Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Tri- and difluoroethylation of alkenes by visible light photoredox catalysis

Xiao-Yang Pan,[ab] Yue Zhao,[ab] Hong-An Qu,[c] Jin-Hong Lin,[b]* Xiao-Chun Hang[a]* and Ji-Chang Xiao[b]*

[a]*Key Laboratory of Flexible Electronics (KLOFE) and Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211800, China*

[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chmistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*

[c]*Shandong NHU Amino Acid Co., LTD*.

Dr. Jin-Hong Lin, Tel: (+86)21-5492-5541; E-mail: jlin@sioc.ac.cn.

Prof. Xiao-Chun Hang, Tel: (+86)25-8358-7982; E-mail: iamxchhang@njtech.edu.cn.

Prof. Ji-Chang Xiao, Tel: (+86)21-5492-5340; E-mail: jchxiao@sioc.ac.cn.

Table of Contents

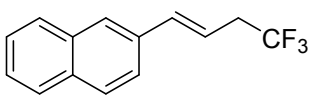
1. General information

^{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 or ESI mode. The mass analyzer types for HRMS-EI, HRMS-ESI, and HRMSMALDI are time-of-flight, Fourier transform mass spectrometer, and Fourier transform mass spectrometer, respectively. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

2. General procedure for trifluoroethylation of alkenes

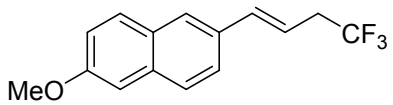
Into a 5 mL sealed tube were added alkene **1** (0.5 mmol, 1.0 equiv.), reagent **I** (1.5 mmol, 3 equiv.), CuO (1.0 mmol, 2 equiv.), $Ir(ppy)_3$ (0.015 mmol, 3 mol%) and DMAc (3 mL) under a N_2 atmosphere. The tube was sealed and the reaction mixture was exposed to blue light and stirred at room temperature for 24 h. The solid was removed by filtration and washed with ethyl acetate (20 mL). The combined organic phase was washed with water (10 mL × 3), dried over Na_2SO_4, and the solvent was removed by concentration.

As the desired product and the byproduct Ph_2S have similar polarity, it was hard to isolate the desired product by direct flash column chromatography. Ph_2S was oxidized first by Me_3O^+ BF_4^-. The procedure is shown as follows. The mixture obtained above was dissolved in dichloromethane (3 mL), and Me_3O^+ BF_4^- (400 mg, 2.7 mmol) was added into the solution. After the mixture was stirred at room temperature overnight, ethyl acetate (20 mL) was added. The mixture was washed with water (10 mL × 3), dried over Na_2SO_4. The solvent was removed by concentration, and the residue was subjected to flash column chromatography to afford the final product.



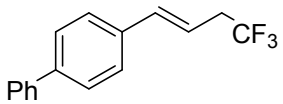
2a

(*E*)-2-(4,4,4-trifluorobut-1-en-1-yl)naphthalene **(2a)**[1]: White solid, 70.9 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.79 (m, 3H), 7.74 (s, 1H), 7.59 (dd, J = 8.7, 1.8 Hz, 1H), 7.50 - 7.44. (m, 2H), 6.77 (d, J = 15.8 Hz, 1H), 6.24 (dt, J = 16.0, 7.2 Hz, 1H), 3.11 – 3.01 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J = 10.6 Hz, 3F).



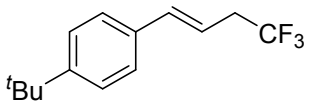
2b

(*E*)-2-methoxy-6-(4,4,4-trifluorobut-1-en-1-yl)naphthalene **(2b)**: White solid. M.p. 102 °C. 73.2 mg, 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 3H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.16 – 7.11 (m, 2H), 6.72 (d, *J* = 15.8 Hz, 1H), 6.18 (dt, *J* = 15.7, 7.3 Hz, 1H), 3.92 (s, 3H), 3.09 – 2.99 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (s), 136.8 (s), 134.4 (s), 131.6 (s), 129.6 (s), 128.9 (s), 127.2 (s), 126.4 (s), 126.0 (q, *J* = 277.8 Hz) 123.9 (s), 119.1 (s), 116.4 (q, *J* = 3.7 Hz), 105.9 (s), 55.3 (s), 37.8 (q, *J* = 29.8 Hz). IR (neat) ν = 3058, 2969, 2849, 1628, 1601, 1260, 1245, 1109, 1031, 970, 857, 818, 770 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{13}F_3O$ [M]$^{+}$: 266.0918, Found: 266.0920.



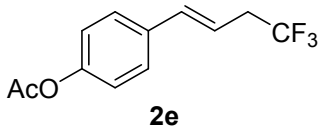
2c

(*E*)-4-(4,4,4-trifluorobut-1-en-1-yl)-1,1'-biphenyl **(2c)**[2]: White solid, 91.8 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 4H), 7.49 – 7.46 (m, 4H), 7.38 (tt, *J* = 7.6, 1.6 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.9, 7.3 Hz, 1H), 3.09 – 2.99 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.7 Hz, 3F).



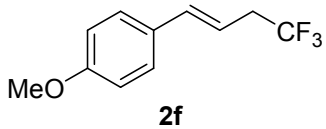
2d

(*E*)-1-(tert-butyl)-4-(4,4,4-trifluorobut-1-en-1-yl)benzene **(2d)**[1]: Colorless oil, 72.7 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.08 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.03 – 2.93 (m, 2H), 1.33 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.6 Hz, 3F).



2e

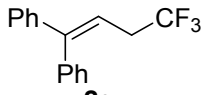
(*E*)-4-(4,4,4-trifluorobut-1-en-1-yl)phenyl acetate **(2e)**[1]: White solid, 86.7 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.06 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.29 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.3 (t, *J* = 10.6 Hz, 3F).



2f

(*E*)-1-methoxy-4-(4,4,4-trifluorobut-1-en-1-yl)benzene **(2f)**[1]: Light yellow oil, 49.7 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.54 (d, *J* = 15.8 Hz, 1H), 5.97 (dt, *J* = 16.0, 7.2 Hz, 1H), 3.81 (s, 3H), 3.01 –

2.92 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.4 (t, J = 10.6 Hz, 3F).

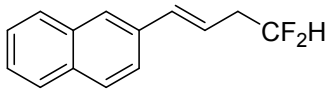


2g

(4,4,4-trifluorobut-1-ene-1,1-diyl)dibenzene **(2g)**[1]: Colorless oil, 102.3 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 3H), 7.30 – 7.22 (m, 5H), 7.18 – 7.16 (m, 2H), 6.06 (t, J = 7.4 Hz, 1H), 2.95 – 2,85 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.7 (t, J = 10.7 Hz, 3F).

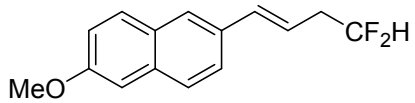
3. General procedure for difluoroethylation of alkenes

Into a 5 mL sealed tube were added alkene **1** (0.5 mmol, 1.0 equiv.), reagent **II** (1.5 mmol, 3 equiv.), CuO (1.0 mmol, 2 equiv.), $Ir(ppy)_3$ (0.015 mmol, 3 mol%) and DMAc (3 mL) under a N_2 atmosphere. The tube was sealed and the reaction mixture was exposed to blue light and stirred at room temperature for 48 h. The solid was removed by filtration and washed with ethyl acetate (20 mL). The combined organic phase was washed with water (10 mL × 3), dried over Na_2SO_4. After the solvent was removed by concentration, the residue was subjected to flash column chromatography to afford the final product.



3a

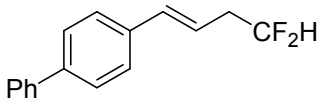
(*E*)-2-(4,4-difluorobut-1-en-1-yl)naphthalene **(3a)**: White solid. M.p. 70 °C. 56.7 mg, 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.80 (m, 3H), 7.74 (s, 1H), 7.61 (dd, J = 8.6, 1.7 Hz, 1H), 7.53 – 7.46 (m, 2H), 6.73 (d, J = 15.9 Hz, 1H), 6.28 (dt, J = 15.9, 7.2 Hz, 1H), 5.93 (tt, J = 56.7, 4.4 Hz, 1H), 2.89 – 2.77 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4 (dt, J = 56.6, 17.2 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4 (s), 134.1 (s), 133.6 (s), 133.1 (s), 128.3 (s), 128.0 (s), 127.7 (s), 126.37 (s), 126.33 (s), 126.0 (s), 123.4 (s), 119.9 (t, J = 6.8 Hz), 116.3 (t, J = 240.7 Hz), 38.2 (t, J = 22.0 Hz). IR (neat) ν = 3053, 2989, 2921, 1594, 1507, 1393, 1208, 1119, 1050, 816, 751, 479 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{12}F_2$ $[M]^+$: 218.0907, Found: 218.0903.



3b

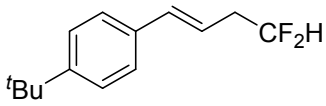
(*E*)-2-(4,4-difluorobut-1-en-1-yl)-6-methoxynaphthalene **(3b)**: White solid. M.p. 95 °C. 63.3 mg, 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 3H), 7.55 (dd, J = 8.6, 1.6 Hz, 1H), 7.15 – 7.11 (m, 2H), 6.68 (d, J = 15.9 Hz, 1H), 6.20 (dt, J = 15.8, 7.2 Hz, 1H), 5.90 (tt, J = 56.8, 4.5 Hz, 1H), 3.92 (s, 3H), 2.86 – 2.74 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.5 (dt, J = 56.7, 17.1 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (s), 135.4 (s), 134.2 (s), 132.0 (s), 129.5 (s), 128.9 (s), 127.1 (s), 126.1 (s),

124.0 (s), 119.1 (s), 118.8 (t, J = 7.0 Hz), 116.3 (t, J = 240.8 Hz), 105.9 (s), 55.3 (s), 38.2 (t, J = 22.0 Hz). IR (neat) ν = 2977, 2851, 1630, 1601, 1244, 1205, 1117, 1024, 858, 822, 772, 478 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{14}F_2O$ $[M]^+$: 248.1013, Found: 248.1020.



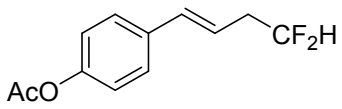
3c

(*E*)-4-(4,4-difluorobut-1-en-1-yl)-1,1'-biphenyl **(3c)**: White solid. M.p. 104 °C. 68.4 mg, 56%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.47 – 7.44 (m, 4H), 7.36 (tt, J = 7.2, 1.6 Hz, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.19 (dt, J = 15.7, 7.3 Hz, 1H), 5.90 (tt, J = 56.7, 4.4 Hz, 1H), 2.85 – 2.74 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6 (dt, J = 56.6, 17.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.63 (s), 140.57 (s), 135.7 (s), 134.9 (s), 128.8 (s), 127.4 (s), 127.3 (s), 127.0 (s), 126.7 (s), 119.7 (t, J = 6.7 Hz), 116.3 (t, J = 240.7 Hz), 38.1 (t, J = 22.0 Hz). IR (neat) ν = 3032, 2972, 1913, 1488, 1408, 1118, 1061, 970, 846, 758, 688, 468 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{14}F_2$ $[M]^+$: 244.1064, Found: 244.1073.



3d

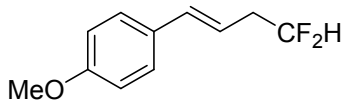
(*E*)-1-(tert-butyl)-4-(4,4-difluorobut-1-en-1-yl)benzene **(3d)**. This product also has similar polarity with that of byproduct Ph_2S. Therefore, the oxidization of Ph_2S was necessary. The oxidization process was shown in trifluoroethylation of alkenes except that the oxidization reaction should be quenched within a period of 3 h as the desired product is slightly sensitive to the oxidization reagent. Colorless oil, 59.4 mg, 53%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 4H), 6.54 (d, J = 15.9 Hz, 1H), 6.09 (dt, J = 15.8, 7.3 Hz, 1H), 5.85 (tt, J = 56.8, 4.5 Hz, 1H), 2.81 – 2.69 (m, 2H), 1.32 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6 (dt, J = 56.6, 17.2 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (s), 135.1 (s), 133.9 (s), 126.0 (s), 125.5 (s), 118.7 (t, J = 6.8 Hz), 116.3 (t, J = 240.7 Hz), 38.1 (t, J = 21.9 Hz), 34.6 (s), 31.3 (s). IR (neat) ν = 2964, 2906, 1515, 1393, 1267, 1209, 1117, 1055, 968, 890, 806, 557 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{18}F_2$ $[M]^+$: 224.1377, Found: 224.1379.



3e

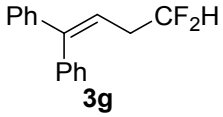
(*E*)-4-(4,4-difluorobut-1-en-1-yl)phenyl acetate **(3e)**: White solid. M.p. 49 °C. 73.5 mg, 65%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 6.08 (dt, J = 15.8, 7.3 Hz, 1H), 5.86 (tt, J = 56.6, 4.4 Hz, 1H), 2.81 – 2.69 (m, 2H), 2.30 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7 (dt, J = 56.6, 17.3 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4 (s), 150.2 (s), 134.5 (s), 134.3 (s), 127.3 (s), 121.7 (s), 119.8 (t, J = 6.8 Hz), 116.1 (t, J = 240.7 Hz), 38.0 (t, J = 22.0 Hz), 21.1 (s). IR (neat) ν = 2986, 1755, 1600, 1508, 1374, 1221, 1116, 1052,

1016, 912, 854, 594, 505 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{12}F_2O_2$ $[M]^+$: 226.0805, Found: 226.0797.



3f

(*E*)-1-(4,4-difluorobut-1-en-1-yl)-4-methoxybenzene **(3f)**[2]: Light yellow oil, 46.6 mg, 47%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 15.9 Hz, 1H), 5.99 (dt, *J* = 15.8, 7.3 Hz, 1H), 5.85 (tt, *J* = 56.8, 4.4 Hz, 1H), 3.81 (s, 3H), 2.79 – 2.67 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6 (dt, *J* = 56.6, 17.1 Hz, 2F).

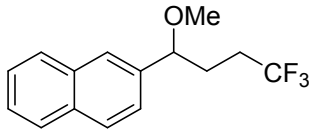


3g

(4,4-difluorobut-1-ene-1,1-diyl)dibenzene **(3g)**: Colorless oil, 86.7 mg, 71%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 3H), 7.30 – 7.23 (m, 5H), 7.18 – 7.16 (m, 2H), 6.07 (t, *J* = 7.5 Hz, 1H), 5.83 (tt, *J* = 56.8, 4.4 Hz, 1H), 2.73 – 2.61 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.5 (dt, *J* = 56.9, 17.6 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6 (s), 141.8 (s), 139.2 (s), 129.6 (s), 128.5 (s), 128.2 (s), 127.6 (s), 127.5 (s), 127.3 (s), 118.2 (t, *J* = 6.5 Hz), 116.3 (t, *J* = 240.8 Hz), 35.06 (t, *J* = 21.8 Hz). IR (neat) ν = 3057, 2977, 1599, 1494, 1445, 1393, 1121, 1052, 888, 762, 702, 592 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{14}F_2$ $[M]^+$: 244.1064, Found: 244.1060.

4. General procedure for methoxytrifluoroethylation of alkenes

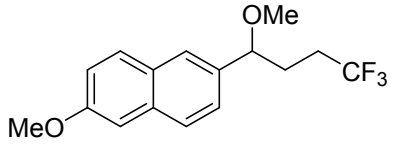
Into a 5 mL sealed tube were added alkenes **1** (0.5 mmol, 1.0 equiv.), reagent **I** (1.0 mmol, 2 equiv.), $Ir(ppy)_3$ (0.01 mmol, 2 mol%) and MeOH (3 mL) under a N_2 atmosphere. The tube was sealed and the reaction mixture was exposed to blue light and stirred at room temperature for 12 h. Ethyl acetate (20 mL) was added, and the resulting organic phase was washed with water (10 mL × 3), dried over Na_2SO_4. After the solvent was removed by concentration, the residue was subjected to flash column chromatography to afford the final product.



4a

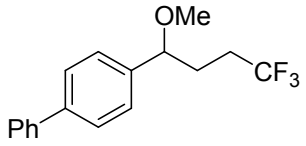
2-(4,4,4-trifluoro-1-methoxybutyl)naphthalene **(4a)**: Colorless oil, 107.3 mg, 80%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90– 7.86 (m, 3H), 7.75 (s, 1H), 7.55 – 7.49 (m, 2H), 7.45 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.35 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.28 (s, 3H), 2.38 – 1.96 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, *J* = 10.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4 (s), 133.24 (s), 133.21 (s), 128.7 (s), 127.84 (s), 127.75 (s),

127.3 (q, J = 276.7 Hz), 126.3 (s), 126.0 (s), 125.8 (s), 124.0 (s), 82.2 (s), 56.8 (s), 30.33 (q, J = 3.0 Hz), 30.26 (q, J = 29.3 Hz). IR (neat) ν = 3057, 2936, 2825, 1508, 1451, 1253, 1195, 1010, 858, 821, 749, 479 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{15}OF_3$ $[M]^+$: 268.1075, Found: 268.1078.



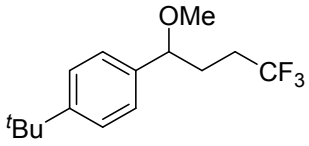
4b

2-methoxy-6-(4,4,4-trifluoro-1-methoxybutyl)naphthalene **(4b)**: White solid. M.p. 65 ^oC. 101.4 mg, 68%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.66 (s, 1H), 7.41 (dd, J = 8.4, 1.8 Hz, 1H), 7.21 – 7.16 (m, 2H), 4.32 – 4.28 (m, 1H), 3.94 (s, 3H), 3.26 (s, 3H), 2.34 – 1.94 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J = 10.8 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (s), 136.0 (s), 134.4 (s), 129.3 (s), 128.6 (s), 127.5 (s), 127.3 (q, J = 276.7 Hz), 125.7 (s), 124.5 (s), 119.1 (s), 105.7 (s), 82.2 (s), 56.6 (s), 55.3 (s), 30.31 (q, J = 3.0 Hz), 30.29 (q, J = 29.3 Hz). IR (neat) ν = 3059, 2939, 2825, 1608, 1508, 1418, 1267, 1172, 1033, 854, 655, 476 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{17}O_2F_3$ $[M]^+$: 298.1181, Found: 298.1185.



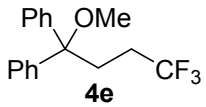
4c

4-(4,4,4-trifluoro-1-methoxybutyl)-1,1'-biphenyl **(4c)**: White solid. M.p. 60 ^oC. 125.1 mg, 85%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 – 7.36 (m, 3H), 4.23 (dd, J = 8.1, 5.0 Hz, 1H), 3.29 (s, 3H), 2.39 – 1.92 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J = 10.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9 (s), 140.7 (s), 140.0 (s), 128.8 (s), 127.4 (s), 127.3 (q, J = 276.7 Hz), 127.1 (s), 126.9 (s), 81.8 (s), 56.8 (s), 30.5 (q, J = 3.0 Hz), 30.3 (q, J = 28.3 Hz). IR (neat) ν = 3000, 2935, 2827, 1567, 1451, 1348, 1249, 1128, 836, 762, 691, 581 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{17}OF_3$ $[M]^+$: 294.1231, Found: 294.1240.



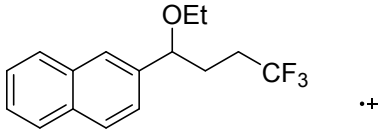
4d

1-(tert-butyl)-4-(4,4,4-trifluoro-1-methoxybutyl)benzene **(4d)**: Colorless oil, 90.5 mg, 66%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 4.15 (dd, J = 8.1, 5.0 Hz, 1H), 3.24 (s, 3H), 2.35 – 1.87 (m, 4H), 1.35 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.2 (t, J = 10.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (s), 137.9 (s), 127.3 (q, J = 277.8 Hz), 126.2 (s), 125.5 (s), 81.9 (s), 56.7 (s), 34.5 (s), 31.4 (s), 30.4 (q, J = 2.7 Hz), 30.3 (q, J = 29.3 Hz). IR (neat) ν = 2964, 2870, 2825, 1510, 1452, 1347, 1253, 1143, 1099, 1008, 834, 589 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{21}OF_3$ $[M]^+$: 274.1544, Found: 274.1544.



4e

(4,4,4-trifluoro-1-methoxybutane-1,1-diyl)dibenzene **(4e)**: White solid. M.p. 62 °C. 91.2 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 8H), 7.24 – 7.20 (m, 2H), 3.06 (s, 3H), 2.58 – 2.54 (m, 2H), 1.97 – 1.85 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 11.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2 (s), 128.2 (s), 127.7 (q, *J* = 276.7 Hz), 127.1 (s), 126.7 (s), 81.2 (s), 49.9 (s), 28.2 (q, *J* = 29.3 Hz), 27.4 (q, *J* = 3.0 Hz). IR (neat) ν = 3061, 2954, 2830, 1600, 1448, 1389, 1320, 1256, 1141, 1093, 1007, 699, 601 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{17}OF_3$ $[M]^+$: 294.1231, Found: 294.1227.

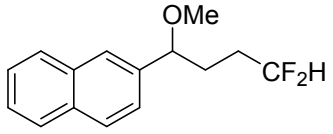


4f

2-(1-ethoxy-4,4,4-trifluorobutyl)naphthalene **(4f)**: EtOH/DMAc (v/v = 1 mL/2 mL) was used as the solvent instead of MeOH. Colorless oil, 80.5 mg, 57%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.83 (m, 3H), 7.74 (s, 1H), 7.54 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.45 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.48 – 3.33 (m, 2H), 2.39 – 1.94 (m, 4H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.1 (t, *J* = 10.7 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2 (s), 133.20 (s), 133.17 (s), 128.6 (s), 127.8 (s) , 127.7 (s), 127.33 (q, *J* = 277.1 Hz), 126.3 (s), 126.0 (s), 125.6 (s), 124.0 (s), 80.3 (s), 64.3 (s), 30.5 (q, *J* = 2.7 Hz), 30.3 (q, *J* = 29.0 Hz), 15.2 (s). IR (neat) ν = 3058, 2977, 2870, 1451, 1387, 1340, 1252, 1141, 1094, 1020, 820, 748, 479 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{17}OF_3$ $[M]^+$: 282.1231, Found: 282.1234.

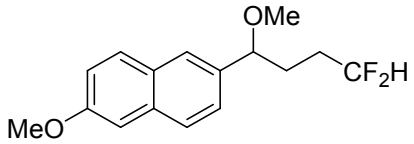
5. General procedure for methoxydifluoroethylation of alkenes

Into a 5 mL sealed tube were added alkenes **1** (0.5 mmol, 1.0 equiv.), reagent **II** (1.0 mmol, 2 equiv.), $Ir(ppy)_3$ (0.01 mmol, 2 mol%) and component solvent (MeOH 1mL and DMAc 2 mL) under a N_2 atmosphere. The tube was sealed and the reaction mixture was exposed to blue light and stirred at room temperature for 30 h. Ethyl acetate (20 mL) was added, and the resulting organic phase was washed with water (10 mL × 3), dried over Na_2SO_4. After the solvent was removed by concentration, the residue was subjected to flash column chromatography to afford the final product.



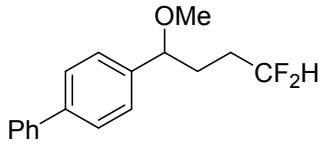
5a

2-(4,4-difluoro-1-methoxybutyl)naphthalene **(5a)**: Colorless oil, 83.8 mg, 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 3H), 7.73 (s, 1H), 7.53 – 7.47 (m, 2H), 7.43 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.85 (tt, *J* = 56.9, 4.1 Hz, 1H), 4.32 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.26 (s, 3H), 2.06 – 1.83 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.34 (ddt, *J* = 280.1, 57.2, 17.3 Hz, 1F), -116.38 (ddt, *J* = 280.1, 57.2, 17.3 Hz, 1F). ^{13}C NMR (101 MHz, CDCl3) δ 138.8 (s), 133.22 (s), 133.20 (s), 128.6 (s), 127.8 (s), 127.7 (s), 126.2 (s), 126.0 (s), 125.8 (s), 124.1 (s), 117.3 (t, *J* = 240.4 Hz), 83.1 (s), 56.8 (s), 30.6 (t, *J* = 22.2 Hz) , 30.4 (t, *J* = 5.1 Hz). IR (neat) ν = 3056, 2934, 2824, 1508, 1403, 1111, 1067, 1018, 859, 821, 749, 479 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{16}OF_2$ $[M]^+$: 250.1169, Found: 250.1176.



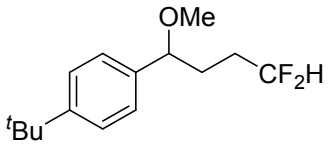
5b

2-(4,4-difluoro-1-methoxybutyl)-6-methoxynaphthalene **(5b)**: White solid. M.p. 42 °C. 99.5 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 9.2 Hz, 1H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.65 (s, 1H), 7.40 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.19 – 7.15 (m, 2H), 5.85 (tt, *J* = 57.3, 4.2 Hz, 1H), 4.28 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.93 (s, 3H), 3.25 (s, 3H), 2.08 – 1.80 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.29 (ddt, *J* = 278.2, 56.4, 15.0 Hz, 1F), -116.32 (ddt, *J* = 278.2, 56.4, 15.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (s), 136.5 (s), 134.4 (s), 129.3 (s), 128.7 (s), 127.4 (s), 125.7 (s), 124.7 (s), 119.1 (s), 117.3 (t, *J* = 240.4 Hz), 105.8 (s), 83.1 (s), 56.7 (s), 55.3 (s), 30.7 (t, *J* = 21.2 Hz) , 30.4 (t, *J* = 5.1 Hz). IR (neat) ν = 3058, 2937, 2824, 1608, 1484, 1390, 1267, 1230, 1111, 1068, 855, 477 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{18}O_2F_2$ $[M]^+$: 280.1275, Found: 280.1274.



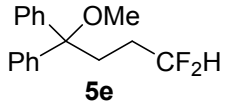
5c

4-(4,4-difluoro-1-methoxybutyl)-1,1'-biphenyl **(5c)**: White solid. M.p. 44 °C. 85.7 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 4H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.35 (m, 3H), 5.86 (tt, *J* = 56.9, 4.1 Hz, 1H), 4.21 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.27 (s, 3H), 2.08 – 1.82 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.30 (ddt, *J* = 279.7, 57.2, 16.9 Hz, 1F), -116.36 (ddt, *J* = 279.7, 57.2, 16.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.79 (s), 140.77 (s), 140.5 (s), 128.8 (s), 127.34 (s), 127.31 (s), 127.1 (s), 127.0 (s), 117.3 (t, *J* = 239.4 Hz), 82.7 (s), 56.8 (s), 30.6 (t, *J* = 22.2 Hz) , 30.5 (t, *J* = 5.1 Hz). IR (neat) ν = 3029, 2934, 2824, 1600, 1487, 1405, 1112, 1008, 979, 841, 765, 698 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{18}OF_2$ $[M]^+$: 276.1326, Found: 276.1330.



5d

1-(tert-butyl)-4-(4,4-difluoro-1-methoxybutyl)benzene **(5d)**: Colorless oil, 76.9 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.83 (tt, *J* = 57.0, 4.1 Hz, 1H), 4.13 (dd, J = 6.8, 4.8 Hz, 1H), 3.22 (s, 3H), 2.05 – 1.78 (m, 4H), 1.33 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.27 (ddt, *J* = 279.7, 57.2, 16.9 Hz, 1F), -116.32 (ddt, *J* = 279.7, 57.2, 16.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7 (s), 138.2 (s), 126.2(s) , 125.4 (s), 117.3 (t, *J* = 240.4 Hz) , 82.7 (s), 56.6 (s), 34.5 (s), 31.4 (s), 30.7 (t, *J* = 21.2 Hz) , 30.5 (t, *J* = 5.1 Hz). IR (neat) ν = 2965, 2870, 2824, 1510, 1449, 1405, 1305, 1112, 1070, 980, 835, 595 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{22}OF_2$ $[M]^+$: 256.1639, Found: 256.1647.



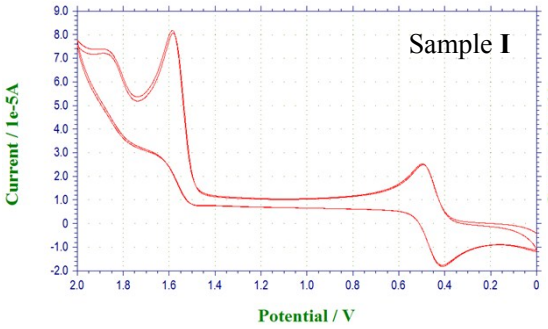
5e

(4,4-difluoro-1-methoxybutane-1,1-diyl)dibenzene **(5e)**: White solid. M.p. 63 °C. 98.1 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 8H), 7.24 – 7.20 (m, 2H), 5.78 (tt, *J* = 57.0, 4.2 Hz, 1H), 3.06 (s, 3H), 2.50 – 2.46 (m, 2H), 1.76 – 1.62 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.04 (dt, *J* = 56.8, 18.4 Hz, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6 (s), 128.1 (s), 126.9 (s), 126.8 (s), 117.3 (t, *J* = 240.4 Hz), 81.6 (s), 49.9 (s), 28.2 (t, *J* = 21.2 Hz) , 27.0 (t, *J* = 5.1 Hz). IR (neat) ν = 3059, 2944, 2828, 1598, 1447, 1404, 1199, 1129, 1065, 976, 753, 700 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{18}OF_2$ $[M]^+$: 276.1326, Found: 276.1335.

6. Cyclic Voltammetry studies

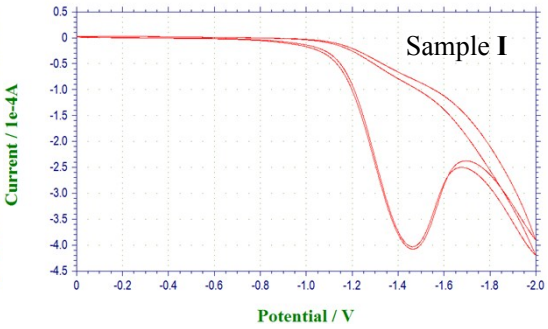
Electrochemical measurements were performed on a CHI660E electrochemical analyzer, using a standard three-electrode setup with a platinum working electrode (2 mm diameter), a platinum wire counter electrode, and a Ag/AgCl reference electrode. Sample **I** were prepared with reagent **I** (0.012 mmol) and Ferrocene (0.012 mmol) in the solution of $^{n}Bu_4NPF_6$ in dry and degassed acetonitrile (2.5 mL, 0.1 M). Sample **II** were prepared with reagent **II** (0.5 mmol) and Ferrocene (0.012 mmol) in the solution of $^{n}Bu_4NPF_6$ in dry and degassed acetonitrile (2.5 mL, 0.1 M). Solutions were kept under a N_2 atmosphere during the measurements. Cyclic voltammetry (CV) with the following settings: Scan Rates = 0.1 V/s, Sweep Segments = 4, Sample Interval = 0.001 V, Quiet Time = 2 sec. Data was analyzed using Origin 2016, and Epc was the peak potential at the maximum current. The obtained value was referenced to Ag/AgCl and converted to Saturated Calomel Electrode (SCE). Reagent **I** : E_{pc} = -1.517 V vs SCE; Reagent **II** : E_{pc} = -1.237 V vs SCE.

Reagent I: $Ph_2S^+CH_2CF_3$ TfO^-



$E_{1/2}(Fc/Fc^+)$ = 0.453 V vs Ag/AgCl

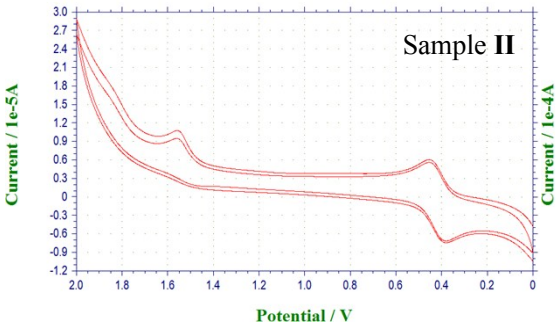
$E_{1/2}(Fc/Fc^+)$ = 0.400 V vs SCE[3]



E_{pc} = -1.464 V vs Ag/AgCl

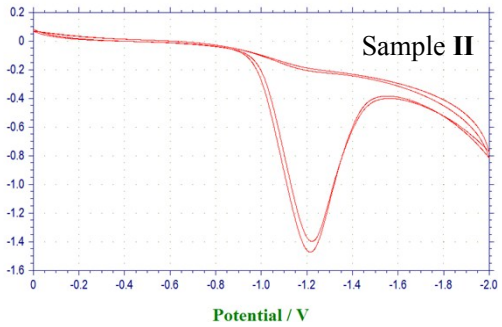
E_{pc} = -1.517 V vs SCE

Reagent II: $Ph_2S^+CH_2CF_2H$ TfO^-



$E_{1/2}(Fc/Fc^+)$ = 0.418 V vs Ag/AgCl

$E_{1/2}(Fc/Fc^+)$ = 0.400 V vs SCE[3]



E_{pc} = -1.219 V vs Ag/AgCl

E_{pc} = -1.237 V vs SCE

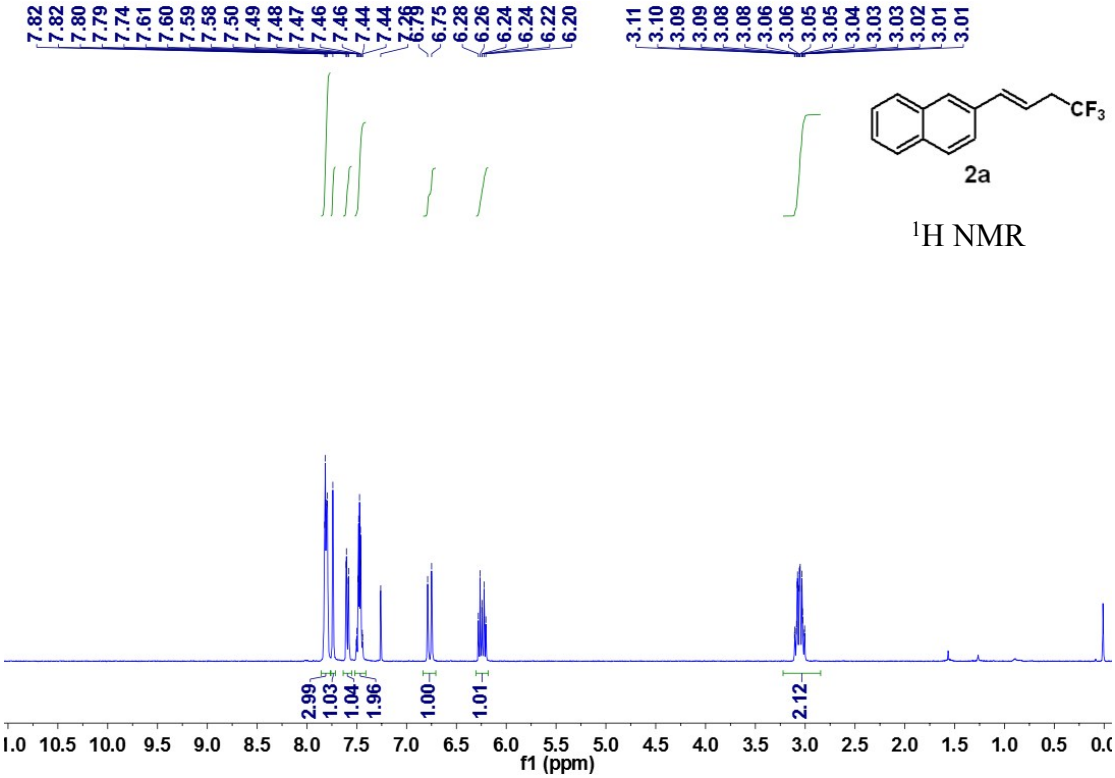
7. References

(1) L. M. Kreis, S. Krautwald, N. Pfeiffer, R. E. Martin, E. M. Carreira, *Org. Lett.* **2013**, 15, 1634–1637.

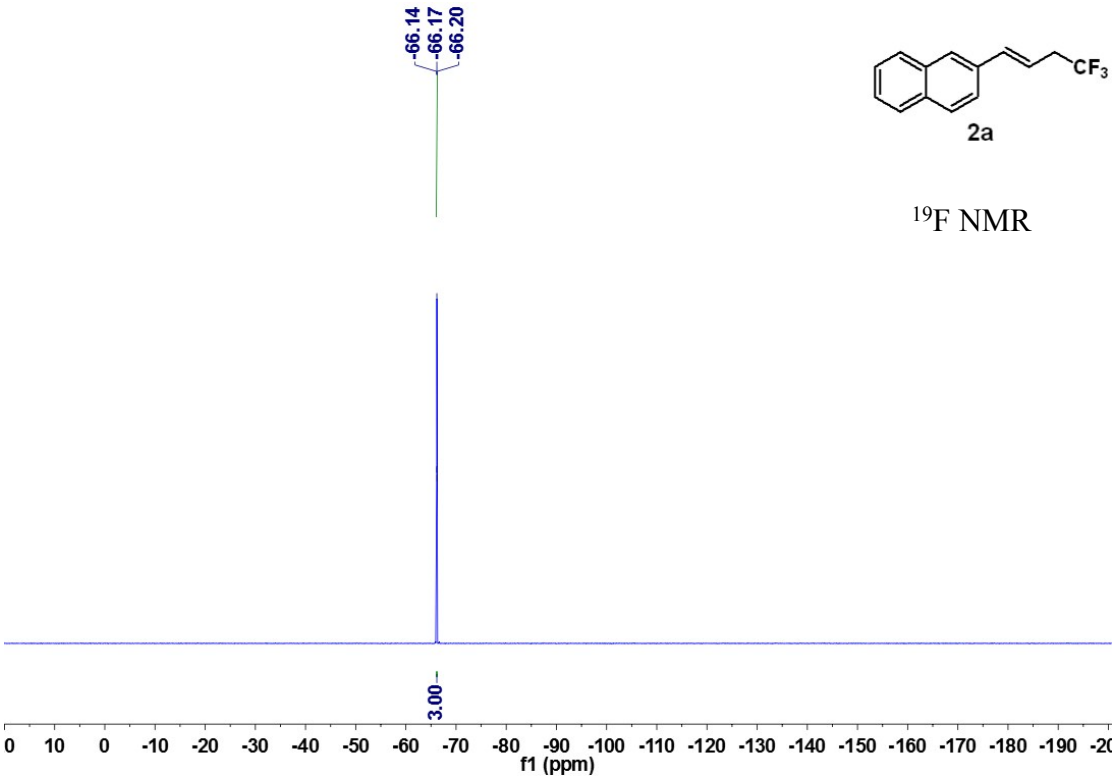
(2) Y. Zhu, J. Gong, Y. Wang, *J. Org. Chem.* **2017**, 82, 7428-7436.

(3) V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta.* **2000**, 298, 97-102.

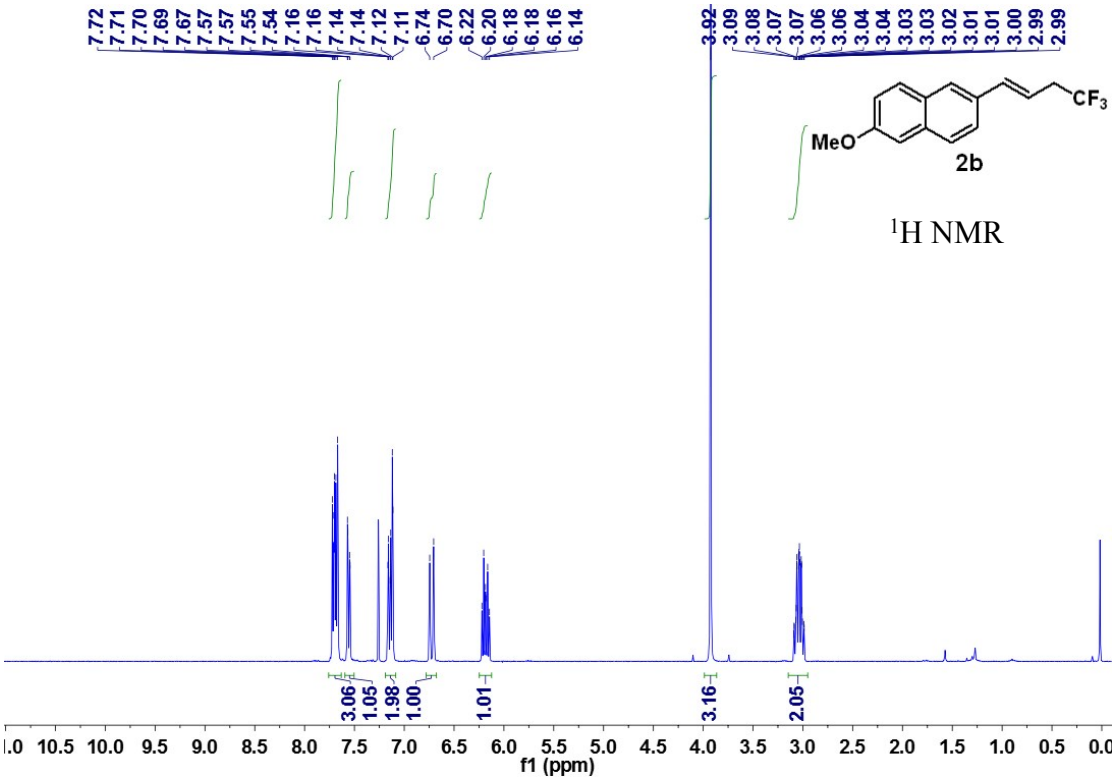
8. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra of products



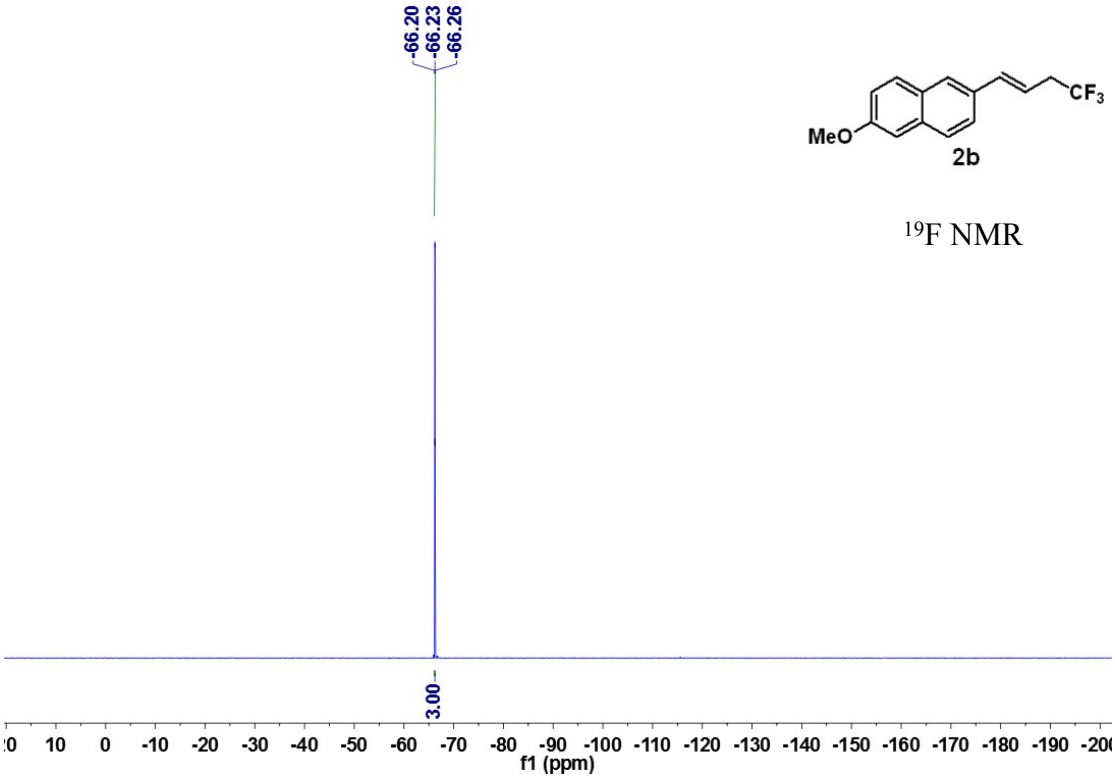
^{1}H NMR



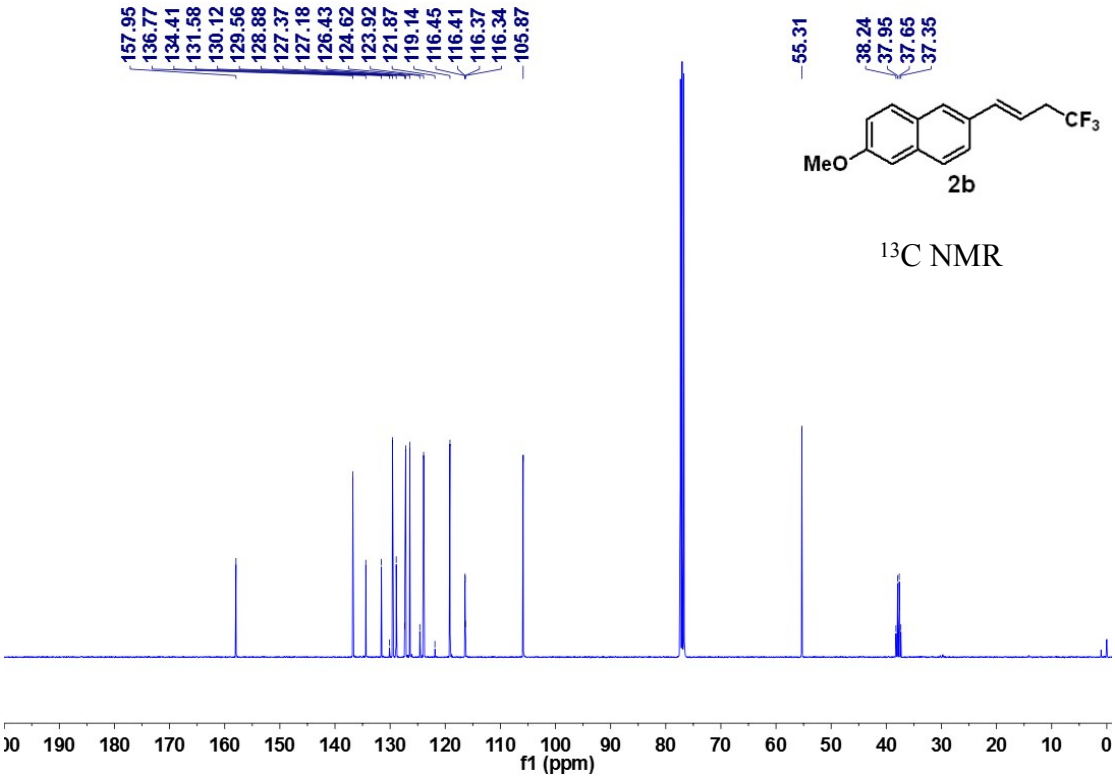
^{19}F NMR



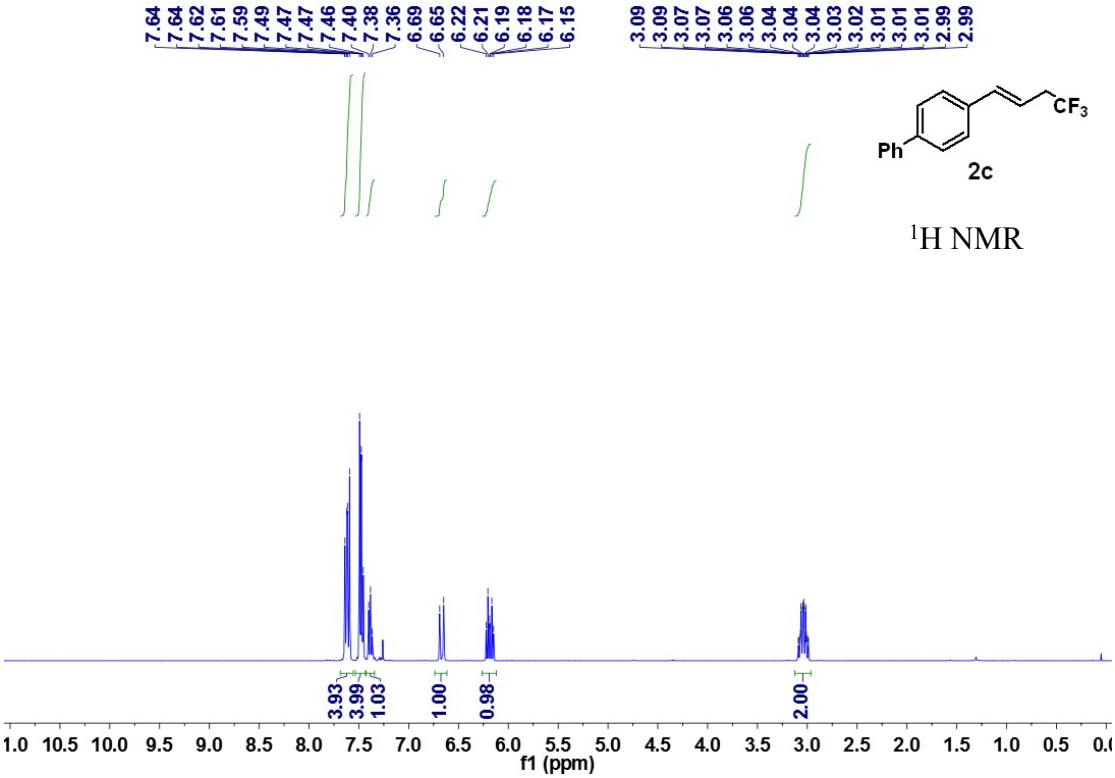
^{1}H NMR



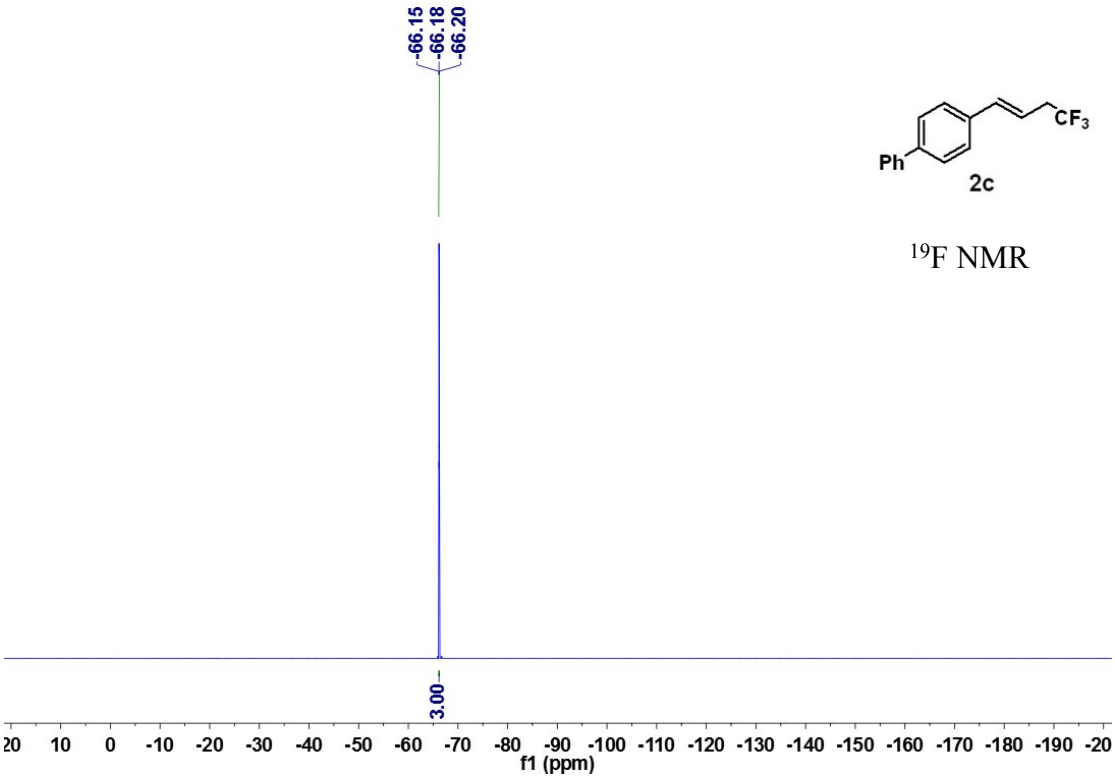
^{19}F NMR



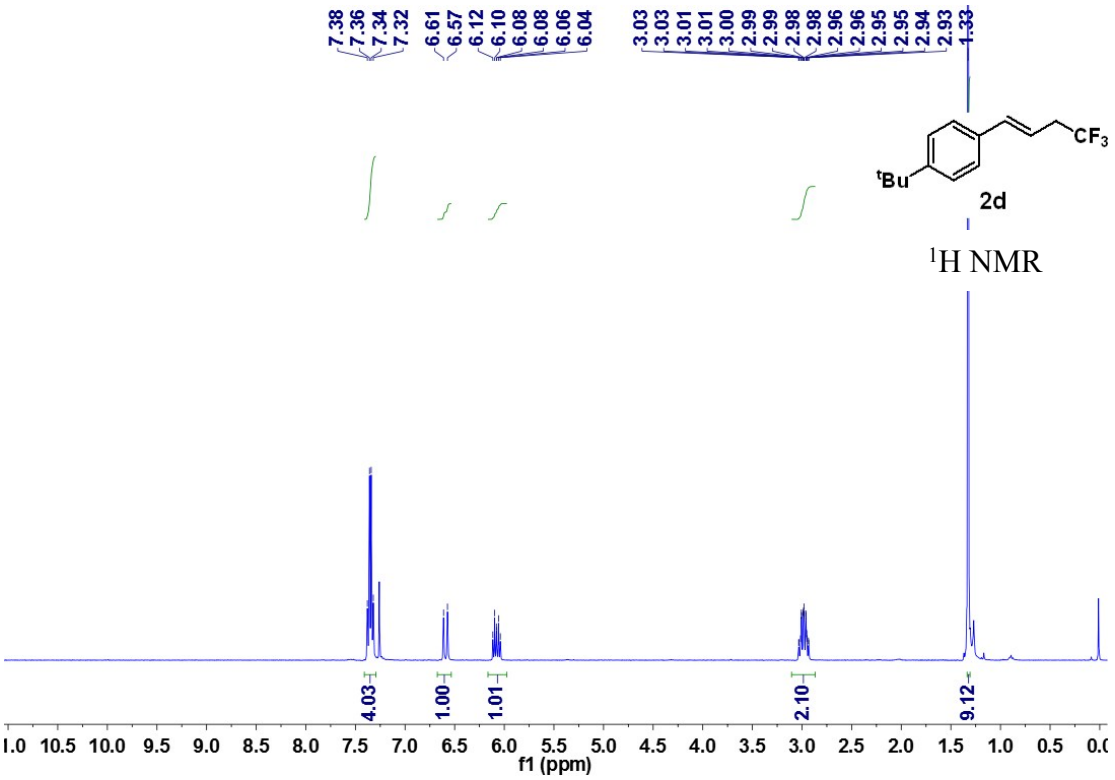
^{13}C NMR



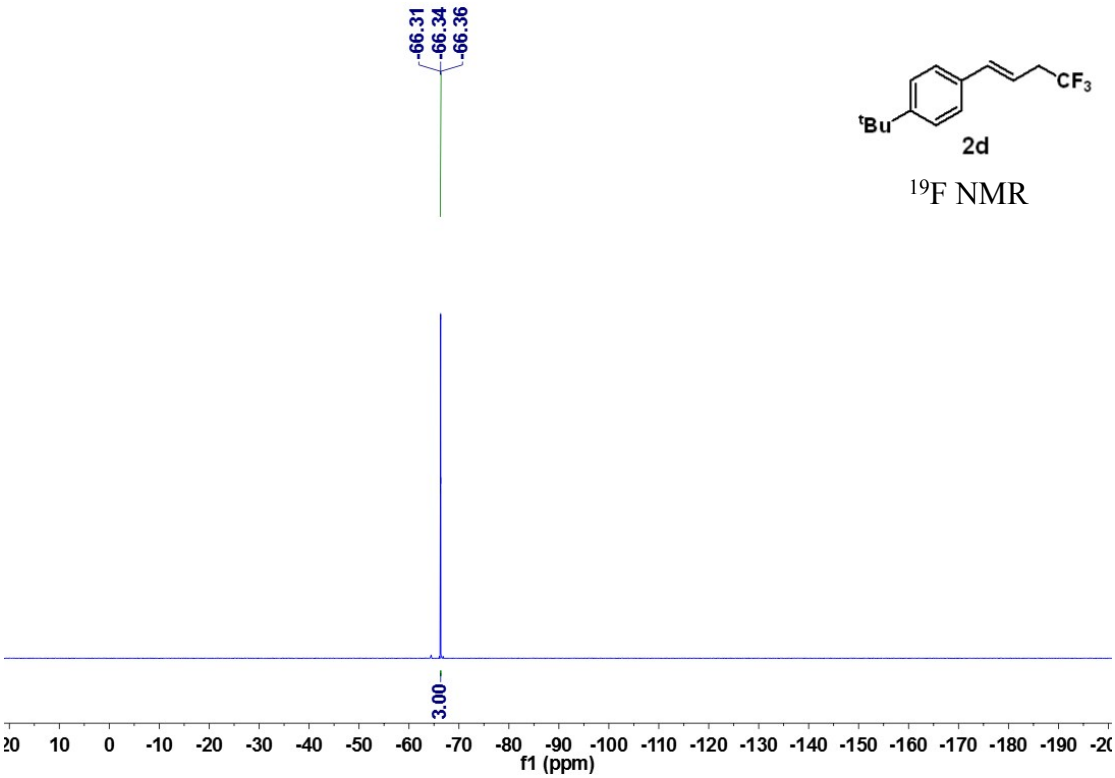
^{1}H NMR

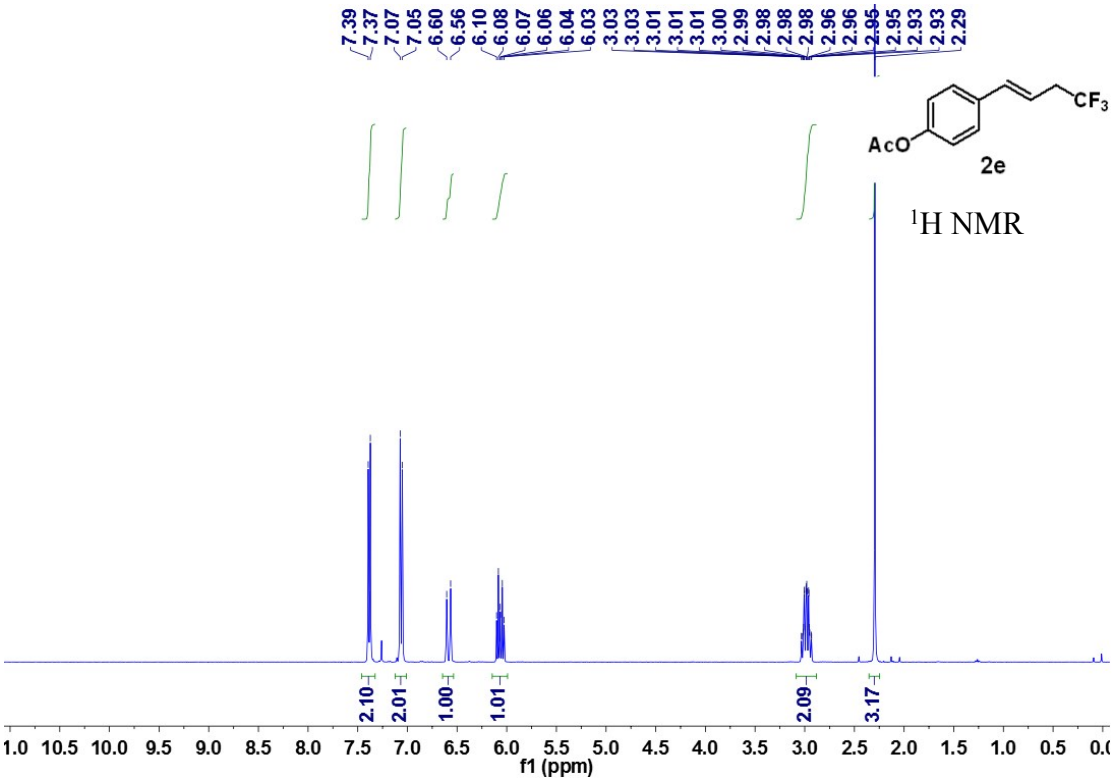


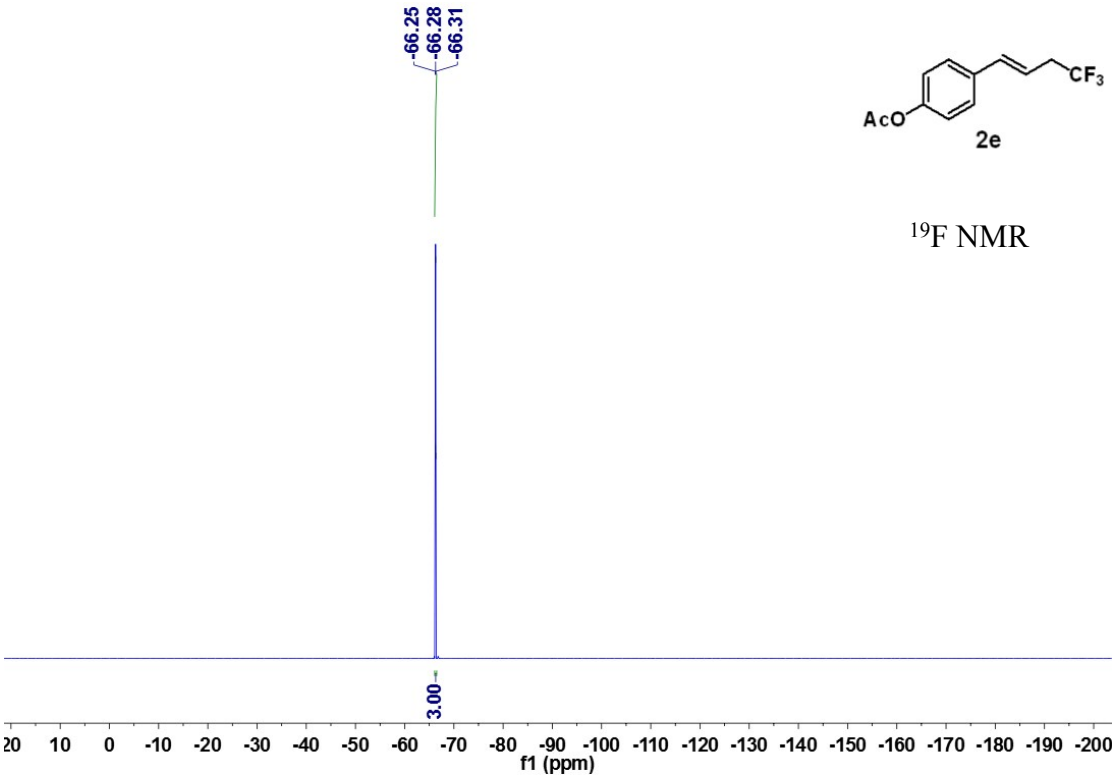
^{19}F NMR

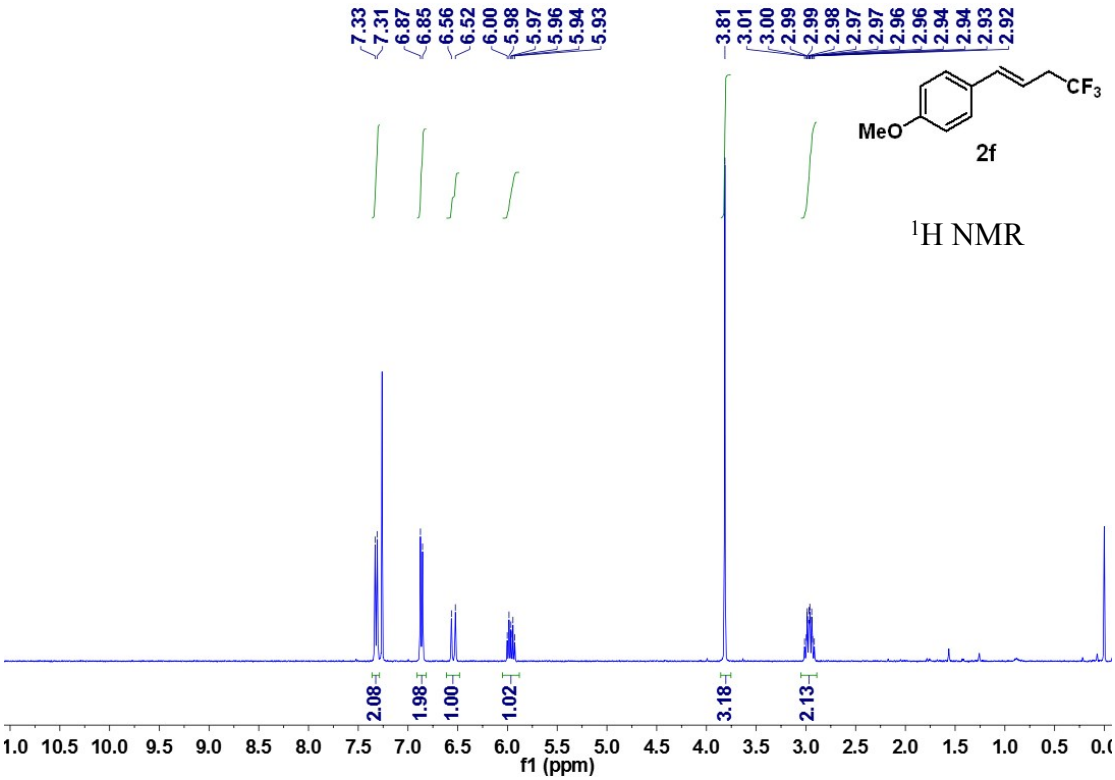


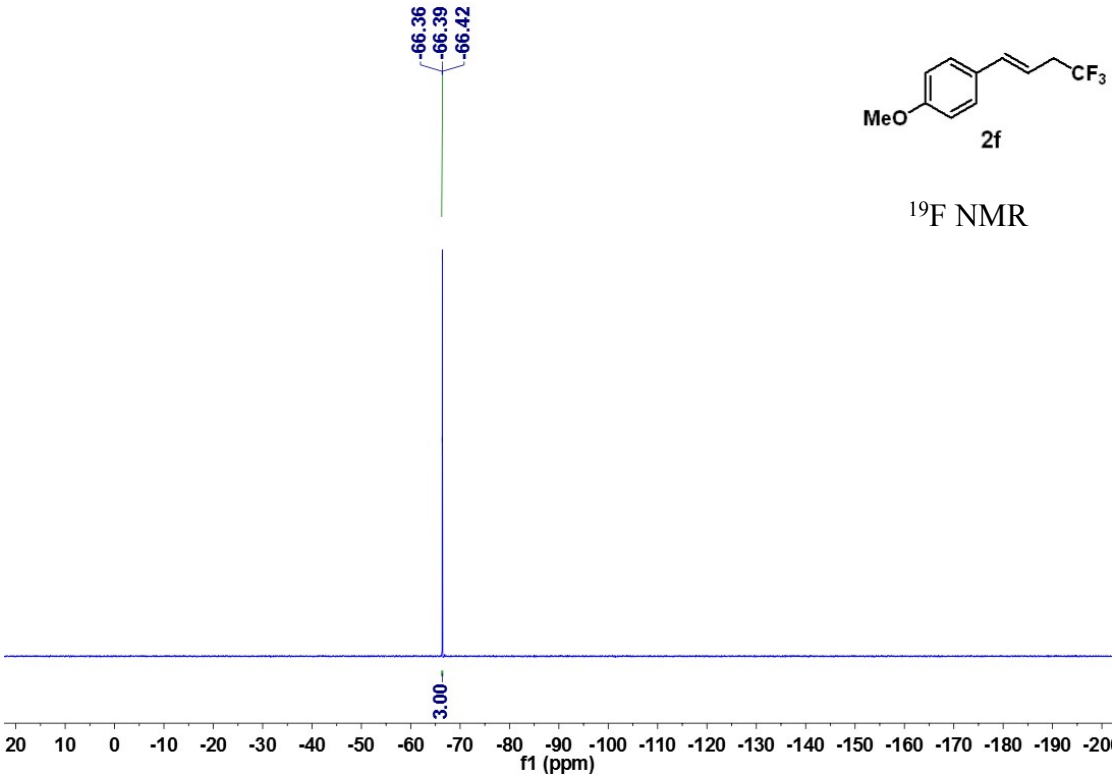
^{1}H NMR


-66.31
-66.34
-66.36
CF3
tBu
2d
19F NMR
3.00
f1 (ppm)


7.39
7.37
7.07
7.05
6.60
6.56
6.10
6.08
6.07
6.06
6.04
6.03
3.03
3.03
3.01
3.01
3.01
3.00
2.99
2.98
2.98
2.98
2.96
2.96
2.95
2.95
2.93
2.93
2.29
CF3
AcO
2e
1H NMR
2.10
2.01
1.00
1.01
2.09
3.17
f1 (ppm)

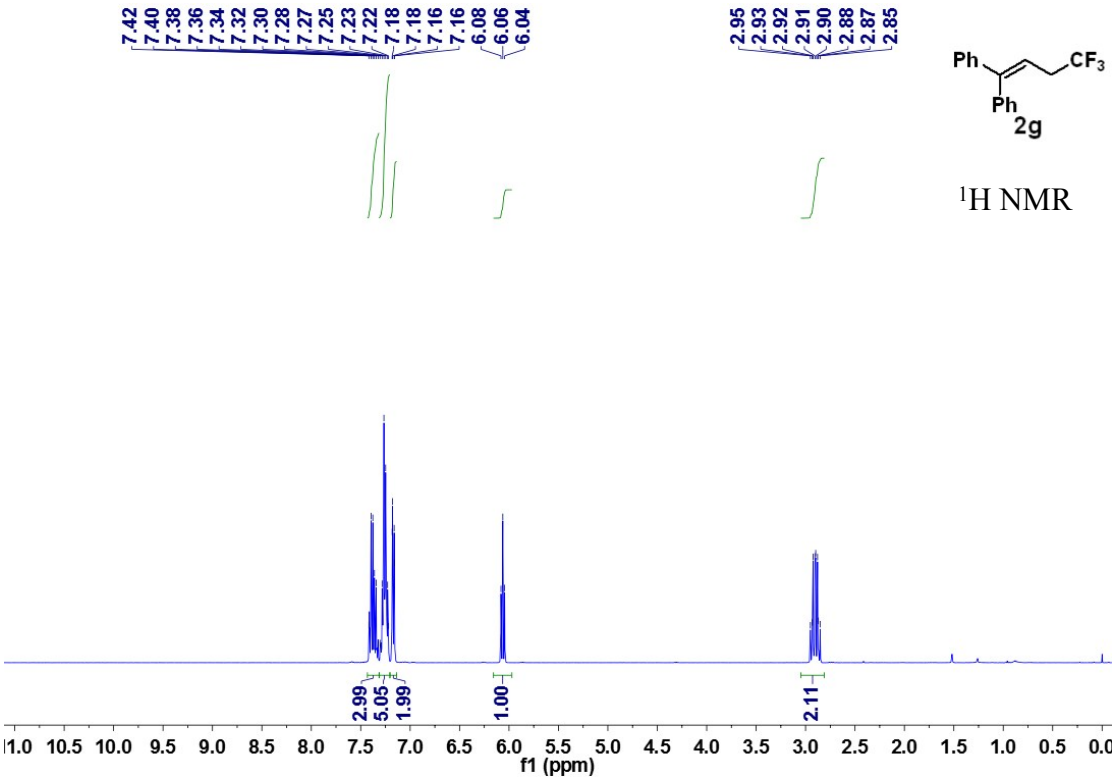

-66.25
-66.28
-66.31
AcO
CF3
2e
19F NMR
3.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


7.33
7.31
6.87
6.85
6.56
6.52
6.00
5.98
5.97
5.96
5.94
5.93
3.81
3.01
3.00
2.99
2.99
2.98
2.97
2.97
2.96
2.96
2.94
2.94
2.93
2.92
MeO
CF3
2f
1H NMR
2.08
1.98
1.00
1.02
3.18
2.13
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



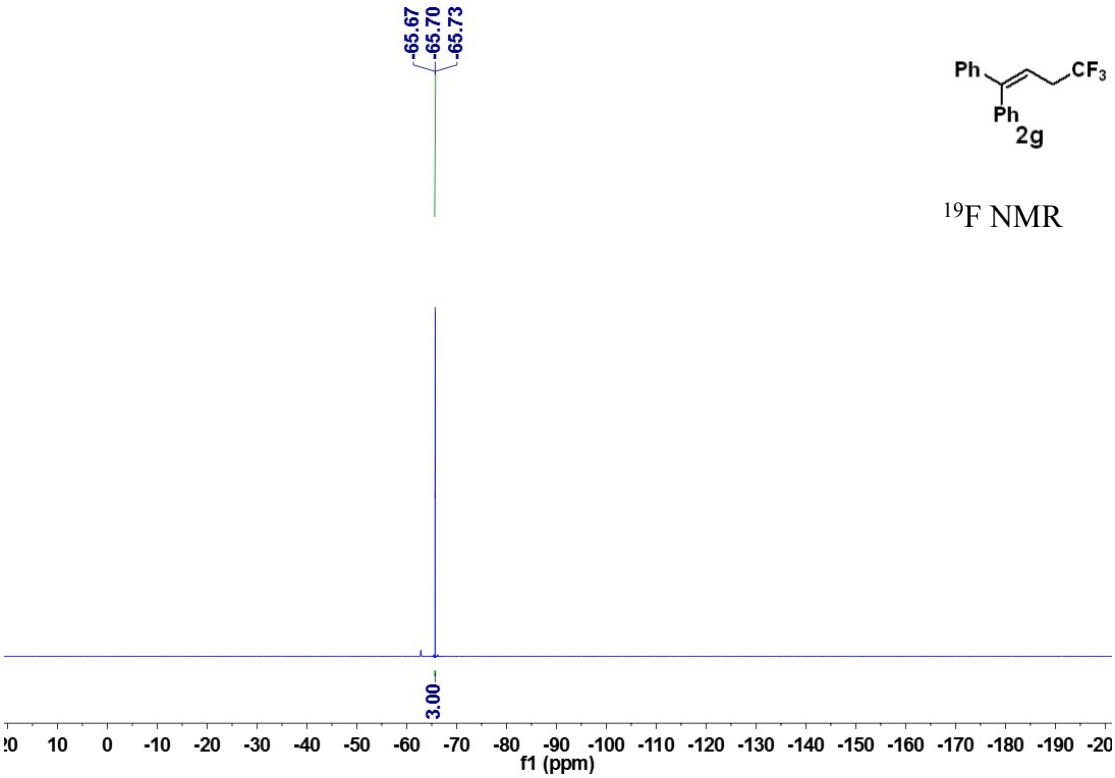
2f

^{19}F NMR

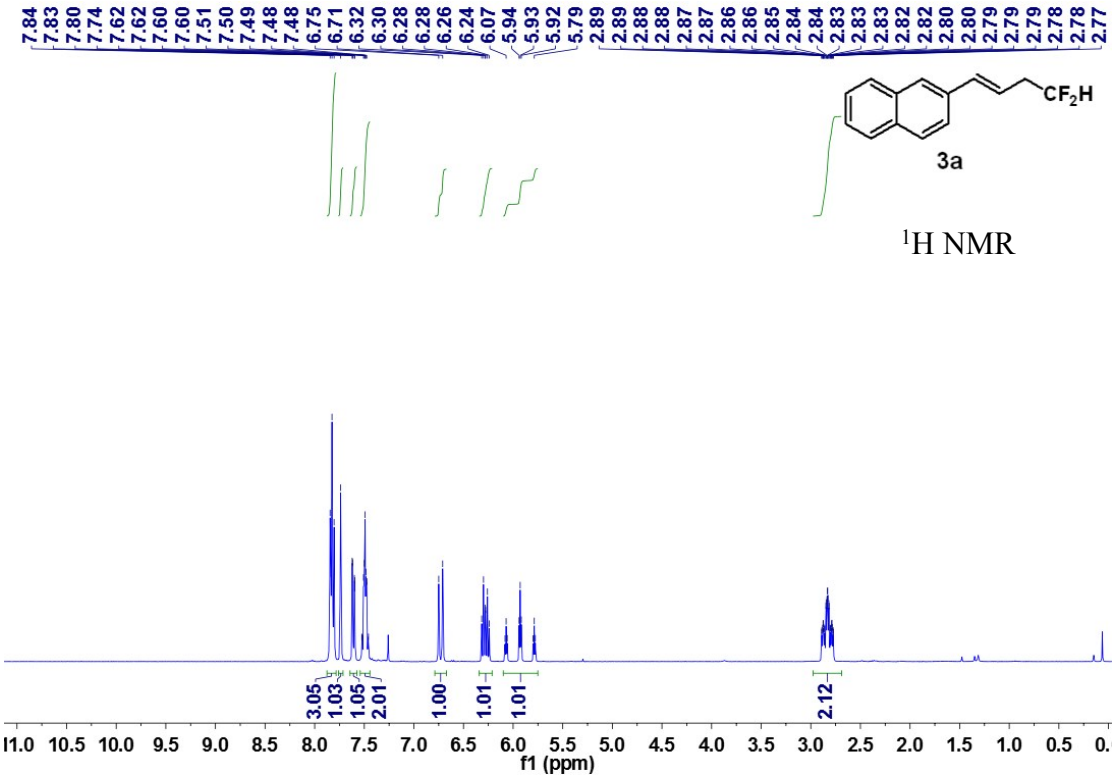


2g

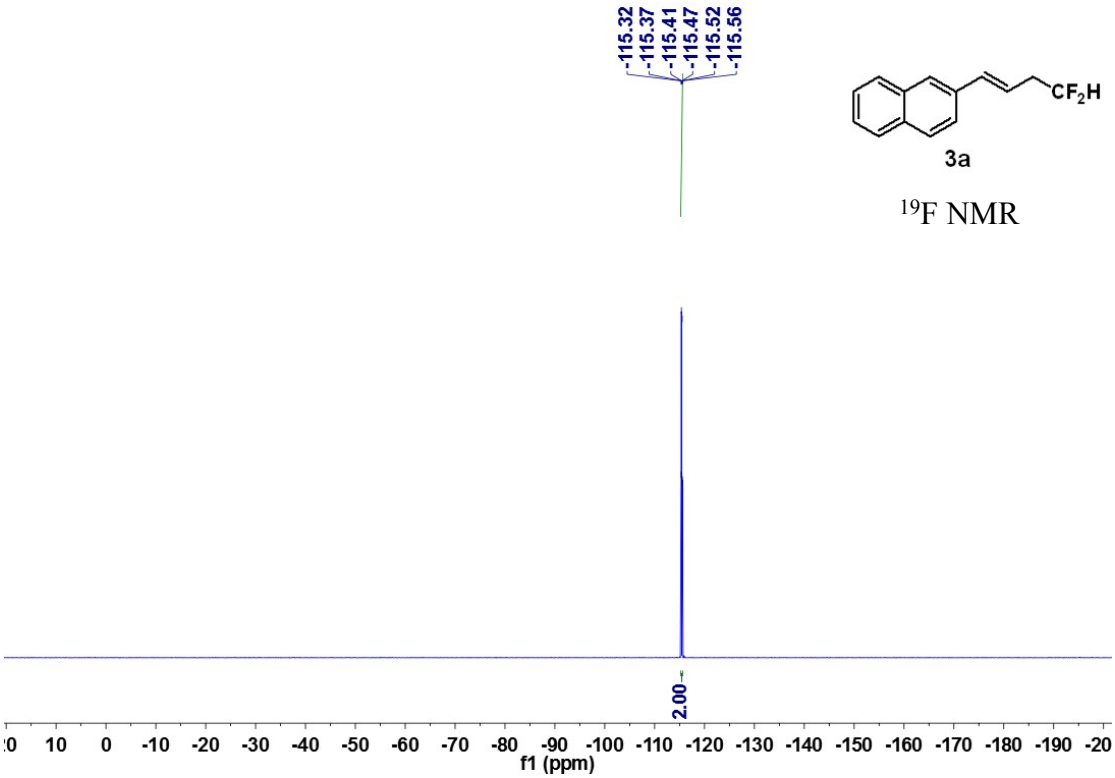
^{1}H NMR



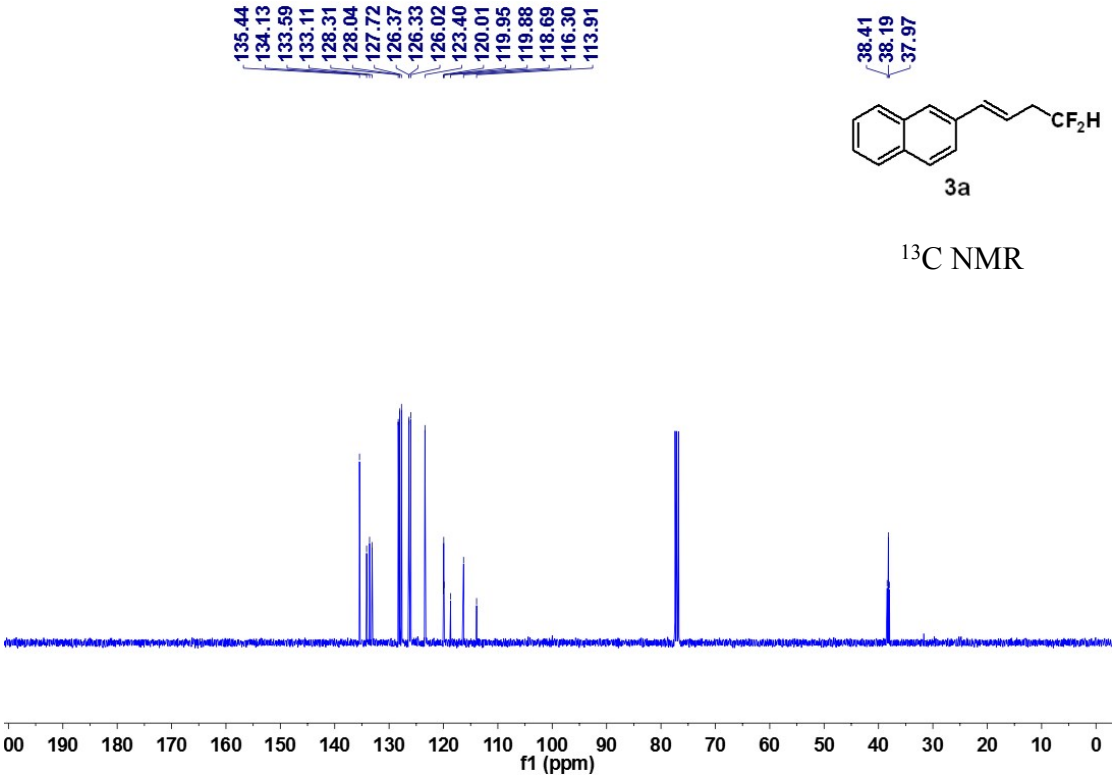
^{19}F NMR



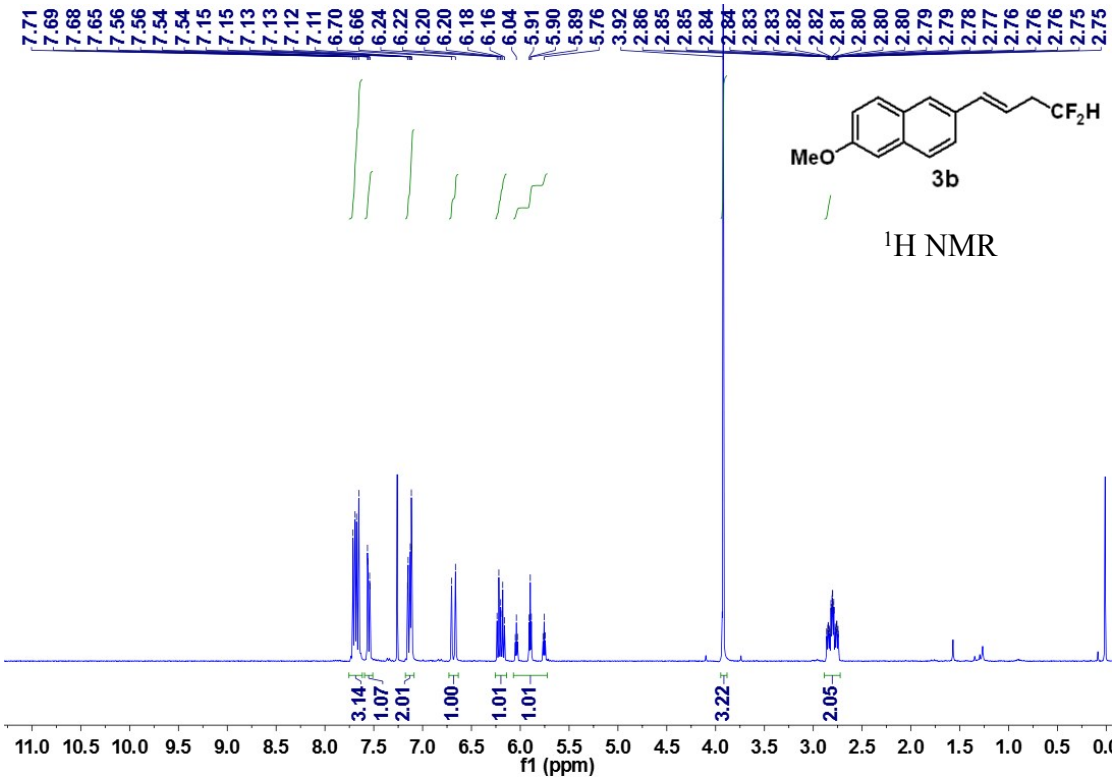
^{1}H NMR

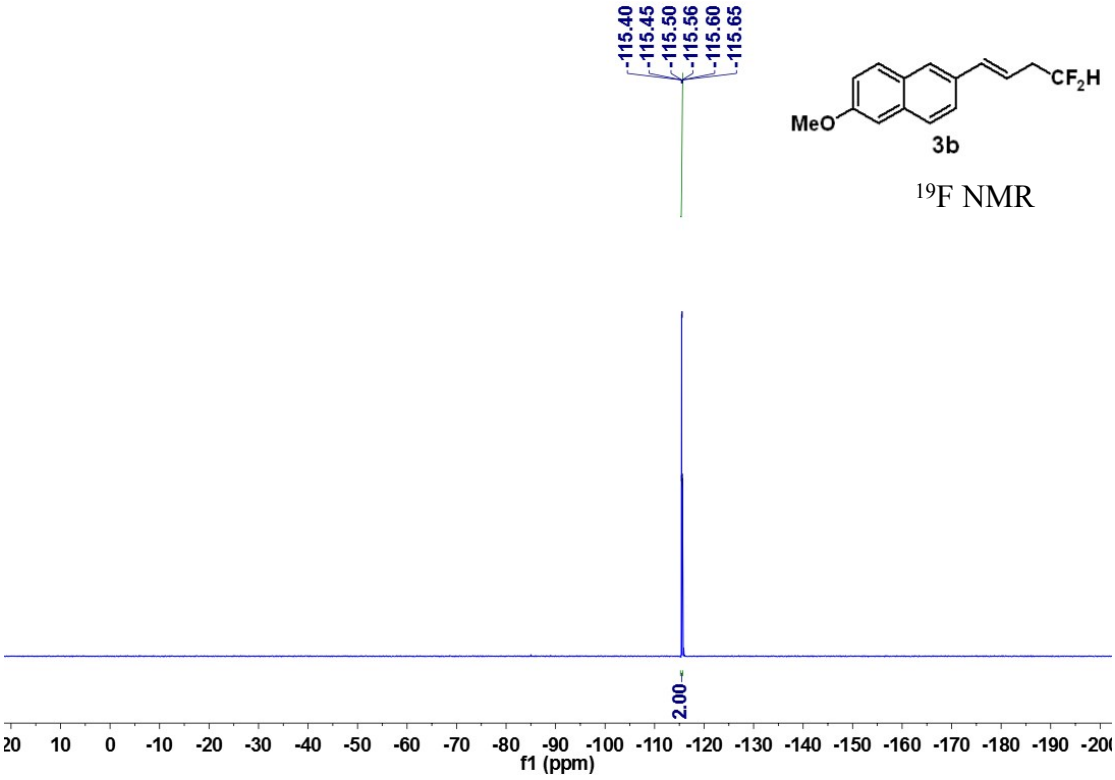


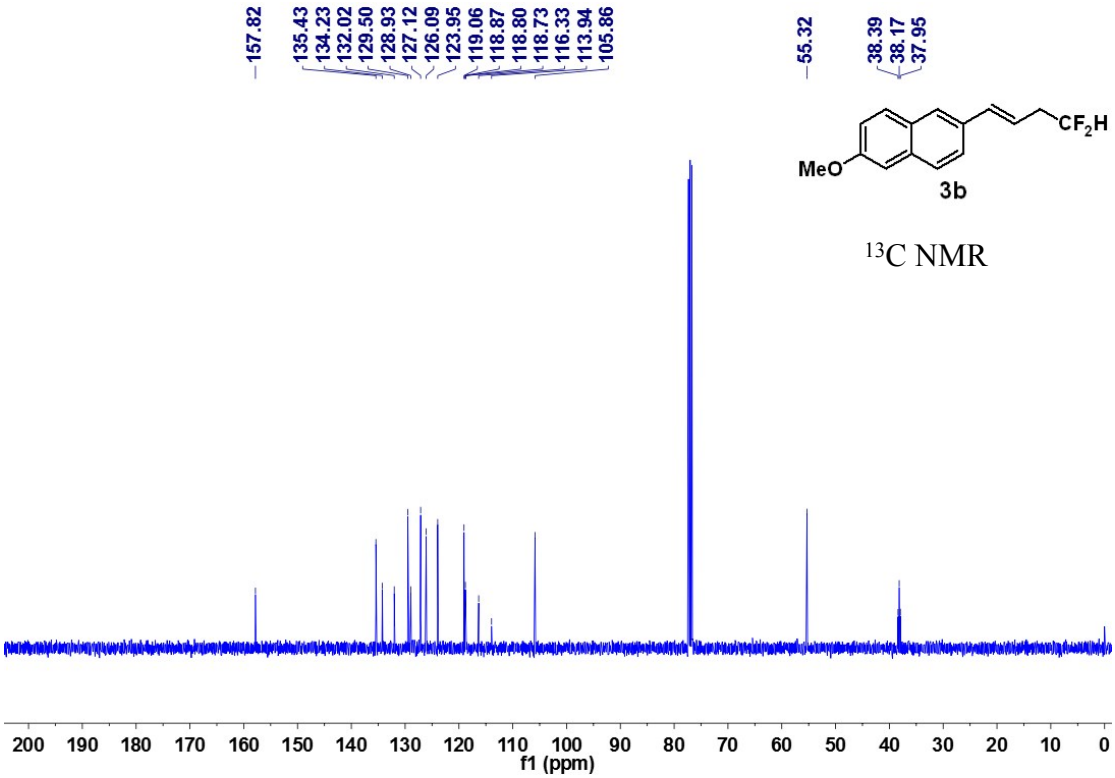
^{19}F NMR

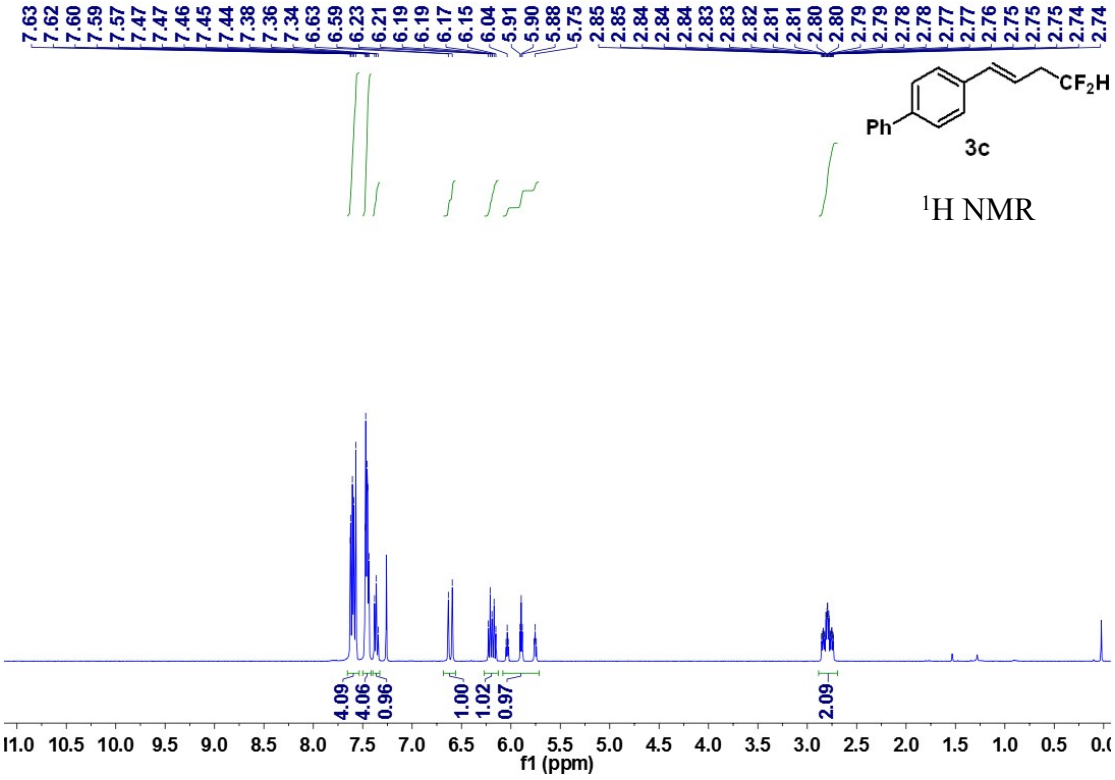


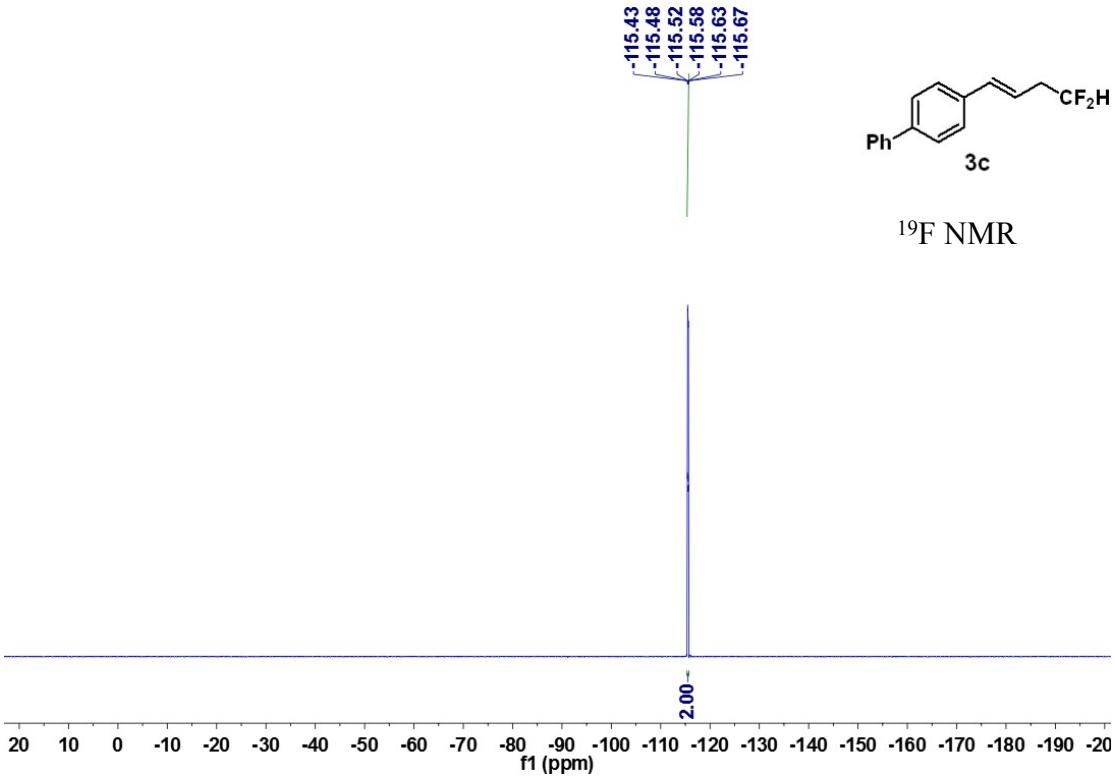
^{13}C NMR


MeO
CF2H
3b
1H NMR
f1 (ppm)

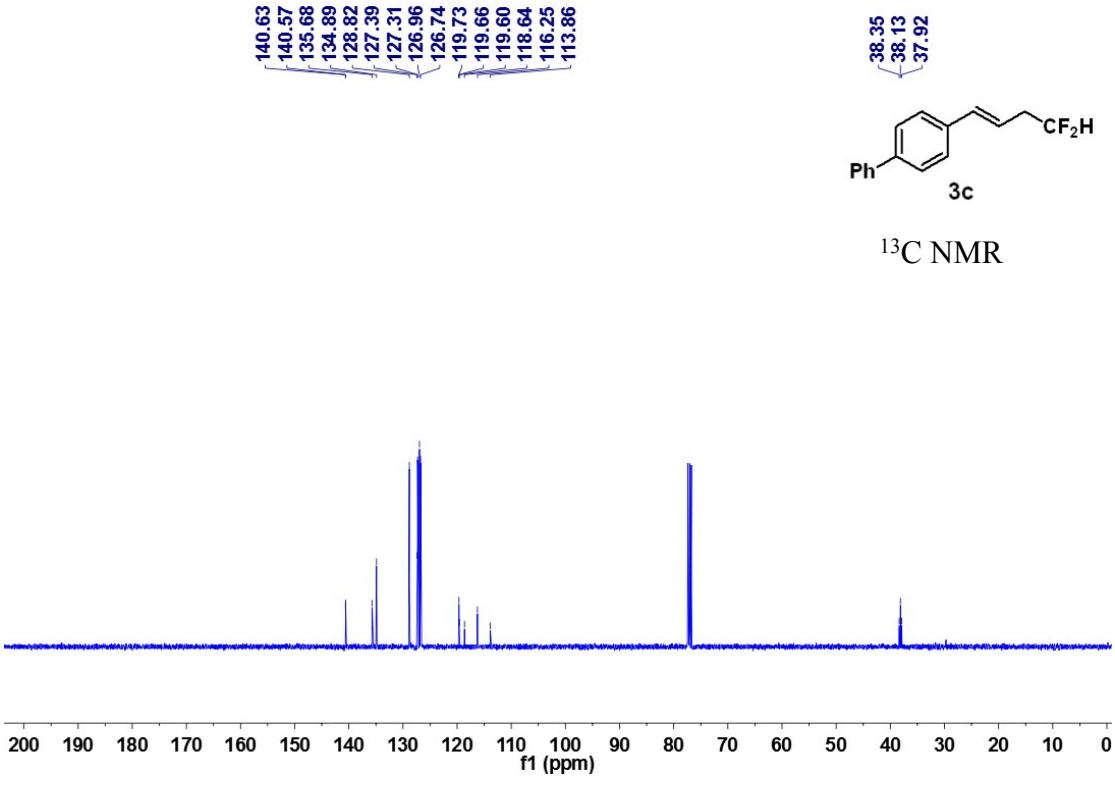

MeO
CF2H
3b
19F NMR
f1 (ppm)


157.82
135.43
134.23
132.02
129.50
128.93
127.12
126.09
123.95
119.06
118.87
118.80
118.73
116.33
113.94
105.86
55.32
38.39
38.17
37.95
MeO
CF2H
3b
13C NMR
f1 (ppm)

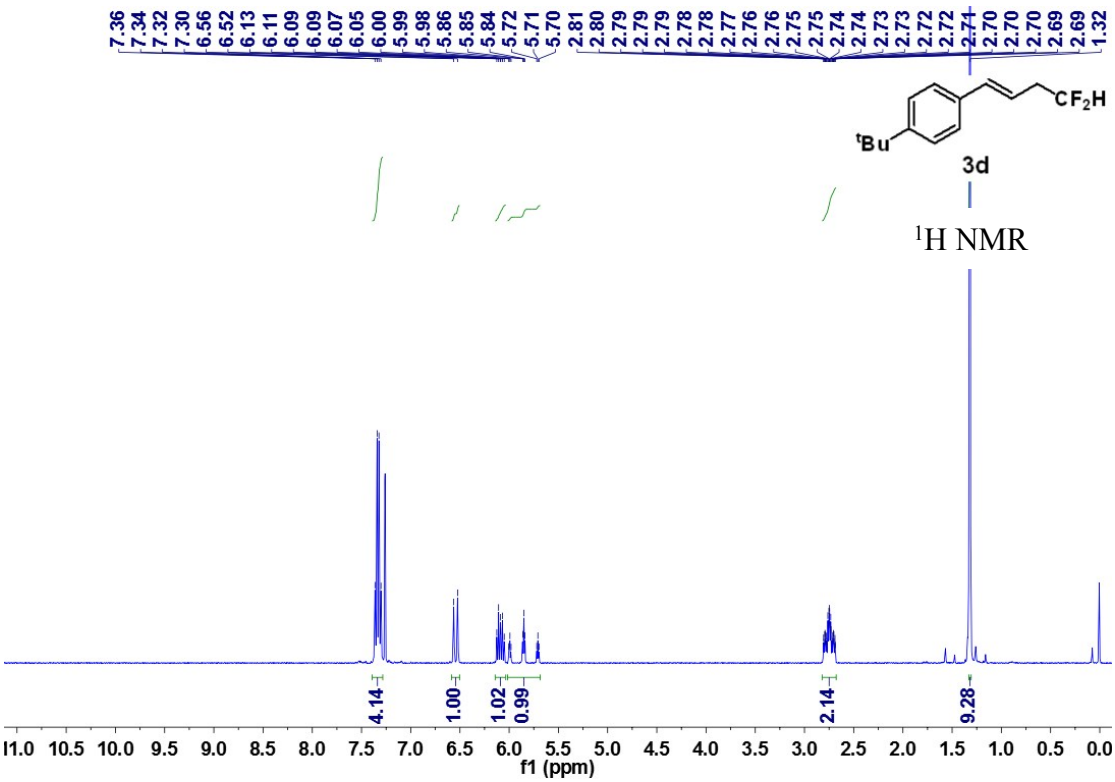

7.63
7.62
7.60
7.59
7.57
7.47
7.47
7.46
7.45
7.44
7.38
7.36
7.34
6.63
6.59
6.23
6.21
6.19
6.19
6.17
6.15
6.04
5.91
5.90
5.88
5.75
2.85
2.85
2.84
2.84
2.84
2.83
2.83
2.82
2.81
2.81
2.80
2.80
2.79
2.79
2.78
2.78
2.77
2.77
2.76
2.75
2.75
2.74
2.74
Ph
CF2H
3c
1H NMR
4.09
4.06
0.96
1.00
1.02
0.97
2.09
f1 (ppm)



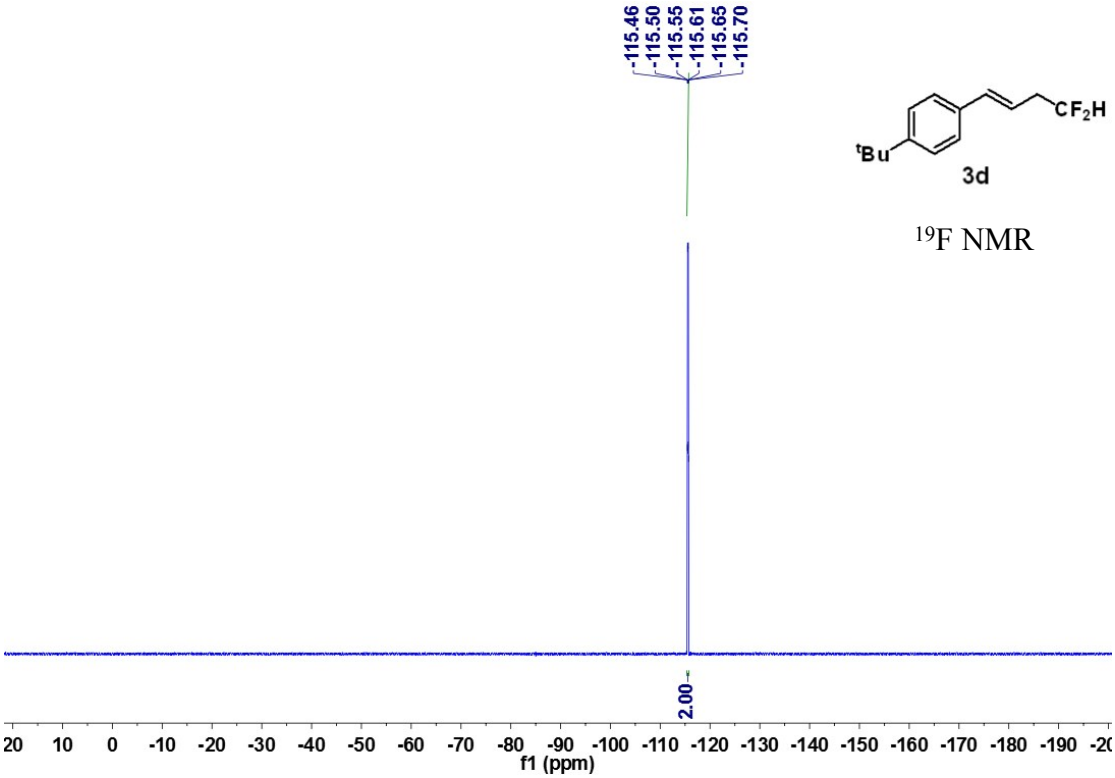
^{19}F NMR



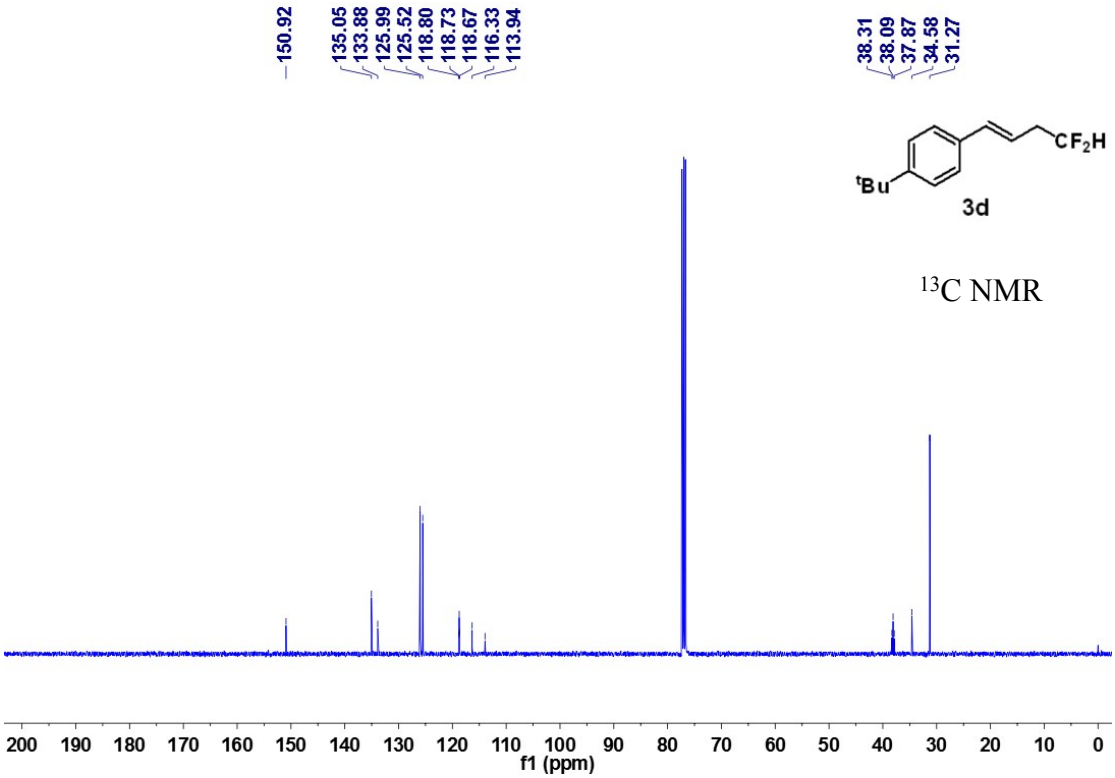
^{13}C NMR

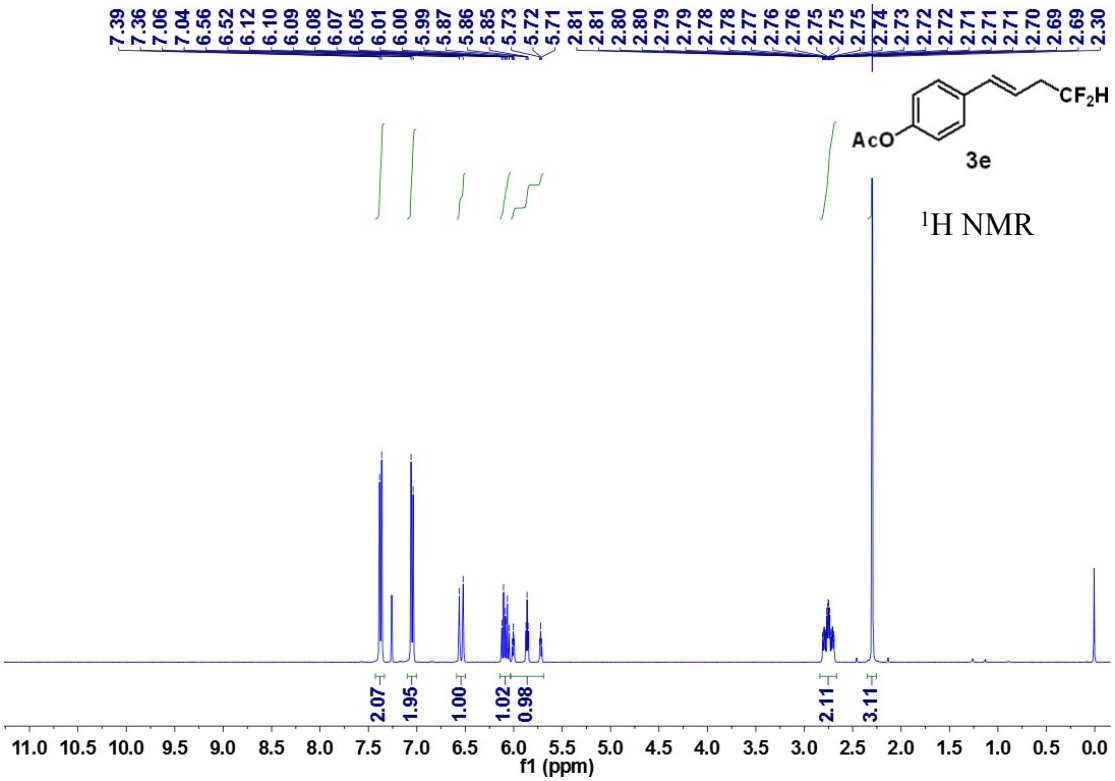


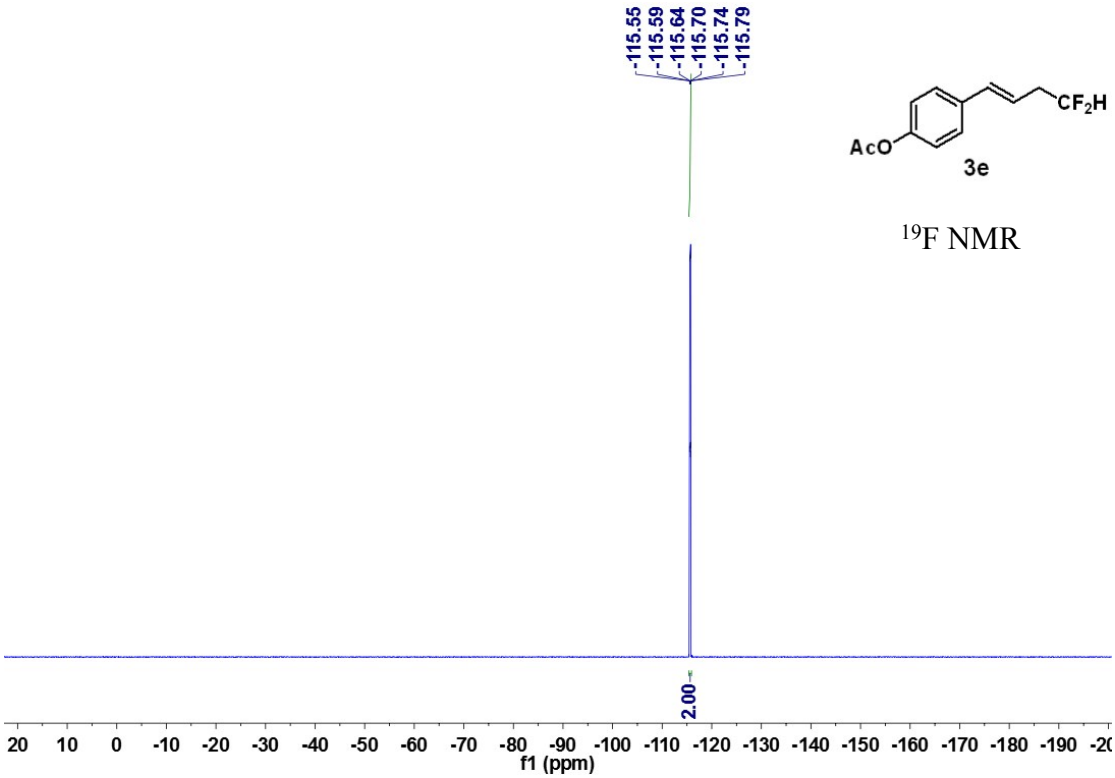
^{1}H NMR



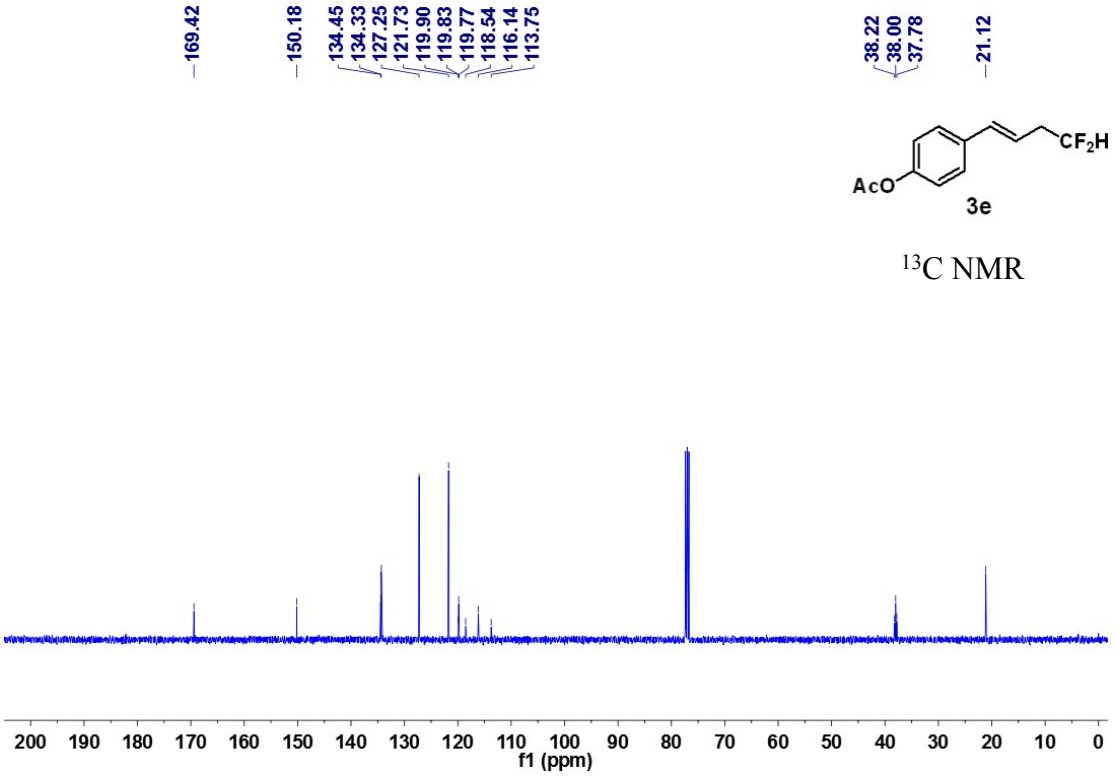
^{19}F NMR


150.92
135.05
133.88
125.99
125.52
118.80
118.73
118.67
116.33
113.94
38.31
38.09
37.87
34.58
31.27
CF2H
tBu
3d
13C NMR
f1 (ppm)

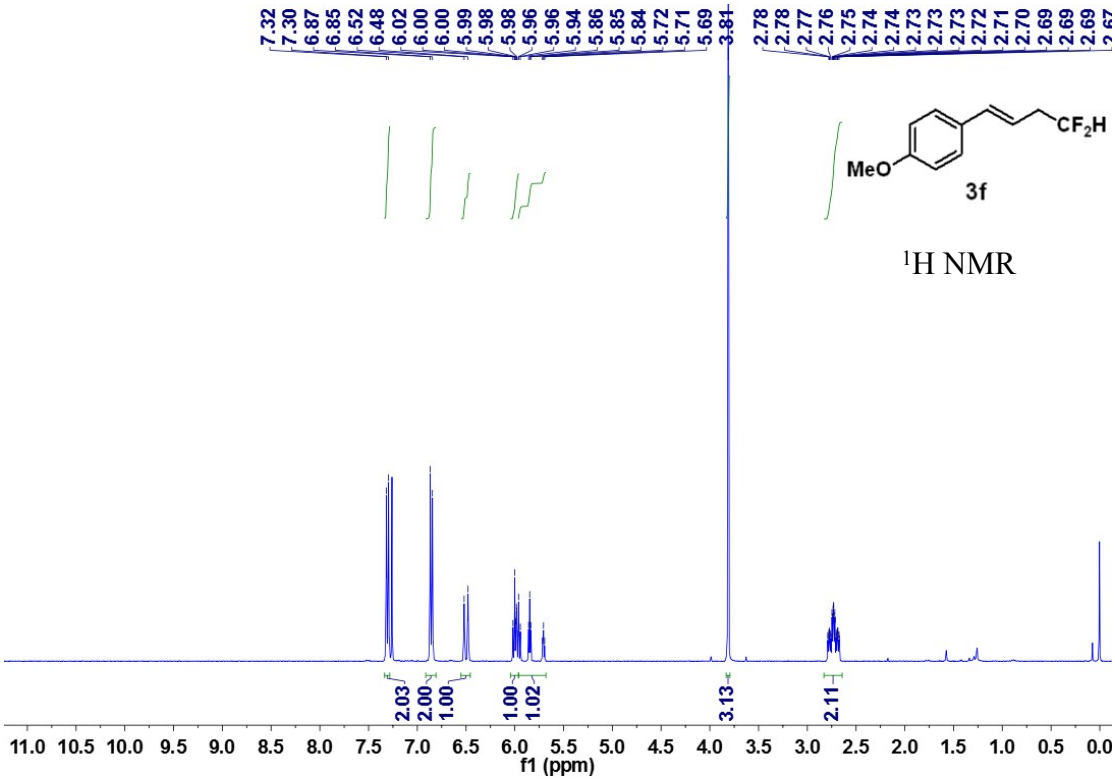

7.39
7.36
7.06
7.04
6.56
6.52
6.12
6.10
6.09
6.08
6.07
6.05
6.01
6.00
5.99
5.87
5.86
5.85
5.73
5.72
5.71
2.81
2.81
2.80
2.80
2.79
2.79
2.78
2.78
2.77
2.76
2.76
2.75
2.75
2.75
2.74
2.73
2.72
2.72
2.71
2.71
2.71
2.70
2.69
2.69
2.30
CF2H
AcO
3e
1H NMR
2.07
1.95
1.00
1.02
0.98
2.11
3.11
f1 (ppm)



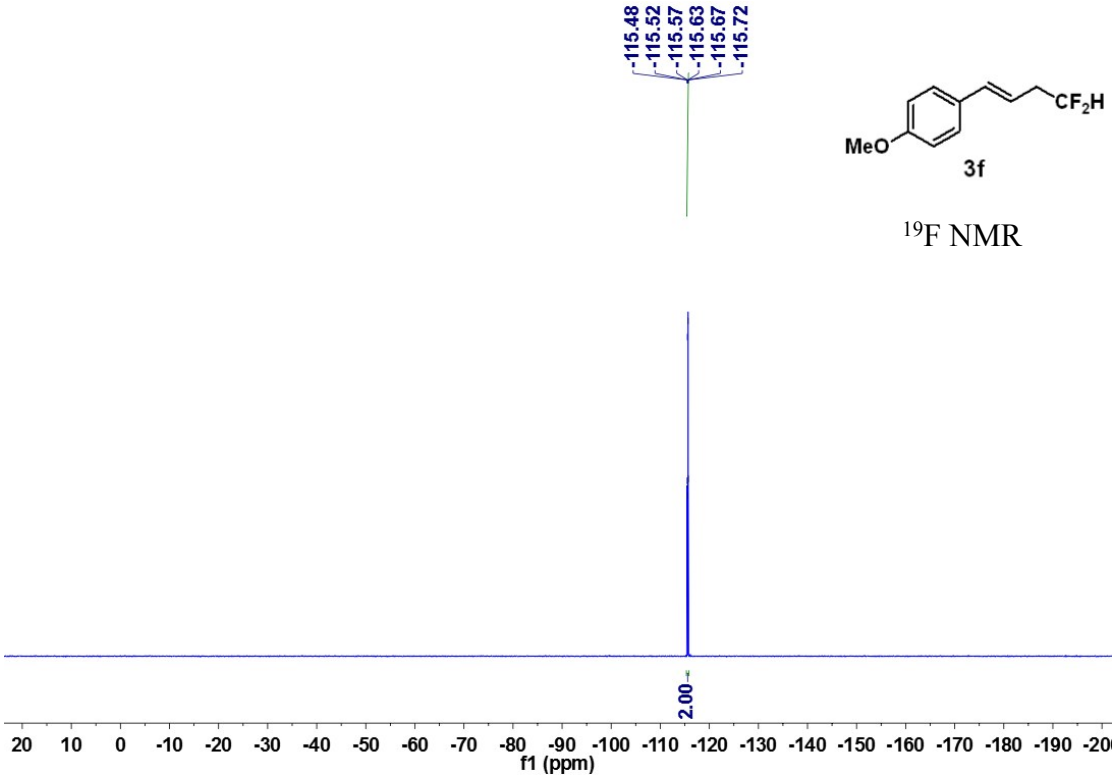
^{19}F NMR



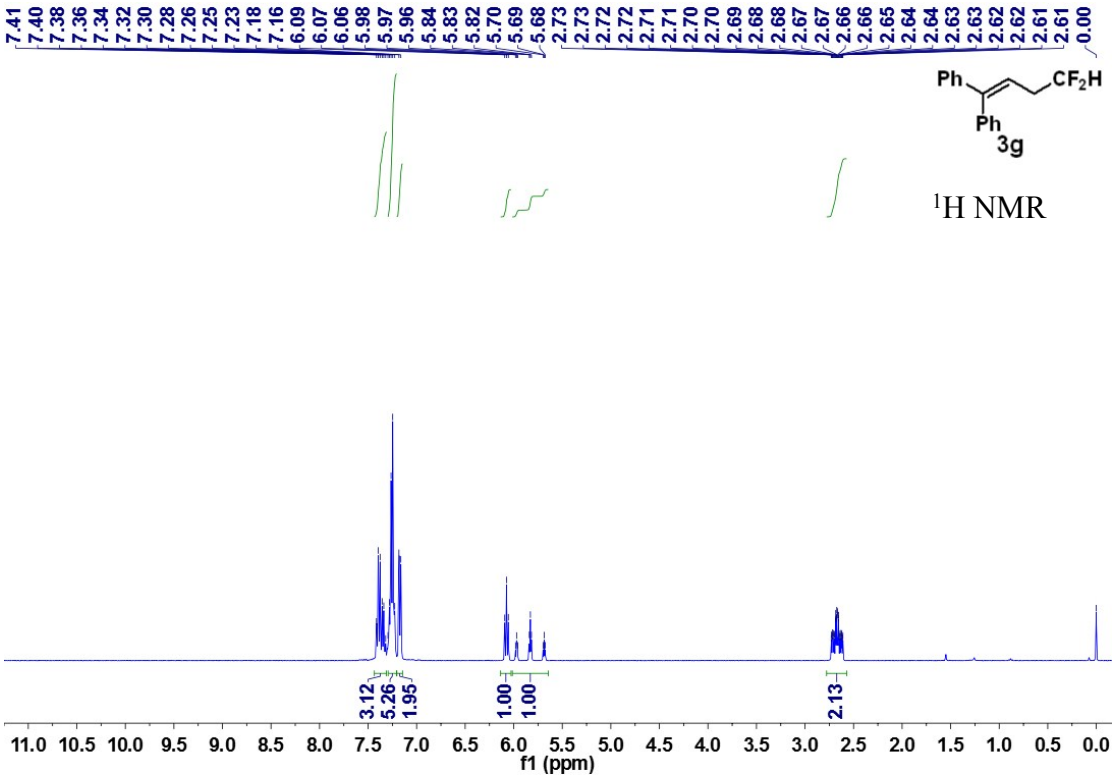
^{13}C NMR



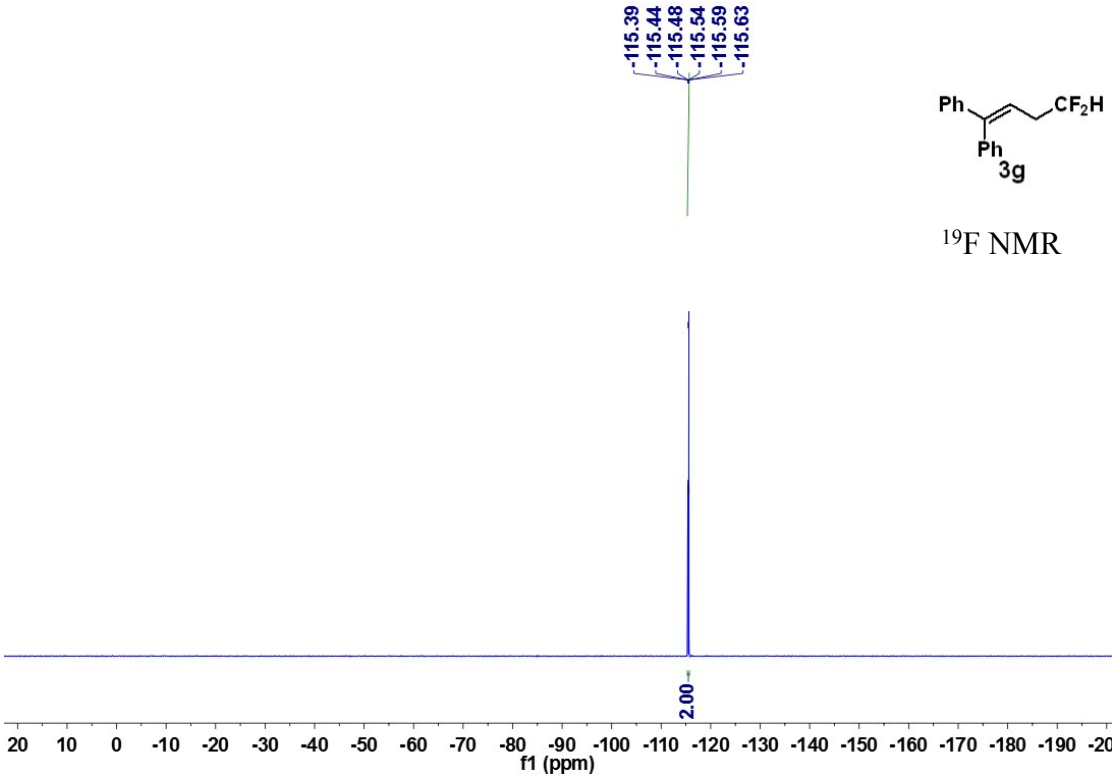
^{1}H NMR



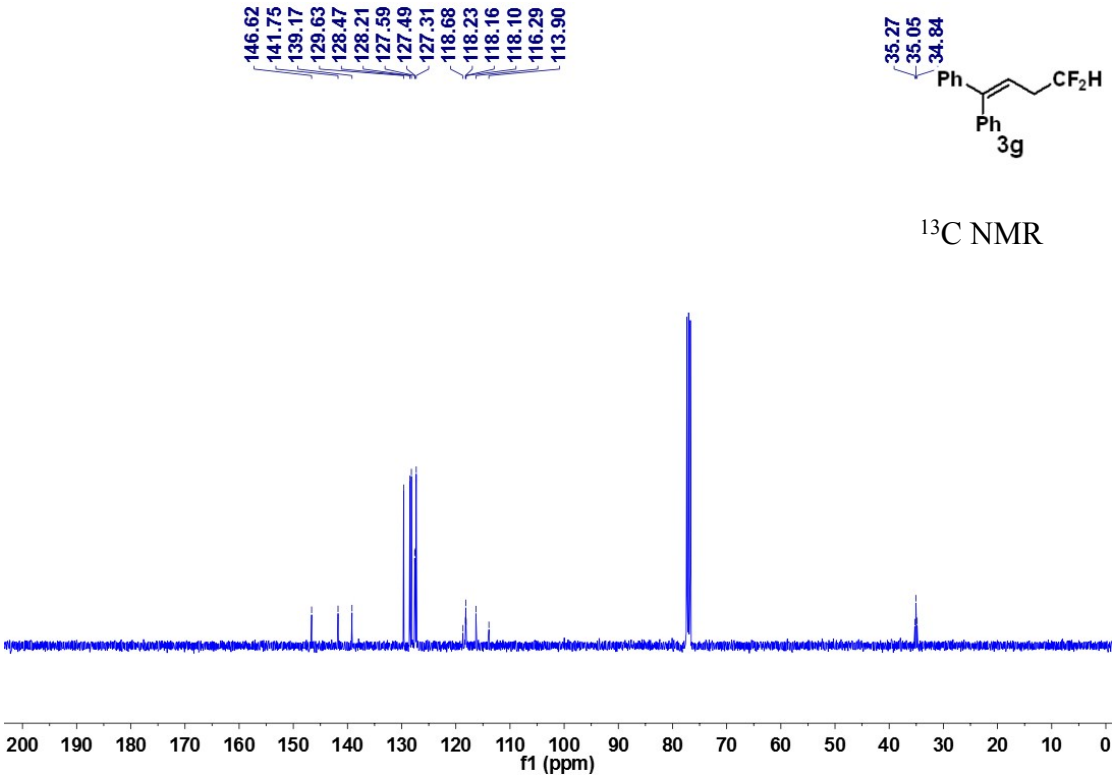
^{19}F NMR



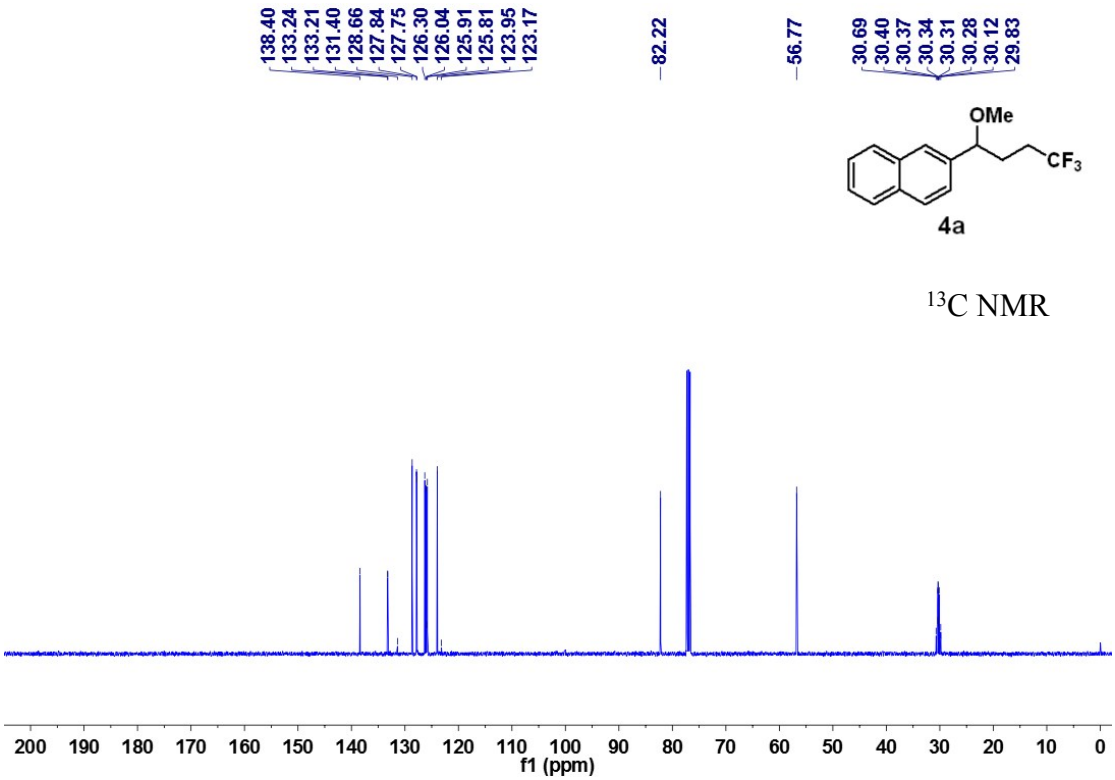
^{1}H NMR



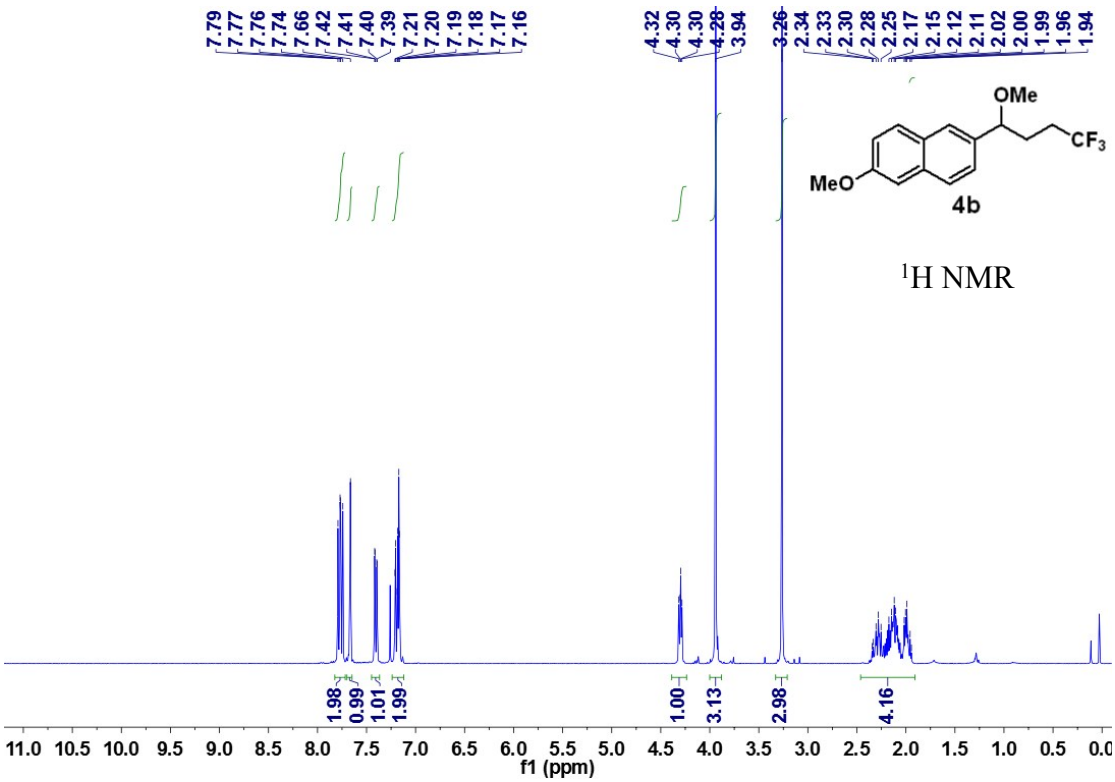
^{19}F NMR


146.62
141.75
139.17
129.63
128.47
128.21
127.59
127.49
127.31
118.68
118.23
118.16
118.10
116.29
113.90
35.27
35.05
34.84
Ph
CF2H
Ph
3g
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
7.90
7.88
7.87
7.87
7.86
7.86
7.75
7.55
7.55
7.53
7.53
7.52
7.51
7.50
7.49
7.49
7.46
7.46
7.44
7.43
4.36
4.34
4.33
3.28
2.38
2.35
2.29
2.24
2.15
2.14
2.14
2.14
2.13
2.05
2.03
2.01
1.96
OMe
CF3
4a
1H NMR
2.87
0.96
1.89
0.96
1.00
3.04
4.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

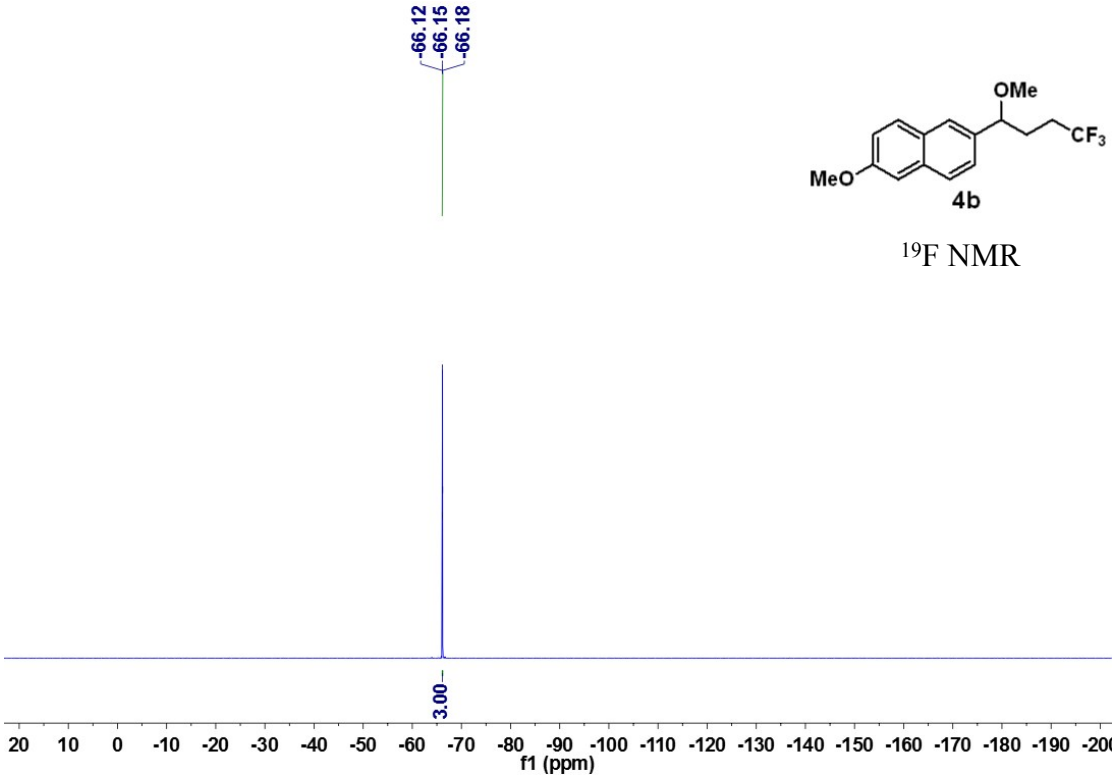
^{19}F NMR



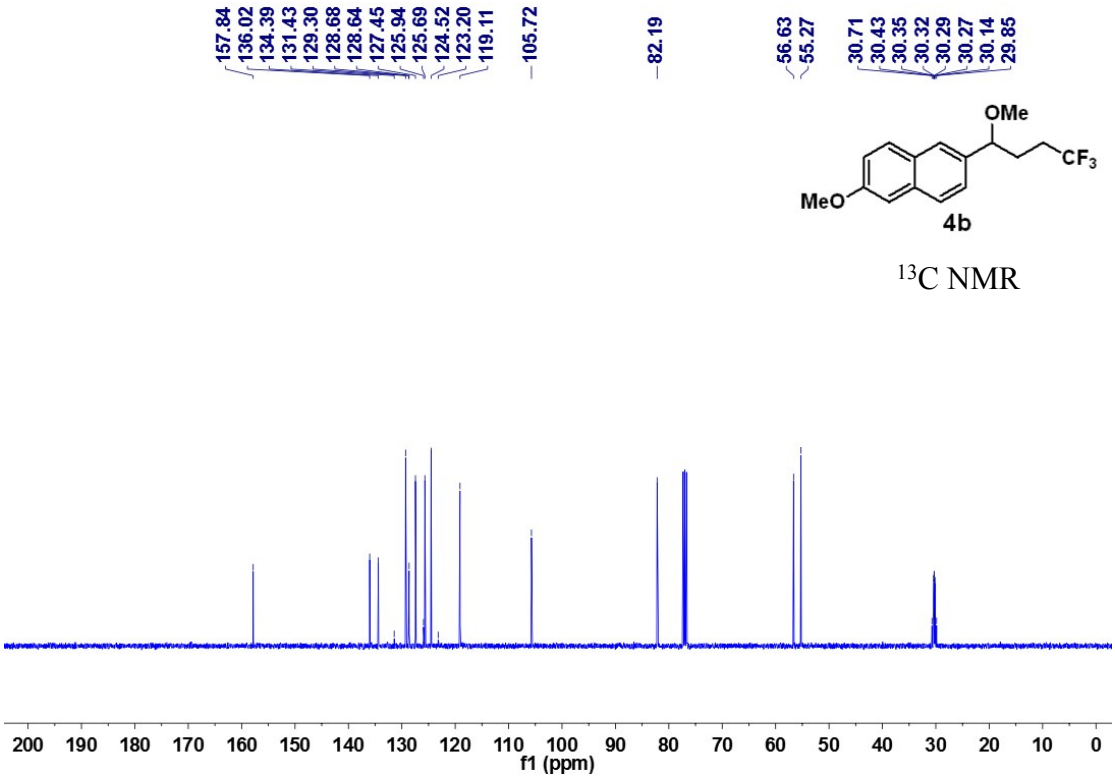
^{13}C NMR



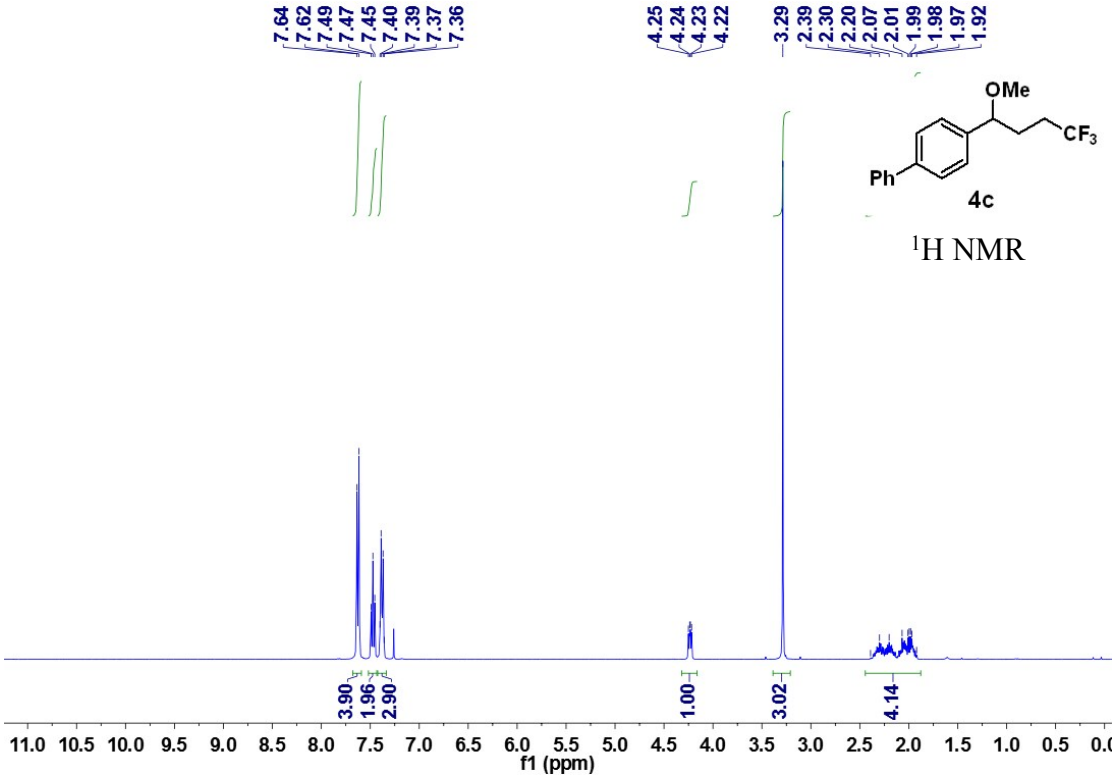
^{1}H NMR



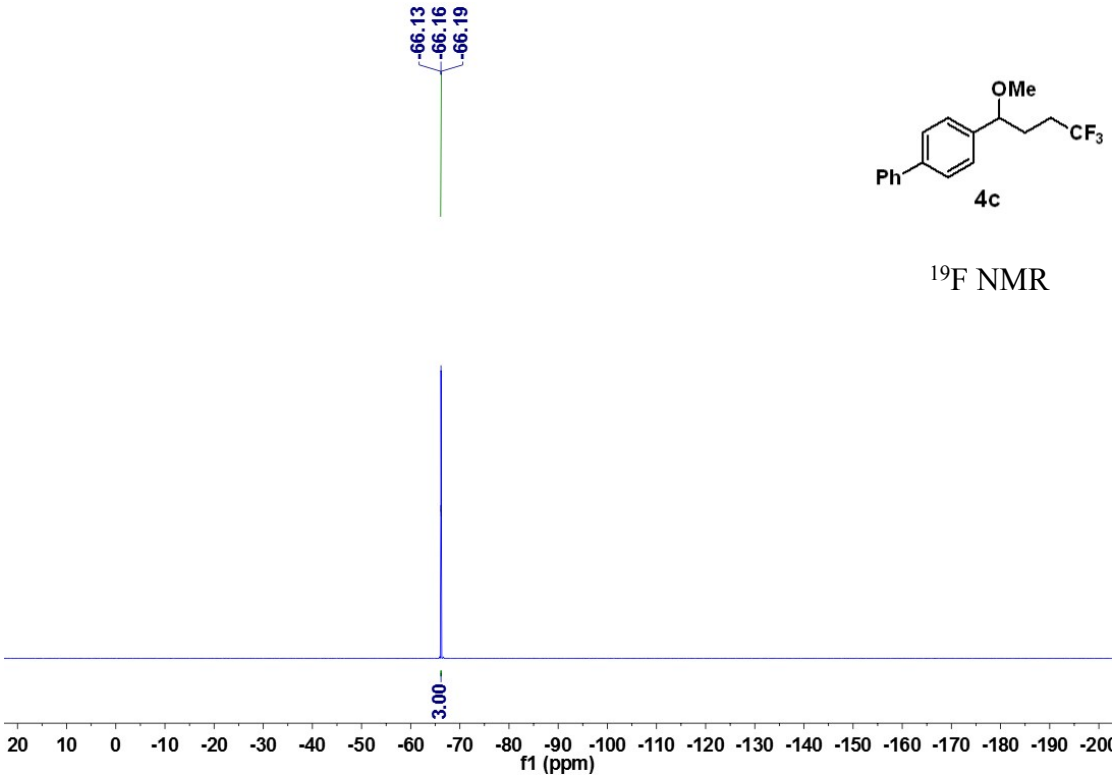
^{19}F NMR



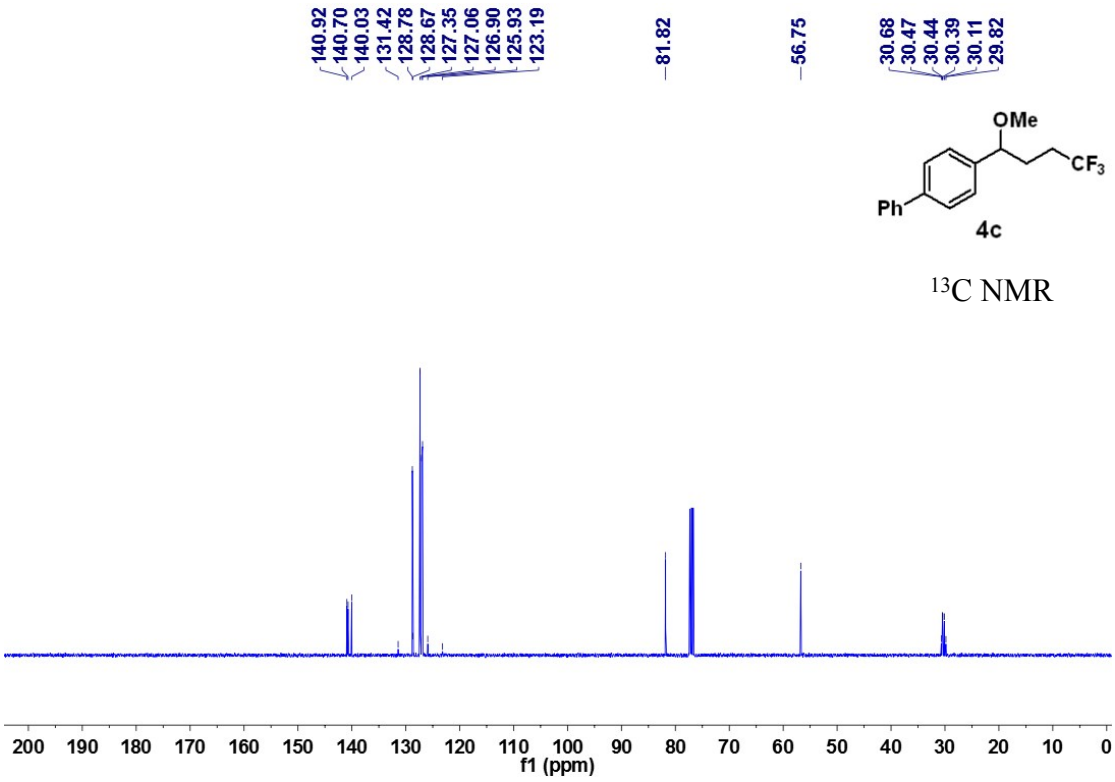
^{13}C NMR



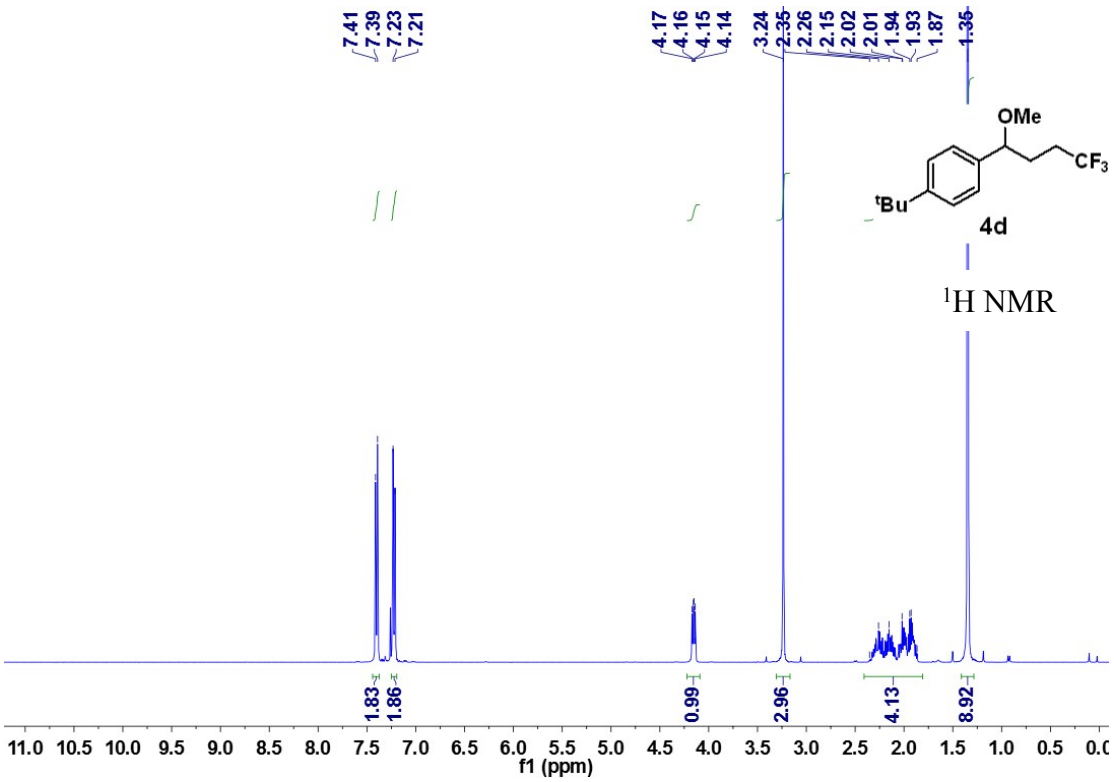
^{1}H NMR



^{19}F NMR

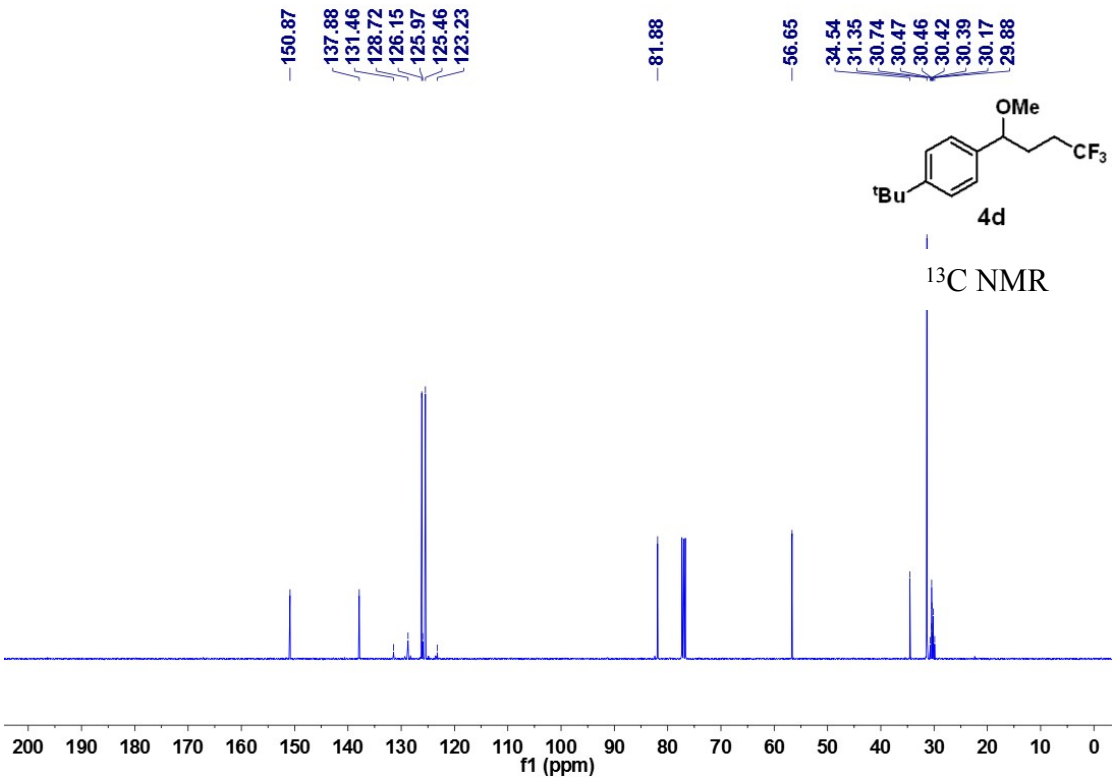


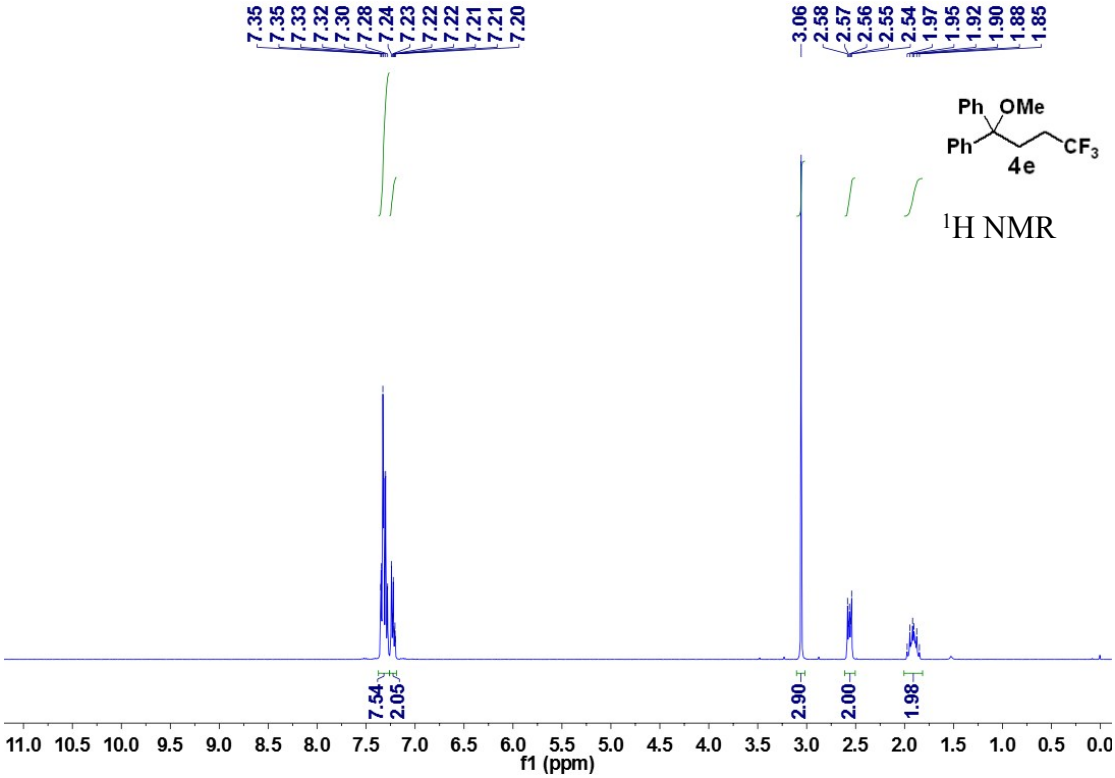
^{13}C NMR

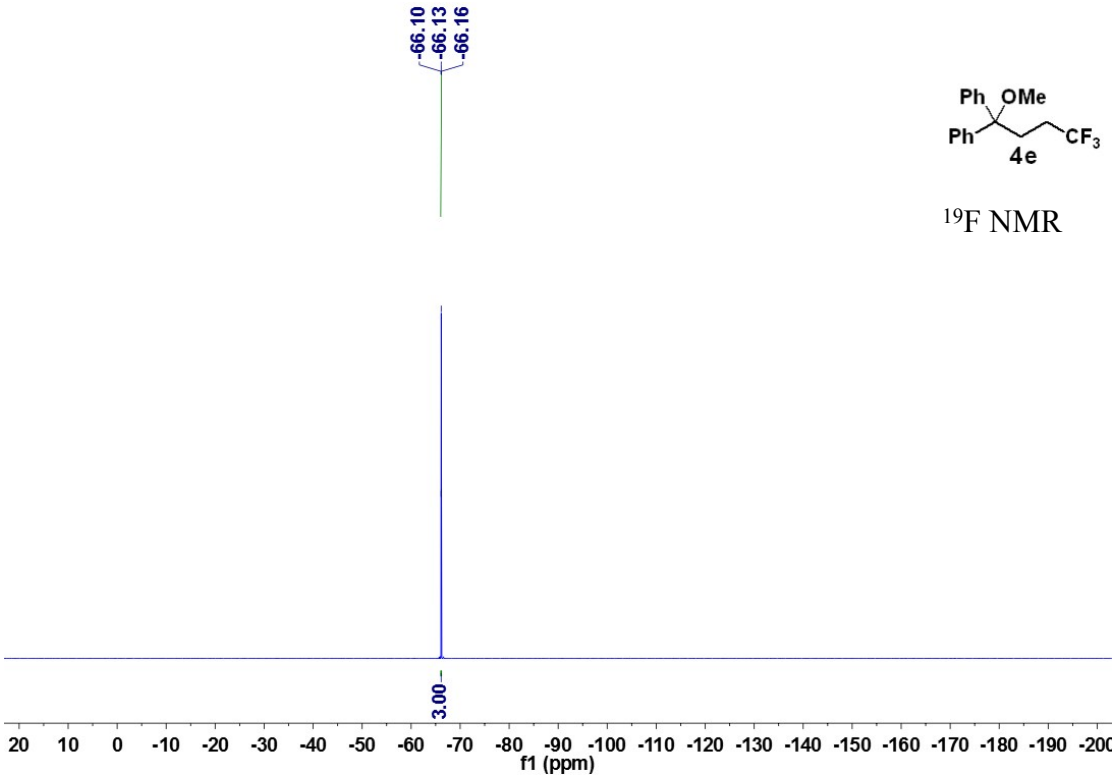


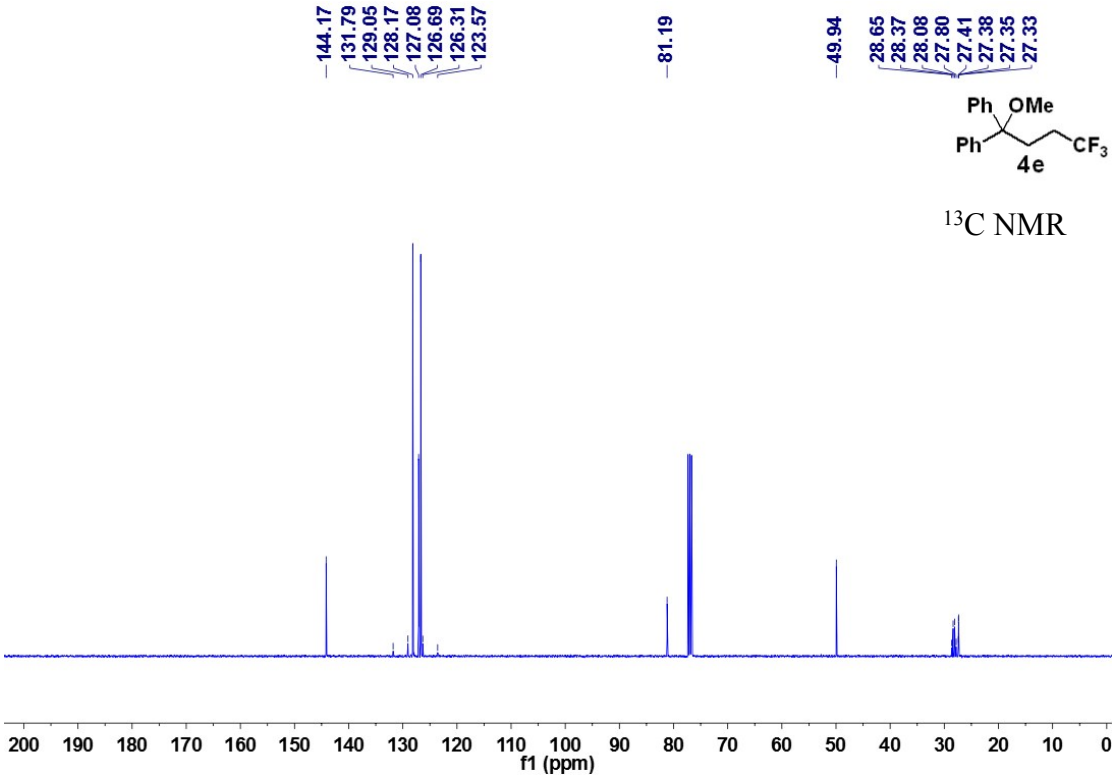
^{1}H NMR

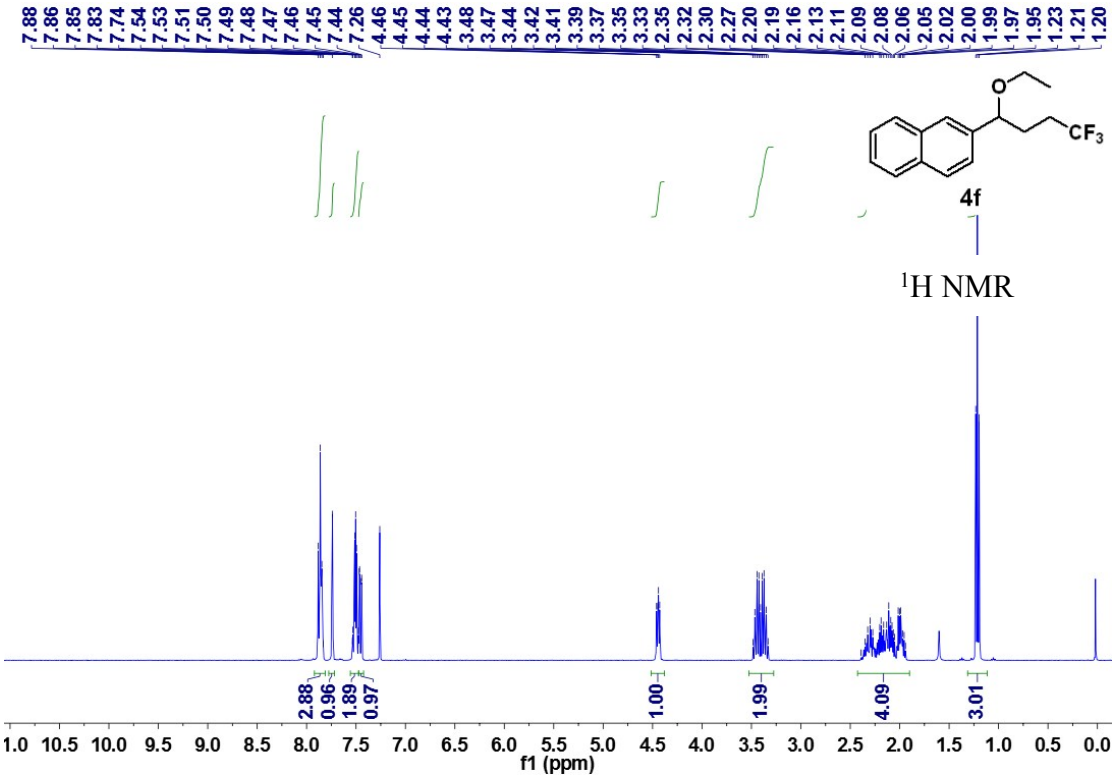
^{19}F NMR


150.87
137.88
131.46
128.72
126.15
125.97
125.46
123.23
81.88
56.65
34.54
31.35
30.74
30.47
30.46
30.42
30.39
30.17
29.88
OMe
CF3
tBu
4d
13C NMR
f1 (ppm)


7.35
7.35
7.33
7.32
7.30
7.28
7.24
7.23
7.22
7.22
7.21
7.21
7.20
3.06
2.58
2.57
2.56
2.55
2.54
1.97
1.95
1.92
1.90
1.88
1.85
Ph
OMe
Ph
CF3
4e
1H NMR
7.54
2.05
2.90
2.00
1.98
f1 (ppm)

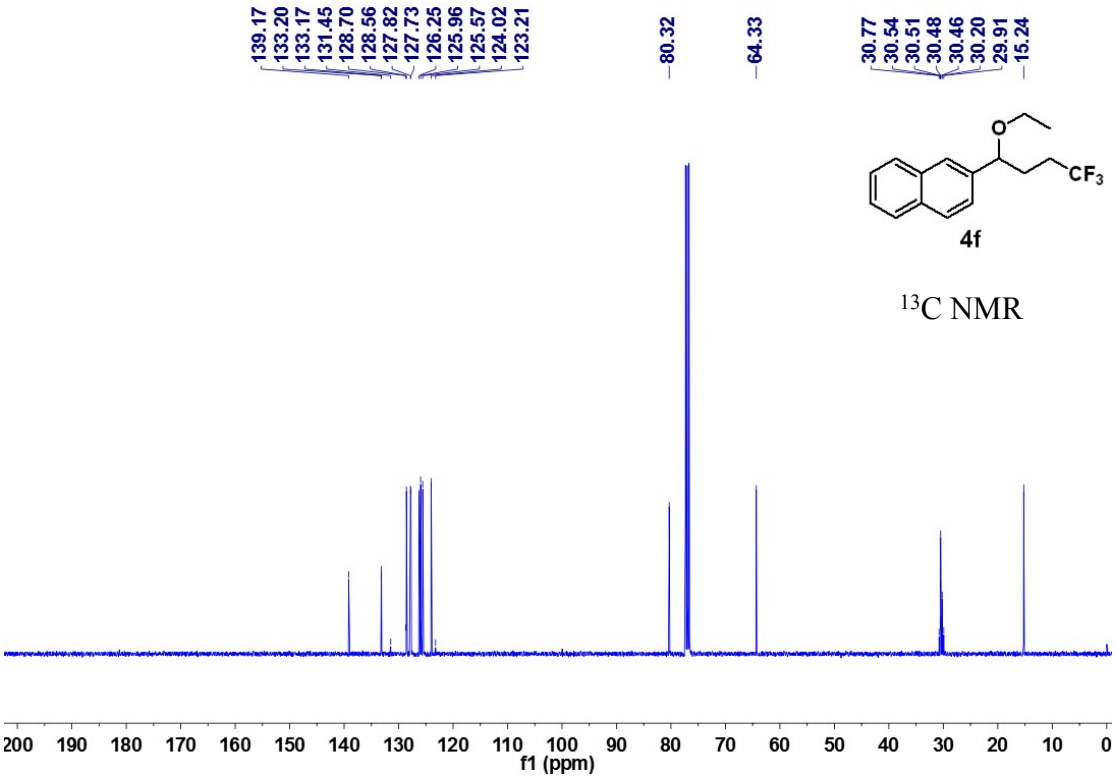

-66.10
-66.13
-66.16
Ph OMe
Ph
CF3
4e
19F NMR
3.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

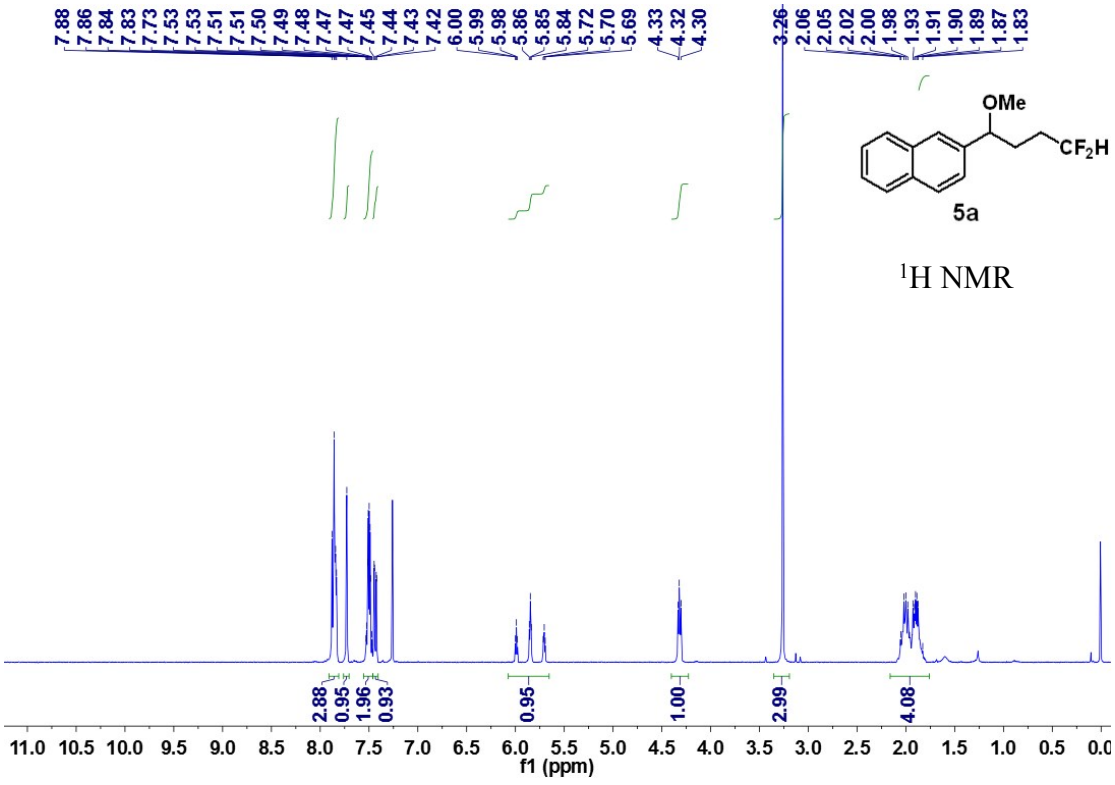

144.17
131.79
129.05
128.17
127.08
126.69
126.31
123.57
81.19
49.94
28.65
28.37
28.08
27.80
27.41
27.38
27.35
27.33
Ph OMe
Ph
CF3
4e
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

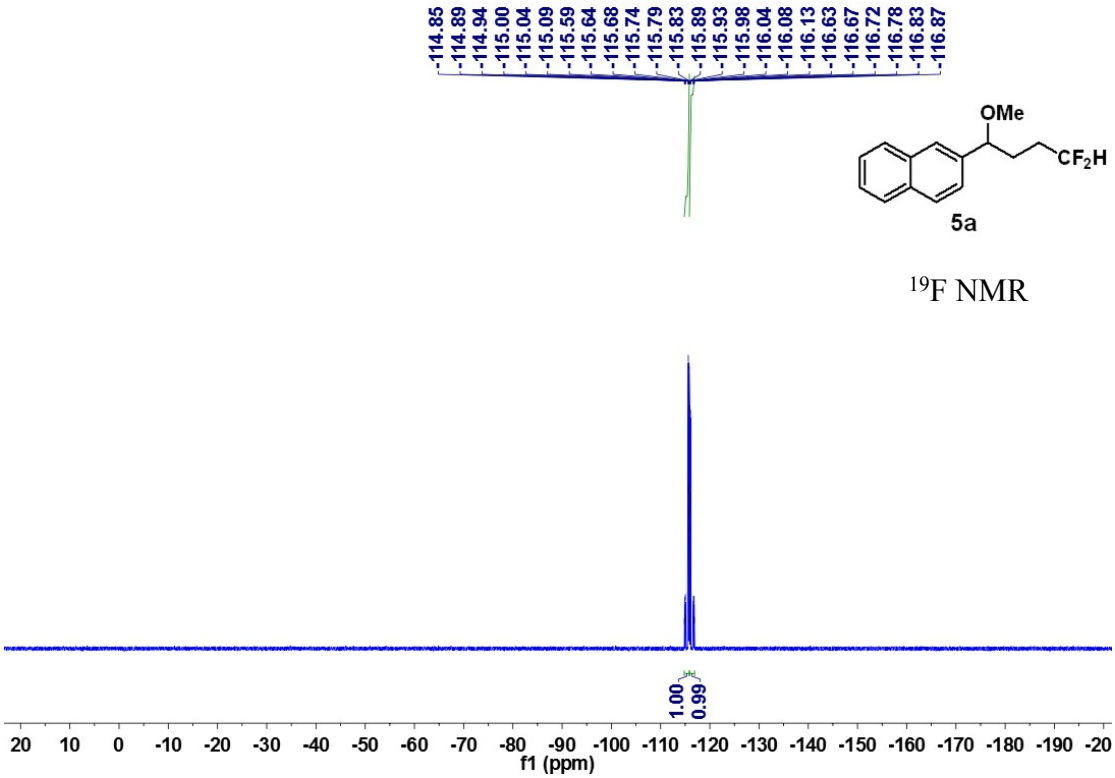


^{1}H NMR

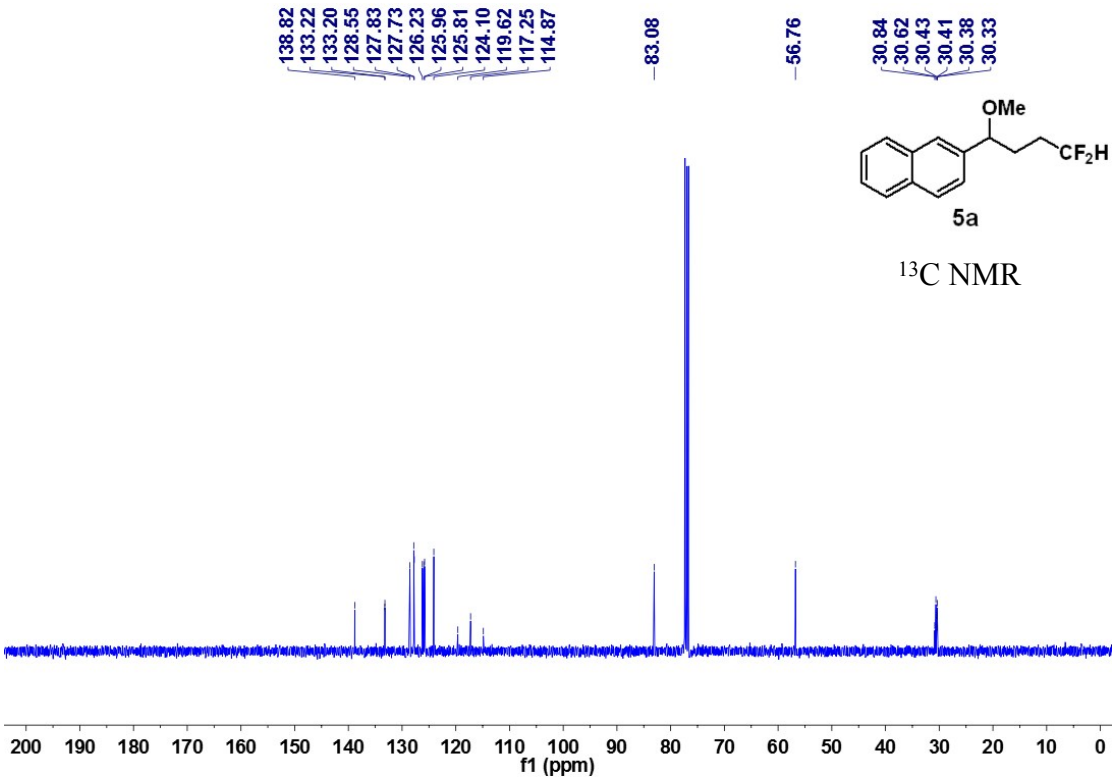
^{19}F NMR


139.17
133.20
133.17
131.45
128.70
128.56
127.82
127.73
126.25
125.96
125.57
124.02
123.21
80.32
64.33
30.77
30.54
30.51
30.48
30.46
30.20
29.91
15.24
O
CF3
4f
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

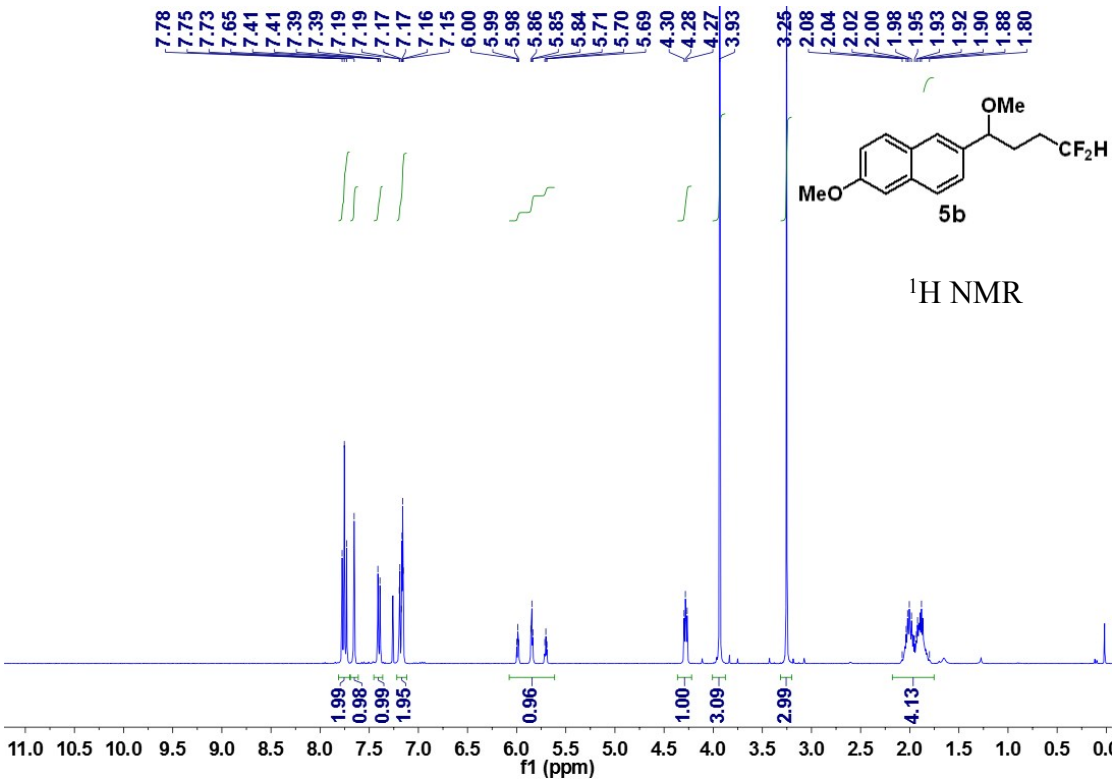

7.88
7.86
7.84
7.83
7.73
7.53
7.53
7.51
7.51
7.50
7.49
7.48
7.47
7.47
7.45
7.44
7.43
7.42
6.00
5.99
5.98
5.86
5.85
5.84
5.72
5.70
5.69
4.33
4.32
4.30
3.26
2.06
2.05
2.02
2.00
1.98
1.93
1.91
1.90
1.89
1.87
1.83
OMe
CF2H
5a
1H NMR
2.88
0.95
1.96
0.93
0.95
1.00
2.99
4.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



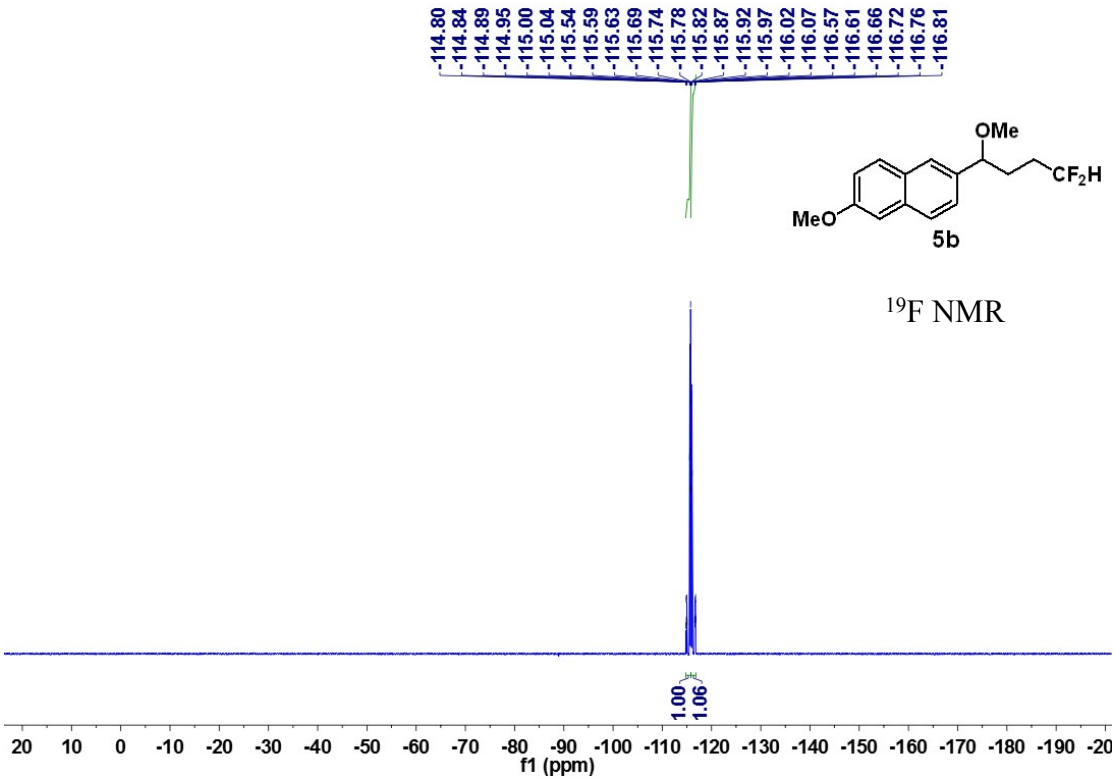
^{19}F NMR



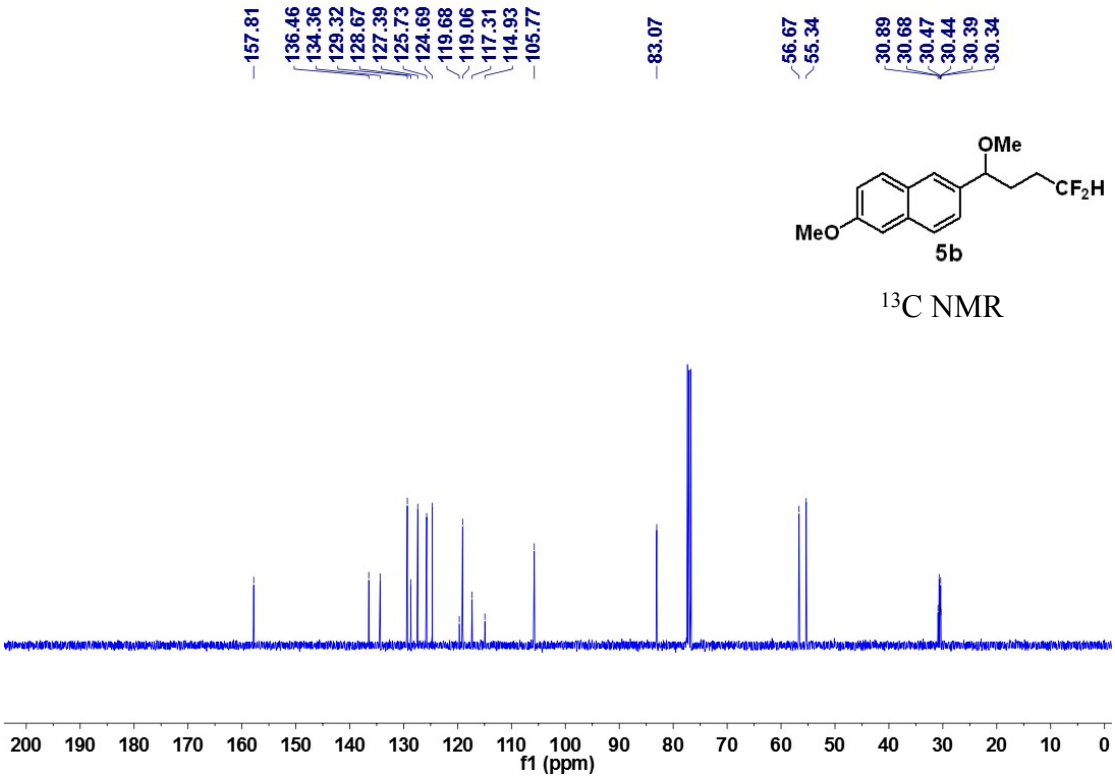
^{13}C NMR

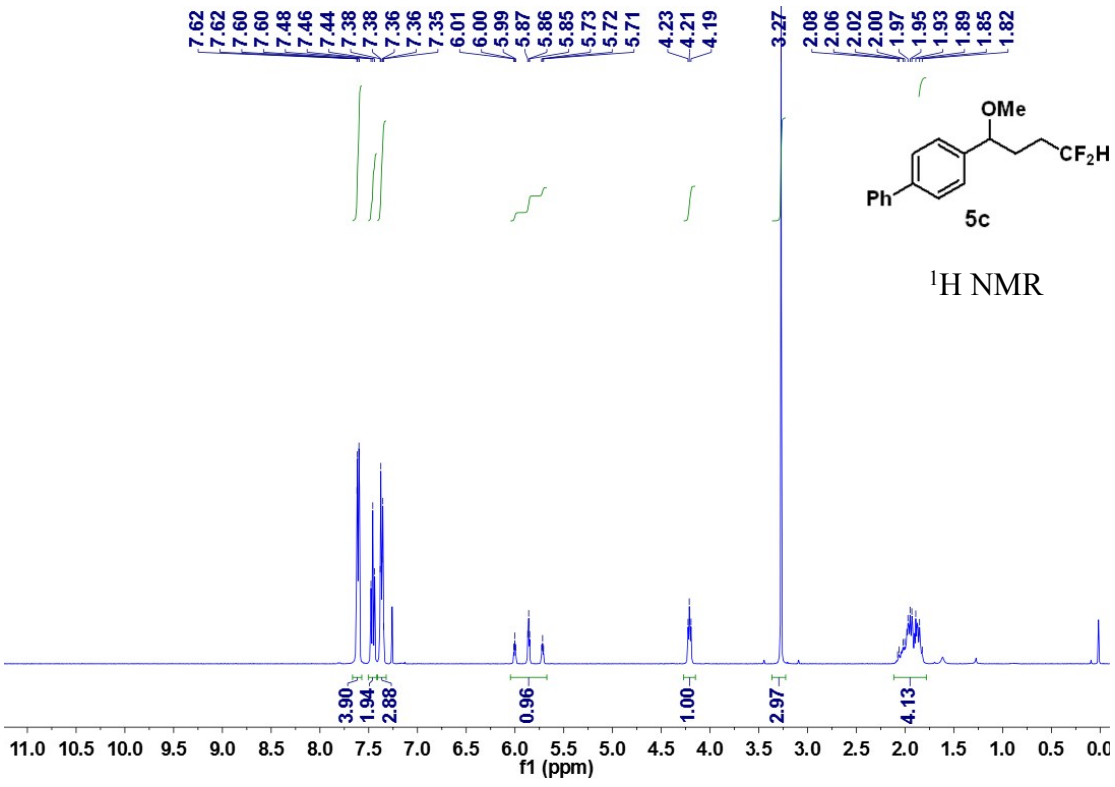


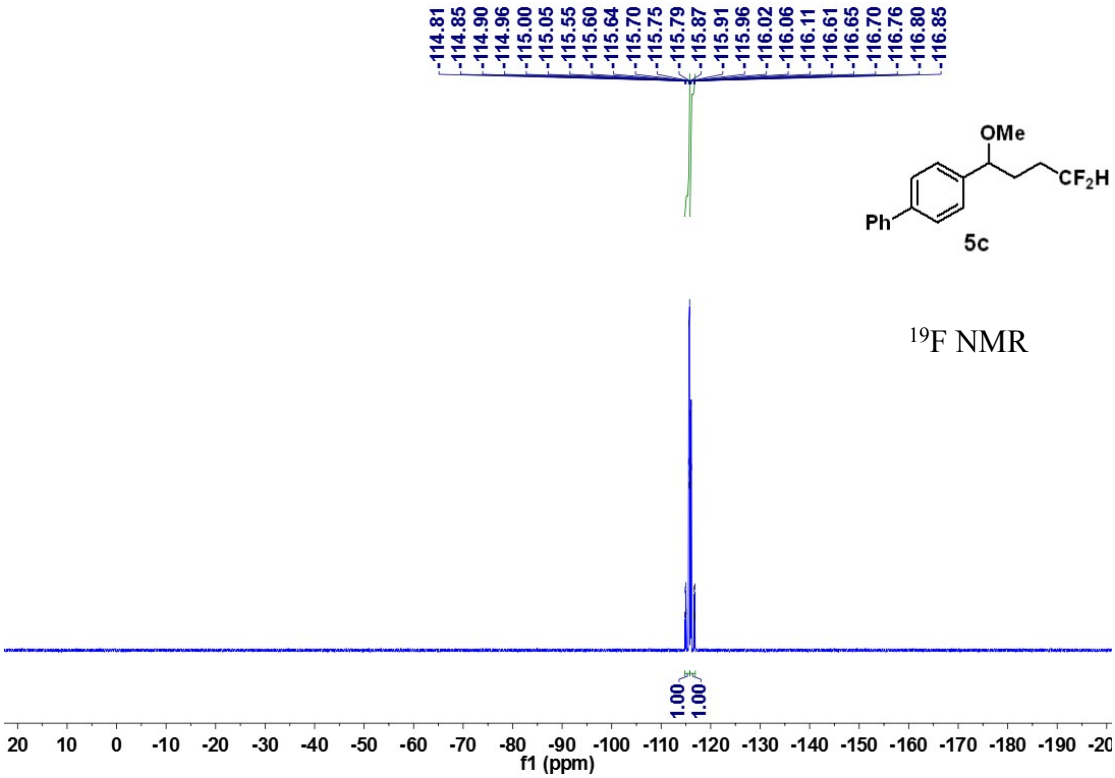
^{1}H NMR



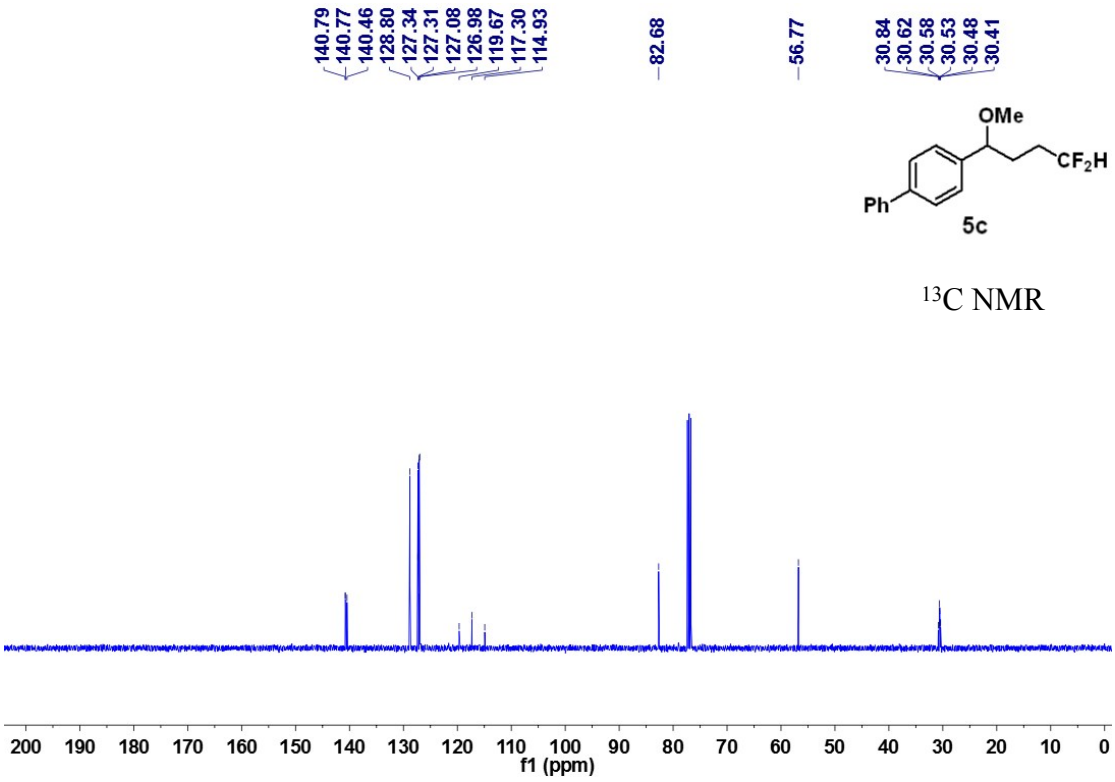
^{19}F NMR


157.81
136.46
134.36
129.32
128.67
127.39
125.73
124.69
119.68
119.06
117.31
114.93
105.77
83.07
56.67
55.34
30.89
30.68
30.47
30.44
30.39
30.34
OMe
CF2H
MeO
5b
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

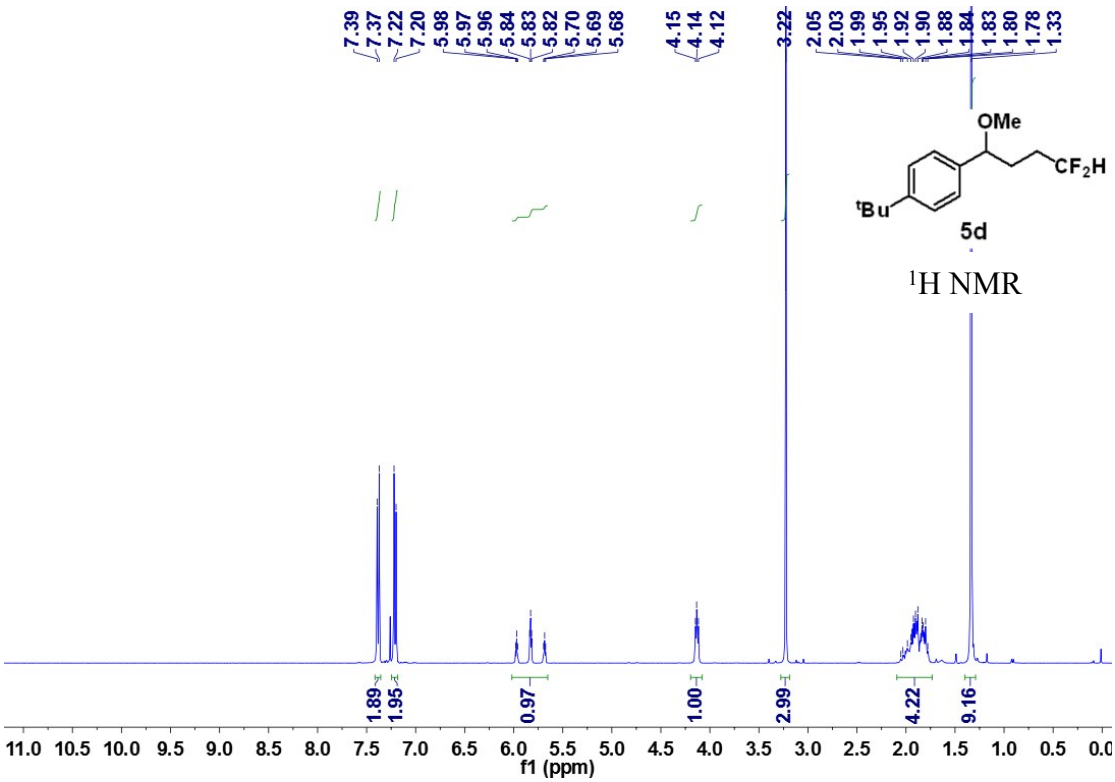

7.62
7.62
7.60
7.60
7.48
7.46
7.44
7.38
7.38
7.36
7.36
7.35
6.01
6.00
5.99
5.87
5.86
5.85
5.73
5.72
5.71
4.23
4.21
4.19
3.27
2.08
2.06
2.02
2.00
1.97
1.95
1.93
1.89
1.85
1.82
OMe
CF2H
Ph
5c
1H NMR
3.90
1.94
2.88
0.96
1.00
2.97
4.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



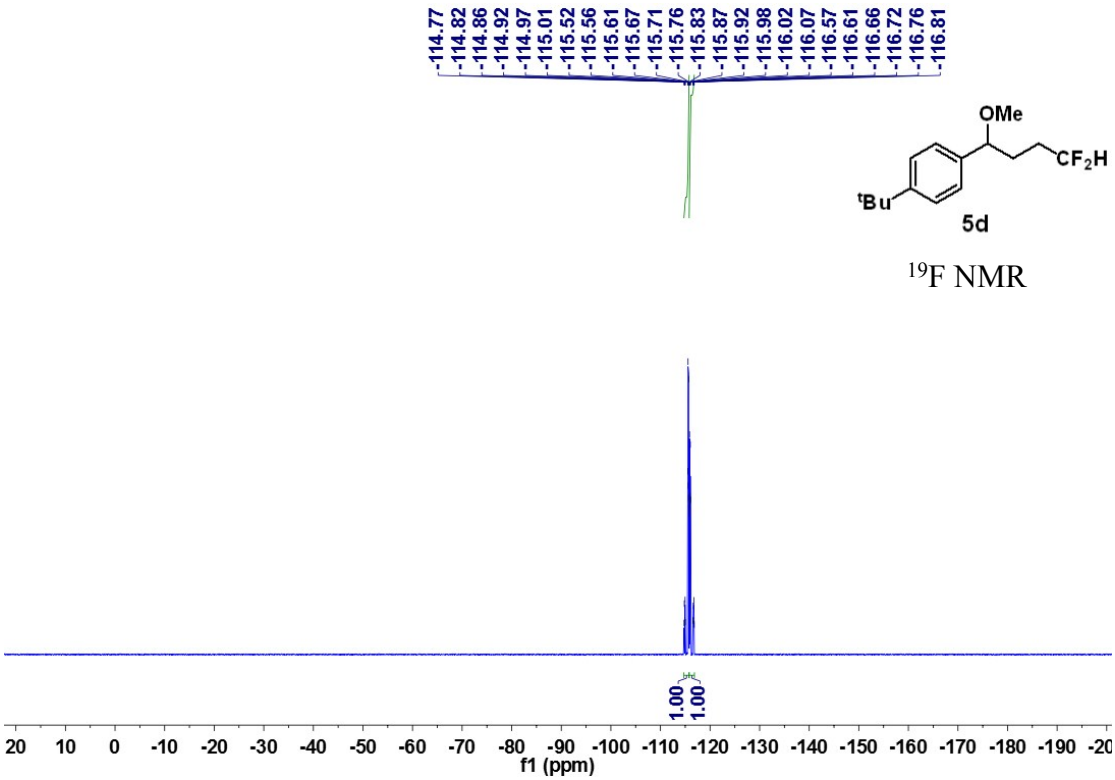
^{19}F NMR



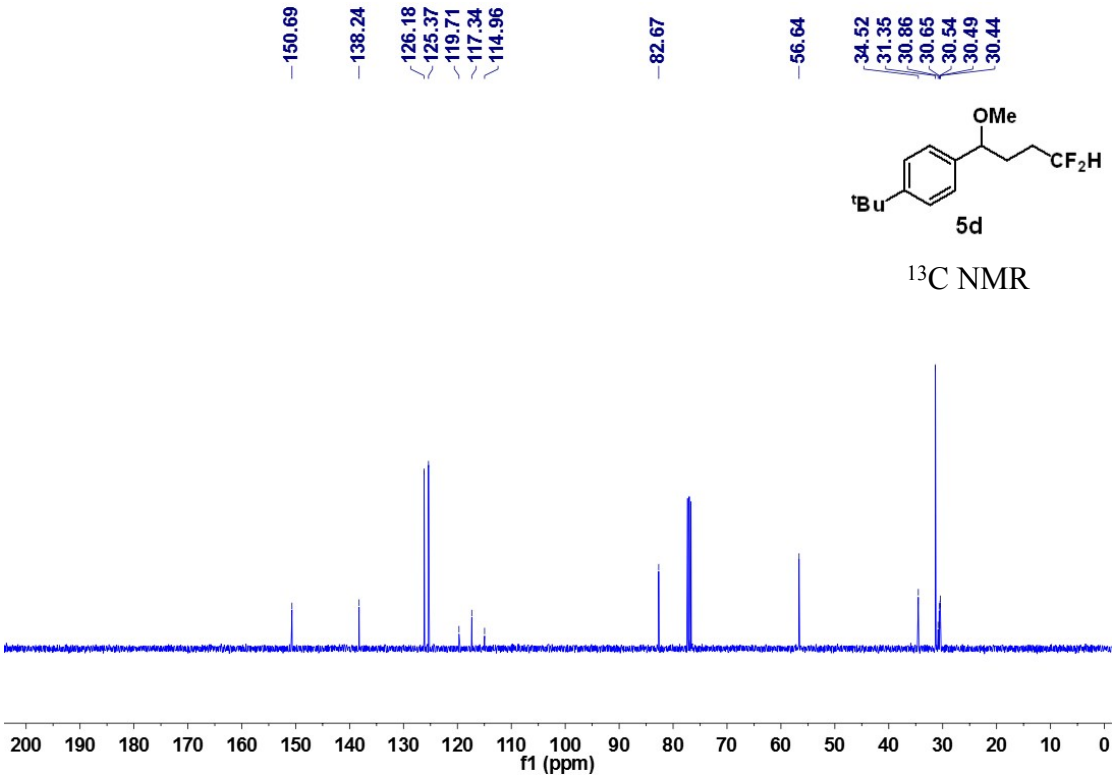
^{13}C NMR

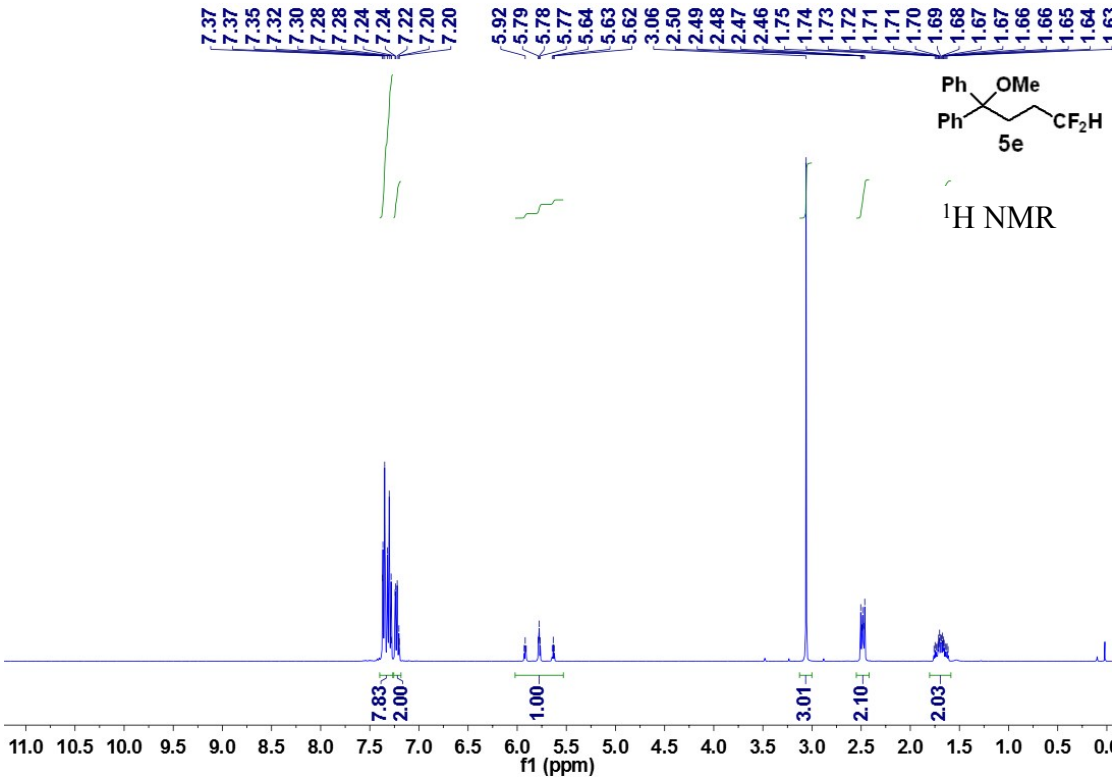


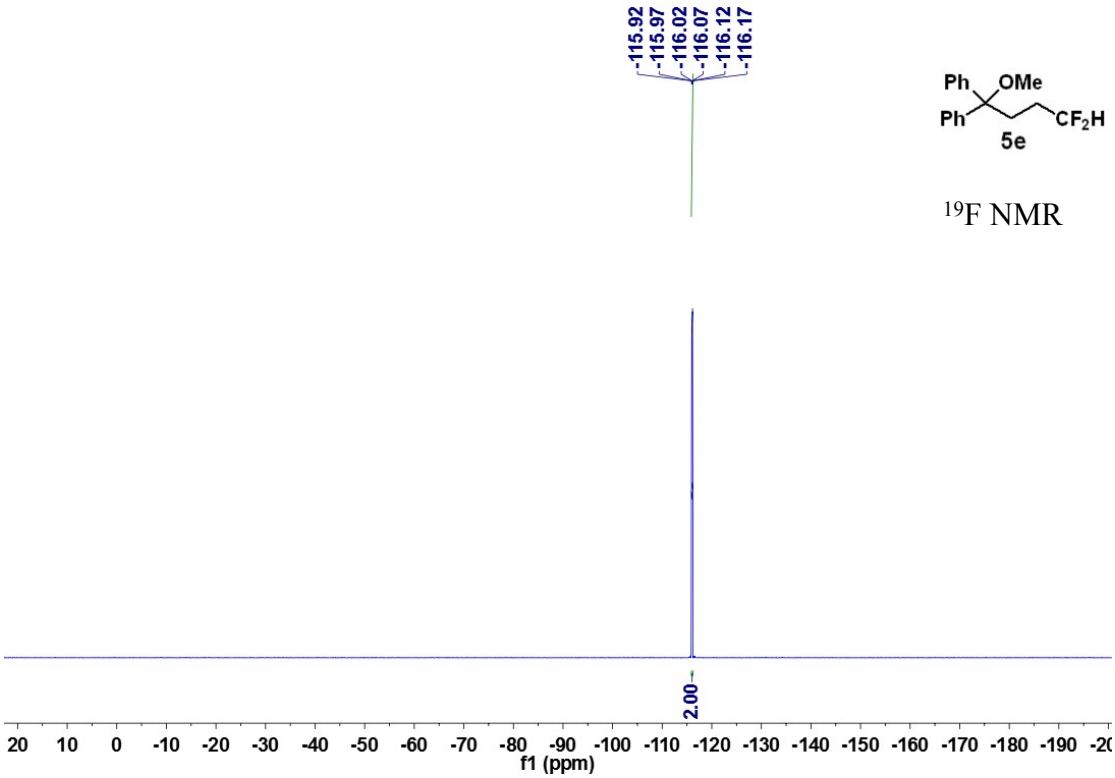
^{1}H NMR

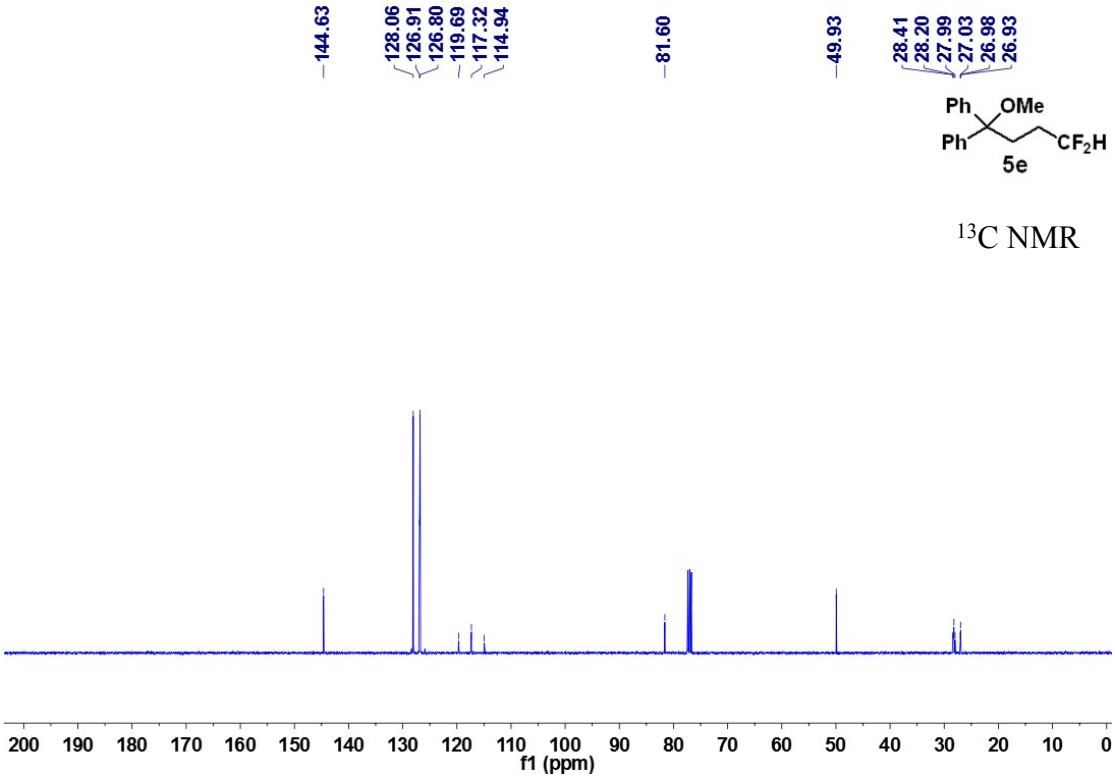


^{19}F NMR


150.69
138.24
126.18
125.37
119.71
117.34
114.96
82.67
56.64
34.52
31.35
30.86
30.65
30.54
30.49
30.44
OMe
CF2H
tBu
5d
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.37 7.37 7.35 7.32 7.30 7.28 7.28 7.24 7.24 7.22 7.20 7.20
5.92 5.79 5.78 5.77 5.64 5.63 5.62
3.06 2.50 2.49 2.48 2.47 2.46 1.75 1.74 1.73 1.72 1.71 1.71 1.70 1.69 1.68 1.67 1.67 1.66 1.66 1.65 1.64
Ph OMe
Ph
CF2H
5e
1H NMR
7.83
2.00
1.00
3.01
2.10
2.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


-115.92
-115.97
-116.02
-116.07
-116.12
-116.17
Ph
OMe
Ph
CF2H
5e
19F NMR
2.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)


144.63
128.06
126.91
126.80
119.69
117.32
114.94
81.60
49.93
28.41
28.20
27.99
27.03
26.98
26.93
Ph
OMe
Ph
CF2H
5e
13C NMR
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)