Electronic Supplementary Material (ESI) for RSC Advances.

Palladium-Catalysed Difluoroolefination of Benzyl Tosylates Toward the Synthesis of *gem*-Difluoro-2-triflurомethyl Styrene Derivatives

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1. General information

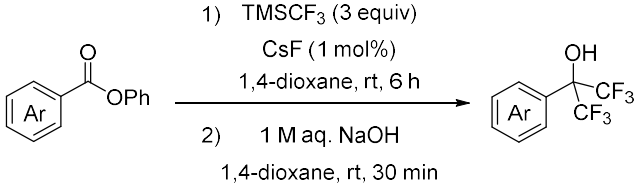
Unless otherwise noted, all reactions or reagents were obtained from commercial suppliers and used as received. Unless otherwise noted, all catalytic reactions were set up in an argon atmosphere glovebox (Vigor, SGI800-750TS-F). The substrates and reagents for catalytic reactions were degassed and stored in the glovebox, unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Thin Layer Chromatography analyses were performed on silica gel coated glass plates (0.25 mm) with fluorescence indicator UV254. For detection of spots, irradiation of UV light at 254 nm or staining reagent using Potassium permanganate solution was used. Flash column chromatography was conducted with silica gel 60 (particle size 230-400 mesh, Huanghai) at room temperature and under elevated pressure.

Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2030 instrument equipped with a Rtx-5 column (30 m × 0.25 mm) with dodecane as an internal standard. GC-MS analysis was conducted on a Agilent 5977B GC/MSD instrument equipped with a HP-5MS UI column (30 m × 0.25 mm). ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded at 400 MHz, 376 MHz and at 101 or 151 MHz, respectively in $CDCl_3$ at room temperature. ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts (δ) were reported with respect to the corresponding solvent residual peak at 7.26 ppm for $CDCl_3$ for ^{1}H NMR. ^{13}C NMR spectra (^{1}H-broadband decoupled) were reported in ppm using the central peak of $CDCl_3$ (77.16 ppm). High-resolution mass spectrometric measurements were provided by the Department of The State Key Laboratory of Biotherapy, Sichuan University. The molecular ion $[M]^+$, $[M+H]^+$ and $[M+Na]^+$ are given in m/z units.

2. General procedure for the synthesis of α, α-bis(trifluoromethyl) tosylate

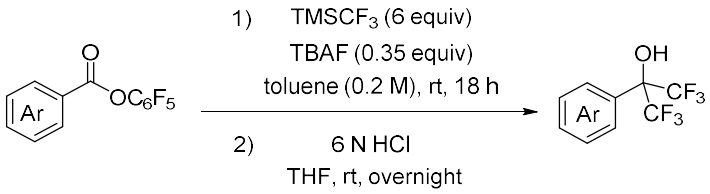
General procedure A:[1]



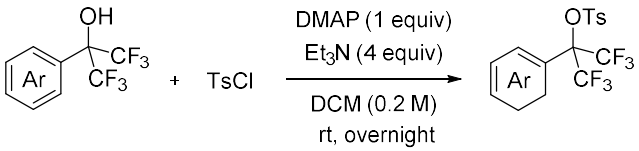
In a glovebox filled with argon, dried CsF (1 mol%), Me_3SiCF_3 (3.0 equiv), phenyl carboxylate (1 equiv) and 1,4-dioxane were added to a two necked flask. After stirring the mixture at room temperature for 6 h, the resulting solution was filtered through a pad of silica gel and further eluted with EtOAc. The crude mixture was concentrated under reduced pressure, and the resulting mixture

was purified by flash column chromatography over silica gel. The product obtained above, 1,4-dioxane and 1 M NaOH were added to a round bottom flask and stirred for 30 min at room temperature. The resulting crude mixture was filtered through silica gel, further eluted with EtOAc and concentrated under reduced pressure. The resulting mixture was purified by flash column chromatography over silica gel and the alcohol was obtained.

General procedure B:[2]

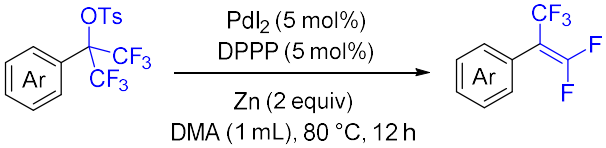


To a stirred solution of pentafluorophenyl ester (1.0 equiv) in toluene (0.2 M) was added trimethyl(trifluoromethyl)silane (6.0 equiv). The reaction mixture was cooled to 0 °C in an ice bath and a solution of tetrabutylammonium fluoride (1 M in THF) (0.35 equiv) was added dropwise. The reaction mixture was allowed to reach room temperature and stirred for 18 h. The reaction was monitored by TLC (petroleum ether), and if necessary, additional trimethyl-(trifluoromethyl)silane could be added. Diethyl ether was added and the organic phase was washed with aqueous HCl (1 M). The aqueous phase was extracted with EtOAc (2 times). The combined etheral phases were washed with H_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the desired product. The product obtained above, THF (0.2 M) and 6 M HCl (half volume of THF) were added and stirred overnight at room temperature. The mixture was diluted with H_2O and the product was extracted with EtOAc (2 times). The organic phases were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the desired product.



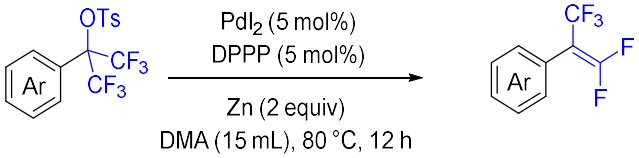
Et_3N (4.0 equiv) was added dropwise to a stirred solution of α-trifluoromethylcarbinol (1.0 equiv) and DMAP (1.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C, and the *p*-toluenesulfonyl chloride (1.1 eq) was added. The solution was stirred at room temperature until completion and quenched with saturated aq. $NaHCO_3$, the layers were separated and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The α, α-bis(trifluoromethyl)-tosylates were purified by silica gel column chromatography. [3]

3. Standard conditions for preparing the *gem*-Difluoro-2-trifluromethyl Styrene Derivatives



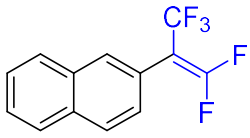
In the glovebox, α, α-bis(trifluoromethyl) tosylates (0.2 mmol), PdI_2 (3.6 mg, 0.01 mmol), DPPP (4.1 mg, 0.01 mmol), and Zn (26.2 mg, 0.4 mmol) were added into an oven-dried 4 mL vial with a magnetic stirring bar, followed by addition of DMA (1.0 mL). The vial was sealed and removed out of the glovebox and heated to 80 °C. After 12 h, the vial was cooled to room temperature. The mixture was passed through a short silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography to give the desired product.

4. The procedure for the gram scale reaction

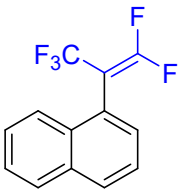


In the glovebox, α, α-bis(trifluoromethyl) tosylates (3.0 mmol), PdI_2 (54.0 mg, 0.15 mmol), DPPP (61.5 mg, 0.15 mmol), and Zn (393.0 mg, 6 mmol) were added into a 50 mL sealed tube with a magnetic stirring bar, followed by addition of DMA (15.0 mL). The tube was sealed and removed out of the glovebox and heated to 80 °C. After 12 h, the vial was cooled to room temperature. The mixture was passed through a silica gel pad with EtOAc. The filtrate was concentrated and the residue was purified by flash column chromatography to give the desired product.

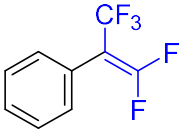
5. Characterization data of products



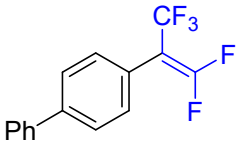
2-(perfluoroprop-1-en-2-yl)naphthalene (2a) Prepared by the general procedure; isolated as a white solid using petroleum as eluent (46.4 mg, 90%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 - 7.85 (m, 4H), 7.58 - 7.52 (m, 2H), 7.40 (dd, J = 8.4, 2.0 Hz, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.01 (dd, J_{FF} = 26.3, 11.3 Hz, 3F), -75.22 (ddd, J_{FF} = 48.9, 26.3, 11.3 Hz, 1F), -77.09 - -77.21 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.6 (ddq, J_{CF} = 308.0, 292.9, 4.0 Hz, CF_2=CAr-CF_3), 133.4, 133.1, 130.1 (t, J_{CF} = 3.0 Hz), 128.7, 128.3, 127.9, 127.3, 126.9, 126.8, 124.1 - 121.3 (m, CF_2=CAr-CF_3), 123.4, 90.5 - 89.8 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: [M] calcd for $C_{13}H_7F_5$ 258.0462; found: 258.0462.



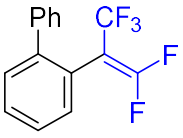
1-(perfluoroprop-1-en-2-yl)naphthalene (2b) Prepared by the general procedure; isolated as a white solid using petroleum as eluent (45.9 mg, 89%). Known compound. [4] **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.98 - 7.89 (m, 3H), 7.62 - 7.50 (m, 4H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.44 (dd, J_{FF} = 18.8, 11.3 Hz, 3F), -74.42 - -74.60 (m, 2F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.6 - 153.5 (m, CF_2=CAr-CF_3), 133.9, 132.4 (dd, J_{CF} = 3.0, 2.0 Hz), 130.6, 129.6 (dd, J_{CF} = 3.0, 2.0 Hz), 128.8, 127.4, 126.6, 125.3, 124.4, 123.1, 122.8 (qdd, J_{CF} = 259.6, 11.1, 5.0 Hz, CF_2=CAr-CF_3), 88.1 - 87.3 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{13}H_7F_5$ 258.0462; found: 258.0460.



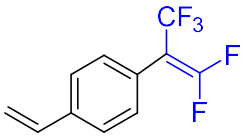
(perfluoroprop-1-en-2-yl)benzene (2c) Prepared by the general procedure; isolated as a colorless liquid using petroleum as eluent (39.1 mg, 94%). Known compound. [5] **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.43 - 7.41 (m, 3H), 7.35 - 7.32 (m, 2H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.58 (dd, J_{FF} = 26.3, 11.3 Hz, 3F), -76.19 (ddd, J_{FF} = 48.9, 26.3, 11.3 Hz, 1F), -77.87 - -77.99 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.4 (ddq, J_{CF} = 308.0, 293.9, 3.0 Hz, CF_2=CAr-CF_3), 130.1 (t, J_{CF} = 3.0 Hz), 129.6, 128.9, 126.1,124.0 - 121.2 (m, CF_2=CAr-CF_3), 90.4 - 89.7 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_9H_5F_5$ 208.0306; found: 208.0304.



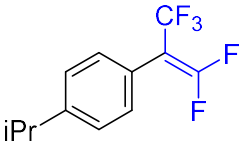
4-(perfluoroprop-1-en-2-yl)-1,1'-biphenyl (2d) Prepared by the general procedure; isolated as a white solid using petroleum as eluent (44.3 mg, 78%). Known compound. [6] **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 (dd, J = 17.2, 8.0 Hz, 4H), 7.49 - 7.37 (m, 5H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.11 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -75.25 (ddd, J_{FF} = 48.9, 26.3, 11.3Hz, 1F), -77.15 - -77.26 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.4 (ddq, J_{CF} = 308.0, 293.9, 2.0 Hz, CF_2=CAr-CF_3), 142.5, 140.2, 130.5 (t, J_{CF} = 3.0 Hz), 129.0, 128.0, 127.6, 127.3, 124.9, 124.1 - 121.2 (m, CF_2=CAr-CF_3), 90.2 - 89.4 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{15}H_9F_5$ 284.0619; found: 284.0614.



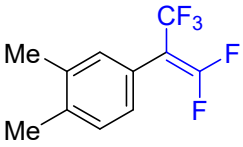
2-(perfluoroprop-1-en-2-yl)-1,1'-biphenyl (2e) Prepared by the general procedure; isolated as a white solid using petroleum as eluent (42.6 mg, 75%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.52 - 7.48 (m, 1H), 7.44 - 7.35 (m, 6H), 7.30 - 7.28 (m, 2H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -58.88 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -74.40 - -74.51 (m, 1F), -76.14 (ddd, J_{FF} = 37.6, 18.8, 7.5 Hz, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.7 (ddq, J_{CF} = 308.0, 292.9, 4.0 Hz, CF_2=CAr-CF_3), 144.0 (t, J_{CF} = 4.0 Hz), 140.4, 131.2 (dd, J_{CF} = 2.0, 4.0 Hz), 130.8, 130.0, 128.8, 128.3, 127.71, 127.68, 124.3, 122.6 (qdd, J_{CF} = 272.7, 12.1, 6.1 Hz, CF_2=CAr-CF_3), 89.3 - 88.5 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{15}H_9F_5$ 284.0619; found: 284.0615.



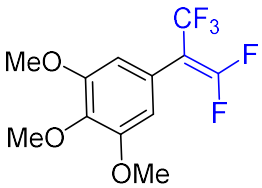
1-(perfluoroprop-1-en-2-yl)-4-vinylbenzene (2f) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a colorless liquid using petroleum as eluent (39.3 mg, 84%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.80 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.94 (d, *J* = 17.6 Hz, 1H), 5.48 (d, *J* = 10.8 Hz, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.18 (dd, J_{FF} = 26.3, 11.3 Hz, 3F), -75.37 (ddd, J_{FF} = 48.9, 22.6, 11.3 Hz, 1F), -77.23 - -77.34 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.4 (ddq, J_{CF} = 308.0, 292.9, 4.0 Hz, CF_2=CAr-CF_3), 138.8, 136.0, 130.3 (t, J_{CF} = 3.0 Hz), 126.6, 125.3, 124.0 - 121.1 (m, CF_2=CAr-CF_3), 115.6, 90.1- 89.4 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{11}H_7F_5$ 234.0462; found: 234.0461.



1-isopropyl-4-(perfluoroprop-1-en-2-yl)benzene (2g) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. isolated as a colorless liquid using petroleum as eluent (36.0 mg, 72%). Known compound. [7] **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.21 - 7.16 (m, 4H), 2.89 - 2.82 (m, 1H), 1.20 (s, 3H), 1.18 (s, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.32 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -76.00 (ddd, J_{FF} = 48.9, 22.6, 11.3 Hz, 1F), -77.78 - -77.91 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.4 (ddq, J_{CF} = 307.0, 292.9, 4.0 Hz, CF_2=CAr-CF_3), 150.4, 130.0 (t, J_{CF} = 2.0 Hz), 127.0, 123.4, 122.7 (qdd, J_{CF} = 272.7, 12.1, 6.1 Hz, CF_2=CAr-CF_3), 90.3 - 89.5(m, CF_2=CAr-CF_3), 34.1, 23.9. HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{12}H_{11}F_5$ 250.0775; found: 250.0773.

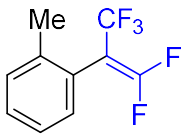


2-1,2-dimethyl-4-(perfluoroprop-1-en-2-yl)benzene (2h) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a colorless liquid using petroleum as eluent (26.9 mg, 57%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.20 (d, *J* = 7.6 Hz, 1H), 7.12 - 7.07 (m, 2H), 2.30 (s, 6H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.41 (dd, J_{FF} = 26.3, 11.3 Hz, 3F), -76.32 (ddd, J_{FF} = 48.9, 22.6, 11.3 Hz, 1F), -77.86 - -77.98 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.4 (ddq, J_{CF} = 307.0, 292.9, 4.0 Hz, CF_2=CAr-CF_3), 138.3, 137.3, 131.1 (t, J_{CF} = 2.0 Hz), 130.1, 127.5 (t, J_{CF} = 2.0 Hz), 123.4, 122.7 (qdd, J_{CF} = 271.7, 12.1, 6.1 Hz, CF_2=CAr-CF_3), 90.3 - 89.5 (m, CF_2=CAr-CF_3), 19.8, 19.7. HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{11}H_9F_5$ 236.0619; found: 236.0617.

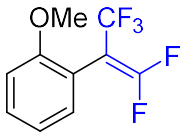


1,2,3-trimethoxy-5-(perfluoroprop-1-en-2-yl)benzene (2i) Prepared by the general procedure; isolated as a colorless liquid using petroleum/EtOAc (50/1) as eluent (20.9 mg, 35%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.52 (s, 2H), 3.87 (s, 3H), 3.86 (s, 6H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.40 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -75.62 (ddd, J_{FF} = 48.9, 26.3, 11.3 Hz, 1F), -76.51 - -76.63 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.4 - 153.8 (m, CF_2=CAr-CF_3), 153.5, 139.1, 124.0 - 121.2 (m, CF_2=CAr-CF_3), 121.1, 107.5,

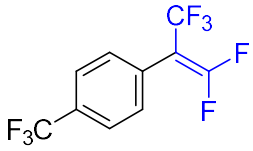
90.3 - 89.5 (m, CF_2=*C*Ar-CF_3), 61.0, 56.4. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{12}H_{11}F_5O_3Na$ 321.0521; found: 321.0521.



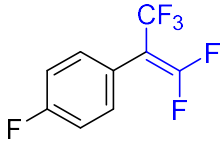
1-methyl-2-(perfluoroprop-1-en-2-yl)benzene (2j) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a colorless liquid using petroleum as eluent (42.2 mg, 95%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.33 - 7.29 (m, 2H), 7.24 - 7.19 (m, 2H), 2.28 (s, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -60.09 - -60.18 (m, 3F), -76.62 - -76.80 (m, 2F). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 158.0 - 153.9 (m, *C*F_2=CAr-CF_3), 138.6, 131.1, 130.7, 130.0, 126.3, 125.2, 123.6 - 121.7 (m, CF_2=CAr-*C*F_3), 88.6 - 88.1 (m, CF_2=*C*Ar-CF_3), 19.6. HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{10}H_7F_5$ 222.0462; found: 222.0459.



1-methoxy-2-(perfluoroprop-1-en-2-yl)benzene (2k) Prepared by the general procedure; isolated as a colorless liquid using petroleum as eluent (40.5 mg, 85%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.43 - 7.38 (m, 1H), 7.23 (d, *J*=7.6 Hz, 1H), 7.00 - 6.94 (m, 2H), 3.84 (s, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.75 (dd, J_{FF} = 18.8, 11.3 Hz, 3F), -75.72 (ddd, J_{FF} = 37.6, 18.8, 7.5 Hz, 1F), -76.38 - -76.49 (m, 1F). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 158.1, 156.3 (ddq, J_{CF} = 304.5, 292.9, 4.5 Hz, *C*F_2=CAr-CF_3), 132.0, 131.4, 122.6 (qdd, J_{CF} = 271.8, 13.6, 6.0 Hz, CF_2=CAr-*C*F_3), 120.7, 114.9, 111.3, 86.4 - 85.8 (m, CF_2=*C*Ar-CF_3), 55.8. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$calcd for $C_{10}H_7F_5ONa$ 261.0309; found: 261.0313.

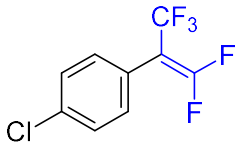


1-(perfluoroprop-1-en-2-yl)-4-(trifluoromethyl)benzene (2l) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a colorless liquid using petroleum as eluent (33.1 mg, 60%). Known compound. [8] **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.02 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -63.06 (s, 3F), -73.80 (ddd, J_{FF} = 45.1, 22.6, 7.5 Hz, 1F), -75.93 - -76.04 (m, 1F). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 156.6 (ddq, J_{CF} = 308.0, 294.4, 3.0 Hz, *C*F_2=CAr-CF_3), 131.8 (q, J_{CF} = 33.2 Hz), 130.6, 129.8, 126.0 (q, J_{CF} = 4.5 Hz), 123.8 (q, J_{CF} = 273.3 Hz), 123.2 - 121.1 (m, CF_2=CAr-*C*F_3), 89.7 - 89.2 (m, CF_2=*C*Ar-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{10}H_4F_8$ 276.0180; found: 276.0176.

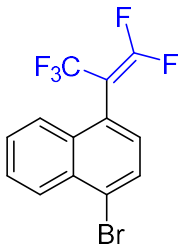


1-fluoro-4-(perfluoroprop-1-en-2-yl)benzene (2m) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a colorless liquid using petroleum as eluent (28.0 mg, 62%). Known compound. [8] **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.33 - 7.30 (m, 2H), 7.14 - 7.10 (m, 2H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.54 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -75.10 (ddd, J_{FF} = 48.9, 22.6, 11.3 Hz, 1F), -76.92 - -77.04 (m, 1F), -111.26 (s, 1F). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 163.4 (d, J_{CF} = 250.7 Hz), 158.4 -

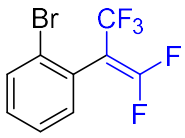
154.4 (m, CF_2=CAr-CF_3), 132.2 (d, J_{CF} = 9.1 Hz), 123.4 - 121.5 (m, CF_2=CAr-CF_3), 121.9, 116.2 (d, J_{CF} = 22.6 Hz), 89.8 - 89.0 (m, CF_2=CAr-CF_3). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_9H_5F_6$ 227.0290; found: 227.0291.



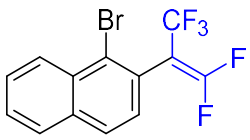
1-chloro-4-(perfluoroprop-1-en-2-yl)benzene (2n) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a white solid using petroleum as eluent (28.6 mg, 59%). Known compound. [5] **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.35 - 7.32 (m, 2H), 7.20 (d, J = 8.8 Hz, 2H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.49 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -74.93 (ddd, J_{FF} = 45.1, 22.6, 7.5 Hz, 1F), -76.86 - -76.98 (m, 1F). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 157.4 - 153.4 (m, $C$$F_2$=CAr-$CF_3$), 134.9, 130.5, 128.3, 123.5, 122.3 - 120.4 (m, CF_2=CAr-$C$$F_3$), 88.5 - 88.1 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_9H_4ClF_5$ 241.9916; found: 241.9915.



1-bromo-4-(perfluoroprop-1-en-2-yl)naphthalene (2o) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a white solid using petroleum as eluent (52.6 mg, 78%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.36 - 8.32 (m, 1H), 7.88 - 7.84 (m, 2H), 7.70 - 7.62 (m, 2H), 7.34 (d, J = 7.6 Hz, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.39 - -59.48 (m, 3F), -73.56 - -73.75 (m, 2F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.6 - 153.5 (m, $C$$F_2$=CAr-$CF_3$), 133.5, 132.5, 129.8 (t, J_{CF} = 2.0 Hz), 129.6, 128.24, 128.16, 128.0, 125.7, 124.9, 124.0 - 121.0 (m, CF_2=CAr-$C$$F_3$), 123.1, 87.8 - 86.9 (m, CF_2=CAr-CF_3). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_7BrF_5$ 336.9646; found: 336.9653.

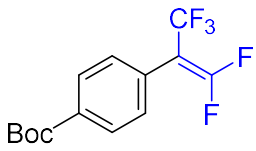


1-bromo-2-(perfluoroprop-1-en-2-yl)benzene (2p) Prepared by the general procedure; 100 °C instead of 80 °C and PdI_2 (7.2 mg, 0.02 mmol), DPPP (8.2 mg, 0.02 mmol) were used. Isolated as a colorless liquid using petroleum as eluent (49.9 mg, 87%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (dd, J = 7.6, 1.2 Hz, 1H), 7.40 - 7.29 (m, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.63 (dd, J_{FF} = 18.8, 11.3 Hz, 3F), -73.70 (ddd, J_{FF} = 22.6, 11.3, 7.5 Hz, 1F), -75.00 (ddd, J_{FF} = 41.4, 18.8, 7.5 Hz, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.3 (ddq, J_{CF} = 309.1, 293.9, 4.0 Hz, $C$$F_2$=CAr-$CF_3$), 133.3, 132.4 (q, J_{CF} = 2.0 Hz), 131.4, 127.7, 127.0, 125.8 (q, J_{CF} = 2.0 Hz), 123.5 - 120.6 (m, CF_2=CAr-$C$$F_3$), 104.1- 102.2 (m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_9H_4BrF_5$ 285.9411; found: 285.9409.

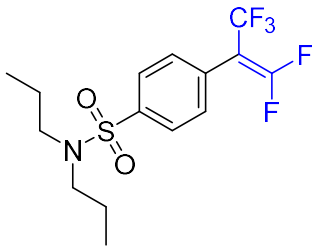


1-bromo-2-(perfluoroprop-1-en-2-yl)naphthalene (2q) Prepared by the general procedure; isolated as a white solid using petroleum as eluent (59.3 mg, 88%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.38 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.69 - 7.59 (m, 2H), 7.39 (d, J = 8.4 Hz, 1H). **^{19}F**

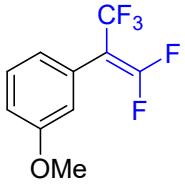
NMR (376 MHz, Chloroform-*d*) δ -59.15 (dd, J_{FF} = 18.8, 7.5 Hz, 3F), -73.70 (ddd, J_{FF} = 22.6, 11.3, 3.8 Hz, 1F), -75.13 (ddd, J_{FF} = 41.4, 18.8, 3.8 Hz, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.5 (ddq, J_{CF} = 308.0, 293.9, 3.0 Hz, CF_2=CAr-CF_3), 134.8, 132.5, 128.4, 128.34, 128.28, 128.0, 127.8, 127.3 (t, J_{CF} = 3.0 Hz), 126.9, 125.1, 123.8 - 120.9 (m, CF_2=CAr-CF_3), 90.8 - 89.6(m, CF_2=CAr-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{13}H_6BrF_5$ 335.9568; found: 335.9563.



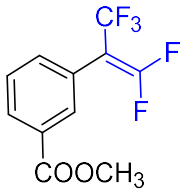
tert-butyl 4-(perfluoroprop-1-en-2-yl)benzoate (2r) Prepared by the general procedure; isolated as a white solid using petroleum/EtOAc (50/1) as eluent (43.1 mg, 70%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.04 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 1.60 (s, 9H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -58.97 (dd, J_{FF} = 26.3, 11.3 Hz, 3F), -74.35 (ddd, J_{FF} = 45.1, 22.6, 7.5 Hz, 1F), -76.32 - -76.43 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 165.0, 156.4 (ddq, J_{CF} = 309.1, 295.9, 4.0 Hz, CF_2=CAr-CF_3), 133.1, 130.0 (t, J_{CF} = 2.0 Hz), 129.9, 123.8 - 120.9 (m, CF_2=CAr-CF_3), 90.1 - 89.3 (m, CF_2=CAr-CF_3), 81.7, 60.5, 28.3. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$calcd for $C_{14}H_{13}F_5O_2Na$ 331.0728; found: 331.0730.



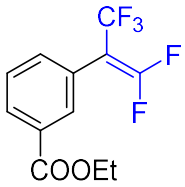
4-(perfluoroprop-1-en-2-yl)-N,N-dipropylbenzenesulfonamide (2s) Prepared by the general procedure; isolated as a white solid using petroleum/EtOAc (10/1) as eluent (64.5 mg, 87%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 3.10 (t, J = 7.6 Hz, 4H), 1.61 - 1.52 (m, 4H), 0.87 (t, J = 7.6 Hz, 6H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -58.84 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -73.38 (ddd, J_{FF} = 48.9, 22.6, 7.5 Hz, 1F), -75.59 - -75.69 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.4 (ddq, J_{CF} = 309.1, 295.9, 3.0 Hz, CF_2=CAr-CF_3), 141.4, 130.6 (t, J_{CF} = 2.0 Hz), 129.9, 127.4, 123.5 - 120.7 (m, CF_2=CAr-CF_3), 89.6 - 88.9 (m, CF_2=CAr-CF_3), 50.1, 22.1, 11.1. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$calcd for $C_{15}H_{18}F_5NO_2SNa$ 394.0871; found: 394.0869.



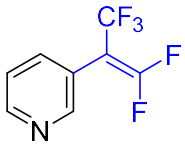
1-methoxy-3-(perfluoroprop-1-en-2-yl)benzene (2t) Prepared by the general procedure; isolated as a colorless liquid using petroleum as eluent (40.5mg, 85%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.26 (t, J = 8.0 Hz, 1H), 6.89 (dd, J = 8.4, 2.4 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.78 (s, 1H), 3.75 (s, 3H). Known compound. [9] **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.26 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -75.60 (ddd, J_{FF} = 48.9, 22.6, 11.3 Hz, 1F), -76.91 - -77.02 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.8, 157.0 (ddq, J_{CF} = 311.1, 293.9, 4.0 Hz, CF_2=CAr-CF_3), 129.9, 127.2, 122.4 (t, J_{CF} = 2.0 Hz), 115.9 (t, J_{CF} = 2.0 Hz), 115.1, 122.6 (qdd, J_{CF} = 272.7, 12.1, 6.0 Hz, CF_2=CAr-CF_3), 90.1 - 89.9 (m, CF_2=CAr-CF_3), 55.5. HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{10}H_7F_5O$ 238.0417; found: 238.0411.



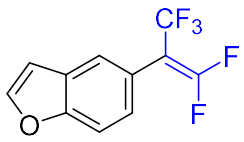
methyl 3-(perfluoroprop-1-en-2-yl)benzoate (2u) Prepared by the general procedure; isolated as a colorless liquid using petroleum/EtOAc (50/1) as eluent (19.2 mg, 36%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.12 - 8.09 (m, 1H), 8.03 (s, 1H), 7.53 - 7.51 (m, 2H), 3.94 (s, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.20 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -74.58 (ddd, J_{FF} = 48.9, 26.3, 11.3 Hz, 1F), -76.40 - -76.51(m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 166.3, 156.5 (ddq, J_{CF} = 308.1, 293.9, 4.0 Hz, *C*F_2=CAr-CF_3), 134.4 (t, J_{CF} = 2.0 Hz), 131.3 (t, J_{CF} = 2.0 Hz), 131.0, 130.7, 129.1, 126.4, 123.8 - 120.9 (m, CF_2=CAr-*C*F_3), 90.1 - 89.1 (m, CF_2=*C*Ar-CF_3), 52.5. HRMS (ESI/Q-TOF) m/z: $[M+Na]^+$ calcd for $C_{11}H_7F_5O_2Na$ 289.0258; found: 289.0265.



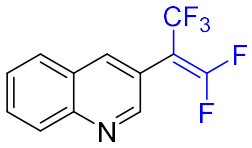
ethyl 3-(perfluoroprop-1-en-2-yl)benzoate (2v) Prepared by the general procedure; isolated as a colorless liquid using petroleum as eluent (22.4 mg, 40% yield). **^{1}H NMR (400 MHz, Chloroform-d)** δ 8.06 – 8.02 (m, 1H), 7.95 (s, 1H), 7.44-7.42 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.22 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -74.66 (ddd, J_{FF} = 48.9, 26.3, 11.3 Hz, 1F), -76.42 - -76.53 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 165.8, 159.6 - 153.6 (m, *C*F_2=CAr-CF_3), 134.4 (t, J_{CF} = 2.0 Hz), 131.5, 131.3 (t, J_{CF} = 2.0 Hz), 130.7, 129.1, 126.4, 123.8 - 121.0 (m, CF_2=CAr-*C*F_3), 90.0 - 89.2 (m, CF_2=*C*Ar-CF_3), 61.5, 14.4. HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{12}H_9F_5O_2$ 280.0517; found: 280.0516.



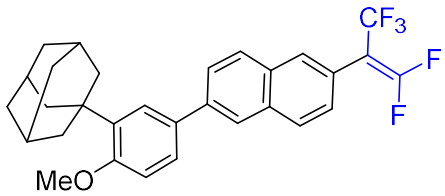
3-(perfluoroprop-1-en-2-yl)pyridine (2w) Prepared by the general procedure; isolated as a colorless liquid using petroleum/EtOAc (5/1) as eluent (36.8 mg, 88%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.68 (d, *J* = 3.6 Hz, 1H), 8.60 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 8.8, 4.8 Hz, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.25 (dd, J_{FF} = 26.3, 11.3 Hz, 3F), -73.20 (ddd, J_{FF} = 45.1, 22.6, 7.5 Hz, 1F), -75.78 - -75.89 (ddd, J_{FF} = 22.5, 11.3, 7.5 Hz, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.7 (ddq, J_{CF} = 309.1, 295.9, 4.0 Hz, *C*F_2=CAr-CF_3), 150.5, 150.4, 137.8, 123.8, 122.8, 122.2 (qdd, J_{CF} = 272.7, 12.1, 6.1 Hz, CF_2=CAr-*C*F_3), 87.9 - 87.2 (m, CF_2=*C*Ar-CF_3). HRMS (ESI/Q-TOF) m/z: $[M+H]^+$ calcd for $C_8H_5F_5N$ 210.0337; found: 210.0341.



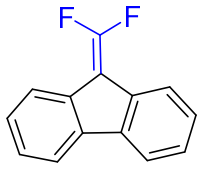
5-(perfluoroprop-1-en-2-yl)benzofuran (2x) Prepared by the general procedure; isolated as a white solid using petroleum as eluent (45.6 mg, 92%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 2.4 Hz, 1H), 7.50 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.18 - 7.15 (m, 1H), 6.72 (dd, *J* = 2.4, 1.2 Hz, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.54 (dd, J_{FF} = 22.6, 7.5 Hz, 3F), -75.83 (ddd, J_{FF} = 48.9, 26.3, 15.2 Hz, 1F), -77.30 - -77.42 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 156.5 (ddq, J_{CF} = 308.0, 296.9, 4.0 Hz, *C*F_2=CAr-CF_3), 155.3, 146.2, 128.1, 126.3, 123.4, 122.7 (qdd, J_{CF} = 272.7, 11.1, 6.1 Hz, CF_2=CAr-*C*F_3), 120.5, 112.0, 106.7, 90.4 - 89.7(m, CF_2=*C*Ar-CF_3). HRMS (EI/Q-TOF) m/z: $[M]^+$ calcd for $C_{11}H_5F_5O$ 248.0255; found: 248.0253.



3-(perfluoroprop-1-en-2-yl)quinoline (2y) Prepared by the general procedure; isolated as a white solid using petroleum/EtOAc (5/1) as eluent (45.1mg, 87%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.84 (s, 1H), 8.18 - 8.14 (m, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.81 - 7.77 (m, 1H), 7.62 - 7.58 (m, 1H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -59.04 (dd, J_{FF} = 22.6, 11.3 Hz, 3F), -72.77 (ddd, J_{FF} = 45.1, 22.6, 7.5 Hz, 1F), -75.57 (ddd, J_{FF} = 22.6, 11.3, 7.5 Hz, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.0 (ddq, J_{CF} = 310.1, 295.9, 3.0 Hz, CF$_2$=CAr-CF$_3$), 150.3, 147.9, 138.0, 131.1, 129.4, 128.2, 127.8, 127.4, 122.4 (qdd, J_{CF} = 272.7, 11.1, 6.0 Hz, CF$_2$=CAr-CF$_3$), 119.5, 88.1 - 87.3 (m, CF$_2$=CAr-CF$_3$). HRMS (ESI/Q-TOF) m/z: [M+H]$^+$ calcd for $C_{12}H_7F_5N$ 260.0493; found: 260.0499.



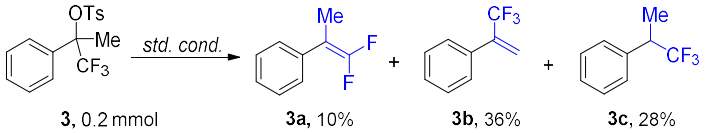
1-(2-methoxy-5-(6-(perfluoroprop-1-en-2-yl)naphthalen-2-yl)phenyl)adamantane (2z) Prepared by the general procedure; isolated as a white solid using petroleum/EtOAc (10/1) as eluent (78.8 mg, 79%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.03 (s, 1H), 7.93 (dd, J = 12.4, 8.4 Hz, 2H), 7.87 (s, 1H), 7.82 (dd, J = 8.4, 1.6 Hz, 1H), 7.63 (d, J = 2.4 Hz, 1H), 7.56 (dd, J = 8.4, 2.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 3.92 (s, 3H), 2.22 (s, 6H), 2.14 (s, 3H), 1.84 (s, 6H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -58.97 (dd, J_{FF} = 22.6, 7.5 Hz, 3F), -75.28 (ddd, J_{FF} = 45.1, 22.6, 11.3 Hz, 1F), -77.15 - -77.27 (m, 1F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.6 - 153.6 (m, CF$_2$=CAr-CF$_3$), 159.0, 140.5, 139.1, 133.8, 132.8, 131.9, 129.8, 128.8, 128.7, 127.1, 126.7, 126.1, 125.8, 124.9, 124.2 - 121.3 (m, CF$_2$=CAr-CF$_3$), 122.9, 112.3, 90.6 - 89.8 (m, CF$_2$=CAr-CF$_3$), 55.3, 40.8, 37.4, 37.3, 29.3. HRMS (ESI/Q-TOF) m/z: [M+H]$^+$ calcd for $C_{30}H_{28}F_5O$ 499.2055; found: 499.2057.



9-(difluoromethylene)-9H-fluorene (2aa) Prepared by the general procedure; isolated as a white solid using petroleum as eluent (25.1 mg, 59%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.78 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 7.2 Hz, 2H), 7.41 - 7.34 (m, 4H). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -75.22 (s, 2F). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.5 (t, J_{CF} = 305.0 Hz), 139.1 (t, J_{CF} = 3.0 Hz), 134.1, 127.9 (t, J_{CF} = 2.0 Hz), 127.4, 123.7 (t, J_{CF} = 5.0 Hz), 120.2, 95.3 (t, J_{CF} = 19.2 Hz). HRMS (EI/Q-TOF) m/z: [M]$^+$ calcd for $C_{14}H_8F_2$ 214.0589; found: 214.0590.

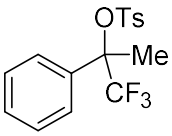
6. Mechanism studies

a). Effect of CF_3 group

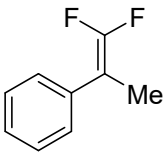


3, 0.2 mmol **3a**, 10% **3b**, 36% **3c**, 28%

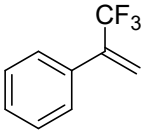
In the glovebox, 1,1,1-trifluoro-2-phenylpropan-2-yl 4-methylbenzenesulfonate (**3**), PdI_2 (5 mol%, 3.6 mg), DPPP (5 mol%, 4.1 mg), and Zn (2.0 equiv, 26.2 mg) were added into an oven-dried 4 mL vial with a magnetic stirring bar, followed by addition of DMA (1.0 mL). The vial was sealed and removed out of the glovebox and heated to 80 °C. After 12 h, the vial was cooled to room temperature. The mixture was passed through a short silica gel pad with EtOAc. The filtrate was analyzed by GC-MS, and the yields were determined by GC-MS analysis using dodecane as the internal standard.



1,1,1-trifluoro-2-phenylpropan-2-yl 4-methylbenzenesulfonate (3) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.42 - 7.31 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.59.[10]

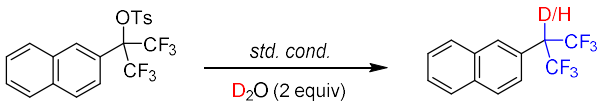


(1,1-difluoroprop-1-en-2-yl) benzene (3a) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 4H), 7.28 - 7.24 (m, 1H), 1.98 (t, *J* = 3.6 Hz, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -90.47 (d, J_{FF} = 45.1, 1F), -90.90 (d, J_{FF} = 41.4, 1F).[11]



(3,3,3-trifluoroprop-1-en-2-yl) benzene (3b) ^{1}H NMR (400 MHz, Chloroform-*d*) δ7.49 - 7.47 (m, 4H), 7.42 - 7.39 (m, 1H), 5.98 (dd, *J* = 2.8, 1.6 Hz, 1H), 5.78 (dd, *J* = 5.4, 2.4 Hz, 1H), ^{19}F NMR (376 MHz, Chloroform-*d*) δ -54.78.[12]

b). D_2O quecing reaction

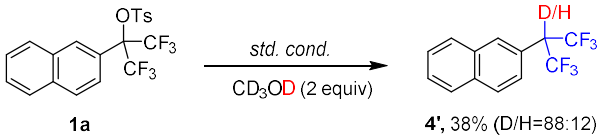


1a **4**, 59% (D/H=90:10)

In the glovebox,**1a**, PdI_2 (3.6 mg, 0.01 mmol), DPPP (4.1 mg, 0.01 mmol), and Zn (26.2 mg, 0.4 mmol) were added into an oven-dried 4 mL vial with a magnetic stirring bar, followed by addition of D_2O (38.0 mg, 0.4 mmol) and DMA (1.0 mL). The vial was sealed and removed out of the glovebox and heated to 80 °C. After 12 h, the vial was cooled to room temperature. The mixture

was passed through a short silica gel pad with EtOAc. The organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated in vacuo. The **4** were purified by silica gel column chromatography.

Compound **4** are all white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95-7.84 (m, 4H), 7.62-7.51 (m, 2H), 7.51 (d, *J* = 8.6 Hz, 1H), 4.23-4.19 (m, 0.1H). ^{19}F NMR (376MHz, Chloroform-*d*) δ -65.19.



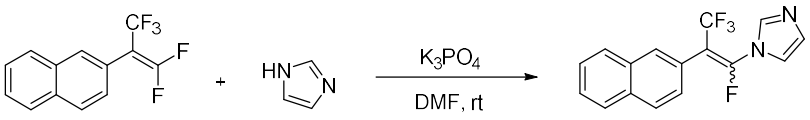
1a **4'**, 38% (D/H=88:12)

In the glovebox,**1a**, PdI_2 (3.6 mg, 0.01 mmol), DPPP (4.1 mg, 0.01 mmol), and Zn (26.2 mg, 0.4 mmol) were added into an oven-dried 4 mL vial with a magnetic stirring bar, followed by addition of CD_3OD (38.0 mg, 0.4 mmol) and DMA (1.0 mL). The vial was sealed and removed out of the glovebox and heated to 80 °C. After 12 h, the vial was cooled to room temperature. The mixture was passed through a short silica gel pad with EtOAc. The organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated in vacuo. The **4'** were purified by silica gel column chromatography.

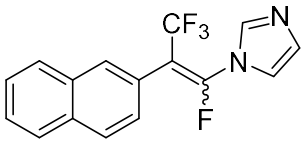
Compound **4'** are all white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93-7.87 (m, 4H), 7.60-7.53 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 4.28-4.19 (m, 0.12H). ^{19}F NMR (376MHz, Chloroform-*d*) δ -65.19.

7. Synthetic utility experiments

a)

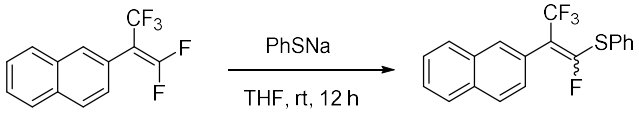


A solution of azole (34.0 mg, 0.5 mmol) in DMF (0.5 mL) was added dropwise to a mixture of **2a** (154.8 mg, 0.6 mmol) and K_3PO_4 (212.0 mg, 1 mmol) in DMF (0.5 mL) via syringe and then stirred at room temperature for 12 h (monitored by TLC). After completion of the reaction, the mixture was quenched with H_2O (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over Na_2SO_4 and filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the pure target compound **9**.[13]

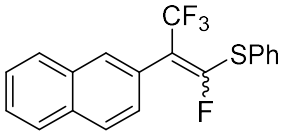


1-(1,3,3,3-tetrafluoro-2-(naphthalen-2-yl)prop-1-en-1-yl)-1H-imidazole (5) was obtained as a colorless oil (104.0 mg, 68%, Z/E = 1/4); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.81 - 7.62 (m, 5H), 7.42 - 7.33 (m, 2H), 7.13 - 7.09 (m, 1H), 6.73 (s, 1H), 6.59 (s, 1H). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -58.32 (d, J_{FF} = 22.6 Hz, 3F), 45.39 (d, J_{FF} = 22.6 Hz, 1F). ^{13}C NMR (151 MHz, Chloroform-d) δ 149.4 - 147.5 (m, *C*F=CAr-CF$_3$), 136.5, 133.4, 133.1, 130.0 (d, J_{CF} = 1.0 Hz), 129.5, 128.6, 128.2, 127.8, 127.6, 127.0, 126.5 (d, J_{CF} = 1.0 Hz), 124.9, 117.7, 124.6 - 119.2 (m, CF=*C*Ar-CF$_3$), 103.5 - 103.2 (m, CF=CAr-*C*F$_3$). HRMS (EI/Q-TOF) m/z: [M]$^+$ calcd for $C_{16}H_{10}F_4N_2$ 306.0775; found: 306.0754.

b)

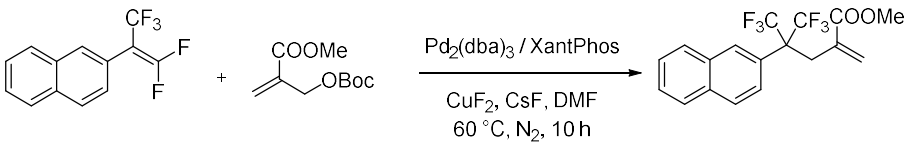


PhSNa(1.2 equiv) was added to a stirred solution of **2a** (1.0 equiv) in THF (0.2 M). The solution was stirred at rt for 12 h and quenched with H_2O, the layers were separated and the aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by silica gel column chromatography afforded the desired product. [14]



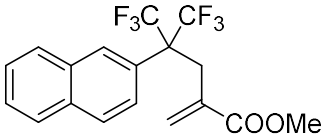
phenyl(1,3,3,3-tetrafluoro-2-(naphthalen-2-yl)prop-1-en-1-yl)sulfane (6) was obtained as a colorless oil (130.5 mg, 75%, Z/E = 7/1); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.96 - 7.85 (m, 4H), 7.69 - 7.54 (m, 3H), 7.50 - 7.47 (m, 2H), 7.44 - 7.36 (m, 3H). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -58.16 (d, J_{FF} = 22.5 Hz, 3F), -78.17 (q, J_{FF} = 22.6, 1F). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0 (dq, J_{CF} = 321.2, 3.0 Hz, *C*F=CAr-CF$_3$), 133.6, 133.4, 133.0, 130.5 (d, J_{CF} = 3.0 Hz), 129.6, 129.5, 129.4, 128. 6, 128.3, 128.1, 127.8, 127.3 (d, J_{CF} = 3.0 Hz), 126.9, 126.5, 123.6 - 20.9 (m, CF=CAr-*C*F$_3$), 1114.7 - 114.1 (m, CF=CAr-*C*F$_3$). HRMS (EI/Q-TOF) m/z: [M]$^+$ calcd for $C_{19}H_{12}F_4S$ 348.0590; found: 348.0587.

c)



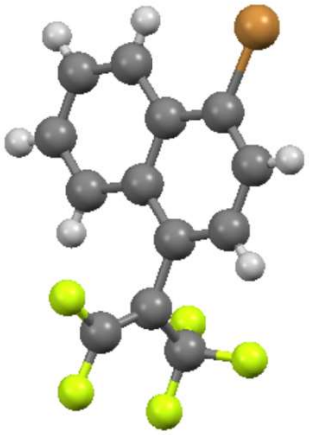
An oven-dried 8 ml Schlenk tube was charged with $Pd_2(dba)_3$ (3.4 mg, 0.015 mmol), Xantphos (8.7 mg, 0.01 mmol), CuF_2 (1.5 mg, 0.01 mmol), CsF (68.4 mg, 0.45 mmol) in sequence under the

glovebox, followed by adding **2a** (37.2 mg, 0.15 mmol) and methyl 2-(((tert-butoxycarbonyl)oxy)methyl)acrylate (64.8 mg, 0.3 mmol) and then anhydrous DMF (1.0 mL) was added through syringe. After stirring at 60 ℃ for 10 h the mixture was washed with water and extracted with EtOAc, the solvent was removed in vacuo. Purification of the residue by silica gel column chromatography afforded the desired product.[15]



Methyl 5,5,5-trifluoro-2-methylene-4-(naphthalen-2-yl)-4-(trifluoromethyl)pentanoate (8) was obtained as a colorless oil (41.7 mg, 74%); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 – 7.77 (m, 3H), 7.77 – 7.73 (m, 1H), 7.51 – 7.41 (m, 3H), 6.23 – 6.18 (m, 1H), 5.57 (d, J = 2.0 Hz, 1H), 3.75 (s, 3H), 3.54 (t, J = 2.0 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*): δ -65.0. ^{13}C NMR (101 MHz, Chloroform-d) δ 167.3, 154.7 (dd, J_{CF} = 293.9, 289.9 Hz), 136.7 (dd, J_{CF} = 3.0, 2.0 Hz), 133.3, 132.6, 130.6 (t, J_{CF} = 4.0 Hz), 128.2, 128.1, 127.7, 127.3 (t, J_{CF} = 3.0 Hz), 126.47, 126.45, 126.4, 125.9 (dd, J_{CF} = 4.0, 2.0 Hz), 89.8 (dd, J_{CF} = 21.2, 14.1 Hz), 52.2, 30.1 (dd, J_{CF} = 2.0, 1.0 Hz). HRMS (EI/Q-TOF) m/z: $[M]^{+}$ calcd for $C_{18}H_{14}F_6O_2$ 376.0893; found: 376.0891.

8. X-ray crystal structure of 2o



CCDC-2074740 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

9. References

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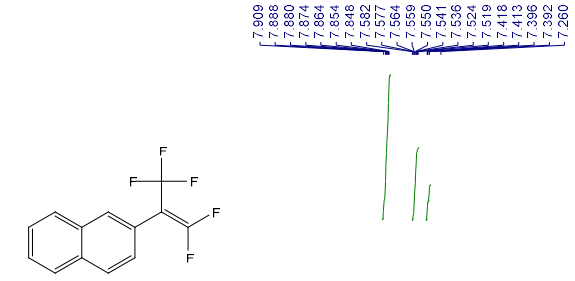
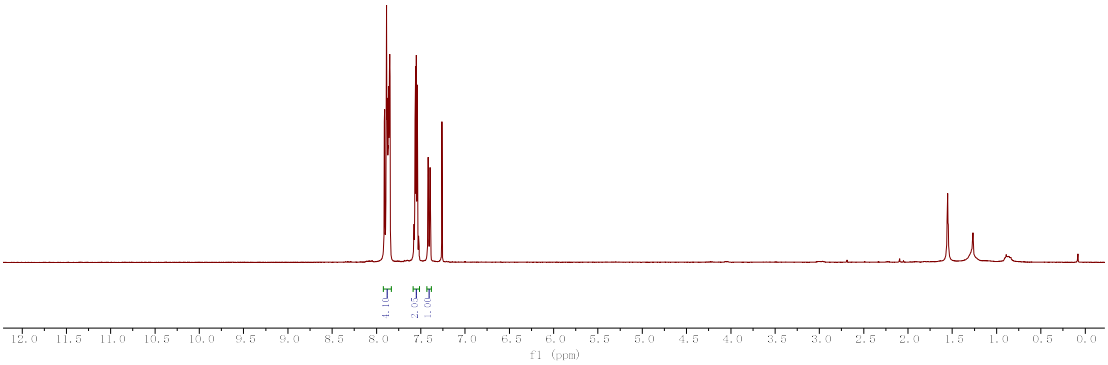
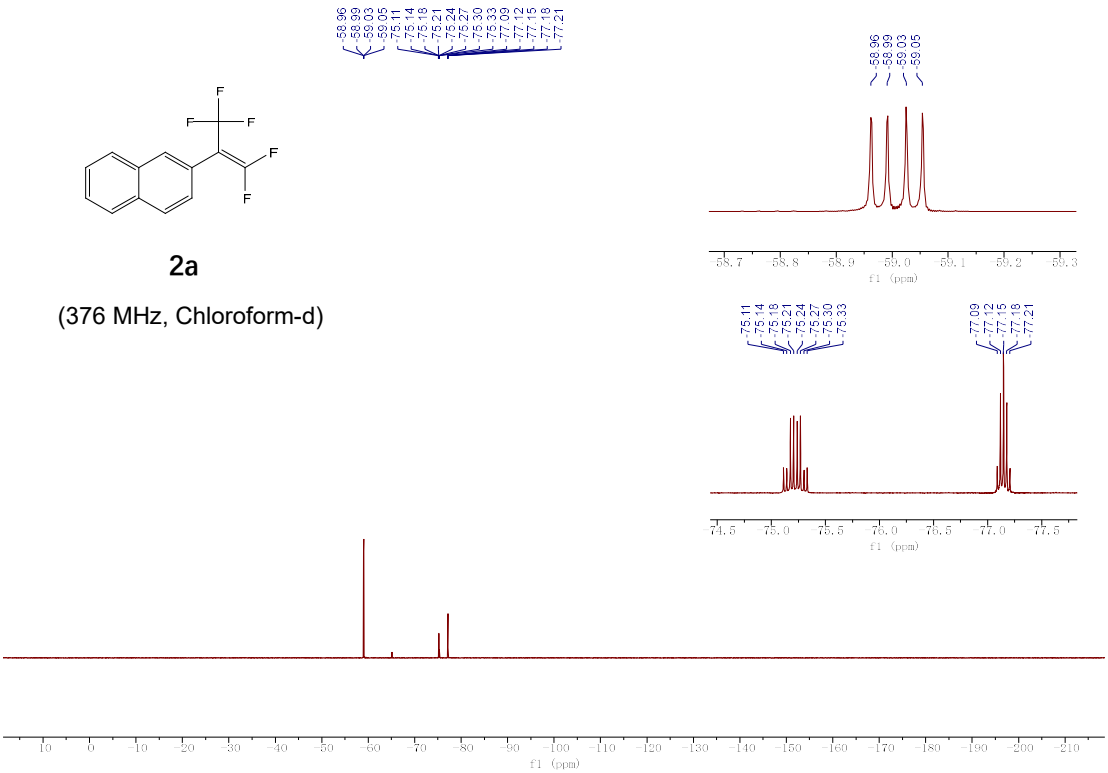
10. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra of Products



2a

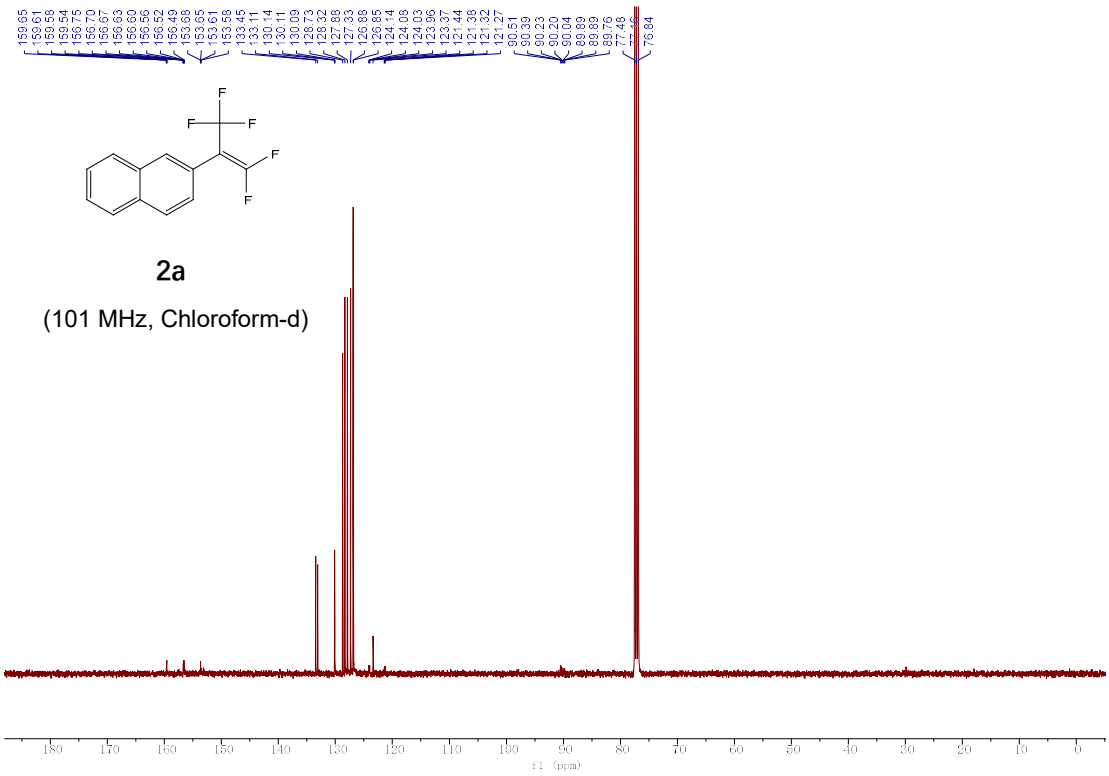
(400 MHz, Chloroform-d)

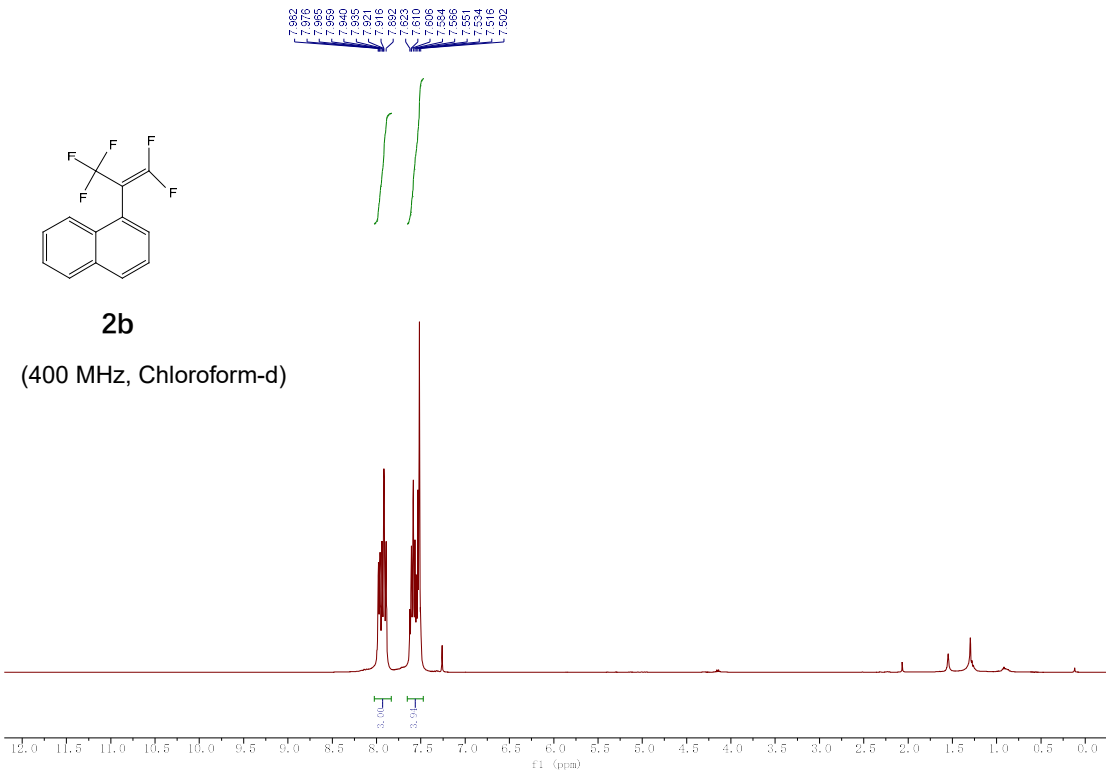


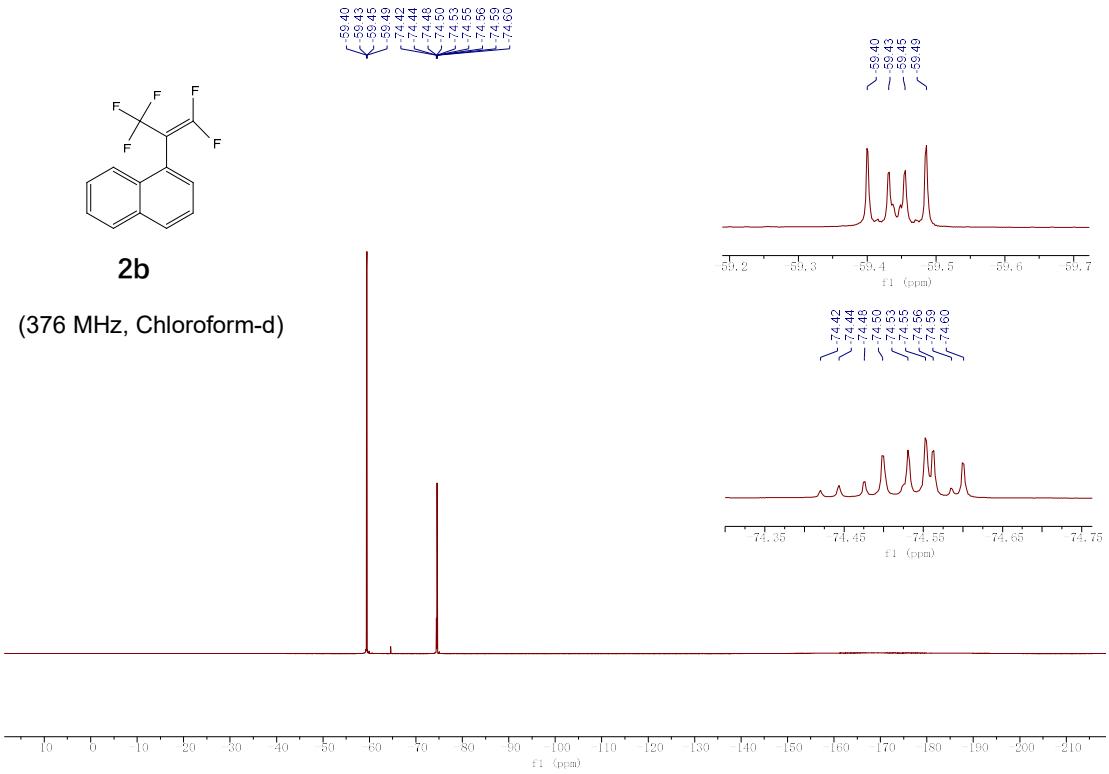


2a

(376 MHz, Chloroform-d)

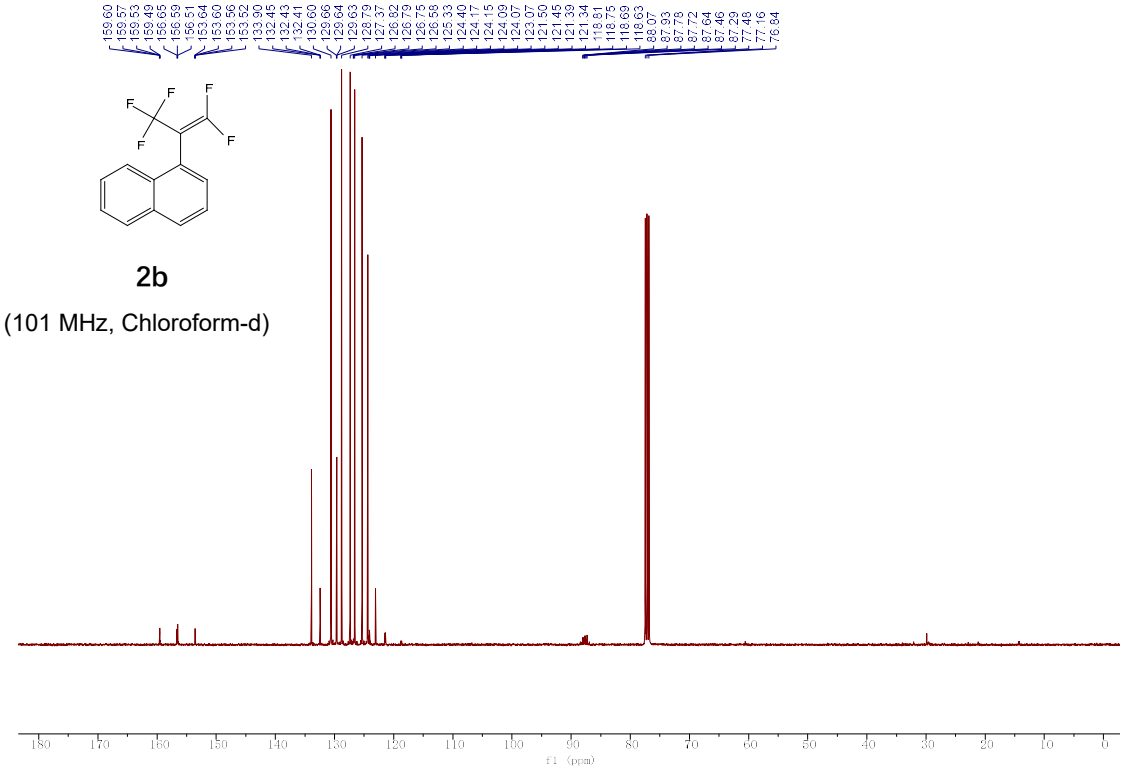

159.65
159.61
159.58
159.54
156.75
156.70
156.67
156.63
156.60
156.56
156.52
156.49
153.68
153.65
153.61
153.58
133.45
133.11
130.14
130.11
130.09
128.73
128.32
127.88
127.33
126.88
126.85
124.14
124.08
124.03
123.96
123.37
121.44
121.36
121.32
121.27
90.51
90.39
90.23
90.20
90.04
89.89
89.89
89.76
77.46
76.84
F
F
F
F
F
2a
(101 MHz, Chloroform-d)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.982
7.975
7.965
7.959
7.940
7.935
7.921
7.916
7.892
7.883
7.610
7.606
7.584
7.566
7.551
7.534
7.516
7.502
F
F
F
F
F
2b
(400 MHz, Chloroform-d)
3.00
3.94
12.0
11.5
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)



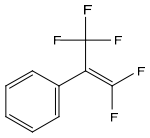
2b

(376 MHz, Chloroform-d)



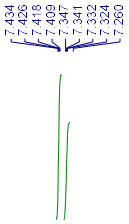
2b

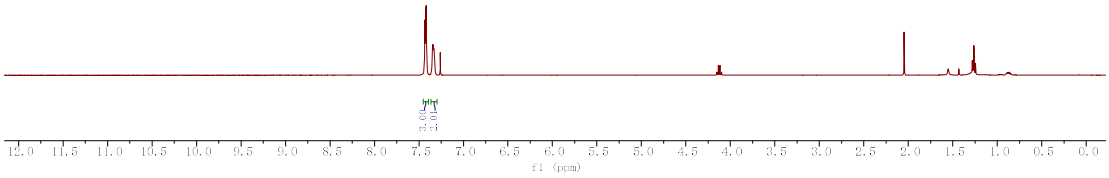
(101 MHz, Chloroform-d)

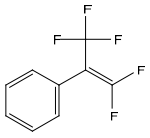


2c

(400 MHz, Chloroform-d)

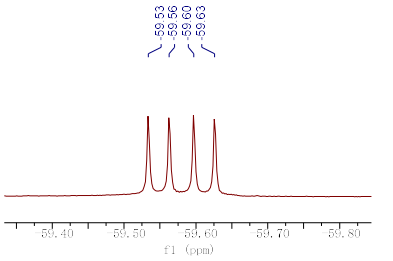


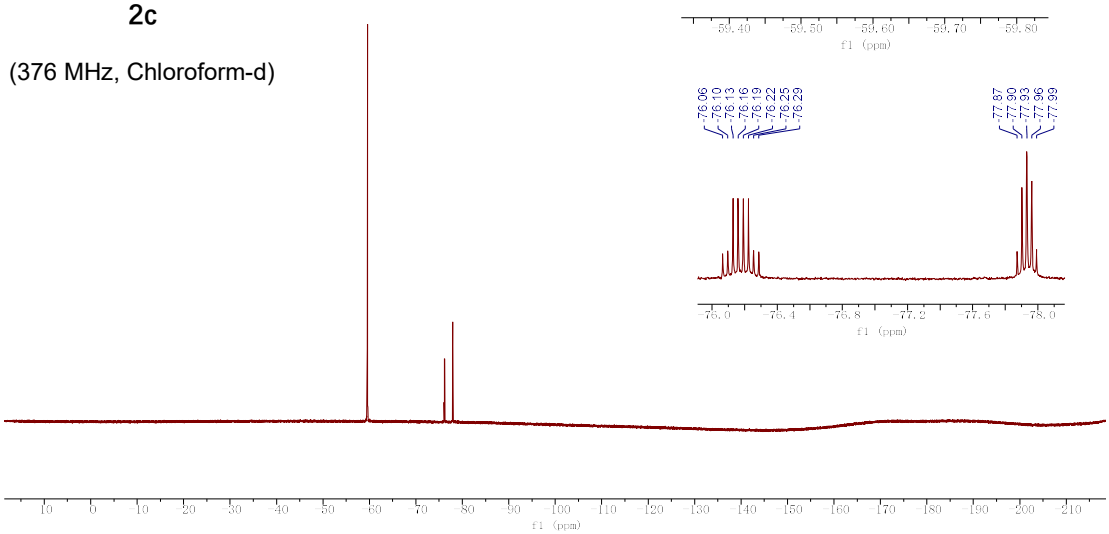


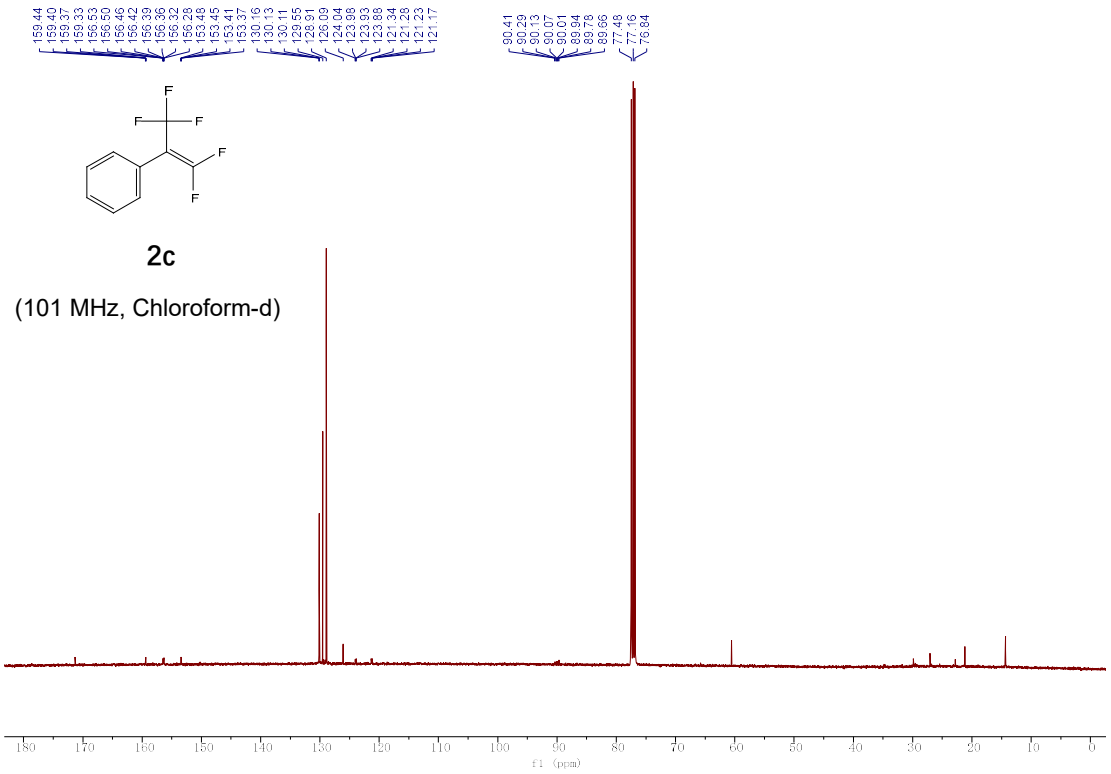


2c

(376 MHz, Chloroform-d)

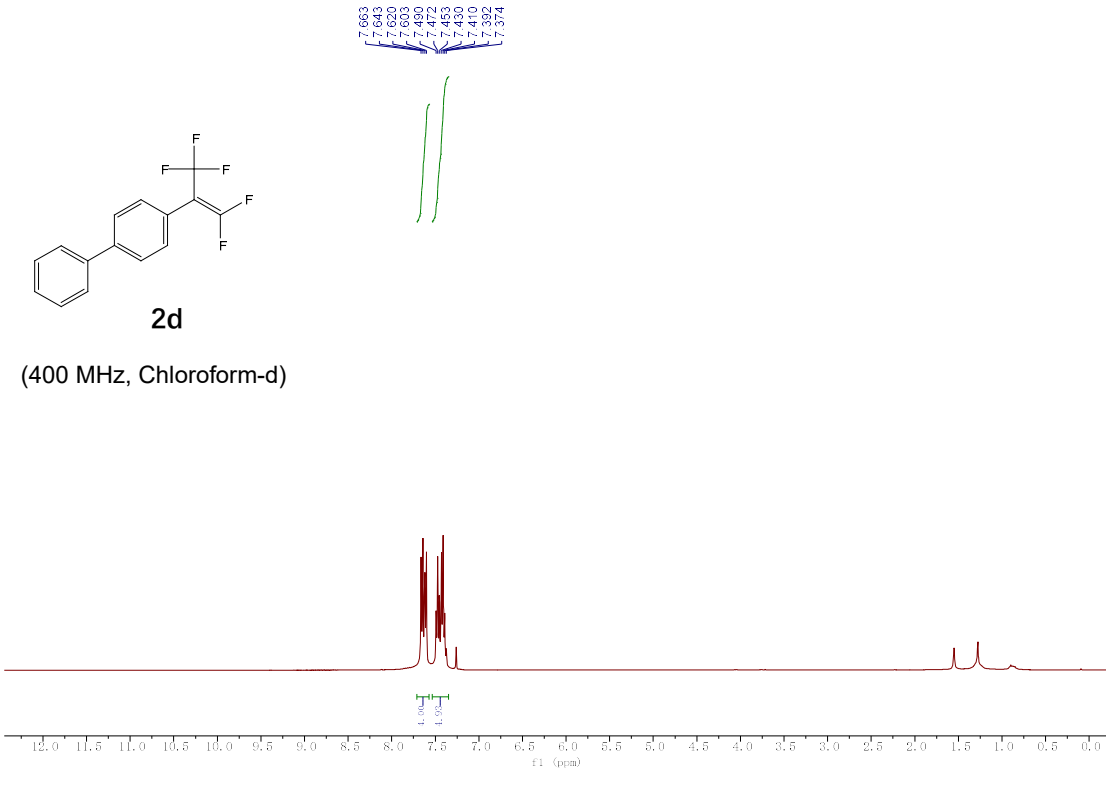






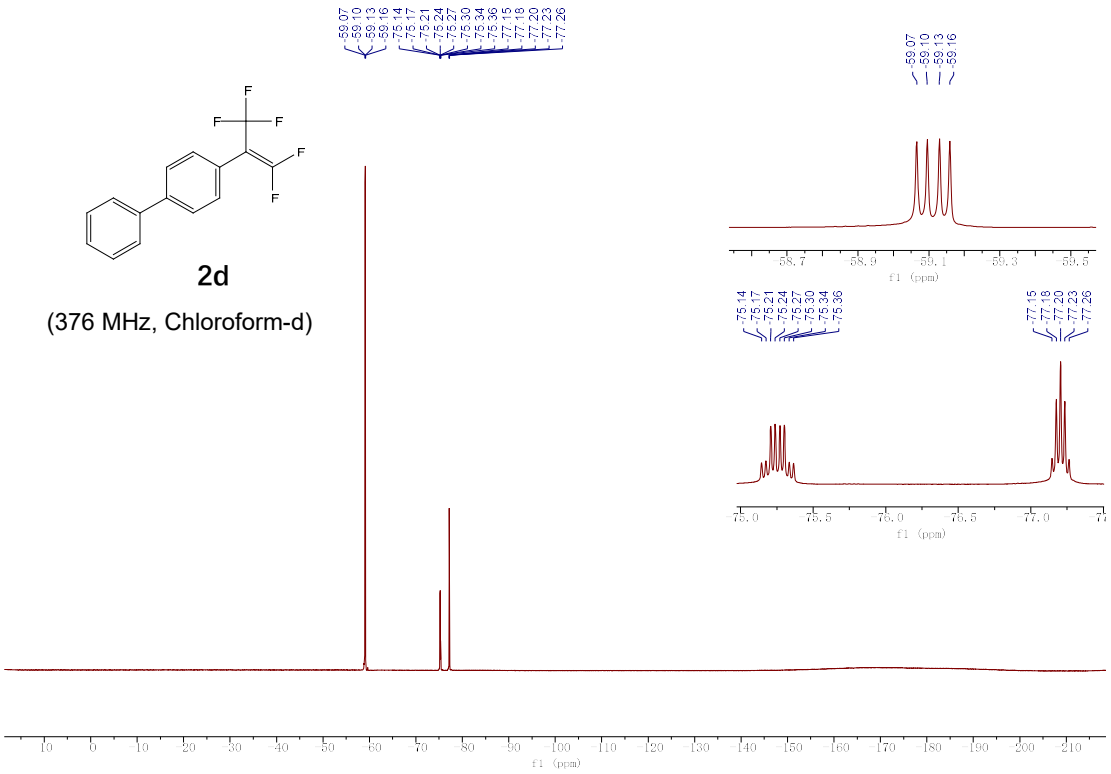
2c

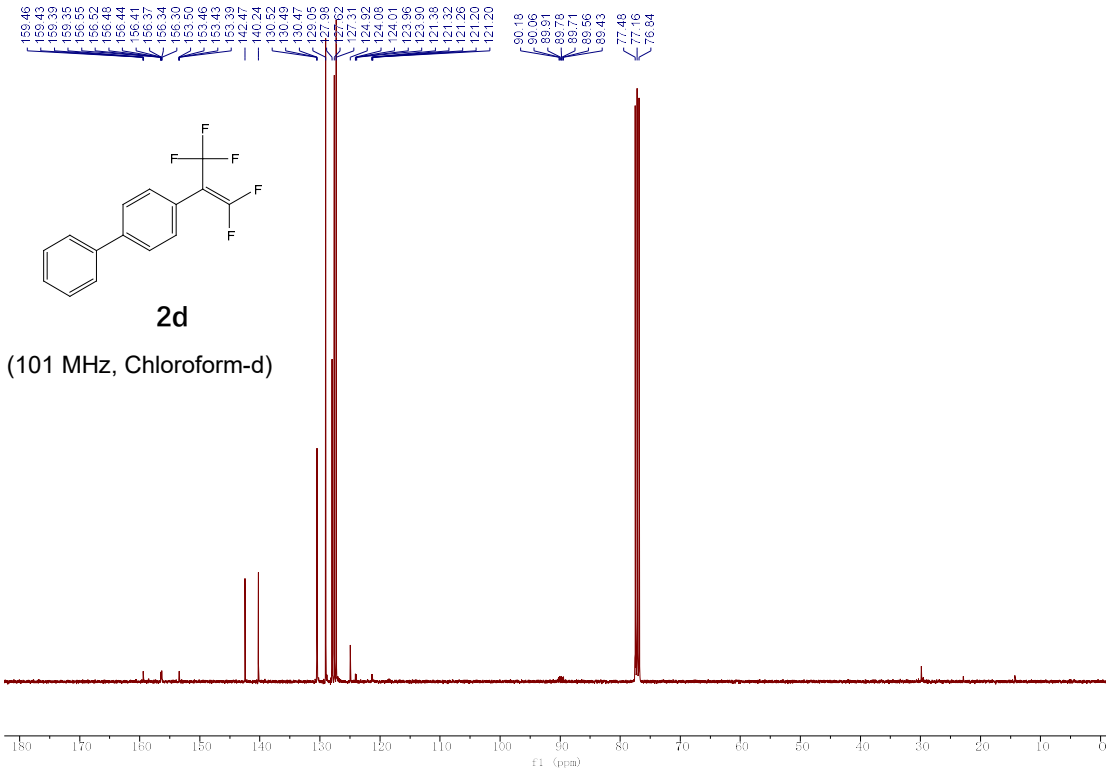
(101 MHz, Chloroform-d)

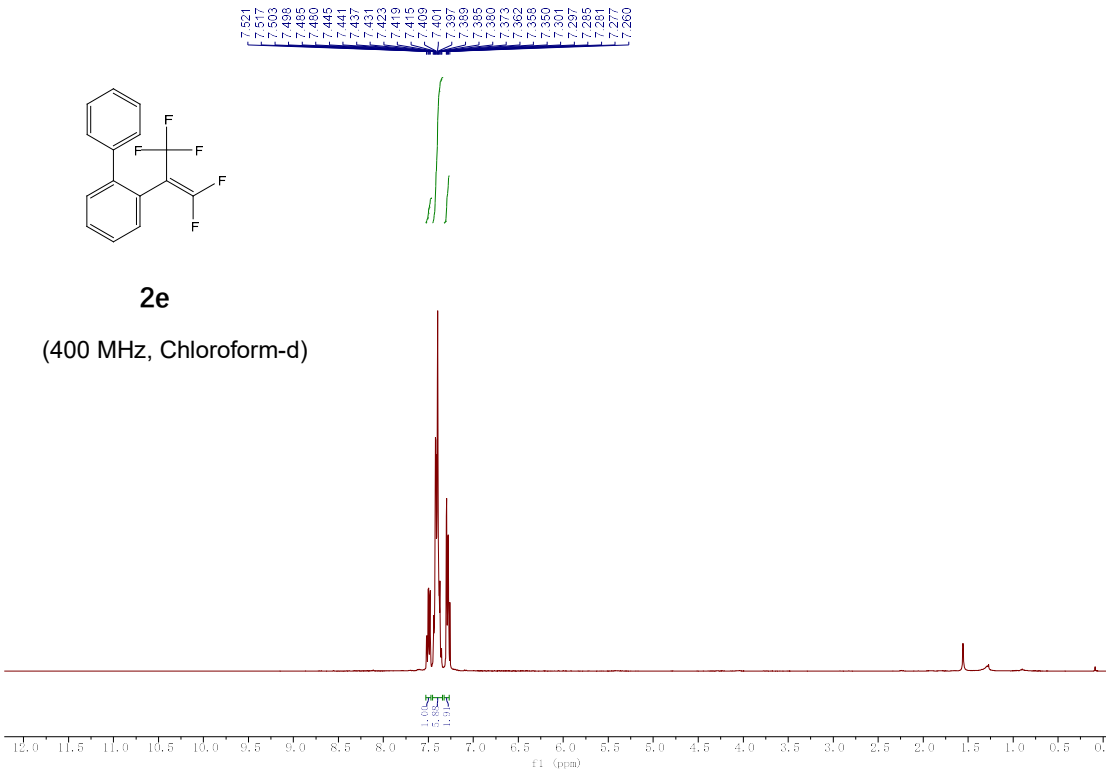


2d

(400 MHz, Chloroform-d)

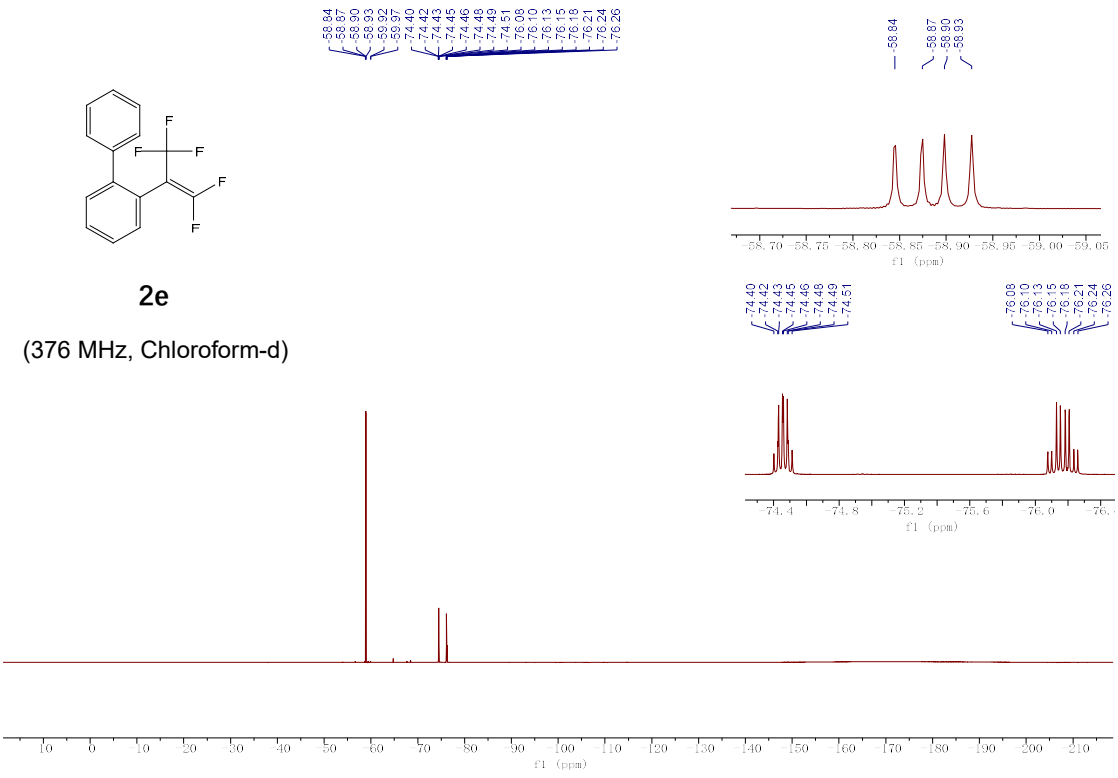

59.07
59.10
59.13
59.16
75.14
75.17
75.21
75.24
75.27
75.30
75.34
75.36
77.15
77.18
77.20
77.23
77.26
F
F
F
F
F
2d
(376 MHz, Chloroform-d)
f1 (ppm)


159.46
159.43
159.39
159.35
156.55
156.52
156.48
156.44
156.41
156.37
156.34
156.30
153.50
153.46
153.43
153.39
142.47
140.24
130.52
130.49
130.47
129.05
127.98
127.62
127.31
124.92
124.08
124.01
123.96
123.90
121.38
121.32
121.26
121.20
90.18
90.06
89.91
89.78
89.71
89.56
89.43
77.48
77.16
76.84
F
F
F
F
F
2d
(101 MHz, Chloroform-d)
f1 (ppm)



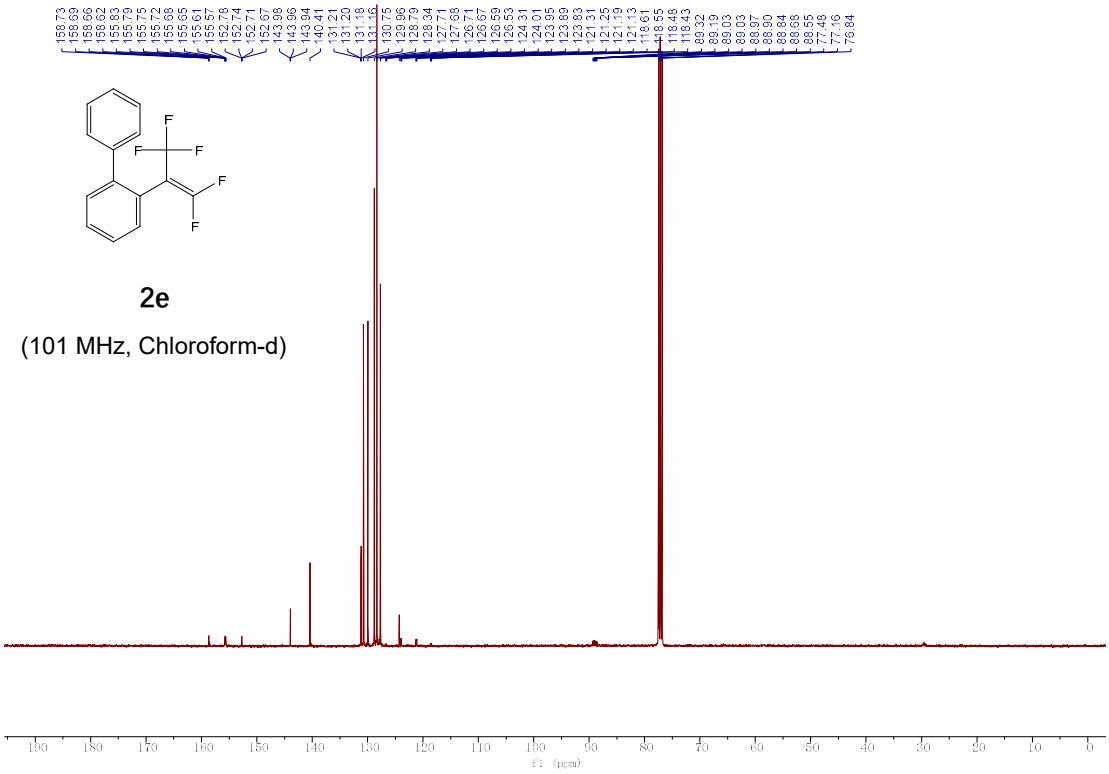
2e

(400 MHz, Chloroform-d)



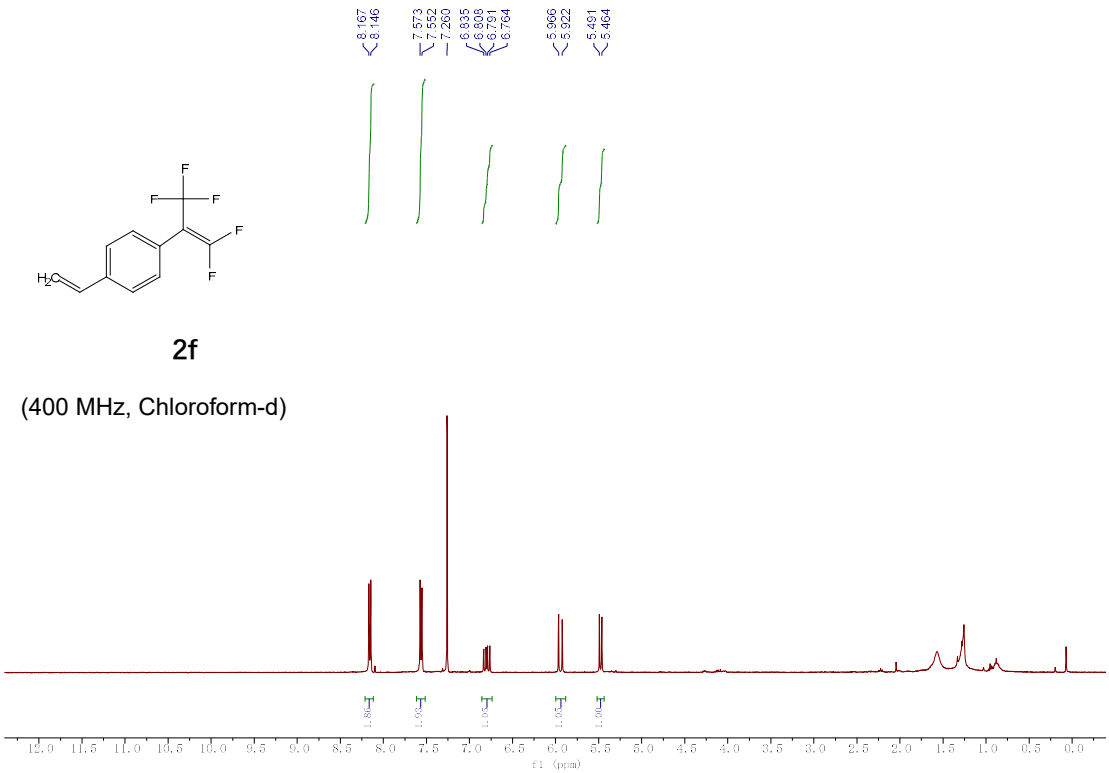
2e

(376 MHz, Chloroform-d)



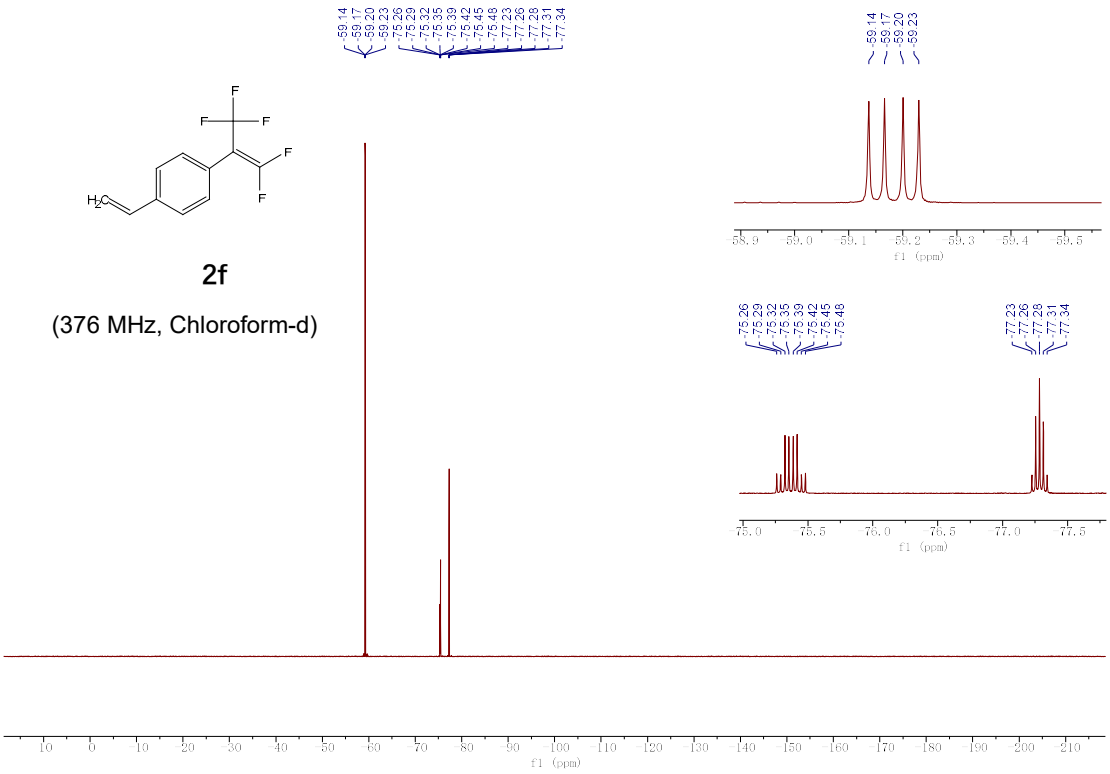
2e

(101 MHz, Chloroform-d)



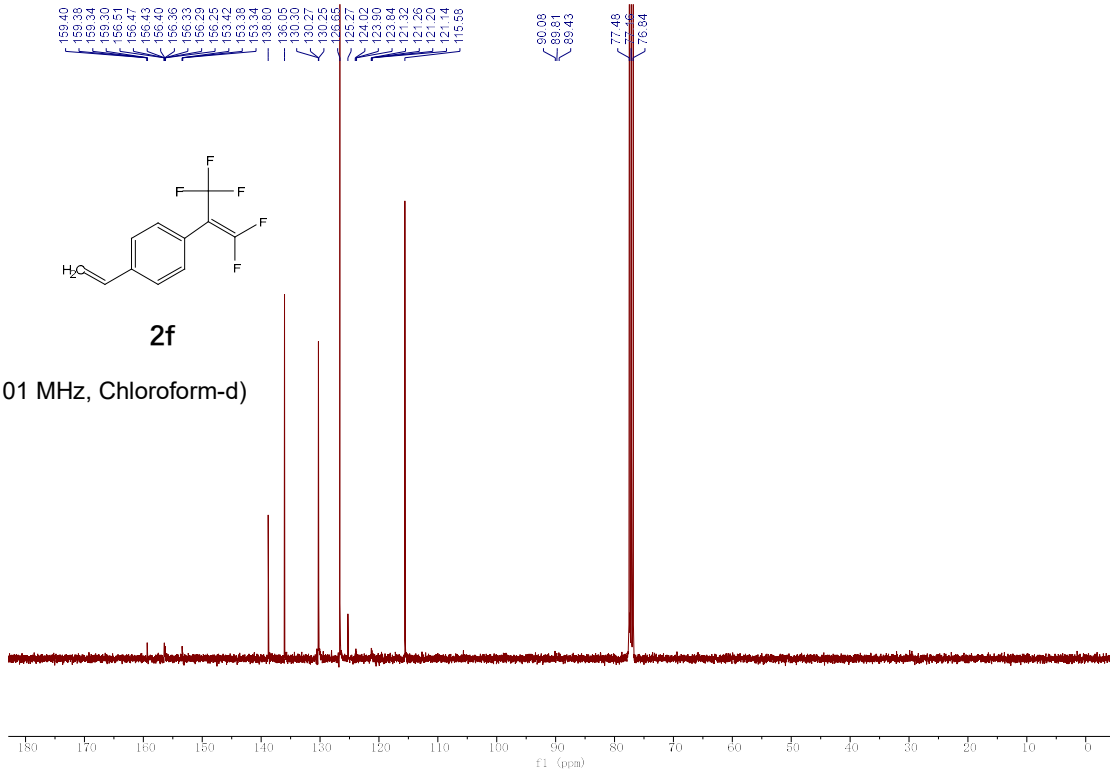
2f

(400 MHz, Chloroform-d)



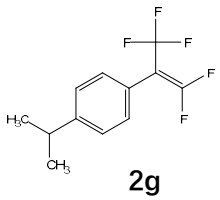
2f

(376 MHz, Chloroform-d)



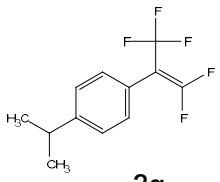
2f

(101 MHz, Chloroform-d)



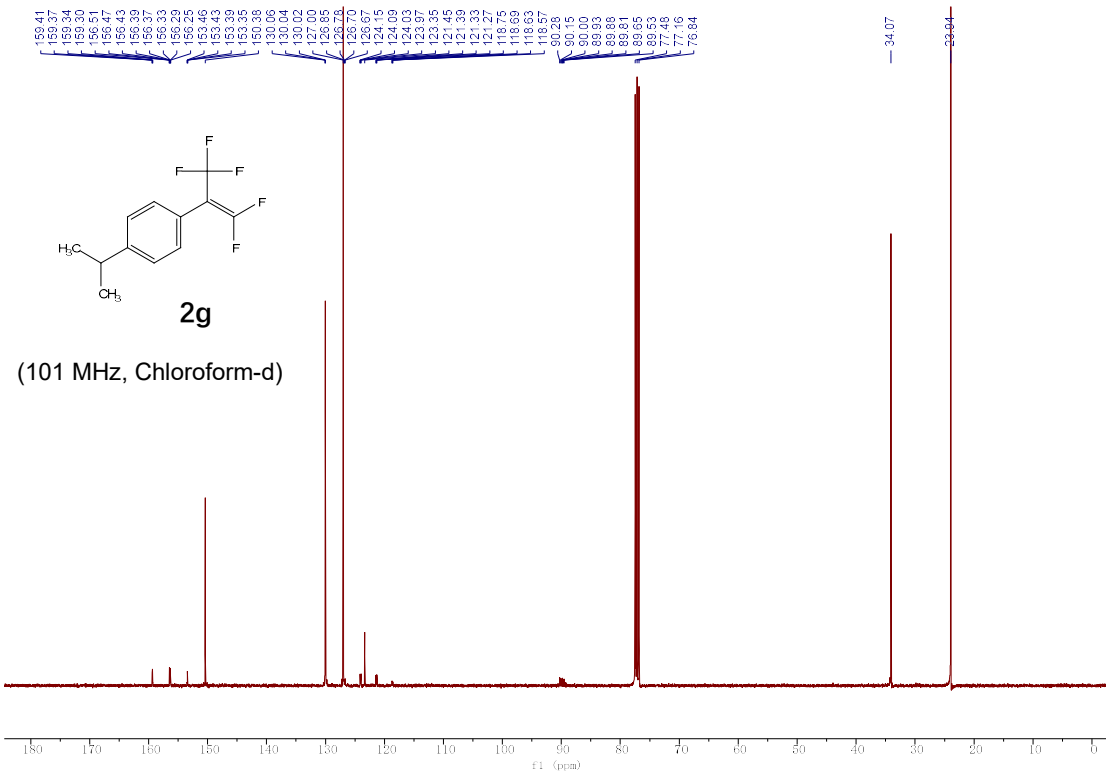
2g

(400 MHz, Chloroform-d)



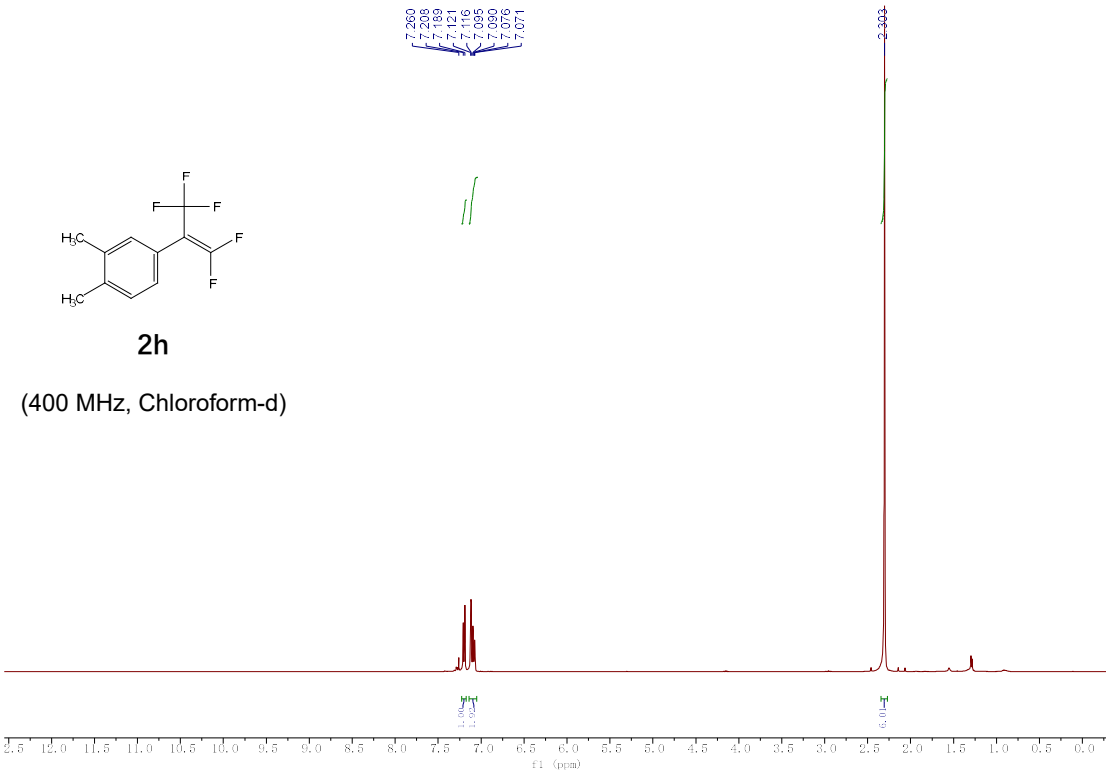
2g

(376 MHz, Chloroform-d)



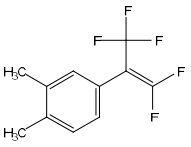
2g

(101 MHz, Chloroform-d)



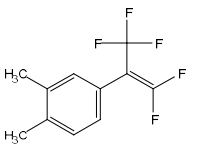
2h

(400 MHz, Chloroform-d)



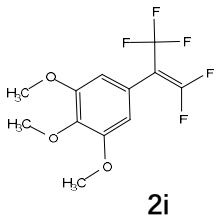
2h

(376 MHz, Chloroform-d)



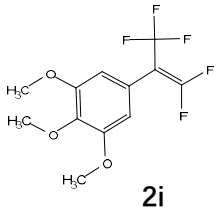
2h

(101 MHz, Chloroform-d)



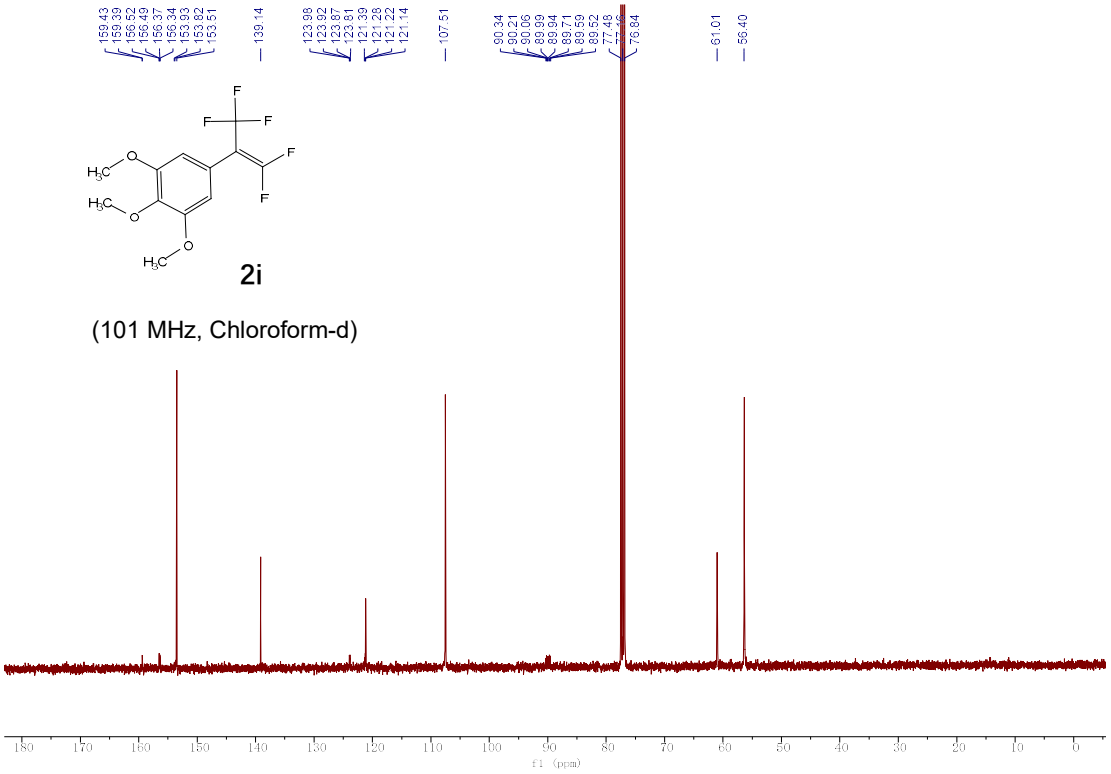
2i

(400 MHz, Chloroform-d)



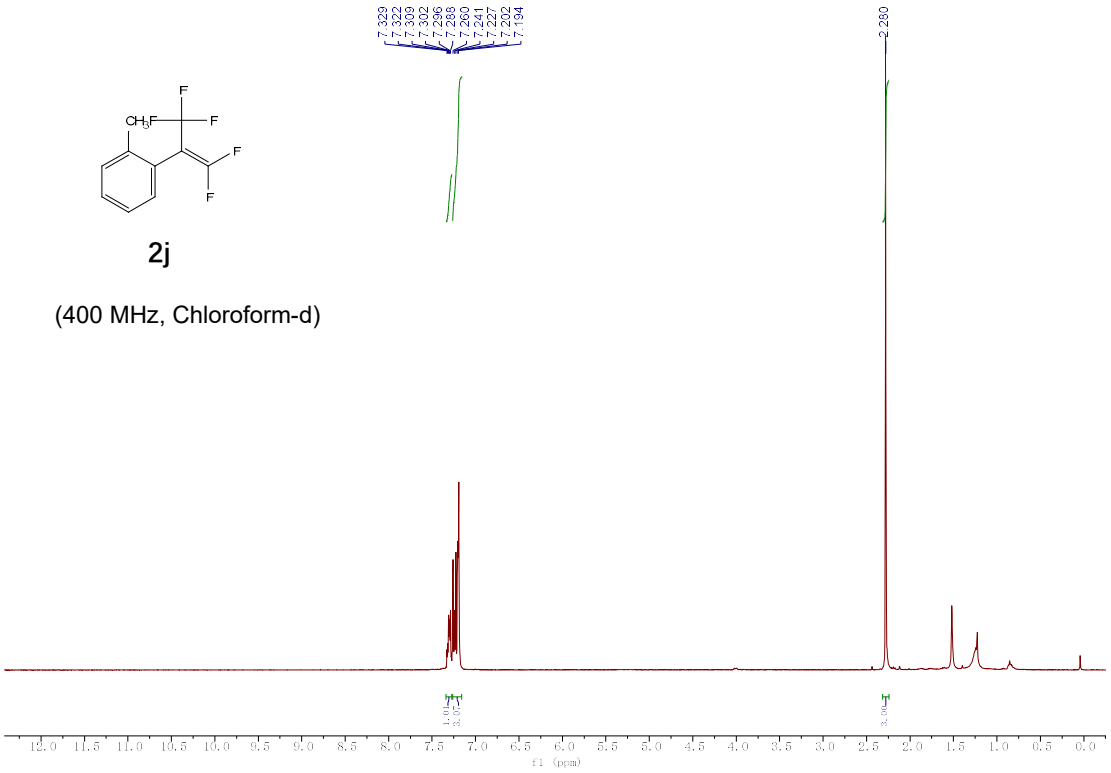
2i

(376 MHz, Chloroform-d)



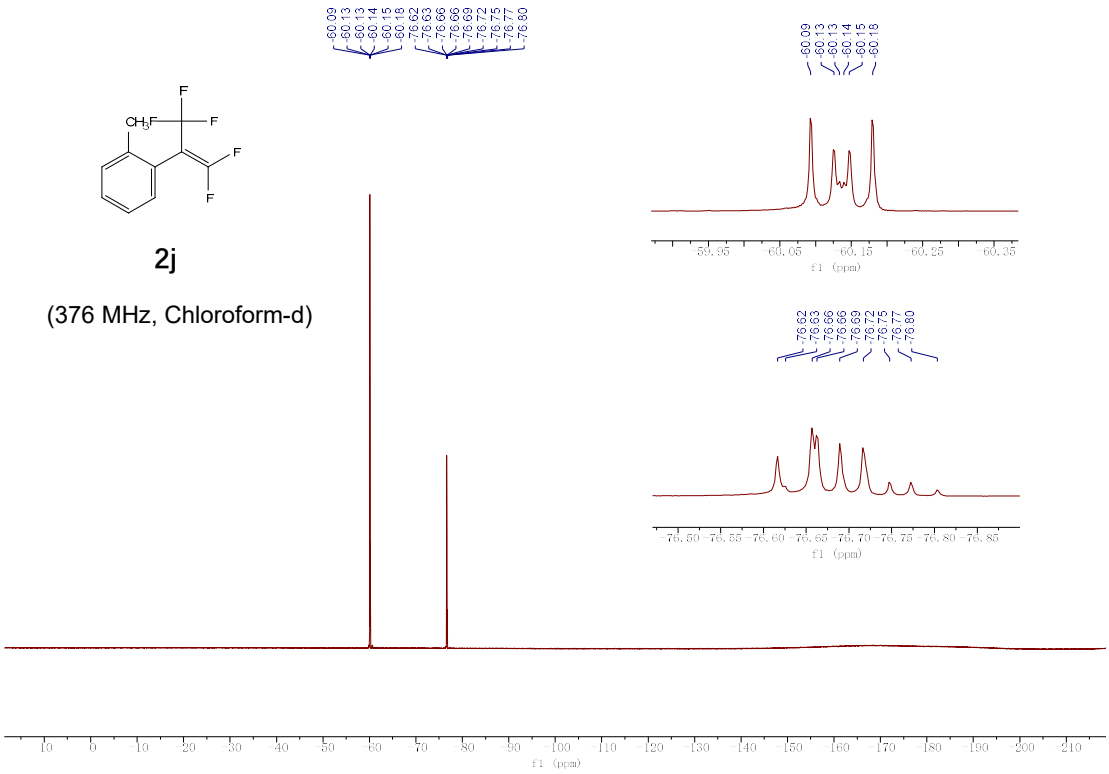
2i

(101 MHz, Chloroform-d)



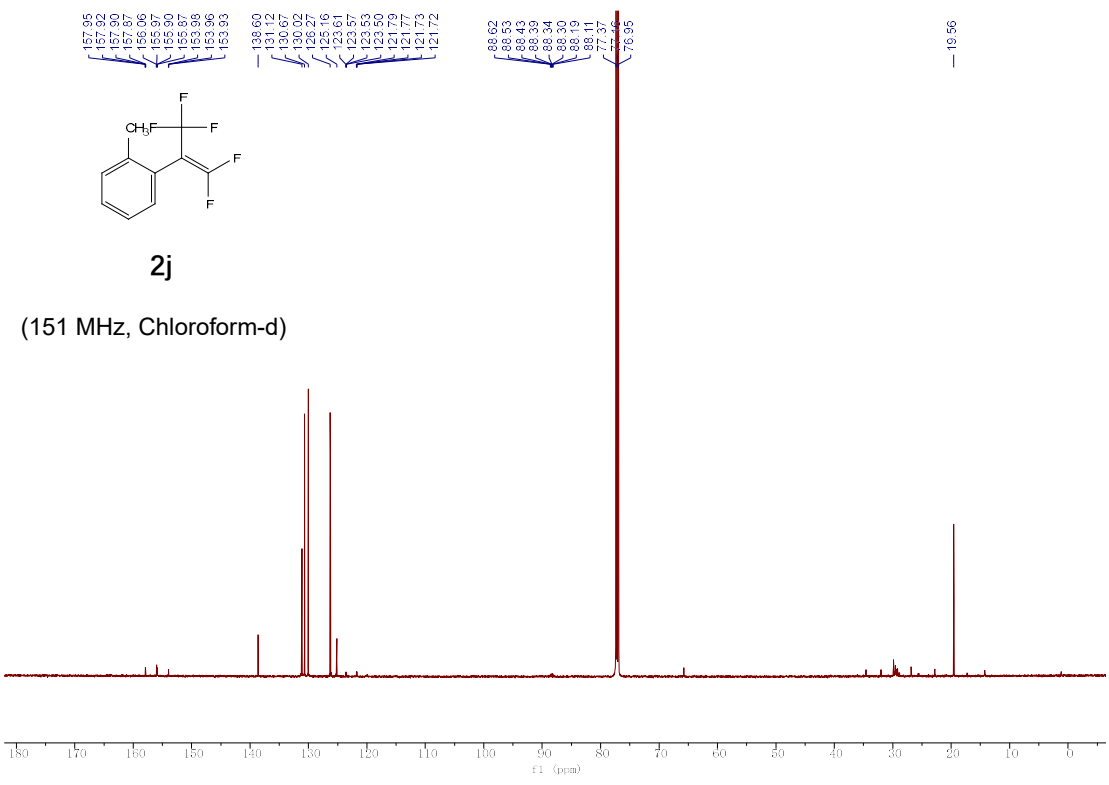
2j

(400 MHz, Chloroform-d)



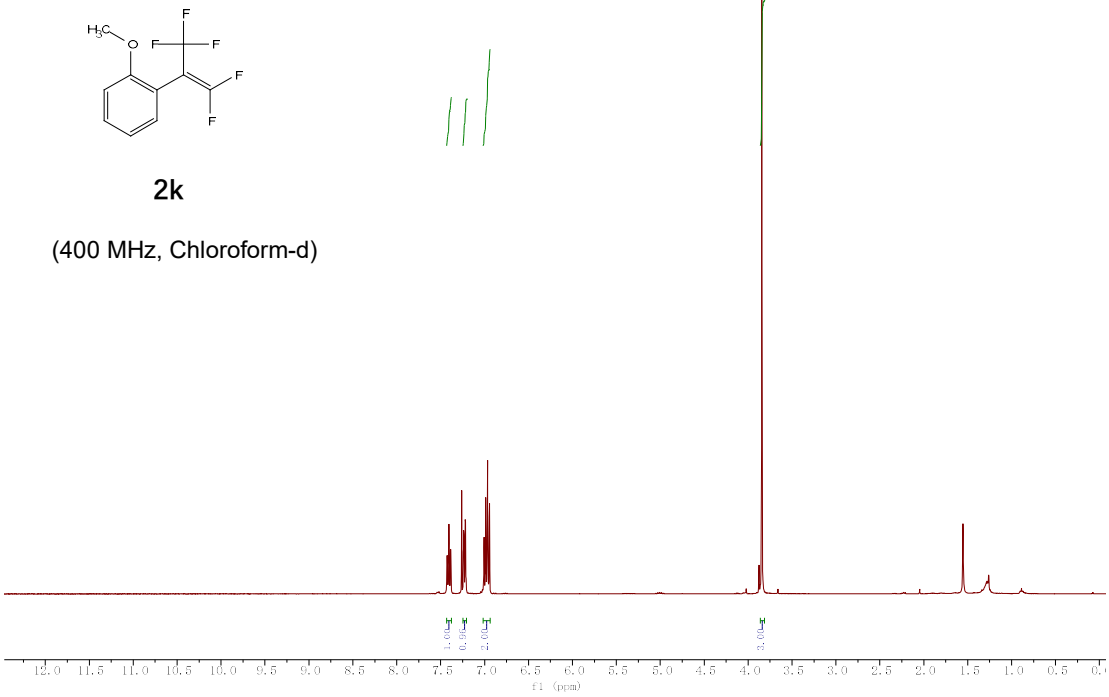
2j

(376 MHz, Chloroform-d)



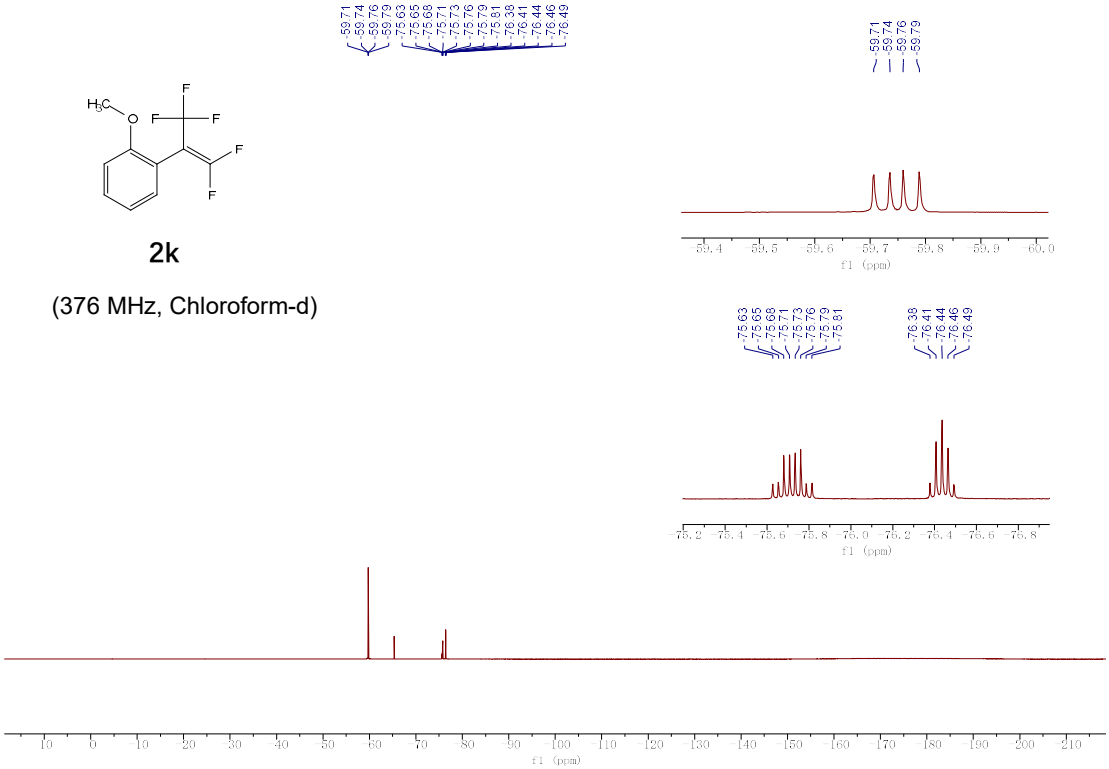
2j

(151 MHz, Chloroform-d)



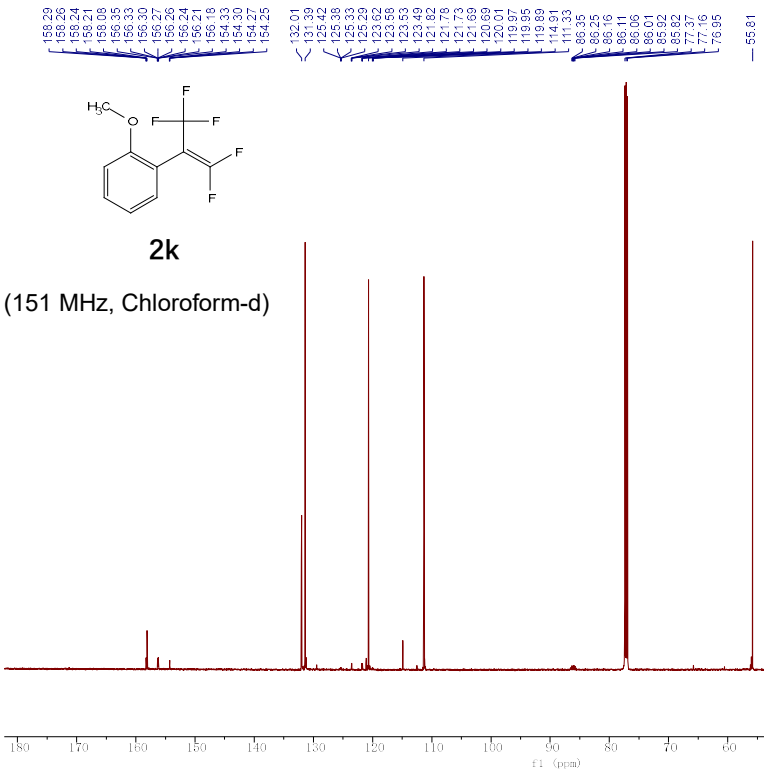
2k

(400 MHz, Chloroform-d)



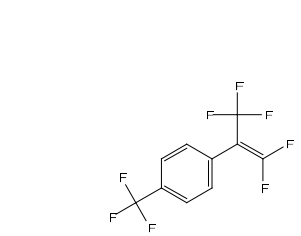
2k

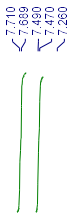
(376 MHz, Chloroform-d)



2k

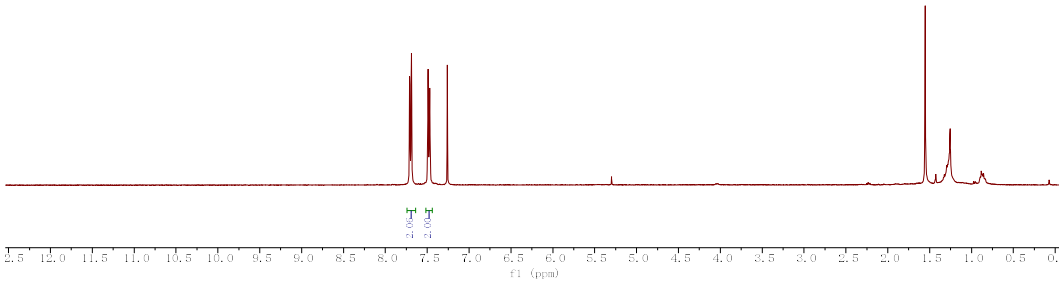
(151 MHz, Chloroform-d)

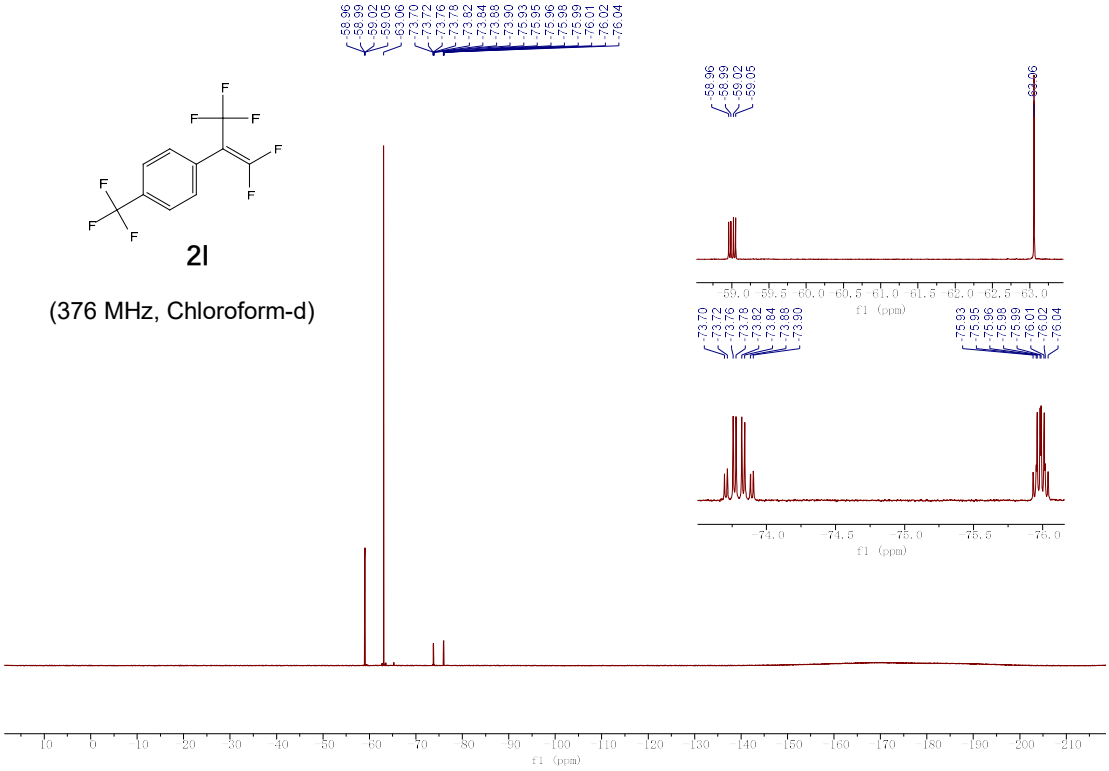




2l

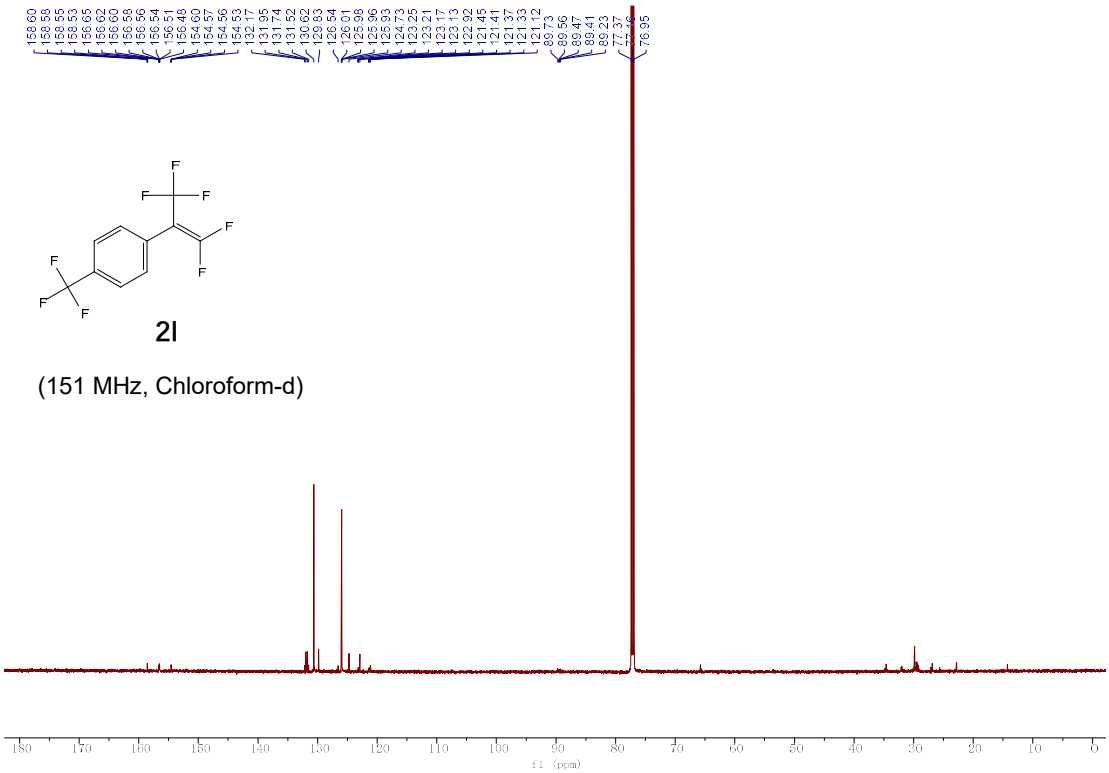
(400 MHz, Chloroform-d)





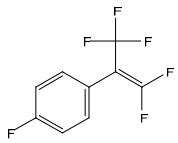
2l

(376 MHz, Chloroform-d)



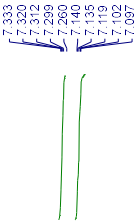
2l

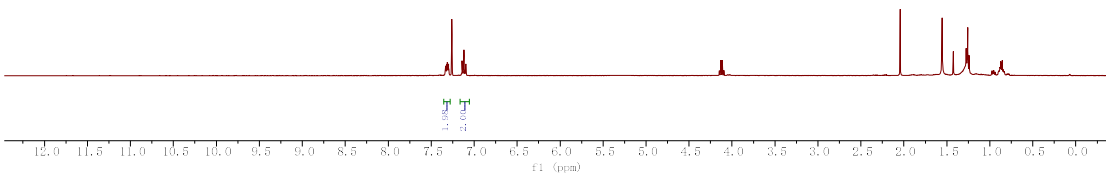
(151 MHz, Chloroform-d)

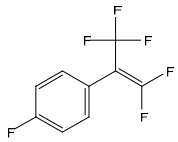


2m

(400 MHz, Chloroform-d)

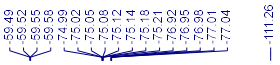


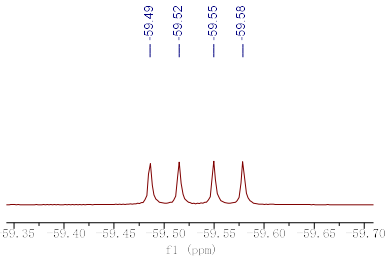


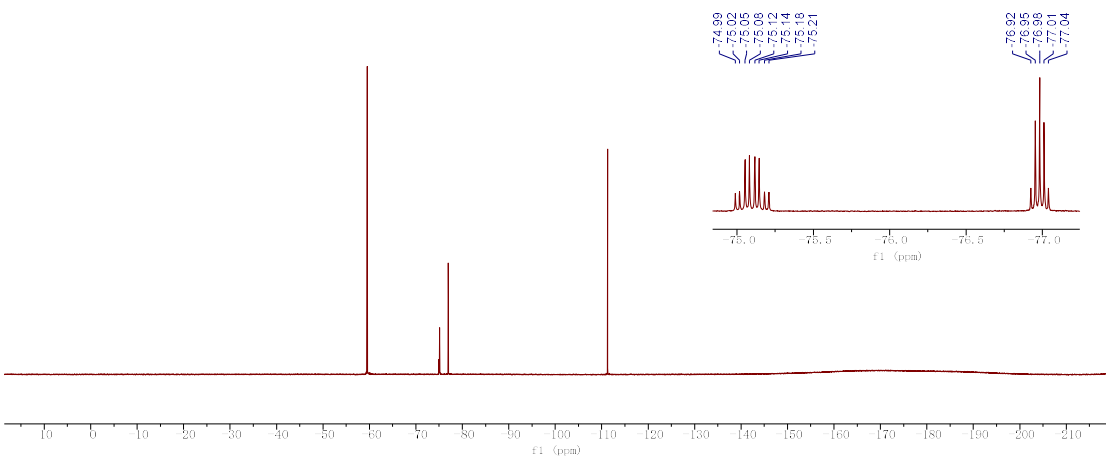


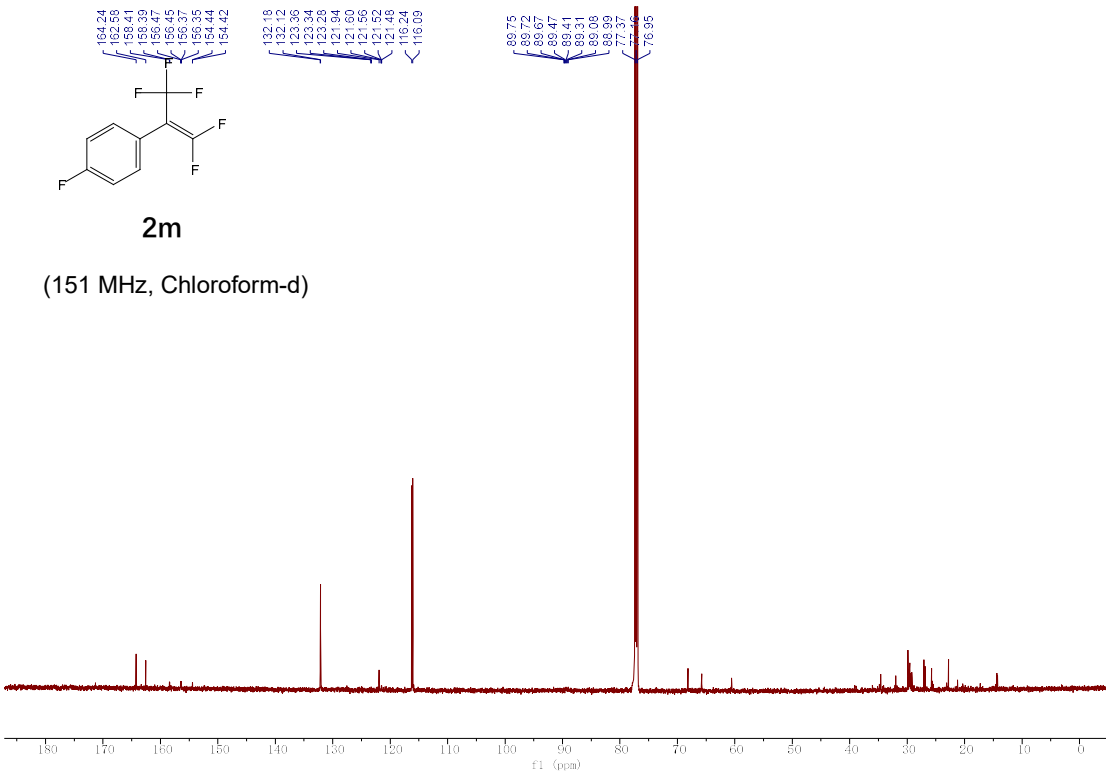
2m

(376 MHz, Chloroform-d)



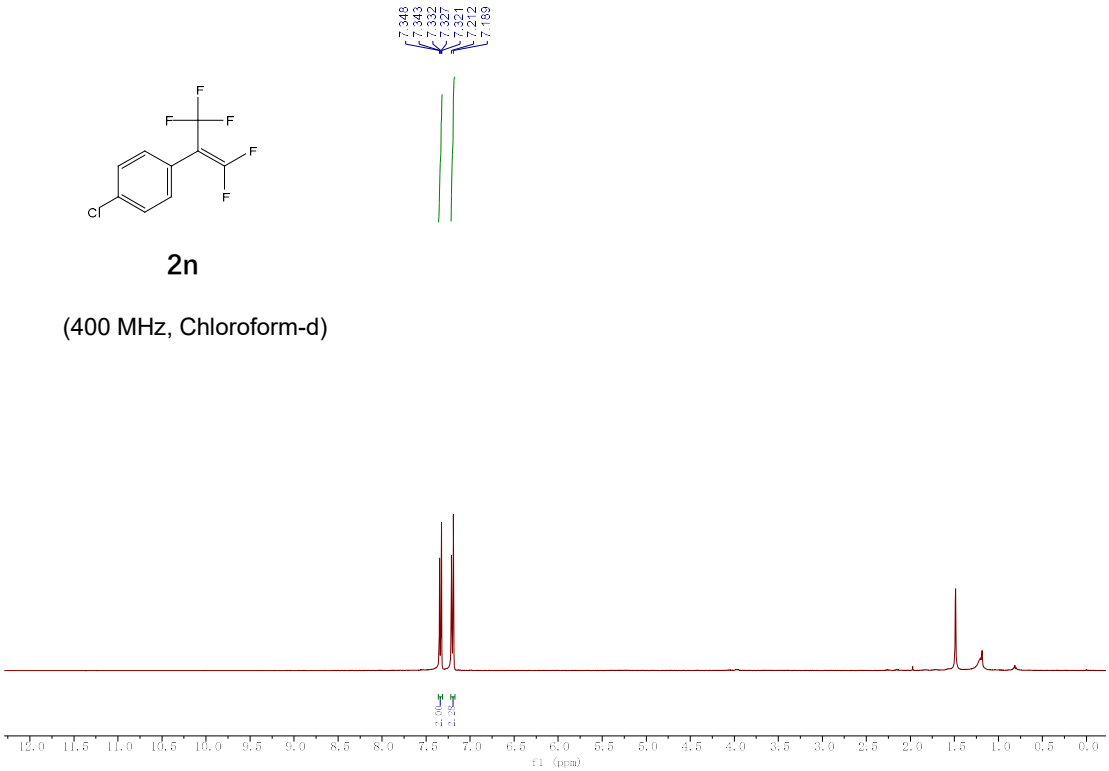






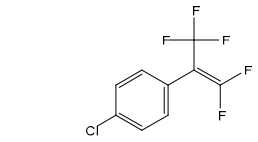
2m

(151 MHz, Chloroform-d)



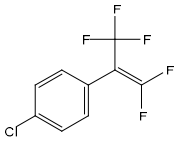
2n

(400 MHz, Chloroform-d)



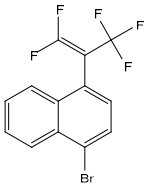
2n

(376 MHz, Chloroform-d)



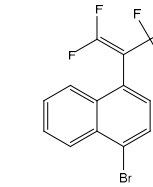
2n

(151 MHz, Chloroform-d)



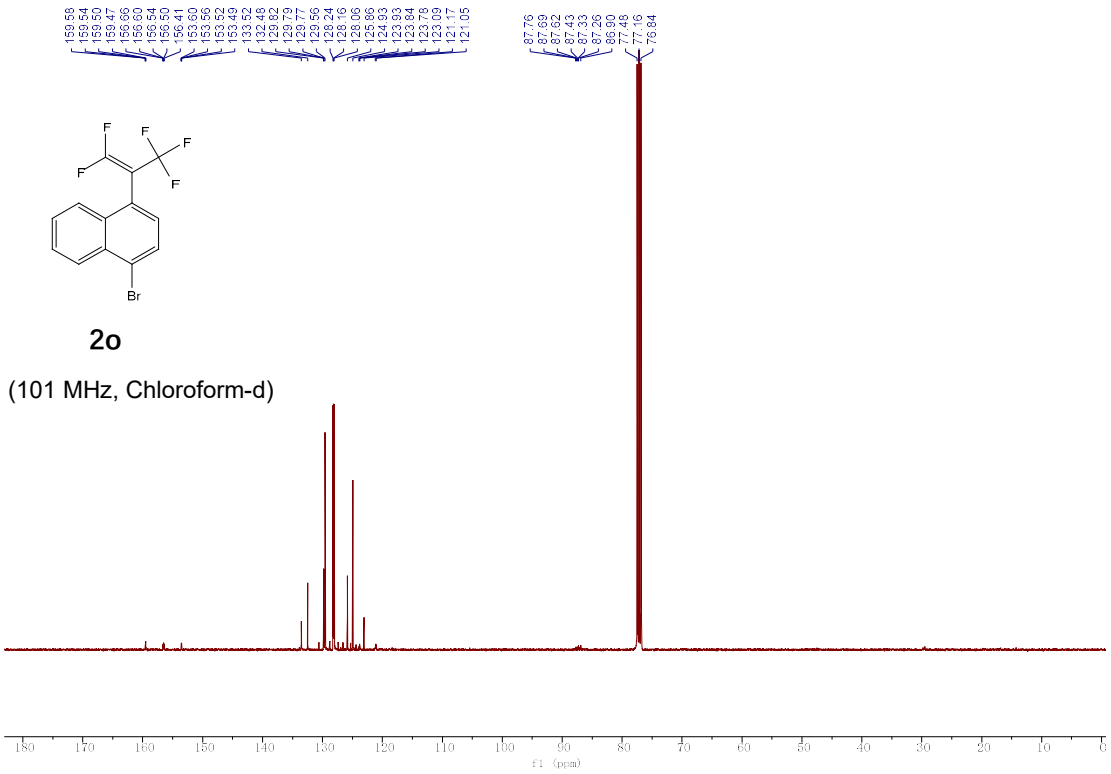
2o

(400 MHz, Chloroform-d)



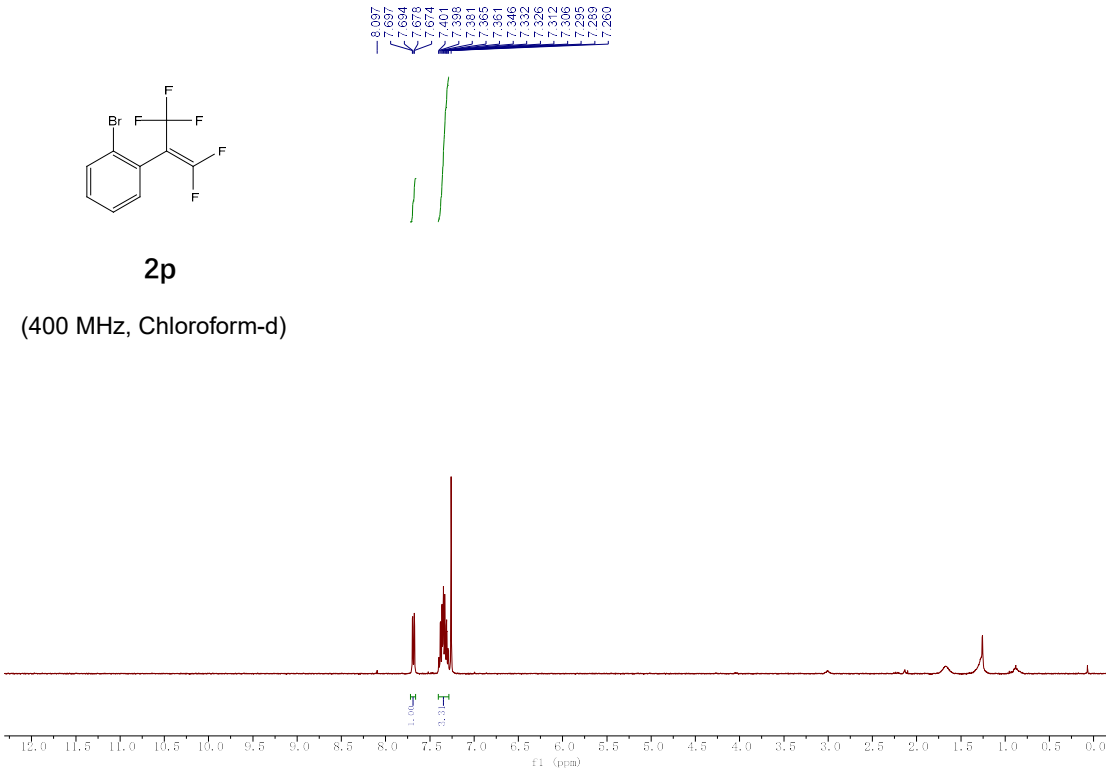
2o

(376 MHz, Chloroform-d)



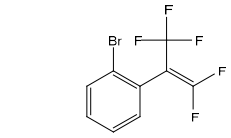
2o

(101 MHz, Chloroform-d)



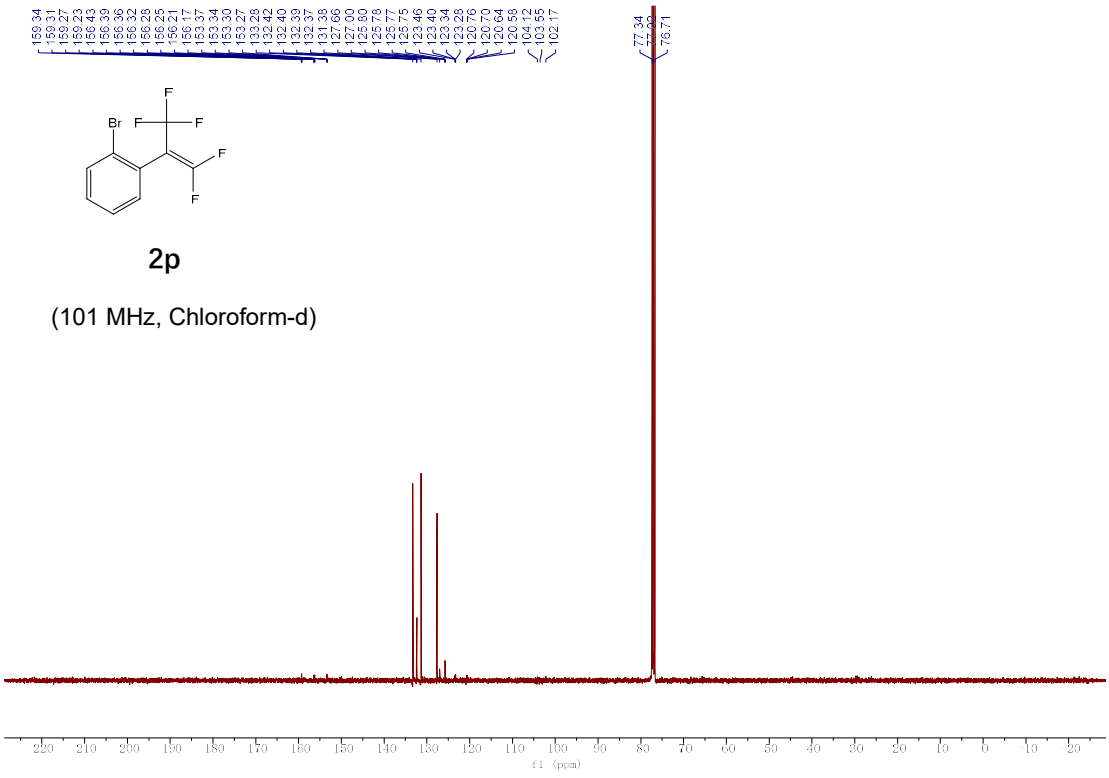
2p

(400 MHz, Chloroform-d)



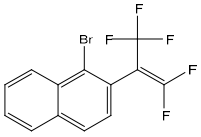
2p

(376 MHz, Chloroform-d)



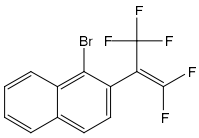
2p

(101 MHz, Chloroform-d)



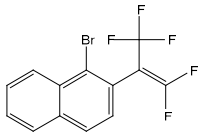
2q

(400 MHz, Chloroform-d)



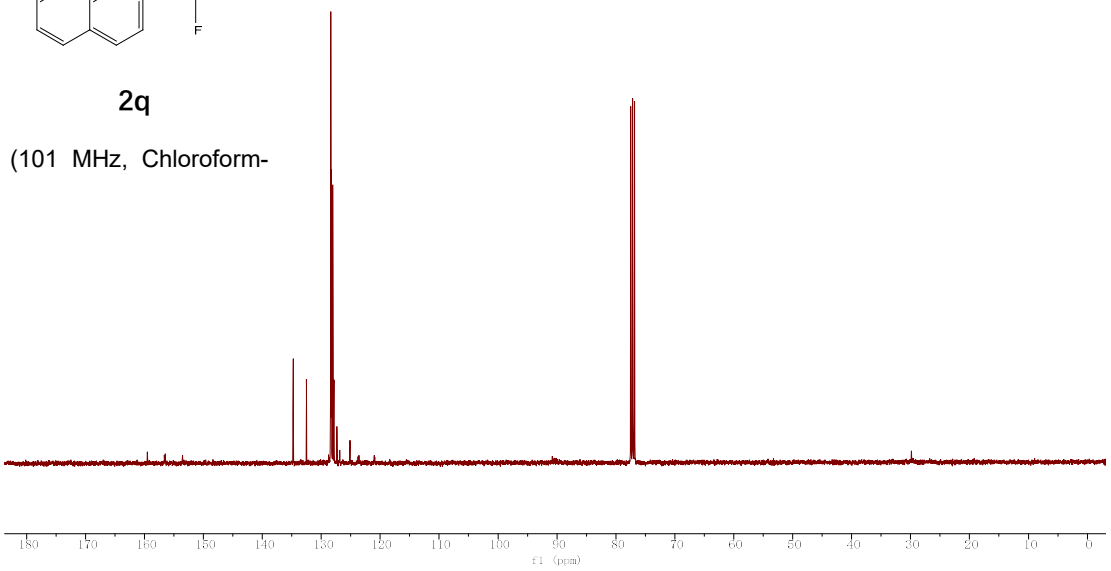
2q

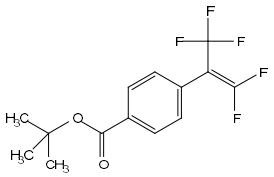
(376 MHz, Chloroform-d)



2q

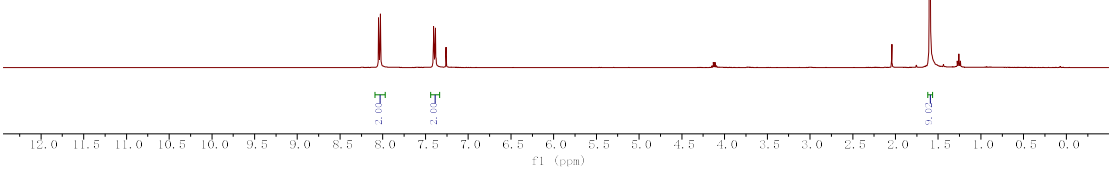
(101 MHz, Chloroform-

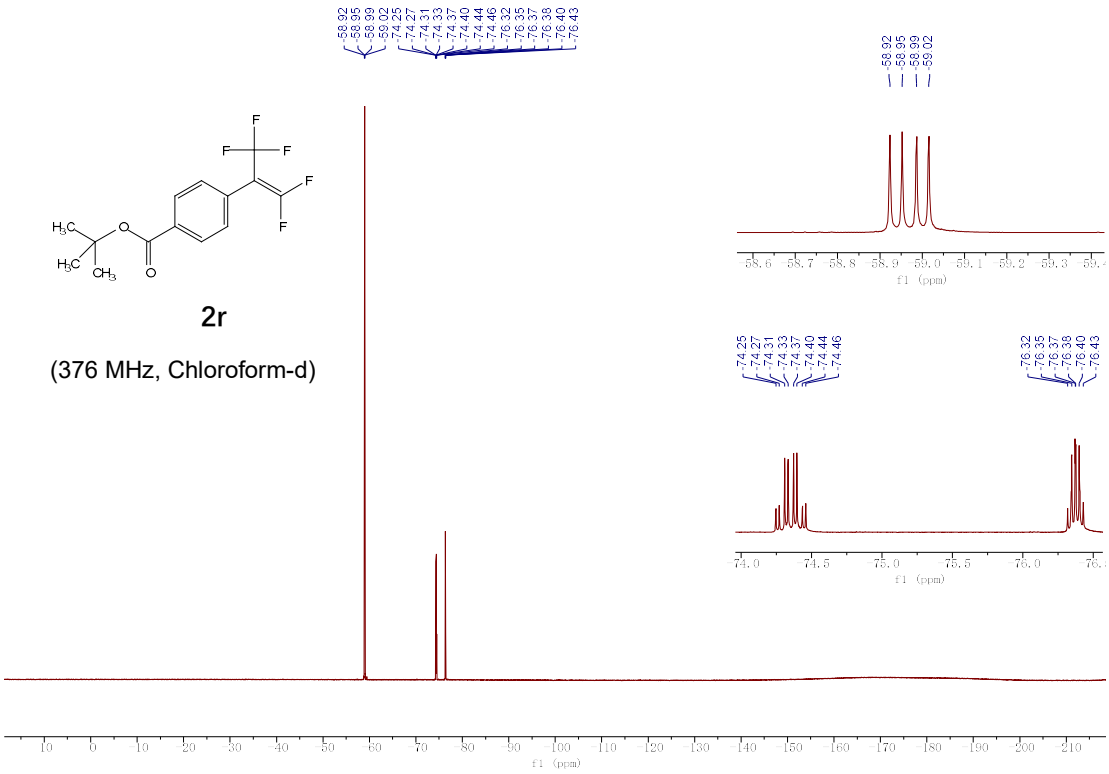




2r

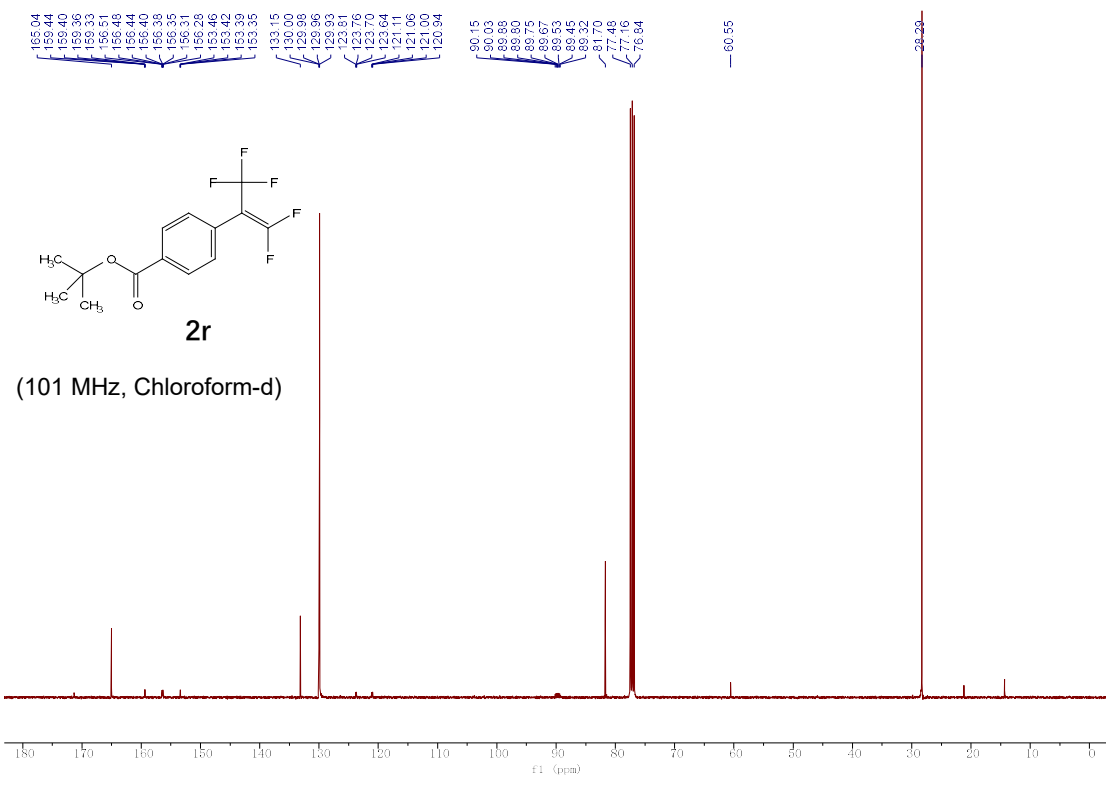
(400 MHz, Chloroform-d)





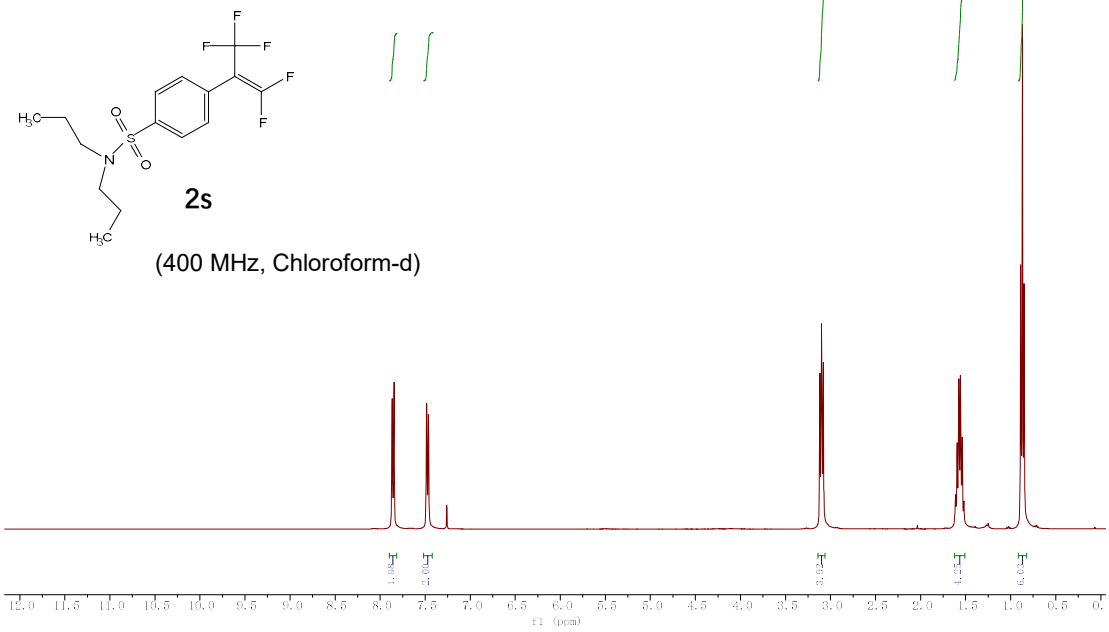
2r

(376 MHz, Chloroform-d)



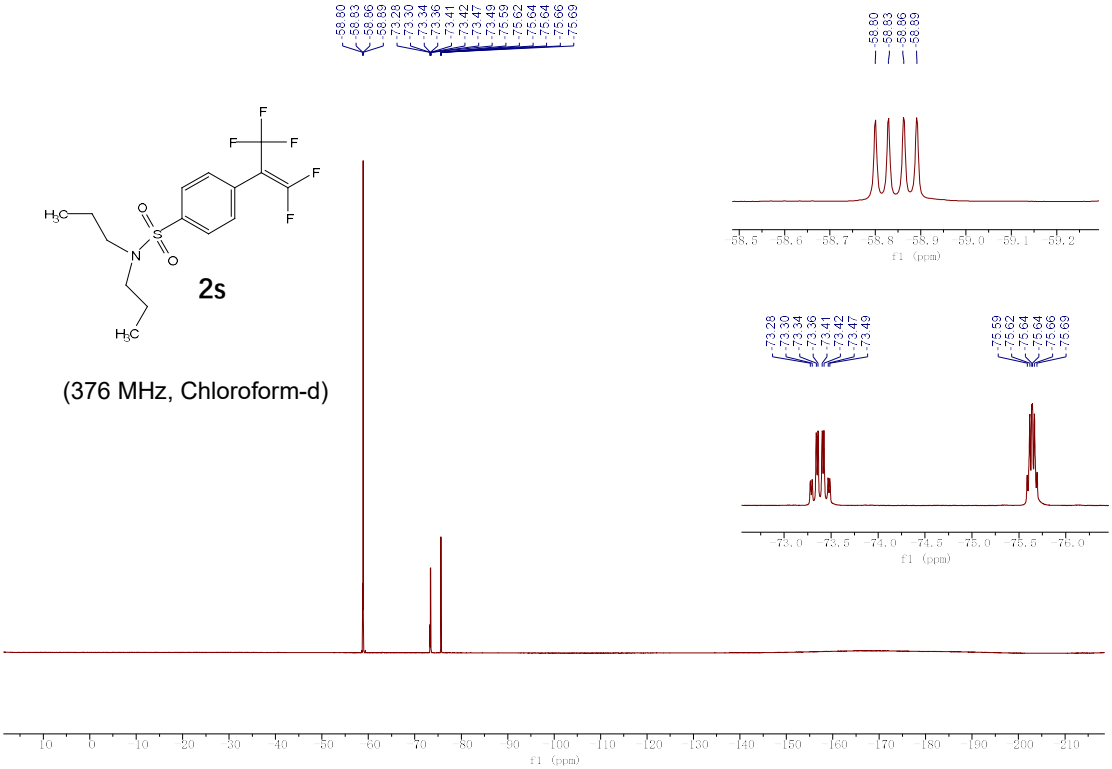
2r

(101 MHz, Chloroform-d)



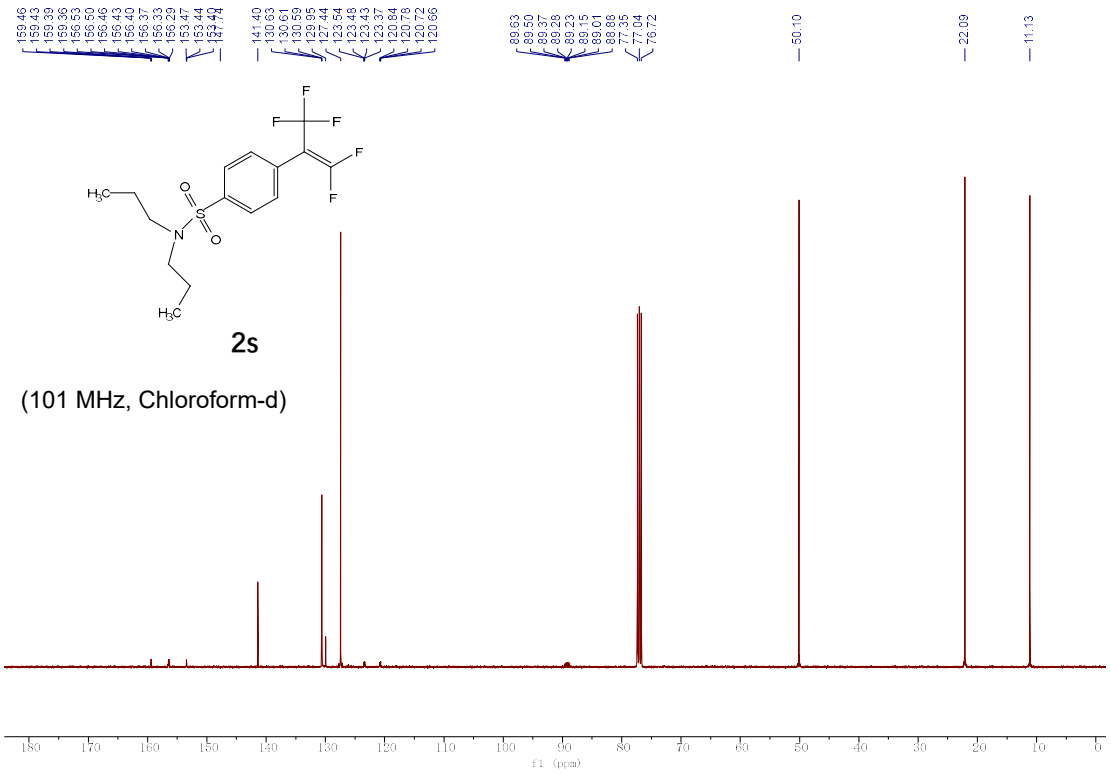
2s

(400 MHz, Chloroform-d)



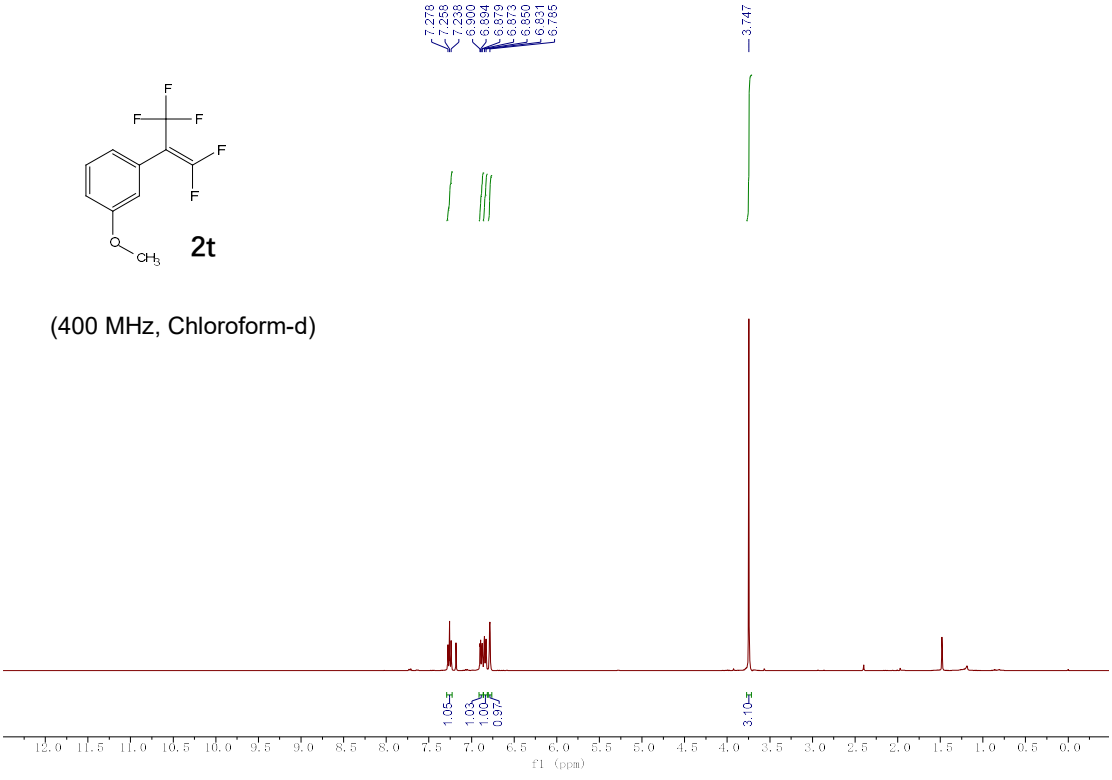
2s

(376 MHz, Chloroform-d)



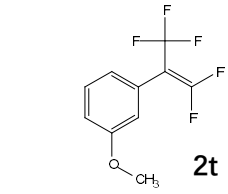
2s

(101 MHz, Chloroform-d)



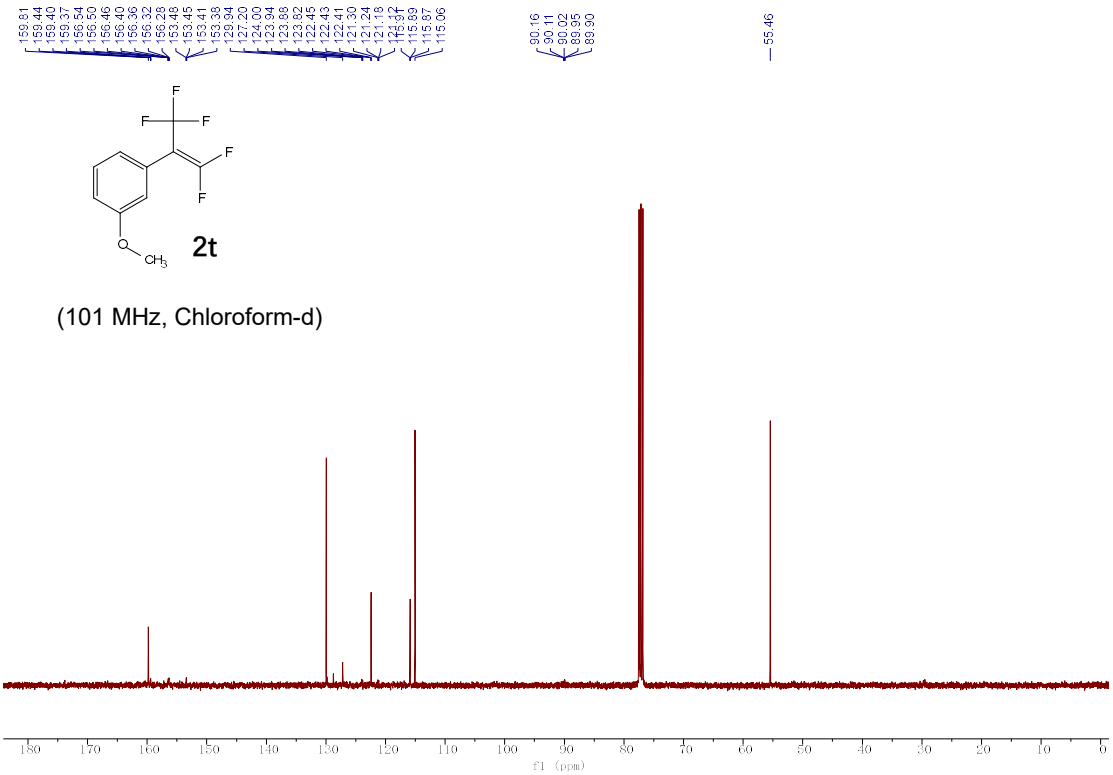
2t

(400 MHz, Chloroform-d)



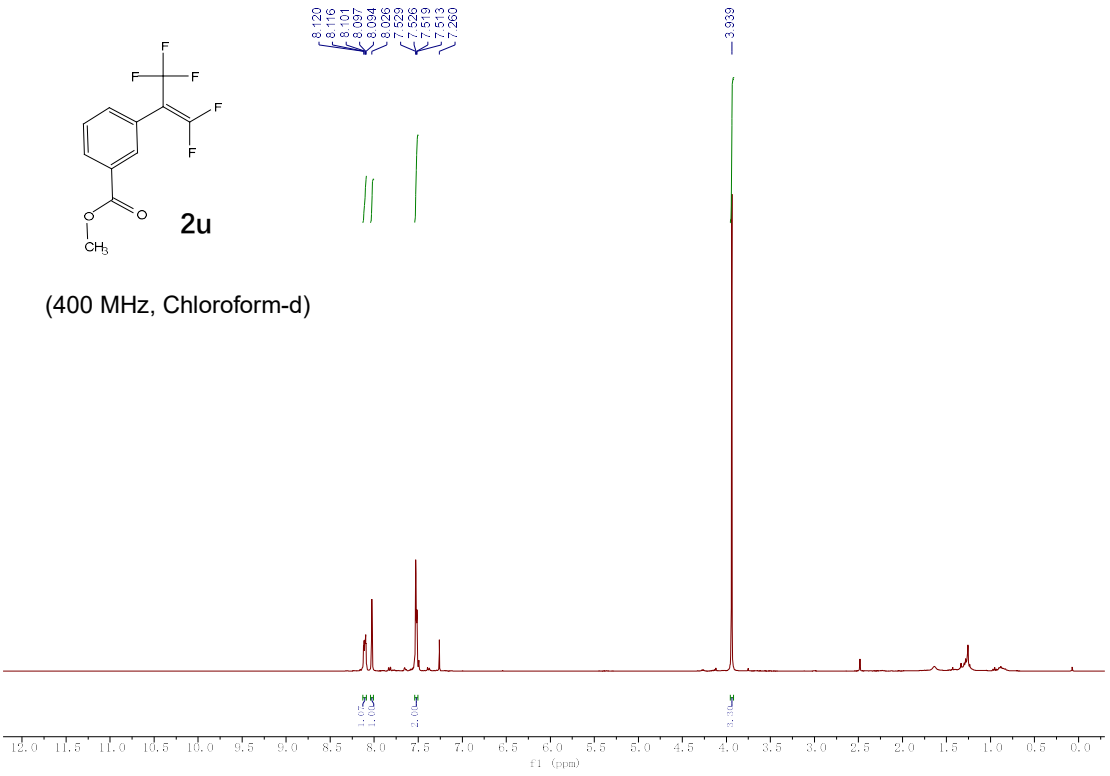
2t

(376 MHz, Chloroform-d)

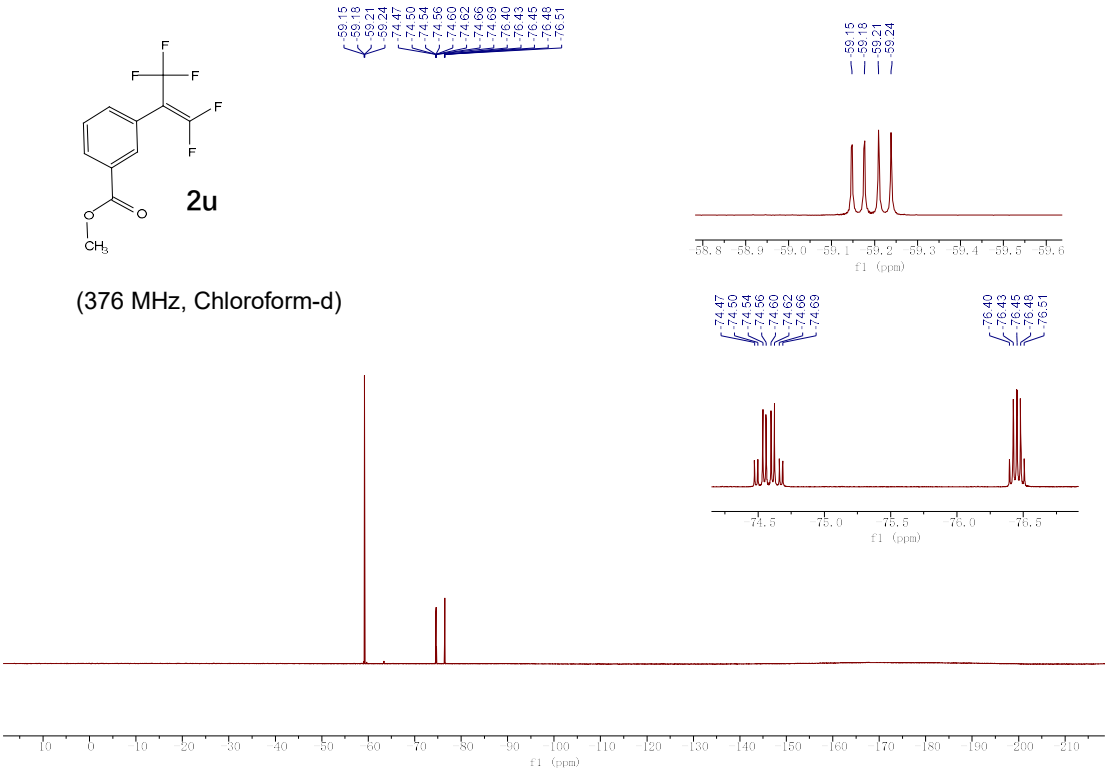


2t

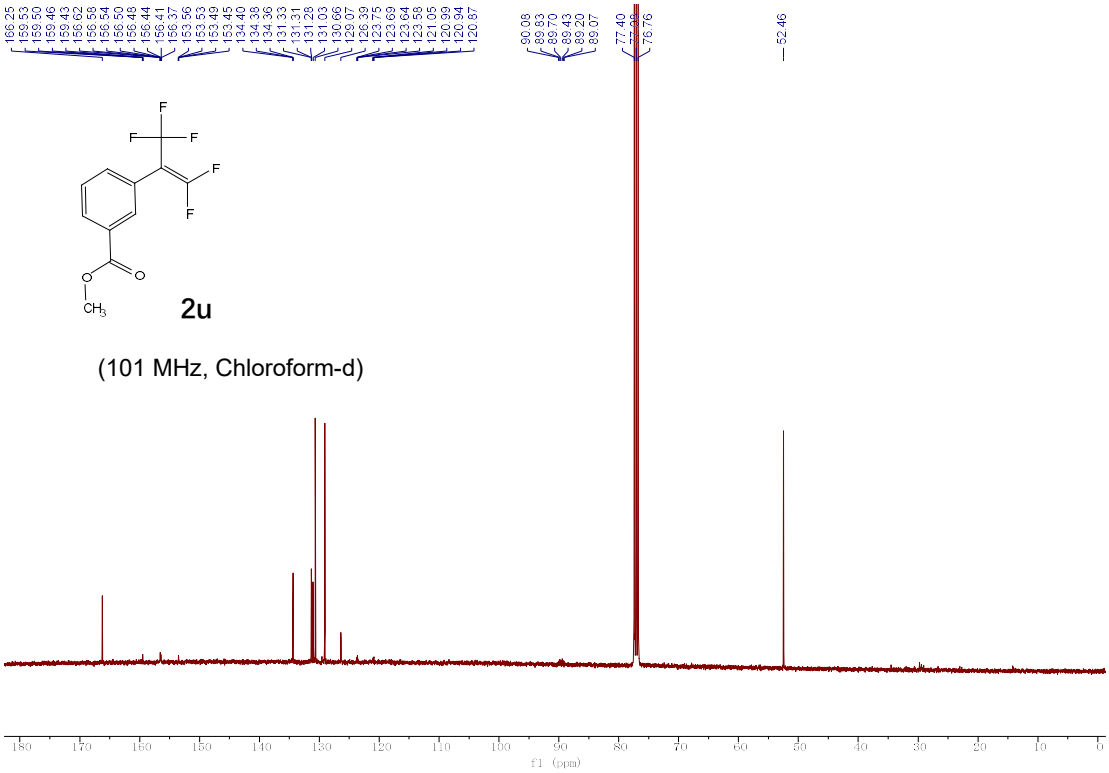
(101 MHz, Chloroform-d)



(400 MHz, Chloroform-d)

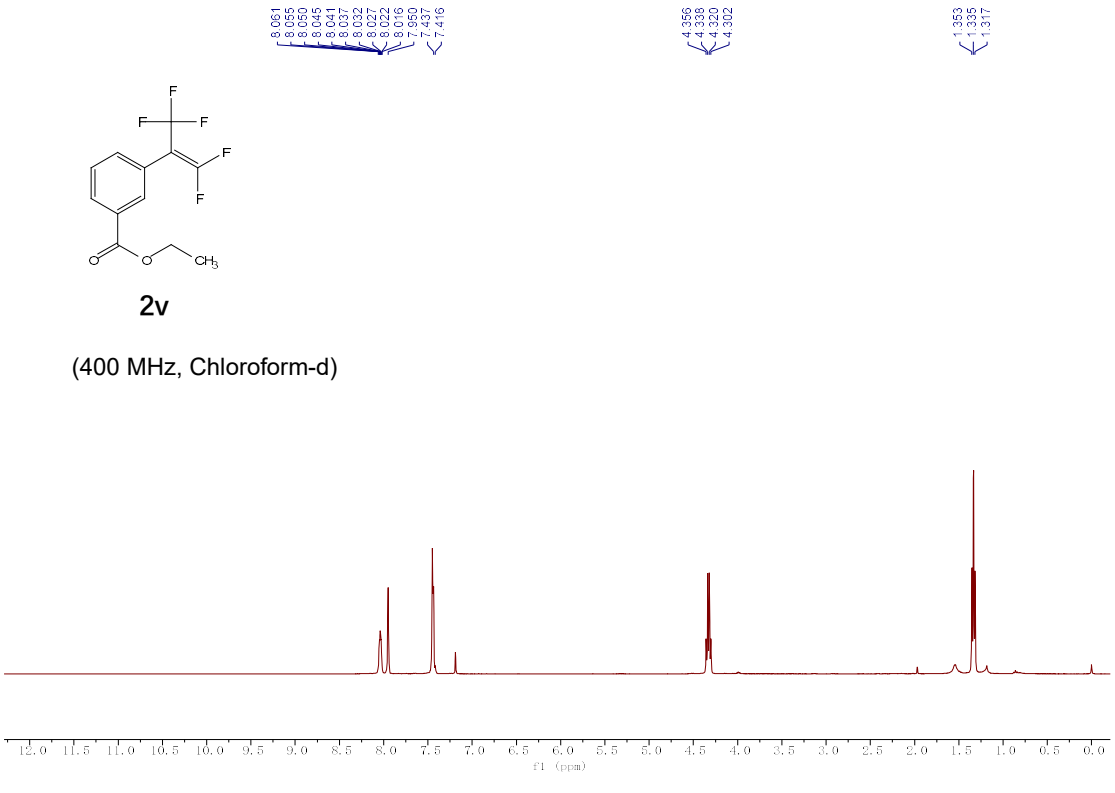


(376 MHz, Chloroform-d)



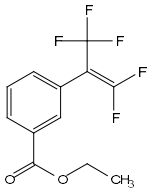
2u

(101 MHz, Chloroform-d)



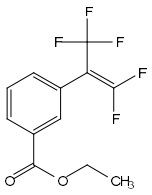
2v

(400 MHz, Chloroform-d)



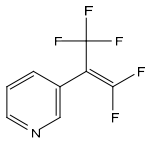
2v

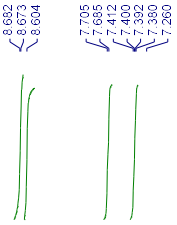
(376 MHz, Chloroform-d)



2v

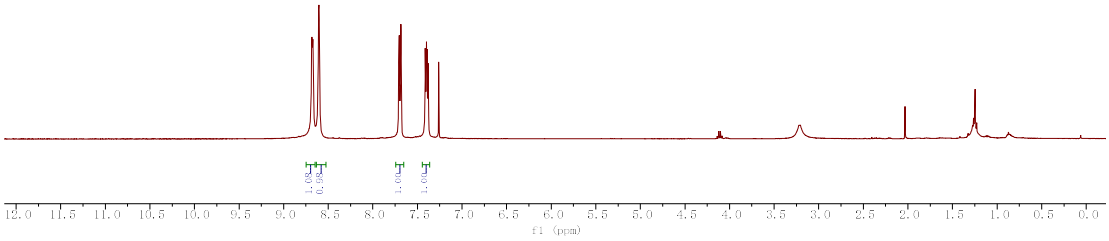
(101 MHz, Chloroform-d)

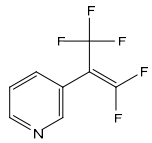




2w

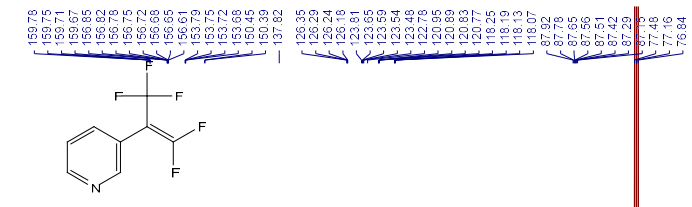
(400 MHz, Chloroform-d)





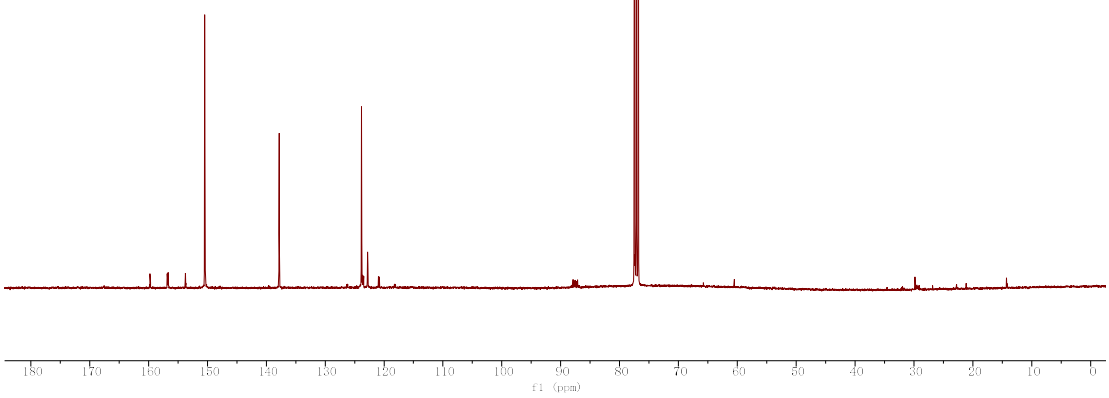
2w

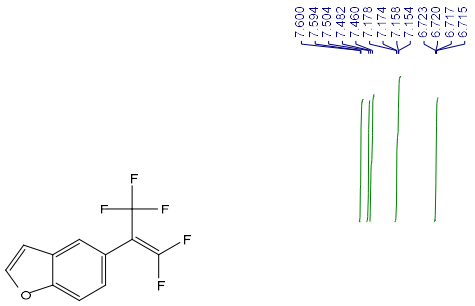
(376 MHz, Chloroform-d)



2w

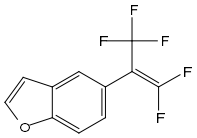
(101 MHz, Chloroform-d)





2x

(400 MHz, Chloroform-d)

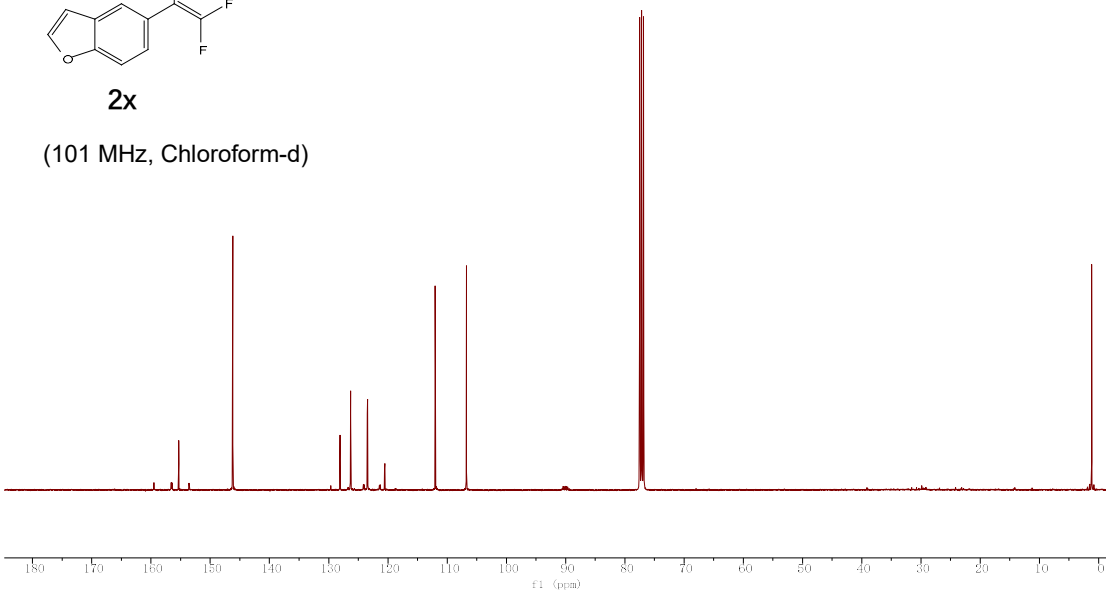


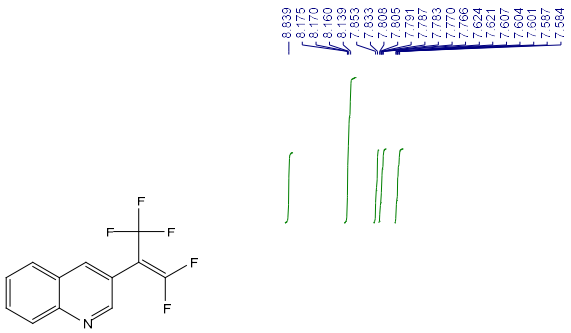
2x

(376 MHz, Chloroform-d)

2x

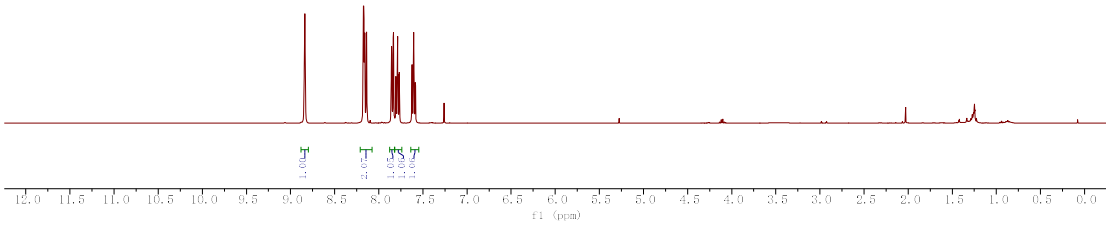
(101 MHz, Chloroform-d)

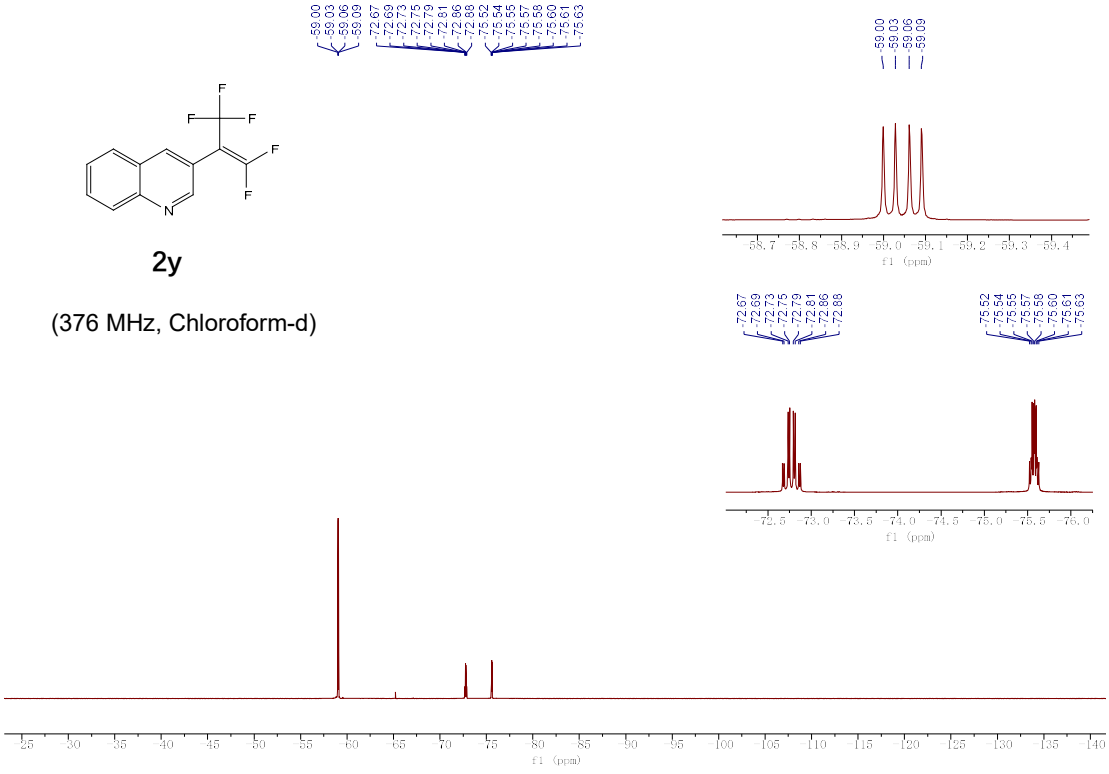




2y

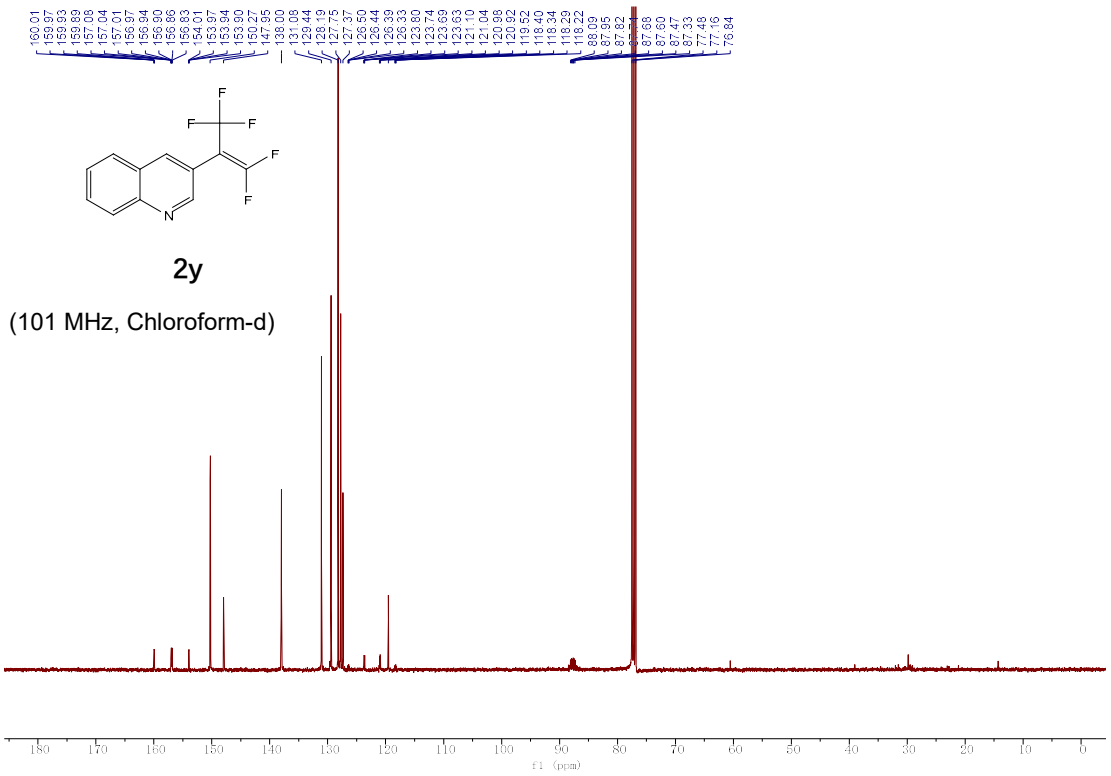
(400 MHz, Chloroform-d)





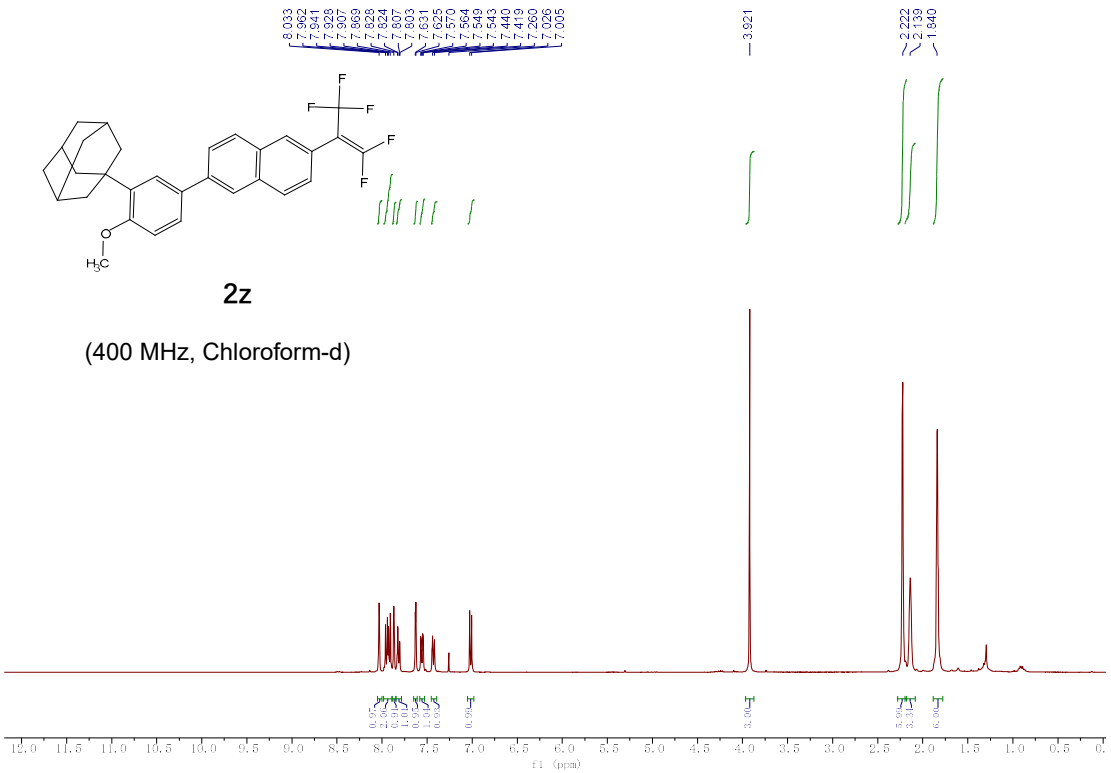
2y

(376 MHz, Chloroform-d)



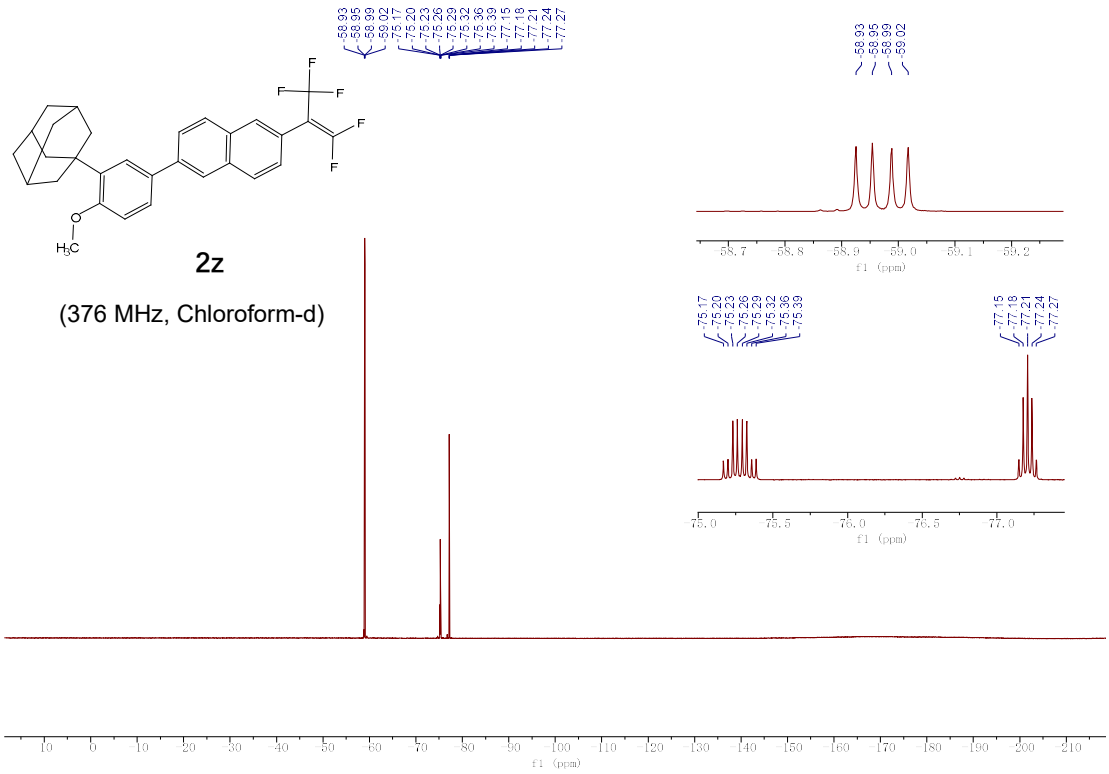
2y

(101 MHz, Chloroform-d)



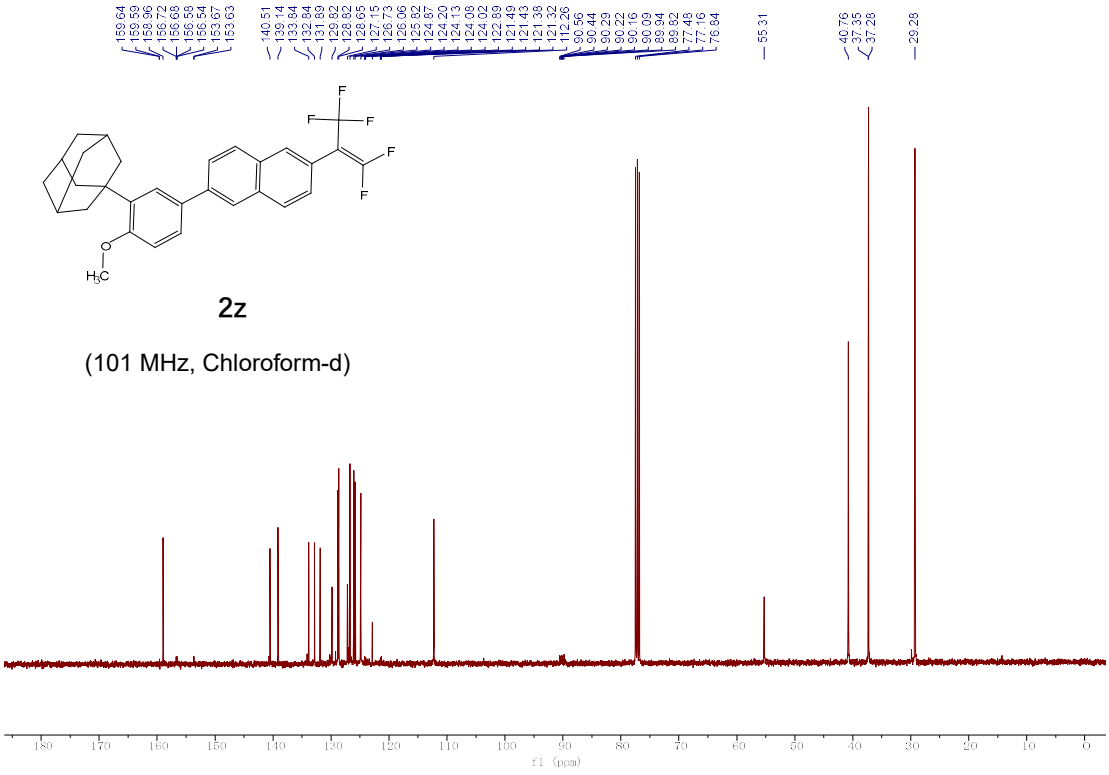
2z

(400 MHz, Chloroform-d)



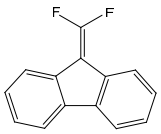
2z

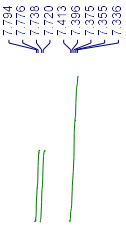
(376 MHz, Chloroform-d)



2z

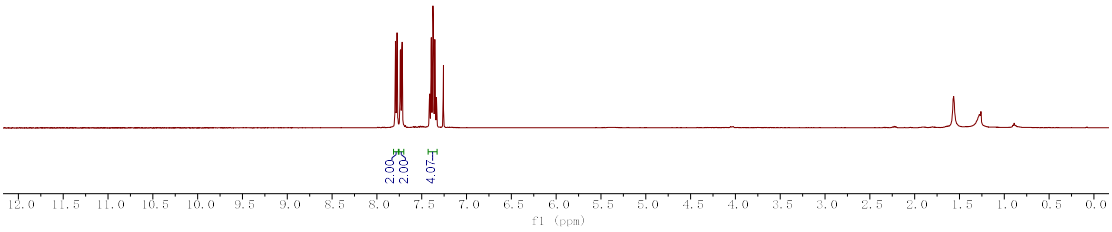
(101 MHz, Chloroform-d)

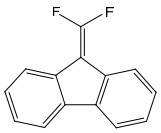




2aa

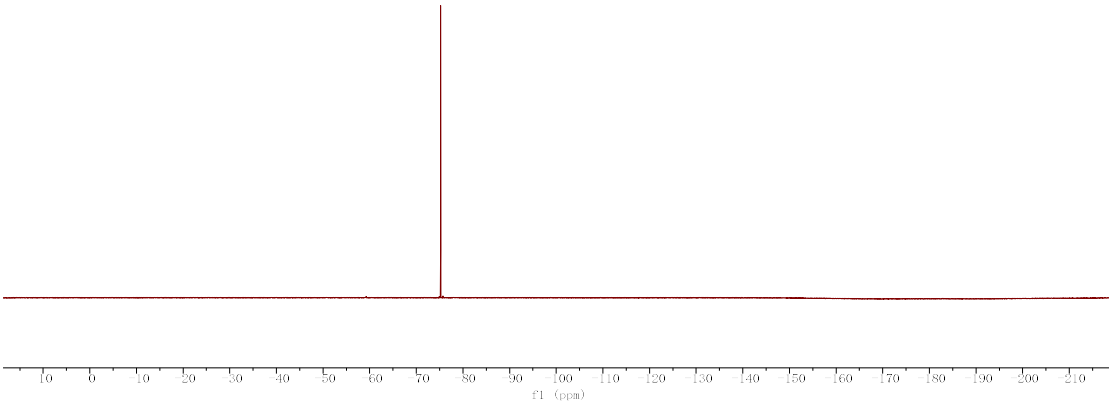
(400 MHz, Chloroform-d)

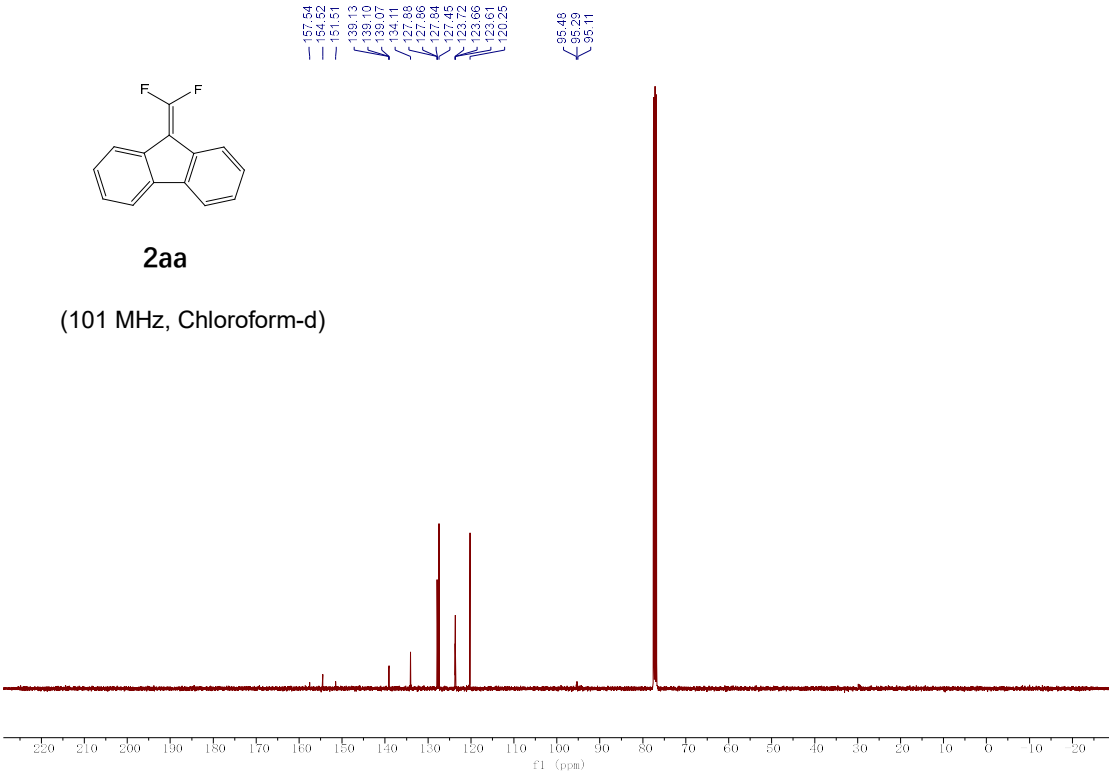




2aa

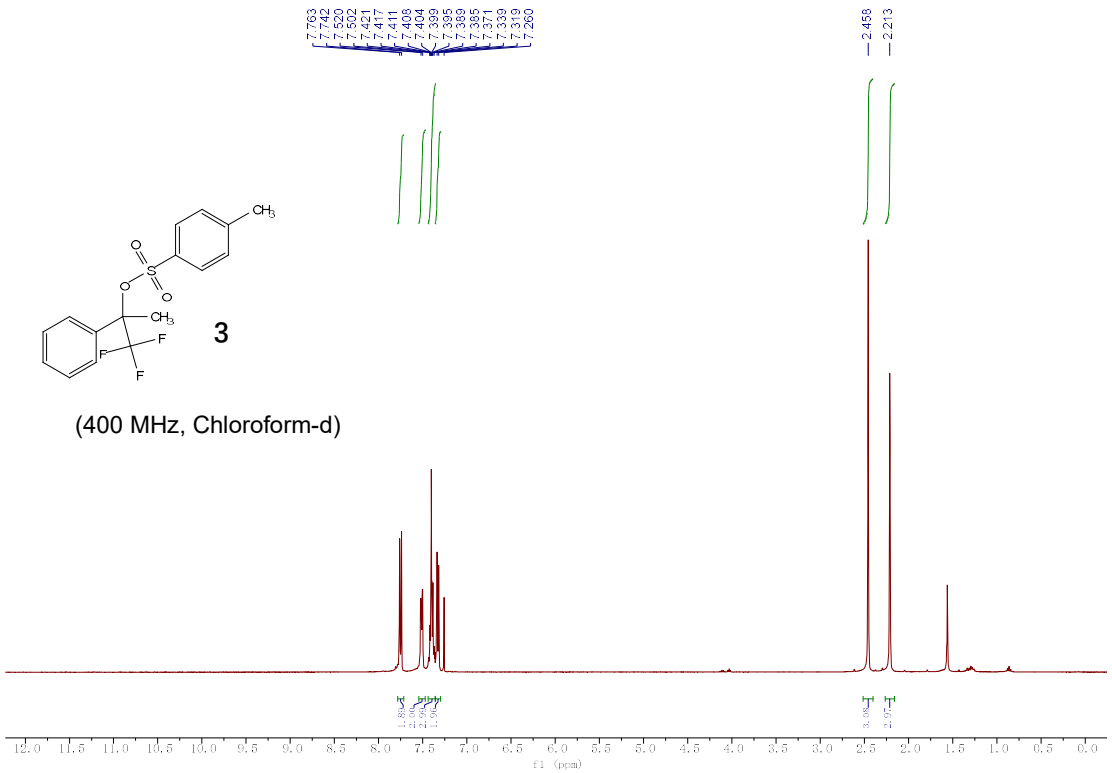
(376 MHz, Chloroform-d)





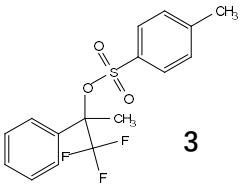
2aa

(101 MHz, Chloroform-d)



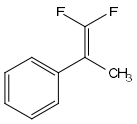
3

(400 MHz, Chloroform-d)



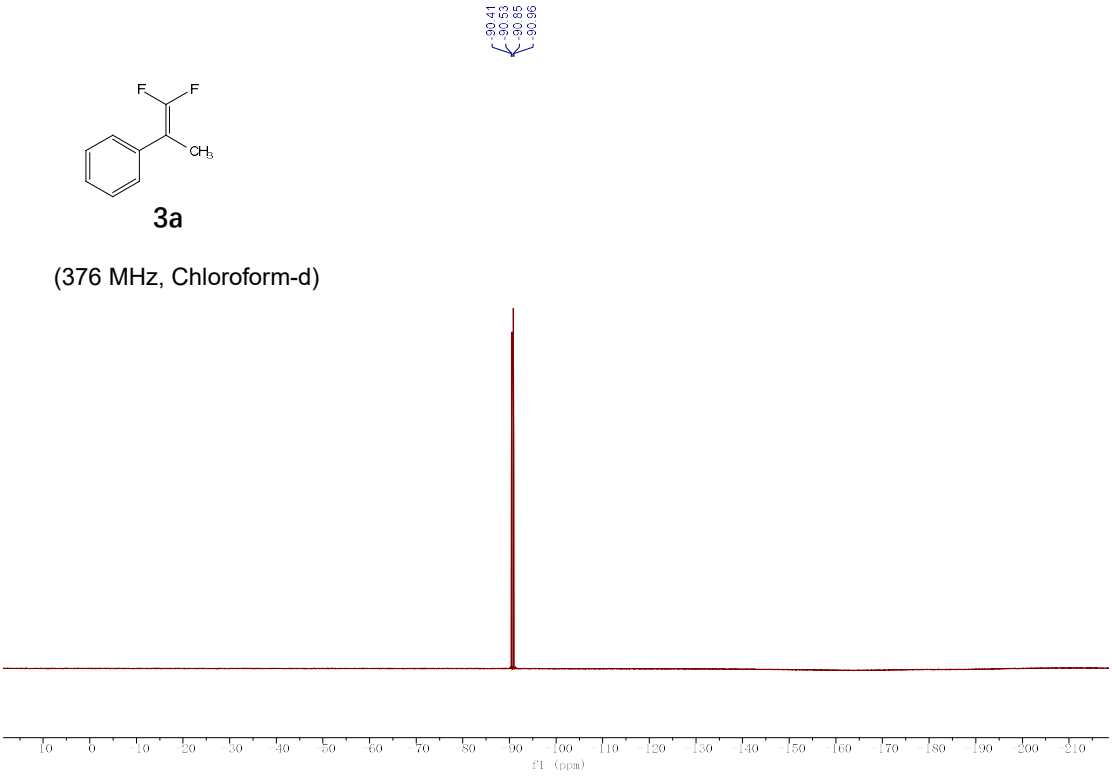
3

(376 MHz, Chloroform-d)



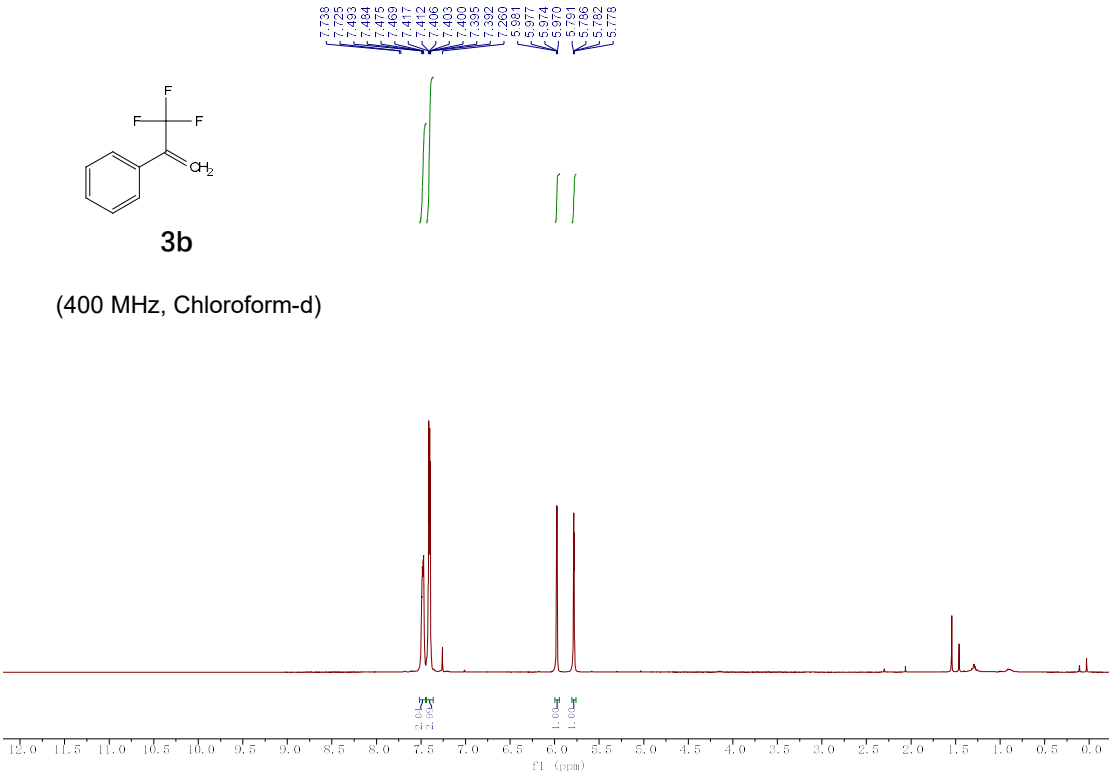
3a

(400 MHz, Chloroform-d)



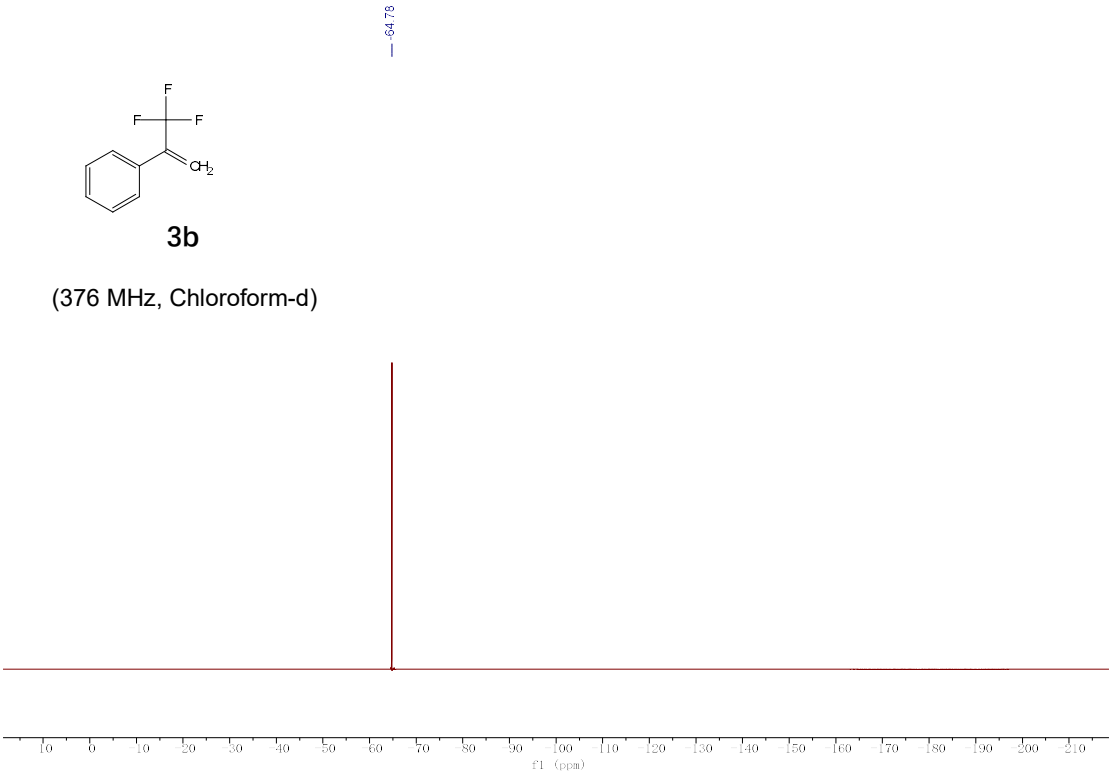
3a

(376 MHz, Chloroform-d)



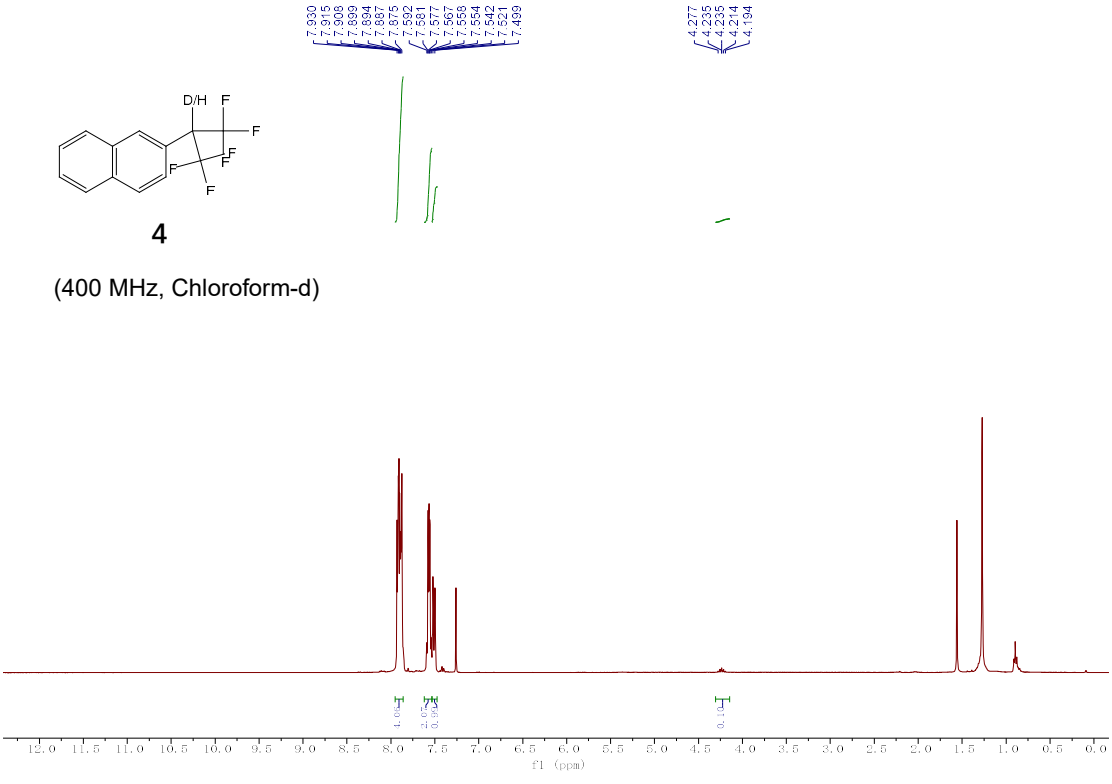
3b

(400 MHz, Chloroform-d)



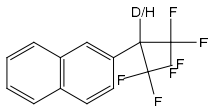
3b

(376 MHz, Chloroform-d)



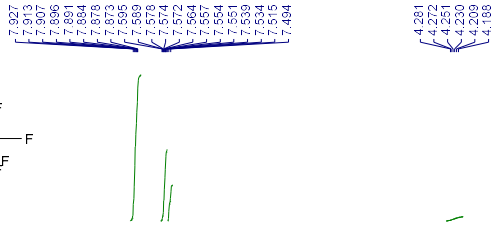
4

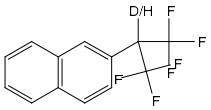
(400 MHz, Chloroform-d)



4

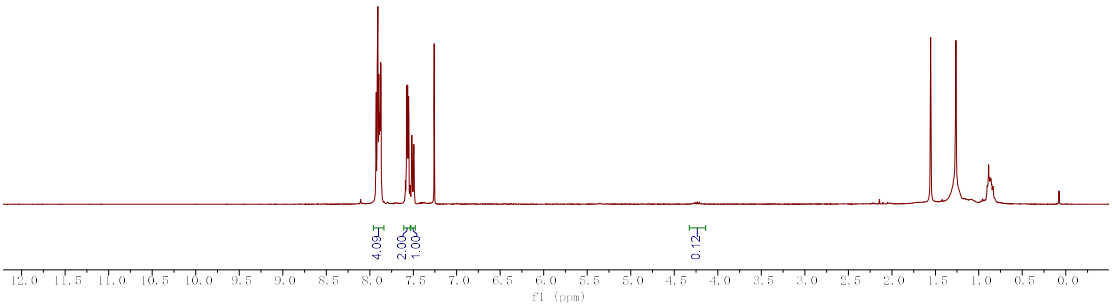
(376 MHz, Chloroform-d)

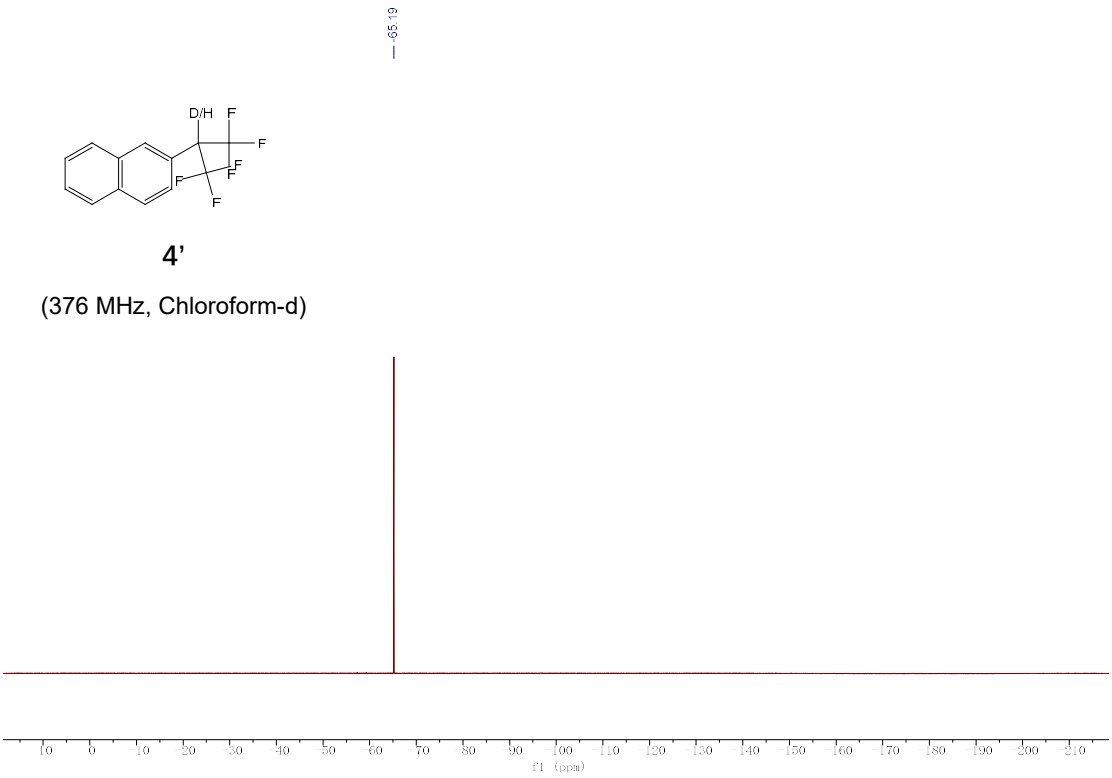




4’

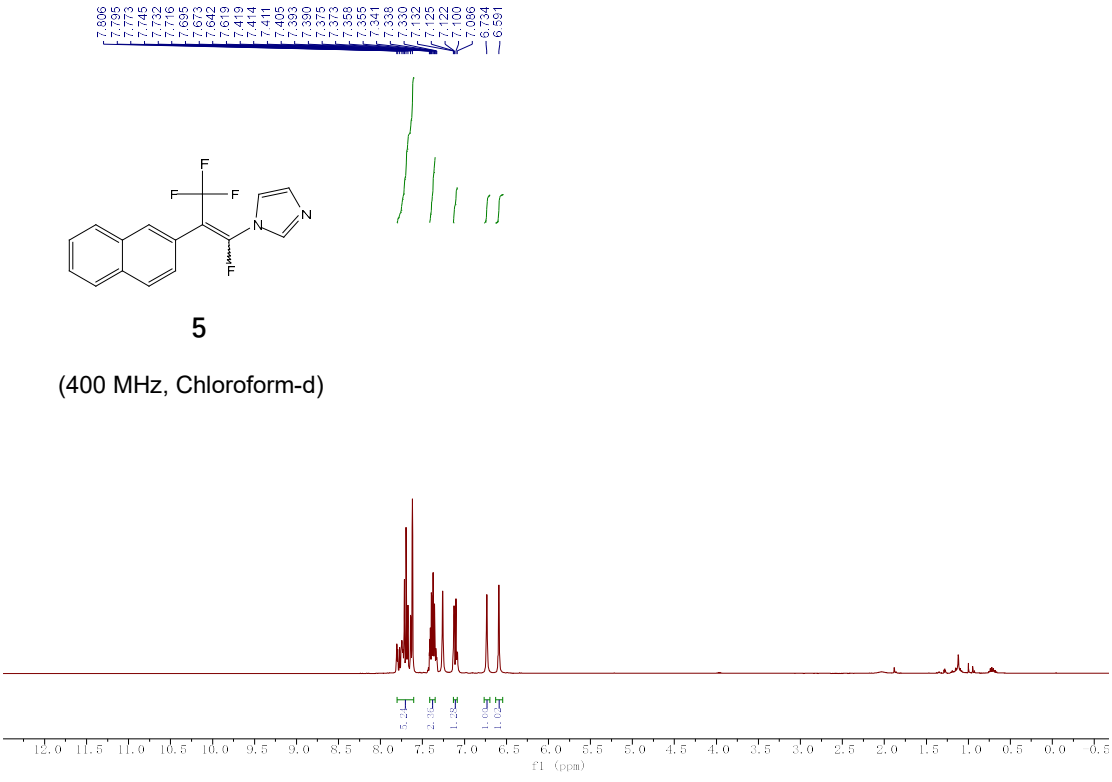
(400 MHz, Chloroform-d)





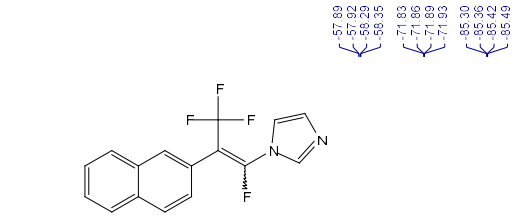
4’

(376 MHz, Chloroform-d)



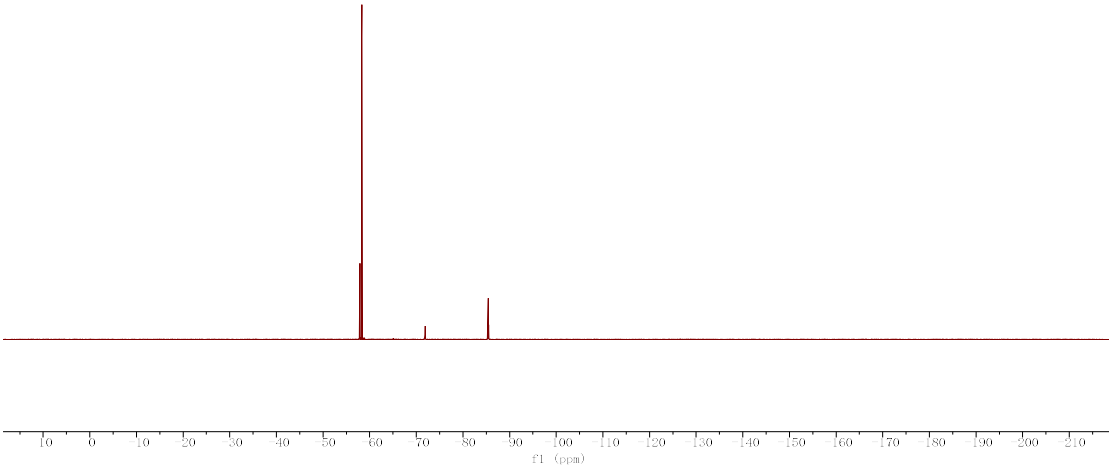
5

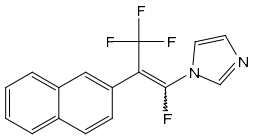
(400 MHz, Chloroform-d)



5

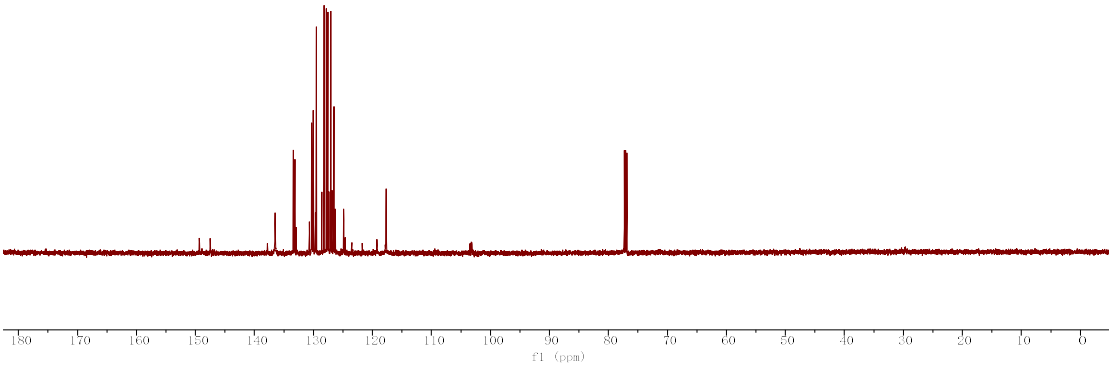
(376 MHz, Chloroform-d)

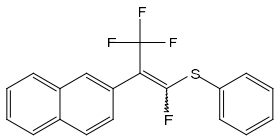




5

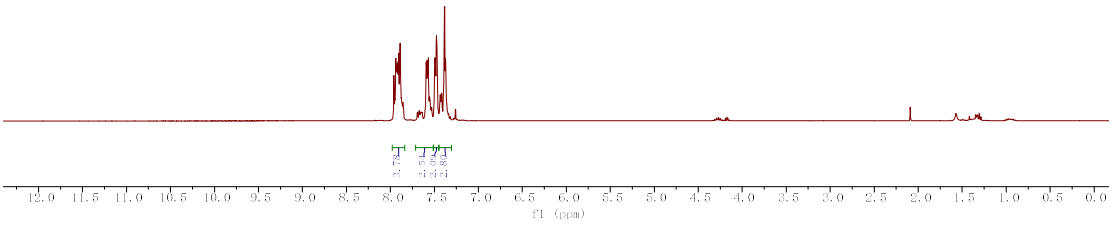
(151 MHz, Chloroform-d)

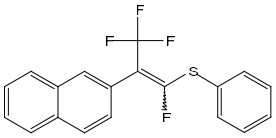




6

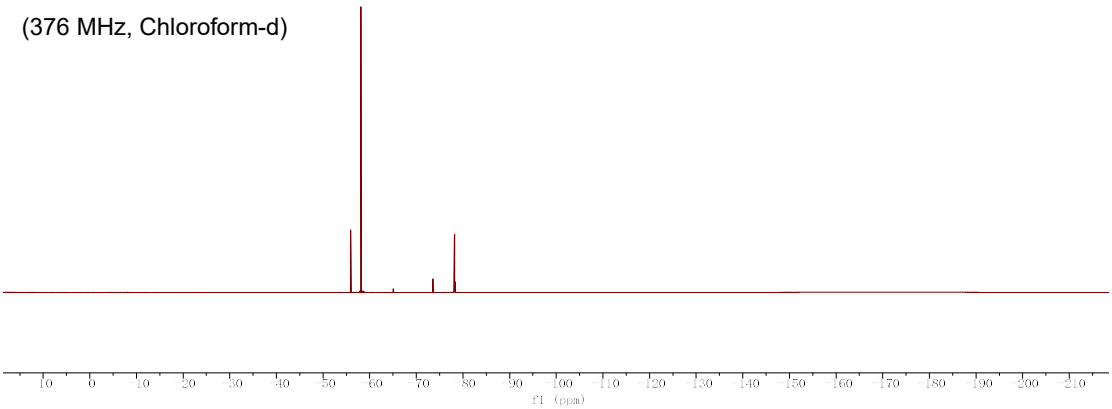
(400 MHz, Chloroform-d)

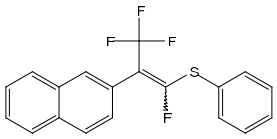




6

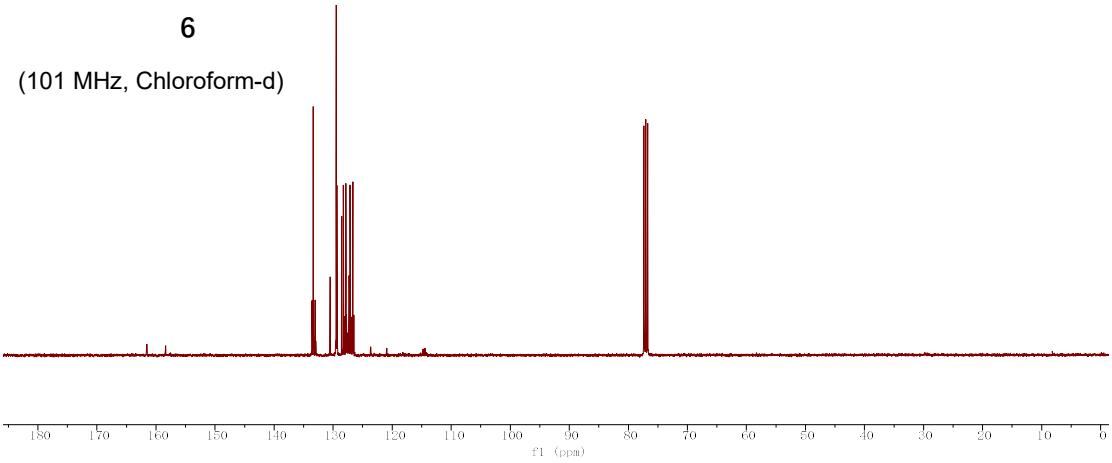
(376 MHz, Chloroform-d)

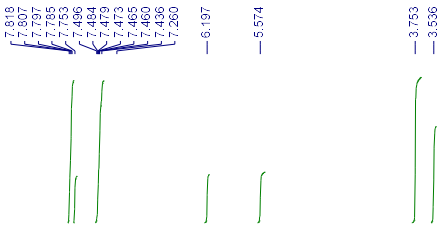


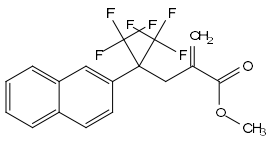


6

(101 MHz, Chloroform-d)

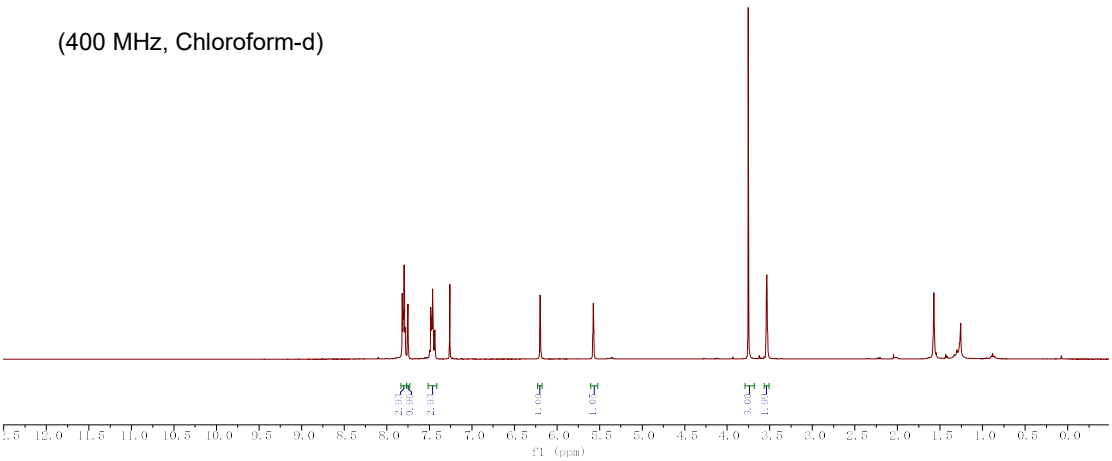


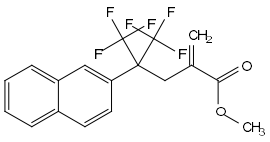




8

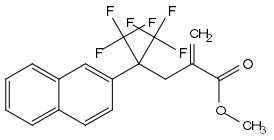
(400 MHz, Chloroform-d)





8

(376 MHz, Chloroform-d)



8

(101 MHz, Chloroform-d)