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Copper-Mediated Oxidative Difluoromethylation of Terminal Alkynes with $TMSCF_2H$

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Supporting Information

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General information.

^{1}H NMR (TMS as the internal standard) and ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a Bruker AM400 spectrometer. ^{13}C NMR was recorded on a Bruker AM400 spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

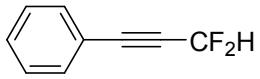
Materials. 1a-o were received from commercial sources. The terminal alkynes **1i**,[1] **1q**[2] and **1r**[3] were prepared as reported procedures. Solvents were freshly dried and degassed before using.

References

(1) Chen, C.; Chu, L.; Qing, F.-L. *J. Am. Chem. Soc.* **2012**, *134*, 12454.
(2) Zhang, Z.; Jiang, X. *Org. Lett.* **2014**, *16*, 4400.
(3) Gómez, A. M.; Company, M. D.; Valverde, S.; López, J. C. *Org. Lett.* **2002**, *4*, 383.

General Procedures for Copper-Mediated Oxidative Difluoromethylation of Terminal Alkynes with $TMSCF_2H$.

In a glove box, ^{t}BuOK (1.2 mmol, 134.6 mg) and CuI (0.4 mmol, 76.2 mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum. DMF (4 mL) was added and the mixture was stirred at room temperature for 10 minutes. Next, $TMSCF_2H$ (0.8 mmol, 99.4 mg) was added under N_2 atmosphere at 0 ℃, followed by the addition of a solution of terminal alkyne **1a** (0.4 mmol) in DMF and 9, 10-phenanthraquinone (0.48 mmol, 100.0 mg). Then, the reaction mixture was stirred at room temperature for 10 h. The reaction was quenched by water and extracted with ethyl acetate, and the organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash column chromatography using pentane and dichloromethane as fluent solvent.

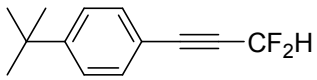


2a

(3,3-difluoroprop-1-yn-1-yl)benzene 2a:

Volatile liquid (31.6 mg, 0.21 mmol, Yield: 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.24 (m, 5H), 6.40 (t, J = 55.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.30 (d, J = 54.8 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (t, J = 2.2 Hz), 130.1, 128.5, 119.9 (t, J = 2.7 Hz), 104.2 (t, J = 230.4 Hz), 88.4 (t, J = 7.3 Hz), 79.8 (t, J = 33.6 Hz). IR (ATR): ν_{max} 2974, 2254, 2222, 1686, 1491, 1445, 1373, 1259, 1091, 1038, 972, 914, 757, 689, 627, 506 cm^{-1}. MS (EI): m/z (%) 152, 151 (100). HRMS: Calculated for $C_9H_6F_2$: 152.0438; Found: 152.0441.

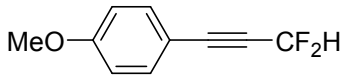


2b

1-(tert-butyl)-4-(3,3-difluoroprop-1-yn-1-yl)benzene 2b:

Colorless oil (60.0 mg, 0.29 mmol, Yield: 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.8 Hz, 2H), 6.40 (t, J = 55.2 Hz, 1H), 1.30 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.92 (d, J = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 132.0 (t, J = 2.2 Hz), 125.6, 116.8, 104.3 (t, J = 230.4 Hz), 88.8 (t, J = 7.3 Hz), 79.3 (t, J = 33.6 Hz), 35.0, 31.1. IR (ATR): ν_{max} 2966, 2907, 2871, 2253, 2226, 1690, 1605, 1506, 1464, 1375, 1267, 1088, 1039, 975, 913, 836, 773, 743, 672, 565 cm^{-1}. MS (EI): m/z (%) 208, 193 (100). HRMS: Calculated for $C_{13}H_{14}F_2$: 208.1064; Found: 208.1070.

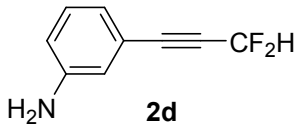


2c

1-(3,3-difluoroprop-1-yn-1-yl)-4-methoxybenzene 2c:

Light yellow oil (54.6 mg, 0.3 mmol, Yield: 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.38 (t, *J* = 55.6 Hz, 1H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.62 (d, *J* = 54.8 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 133.8 (t, *J* = 2.9 Hz), 114.2, 111.8 (t, *J* = 2.9 Hz), 104.4 (t, *J* = 229.7 Hz), 88.8 (t, *J* = 7.3 Hz), 78.8 (t, *J* = 34.3 Hz). IR (ATR): ν_{max} 2966, 2842, 2250, 2222, 1607, 1511, 1465, 1443, 1374, 1296, 1255, 1175, 1088, 1030, 973, 833, 807, 596 cm^{-1}. MS (EI): m/z (%) 182 (100). HRMS: Calculated for $C_{10}H_8F_2O$: 182.0543; Found: 182.0541.

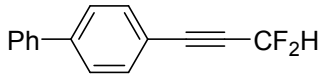


2d

3-(3,3-difluoroprop-1-yn-1-yl)aniline 2d:

Yellow oil (35.4 mg, 0.21 mmol, Yield: 53%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.38 (t, *J* = 55.2 Hz, 1H), 3.70 (br, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.13 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 129.5, 122.4 (t, *J* = 2.1 Hz), 120.5, 118.1 (t, *J* = 2.9 Hz), 117.0, 104.3 (t, *J* = 230.5 Hz), 88.8 (t, *J* = 7.3 Hz), 79.1 (t, *J* = 33.5 Hz). IR (ATR): ν_{max} 3469, 3385, 3220, 3052, 2925, 2243, 1623, 1601, 1581, 1491, 1450, 1374, 1320, 1309, 1295, 1210, 1168, 1088, 1032, 1000, 895, 865, 785, 684, 506, 458 cm^{-1}. MS (EI): m/z (%) 167 (100). HRMS: Calculated for $C_9H_7F_2N$: 167.0547; Found: 167.0549.

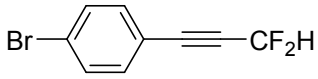


2e

4-(3,3-difluoroprop-1-yn-1-yl)-1,1'-biphenyl 2e:

Light yellow solid (65.7 mg, 0.29 mmol, Yield: 72%), mp 52-54 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 6H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.43 (t, *J* = 55.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.19 (d, *J* = 55.1 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.0, 132.6 (t, *J* = 2.9 Hz), 129.0, 128.1, 127.2, 127.1, 118.7, 104.3 (t, *J* = 234.8 Hz), 88.4 (t, *J* = 7.3 Hz), 80.3 (t, *J* = 33.6 Hz). IR (ATR): ν_{max} 3300, 3033, 2250, 2224, 1924, 1684, 1603, 1487, 1448, 1375, 1088, 1036, 972, 783, 764, 696, 561 cm^{-1}. MS (EI): m/z (%) 228 (100). HRMS: Calculated for $C_{15}H_{10}F_2$: 228.0751; Found: 228.0756.

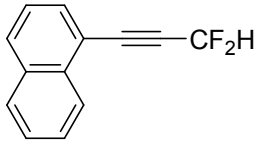


2f

1-bromo-4-(3,3-difluoroprop-1-yn-1-yl)benzene 2f:

Light yellow solid (60.1 mg, 0.26 mmol, Yield: 65%), mp 32-35 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.40 (t, *J* = 54.9 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.78 (d, *J* = 54.9 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 131.9, 124.8, 118.8, 104.1 (t, *J* = 231.2 Hz), 87.3 (t, *J* = 7.3 Hz), 80.8 (t, *J* = 32.8 Hz). IR (ATR): ν_{max} 2925, 2853, 2253, 2223, 1679, 1586, 1487, 1373, 1261, 1090, 1071, 1042, 1012, 972, 824, 767 cm^{-1}. MS (EI): m/z (%) 232 (100), 230 (100). HRMS: Calculated for $C_9H_5BrF_2$: 229.9543; Found: 229.9545.

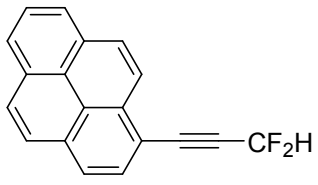


2g

1-(3,3-difluoroprop-1-yn-1-yl)naphthalene 2g:

Light yellow oil (50.1 mg, 0.25 mmol, Yield: 62%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.59 (dt, *J* = 24.7, 7.5 Hz, 2H), 7.49 – 7.43 (m, 1H), 6.57 (t, *J* = 55.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.91 (d, *J* = 55.1 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1 (t, *J* = 1.9 Hz), 133.0, 131.9 (t, *J* = 3.0 Hz), 130.7, 128.5, 127.5, 126.8, 125.6, 125.0, 117.4 (t, *J* = 3.4 Hz), 104.4 (t, *J* = 231.2 Hz), 86.8 (t, *J* = 7.2 Hz), 84.4 (t, *J* = 33.8 Hz). IR (ATR): ν_{max} 3061, 2240, 1588, 1508, 1397, 1369, 1338, 1280, 1179, 1116, 1074, 1041, 952, 841, 799, 772, 706, 627, 435 cm^{-1}. MS (EI): m/z (%) 202 (100). HRMS: Calculated for $C_{13}H_8F_2$: 202.0594; Found: 202.0593.



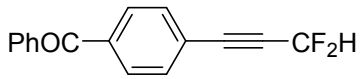
2h

1-(3,3-difluoroprop-1-yn-1-yl)pyrene 2h:

Light yellow solid (82.8 mg, 0.3 mmol, Yield: 75%), mp 85-87 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 9.1 Hz, 1H), 8.24 – 7.92 (m, 8H), 6.65 (t, *J* = 55.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.50 (d, *J* = 55.2 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 132.5, 131.0, 130.7, 130.0 (t, *J* = 2.2 Hz), 129.1, 127.0, 126.4, 126.2, 126.1, 124.6, 124.3, 124.1, 123.9, 113.7, 104.6 (t, *J* = 230.4 Hz), 87.9 (t, *J* = 8.0 Hz), 84.9 (t, *J* = 33.6 Hz). IR (ATR): ν_{max} 3042, 2227, 1597, 1584,

1435, 1373, 1190, 1117, 1106, 1024, 981, 962, 843, 825, 759, 714, 697, 611 cm^{-1}. MS (EI): m/z (%) 276 (100). HRMS: Calculated for $C_{19}H_{10}F_2$: 276.0751; Found: 276.0753.

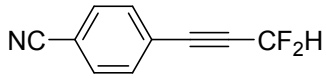


2i

(4-(3,3-difluoroprop-1-yn-1-yl)phenyl)(phenyl)methanone 2i:

White solid (64.0 mg, 0.25 mmol, Yield: 62%), 67-68 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, *J* = 6.9 Hz, 4H), 7.62-7.58 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 6.44 (t, *J* = 54.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.05 (d, *J* = 54.8 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 138.7, 137.0, 132.9, 132.1 (t, *J* = 2.5 Hz), 130.1, 130.0, 128.5, 123.8 (t, *J* = 3.7 Hz), 104.0 (t, *J* = 231.2 Hz), 87.3 (t, *J* = 7.3 Hz), 82.1 (t, *J* = 33.5 Hz). IR (ATR): ν_{max} 3062, 2252, 1661, 1601, 1448, 1373, 1309, 1275, 1178, 1088, 1039, 972, 925, 853, 741, 699, 638 cm^{-1}. MS (EI): m/z (%) 256 (100). HRMS: Calculated for $C_{16}H_{10}F_2O$: 256.0700; Found: 256.0703.

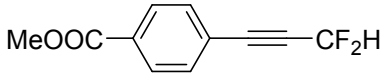


2j

4-(3,3-difluoroprop-1-yn-1-yl)benzonitrile 2j:

Light yellow oil (35.0 mg, 0.19 mmol, Yield: 48%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 6.43 (t, *J* = 54.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.68 (d, *J* = 54.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.7 (t, *J* = 3.0 Hz), 132.2, 124.6 (t, *J* = 2.9 Hz), 117.9, 113.8, 103.8 (t, *J* = 231.9 Hz), 86.1 (t, *J* = 7.3 Hz), 83.3 (t, *J* = 34.3 Hz). IR (ATR): ν_{max} 2255, 2232, 1607, 1503, 1373, 1262, 1181, 1093, 1042, 972, 841, 693, 559, 465 cm^{-1}. MS (EI): m/z (%) 177 (100). HRMS: Calculated for $C_{10}H_5F_2N$: 177.0390; Found: 177.0385.



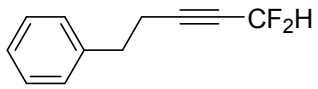
2k

methyl 4-(3,3-difluoroprop-1-yn-1-yl)benzoate 2k:

Light yellow solid (37.8 mg, 0.18 mmol, Yield: 45%), 62-64 ^oC.

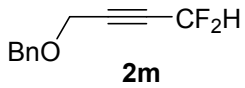
^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 6.43 (t, *J* = 54.8 Hz, 1H), 3.94 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.11 (d, *J* = 54.8 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.2 (t, *J* = 2.2 Hz), 131.4, 129.6, 124.3 (t, *J* = 3.6 Hz), 104.0 (t, *J* = 231.2 Hz), 87.3 (t, *J* = 7.3 Hz), 82.1 (t, *J* = 33.5 Hz), 52.4. IR (ATR): ν_{max} 2956, 2253, 2225, 1727, 1607, 1438, 1371, 1310, 1278, 1178, 1091, 1040,

1020, 973, 859, 769, 694, 654 cm^{-1}. MS (EI): m/z (%) 210, 179 (100). HRMS: Calculated for $C_{11}H_8F_2O_2$: 210.0492; Found: 210.0496.



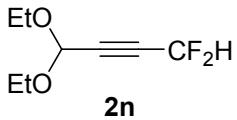
2l

(5,5-difluoropent-3-yn-1-yl)benzene 2l:
Colorless liquid (63.0 mg, 0.3 mmol, Yield: 75%).
^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.24-7.19 (m, 3H), 6.14 (t, *J* = 54.7 Hz, 1H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.70 – 2.44 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.40 (dt, *J* = 55.3, 5.7 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 128.6, 128.4, 126.7, 103.8 (t, *J* = 229.7 Hz), 89.8 (t, *J* = 7.3 Hz), 72.9 (t, *J* = 33.6 Hz), 34.0, 20.6. IR (ATR): ν_{max} 3065, 3030, 2933, 2866, 2333, 2255, 1604, 1497, 1455, 1375, 1165, 1043, 858, 795, 748, 699, 507 cm^{-1}. MS (EI): m/z (%) 180, 91 (100). HRMS: Calculated for $C_{11}H_{10}F_2$: 180.0751; Found: 180.0746.



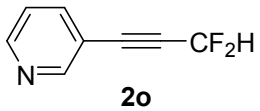
2m

(((4,4-difluorobut-2-yn-1-yl)oxy)methyl)benzene 2m:
Colorless liquid (37.6 mg, 0.19 mmol, Yield: 48%).
^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 5H), 6.22 (t, *J* = 54.4 Hz, 1H), 4.60 (s, 2H), 4.24 (t, *J* = 4.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.25 (dt, *J* = 53.4, 5.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 128.6, 128.2, 103.5 (t, *J* = 230.4 Hz), 85.2 (t, *J* = 7.3 Hz), 77.3 (t, *J* = 34.3 Hz), 72.1, 56.6 (t, *J* = 3.0 Hz). IR (ATR): ν_{max} 3033, 2862, 2253, 1497, 1455, 1375, 1355, 1151, 1092, 1046, 913, 830, 743, 699, 648, 602 cm^{-1}. MS (EI): m/z (%) 196, 91 (100). HRMS: Calculated for $C_{11}H_{10}F_2O$: 196.0700; Found: 196.0697.



2n

1,1-diethoxy-4,4-difluorobut-2-yne 2n:
Colorless liquid (40.8 mg, 0.21 mmol, Yield: 52%).
^1H NMR (400 MHz, $CDCl_3$) δ 6.24 (t, *J* = 54.3 Hz, 1H), 5.34 (t, *J* = 3.4 Hz, 1H), 3.79 – 3.57 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.36 (dd, *J* = 54.3, 3.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.4 (t, *J* = 231.9 Hz), 90.7 (t, *J* = 1.5 Hz), 83.9 (t, *J* = 7.3 Hz), 75.9 (t, *J* = 34.3 Hz), 61.4, 14.9. IR (ATR): ν_{max} 2982, 2935, 2892, 2257, 1482, 1447, 1375, 1356, 1329, 1152, 1117, 1211, 918, 866, 829, 636, 513 cm^{-1}. MS (EI): m/z (%) 177, 105 (100). HRMS: Calculated for [M-H, $C_8H_{11}F_2O_2$]: 177.0727; Found: 177.0725.

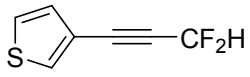


2o

3-(3,3-difluoroprop-1-yn-1-yl)pyridine 2o:

Red liquid (29.4 mg, 0.19 mmol, Yield: 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 1.2 Hz, 1H), 8.64 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.81 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.32 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.42 (t, *J* = 54.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.29 (d, *J* = 53.4 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (t, *J* = 2.2 Hz), 150.4, 139.1 (t, *J* = 2.2 Hz), 123.1, 117.2 (t, J = 3.4 Hz), 103.9 (t, *J* = 231.1 Hz), 85.0 (t, *J* = 7.3 Hz), 82.9 (t, *J* = 34.3 Hz). IR (ATR): ν_{max} 3036, 2257, 2226, 1564, 1478, 1412, 1374, 1266, 1189, 1093, 1038, 971, 807, 773, 704, 644, 512. MS (EI): m/z (%) 153 (100). HRMS: Calculated for $C_8H_5F_2N$: 153.0390; Found: 153.0385.

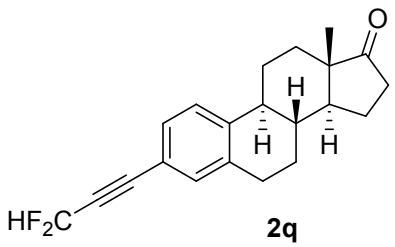


2p

3-(3,3-difluoroprop-1-yn-1-yl)thiophene 2p:

Light yellow oil (28.5 mg, 0.18 mmol, Yield: 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 1H), 7.32 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.18 (d, *J* = 5.0 Hz, 1H), 6.40 (t, *J* = 55.1 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.23 (d, *J* = 55.1 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.9 (t, *J* = 2.9 Hz), 129.7 (t, *J* = 2.2 Hz), 126.0, 119.0 (t, *J* = 2.9 Hz), 104.2 (t, *J* = 230.4 Hz), 83.9 (t, *J* = 7.3 Hz), 79.6 (t, *J* = 33.6 Hz). IR (ATR): ν_{max} 2252, 2226, 1368, 1187, 1077, 1035, 997, 913, 822, 785, 744, 676, 625 cm^{-1}. MS (EI): m/z (%) 158 (100). HRMS: Calculated for $C_7H_4F_2S$: 158.0002; Found: 158.0006.



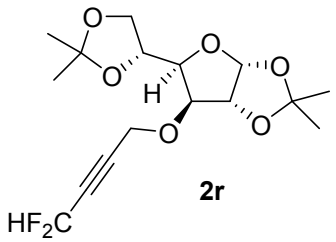
2q

(8R,9S,13S,14S)-3-(3,3-difluoroprop-1-yn-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one 2q:

White solid (68.3 mg, 0.21 mmol, 52%), mp 141-143 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.21 (m, 3H), 6.40 (t, *J* = 55.2 Hz, 1H), 2.97 – 2.79 (m, 2H), 2.58 – 1.92 (m, 7H), 1.73 – 1.33 (m, 6H), 0.92 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.92 (d, *J* = 55.2 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.4, 142.4, 137.0, 132.6 (t, *J* = 2.2 Hz), 129.4 (t, *J* = 2.2 Hz), 125.5, 117.2 (t, *J* = 2.9 Hz),

104.3 (t, *J* = 230.4 Hz), 88.7 (t, *J* = 7.3 Hz), 79.3 (t, *J* = 33.5 Hz), 50.5, 47.9, 44.5, 37.8, 35.8, 31.5, 29.0, 26.2, 25.5, 21.5, 13.8. IR (ATR): ν_{max} 2933, 2864, 2231, 1738, 1496, 1454, 1373, 1260, 1082, 1033, 823, 508 cm^{-1}. MS (EI): m/z (%) 328 (100). HRMS: Calculated for $C_{21}H_{22}F_2O$: 328.1639; Found: 328.1646.



2r

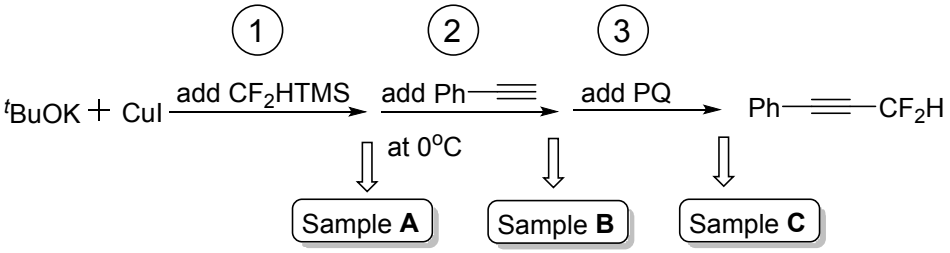
(3aR,5R,6S,6aR)-6-((4,4-difluorobut-2-yn-1-yl)oxy)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole 2r:

Colorless oil (99.1 mg, 0.28 mmol, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (t, *J* = 54.8 Hz, 1H), 5.85 (d, *J* = 3.6 Hz, 1H), 4.57 (d, *J* = 3.6 Hz, 1H), 4.36 (td, *J* = 4.4, 0.8 Hz, 2H), 4.23-4.20 (m, 1H), 4.09-4.06 (m, 2H), 4.04 (d, *J* = 3.2 Hz, 1H), 4.00-3.95 (m, 1H), 1.48 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1.29 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.64 (dt, *J* = 53.0, 5.5 Hz, 2F). ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.1, 109.2, 105.3, 103.4 (t, *J* = 231.2 Hz), 84.7 (t, *J* = 7.3 Hz), 82.6, 82.0, 81.0, 77.6 (t, *J* = 34.2 Hz), 72.3, 67.4, 57.7 (t, *J* = 2.2 Hz), 26.9, 26.8, 26.2, 26.3. IR (ATR): ν_{max} 2989, 2939, 2894, 2255, 1456, 1375, 1255, 1217, 1152, 1117, 1084, 1045, 889, 846, 638, 515 cm^{-1}. MS (EI): m/z (%) 333, 101 (100). HRMS: Calculated for [M-CH_3, $C_{14}H_{16}F_2O_6$]: 333.1150; Found: 333.1146.

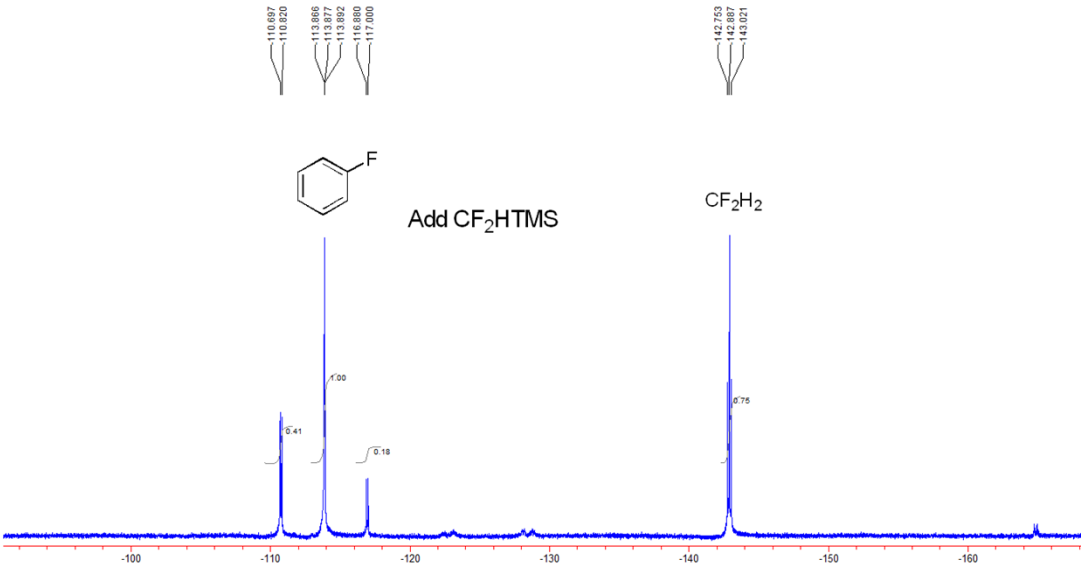
Experiments for Mechanistic Investigation.

Tracking the reaction mixture by ^{19}F NMR



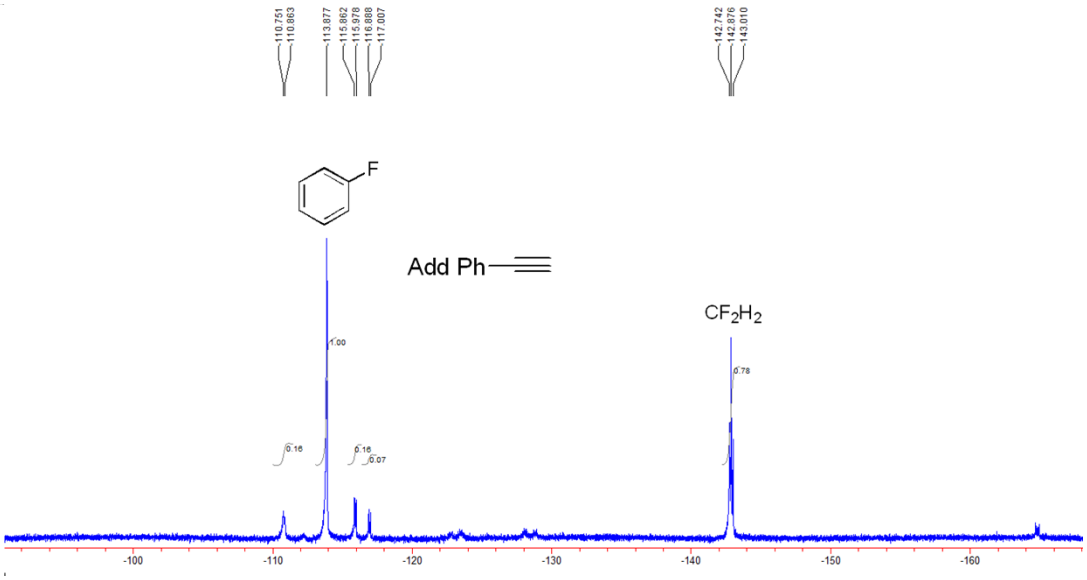
In a glove box, ^{t}BuOK (0.2 mmol, 22.4 mg) and CuI (0.2 mmol, 38.1 mg) were added to an oven-dried reaction tube containing a magnetic stir bar. The tube was capped with a septum. DMF (2 mL) and fluorobenzene (0.2 mmol, 19 μL) were added and the mixture was stirred at room temperature for 10 minutes. Next, $TMSCF_2H$ (0.4 mmol, 50.0 mg) was added under N_2 atmosphere at 0 ℃. Sample **A** was taken and then analyzed by ^{19}F NMR. After the addition of terminal alkyne **1a** (0.2 mmol) in DMF, sample **B** was taken and then analyzed by ^{19}F NMR. Next, 9,10-Phenanthraquinone (0.24 mmol, 50.0 mg) in DMF was added, the resulting reaction mixture was stirred at room temperature for 5 minutes. Sample **C** was taken and then analyzed by ^{19}F NMR.

^{19}F NMR spectrum of sample **A** (after addition of the CF_2HTMS):



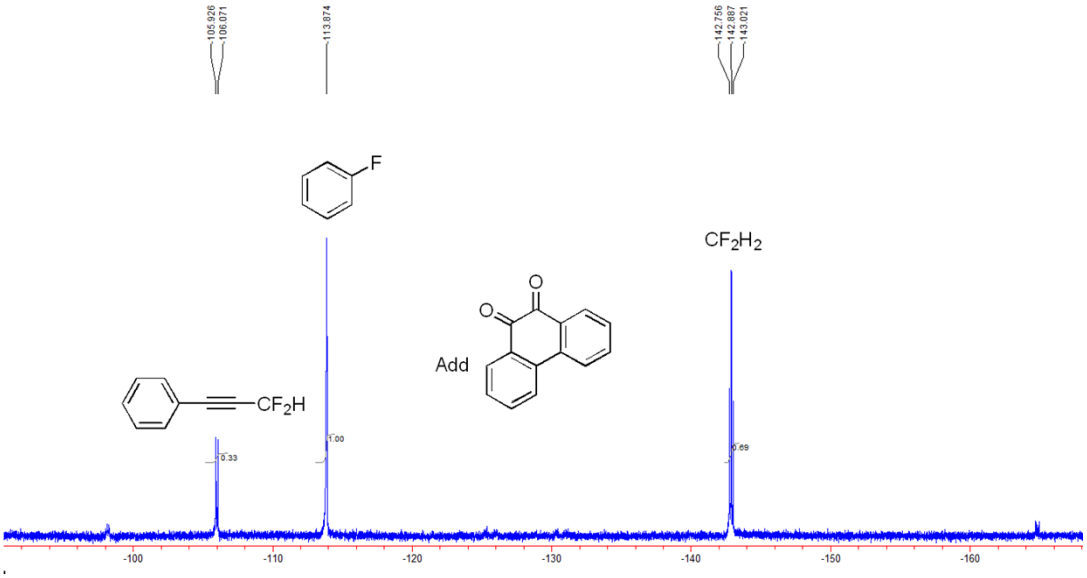
The ^{19}F NMR spectrum of the reaction mixture clearly shows two $CuCF_2H$ species: [$(CF_2H)Cu$] (resonates at δ = -110.8 ppm, d, J = 45.3 Hz) and [$Cu(CF_2H)_2$] (resonates at δ = -116.9 ppm, d, J = 44.2 Hz), which are similar to the literature data (Eujen, R.; Hoge, B.; Brauer, D. J. *J. Organomet. Chem.* **1996,** *519*, 7.).

^{19}F NMR spectrum for sample **B** (after addition of phenylacetylene):



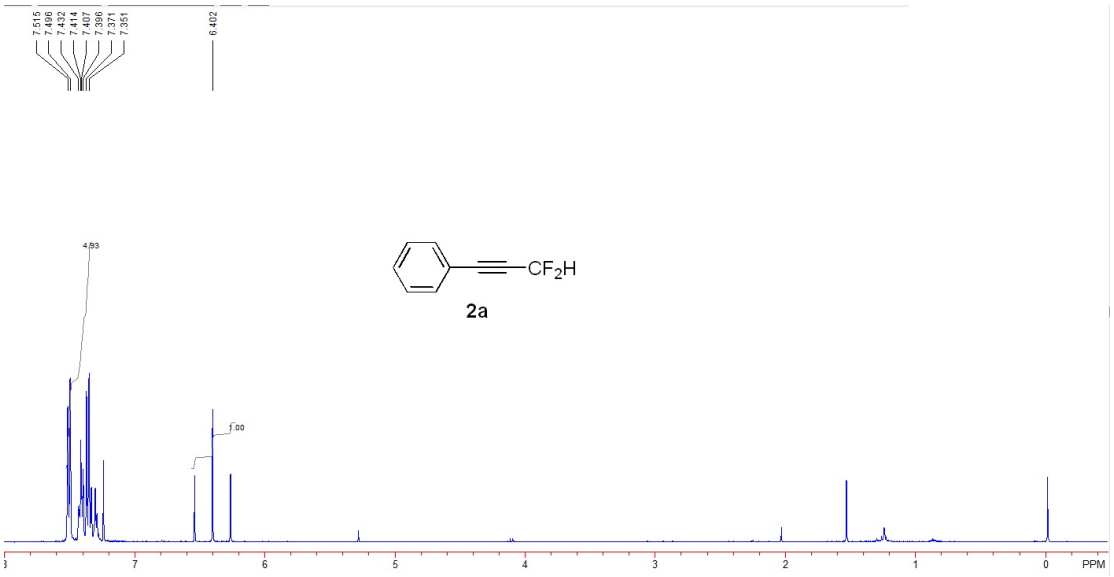
After addition of the phenylacetylene, a new peak emerged (resonates at δ = -115.9 ppm, d, J = 42.7 Hz).

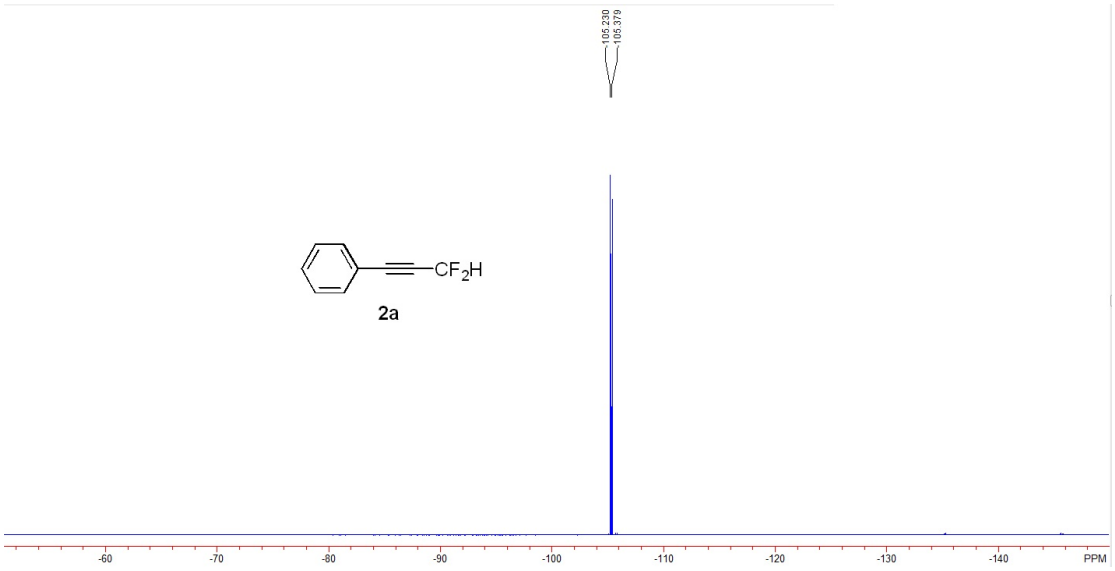
^{19}F NMR spectrum for sample **C** (after addition of 9,10-phenanthraquinone):

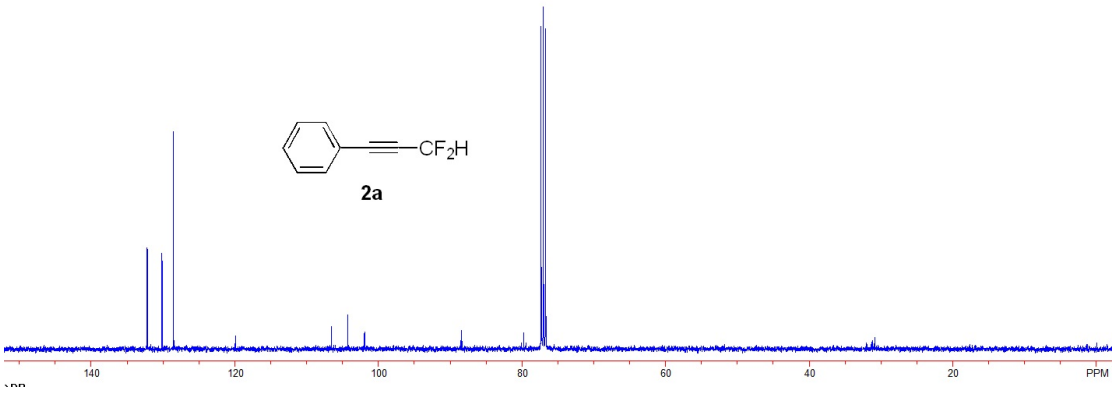


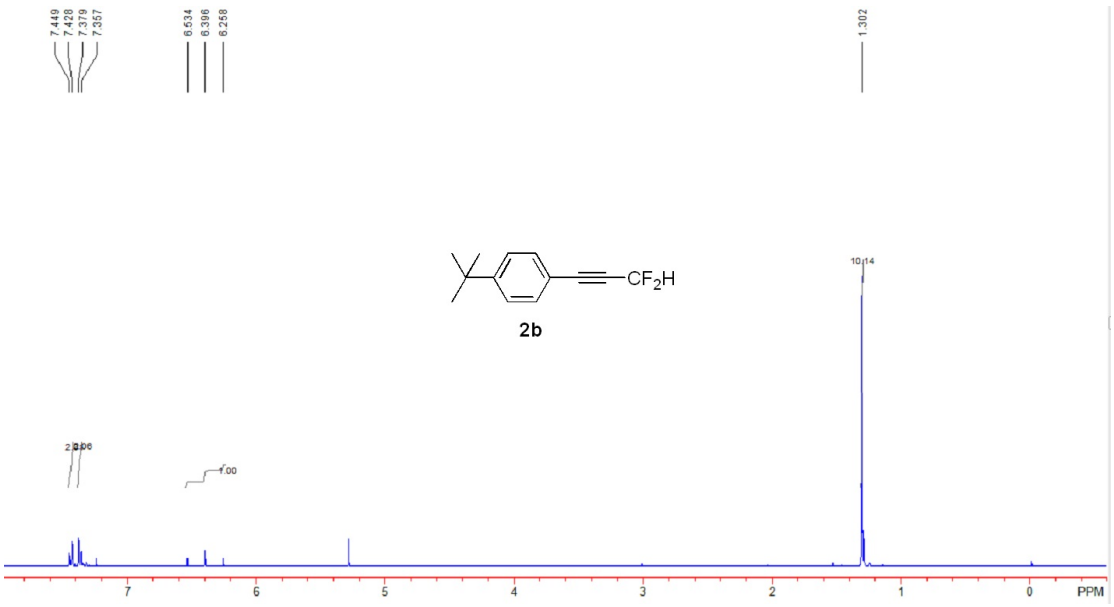
Finally, the oxidant 9,10-phenanthraquinone was added. All the $CuCF_2H$ species were consumed and the product was obtained (resonates at δ = -106.0 ppm, d, J = 53.4 Hz).

Copies of NMR Spectra.





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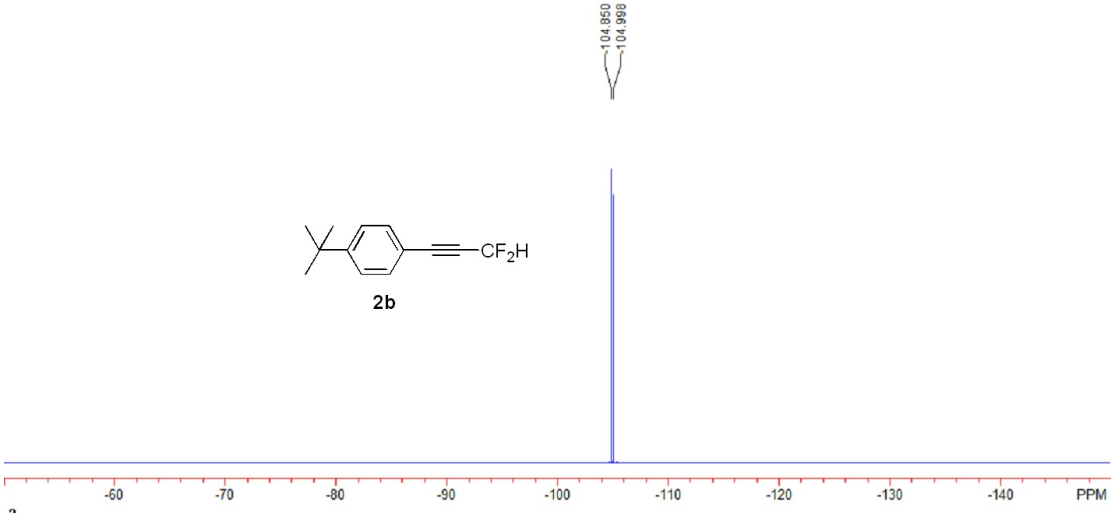
6
5
4
3
2
1
0
PPM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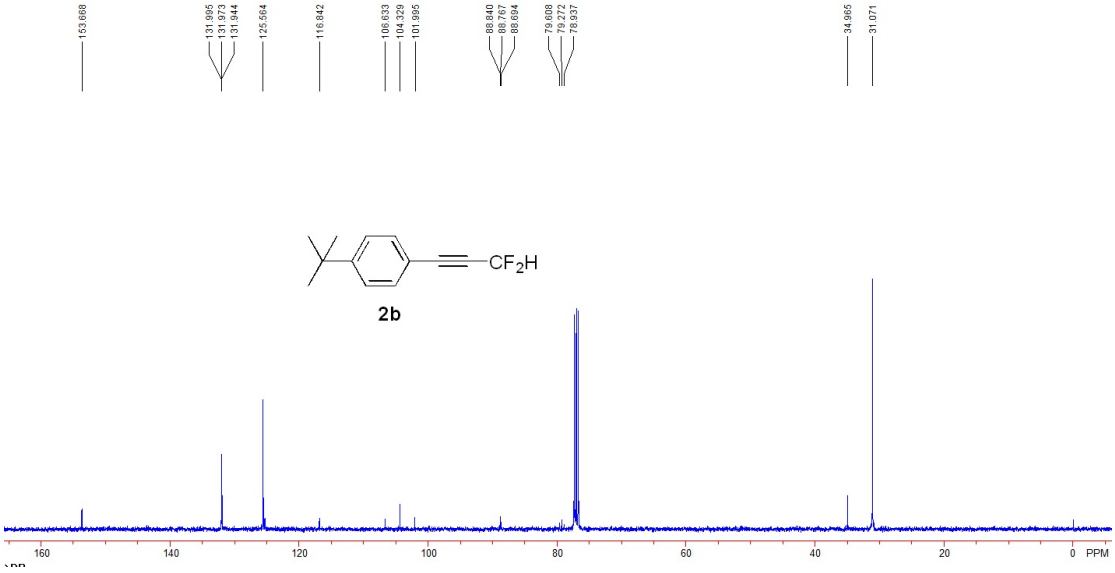
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60
40
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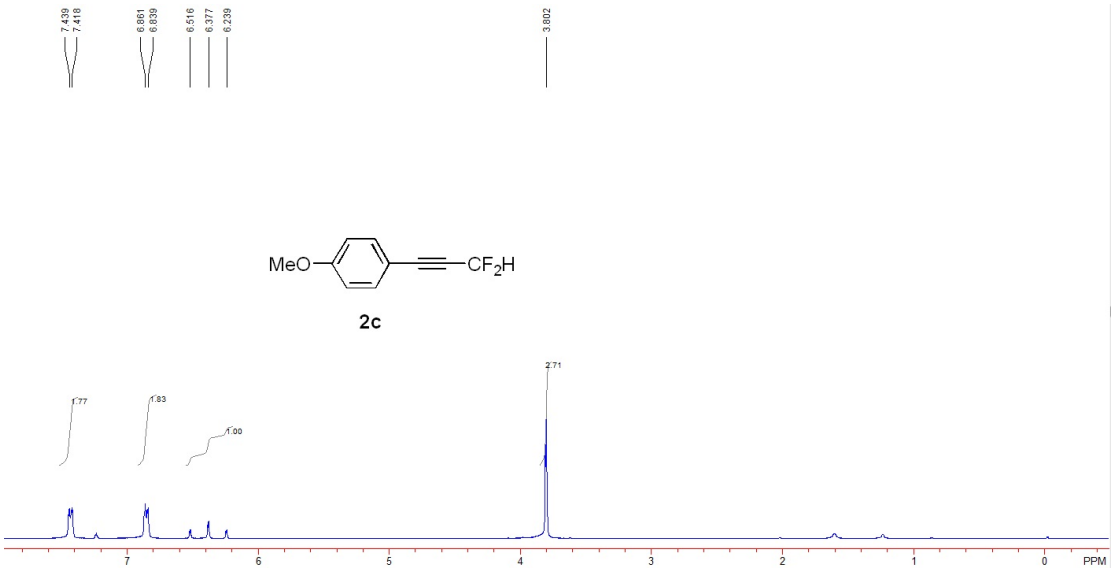
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6
5
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2
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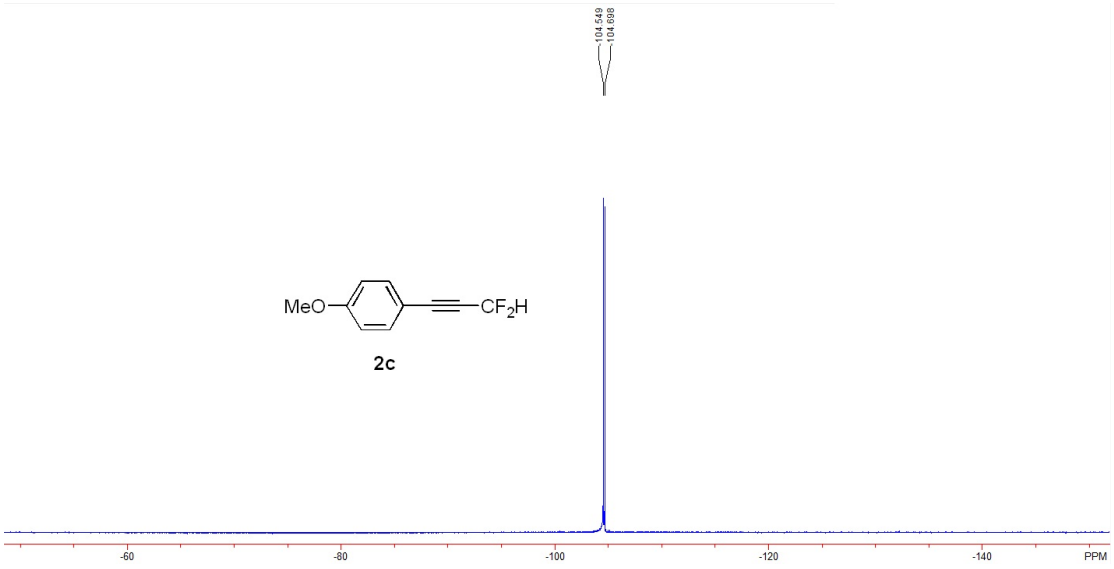
PPM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-120
-140
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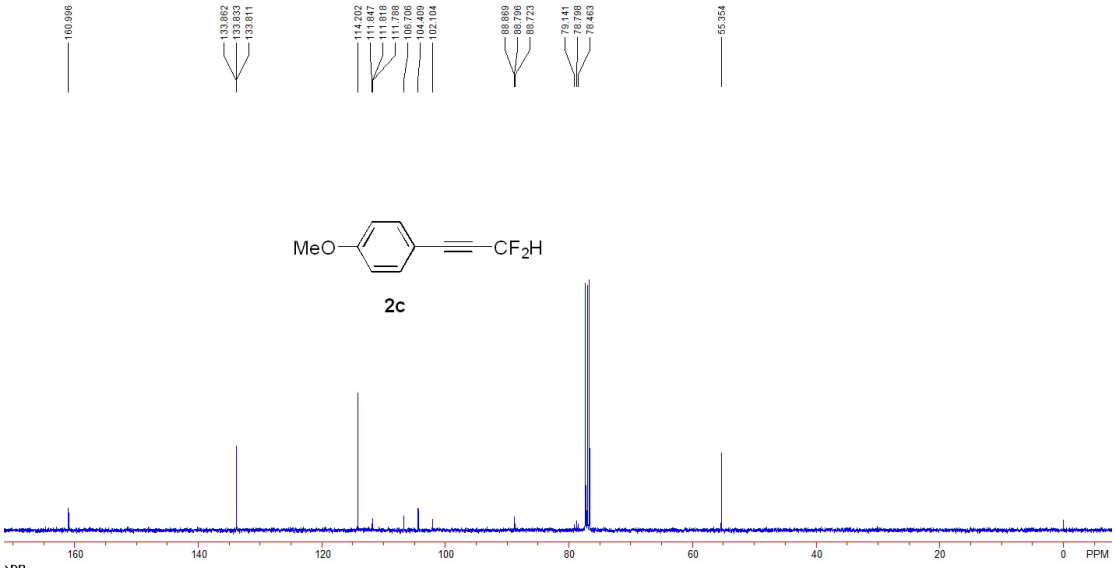
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79.141
78.798
78.463
55.354
MeO
CF2H
2c
160
140
120
100
80
60
40
20
0
PPM


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7.137
7.117
7.098
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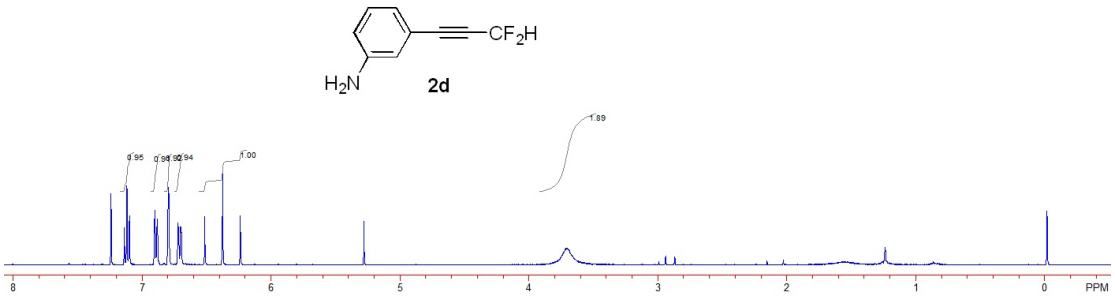
3.686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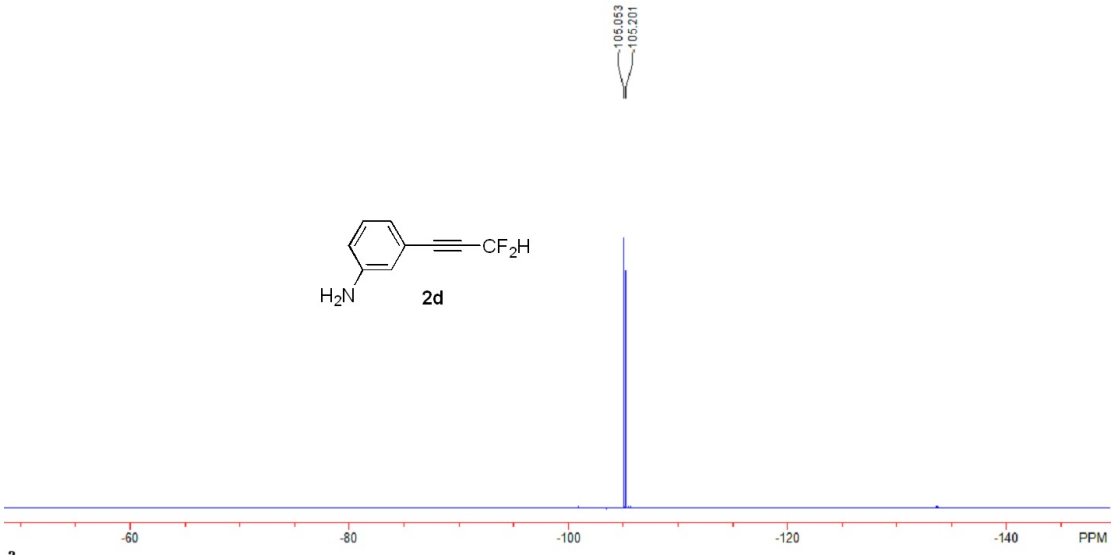
PPM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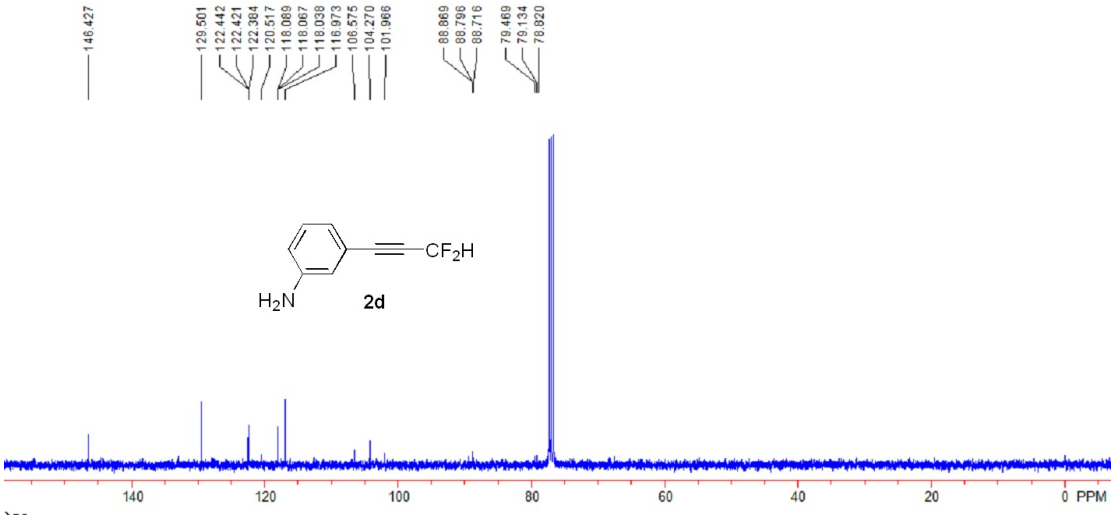
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88.869
88.796
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2d
140
120
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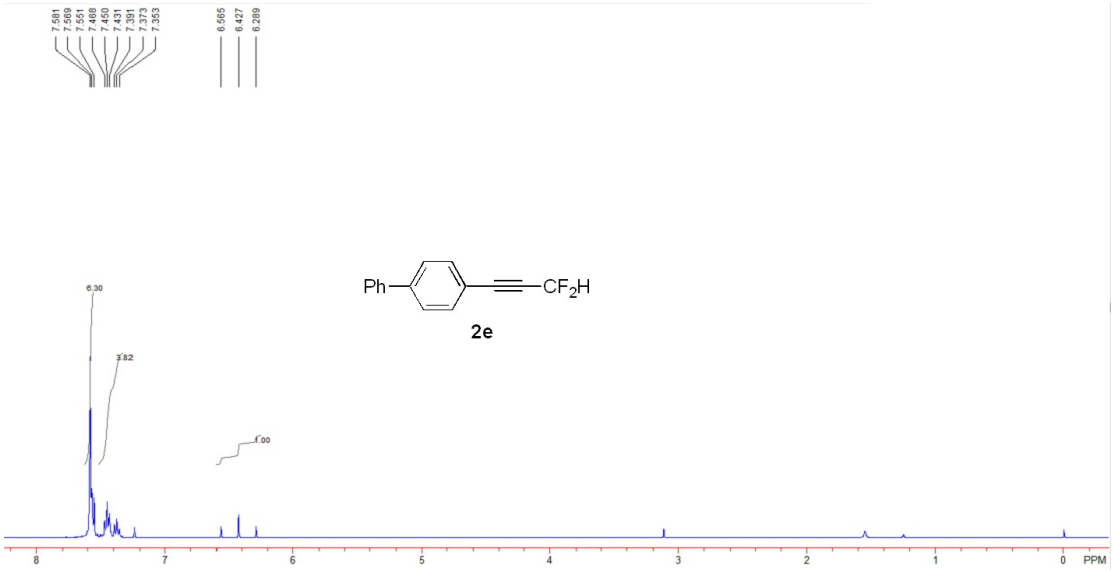
80
60
40
20
0 PPM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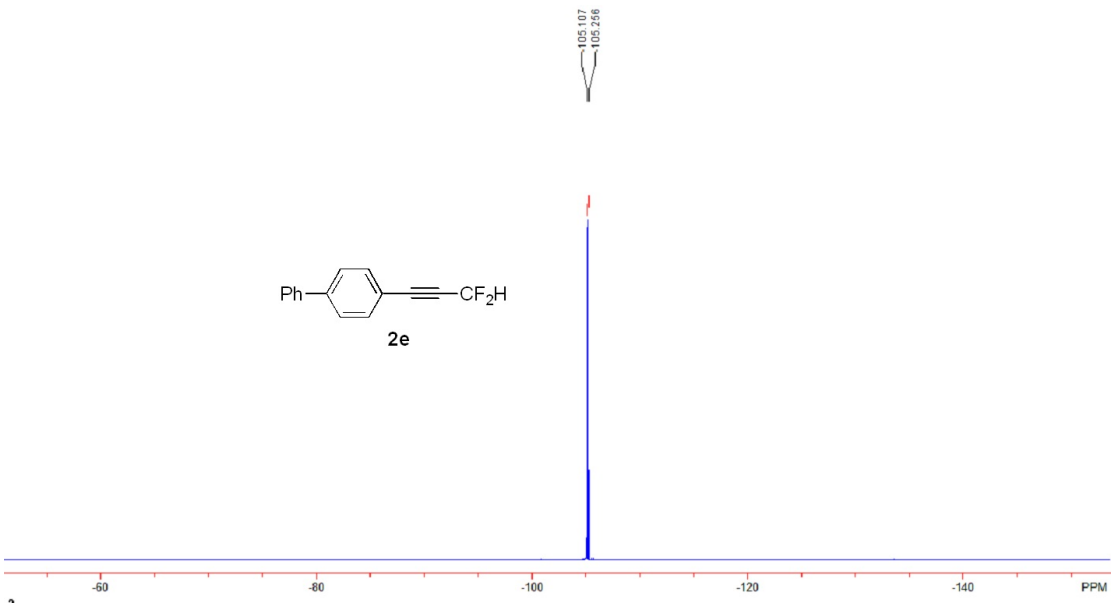
PPM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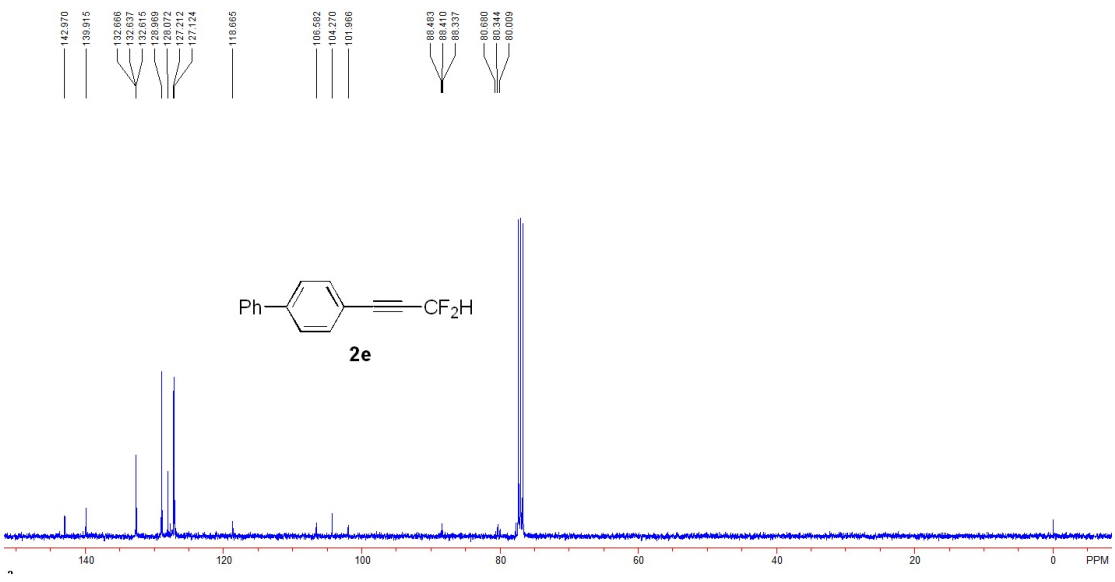
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40
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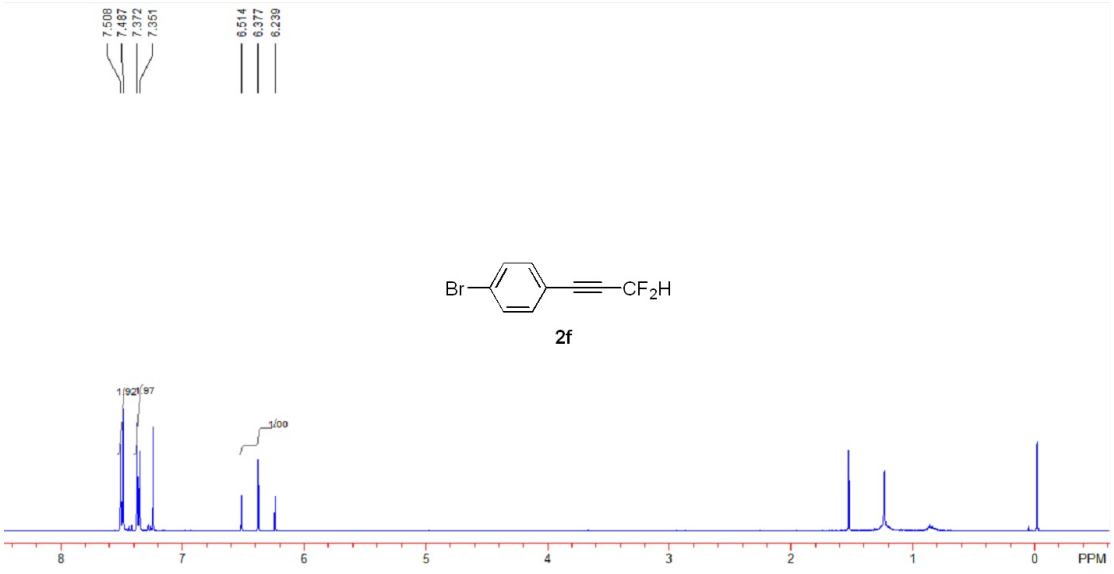
PPM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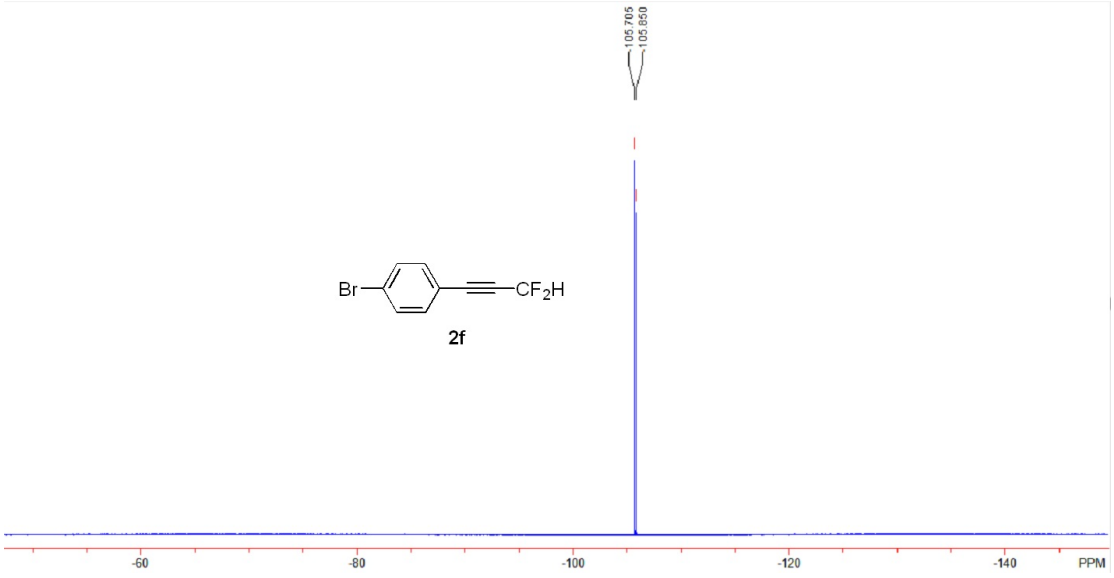
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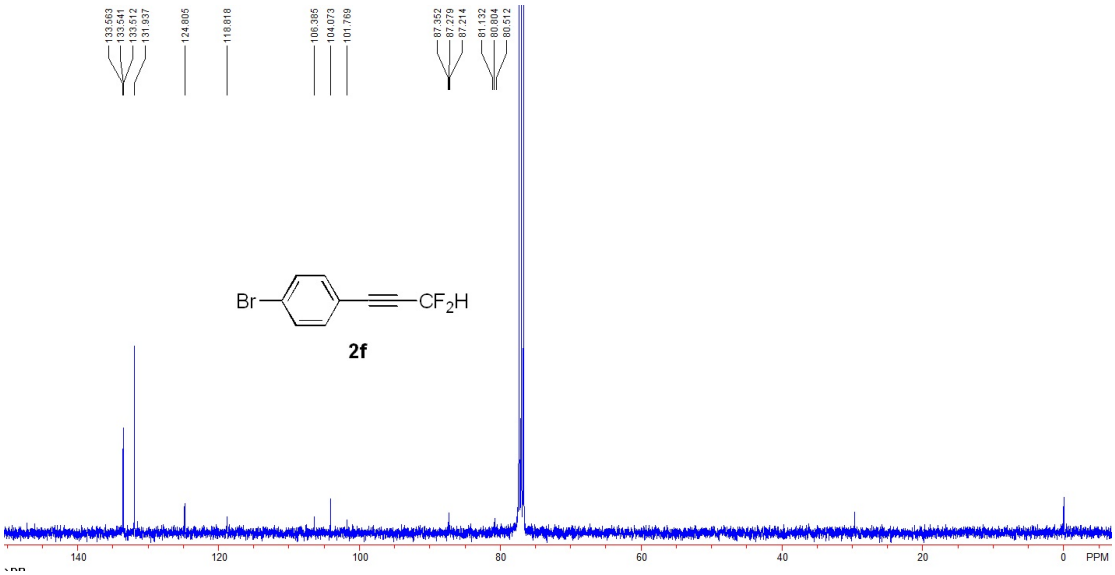
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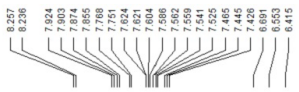
PPM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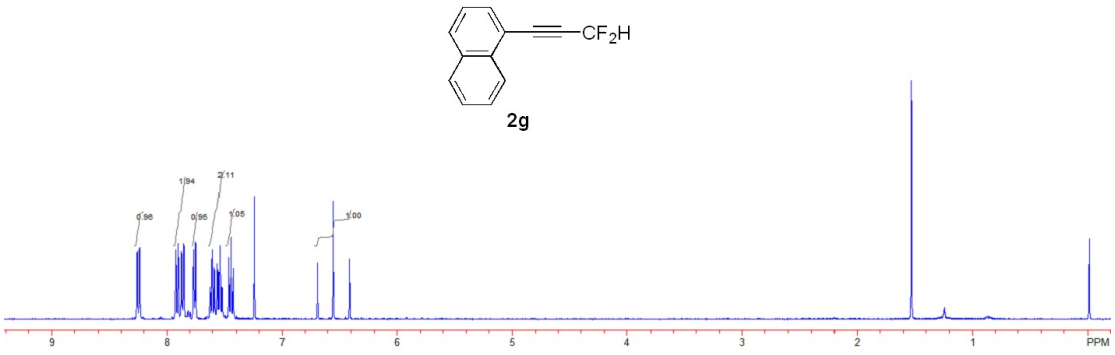
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2
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PPM


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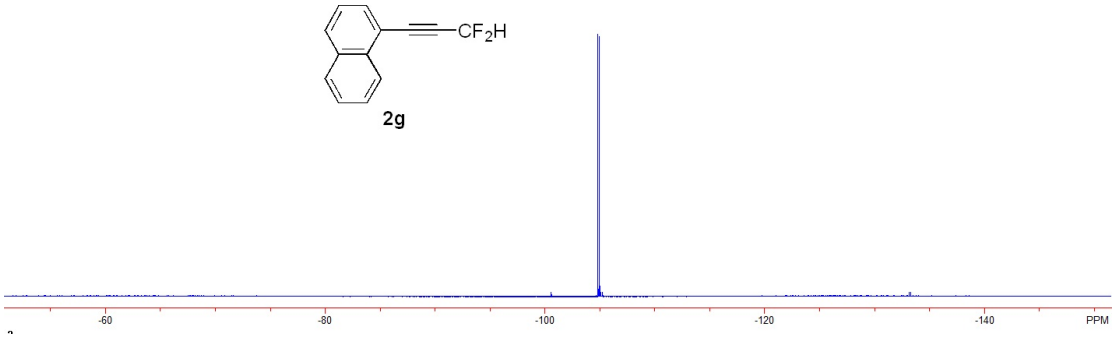
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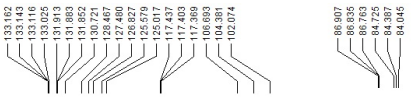
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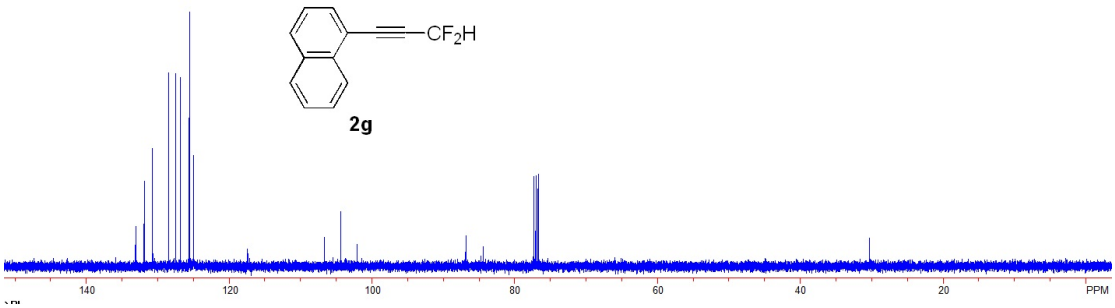
CF2H
2g
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120
100
80
60
40
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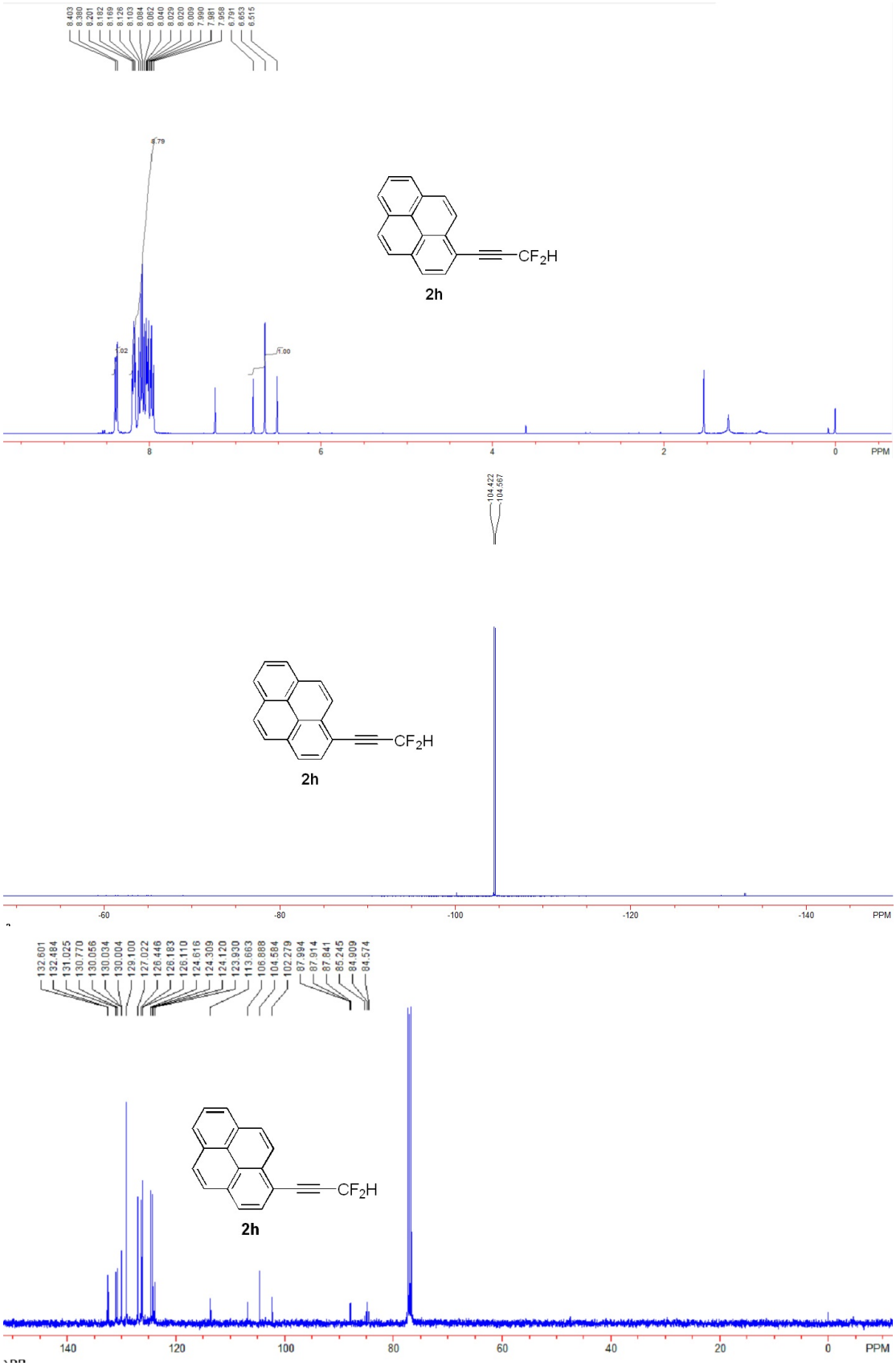
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124.309
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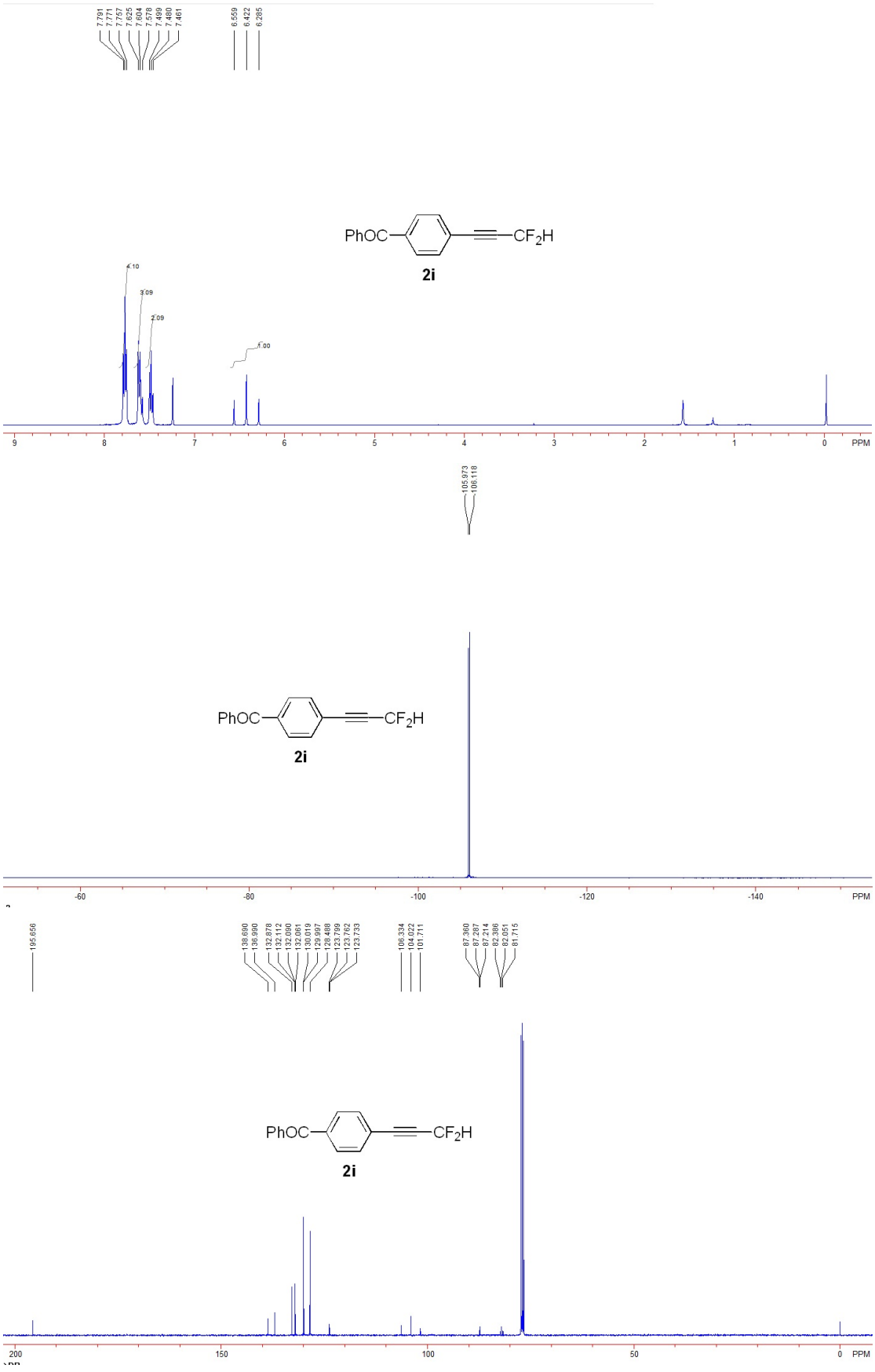
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2i
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2.09
1.00
9
8
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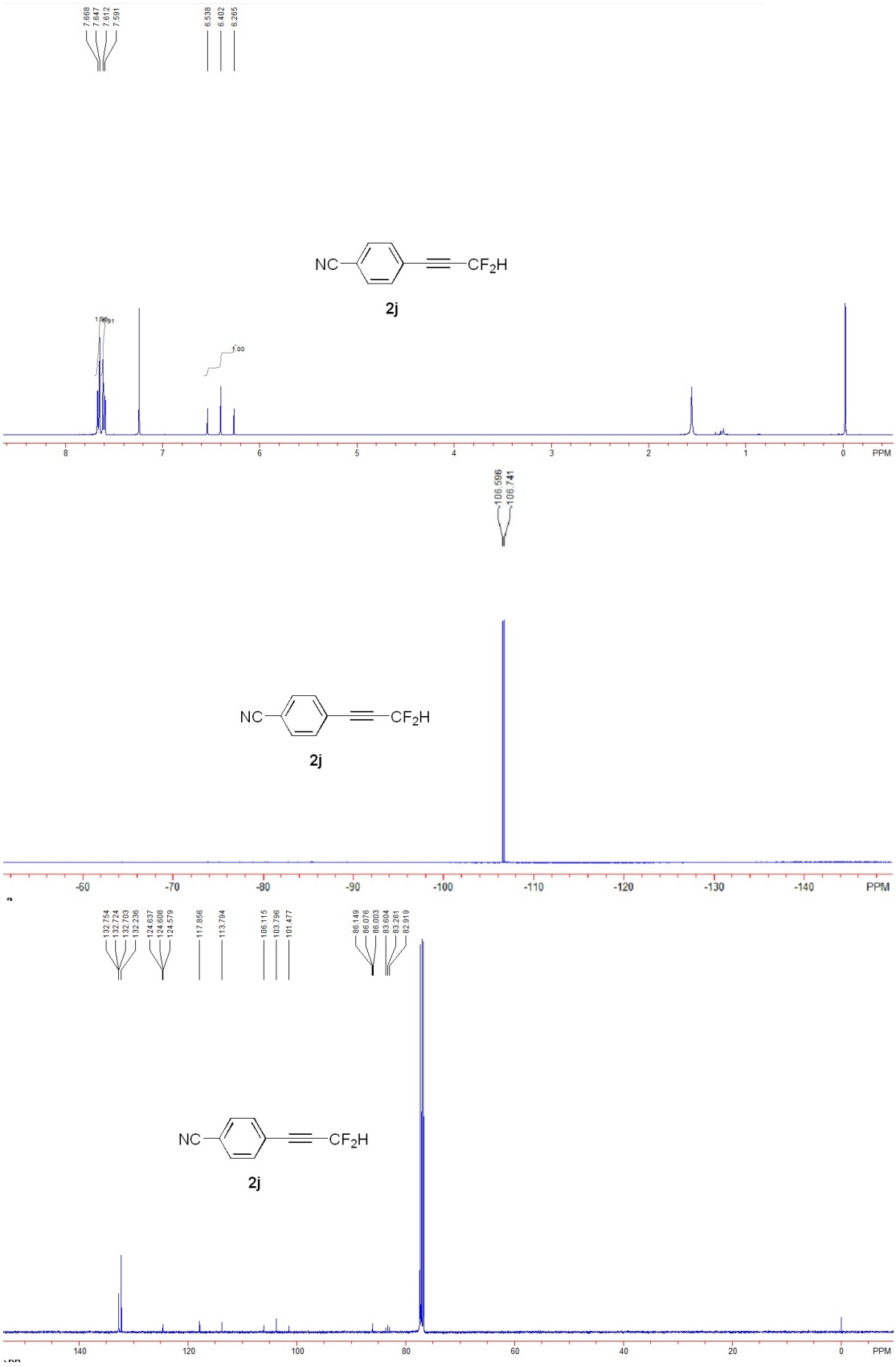
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5
4
3
2
1
0
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CF2H
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-120
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-140
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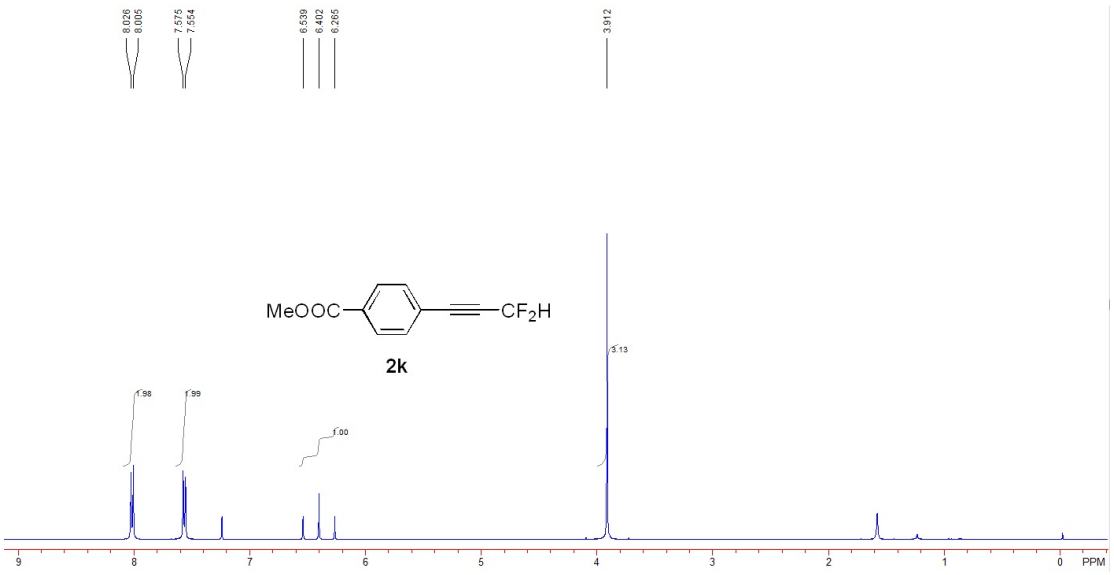
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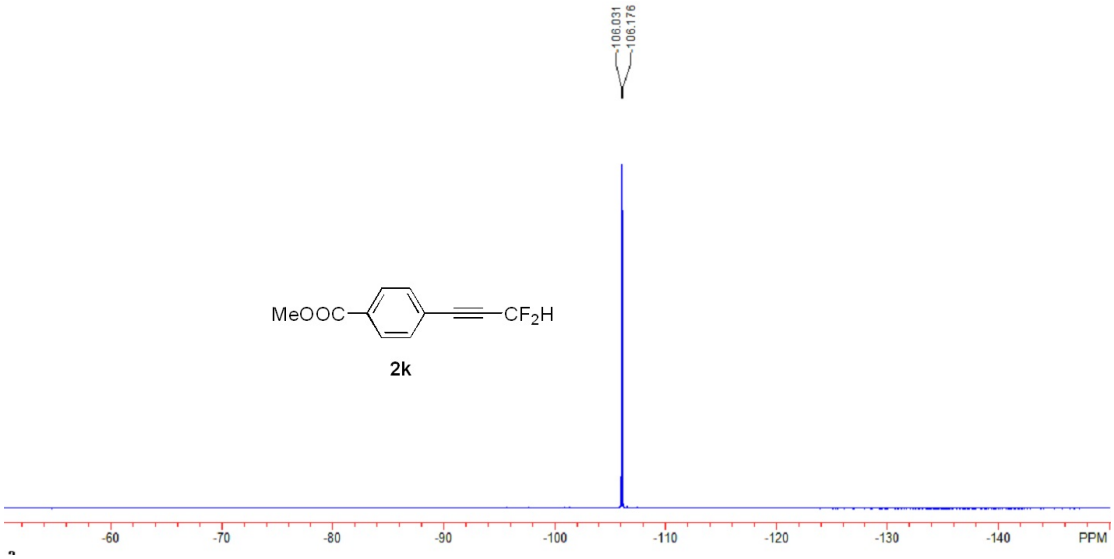
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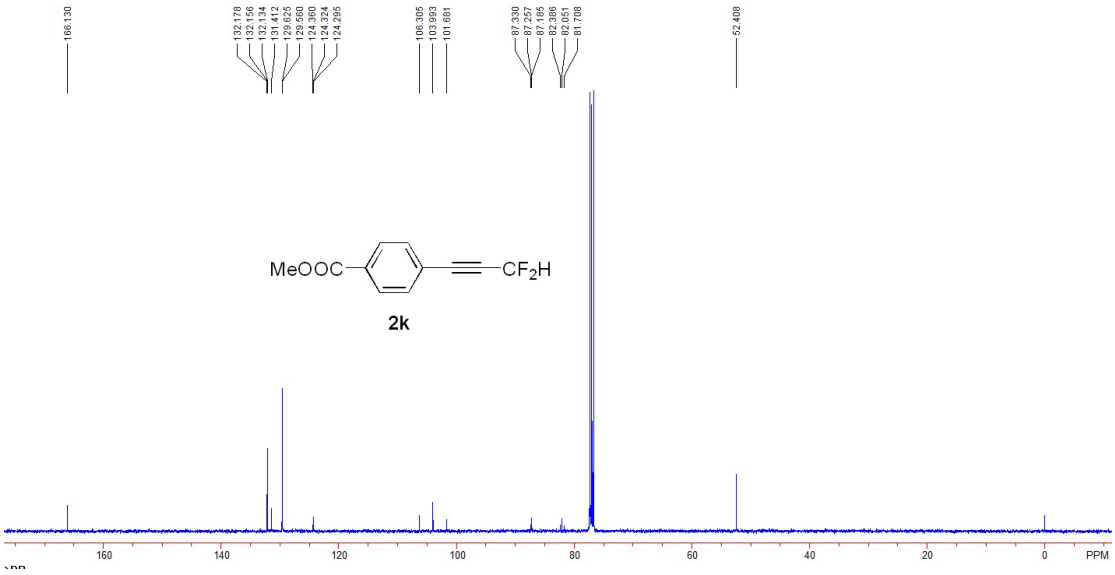
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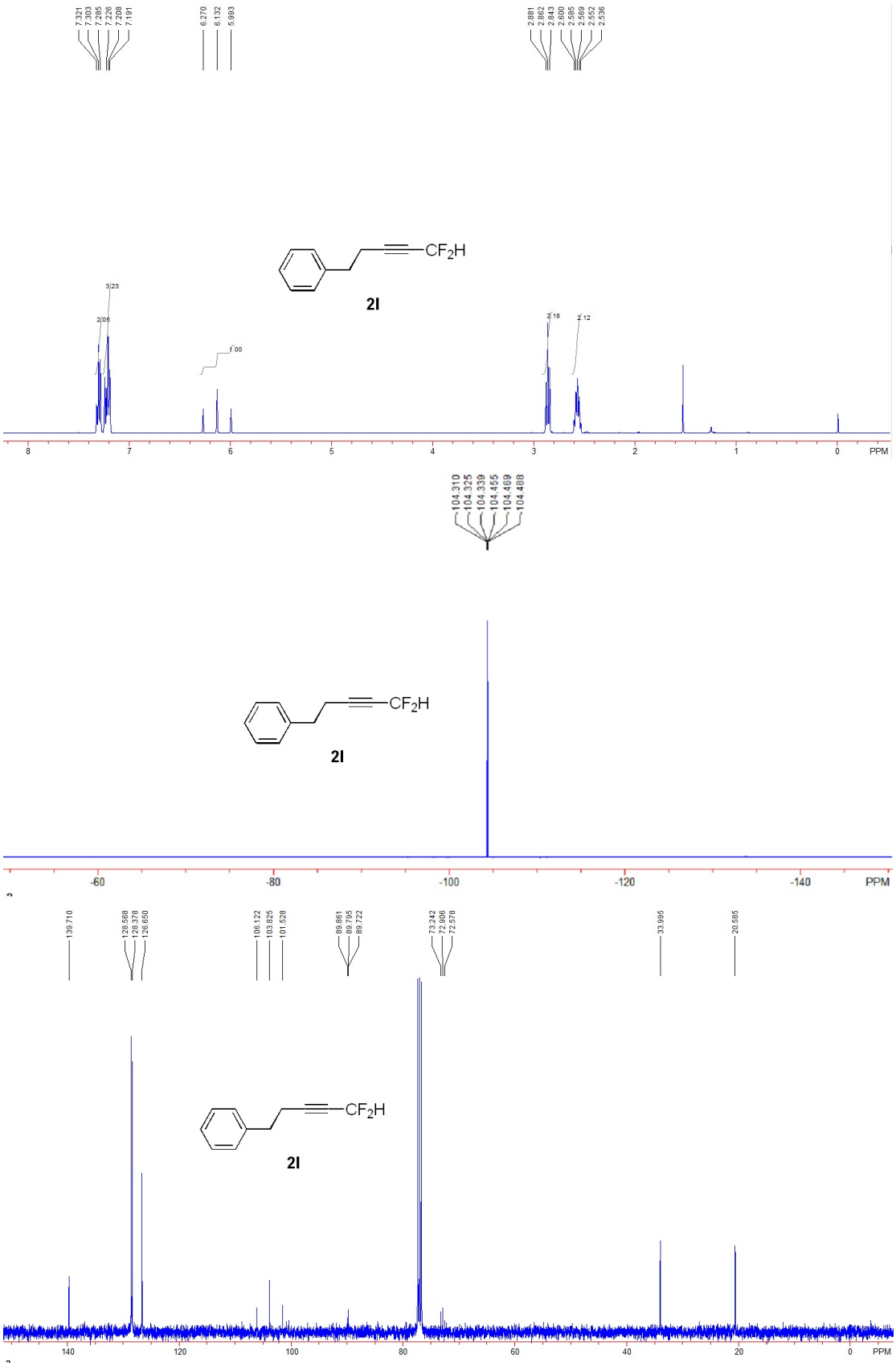
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2.585
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2.552
2.536
CF2H
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1.00
2.18
2.12
8
7
6
5
4
3
2
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PPM
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-120
-140
PPM
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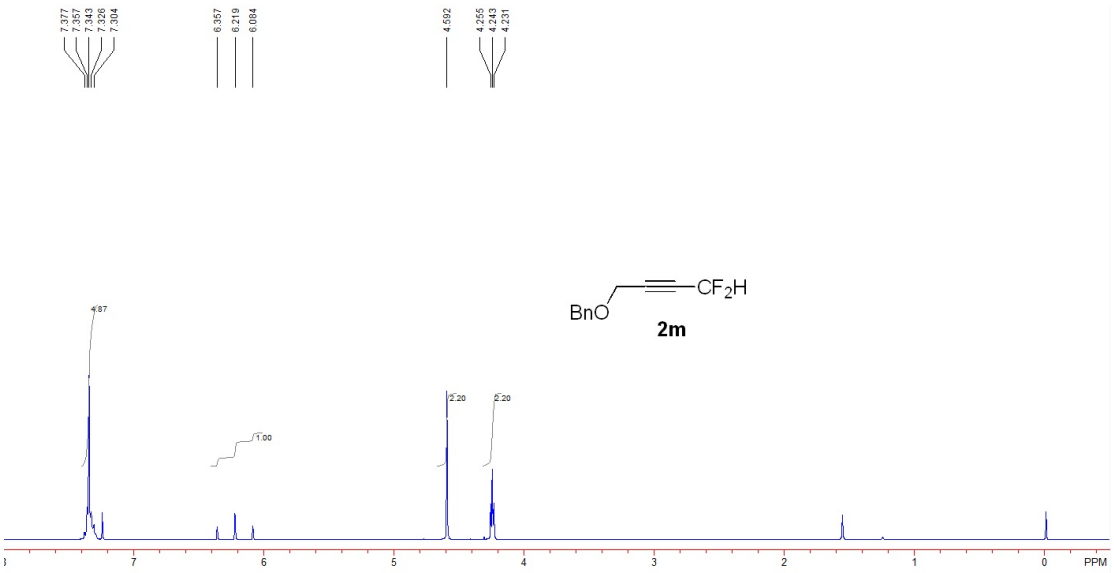
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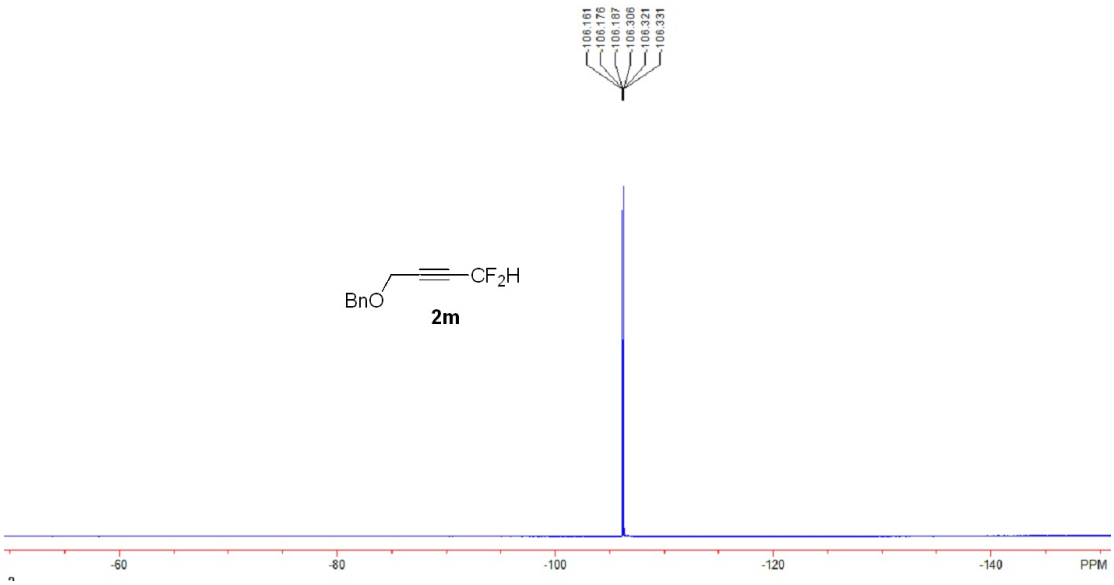
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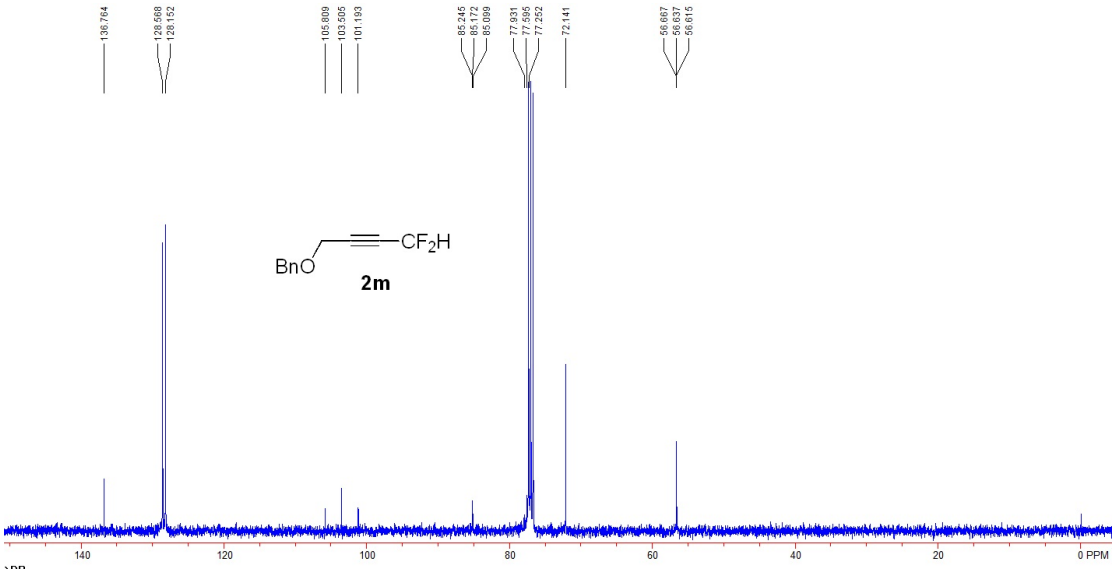
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CF2H
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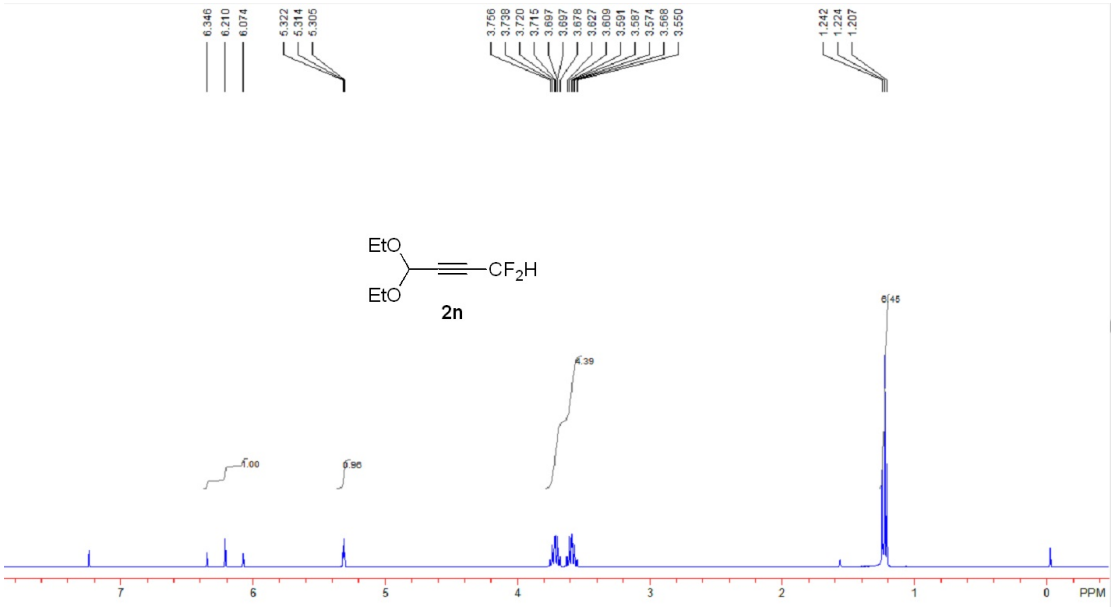
120
100
80
60
40
20
0 PPM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3.591
3.587
3.574
3.568
3.550
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1.224
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EtO
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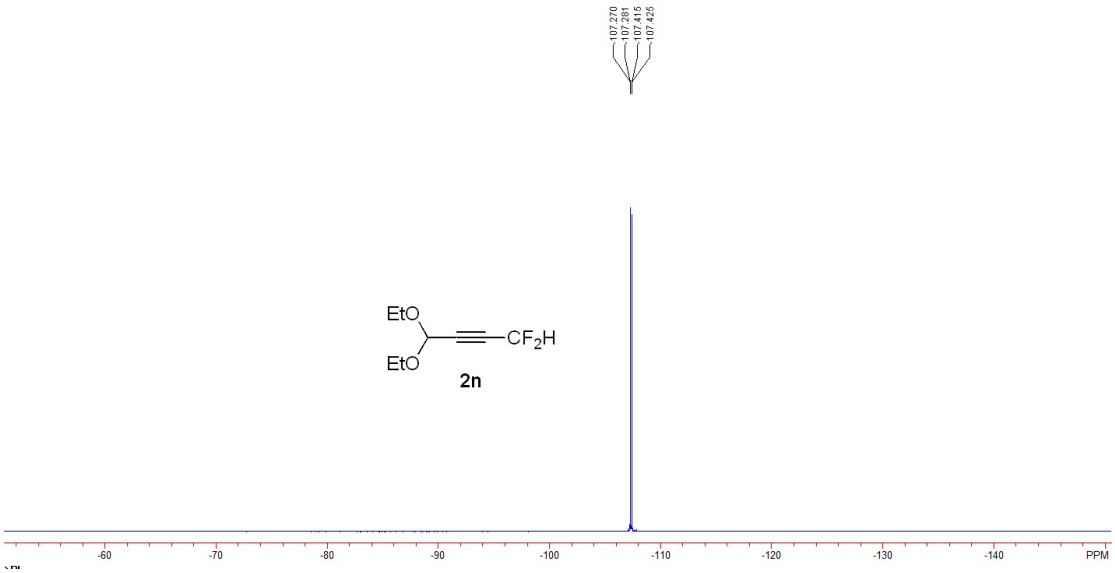
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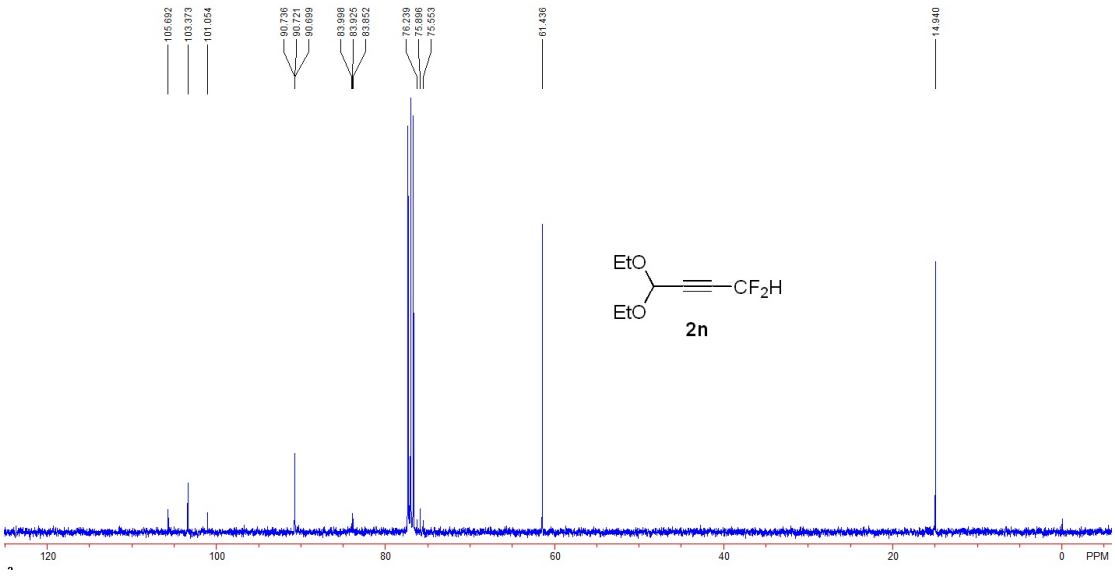
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EtO
CF2H
2n
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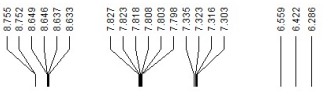
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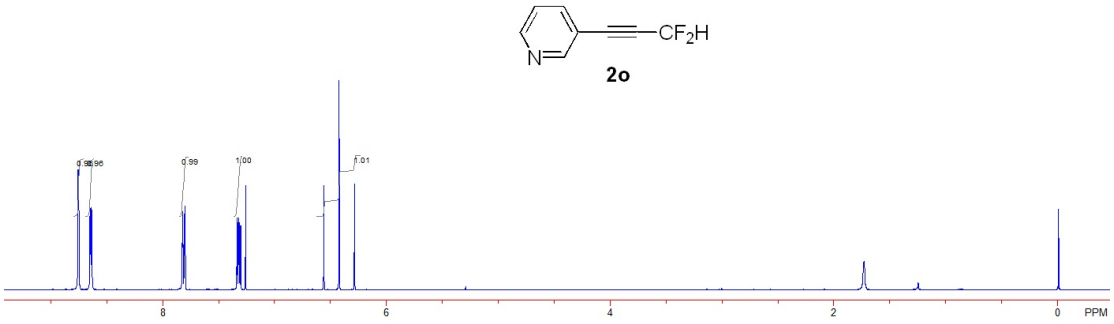
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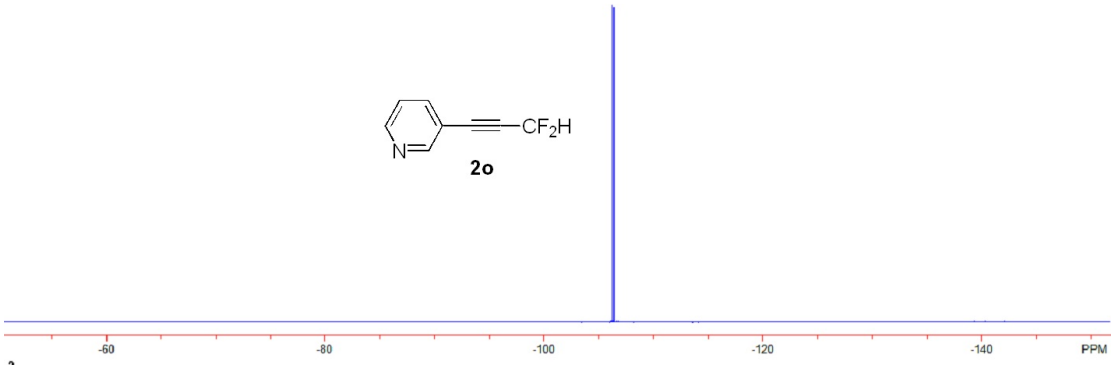
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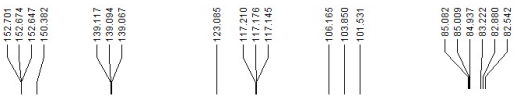
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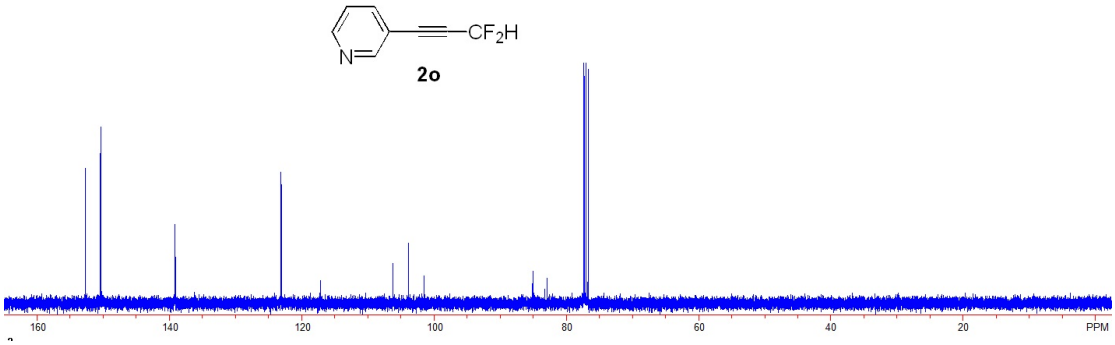
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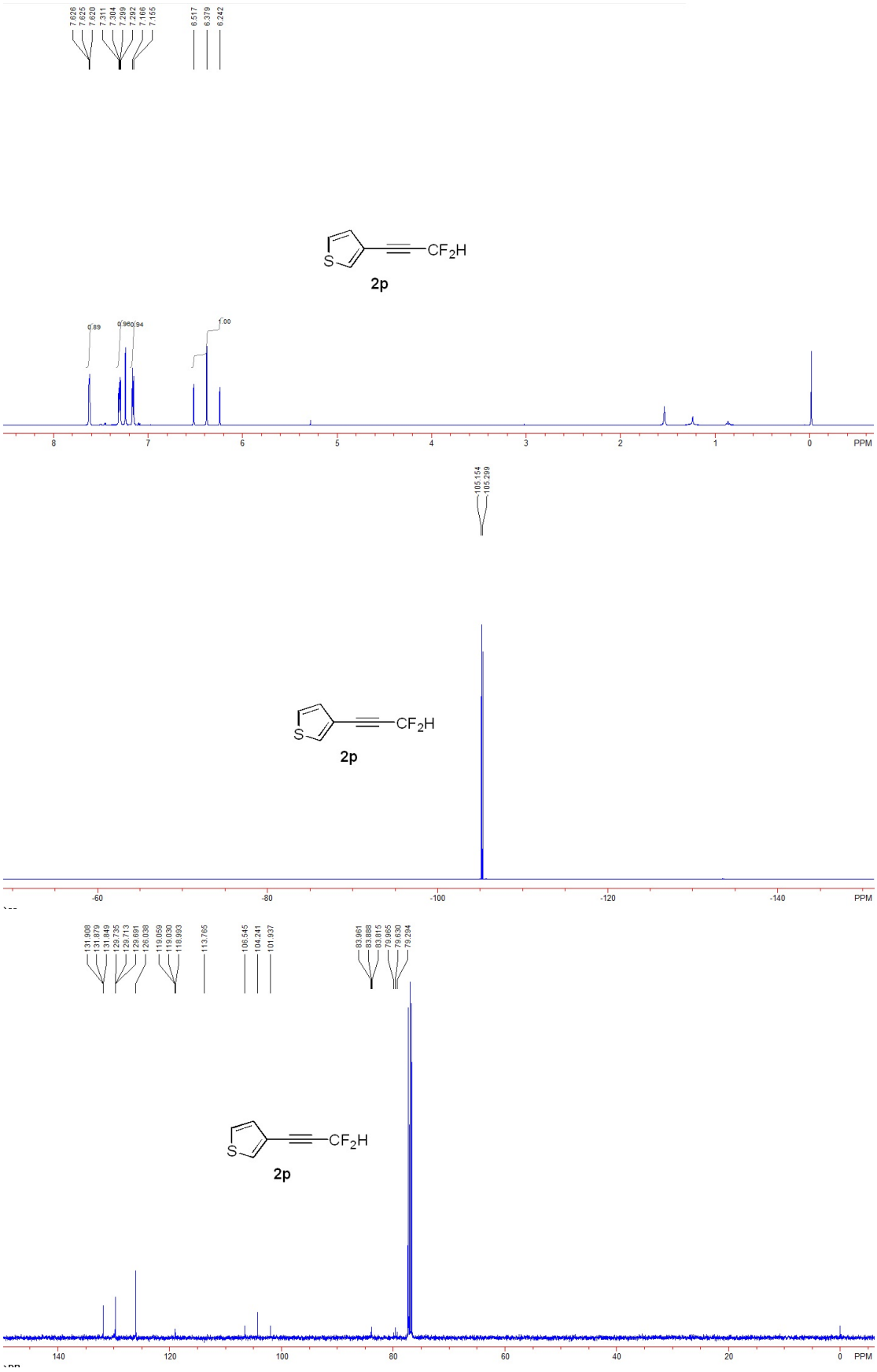
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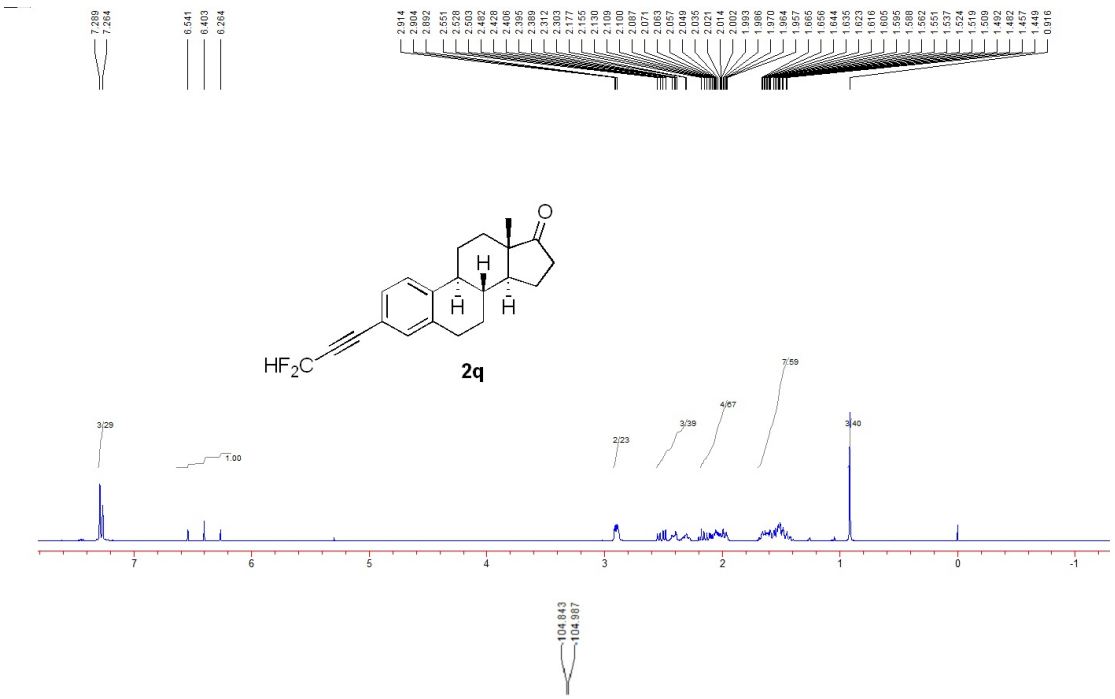
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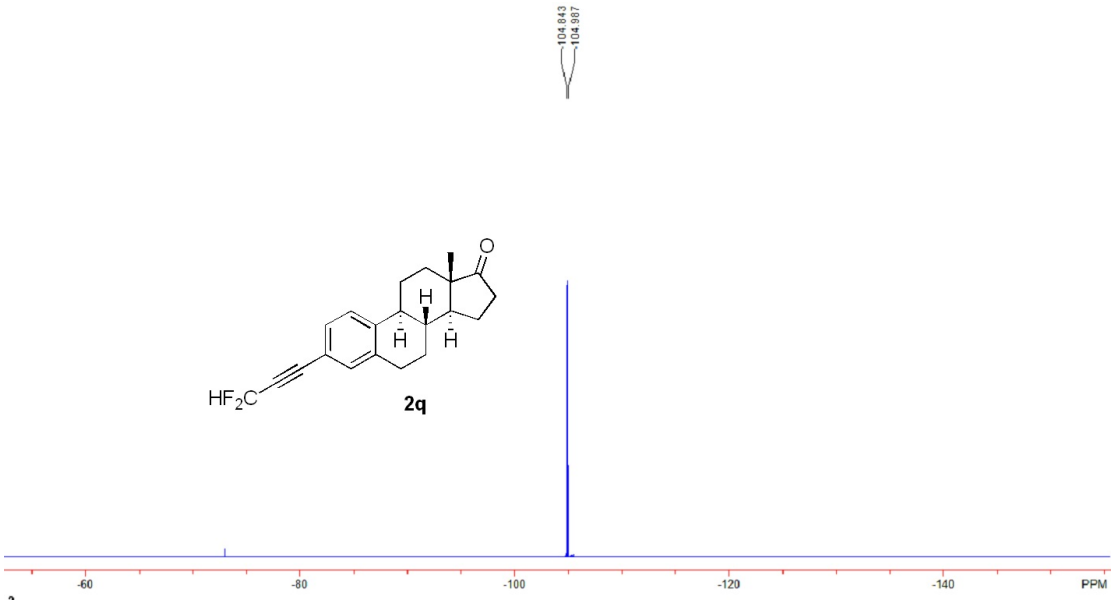
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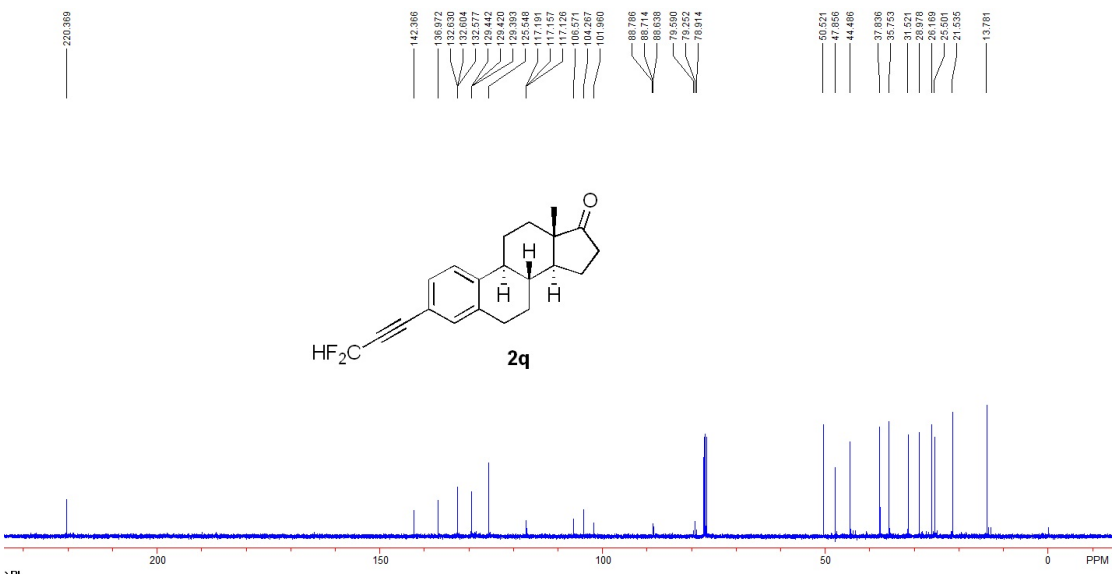
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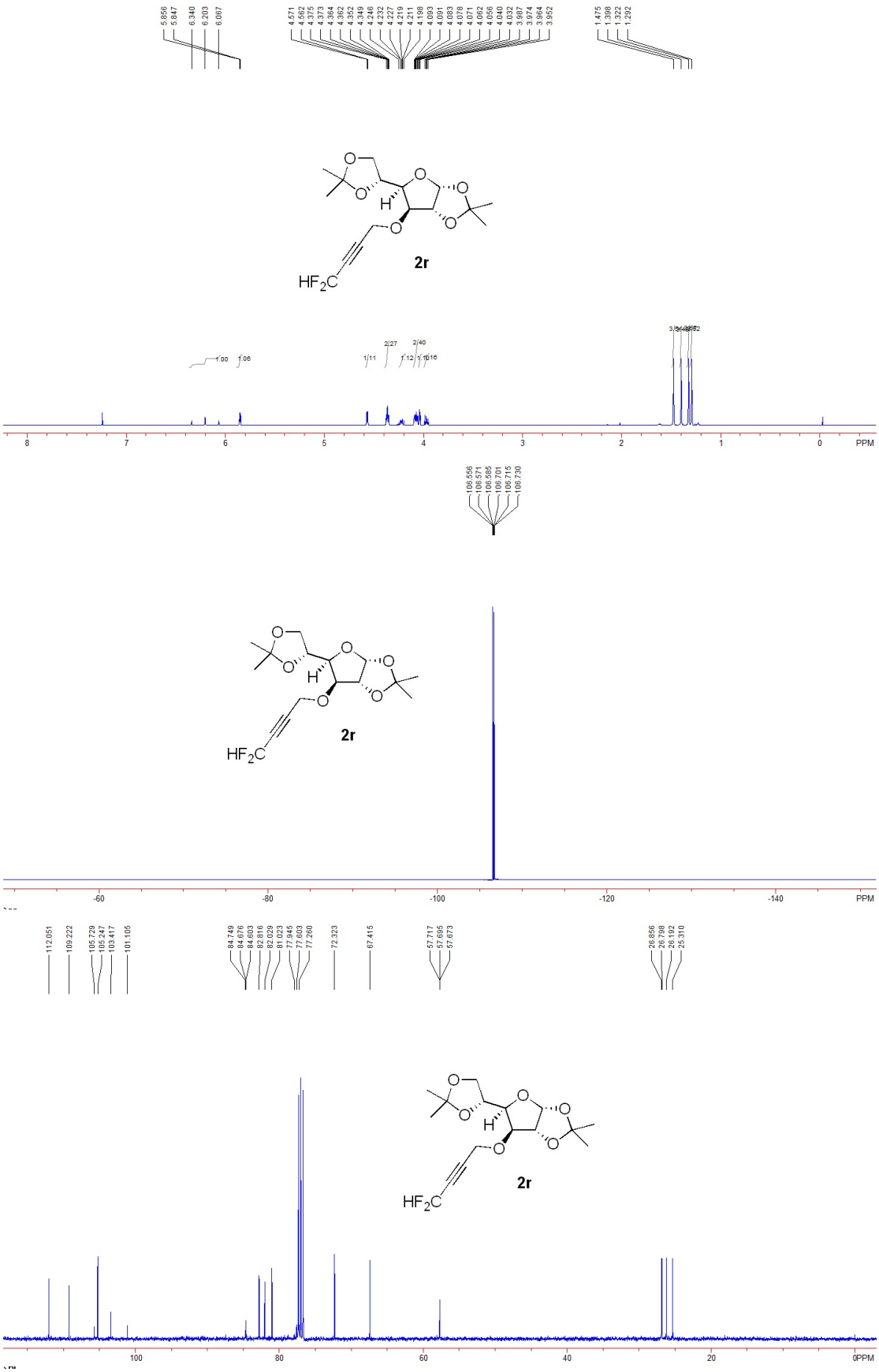
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