Difluoromethylation and *gem*-difluorocyclopropenation with difluorocarbene generated by decarboxylation

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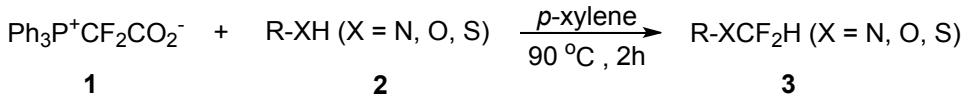
Electronic Supporting Information

Contents

1. General information

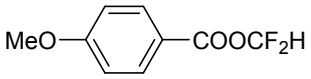
Solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. The solvent *p*-xylene was distilled from CaH_2. ^1H, ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^1H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (s) in Hz). Mass spectra were obtained on a GC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI or ESI mode.

2. Difluoromethylation of activated X-H bond (X = N, O and S)



1 **2** **3**

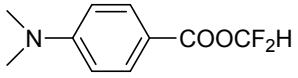
A dried Schlenk tube was charged with **2** (0.6 mmol), $Ph_3P^+CF_2CO_2^-$ (428 mg, 1.2 mmol) and *p*-xylene (3 mL) under N_2. The resulting mixture was stirred at 90 °C for 2h. After being cooled to room temperature, the mixture was subjected to flash column chromatography to afford pure product.



3a

Difluoromethyl 4-methoxybenzoate (3a):

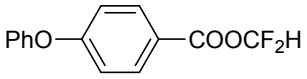
White solid. 84%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.28 (t, *J* = 71.4 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.27 (d, *J* = 71.4 Hz, 2F). GC-MS(EI) calcd. for $C_9H_8F_2O_3$ $[M]^+$: 202.0. Found: 202.0.



3b

Difluoromethyl 4-(dimethylamino)benzoate (3b):

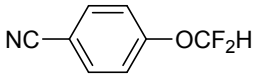
White solid. M.p. 101 – 102 °C. 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.2 Hz, 2H), 7.27 (t, *J* = 72.0 Hz, 1H), 6.62 (d, *J* = 9.2 Hz, 2H), 3.05 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.90 (d, *J* = 72.0 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.68 (t, *J* = 3.1 Hz), 154.30 (s), 132.28 (s), 113.12 (t, *J* = 255.2 Hz), 112.95 (s), 110.71 (s), 39.92 (s). IR (neat) ν = 2922, 2831, 1740, 1617, 1537, 1484, 1450, 1379, 1318, 1280, 1232, 1190, 1070, 1042, 997, 943, 825, 762, 749, 698, 655, 629, 552, 511, 499, 476 cm^{-1}. HRMS (EI) calcd. for $C_{10}H_{11}F_2NO_2$ $[M]^+$: 251.0758. Found: 251.0759.



3c

Difluoromethyl 4-phenoxybenzoate (3c):

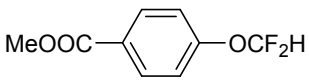
Light yellow liquid. 67%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.23 – 7.06 (m, 4H), 7.00 (d, *J* = 8.8 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.25 (d, *J* = 71.3 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.50 (s), 162.03 (t, *J* = 3.2 Hz), 154.98 (s), 132.66 (s), 130.18 (s), 125.06 (s), 121.12 (s), 120.44 (s), 117.28 (s), 112.97 (t, *J* = 257.3 Hz). IR (neat) ν = 3042, 1751, 1609, 1588, 1506, 1490, 1457, 1422, 1360, 1247, 1199, 1167, 1142, 1074, 1024, 1010, 910, 875, 851, 754, 693, 659, 631, 550, 497 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{10}F_2O_3$ $[M]^+$: 264.0598. Found: 264.0600.



3d

4-(difluoromethoxy)benzonitrile (3d):

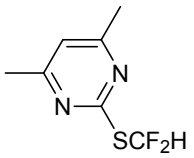
White solid. 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.61 (t, *J* = 72.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.35 (d, *J* = 72.5 Hz, 2F). GC-MS(EI) calcd. for $C_8H_5F_2NO$ $[M]^+$: 169.0. Found: 169.0.



3e

Methyl 4-(difluoromethoxy)benzoate (3e):

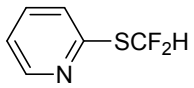
White solid. 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.59 (t, *J* = 73.2 Hz, 1H), 3.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.80 (d, *J* = 73.2 Hz, 2F). GC-MS(EI) calcd. for $C_9H_8F_2O_3$ $[M]^+$: 202.0. Found: 202.0.



3f

2-((difluoromethyl)thio)-4,6-dimethylpyrimidine (3f):

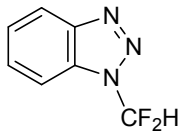
Light yellow solid. 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 56.0 Hz, 1H), 6.79 (s, 1H), 2.39 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.11 (d, *J* = 56.0 Hz, 2F). GC-MS(EI) calcd. for $C_7H_8F_2N_2S$ $[M]^+$: 190.0. Found: 190.0.



3g

2-((difluoromethyl)thio)pyridine (3g):

Light yellow liquid. 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.7 Hz, 1H), 7.70 (t, *J* = 56.3 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.13 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.26 (d, *J* = 56.3 Hz, 2F). GC-MS(EI) calcd. for $C_6H_5F_2NS$ $[M]^+$: 161.0. Found: 161.0.

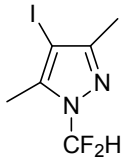


3h

1-(difluoromethyl)-1H-benzo[d][1,2,3]triazole (3h):

White solid. 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.89

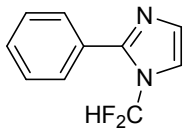
(t, J = 58.6 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.51 – 7.46 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.22 (d, J = 58.6 Hz, 2F). GC-MS(EI) calcd. for $C_7H_5F_2N_3$ $[M]^+$: 169.1. Found: 169.1.



3i

1-(difluoromethyl)-4-iodo-3,5-dimethyl-1H-pyrazole (3i):

White solid. 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 59.0 Hz, 1H), 2.44 (s, 3H), 2.23 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.12 (d, J = 59.0 Hz, 2F). GC-MS(EI) calcd. for $C_6H_7F_2IN_2$ $[M]^+$: 272.0. Found: 272.0.

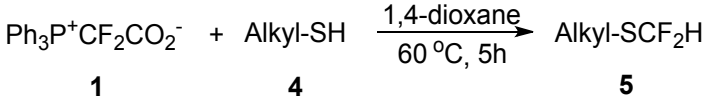


3j

1-(difluoromethyl)-2-phenyl-1H-imidazole (3j):

White solid. 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.51 – 7.46 (m, 3H), 7.37 (d, J = 1.3 Hz, 1H), 7.20 – 6.90 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.56 (d, J = 59.8 Hz, 2F). GC-MS(EI) calcd. for $C_{10}H_8F_2N_2$ $[M]^+$: 194.1. Found: 194.1.

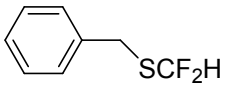
3. Difluoromethylation of aliphatic thiols



1 **4** **5**

A dried Schlenk tube was charged with **4** (0.6 mmol), $Ph_3P^+CF_2CO_2^-$ (428 mg, 1.2 mmol) and 1,4-dioxane (3 mL) under N_2. The resulting mixture was stirred at 60 °C for 5h. After being cooled to room temperature, the mixture was subjected to flash

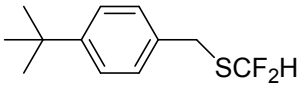
column chromatography to afford pure product.



5a

Benzyl(difluoromethyl)sulfane (5a):

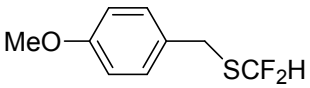
Colourless liquid. 43%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 5H), 6.71 (t, *J* = 56.6 Hz, 1H), 4.01 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.43 (d, *J* = 56.6 Hz, 2F). GC-MS(EI) calcd. for $C_8H_8F_2S$ $[M]^+$ 174.0. Found 174.0.



5b

(4-(tert-butyl)benzyl)(difluoromethyl)sulfane (5b):

Colourless liquid. 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.70 (t, *J* = 56.7 Hz, 1H), 3.98 (s, 2H), 1.30 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.52 (d, *J* = 56.7 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.71 (s), 133.08 (s), 128.62 (s), 125.77 (s), 120.38 (t, *J* = 272.7 Hz), 34.58 (s), 31.41 (t, *J* = 3.6 Hz), 31.33 (s). IR (neat) ν = 3029, 2965, 2908, 2870, 1910, 1612, 1516, 1465, 1414, 1395, 1365, 1323, 1305, 1269, 1250, 1204, 1108, 1059, 1027, 883, 837, 778, 746, 698, 657, 558, 517, 440 cm^{-1}. HRMS (EI) calcd. for $C_{12}H_{16}F_2S$ $[M]^+$: 230.0941. Found: 230.0938.

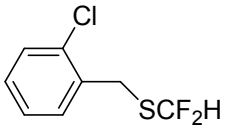


5c

(Difluoromethyl)(4-methoxybenzyl)sulfane (5c):

Colourless liquid. 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.72 (t, *J* = 56.6 Hz, 1H), 3.98 (s, 2H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.49 (d, *J* = 56.6 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$)

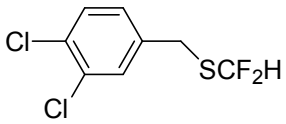
δ 159.06 (s), 130.06 (s), 128.04 (s), 120.34 (t, *J* = 272.6 Hz), 114.18 (s), 55.30 (s), 31.28 (t, *J* = 3.7 Hz). IR (neat) ν = 3005, 2959, 2838, 1612, 1585, 1514, 1465, 1442, 1320, 1303, 1246, 1178, 1059, 1033, 878, 832, 779, 743, 733, 670, 545, 516 cm^{-1}. HRMS (EI) calcd. for $C_9H_{10}F_2OS$ $[M]^+$: 204.0420. Found: 204.0416.



5d

(2-chlorobenzyl)(difluoromethyl)sulfane (5d):

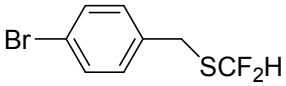
Light yellow liquid. 56%; ^1H NMR (400 MHz, $CDCl_3$)δ 7.41 – 7.38 (m, 2H), 7.25 – 7.22 (m, 2H), 6.81 (t, *J* = 56.3 Hz, 1H), 4.13 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.90 (d, *J* = 56.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.56 (s), 134.11 (s), 130.85 (s), 129.88 (s), 129.15 (s), 127.12 (s), 120.29 (t, *J* = 273.5 Hz), 29.45 (t, *J* = 3.8 Hz). IR (neat) ν = 3071, 2926, 1593, 1574, 1474, 1446, 1422, 1384, 1324, 1248, 1206, 1123, 1053, 1037, 947, 875, 825, 784, 755, 735, 688, 672, 438 cm^{-1}. HRMS (EI) calcd. for $C_8H_7ClF_2S$ $[M]^+$: 207.9925. Found: 207.9927.



5e

(3,4-dichlorobenzyl)(difluoromethyl)sulfane (5e):

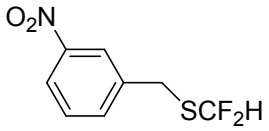
Light yellow liquid. 61%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 6.76 (t, *J* = 56.0 Hz, 1H), 3.96 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.00 (d, *J* = 56.0 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.86 (s), 132.76 (s), 131.78 (s), 130.77 (s), 130.69 (s), 128.20 (s), 119.83 (t, *J* = 274.0 Hz), 30.39 (t, *J* = 4.0 Hz). IR (neat) ν = 2967, 1728, 1593, 1563, 1538, 1514, 1472, 1423, 1396, 1324, 1282, 1244, 1206, 1135, 1063, 1032, 893, 823, 777, 760, 721, 699, 684, 653, 560, 466, 439 cm^{-1}. HRMS (EI) calcd. for $C_8H_6Cl_2F_2S$ $[M]^+$: 241.9535. Found: 241.9533.



5f

(4-bromobenzyl)(difluoromethyl)sulfane (5f):

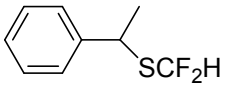
Light yellow liquid. 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.73 (t, *J* = 56.3 Hz, 1H), 3.96 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.20 (d, *J* = 56.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.49 (s), 131.94 (s), 130.58 (s), 121.63 (s), 120.03 (t, *J* = 273.5 Hz), 31.01 (t, *J* = 3.8 Hz). IR (neat) ν = 3848, 3814, 3699, 3452, 2925, 2286, 1902, 1591, 1548, 1488, 1422, 1404, 1324, 1248, 1200, 1180, 1071, 1012, 882, 806, 773, 758, 724, 683, 613, 494 cm^{-1}. HRMS (EI) calcd. for $C_8H_7BrF_2S$ $[M]^+$: 251.9420. Found: 251.9422.



5g

(Difluoromethyl)(3-nitrobenzyl)sulfane (5g):

Light yellow liquid. 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 6.81 (t, *J* = 55.8 Hz, 1H), 4.12 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.69 (d, *J* = 55.8 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.39 (s), 138.99 (s), 134.92 (s), 129.74 (s), 123.76 (s), 122.65 (s), 119.73 (t, *J* = 274.3 Hz), 30.60 (t, *J* = 4.0 Hz). IR (neat) ν = 3440, 3092, 2935, 1619, 1584, 1563, 1531, 1481, 1443, 1423, 1352, 1319, 1250, 1027, 922, 906, 865, 811, 780, 761, 742, 708, 680 cm^{-1}. HRMS (EI) calcd. for $C_8H_7F_2NO_2S$ $[M]^+$: 219.0166. Found: 219.0162.

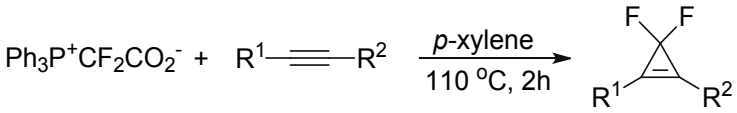


5h

(Difluoromethyl)(1-phenylethyl)sulfane (5h):

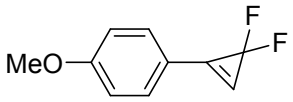
Colourless liquid. 59%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 2H), 7.26 – 7.19 (m, 3H), 6.77 (t, *J* = 56.3 Hz, 1H), 3.08 – 2.95 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.78 (d, *J* = 56.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.51 (s), 128.61 (s), 128.54 (s), 126.72 (s), 120.60 (t, *J* = 272.8 Hz), 36.74 (s), 28.55 (t, *J* = 3.0 Hz). IR (neat) ν = 3087, 3065, 3030, 2930, 2857, 1736, 1604, 1497, 1455, 1325, 1233, 1180, 1142, 1059, 1023, 880, 799, 775, 755, 713, 698, 561, 492, 442 cm^{-1}. HRMS (EI) calcd. for $C_9H_{10}F_2S$ $[M]^+$: 188.0471. Found: 188.0475.

4. *gem*-Difluorocyclopropenation of alkynes



1 **6** **7**

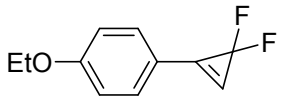
A dried Schlenk tube was charged with **6** (0.6 mmol), $Ph_3P^+CF_2CO_2^-$ (428 mg, 1.2 mmol) and *p*-xylene (3 mL) under N_2. The resulting mixture was stirred at 110 °C for 2h. After being cooled to room temperature, the mixture was subjected to flash column chromatography to afford pure product.



7a

1-(3,3-fluoroscopically-1-en-1-yl)-4-methoxybenzene (7a):

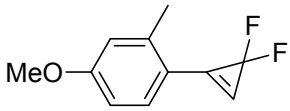
Yellow liquid. 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), δ (t, *J* = 1.8 Hz, 1H), δ 6.96 (d, *J* = 8.9 Hz, 2H), δ 3.83 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.24 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.22 (s), 133.19 (t, *J* = 10.3 Hz), 131.97 (s), 115.89 (s), 114.53 (s), 110.32 (t, *J* = 12.5 Hz), 102.06 (t, *J* = 269.3 Hz), 55.40 (s). IR (neat) ν = 3132, 2937, 2843, 1720, 1605, 1575, 1506, 1464, 1443, 1424, 1312, 1286, 1257, 1172, 1114, 1016, 838, 824, 792, 773, 717, 672, 598, 504, 412 cm^{-1}. HRMS (EI) calcd. for $C_{10}H_8F_2O$ $[M]^+$: 182.0543. Found: 182.0539.



7b

1-(3,3-difluorocycloprop-1-en-1-yl)-4-ethoxybenzene (7b):

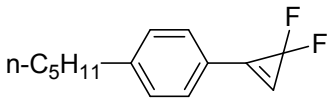
Light yellow liquid. 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.26 (t, *J* = 1.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.26 (d, *J* = 1.8 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.66 (s), 133.24 (t, *J* = 10.2 Hz), 131.99 (s), 115.70 (s), 115.01 (s), 110.16 (t, *J* = 12.6 Hz), 102.11 (t, *J* = 269.3 Hz), 63.76 (s), 14.64 (s). IR (neat) ν = 3131, 2985, 2938, 1720, 1605, 1575, 1506, 1478, 1445, 1396, 1287, 1256, 1173, 1117, 1043, 1014, 922, 841, 826, 798, 772, 717, 689, 645, 610, 504 cm^{-1}. HRMS (EI) calcd. for $C_{11}H_{10}F_2O$ $[M]^+$: 196.0700. Found: 196.0698.



7c

1-(3,3-difluorocycloprop-1-en-1-yl)-4-methoxy-2-methylbenzene (7c):

Light yellow liquid. 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 1H), 7.26 (t, *J* = 2.2 Hz, 1H), 6.82 – 6.78 (m, 2H), 3.83 (s, 3H), 2.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.22 (s, 2F). GC-MS(EI) calcd. for $C_{11}H_{10}F_2O$ $[M]^+$: 196.1. Found: 196.1.

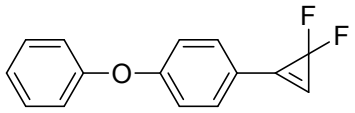


7d

1-(3,3-difluorocycloprop-1-en-1-yl)-4-pentylbenzene (7d):

Yellow liquid. 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 1.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.67 (t, 7.6 Hz, 2H), 1.68 – 1.61 (m, 2H), 1.39 – 1.29 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{19}F NMR (376 MHz, CDCl3) δ -106.34 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.26 (s), 133.81 (t, *J* = 10.4 Hz),

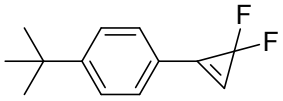
130.15 (s), 129.15 (s), 120.77 (s), 112.13 (t, J = 12.4 Hz), 101.90 (t, J = 269.7 Hz), 36.02 (s), 31.40 (s), 30.88 (s), 22.50 (s), 13.98 (s). IR (neat) ν = 3131, 3030, 2958, 2932, 2859, 1719, 1608, 1506, 1467, 1417, 1379, 1310, 1287, 1234, 1181, 1178, 1023, 972, 846, 823, 803, 774, 503 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{16}F_2$ $[M]^+$: 222.1220. Found: 222.1217.



7e

1-(3,3-difluorocycloprop-1-en-1-yl)-4-phenoxybenzene (7e):

Yellow solid. M.p. 58 – 59 °C. 76%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 8.6 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.24 – 7.16 (m, 1H), 7.07 – 7.03 (m, 4H). ^{19}F NMR (282 MHz, CDCl3) δ -106.42 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.61 (s), 155.65 (s), 133.11 (t, J = 10.4 Hz), 132.05 (s), 130.08 (s), 124.55 (s), 120.00 (s), 118.31 (s), 117.84 (s), 111.58 (t, J = 12.5 Hz), 101.79 (t, J = 268.0 Hz). IR (neat) ν = 3393, 3205, 3132, 2938, 1913, 1723, 1604, 1586, 1500, 1489, 1455, 1422, 1310, 1287, 1245, 1195, 1167, 1156, 1109, 1071, 1045, 1000, 915, 869, 842, 817, 780, 759, 716, 696, 648, 610, 587, 502, 426, 409 cm^{-1}. HRMS (EI) calcd. for $C_{15}H_{10}F_2O$ $[M]^+$: 244.0700. Found: 244.0702.

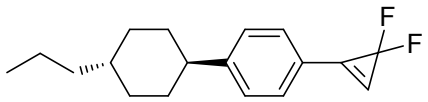


7f

1-(tert-butyl)-4-(3,3-difluorocycloprop-1-en-1-yl)benzene (7f):

Light yellow liquid. 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.5Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.40 (t, J = 1.7 Hz, 1H), 1.36 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.34 (d, J = 1.6 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.33 (s), 133.73 (t, J = 10.4 Hz), 129.98 (s), 126.06 (s), 120.57 (s), 112.31 (t, J = 12.4 Hz), 101.87 (t, J = 269.7 Hz), 35.11 (s), 31.11 (s). IR (neat) ν = 3130, 2966, 2907, 2871, 1719, 1606, 1508, 1464, 1411, 1396, 1366, 1318, 1300, 1285, 1232, 1191, 1122, 1094,

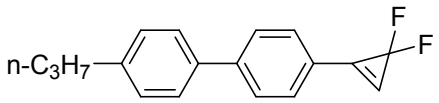
1023, 973, 843, 817, 779, 749, 733, 541, 504 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{14}F_2$ $[M]^+$: 208.1064. Found: 208.1065.



7g

1-(3,3-difluorocycloprop-1-en-1-yl)-4-((1s,4r)-4-propylcyclohexyl)benzene (7g):

Yellow solid. M.p. 37 – 38 °C. 76%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 1.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.55 – 2.48 (m, 1H), 1.90 – 1.85 (m, 4H), 1.52 – 1.39 (m, 2H), 1.35 (m, 3H), 1.26 – 1.17 (m, 2H), 1.12 – 0.98 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.33 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.09 (s), 133.81 (t, *J* = 10.4 Hz), 130.22 (s), 127.61 (s), 120.93 (s), 112.12 (t, *J* = 12.3 Hz), 101.89 (t, *J* = 269.7 Hz), 44.80 (s), 39.65 (s), 36.96 (s), 34.09 (s), 33.40 (s), 20.03 (s), 14.40 (s). IR (neat) ν = 3133, 3031, 2959, 2926, 2869, 2848, 1914, 1718, 1607, 1553, 1505, 1466, 1446, 1418, 1377, 1312, 1288, 1233, 1216, 1178, 1153, 1109, 1012, 976, 968, 839, 826, 812, 778, 730, 712, 621, 528, 503 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{22}F_2$ $[M]^+$: 276.1690. Found: 276.1692.

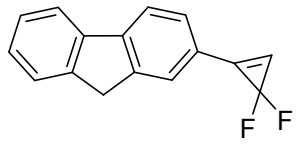


7h

4-(3,3-difluorocycloprop-1-en-1-yl)-4'-propyl-1,1'-biphenyl (7h):

Yellow solid. M.p. 121 – 122 °C. 59%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 4H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 1.2 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.68 (t, *J* = 7.4, 2H), 1.78 – 1.67 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.20 (d, *J* = 1.2 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.38 (s), 143.00 (s), 137.14 (s), 133.61 (t, *J* = 10.4 Hz), 130.57 (s), 129.12 (s), 127.46 (s), 127.00 (s), 121.81 (s), 113.00 (t, *J* = 12.3 Hz), 101.79 (t, *J* = 270.0 Hz), 37.70 (s), 24.51 (s), 13.85 (s). IR (neat) ν = 3136, 3030, 2960, 2927, 2855, 1918, 1716, 1604,

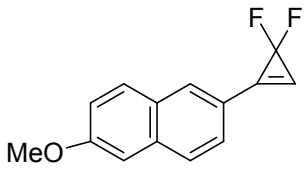
1492, 1466, 1401, 1383, 1318, 1297, 1194, 1184, 1136, 1096, 1031, 974, 821, 779, 753, 661, 591, 551, 503, 475, 416 cm^{-1}. HRMS (EI) calcd. for $C_{18}H_{16}F_2$ $[M]^+$: 270.1220. Found: 270.1218.



7i

2-(3,3-difluorocycloprop-1-en-1-yl)-9H-fluorene (7i):

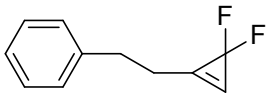
Yellow solid. M.p. 104 – 105 °C. 67%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 3H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.41 – 7.29 (m, 3H), 3.83 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.08 (s, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.09 (s), 143.98 (s), 143.76 (s), 140.48 (s), 134.01 (t, *J* = 10.3 Hz), 129.19 (s), 127.97 (s), 127.09 (s), 126.74 (s), 125.23 (s), 121.33 (s), 120.66 (s), 120.31 (s), 112.21 (t, *J* = 12.4 Hz), 102.04 (t, *J* = 269.8 Hz), 36.74 (s). IR (neat) ν = 3127, 2903, 1719, 1608, 1481, 1469, 1453, 1427, 1398, 1338, 1283, 1273, 1222, 1198, 1181, 1152, 1125, 1102, 1004, 953, 900, 886, 845, 826, 804, 790, 764, 748, 738, 684, 654, 644, 504, 417 cm^{-1}. HRMS (EI) calcd. for $C_{16}H_{10}F_2$ $[M]^+$: 240.0751. Found: 240.0748.



7j

2-(3,3-difluorocycloprop-1-en-1-yl)-6-methoxynaphthalene (7j):

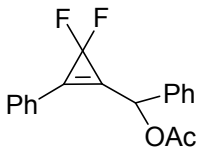
White solid. 78%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.83 – 7.79 (m, 2H), 7.64 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.45 (t, *J* = 1.7 Hz, 1H), 7.21 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 3.95 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.17 (s, 2F). GC-MS(EI) calcd. for $C_{14}H_{10}F_2O$ $[M]^+$: 232.1. Found: 232.2.



7l

(2-(3,3-difluorocycloprop-1-en-1-yl)ethyl)benzene (7l):

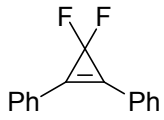
Light yellow liquid. 60%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 2H), 7.25 – 7.18 (m, 4H), 2.95 (t, *J* = 6.9 Hz, 2H), 2.82 (t, *J* = 6.9 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -103.96 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.66 (s), 133.24 (t, *J* = 10.2 Hz), 131.99 (s), 115.70 (s), 115.01 (s), 110.16 (t, *J* = 12.6 Hz), 102.11 (t, *J* = 269.3 Hz), 63.76 (s), 14.64 (s). IR (neat) ν = 3307, 3127, 3088, 3065, 3030, 2930, 2864, 1723, 1604, 1538, 1497, 1455, 1423, 1309, 1250, 1078, 1017, 935, 815, 790, 750, 700, 554, 498 cm^{-1}. HRMS (EI) calcd. for $C_{11}H_{10}F_2$ $[M]^+$: 180.0751. Found: 180.0747.



7m

(3,3-difluoro-2-phenylcycloprop-1-en-1-yl)(phenyl)methyl acetate (7m):

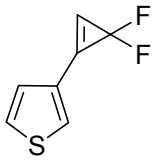
Light yellow solid. 45%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 10H), 6.87 (t, *J* = 2.1 Hz, 1H), 2.20 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.76 – -108.51 (m, 2F). MS(ESI) calcd. for $C_{18}H_{14}F_2O_2$ $[M+Na]^+$: 323.1. Found: 323.1.



7n

(3,3-difluorocycloprop-1-ene-1,2-diyl)dibenzene (7n):

White solid. 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.9 Hz, 4H), 7.55 – 7.46 (m, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.14 (s, 2F). GC-MS(EI) calcd. for $C_{15}H_{10}F_2$ $[M]^+$: 228.1. Found: 228.0.



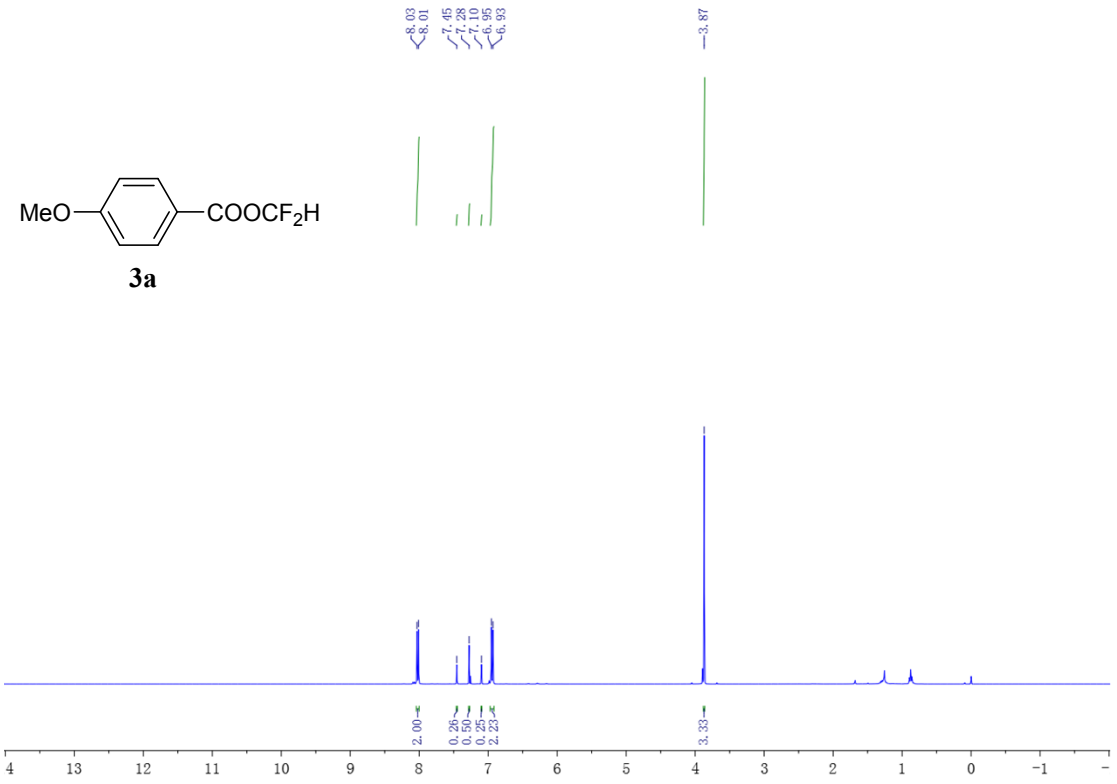
7o

3-(3,3-difluorocycloprop-1-en-1-yl)thiophene (7o):

Light yellow liquid. 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.4 Hz, 1H), 7.42 (dd, *J* = 4.5, 2.9 Hz, 1H), 7.34 (d, *J* = 5.0 Hz, 1H), 7.28 (t, *J* = 1.6 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.18 (s, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 130.84 (t, *J* = 1.5 Hz), 128.29 (t, *J* = 10.5 Hz), 127.70 (s), 127.17 (s), 124.37 (s), 110.86 (t, *J* = 12.4 Hz), 100.83 (t, *J* = 270.1 Hz). IR (neat) ν = 3132, 1725, 1508, 1409, 1379, 1298, 1244, 1204, 1183, 1102, 1077, 1017, 910, 867, 829, 820, 795, 766, 698, 636, 504 cm^{-1}. HRMS (EI) calcd. for $C_7H_4F_2S$ $[M]^+$: 158.0002. Found: 158.0004.

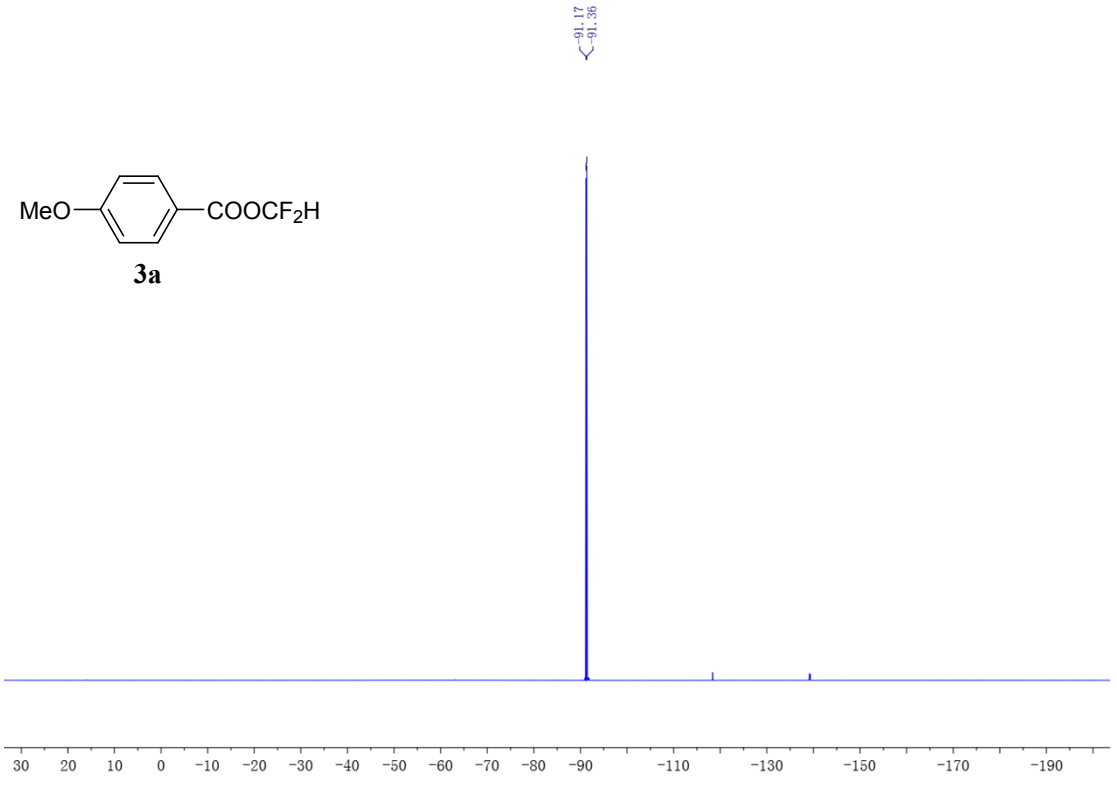
5. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra.

^{1}H NMR



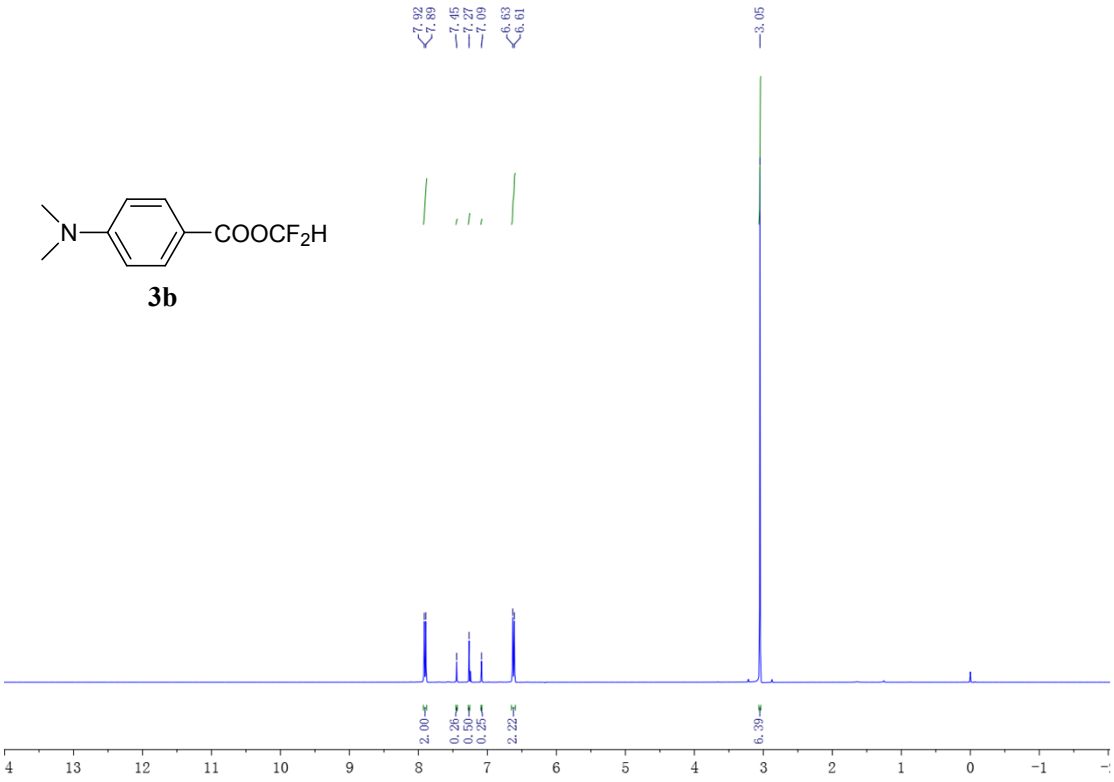
3a

^{19}F NMR



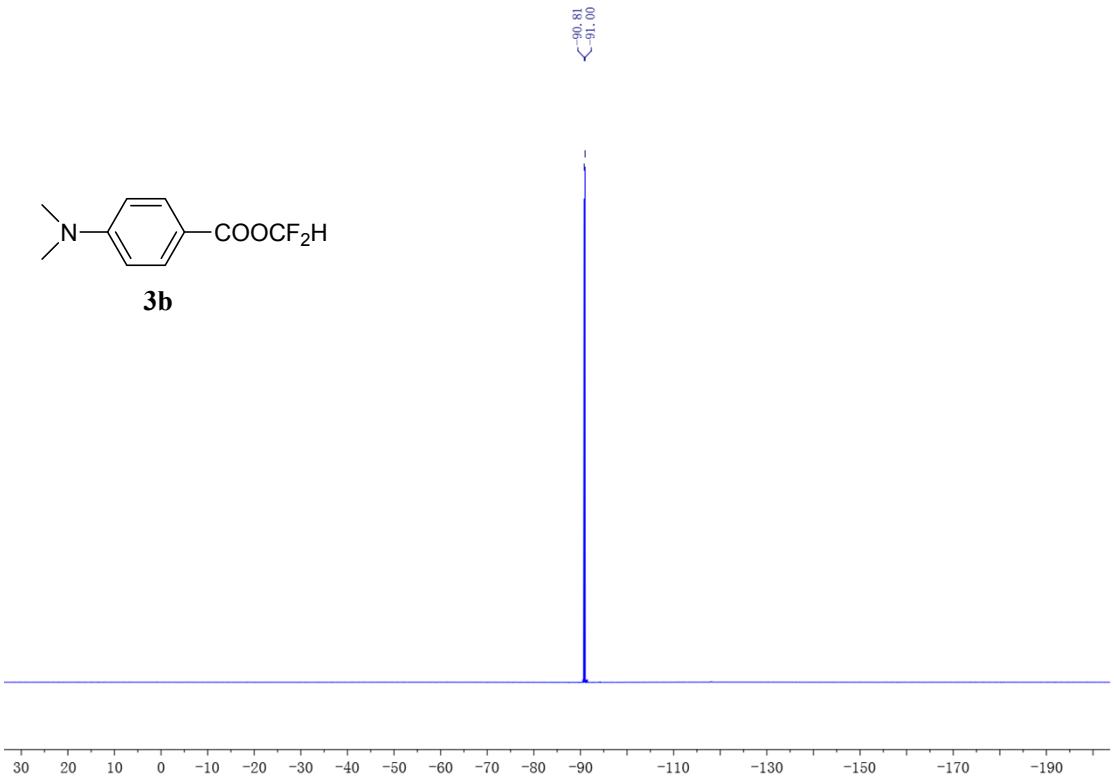
3a

^{1}H NMR



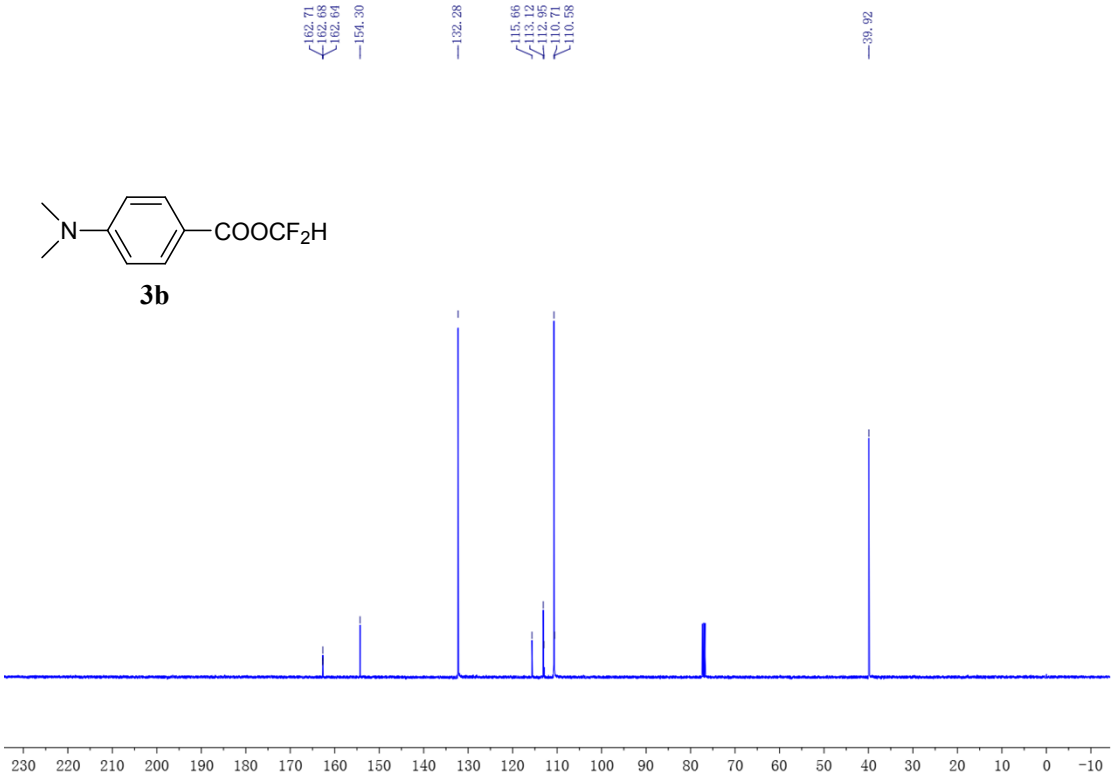
3b

^{19}F NMR



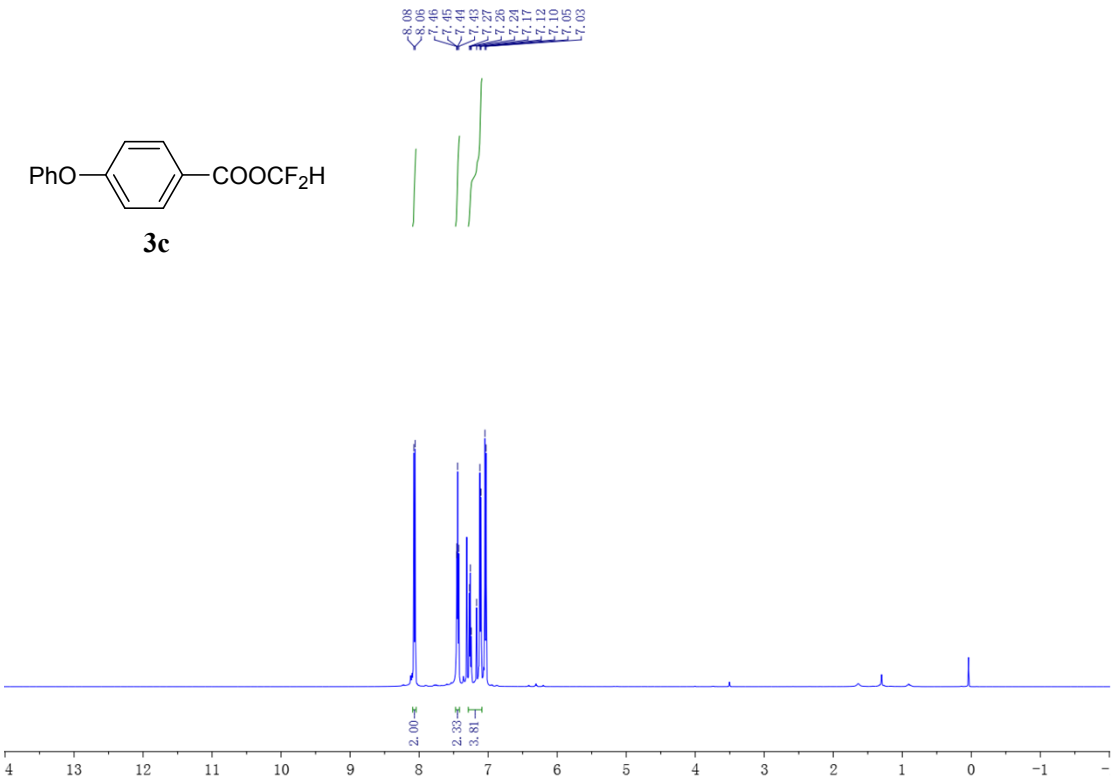
3b

^{13}C NMR



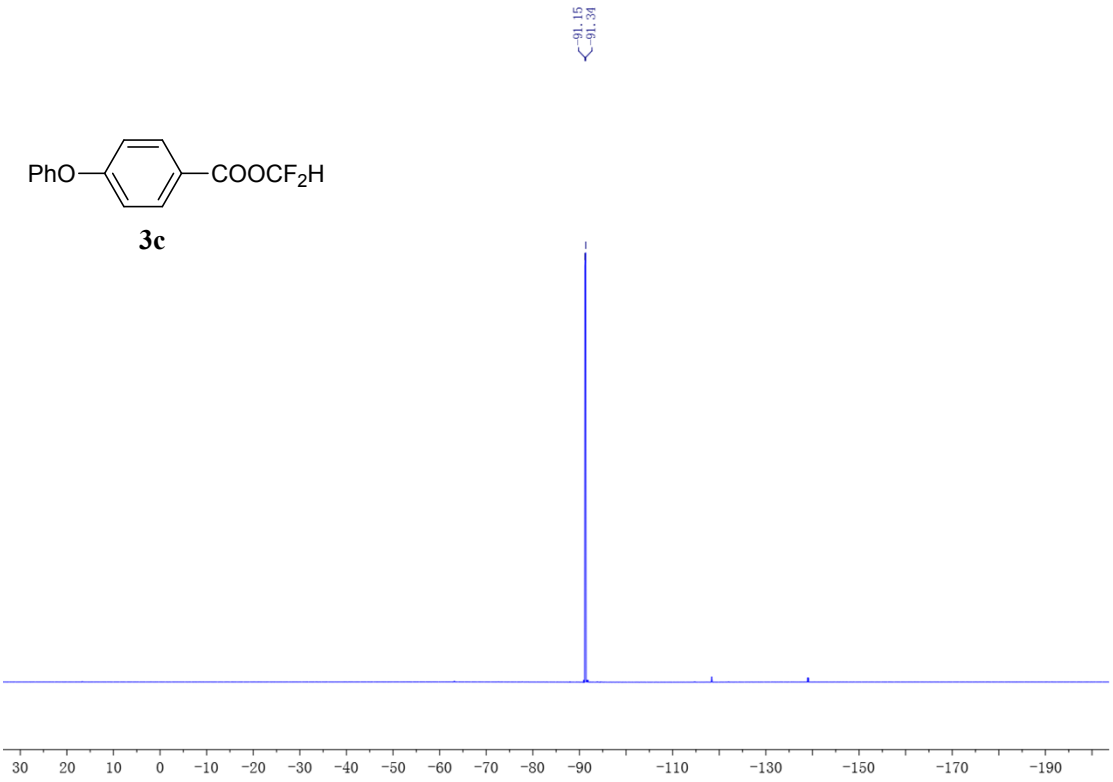
3b

^{1}H NMR

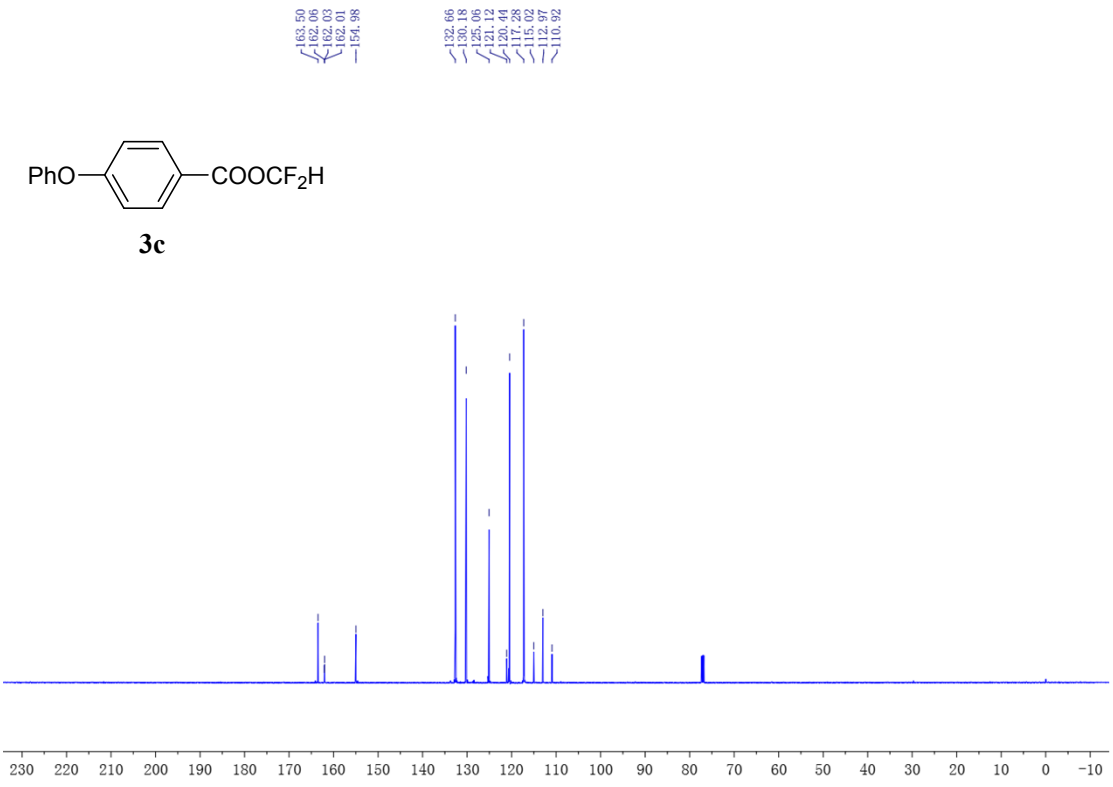


3c

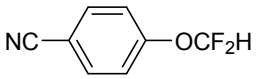
^{19}F NMR



^{13}C NMR

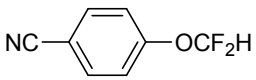


^{1}H NMR



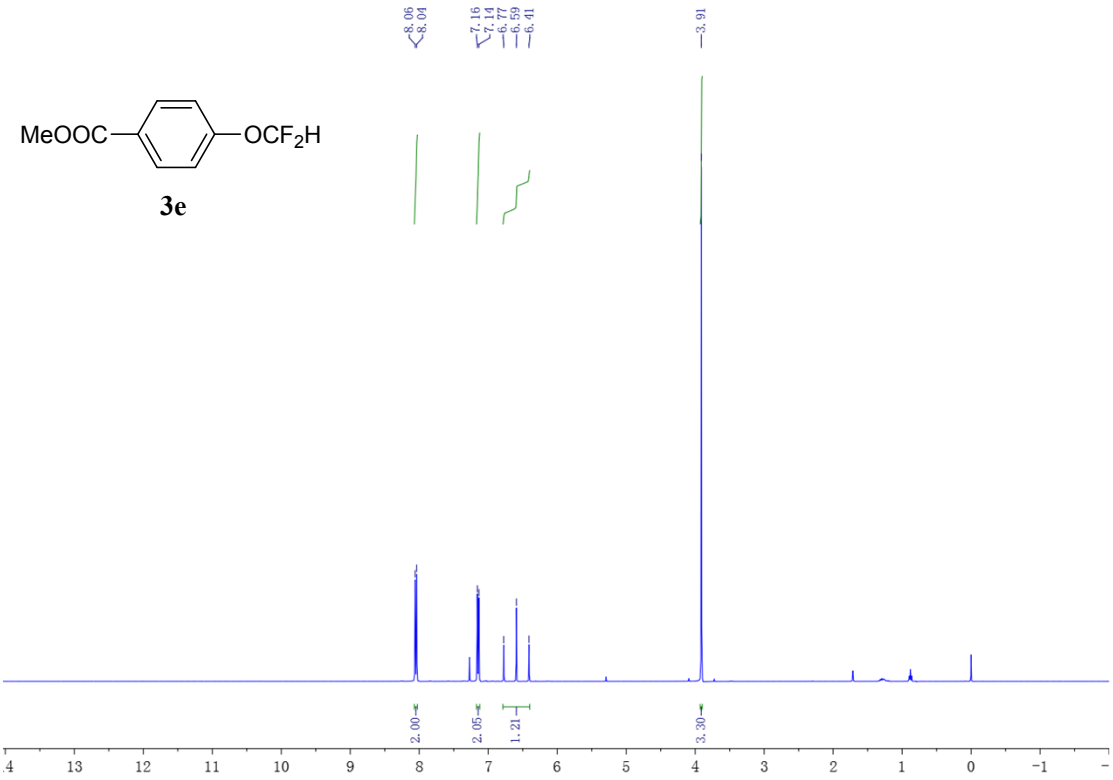
3d

^{19}F NMR



3d

^{1}H NMR



3e

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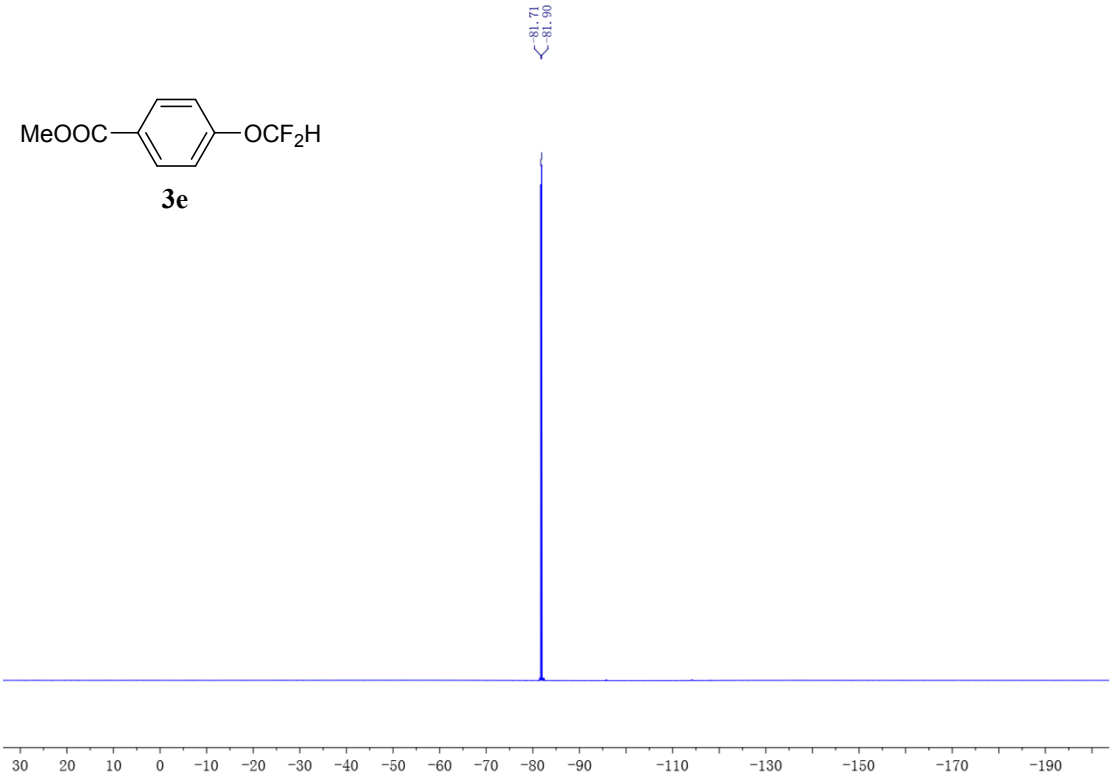

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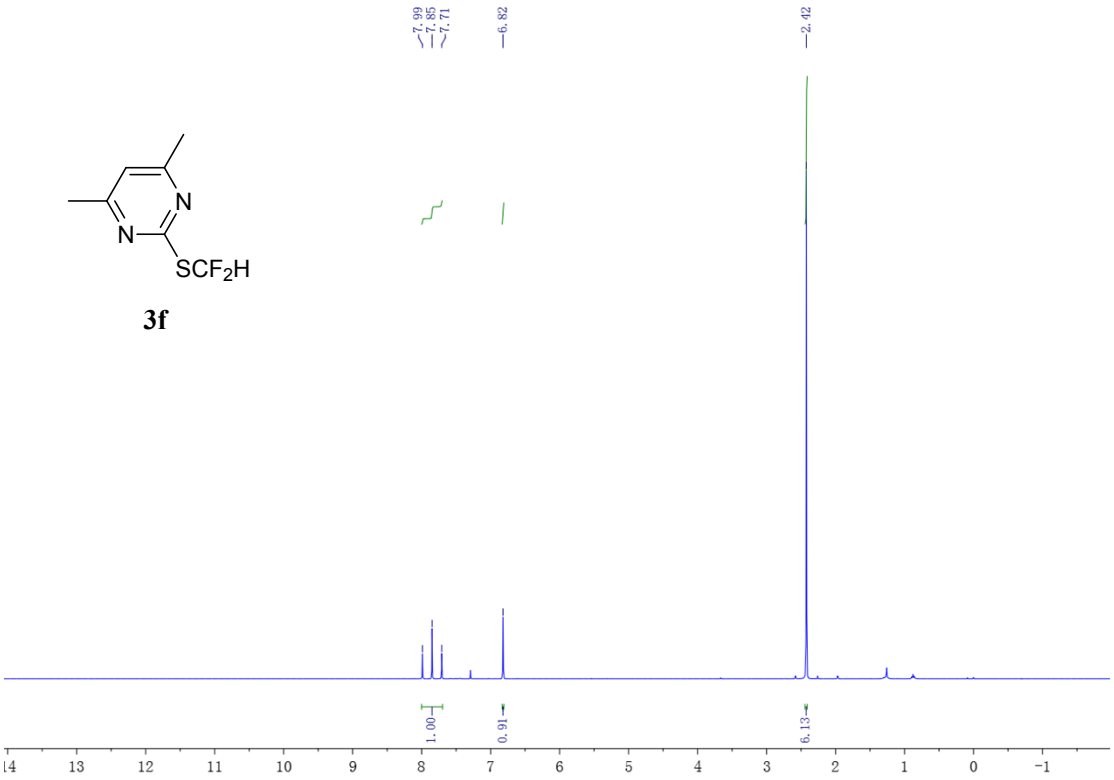
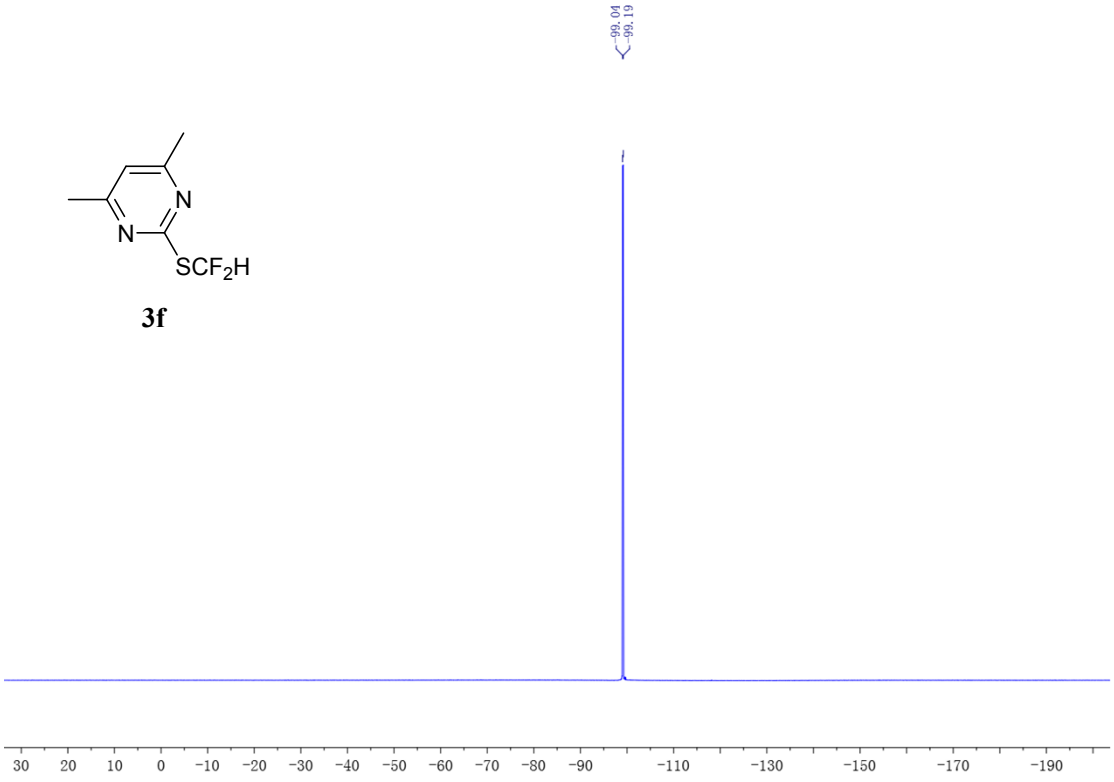


3f

^{19}F NMR



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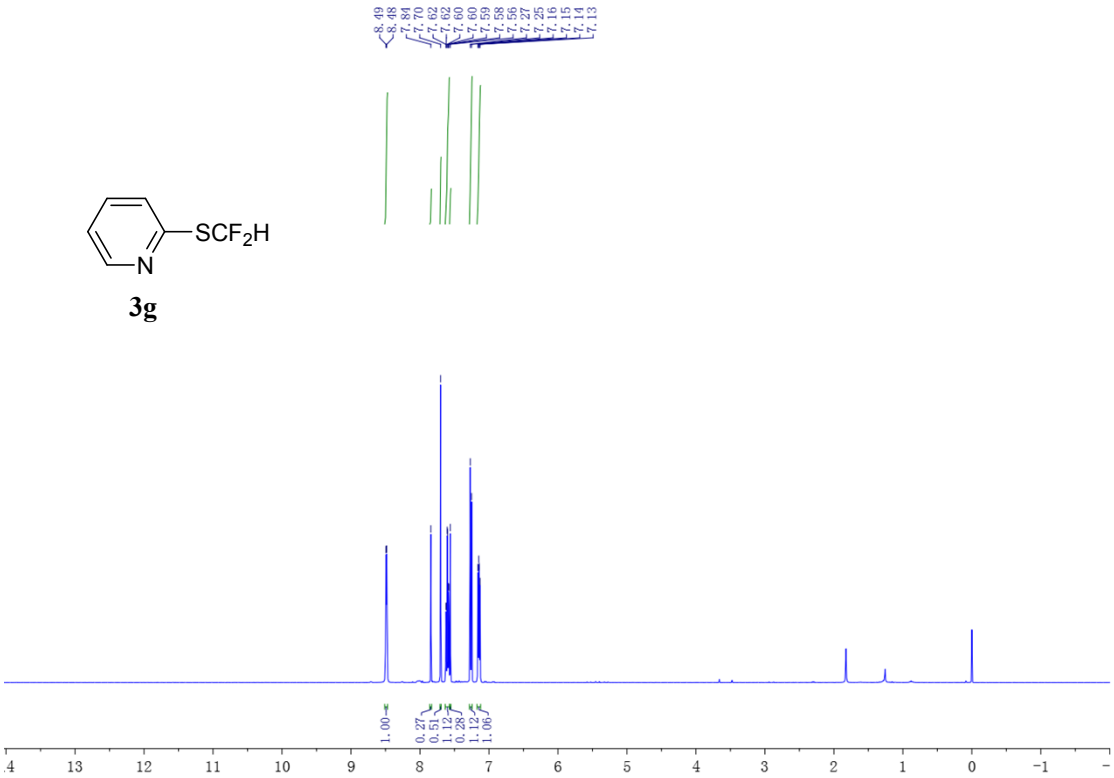

3g

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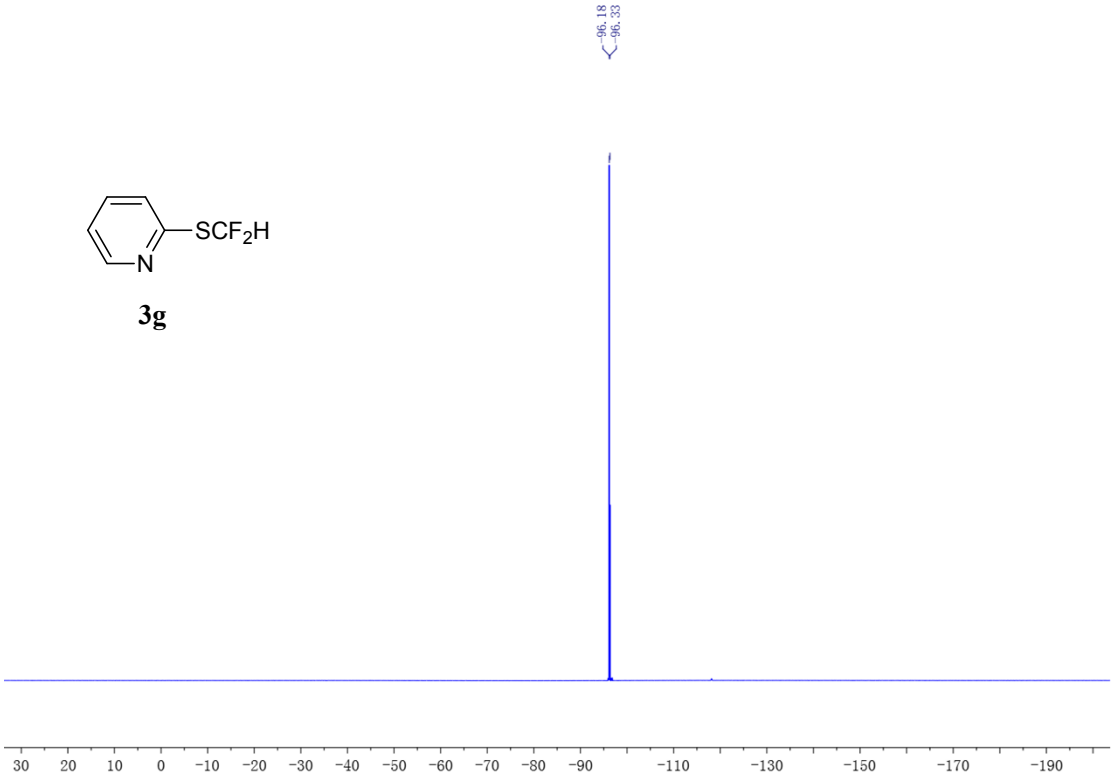

3g

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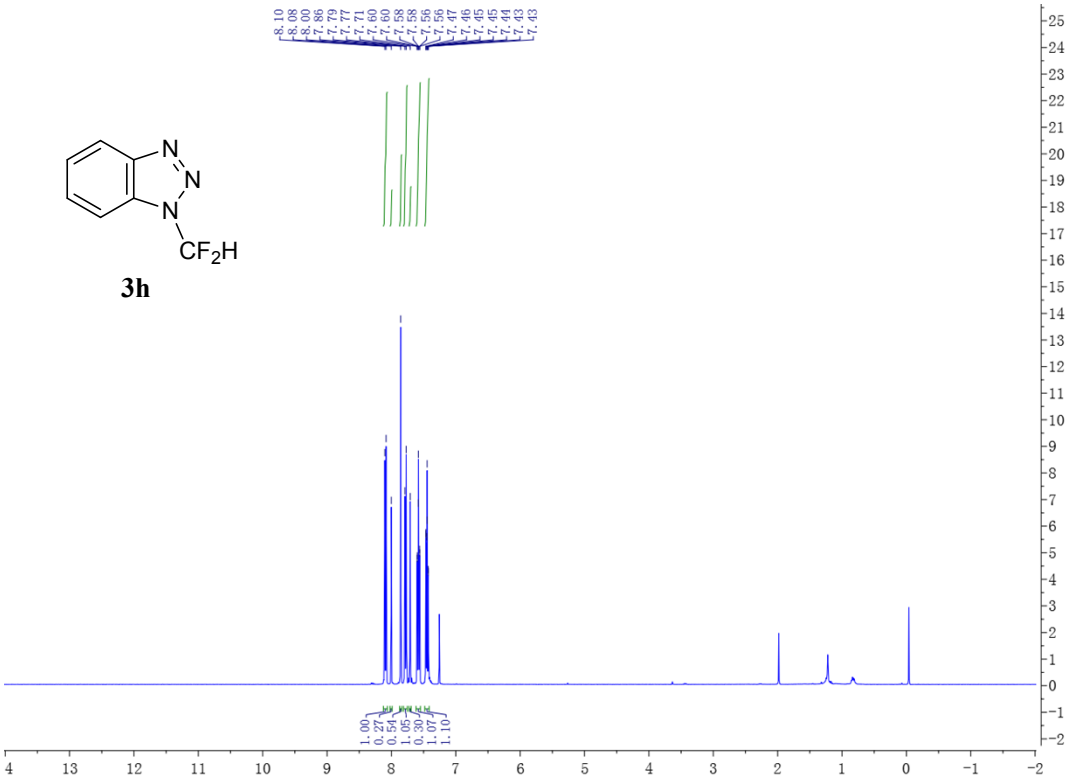

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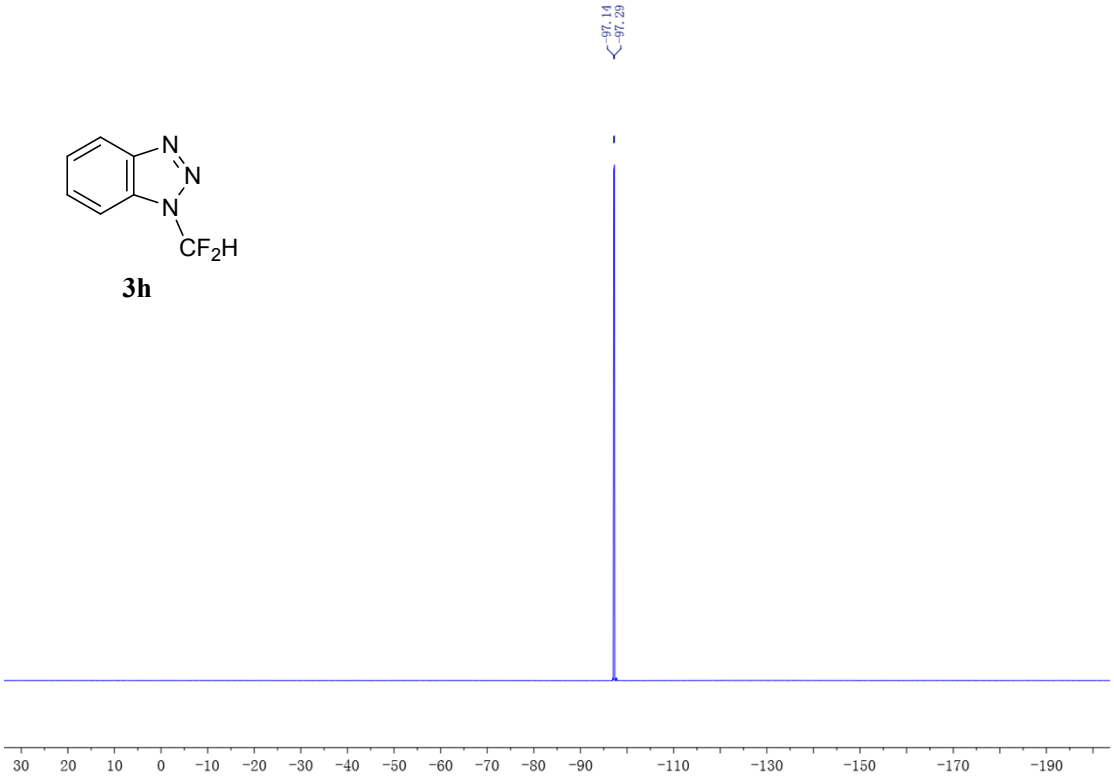

3h

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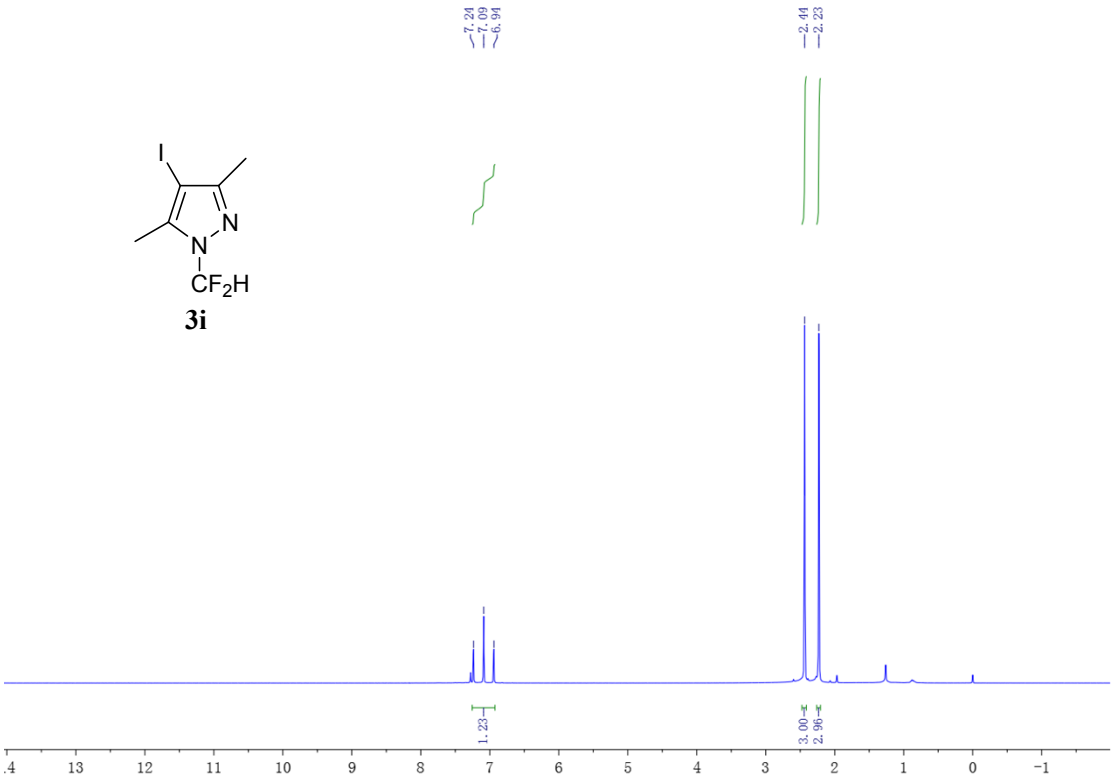

3i

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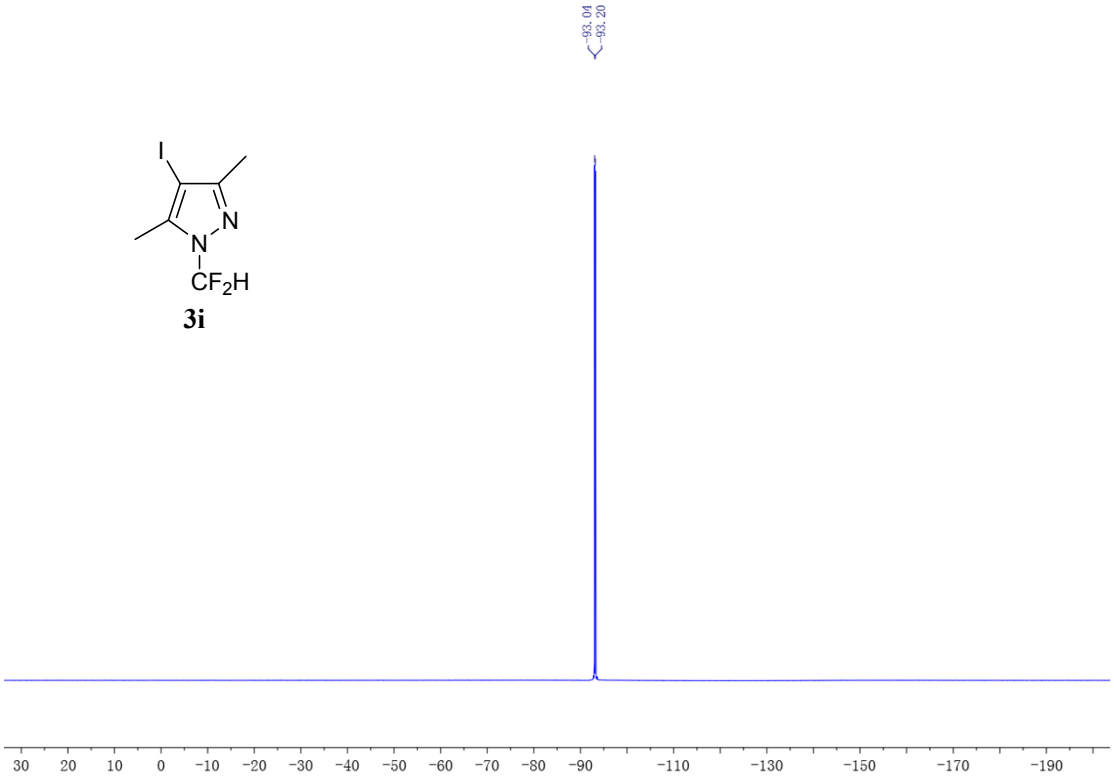

3i

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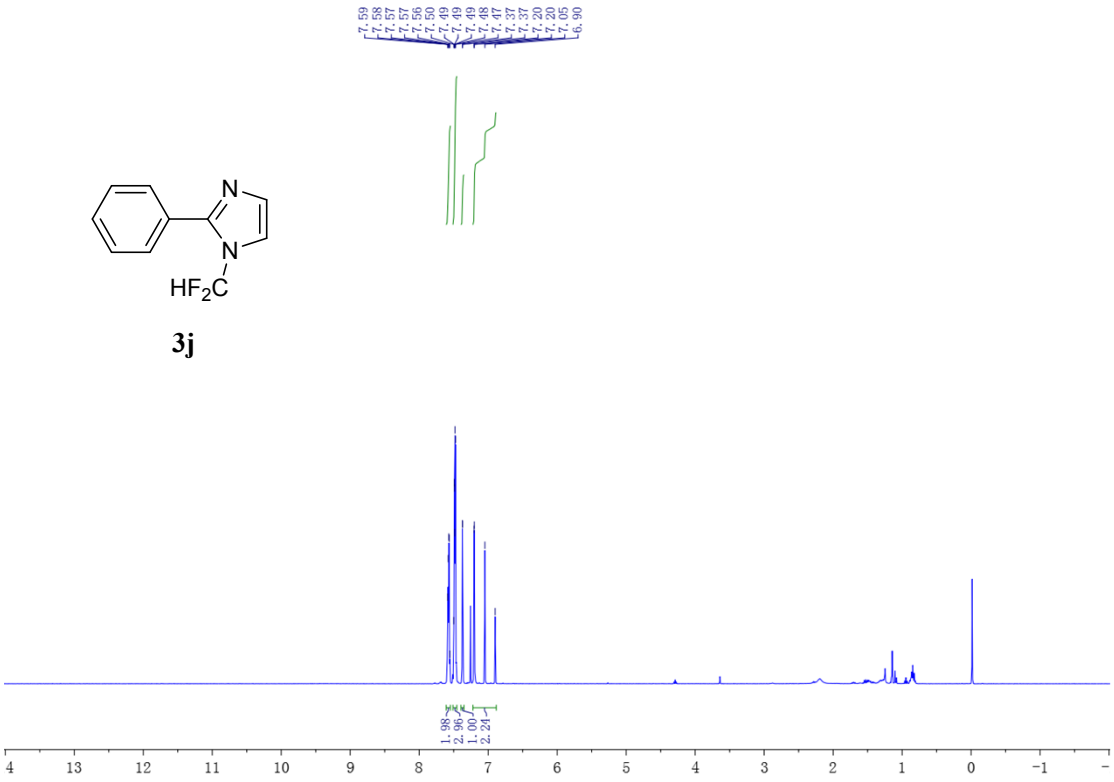

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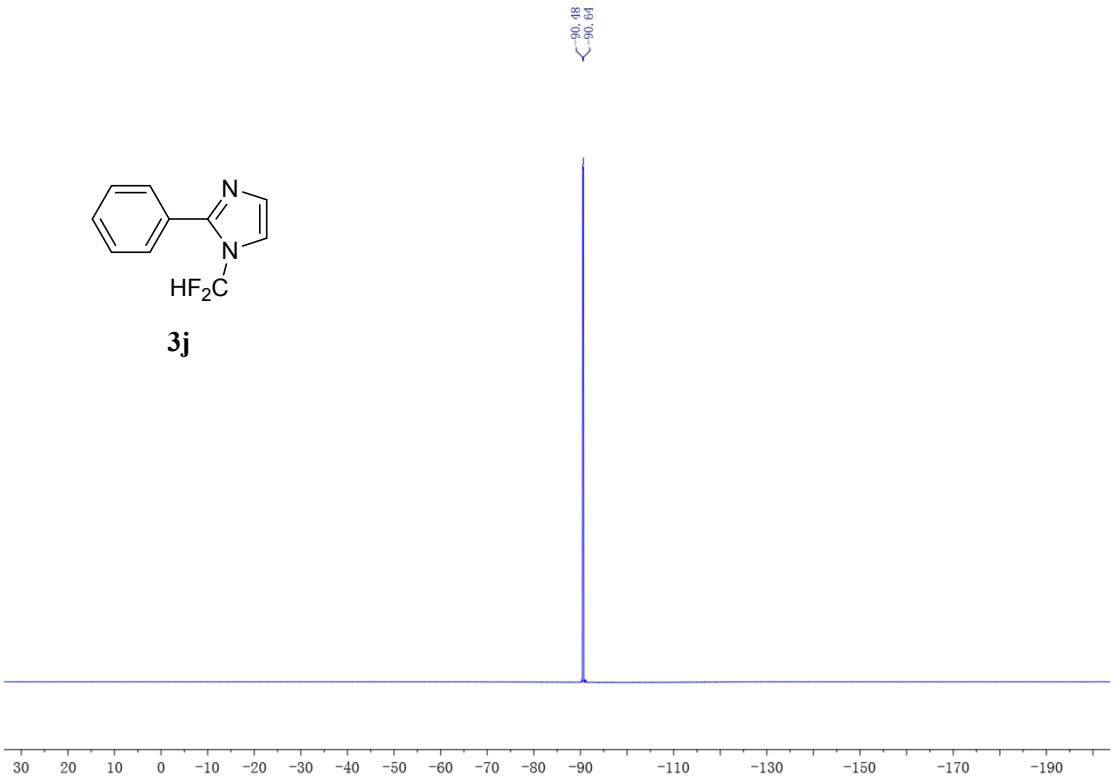

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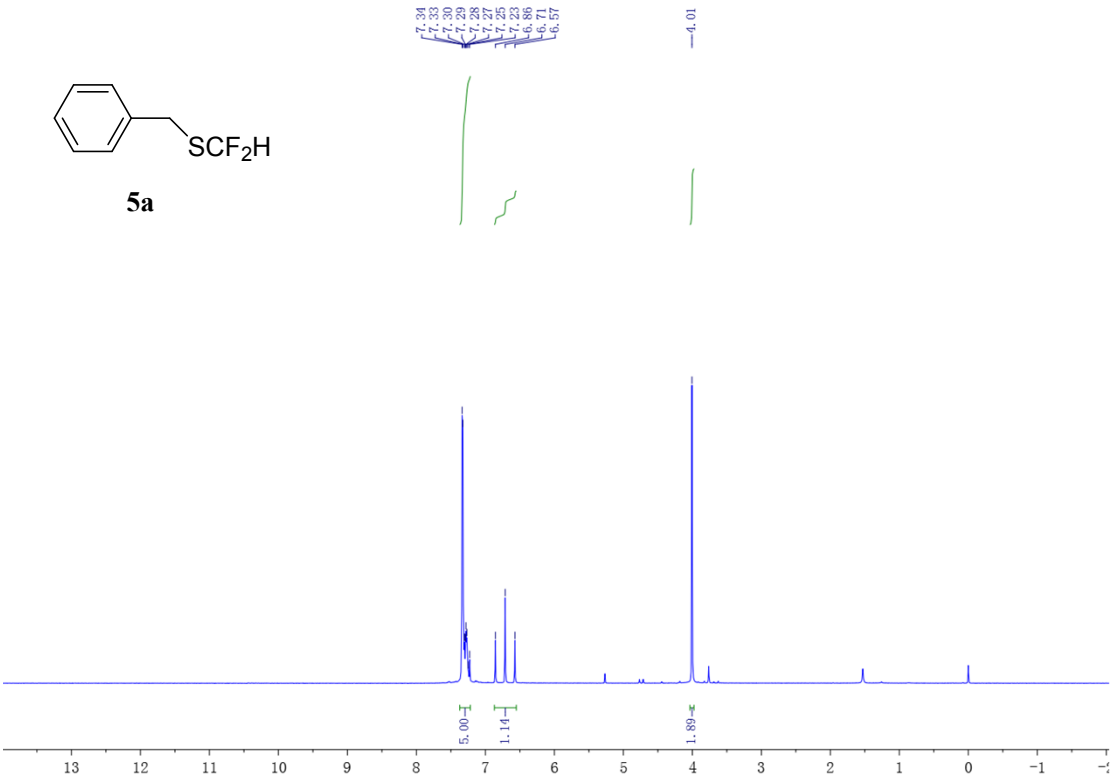

5a

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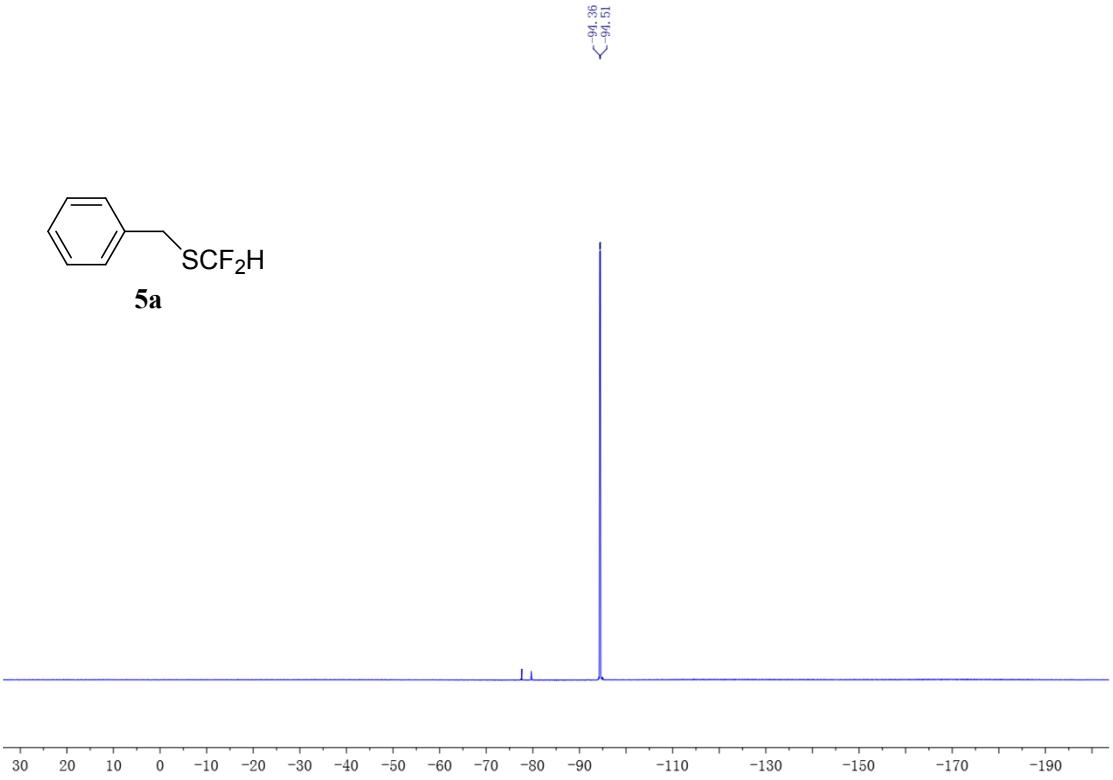
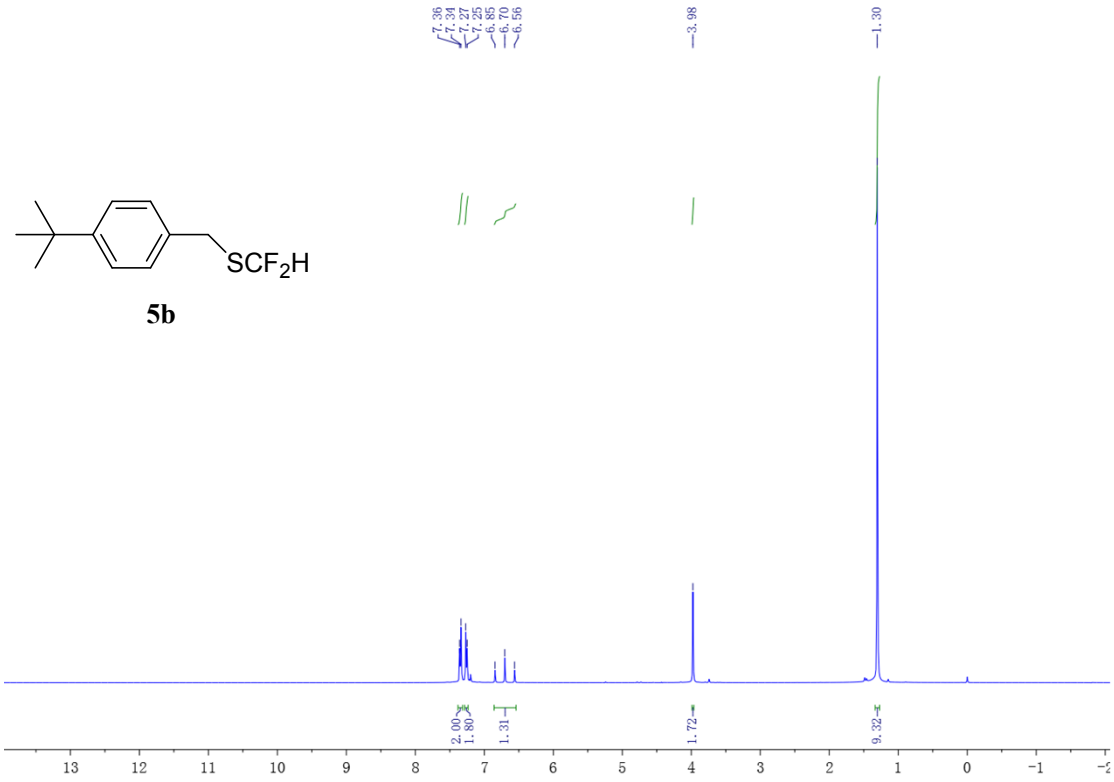


5a

^{1}H NMR

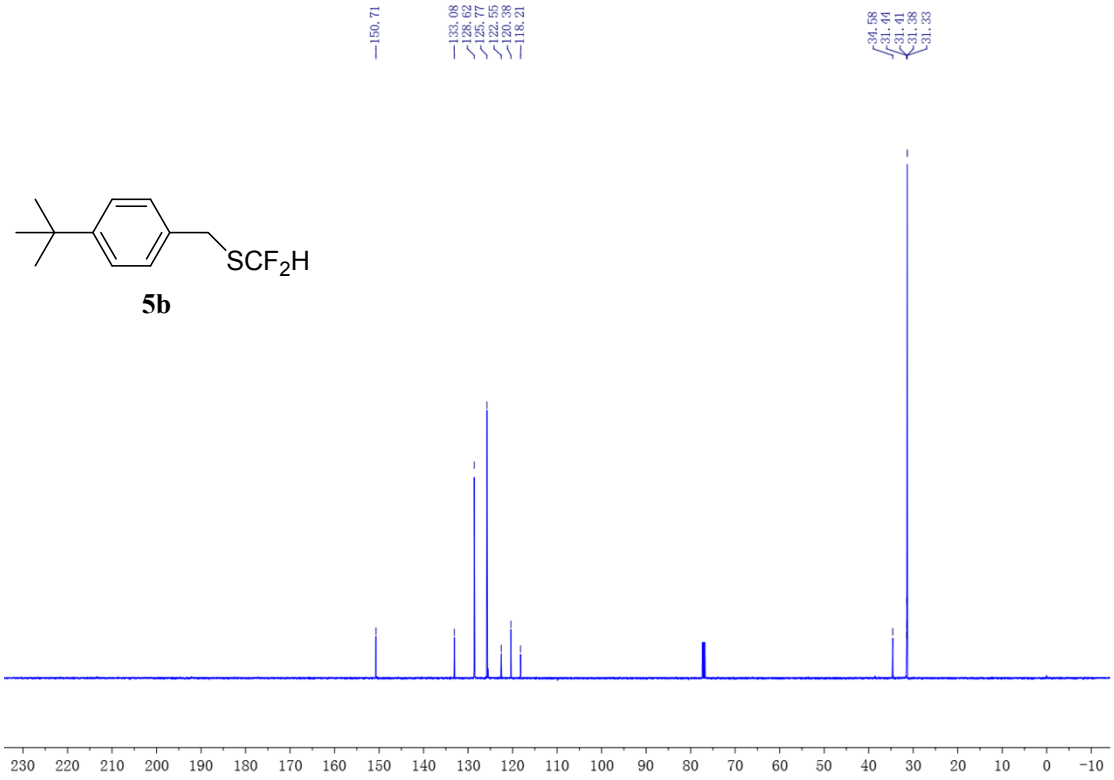


5b

^{19}F NMR

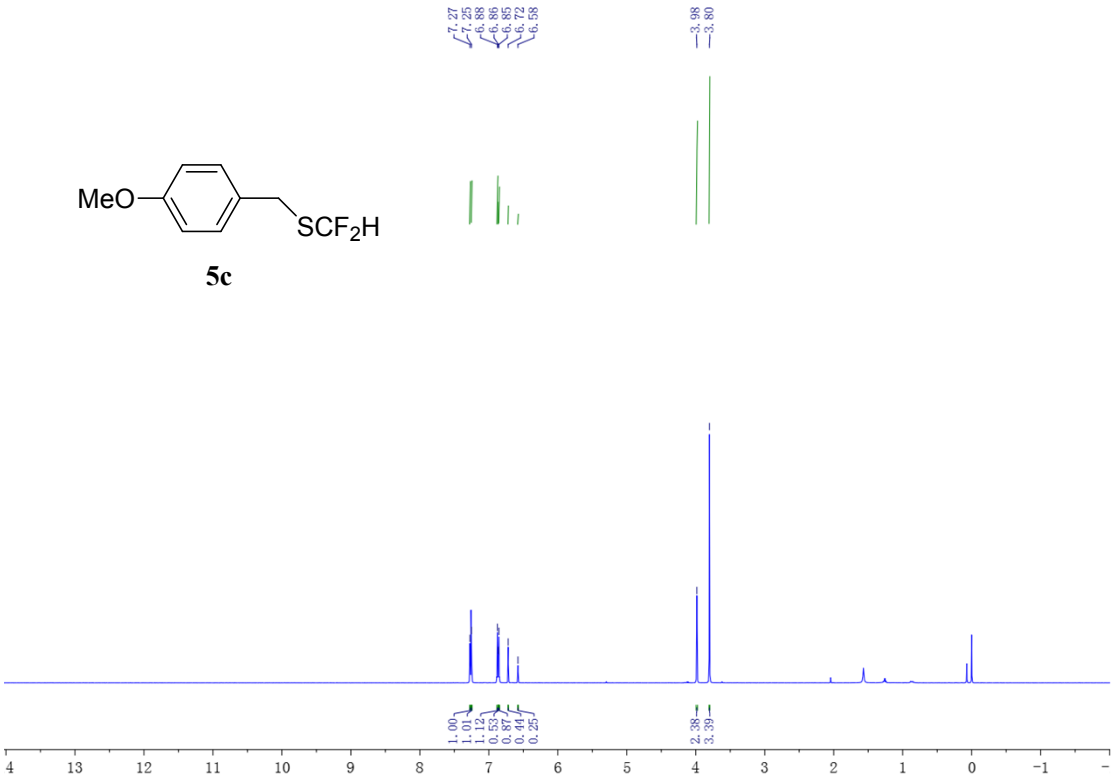
5b

^{13}C NMR



5b

^{1}H NMR



5c

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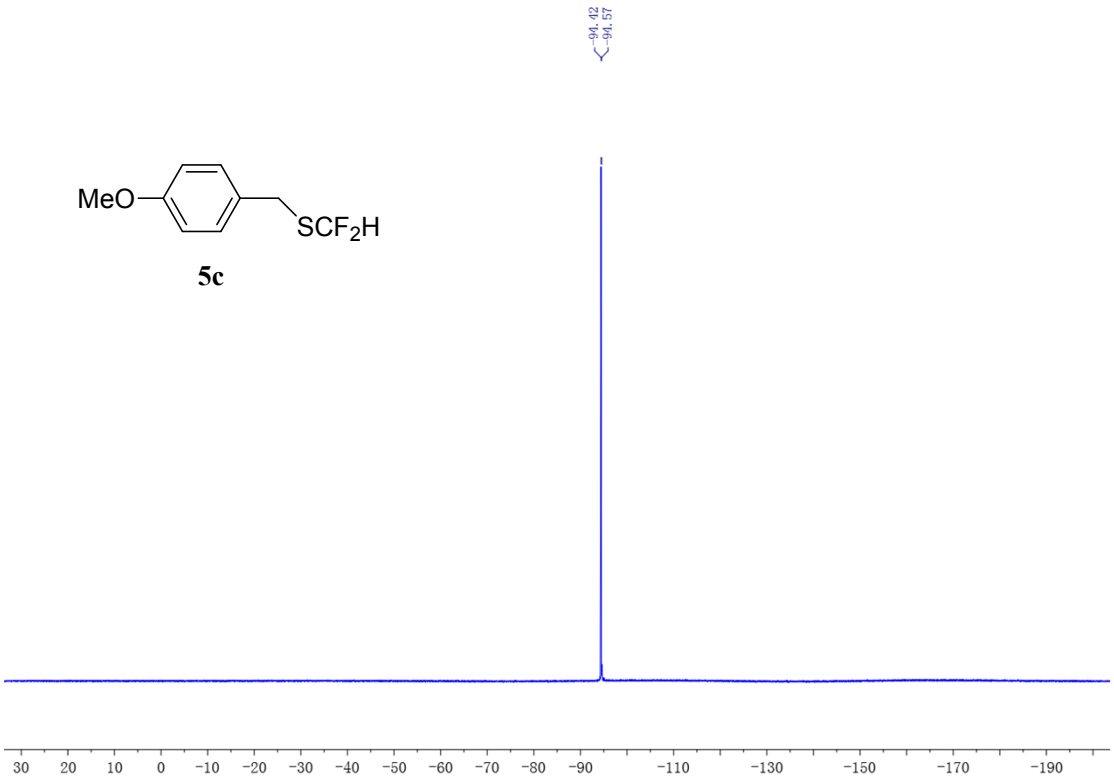
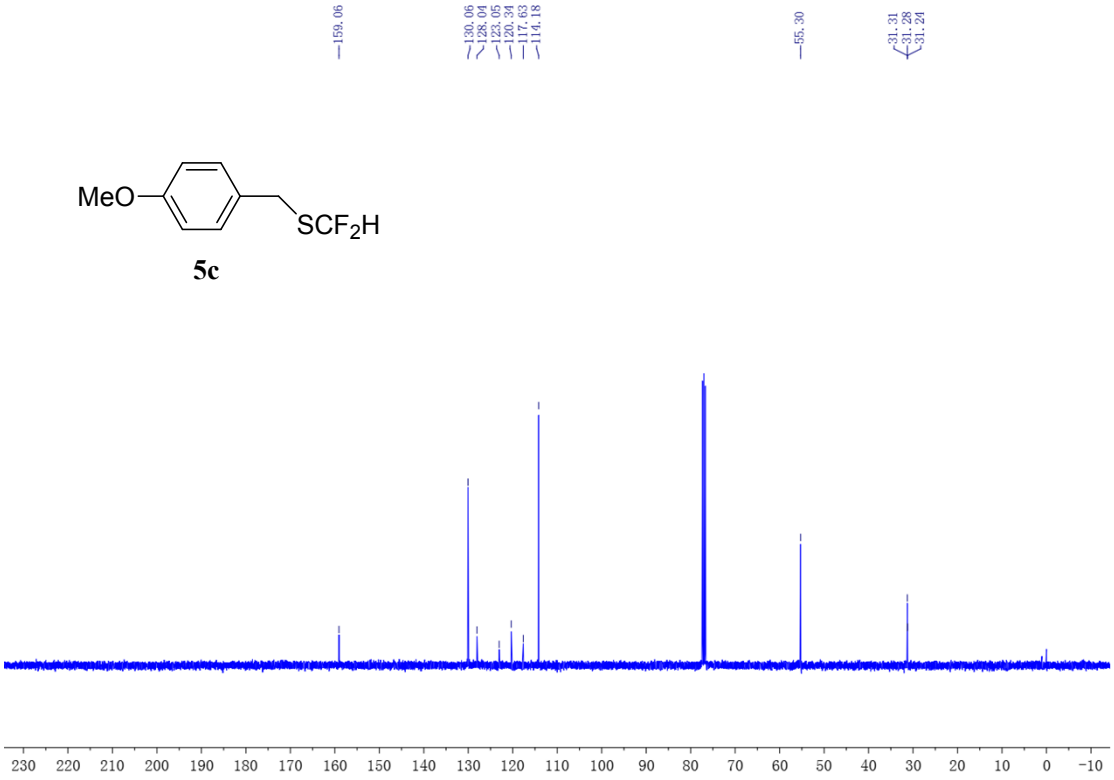
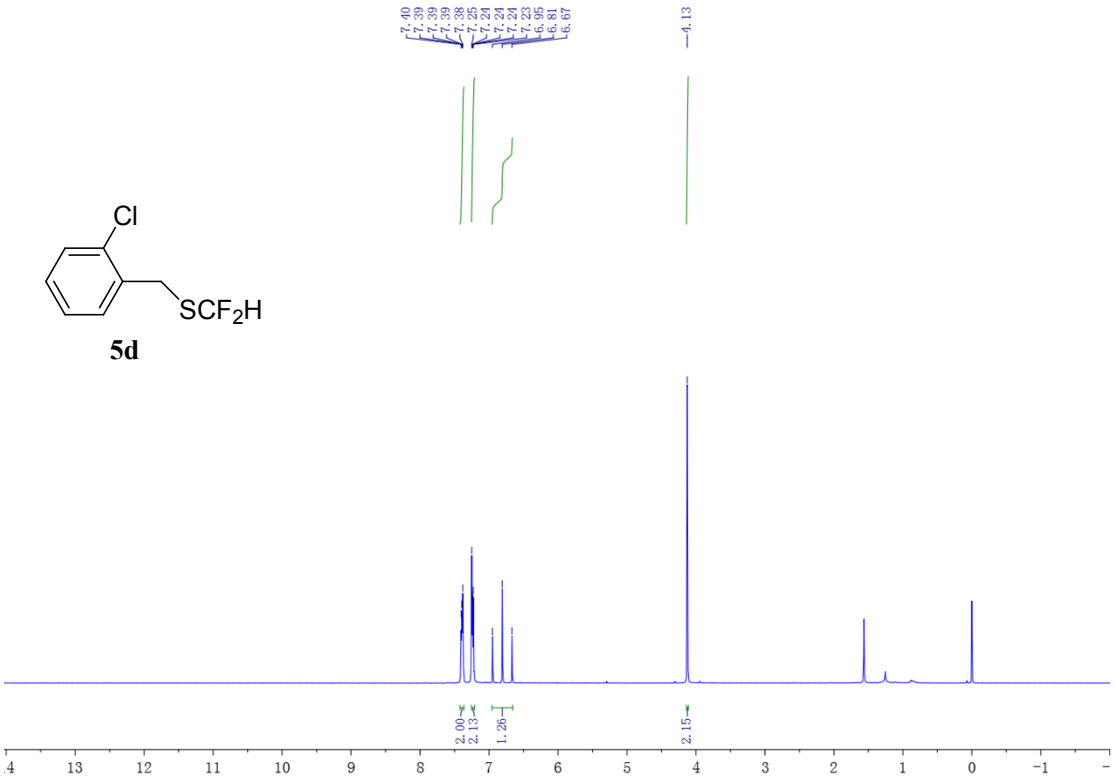


^{13}C NMR

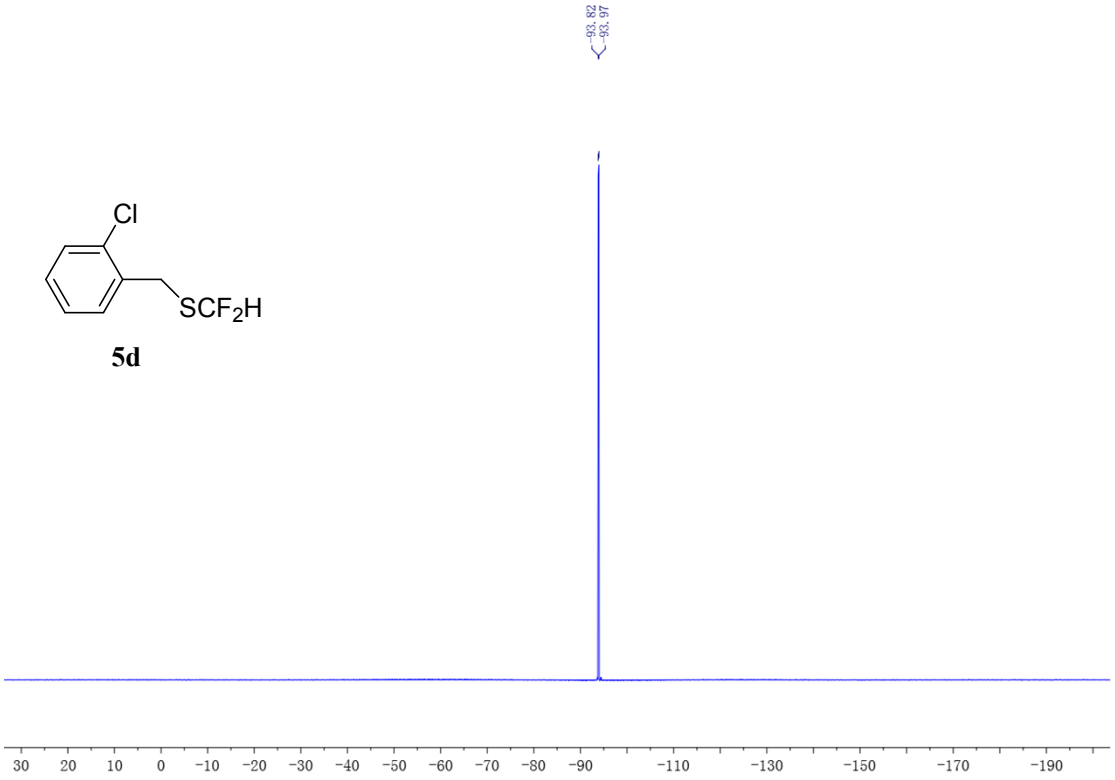


^{1}H NMR



5d

^{19}F NMR



5d

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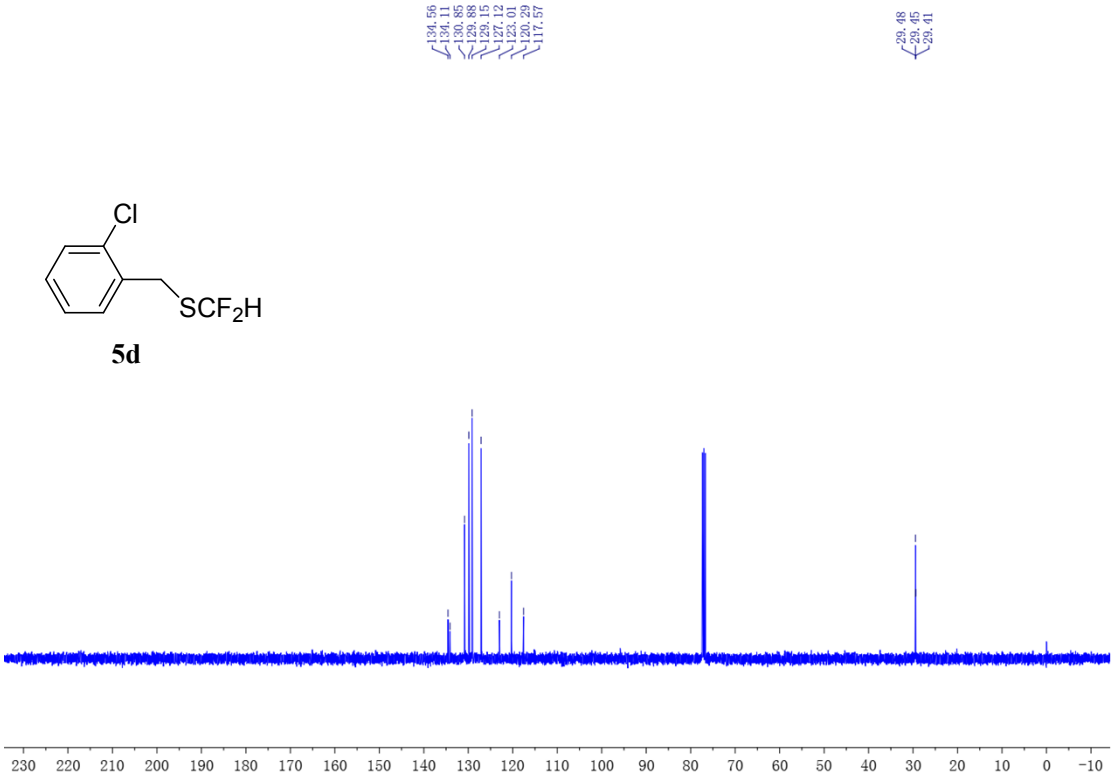
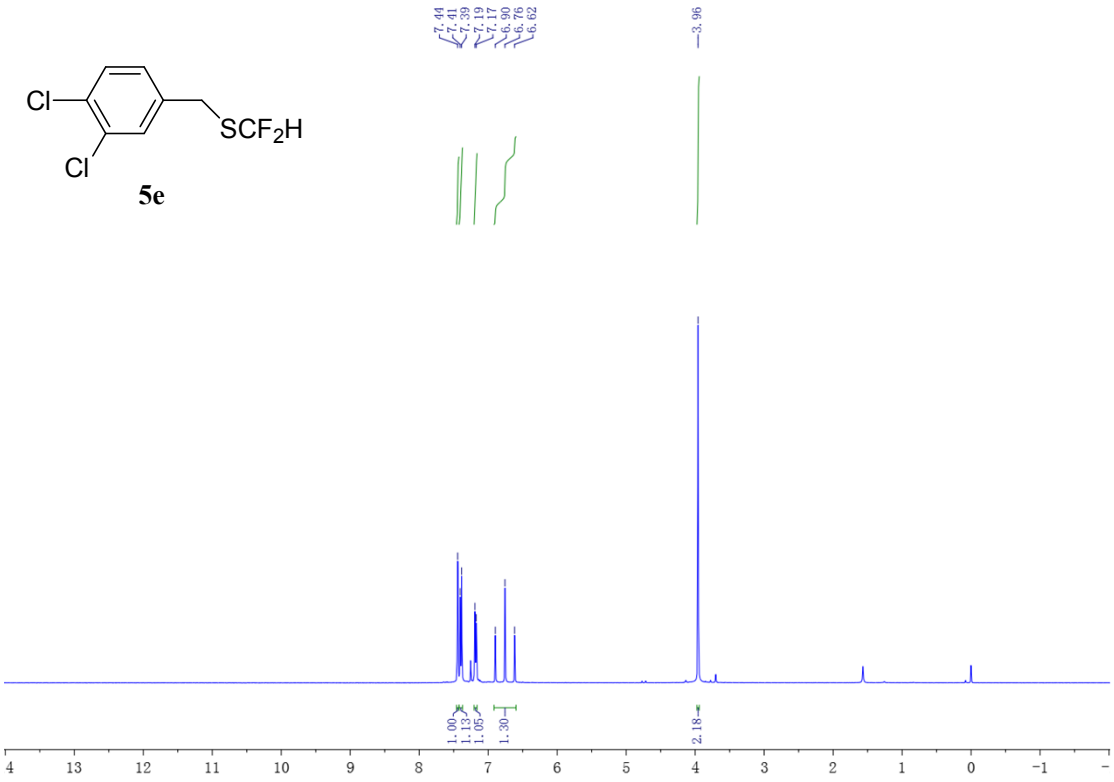


5d

^{1}H NMR



5e

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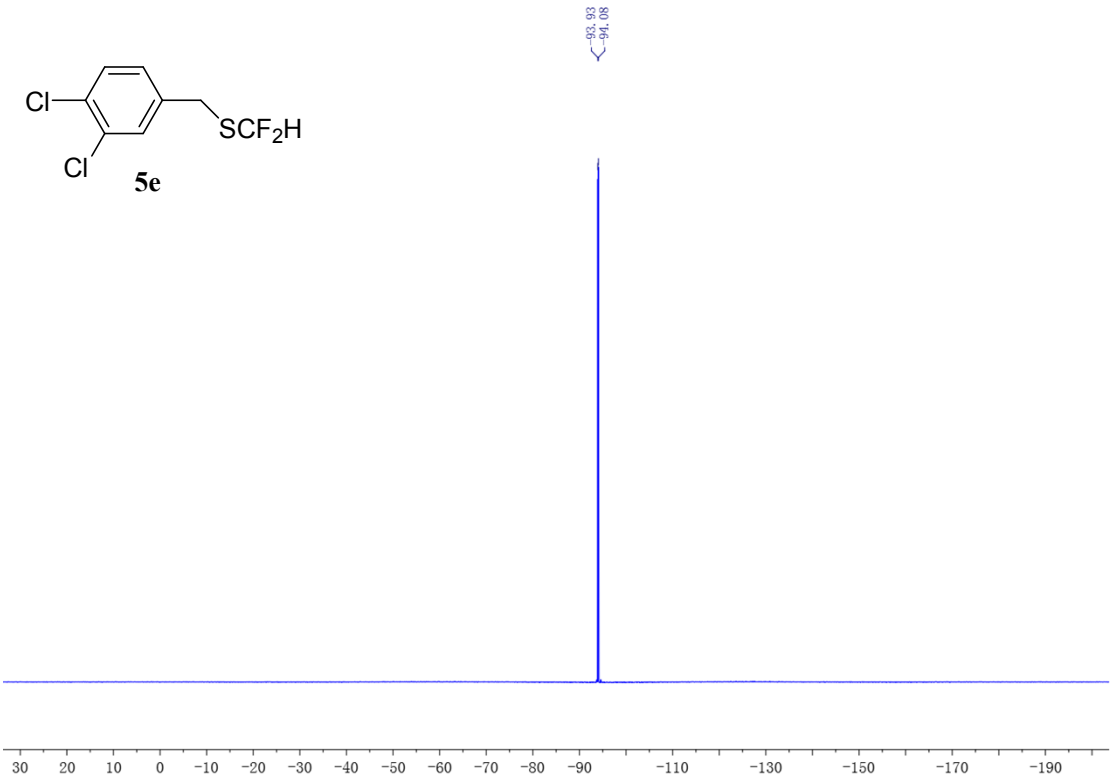
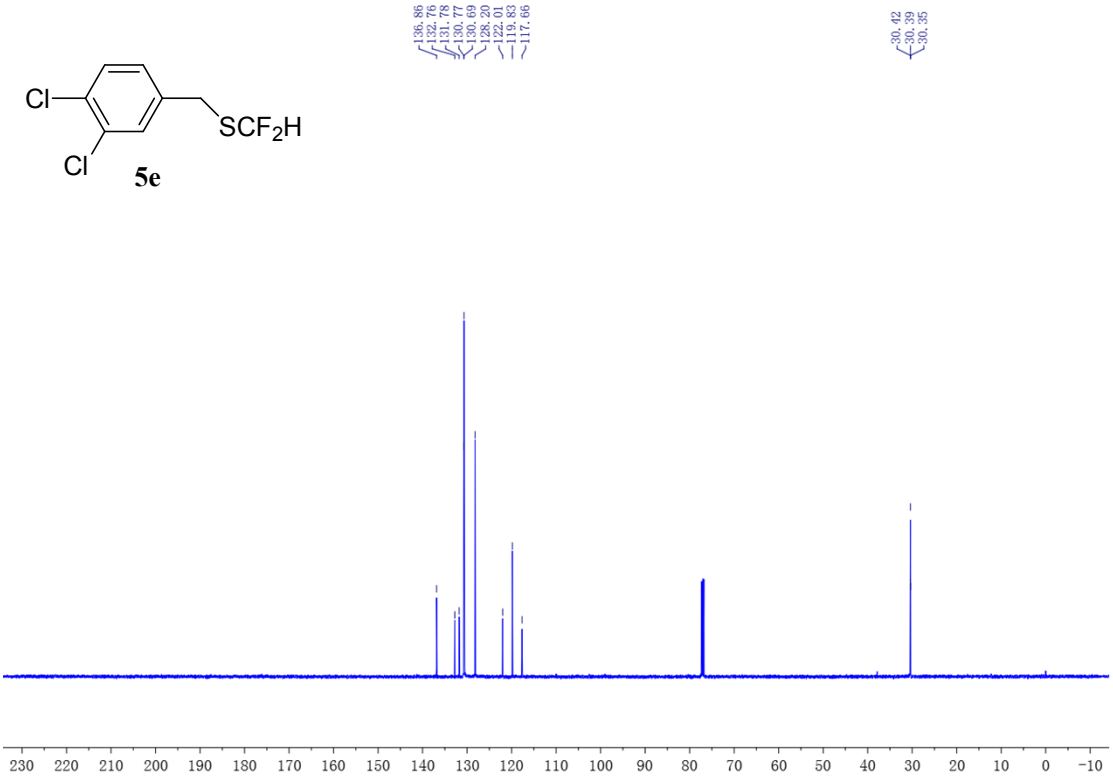
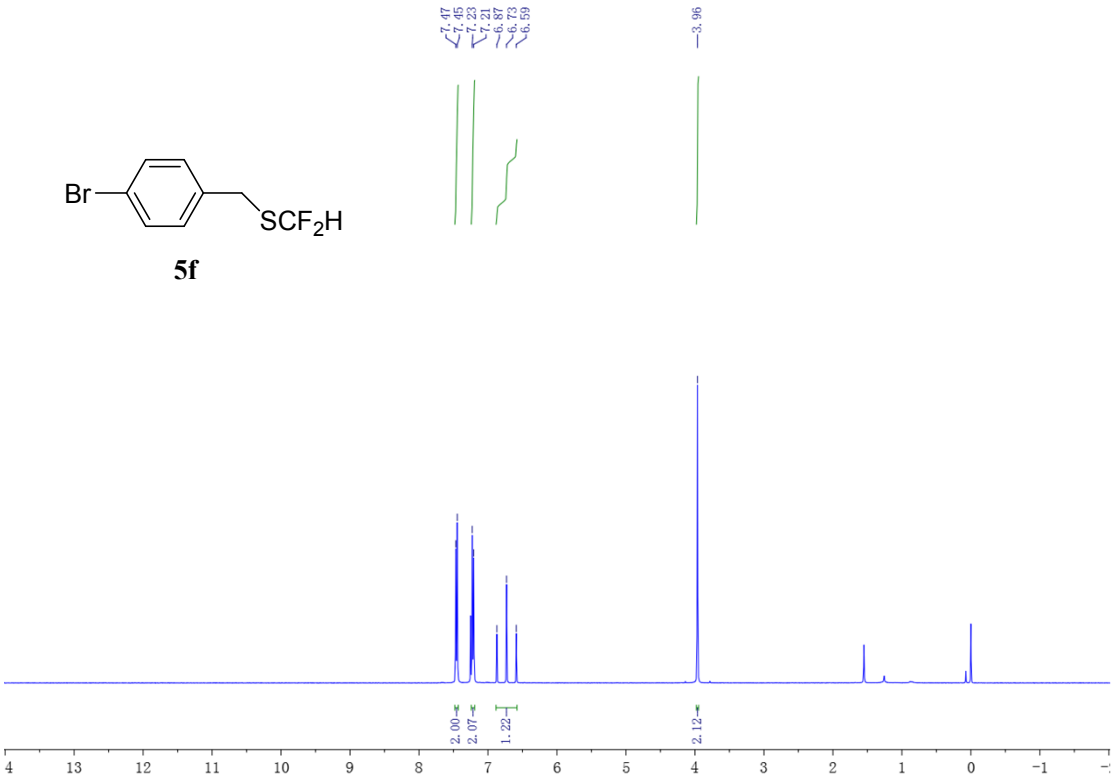


^{13}C NMR



^{1}H NMR



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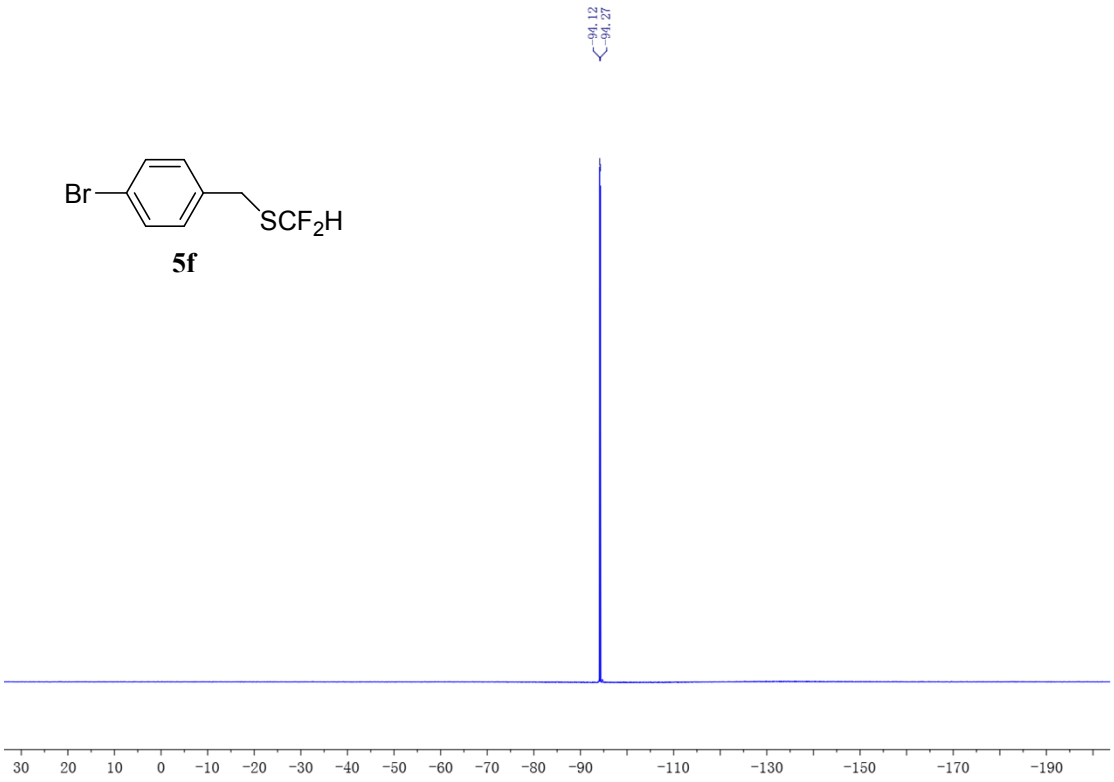
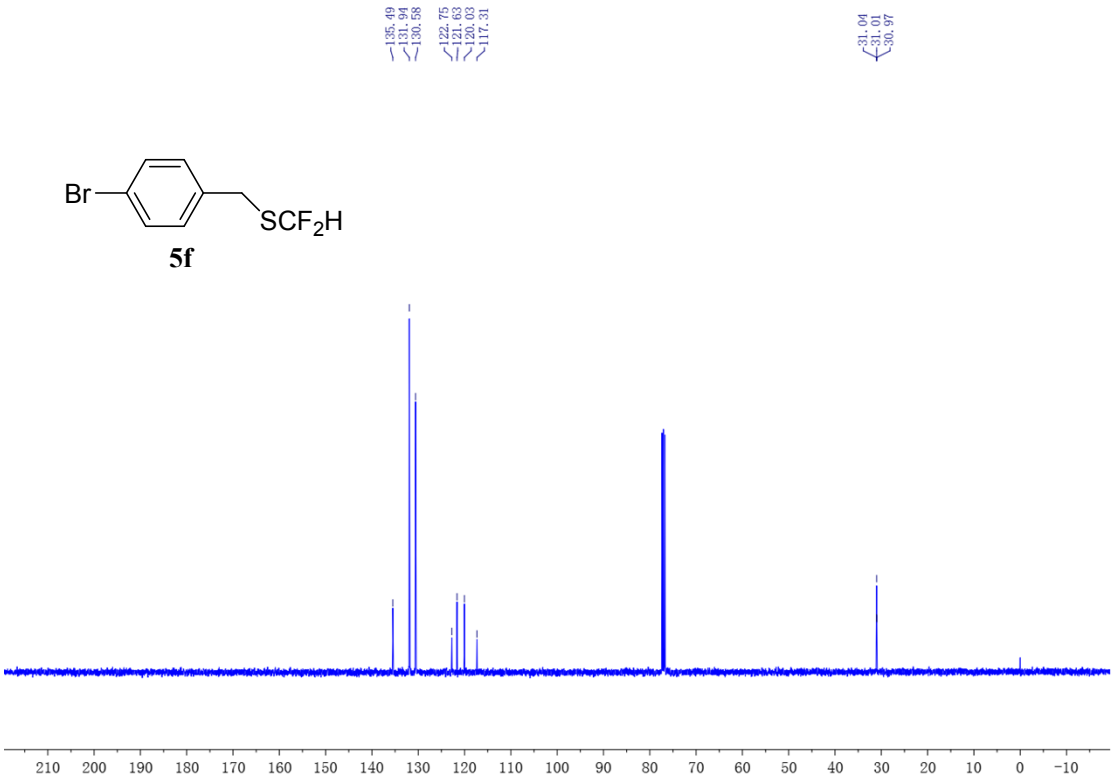


^{13}C NMR



5f

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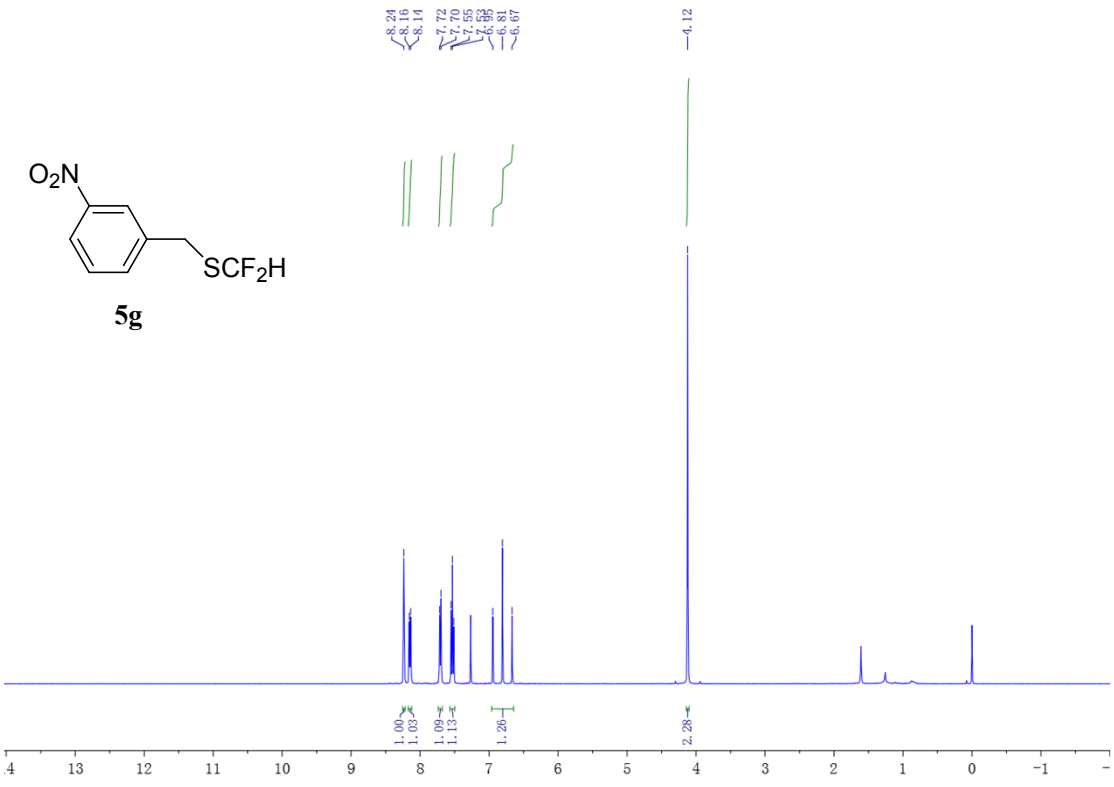
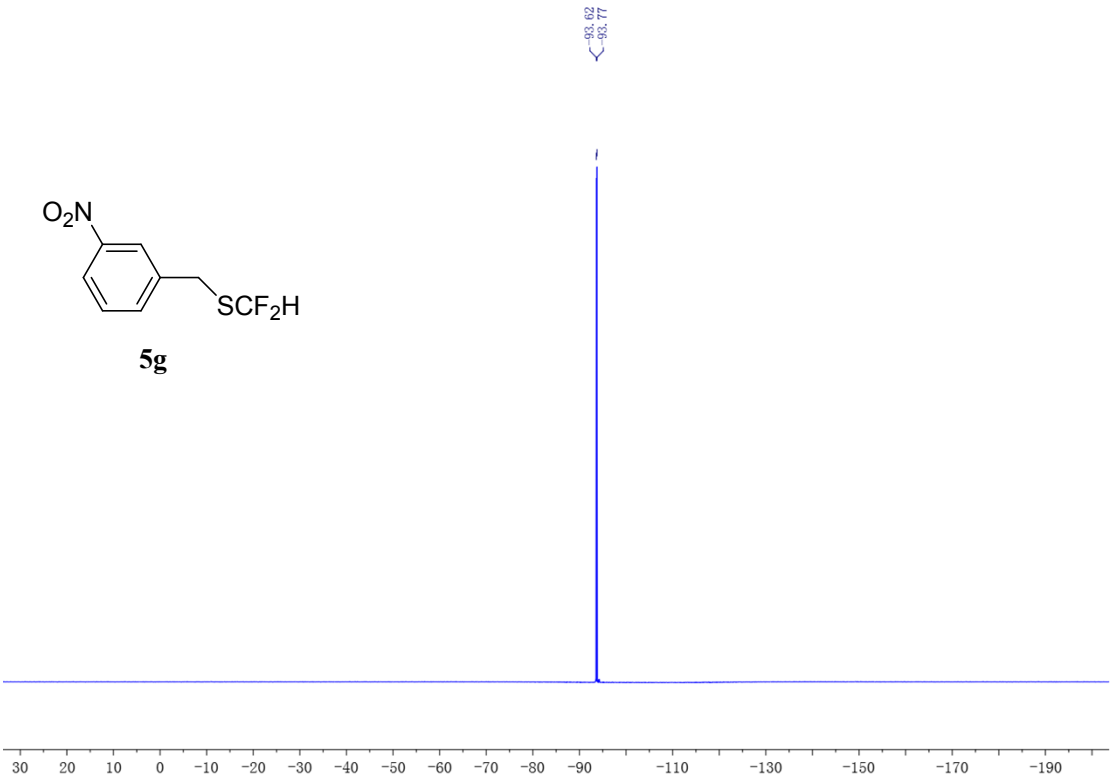
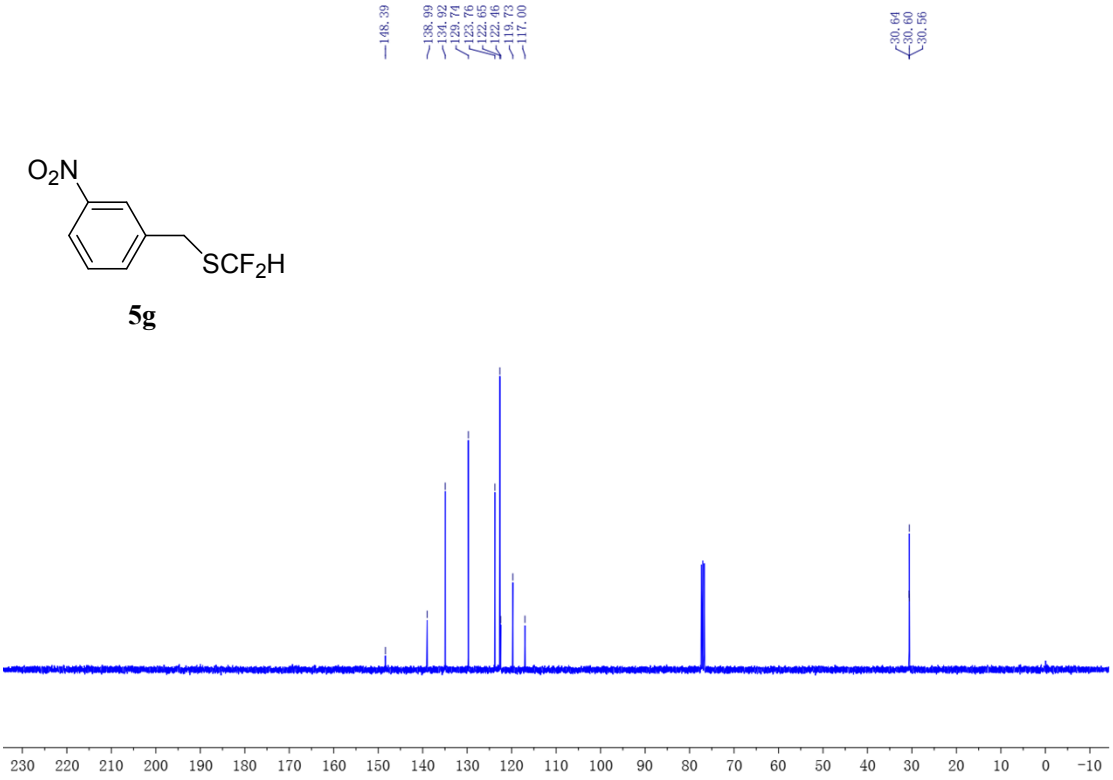


5g

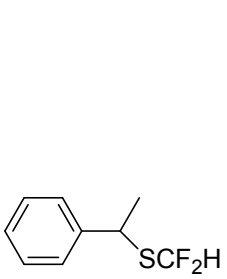
^{19}F NMR



^{13}C NMR



^{1}H NMR



5h

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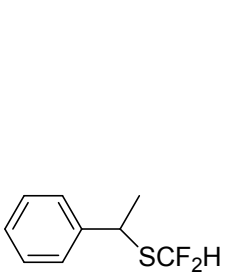

5h

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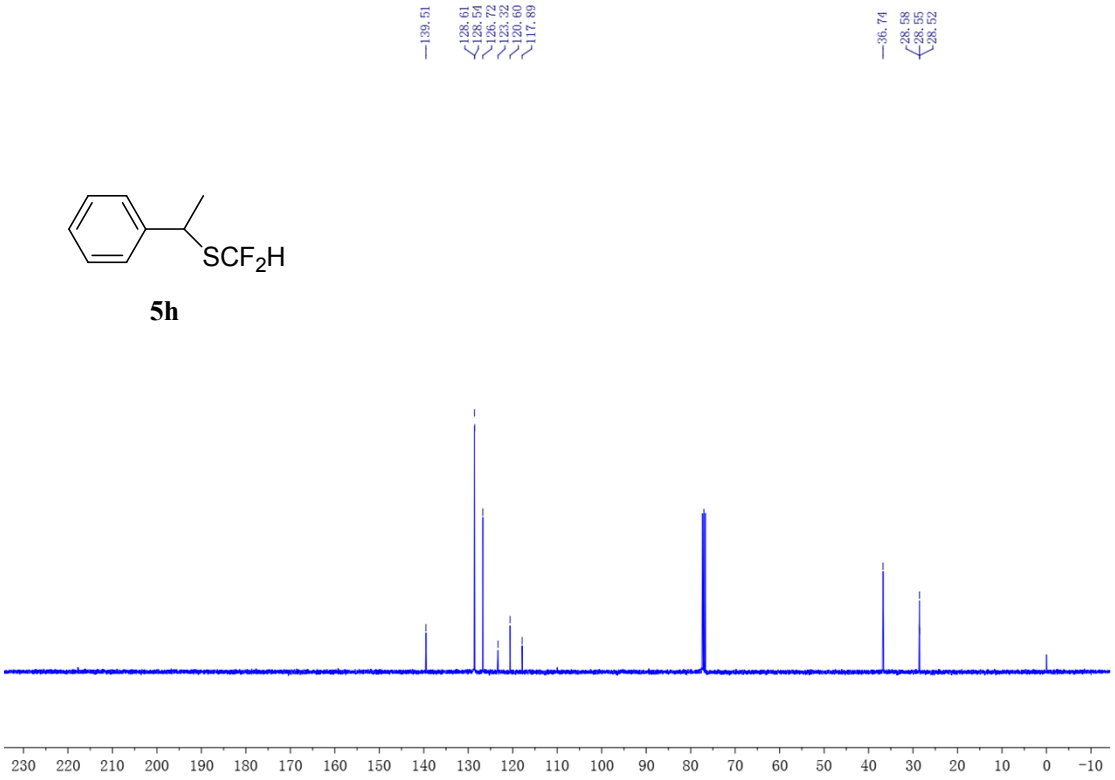
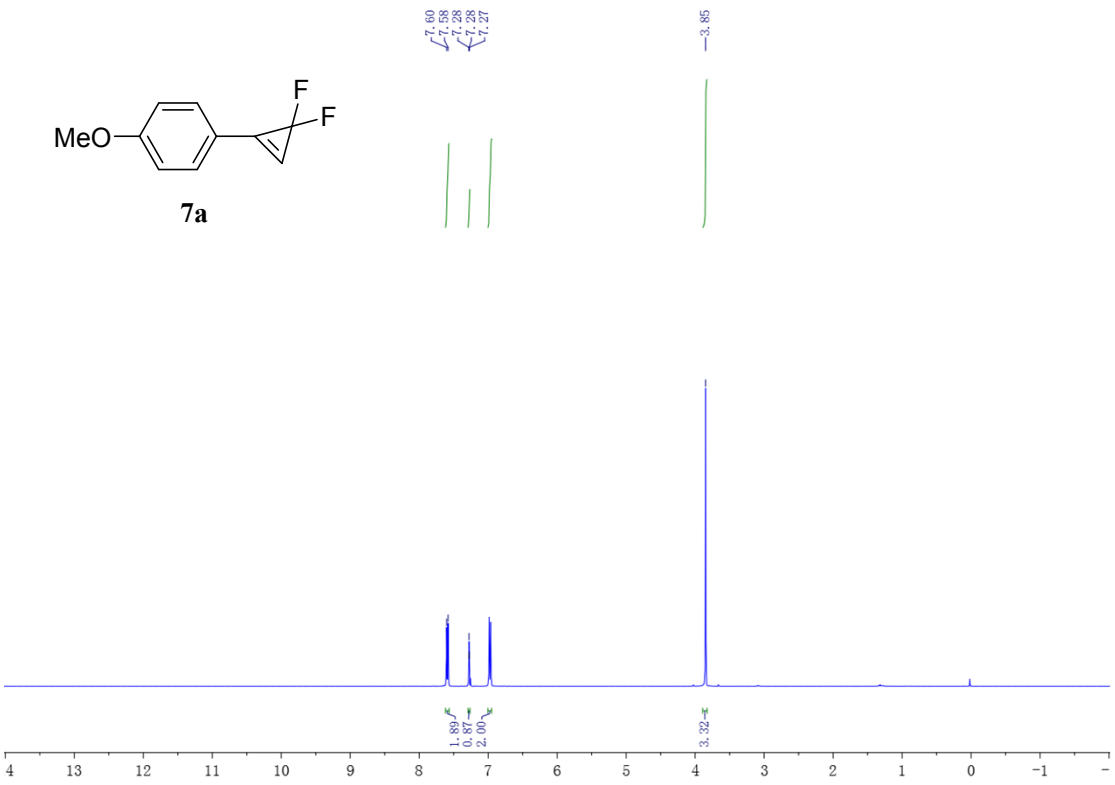


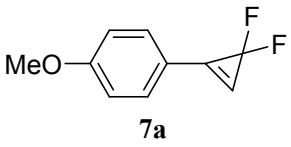
5h

^{1}H NMR



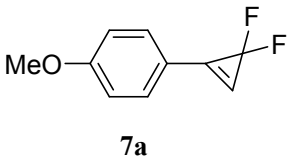
7a

^{19}F NMR



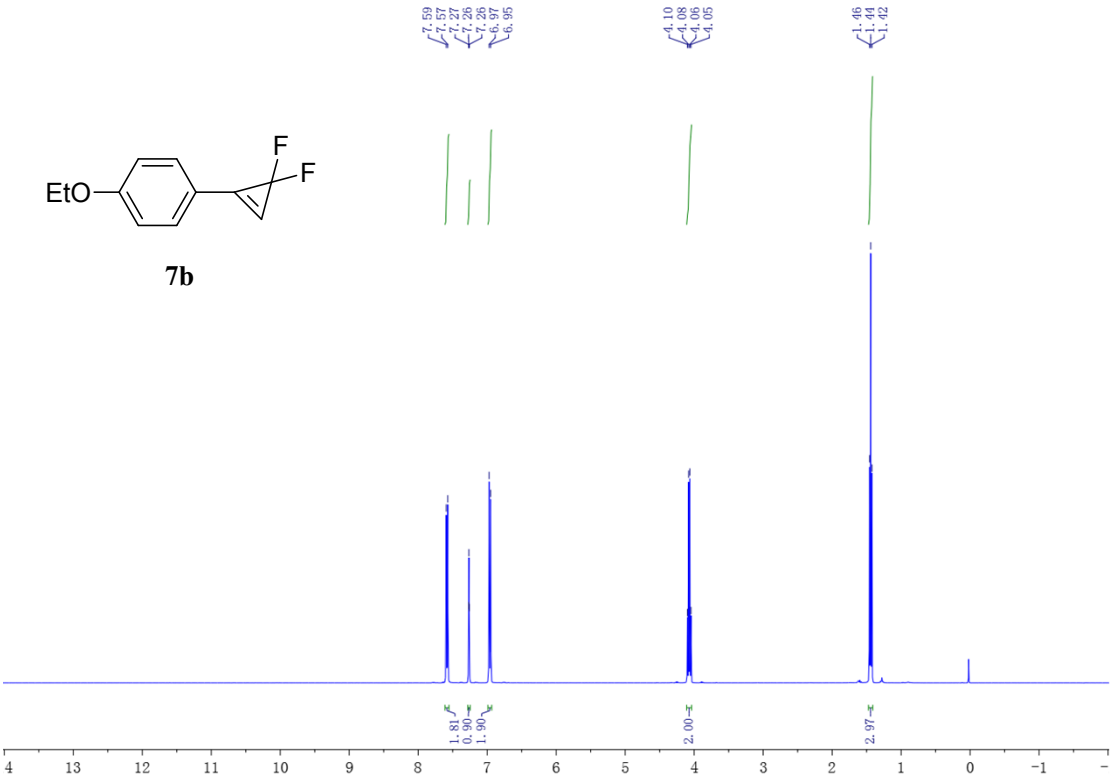
7a

^{13}C NMR



7a

^{1}H NMR



7b

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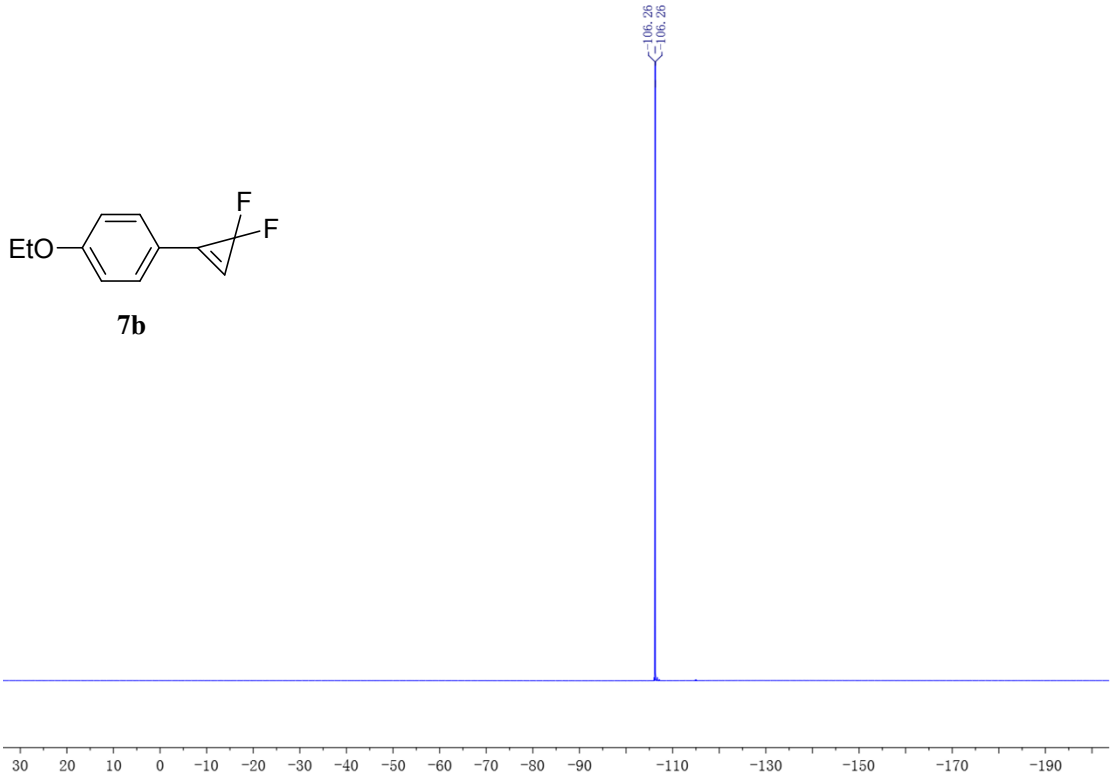

7b

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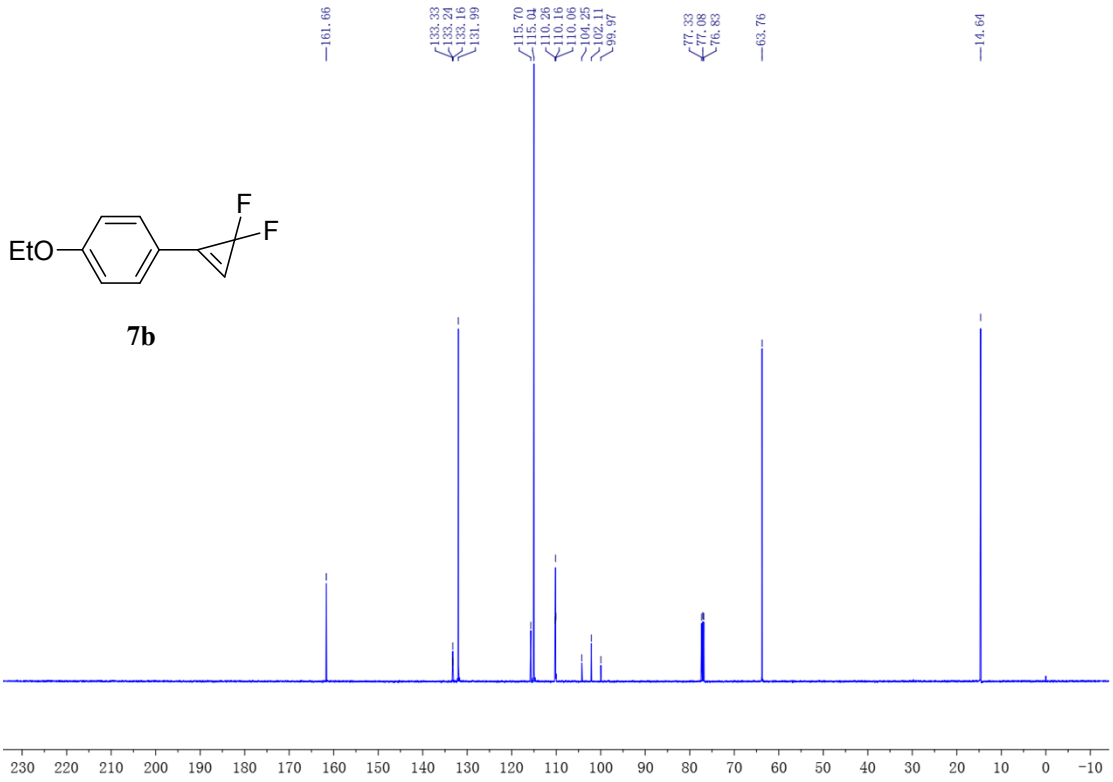

7b

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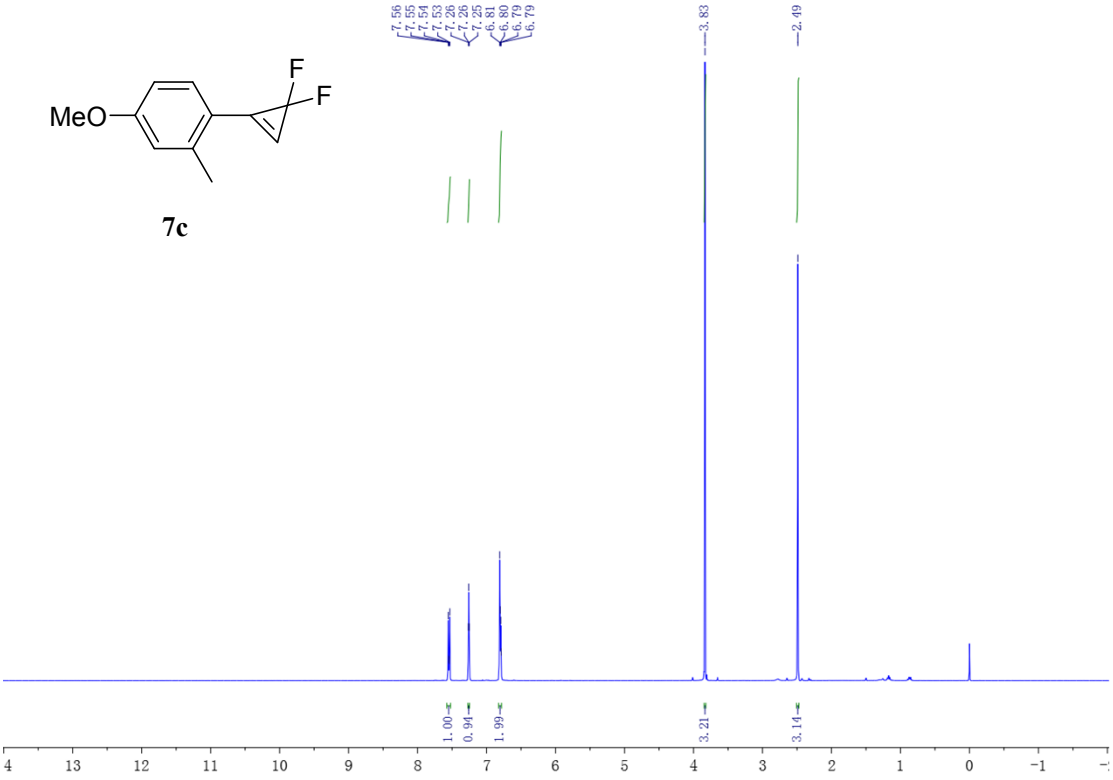
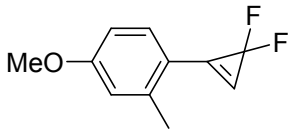


7c

^{19}F NMR



7c

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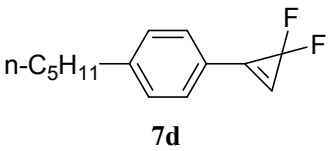

7d

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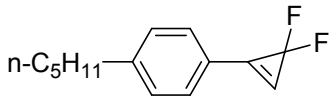

7d

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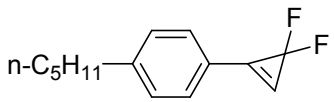

7d

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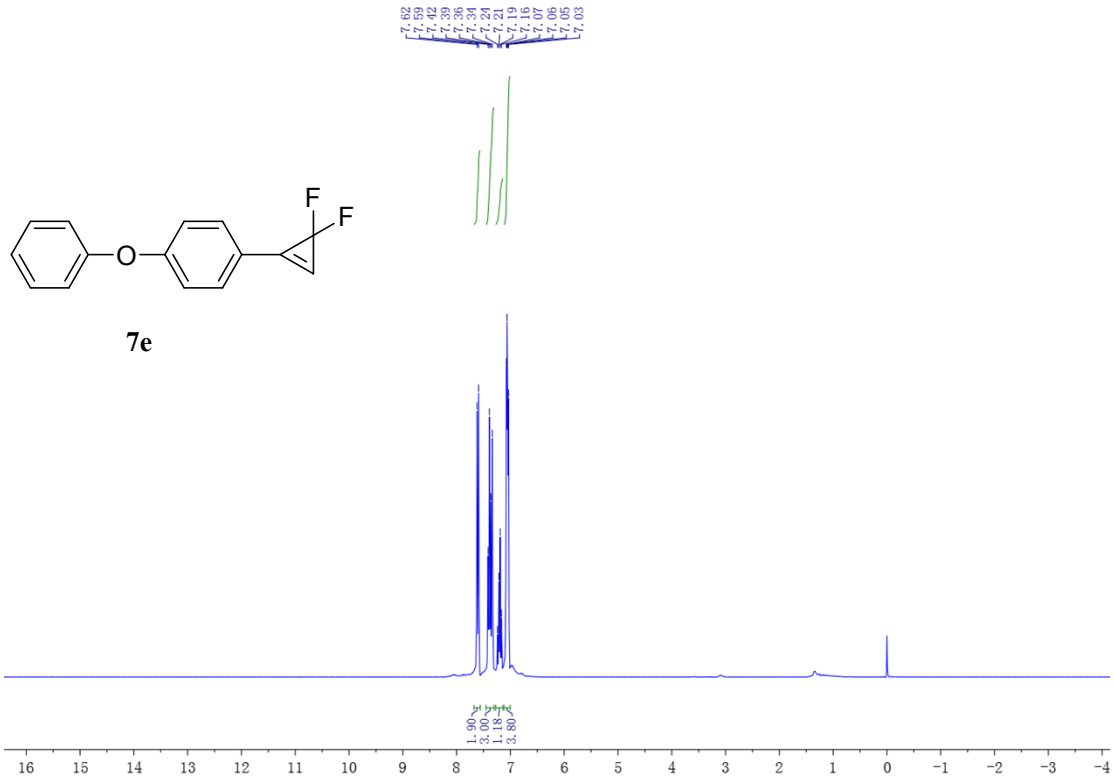
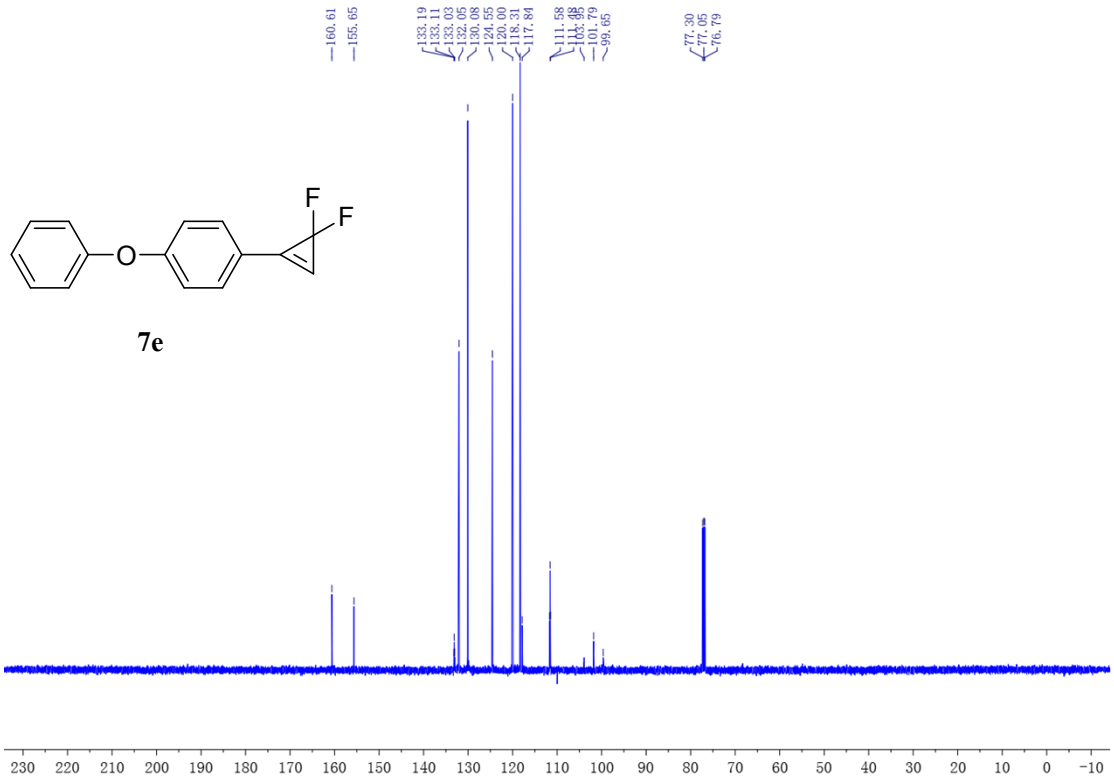


7e

^{19}F NMR

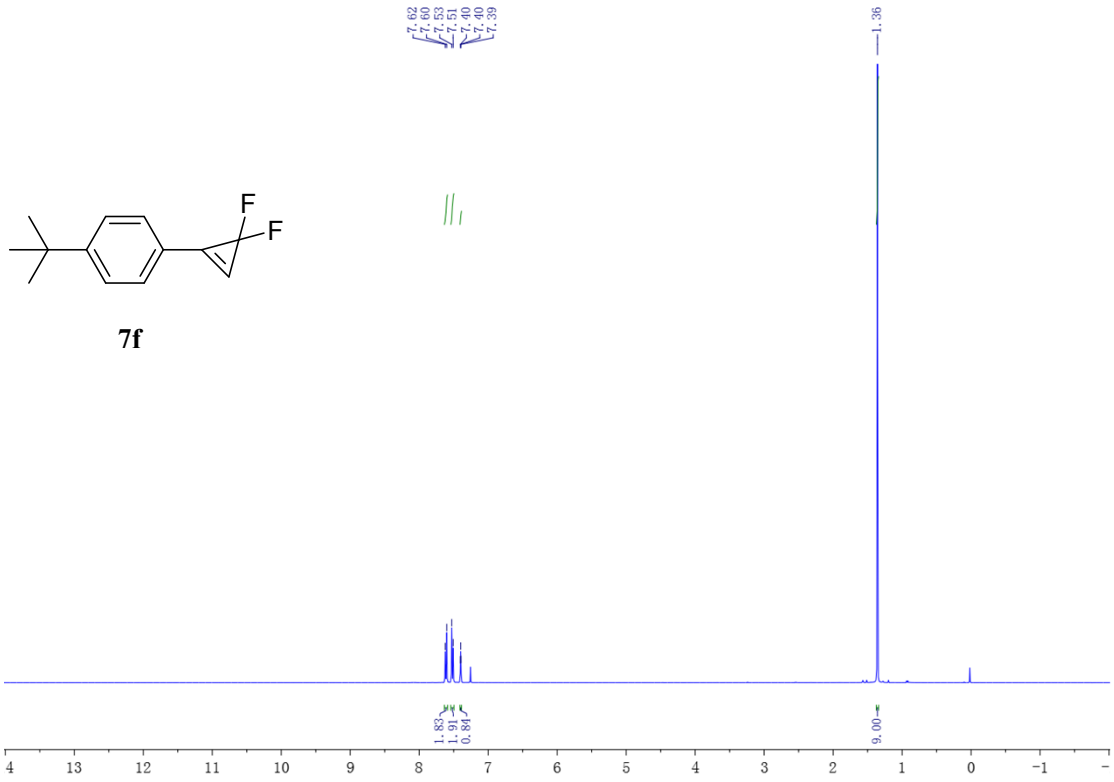
7e

^{13}C NMR



7e

^{1}H NMR



7f

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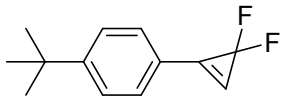

7f

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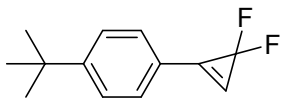

7f

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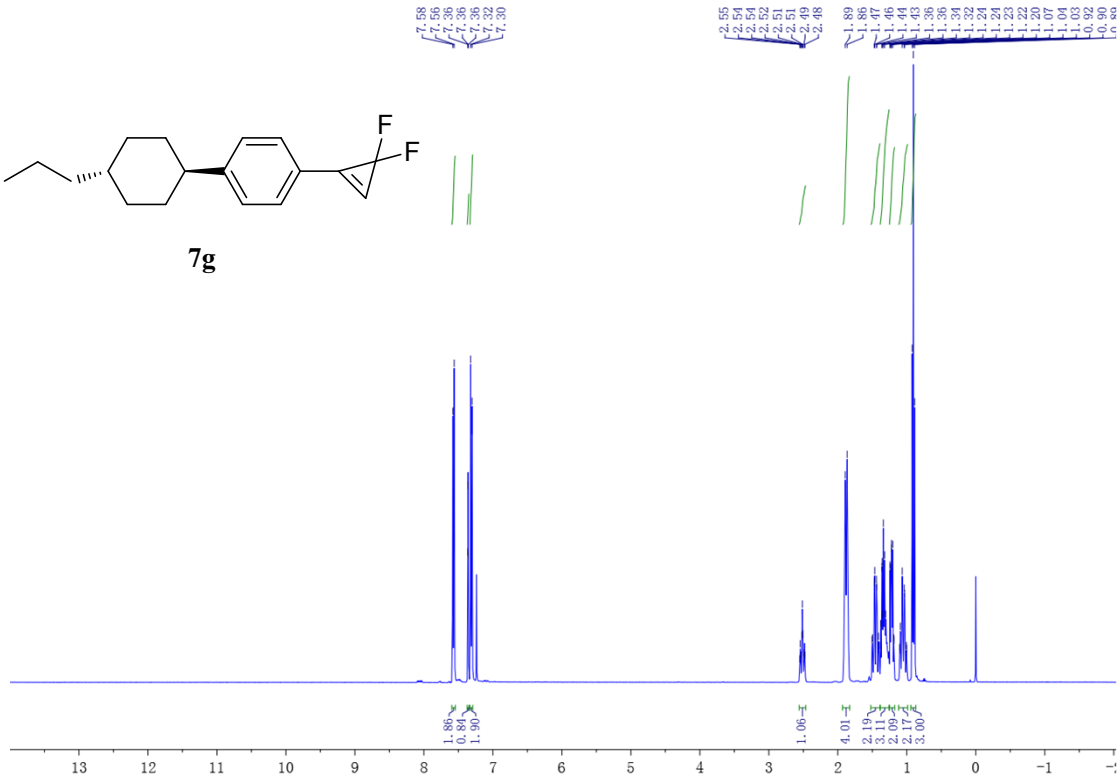

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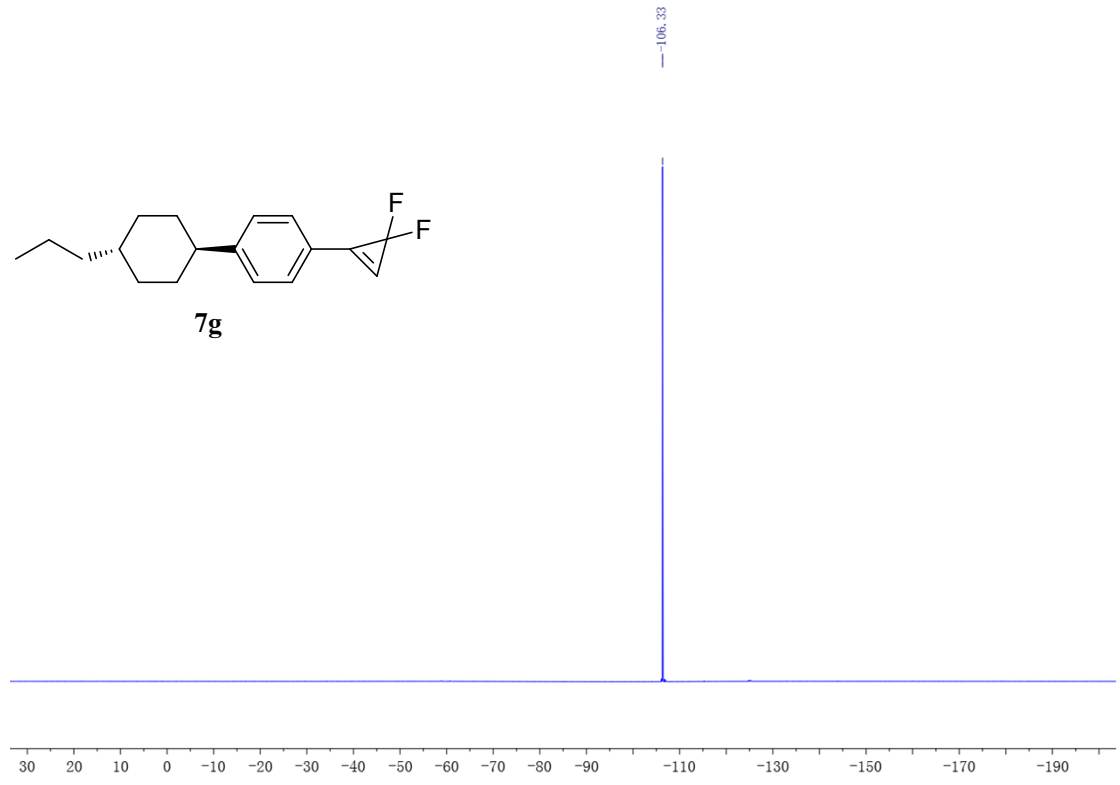

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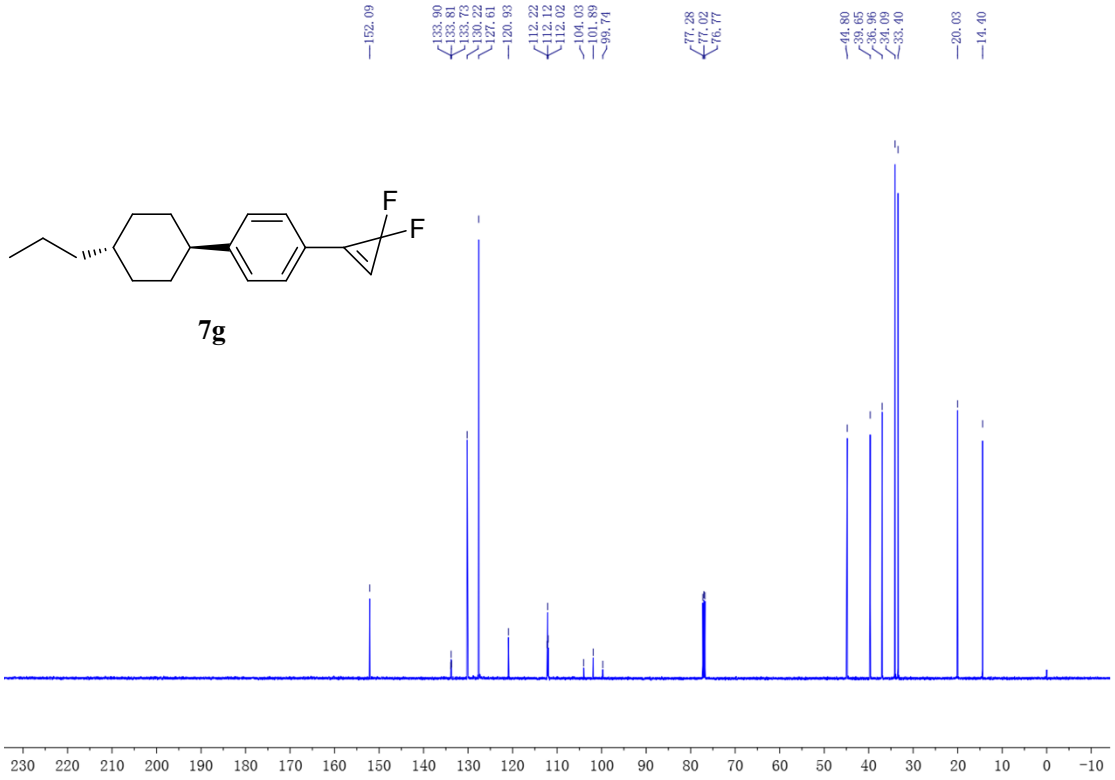

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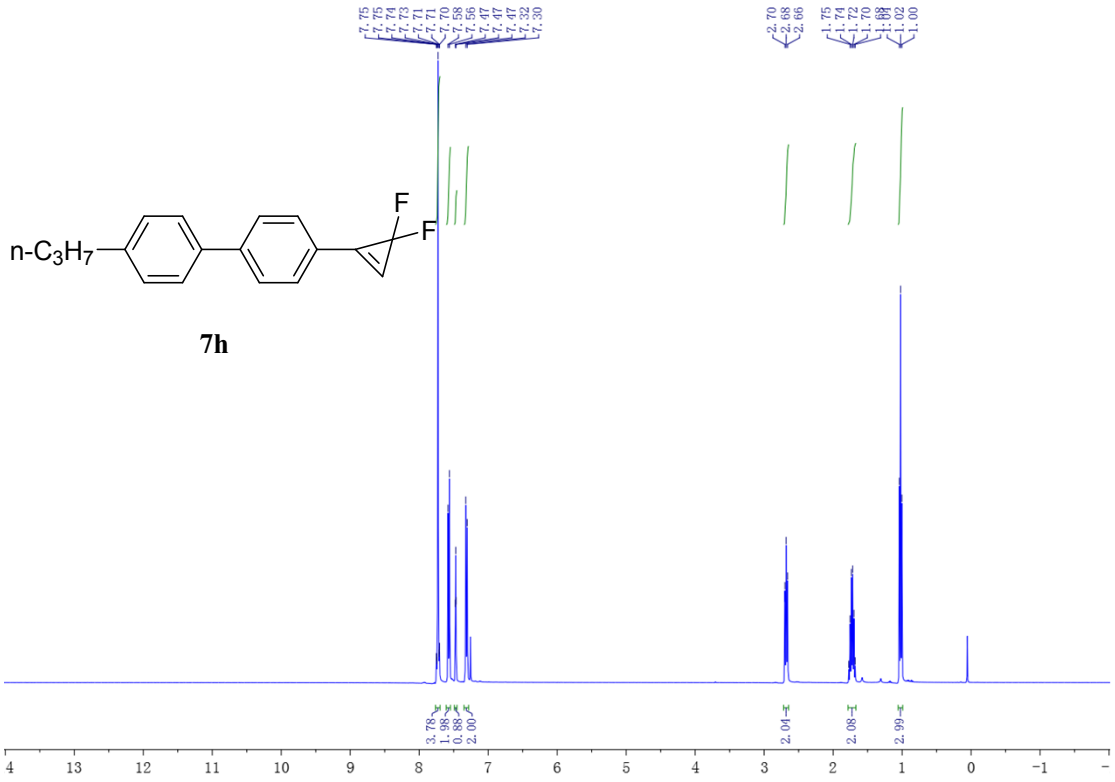
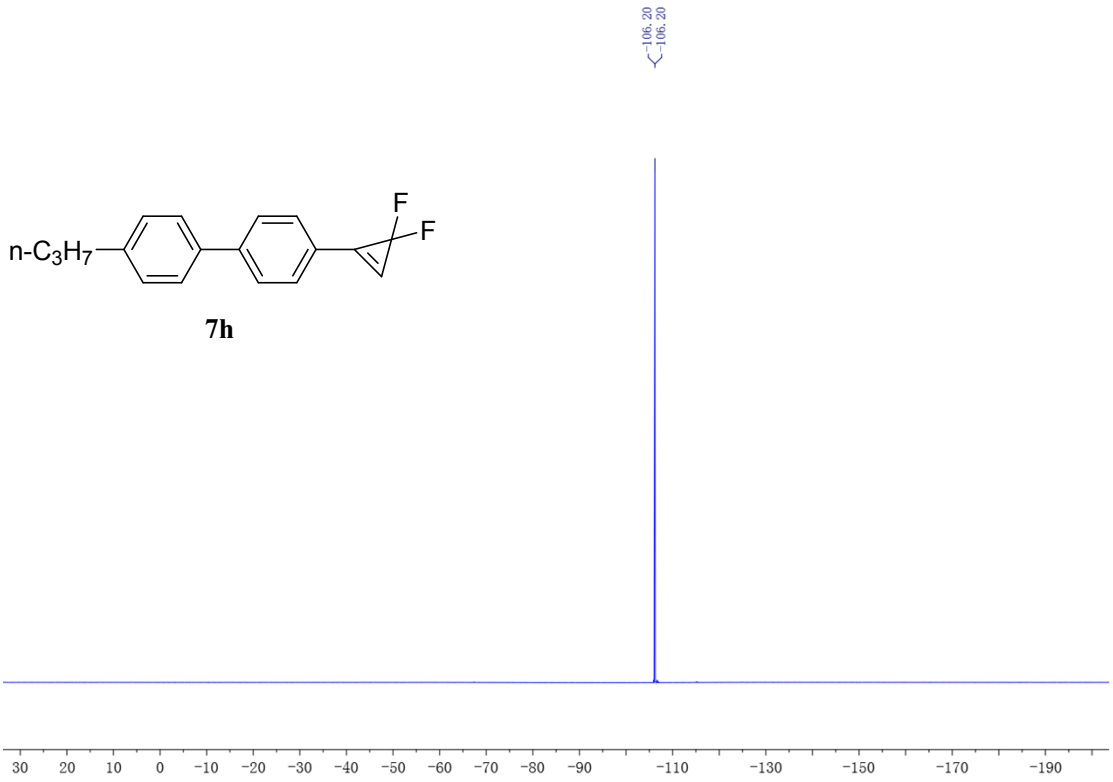
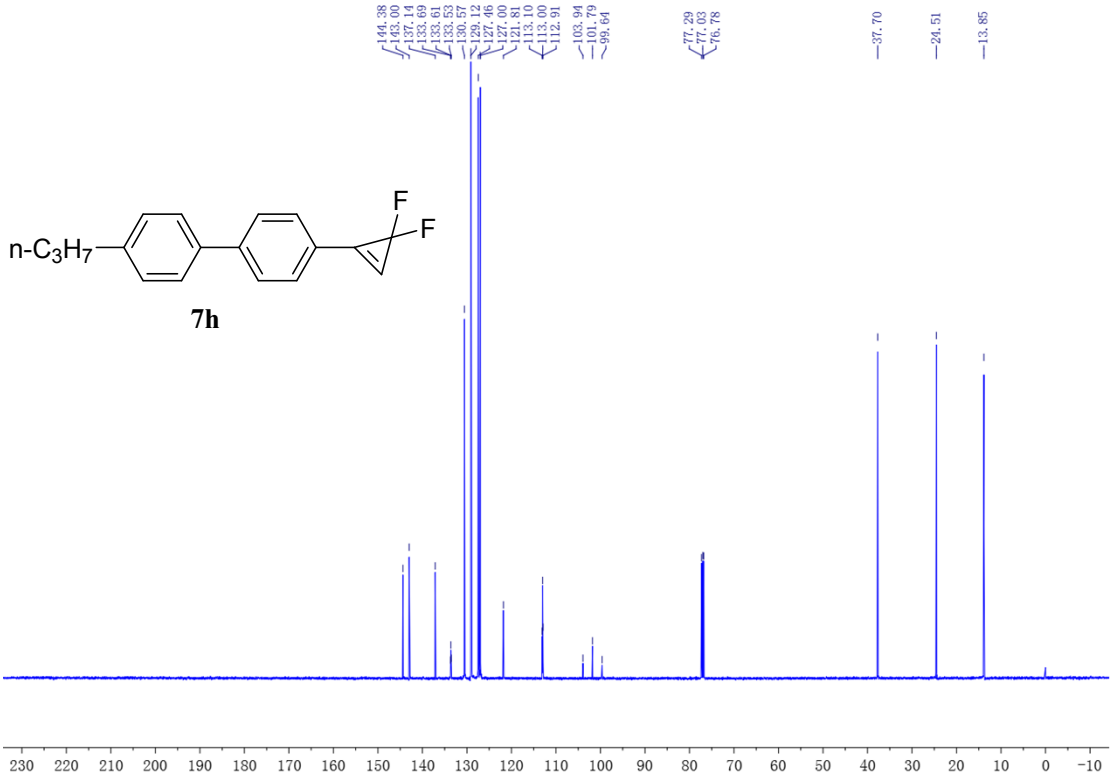


^{19}F NMR



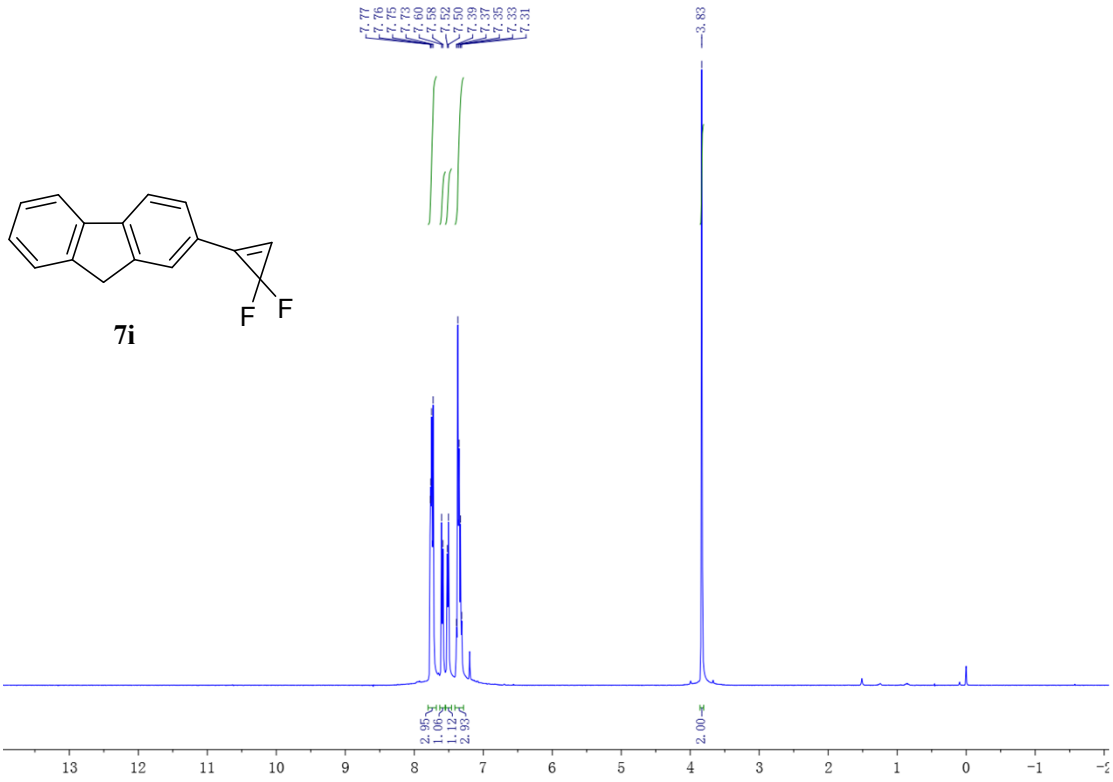
7h

^{13}C NMR



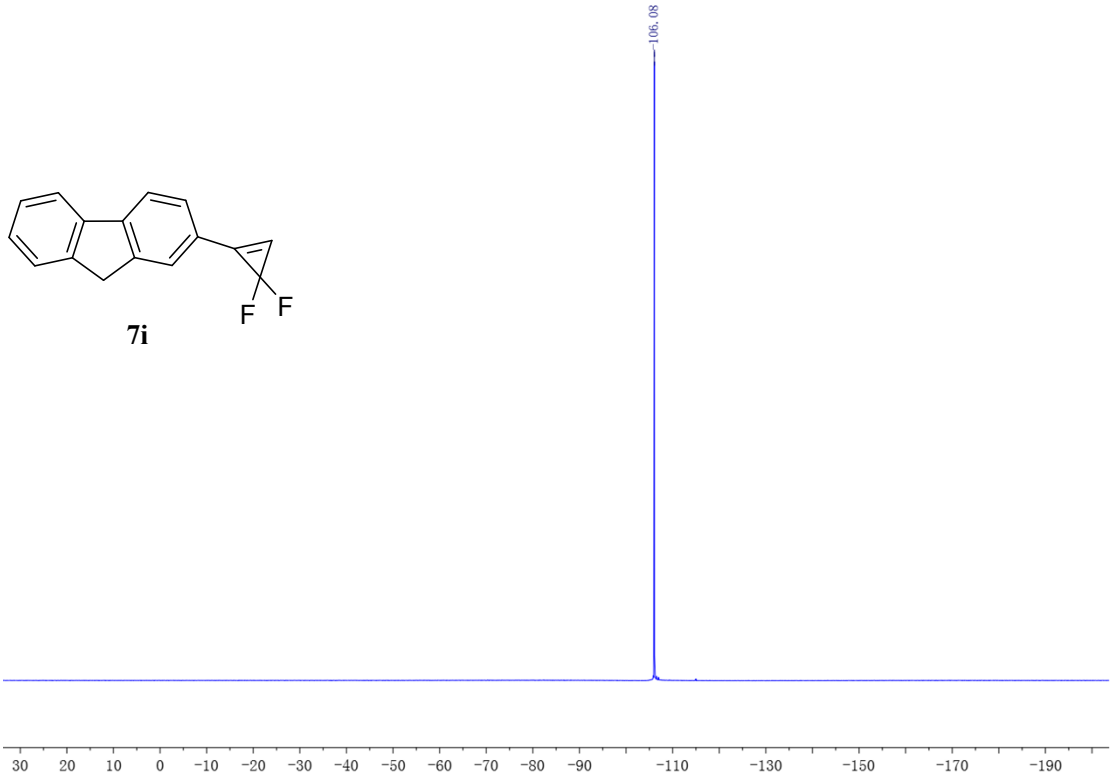
7h

^{1}H NMR



7i

^{19}F NMR



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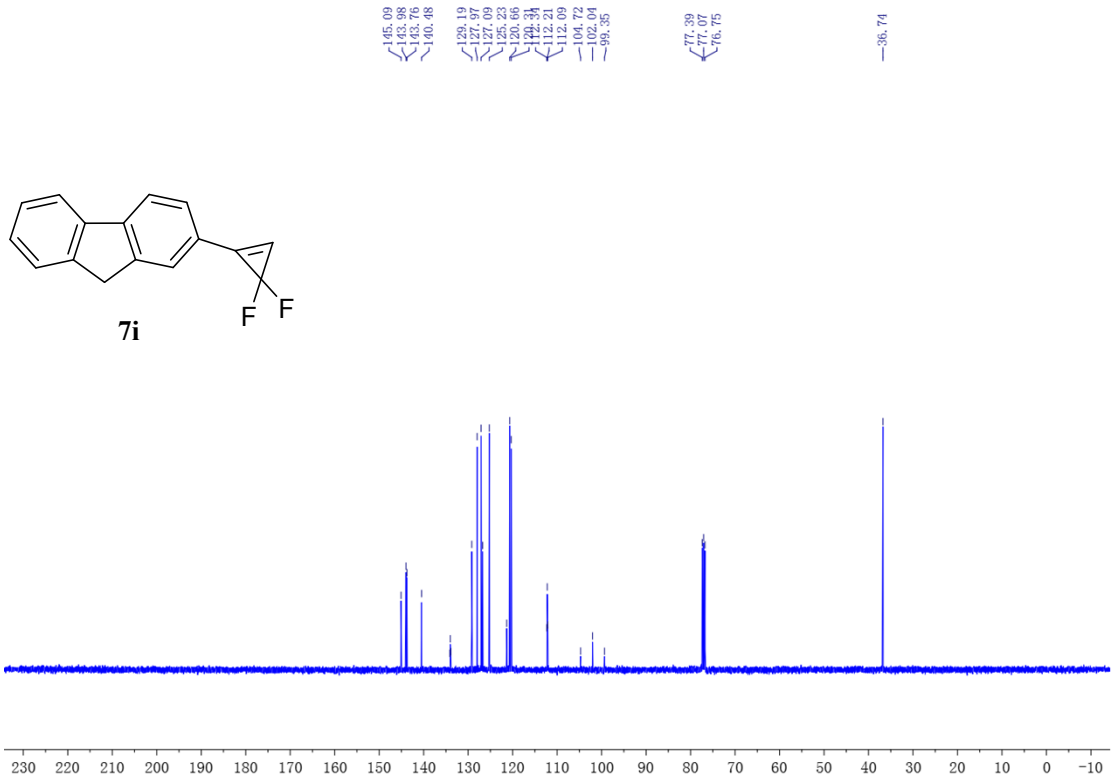

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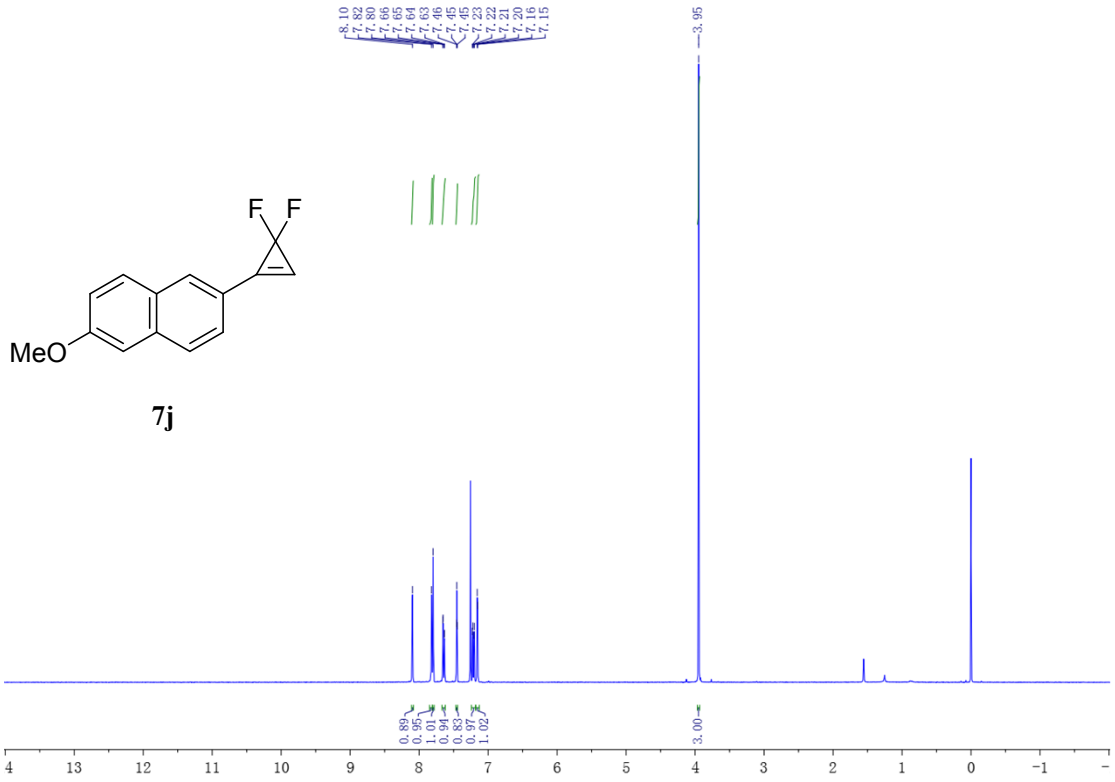

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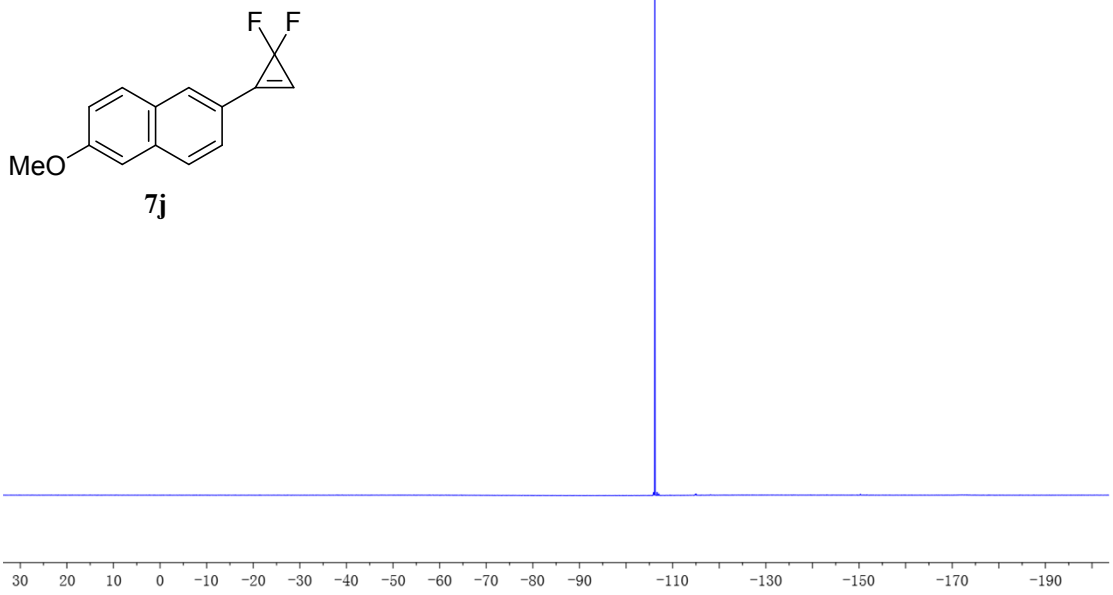

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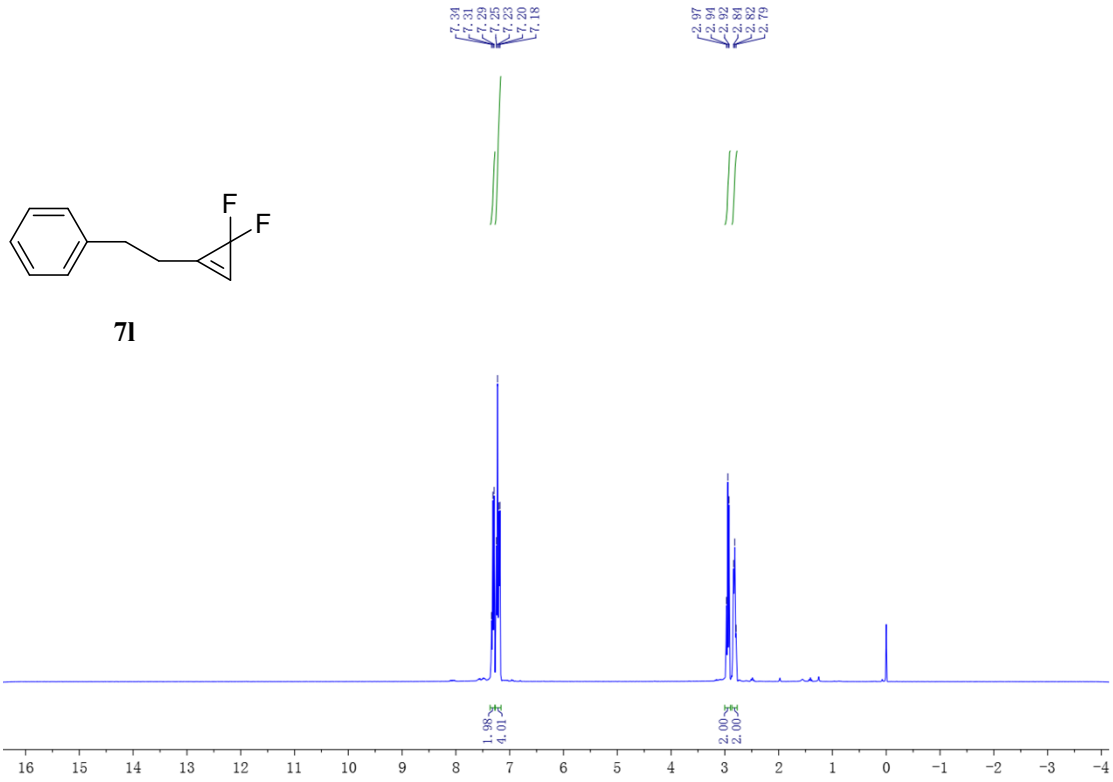
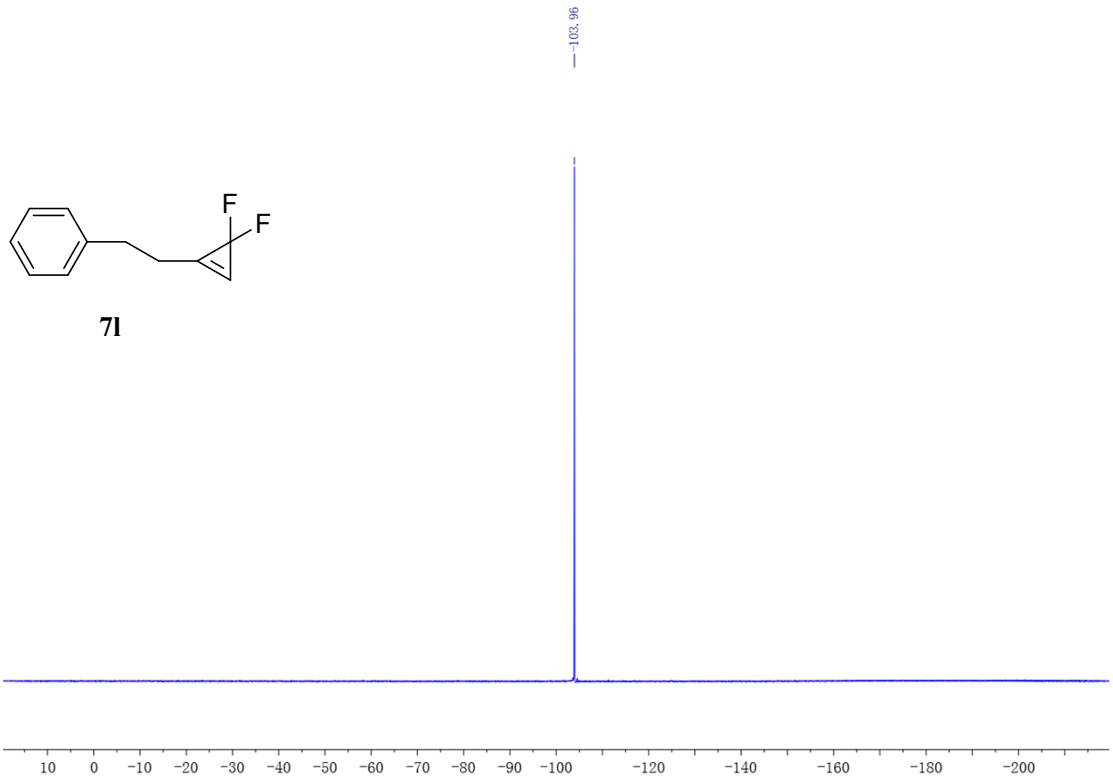
^{1}H NMR



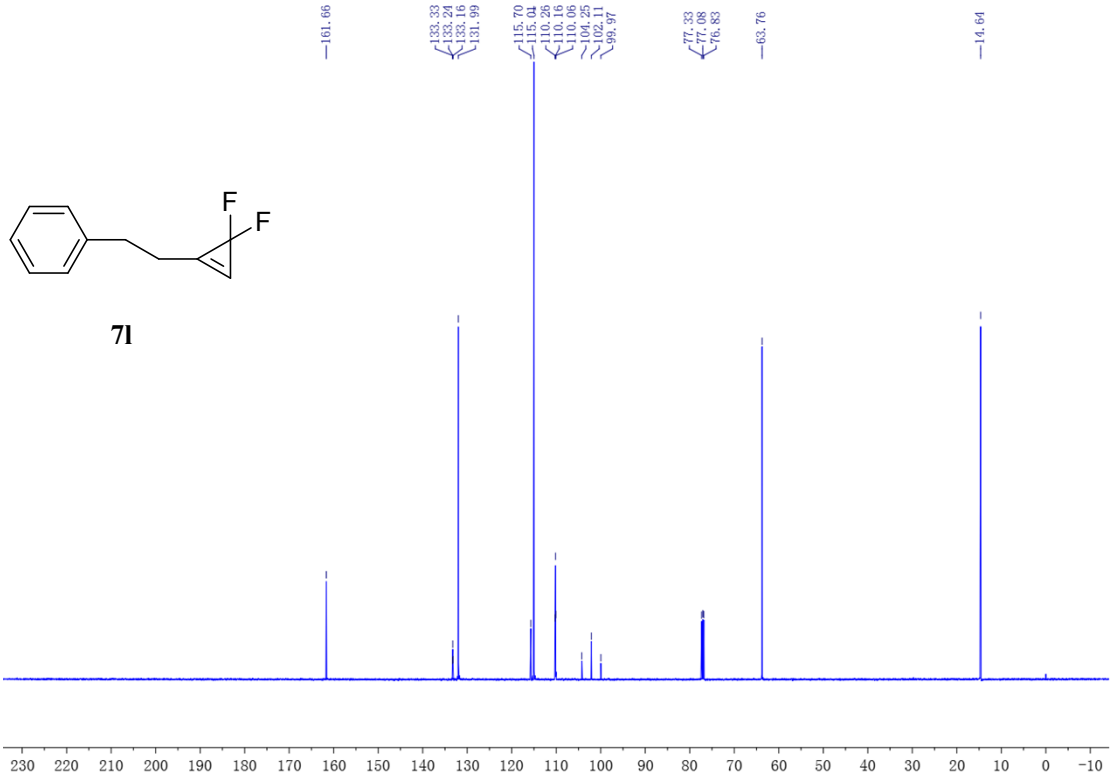
7l

^{19}F NMR



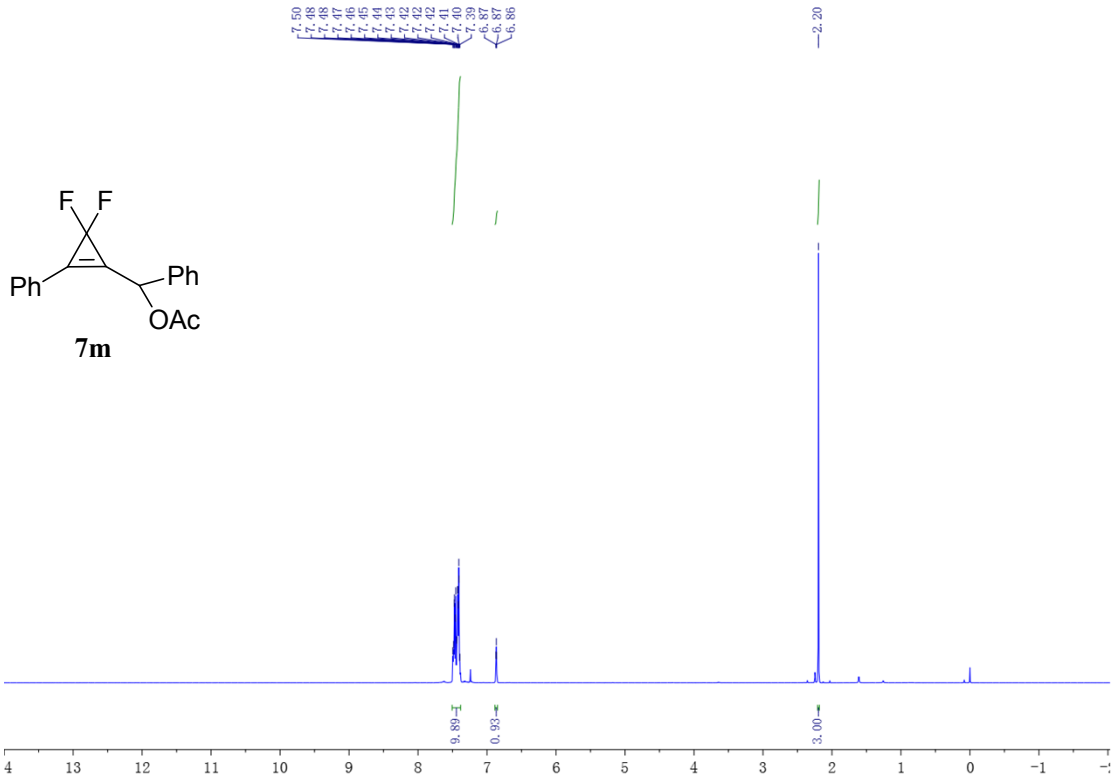
7l

^{13}C NMR



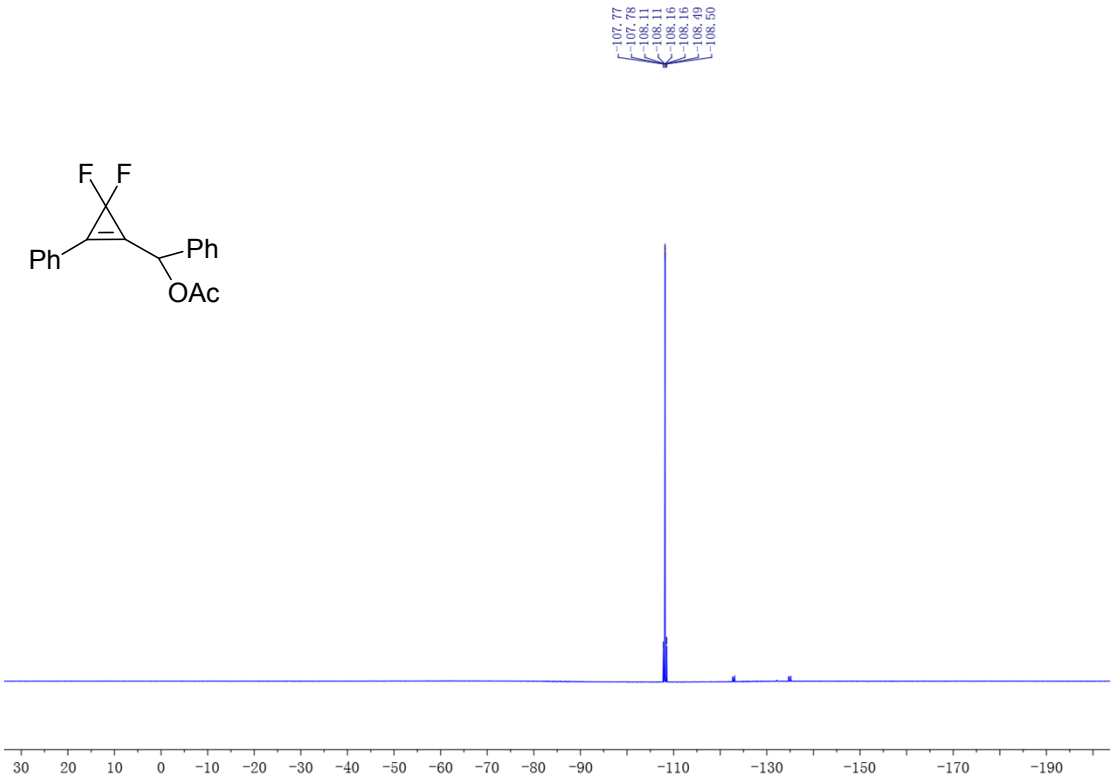
7l

^{1}H NMR

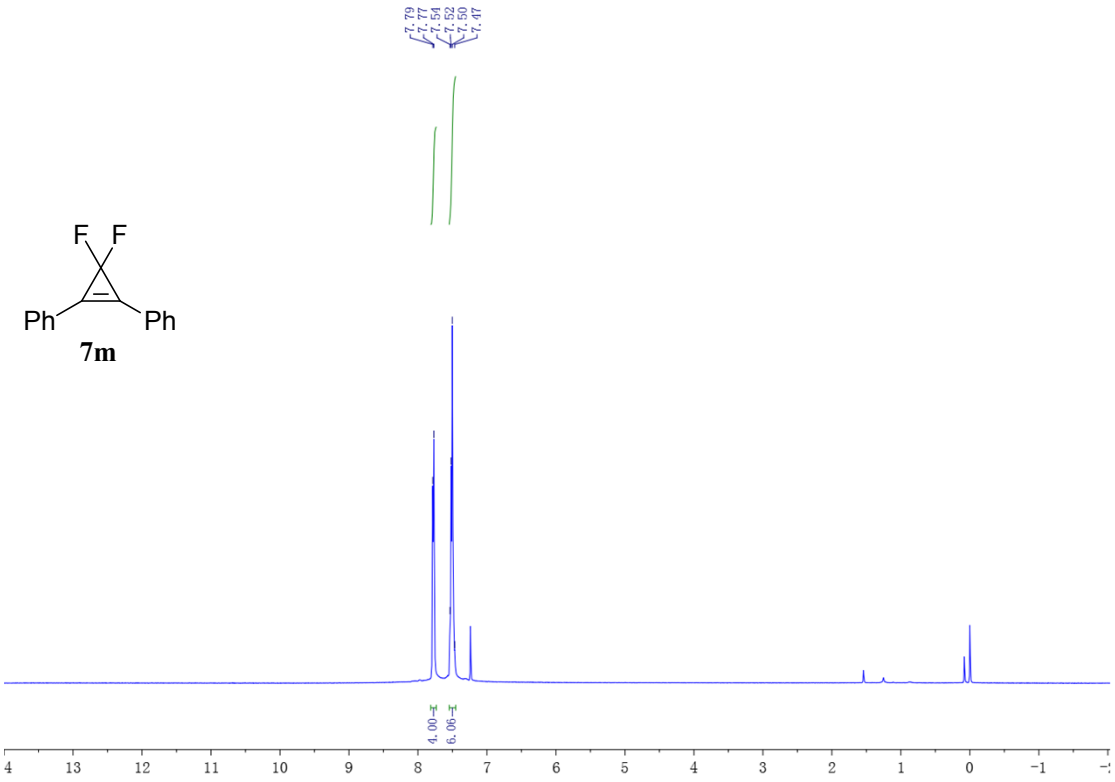


7m

^{19}F NMR

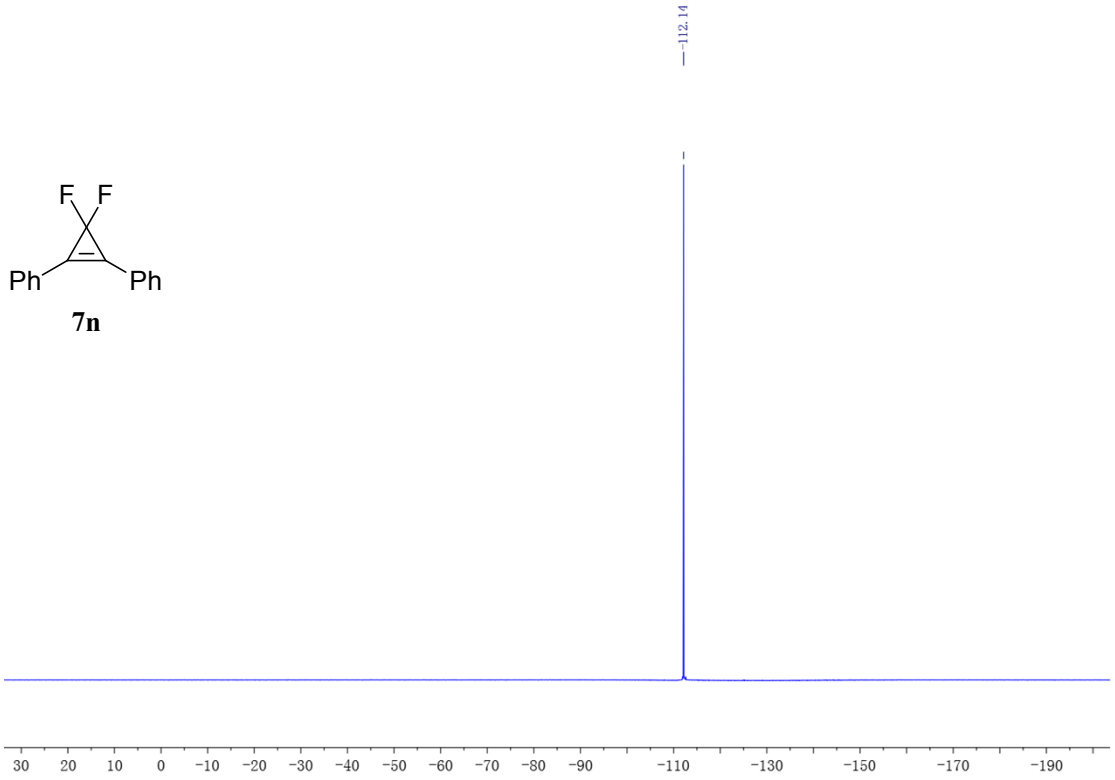


^{1}H NMR



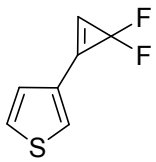
7m

^{19}F NMR

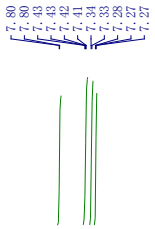


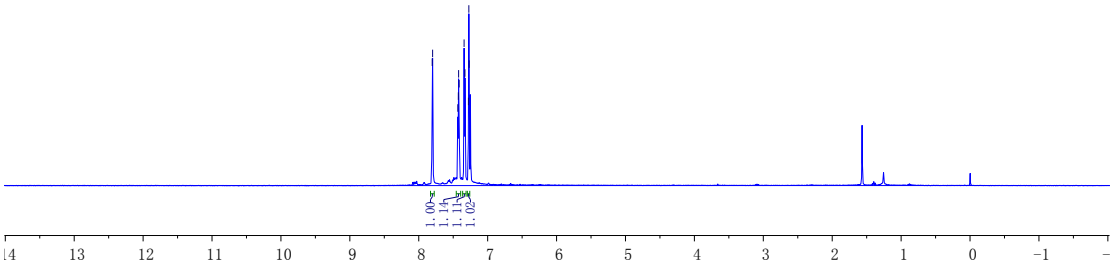
7n

^{1}H NMR

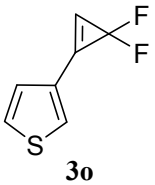


3o



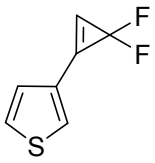


^{19}F NMR



3o

^{13}F NMR


F
F
S

3o

130.86
130.84
130.83
128.38
128.29
128.21
127.70
127.17
124.37
110.96
110.86
110.76
102.98
100.83
98.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10