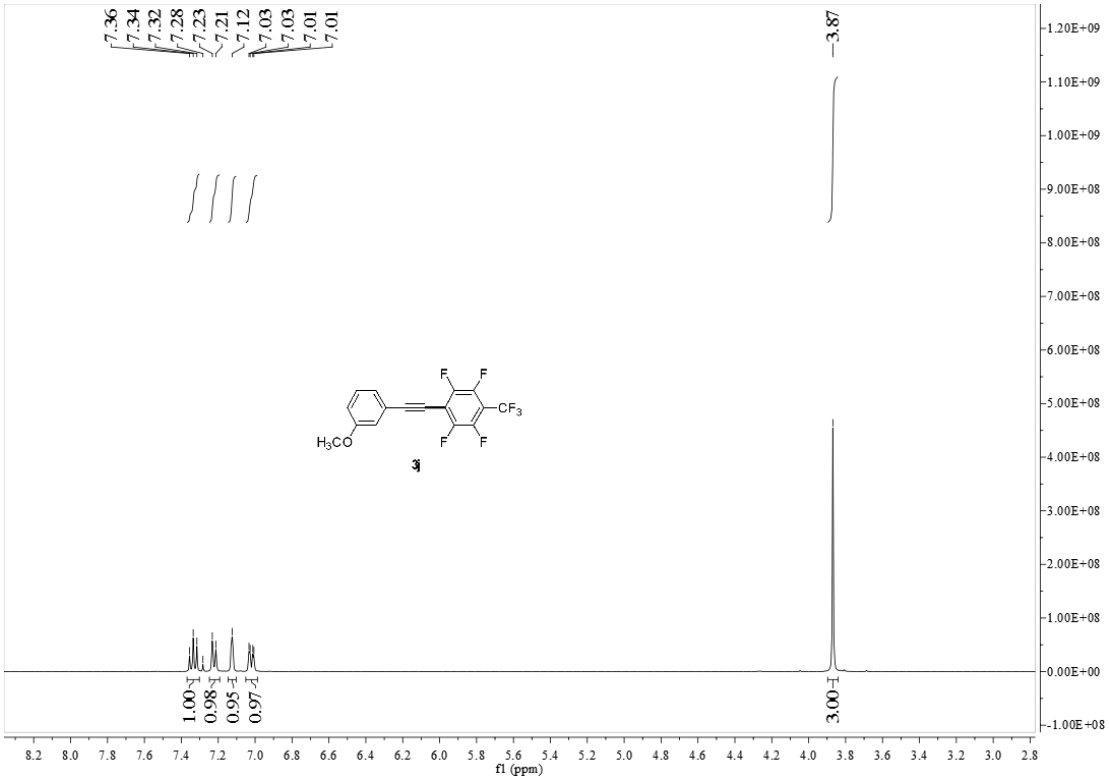
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.56 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.3 (t, J = 22.6 Hz, 3F), -134.5 to -134.6 (m, 2F), -140.6 to -140.8 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 74.2 (t, J = 4.0 Hz), 103.5 (t, J = 3.5 Hz), 108.7 – 110.0 (m), 119.4, 120.7 (q, $^{1}J_{CF}$ = 273.0 Hz),

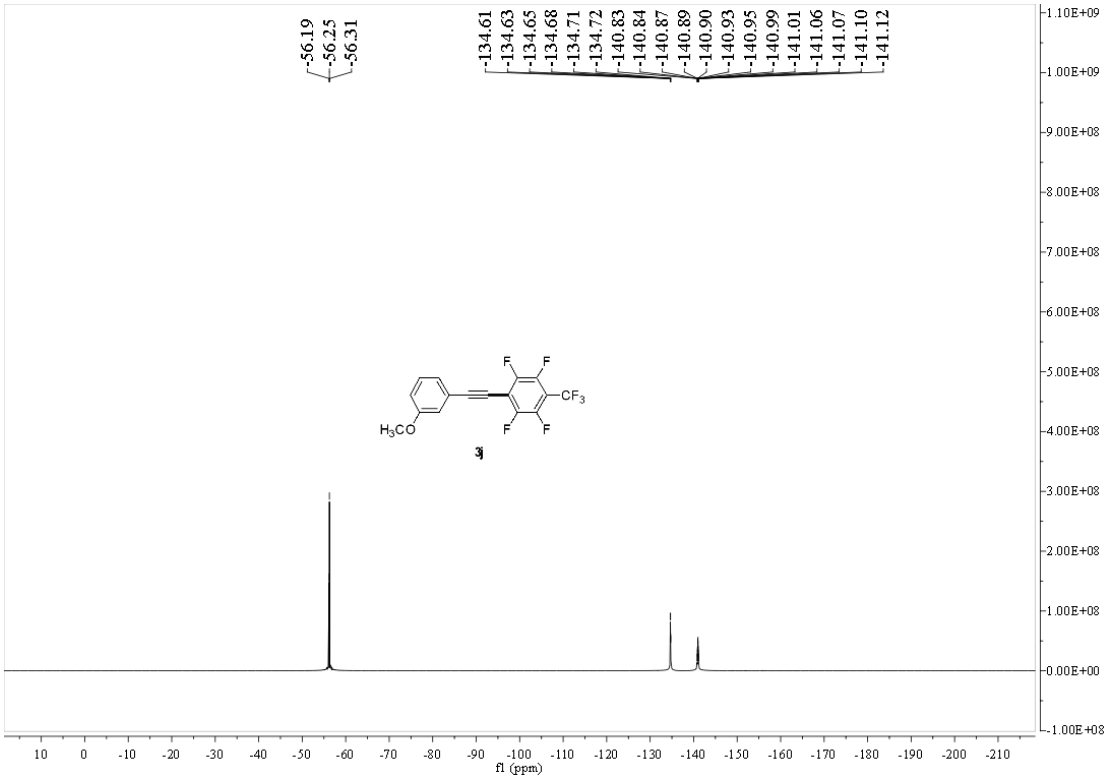
129.1, 133.3, 136.6, 142.7 – 142.9 (m), 145.3 – 145.7 (m), 148.0 – 148.2 (m); **IR** (KBr) v (cm^{-1}): 2226, 1763, 1651, 1595, 1486, 1403, 1343, 1272, 1188, 1142, 1092, 984, 873, 826, 744, 711, 524; **HRMS** (EI) found: m/z 351.9890 [M]; calcd. for $C_{15}H_4ClF_7$ 351.9890.

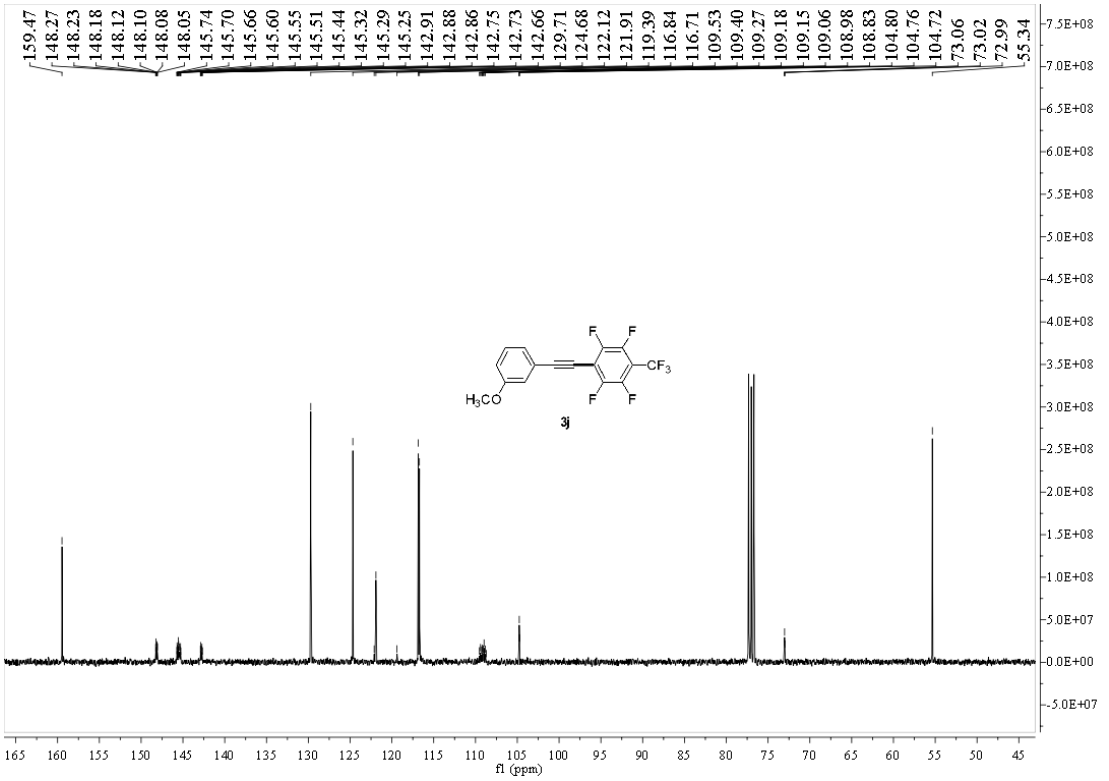
1,2,4,5-tetrafluoro-3-((3-methoxyphenyl)ethynyl)-6-(trifluoromethyl)benzene



3j



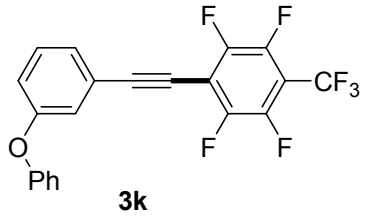




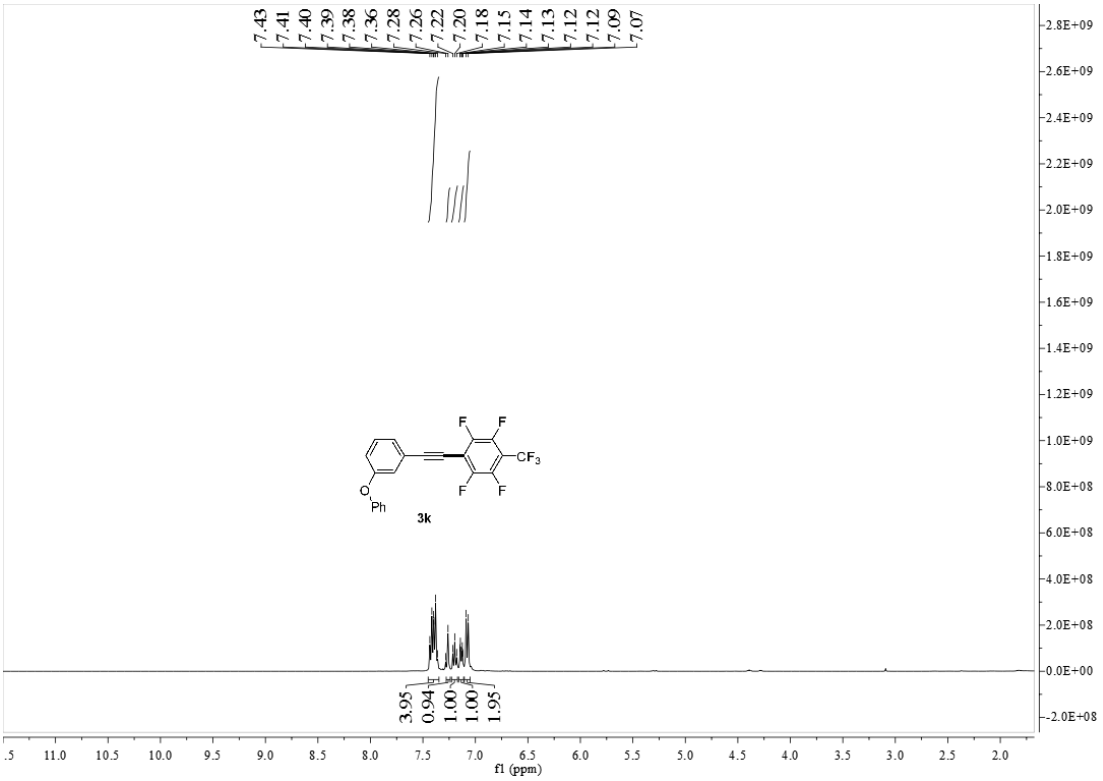
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.34 (t, J = 7.9 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.12 (s, 1H), 7.02 (dd, J = 8.3, 2.4 Hz, 1H), 3.87 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.3 (t, J = 22.6 Hz, 3F), -134.6 to -134.7 (m, 2F), -140.8 to -141.1 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 55.3, 73.0 (t, J = 3.5 Hz), 104.8 (t, J = 4.0

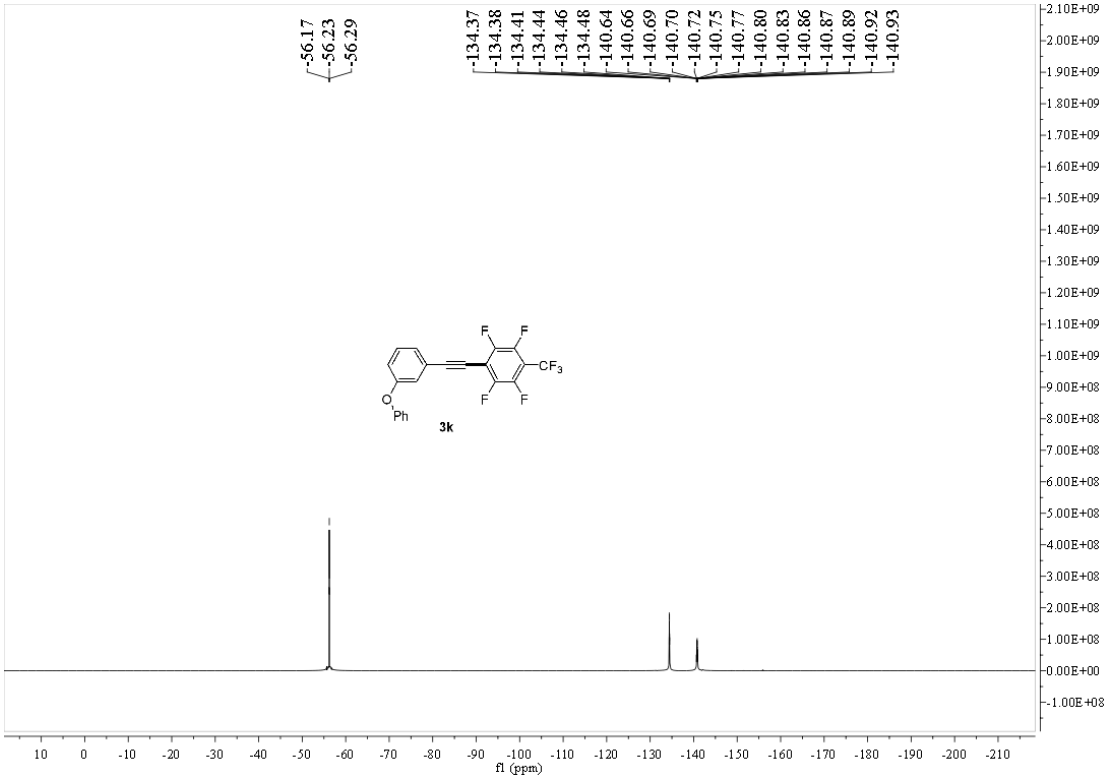
Hz), 108.7 – 109.5 (m), 116.7, 116.8, 120.7 (q, $^1J_{CF}$ = 273.0 Hz), 121.9, 124.7, 129.7, 142.7 – 142.9 (m), 145.3 – 145.7 (m), 148.1 – 148.3 (m), 159.5; **IR** (KBr) v (cm^{-1}): 2944, 2226, 1648, 1603, 1491, 1341, 1271, 1147, 988, 873, 837, 712, 687, 561, 528; **HRMS** (EI) found: m/z 348.0378 [M]; calcd. for $C_{16}H_7F_7O$ 348.0385.

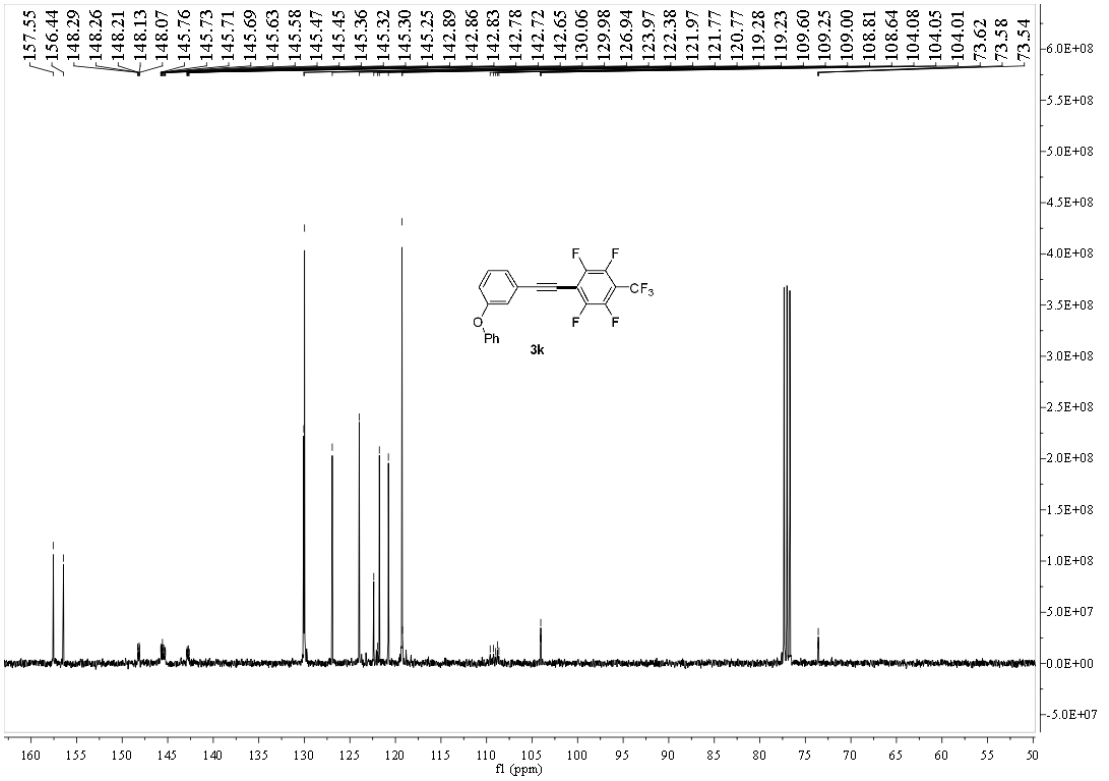
1,2,4,5-tetrafluoro-3-((3-phenoxyphenyl)ethynyl)-6-(trifluoromethyl)benzene



3k



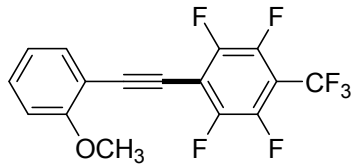




^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.40 (dt, J = 14.0, 7.8 Hz, 4H), 7.26 (s, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.08 (d, J = 7.9 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.4 to -134.5 (m, 2F), -140.6 to -140.9 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 73.6 (t, J = 3.5 Hz), 104.1 (t, J = 3.5

Hz), 108.6 – 109.6 (m), 119.3, 120.6 (q, $^{1}J_{CF}$ = 274.0 Hz), 120.8, 121.8, 122.4, 124.0, 126.9, 130.0, 130.1, 142.7 – 142.9 (m), 145.3 – 145.8 (m), 148.1 – 148.3 (m), 156.4, 157.6; **IR** (KBr) ν (cm^{-1}): 2226, 1653, 1576, 1489, 1429, 1345, 1281, 1229, 1192, 1151, 1075, 989, 936, 872, 777, 716, 688, 579, 483; **HRMS** (EI) found: m/z 410.0541 [M]; calcd. for $C_{21}H_9F_7O$ 410.0542.

1,2,4,5-tetrafluoro-3-((2-methoxyphenyl)ethynyl)-6-(trifluoromethyl)benzene



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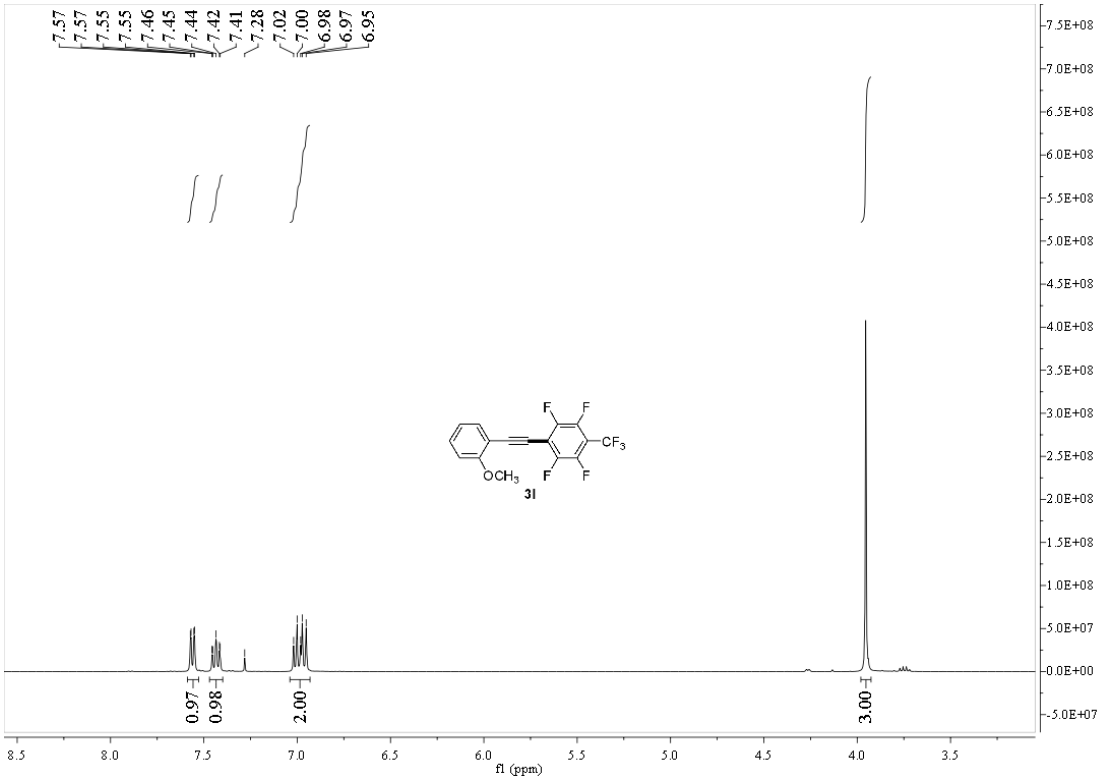
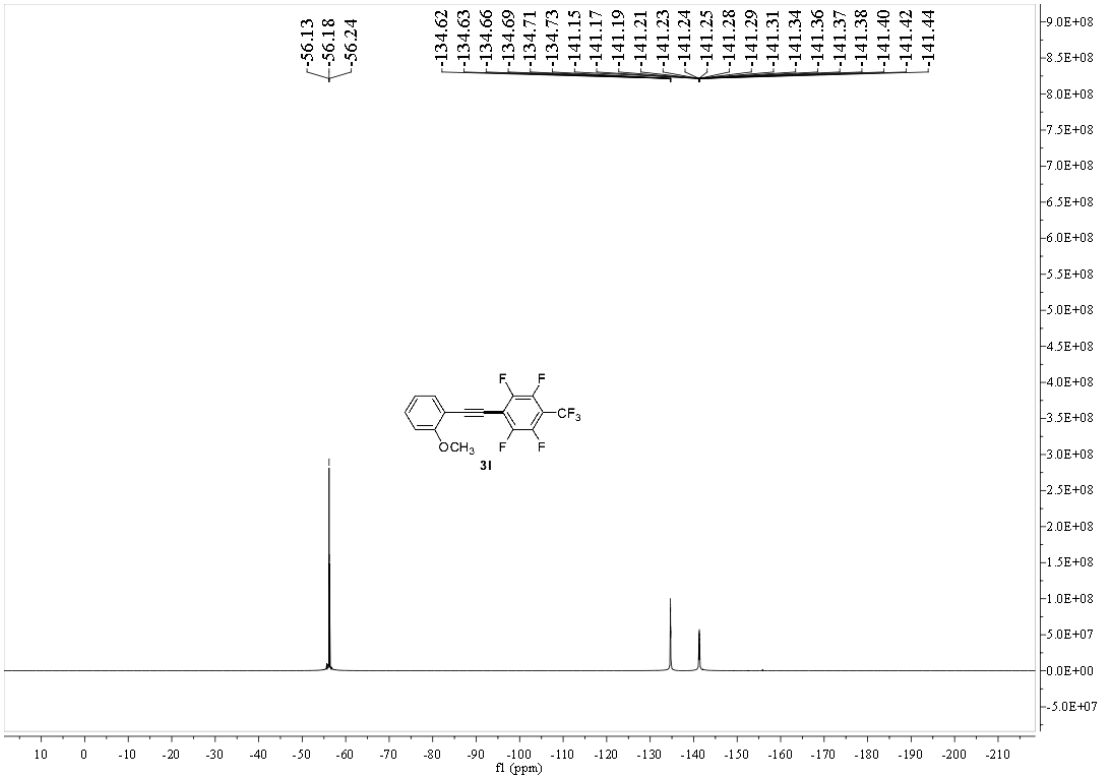
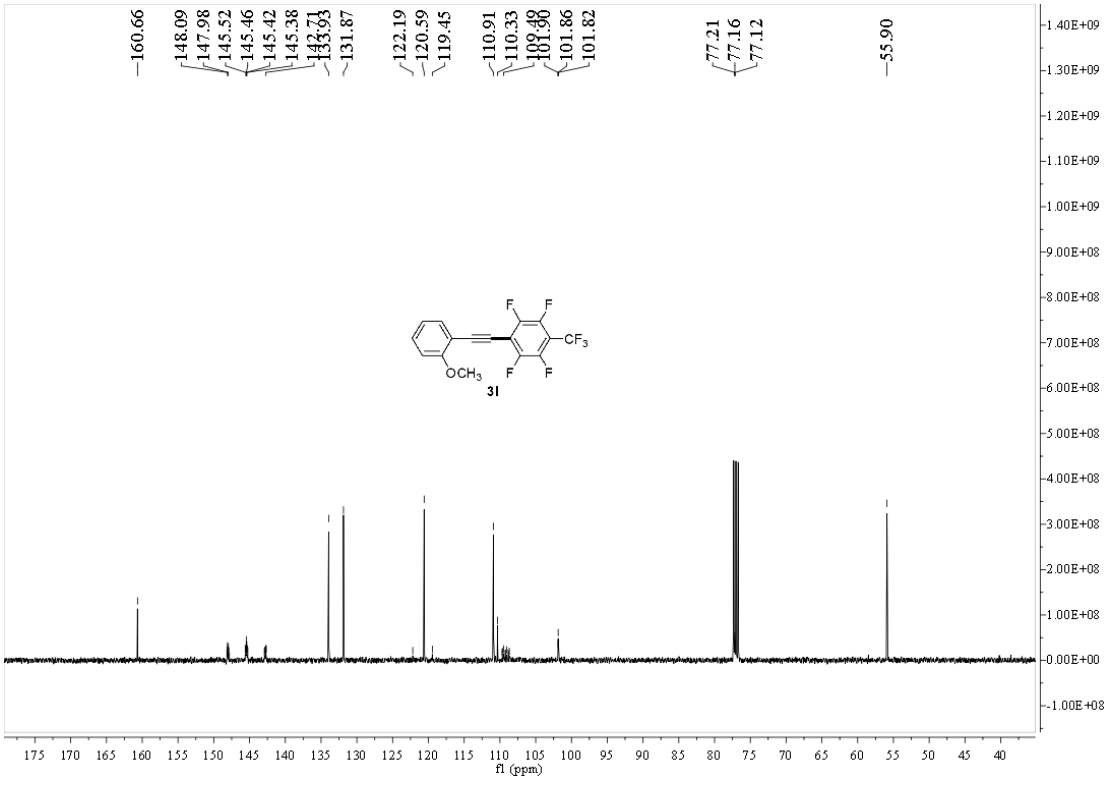


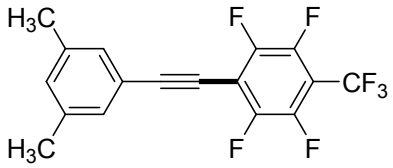




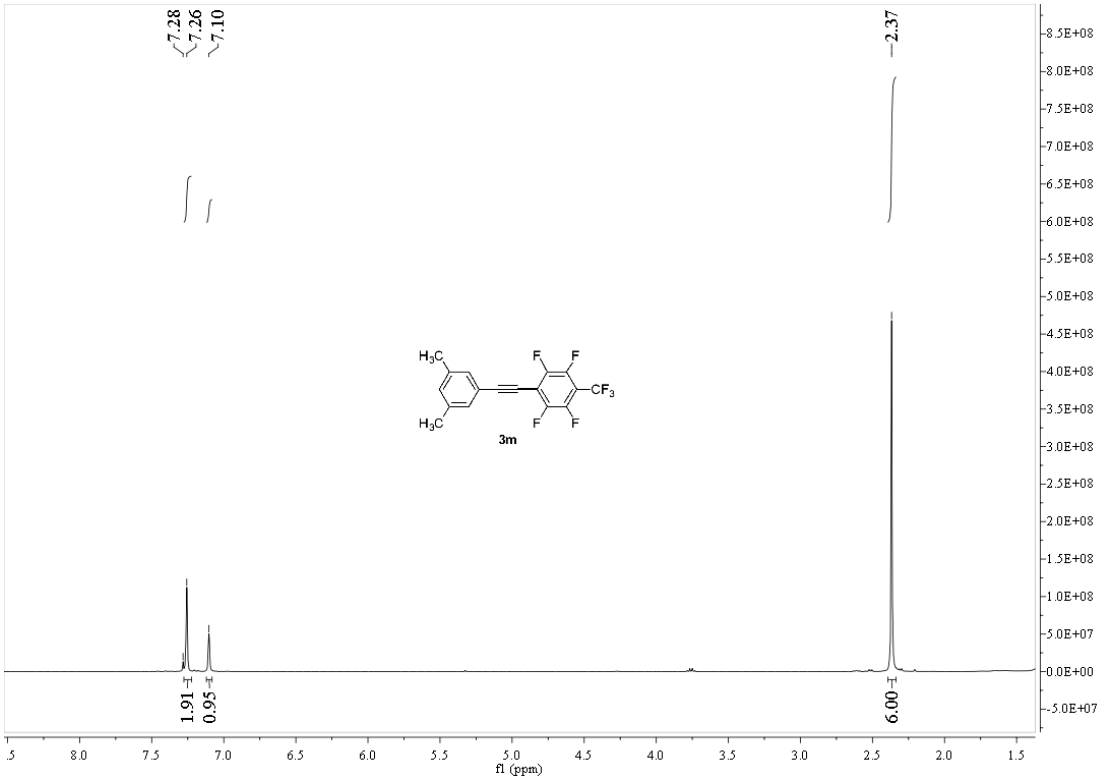
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.56 (dd, J = 7.6, 1.5 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.04 – 6.93 (m, 2H), 3.95 (d, J = 5.6 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 20.7 Hz, 3F), -134.6 to -134.7 (m, 2F), -141.2 to -141.4 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 55.9, 77.2 (t, J = 4.5 Hz), 101.9 (t, J = 4.0 Hz),

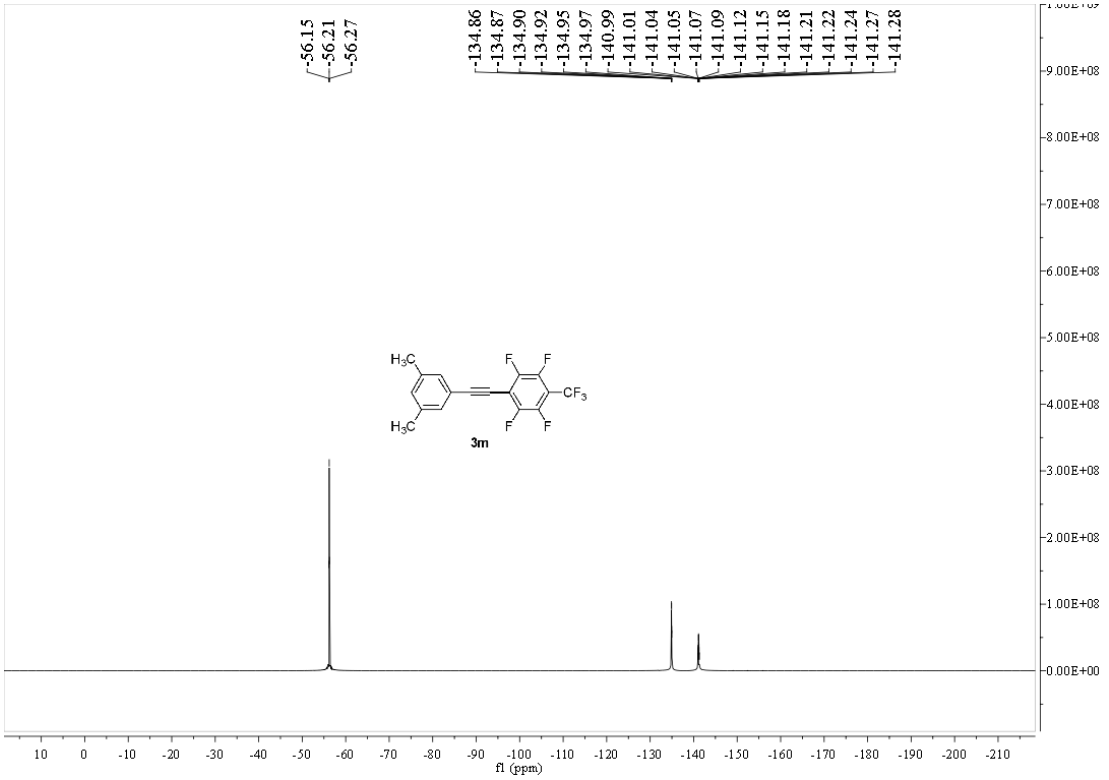
108.7 – 109.7 (m), 110.3, 110.9, 120.6, 120.8 (q, $^1J_{CF}$ = 274.0 Hz), 131.9, 133.9, 142.7 – 142.9 (m), 145.2 – 145.6 (m), 147.8 – 148.2 (m), 160.7; **IR** (KBr) ν (cm^{-1}): 2961, 2848, 2220, 1654, 1594, 1490, 1344, 1272, 1246, 1187, 1133, 1022, 986, 874, 804, 755, 713, 552, 491; **HRMS** (EI) found: m/z 348.0378 [M]; calcd. for $C_{16}H_7F_7O$ 348.0385.

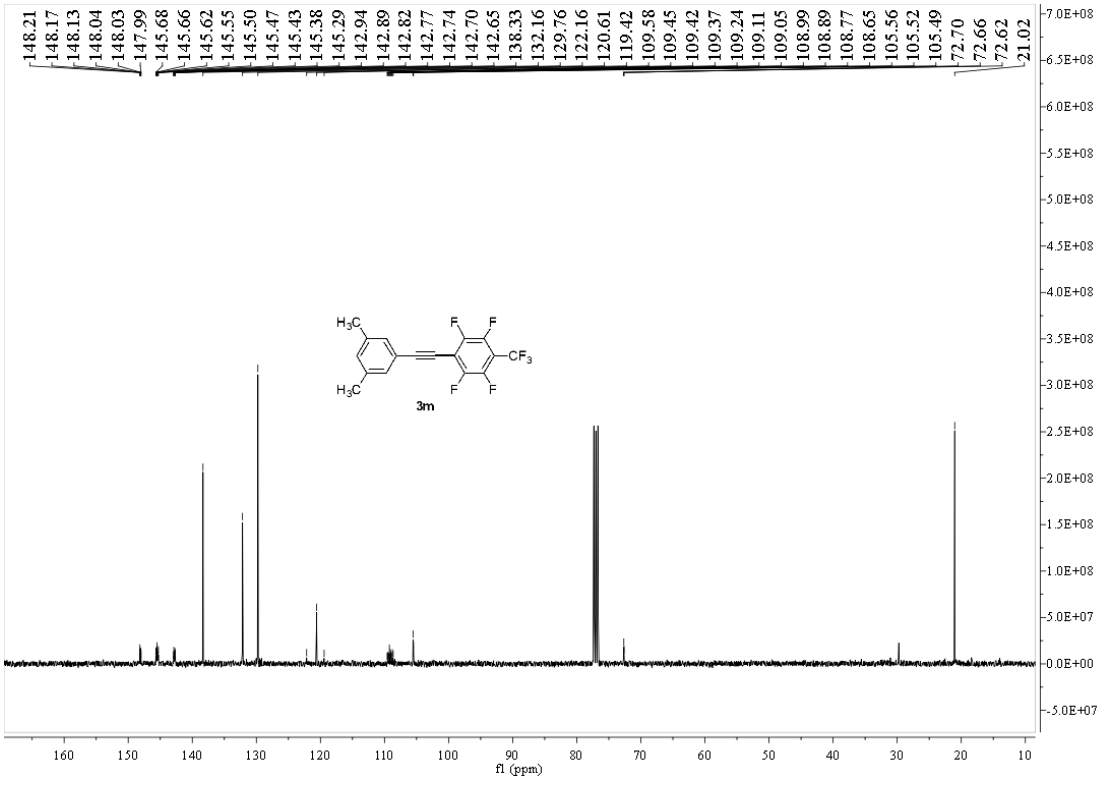
1-((3,5-dimethylphenyl)ethynyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene



3m



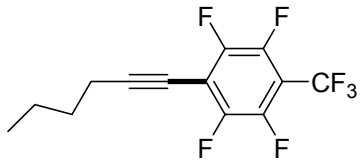




^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.26 (s, 2H), 7.10 (s, 1H), 2.37 (s, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.9 to -135.0 (m, 2F), -141.0 to -141.3 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 21.0, 72.3 (t, J = 4.0 Hz), 105.5 (t, J = 3.5 Hz), 108.7 – 109.6 (m), 120.6, 120.8 (q, $^{1}J_{CF}$ = 274.0 Hz),

129.8, 132.2, 138.3, 142.7 – 142.9 (m), 145.3 – 145.7 (m), 148.0 – 148.2 (m); **IR** (KBr) v (cm^{-1}): 2923, 2855, 2219, 1653, 1596, 1487, 1384, 1344, 1305, 1232, 1195, 1138, 1041, 986, 850, 715, 684; **HRMS** (EI) found: m/z 346.0589 [M]; calcd. for $C_{17}H_9F_7$ 346.0592.

1,2,4,5-tetrafluoro-3-(hex-1-ynyl)-6-(trifluoromethyl)benzene



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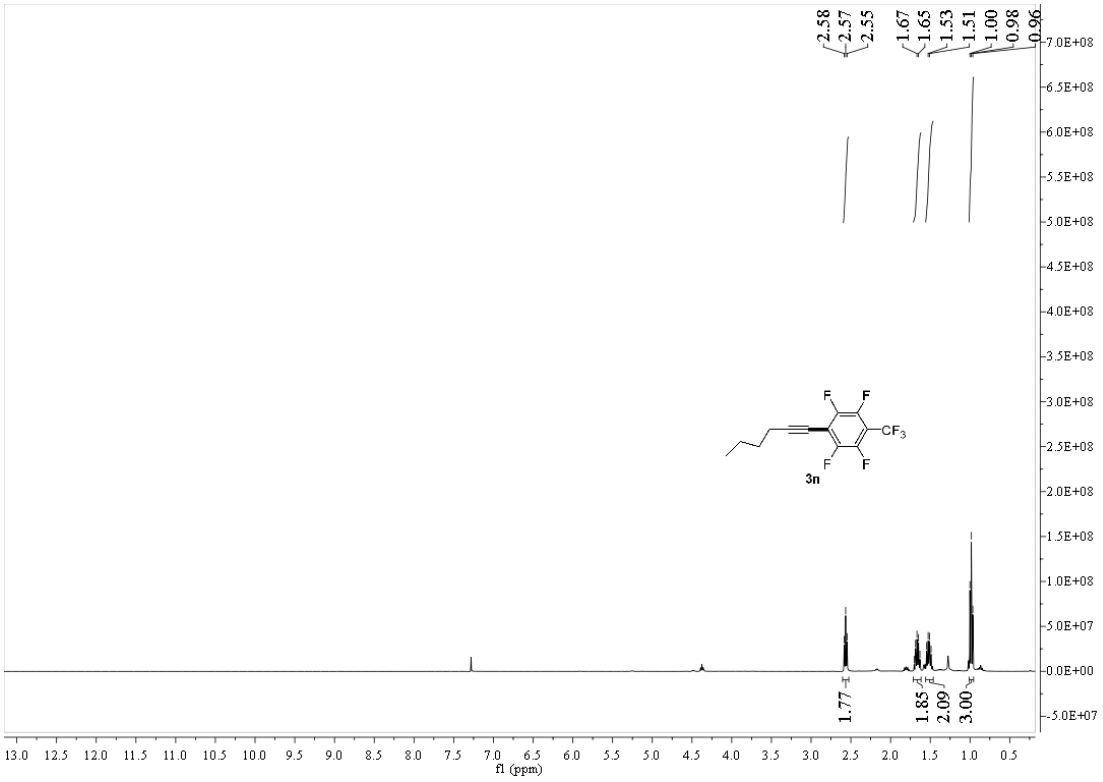
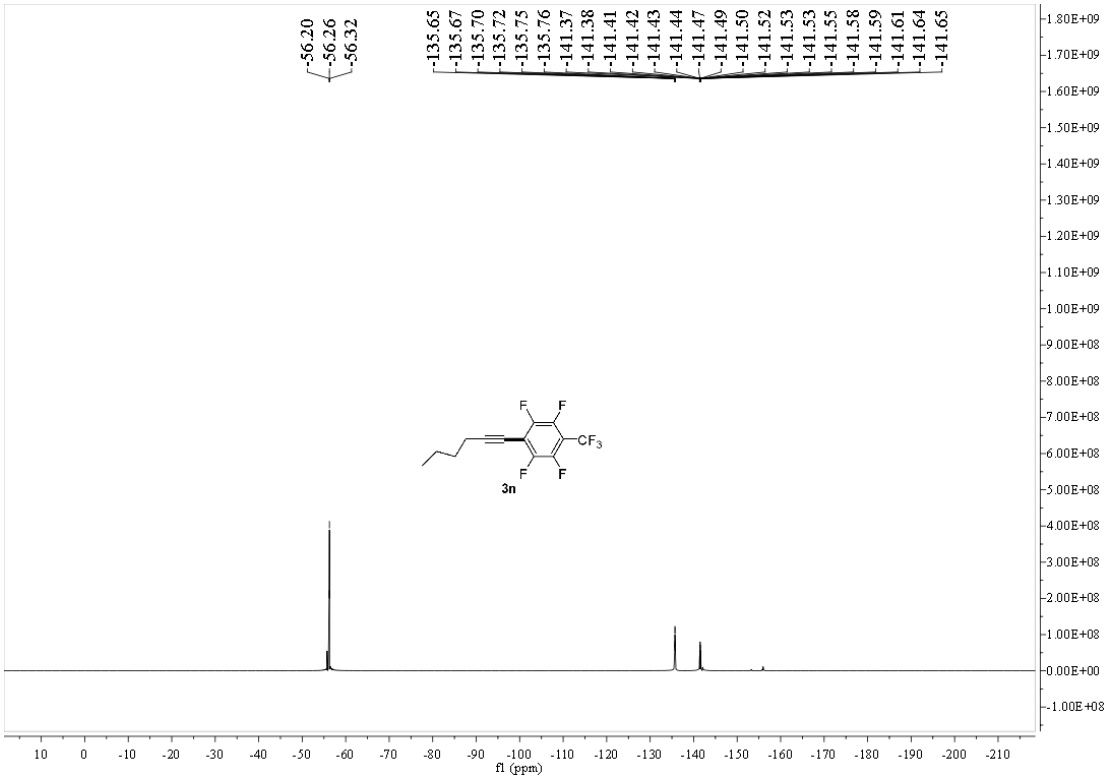
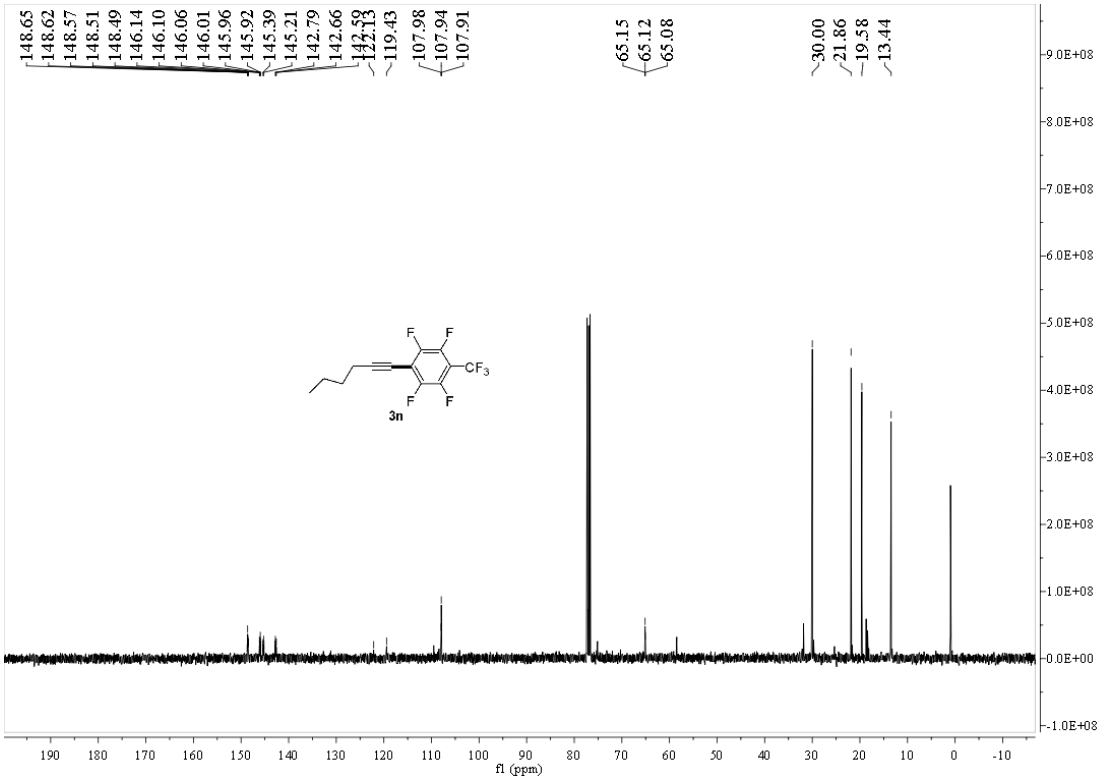


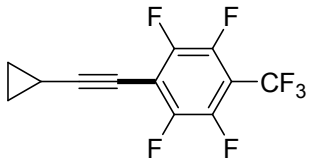




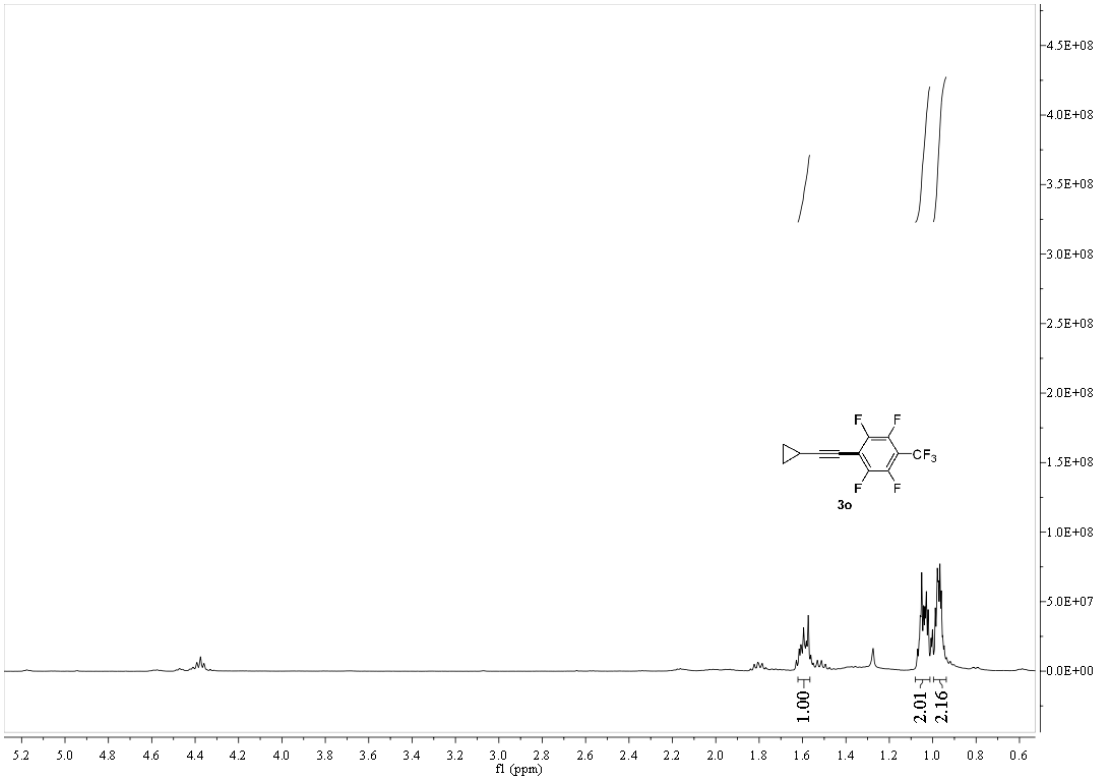
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 2.57 (t, J = 7.0 Hz, 2H), 1.71 – 1.62 (m, 2H), 1.52 (dd, J = 15.0, 7.4 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.3 (t, J = 22.6 Hz, 3F), -135.7 to -135.8 (m, 2F), -141.4 to -141.7 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 13.4, 19.6, 21.9, 30.0, 65.1 (t, J = 3.5 Hz),

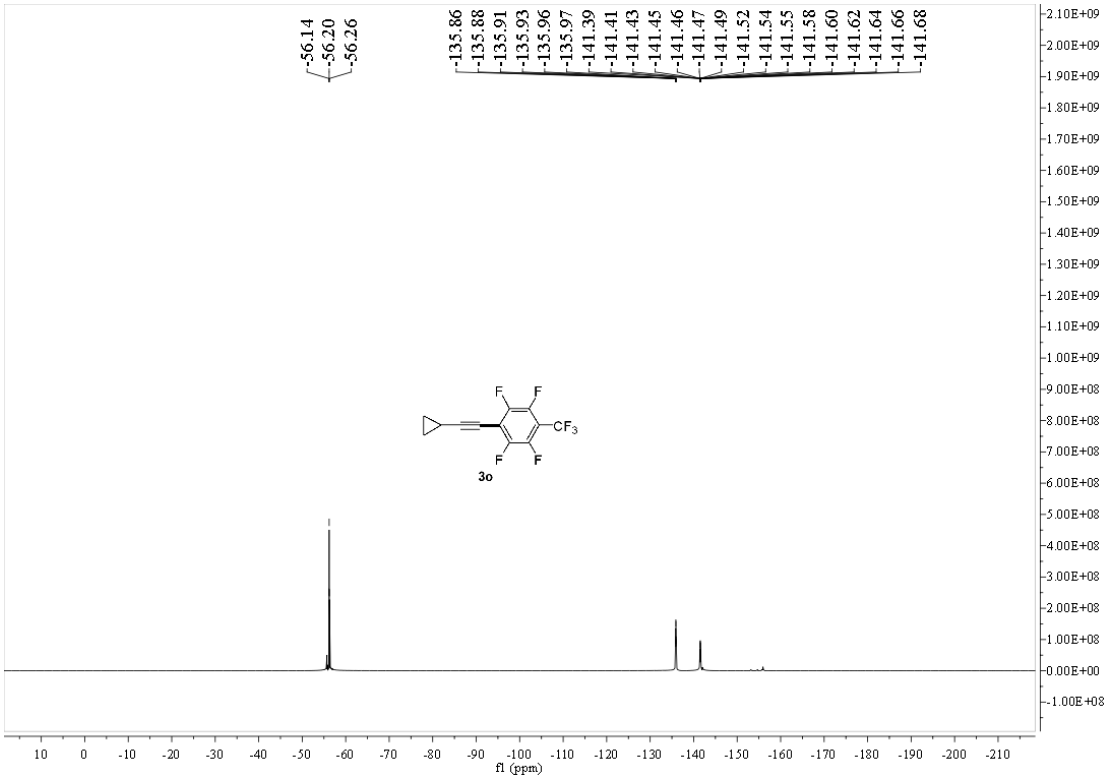
107.9 (t, J = 3.5 Hz), 120.8 (q, $^1J_{CF}$ = 270.0 Hz), 142.6 – 142.9 (m), 145.2 – 145.5 (m), 145.9 – 146.1, 148.0 – 148.2 (m); **IR** (KBr) ν (cm^{-1}): 2961, 2928, 2861, 2241, 1728, 1654, 1611, 1501, 1429, 1378, 1340, 1260, 1228, 1186, 1146, 1096, 999, 872, 799, 712, 400; **HRMS** (EI) found: m/z 298.0580 [M]; calcd. for $C_{13}H_9F_7$ 298.0592.

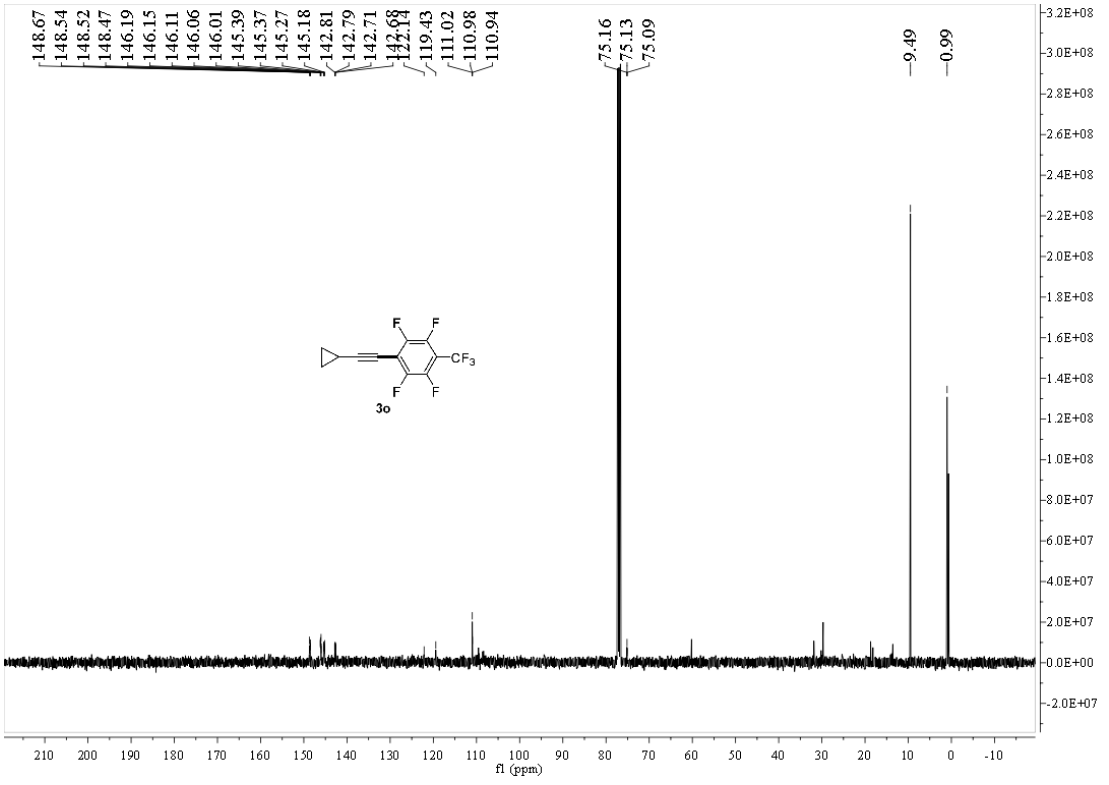
1-(cyclopropylethynyl)-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene



3o



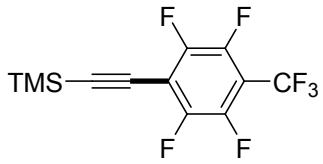




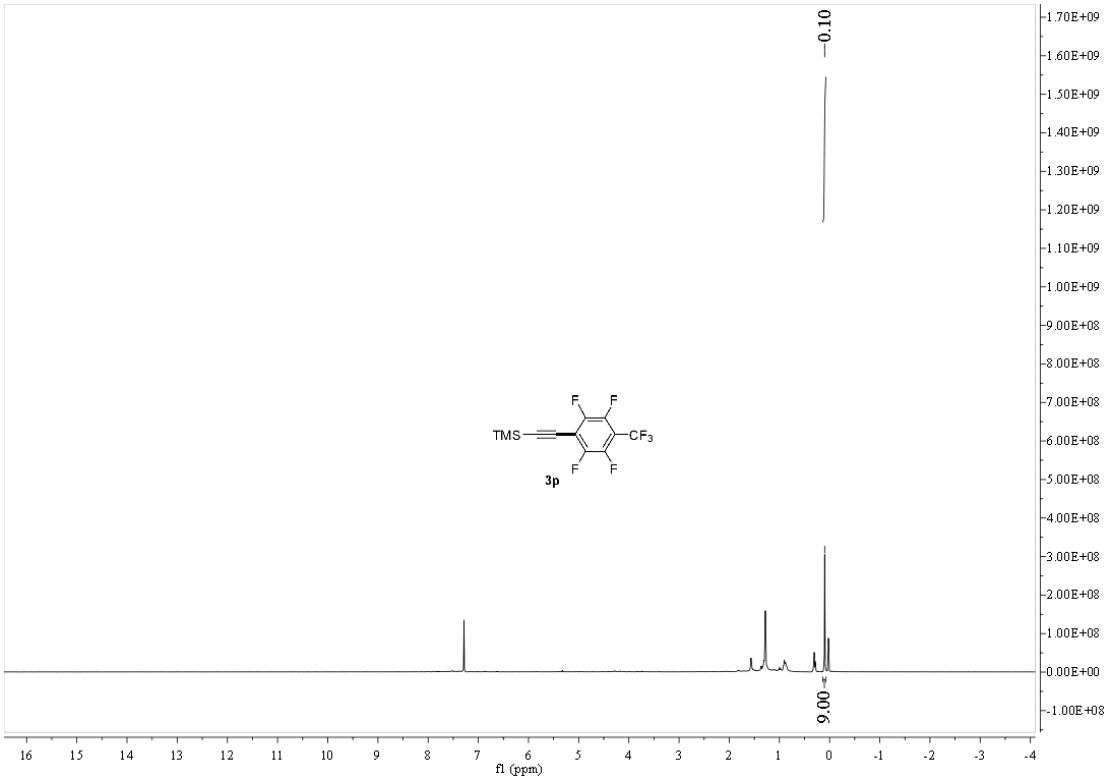
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 1.62 – 1.57 (m, 1H), 1.05 (ddd, J = 8.3, 5.6, 3.3 Hz, 2H), 0.96 (ddd, J = 9.0, 6.0, 3.7 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -135.9 to -136.0 (m, 2F), -141.4 to -141.7 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 1.0, 9.5, 75.1 (t, J = 3.5 Hz), 111.0 (t, J = 4.0 Hz),

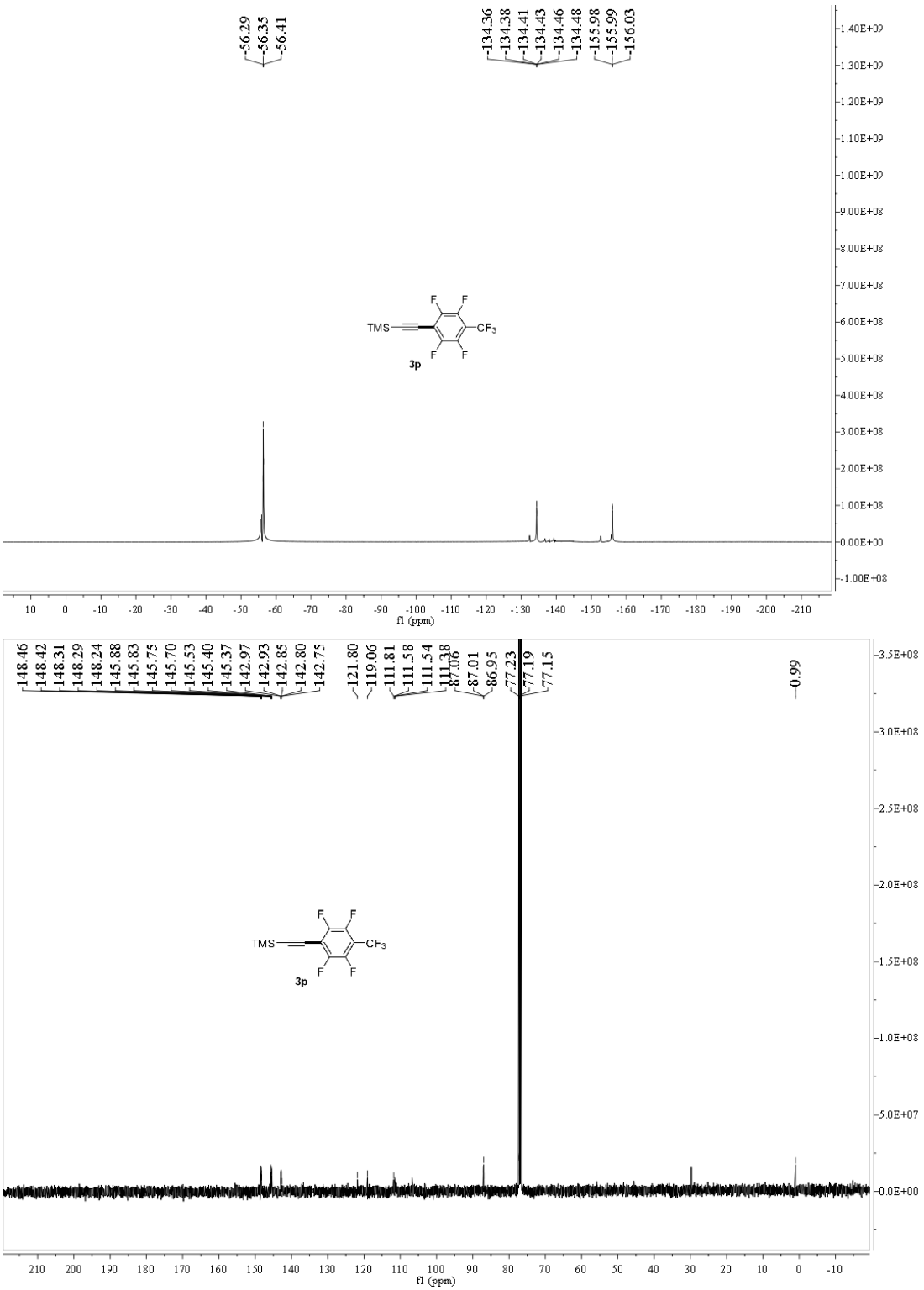
120.8 (q, $^{1}J_{CF}$ = 271.0 Hz), 142.6 – 142.8 (m), 145.2 – 145.4 (m), 146.0 – 146.2, 148.5 – 148.8 (m); **IR** (KBr) ν (cm^{-1}): 3067, 2923, 1642, 1508, 1453, 1318, 1259, 1177, 1131, 952, 929, 848, 787, 741, 608, 431; **HRMS** (EI) found: m/z 282.0270 [M]; calcd. for $C_{12}H_5F_7$ 282.0279.

Trimethyl((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethynyl)silane



3p

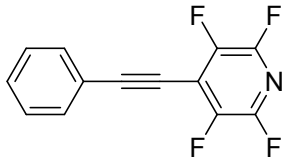




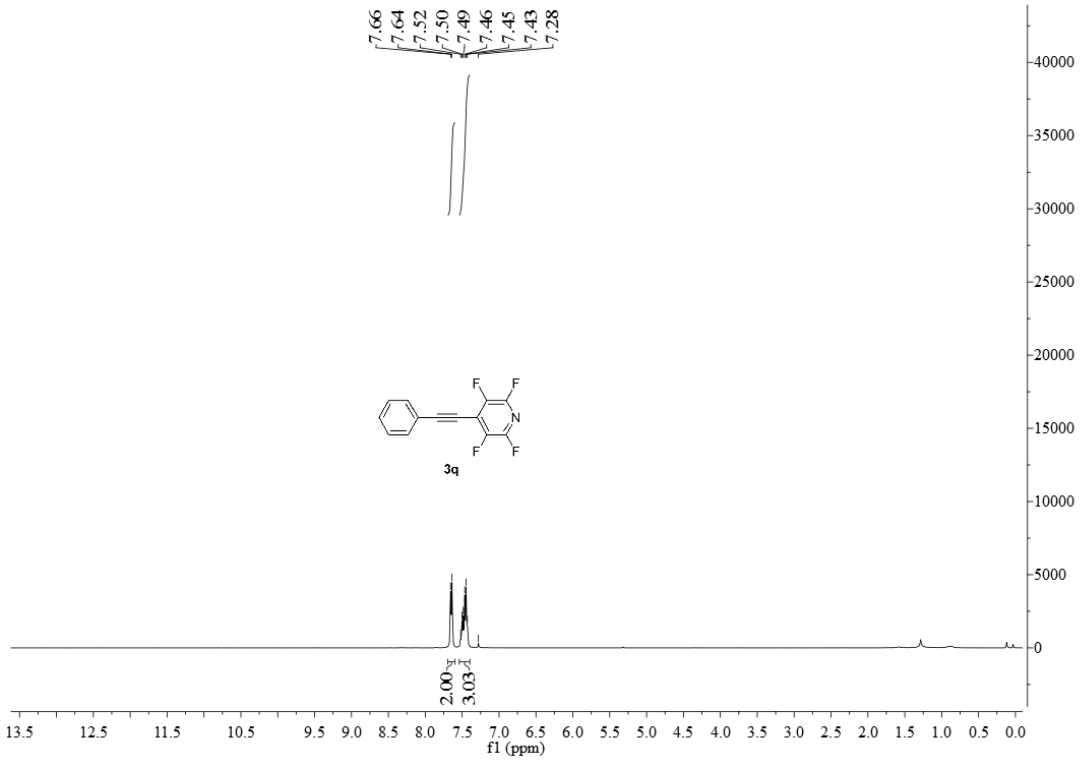
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 0.10 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.4 (t, J = 22.6 Hz, 3F), -134.4 to -134.5 (m, 2F), -155.9 to -156.0 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 29.7, 77.2 (t, J = 4.0 Hz), 87.0 (t, J = 5.5 Hz), 120.4 (q, $^{1}J_{CF}$ = 274.0 Hz), 111.1 – 111.8 (m), 142.7 – 143.0 (m), 145.4 – 145.9, 148.2 – 148.6 (m); **IR** (KBr) v (cm^{-1}): 2961, 2920, 2852, 2218, 1731, 1656, 1604, 1500,

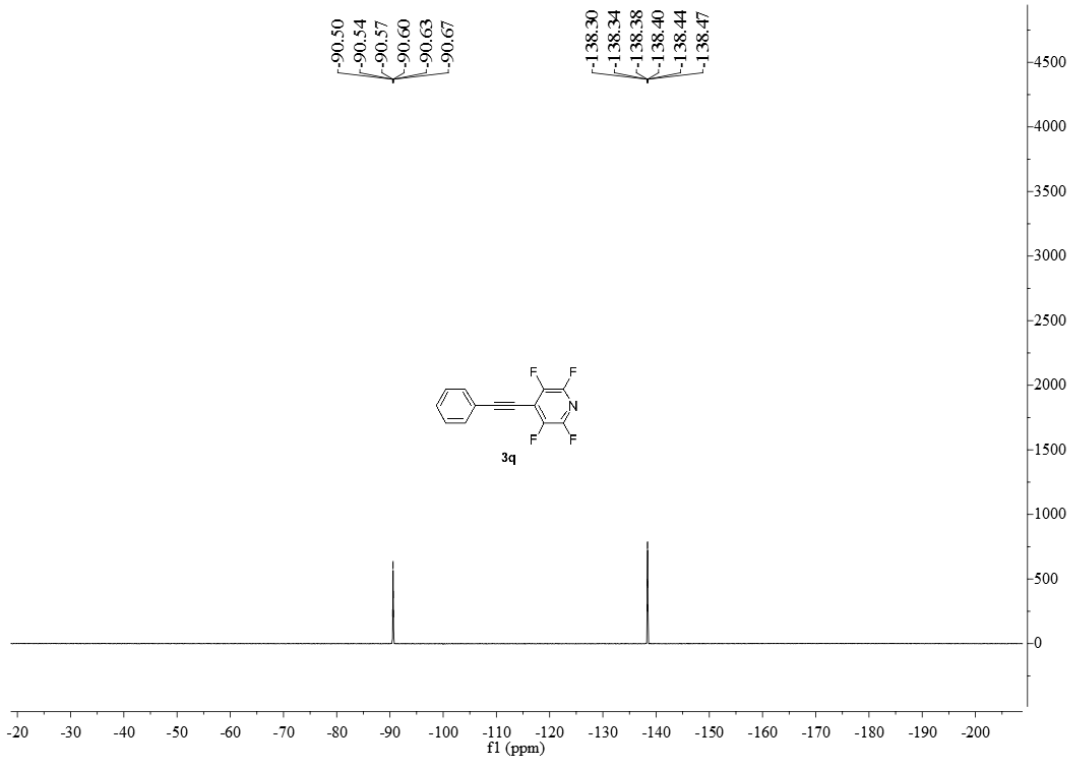
1427, 1340, 1259, 1229, 1187, 1149, 1002, 801, 714, 402; **HRMS** (EI) found: m/z 314.0364 [M]; calcd. for $C_{12}H_9F_7Si$ 314.0362.

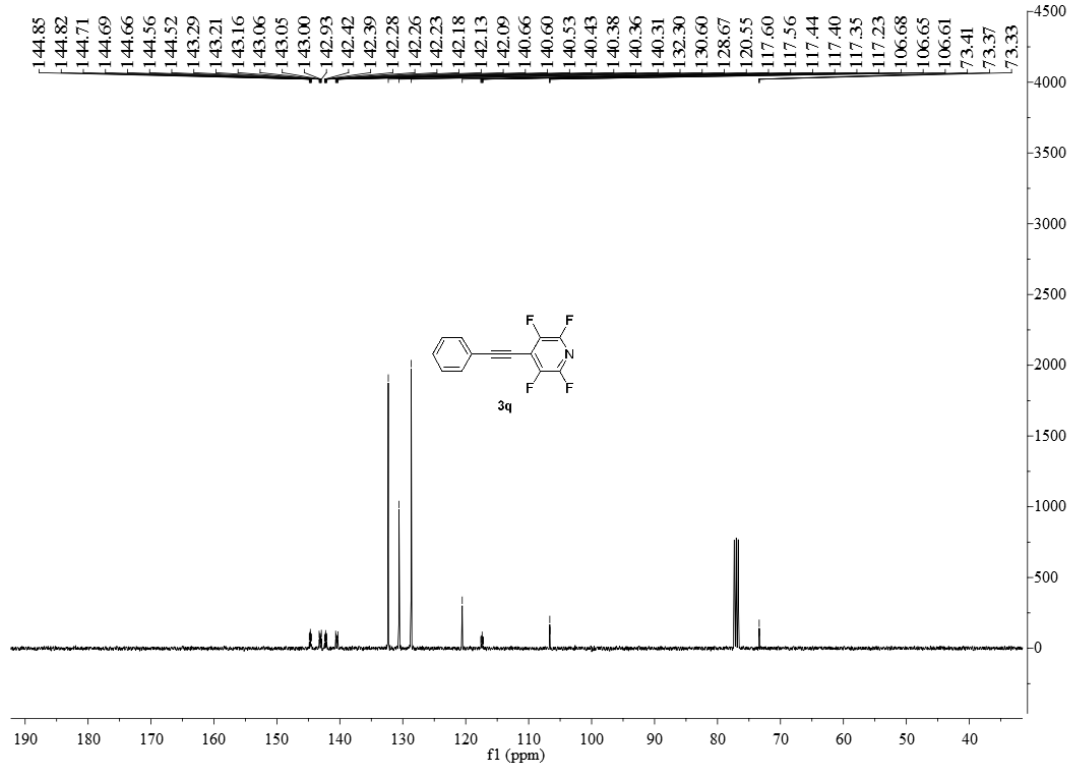
2,3,5,6-tetrafluoro-4-(phenylethynyl)pyridine



3q



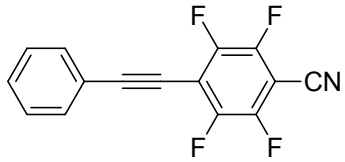




^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.65 (d, J = 7.2 Hz, 2H), 7.47 (dq, J = 14.4, 7.0 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -90.50 to -90.67 (m, 2F), -138.30 to -138.47 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 73.4 (t, J = 4.0 Hz), 106.6 (t, J = 3.5 Hz), 117.2 – 117.6 (m), 120.6, 128.7, 130.6, 132.3, 140.3 – 140.7 (m), 142.1

– 142.4 (m), 142.9 – 143.3 (m), 144.5 – 144.8 (m); **IR** (KBr) ν (cm^{-1}): 2216, 1637, 1579, 1491, 1414, 1308, 1279, 1210, 994, 964, 759, 728, 613, 580, 529.

2,3,5,6-tetrafluoro-4-(phenylethynyl)benzonitrile



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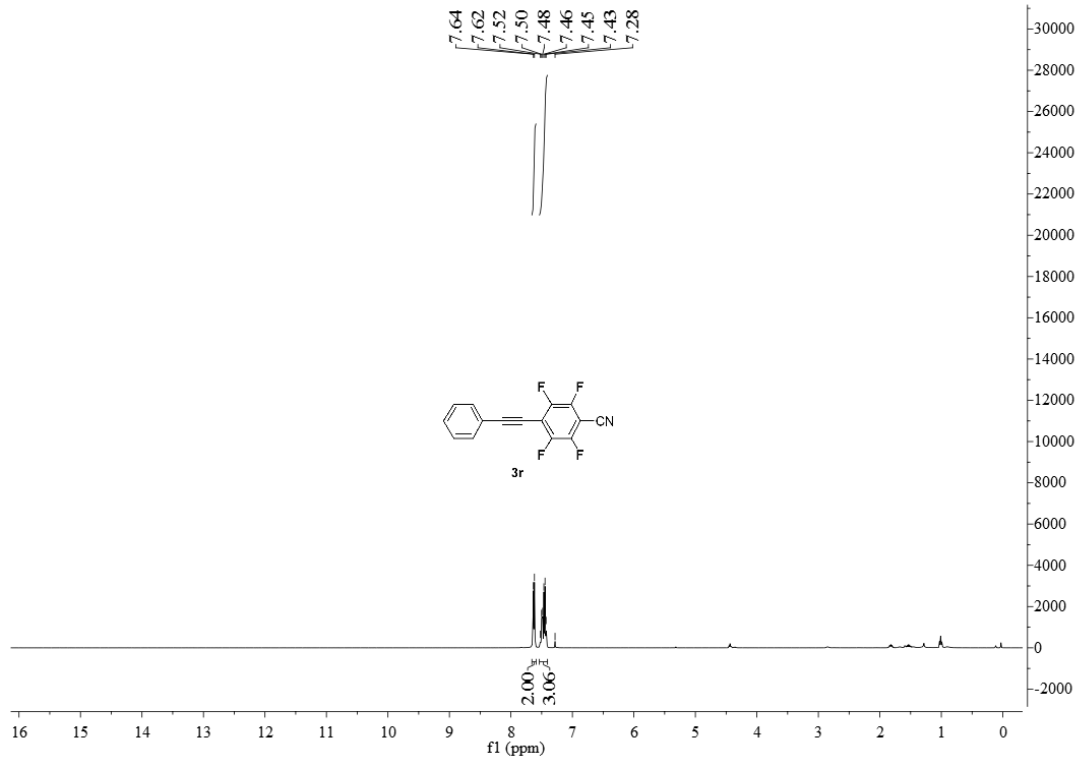
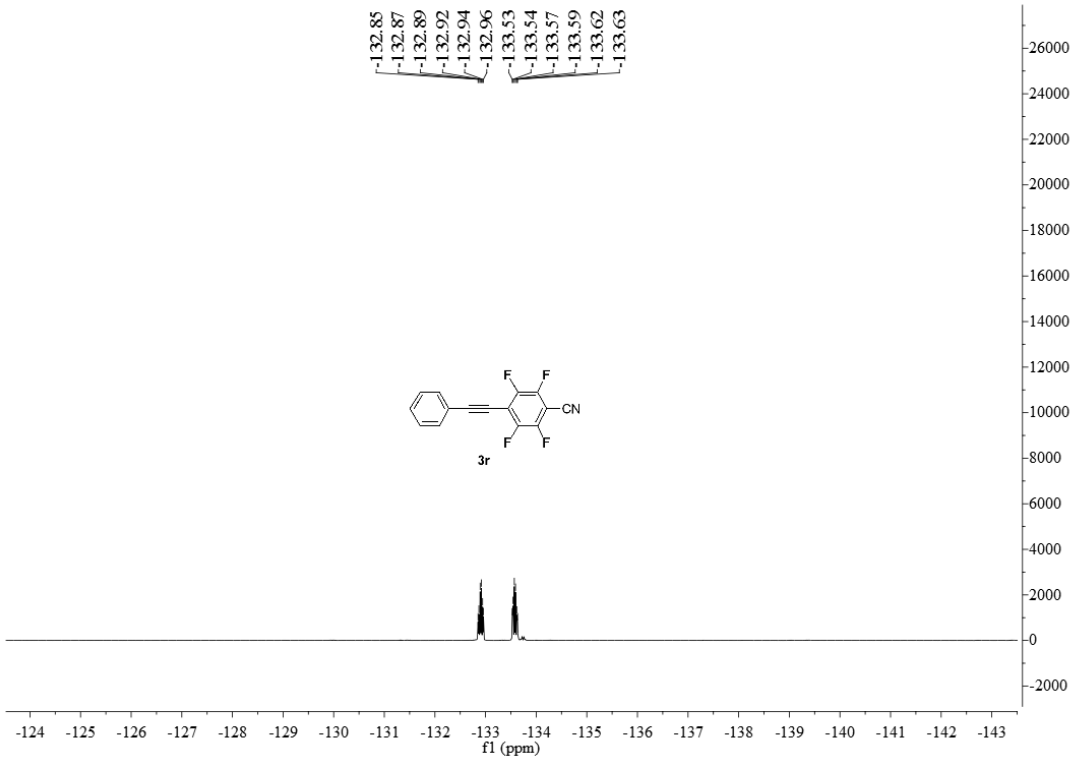
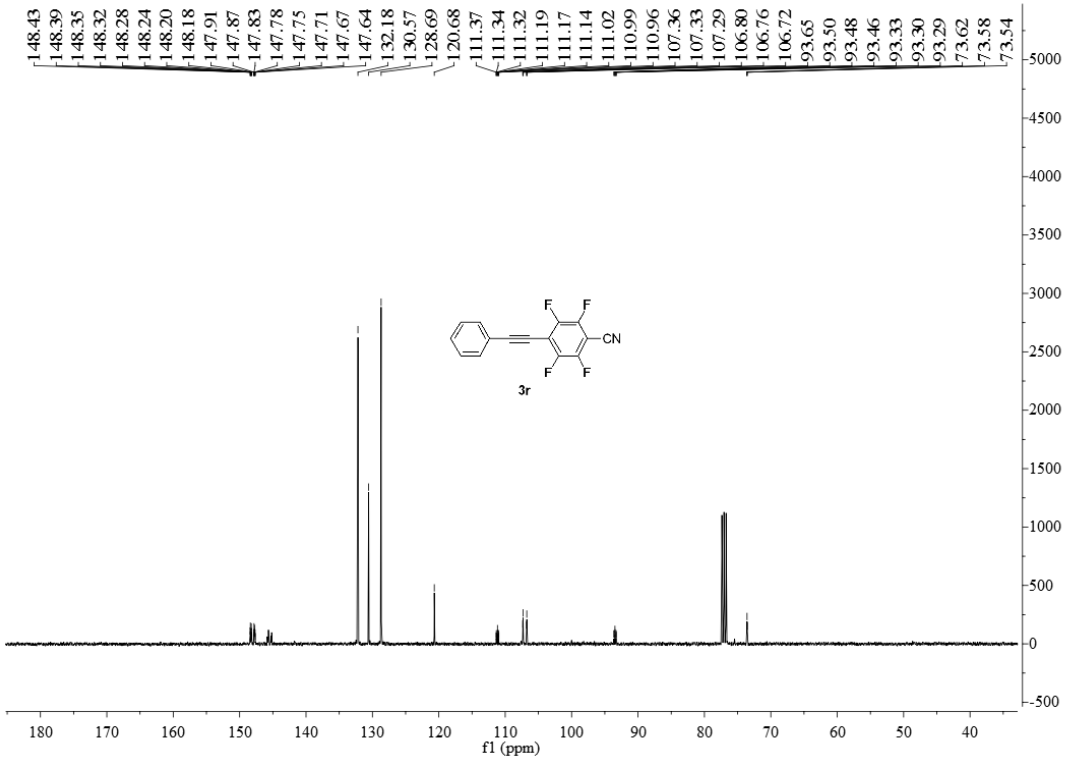


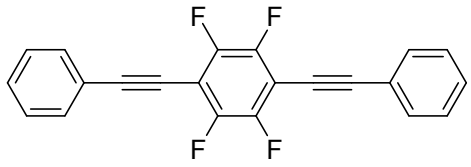




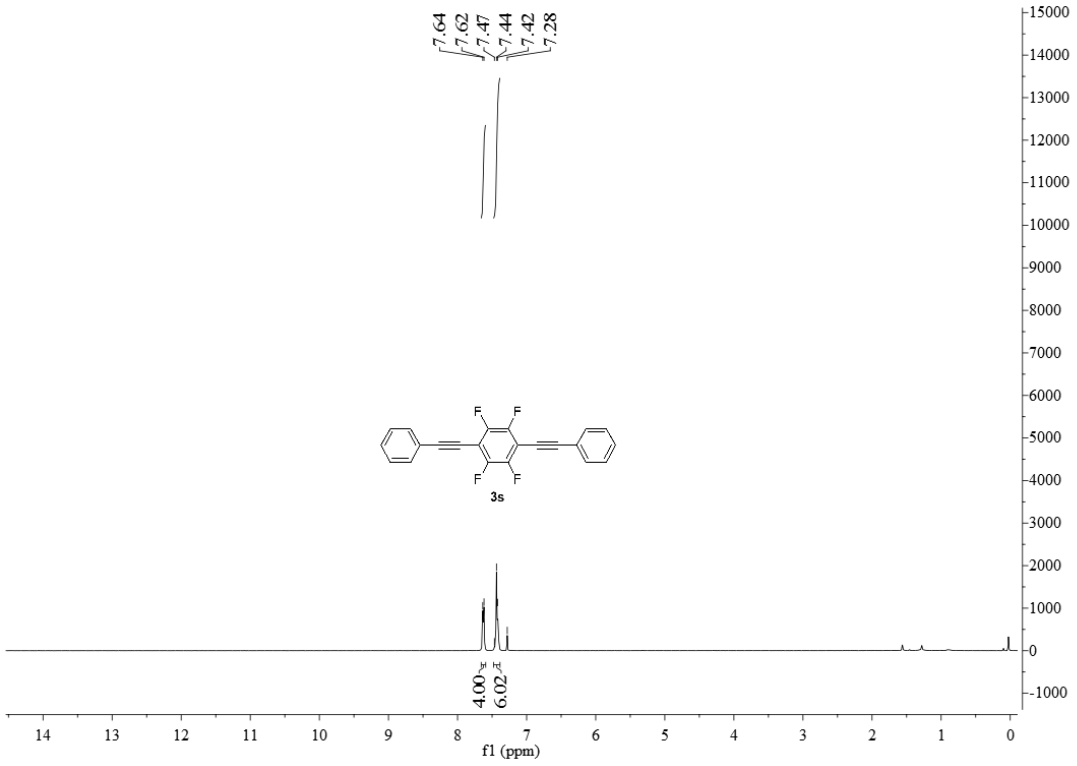
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.1 Hz, 2H), 7.57 – 7.38 (m, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -132.85 to -132.96 (m, 2F), -133.53 to -133.63 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 73.6 (t, J = 4.0 Hz), 93.3 – 93.6 (m), 106.8 (t, J = 4.0 Hz), 107.3 (t, J = 3.5 Hz), 111.0 – 111.4 (m), 120.7, 128.7, 130.6, 132.2,

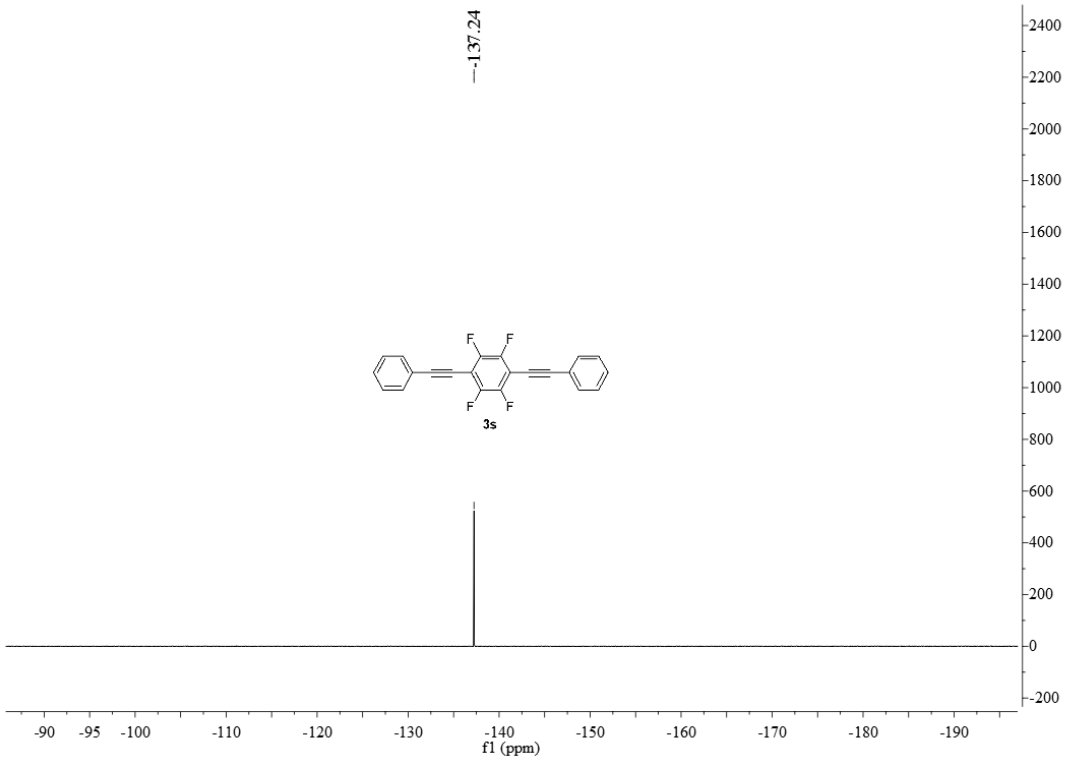
145.1 – 145.3 (m), 145.6 – 145.8 (m), 147.6 – 147.9 (m), 148.2 – 148.4 (m); **IR** (KBr) v (cm^{-1}): 2218, 1638, 1484, 1383, 1326, 1270, 1066, 981, 926, 759, 690, 657, 530.

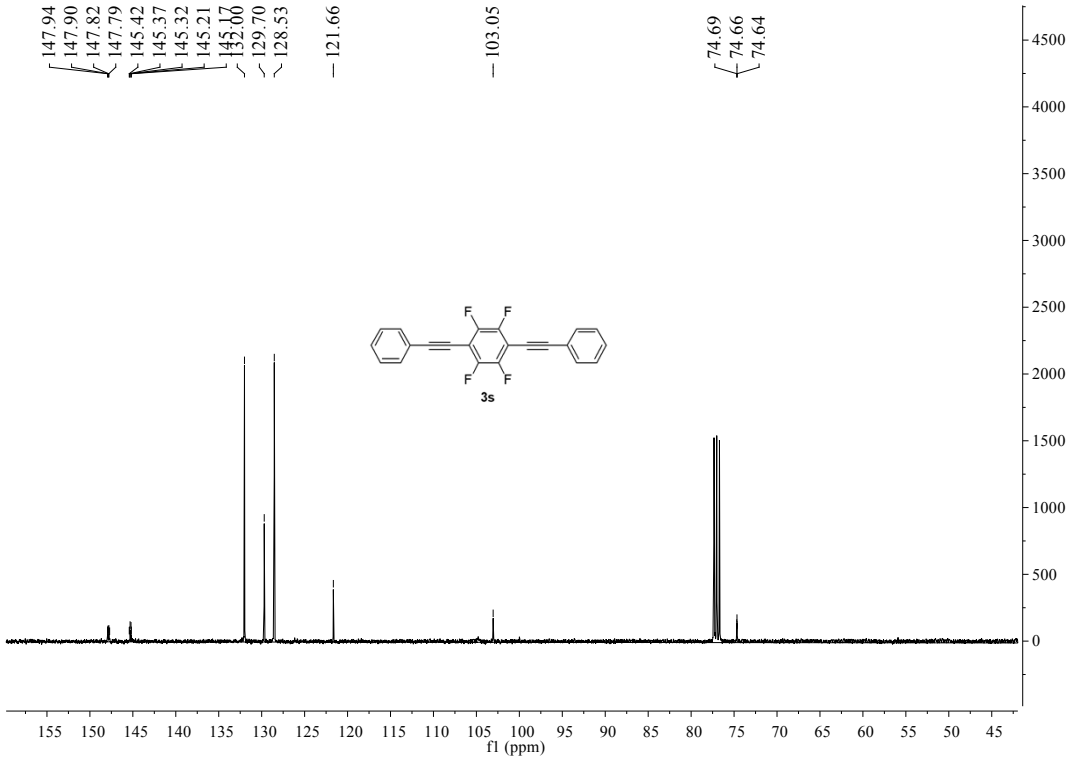
((perfluoro-1,4-phenylene)bis(ethyne-2,1-diyl))dibenzene



3s



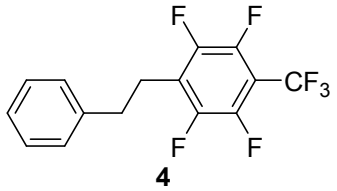




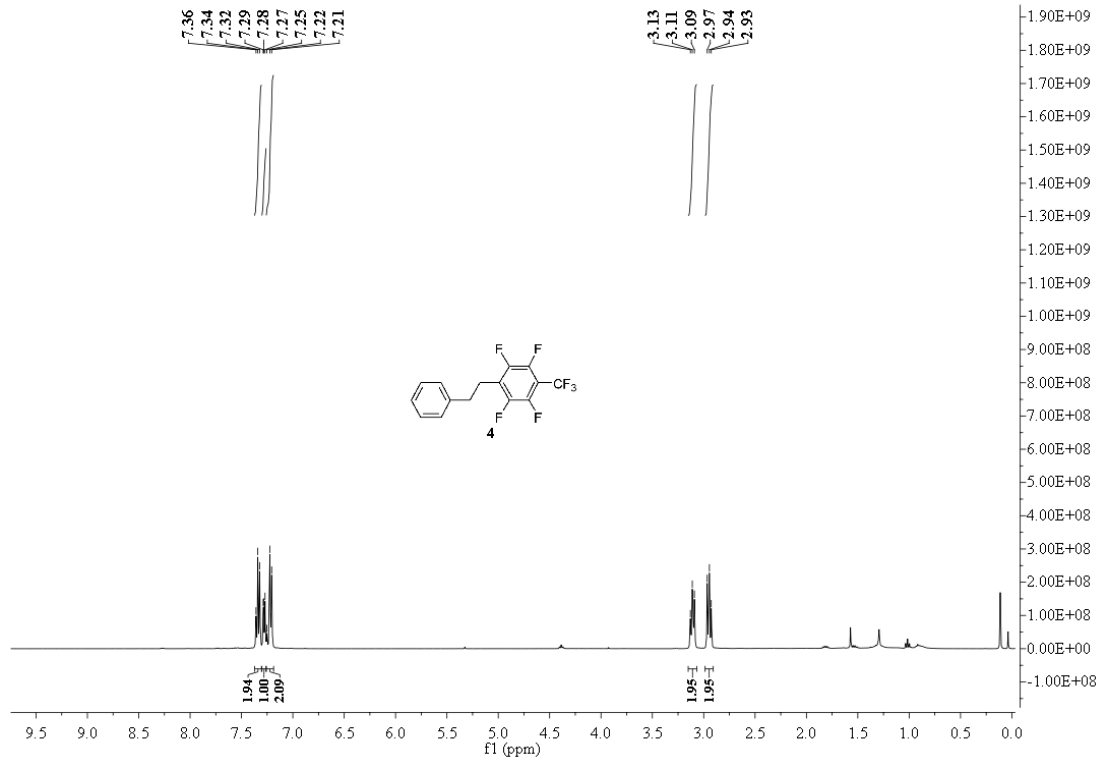
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.3 Hz, 4H), 7.44 (t, J = 9.3 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -137.24 (s, 4F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 74.7 (t, J = 2.5 Hz), 103.0, 121.7, 128.5, 129.7, 132.0, 145.2 – 145.4 (m), 147.7 – 147.9 (m); **IR** (KBr) v (cm^{-1}): 1519, 1484, 1446, 1400, 1333, 1068, 974, 754, 686,

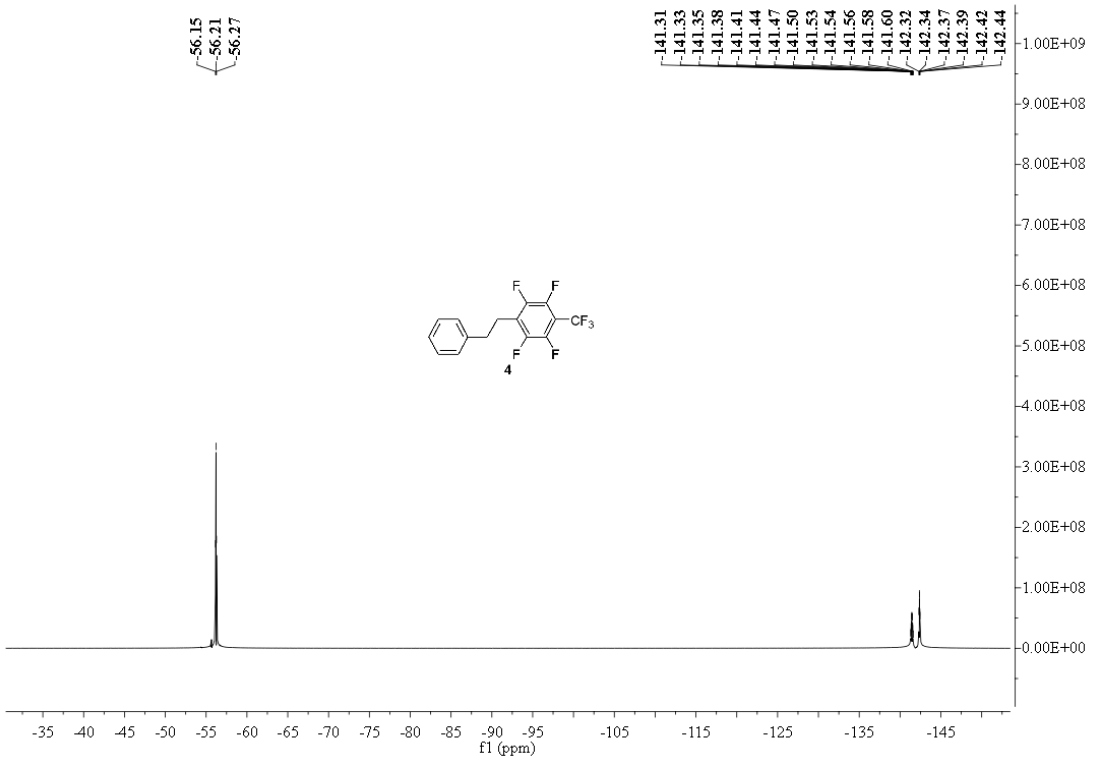
585, 526; **HRMS** (EI) found: m/z 350.0721 [M]; calcd. for $C_{22}H_{10}F_4$ 350.0719.

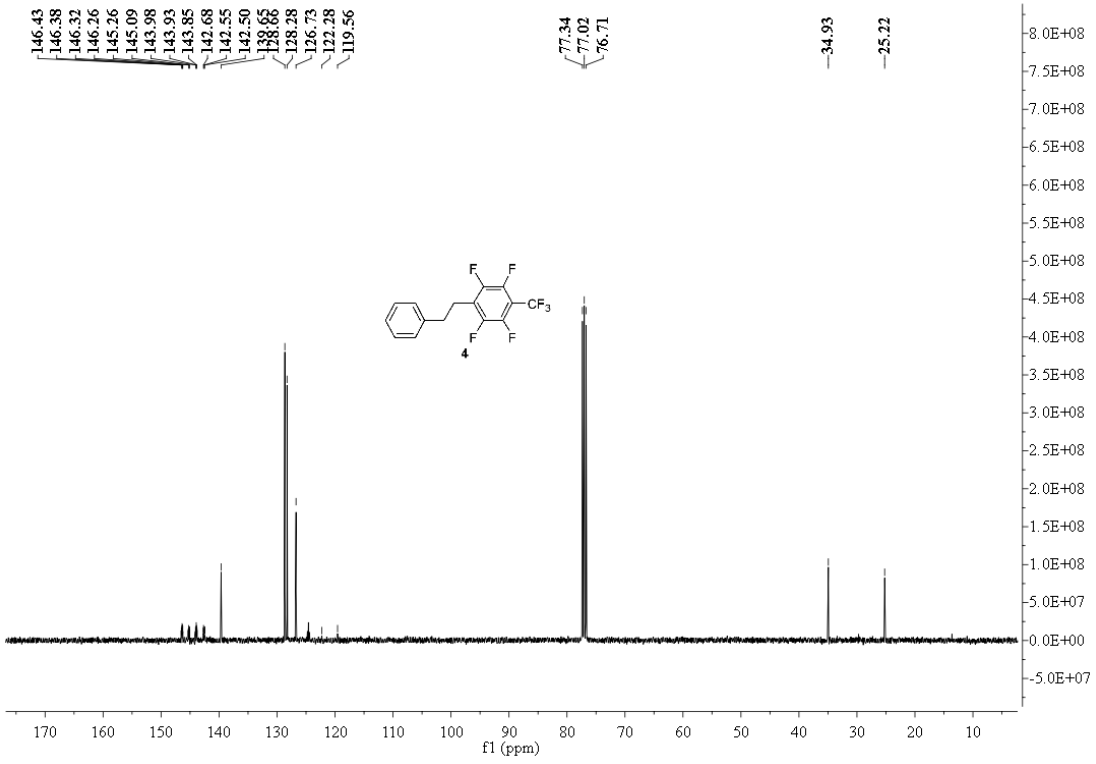
1,2,4,5-tetrafluoro-3-phenethyl-6-(trifluoromethyl)benzene



4



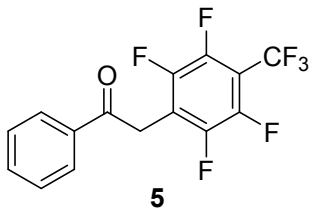




^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.34 (t, J = 7.3 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.23 (t, J = 9.3 Hz, 2H), 3.15 – 3.07 (m, 2H), 2.99 – 2.91 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -141.3 to -141.6 (m, 2F), -142.3 to -142.4 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 25.2, 34.9, 120.9 (q, $^{1}J_{CF}$ = 272.0

Hz), 126.7, 128.3, 128.7, 139.6, 142.5 – 142.7 (m), 143.8 – 144.1 (m), 145.0 – 145.3 (m), 146.2 – 146.6 (m); **IR** (KBr) ν (cm^{-1}): 2928, 2861, 1721, 1663, 1603, 1492, 1328, 1264, 1215, 1180, 1141, 940, 868, 800, 750, 704, 629, 548, 493; **HRMS** (EI) found: m/z 322.0601 [M]; calcd. for $C_{15}H_9F_7$ 322.0592.

1-phenyl-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethanone



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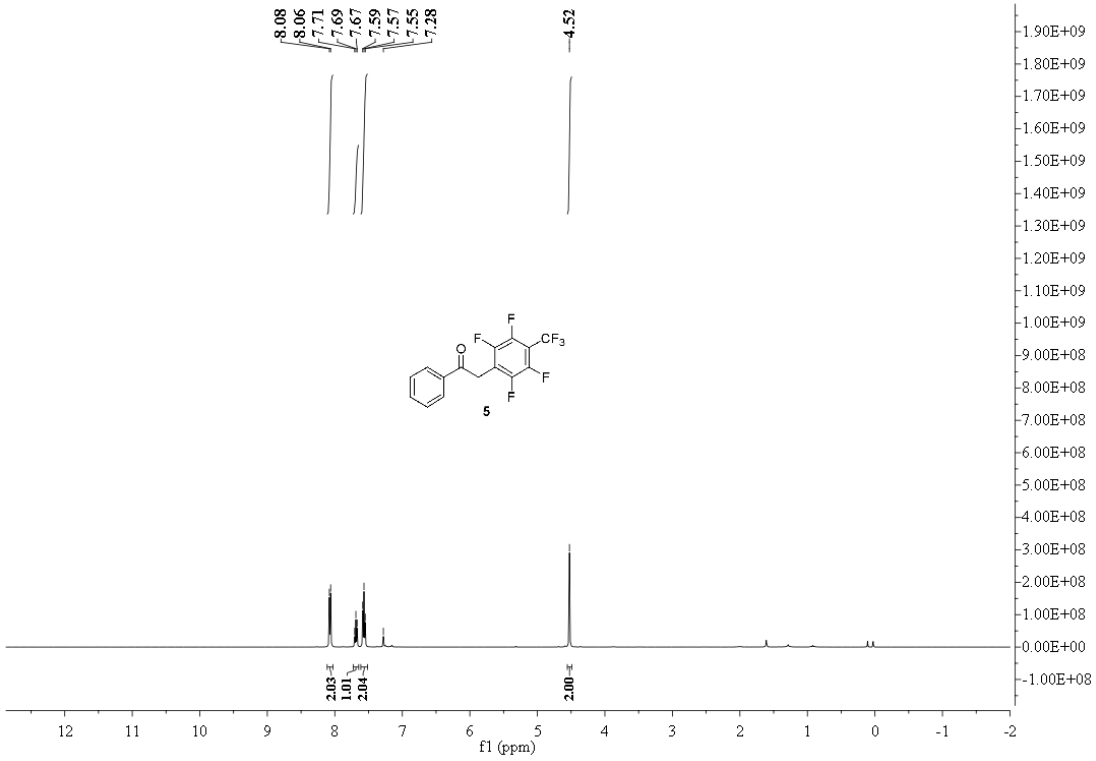
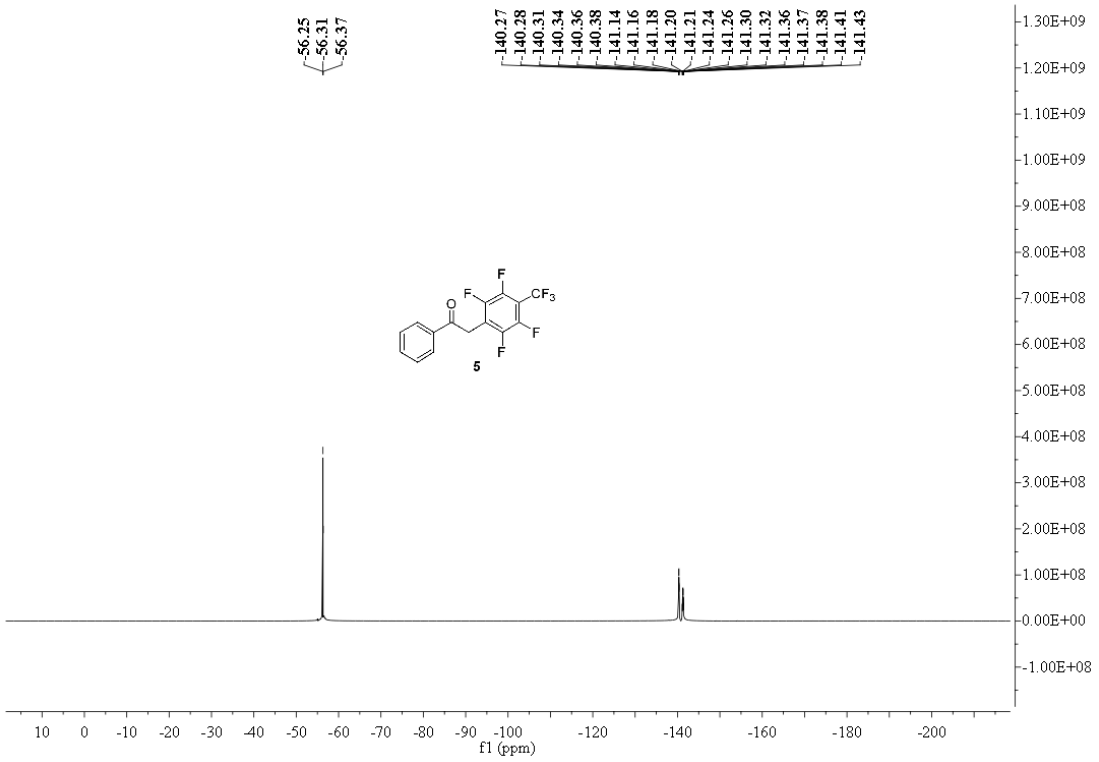
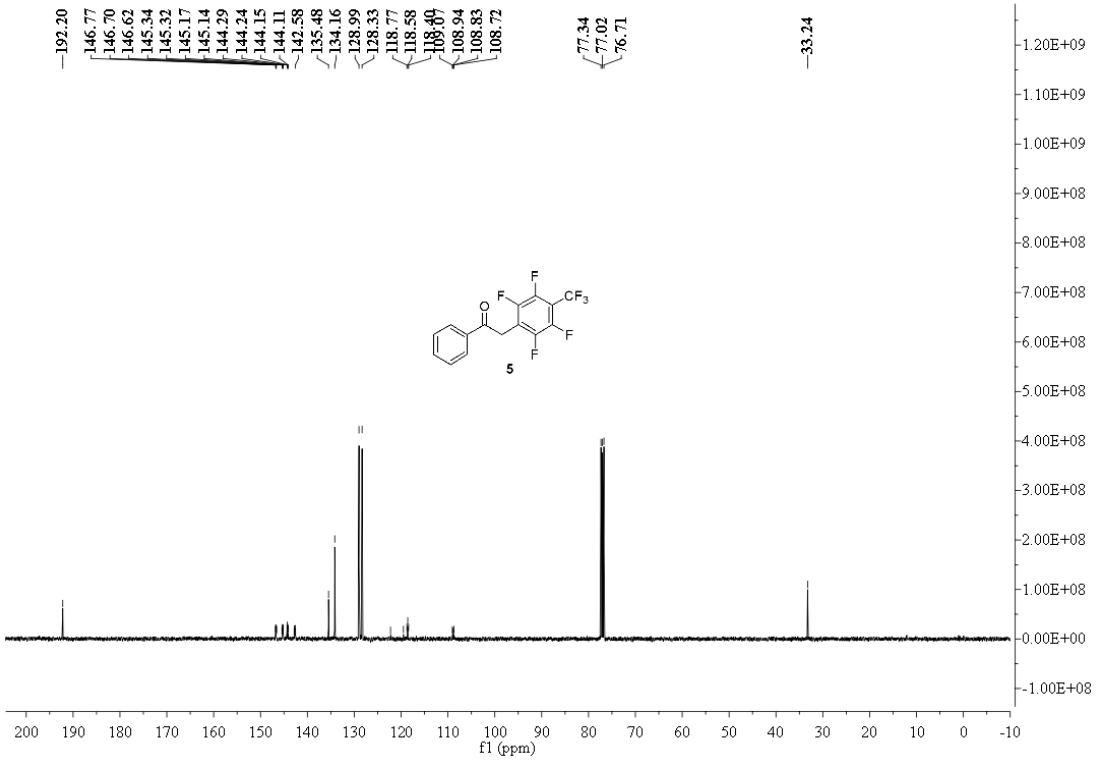


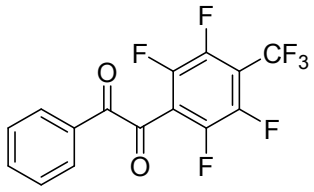


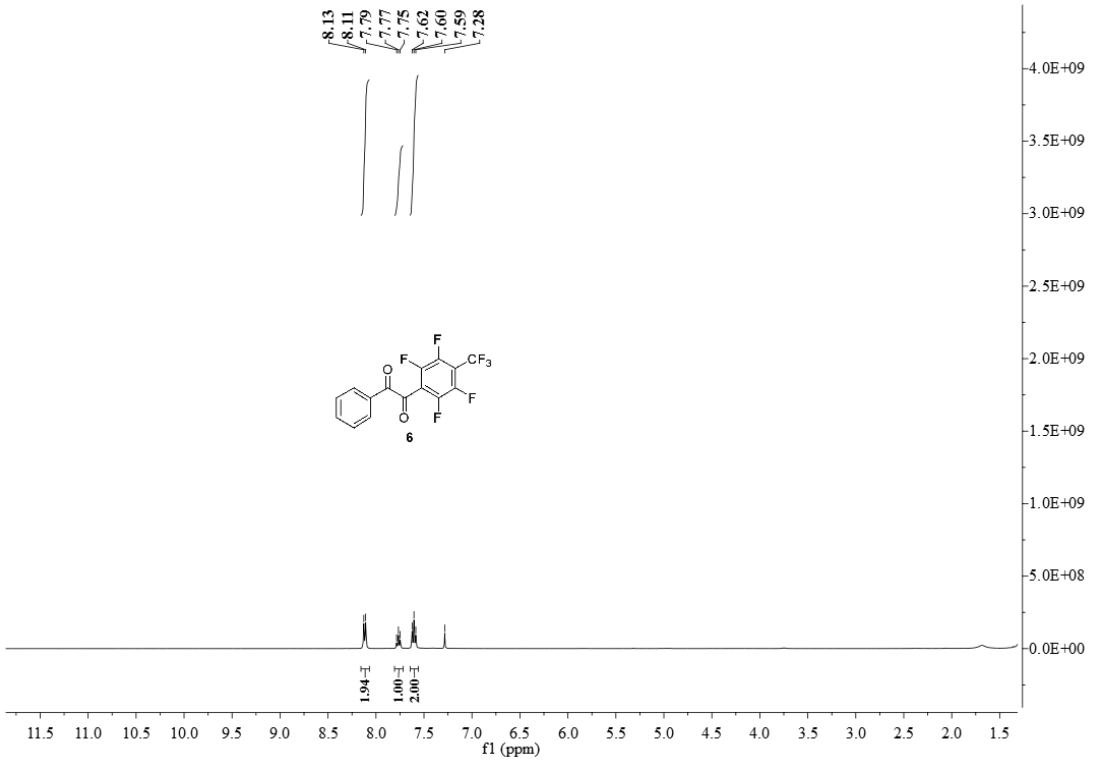


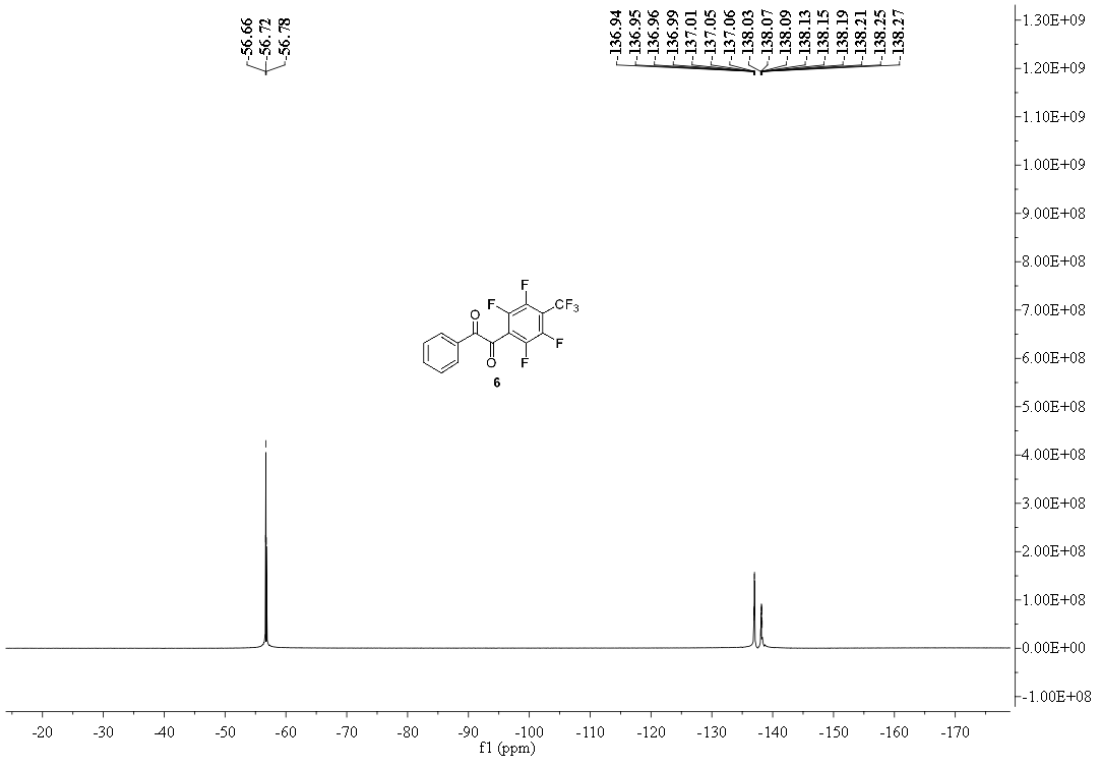
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.07 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 4.52 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.3 (t, J = 22.6 Hz, 3F), -140.3 to -140.4 (m, 2F), -141.1 to -141.4 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 33.2, 108.7 – 109.1 (m), 118.4 – 118.8 (m), 120.9 (q, $^{1}J_{CF}$ =

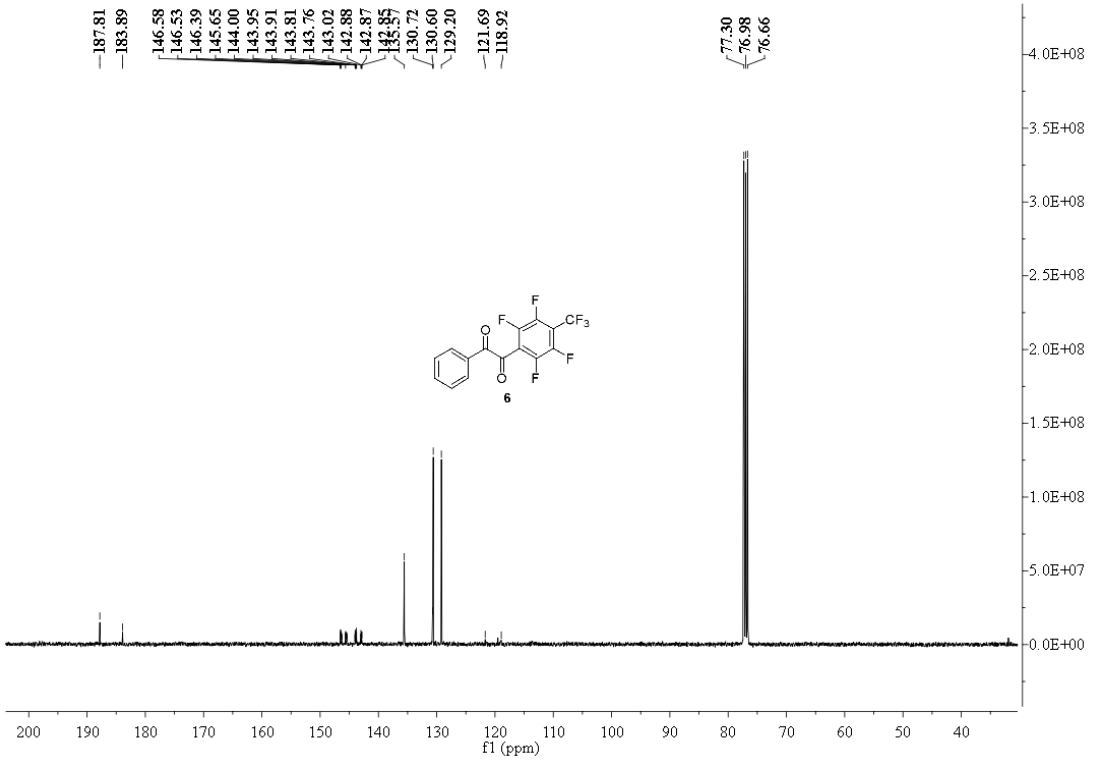
275.0 Hz), 128.3, 129.0, 134.2, 135.5, 142.5 – 142.8 (m), 144.1 – 144.4 (m), 145.1 – 145.4 (m), 146.6 – 146.8 (m), 192.2; **IR** (KBr) v (cm^{-1}): 3056, 2987, 2957, 2933, 2306, 1686, 1593, 1493, 1451, 1419, 1332, 1266, 1210, 1146, 989, 936, 902, 740, 605, 564; **HRMS** (ESI) found: m/z 335.0310 $[M-H]^-$; calcd. for $C_{15}H_7F_7O$-H 335.0307.

1-phenyl-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethane-1,2-dione





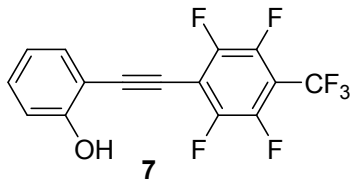




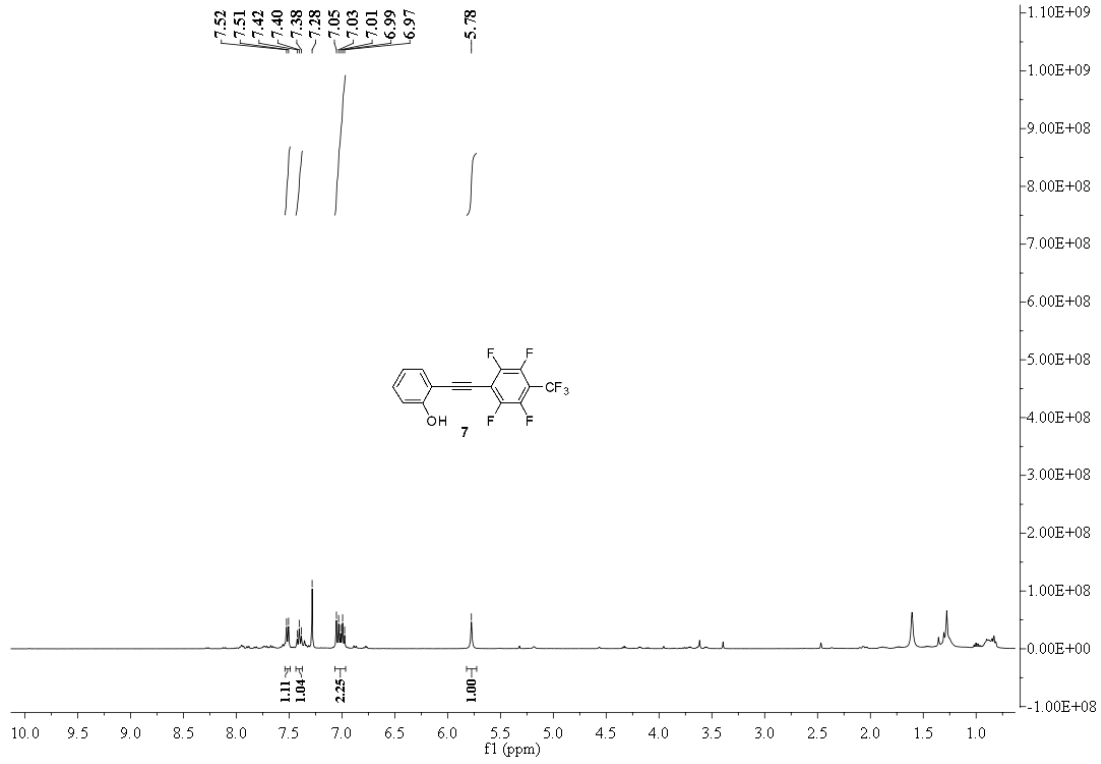
^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 8.12 (d, J = 7.7 Hz, 9H), 7.77 (t, J = 7.4 Hz, 5H), 7.60 (t, J = 7.7 Hz, 10H), 7.28 (s, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.7 (t, J = 22.6 Hz, 3F), -136.9 to -137.1 (m, 2F), -138.0 to -138.3 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 120.3 (q, $^{1}J_{CF}$ = 277.0 Hz), 129.2, 130.6, 130.7, 135.6, 142.9 –

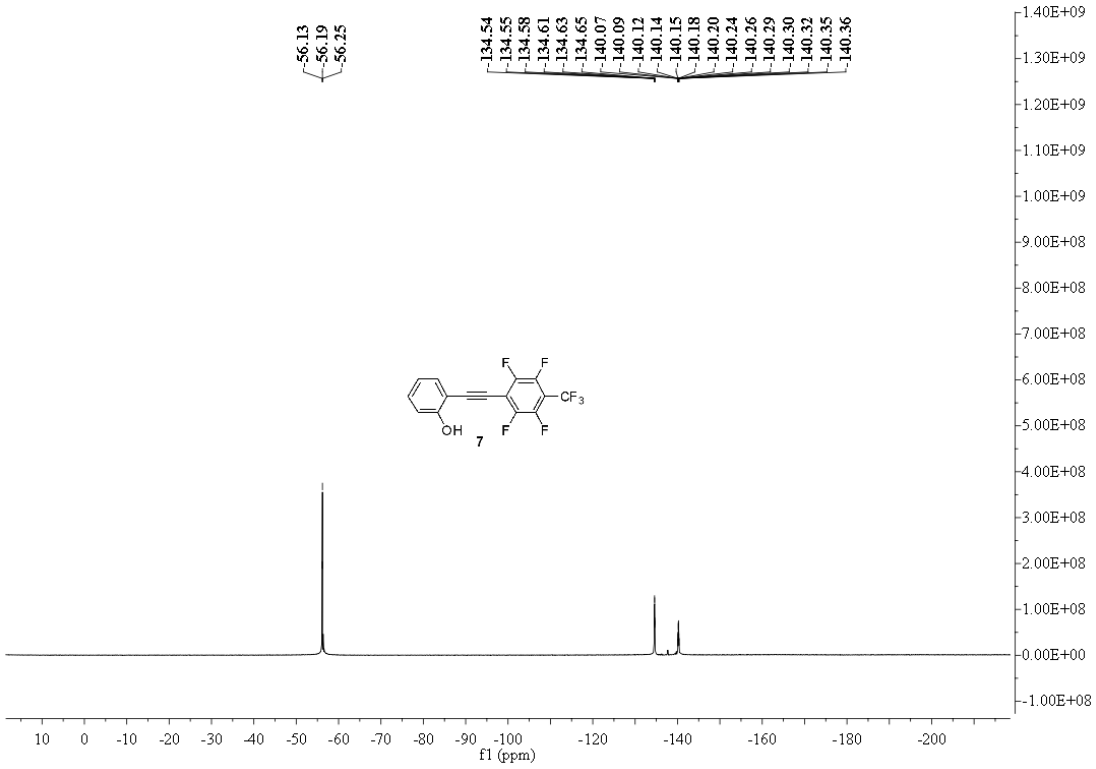
143.0 (m), 143.8 – 144.1 (m), 145.4 – 145.7 (m), 146.2 – 146.6 (m), 183.9, 187.8; **IR** (KBr) v (cm^{-1}): 2924, 2854, 17346, 1675, 1593, 1486, 1337, 1282, 1182, 1153, 1107, 994, 870, 807, 747, 710, 681, 647, 464; **HRMS** (ESI) found: m/z 351.0253 $[M+H]^+$; calcd. for $C_{15}H_5F_7O_2$+H 351.0256.

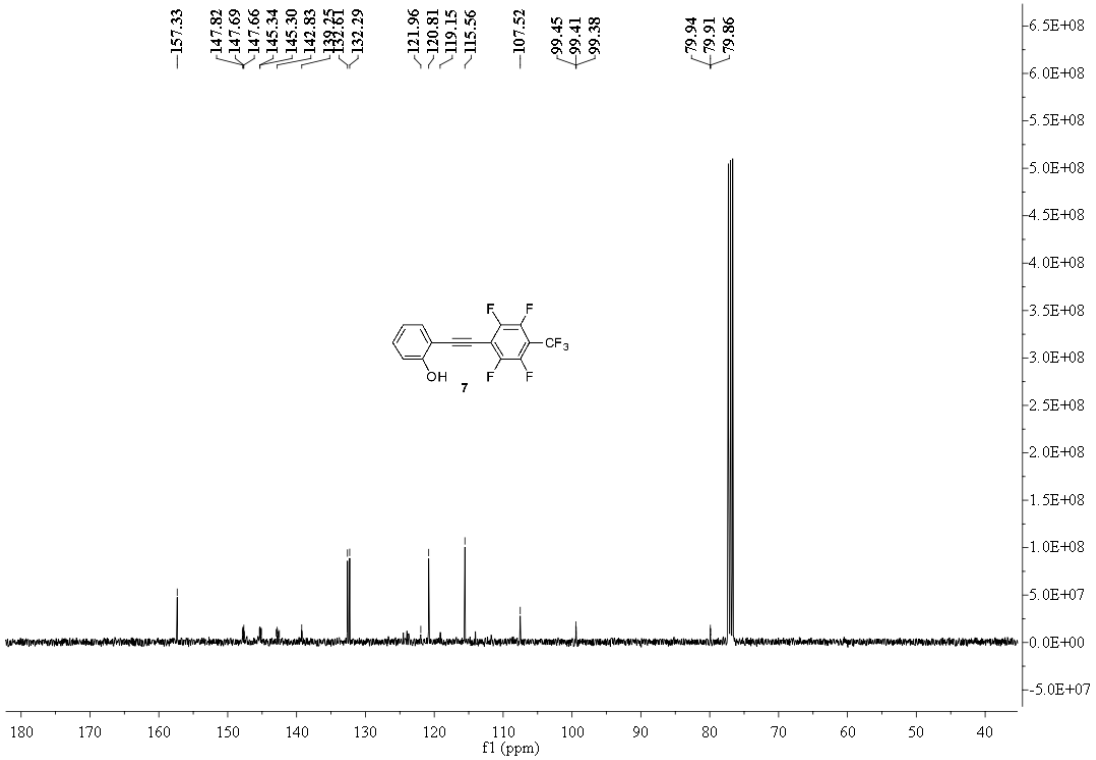
2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethynyl)phenol



7







^{1}H NMR (400 MHz, $CDCl_3$) [ppm] δ 7.51 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.07 – 6.97 (m, 2H), 5.78 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) [ppm] δ -56.2 (t, J = 22.6 Hz, 3F), -134.5 to -134.6 (m, 2F), -140.1 to -140.4 (m, 2F); **^{13}C NMR** (100 MHz, $CDCl_3$) [ppm] δ 79.9 (t, J = 4.0 Hz), 99.4 (t, J = 3.5 Hz), 107.5, 115.6, 120.6 (q, $^{1}J_{CF}$

= 281.0 Hz), 120.8, 132.3, 132.6, 139.2 – 139.3 (m), 142.5 – 143.0 (m), 145.1 – 145.4 (m), 147.6 – 147.9 (m), 157.3; **IR** (KBr) v (cm^{-1}): 3690, 1571, 1485, 1340, 1264, 1178, 1138, 1023, 982, 876, 800, 758, 712, 450; **HRMS** (EI) found: m/z 334.0215 [M]; calcd. for $C_{15}H_5F_7O$ 334.0229.

Computational Details:

Molecular geometries of the model complexes were optimized without constraints via DFT calculations using the Becke3LYP(B3LYP) functional,[1] as implemented in the Gaussian 09 suite of programs.[2] The 6-31G* basis set[3] was used for all atoms. Frequency calculations at the same level of theory have also been performed to identify all of the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Transition states were located using the Berny algorithm. Intrinsic reaction coordinates (IRC)[4] were calculated for the transition states to confirm that such structures indeed connect two relevant minima.

References:

1 (a) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623; (c) X. Y. Ren, C. F. Xiao and H. M. Wang, *Dalton Trans.*, 2011, **40**, 3576; (d) H. M. Wang, Y. Wang, K.-L. Han and X.-J. Peng, *J. Org. Chem.*, 2005, **70**, 4910.

2 M. J. Frisch, *et al.*, Gaussian, Inc., *Gaussian 09*, revision A.02, Gaussian, Inc., Wallingford, CT 2009.

3 P. C. Hariharan and J. A. Pople, *Theoret. chim. Acta (Berl.)*, 1973, **28**, 213.

4 (a) K. Ishida, K. Morokuma and A. Komornicki, *J. Chem. Phys.*, 1977, **66**, 2153; (b) K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363.

Cartesian coordinates for all of the species calculated in this study

octafluorotoluene

E = -1065.406823

C	0.00450100	-1.16379100	-0.00008400
C	-0.67412000	0.06082500	-0.00006200
C	0.09241500	1.22981100	-0.00006800
C	1.48670800	1.17597800	-0.00001200
C	2.13642700	-0.05405400	0.00001100
C	1.39250000	-1.23287300	-0.00006900
C	-2.18720400	0.03832900	0.00000000
F	2.01263500	-2.41493300	-0.00004200
F	-0.68506600	-2.30845800	-0.00003000
F	3.46722200	-0.10712900	0.00008900
F	2.19817800	2.30601400	0.00005900
F	-0.46685000	2.44173000	-0.00011600
F	-2.72199000	1.26820500	0.00010500
F	-2.65257700	-0.61073100	-1.08661300
F	-2.65237000	-0.61084700	1.08673800

I

E = -780.297881

C	3.76642200	0.14884200	1.22346000
C	3.18575300	-0.03031300	-0.05115400
C	4.05423500	-0.22942500	-1.14663400
C	5.43593500	-0.24786500	-0.97282600
C	5.99306400	-0.06864500	0.29610500
C	5.14879800	0.12959200	1.39180700
H	3.11150200	0.30275300	2.07634200
H	3.62306000	-0.36833500	-2.13387200
H	6.08316300	-0.40287800	-1.83320400
H	7.07179800	-0.08338200	0.42942700
H	5.57092200	0.27001800	2.38445100
C	1.76820400	-0.01095500	-0.22599600
C	0.53995400	0.00563100	-0.37713100
Li	-1.43764800	0.01023600	-0.56525800
O	-2.40507000	1.69099400	-0.58090800
C	-3.37863500	2.09403300	0.41101800
C	-1.52822800	2.80879400	-0.90510200
C	-3.16908900	3.59741900	0.62902200
H	-4.37844500	1.84458600	0.04093400
H	-3.19085900	1.52276700	1.32984100
C	-1.68877500	3.78252400	0.25800500
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H	-1.86374900	3.24636900	-1.85436200
H	-3.40172300	3.90253400	1.65347600
H	-3.80769200	4.17486400	-0.04938800
H	-1.03946400	3.48549400	1.08930400
H	-1.44092000	4.81086100	-0.02073600
O	-2.40370600	-1.66605800	-0.54927500
C	-1.52347800	-2.81983300	-0.66637900
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C	-1.91273300	-3.71848800	0.50205100
H	-1.71155000	-3.30545800	-1.63321200
H	-0.49987000	-2.43905000	-0.63540100
C	-3.43290100	-3.49983700	0.57742900
H	-3.58960700	-1.38067200	1.12216800
H	-4.46873900	-1.79374400	-0.37017000
H	-1.42363900	-3.37487900	1.42080200
H	-1.63689900	-4.76409800	0.33706500
H	-3.85809000	-3.73423700	1.55771700
H	-3.94324200	-4.11982700	-0.16848000

IIp

E = -1273.400331

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C	-4.11103900	-0.00714800	-0.00004300
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C	-6.20132500	-1.24104600	0.00001500
C	-6.91400800	-0.03903000	0.00006200
C	-6.22881900	1.17887200	0.00005500
H	-4.29882600	2.14306900	-0.00000600
H	-4.24989400	-2.16110800	-0.00007700
H	-6.73204500	-2.18896200	0.00002100
H	-8.00037800	-0.05140800	0.00010600
H	-6.78096900	2.11446100	0.00009100
C	-2.68785000	0.00835900	-0.00009100
C	-1.47272200	0.02105300	0.00000000
C	-0.05857000	0.02860700	-0.00002200
C	0.68278500	-1.16679300	-0.00000800
C	0.67192800	1.22735800	-0.00001700
C	2.06911500	-1.15257800	-0.00000400
C	2.06412500	1.24020200	-0.00001400
C	2.79237800	0.04661400	-0.00000400
F	0.02319800	2.39664500	-0.00001900
F	0.04577900	-2.34206700	-0.00000600
F	2.72153100	-2.32149800	0.00001200
F	2.66775400	2.43320700	-0.00000900

TSp

E = -1845.705203

C	0.42271900	3.91783900	0.73626500
C	0.17899100	3.09724100	-0.38619000
C	0.48205900	3.60774400	-1.66685400
C	1.00642800	4.88860700	-1.81509400
C	1.24065300	5.68981100	-0.69439900
C	0.94700100	5.19773900	0.58012100
H	0.20005100	3.53215000	1.72668300
H	0.30487600	2.98224900	-2.53671600
H	1.23631300	5.26348900	-2.80914400
H	1.65127000	6.68885100	-0.81313500
H	1.13044100	5.81407700	1.45650100
C	-0.35495000	1.78473600	-0.22892600
C	-0.83700300	0.65229400	-0.09038000
C	0.01341500	-1.20796800	0.17956900
C	0.76343000	-1.49791900	-0.98070700
C	0.73759000	-1.16195700	1.38829200
C	2.14026700	-1.43028300	-0.96618800
C	2.11848700	-1.09375200	1.39684600
C	2.86895500	-1.23034700	0.21850100
F	-1.23582600	-1.86655400	0.25761400
F	0.04601600	-0.99245000	2.53790200
F	0.09927300	-1.66413400	-2.14625100
F	2.79235400	-1.60777600	-2.12632300
F	2.71407200	-0.93563400	2.58812000
C	4.36940000	-1.22979600	0.16896300
F	4.83049400	-0.41982500	-0.81056900
F	4.86188200	-2.46650100	-0.08895700
F	4.92564900	-0.81536700	1.32214700
Li	-2.58696100	-0.47547800	0.02780100
O	-3.54803400	-0.32557900	1.71099200
C	-3.43984300	-1.38589200	2.70122200
C	-3.45761900	0.97141400	2.36269500
C	-3.49849600	-0.69133700	4.06371100
H	-4.25701800	-2.09346700	2.53143900
H	-2.48166700	-1.89362400	2.55120800
C	-2.88905200	0.68372600	3.74980700
H	-2.81443000	1.60479400	1.74653100
H	-4.46513100	1.40400500	2.41270600
H	-2.94645200	-1.24337600	4.82970400
H	-4.53661200	-0.58504200	4.39990400
H	-1.79766500	0.61232300	3.69860400
H	-3.15689000	1.45367400	4.47932300
O	-3.47135700	-0.80516700	-1.66814300
C	-3.33045500	0.24088000	-2.66813800
C	-3.37350600	-2.11152900	-2.30006700
C	-2.73202700	-0.45212100	-3.88955300
H	-4.32494600	0.65584200	-2.87731600
H	-2.68959800	1.01766600	-2.24350900
C	-3.37169500	-1.84697700	-3.80773600
H	-2.43824000	-2.57718600	-1.97290700
H	-4.21911700	-2.71743500	-1.96073100
H	-1.64490400	-0.52538800	-3.78210900
H	-2.95802000	0.07443100	-4.82149500
H	-2.81401700	-2.61045800	-4.35758100
H	-4.39595500	-1.82394900	-4.19787100

IIm

E = -1273.400999

C	4.41298400	-1.44255200	0.00021700
C	3.88787700	-0.13483800	-0.00004900
C	4.77330600	0.96147100	-0.00023700
C	6.14882400	0.74929700	-0.00015400
C	6.66129800	-0.55065400	0.00011400
C	5.79021100	-1.64322500	0.00029700
H	3.73122700	-2.28727800	0.00035900
H	4.36950200	1.96909900	-0.00044200
H	6.82366300	1.60075400	-0.00029800
H	7.73576100	-0.71157600	0.00018000
H	6.18555900	-2.65516400	0.00050500
C	2.47969200	0.07596200	-0.00011100
C	1.27791000	0.25470100	-0.00010700
C	-0.12125700	0.46979000	-0.00010200
C	-0.65987700	1.76632400	-0.00000200
C	-1.03537700	-0.60317100	-0.00015100
C	-2.03217300	1.98746600	0.00004100
C	-2.41851200	-0.41988000	-0.00013800
C	-2.89426200	0.89781200	0.00000700
F	-0.51815100	-1.83498000	-0.00020700
F	0.15507300	2.82158800	0.00005000
F	-2.51840300	3.23274900	0.00015000
C	-3.43551500	-1.53911900	-0.00001900
F	-4.20922600	1.13165900	0.00011200
F	-2.87382400	-2.75677500	-0.00076200
F	-4.23140000	-1.45818900	1.08737600
F	-4.23256700	-1.45740200	-1.08648900

TSm

E = -1845.693761

C	-0.11521700	4.16490600	0.98928100
C	0.63464900	3.05922900	0.54216600
C	2.03692500	3.18310100	0.44788100
C	2.66022000	4.37922700	0.79382300
C	1.90765800	5.46723100	1.24341500
C	0.51885200	5.35420100	1.34050600
H	-1.19613400	4.07898100	1.05745900
H	2.61886500	2.33689200	0.09777700
H	3.74095500	4.46111000	0.71320900
H	2.39992800	6.39719900	1.51488200
H	-0.07350800	6.19727300	1.68688800
C	0.00562800	1.82800700	0.17971500
C	-0.49162400	0.73414600	-0.12086500
C	-0.21393500	-1.95455000	-0.52104900
C	0.18345700	-0.73152900	-1.11808800
C	0.63159200	-2.77490200	0.19698500
C	1.60128800	-0.62095400	-1.21334000
C	2.00564900	-2.54879900	0.17559300
C	2.49626100	-1.43851200	-0.52818700
F	-1.57936800	-2.11980900	-0.36315200
F	0.12056600	-3.81255400	0.88632900
F	-0.53840100	-0.38921700	-2.27267100
F	2.06726500	0.49789300	-1.81073700
F	2.80272100	-3.41799100	0.82545700
C	3.96173800	-1.08473300	-0.59708400
F	4.19540900	0.13461800	-0.04935200
F	4.39854600	-1.03043600	-1.87336800
F	4.74360600	-1.96166800	0.05554800
Li	-2.35422000	-0.29986000	0.08277100
O	-2.89189200	-0.63449800	1.92098000
C	-2.92648200	-1.96378600	2.51264100
C	-2.56819400	0.35136500	2.93469900
C	-2.71451400	-1.76053100	4.01680200
H	-3.88976300	-2.42212000	2.26766400
H	-2.12629600	-2.55774800	2.06039900
C	-1.92433000	-0.44305600	4.06692900
H	-1.90657500	1.08945400	2.47494300
H	-3.49643900	0.84093600	3.25838800
H	-2.18271400	-2.60034100	4.47278200
H	-3.67603500	-1.64795600	4.53085400
H	-0.86482500	-0.61853900	3.84888400
H	-1.99701300	0.06795800	5.03137400
O	-3.65139200	0.16192800	-1.27517200
C	-3.58613900	1.52937200	-1.76503700
C	-3.88115400	-0.75157600	-2.38461000
C	-3.36319100	1.40603600	-3.26951900
H	-4.53573400	2.02678200	-1.52814000
H	-2.76711800	2.02835000	-1.24100000
C	-4.15445000	0.13185800	-3.60465800
H	-2.97813200	-1.35511300	-2.51753000
H	-4.71819900	-1.40410400	-2.11836700
H	-2.29789500	1.26085700	-3.47413400
H	-3.71026100	2.28729600	-3.81690500
H	-3.83080300	-0.34342200	-4.53502600
H	-5.22460900	0.35435600	-3.68965900

IIo

E = -1273.394937

C	4.06552600	-0.97850900	-0.00016800
C	3.39919100	0.26358700	0.00002300
C	4.15670800	1.45156500	0.00014700
C	5.54729700	1.39367700	0.00006800
C	6.20029800	0.15825500	-0.00013000
C	5.45632800	-1.02485700	-0.00024700
H	3.47938600	-1.89219500	-0.00025900
H	3.64264000	2.40767700	0.00030000
H	6.12383800	2.31450800	0.00016200
H	7.28601900	0.11747400	-0.00019100
H	5.96229200	-1.98627000	-0.00040200
C	1.97682500	0.31148000	0.00008100
C	0.76199200	0.30788600	-0.00004000
C	-0.65301800	0.40549900	-0.00001100
C	-1.20574700	1.70074600	-0.00000700
C	-1.54831800	-0.69517600	-0.00024000
C	-2.57702900	1.91945500	0.00001100
C	-2.92270300	-0.45618600	-0.00018900
C	-3.44638000	0.83303500	-0.00019400
F	-0.39994700	2.76798900	0.00011900
F	-3.06306400	3.16162100	0.00008900
F	-4.76628600	1.02776600	-0.00020500
C	-1.11855800	-2.14769300	0.00010000
F	0.21403100	-2.30745100	-0.00068400
F	-1.60127100	-2.78802100	-1.08657700
F	-1.59990900	-2.78700600	1.08802400
F	-3.78895900	-1.47687400	-0.00019300

TSo

E = -1845.704728

C	-2.14031400	0.07760600	3.63969400
C	-1.83355000	-0.65182500	2.47192900
C	-2.54246900	-1.84661600	2.21831500
C	-3.51853800	-2.29207300	3.10463800
C	-3.80891100	-1.56199900	4.26073000
C	-3.11655700	-0.37662600	4.52232100
H	-1.60399600	1.00056800	3.83988800
H	-2.31856700	-2.40151300	1.31229900
H	-4.05762500	-3.21187000	2.89245900
H	-4.57091300	-1.91289600	4.95151900
H	-3.34050500	0.19724200	5.41801900
C	-0.83822600	-0.20883500	1.55353600
C	0.02767900	0.10919100	0.72727700
C	-1.89265500	2.39351200	-1.45671200
C	-0.59364900	2.07208400	-1.13380000
C	-2.73664400	1.43280400	-2.02687200
C	-0.12286700	0.73647200	-1.20290400
C	-2.24116200	0.15472000	-2.22827700
C	-0.92406600	-0.20123800	-1.91498600
F	-2.34334800	3.63951900	-1.26786900
F	-3.99689000	1.75205200	-2.36346100
F	0.20218400	3.00032100	-0.55776500
F	1.27671500	0.67779100	-1.43367600
F	-3.06247800	-0.75746900	-2.77346900
C	-0.51622800	-1.63338200	-2.07041200
F	-1.11521600	-2.45034400	-1.16207800
F	0.82147000	-1.81130600	-1.90546000
F	-0.82662500	-2.12465900	-3.28726900
Li	2.06258200	0.08590300	0.26784300
O	3.14445800	1.57153300	0.92488600
C	3.47620500	2.71235900	0.08609300
C	2.74328500	2.02697400	2.24530100

C	3.45698200	3.93209600	1.01180800
H	4.45278200	2.52572200	-0.37127500
H	2.71648900	2.78819600	-0.69724600
C	2.43531600	3.51288800	2.08021000
H	1.87954000	1.43092100	2.55177800
H	3.57505200	1.85378800	2.94049700
H	3.17502400	4.84582400	0.48087600
H	4.44317600	4.09035900	1.46393700
H	1.41589300	3.64343700	1.70331700
H	2.53672200	4.06745400	3.01781900
O	2.97656900	-1.61631200	0.35229600
C	2.24143700	-2.80423000	0.75964200
C	4.08118100	-1.98073700	-0.50952600
C	2.72346000	-3.91402600	-0.17196400
H	2.48718600	-3.01427100	1.80813500
H	1.17696200	-2.57905500	0.67732100
C	4.18220900	-3.50621600	-0.43300500
H	3.85389300	-1.64303600	-1.52889400
H	4.97723600	-1.46227200	-0.15514400
H	2.14669900	-3.89700700	-1.10201300
H	2.62709800	-4.90632600	0.27821400
H	4.59732700	-3.93964500	-1.34760300
H	4.82073700	-3.80563800	0.40632600

Li(thf)$_2$F

E = -572.3867838

F	-0.00015700	2.14557800	0.36284000
Li	-0.00035800	0.85987800	-0.65050700
O	1.76947200	0.07313300	-0.93135600
C	2.68944800	0.97443400	-0.23171200
C	2.15484900	-1.27674400	-0.63997100
C	3.38852000	0.12016600	0.84933500
H	3.39804300	1.37576800	-0.96488100
H	2.05543600	1.77036200	0.16966800
C	2.63522200	-1.22553100	0.80830900
H	1.28352300	-1.91681200	-0.80942900
H	2.95829800	-1.59239400	-1.32237200
H	3.33431300	0.59172300	1.83424100
H	4.44671400	-0.02630700	0.60691900
H	1.77053500	-1.20302200	1.48141800
H	3.26263000	-2.07957500	1.08148600
O	-1.76980400	0.07297900	-0.93165400
C	-2.15446500	-1.27698200	-0.63965400
C	-2.68991100	0.97415400	-0.23194100
C	-2.63453400	-1.22544800	0.80871300
H	-2.95790500	-1.59328500	-1.32175900
H	-1.28286200	-1.91668800	-0.80905300
C	-3.38853900	0.11985400	0.84934300
H	-2.05604000	1.77028500	0.16926300
H	-3.39871500	1.37521800	-0.96504800
H	-1.76970500	-1.20218700	1.48161500
H	-3.26142500	-2.07971400	1.08238100
H	-3.33458900	0.59173700	1.83410800
H	-4.44665300	-0.02725100	0.60695900