Supporting Information

Syn Fluoro- and Oxy-Trifluoromethylation of Arylacetylenes

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Contents

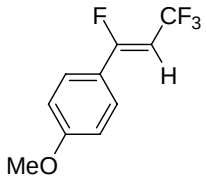
1. General experimental details

All chemicals were purchased commercially except complex **1**, which was prepared according to the method we reported recently (S.-L. Zhang, W.-F. Bie, *RSC Adv.* **2016**, *6*, 70902). DMF, toluene and CH_2Cl_2 solvents were simply dried over Na_2SO_4 before use to extrude adventitious water. Other reactants were used as received without further purification. CsF was received as crystalline solid purchased from J&K Scientific Ltd. All the reactions were performed in a Schlenk tube under N_2 or O_2 balloon atmosphere which was realized through evacuation/backfill techniques after three times. NMR spectra were recorded on a Bruker Advance III HD 400 MHz spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent peak or TMS. Coupling constants are reported in Hertz.

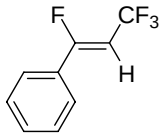
2. General procedure for fluoro-trifluoromethylation reactions

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added phenCu$(CF_3)_3$ (**1**) (45 mg, 0.1 mmol), alkynes (**2**) (0.1 mmol) and fluoride salt (0.5 mmol). The Schlenk tube was evacuated and refilled with dry nitrogen. Dry DMF (2 mL) was then added by syringe. The contents in the tube were vigorously stirred for 6 hours at 100 ^oC (heated in an oil bath). The reaction mixture was then allowed to cool to room temperature, and water was added at 0 ^oC. The resulting mixture was extracted by dichloromethane. The combined organic layers were washed with a large amount of water for 5 times, with brine for once and then dried over magnesium sulfate. The solvent was removed by vacuum evaporation in an ice-water bath. The resulting residual was purified by column chromatography on silica gel eluted with *n*-hexane to provide fluoro-trifluoromethylation products **3**.

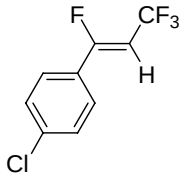
A representative example of fluoro-trifluoromethylation reaction at 1.0 mmol scale: Following the procedure described above, reaction of phenCu$(CF_3)_3$ (**1**) (450 mg, 1.0 mmol), *para*-chlorophenyl acetylene (136 mg, 1.0 mmol) and CsF (760 mg, 5.0 mmol) in 20 mL DMF at 100 ^oC for 6 hours produced **3c** in a ^{19}F NMR yield of 93% and an isolated yield of 77% (174 mg), which are only slightly lower than the yields of 99% (81%) obtained at a 0.1 mmol scale as reported in the main text.



(Z)-1-methoxy-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3a**; 14 mg, 63%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.57 (dq, *J* = 33.9, 7.5 Hz, 1H), 3.88 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.6 (d, *J* = 16.3 Hz, 3F), -102.2 (q, *J* = 16.3 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (dq, *J* = 269.1, 5.8 Hz), 162.1 (s), 127.1 (d, *J* = 7.8 Hz), 122.9 (q, *J* = 269.9 Hz), 121.9 (d, *J* = 26.3 Hz), 114.3 (d, *J* = 1.7 Hz), 93.6 (qd, *J* = 36.2, 11.9 Hz), 55.5 (s). GC-MS: 220 (M^+).

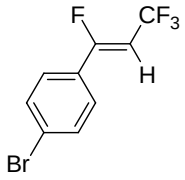


(Z)-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3b**; 12 mg, 63%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.0 Hz, 2H), 7.53–7.45 (m, 3H), 5.72 (dq, *J* = 33.4, 7.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.10 (d, *J* = 16.5 Hz, 3F), -102.38 (q, *J* = 16.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 (dq, *J* = 269.9, 5.8 Hz), 131.5 (s), 129.6 (d, *J* = 26.1 Hz), 128.9 (d, *J* = 1.8 Hz), 125.4 (d, *J* = 7.5 Hz), 122.6 (q, *J* = 268.9 Hz), 95.6 (qd, *J* = 36.3, 11.6 Hz).

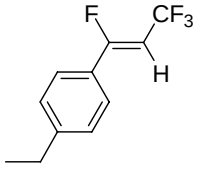


(Z)-1-chloro-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3c**; 18 mg**,** 81%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.70 (dq, *J* = 33.3, 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.14 (d, *J* = 16.5 Hz, 3F), -102.50 (q, *J* = 16.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (dq, *J* = 269.5, 5.8 Hz), 137.8 (s), 129.3 (d, *J* = 1.7 Hz), 128.0 (d, *J* = 26.8 Hz), 126.7 (d, *J*

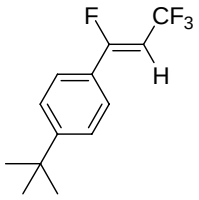
= 7.4 Hz), 122.4 (q, *J* = 269.5 Hz), 96.1 (qd, *J* = 36.5, 11.4 Hz).



(Z)-1-bromo-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3d**; 12 mg, 41%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 5.72 (dq, *J* = 33.2, 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.17 (d, *J* = 16.6 Hz, 3F), -102.64 (q, *J* = 16.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (dq, *J* = 269.5, 5.8 Hz), 132.2 (d, *J* = 1.9 Hz), 128.4 (d, *J* = 26.8 Hz), 126.8 (d, *J* = 7.4 Hz), 126.2 (s), 122.4 (q, *J* = 269.5 Hz), 96.2 (qd, *J* = 36.5, 11.4 Hz).

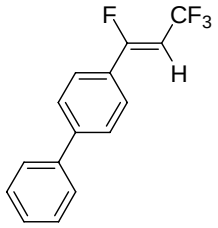


(Z)-1-ethyl-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3e**; 12 mg, 54%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.66 (dq, *J* = 33.6, 7.5 Hz, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.86 (d, *J* = 16.4 Hz, 3F), -102.35 (q, *J* = 16.4 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (dq, *J* = 269.1, 5.8 Hz), 148.3 (s), 128.4 (d, *J* = 1.8 Hz), 127.0 (d, *J* = 26.2 Hz), 125.5 (d, *J* = 7.5 Hz), 122.8 (q, *J* = 268.6 Hz), 94.7 (qd, *J* = 36.2, 11.6 Hz), 28.8 (s), 15.2 (s).

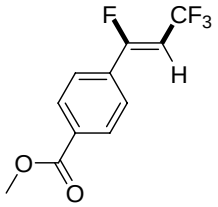


(Z)-1-(tert-butyl)-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3f**; 13 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 5.66 (dq, *J* = 33.6, 7.5 Hz, 1H), 1.36 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.86 (d, *J* =

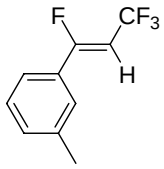
16.4 Hz, 3F), -102.44 (q, *J* = 16.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (dq, *J* = 269.4, 5.8 Hz), 155.2 (s), 131.9 (s), 125.9 (d, *J* = 1.7 Hz), 125.3 (d, *J* = 7.5 Hz), 122.8 (q, *J* = 273.0 Hz), 94.8 (qd, *J* = 36.2, 11.6 Hz), 35.0 (s), 31.1 (s).



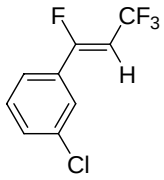
(Z)-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)-1,1'-biphenyl (**3g**; 18 mg, 69%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 3H), 7.66–7.59 (m, 3H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 5.76 (dq, *J* = 33.5, 7.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.86 (d, *J* = 16.5 Hz, 3F), -102.65 (q, *J* = 16.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (dq, *J* = 272.1, 5.6 Hz), 144.3 (s), 139.7 (s), 132.6 (s), 129.0 (d, *J* = 12.6 Hz), 127.5 (d, *J* = 1.7 Hz), 127.1 (s), 127.0 (d, *J* = 5.1 Hz), 125.9 (d, *J* = 7.5 Hz), 122.7 (q, *J* = 269.0 Hz), 95.5 (qd, *J* = 36.3, 11.6 Hz).



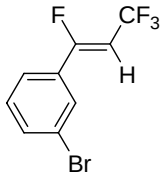
(Z)-methyl 4-(1,3,3,3-tetrafluoroprop-1-enyl)benzoate (**3h**; 36 mg, 73%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 1H), 5.82 (dq, *J* = 33.1, 7.4 Hz, 1H), 3.97 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.31 (d, *J* = 16.7 Hz, 3F), -102.69 (q, *J* = 16.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.02 (s), 162.30 (dq, *J* = 276.9, 5.6 Hz), 133.43 (d, *J* = 26.5 Hz), 132.75 (s), 130.07 (d, *J* = 1.8 Hz), 125.39 (d, *J* = 7.4 Hz), 122.27 (q, *J* = 270.2 Hz), 97.57 (qd, *J* = 36.6, 11.3 Hz), 52.46 (s), 50.78 (s).



(Z)-1-methyl-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3k**; 12 mg, 61%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 6.4 Hz, 2H), 7.38–7.30 (m, 2H), 5.69 (dq, *J* = 33.5, 7.5 Hz, 1H), 2.42 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.00 (d, *J* = 16.6 Hz, 3F), -102.10 (q, *J* = 16.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (dq, *J* = 269.8, 6.0 Hz), 138.8 (d, *J* = 1.8 Hz), 132.3 (s), 129.5 (d, *J* = 25.8 Hz), 128.8 (d, *J* = 1.8 Hz), 126.0 (d, *J* = 7.4 Hz), 122.7 (q, *J* = 268.8 Hz), 122.6 (d, *J* = 7.6 Hz), 95.4 (qd, *J* = 36.2, 11.6 Hz), 21.3 (s).

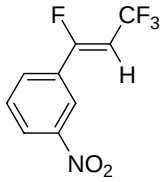


(Z)-1-chloro-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3l**; 15 mg, 68%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.49 (s, 2H), 7.44–7.38 (m, 1H), 5.73 (dq, *J* = 33.1, 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.29 (d, *J* = 16.6 Hz, 3F), -102.43 (q, *J* = 16.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9 (dq, *J* = 270.1, 5.7 Hz), 135.2 (s), 131.6 (s), 131.3 (d, *J* = 26.9 Hz), 130.2 (d, *J* = 1.7 Hz), 125.6 (d, *J* = 7.8 Hz), 123.5 (d, *J* = 7.3 Hz), 122.3 (q, *J* = 270.5 Hz), 96.8 (qd, *J* = 36.5, 11.2 Hz).

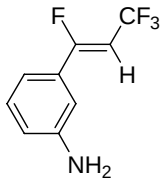


(Z)-1-bromo-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3m**; 16 mg, 61%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 5.73 (dq, *J* = 33.1, 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.27 (d, *J* = 16.7 Hz, 3F), -102.43 (q, *J* = 16.7 Hz, 1F). ^{13}C

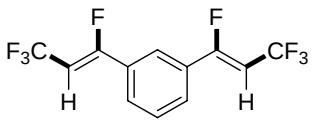
NMR (101 MHz, $CDCl_3$) δ 162.7 (dq, *J* = 269.2, 5.5 Hz), 135.1 (s), 131.5 (s), 131.2 (d, *J* = 26.7 Hz), 130.1 (d, *J* = 1.7 Hz), 125.5 (d, *J* = 7.7 Hz), 123.4 (d, *J* = 7.2 Hz), 122.2 (q, *J* = 268.4 Hz), 96.7 (qd, *J* = 36.4, 11.1 Hz).



(Z)-1-nitro-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3n**; 13 mg, 54%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.38 (d, *J* = 10.4 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 8.1 Hz, 1H), 5.90 (dq, *J* = 32.8, 7.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.47 (d, *J* = 16.8 Hz, 3F), -102.52 (q, *J* = 16.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (dq, *J* = 270.3, 5.7 Hz), 148.6 (s), 131.3 (d, *J* = 27.9 Hz), 130.9 (d, *J* = 7.0 Hz), 130.3 (d, *J* = 1.6 Hz), 126.0 (s), 123.3 (d, *J* = 257.1 Hz), 120.6 (t, *J* = 7.8 Hz), 98.3 (qd, *J* = 36.9, 10.9 Hz).

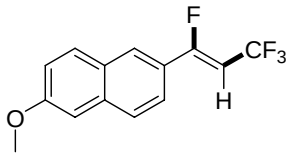


(Z)-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)aniline (**3o**; 12 mg, 59%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.90 (s, 1H), 6.80 (d, *J* = 6.1 Hz, 1H), 5.65 (dq, *J* = 33.5, 7.5 Hz, 1H), 3.83 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.01 (d, *J* = 16.4 Hz), -102.00 (q, *J* = 16.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9 (dq, *J* = 271.4, 5.6 Hz), 162.3 (d, *J* = 6.0 Hz), 146.8, 130.6 (d, *J* = 25.6 Hz), 129.8, 122.7 (q, *J* = 268.9 Hz), 118.0, 115.6 (d, *J* = 7.6 Hz), 111.5 (d, *J* = 8.0 Hz), 95.4 (qd, *J* = 36.2, 11.7 Hz).

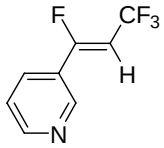


1,3-bis((Z)-1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3q**; 19 mg, 63%). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.74 (d, *J* = 9.5 Hz, 2H), 7.58 (t, *J* = 7.9

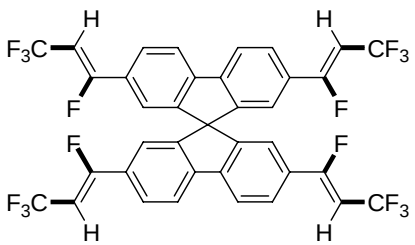
Hz, 1H), 5.80 (dq, *J* = 33.2, 7.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.30 (d, *J* = 16.7 Hz, 3F), -102.50 (q, *J* = 16.7 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8, 129.3–128.8 (m), 125.5 (d, *J* = 7.4 Hz), 123.7, 123.3 (d, *J* = 2.1 Hz), 96.7 (d, *J* = 11.4 Hz), 96.3 (d, *J* = 11.3 Hz).



(Z)-2-methoxy-6-(1,3,3,3-tetrafluoroprop-1-en-1-yl)naphthalene (**3r**; 18 mg, 67%). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.80 (dd, *J* = 12.6, 8.9 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.24 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 5.77 (dq, *J* = 33.8, 7.5 Hz, 1H), 3.97 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.69 (d, *J* = 16.4 Hz, 3F), -102.83 (q, *J* = 16.6 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 (dq, *J* = 262.6, 3.9 Hz), 159.4 (s), 136.1 (s), 130.4 (s), 128.1 (d, *J* = 1.2 Hz), 127.6 (d, *J* = 2.4 Hz), 125.8 (d, *J* = 8.2 Hz), 124.4 (d, *J* = 25.6 Hz), 122.8 (q, *J* = 268.9 Hz), 122.2 (d, *J* = 7.1 Hz), 120.0 (s), 105.9 (s), 94.9 (qd, *J* = 36.3, 11.7 Hz), 55.4 (s).



(Z)-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)pyridine (**3s**; 12 mg, 63%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 2H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.57 (s, 1H), 5.80 (dq, *J* = 33.2, 7.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.31 (d, *J* = 16.7 Hz, 3F), -103.47 (q, *J* = 16.2 Hz, 1F).



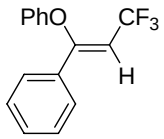
2,2',7,7'-Tetrakis((Z)-1,3,3,3-tetrafluoroprop-1-en-1-yl)-9,9'-spirobi[fluorene] (**3u**;

30 mg, 40%). Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 4H), 7.76 (d, *J* = 6.8 Hz, 4H), 6.91 (s, 4H), 5.59 (dq, *J* = 33.4, 7.4 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.09 (d, *J* = 16.4 Hz, 12F), -102.23 (q, *J* = 16.4 Hz, 4F).

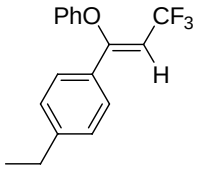
3. General procedure for oxy-trifluoromethylation reactions

In an oven-dried 25-mL Schlenk tube equipped with a stir bar were added phenCu(CF_3)$_3$ (**1**) (45 mg, 0.1 mmol), alkynes (**2**) (0.1 mmol) and phenoxides or alkoxides (0.5 mmol). The Schlenk tube was evacuated and refilled with dry nitrogen. Dry DMF (2 mL) was then added by syringe. The contents in the tube were vigorously stirred for 6 hours at 100 ^{o}C (heated in an oil bath). The reaction mixture was then allowed to cool to room temperature, and water was added at 0 ^{o}C. The resulting mixture was extracted by dichloromethane. The combined organic layers were washed with a large amount of water 5 times, with brine for once and then dried over magnesium sulfate. The solvent was removed by vacuum evaporation in an ice-water bath. The resulting residual was purified by column chromatography on silica gel eluted with *n*-hexane or mixed PE/EA = 10:1 (v/v) to provide oxy-trifluoromethylation products **5**.

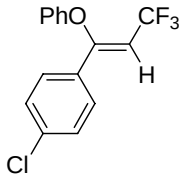
A representative example of oxy-trifluoromethylation reaction at 1.0 mmol scale: Following the procedure described above, reaction of phenCu(CF_3)$_3$ (**1**) (450 mg, 1.0 mmol), *para*-ethylphenyl acetylene (130 mg, 1.0 mmol) and NaOPh (580 mg, 5.0 mmol) in 20 mL DMF at 100 ^{o}C for 6 hours produced **5b** in a ^{19}F NMR yield of 90% and an isolated yield of 74% (216 mg), which are slightly lower than the yields of 99% (86%) obtained at a 0.1 mmol scale as reported in the main text.



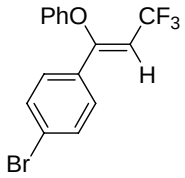
(Z)-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5a**; 18 mg, 68%; *n*-hexane as eluent). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 3H), 7.29–7.21 (m, 2H), 6.98 (dd, *J* = 19.9, 7.6 Hz, 3H), 5.87 (q, *J* = 7.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.76 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8 (q, *J* = 5.7 Hz), 156.2, 132.8, 130.5, 129.5, 128.8, 127.2, 122.9 (q, *J* = 269.7 Hz), 122.8, 117.1, 105.1 (q, *J* = 34.9 Hz).



(Z)-1-ethyl-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5b**; 25 mg, 86%; *n*-hexane as eluent). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.40–7.34 (m, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 3H), 6.97 (d, *J* = 7.8 Hz, 2H), 5.85 (q, *J* = 7.6 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.58 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9 (q, *J* = 5.8 Hz), 156.3, 153.9, 147.1, 129.5, 128.3, 127.2, 123.0 (q, *J* = 269.6 Hz), 122.7, 117.0, 104.4 (q, *J* = 34.8 Hz), 28.6, 15.1.

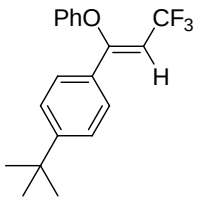


(Z)-1-chloro-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5c**; 15 mg**,** 52%; *n*-hexane as eluent). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.27–7.22 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 2H), 5.85 (q, *J* = 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (q, *J* = 5.4 Hz), 155.9, 136.6, 131.3, 129.7, 129.2, 128.5, 123.1, 122.7 (q, *J* = 269.9 Hz), 117.0, 105.6 (q, *J* = 35.1 Hz).

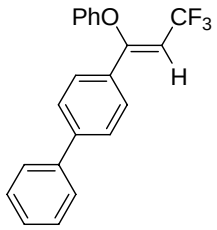


(Z)-1-bromo-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5d**; 14 mg, 42%; *n*-hexane as eluent). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.27–7.22 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.85 (q, *J* = 7.4 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.90 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8 (q, *J* = 5.3 Hz), 155.9, 132.1, 129.7, 128.7, 125.0,

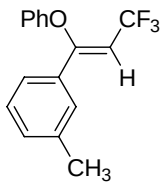
123.1, 117.0, 105.6 (q, J = 35.0 Hz).



(Z)-1-(tert-butyl)-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5e**; 21 mg, 64%; *n*-hexane as eluent). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.29–7.23 (m, 2H), 6.99 (dd, J = 18.3, 7.6 Hz, 3H), 5.85 (q, J = 7.6 Hz, 1H), 1.30 (s, 9H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.62 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7 (q, J = 5.8 Hz), 156.4, 154.0, 129.8, 129.5, 126.9, 125.8, 123.0 (q, J = 269.6 Hz), 122.7, 116.9, 104.5 (q, J = 34.8 Hz), 35.0, 31.1.

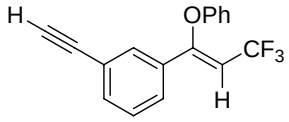


(Z)-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)-1,1'-biphenyl (**5f**; 18 mg, 54%; PE:EA = 10:1 (v/v) as eluent). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (q, J = 8.4 Hz, 6H), 7.46 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.27 (d, J = 16.1 Hz, 2H), 7.02 (dd, J = 10.9, 8.1 Hz, 3H), 5.93 (q, J = 7.5 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.65 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (q, J = 5.7 Hz), 156.3, 143.3, 139.8, 131.6, 129.6, 128.9, 128.0, 127.6, 127.4, 127.1, 123.0 (q, J = 276.9 Hz), 122.9, 117.0, 105.0 (q, J = 34.9 Hz).

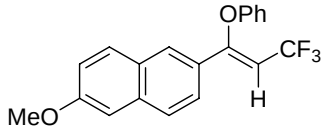


(Z)-1-methyl-3-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5g**; 20 mg, 72%; *n*-hexane as eluent). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 2H), 7.28–7.16 (m, 4H), 6.99 (dd, J = 18.7, 7.6 Hz, 3H), 5.85 (q, J = 7.6 Hz, 1H), 2.34

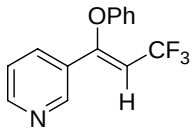
(s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.72 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (q, *J* = 5.8 Hz), 156.3, 138.6, 132.8, 131.3, 129.5, 128.7, 127.8, 124.4, 123.0 (q, *J* = 269.7 Hz), 122.8, 117.1, 105.0 (q, *J* = 34.8 Hz), 21.4.



(Z)-1-ethynyl-3-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5h**; 15 mg, 51%; PE:EA = 10:1 (v/v) as eluent). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.50–7.46 (m, 2H), 7.32–7.23 (m, 3H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 2H), 5.86 (q, *J* = 7.4 Hz, 1H), 3.12 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.95 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9 (q, *J* = 5.6 Hz), 155.9, 134.0, 133.2, 130.8, 129.6, 128.9, 127.4, 123.1, 122.7 (q, *J* = 269.8 Hz), 117.1, 105.94 (q, *J* = 35.0 Hz), 82.5, 78.3.

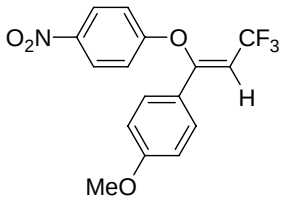


(Z)-2-methoxy-6-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)naphthalene (**5i**; 21 mg, 61%; PE:EA = 10:1 (v/v) as eluent). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.70 (dd, *J* = 11.4, 8.9 Hz, 2H), 7.54 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.23 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.17 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.10 (d, *J* = 2.4 Hz, 1H), 7.05–6.94 (m, 3H), 5.96 (q, *J* = 7.6 Hz, 1H), 3.93 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.48 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (q, *J* = 4.9 Hz), 156.4, 130.2, 129.6, 127.5, 124.2, 123.4 (q, *J* = 269.0 Hz), 122.8, 119.7, 117.0, 115.3, 105.7, 104.6 (q, *J* = 34.8 Hz), 55.4.

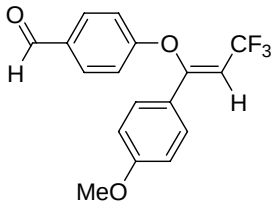


(Z)-3-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)pyridine (**5j**; 15 mg, 57%; PE:EA = 10:1 (v/v) as eluent). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 2H), 7.80

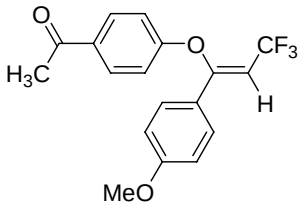
(d, *J* = 7.8 Hz, 1H), 7.43 (s, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 5.90 (q, *J* = 7.3 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.99 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (q, *J* = 4.3 Hz), 134.3, 129.8, 123.4, 122.5 (q, *J* = 270.0 Hz), 117.2, 106.7 (q, *J* = 35.2 Hz).



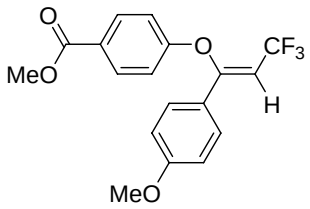
(Z)-1-methoxy-4-(3,3,3-trifluoro-1-(4-nitrophenoxy)prop-1-en-1-yl)benzene (**5k**; 23 mg, 69%; PE:EA = 10:1 (v/v) as eluent). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.2 Hz, 2H), 7.44 (d, *J* = 11.8 Hz, 2H), 7.04 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.91 (q, *J* = 7.5 Hz, 1H), 3.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.72 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 161.2, 157.4 (q, *J* = 5.7 Hz), 143.1, 128.4, 125.9, 123.6, 122.7 (q, *J* = 269.7 Hz), 116.9, 114.6, 104.3 (q, *J* = 35.2 Hz), 55.4.



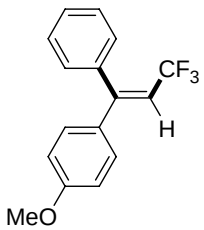
(Z)-4-((3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)oxy)benzaldehyde (**5l**; 19 mg, 59%; PE:EA = 10:1 (v/v) as eluent). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.88 (q, *J* = 7.5 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 161.7, 161.2, 157.6 (q, *J* = 5.8 Hz), 131.8, 131.5, 128.5, 124.1, 122.8 (q, *J* = 269.6 Hz), 117.2, 114.5, 104.1 (q, *J* = 35.1 Hz), 55.4.



(Z)-1-(4-((3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)oxy)phenyl)ethan-1-one (**5n**; 16 mg, 49%; PE:EA = 10:1 (v/v) as eluent). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.86 (q, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 2.54 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.63 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 161.6, 160.2, 157.8 (q, *J* = 5.5 Hz), 132.1, 130.5, 128.5, 124.3, 122.9 (q, *J* = 269.6 Hz), 116.6, 114.4, 103.9 (q, *J* = 35.1 Hz), 55.4, 26.3.



Methyl (Z)-4-((3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)oxy)benzoate (**5o**; 25 mg, 71%; PE:EA = 10:1 (v/v) as eluent). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.84 (q, *J* = 7.5 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.62 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 161.6, 160.0, 157.9 (q, *J* = 5.8 Hz), 131.6, 128.5, 124.7, 124.3, 122.9 (q, *J* = 269.6 Hz), 116.6, 114.4, 103.8 (q, *J* = 35.1 Hz), 55.3, 52.0.

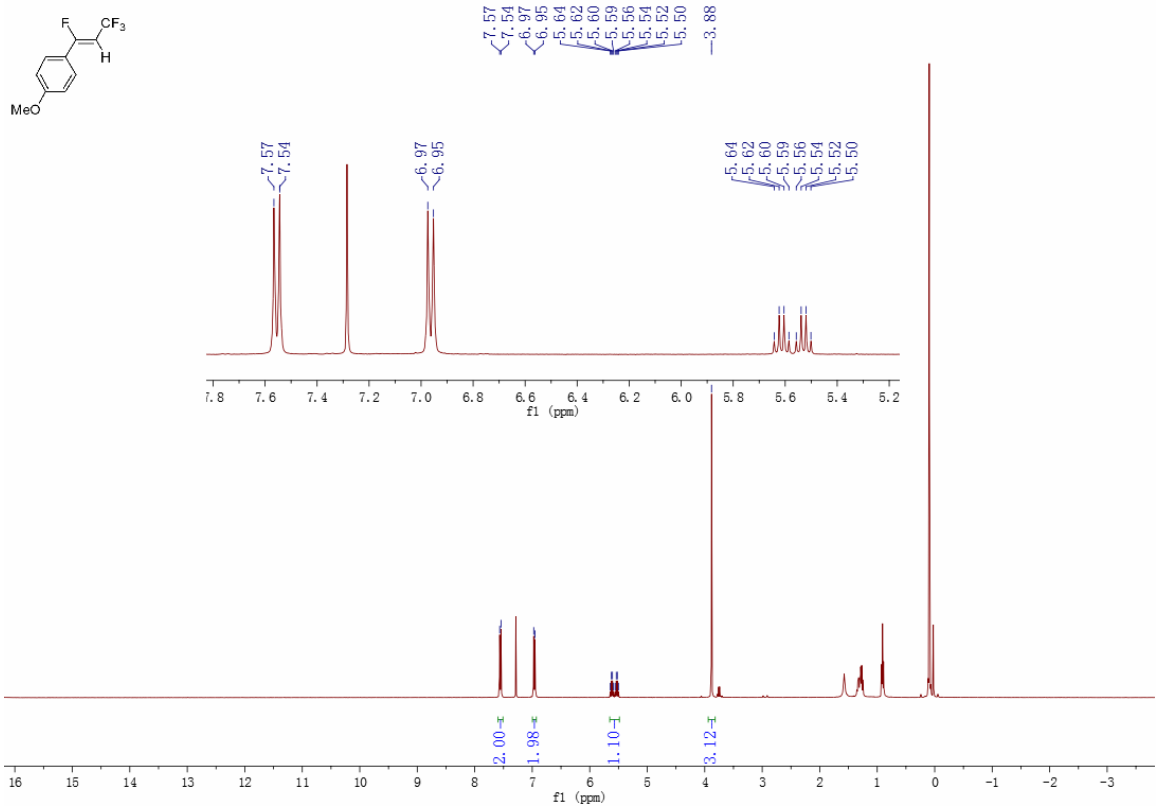


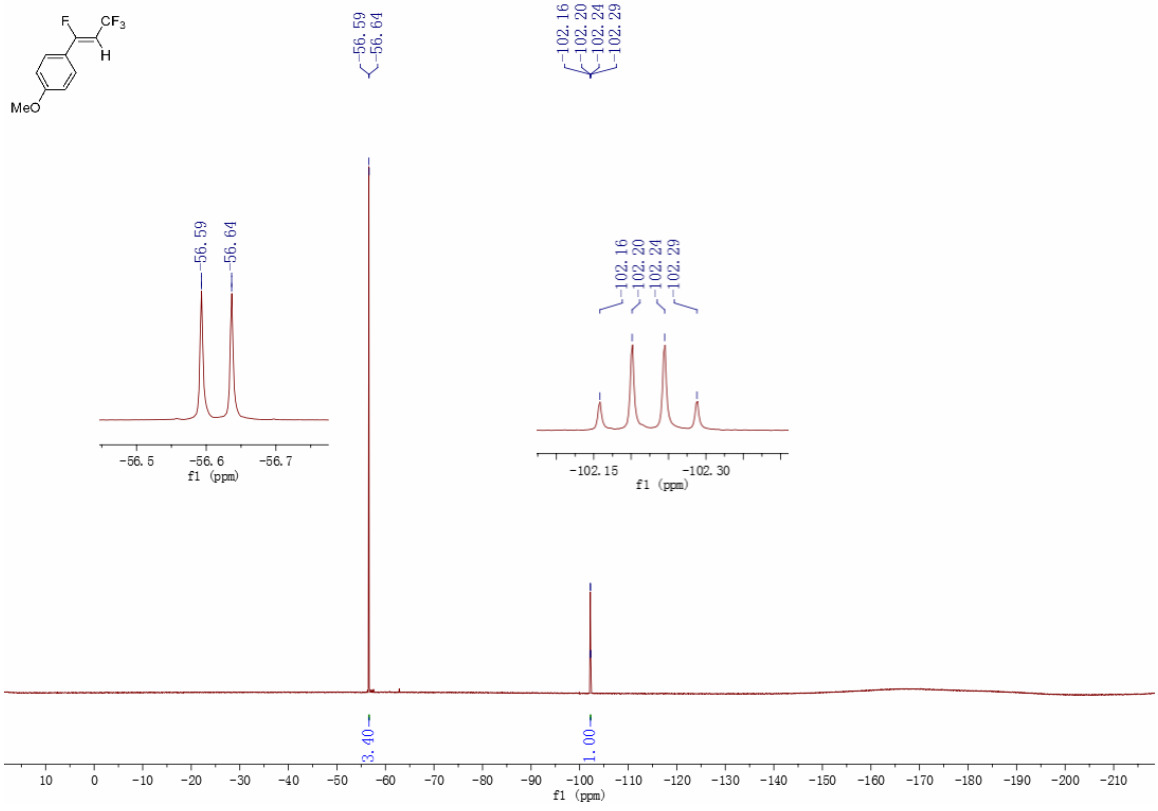
(E)-1-methoxy-4-(3,3,3-trifluoro-1-phenylprop-1-enyl)benzene (**7**; 16 mg, 57%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 3H), 7.30–7.26 (m, 2H),

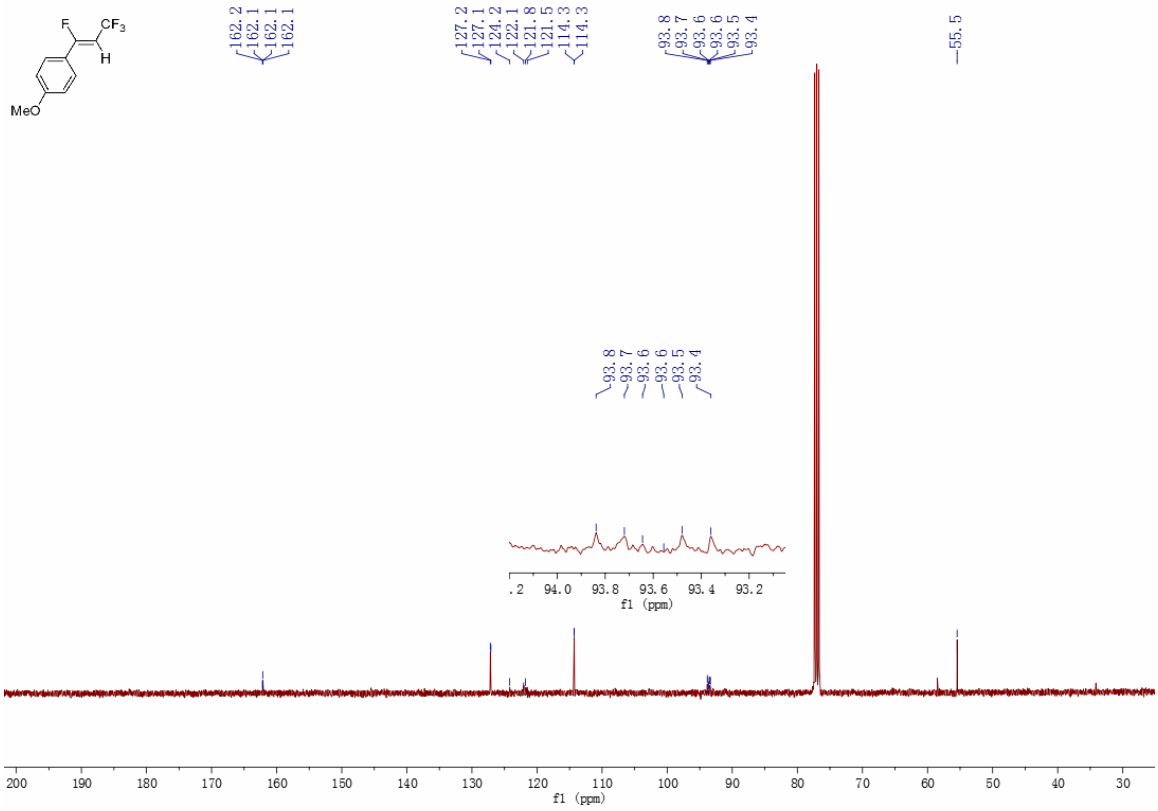
7.21 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.07 (q, J = 8.4 Hz, 1H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.49 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.88 (s), 152.37 (q, J = 5.6 Hz), 140.76 (s), 130.66 (q, J = 1.8 Hz), 129.58 (s), 129.31 (s), 128.41 (s), 128.17 (s), 123.23 (q, J = 270.5 Hz), 114.95 (q, J = 33.7 Hz), 113.46 (s), 55.24 (s).

4. ^{1}H, ^{19}F and ^{13}C NMR spectra for all the products

(Z)-1-methoxy-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3a**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)






F
CF3
H
MeO
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162.1
162.1
162.1
127.2
127.1
124.2
122.1
121.8
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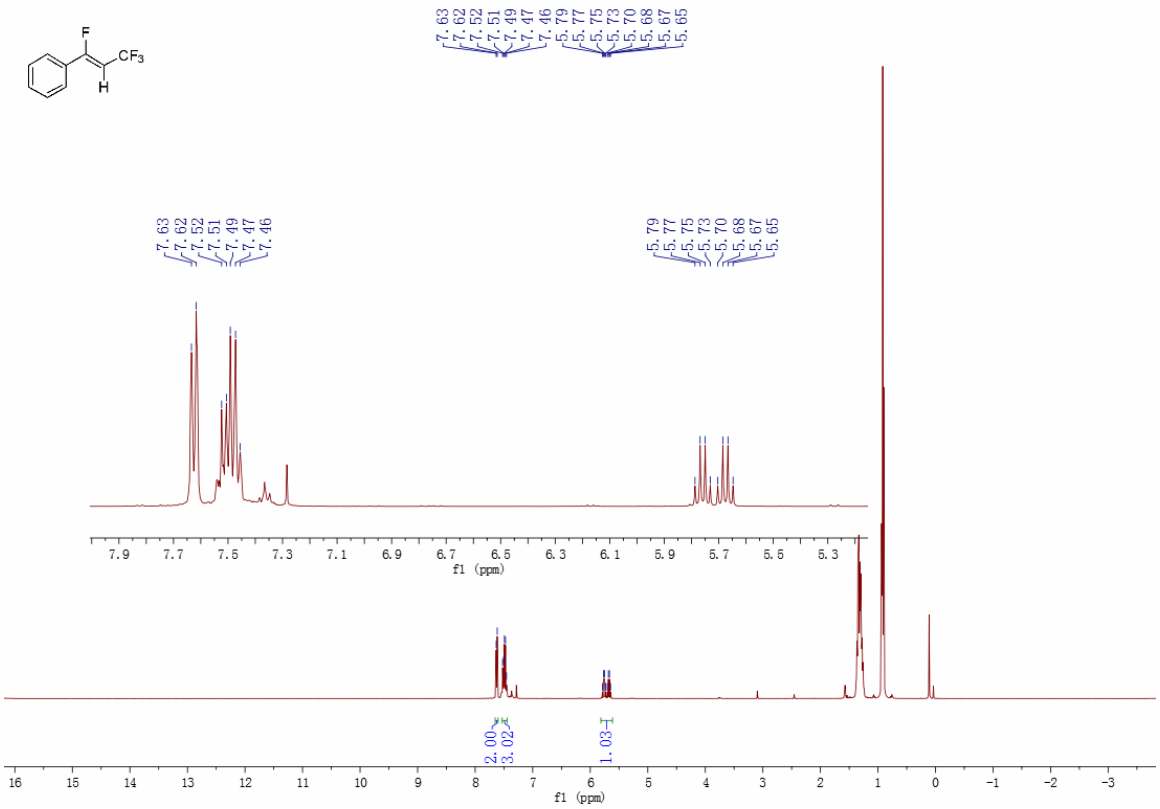
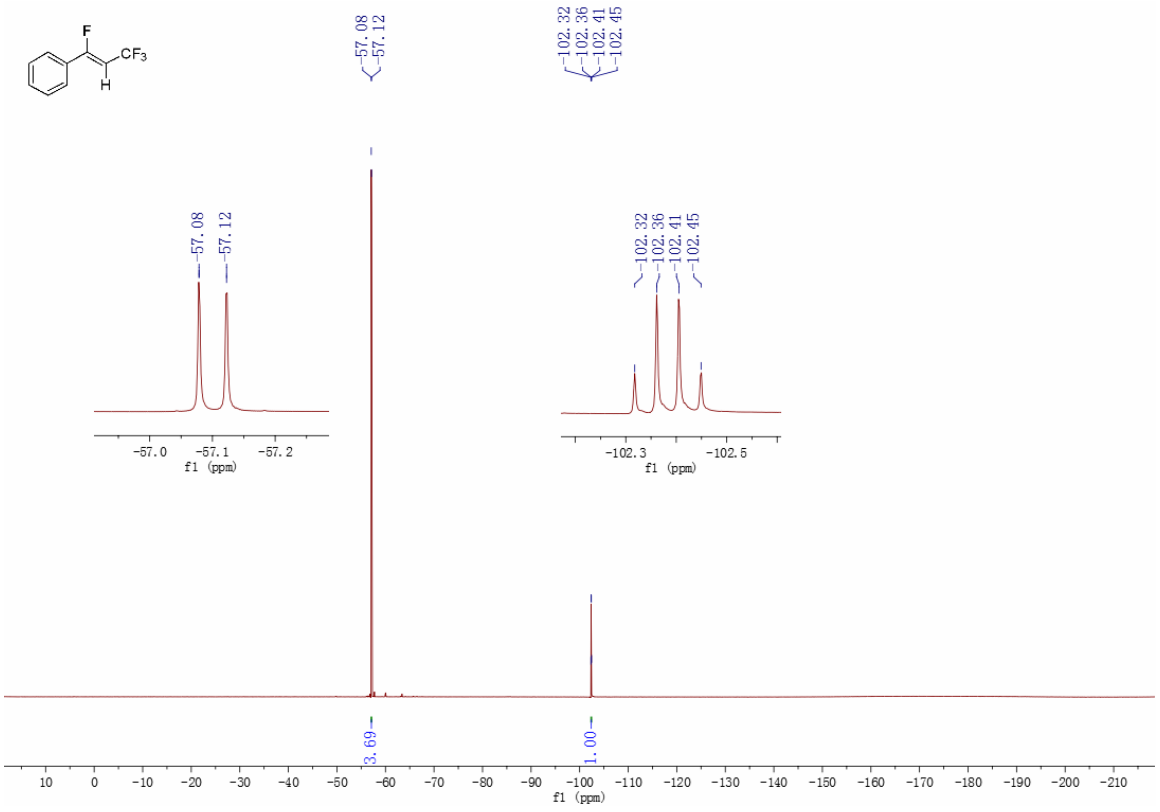
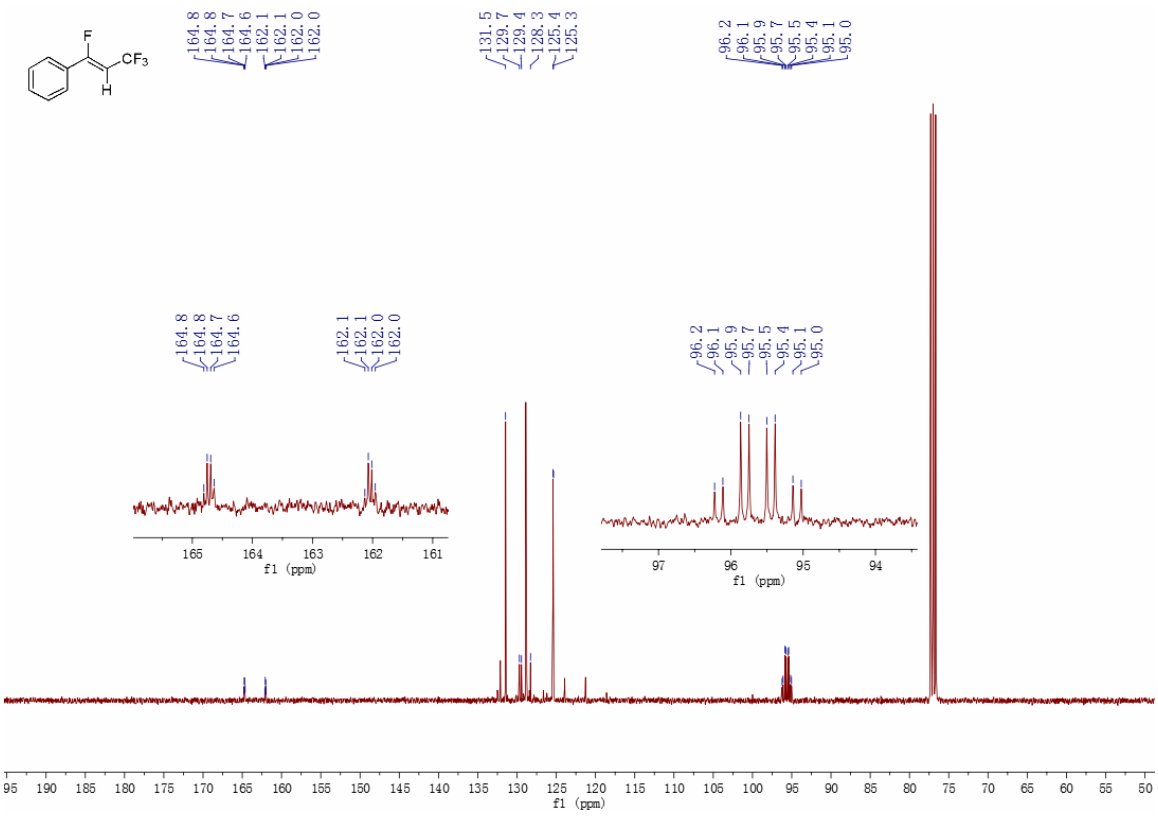
114.3
114.3
93.8
93.7
93.6
93.5
93.4
55.5
93.8
93.7
93.6
93.5
93.4
94.0
93.8
93.6
93.4
93.2
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

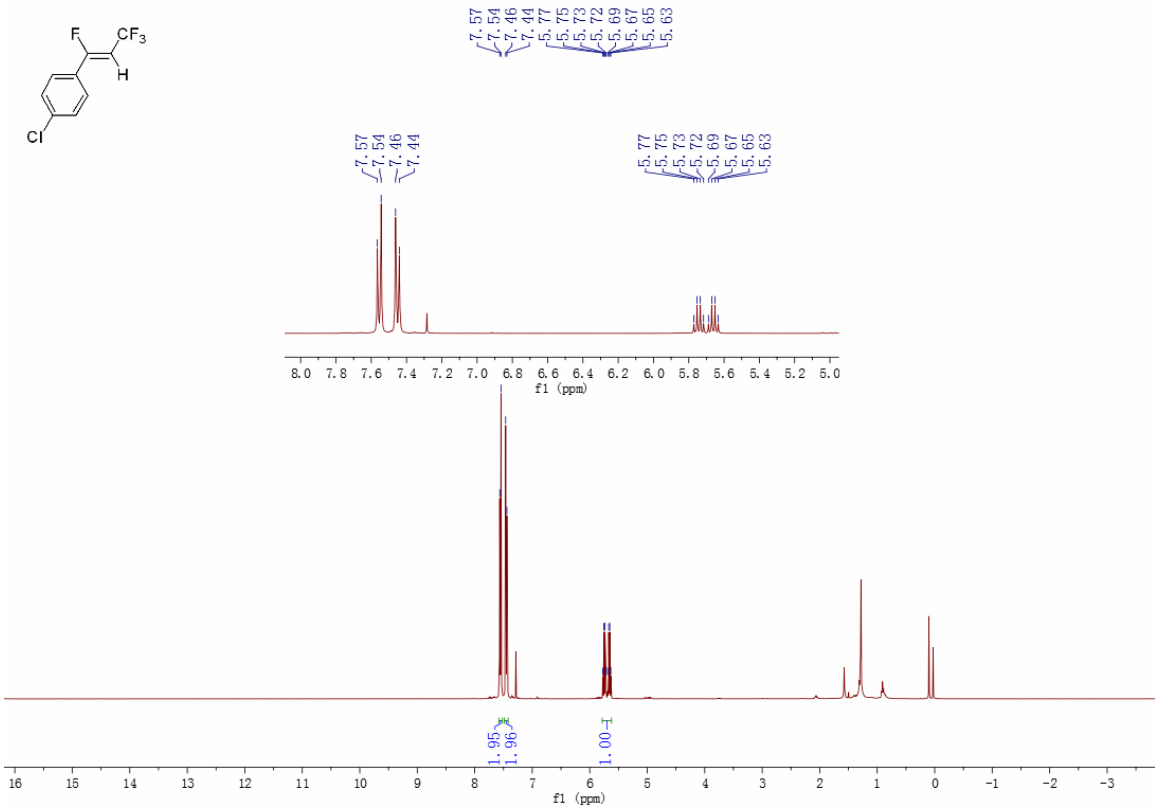
(Z)-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3b**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

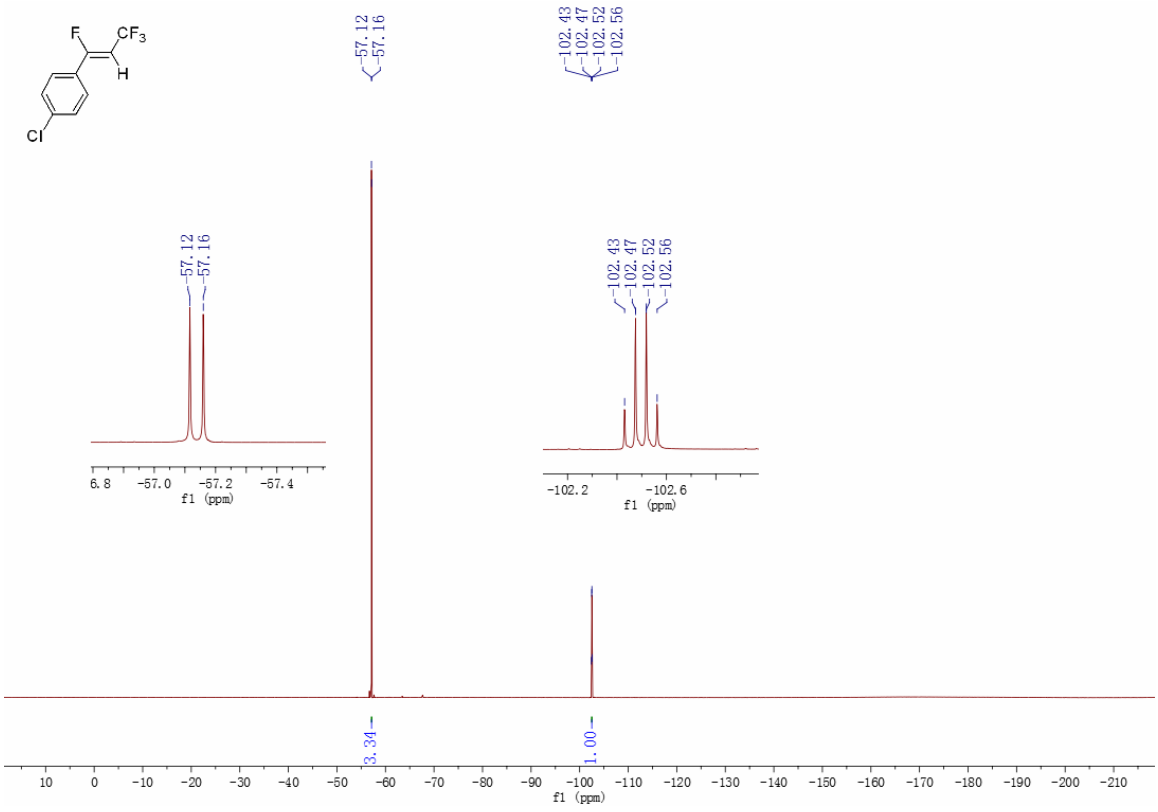


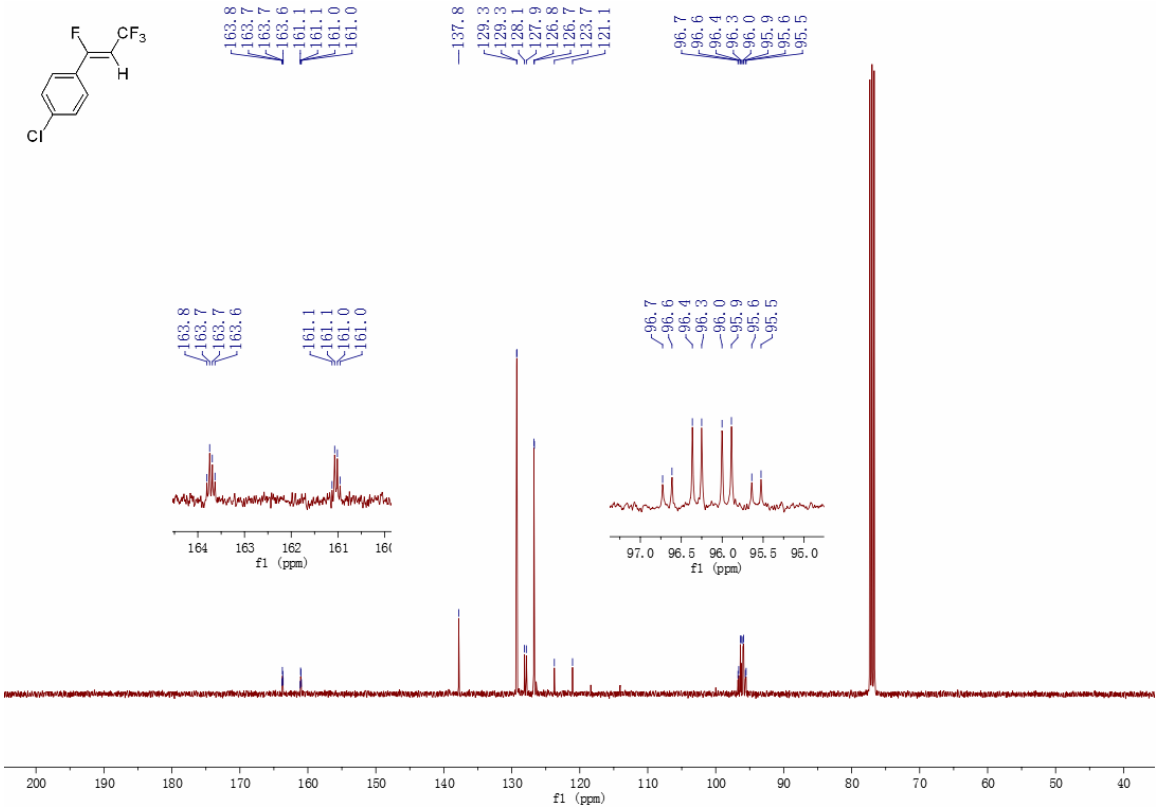



F
CF3
H
164.8
164.8
164.7
164.6
162.1
162.1
162.0
162.0
131.5
129.7
129.4
128.3
125.4
125.3
96.2
96.1
95.9
95.7
95.5
95.4
95.1
95.0
f1 (ppm)
f1 (ppm)
f1 (ppm)

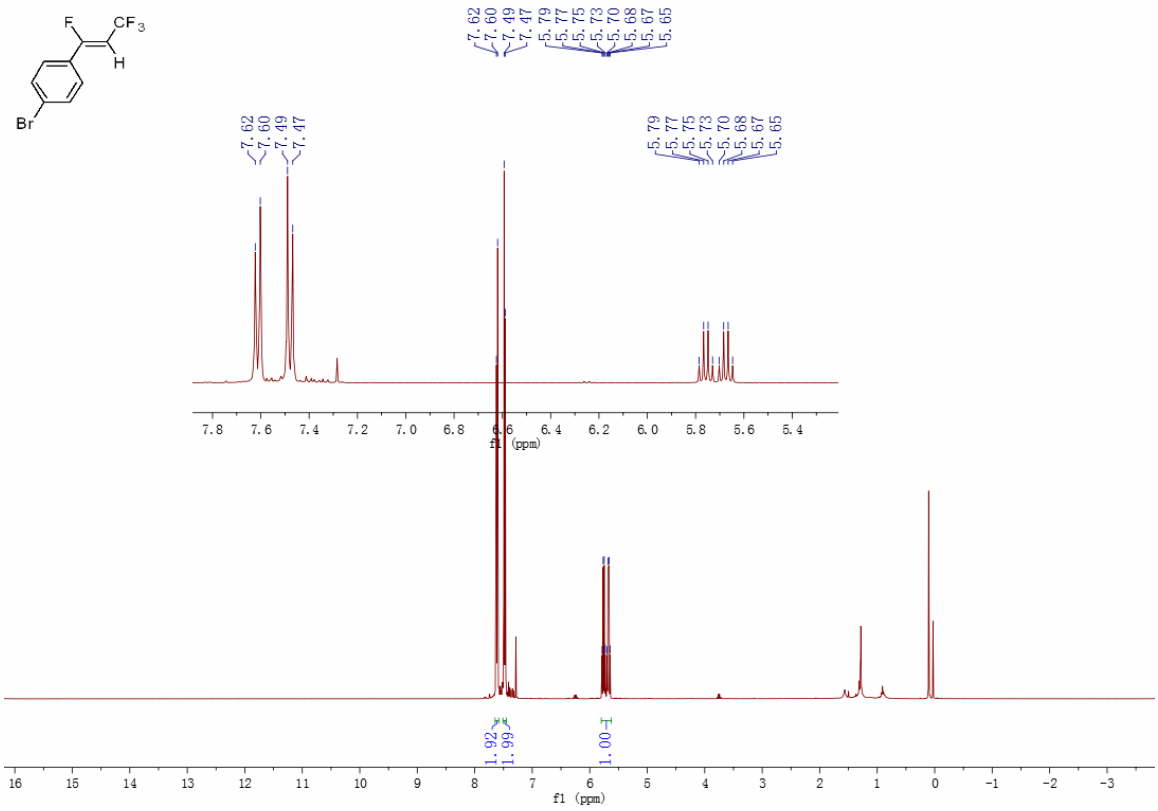
(Z)-1-chloro-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3c**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

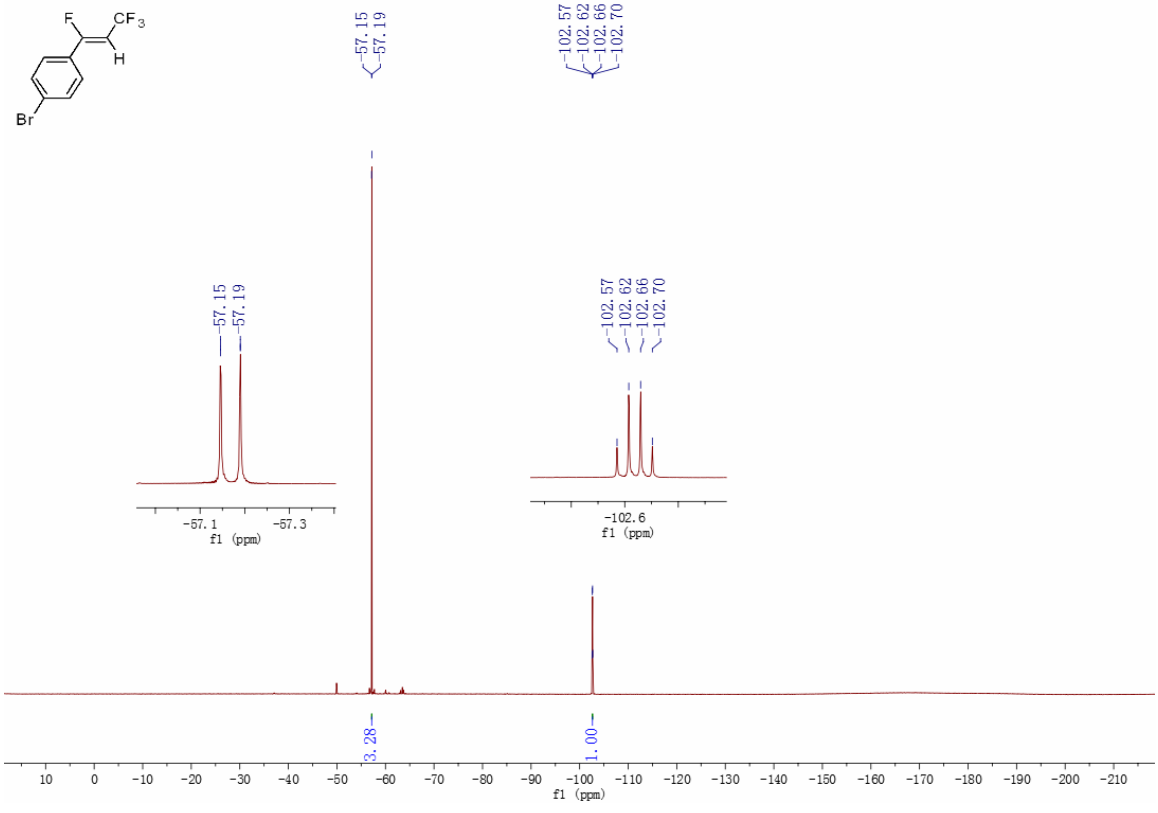


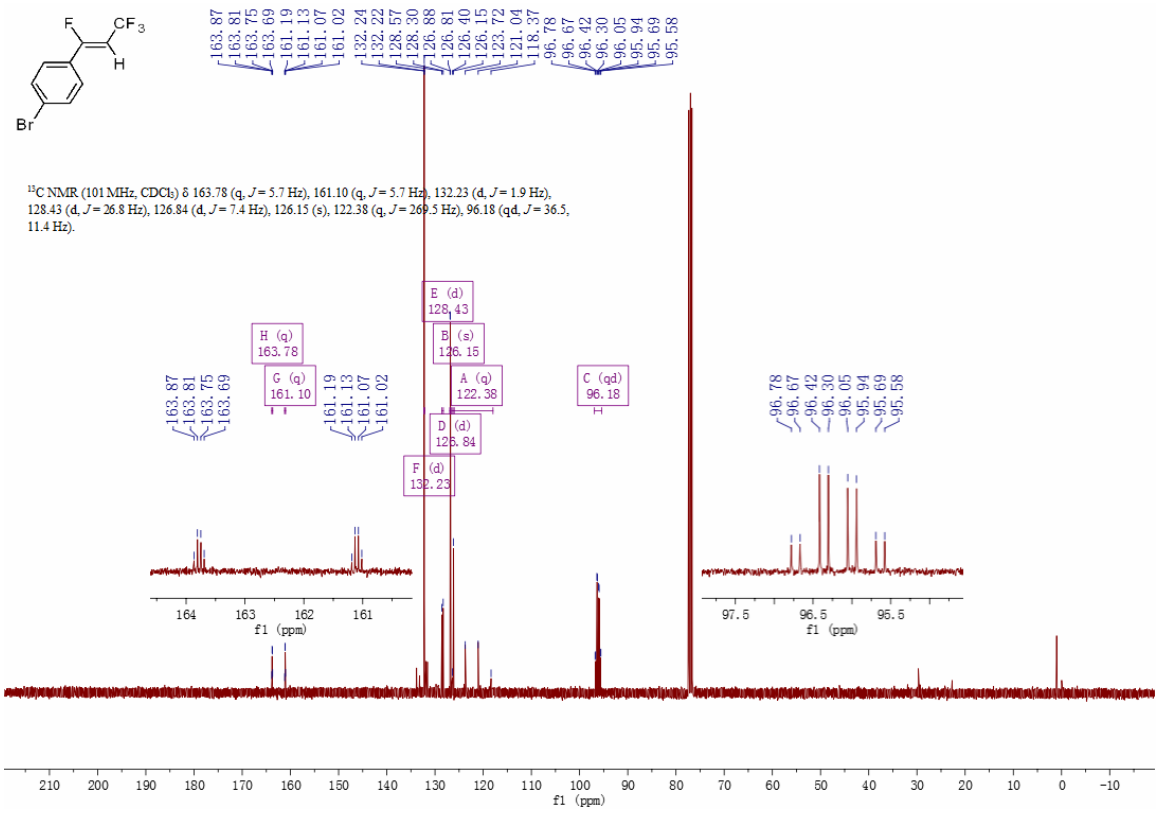



F
CF3
H
Cl
163.8
163.7
163.7
163.6
161.1
161.1
161.0
161.0
137.8
129.3
129.3
128.1
127.9
126.8
126.7
123.7
121.1
96.7
96.6
96.4
96.3
96.0
95.9
95.6
95.5
f1 (ppm)
f1 (ppm)
f1 (ppm)

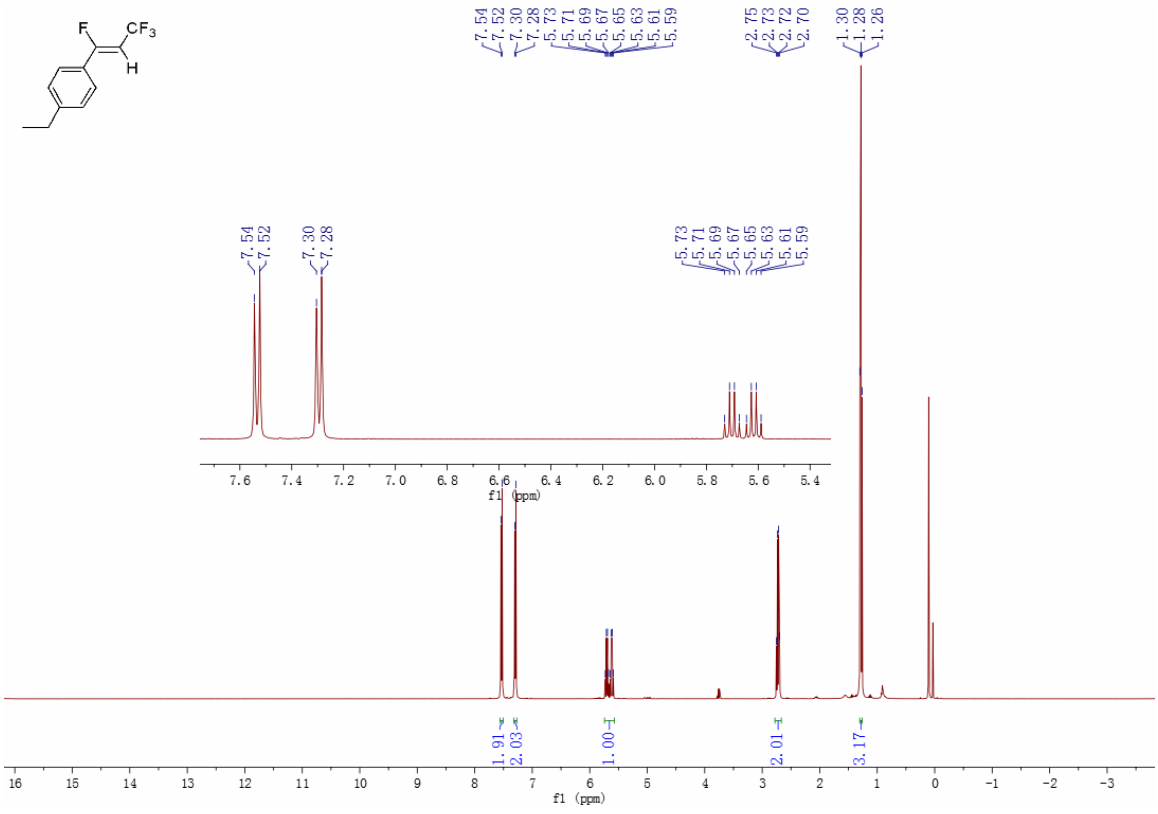
(Z)-1-bromo-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3d**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

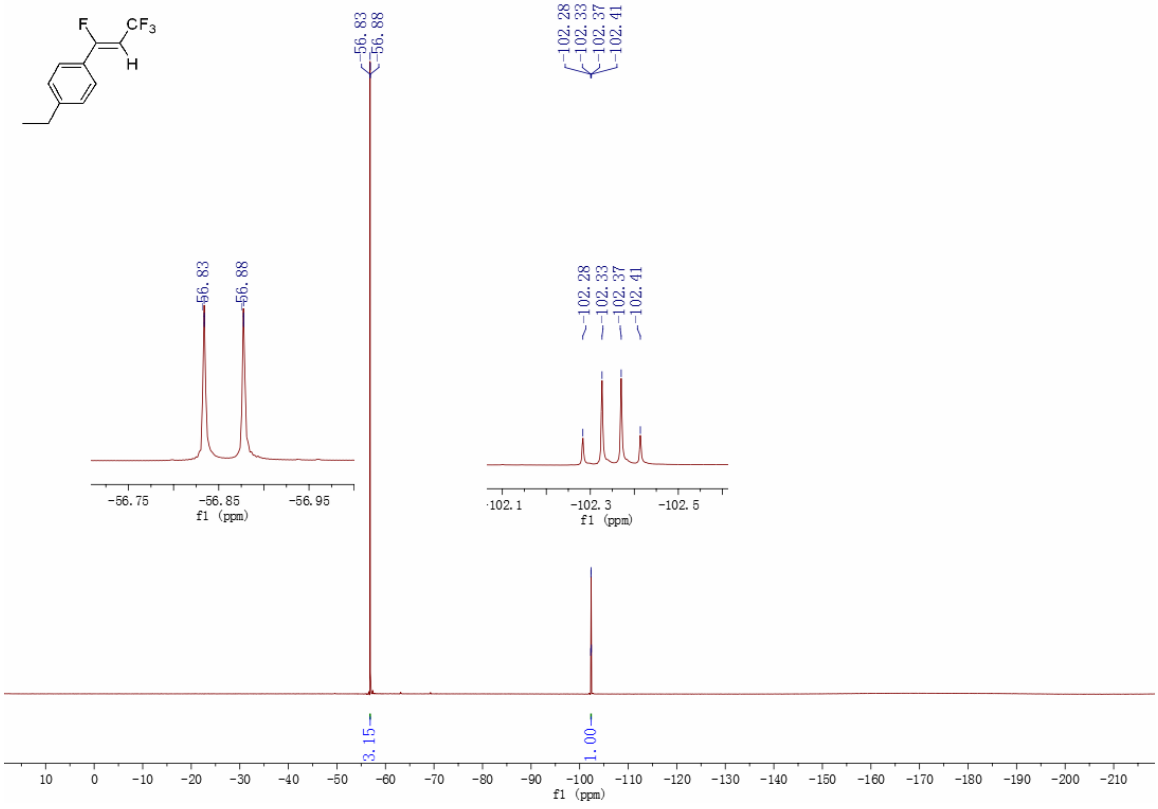


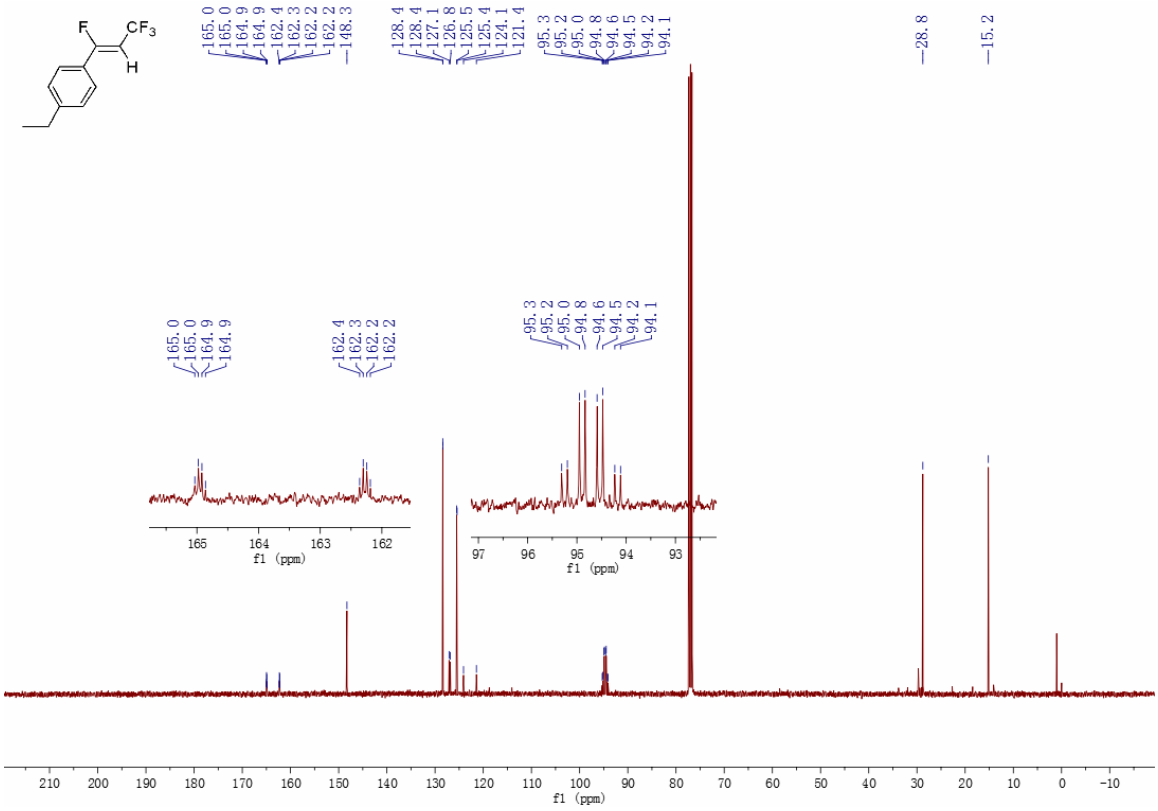



F
CF3
H
Br
163.87
163.81
163.75
163.69
161.19
161.13
161.07
161.02
132.24
132.22
128.57
128.30
126.88
126.81
126.40
126.15
123.72
121.04
118.37
96.78
96.67
96.42
96.30
96.05
95.94
95.69
95.58
13C NMR (101 MHz, CDCl3) δ 163.78 (q, J = 5.7 Hz), 161.10 (q, J = 5.7 Hz), 132.23 (d, J = 1.9 Hz), 128.43 (d, J = 26.8 Hz), 126.84 (d, J = 7.4 Hz), 126.15 (s), 122.38 (q, J = 269.5 Hz), 96.18 (qd, J = 36.5, 11.4 Hz).
E (d) 128.43
B (s) 126.15
H (q) 163.78
G (q) 161.10
A (q) 122.38
C (qd) 96.18
D (d) 126.84
F (d) 132.23
164
163
162
161
f1 (ppm)
97.5
96.5
95.5
f1 (ppm)
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)

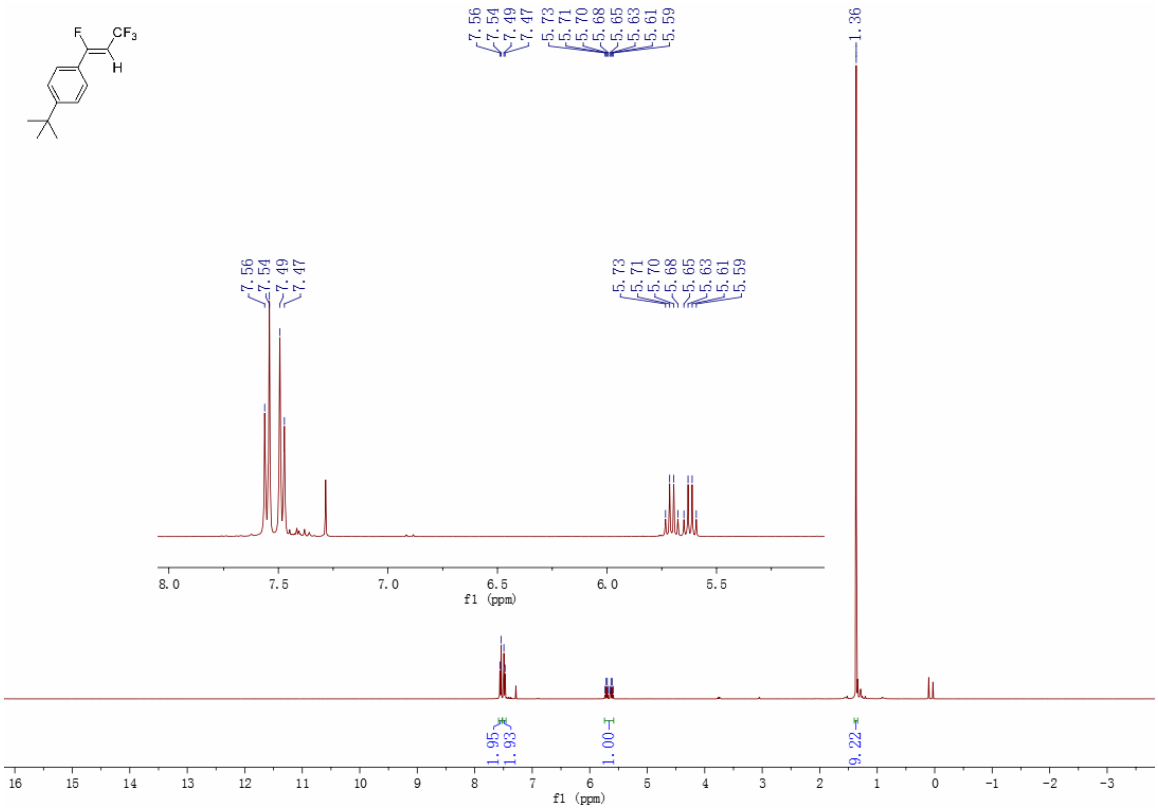
(Z)-1-ethyl-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3e**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

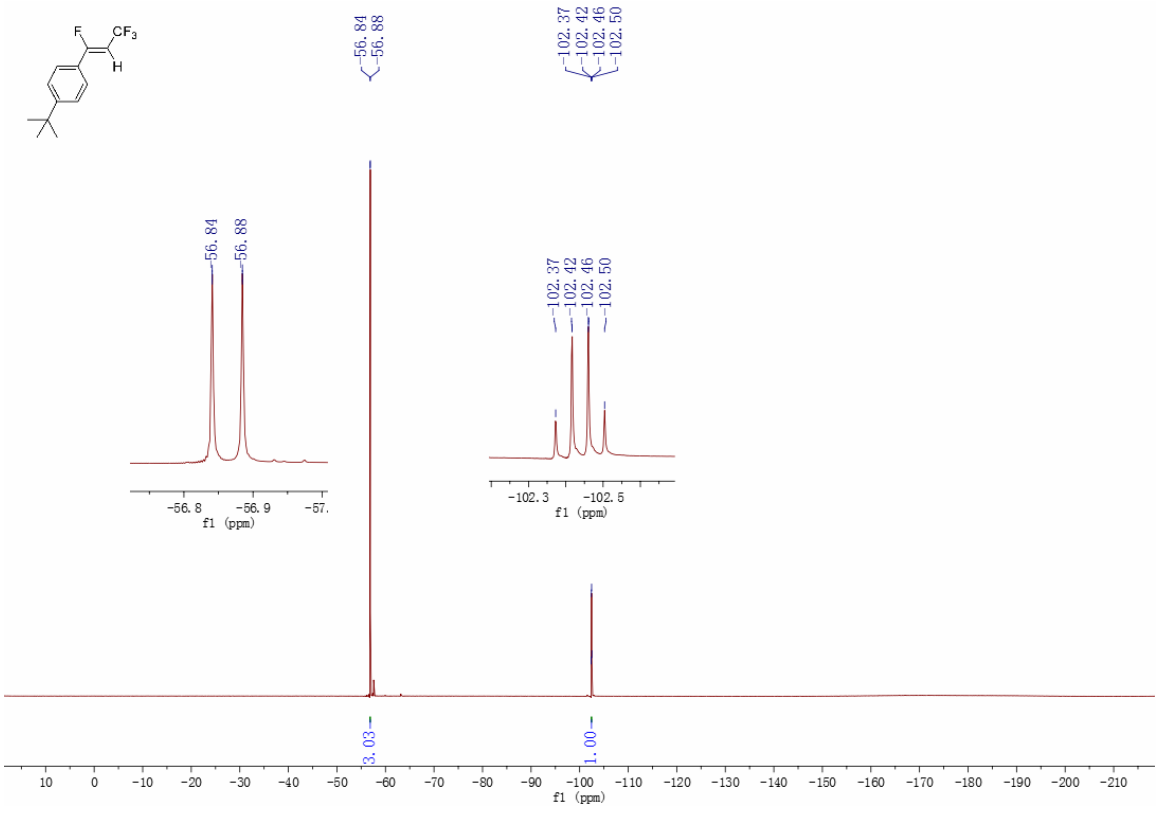


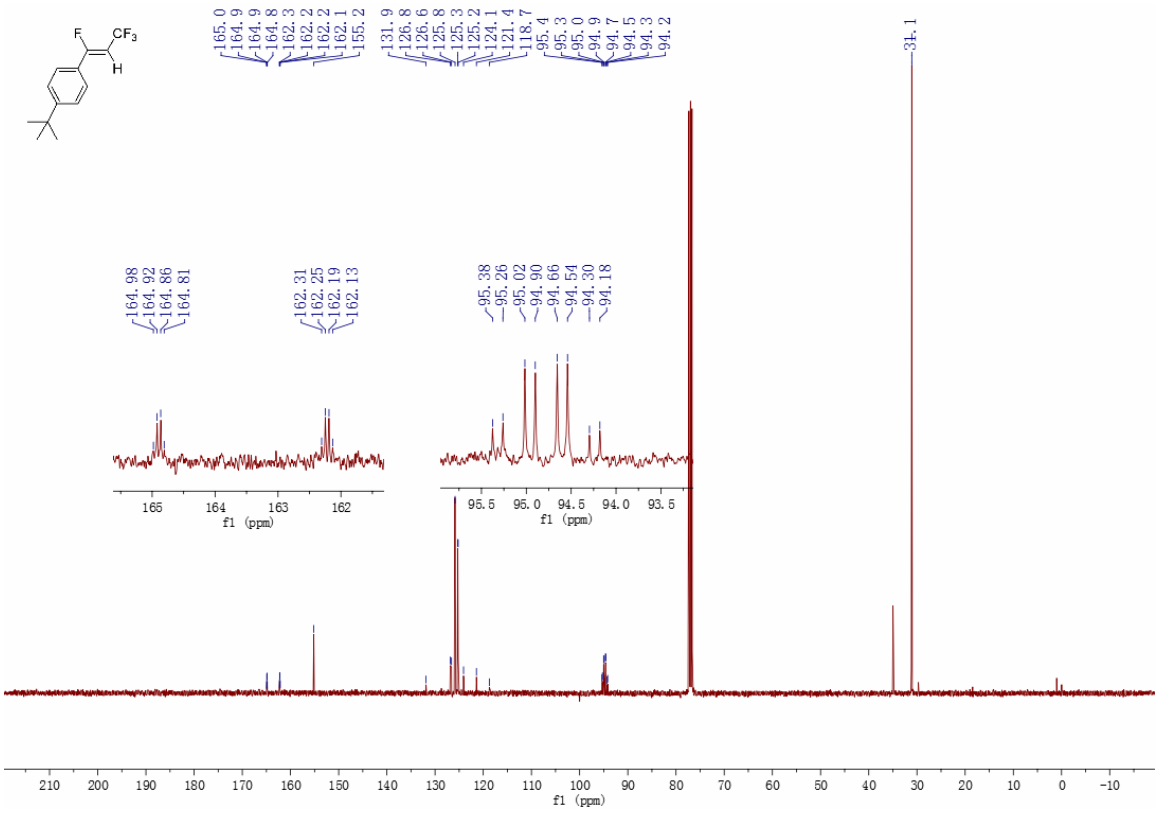



F
CF3
H
165.0
165.0
164.9
164.9
162.4
162.3
162.2
162.2
148.3
128.4
128.4
127.1
126.8
125.5
125.4
124.1
121.4
95.3
95.2
95.0
94.8
94.6
94.5
94.2
94.1
28.8
15.2
f1 (ppm)
f1 (ppm)
f1 (ppm)

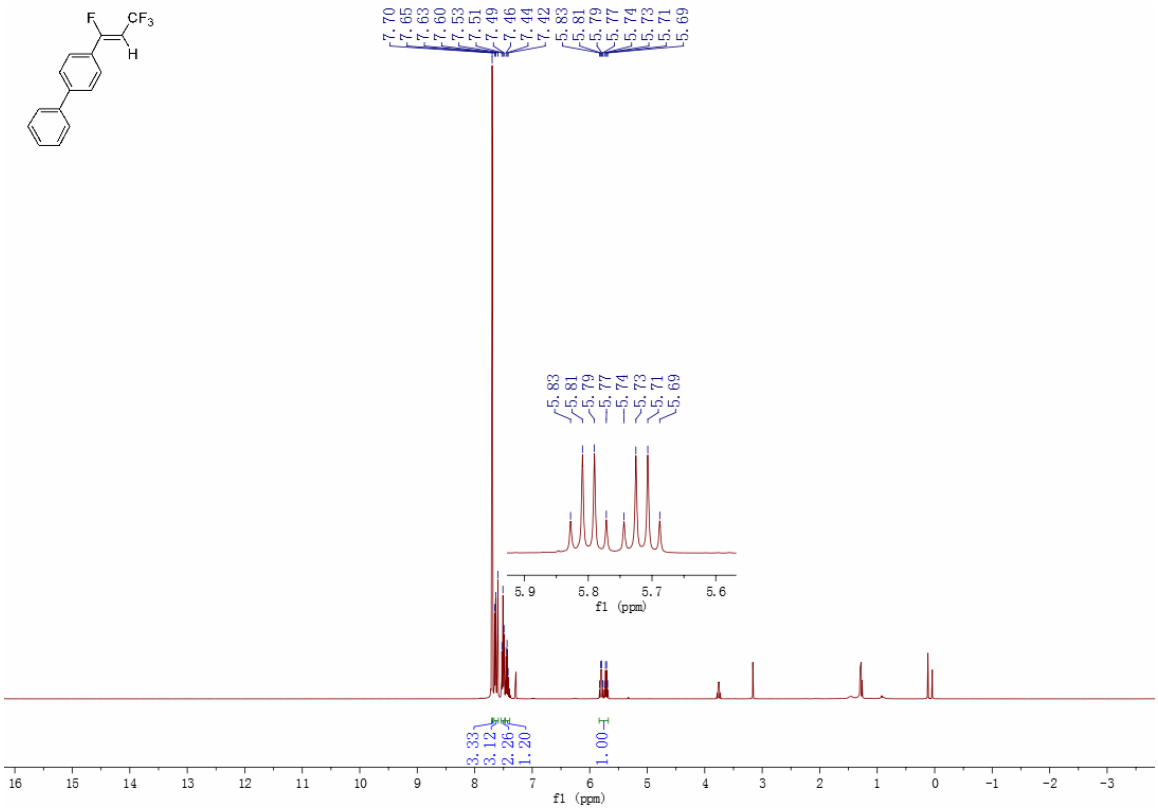
(Z)-1-(tert-butyl)-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3f**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

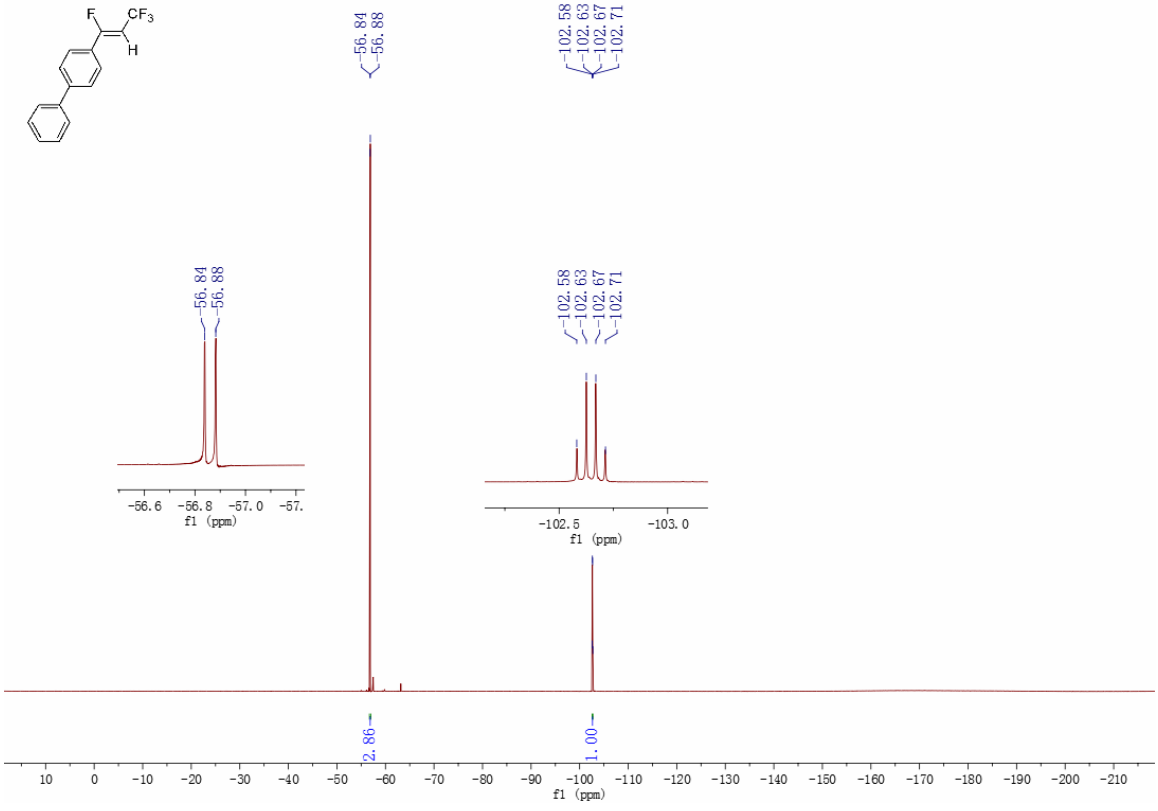


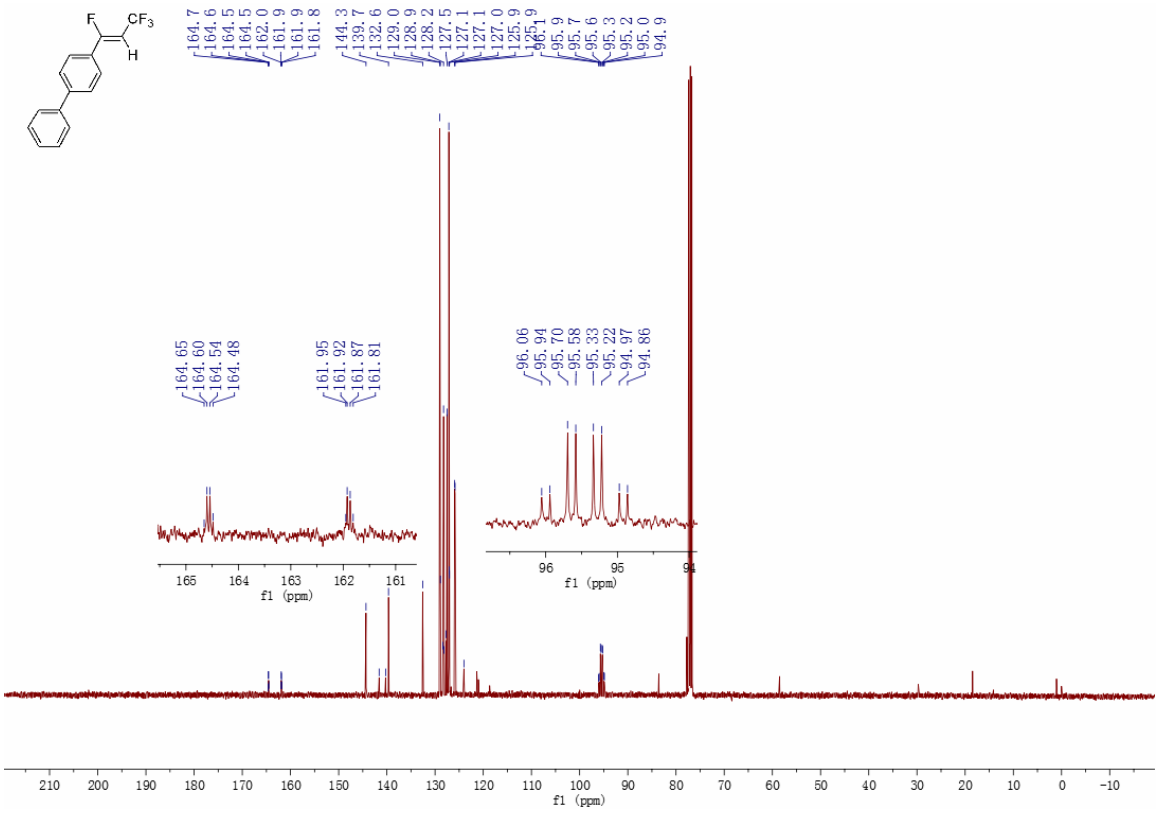



F
CF3
H
165.0
164.9
164.9
164.8
162.3
162.2
162.2
162.1
155.2
131.9
126.8
126.6
125.8
125.3
125.2
124.1
121.4
118.7
95.4
95.3
95.0
94.9
94.7
94.5
94.3
94.2
34.1
164.98
164.92
164.86
164.81
162.31
162.25
162.19
162.13
95.38
95.26
95.02
94.90
94.66
94.54
94.30
94.18
165
164
163
162
f1 (ppm)
95.5
95.0
94.5
94.0
93.5
f1 (ppm)
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)

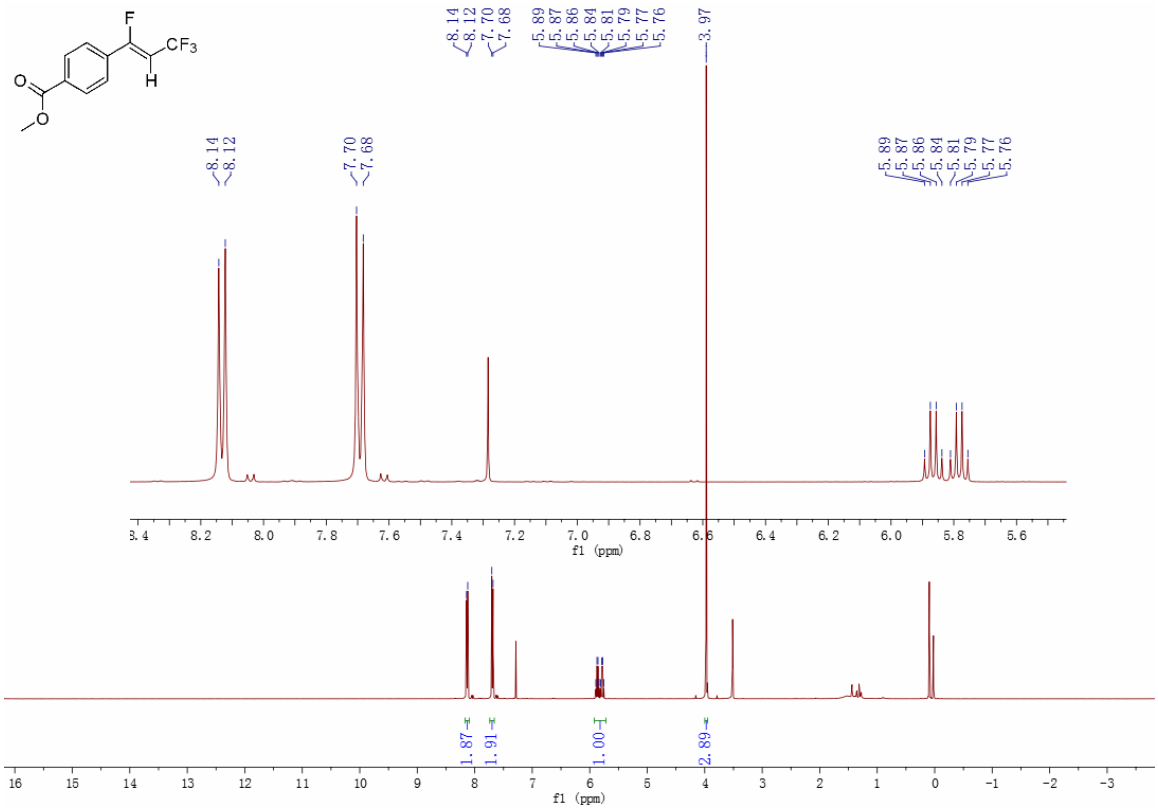
(Z)-4-(1,3,3,3-tetrafluoroprop-1-en-1-yl)-1,1'-biphenyl (**3g**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

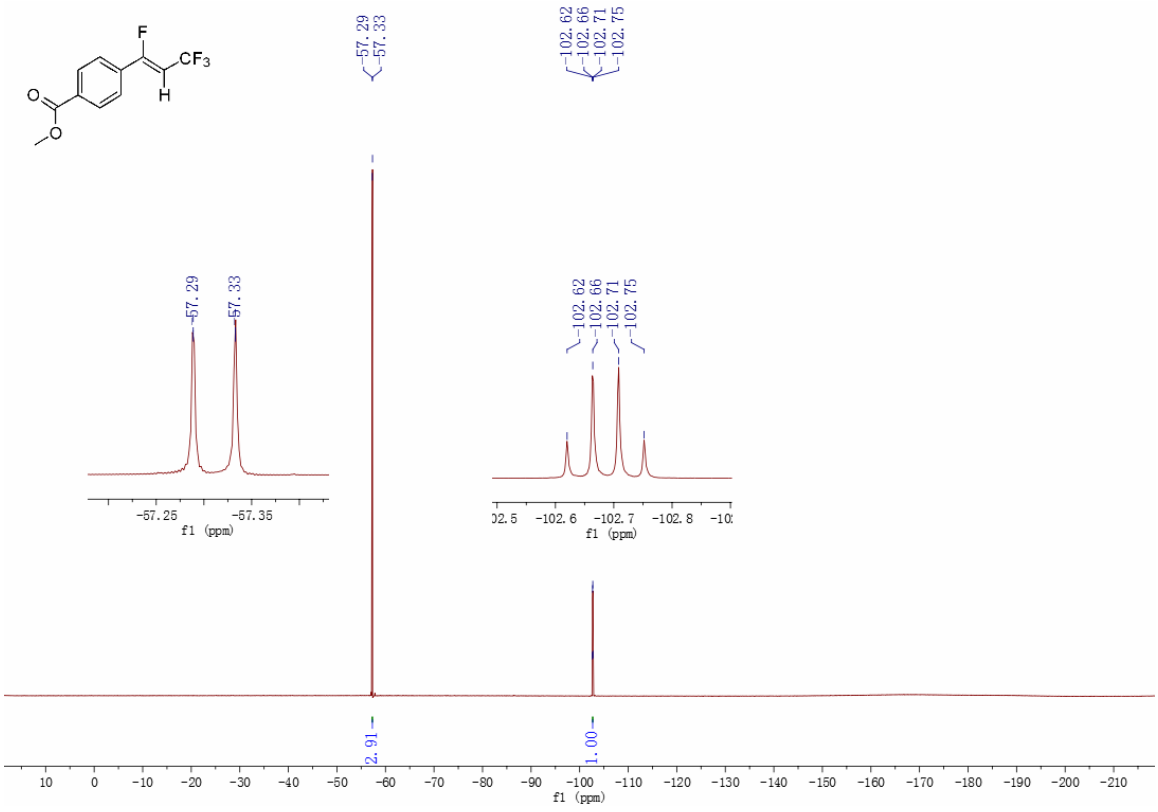


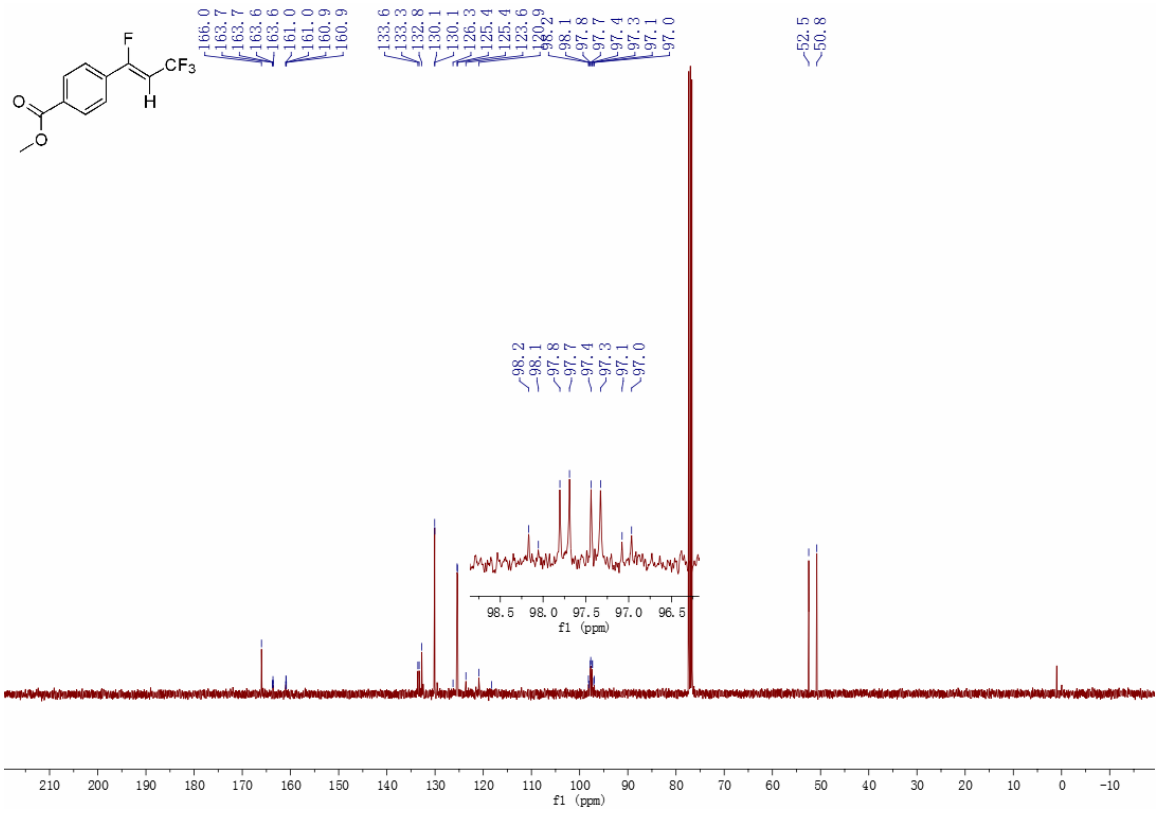



F
CF3
H
164.7
164.6
164.5
164.5
162.0
161.9
161.9
161.8
144.3
139.7
132.6
129.0
128.9
128.2
127.5
127.1
127.1
127.0
125.9
125.9
96.1
95.9
95.7
95.6
95.3
95.2
95.0
94.9
164.65
164.60
164.54
164.48
161.95
161.92
161.87
161.81
96.06
95.94
95.70
95.58
95.33
95.22
94.97
94.86
f1 (ppm)
f1 (ppm)
f1 (ppm)

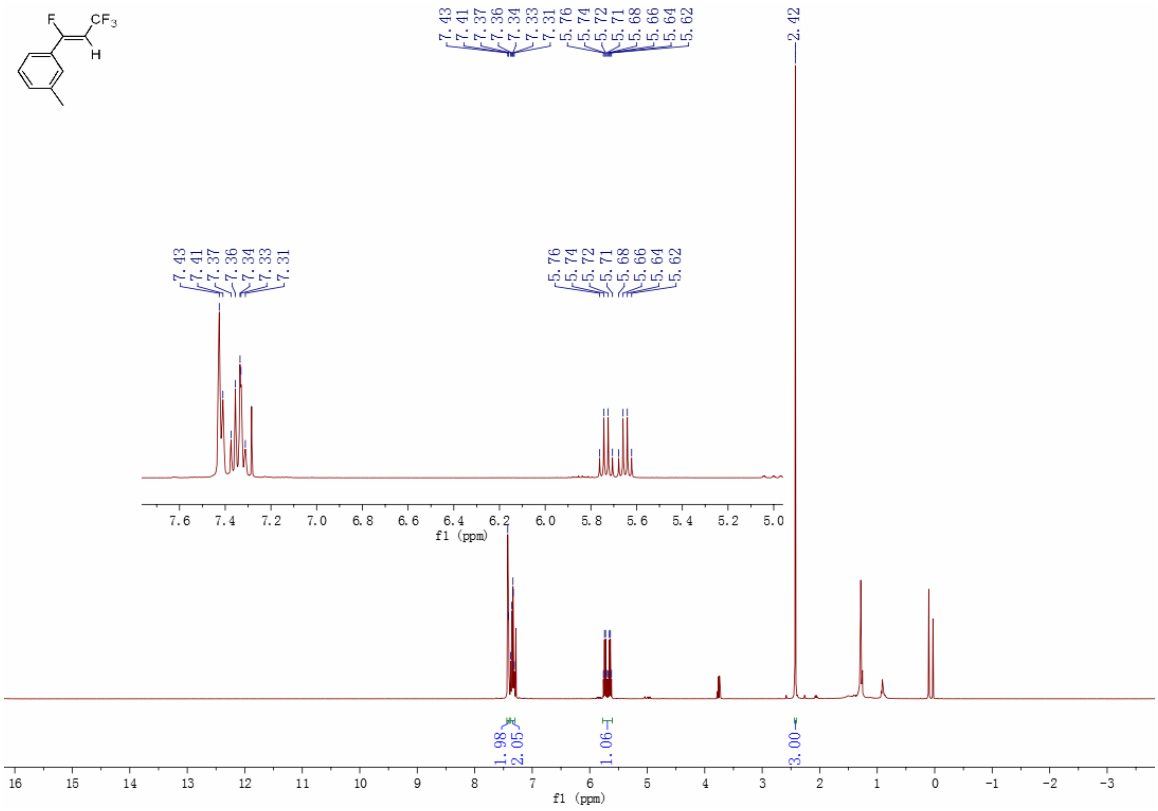
(Z)-Methyl 4-(1,3,3,3-tetrafluoroprop-1-enyl)benzoate (3h. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

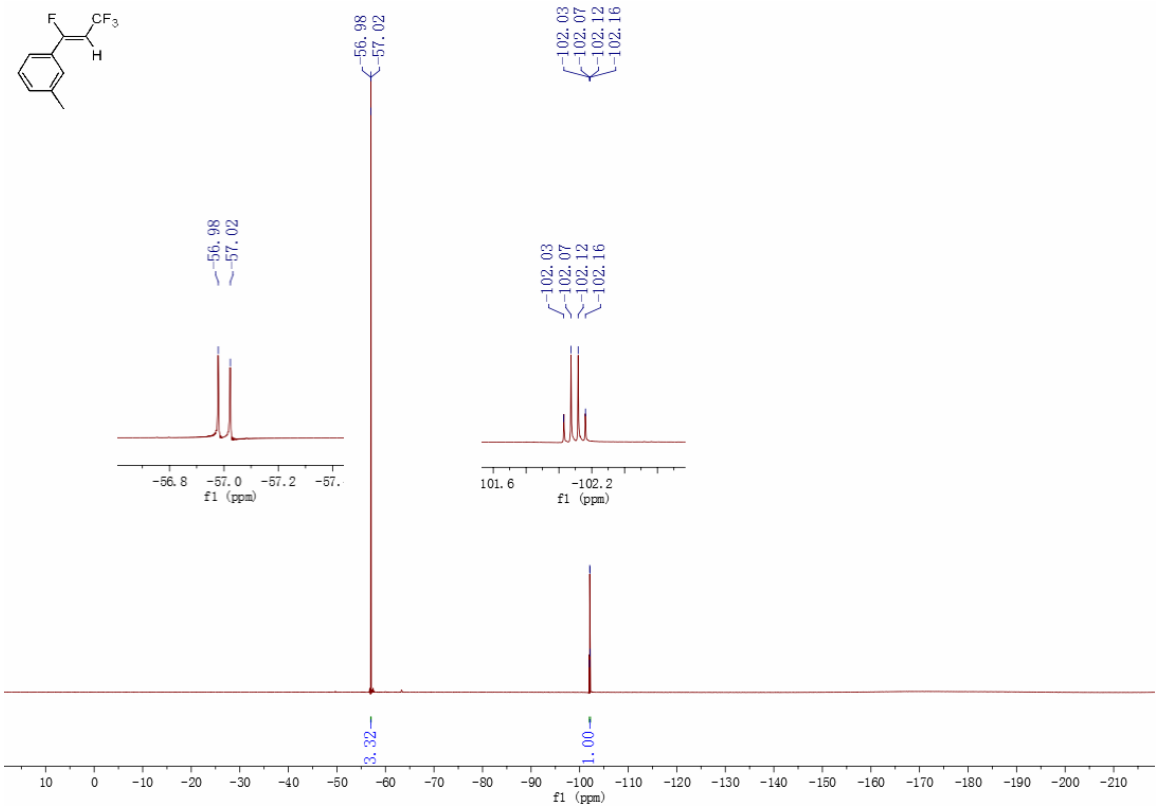


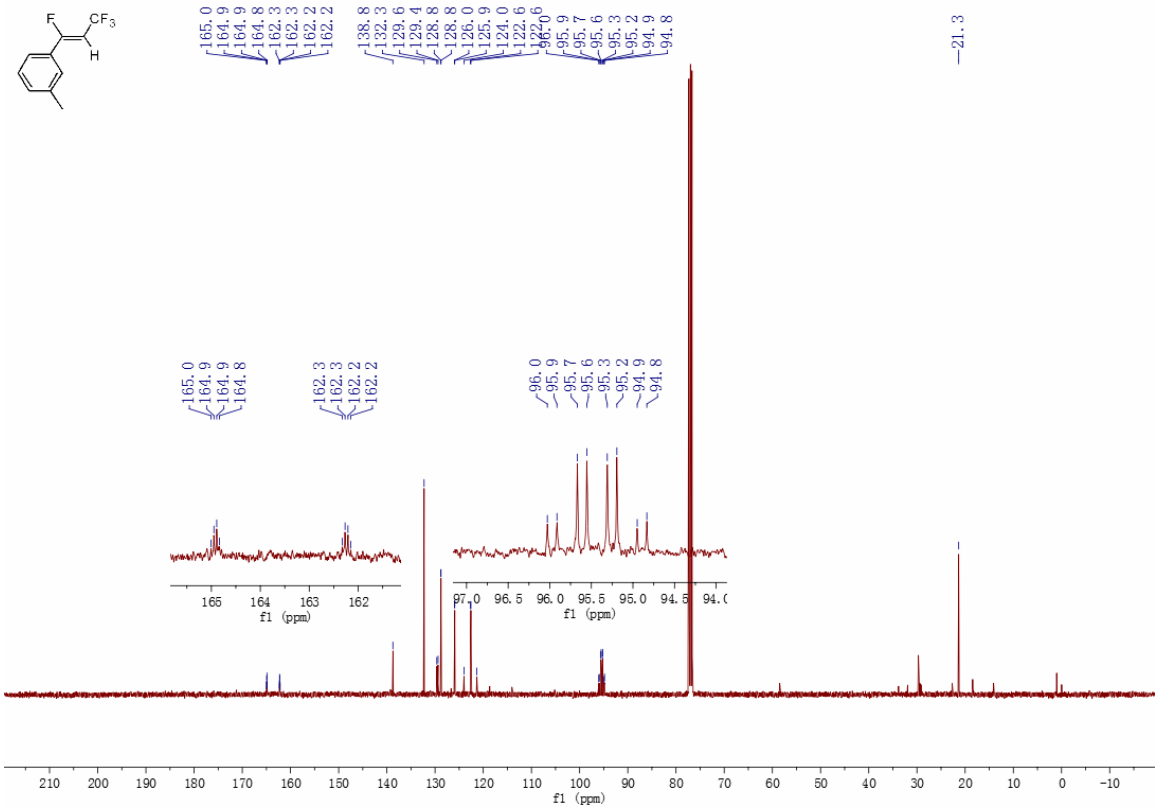



F
CF3
H
O
O
166.0
163.7
163.7
163.6
163.6
161.0
161.0
160.9
160.9
133.6
133.3
132.8
130.1
130.1
126.3
125.4
125.4
123.6
120.9
98.2
98.1
97.8
97.7
97.4
97.3
97.1
97.0
52.5
50.8
98.2
98.1
97.8
97.7
97.4
97.3
97.1
97.0
98.5 98.0 97.5 97.0 96.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

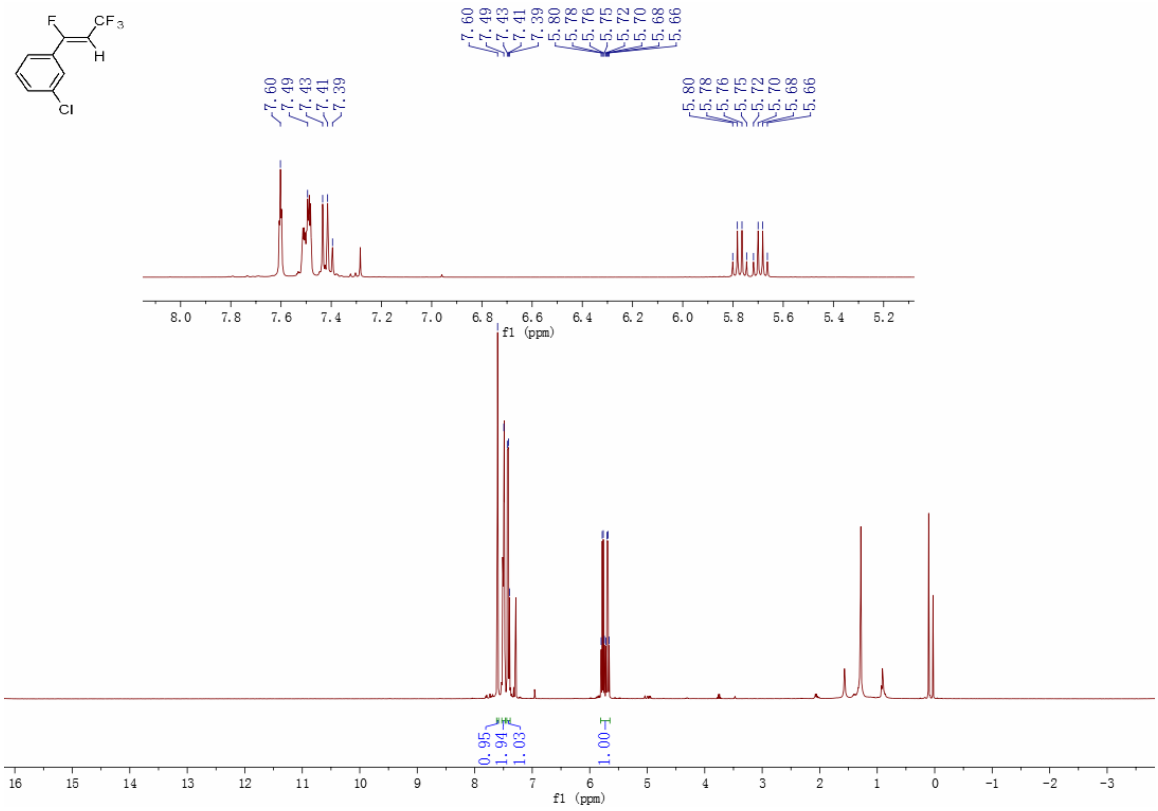
(Z)-1-methyl-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3k**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

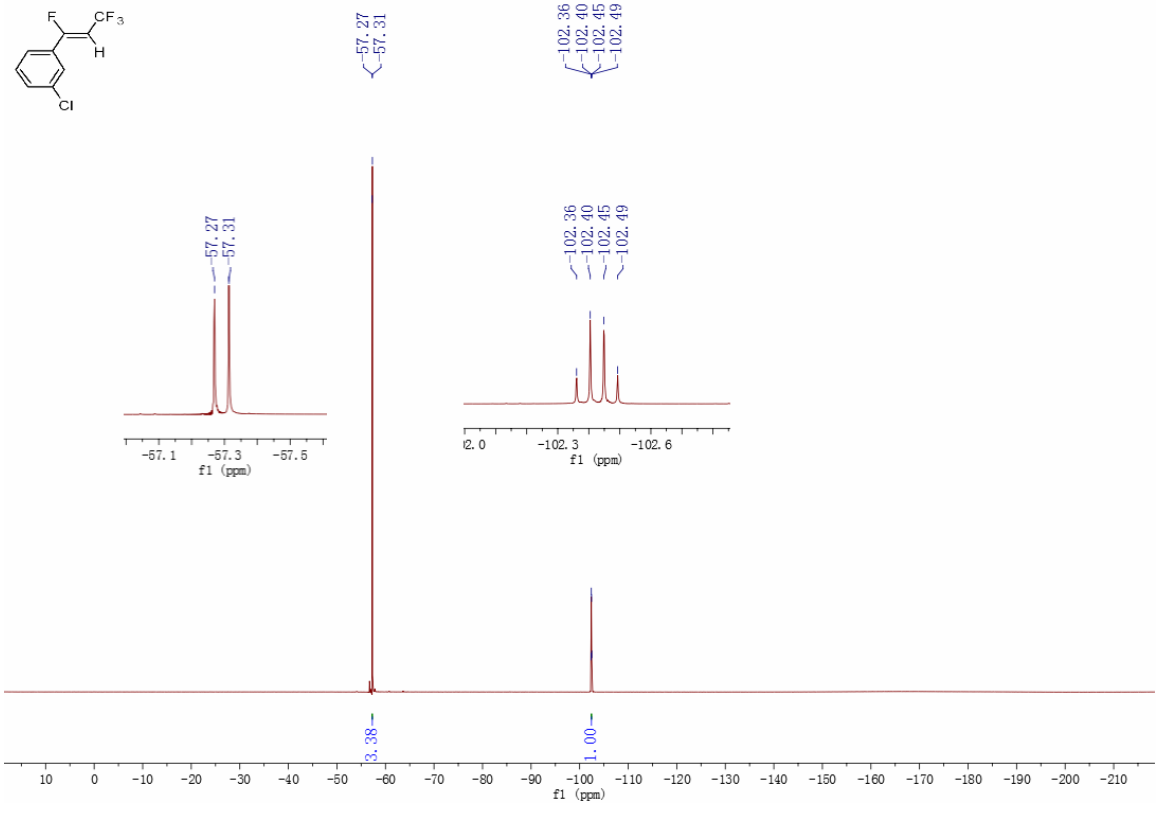


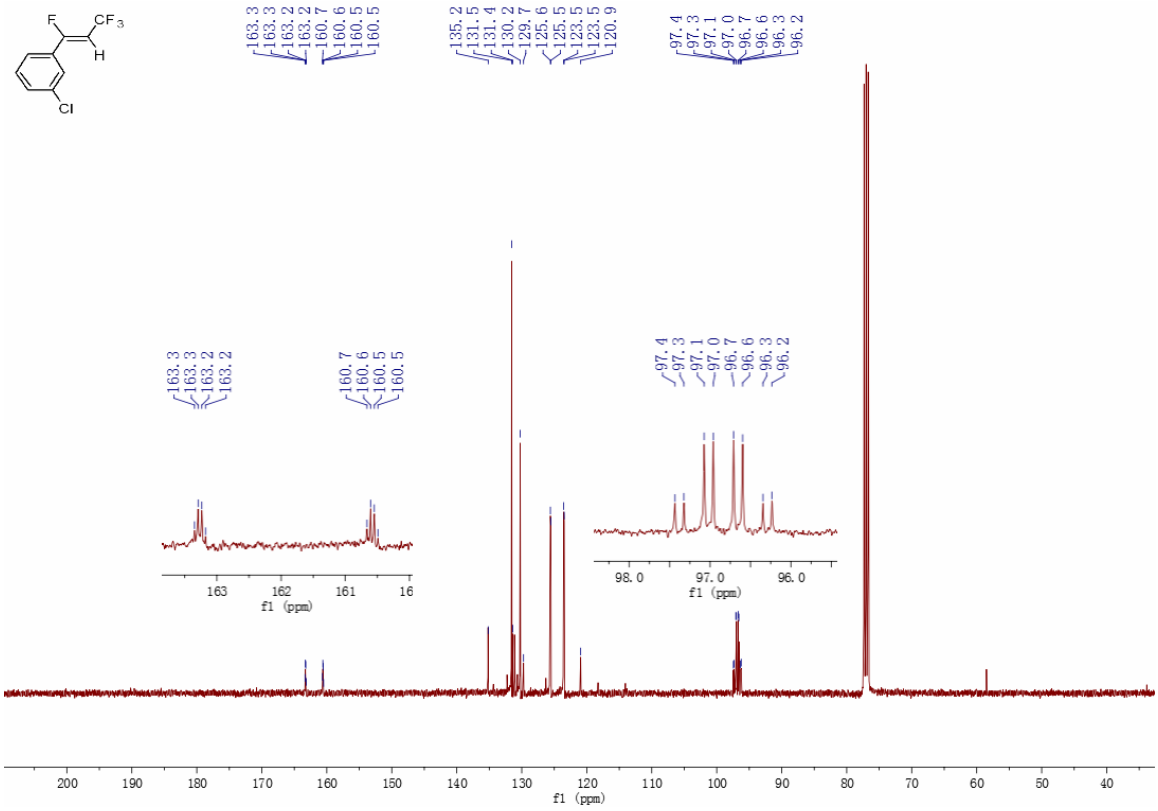



F
CF3
H
165.0
164.9
164.9
164.8
162.3
162.3
162.2
162.2
138.8
132.3
129.6
129.4
128.8
128.8
126.0
125.9
124.0
122.6
96.0
95.9
95.7
95.6
95.3
95.2
94.9
94.8
21.3
f1 (ppm)
f1 (ppm)
f1 (ppm)

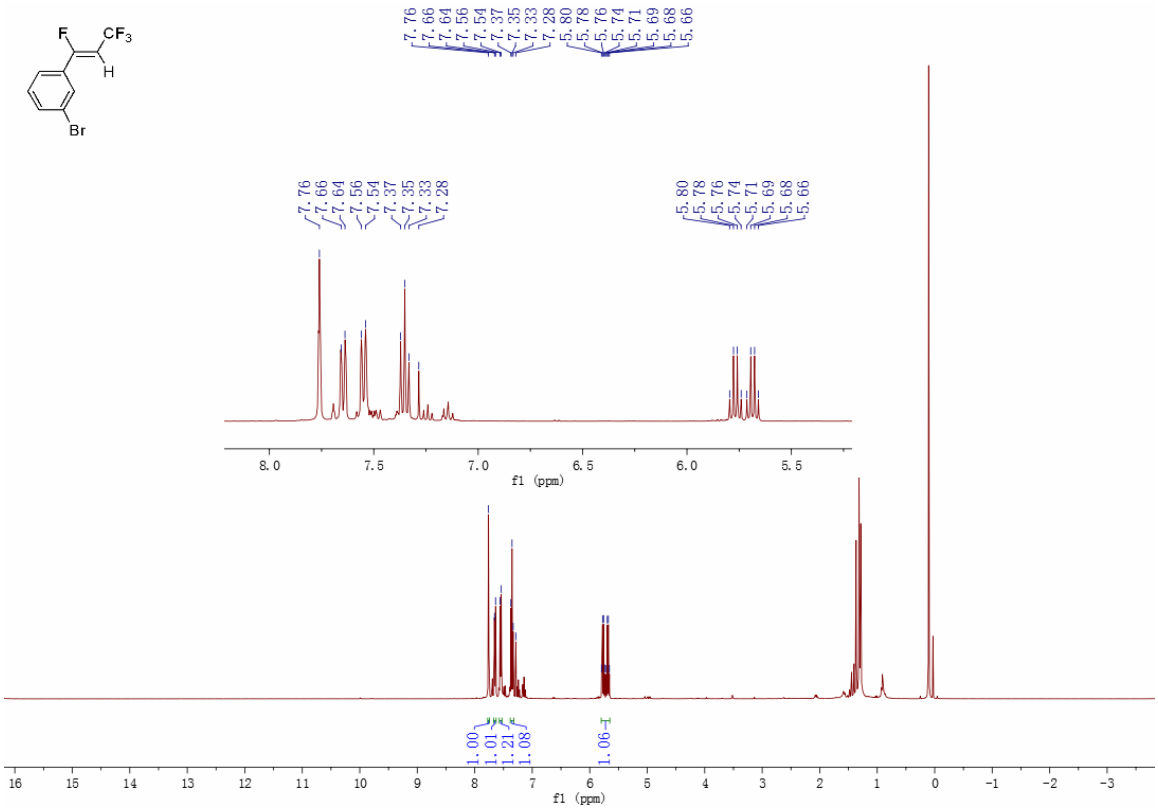
(Z)-1-chloro-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3l**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

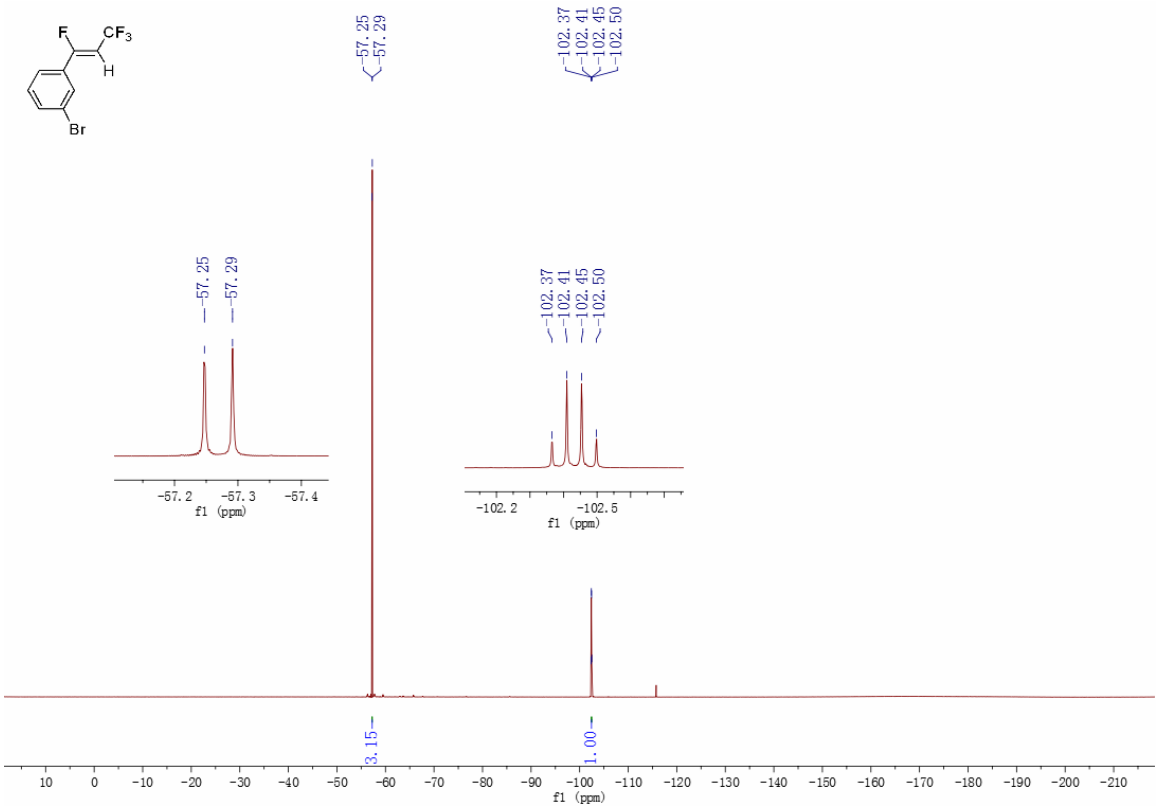


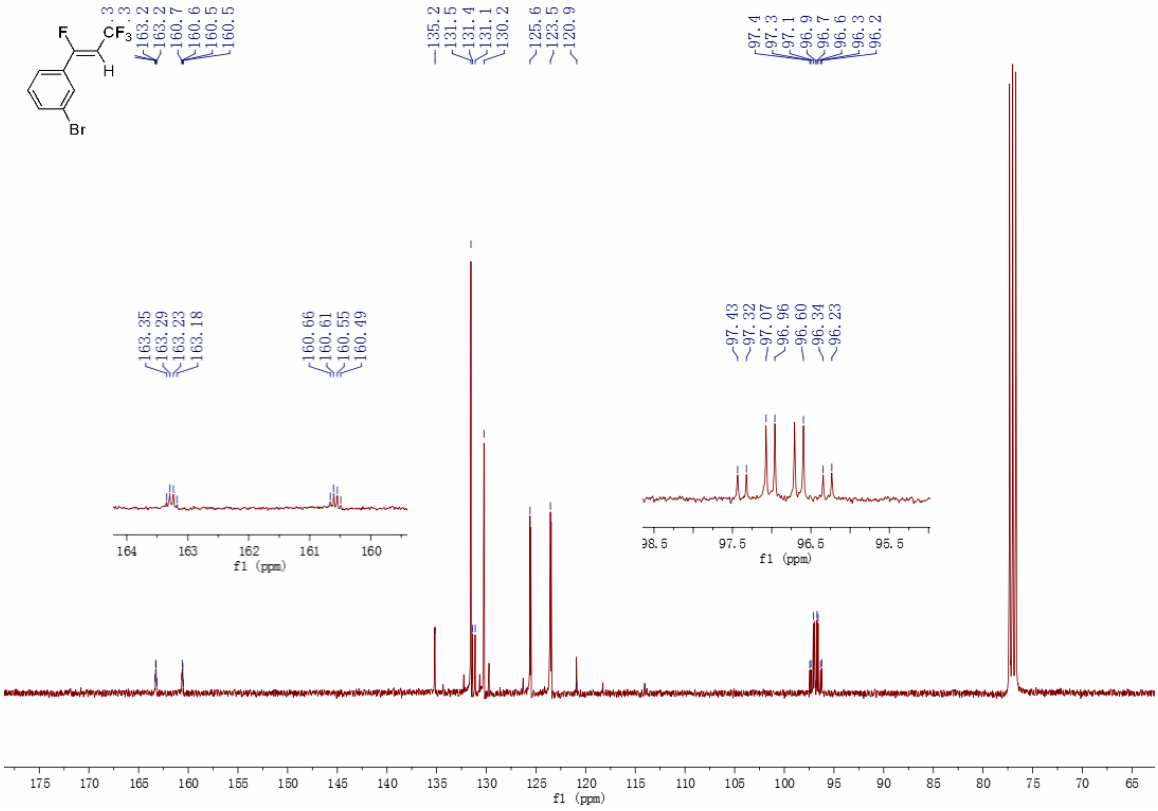



F
CF3
H
Cl
163.3
163.3
163.2
163.2
160.7
160.6
160.5
160.5
135.2
131.5
131.4
130.2
129.7
125.6
125.5
123.5
123.5
120.9
97.4
97.3
97.1
97.0
96.7
96.6
96.3
96.2
f1 (ppm)
f1 (ppm)
f1 (ppm)

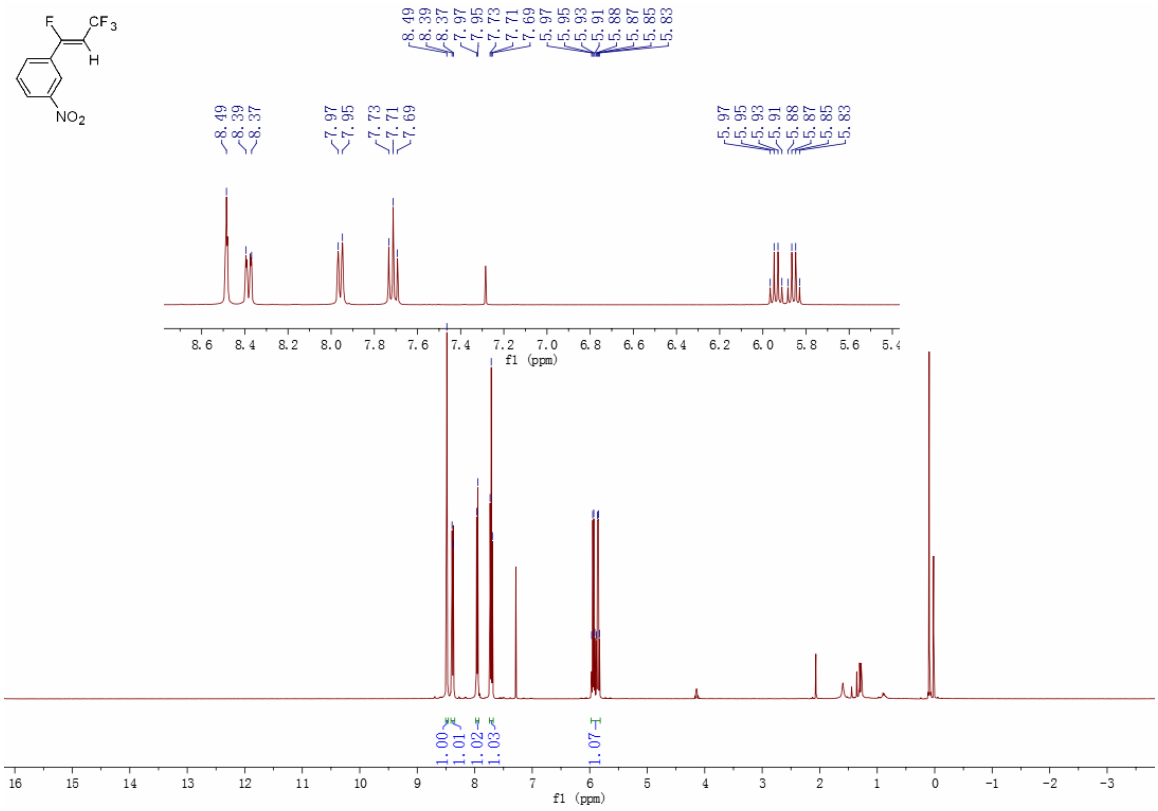
(Z)-1-bromo-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3m**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

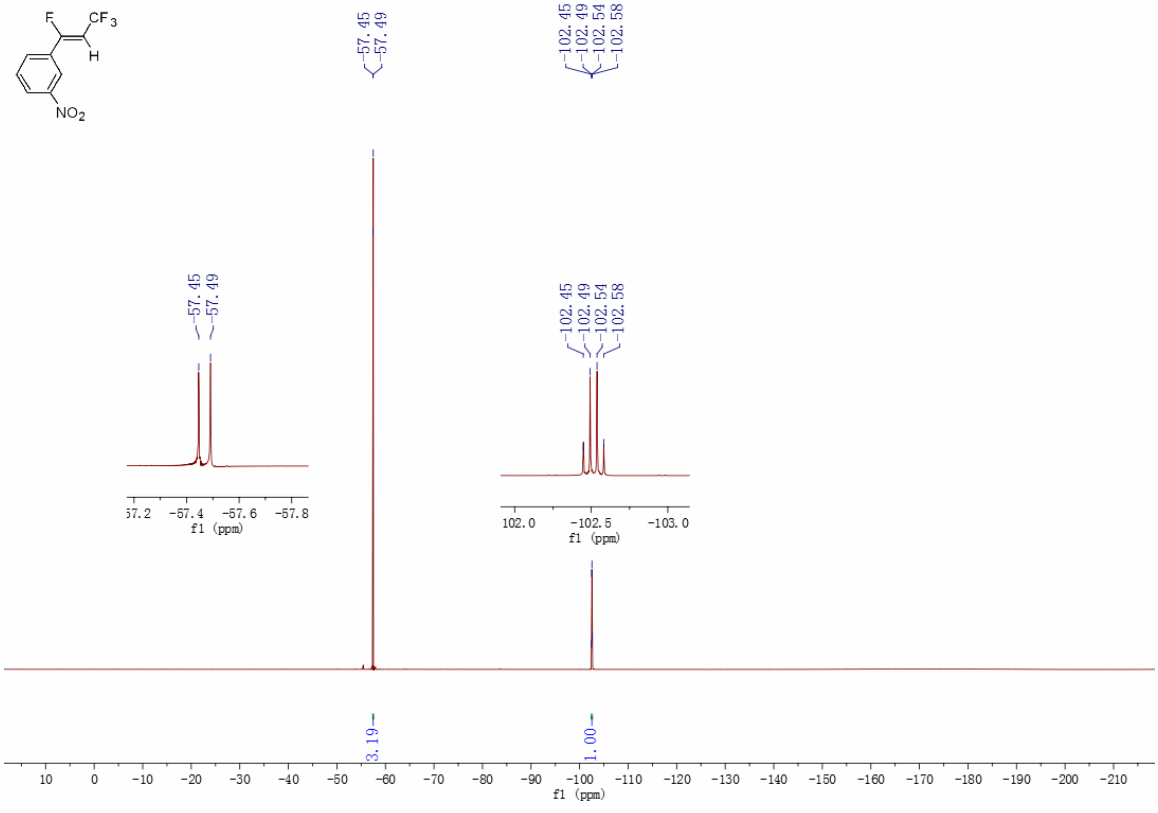


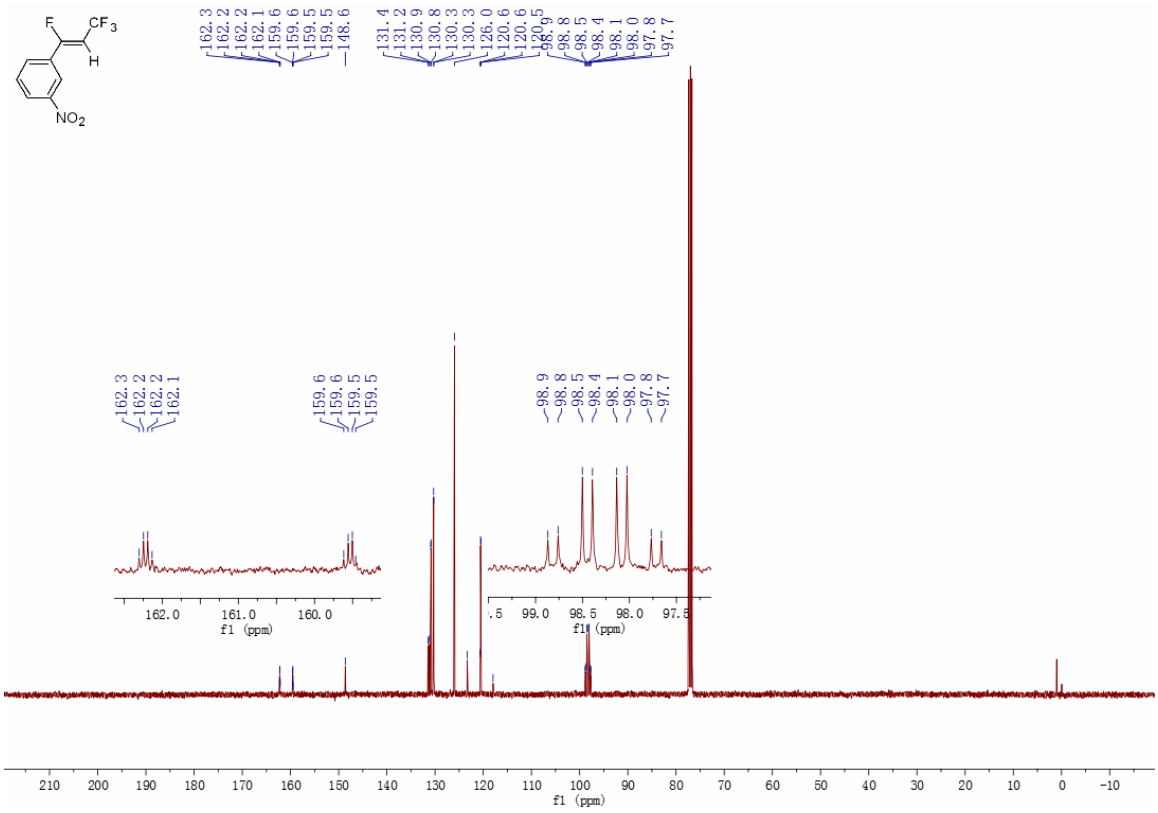



F
CF3
H
Br
163.3
163.2
163.2
160.7
160.6
160.5
160.5
135.2
131.5
131.4
131.1
130.2
125.6
123.5
120.9
97.4
97.3
97.1
96.9
96.7
96.6
96.3
96.2
163.35
163.29
163.23
163.18
160.66
160.61
160.55
160.49
97.43
97.32
97.07
96.96
96.60
96.34
96.23
f1 (ppm)
f1 (ppm)
f1 (ppm)

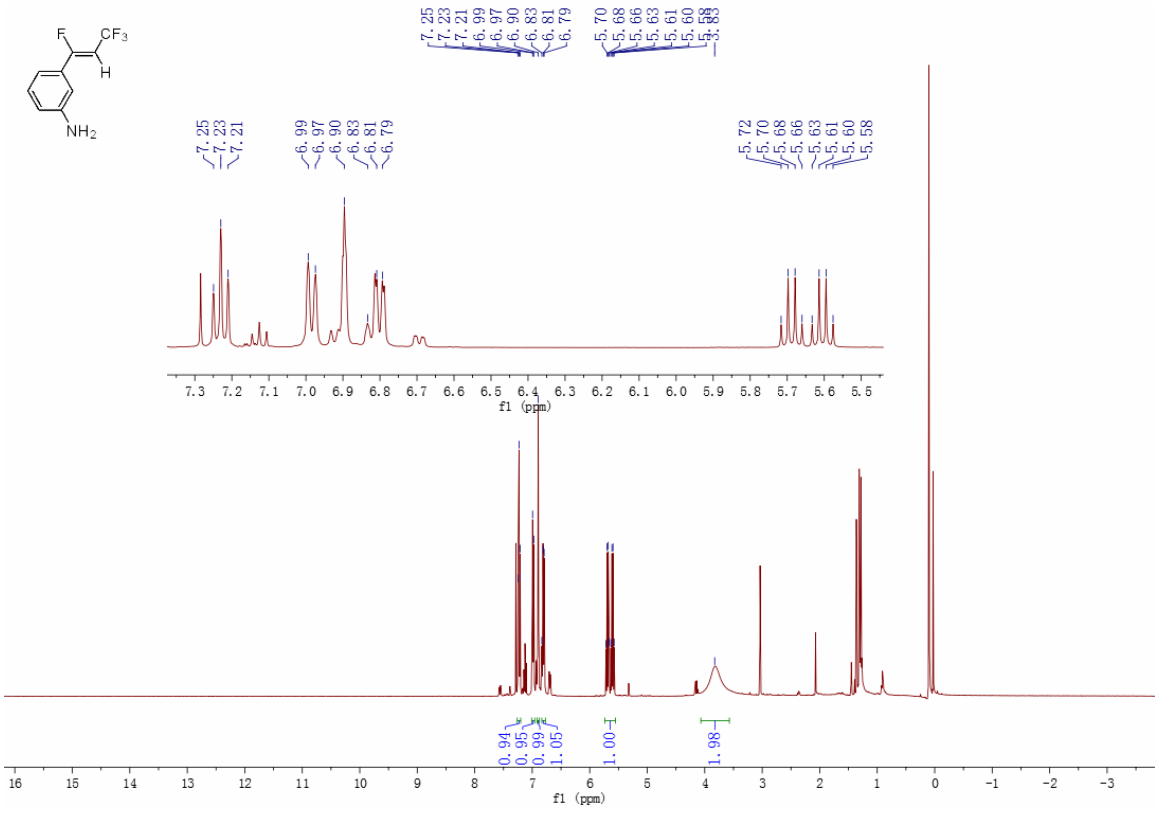
(Z)-1-nitro-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3n**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

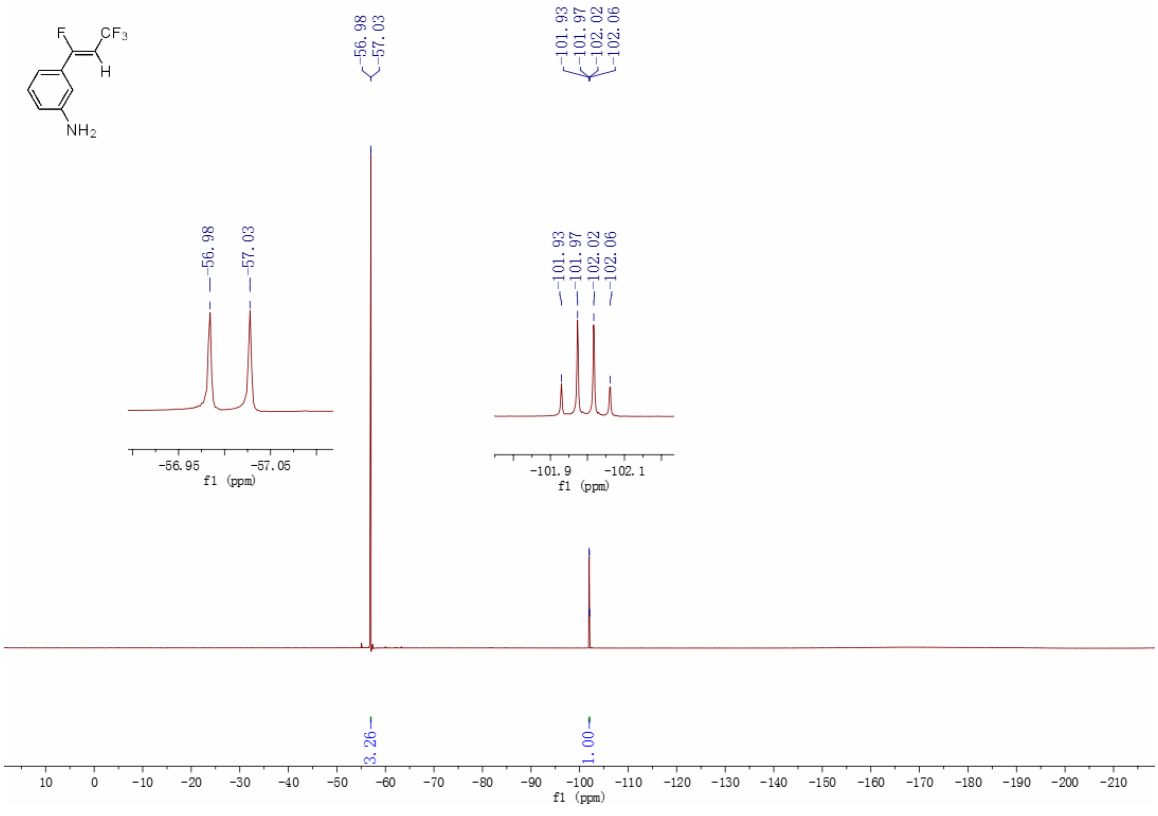


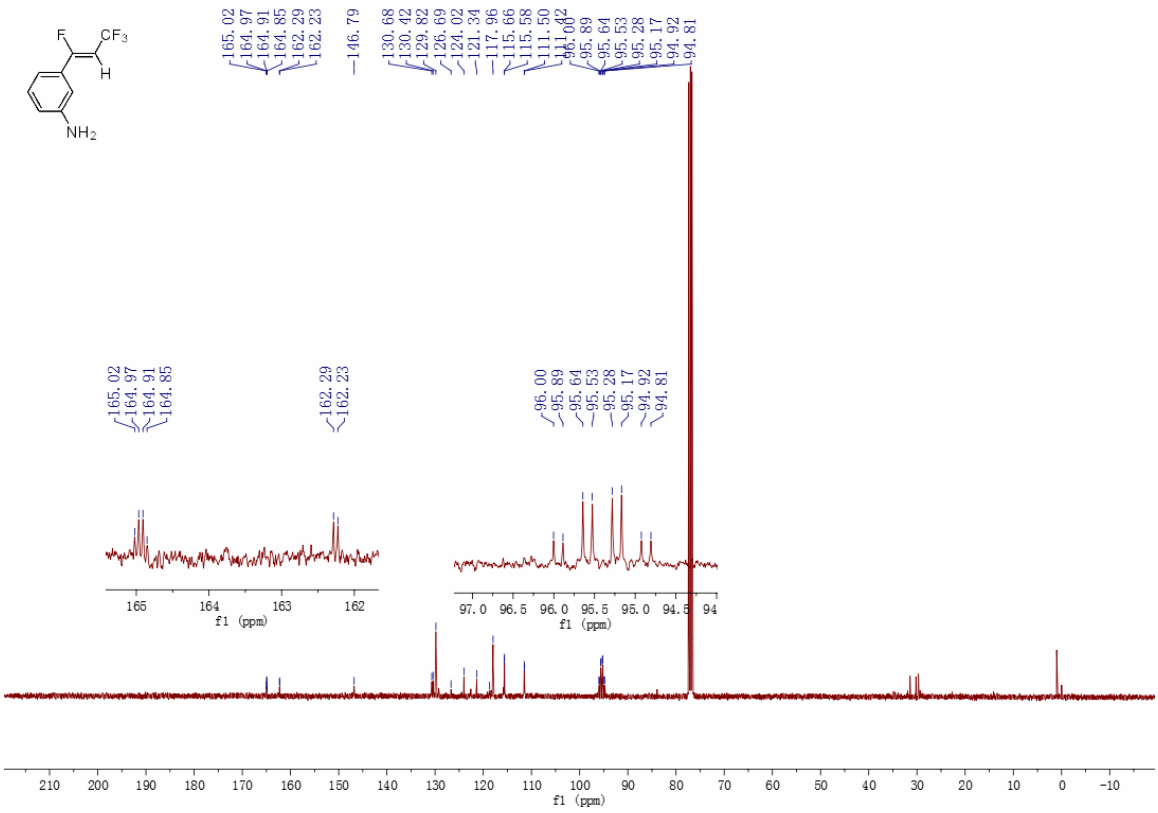



F
CF3
H
NO2
162.3
162.2
162.2
162.1
159.6
159.5
159.5
148.6
131.4
131.2
130.9
130.8
130.3
130.3
126.0
120.6
120.6
98.9
98.8
98.5
98.4
98.1
98.0
97.8
97.7
f1 (ppm)

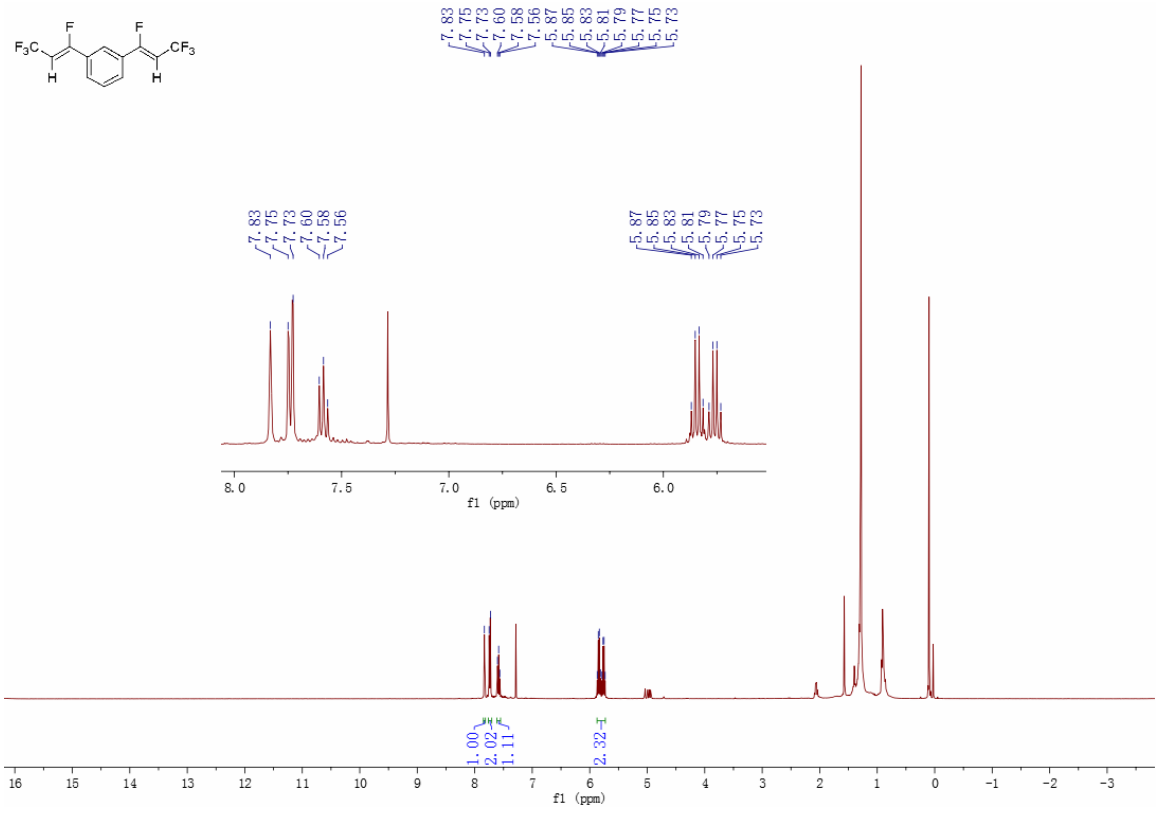
(Z)-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)aniline (3o. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

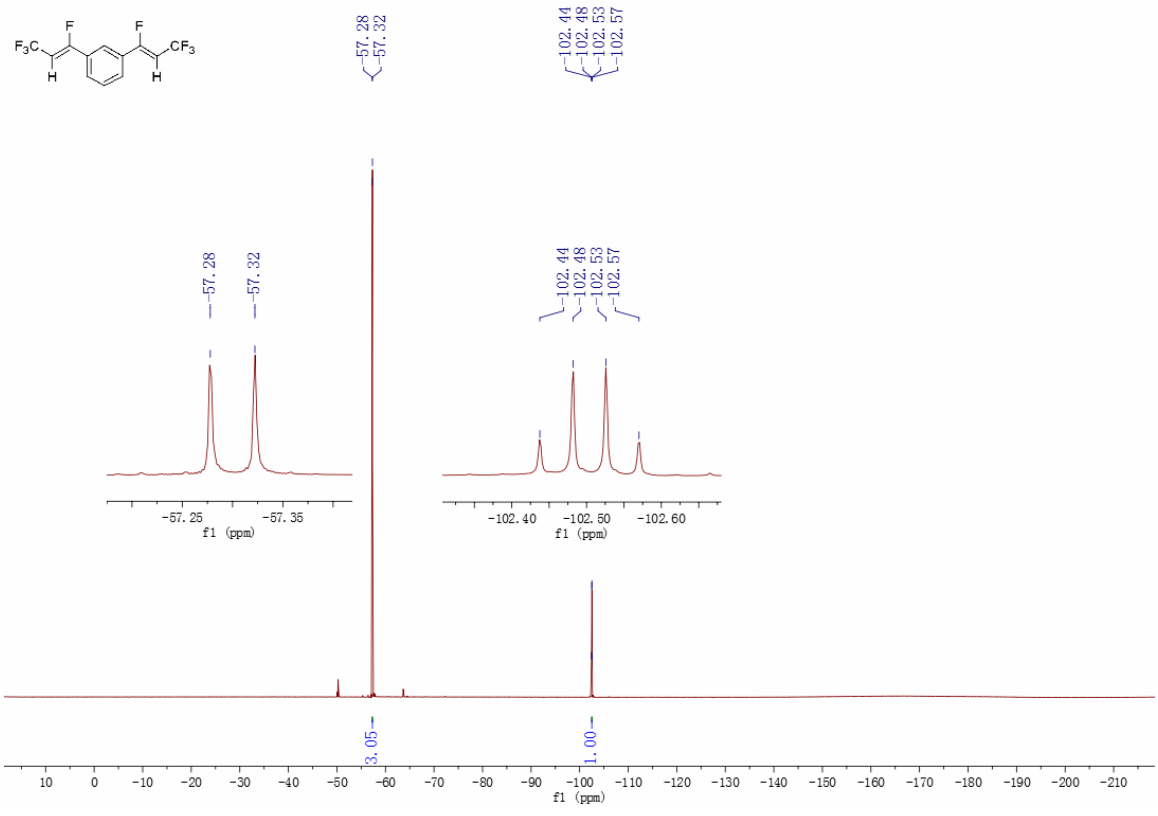


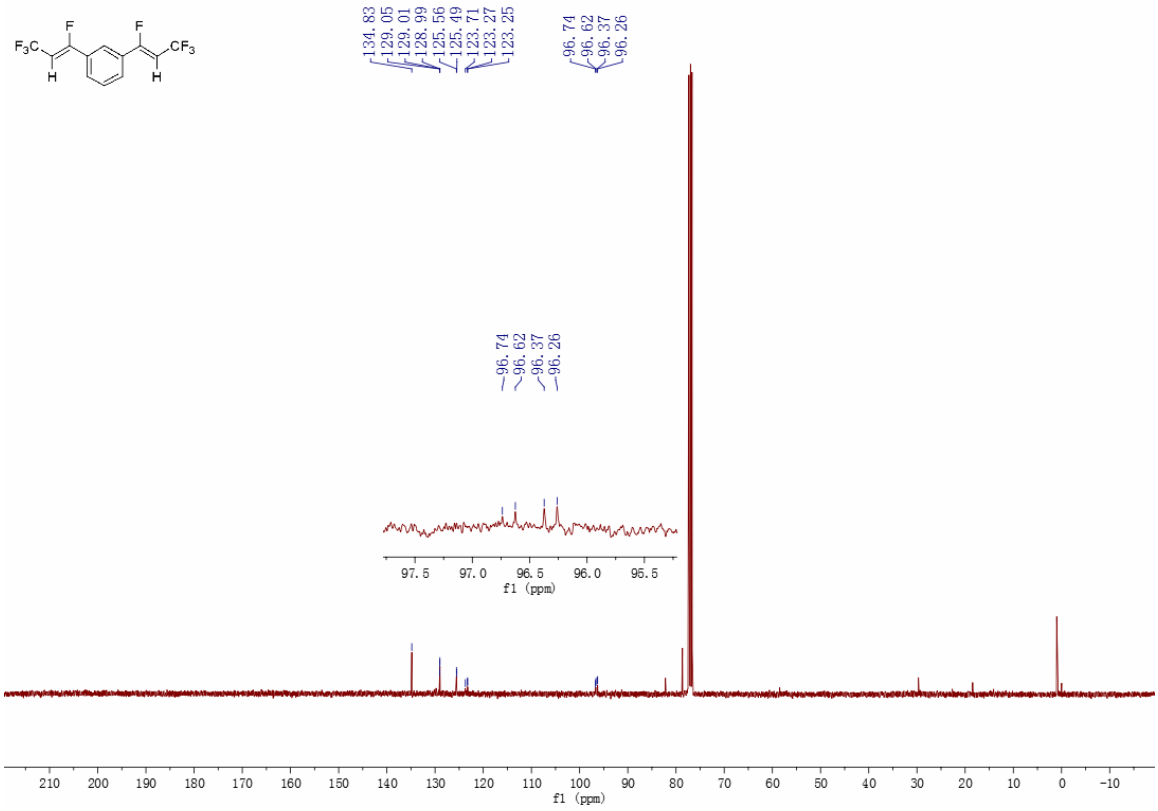



F
CF3
H
NH2
165.02
164.97
164.91
164.85
162.29
162.23
146.79
130.68
130.42
129.82
126.69
124.02
121.34
117.96
115.66
115.58
111.50
111.42
96.00
95.89
95.64
95.53
95.28
95.17
94.92
94.81
f1 (ppm)

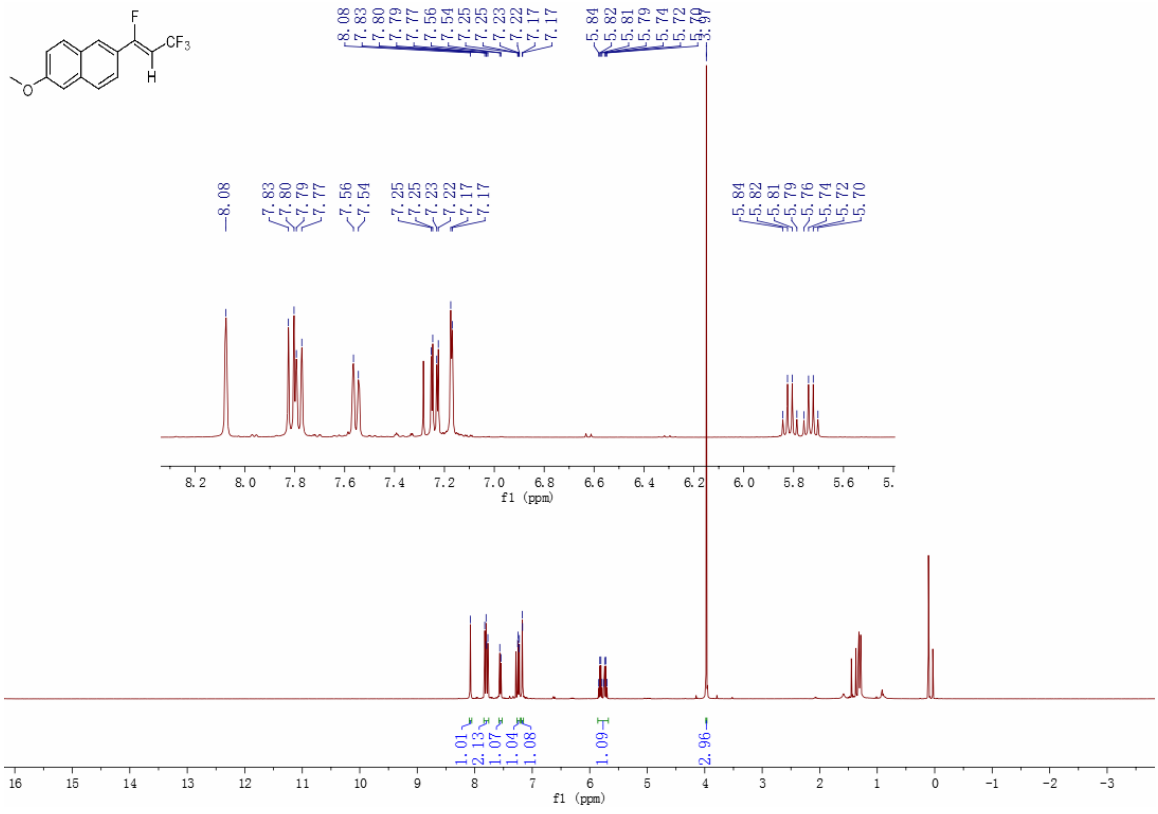
1,3-bis((Z)-1,3,3,3-tetrafluoroprop-1-en-1-yl)benzene (**3q**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

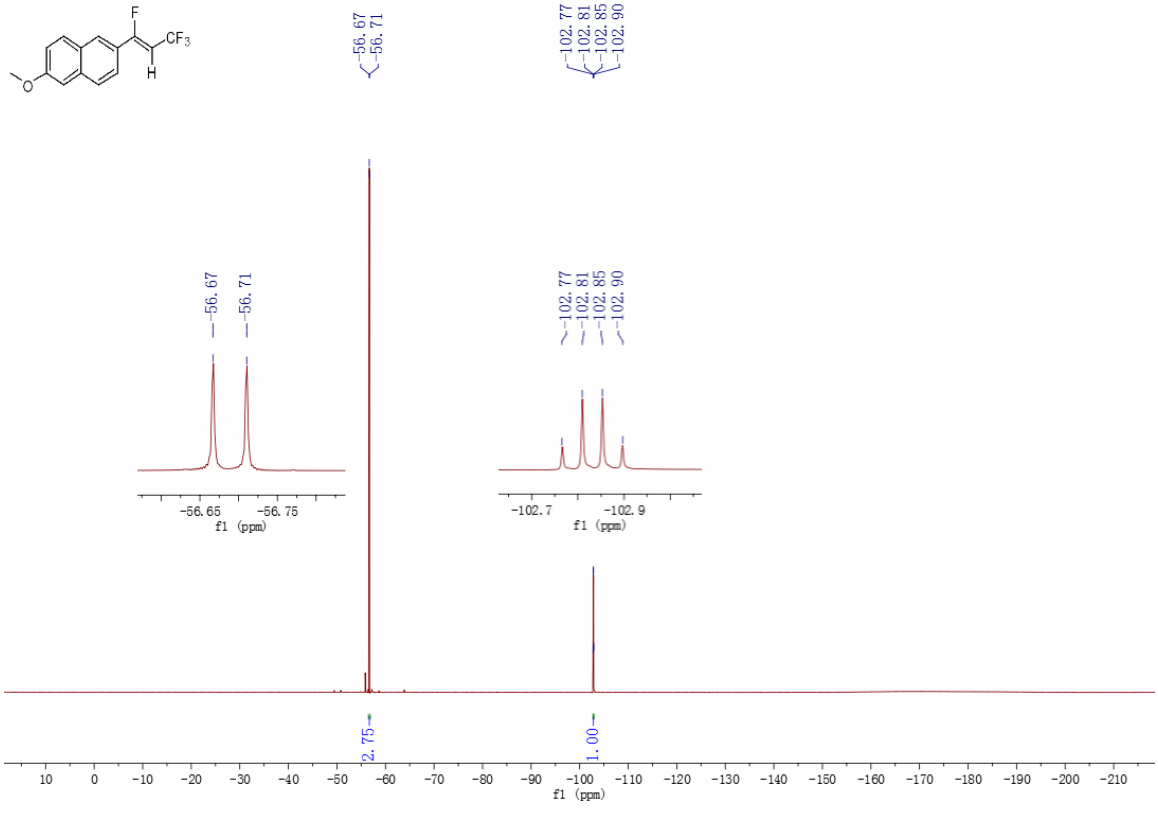


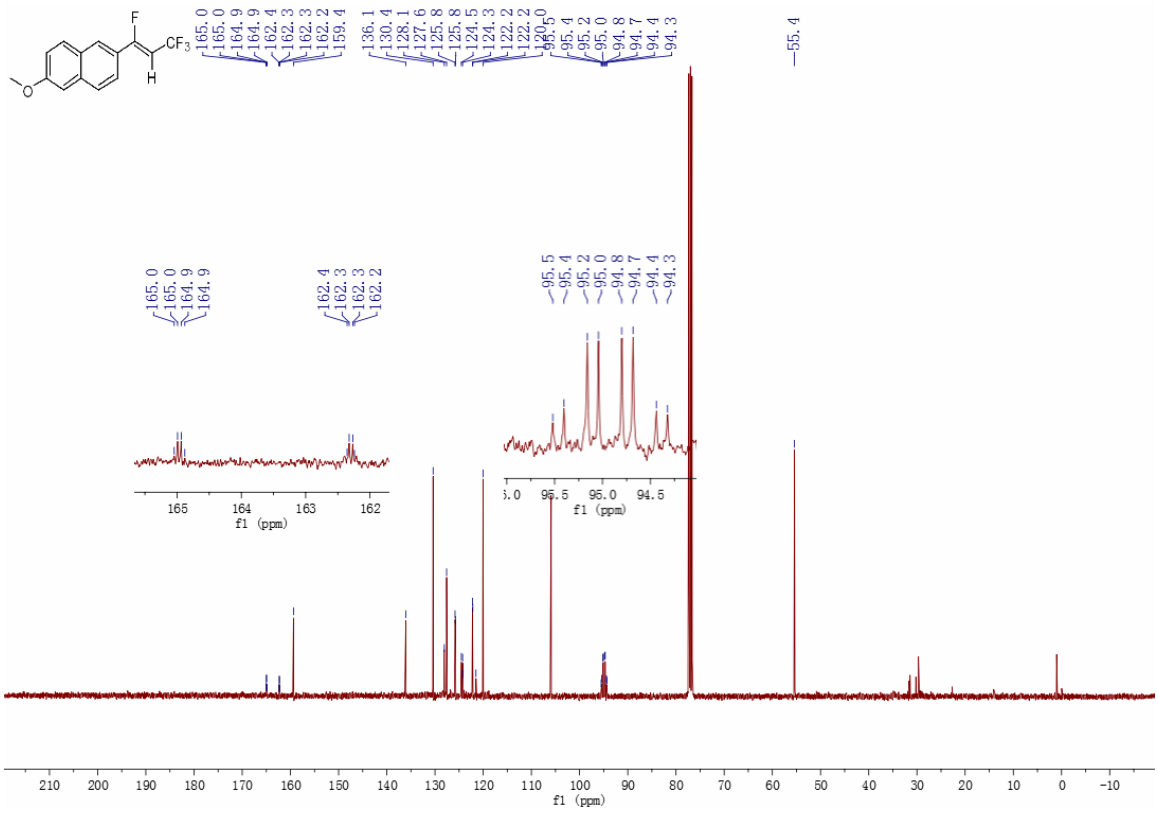



F
F
F3C
CF3
H
H
134.83
129.05
129.01
128.99
125.56
125.49
123.71
123.27
123.25
96.74
96.62
96.37
96.26
96.74
96.62
96.37
96.26
97.5
97.0
96.5
96.0
95.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

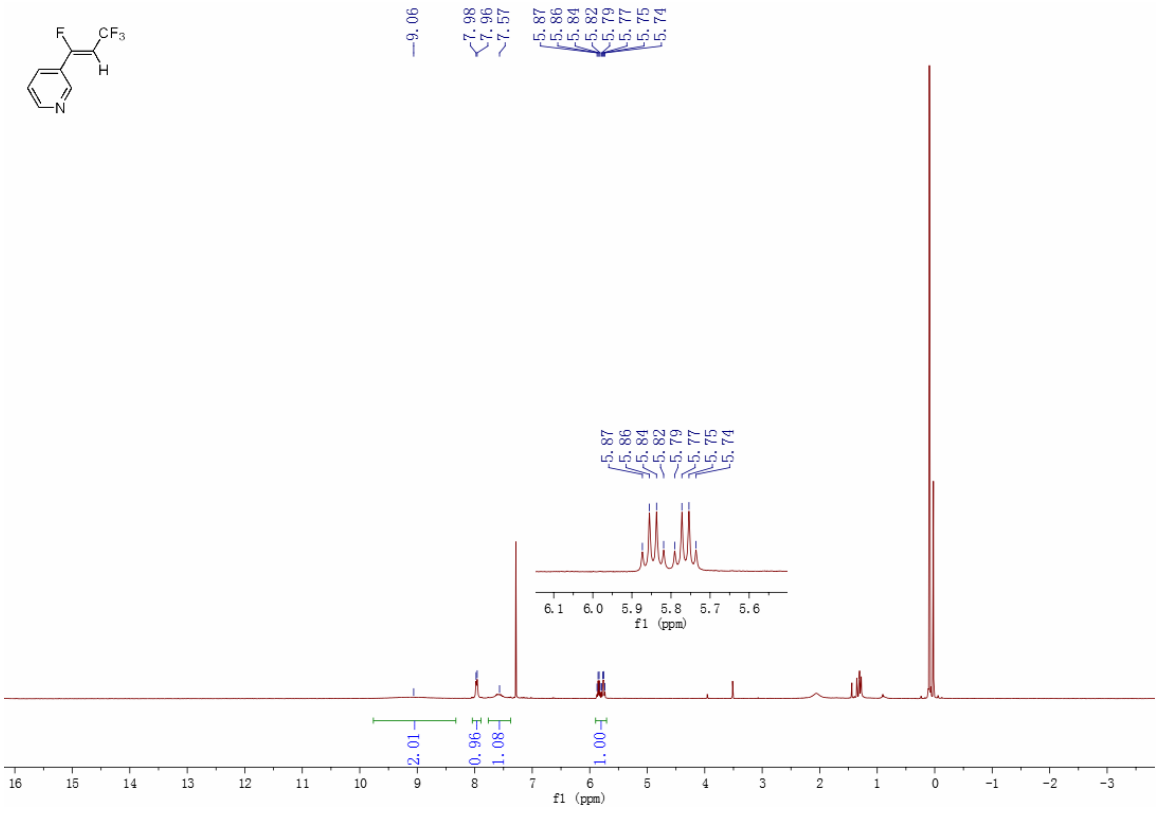
(Z)-2-methoxy-6-(1,3,3,3-tetrafluoroprop-1-en-1-yl)naphthalene (**3r**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

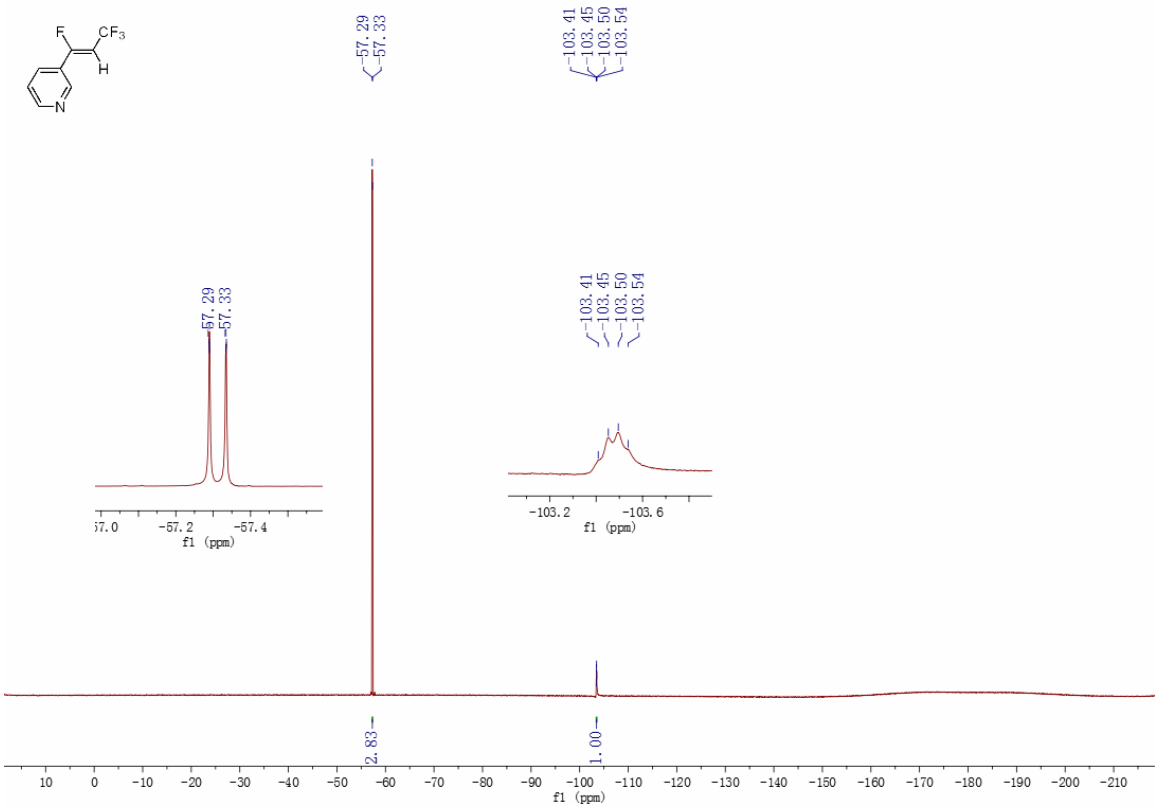




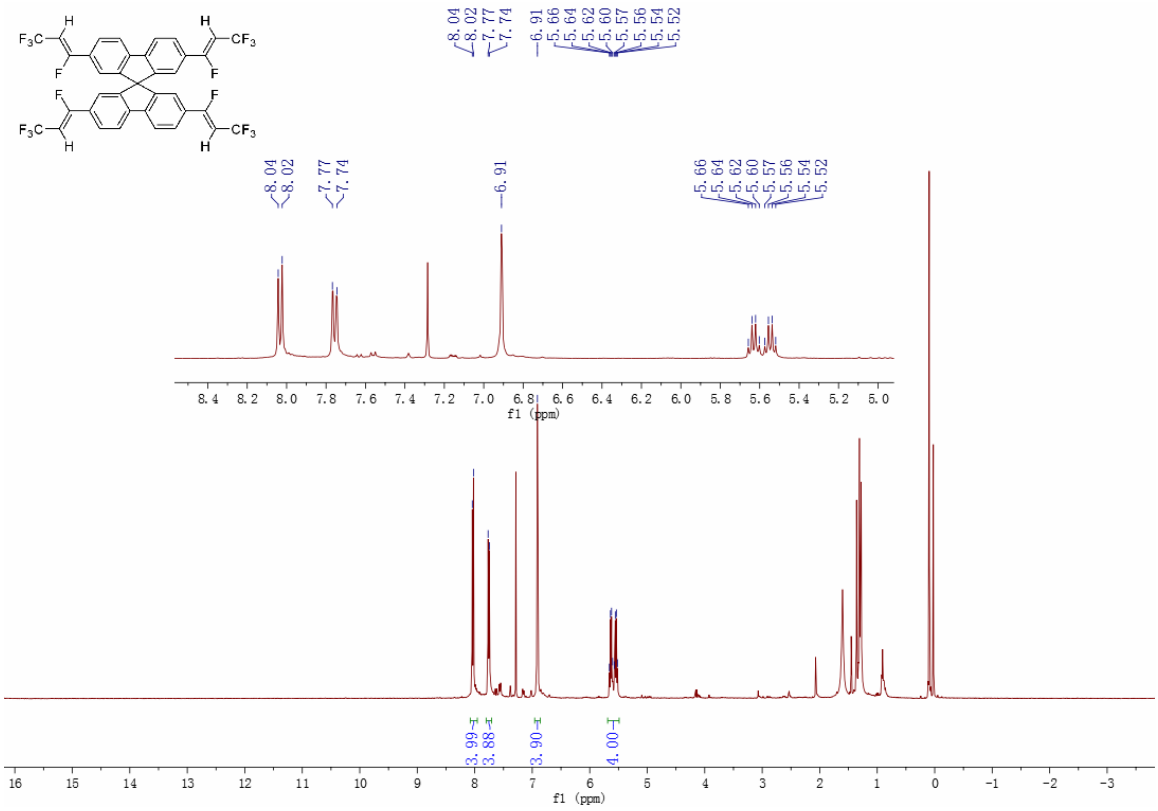

F
CF3
H
O
165.0
165.0
164.9
164.9
162.4
162.3
162.3
162.2
159.4
136.1
130.4
128.1
127.6
125.8
125.8
124.5
124.3
122.2
122.2
120.0
95.5
95.4
95.2
95.0
94.8
94.7
94.4
94.3
55.4
f1 (ppm)
f1 (ppm)
f1 (ppm)

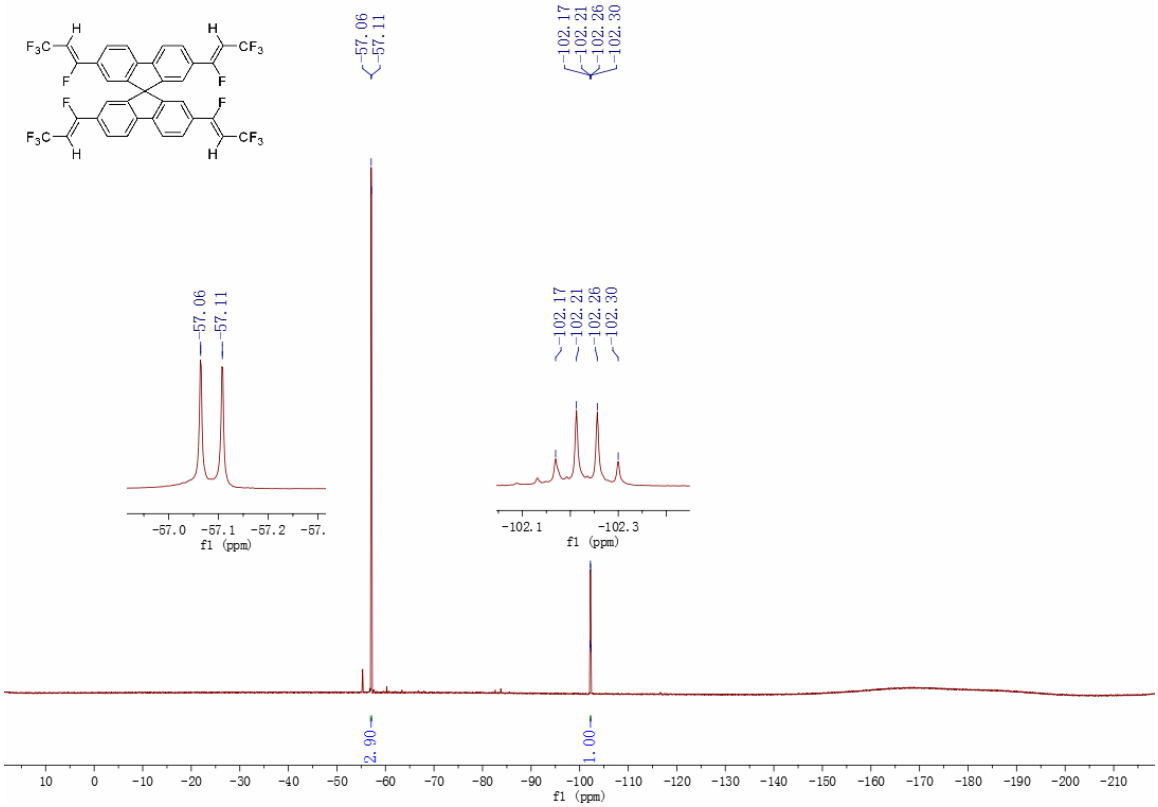
(Z)-3-(1,3,3,3-tetrafluoroprop-1-en-1-yl)pyridine (3s. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)





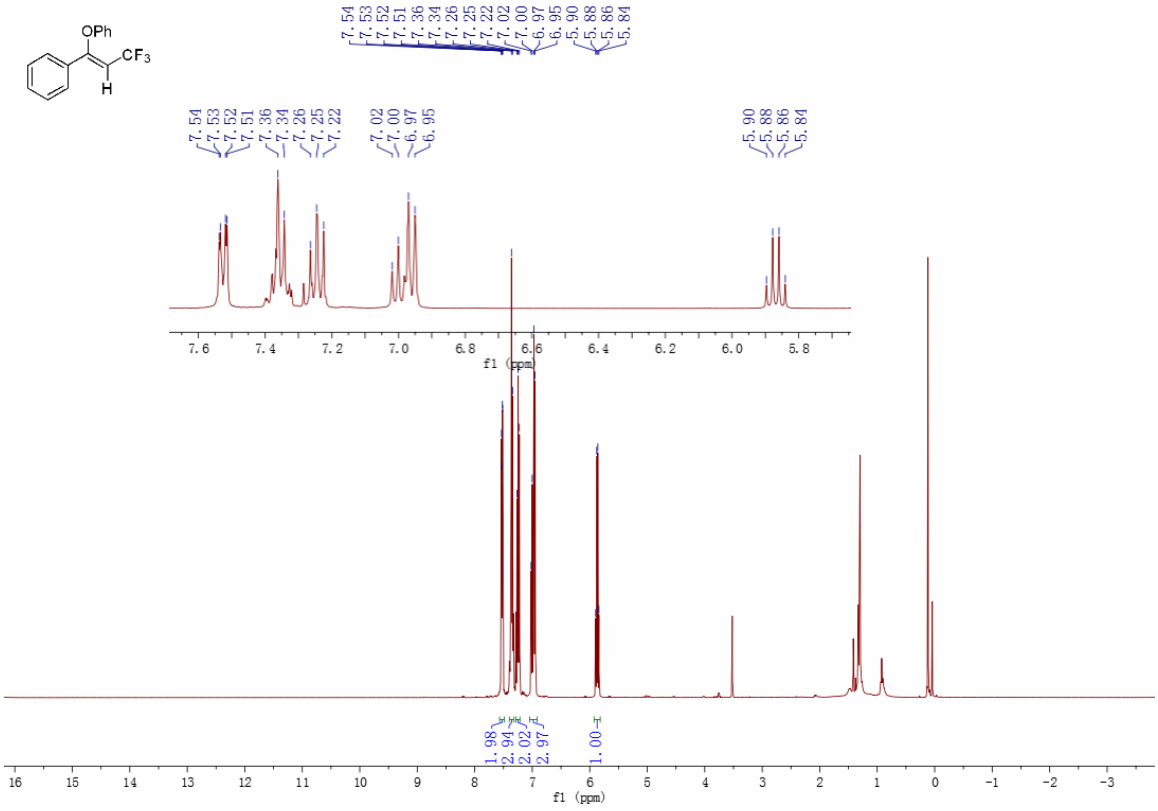
2,2',7,7'-tetrakis((Z)-1,3,3,3-tetrafluoroprop-1-en-1-yl)-9,9'-spirobi[fluorene] (**3u**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

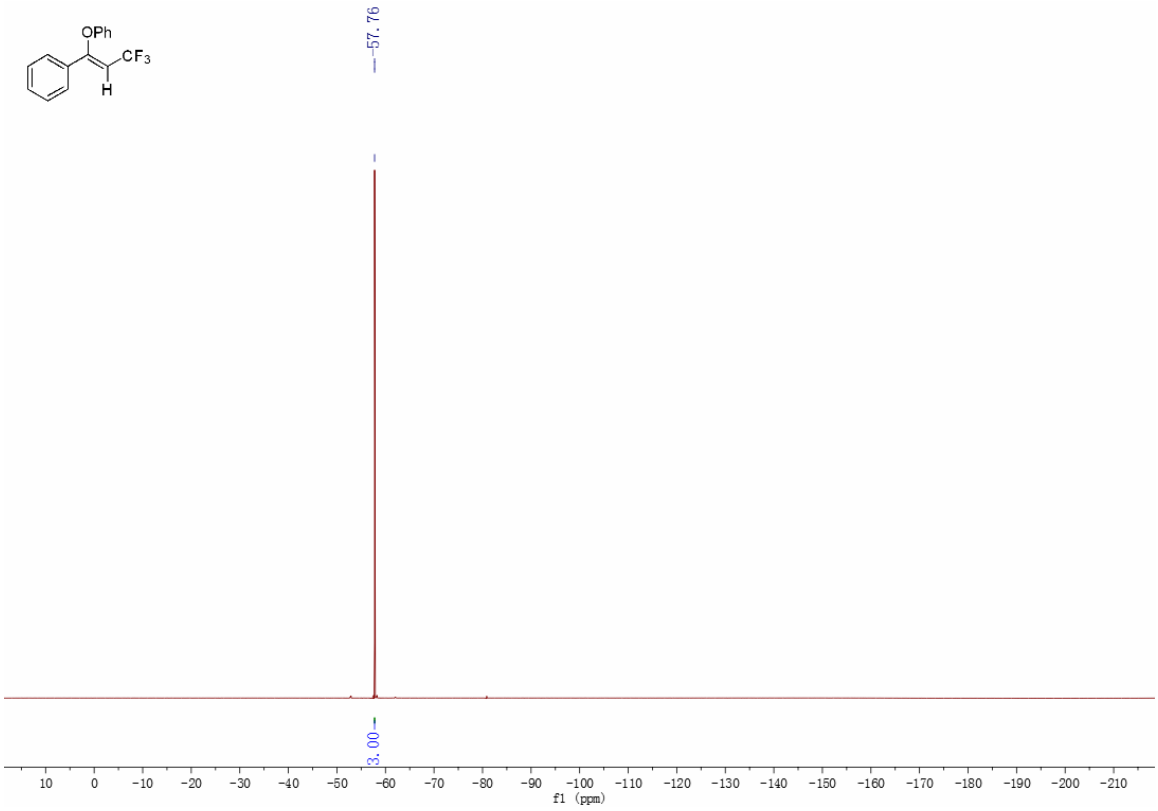


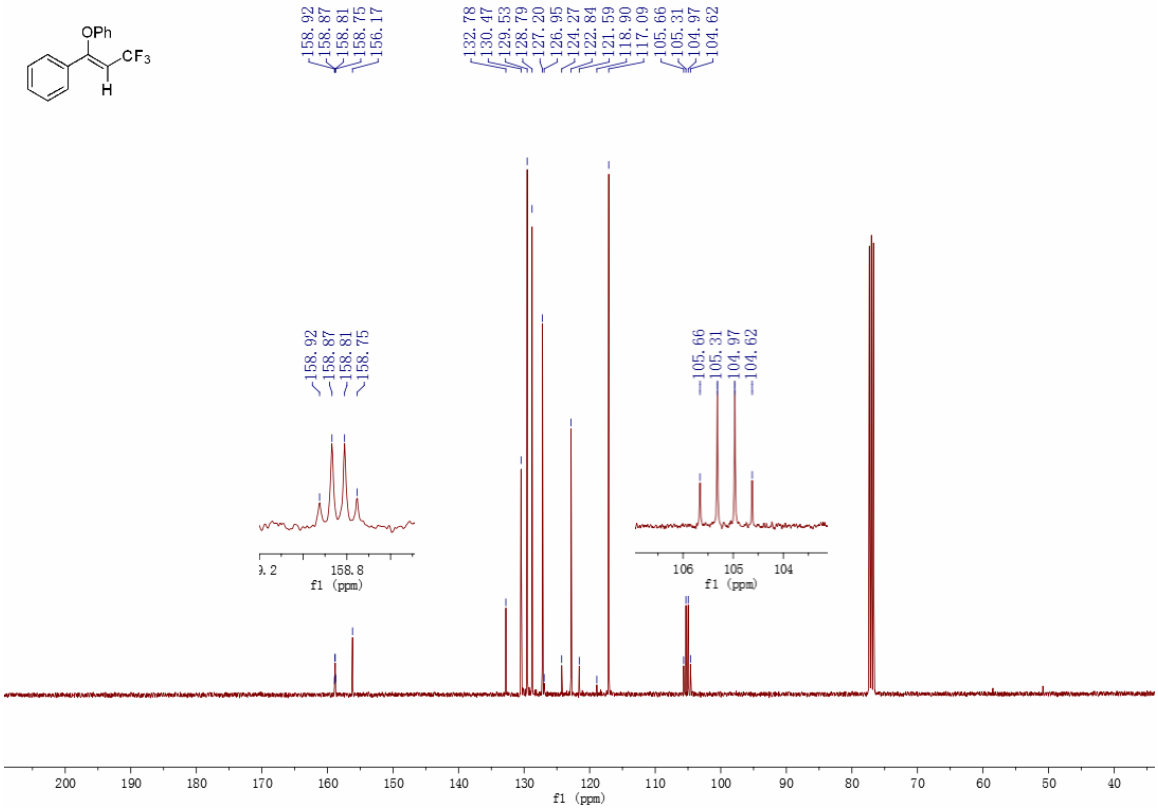


From here on, oxy-CF_3 products

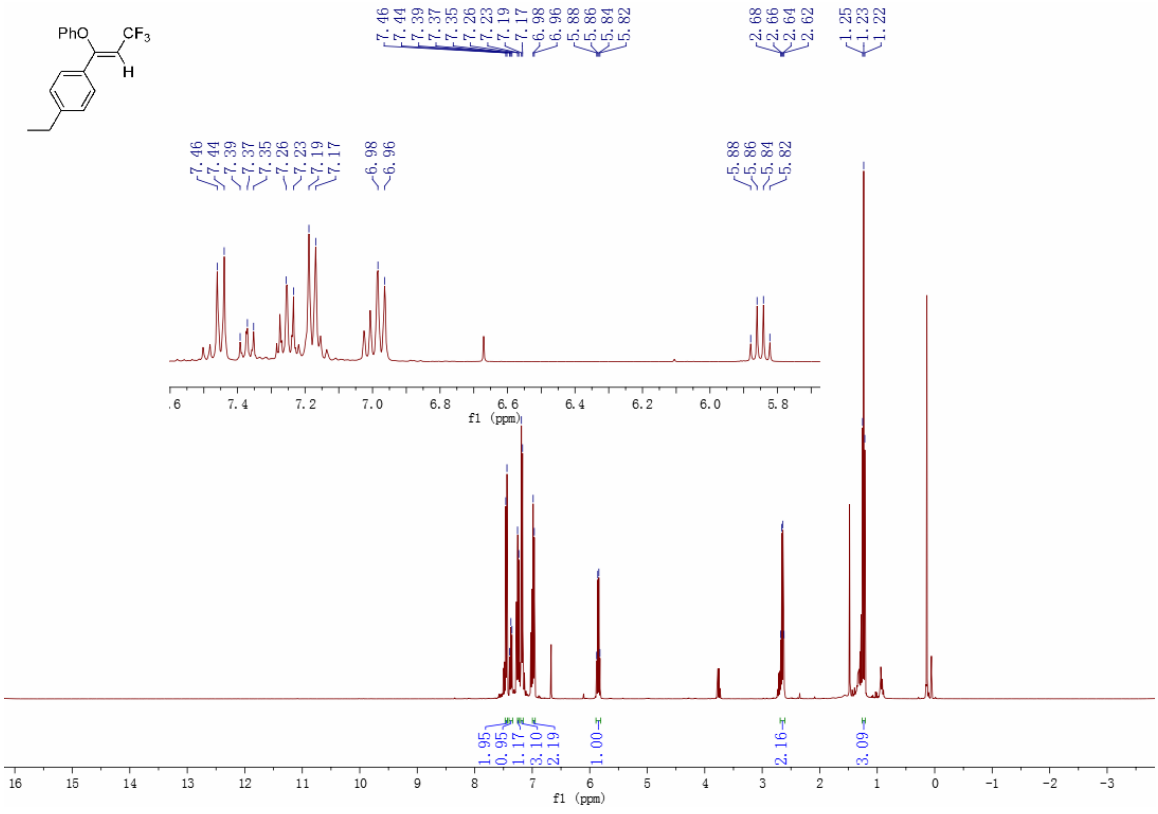
(Z)-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5a**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

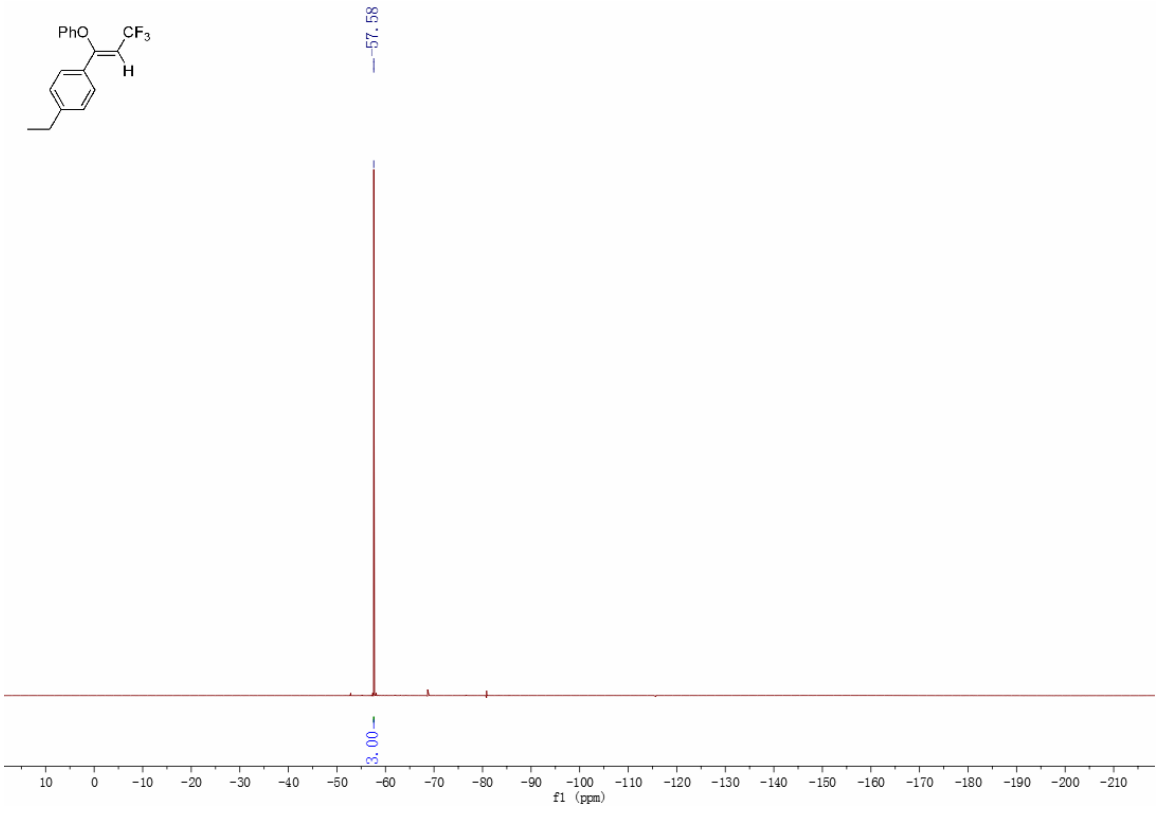


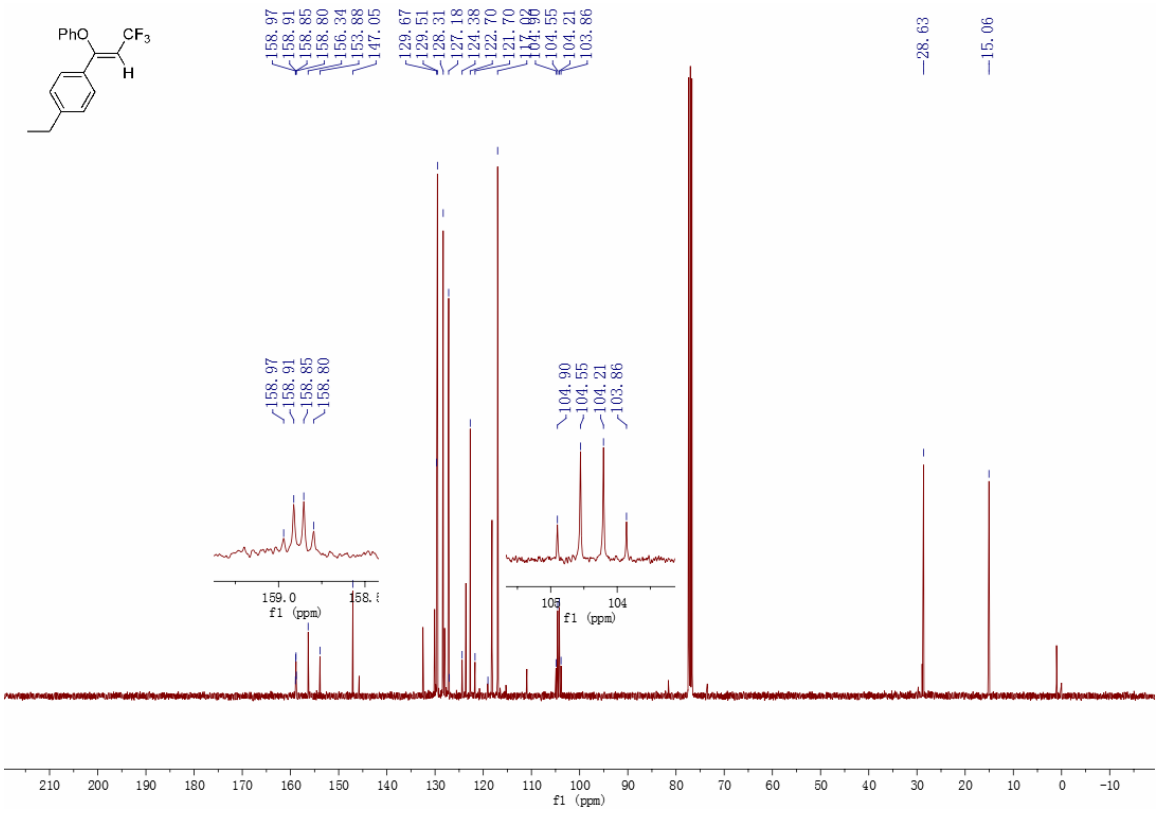



OPh
CF3
H
158.92
158.87
158.81
158.75
156.17
132.78
130.47
129.53
128.79
127.20
126.95
124.27
122.84
121.59
118.90
117.09
105.66
105.31
104.97
104.62
158.8
f1 (ppm)
106
105
104
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

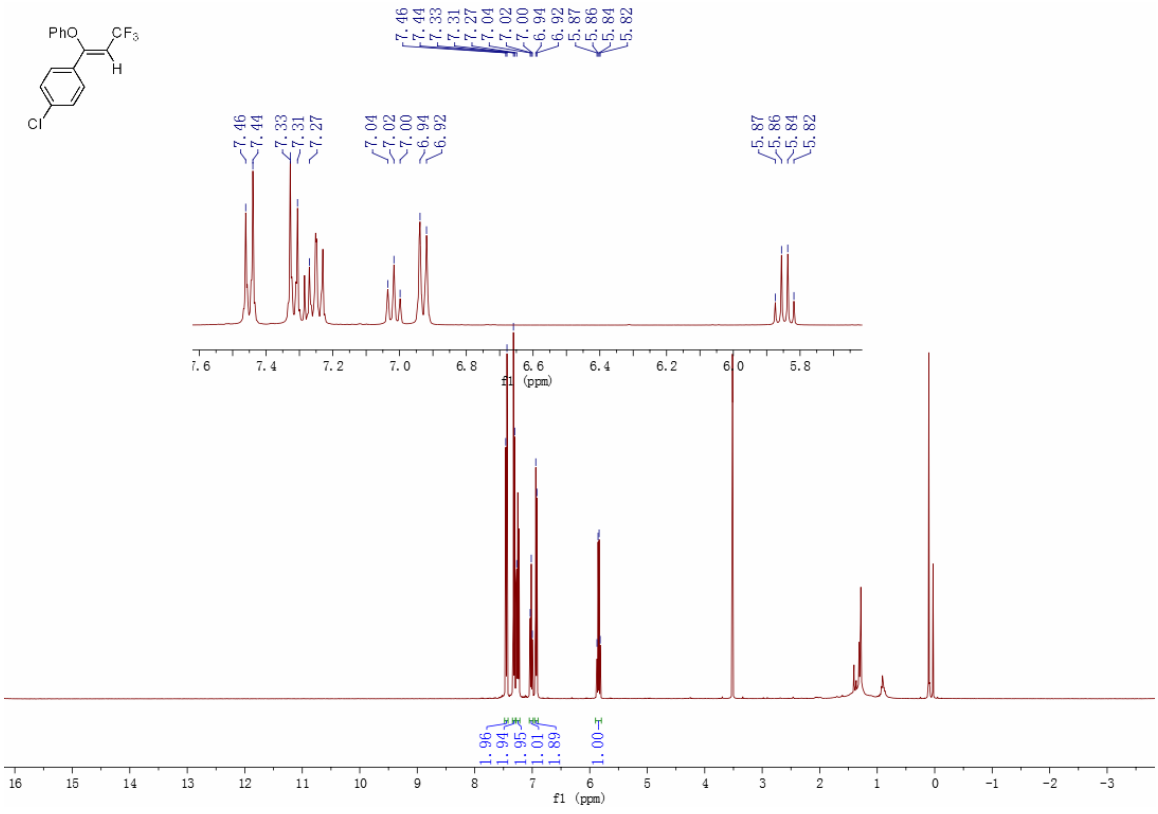
(Z)-1-ethyl-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5b**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

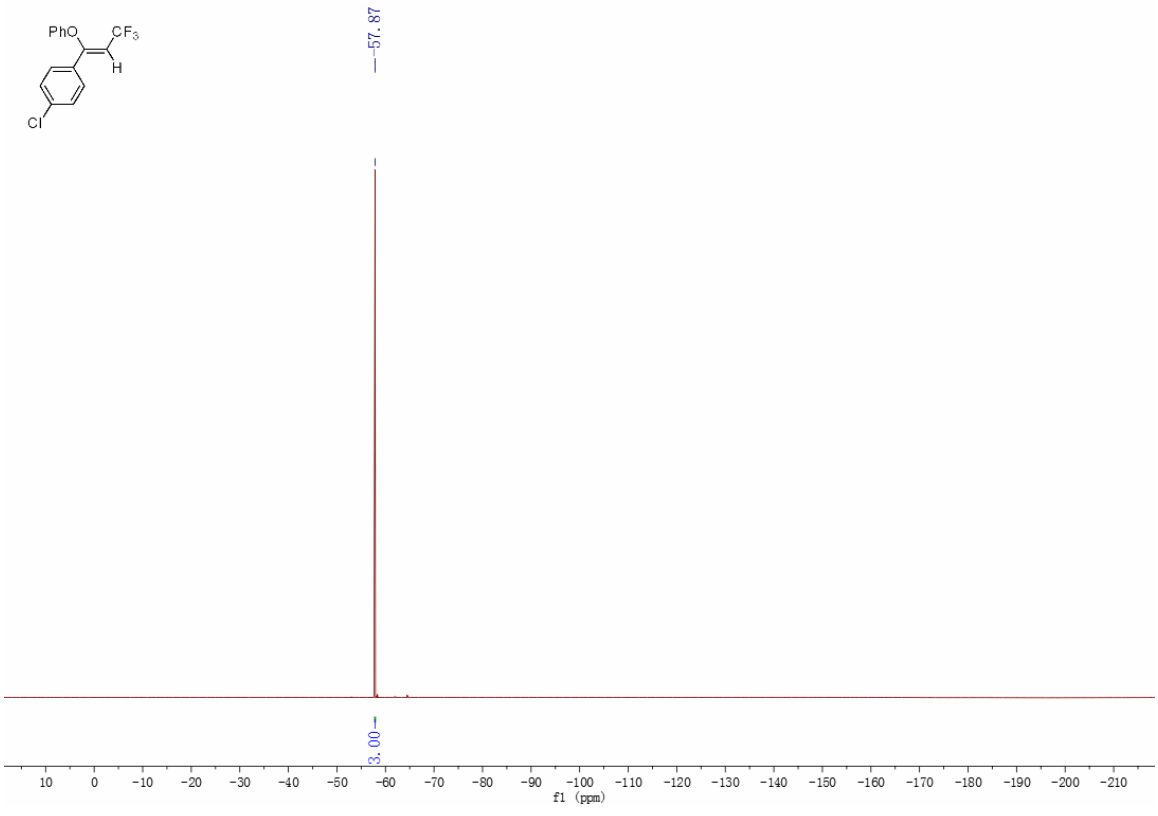


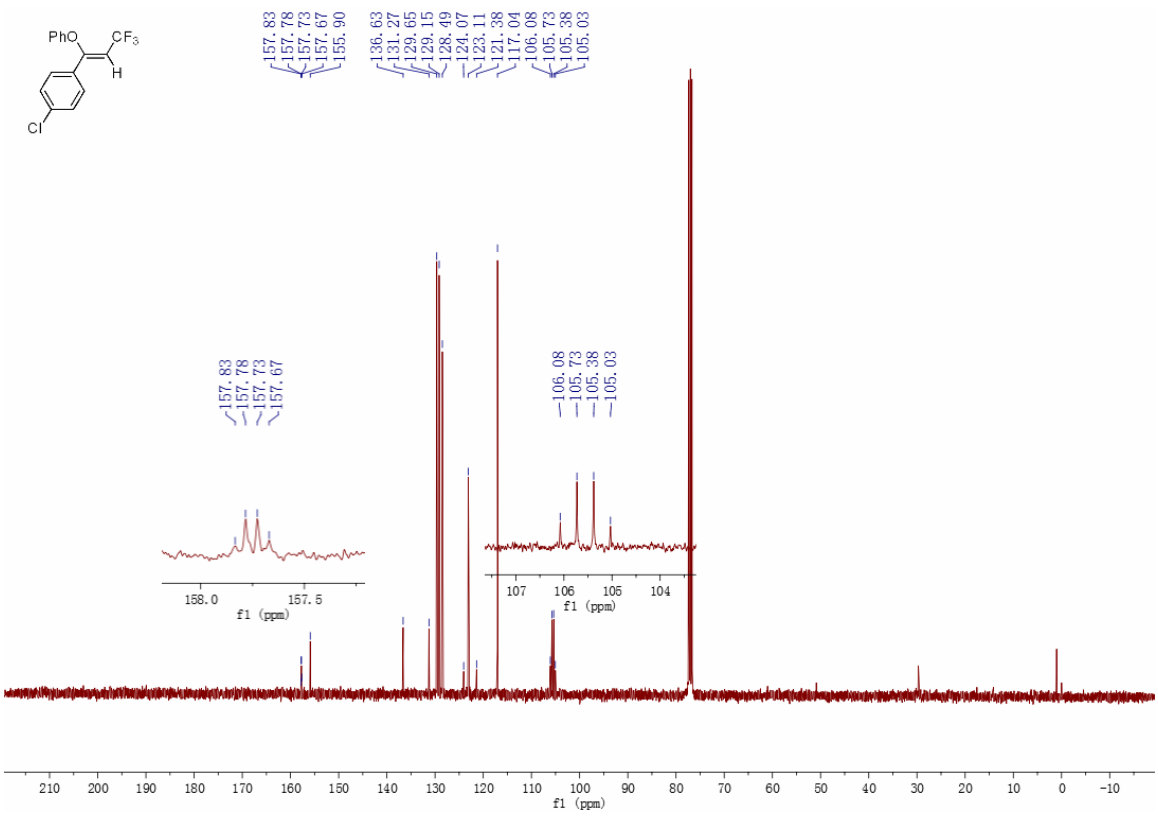



PhO
CF3
H
158.97
158.91
158.85
158.80
156.34
153.88
147.05
129.67
129.51
128.31
127.18
124.38
122.70
121.70
104.90
104.55
104.21
103.86
28.63
15.06
f1 (ppm)

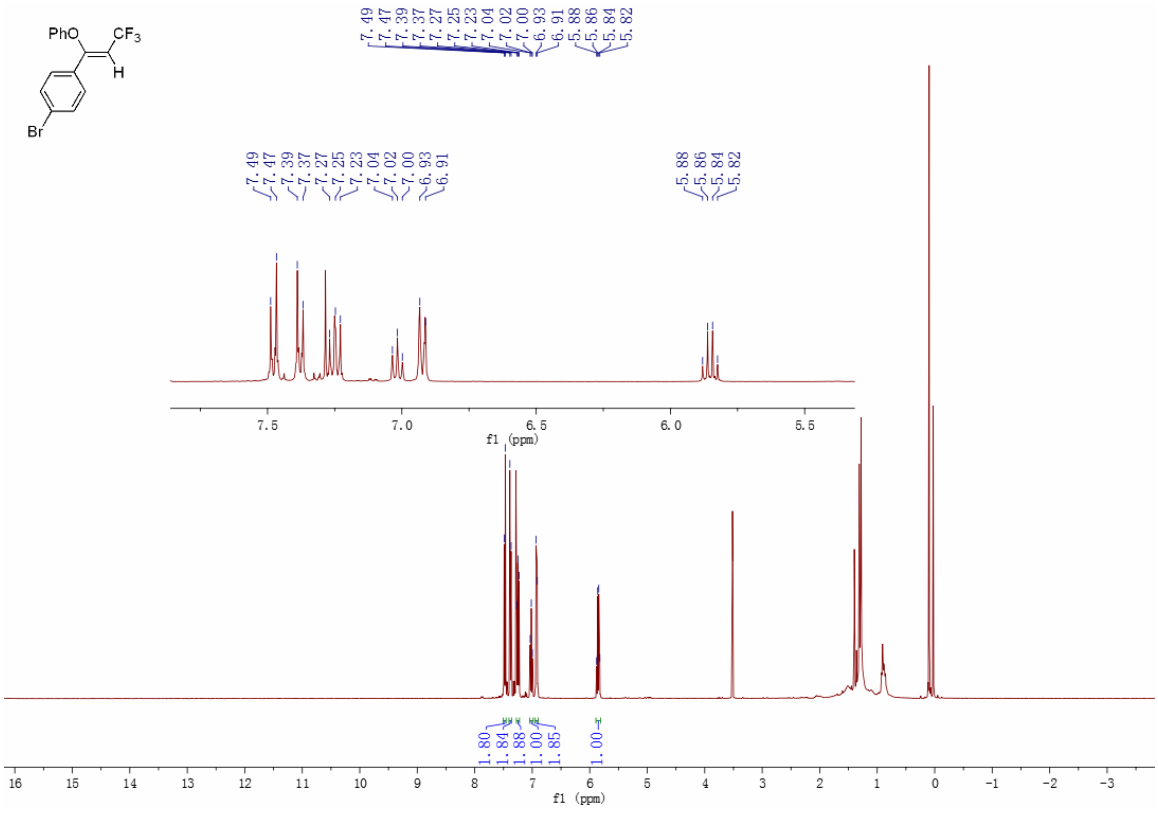
(Z)-1-chloro-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5c**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

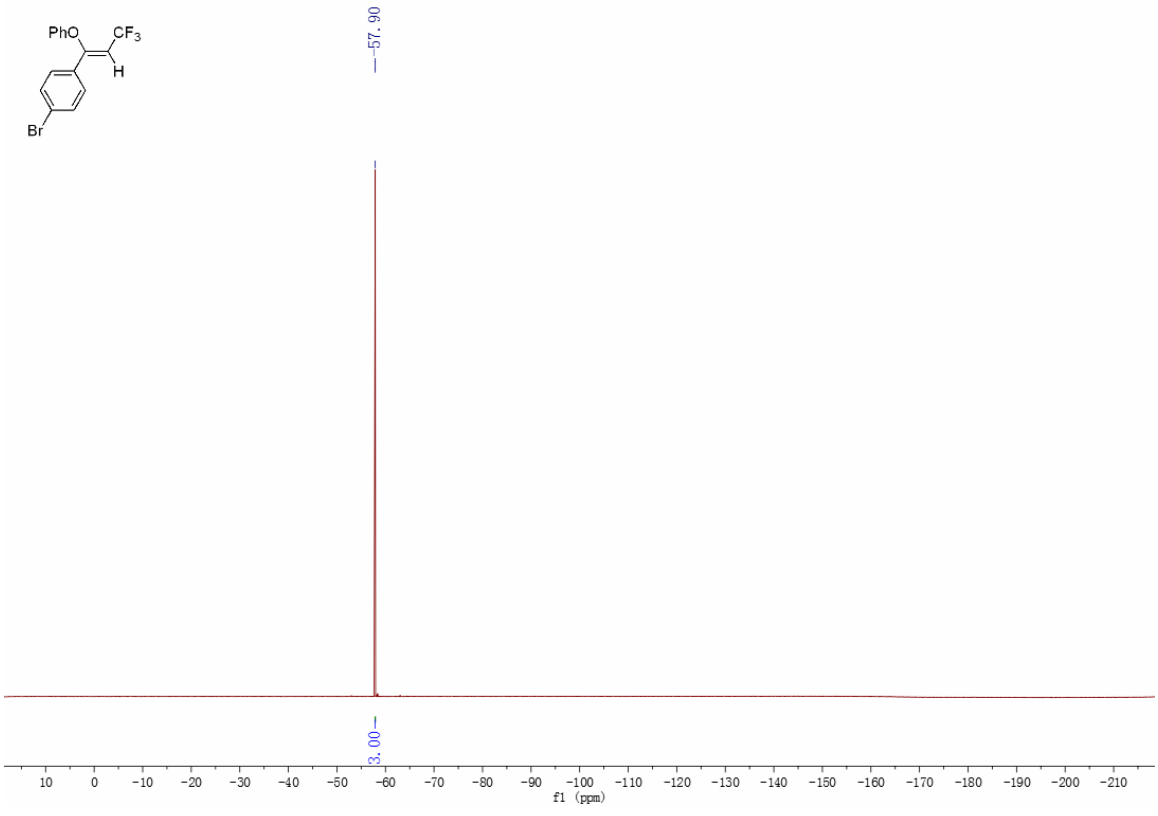


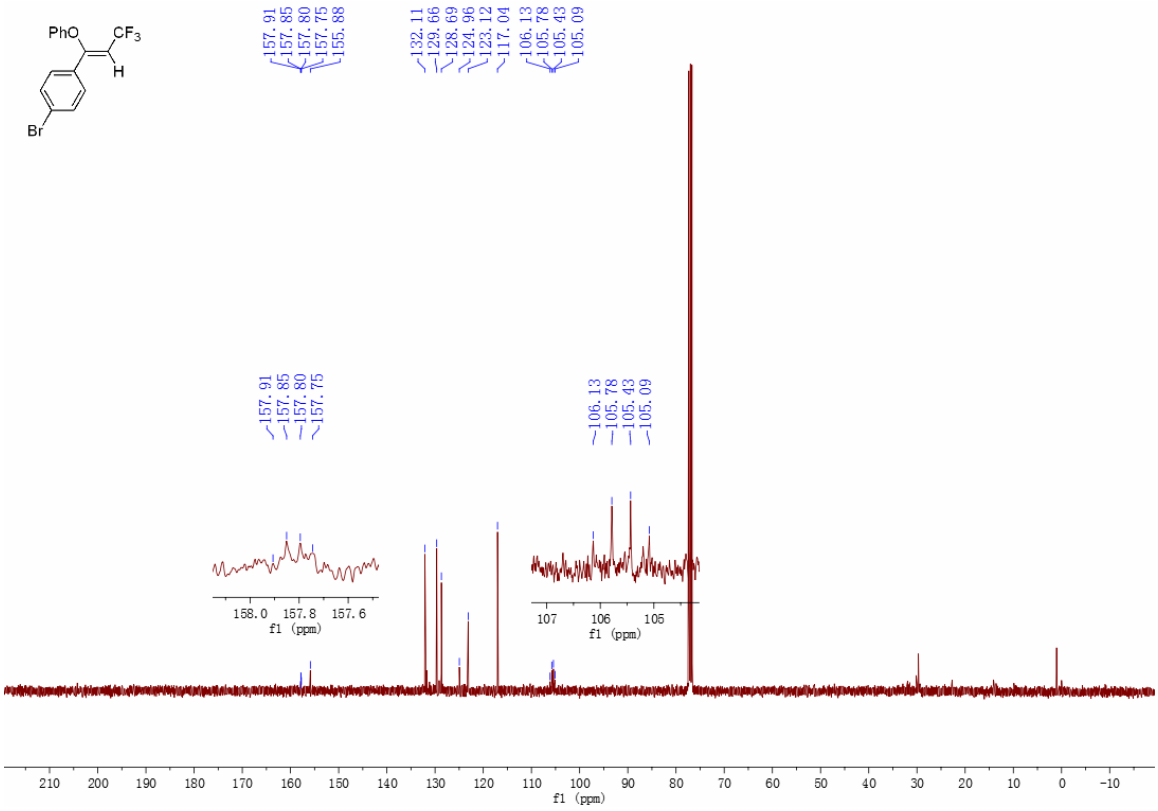



PhO
CF3
H
Cl
157.83
157.78
157.73
157.67
155.90
136.63
131.27
129.65
129.15
128.49
124.07
123.11
121.38
117.04
106.08
105.73
105.38
105.03
158.0
157.5
f1 (ppm)
107
106
105
104
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

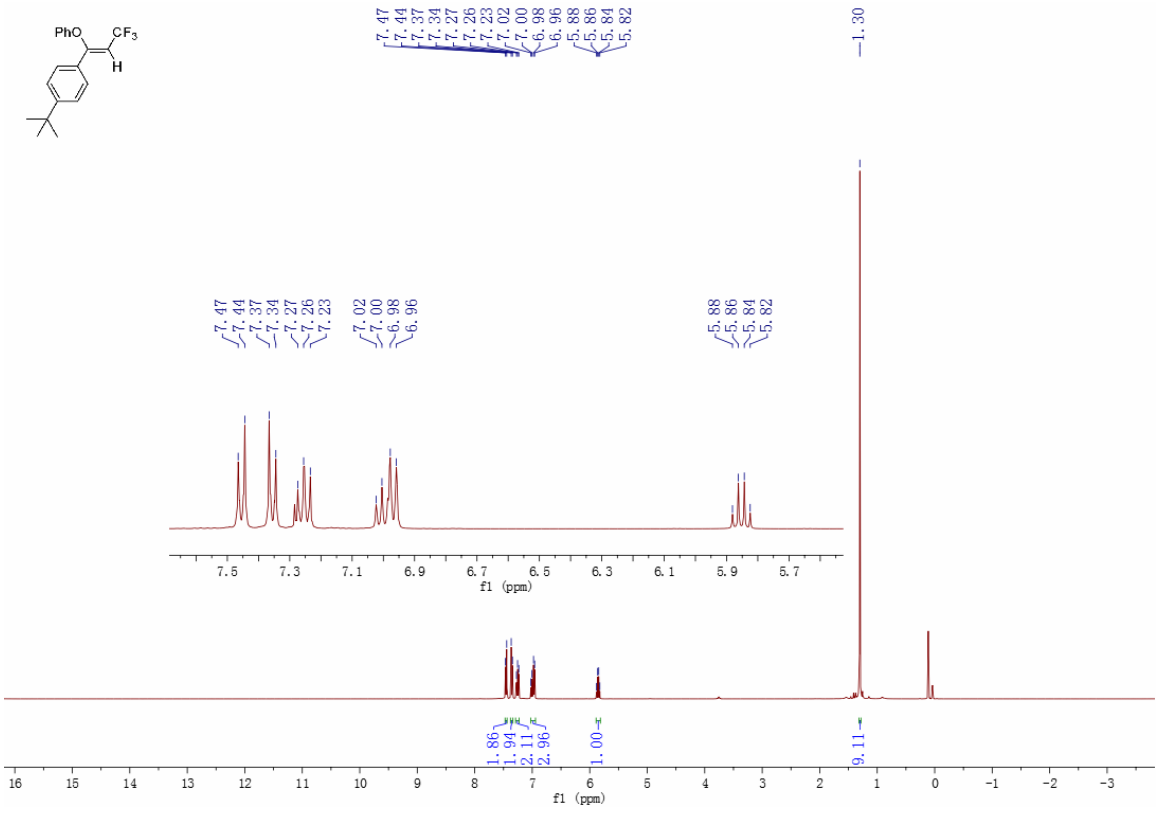
(Z)-1-bromo-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5d**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

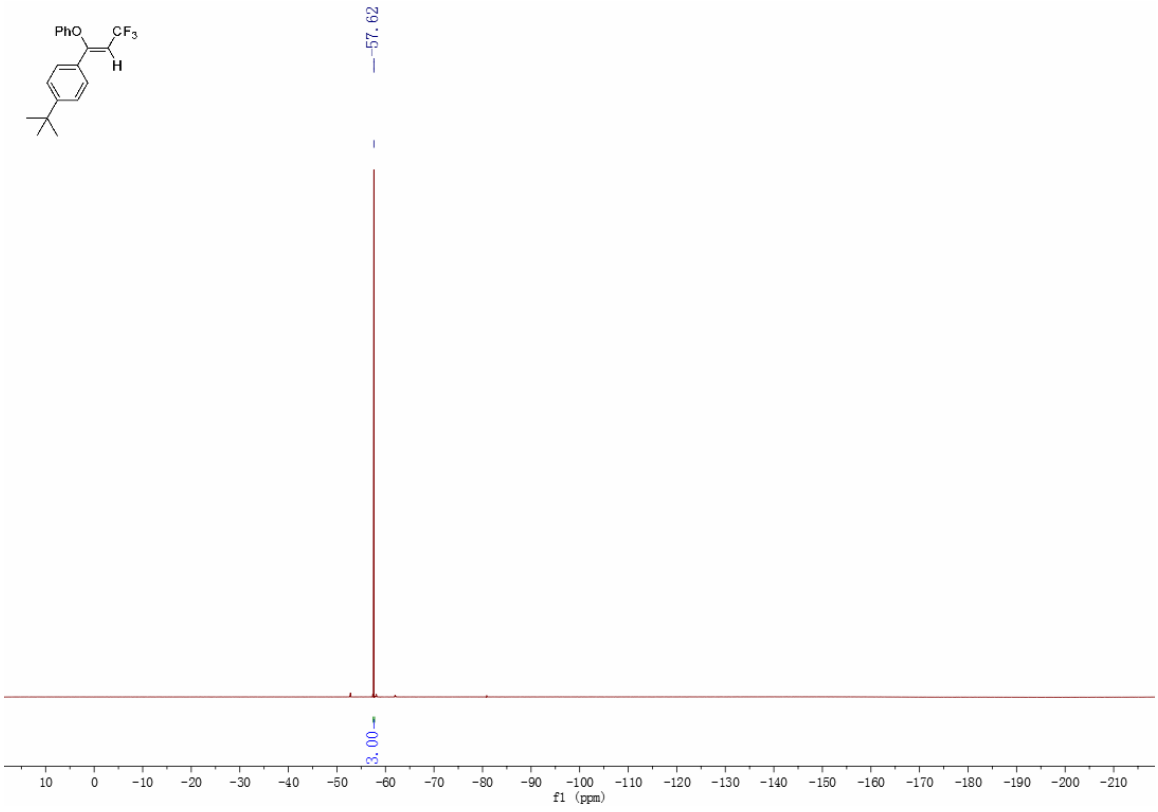


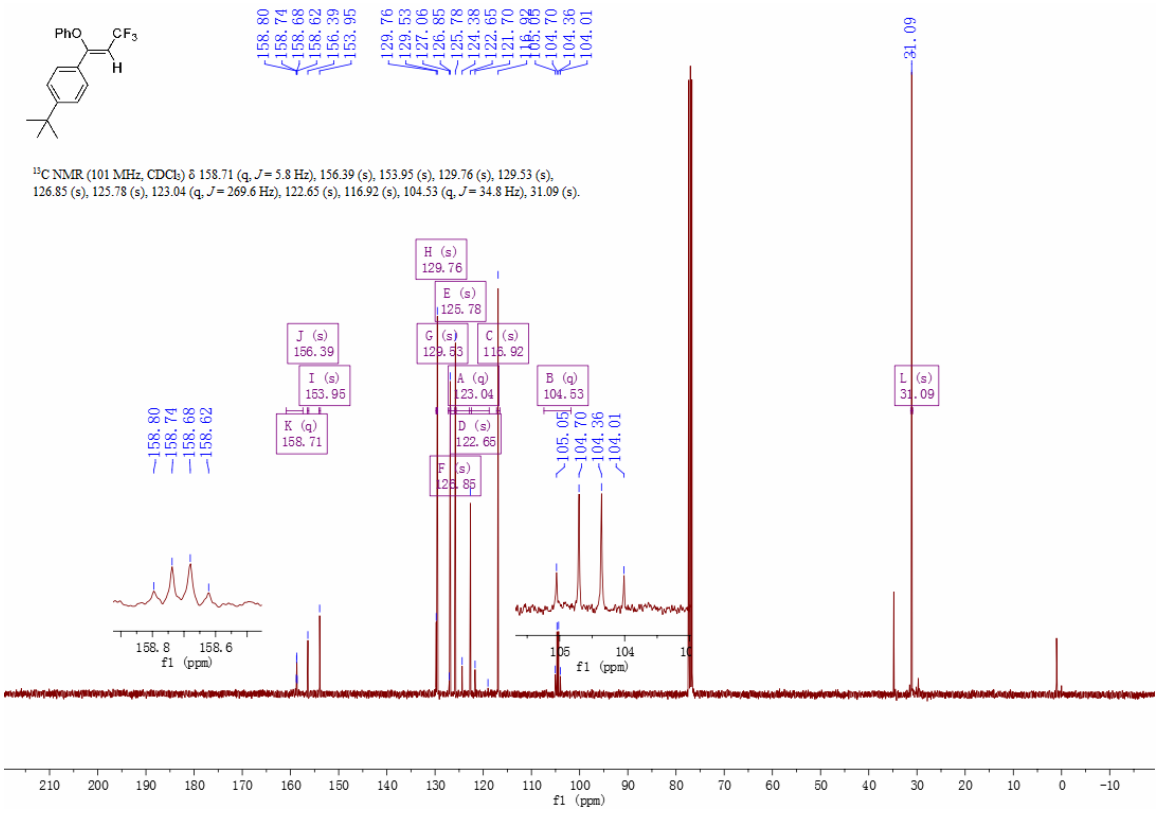



PhO
CF3
H
Br
157.91
157.85
157.80
157.75
155.88
132.11
129.66
128.69
124.96
123.12
117.04
106.13
105.78
105.43
105.09
158.0
157.8
157.6
f1 (ppm)
107
106
105
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

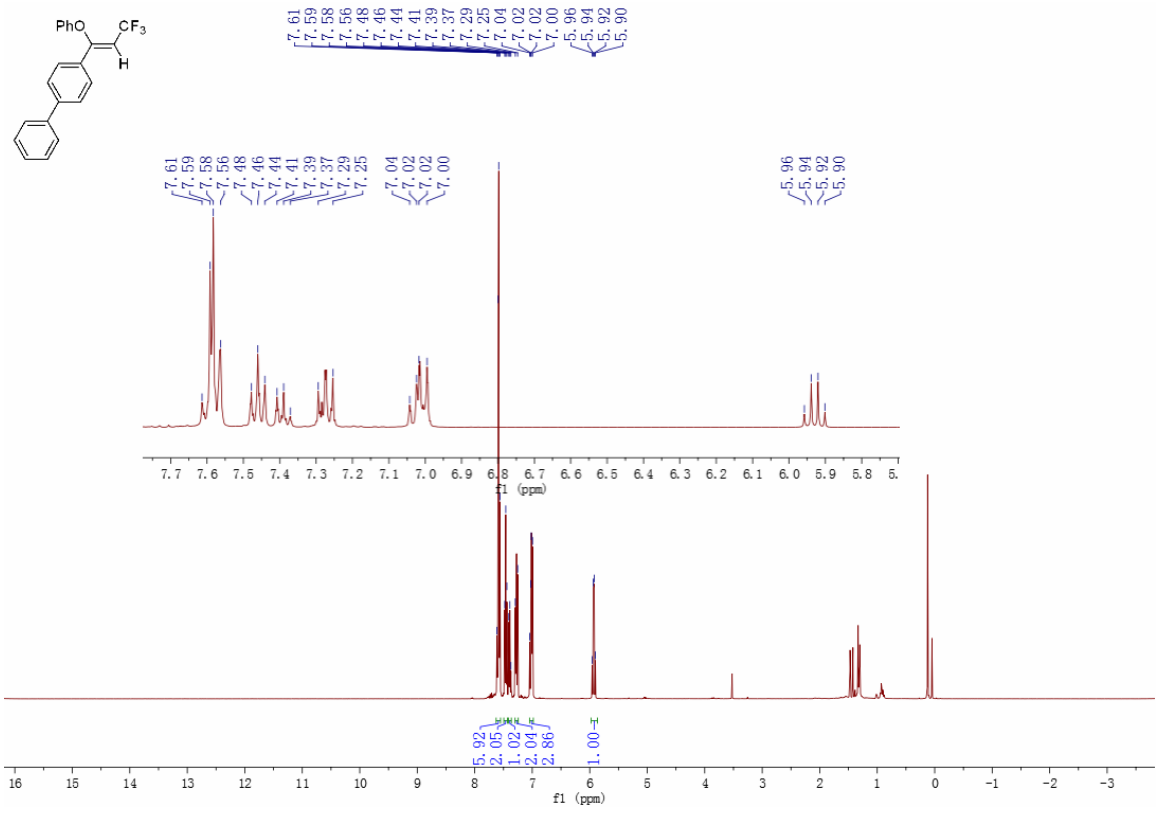
(Z)-1-(tert-butyl)-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5e**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

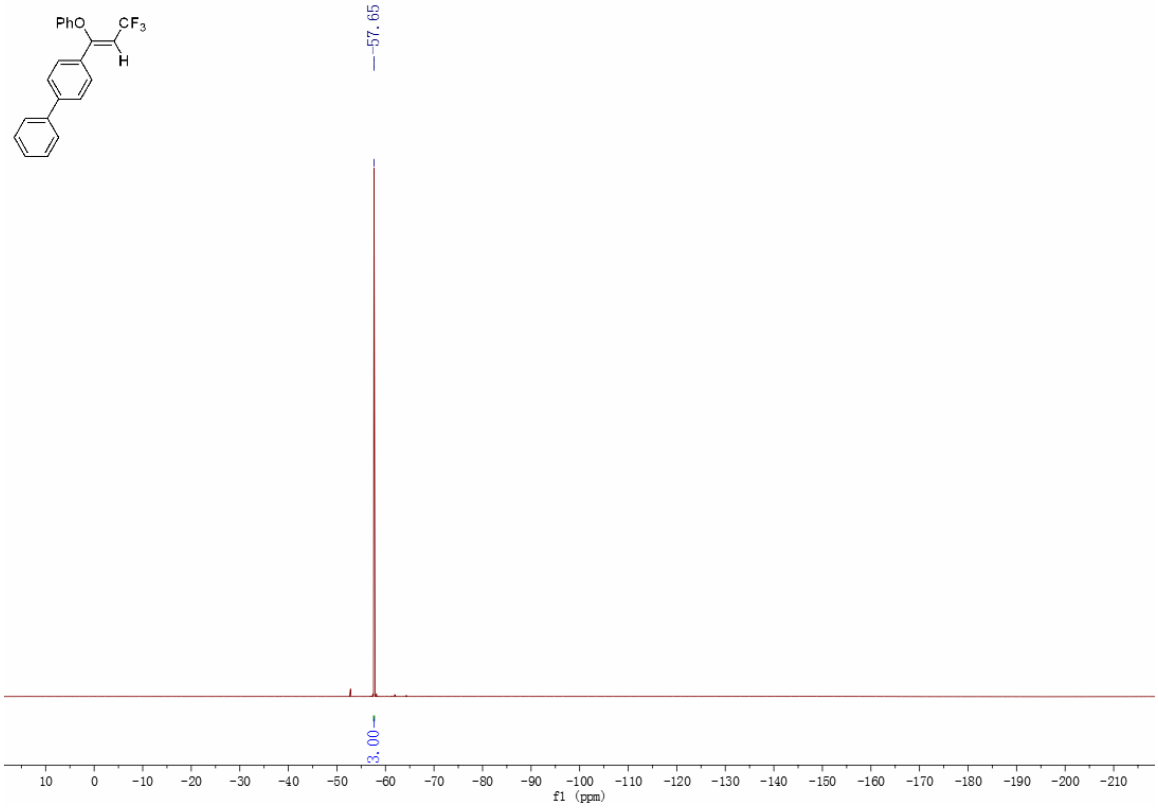


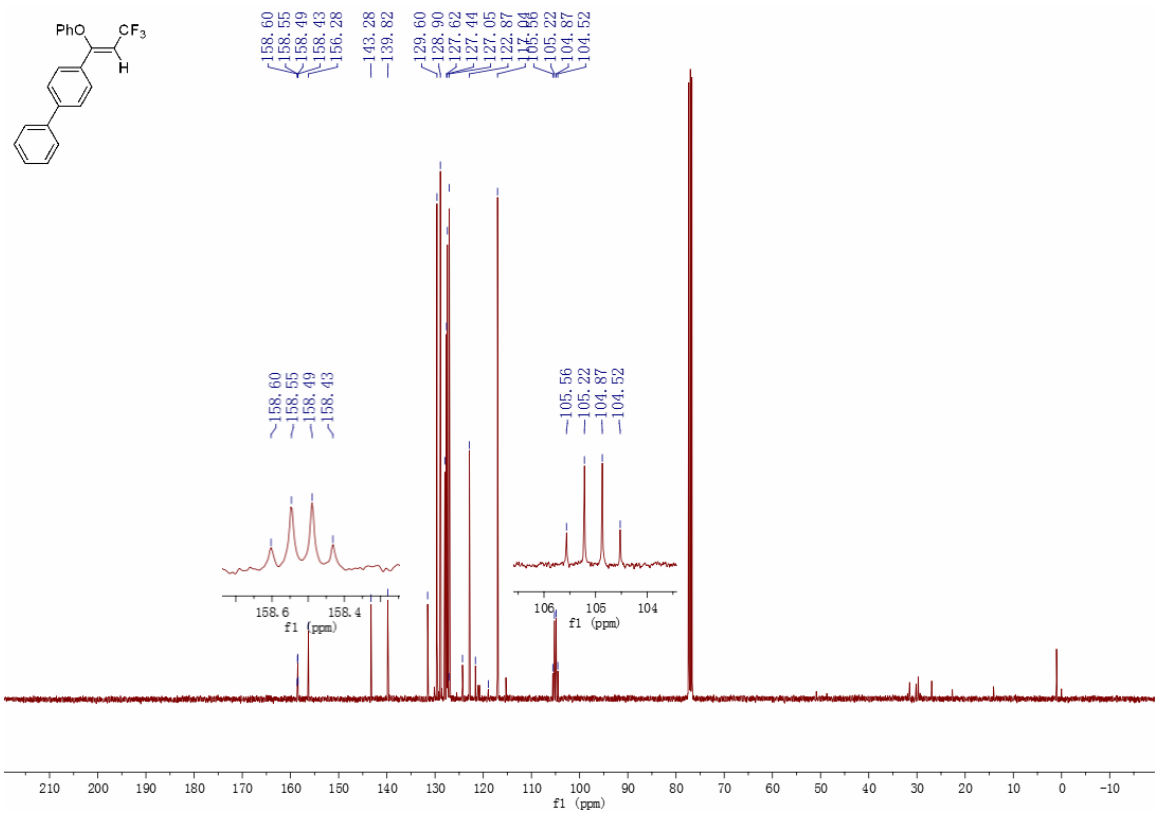



PhO
CF3
H
158.80
158.74
158.68
158.62
156.39
153.95
129.76
129.53
127.06
126.85
125.78
124.38
122.65
121.70
116.92
105.05
104.70
104.36
104.01
31.09
13C NMR (101 MHz, CDCl3) δ 158.71 (q, J = 5.8 Hz), 156.39 (s), 153.95 (s), 129.76 (s), 129.53 (s), 126.85 (s), 125.78 (s), 123.04 (q, J = 269.6 Hz), 122.65 (s), 116.92 (s), 104.53 (q, J = 34.8 Hz), 31.09 (s).
H (s) 129.76
E (s) 125.78
J (s) 156.39
G (s) 129.53
C (s) 116.92
I (s) 153.95
A (q) 123.04
B (q) 104.53
L (s) 31.09
K (q) 158.71
D (s) 122.65
F (s) 125.85
158.8
158.6
f1 (ppm)
105
104
f1 (ppm)
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)

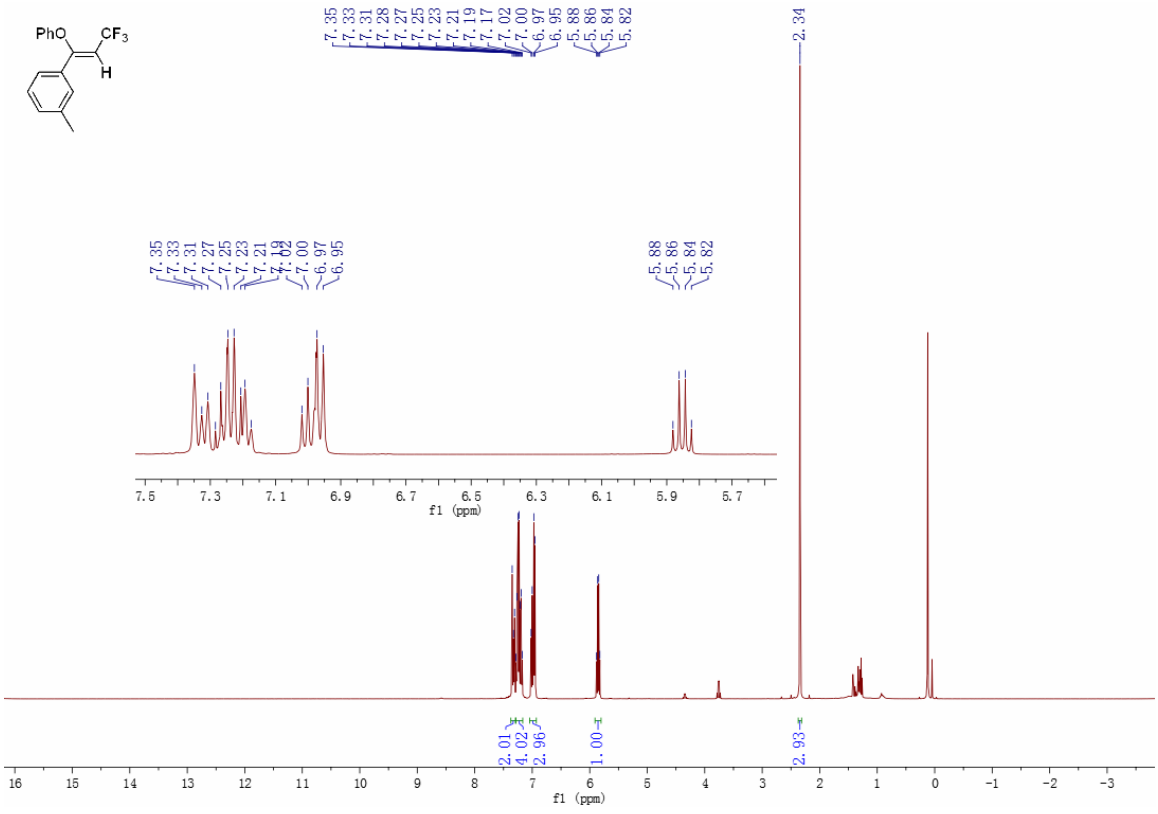
(Z)-4-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)-1,1'-biphenyl (**5f**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

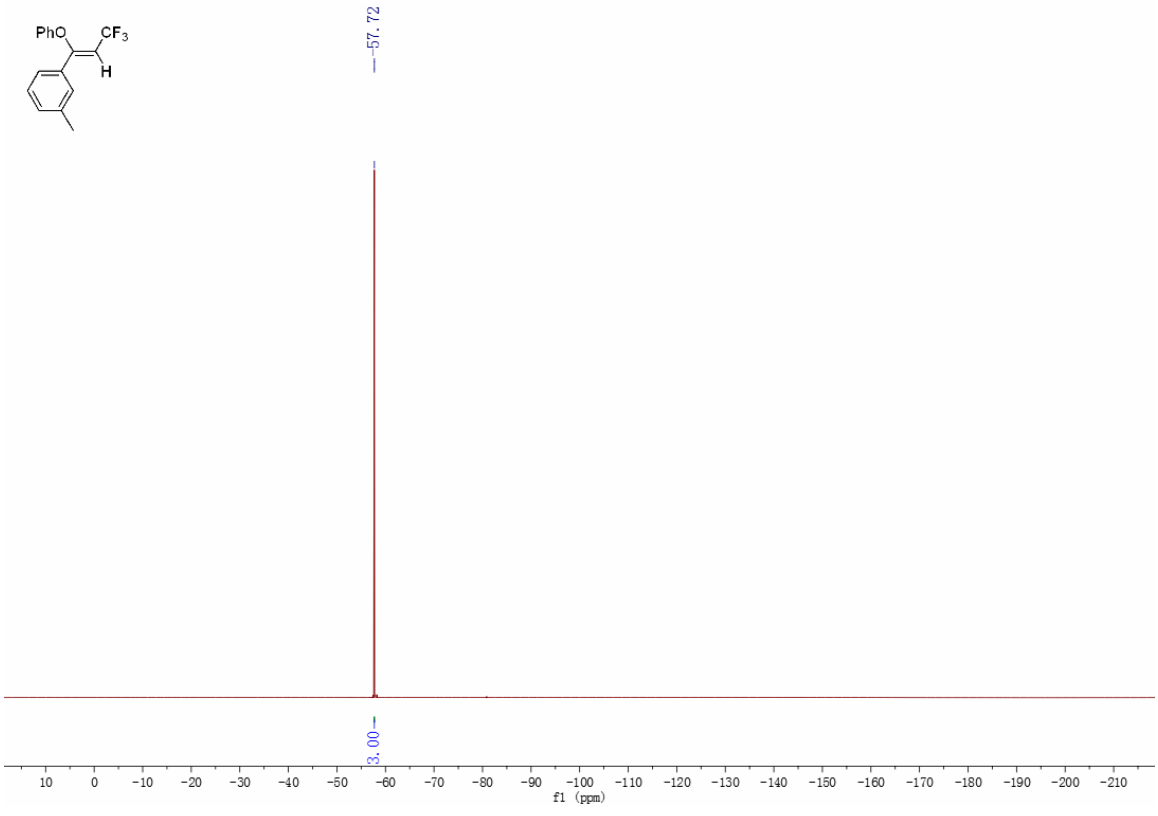


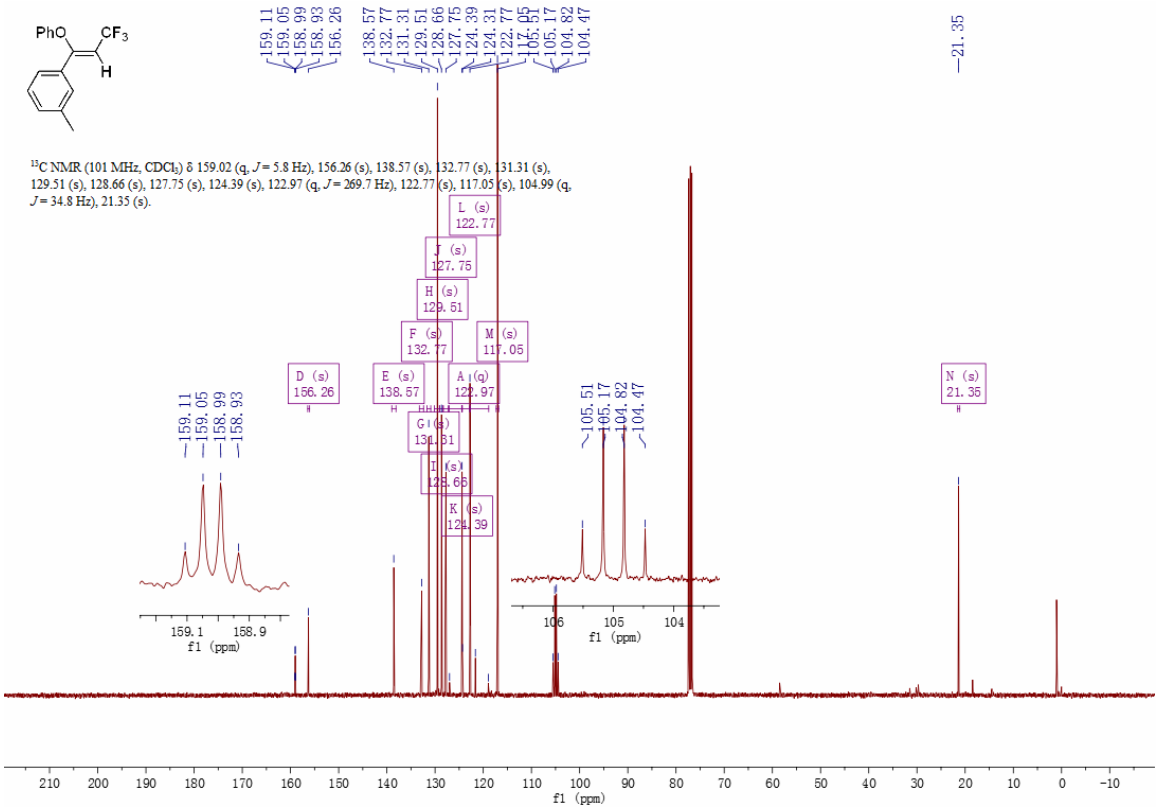



PhO
CF3
H
158.60
158.55
158.49
158.43
156.28
143.28
139.82
129.60
128.90
127.62
127.44
127.05
122.87
105.56
105.22
104.87
104.52
158.6
158.4
f1 (ppm)
106
105
104
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

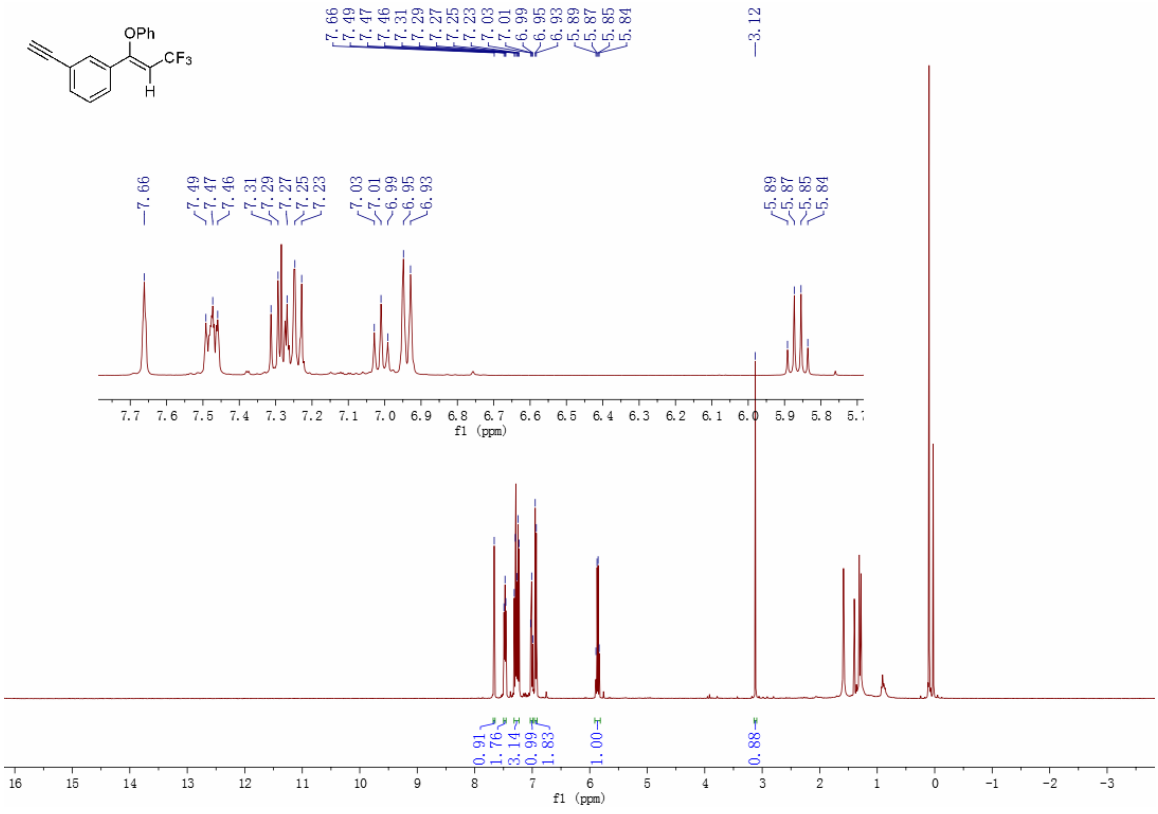
(Z)-1-methyl-3-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5g**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

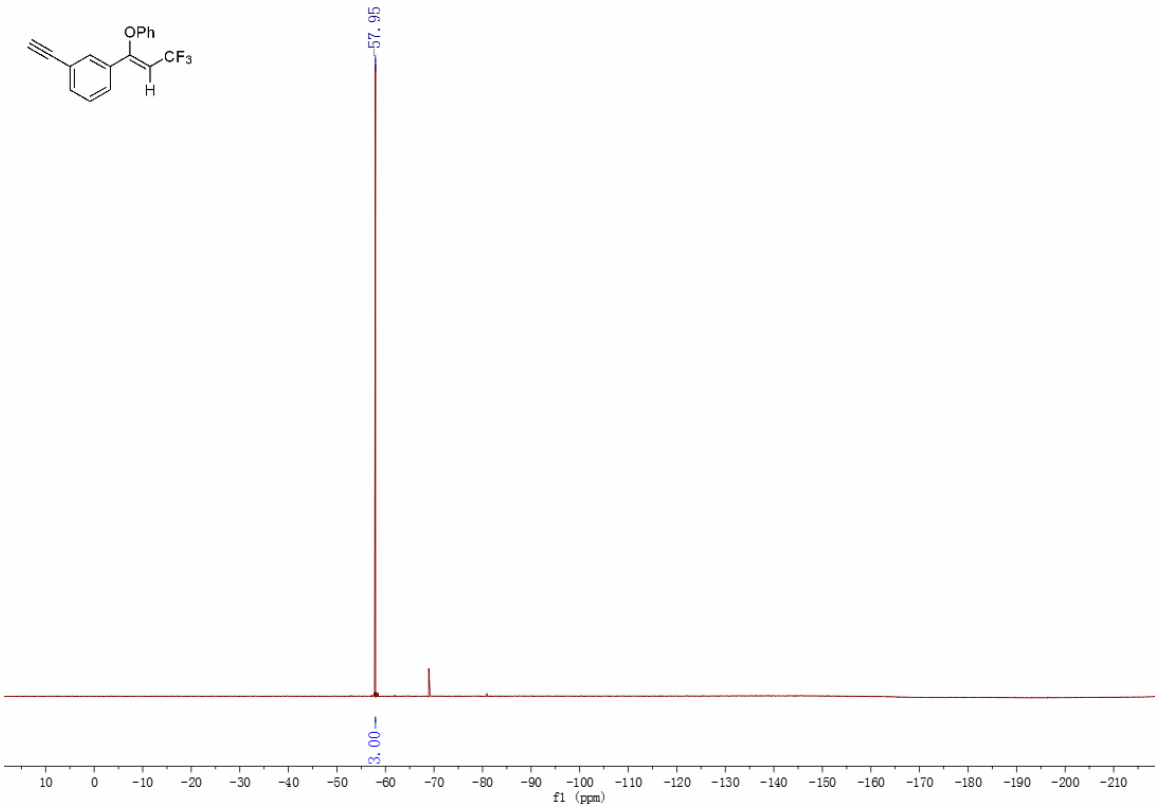


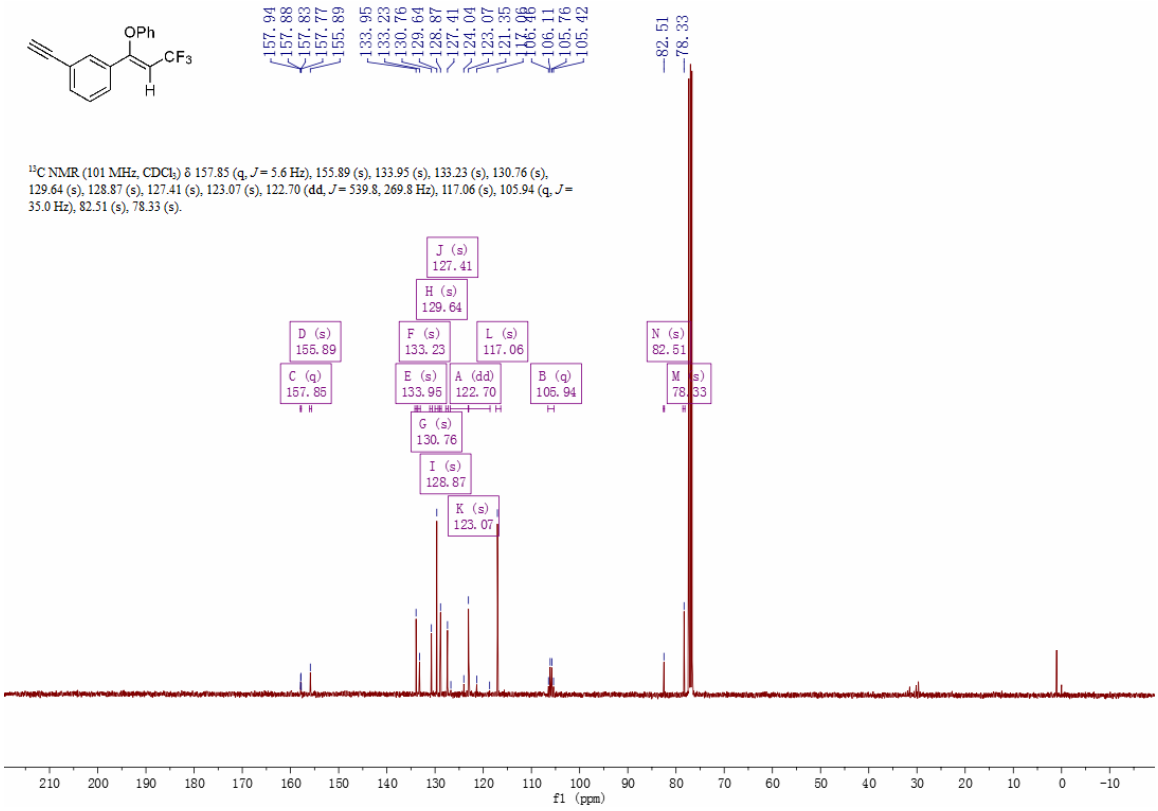



PhO
CF3
H
159.11
159.05
158.99
158.93
156.26
138.57
132.77
131.31
129.51
128.66
127.75
124.39
124.31
122.77
117.05
105.51
105.17
104.82
104.47
21.35
13C NMR (101 MHz, CDCl3) δ 159.02 (q, J = 5.8 Hz), 156.26 (s), 138.57 (s), 132.77 (s), 131.31 (s), 129.51 (s), 128.66 (s), 127.75 (s), 124.39 (s), 122.97 (q, J = 269.7 Hz), 122.77 (s), 117.05 (s), 104.99 (q, J = 34.8 Hz), 21.35 (s).
L (s) 122.77
J (s) 127.75
H (s) 129.51
F (s) 132.77
M (s) 117.05
D (s) 156.26
E (s) 138.57
A (q) 122.97
G (s) 131.31
I (s) 128.66
K (s) 124.39
N (s) 21.35
159.1
158.9
f1 (ppm)
106
105
104
f1 (ppm)
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)

(Z)-1-ethynyl-3-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)benzene (**5h**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

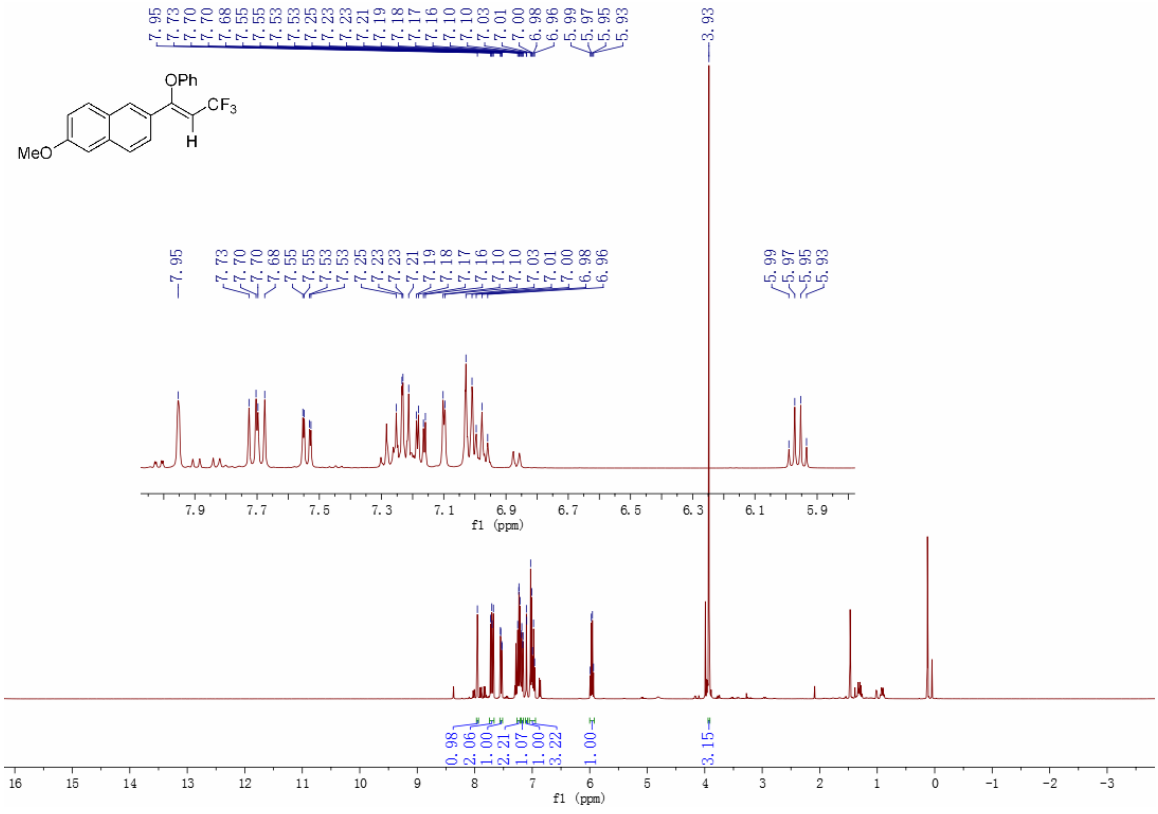


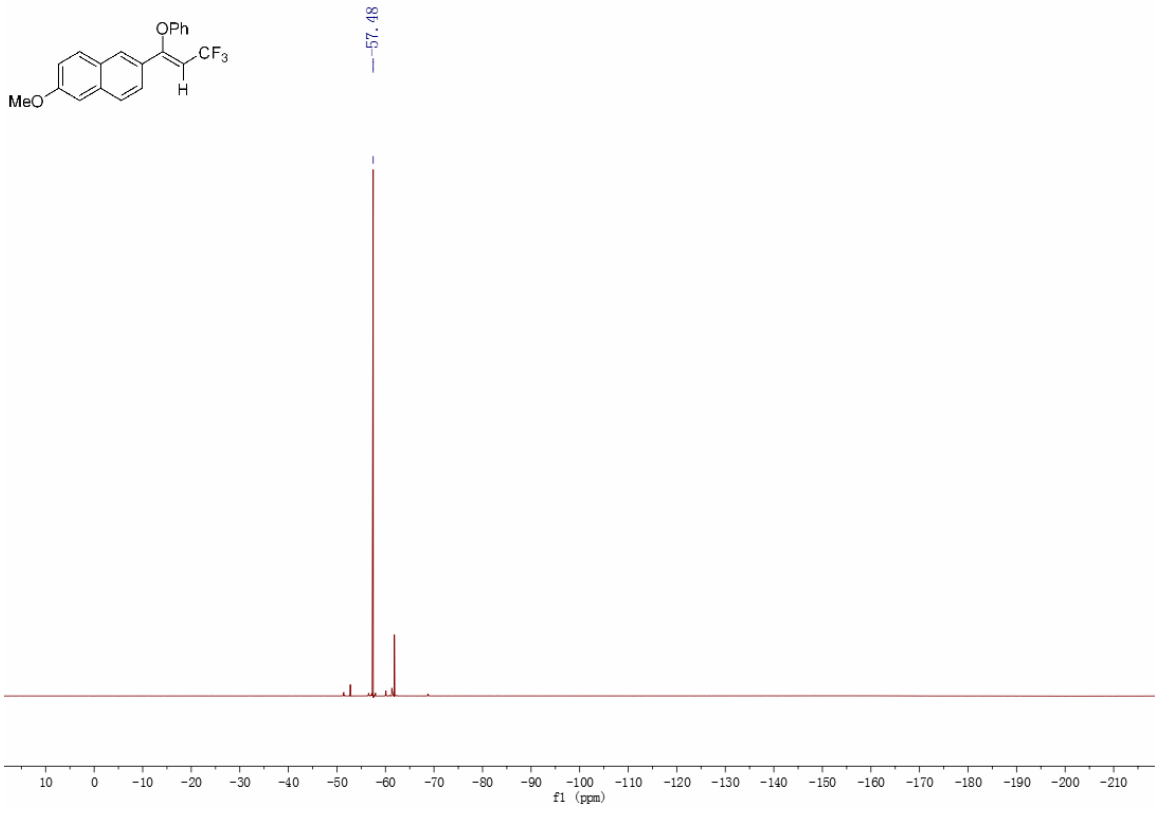


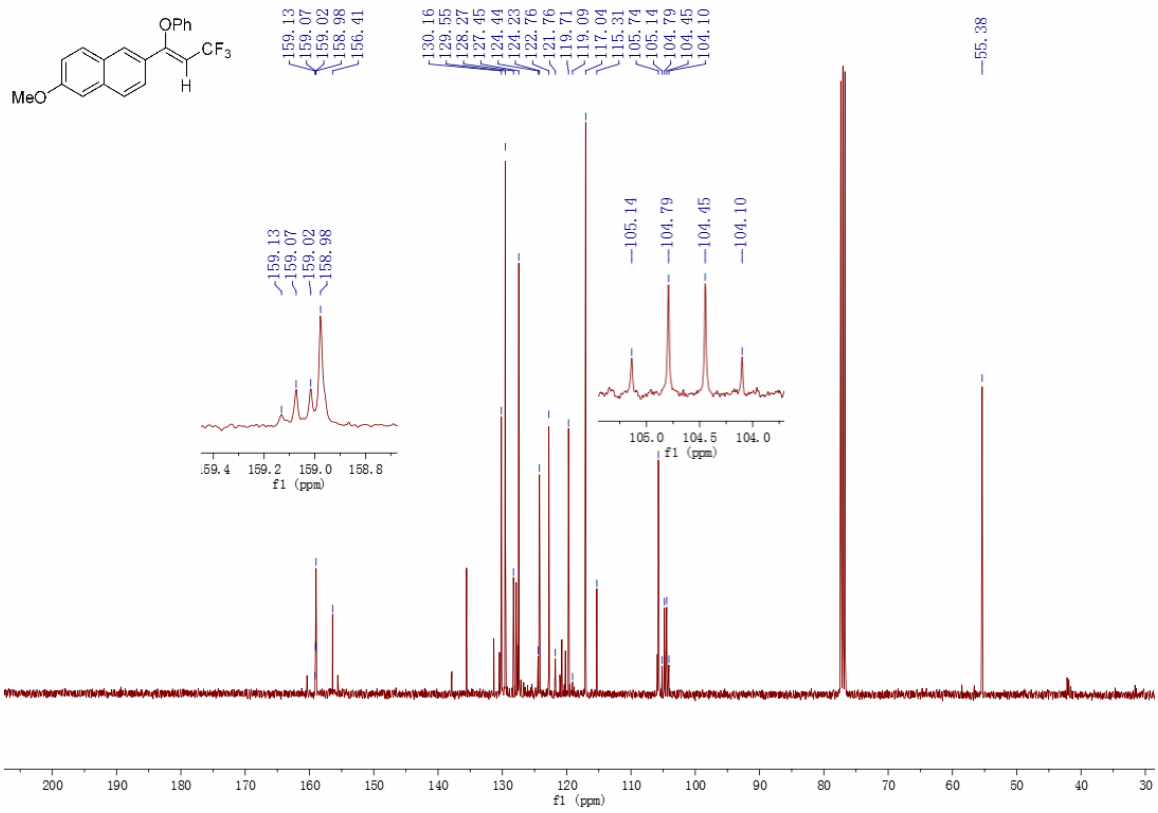


^{13}C NMR (101 MHz, $CDCl_3$) δ 157.85 (q, J = 5.6 Hz), 155.89 (s), 133.95 (s), 133.23 (s), 130.76 (s), 129.64 (s), 128.87 (s), 127.41 (s), 123.07 (s), 122.70 (dd, J = 539.8, 269.8 Hz), 117.06 (s), 105.94 (q, J = 35.0 Hz), 82.51 (s), 78.33 (s).

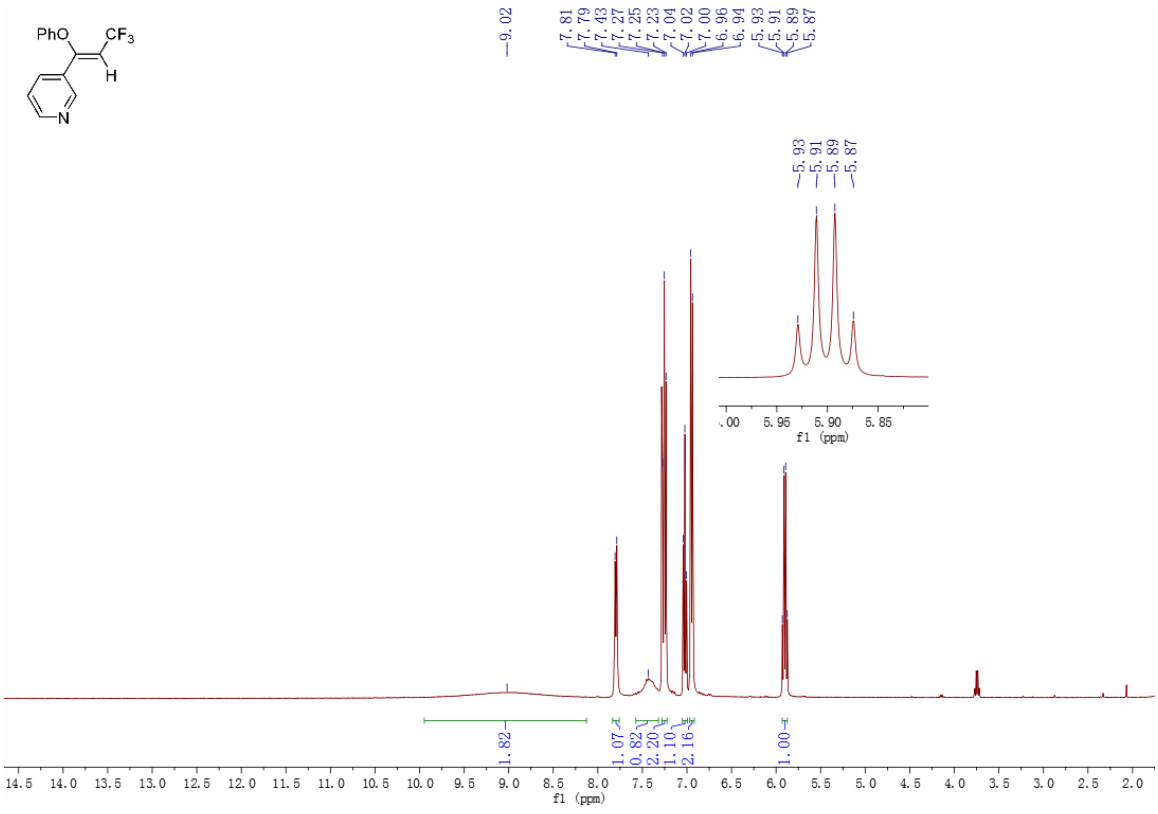
(Z)-2-methoxy-6-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)naphthalene (**5i**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

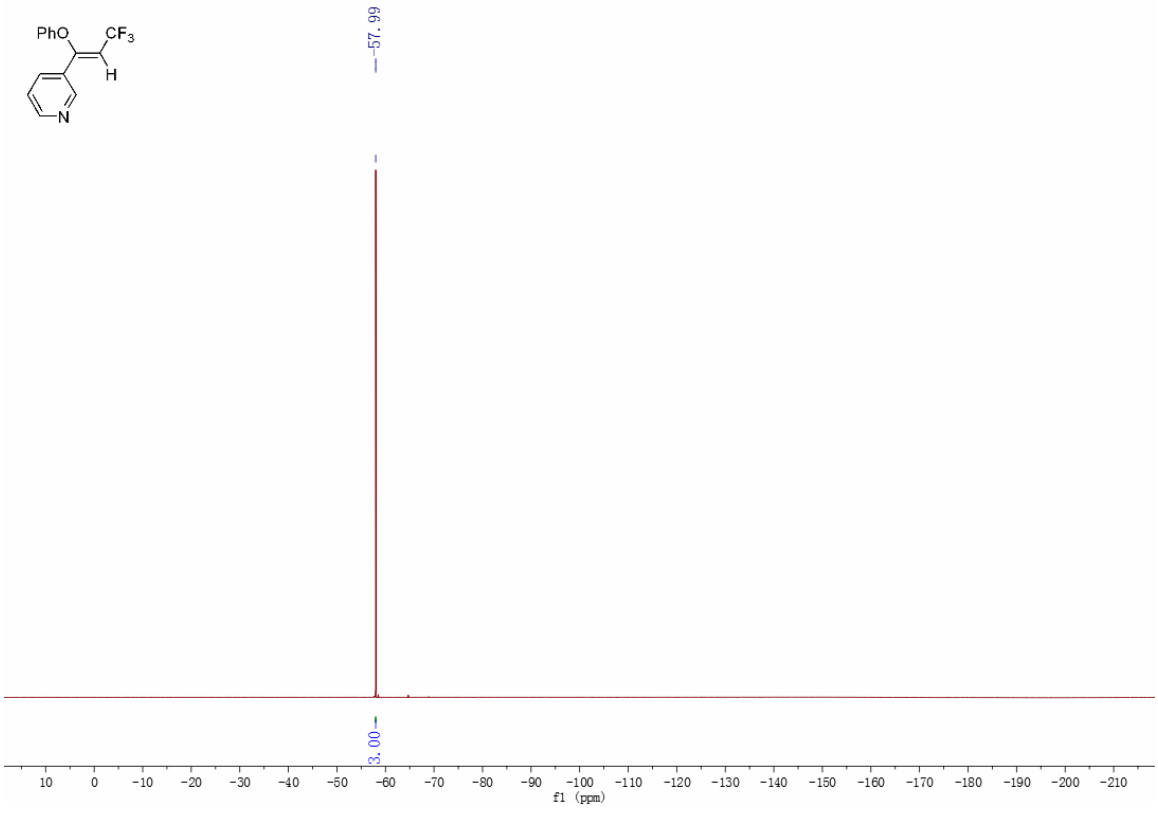


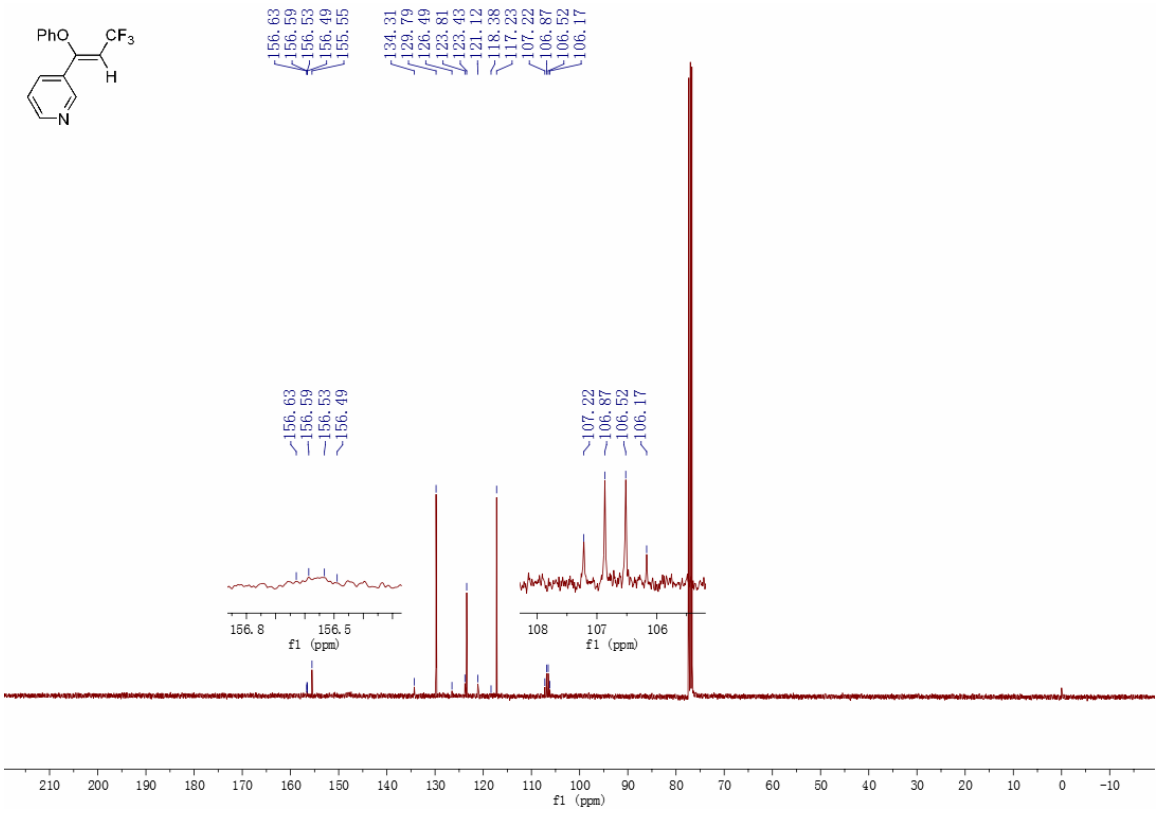



OPh
CF3
H
MeO
159.13
159.07
159.02
158.98
156.41
130.16
129.55
128.27
127.45
124.44
124.23
122.76
121.76
119.71
119.09
117.04
115.31
105.74
105.14
104.79
104.45
104.10
55.38
f1 (ppm)

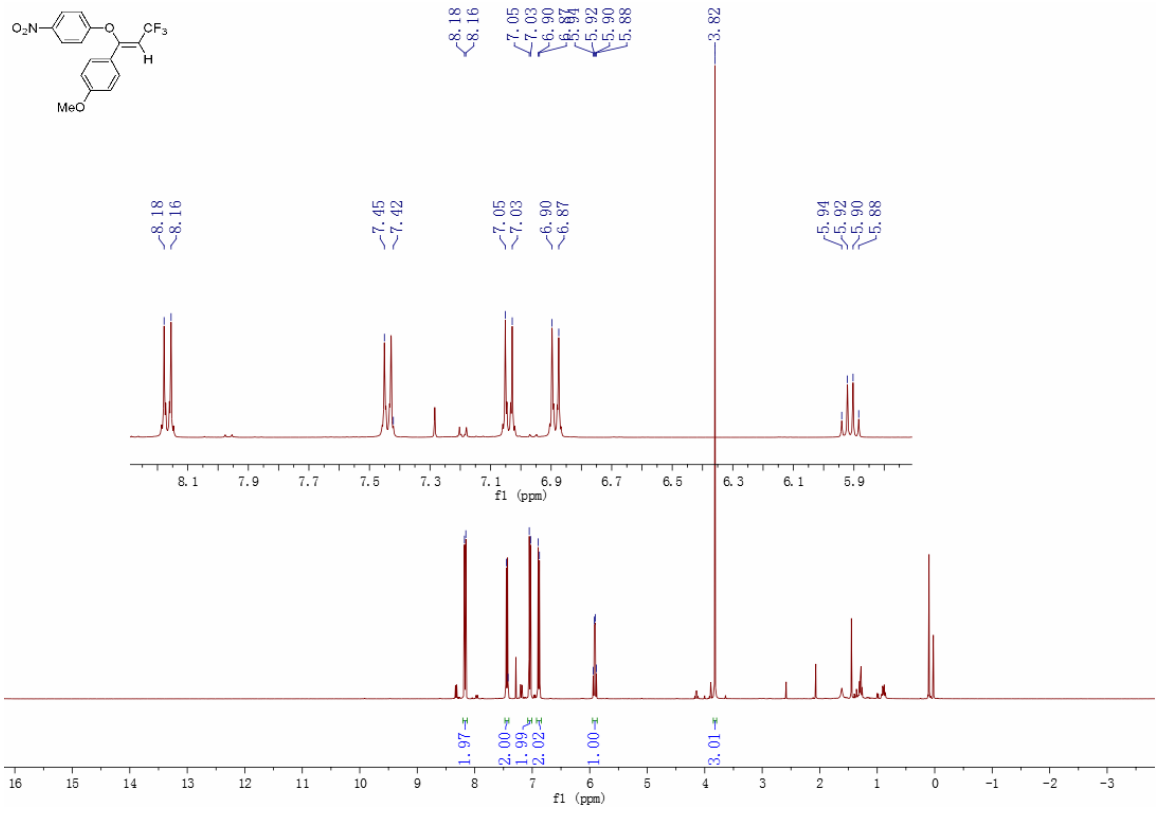
(Z)-3-(3,3,3-trifluoro-1-phenoxyprop-1-en-1-yl)pyridine (**5j**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

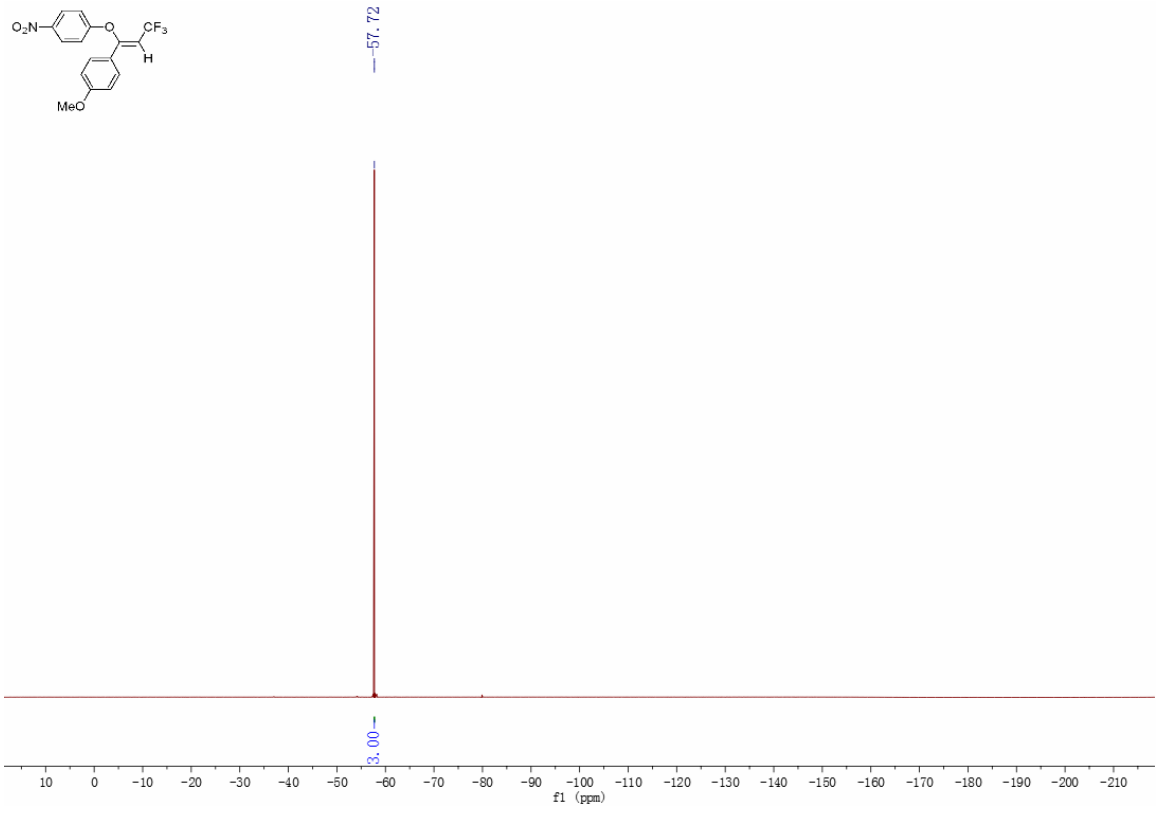


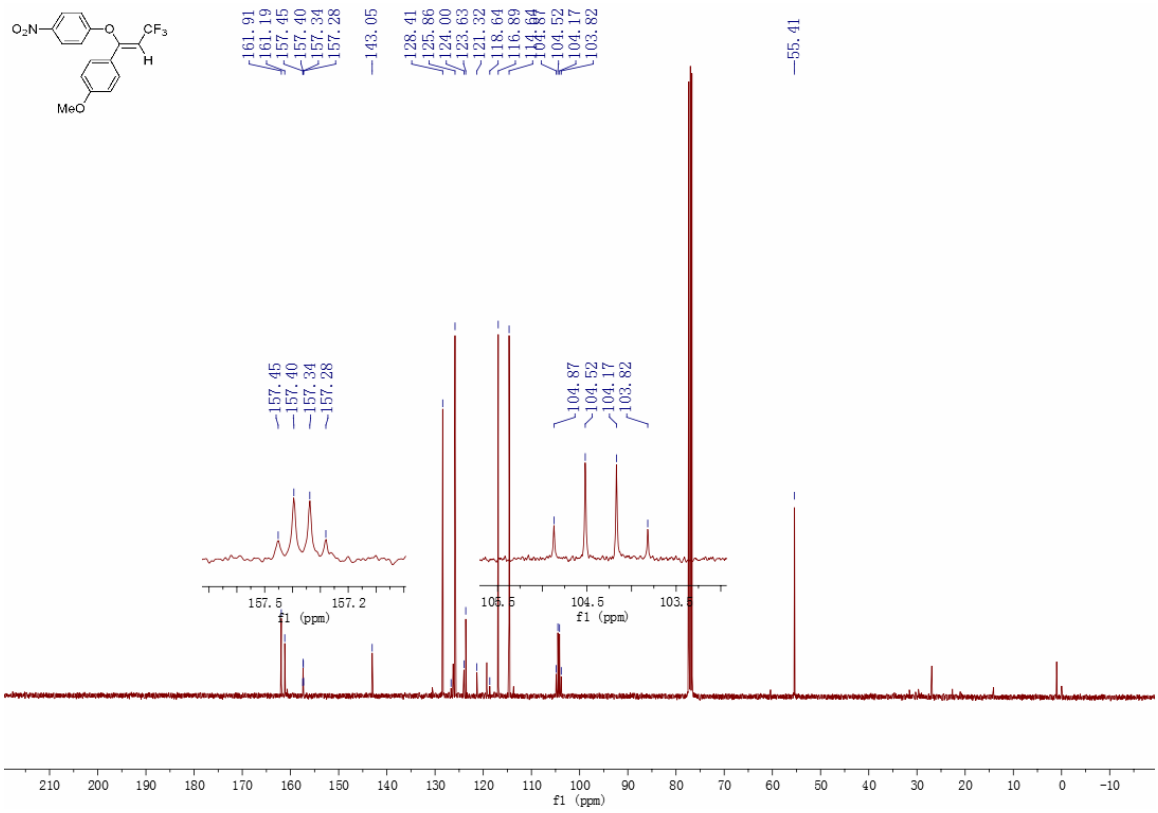



PhO
CF3
H
N
156.63
156.59
156.53
156.49
155.55
134.31
129.79
126.49
123.81
123.43
121.12
118.38
117.23
107.22
106.87
106.52
106.17
156.8
156.5
f1 (ppm)
108
107
106
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

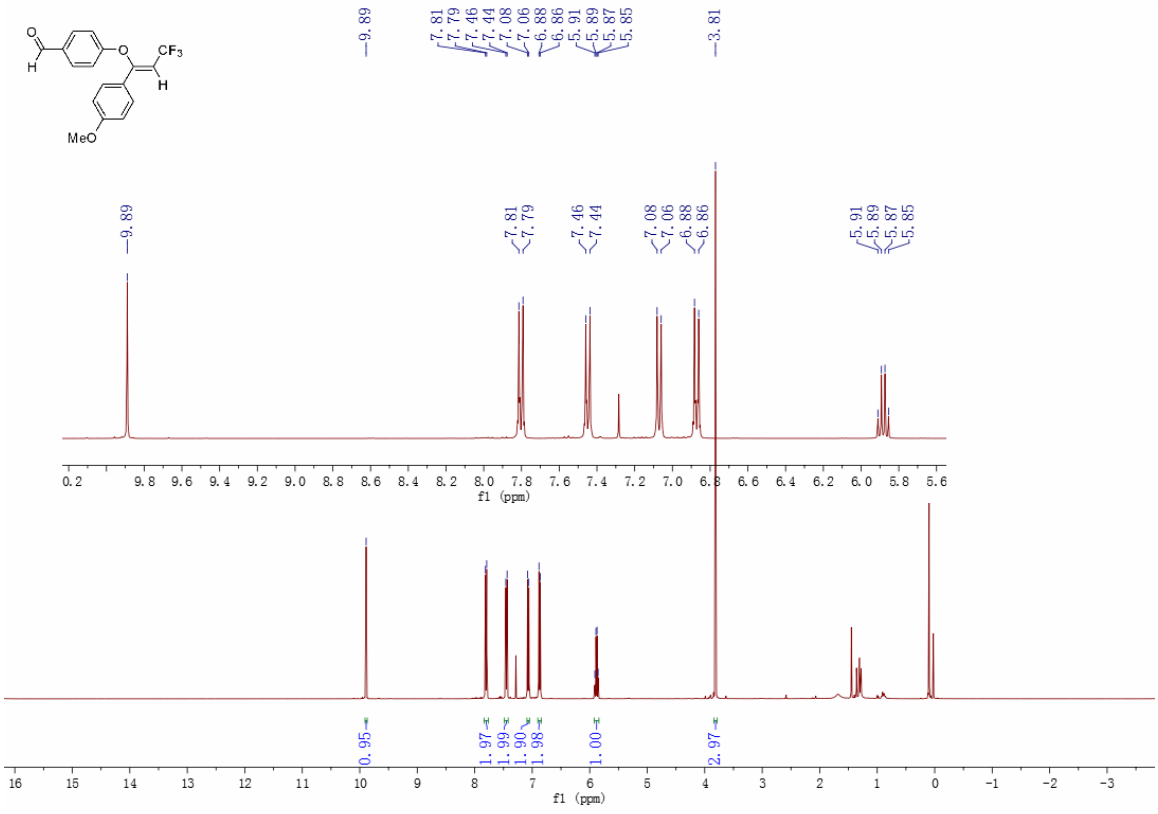
(Z)-1-methoxy-4-(3,3,3-trifluoro-1-(4-nitrophenoxy)prop-1-en-1-yl)benzene (5k. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

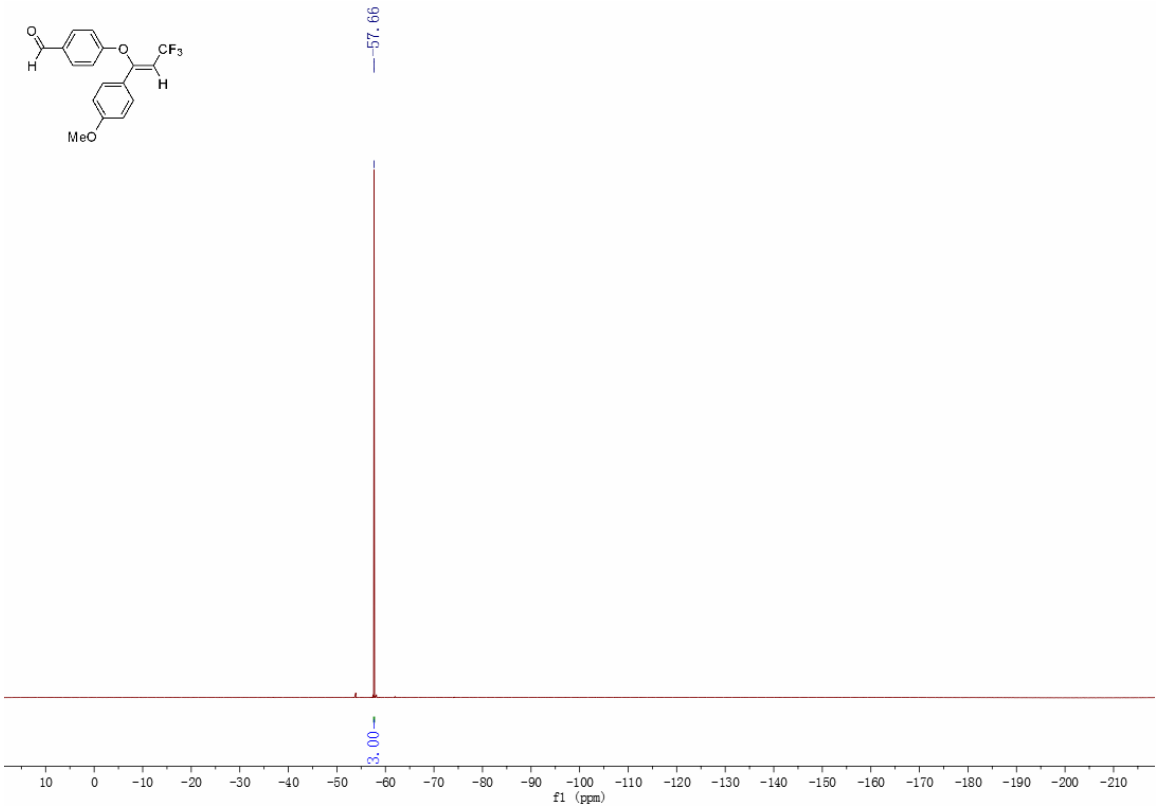


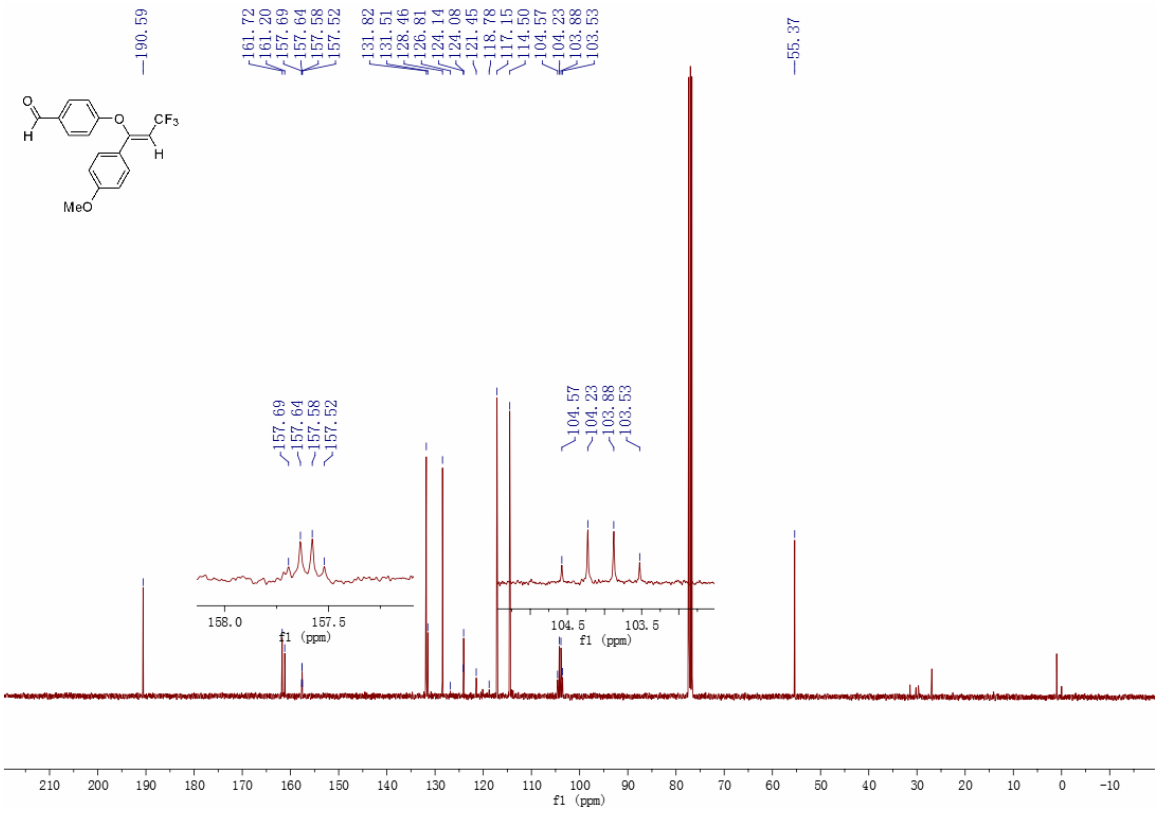



O2N
O
CF3
H
MeO
161.91
161.19
157.45
157.40
157.34
157.28
143.05
128.41
125.86
124.00
123.63
121.32
118.64
116.89
104.87
104.52
104.17
103.82
55.41
157.5
157.2
f1 (ppm)
104.5
103.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

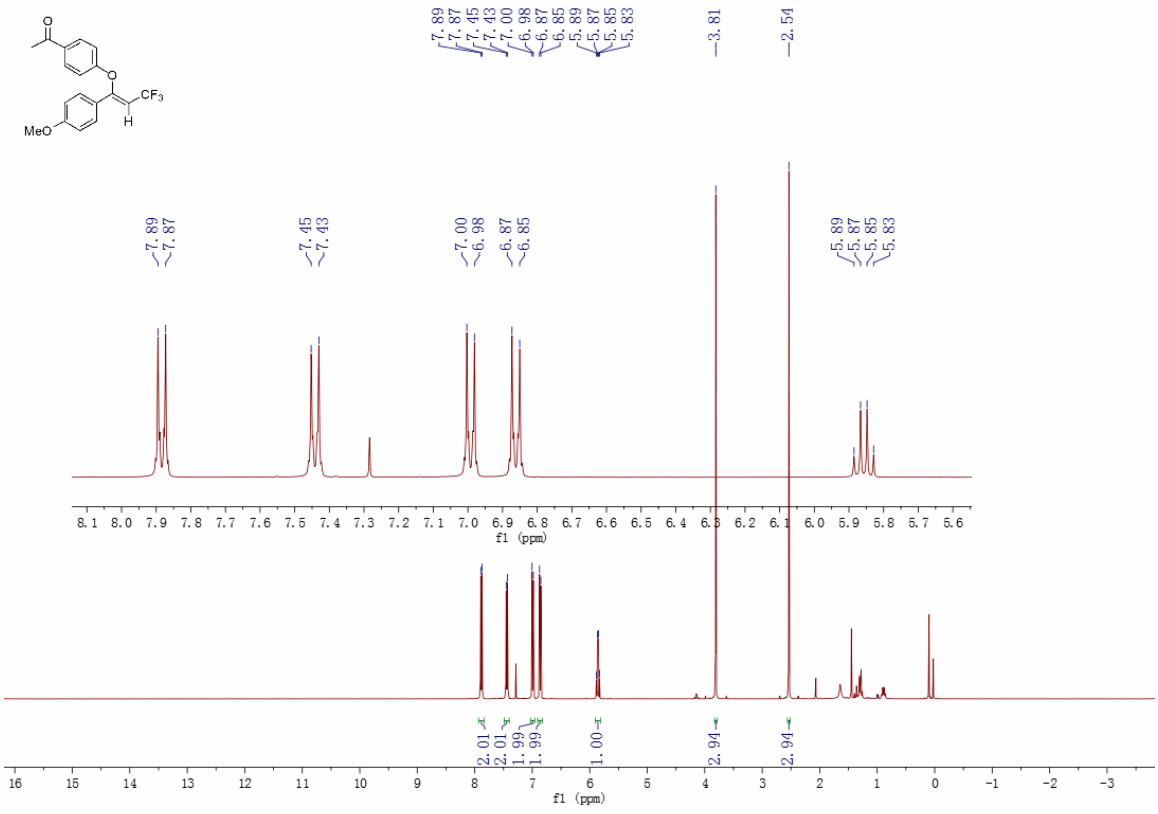
(Z)-4-((3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)oxy)benzaldehyde (5l. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

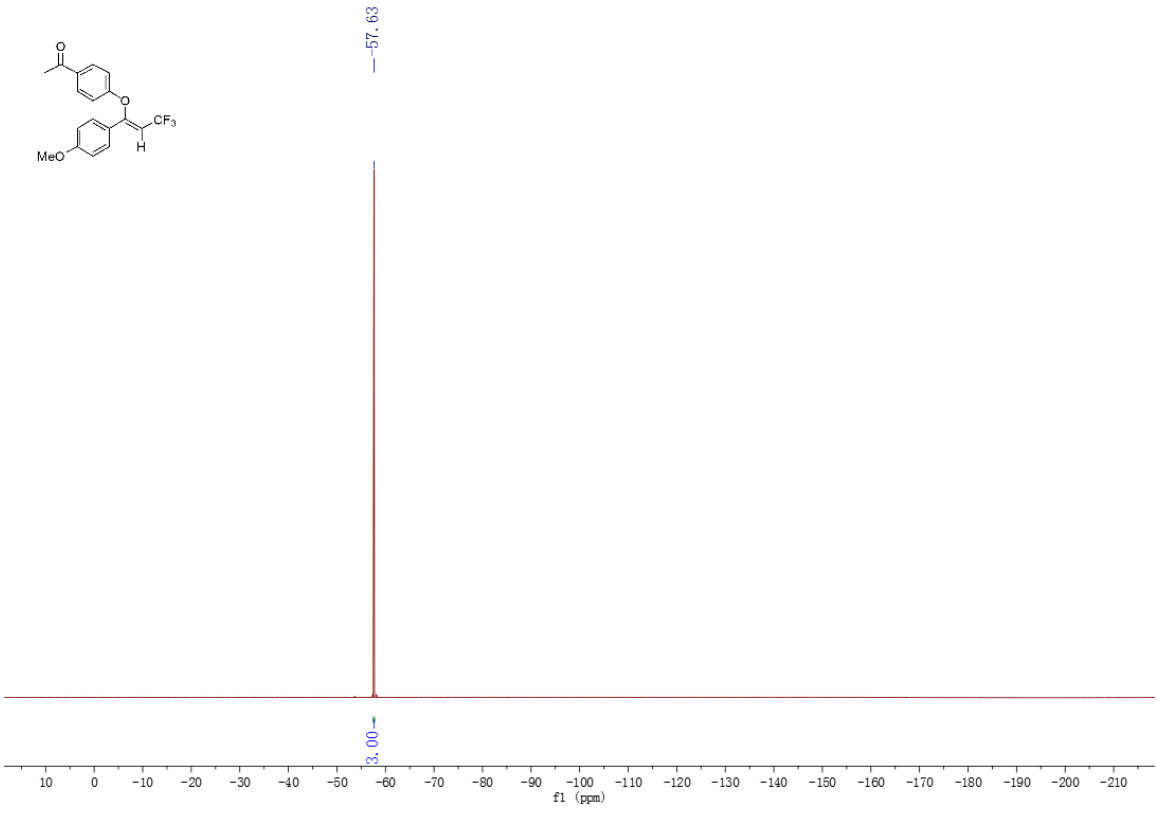


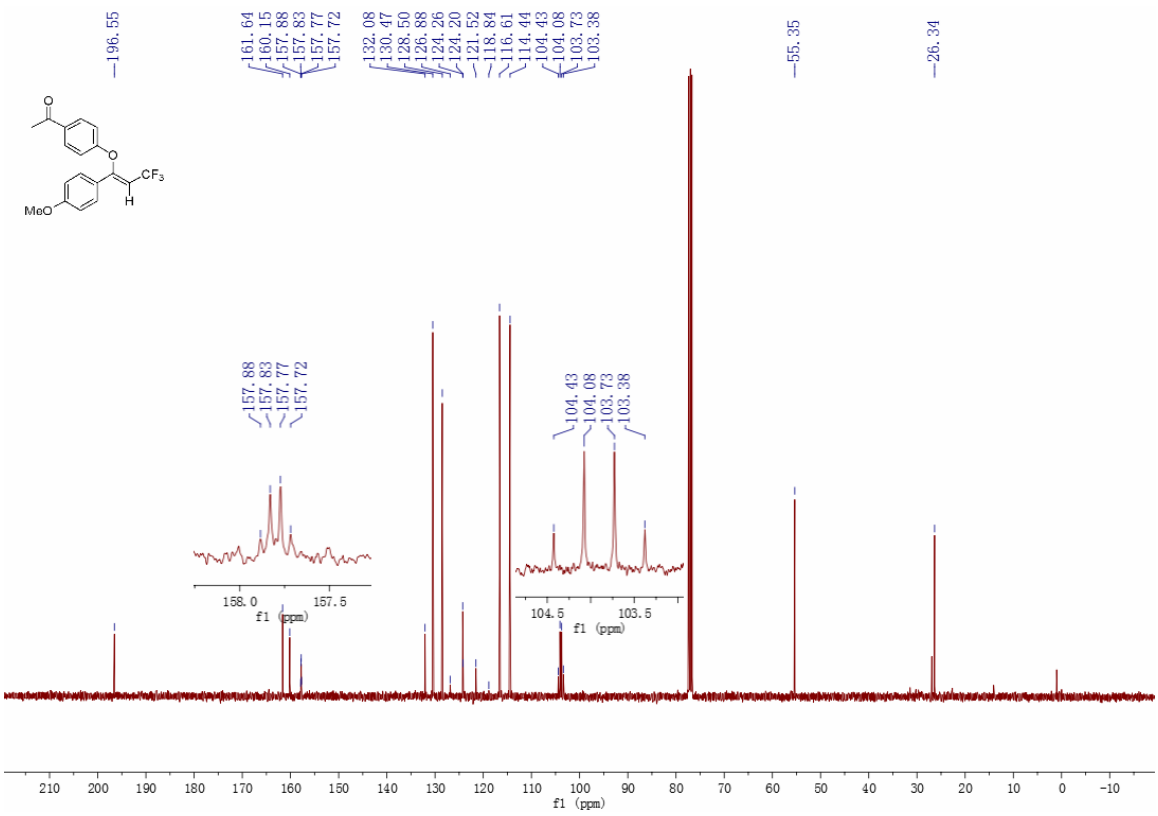



190.59
161.72
161.20
157.69
157.64
157.58
157.52
131.82
131.51
128.46
126.81
124.14
124.08
121.45
118.78
117.15
114.50
104.57
104.23
103.88
103.53
55.37
O
H
O
CF3
H
MeO
157.69
157.64
157.58
157.52
104.57
104.23
103.88
103.53
158.0
157.5
f1 (ppm)
104.5
103.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(Z)-1-(4-((3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)oxy)phenyl)ethan-1-one (5n. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

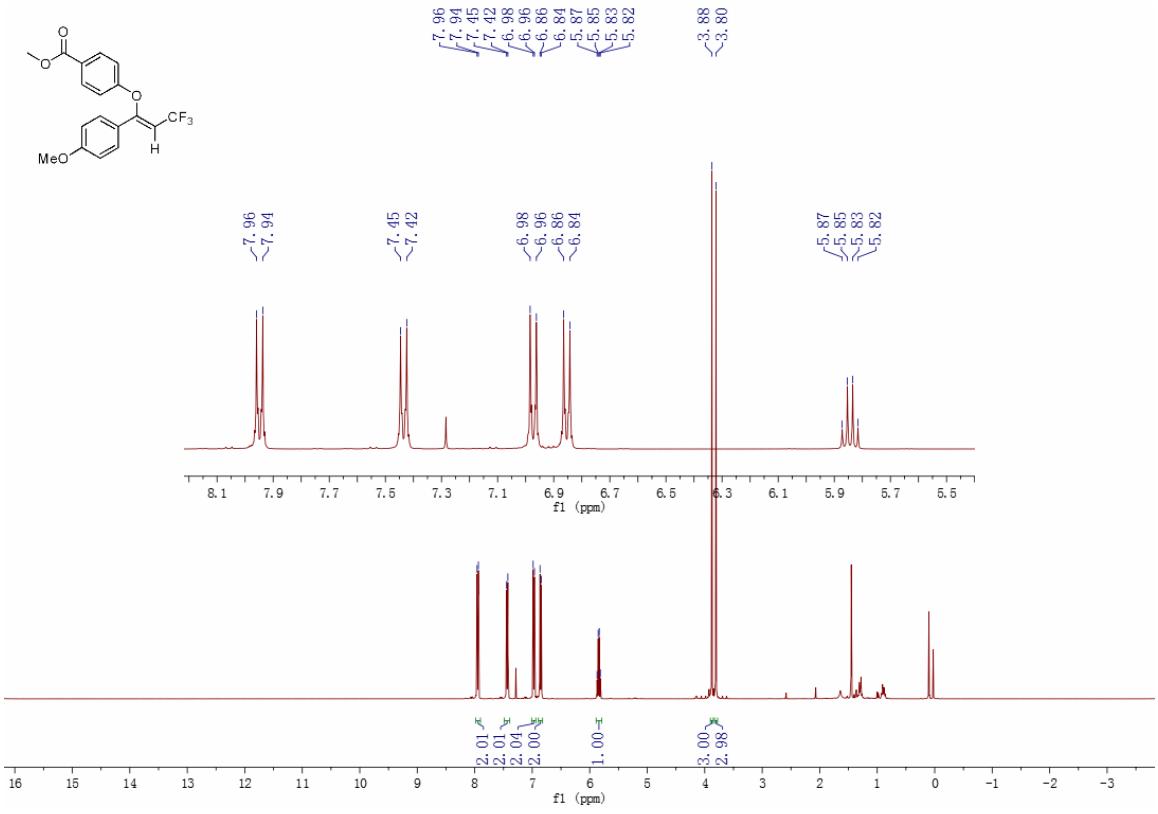


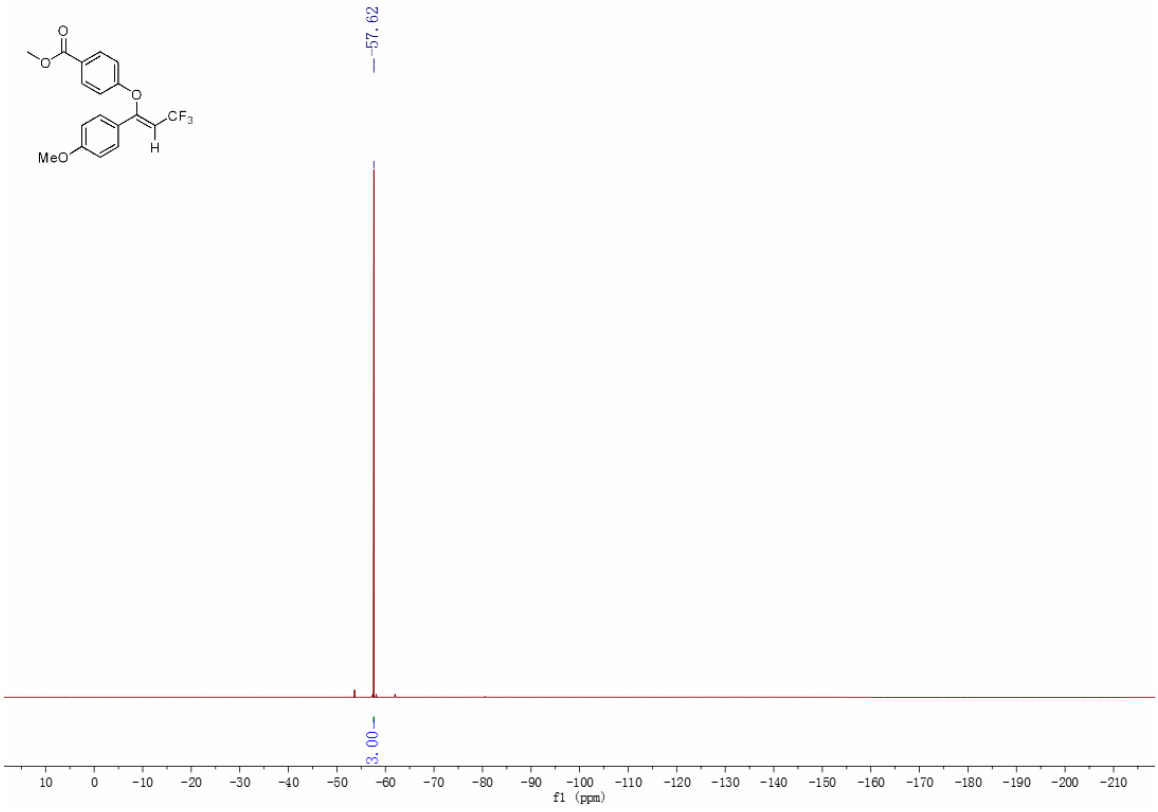


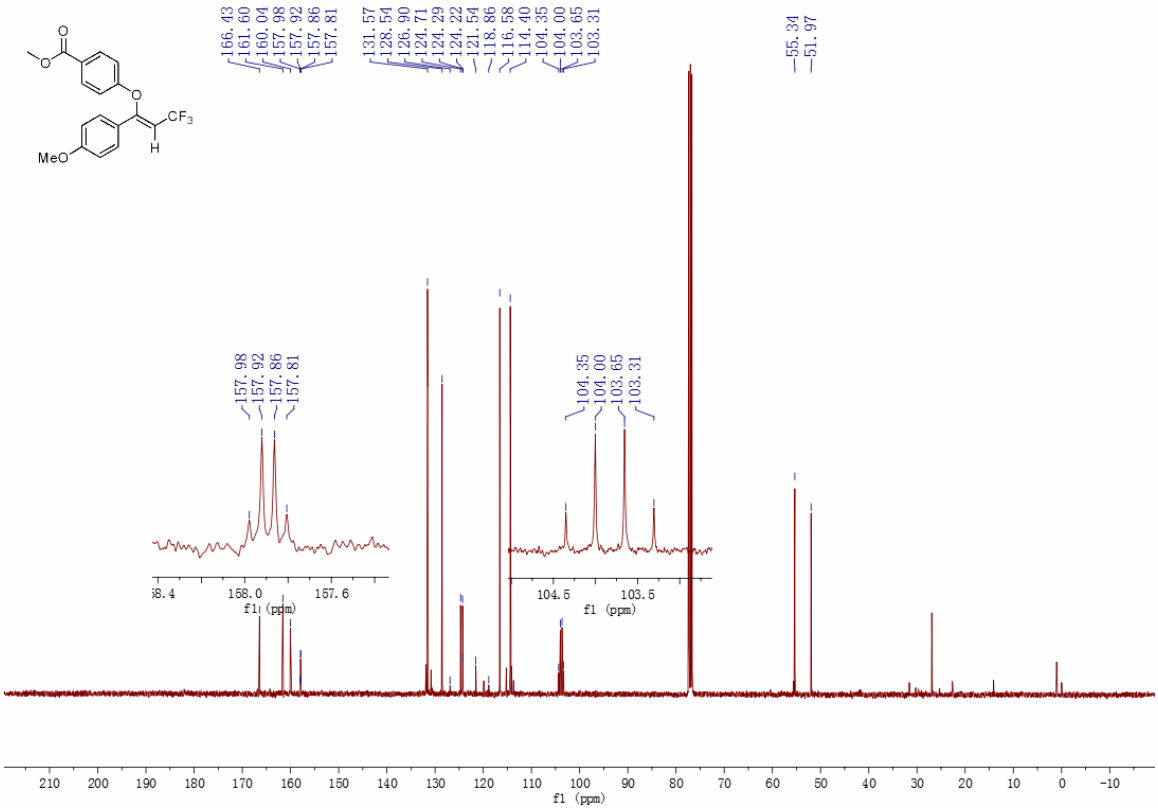

196.55
161.64
160.15
157.88
157.83
157.77
157.72
132.08
130.47
128.50
126.88
124.26
124.20
121.52
118.84
116.61
114.44
104.43
104.08
103.73
103.38
55.35
26.34
MeO
CF3
158.0
157.5
f1 (ppm)
104.5
103.5
f1 (ppm)
f1 (ppm)

Methyl (Z)-4-((3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)oxy)benzoate

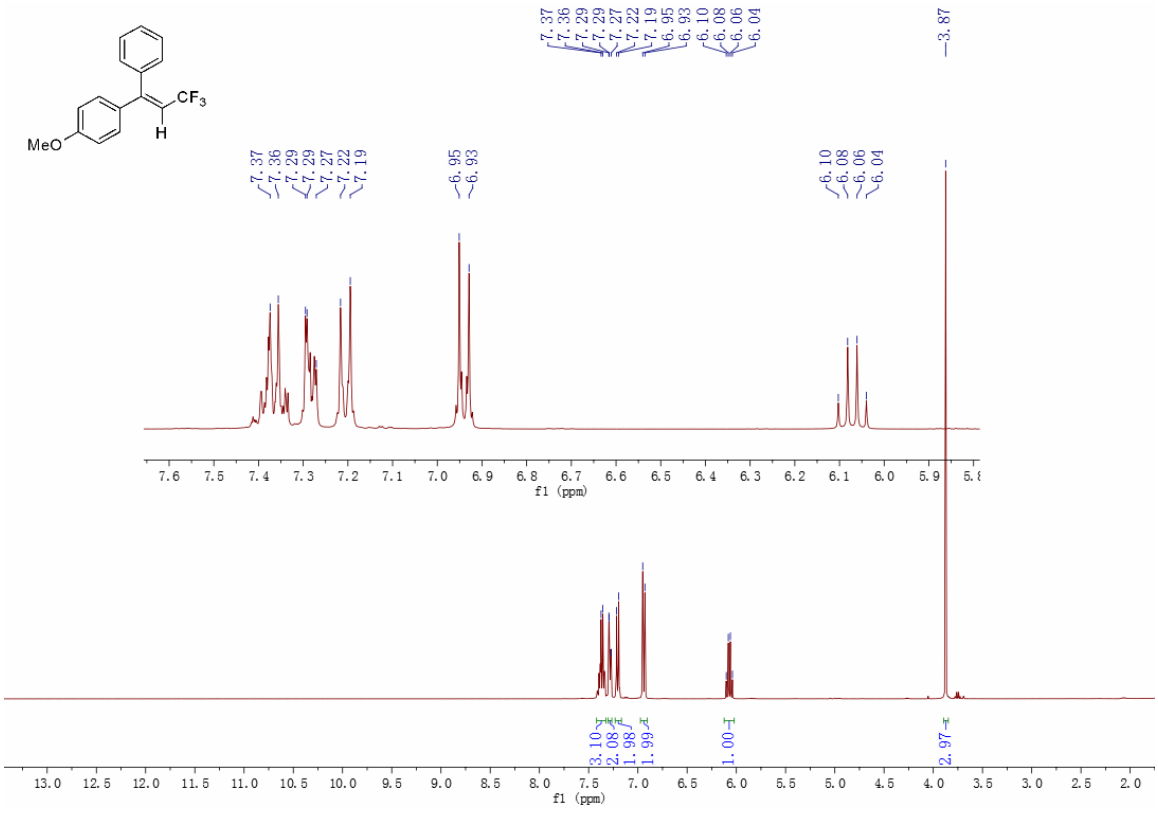
(**5o**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)

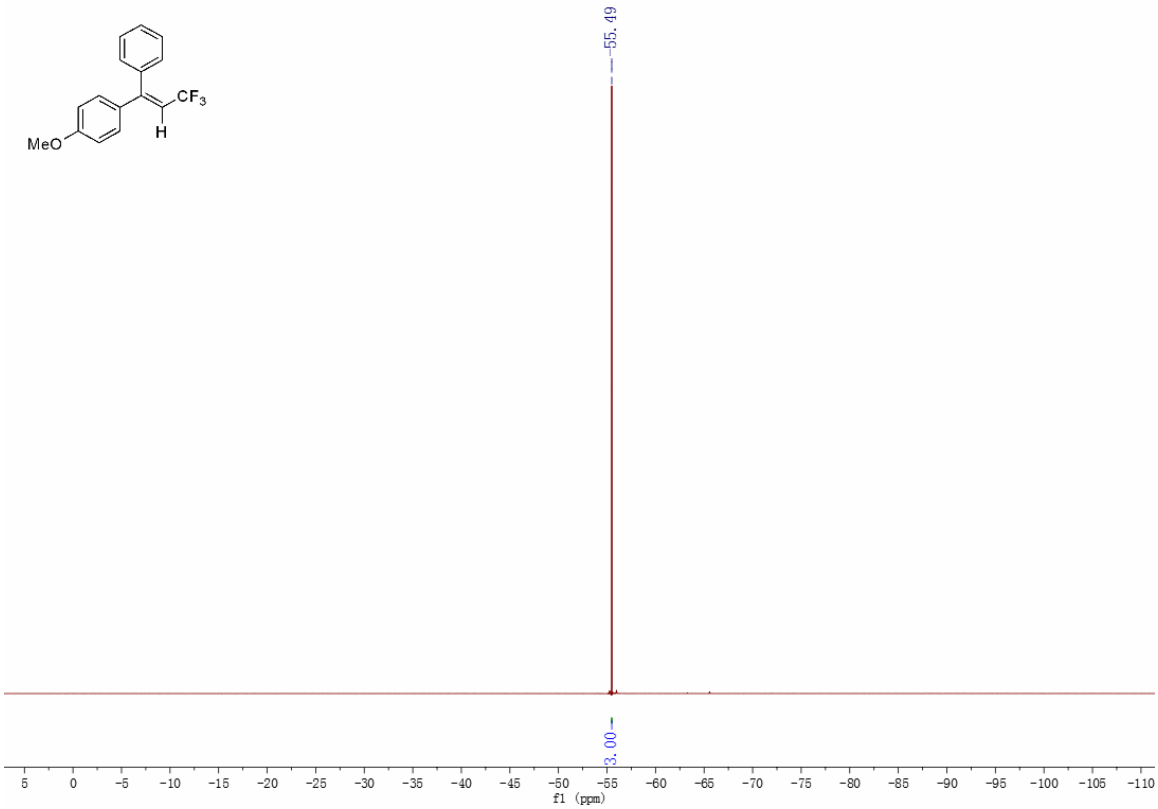


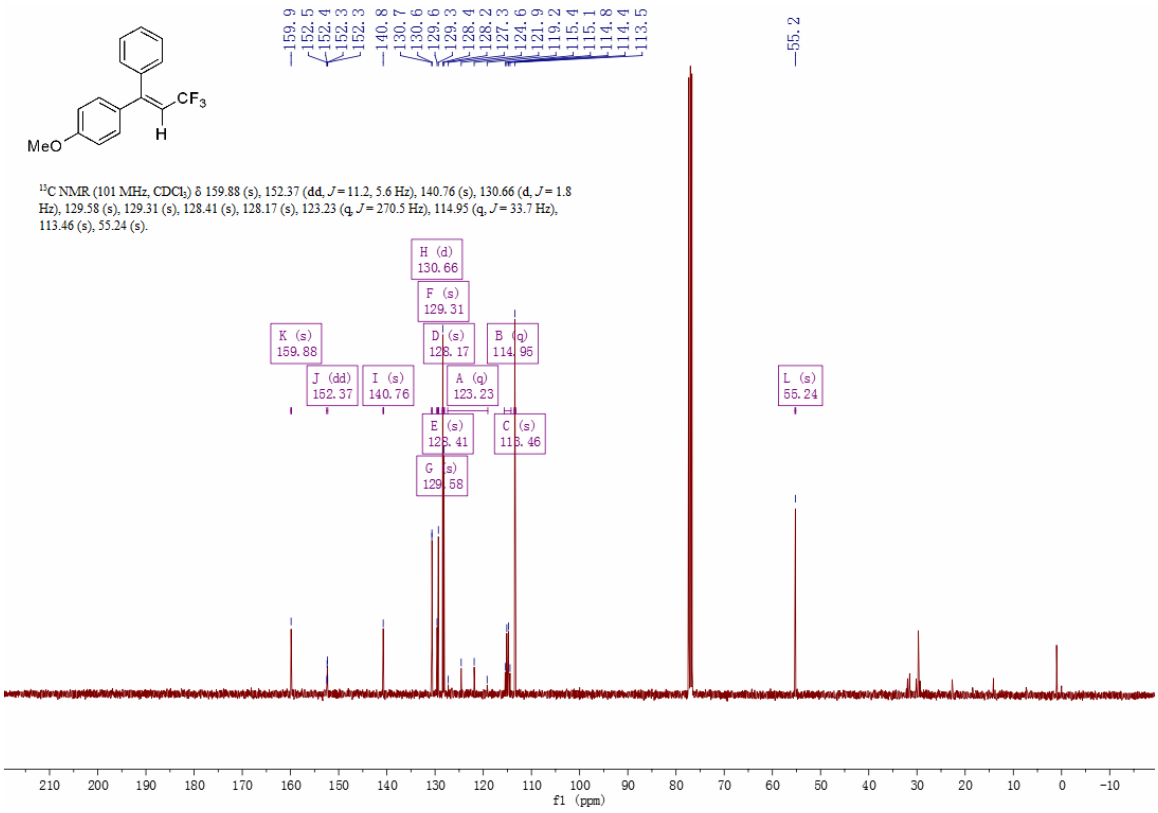



166.43
161.60
160.04
157.98
157.92
157.86
157.81
131.57
128.54
126.90
124.71
124.29
124.22
121.54
118.86
116.58
114.40
104.35
104.00
103.65
103.31
55.34
51.97
MeO
CF3
H
157.98
157.92
157.86
157.81
104.35
104.00
103.65
103.31
158.0
157.6
104.5
103.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

(E)-1-methoxy-4-(3,3,3-trifluoro-1-phenylprop-1-enyl)benzene (**7**. ^{1}H NMR 400 MHz, $CDCl_3$; ^{19}F NMR 376 MHz, $CDCl_3$; ^{13}C NMR 101 MHz, $CDCl_3$)







^{13}C NMR (101 MHz, $CDCl_3$) δ 159.88 (s), 152.37 (dd, J = 11.2, 5.6 Hz), 140.76 (s), 130.66 (d, J = 1.8 Hz), 129.58 (s), 129.31 (s), 128.41 (s), 128.17 (s), 123.23 (q, J = 270.5 Hz), 114.95 (q, J = 33.7 Hz), 113.46 (s), 55.24 (s).

5. ^{19}F NMR spectrum of the reaction mixtures in Table 1

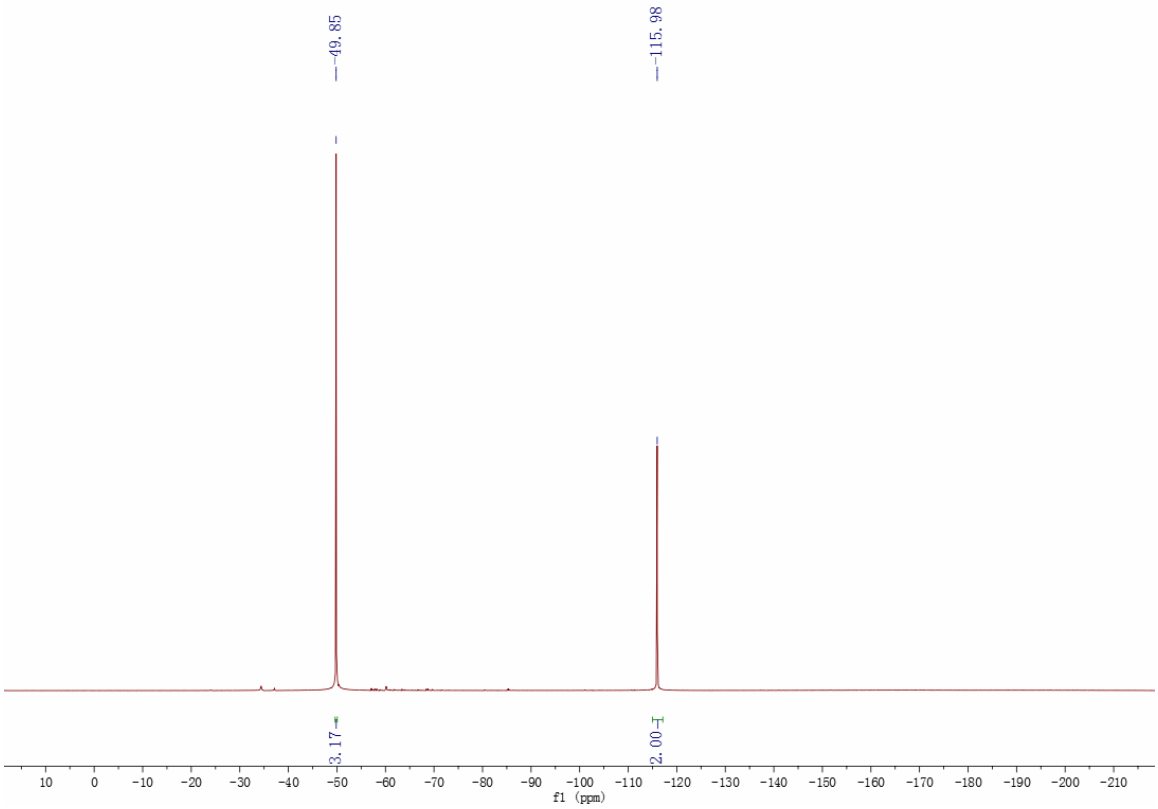


Figure S1. In the presence of NaO*t*Bu (entry 1).

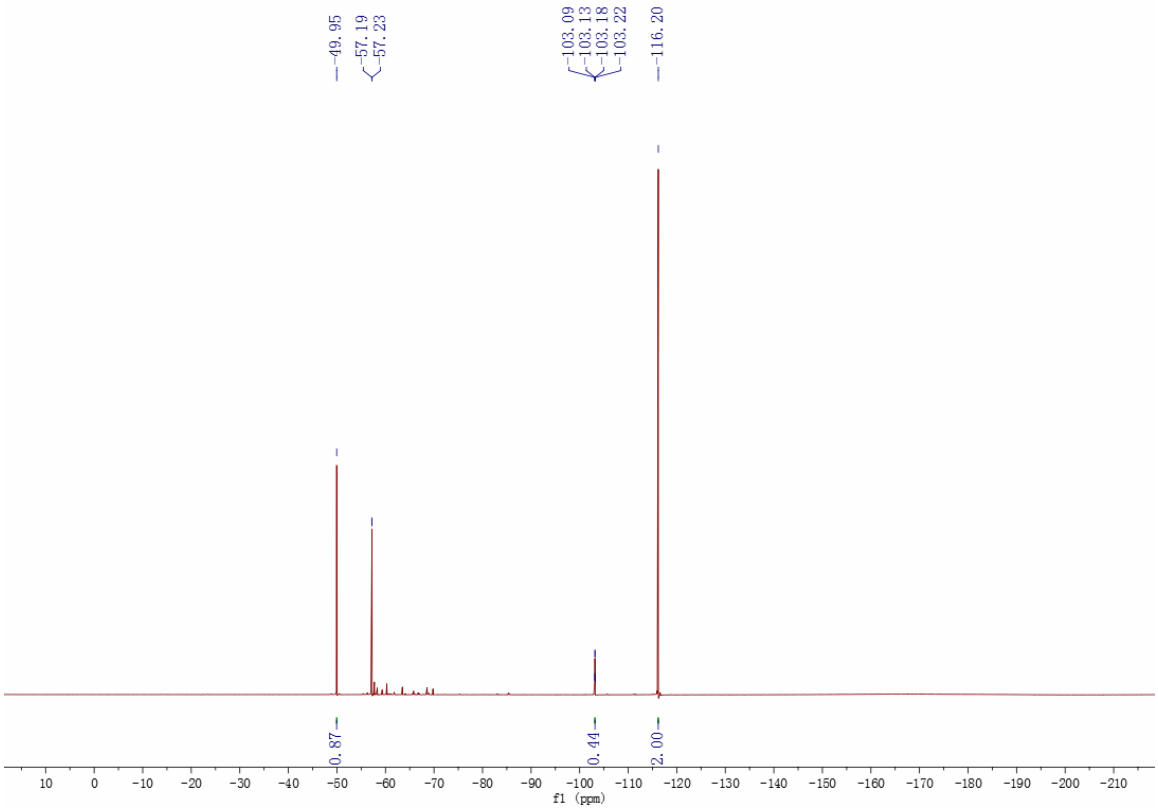


Figure S2. In the presence of KF (entry 2).

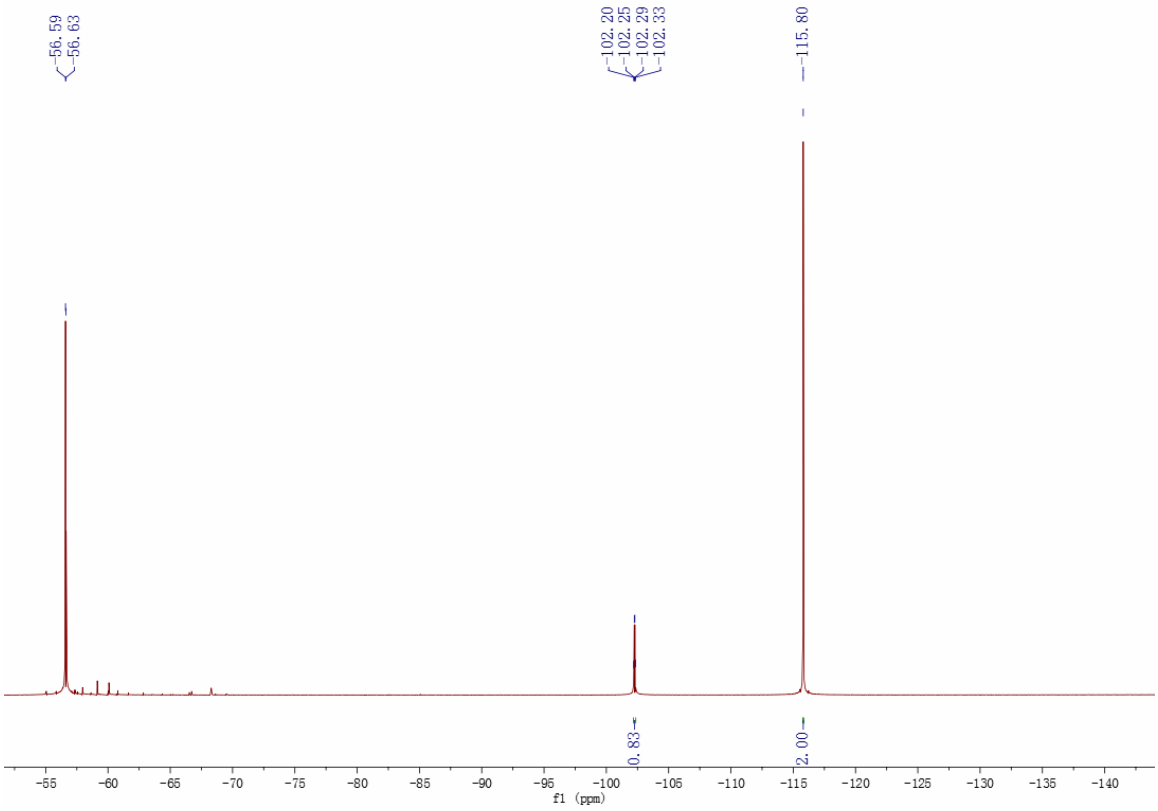


Figure S3. In the presence of CsF (entry 3).

Figures S1-S3 show the ^{19}F NMR spectra of reaction mixtures of complex **1** with *para*-methoxyphenyl acetylene (**2a**) in the presence of different salts: NaO*t*Bu, KF and CsF. For reaction conditions, please refer to Table 1 and related discussions in the main text. One equivalent of 4,4′-difluorobiphenyl (0.1 mmol) was used as the internal standard (with ^{19}F signal at *ca*. 116 ppm) to determine the NMR yield of the reactions.

6. ^{19}F NMR monitoring of reaction course of fluoro-trifluoromethylation of 2a

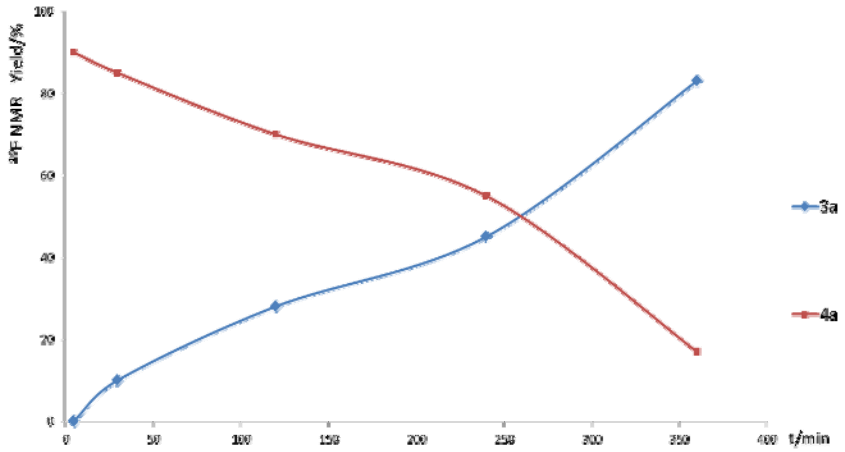


Figure S4. ^{19}F NMR monitoring of the reaction mixture in 5 mins, 0.5 hour, 2 hours, 4 hours and 6 hours.

7. Control experiments

All the control experiments were performed with one equivalent of 4,4′-difluorobiphenyl (0.1 mmol) as the internal standard (with ^{19}F signal at *ca*. 116 ppm) to determine the NMR yields of the reactions. The desired product **3a** features two signals at ca. -56 (d) and -102 (q) ppm in a 3:1 ratio. The intermediate **4a** has a singlet resonance at *ca*. -50 ppm.

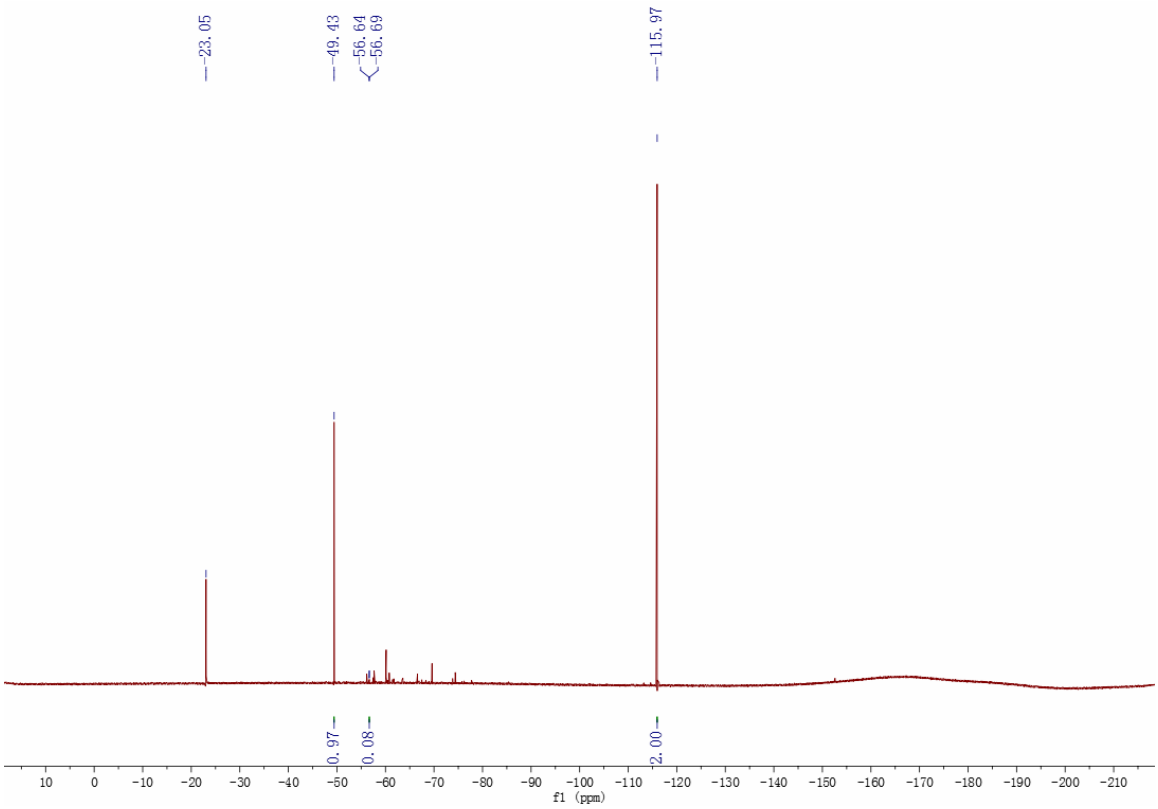


Figure S5. ^{19}F NMR spectrum of the reaction crude mixture of Eqn 1 in Scheme 7.

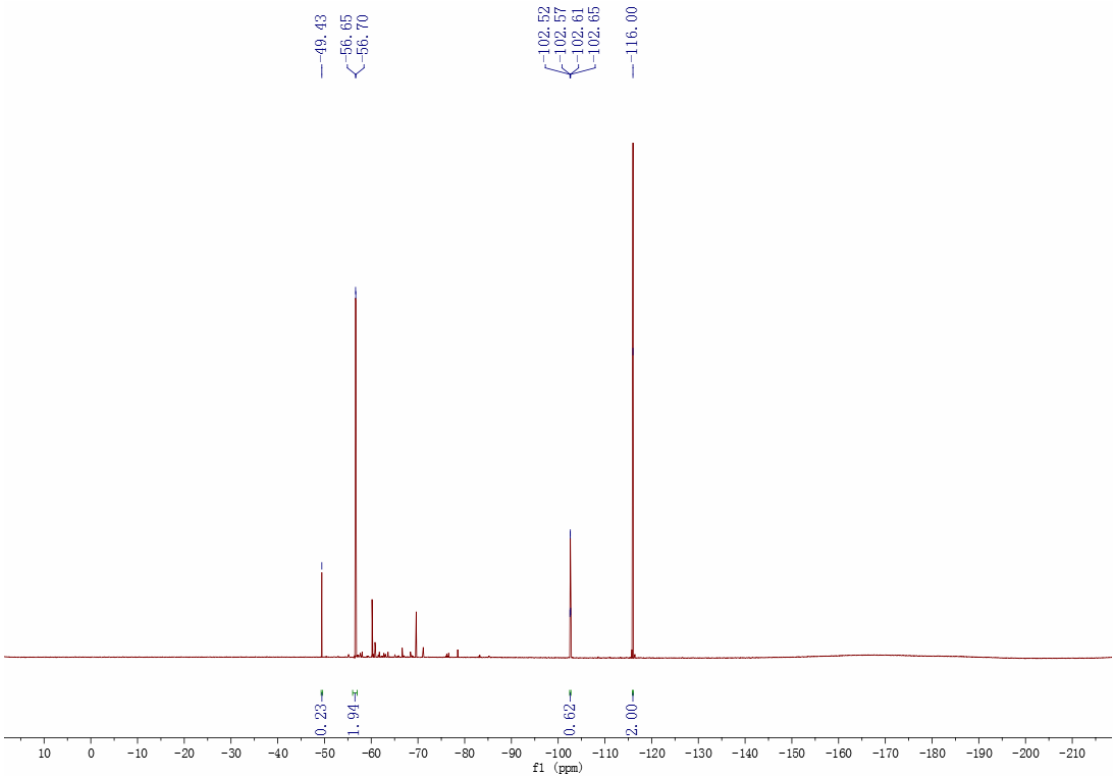


Figure S6. ^{19}F NMR spectrum of the reaction crude mixture of Eqn 2 in Scheme 7 in the presence of *t*BuOH as the proton source.

8. Radical trapping experiments

Radical trapping experiments were performed with one equivalent of 4,4′-difluorobiphenyl (0.1 mmol) as the internal standard (with ^{19}F signal at *ca*. 116 ppm) to determine the NMR yield of the reaction. The detailed reaction conditions are shown in Eqn 3 in Scheme 7 in the main text.

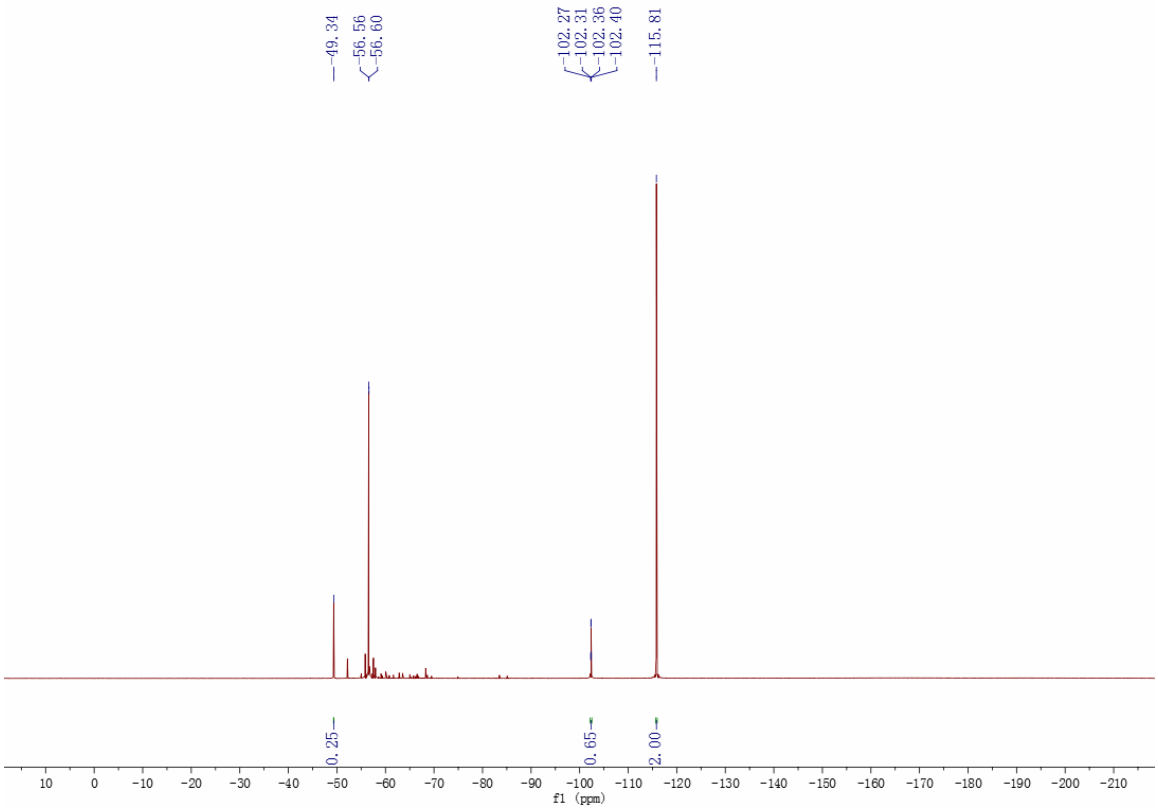


Figure S7. ^{19}F NMR spectrum of the reaction crude mixture of Eqn 3 with radical scavenger BHT.

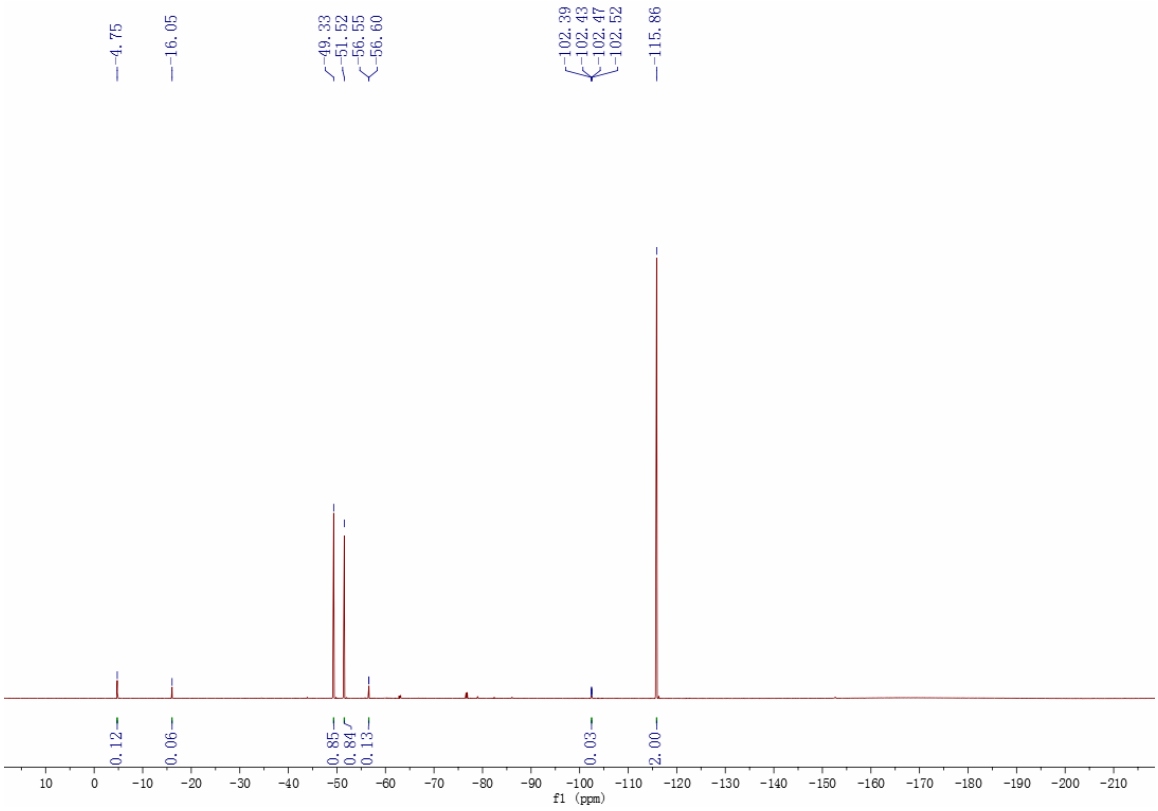


Figure S8. ^{19}F NMR spectrum of the reaction crude mixture of Eqn 3 with radical scavenger TEMPO.

As can be seen in Figure S7, in the presence of one equivalent of radical scavenger BHT, a significantly lower yield of 65% of the desired fluoro-trifluoromethylation product (**3a**) was observed. When TEMPO was present, the desired fluoro-trifluoromethylation reaction was almost completely inhibited (Figure S8).

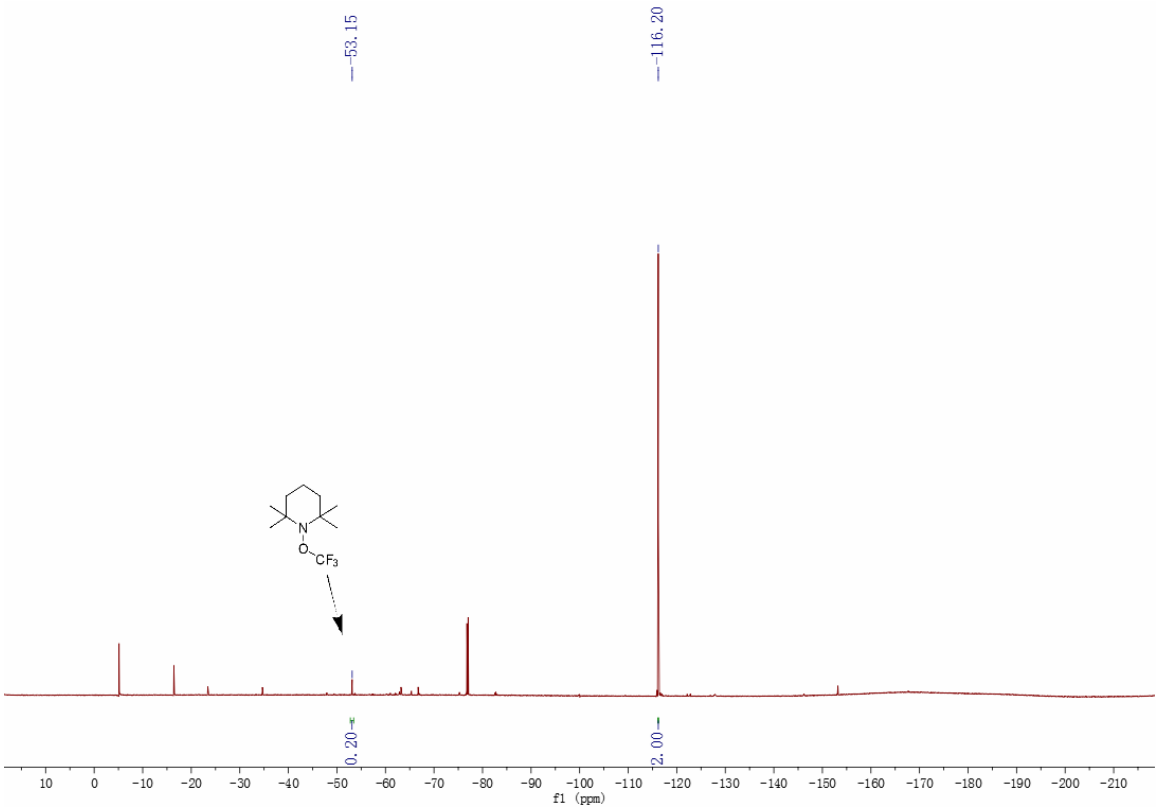


Figure S9. ^{19}F NMR spectrum of direct heating of DMF solution of **1** at 100 ^{o}C in the presence of 2 equivalents of TEMPO.

As shown by Figure S9, there are significant formation of TEMPO-CF_3 adduct (signal at *ca* -53 ppm) arising from trapping of CF_3 radical by TEMPO, which suggests the ability of CF_3 radical generation from **1** under the reaction conditions. For the assignment of TEMPO-CF_3 adduct, please refer to: Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 16410.