Visible-Light-Induced Metal-Free Decarboxylative Perfluoroalkylation of Aryl Acrylic Acids

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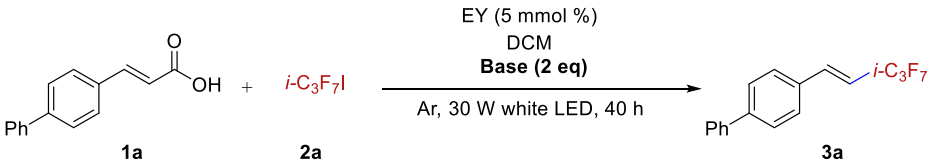
Supporting Information

1. General Information

All commercially available reagents were used without further purification unless mentioned otherwise. ^{1}H, ^{13}C and ^{19}F Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometer. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an GC-MS instrument (Ionspec 7.0 T, EI/ Quadrupole Mass Analyzer, EI-QMA). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). White LED (30 W) was purchased from JIADENG (LS) and used for white light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.

2. Reaction of optimization

Table S1. Screening of bases.[a]

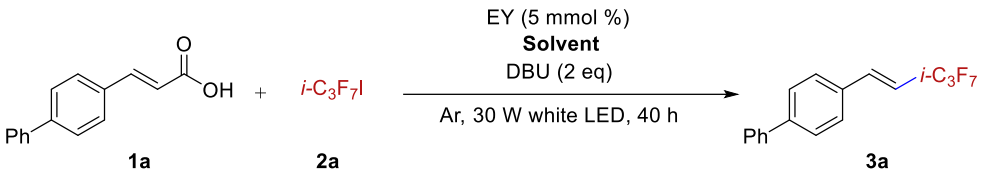


1a 2a 3a

Entry	Bases	Yield (%)[b]
1	DBU	46
2	Cs_2CO_3	0
3	Na_2CO_3	0
4	K_2CO_3	0
5	NaOAc	0
6	K_3PO_4	0
7	DIPEA	20

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a** (1.0 mmol, 5 equiv.), **EY** (5 mol%), **bases** (0.4 mmol, 2 equiv.) in **DCM** (0.1 M) were irradiated using a 30 W white LED at room temperature under an argon atmosphere for 40 h. [b]Yields were determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as an internal standard.

Table S2. Screening of solvents.[a]



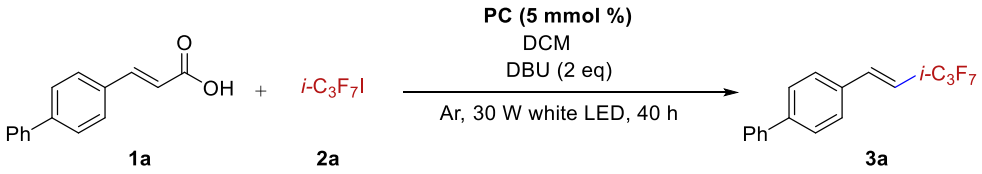
1a 2a 3a

Entry	Solvents	Yield (%)[b]
1	DCM	46
2	MeCN	22

3	DMSO	0
4	THF	0
5	DMF	0

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a** (1.0 mmol, 5 equiv.), **EY** (5 mol%), **DBU** (0.4 mmol, 2 equiv.) in **solvent** (0.1 M) were irradiated using a 30 W white LED at room temperature under an argon atmosphere for 40 h. [b]Yields were determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as an internal standard.

Table S3. Screening of photocatalysts.[a]

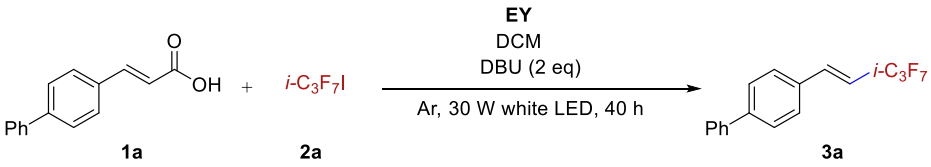


1a **2a** **3a**

Entry	Photocatalysts	Yield (%)[b]
1	Eosin Y	46
2	*fac*-Ir(ppy)$_3$	20
3	4CzIPN	14

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a** (1.0 mmol, 5 equiv.), **photocatalyst** (5 mol%), **DBU** (0.4 mmol, 2 equiv.) in **DCM** (0.1 M) were irradiated using a 30 W white LED at room temperature under an argon atmosphere for 40 h. [b]Yields were determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as an internal standard.

Table S4. Screening of amount of photocatalyst.[a]

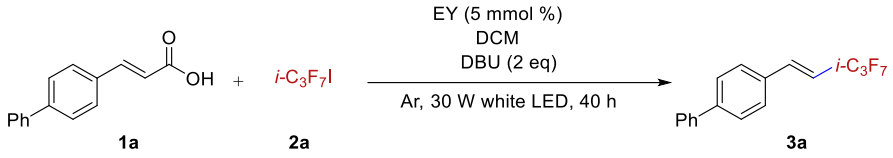


1a **2a** **3a**

Entry	Amount of **EY** (%)	Yield (%)[b]
1	0.5	6
2	2	30
3	5	46

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a** (1.0 mmol, 5 equiv.), **Eosin Y**, **DBU** (0.4 mmol, 2 equiv.) in **DCM** (0.1 M) were irradiated using a 30 W white LED at room temperature under an argon atmosphere for 40 h. [b]Yields were determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as an internal standard.

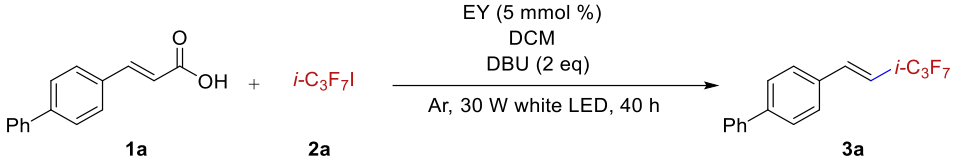
Table S5. Screening of equivalent of 2a[a]



Entry	Equivalent of **2a**	Yield (%)[b]
1	1.5	11
2	2	22
3	3	38
4	5	46

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a**, **Eosin Y** (5 mol%), **DBU** (0.4 mmol, 2 equiv.) in **DCM** (0.1 M) were irradiated using a 30 W white LED at room temperature under an argon atmosphere for 40 h. [b]Yields were determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as an internal standard.

Table S6. Screening of concentration of 1a[a]

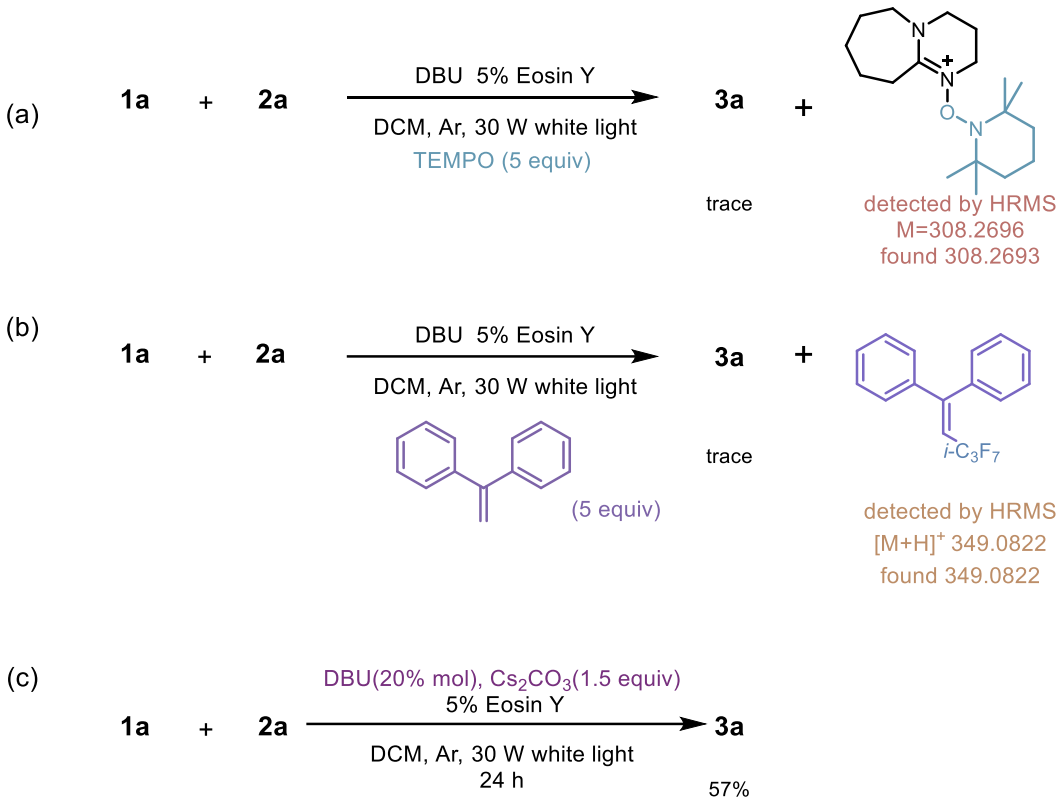


Entry	Concentration of **1a**	Yield (%)[b]
1	0.2 M	11
2	0.1 M	46
3	**0.0677 M**	**93**

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a**, **Eosin Y** (5 mol%), **DBU** (0.4 mmol, 2 equiv.) in **DCM** were irradiated using a 30 W white LED at room temperature under an argon atmosphere for 40 h. [b]Yields were determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as an internal standard.

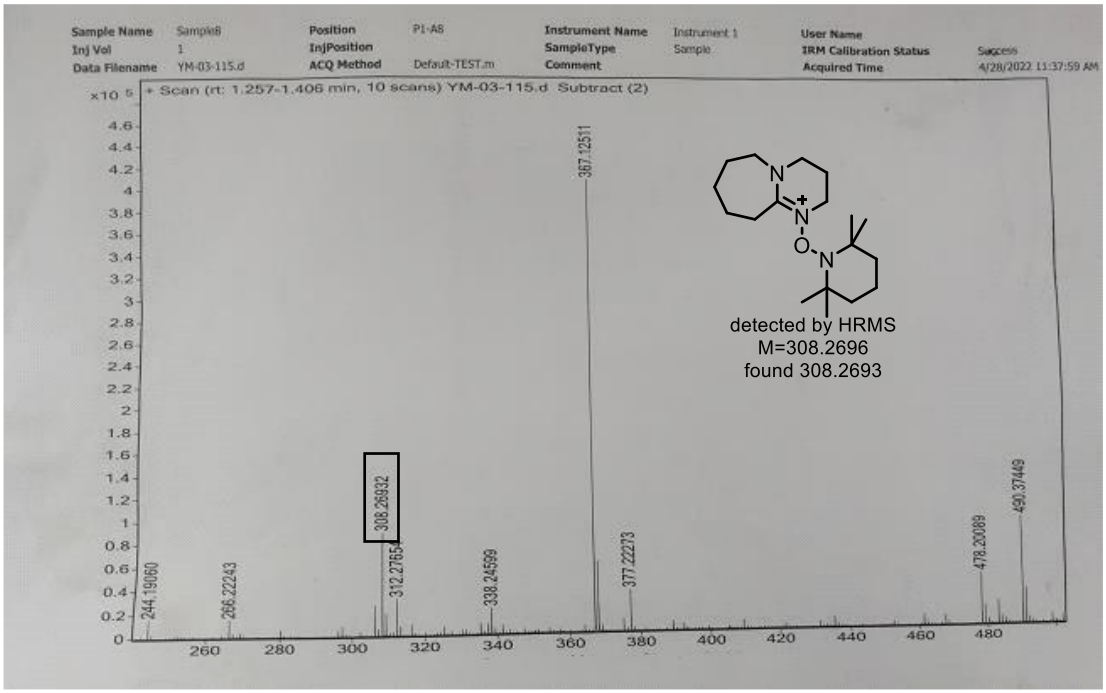
3. Investigation of the mechanism

3.1 Radical inhibition experiment

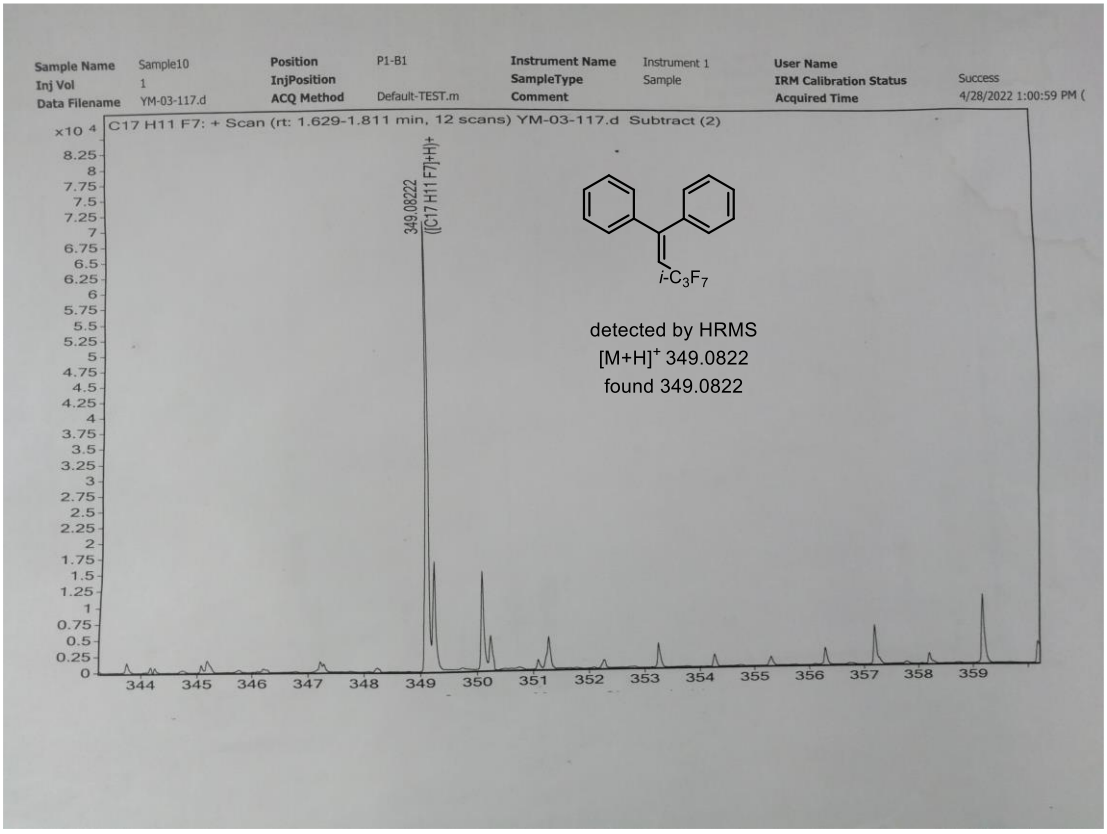


Scheme S1

a) To an 8 mL glass vial was added **1a** (0.2 mmol, 1 equiv.), **2a** (1 mmol, 5 equiv.), Eosin Y (5 mol%), DBU (0.4 mmol, 2 equiv.), DCM (3 mL, 0.067 M) and TEMPO (156 mg, 1 mmol). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. The HRMS is detected.



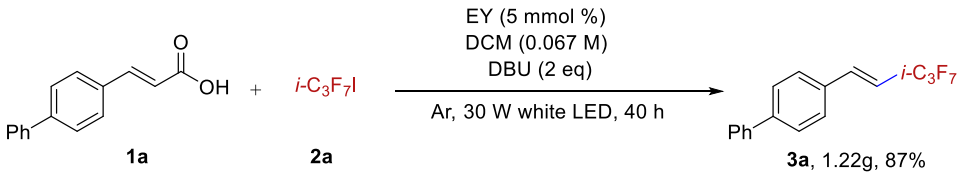
b) To an 8 mL glass vial was added **1a** (0.2 mmol, 1 equiv.), **2a** (1 mmol, 5 equiv.), Eosin Y (5 mol%), DBU (0.4 mmol, 2 equiv.), DCM (3 mL,0.067 M) and 1,1-diphenylethylene (108 mg, 0.6 mmol)). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. The HRMS is detected.



3.2 Proof of DBU as a SET reagent

c) To an 8 mL glass vial was added **1a** (0.2 mmol, 1 equiv.), **2a** (1 mmol, 5 equiv.), Eosin Y (5 mol%), DBU (0.04 mmol, 20 mol %), DCM (3 mL,0.067 M) and Cs_2CO_3 (3 mmol, 1.5 equiv.). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. Yield was determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as an internal standard.[1]

4.Gram-scale preparation

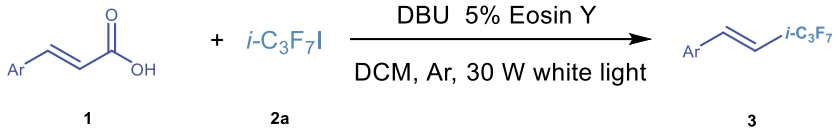


1a **2a** **3a**, 1.22g, 87%

To an 8 mL glass vial was added **1a** (0.90 g, 4.0 mmol, 1 equiv.), **2a** (6.0 g, 20.0 mmol, 5 equiv.), Eosin Y (130 mg, 0.2 mmol, 5 mol%), DBU (1.2 g, 0.4 mmol, 2 equiv.), DCM (60 mL, 0.067 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. The HRMS is detected. When the reaction is completed, extracted with DCM (3 × 30 mL), washed with brine (3 × 30 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (petroleum ether) to afford the

corresponding target compounds.

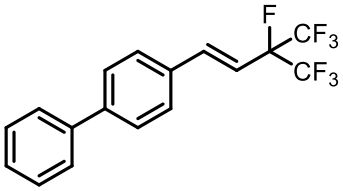
5.Experimental procedures and product characterization



1 2a 3

To an 8 mL glass vial was added **1** (0.2 mmol, 1 equiv.), **2a** (296 mg, 1.0 mmol, 5 equiv.), Eosin Y (6.4 mg, 0.01 mmol, 5 mol%), DBU (61 mg, 0.4 mmol, 2 equiv.), DCM (3 mL, 0.067 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. When the reaction is completed, extracted with DCM (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography on a silica gel using petroleum ether and ethyl acetate to afford the corresponding target compounds **3**.

(*E*)-4-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)-1,1'-biphenyl (**3a**)



White solid, yield 90% (62.6 mg). M.p. = 116 – 118 ºC.

R_f 0.90 (Petroleum ether).

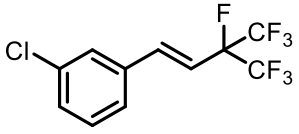
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 4H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 16.1 Hz, 1H), 6.32 (dd, *J* = 19.8, 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.2, 138.2 (d, *J* = 11.2 Hz), 132.9, 129.0, 128.0, 127.7, 127.1, 125.6 – 115.4 (m), 111.9, 111.7, 94.2 – 88.4 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.05 (d, *J* = 8.4 Hz), -180.82 – -188.98 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{11}F_7$ 348.0743; found 348.0743.

(*E*)-1-chloro-3-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3b**)



Colorless oil, yield 51% (31.0 mg).

R_f 0.70 (Petroleum ether).

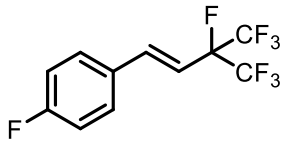
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.38 – 7.32 (m, 3H), 7.09 (d, *J* = 16.1 Hz, 1H), 6.16 (dd, *J* = 19.8, 16.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4 (d, *J* = 11.4 Hz), 135.7, 135.2, 130.3, 130.0, 127.4, 125.8, 125.2 – 115.6 (m), 113.6 (d, *J* = 16.8 Hz), 94.1 – 88.3 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -76.97 (d, *J* = 8.2 Hz), -184.98 – -190.74 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_6ClF_7$ 306.0041; found 306,0040.

(*E*)-1-fluoro-4-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3c**)



Colorless oil, yield 81% (31.0 mg).

R_f 0.90 (Petroleum ether).

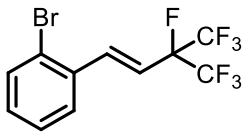
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.81 – 7.70 (m, 2H), 7.26 (d, *J* = 16.2 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.52 (dd, *J* = 20.8, 16.2 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.6 (d, *J* = 248.5 Hz), 138.7 (d, *J* = 11.7 Hz), 131.4 (d, *J* = 3.4 Hz), 130.9 (d, *J* = 8.4 Hz), 121.4 (qd, *J* = 284.4, 27.1 Hz), 116.7 (d, *J* = 22.0 Hz), 112.1 (d, *J* = 16.8 Hz), 94.4 – 89.5 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.59 (d, *J* = 7.9 Hz), 65.12 (s), -4.42 – -15.92 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_6F_8$ 290.0336; found 290.0337.

(*E*)-1-bromo-2-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3d**)



Colorless oil, yield 65% (45.0 mg).

R_f 0.80 (Petroleum ether).

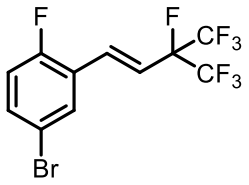
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.18 (m, 1H), 6.10 (dd, *J* = 19.9, 16.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9 (d, *J* = 11.8 Hz), 134.3, 133.5, 131.1, 128.0, 127.7, 124.6, 120.4 (qd, *J* = 285.6, 26.9 Hz), 115.1 (d, *J* = 16.9 Hz), 92.6 – 88.7 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -76.92 (d, *J* = 8.3 Hz), -183.86 – -188.98 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_6BrF_7$ 349.9536; found 349.9534.

(*E*)-4-bromo-1-fluoro-2-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3e**)



Colorless oil, yield 74% (63.2 mg).

R_f 0.70 (Petroleum ether).

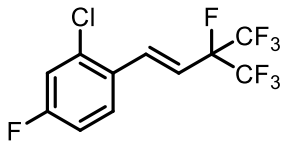
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.12 (dd, *J* = 6.6, 1.8 Hz, 1H), 7.79 (s, 1H), 7.43 – 7.15 (m, 2H), 6.70 (dd, *J* = 20.8, 16.2 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 159.7 (d, *J* = 249.5 Hz), 136.6 (d, *J* = 12.0 Hz), 132.8, 132.1 (d, *J* = 3.7 Hz), 129.3 (d, *J* = 7.8 Hz), 120.5 (qd, *J* = 285.0, 25.7 Hz), 117.0 (d, *J* = 22.9 Hz), 113.0 (d, *J* = 16.1 Hz), 109.0 (d, *J* = 21.6 Hz), 93.0 – 86.2 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.67 (d, *J* = 8.0 Hz), 70.29 (s), -7.51 – -20.79 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_6BrF_7$ 367.9447; found 367.9440.

(*E*)-2-chloro-4-fluoro-1-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3f**)



Colorless oil, yield 72% (46.8 mg).

R_f 0.70 (Petroleum ether).

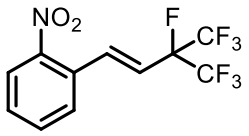
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.01 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.54 (d, *J* = 16.1 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.24 (td, *J* = 8.3, 2.3 Hz, 1H), 6.66 (dd, *J* = 20.3, 16.3 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 164.2 (d, *J* = 252.1 Hz), 135.6 (d, *J* = 10.6 Hz), 134.7 (d, *J* = 12.9 Hz), 130.8 (d, *J* = 8.8 Hz), 129.5 (d, *J* = 3.8 Hz), 121.4 (qd, *J* = 286.4, 27.5 Hz), 118.06 (d, *J* = 25.4 Hz), 116.1 (d, *J* = 21.8 Hz), 115.7 (d, *J* = 15.8 Hz), 96.9 – 84.7 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.71 (d, *J* = 7.9 Hz), 67.29 (s), -4.00 – -14.39 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_5BrF_8$ 323.9952; found 323.9949.

(*E*)-1-nitro-2-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3g**)



Colorless oil, yield 70% (49.5 mg).

R_f 0.30 (Petroleum ether/ EtOAc, 10/1).

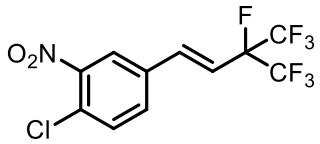
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.14 (dd, J = 8.2, 1.2 Hz, 1H), 7.90 (dd, J = 7.8, 1.3 Hz, 1H), 7.82 (td, J = 7.5, 1.0 Hz, 1H), 7.77 – 7.66 (m, 2H), 6.58 (dd, J = 20.6, 16.0 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 149.1, 136.9 (d, J = 12.9 Hz), 135.0, 131.7, 130.64, 130.61, 125.8, 121.4 (qd, J = 286.2, 27.7 Hz), 117.0 (d, J = 16.3 Hz), 95.4 – 88.1 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.85 (d, J = 7.8 Hz), -1.60 – -19.67 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_6F_7NO_2$ 317.0287; found 317.0281.

(*E*)-1-chloro-2-nitro-4-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3h**)



Colorless oil, yield 76% (61.4 mg).

R_f 0.80 (Petroleum ether/ EtOAc, 5/1).

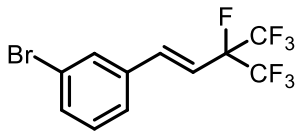
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.41 (d, J = 2.0 Hz, 1H), 8.06 (dd, J = 8.4, 2.0 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 16.2 Hz, 1H), 6.92 (dd, J = 20.7, 16.2 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 153.8, 141.2 (d, J = 12.1 Hz), 139.7, 137.6 (d, J = 8.3 Hz), 137.4, 131.7, 129.5 (d, J = 15.8 Hz), 125.6 (qd, J = 286.3, 27.9 Hz), 120.6 (d, J = 16.1 Hz), 98.8 – 92.4 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.80 (d, J = 7.9 Hz), -4.63 – -16.79 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_5F_7NO_2Cl$ 350.9892; found 350.9892.

(*E*)-1-bromo-3-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3i**)



Colorless oil, yield 89% (45.0 mg).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.97 (s, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.9 Hz,

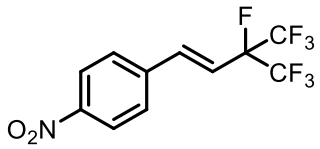
1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 16.2 Hz, 1H), 6.74 (dd, *J* = 20.8, 16.2 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 138.4 (d, *J* = 11.9 Hz), 137.1, 133.6, 131.8, 131.2, 127.7, 123.5, 121.4 (qd, *J* = 286.2, 27.7 Hz), 114.2 (d, *J* = 16.2 Hz), 94.1 – 90.0 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 97.95 (d, *J* = 66.0 Hz), 0.00 – -17.91 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_6F_7Br$ 292.0157; found 292.0151.

(*E*)-1-nitro-4-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3j**)



Colorless oil, yield 54% (39.2 mg).

R_f 0.60 (Petroleum ether/ EtOAc, 20/1).

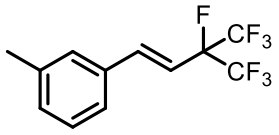
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 16.2 Hz, 1H), 6.89 (dd, *J* = 20.7, 16.2 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 149.5, 141.0, 138.1 (d, *J* = 12.0 Hz), 129.9, 125.0, 121.4 (qd, *J* = 286.3, 27.6 Hz), 117.0 (d, *J* = 16.2 Hz), 95.4 – 85.1 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.81 (d, *J* = 7.9 Hz), -4.00 – -14.39 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{11}H_6F_7NO_2$ 317.0287; found 317.0284.

(*E*)-1-methyl-3-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3k**)



Colorless oil, yield 82% (49.9 mg).

R_f 0.90 (Petroleum ether).

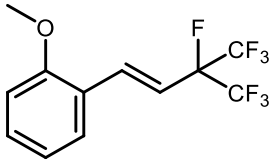
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.46 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.48 (dd, *J* = 20.8, 16.2 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 139.3 (d, *J* = 11.4 Hz), 138.8, 134.1, 130.9, 129.0, 128.4, 125.2, 120.8 (qd, *J* = 286.0, 27.9 Hz), 111.3 (d, *J* = 16.3 Hz), 96.23 – 88.2 (m), 20.6.

^{19}F NMR (376 MHz, Acetone-d_6) δ 95.41 (d, *J* = 8.2 Hz), -1.60 – -26.71 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_9F_7$ 286.0592; found 286.0598.

(*E*)-1-methoxy-2-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3l**)



Colorless oil, yield 81% (48.9 mg).

R_f 0.70 (Petroleum ether).

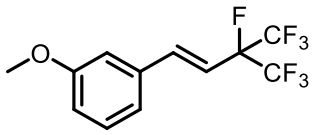
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.29 (m, 3H), 7.04 – 6.89 (m, 2H), 6.29 (dd, *J* = 20.4, 16.3 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9 , 134.0 (d, *J* = 12.0 Hz), 131.1 , 128.7 , 123.0 , 120.9 , 120.7 (qd, *J* = 285.4, 27.3 Hz), 112.5 (d, *J* = 16.2 Hz), 111.3 , 94.3 – 88.2 (m), 55.6 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -77.13 (d, *J* = 8.3 Hz), -181.46 – -193.14 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_9F_7O$ 302.0536; found 302.0540.

(*E*)-1-methoxy-3-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3m**)



Colorless oil, yield 92% (69.8 mg).

R_f 0.50 (Petroleum ether).

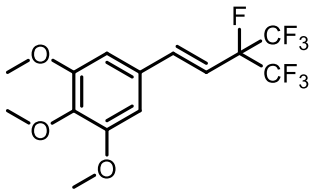
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.37 (t, *J* = 7.9 Hz, 1H), 7.33 – 7.23 (m, 3H), 7.01 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.61 (dd, *J* = 20.8, 16.2 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 161.2, 139.9 (d, *J* = 11.6 Hz), 136.2, 130.9, 121.5 (qd, *J* = 316.4, 29.5 Hz), 121.2, 117.0, 113.4, 112.5 (d, *J* = 16.3 Hz), 96.6 – 85.8 (m), 55.8.

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.62 (d, *J* = 7.5 Hz), -3.36 – -17.91 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_9F_7O$ 302.0536; found 302.0541.

(*E*)-1,2,3-trimethoxy-5-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3n**)



Colorless oil, yield 70% (48.5 mg).

R_f 0.50 (Petroleum ether/ EtOAc, 10/1).

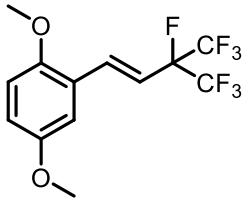
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.22 (d, J = 16.1 Hz, 1H), 7.09 (s, 2H), 6.56 (dd, J = 20.9, 16.1 Hz, 1H), 3.87 (s, 6H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 154.8, 141.0, 140.1 (d, J = 11.7 Hz), 130.3, 121.6 (qd, J = 284.4, 27.6 Hz), 111.2 (d, J = 16.1 Hz), 106.4, 95.5 – 88.6 (m), 60.7, 56.6.

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.61 (d, J = 8.0 Hz), -6.39 – -14.39 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{13}F_7O_3$ 362.0749; found 362.0749.

(*E*)-1,4-dimethoxy-2-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3o$_1$**)



Colorless oil, yield 64% (42.5 mg).

R_f 0.30 (Petroleum ether).

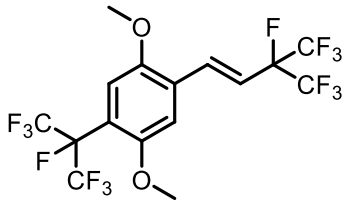
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.47 (d, J = 16.3 Hz, 1H), 7.29 (d, J = 2.9 Hz, 1H), 7.00 (dt, J = 9.0, 6.0 Hz, 2H), 6.63 (dd, J = 20.8, 16.4 Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 154.8, 153.1, 134.7 (d, J = 12.4 Hz), 123.6, 121.5 (qd, J = 285.9, 28.0 Hz), 117.9, 114.0, 113.7, 112.7 (d, J = 15.6 Hz), 93.9 – 89.1 (m), 56.5, 56.1 (s).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.58 (d, J = 8.0 Hz), -4.63 – -15.67 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{11}F_7O_2$ 332.0642; found 332.0641.

(*E*)-2,5-dimethoxy-1-(perfluoropropan-2-yl)-3-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3o$_2$**)



Colorless oil, yield 22% (20.3 mg).

R_f 0.60 (Petroleum ether).

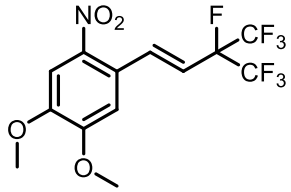
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.67 (d, J = 1.0 Hz, 1H), 7.51 (d, J = 16.3 Hz, 1H), 7.28 (d, J = 0.6 Hz, 1H), 6.85 (dd, J = 20.8, 16.3 Hz, 1H), 3.98 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 151.9 (d, J = 3.0 Hz), 151.2 (d, J = 5.0 Hz), 132.6 (d, J = 12.7 Hz), 126.4, 122.6 – 121.4 (m), 120.2 – 118.5 (m), 117.2 (d, J = 21.6 Hz), 114.7 (d, J = 15.7 Hz), 113.2, 111.2 (d, J = 20.4 Hz), 95.3 – 89.2 (m), 56.2, 56.0 (s).

^{19}F NMR (376 MHz, Acetone-d_6) δ 102.59 (d, J = 4.6 Hz), 99.72 (d, J = 7.9 Hz), 7.68 – 0.00 (m), -6.39 – -14.39 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{10}F_{14}O_2$ 500.0457; found 500.0447.

(*E*)-1,2-dimethoxy-4-nitro-5-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzene (**3p**)



Colorless oil, yield 68% (51.0 mg).

R_f 0.50 (Petroleum ether/ EtOAc, 5/1).

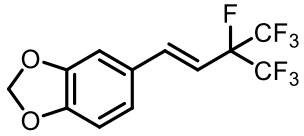
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.75 (d, J = 15.9 Hz, 1H), 7.67 (s, 1H), 7.36 (s, 1H), 6.58 (dd, J = 20.4, 16.0 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 154.6, 151.2, 142.1, 136.9 (d, J = 13.0 Hz), 124.7, 121.5 (qd, J = 286.3, 27.8 Hz), 115.5 (d, J = 16.3 Hz), 111.4, 108.8, 97.1 – 88.1 (m), 57.0, 56.8.

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.85 (d, J = 8.1 Hz), -6.39 – -12.15 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{10}F_7NO_4$ 377.0493; found 377.0494.

(*E*)-5-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)benzo[d][1,3]dioxole (**3q**)



Colorless oil, yield 52% (33.1 mg).

R_f 0.30 (Petroleum ether).

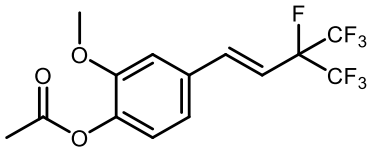
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.34 (s, 1H), 7.24 – 7.10 (m, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6.41 (dd, J = 20.8, 16.1 Hz, 1H), 6.06 (s, 2H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 150.3, 149.5, 139.5 (d, J = 11.3 Hz), 129.2, 124.8, 121.5 (qd, J = 286.1, 27.6 Hz), 110.0 (d, J = 16.3 Hz), 109.2, 107.1, 102.6 – 102.1 (m), 95.0 – 90.3 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.51 (d, J = 8.1 Hz), -5.11 – -11.51 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_7F_7O_2$ 316.0334; found 316.0328.

(*E*)-2-methoxy-4-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)phenyl acetate (**3r**)



Colorless oil, yield 76% (54.6 mg).

R_f 0.70 (Petroleum ether/ EtOAc, 5/1).

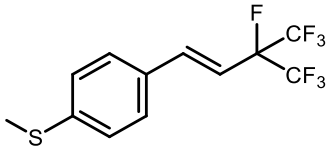
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.52 (s, 1H), 7.33 – 7.17 (m, 2H), 7.12 (d, J = 8.1 Hz, 1H), 6.61 (dd, J = 20.8, 16.2 Hz, 1H), 3.87 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 168.0, 151.9, 141.5, 138.4 (d, J = 11.8 Hz), 132.7, 123.3, 120.8, 120.5 (dd, J = 286.2, 28.0 Hz), 111.4, 111.3, 93.8 – 85.7 (m), 55.5, 19.6 (s).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.63 (d, J = 8.0 Hz), -5.75 – -13.91 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{11}F_7O_3$ 360.0596; found 360.0597.

(*E*)-methyl(4-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)phenyl)sulfane (**3s**)



Colorless oil, yield 74% (49.0 mg).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.65 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 16.1 Hz, 1H), 6.52 (dd, J = 20.8, 16.1 Hz, 1H), 2.52 (s, 3H).

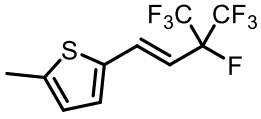
^{13}C NMR (100 MHz, Acetone-d_6) δ 142.7, 139.4 (d, J = 11.6 Hz), 131.3, 129.1, 126.9 (s), 121.5 (qd), 111.2 (d, J = 16.3 Hz), 96.1 – 86.5 (m).

^{13}C NMR (100 MHz, Acetone-d_6) δ 141.7, 138.4 (d, J = 11.6 Hz), 130.3, 128.1, 125.9, 120.6 (qd, J = 286.2, 27.6 Hz), 110.2 (d, J = 16.3 Hz), 95.8 – 86.9 (m), 14.00.

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.56 (d, J = 8.0 Hz), -5.11 – -17.91 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_9F_7S$ 318.0308; found 318.0306.

(*E*)-2-methyl-5-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)thiophene (**3t**)



Colorless oil, yield 52% (33.1 mg).

R_f 0.90 (Petroleum ether).

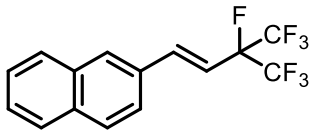
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.31 (d, J = 15.9 Hz, 1H), 7.19 (d, J = 3.5 Hz, 1H), 6.76 (d, J = 3.4 Hz, 1H), 6.00 (dd, J = 20.6, 15.9 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 144.3, 137.2, 133.4 (d, J = 13.4 Hz), 132.1, 127.5, 121.4 (qd, J = 285.5, 27.7 Hz), 108.8, 94.0 – 84.9 (m), 15.5 (s).

^{19}F NMR (376 MHz, Acetone-d_6) δ 100.66 (d, J = 8.2 Hz), -3.94 – -11.46 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{10}H_7F_7S$ 292.0157; found 292.0151.

(*E*)-2-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)naphthalene (**3u**)



Colorless oil, yield 95% (57.9 mg).

R_f 0.90 (Petroleum ether).

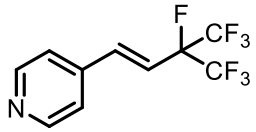
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.16 (s, 1H), 8.04 – 7.83 (m, 4H), 7.59 – 7.53 (m, 2H), 7.46 (d, J = 16.1 Hz, 1H), 6.71 (dd, J = 20.8, 16.2 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 139.9 (d, J = 11.5 Hz), 135.0, 134.3, 132.3, 130.1 (d, J = 6.3 Hz), 129.7, 129.4, 128.7, 128.2, 127.7, 124.4, 121.5 (qd, J = 286.7, 27.3 Hz), 112.5 (d, J = 15.5 Hz), 95.3 – 88.8 (m).

^{19}F NMR (376 MHz, Acetone-d_6) δ 99.69 (d, J = 8.1 Hz), -6.39 – -16.79 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_9F_7$ 322.0587; found 322.0585.

(*E*)-4-(3,4,4,4-tetrafluoro-3-(trifluoromethyl)but-1-en-1-yl)pyridine (**3v**)



Colorless oil, yield 51% (28.0 mg).

R_f 0.60 (Petroleum ether/ EtOAc, 1/1).

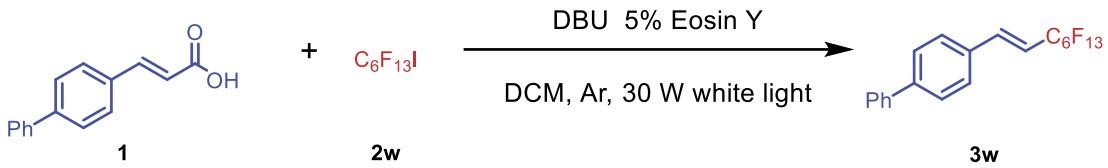
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 7.34 (d, J = 5.2 Hz, 2H), 7.11 (d, J = 16.1 Hz, 1H), 6.36 (dd, J = 19.8, 16.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 141.0, 136.5 (d, J = 11.7 Hz), 129.7, 124.8 (qd, J = 654.8, 20.2 Hz), 116.9 (d, J = 16.9 Hz), 96.6 – 83.3 (m).

^{19}F NMR (376 MHz, $CDCl_3$) δ -76.76 (d, *J* = 8.1 Hz), -180.34 – -190.10 (m).

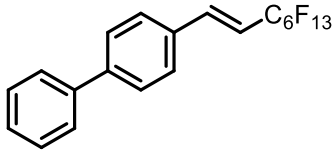
HRMS (EI) m/z: $[M]^+$ Calcd for $C_{10}H_6F_7N$ 273.0383; found 273.0383.

General procedure 2



To an 8 mL glass vial was added **1a** (44.8 mg, 0.2 mmol, 1 equiv.), **2w** (446.0 mg, 1.0 mmol, 5 equiv.), Eosin Y (6.4 mg, 0.01 mmol, 5 mol%), DBU (60.8 mg, 0.4 mmol, 2 equiv.), DCM (3 mL,0.067 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. When the reaction is completed, extracted with DCM (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography on a silica gel using petroleum ether and ethyl acetate to afford the corresponding target compound **3w**.

(*E*)-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-en-1-yl)-1,1'-biphenyl (**3w**)



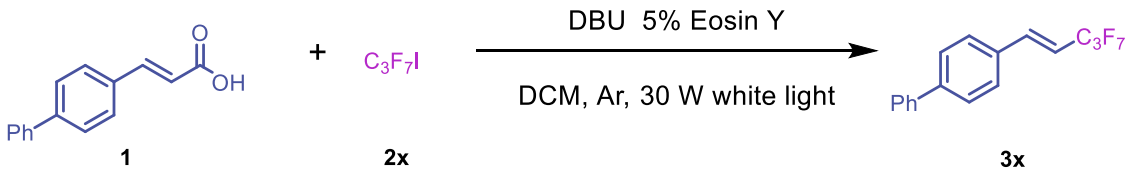
White solid, yield 32% (31.4 mg). M.p. = 88 – 90 ºC.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.35 (m, 2H), 6.66 (m, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 143.9, 141.0 (t, *J* = 10.2 Hz), 140.9, 133.6, 130.0, 129.6, 128.9, 128.4, 127.9, 127.6, 123.4 – 107.7 (m, -C_6F_{13}), 114.6 (t, *J* = 22.8 Hz).

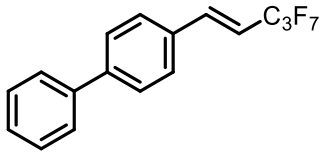
^{19}F NMR (376 MHz, Acetone-d_6) δ 96.17 – 94.62 (m), 66.36 (dd, *J* = 28.7, 14.4 Hz), 55.35 (s), 54.15 – 53.95 (m), 53.83 – 53.60 (m), 50.82 – 50.48 (m).

General procedure 3



To an 8 mL glass vial was added **1a** (44.8 mg, 0.2 mmol, 1 equiv.), **2x** (446.0 mg, 1.0 mmol, 5 equiv.), Eosin Y (6.4 mg, 0.01 mmol, 5 mol%), DBU (60.8 mg, 0.4 mmol, 2 equiv.), DCM (3 mL,0.067 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. When the reaction is completed, extracted with DCM (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography on a silica gel using petroleum ether and ethyl acetate to afford the corresponding target compound **3x**.

(*E*)-4-(3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl)-1,1'-biphenyl (**3x**)



White solid, yield 66% (46.0 mg). M.p. = 132 – 133 °C.

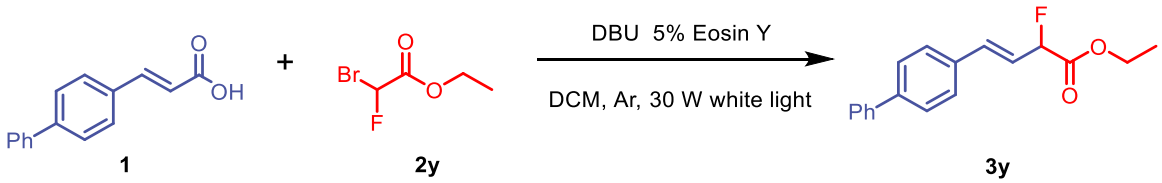
R_f 0.90 (Petroleum ether).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.78 (d, J = 8.3 Hz, 2H), 7.74 – 7.63 (m, 4H), 7.44 (t, J = 7.5 Hz, 2H), 7.41 – 7.31 (m, 2H), 6.61 (m, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 143.8, 140.9 (t, J = 9.7 Hz), 140.8, 133.6, 130.5 (t, J = 3.5 Hz), 129.9, 129.6, 128.9, 128.3, 127.8, 122.1 – 108.6 (m, -C_3F_7).

^{19}F NMR (376 MHz, Acetone-d_6) δ 96.69 – 95.46 (m), 66.27 – 63.53 (m), 49.26 (s).

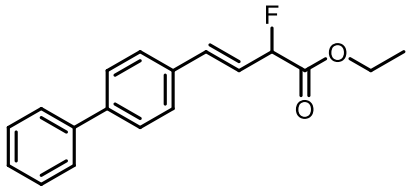
HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{11}F_7$ 346.0749; found 346.0737.



To an 8 mL glass vial was added **1a** (44.8 mg, 0.2 mmol, 1 equiv.), **2y** (185.0 mg, 1.0 mmol, 5 equiv.), Eosin Y (6.4 mg, 0.01 mmol, 5 mol%), DBU (60.8 mg, 0.4 mmol, 2 equiv.), DCM (3 mL,0.067 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. When the reaction is completed, extracted with DCM (3 × 10 mL), washed

with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography on a silica gel using petroleum ether and ethyl acetate to afford the corresponding target compound **3y**.

Ethyl (*E*)-4-([1,1'-biphenyl]-4-yl)-2-fluorobut-3-enoate (**3y**)



White solid, yield 92% (52.3 mg). M.p. = 65 – 68 ºC.

R_f 0.65 (Petroleum ether/ EtOAc, 10/1).

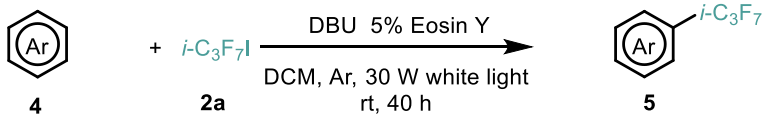
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.0 Hz, 1H), 7.69 – 7.58 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.1 Hz, 1H), 6.68 – 6.51 (m, 2H), 4.37 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, *J* = 29.9 Hz), 164.0, 148.1, 144.0, 139.9, 132.6, 129.0 (d, *J* = 9.5 Hz), 128.1, 127.7, 127.1, 115.1, 95.1 (d, *J* = 231.9 Hz), 62.8, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -139.39 (d, *J* = 53.2 Hz).

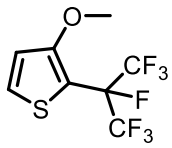
HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{17}FO_2$ 284.1213; found 284.1217.

General procedure 5



To an 8 mL glass vial was added **4** (0.2 mmol, 1 equiv.), **2a** (296 mg, 1.0 mmol, 5 equiv.), Eosin Y (6.4 mg, 0.01 mmol, 5 mol%), DBU (91.2 mg, 0.6 mmol, 3 equiv.), DCM (3 mL,0.067 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. When the reaction is completed, extracted with DCM (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography on a silica gel using petroleum ether and ethyl acetate to afford the corresponding target compounds **5**.

3-methoxy-2-(perfluoropropan-2-yl)thiophene (**5a**)



Yellow oil, yield 64% (35.8 mg).

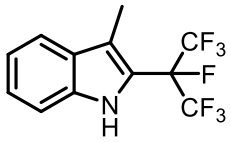
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 5.6, 1.0 Hz, 1H), 6.91 (dd, *J* = 5.6, 2.9 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 127.4, 120.6 (qd, *J* = 286.9, 27.4 Hz), 117.0, 104.0, 95.0 – 88.4 (m), 59.1 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.87 (d, *J* = 8.3 Hz), -165.15 – -186.74 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_8H_5F_7OS$ 281.9949; found 281.9943.

3-methyl-2-(perfluoropropan-2-yl)-1H-indole (**5b**)



Yellow solid, yield 59% (33.1 mg). M.p. = 65 – 68 °C.

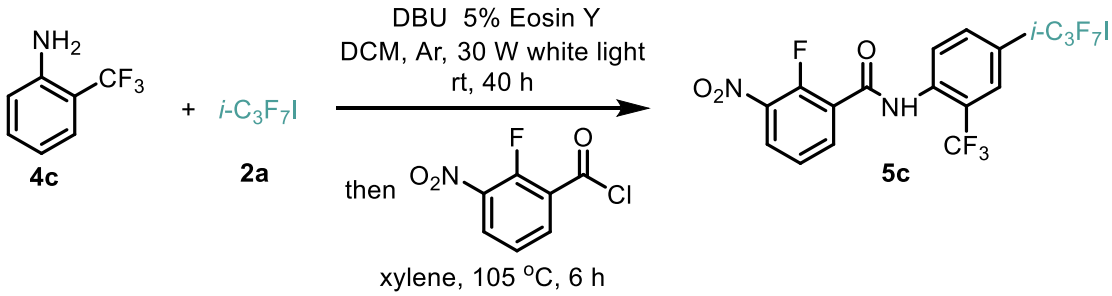
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.13 (m, 1H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 128.6, 124.6, 120.6 (qd), 120.4, 119.6, 116.7 (d, *J* = 24.6 Hz), 116.0, 111.3, 93.2 – 89.0 (m), 8.8 (d, *J* = 5.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.70 (d, *J* = 9.5 Hz), -172.83 – -191.86 (m).

HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_8F_7N$ 299.0545; found 299.0534.

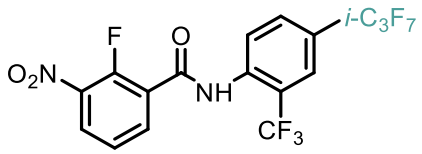
General procedure 6



To an 8 mL glass vial was added **4c** (32 mg, 0.2 mmol, 1 equiv.), **2a** (296 mg, 1.0 mmol, 5 equiv.), Eosin Y (6.4 mg, 0.01 mmol, 5 mol%), DBU (91.2 mg, 0.6 mmol, 3 equiv.), DCM (3 mL,0.067 M). The reaction mixture was degassed by bubbling with argon for 10 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and

irradiated with a 30 W white LED (approximately 5 cm away from the light source) at room temperature for 40 h. When the reaction is completed, extracted with DCM (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo. Meanwhile, to an another 8 mL glass vial was added 2-Fluoro-3-nitrobenzoic acid (40.7 mg, 0.22 mmol, 1.1 equiv.) and $SOCl_2$ (130.9 mg, 1.1 mmol, 5.5 equiv.). The mixture was stirred at 65 ºC for 6 h. After the reaction, the mixture was concentrated in vacuo to removing $SOCl_2$ to obtain 2-fluoro-3-nitrobenzoyl chloride. Then, the chloride was added to the crude perfluoroalkyled product and 2 mL xylene was added. The system was stirred at 105 ºC for 6 h. When the reaction is completed, extracted with DCM (3 × 10 mL), washed with brine (3 × 10 mL), dried over anhydrous sodium sulfate, concentrated in vacuo and purified by column chromatography on a silica gel using petroleum ether and ethyl acetate to afford the corresponding target compounds **5c**.

2-Fluoro-3-nitro-N-(4-(perfluoropropan-2-yl)-2-(trifluoromethyl)phenyl)benzamide (**5c**)



Yellow solid, yield 68% (67.5 mg).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.76 (s, 1H), 8.39 – 8.32 (m, 1H), 8.18 – 8.02 (m, 3H), 7.96 (s, 1H), 7.62 (t, J = 8.0 Hz, 1H).

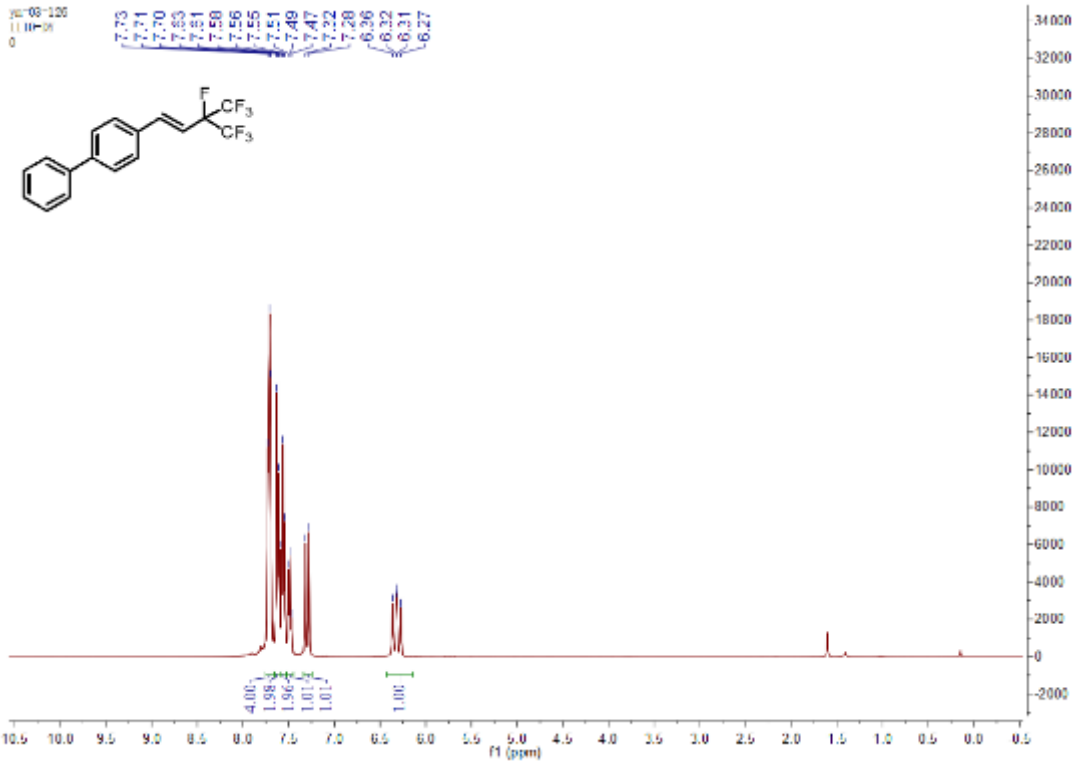
The data are in accord with the previous literature.[2]

Reference：

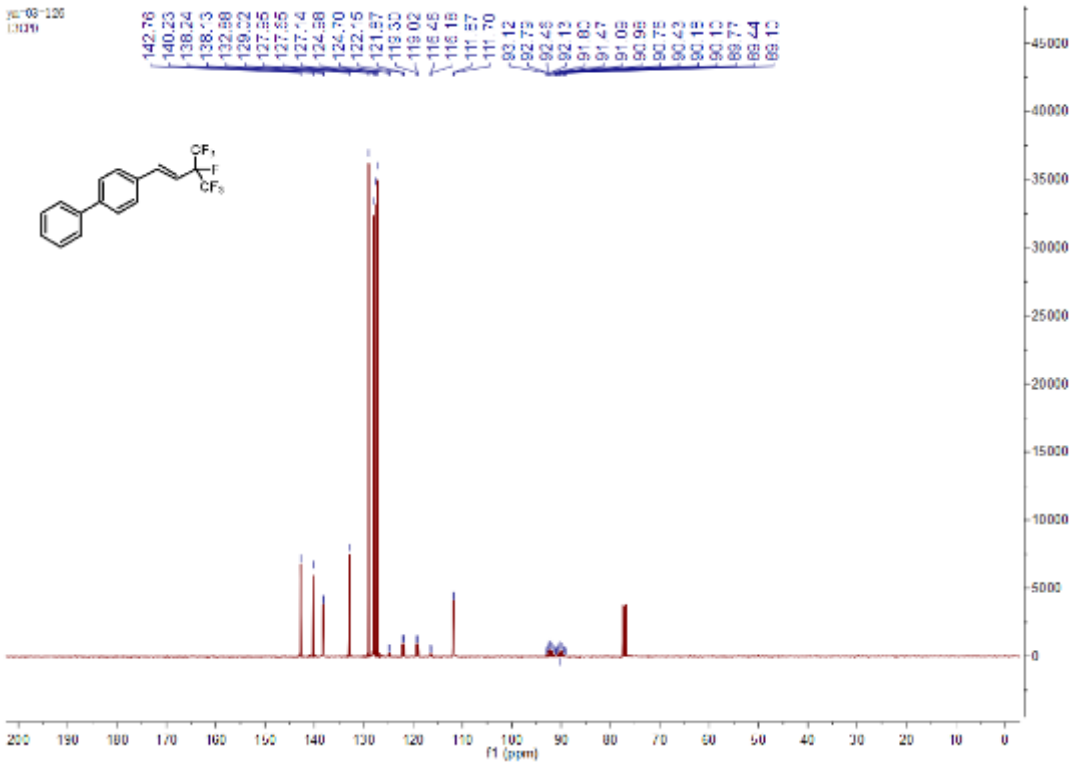
(1) Han, Y. Z.; Jin, Y. H.; Jiang, M.; Yang, H. J.; Fu, H. Photocatalyst-Free Visible-Light Photoredox Dearomatization of Phenol Derivatives Containing Ketoximes: An Easy Access to Spiropyrrolines. *Org. Lett.* **2019**, *21* (6), 1799-1803.

(2) Luo, C.; Xu, Q.; Huang, C.; Luo, L.; Zhu, J.; Zhang, R.; Huang, G.; Yin, D. Development of an Efficient Synthetic Process for Broflanilide. *Org. Process Res. Dev.* **2020**, *24* (6), 1024-1031.

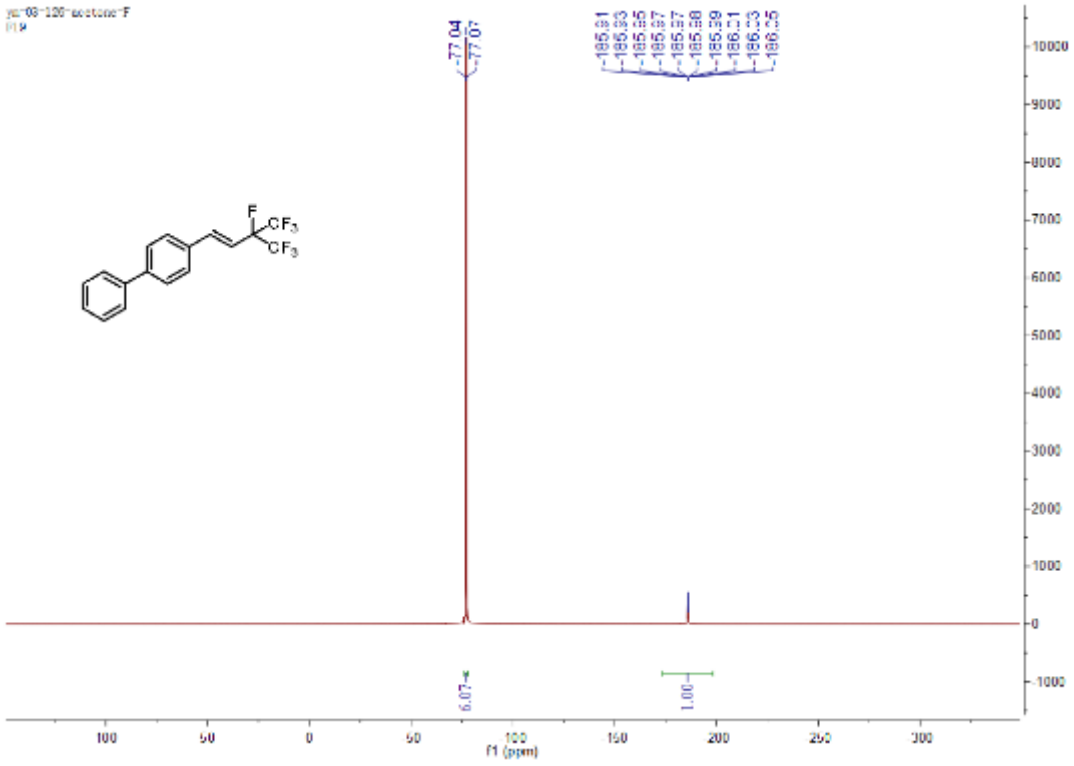
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3a**



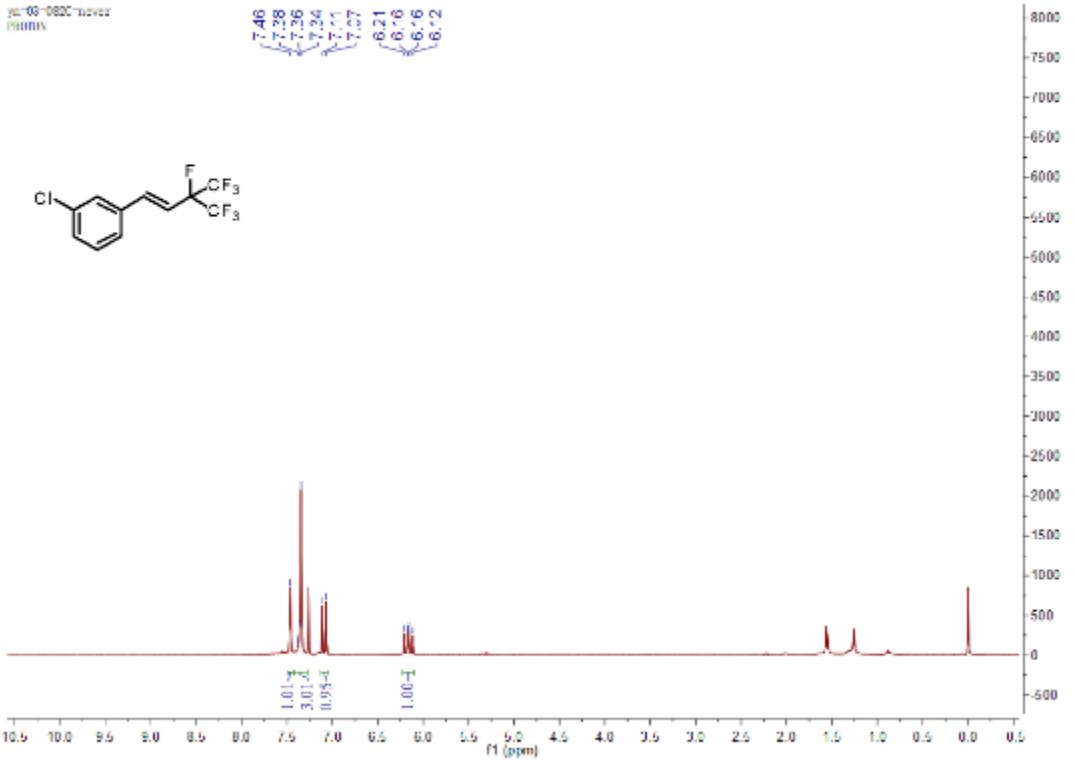
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3a**



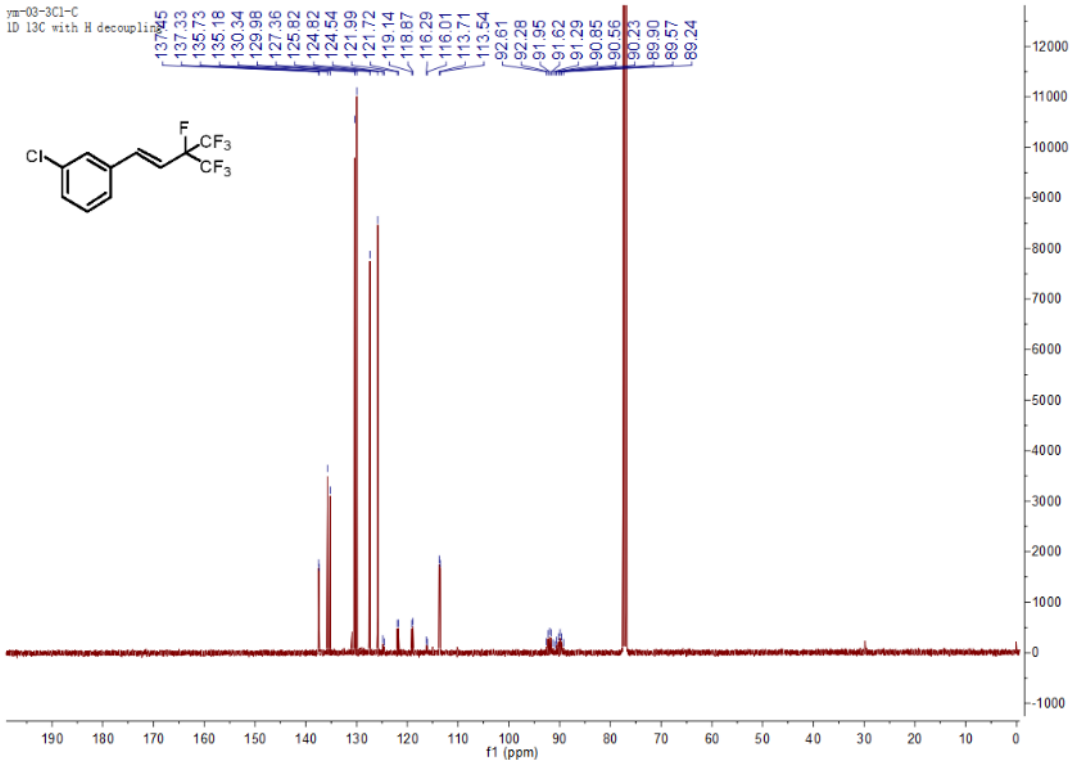
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3a**



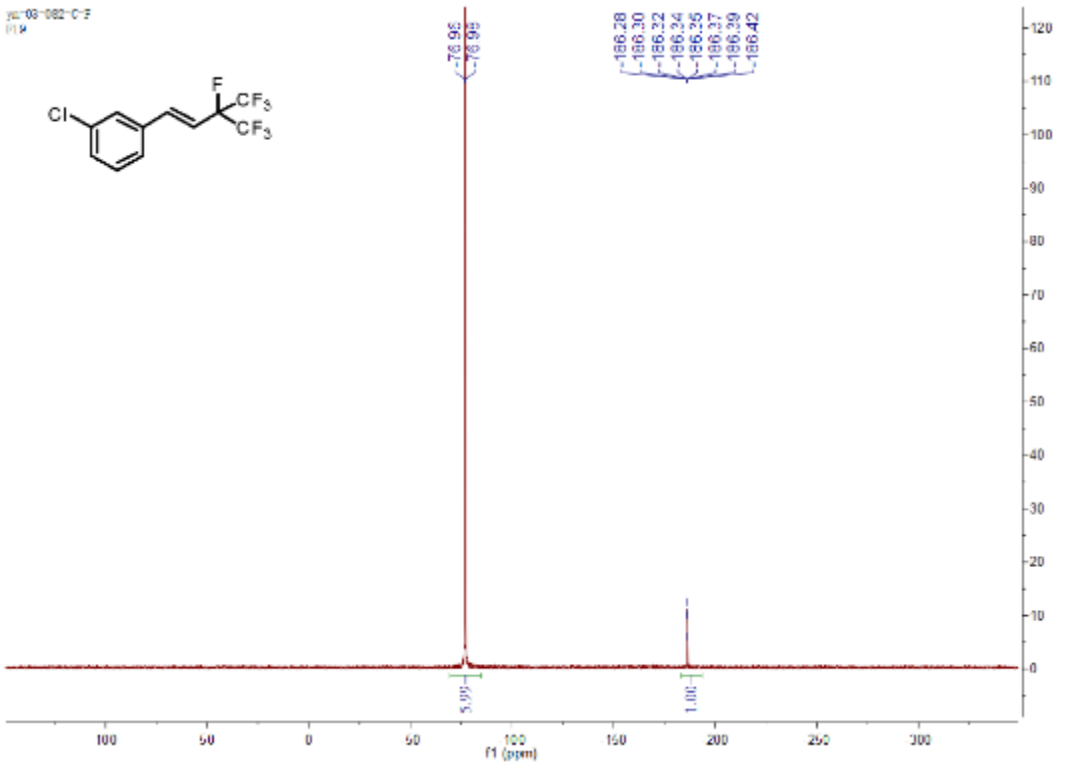
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3b**



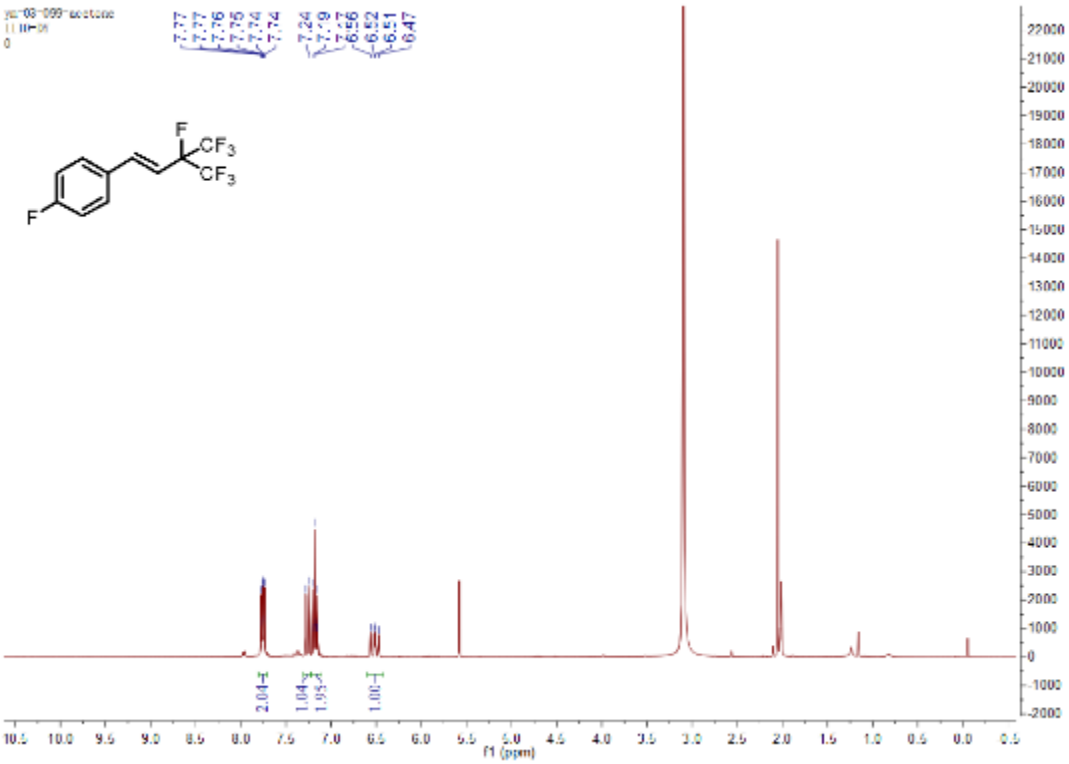
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3b**



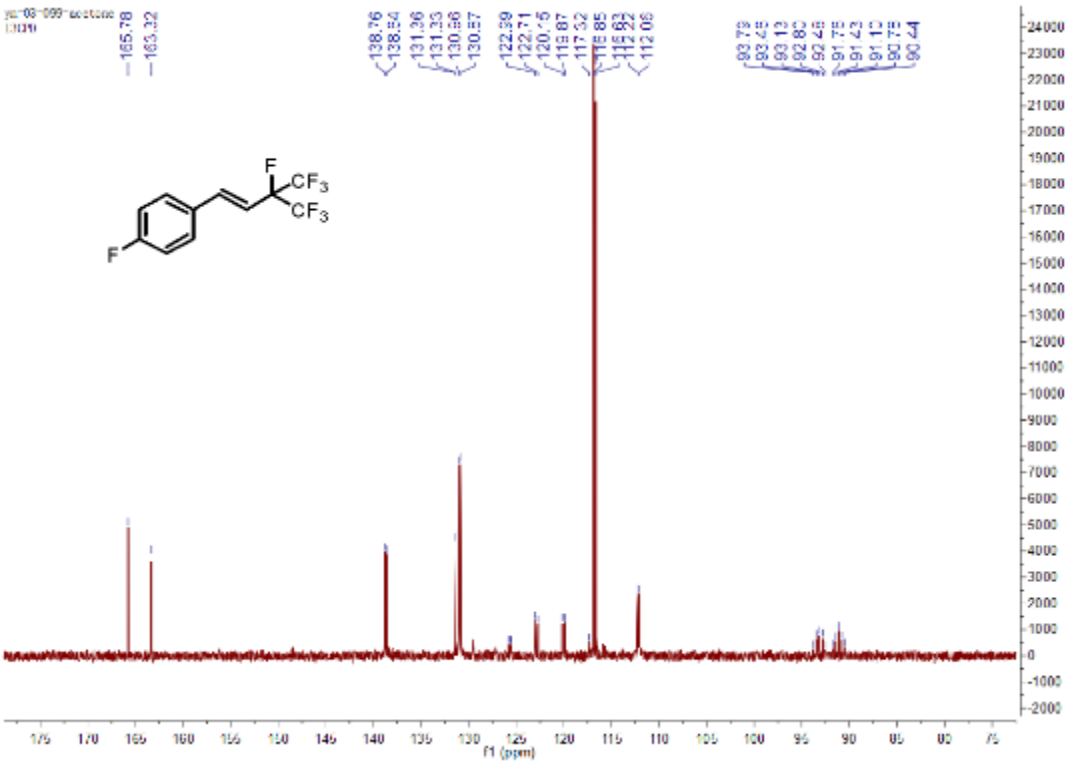
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3b**



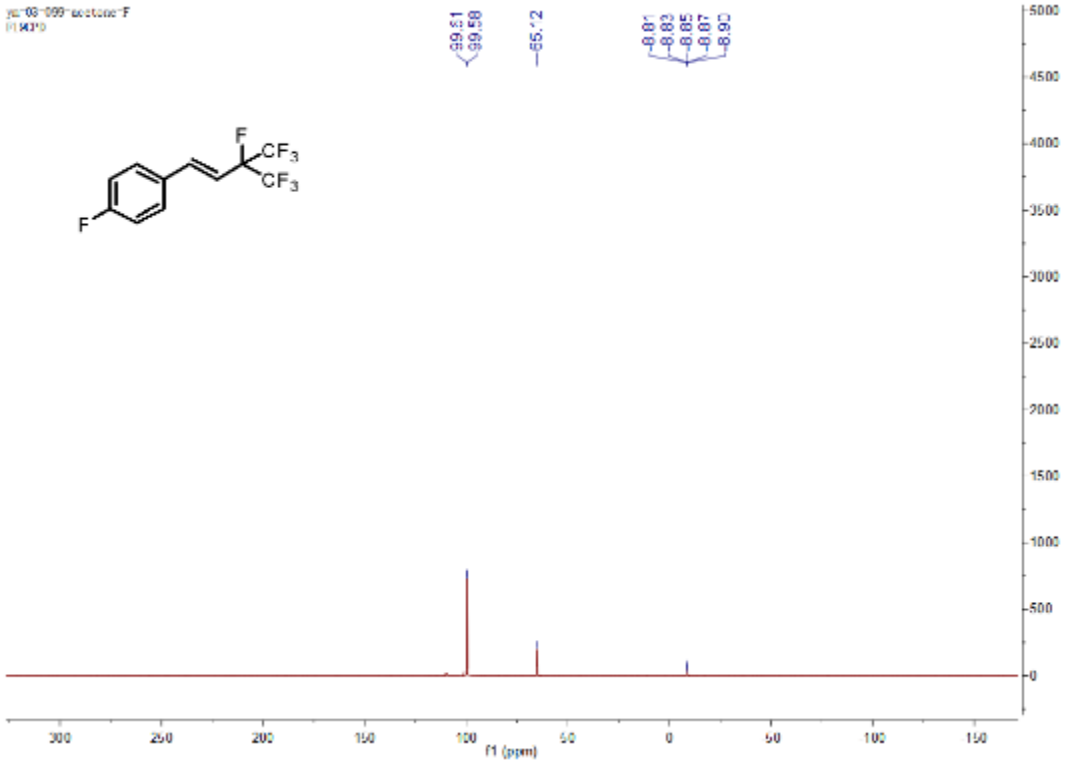
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3c**



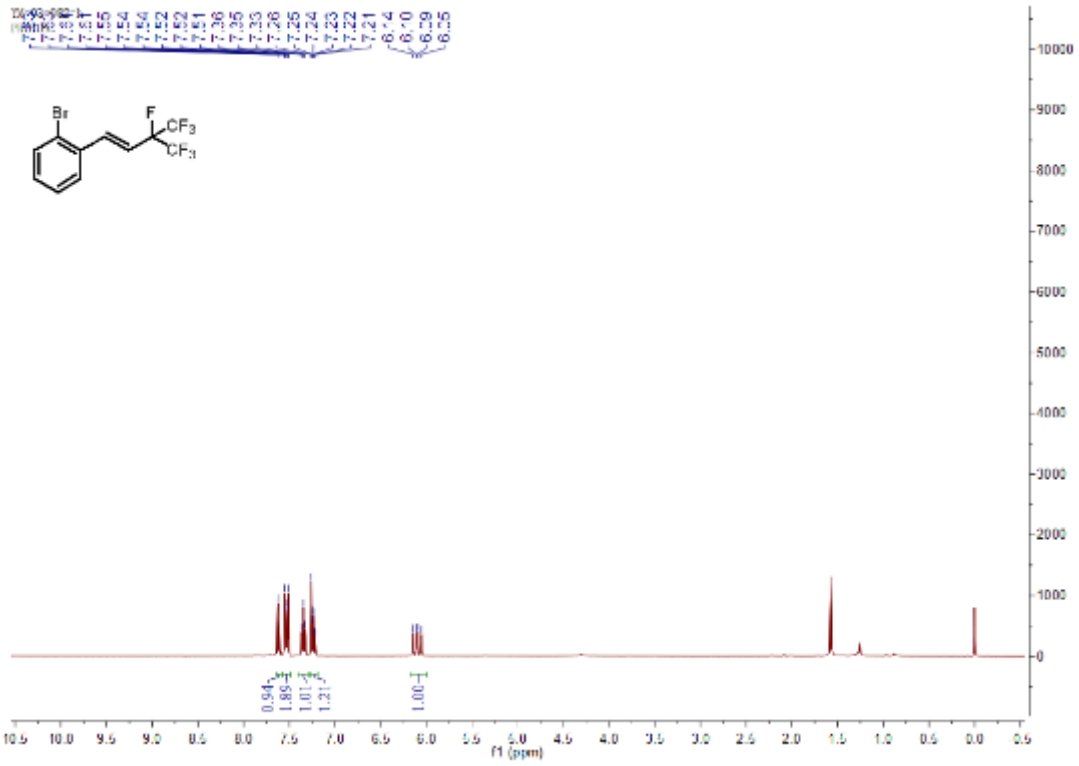
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3c**



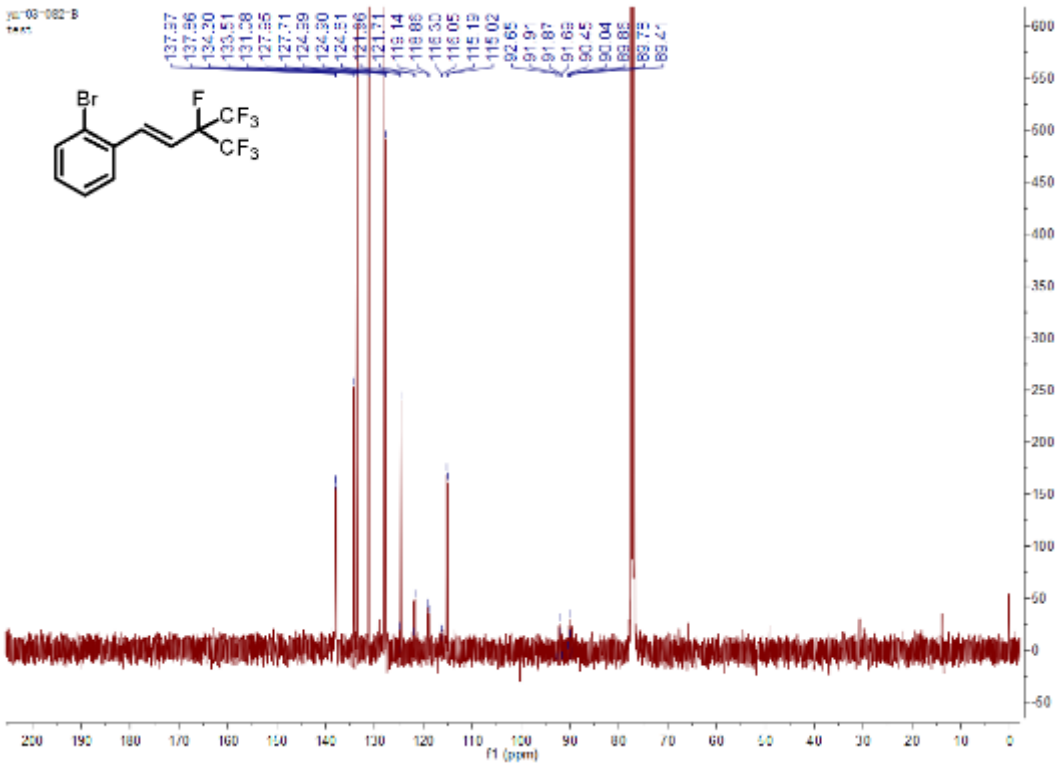
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3c**



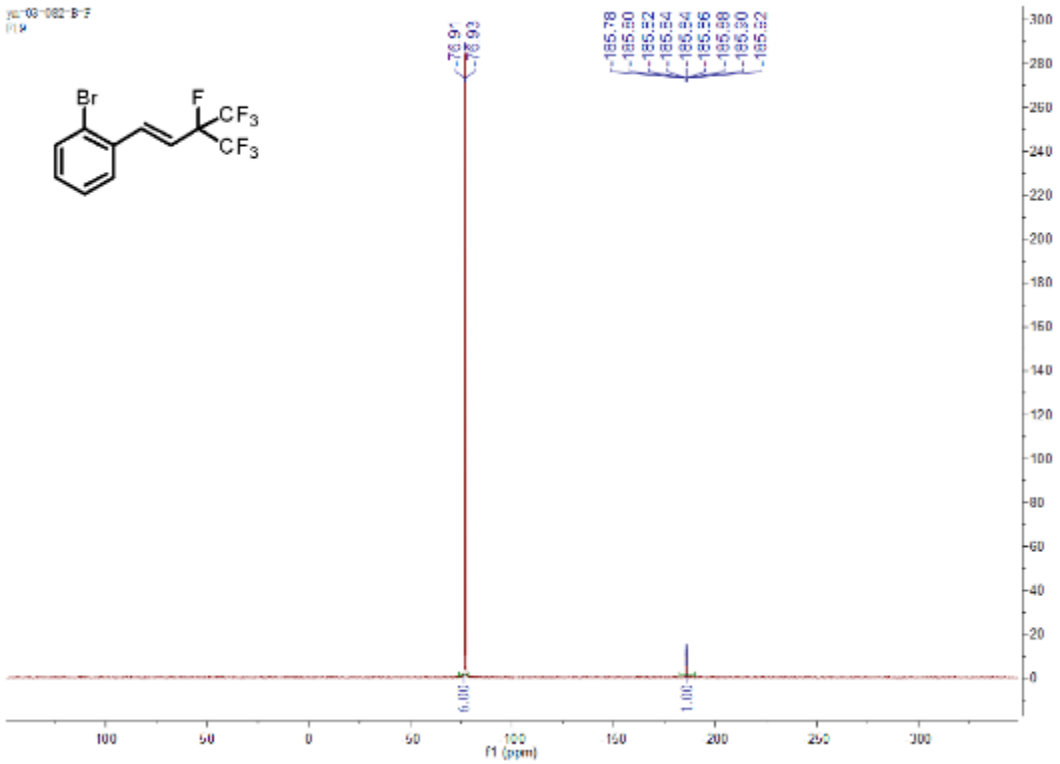
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3d**



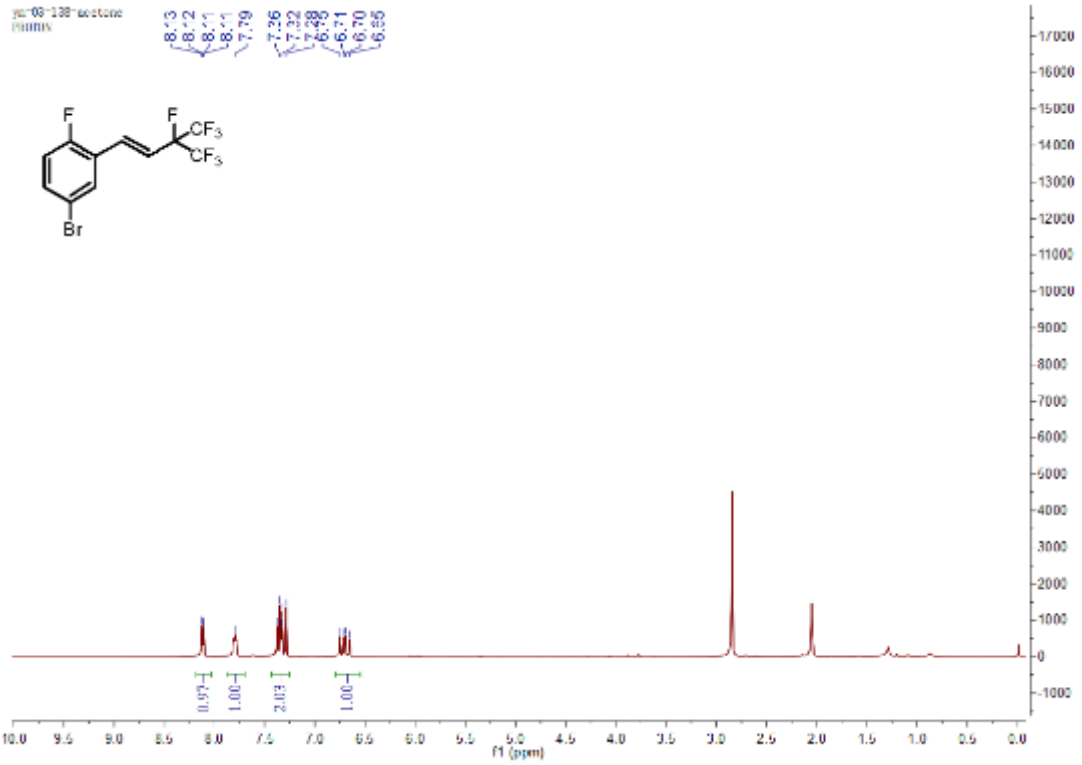
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3d**



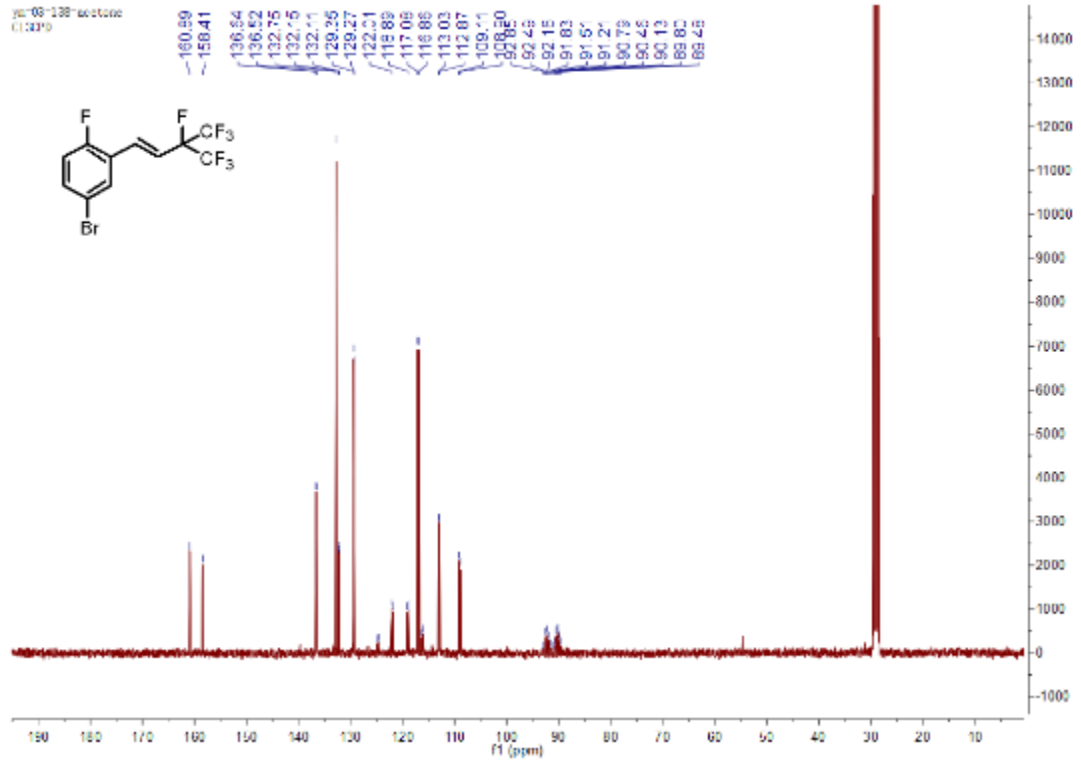
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3d**



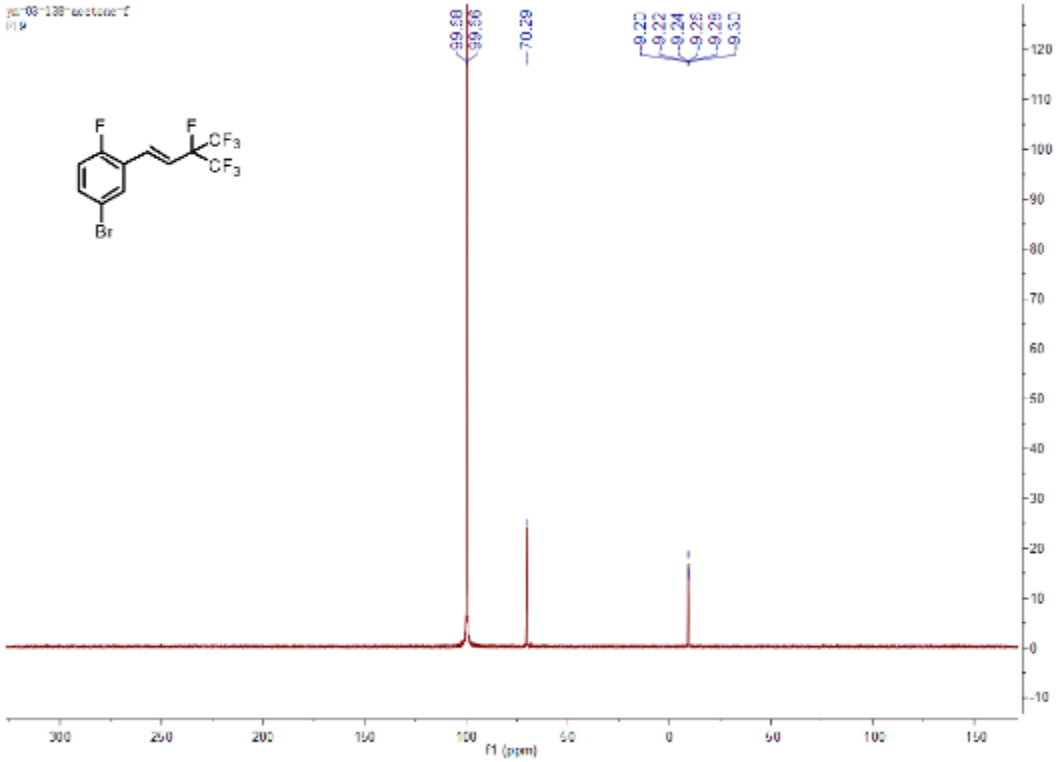
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3e**



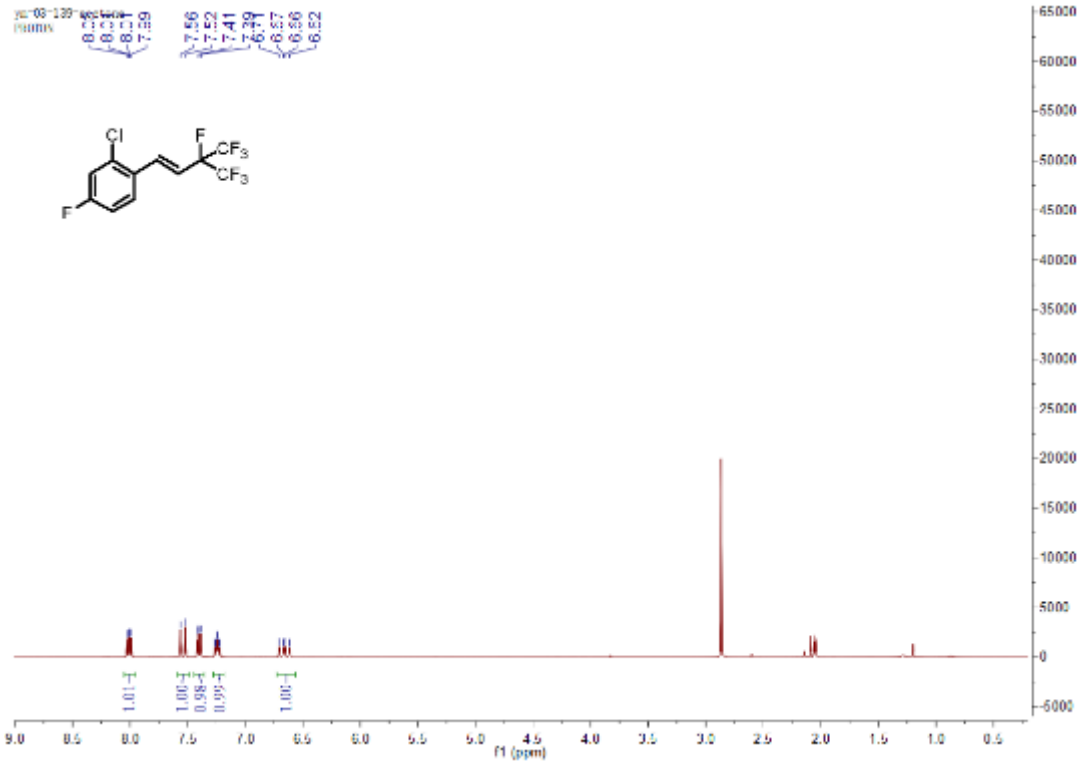
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3e**



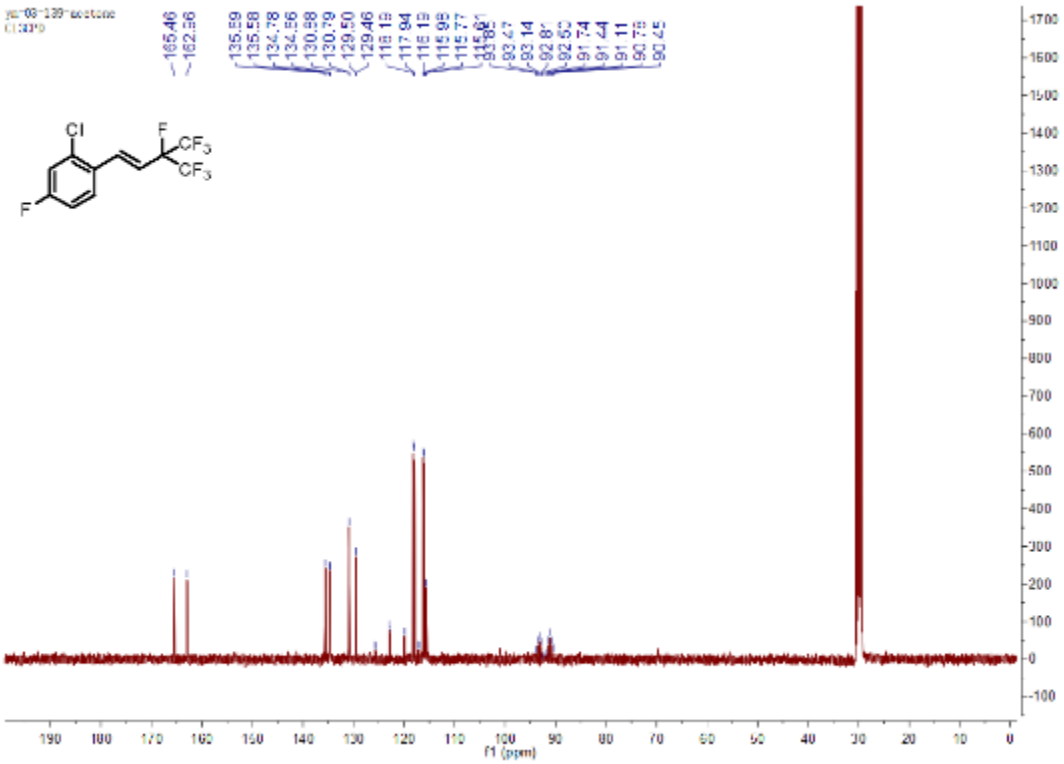
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3e**



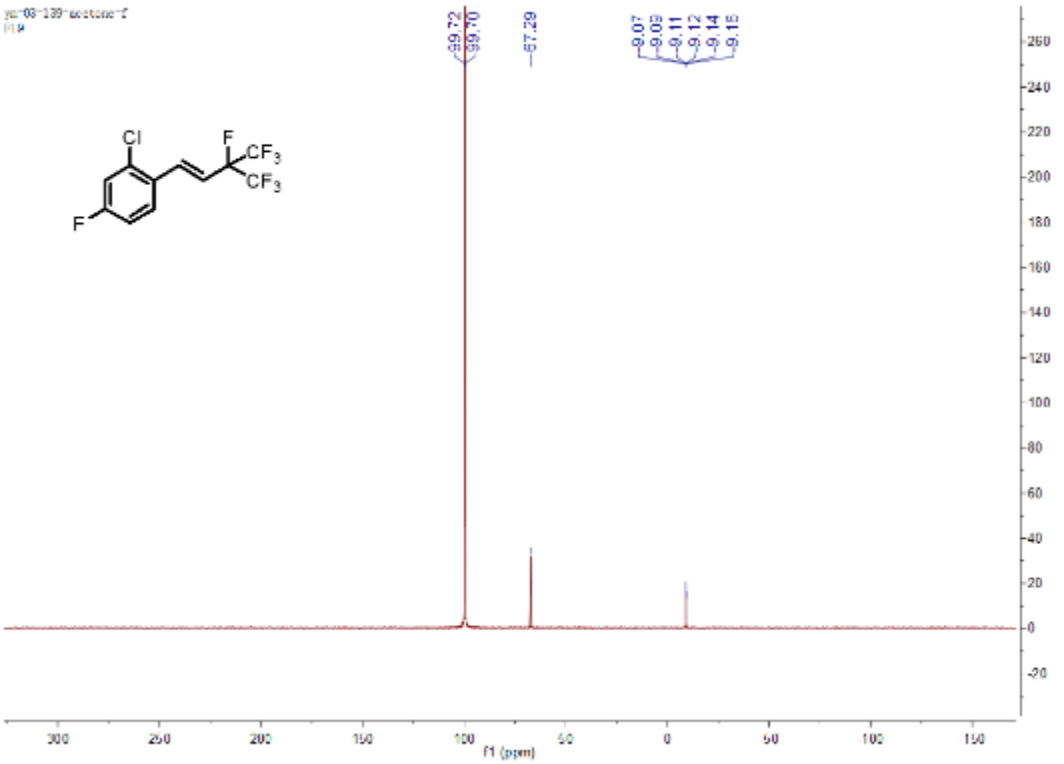
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3f**



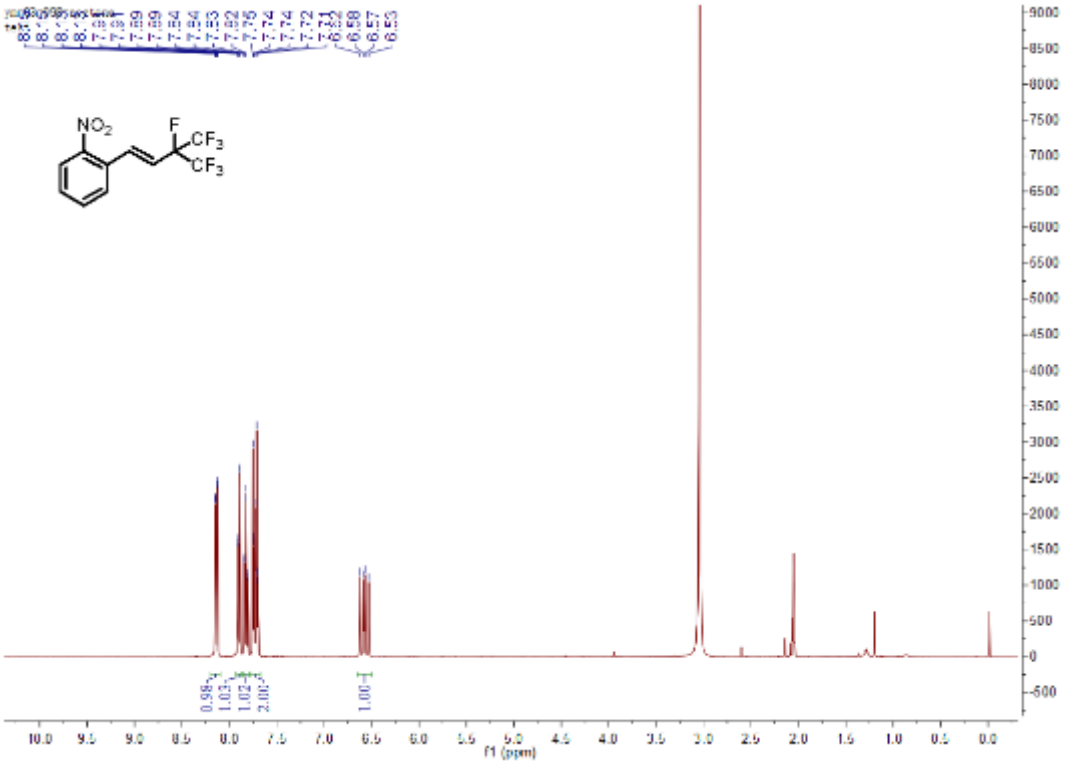
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3f**



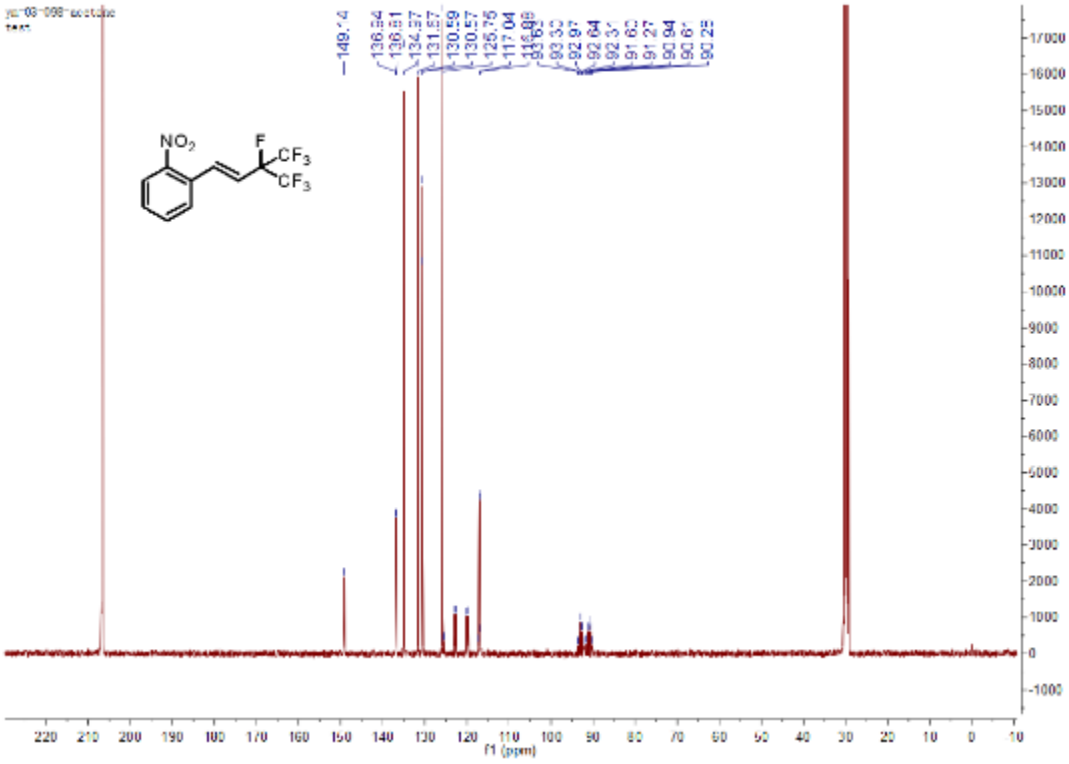
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3f**



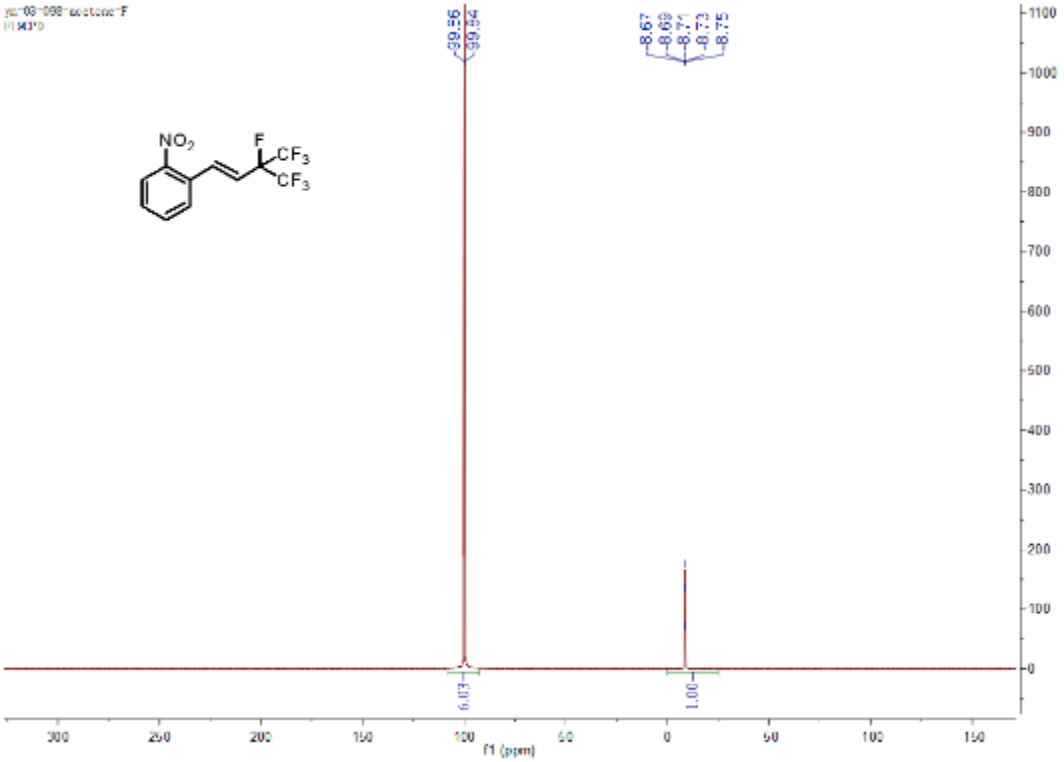
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3g**



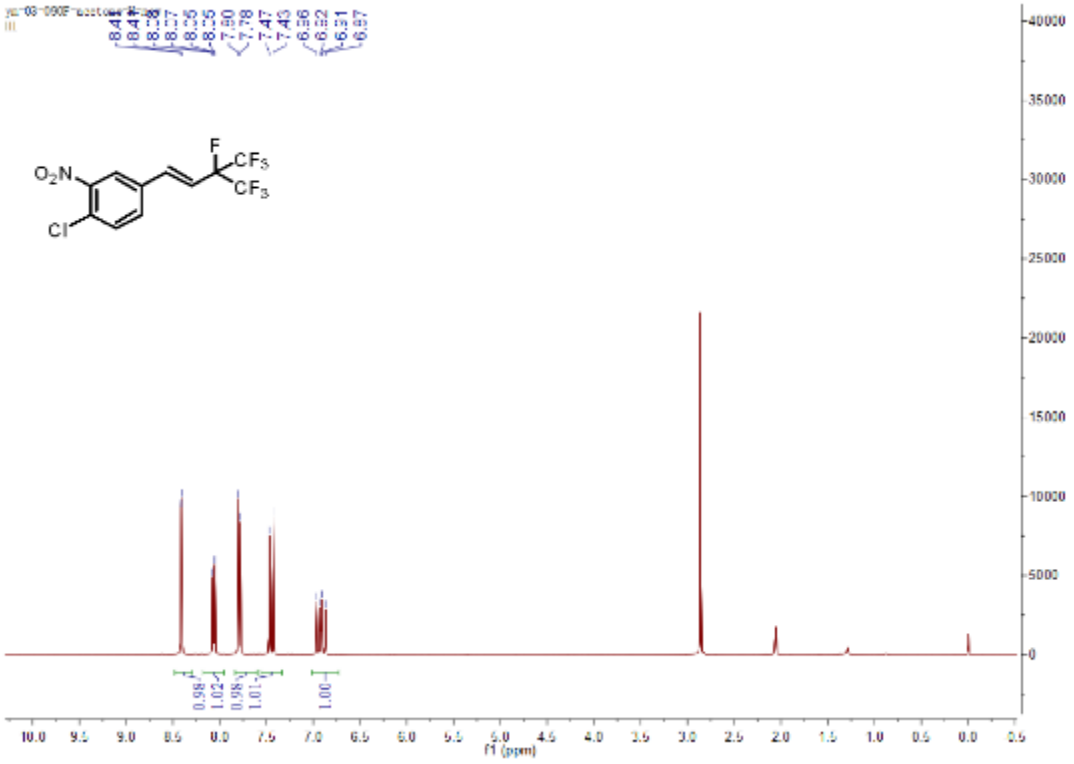
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3g**



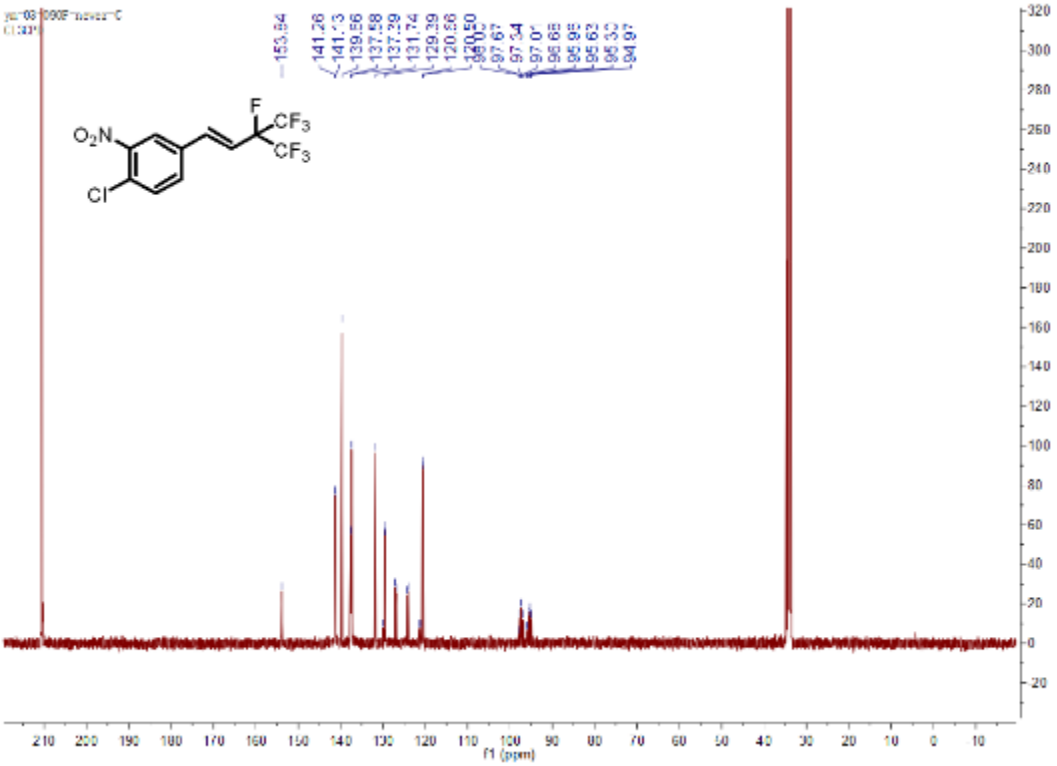
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3g**



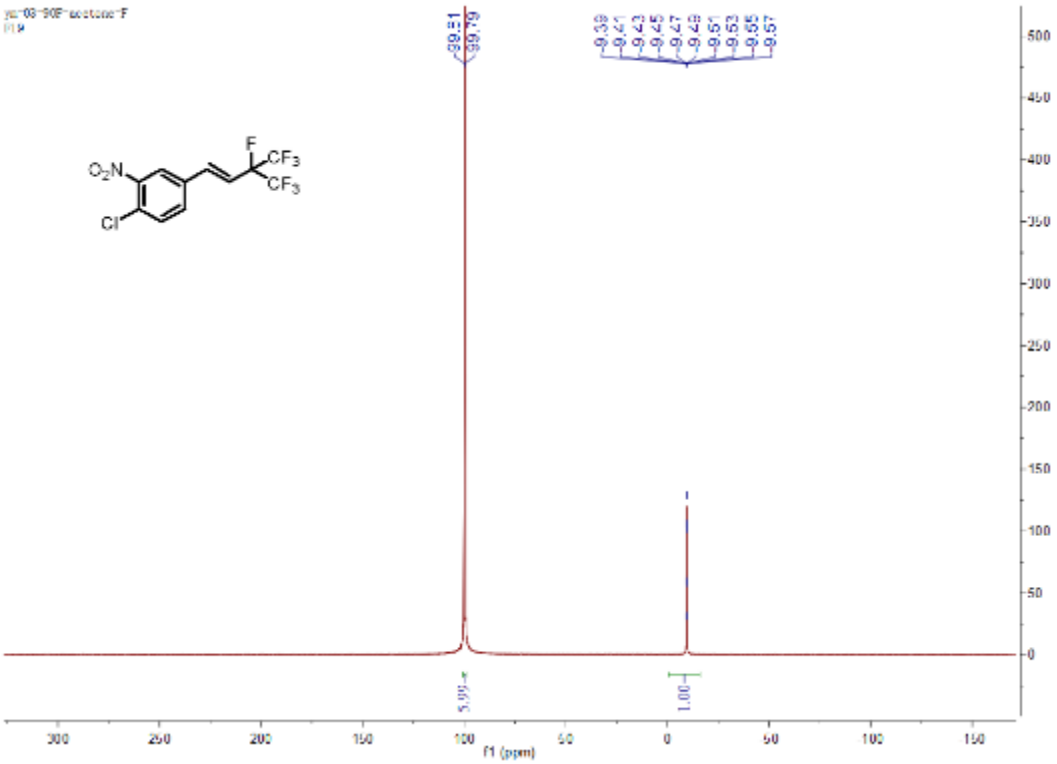
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3h**



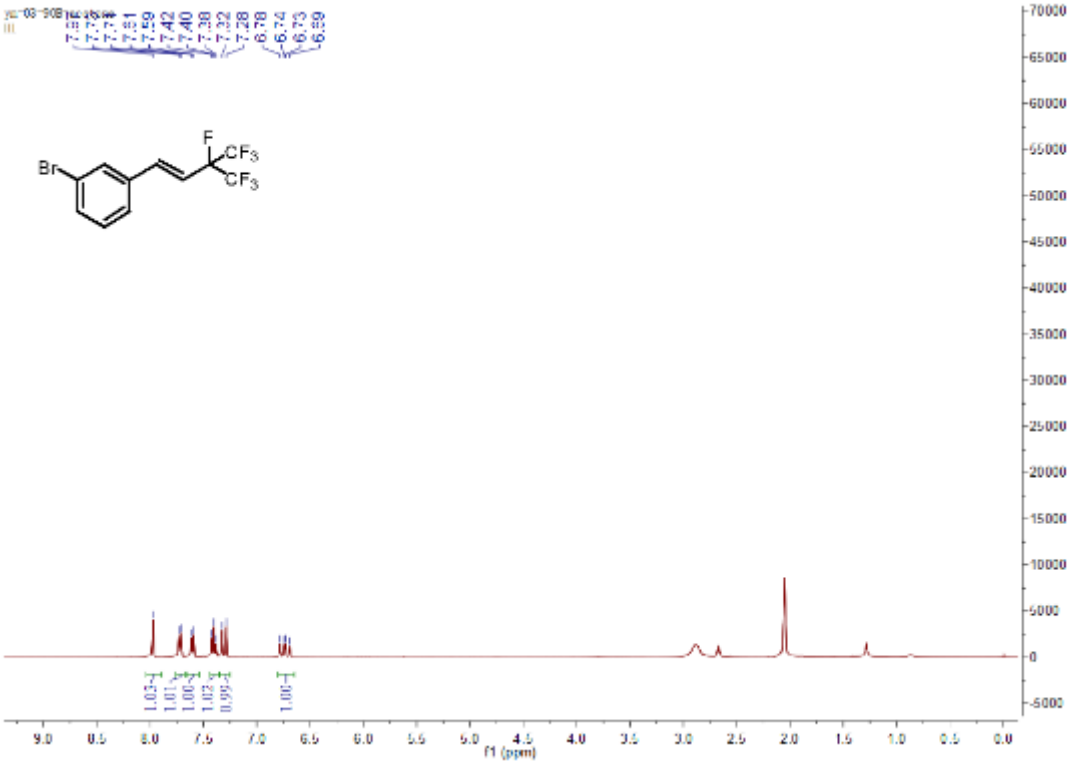
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3h**



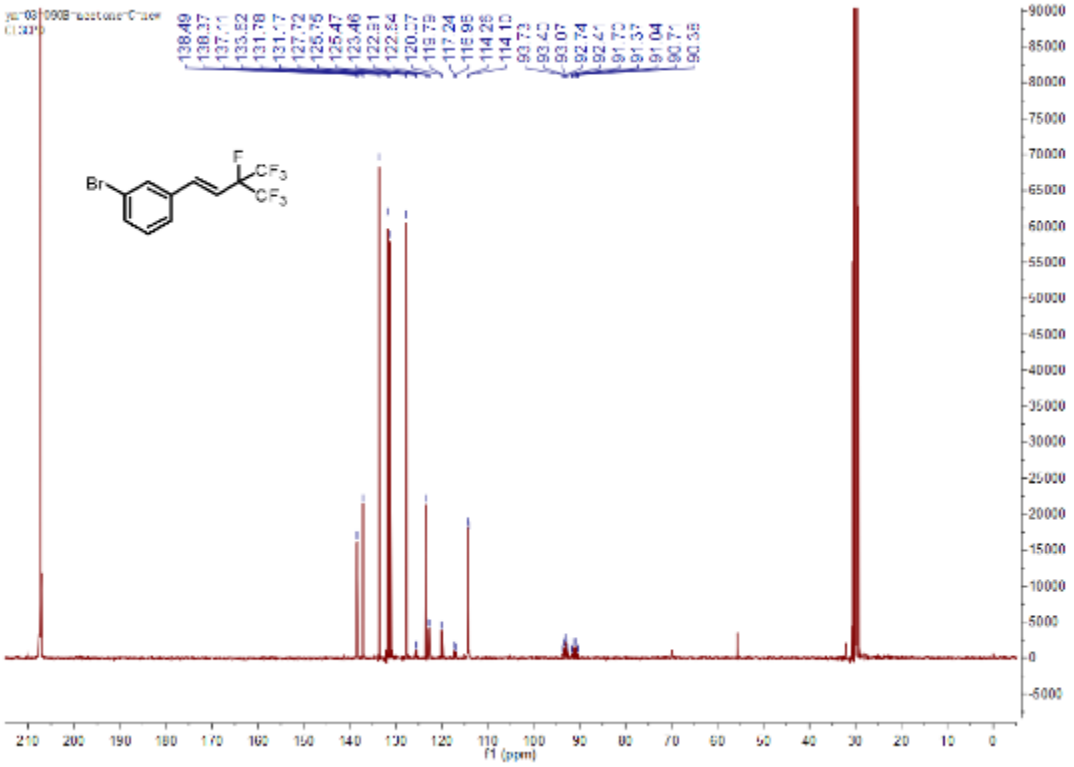
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3h**



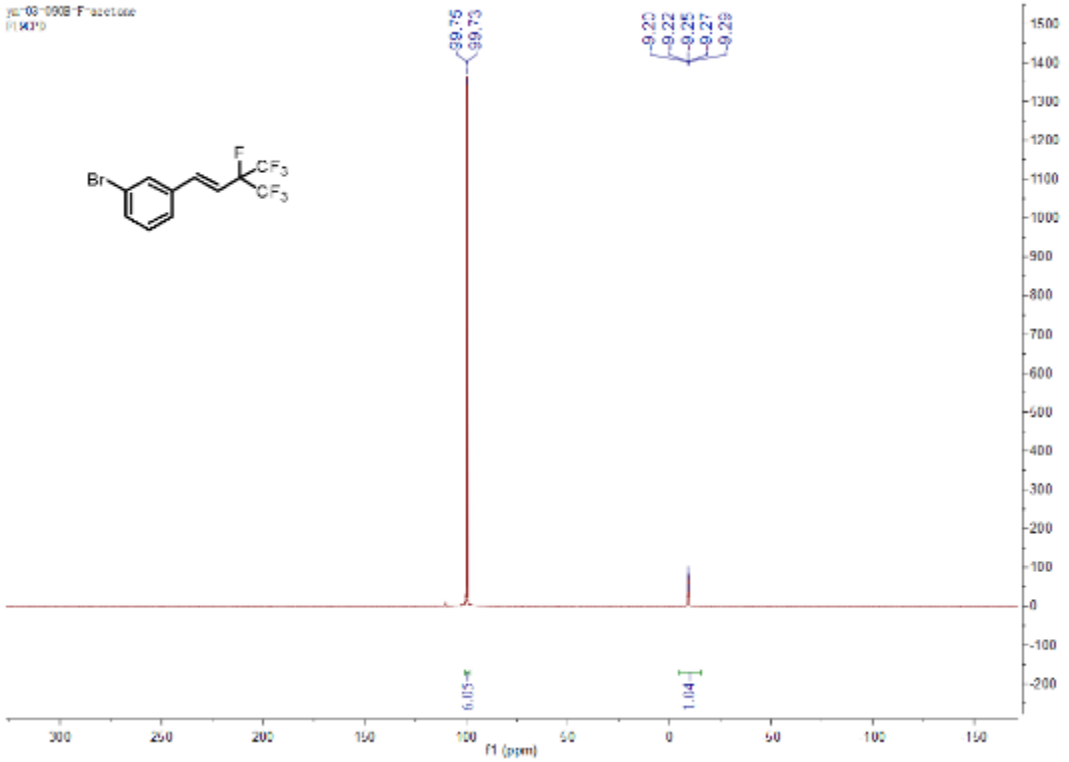
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3i**



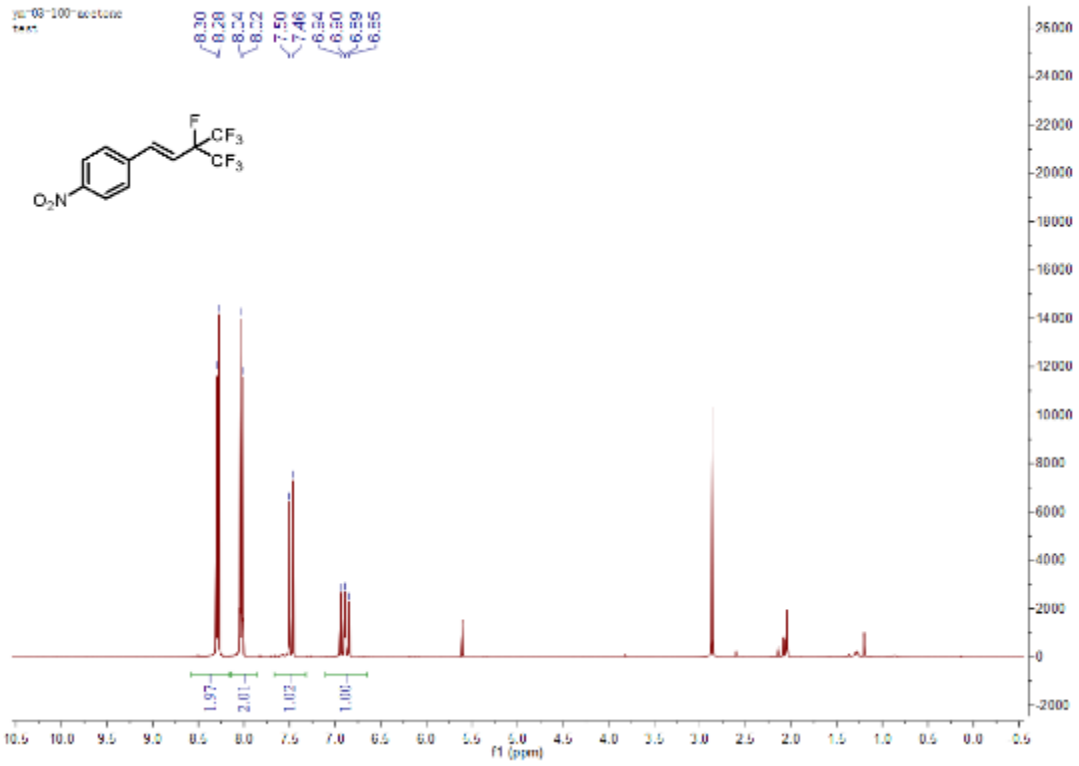
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3i**



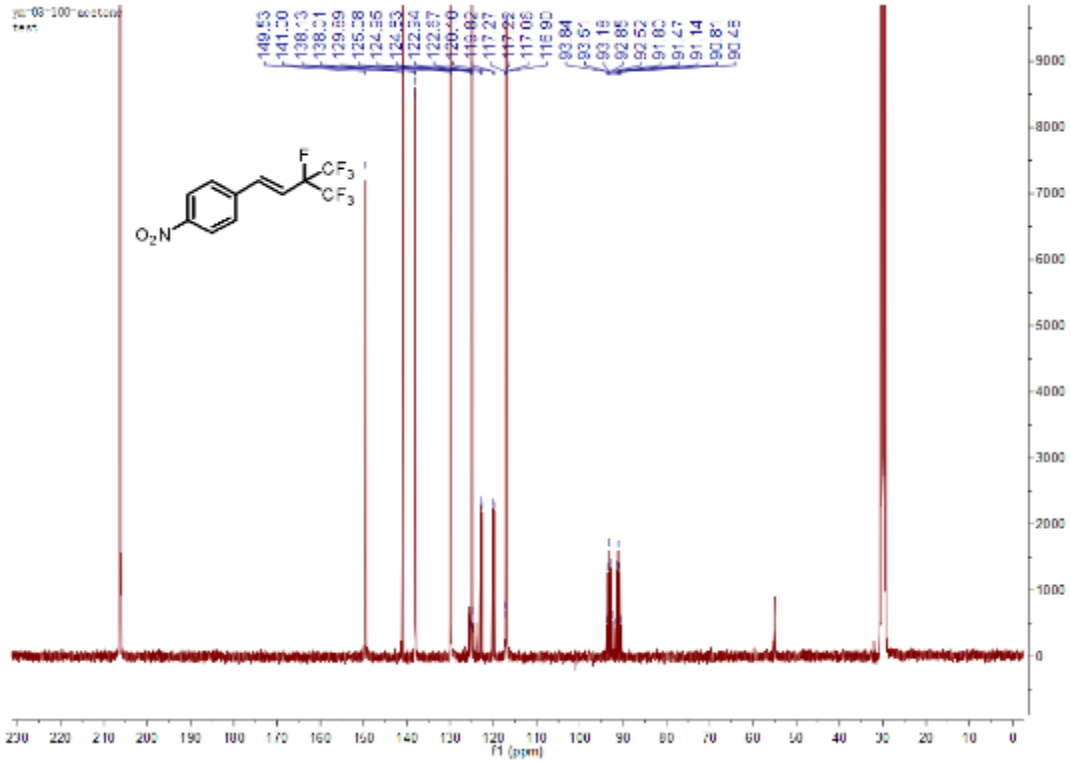
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3i**



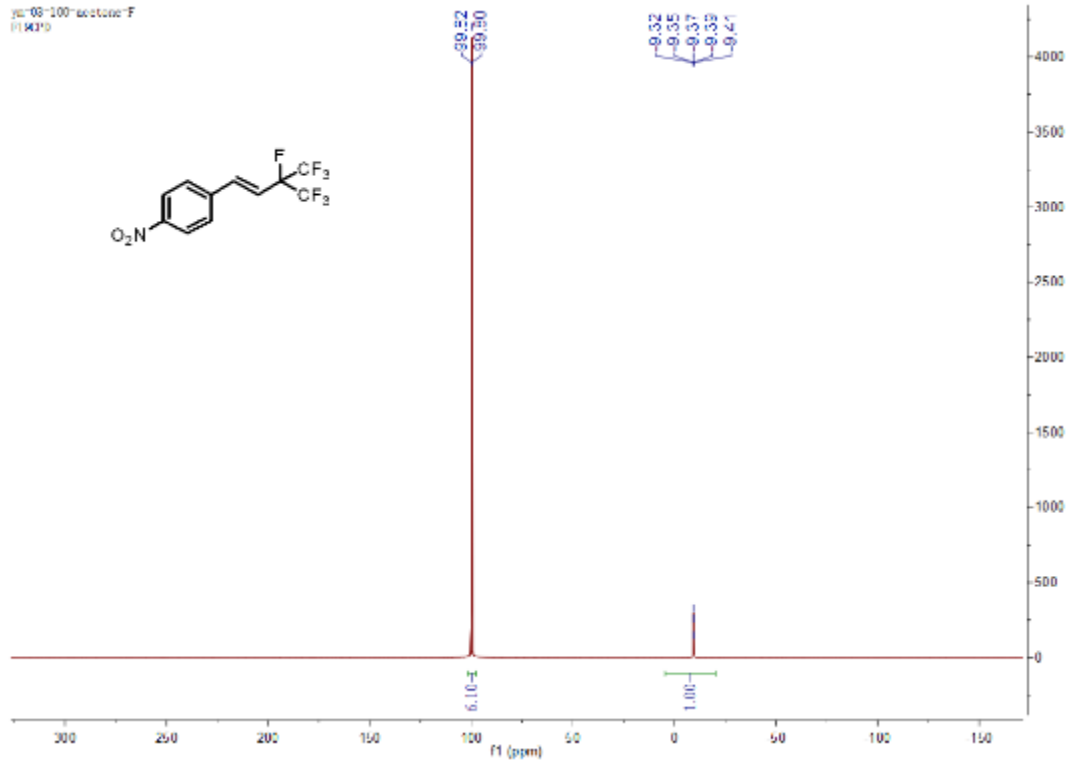
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3j**



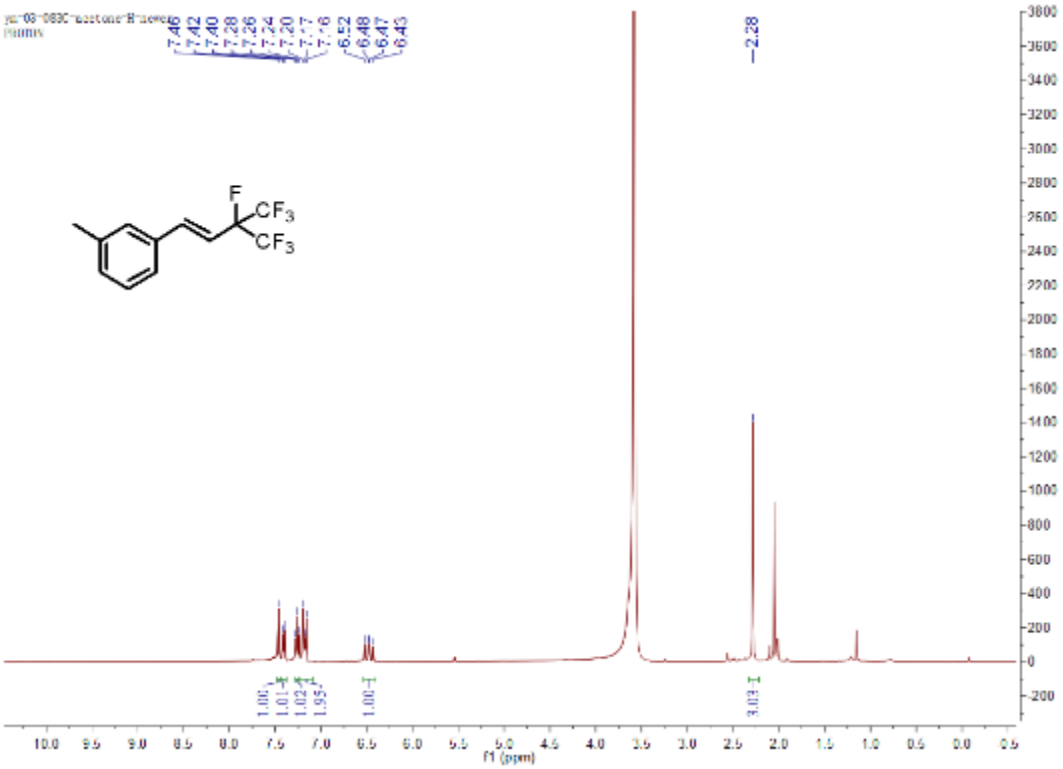
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3j**



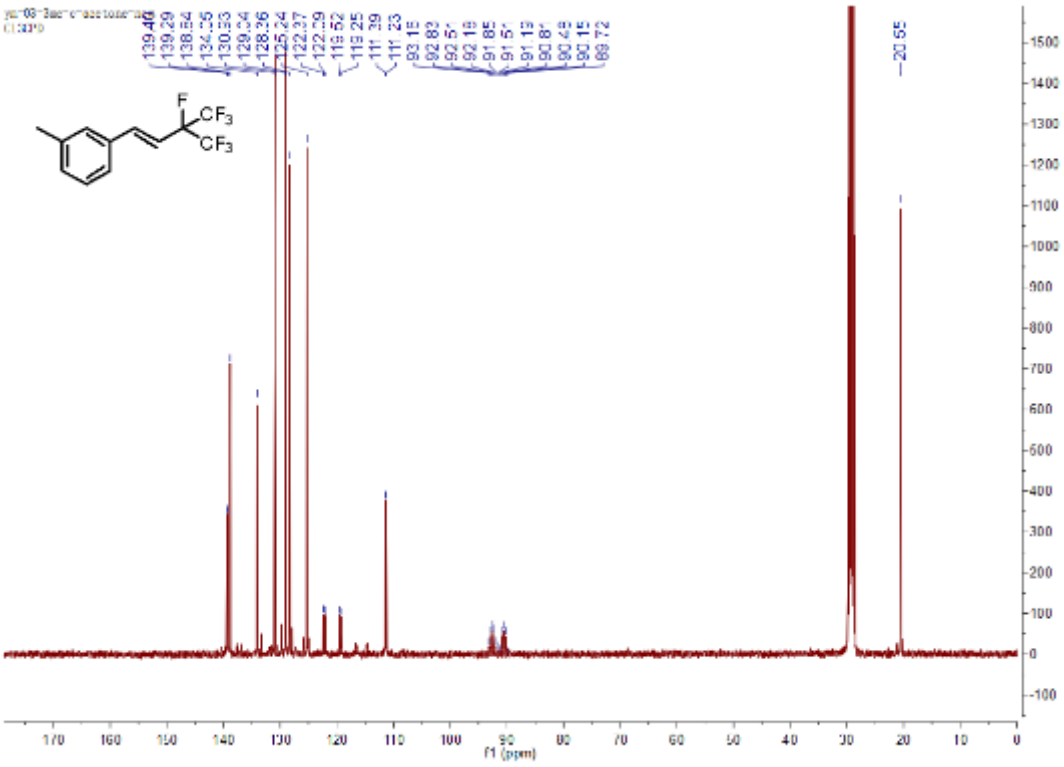
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3j**



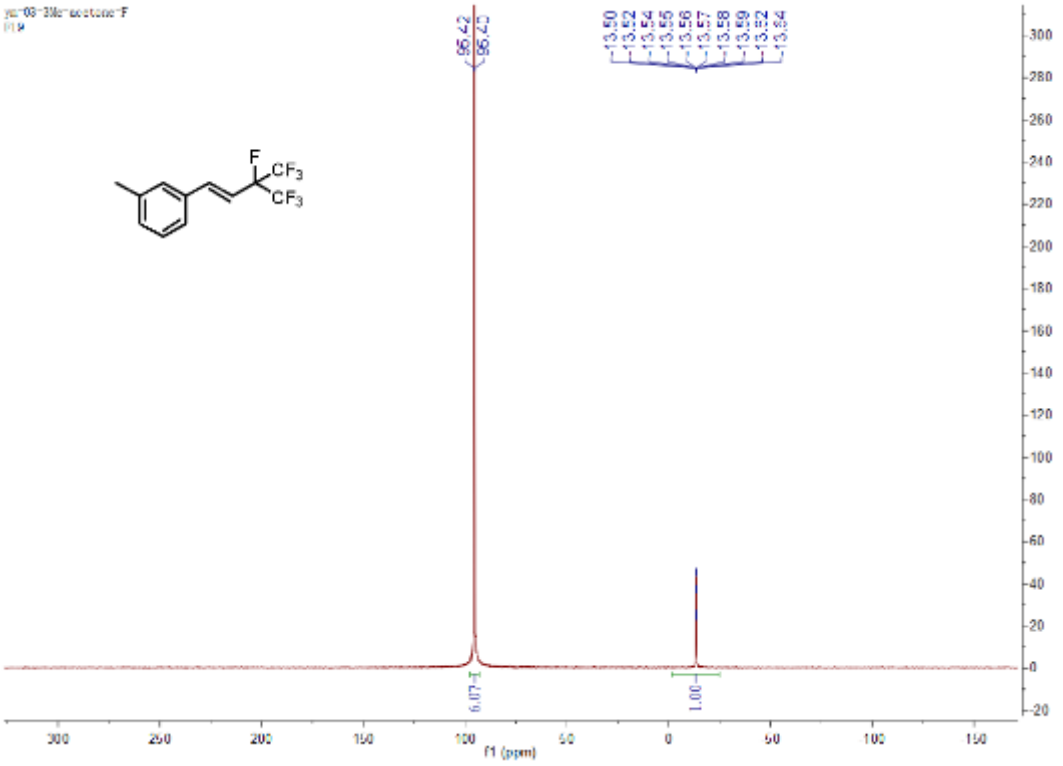
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3k**



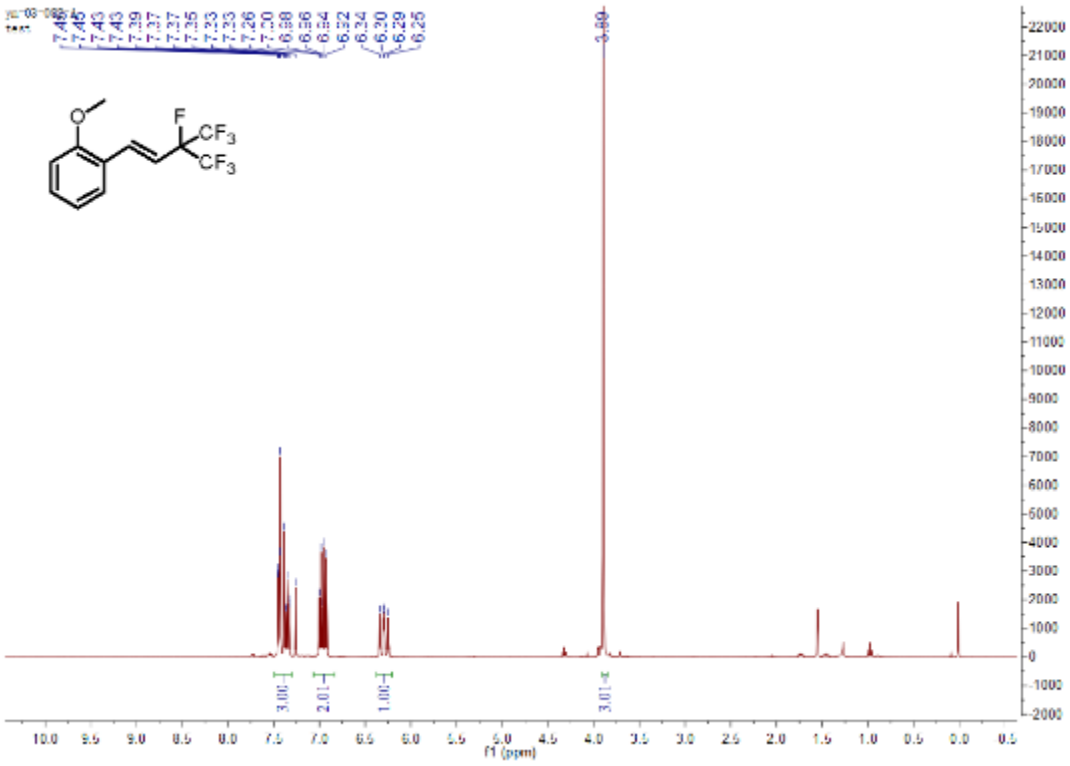
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3k**



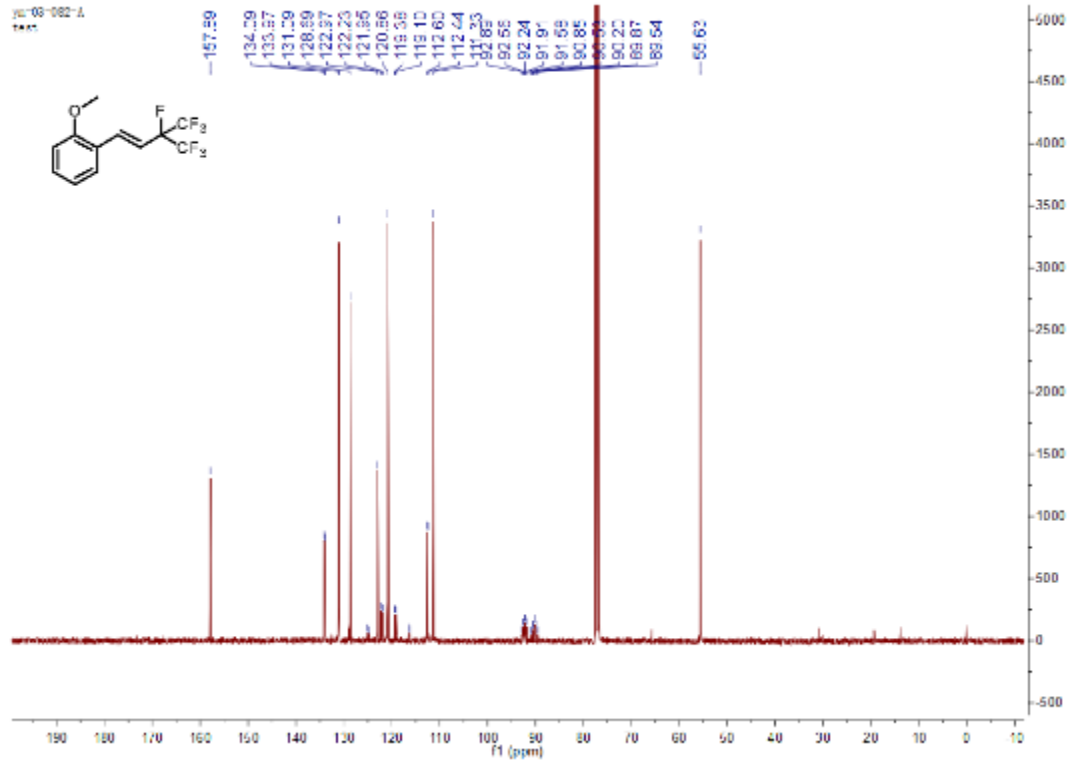
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3k**



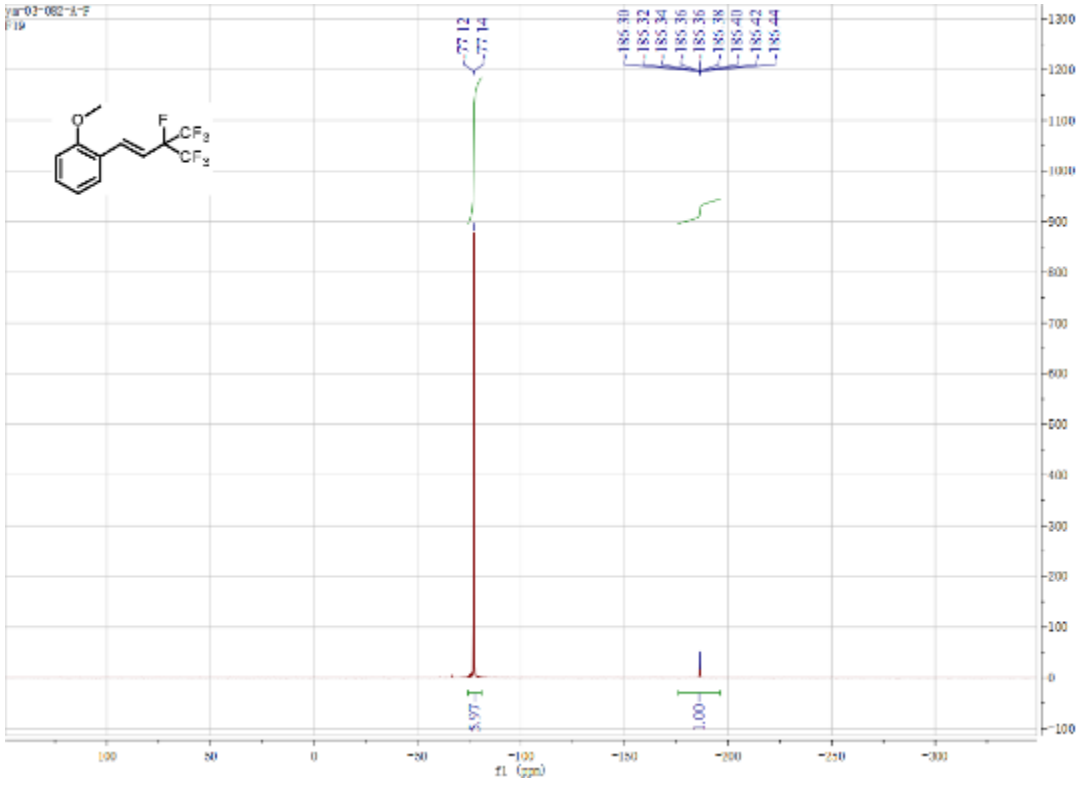
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3l**



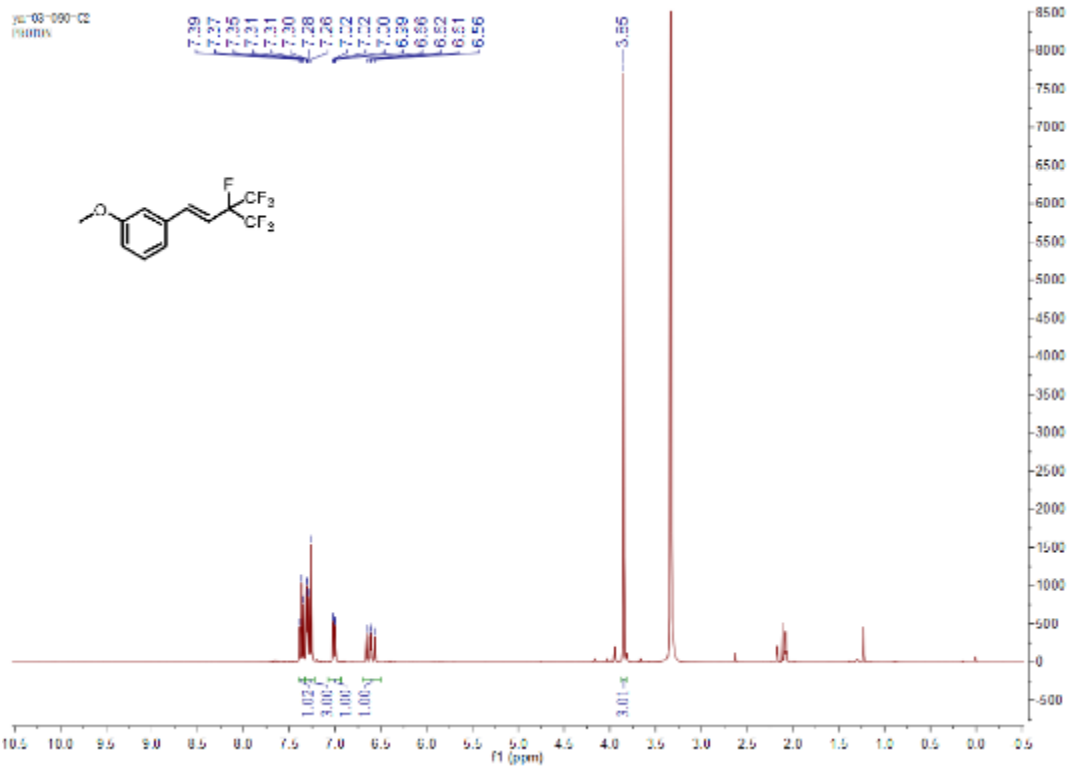
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3l**



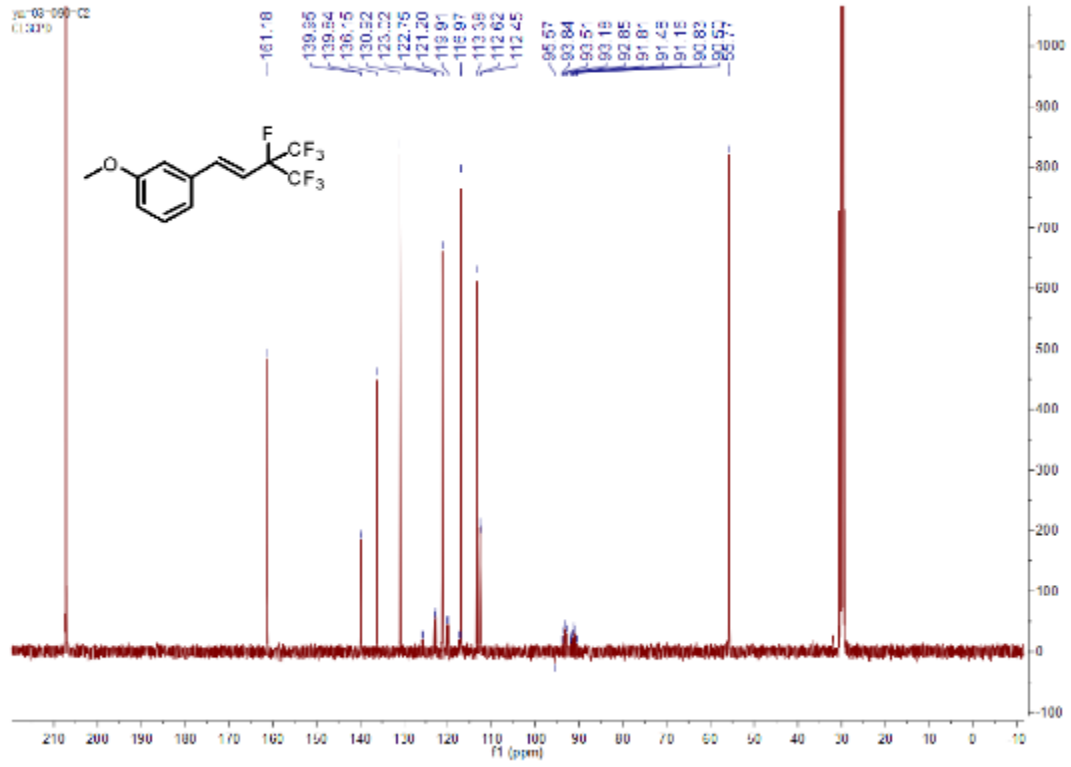
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3l**



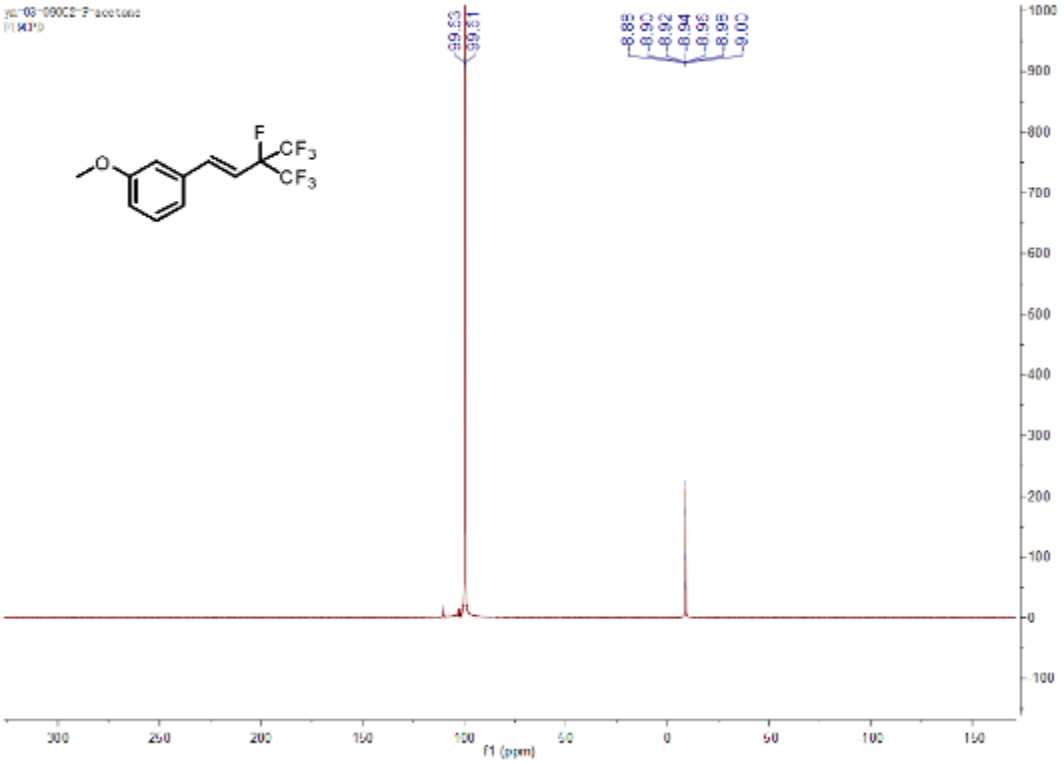
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3m**



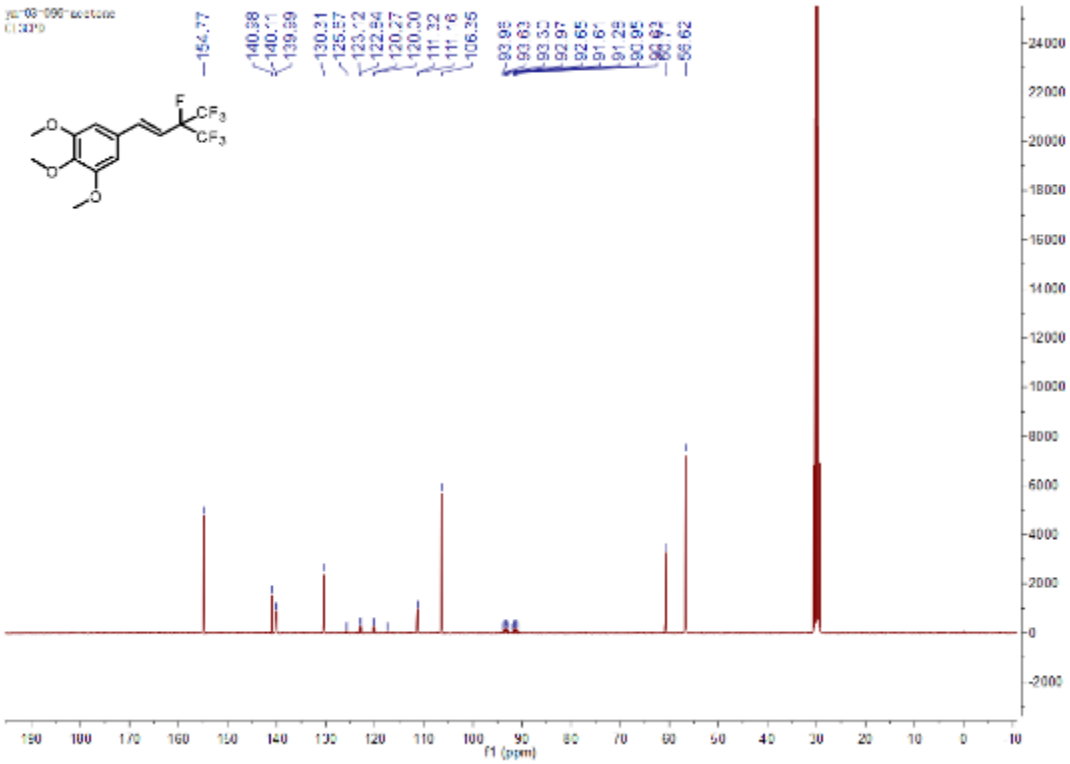
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3m**



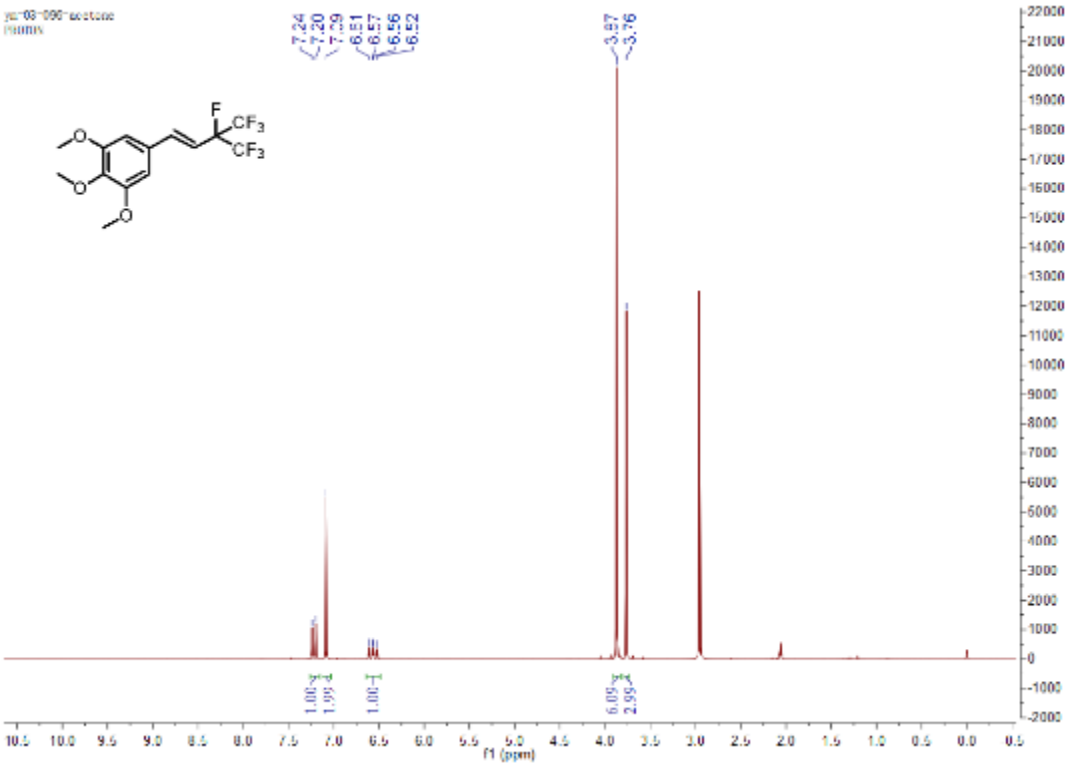
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3m**



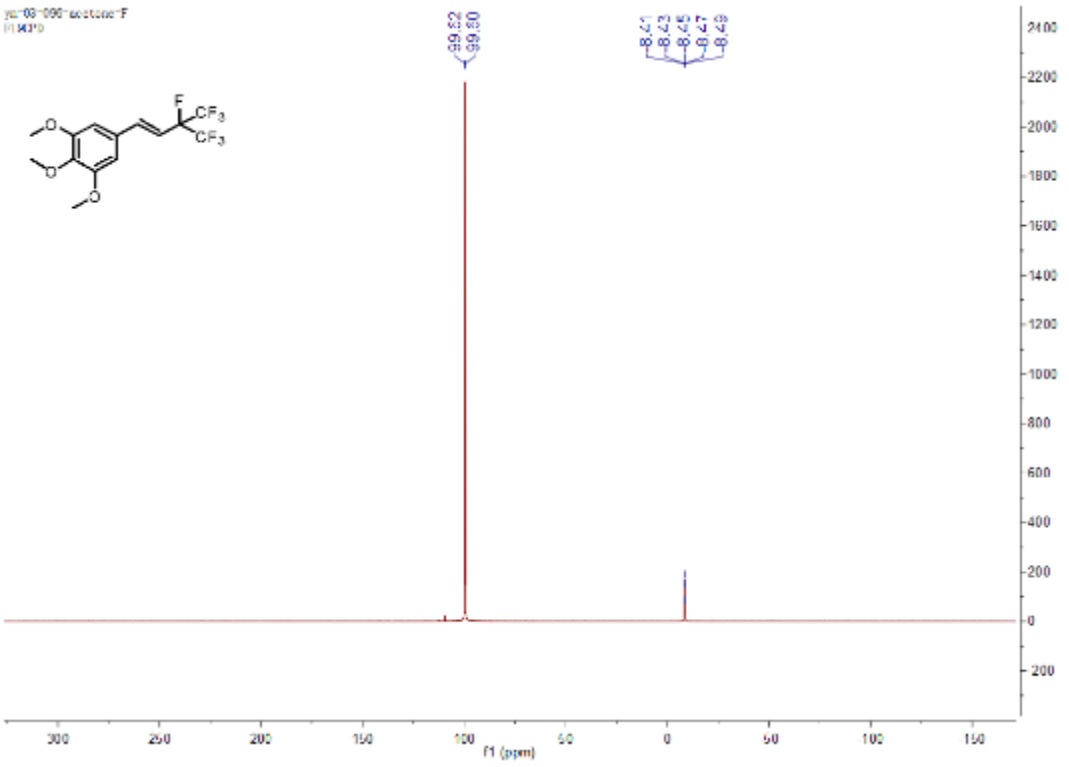
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3n**



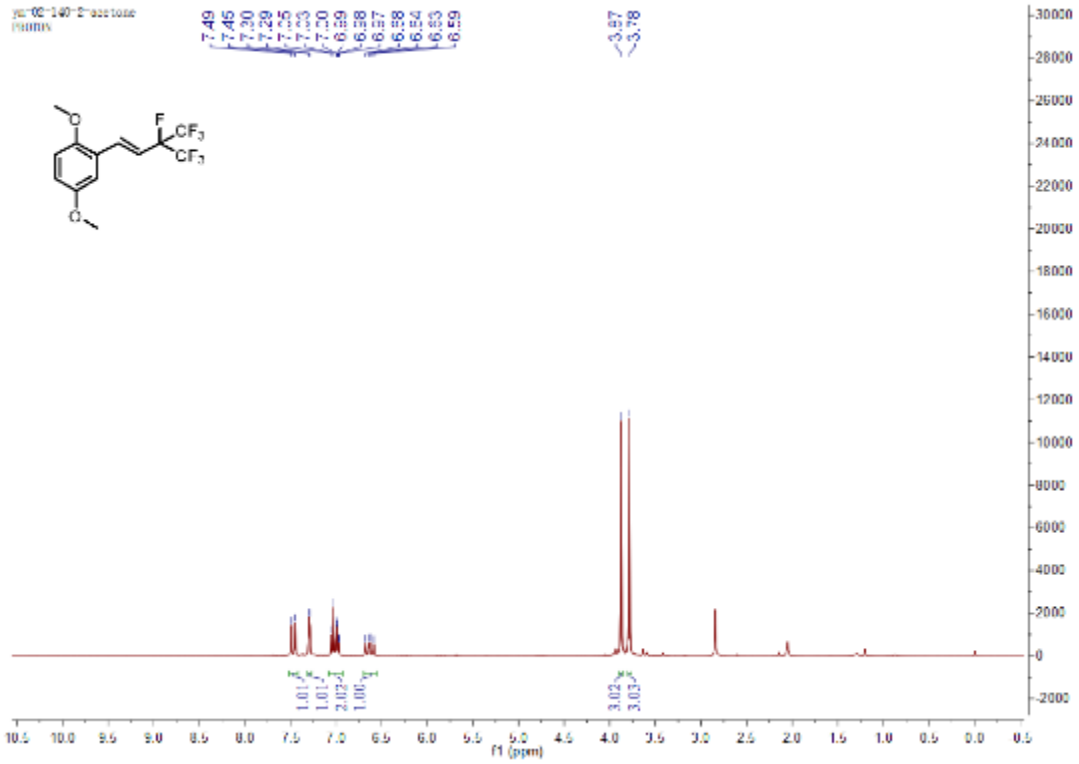
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3n**



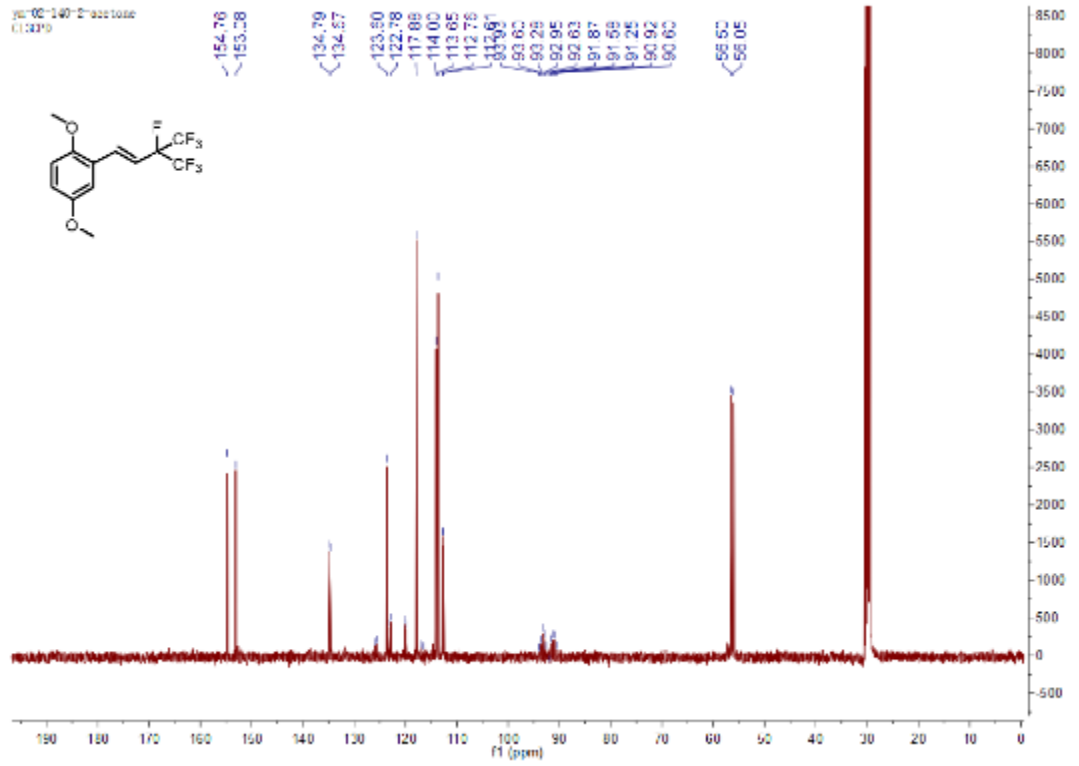
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3n**



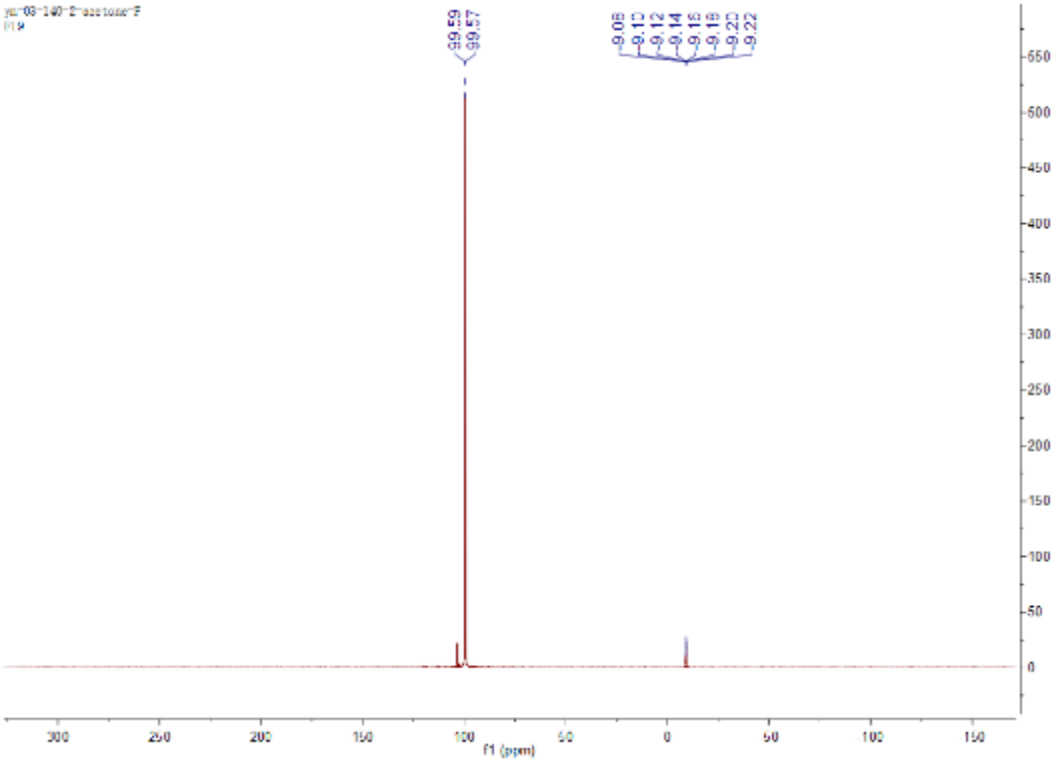
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3o$_1$**



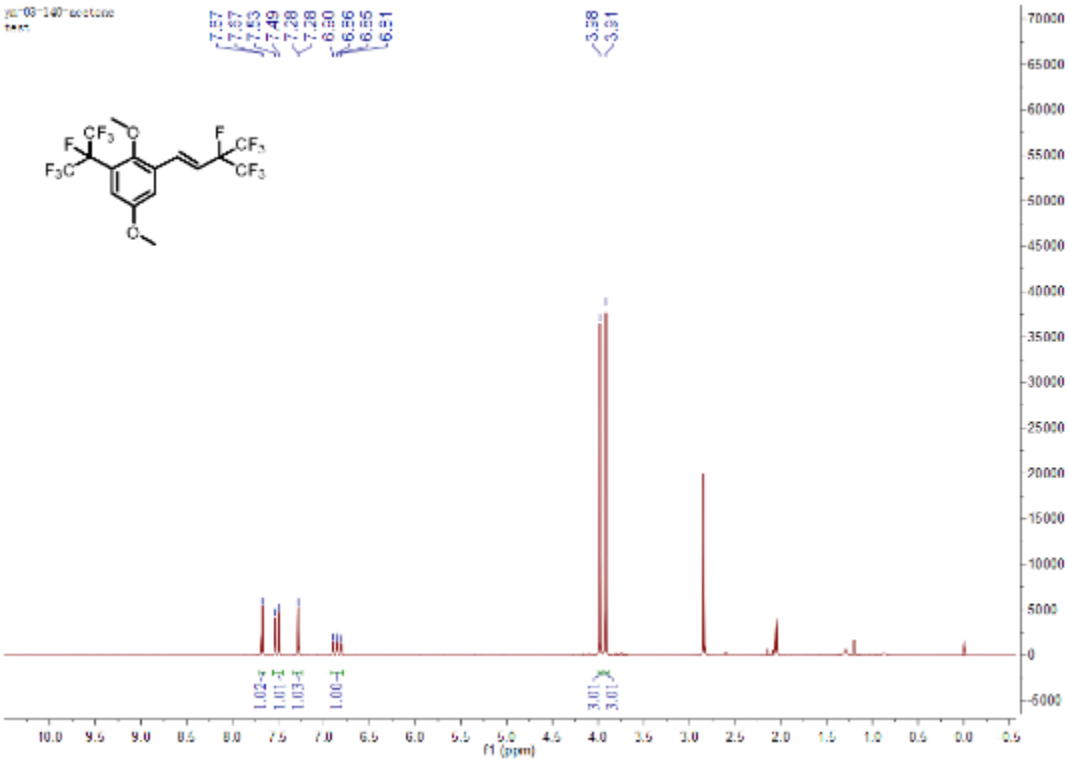
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3o$_1$**



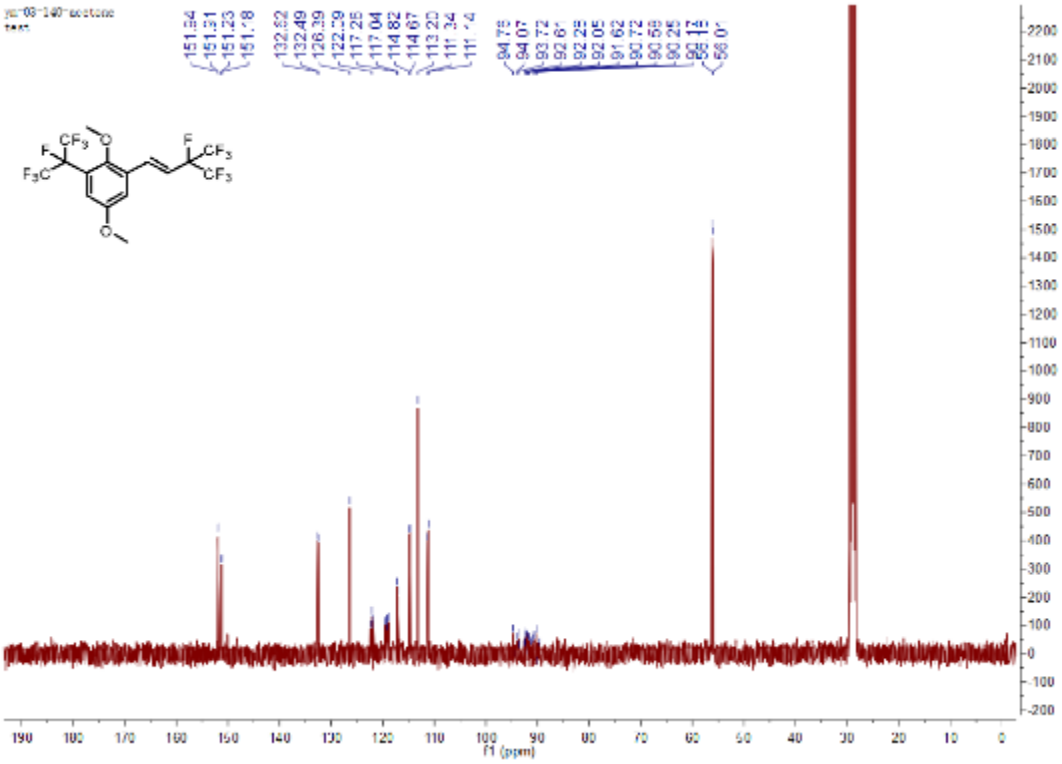
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3o1**



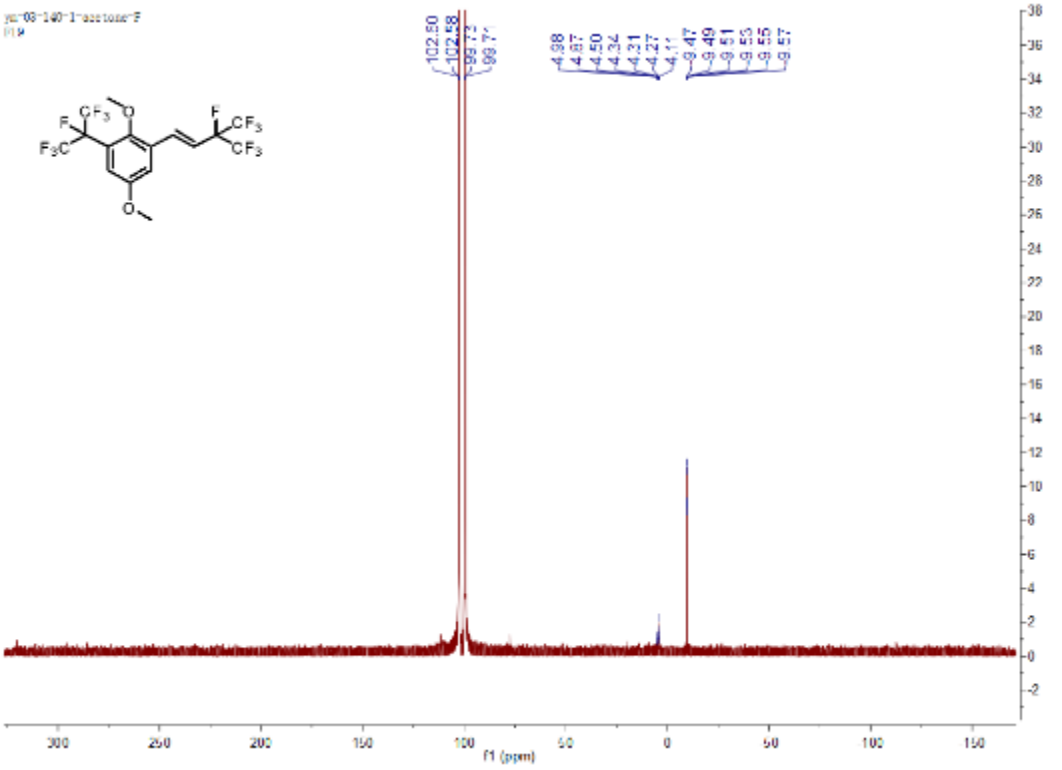
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3o2**



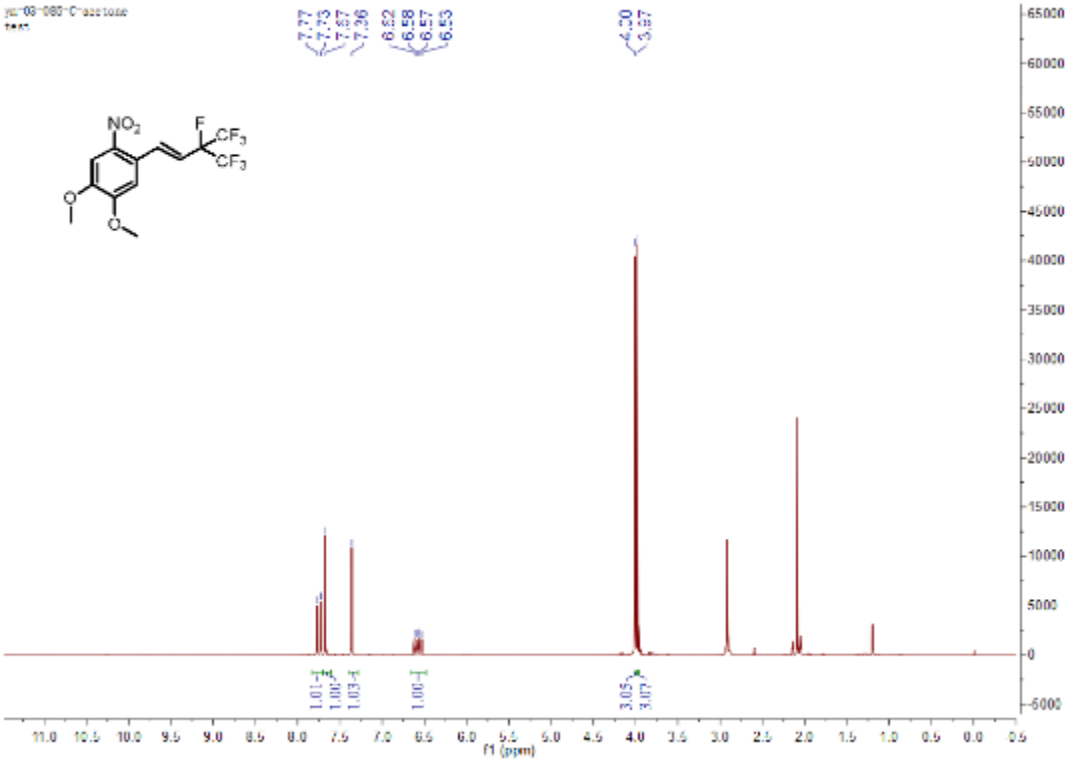
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3o2**



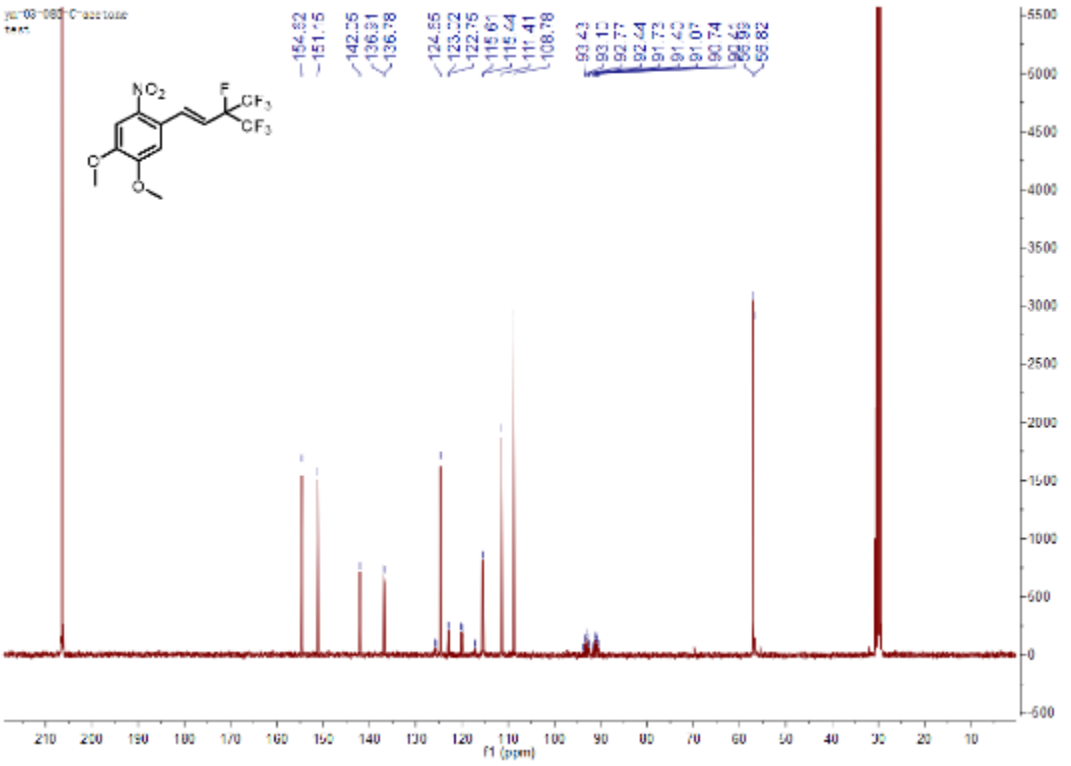
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3o2**



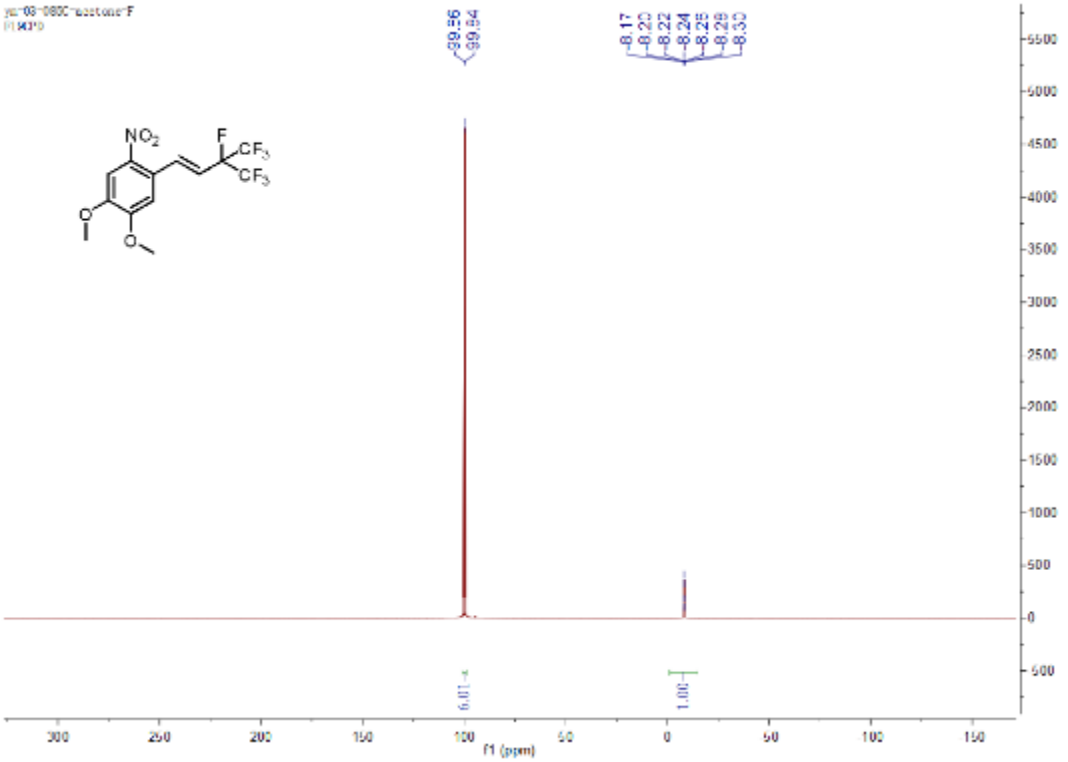
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3p**



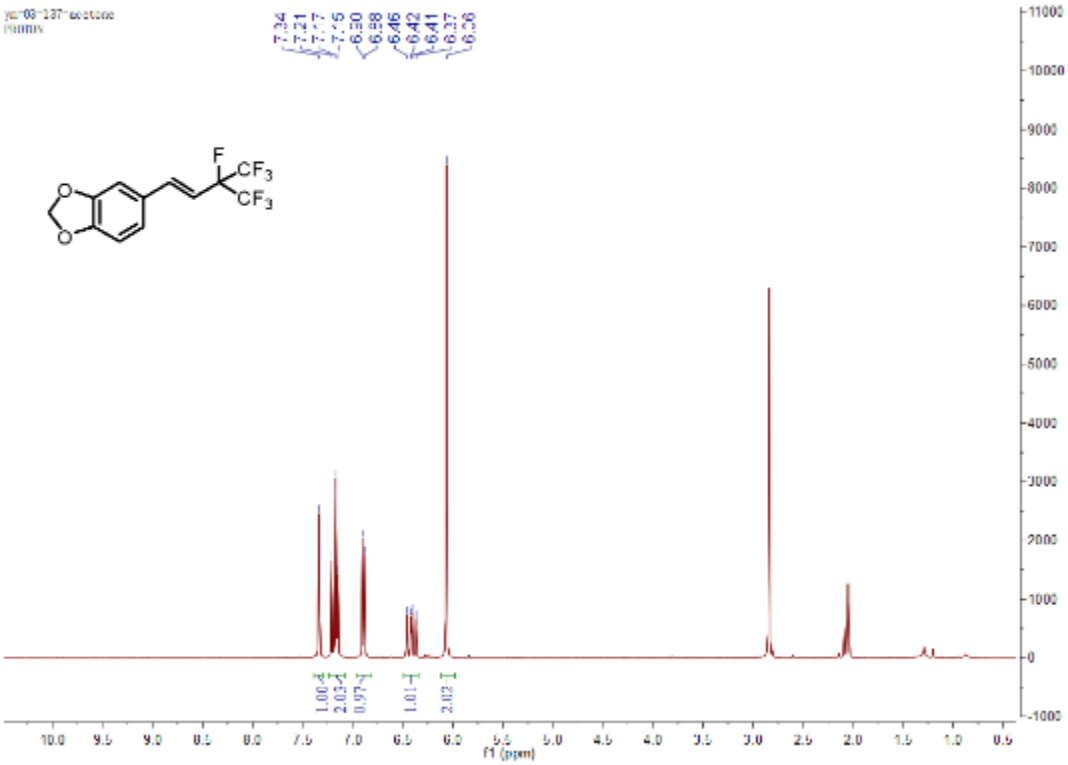
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3p**



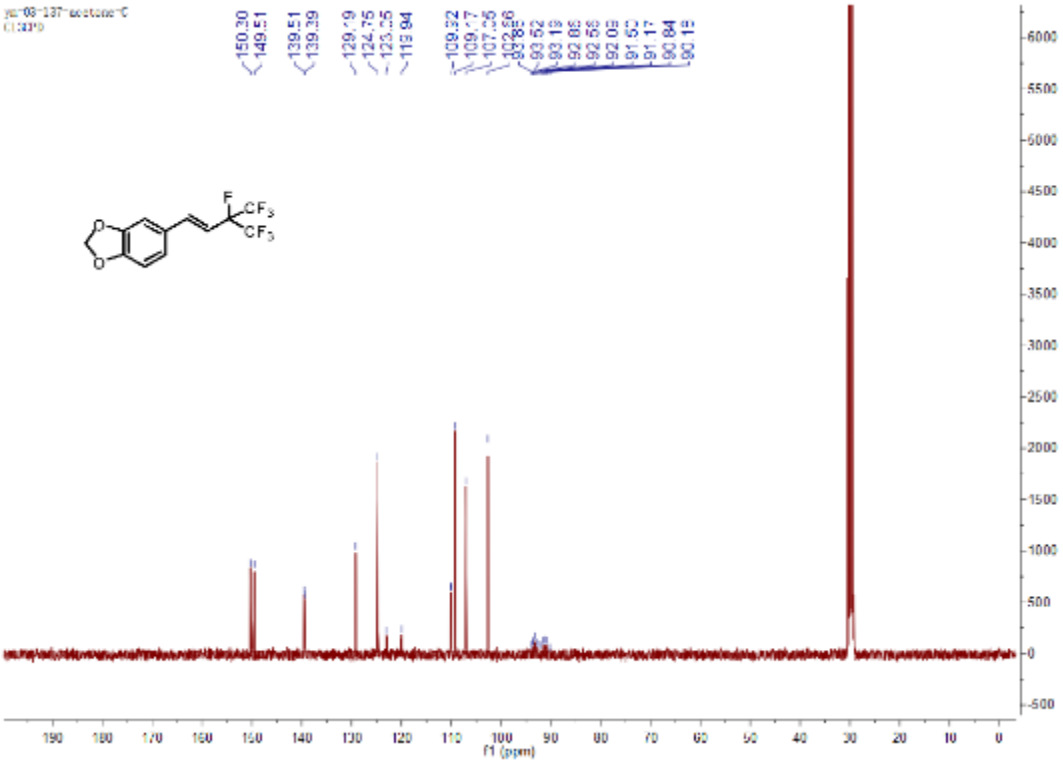
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3p**



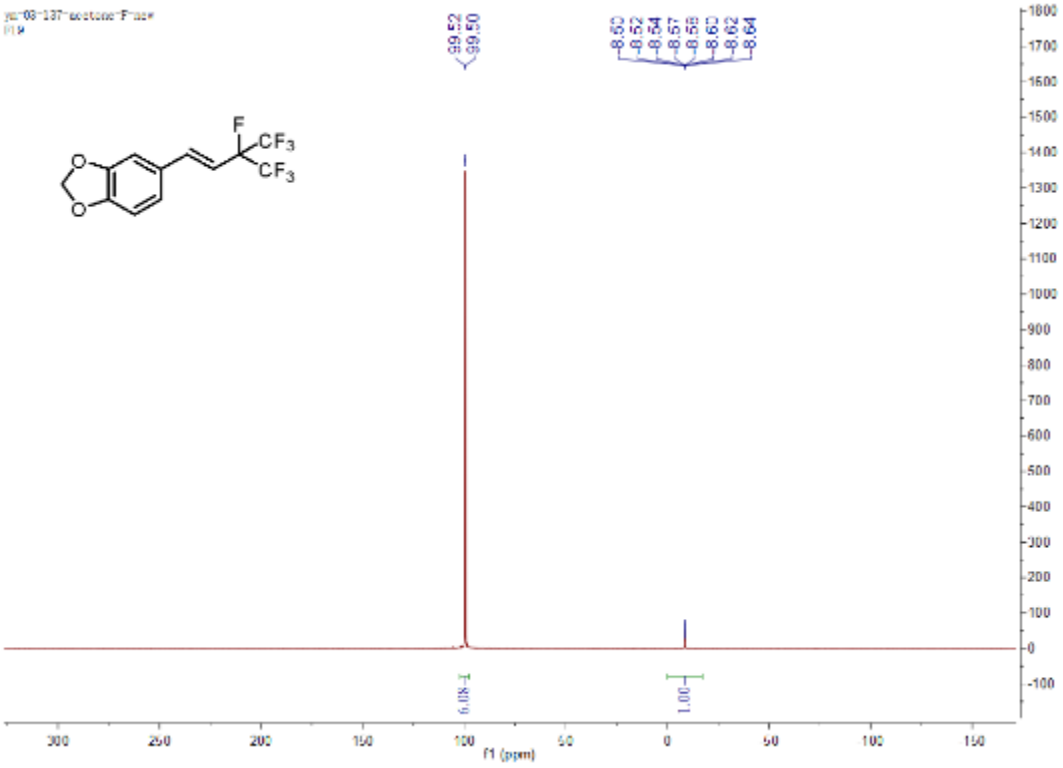
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3q**



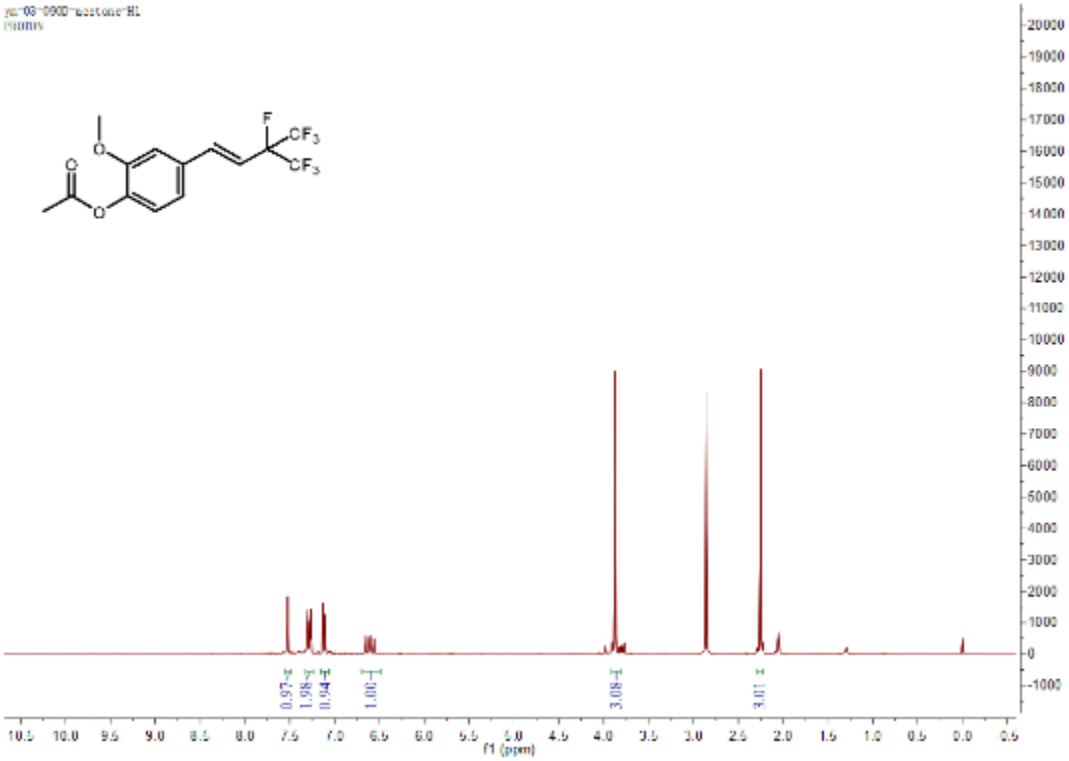
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3q**



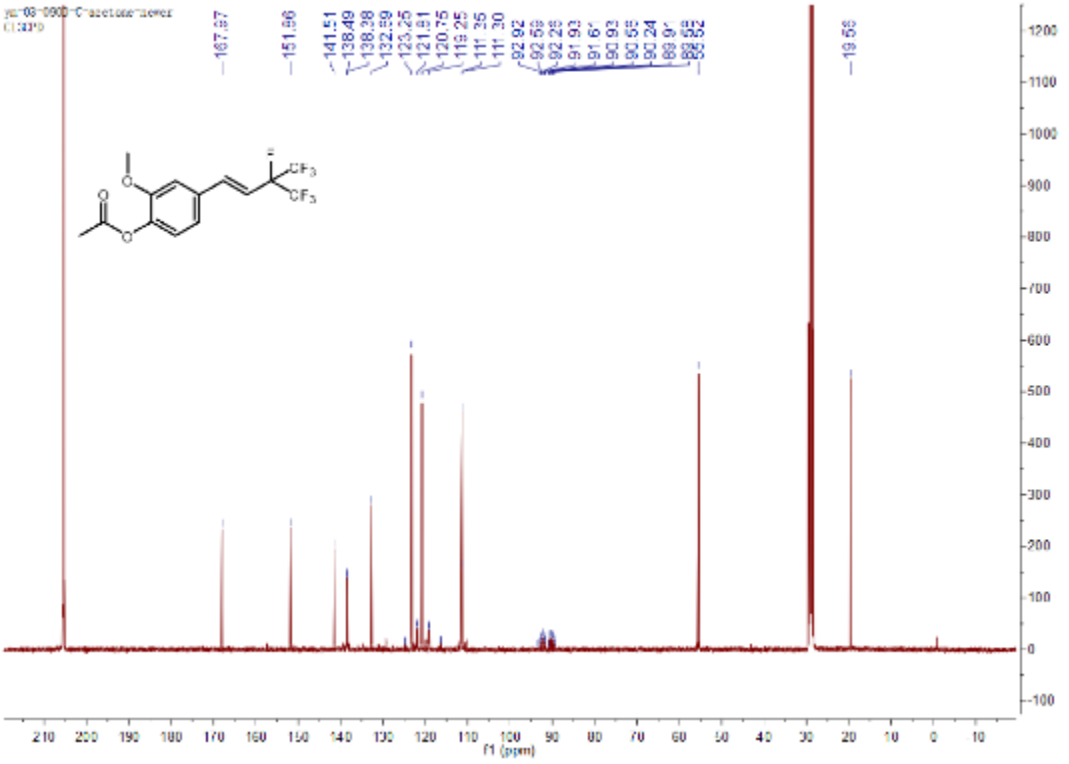
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3q**



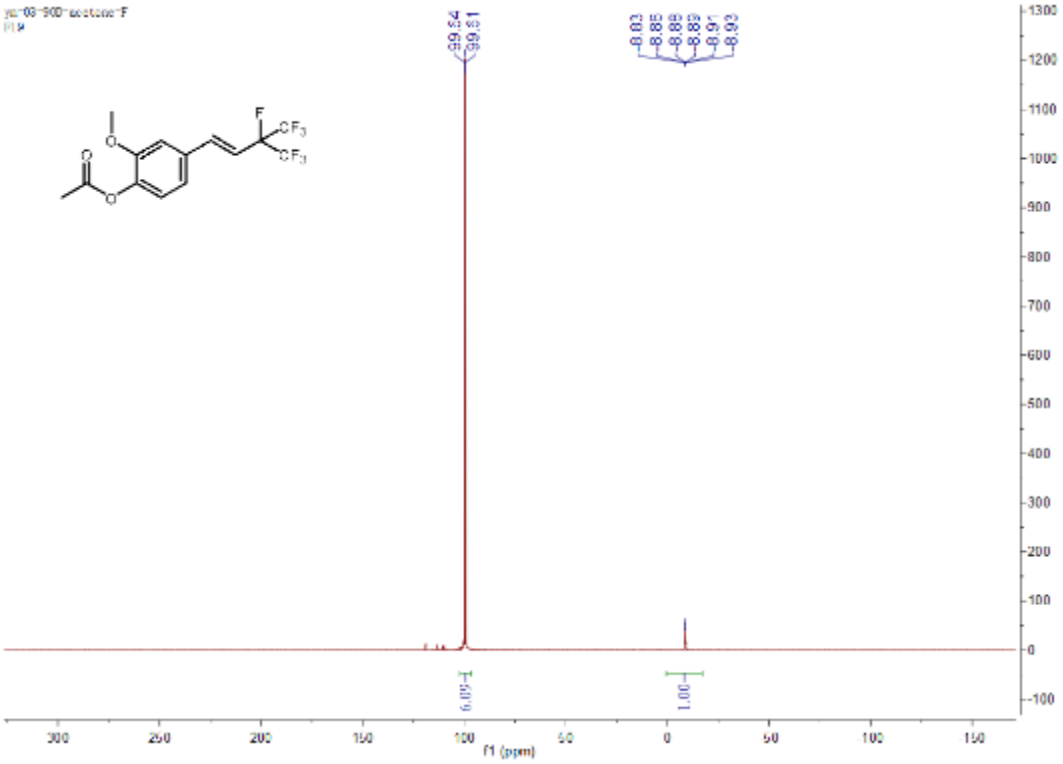
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3r**



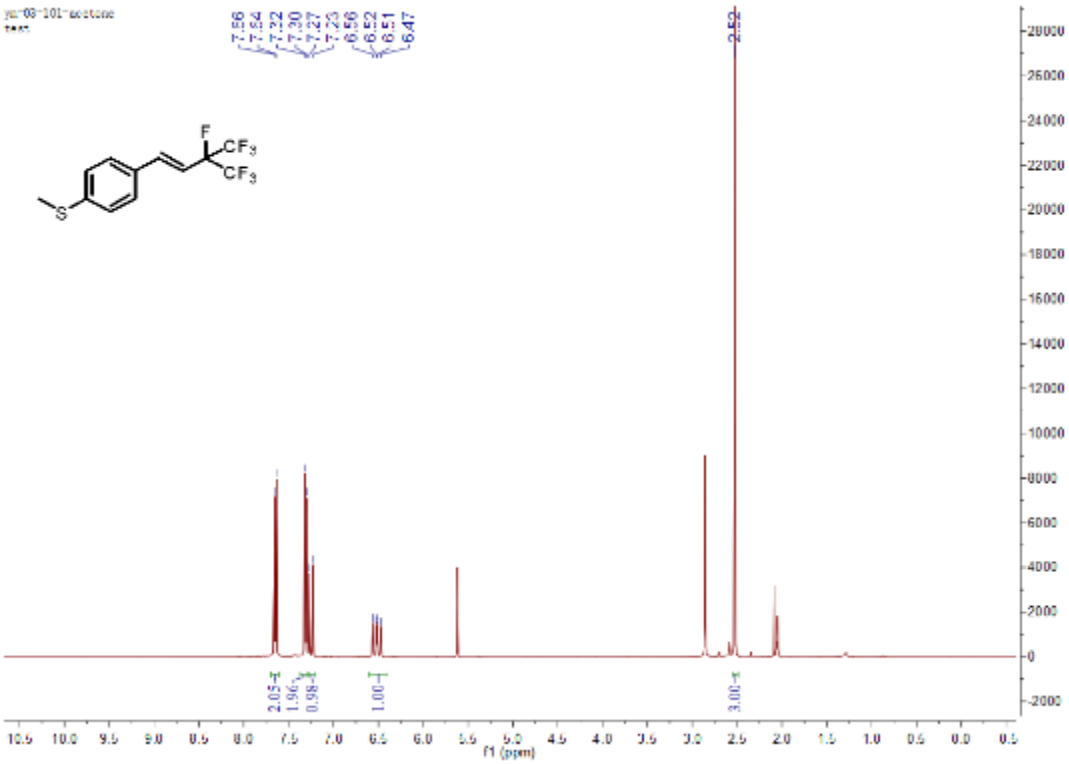
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3r**



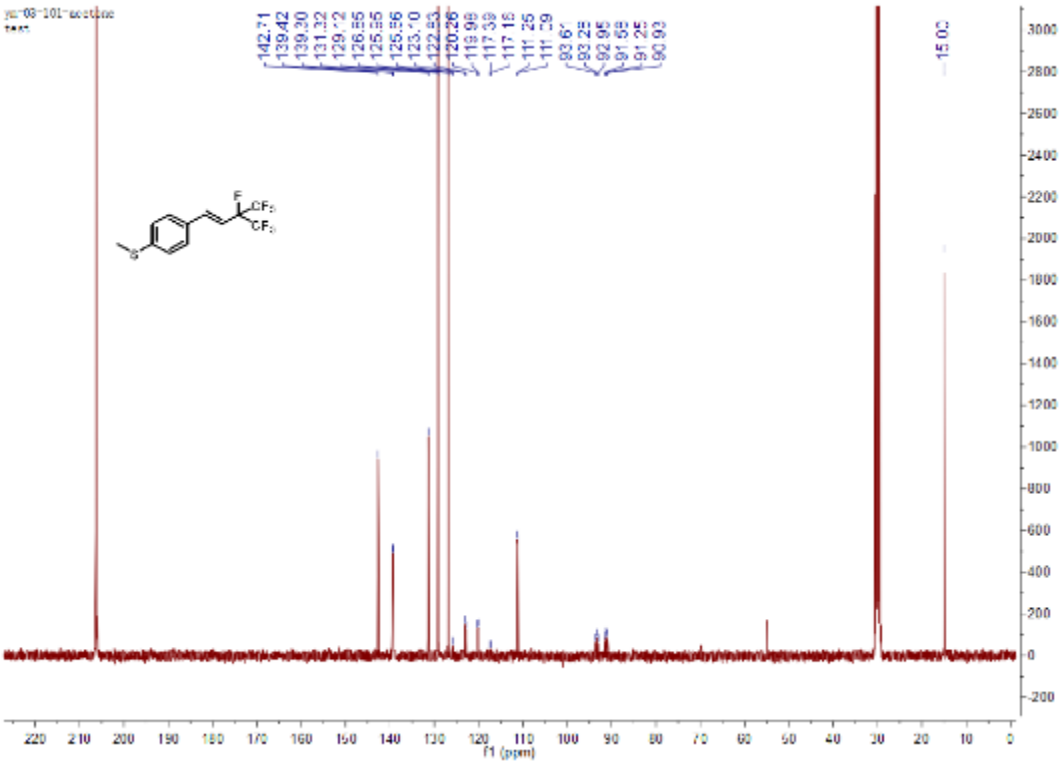
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3r**



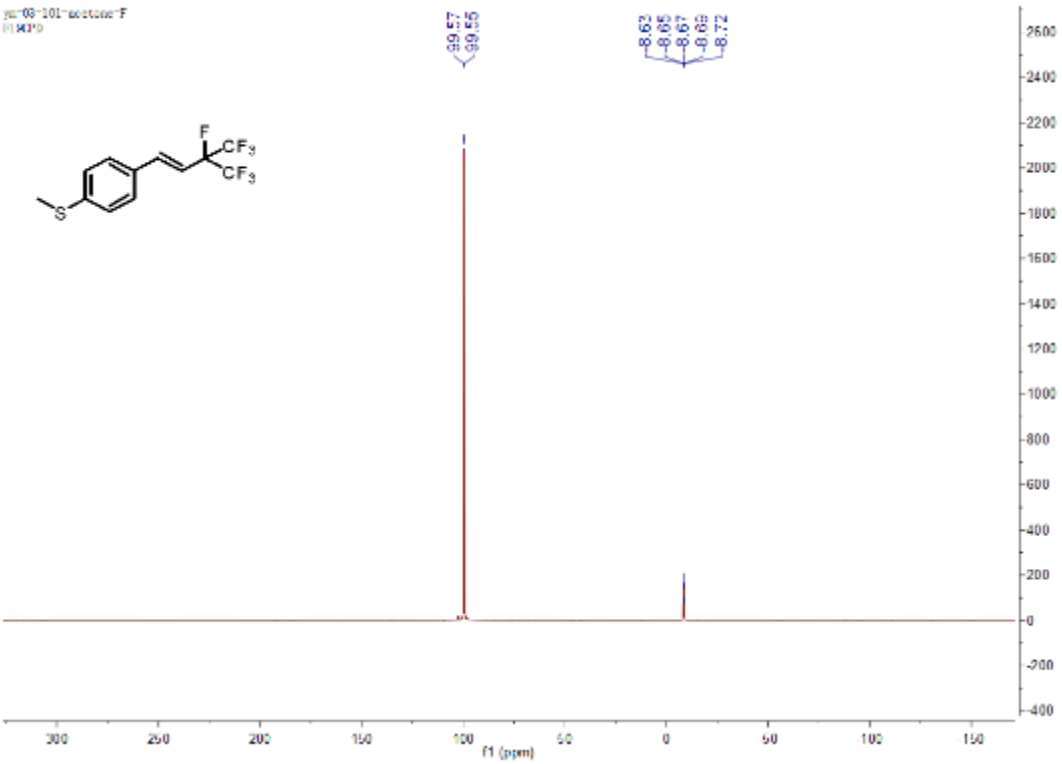
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3s**



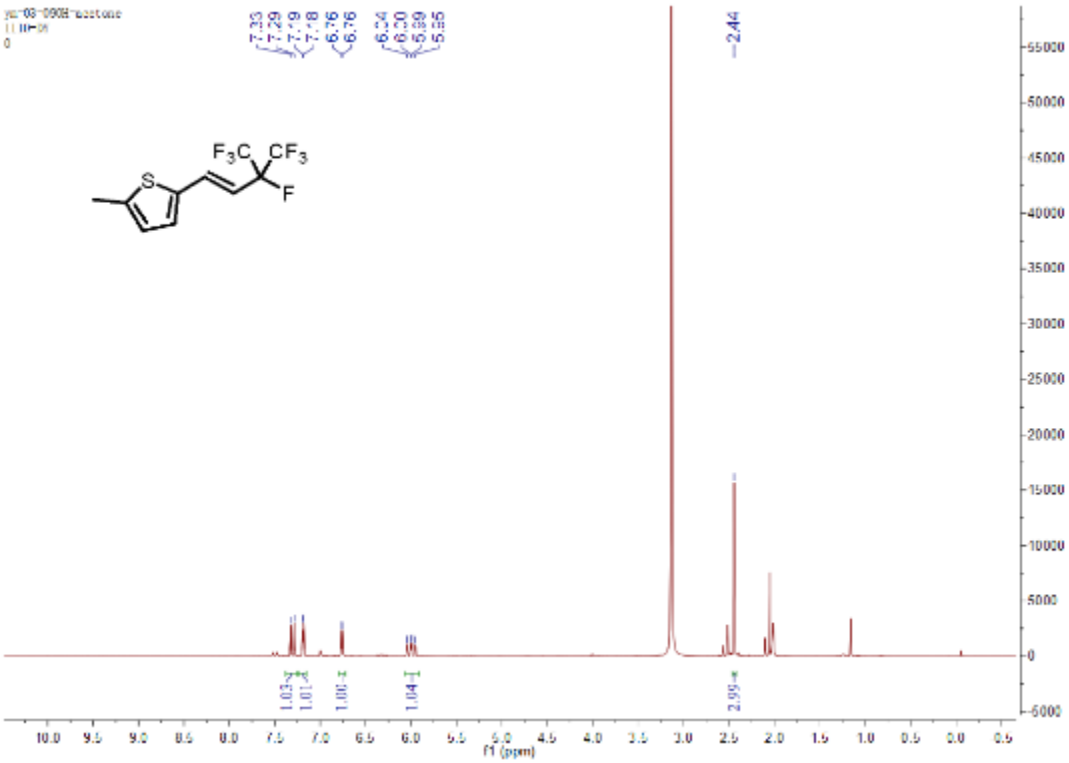
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3s**



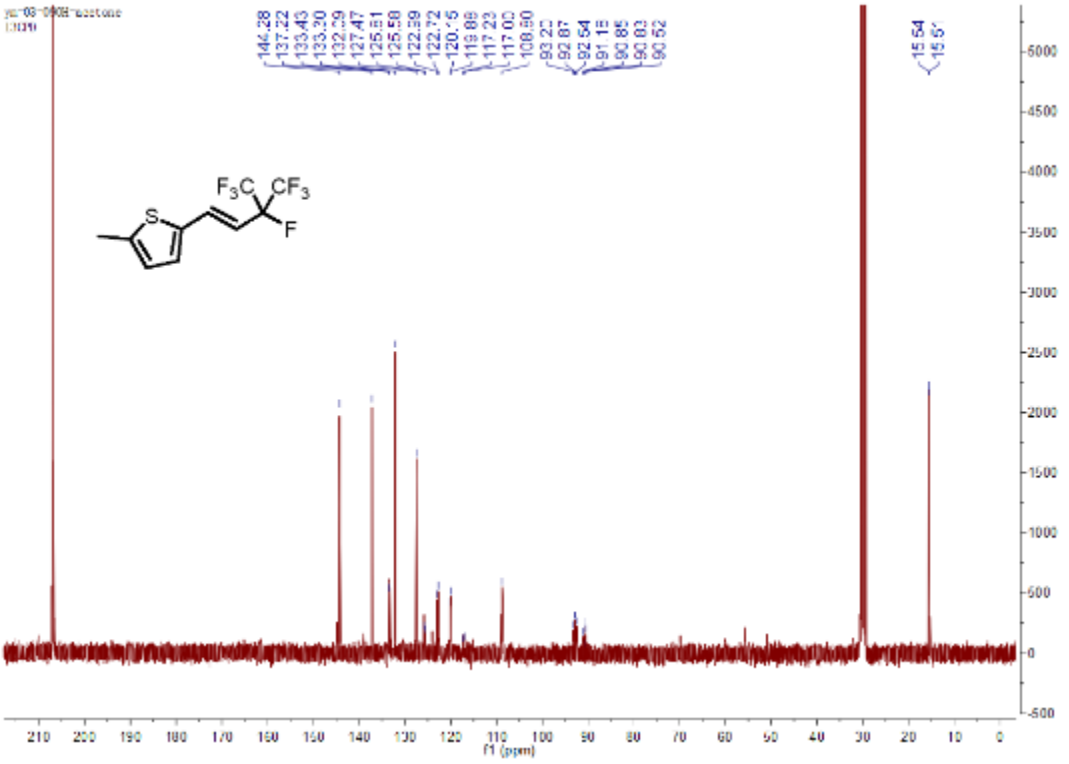
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3s**



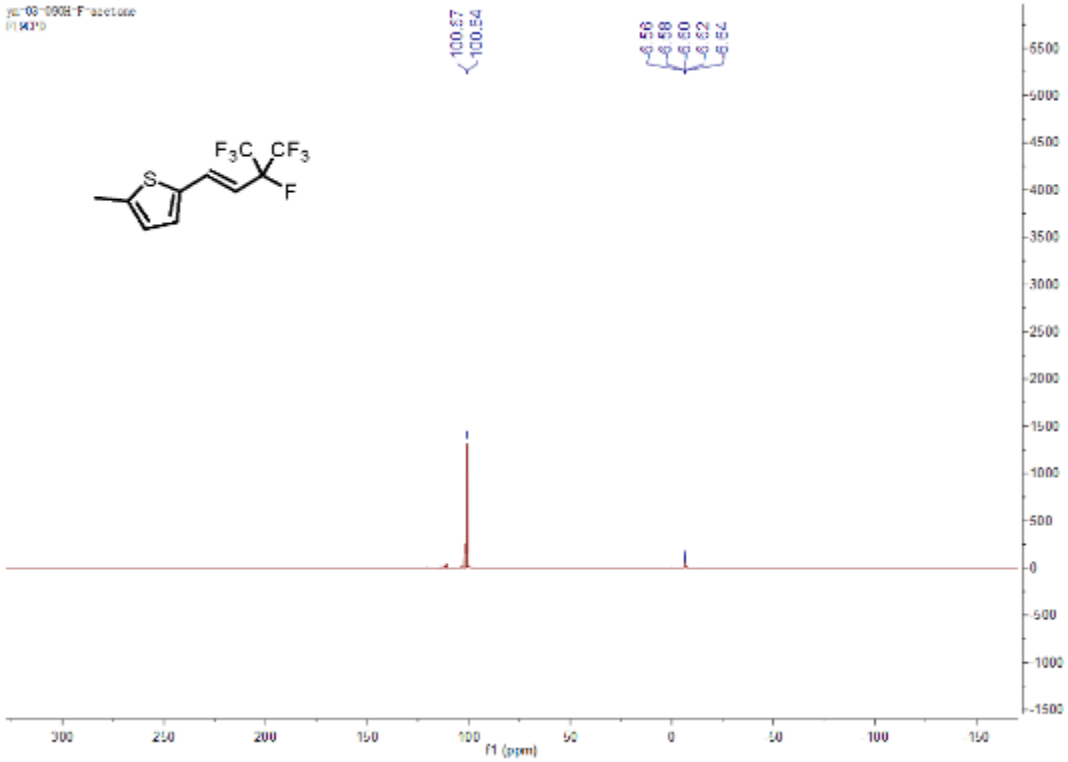
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3t**



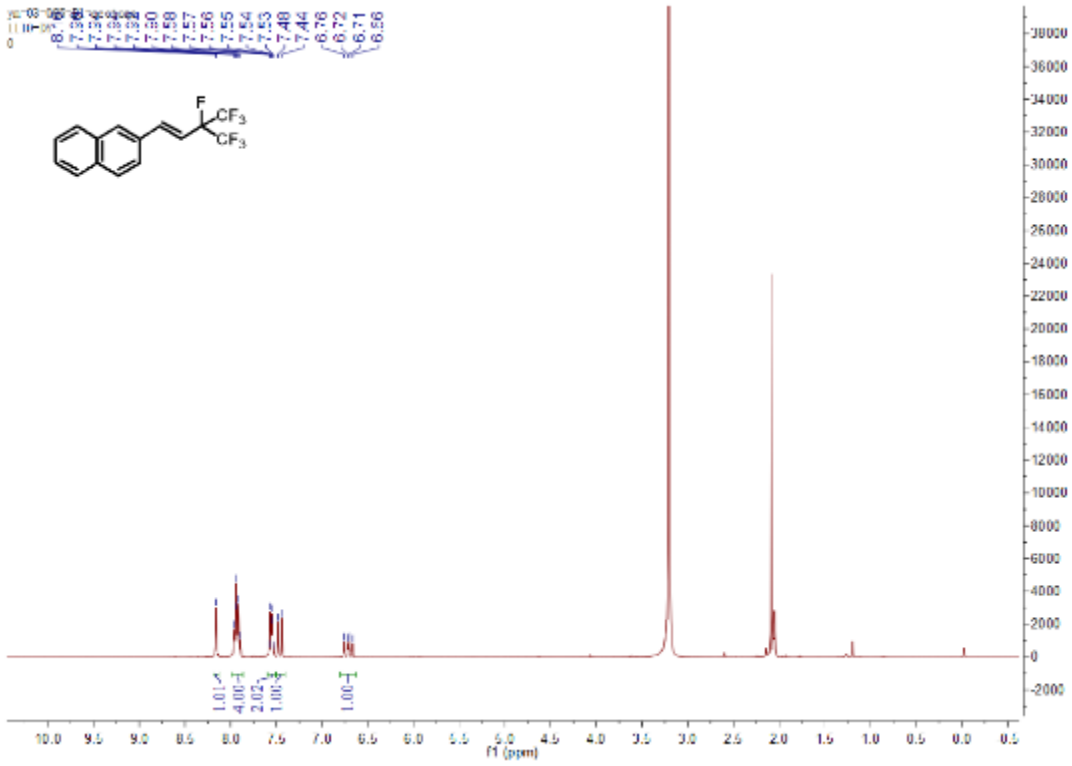
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3t**



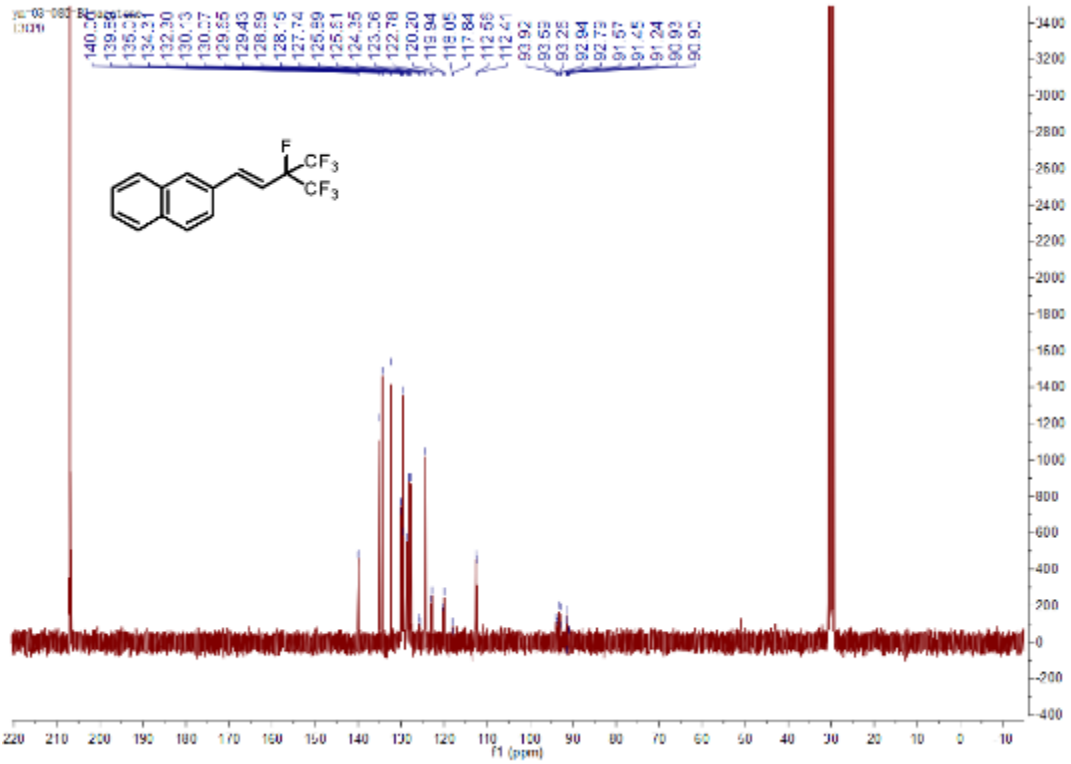
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3t**



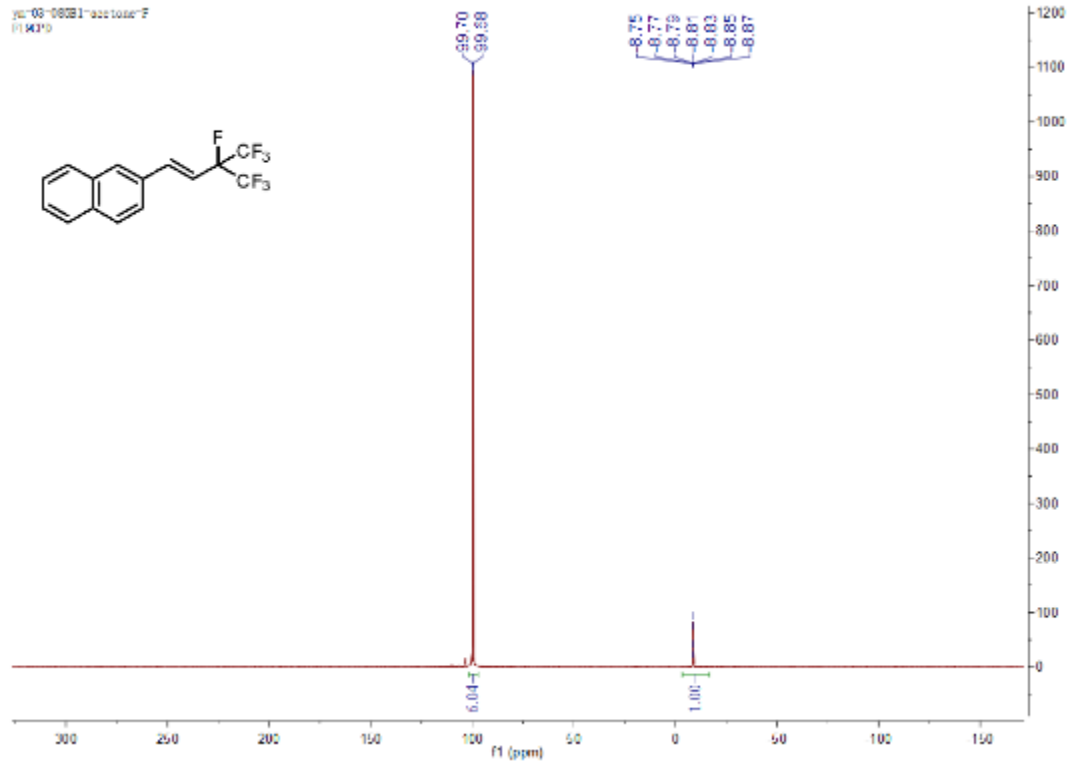
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3u**



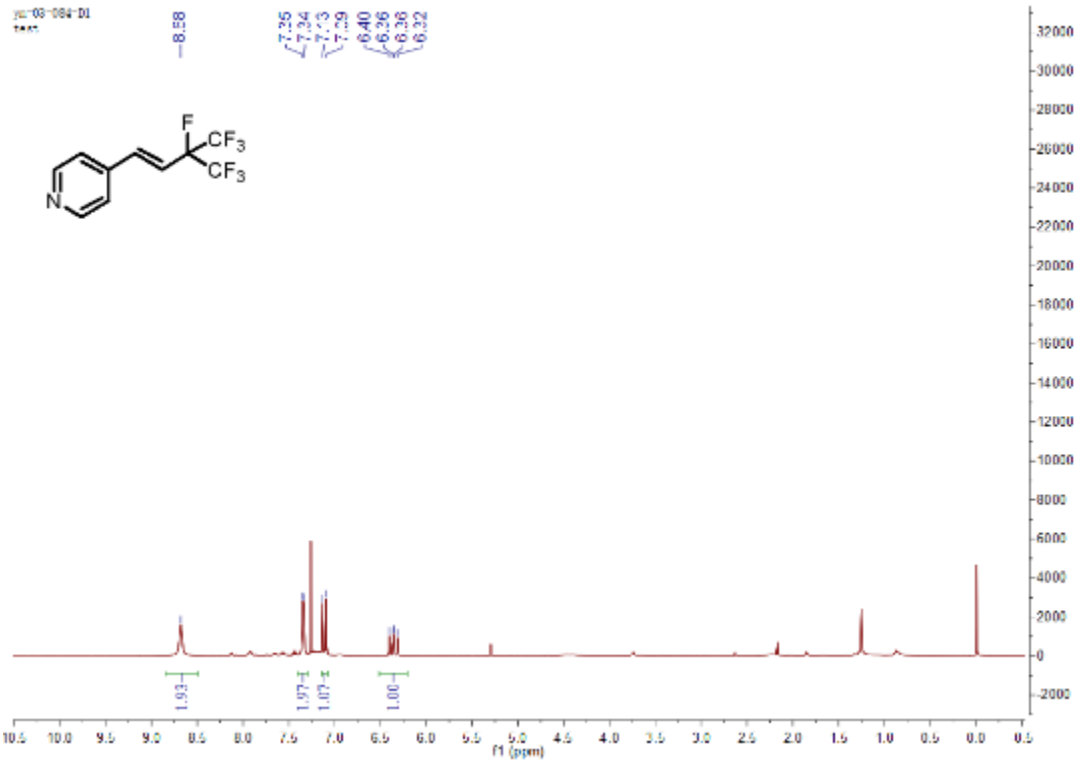
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3u**



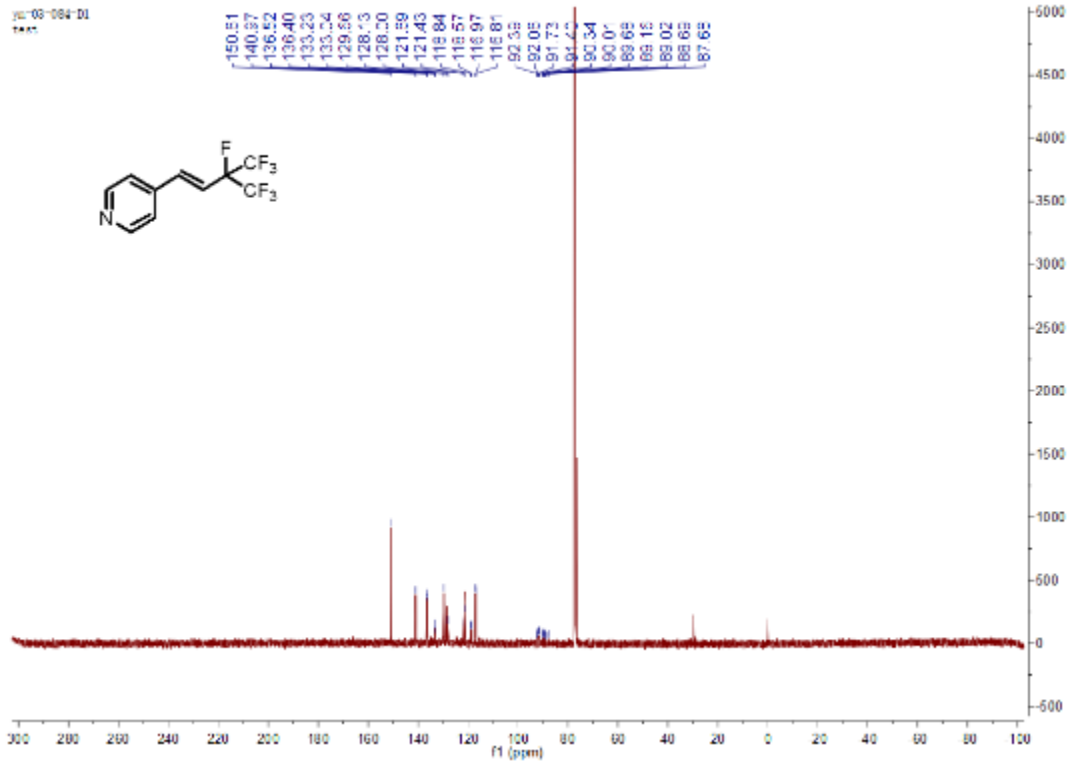
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3u**



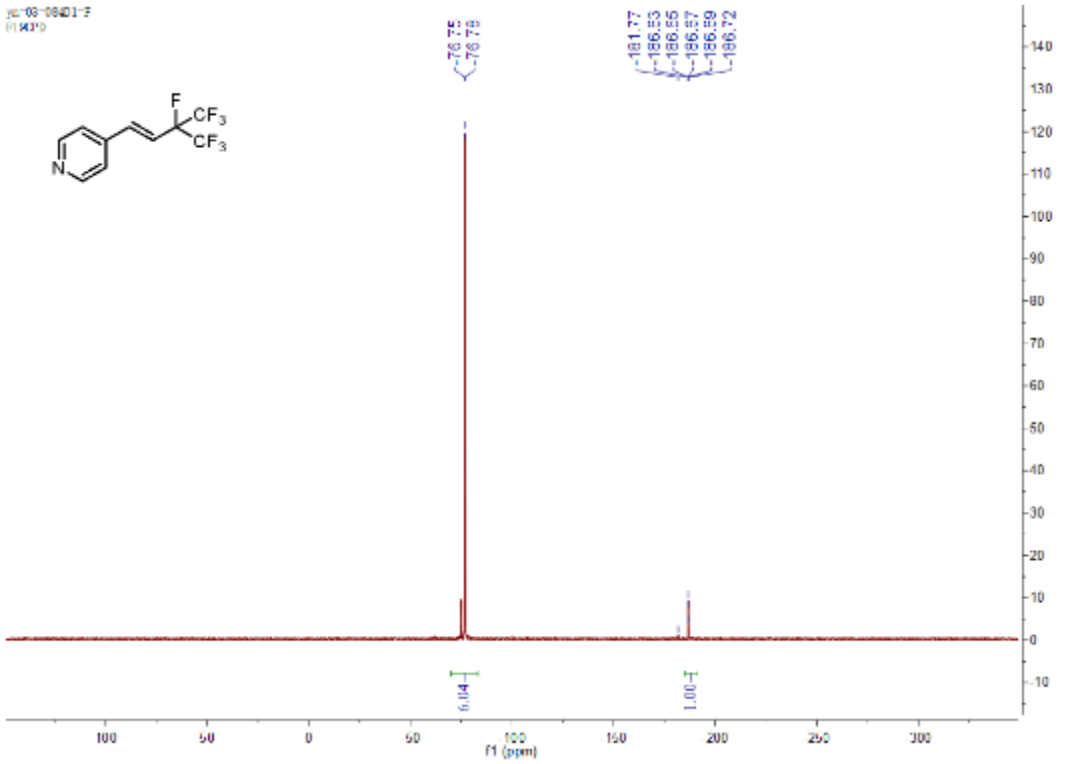
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3v**



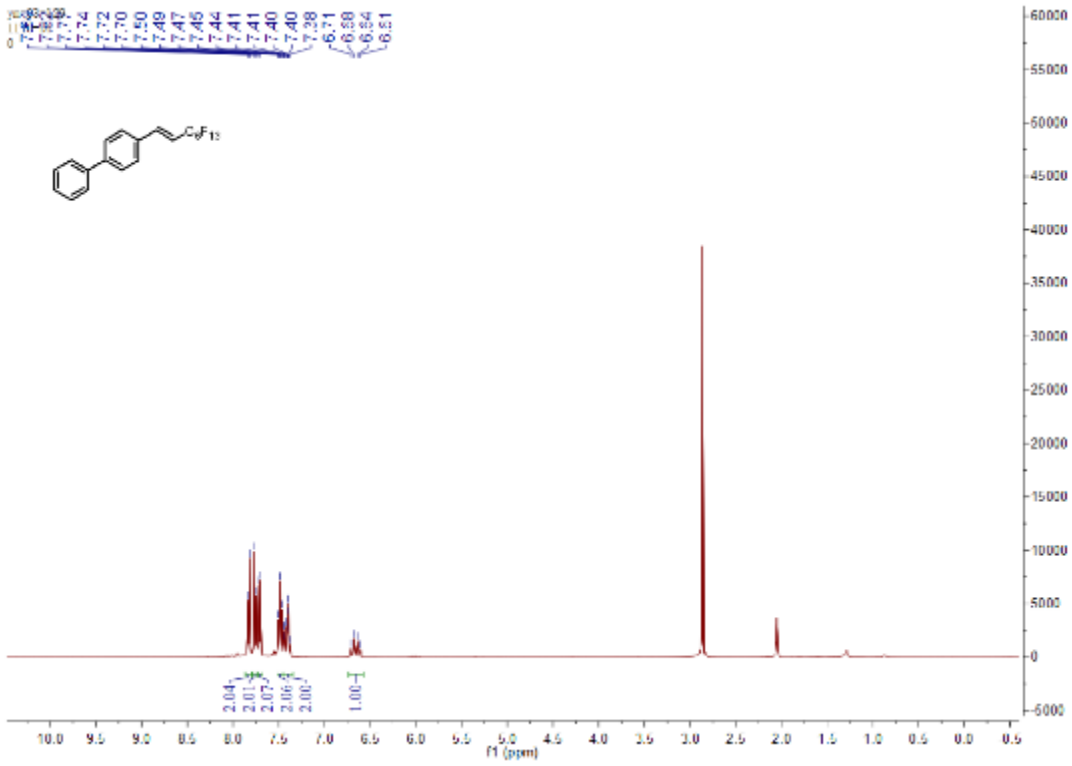
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3v**



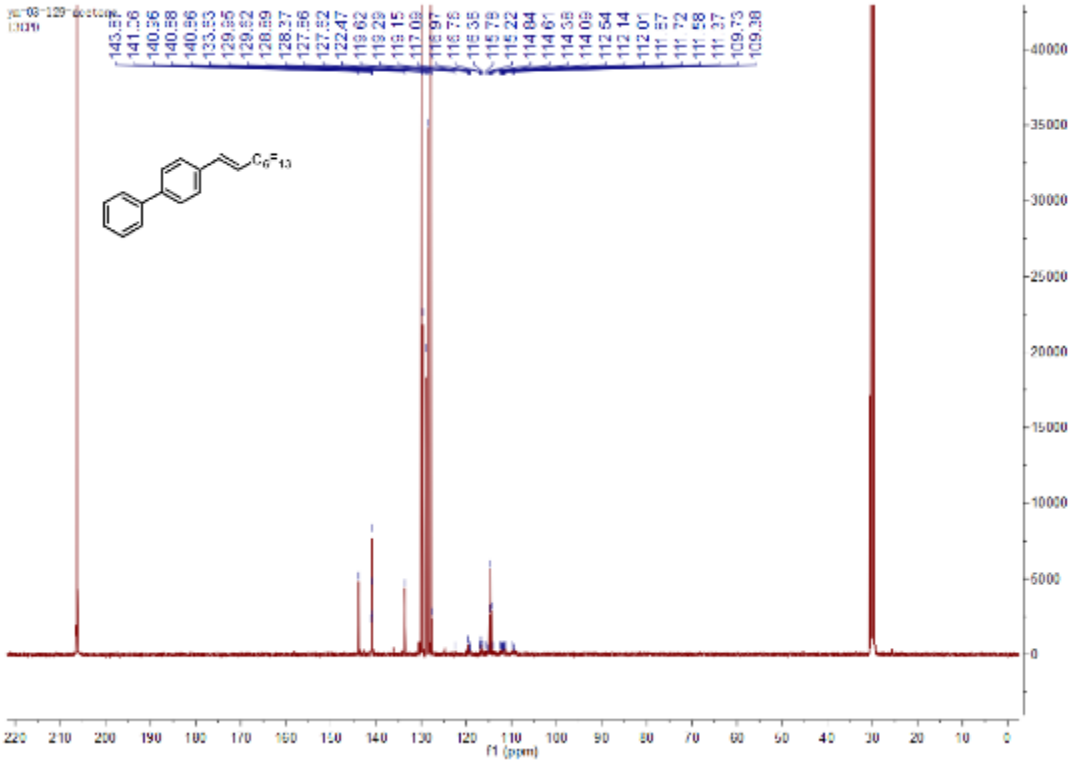
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3v**



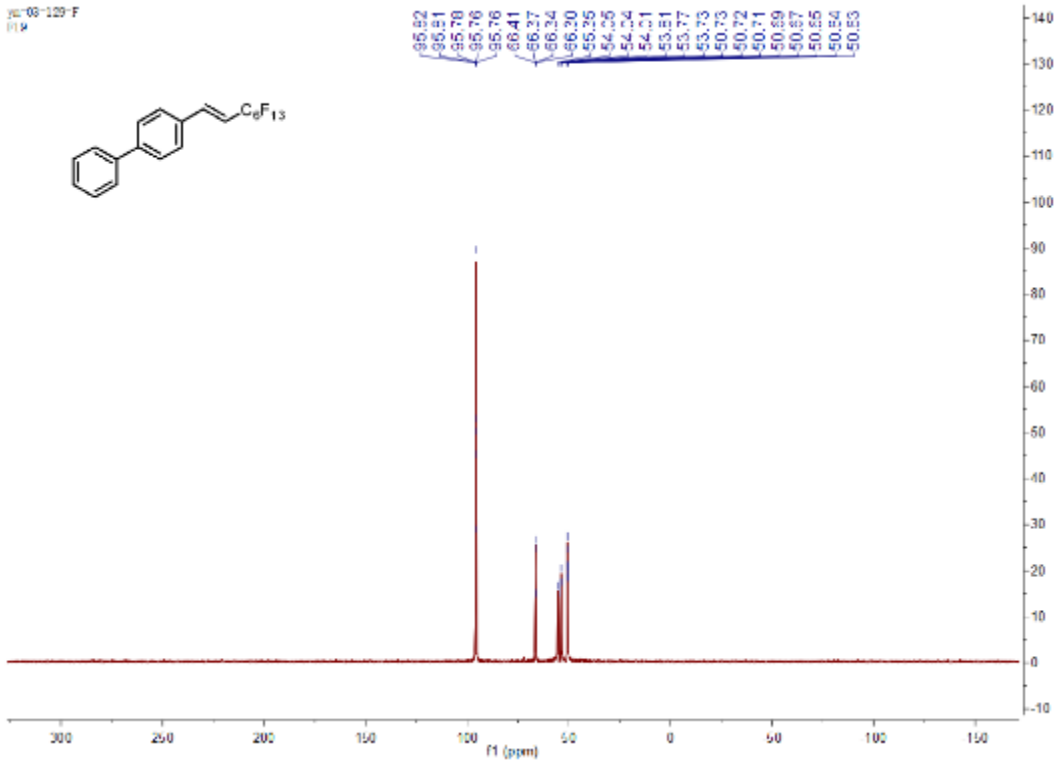
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3w**



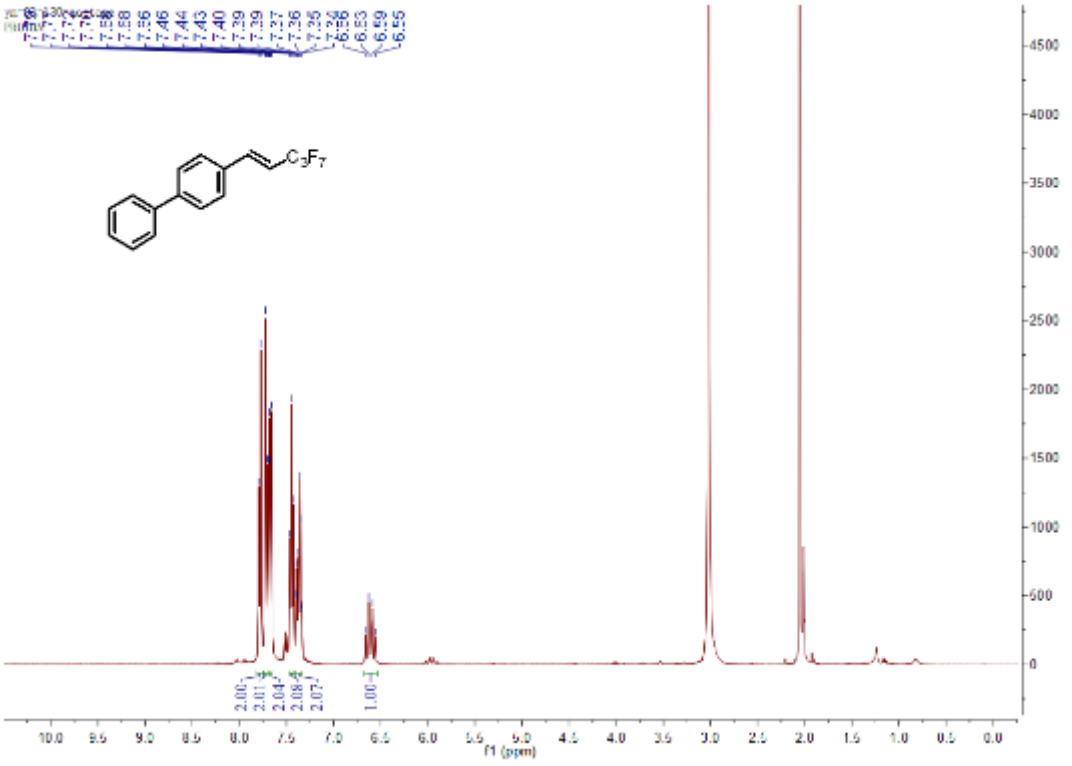
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3w**



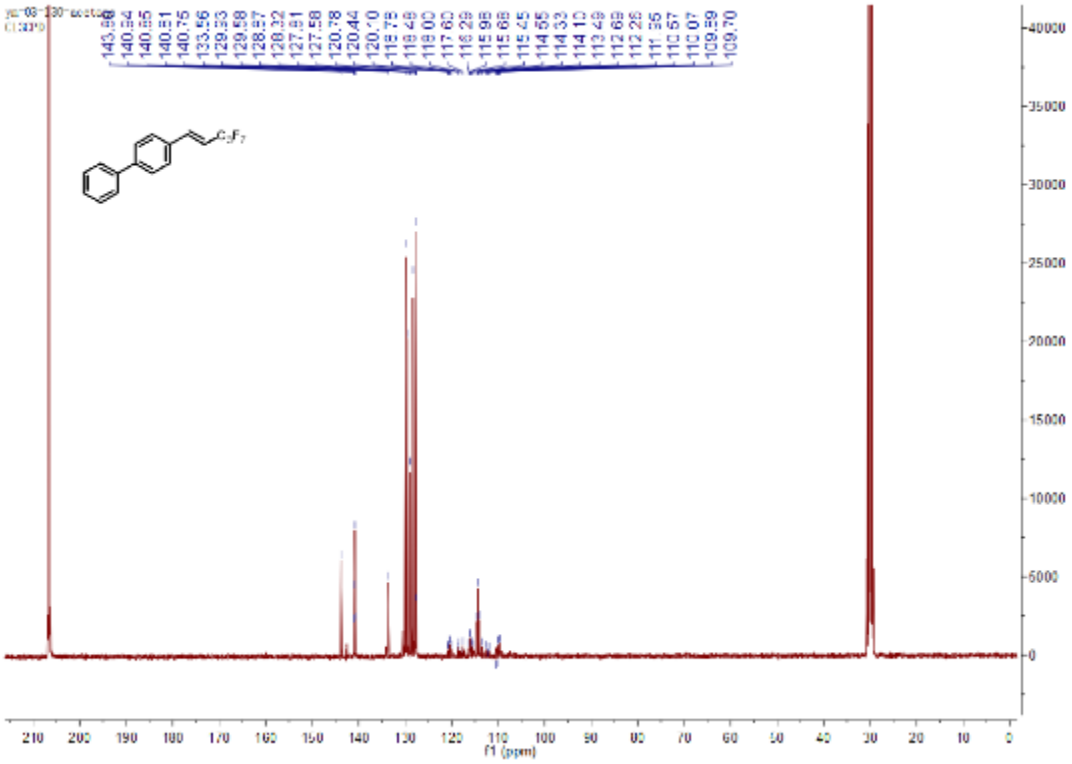
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3w**



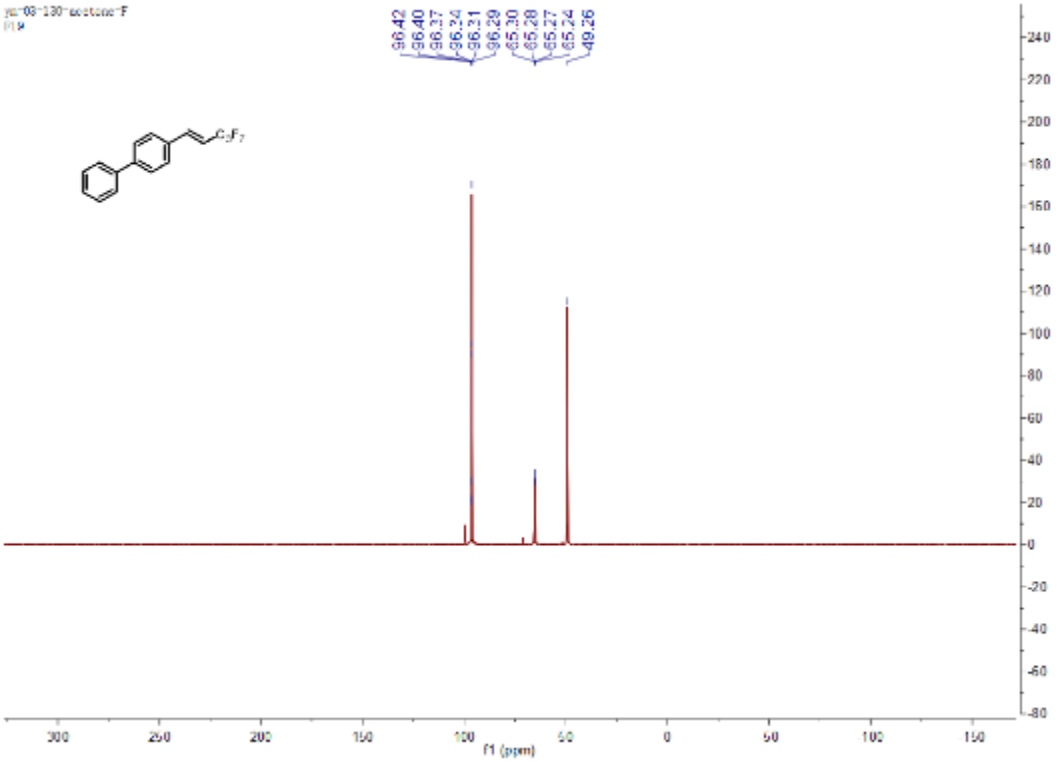
^{1}H NMR spectrum (400 MHz, Acetone-d_6) of compound **3x**



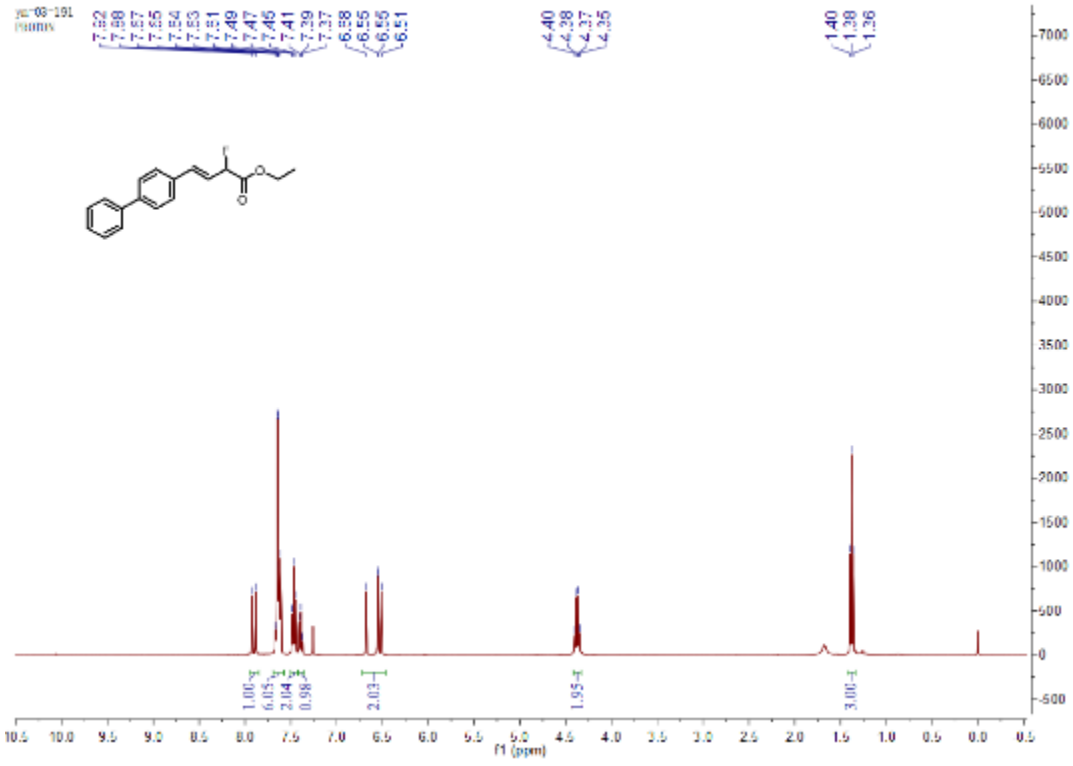
^{13}C NMR spectrum (100 MHz, Acetone-d_6) of compound **3x**



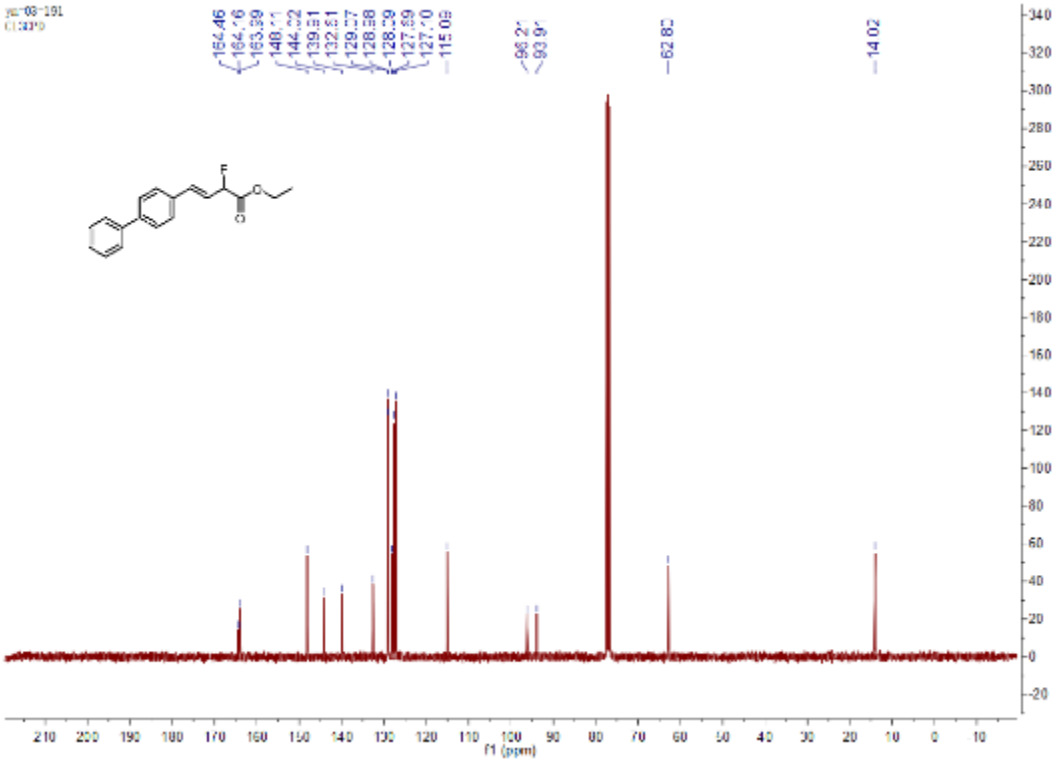
^{19}F NMR spectrum (376 MHz, Acetone-d_6) of compound **3x**



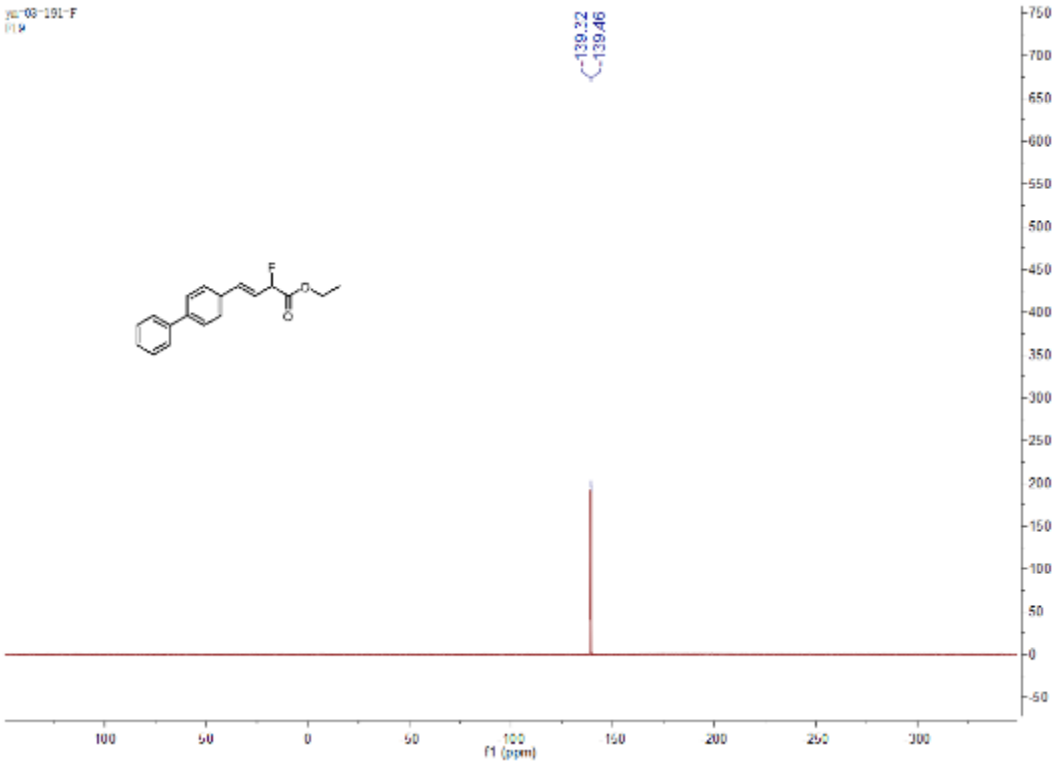
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3y**



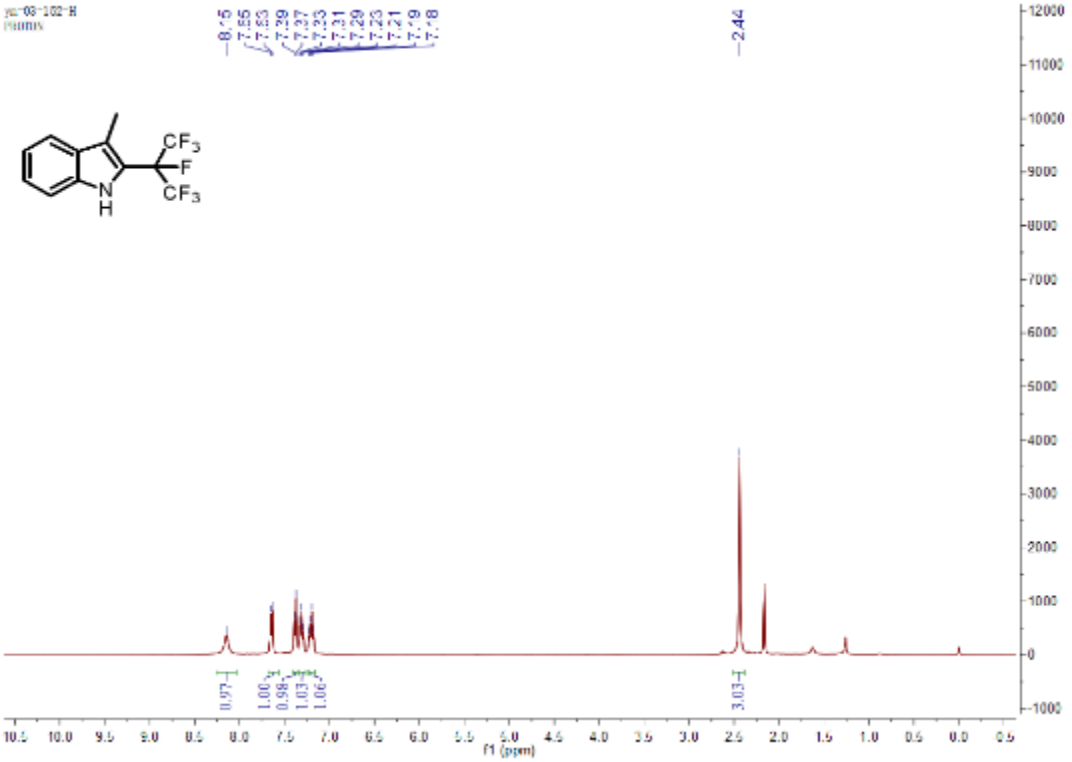
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **3y**



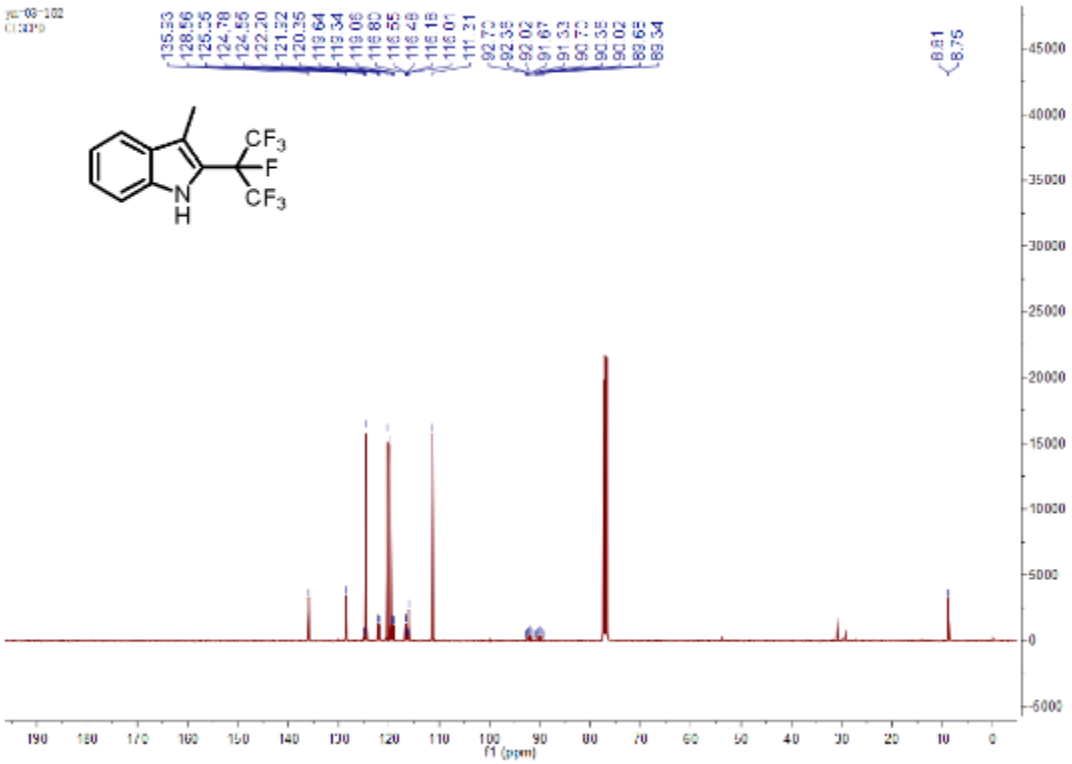
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3y**



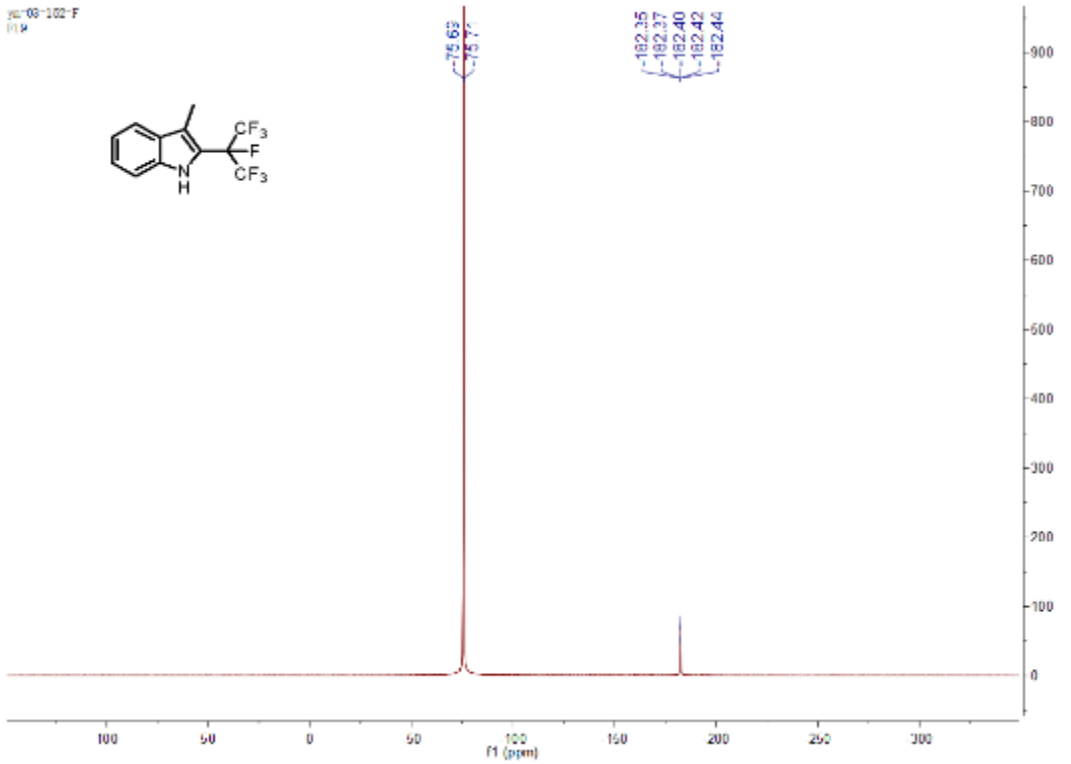
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5a**



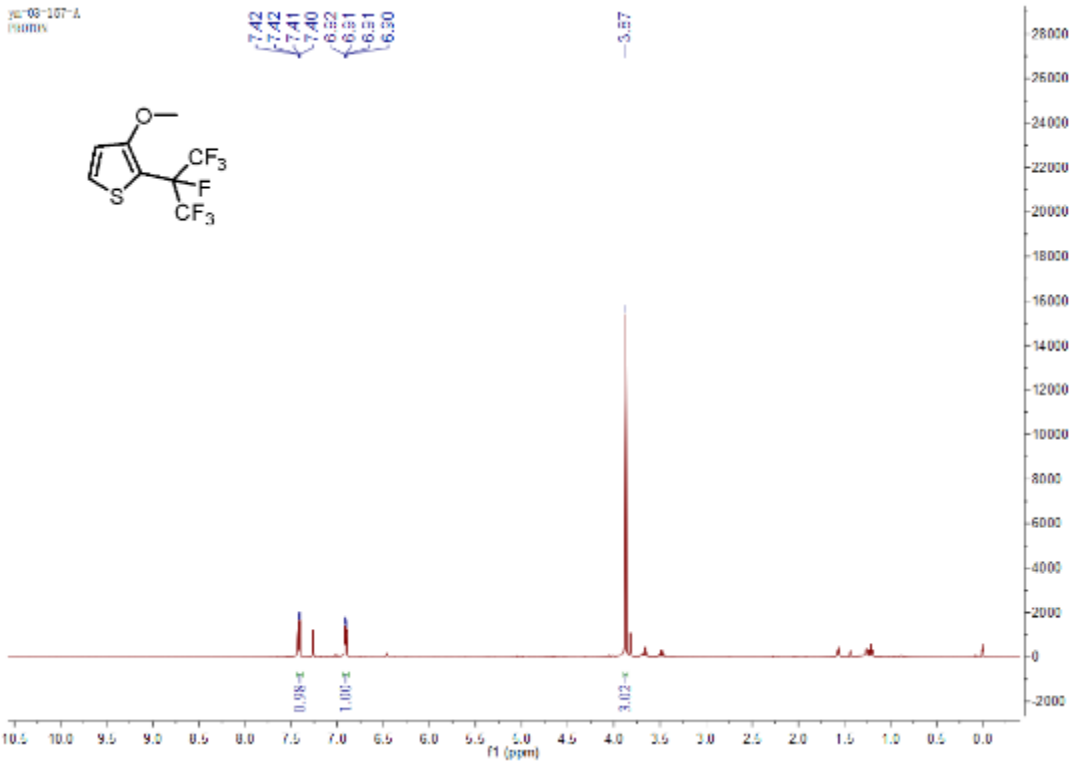
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5a**



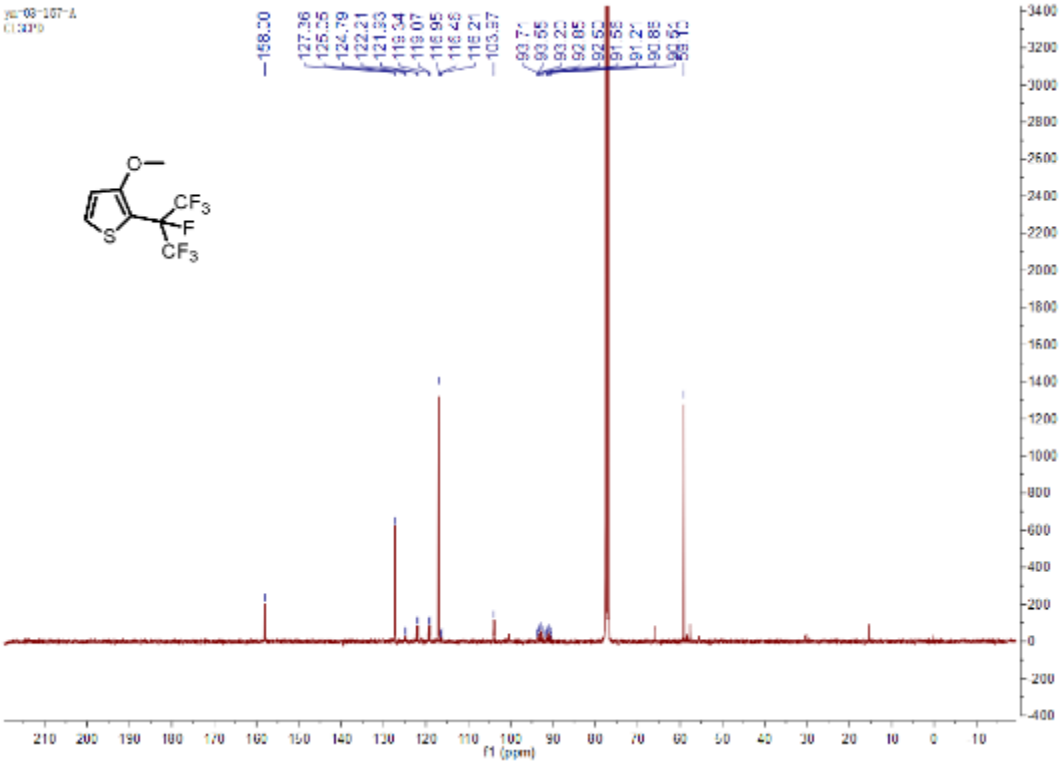
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5a**



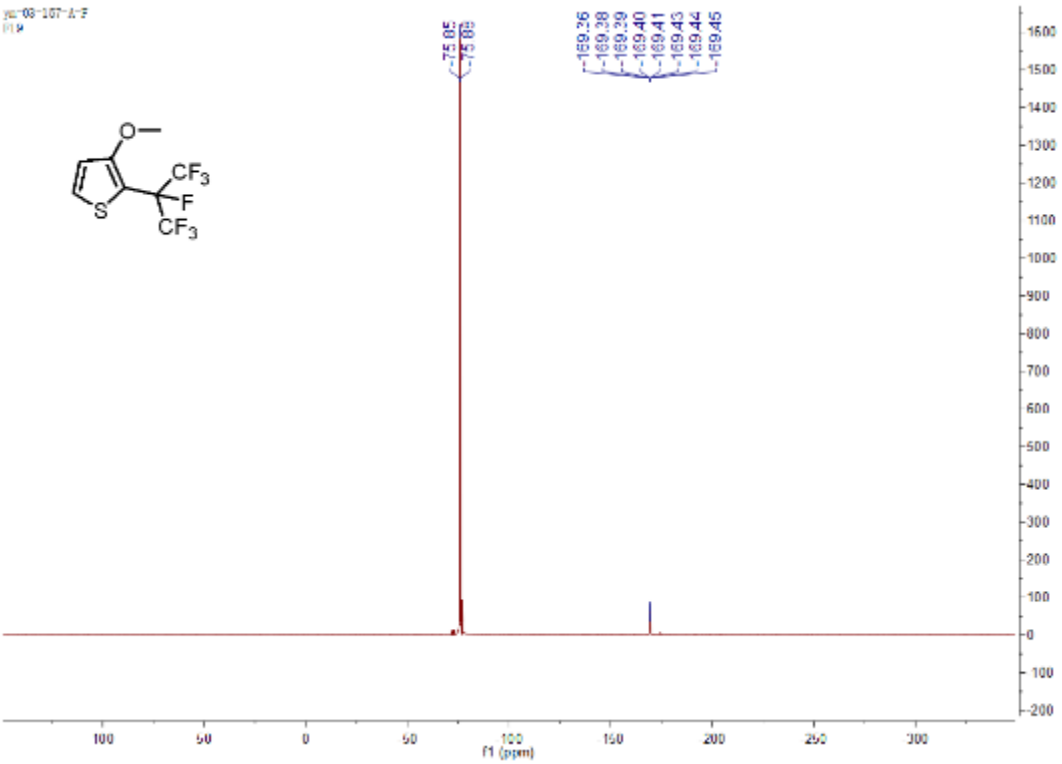
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5b**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5b**



^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5b**



^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **5c**