Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION FOR:

Photocatalytic alkene reduction by B_{12}-TiO_2 hybrid catalyst coupled with C-F bond cleavage for *gem*-difluoroolefin synthesis

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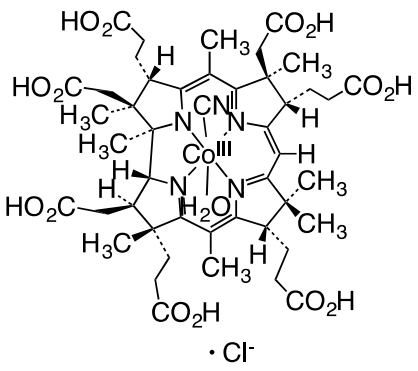
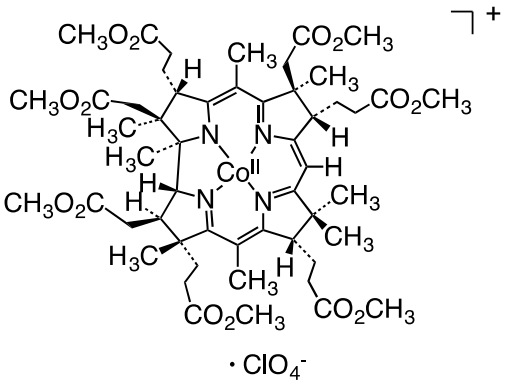
Chemicals

All solvents and chemicals used in this study were of reagent grade and were used without further purification. Deuterium methanol (CH_3OD) (99.9 % atom D) was purchased from CEA and was used as received. TiO_2 (anatase, AMT-600, surface area=52 m^2g^{-1}, diameter size=ca. 30 nm) was obtained from Tayca Co., Ltd. Pt-TiO_2 (0.15 wt% Pt loaded P-25 TiO_2; a mixture of rutile (20%) and anatase (80%), surface area= 50 m^2g^{-1}) was obtained from NSG Co., Ltd. Aquacyano cobyrinic acid (Chart S1) was synthesized by a previously reported method.[S1] Heptamethyl cobyrinate perchlorate (Chart S1) was synthesized by a previously reported method.[S2,3] The substrate, α-trifluoromethyl styrene (**1**) and an authentic sample of 3,3,3-trifluoropropylbenzene (**25**) were purchased from Wako Chemical Industries, Ltd. The authentic sample of α-trifluoromethyl ethylethylbenzene (**3**) was purchased from Fluorochem. Alfusone^R as an F^- quantification reagent was purchased from DOJINDO.



Cyanoaqua cobyrinic acid



Heptamethyl cobyrinate perchlorate

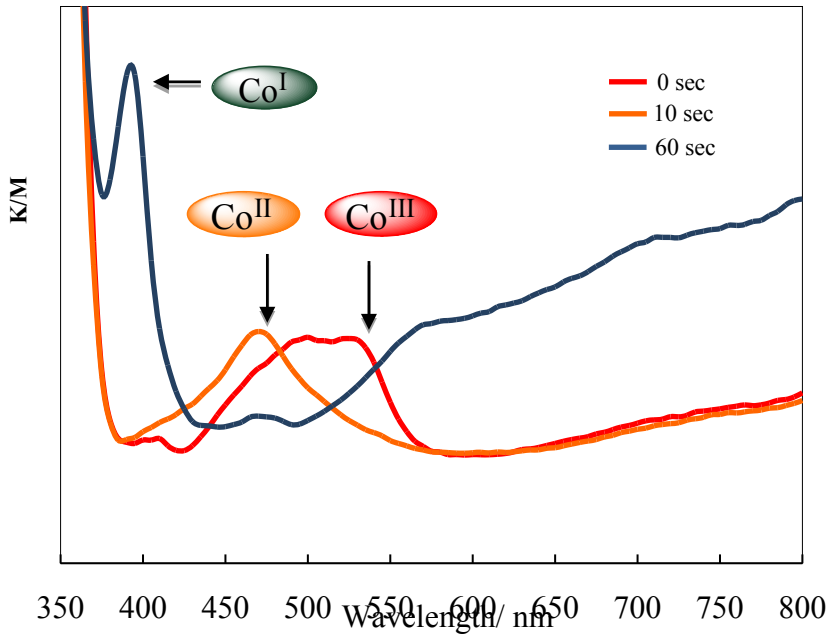
Chart S1.

Measurements

The NMR spectra were recorded by Bruker Avance 500 and 300 spectrometers at the Center of Advanced Instrumental Analysis of Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. The GC-

mass spectra were obtained using a Shimadzu GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μm). The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer at room temperature. The diffuse reflectance (DR) UV-vis reflectance spectra were measured by a Hitachi U-3300 spectrophotometer equipped with a Φ 60 integrating sphere at room temperature under nitrogen. The ESR spectra were obtained using a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter at room temperature. The cyclic voltammograms (CV) were obtained using a BAS CV 50W electrochemical analyzer. A three-electrode cell equipped with 3-mm diameter glassy carbon wires as the working and platinum counter electrodes was used. An Ag/AgCl (3.0 M NaCl) electrode served as the reference. The $E_{1/2}$ value of the ferrocene–ferrocenium (Fc/Fc^{+}) was 0.45 V *vs*. Ag/AgCl with this setup.

(a)



(b)

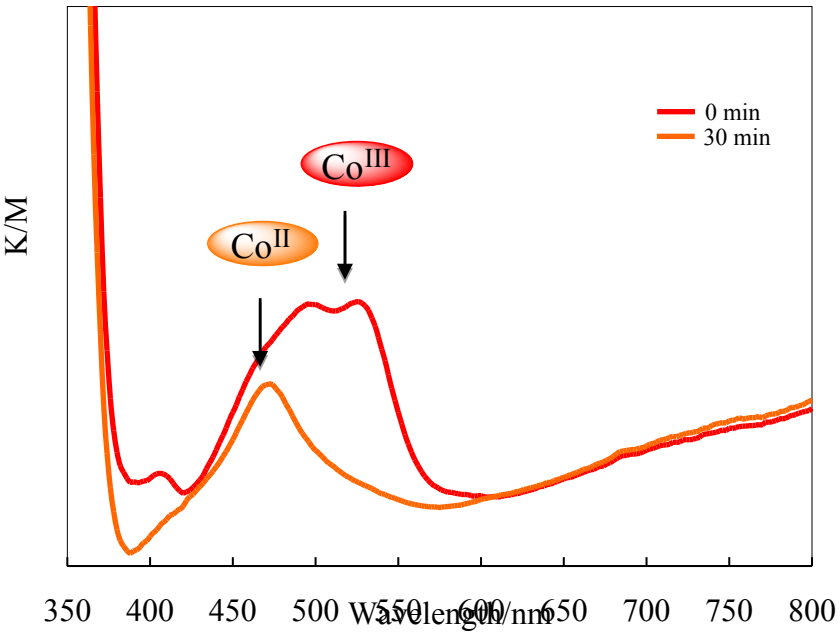


Fig S1. Diffuse reflectance (DR) UV-VIS spectral change of the B_{12}-TiO_2 during UV light irradiation in the absence (a) and in the presence of (b) **1** in MeOH under N_2.

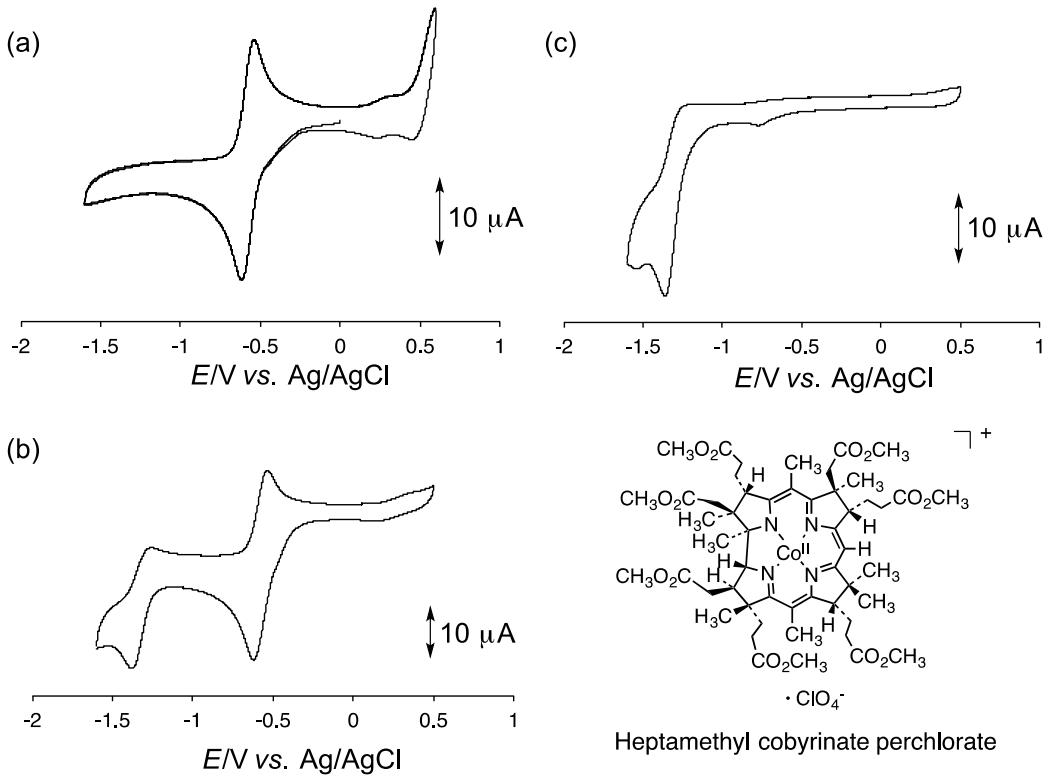


Fig. S2. CVs of B_{12}, heptamethyl cobyrinate perchlorate (1mM), in CH_3CN containing of 0.1 M *n*-Bu_4NClO_4 under N_2 (a) and in the presence of 0.2 M of **1** (b). CV of **1** (c).

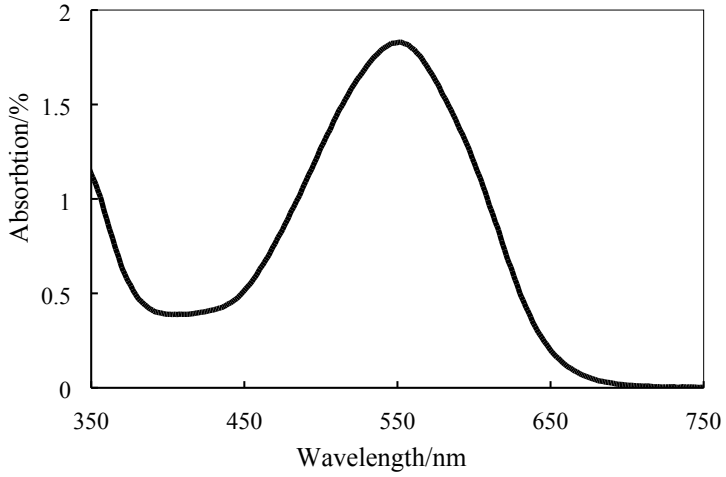
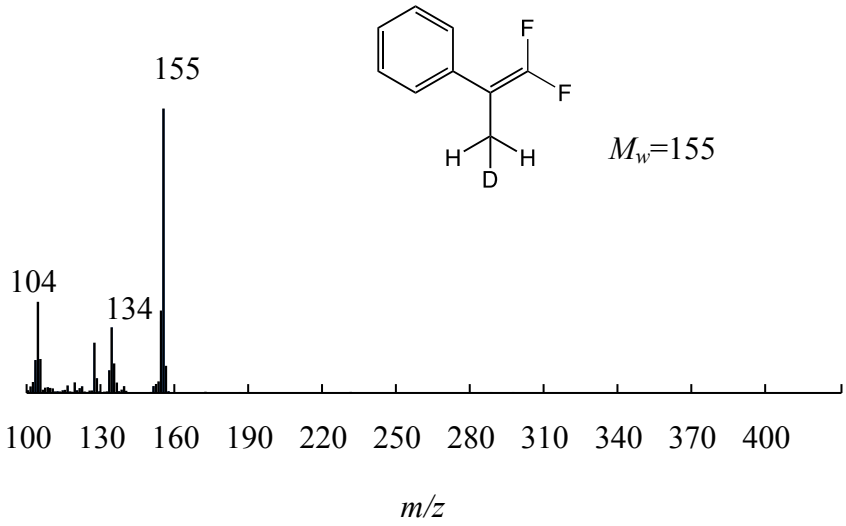


Fig. S3. UV-VIS spectrum for F^- quantification after catalytic reaction of entry 1 in Table 1.

(a)



(b)

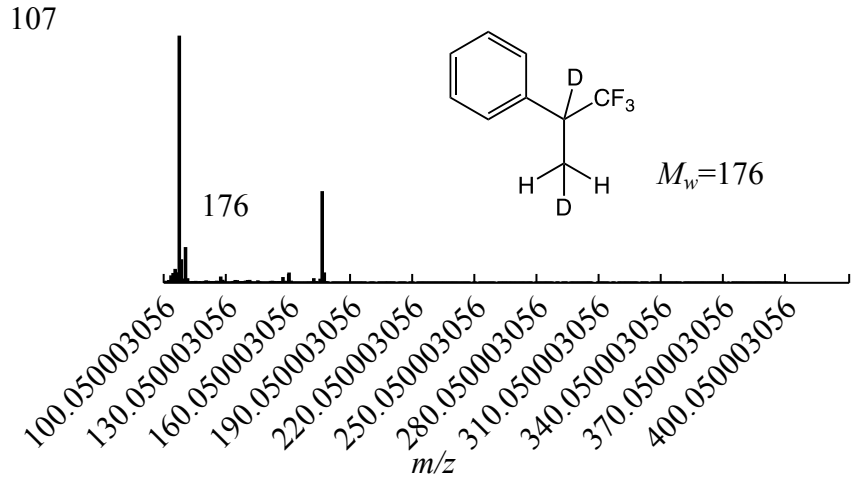


Fig. S4. GS-MS of products from **1** in CH_3OD, *gem*-difluoroolefin (**2-d$_1$**) (a) and reduced product (**3-d$_2$**) (b).

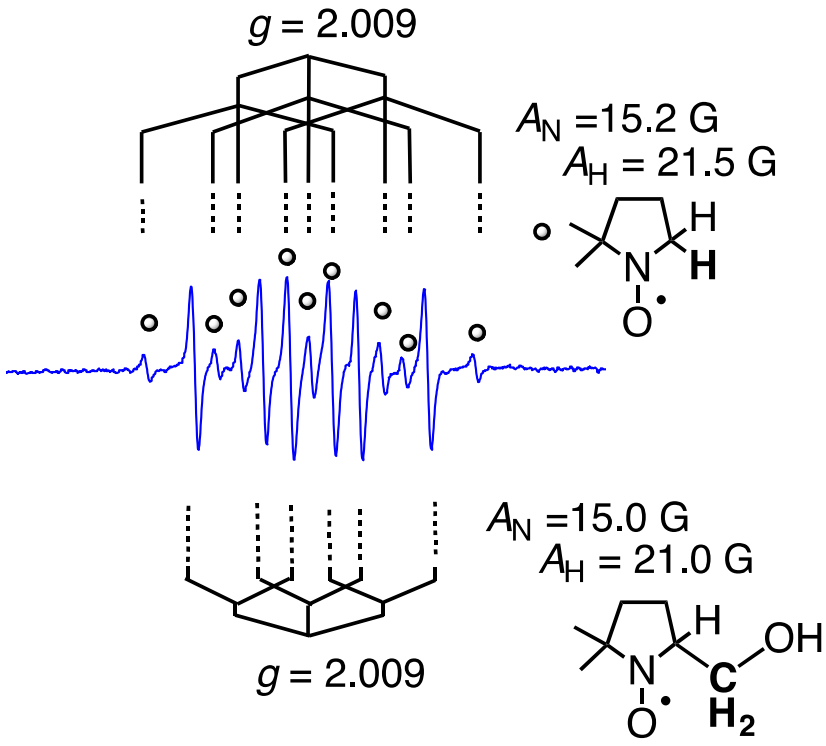


Fig. S5. ESR spectra observed during the UV light irradiation of the B_{12}-TiO_2 without **1**; [DMPO]=1 M, 2 mg of B_{12}-TiO_2 under N_2 at room temperature in MeOH.

General procedure for catalytic reaction by the B_{12}-TiO_2

A mixture of an alkene (**1**) (4.1 mg, 4 mM) and B_{12}-TiO_2 (anatase, AMT-600, 10 mg, B_{12}=1.60x10^{-5} M) was stirred in 6 mL of CH_3OH under nitrogen. After the solution was stirred for 24 hours during irradiation by 365 nm UV light (black light, 10 cm distance), the B_{12}-TiO_2 was removed by filtration. The resulting solution was analyzed by GC-MS and yields of the products were calculated by comparison to the ratio of the peak area using diphenyl as an internal standard.

F^- Quantification experiment

First, a 5% Alfusone^R aqueous solution and 0.001 mg F^-/mL sodium fluoride aqueous solution were prepared. The 5% Alfusone^R aqueous solution (5 mL), acetone (20 mL) and 0.001 mg F^-/mL sodium fluoride aqueous solution (0 mL, 1 mL, 2 mL, 3 mL, 4 mL, 5 mL) were mixed and diluted to 50 mL by water. After 1 hour, the UV-vis absorbance was measured at 620 nm to make the calibration curve. F^- generated from the catalytic reaction was then quantified by the same method according to the calibration curve.

ESR spin-trapping experiment

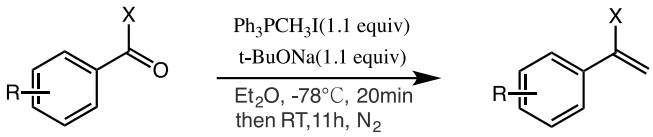
The ESR spectra for the DMPO spin-adducts were observed after 1 hour of UV-light irradiation of B_{12}-TiO_2 (2 mg) in the presence of **1** (9.4 mM) and DMPO (1.0 M) in 2 mL of MeOH or MeOD under nitrogen at room temperature. The settings for the ESR measurements were a frequency of 9.78 GHz, power of 1.0 mW, a center field of 3515 G, a sweep width of 150 G, a modulation amplitude of 5.0 G, a time constant of 40 ms, and a sweep time of 20 s.

DR-UV-VIS measurement

The DR-UV-VIS spectral change for the B_{12}-TiO_2 with substrate **1** (0.06 M) during UV-light irradiation was observed from the B_{12}-TiO_2 (4mg) suspended methanol (5mL) solution under nitrogen at room temperature.

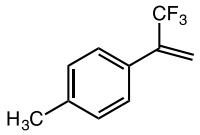
[Preparation of substrates]

Preparation of *α*-(tri/difluoromethyl) styrenes



The compounds were prepared according to a previously described procedure.[S4] To a diethyl ether solution (5 mL) of Ph_3PCH_3I (1.055 mmol), *t*-BuONa (1.055 mmol) was added at 0°C. The reaction mixture was stirred for 30 min at room temperature, then cooled to -78°C. To the mixture was slowly added a diethyl ether solution (2 mL) of tri/difluoroacetophenones (0.9589 mmol) at -78°C over 10 min. The mixture was gradually warmed to room temperature and stirred for 11h, then saturated aqueous NH_4Cl was added. The organic materials were extracted three times with Et_2O. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane) and further distillation under reduced pressure to give the products.

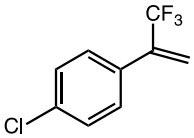
α-Trifluoromethyl-*p*-methyl styrene (4)



For the preparation of *α*-trifluoromethyl-*p*-methyl styrene, 4'-methyl-2,2,2-trifluoroacetopheneone was used as the reactant.

Colorless liquid, yield (26%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 and 7.20 (A_2B_2, J=10 Hz, 4H), 5.91 (s, 1H), 5.74 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.85 (q, J=30 Hz), 138.98, 130.84, 129.27, 127.27, 122.37 (q, J=272.5 Hz), 119.56 (q, J=6.25 Hz), 21.26. ^{19}F NMR (282 MHz, $CDCl_3$): δ -65.98; GC-MS: M^+=186.

α-Trifluoromethyl-*p*-chloro styrene (13)

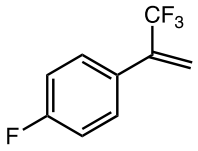


For the preparation of *α*-trifluoromethyl-*p*-chloro styrene, 4'-chloro-2,2,2-trifluoroacetopheneone was used as the reactant.

Colorless liquid, yield (65%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.37 (m, 4H), 5.98 (s, 1H), 5.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.05 (q, J=30 Hz), 135.24, 132.11,

128.86, 128.80, 120.90 (q, *J*=272.5 Hz), 120.81 (*q*, *J*= 5Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.13; GC-MS: M^+=206.

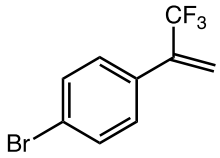
α-Trifluoromethyl-*p*-fluoro styrene (10)



For the preparation of α-trifluoromethyl-*p*-fluoro styrene, 4'-fluoro-2,2,2-trifluoroacetopheneone was used as reactant.

Colorless liquid, yield (20%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 and 7.07 (A_2B_2, *J*=5 Hz, 4H), 5.95 (s, 1H), 5.73 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.21, 162.23, 138.34 (q, *J*=30 Hz), 129.42 (d, *J*=8.75Hz), 124.32 (q, *J*=272.5Hz), 120.50 (*q*, *J*= 6.25Hz), 115.71(d, *J*=22.5Hz); GC-MS: M^+=190.

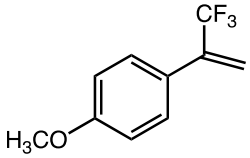
α-Trifluoromethyl-*p*-bromo styrene (16)



For the preparation of α-trifluoromethyl-*p*-bromo styrene, 4'-bromo-2,2,2-trifluoroacetopheneone was used as reactant.

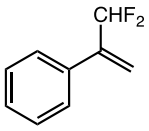
Colorless liquid, yield (44%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 and 7.33 (A_2B_2, *J*=10 Hz, 4H), 5.98 (s, 1H), 5.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.36(q, *J*=30Hz), 132.59, 131.84, 129.06, 124.18(q, *J*=272.5Hz), 123.43, 120.90 (q, *J*=6.25Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.12; GC-MS: M^+=250.

α-Trifluoromethyl-*p*-methoxy styrene (7)



For the preparation of α-trifluoromethyl-*p*-bromo styrene, 4'-methoxy-2,2,2-trifluoroacetopheneone was used as reactant.

Colorless liquid, yield (33%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 and 6.91 (A_2B_2, *J*=5Hz, 4H), 5.87 (d, *J*=5Hz, 1H), 5.70 (d, *J*=5Hz, 1H). 3.83 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.21, 138.59(q, *J*=30Hz), 128.67, 126.09, 124.58(q, *J*=272.5Hz), 118.85 (q, *J*=5Hz), 114.00, 55.33. ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.03; GC-MS: M^+=202.

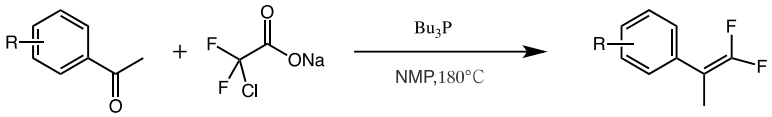
α-Difluoromethyl styrene (19) 

For the preparation of α-difluoromethyl styrene**,** 2,2-difluoroacetophenone was used as the reactant.

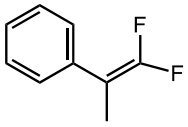
Colorless liquid, yield (60%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49-7.37 (m, 5H), 6.40 (t, J=55 Hz, 1H), 5.73 (t, J=5 Hz, 1H), 5.67 (t, J=2.5Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.13 (t, J=20 Hz), 134.83, 128.64, 128.59, 126.99, 118.84 (t, J=10 Hz), 115.40 (t, J=237.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -114.49 (d, J=54 Hz); GC-MS: M^{+}=154.

[Preparation of authentic samples of products]

Preparation of β, β-difluoro-α-methyl styrenes



The compounds were prepared according to a procedure analogous to that previously described.[S5] To a stirred hot (180° bath) solution of 0.012 mol of the ketone, 0.0132 mol of tributylphosphine and 2mL of *N*-methylpyrrolidone, was added dropwise from an equilibrating dropping funnel over a period of about 30 min, a warm (60°) solution of 0.024 mol of sodium chlorodifluoroacetate in 10mL *N*-methylpyrrolidone. The flask contents were distilled at 85°C, and the fractional distillations were further purified by silica gel column chromatography to give the corresponding products.

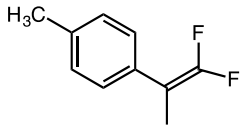
β, β-Difluoro-α-methyl styrene (2) 

For preparation of the β, β-difluoro-α-methyl styrenes, acetophenone was used as the reactant.

Colorless liquid, yield (10%); ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 7.46-7.31(m, 5H), 2.00 (t, J=5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.52 (dd, J=284.4, 287.5 Hz), 134.97 (t, J=3.75 Hz), 128.39, 127.53 (t, J=3.75Hz), 127.09, 87.51(dd, J=15, 22.5 Hz),

13.26. ^{19}F NMR (282 MHz, $CDCl_3$): δ -91.46 (dq, J=47.94, 2.82 Hz), -91.73 (dq, J=47.94, 2.82 Hz); GC-MS: M^+=154.

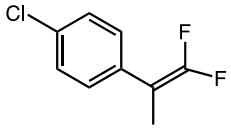
4-Methyl-β, β-difluoro-α-methyl styrene (5)



For preparation of the 4-methyl-β, β-difluoro-α-methyl styrene, *p*-acetyltoluene was used as the reactant.

Colorless liquid, yield (28%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.26-7.16(m, 4H), 2.35 (s, 3H), 1.95 (t, J=5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.41 (dd, J=287.5, 287.5 Hz), 136.82, 131.97 (t, 3.75 Hz), 129.08, 127.38 (t, 3.75Hz), 87.29 (dd, J=21.25, 22.5 Hz), 21.08, 13.28; ^{19}F NMR (282 MHz, $CDCl_3$): -92.29 (dd, J=46.53, 2.82 Hz), -90.75 (dd, J=46.53, 2.82 Hz); GC-MS: M^+=168.

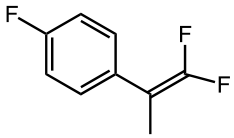
4-Chloro-β, β-difluoro-α-methyl styrene (14)



For preparation of the 4-chloro-β,β-difluoro-α-methyl styrene, *p*-chloroacetophenone was used as the reactant.

Colorless liquid, yield (16%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.33-7.28 (m, 4H), 1.95 (t, J=2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.54 (dd, J=285, 290 Hz), 133.37 (t, J=3.75 Hz), 132.93, 128.80 (t, J=3.75 Hz), 128.59, 86.78 (dd, J=14, 22.5 Hz), 13.15; ^{19}F NMR (282 MHz, $CDCl_3$): -90.75 (dq, J=42.3, 2.82Hz), -91.2 (dq, J=42.3, 2.82 Hz); GC-MS: M^+=188.

4-Fluoro-β, β-difluoro-α-methyl styrene (11)

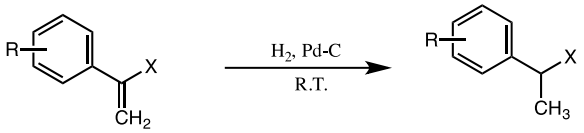


For the preparation of 4-fluoro-β,β-difluoro-α-methyl styrene, *p*-fluoroacetophenone was used as reactant.

Colorless liquid, yield (15%); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 and 7.07 (A_2B_2, J=5Hz, 4H), 1.98 (t, J=5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.76, 160.80, 129.18 (t, J=7.5 Hz), 115.41, 115.24, 86.82 (dd, J=15, 23.75 Hz), 13.15; GC-MS:

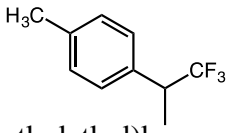
M^+=172.

Preparation of (tri or difluoro-1-methylethyl)benzenes



α-(Tri or difluoromethyl) styrenes (0.49 mmol), Pd-C (30mg), MeOH (10mL) and THF (5 mL) were placed in a reactor. After degassing, H_2 gas filled the reactor. The solution was then stirred at room temperature for 3 hours. The solution was purified by filtration and the solvent was removed under reduced pressure.

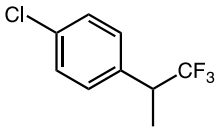
4-Methyl-(2,2,2-trifluoro-1-methylethyl)benzene (6)



For preparation of the 4-methyl-(2,2,2-trifluoro-1-methylethyl)benzene, 4-methyl-1-(trifluoromethyl)vinylbenzene was used as the reactant.

Colorless liquid, yield (92%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 and 7.17(A_2B_2, J=7.5 Hz, 4H), 3.44-3.37 (m, 1H), 2.35(s, 3H), 1.48 (d, J=10 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.82, 133.53 (d, 1.25 Hz), 129.31, 128.37, 126.17, 43.75 (q, 27.5 Hz), 21.06, 14.64 (q, 2.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -72.85 (d, 11.28 Hz); GC-MS: M^+=188.

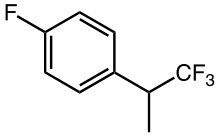
4-Chloro-(2,2,2-trifluoro-1-methylethyl)benzene (15)



For preparation of the 4-chloro-(2,2,2-trifluoro-1-methylethyl)benzene, 4-chloro-1-(trifluoromethyl)vinylbenzene was used as the reactant.

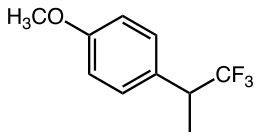
Colorless liquid, yield (90%); ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 7.46-7.42(m, 4H), 3.77-3.72 (m, 1H), 1.50 (d, J= 5Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.85 (d, 2.5Hz), 134.07, 129.85, 128.82, 127.98, 43.53 (q, 27.5 Hz), 14.52 (q, 2.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -72.90 (d, 11.28 Hz) ; GC-MS: M^+=206.

4-Fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene (12)



For the preparation of 4-fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene, 4-fluoro-1-(trifluoromethyl)vinylbenzene was used as reactant.

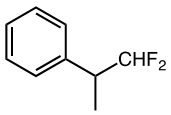
Colorless liquid, yield (60%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 and 7.04 (A_2B_2, J=5 Hz, 4H), 3.45-3.38 (m, 1H), 1.50(d, J= 5Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.56, 161.60, 130.15, 128.12(q, J= 277.5Hz), 115.63(d, J= 22.5Hz), 43.67(q, J= 27.5Hz), 14.68; ^{19}F NMR (282 MHz, $CDCl_3$): -115.48, -73.04; GC-MS: M^+=192.



4-Methoxy-(2,2,2-trifluoro-1-methylehtyl)benzene (9)

For the preparation of 4-methoxy-(2,2,2-trifluoro-1-methylehtyl)benzene, 4-methoxy-1-(trifluoromethyl)vinylbenzene was used as reactant.

Colorless liquid, yield (99%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 and 6.89 (A_2B_2, J=5 Hz, 4H), 3.41-3.36 (m, 1H), 1.49(d, J= 10Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.44, 129.56, 128.54, 128.40(q, J= 277.5 Hz), 114.05, 55.29, 43.53(q, J= 2.5Hz), 14.65; GC-MS: M^+=204.

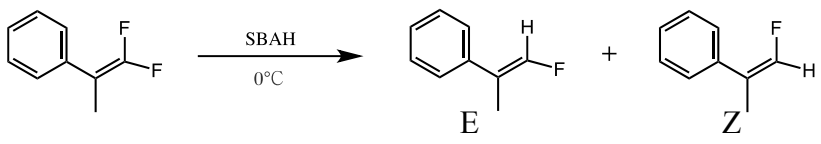


2,2-Difluoro-1-methylethylbenzene (22)

For preparation of the (2,2-difluoro-1-methylethyl)benzene, (3,3-difluoroprop-1-en-2yl)benzene was used as the reactant.

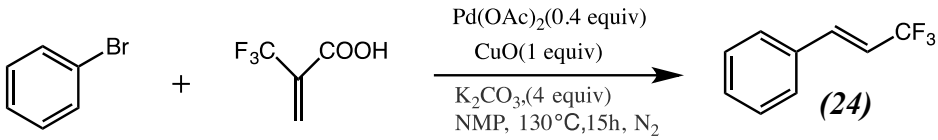
Colorless liquid, yield (80%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.27 (m, 5H), 5.81 (td, J=55Hz, 5 Hz 1H), 3.17 (m, 1H), 1.40 (d, J=5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.69 (t, J=3.75 Hz), 128.67, 128.24, 127.51, 118.28 (t, J=242.5 Hz), 43.98(t, J=20.63 Hz), 13.73 (t, J=5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -124.43 (ddq, J=666.93 Hz, 138.18 Hz, 19.74 Hz); GC-MS: M^+=156.

Preparation of β-fluoro-α-methylstyrenes (*E/(Z*) (20/21)



The compounds were prepared according to a procedure analogous to that previously described.[S6] A mixture of **(2)** (1.3 mmol), a benzene solution of 70% sodium bis(2-methoxyethoxy)aluminum (70% SBAH)(0.6 mL), and dry benzene(3 mL) was stirred at -5~0°C for 1 hour. The mixture was then poured into ice-water and acidified with concentrated hydrochloric acid until the pH of the solution was 6. The organic layer was washed with saturated aqueous NaCl, and dried by Na_2SO_4. The products were obtained after evaporation. Yield: 60% as colorless oil (*E*/*Z* mixture with ratio 2.8). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5-7.28 (m, 7H), 6.98-6.57 (m, 1H), 2.05-1.91(m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.04, 145.24, 144.99, 130.47 (dq, 37.5, 1.25 Hz), 132.58 (dq, 37.5, 1.25 Hz), 128.56, 128.23, 127.78, 127.73, 127.41,125.96, 126.93, 16.03 (d, *J*=6.25 Hz), 12.26 (d, *J*=5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -130.47(dq, *J*=84.6, 2.82 Hz), -132.60(dq, *J*=87.42, 2.82 Hz); GC-MS: M^+=136.

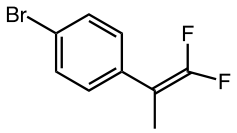
Preparation of β-trifluoromethyl styrene (24)



The compound was prepared according to a procedure analogous to that previously described.[S7] A 100-mL pressure tube was charged with bromobenzene (10 mmol), 3,3,3-trifluoromethyl acrylic acid (20 mmol), palladium acetate (4 mmol), copper oxide (10mmol), and potassium carbonate (40 mmol), then 1-methyl-2-pyrrolidinone (NMP) (1.5 mL) was added, and the mixture was stirred at 130 °C for 15 hours under an nitrogen atmosphere. After cooling, the reaction mixture was diluted with ethyl acetate, filtered through celite and the filtrate was washed with water. The aqueous layer was extracted with ethyl acetate (3 times), the organic layers were washed with water, and brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography with dichloromethane. Yield: 68% as brown liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.31 (m, 5H), 7.10-7.07 (m, 1H), 6.16-6.11 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.70 (q, *J*=7.5 Hz), 133.52, 130.02, 128.96, 127.55, 115.87 (q, *J*=33.75 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -63.34 (dd, *J*=5.64 Hz, 2.82 Hz); GC-MS: M^+=172.

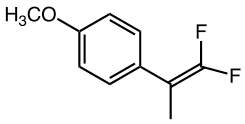
Preparation of 4-bromo-β,β-difluoro-α-methyl styrene, 4-methoxy-β, β-difluoro-α-methylstyrene and 4-bromo-(2,2,2-trifluoro-1-methylehtyl)benzene

The compounds were prepared by referring to literature [S8] and purified by GPC.



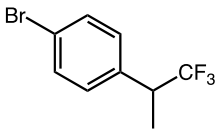
4-Bromo-β,β-difluoro-α-methyl styrene (17)

Colorless liquid, yield (46%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 and 7.24 (A_2B_2, J=10Hz, 4H), 1.95 (t, J=5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.46, 133.88(t, J=4 Hz), 131.56, 129.13 (t, J=4 Hz), 121.02, 86.92 (dd, J=13.75, 23.75 Hz), 13.09; GC-MS: M^+=234.



4-Methoxy-β,β-difluoro-α-methyl styrene (8)

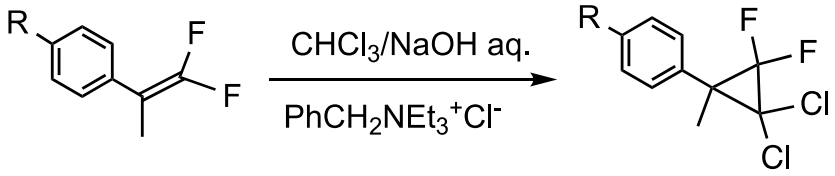
Colorless liquid, yield (46%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 and 6.90 (A_2B_2, J=10Hz, 4H), 3.81 (s, 3H), 1.94 (t, J=5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.63, 153.33(t, J=286.25 Hz), 128.63(t, J=4 Hz), 127.22(t, J=24 Hz), 113.89, 87.00(dd, J=15, 21.88 Hz), 55.30, 13.37; GC-MS: M^+=184.



4-Bromo-(2,2,2-trifluoro-1-methylehtyl)benzene (18)

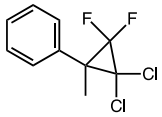
Colorless liquid, yield (17%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 and 7.20 (A_2B_2, J=10 Hz, 4H), 3.43-3.37 (m, 1H), 1.50(d, J= 10Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.46, 131.83, 130.19, 127.94, 122.23, 43.70, 14.52; GC-MS: M^+=252.

Preparation of 1-aryl-1-methyl-2,2-dichloro-3,3-difluorocyclopropanes (26, 27, 28)



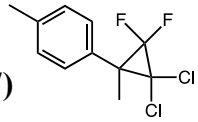
R=H (**2**), R=CH_3 (**5**), R=Cl (**14**) R=H (**26**), R=CH_3(**27**), R=Cl (**28**)

The compounds were prepared according to a procedure analogous to that previously described.[S8]



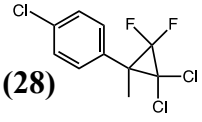
2,2-Dichloro-3,3-difluoro-1-methyl-1-phenylcyclopropane (26)

Colorless liquid, yield (98%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26~7.29 (m, 5H), 1.66 (t, J=2.5Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.33, 133.08, 128.86, 128.72, 108.98 (t, 303 Hz), 64.09, 42.69, 20.75; GC-MS: M^+=236.



2,2-Dichloro-3,3-difluoro-1-methyl-1-*p*-methylphenylcyclopropane (27)

Colorless liquid, yield (97%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21~7.17 (m, 4H), 2.35 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.91, 132.33, 129.42, 128.70, 109.09 (t, 303 Hz), 74.84, 42.49, 21.18, 20.83; GC-MS: M^+=254.



2,2-Difluoro-3,3-difluoro-1-methyl-1-*p*-chlorophenylcyclopropane (28)

Colorless liquid, yield (81%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 and 7.23 (A_2B_2, J=5 Hz, 4H), 1.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.27, 133.70, 130.27, 129.07, 108.77 (t, 303 Hz), 63.81 (t, 13.75 Hz), 42.02, 20.53; GC-MS: $[M\text{-}Cl^-]^+$=235.

Theoretical calculations.

Geometry optimizations were performed using the hybrid (Hartree-Fock/DFT) B3LYP functional[S9,S10] combined with the 6-31G** basis set.[S11] The RB3LYP functional was used for the closed-shell molecules. Solvent effects are estimated for methanol by using the PCM method. The Gaussian 09 program[S12] was used for all calculations.

DFT calculations also demonstrate that MeOH plays a role of proton source in the protonation of **CB**$^-$ (Fig. S45(b)). In the first step **CB**$^-$ and MeOH form **CB—MeOH** with a binding energy of 12.0 kcal/mol. The hydroxy group of methanol is anchored to the anionic carbon of the **CB**$^-$ moiety through a hydrogen bond of 1.924 Å. **TS2** is a transition state, which connects **CB**$^-$**-MeOH** and **3-MeO**$^-$. Computed activation energy of **TS2** is only 5.5 kcal/mol relative to **CB**$^-$**-MeOH**, and the relative energy of **3-MeO**$^-$ is -7.8 kcal/mol. Thus, computed results suggest that the protonation of **CB**$^-$ is likely to occur in MeOH. In **TS2** the O-H bond and the C-H bond were computed to be 1.229 Å and 1.393 Å, respectively, which is consistent with a transition structure leading to the cleavage of an O-H bond and the formation of a C-H bond. After formation of the C-H bond the two C-C bonds are increased to 1.523 Å (C-C_F) and 1.523 Å (C-C_{Ph}).

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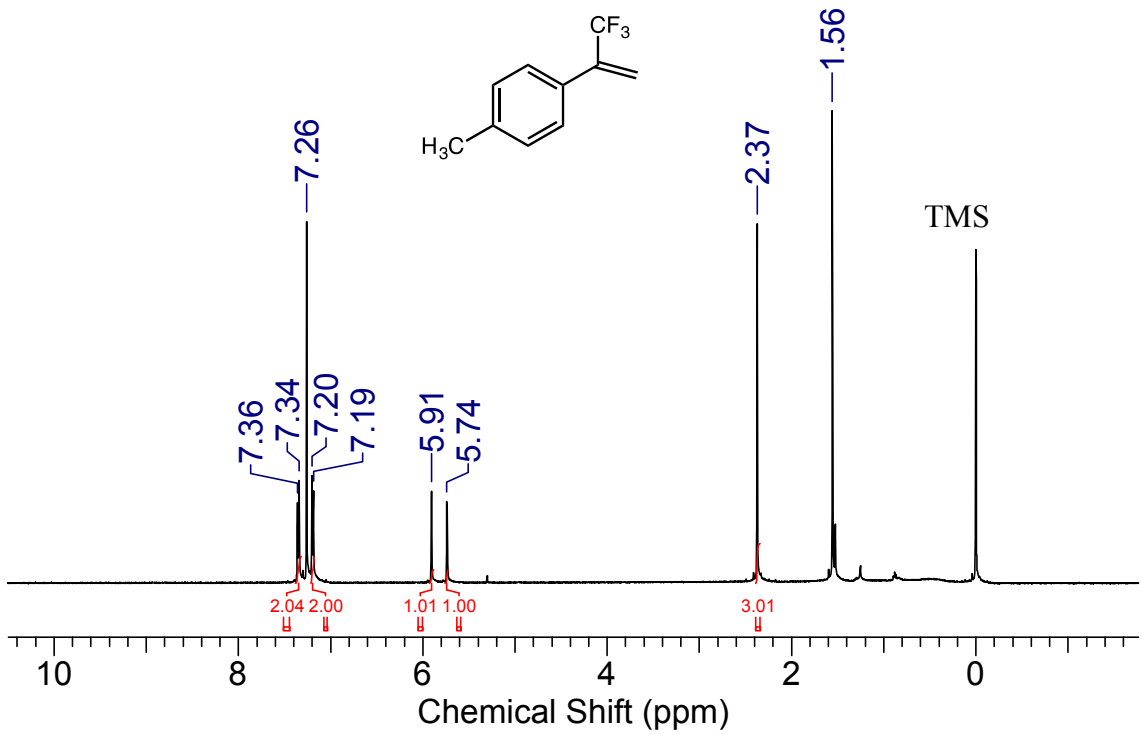


Fig. S6 ^{1}H NMR spectrum of α-trifluoromethyl-*p*-methyl styrene (**4**).

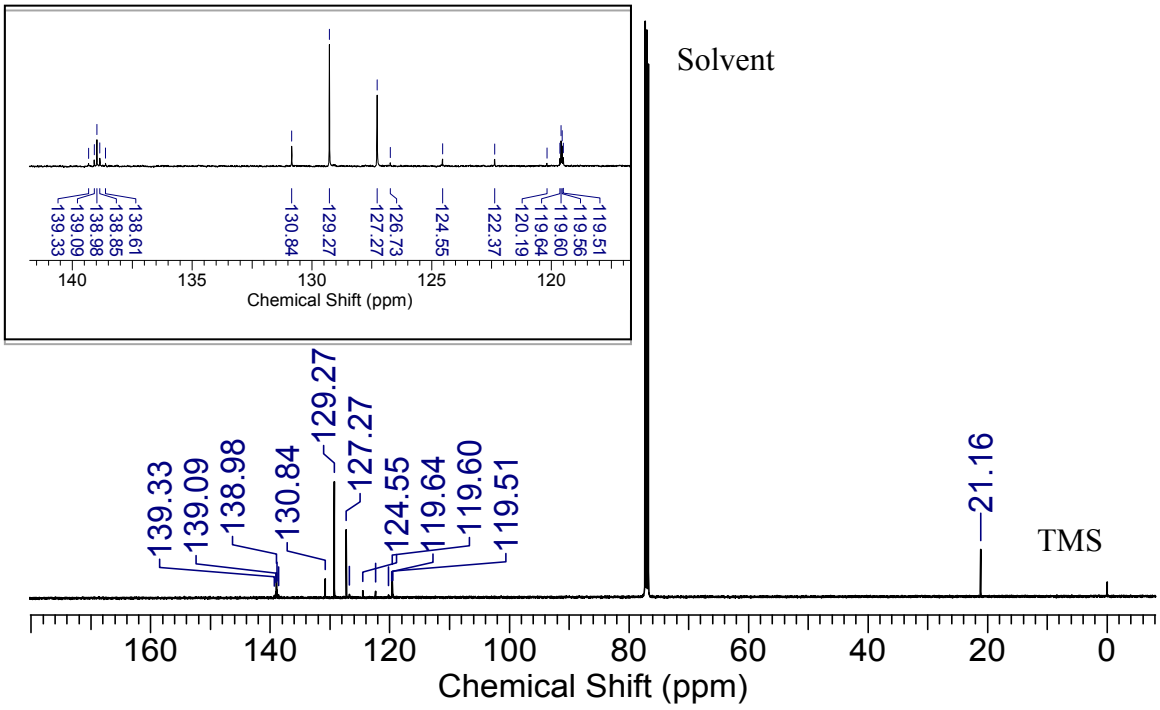

Solvent
139.33
139.09
138.98
138.85
138.61
130.84
129.27
127.27
126.73
124.55
122.37
120.19
119.64
119.60
119.56
119.51
140
135
130
125
120
Chemical Shift (ppm)
139.33
139.09
138.98
130.84
129.27
127.27
124.55
119.64
119.60
119.51
21.16
TMS
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Fig. S7 ^{13}C NMR spectrum of α-trifluoromethyl-*p*-methyl styrene (**4**).

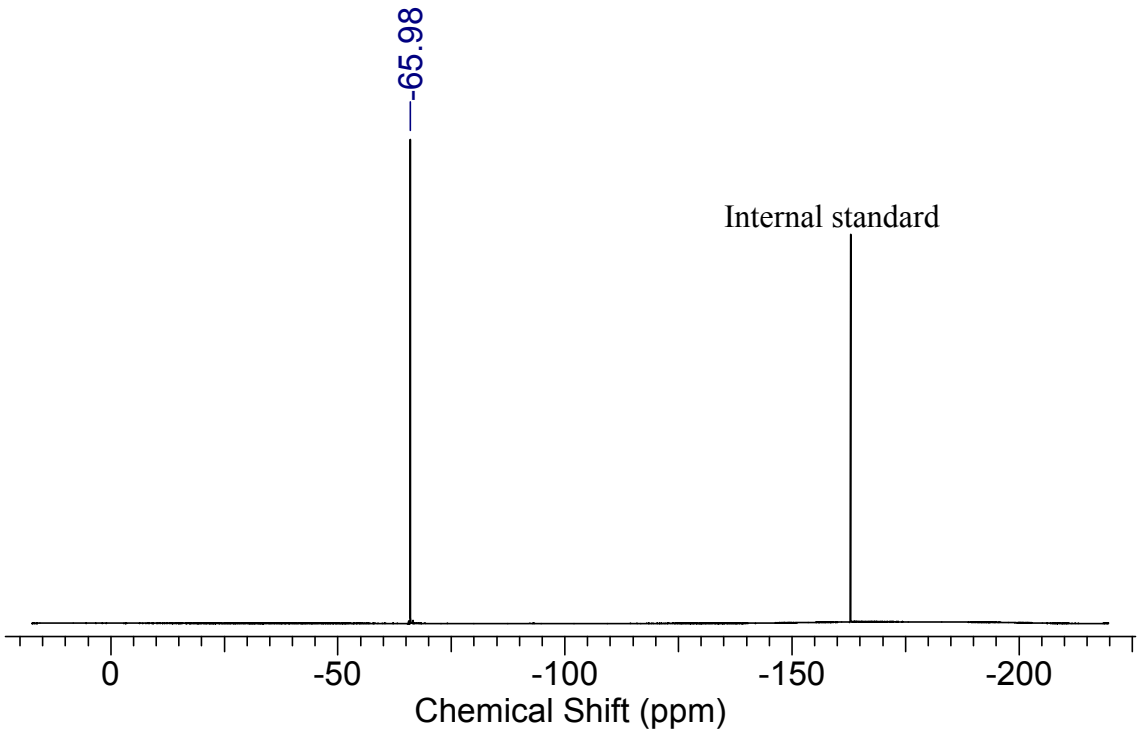


Fig. S8 ^{19}F NMR spectrum of α-trifluoromethyl-*p*-methyl styrene (**4**).

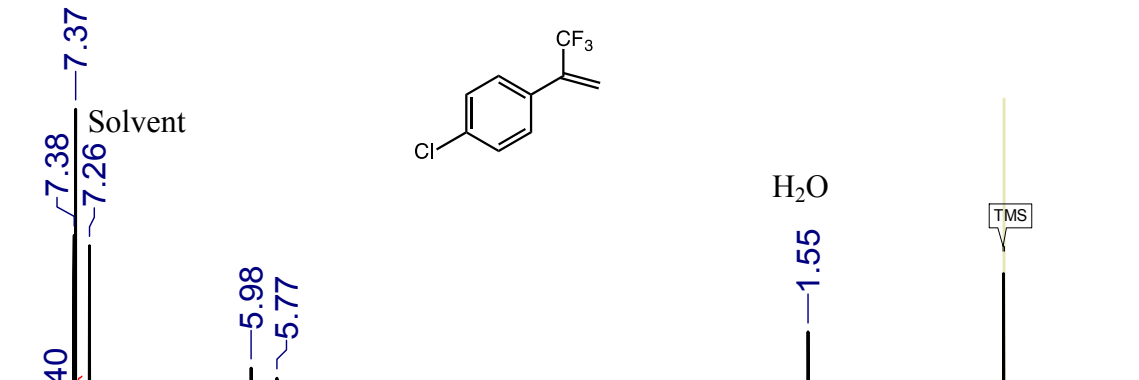


Fig. S9. ^{1}H NMR spectrum of α-trifluoromethyl-*p*-chloro styrene (**13**).

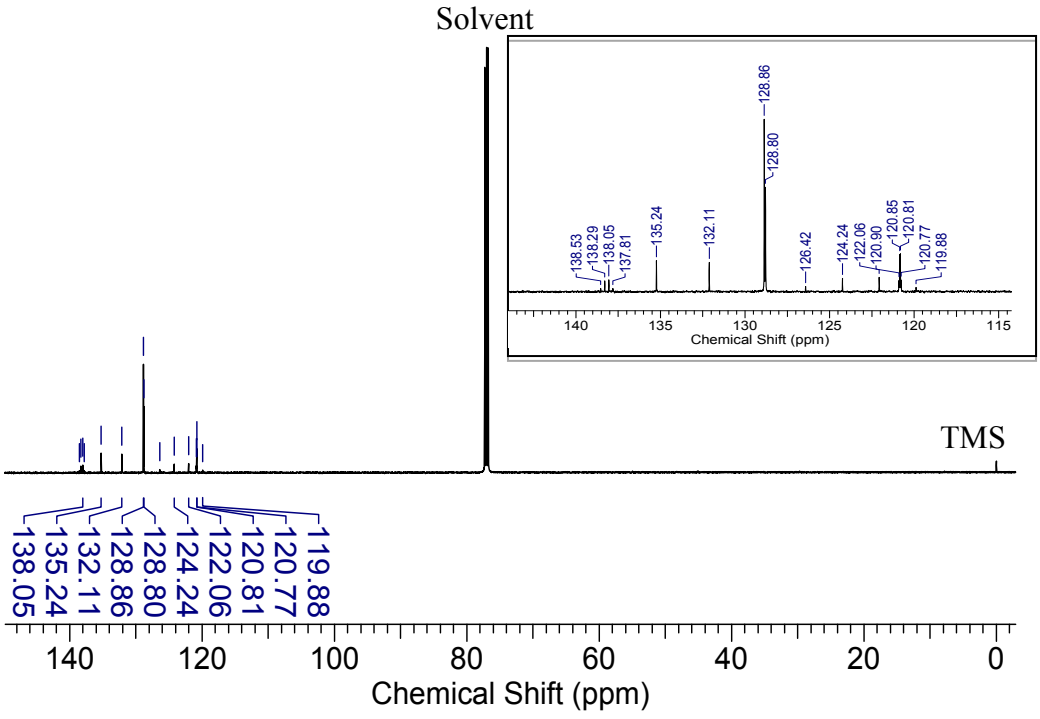


Fig. S10. ^{13}C NMR spectrum ofα-trifluoromethyl-*p*-chloro styrene (**13**).

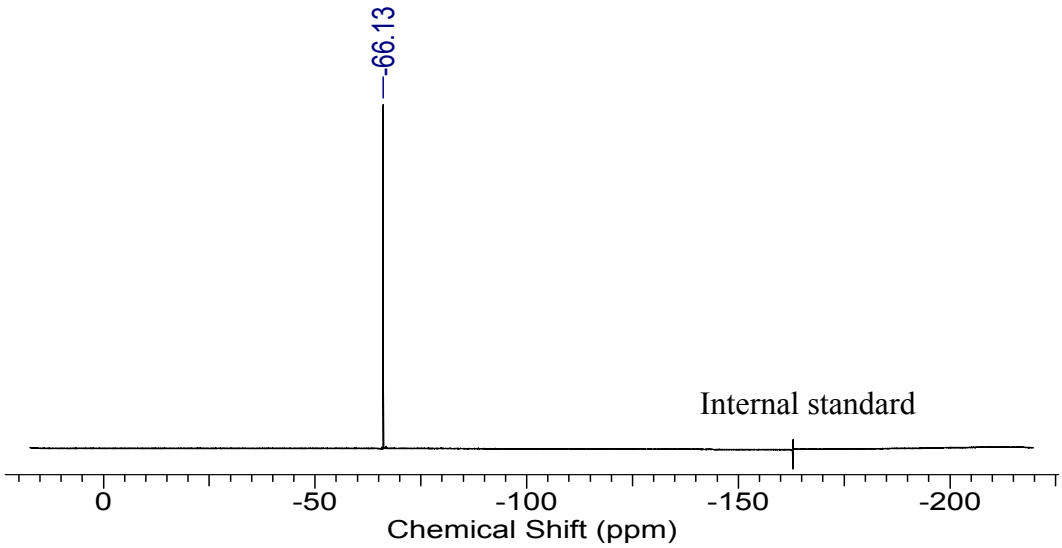


Fig. S11. ^{19}F NMR spectrum ofα-trifluoromethyl-*p*-chloro styrene (**13**).

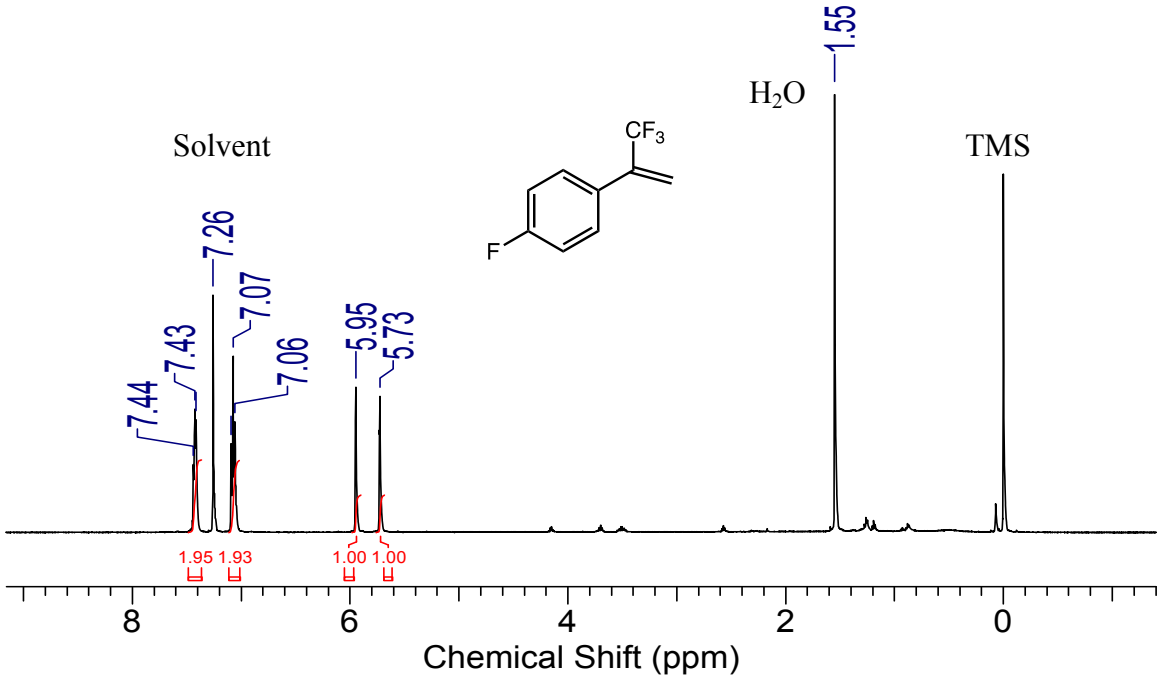


Fig. S12. ^{1}H NMR spectrum of α-trifluoromethyl-*p*-fluoro styrene (**10**).

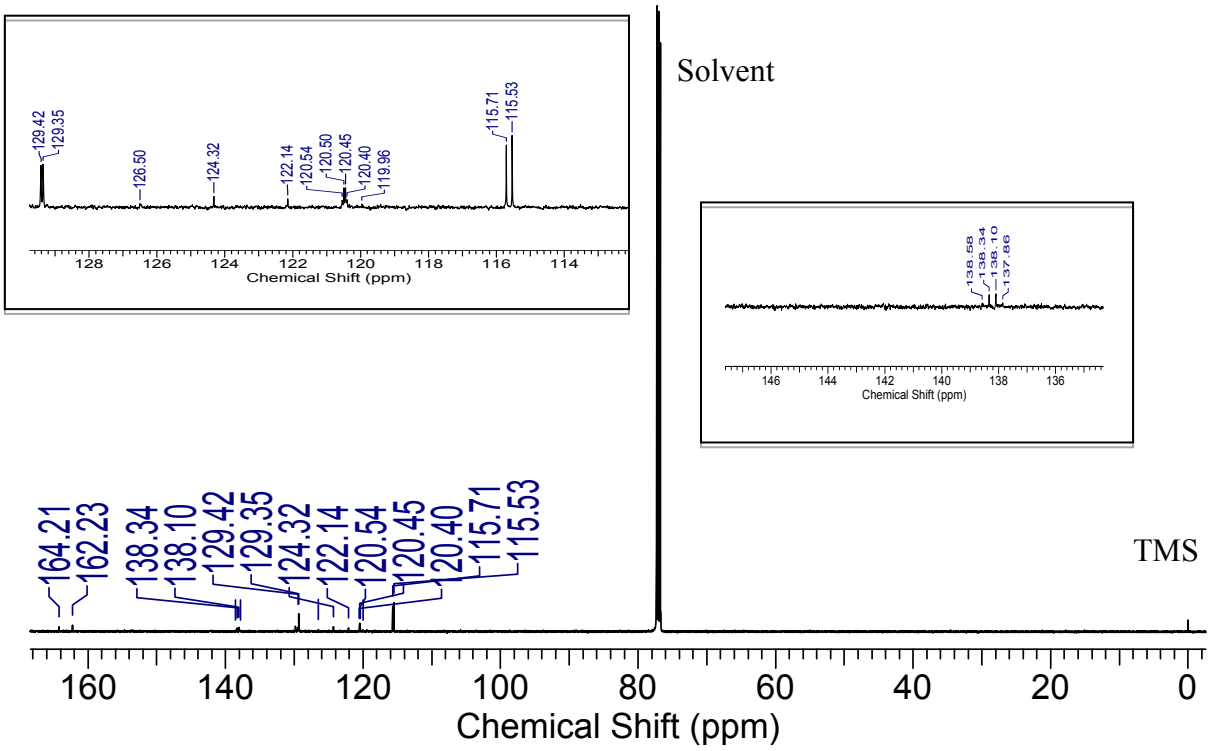


Fig. S13. ^{13}C NMR spectrum of α-trifluoromethyl-*p*-fluoro styrene (**10**).

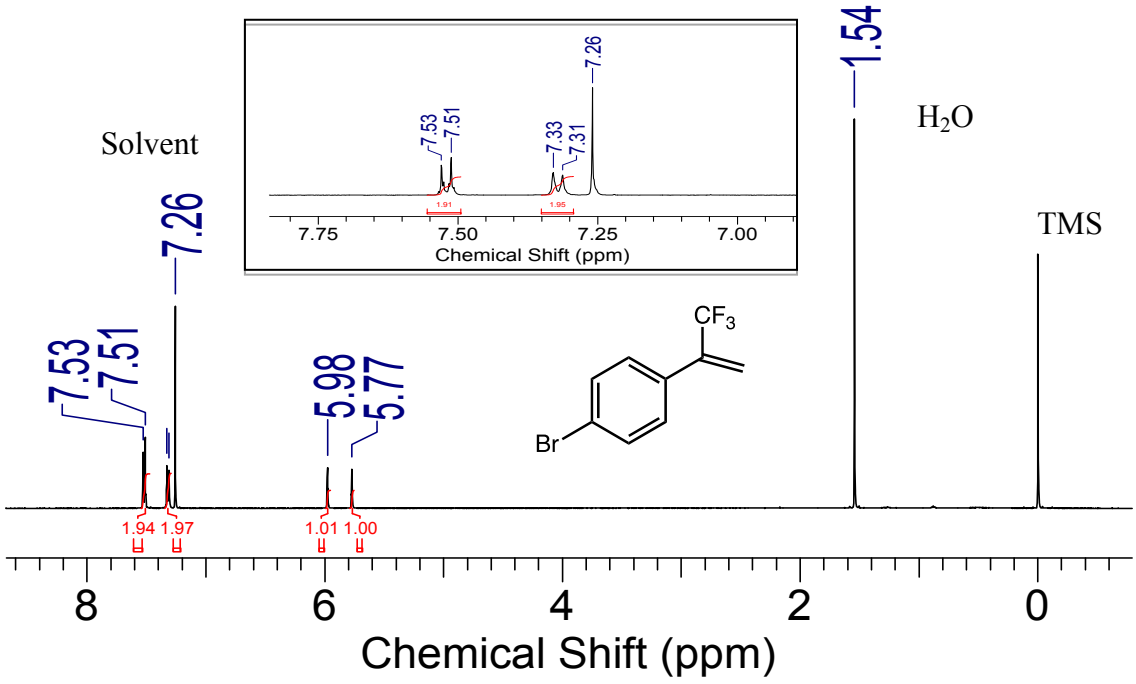


Fig. S14. ^{1}H NMR spectrum of α-trifluoromethyl-*p*-bromo styrene (**16**).

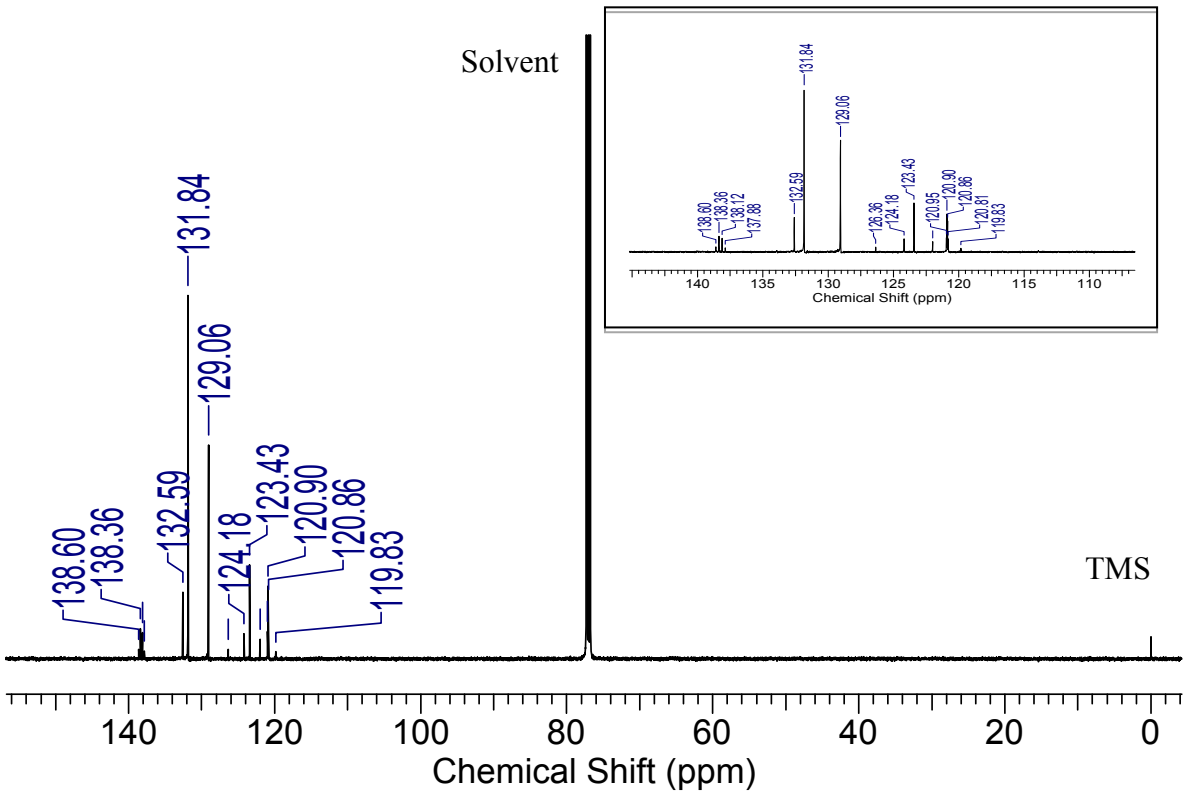


Fig. S15. ^{13}C NMR spectrum of α-trifluoromethyl-*p*-bromo styrene (**16**).

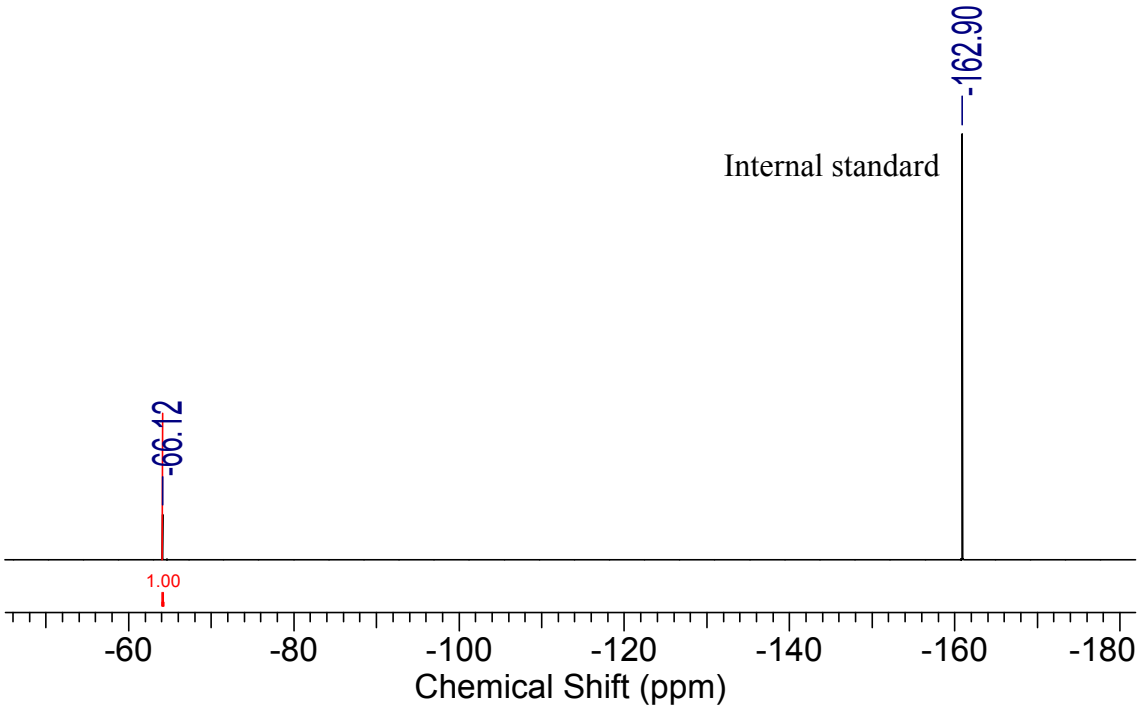


Fig. S16. ^{19}F NMR spectrum of α-trifluoromethyl-*p*-bromo styrene (**16**).

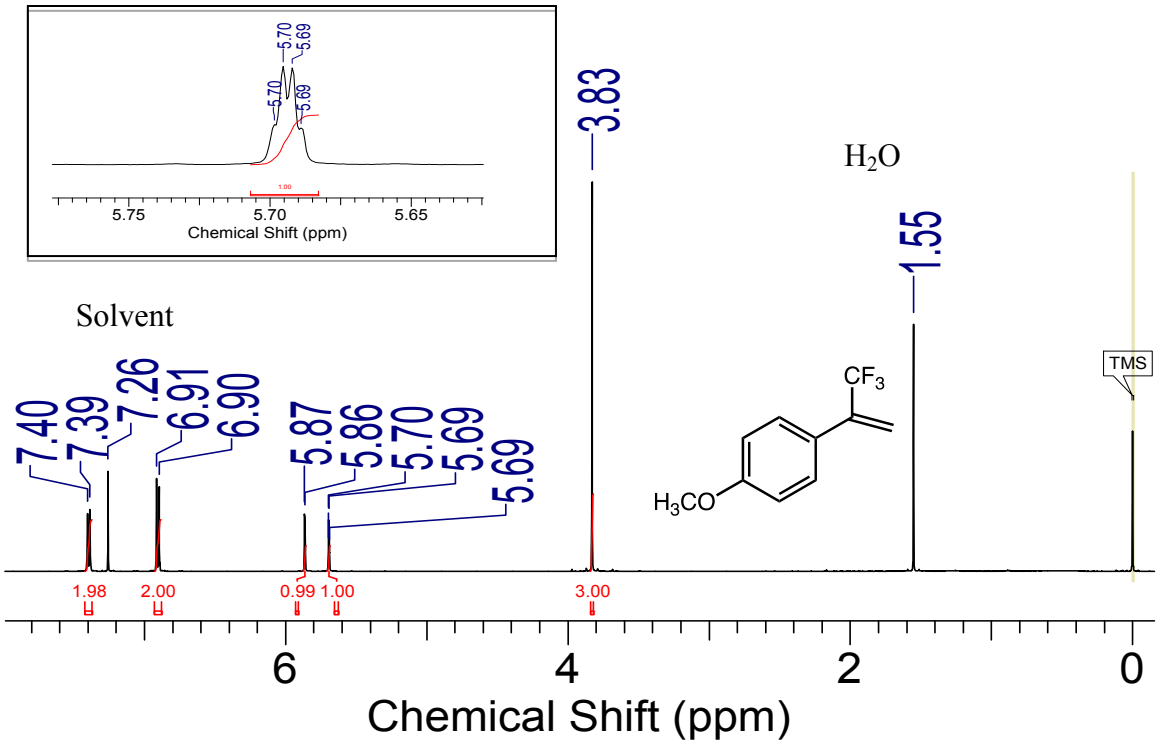


Fig. S17. ^{1}H NMR spectrum of α-trifluoromethyl-*p*-methoxy styrene (**7**).

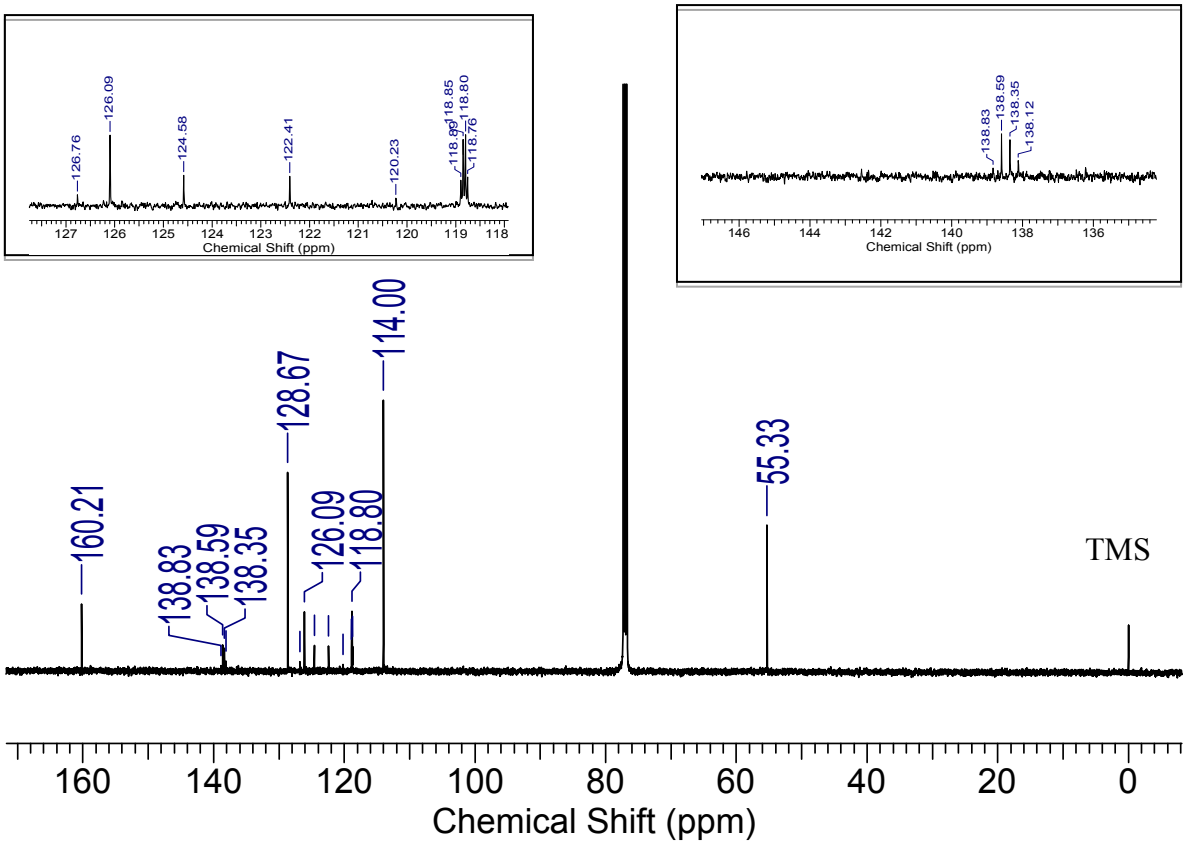


Fig. S18. ^{13}C NMR spectrum of α-trifluoromethyl-*p*-methoxy styrene (**7**).

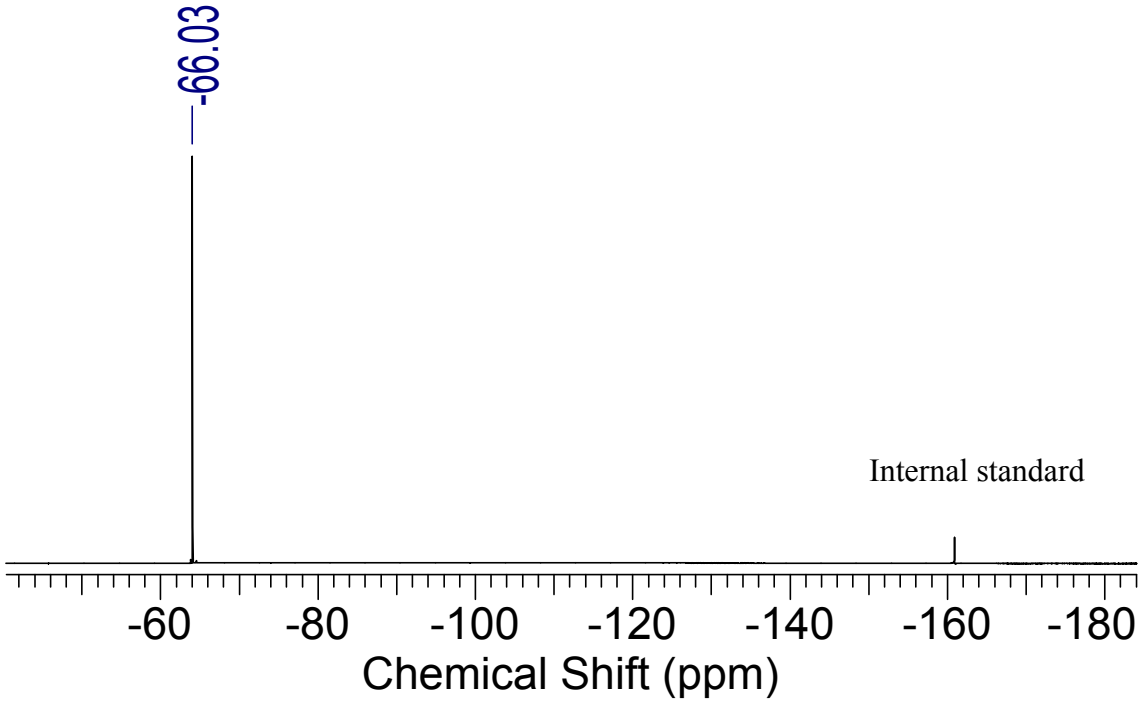


Fig. S19. ^{19}F NMR spectrum of α-trifluoromethyl-*p*-methoxy styrene (**7**).

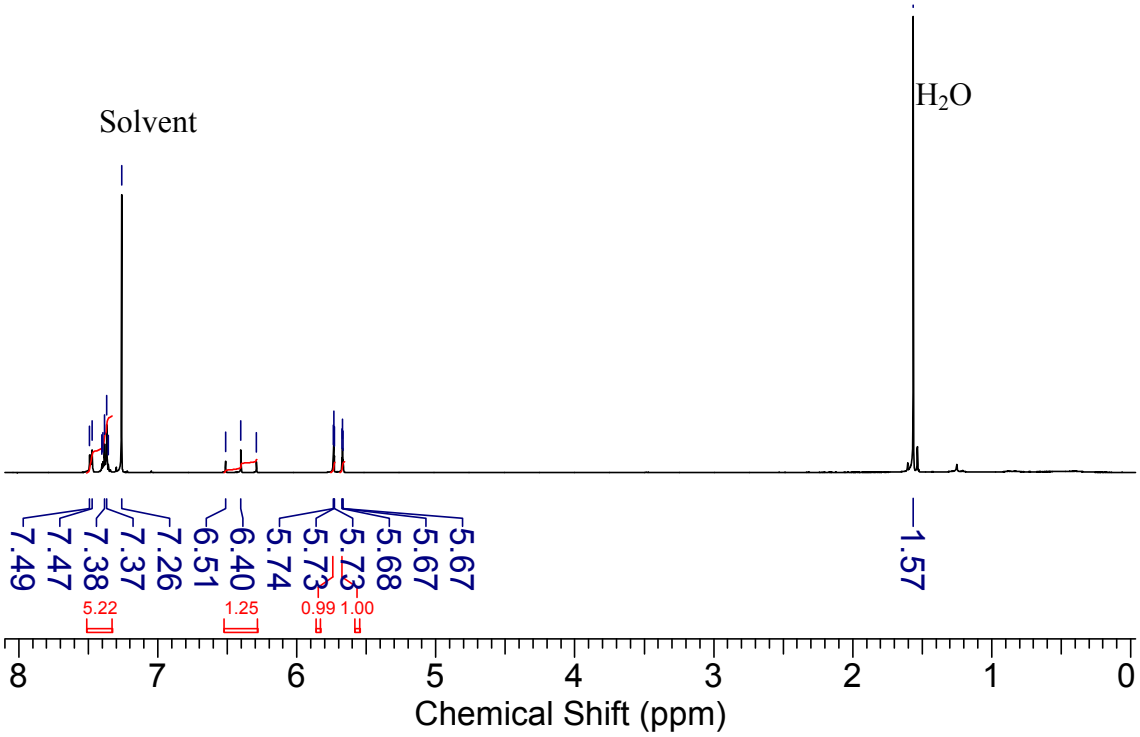

Solvent
H2O
7.49
7.47
7.38
7.37
7.26
6.51
6.40
5.74
5.73
5.73
5.68
5.67
5.67
1.57
5.22
1.25
0.99
1.00
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Fig. S20. ^{1}H NMR spectrum of α-difluoromethyl styrene (**19**).

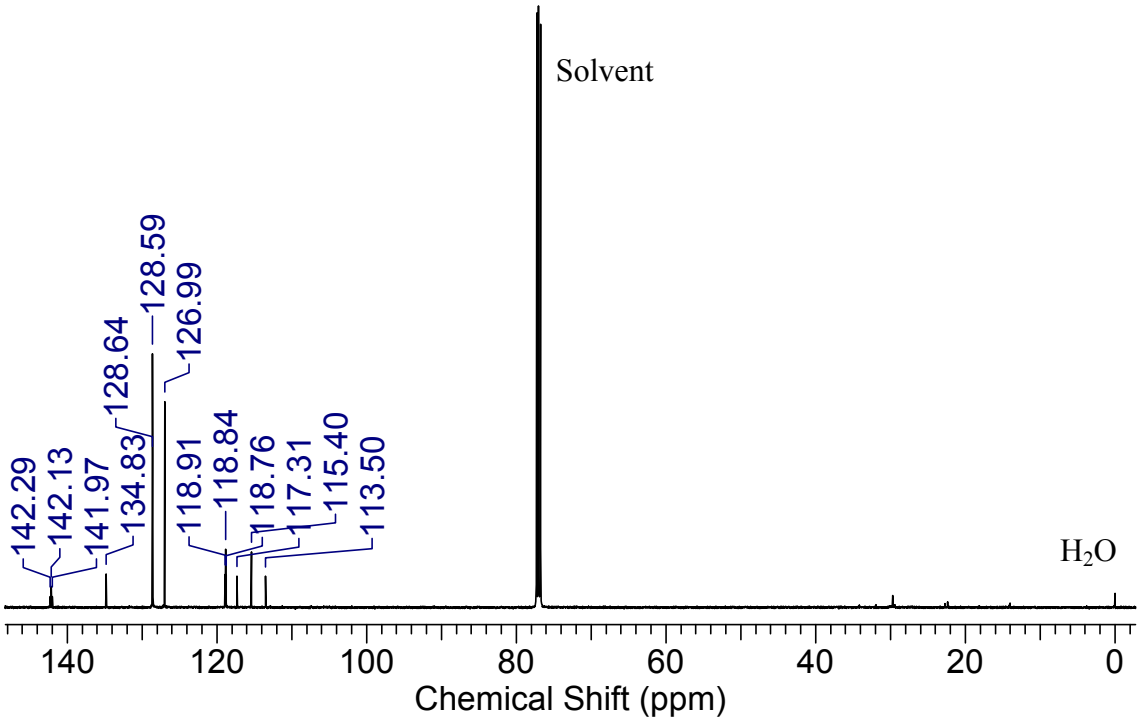

Solvent
142.29
142.13
141.97
134.83
128.64
128.59
126.99
118.91
118.84
118.76
117.31
115.40
113.50
H2O
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Fig. S21. ^{13}C NMR spectrum of α-difluoromethyl styrene (**19**).

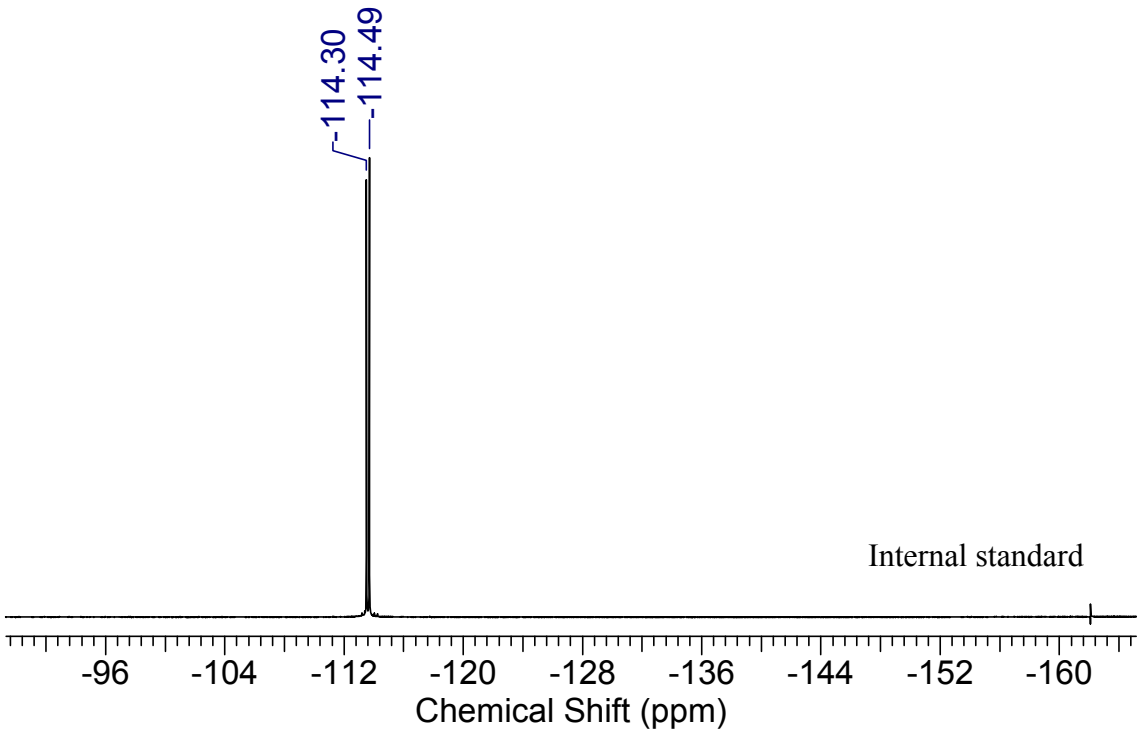
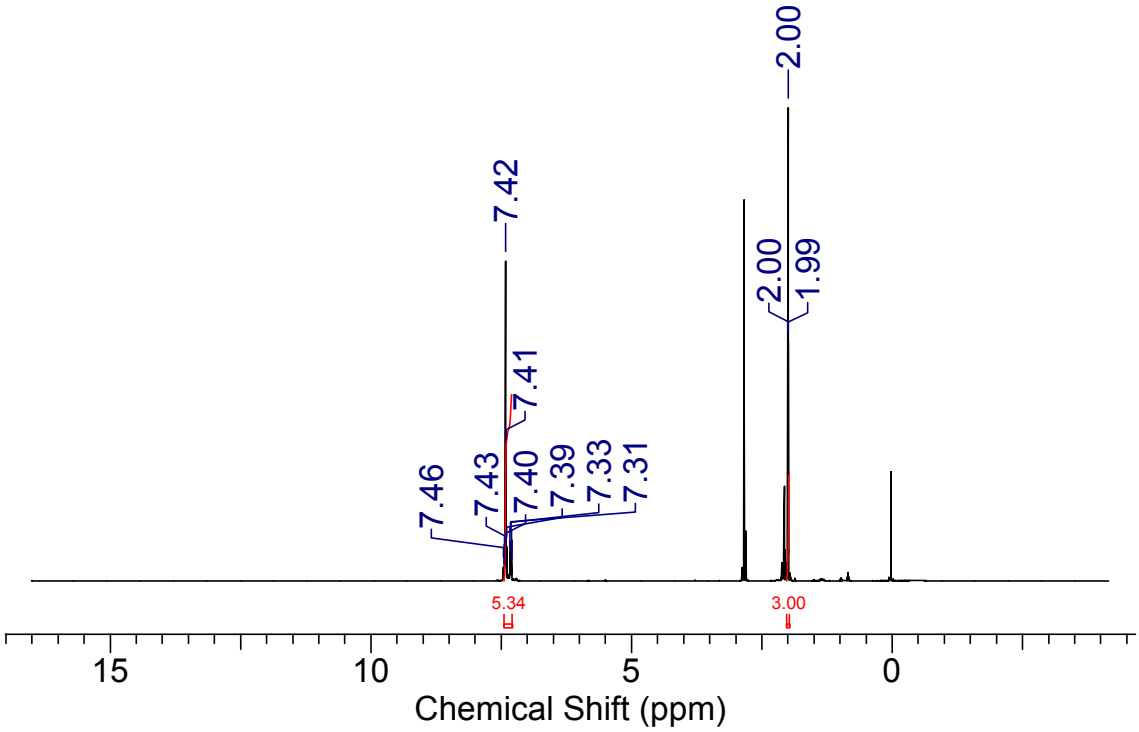
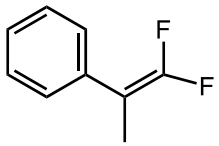

-114.30
-114.49
Internal standard
-96
-104
-112
-120
-128
-136
-144
-152
-160
Chemical Shift (ppm)

Fig. S22. ^{19}F NMR spectrum of α-difluoromethy styrene (**19**).





H_2O

TMS

Fig. S23. ^{1}H NMR spectrum of β, β-difluoro-α-methyl styrene (**2**).

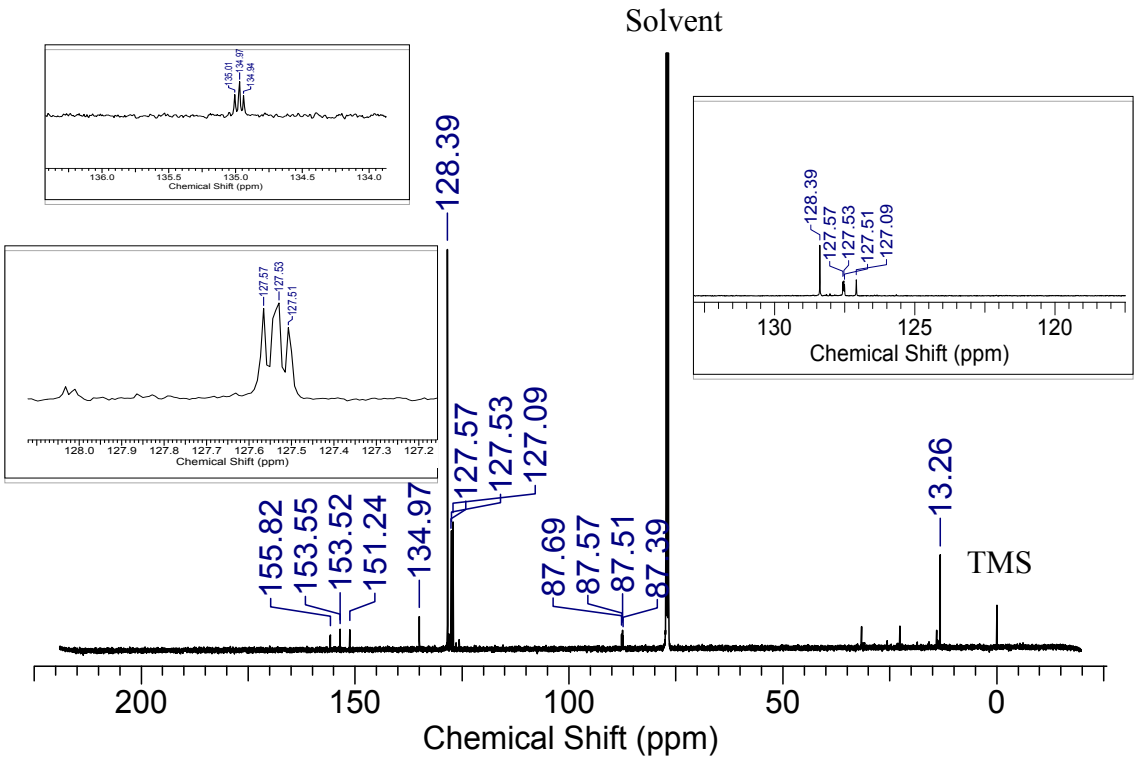
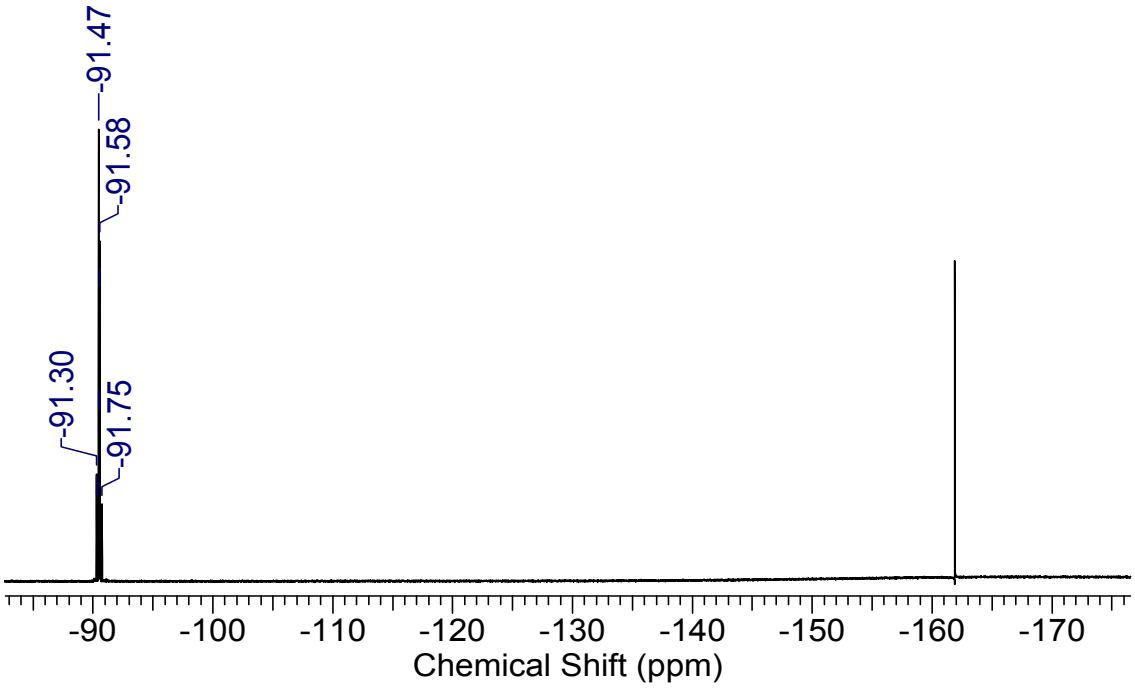
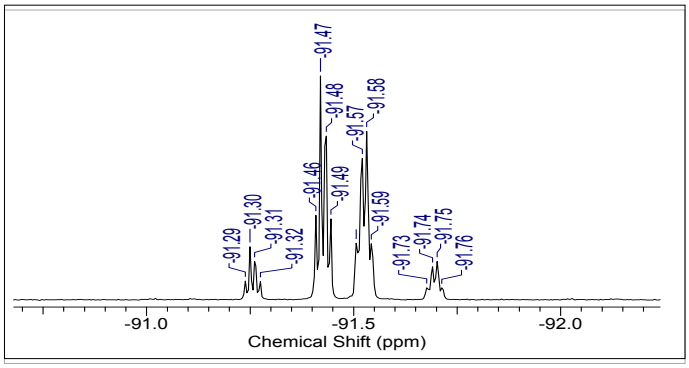

Solvent
128.39
127.57
127.53
127.09
155.82
153.55
153.52
151.24
134.97
87.69
87.57
87.51
87.39
13.26
TMS
200
150
100
50
0
Chemical Shift (ppm)
135.01
134.97
134.94
136.0
135.5
135.0
134.5
134.0
Chemical Shift (ppm)
127.57
127.53
127.51
128.0
127.9
127.8
127.7
127.6
127.5
127.4
127.3
127.2
Chemical Shift (ppm)
128.39
127.57
127.53
127.51
127.09
130
125
120
Chemical Shift (ppm)

Fig. S24. ^{13}C NMR spectrum of β, β-difluoro-α-methyl styrene (**2**).





Internal standard

Fig. S25. ^{19}F NMR spectrum of *β, β*-difluoro-*α*-methyl styrene (**2**).

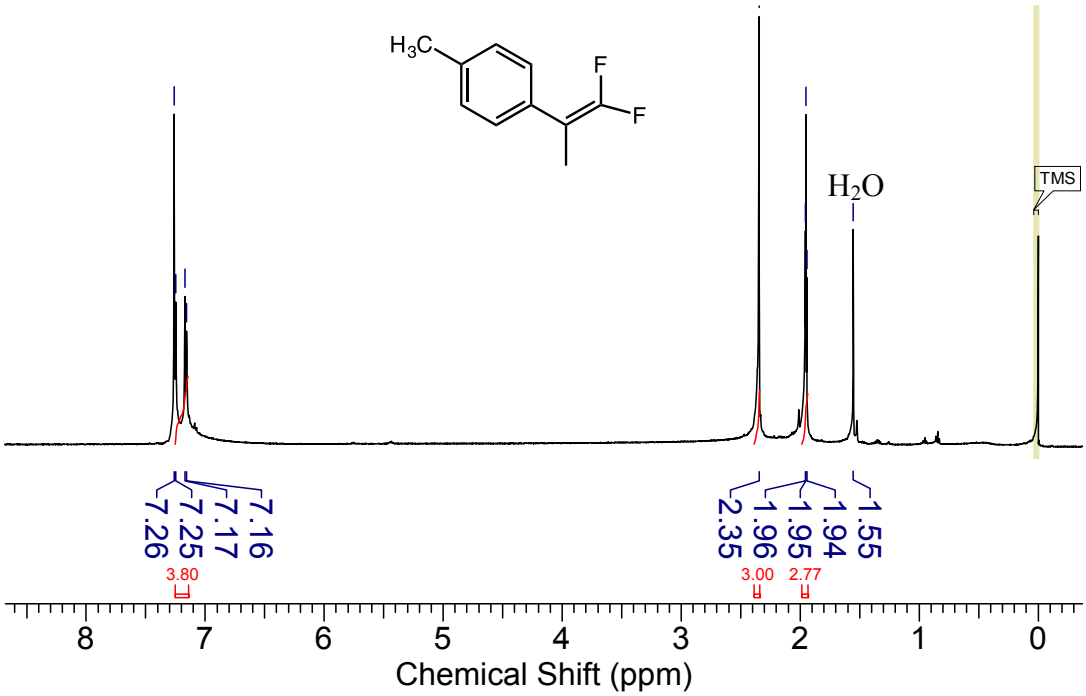


Fig. S26. ^{1}H NMR spectrum of 1-(1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (**5**).

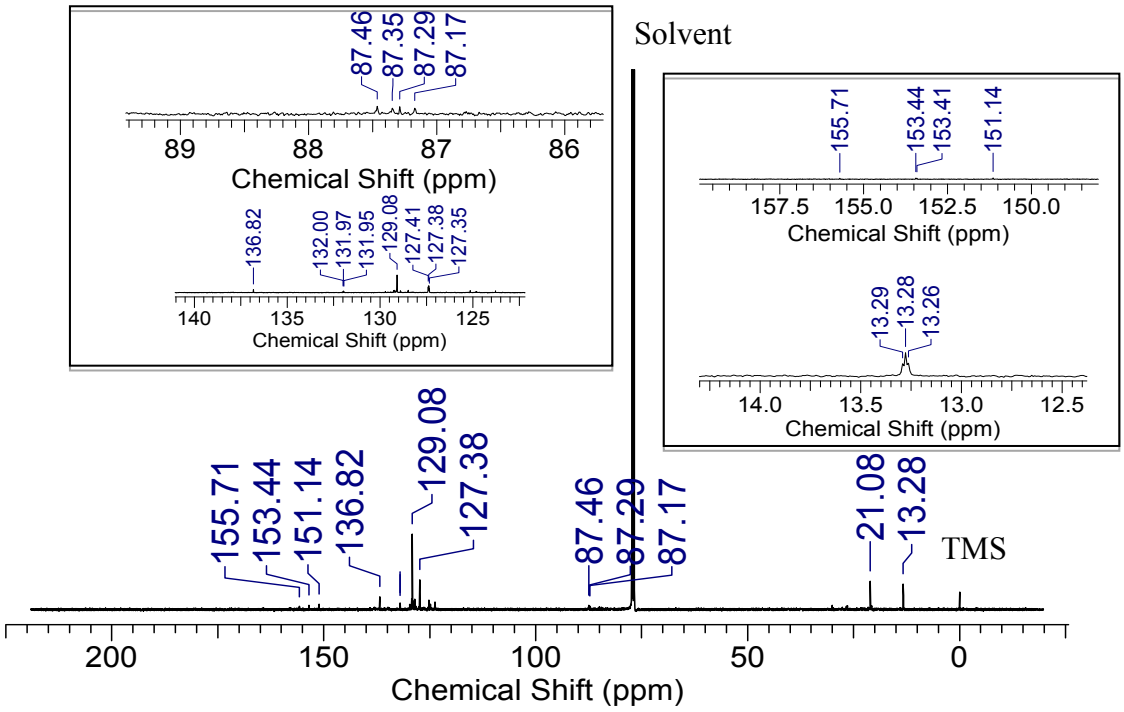

87.46
87.35
87.29
87.17
89
88
87
86
Chemical Shift (ppm)
136.82
132.00
131.97
131.95
129.08
127.41
127.38
127.35
140
135
130
125
Chemical Shift (ppm)
Solvent
155.71
153.44
153.41
151.14
157.5
155.0
152.5
150.0
Chemical Shift (ppm)
13.29
13.28
13.26
14.0
13.5
13.0
12.5
Chemical Shift (ppm)
155.71
153.44
151.14
136.82
129.08
127.38
87.46
87.29
87.17
21.08
13.28
TMS
200
150
100
50
0
Chemical Shift (ppm)

Fig. S27. ^{13}C NMR spectrum of 1-(1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (**5**).

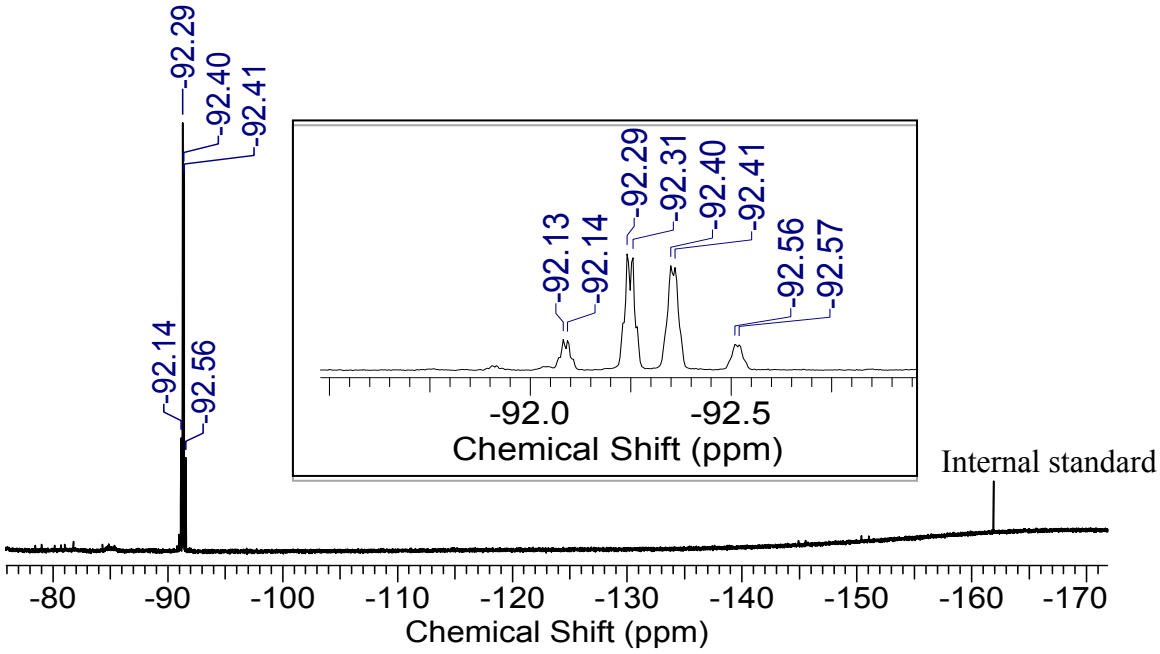


Fig. S28. ^{13}C NMR spectrum of 1-(1,1-difluoroprop-1-en-2-yl)-4-methylbenzene (**5**).

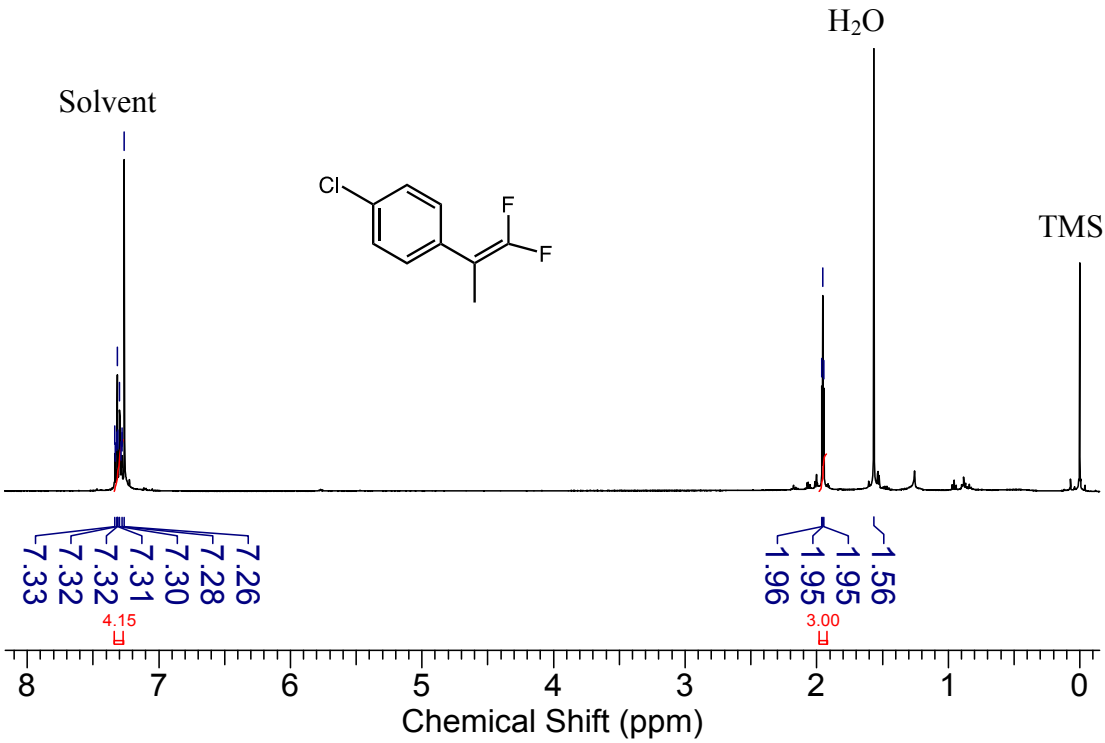


Fig. S29. ^{1}H NMR spectrum of 1,1-difluoro-2-(4'-chlorophenyl)propene (**14**).

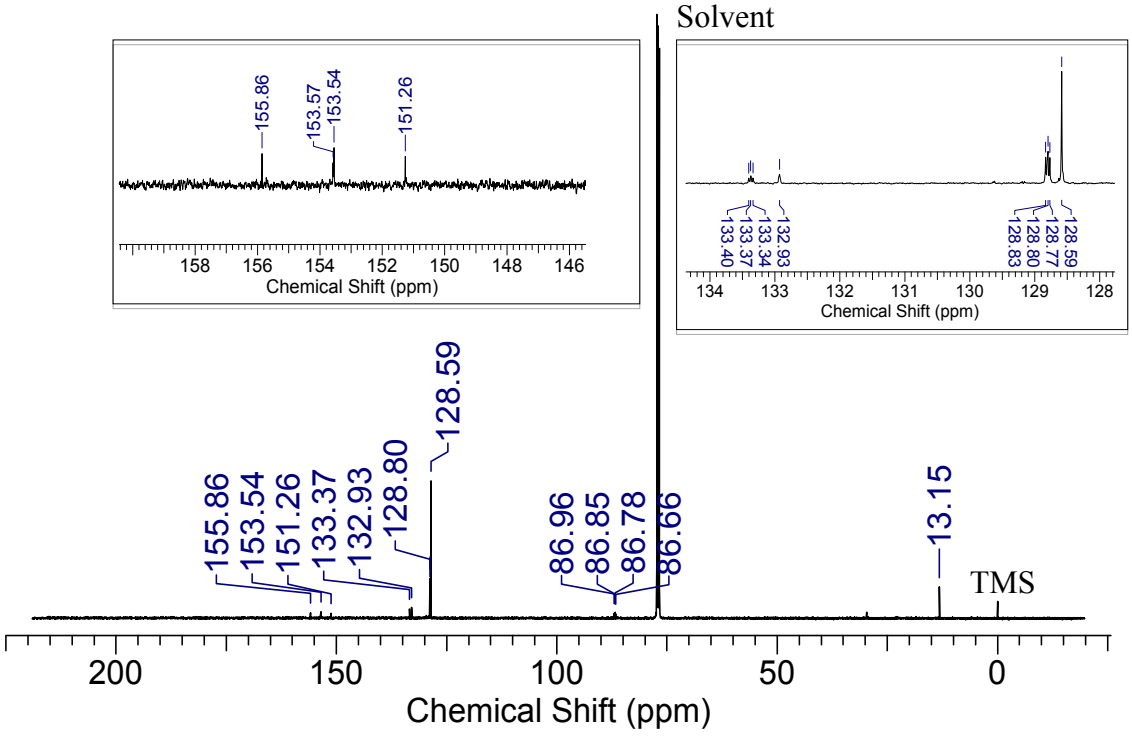

Solvent
155.86
153.57
153.54
151.26
158
156
154
152
150
148
146
Chemical Shift (ppm)
133.40
133.37
133.34
132.93
128.83
128.80
128.77
128.59
134
133
132
131
130
129
128
Chemical Shift (ppm)
128.59
155.86
153.54
151.26
133.37
132.93
128.80
86.96
86.85
86.78
86.66
13.15
TMS
200
150
100
50
0
Chemical Shift (ppm)

Fig. S30. ^{13}C NMR spectrum of 1,1-difluoro-2-(4'-chlorophenyl)propene (**14**).

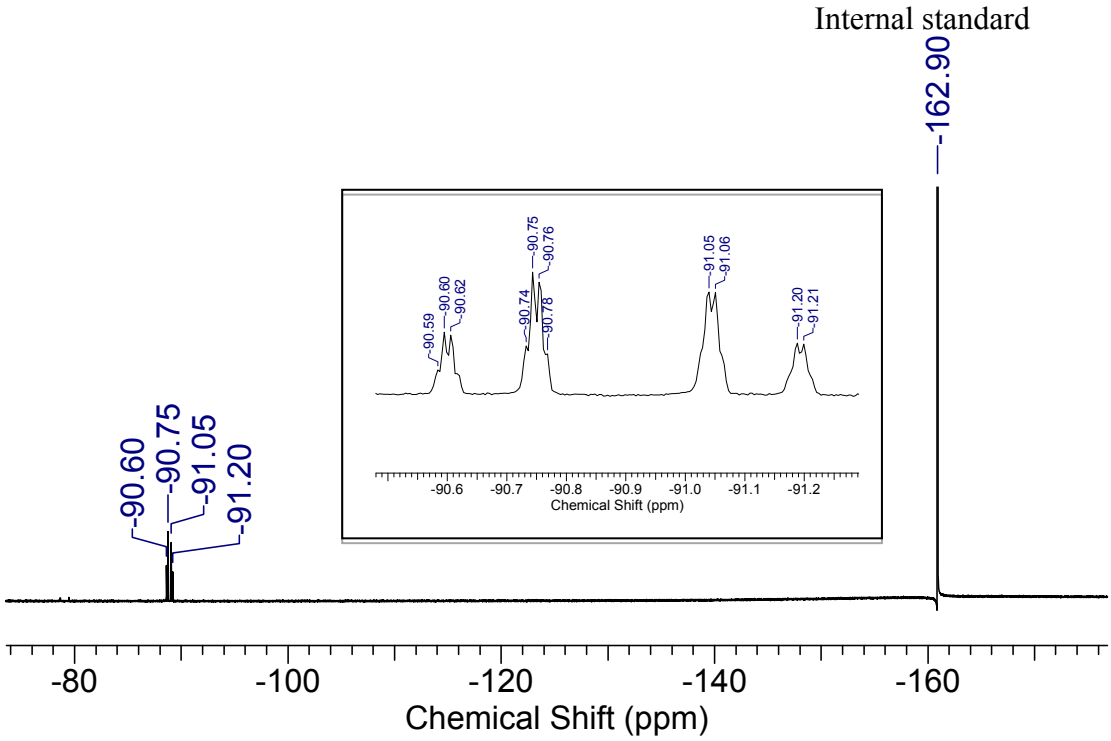


Fig. S31. ^{19}F NMR spectrum of 1,1-difluoro-2-(4'-chlorophenyl)propene (**14**).

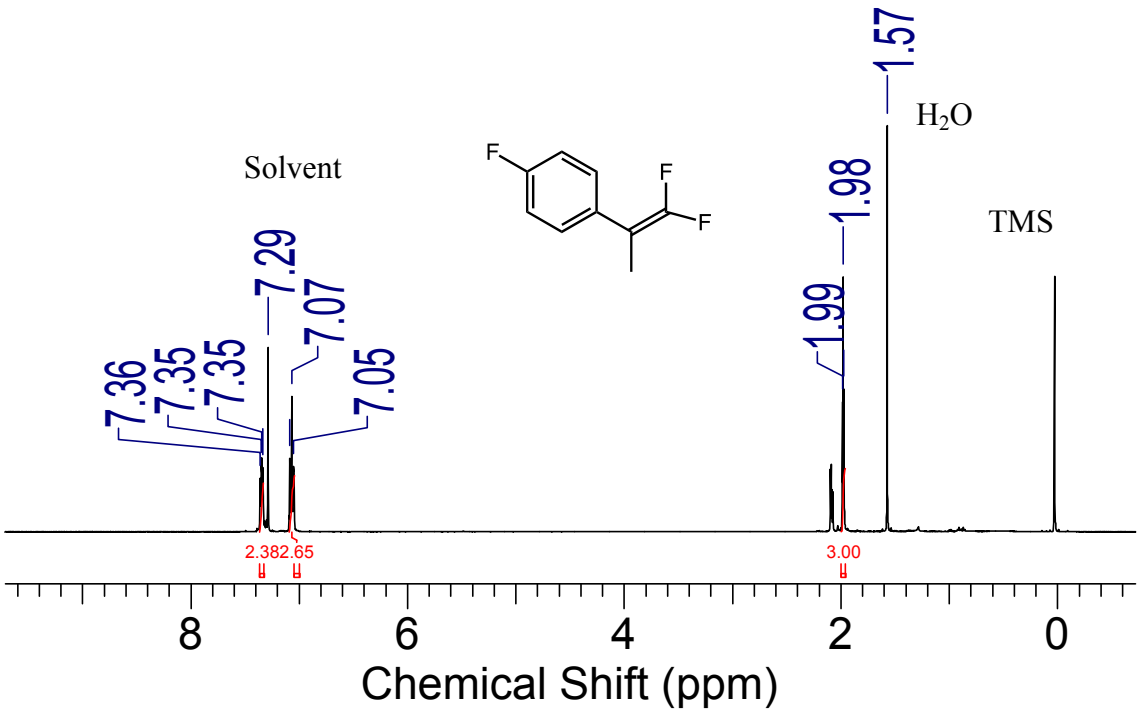


Fig. S32. ^{1}H NMR spectrum of 4-fluoro-β,β-difluoro-α-methyl styrene (**11**).

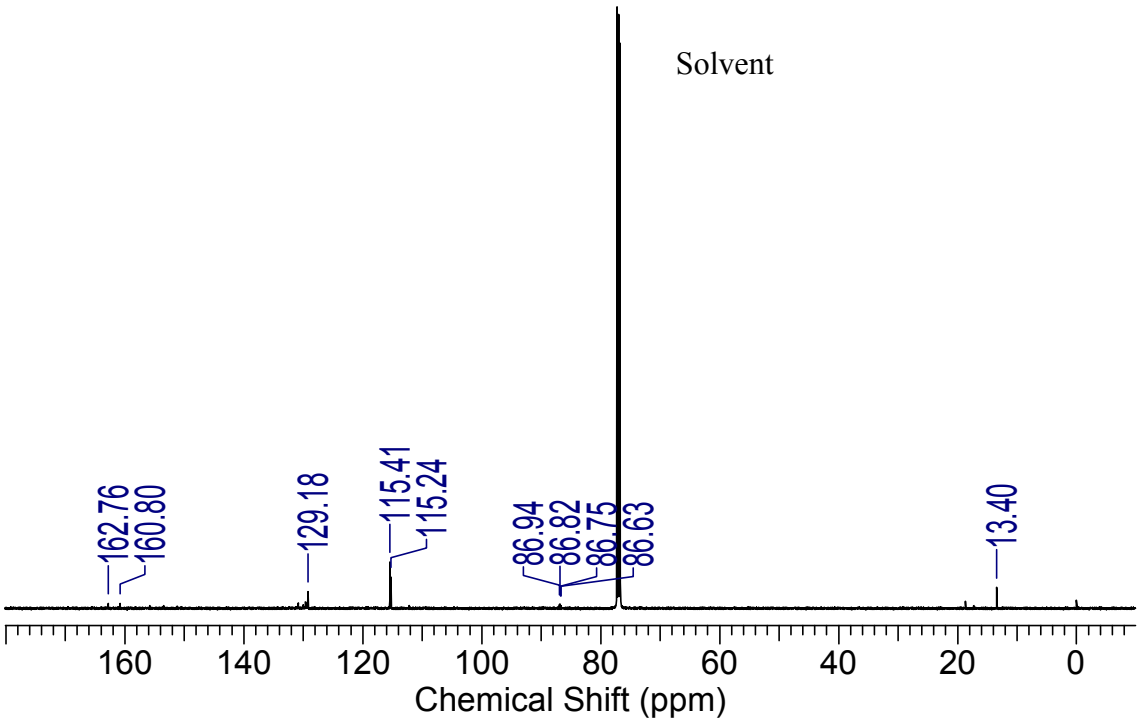


Fig. S33. ^{13}C NMR spectrum of 4-fluoro-β,β-difluoro-α-methyl styrene (**11**).

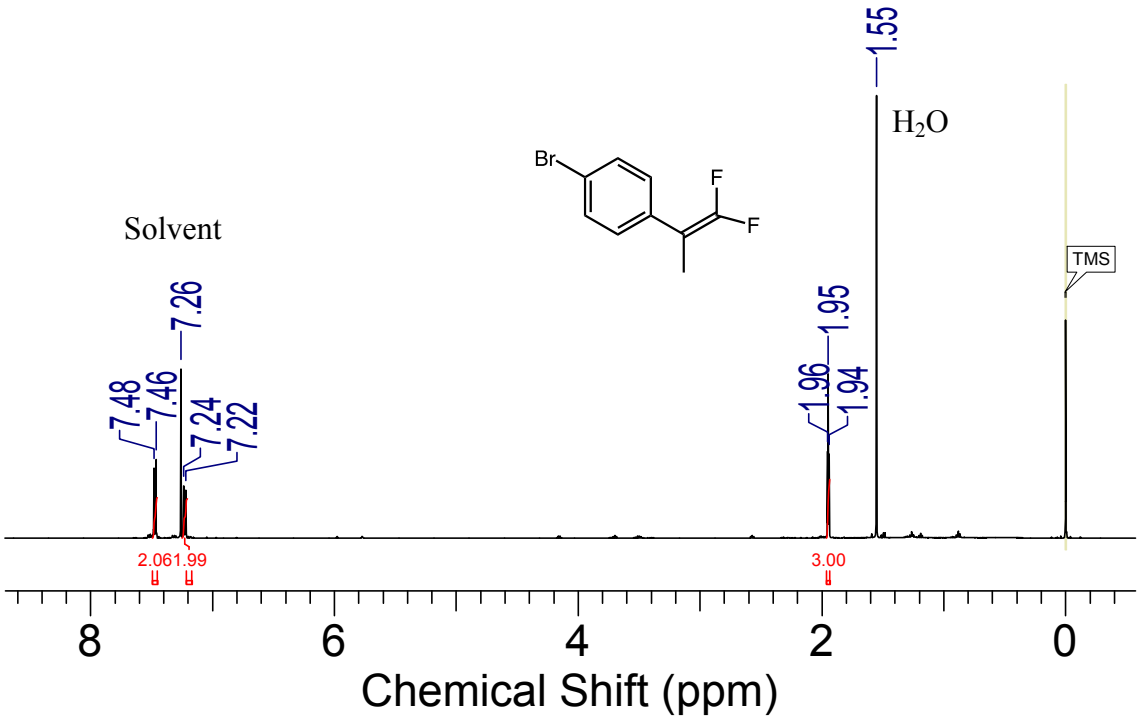
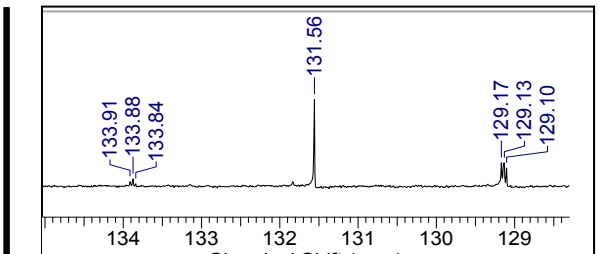


Fig. S34. ^{1}H NMR spectrum of 4-bromo-β,β-difluoro-α-methyl styrene (**17**).



Solvent

TMS

Fig. S35. ^{13}C NMR spectrum of 4-bromo-β,β-difluoro-α-methyl styrene (**17**).

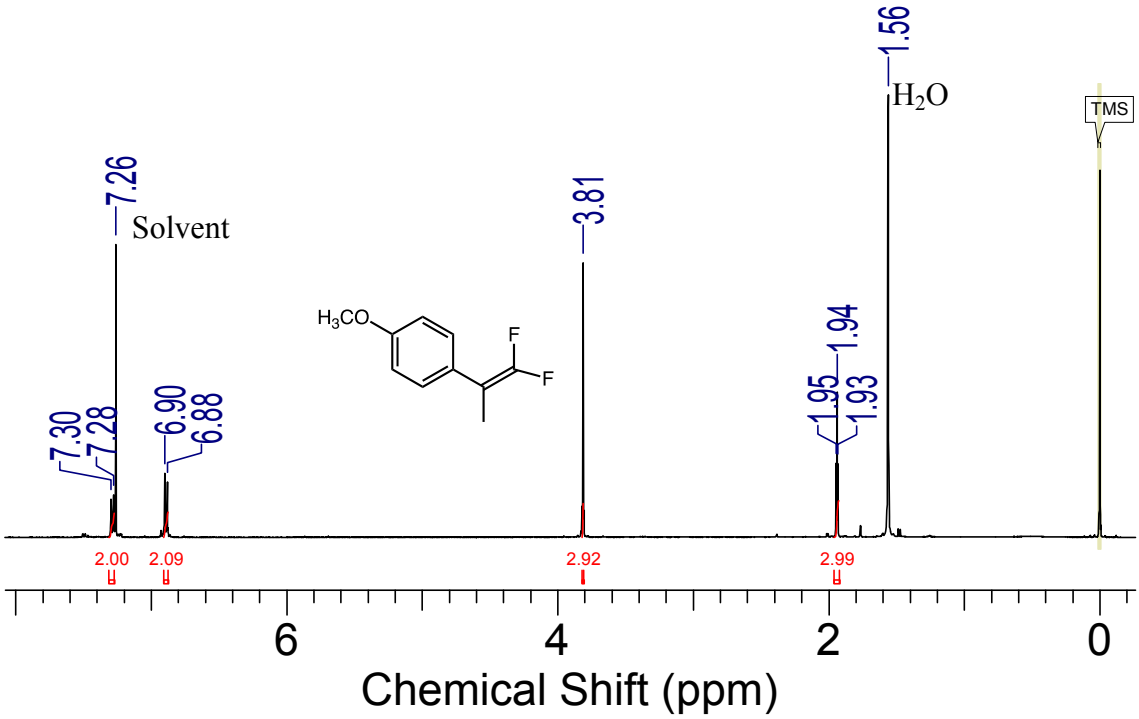


Fig. S36. ^{1}H NMR spectrum of 4-methoxy-β,β-difluoro-□-methyl styrene (**8**).

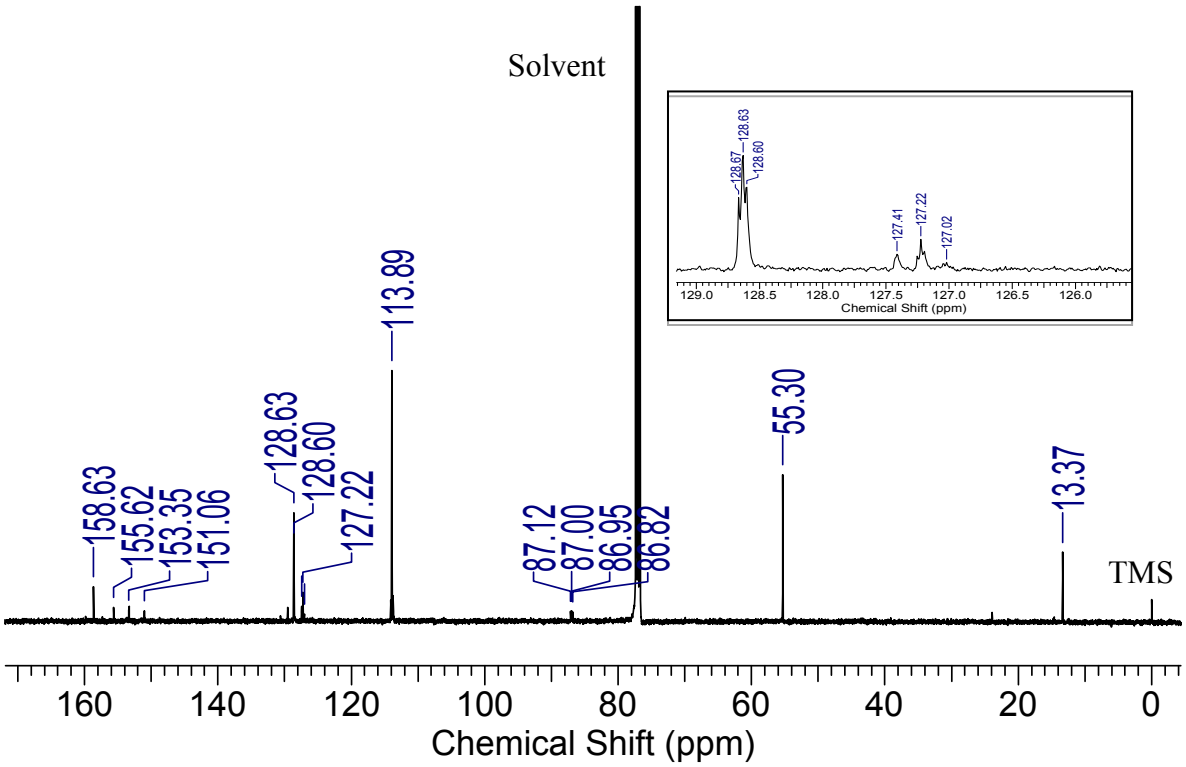


Fig. S37. ^{13}C NMR spectrum of 4-methoxy-β,β-difluoro-α-methyl styrene (**8**).

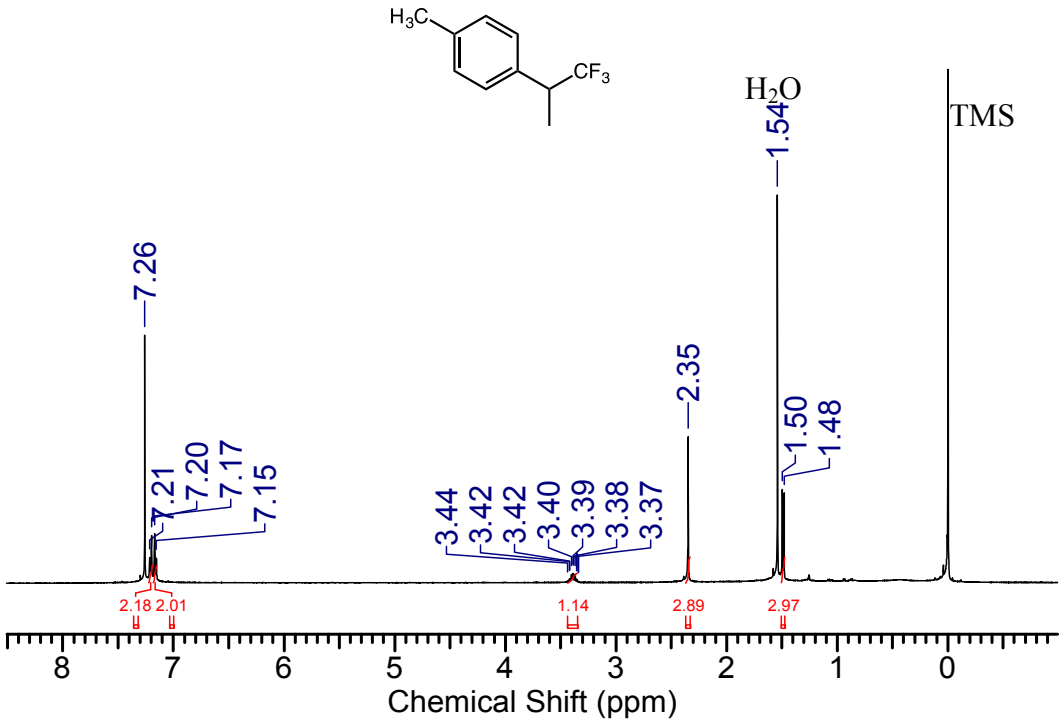


Fig. S38. ^{1}H NMR spectrum of 4-methyl-(2,2,2-trifluoro-1-methylehtyl)benzene (**6**).

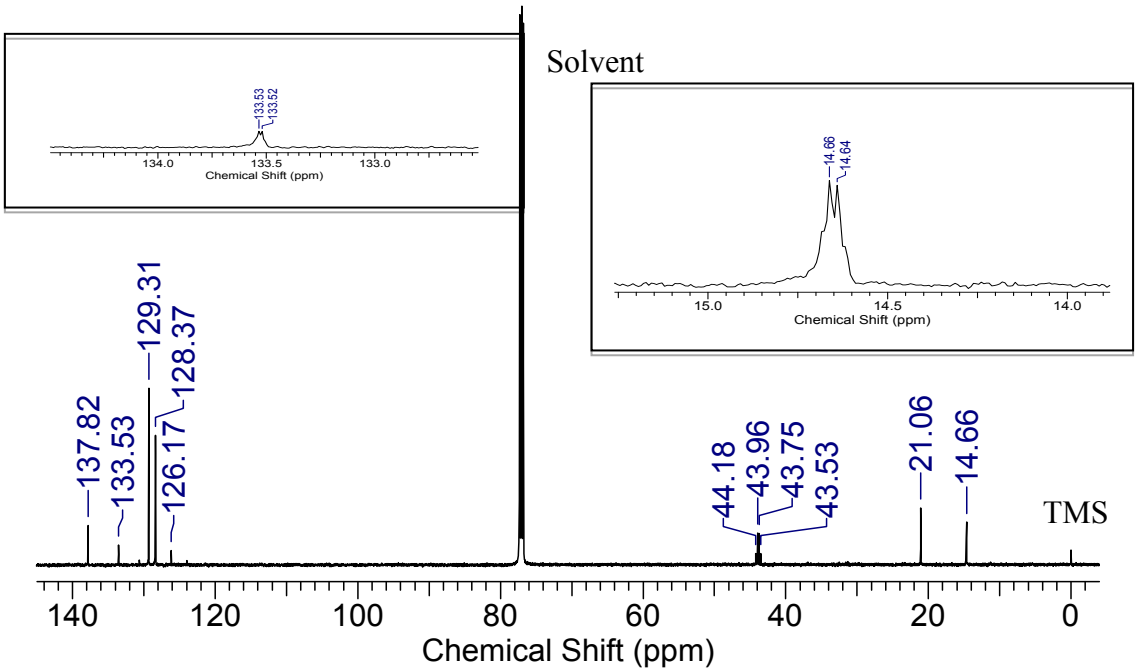

Solvent
133.53
133.52
134.0
133.5
133.0
Chemical Shift (ppm)
14.66
14.64
15.0
14.5
14.0
Chemical Shift (ppm)
137.82
133.53
129.31
128.37
126.17
44.18
43.96
43.75
43.53
21.06
14.66
TMS
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Fig. S39. ^{13}C NMR spectrum of 4-methyl-(2,2,2-trifluoro-1-methylehtyl)benzene (**6**).

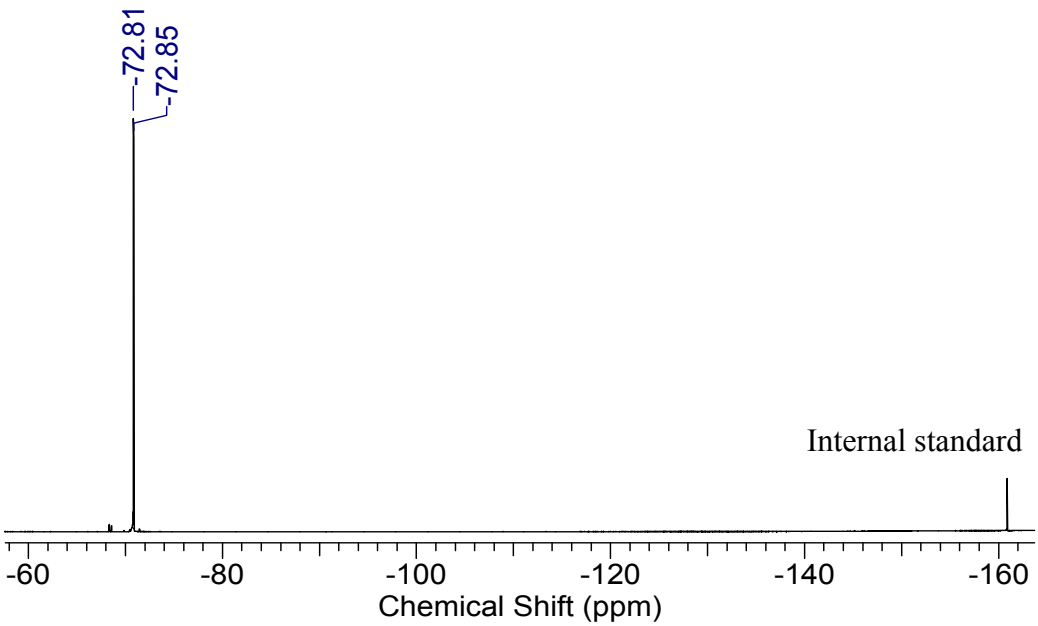


Fig.

S40. ^{19}F NMR spectrum of 4-methyl-(2,2,2-trifluoro-1-methylehtyl)benzene (**6**).

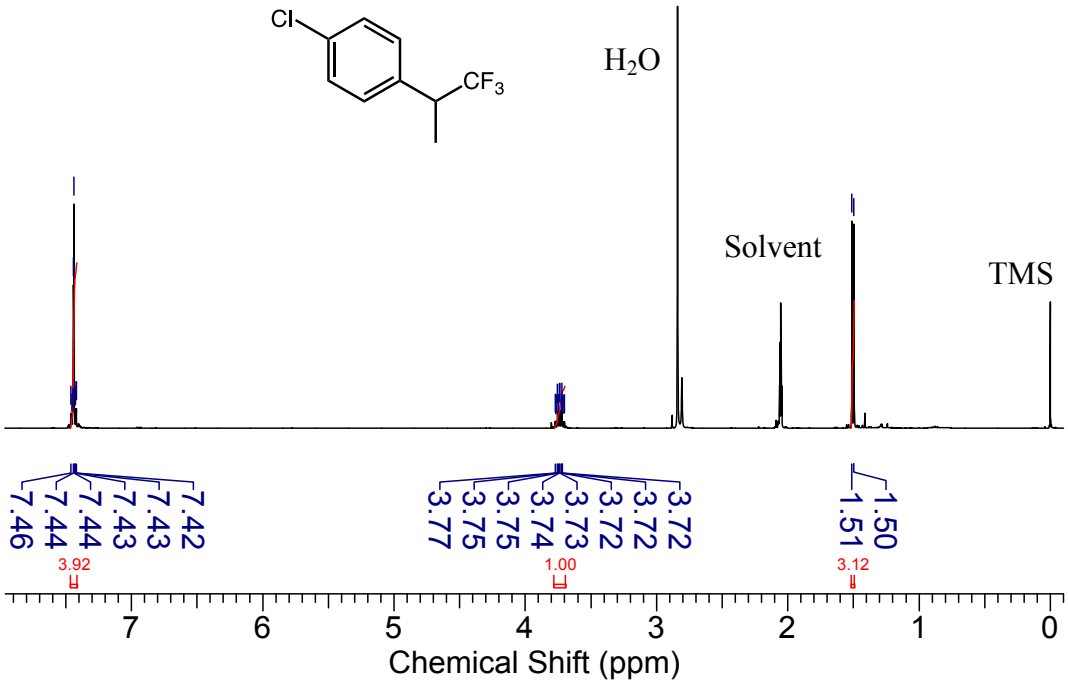


Fig. S41. ^{1}H NMR spectrum of 4-chloro-(2,2,2-trifluoro-1-methylehtyl)benzene (**15**).

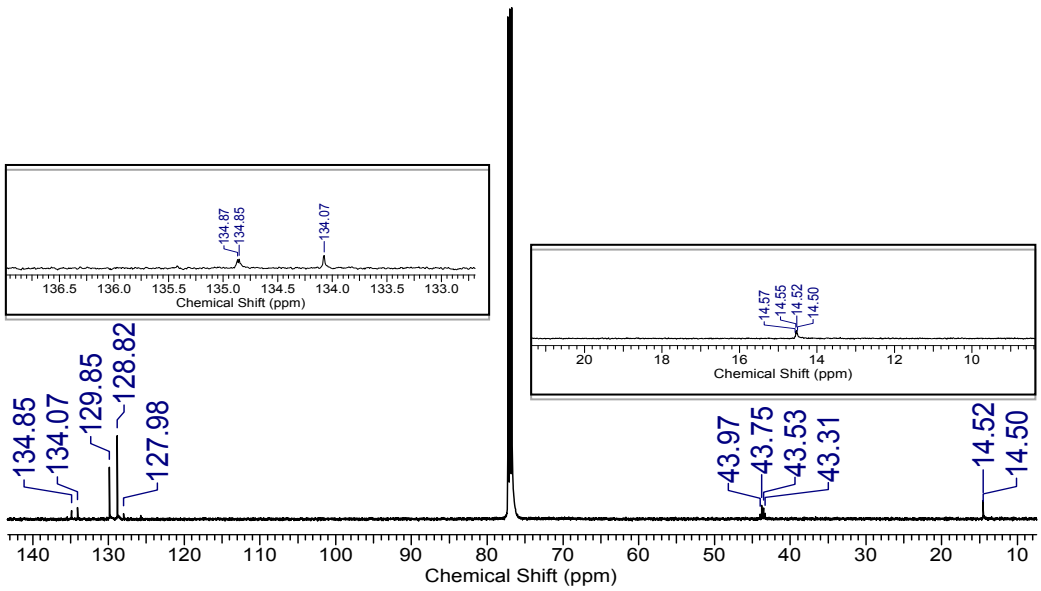


Fig. S42. ^{13}C NMR spectrum of 4-chloro-(2,2,2-trifluoro-1-methylehtyl)benzene (**15**).

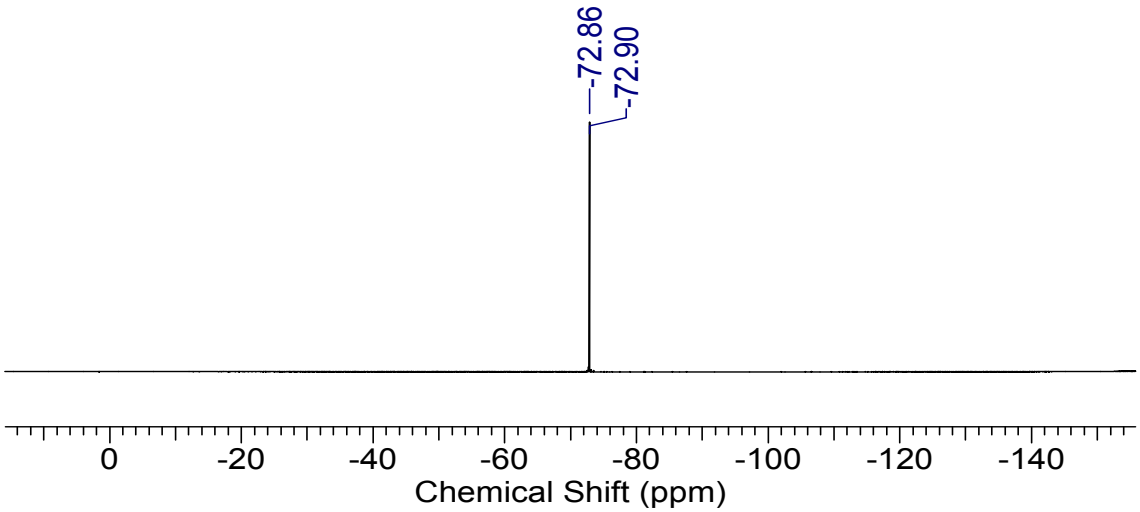

-72.86
-72.90
0
-20
-40
-60
-80
-100
-120
-140
Chemical Shift (ppm)

Fig. S43. ^{19}F NMR spectrum of 4-chloro-(2,2,2-trifluoro-1-methylehtyl)benzene (**15**).

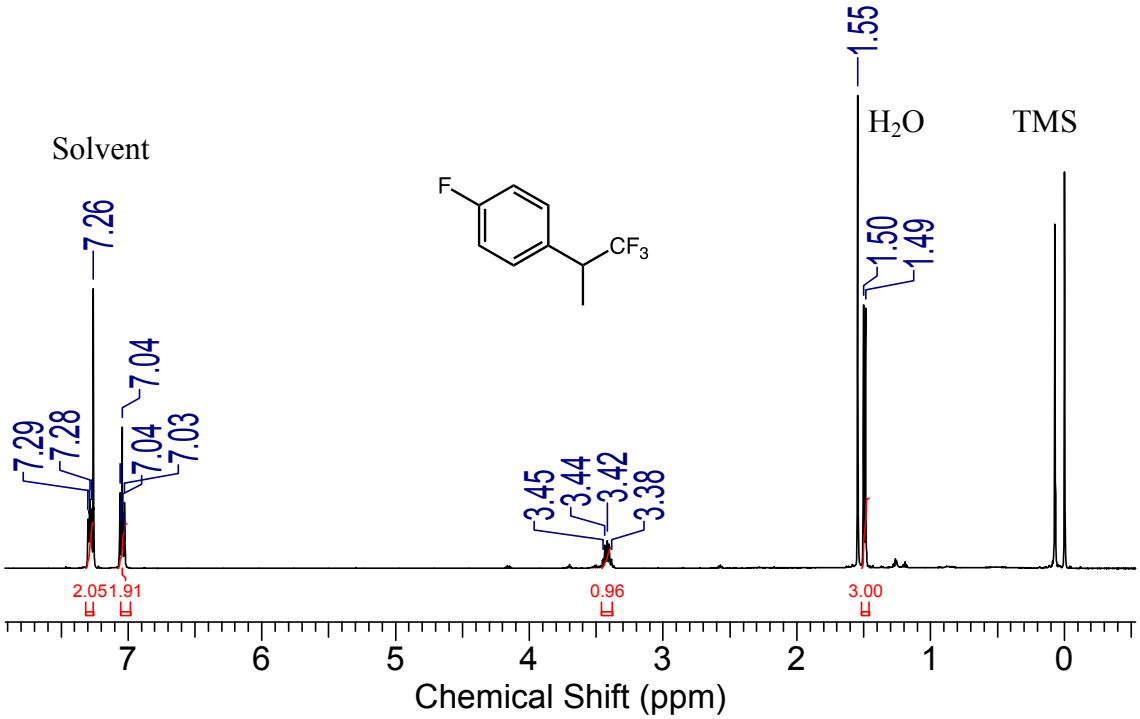
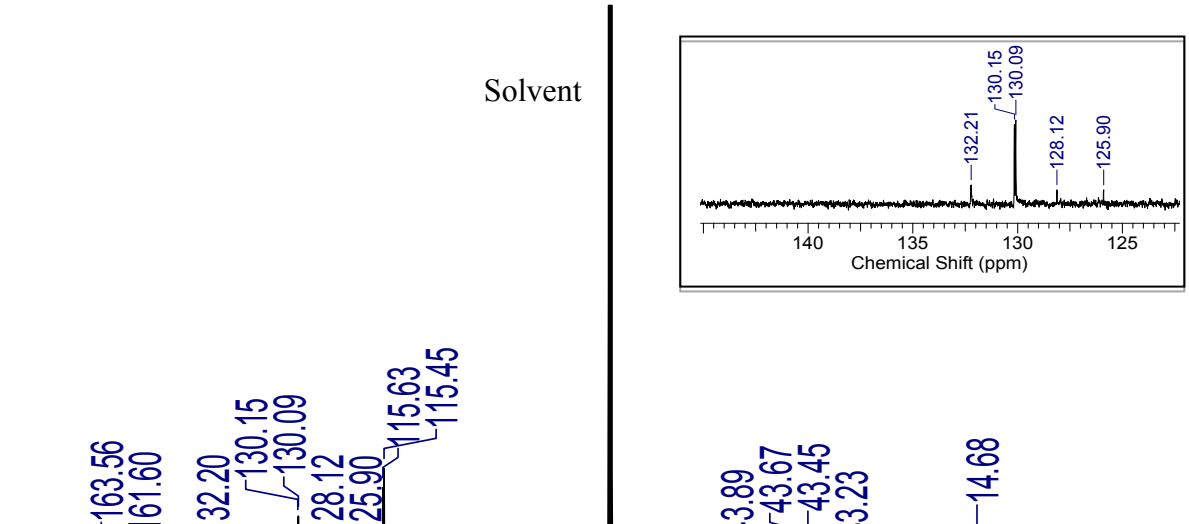


Fig. S44. ^{1}H NMR spectrum of 4-fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene (**12**).



TMS

Fig. S45. ^{13}C NMR spectrum of 4-fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene (**12**).

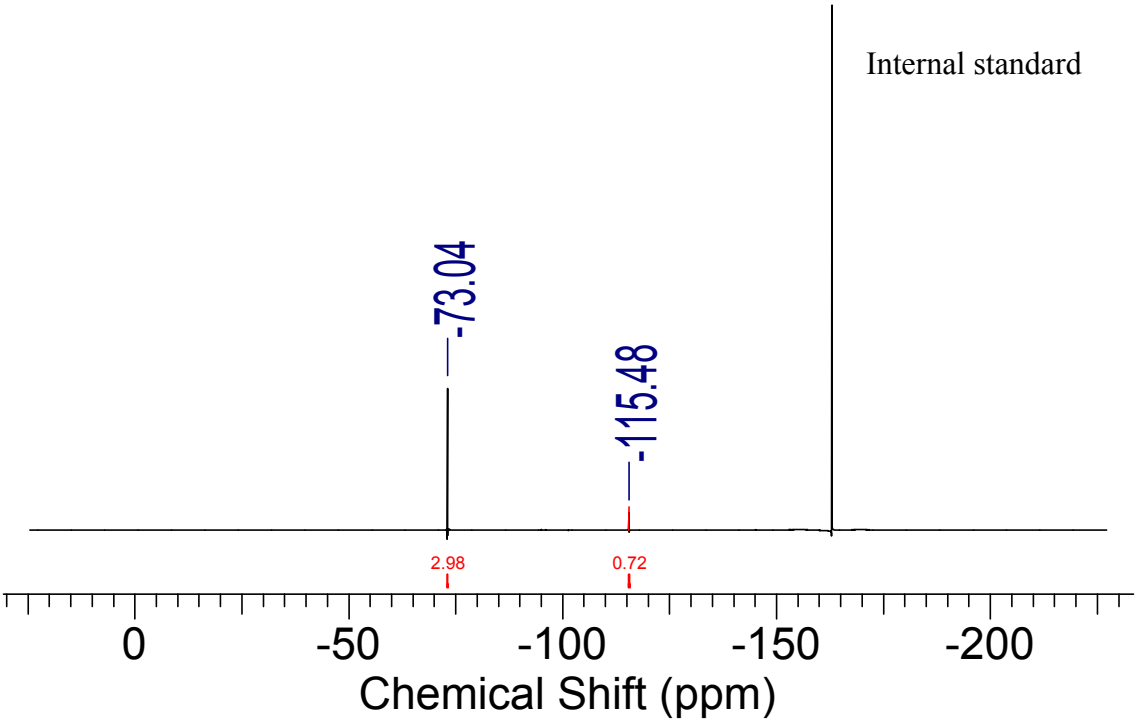


Fig. S46. ^{19}F NMR spectrum of 4-fluoro-(2,2,2-trifluoro-1-methylehtyl)benzene (**12**).

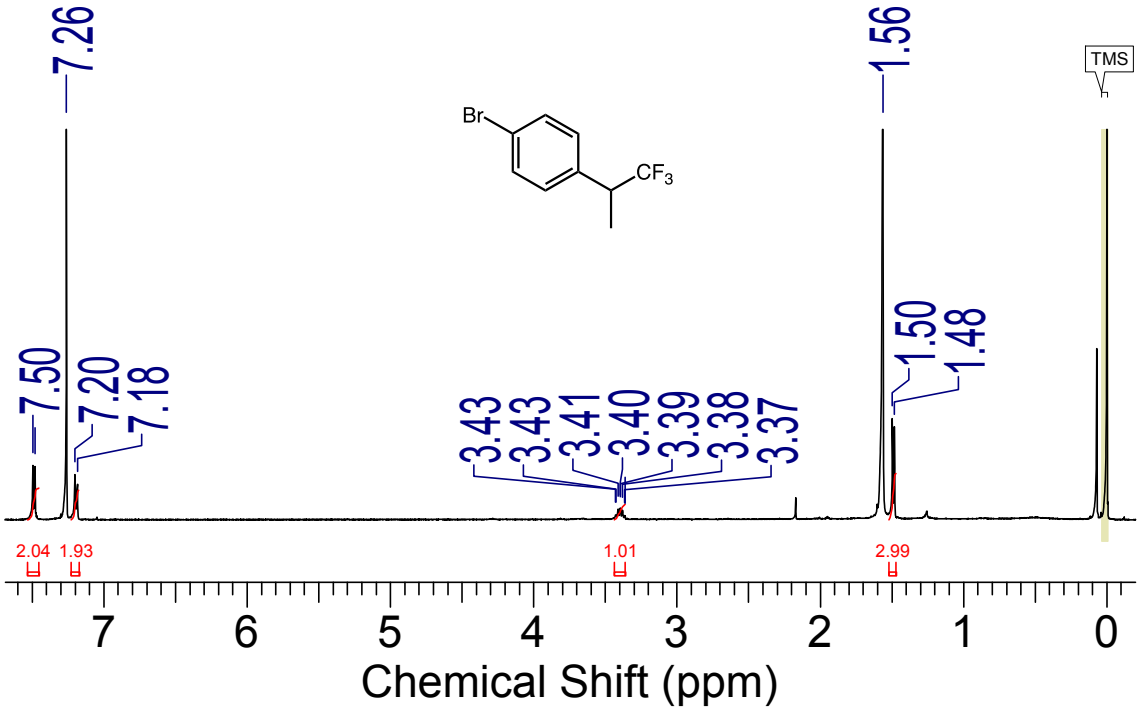


Fig. S47. ^{1}H NMR spectrum of 4-bromo-(2,2,2-trifluoro-1-methylehtyl)benzene (**18**).

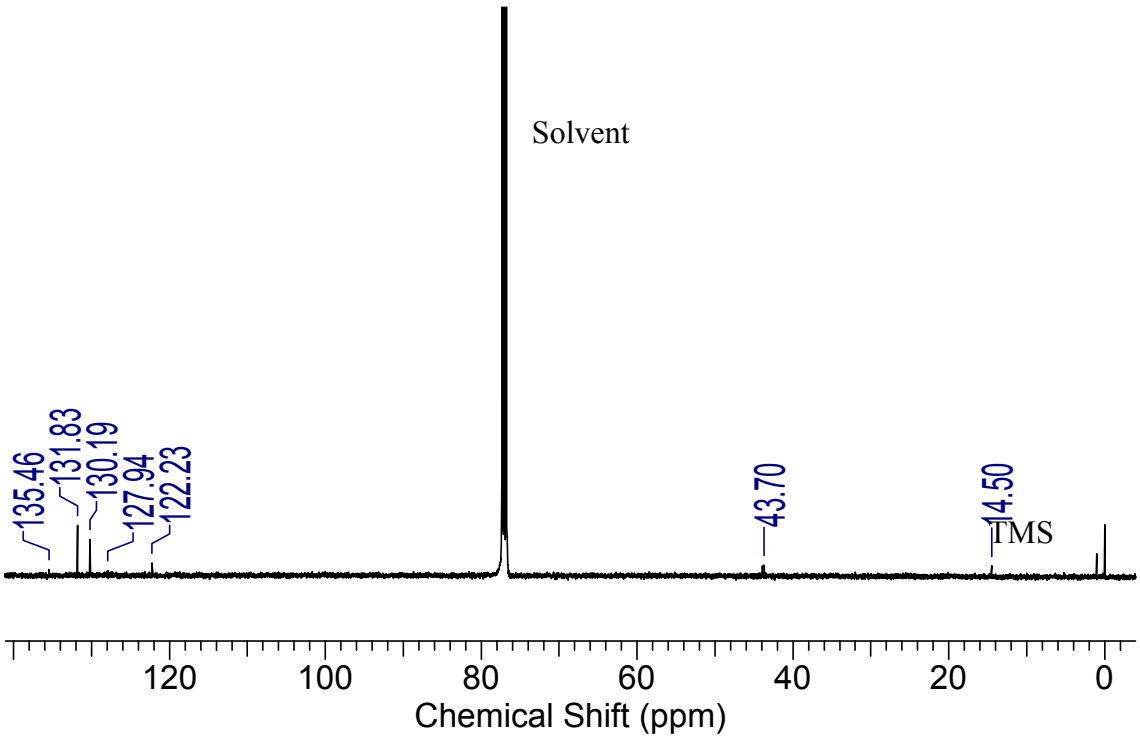


Fig. S48. ^{13}C NMR spectrum of 4-bromo-(2,2,2-trifluoro-1-methylehtyl)benzene (**18**).

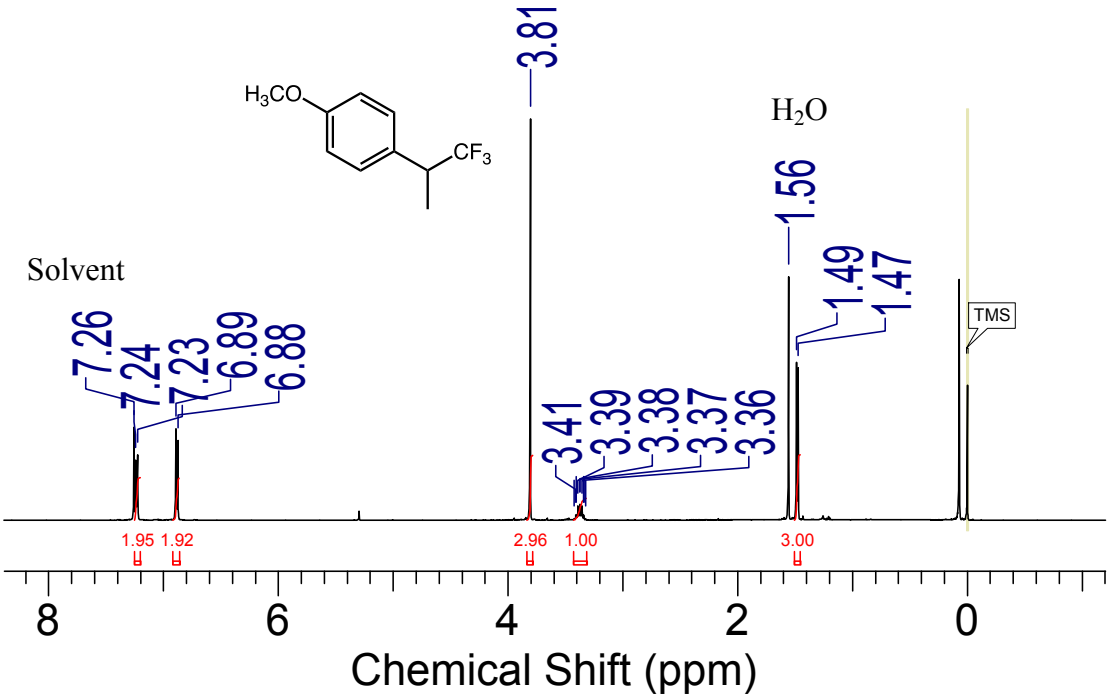


Fig. S49. [1]H NMR spectrum of 4-methoxy-(2,2,2-trifluoro-1-methylehtyl)benzene (**9**).

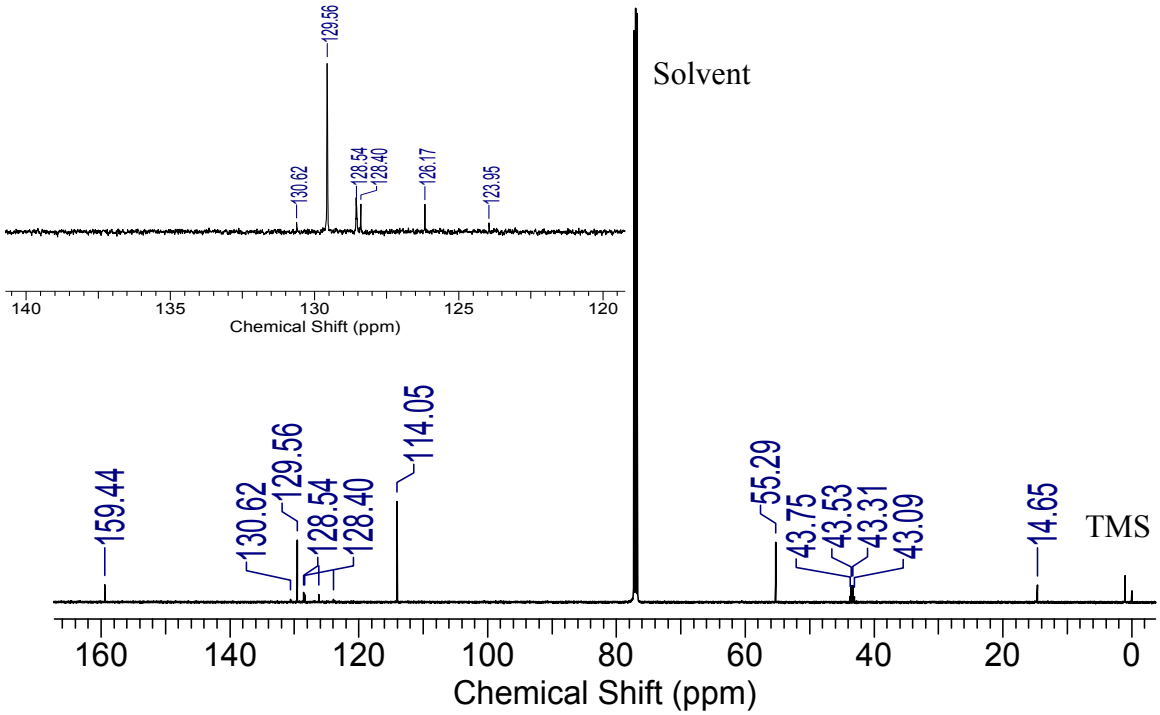


Fig. S50. [13]C NMR spectrum of 4-methoxy-(2,2,2-trifluoro-1-methylehtyl)benzene (**9**).

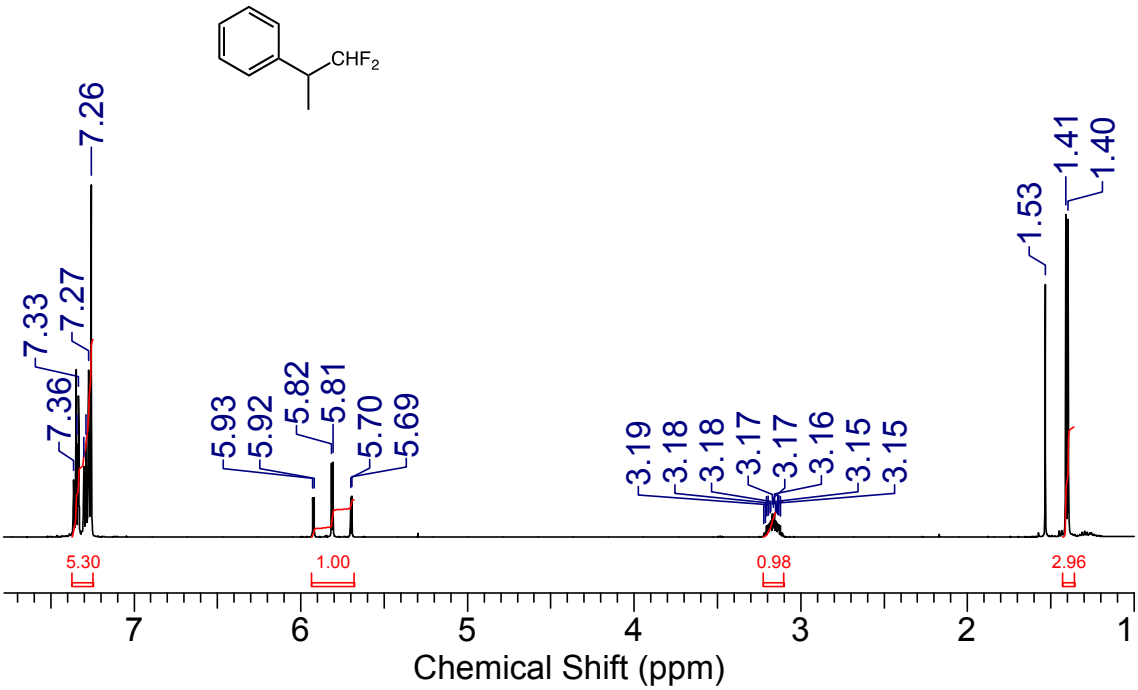

CHF2
7.26
7.33
7.27
7.36
5.93
5.92
5.82
5.81
5.70
5.69
3.19
3.18
3.18
3.17
3.17
3.16
3.15
3.15
1.53
1.41
1.40
5.30
1.00
0.98
2.96
7
6
5
4
3
2
1
Chemical Shift (ppm)

Fig. S51. ^{1}H NMR spectrum of 2,2-difluoro-1-methylehtylbenzene **(22)**.

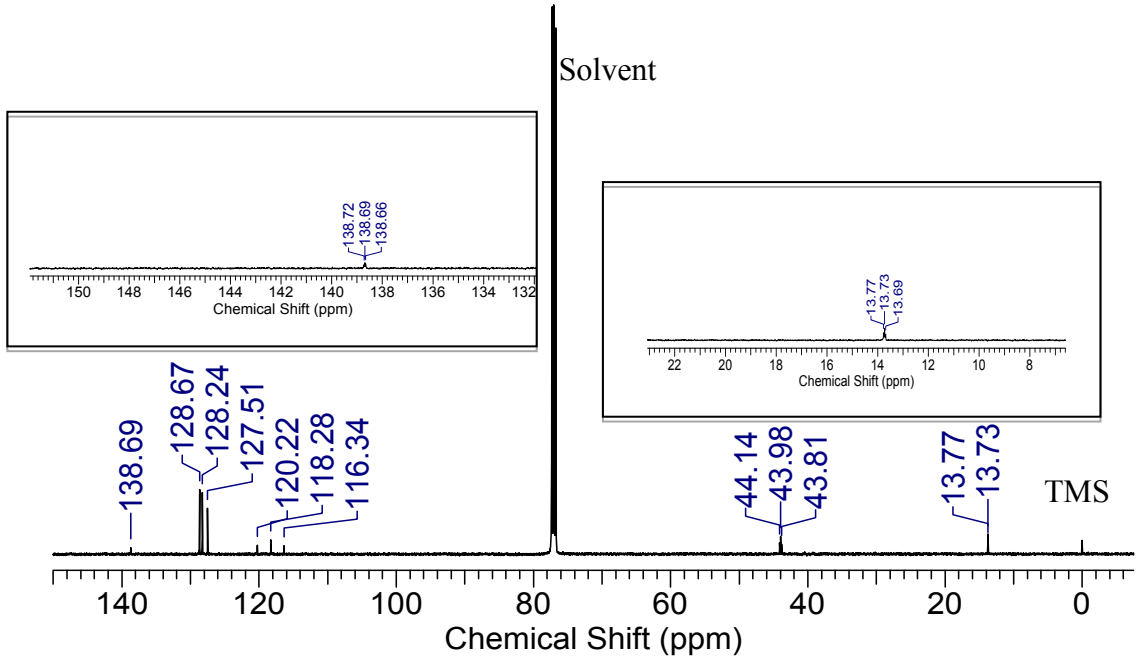

Solvent
138.72
138.69
138.66
150 148 146 144 142 140 138 136 134 132
Chemical Shift (ppm)
13.77
13.73
13.69
22 20 18 16 14 12 10 8
Chemical Shift (ppm)
138.69
128.67
128.24
127.51
120.22
118.28
116.34
44.14
43.98
43.81
13.77
13.73
TMS
140 120 100 80 60 40 20 0
Chemical Shift (ppm)

Fig. S52. ^{13}C NMR spectrum of 2,2-difluoro-1-methylehtylbenzene (**22**).

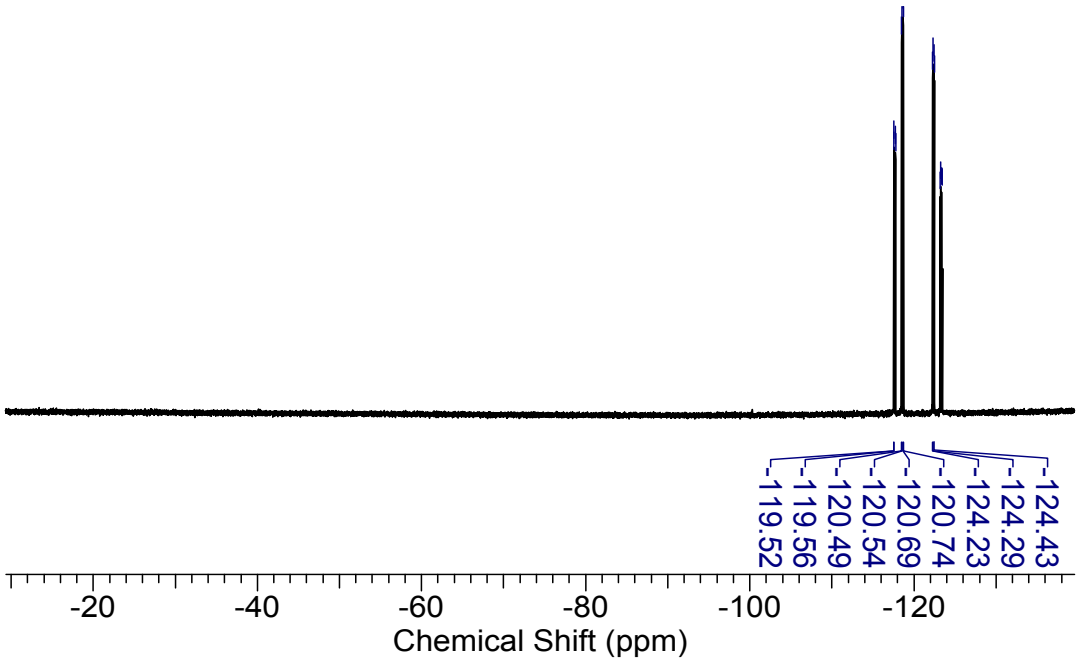


Fig. S53. ^{19}F NMR spectrum of 2,2-difluoro-1-methylehtylbenzene (**22**).

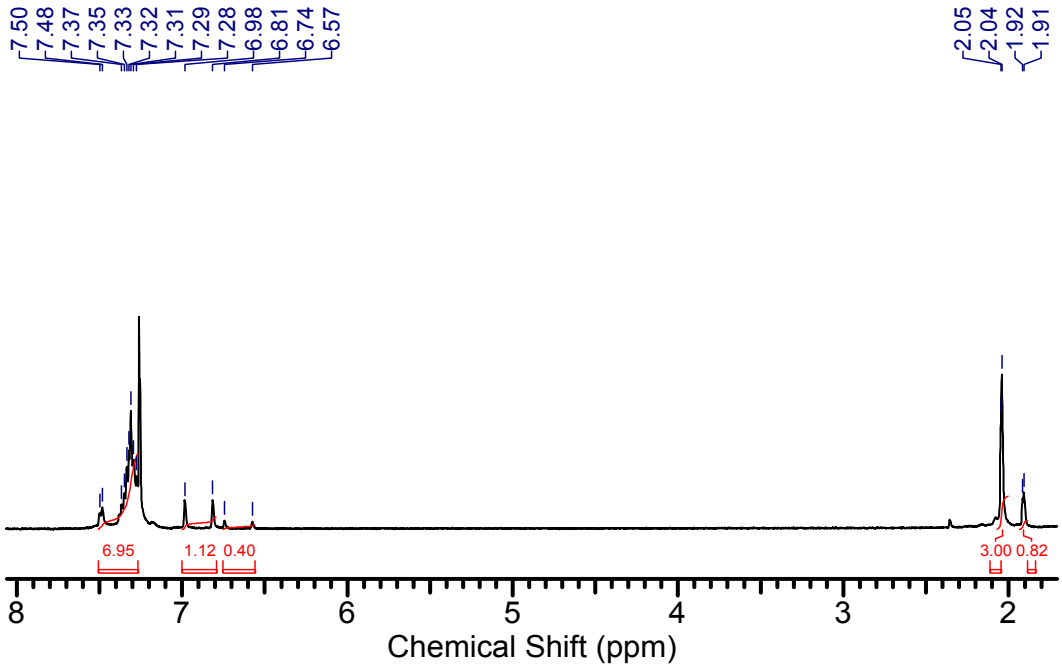

7.50
7.48
7.37
7.35
7.33
7.32
7.31
7.29
7.28
6.98
6.81
6.74
6.57
2.05
2.04
1.92
1.91
6.95
1.12
0.40
3.00
0.82
8
7
6
5
4
3
2
Chemical Shift (ppm)

Fig. S54. ^{1}H NMR spectrum of β-fluoro-α-methyl styrenes (*E*/*Z*) (**20**/**21**).

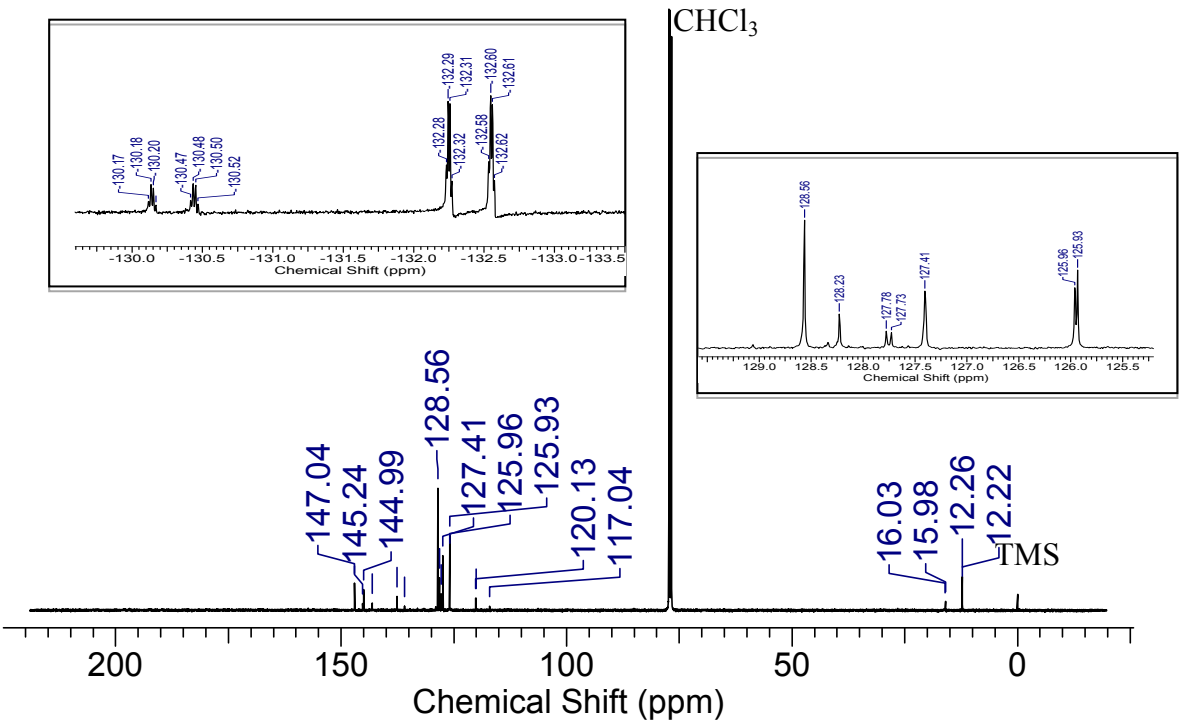


Fig. S55. ^{13}C NMR spectrum of β-fluoro-α-methyl styrenes (*E*/*Z*) (**20**/**21**).

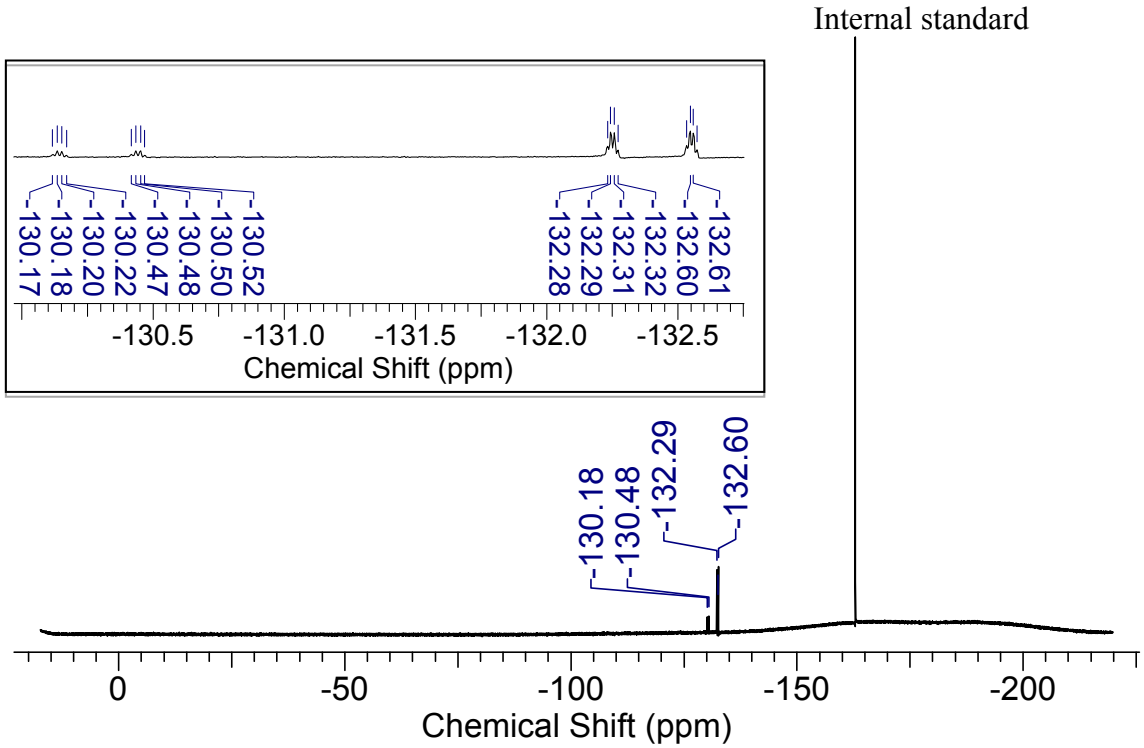

Internal standard
-130.17
-130.18
-130.20
-130.22
-130.47
-130.48
-130.50
-130.52
-132.28
-132.29
-132.31
-132.32
-132.60
-132.61
-130.5
-131.0
-131.5
-132.0
-132.5
Chemical Shift (ppm)
-130.18
-130.48
-132.29
-132.60
0
-50
-100
-150
-200
Chemical Shift (ppm)

Fig. S56. ^{19}F NMR spectrum of β-fluoro-α-methyl styrenes (*E*/*Z*) (**20**/**21**).

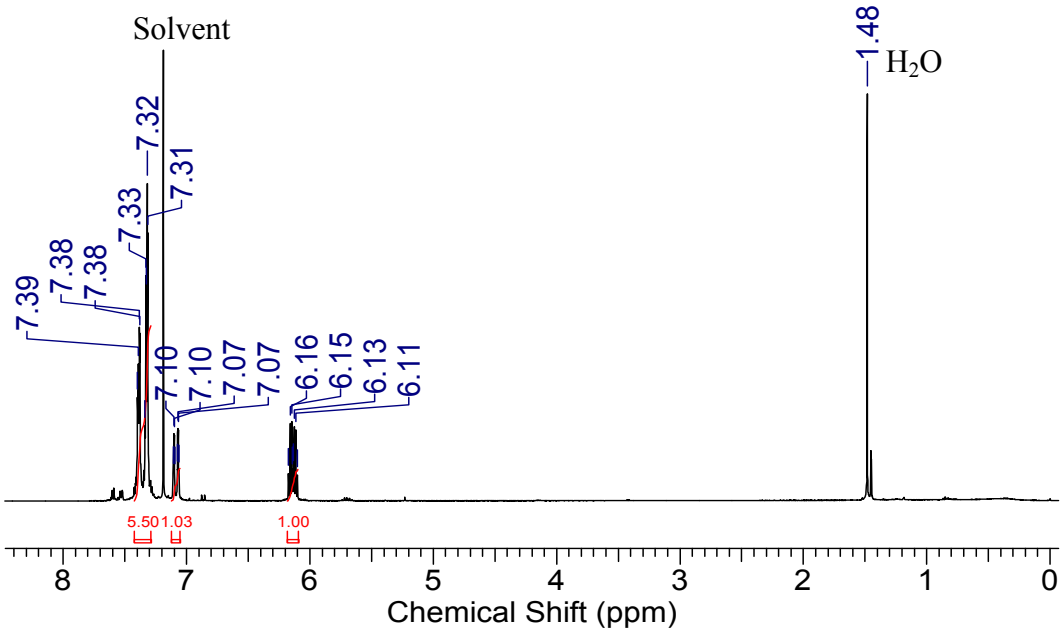


Fig. S57. ^{1}H NMR spectrum of β-trifluoromethyl styrene (**24**).

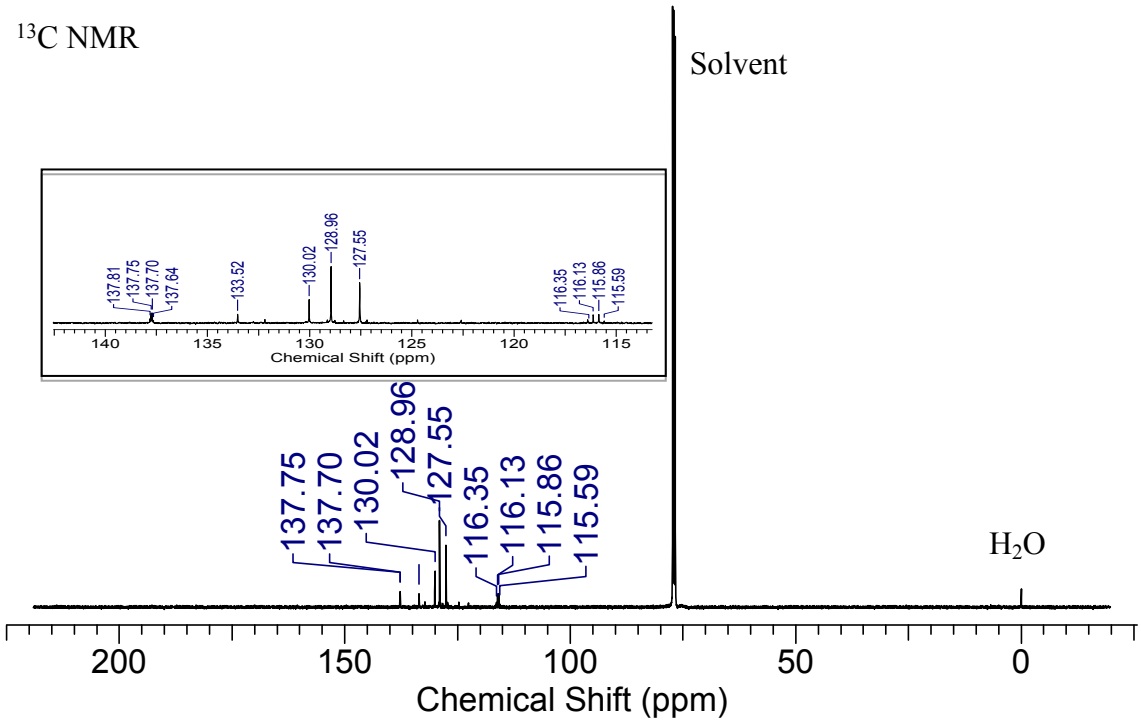

13C NMR
Solvent
137.81
137.75
137.70
137.64
133.52
130.02
128.96
127.55
116.35
116.13
115.86
115.59
140
135
130
125
120
115
Chemical Shift (ppm)
137.75
137.70
130.02
128.96
127.55
116.35
116.13
115.86
115.59
H2O
200
150
100
50
0
Chemical Shift (ppm)

Fig. S58. ^{13}C NMR spectrum of β-trifluoromethyl styrene (**24**).

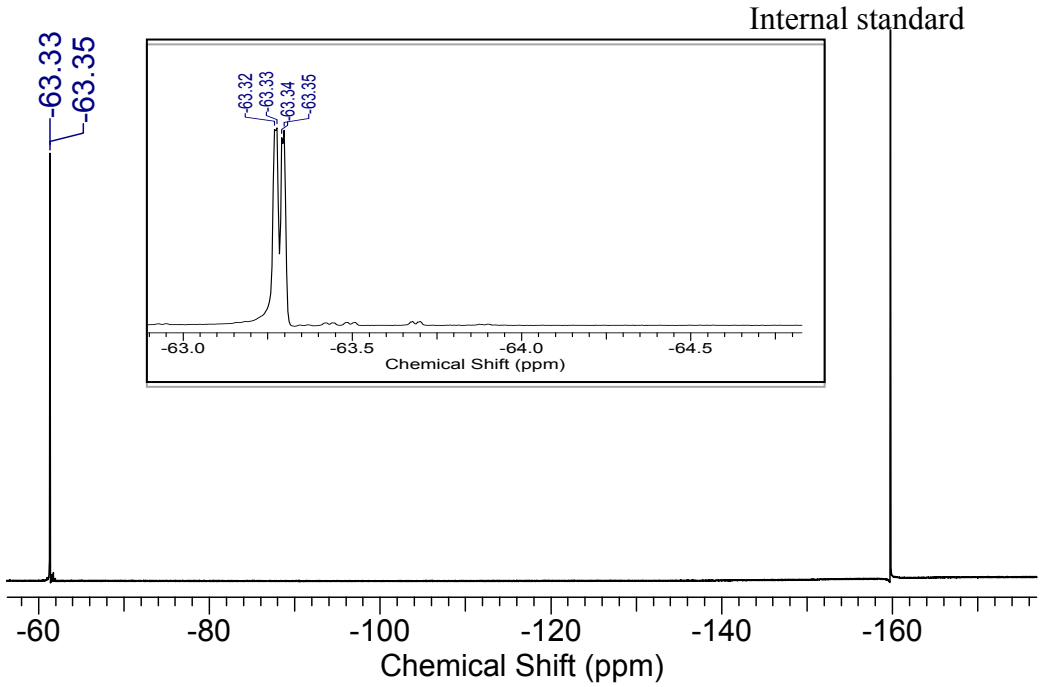


Fig. S59. ^{19}F NMR spectrum of β-trifluoromethyl styrene (**24**).

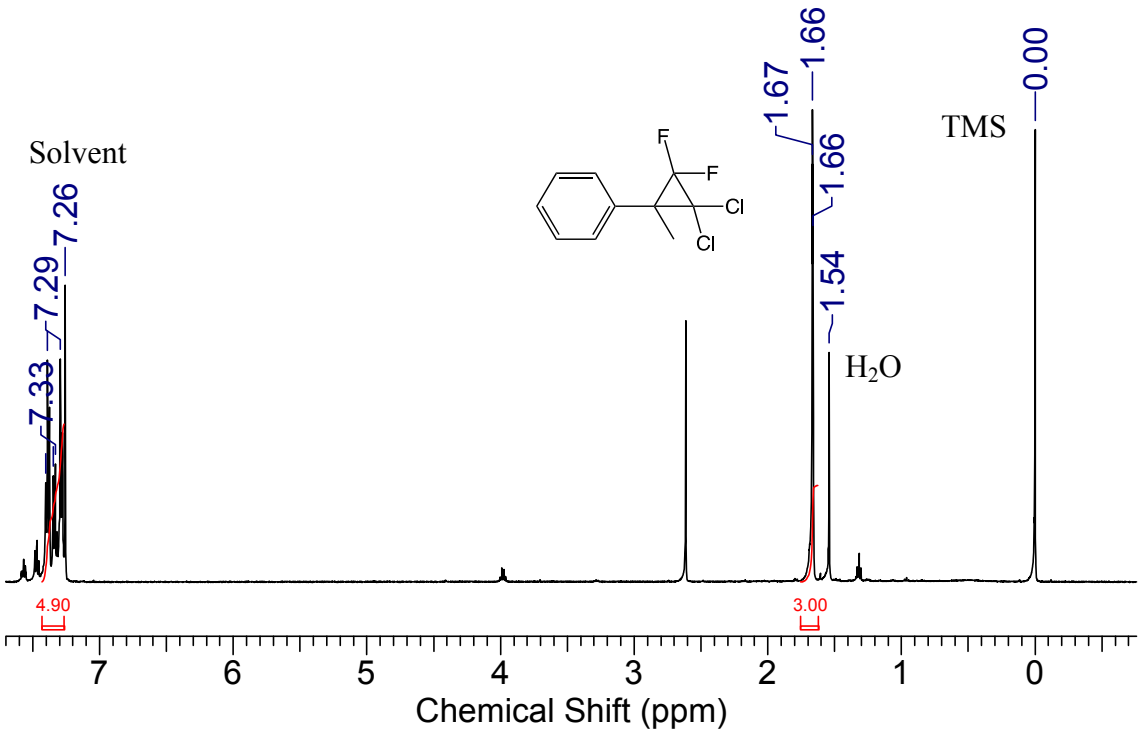

Solvent
7.26
7.29
7.33
1.67
1.66
1.66
1.54
H2O
TMS
0.00
F
F
Cl
Cl
4.90
3.00
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Fig. S60. ^{1}H NMR spectrum of **26**.

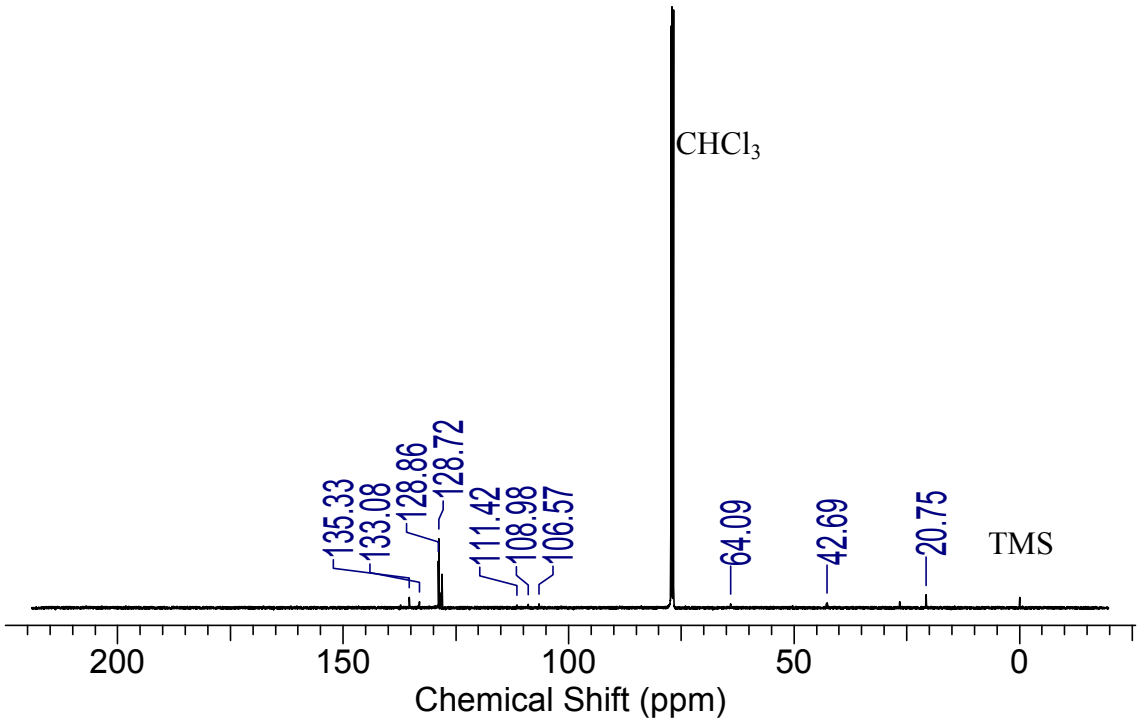


Fig. S61. ^{13}C NMR spectrum of **26**.

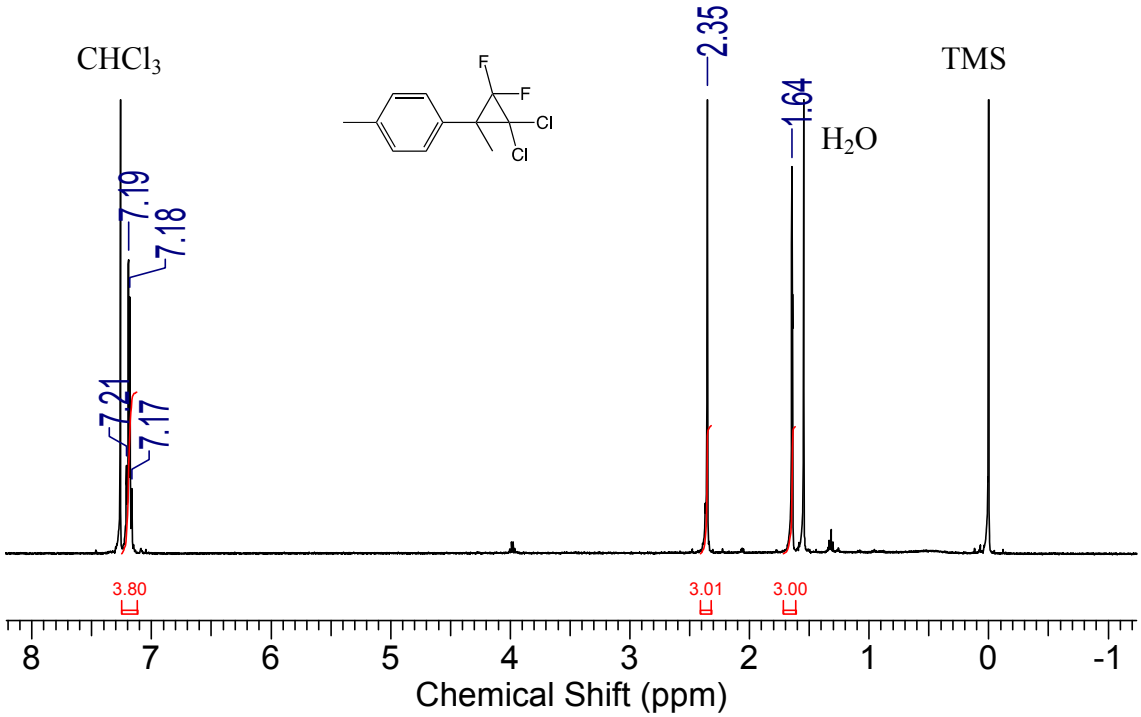


Fig. S62. ^{1}H NMR spectrum of **27**.

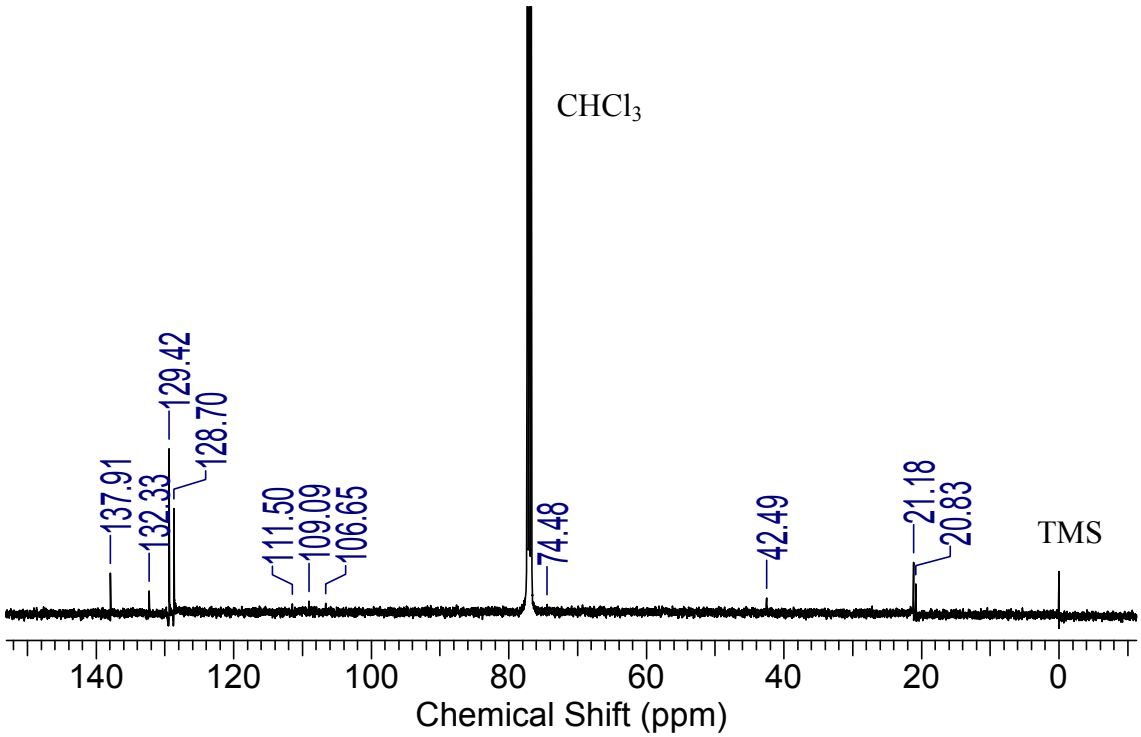


Fig. S63. ^{13}C NMR spectrum of **27**.

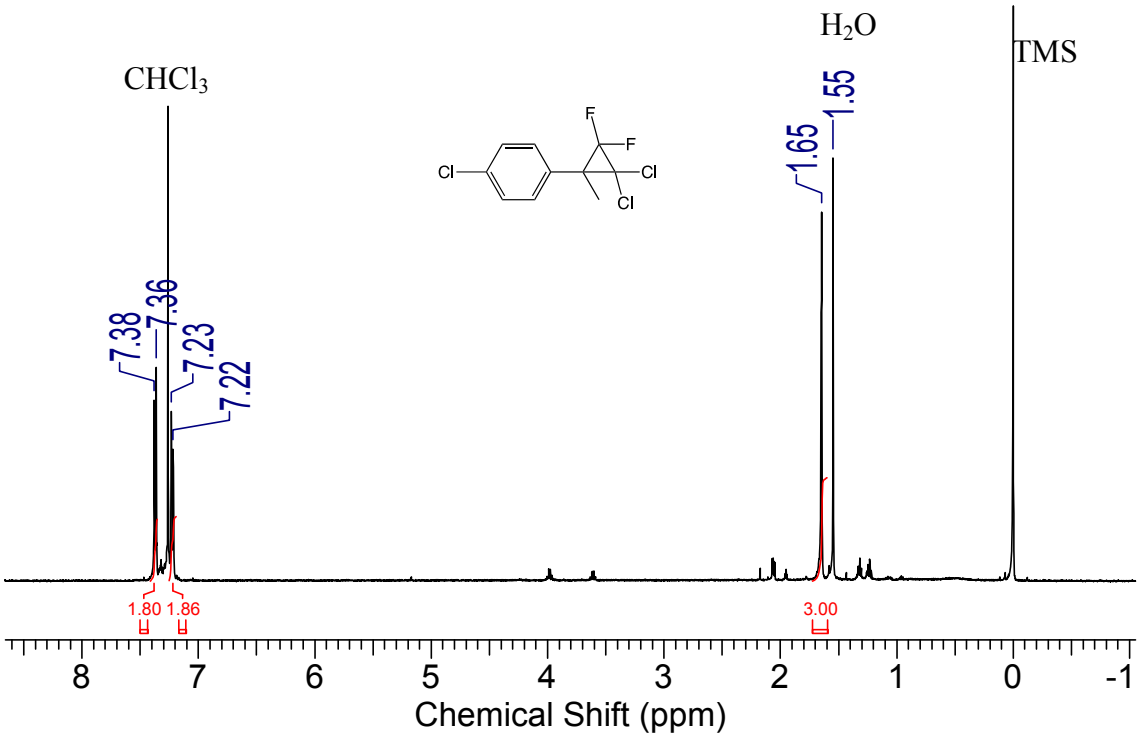


Fig. S64. ^{1}H NMR spectrum of **28**.

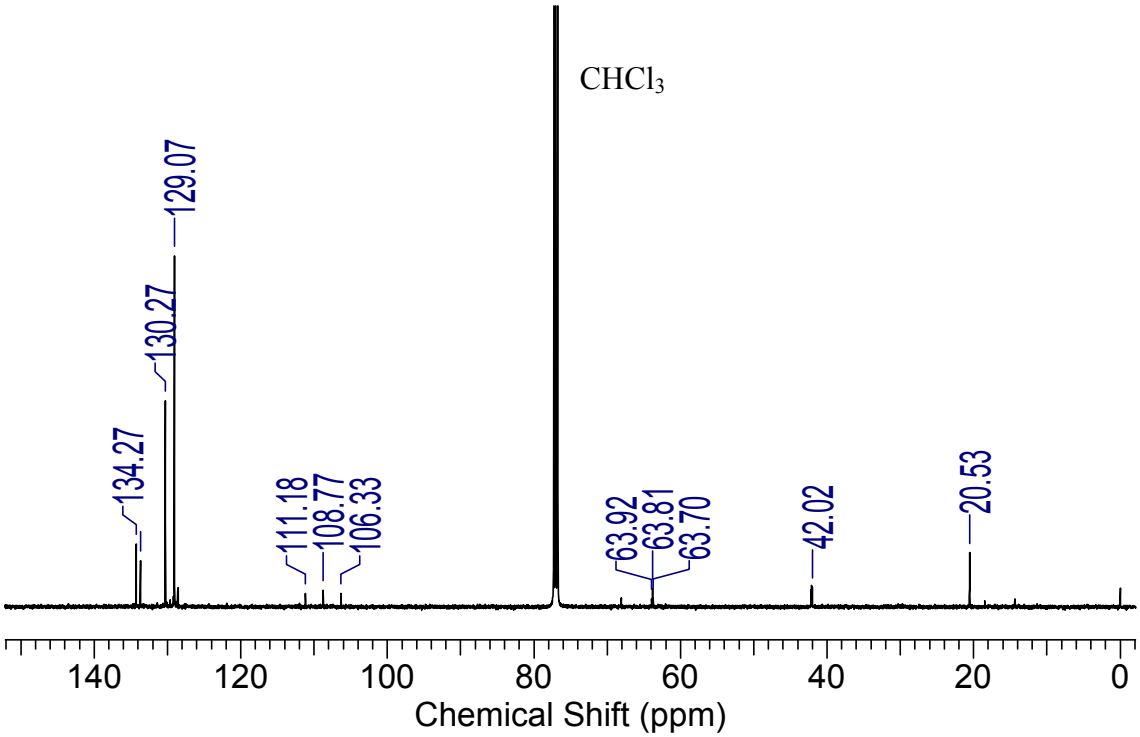


Fig. S65. ^{13}C NMR spectrum of **28**.

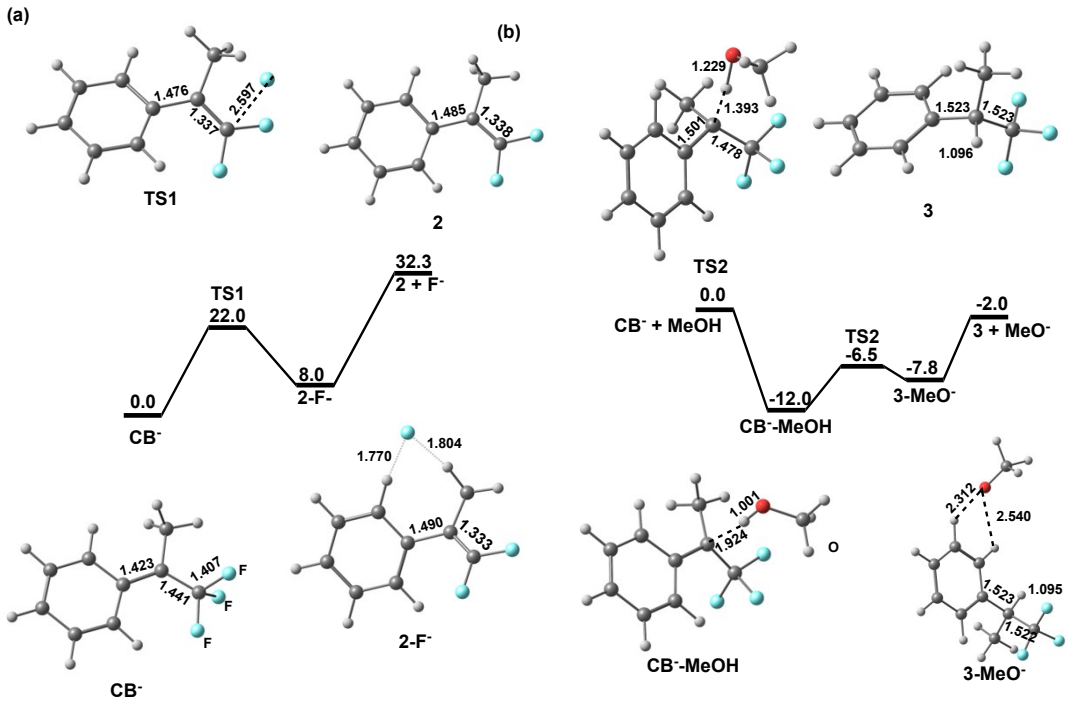


Fig. S66. Optimized structures and computed energy diagrams for (a) *β*-fluorine elimination and (b) protonation in carbanion intermediate (**CB**$^-$). Units are in kcal/mol and angstrom**.**