Supporting information

O-difluoromethylation of 1,3-diones with *S*-difluoromethyl sulfonium salt

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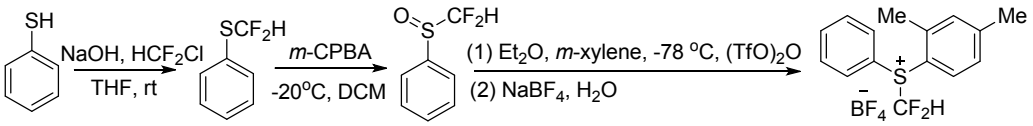
1. General Information

^{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 constants 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.

2. The Procedure for the Synthesis of compound 3



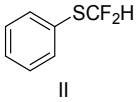
I II III **3**

Into the solution of thiophenol (32.18 g, 292.5 mmol), THF (30 mL) and H_2O (5 mL) was added sodium hydroxide (30 g, 0.75 mol). HCF_2Cl was bubbled into the system slowly at room temperature for 4 h. After the resulting mixture was further stirred for 2 h, the solid was removed by filtration. Into the filtrate were added water (30 mL) and THF (50 mL). THF phase was separated, and the aqueous phase was extracted with THF (30 mL × 2). The organic phase was combined and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by concentration in vacuo to afford **II** as a slightly yellow liquid (35.67 g, 78 %).

Into the solution of compound **II** (35.67 g, 229.3 mmol) in DCM (20 mL) was added the saturated solution of 3-chloroperbenzoic acid (46 g, 261.3 mmol) in DCM dropwise at -20 °C. The resulting mixture was further stirred at this temperature for 10 min. Saturated sodium carbonate (50 mL) was added into the reaction system. The mixture was extracted with DCM (50 mL × 3). The combined organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by concentration in vacuo, and the residue was subjected to flash column chromatography with the use of hexane/ethyl acetate (23 : 2) as eluent to afford the product **III** (30.43 g, 75 %).

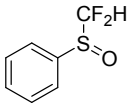
Into the solution of compound **III** (4.0 g, 22.7 mmol) and *m*-xylene (2.65 g, 25 mmol) in diethyl ether (20 mL) was added the solution of trifluoromethanesulfonic anhydride (7.0 g, 25 mmol) in diethyl ether (50 mL) dropwise at -78 °C under N_2 atmosphere for 2 h. The resulting reaction mixture was further stirred for 20 min. Two phases were observed. The upper layer phase was discarded. The residue was washed with diethyl ether (40 mL × 3), and was then dissolved in DCM (50 mL). Into the DCM solution was added aqueous solution of sodium tetrafluoroborate (1 M, 100 mL). The resulting mixture was stirred for 2 min, and then the aqueous phase was discarded (anion metathesis). This anion metathesis procedure was further repeated twice. The organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was

removed by concentration to give a white solid product **3** (4.3 g, 53 %).



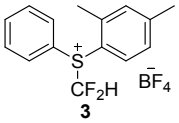
II

(Difluoromethyl)(phenyl)sulfane[1], 78 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.2 Hz, 2 H), 7.47 – 7.33 (m, 3 H), 6.83 (td, *J* = 57.0 0.5Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.39 (d, *J* = 57.0 Hz, 2 F).



III

((Difluoromethyl)sulfinyl)benzene[1], 75 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 2 H), 7.62 – 7.57 (m, 3 H), 6.02 (t, *J* = 55.4 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.25 (dd, *J* = 55.4, 13.0 Hz, 2 F).

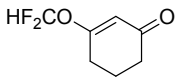


3

(Difluoromethyl)(2,4-dimethylphenyl)(phenyl) sulfonium tetrafluoroborate, white solid, 53 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (t, *J* = 52.9 Hz, 1 H), 7.85 (d, *J* = 8.0 Hz, 2 H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.72 (dd, *J* = 17.2, 8.6 Hz, 3 H), 7.40 (d, *J* = 8.6 Hz, 1 H), 7.34 (s, 1 H), 2.60 (s, 3 H), 2.43 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.45 (dd, *J* = 53.0, 3.4 Hz, 2 F), -151.44 (s, 1F), -151.49 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.88 (s), 143.52 (s), 135.59 (s), 134.28 (s), 131.86 (s), 131.71 (s), 131.37 (s), 130.53 (s), 118.74 (t, *J* = 298.2 Hz), 118.34 (s), 112.90 (s), 21.62 (s), 19.99 (s).HRMS (ESI) Calcd for $C_{15}H_{15}F_2S^+$ $[M\text{-}BF_4]^+$: 265.0857, Found: 265.0857. IR: 3389, 3058, 1601, 1583, 1476, 1446, 1438, 1377, 1275, 1234, 1100, 1033, 814, 738,715, 689, 552, 542, 533, 521, 496 cm^{-1}.

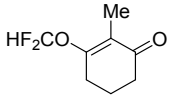
3. The Procedure for *O*-difluoromethylation

Into a mixture of salt **3** (53.6 mg, 0.15 mmol), 1,3-cyclohexanedione (**5a**, 11.2 mg, 0.1 mmol) and potassium carbonate (20.8 mg, 0.15 mmol) were added the deionized water (2.9 mg, 0.16 mmol) and dry DCM (1.5 mL) under N_2 atmosphere. The resulting mixture was stirred at room temperature for 2 h. The solvent was removed by concentration, and the residue was subjected to flash column chromatography with the use of *n*-pentane/ether (3 : 2) as eluent to afford the pure product **6a** (85%).



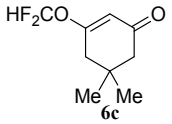
6a

3-(Difluoromethoxy)cyclohex-2-enone[4], 85 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (t, *J* = 72.0 Hz, 1 H), 5.52 (s, 1 H), 2.49 (t, *J* = 6.2 Hz, 2 H), 2.36 (t, *J* = 6.7 Hz, 2 H), 2.02 (p, *J* = 6.4 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.26 (d, *J* = 72.0 Hz, 2 F).



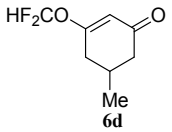
6b

3-(Difluoromethoxy)-2-methylcyclohex-2-enone[4], 70 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (t, *J* = 73.4 Hz, 1 H), 2.63-2.60 (m, 2 H), 2.46 – 2.34 (m, 2 H), 2.10 – 1.90 (m, 2 H), 1.75 (t, *J* = 1.7 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.10 (d, *J* = 73.4 Hz, 2 F).



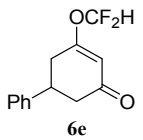
6c

3-(Difluoromethoxy)-5,5-dimethylcyclohex-2-enone[4], 86 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (t, *J* = 72.1 Hz, 1 H), 5.53 (s, 1 H), 2.34 (s, 2 H), 2.22 (s, 2 H), 1.07 (s, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.29 (d, *J* = 72.0 Hz, 2 F).



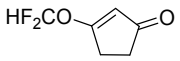
6d

3-(Difluoromethoxy)-5-methylcyclohex-2-enone[4], 71 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (t, *J* = 72.0 Hz, 1 H), 5.51 (s, 1 H), 2.58 – 2.39 (m, 2 H), 2.33 – 2.17 (m, 2 H), 2.08-2.01 (m, 1 H), 1.09 (d, *J* = 6.3 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.69 (dd, *J* = 173.6, 72.0 Hz, 1 F), -85.93 (dd, *J* = 173.6, 71.0 Hz, 1 F).



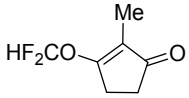
6e

5-(Difluoromethoxy)-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one[5], 76 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 –7.24 (m, 5 H), 6.53 (t, *J* = 72.0 Hz, 1 H), 5.63 (s, 1 H), 3.48 – 3.23 (m, 1 H), 2.87 – 2.32 (m, 4 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -84.88 (dd, *J* = 173.1, 72.3 Hz 1 F), -86.54 (dd, *J* = 173.0, 70.9 Hz, 1 F).



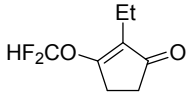
6f

3-(Difluoromethoxy)cyclopent-2-enone[4] , 0.3 mmol scale was used, 76 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (t, *J* = 71.6 Hz, 1H), 5.55 (s, 1 H), 2.87 – 2.65 (m, 2 H), 2.61 – 2.42 (m, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.79 (d, *J* = 71.5 Hz, 2 F).



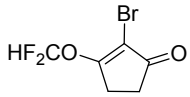
6g

3-(Difluoromethoxy)-2-methylcyclopent-2-enone[3], 69 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (t, *J* = 72.2 Hz, 1 H), 2.81 – 2.75 (m, 2 H), 2.55 – 2.50 (m, 2 H), 1.68 (t, *J* = 1.9 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.33 (d, *J* = 72.3 Hz, 2 F).



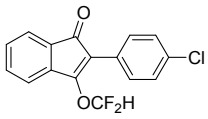
6h

3-(Difluoromethoxy)-2-ethylcyclopent-2-enone[4], 84 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65 (t, *J* = 72.3 Hz, 1 H), 2.83 – 2.65 (m, 2 H), 2.64 – 2.43 (m, 2 H), 2.18 (q, *J* = 7.6 Hz, 2 H), 1.00 (t, *J* = 7.6 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.39 (d, *J* = 72.3 Hz, 2 F).



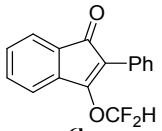
6i

2-Bromo-3-(difluoromethoxy)cyclopent-2-enone[4], 79 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (t, *J* = 70.9 Hz, 1 H), 3.07 – 2.87 (m, 2 H), 2.78 – 2.61 (m, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.48 (d, *J* = 70.9 Hz, 2 F).



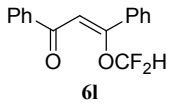
6j

2-(4-Chlorophenyl)-3-(difluoromethoxy)-1H-inden-1-one, Red solid, 77 %, M.P.: 71.8 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2 H), 7.53 (d, *J* = 7.3 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.40 (d, *J* = 8.1 Hz, 2 H), 7.37 – 7.27 (m, 2 H), 6.64 (t, *J* = 72.4 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.35 (d, *J* = 72.4 Hz, 2 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.73 (s), 163.91 (t, *J* = 2.9 Hz), 138.78 (s), 134.72 (s), 133.77 (s), 130.64 (s), 130.43 (s), 130.25 (s), 128.92 (s), 126.90 (s), 122.75 (s), 119.64 (t, *J* = 1.4 Hz), 117.69 (s), 114.60 (t, *J* = 264.0 Hz). HRMS (EI) Calcd for $C_{16}H_9F_2O_2Cl$, $[M]^+$: 306.0259, Found: 306.0254. IR (KBr): 3060, 1715, 1588, 1491, 1457, 1364, 1309, 1123, 1074, 1036, 913, 841, 756, 698, 597, 511 cm^{-1}.



6k

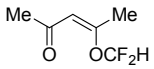
3-(Difluoromethoxy)-2-phenyl-1H-inden-1-one, Red solid, 76 %, M.P.: 97.8 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56– 7.53 (m, 3 H), 7.47 – 7.41 (m, 3 H), 7.38 – 7.30 (m, 3 H),6.65 (t, *J* = 72.1 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.67 (d, *J* = 72.1 Hz, 2F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.09 (s), 163.75 (t, *J* = 2.9 Hz), 139.12 (s), 133.62 (s), 130.27 (s), 130.24 (s), 129.47 (s), 128.69 (s), 128.68 (s), 128.46 (s), 122.58 (s), 119.45 (t, *J* = 1.0 Hz), 118.20 (s), 114.51 (t, *J* = 263.3 Hz). HRMS (EI) Calcd for $C_{16}H_{10}F_2O_2$, $[M]^+$: 272.0649, Found: 272.0648, IR (KBr): 3072, 1712, 1620, 1589, 1490, 1458, 1370, 1321, 1299, 1216, 1086, 1033, 1014, 947,872, 829, 793,764,741, 724, 629, 461 cm^{-1}.



6l

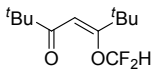
(*Z*)-3-(Difluoromethoxy)-1,3-diphenylprop-2-en-1-one,wite solid, 79 %. M.P.: 72.6 °C. Only *Z*-isomer was observed before isolation. But after isolation, both *Z*- and *E*- isomers were observed. *Z* : *E* = 76:24, Characterization data of *Z*-isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2 H), 7.80 – 7.72 (m, 2 H), 7.62 (tt, *J* = 7.3, 1.3 Hz, 1 H), 7.51 – 7.41 (m, 5 H), 7.03 (s, 1 H), 6.89 (t, *J* =

75.3 Hz, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.20 (d, *J* = 75.2 Hz, 2 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.80 (s), 157.12 (s), 138.20 (s), 133.93 (s), 133.20 (s), 131.38 (s), 128.90 (s), 128.69 (s), 128.41 (s), 127.16 (s), 116.81 (t, *J* = 261.6 Hz), 109.80 (s). HRMS (EI) Calcd for $C_{16}H_{12}F_2O_2$, $[M]^+$: 274.0805, Found: 274.0804, IR (KBr): 3061, 1665, 1599, 1574, 1493, 1448, 1351, 1271, 1213, 1119, 1055, 913, 846, 769, 689, 591 cm^{-1}.



6m

(*Z*)-4-(Difluoromethoxy)pent-3-en-2-one，0.3 mmol scales was used, colorless oil, 30 %. Only *Z*-isomer was observed before isolation. But after isolation, both *Z*- and *E*- isomers were observed. *Z* : *E* = 82 : 18, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (t, *J* = 73.8 Hz, 1 H), 5.45 (s, 1 H), 2.32 (s, 3 H), 2.11 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.74 (d, *J* = 73.8 Hz, 2 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.67 (s), 156.17 (t, *J* = 2.4 Hz), 115.35 (s), 114.61 (t, *J* = 261.6 Hz), 31.34 (s), 20.41 (s). HRMS (EI) Calcd for $C_6H_8F_2O_2$, $[M]^+$: 150.0492, Found: 150.0497. IR (KBr): 2921, 2849, 1725,1639, 1562, 1544, 1509, 1460, 1408, 1188, 799, 763, 750, 688, 659 cm^{-1}.



6n

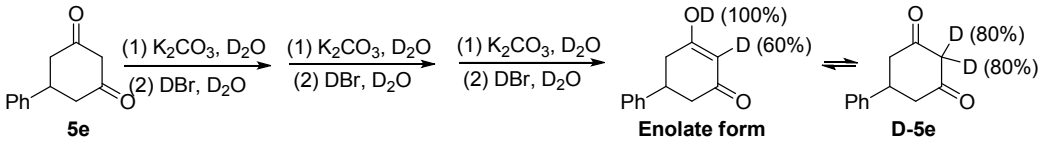
(*Z*)-5-(Difluoromethoxy)-2,2,6,6-tetramethylhept-4-en-3-one, 0.3 mmol scales was used, colorless oil, 68 %, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (t, *J* = 76.0 Hz, 1 H), 6.06 (s, 1 H), 1.17 (s, 9 H), 1.14 (s, 9 H)., ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.98 (d, *J* = 76.0 Hz, 2 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.01 (s), 168.89 (t, *J* = 2.5 Hz), 116.65 (t, *J* = 259.3 Hz), 103.21 (s), 44.26 (s), 37.98 (s), 27.88 (s), 26.47 (s). HRMS (EI) Calcd for $C_{12}H_{20}F_2O_2$, $[M]^+$: 234.1431, Found: 234.1434. IR (KBr): 2962,1260,1188, 1149, 1084, 1021, 799, 763,750,688, 659 cm^{-1}.

4. The procedure for the preparation of compound D-5e

Into a mixture of 5-phenylcyclohexane-1,3-dione (377 mg, 2 mmol) and potassium carbonate (277mg, 2mmol) was added deuterated water (1.5mL) under N_2 atmosphere. The resulting mixture was stirred at room temperature for 20 min. Dry THF (5 mL) and a solution of deuterium bromide in D_2O (2 M, 0.5 mL) were added to quench the reaction. Two phases were observed. The upper layer phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was

removed by concentration to give partially deuterated 5-phenylcyclohexane-1,3-dione.

The deuteration of the above partially deuterated 5-phenylcyclohexane-1,3-dione was repeated twice to afford the final deuterated 5-phenylcyclohexane-1,3-dione (**D-5e)** (331 mg, 88 % yield, 80 % deuterated).

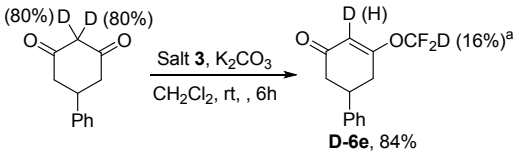


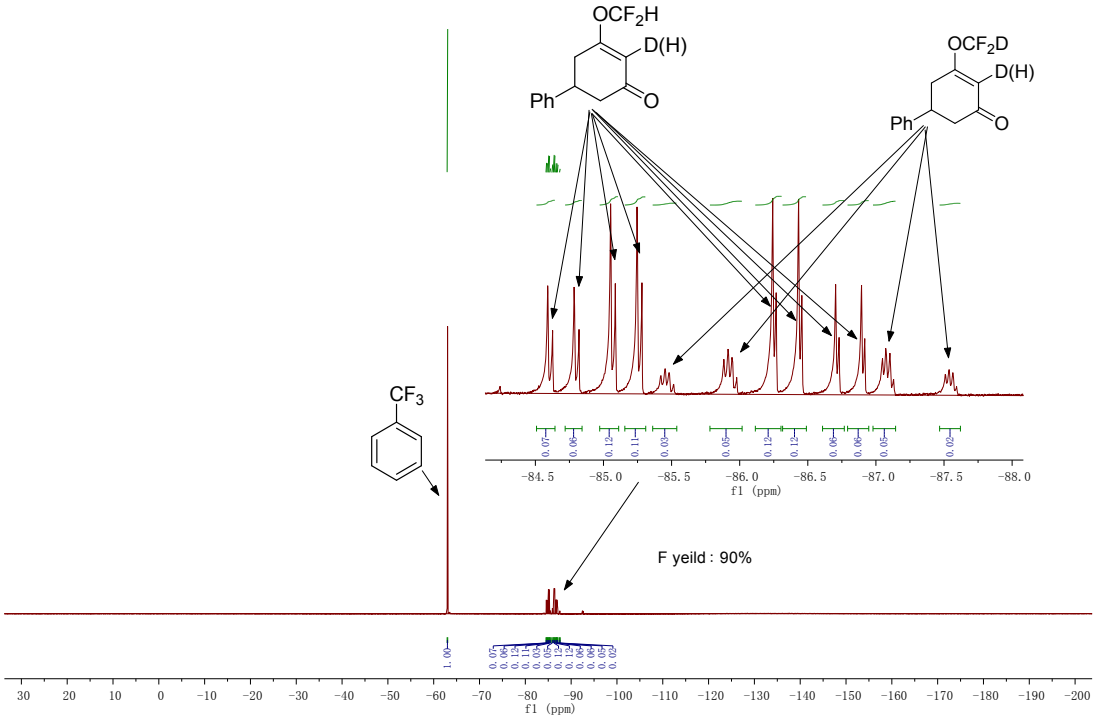
Poor solubility of **D-5e** in $CDCl_3$ was observed. The ^1H NMR spectrum of **D-5e** in D-DMSO reveals that only enolate form was observed. The characterization data of **D-5e** in D-DMSO is shown as follows. ^1H NMR (400 MHz, DMSO) δ 7.31 – 7.24 (m, 4 H), 7.23 – 7.17 (m, 1 H), 5.24 (s, 0.4 H), 3.31 – 3.23 (m, 1 H), 2.59 – 2.52 (m, 2 H), 2.38 – 2.32 (m, 2 H). ^{13}C NMR (126 MHz, DMSO) δ 187.43 (br), 172.41 (s). 144.03 (s), 128.91 (s), 127.35 (s), 127.01 (s), 103.68 (t, J = 20.3 Hz), 39.21 (s), 25.59 (s), 21.48 (s). IR (KBr):2922, 2348, 1622, 1555, 1371, 1247, 1187, 1141, 1099, 1060, 996, 862, 834, 752, 696, 646, 555, 489cm^{-1}, HRMS (EI) Calcd for $C_{12}H_{11}DO_2$: 189.0900, Found: 189.0893; $C_{12}H_{10}D_2O_2$: 190.0963, Found: 190.0966.

5. The *O*-difluoromethylation of compound D-5e

(1) *O*-difluoromethylation without water

Into the mixture of **D-5e** (18.8 mg, 0.1 mmol), salt **3** (54.3 mg, 0.15 mmol) and potassium carbonate (20.7mg 0.15mmol) was added dry DCM (1.5 mL) under N_2 atmosphere. The resulting mixture was stirred at room temperature for 6 h. The solvent was removed by concentration, and the residue was subjected to flash column chromatography with the use of *n*-pentane/ether (3:2) to afford the product **D-6e** (84 % yield, 16 % deuterated).

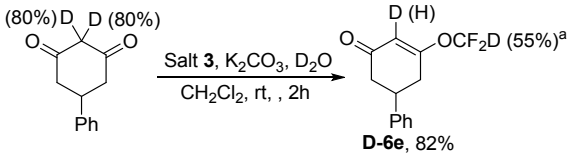


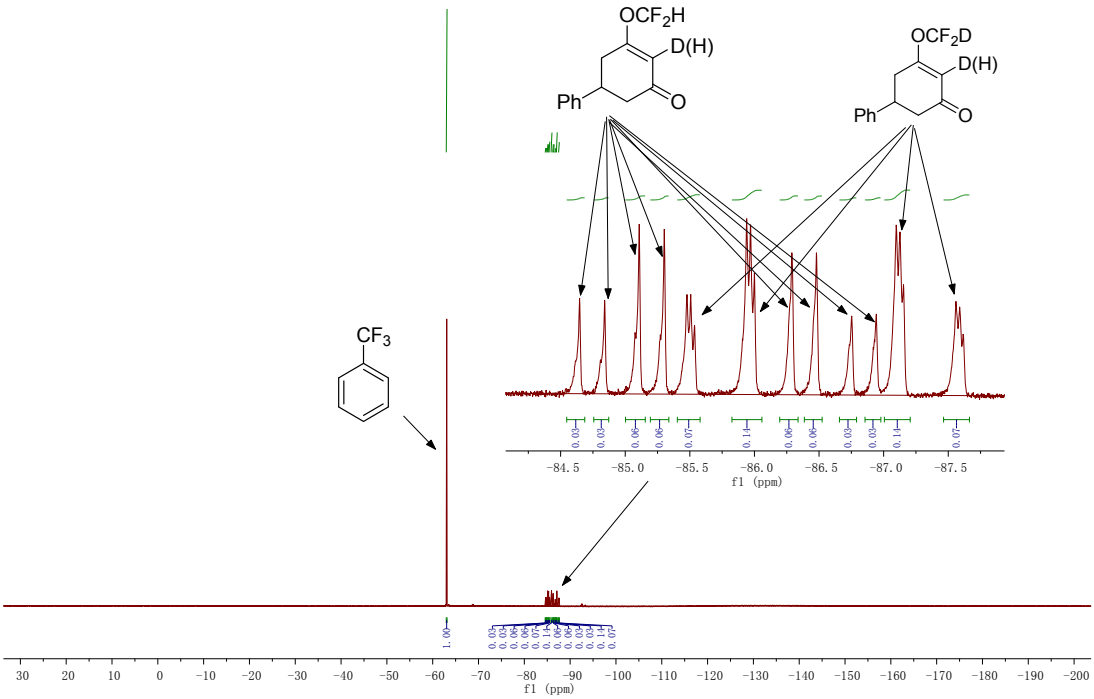


Scheme 1 ^{19}F NMR spectra of the reaction mixture with the use of trifluoromethylbenzene as an internal standard.

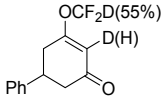
(2) *O*-difluoromethylation in the presence of D_2O

Into the mixture of **D-5e** (18.8 mg, 0.1 mmol), salt **3** (54.5 mg, 0.15 mmol) and potassium carbonate (20.6 mg 0.15 mmol) were added D_2O (3 mg, 0.15 mmol) and dry DCM (1.5 mL) under N_2 atmosphere. The resulting mixture was stirred for 2 h. The solvent was removed by concentration, and the residue was subjected to flash column chromatography to afford the product **D-6e** (82 % yield, 55 % deuterated).





Scheme 2 ^{19}F NMR spectra of the reaction mixture with the use of trifluoromethylbenzene as an internal standard.

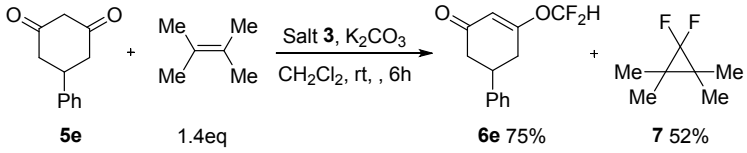


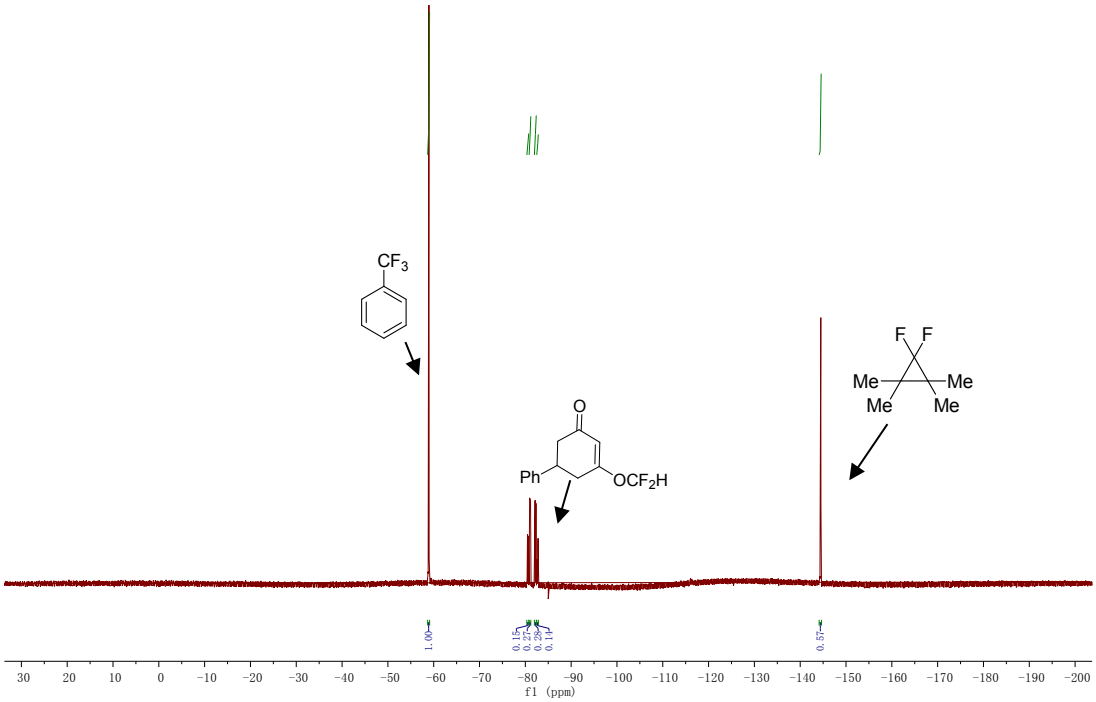
D-6e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2 H), 7.31 – 7.18 (m, 3 H), 6.54 (t, *J* = 71.8, Hz, 0.45 H), 5.63 (s, 0.15 H), 3.44 – 3.35 (m, 1 H), 2.80 – 2.55 (m, 4 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.33 (dt, *J* = 173.8, 10.8 Hz, 1 F), -86.85 (dt, *J* = 173.8, 10.8 Hz, 1 F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.61 (s), 168.73 (t, *J* = 3.1 Hz), 141.75 (s), 128.97 (s), 127.40 (s), 126.62 (s), 113.66 (tt, *J* = 259.9, 33.8 Hz), 107.96 (t, *J* = 24.6 Hz), 43.56 (s), 38.90 (s), 35.43 (s). ^{2}D NMR (61 MHz, CH_2Cl_2) δ 6.57 (t, *J* = 10.9 Hz, 1 D), 5.62 (s, 1.15 D). IR (KBr):1672, 1612, 1496, 1454, 1427, 1374, 1341, 1299, 1189,1128, 1079, 971, 910, 795, 757, 699, 628, 470cm^{-1}. HRMS (EI) Calcd for $C_{13}H_{11}D_1F_2O_2$: 239.0868, Found: 239.0872, $C_{13}H_{10}D_2F_2O_2$: 240.0931, Found: 240.0929.

6. The trap of difluorocarbene

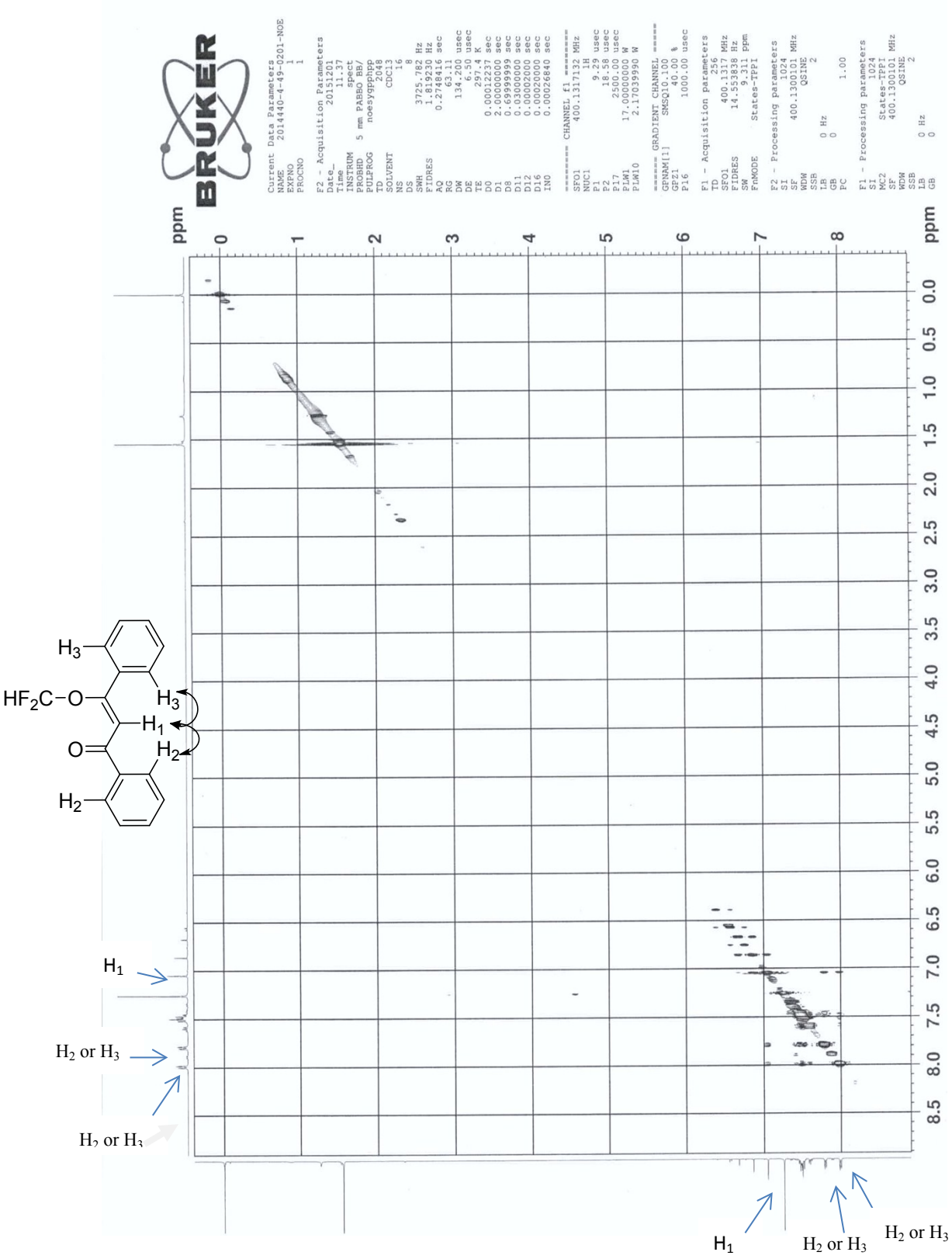
Into a mixture of **D-5e** (18.8 mg, 0.1 mmol), salt **3** (54.4 mg, 0.15 mmol) and potassium carbonate (20.6 mg 0.15 mmol) were added 2,3-dimethyl-2-butene (11.8mg, 0.14mmol) and dry DCM (1.5 mL) under N_2 atmosphere. The resulting mixture was stirred for 6 h. The yields of compounds **6e** and **7** were determined by ^{19}F NMR with the use of trifluoromethylbenzene as an internal standard (the spectrum is shown as follows).



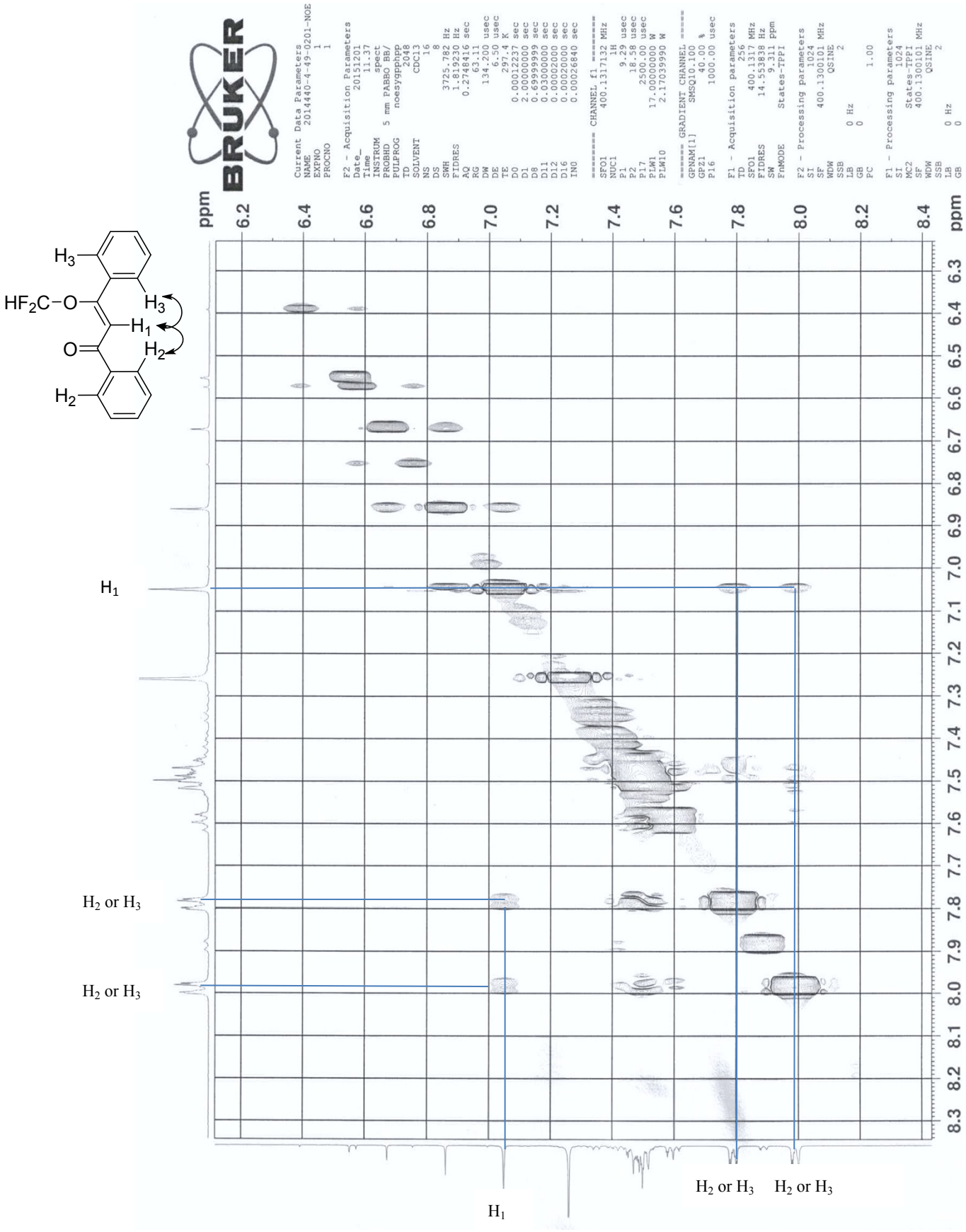


Scheme 3 ^{19}F NMR spectra of the reaction mixture with the use of trifluoromethylbenzene as an internal standard.

7. The determination of the configuration of product 6l

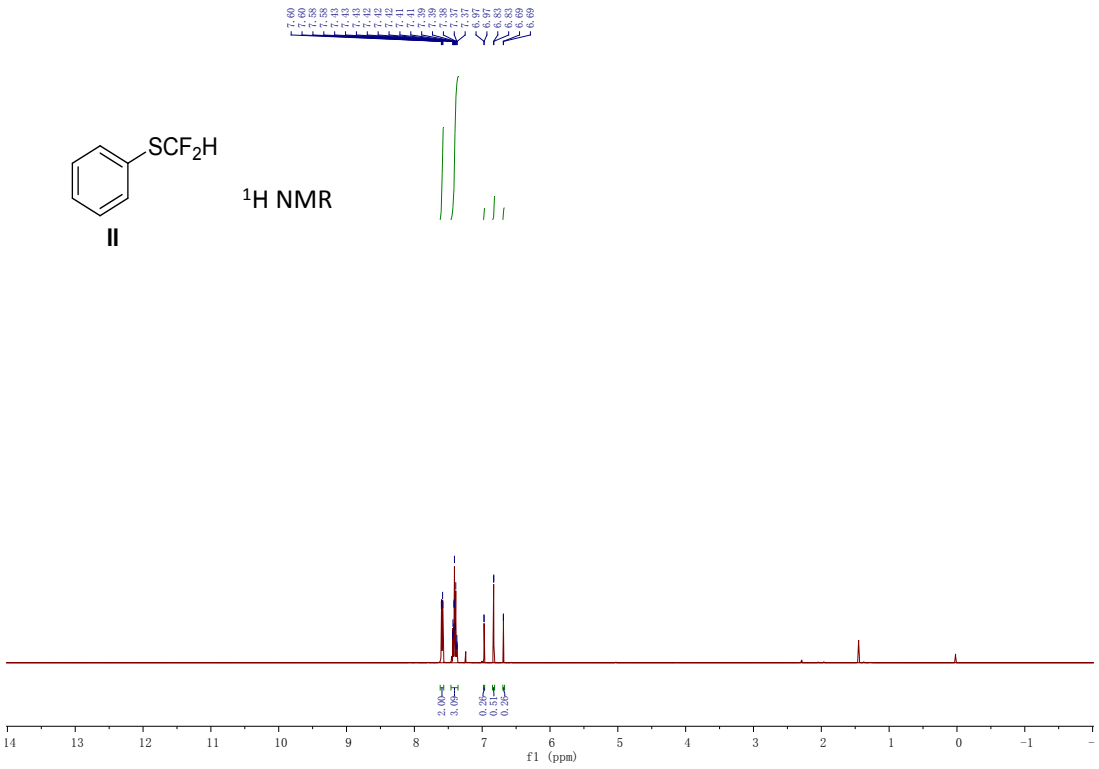


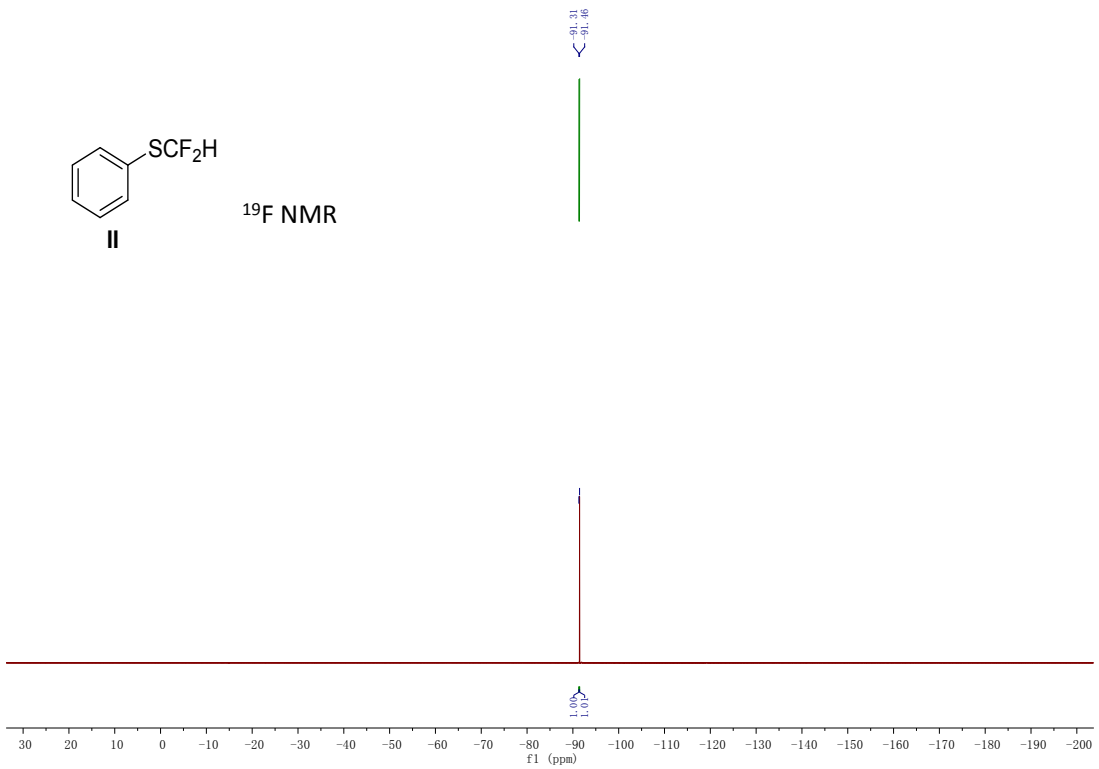
NOE spectrum of **6l**

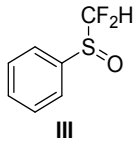


NOE spectrum of **6l**

8. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of compounds 3 and 6

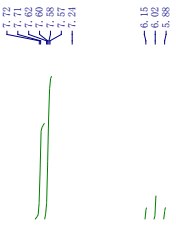


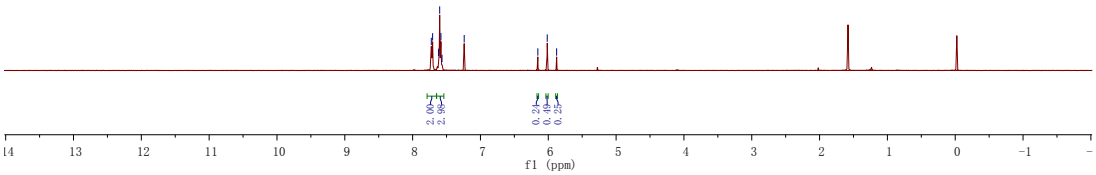


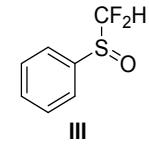


III

^{1}H NMR

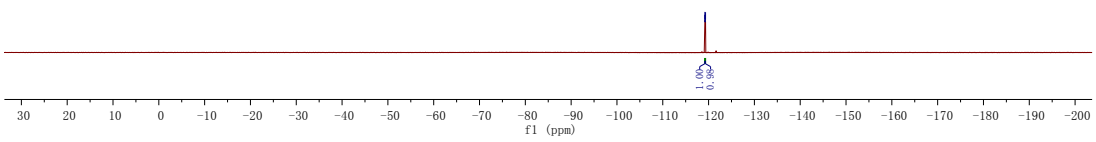


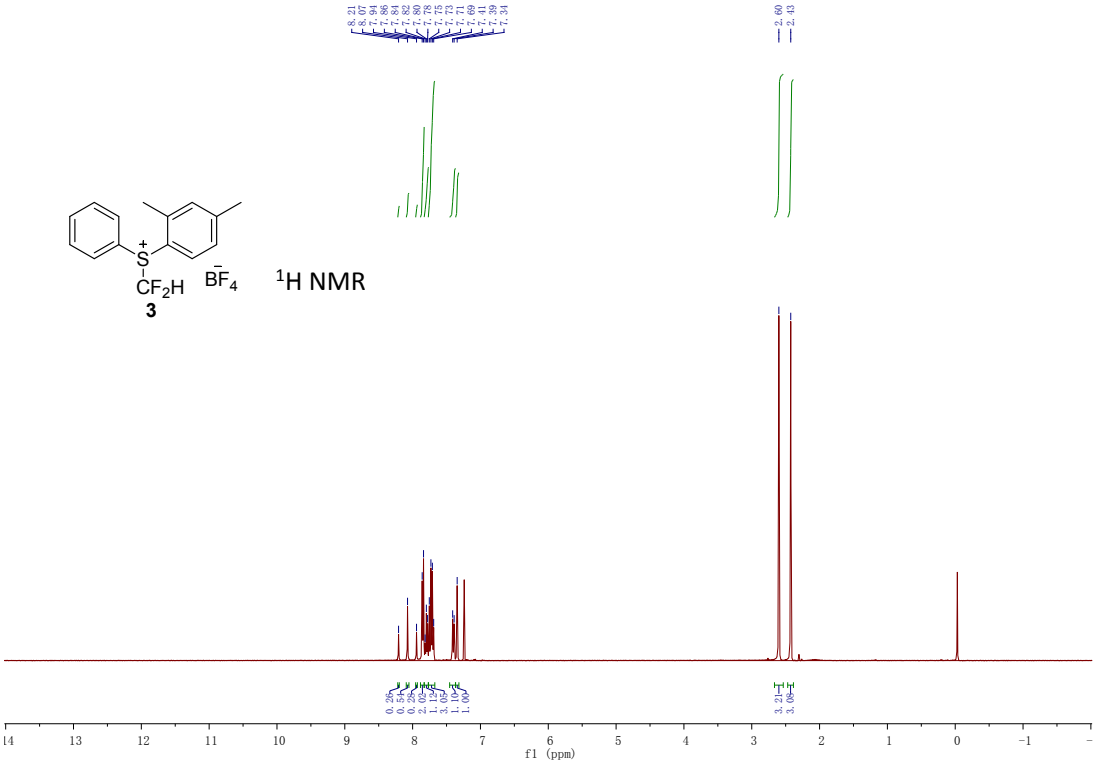




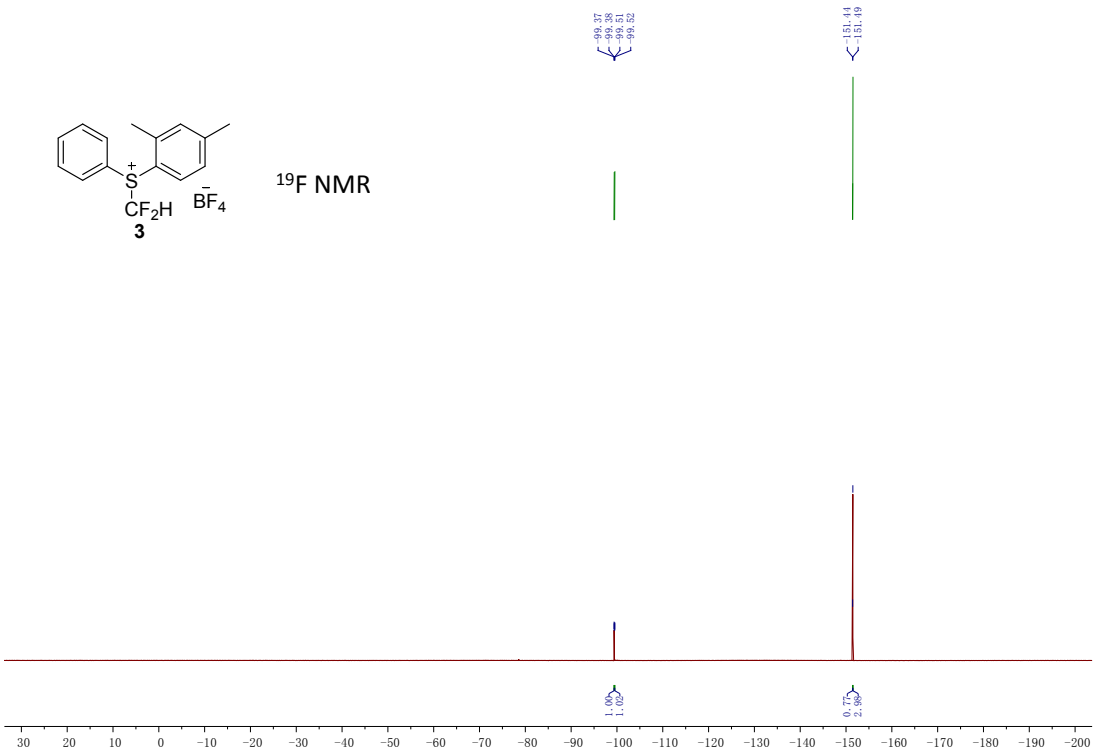
III

^{19}F NMR

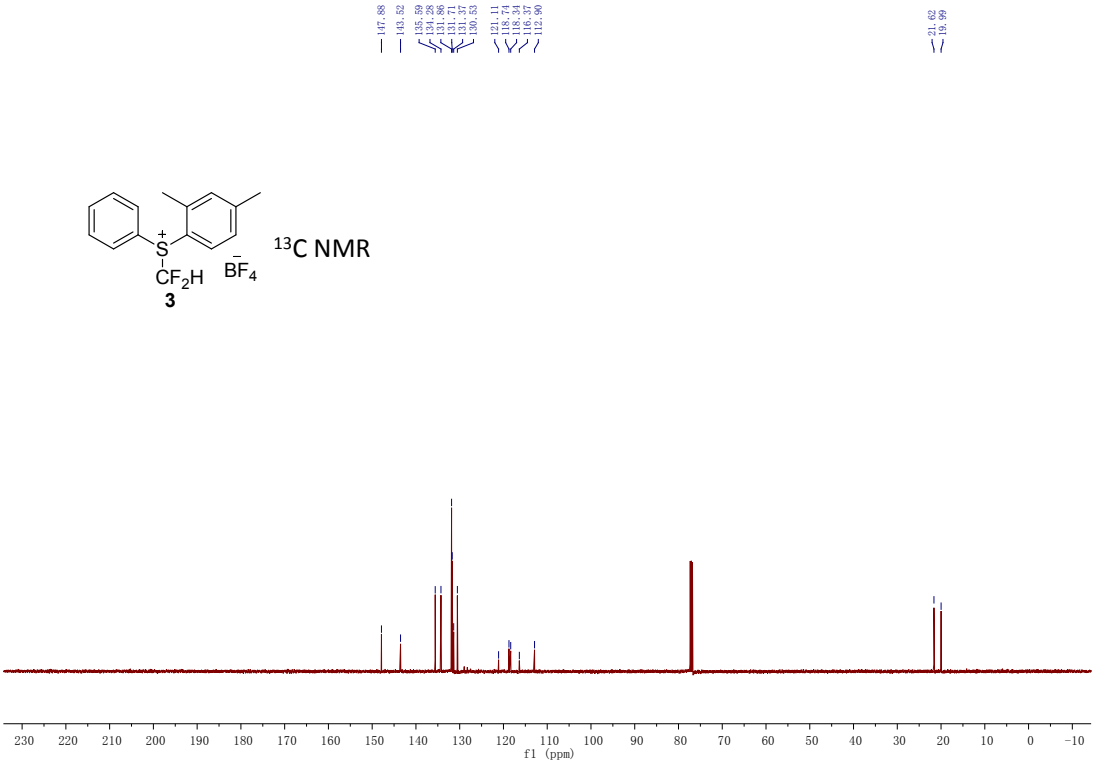


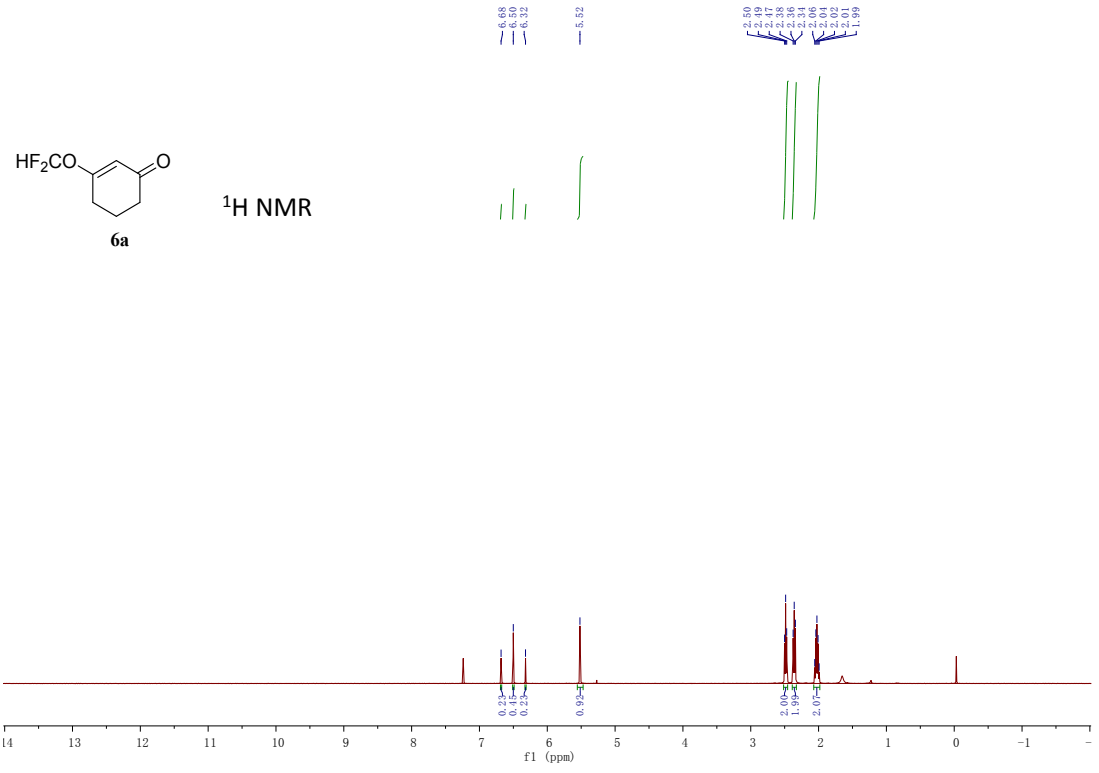


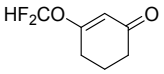
^{1}H NMR



^{19}F NMR

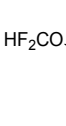

147.88
143.52
135.59
134.28
131.86
131.71
131.37
130.53
121.11
118.74
116.34
112.90
21.62
19.99
S
CF2H
BF4
3
13C NMR
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


6.68
6.50
6.32
5.52
2.50
2.49
2.47
2.38
2.36
2.34
2.06
2.04
2.02
2.01
1.99
HF2CO
O
6a
1H NMR
0.23
0.45
0.23
0.92
2.00
1.99
2.07
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)



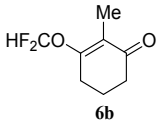
6a

^{19}F NMR



6b

^{1}H NMR

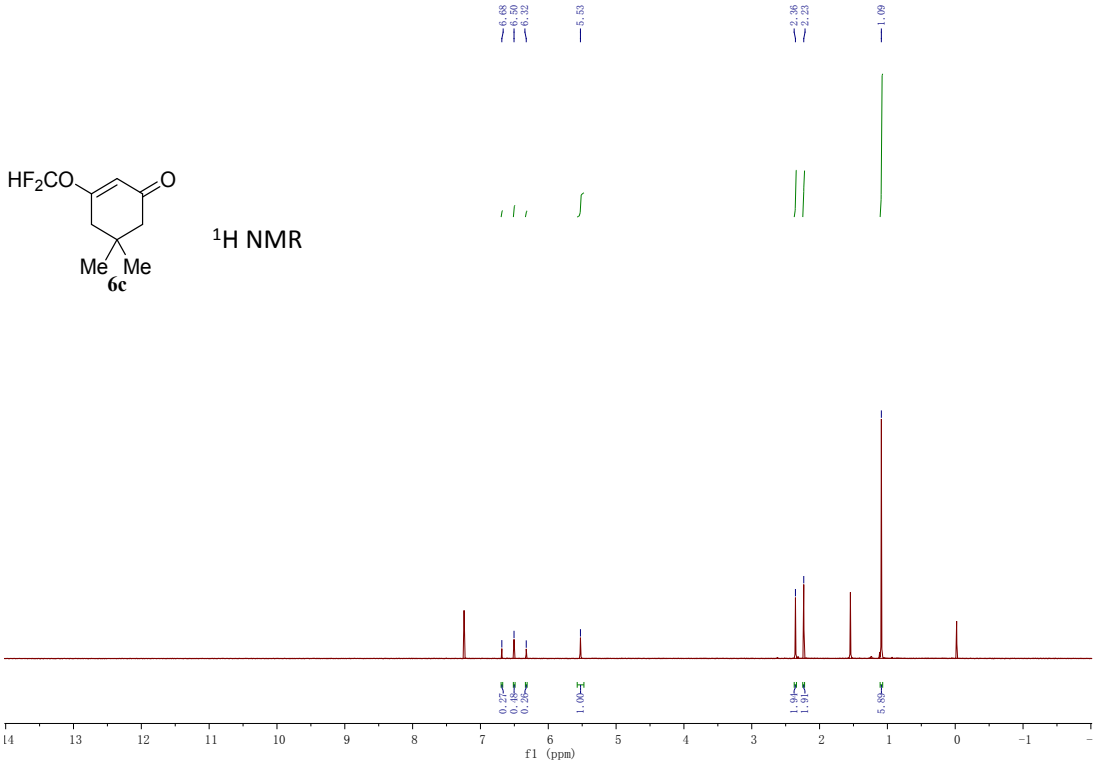


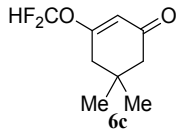
6b

^{19}F NMR

6c

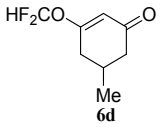
^{1}H NMR





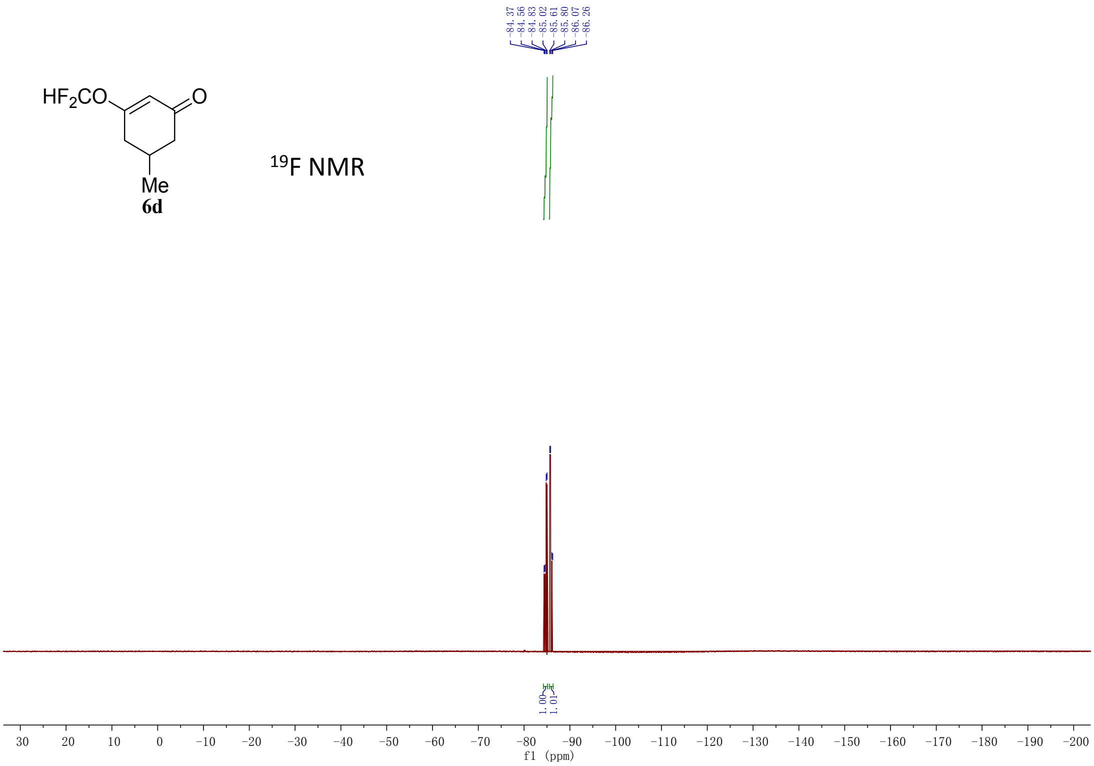
6c

^{19}F NMR



6d

^{1}H NMR



6d

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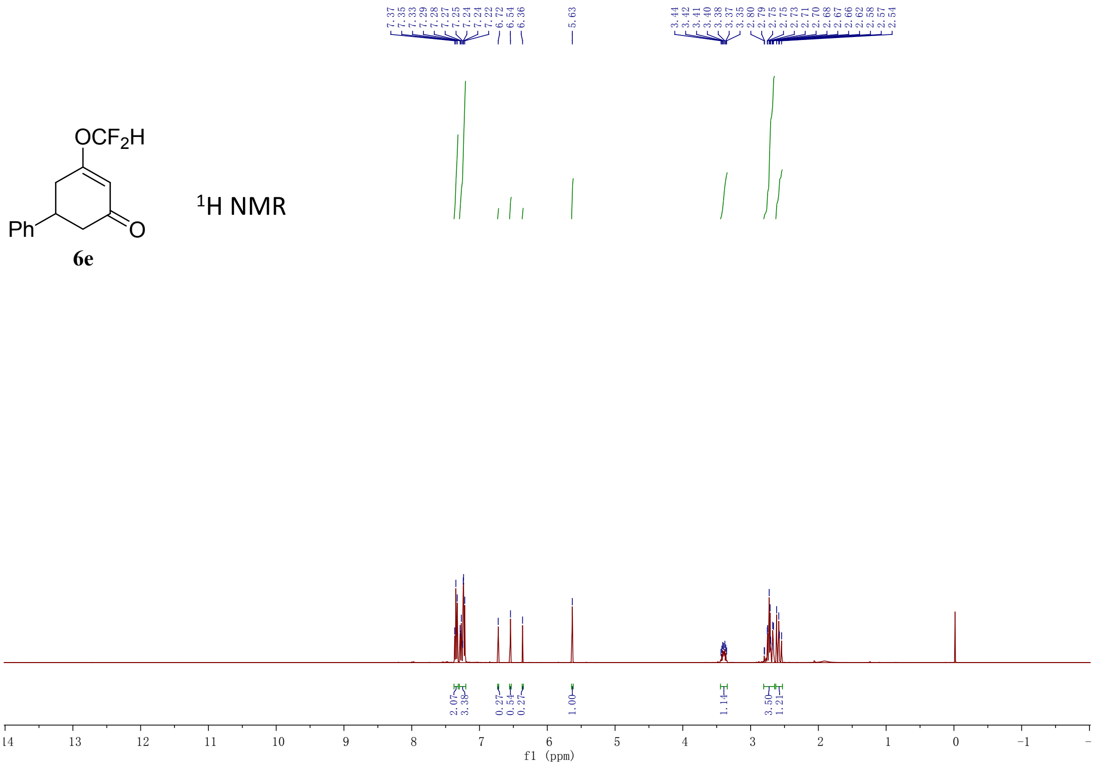
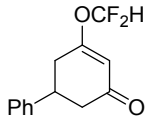


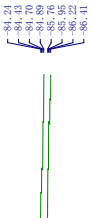
6e

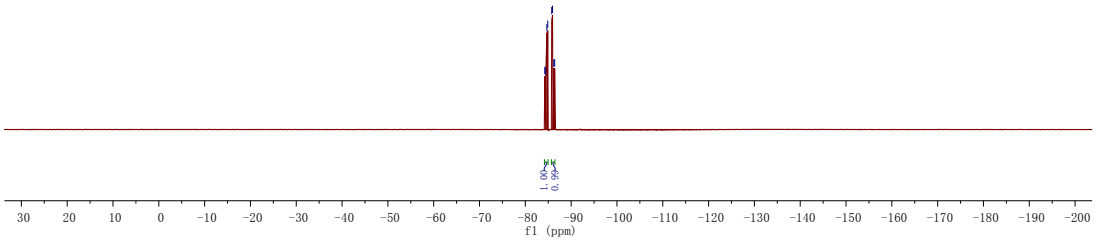
^{1}H NMR



6e

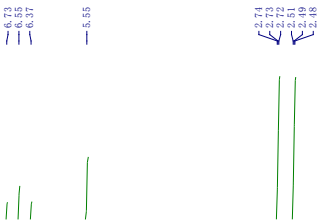
^{19}F NMR

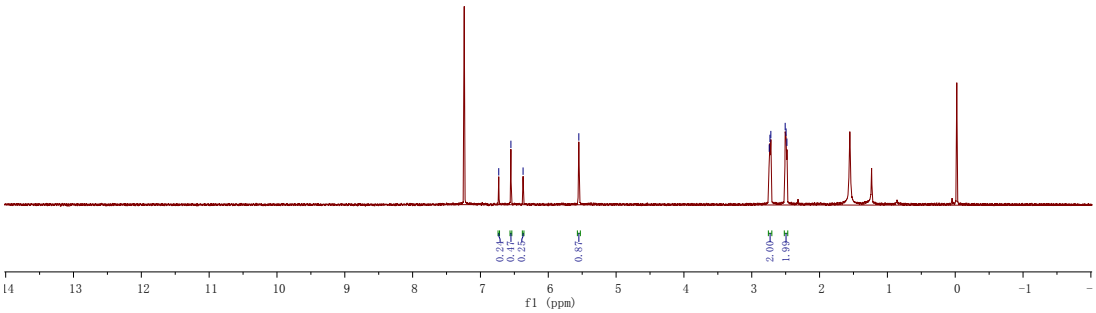


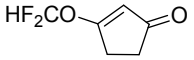


6f

^{1}H NMR





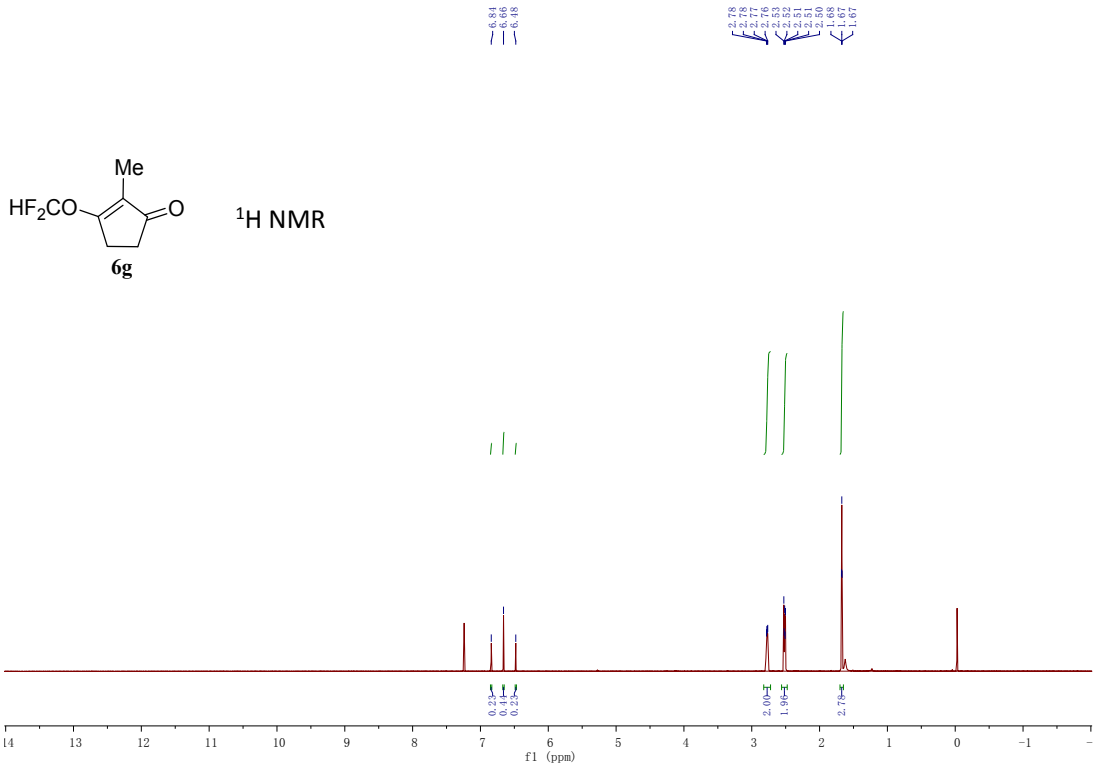


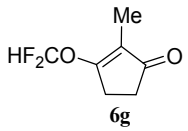
6f

^{19}F NMR

6g

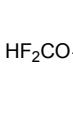
^{1}H NMR





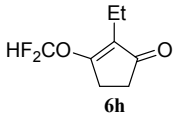
6g

^{19}F NMR



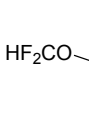
6h

^{1}H NMR



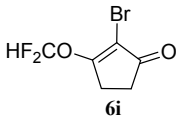
6h

^{19}F NMR



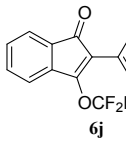
6i

^{1}H NMR



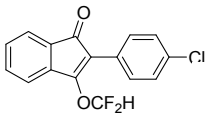
6i

^{19}F NMR



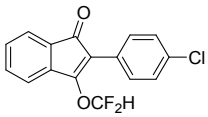
6j

^{1}H NMR



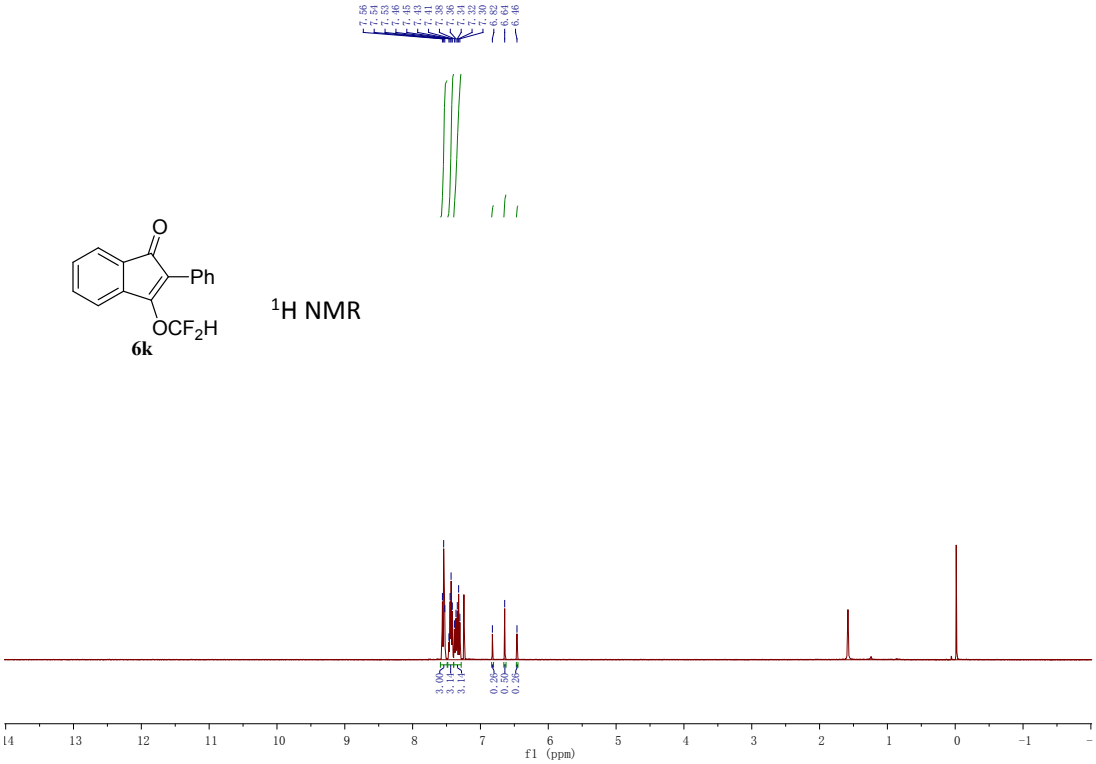
6j

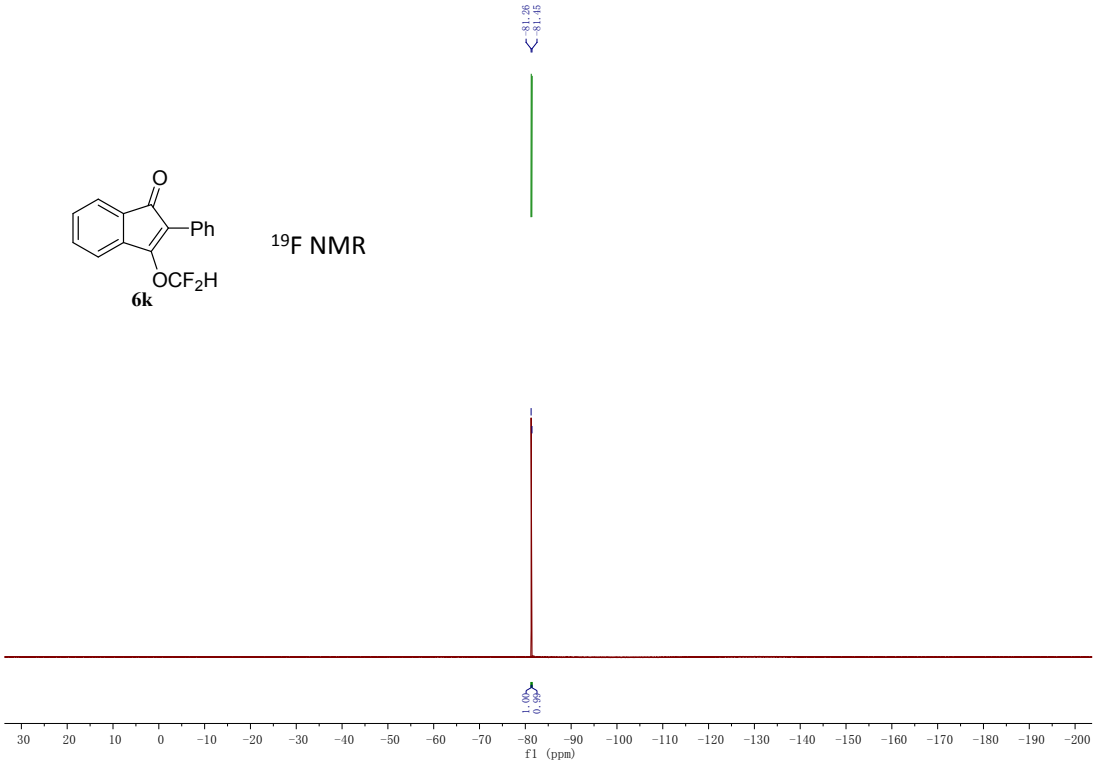
^{19}F NMR

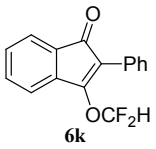


6j

^{13}C NMR

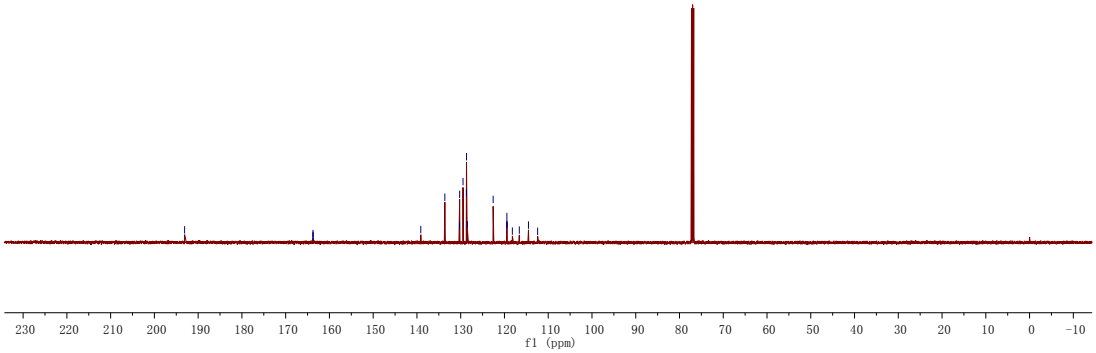

O
Ph
OCF2H
6k
1H NMR
f1 (ppm)

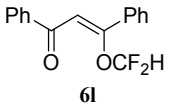

O
Ph
OCF2H
6k
19F NMR
f1 (ppm)



6k

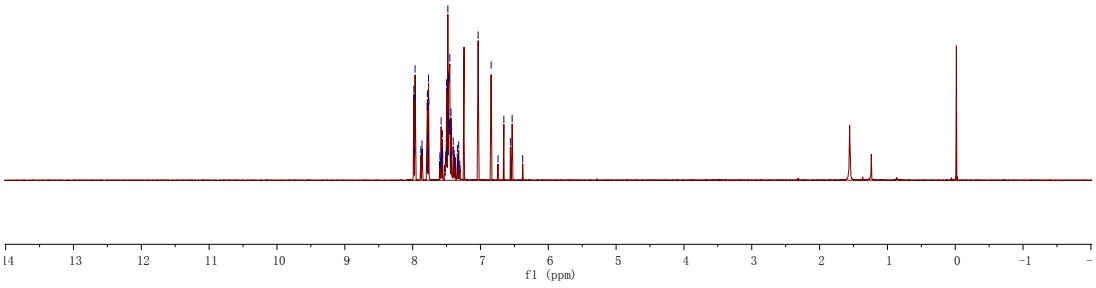
^{13}C NMR

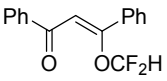




6l

^{1}H NMR



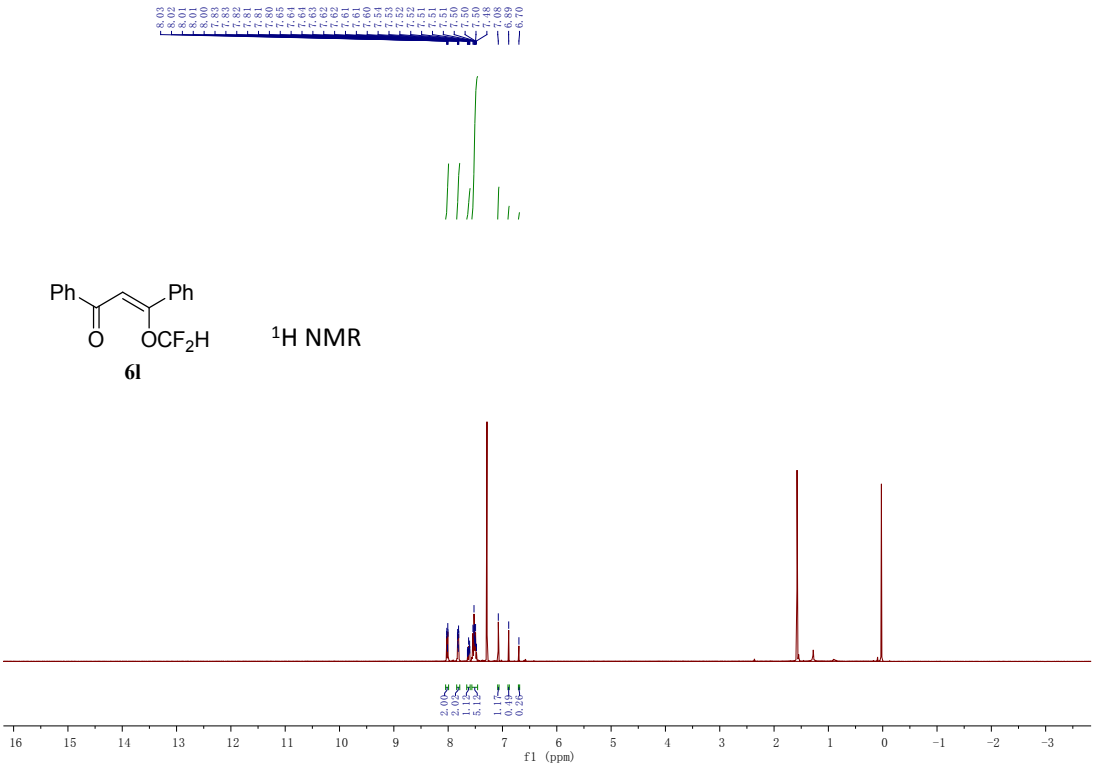


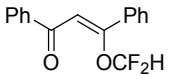
6l

^{19}F NMR

6l

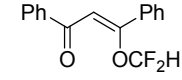
^{1}H NMR





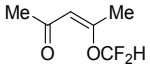
6l

^{19}F NMR



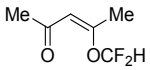
6l

^{13}C NMR



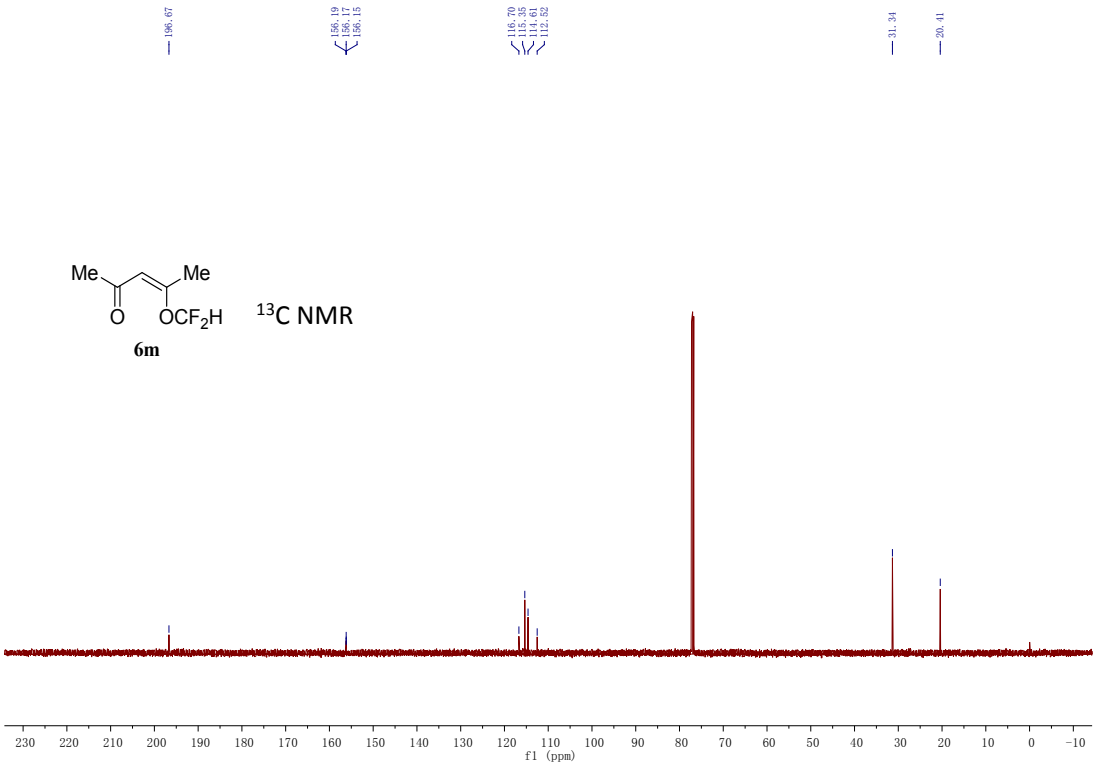
6m

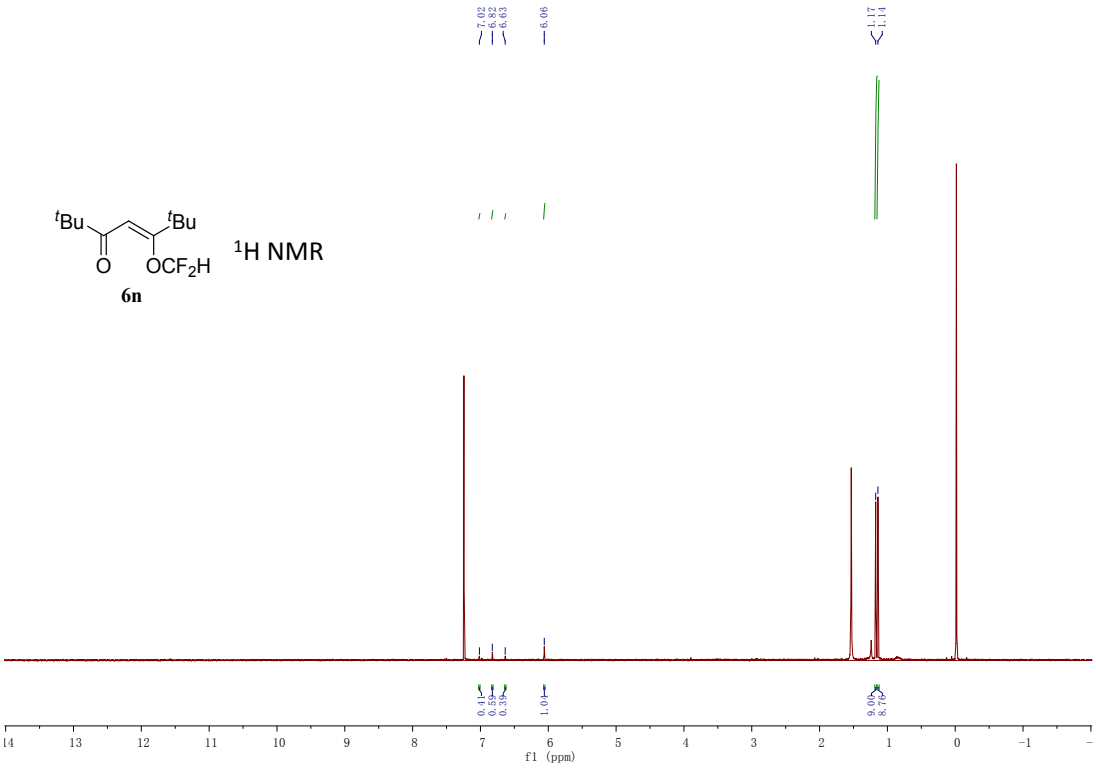
^{1}H NMR

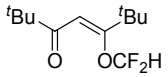


6m

^{19}F NMR

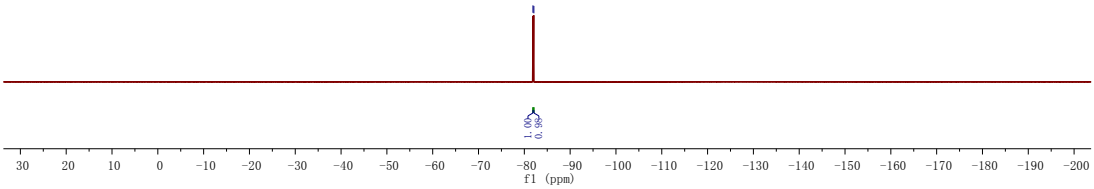

196.67
156.19
156.17
156.15
116.70
115.35
114.61
112.52
31.34
20.41
Me
Me
O
OCF2H
13C NMR
6m
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

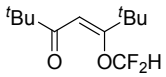

7.02
6.82
6.63
6.06
1.17
1.14
tBu
tBu
O
OCF2H
1H NMR
6n
0.41
0.84
0.39
1.00
9.09
8.78
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)



6n

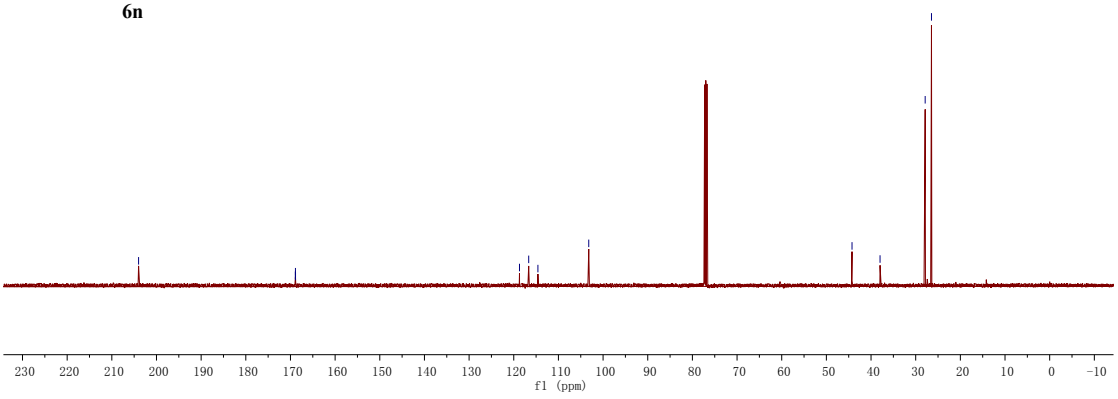
^{19}F NMR



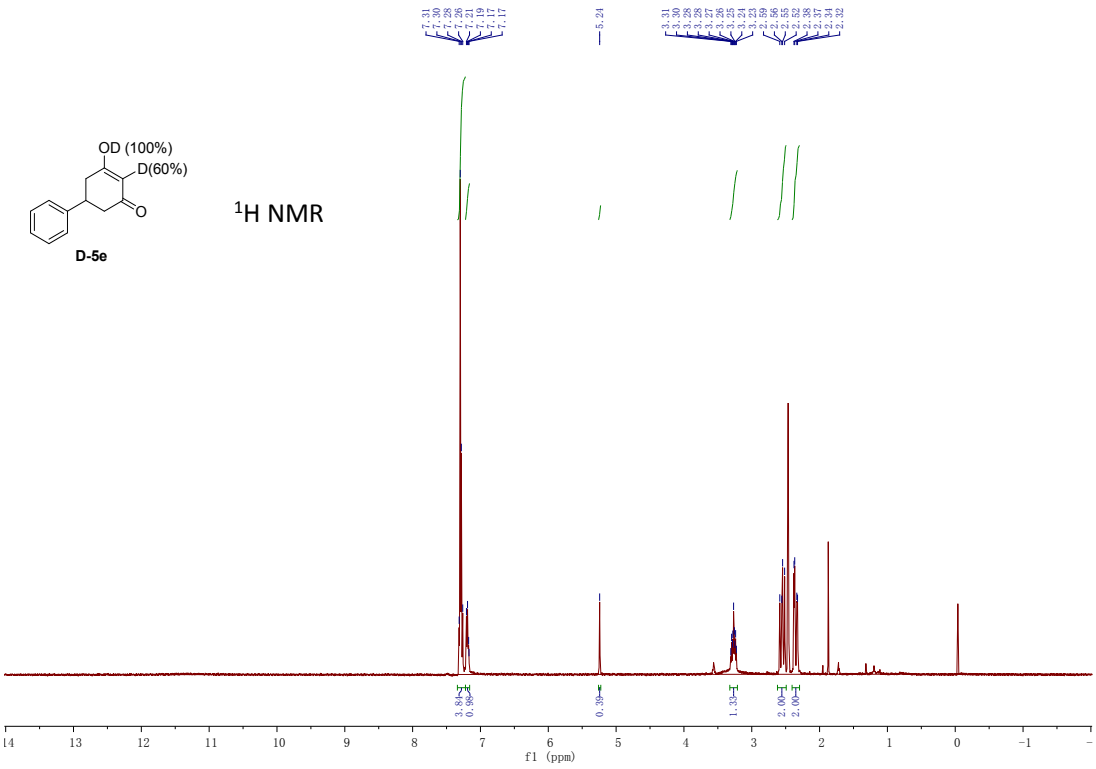


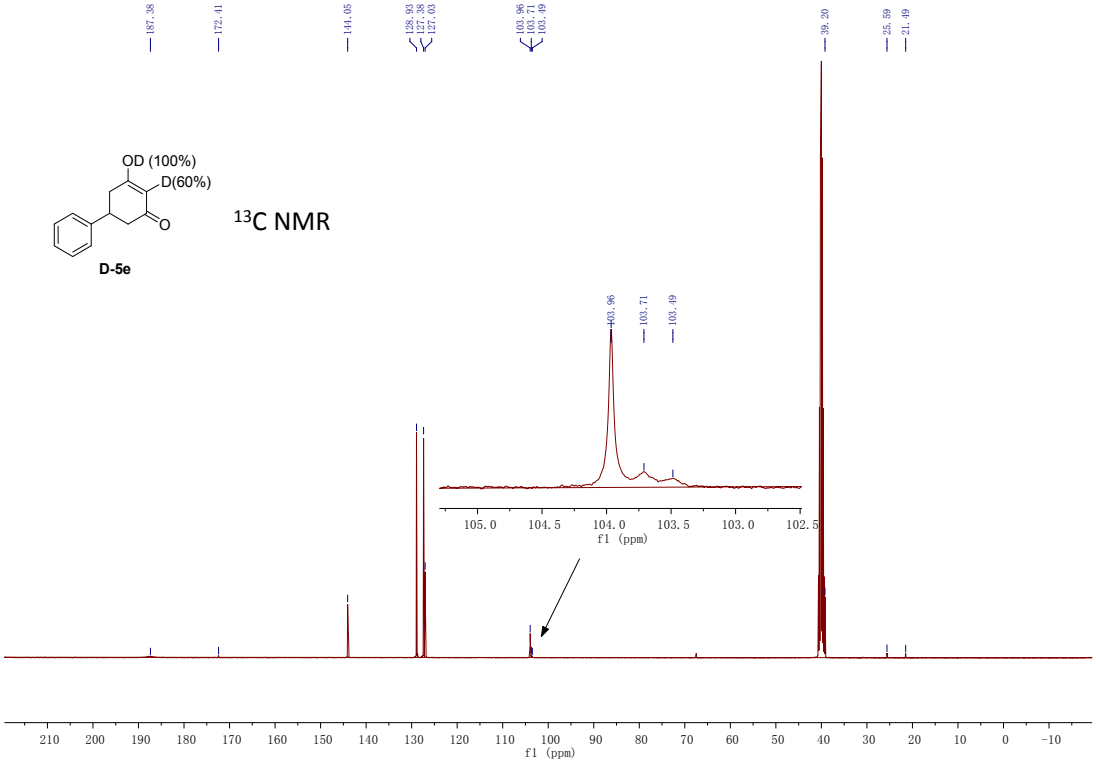
6n

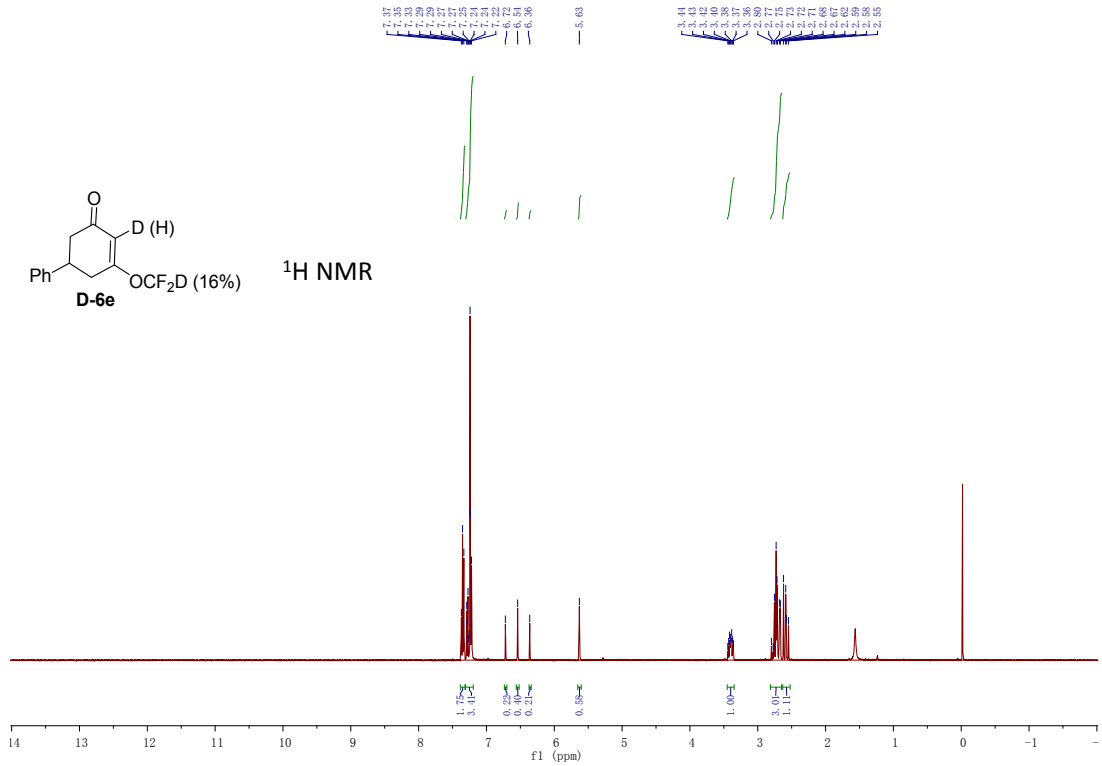
^{13}C NMR

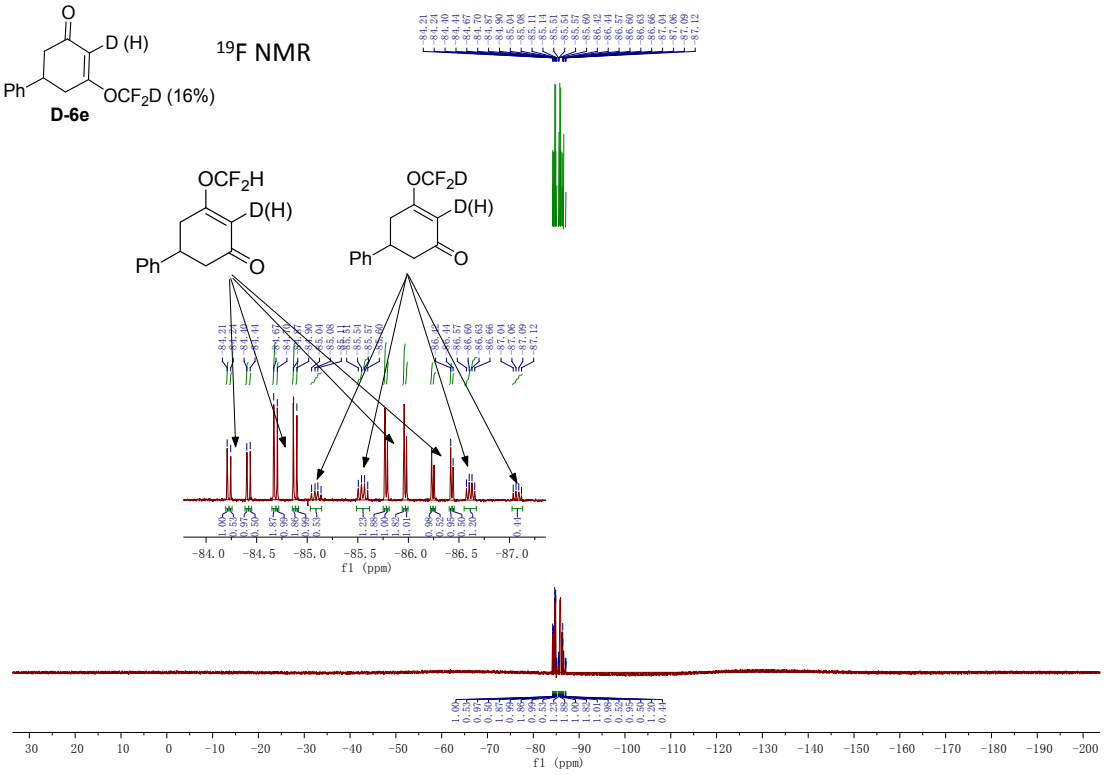


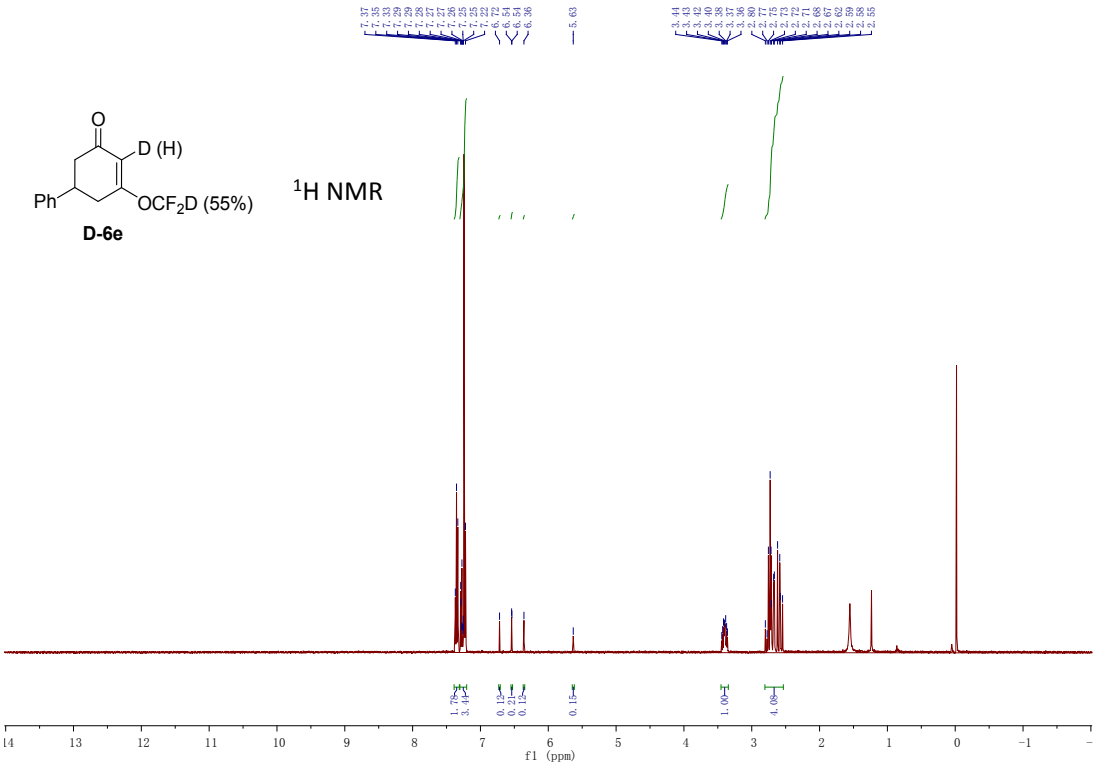
9. Copies of ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and ^{2}D NMR of compound D-5e and D-6e

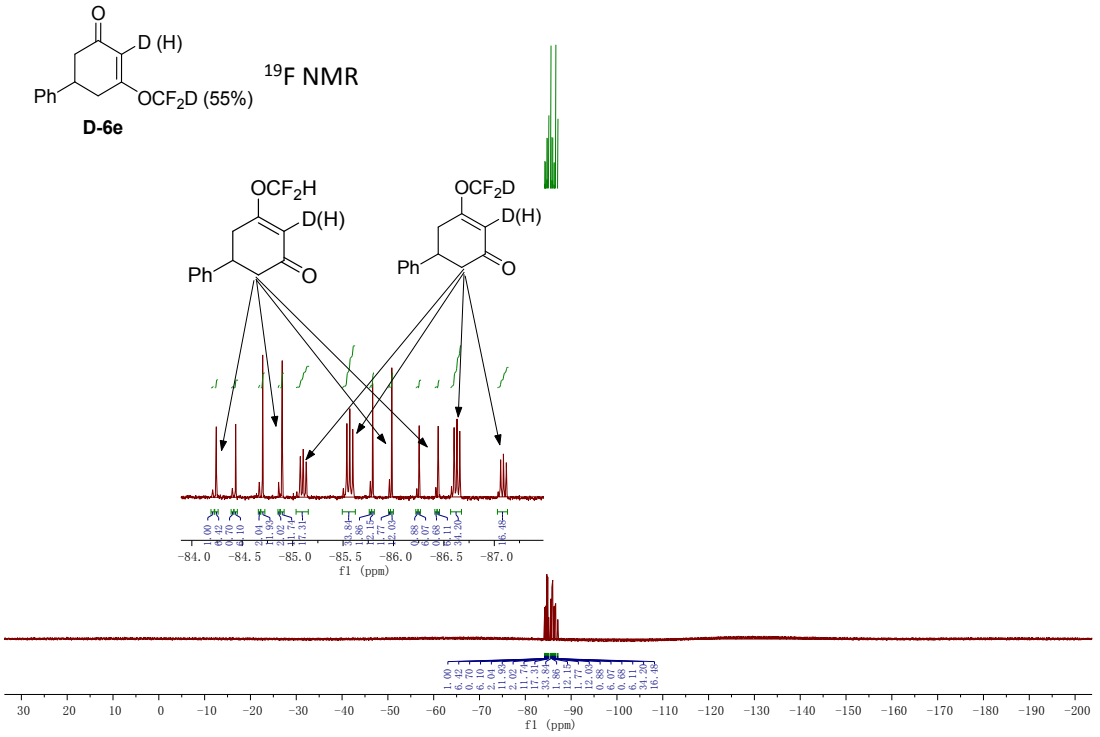


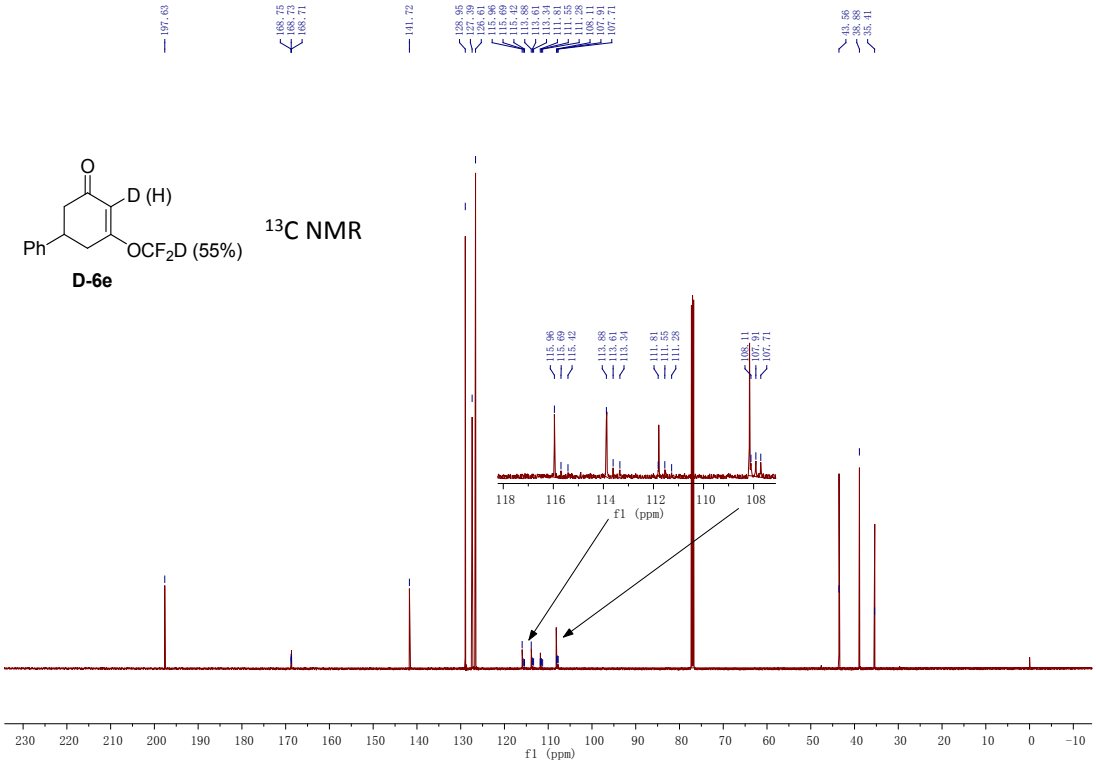


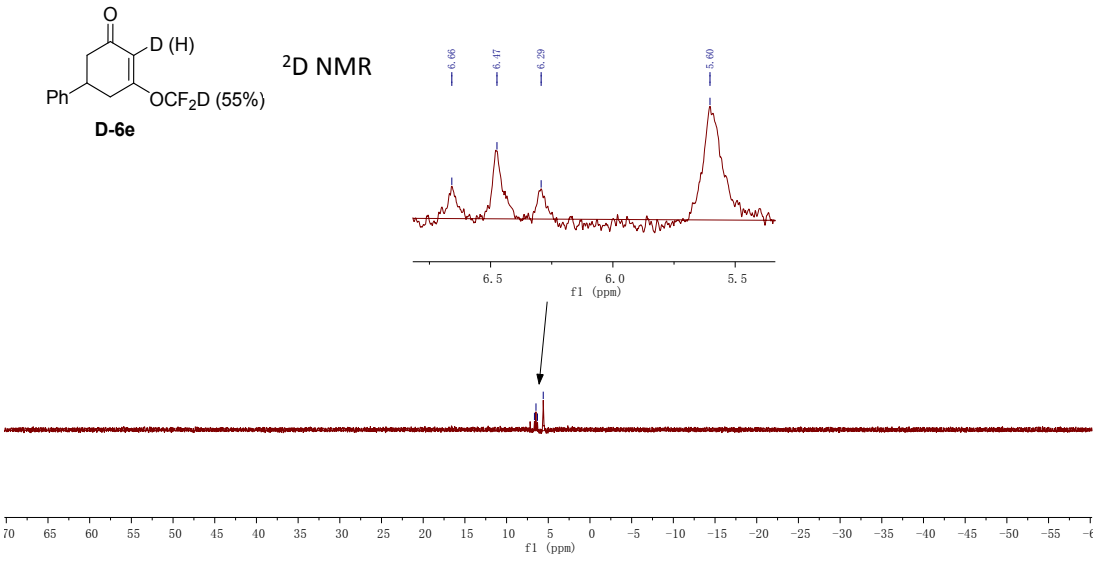

O
D (H)
Ph
OCF2D (16%)
D-6e
1H NMR
f1 (ppm)


O
D (H)
Ph
OCF2D (16%)
D-6e
19F NMR
OCF2H
D(H)
Ph
O
OCF2D
D(H)
Ph
O
f1 (ppm)


O
D (H)
Ph
OCF2D (55%)
D-6e
1H NMR
f1 (ppm)


O
D (H)
Ph
OCF2D (55%)
D-6e
19F NMR
OCF2H
D(H)
Ph
O
OCF2D
D(H)
Ph
O
f1 (ppm)


O
D (H)
Ph
OCF2D (55%)
D-6e
13C NMR
f1 (ppm)


O
D (H)
Ph
OCF2D (55%)
D-6e
2D NMR
f1 (ppm)