Supporting Information

Difluoromethylcarbene for Iron-catalyzed cyclopropanation

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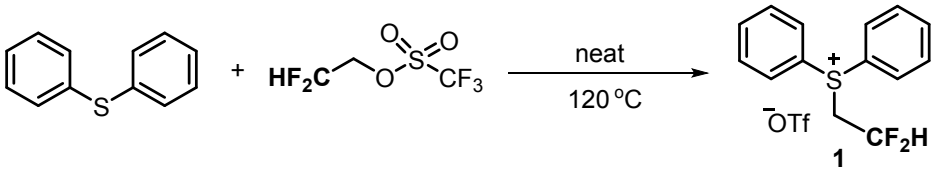
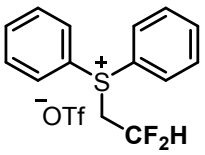
1. General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^{1}H 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 GC-MS or LC-MS (ESI). High resolution mass data were recorded on a high resolution mass spectrometer in the EI, ESI or MALDI mode. Unless otherwise noted, all reagents were obtained commercially and used without further purification. Substrates **2s**[1], **2v**[2] and **2w**[2] were prepared according to literature.

2. Procedure for the preparation of sulfonium salt 1



The mixture of 2,2-difluoroethyl triflate (8.56 g, 40 mmol, 1.0 equiv.) and diphenyl sulfide (22.32 g, 120 mmol, 3.0 equiv.) in a sealed tube was stirred at 120 °C for 20 hours. After the reaction mixture was cooled to room temperature, diethyl ether (10 mL) was added to precipitate the crude product, which was then washed by dry diethyl ether to give the final product **1** (15.69 g, yield 98%).



1

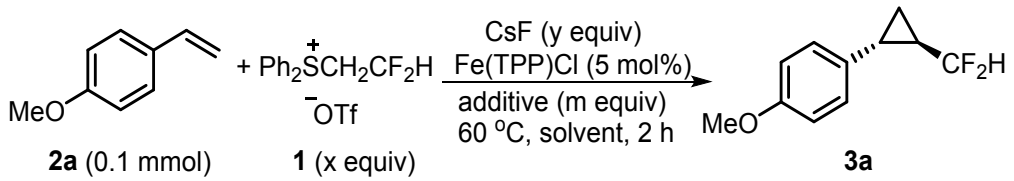
Diphenyl(2,2-difluoroethyl)sulfonium triflate (**1**)[3]: White solid. M.P.: 81.6 - 82.3 °C; ^{1}H NMR (400 MHz, Acetone) δ 8.28 (d, J = 7.6 Hz, 4H), 7.90 (t, J = 7.4 Hz, 2H), 7.82 (t, J = 7.6 Hz, 4H), 6.82 (t, J = 53.6 Hz, 1H), 5.25 (t, J = 15.2 Hz, 2H); ^{19}F NMR (376 MHz, Acetone-d_6) δ -78.94 (s, 3F), -115.27 (dt, J = 53.6, 15.2 Hz, 2F); ^{13}C NMR (101 MHz, Acetone-d_6) δ 134.97 (s), 131.51 (s), 130.83 (s), 125.22 (s), 121.40 (q, J = 321.4 Hz), 112.55 (t, J = 243.0 Hz), 46.37 (t, J = 23.6 Hz).

3. Screening Reaction Conditions for Cyclopropanation

Using the same reaction conditions as the cyclopropanation of aryl olefins with trifluoromethylcarbene catalyzed by Fe(TPP)Cl (TPP = 5,10,15,20-tetraphenyl-21*H*,23*H* -porphine) described by us recently[1], we did not observe the desired product in attempts to perform the cyclopropanation of olefin **2a** with difluoromethylcarbene produced from sulfonium salt **1** ($Ph_2S^+CH_2CF_2H$ TfO^-) (Table 1, entry 1). However, elevating the reaction temperature led to the observation of trace amounts of product **3a** (Table 1, entry 2). A brief survey of reaction

solvents (Table 1, entries 2-7) revealed that product was produced only with highly polar solvents (Table 1, entries 2-3).

Table 1. Optimization of Reaction Conditions[a].



2a (0.1 mmol) **1** (x equiv) **3a**

Entry	Solvent	Additive	x:y:m	Yield (%)[b]
1[c]	DMA	-	1.1 : 1.2 : 0	N.D.
2	DMA	-	1.1 : 1.2 : 0	trace
3	DMF	-	1.1 : 1.2 : 0	trace
4	CH_3CN	-	1.1 : 1.2 : 0	N.D.
5	DMSO	-	1.1 : 1.2 : 0	N.D.
6	Toluene	-	1.1 : 1.2 : 0	N.D.
7	THF	-	1.1 : 1.2 : 0	N.D.
8	DMF	DMAP	1.1 : 1.2 : 2	N.D.
9	DMF	Imidazole	1.1 : 1.2 : 2	N.D.
10	DMF	1-Methylimidazole	1.1 : 1.2 : 2	N.D.
11	DMF	$Na_2S_2O_4$	1.1 : 1.2 : 2	N.D.
12	DMF	Fe	1.1 : 1.2 : 2	N.D.
13	DMF	Zn[f]	1.1 : 1.2 : 2	63
14	DMF	Zn[f]	2 : 4 : 2	12-69
15[d]	DMF	Zn[f]	2 : 4 : 2	69
16[d]	DMF	Zn[f]	2 : 4 : 0.2	86
17	DMF	-	2 : 4 : 0	N.D.
18[e]	DMF	Zn[f]	2 : 4 : 0.2	N.D.
19[d]	DMF	Zn[f]	2 : 4 : 0.2	100

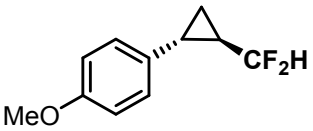
[a]Reaction conditions: The mixture of **2a**, Fe(TPP)Cl, **1**, CsF and the additive in the solvent (1.5 mL) was stirred at 60 °C for 2 h under a N_2 atmosphere. N.D. = Not detected. [b]The yields were determined by ^{19}F NMR spectroscopy. [c] The reaction mixture was stirred at room temperature under a N_2 atmosphere. [d]The mixture of Zn and Fe(TPP)Cl in DMF (0.5 mL) was stirred at 60 °C for 10 min under a N_2 atmosphere and then a mixture of **2a**, **1**, CsF and DMF (1 mL) was added. The resulting mixture was stirred at 60 °C for a further 2 h. [e]Fe(TPP)Cl was not used. [f]Zinc powder was used after being activated by aq. HCl.

Recent studies have shown that the presence of axial ligands such as *N,N*-4-dimethylaminopyridine (DMAP) favors the porphyrin-coordinated-transition-metal -catalyzed cyclopropanation of olefins with trifluoromethylcarbene.[4] Various ligands were screened, but none were favorable for the conversion (Table 1, entries 8-10). It is also believed that Fe^{III} must be reduced to Fe^{II} to promote the cyclopropanation reaction. [5] The examination of a series of

reducing agents (Table 1, entries 11-13) indicated that activated zinc powder (Table 1, entry 13) was efficient at reducing Fe^{III}. Increasing the loading of salt **1**, CsF and Zn slightly increased the yield (Table 1, entry 14). However, to our surprise, these results were not reproducible and the yields varied dramatically (Table 1, entries 13-14). Much effort was then put into optimizing the reaction process, and we realized that mixing Fe(TPP)Cl and Zn in advance was necessary to obtain good yields of product **3a** (Table 1, entry 15). We also found that Zn could result in the decomposition of salt **1**, the loading of Zn should therefore be minimized. Indeed, reactions with decreased Zn loadings had considerably improved yields (Table 1, entry 16). Omitting either the catalyst [Fe(TPP)Cl] or the reducing agent (Zn) from the reaction mixture completely suppressed the desired conversion (Table 1, entries 17-18). The reaction scale was increased to five times to demonstrate the practicality of the conversion (Table 1, entry 19). Interestingly, the yield of **3a** was increased by increasing the scale of the reaction (entry 19 vs entry 16).

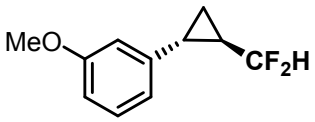
4. General procedure for cyclopropanation

Into a mixture of Fe(TPP)Cl (0.025 mmol, 17.6 mg, 5 mol %) and Zinc powder (0.1 mmol, 6.5 mg, 20 mol %) was added DMF (1 mL) under N_2 atmosphere. The mixture was stirred at 60°C for 10 min. Substrate (0.5 mmol, 1.0 equiv), sulfonium salt **1** (1.0 mmol, 400.4 mg, 2.0 equiv), cesium fluoride (2.0 mmol, 303.8 mg, 4.0 equiv) and DMF (4 mL) were then added. The resulting mixture was stirred at 60 °C for another 2 h, and was then diluted with CH_2Cl_2 (15 mL) and water (15 mL). The organic phase was separated and washed with water (15 mL, three times), and then dried over Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane/dichloromethane as eluent to give the final product.



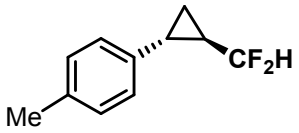
3a

1-(*trans*-2-(Difluoromethyl)cyclopropyl)-4-methoxybenzene **(3a)**: 97%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.73 (td, *J* = 57.5, 4.3 Hz, 1H), 3.80 (s, 3H), 2.20 - 2.14 (m, 1H), 1.63 - 1.50 (m, 1H), 1.23 - 1.16 (m, 1H), 1.07 - 1.00 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.59 (dddd, *J* = 280.4, 57.7, 10.7, 1.7 Hz, 1F), -115.53 (ddd, *J* = 280.4, 57.5, 10.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.34 (s), 132.20 (s), 127.58 (s), 116.83 (t, *J* = 238.1 Hz), 113.99 (s), 55.28 (s), 23.62 (t, *J* = 26.8 Hz), 18.15 (t, *J* = 4.6 Hz), 10.08 (t, *J* = 4.6 Hz). IR (neat) ν = 2903, 2838, 1520, 1461, 1402, 1378, 1249, 1181, 1148, 1100, 1033, 821 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{12}F_2O$ $[M]^+$: 198.0856, Found: 198.0857.



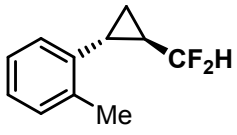
3b

1-(*trans*-2-(Difluoromethyl)cyclopropyl)-3-methoxybenzene (**3b**): 95%. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 5.75 (td, *J* = 57.4, 4.1 Hz, 1H), 3.80 (s, 3H), 2.21 - 2.13 (m, 1H), 1.69 - 1.55 (m, 1H), 1.26 - 1.19 (m, 1H), 1.13 - 1.05 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.08 (ddd, *J* = 280.8, 57.4, 10.7 Hz, 1F), -116.07 (ddd, *J* = 280.8, 57.4, 10.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.84 (s), 141.97 (s), 129.55 (s), 118.60 (s), 116.50 (t, *J* = 238.4 Hz), 112.37 (s), 111.61 (s), 55.18 (s), 24.01 (t, *J* = 26.8 Hz), 18.85 (t, *J* = 4.6 Hz), 10.52 (t, *J* = 4.6 Hz).IR (neat) ν = 3008, 2962, 2838, 1604, 1585, 1496, 1467, 1431, 1377, 1320, 1255, 1211, 1160, 1105, 1043, 989, 870, 777, 734, 695 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{12}F_2O$ $[M]^+$: 198.0856, Found: 198.0860.



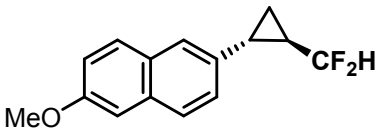
3c

1-(*trans*-2-(Difluoromethyl)cyclopropyl)-4-methylbenzene (**3c**): 92%. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 5.74 (td, *J* = 57.5, 4.1 Hz, 1H), 2.33 (s, 3H), 2.20 - 2.13 (m, 1H), 1.64 - 1.53 (m, 1H), 1.25 - 1.18 (m, 1H), 1.10 - 1.02 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.82 (ddd, *J* = 280.5, 57.5, 10.7 Hz, 1F), -115.90 (ddd, *J* = 280.5, 57.5, 10.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.17 (s), 136.00 (s), 129.20 (s), 126.30 (s), 116.66 (t, *J* = 238.2 Hz), 23.82 (t, *J* = 26.8 Hz), 20.98 (s), 18.50 (t, *J* = 4.6 Hz), 10.31 (t, *J* = 4.5 Hz). IR (neat) ν = 3020, 2964, 2925, 1519, 1466, 1431, 1416, 1378, 1225, 1184, 1149, 1101, 1081, 1034, 995, 947, 812, 662, 538 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{12}F_2$ $[M]^+$: 182.0907, Found: 182.0911.



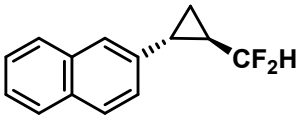
3d

1-(*trans*-2-(Difluoromethyl)cyclopropyl)-2-methylbenzene (**3d**): 92%. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.15 (m, 3H), 7.08 - 6.99 (m, 1H), 5.79 (td, *J* = 57.5, 4.3 Hz, 1H), 2.46 (s, 3H), 2.26 - 2.18 (m, 1H), 1.61 - 1.49 (m, 1H), 1.26 - 1.19 (m, 1H), 1.16 - 1.09 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.87 (ddd, *J* = 280.5, 57.5, 10.2 Hz, 1F), -114.95 (ddd, *J* = 280.5, 57.5, 10.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.07 (s), 137.79 (s), 129.96 (s), 126.72 (s), 126.20 (s), 125.99 (s), 117.12 (t, *J* = 238.2 Hz), 22.60 (t, *J* = 26.8 Hz), 19.53 (s), 17.24 (dd, *J* = 5.1, 4.0 Hz), 8.62 (dd, *J* = 4.7, 4.1 Hz). IR (neat) ν = 3022, 2959, 1494, 1461, 1430, 1411, 1379, 1185, 1150, 1103, 1083, 1034, 989, 910, 759, 733, 438 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{12}F_2$ $[M]^+$: 182.0907, Found: 180.0911.



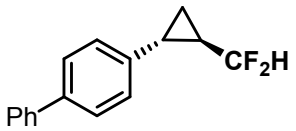
3e

2-(*trans*-2-(Difluoromethyl)cyclopropyl)-6-methoxynaphthalene (**3e**): Quantitative. White solid. M.p.: 78.0-78.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.53 (s, 1H), 7.23 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.17 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 5.83 (td, *J* = 57.5, 4.1 Hz, 1H), 3.94 (s, 3H), 2.40 - 2.32 (m, 1H), 1.77 - 1.66 (m, 1H), 1.34 - 1.27 (m, 1H), 1.24 - 1.16 (m, 1H). ^{19}F NMR (376 MHz,$CDCl_3$) δ -114.88 (ddd, *J* = 280.5, 58.7, 10.6 Hz, 1F), -115.78 (ddd, *J* = 280.5, 57.8, 10.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.44 (s), 135.24 (s), 133.33 (s), 128.91 (s), 128.89 (s), 127.06 (s), 125.46 (s), 124.73 (s), 119.09 (s), 116.64 (t, *J* = 238.3 Hz), 105.69 (s), 55.30 (s), 23.78 (t, *J* = 26.8 Hz), 18.90 (t, *J* = 4.6 Hz), 10.25 (t, *J* = 4.5 Hz). IR (neat) ν = 3012, 2967, 2939, 1632, 1605, 1507, 1491, 1405, 1394, 1375, 1275, 1265, 1241, 1207, 1179, 1161, 1123, 1108, 1061, 1028, 994, 880, 855, 818, 697 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{14}F_2O$ $[M]^+$: 248.1013, Found: 248.1018.



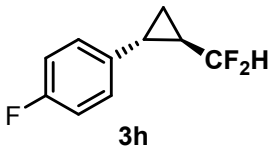
3f

2-(*trans*-2-(Difluoromethyl)cyclopropyl)naphthalene (**3f**): 90%. White solid. M.p.: 39.8-40.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.74 (m, 3H), 7.57 (s, 1H), 7.51 - 7.40 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 5.81 (td, *J* = 57.5, 4.1 Hz, 1H), 2.40 - 2.33 (m, 1H), 1.79 - 1.66 (m, 1H), 1.35 - 1.27 (m, 1H), 1.24 - 1.17 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.01 (ddd, *J* = 275.5, 57.5, 10.8 Hz, 1F), -115.90 (ddd, *J* = 275.5, 57.5, 10.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.64 (s), 133.44 (s), 132.27 (s), 128.23 (s), 127.66 (s), 127.40 (s), 126.29 (s), 125.50 (s), 124.87 (s), 124.81 (s), 116.52 (t, *J* = 238.4 Hz), 23.96 (t, *J* = 26.7 Hz), 19.05 (t, *J* = 4.6 Hz), 10.45 (t, *J* = 4.5 Hz). IR (neat) ν = 3059, 3018, 2982, 1635, 1601, 1508, 1458, 1430, 1416, 1382, 1364, 1271, 1207, 1177, 1152, 1103, 1079, 1041, 1003, 975, 890, 855, 821, 809, 751, 669, 479 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{12}F_2$ $[M]^+$: 218.0907, Found: 218.0905.



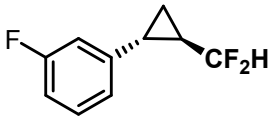
3g

4-(*trans*-2-(Difluoromethyl)cyclopropyl)-1,1'-biphenyl (**3g**): 99%. White solid. M.p.: 73.4-73.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.78 (td, *J* = 57.5, 4.0 Hz, 1H), 2.31 - 2.19 (m, 1H), 1.72 - 1.60 (m, 1H), 1.32 - 1.22 (m, 1H), 1.18 - 1.08 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.15 (ddd, *J* = 279.6, 57.5, 10.7 Hz, 1F), -116.05 (ddd, *J* = 279.6, 57.5, 10.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.75 (s), 139.38 (s), 139.34 (s), 128.77 (s), 127.21 (s), 127.20 (s), 126.96 (s), 126.70 (s), 116.43 (t, *J* = 238.4 Hz), 24.06 (t, *J* = 26.8 Hz), 18.51 (t, *J* = 4.7 Hz), 10.59 (t, *J* = 4.6 Hz). IR (neat) ν = 3032, 2987, 1611, 1527, 1488, 1465, 1435, 1409, 1374, 1192, 1123, 1105, 1017, 943, 832, 762, 724, 690, 513 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{14}F_2$ $[M]^+$: 244.1064, Found: 244.1059.



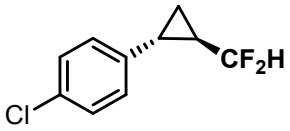
3h

1-(*trans*-2-(Difluoromethyl)cyclopropyl)-4-fluorobenzene (**3h**): 84%. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.07 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.96 (t, *J* = 8.5 Hz, 2H), 5.74 (td, *J* = 57.5, 4.0 Hz, 1H), 2.21 - 2.14 (m, 1H), 1.60 - 1.49 (m, 1H), 1.25 - 1.18 (m, 1H), 1.06 - 0.99 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.65 (dd, *J* = 57.5, 10.7 Hz, 2F), -116.61 - -116.71 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.56 (d, *J* = 244.5 Hz), 135.80 (d, *J* = 3.1 Hz), 127.98 (d, *J* = 7.9 Hz), 116.40 (t, *J* = 238.4 Hz), 115.30 (d, *J* = 21.4 Hz), 23.81 (t, *J* = 26.8 Hz), 18.11 (t, *J* = 4.6 Hz), 10.29 (t, *J* = 4.6 Hz). IR (neat) ν = 2954, 2921, 1653, 1559, 1541, 1507, 1458, 1376, 1098, 1023 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_9F_3$ $[M]^+$: 186.0656, Found: 186.0659.



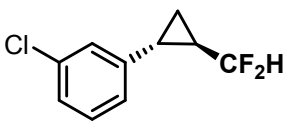
3i

1-(*trans*-2-(Difluoromethyl)cyclopropyl)-3-fluorobenzene (**3i**): 60%. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.19 (m, 1H), 6.92 - 6.84 (m, 2H), 6.78 (dd, *J* = 10.0, 8.7 Hz, 1H), 5.75 (td, *J* = 57.5, 3.8 Hz, 1H), 2.22 - 2.14 (m, 1H), 1.66 - 1.54 (m, 1H), 1.28 - 1.21 (m, 1H), 1.11 - 1.02 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.34 - -113.45 (m，1F), -116.11 (dd, *J* = 57.5, 10.8 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.02 (d, *J* = 245.7 Hz), 142.96 (d, *J* = 7.7 Hz), 129.96 (d, *J* = 8.5 Hz), 122.08 (d, *J* = 2.7 Hz), 116.09 (t, *J* = 238.6 Hz), 113.28 (d, *J* = 21.1 Hz), 113.19 (d, *J* = 21.9 Hz), 24.17 (t, *J* = 26.8 Hz), 18.49 (dd, *J* = 4.7, 2.2 Hz), 10.67 (t, *J* = 4.6 Hz). IR (neat) ν = 2960, 2925, 2854, 1590, 1460, 1412, 1377, 1261, 1099, 1023, 859, 800, 690, 669 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_9F_3$ $[M]^+$: 186.0656, Found: 186.0652.



3j

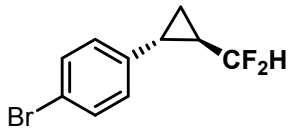
1-Chloro-4-(*trans*-2-(difluoromethyl)cyclopropyl)benzene (**3j**): Quantitative. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 5.75 (td, *J* = 57.4, 4.0 Hz, 1H), 2.19 - 2.12 (m, 1H), 1.62 - 1.51 (m, 1H), 1.26 - 1.20 (m, 1H), 1.07 - 1.00 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.87 (dd, *J* = 57.4, 10.8 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.75 (s), 132.10 (s), 128.61 (s), 127.76 (s), 116.23 (t, *J* = 238.5 Hz), 24.01 (t, *J* = 26.8 Hz), 18.23 (t, *J* = 4.7 Hz), 10.50 (t, *J* = 4.6 Hz). IR (neat) ν = 3015, 2967, 1498, 1466, 1432, 1401, 1376, 1187, 1151, 1097, 1081, 1035, 1014, 996, 909, 82,735, 533, 512 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_9F_2Cl$ $[M]^+$: 202.0361, Found: 202.0359.



3k

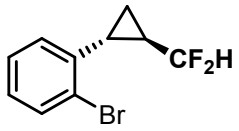
1-Chloro-3-(*trans*-2-(difluoromethyl)cyclopropyl)benzene (**3k**): 84%. Colourless oil. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.22 - 7.14 (m, 2H), 7.07 (s, 1H), 6.98 (d, *J* = 7.1 Hz, 1H), 5.75 (td, *J* = 57.4, 3.9 Hz, 1H), 2.20 - 2.11 (m, 1H), 1.66 - 1.54 (m, 1H), 1.28 - 1.21 (m, 1H), 1.11 - 1.03 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.10 (dd, *J* = 57.4, 10.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.37 (s), 134.40 (s), 129.74 (s), 126.57 (s), 126.53 (s), 124.65 (s), 116.07 (t, *J* = 238.6 Hz), 24.07 (t, *J* = 26.8 Hz), 18.43 (t, *J* = 4.7 Hz), 10.57 (t, *J* = 4.7 Hz). IR (neat) ν = 3017, 2967, 1601, 1573, 1466, 1431, 1413, 1376, 1188, 1151, 1096, 1082, 1035, 9989, 954, 871, 781, 692, 667, 594, 445 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_9F_2Cl$ $[M]^+$: 202.0361, Found: 202.0369.



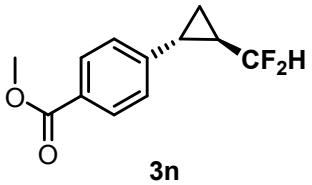
3l

1-Bromo-4-(*trans*-2-(difluoromethyl)cyclopropyl)benzene (**3l**): 90%. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.75 (td, *J* = 57.4, 4.0 Hz, 1H), 2.18 - 2.11 (m, 1H), 1.63 - 1.50 (m, 1H), 1.27 - 1.20 (m, 1H), 1.07 - 1.00 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.90 (dd, *J* = 57.4, 10.8 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.29 (s), 131.55 (s), 128.13 (s), 120.05 (s), 116.18 (t, *J* = 238.6 Hz), 24.01 (t, *J* = 26.8 Hz), 18.30 (t, *J* = 4.7 Hz), 10.51 (t, *J* = 4.6 Hz). IR (neat) ν = 3030, 2967, 1494, 1465, 1432, 1398, 1376, 1184, 1150, 1099, 1075, 1035, 1010, 996, 908, 819, 765, 734, 532, 509 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_9F_2Br$ $[M]^+$: 245.9856, Found: 245.9855.



3m

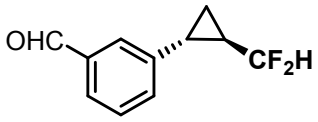
1-Bromo-2-(*trans*-2-(difluoromethyl)cyclopropyl)benzene (**3m**): 93%. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 5.89 (td, *J* = 57.6, 3.7 Hz, 1H), 2.39 - 2.31 (m, 1H), 1.61 - 1.48 (m, 1H), 1.35 - 1.27 (m, 1H), 1.11 - 1.03 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.92 (ddd, *J* = 281.2, 57.8, 9.0 Hz, 1F), -118.39 (ddd, *J* = 281.2, 57.5, 13.1 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.06 (s), 132.65 (s), 128.12 (s), 127.61 (s), 127.45 (s), 126.04 (s), 116.23 (t, *J* = 238.8 Hz), 23.22 (dd, *J* = 27.5, 25.7 Hz), 20.04 (t, *J* = 5.1 Hz), 9.23 (t, *J* = 4.3 Hz). IR (neat) ν = 3060, 2967, 1592, 1567, 1480, 1458, 1430, 1412, 1377, 1188, 1151, 1101, 1081, 1053, 1026, 984, 46, 922, 750, 655, 446 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_9F_2Br$ $[M]^+$: 245.9856, Found: 245.9862.



3n

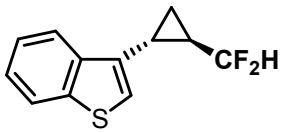
Methyl 4-(*trans*-2-(difluoromethyl)cyclopropyl)benzoate (**3n**): Quantitative. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.76 (td, *J* = 57.4, 3.8 Hz, 1H), 3.87 (s, 3H), 2.24 - 2.16 (m, 1H), 1.71 - 1.57 (m, 1H), 1.32 - 1.23 (m, 1H), 1.14 - 1.06 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.20 (ddd, *J* = 57.4, 10.8, 5.7 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.84 (s), 145.82 (s), 129.82 (s), 128.28 (s), 126.09 (s), 116.00 (t, *J* = 238.7 Hz), 52.00 (s), 24.58 (t, *J* = 26.9 Hz), 18.78 (t, *J* = 4.7 Hz), 11.14 (t, *J* = 4.6 Hz). IR (neat) ν

= 3015, 2955, 1718, 1613, 1458, 1436, 1408, 1377, 1314, 1282, 1183, 1150, 1112, 1034, 1019, 994, 850, 771, 703, 536 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{12}F_2O_2$ $[M]^+$: 226.0817, Found: 226.0811.



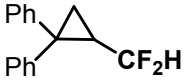
3o

3-(*trans*-2-(Difluoromethyl)cyclopropyl)benzaldehyde (**3o**): 93%. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.58 (s, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 5.77 (td, *J* = 57.4, 3.7 Hz, 1H), 2.30 - 2.19 (m, 1H), 1.71 - 1.56 (m, 1H), 1.33 - 1.23 (m, 1H), 1.16 - 1.06 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.61 (ddd, *J* = 280.3, 57.4, 10.5 Hz, 1F), -116.50 (ddd, *J* = 280.3, 57.4, 10.5 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.17 (s), 141.50 (s), 136.62 (s), 132.68 (s), 129.16 (s), 128.26 (s), 126.73 (s), 116.04 (t, *J* = 238.6 Hz), 24.17 (t, *J* = 26.9 Hz), 18.39 (t, *J* = 4.7 Hz), 10.68 (t, *J* = 4.6 Hz). IR (neat) ν = 3016, 2988, 1698, 1607, 1588, 1489, 1432, 1412, 1378, 1293, 1243, 1188, 1150, 1105, 1084, 1035, 989, 937, 758, 738, 691, 650 cm^{-1}. HRMS (EI): calcd. for $C_{11}H_{10}F_2O$ $[M]^+$: 196.0700, Found: 196.0704.



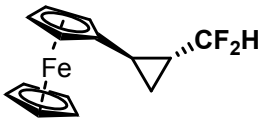
3p

3-(*trans*-2-(Difluoromethyl)cyclopropyl)benzo[b]thiophene (**3p**): 91%. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 5.84 (td, *J* = 57.5, 4.2 Hz, 1H), 2.38 - 2.30 (m, 1H), 1.65 - 1.53 (m, 1H), 1.30 - 1.23 (m, 1H), 1.21 - 1.13 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.92 (ddd, *J* = 281.2, 57.5, 9.4 Hz, 1F), -116.04 (ddd, *J* = 281.2, 57.4, 11.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.48 (s), 139.29 (s), 135.19 (s), 124.69 (s), 124.27 (s), 122.89 (s), 121.94 (s), 121.60 (s), 116.73 (t, *J* = 238.3 Hz), 22.02 (t, *J* = 26.8 Hz), 12.71 (dd, *J* = 5.5, 4.1 Hz), 8.42 (dd, *J* = 4.9, 4.0 Hz). IR (neat) ν = 3086, 2967, 1464, 1430, 1414, 1380, 1254, 1182, 1150, 1094, 1036, 991, 909, 830, 764, 733, 436 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{10}F_2S$ $[M]^+$: 224.0471, Found: 224.0469.



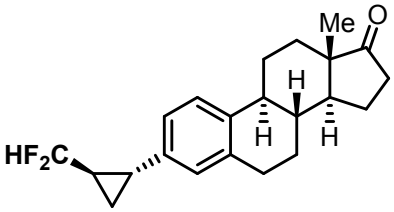
3q

(2-(Difluoromethyl)cyclopropane-1,1-diyl)dibenzene (**3q**): 86%. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.29 - 7.21 (m, 5H), 7.22 - 7.15 (m, 1H), 5.01 (td, *J* = 55.2, 7.6 Hz, 1H), 2.27 - 2.14 (m, 1H), 1.68 - 1.62 (m, 1H), 1.50 - 1.44 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.99 (ddd, *J* = 283.8, 54.5, 8.6 Hz, 1F), -113.99 (ddd, *J* = 283.9, 56.0, 6.1 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.53 (s), 139.70 (s), 130.07 (s), 128.80 (s), 128.58 (s), 127.83 (s), 127.35 (s), 126.68 (s), 118.23 (t, *J* = 236.1 Hz), 35.27 (d, *J* = 9.4 Hz), 27.22 (dd, *J* = 31.8, 28.3 Hz), 15.65 (dd, *J* = 7.6, 7.0 Hz). IR (neat) ν = 3053, 2980, 1601, 1579, 1494, 1457, 1447, 1421, 1342, 1180, 1082, 1071, 1027, 965, 933, 862, 776, 756, 705, 645, 560, 479, 422 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{14}F_2$ $[M]^+$: 244.1064, Found: 244.1062.



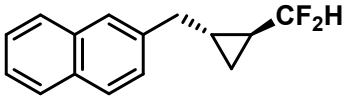
3r

(*trans*-2-(Drifluoromethyl)cyclopropyl)ferrocene (**3r**): 89%. Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (td, *J* = 57.4, 4.4 Hz, 1H), 4.16 (s, 5H), 4.09 - 4.03 (m, 3H), 3.99 (s, 1H), 1.87 - 1.79 (m, 1H), 1.53 - 1.42 (m, 1H), 1.11 - 1.03 (m, 1H), 0.88 - 0.80 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.90 (ddd, *J* = 280.1, 57.4, 9.9 Hz, 1F), -115.15 (ddd, *J* = 280.1, 57.4, 11.1 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 116.96 (t, *J* = 238.0 Hz), 88.55 (s), 68.68 (s), 67.29 (s), 67.22 (s), 67.02 (s), 66.07 (s), 23.83 (t, *J* = 26.8 Hz), 14.10 (dd, *J* = 5.5, 3.8 Hz), 11.67 (dd, *J* = 5.1, 4.1 Hz). IR (neat) ν = 3093, 2923, 2851, 1456, 1428, 1411, 1379, 1149, 1105, 1081, 1024, 1000, 819, 485 cm^{-1}. HRMS (MALDI-FT-DHB): calcd. for $C_{14}H_{14}F_2{}^{54}Fe$ $[M]^+$: 274.0454, Found: 274.0454.



3s

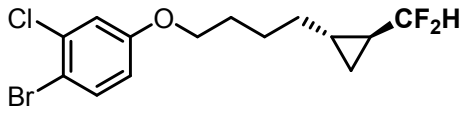
(8R,9S,13S,14S)-3-(*trans*-2-(Difluoromethyl)cyclopropyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (**3s**): 90%. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 1H), 5.72 (td, *J* = 57.5, 4.2 Hz, 1H), 2.93 - 2.85 (m, 2H), 2.55 - 2.45 (m, 1H), 2.44 - 2.37 (m, 1H), 2.31 - 2.22 (m, 1H), 2.19 - 1.92 (m, 5H), 1.69 - 1.38 (m, 7H), 1.23 - 1.15 (m, 1H), 1.09 - 1.02 (m, 1H), 0.90 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.34 - -116.21 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.77 (s), 138.00 (s), 137.72 (s), 136.68 (s), 127.04 (d, *J* = 10.8 Hz), 125.59 (s), 123.70 (d, *J* = 9.6 Hz), 116.64 (t, *J* = 238.3 Hz), 50.50 (s), 48.00 (s), 44.30 (s), 38.22 (s), 35.87 (s), 31.63 (s), 29.41 (s), 26.52 (s), 25.79 (s), 23.85 (t, *J* = 26.8 Hz), 21.61 (s), 18.35 (t, *J* = 4.6 Hz), 13.86 (s), 10.38 (t, *J* = 4.3 Hz). IR (neat) ν = 3007, 2924, 2865, 1735, 1614, 1505, 1455, 1432, 1403, 1374, 1255, 1198, 1161, 1149, 1101, 1078, 1046, 987, 823 cm^{-1}. HRMS (EI): calcd. for $C_{22}H_{26}F_2O$ $[M]^+$: 344.1952, Found: 344.1946.



3u

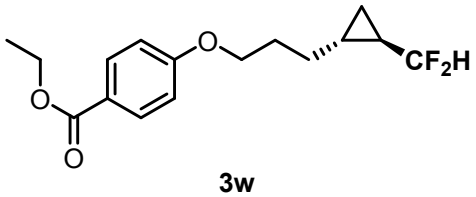
2-(((*trans*)-2-(Difluoromethyl)cyclopropyl)methyl)naphthalene (**3u**): 63%. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.76 - 7.69 (m, 1H), 7.54 - 7.44 (m, 2H), 7.44 - 7.38 (m, 2H), 5.57 (td, *J* = 57.0, 4.6 Hz, 1H), 3.18 (dd, *J* = 15.4, 6.2 Hz, 1H), 3.04 (dd, *J* = 15.3, 6.7 Hz, 1H), 1.52 - 1.43 (m, 1H), 1.29 - 1.19 (m, 1H), 0.90 - 0.82 (m, 1H), 0.68 - 0.60 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.51 (ddd, *J* = 279.7, 57.8, 10.5 Hz, 1F), -114.46 (ddd, *J* = 279.7, 57.9, 10.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.13 (s), 133.68 (s), 131.88 (s), 128.77 (s), 127.01 (s), 125.96 (s), 125.60 (s), 125.57 (s), 125.55 (s), 123.48 (s), 117.29 (t, *J* = 237.7 Hz), 34.99 (s), 20.84 (t, *J* = 26.8 Hz), 14.50 (dd, *J* = 4.8, 3.8 Hz), 8.05 (dd, *J* = 4.8, 3.8 Hz). IR (neat) ν = 3048, 3008, 2961, 2927, 1597, 1509, 1466, 1457, 1429, 1414,

1380, 1260, 1188, 1155, 1096, 1080, 1029, 792, 775 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{14}F_2$ $[M]^+$: 232.1064, Found: 232.1068.



3v

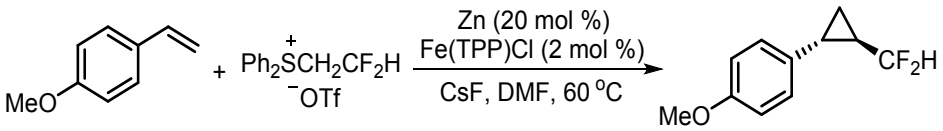
1-Bromo-2-chloro-4-(4-(*trans*-2-(difluoromethyl)cyclopropyl)butoxy)benzene (**3v**): 75%. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.1 Hz, 1H), 7.27 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 1H), 5.49 (td, *J* = 57.5, 4.7 Hz, 1H), 3.97 (t, *J* = 6.3 Hz, 2H), 1.90 - 1.78 (m, 2H), 1.64 - 1.53 (m, 2H), 1.44 - 1.25 (m, 2H), 1.10 - 0.92 (m, 2H), 0.78 - 0.68 (m, 1H), 0.52 - 0.43 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.10 - -113.40 (m, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.88 (s), 132.60 (s), 130.45 (s), 124.04 (s), 117.66 (t, *J* = 237.2 Hz), 114.50 (s), 112.32 (s), 69.23 (s), 32.43 (s), 28.57 (s), 25.64 (s), 20.56 (t, *J* = 26.9 Hz), 14.63 (t, *J* = 4.1 Hz), 7.89 (t, *J* = 4.5 Hz). IR (neat) ν = 3007, 2939, 2859, 1582, 1485, 1430, 1417, 1385, 1289, 1265, 1249, 1210, 1187, 1062, 1027, 910, 870, 803, 728, 639, 554 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{16}BrClF_2O$ $[M]^+$: 352.0041, Found: 352.0036.



3w

Ethyl 4-(3-(*trans*-2-(difluoromethyl)cyclopropyl)propoxy)benzoate (**3w**): 65%. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.50 (td, *J* = 57.4, 4.6 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.03 (t, *J* = 6.3 Hz, 2H), 1.96 - 1.85 (m, 2H), 1.57 - 1.47 (m, 1H), 1.46 - 1.39 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.12 - 0.95 (m, 2H), 0.79 - 0.71 (m, 1H), 0.54 - 0.45 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.97 (ddd, *J* = 278.7, 57.4, 9.5 Hz, 1F), -114.13 (ddd, *J* = 278.7, 57.4, 10.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.39 (s), 162.63 (s), 131.51 (s), 122.80 (s), 117.47 (t, *J* = 237.4 Hz), 113.93 (s), 67.20 (s), 60.61 (s), 29.18 (s), 28.70 (s), 20.62 (t, *J* = 27.0 Hz), 14.37 (s), 14.24 (dd, *J* = 5.0, 3.2 Hz), 7.92 (dd, *J* = 5.3, 3.6 Hz). IR (neat) ν = 2941, 2874, 1709, 1607, 1580, 1511, 1471, 1421, 1386, 1367, 1314, 1277, 1255, 1168, 1104, 1024, 848, 771, 697, 646 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{20}F_2O_3$ $[M]^+$: 298.1381, Found: 298.1384.

5. Large scale reaction



2a (1.34 g, 10 mmol) **1** (8.0 g, 20 mmol) **3a** (1.35 g, 68%)

Into a mixture of Fe(TPP)Cl (0.2 mmol, 140.6 mg, 2 mol %) and Zinc powder (2 mmol, 6.5 mg, 20 mol %) was added DMF (2 mL) under N_2 atmosphere. The mixture was stirred at 60°C for 10 min. **2a** (1.368 g, 10 mmol, 1.0 equiv), sulfonium salt **1** (20 mmol, 8.008 g, 2.0 equiv), cesium fluoride (40 mmol, 6.076 g, 4.0 equiv) and DMF (8 mL) were added. The resulting mixture was stirred at 60 °C for another 3 h, and was then diluted with CH_2Cl_2 (50 mL) and water (50 mL). The organic phase was separated and washed with water (50 mL, three times), and then dried over Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane/dichloromethane as eluent to give the final product (1.348 g, 68% yield).

6. The determination of the relative configuration of 3g by NOESY Spectrometry

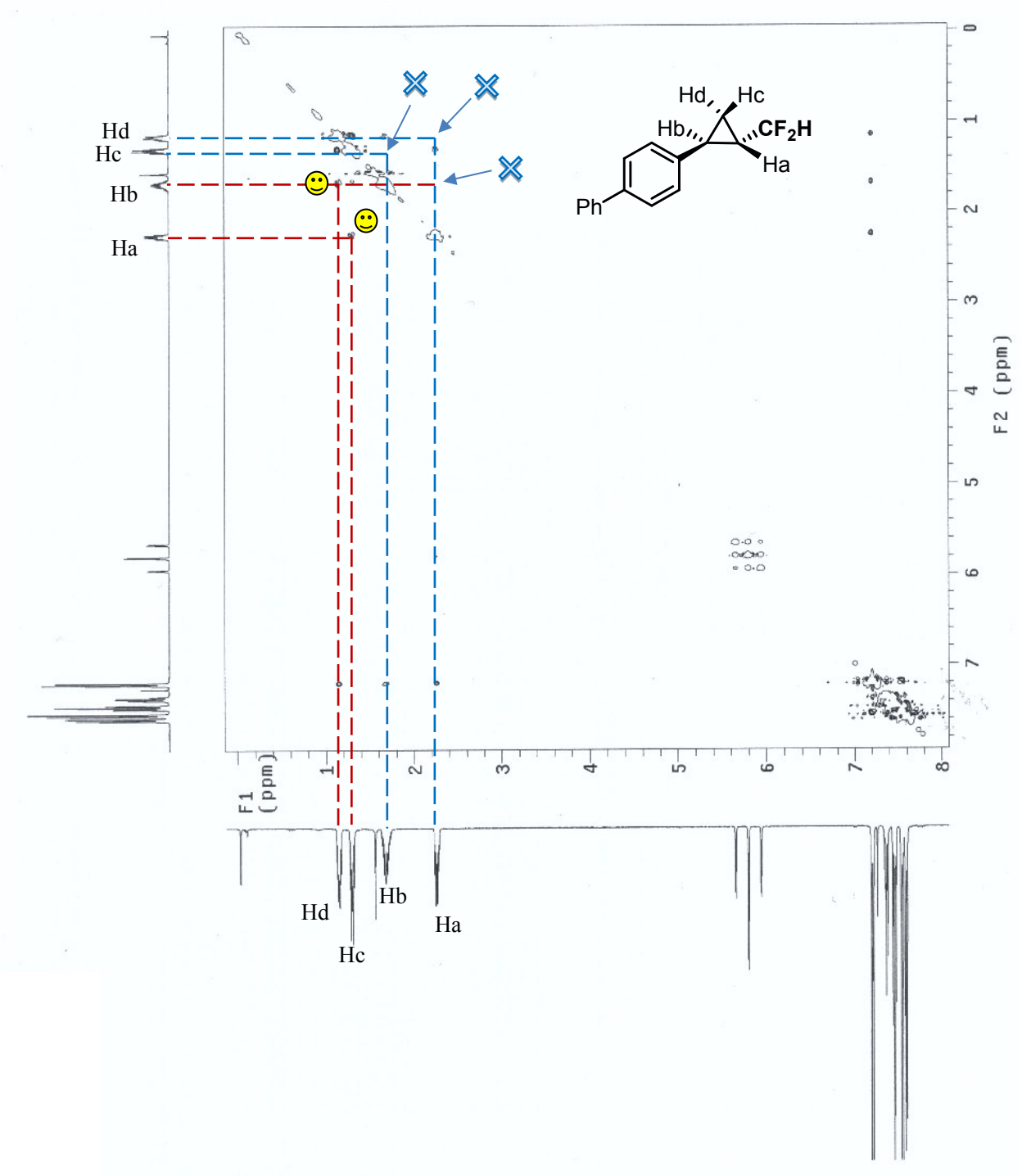
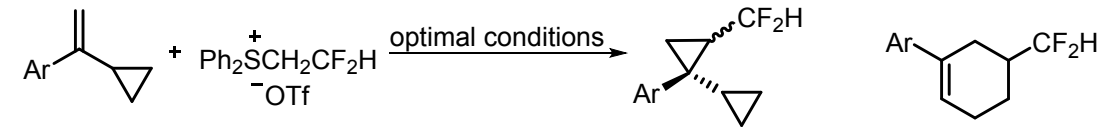


Figure 6.1 Expanded NOE spectrum

Figure 6.2 Full NOE spectrum

7. Mechanism studies

7.1 Radical clock



2x (radical clock) Ar = 4-$MeOC_6H_4$ | **1** | **3x** (dr = 3:1, 87% total yield)[a] | **3x'** (not observed)

Into a mixture of Fe(TPP)Cl (0.025 mmol, 17.6 mg, 5 mol %) and Zinc powder (0.1 mmol, 6.5 mg, 20 mol %) was added DMF (1 mL) under N_2 atmosphere. The mixture was stirred at 60°C for 10 min. 1-(1-Cyclopropylvinyl)-4-methoxybenzene (0.5 mmol, 1.0 equiv), sulfonium salt **1** (1.0 mmol, 400.4 mg, 2.0 equiv), cesium fluoride (2.0 mmol, 303.8 mg, 4.0 equiv) and DMF (4 mL) were added. The resulting mixture was stirred at 60 °C for another 2 h, and was then diluted with CH_2Cl_2 (15 mL) and water (15 mL). The organic phase was separated and washed with water (15 mL, three times), and then dried over Na_2SO_4. After filtration, the solvent was removed by concentration. The residue was subjected to flash column chromatography with the use of hexane/dichloromethane as eluent to give the mixture of two isomers (3:1, isolated yield: 87%).

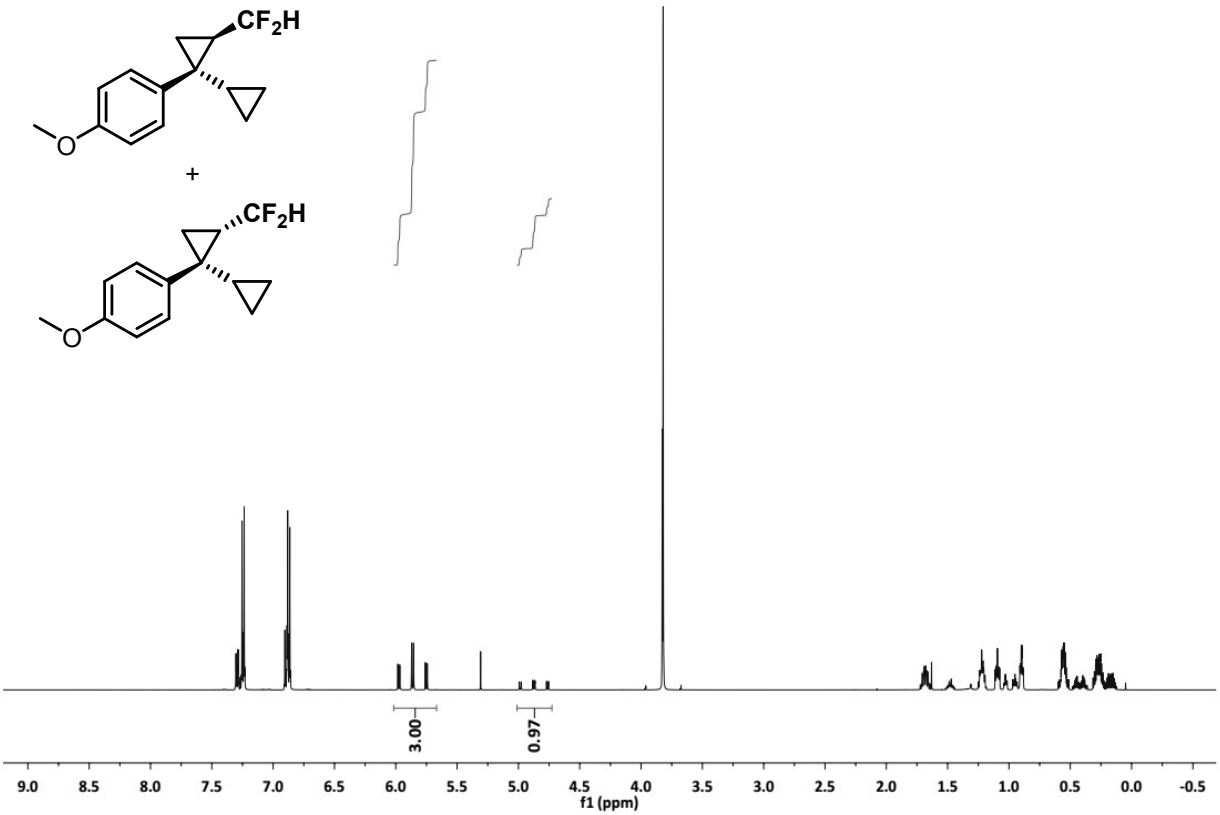


Figure 7.1 a ^1H NMR Spectram of Two Isomers

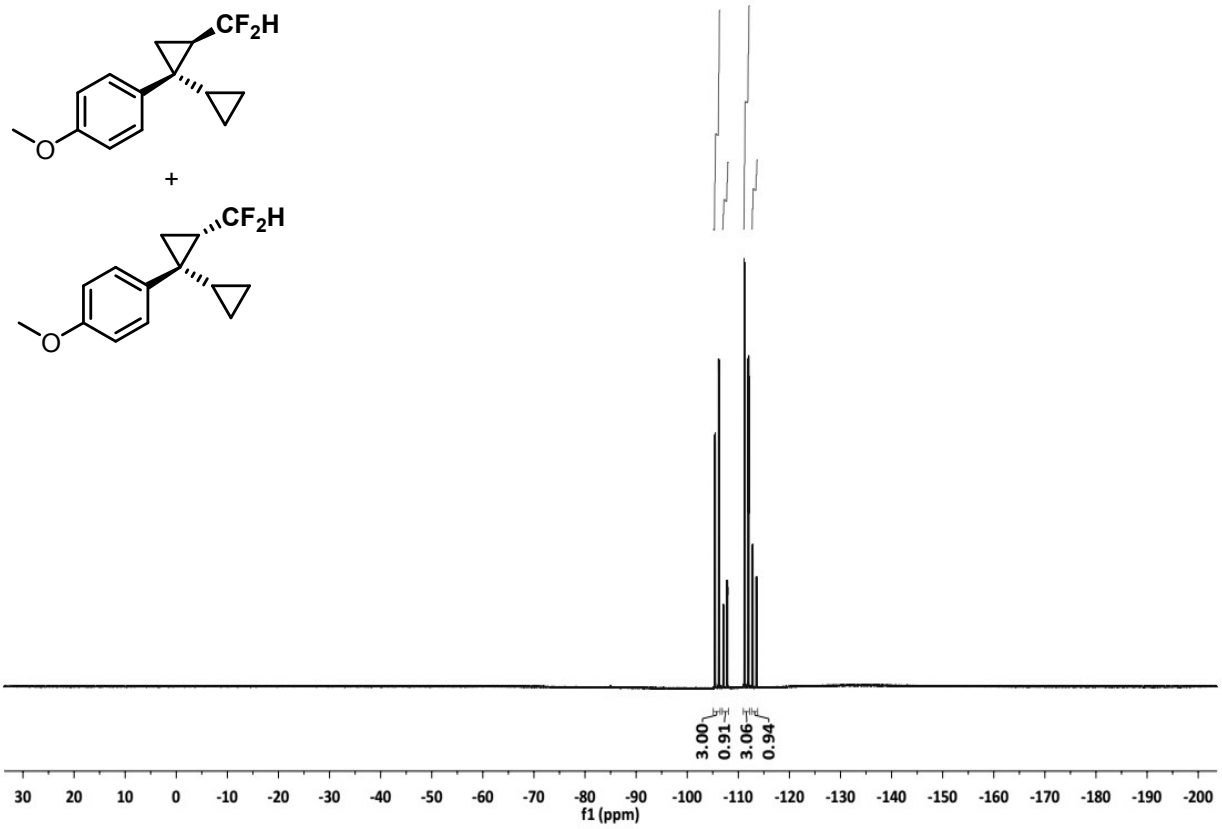
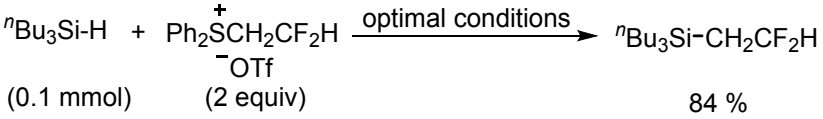


Figure 7.1 b ^{19}F NMR Spectram of Two Isomers

7.2 Insertion into X-H bond

(1) Insertion into Si-H bond:



Under the optimal reaction condition, the Si-H bond insertion product was obtained in 84% yield determined by ^{19}F NMR spectrometry (see Figure 6.2a) with (trifluoromethyl)benzene (14.6 mg, 0.1 mmol) as an internal standard.

^{19}F NMR (376 MHz, $CDCl_3$) δ - 101.01 ppm (dt, J = 58.3, 21.9 Hz, 2F).

MS (EI): 264.2.

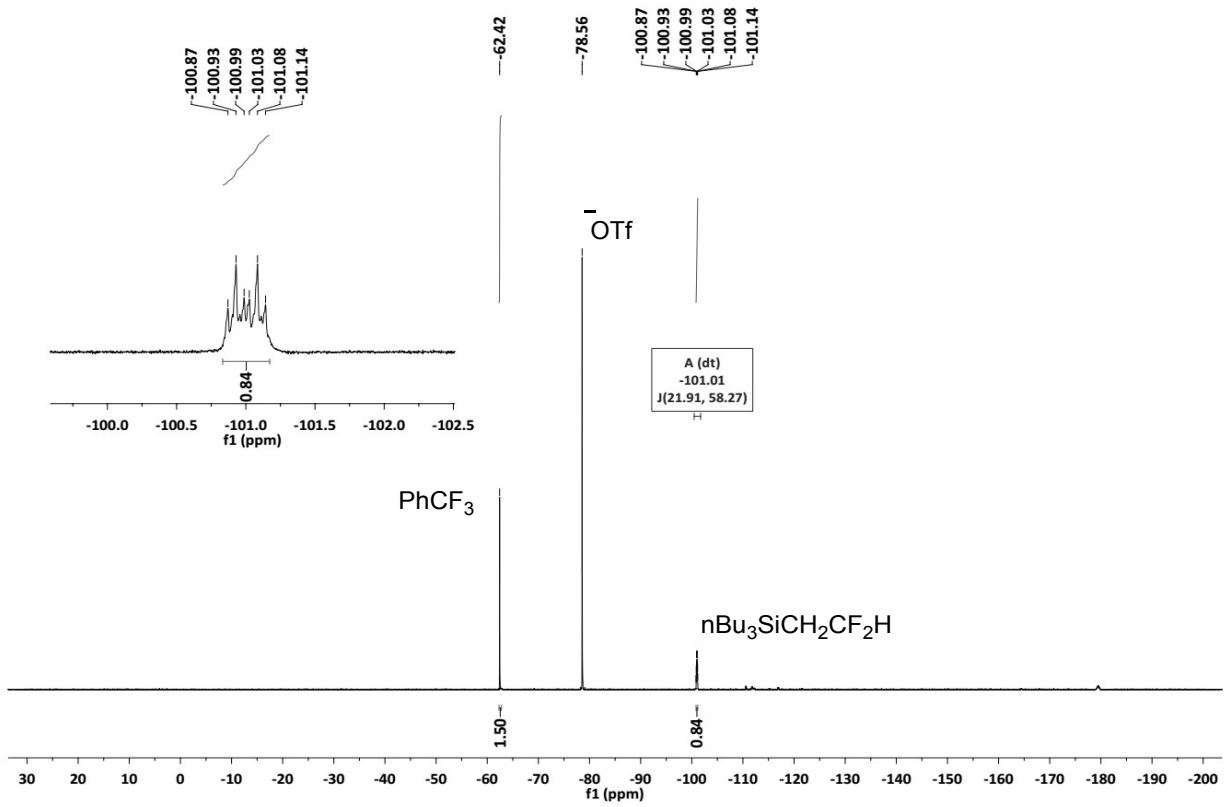
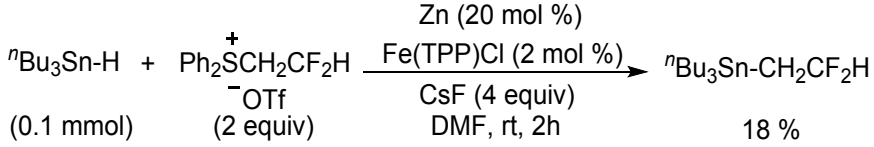


Figure 7.2 a ^{19}F NMR Spectra of the reaction mixture with the use of (trifluoromethyl)benzene as an internal standard.

(2) Insertion into Sn-H bond:



Into a mixture of Fe(TPP)Cl (0.002 mmol, 1.4 mg, 2 mol %), Zinc powder (0.02 mmol, 1.3 mg, 20 mol %), $^{n}Bu_3SnH$ (0.1 mmol, 1.0 equiv.), sulfonium salt **1** (0.2 mmol, 80.1 mg, 2.0 equiv) and cesium fluoride (0.4 mmol, 60.8 mg, 4 equiv) was added DMF (1.5 mL) under N_2 atmosphere. The mixture was stirred for 2 h at room temperature. The product was detected in the reaction mixture both by ^{19}F NMR and EI spectrometry. The yield was determined by ^{19}F NMR spectrometry (see Figure 6.2b) with (trifluoromethyl)benzene (14.6 mg, 0.1 mmol) as an internal standard.

^{19}F NMR (376 MHz, $CDCl_3$) δ - 96.11 ppm (dt, J = 48.4, 23.6 Hz, 2F).

MS (EI): 356.1.

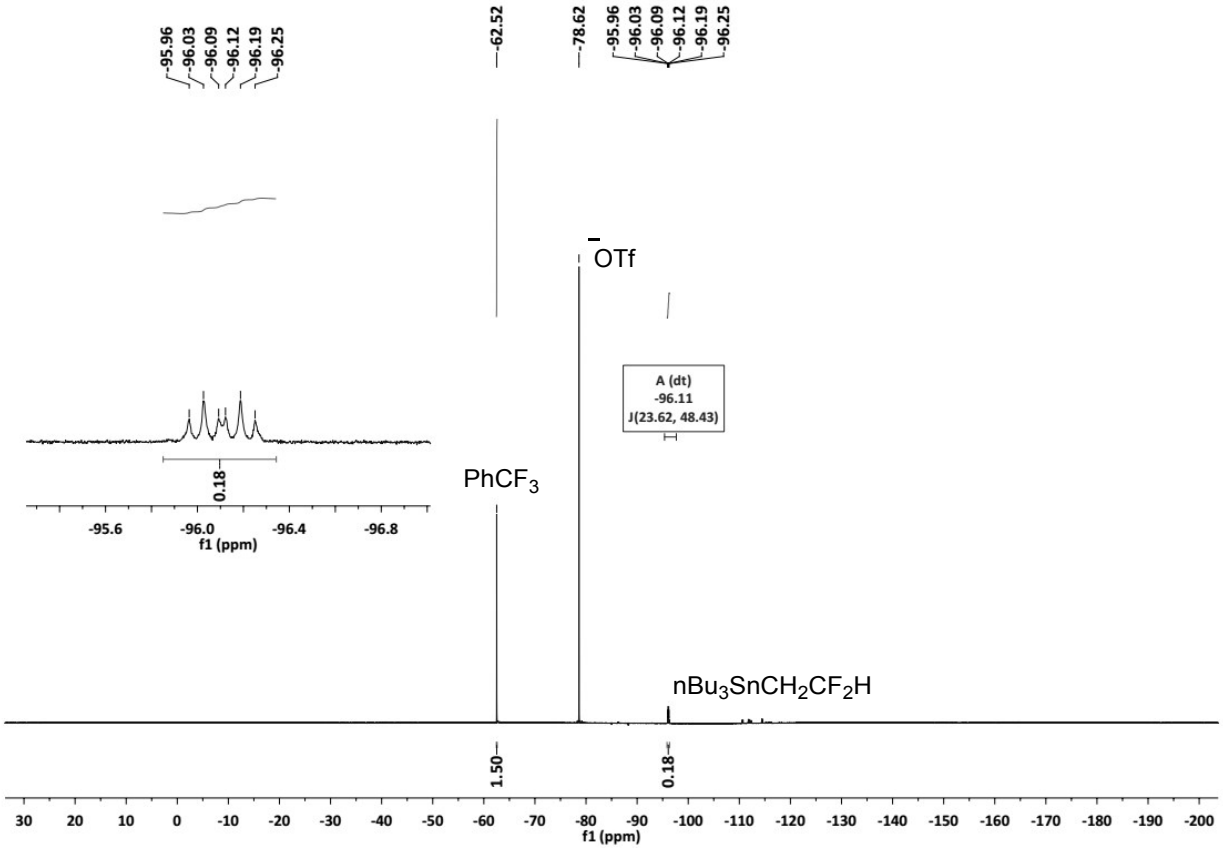


Figure 7.2 b ^{19}F NMR Spectra of the reaction mixture with the use of (trifluoromethyl)benzene as an internal standard.

8. References

[1] Y. Duan, J. -H. Lin, J. -C. Xiao, Y. -C. Gu, *Org. Lett.*, 2016, **18**, 2471-2474.

[2] B. H. Lipshutz, S. Ghorai, W. W. Y. Leong, *J. Org. Chem.* 2009, **74**, 2854-2857.

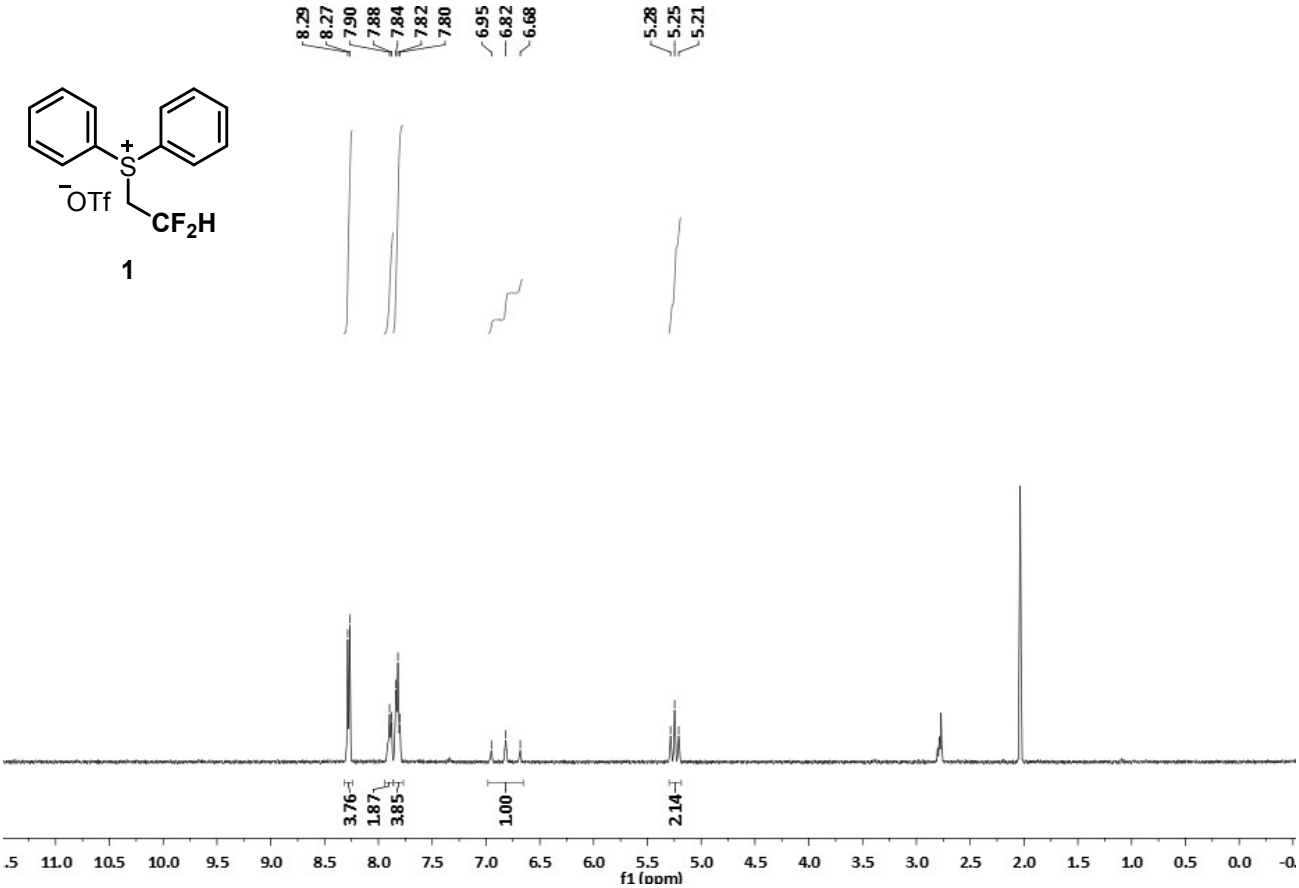
[3] X. -Y. Wang, H. -X. Song, S. -M. Wang, J. Yang, H. -L. Qin, X. Jiang, C. -P. Zhang, *Tetrahedron*, 2016, **72**, 7606-7612.

[4] For selected review, please see: a) S. F. Zhu, Q. L. Zhou, *Natl. Sci. Rev.* 2014, **1**, 580-603; For selected examples, please see: b) Y. Urano, T. Higuchi, M. Hirobe, T. Nagano, *J. Am. Chem. Soc.* 1997, **119**, 12008-12009; c) M. K. Safo, G. P. Gupta, F. A. Walker, W. R. Scheidt, *J. Am. Chem. Soc.* 1991, **113**, 5497-5510.

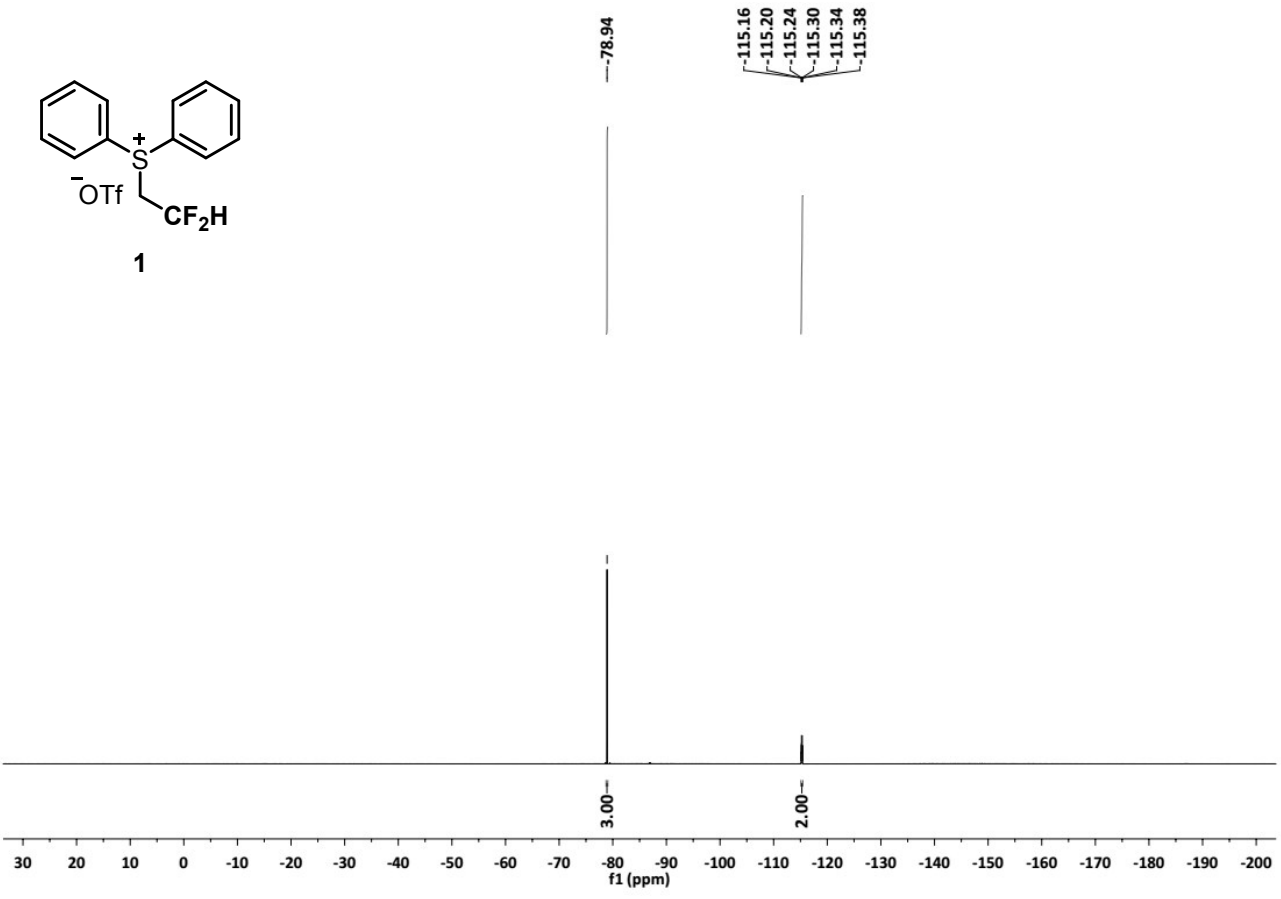
[5] J. R. Wolf, C. G. Hamaker, J.-P. Djukic, T. Kodadek, L. K. Woo, *J. Am. Chem. Soc.* 1995, **117**, 9194-9199.

9. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of 1 and 3

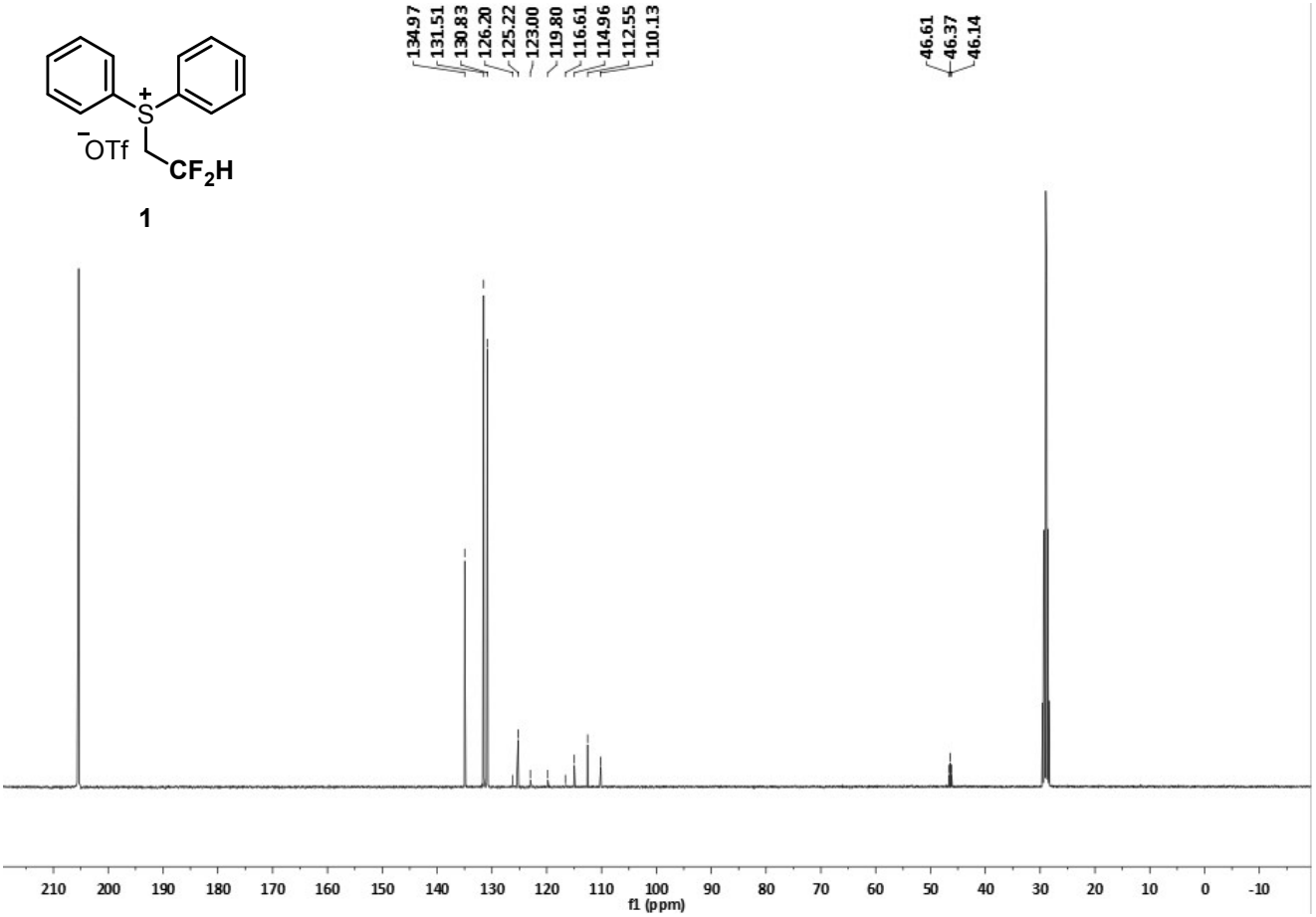
^{1}H NMR:



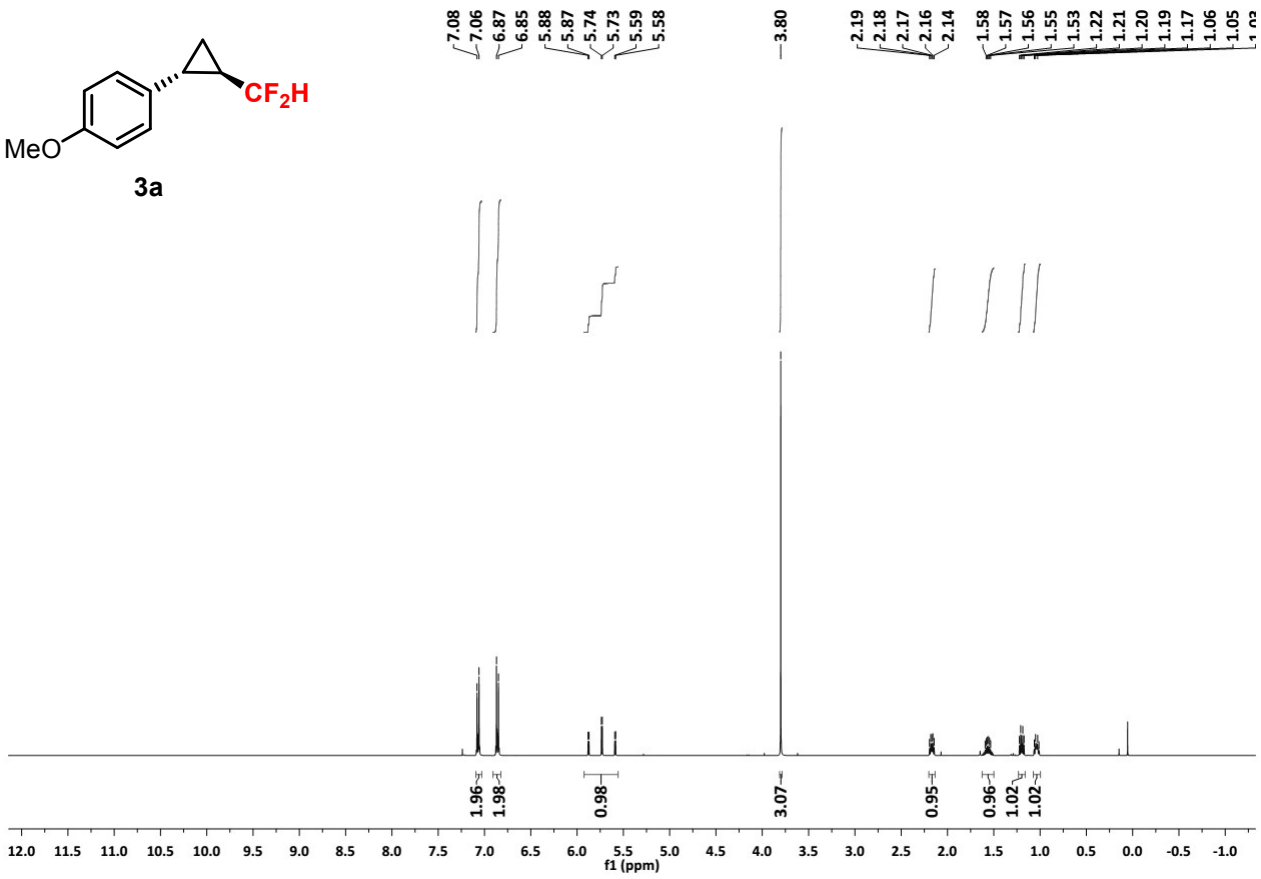
^{19}F NMR:



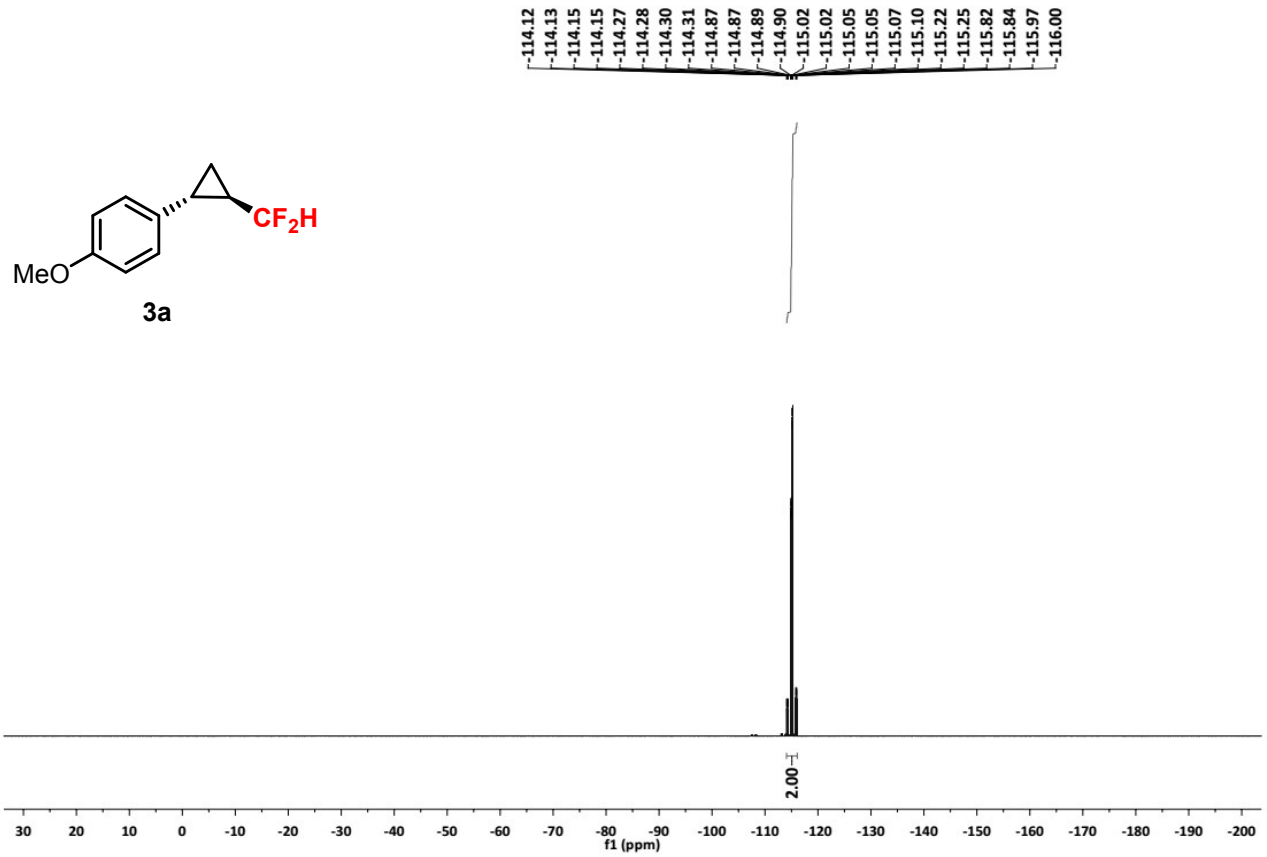
^{13}C NMR：



^{1}H NMR：



^{19}F NMR：



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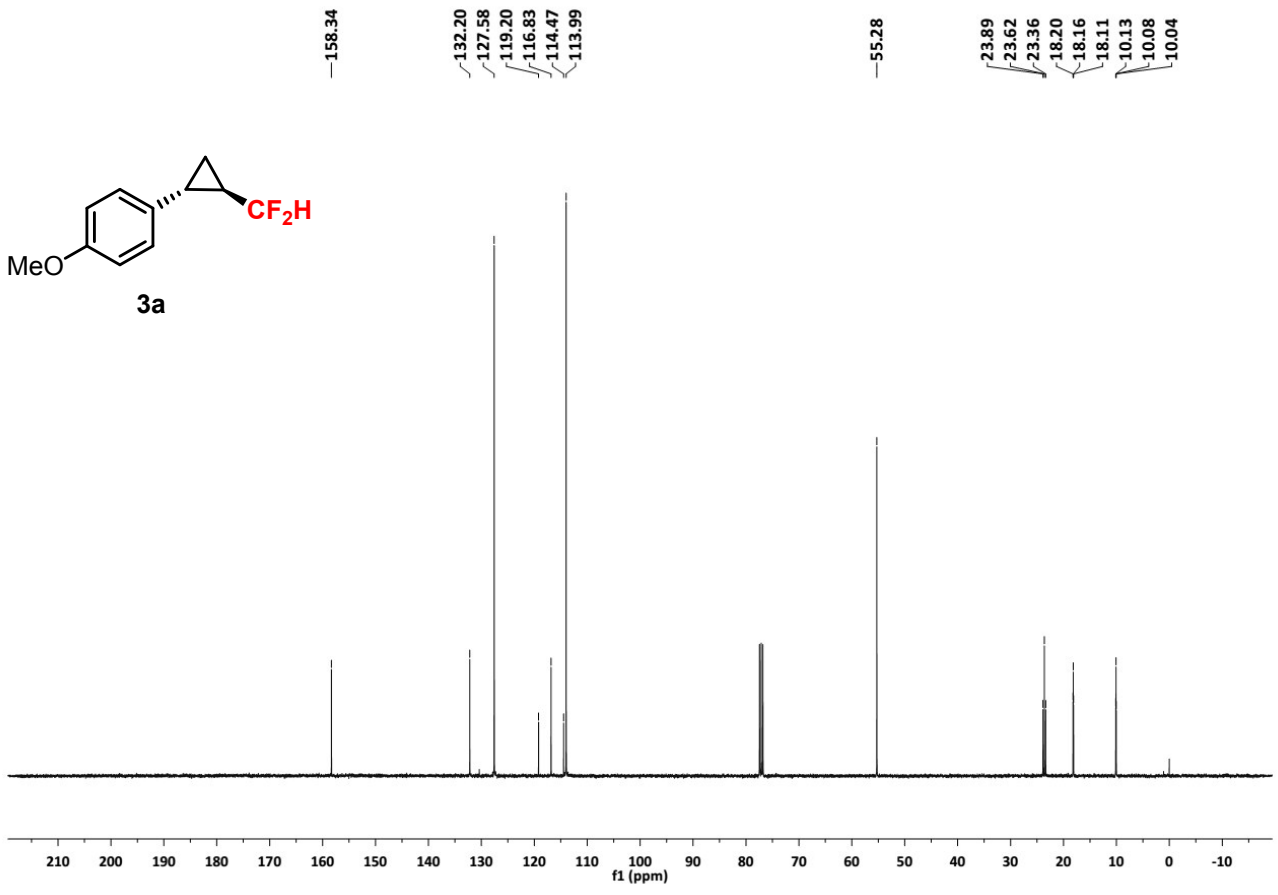

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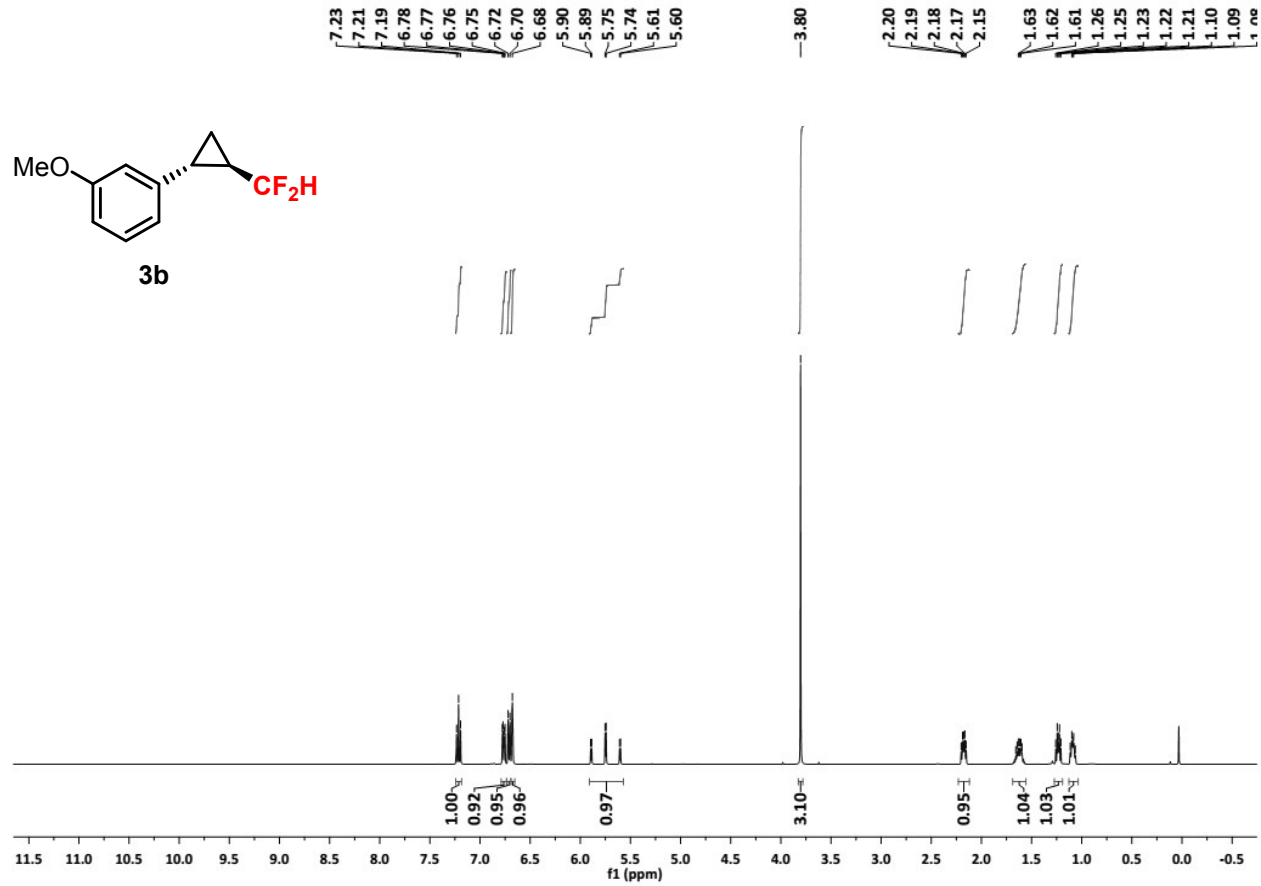

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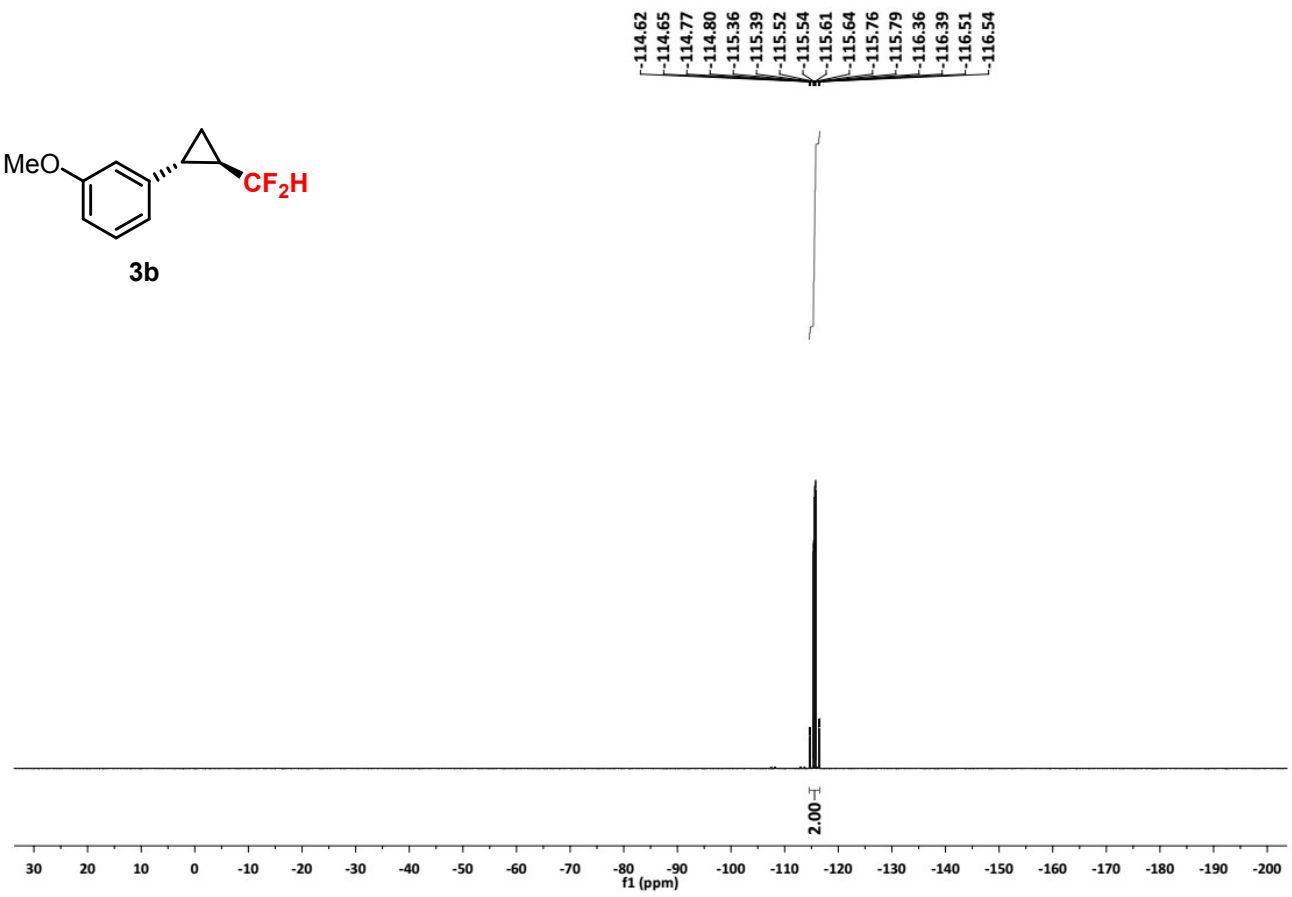

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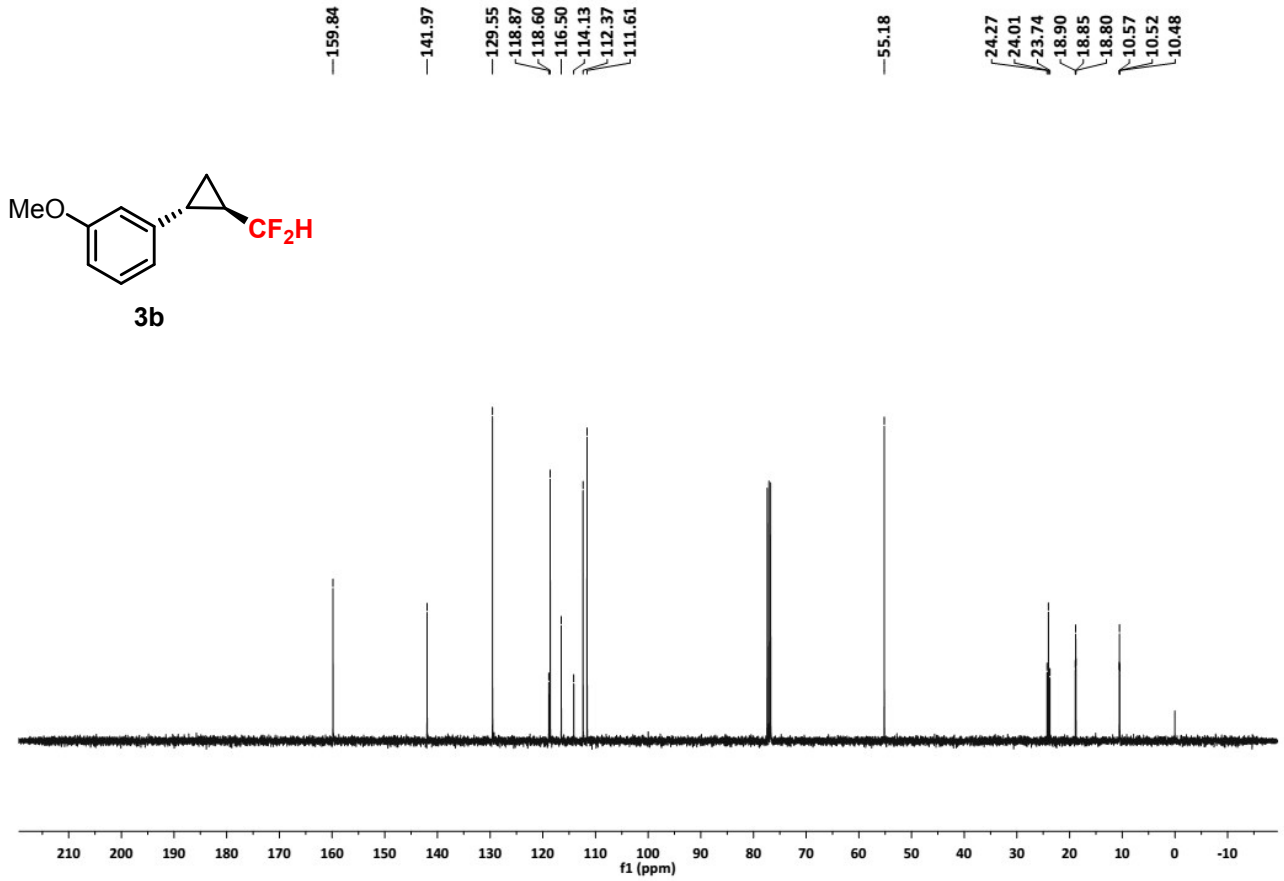

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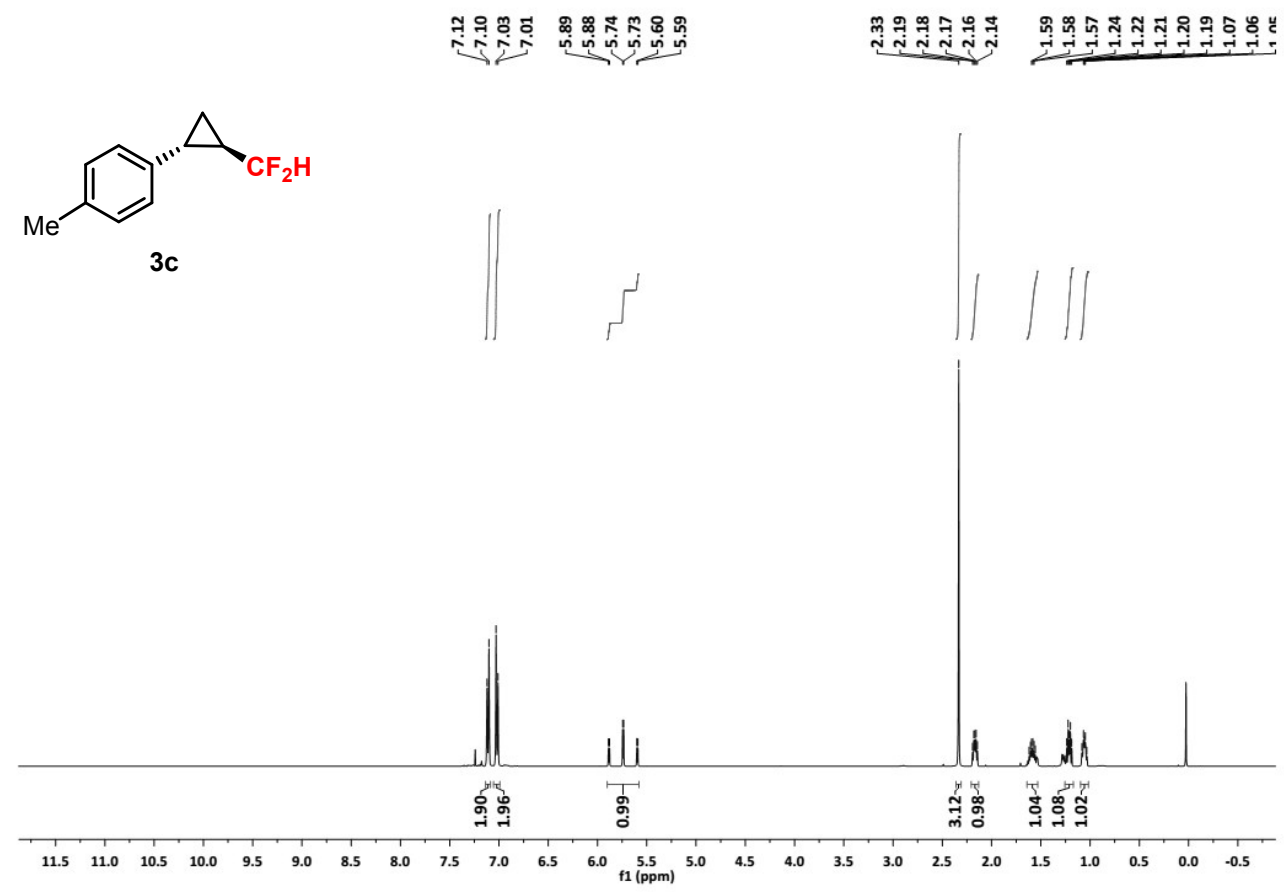

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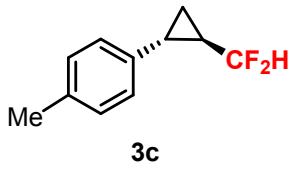
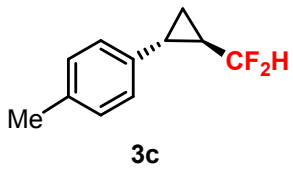


3c

^{13}C NMR：



3c

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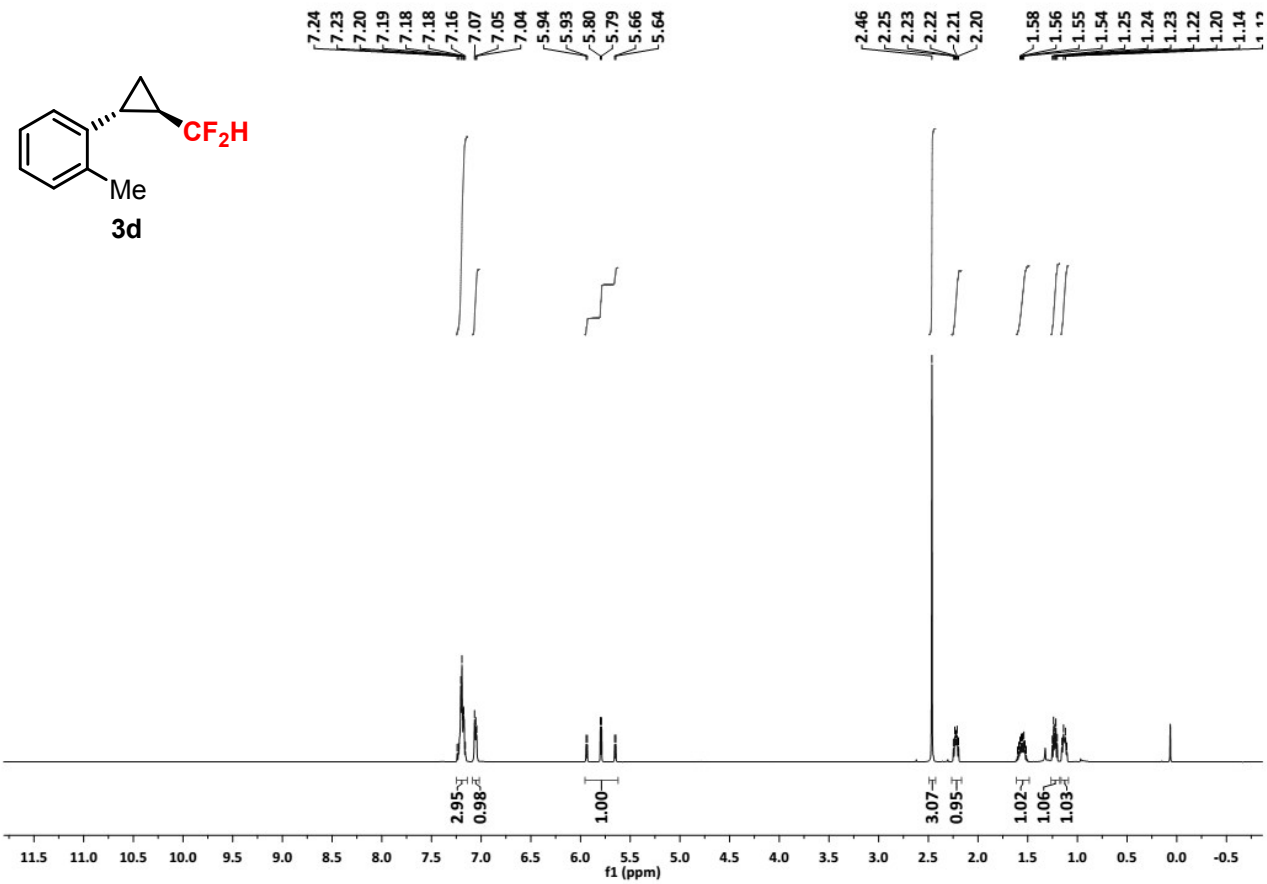
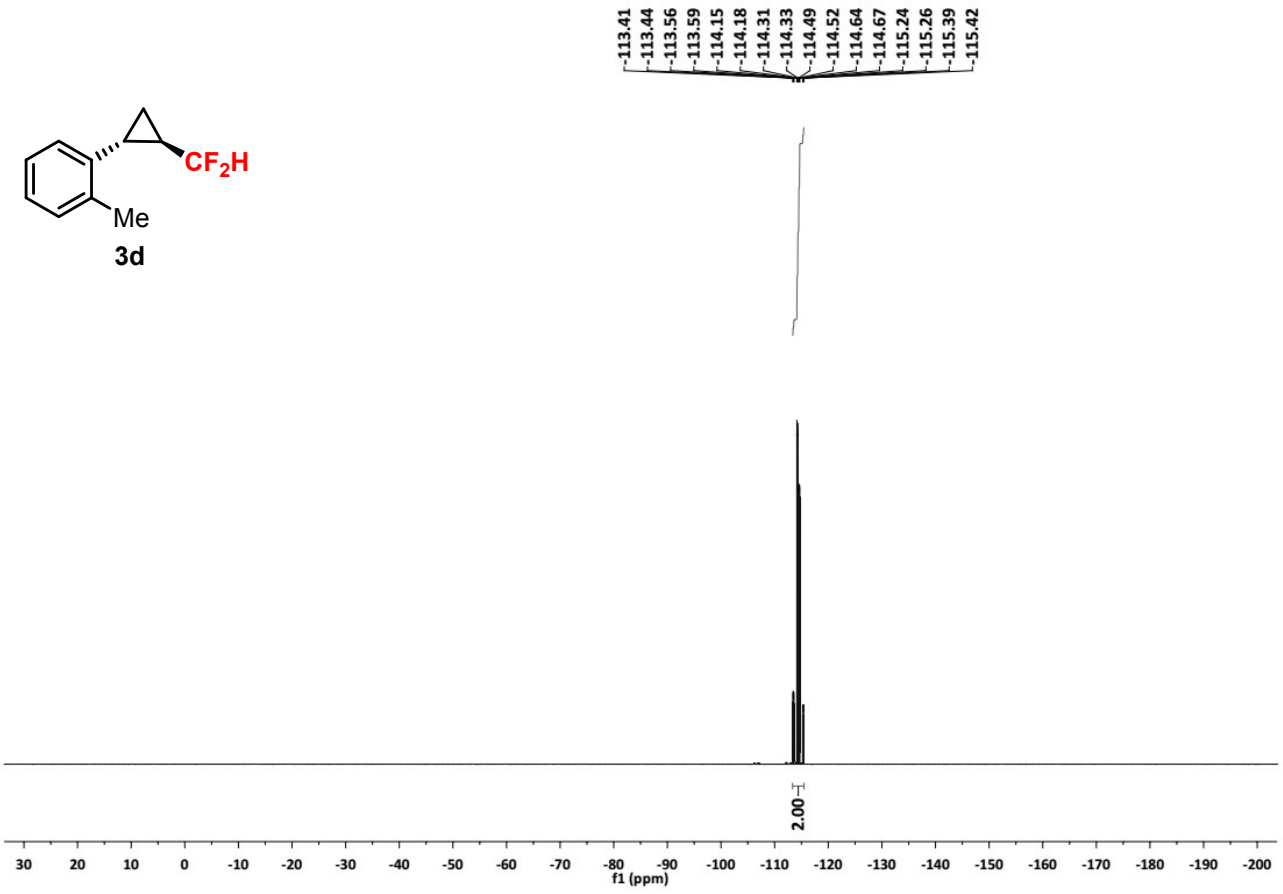
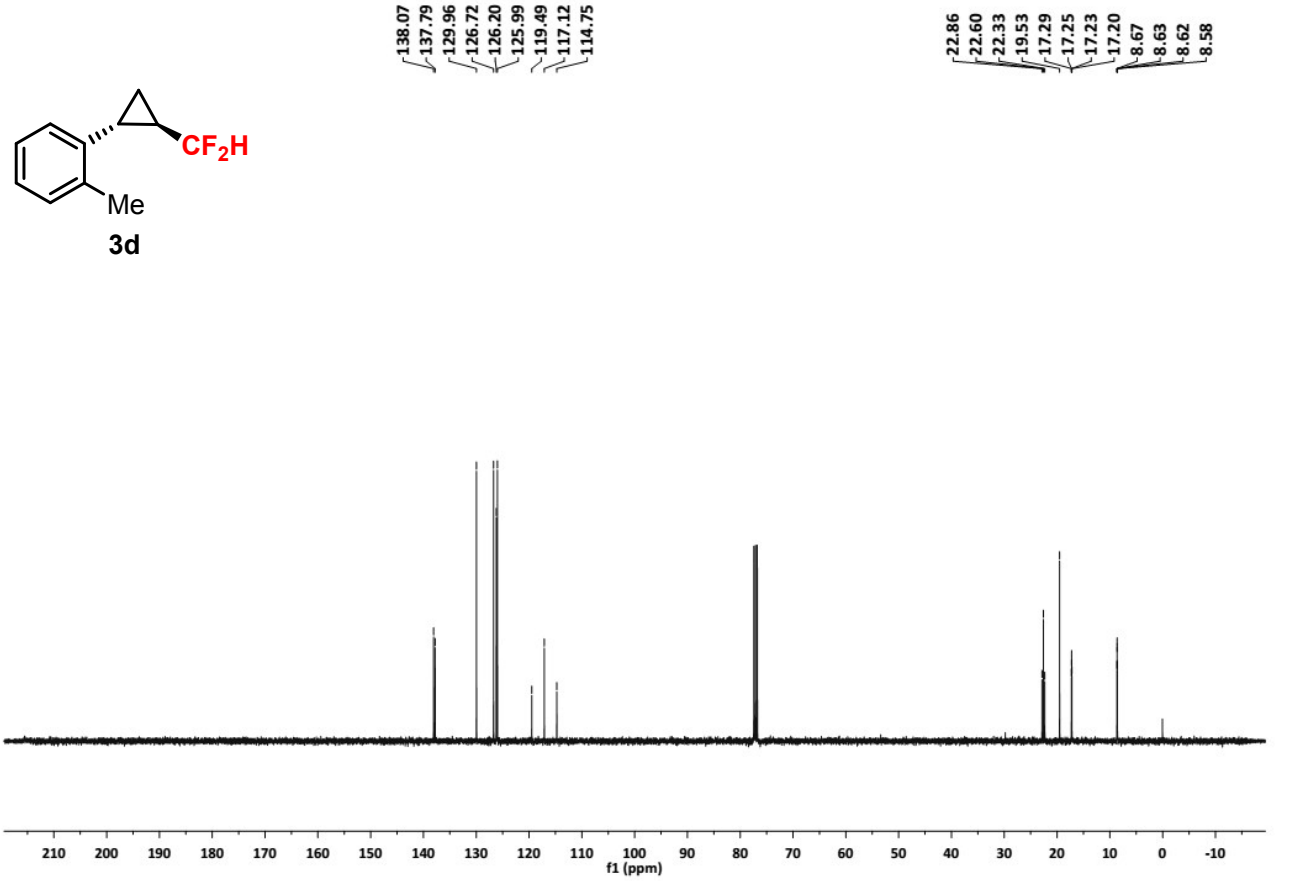


^{19}F NMR：



^{13}C NMR：



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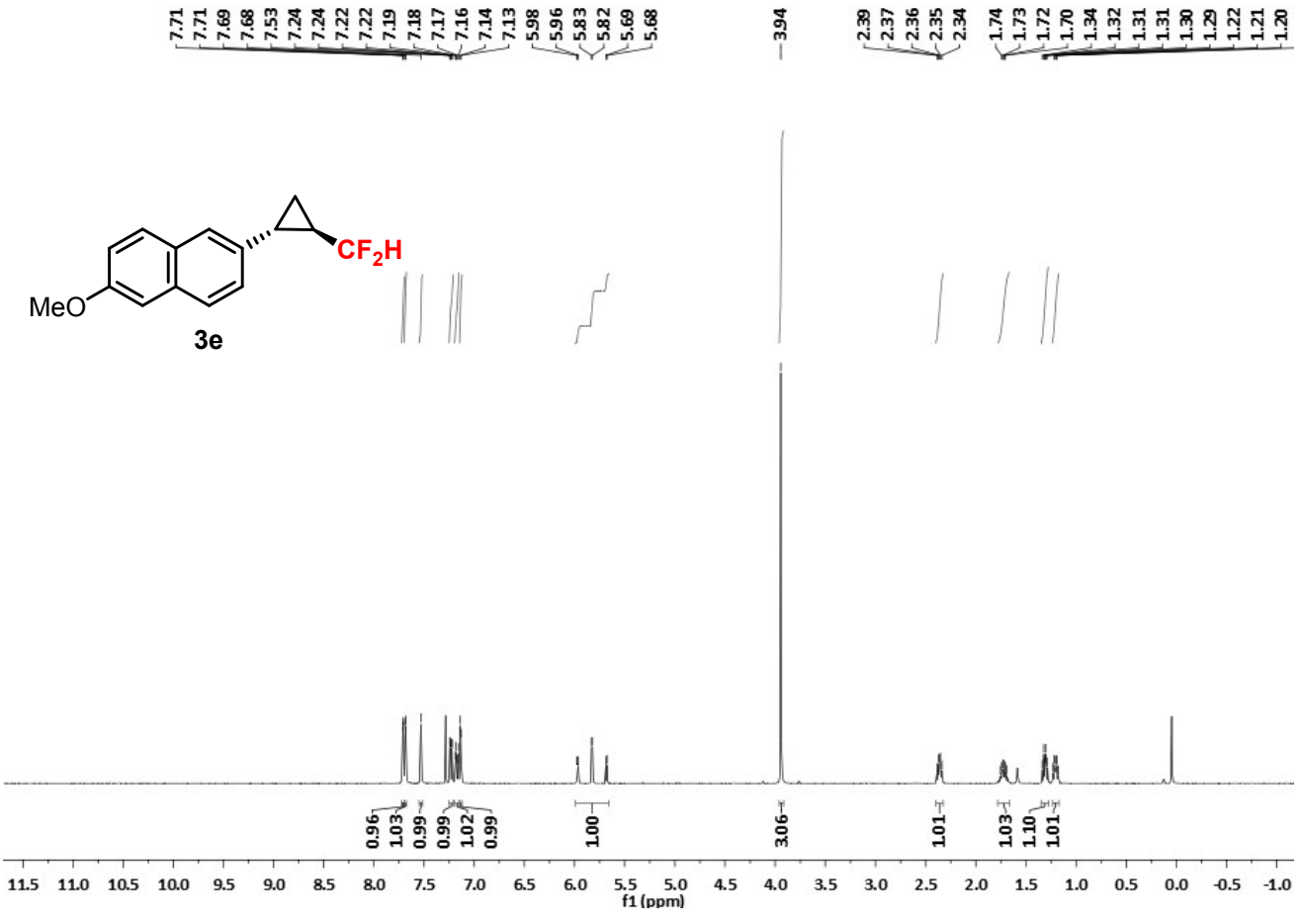
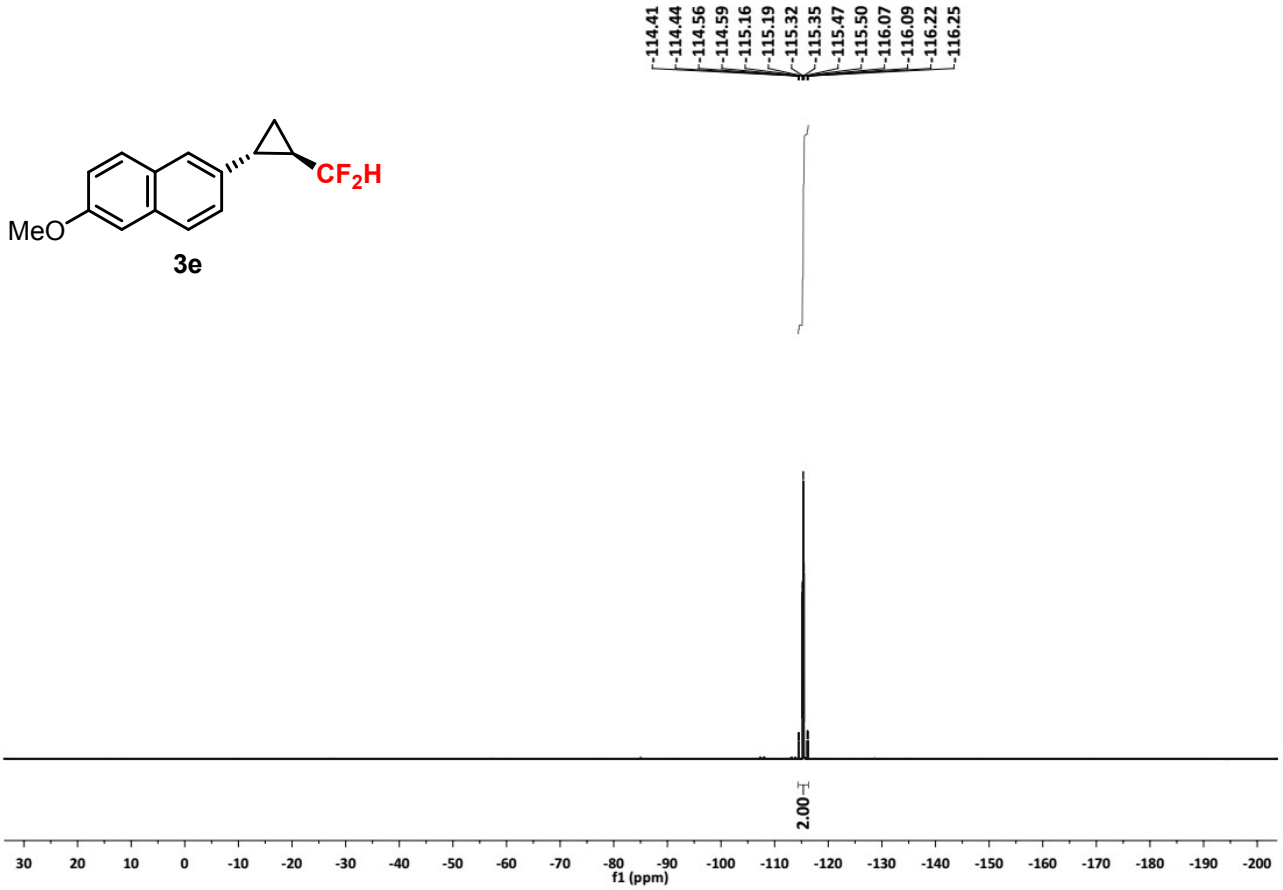


^{19}F NMR：



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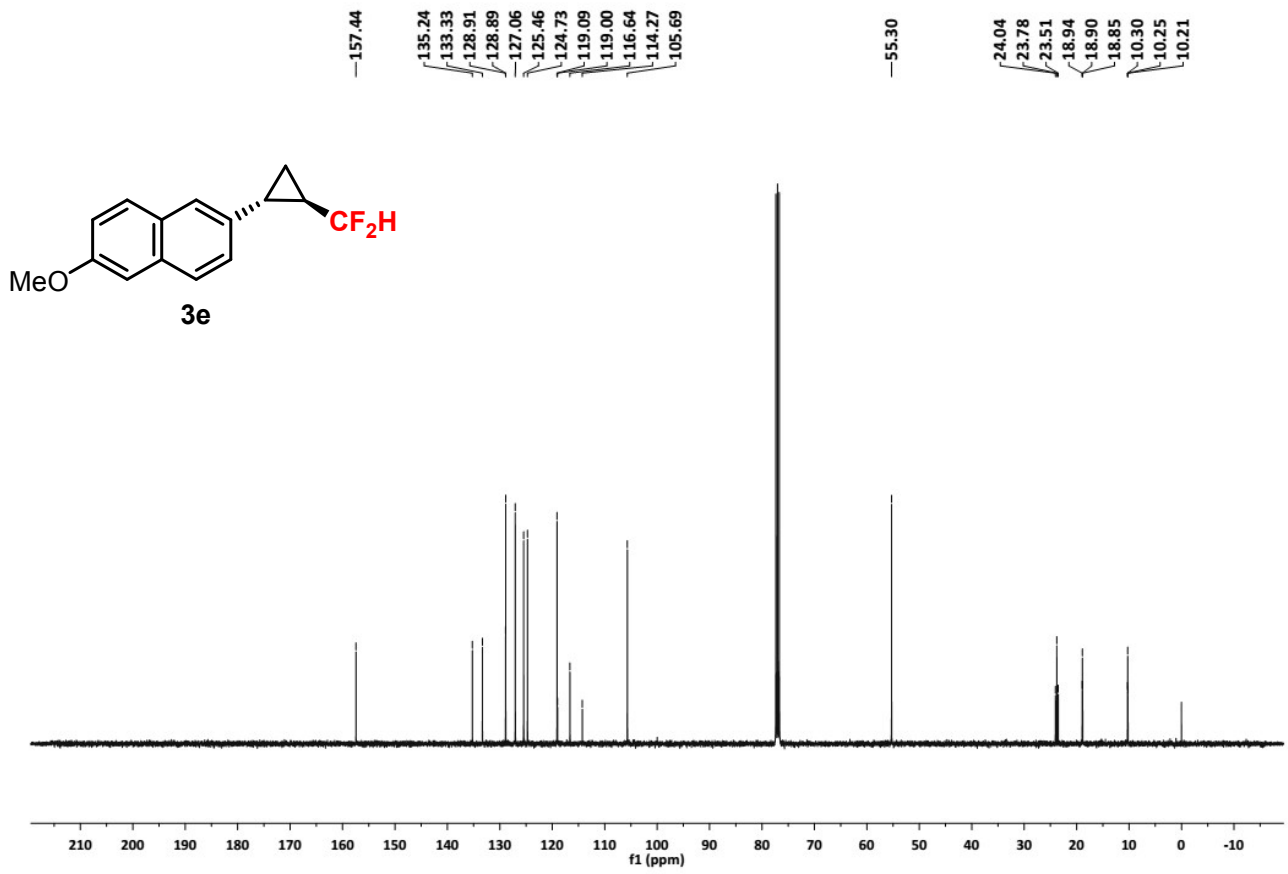

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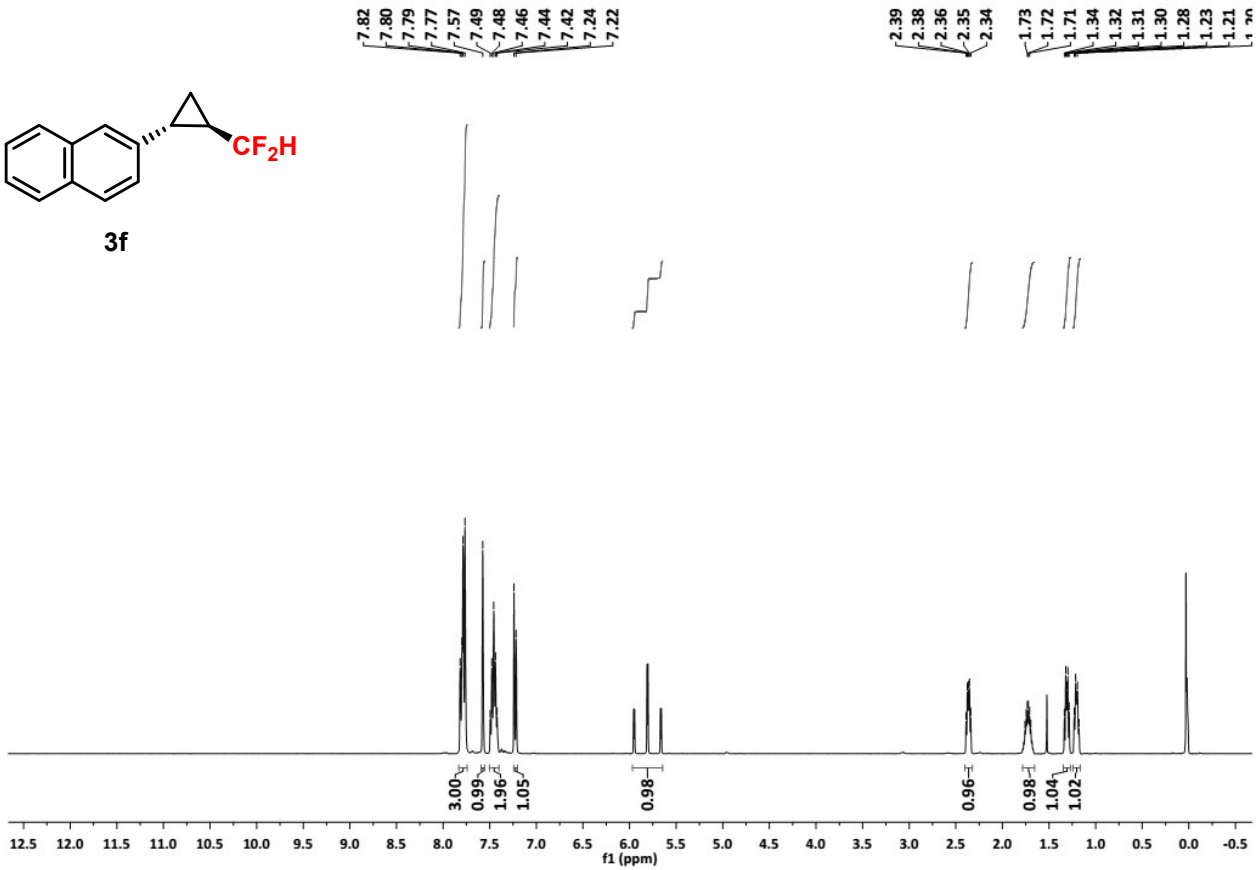

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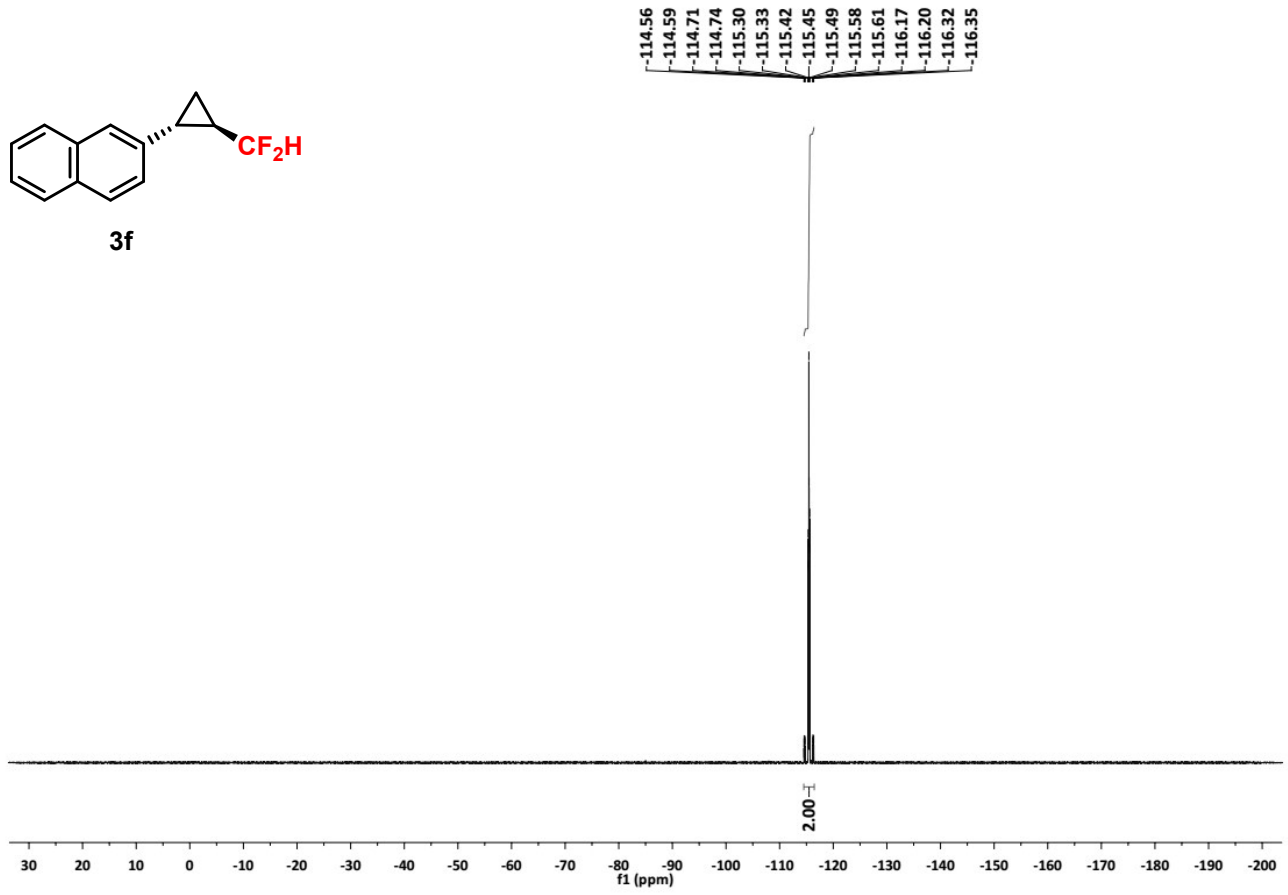

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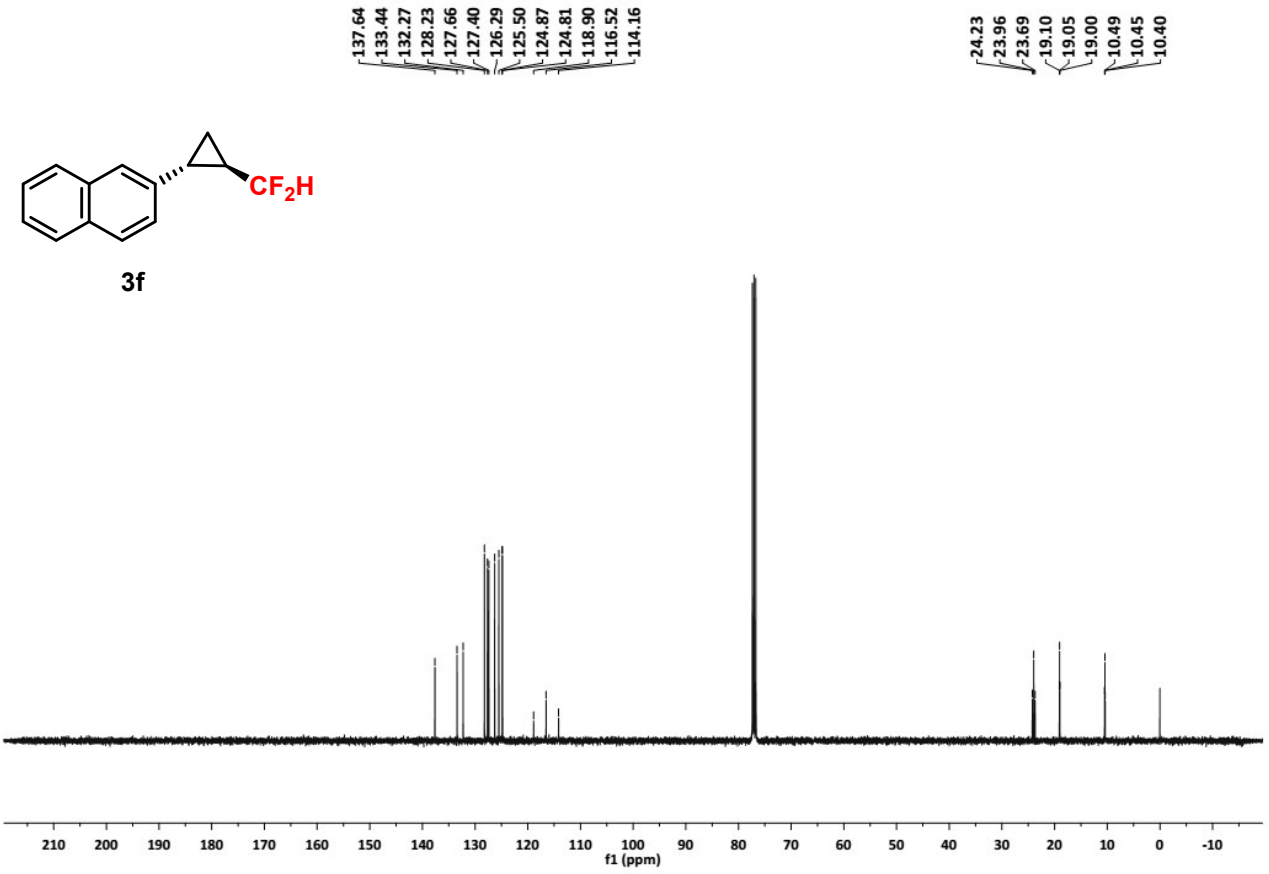

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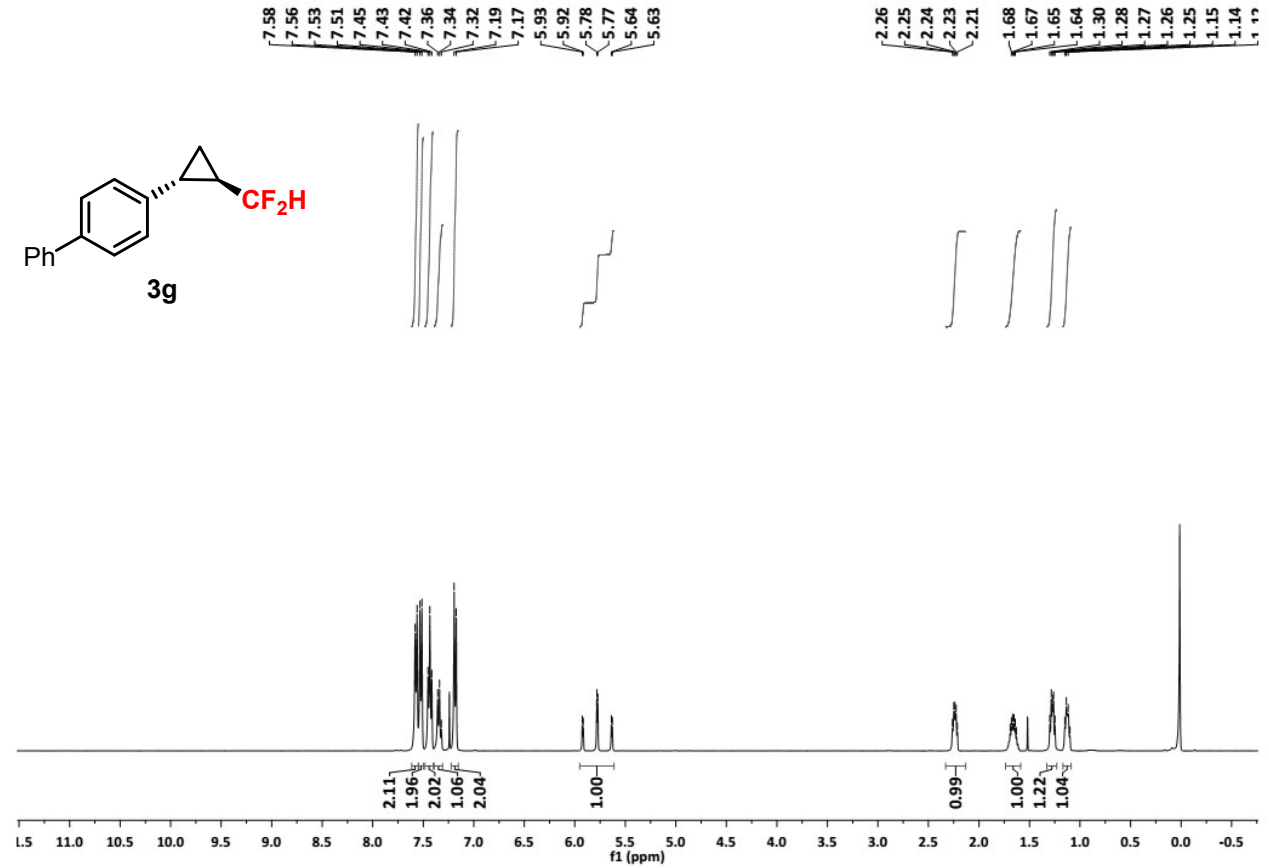
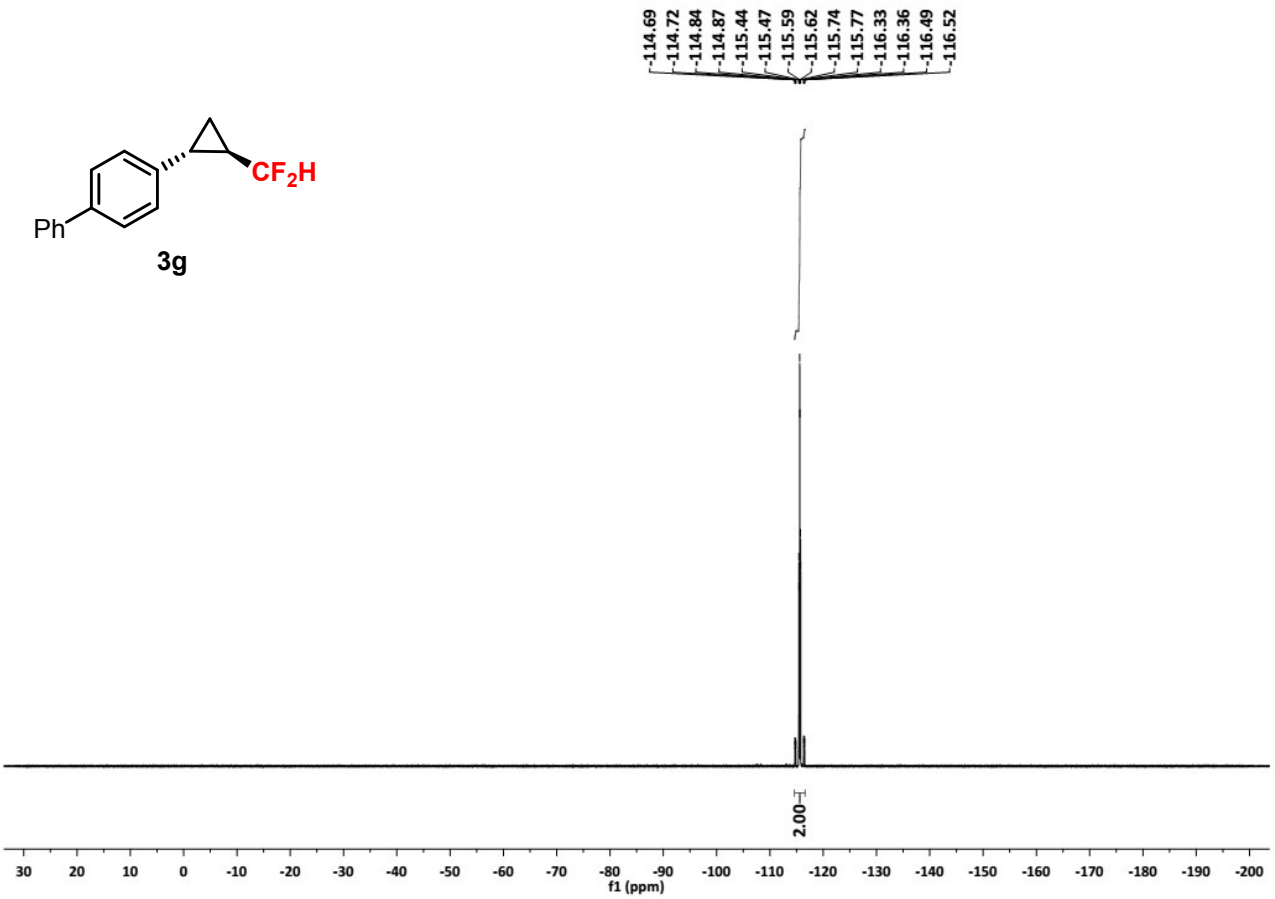


^{19}F NMR：


-114.69
-114.72
-114.84
-114.87
-115.44
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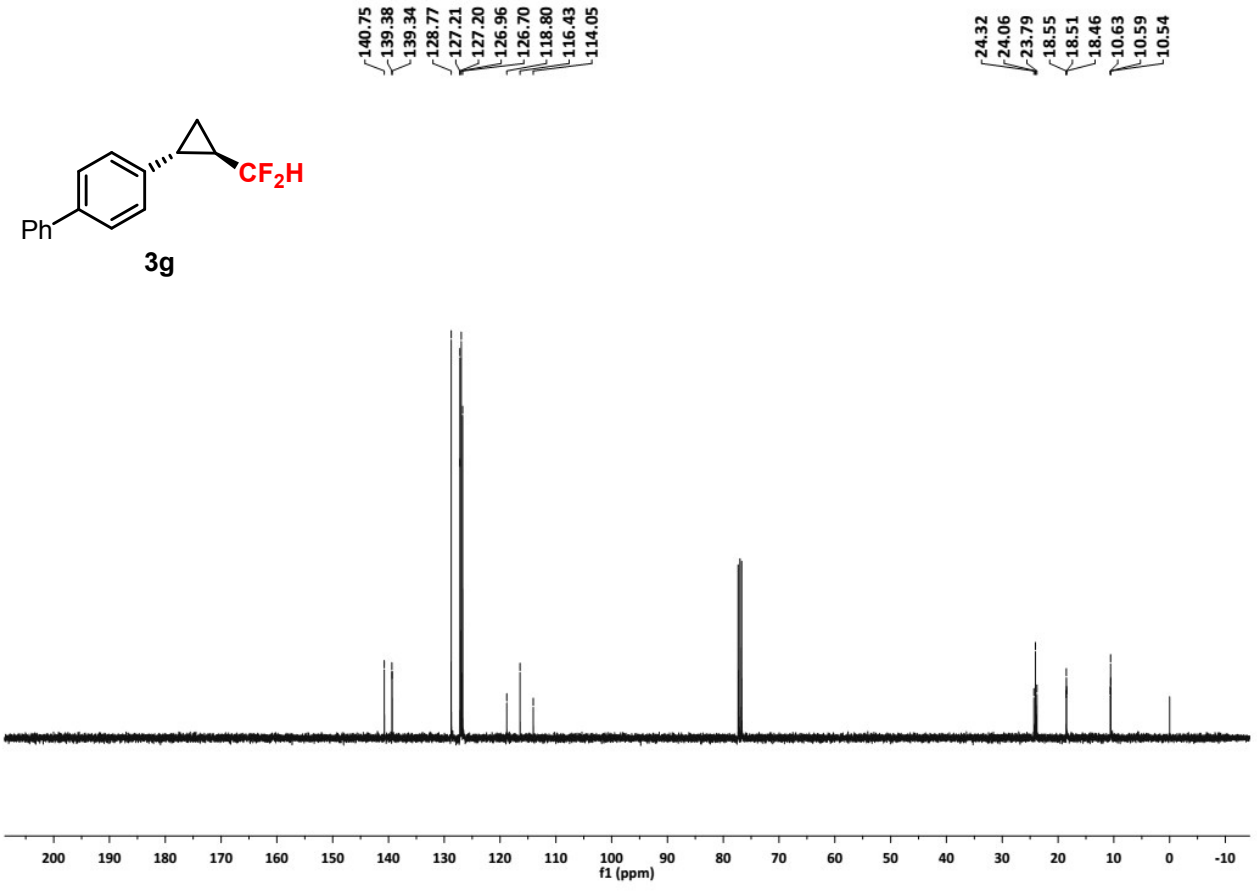
-115.59
-115.62
-115.74
-115.77
-116.33
-116.36
-116.49
-116.52
CF2H
Ph
3g
2.00
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{13}C NMR：


140.75
139.38
139.34
128.77
127.21
127.20
126.96
126.70
118.80
116.43
114.05
24.32
24.06
23.79
18.55
18.51
18.46
10.63
10.59
10.54
CF2H
Ph
3g
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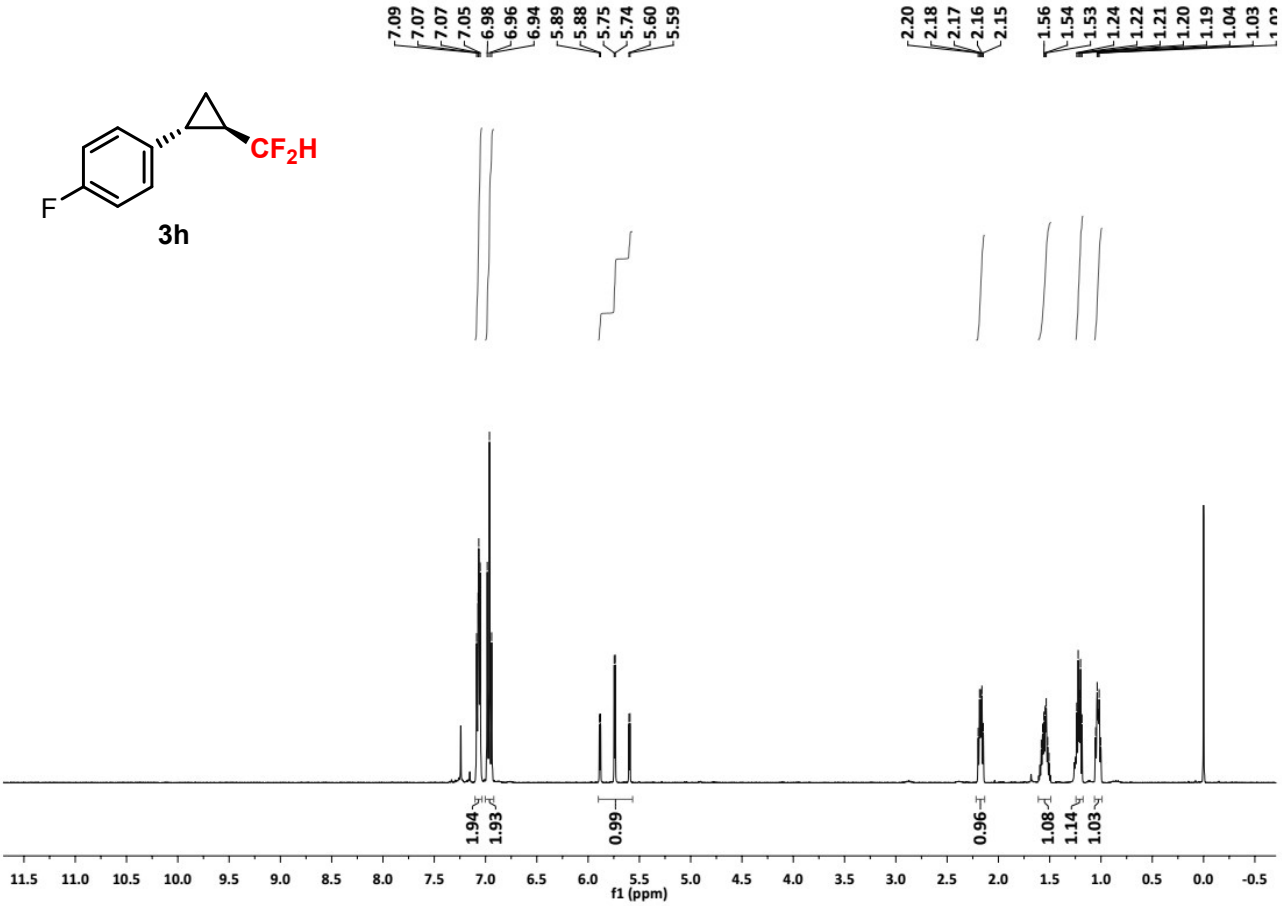
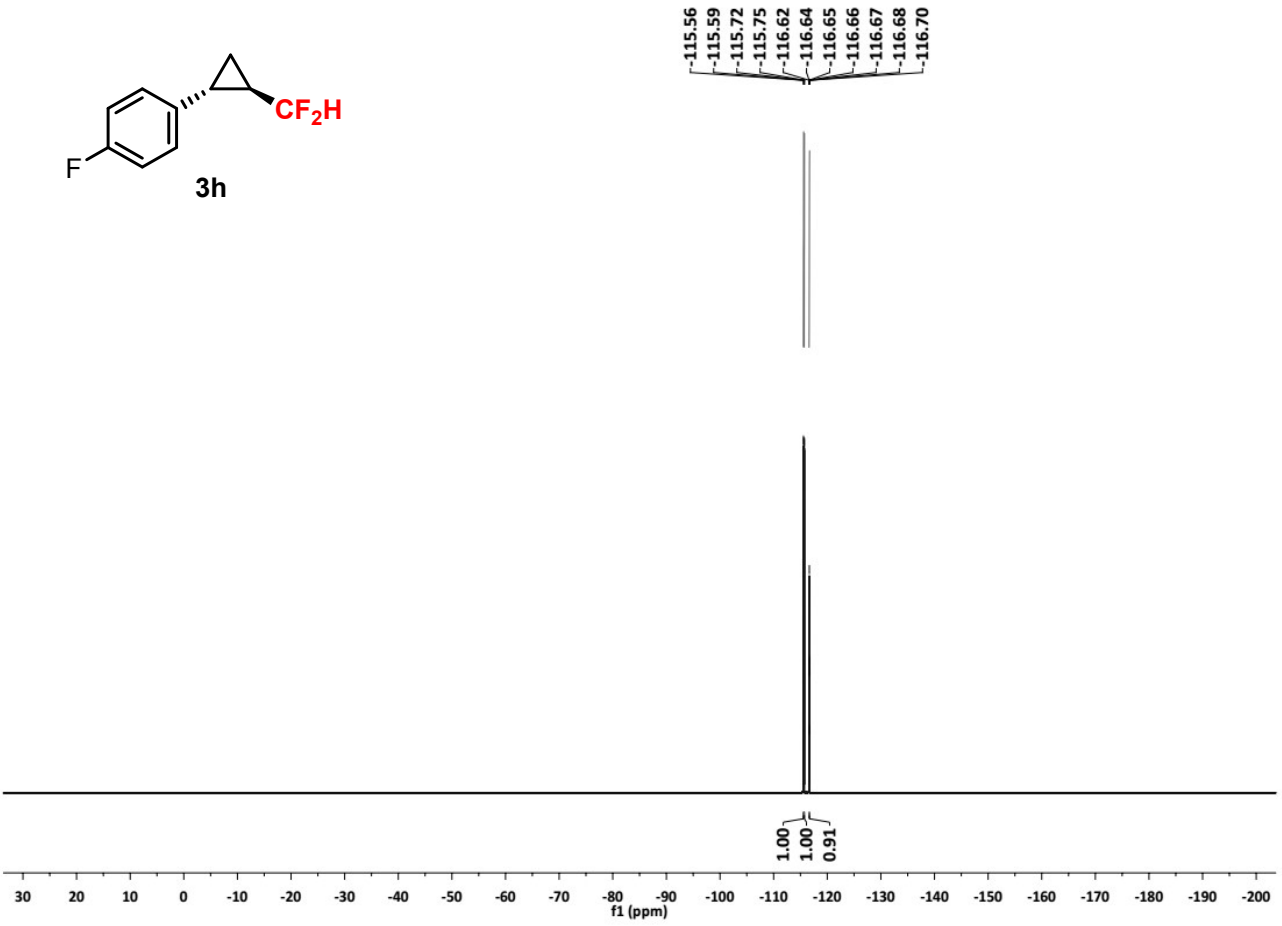
f1 (ppm)

^{1}H NMR：



^{19}F NMR：



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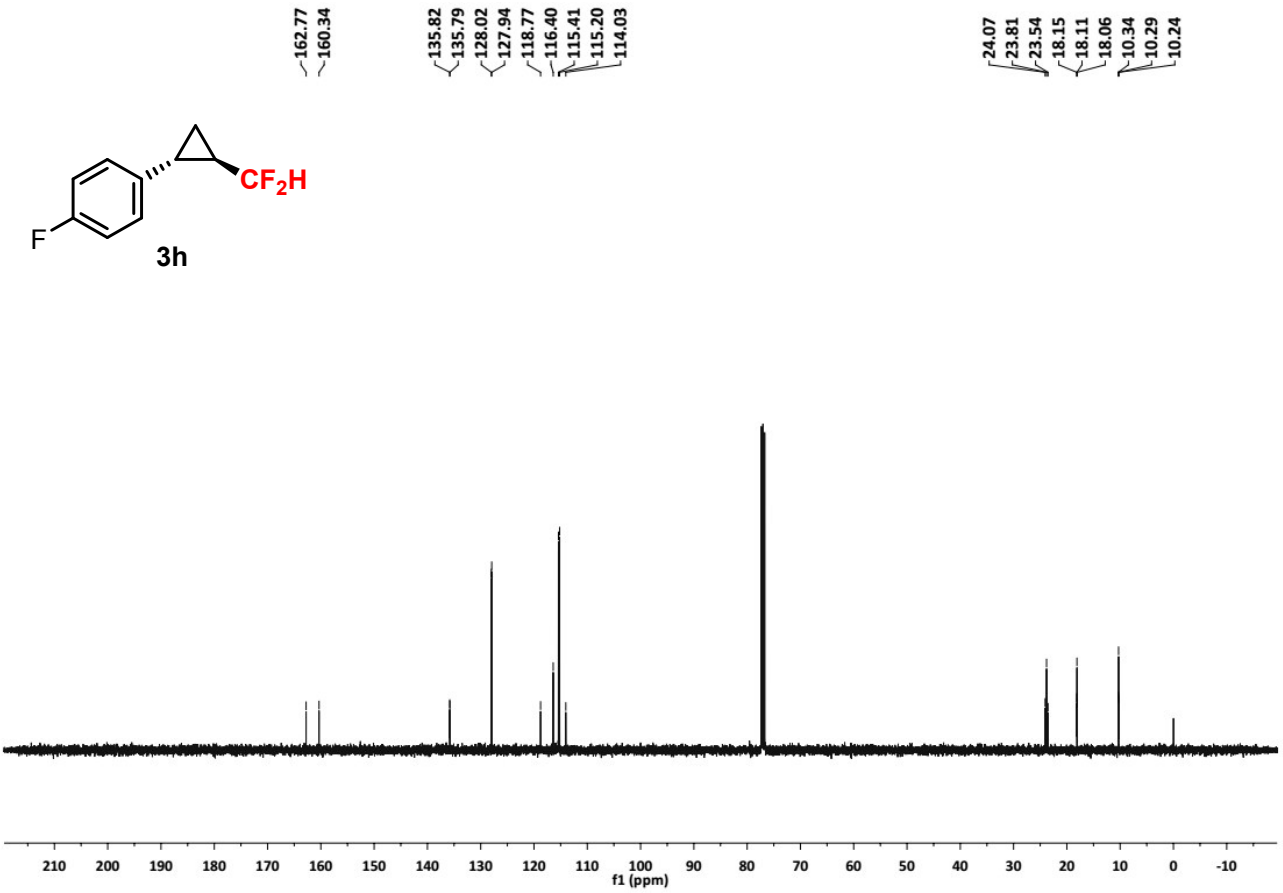
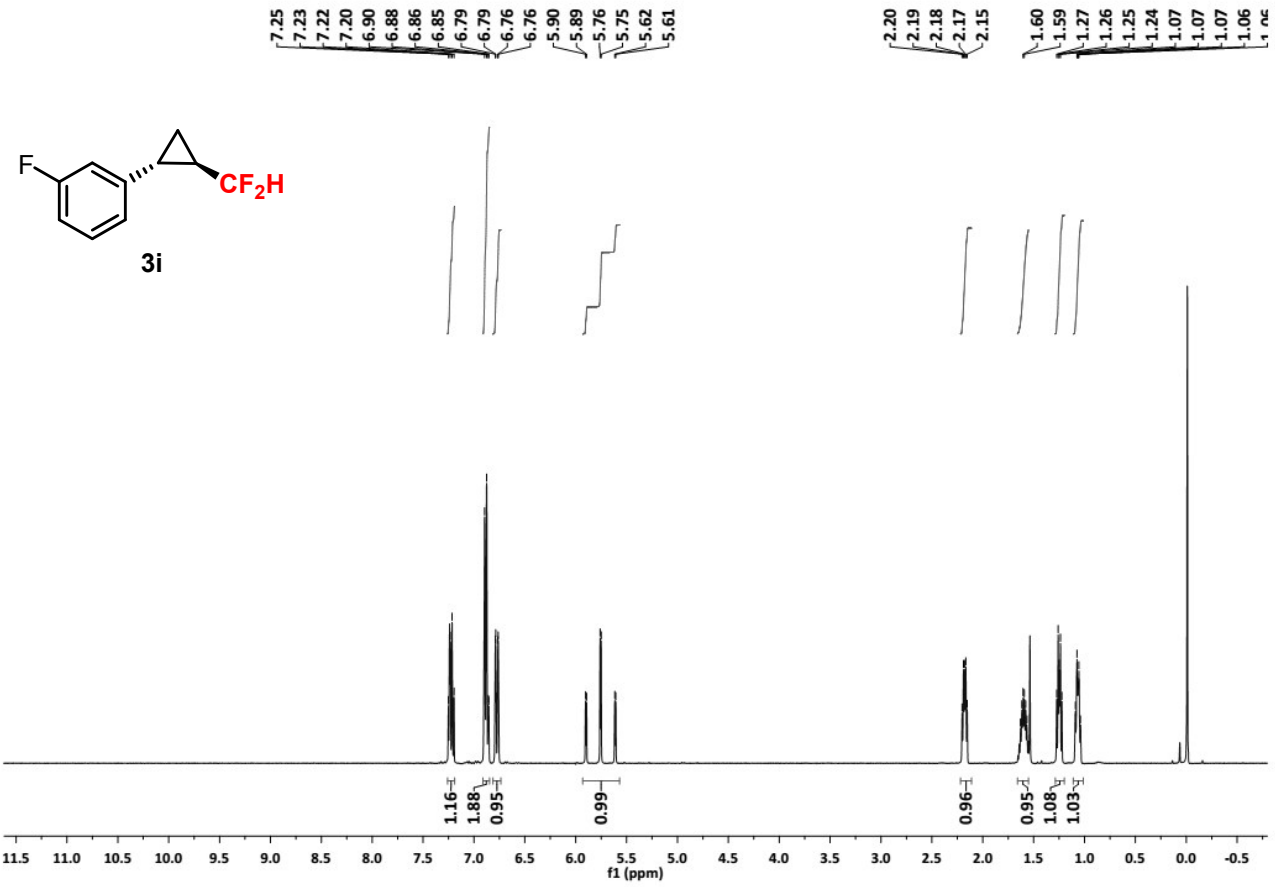


^{1}H NMR：



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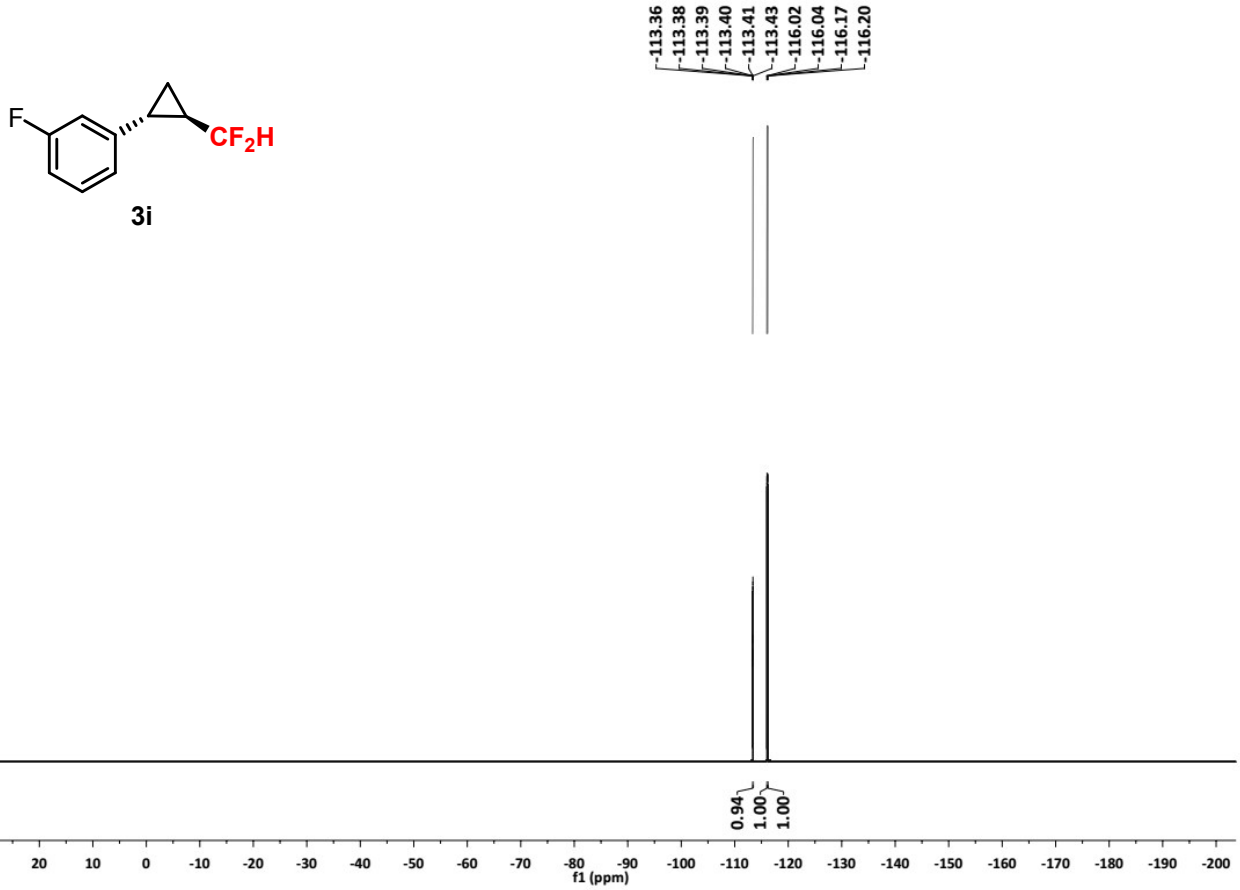

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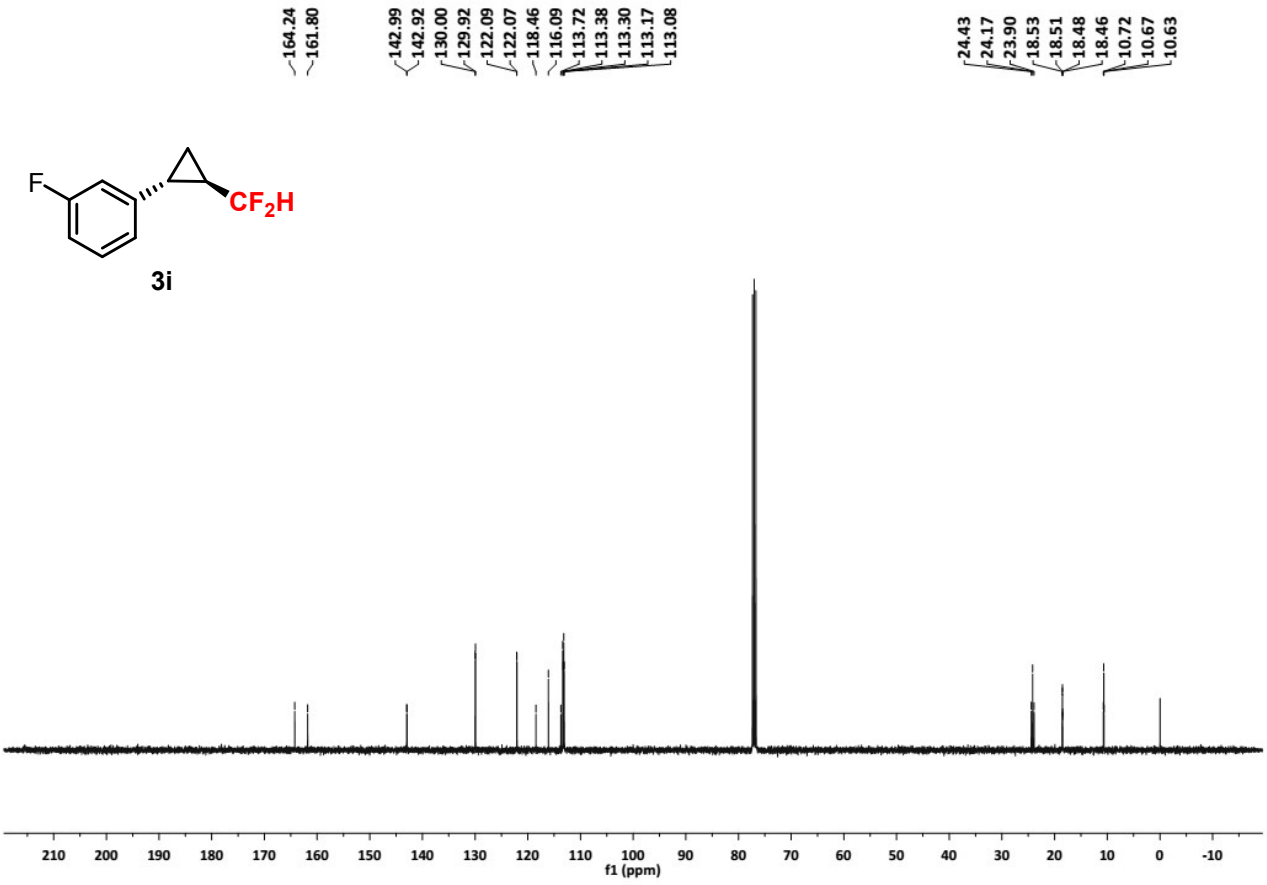

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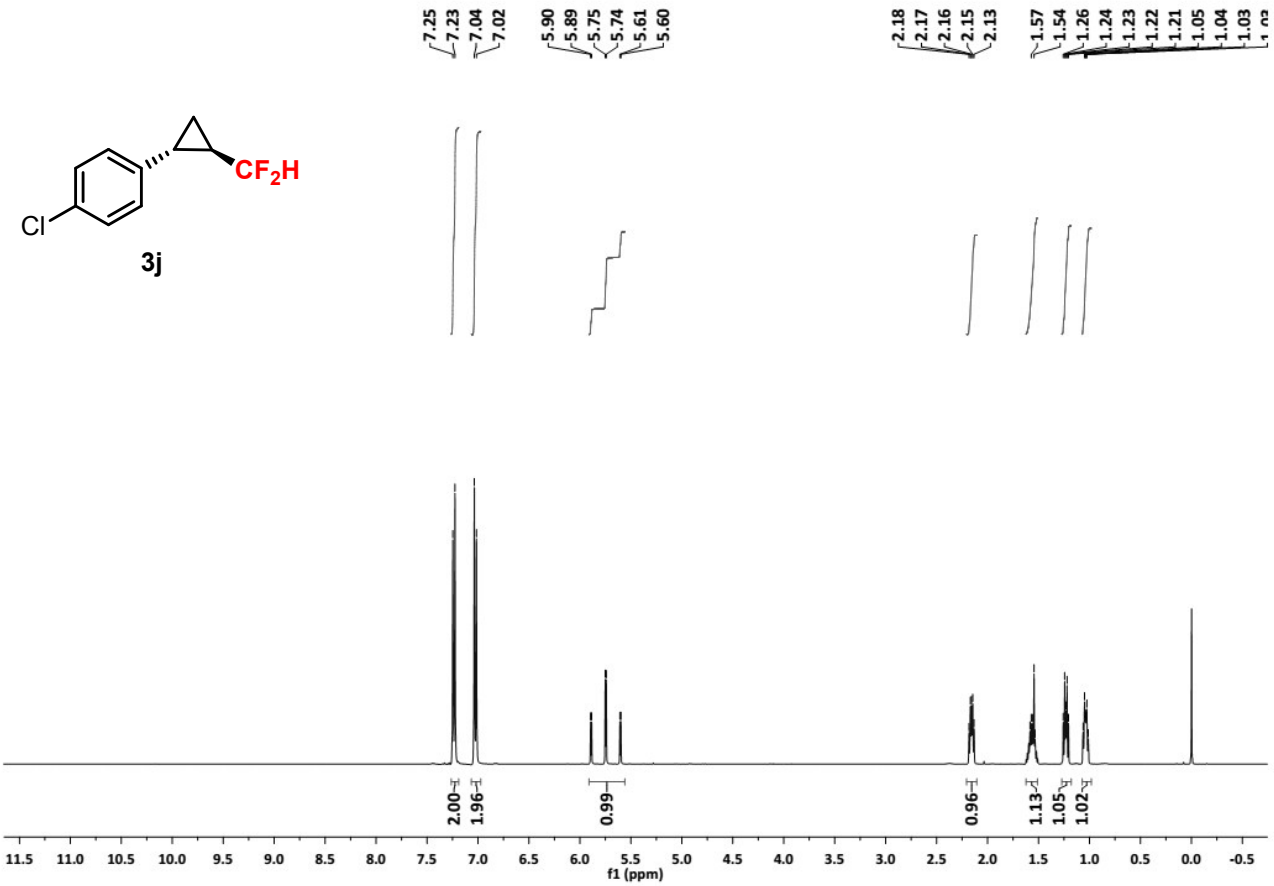

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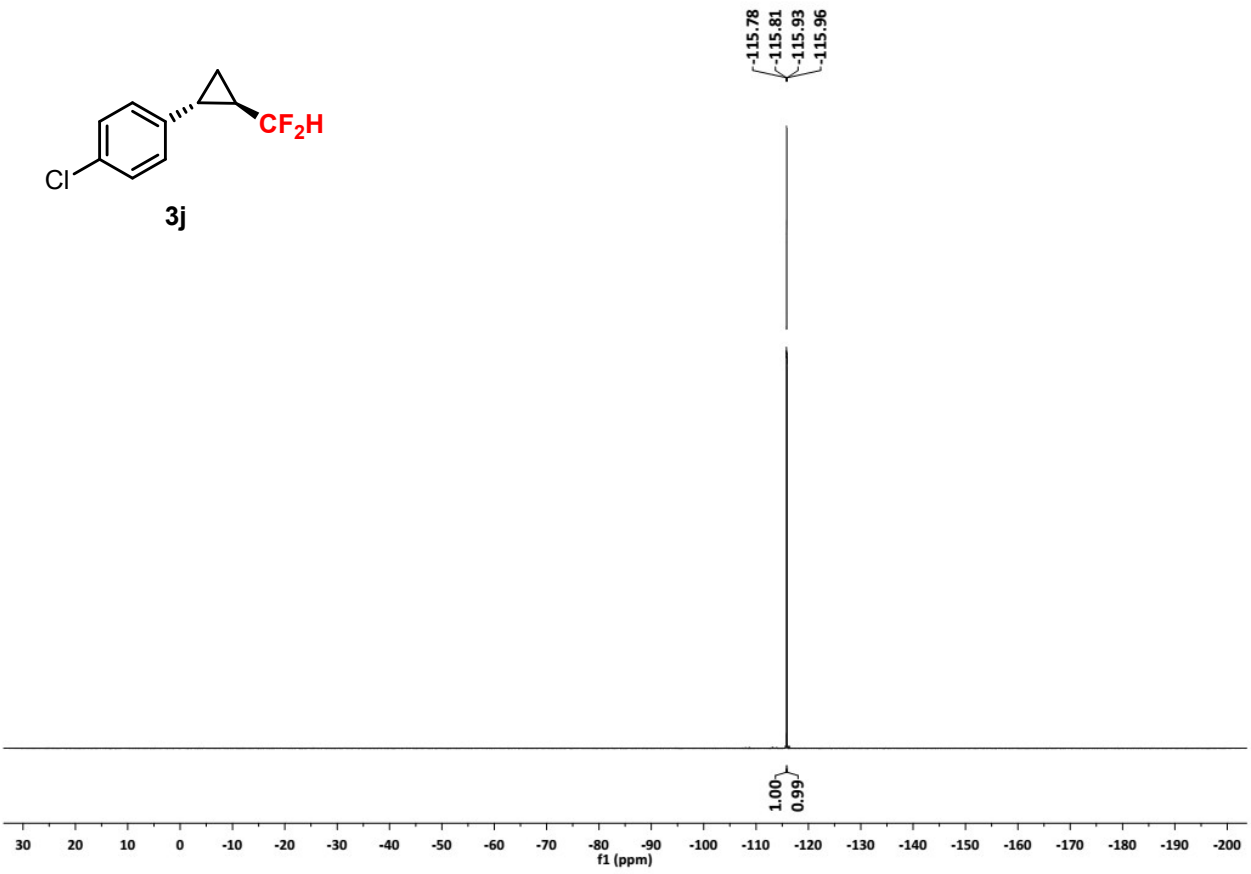

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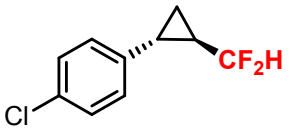

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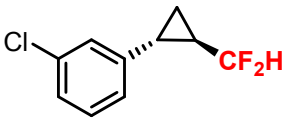

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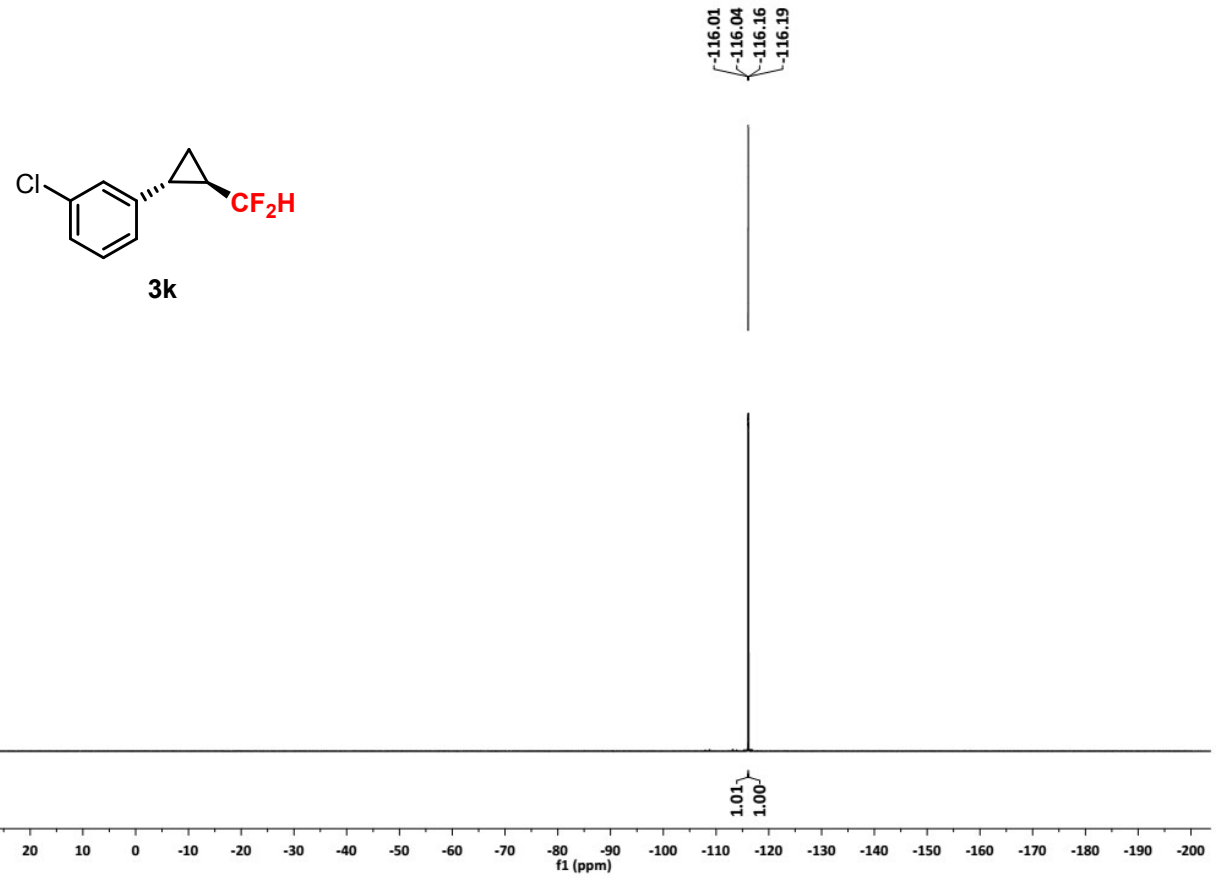

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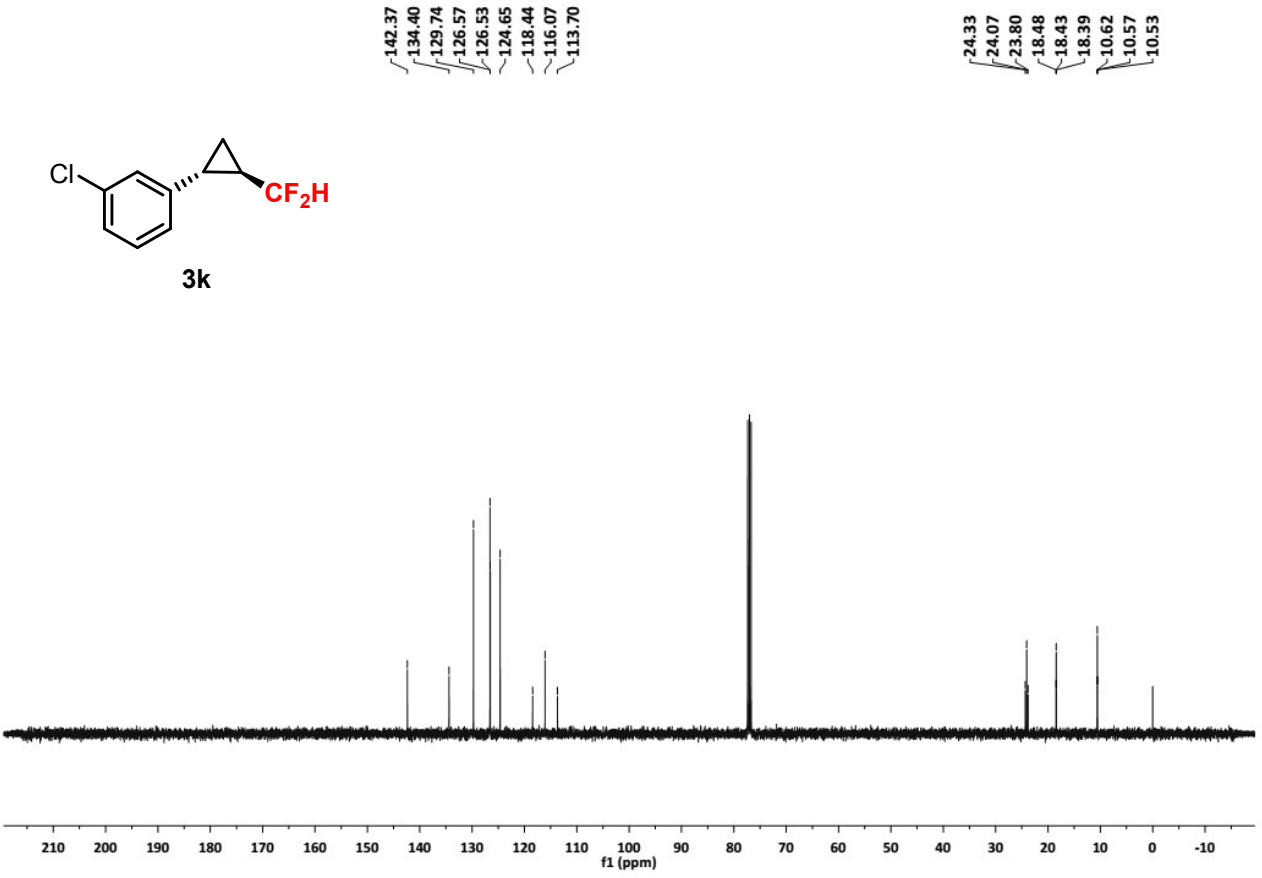

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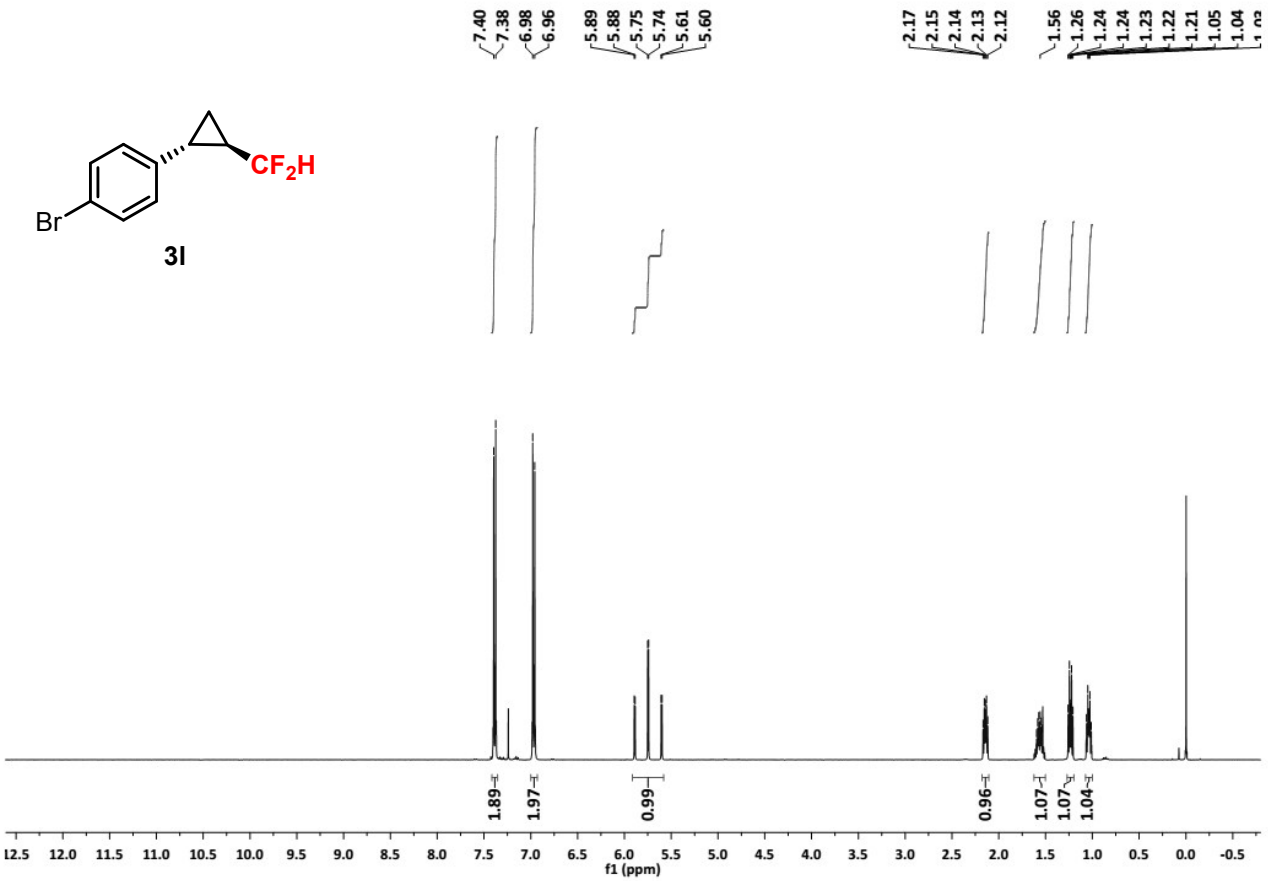

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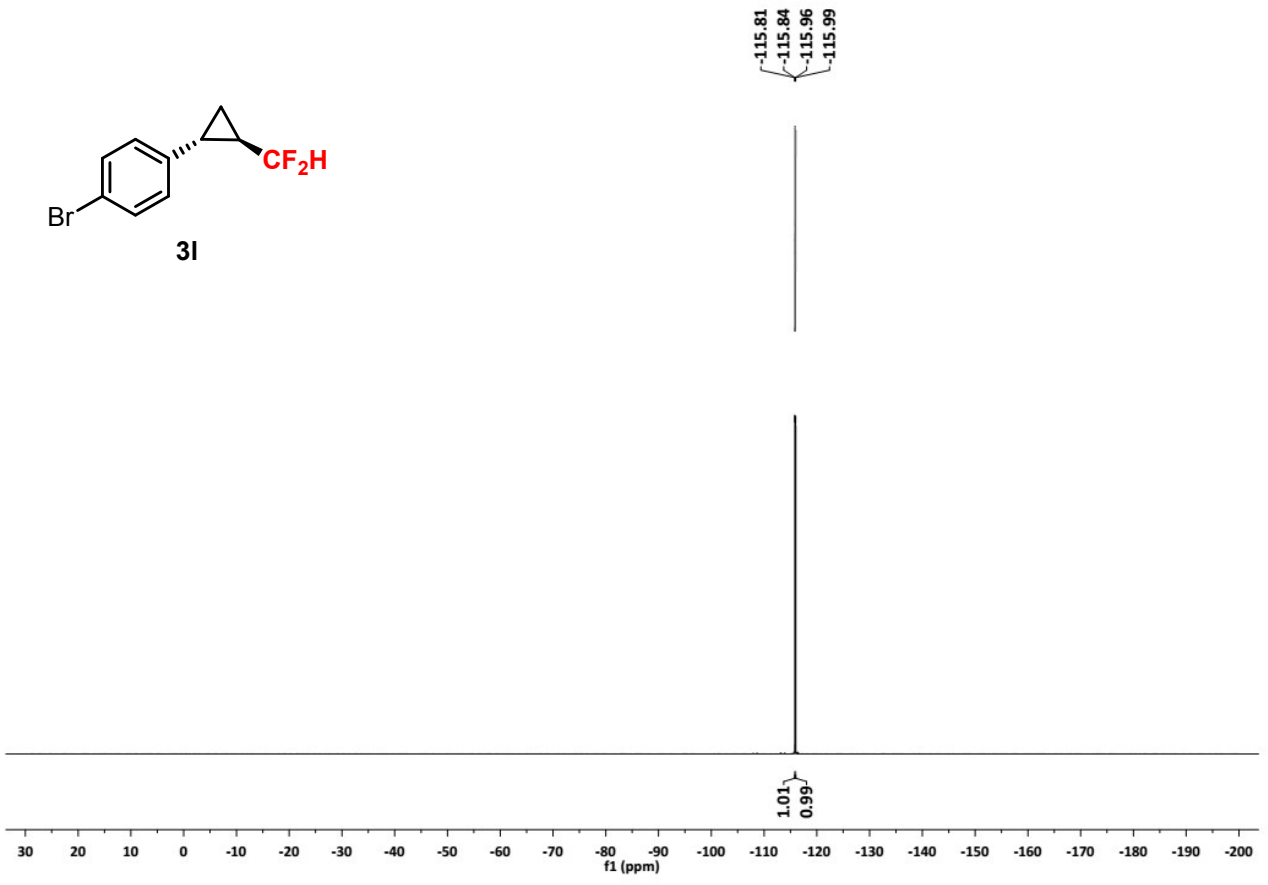

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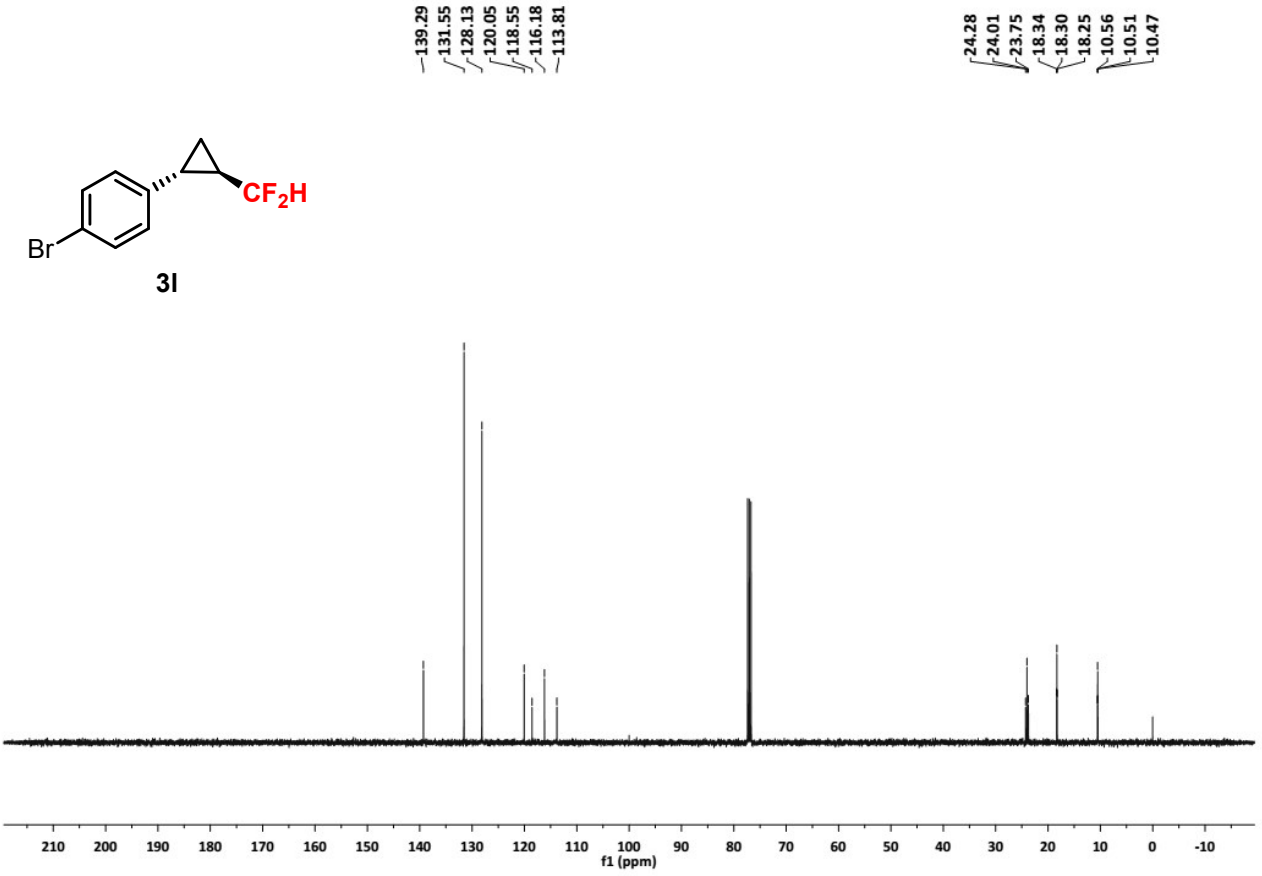

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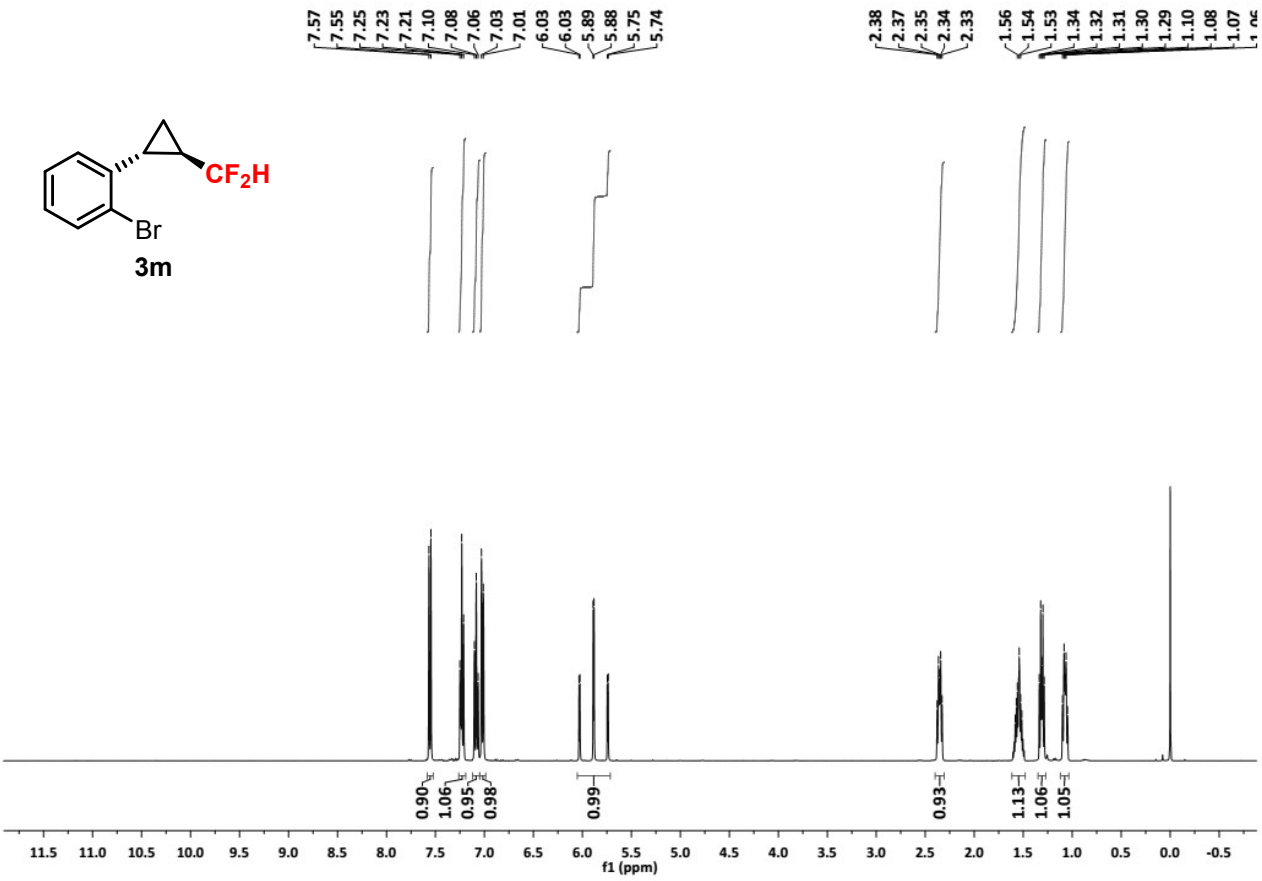

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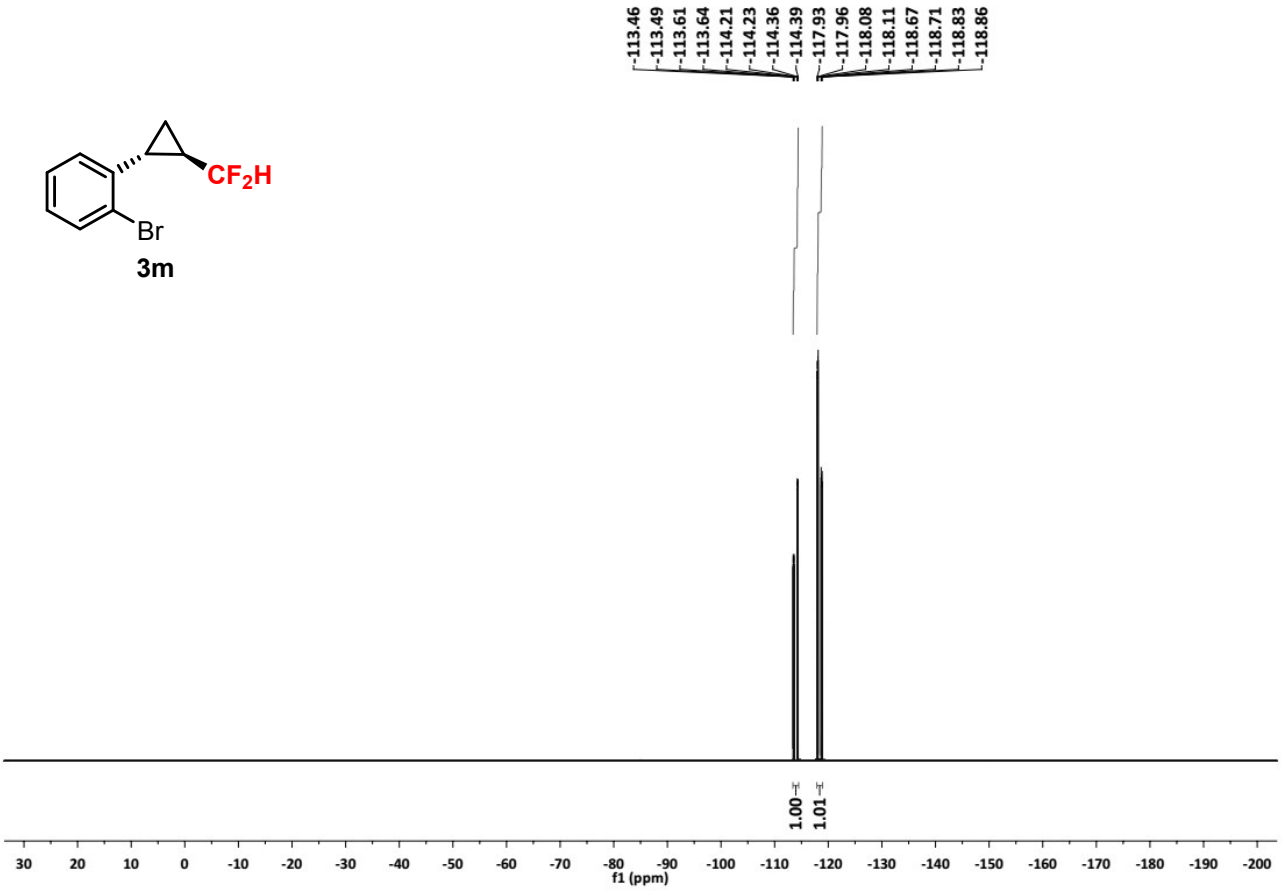

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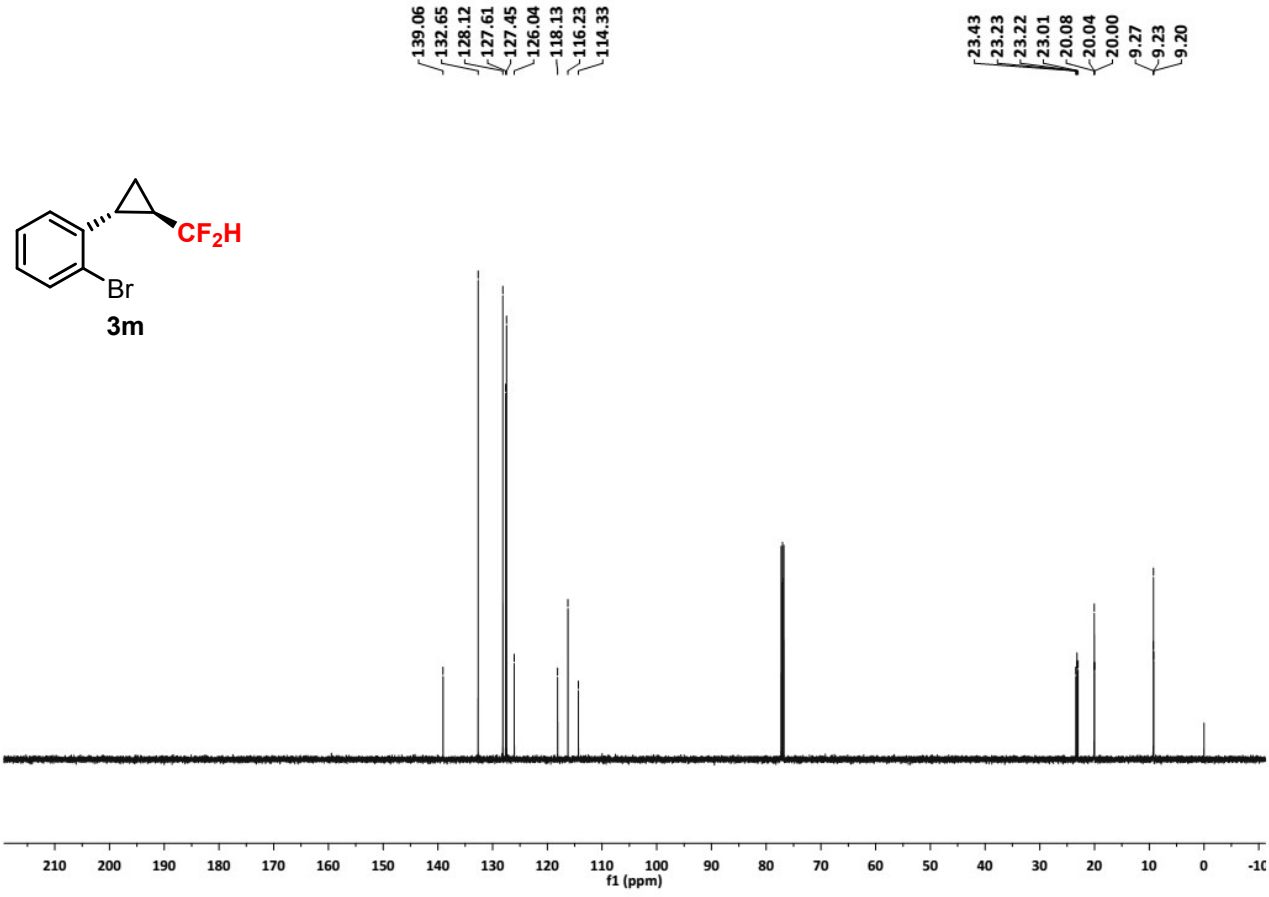

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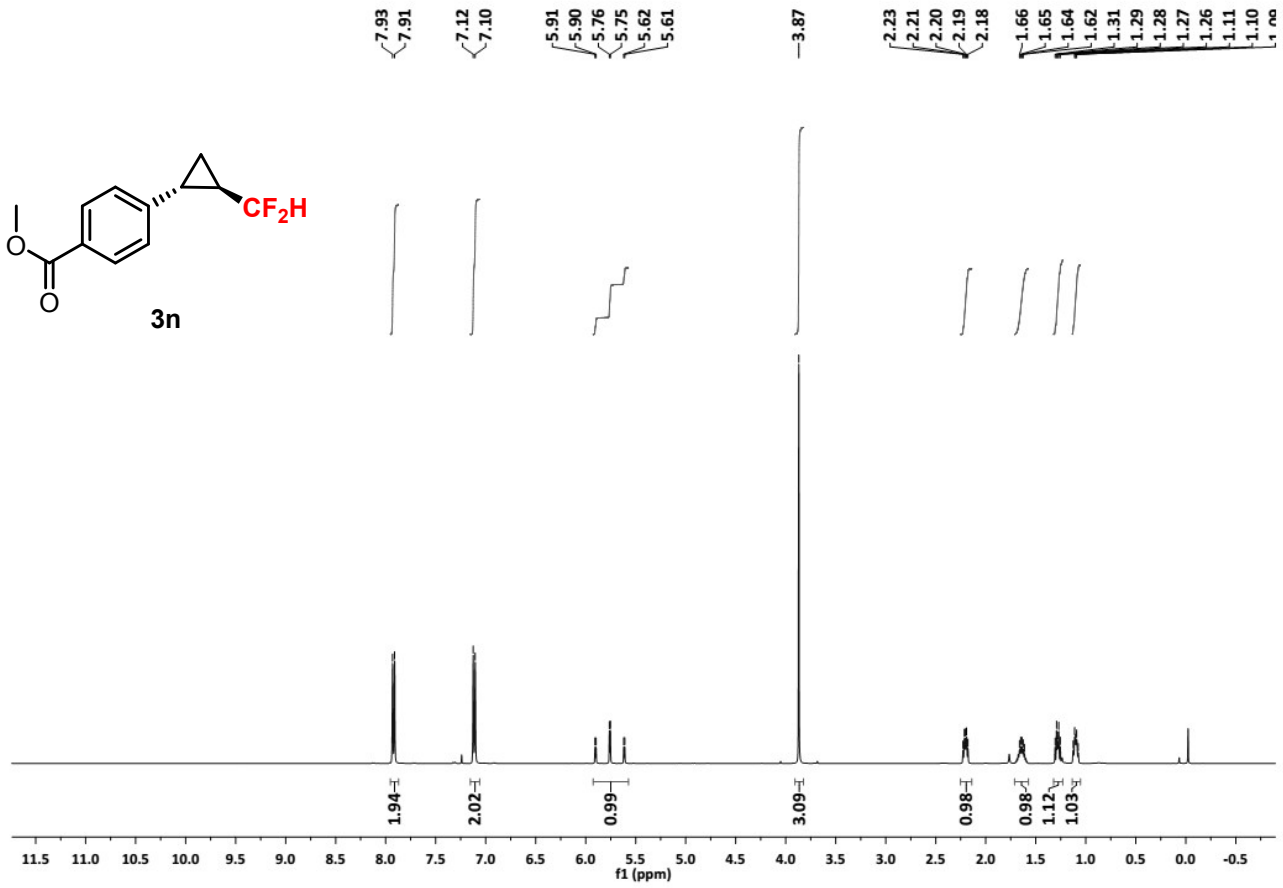

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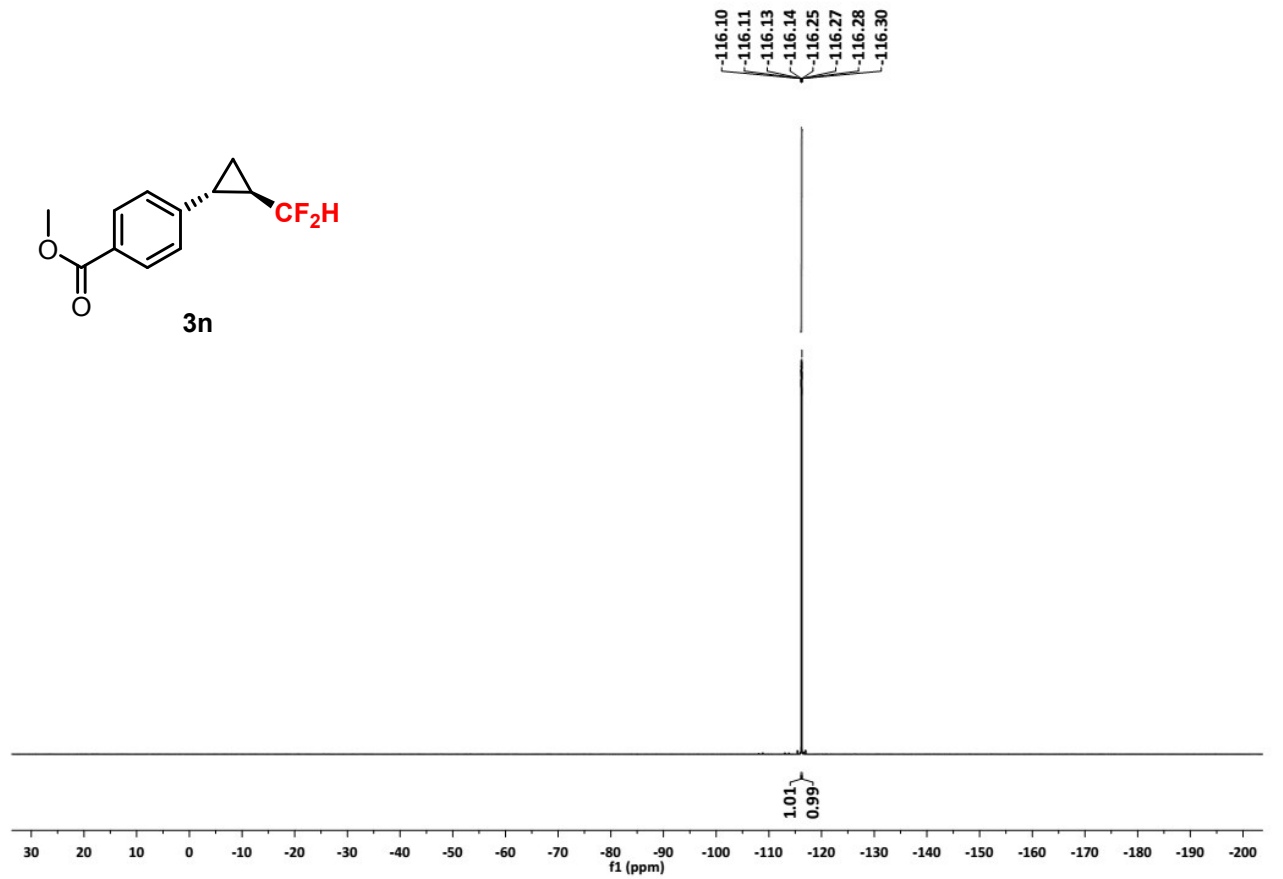

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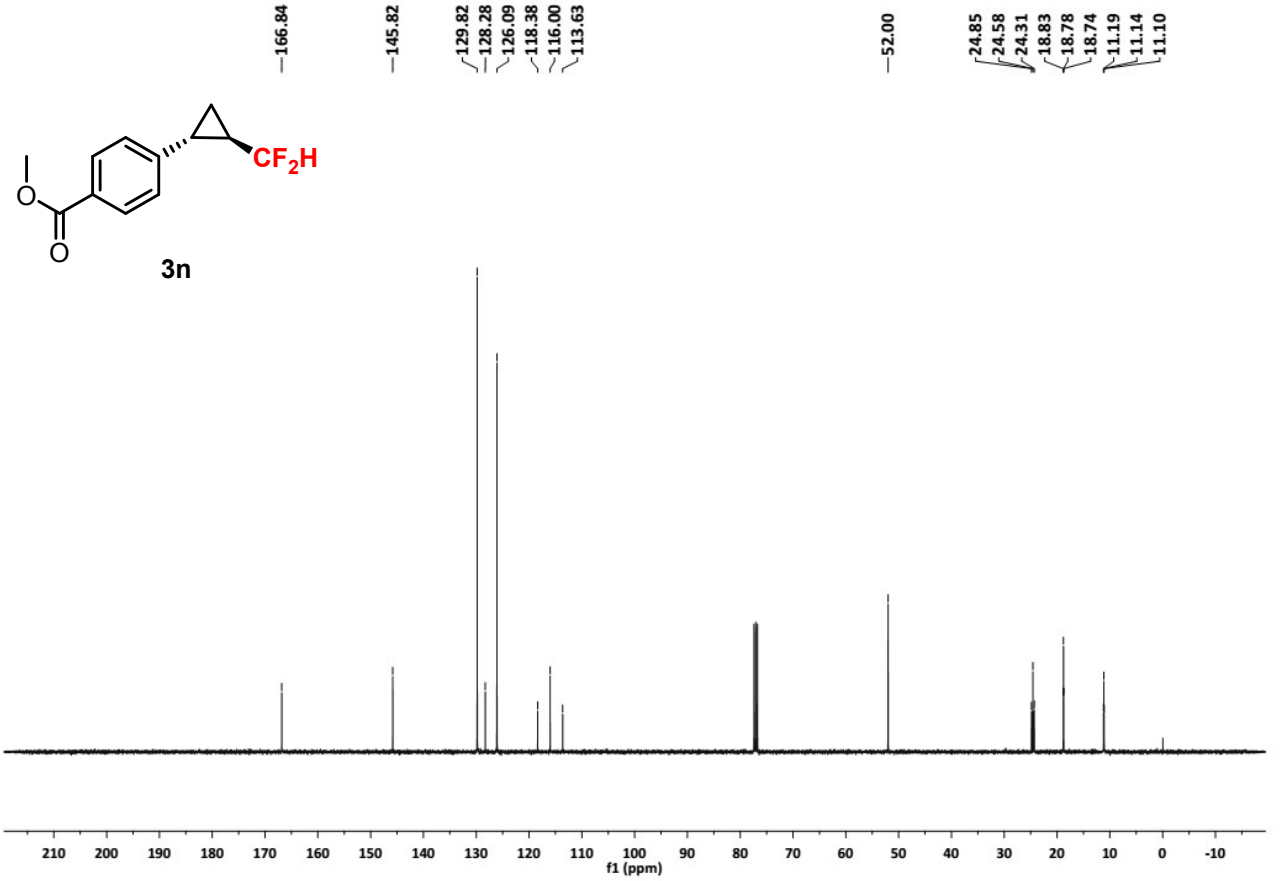

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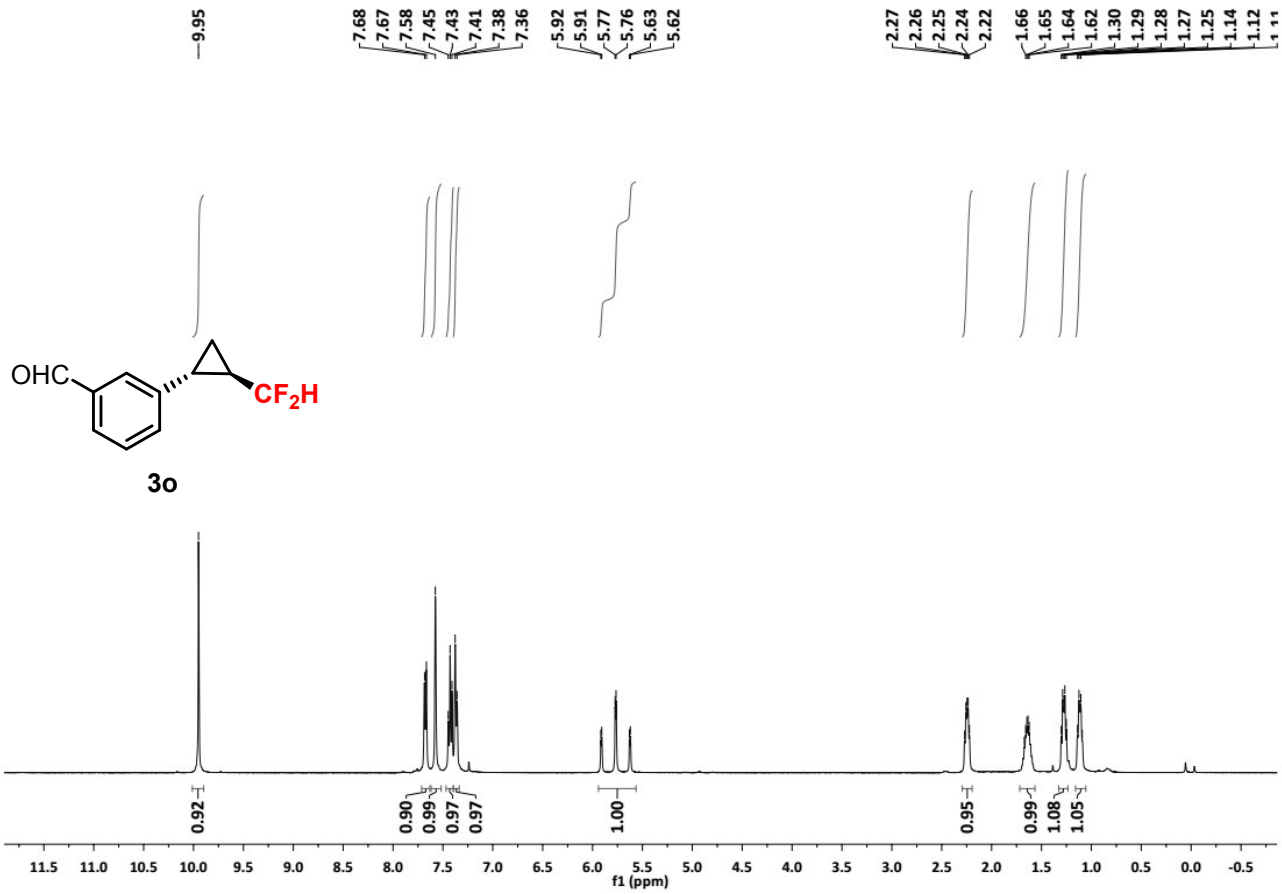

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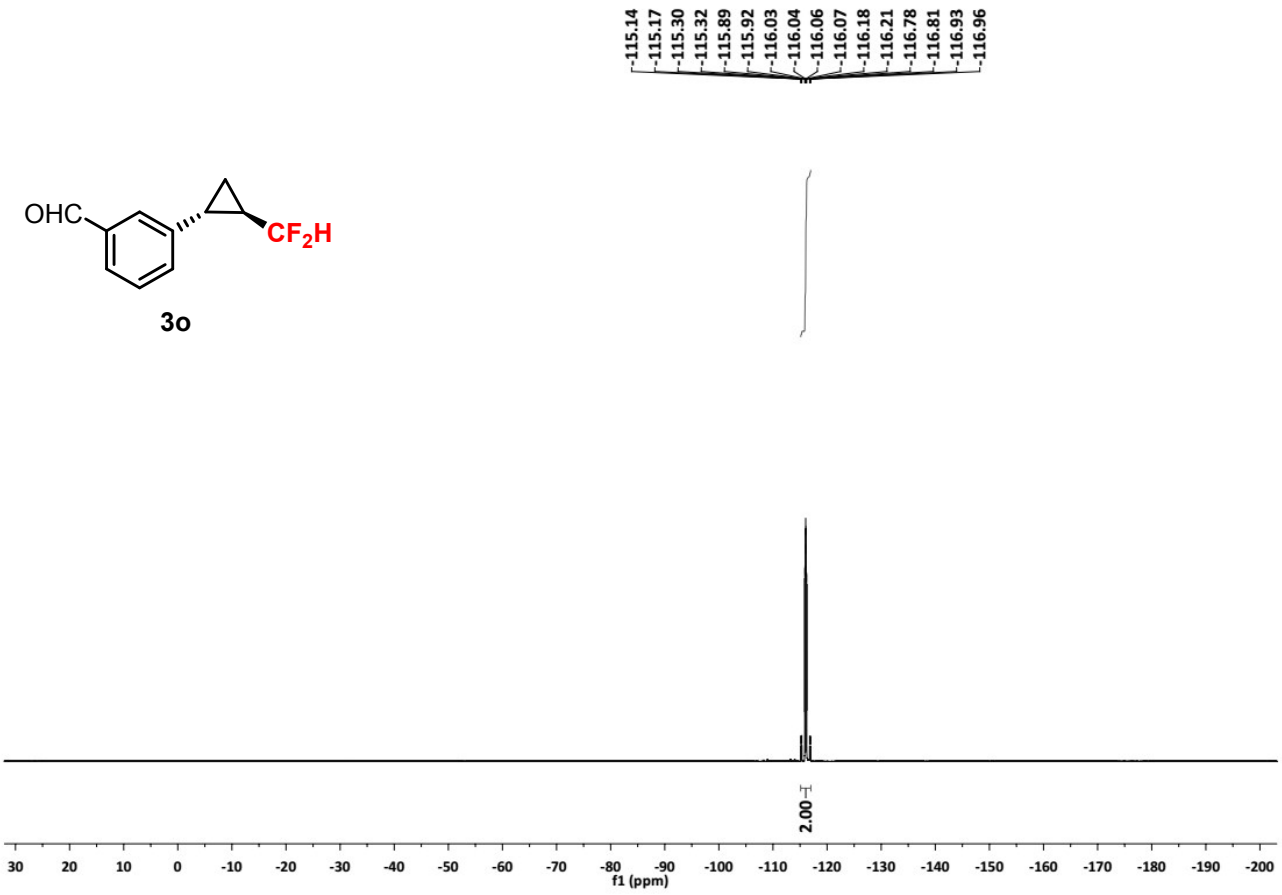

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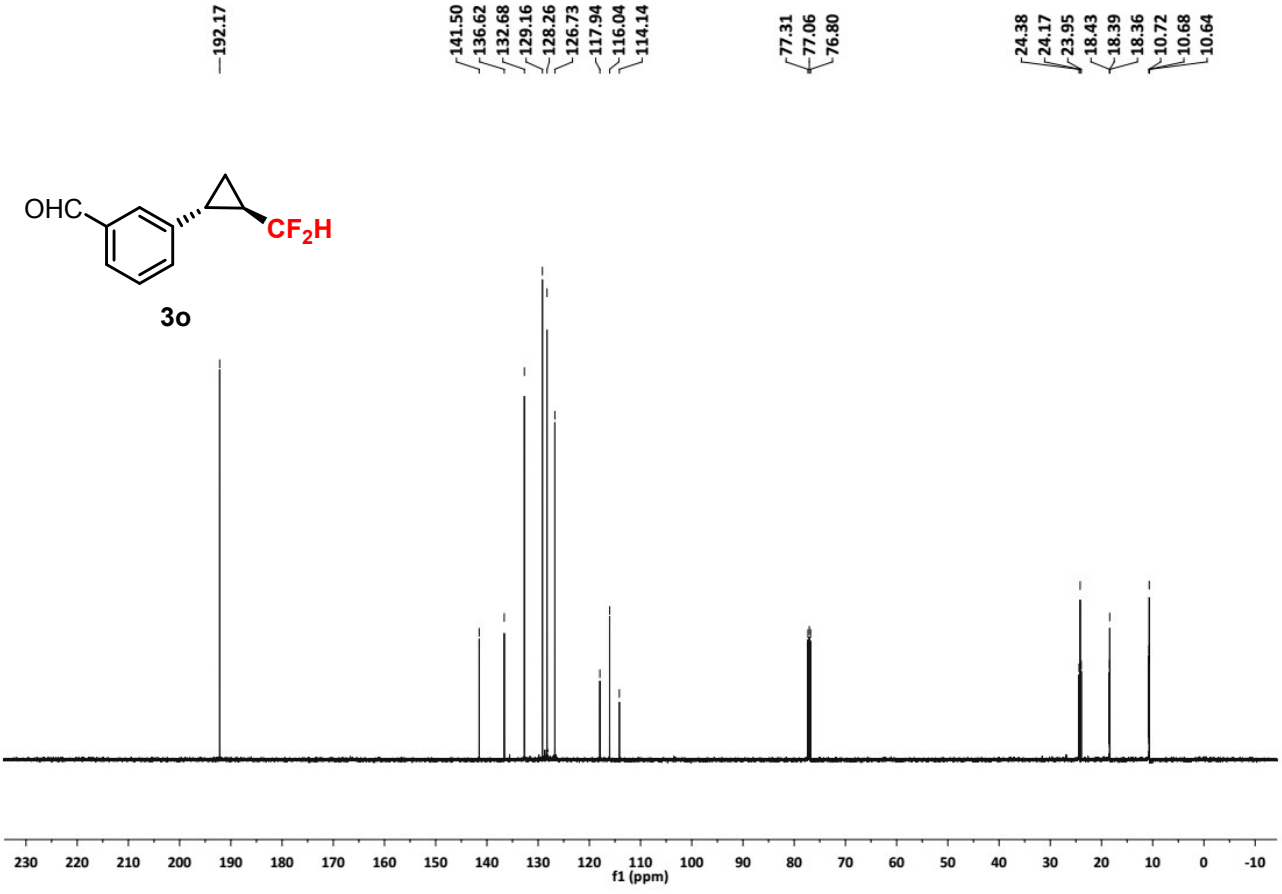

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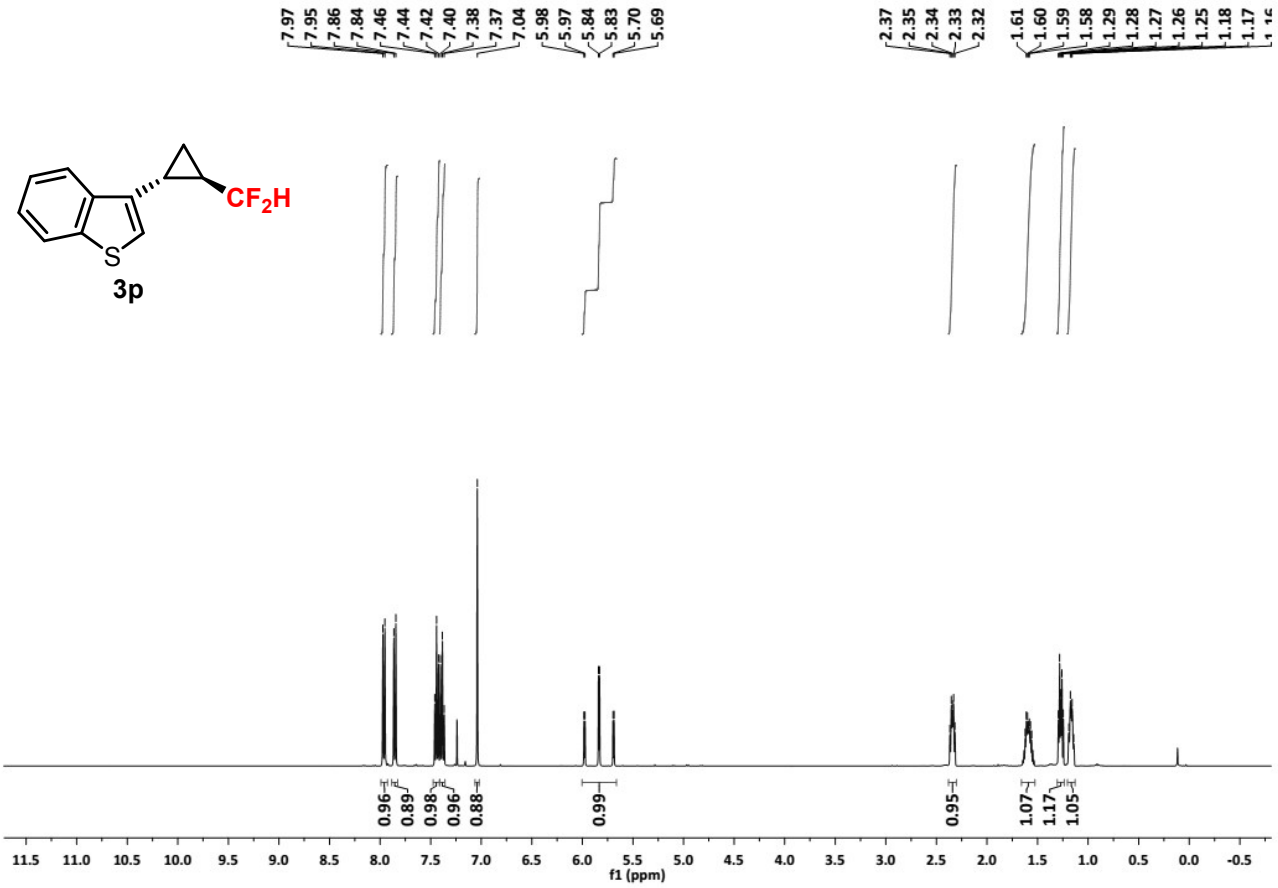

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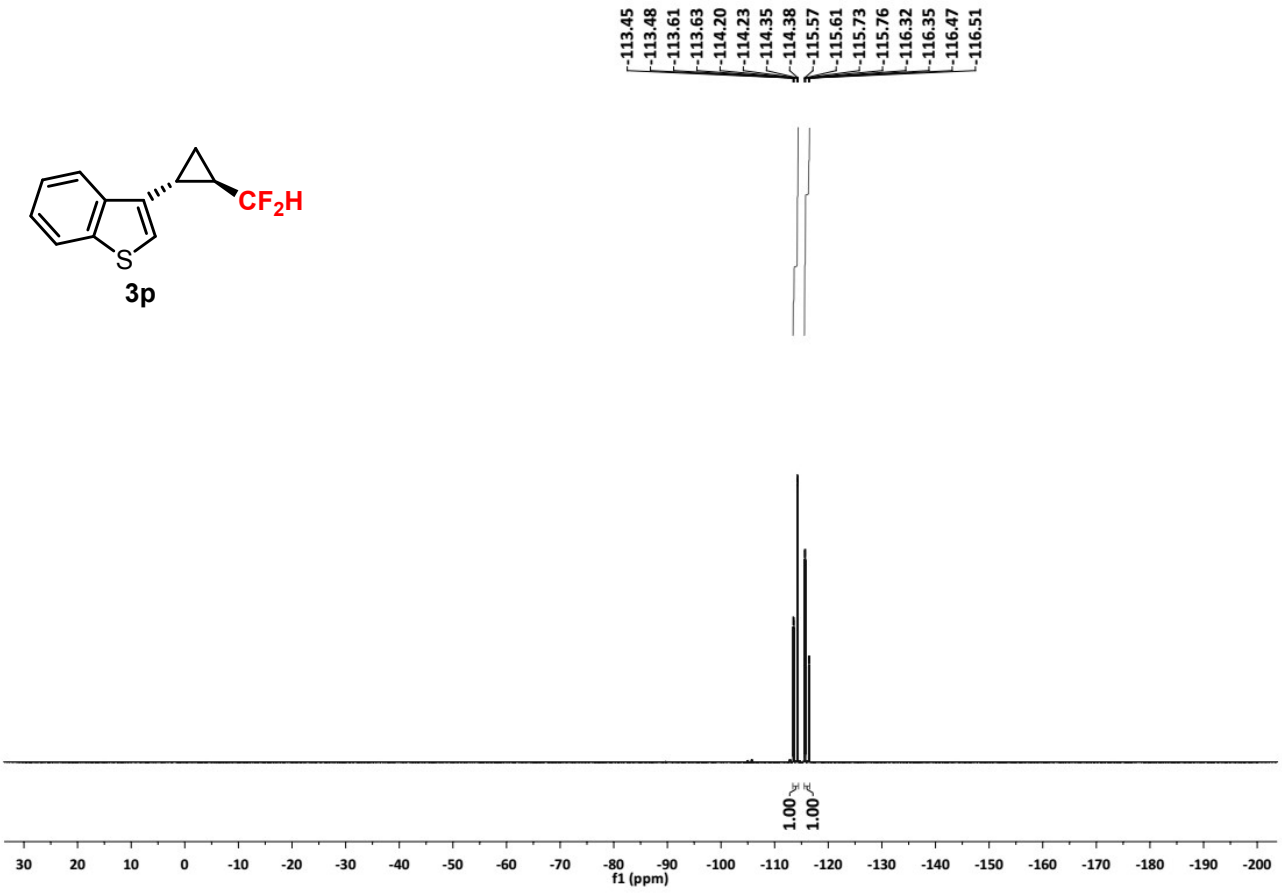

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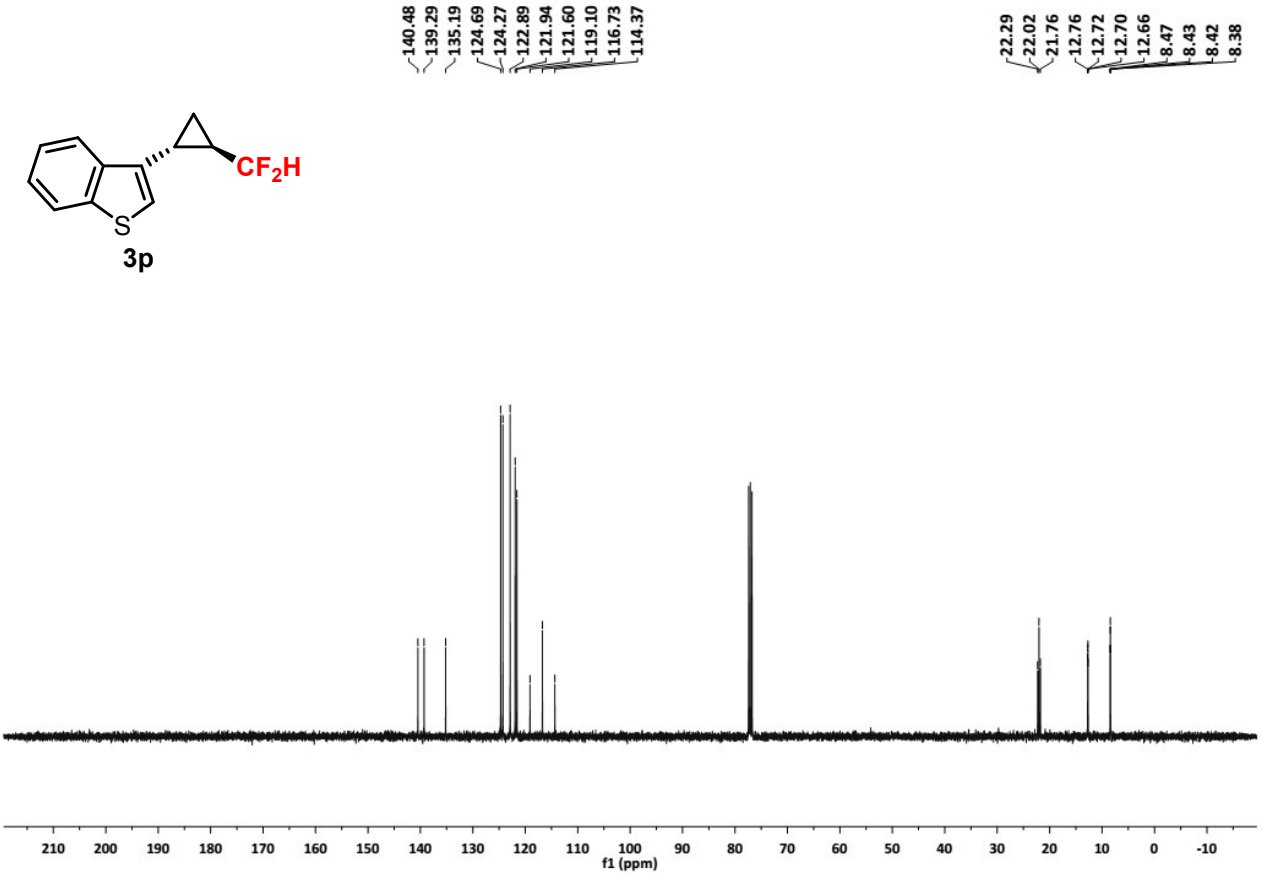

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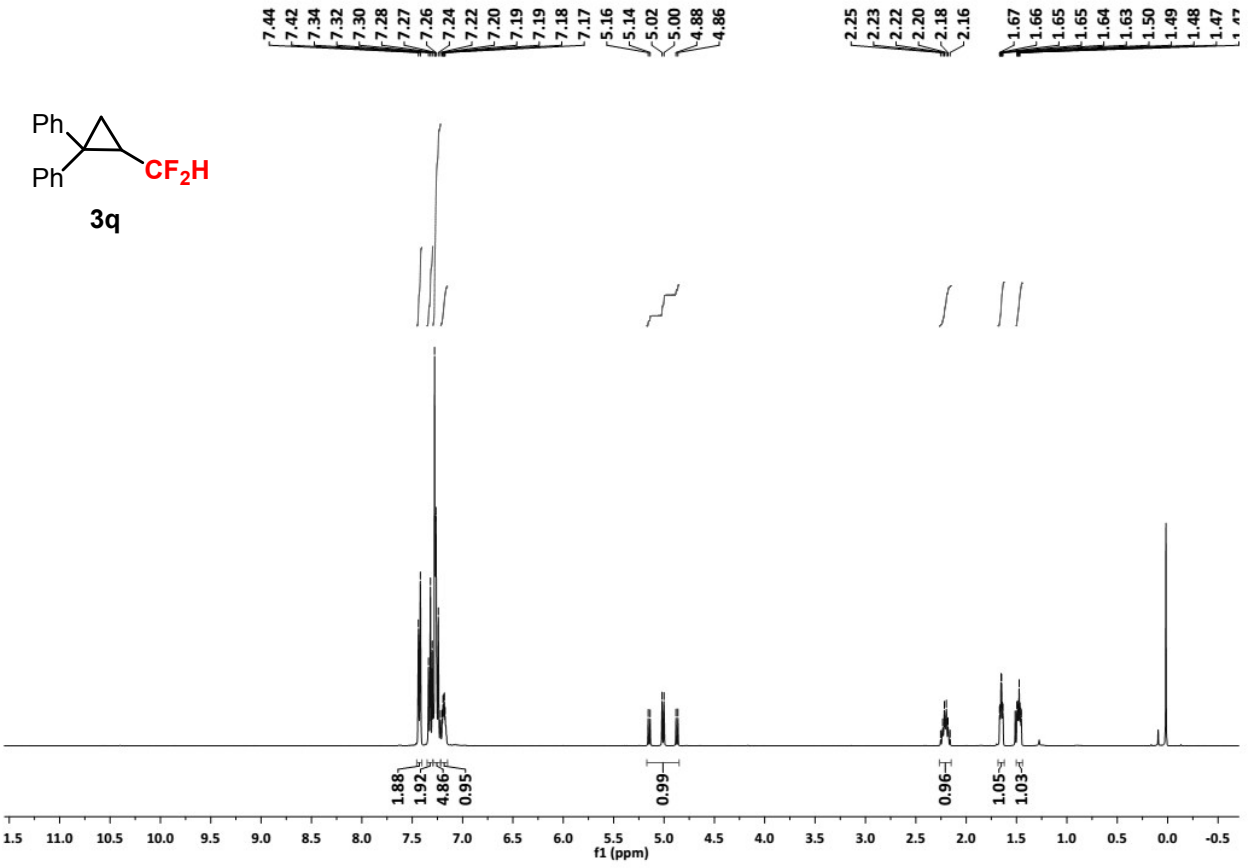

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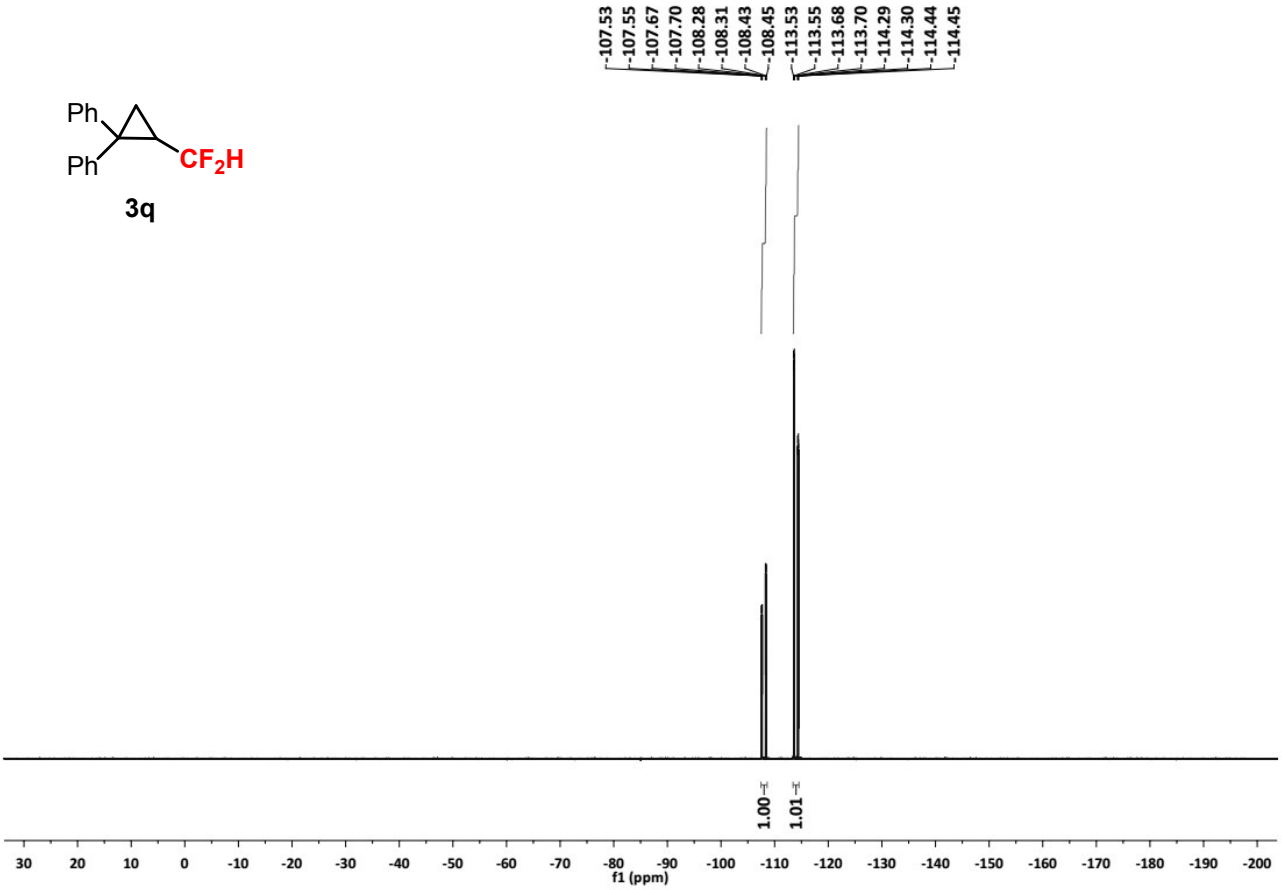

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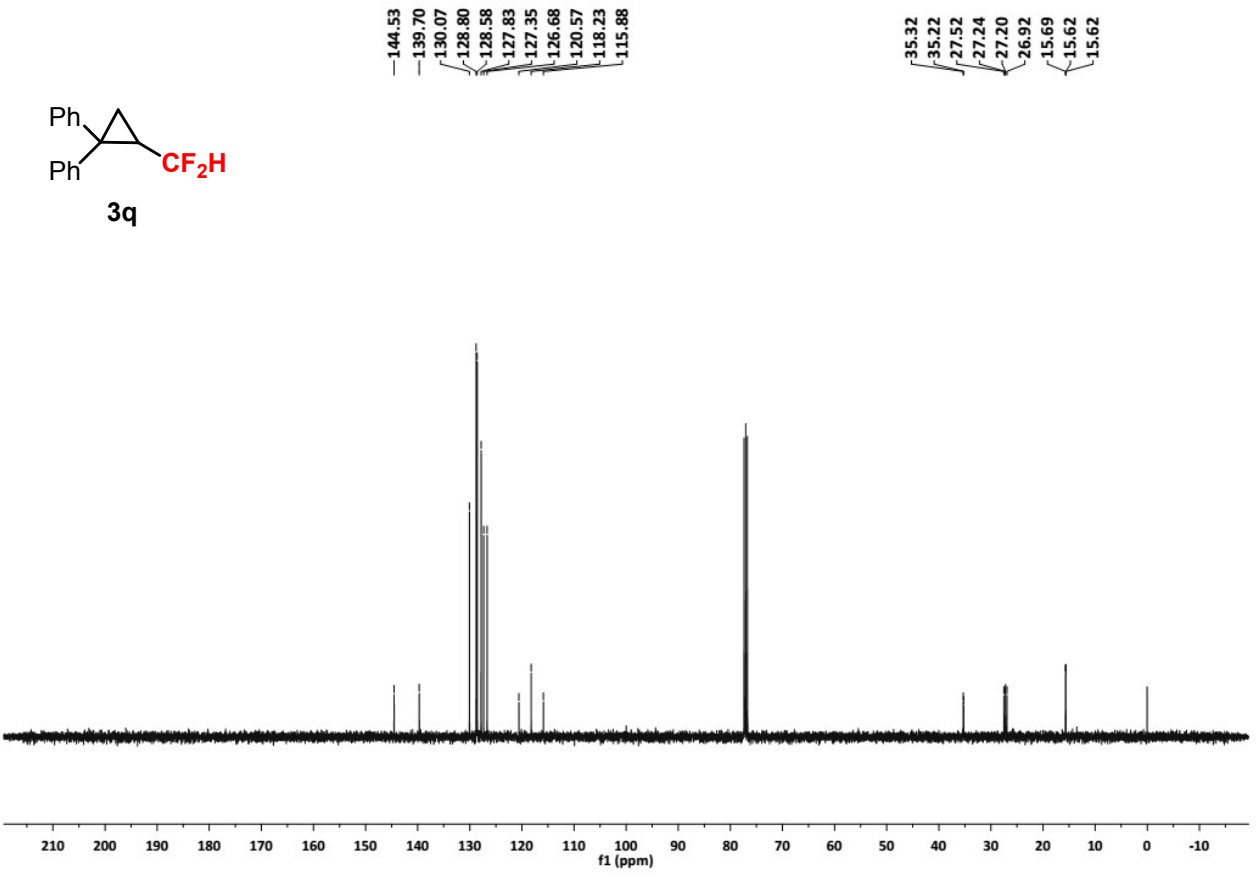

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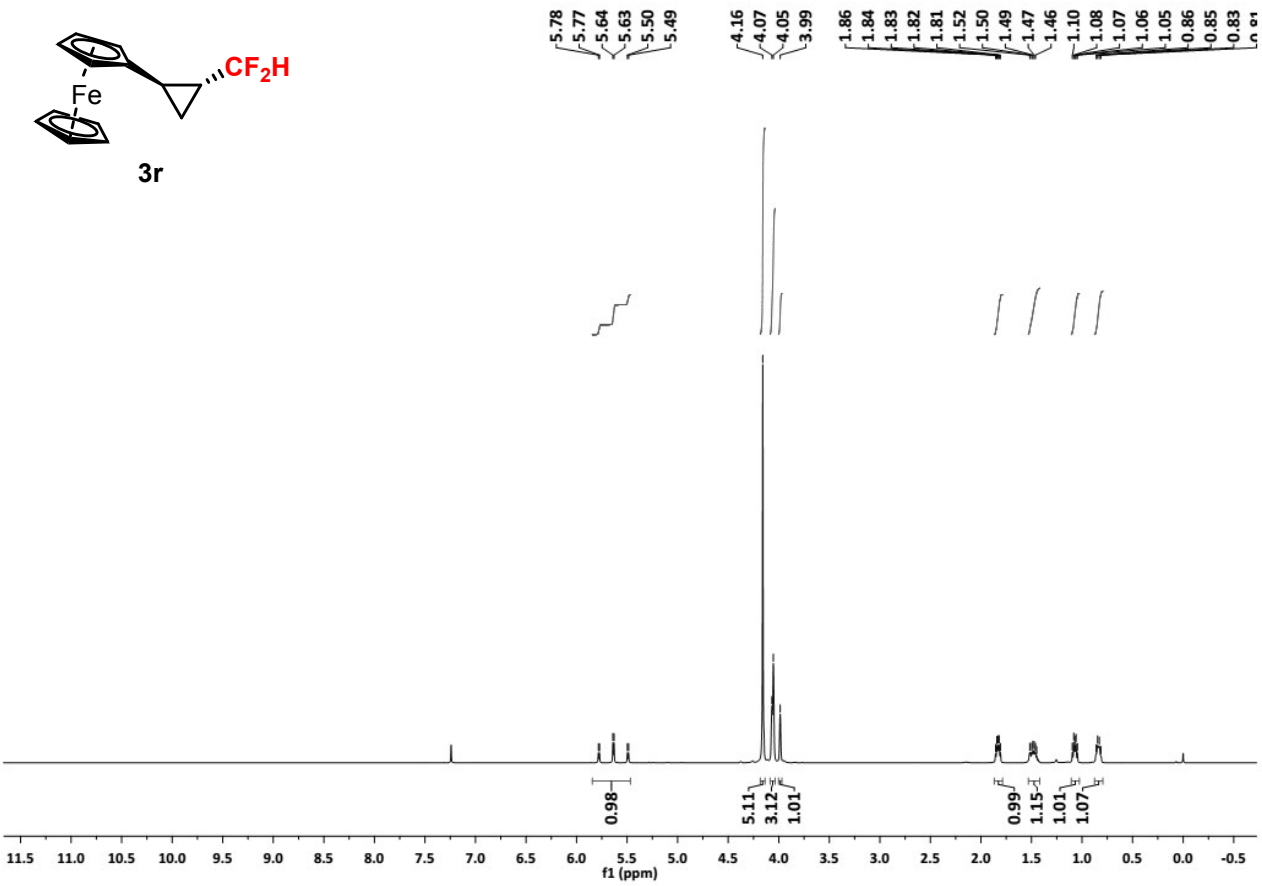

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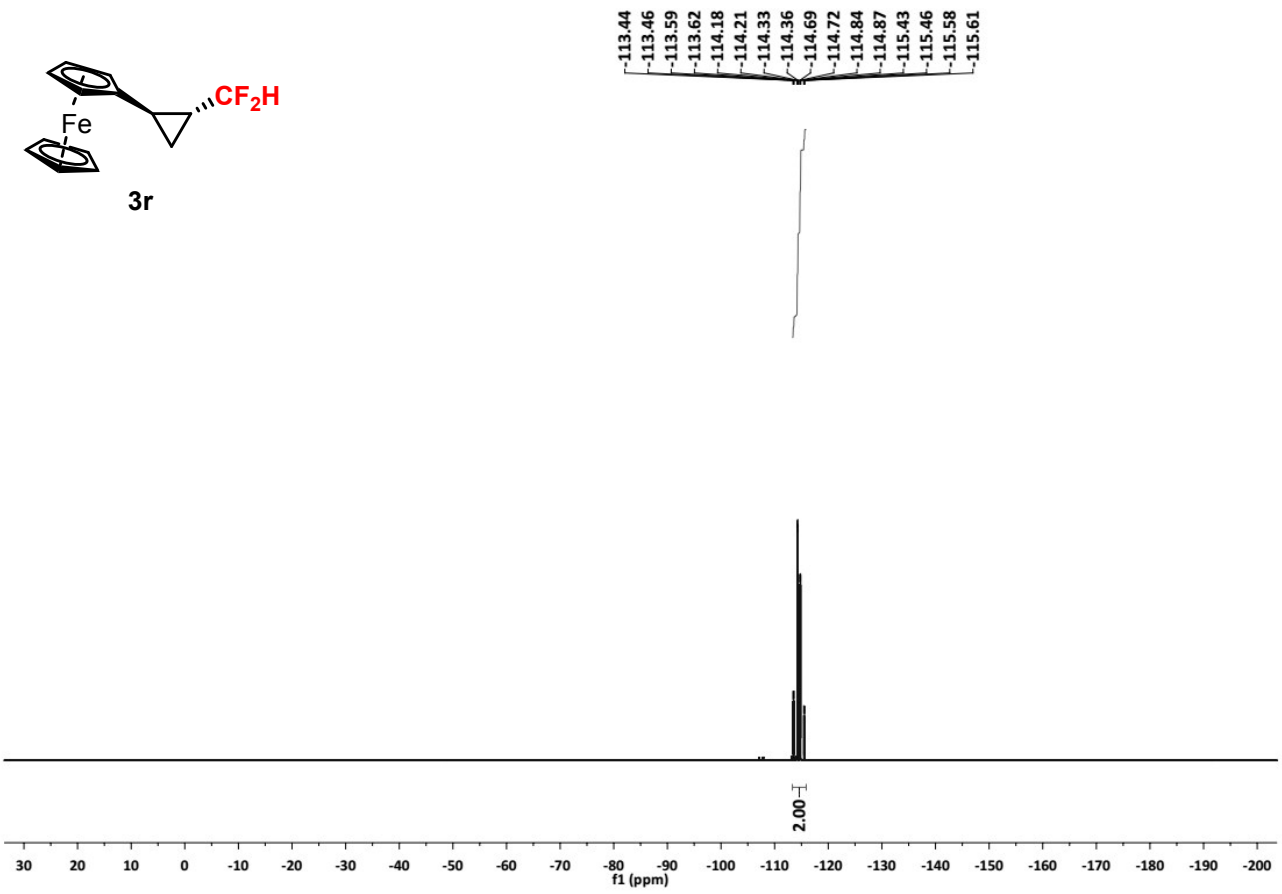

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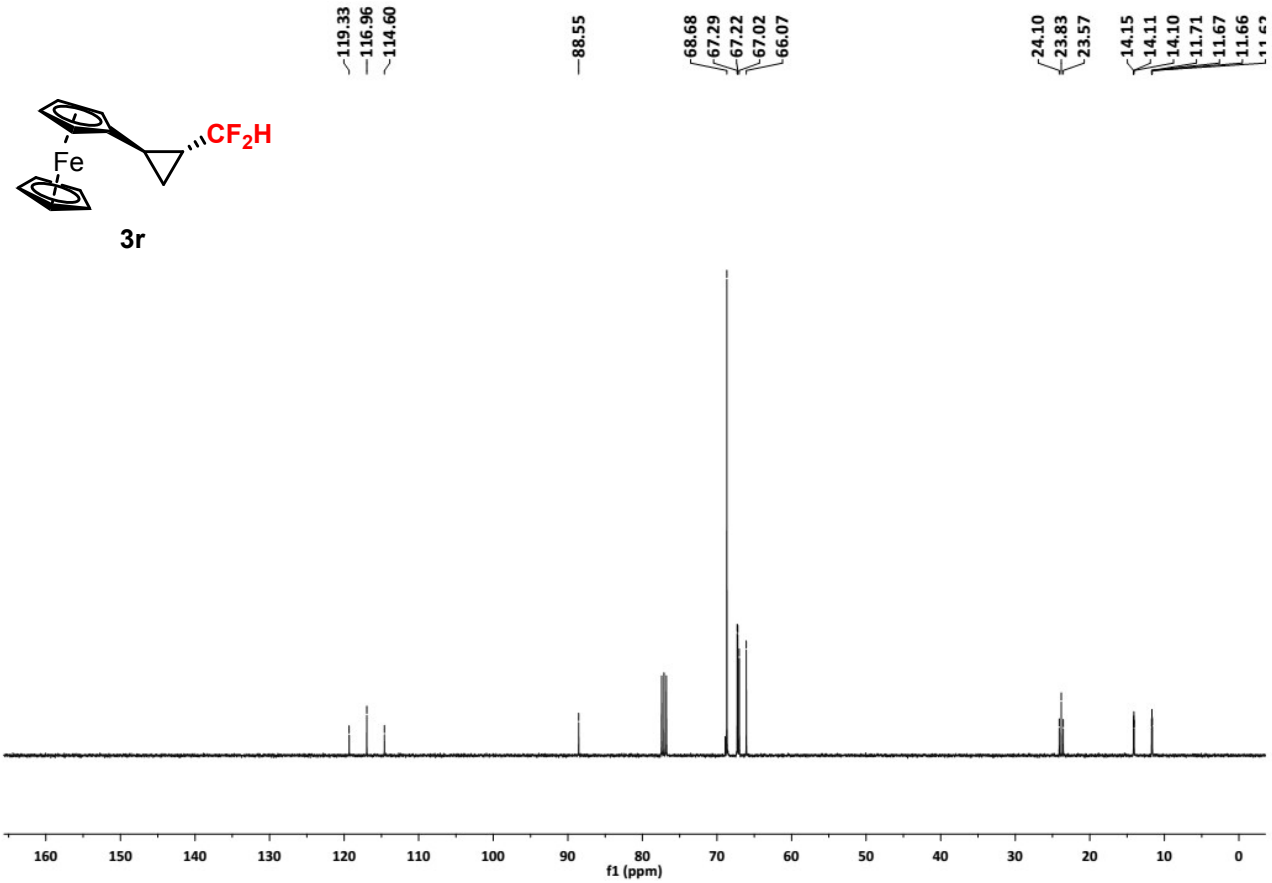

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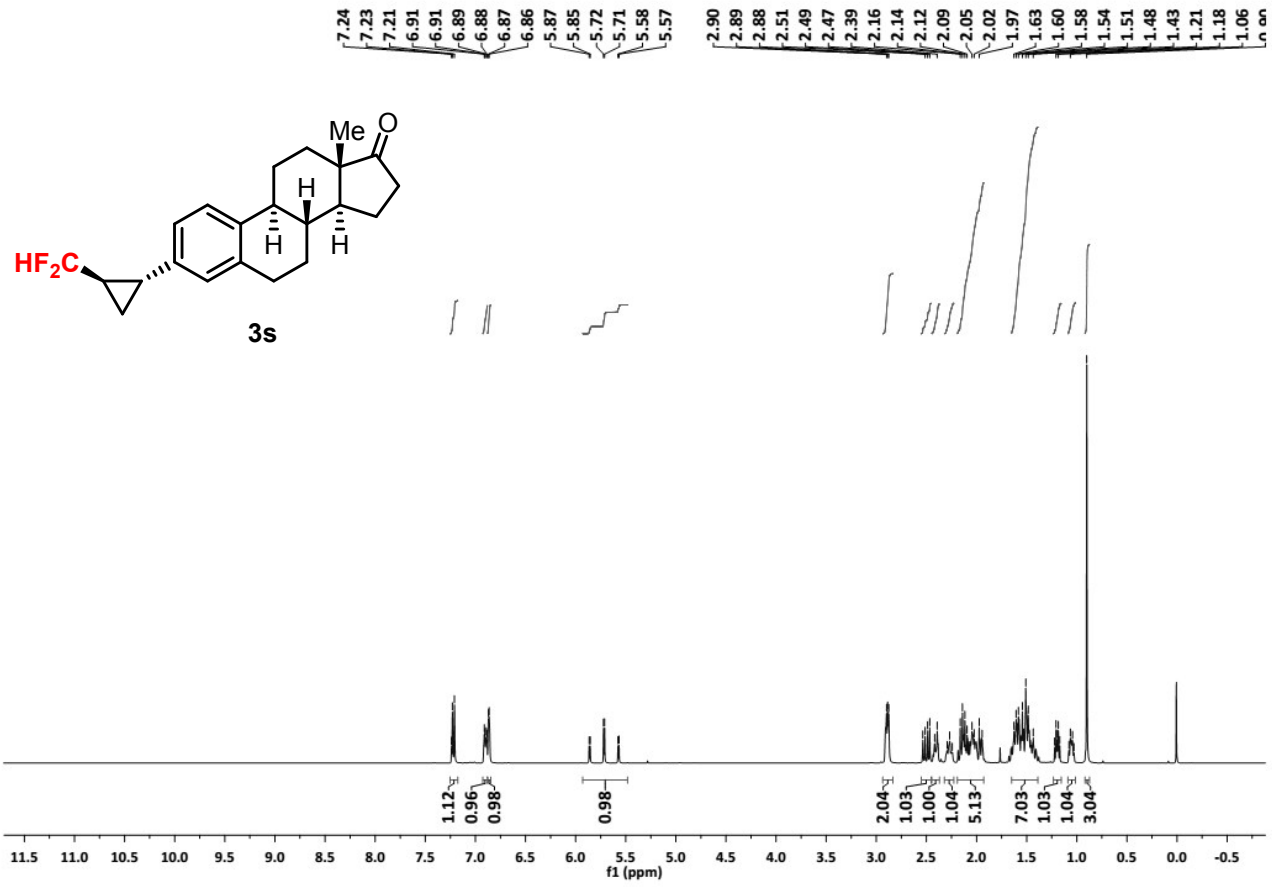

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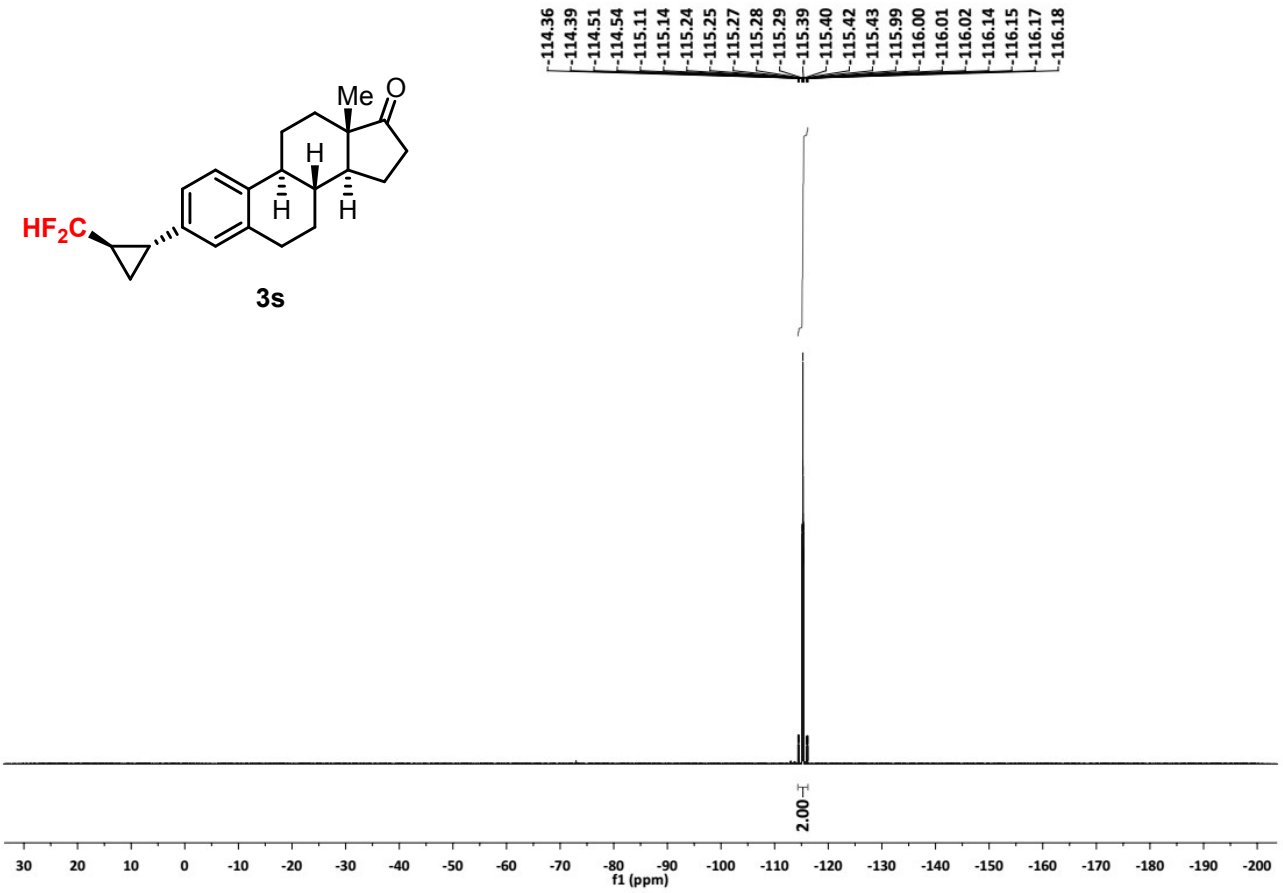

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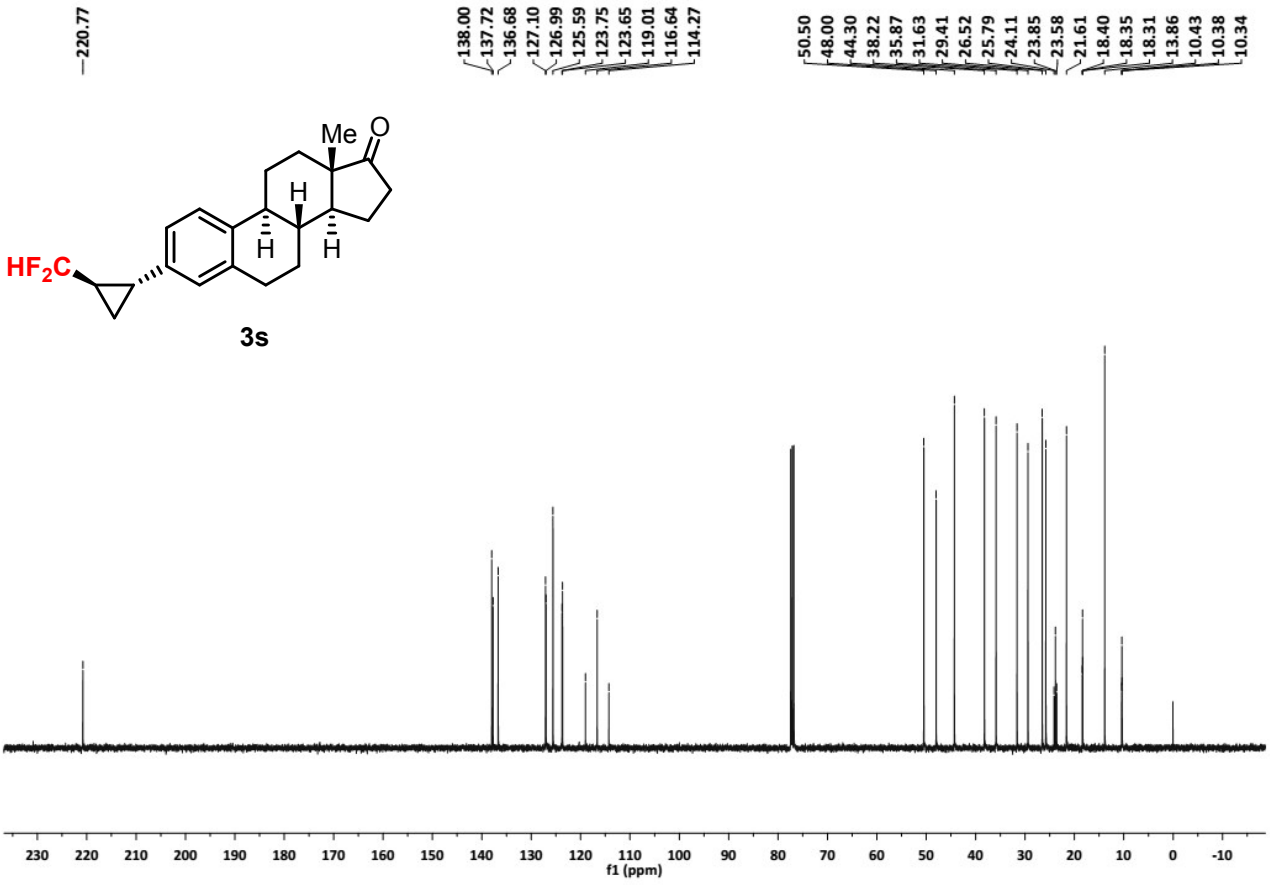

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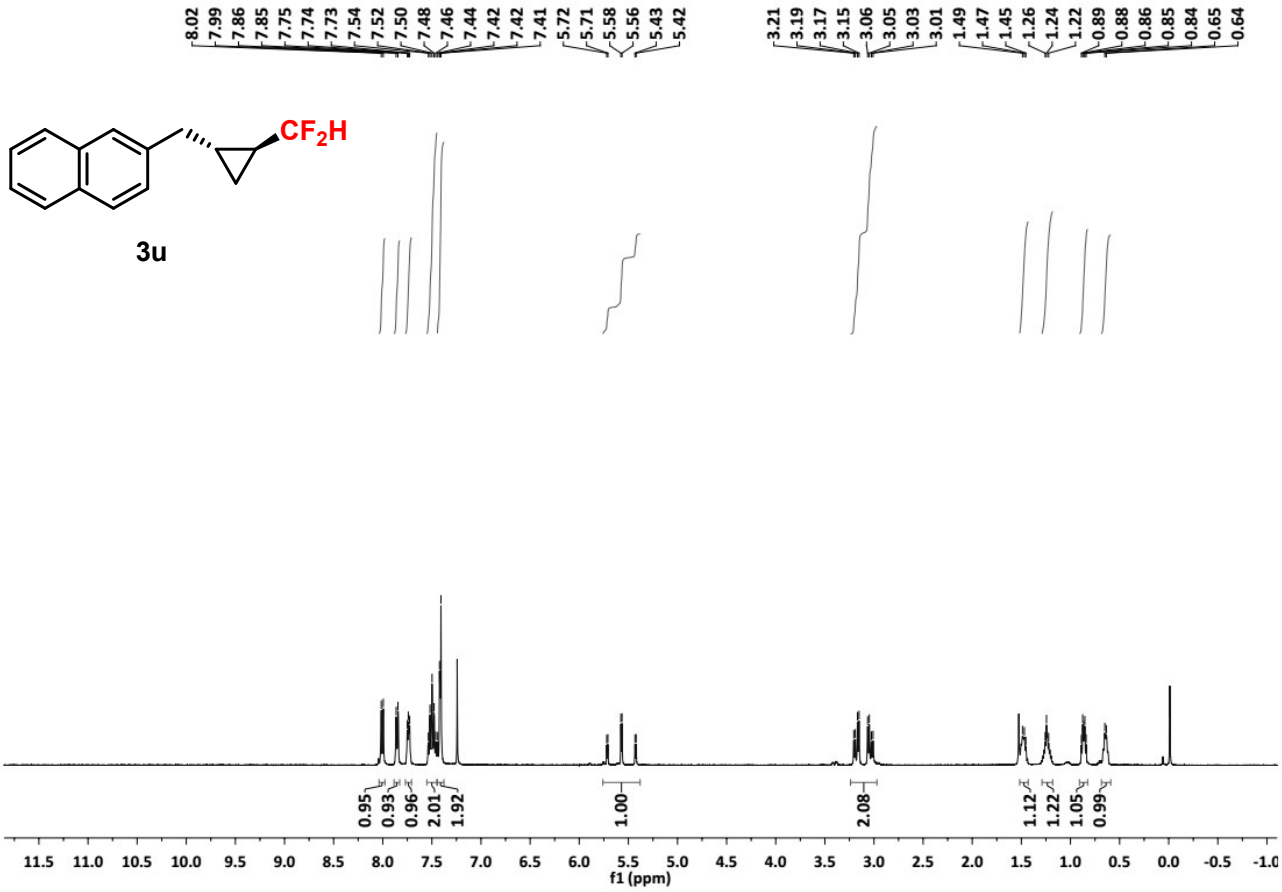

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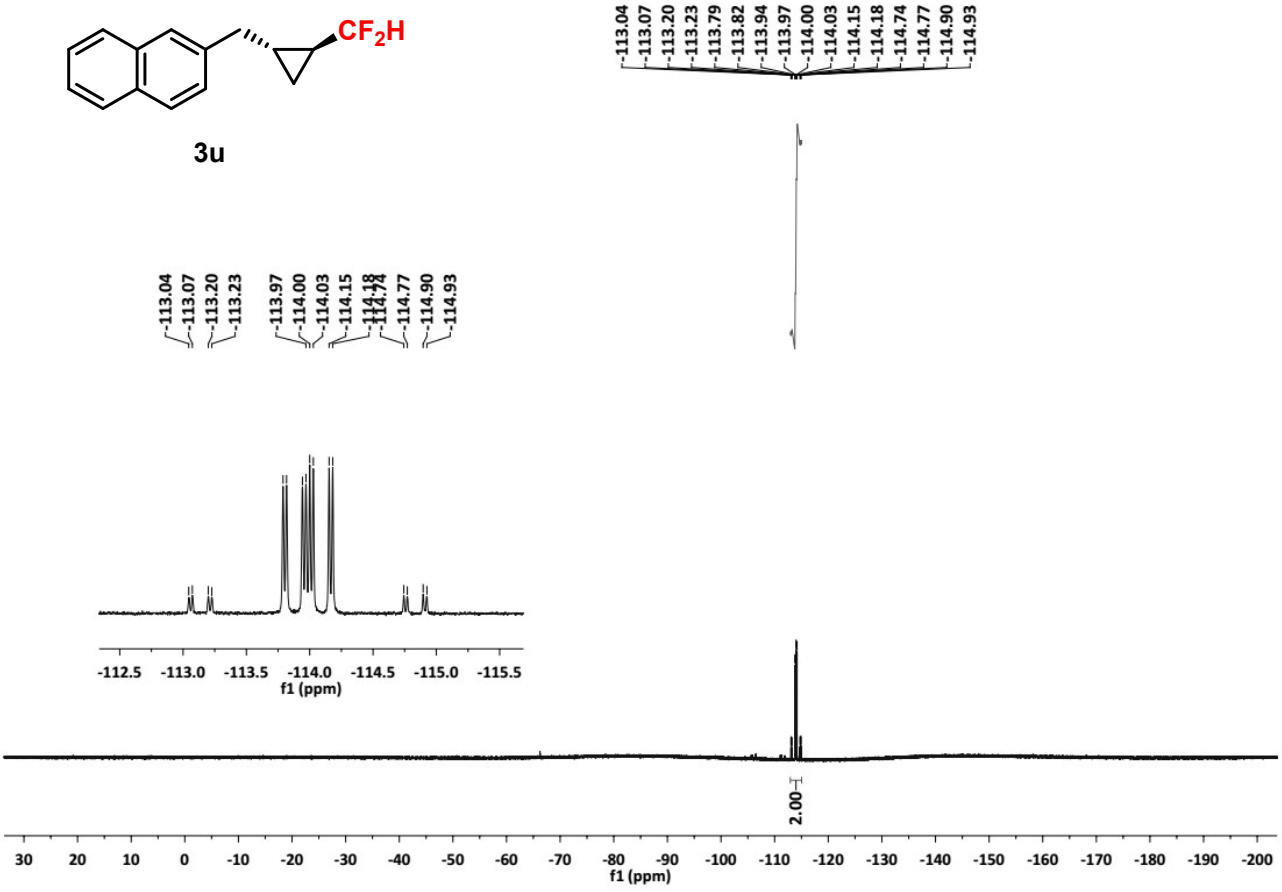

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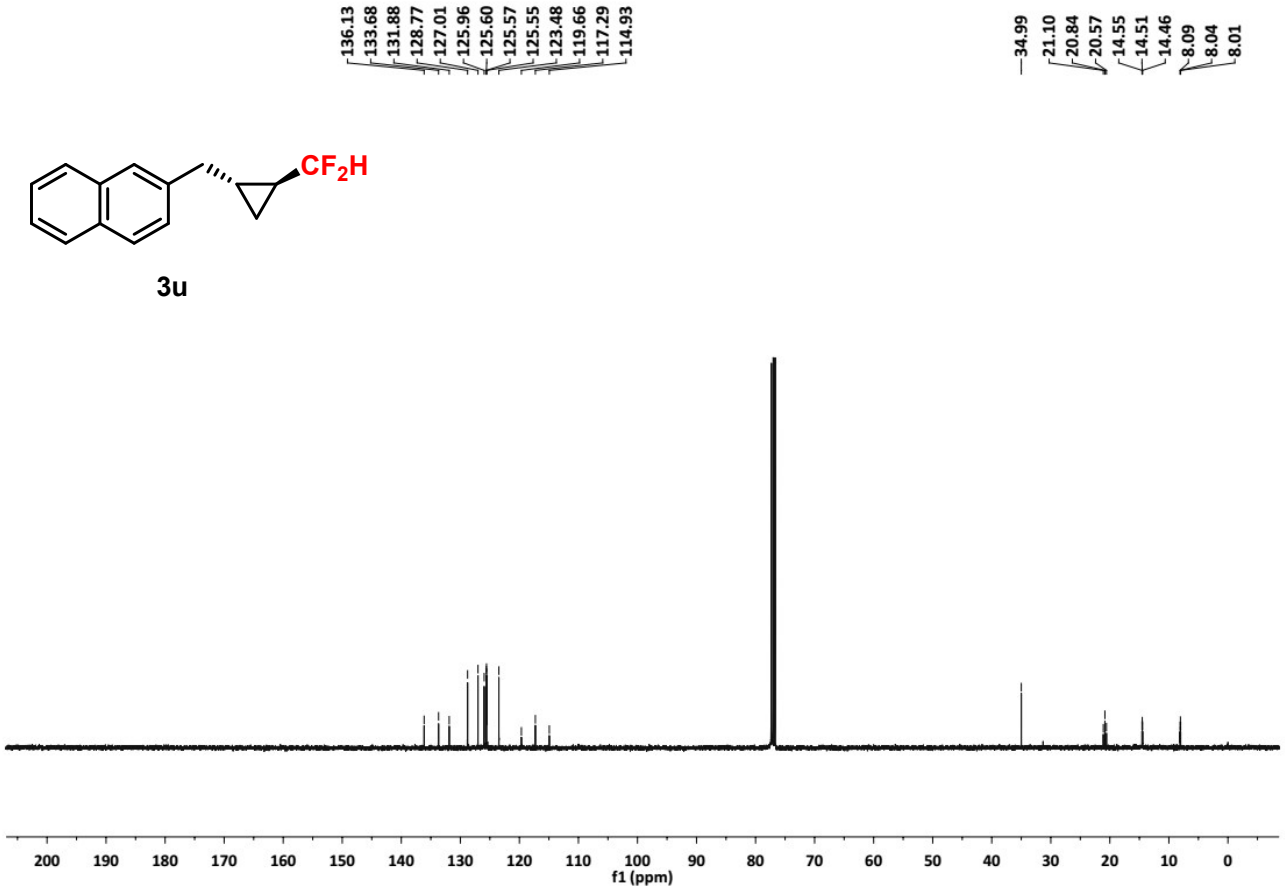

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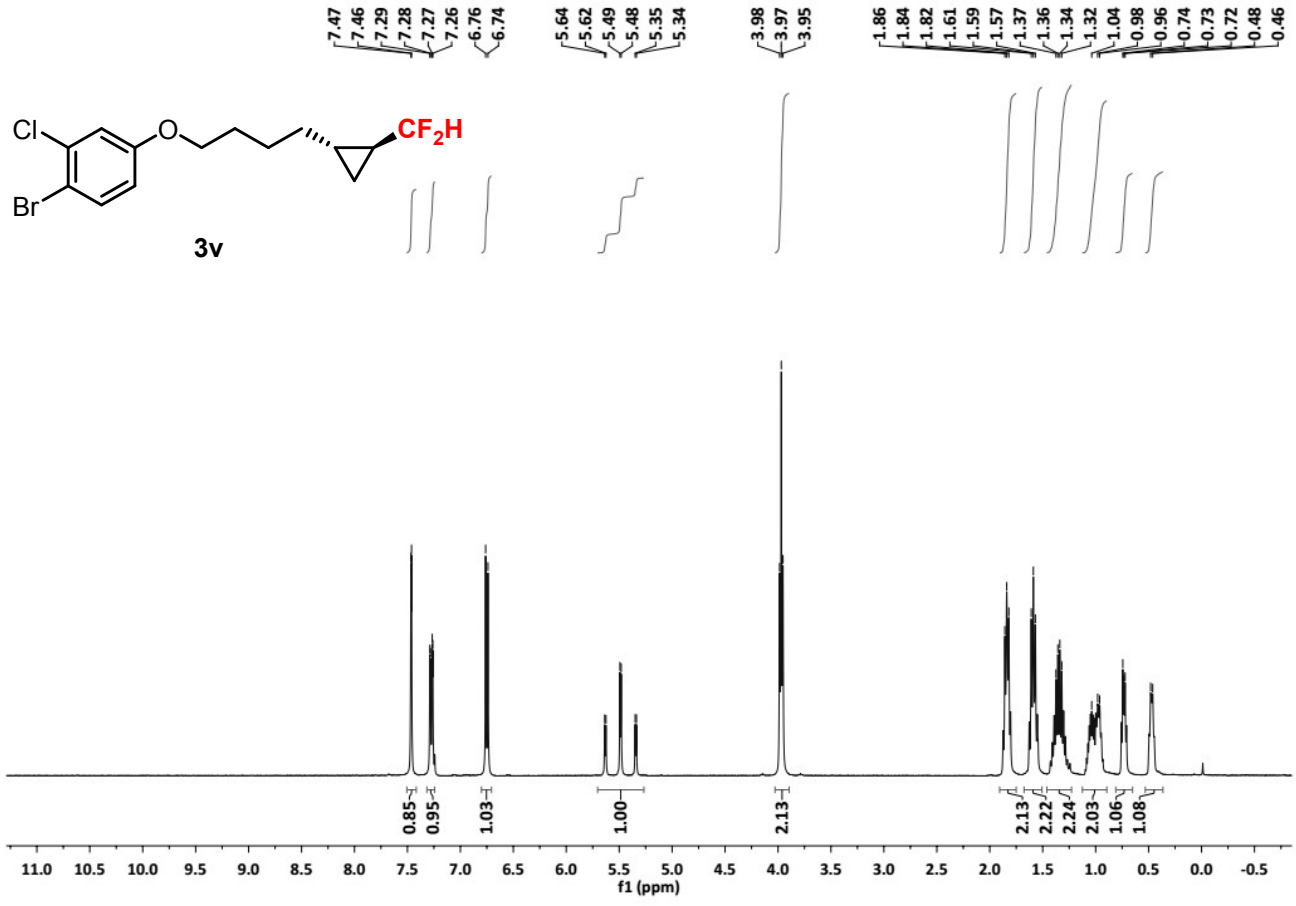

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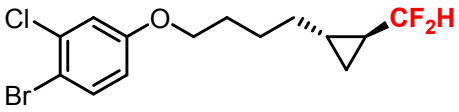

3v

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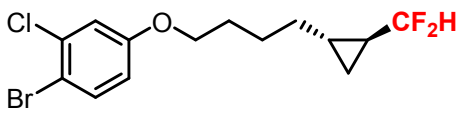

3v

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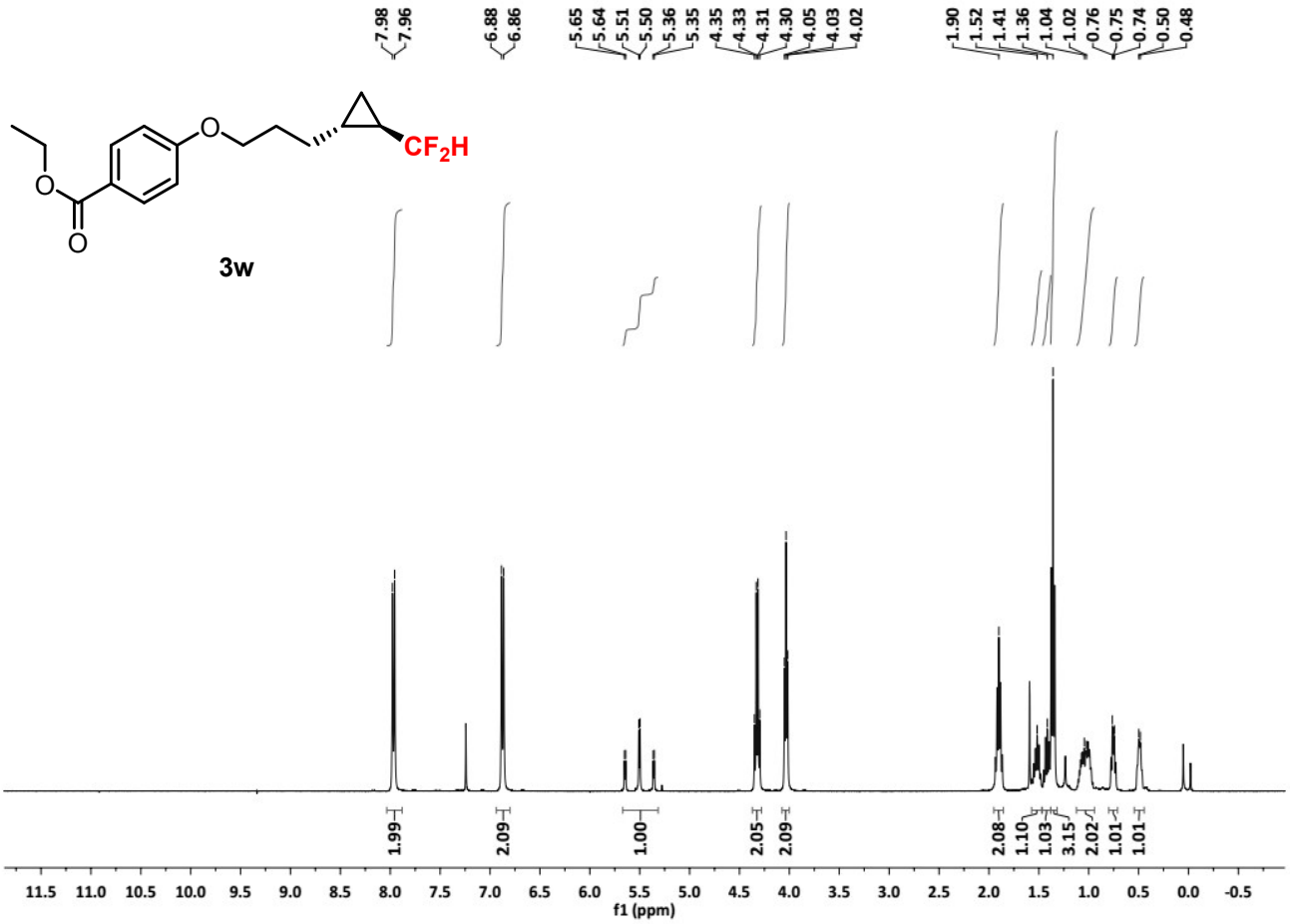

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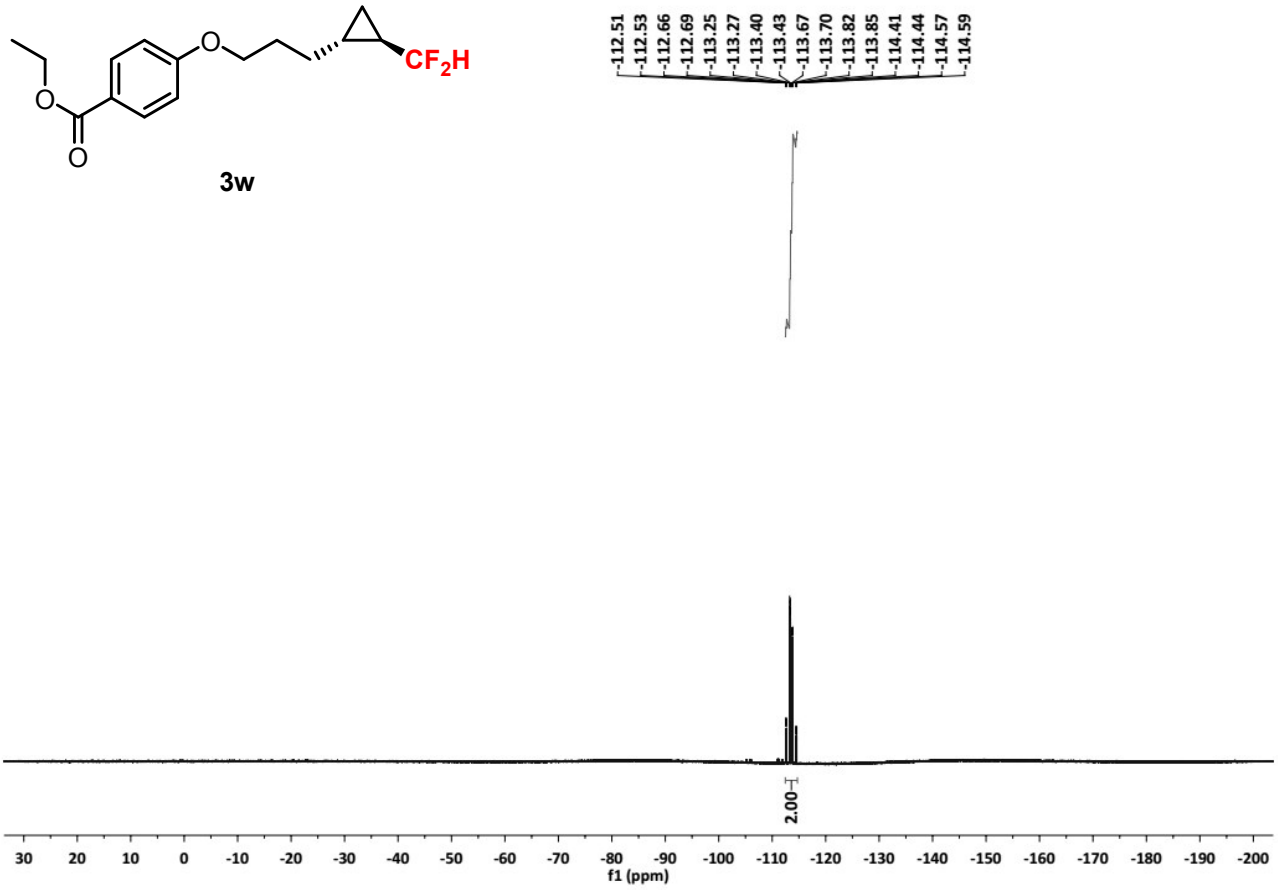

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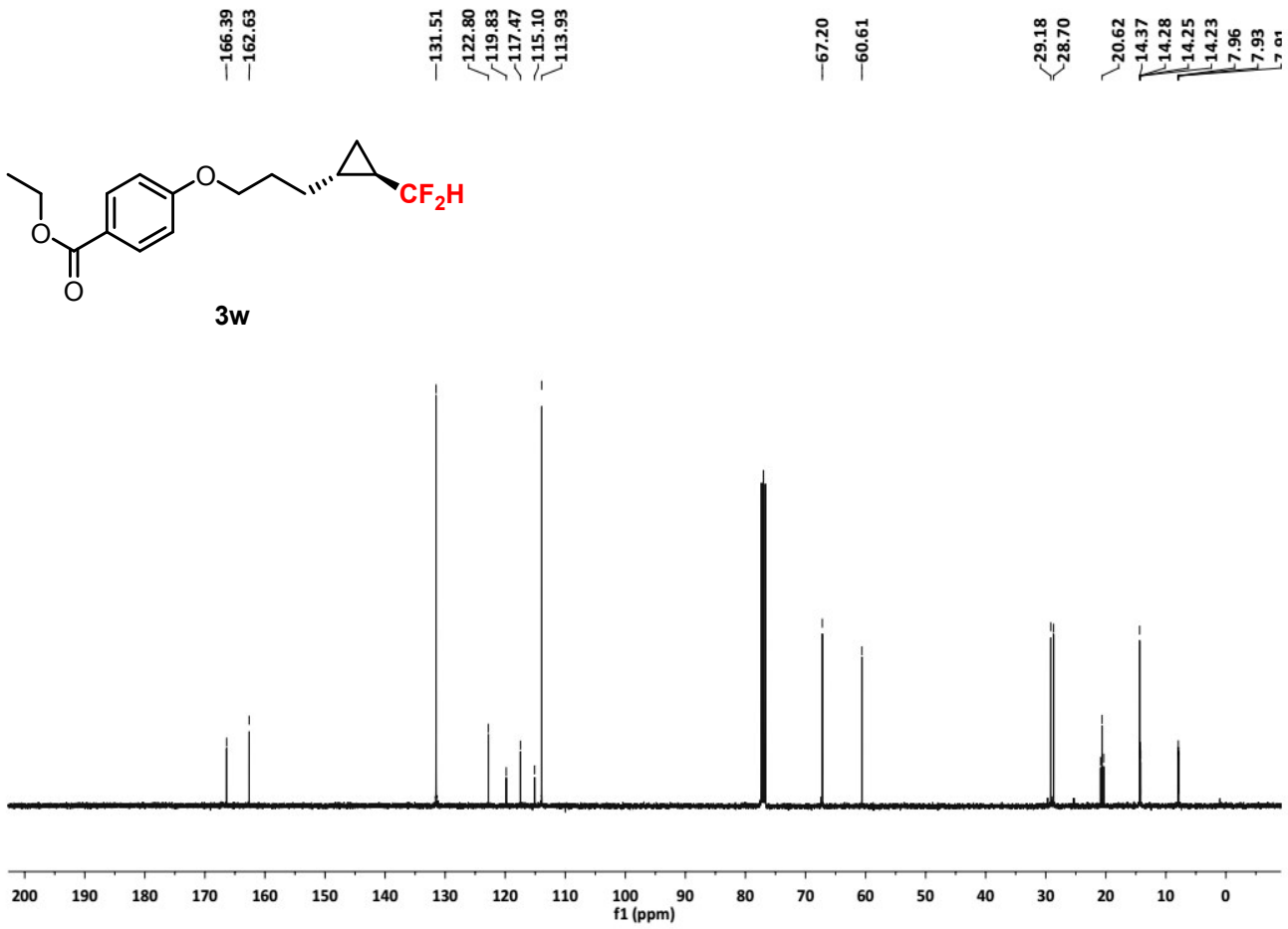
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f1 (ppm)