Supporting Information

Chemo-, Regio-, and Stereoselective Tetrafunctionalization of Fluoroalkynes Enables Divergent Synthesis of 5–7-Membered Azacycles

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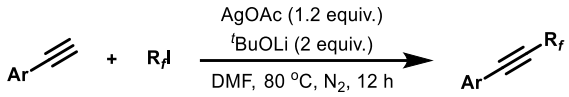
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N_2 or air atmosphere using undistilled solvent. Melting points were recorded on an electrothermal digital melting point apparatus. ^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Joel 400 MHz spectrometers. NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), *etc*. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. A suitable crystal was selected and recorded on a XtaLAB AFC12 (RINC): Kappa single diffractometer. Column chromatography was generally performed on neutral alumina (200–300 mesh) or silica gel (300–400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light or $KMnO_4$ to visualize the course of the reactions.

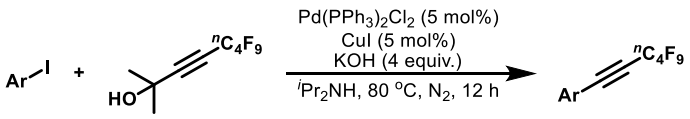
General procedures for the synthesis of polyfluoroalkynes

a) General procedure A (GPA)[1]



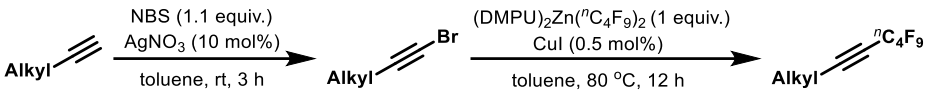
Terminal aryl alkyne (5 mmol, 1 equiv.) and perfluoroalkyl iodide (15 mmol, 3 equiv.) were added dropwise to a solution of AgOAc (1.0 g, 6 mmol, 1.2 equiv.) and ^{t}BuOLi (0.8 g, 10 mmol, 2 equiv.) in DMF (20 mL) under N_2 at 80 °C (oil bath). The mixture was stirred at 80 °C (oil bath) for 12 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (50 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the pure perfluoroalkylated aryl alkynes [petroleum ether/ethyl acetate (100/1–4/1) as eluent, or petroleum ether as eluent].

b) General procedure B (GPB)[2]



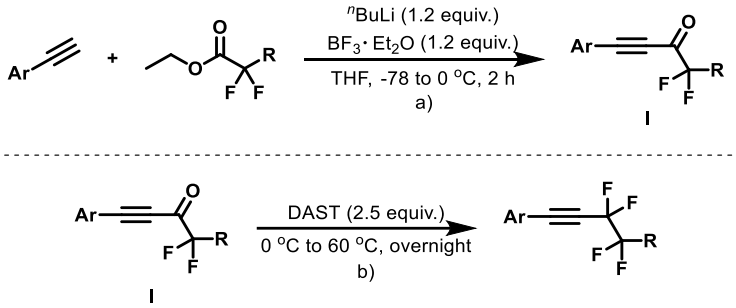
Perfluorobutylated propargyl alcohol (1.8 g, 6 mmol, 1.2 equiv.) was added dropwise to a solution of aryl iodide (5 mmol, 1 equiv.), $Pd(PPh_3)_2Cl_2$ (175.4 mg, 0.25 mmol, 0.05 equiv.), CuI (47.5 mg, 0.25 mmol, 0.05 equiv.), and KOH (1.1 g, 20 mmol, 4 equiv.) in $^{i}Pr_2NH$ (30 mL) under N_2 at 80 ºC (oil bath). The mixture was stirred at 80 ºC (oil bath) for 12 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (30 mL) and extracted with ethyl acetate (30 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the pure perfluorobutylated aryl alkynes [petroleum ether/ethyl acetate (8/1–4/1) as eluent].

c) General procedure C (GPC)[3]



$AgNO_3$ (84.9 mg, 0.5 mmol, 0.1 equiv.) and NBS (1.0 g, 5.5 mmol, 1.1 equiv.) was added to a solution of alkyl alkyne (5 mmol, 1 equiv.) in toluene (30 mL) at room temperature. The mixture was stirred at room temperature for 3 h, then CuI (4.8 mg, 0.025 mmol, 0.005 equiv.) and $(DMPU)_2Zn(^nC_4F_9)_2$ (2.7 g, 5 mmol, 1 equiv.) were added under N_2. The mixture was stirred at 80 ºC (oil bath) for 12 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (30 mL) and extracted with ethyl acetate (30 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford pure perfluorobutylated alkyl alkynes [petroleum ether/ethyl acetate (100/1–1/1) as eluent, or petroleum ether as eluent].

d) General procedure D (GPD)[4]



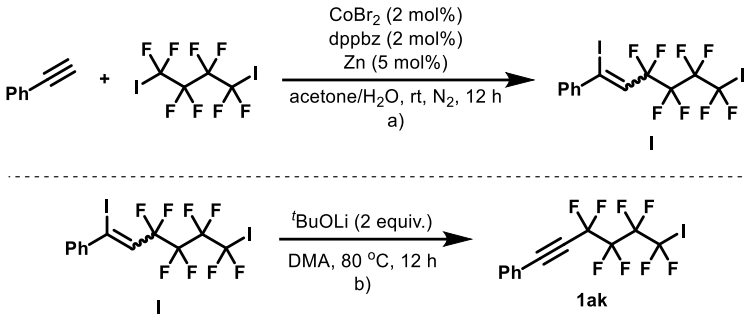
Step a):

^{n}BuLi (12 mmol, 4.8 mL, 2.5 M in hexane, 1.2 equiv.) was added dropwise to a solution of alkyne (12 mmol, 1.2 equiv.) in THF (20 mL) under N_2 at -78 ºC. After stirring at -78 ºC for 30 min, a solution of ester (10 mmol, 1.0 equiv.) and BF_3•Et_2O (1.7 g, 12 mmol, 1.2 equiv.) in THF (10 mL) was added, and the mixture was warmed to room temperature. After the consumption of ester, the mixture was quenched by saturated NH_4Cl solution (50 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude ketone **I**, which could be used directly in the next step without further purification.

Step b):

1 drop of ethanol was added to the ketone **I** obtained above, and then DAST (4.0 g, 25 mmol, 2.5 equiv.) was added in one portion at 0 ºC. After stirring at 0 ºC for 30 min, the mixture was warmed to 60 ºC and stirred overnight. The mixture was quenched by saturated NH_4Cl solution (30 mL) and extracted with DCM (30 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford pure α,β-tetrafluoroalkyne [petroleum ether/ethyl acetate (100/1–4/1) as eluent, or petroleum ether as eluent].

e) General procedure E (GPE)



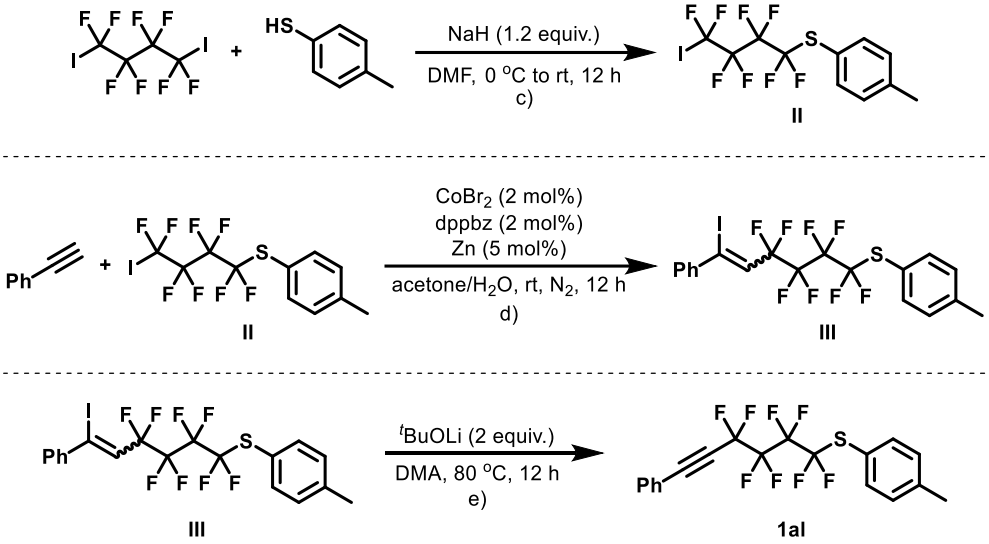
Step a):[5]

A solution of $CoBr_2$ (43.7 mg, 0.2 mmol, 0.02 equiv.), dppbz (89.3 mg, 0.2 mmol, 0.02 equiv.), and Zn (32.7 mg, 0.5 mmol, 0.05 equiv.) in acetone/H_2O (31 mL, v/v = 30/1) were stirred under N_2 at room temperature for 2 min. Phenylacetylene (1.0 g, 10 mmol, 1 equiv.) and perfluoroalkylated diiodide (9.1 g, 20 mmol, 2 equiv.) were added to the above solution under N_2. The mixture was stirred at room temperature for 12 h. The solvent was directly removed to leave a crude product, which was purified by flash silica gel column chromatography to afford the polyfluoroalkyl alkenyl iodide **I** (petroleum ether as eluent, 2.5 g, 45% yield).

Step b):[1]

A solution of polyfluoroalkyl alkenyl iodide (2.3 g, 4.2 mmol, 1 equiv., **I**) and ^{t}BuOLi (0.7 g, 8.4 mmol, 2 equiv.) in DMA (15 mL) was stirred at 80 °C (oil bath) for 12 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (50 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the pure polyfluoroalkyne **1ak** (petroleum ether as eluent, 1.3 g, 75% yield).

f) General procedure F (GPF)



step a):[6]

NaH (1.0 g, 60% in mineral oil, 24 mmol, 1.2 equiv.) was added to a solution of *p*-toluene thiol (2.5 g, 20 mmol, 1 equiv.) in DMF (80 mL) at 0 °C. After stirring at 0 °C for 15 min, perfluoroalkylated diiodide (13.6 g, 30 mmol, 1.5 equiv.) was added slowly. After stirring at 0 °C for another 30 min,

the mixture was warmed to room temperature and stirred for 12 h. The mixture was quenched by saturated NH_4Cl solution (50 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford pure polyfluoroalkyl iodide **II** (petroleum ether as eluent, 4.6 g, 69% yield).

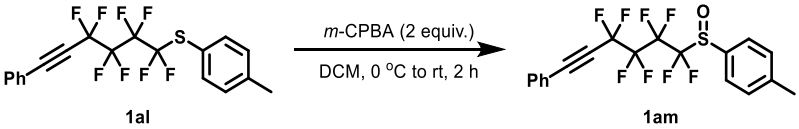
step b):[5]

A solution of $CoBr_2$ (37.2 mg, 0.17 mmol, 0.02 equiv.), dppbz (75.9 mg, 0.17 mmol, 0.02 equiv.), Zn (28.2 mg, 0.43 mmol, 0.05 equiv.) in acetone/H_2O (15.5 mL, v/v = 30/1) were stirred under N_2 at room temperature for 2 min. Phenylacetylene (0.9 g, 8.6 mmol, 1 equiv.) and polyfluoroalkyl iodide (4.7 g, 10.4 mmol, 1.2 equiv., **II**) were added to the solution under N_2. The mixture was stirred at room temperature for 12 h. The solvent was directly removed to leave a crude product, which was purified by flash silica gel column chromatography to afford the polyfluoroalkyl alkenyl iodide **III** (petroleum ether as eluent, 1.4 g, 30% yield).

step c):[1]

A solution of polyfluoroalkyl alkenyl iodide (1.4 g, 2.6 mmol, 1 equiv., **III**) and ^{t}BuOLi (0.4 g, 5.2 mmol, 2 equiv.) in DMA (10 mL) was stirred at 80 °C (oil bath) for 12 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (30 mL) and extracted with ethyl acetate (30 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the pure polyfluoroalkyne **1al** (petroleum ether as eluent, 0.88 g, 79% yield).

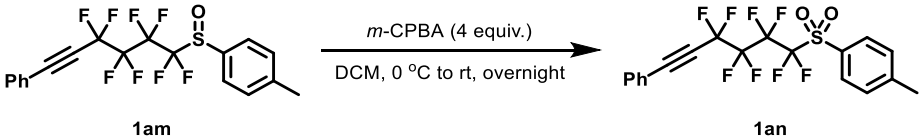
g) General procedure G (GPG)[7]



1al **1am**

m-CPBA (5 mL, 0.4 M in DCM, 2 mmol, 2 equiv.) was added dropwise to a solution of polyfluoroalkyne (0.42 g, 1 mmol, 1 equiv., **1al**) in DCM (5 mL) at 0 °C over 30 min. The mixture was warmed to room temperature and stirred for 2 h. The mixture was quenched by saturated $Na_2S_2O_3$ solution (15 mL) and saturated $NaHCO_3$ solution (15 mL) and extracted with DCM (20 x 3 mL). The organic extract was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford pure polyfluoroalkyne **1am** [petroleum ether/ethyl acetate (20/1) as eluent, 0.31 g, 69% yield].

h) General procedure H (GPH)[7]

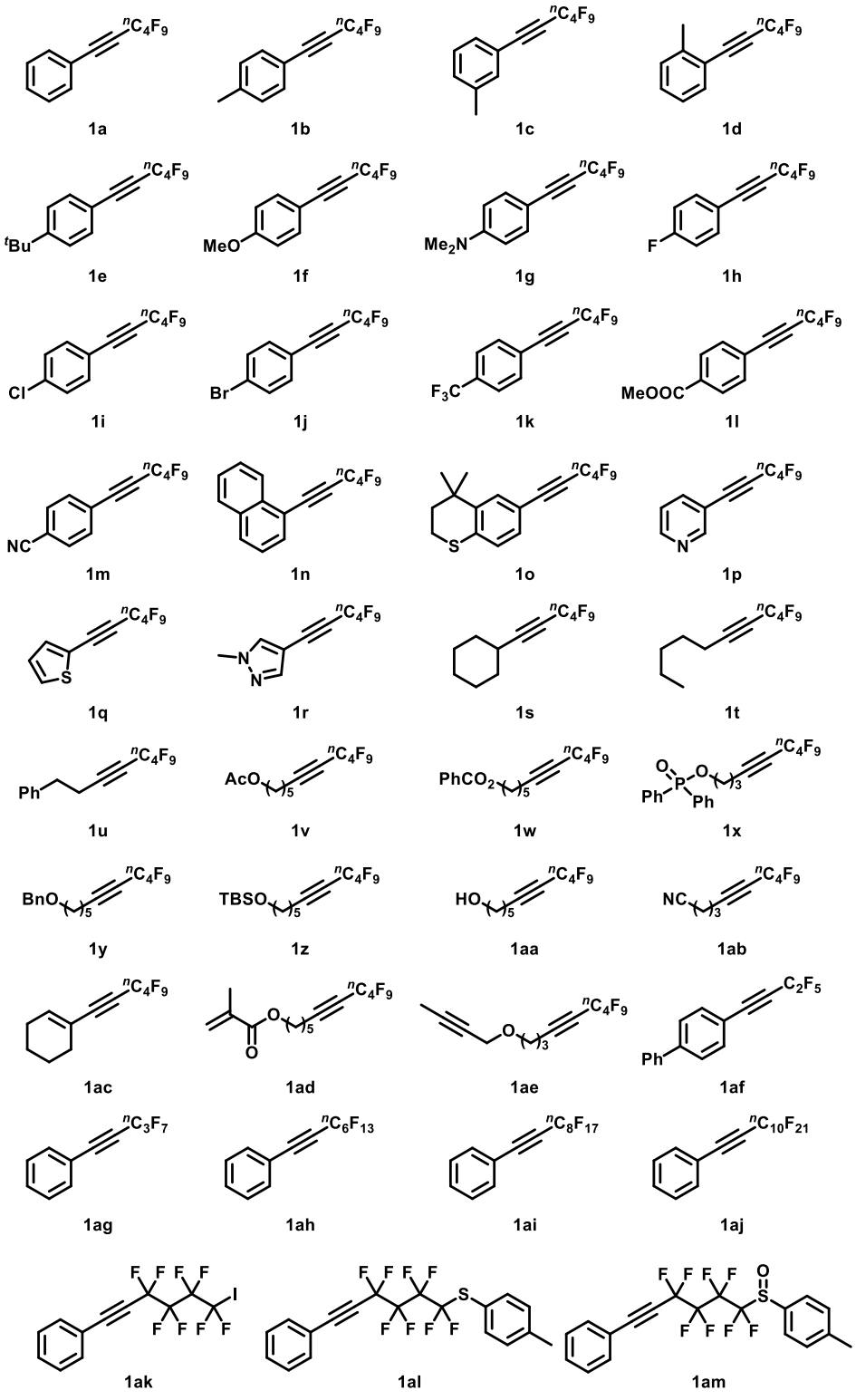


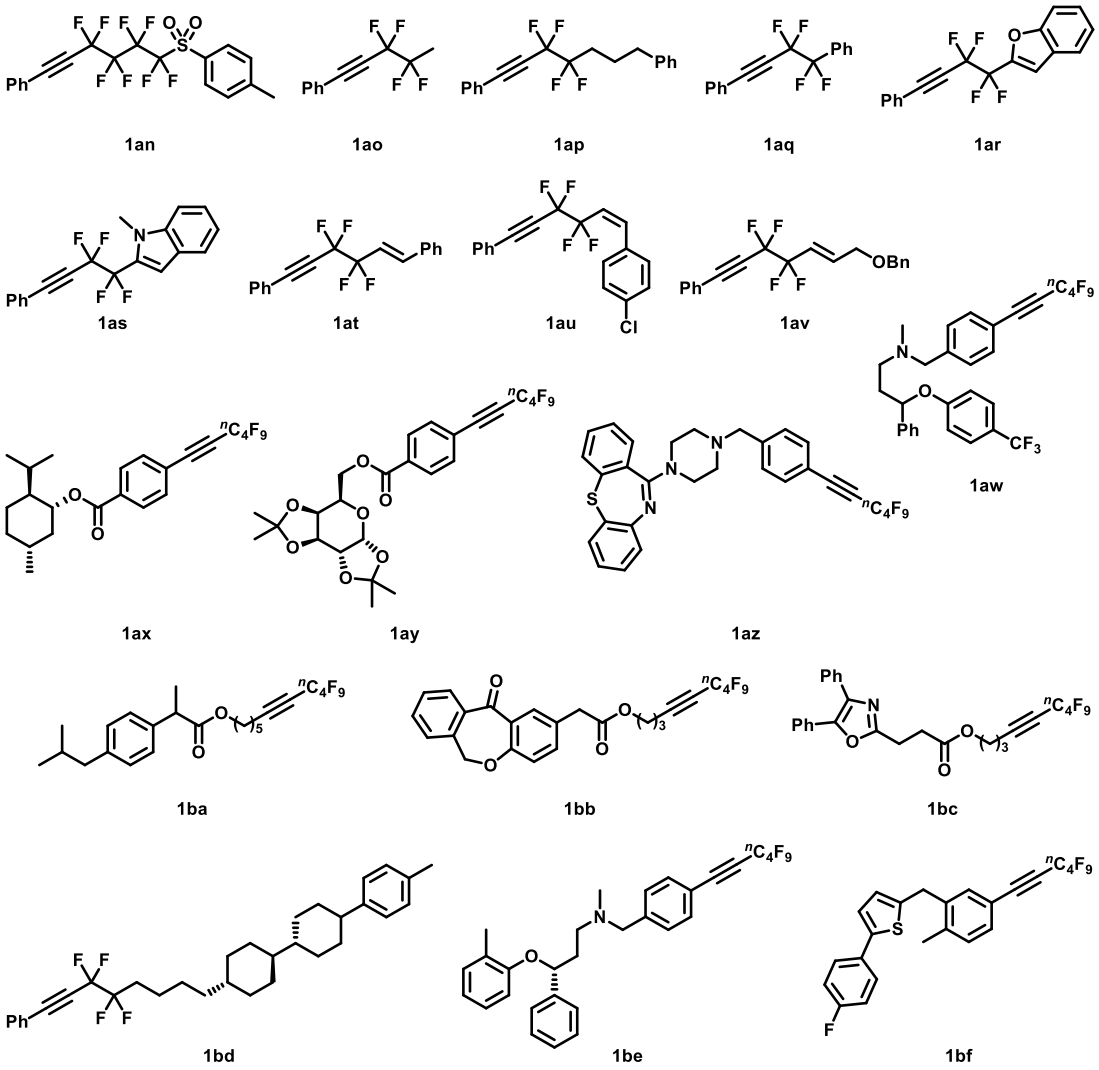
1am **1an**

m-CPBA (4 mL, 0.4 M in DCM, 1.6 mmol, 4 equiv.) was added dropwise to a solution of polyfluoroalkyne (0.18 g, 0.4 mmol, 1 equiv., **1am**) in DCM (2 mL) at 0 °C over 30 min. The mixture was warmed to room temperature and stirred for 12 h. The mixture was quenched by saturated $Na_2S_2O_3$ solution (15 mL) and saturated $NaHCO_3$ solution (15 mL) and extracted with DCM (20 x

3 mL). The organic extract was washed with water, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford pure polyfluoroalkyne **1an** [petroleum ether/ethyl acetate (40/1) as eluent, 0.13 g, 74% yield].

Polyfluoroalkynes used in the reaction:





a) Perfluoroalkylated aryl alkynes **1a-1f**,[8] **1h-1j**,[8] **1l**,[1] **1n**,[8] **1p**,[8] **1q**,[8] **1ag-1aj**,[8] **1ax**,[8] and **1ay**[8] are known compounds and synthesized according to GPA;

b) Perfluorobutyl alkyl alkyne **1t**[3] is known compound and synthesized according to GPC;

c) Perfluorobutyl aryl alkynes **1g**, **1k**, **1o**, and **1af** are new compounds and synthesized according to GPA;

d) Perfluorobutyl aryl alkynes **1m**, **1r**, **1aw**, **1az**, **1be**, and **1bf** are new compounds and synthesized according to GPB;

e) Perfluorobutyl alkyl alkynes **1s**, **1u-1ae**, and **1ba-1bc** are new compounds and synthesized according to GPC;

f) Polyfluoroalkyl aryl alkynes **1ao-1av**, and **1bd** are new compounds and synthesized according to GPD;

g) Polyfluoro alkyne **1ak** is new compound and synthesized according to GPE;

h) Polyfluoro alkyne **1al** is new compound and synthesized according to GPF;

i) Polyfluoro alkyne **1am** is new compound and synthesized according to GPG;

j) Polyfluoro alkyne **1an** is new compound and synthesized according to GPH.

Representative examples:

***N*,*N*-Dimethyl-4-(perfluorohex-1-yn-1-yl)aniline (1g): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.43–7.37 (m, 2H), 6.66–6.58 (m, 2H), 3.02 (s, 6H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.86 (t, *J* = 9.8 Hz, 3F), -95.55–-95.65 (m, 2F), -123.18–-123.28 (m, 2F), -125.30 (t, *J* = 9.5 Hz, 2F) ppm.

1-(Perfluorohex-1-yn-1-yl)-4-(trifluoromethyl)benzene (1k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.65 (m, 4H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -63.25 (s, 3F), -80.95 (t, *J* = 9.6 Hz, 3F), -98.14 (q, *J* = 8.0 Hz, 2F), -123.20–-123.37 (m, 2F), -125.25–-125.53 (m, 2F) ppm.

4-(Perfluorohex-1-yn-1-yl)benzonitrile (1m): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.50 (s, 3F), -98.75 (s, 2F), -123.63 (s, 2F), -125.78 (s, 2F) ppm.

4,4-Dimethyl-6-(perfluorohex-1-yn-1-yl)thiochromane (1o): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 1.8 Hz, 1H), 7.19 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 3.08–3.03 (m, 2H), 1.98–1.91 (m, 2H), 1.33 (s, 6H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.90 (s, 3F), -96.65 (s, 2F), -123.15 (s, 2F), -125.35 (s, 2F) ppm.

1-Methyl-4-(perfluorohex-1-yn-1-yl)-1*H*-pyrazole (1r): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 1H), 7.67 (s, 1H), 3.92 (s, 3H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.92 (t, *J* = 9.8 Hz, 3F), -96.75 (q, *J* = 8.2 Hz, 2F), -123.15–-123.30 (m, 2F), -125.25–-125.58 (m, 2F) ppm.

(Perfluorohex-1-yn-1-yl)cyclohexane (1s): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59–2.52 (m, 1H), 1.89–1.79 (m, 2H), 1.75–1.65 (m, 2H), 1.58–1.45 (m, 2H), 1.40–1.31 (m, 2H), 1.30–1.24 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.00 (s, 3F), -96.34 (s, 2F), -123.55 (s, 2F), -125.31 (s, 3F) ppm.

(5,5,6,6,7,7,8,8,8-Nonafluorooct-3-yn-1-yl)benzene (1u): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.28 (m, 2H), 7.27–7.24 (m, 1H), 7.22–7.18 (m, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.67–2.61 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.96 (t, *J* = 9.7 Hz, 3F), -96.64 (d, *J* = 13.6 Hz, 2F), -123.29–-123.39 (m, 2F), -125.41 (t, *J* = 11.6 Hz, 2F) ppm.

8,8,9,9,10,10,11,11,11-Nonafluoroundec-6-yn-1-yl acetate (1v): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.06 (td, *J* = 6.6, 2.0 Hz, 2H), 2.43–2.32 (m, 2H), 2.04 (dd, *J* = 2.9, 0.8 Hz, 3H), 1.70–1.57 (m, 4H), 1.55–1.41 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.00 (d, *J* = 9.4 Hz, 3F), -96.55 (s, 2F), -123.45 (d, *J* = 11.9 Hz, 2F), -125.44 (d, *J* = 11.1 Hz, 2F) ppm.

8,8,9,9,10,10,11,11,11-Nonafluoroundec-6-yn-1-yl benzoate (1w): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–8.00 (m, 2H), 7.60–7.52 (m, 1H), 7.49–7.39 (m, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.46–2.33 (m, 2H), 1.80 (dt, *J* = 8.0, 6.6 Hz, 2H), 1.72–1.65 (m, 2H), 1.63–1.55 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.97 (s, 3F), -96.50 (s, 2F), -123.38 (s, 2F), -125.37 (s, 2F) ppm.

6,6,7,7,8,8,9,9,9-Nonafluorononon-4-yn-1-yl diphenylphosphinate (1x): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.74 (m, 4H), 7.56–7.50 (m, 2H), 7.49–7.42 (m, 4H), 4.13–4.07 (m, 2H), 2.59–

2.53 (m, 2H), 2.04–1.98 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.94 (t, *J* = 9.7 Hz, 3F), -96.55–-96.93 (m, 2F), -123.34 (dd, *J* = 14.4, 6.8 Hz, 2F), -125.42 (t, *J* = 11.9 Hz, 2F) ppm.

(((8,8,9,9,10,10,11,11,11-Nonafluoroundec-6-yn-1-yl)oxy)methyl)benzene (1y): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.32 (m, 4H), 7.32–7.26 (m, 1H), 4.51 (s, 2H), 3.48 (t, *J* = 6.3 Hz, 2H), 2.42–2.31 (m, 2H), 1.70–1.56 (m, 4H), 1.56–1.44 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.86–-81.04 (m, 3F), -96.41 (s, 2F), -123.40 (t, *J* = 10.0 Hz, 2F), -125.39 (t, *J* = 10.8 Hz, 2F) ppm.

***tert*-Butyldimethyl((8,8,9,9,10,10,11,11,11-nonafluoroundec-6-yn-1-yl)oxy)silane (1z): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 3.61 (td, *J* = 6.2, 1.9 Hz, 2H), 2.41–2.32 (m, 2H), 1.64–1.46 (m, 6H), 0.89 (s, 9H), 0.03 (s, 6H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.98 (t, *J* = 9.9 Hz, 3F), -96.19–-96.64 (m, 2F), -123.44 (d, *J* = 10.0 Hz, 2F), -125.41 (t, *J* = 11.5 Hz, 2F) ppm.

8,8,9,9,10,10,11,11,11-Nonafluoroundec-6-yn-1-ol (1aa): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (t, *J* = 6.4 Hz, 2H), 2.40–2.31 (m, 2H), 1.68–1.53 (m, 6H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.06 (t, *J* = 9.8 Hz, 3F), -96.29–-96.72 (m, 2F), -123.50 (t, *J* = 9.3 Hz, 2F), -125.27–-125.66 (m, 2F) ppm.

7,7,8,8,9,9,10,10,10-Nonafluorodec-5-ynenitrile (1ab): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62–2.55 (m, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 2.01–1.93 (m, 2H). ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.96 (t, *J* = 10.2 Hz, 3F), -97.27 (s, 2F), -123.38 (tt, *J* = 11.2, 4.2 Hz, 2F), -125.43 (t, *J* = 10.2 Hz, 2F) ppm.

1-(Perfluorohex-1-yn-1-yl)cyclohex-1-ene (1ac): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.48–6.41 (m, 1H), 2.15 (td, *J* = 4.3, 2.2 Hz, 2H), 1.69–1.56 (m, 2H), 1.32–1.18 (m, 2H), 0.90–0.78 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.96 (d, *J* = 10.3 Hz, 3F), -96.42 (t, *J* = 9.3 Hz, 2F), -123.45 (d, *J* = 16.1 Hz, 2F), -125.14–-126.30 (m, 2F) ppm.

8,8,9,9,10,10,11,11,11-Nonafluoroundec-6-yn-1-yl methacrylate (1ad): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.11–6.05 (m, 1H), 5.54–5.53 (m, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 2.42–2.32 (m, 2H), 1.92 (t, *J* = 1.3 Hz, 3H), 1.76–1.59 (m, 4H), 1.54–1.45 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.14 (t, *J* = 9.8 Hz, 3F), -96.28–-97.10 (m, 2F), -123.49–-124.07 (m, 2F), -125.55 (t, *J* = 11.1 Hz, 2F) ppm.

1-(But-2-yn-1-yloxy)-6,6,7,7,8,8,9,9,9-nonafluorononon-4-yne (1ae): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.07 (q, *J* = 2.3 Hz, 2H), 3.54 (t, *J* = 5.9 Hz, 2H), 2.52–2.41 (m, 2H), 1.90–1.77 (m, 5H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.10 (d, *J* = 10.5 Hz, 3F), -96.63 (s, 2F), -123.51 (s, 2F), -125.50 (t, *J* = 11.7 Hz, 2F) ppm.

4-(Perfluorobut-1-yn-1-yl)-1,1'-biphenyl (1af): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 1.0 Hz, 4H), 7.62–7.58 (m, 2H), 7.50–7.45 (m, 2H), 7.43–7.38 (m, 1H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -85.04 (s, 3F), -100.79–-100.95 (m, 2F) ppm.

(3,3,4,4,5,5,6,6-Octafluoro-6-iodohex-1-yn-1-yl)benzene (1ak): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.54 (m, 2H), 7.52–7.46 (m, 1H), 7.40 (dd, *J* = 8.2, 6.8 Hz, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -58.39 (t, *J* = 14.7 Hz, 2F), -97.11–-97. 20 (m, 2F), -112.14 (tt, *J* = 11.6, 5.9 Hz, 2F), -121.44 (tt, *J* = 12.8, 6.5 Hz, 2F) ppm.

(1,1,2,2,3,3,4,4-Octafluoro-6-phenylhex-5-yn-1-yl)(*p*-tolyl)sulfane (1al): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.2, 1.8 Hz, 4H), 7.50–7.45 (m, 1H), 7.42–7.36 (m, 2H), 7.24–7.20 (m, 2H), 2.39 (s, 3H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -86.92 (t, *J* = 13.3 Hz, 2F), -97.17–-97.27 (m, 2F), -118.11–-118.37 (m, 2F), -121.79 (dd, *J* = 13.4, 6.8 Hz, 2F) ppm.

1-Methyl-4-((1,1,2,2,3,3,4,4-octafluoro-6-phenylhex-5-yn-1-yl)sulfinyl)benzene (1am): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.67 (m, 2H), 7.58–7.53 (m, 2H), 7.51–7.45 (m, 1H), 7.43–7.36 (m, 4H), 2.47 (s, 3H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -97.00–-97.09 (m, 2F), -110.61–-111.91 (m, 1F), -118.19–-120.51 (m, 2F), -121.35–-123.47 (m, 3F). ppm. **^{13}C NMR (101 MHz, $CDCl_3$):** δ = 144.7, 132.5 (t, *J* = 2.7 Hz), 131.9, 131.0, 130.2, 128.6, 126.9, 118.5, 92.2 (t, *J* = 6.3 Hz), 74.8 (t, *J* = 36.2 Hz), 21.7 ppm.

1-Methyl-4-((1,1,2,2,3,3,4,4-octafluoro-6-phenylhex-5-yn-1-yl)sulfonyl)benzene (1an): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.89 (m, 2H), 7.57–7.53 (m, 2H), 7.46 (t, *J* = 8.1 Hz, 3H), 7.39 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.51 (s, 3H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -96.75–-97.21 (m, 2F), -111.35 (t, *J* = 14.6 Hz, 2F), -119.03 (dq, *J* = 11.8, 6.3 Hz, 2F), -122.29 (tt, *J* = 12.8, 6.6 Hz, 2F) ppm.

(3,3,4,4-Tetrafluoropent-1-yn-1-yl)benzene (1ao): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 2H), 7.49–7.43 (m, 1H), 7.42–7.35 (m, 2H), 1.83 (tt, *J* = 18.4, 1.5 Hz, 3H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -100.05 (s, 2F), -107.49 (q, *J* = 20.1 Hz, 2F) ppm.

(3,3,4,4-Tetrafluorohept-1-yne-1,7-diyl)dibenzene (1ap): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 2H), 7.49–7.43 (m, 1H), 7.38 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.34–7.28 (m, 2H), 7.25–7.19 (m, 3H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.19–2.10 (m, 2H), 2.04–1.93 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -99.62–-99.83 (m, 2F), -115.23 (tt, *J* = 18.3, 4.9 Hz, 2F) ppm.

(Perfluorobut-1-yne-1,4-diyl)dibenzene (1aq): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.64 (m, 2H), 7.59–7.43 (m, 6H), 7.38 (dd, *J* = 8.1, 6.6 Hz, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -98.94 (s, 2F), -111.69 (s, 2F) ppm.

2-(1,1,2,2-Tetrafluoro-4-phenylbut-3-yn-1-yl)3benzofuran (1ar): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.59 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.57–7.52 (m, 2H), 7.49–7.42 (m, 2H), 7.42–7.36 (m, 2H), 7.34–7.30 (m, 1H), 7.24 (q, *J* = 1.1 Hz, 1H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -98.37 (t, *J* = 8.2 Hz, 2F), -111.82 (t, *J* = 8.2 Hz, 2F) ppm.

1-Methyl-2-(1,1,2,2-tetrafluoro-4-phenylbut-3-yn-1-yl)-1*H*-indole (1as): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.9 Hz, 1H), 7.57–7.52 (m, 2H), 7.42–7.33 (m, 5H), 7.21–7.17 (m, 1H),

7.03 (s, 1H), 3.91 (s, 3H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -96.94 (t, J = 9.2 Hz, 2F), -104.83 (t, J = 8.9 Hz, 2F) ppm.

(*E*)-(3,3,4,4-Tetrafluorohex-1-en-5-yne-1,6-diyl)dibenzene (1at): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.53 (m, 2H), 7.49 (dq, J = 8.0, 2.3 Hz, 2H), 7.47–7.43 (m, 1H), 7.43–7.35 (m, 5H), 7.19 (dt, J = 16.2, 2.3 Hz, 1H), 6.36–6.25 (m, 1H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -98.99 (s, 2F), -111.88 (s, 2F) ppm.

(*Z*)-1-Chloro-4-(3,3,4,4-tetrafluoro-6-phenylhex-1-en-5-yn-1-yl)benzene (1au): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 2H), 7.48–7.43 (m, 1H), 7.40–7.35 (m, 4H), 7.34–7.29 (m, 2H), 7.02 (dt, J = 12.8, 2.8 Hz, 1H), 5.95–5.79 (m, 1H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -99.44 (t, J = 7.5 Hz, 2F), -106.04 (dt, J = 15.8, 7.5 Hz, 2F) ppm.

(*E*)-(7-(Benzyloxy)-3,3,4,4-tetrafluorohept-5-en-1-yn-1-yl)benzene (1av): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (dt, J = 7.1, 1.5 Hz, 2H), 7.48–7.43 (m, 1H), 7.40–7.33 (m, 7H), 6.51–6.44 (m, 1H), 6.12–5.98 (m, 1H), 4.58 (s, 2H), 4.19–4.16 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -99.43 (t, J = 7.1 Hz, 2F), -112.64 (dp, J = 12.7, 4.9 Hz, 2F) ppm.

***N*-Methyl-*N*-(4-(perfluorohex-1-yn-1-yl)benzyl)-3-phenyl-3-(4-(trifluoromethyl)phenoxy)propan-1-amine (1aw): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.34 (d, J = 8.6 Hz, 2H), 7.26 (t, J = 6.4 Hz, 3H), 7.23–7.20 (m, 3H), 7.20–7.16 (m, 3H), 6.75 (d, J = 8.5 Hz, 2H), 5.24 (dd, J = 8.7, 4.2 Hz, 1H), 3.48 (d, J = 13.6 Hz, 1H), 3.35 (d, J = 13.6 Hz, 1H), 2.58–2.52 (m, 1H), 2.35–2.29 (m, 1H), 2.15 (s, 3H), 2.11–2.01 (m, 1H), 1.97–1.87 (m, 1H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -61.48 (s, 3F), -80.88 (t, J = 9.7 Hz, 3F), -97.13 (t, J = 8.6 Hz, 2F), -123.23–-123.35 (m, 2F), -125.28–-125.40 (m, 2F) ppm.

11-(4-(4-(Perfluorohex-1-yn-1-yl)benzyl)piperazin-1-yl)dibenzo[*b*,*f*][1,4]thiazepine (1az): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.46 (m, 3H), 7.38 (dt, J = 7.8, 1.6 Hz, 3H), 7.34–7.26 (m, 3H), 7.16 (ddd, J = 8.6, 7.3, 1.5 Hz, 1H), 7.05 (dd, J = 8.0, 1.5 Hz, 1H), 6.87 (td, J = 7.5, 1.5 Hz, 1H), 3.57 (d, J = 1.7 Hz, 4H), 2.74–2.35 (m, 4H), 1.63 (brs, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.84 (t, J = 9.5 Hz, 3F), -97.14 (t, J = 8.3 Hz, 2F), -123.28 (td, J = 10.6, 5.6 Hz, 2F), -125.32 (t, J = 10.7 Hz, 2F) ppm.

8,8,9,9,10,10,11,11,11-Nonafluoroundec-6-yn-1-yl 2-(4-isobutylphenyl)propanoate (1ba): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.16 (m, 2H), 7.13–7.05 (m, 2H), 4.14–3.99 (m, 2H), 3.68 (q, J = 7.1 Hz, 1H), 2.44 (d, J = 7.2 Hz, 2H), 2.34–2.23 (m, 2H), 1.83 (dq, J = 13.6, 6.8 Hz, 1H), 1.65–1.51 (m, 4H), 1.48 (d, J = 7.2 Hz, 3H), 1.40–1.31 (m, 2H), 0.89 (d, J = 6.6 Hz, 6H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.95 (s, 3F), -96.47 (s, 2F), -123.37 (s, 2F), -125.37 (s, 2F) ppm.

6,6,7,7,8,8,9,9,9-Nonafluorononon-4-yn-1-yl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl) acetate (1bb): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 2.4 Hz, 1H), 7.86 (dd, J = 7.7, 1.4 Hz, 1H), 7.52 (tq, J = 7.5, 1.6 Hz, 1H), 7.46–7.37 (m, 2H), 7.32 (dd, J = 7.5, 1.5 Hz, 1H), 7.01 (dd, J = 8.5, 1.7 Hz, 1H), 5.15 (d, J = 1.6 Hz, 2H), 4.16 (t, J = 6.1 Hz, 2H), 3.63 (s, 2H), 2.48–2.37 (m, 2H),

1.97–1.86 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -81.04 (d, J = 10.5 Hz, 3F), -96.80 (s, 2F), -123.44 (s, 2F), -125.48 (t, J = 11.3 Hz, 2F) ppm.

6,6,7,7,8,8,9,9,9-Nonafluorononon-4-yn-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (1bc): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.61 (m, 2H), 7.60–7.55 (m, 2H), 7.38–7.27 (m, 6H), 4.21 (t, J = 6.1 Hz, 2H), 3.19 (t, J = 7.4 Hz, 2H), 2.93 (t, J = 7.4 Hz, 2H), 2.49–2.38 (m, 2H), 1.98–1.87 (m, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.98 (d, J = 10.0 Hz, 3F), -96.78 (s, 2F), -123.39 (t, J = 10.2 Hz, 2F), -125.43 (t, J = 11.0 Hz, 2F) ppm.

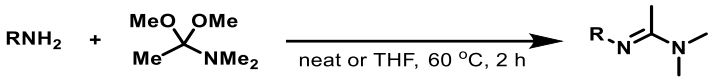
(1*S*,4*R*)-4-(5,5,6,6-Tetrafluoro-8-phenyloct-7-yn-1-yl)-4'-(*p*-tolyl)-1,1'-bi(cyclohexane) (1bd): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 2H), 7.49–7.43 (m, 1H), 7.41–7.35 (m, 2H), 7.10 (s, 4H), 2.41 (tt, J = 12.1, 3.4 Hz, 1H), 2.31 (s, 3H), 2.08 (tt, J = 18.1, 8.2 Hz, 2H), 1.90 (d, J = 12.9 Hz, 2H), 1.86–1.80 (m, 2H), 1.80–1.71 (m, 4H), 1.65–1.57 (m, 2H), 1.56 (s, 2H), 1.39 (q, J = 10.1 Hz, 4H), 1.25–1.10 (m, 6H), 1.08–0.95 (m, 3H), 0.89 (dd, J = 13.0, 10.2 Hz, 2H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -99.73 (d, J = 5.4 Hz, 2F), -115.15–-115.53 (m, 2F) ppm.

(*R*)-*N*-Methyl-*N*-(4-(perfluorohex-1-yn-1-yl)benzyl)-3-phenyl-3-(*o*-tolyloxy)propan-1-amine (1be): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.28 (m, 6H), 7.26–7.22 (m, 3H), 7.09–7.06 (m, 1H), 6.96 (td, J = 7.8, 1.8 Hz, 1H), 6.77 (td, J = 7.4, 1.1 Hz, 1H), 6.56 (dd, J = 8.2, 1.1 Hz, 1H), 5.27 (dd, J = 8.9, 3.9 Hz, 1H), 3.57 (d, J = 13.6 Hz, 1H), 3.41 (d, J = 13.6 Hz, 1H), 2.66 (dt, J = 12.4, 7.5 Hz, 1H), 2.42–2.36 (m, 1H), 2.26 (s, 3H), 2.17–2.07 (m, 4H), 2.05–1.95 (m, 1H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.83 (t, J = 9.5 Hz, 3F), -97.00 (t, J = 8.8 Hz, 2F), -123.23-123.35 (m, 2F), -125.31 (t, J = 10.9 Hz, 2F) ppm.

2-(4-Fluorophenyl)-5-(2-methyl-5-(perfluorohex-1-yn-1-yl)benzyl)thiophene (1bf): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.48 (m, 2H), 7.47 (d, J = 1.7 Hz, 1H), 7.43 (dd, J = 7.8, 1.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.09–7.03 (m, 3H), 6.70 (dt, J = 3.6, 1.1 Hz, 1H), 4.14 (s, 2H), 2.40 (s, 3H) ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ = -80.94 (t, J = 9.7 Hz, 3F), -96.95–-97.04 (m, 2F), -114.72 (dd, J = 13.6, 6.8 Hz, 1F), -122.77–-123.78 (m, 2F), -124.96–-125.58 (m, 2F) ppm.

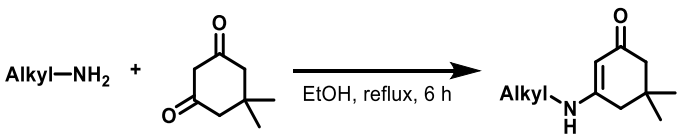
General procedures for the synthesis of difunctional reagents

a) General procedure I (GPI)[9]



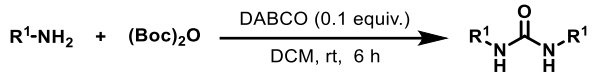
A mixture of amine (5 mmol, 1 equiv.) and 1,1-dimethoxy-*N*,*N*-dimethylethylamine (0.67 g, 6 mmol, 1.2 equiv.) was stirred at 60 °C for 2 h. The mixture was evaporated at 40 °C on a rotary evaporator. The contents were further heated at 55 °C on high vacuum for 8 h to yield the product. As for solid amines, THF (5 mL) was used as a solvent.

b) General Procedure J (GPJ)[10]



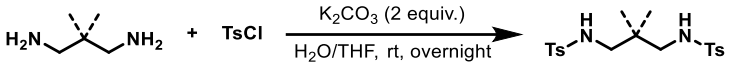
A solution of amine (20 mmol, 1.0 equiv.) and 5,5-dimethylcyclohexane-1,3-dione (2.8 g, 20 mmol, 1 equiv.) in EtOH (30 mL) was refluxed for 6 h. The solvent was directly removed to leave a crude product, which was recrystallized with EtOH, washed with petroleum ether/EtOH (100/1, 30 mL x 3), and dried under vacuum, affording pure product enaminone.

c) General procedure K (GPK)[11]



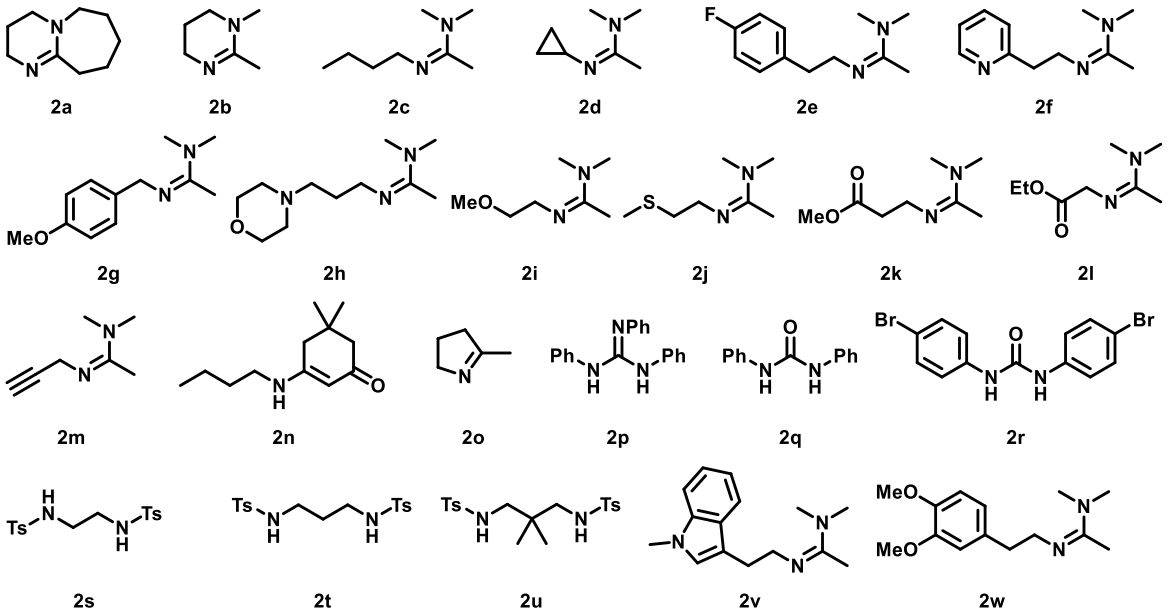
A solution of amine (2 mmol, 1.0 equiv.), DABCO (22.4 mg, 0.2 mmol, 0.1 equiv.), and $(Boc)_2O$ (218 mg, 1.0 mmol, 0.5 equiv.) in CH_2Cl_2 (10 mL) was stirred at room temperature for 6 h. After being cooled to 0 °C, *n*-hexane was then added to the mixture. The resulting solid was collected and further washed with cold water (20 mL x 3) and diethyl ether (15 mL x 3) to afford the product diarylurea.

d) General procedure L (GPL)[12]



TsCl (9.5 g, 50 mmol, 2 equiv.) in THF (40 mL) was added dropwise to a solution of 1,3-propanediamine (25 mmol, 1 equiv.) and K_2CO_3 (6.9 g, 50 mmol, 2 equiv.) in water (20 mL) at room temperature overnight. The solvent was directly removed to leave a crude product, which was poured into ice-cold water, filtered, washed with cold EtOH (30 mL x 3), and dried under vacuum, affording pure sulfamide as white solid in quantitative yield.

Difunctional reagents used in the reaction:



a) Amidines **2c**,[9] and **2i**[9] are known compounds and synthesized according to GPI;

b) Enaminone **2n**[10] is known compound and synthesized according to GPJ;

c) Diarylurea **2r**[13] is known compound and synthesized according to GPK;

d) Sulfamides **2t**,[14] and **2u**[15] are known compounds and synthesized according to GPL;

e) Amidines **2d**-**2h**, **2j**-**2m**, **2v**, and **2w** are new compounds and synthesized according to GPI;

f) Difunctional reagents **2a**, **2b**, **2o-q**, and **2s** are commercially available.

Representative examples:

***N*'-Cyclopropyl-*N*,*N*-dimethylacetimidamide (2d): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 2.83 (s, 6H), 2.57 (tt, *J* = 7.3, 3.9 Hz, 1H), 2.04 (s, 3H), 0.68–0.60 (m, 2H), 0.44–0.37 (m, 2H) ppm.

***N*,*N*-Dimethyl-*N*'-(2-(pyridin-2-yl)ethyl)acetimidamide (2f): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.50–8.47 (m, 1H), 7.56–7.51 (m, 1H), 7.21–7.16 (m, 1H), 7.09–7.02 (m, 1H), 3.54 (t, *J* = 7.6 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.82 (s, 6H), 1.77 (s, 3H) ppm.

***N*'-(4-Methoxybenzyl)-*N*,*N*-dimethylacetimidamide (2g): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.25–7.21 (m, 2H), 6.86–6.81 (m, 2H), 4.42 (s, 2H), 3.77 (s, 3H), 2.94 (s, 6H), 1.90 (s, 3H) ppm.

***N*,*N*-Dimethyl-*N*'-(3-morpholinopropyl)acetimidamide (2h): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 3.64 (t, *J* = 4.7 Hz, 4H), 3.14 (t, *J* = 7.1 Hz, 2H), 2.79 (d, *J* = 0.8 Hz, 6H), 2.41–2.31 (m, 6H), 1.81 (d, *J* = 0.7 Hz, 3H), 1.68–1.59 (m, 2H) ppm.

***N*,*N*-Dimethyl-*N*'-(2-(methylthio)ethyl)acetimidamide (2j): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 3.43–3.35 (m, 2H), 2.86 (s, 6H), 2.68–2.58 (m, 2H), 2.14 (s, 3H), 1.87 (s, 3H) ppm.

Methyl 3-((1-(dimethylamino)ethylidene)amino)propanoate (2k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3H), 3.46 (t, *J* = 7.3 Hz, 2H), 2.85 (s, 6H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.89 (s, 3H) ppm.

Ethyl 2-((1-(dimethylamino)ethylidene)amino)acetate (2l): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 2.89 (s, 6H), 1.81 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm.

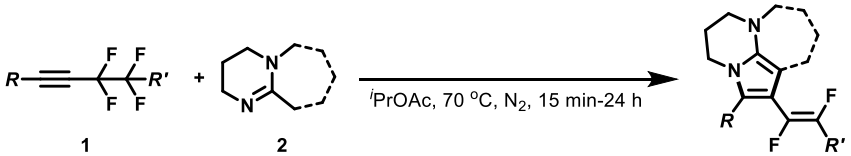
***N*,*N*-Dimethyl-*N*'-(prop-2-yn-1-yl)acetimidamide (2m): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 3.96 (d, *J* = 2.6 Hz, 2H), 2.87 (s, 6H), 2.13 (t, *J* = 2.6 Hz, 1H), 1.93 (s, 3H) ppm.

***N*,*N*-Dimethyl-*N*'-(2-(1-methyl-1H-indol-3-yl)ethyl)acetimidamide (2v): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.69–7.65 (m, 1H), 7.31–7.27 (m, 1H), 7.23–7.19 (m, 1H), 7.13–7.07 (m, 1H), 6.91 (s, 1H), 3.75 (s, 3H), 3.53 (t, *J* = 8.2 Hz, 2H), 2.99 (t, *J* = 8.4 Hz, 2H), 2.92 (s, 6H), 1.85 (s, 3H) ppm.

***N*'-(3,4-Dimethoxyphenethyl)-*N*,*N*-dimethylacetimidamide (2w): ^{1}H NMR (400 MHz, $CDCl_3$):** δ = 6.78–6.75 (m, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.40 (t, *J* = 8.7 Hz, 2H), 2.87 (s, 6H), 2.75 (t, *J* = 8.7 Hz, 2H), 1.75 (s, 3H) ppm.

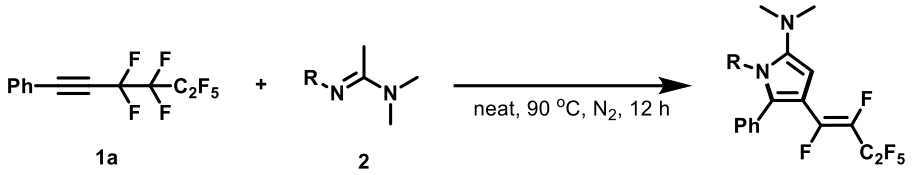
General procedures for the synthesis of 1,2-difluorovinyl azacycles

a) General procedure M (GPM)



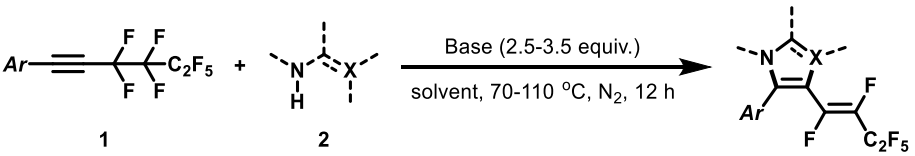
A solution of polyfluoroalkyne (0.3 mmol, 1 equiv., **1**) and difunctional reagent (1.05 mmol, 3.5 equiv., **2**) in ^{i}PrOAc (2 mL) was stirred under N_2 at 70 °C for 15 min–24 h. After being cooled to room temperature, the mixture was quenched by water or saturated NH_4Cl solution (30 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product [petroleum ether/ethyl acetate (20/1–1/1) as eluent].

b) General procedure N (GPN)



A mixture of (perfluorohex-1-yn-1-yl)benzene (96.0 mg, 0.3 mmol, 1 equiv., **1a**) and difunctional reagent (1.05 mmol, 3.5 equiv., **2**) was stirred under N_2 at 90 °C for 12 h. After being cooled to room temperature, the mixture was quenched by water or saturated NH_4Cl solution (30 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product [petroleum ether/ethyl acetate (100/1–1/1) as eluent].

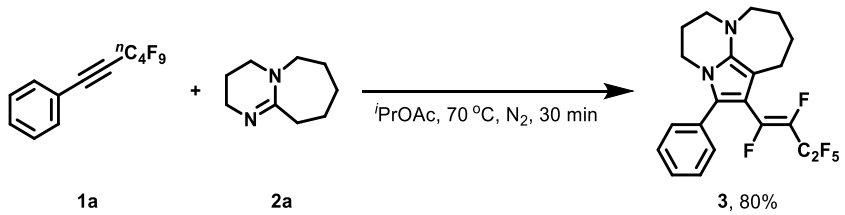
c) General procedure O (GPO)



A solution of polyfluoroalkyne (0.3 mmol, 1 equiv., **1**), difunctional reagent (0.45–1.05 mmol, 1.5–3.5 equiv., **2**), and base (e.g., Cs_2CO_3, 1-methylimidazole, 0.75-1.05 mmol, 2.5-3.5 equiv.) in solvent (e.g., ^{i}PrOAc, DMF, DMSO, 2 mL) was stirred under N_2 at 70–110 °C for 12 h. After being cooled to room temperature, the mixture was quenched by water or saturated NH_4Cl solution (30 mL) and extracted with ethyl acetate (30 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product [petroleum ether/ethyl acetate (100/1–4/1) or DCM/MeOH (100/1) as eluent].

Scale-up synthesis of products

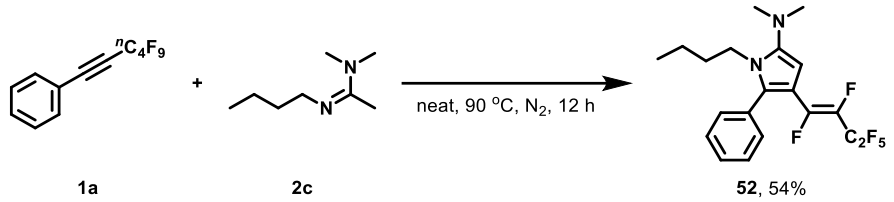
1) Scale-up synthesis of product 3



A solution of (perfluorohex-1-yn-1-yl)benzene (1.6 g, 5 mmol, 1 equiv., **1a**) and DBU (2.7 g, 17.5

mmol, 3.5 equiv., **2a**) in ^{i}PrOAc (30 mL) was stirred under N_2 at 70 °C for 30 min. After being cooled to room temperature, the mixture was quenched by water (50 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **3** [petroleum ether/ethyl acetate (10/1) as eluent, 1.72 g, 80% yield].

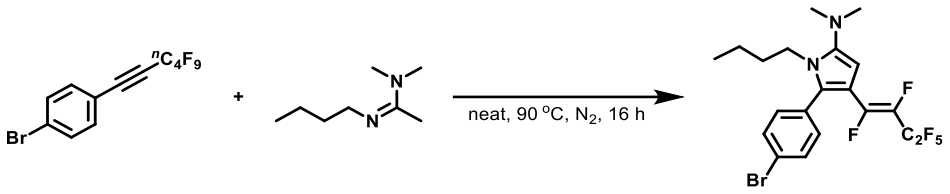
2) Scale-up synthesis of product 52



1a **2c** **52**, 54%

A mixture of (perfluorohex-1-yn-1-yl)benzene (1.6 g, 5 mmol, 1 equiv., **1a**) and *N*'-butyl-*N*,*N*-dimethylacetimidamide (2.5 g, 17.5 mmol, 3.5 equiv., **2c**) was stirred under N_2 at 90 °C for 12 h. After being cooled to room temperature, the mixture was quenched by water (50 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **52** [petroleum ether/ethyl acetate (100/1) as eluent, 1.14 g, 54% yield].

3) Scale-up synthesis of product 88

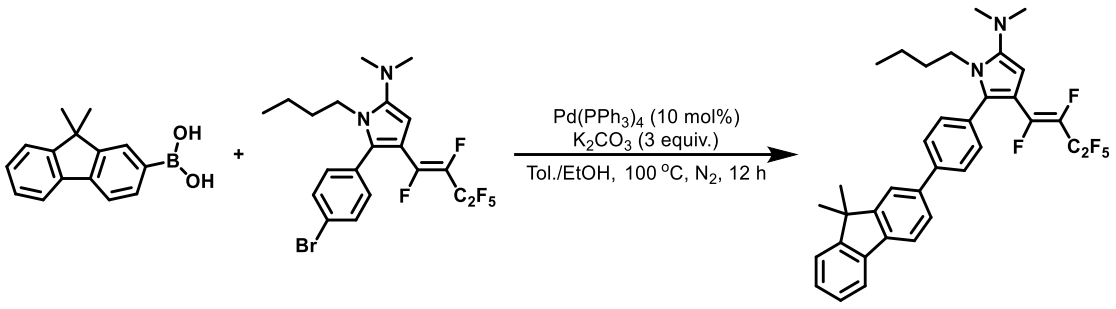


1j **2c** **88**, 73%

A mixture of 1-bromo-4-(perfluorohex-1-yn-1-yl)benzene (2.0 g, 5 mmol, 1 equiv., **1j**) and *N*'-butyl-*N*,*N*-dimethylacetimidamide (2.5 g, 17.5 mmol, 3.5 equiv., **2c**) was stirred under N_2 at 90 °C for 16 h. After being cooled to room temperature, the mixture was quenched by water (50 mL) and extracted with ethyl acetate (50 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **88** [petroleum ether/ethyl acetate (100/1) as eluent, 1.83 g, 73% yield].

Further transformations

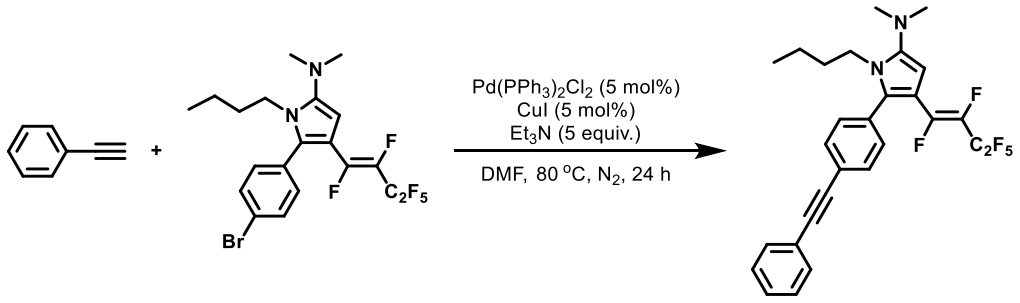
1) Suzuki coupling reaction of product 88 with (9,9-dimethyl-9*H*-fluoren-2-yl)boronic acid



88 **89**, 91%

A solution of (*E*)-5-(4-bromophenyl)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-1*H*-pyrrol-2-amine (150.4 mg, 0.3 mmol, 1 equiv., **88**), (9,9-dimethyl-9*H*-fluoren-2-yl)boronic acid (142.9 mg, 0.6 mmol, 2 equiv.), $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 0.1 equiv.), and K_2CO_3 (124.4 mg, 0.9 mmol, 3 equiv.) in toluene/EtOH (2 mL, v/v = 1/1) was stirred under N_2 at 100 °C for 12 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **89** [petroleum ether/ethyl acetate (100/1) as eluent, 166.9 mg, 91% yield].

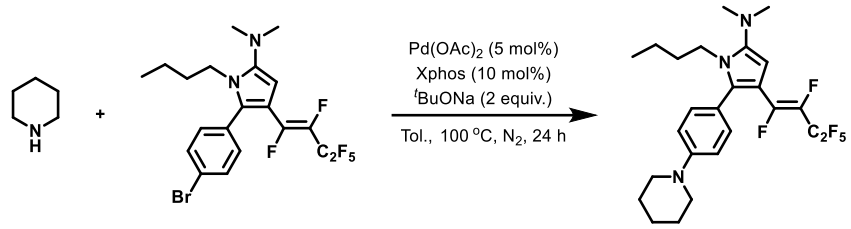
2) Sonogashira coupling reaction of product 88 with ethynylbenzene



88 **90**, 98%

A solution of (*E*)-5-(4-bromophenyl)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-1*H*-pyrrol-2-amine (150.4 mg, 0.3 mmol, 1 equiv., **88**), ethynylbenzene (91.9 mg, 0.9 mmol, 3 equiv.), $Pd(PPh_3)_2Cl_2$ (10.5 mg, 0.015 mmol, 0.05 equiv.), CuI (2.9 mg, 0.015 mmol, 0.05 equiv.), and Et_3N (151.8 mg, 1.5 mmol, 5 equiv.) in DMF (2 mL) was stirred under N_2 at 80 °C for 24 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **90** [petroleum ether/ethyl acetate (400/1) as eluent, 153.7 mg, 98% yield].

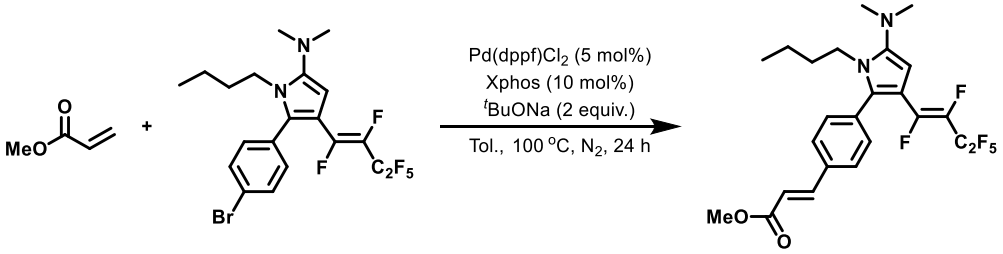
3) Buchwald-Hartwig coupling reaction of product 88 with piperidine



88 **91**, 99%

A solution of (*E*)-5-(4-bromophenyl)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-1*H*-pyrrol-2-amine (150.4 mg, 0.3 mmol, 1 equiv., **88**), piperidine (51.1 mg, 0.6 mmol, 2 equiv.), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.05 equiv.), Xphos (14.3 mg, 0.03 mmol, 0.1 equiv.), and ^{t}BuONa (57.7 mg, 0.6 mmol, 2 equiv.) in toluene (2 mL) was stirred under N_2 at 100 °C for 24 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **91** [petroleum ether/ethyl acetate (100/1) as eluent, 150.2 mg, 99% yield].

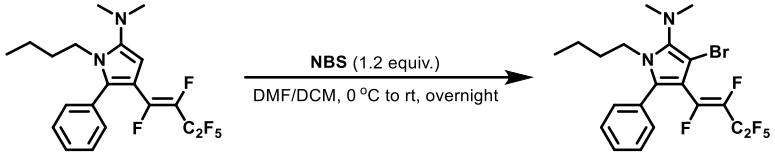
4) Heck reaction of product 88 with methyl acrylate



88 **92**, 84%

A solution of (*E*)-5-(4-bromophenyl)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-1*H*-pyrrol-2-amine (150.4 mg, 0.3 mmol, 1 equiv., **88**), methyl acrylate (77.5 mg, 0.9 mmol, 3 equiv.), $Pd(dppf)Cl_2$ (11.0 mg, 0.015 mmol, 0.05 equiv.), Xphos (14.3 mg, 0.03 mmol, 0.1 equiv.), and ^{t}BuONa (57.7 mg, 0.6 mmol, 2 equiv.) in toluene (2 mL) was stirred under N_2 at 100 °C for 24 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **92** [petroleum ether/ethyl acetate (40/1–10/1) as eluent, 126.9 mg, 84% yield].

5) Bromination of product 52 with NBS

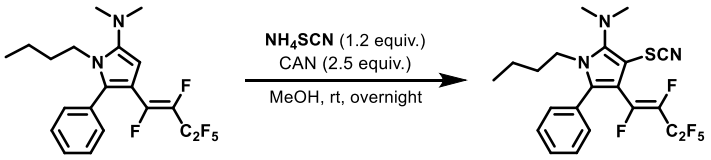


52 **93**, 90%

N-Bromosuccinimide (64.0 mg, 0.36 mmol, 1.2 equiv., NBS) was added to a solution of (*E*)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (126.7 mg, 0.3 mmol, 1 equiv., **52**) in DMF/DCM (2 mL, v/v = 1/1) at 0 °C. After stirring at 0 °C for 30 min, the mixture

was warmed to room temperature and stirred overnight. The mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **93** [petroleum ether/ethyl acetate (100/1) as eluent, 135.1 mg, 90% yield].

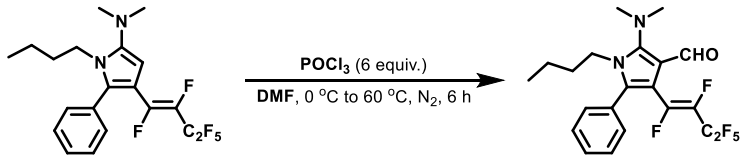
6) Thiocyanation of product 52 with NH_4SCN



52 **94**, 71%

$(NH_4)_2Ce(NO_3)_6$ (397.6 mg, 0.75 mmol, 2.5 equiv., CAN) in MeOH (5 mL) was added to a solution of (*E*)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (126.7 mg, 0.3 mmol, 1 equiv., **52**) and NH_4SCN (27.4 mg, 0.36 mmol, 1.2 equiv.) in MeOH (1 mL) at room temperature. After stirring at room temperature overnight, the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **94** [petroleum ether/ethyl acetate (100/1) as eluent, 102.3 mg, 71% yield].

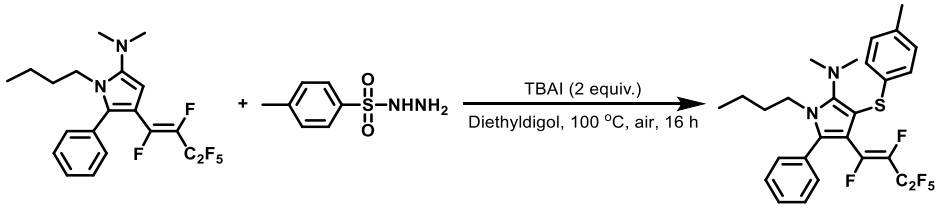
7) Vilsmeier-Haack formylation of product 52



52 **95**, 87%

$POCl_3$ (276.0 mg, 1.8 mmol, 6 equiv.) was added dropwise to DMF (3.5 mL) under N_2 at 0 °C. The mixture was stirred at room temperature for 15 min, and then a solution of (*E*)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (126.7 mg, 0.3 mmol, 1 equiv., **52**) in DMF (1.5 mL) was added. After stirring at 60 °C for 6 h, the mixture was quenched by saturated $NaHCO_3$ solution (30 mL) and extracted with ethyl acetate (30 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **95** [petroleum ether/ethyl acetate (50/1–30/1) as eluent, 117.6 mg, 87% yield].

8) Sulfenylation of product 52 with benzenesulfonohydrazide

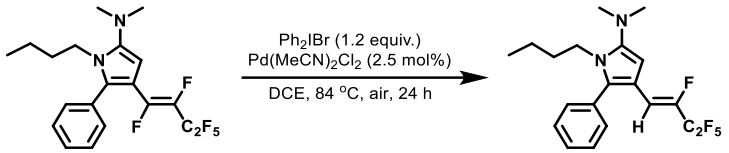


52 **96**, 80%

A solution of (*E*)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine

(126.7 mg, 0.3 mmol, 1 equiv., **52**), 4-methylbenzenesulfonohydrazide (167.6 mg, 0.9 mmol, 3 equiv.), and tetrabutylammonium iodide (221.6 mg, 0.6 mmol, 2 equiv., TBAI) in diethyldigol (0.5 mL) was stirred at 100 °C for 16 h. After being cooled to room temperature, the mixture was quenched by saturated NH_4Cl solution (20 mL) and extracted with DCM (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **96** [petroleum ether as eluent, 130.5 mg, 80% yield].

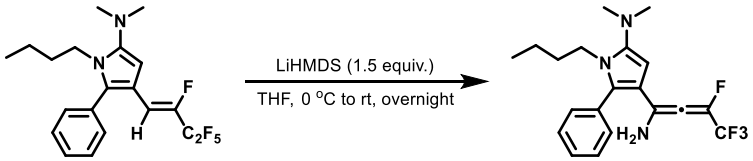
9) Hydrodefluorination of product 52



52 **97**, 72%

A solution of (*E*)-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (126.7 mg, 0.3 mmol, 1 equiv., **52**) and $Pd(MeCN)_2Cl_2$ (1.9 mg, 0.0075 mmol, 0.025 equiv.) in DCE (1.5 mL) was stirred at room temperature for 5 min. Then Ph_2IBr (130.0 mg, 0.36 mmol, 1.2 equiv.) was added. After stirring at 84 °C for 24 h, the mixture was quenched by saturated $NaHCO_3$ solution (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **97** [petroleum ether/ethyl acetate (200/1) as eluent, 87.8 mg, 72% yield].

10) Defluoroamination of product 97

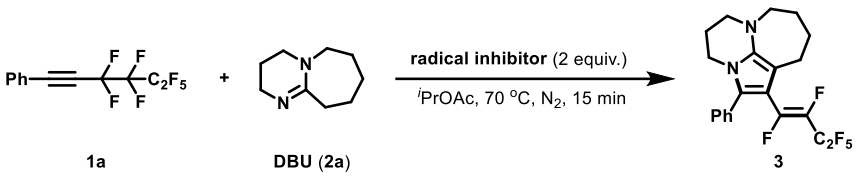


97 **98**, 86%

LiHMDS (0.35 mL, 1.3 M in THF, 0.45 mmol, 1.5 equiv.) was added dropwise to a solution of (*Z*)-1-butyl-4-(2,3,3,4,4,4-hexafluorobut-1-en-1-yl)-*N*,*N*-dimethyl-5-phenyl-1*H*-pyrrol-2-amine (121.3 mg, 0.3 mmol, 1 equiv., **97**) in THF (2 mL) at 0 °C. After stirring at room temperature overnight, the mixture was quenched by saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatography to afford the pure product **98** [petroleum ether/ethyl acetate (20/1–10/1) as eluent, 98.3 mg, 86% yield].

Mechanistic studies

1) Verification experiments of radical process



1a DBU (2a) 3

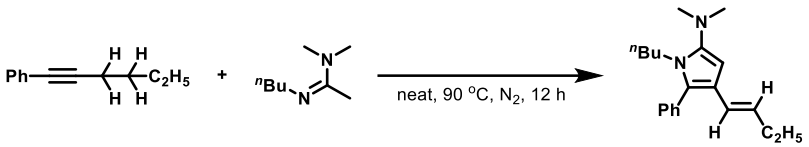
entry	radical inhibitor	NMR yield (%)
1	none	>99
2	TEMPO	82
3	BHT	80
4	1,1-diphenylethylene	90

A solution of (perfluorohex-1-yn-1-yl)benzene (96.0 mg, 0.3 mmol, 1 equiv., **1a**), DBU (159.9 mg, 1.05 mmol, 3.5 equiv., **2a**), and radical inhibitor (0 or 2 equiv.) in ^{i}PrOAc (2 mL) was stirred under N_2 at 70 °C for 15 min. After being cooled to room temperature, the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The yields of product **3** were determined by ^{19}F NMR analysis.

<u>The reactions were not inhibited by the addition of radical inhibitors. These results suggested that a radical pathway could be excluded at this stage.</u>

2) Verification experiments of the fluorine substitution effect

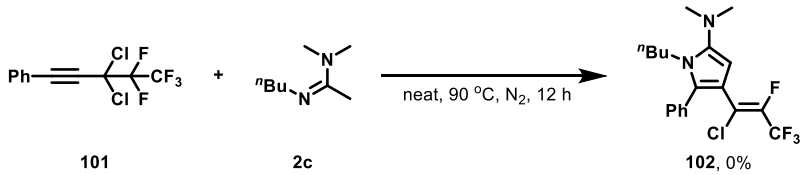
a) The use of nonfluorinated hex-1-yn-1-ylbenzene (**99**)



99 **2c** **100**, 0%

A mixture of hex-1-yn-1-ylbenzene (47.5 mg, 0.3 mmol, 1 equiv., **99**) and *N*'-butyl-*N*,*N*-dimethylacetimidamide (149.4 mg, 1.05 mmol, 3.5 equiv., **2c**) was stirred under N_2 at 90 °C for 12 h. After being cooled to room temperature, the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. No desired product **100** was obtained.

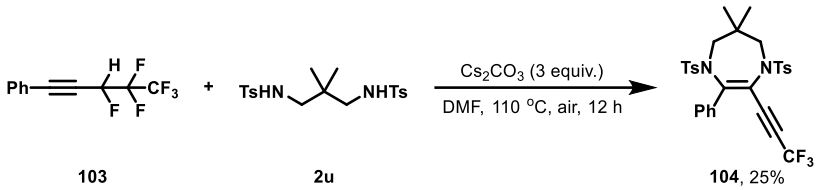
b) The use of *gem*-dichlorine congener **101**



101 **2c** **102**, 0%

A mixture of (3,3-dichloro-4,4,5,5,5-pentafluoropent-1-yn-1-yl)benzene (90.9 mg, 0.3 mmol, 1 equiv., **101**) and *N*'-butyl-*N*,*N*-dimethylacetimidamide (149.4 mg, 1.05 mmol, 3.5 equiv., **2c**) was stirred under N_2 at 90 °C for 12 h. After being cooled to room temperature, the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. No desired product **102** was obtained.

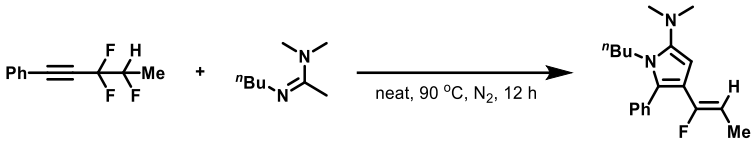
c) The use of (3,4,4,5,5,5-hexafluoropent-1-yn-1-yl)benzene (**103**)



103 **2u** **104**, 25%

A solution of (3,4,4,5,5,5-hexafluoropent-1-yn-1-yl)benzene (75.6 mg, 0.3 mmol, 1 equiv., **103**), *N*,*N*'-(2,2-dimethylpropane-1,3-diyl)bis(4-methylbenzenesulfonamide) (184.7 mg, 0.45 mmol, 1.5 equiv., **2u**), and Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.) in DMF (2 mL) was stirred at 110 °C for 12 h. After being cooled to room temperature, the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the pure product **104** [DCM/MeOH (100/1) as eluent, 45.2 mg, 25% yield].

d) The use of (3,3,4-trifluoropent-1-yn-1-yl)benzene (**105**)



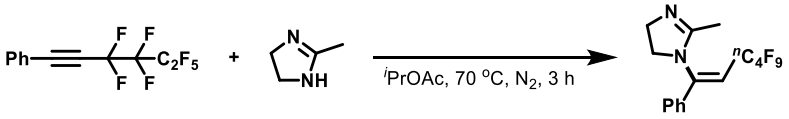
105 **2c** **106**, trace

A mixture of (3,3,4-trifluoropent-1-yn-1-yl)benzene (59.5 mg, 0.3 mmol, 1 equiv., **105**) and *N*'-butyl-*N*,*N*-dimethylacetimidamide (149.4 mg, 1.05 mmol, 3.5 equiv., **2c**) was stirred under N_2 at 90 °C for 12 h. After being cooled to room temperature, the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Only trace amount of product **106** was observed.

Together with the experiments described above, these observations demonstrate the indispensability of the perfluoroethane-1,2-diyl group on substrates.

3) Verification experiments for the involvement of allenyl intermediates

a) The reaction of fluoroalkyne (**1a**) with (**86**)



1a **86** **107**, 35%

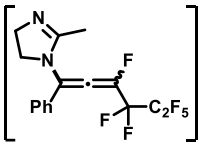
A solution of (perfluorohex-1-yn-1-yl)benzene (96.0 mg, 0.3 mmol, 1 equiv., **1a**) and 2-methyl-4,5-dihydro-1*H*-imidazole (88.3 mg, 1.05 mmol, 3.5 equiv., **86**) in ^{i}PrOAc (2 mL) was stirred under N_2 at 70 °C for 3 h. After being cooled to room temperature, the mixture was passed through a short pad of Celite followed by rinse with MeCN. A sample was taken from the filtrate and was directly analyzed by HRMS. Then the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the pure hydroaminated product **107** [DCM/MeOH (10/1) as eluent, 42.4 mg, 35% yield].

The intermediate **108** was detected by HRMS analysis of the mixture:

Elemental Composition Report Page 1

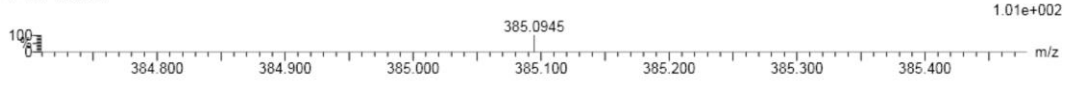
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
51 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-20 H: 0-24 N: 0-3 F: 0-9
CJW-INT1 39 (0.298)
1: TOF MS ES+



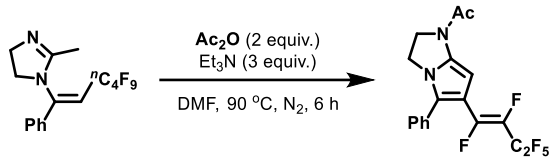
108

$C_{16}H_{13}F_8N_2^+$ $[M+H]^+$
Exact mass: 385.0946; found: 385.0945



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
385.0945	385.0951	-0.6	-1.6	7.5	17.5	n/a	n/a	C16 H13 N2 F8

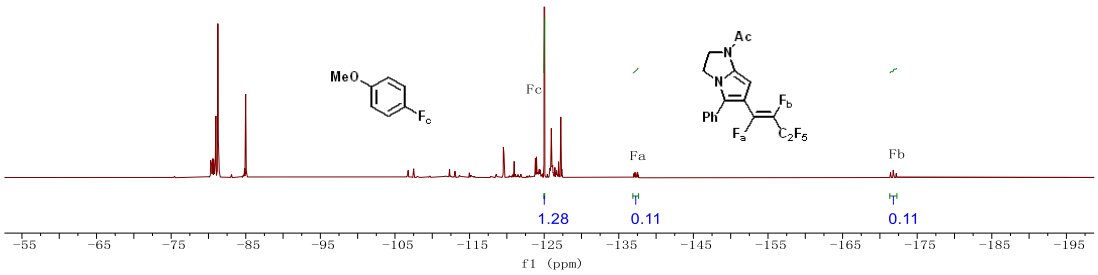
b) The further cyclization of hydroaminated product **107**



107 **109**, 11% NMR yield

A solution of 2-methyl-1-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)-4,5-dihydro-1*H*-imidazole (121.3 mg, 0.3 mmol, 1 equiv., **107**), Ac_2O (61.3 mg, 0.6 mmol, 2 equiv.), and Et_3N (91.1 mg, 0.9 mmol, 3 equiv.) in DMF (2 mL) was stirred under N_2 at 90 °C for 6 h. After being cooled to room temperature, the mixture was passed through a short pad of Celite followed by rinse with MeCN. A sample was taken from the filtrate and was directly analyzed by HRMS. Then the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was directly analyzed by NMR analysis. 11% NMR yield of (*E*)-1-(6-(perfluorobut-1-en-1-yl)-5-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl)ethan-1-one (**109**) was determined by ^{19}F NMR analysis of the residue using 1-fluoro-4-methoxybenzene (0.384 mmol) as an internal standard.

^{19}F NMR analysis of the residue:

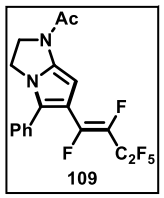


The desired product **109** was also detected by HRMS analysis of the mixture:

Elemental Composition Report Page 1

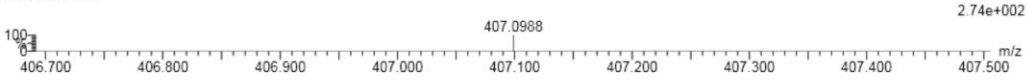
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
97 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-20 H: 0-24 N: 0-3 O: 0-2 F: 0-7
CJW-INT3 78 (0.576)
1: TOF MS ES+



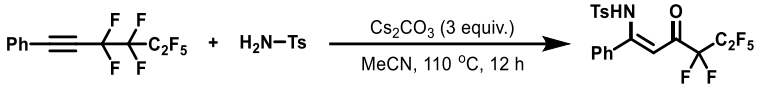
109

$C_{18}H_{14}F_7N_2O^+$ [M+H]$^+$
Exact mass: 407.0989; found: 407.0988



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
407.0988	407.0994	-0.6	-1.5	9.5	20.5	n/a	n/a	C18 H14 N2 O F7

c) The reaction of fluoroalkyne (**1a**) with $TsNH_2$



1a **110** **111**, 71% (*Z* only)

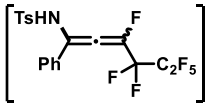
A solution of (perfluorohex-1-yn-1-yl)benzene (96.0 mg, 0.3 mmol, 1 equiv., **1a**), 4-methylbenzenesulfonamide (77.0 mg, 0.45 mmol, 1.5 equiv., **110**), and Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.) in MeCN (2 mL) was stirred at 110 °C for 12 h. After being cooled to room temperature, the mixture was passed through a short pad of Celite followed by rinse with MeCN. A sample was taken from the filtrate and was directly analyzed by HRMS. Then the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to afford the pure product **111** [petroleum ether/ethyl acetate (20/1–10/1) as eluent, 99.4 mg, 71% yield].

The intermediate **112** was detected by HRMS analysis of the mixture:

Elemental Composition Report Page 1

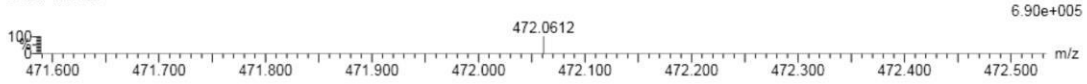
Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
239 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-20 H: 0-24 N: 0-3 O: 0-2 F: 0-9 S: 0-1
CJW-INT2 322 (2.316)
1: TOF MS ES+



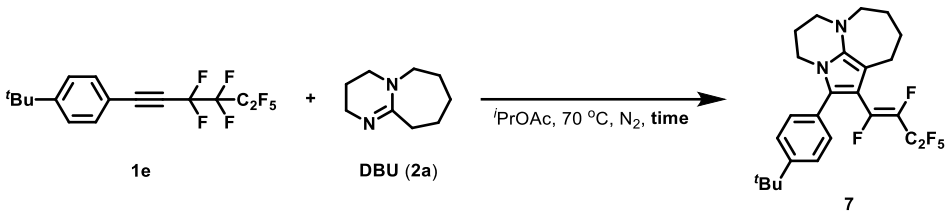
112

$C_{19}H_{14}F_8NO_2S^+$ [M+H]$^+$
Exact mass: 472.0612; found: 472.0612



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
472.0612	472.0618	-0.6	-1.3	9.5	40.4	n/a	n/a	C19 H14 N O2 F8 S

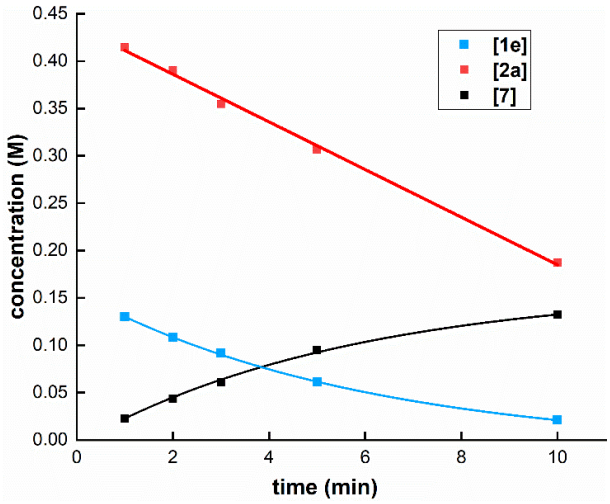
4）Kinetic experiments



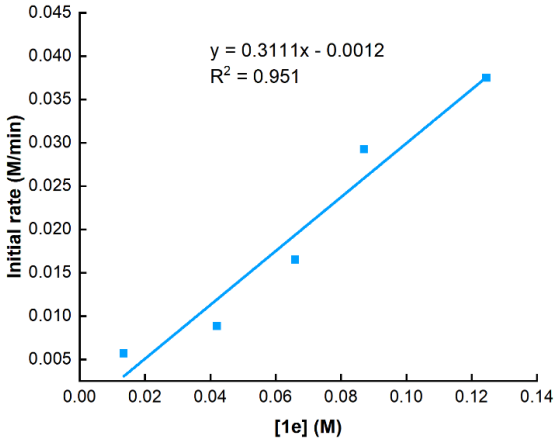
entry	**time** (min)	residual **1e** (%)	NMR yield of product **7** (%)
1	1	83	16
2	2	58	38
3	3	44	50
4	5	28	60
5	10	9	78

A mixture of 1-(*tert*-butyl)-4-(perfluorohex-1-yn-1-yl)benzene (112.9 mg, 0.3 mmol, 1 equiv., **1e**) and DBU (159.9 mg, 1.05 mmol, 3.5 equiv., **2a**) in ^{i}PrOAc (2 mL) was stirred under N_2 at 70 °C for 1–10 min. After being cooled to room temperature, the mixture was quenched by water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was directly analyzed by NMR analysis. The amount of residue fluoroalkyne **1e** and the yield of product **7** were determined by ^{19}F NMR analysis of the residue using 1-fluoro-4-methoxybenzene (0.3 mmol) as an internal standard. Another set of parallel experiments was diluted with EtOH, and the amount of residue DBU **2a** was determined by GC using tetradecane (0.15 mmol) as an internal standard.

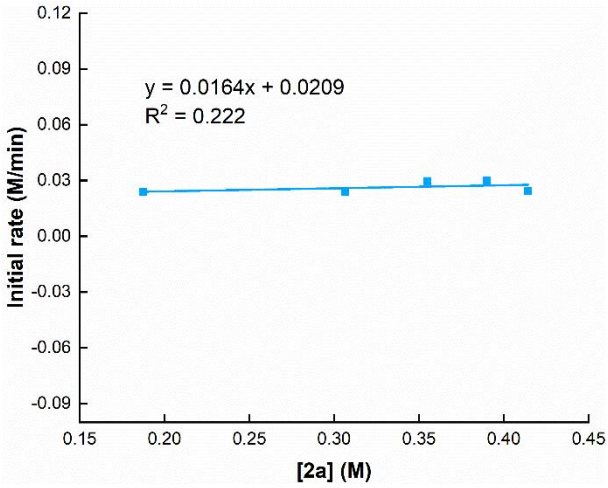
a) Reaction progress data for the reaction of fluoroalkyne **1e** with DBU (**2a**)



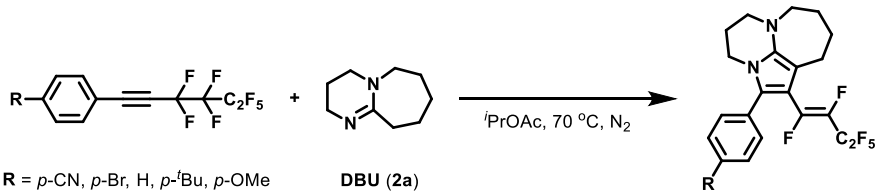
b) A first-order kinetic dependence on fluoroalkyne **1e**



c) A zero-order kinetic dependence on DBU (**2a**)



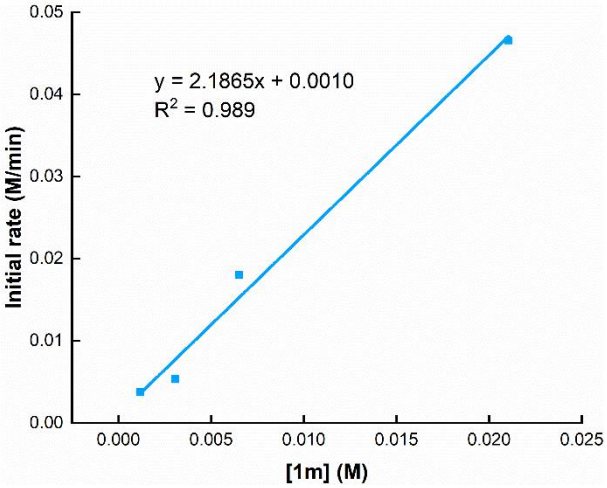
5）Hammett plot



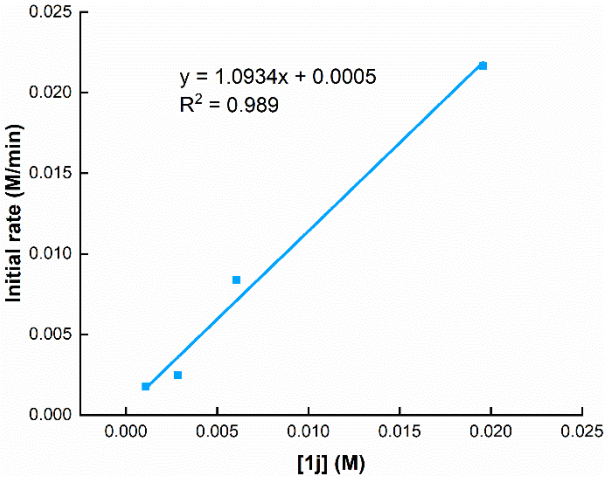
R = *p*-CN, *p*-Br, H, *p*-^{t}Bu, *p*-OMe **DBU** (**2a**)

A solution of perfluoroalkyne (0.3 mmol, 1 equiv., **1**), DBU (159.9 mg, 1.05 mmol, 3.5 equiv., **2a**), and tetradecane (59.5 mg, 0.3 mmol, 1 equiv.) in ^{i}PrOAc (2 mL) was stirred under N_2 at 70 °C for 0.5-10 min. After being cooled to room temperature, the mixture was quenched by water (2 mL), and the reaction solution was analyzed by GC using tetradecane as internal standard. The concentrations of the perfluoroalkynes **1** are plotted to yield the initial rates for the consumption of perfluoroalkynes **1**.

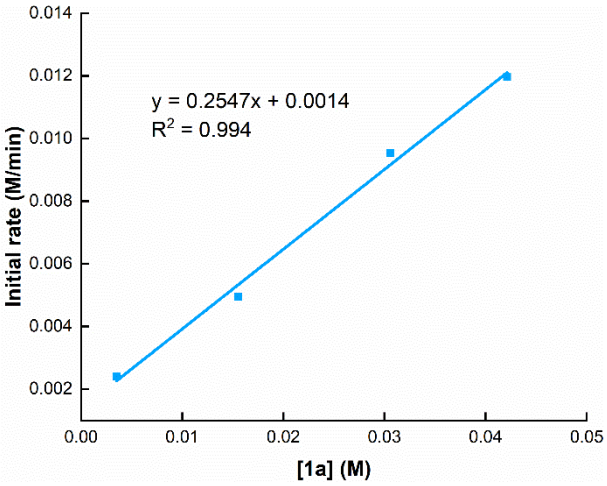
a) Determination of the rate constant of **1m**



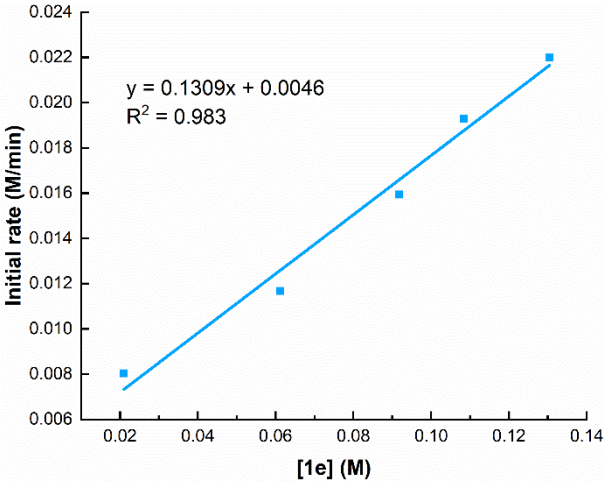
b) Determination of the rate constant of **1j**



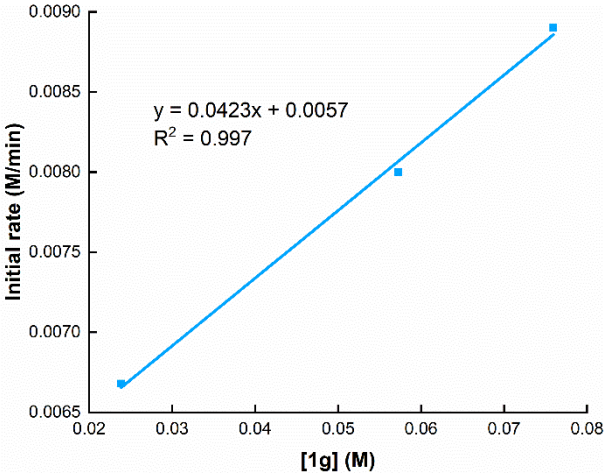
c) Determination of the rate constant of **1a**



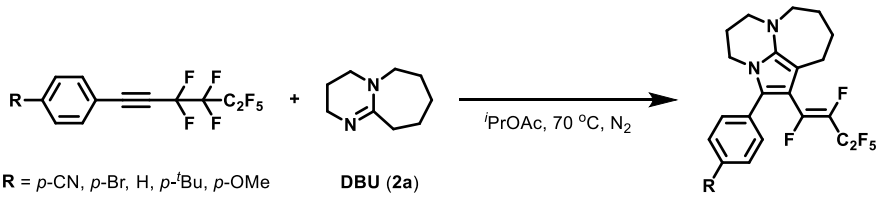
d) Determination of the rate constant of **1e**



e) Determination of the rate constant of **1g**

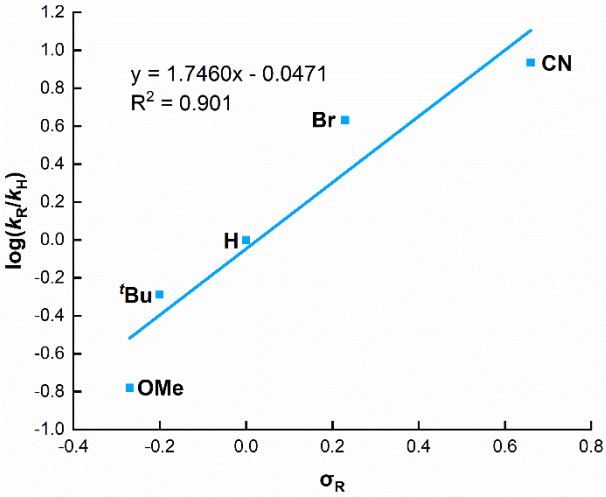


f) Hammett plot



R = *p*-CN, *p*-Br, H, *p*-^{t}Bu, *p*-OMe **DBU** (**2a**)

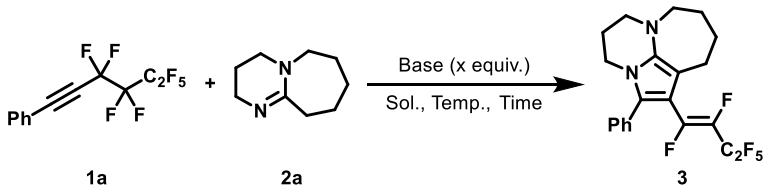
R	σ_R	$\log(k_R/k_H)$
p-CN	0.66	0.93
p-Br	0.23	0.63
H	0	0
p-^{t}Bu	-0.20	-0.29
p-OMe	-0.27	-0.78



The positive slope (ρ = 1.746) in the Hammett plot might suggest that electron-deficient aryl intermediates would be more favourable during the defluorocyclization process.

Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions[a]



1a 2a 3

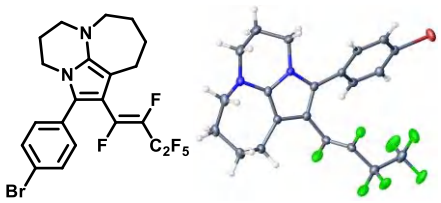
Entry	1a/2a	Base (x equiv)	Solvent	Temp. (°C)	Time	Yield (%)[b] (*E*/*Z*)
1	1/2	--	DMSO	rt	6 h	22 (7.4/1)
2	1/3	--	DMSO	rt	6 h	26 (7.1/1)
3	1/3.5	NH_2Bn (3.5)	DMA (dry)	90	5 min	61 (8.7/1) (56)[c]
4	1/3.5	NH_2Bn (3.5)	DMA	90	12 h	45 (>20/1)
5	1/3.5	DABCO (3.5)	DMA (dry)	90	5 min	59 (6.6/1)
6	1/3.5	--	DMA (dry)	90	5 min	64 (9.1/1)
7	1/3.5	--	DMA (dry)	50	7 min	59 (<10/1)
8	1/3.5	--	DMA (dry)	70	7 min	64 (<10/1)
9	1/3.5	--	DMA (dry)	110	5 min	64 (<10/1)
10	1/3.5	--	DMSO (dry)	70	8 min	62 (>20/1)
11	1/3.5	--	EtOAc	70	13 min	84 (>30/1)
12	1/3.5	--	MeCN	70	10 min	55 (>20/1)
13	1/3.5	--	DCE	70	18 min	61 (>30/1)
14	1/3.5	--	Toluene	70	13 min	76 (>30/1)
15	1/3.5	--	EtOH	70	15 min	trace
16	1/3.5	--	THF (dry)	70	15 min	82 (>30/1)
17	**1/3.5**	**--**	**^{i}PrOAc**	**70**	**15 min**	**99 (>30/1) (80)[c]**
18	1/3.5	--	$EtCO_2Me$	70	15 min	95 (>30/1)
19	1/3.5	--	H_2O	70	12 h	17 (>30/1)
20	1/2.5	--	^{i}PrOAc	70	15 min	84 (>30/1)

21	1/1.5	--	^{i}PrOAc	70	15 min	62 (>30/1)

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45-1.05 mmol), and base (0-1.05 mmol) in solvent (2 mL) at rt-110 °C under N_2 for 5 min-12 h. [b] Yields and *E*/*Z* ratio in parentheses were determined by ^{19}F NMR analysis with 1-fluoro-4-methoxybenzene (0.3 mmol) as an internal standard. [c] Isolated yield.

The X-ray crystal structures of products

a) (*E*)-2-(4-Bromophenyl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene [12; displacement ellipsoids are drawn at the 50% probability levels**]:**



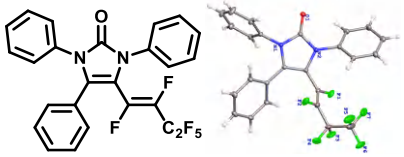
The single crystal was grown from the mixed solution of petroleum ether/EtOAc (v/v = 1/1) by slowly evaporating the above solvents at room temperature.

Table S2. Crystal data and structure refinement for product **12**.

Identification code	**12**
Empirical formula	$C_{21}H_{18}BrF_7N_2$
Formula weight	511.28
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.0199(4)
b/Å	9.6664(5)
c/Å	12.1317(5)
α/°	80.233(4)
β/°	78.910(4)
γ/°	79.201(4)
Volume/Å^3	1009.79(8)
Z	2
ρ_{calc}g/cm^3	1.682
μ/mm^{-1}	1.542
F(000)	512
Crystal size/mm^3	0.10 × 0.10 × 0.10
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	3.749 to 69.966
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -14 ≤ l ≤ 13
Reflections collected	8740
Data/restraints/parameters	3689/0/280

Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0260, wR_2 = 0.0653
Final R indexes [all data]	R_1 = 0.0271, wR_2 = 0.0662
Largest diff. peak/hole / e $Å^{-3}$	0.328/-0.421

b) (*E*)-4-(Perfluorobut-1-en-1-yl)-1,3,5-triphenyl-1,3-dihydro-2*H*-imidazol-2-one [(*E*)-66; displacement ellipsoids are drawn at the 50% probability levels**]:**



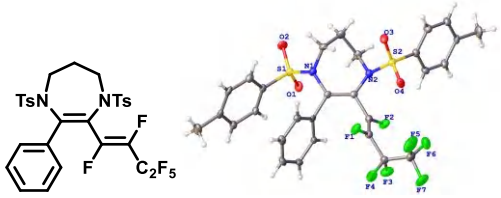
The single crystal was grown from the solution of EtOH by slowly evaporating the above solvents at room temperature.

Table S3. Crystal data and structure refinement for product **(*E*)-66**.

Identification code	**(*E*)-66**
Empirical formula	$C_{25}H_{15}F_7N_2O$
Formula weight	492.39
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8721(3)
b/Å	42.5797(9)
c/Å	10.9151(3)
α/°	90
β/°	118.699(4)
γ/°	90
Volume/$Å^3$	4432.2(2)
Z	8
ρ_{calc}g/cm^3	1.476
μ/mm^{-1}	1.154
F(000)	2000.0
Crystal size/mm^3	0.15 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.306 to 133.186
Index ranges	-12 ≤ h ≤ 12, -50 ≤ k ≤ 50, -12 ≤ l ≤ 12
Reflections collected	18370
Independent reflections	7804 [R_{int} = 0.0510, R_{sigma} = 0.0485]
Data/restraints/parameters	7804/694/722
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0938, wR_2 = 0.2539

Final R indexes [all data]	R_1 = 0.1053, wR_2 = 0.2686
Largest diff. peak/hole / e Å^{-3}	0.50/-0.45

c) (*E*)-2-(Perfluorobut-1-en-1-yl)-3-phenyl-1,4-ditosyl-4,5,6,7-tetrahydro-1*H*-1,4-diazepine [69; displacement ellipsoids are drawn at the 50% probability levels**]:**



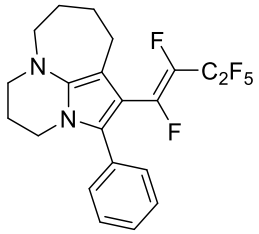
The single crystal was grown from the solution of MeCN by slowly evaporating the above solvents at room temperature.

Table S4. Crystal data and structure refinement for product **69**.

Identification code	**69**
Empirical formula	$C_{29}H_{25}F_7N_2O_4S_2$
Formula weight	662.63
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	Pn
a/Å	18.8892(5)
b/Å	5.71600(10)
c/Å	27.6517(7)
α/°	90
β/°	107.953(3)
γ/°	90
Volume/Å^3	2840.20(12)
Z	4
ρ_{calc}g/cm^3	1.550
μ/mm^{-1}	2.480
F(000)	1360.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.028 to 147.068
Index ranges	-23 ≤ h ≤ 18, -6 ≤ k ≤ 5, -29 ≤ l ≤ 33
Reflections collected	10438
Independent reflections	7478 [R_{int} = 0.0445, R_{sigma} = 0.0676]
Data/restraints/parameters	7478/740/791
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1347
Final R indexes [all data]	R_1 = 0.0679, wR_2 = 0.1506

Largest diff. peak/hole / e Å^{-3} 0.40/-0.45

Characterization data for products



(*E*)-1-(Perfluorobut-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (3):

Yield = 80% (103.3 mg). Yellow solid. M.p. 78.3–79.0 °C.

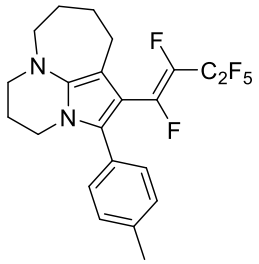
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.34 (m, 2H), 7.30 (qd, *J* = 7.0, 6.4 Hz, 3H), 3.80 (t, *J* = 6.0 Hz, 2H), 3.23–3.17 (m, 2H), 3.03–2.98 (m, 2H), 2.58–2.51 (m, 2H), 2.02 (p, *J* = 5.8 Hz, 2H), 1.93–1.84 (m, 2H), 1.70–1.62 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.49–-84.58 (m, 3F), -119.65 (d, *J* = 10.7 Hz, 2F), -121.82 (dtd, *J* = 146.8, 25.2, 5.5 Hz, 1F), -166.43 (dtd, *J* = 145.9, 13.8, 5.9 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8 (dd, *J* = 258.4, 43.8 Hz), 138.5, 137.6–134.2 (m, 1C), 130.8, 129.3, 128.3, 127.4, 127.2, 106.8–106.5 (m, 1C), 104.6, 56.9, 50.6, 43.2, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{20}F_7N_2$ $[M+H]^+$ 433.1509, found: 433.1511.



(*E*)-1-(Perfluorobut-1-en-1-yl)-2-(*p*-tolyl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (4):

Yield = 93% (124.4 mg). Yellow solid. M.p. 102.4–103.5 °C.

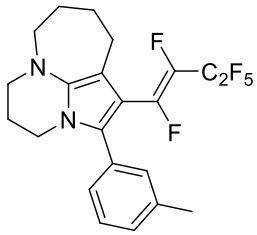
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (s, 4H), 3.80 (t, *J* = 5.3 Hz, 2H), 3.23–3.18 (m, 2H), 3.04–2.99 (m, 2H), 2.59–2.51 (m, 2H), 2.39 (s, 3H), 2.06–1.98 (m, 2H), 1.93–1.86 (m, 2H), 1.67 (p, *J* = 5.8 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.54 (m, 3F), -119.40–-119.70 (m, 2F), -121.62 (dt, *J* = 145.0, 24.5 Hz, 1F), -166.59 (dt, *J* = 148.6, 16.5 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.9 (dd, *J* = 256.6, 43.0 Hz), 138.3, 137.6–134.1 (m, 1C), 137.3, 129.2, 129.1, 128.0, 127.2, 106.5 (dd, *J* = 25.2, 3.4 Hz), 104.4, 56.9, 50.6, 43.1, 31.5, 27.2, 26.0, 22.6, 21.1 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{22}F_7N_2$ $[M+H]^+$ 447.1666, found: 447.1662.



(*E*)-1-(Perfluorobut-1-en-1-yl)-2-(*m*-tolyl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (5):

Yield = 91% (122.0 mg). Yellow solid. M.p. 71.8–72.9 °C.

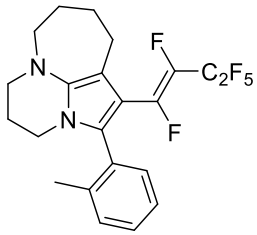
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, J = 7.7 Hz, 1H), 7.16–7.08 (m, 3H), 3.82 (t, J = 6.0 Hz, 2H), 3.23–3.16 (m, 2H), 3.04–2.97 (m, 2H), 2.56 (m, 2H), 2.36 (s, 3H), 2.02 (p, J = 6.0 Hz, 2H), 1.89 (p, J = 5.3 Hz, 2H), 1.66 (p, J = 5.3 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.66 (d, J = 4.7 Hz, 3F), -119.65 (dd, J = 25.6, 13.4 Hz, 2F), -121.44–-122.05 (m, 1F), -166.28–-166.82 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.9 (dd, J = 257.5, 43.5 Hz), 138.4, 138.0, 137.6–136.5 (m, 1C), 130.7, 129.9, 128.2, 127.3, 126.3, 106.5 (dd, J = 25.4, 3.8 Hz), 104.6, 92.4, 56.9, 50.6, 43.2, 31.5, 27.2, 26.0, 22.6, 21.2 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{22}F_7N_2$ $[M+H]^+$ 447.1666, found: 447.1669.



(*E*)-1-(Perfluorobut-1-en-1-yl)-2-(*o*-tolyl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (6):

Yield = 93% (124.7 mg). Yellow solid. M.p. 73.6–74.8 °C.

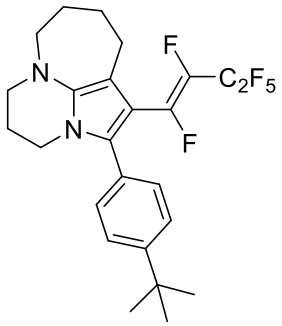
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.22 (m, 2H), 7.17 (dt, J = 3.6, 1.8 Hz, 2H), 3.56–3.41 (m, 2H), 3.23–3.09 (m, 2H), 3.05–2.93 (m, 2H), 2.62–2.46 (m, 2H), 2.14 (s, 3H), 2.01 (p, J = 5.9 Hz, 2H), 1.95–1.82 (m, 2H), 1.77–1.58 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.89 (d, J = 5.1 Hz, 3F), -119.59 (dd, J = 25.7, 14.2 Hz, 2F), -124.02 (dtd, J = 145.3, 25.5, 5.6 Hz, 1F), -167.22–-167.74 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8 (dd, J = 256.6, 42.9 Hz), 138.5, 137.8, 137.1–133.6 (m, 1C), 131.2, 130.7, 129.9, 128.6, 126.7 (d, J = 4.6 Hz), 106.8 (dd, J = 25.5, 3.9 Hz), 103.5, 91.8, 57.0, 50.8, 42.1, 31.4, 27.7, 26.1, 22.6, 19.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{22}F_7N_2$ $[M+H]^+$ 447.1666, found: 447.1664.



(*E*)-2-(4-(*tert*-Butyl)phenyl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (7):

Yield = 93% (135.7 mg). Yellow solid. M.p. 121.7–122.0 °C.

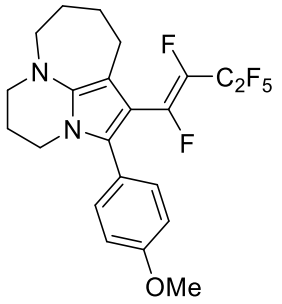
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 3.83 (t, J = 5.9 Hz, 2H), 3.24–3.18 (m, 2H), 3.06–2.99 (m, 2H), 2.57 (t, J = 5.8 Hz, 2H), 2.03 (p, J = 6.0 Hz, 2H), 1.90 (p, J = 5.0 Hz, 2H), 1.68 (p, J = 5.7 Hz, 2H), 1.37 (d, J = 1.2 Hz, 9H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.53 (s, 3F), -119.62 (dd, J = 25.8, 14.5 Hz, 2F), -121.69 (dtd, J = 146.5, 25.4, 5.2 Hz, 1F), -166.12–-166.67 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0 (dd, J = 257.2, 43.1 Hz), 150.4, 138.3, 137.6–134.1 (m, 1C), 129.0, 127.8, 127.4 (d, J = 4.8 Hz), 125.2, 106.4 (dd, J = 25.7, 3.9 Hz), 104.4, 57.0, 50.6, 43.1, 34.5, 31.5, 31.2, 27.3, 26.1, 22.7 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{25}H_{28}F_7N_2$ $[M+H]^+$ 489.2135, found: 489.2136.



(*E*)-2-(4-Methoxyphenyl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (8):

Yield = 63% (87.4 mg). Yellow solid. M.p. 105.0–105.8 °C.

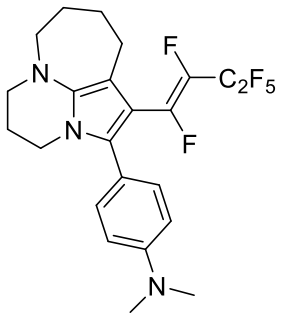
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.19 (m, 2H), 6.94–6.88 (m, 2H), 3.83 (s, 3H), 3.75 (t, J = 6.0 Hz, 2H), 3.21–3.15 (m, 2H), 3.02–2.95 (m, 2H), 2.52 (t, J = 5.9 Hz, 2H), 2.01 (dt, J = 11.5, 5.8 Hz, 2H), 1.87 (q, J = 5.6 Hz, 2H), 1.65 (p, J = 5.9 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.54 (d, J = 4.9 Hz, 3F), -119.53 (dd, J = 25.5, 14.7 Hz, 2F), -121.75 (dtd, J = 146.2, 25.3, 5.9 Hz, 1F), -166.65 (dtd, J = 146.2, 14.0, 5.9 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.1, 152.9 (dd, J = 257.3, 43.3 Hz), 138.1, 137.5–134.0 (m, 1C), 130.7, 127.0 (d, J = 4.8 Hz), 123.3, 113.8, 106.1 (dd, J = 25.2, 3.4 Hz), 104.2, 56.9, 55.2, 50.6, 43.0, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{22}F_7N_2O$ $[M+H]^+$ 463.1615, found: 463.1610.



(*E*)-*N*,*N*-Dimethyl-4-(1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulen-2-yl)aniline (9):

Yield = 77% (110.3 mg). Yellow oil.

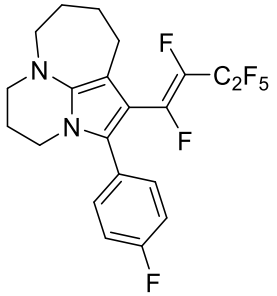
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1–4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.17 (m, 2H), 6.77–6.71 (m, 2H), 3.80 (t, J = 6.0 Hz, 2H), 3.22–3.17 (m, 2H), 3.04–3.00 (m, 8H), 2.58–2.52 (m, 2H), 2.02 (p, J = 5.8 Hz, 2H), 1.89 (p, J = 5.5 Hz, 2H), 1.67 (p, J = 5.4 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.45 (d, J = 5.2 Hz, 3F), -119.32 (dd, J = 25.3, 14.8 Hz, 2F), -121.36 (dtd, J = 146.2, 25.3, 5.7 Hz, 1F), -166.71–-167.24 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.1 (dd, J = 257.3, 43.1 Hz), 149.7, 137.8, 137.4–133.9 (m, 1C), 130.2, 127.9 (d, J = 4.3 Hz), 120.4, 118.5, 112.0, 105.6 (dd, J = 25.2, 3.8 Hz), 104.1, 56.9, 50.7, 43.1, 40.2, 31.6, 27.3, 26.0, 22.7 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{25}F_7N_3$ $[M+H]^+$ 476.1931, found: 476.1929.



(*E*)-2-(4-Fluorophenyl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (10):

Yield = 81% (109.9 mg). Yellow solid. M.p. 188.6–189.0 °C.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

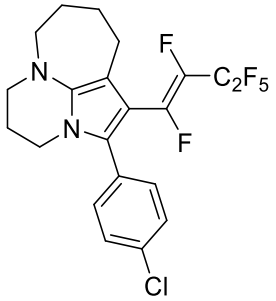
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (ddd, J = 7.2, 6.1, 1.9 Hz, 2H), 7.10–7.02 (m, 2H), 3.74 (t, J = 6.1 Hz, 2H), 3.24–3.14 (m, 2H), 3.05–2.95 (m, 2H), 2.52 (t, J = 5.8 Hz, 2H), 2.02 (p, J = 5.8 Hz, 2H), 1.91–1.83 (m, 2H), 1.65 (q, J = 5.7 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.55–-84.66 (m, 3F), -113.95–-114.12 (m, 1F), -119.69 (dd, J = 25.6, 14.4 Hz, 2F), -122.03 (dtd, J = 146.4, 25.0, 5.7 Hz, 1F), -166.04 – -166.57 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.3 (d, J = 248.7 Hz), 152.7 (dd, J = 257.3, 43.0 Hz), 138.6, 137.7–134.2 (m, 1C), 131.1 (d, J = 8.1 Hz), 127.0 (d, J = 1.2 Hz), 126.0 (d, J = 4.0 Hz), 115.4 (d, J

= 21.7 Hz), 106.8 (dd, *J* = 25.6, 3.9 Hz), 104.5, 56.9, 50.5, 43.0, 27.2, 26.0, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{19}F_8N_2$ $[M+H]^+$ 451.1415, found: 451.1417.



(*E*)-2-(4-Chlorophenyl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (11):

Yield = 73% (102.7 mg). Yellow solid. M.p. 144.1–144.4 °C.

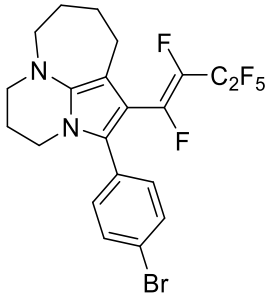
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 2H), 7.25–7.20 (m, 2H), 3.81–3.73 (m, 2H), 3.24–3.16 (m, 2H), 3.03–2.97 (m, 2H), 2.51 (d, *J* = 5.9 Hz, 2H), 2.02 (p, *J* = 5.7 Hz, 2H), 1.92–1.84 (m, 2H), 1.65 (q, *J* = 5.8 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.42–-84.63 (m, 3F), -119.67 (dd, *J* = 25.0, 13.7 Hz, 2F), -122.00 (dtd, *J* = 146.6, 25.3, 5.8 Hz, 1F), -165.81–-166.34 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.5 (dd, *J* = 257.1, 43.0 Hz), 138.9, 137.8–134.3 (m, 1C), 133.4, 130.5, 129.3, 128.6, 125.6 (d, *J* = 3.2 Hz), 107.0 (dd, *J* = 25.6, 3.8 Hz), 104.8, 56.9, 50.5, 43.2, 31.4, 27.1, 26.0, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{19}ClF_7N_2$ $[M+H]^+$ 467.1120, found: 467.1117.



(*E*)-2-(4-Bromophenyl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (12):

Yield = 66% (101.0 mg). Yellow solid. M.p. 139.0–139.9 °C.

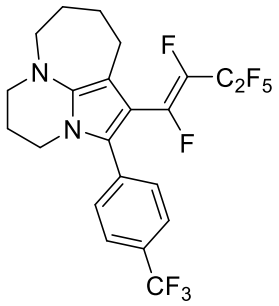
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.47 (m, 2H), 7.18–7.13 (m, 2H), 3.77 (t, *J* = 6.0 Hz, 2H), 3.22–3.17 (m, 2H), 3.02–2.98 (m, 2H), 2.54–2.49 (m, 2H), 2.06–1.98 (m, 2H), 1.91–1.84 (m, 2H), 1.64 (p, *J* = 5.8 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.45–-84.54 (m, 3F), -119.54–-119.71 (m, 2F), -121.93 (dt, *J* = 146.3, 23.9 Hz, 1F), -166.01 (dt, *J* = 143.4, 17.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.5 (dd, J = 256.9, 42.8 Hz), 138.9, 137.9–134.4 (m, 1C), 131.6, 130.8, 129.8, 125.6 (d, J = 2.9 Hz), 121.6, 107.1 (dd, J = 25.6, 3.5 Hz), 104.9, 56.9, 50.5, 43.2, 31.4, 27.1, 26.0, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{19}BrF_7N_2$ $[M+H]^+$ 511.0614, found: 511.0615.



(*E*)-1-(Perfluorobut-1-en-1-yl)-2-(4-(trifluoromethyl)phenyl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (13):

Yield = 45% (67.5 mg). Yellow solid. M.p. 114.0–115.3 ºC.

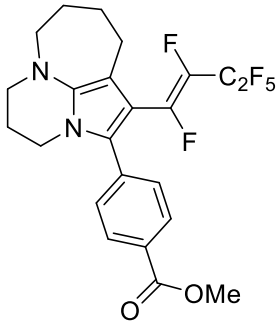
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 3.81 (t, J = 6.0 Hz, 2H), 3.33–3.18 (m, 2H), 3.12–2.96 (m, 2H), 2.67–2.49 (m, 2H), 2.03 (p, J = 5.8 Hz, 2H), 1.88 (p, J = 5.3 Hz, 2H), 1.77–1.59 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.51 (s, 3F), -84.55 (t, J = 4.4 Hz, 3F), -119.79 (dd, J = 26.1, 15.9 Hz, 2F), -122.18 (dtd, J = 146.3, 25.3, 5.7 Hz, 1F), -165.43–-166.00 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.3 (dd, J = 258.0, 42.8 Hz), 139.4, 137.7–134.6 (m, 1C), 134.5, 128.9, 125.5, 125.4 (q, J = 3.9 Hz), 122.8, 120.5–116.6 (m, 1C), 107.8 (dd, J = 25.9, 4.1 Hz), 105.4, 56.9, 50.5, 43.4, 31.4, 27.1, 26.0, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{22}H_{19}F_{10}N_2$ $[M+H]^+$ 501.1383, found: 501.1385.



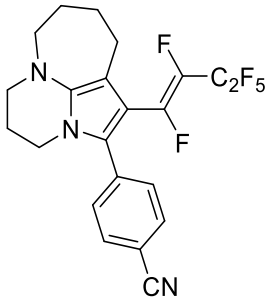
Methyl (*E*)-4-(1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulen-2-yl)benzoate (14):

Yield = 61% (90.0 mg). Yellow solid. M.p. 183.5–183.6 ºC.

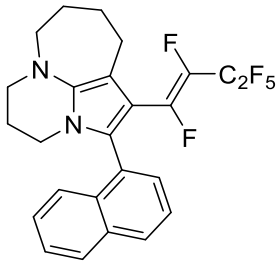
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–8.00 (m, 2H), 7.36–7.32 (m, 2H), 3.92 (s, 3H), 3.86–3.79 (m, 2H), 3.24–3.18 (m, 2H), 3.04–2.97 (m, 2H), 2.53–2.47 (m, 2H), 2.06–1.98 (m, 2H), 1.91–1.84 (m, 2H), 1.63 (p, J = 6.1 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.45 (d, J = 3.6 Hz, 3F), -119.74 (dd, J = 25.2, 13.6 Hz, 2F), -122.05 (dtd, J = 147.1, 25.3, 5.7 Hz, 1F), -165.51–-166.04 (m, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.8, 152.3 (dd, J = 257.1, 43.1 Hz), 139.5, 137.4–134.6 (m, 1C), 135.3, 129.7, 128.7, 128.5, 125.6, 107.8 (dd, J = 25.2, 3.7 Hz), 105.6, 56.9, 52.1, 50.5, 43.5, 31.4, 27.1, 25.9, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{23}H_{22}F_7N_2O_2$ $[M+H]^+$ 491.1564, found: 491.1567.



(*E*)-4-(1-(Perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulen-2-yl)benzonitrile (15):
Yield = 31% (43.0 mg). Yellow solid. M.p. 154.5–156.0 °C.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1–6/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.61 (m, 2H), 7.39–7.34 (m, 2H), 3.82 (t, J = 5.8 Hz, 2H), 3.26–3.19 (m, 2H), 3.07–2.98 (m, 2H), 2.54–2.46 (m, 2H), 2.03 (p, J = 5.7 Hz, 2H), 1.92–1.84 (m, 2H), 1.64 (q, J = 5.8 Hz, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.42 (d, J = 4.2 Hz, 3F), -119.81 (dd, J = 25.4, 13.2 Hz, 2F), -122.27 (dtd, J = 146.2, 25.2, 5.8 Hz, 1F), -165.07–-165.61 (m, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.1 (dd, J = 258.4, 44.2 Hz), 140.0, 137.8–134.8 (m, 1C), 135.4, 132.2, 129.2, 124.5, 118.9, 110.2, 108.4 (dd, J = 25.6, 3.5 Hz), 106.0, 56.8, 50.4, 43.5, 31.4, 27.0, 25.9, 22.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{22}H_{19}F_7N_3$ $[M+H]^+$ 458.1462, found: 458.1460.



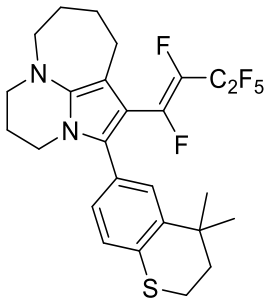
(*E*)-2-(Naphthalen-1-yl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (16):
Yield = 83% (120.3 mg). Yellow oil.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.86 (m, 2H), 7.71–7.64 (m, 1H), 7.54–7.43 (m, 4H), 3.55–3.44 (m, 2H), 3.28–3.13 (m, 2H), 3.10–3.02 (m, 2H), 2.75–2.57 (m, 2H), 2.00–1.92 (m, 4H), 1.76

(p, J = 6.0 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.90 (d, J = 5.4 Hz, 3F), -119.54–-119.81 (m, 2F), -123.42 (dtd, J = 144.8, 25.3, 5.2 Hz, 1F), -166.32–-166.85 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.9 (dd, J = 257.0, 43.1 Hz), 138.4, 137.4–133.9 (m, 1C), 133.6, 133.0, 129.0, 128.8, 128.7, 128.3, 126.5, 125.9, 125.6, 125.3 (d, J = 3.6 Hz), 125.2, 108.2 (dd, J = 25.4, 3.7 Hz), 104.0, 57.0, 50.7, 42.4, 31.4, 27.2, 26.2, 22.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{25}H_{22}F_7N_2$ $[M+H]^+$ 483.1666, found: 483.1668.



(*E*)-2-(4,4-Dimethylthiochroman-6-yl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (17):

Yield = 88% (140.4 mg). Yellow solid. M.p. 62.4–62.6 °C.

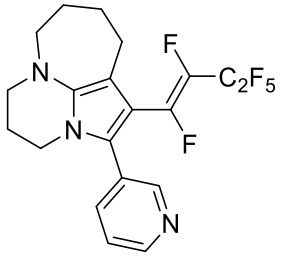
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, J = 1.9 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.98 (dd, J = 8.1, 1.9 Hz, 1H), 3.79 (t, J = 6.0 Hz, 2H), 3.23–3.17 (m, 2H), 3.09–3.03 (m, 2H), 3.03–2.98 (m, 2H), 2.55–2.50 (m, 2H), 2.05–1.98 (m, 4H), 1.89 (p, J = 5.2 Hz, 2H), 1.66 (p, J = 5.7 Hz, 2H), 1.33 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.46 (q, J = 4.4 Hz, 3F), -119.12 (dd, J = 25.6, 14.8 Hz, 2F), -120.68 (dtd, J = 146.8, 25.3, 5.7 Hz, 1F), -166.07–-166.60 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.7 (dd, J = 258.1, 42.8 Hz), 142.0, 138.4, 137.8–134.3 (m, 1C), 131.3, 127.7, 127.1 (d, J = 3.0 Hz), 126.7, 126.4, 126.3, 106.2 (dd, J = 25.0, 3.4 Hz), 104.4, 56.9, 50.6, 43.2, 37.4, 32.9, 31.5, 30.0, 27.2, 25.9, 23.0, 22.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{28}F_7N_2S$ $[M+H]^+$ 533.1856, found: 533.1860.

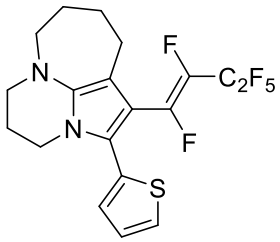


(*E*)-1-(Perfluorobut-1-en-1-yl)-2-(pyridin-3-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (18):

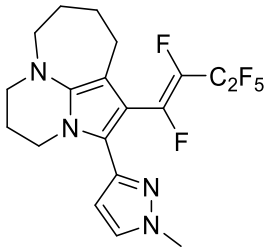
Yield = 68% (88.6 mg). Yellow solid. M.p. 62.4–62.6 °C.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1–4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57–8.51 (m, 2H), 7.59 (dt, J = 7.9, 1.9 Hz, 1H), 7.30 (dd, J = 7.8, 4.8 Hz, 1H), 3.78 (t, J = 6.0 Hz, 2H), 3.24–3.18 (m, 2H), 3.00 (d, J = 5.5 Hz, 2H), 2.55–2.47 (m, 2H), 2.04 (p, J = 5.8 Hz, 2H), 1.93–1.83 (m, 2H), 1.68–1.60 (m, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.56 (d, J = 4.7 Hz, 3F), -119.73 (dd, J = 25.0, 13.7 Hz, 2F), -122.34 (m, 1F), -165.50–-166.03 (m, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.2 (dd, J = 257.1, 44.5 Hz), 149.9, 148.4, 139.4, 138.1–134.4 (m, 1C), 136.5, 127.1, 123.3, 123.0 (d, J = 4.7 Hz), 108.0 (dd, J = 25.5, 3.5 Hz), 105.2, 56.9, 50.4, 43.1, 31.4, 27.1, 26.0, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{20}H_{19}F_7N_3$ $[M+H]^+$ 434.1462, found: 434.1458.



(*E*)-1-Perfluorobut-1-en-1-yl)-2-(thiophen-2-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (19):
Yield = 53% (69.6 mg). Yellow solid. M.p. 75.0-75.7 °C.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 5.2 Hz, 1H), 7.05 (dd, J = 5.2, 3.5 Hz, 1H), 6.97 (d, J = 3.5 Hz, 1H), 3.90–3.84 (m, 2H), 3.24–3.13 (m, 2H), 3.06–2.94 (m, 2H), 2.57–2.45 (m, 2H), 2.05 (p, J = 5.9 Hz, 2H), 1.93–1.82 (m, 2H), 1.65 (p, J = 5.6 Hz, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.33–-84.57 (m, 3F), -119.64 (dd, J = 24.6, 14.9 Hz, 2F), -121.48 (dtd, J = 146.9, 25.2, 5.6 Hz, 1F), -164.86–-165.85 (m, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.1 (dd, J = 257.8, 43.3 Hz), 139.2, 138.2–134.8 (m, 1C), 131.4, 127.6, 127.1, 126.4, 119.0, 108.5 (dd, J = 24.9, 3.2 Hz), 105.0, 56.9, 50.4, 43.0, 31.4, 27.1, 25.9, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{19}H_{18}F_7N_2S$ $[M+H]^+$ 439.1073, found: 439.1072.



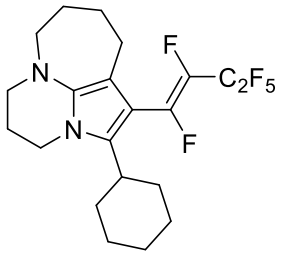
(*E*)-2-(1-Methyl-1H-pyrazol-3-yl)-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (20):
Yield = 80% (105.1 mg). Yellow solid. M.p. 109.1–110.1 °C.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1–8/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, J = 0.8 Hz, 1H), 7.32 (s, 1H), 3.90 (s, 3H), 3.82–3.74 (m, 2H), 3.19–3.12 (m, 2H), 2.99–2.92 (m, 2H), 2.50–2.43 (m, 2H), 2.08–1.98 (m, 2H), 1.85 (dq, J

= 7.2, 4.9 Hz, 2H), 1.66–1.56 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.58 (t, J = 4.2 Hz, 3F), -119.46 (dd, J = 25.5, 14.0 Hz, 2F), -119.92–-120.53 (m, 1F), -165.47–-166.01 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.5 (dd, J = 258.1, 43.0 Hz), 138.9, 138.4, 137.6–134.1 (m, 1C), 129.2, 118.2, 111.5, 106.4 (dd, J = 24.9, 2.9 Hz), 104.2, 56.9, 50.4, 42.7, 38.9, 31.4, 27.1, 25.9, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{20}F_7N_4$ $[M+H]^+$ 437.1571, found: 437.1575.



(*E*)-2-Cyclohexyl-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (21):

Yield = 76% (98.5 mg). Yellow oil.

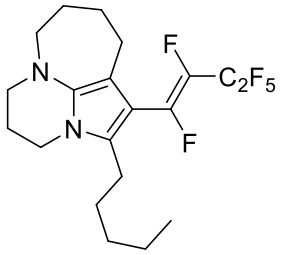
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (td, J = 6.1, 1.9 Hz, 2H), 3.15–3.08 (m, 2H), 2.96–2.89 (m, 2H), 2.58–2.46 (m, 1H), 2.41–2.33 (m, 2H), 2.08 (p, J = 6.0 Hz, 2H), 1.81 (dt, J = 10.5, 3.4 Hz, 6H), 1.63–1.47 (m, 4H), 1.26 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.34–-84.43 (m, 3F), -112.04 (dt, J = 150.7, 24.9 Hz, 1F), -119.41 (dd, J = 24.7, 14.3 Hz, 2F), -164.13 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8 (dd, J = 259.8, 43.2 Hz), 137.7–134.8 (m, 1C), 136.8, 130.7, 103.7 (d, J = 25.0 Hz), 103.0, 57.2, 50.6, 41.6, 37.0, 32.0 (d, J = 1.3 Hz), 31.4, 27.1, 27.0, 26.0, 25.4, 22.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{26}F_7N_2$ $[M+H]^+$ 437.1571, found: 437.1575.



(*E*)-2-Pentyl-1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (22):

Yield = 58% (74.3 mg). Brown oil.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

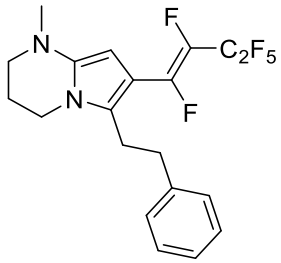
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (dp, J = 13.5, 7.5, 6.8 Hz, 2H), 3.14 (q, J = 5.3 Hz, 2H), 2.94 (q, J = 5.2 Hz, 2H), 2.60–2.33 (m, 4H), 2.09 (dt, J = 11.5, 6.0 Hz, 2H), 1.83 (h, J = 4.8 Hz, 2H), 1.62 (q, J = 5.8 Hz, 2H), 1.49 (p, J = 7.3 Hz, 2H), 1.33 (tq, J = 7.8, 3.9 Hz, 4H), 0.90 (t, J =

6.4 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.71 (d, J = 4.3 Hz, 3F), -119.17 (dd, J = 26.2, 14.1 Hz, 2F), -121.18–-121.79 (m, 1F), -167.41–-167.98 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.1 (dd, J = 257.0, 41.9 Hz), 137.6–134.0 (m, 1C), 137.4, 127.2, 105.1 (dd, J = 25.1, 2.5 Hz), 102.7, 57.1, 50.6, 41.3, 31.6, 31.4, 29.4, 27.2, 25.9, 25.2, 22.5, 22.3, 13.9 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{26}F_7N_2$ $[M+H]^+$ 427.1979, found: 427.1976.



(*E*)-1-Methyl-7-(perfluorobut-1-en-1-yl)-6-phenethyl-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidine (23):

Yield = 47% (59.2 mg). Yellow oil.

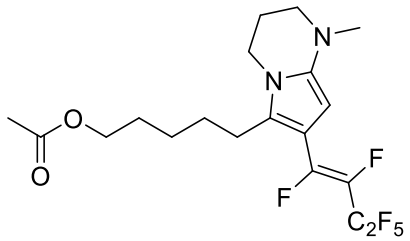
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 2H), 7.26–7.18 (m, 1H), 7.17–7.09 (m, 2H), 5.40 (dt, J = 3.5, 1.1 Hz, 1H), 3.53 (t, J = 6.3 Hz, 2H), 2.99 (dd, J = 6.0, 4.9 Hz, 2H), 2.92 (ddd, J = 8.9, 7.0, 1.7 Hz, 2H), 2.82 (dd, J = 8.6, 5.7 Hz, 2H), 2.76 (d, J = 0.9 Hz, 3H), 2.11–2.01 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.53 (t, J = 6.1 Hz, 3F), -118.39 (dd, J = 27.3, 13.9 Hz, 2F), -143.55–-144.17 (m, 1F), -174.88–-175.40 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.9 (dd, J = 248.7, 37.9 Hz), 141.3, 141.0, 134.8–131.4 (m, 1C), 128.5 (d, J = 3.0 Hz), 127.8, 126.2, 105.4 (dd, J = 22.6, 5.5 Hz), 83.5 (dd, J = 12.5, 8.2 Hz), 48.1, 40.6, 39.7, 37.0, 27.9 (d, J = 6.1 Hz), 22.7 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{20}F_7N_2$ $[M+H]^+$ 421.1509, found: 421.1512.



(*E*)-5-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)pentyl acetate (24):

Yield = 38% (50.1 mg). Yellow oil.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

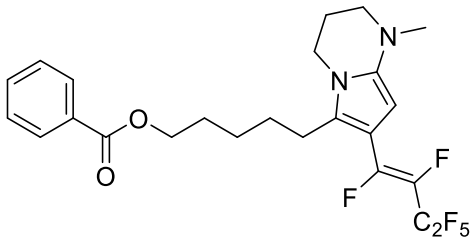
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.32 (dd, J = 3.6, 1.3 Hz, 1H), 4.04 (t, J = 6.7 Hz, 2H), 3.79 (t, J = 6.3 Hz, 2H), 3.07–2.99 (m, 2H), 2.74 (s, 3H), 2.61 (td, J = 7.6, 1.8 Hz, 2H), 2.24–2.14 (m, 2H), 2.04 (s, 3H), 1.70–1.59 (m, 2H), 1.51 (p, J = 7.3 Hz, 2H), 1.43–1.35 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.55–-84.68 (m, 3F), -118.42–-118.62 (m, 2F), -142.66–-

143.26 (m, 1F), -174.82–-175.44 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.3, 153.9 (dd, J = 249.3, 38.0 Hz), 141.3, 134.1–131.3 (m, 1C), 128.5, 105.2 (dd, J = 22.1, 4.3 Hz), 83.3 (dd, J = 12.2, 7.9 Hz), 64.3, 48.1, 40.6, 39.6, 29.9, 28.3, 25.6, 25.4 (d, J = 5.7 Hz), 22.8, 20.9 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{24}F_7N_2O_2$ $[M+H]^+$ 427.1979, found: 427.1976.



(*E*)-5-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)pentyl benzoate (25):

Yield = 50% (76.1 mg). Yellow oil.

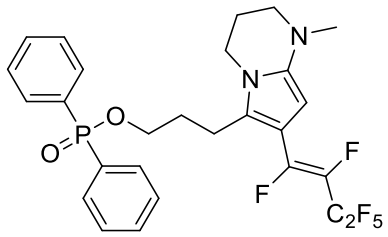
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08–8.02 (m, 2H), 7.60–7.54 (m, 1H), 7.45 (dd, J = 8.5, 7.0 Hz, 2H), 5.34 (dd, J = 3.5, 1.2 Hz, 1H), 4.33 (t, J = 6.6 Hz, 2H), 3.80 (t, J = 6.3 Hz, 2H), 3.05–3.00 (m, 2H), 2.75 (s, 3H), 2.69–2.62 (m, 2H), 2.22–2.14 (m, 2H), 1.80 (p, J = 6.8 Hz, 2H), 1.63–1.46 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.58 (t, J = 5.7 Hz, 3F), -118.46 (dd, J = 27.0, 13.5 Hz, 2F), -142.93 (dtd, J = 129.6, 26.5, 6.2 Hz, 1F), -175.16 (ddq, J = 129.9, 13.4, 7.6 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.6, 153.9 (dd, J = 250.2, 40.4 Hz), 141.3, 134.8–131.3 (m, 2C), 132.8, 130.3, 129.5, 128.5, 128.3, 105.2 (dd, J = 20.5, 4.8 Hz), 83.2 (dd, J = 12.1, 7.8 Hz), 64.8, 48.1, 40.6, 39.6, 29.9, 28.4, 25.7, 25.4 (d, J = 6.1 Hz), 22.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{26}F_7N_2O_2$ $[M+H]^+$ 507.1877, found: 507.1873.



(*E*)-3-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)propyl diphenylphosphinate (26):

Yield = 44% (75.4 mg). Yellow oil.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 1/1).

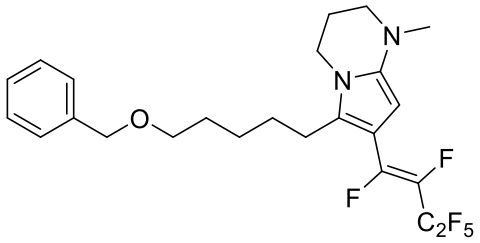
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.76 (m, 4H), 7.56–7.50 (m, 2H), 7.45 (tdd, J = 8.2, 3.0, 1.3 Hz, 4H), 5.33 (dd, J = 3.6, 1.3 Hz, 1H), 4.09–4.02 (m, 2H), 3.75 (t, J = 6.3 Hz, 2H), 3.02–2.97 (m, 2H), 2.78 (td, J = 7.7, 1.6 Hz, 2H), 2.73 (s, 3H), 2.17–2.08 (m, 2H), 1.96–1.87 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.55 (d, J = 7.2 Hz, 3F), -118.30–-118.60 (m, 2F), -143.51–-144.09 (m, 1F), -174.82–-175.34 (m, 1F) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 32.35 (s, 1P) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.8 (dd, J = 252.4, 34.9 Hz), 141.5, 134.9–131.9 (m, 1C), 132.2 (d, J = 2.9 Hz), 132.0, 131.5 (d, J = 10.1 Hz), 130.6, 128.6 (d, J = 13.1 Hz), 127.3, 83.4 (dd, J = 12.9, 8.5 Hz), 64.2 (d, J = 6.0 Hz), 48.1, 40.6, 39.6, 31.2 (d, J = 6.3 Hz), 22.7, 22.0 (d, J = 5.8 Hz) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{27}H_{27}F_7N_2O_2P$ $[M+H]^+$ 575.1693, found: 575.1696.



(*E*)-6-(5-(Benzyloxy)pentyl)-1-methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidine (27):

Yield = 55% (81.2 mg). Yellow oil.

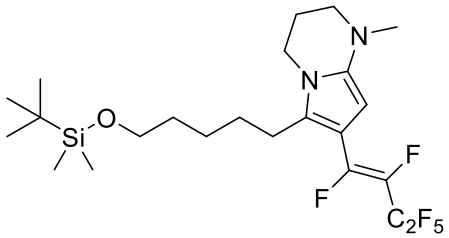
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 5H), 5.34 (dd, J = 3.6, 1.3 Hz, 1H), 4.51 (s, 2H), 3.78 (t, J = 6.3 Hz, 2H), 3.48 (t, J = 6.5 Hz, 2H), 3.07–2.99 (m, 2H), 2.75 (s, 3H), 2.67–2.58 (m, 2H), 2.23–2.13 (m, 2H), 1.71–1.60 (m, 2H), 1.58–1.37 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.48–-84.63 (m, 3F), -118.35–-118.53 (m, 2F), -142.59–-143.50 (m, 1F), -174.95–-175.72 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.0 (dd, J = 238.3, 47.6 Hz), 141.3, 138.5, 134.7–131.3 (m, 1C), 128.9, 128.3, 127.6, 127.5, 105.0 (dd, J = 22.7, 5.4 Hz), 83.2 (dd, J = 12.2, 7.9 Hz), 72.9, 70.2, 48.1, 40.6, 39.6, 30.1, 29.4, 26.0, 25.5 (d, J = 5.7 Hz), 22.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{28}F_7N_2O$ $[M+H]^+$ 493.2084, found: 493.2083.



(*E*)-6-(5-((*tert*-Butyldimethylsilyl)oxy)pentyl)-1-methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidine (28):

Yield = 56% (86.1 mg). Yellow oil.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

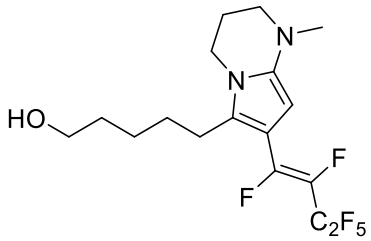
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.33 (dd, J = 3.6, 1.2 Hz, 1H), 3.80 (t, J = 6.3 Hz, 2H), 3.60 (t, J = 6.4 Hz, 2H), 3.07–3.00 (m, 2H), 2.75 (s, 3H), 2.65–2.56 (m, 2H), 2.24–2.13 (m, 2H), 1.58–1.45 (m, 4H), 1.38 (tt, J = 10.8, 4.1 Hz, 2H), 0.89 (d, J = 0.9 Hz, 9H), 0.04 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.60 (p, J = 4.6 Hz, 3F), -118.39–-118.56 (m, 2F), -142.60–-143.44 (m, 1F), -174.93–-175.74 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.0 (dd, J = 251.5, 40.3 Hz), 141.2, 132.4–130.3 (m, 1C),

129.0, 105.1 (dd, J = 23.1, 5.8 Hz), 83.3 (dd, J = 12.5, 7.9 Hz), 63.0, 48.2, 40.7, 39.7, 32.5, 30.1, 25.9, 25.6, 25.5, 22.8, 18.4, -5.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{36}F_7N_2OSi$ $[M+H]^+$ 517.2480, found: 517.2477.



(*E*)-5-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)pentan-1-ol (29):

Yield = 45% (54.0 mg). Yellow oil.

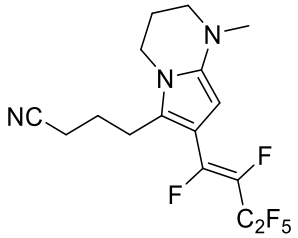
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 1/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.32 (dd, J = 3.5, 1.3 Hz, 1H), 3.79 (t, J = 6.3 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 3.07–2.99 (m, 2H), 2.74 (s, 3H), 2.61 (td, J = 7.8, 1.8 Hz, 2H), 2.18 (qd, J = 6.5, 5.1 Hz, 2H), 1.62–1.47 (m, 5H), 1.45–1.37 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.60 (p, J = 4.9 Hz, 3F), -118.40–-118.58 (m, 2F), -142.67–-143.31 (m, 1F), -174.95–-175.47 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.9 (dd, J = 246.0, 41.6 Hz), 141.3, 134.7–131.6 (m, 1C), 128.8, 105.1 (dd, J = 20.8, 5.1 Hz), 83.3 (dd, J = 12.1, 7.8 Hz), 62.8, 48.2, 40.7, 39.7, 32.4, 30.1, 25.5, 25.4, 22.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{17}H_{22}F_7N_2O$ $[M+H]^+$ 403.1615, found: 403.1618.



(*E*)-4-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)butanenitrile (30):

Yield = 36% (41.4 mg). Yellow oil.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1–8/1).

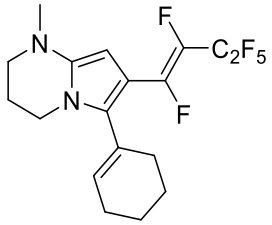
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.35 (dd, J = 3.6, 1.3 Hz, 1H), 3.83 (t, J = 6.3 Hz, 2H), 3.09–3.02 (m, 2H), 2.82–2.73 (m, 5H), 2.38 (t, J = 7.1 Hz, 2H), 2.21 (qd, J = 6.2, 4.2 Hz, 2H), 1.86 (p, J = 7.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.96–-84.64 (m, 3F), -118.62 (dd, J = 27.1, 13.7 Hz, 2F), -144.16 (dtd, J = 128.5, 26.9, 6.2 Hz, 1F), -173.57–-174.46 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.5 (dd, J = 248.4, 39.8 Hz), 141.8, 134.8–132.0 (m, 1C), 125.4, 119.4, 106.2 (dd, J = 22.5, 5.2 Hz), 83.5 (dd, J = 12.6, 8.2 Hz), 47.8, 40.7, 39.6, 25.8, 24.3 (d, J = 5.8 Hz), 22.7, 16.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due

to C-F coupling.

HRMS (m/z): calcd for $C_{16}H_{17}F_7N_3$ $[M+H]^+$ 384.1305, found: 384.1310.



(*E*)-6-(Cyclohex-1-en-1-yl)-1-methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidine (31):

Yield = 73% (87.3 mg). Yellow oil.

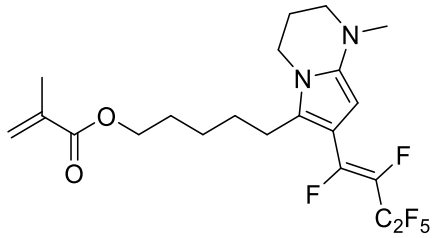
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73 (dq, J = 3.5, 1.8 Hz, 1H), 5.35 (dd, J = 2.9, 0.9 Hz, 1H), 3.76 (t, J = 6.3 Hz, 2H), 3.10–3.02 (m, 2H), 2.78 (s, 3H), 2.18–2.11 (m, 6H), 1.76–1.62 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.61 (t, J = 3.9 Hz, 3F), -118.62–-118.79 (m, 2F), -139.79–-140.40 (m, 1F), -174.09–-174.66 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.5 (dd, J = 250.5, 39.9 Hz), 141.2, 134.9–131.4 (m, 1C), 131.1, 130.9 , 129.4, 105.3 (dd, J = 23.7, 5.3 Hz), 83.2 (dd, J = 9.9, 6.3 Hz), 48.3, 41.3, 39.5, 29.6, 25.5, 22.9, 22.8, 21.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{18}H_{20}F_7N_2$ $[M+H]^+$ 397.1509, found: 397.1512.



(*E*)-5-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)pentyl methacrylate (32):

Yield = 50% (69.9 mg). Yellow oil.

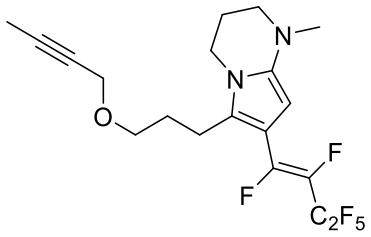
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.09 (dq, J = 2.0, 1.0 Hz, 1H), 5.55 (p, J = 1.6 Hz, 1H), 5.32 (dd, J = 3.5, 1.3 Hz, 1H), 4.13 (t, J = 6.6 Hz, 2H), 3.79 (t, J = 6.3 Hz, 2H), 3.07–2.99 (m, 2H), 2.74 (s, 3H), 2.66–2.58 (m, 2H), 2.24–2.14 (m, 2H), 1.94 (t, J = 1.3 Hz, 3H), 1.75–1.63 (m, 2H), 1.59–1.48 (m, 2H), 1.47–1.37 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.61 (t, J = 3.9 Hz, 3F), -118.62–-118.79 (m, 2F), -139.79–-140.40 (m, 1F), -174.09–-174.66 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.5, 153.9 (dd, J = 247.4, 39.7 Hz), 141.3, 136.4, 134.8–131.6 (m, 1C), 128.5, 125.3, 105.2 (dd, J = 22.7, 5.2 Hz), 83.3 (dd, J = 12.2, 7.9 Hz), 64.5, 48.1, 40.7, 39.6, 29.8, 28.3, 25.7, 25.4 (d, J = 5.7 Hz), 22.8, 18.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{26}F_7N_2O_2$ $[M+H]^+$ 471.1877, found: 471.1882.



(*E*)-6-(3-(But-2-yn-1-yloxy)propyl)-1-methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidine (33):

Yield = 50% (63.4 mg). Yellow oil.

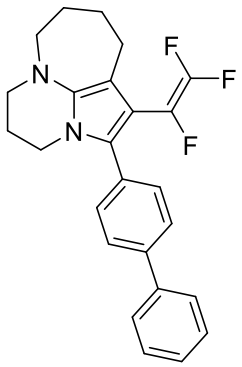
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.34 (dd, J = 3.6, 1.4 Hz, 1H), 4.09 (q, J = 2.3 Hz, 2H), 3.83 (t, J = 6.3 Hz, 2H), 3.48 (t, J = 6.1 Hz, 2H), 3.07–2.99 (m, 2H), 2.77–2.68 (m, 5H), 2.23–2.13 (m, 2H), 1.89–1.73 (m, 5H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.56–-84.65 (m, 3F), -118.48 (dd, J = 27.3, 12.8 Hz, 2F), -143.26–-143.86 (m, 1F), -175.30 (ddt, J = 129.7, 17.0, 8.5 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.9 (dd, J = 248.6, 38.6 Hz), 141.3, 134.7–131.3 (m, 1C), 128.2, 105.3 (dd, J = 22.5, 5.3 Hz), 83.3 (dd, J = 12.5, 8.1 Hz), 82.4, 75.1, 68.9, 58.6, 48.2, 40.7, 39.6, 30.1, 22.8, 22.1 (d, J = 6.1 Hz), 3.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{22}F_7N_2O$ $[M+H]^+$ 427.1615, found: 427.1621.



2-([1,1'-Biphenyl]-4-yl)-1-(1,2,2-trifluorovinyl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (34):

Yield = 11% (13.4 mg). Yellow oil.

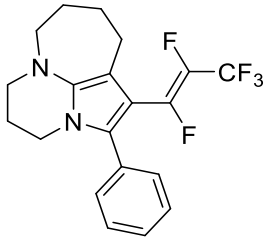
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.59 (m, 4H), 7.46 (dd, J = 8.5, 6.9 Hz, 2H), 7.42–7.32 (m, 3H), 3.86 (td, J = 5.9, 1.6 Hz, 2H), 3.27–3.13 (m, 2H), 3.08–2.95 (m, 2H), 2.61–2.48 (m, 2H), 2.10–2.00 (m, 2H), 1.95–1.82 (m, 2H), 1.65 (ddt, J = 11.4, 7.6, 4.4 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -102.14 (dd, J = 75.8, 23.9 Hz, 1F), -117.62 (dd, J = 120.3, 76.9 Hz, 1F), -151.89 (dd, J = 121.0, 23.4 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.6, 139.6, 138.3, 130.1, 129.7, 128.8, 127.3, 127.02 (d, J = 1.5 Hz), 126.95, 126.9, 126.5, 106.0 (d, J = 1.9 Hz), 105.8 (d, J = 3.2 Hz), 105.5, 57.0, 50.7, 43.3, 31.6, 27.3, 26.0, 22.8 ppm.

HRMS (m/z): calcd for $C_{25}H_{24}F_3N_2$ $[M+H]^+$ 409.1886, found: 409.1886.



(*E*)-1-(Perfluoroprop-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (35):

Yield = 94% (107.9 mg). White solid. M.p. 153.2–154.3 °C.

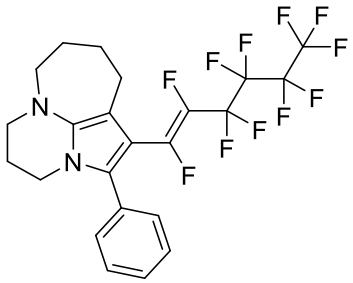
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (dd, J = 8.7, 6.4 Hz, 2H), 7.32 (td, J = 6.0, 5.5, 2.0 Hz, 3H), 3.80 (t, J = 5.9 Hz, 2H), 3.29–3.14 (m, 2H), 3.10–2.90 (m, 2H), 2.63–2.44 (m, 2H), 2.02 (p, J = 5.8 Hz, 2H), 1.89 (ddt, J = 10.8, 7.2, 3.9 Hz, 2H), 1.66 (p, J = 5.8 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -67.01 (dd, J = 21.4, 12.7 Hz, 3F), -122.77 (dq, J = 145.8, 21.4 Hz, 1F), -168.18 (dq, J = 146.0, 12.1 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.5 (dd, J = 253.5, 42.4 Hz), 136.4–135.5 (m, 1C), 130.9, 129.4, 128.3, 127.5, 127.0 (d, J = 4.7 Hz), 106.4 (dd, J = 25.7, 3.7 Hz), 104.6, 57.0, 50.6, 43.2, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the CF_3 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{20}F_5N_2$ $[M+H]^+$ 383.1541, found: 383.1544.



(*E*)-1-(Perfluorohex-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (36):

Yield = 79% (125.4 mg). Yellow solid. M.p. 66.2–67.8 °C.

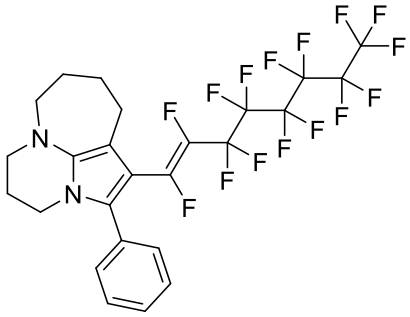
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.29 (m, 5H), 3.87–3.77 (m, 2H), 3.22 (dt, J = 10.7, 5.1 Hz, 2H), 3.04 (dt, J = 14.7, 5.3 Hz, 2H), 2.60–2.54 (m, 2H), 2.04 (dp, J = 11.2, 5.4 Hz, 2H), 1.91 (dp, J = 10.7, 5.1 Hz, 2H), 1.69 (dp, J = 11.2, 6.0 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.98 (t, J = 10.3 Hz, 3F), -116.46 (dq, J = 26.1, 13.1 Hz, 2F), -120.70–-121.47 (m, 1F), -124.17–-124.73 (m, 2F), -126.39 (t, J = 13.0 Hz, 2F), -165.23 (dt, J = 146.4, 14.8 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0 (dd, J = 258.2, 43.6 Hz), 138.5, 137.8–134.3 (m, 1C), 130.9, 129.4, 128.3, 127.5, 127.1 (d, J = 3.1 Hz), 106.7 (dd, J = 25.5, 2.8 Hz), 104.6, 56.9, 50.6, 43.2, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{20}F_{11}N_2$ $[M+H]^+$ 533.1445, found: 533.1445.



(*E*)-1-(Perfluorooct-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (37):

Yield = 83% (157.0 mg). Yellow solid. M.p. 86.6–87.5 °C.

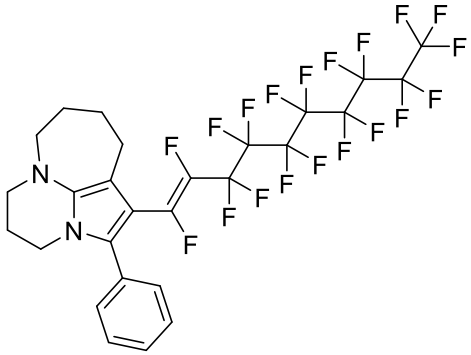
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.35 (m, 2H), 7.34–7.29 (m, 3H), 3.80 (t, J = 6.0 Hz, 2H), 3.24–3.17 (m, 2H), 3.05–2.98 (m, 2H), 2.55 (t, J = 5.8 Hz, 2H), 2.08–1.97 (m, 2H), 1.89 (p, J = 5.1 Hz, 2H), 1.67 (p, J = 5.6 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.82 (t, J = 9.8 Hz, 3F), -116.30 (dq, J = 26.8, 13.5 Hz, 2F), -121.03 (dtt, J = 146.2, 26.6, 7.1 Hz, 1F), -122.28 (q, J = 14.4 Hz, 2F), -122.71–-123.02 (m, 2F), -123.65 (dt, J = 22.6, 9.4 Hz, 2F), -126.18 (td, J = 15.0, 6.5 Hz, 2F), -165.12 (dt, J = 146.3, 15.1 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0 (dd, J = 258.2, 43.2 Hz), 138.5, 137.8–134.3 (m, 1C), 130.9, 129.4, 128.3, 127.5, 127.2 (d, J = 3.9 Hz), 106.8 (dd, J = 25.6, 3.8 Hz), 104.6, 57.0, 50.6, 43.2, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the C_6F_{13} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{25}H_{20}F_{15}N_2$ $[M+H]^+$ 633.1381, found: 633.1383.



(*E*)-1-(Perfluorodec-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (38):

Yield = 84% (185.5 mg). Yellow solid. M.p. 90.8–91.9 °C.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

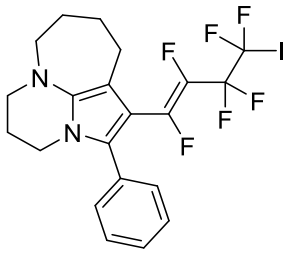
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.35 (m, 2H), 7.33–7.28 (m, 3H), 3.83–3.76 (m, 2H), 3.24–3.16 (m, 2H), 3.04–2.98 (m, 2H), 2.55 (t, J = 5.8 Hz, 2H), 2.07–1.98 (m, 2H), 1.90 (ddt, J = 10.9, 7.3, 3.6 Hz, 2H), 1.67 (ddt, J = 9.7, 5.8, 3.5 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.89 (t, J = 9.8 Hz, 3F), -116.34 (dq, J = 24.9, 12.4 Hz, 2F), -

121.06 (dtd, *J* = 147.3, 26.5, 7.6 Hz, 1F), -121.85–-122.30 (m, 6F), -122.79 (dt, *J* = 22.1, 11.0 Hz, 2F), -123.48–-123.90 (m, 2F), -126.22 (q, *J* = 9.9 Hz, 2F), -164.82–-165.42 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0 (dd, *J* = 257.8, 43.3 Hz), 138.5, 137.9–134.4 (m, 1C), 130.9, 129.4, 128.3, 127.5, 127.2 (d, *J* = 3.7 Hz), 106.8 (dd, *J* = 25.7, 3.2 Hz), 104.6, 57.0, 50.6, 43.2, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the C_8F_{17} group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{27}H_{20}F_{19}N_2$ $[M+H]^+$ 733.1318, found: 733.1321.



(*E*)-1-(1,2,3,3,4,4-Hexafluoro-4-iodobut-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (39):

Yield = 67% (107.9 mg). Yellow solid. M.p. 125.6–126.4 ºC.

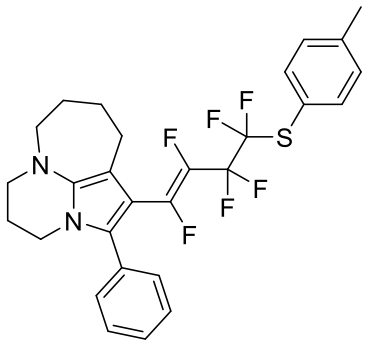
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 2H), 7.31 (d, *J* = 7.2 Hz, 3H), 3.79 (t, *J* = 5.9 Hz, 2H), 3.23–3.16 (m, 2H), 3.04–2.97 (m, 2H), 2.54 (t, *J* = 5.7 Hz, 2H), 2.02 (h, *J* = 6.1 Hz, 2H), 1.88 (p, *J* = 5.7 Hz, 2H), 1.66 (p, *J* = 5.5 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -60.51 (d, *J* = 5.3 Hz, 2F), -110.34 (ddt, *J* = 23.8, 14.8, 8.9 Hz, 2F), -120.49–-121.09 (m, 1F), -163.01–-163.50 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.7 (dd, *J* = 255.8, 42.1 Hz), 138.4, 136.8–132.4 (m, 1C), 130.9, 129.4, 128.3, 127.4, 127.0, 106.9 (d, *J* = 25.2 Hz), 104.6, 96.0 (tt, *J* = 320.9, 44.1 Hz), 56.9, 50.6, 43.1, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the $-CF_2-$ group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{20}F_6IN_2$ $[M+H]^+$ 541.0570, found: 541.0565.



(*E*)-1-(1,2,3,3,4,4-Hfexafluoro-4-(*p*-tolylthio)but-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (40):

Yield = 79% (126.6 mg). Yellow solid. M.p. 82.2–83.5 ºC.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

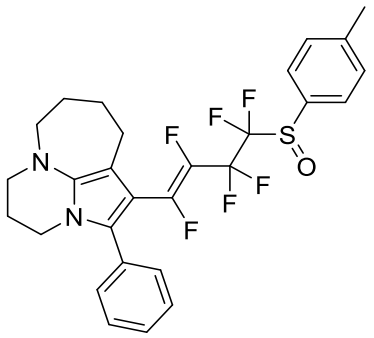
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.52 (m, 2H), 7.42–7.36 (m, 4H), 7.31 (ddt, *J* = 7.0, 6.0,

2.5 Hz, 1H), 7.27–7.20 (m, 2H), 3.82 (t, *J* = 5.9 Hz, 2H), 3.25–3.18 (m, 2H), 3.06–2.99 (m, 2H), 2.64–2.56 (m, 2H), 2.41 (s, 3H), 2.09–1.97 (m, 2H), 1.92 (dq, *J* = 10.5, 5.0 Hz, 2H), 1.70 (q, *J* = 5.7 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -88.88 (t, *J* = 7.5 Hz, 2F), -113.96 (ddt, *J* = 23.8, 15.8, 8.1 Hz, 2F), -121.82 (dtd, *J* = 146.2, 25.4, 5.2 Hz, 1F), -162.96 (dtd, *J* = 145.5, 13.3, 12.6 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.8 (dd, *J* = 256.3, 44.2 Hz), 141.0, 139.0–136.0 (m, 1C), 138.4, 137.1, 131.0, 130.0, 129.4, 128.3, 127.2, 126.7, 123.6 (t, *J* = 37.2 Hz), 120.2, 112.3 (t, *J* = 35.3 Hz), 107.2 (dd, *J* = 25.6, 3.5 Hz), 104.7, 56.9, 50.6, 43.2, 31.5, 27.2, 26.0, 22.6, 21.2 ppm.

HRMS (m/z): calcd for $C_{28}H_{27}F_6N_2S$ $[M+H]^+$ 537.1794, found: 537.1797.



(*E*)-1-(1,2,3,3,4,4-Hexafluoro-4-(*p*-tolylsulfinyl)but-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (41):

Yield = 88% (145.6 mg). Yellow oil.

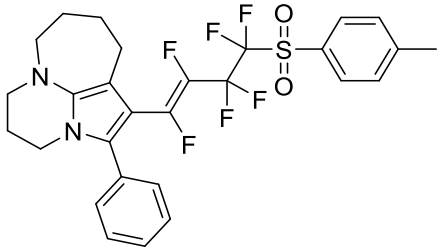
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.33–7.22 (m, 5H), 3.79–3.71 (m, 2H), 3.19–3.12 (m, 2H), 3.00–2.93 (m, 2H), 2.55–2.47 (m, 2H), 2.42 (s, 3H), 1.97 (p, *J* = 5.8 Hz, 2H), 1.88–1.80 (m, 2H), 1.66–1.58 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -112.73–-114.82 (m, 3F), -121.30 (dtd, *J* = 146.0, 25.0, 6.1 Hz, 1F), -123.19 (dt, *J* = 238.5, 6.2 Hz, 1F), -164.87 (dddd, *J* = 146.3, 21.1, 14.4, 6.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.5 (dd, *J* = 255.9, 43.4 Hz), 144.1, 138.4, 138.1–134.8 (m, 1C), 132.6, 130.9, 129.9, 129.4, 128.3, 127.3, 126.9, 126.7, 106.8 (dd, *J* = 25.3, 3.5 Hz), 104.6, 56.9, 50.5, 43.1, 31.4, 27.1, 25.9, 22.5, 21.5 ppm, carbons corresponding to the -C_2F_4- group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{27}F_6N_2OS$ $[M+H]^+$ 553.1743, found: 553.1739.



(*E*)-1-(1,2,3,3,4,4-Hexafluoro-4-tosylbut-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (42):

Yield = 75% (127.2 mg). Yellow oil.

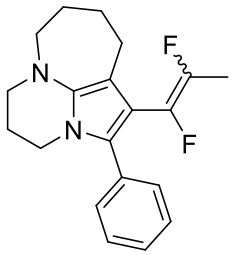
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.37–7.25 (m, 5H), 3.78 (t, J = 5.9 Hz, 2H), 3.22–3.15 (m, 2H), 3.02–2.95 (m, 2H), 2.56–2.50 (m, 2H), 2.49 (s, 3H), 2.05–1.95 (m, 2H), 1.91–1.82 (m, 2H), 1.64 (q, J = 5.8 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -113.26–-113.50 (m, 4F), -121.26 (dtt, J = 145.6, 25.5, 6.8 Hz, 1F), -164.43–-165.01 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.6 (dd, J = 256.9, 43.3 Hz), 147.6, 138.5, 137.9–134.9 (m, 1C), 130.9, 130.8, 130.1, 130.0, 129.3, 128.3, 127.3, 126.9, 125.7 (t, J = 66.6 Hz), 115.0 (tt, J = 300.3, 40.5 Hz), 106.8 (dd, J = 25.1, 3.8 Hz), 104.7, 56.9, 50.6, 43.2, 31.5, 27.1, 25.9, 22.5, 21.8 ppm.

HRMS (m/z): calcd for $C_{28}H_{27}F_6N_2O_2S$ $[M+H]^+$ 569.1692, found: 569.1687.



1-(1,2-Difluoroprop-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (43):

Yield = 74% (73.3 mg, E/Z = 4.4/1). Orange solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 6/1).

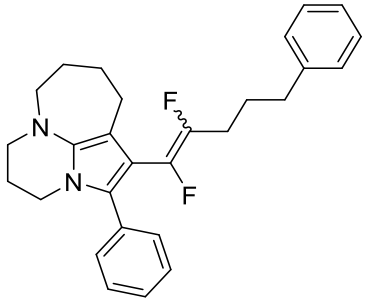
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.37–7.21 (m, 5H), 3.78 (td, J = 6.0, 1.5 Hz, 2H), 3.20–3.13 (m, 2H), 3.00–2.92 (m, 2H), 2.56–2.46 (m, 2H), 2.05–1.94 (m, 4.5H), 1.90–1.81 (m, 2H), 1.62 (p, J = 5.7 Hz, 2H), 1.46 (dd, J = 17.3, 3.7 Hz, 0.5H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -136.22 (d, J = 137.6 Hz, 1F), -139.66 (d, J = 137.6 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -122.41 (d, J = 22.5 Hz, 1F), -128.50 (d, J = 22.5 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 148.3 (dd, J = 234.8, 62.1 Hz), 144.4 (dd, J = 227.9, 51.2 Hz), 138.0, 131.9 (d, J = 1.6 Hz), 129.4 (d, J = 1.4 Hz), 128.0, 126.6, 125.6 (dd, J = 4.3, 2.1 Hz), 108.9 (dd, J = 26.5, 2.9 Hz), 105.0, 57.0, 50.7, 43.1, 31.7, 27.3, 26.1, 22.8, 12.9 (dd, J = 26.6, 1.2 Hz) ppm.

HRMS (m/z): calcd for $C_{20}H_{23}F_2N_2$ $[M+H]^+$ 329.1824, found: 329.1826.



1-(1,2-Difluoro-5-phenylpent-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (44):

Yield = 80% (103.2 mg, *E*/*Z* = 7.3/1). Yellow solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

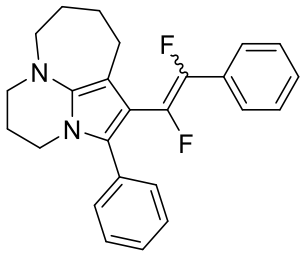
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.40–7.32 (m, 4H), 7.31–7.11 (m, 6H), 3.80 (td, *J* = 6.0, 1.5 Hz, 2H), 3.26–3.15 (m, 2H), 3.07–2.94 (m, 2H), 2.57 (ddd, *J* = 11.8, 8.6, 5.9 Hz, 4H), 2.46 (dtd, *J* = 22.4, 7.2, 4.8 Hz, 2H), 2.04–1.98 (m, 2H), 1.92–1.75 (m, 4H), 1.66 (tdd, *J* = 7.8, 4.7, 1.9 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -136.12–-136.51 (m, 1F), -147.02 (dt, *J* = 137.8, 22.6 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -120.32 (d, *J* = 26.3 Hz, 1F), -136.39–-136.57 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 151.1 (dd, *J* = 237.8, 61.3 Hz), 144.6 (dd, *J* = 229.0, 51.9 Hz), 141.9, 138.0, 131.9, 129.5, 128.4, 128.2, 128.0, 126.7, 125.7, 125.6 (d, *J* = 2.2 Hz), 108.9 (dd, *J* = 26.8, 2.4 Hz), 104.8, 57.1, 50.7, 43.0, 34.9, 31.7, 27.6, 27.3, 26.4 (d, *J* = 25.1 Hz), 26.1, 22.8 ppm.

HRMS (m/z): calcd for $C_{28}H_{31}F_2N_2$ $[M+H]^+$ 433.2450, found: 433.2455.



1-(1,2-Difluoro-2-phenylvinyl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (45):

Yield = 78% (91.9 mg, *E*/*Z* = 5/1). Yellow solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

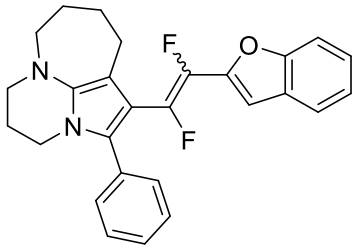
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.65–7.06 (m, 10H), 3.83–3.69 (m, 2H), 3.20–3.13 (m, 2H), 3.02–2.91 (m, 2H), 2.62–2.38 (m, 2H), 2.03–1.95 (m, 2H), 1.90–1.79 (m, 2H), 1.68–1.46 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -128.67 (d, *J* = 136.3 Hz, 1F), -152.12 (d, *J* = 136.5 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -110.67 (d, *J* = 25.9 Hz, 1F), -136.18 (d, *J* = 25.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 148.0 (dd, *J* = 51.6, 38.7 Hz), 145.7 (dd, *J* = 54.3, 51.9 Hz), 138.1, 131.8 (d, *J* = 1.0 Hz), 130.6 (dd, *J* = 28.5, 7.3 Hz), 129.4 (d, *J* = 1.5 Hz), 128.2 (d, *J* = 2.2 Hz), 128.1, 127.7, 126.7, 125.8 (dd, *J* = 4.1, 2.2 Hz), 125.3 (dd, *J* = 9.0, 7.2 Hz), 109.65 (dd, *J* = 25.9, 2.9 Hz), 105.16 (d, *J* = 0.7 Hz), 57.0, 50.7, 43.2, 31.7, 27.3, 26.2 (d, *J* = 1.1 Hz), 22.7 ppm.

HRMS (m/z): calcd for $C_{25}H_{25}F_2N_2$ $[M+H]^+$ 391.1980, found: 391.1974.



1-(2-(Buenzofuran-2-yl)-1,2-difluorovinyl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (46):

Yield = 68% (68.2 mg, *E*/*Z* = 1.2/1). Yellow solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1–10/1).

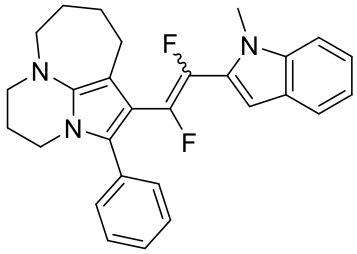
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.60–7.39 (m, 2H), 7.39–7.30 (m, 3H), 7.28–7.16 (m, 4H), 6.90 (s, 0.7H) , 6.32 (s, 0.3H), 3.84–3.72 (m, 2H), 3.25–3.15 (m, 2H), 3.07–2.92 (m, 2H), 2.54 (dt, *J* = 45.7, 5.5 Hz, 2H), 2.06–1.97 (m, 2H), 1.91–1.80 (m, 2H), 1.68–1.49 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -124.82 (d, *J* = 137.2 Hz, 1F), -162.20 (d, *J* = 136.9 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -105.76 (d, *J* = 28.9 Hz, 1F), -144.42 (d, *J* = 28.3 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 154.6, 154.4 (d, *J* = 1.8 Hz), 148.7–144.8 (m, 2C), 142.4–139.6 (m, 2C), 138.32, 138.28, 131.6, 131.1, 129.5, 129.2, 128.21, 128.15, 128.1, 128.0, 127.0, 126.9, 126.5–126.3 (m, 2C), 124.7, 124.4, 123.1, 122.9, 121.0, 120.9, 111.3, 111.2, 108.6–108.3 (m, 2C), 105.4–105.1 (m, 2C), 57.2, 57.0, 50.8, 50.7, 43.2, 31.6, 27.3, 27.2, 26.2, 25.8, 22.74, 22.68, 22.6 ppm.

HRMS (m/z): calcd for $C_{27}H_{25}F_2N_2O$ $[M+H]^+$ 431.1929, found: 431.1930.



1-(1,2-Difluoro-2-(1-methyl-1*H*-indol-2-yl)vinyl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (47):

Yield = 51% (68.2 mg, *E*/*Z* = 1.2/1). Yellow solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1–10/1).

^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.62 (dd, *J* = 8.0, 1.0 Hz, 0.55H), 7.49 (d, *J* = 7.9 Hz, 0.45H), 7.46–7.35 (m, 2H), 7.33–7.04 (m, 5H), 6.89 (dq, *J* = 6.8, 1.2 Hz, 1H) , 6.82–6.80 (m, 0.55H), 6.07 (dt, *J* = 3.3, 0.7 Hz, 0.45H), 3.85 (td, *J* = 6.1, 1.3 Hz, 1.1H), 3.60–3.52 (m, 2.25H), 3.25–3.19 (m, 1.1H), 3.16–3.09 (m, 2.55H), 3.08–3.02 (m, 1.1H), 3.00–2.93 (m, 0.9H), 2.69 (dt, *J* = 7.3, 2.8 Hz, 2H), 2.05 (tt, *J* = 6.7, 5.4 Hz, 1.1H), 1.96–1.87 (m, 2.9H), 1.75–1.65 (m, 2H) ppm.

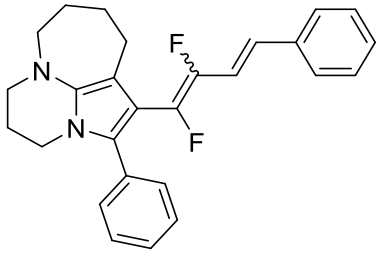
^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -125.89 (d, *J* = 147.2 Hz, 1F), -143.12 (d, *J* = 147.5

Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -108.53 (d, J = 31.1 Hz, 1F), -126.07 (d, J = 30.6 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 149.0–145.8 (m, 2C), 143.6–140.3 (m, 2C), 138.3, 138.0, 137.9, 137.4, 131.8, 131.3, 129.7, 129.6, 129.3–128.4 (m, 2C), 128.2, 127.9, 127.3, 127.03, 126.96, 126.8, 126.3 (dd, J = 4.6, 1.9 Hz), 122.6, 122.2, 121.1, 121.0, 119.8, 119.3, 109.4, 109.2, 108.9, 108.8 (d, J = 4.0 Hz), 108.5 (d, J = 3.5 Hz), 105.4 (t, J = 2.7 Hz), 104.8, 104.5–104.4 (m, 2C), 57.1, 57.0, 50.70, 50.67, 43.1, 42.7, 31.6, 31.1 (d, J = 5.4 Hz), 29.9 (d, J = 3.4 Hz), 27.5, 27.4, 26.3, 26.2, 22.7, 22.6 ppm.

HRMS (m/z): calcd for $C_{28}H_{28}F_2N_3$ $[M+H]^+$ 444.2246, found: 444.2251.



1-((3*E*)-1,2-Difluoro-4-phenylbuta-1,3-dien-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (48):

Yield = 86% (107.6 mg, *E*/*Z* = 3/1). Orange solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

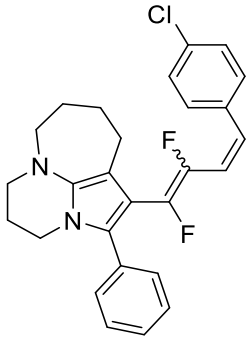
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.41–7.39 (m, 1.56H), 7.36–7.32 (m, 2.92H), 7.31–7.28 (m, 2.20H), 7.27–7.15 (m, 3.66H), 7.05–6.92 (m, 0.66H), 6.70–6.57 (m, 0.89H), 6.30–6.16 (m, 0.11H), 3.84–3.75 (m, 2H), 3.23–3.12 (m, 2H), 3.00–2.95 (m, 2H), 2.58–2.51 (m, 2H), 2.04–1.94 (m, 2H), 1.92–1.81 (m, 2H), 1.67–1.56 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -130.98 (d, J = 130.5 Hz, 1F), -157.94 (d, J = 124.9 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -113.18 (d, J = 23.7 Hz, 1F), -146.92 (t, J = 24.1 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 149.1–144.3 (m, 4C), 138.22, 138.18, 136.53, 136.46, 131.7, 131.3, 129.5, 129.4, 128.6, 128.4, 128.3, 128.1, 127.8, 127.5, 127.2, 127.1, 126.9, 126.8, 126.7–126.6 (m, 2C), 126.4, 126.12–126.06 (m, 1C), 117.0 (d, J = 19.3 Hz), 114.8 (dd, J = 19.7, 2.5 Hz), 108.9–108.4 (m, 2C), 105.8, 105.2, 57.03, 56.96, 50.8, 50.7, 43.3, 43.2, 31.6 (2C), 27.34, 27.26, 26.2, 26.1, 22.7 (2C) ppm.

HRMS (m/z): calcd for $C_{27}H_{27}F_2N_2$ $[M+H]^+$ 417.2137, found: 417.2141.



1-((3*Z*)-4-(4-Chlorophenyl)-1,2-difluorobuta-1,3-dien-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (49):

Yield = 41% (55.5 mg, *E*/*Z* = 2.8/1). Yellow solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

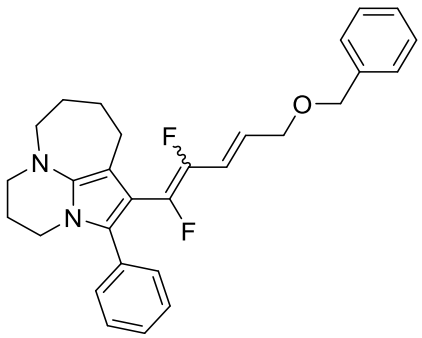
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.44–7.30 (m, 5.08H), 7.24–7.18 (m, 0.76H), 7.13–7.09 (m, 1.37H), 7.02–6.98 (m, 0.46H), 6.96–6.91 (m, 1.46H), 6.41–6.27 (m, 1.48H), 6.09–6.04 (m, 0.22H), 5.69–5.57 (m, 0.17H), 3.85–3.74 (m, 2H), 3.24–3.14 (m, 2H), 3.04–2.95 (m, 2H), 2.61–2.53 (m, 2H), 2.05–1.97 (m, 2H), 1.91–1.83 (m, 2H), 1.68–1.60 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -126.92 (d, *J* = 131.0 Hz, 1F), -146.83 (dd, *J* = 129.6, 29.8 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -112.01 (d, *J* = 23.0 Hz, 1F), -136.33–-136.62 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 149.3–145.2 (m, 4C), 138.3, 138.1, 135.2, 135.1, 132.8, 132.7, 132.0, 131.4, 130.4 (d, *J* = 5.8 Hz), 130.0 (d, *J* = 5.2 Hz), 129.7, 129.6, 128.3, 128.2, 128.0, 127.9 (d, *J* = 1.2 Hz), 127.7, 127.6, 127.5–127.4 (m, 1C), 127.0, 126.9, 126.5–126.4 (m, 1C), 117.9 (d, *J* = 17.9 Hz), 115.5–115.3 (m, 1C), 108.8–108.2 (m, 2C), 105.5, 104.8, 57.1, 57.0, 50.72, 50.68, 43.2, 43.1, 31.60, 31.56, 27.4, 27.3, 26.23, 26.15, 22.7 (2C) ppm.

HRMS (m/z): calcd for $C_{27}H_{26}ClF_2N_2$ $[M+H]^+$ 451.1747, found: 451.1741.



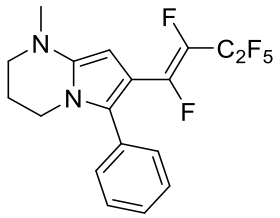
1-((3*E*)-5-(Benzyloxy)-1,2-difluoropenta-1,3-dien-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (50):

Yield = 75% (103.2 mg, *E*/*Z* = 3.6/1). Yellow solid.

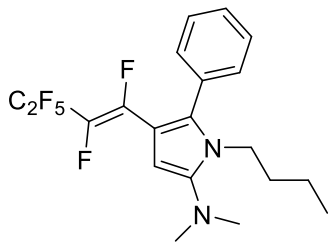
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.37–7.22 (m, 10H), 6.63–6.51 (m, 0.59H), 5.97–5.90 (m, 0.59H), 5.85–5.79 (m, 0.25H), 4.53 (s, 1.28H), 4.34 (s, 0.31H), 4.27–4.24 (m, 0.25H), 4.11 (dt, *J* = 5.8, 1.4 Hz, 1.46H), 3.92–3.91 (m, 2H), 3.80–3.76 (m, 2H), 3.23–3.12 (m, 2H), 3.05–

2.90 (m, 2H), 2.55–2.45 (m, 2H), 2.04–1.95 (m, 2H), 1.89–1.83 (m, 2H), 1.65–1.58 (m, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -131.63 (d, J = 128.1 Hz, 1F), -157.98 (dd, J = 128.6, 26.8 Hz, 1F) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -113.95 (d, J = 23.9 Hz, 1F), -146.24–-146.98 (m, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 148.7–143.4 (m, 2C), 138.1 (d, J = 7.8 Hz), 131.7, 129.5, 128.4, 128.1, 127.8, 127.6, 126.8, 126.0, 125.5, 124.90–124.85 (m, 1C), 118.8 (dd, J = 20.5, 1.8 Hz), 108.6 (dd, J = 26.0, 2.7 Hz), 105.2, 72.4, 70.0, 57.0, 50.7, 43.2, 31.7, 27.3, 26.2, 22.7 ppm.
HRMS (m/z): calcd for $C_{29}H_{31}F_2N_2O$ $[M+H]^+$ 461.2399, found: 461.2400.



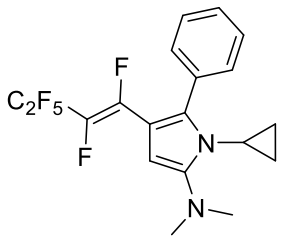
(*E*)-1-Methyl-7-(perfluorobut-1-en-1-yl)-6-phenyl-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidine (51):
Yield = 83% (98.2 mg). Yellow oil.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.30 (m, 5H), 5.53 (t, J = 1.9 Hz, 1H), 3.70 (td, J = 6.2, 1.4 Hz, 2H), 3.19–3.05 (m, 2H), 2.86 (d, J = 1.5 Hz, 3H), 2.21–2.05 (m, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.56 (q, J = 5.0 Hz, 3F), -118.87 (dd, J = 26.9, 13.6 Hz, 2F), -138.72 (dtd, J = 131.7, 27.2, 5.8 Hz, 1F), -173.18–-173.71 (m, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.1 (dd, J = 251.5, 39.3 Hz), 142.0, 135.3–131.9 (m, 1C), 131.6, 130.1, 128.1, 127.92, 127.87, 106.9 (dd, J = 23.1, 5.5 Hz), 84.2 (dd, J = 10.6, 6.3 Hz), 48.1, 42.1, 39.5, 22.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{18}H_{16}F_7N_2$ $[M+H]^+$ 393.1196, found: 393.1196.



(*E*)-1-Butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (52):
Yield = 70% (88.5 mg). Yellow oil.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.38 (m, 3H), 7.38–7.32 (m, 2H), 6.12 (qd, J = 1.7, 1.1 Hz, 1H), 3.78 (td, J = 7.5, 1.7 Hz, 2H), 2.71 (d, J = 1.3 Hz, 6H), 1.37 (dtd, J = 9.2, 7.5, 5.8 Hz, 2H), 1.08 (hd, J = 7.3, 1.5 Hz, 2H), 0.74 (td, J = 7.4, 1.4 Hz, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.55–-84.62 (m, 3F), -118.93 (dd, J = 26.6, 14.6 Hz, 2F), -138.55–-139.07 (m, 1F), -173.57–-174.01 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0 (dd, *J* = 251.2, 38.9 Hz), 146.2, 135.3–131.8 (m, 1C), 132.3, 130.7, 130.1, 128.13, 128.09, 106.8 (dd, *J* = 23.0, 5.3 Hz), 95.2 (dd, *J* = 10.6, 6.2 Hz), 45.7, 43.1, 32.4, 19.6, 13.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{22}F_7N_2$ $[M+H]^+$ 423.1666, found: 423.1662.



(*E*)-1-Cyclopropyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (53):

Yield = 67% (81.7 mg). Yellow solid. M.p. 36.8–37.8 °C.

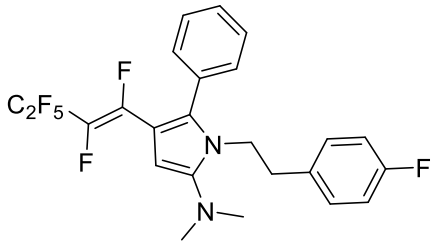
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.32 (m, 5H), 5.77 (dd, *J* = 2.5, 0.8 Hz, 1H), 2.96 (tt, *J* = 6.8, 4.1 Hz, 1H), 2.80 (s, 6H), 0.78–0.66 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.55 (q, *J* = 4.0 Hz, 3F), -119.08 (dd, *J* = 26.8, 13.5 Hz, 2F), -136.88–-137.48 (m, 1F), -172.71 (dtd, *J* = 133.8, 13.3, 6.1 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.9 (dd, *J* = 252.8, 39.8 Hz), 147.8, 135.7–132.2 (m, 1C), 132.6, 132.5, 129.6, 127.9, 127.5, 106.0 (dd, *J* = 23.6, 4.9 Hz), 91.7 (dd, *J* = 9.4, 5.7 Hz), 43.6, 27.2, 9.2 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{18}F_7N_2$ $[M+H]^+$ 407.1353, found: 407.1353.



(*E*)-1-(4-Fluorophenethyl)-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (54):

Yield = 53% (77.3 mg). Yellow solid. M.p. 39.9–40.1 °C.

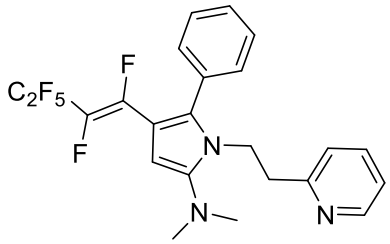
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 80/1–60/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.39 (m, 3H), 7.25 (ddq, *J* = 6.0, 2.3, 1.3 Hz, 2H), 6.92–6.85 (m, 2H), 6.79–6.73 (m, 2H), 6.11 (dt, *J* = 2.8, 1.4 Hz, 1H), 4.01–3.95 (m, 2H), 2.68 (s, 6H), 2.64 (ddd, *J* = 9.7, 5.6, 2.0 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.47–-84.59 (m, 3F), -116.52 (q, *J* = 6.9 Hz, 1F), -118.82–-119.03 (m, 2F), -138.42–-139.00 (m, 1F), -173.06–-173.60 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.6 (d, *J* = 245.5 Hz), 152.8 (dd, *J* = 252.1, 38.9 Hz), 146.1, 135.5–132.3 (m, 1C), 133.8 (d, *J* = 3.1 Hz), 132.1, 130.6, 130.1, 130.0, 128.2, 115.3, 115.1, 107.1 (dd, *J* = 23.2, 5.3 Hz), 95.5 (dd, *J* = 10.6, 6.2 Hz), 45.6, 44.9, 35.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{21}F_8N_2$ $[M+H]^+$ 489.1572, found: 489.1578.



(*E*)-*N*,*N*-Dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1-(2-(pyridin-2-yl)ethyl)-1*H*-pyrrol-2-amine (55):

Yield = 41% (57.8 mg). Yellow oil.

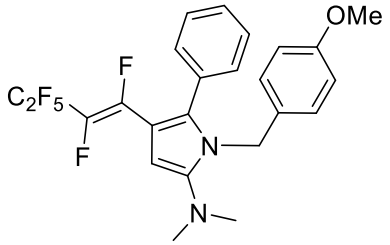
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 4/1–2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 7.47 (td, J = 7.7, 1.8 Hz, 1H), 7.40–7.35 (m, 3H), 7.24–7.20 (m, 2H), 7.07 (ddd, J = 7.6, 4.9, 1.2 Hz, 1H), 6.65 (dt, J = 7.8, 1.1 Hz, 1H), 6.07 (dd, J = 2.9, 1.1 Hz, 1H), 4.22–4.16 (m, 2H), 2.88–2.83 (m, 2H), 2.65 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.55(s, 3F), -118.95 (dd, J = 27.4, 14.3 Hz, 2F), -138.52 (dt, J = 131.4, 26.7 Hz, 1F), -173.33 (d, J = 130.7 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.3, 152.8 (dd, J = 251.0, 39.2 Hz), 149.3, 146.2, 136.3, 135.5–132.1 (m, 1C),132.0, 130.7, 130.0, 128.4, 128.2, 123.1, 121.5, 107.1 (dd, J = 23.2, 5.2 Hz), 95.4 (dd, J = 10.2, 5.9 Hz), 45.6, 43.2, 38.7 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{21}F_7N_3$ $[M+H]^+$ 472.1624, found: 472.1618.



(*E*)-1-(4-Mxzcethoxybenzyl)-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (56):

Yield = 42% (61.9 mg). Yellow solid. M.p. 49.7–50.4 °C.

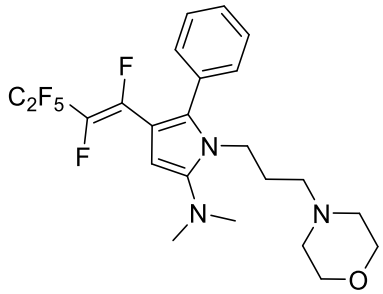
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1–20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 3H), 7.19–7.14 (m, 2H), 6.75–6.65 (m, 4H), 6.19 (dd, J = 2.9, 1.1 Hz, 1H), 4.94 (s, 2H), 3.75 (s, 3H), 2.68 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.53 (d, J = 5.0 Hz, 3F), -118.66–-119.26 (m, 2F), -138.86–-139.46 (m, 1F), -173.11–-173.62 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.5, 152.8 (dd, J = 252.1, 39.0 Hz), 146.3, 135.4–132.1 (m, 1C), 132.0, 131.0, 130.3, 130.2, 128.1, 128.0, 127.5, 113.6, 107.3 (dd, J = 23.0, 5.2 Hz), 95.7 (dd, J = 10.8, 6.3 Hz), 55.1, 45.9, 45.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{22}F_7N_2O$ $[M+H]^+$ 487.1615, found: 487.1608.



(*E*)-*N*,*N*-Dimethyl-1-(3-morpholinopropyl)-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (57):

Yield = 62% (91.5 mg). Light yellow solid. M.p. 74.5–75.0 °C.

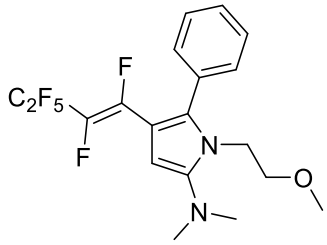
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1–20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.30 (m, 5H), 6.09 (dd, J = 2.8, 1.1 Hz, 1H), 3.89–3.80 (m, 2H), 3.55 (t, J = 4.6 Hz, 4H), 2.69 (s, 6H), 2.12 (q, J = 6.5 Hz, 6H), 1.54 (dq, J = 12.1, 6.9 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.58 (t, J = 4.7 Hz, 3F), -118.95 (dd, J = 26.5, 13.7 Hz, 2F), -138.64–-139.27 (m, 1F), -173.64 (dtd, J = 131.3, 13.4, 6.0 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8 (dd, J = 251.9, 39.2 Hz), 146.0, 135.3–131.9 (m, 1C), 132.2, 130.5, 130.1, 128.2, 128.1, 107.0 (dd, J = 23.2, 5.3 Hz), 95.2 (dd, J = 10.6, 6.3 Hz), 66.8, 55.6, 53.1, 45.6, 41.5, 27.0 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{27}F_7N_3O$ $[M+H]^+$ 494.2037, found: 494.2045.



(*E*)-1-(2-Methoxyethyl)-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (58):

Yield = 56% (70.9 mg). Yellow oil.

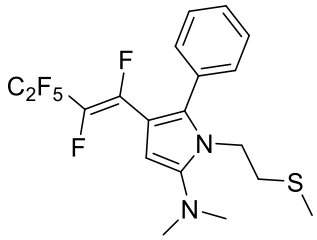
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 40/1–20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.38 (m, 3H), 7.37–7.32 (m, 2H), 6.14 (dh, J = 3.0, 1.0 Hz, 1H), 4.02–3.96 (m, 2H), 3.35–3.28 (m, 2H), 3.14 (s, 3H), 2.72 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.59 (s, 3F), -118.99 (dd, J = 26.4, 13.1 Hz, 2F), -138.91 (dtd, J = 132.7, 26.9, 5.9 Hz, 1F), -173.13–-173.62 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8 (dd, J = 253.1, 39.9 Hz), 146.3, 135.4–132.2 (m, 1C), 132.0, 130.8, 130.3, 128.3, 128.2, 107.2 (dd, J = 22.9, 5.5 Hz), 95.7 (dd, J = 10.6, 6.1 Hz), 70.9, 58.6, 45.8, 42.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{20}F_7N_2O$ $[M+H]^+$ 425.1458, found: 425.1460.



(*E*)-*N*,*N*-Dimethyl-1-(2-(methylthio)ethyl)-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (59):

Yield = 40% (53.5 mg). Yellow oil.

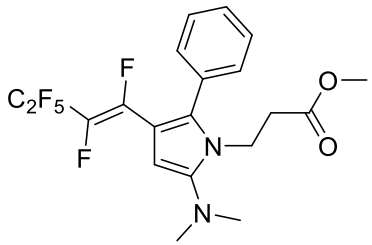
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.38 (m, 3H), 7.35–7.31 (m, 2H), 6.11 (dt, J = 2.9, 0.8 Hz, 1H), 3.99–3.91 (m, 2H), 2.71 (s, 6H), 2.47–2.40 (m, 2H), 1.78 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.56 (d, J = 7.6 Hz, 3F), -118.96 (dd, J = 26.8, 13.2 Hz, 2F), -139.02 (dtd, J = 132.3, 26.6, 5.7 Hz, 1F), -173.19 (dtd, J = 131.8, 13.3, 6.4 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.7 (dd, J = 252.2, 39.4 Hz), 146.1, 135.4–132.2 (m, 1C), 131.9, 130.4, 130.2, 128.4, 128.3, 107.3 (dd, J = 23.1, 5.0 Hz), 95.6 (dd, J = 10.6, 6.3 Hz), 45.7, 42.6, 33.5, 14.9 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{20}F_7N_2S$ $[M+H]^+$ 441.1230, found: 441.1235.



Methyl (*E*)-3-(5-(dimethylamino)-3-(perfluorobut-1-en-1-yl)-2-phenyl-1*H*-pyrrol-1-yl) propanoate (60):

Yield = 35% (47.8 mg). Yellow solid. M.p. 52.6–53.3 ºC.

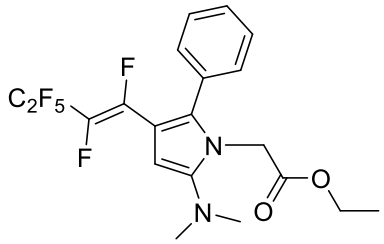
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.35 (m, 3H), 7.33–7.28 (m, 2H), 6.09 (dd, J = 2.8, 1.1 Hz, 1H), 4.11–4.01 (m, 2H), 3.59 (s, 3H), 2.69 (s, 6H), 2.47–2.41 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.58 (d, J = 6.0 Hz, 3F), -119.04 (dd, J = 26.6, 13.7 Hz, 2F), -138.44–-139.24 (m, 1F), -172.83–-173.27 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.12, 152.7 (dd, J = 252.5, 38.8 Hz), 145.9, 135.0–132.4 (m, 1C), 131.6, 130.5, 130.0, 128.44, 128.40, 107.5 (dd, J = 23.5, 5.5 Hz), 95.7 (dd, J = 10.5, 5.9 Hz), 51.7, 45.7, 39.0, 34.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{20}F_7N_2O_2$ $[M+H]^+$ 453.1408, found: 453.1400.



Ethyl (*E*)-2-(5-(dimethylamino)-3-(perfluorobut-1-en-1-yl)-2-phenyl-1*H*-pyrrol-1-yl)acetate (61):

Yield = 33% (44.3 mg). Yellow oil.

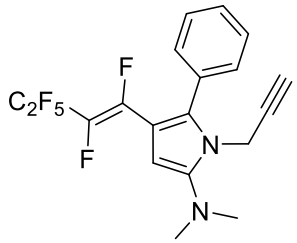
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 40/1–30/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.36 (m, 3H), 7.28 (ddt, J = 5.2, 3.1, 1.0 Hz, 2H), 6.16 (dd, J = 2.9, 1.1 Hz, 1H), 4.44 (s, 2H), 4.13 (q, J = 7.1 Hz, 2H), 2.67 (s, 6H), 1.19 (t, J = 7.1 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.56 (t, J = 4.5 Hz, 3F), -119.04 (ddd, J = 26.9, 13.4, 4.4 Hz, 2F), -134.49–-140.02 (m, 1F), -172.77–-173.27 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.0, 152.7 (dd, J = 253.3, 39.3 Hz), 146.1, 135.4–132.4 (m, 1C),, 131.5, 130.9, 130.2, 128.5, 128.3, 107.4 (dd, J = 23.5, 5.5 Hz), 95.9 (dd, J = 11.0, 6.2 Hz), 61.4, 45.5, 44.9, 14.1 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{20}F_7N_2O_2$ $[M+H]^+$ 453.1408, found: 453.1404.



(*E*)-*N*,*N*-Dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1-(prop-2-yn-1-yl)-1*H*-pyrrol-2-amine (62):

Yield = 38% (45.7 mg). Light yellow solid. M.p. 57.3–58.1 °C.

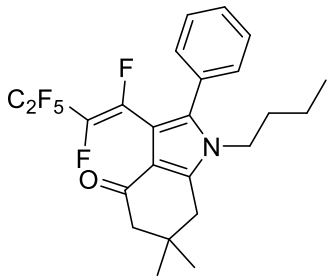
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1–20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.39 (m, 5H), 6.09 (dd, J = 2.6, 1.0 Hz, 1H), 4.48 (d, J = 2.5 Hz, 2H), 2.78 (s, 6H), 2.29 (t, J = 2.5 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.45–-84.68 (m, 3F), -119.12 (dd, J = 27.3, 13.6 Hz, 2F), -138.39–-138.97 (m, 1F), -172.62 (dtd, J = 133.3, 12.6, 6.4 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.6 (dd, J = 252.1, 39.8 Hz), 145.9, 135.7–132.3 (m, 1C), 131.3, 130.9, 130.3, 128.5, 128.2, 107.2 (dd, J = 23.2, 5.1 Hz), 95.3 (dd, J = 10.1, 5.8 Hz), 79.9, 72.3, 45.5, 32.9 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{16}F_7N_2$ $[M+H]^+$ 405.1196, found: 405.1192.



(*E*)-1-Butyl-6,6-dimethyl-3-(perfluorobut-1-en-1-yl)-2-phenyl-1,5,6,7-tetrahydro-4*H*-indol-4-one (63):

Yield = 33% (47.5 mg). Light yellow oil.

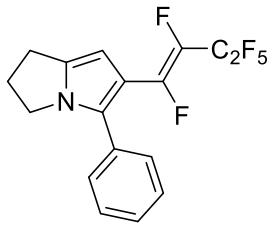
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1–10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 3H), 7.30 (qd, J = 4.3, 2.6 Hz, 2H), 3.82–3.76 (m, 2H), 2.69 (s, 2H), 2.41 (s, 2H), 1.52–1.42 (m, 2H), 1.19–1.10 (m, 8H), 0.77 (t, J = 7.4 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.68 (s, 3F), -120.13–-120.57 (m, 2F), -122.64 (dt, J = 143.9, 24.2 Hz, 1F), -164.39 (dd, J = 143.8, 17.0 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.0, 150.5 (dd, J = 257.9, 44.0 Hz), 143.0, 138.1–134.7 (m, 1C), 137.7 (d, J = 3.4 Hz), 129.9, 129.5, 129.1, 128.6, 117.4, 105.4 (dd, J = 27.8, 3.2 Hz), 52.1, 44.4, 36.3, 35.3, 32.6, 28.7, 19.6, 13.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{25}F_7NO$ $[M+H]^+$ 476.1819, found: 476.1812.



(*E*)-6-(Perfluorobut-1-en-1-yl)-5-phenyl-2,3-dihydro-1*H*-pyrrolizine (64):

Yield = 44% (47.8 mg). Yellow oil.

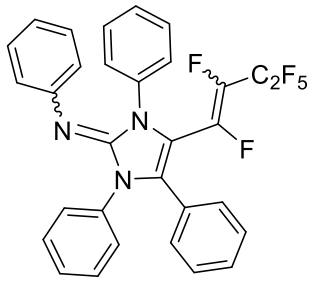
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.39 (m, 2H), 7.39–7.33 (m, 3H), 6.21 (dt, J = 2.5, 1.2 Hz, 1H), 3.93 (t, J = 7.0 Hz, 2H), 2.94 (t, J = 7.3 Hz, 2H), 2.51 (p, J = 7.2 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.52 (q, J = 3.7 Hz, 3F), -119.03 (dd, J = 26.4, 13.8 Hz, 2F), -136.03–-136.79 (m, 1F), -172.23 (dtd, J = 134.5, 13.4, 6.5 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8 (dd, J = 252.6, 40.6 Hz), 138.3, 135.6–132.1 (m, 1C), 131.9, 129.4, 128.7 (d, J = 0.8 Hz), 128.3, 127.8, 110.9 (dd, J = 23.9, 5.0 Hz), 100.1 (dd, J = 9.2, 5.7 Hz), 46.1, 27.6, 24.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{17}H_{13}F_7N$ $[M+H]^+$ 364.0931, found: 364.0934.



4-(Perfluorobut-1-en-1-yl)-*N*,1,3,5-tetraphenyl-1,3-dihydro-2*H*-imidazol-2-imine (65):

Yield = 77% (131.5 mg, undefined *Z*/*E* ratio). Yellow solid.

Purified by silica gel chromatography (petroleum ether/ethyl acetate, 20/1).

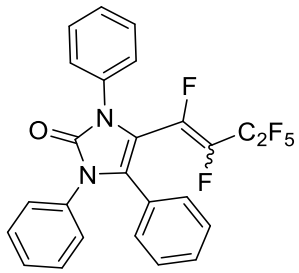
^{1}H NMR (400 MHz, $CDCl_3$) of undefined *Z*- /*E*-isomers: δ = 7.52–6.92 (m, 15H), 6.80–6.62 (m, 2H), 6.56–6.33 (m, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of isomer 1: δ = -84.52 (d, J = 4.6 Hz, 3F), -120.74 (dd, J = 24.4, 14.1 Hz, 2F), -125.67–-126.32 (m, 1F), -156.03 (dddt, J = 148.8, 14.7, 10.1, 4.7 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of isomer 2: δ = -83.16 (d, J = 9.1 Hz, 3F), -96.57 (d, J = 24.3 Hz, 1F), -119.18 (dd, J = 30.5, 18.0 Hz, 2F), -141.48 (dtt, J = 32.9, 18.0, 9.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of undefined *Z*- /*E*-isomers: δ = 147.9, 145.2 (dd, J = 258.4, 42.5 Hz), 144.0, 141.4–137.8 (m, 1C), 135.9, 135.6, 132.1 (dd, J = 7.0, 2.3 Hz), 129.1, 128.9, 128.7, 128.6, 128.5, 128.4, 127.8, 127.7, 127.5, 127.2, 127.0 (d, J = 2.8 Hz), 122.2, 120.0, 110.3 (dd, J = 26.0, 4.8 Hz) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{31}H_{21}F_7N_3$ $[M+H]^+$ 568.1618, found: 568.1624.



4-(Perfluorobut-1-en-1-yl)-1,3,5-triphenyl-1,3-dihydro-2*H*-imidazol-2-one (66):

Yield = 63% (93.8 mg, *E*/*Z* = 5/1). Light yellow oil.

Purified by silica gel chromatography (petroleum ether/ethyl acetate, 10/1).

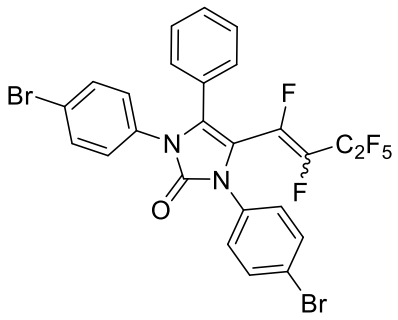
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.53–7.45 (m, 4H), 7.44–7.38 (m, 1H), 7.37–7.30 (m, 4H), 7.30–7.26 (m, 2H), 7.26–7.21 (m, 2H), 7.19–7.11 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -84.37 (t, J = 3.9 Hz, 3F), -120.62–-120.85 (m, 2F), -127.14–-127.74 (m, 1F), -155.75–-156.87 (m, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -83.25 (d, J = 9.0 Hz, 3F), -96.00 (d, J = 355.7 Hz, 1F), -119.65 (d, J = 17.4 Hz, 2F), -140.84 (ddp, J = 26.7, 17.8, 9.0 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 151.5, 145.1 (dd, J = 258.8, 43.1 Hz), 141.3–138.0 (m, 1C), 134.2, 134.1, 129.9–129.8 (m, 1C), 129.4, 129.0, 128.8, 128.7, 128.2, 127.9, 127.4, 126.8 (d, J = 2.4 Hz), 126.3, 125.9, 107.6 (dd, J = 26.9, 4.9 Hz) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{25}H_{16}F_7N_2O$ $[M+H]^+$ 493.1145, found: 493.1147.



1,3-Bis(4-bromophenyl)-4-(perfluorobut-1-en-1-yl)-5-phenyl-1,3-dihydro-2*H*-imidazol-2-one (67):

Yield = 70% (138.3 mg, *E*/*Z* = 3.3/1). Yellow oil.

Purified by silica gel chromatography (petroleum ether/ethyl acetate, 10/1).

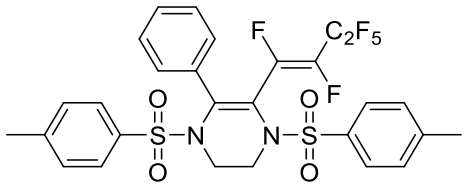
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.66–7.60 (m, 2H), 7.50–7.43 (m, 2H), 7.41–7.29 (m, 5H), 7.19–7.07 (m, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -84.29 (d, *J* = 5.6 Hz, 3F), -120.68 (dd, *J* = 25.1, 13.1 Hz, 2F), -127.72–-128.27 (m, 1F), -155.20–-155.95 (m, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -83.24 (d, *J* = 8.8 Hz, 3F), -96.29 (d, *J* = 20.8 Hz, 1F), -119.63 (dd, *J* = 17.6, 9.7 Hz, 2F), -139.68 (ddp, *J* = 26.8, 17.8, 8.8 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 151.0, 144.6 (dd, *J* = 258.9, 43.1 Hz), 141.5–137.9 (m, 1C), 133.1, 132.6, 132.2, 129.8, 128.9, 128.74, 128.69, 127.8, 127.3, 126.17, 126.15 (d, *J* = 2.4 Hz), 122.1, 121.9, 107.5 (dd, *J* = 27.0, 5.1 Hz) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{25}H_{14}Br_2F_7N_2O$ $[M+H]^+$ 648.9356, found: 648.9356.



(*E*)-5-(Perfluorobut-1-en-1-yl)-6-phenyl-1,4-ditosyl-1,2,3,4-tetrahydropyrazine (68):

Yield = 28% (55.2 mg). Light yellow solid. M.p. 115.8–116.8 °C.

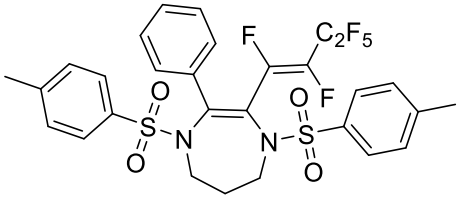
Purified by silica gel chromatography (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.62 (m, 2H), 7.39–7.34 (m, 2H), 7.34–7.28 (m, 1H), 7.21–7.07 (m, 8H), 3.50–3.32 (m, 4H), 2.48 (s, 3H), 2.40 (s, 3H) ppm.

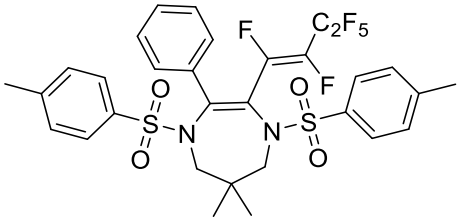
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.21–-84.31 (m, 3F), -121.01 (dd, *J* = 24.9, 12.8 Hz, 2F), -124.40–-124.92 (m, 1F), -158.17–-159.14 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.3 (dd, *J* = 262.6, 43.6 Hz), 145.1, 144.6, 138.5–135.1 (m, 1C), 135.4, 133.9 (d, *J* = 3.5 Hz), 133.6, 132.2 (2C), 130.2, 129.6, 129.3, 127.6, 127.3, 127.1, 109.9 (dd, *J* = 24.8, 4.5 Hz), 43.9, 43.3, 21.6, 21.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

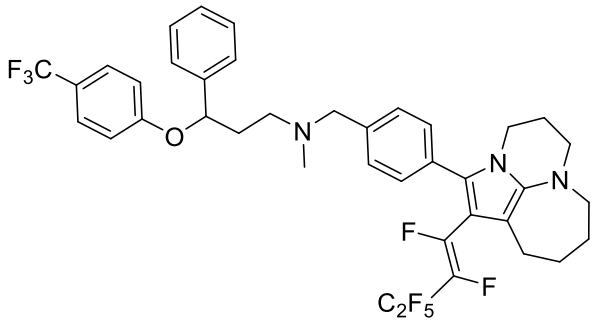
HRMS (m/z): calcd for $C_{28}H_{24}F_7N_2O_4S_2$ $[M+H]^+$ 649.1060, found: 649.1058.



(*E*)-2-(Perfluorobut-1-en-1-yl)-3-phenyl-1,4-ditosyl-4,5,6,7-tetrahydro-1*H*-1,4-diazepine (69):
Yield = 81% (161.6 mg). Light yellow solid. M.p. 182.7–183.1 ºC.
Purified by silica gel chromatography (DCM/MeOH, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 (dq, *J* = 6.3, 3.8 Hz, 1H), 7.07–6.95 (m, 8H), 3.95 (brs, 4H), 2.41 (s, 3H), 2.35–2.18 (m, 5H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.48 (s, 3F), -120.89 (dd, *J* = 24.4, 13.0 Hz, 2F), -124.8–-129.4 (m, 1F), -157.41 (d, *J* = 141.1 Hz, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.1 (dd, *J* = 262.4, 42.1 Hz), 144.3, 143.5, 138.8–135.3 (m, 1C), 137.5, 136.5, 132.1, 130.2, 129.7, 129.3, 129.1, 127.4, 127.2, 126.8, 50.5, 49.0, 28.6, 21.5, 21.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{29}H_{26}F_7N_2O_4S_2$ $[M+H]^+$ 663.1217, found: 663.1226.



(*E*)-6,6-Dimethyl-2-(perfluorobut-1-en-1-yl)-3-phenyl-1,4-ditosyl-4,5,6,7-tetrahydro-1*H*-1,4-diazepine (70):
Yield = 77% (160.5 mg). Light yellow solid. M.p. 185.0–186.3 ºC.
Purified by silica gel chromatography (petroleum ether/ethyl acetate, 4/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.80 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.10–6.99 (m, 4H), 6.97–6.89 (m, 4H), 3.97–2.67 (brs, 4H), 2.41 (s, 3H), 2.29 (s, 3H), 1.06 (s, 6H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -85.05 (t, *J* = 4.2 Hz, 3F), -117.01 (s, 1F), -121.33 (s ,2F), -156.95 (d, *J* = 144.3 Hz, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.9 (dd, *J* = 266.5, 48.4 Hz), 148.2, 144.1, 143.1, 139.2–135.7 (m, 1C), 137.0, 136.8, 131.5, 129.58, 129.55, 129.5, 129.0, 127.5, 127.3, 126.8, 122.51 (dd, *J* = 24.3, 3.1 Hz), 59.3, 57.8, 36.1, 23.8, 23.7, 21.4, 21.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{31}H_{30}F_7N_2O_4S_2$ $[M+H]^+$ 691.1530, found: 691.1525.



(*E*)-*N*-Methyl-*N*-(4-(1-(perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulen-2-yl)benzyl)-3-phenyl-3-(4-(trifluoromethyl)phenoxy)propan-1-amine (71):

Yield = 90% (203.7 mg). Yellow solid. M.p. 78.9–80.3 °C.

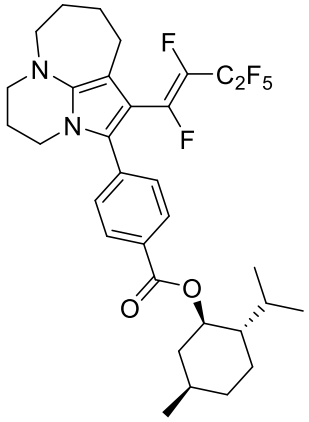
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 4/1–2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.5 Hz, 2H), 7.42–7.35 (m, 4H), 7.30 (td, J = 8.5, 3.6 Hz, 3H), 7.25–7.20 (m, 2H), 6.97 (d, J = 8.5 Hz, 2H), 5.45 (dd, J = 8.3, 4.6 Hz, 1H), 3.81 (t, J = 6.0 Hz, 2H), 3.57 (q, J = 13.3 Hz, 2H), 3.27 – 3.17 (m, 2H), 3.04 (dd, J = 6.6, 4.0 Hz, 2H), 2.78 – 2.66 (m, 1H), 2.65 – 2.48 (m, 3H), 2.28 (s, 4H), 2.07 (ddt, J = 31.2, 11.3, 5.4 Hz, 3H), 1.93 (h, J = 5.2 Hz, 2H), 1.71 (h, J = 5.5 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -61.27 (s, 3F), -84.42 (q, J = 3.8 Hz, 3F), -119.51 (dd, J = 25.2, 14.1 Hz, 2F), -121.60 (dt, J = 145.3, 25.6 Hz, 1F), -166.37 (dtd, J = 147.0, 14.1, 5.7 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.8, 153.0 (dd, J = 257.0, 43.0 Hz), 141.3, 138.5, 138.4, 137.6–134.1 (m, 1C), 129.5, 129.1, 128.8, 128.7, 127.7, 127.0 (d, J = 3.9 Hz), 126.6 (q, J = 3.8 Hz), 125.8, 122.5 (q, J = 3.8 Hz), 115.7, 106.5 (dd, J = 25.7, 3.4 Hz), 104.5, 78.2, 62.1, 56.9, 53.4, 50.5, 43.2, 41.9, 36.6, 31.5, 27.2, 26.0, 22.6 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{39}H_{38}F_{10}N_3O$ $[M+H]^+$ 754.2850, found: 754.2851.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(1-((*E*)-perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulen-2-yl)benzoate (72):

Yield = 40% (73.3 mg). Yellow solid. M.p. 88.4-89.9 °C.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

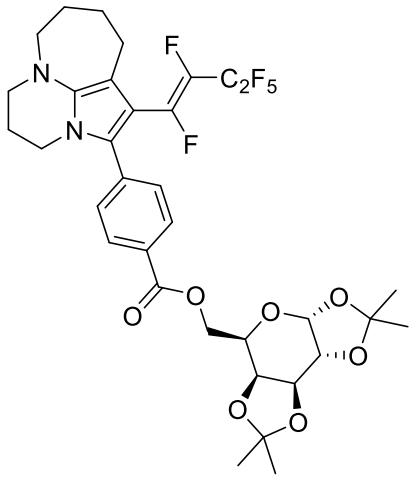
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–8.01 (m, 2H), 7.38–7.32 (m, 2H), 4.95 (td, J = 10.9, 4.4 Hz, 1H), 3.83 (t, J = 6.0 Hz, 2H), 3.27–3.16 (m, 2H), 3.06–2.94 (m, 2H), 2.51 (t, J = 5.8 Hz, 2H), 2.19–

2.10 (m, 1H), 2.00 (dddd, *J* = 16.9, 9.7, 6.9, 4.0 Hz, 3H), 1.87 (p, *J* = 5.8 Hz, 2H), 1.78–1.70 (m, 2H), 1.60 (dddd, *J* = 26.3, 10.8, 8.7, 4.6 Hz, 4H), 1.21–1.05 (m, 2H), 0.93 (dd, *J* = 6.8, 2.2 Hz, 6H), 0.90 – 0.83 (m, 1H), 0.81 (d, *J* = 6.9 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.46 (t, *J* = 4.4 Hz, 3F), -119.60–-119.81 (m, 2F), -121.64–-122.26 (m, 1F), -165.80 (ddd, *J* = 145.1, 18.0, 8.5 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.8, 152.4 (dd, *J* = 256.9, 42.7 Hz), 139.4, 137.7–134.2 (m, 1C), 135.1, 129.7, 129.2, 128.7, 125.7 (d, *J* = 4.7 Hz), 107.7 (dd, *J* = 25.6, 3.3 Hz), 105.5, 74.9, 56.9, 50.5, 47.2, 43.5, 40.9, 34.3, 31.4, 27.1, 26.4, 25.9, 23.6, 22.5, 22.0, 20.7, 16.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{32}H_{38}F_7N_2O_2$ $[M+H]^+$ 615.2816, found: 615.2819.



((3*aR*,5*R*,5*aS*,8*aS*,8*bR*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-(1-((*E*)-perfluorobut-1-en-1-yl)-4, 5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulen-2-yl)benzoate (73):

Yield = 51% (109.9 mg). Yellow oil.

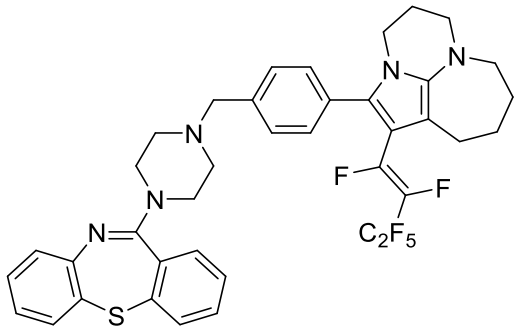
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.33 (dd, *J* = 8.5, 2.1 Hz, 2H), 5.57 (d, *J* = 4.9 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.53 (dd, *J* = 11.5, 4.8 Hz, 1H), 4.43 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.37–4.31 (m, 2H), 4.19 (ddd, *J* = 7.2, 4.9, 1.9 Hz, 1H), 3.82 (t, *J* = 5.9 Hz, 2H), 3.24–3.17 (m, 2H), 3.04–2.96 (m, 2H), 2.50 (t, *J* = 5.7 Hz, 2H), 2.06–1.97 (m, 2H), 1.90–1.82 (m, 2H), 1.63 (h, *J* = 5.5 Hz, 2H), 1.52 (s, 3H), 1.48 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.45 (d, *J* = 5.1 Hz, 3F), -119.75 (dd, *J* = 25.6, 14.5 Hz, 2F), -122.07 (dtd, *J* = 146.9, 24.9, 5.4 Hz, 1F), -165.52–-166.05 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1, 152.3 (dd, *J* = 257.3, 43.3 Hz), 139.5, 137.7–134.2 (m, 1C), 135.4, 129.8, 128.7, 128.3, 125.6 (d, *J* = 4.3 Hz), 109.7, 108.8, 107.7 (dd, *J* = 25.7, 3.4 Hz), 105.6, 96.3, 71.1, 70.7, 70.5, 66.1, 63.9, 56.8, 50.4, 43.5, 31.4, 27.1, 25.9, 24.9, 24.4, 22.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{34}H_{38}F_7N_2O_7$ $[M+H]^+$ 719.2562, found: 719.2567.



(*E*)-11-(4-(4-(1-(Perfluorobut-1-en-1-yl)-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulen-2-yl)benzyl)piperazin-1-yl)dibenzo[*b*,*f*][1,4]thiazepine (74):

Yield = 93% (206.6 mg). Yellow solid. M.p. 139.6–141.2 °C.

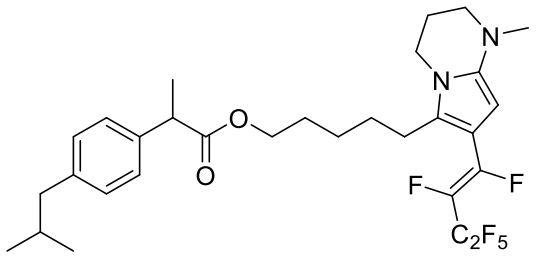
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.28 (td, *J* = 6.9, 2.1 Hz, 2H), 7.23 (dq, *J* = 7.1, 2.6 Hz, 3H), 7.14 (td, *J* = 7.6, 1.5 Hz, 1H), 7.07 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.85 (td, *J* = 7.4, 1.6 Hz, 1H), 3.79–3.46 (m, 6H), 3.17–3.05 (m, 2H), 3.01–2.89 (m, 2H), 2.49 (ddd, *J* = 17.0, 10.9, 5.1 Hz, 6H), 1.93 (p, *J* = 5.8 Hz, 2H), 1.84 (p, *J* = 4.9 Hz, 2H), 1.62 (p, *J* = 5.4 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.39 (q, *J* = 4.5 Hz, 3F), -119.54 (dd, *J* = 26.0, 14.4 Hz, 2F), -121.83 (dtd, *J* = 146.8, 24.9, 5.4 Hz, 1F), -166.18–-166.70 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.7, 152.9 (dd, *J* = 256.7, 43.0 Hz), 148.8, 139.7, 138.4, 137.4–134.2 (m, 1C), 137.1, 134.0, 132.04, 131.99, 130.6, 129.6, 129.1, 129.04, 128.97, 128.9, 128.1, 127.9, 126.9 (d, *J* = 3.6 Hz), 125.2, 122.6, 106.4 (dd, *J* = 25.3, 3.0 Hz), 104.4, 62.6, 56.8, 52.8, 50.4, 43.1, 31.4, 27.1, 26.0, 22.5, 21.7 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{39}H_{35}F_7N_5S$ $[M+H]^+$ 740.2652, found: 740.2656.



(*E*)-5-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)pentyl 2-(4-isobutylphenyl)propanoate (75):

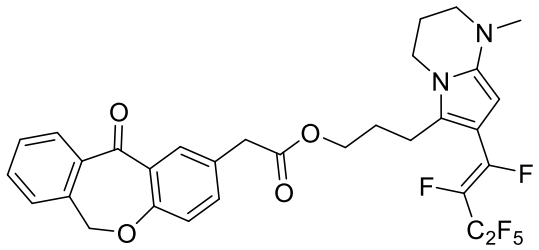
Yield = 61% (108.1 mg). Yellow oil.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 8/1).

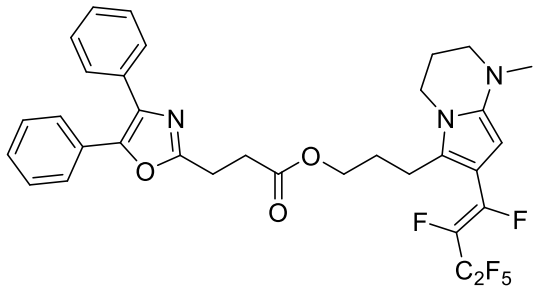
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.19 (m, 2H), 7.14–7.07 (m, 2H), 5.35 (dd, *J* = 3.5, 1.2 Hz, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 3.77 (t, *J* = 6.3 Hz, 2H), 3.70 (q, *J* = 7.1 Hz, 1H), 3.09–3.01 (m, 2H), 2.76 (s, 3H), 2.62–2.53 (m, 2H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.25–2.12 (m, 2H), 1.86 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.61 (p, *J* = 6.8 Hz, 2H), 1.48 (dd, *J* = 14.6, 7.5 Hz, 5H), 1.32 (td, *J* = 8.5, 4.1 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.56 (q, *J* = 4.0 Hz, 3F), -118.33–-118.52 (m, 2F), -142.73–-143.36 (m, 1F), -175.22 (ddt, *J* = 130.0, 18.4, 8.1 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.8, 153.9 (dd, J = 247.8, 40.5 Hz), 141.3, 140.4, 137.8, 134.7–131.2 (m, 1C), 129.2, 128.6, 127.1, 105.1 (dd, J = 22.7, 5.3 Hz), 83.2 (dd, J = 12.2, 7.9 Hz), 64.3, 48.1, 45.1, 45.0, 40.6, 39.6, 30.2, 29.8, 28.2, 25.4, 25.3 (d, J = 5.8 Hz), 22.8, 22.3, 18.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{30}H_{38}F_7N_2O_2$ $[M+H]^+$ 591.2816, found: 591.2819.



(*E*)-3-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)propyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (76):
Yield = 42% (79.3 mg). Orange oil.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1–1/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 2.4 Hz, 1H), 7.87 (dd, J = 7.7, 1.4 Hz, 1H), 7.59–7.53 (m, 1H), 7.50–7.41 (m, 2H), 7.36 (dd, J = 7.4, 1.3 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 5.32 (dd, J = 3.6, 1.3 Hz, 1H), 5.18 (s, 2H), 4.12 (t, J = 6.2 Hz, 2H), 3.71–3.63 (m, 4H), 3.01–2.95 (m, 2H), 2.72 (d, J = 0.8 Hz, 3H), 2.65 (ddd, J = 9.7, 5.7, 1.7 Hz, 2H), 2.16–2.07 (m, 2H), 1.87–1.77 (m, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.53 (t, J = 5.3 Hz, 3F), -118.44 (dd, J = 27.0, 13.5 Hz, 2F), -143.35–-144.19 (m, 1F), -174.56–-175.33 (m, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.8, 171.3, 160.4, 153.7 (dd, J = 248.6, 36.6 Hz), 141.4, 140.3, 136.4, 135.4, 135.0–131.4 (m, 1C), 132.8, 132.3, 129.3, 129.2, 127.80, 127.78, 127.1, 125.0, 121.0, 105.5 (dd, J = 22.5, 5.0 Hz), 83.4 (dd, J = 12.4, 7.8 Hz), 73.5, 64.1, 48.0, 40.5, 40.2, 39.5, 29.0, 22.7, 22.0 (d, J = 5.9 Hz) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{31}H_{28}F_7N_2O_4$ $[M+H]^+$ 625.1932, found: 625.1931.



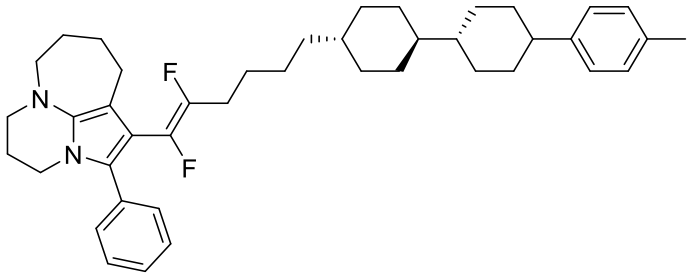
(*E*)-3-(1-Methyl-7-(perfluorobut-1-en-1-yl)-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrimidin-6-yl)propyl 3-(4,5-diphenyloxazol-2-yl)propanoate (77):
Yield = 45% (87.9 mg). Orange oil.
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.60 (m, 2H), 7.60–7.55 (m, 2H), 7.38–7.30 (m, 6H), 5.34 (dd, J = 3.6, 1.3 Hz, 1H), 4.16 (t, J = 6.2 Hz, 2H), 3.74 (t, J = 6.3 Hz, 2H), 3.20 (dd, J = 8.0, 6.9 Hz,

2H), 3.03–2.97 (m, 2H), 2.93 (t, J = 7.5 Hz, 2H), 2.74 (s, 3H), 2.72–2.66 (m, 2H), 2.17–2.09 (m, 2H), 1.85 (dq, J = 12.8, 6.4 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.52 (d, J = 5.8 Hz, 3F), -118.43 (dd, J = 27.3, 13.7 Hz, 2F), -143.58 (ddd, J = 130.2, 30.9, 24.7 Hz, 1F), -174.59–-175.12 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.0, 161.7, 153.7 (dd, J = 251.4, 41.1 Hz), 145.4, 141.4, 135.0, 134.9–131.5 (m, 1C), 132.4, 128.8, 128.6, 128.5, 128.4, 128.0, 127.8, 127.1, 126.4, 105.6 (dd, J = 22.5, 5.3 Hz), 83.4 (dd, J = 12.4, 8.1 Hz), 63.9, 48.0, 40.6, 39.6, 31.0, 29.0, 23.4, 22.7, 22.0 (d, J = 5.8 Hz) ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{33}H_{31}F_7N_3O_3$ $[M+H]^+$ 650.2248, found: 650.2250.



1-((*E*)-1,2-Difluoro-6-((1*S*,4*R*)-4'-(*p*-tolyl)-[1,1'-bi(cyclohexan)]-4-yl)hex-1-en-1-yl)-2-phenyl-4,5,6,7,8,9-hexahydro-3*H*-2*a*,5*a*-diazabenzo[*cd*]azulene (78):

Yield = 72% (135.6 mg, E/Z = 7.2/1). Light yellow solid.

Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 10/1).

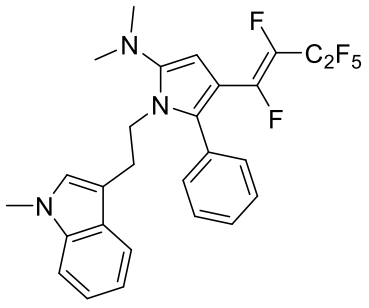
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.40–7.25 (m, 5H), 7.14 (s, 4H), 3.87–3.79 (m, 2H), 3.23–3.18 (m, 2H), 3.05–2.99 (m, 2H), 2.60–2.54 (m, 2H), 2.51–2.38 (m, 3H), 2.36 (s, 3H), 2.04 (td, J = 6.4, 3.4 Hz, 2H), 1.98–1.85 (m, 6H), 1.78 (d, J = 11.0 Hz, 4H), 1.72–1.64 (m, 2H), 1.55–1.41 (m, 4H), 1.32 (q, J = 9.1, 8.6 Hz, 3H), 1.20 (d, J = 8.5 Hz, 5H), 1.09–1.01 (m, 3H), 0.94–0.86 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -136.75–-137.22 (m, 1F), -146.84 (dt, J = 138.6, 23.1 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -120.93 (d, J = 23.7 Hz, 1F), -136.49 (q, J = 22.3 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 151.5 (dd, J = 238.4, 61.4 Hz), 144.9, 144.3 (dd, J = 228.8, 52.7 Hz), 138.0, 135.1, 131.9, 129.5, 128.9, 127.9, 126.63, 126.55, 125.6–125.5 (m, 1C), 109.1 (dd, J = 27.0, 2.6 Hz), 105.0, 57.1, 50.7, 44.2, 43.4, 43.1, 42.9, 37.8, 37.1, 34.7, 33.5, 31.7, 30.4, 30.0, 27.4, 26.1, 22.8 , 20.9 ppm.

HRMS (m/z): calcd for $C_{42}H_{55}F_2N_2$ $[M+H]^+$ 625.4328, found: 625.4329.



(*E*)-*N*,*N*-Dimethyl-1-(2-(1-methyl-1*H*-indol-3-yl)ethyl)-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (79):

Yield = 59% (92.0 mg). Yellow solid. M.p. 112.9–113.9 °C.

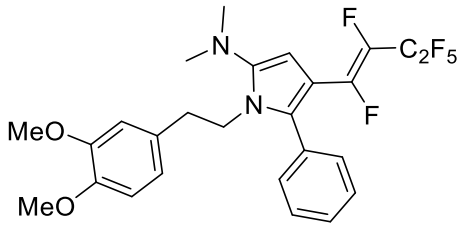
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 40/1–20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (qd, J = 4.3, 1.5 Hz, 3H), 7.30–7.26 (m, 2H), 7.22 (dt, J = 8.3, 1.0 Hz, 1H), 7.16 (ddt, J = 8.2, 5.4, 2.6 Hz, 1H), 7.00–6.93 (m, 2H), 6.60 (s, 1H), 6.13 (dd, J = 2.9, 1.0 Hz, 1H), 4.04–3.96 (m, 2H), 3.64 (s, 3H), 2.83–2.77 (m, 2H), 2.72 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.47 (q, J = 4.2, 3.6 Hz, 3F), -118.82 (dd, J = 26.6, 13.5 Hz, 2F), -138.32–-138.89 (m, 1F), -173.64 (ddt, J = 133.4, 13.4, 8.0 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.0 (dd, J = 252.7, 38.8 Hz), 146.1, 136.8, 135.3–132.0 (m, 1C), 132.2, 130.7, 130.2, 128.3, 128.1, 127.5, 126.6, 121.5, 118.7, 118.6, 110.8, 109.1, 107.0 (dd, J = 22.9, 4.9 Hz), 95.5 (dd, J = 10.6, 6.2 Hz), 45.8, 44.5, 32.4, 26.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{27}H_{25}F_7N_3$ $[M+H]^+$ 524.1931, found: 524.1937.



(*E*)-1-(3,4-Dimethoxyphenethyl)-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (80):

Yield = 56% (88.4 mg). Yellow solid. M.p. 54.2–54.4 °C.

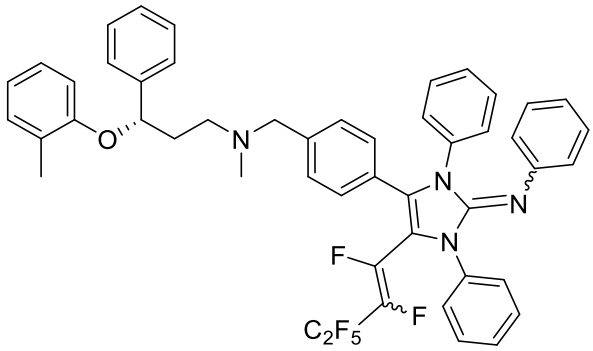
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1–20/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.36 (m, 3H), 7.22–7.18 (m, 2H), 6.69 (d, J = 8.1 Hz, 1H), 6.39 (dd, J = 8.1, 1.9 Hz, 1H), 6.15–6.09 (m, 2H), 4.00–3.94 (m, 2H), 3.83 (s, 3H), 3.73 (s, 3H), 2.68 (s, 6H), 2.62 (dd, J = 8.3, 6.6 Hz, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.57 (s, 3F), -118.85–-119.05 (m, 2F), -138.67 (dt, J = 132.9, 25.9 Hz, 1F), -173.27–-173.80 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.8 (dd, J = 251.3, 38.2 Hz), 148.7, 147.5, 146.2, 135.1–131.9 (m, 1C), 132.1, 130.8, 130.7, 130.1, 128.10, 128.05, 120.6, 111.5, 111.0, 106.9 (dd, J = 22.8, 5.3 Hz), 95.4 (dd, J = 10.6, 6.1 Hz), 55.8, 55.5, 45.6, 45.2, 36.1 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{26}H_{26}F_7N_2O_2$ $[M+H]^+$ 531.1877, found: 531.1872.



(*R*)-*N*-Methyl-*N*-(4-(5-(perfluorobut-1-en-1-yl)-1,3-diphenyl-2-(phenylimino)-2,3-dihydro-1*H*-imidazol-4-yl)benzyl)-3-phenyl-3-(*o*-tolyloxy)propan-1-amine (81):

Yield = 61% (152.3 mg, undefined *Z*/*E* ratio). Yellow oil.

Purified by silica gel chromatography (petroleum ether/ethyl acetate, 20/1).

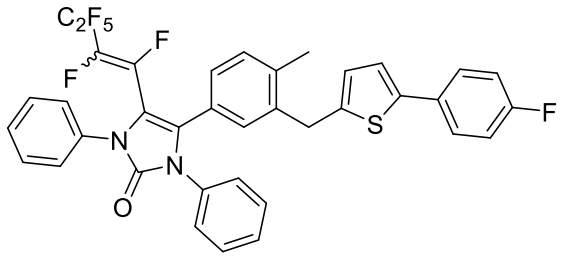
^{1}H NMR (400 MHz, $CDCl_3$) of undefined *Z*- /*E*-isomers: δ = 7.30 (q, *J* = 7.1 Hz, 4H), 7.16 (ddt, *J* = 20.2, 16.4, 10.4 Hz, 14H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.75 (q, *J* = 7.1 Hz, 3H), 6.60 (d, *J* = 8.3 Hz, 1H), 6.55–6.45 (m, 3H), 5.25 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.41 (d, *J* = 2.8 Hz, 2H), 2.65–2.45 (m, 2H), 2.26 (d, *J* = 7.2 Hz, 3H), 2.19 (p, *J* = 9.0, 8.5 Hz, 1H), 2.09 (d, *J* = 5.4 Hz, 3H), 2.00 (dt, *J* = 13.9, 7.0 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of isomer 1: δ = -84.50 (p, *J* = 3.9 Hz, 3F), -120.76 (ddd, *J* = 24.1, 14.0, 3.3 Hz, 2F), -125.62–-126.26 (m, 1F), -156.14 (dtt, *J* = 152.7, 13.6, 4.4 Hz, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of isomer 2: δ = -83.13 (t, *J* = 8.1 Hz, 3F), -96.48 (t, *J* = 24.5 Hz, 1F), -119.31 (dt, *J* = 33.2, 17.0 Hz, 2F), -141.65 (dddd, *J* = 43.3, 27.6, 18.3, 9.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of undefined *Z*- /*E*-isomers: δ = 156.1, 147.9, 145.2 (dd, *J* = 265.2, 41.7 Hz), 144.0, 142.2, 141.0–137.7 (m, 1C), 140.5, 135.9, 135.6, 132.2–132.1(m, 1C), 130.5, 128.8, 128.70, 128.67, 128.53, 128.50, 128.46, 127.8, 127.6, 127.43, 127.37, 127.2, 126.9, 126.5, 125.7, 125.5 (d, *J* = 2.8 Hz), 122.2, 120.1, 120.0, 112.6, 110.2 (dd, *J* = 26.1, 4.8 Hz), 77.6, 61.7, 54.0, 41.9, 36.7, 16.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{49}H_{42}F_7N_4O$ $[M+H]^+$ 835.3241, found: 835.3260.



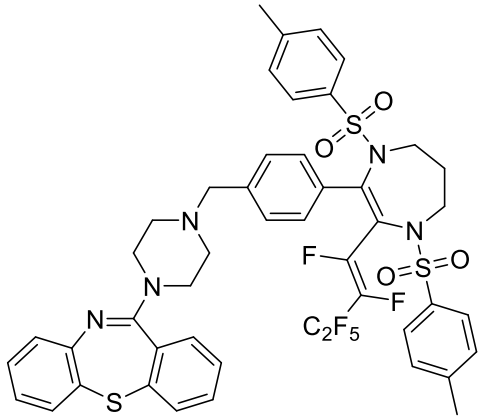
4-(3-((5-(4-Fluorophenyl)thiophen-2-yl)methyl)-4-methylphenyl)-5-(perfluorobut-1-en-1-yl)-1,3-diphenyl-1,3-dihydro-2*H*-imidazol-2-one (82):

Yield = 65% (136.0 mg, *E*/*Z* = 4/1). Pale yellow solid.

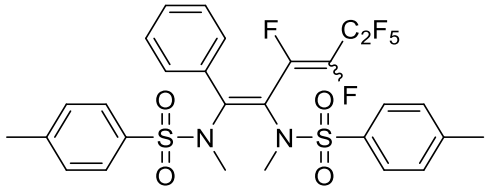
Purified by silica gel chromatography (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.50–7.42 (m, 6H), 7.41–7.35 (m, 1H), 7.32–7.27 (m, 2H), 7.25–7.18 (m, 3H), 7.14–7.09 (m, 1H), 7.08–7.00 (m, 3H), 6.98 (t, *J* = 3.5 Hz, 1H), 6.95 (dd, *J* = 6.0, 1.9 Hz, 1H), 6.42 (dd, *J* = 26.8, 3.5 Hz, 1H), 3.97 (s, 2H), 2.27 (d, *J* = 2.2 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -84.32–-84.34 (m, 3F), -114.74–-114.83 (m, 1F), -120.54 (dd, J = 24.1, 13.8 Hz, 2F), -126.68–-127.48 (m, 1F), -155.91–-156.86 (m, 1F) ppm.
^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -83.11 (d, J = 8.9 Hz, 3F), -95.45 (d, J = 20.9 Hz, 1F), -114.86 (d, J = 7.2 Hz, 1F), -119.44 (dd, J = 97.0, 17.5 Hz, 2F), -140.80 (dtt, J = 26.8, 17.8, 8.9 Hz, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 162.1 (d, J = 248.2 Hz), 151.5, 145.1 (dd, J = 258.7, 42.5 Hz), 141.9, 141.6, 140.8–137.5 (m, 1C), 138.7, 138.1, 134.3, 134.2, 130.8, 130.7, 129.8, 129.3, 129.0, 128.1, 127.8, 127.4, 127.1, 127.0, 126.1, 125.9, 124.6 (d, J = 1.9 Hz), 122.6, 115.7 (d, J = 21.8 Hz), 110.2 (dd, J = 26.1, 4.8 Hz), 107.3 (dd, J = 27.4, 4.6 Hz), 33.6, 19.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{37}H_{25}F_8N_2OS$ $[M+H]^+$ 697.1554, found: 697.1548.



(*E*)-11-(4-(4-(3-(Perfluorobut-1-en-1-yl)-1,4-ditosyl-4,5,6,7-tetrahydro-1H-1,4-diazepin-2-yl)benzyl)piperazin-1-yl)dibenzo[*b*,*f*][1,4]thiazepine (83):
Yield = 83% (240.6 mg). Light yellow solid. M.p. 115.8–117.5 °C.
Purified by silica gel chromatography (petroleum ether/ethyl acetate, 10/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.74 (m, 2H), 7.54–7.48 (m, 1H), 7.40 (dd, J = 7.7, 1.5 Hz, 1H), 7.35–7.26 (m, 5H), 7.18 (ddd, J = 8.5, 7.2, 1.6 Hz, 1H), 7.13–7.08 (m, 3H), 7.07–6.95 (m, 6H), 6.89 (td, J = 7.4, 1.5 Hz, 1H), 4.05–3.45 (m, 8H), 2.69–2.39 (m, 7H), 2.33 (s, 3H), 2.30–2.15 (m, 2H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.29 (s, 3F), -120.70 (dd, J = 24.2, 13.4 Hz, 2F), -126.73 (s, 1F), -157.72 (d, J = 140.9 Hz, 1F) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.7, 150.2 (dd, J = 264.5, 43.8 Hz), 148.8, 144.2, 143.5, 139.7, 139.5, 138.7–135.1 (m, 1C), 137.4, 136.4, 134.0, 132.07, 132.05, 131.2, 130.7, 130.2, 129.7, 129.0, 128.9, 128.2, 127.94, 127.87, 127.2, 126.9, 125.2, 122.7, 62.3, 52.7, 50.4, 48.8, 28.5, 21.5, 21.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{47}H_{43}F_7N_5O_4S_3$ $[M+H]^+$ 970.2360, found: 970.2360.



***N*,*N'*-((1*Z*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(*N*,4-dimethylbenzenesulfonamide) (85):**

Yield = 80% (155.2 mg, *E*/*Z* = 3.4/1). Light yellow solid.

Purified by silica gel chromatography (petroleum ether/ethyl acetate, 4/1).

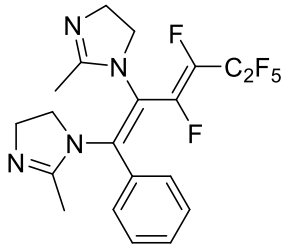
^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 7.90–7.81 (m, 0.54H), 7.78–7.76 (m, 1.39H), 7.68–7.63 (m, 0.67H), 7.48–7.46 (m, 1.4H), 7.41–7.30 (m, 3.23H), 7.29–7.25 (m, 1.04H), 7.23–7.20 (m, 2.90H), 7.15–7.03 (m, 1.83H), 3.23 (d, *J* = 6.0 Hz, 4.25H), 2.81 (d, *J* = 12.3 Hz, 1.40H), 2.68 – 2.67 (m, 0.35H), 2.50–2.39 (m, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*-isomers: δ = -84.30–-84.41 (m, 3F), -120.69 (dd, *J* = 25.1, 13.2 Hz, 2F), -135.61 (dt, *J* = 138.7, 24.4 Hz, 1F), -156.90–-157.69 (m, 1F) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *Z*-isomers: δ = -83.87 (s, 3F), -119.87 (s, 2F), -139.12 (s, 1F), -158.68 (d, *J* = 136.1 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) of *E*-isomers: δ = 150.5 (dd, *J* = 262.5, 42.1 Hz), 148.3–148.2 (m, 1C), 144.1, 144.0, 139.7–136.0 (m, 1C), 135.8, 135.0, 130.2, 129.9, 129.6, 129.44, 129.41, 128.6, 128.3, 127.7, 127.6, 37.8, 36.2, 21.49, 21.46 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{26}F_7N_2O_4S_2$ $[M+H]^+$ 651.1217, found: 651.1221.



1,1'-((1*Z*,3*E*)-3,4,5,5,6,6,6-Heptafluoro-1-phenylhexa-1,3-diene-1,2-diyl)bis(2-methyl-4,5-dihydro-1*H*-imidazole) (87):

Yield = 48% (64.6 mg). Red oil.

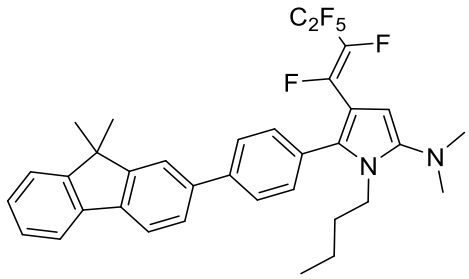
Purified by silica gel chromatography (DCM/MeOH, 50/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.43 (m, 1H), 7.42–7.37 (m, 2H), 7.36–7.32 (m, 2H), 3.95–3.84 (m, 4H), 3.70 (t, *J* = 9.2 Hz, 2H), 3.48 (t, *J* = 9.7 Hz, 2H), 1.95 (s, 3H), 1.40 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.50 (t, *J* = 4.3 Hz, 3F), -120.40–-120.54 (m, 2F), -134.20 (d, *J* = 141.5 Hz, 1F), -161.79 (d, *J* = 140.9 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.2, 159.9, 151.0 (dd, *J* = 259.5, 40.2 Hz), 143.2 (d, *J* = 3.8 Hz), 138.7–135.2 (m, 1C), 134.6 (d, *J* = 1.4 Hz), 130.5, 128.8, 128.7, 109.7–109.3 (m, 1C), 53.3, 52.6, 51.0, 48.4, 16.6, 13.8 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{20}F_7N_4$ $[M+H]^+$ 449.1571, found: 449.1568.



(*E*)-1-Butyl-5-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl)-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-1*H*-pyrrol-2-amine (89):

Yield = 91% (166.9 mg). Yellow oil.

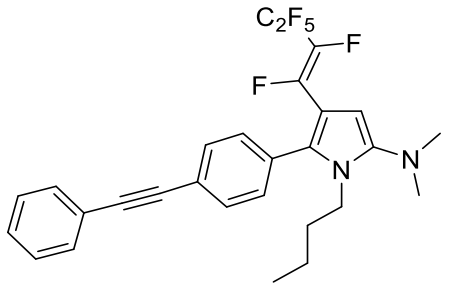
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 400/1–100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 7.9 Hz, 1H), 7.85–7.81 (m, 1H), 7.79 (d, J = 8.2 Hz, 3H), 7.71 (dd, J = 7.9, 1.7 Hz, 1H), 7.55–7.52 (m, 1H), 7.51–7.47 (m, 2H), 7.46–7.38 (m, 2H), 6.21 (dd, J = 3.1, 1.0 Hz, 1H), 3.93–3.87 (m, 2H), 2.78 (s, 6H), 1.62 (s, 6H), 1.52–1.44 (m, 2H), 1.16 (h, J = 7.3 Hz, 2H), 0.83 (t, J = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.40 (d, J = 7.1 Hz, 3F), -118.74 (dd, J = 27.2, 13.5 Hz, 2F), -138.44–-139.02 (m, 1F), -173.28–-173.83 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.3, 153.9, 153.0 (dd, J = 253.1, 39.4 Hz), 146.4, 141.0, 139.5, 138.8, 138.7, 135.3–131.9 (m, 1C), 131.1, 130.5, 130.3, 127.3, 127.1, 126.8, 126.1, 122.6, 121.2, 120.3, 120.1, 107.0 (dd, J = 22.7, 5.4 Hz), 95.3 (dd, J = 10.8, 6.3 Hz), 46.9, 45.7, 43.2, 32.5, 27.2, 19.6, 13.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{35}H_{34}F_7N_2$ $[M+H]^+$ 615.2605, found: 615.2609.



(*E*)-1-Butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-(4-(phenylethynyl)phenyl)-1*H*-pyrrol-2-amine (90):

Yield = 98% (153.7 mg). Brown oil.

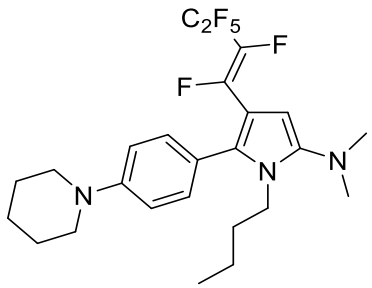
Purified by neutral alumina column chromatography (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.56 (m, 4H), 7.41–7.36 (m, 3H), 7.36–7.32 (m, 2H), 6.12 (dd, J = 2.9, 1.0 Hz, 1H), 3.84–3.78 (m, 2H), 2.72 (s, 6H), 1.42–1.32 (m, 2H), 1.08 (h, J = 7.4 Hz, 2H), 0.77 (t, J = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.50 (d, J = 5.3 Hz, 3F), -118.94 (dd, J = 25.4, 13.1 Hz, 2F), -138.40–-138.99 (m, 1F), -172.93–-173.37 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.7 (dd, J = 251.9, 39.4 Hz), 146.6, 135.4–131.9 (m, 1C), 132.3, 131.6, 131.4, 130.0, 129.8, 128.40, 128.37, 123.0, 122.9, 107.2 (dd, J = 23.0, 5.3 Hz), 95.3 (dd, J = 10.3, 6.0 Hz), 90.3, 89.0, 45.6, 43.2, 32.4, 19.6, 13.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{28}H_{26}F_7N_2$ $[M+H]^+$ 523.1979, found: 523.1976.



(*E*)-1-Butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-(4-(piperidin-1-yl)phenyl)-1*H*-pyrrol-2-amine (91):

Yield = 99% (150.2 mg). Orange oil.

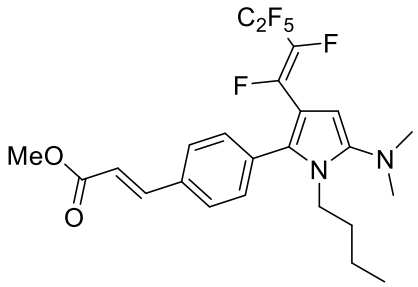
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.14 (m, 2H), 6.98–6.91 (m, 2H), 6.07 (dt, *J* = 3.1, 1.0 Hz, 1H), 3.80–3.72 (m, 2H), 3.27–3.19 (m, 4H), 2.69 (s, 6H), 1.77–1.71 (m, 4H), 1.60 (dtd, *J* = 9.6, 5.4, 2.2 Hz, 2H), 1.38 (tt, *J* = 7.7, 6.3 Hz, 2H), 1.08 (h, *J* = 7.4 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.52 (d, *J* = 6.0 Hz, 3F), -118.61–-118.88 (m, 2F), -138.92–-139.50 (m, 1F), -174.28–-174.72 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 153.2 (dd, *J* = 252.0, 38.4 Hz), 151.5, 145.8, 135.0–131.5 (m, 1C), 131.2, 130.8, 122.2, 115.4, 106.3 (dd, *J* = 22.5, 5.2 Hz), 94.9 (dd, *J* = 11.2, 6.5 Hz), 49.9, 45.7, 43.0, 32.5, 25.8, 24.2, 19.7, 13.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{25}H_{31}F_7N_3$ $[M+H]^+$ 506.2401, found: 506.2403.



Methyl (*E*)-3-(4-(1-butyl-5-(dimethylamino)-3-((*E*)-perfluorobut-1-en-1-yl)-1*H*-pyrrol-2-yl)phenyl)acrylate (92):

Yield = 84% (127.0 mg). Yellow-green solid. M.p. 44.5–45.7 °C.

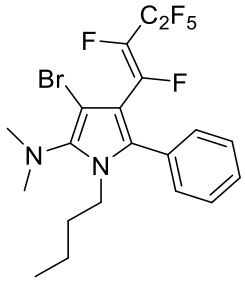
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 40/1–10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 16.0 Hz, 1H), 7.59–7.53 (m, 2H), 7.37–7.30 (m, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.08 (dd, *J* = 2.8, 1.1 Hz, 1H), 3.82 (s, 3H), 3.81–3.75 (m, 2H), 2.69 (s, 6H), 1.38–1.27 (m, 2H), 1.04 (h, *J* = 7.4 Hz, 2H), 0.72 (t, *J* = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.56 (q, *J* = 3.6 Hz, 3F), -119.05 (dd, *J* = 27.0, 13.5 Hz, 2F), -138.81 (dtd, *J* = 132.3, 27.0, 5.9 Hz, 1F), -172.72–-173.27 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.4, 152.7 (dd, *J* = 252.1, 39.3 Hz), 146.8, 144.2, 135.5–132.0 (m, 1C), 134.3, 133.9, 130.4, 129.6, 127.9, 118.1, 107.4 (dd, *J* = 23.2, 5.3 Hz), 95.4 (dd, *J* = 10.6, 6.3 Hz), 51.8, 45.6, 43.2, 32.4, 19.5, 13.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{24}H_{26}F_7N_2O_2$ $[M+H]^+$ 507.1877, found: 507.1877.



(*E*)-3-Bromo-1-butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrol-2-amine (93):

Yield = 90% (135.1 mg). Light yellow solid. M.p. 42.3–43.3 °C.

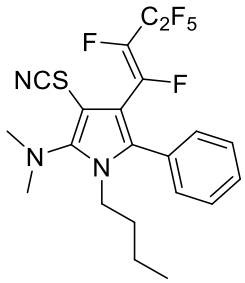
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 200/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.38 (m, 3H), 7.31–7.27 (m, 2H), 3.86–3.79 (m, 2H), 2.90 (s, 6H), 1.48–1.39 (m, 2H), 1.12 (h, J = 7.4 Hz, 2H), 0.77 (t, J = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.69 (d, J = 4.1 Hz, 3F), -120.08 (dd, J = 25.4, 14.5 Hz, 2F), -124.41 (dtd, J = 144.4, 25.5, 5.4 Hz, 1F), -164.00–-164.54 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.6 (dd, J = 257.8, 43.6 Hz), 139.8, 138.4–134.9 (m, 1C), 131.8, 130.7, 129.6, 128.6 (2C), 107.5 (dd, J = 26.6, 4.2 Hz), 89.8, 43.5, 43.3, 33.3, 19.7, 13.4 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{21}BrF_7N_2$ $[M+H]^+$ 501.0771, found: 501.0774.



(*E*)-1-Butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-3-thiocyanato-1*H*-pyrrol-2-amine (94):

Yield = 71% (102.3 mg). Light yellow oil.

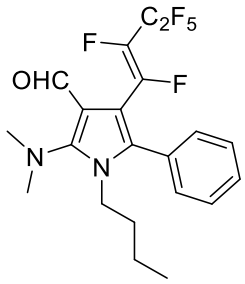
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 3H), 7.31–7.26 (m, 2H), 3.86–3.80 (m, 2H), 3.02 (s, 6H), 1.39 (tt, J = 7.6, 6.5 Hz, 2H), 1.09 (h, J = 7.4 Hz, 2H), 0.75 (t, J = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.67 (t, J = 4.3 Hz, 3F), -120.18 (dd, J = 24.1, 14.7 Hz, 2F), -124.16–-124.75 (m, 1F), -163.17–-163.74 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.5 (dd, J = 257.6, 43.7 Hz), 147.9, 139.0–135.5 (m, 1C), 133.5, 129.9, 129.4, 129.0, 128.7, 111.8, 110.2 (dd, J = 26.0, 4.0 Hz), 91.1, 44.0, 43.8, 32.5, 19.6, 13.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{21}F_7N_3S$ $[M+H]^+$ 480.1339, found: 480.1341.



(*E*)-1-Butyl-2-(dimethylamino)-4-(perfluorobut-1-en-1-yl)-5-phenyl-1*H*-pyrrole-3-carbaldehyde (95):

Yield = 87% (117.6 mg). Light yellow oil.

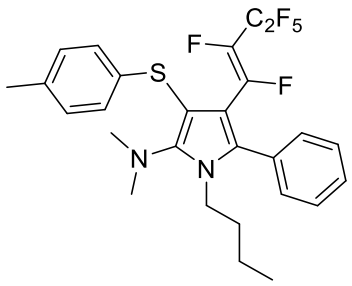
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 50/1–30/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (dd, J = 1.8, 0.8 Hz, 1H), 7.44–7.39 (m, 3H), 7.30–7.26 (m, 2H), 3.87–3.82 (m, 2H), 2.94 (s, 6H), 1.43–1.34 (m, 2H), 1.08 (h, J = 7.4 Hz, 2H), 0.74 (t, J = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.71 (t, J = 4.4 Hz, 3F), -120.29 (dd, J = 25.3, 13.7 Hz, 2F), -121.95 (dtd, J = 145.6, 25.0, 5.2 Hz, 1F), -164.46 (dtd, J = 145.7, 14.1, 6.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.1, 150.4 (dd, J = 256.9, 43.8 Hz), 149.9, 138.3–134.8 (m, 1C), 133.6 (d, J = 4.9 Hz), 129.8, 129.5, 128.9, 128.6, 115.4, 106.9 (dd, J = 27.8, 3.6 Hz), 44.0, 43.6, 32.3, 19.6, 13.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{21}H_{22}F_7N_2O$ $[M+H]^+$ 451.1615, found: 451.1615.



(*E*)-1-Butyl-*N*,*N*-dimethyl-4-(perfluorobut-1-en-1-yl)-5-phenyl-3-(*p*-tolylthio)-1*H*-pyrrol-2-amine (96):

Yield = 80% (130.6 mg). Light yellow solid. M.p. 80.7–82.1 °C.

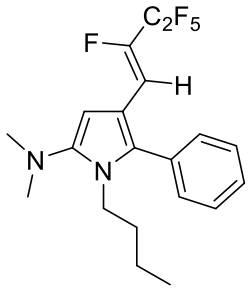
Purified by neutral alumina column chromatography (petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.39 (m, 3H), 7.37–7.32 (m, 2H), 7.04 (s, 4H), 3.92–3.86 (m, 2H), 2.85 (s, 6H), 2.28 (s, 3H), 1.50–1.40 (m, 2H), 1.13 (h, J = 7.4 Hz, 2H), 0.78 (t, J = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -84.83 (d, J = 5.0 Hz, 3F), -120.23 (dd, J = 25.3, 14.3 Hz, 2F), -121.98–-122.66 (m, 1F), -164.07–-164.64 (m, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.1 (dd, J = 258.4, 43.6 Hz), 147.0, 138.4–134.9 (m, 1C), 136.0, 134.4, 132.7 (d, J = 4.2 Hz), 130.9, 129.5, 129.3, 128.5, 128.4, 125.9, 111.1 (dd, J = 26.5, 4.0 Hz), 102.0, 44.2, 43.6, 32.8, 20.8, 19.7, 13.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{27}H_{28}F_7N_2S$ $[M+H]^+$ 545.1856, found: 545.1859.



(*Z*)-1-Butyl-4-(2,3,3,4,4,4-hexafluorobut-1-en-1-yl)-*N*,*N*-dimethyl-5-phenyl-1*H*-pyrrol-2-amine (97):

Yield = 72% (87.8 mg). Light yellow oil.

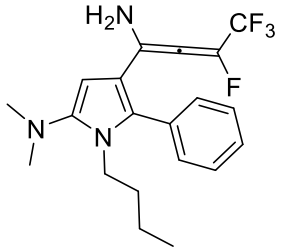
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 200/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.43 (m, 3H), 7.38–7.29 (m, 2H), 6.30 (d, J = 1.6 Hz, 1H), 5.21 (ddd, J = 46.6, 18.6, 3.8 Hz, 1H), 3.81–3.60 (m, 2H), 2.69 (s, 6H), 1.44–1.31 (m, 2H), 1.07 (h, J = 7.4 Hz, 2H), 0.72 (t, J = 7.3 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -82.70 (d, J = 10.4 Hz, 3F), -120.83–-128.72 (m, 2F), -202.41 (ddt, J = 46.1, 22.1, 11.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.6 (d, J = 18.7 Hz), 146.0, 136.8, 131.5, 130.4, 129.1, 128.6, 118.8, 97.1 (d, J = 5.5 Hz), 85.3 (ddd, J = 196.1, 31.5, 24.3 Hz), 45.6, 43.2, 32.3, 19.6, 13.3 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{23}F_6N_2$ $[M+H]^+$ 405.1760, found: 405.1753.



4-(1-Amino-3,4,4,4-tetrafluorobuta-1,2-dien-1-yl)-1-butyl-*N*,*N*-dimethyl-5-phenyl-1*H*-pyrrol-2-amine (98):

Yield = 86% (98.3 mg). Yellow oil.

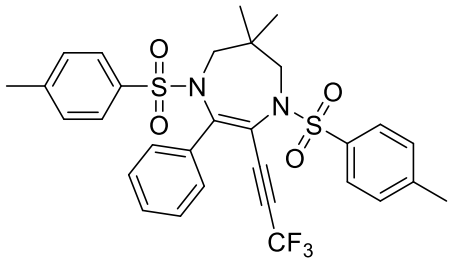
Purified by neutral alumina column chromatography (petroleum ether/ethyl acetate, 20/1–10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.38 (m, 3H), 7.38–7.34 (m, 2H), 6.39 (d, J = 5.6 Hz, 1H), 6.02 (brs, 2H), 3.82–3.71 (m, 2H), 2.71 (s, 6H), 1.38 (tt, J = 7.6, 6.5 Hz, 2H), 1.08 (h, J = 7.4 Hz, 2H), 0.74 (t, J = 7.4 Hz, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -67.21 (d, J = 17.4 Hz, 3F), -161.91 (qd, J = 17.4, 5.2 Hz, 1F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 182.8 (d, J = 23.7 Hz), 145.1 (d, J = 4.5 Hz), 139.8 (dd, J = 246.0, 2.1 Hz), 135.5, 133.1, 132.6–131.4 (m, 1C), 130.1, 128.2, 128.0, 120.6 (q, J = 277.7 Hz), 117.6 (d, J = 6.4 Hz), 97.2 (d, J = 50.0 Hz), 45.7, 42.8, 32.4, 19.6, 13.4 ppm.

HRMS (m/z): calcd for $C_{20}H_{24}F_4N_3$ $[M+H]^+$ 382.1901, found: 382.1897.



6,6-Dimethyl-2-phenyl-1,4-ditosyl-3-(3,3,3-trifluoroprop-1-yn-1-yl)-4,5,6,7-tetrahydro-1*H*-1,4-diazepine (104):

Yield = 25% (45.2 mg). White solid. 177.3–178.8 ºC.

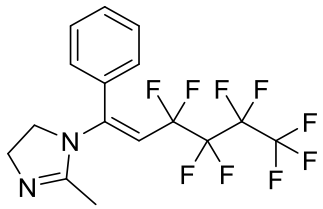
Purified by silica gel chromatography (DCM/MeOH, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 3H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 5.5 Hz, 4H), 7.06 (d, J = 8.0 Hz, 2H), 2.90 (d, J = 310.0 Hz, 3H), 2.41 (s, 3H), 2.36 (s, 3H), 1.05 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -50.78 (s, 3F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 152.7, 144.1, 143.6, 137.1, 136.6, 132.3, 130.1, 129.8, 129.5, 129.2, 127.9, 127.7, 127.5, 115.2, 114.1, 113.9 (q, J = 258.9 Hz), 82.0 (q, J = 6.8 Hz), 78.9 (q, J = 53.0 Hz), 59.8, 56.6, 36.1, 24.1, 21.5 ppm.

HRMS (m/z): calcd for $C_{30}H_{30}F_3N_2O_4S_2$ $[M+H]^+$ 603.1594, found: 603.1597.



(*E*)-2-Methyl-1-(3,3,4,4,5,5,6,6,6-nonafluoro-1-phenylhex-1-en-1-yl)-4,5-dihydro-1*H*-imidazole (107):

Yield = 35% (42.4 mg). Yellow oil.

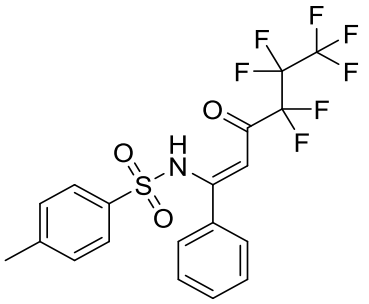
Purified by silica gel chromatography (DCM/MeOH, 70/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 3H), 7.38–7.33 (m, 2H), 5.62 (t, J = 14.6 Hz, 1H), 3.88 (t, J = 9.5 Hz, 2H), 3.67 (t, J = 9.5 Hz, 2H), 1.77 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.85 (d, J = 10.3 Hz, 3F), -106.96 (q, J = 13.3 Hz, 2F), -124.19 (q, J = 10.1 Hz, 2F), -125.38 (t, J = 11.3 Hz, 2F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.5, 149.3, 136.2, 130.9, 129.2, 127.3, 106.6 (t, J = 20.6 Hz), 53.0, 52.4, 14.7 ppm, carbons corresponding to the C_4F_9 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{16}H_{14}F_9N_2$ $[M+H]^+$ 405.1008, found: 405.1010.



(*Z*)-*N*-(4,4,5,5,6,6,6-Heptafluoro-3-oxo-1-phenylhex-1-en-1-yl)-4-methylbenzenesulfonamide (111):

Yield = 71% (99.4 mg). Yellow solid. M.p. 83.7–85.1 °C.

Purified by silica gel chromatography (petroleum ether/ethyl acetate, 20/1–10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.82 (brs, 1H), 7.54–7.49 (m, 1H), 7.39–7.32 (m, 4H), 7.28–7.25 (m, 2H), 7.21–7.17 (m, 2H), 5.79 (s, 1H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.48 (t, J = 9.0 Hz, 3F), -121.52 (q, J = 8.7 Hz, 2F), -126.65 (s, 2F) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 182.3 (t, J = 25.7 Hz), 163.2, 145.2, 135.8, 132.2, 131.8, 129.7, 129.1, 128.1, 127.6, 100.5, 21.6 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{15}F_7NO_3S$ $[M+H]^+$ 382.1901, found: 382.1897.

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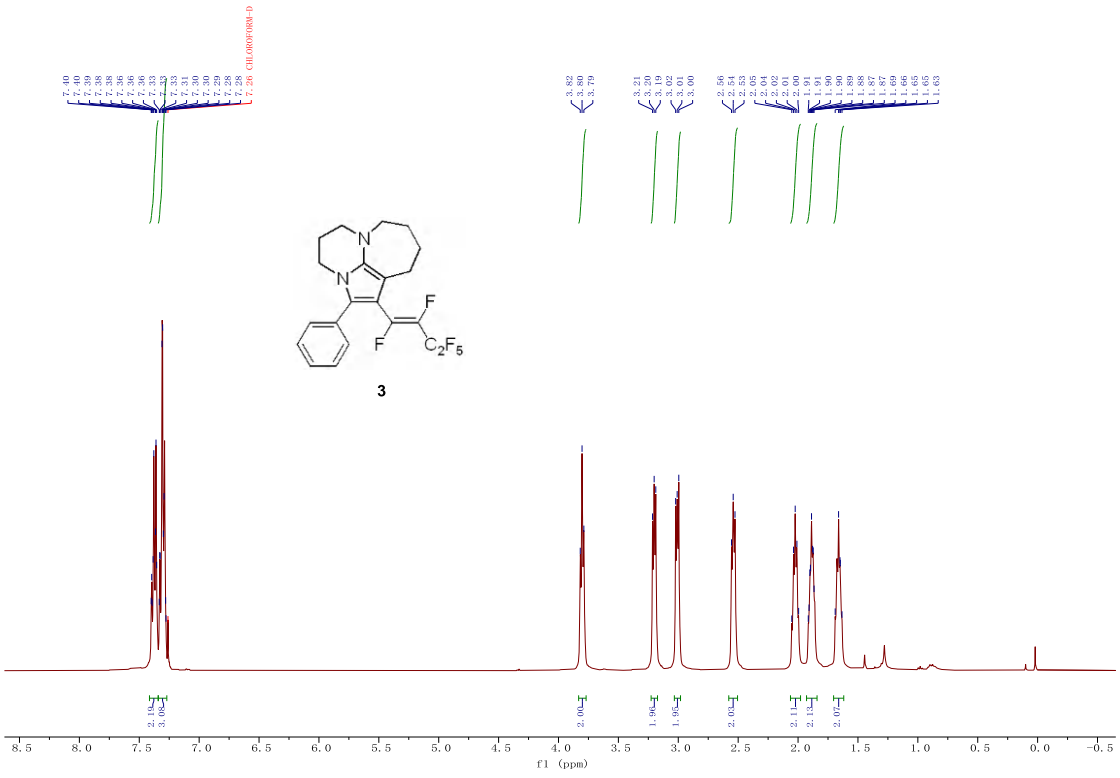
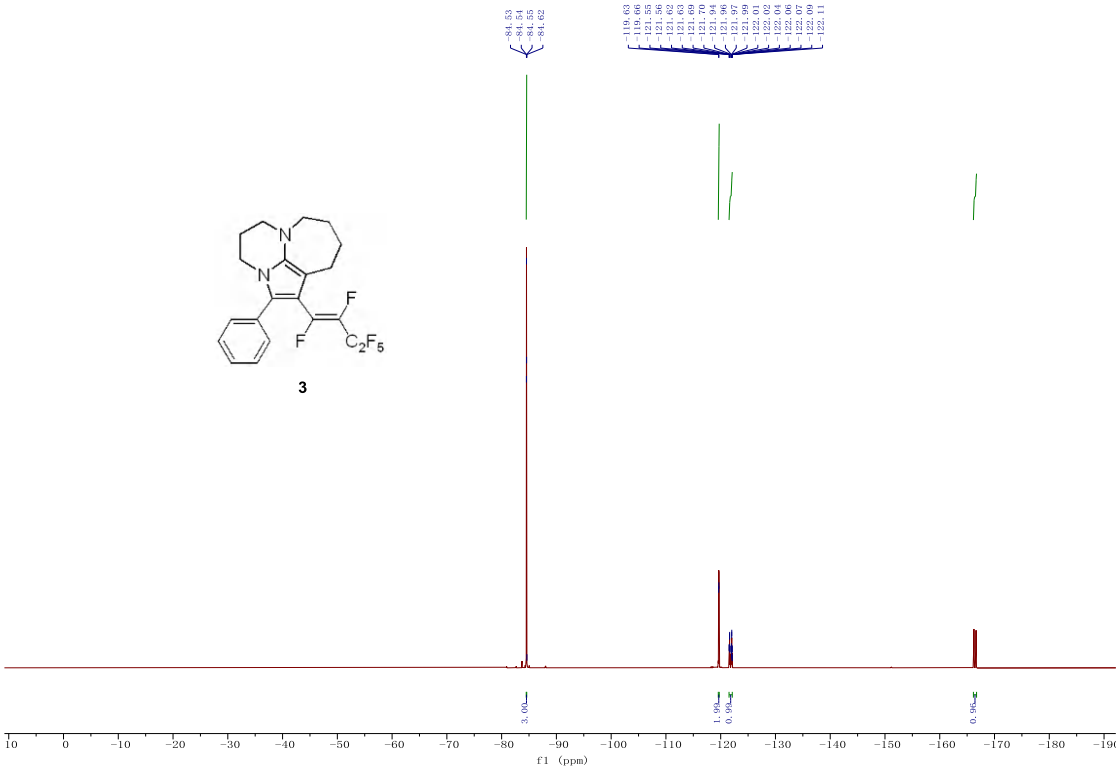
^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra of products

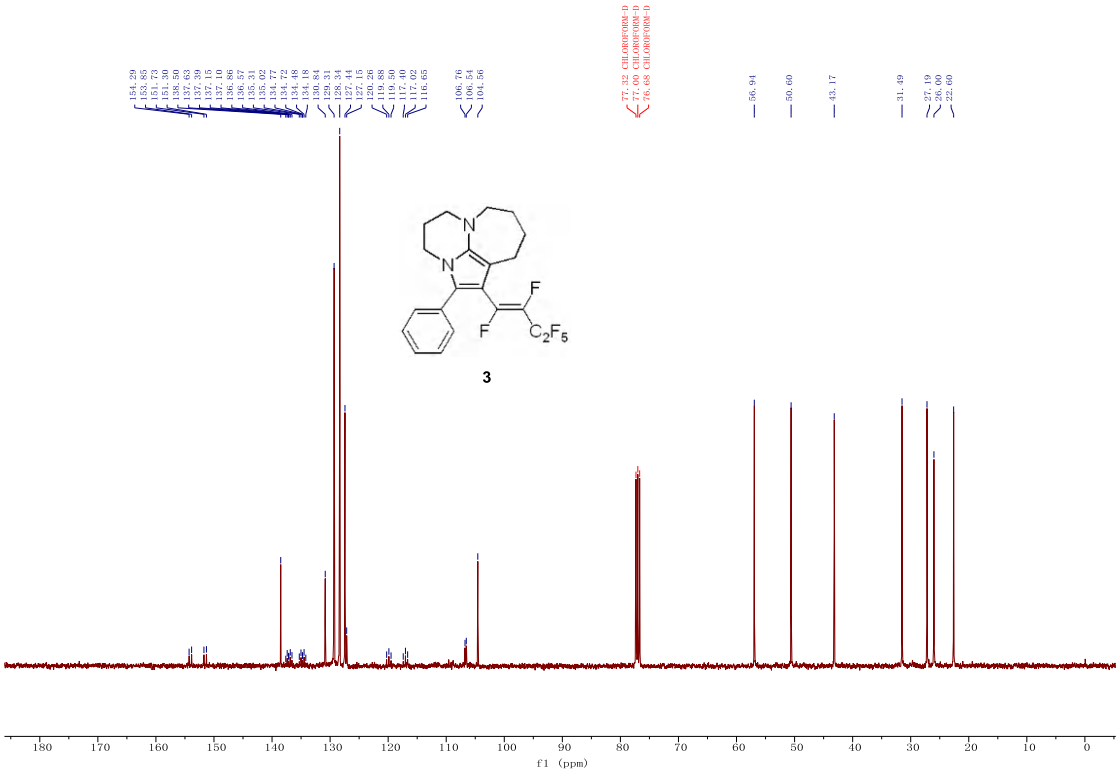
^{1}H NMR spectra of the product **3** (400 MHz, $CDCl_3$):



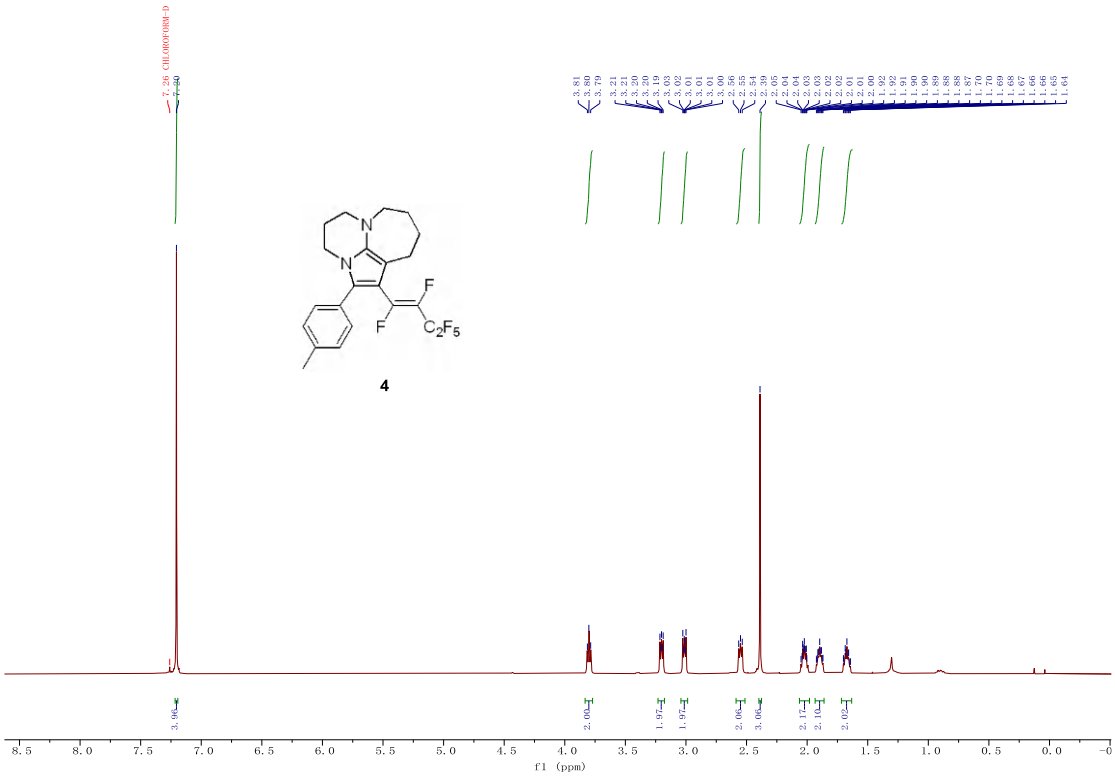
^{19}F NMR spectra of the product **3** (376 MHz, $CDCl_3$):



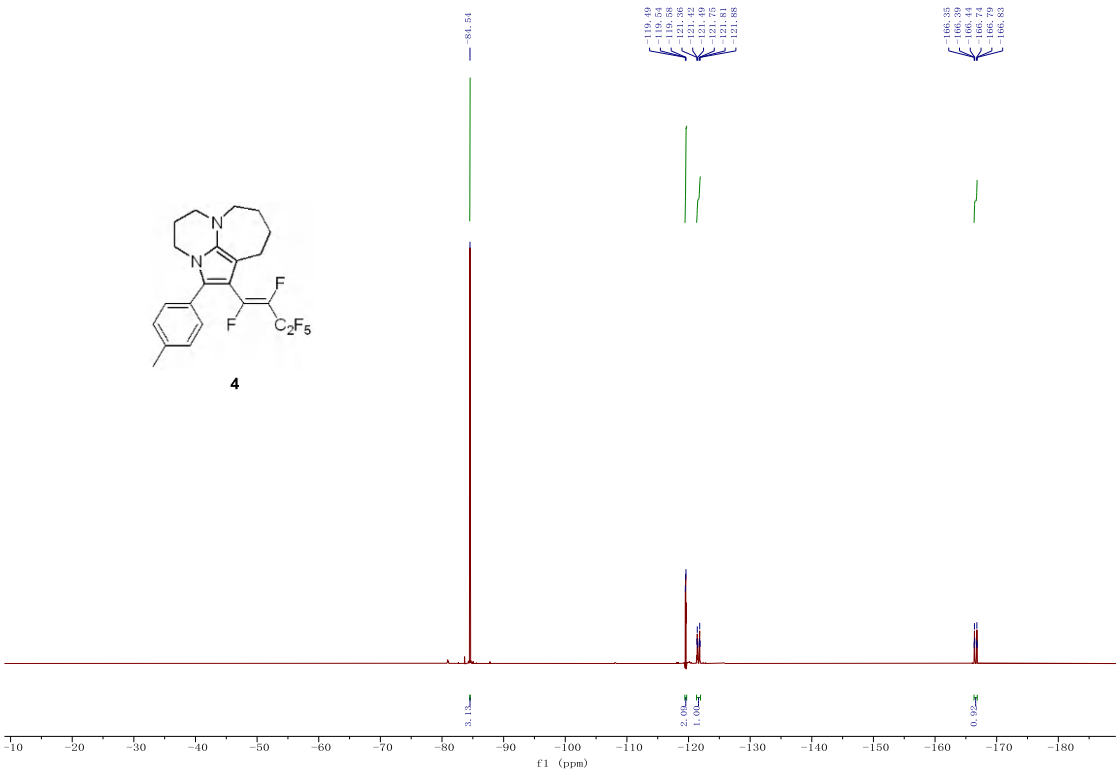
^{13}C NMR spectra of the product **3** (101 MHz, $CDCl_3$):



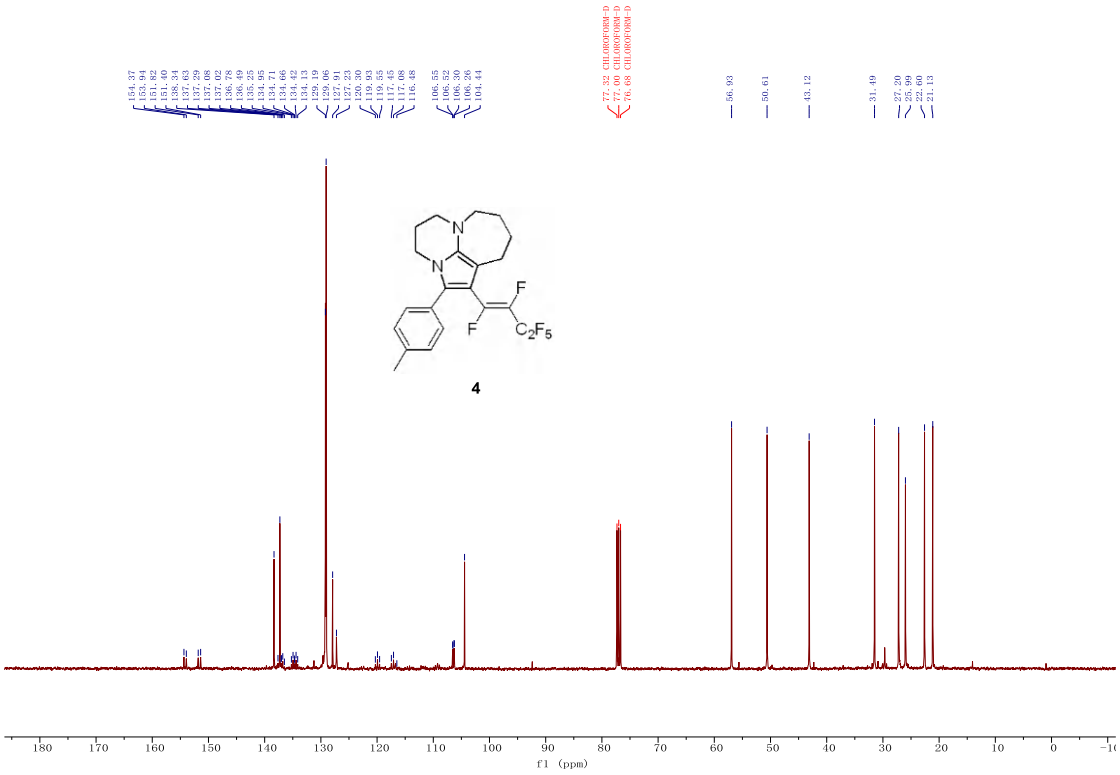
^{1}H NMR spectra of the product **4** (400 MHz, $CDCl_3$):



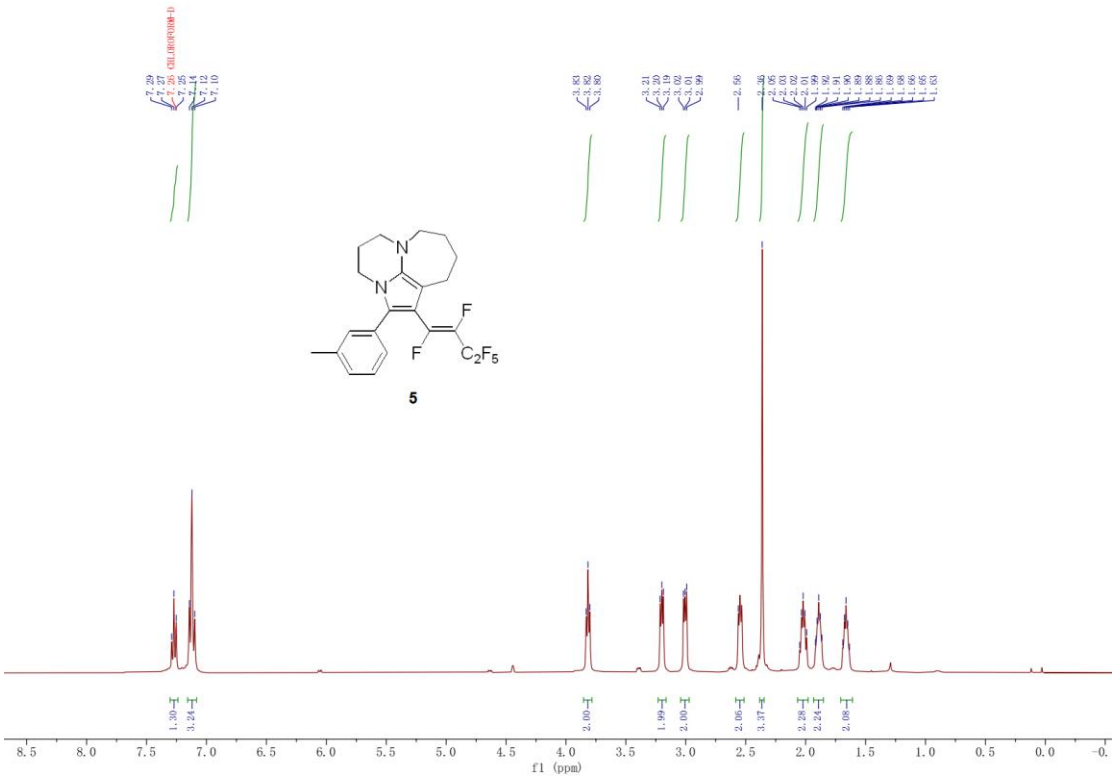
^{19}F NMR spectra of the product **4** (376 MHz, $CDCl_3$):



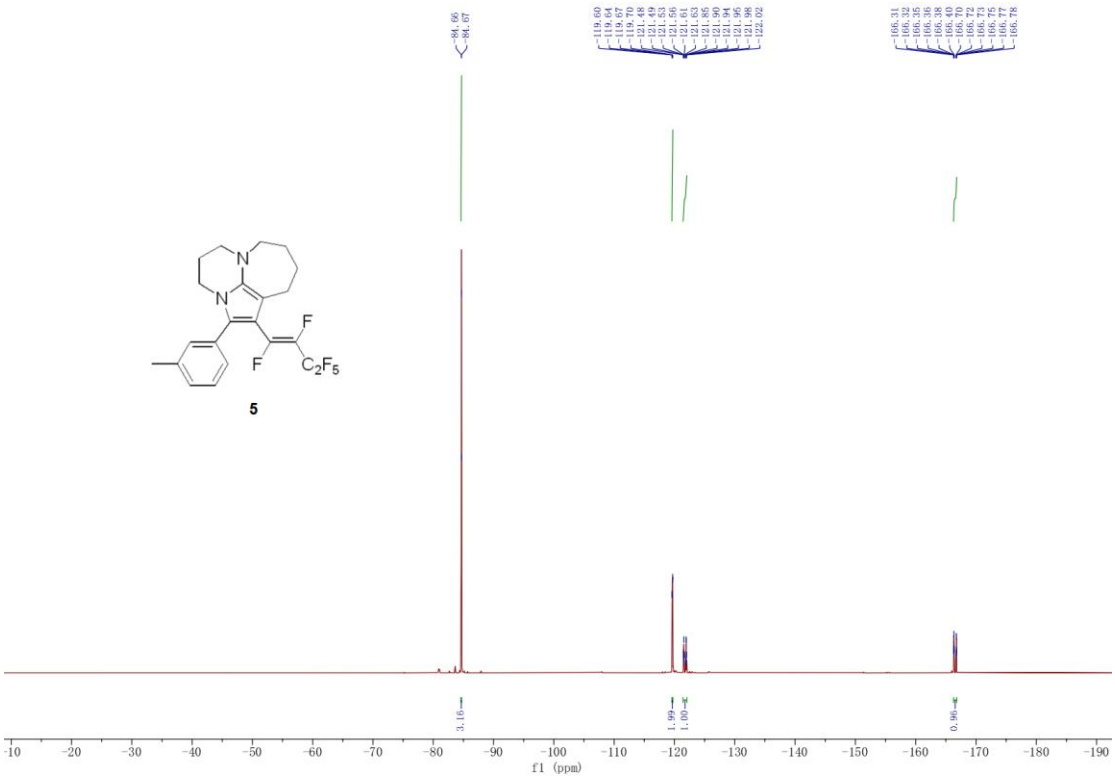
^{13}C NMR spectra of the product **4** (101 MHz, $CDCl_3$):



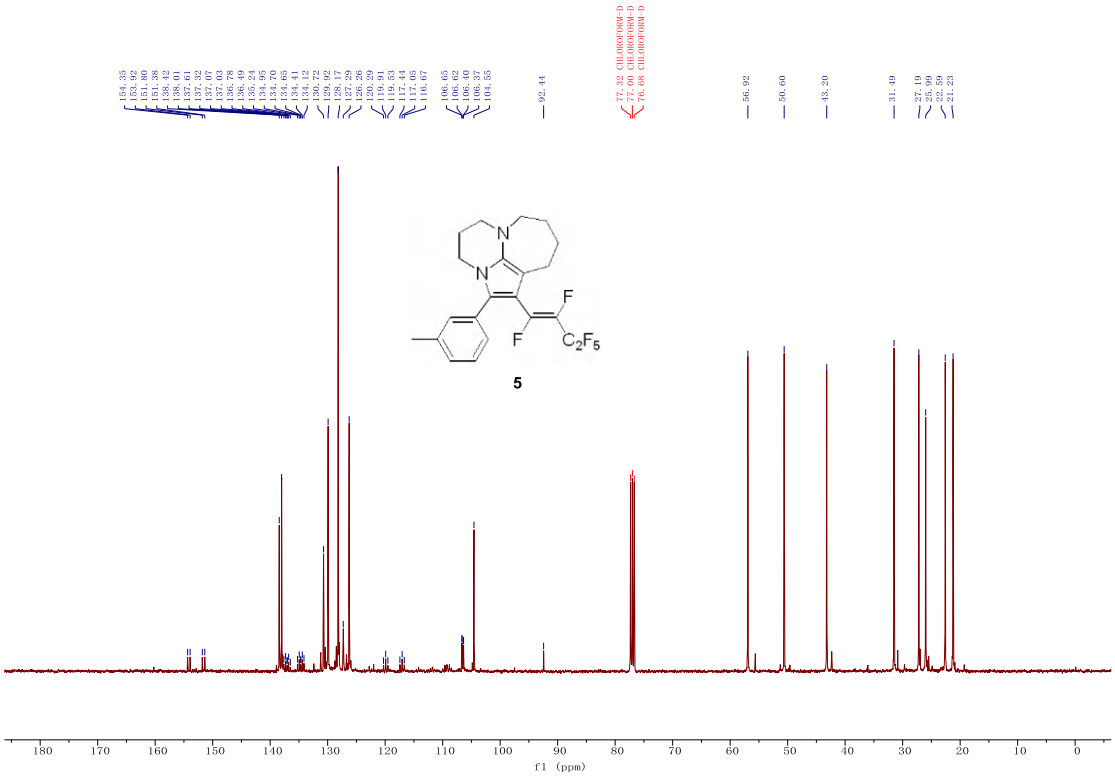
^{1}H NMR spectra of the product **5** (400 MHz, $CDCl_3$):



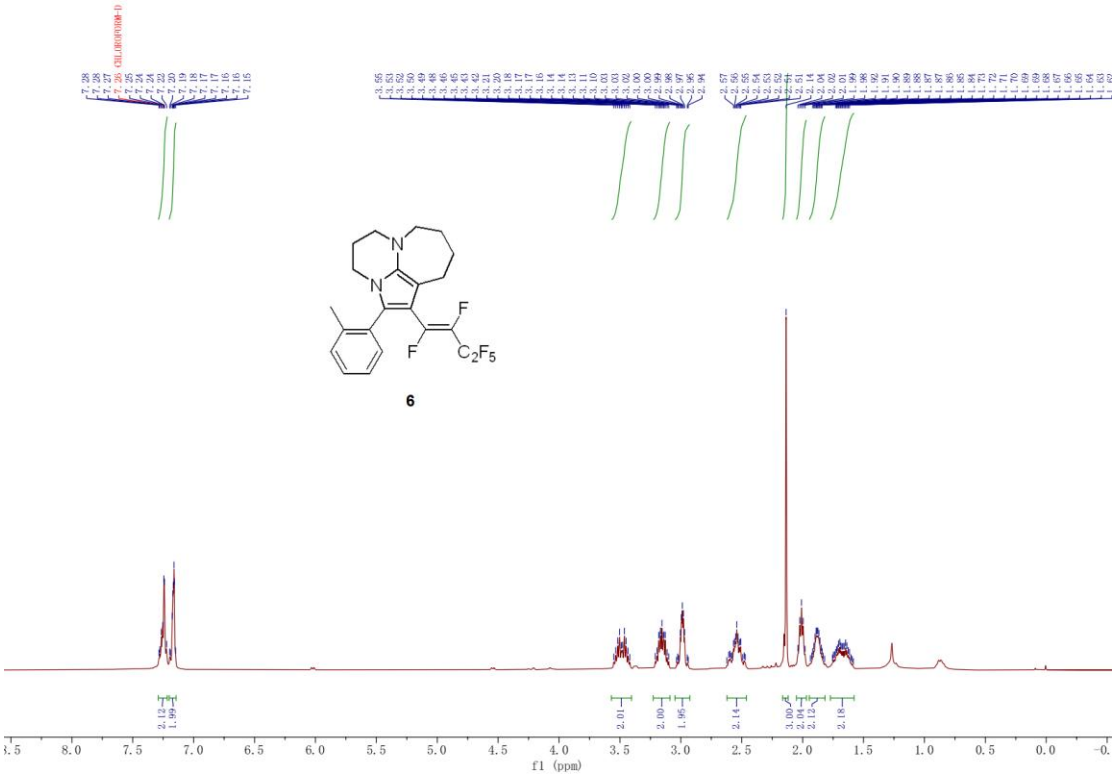
^{19}F NMR spectra of the product **5** (376 MHz, $CDCl_3$):



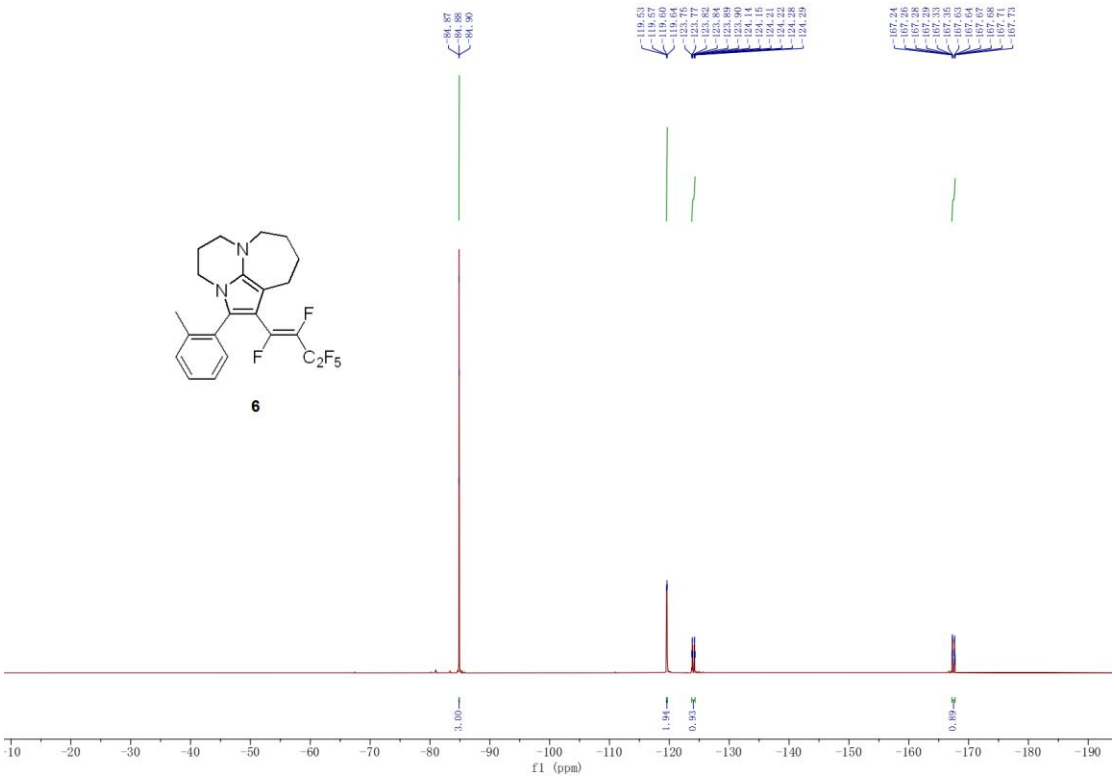
^{13}C NMR spectra of the product **5** (101 MHz, $CDCl_3$):



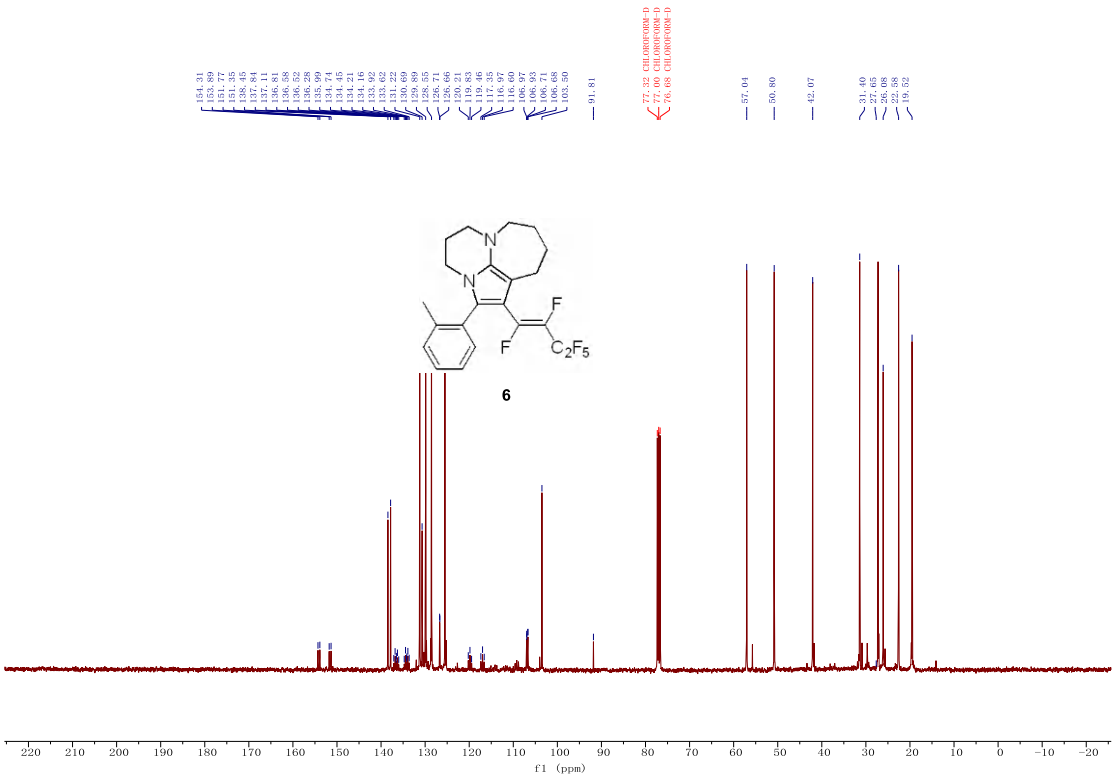
^{1}H NMR spectra of the product **6** (400 MHz, $CDCl_3$):



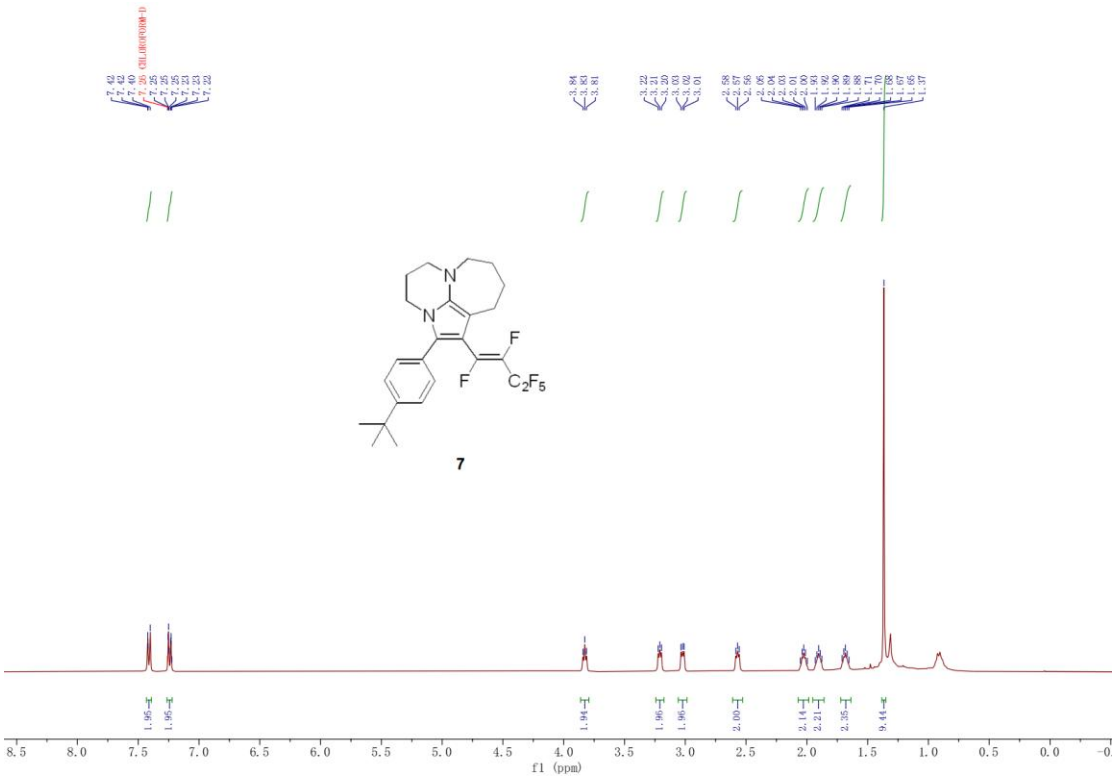
^{19}F NMR spectra of the product **6** (376 MHz, $CDCl_3$):



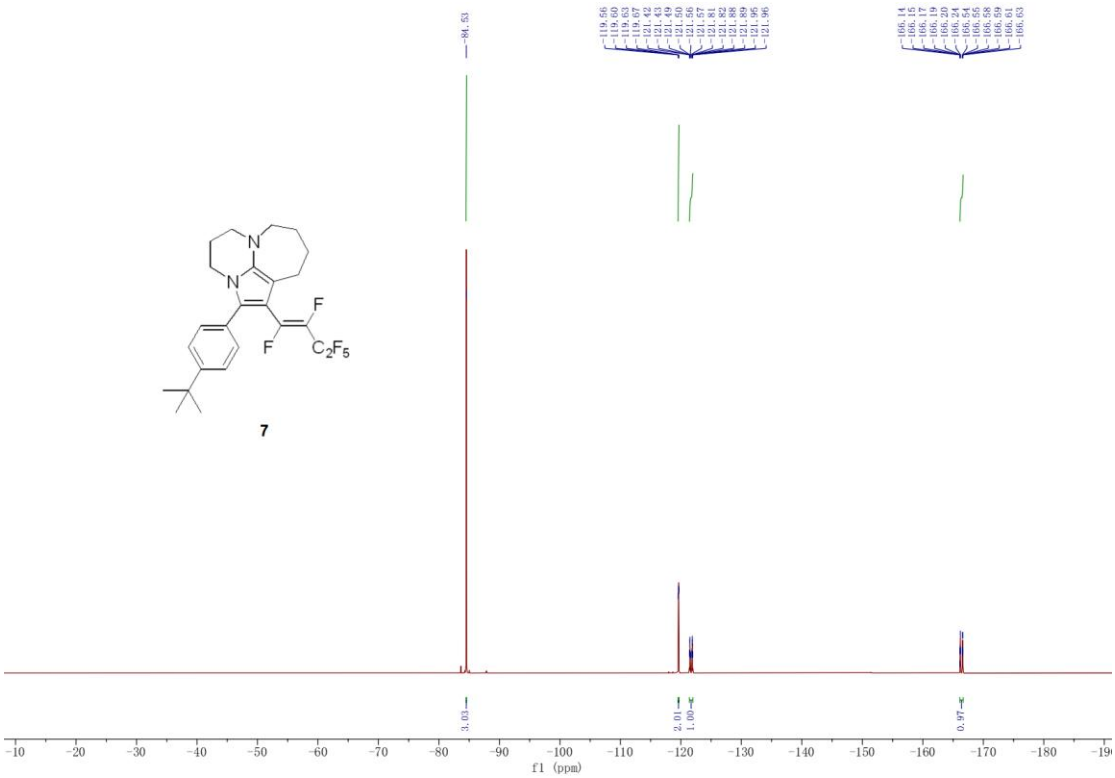
^{13}C NMR spectra of the product **6** (101 MHz, $CDCl_3$):



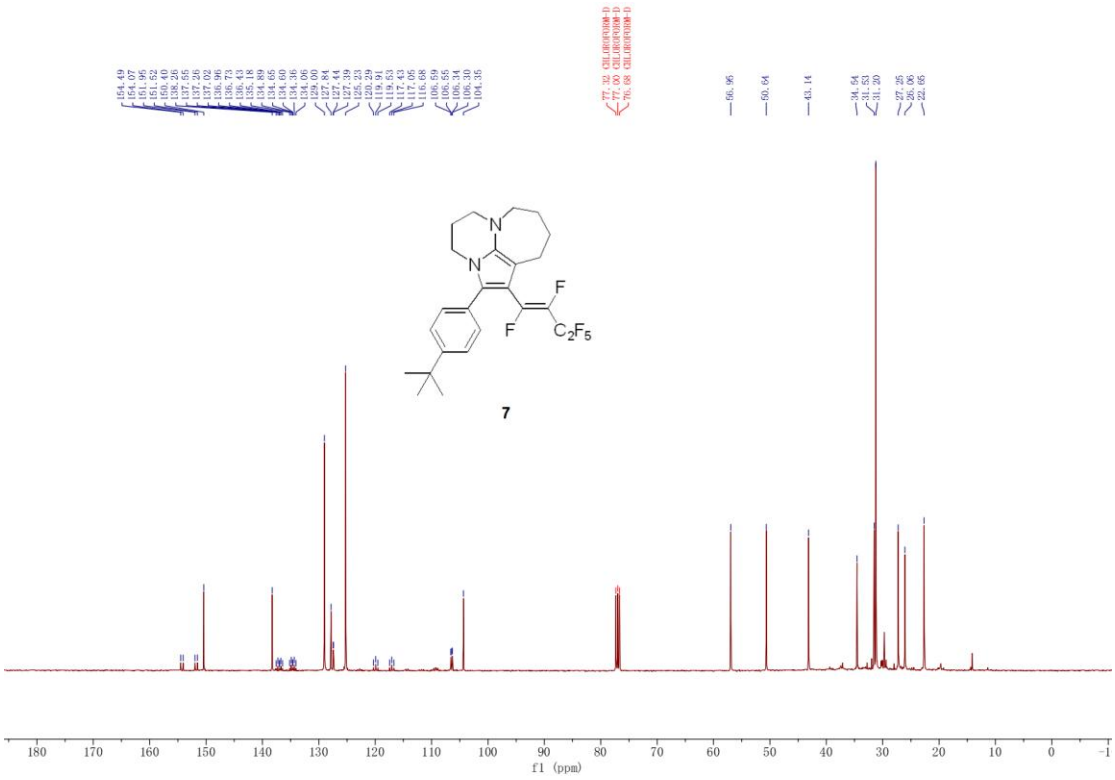
^{1}H NMR spectra of the product **7** (400 MHz, $CDCl_3$):



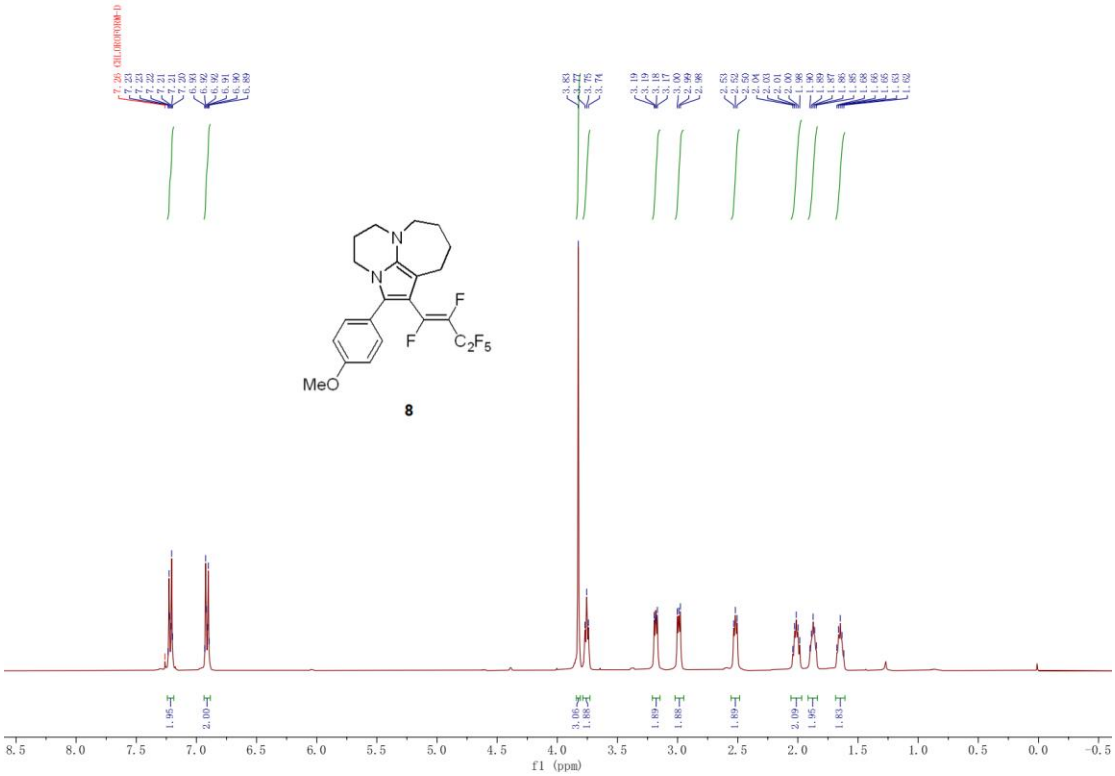
^{19}F NMR spectra of the product **7** (376 MHz, $CDCl_3$):



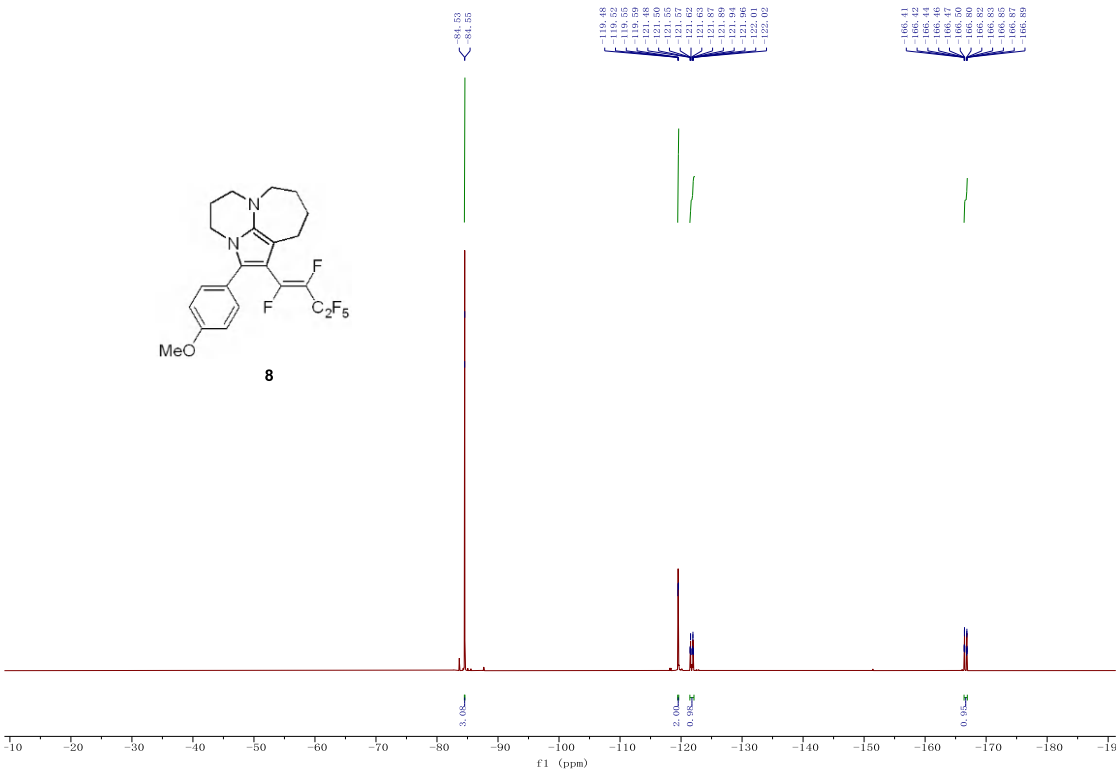
^{13}C NMR spectra of the product **7** (101 MHz, $CDCl_3$):



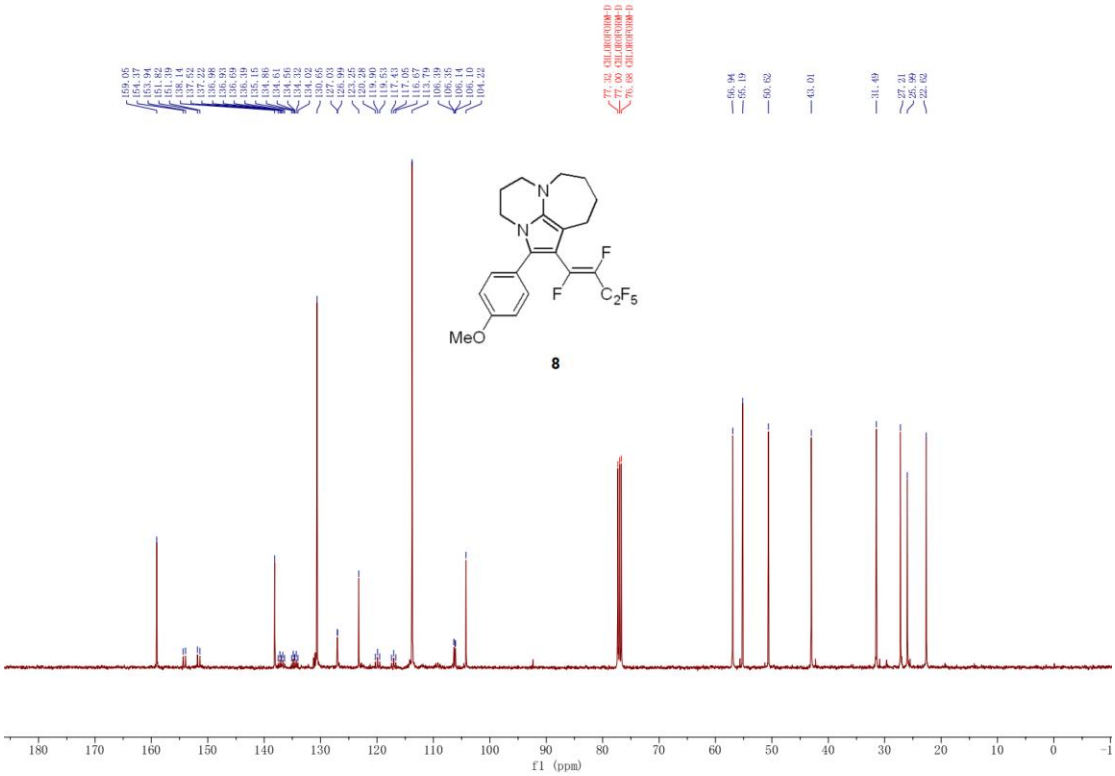
^{1}H NMR spectra of the product **8** (400 MHz, $CDCl_3$):



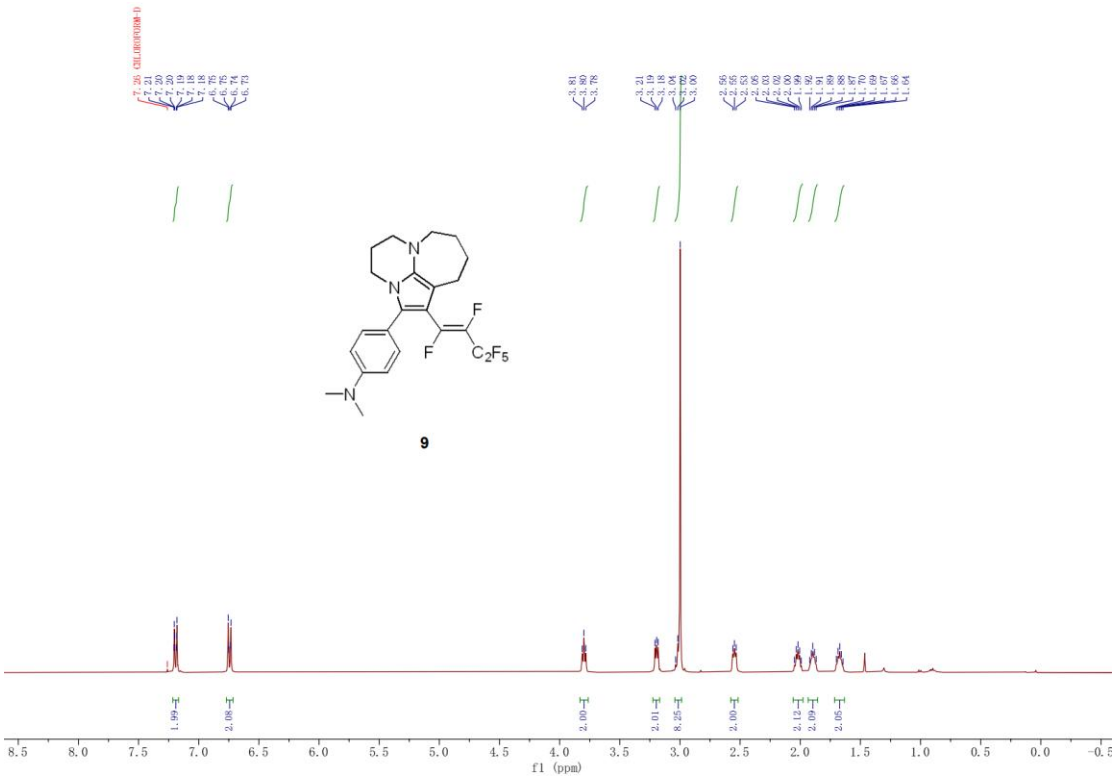
^{19}F NMR spectra of the product **8** (376 MHz, $CDCl_3$):



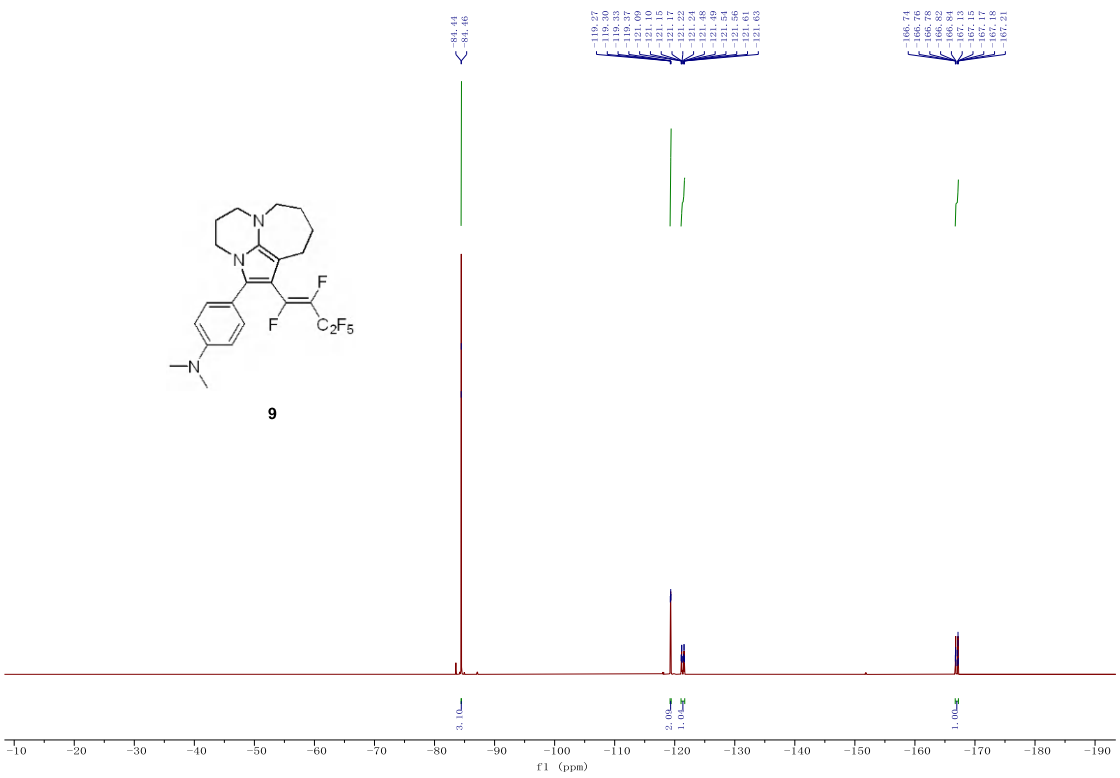
^{13}C NMR spectra of the product **8** (101 MHz, $CDCl_3$):



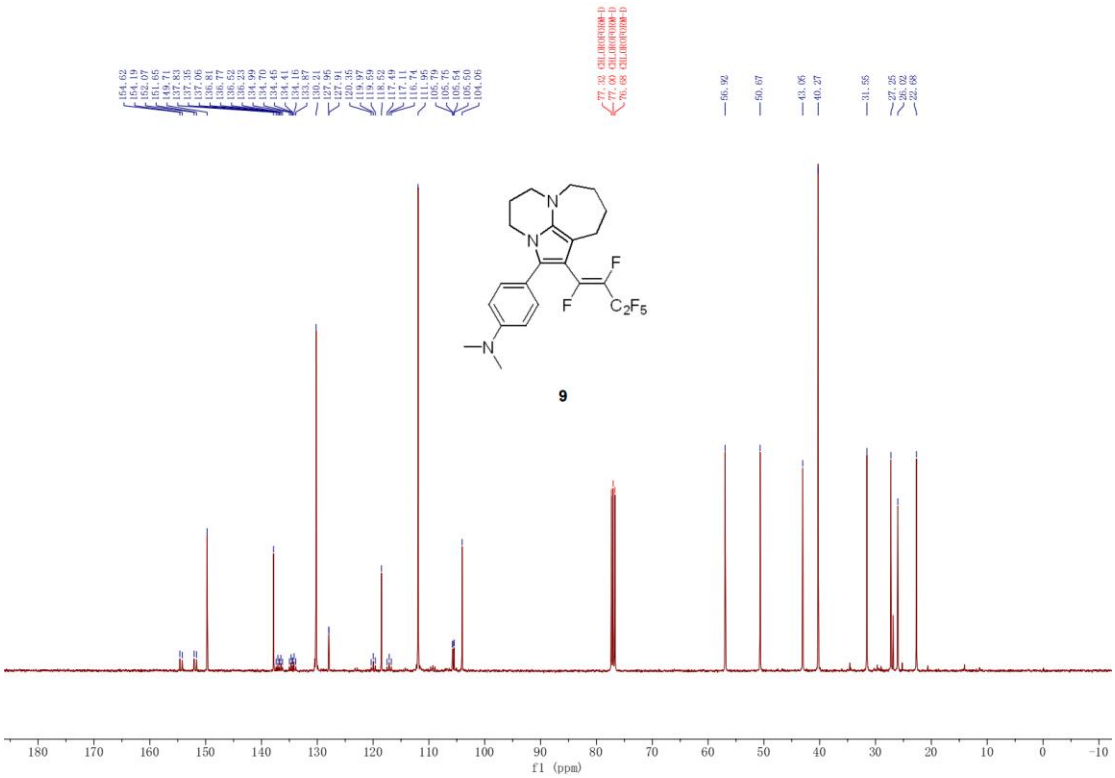
^{1}H NMR spectra of the product **9** (400 MHz, $CDCl_3$):



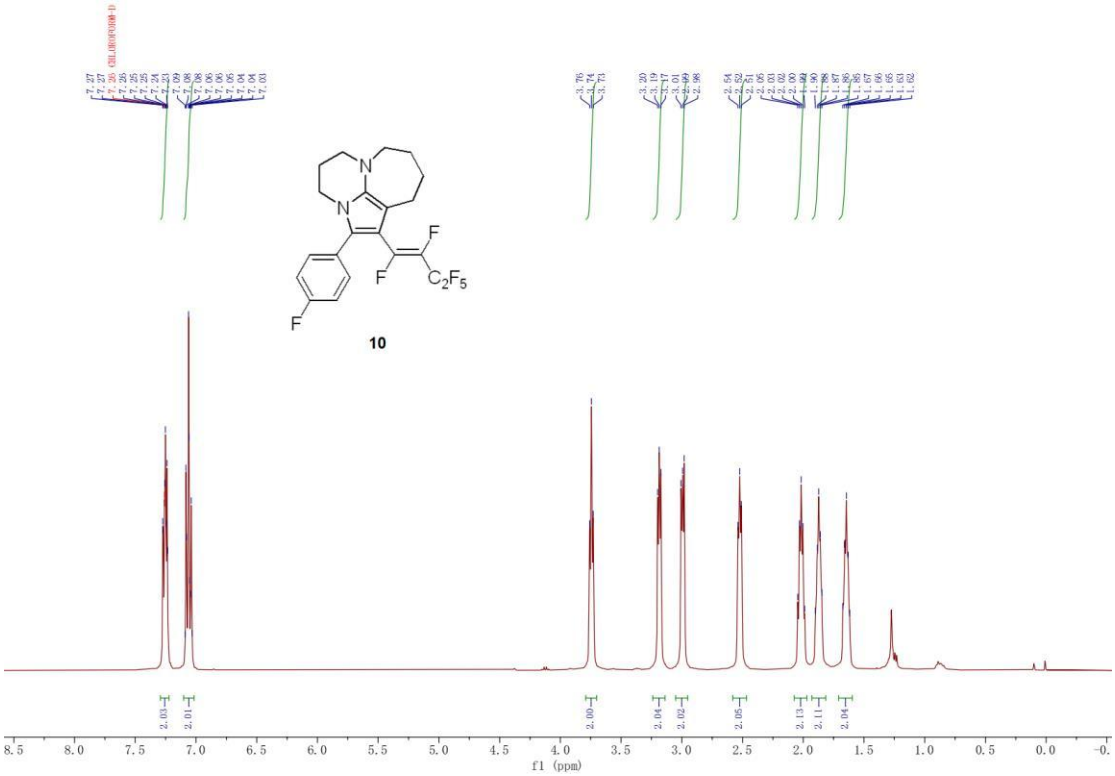
^{19}F NMR spectra of the product **9** (376 MHz, $CDCl_3$):



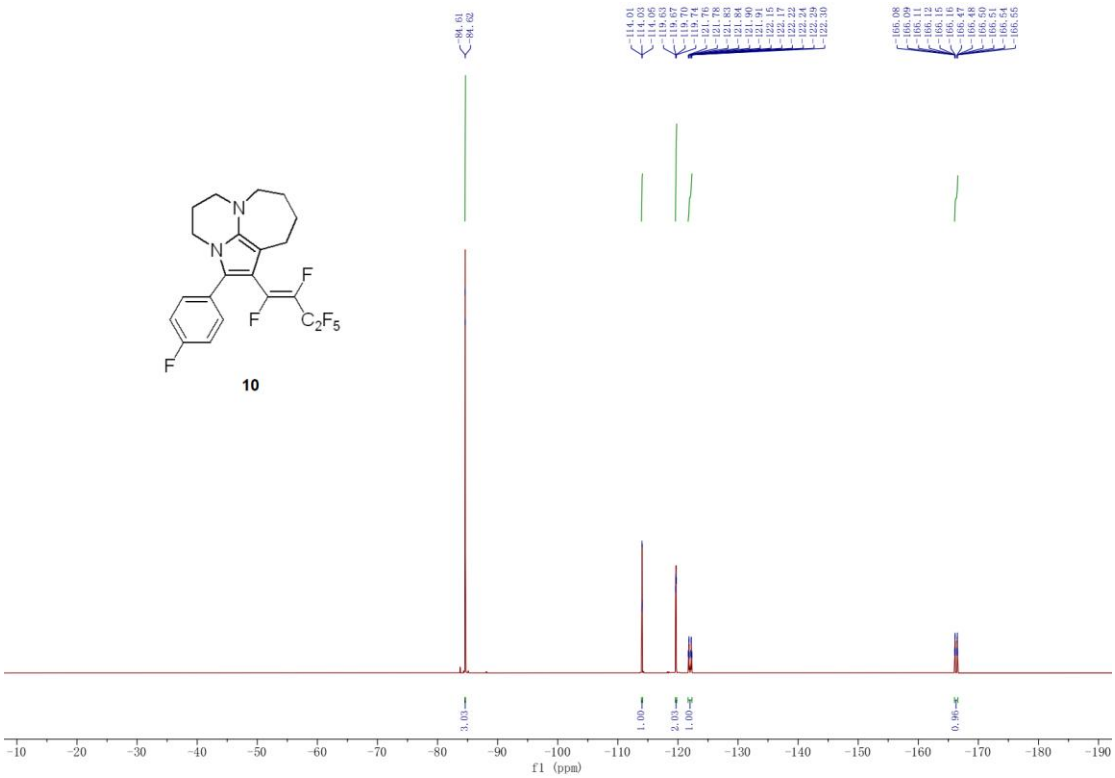
^{13}C NMR spectra of the product **9** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **10** (400 MHz, $CDCl_3$):

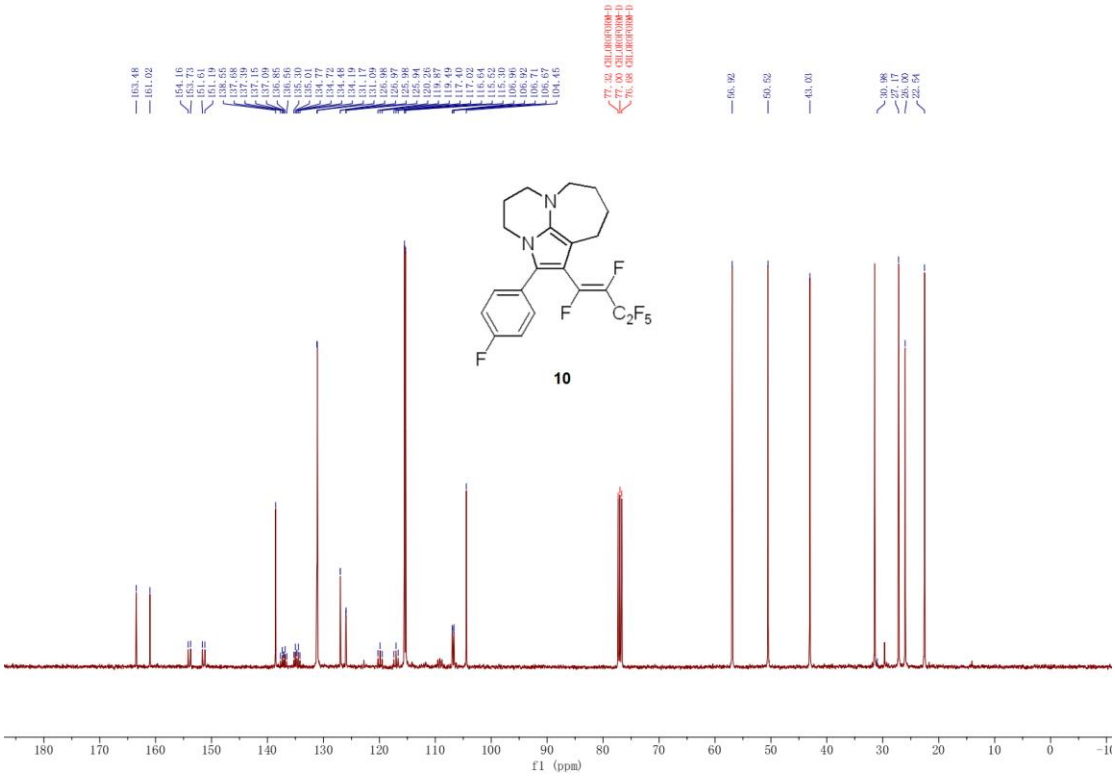


^{19}F NMR spectra of the product **10** (376 MHz, $CDCl_3$):



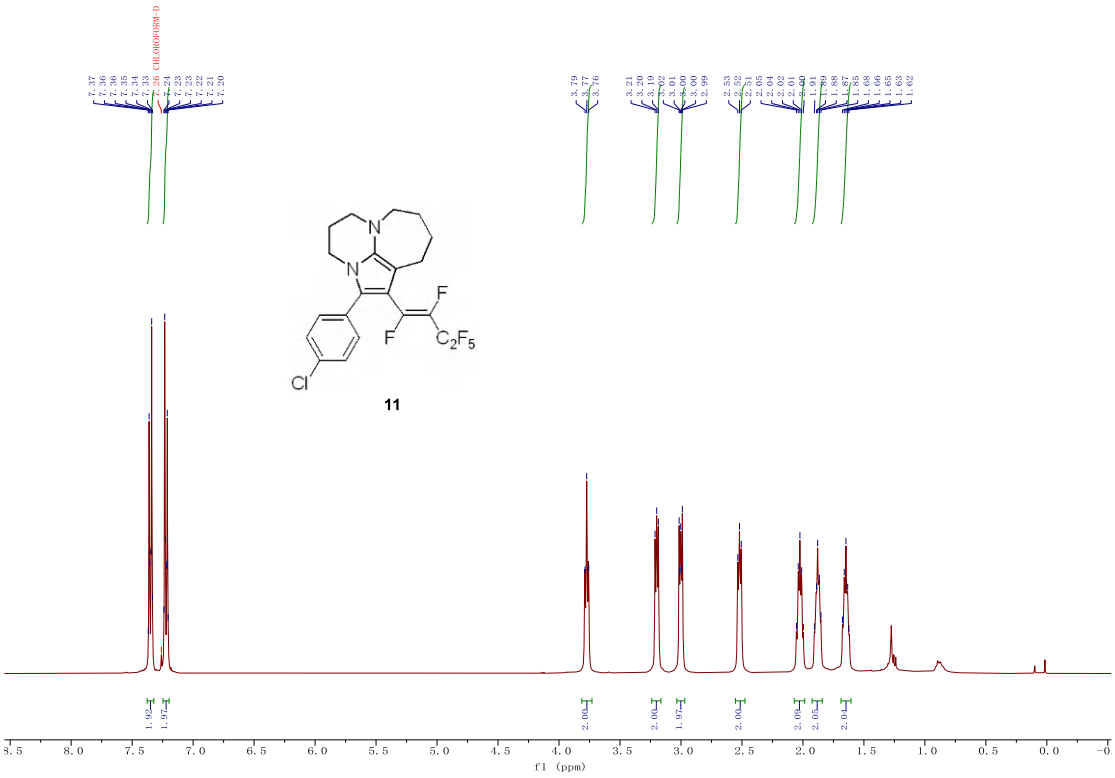
10

^{13}C NMR spectra of the product **10** (101 MHz, $CDCl_3$):

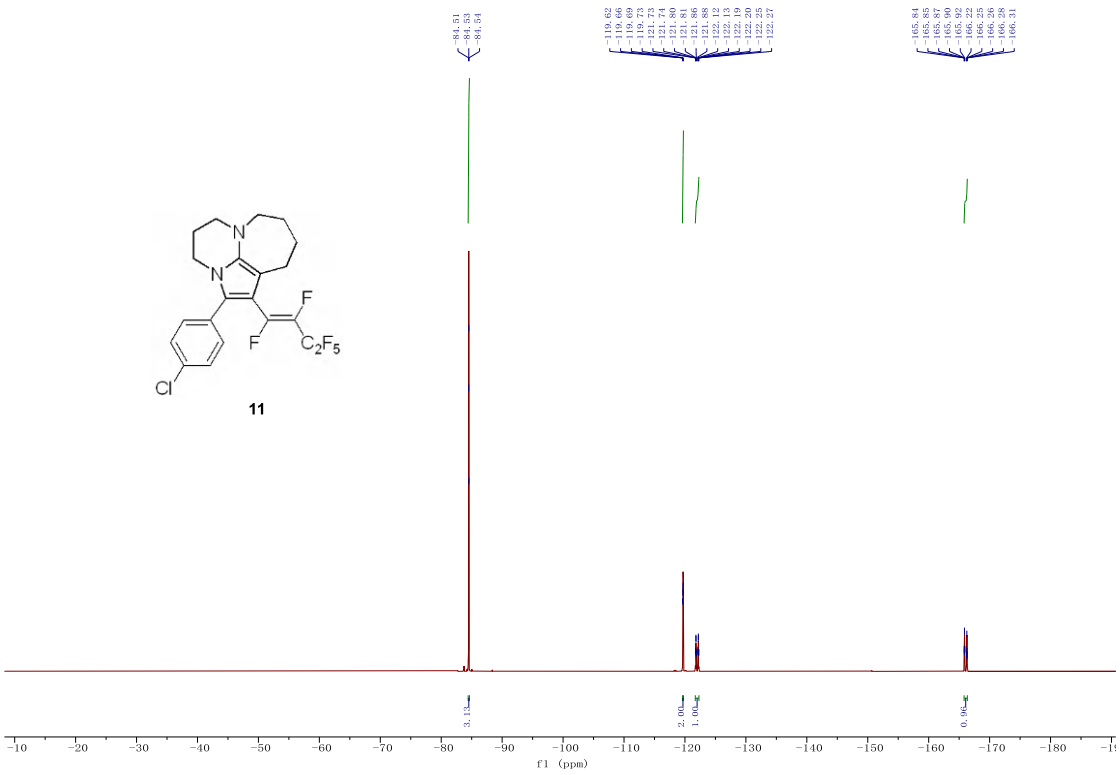


10

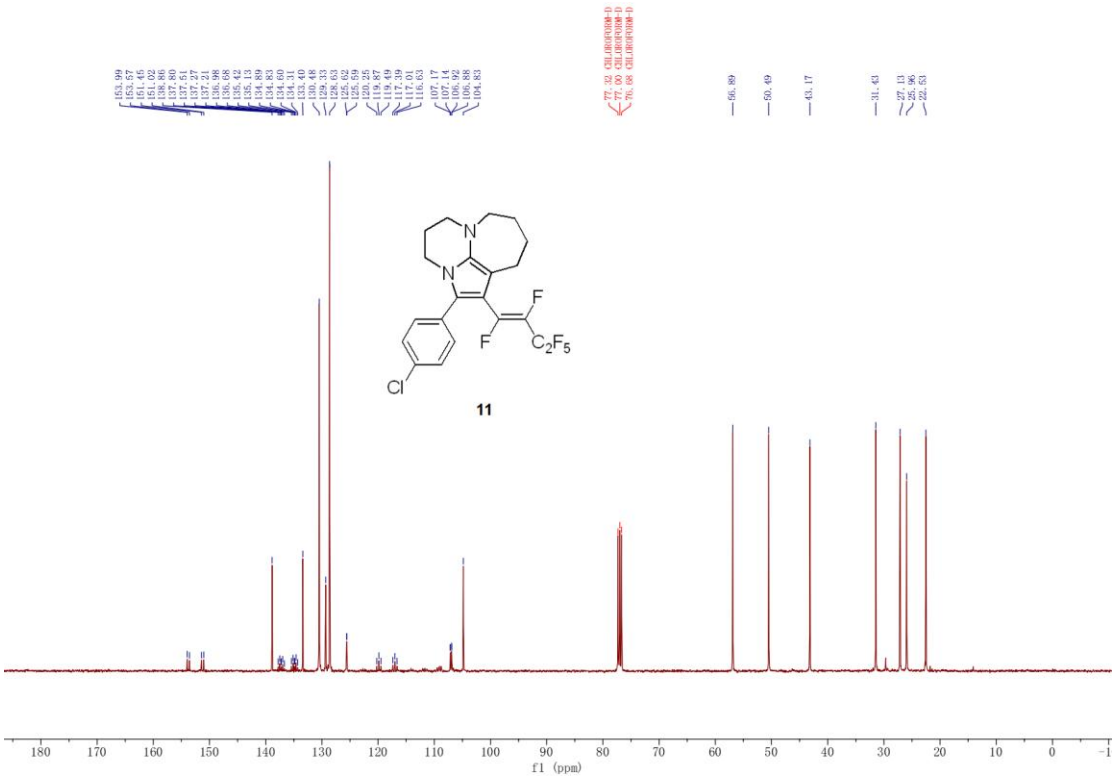
^{1}H NMR spectra of the product **11** (400 MHz, $CDCl_3$):



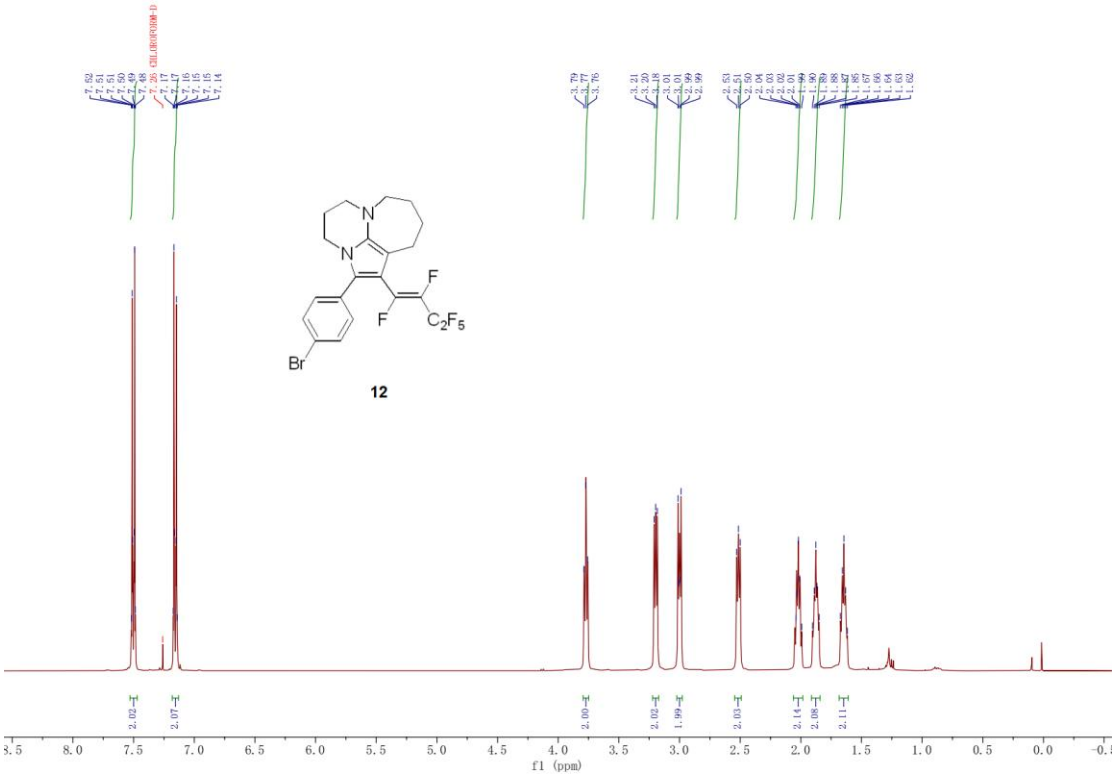
^{19}F NMR spectra of the product **11** (376 MHz, $CDCl_3$):



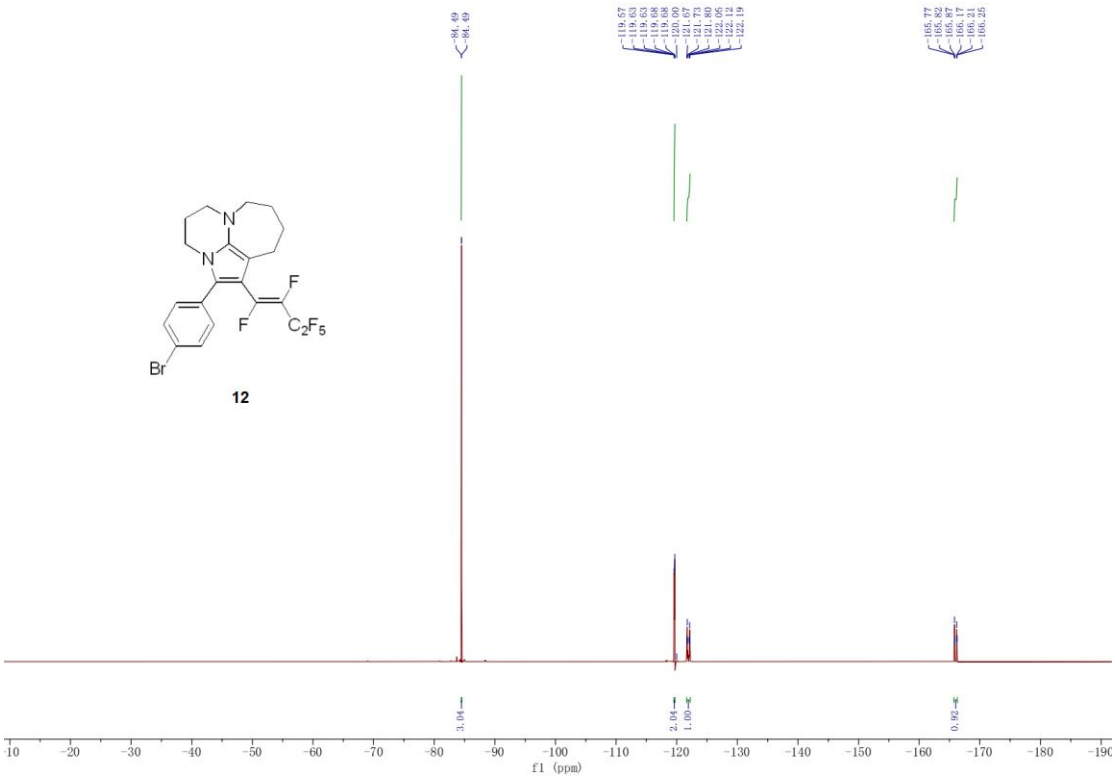
^{13}C NMR spectra of the product **11** (101 MHz, $CDCl_3$):



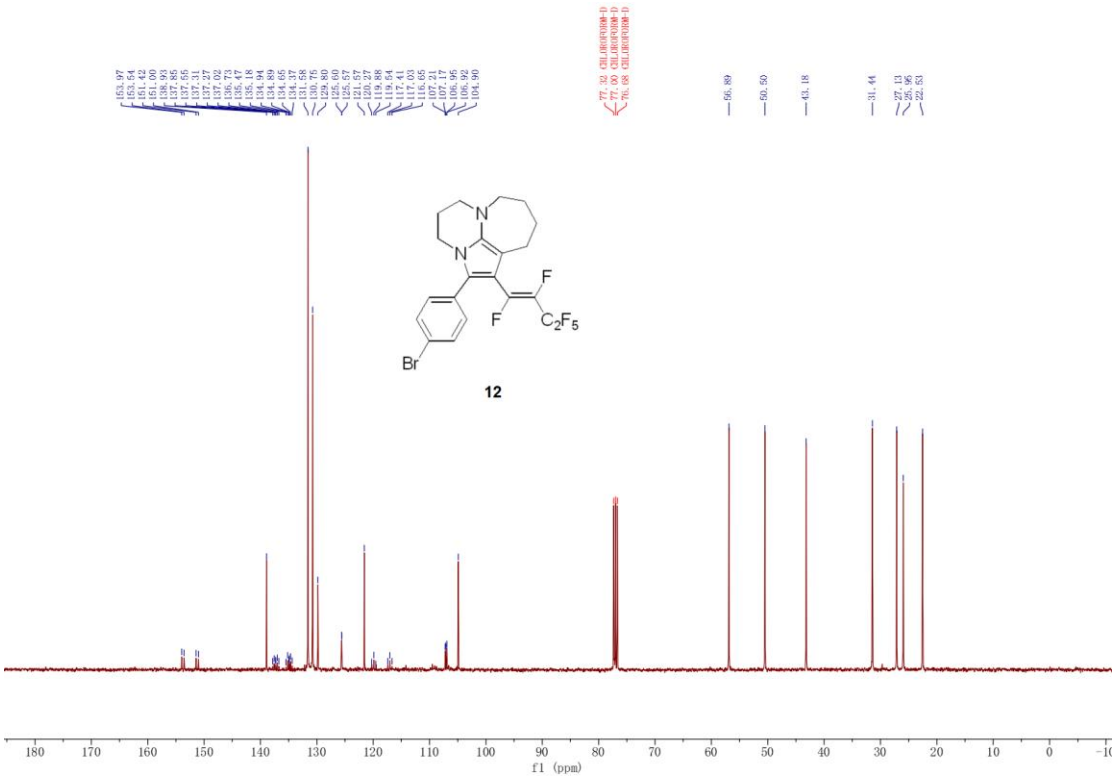
^{1}H NMR spectra of the product **12** (400 MHz, $CDCl_3$):



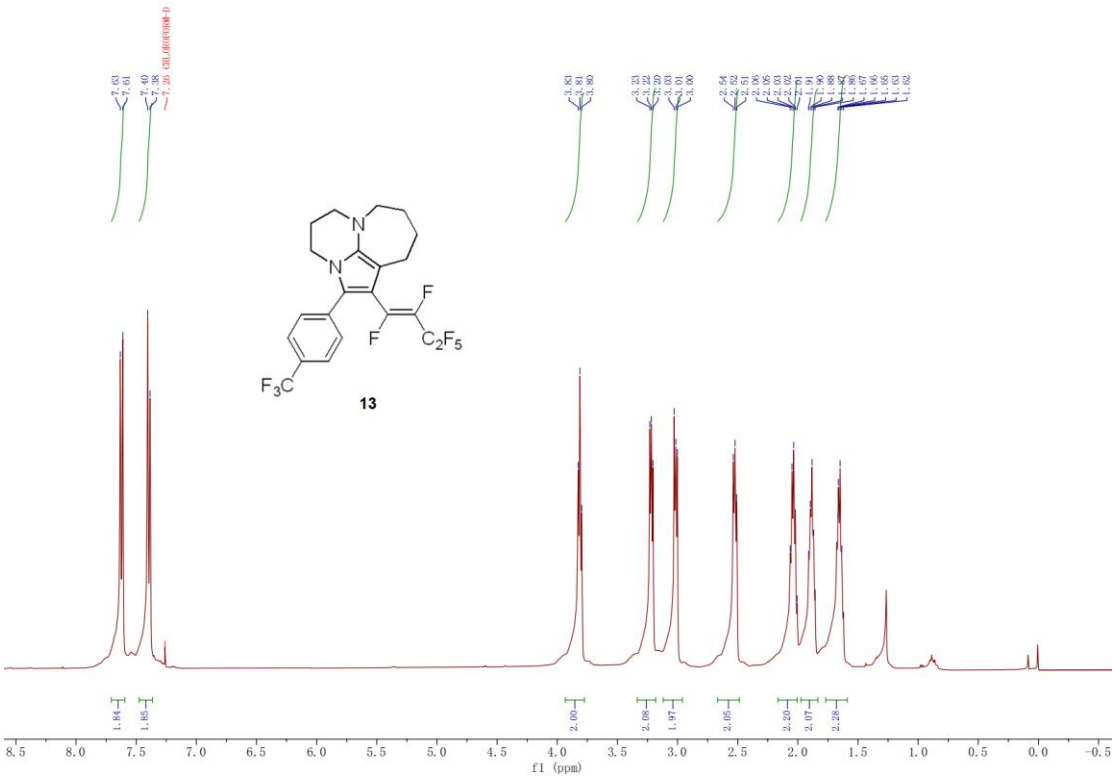
^{19}F NMR spectra of the product **12** (376 MHz, $CDCl_3$):



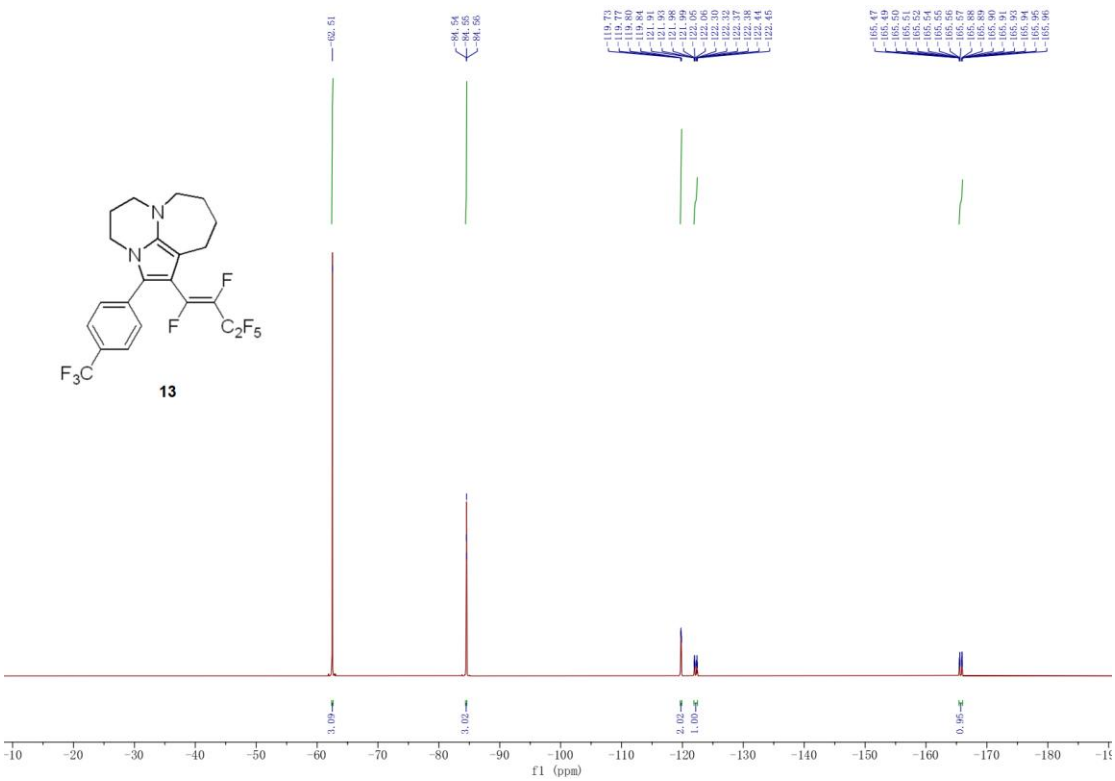
^{13}C NMR spectra of the product **12** (101 MHz, $CDCl_3$):



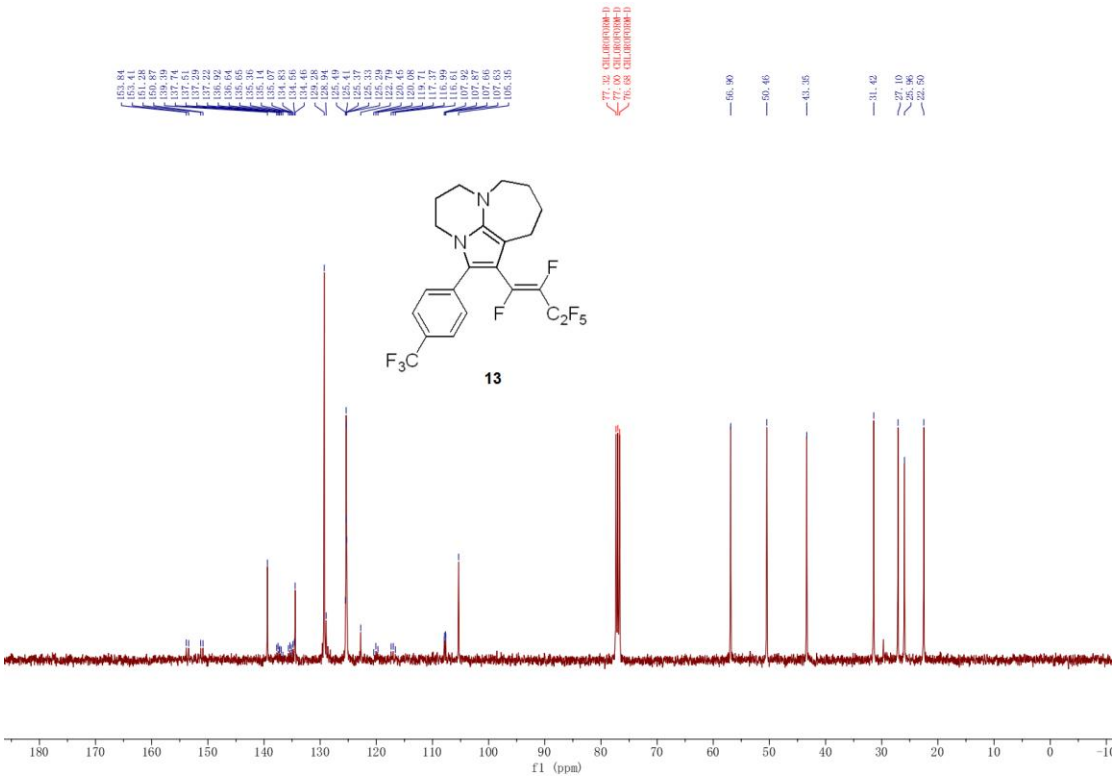
^{1}H NMR spectra of the product **13** (400 MHz, $CDCl_3$):



^{19}F NMR spectra of the product **13** (376 MHz, $CDCl_3$):



^{13}C NMR spectra of the product **13** (101 MHz, $CDCl_3$):



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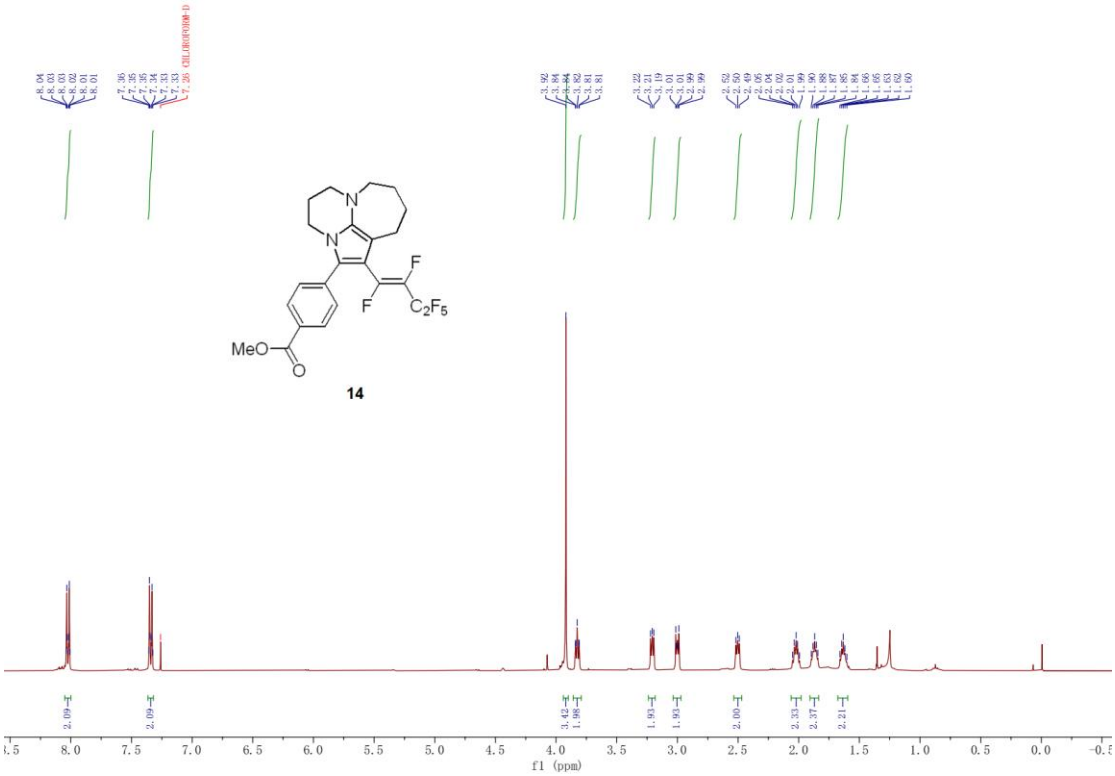
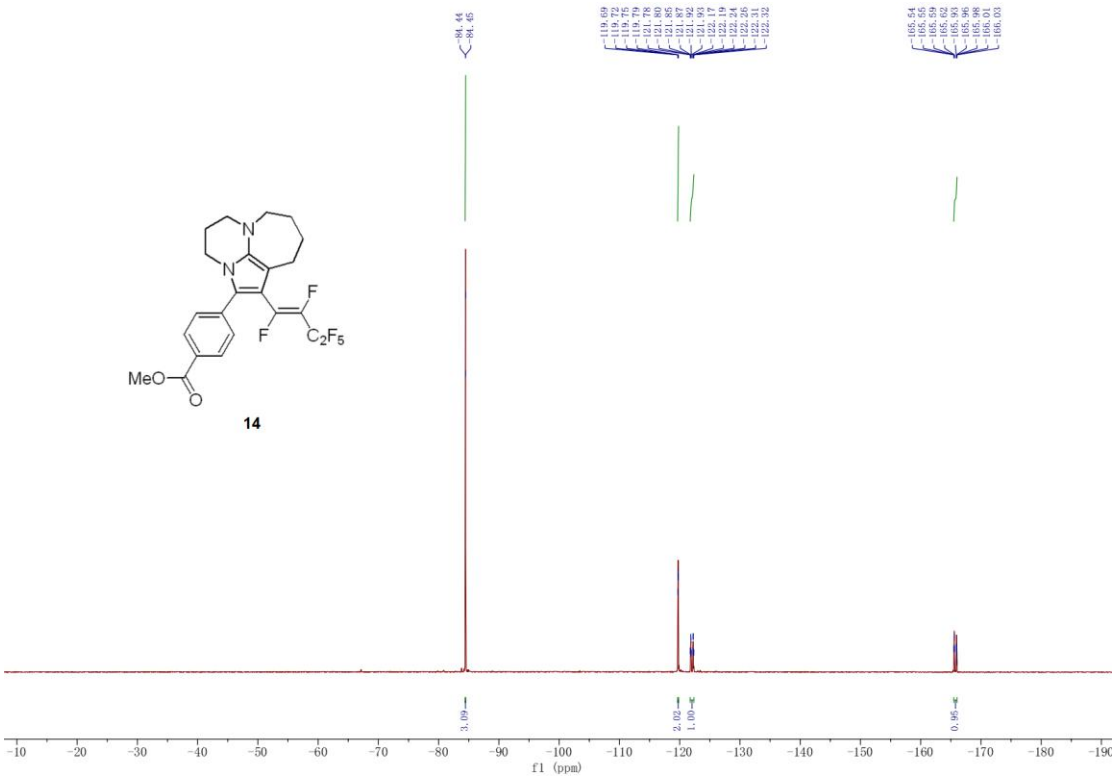
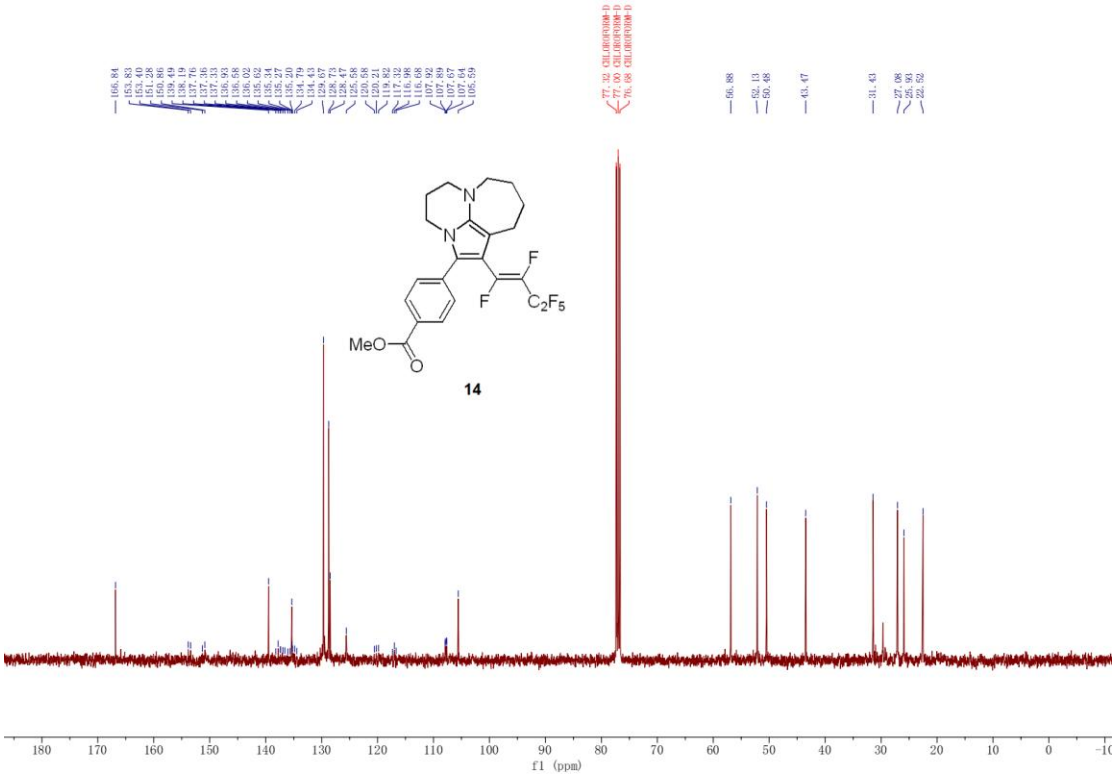


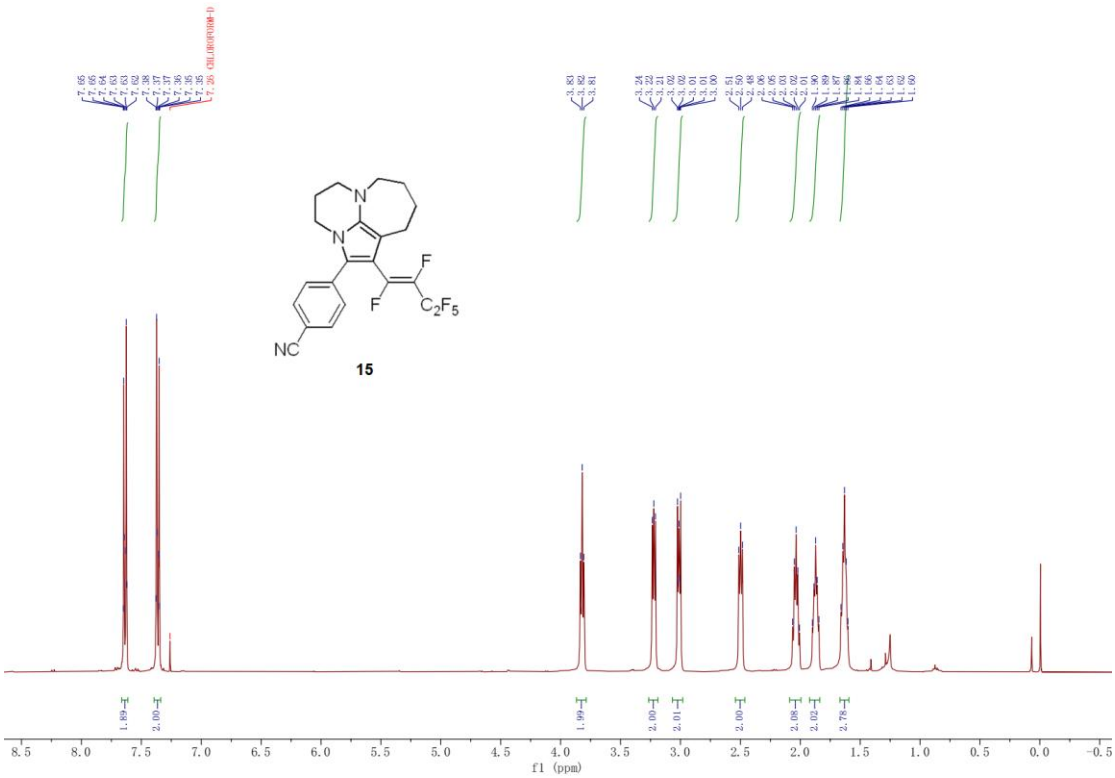
^{19}F NMR spectra of the product **14** (376 MHz, $CDCl_3$):



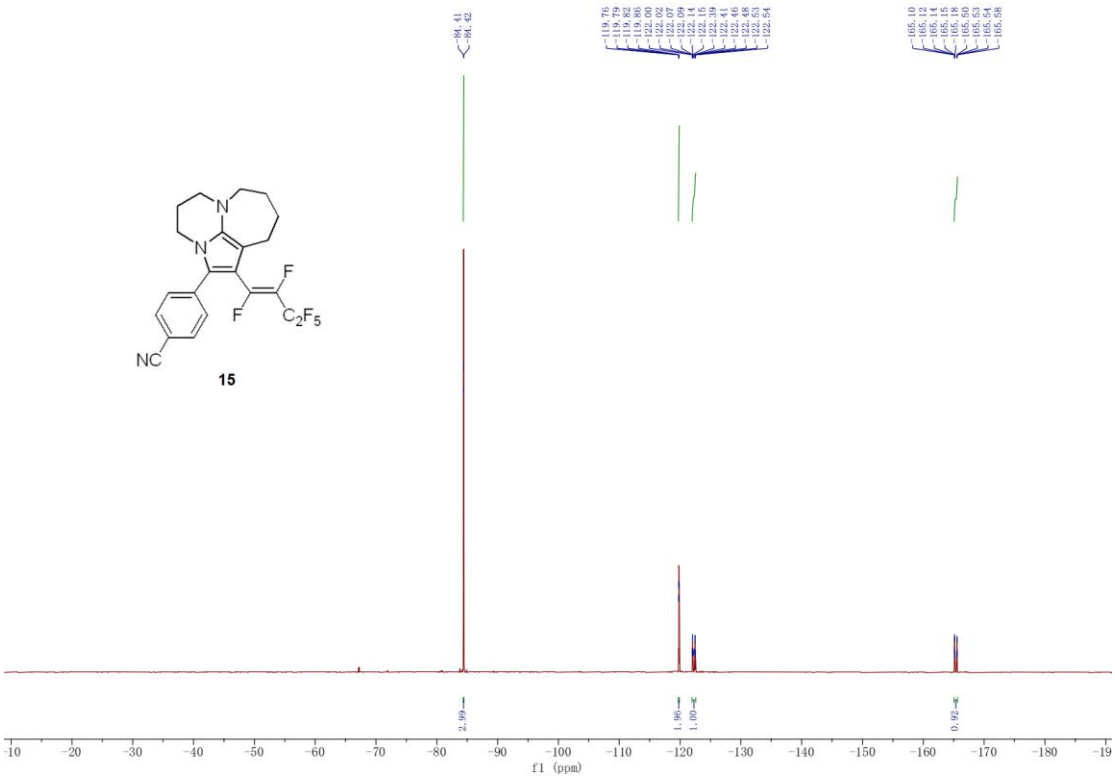
^{13}C NMR spectra of the product **14** (101 MHz, $CDCl_3$):



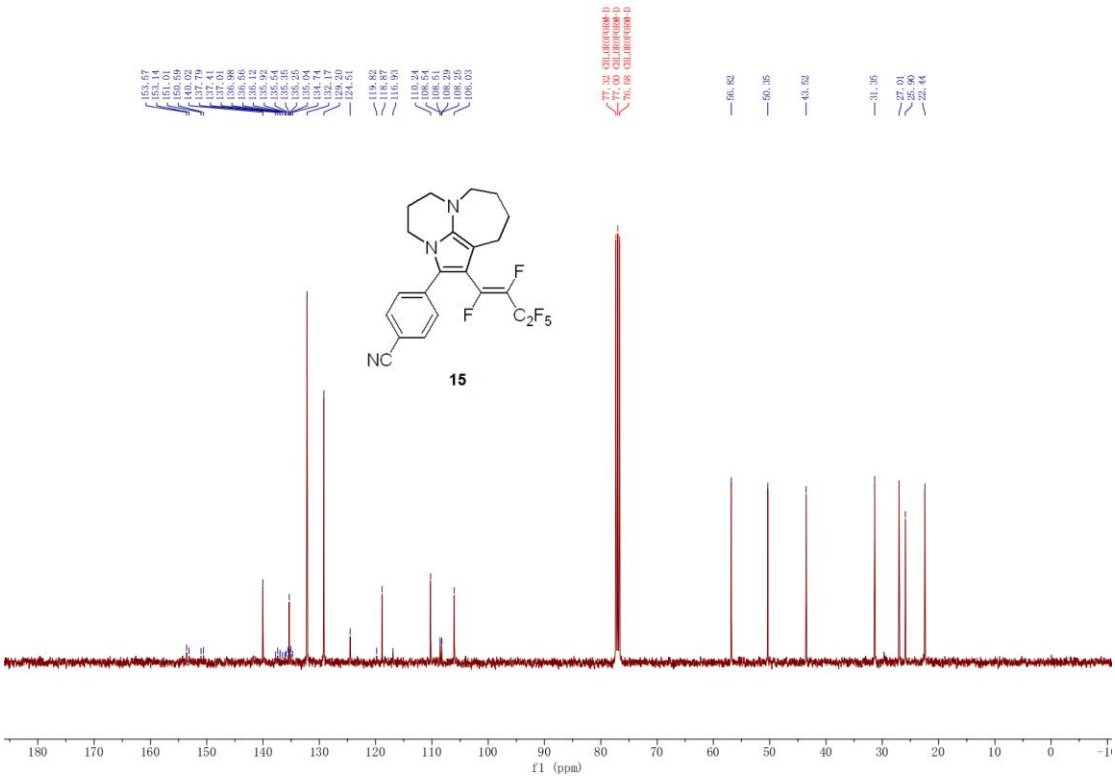
^{1}H NMR spectra of the product **15** (400 MHz, $CDCl_3$):



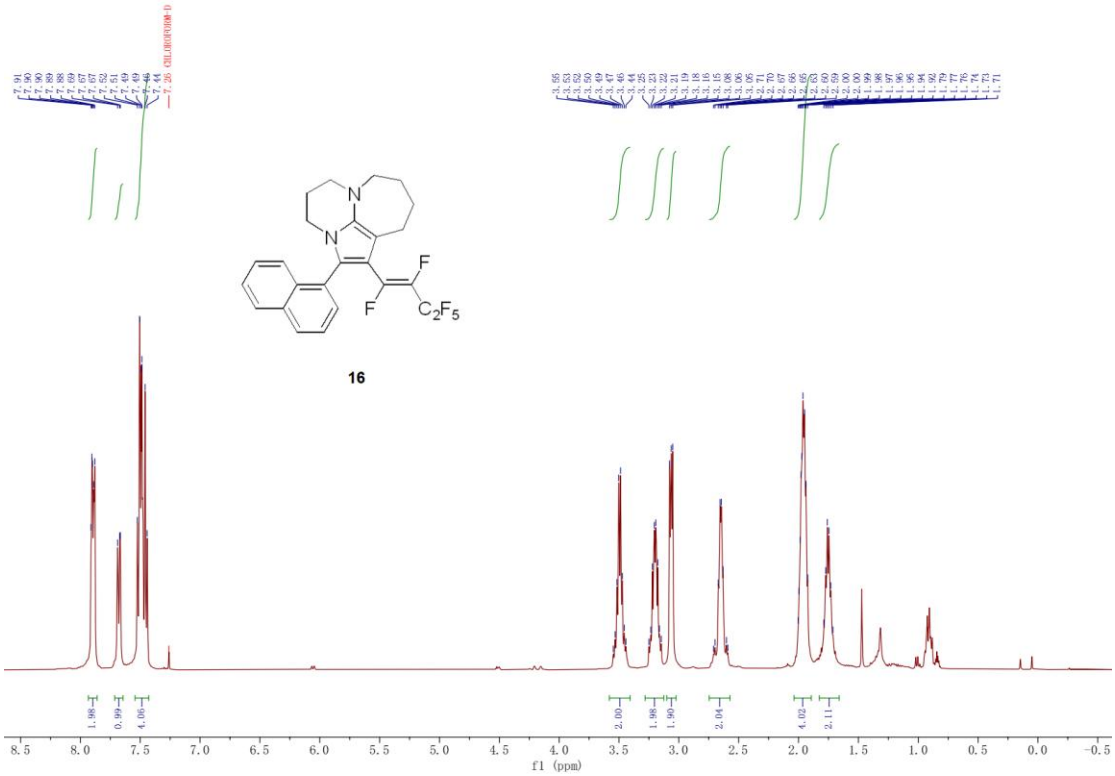
^{19}F NMR spectra of the product **15** (376 MHz, $CDCl_3$):



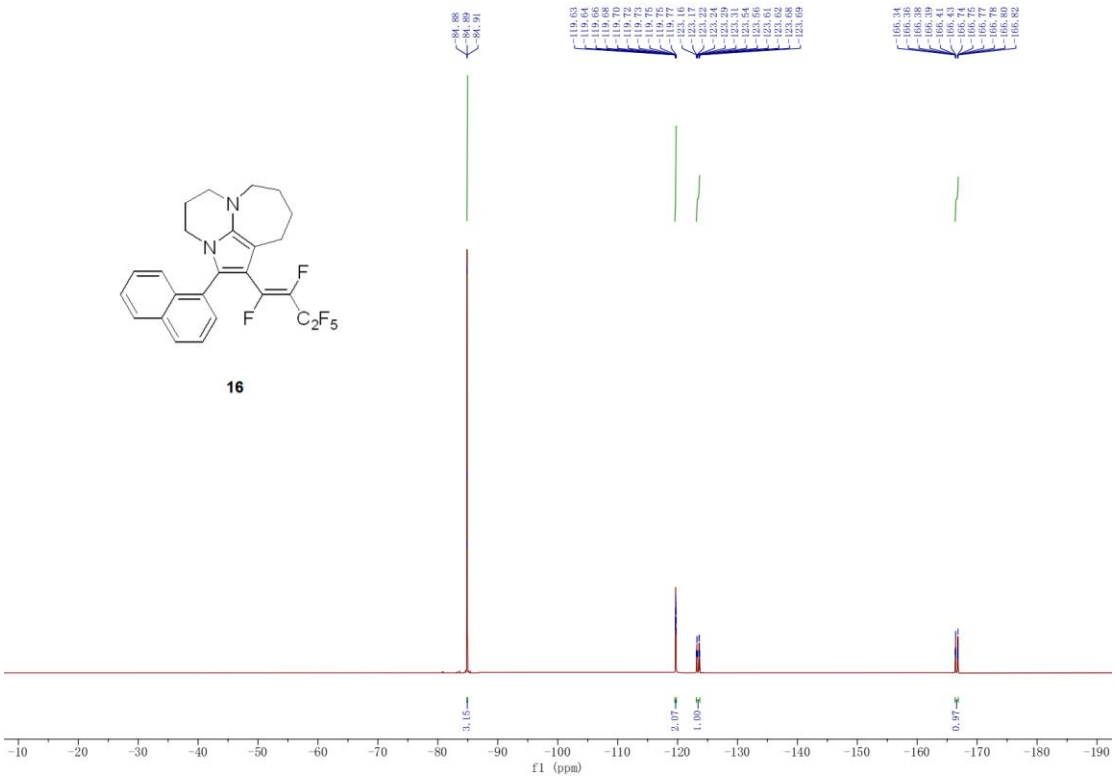
^{13}C NMR spectra of the product **15** (101 MHz, $CDCl_3$):



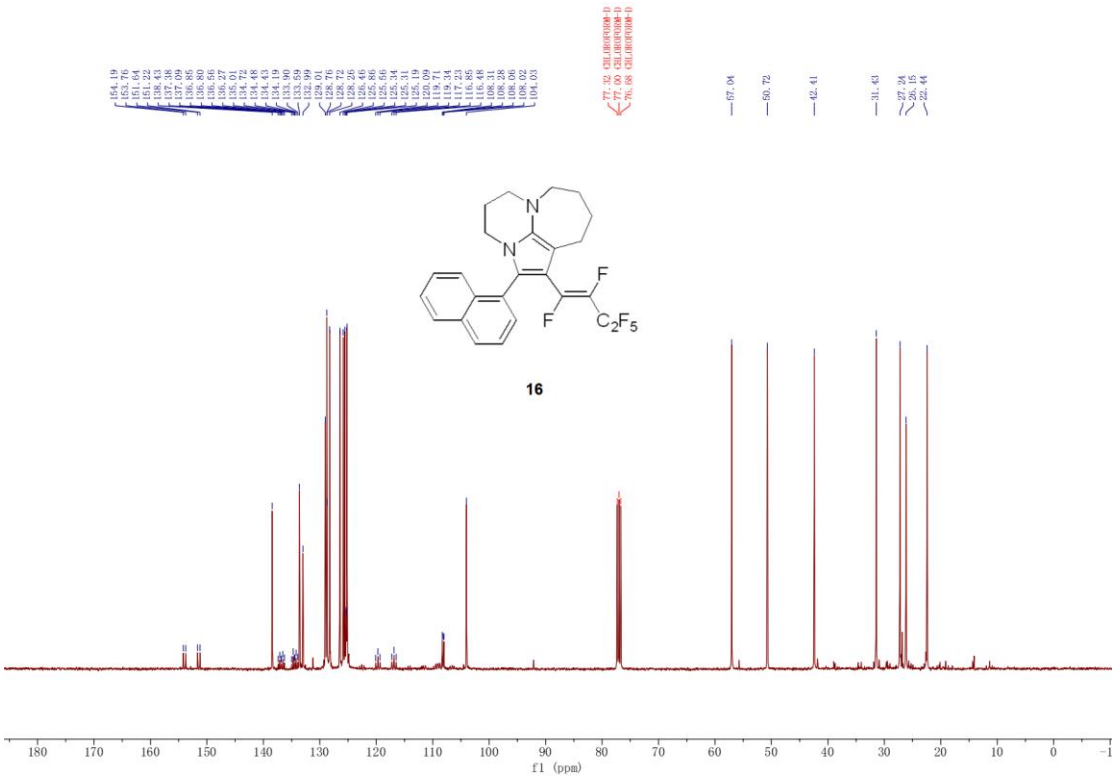
^{1}H NMR spectra of the product **16** (400 MHz, $CDCl_3$):



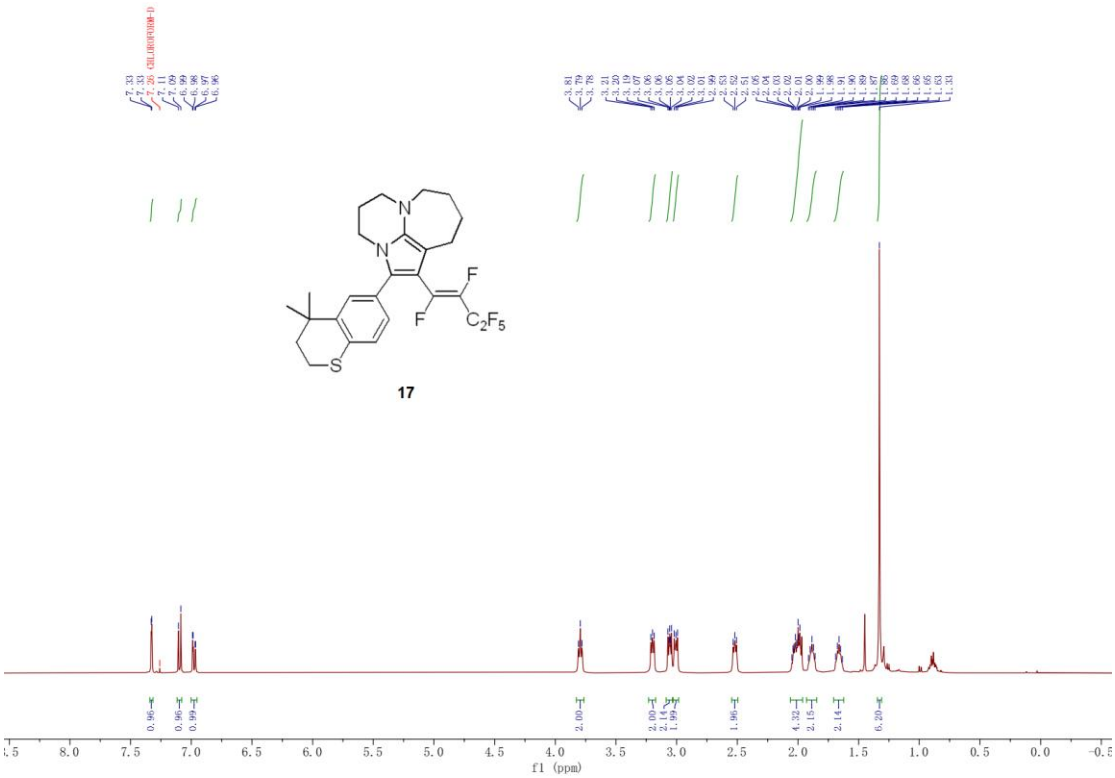
^{19}F NMR spectra of the product **16** (376 MHz, $CDCl_3$):



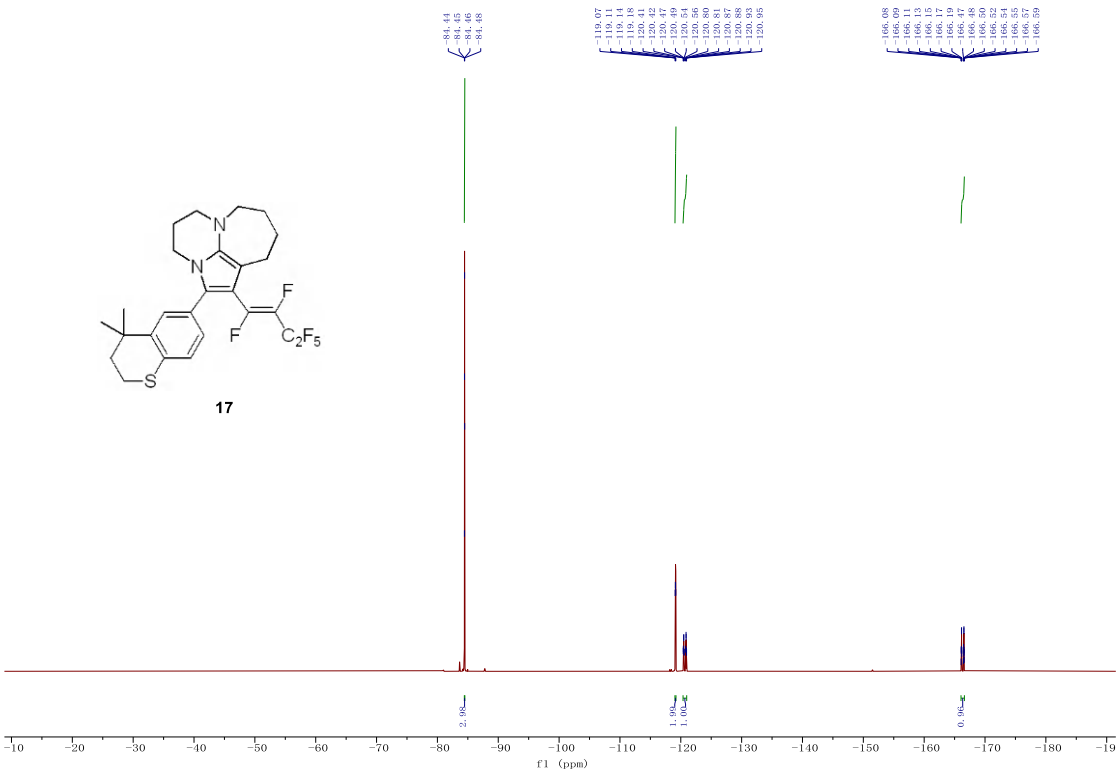
^{13}C NMR spectra of the product **16** (101 MHz, $CDCl_3$):



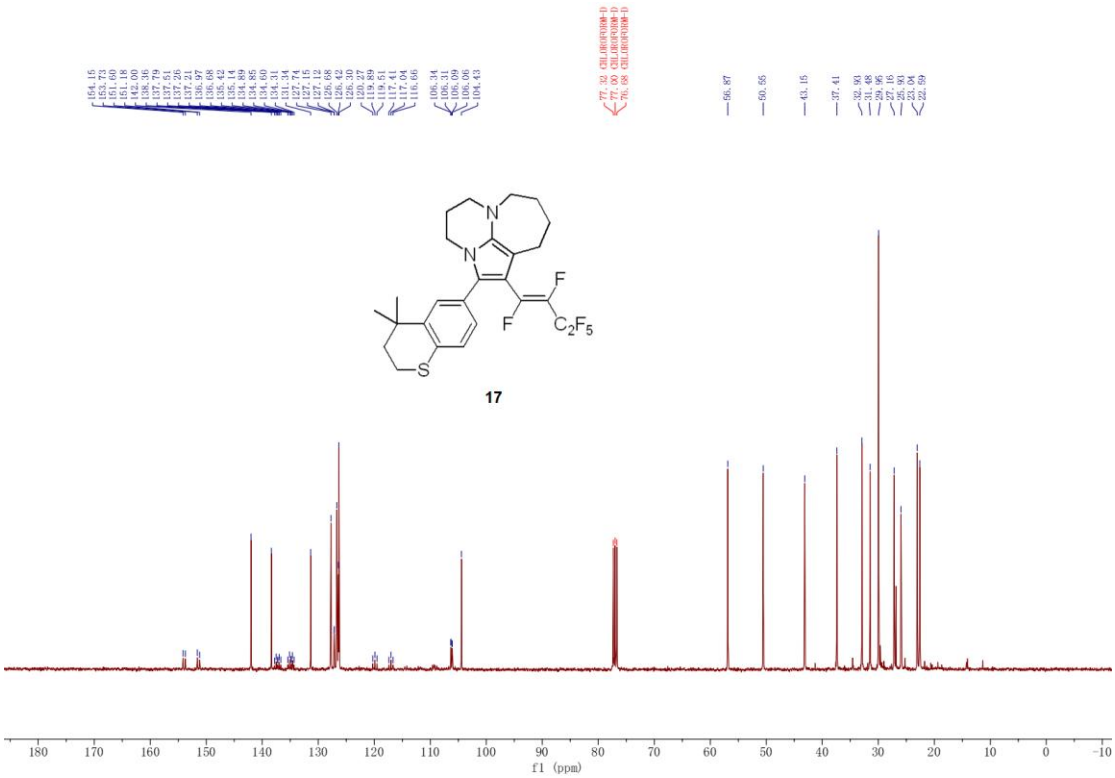
^{1}H NMR spectra of the product **17** (400 MHz, $CDCl_3$):



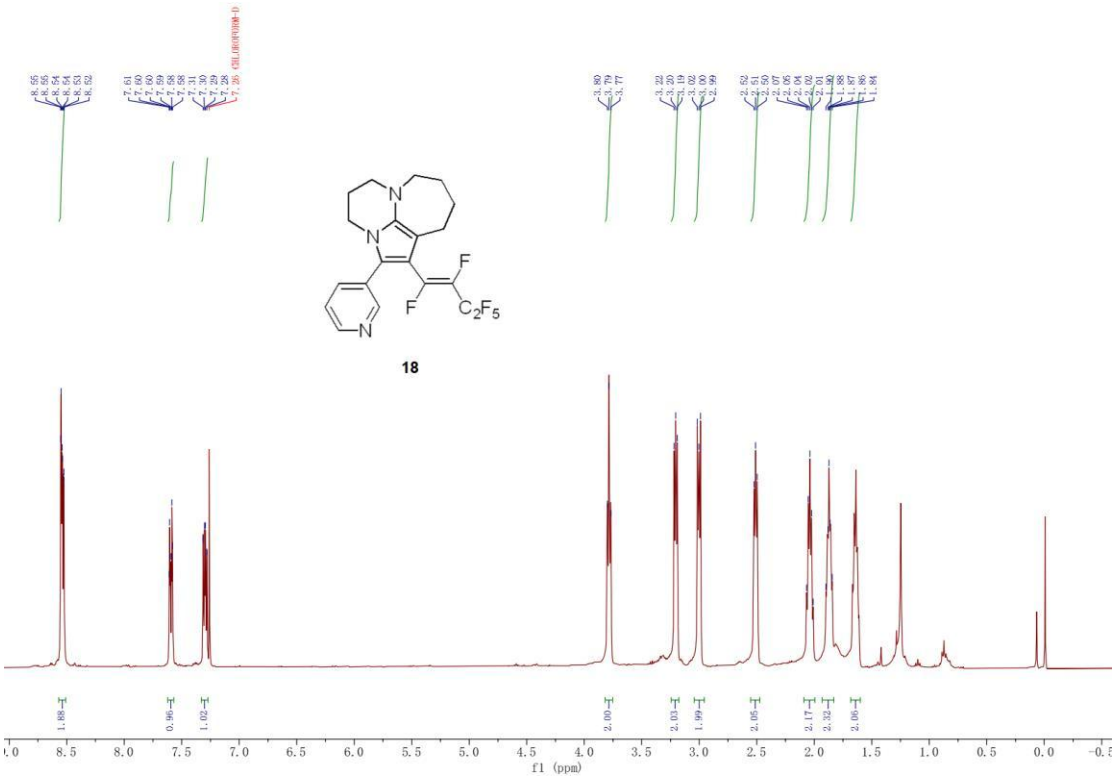
^{19}F NMR spectra of the product **17** (376 MHz, $CDCl_3$):



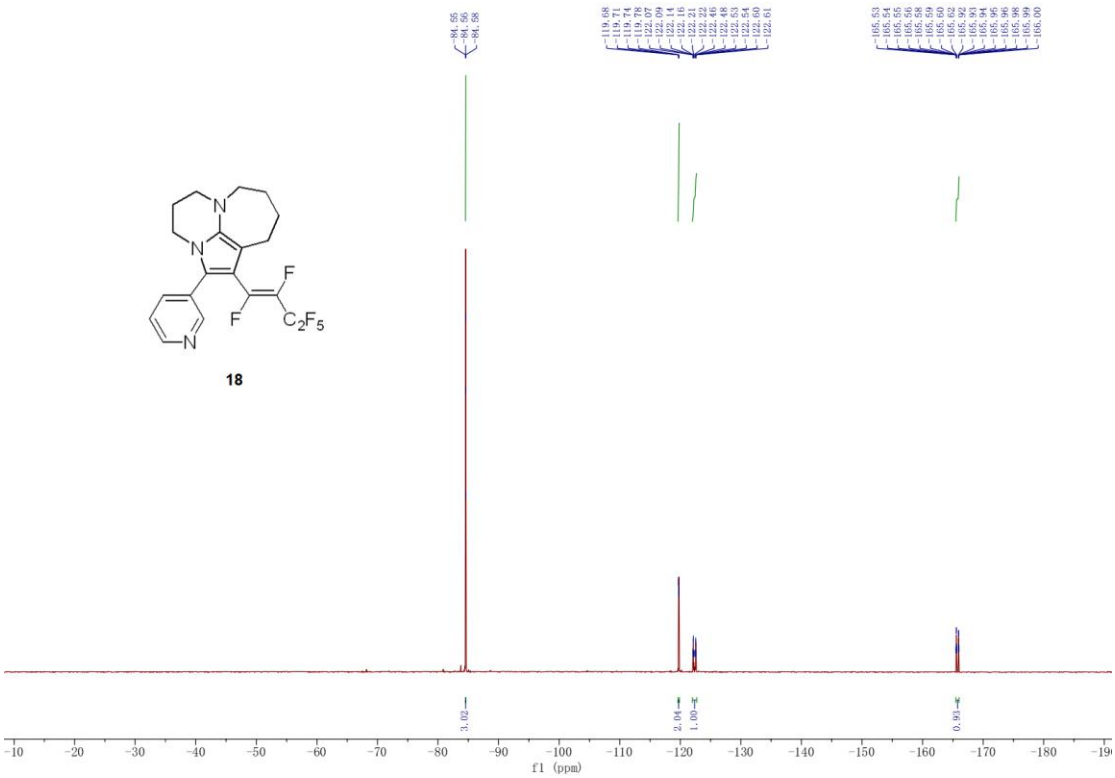
^{13}C NMR spectra of the product **17** (101 MHz, $CDCl_3$):



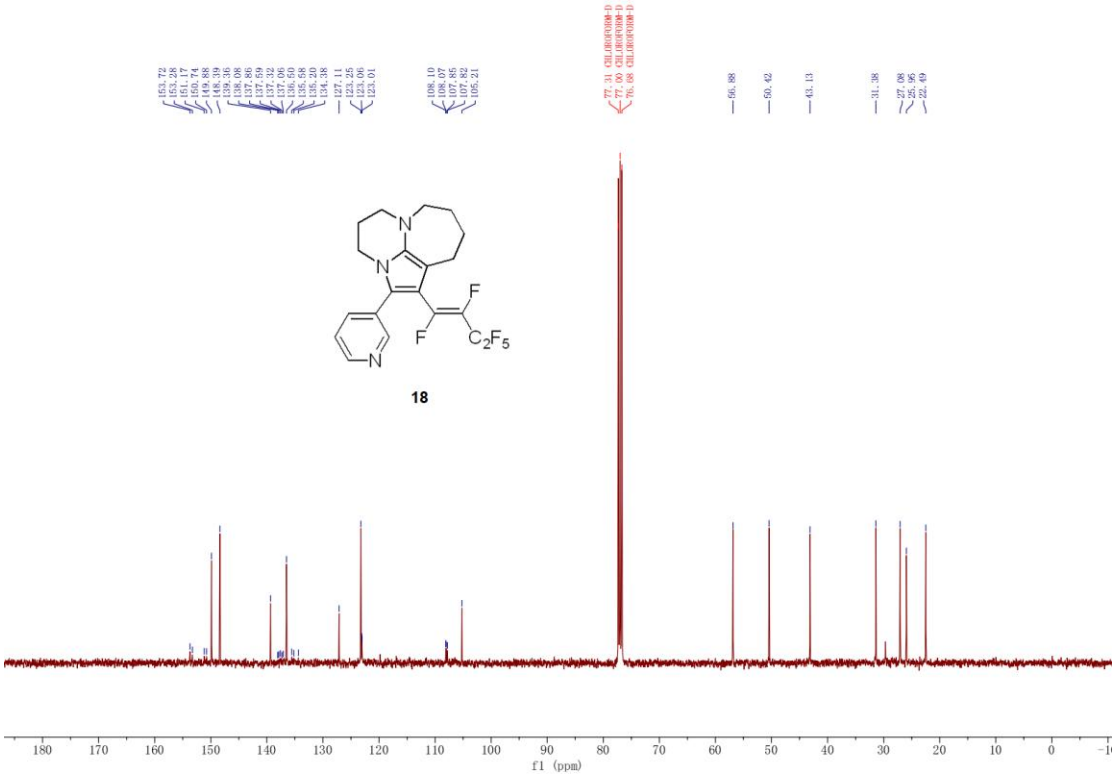
^{1}H NMR spectra of the product **18** (400 MHz, $CDCl_3$):



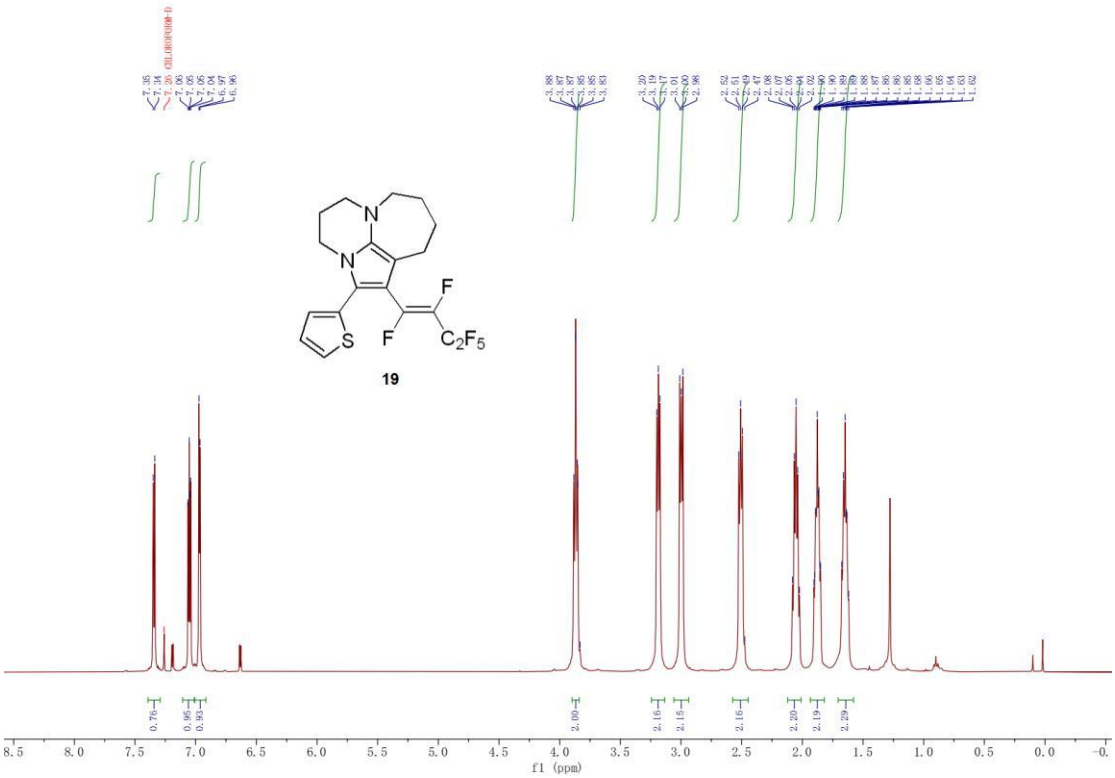
^{19}F NMR spectra of the product **18** (376 MHz, $CDCl_3$):



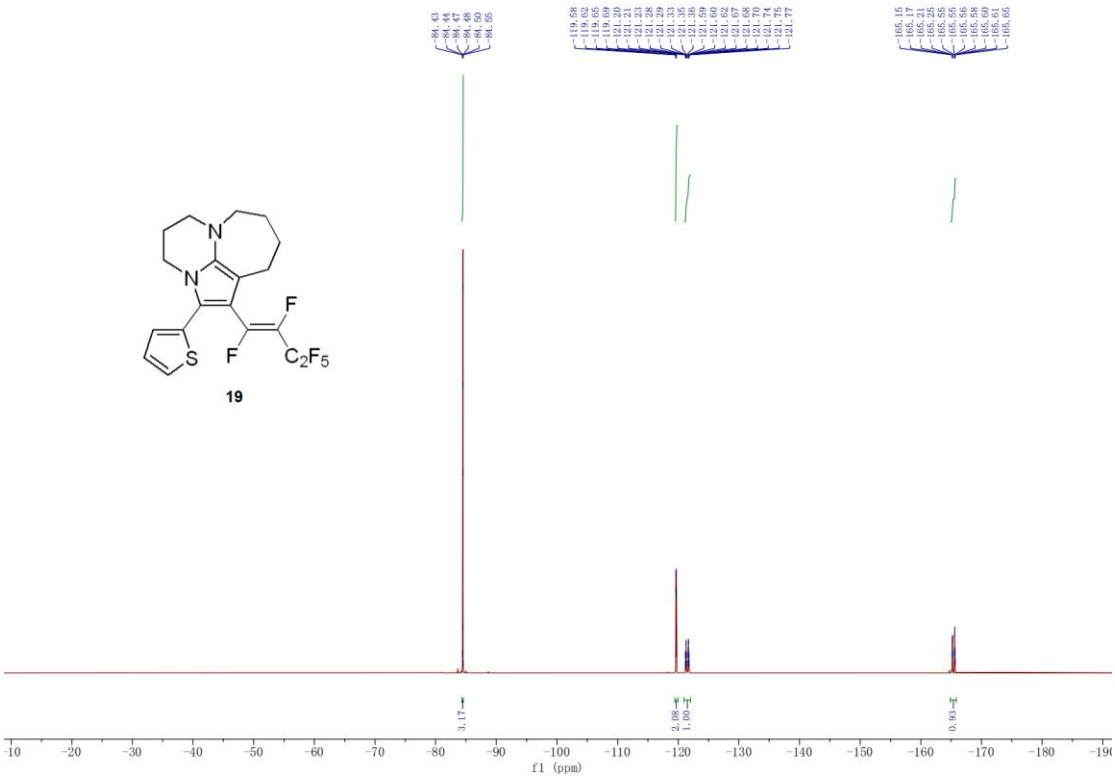
^{13}C NMR spectra of the product **18** (101 MHz, $CDCl_3$):



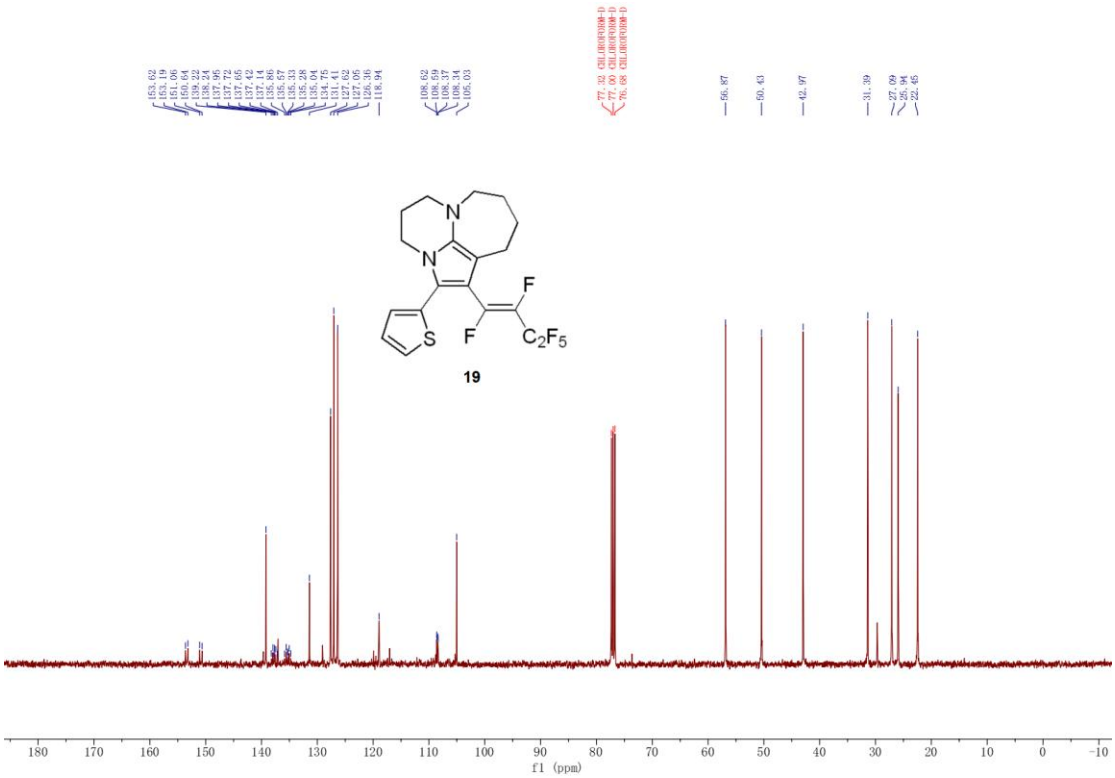
^{1}H NMR spectra of the product **19** (400 MHz, $CDCl_3$):



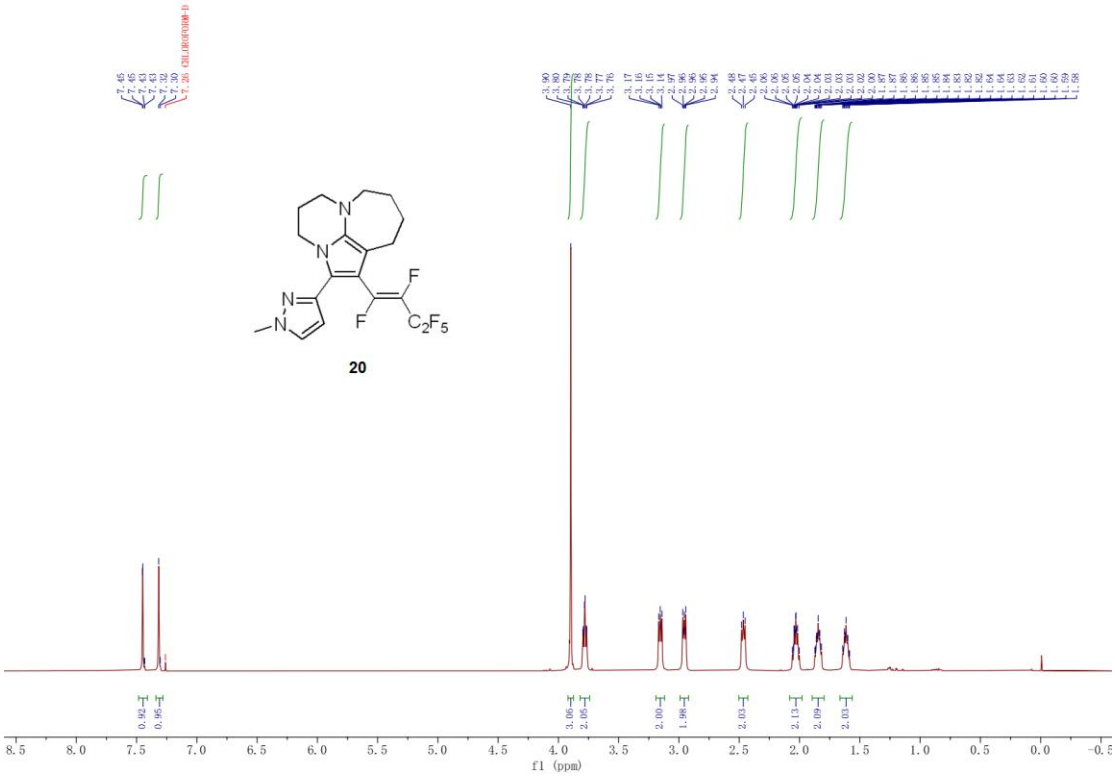
^{19}F NMR spectra of the product **19** (376 MHz, $CDCl_3$):



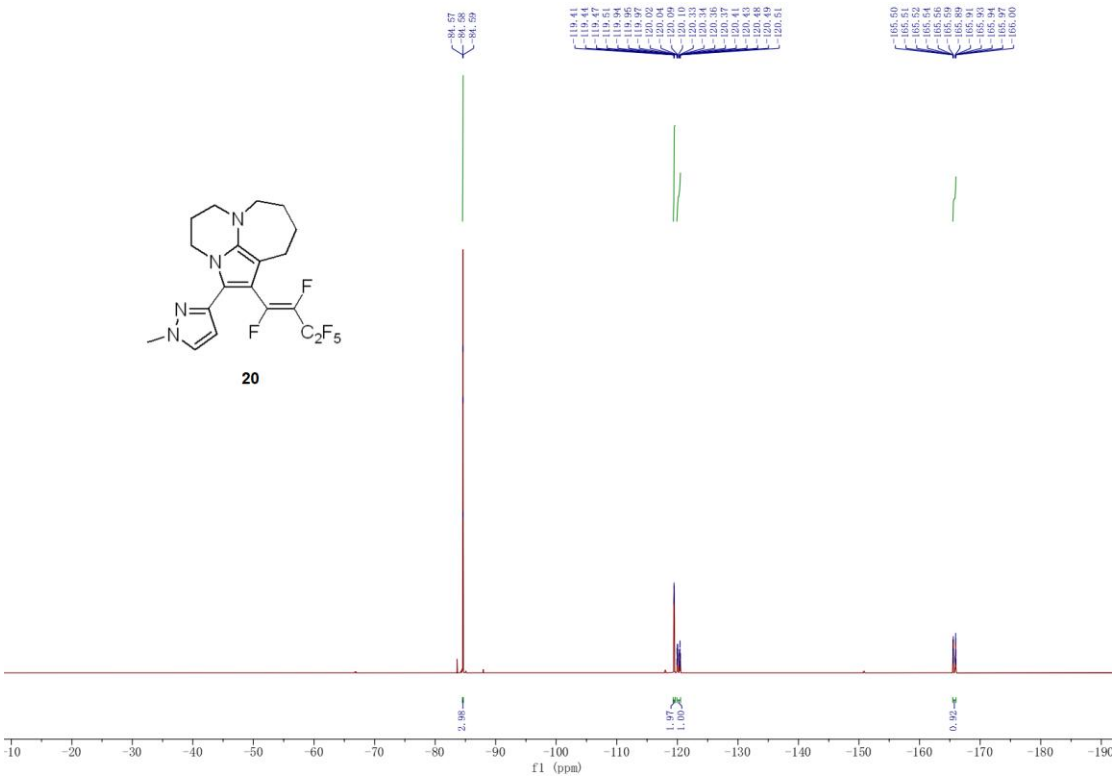
^{13}C NMR spectra of the product **19** (101 MHz, $CDCl_3$):



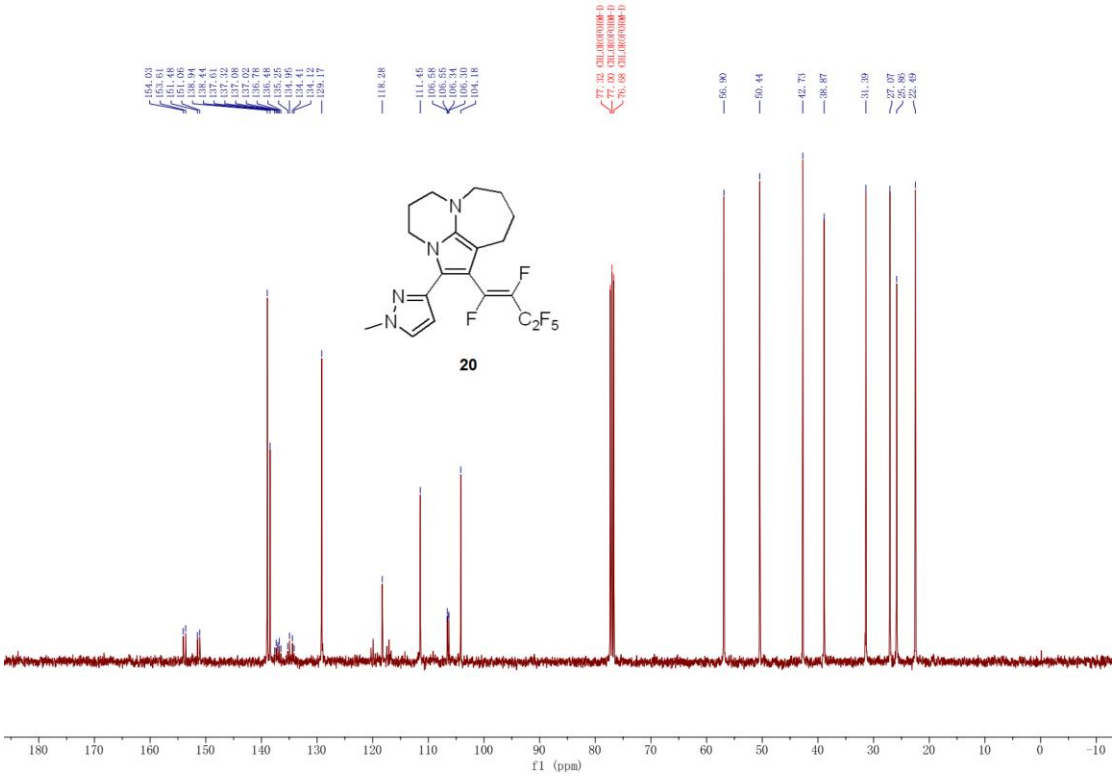
^{1}H NMR spectra of the product **20** (400 MHz, $CDCl_3$):



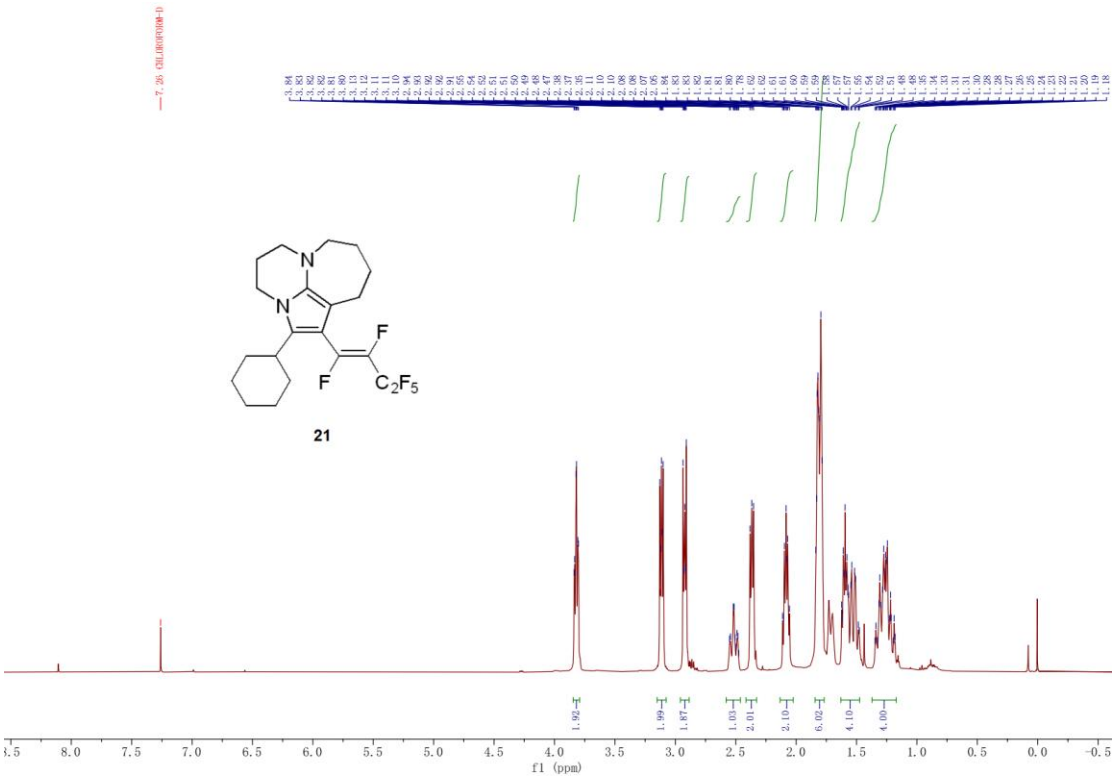
^{19}F NMR spectra of the product **20** (376 MHz, $CDCl_3$):



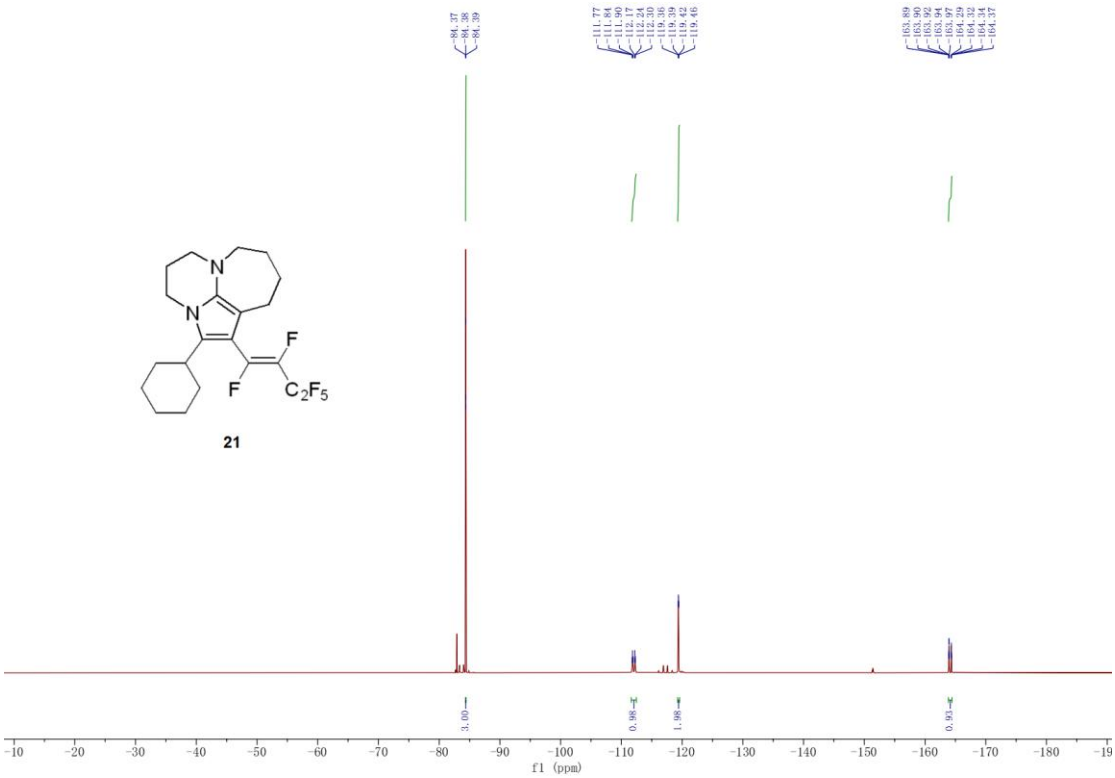
^{13}C NMR spectra of the product **20** (101 MHz, $CDCl_3$):



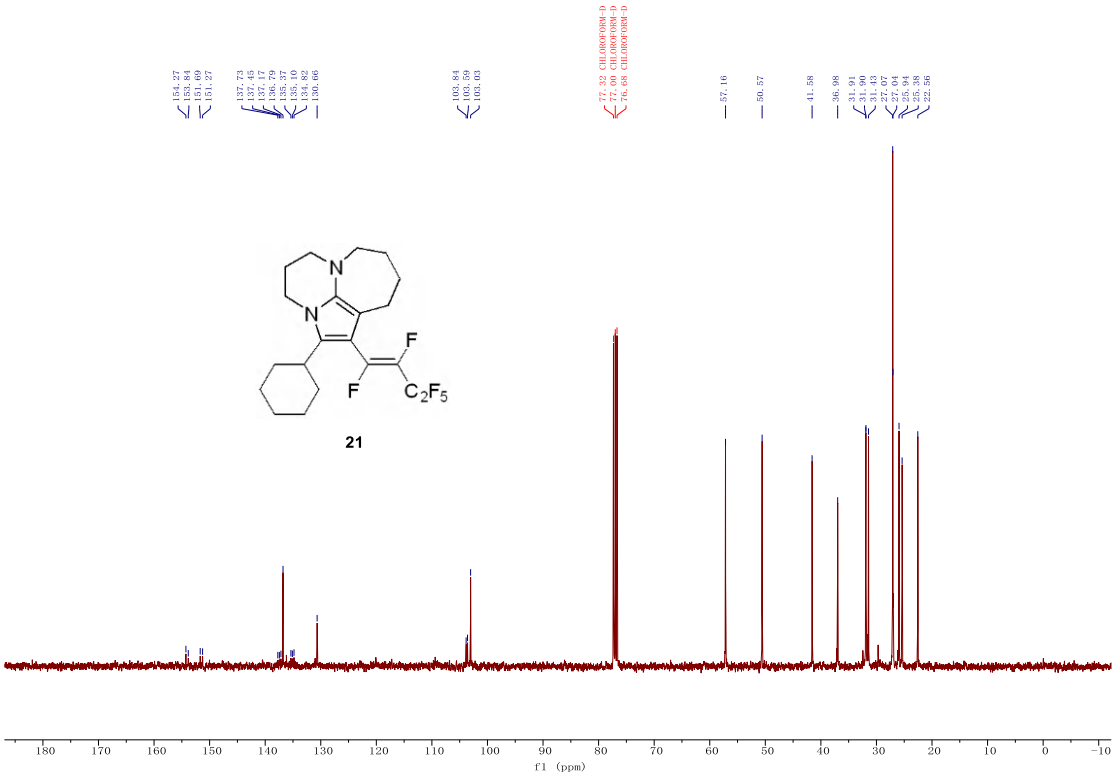
^{1}H NMR spectra of the product **21** (400 MHz, $CDCl_3$):



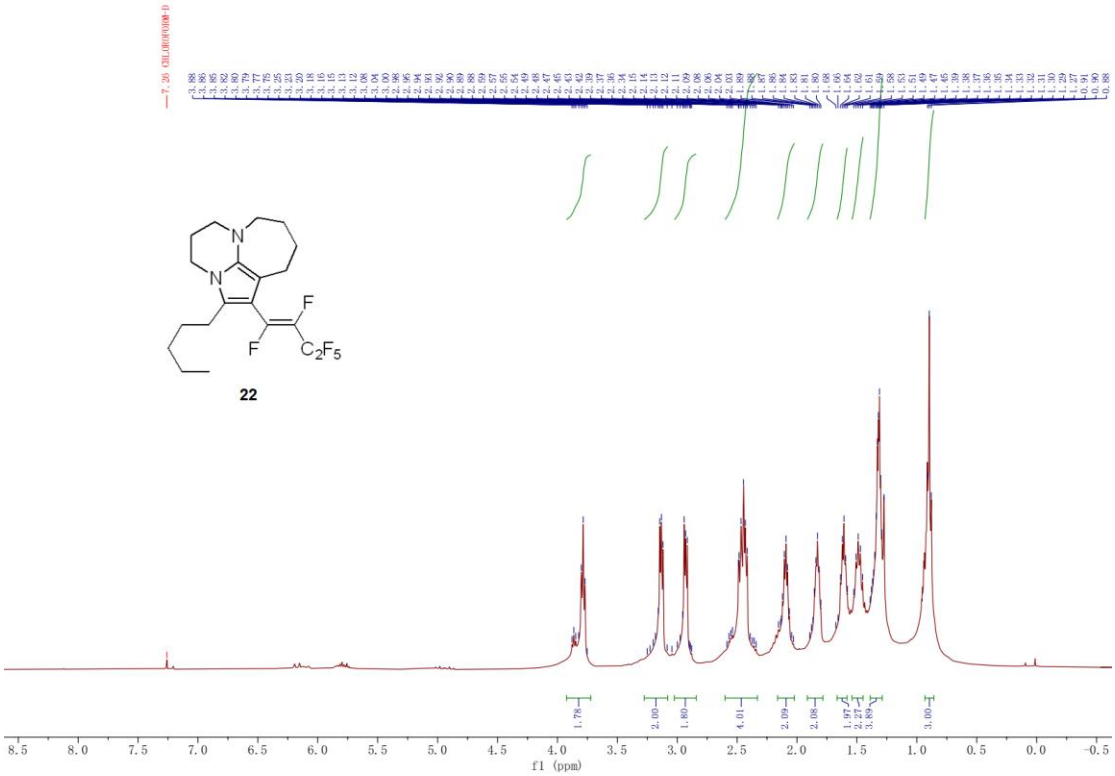
^{19}F NMR spectra of the product **21** (376 MHz, $CDCl_3$):



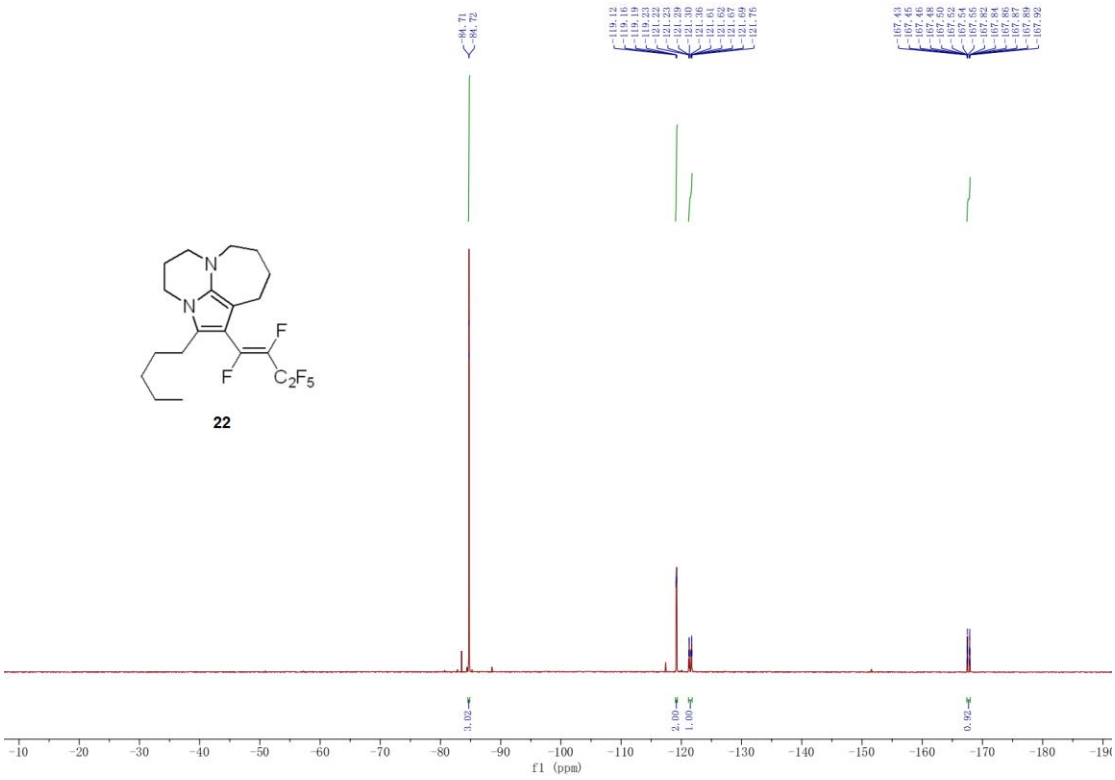
^{13}C NMR spectra of the product **21** (101 MHz, $CDCl_3$):



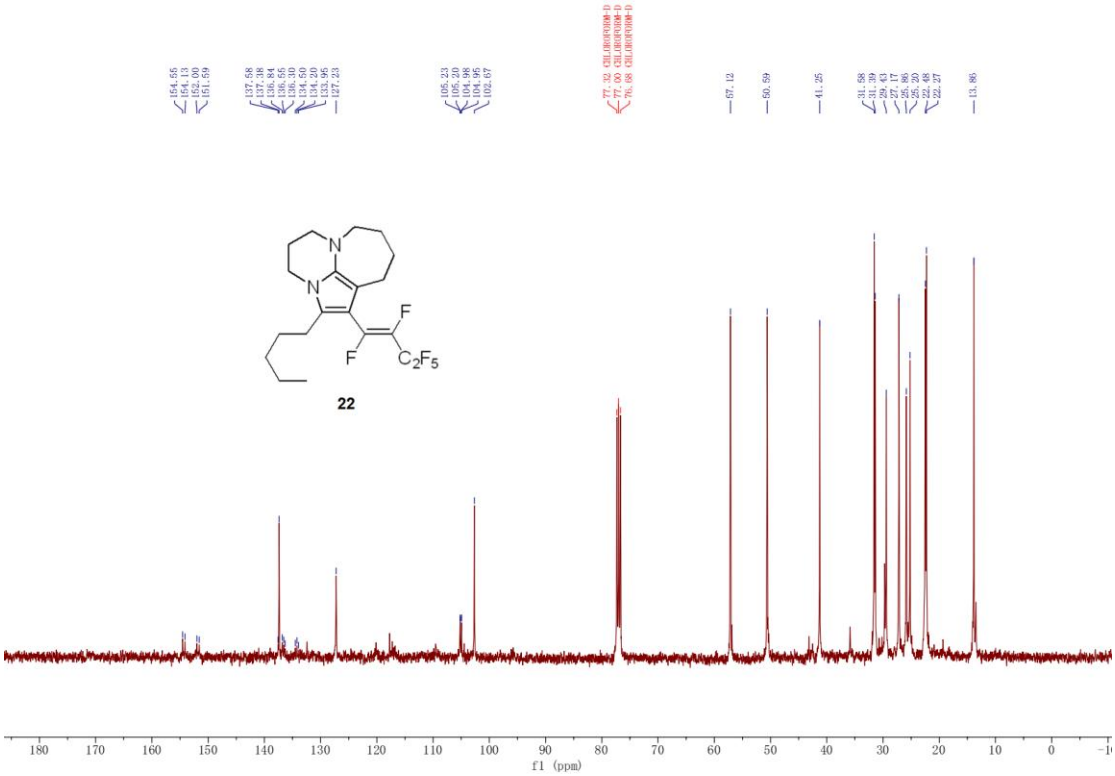
^{1}H NMR spectra of the product **22** (400 MHz, $CDCl_3$):



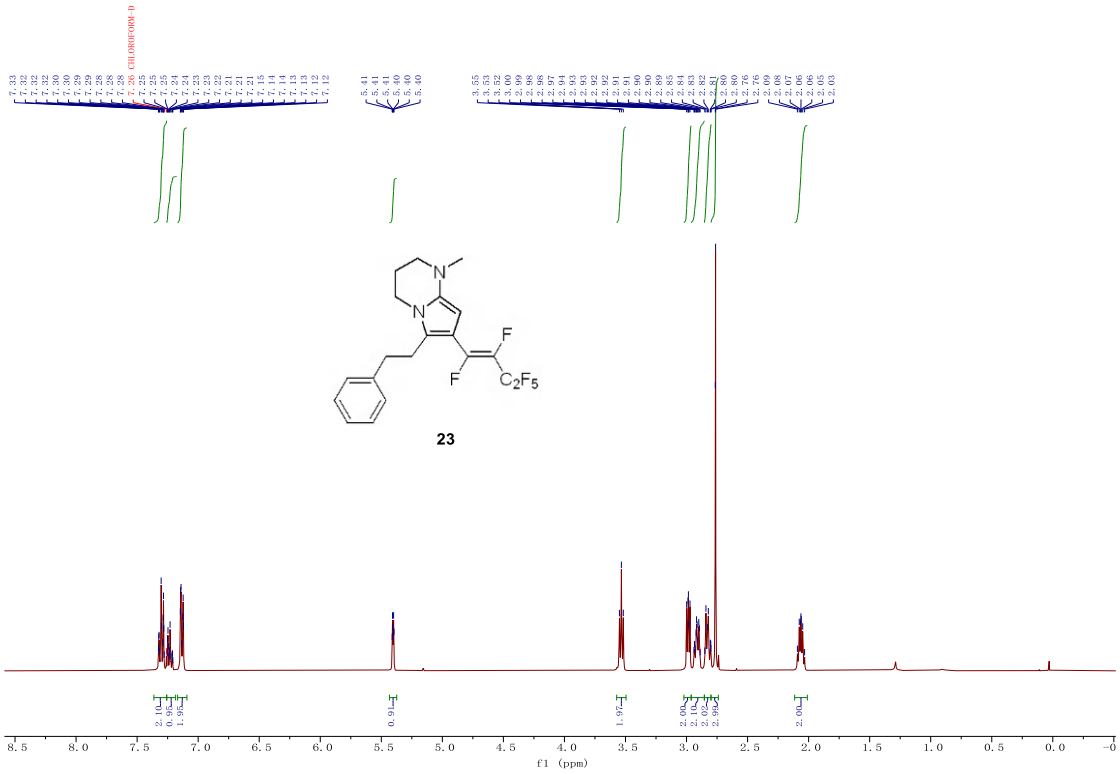
^{19}F NMR spectra of the product **22** (376 MHz, $CDCl_3$):



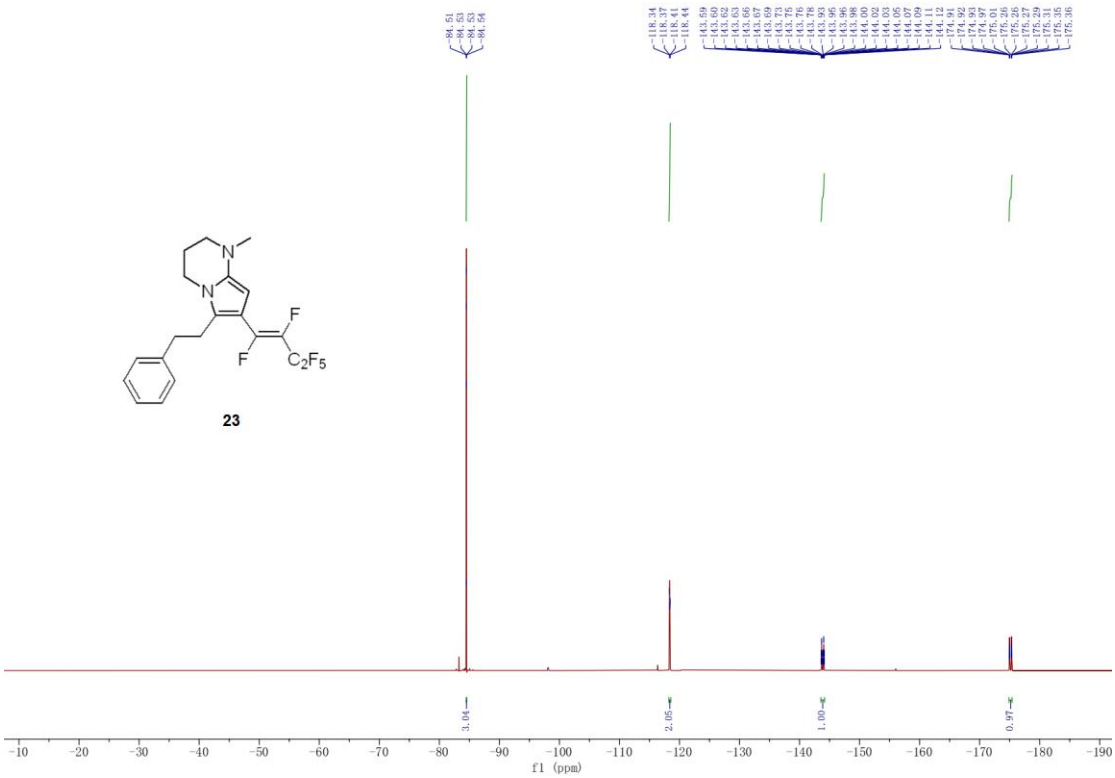
^{13}C NMR spectra of the product **22** (101 MHz, $CDCl_3$):



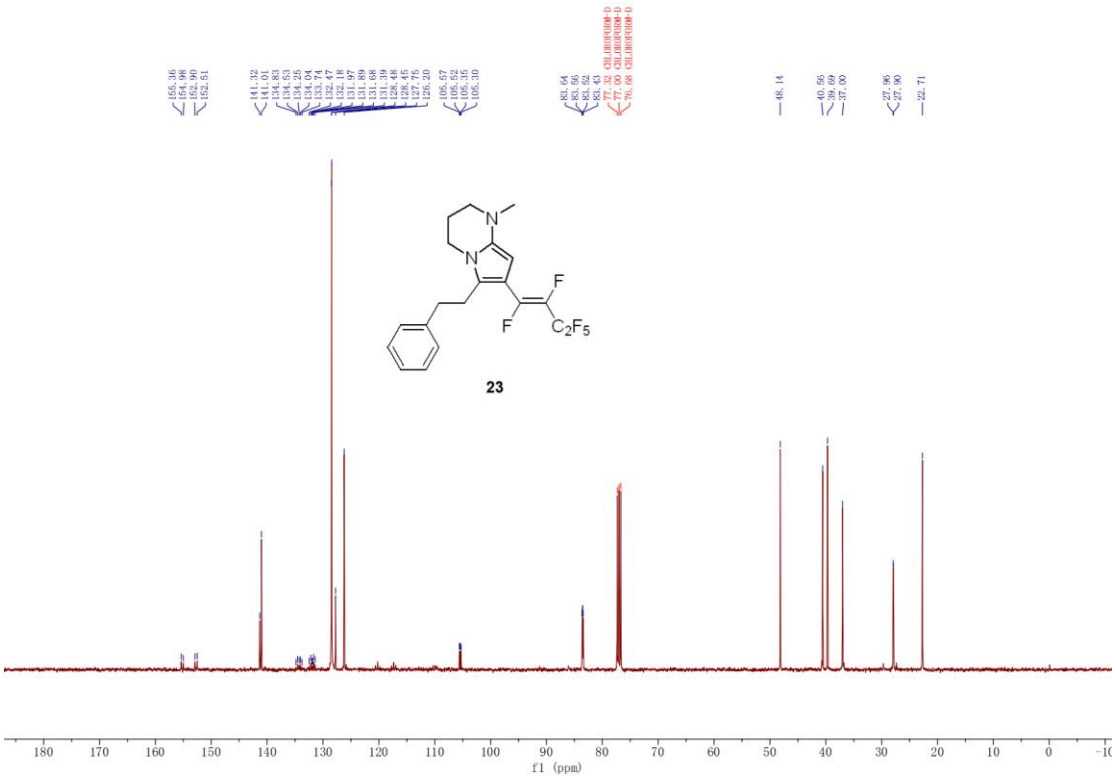
^{1}H NMR spectra of the product **23** (400 MHz, $CDCl_3$):



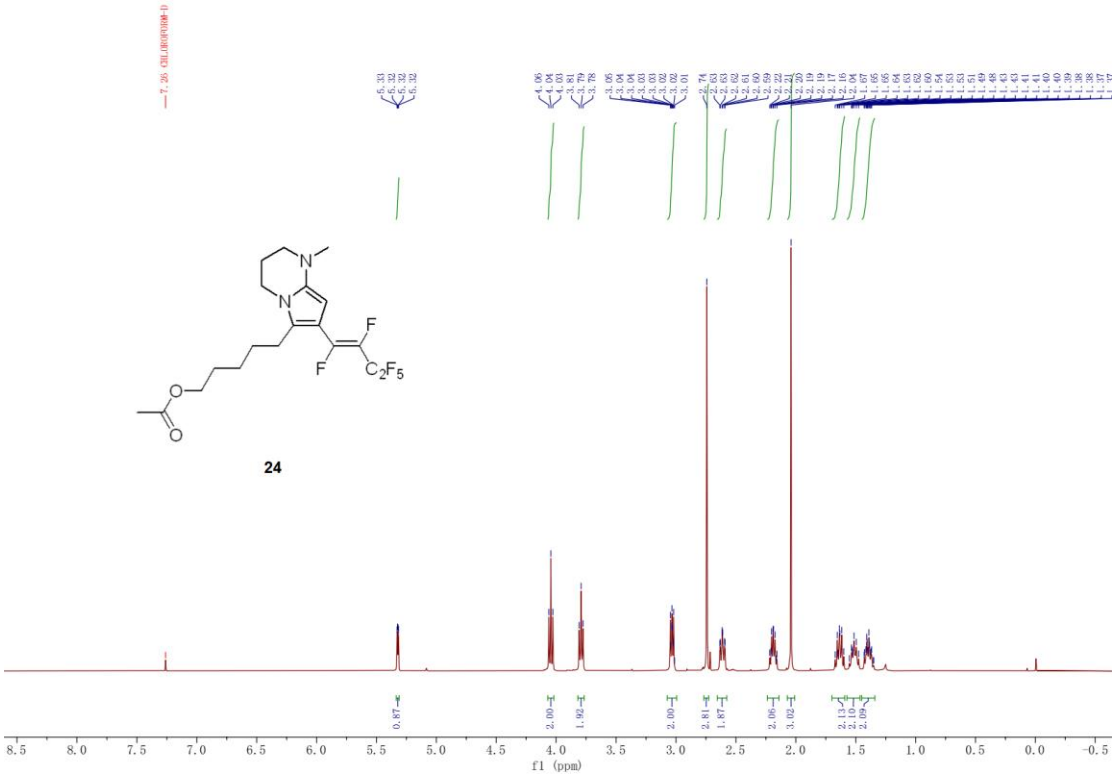
^{19}F NMR spectra of the product **23** (376 MHz, $CDCl_3$):



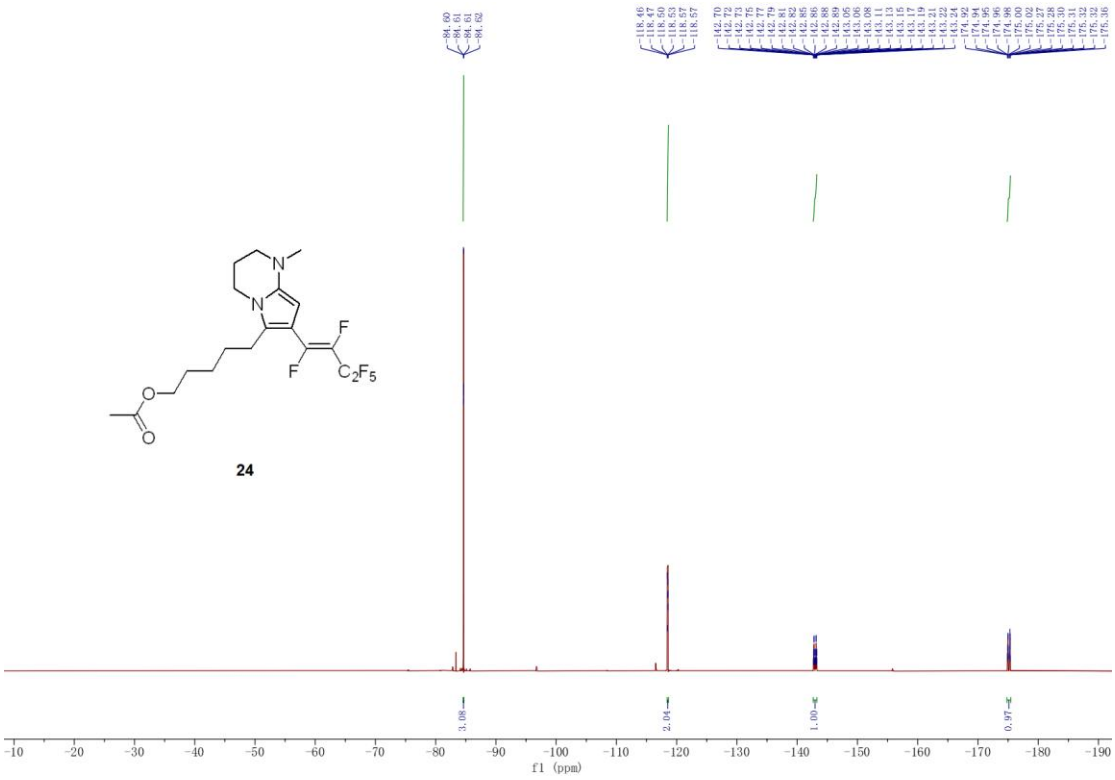
^{13}C NMR spectra of the product **23** (101 MHz, $CDCl_3$):



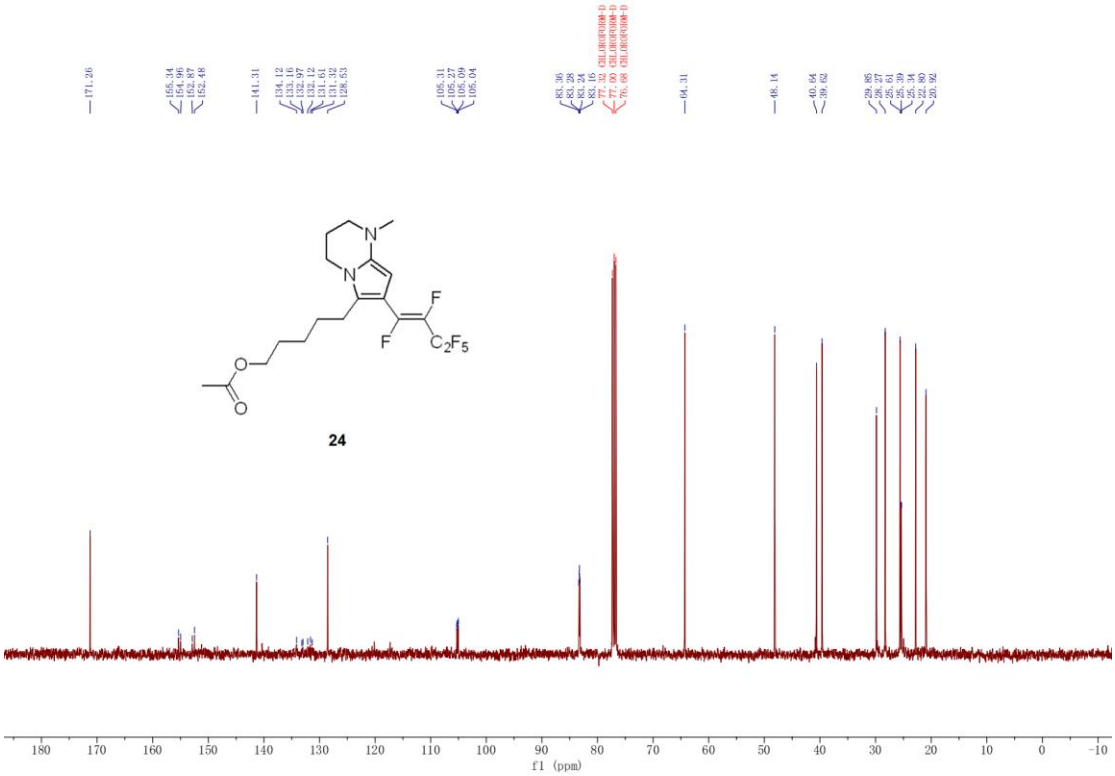
^{1}H NMR spectra of the product **24** (400 MHz, $CDCl_3$):



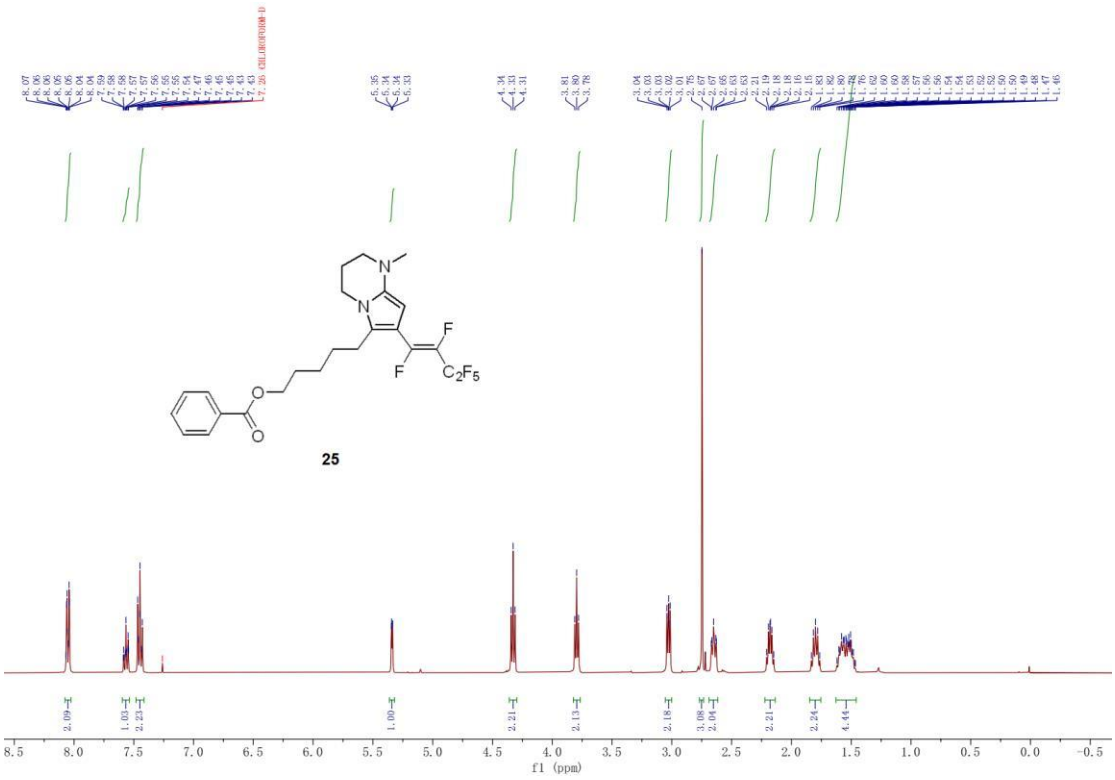
^{19}F NMR spectra of the product **24** (376 MHz, $CDCl_3$):



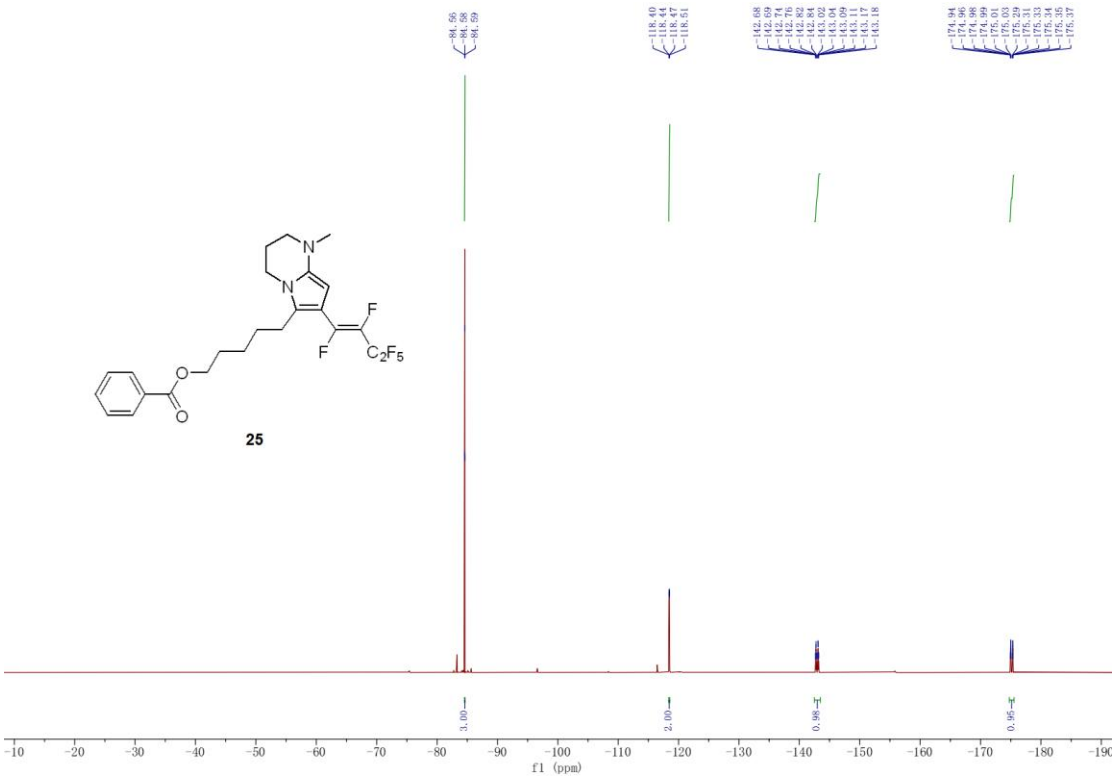
^{13}C NMR spectra of the product **24** (101 MHz, $CDCl_3$):



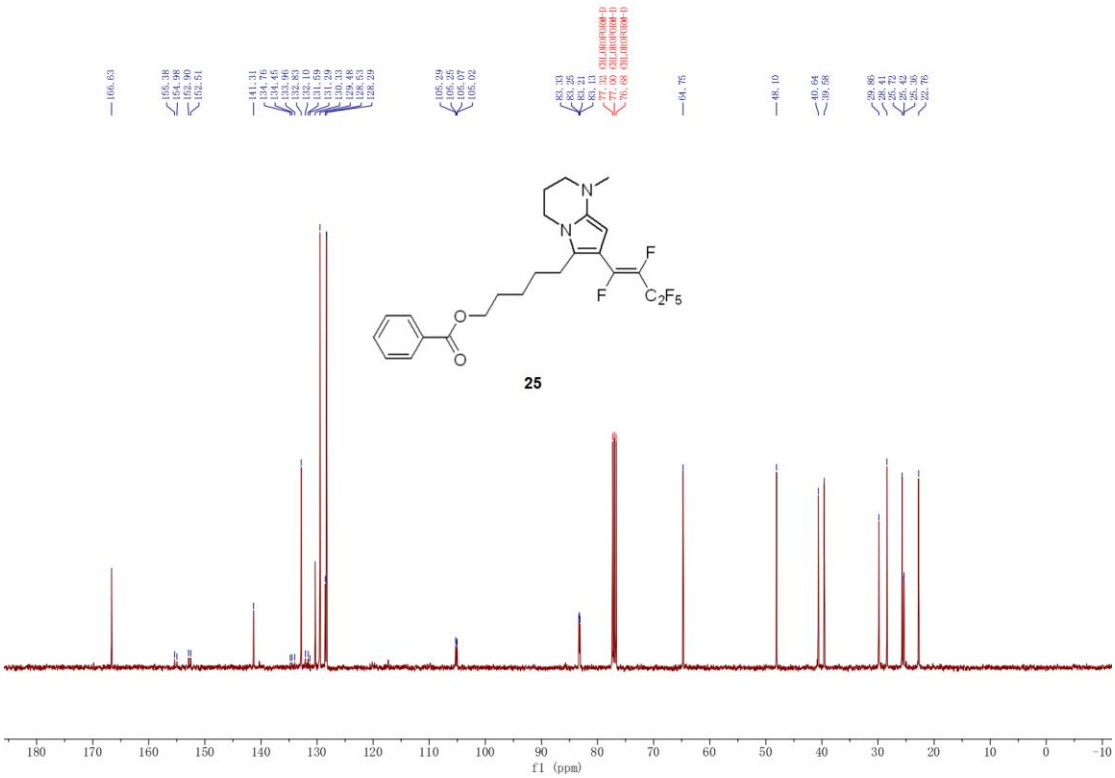
^{1}H NMR spectra of the product **25** (400 MHz, $CDCl_3$):



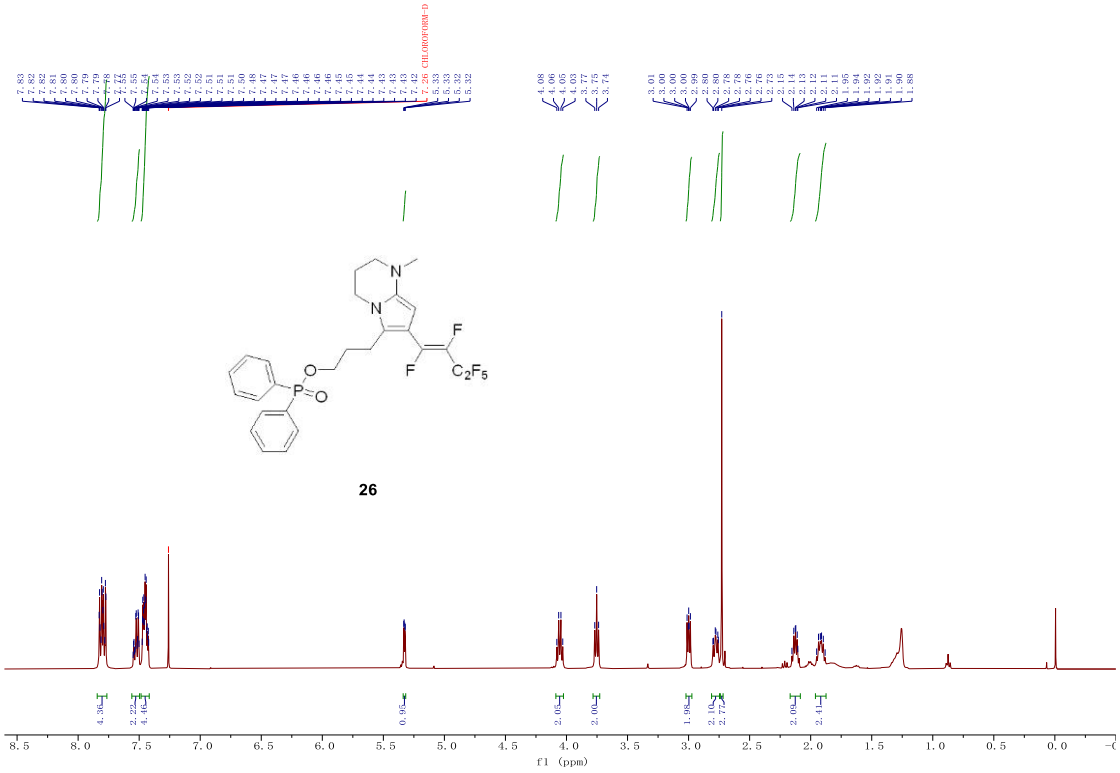
^{19}F NMR spectra of the product **25** (376 MHz, $CDCl_3$):



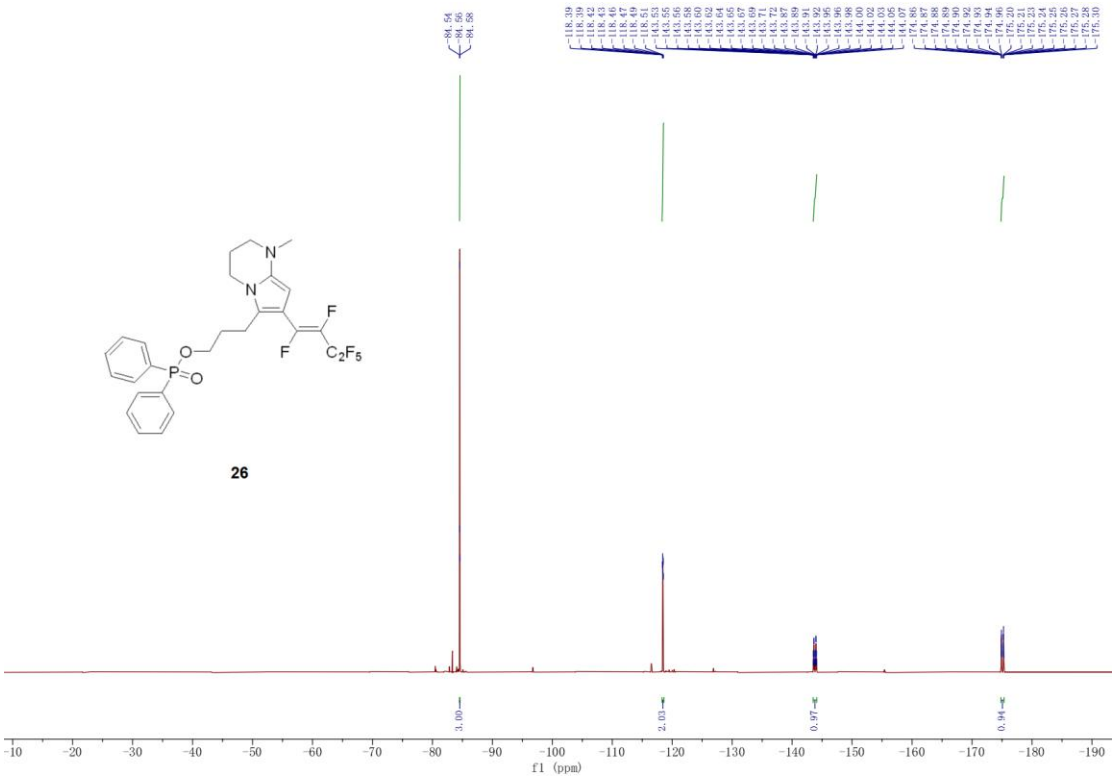
^{13}C NMR spectra of the product **25** (101 MHz, $CDCl_3$):



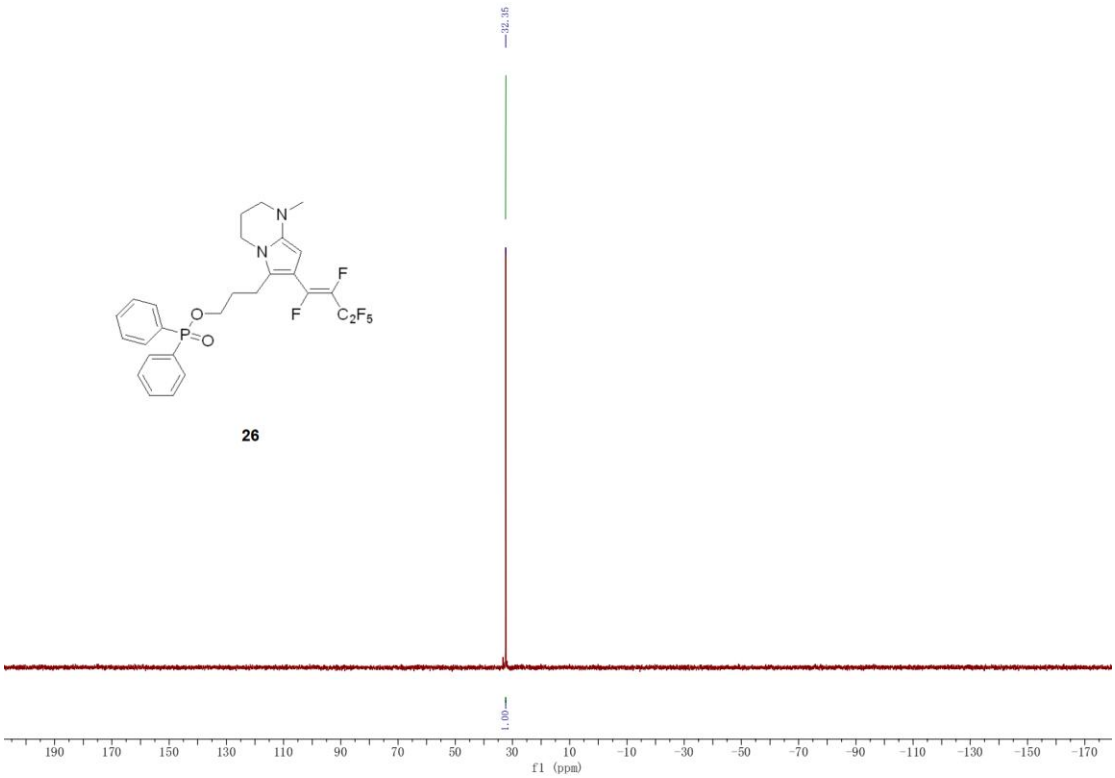
^{1}H NMR spectra of the product **26** (400 MHz, $CDCl_3$):



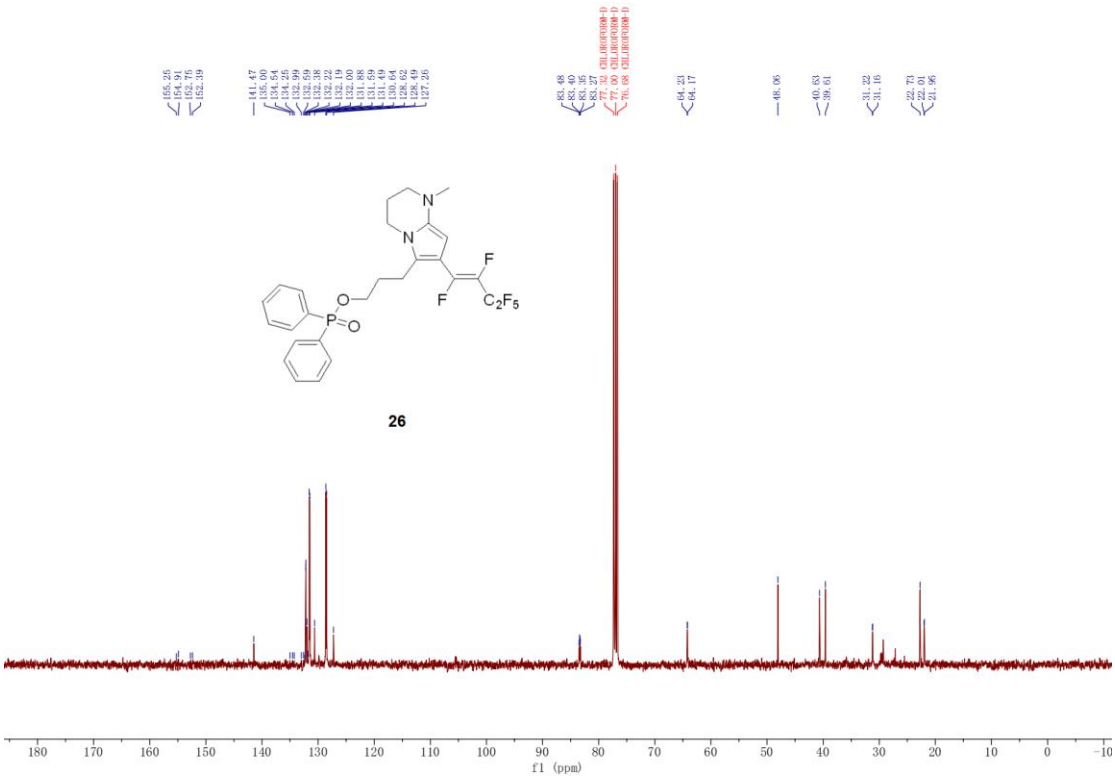
^{19}F NMR spectra of the product **26** (376 MHz, $CDCl_3$):



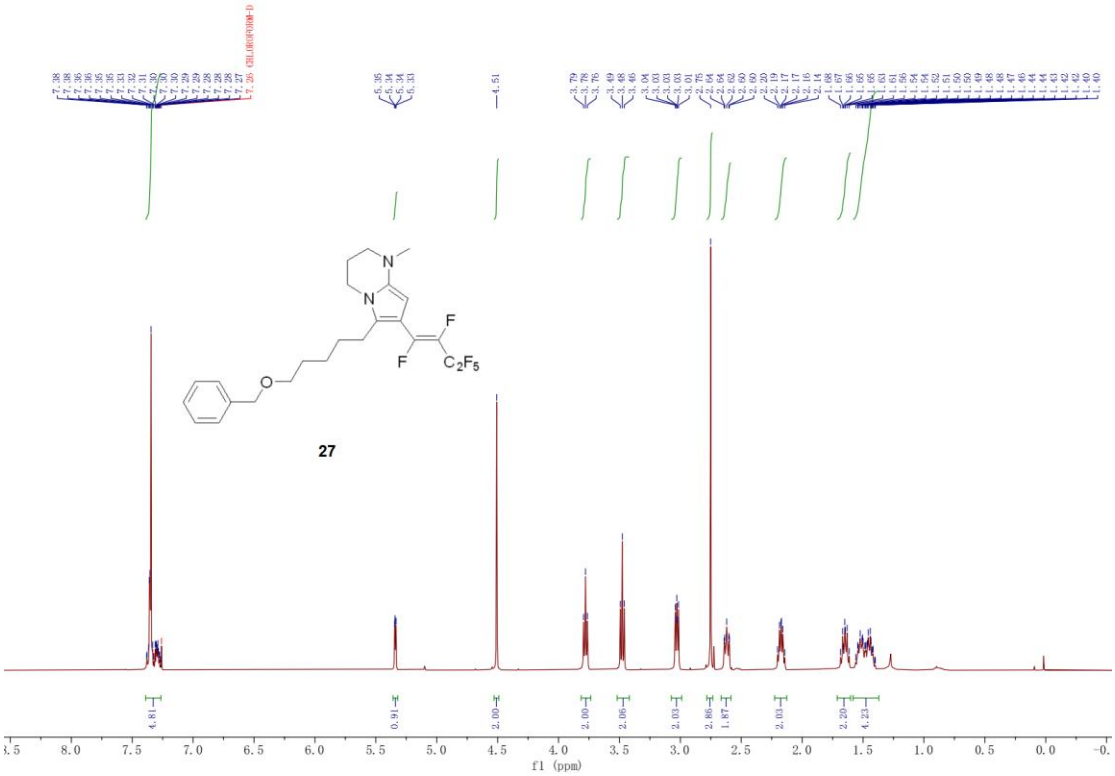
^{31}P NMR spectra of the product **26** (162 MHz, $CDCl_3$):



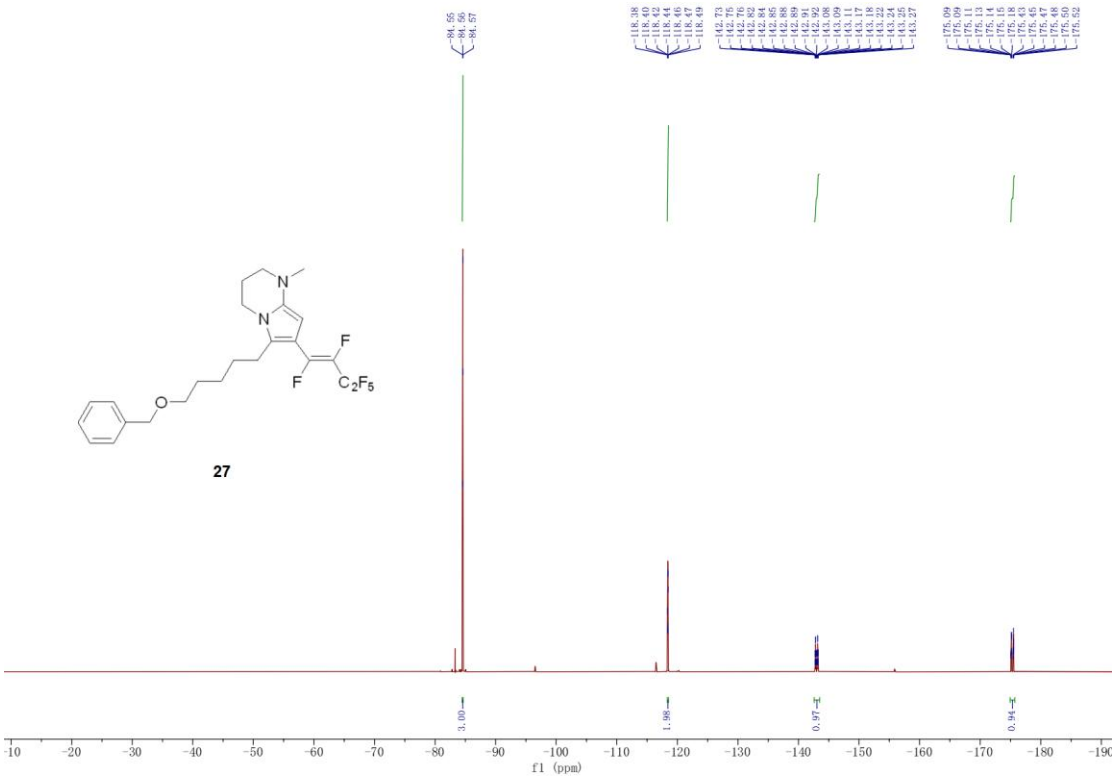
^{13}C NMR spectra of the product **26** (101 MHz, $CDCl_3$):



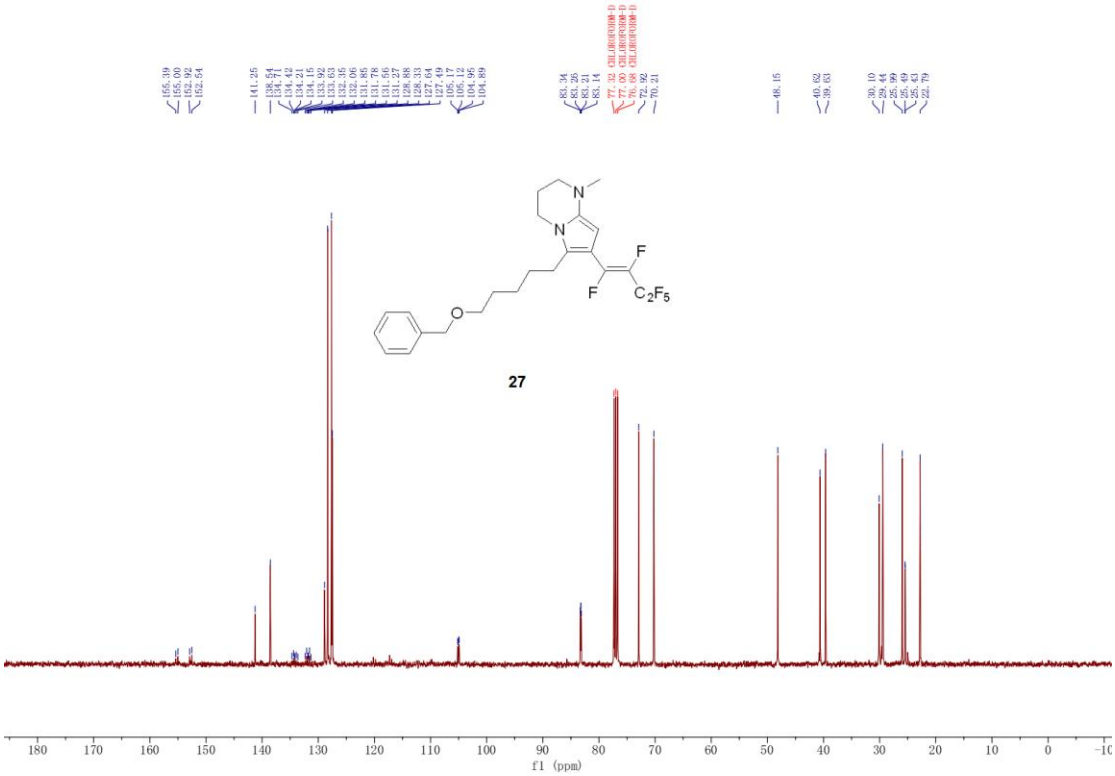
^{1}H NMR spectra of the product **27** (400 MHz, $CDCl_3$):



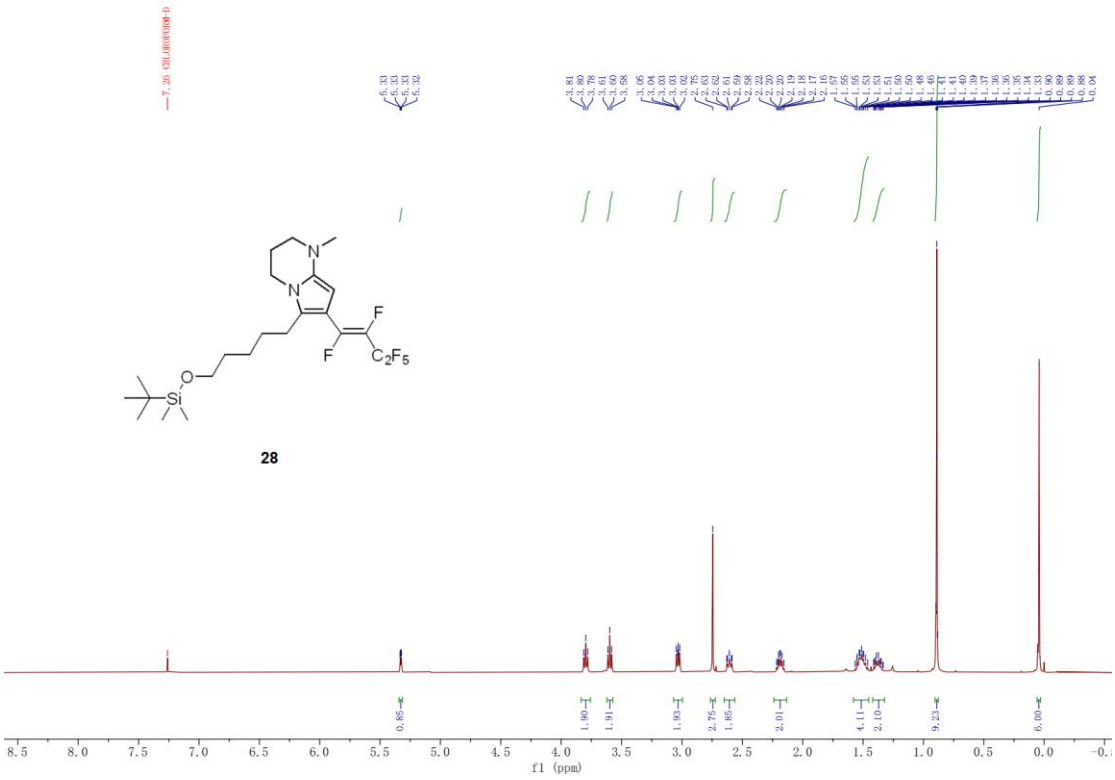
^{19}F NMR spectra of the product **27** (376 MHz, $CDCl_3$):



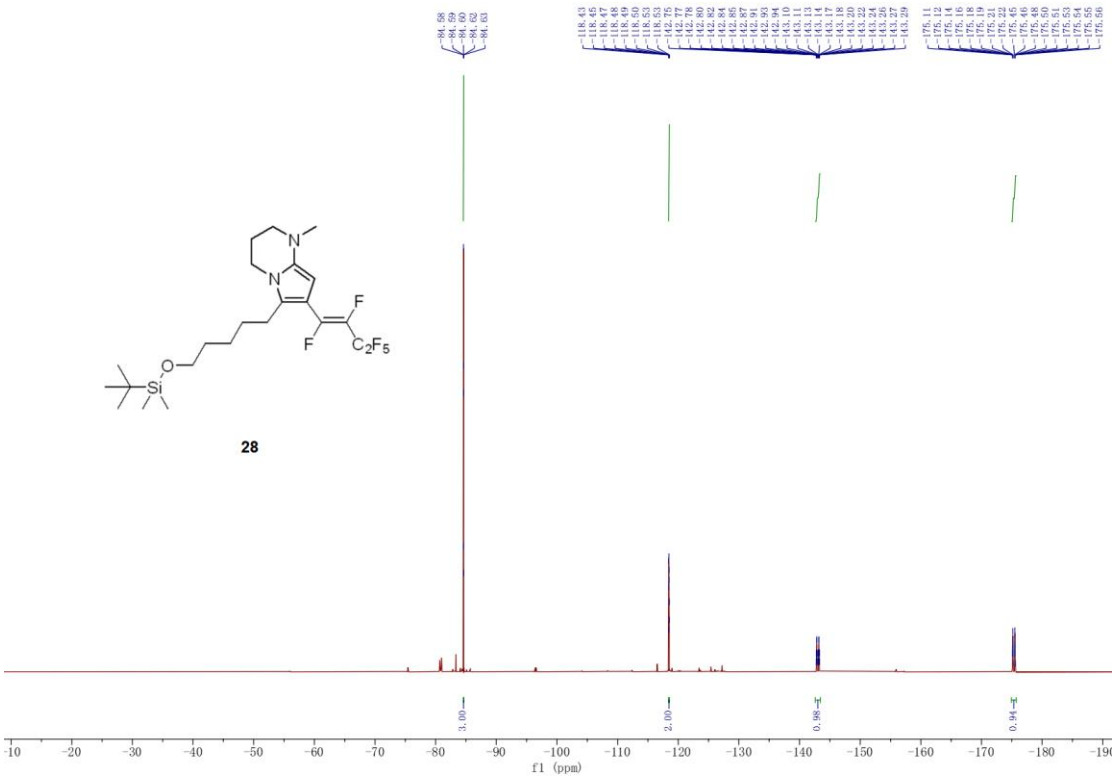
^{13}C NMR spectra of the product **27** (101 MHz, $CDCl_3$):



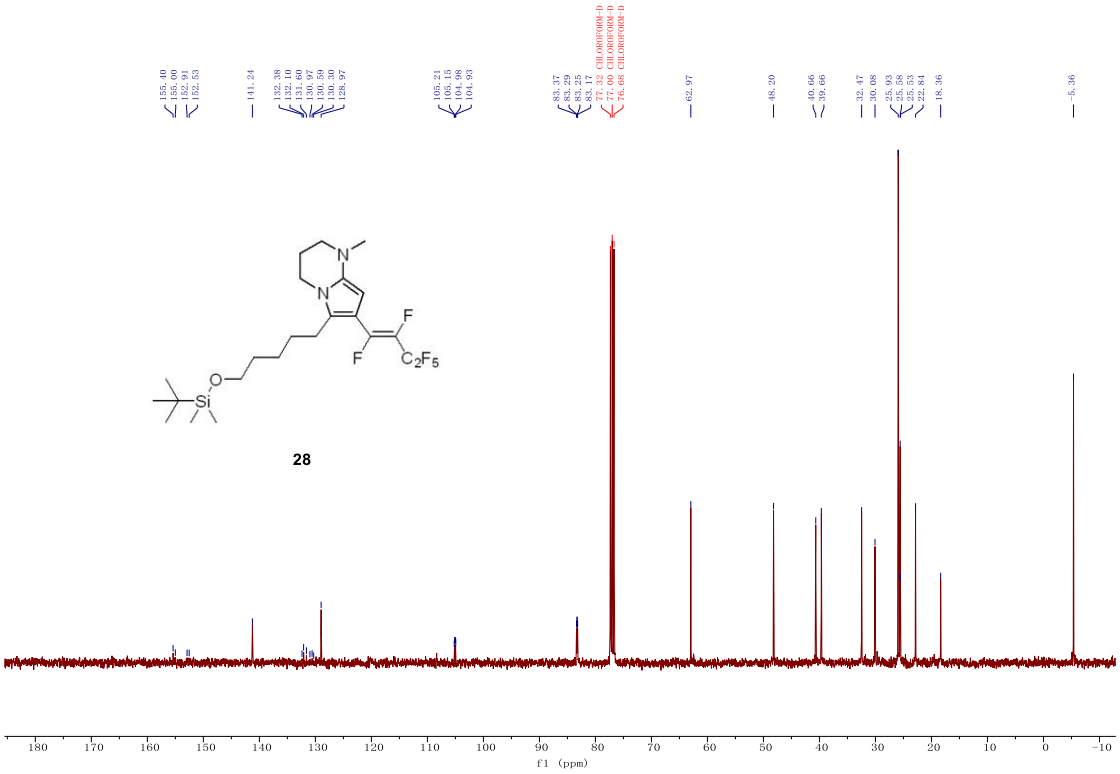
^{1}H NMR spectra of the product **28** (400 MHz, $CDCl_3$):



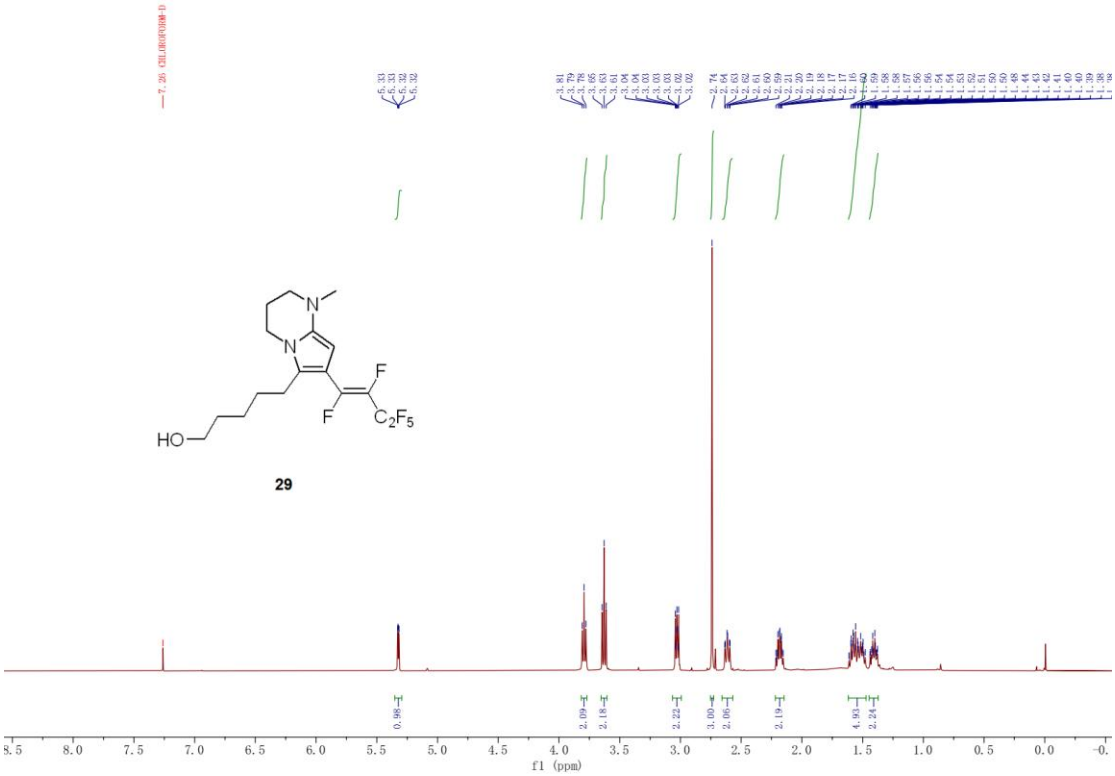
^{19}F NMR spectra of the product **28** (376 MHz, $CDCl_3$):



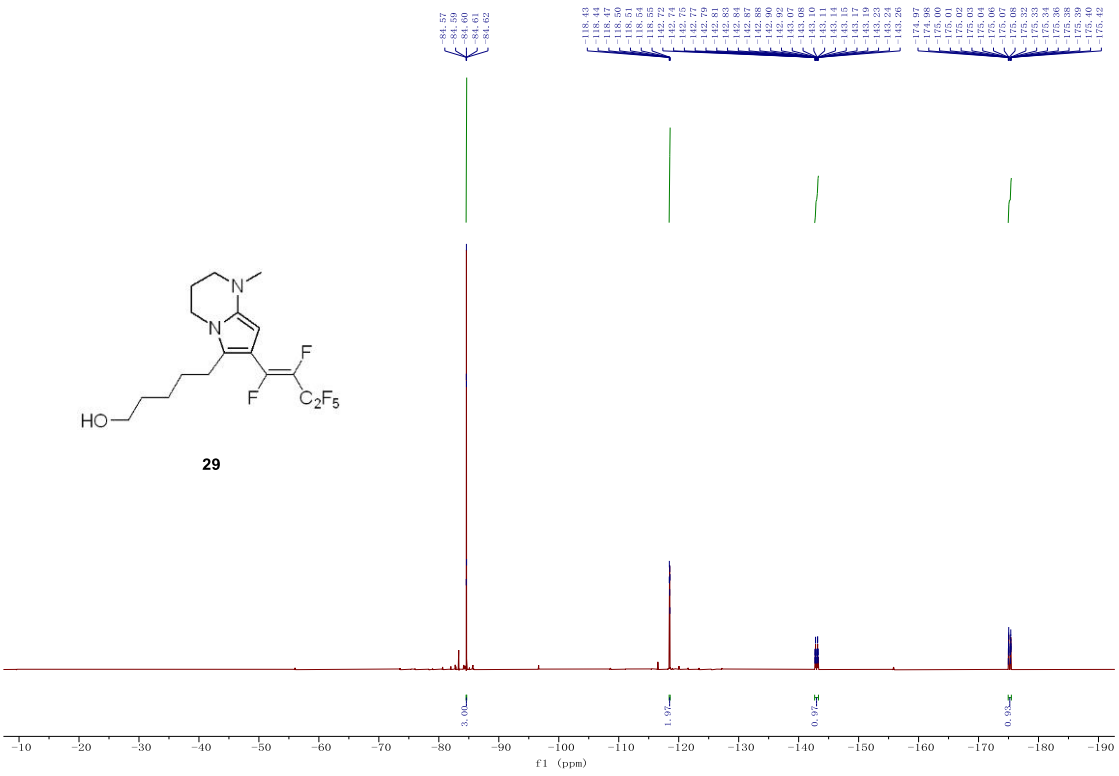
^{13}C NMR spectra of the product **28** (101 MHz, $CDCl_3$):



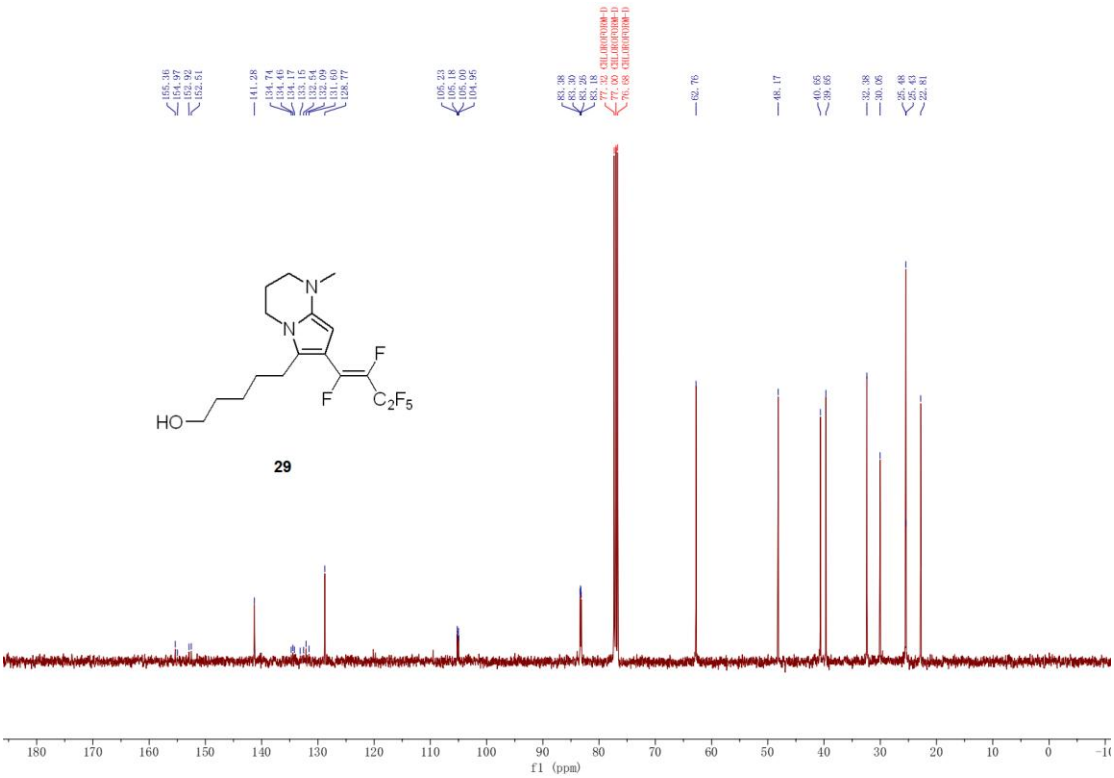
^{1}H NMR spectra of the product **29** (400 MHz, $CDCl_3$):



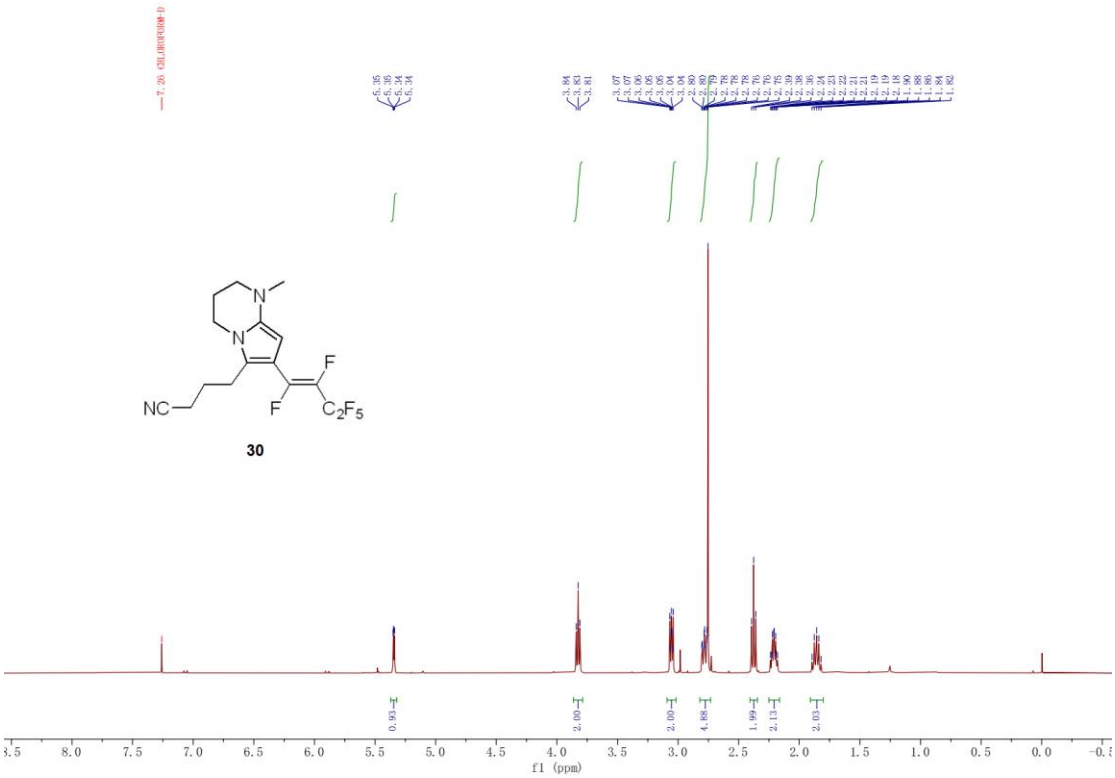
^{19}F NMR spectra of the product **29** (376 MHz, $CDCl_3$):



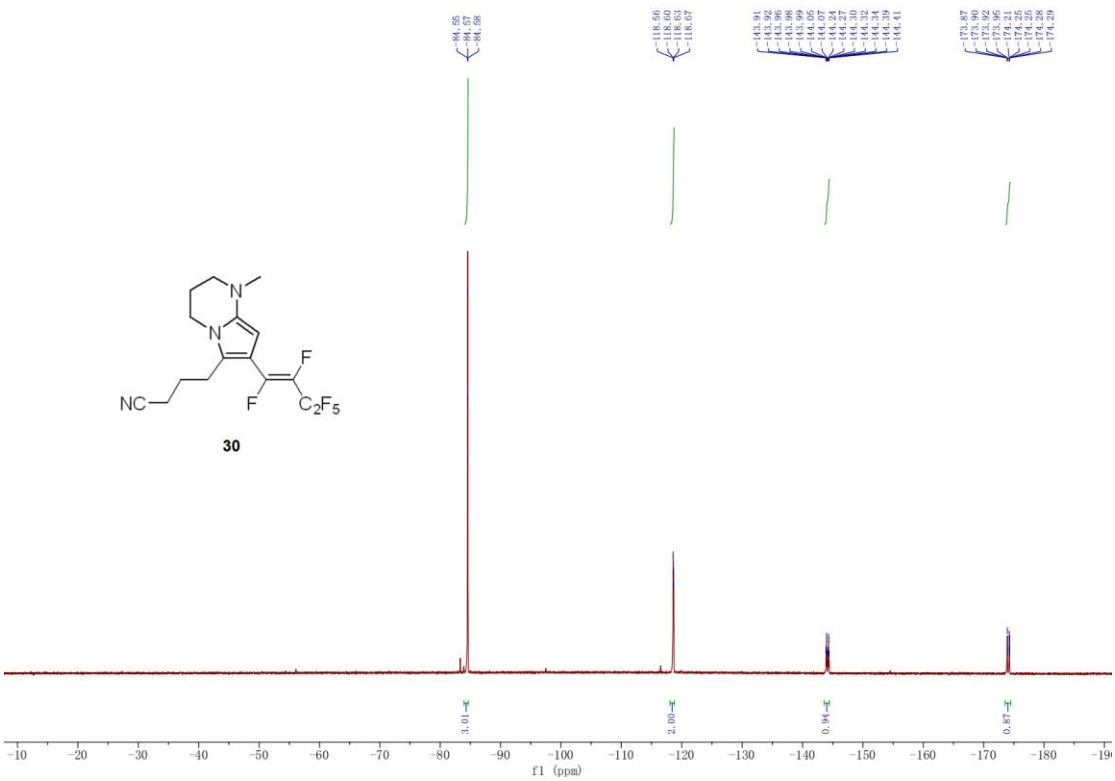
^{13}C NMR spectra of the product **29** (101 MHz, $CDCl_3$):



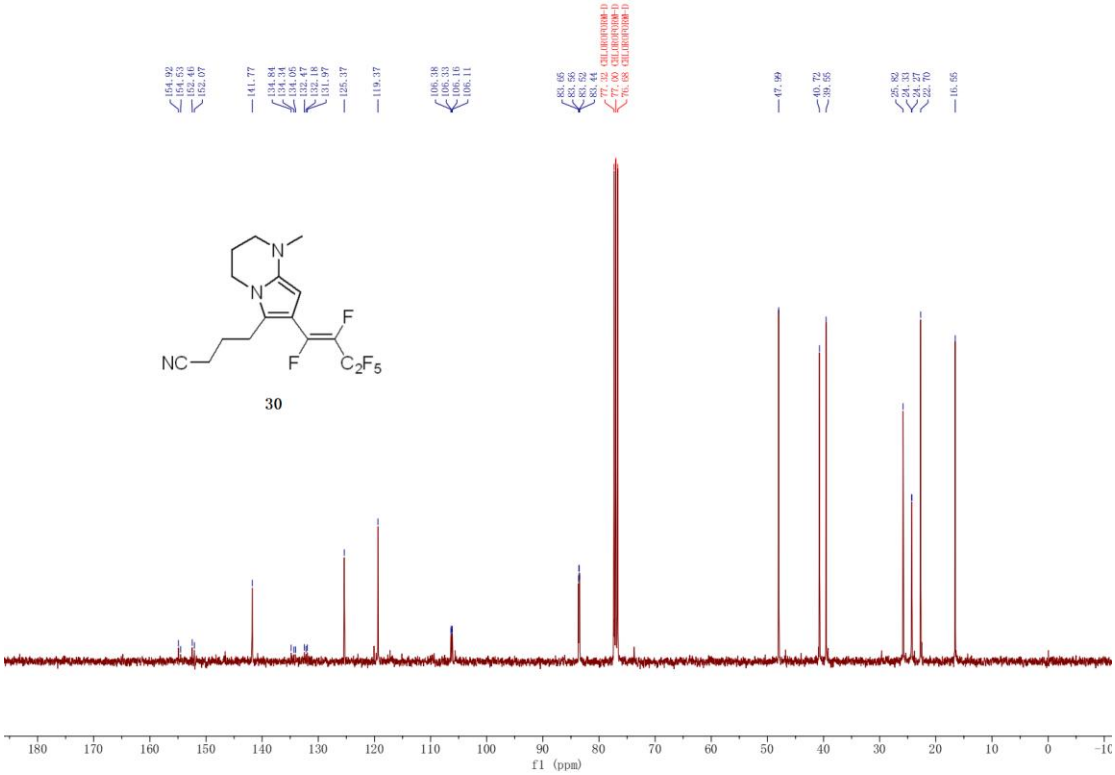
^{1}H NMR spectra of the product **30** (400 MHz, $CDCl_3$):



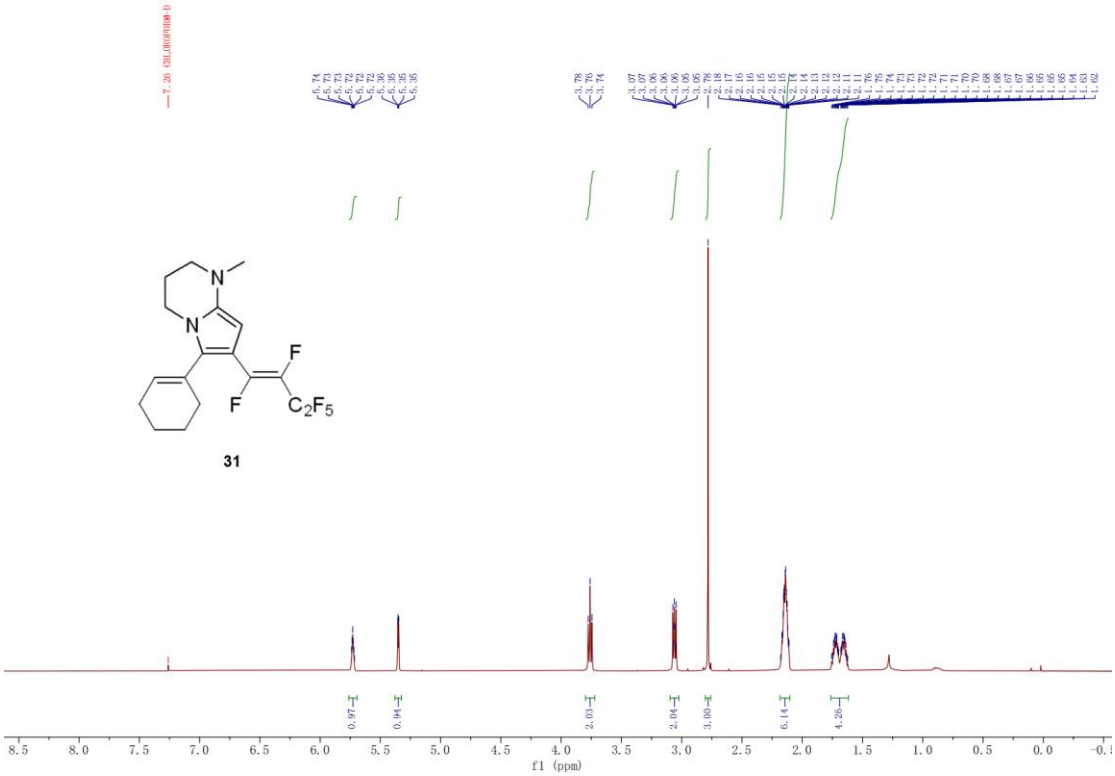
^{19}F NMR spectra of the product **30** (376 MHz, $CDCl_3$):



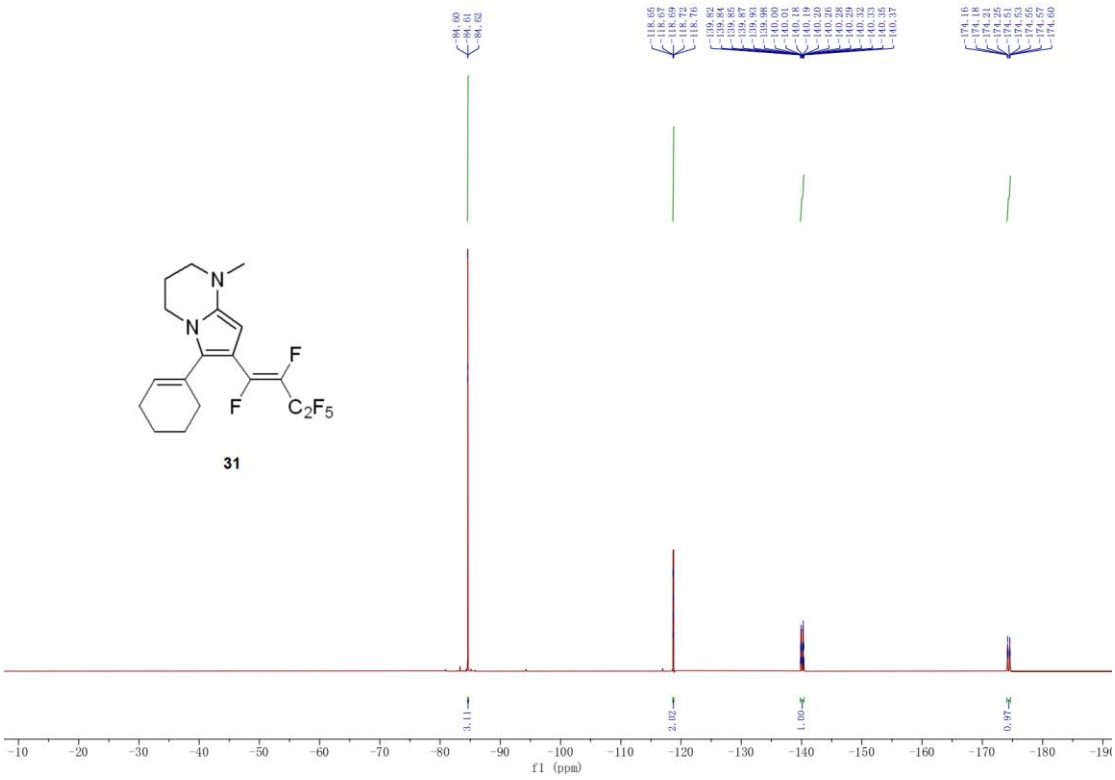
^{13}C NMR spectra of the product **30** (101 MHz, $CDCl_3$):



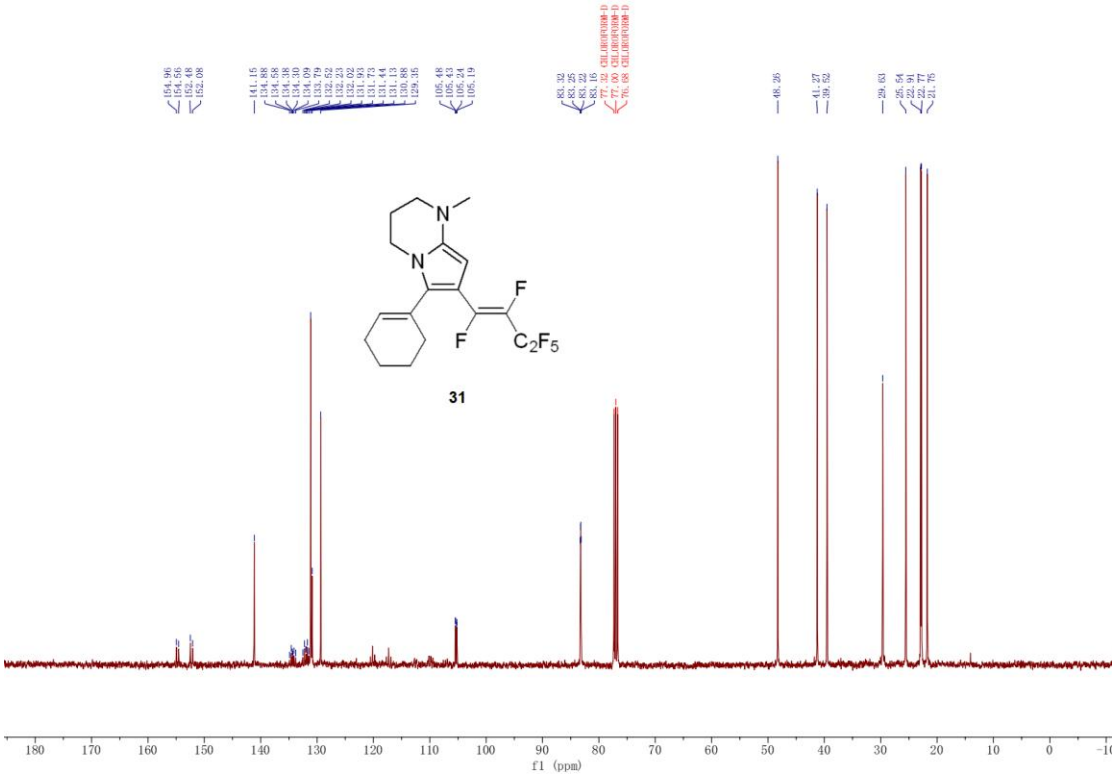
^{1}H NMR spectra of the product **31** (400 MHz, $CDCl_3$):



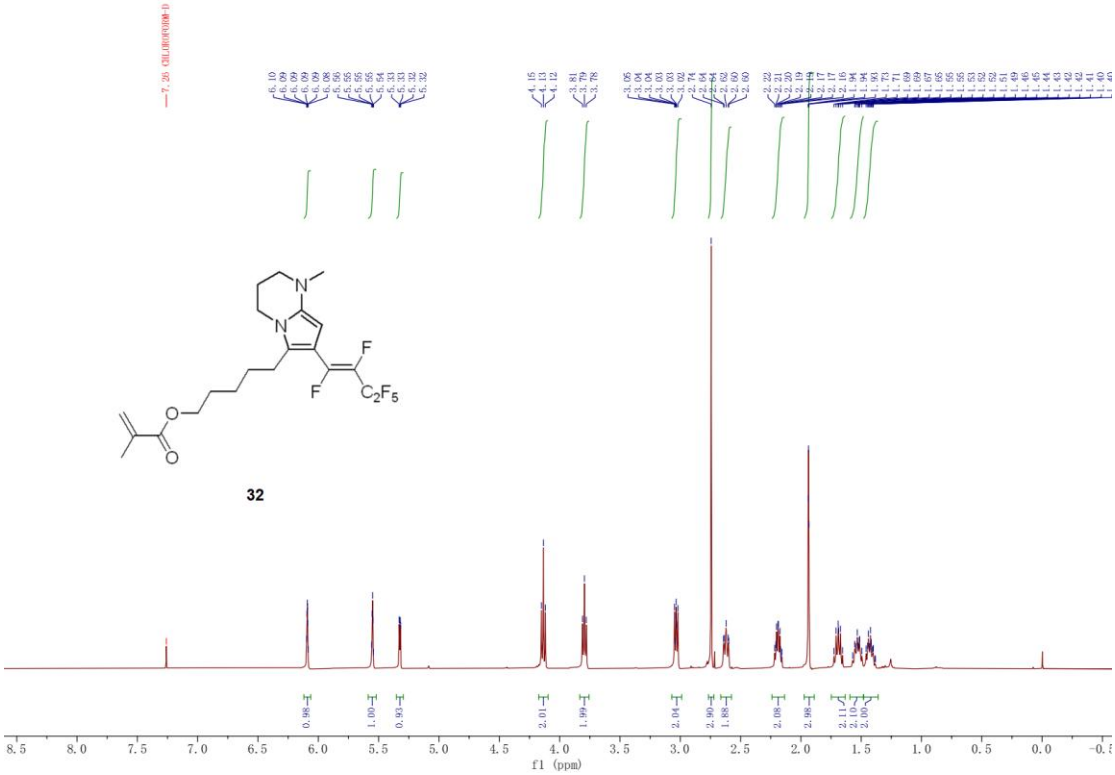
^{19}F NMR spectra of the product **31** (376 MHz, $CDCl_3$):



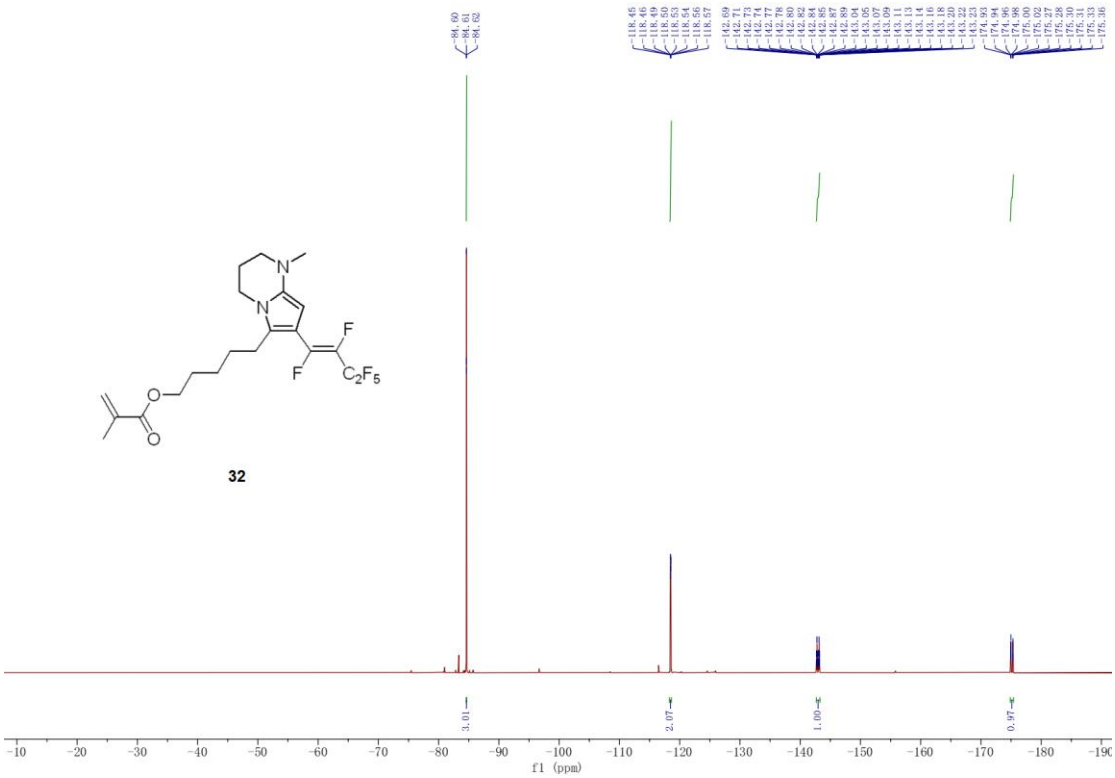
^{13}C NMR spectra of the product **31** (101 MHz, $CDCl_3$):



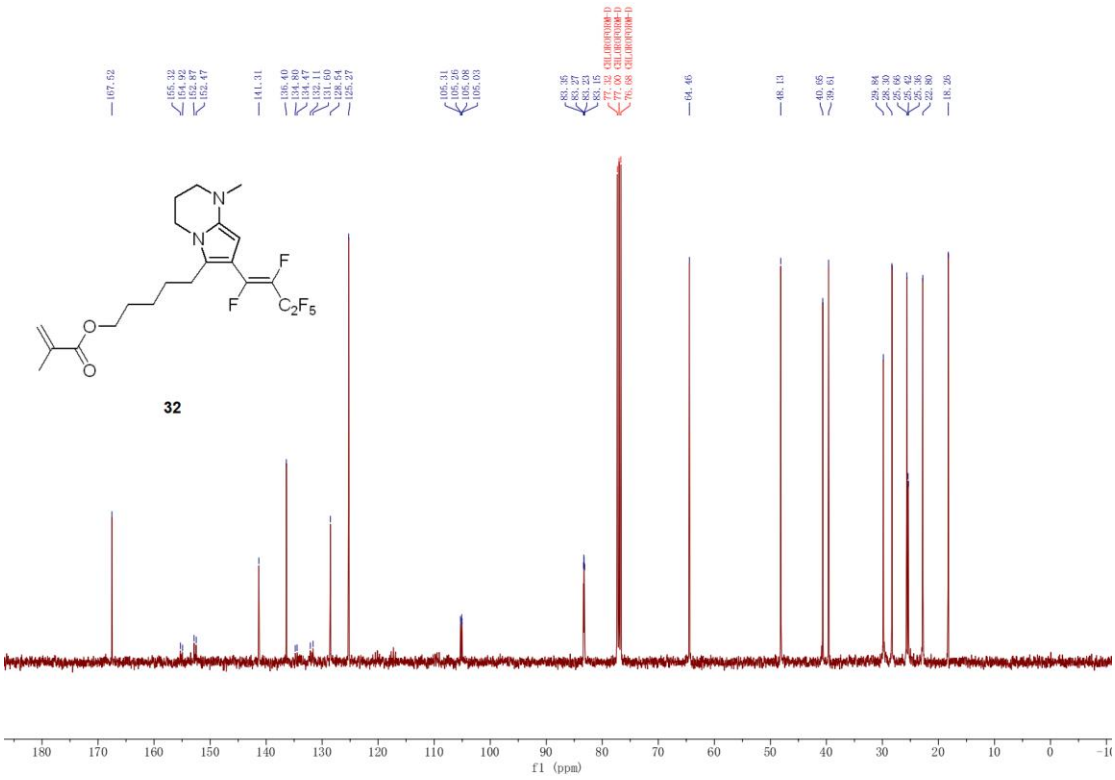
^{1}H NMR spectra of the product **32** (400 MHz, $CDCl_3$):



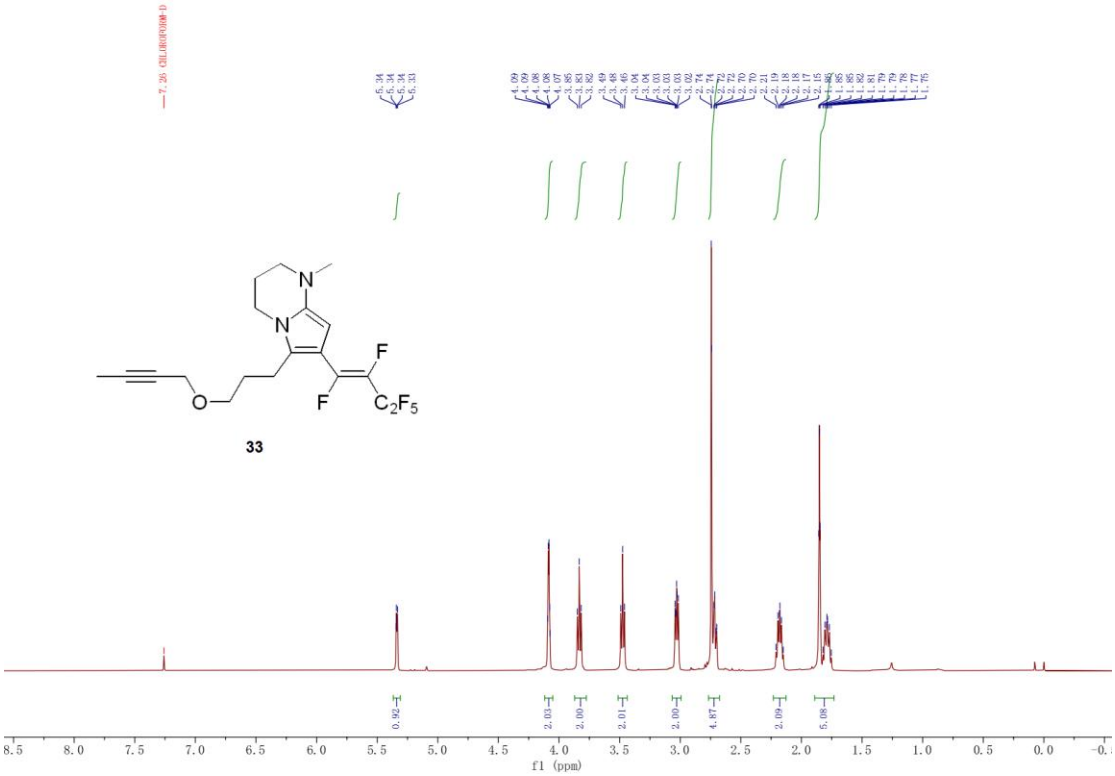
^{19}F NMR spectra of the product **32** (376 MHz, $CDCl_3$):



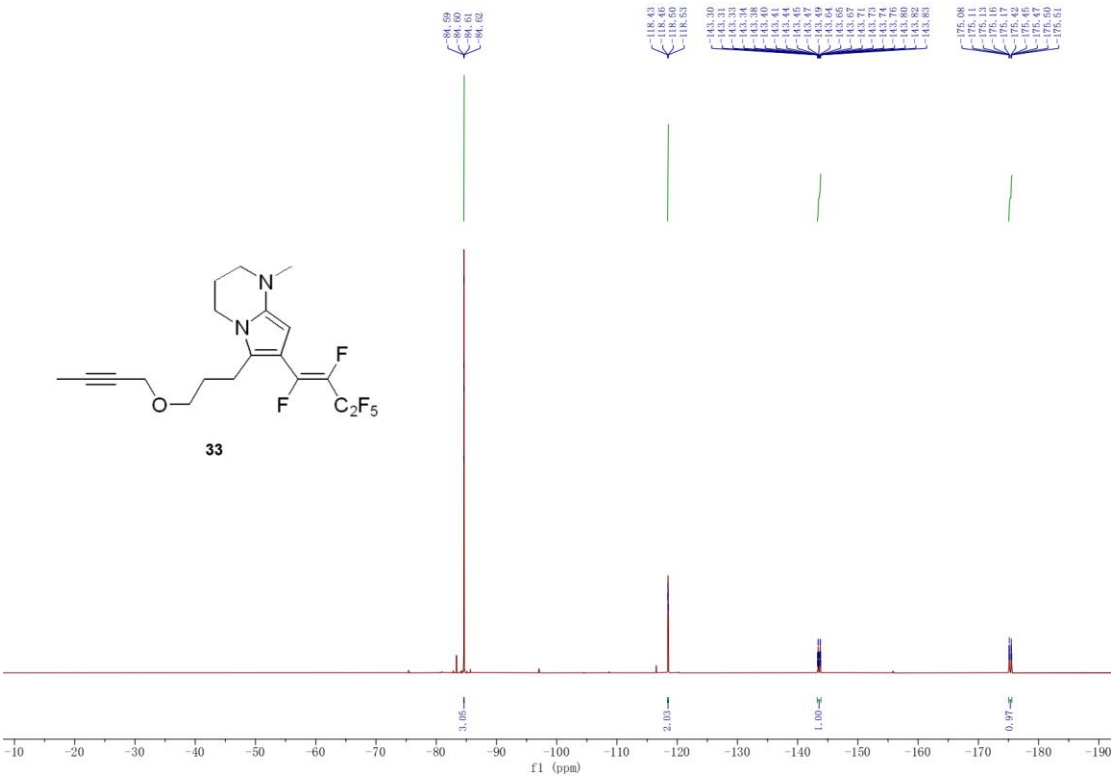
^{13}C NMR spectra of the product **32** (101 MHz, $CDCl_3$):



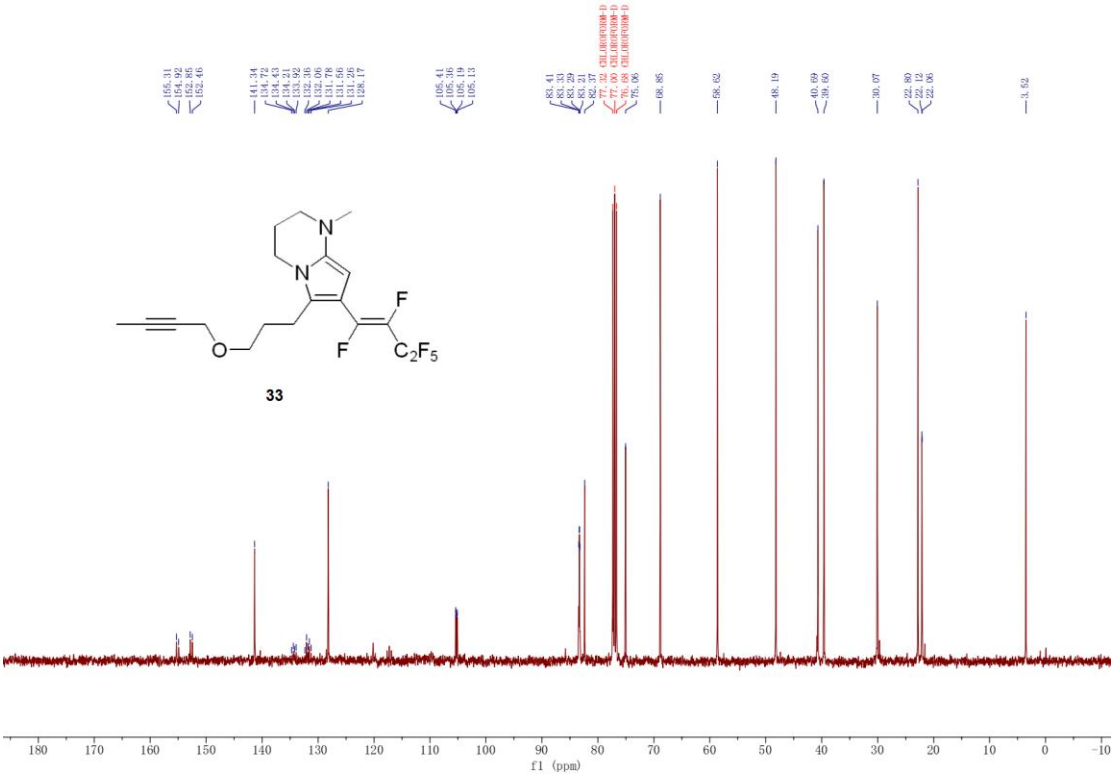
^{1}H NMR spectra of the product **33** (400 MHz, $CDCl_3$):



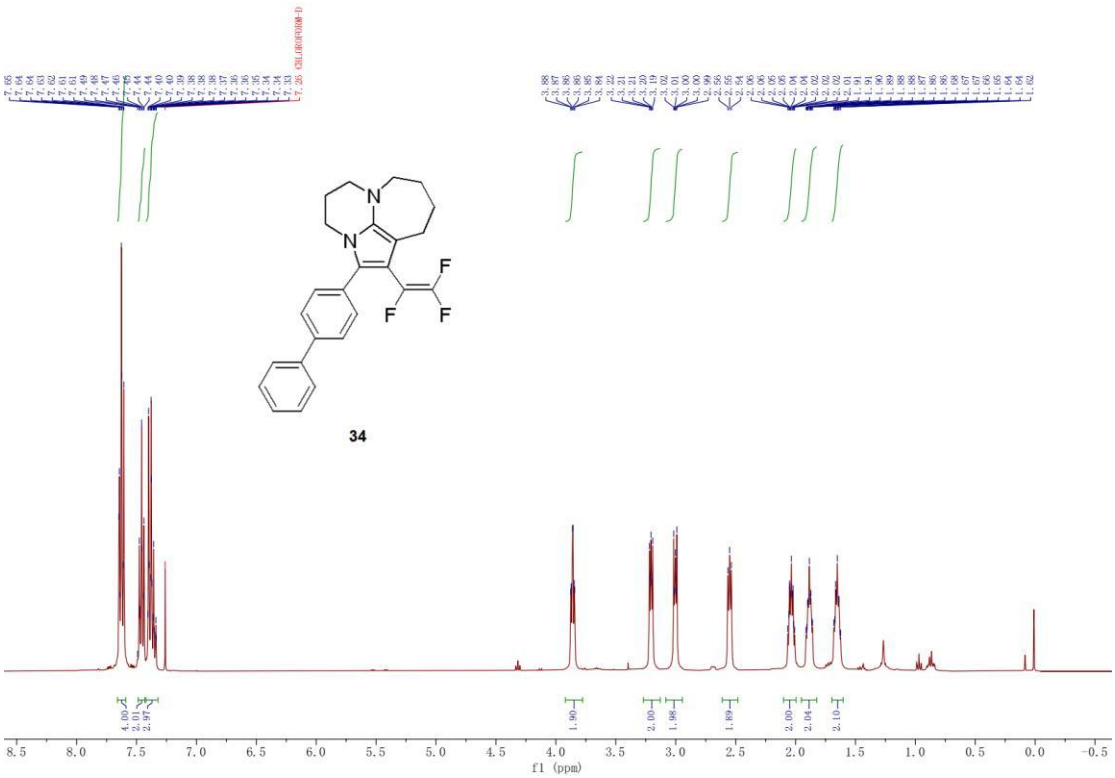
^{19}F NMR spectra of the product **33** (376 MHz, $CDCl_3$):



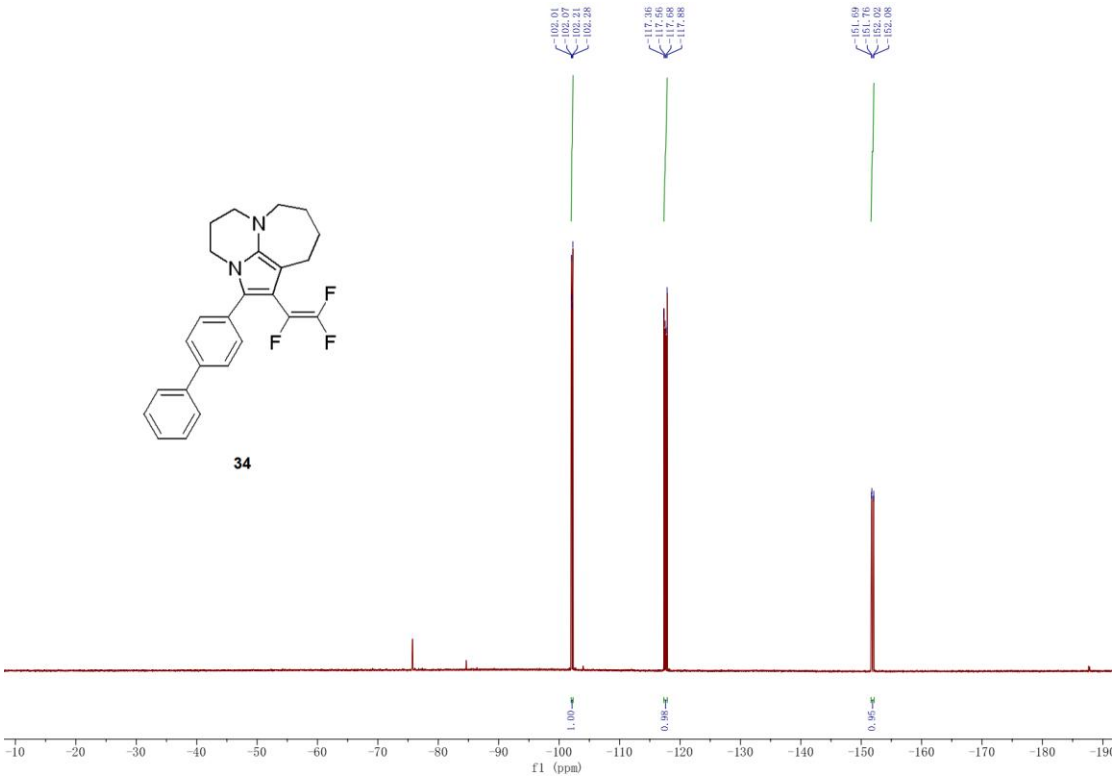
^{13}C NMR spectra of the product **33** (101 MHz, $CDCl_3$):



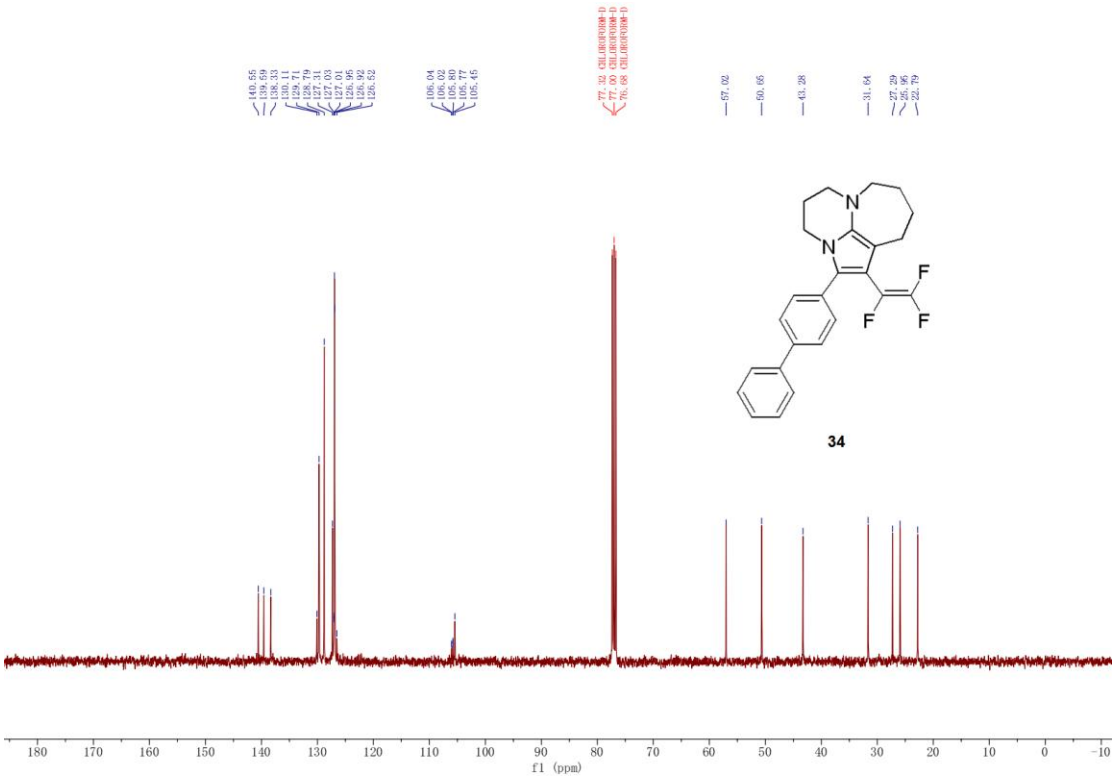
^{1}H NMR spectra of the product **34** (400 MHz, $CDCl_3$):



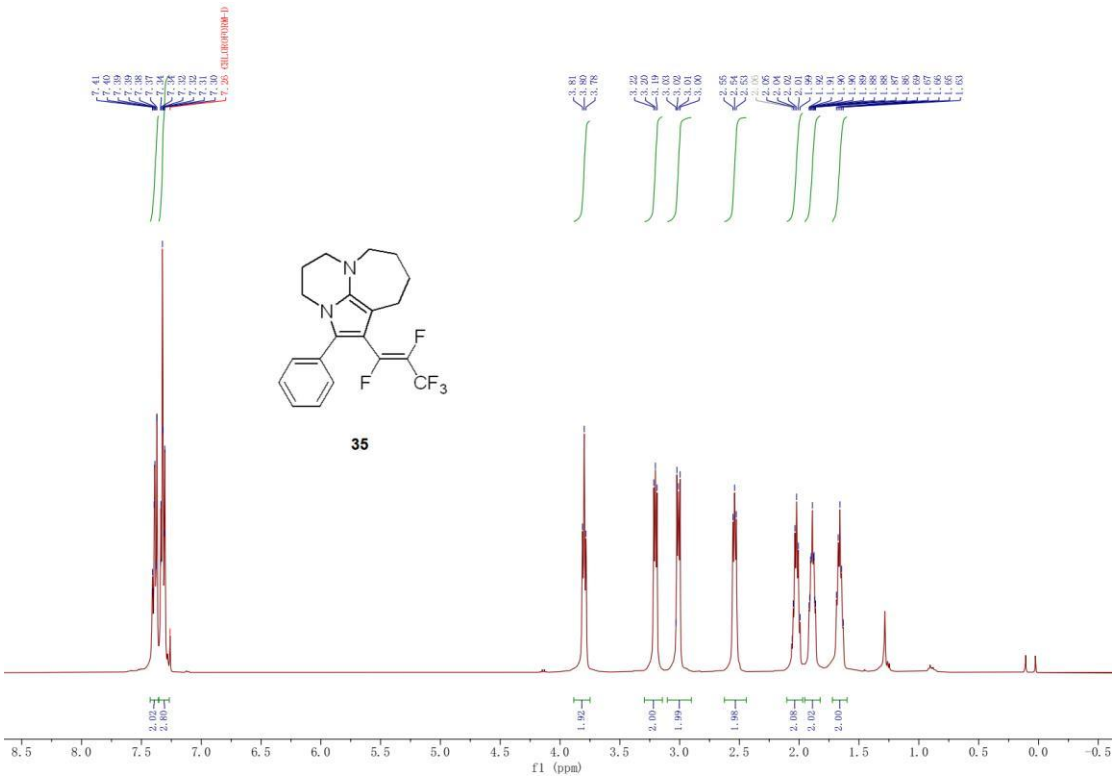
^{19}F NMR spectra of the product **34** (376 MHz, $CDCl_3$):



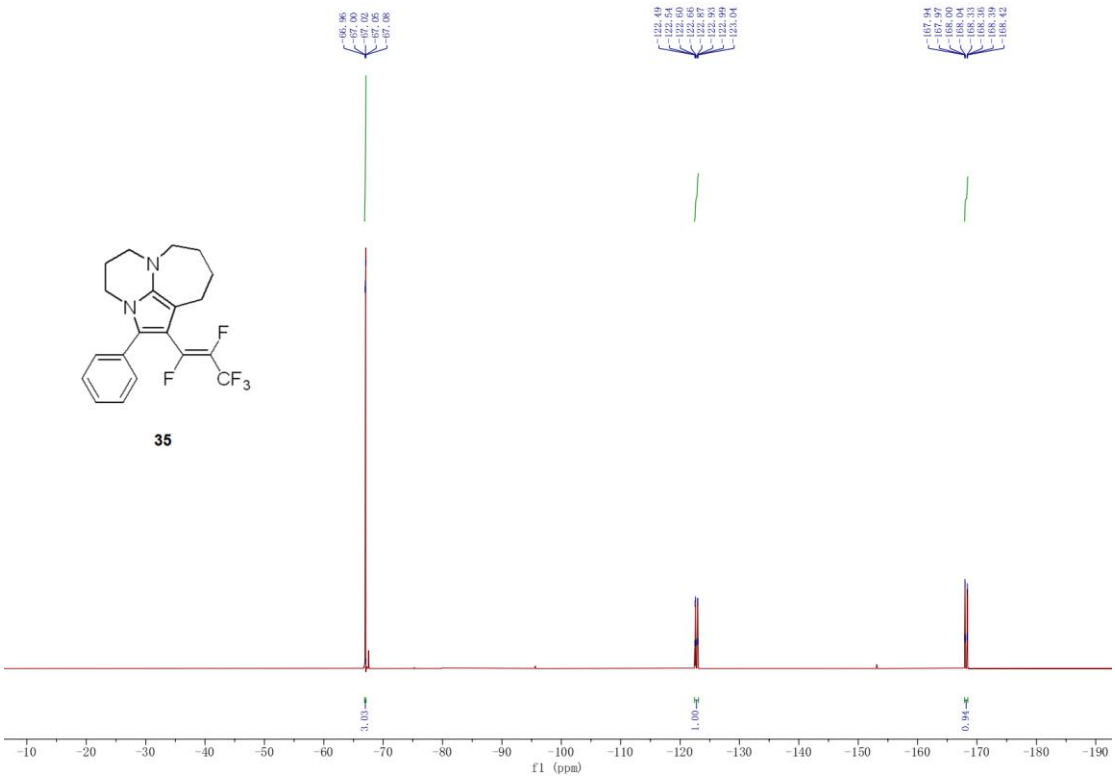
^{13}C NMR spectra of the product **34** (101 MHz, $CDCl_3$):



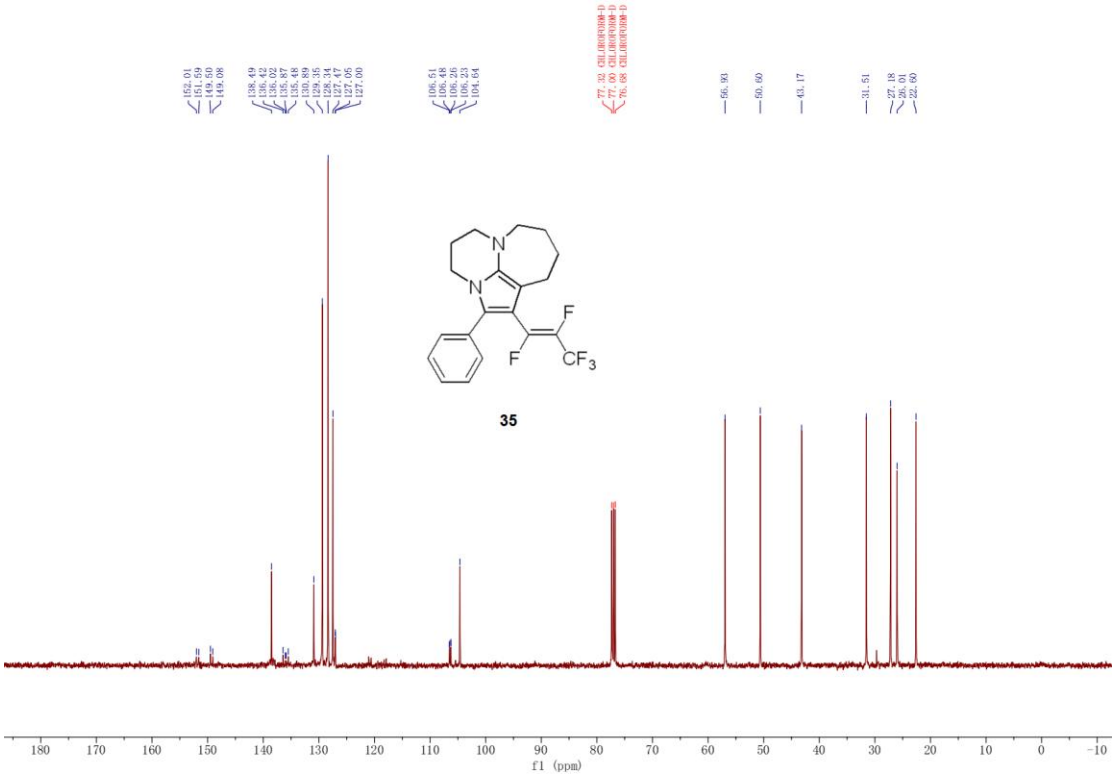
^{1}H NMR spectra of the product **35** (400 MHz, $CDCl_3$):



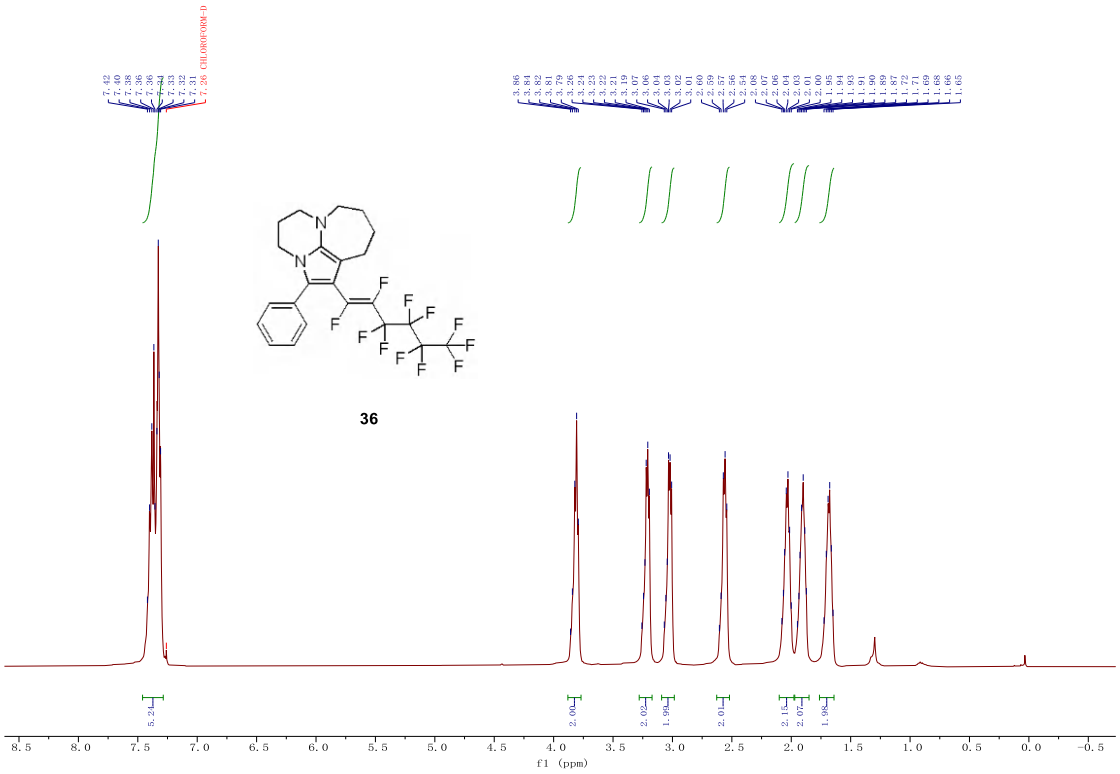
^{19}F NMR spectra of the product **35** (376 MHz, $CDCl_3$):



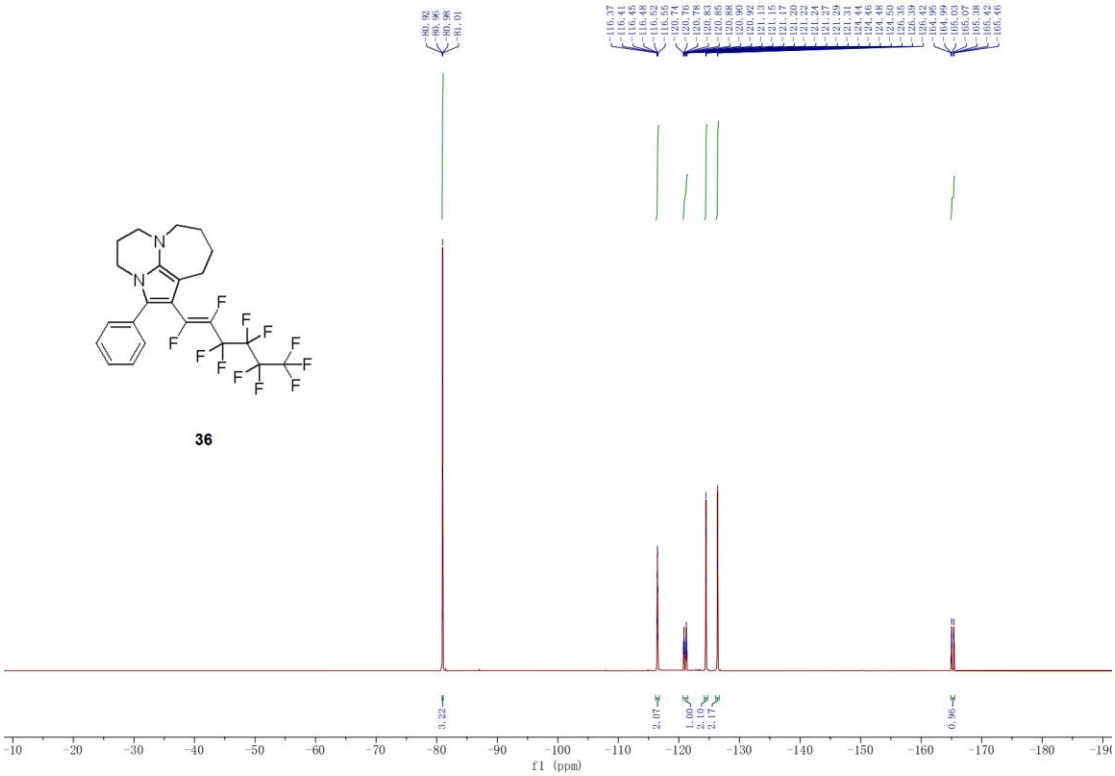
^{13}C NMR spectra of the product **35** (101 MHz, $CDCl_3$):



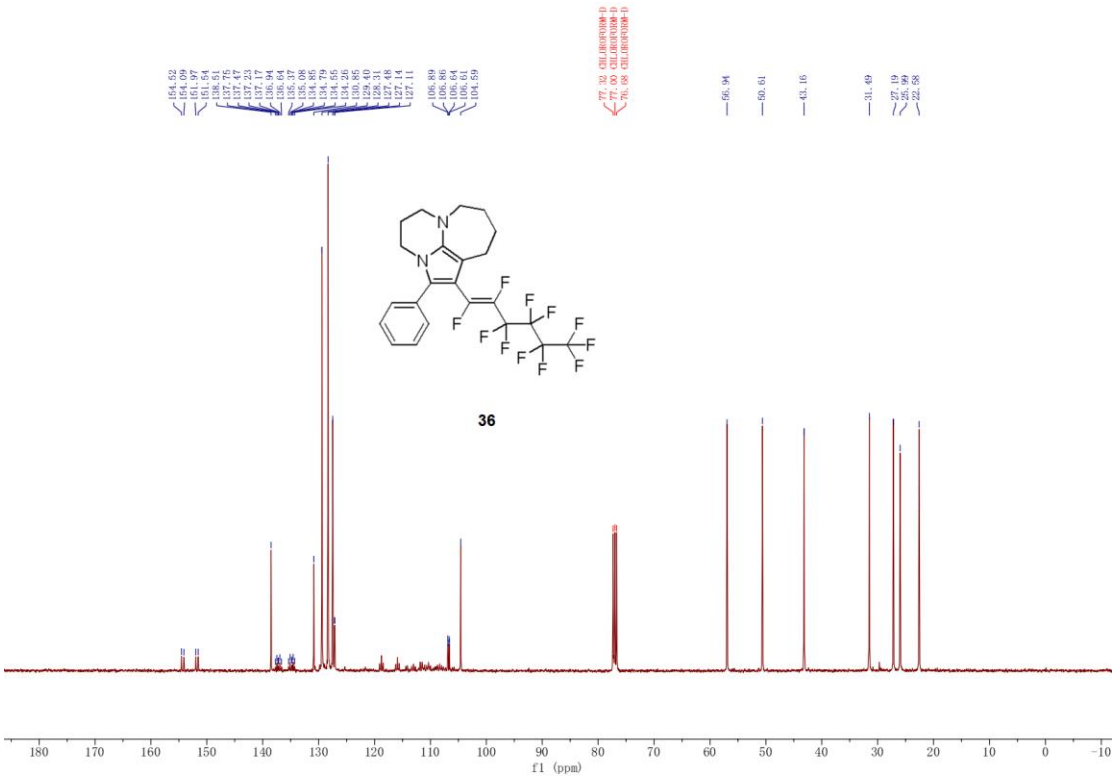
^{1}H NMR spectra of the product **36** (400 MHz, $CDCl_3$):



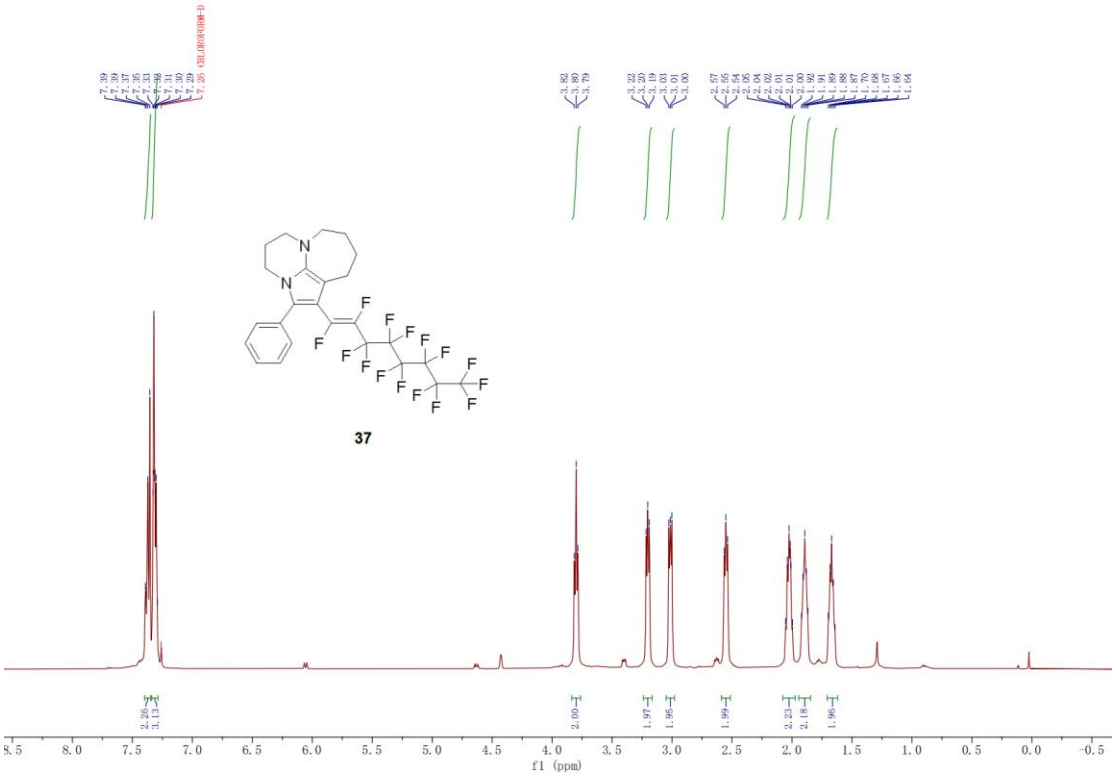
^{19}F NMR spectra of the product **36** (376 MHz, $CDCl_3$):



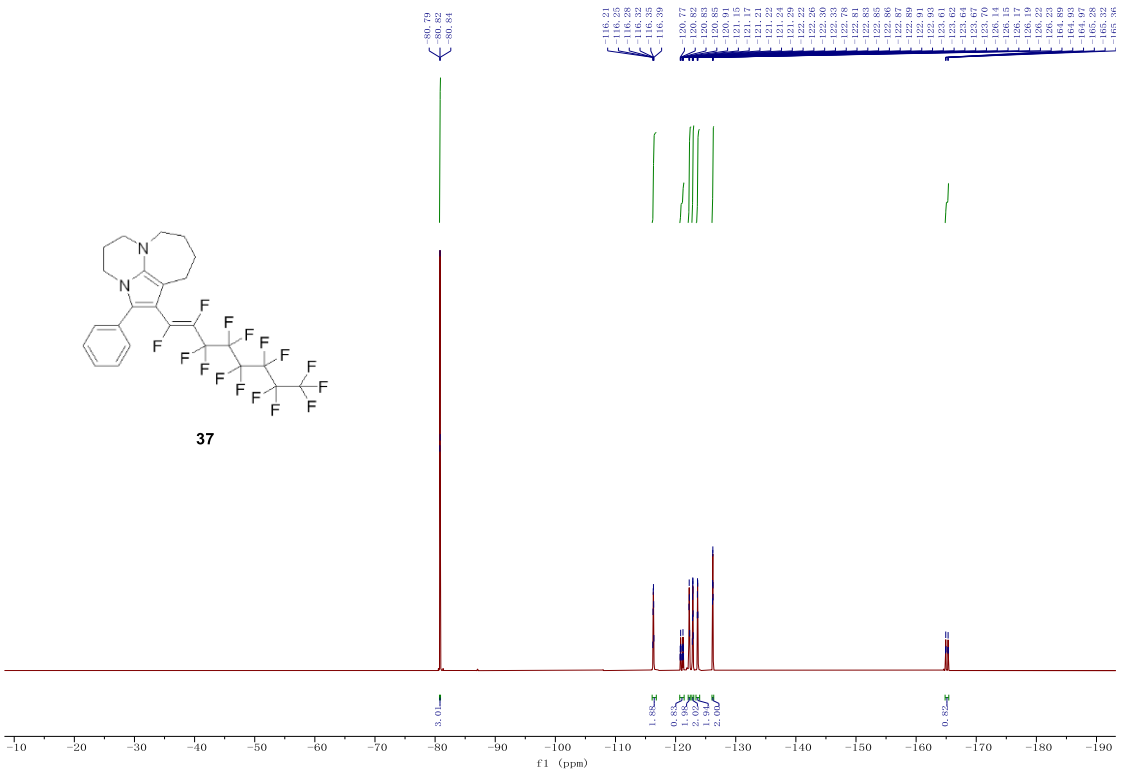
^{13}C NMR spectra of the product **36** (101 MHz, $CDCl_3$):



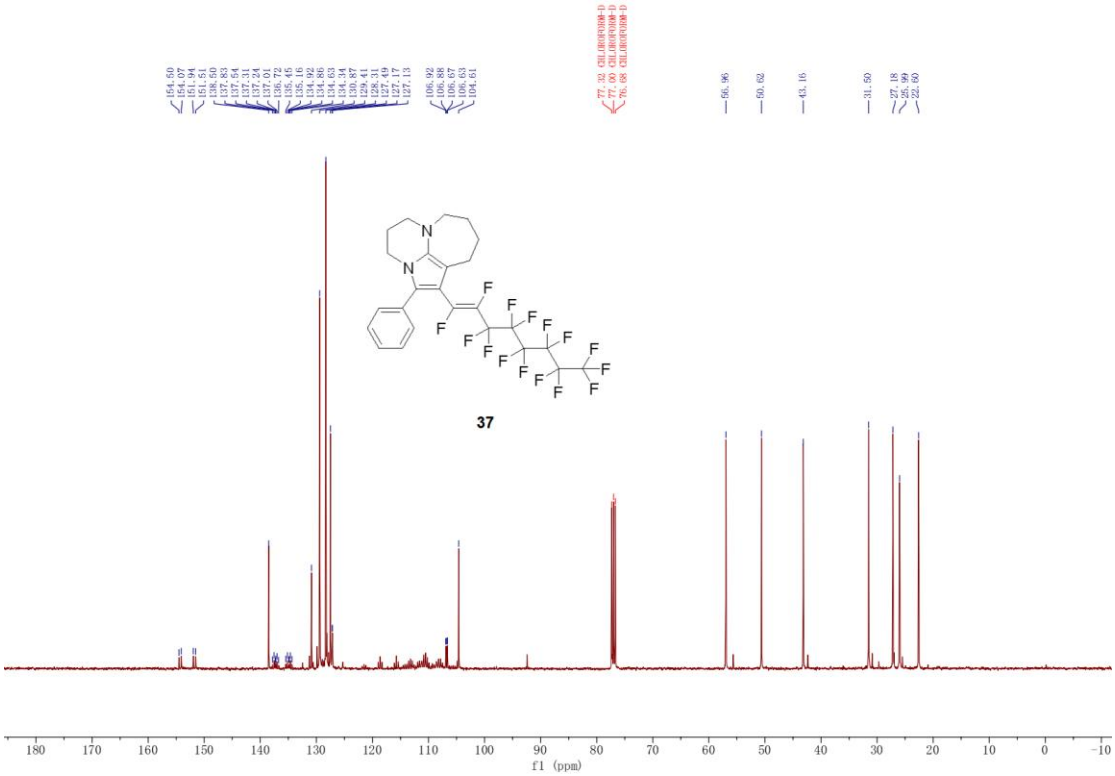
^{1}H NMR spectra of the product **37** (400 MHz, $CDCl_3$):



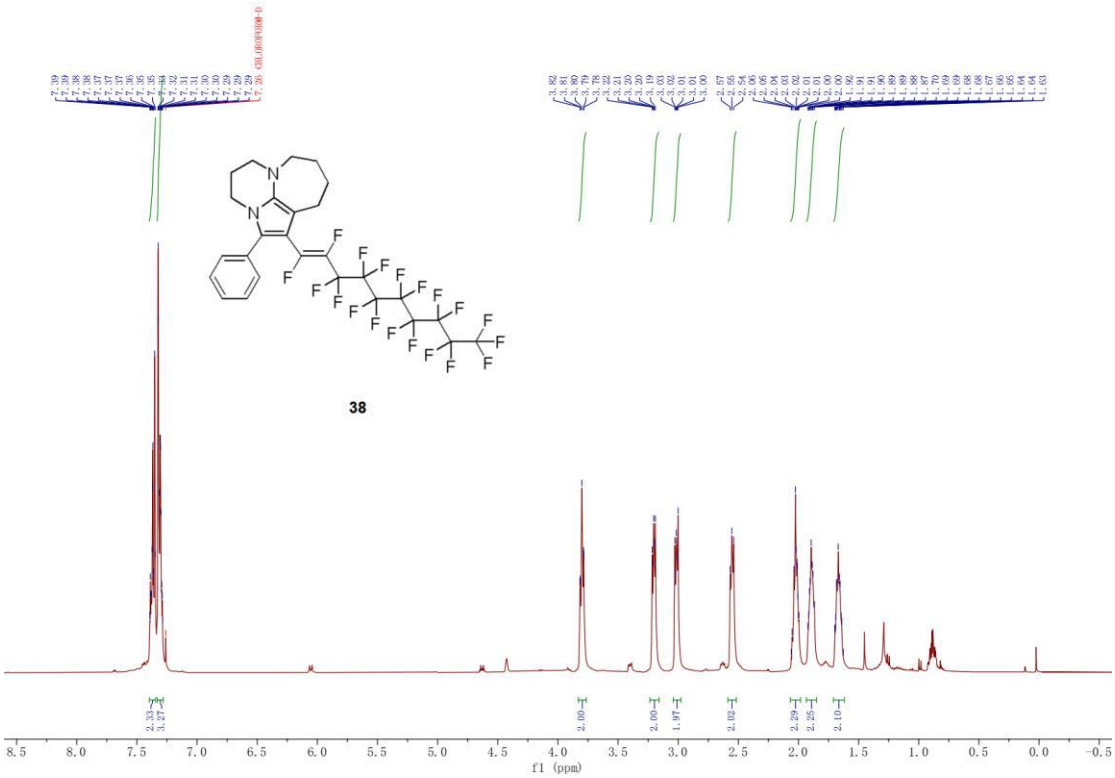
^{19}F NMR spectra of the product **37** (376 MHz, $CDCl_3$):



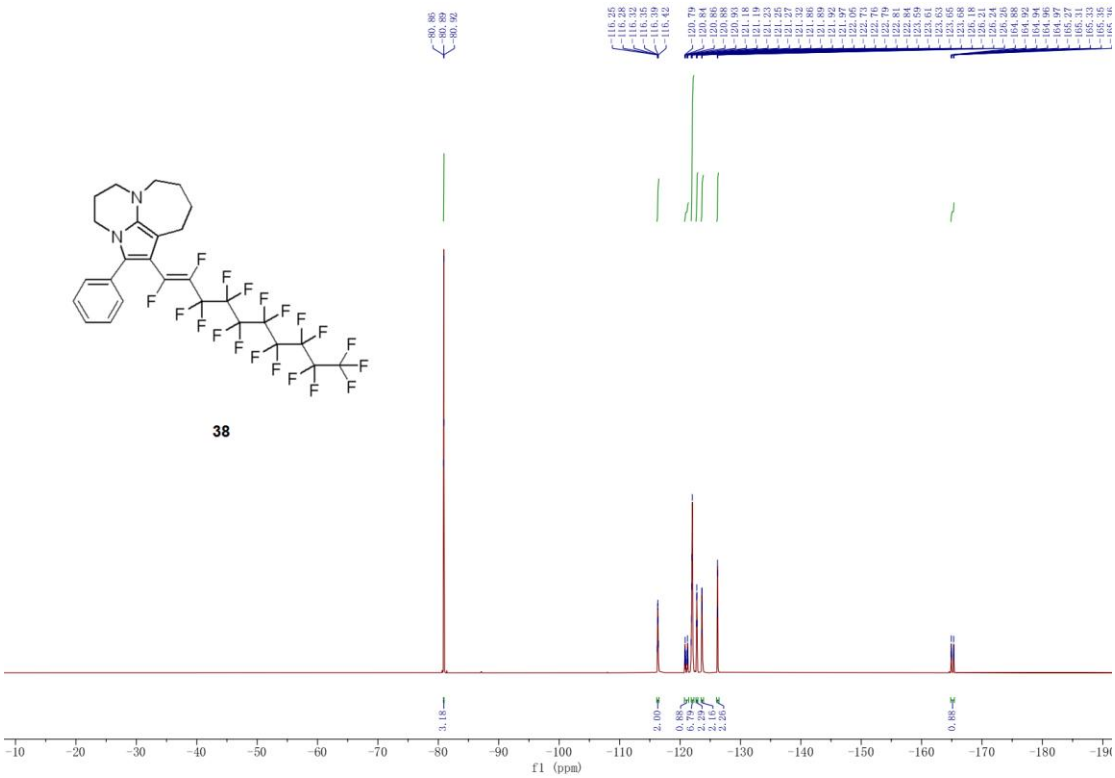
^{13}C NMR spectra of the product **37** (101 MHz, $CDCl_3$):



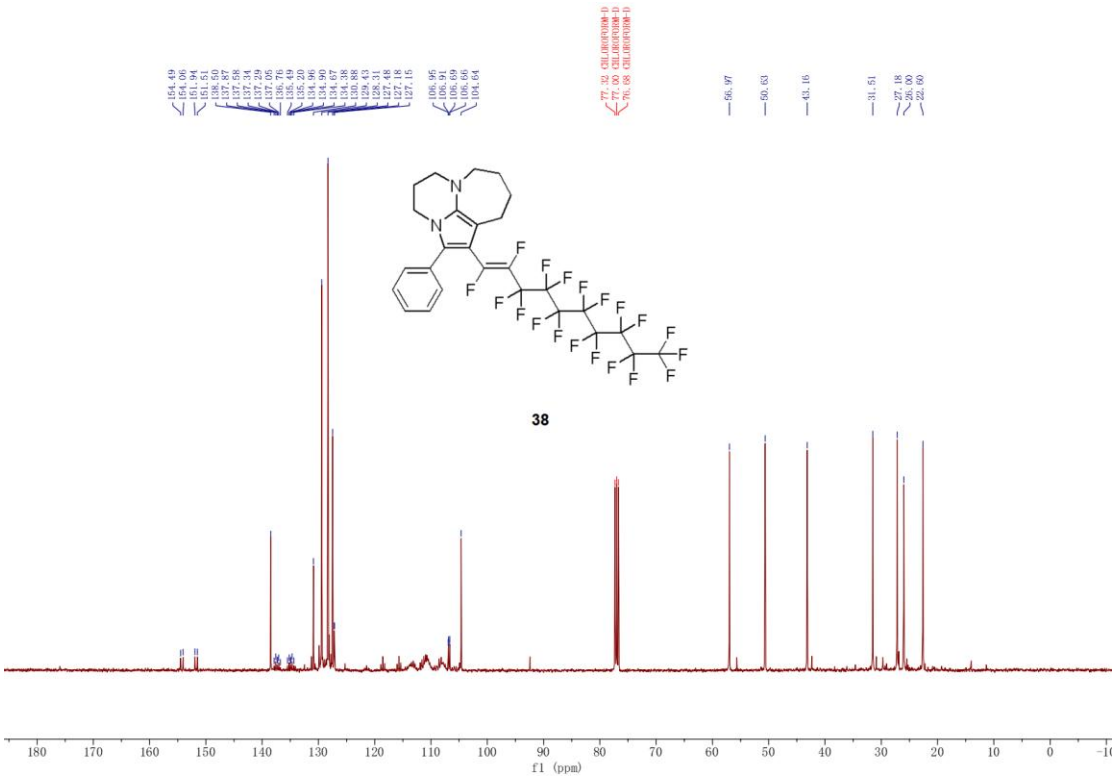
^{1}H NMR spectra of the product **38** (400 MHz, $CDCl_3$):



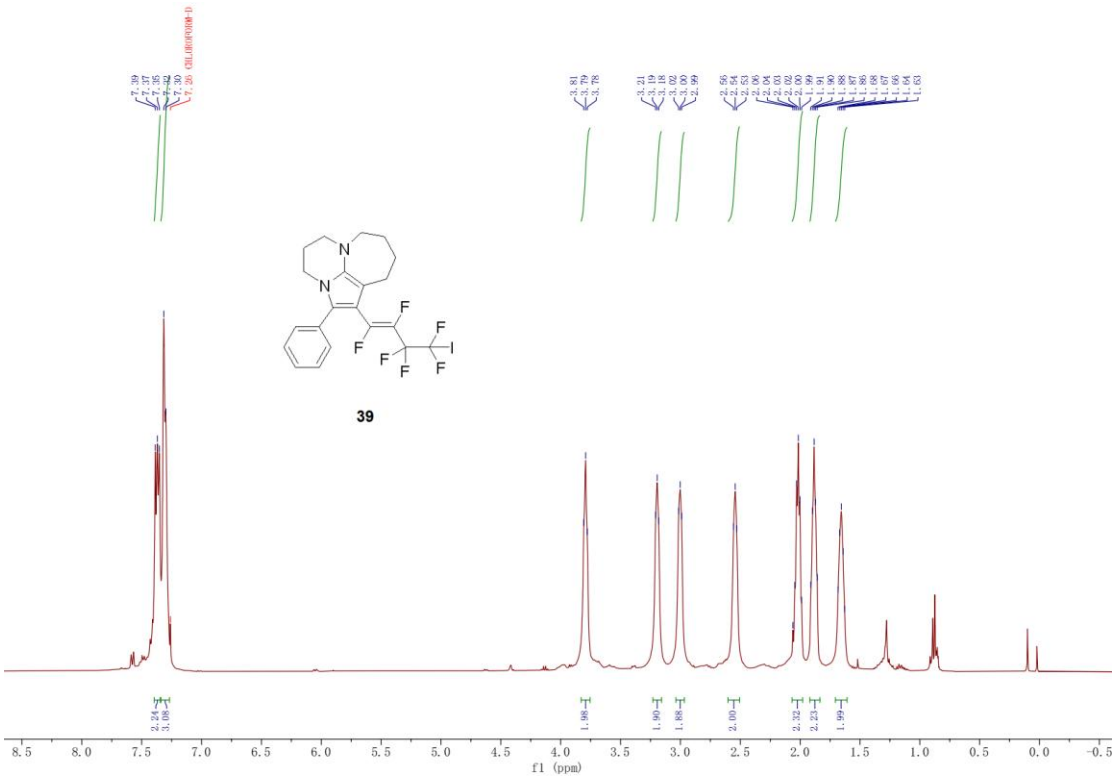
^{19}F NMR spectra of the product **38** (376 MHz, $CDCl_3$):



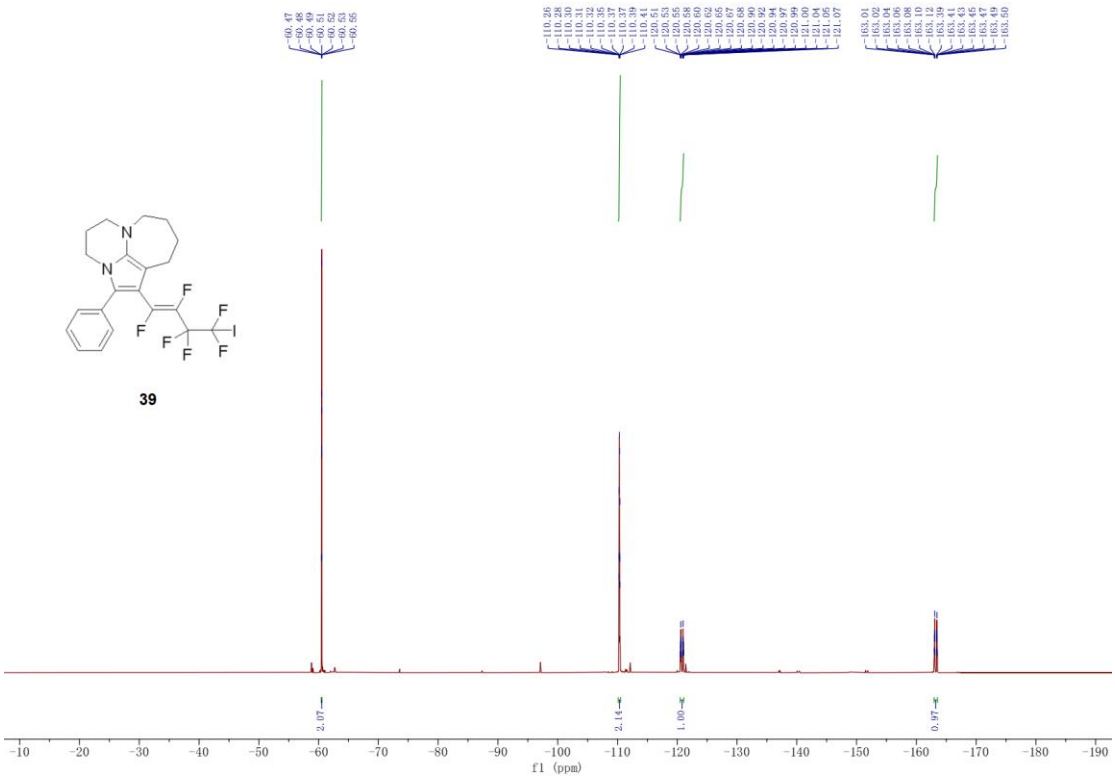
^{13}C NMR spectra of the product **38** (101 MHz, $CDCl_3$):



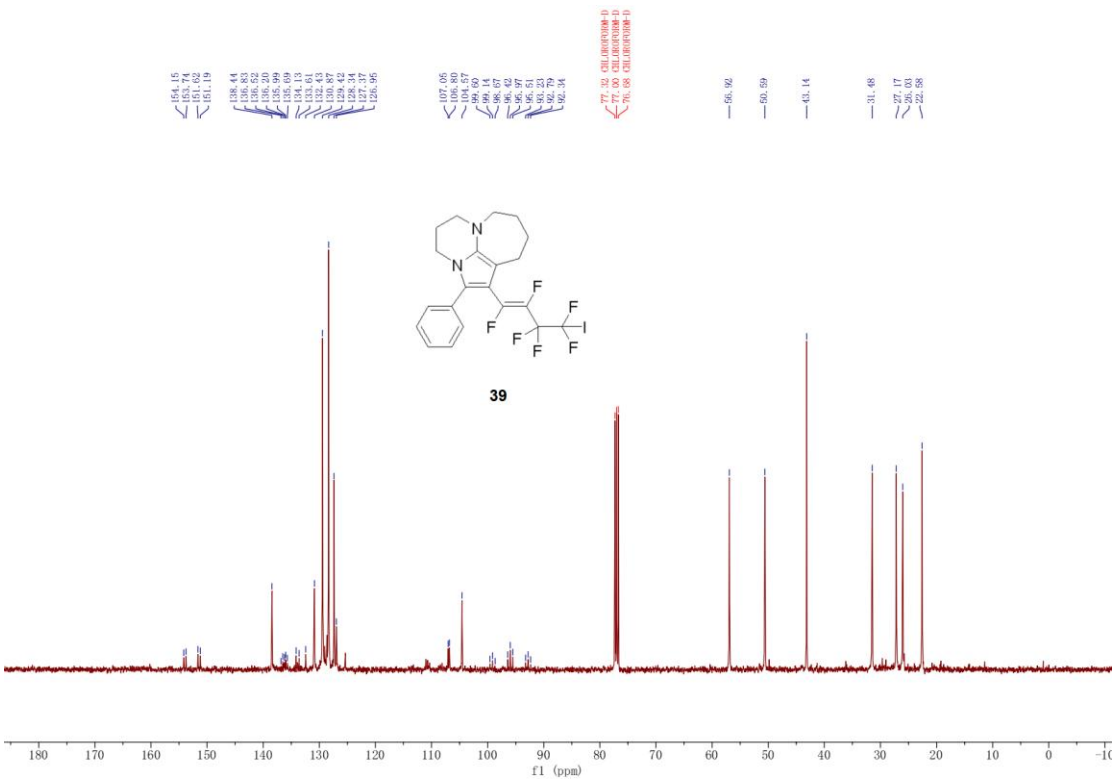
^{1}H NMR spectra of the product **39** (400 MHz, $CDCl_3$):



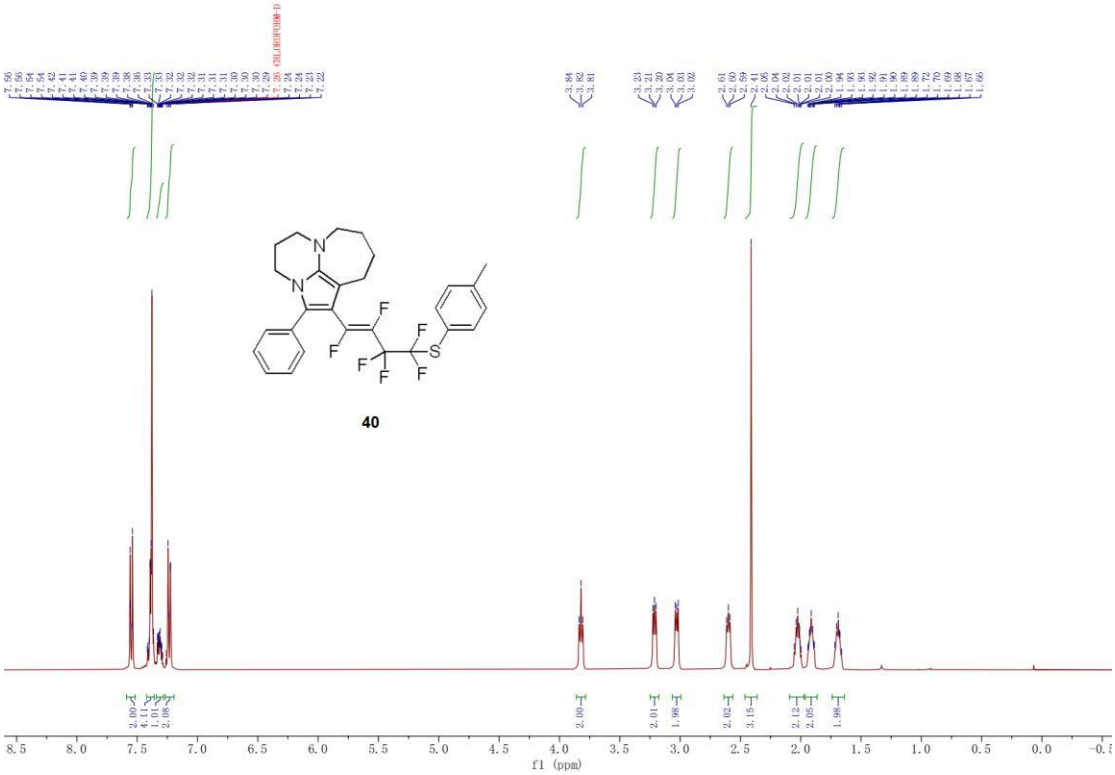
^{19}F NMR spectra of the product **39** (376 MHz, $CDCl_3$):



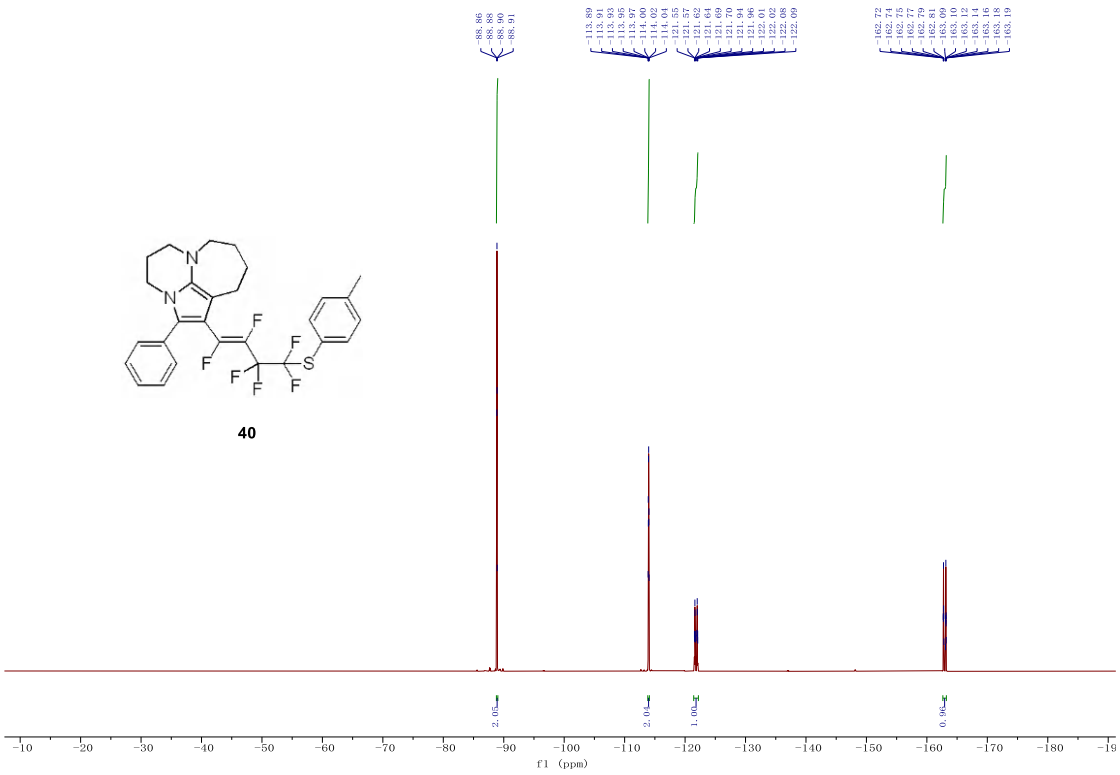
^{13}C NMR spectra of the product **39** (101 MHz, $CDCl_3$):



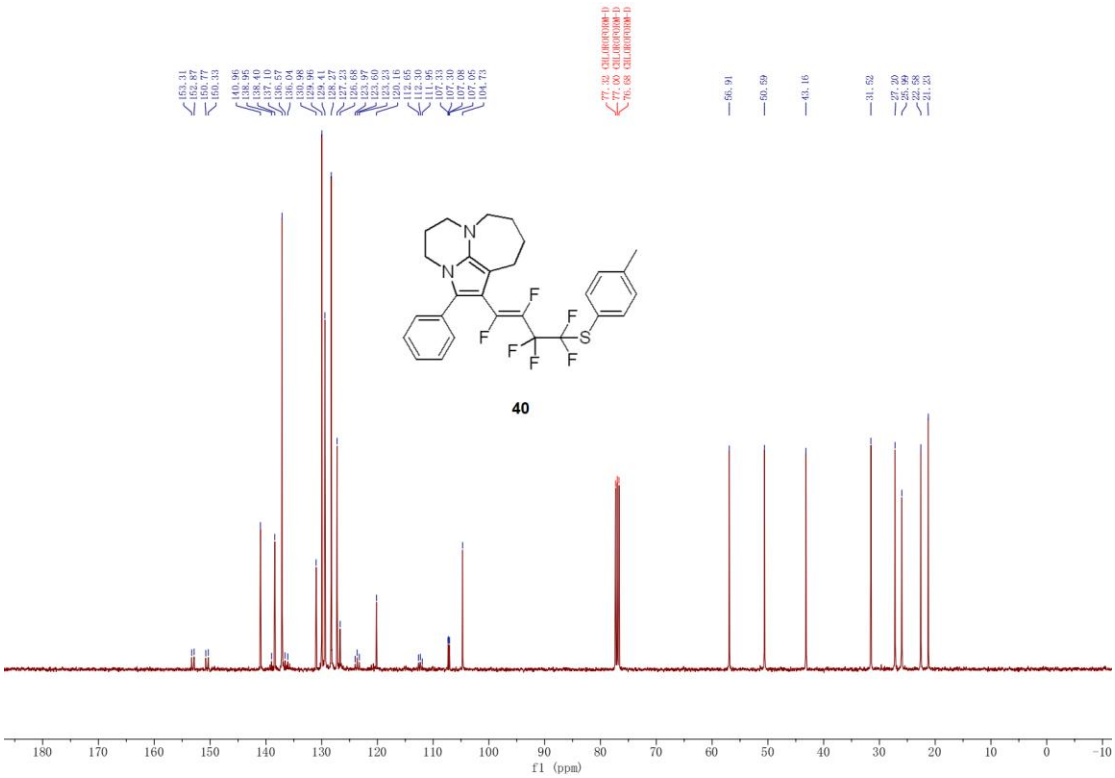
^{1}H NMR spectra of the product **40** (400 MHz, $CDCl_3$):



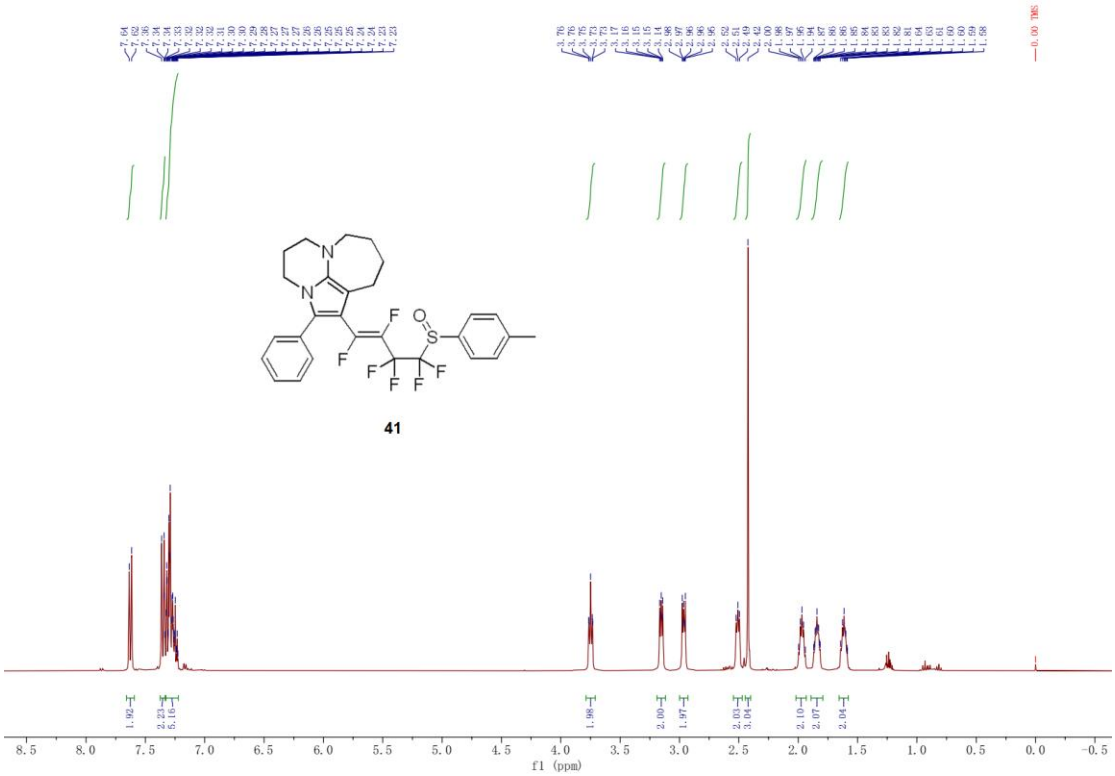
^{19}F NMR spectra of the product **40** (376 MHz, $CDCl_3$):



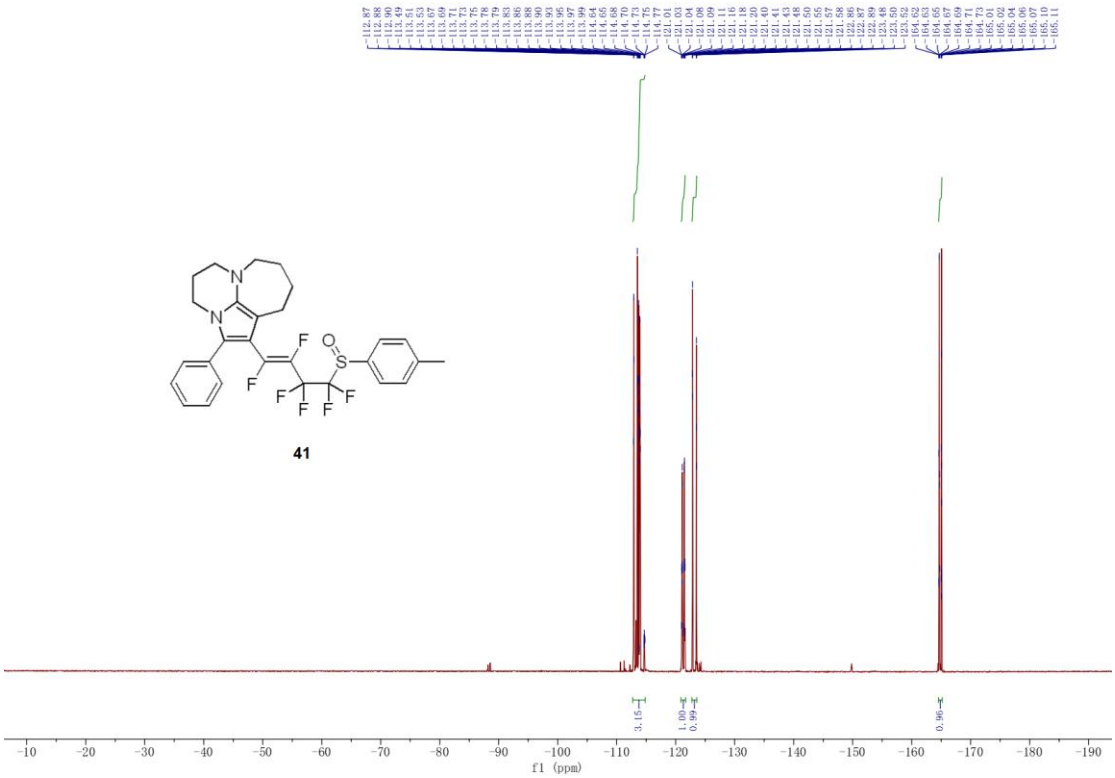
^{13}C NMR spectra of the product **40** (101 MHz, $CDCl_3$):



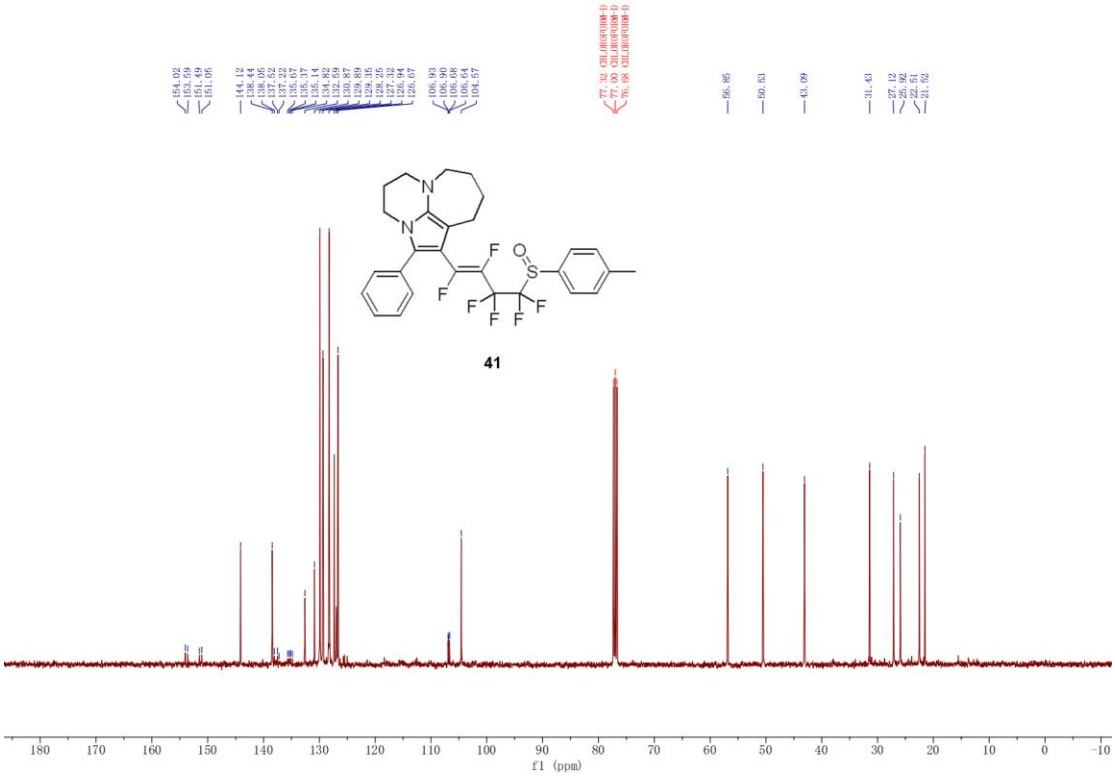
^{1}H NMR spectra of the product **41** (400 MHz, $CDCl_3$):



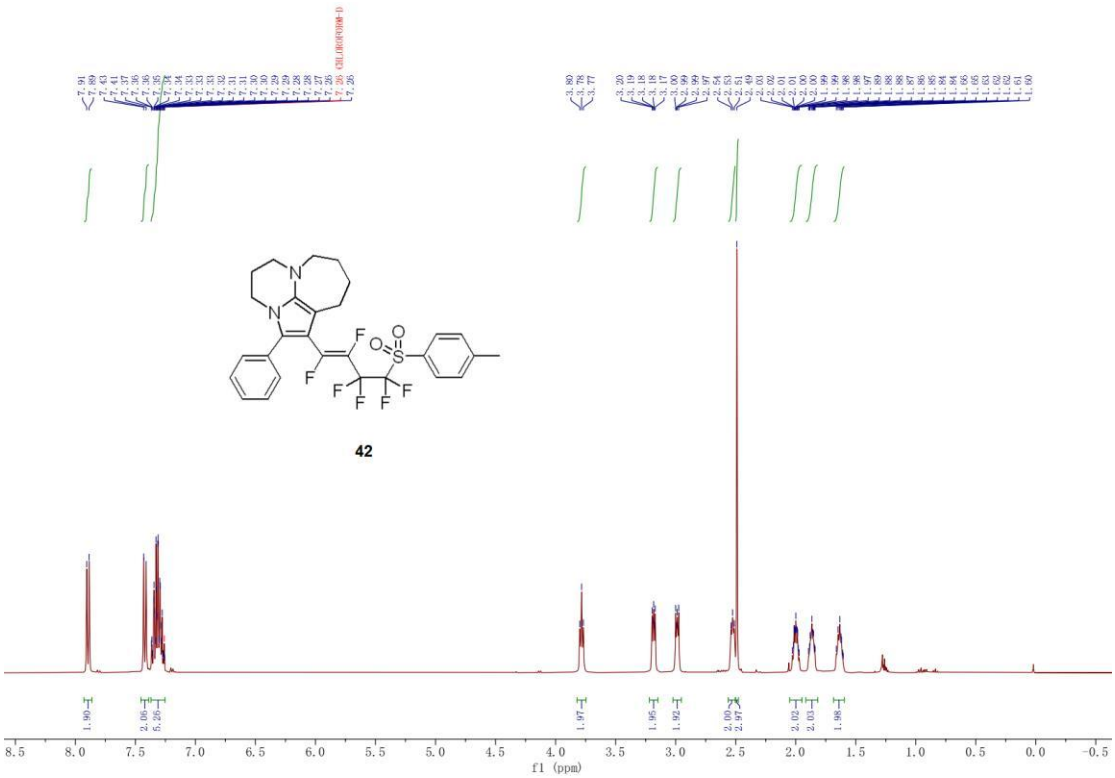
^{19}F NMR spectra of the product **41** (376 MHz, $CDCl_3$):



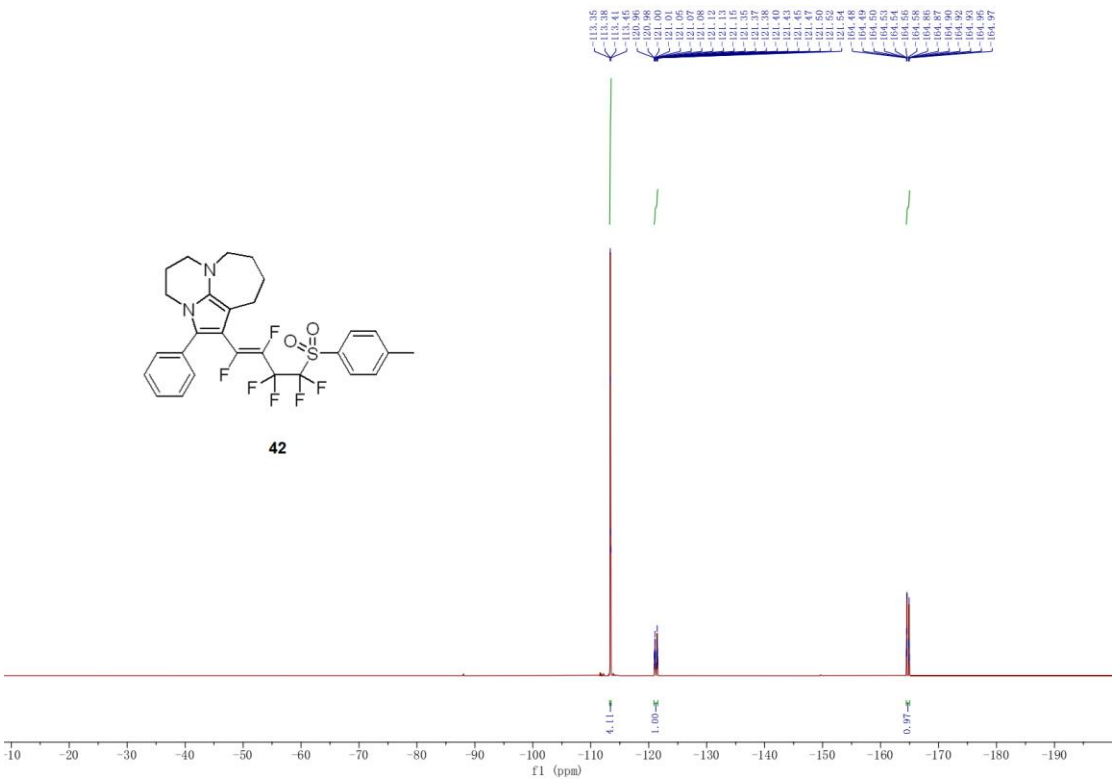
^{13}C NMR spectra of the product **41** (101 MHz, $CDCl_3$):



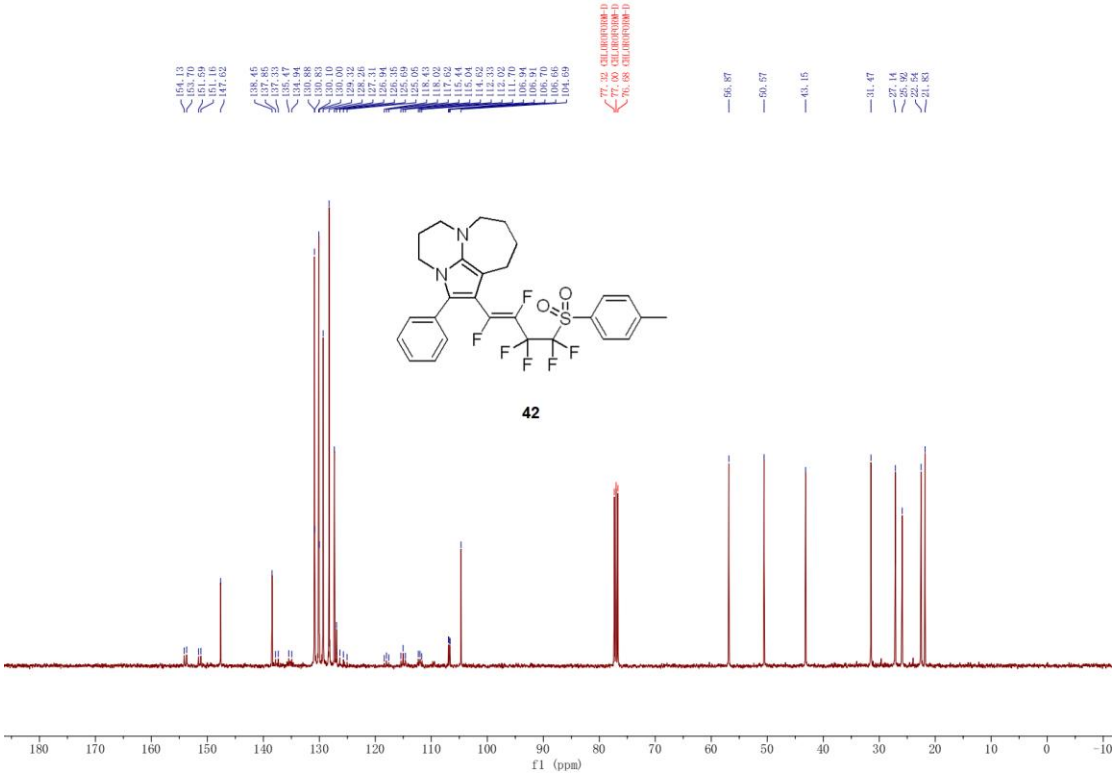
^{1}H NMR spectra of the product **42** (400 MHz, $CDCl_3$):



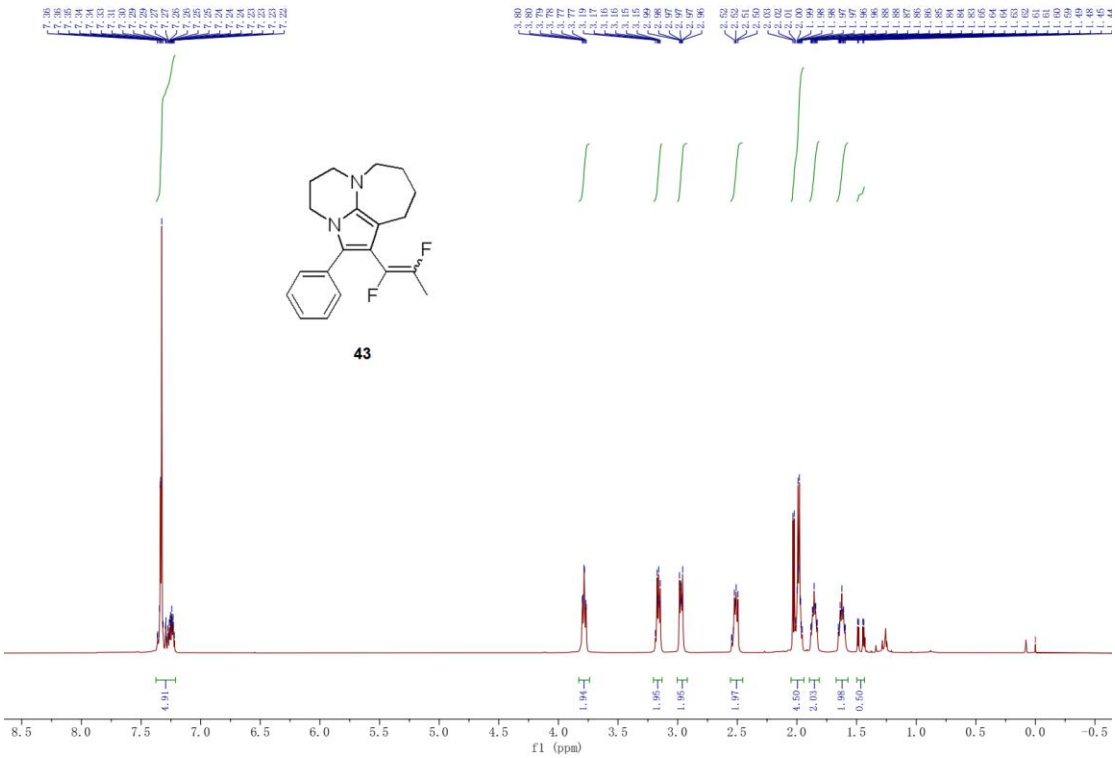
^{19}F NMR spectra of the product **42** (376 MHz, $CDCl_3$):



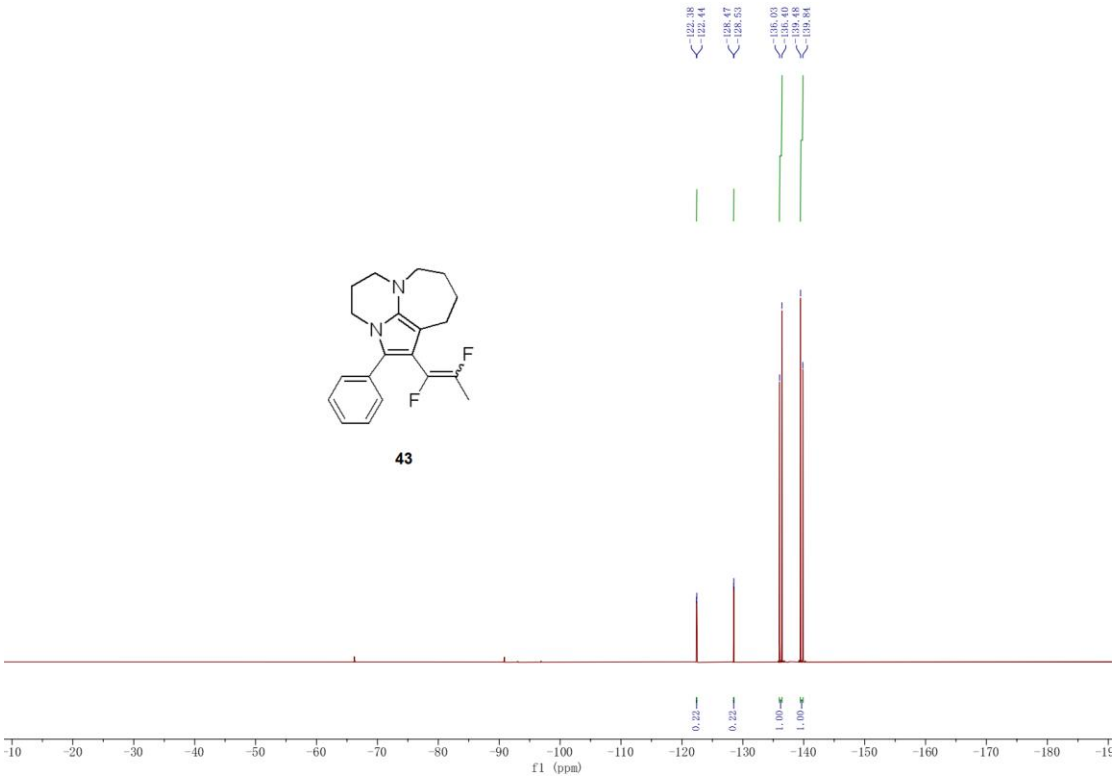
^{13}C NMR spectra of the product **42** (101 MHz, $CDCl_3$):



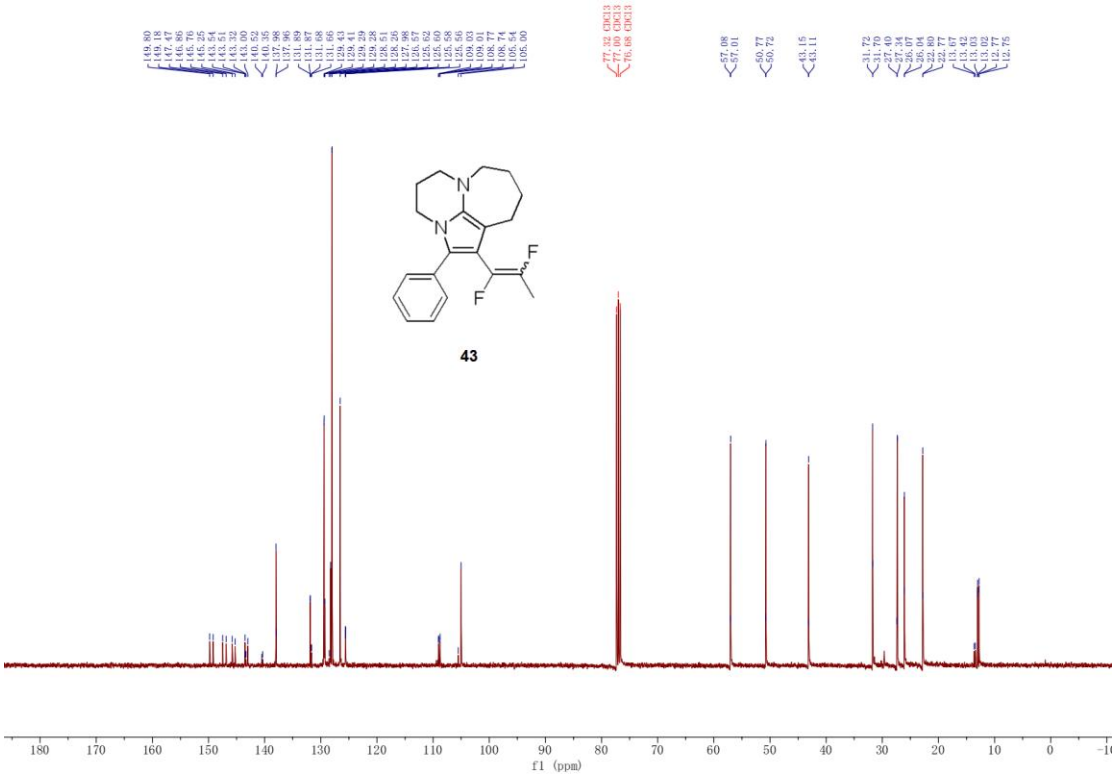
^{1}H NMR spectra of the product **43** (400 MHz, $CDCl_3$):



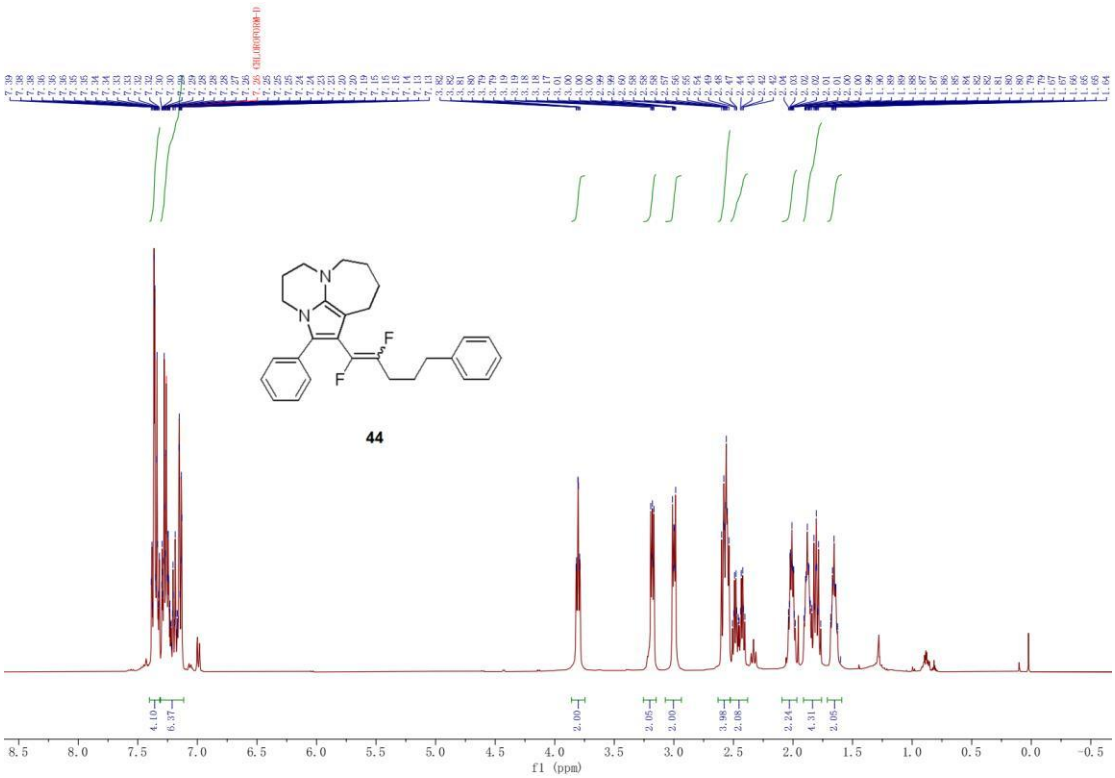
^{19}F NMR spectra of the product **43** (376 MHz, $CDCl_3$):



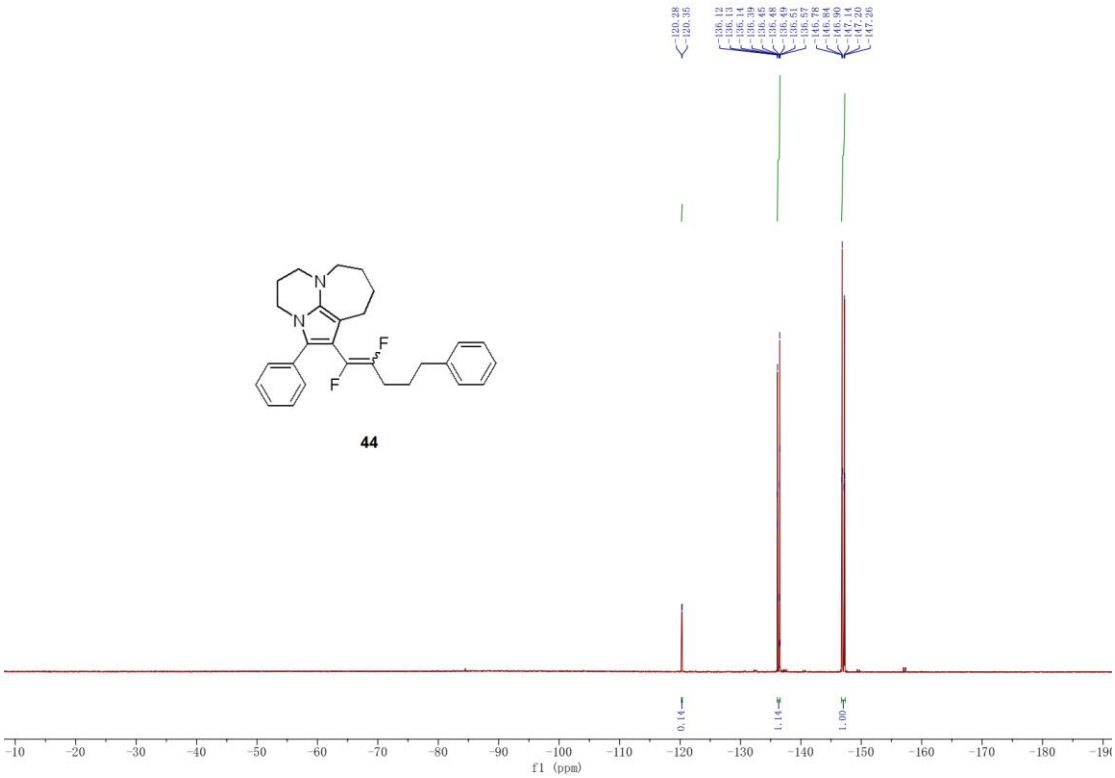
^{13}C NMR spectra of the product **43** (101 MHz, $CDCl_3$):



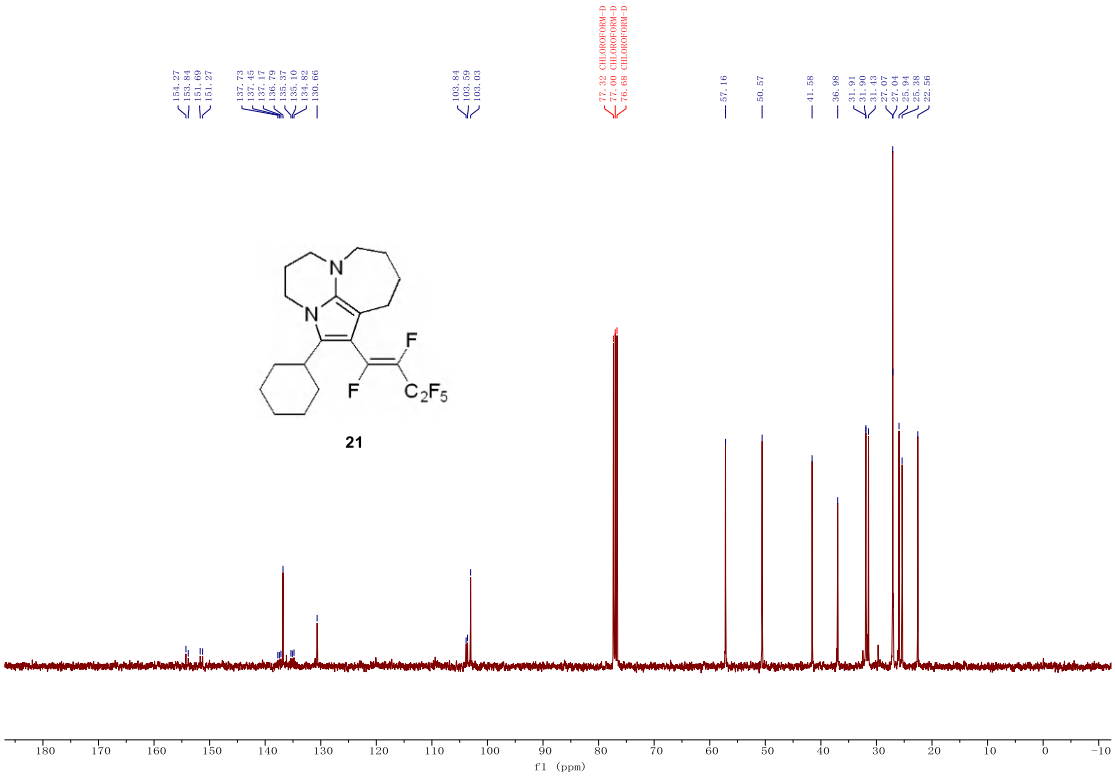
^{1}H NMR spectra of the product **44** (400 MHz, $CDCl_3$):



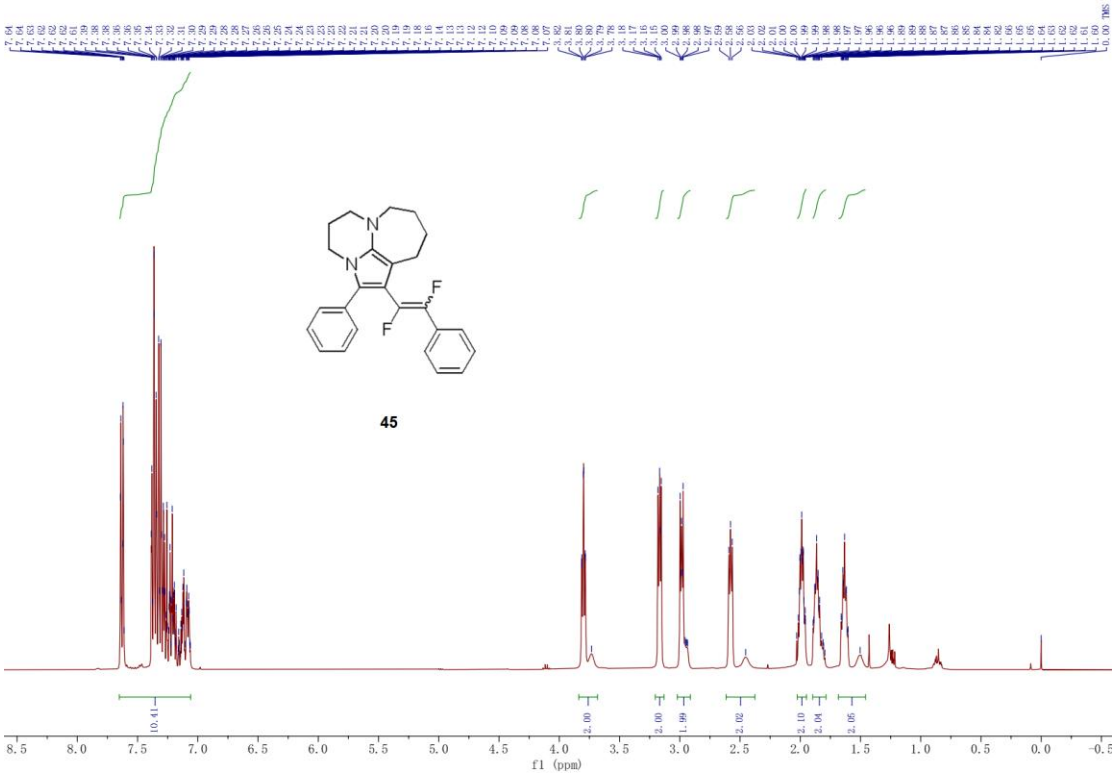
^{19}F NMR spectra of the product **44** (376 MHz, $CDCl_3$):



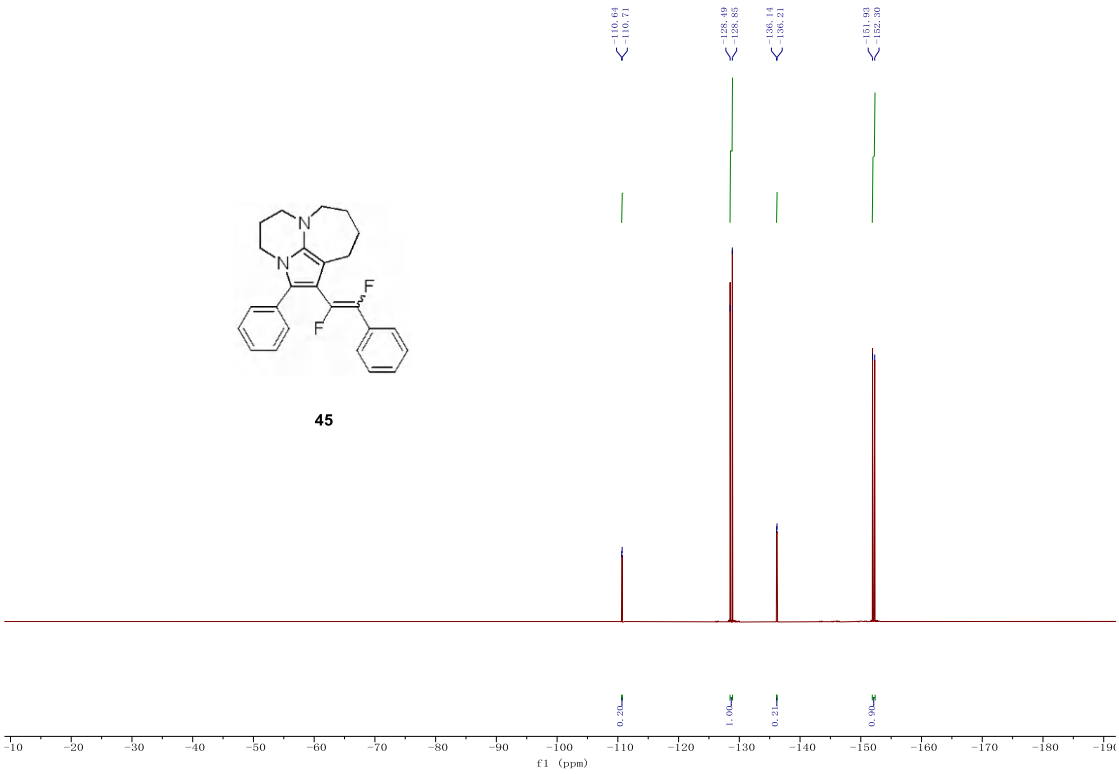
^{13}C NMR spectra of the product **44** (101 MHz, $CDCl_3$):



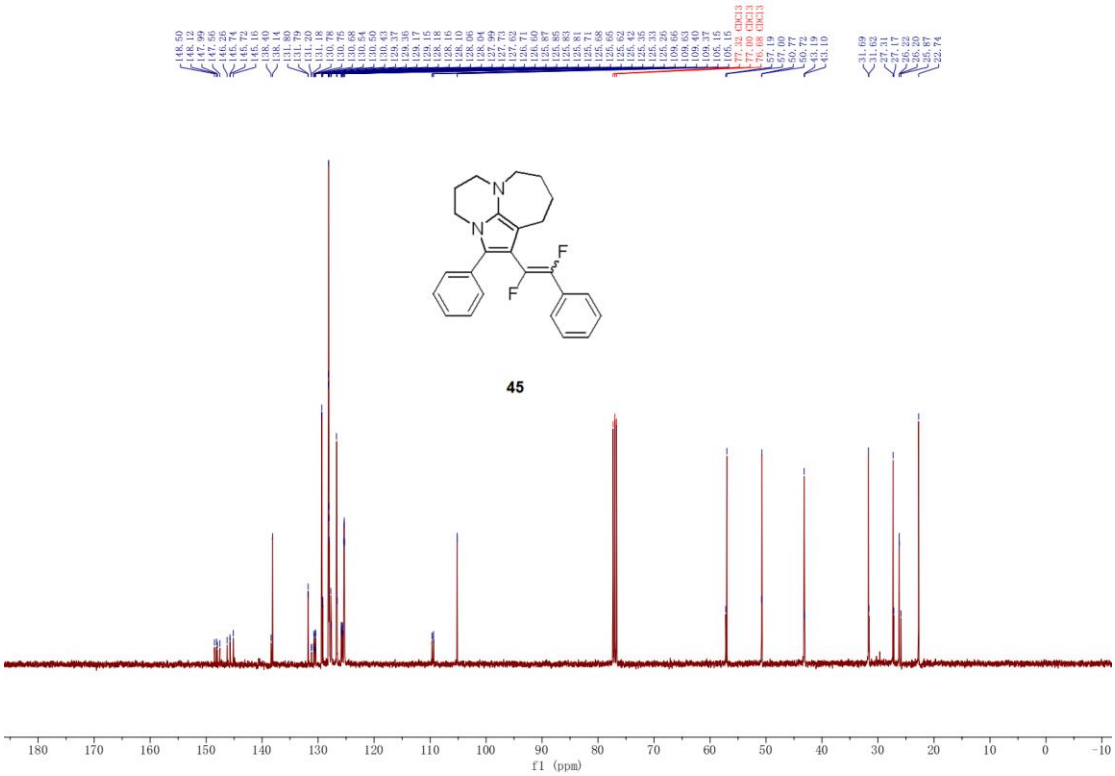
^{1}H NMR spectra of the product **45** (400 MHz, $CDCl_3$):



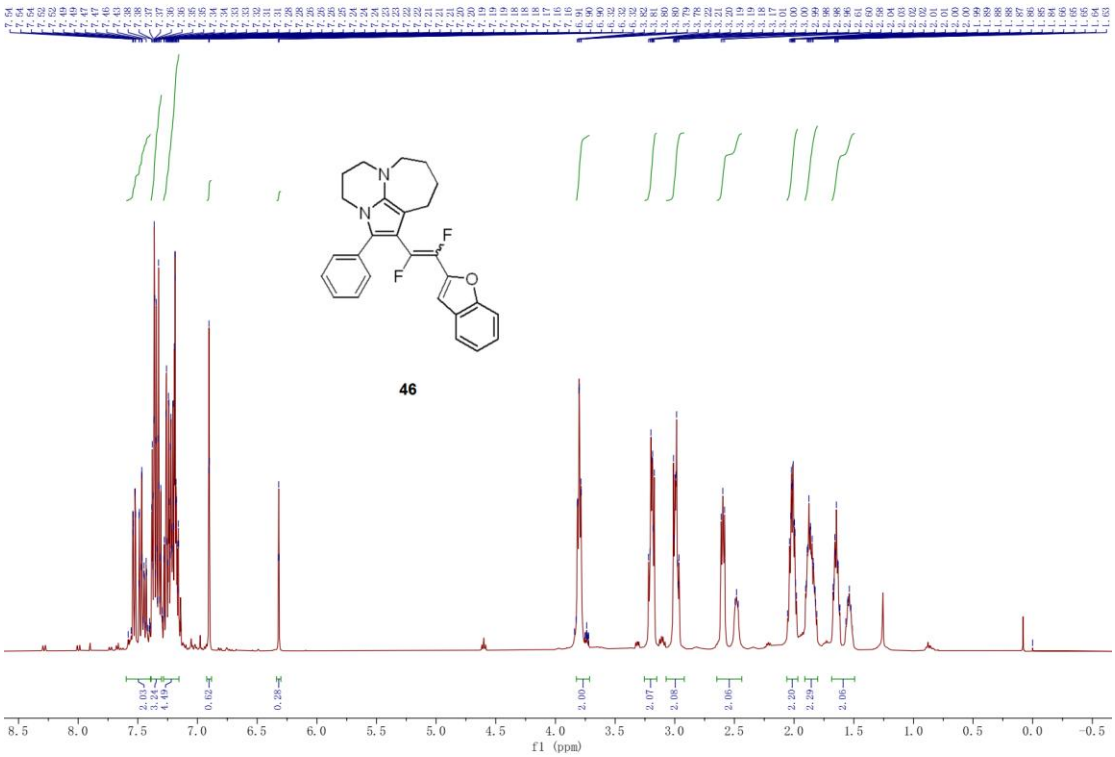
^{19}F NMR spectra of the product **45** (376 MHz, $CDCl_3$):



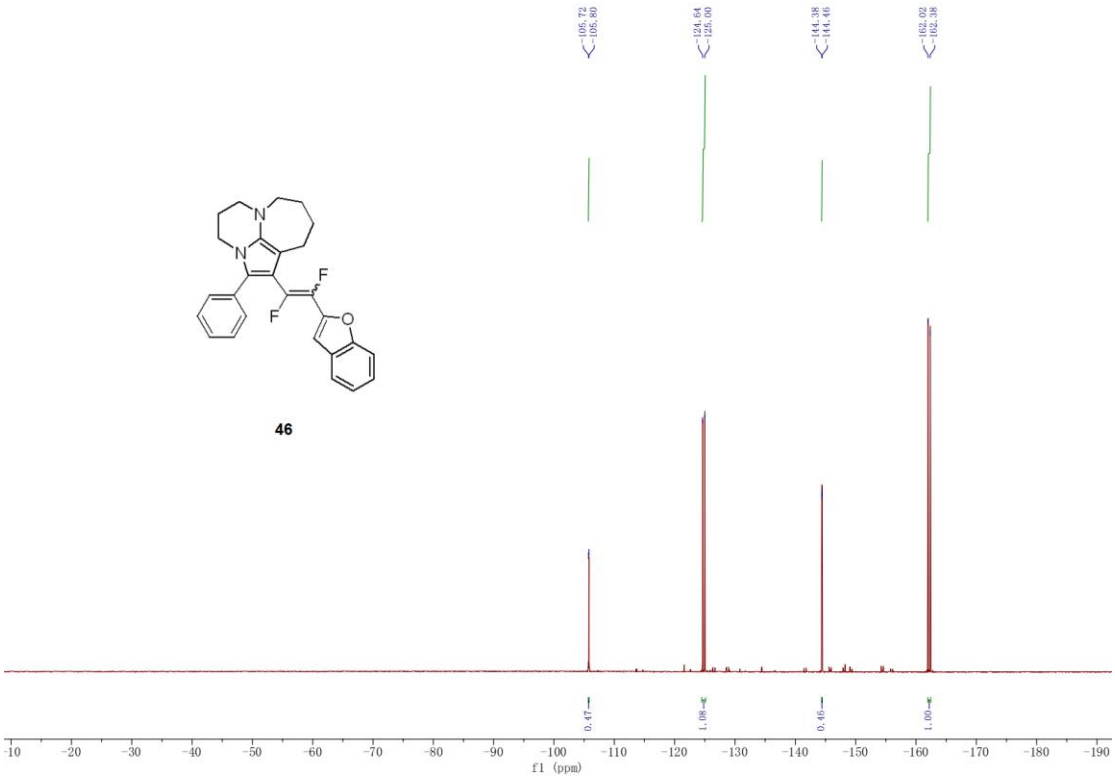
^{13}C NMR spectra of the product **45** (101 MHz, $CDCl_3$):



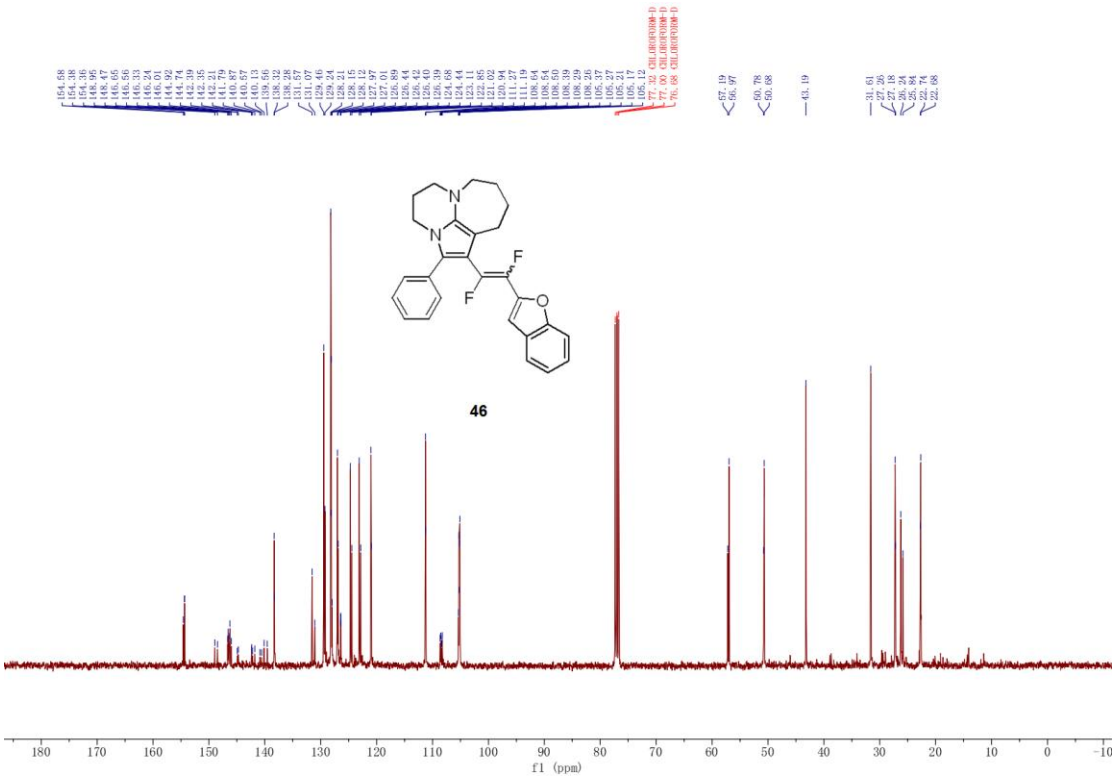
^{1}H NMR spectra of the product **46** (400 MHz, $CDCl_3$):



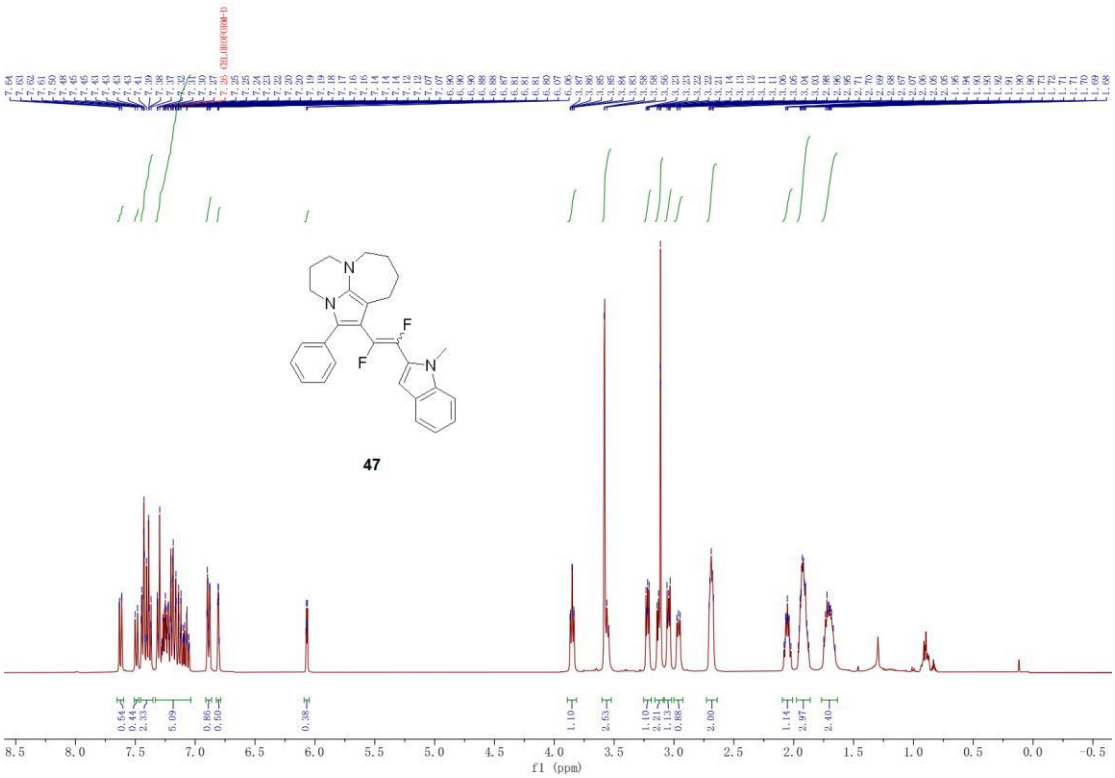
^{19}F NMR spectra of the product **46** (376 MHz, $CDCl_3$):



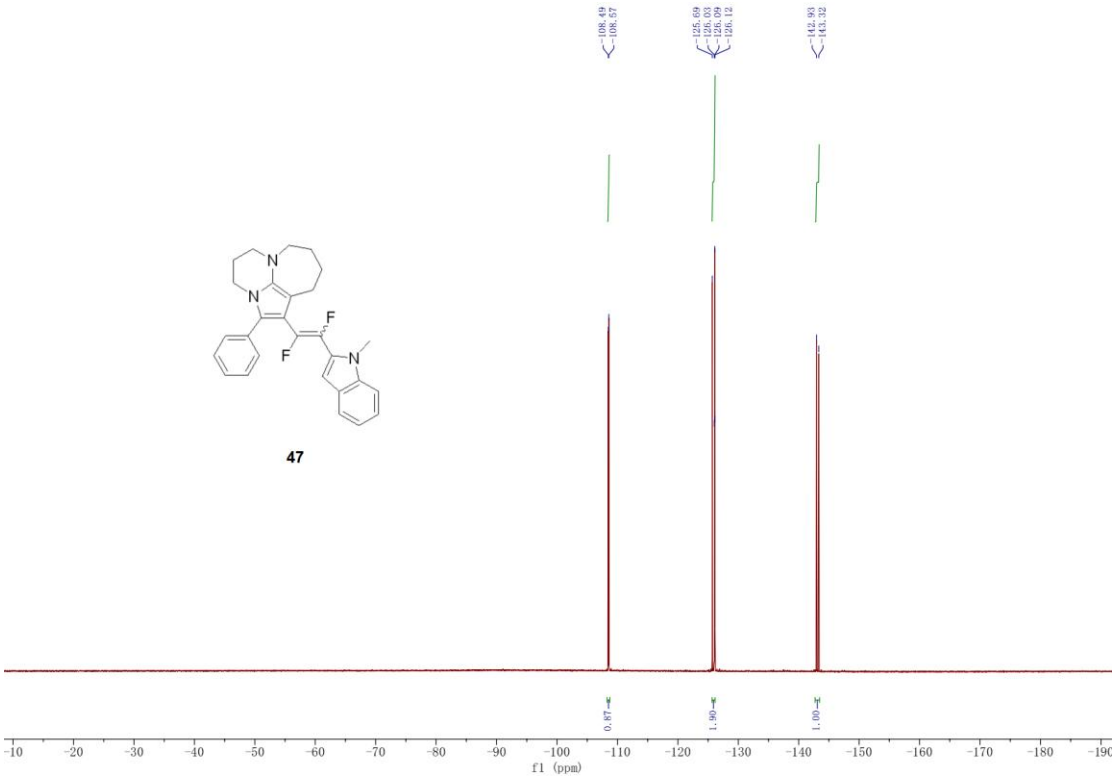
^{13}C NMR spectra of the product **46** (101 MHz, $CDCl_3$):



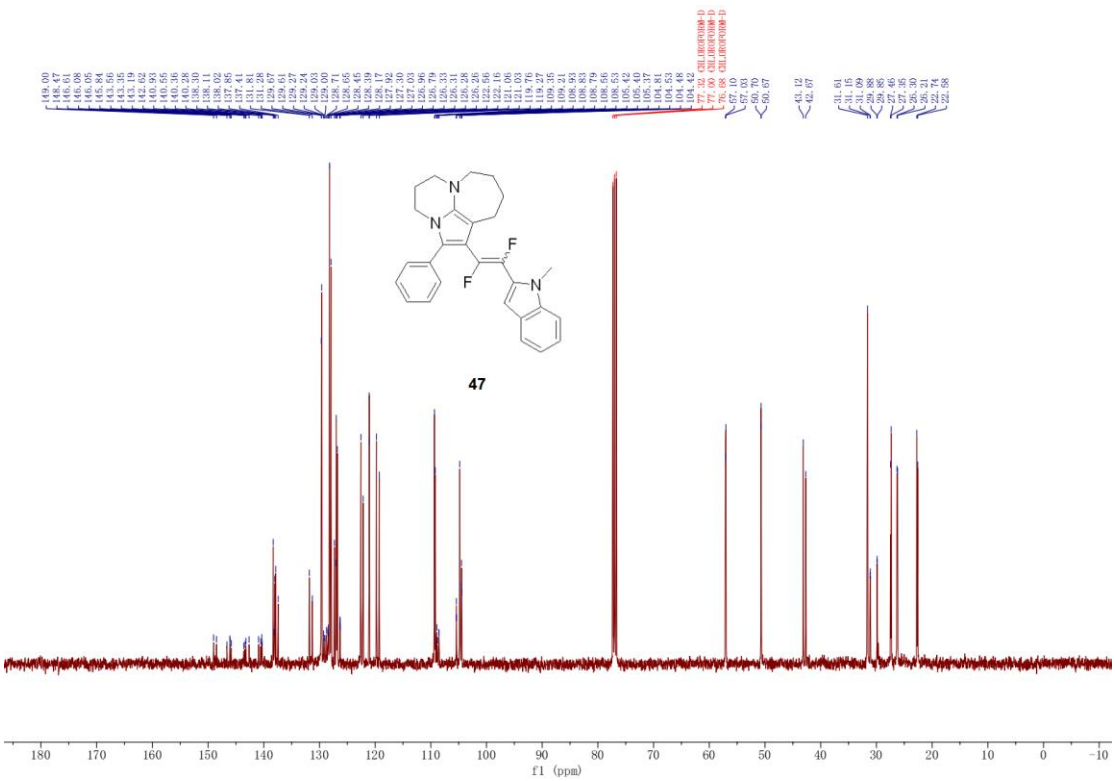
^{1}H NMR spectra of the product **47** (400 MHz, $CDCl_3$):



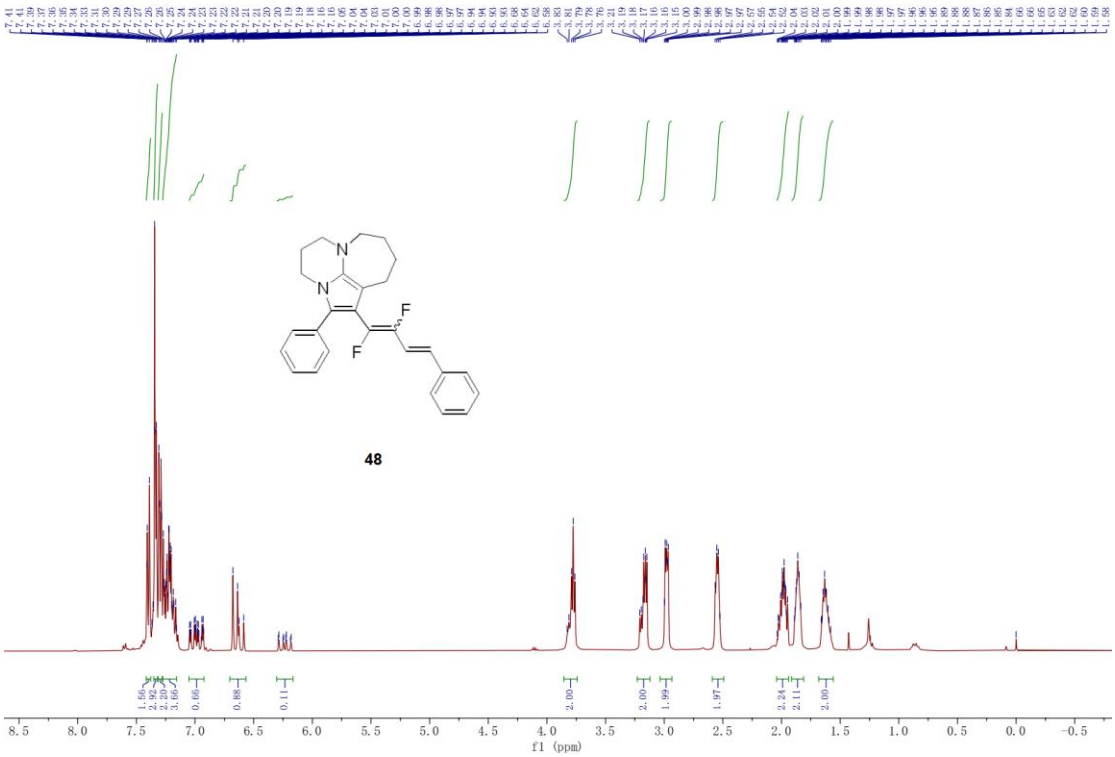
^{19}F NMR spectra of the product **47** (376 MHz, $CDCl_3$):



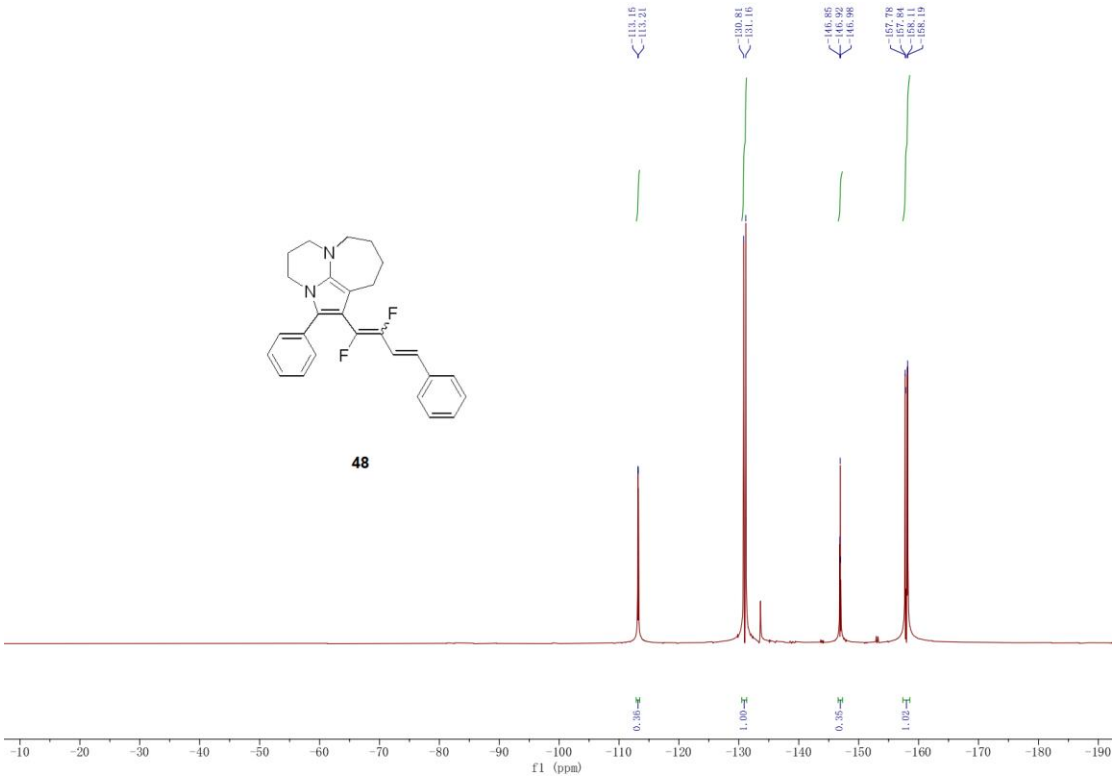
^{13}C NMR spectra of the product **47** (101 MHz, $CDCl_3$):



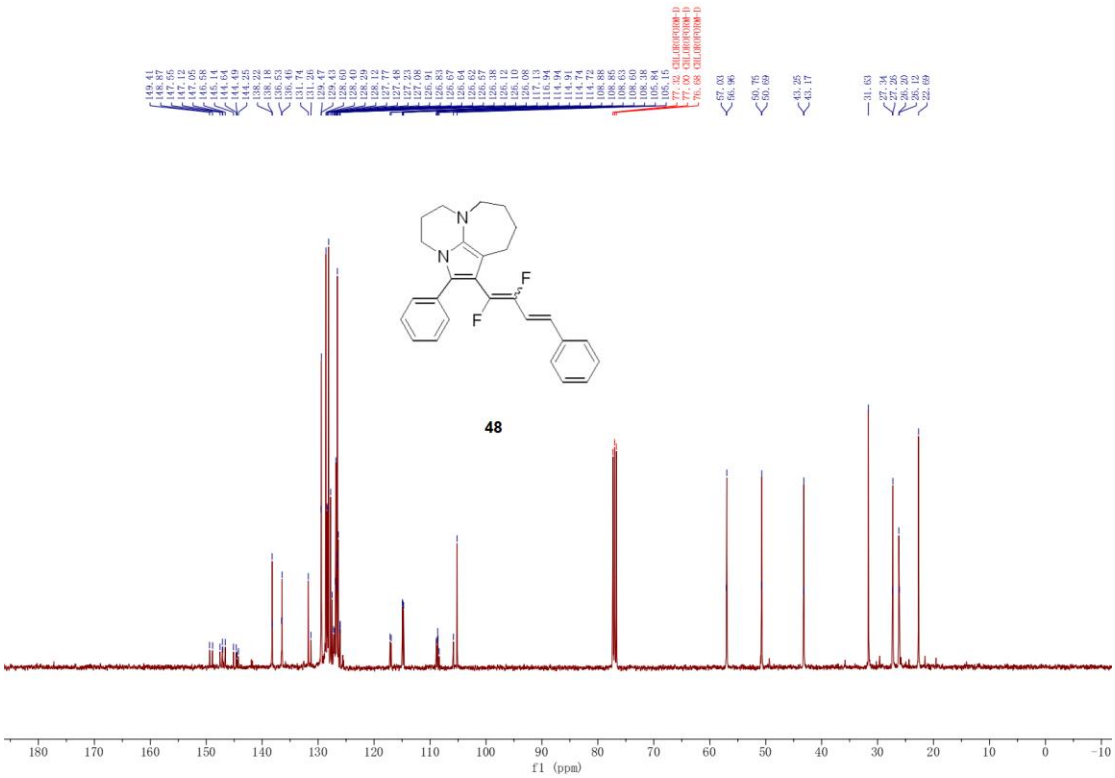
^{1}H NMR spectra of the product **48** (400 MHz, $CDCl_3$):



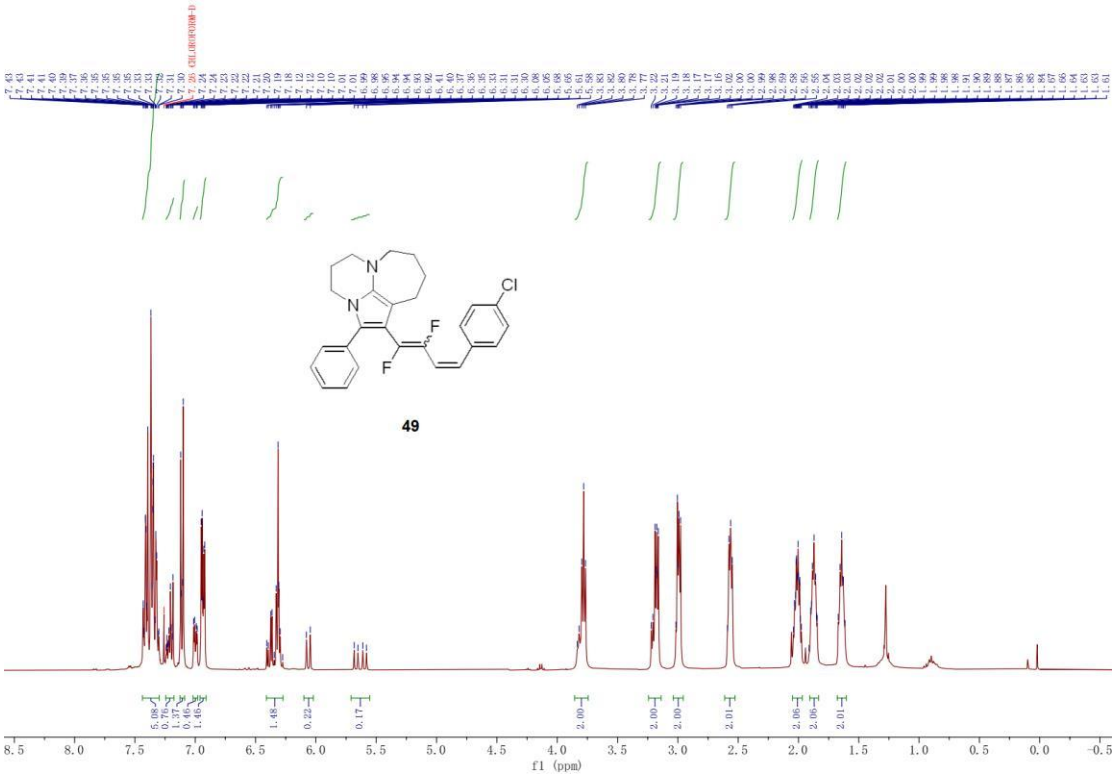
^{19}F NMR spectra of the product **48** (376 MHz, $CDCl_3$):



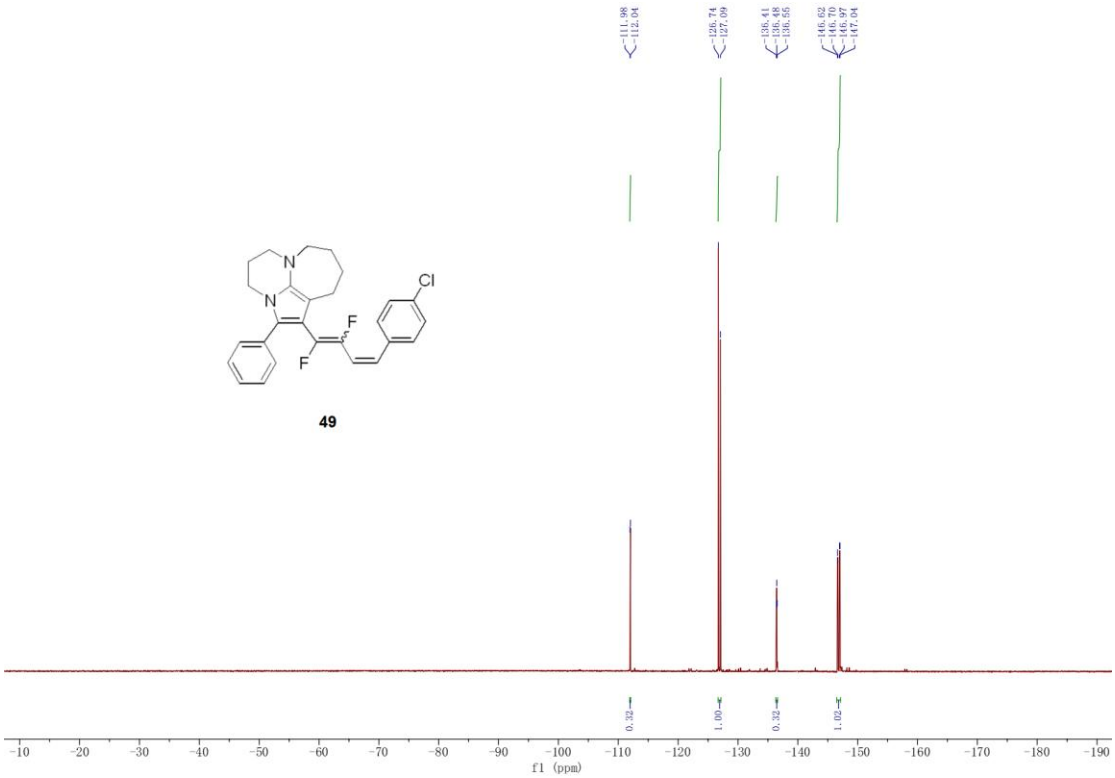
^{13}C NMR spectra of the product **48** (101 MHz, $CDCl_3$):



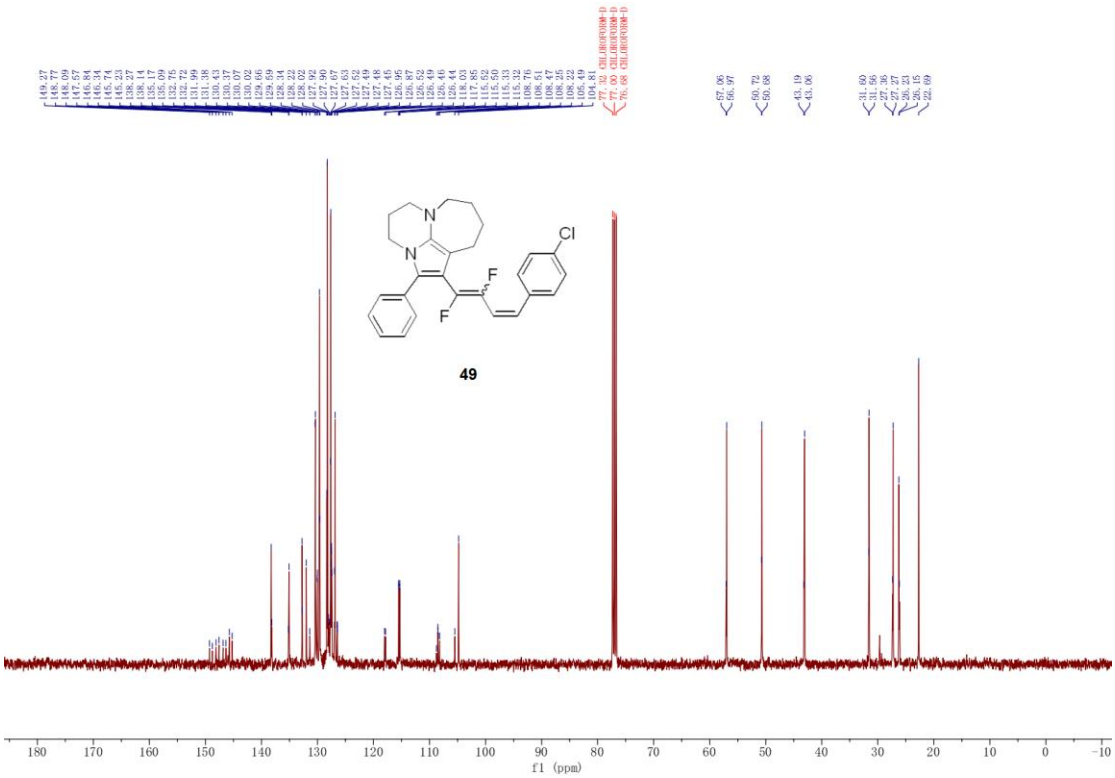
^{1}H NMR spectra of the product **49** (400 MHz, $CDCl_3$):



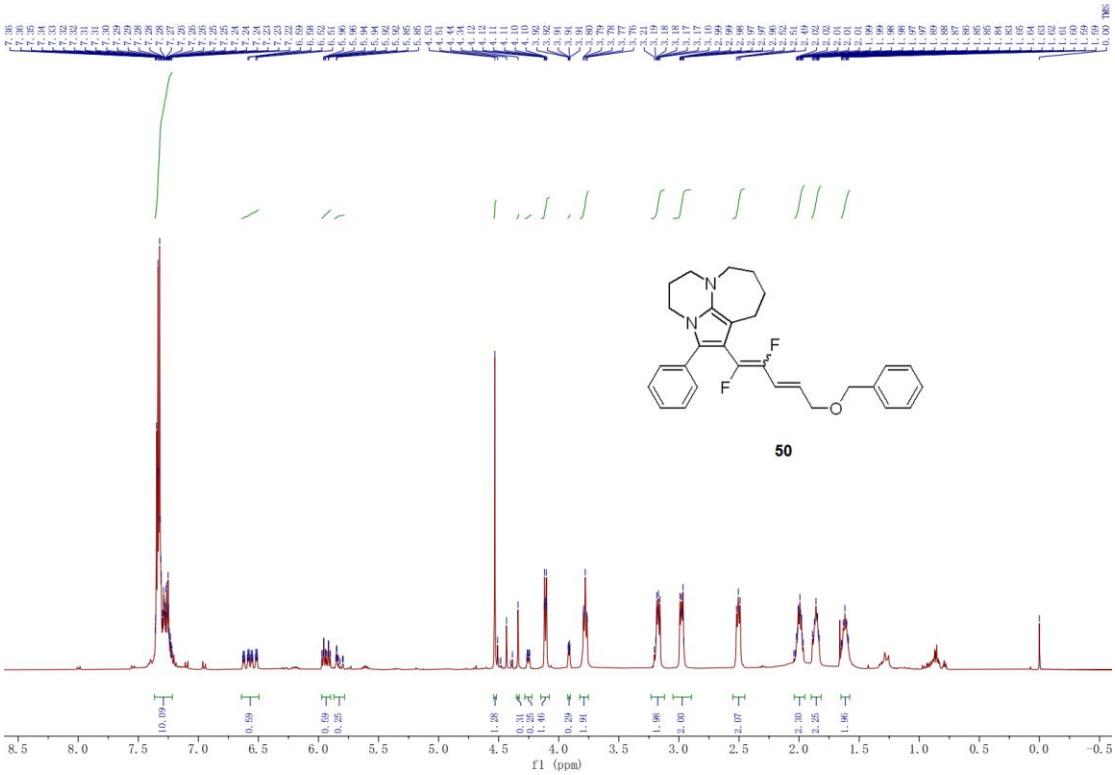
^{19}F NMR spectra of the product **49** (376 MHz, $CDCl_3$):



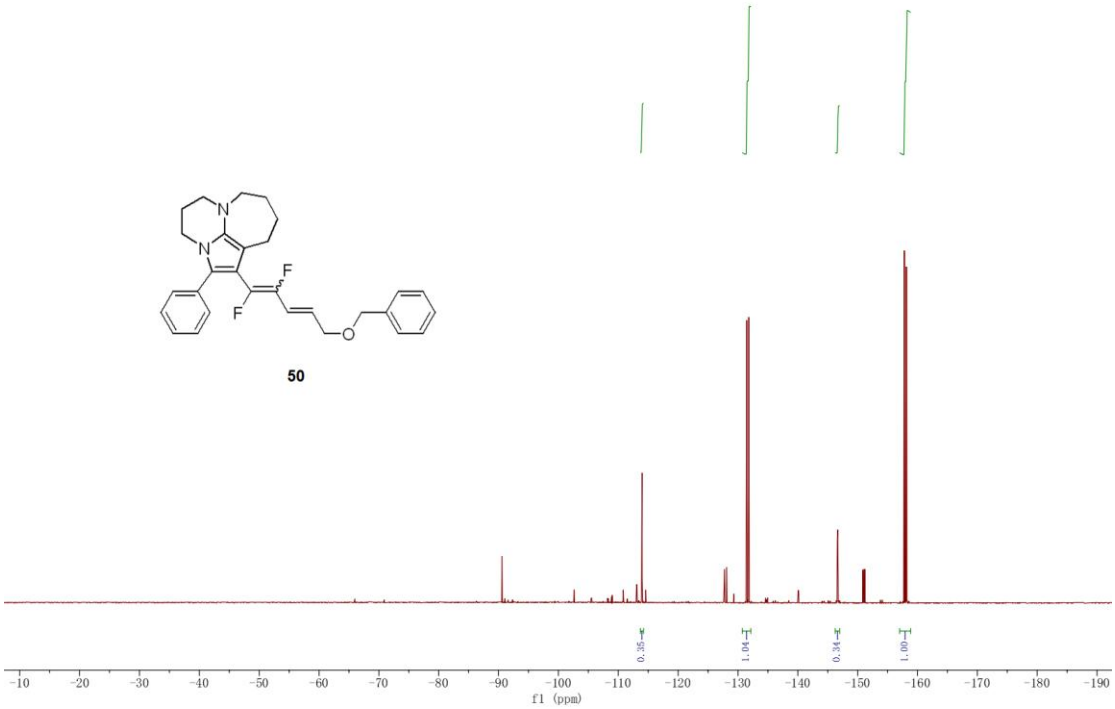
^{13}C NMR spectra of the product **49** (101 MHz, $CDCl_3$):



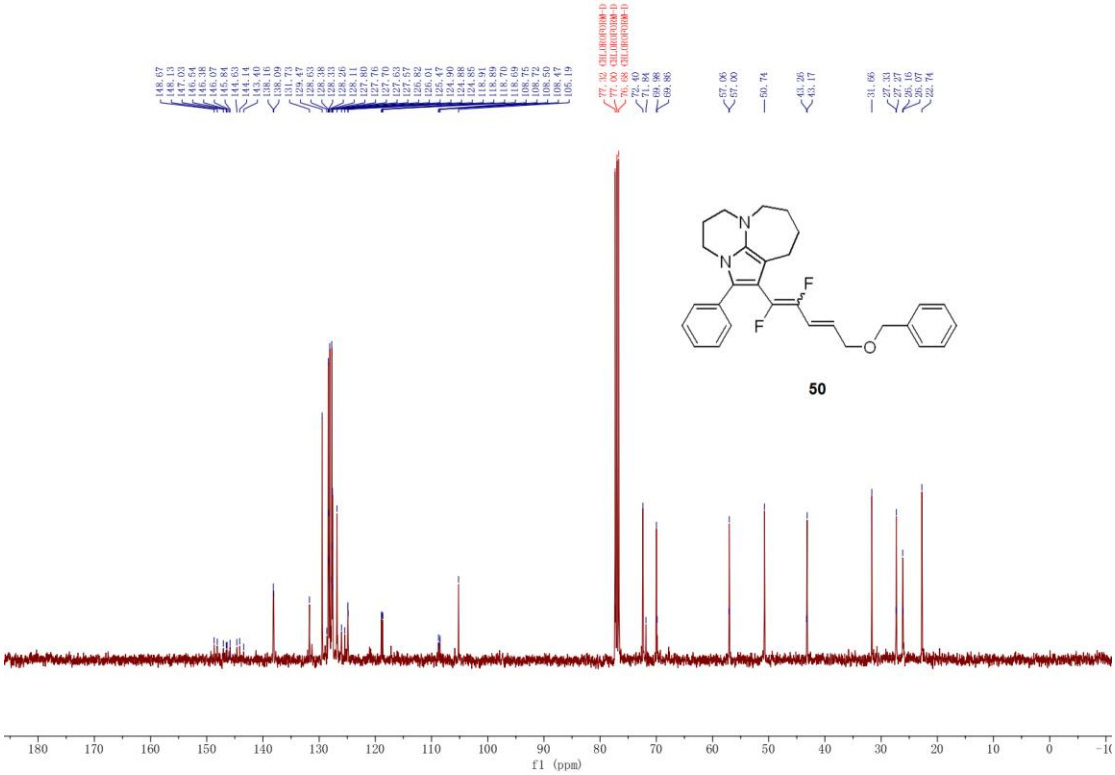
^{1}H NMR spectra of the product **50** (400 MHz, $CDCl_3$):



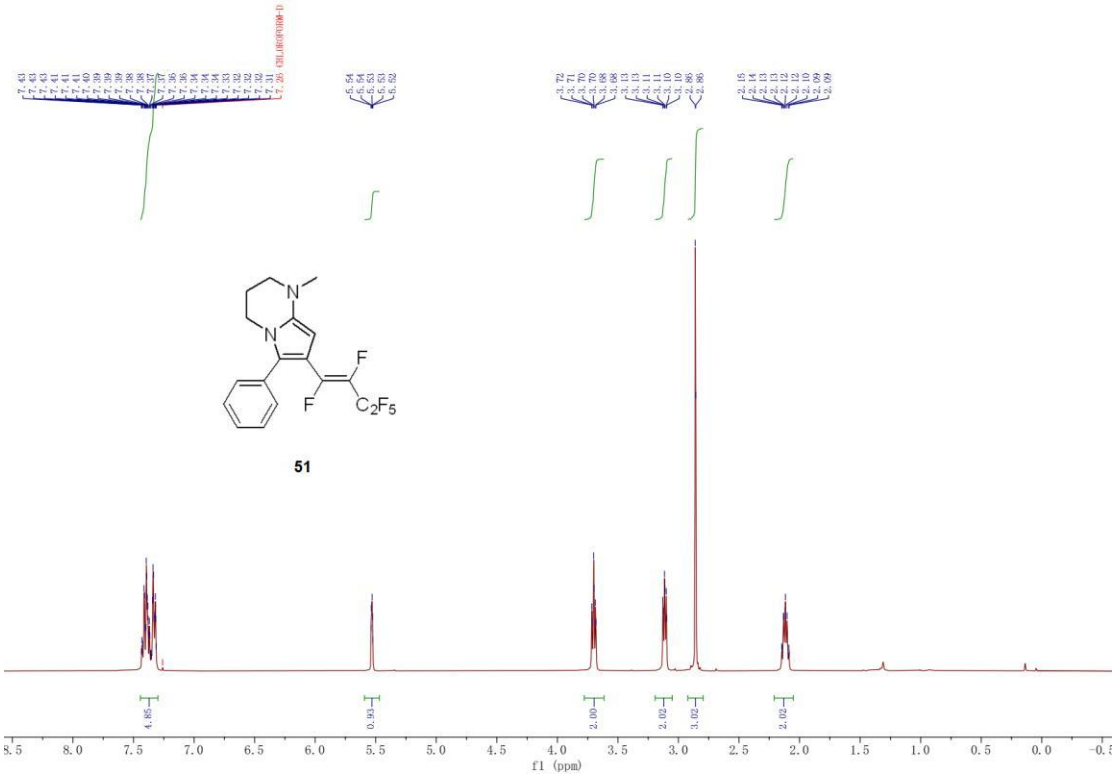
^{19}F NMR spectra of the product **50** (376 MHz, $CDCl_3$):



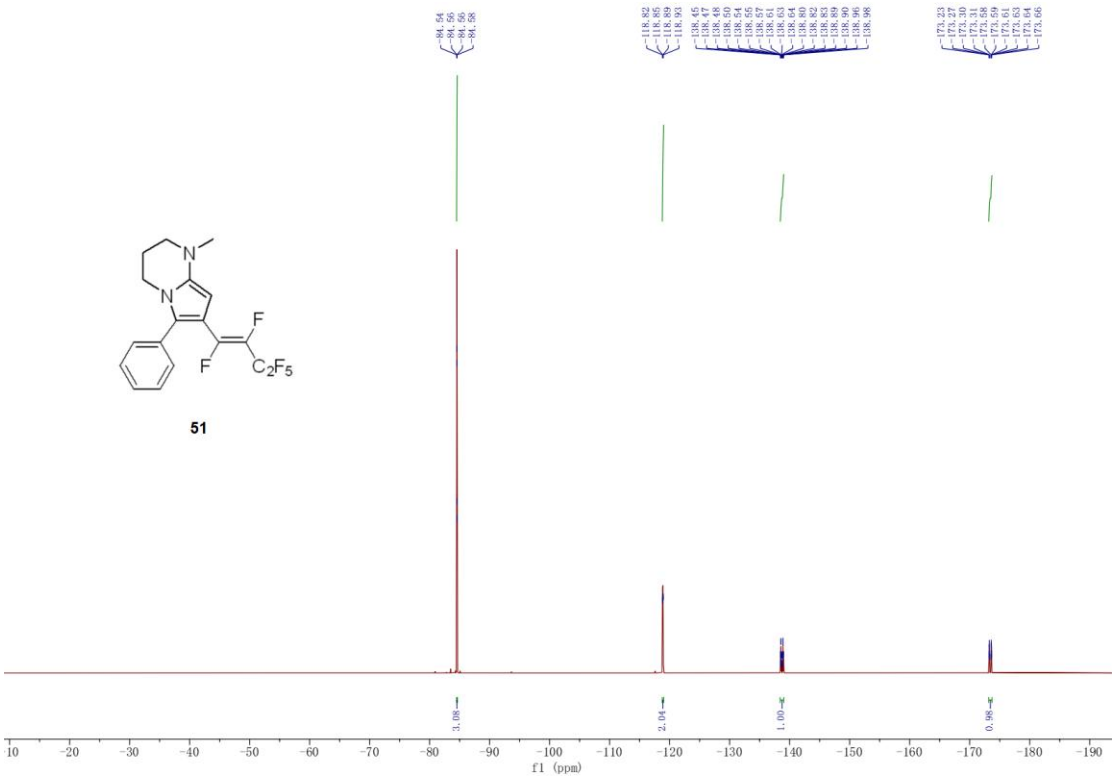
^{13}C NMR spectra of the product **50** (101 MHz, $CDCl_3$):



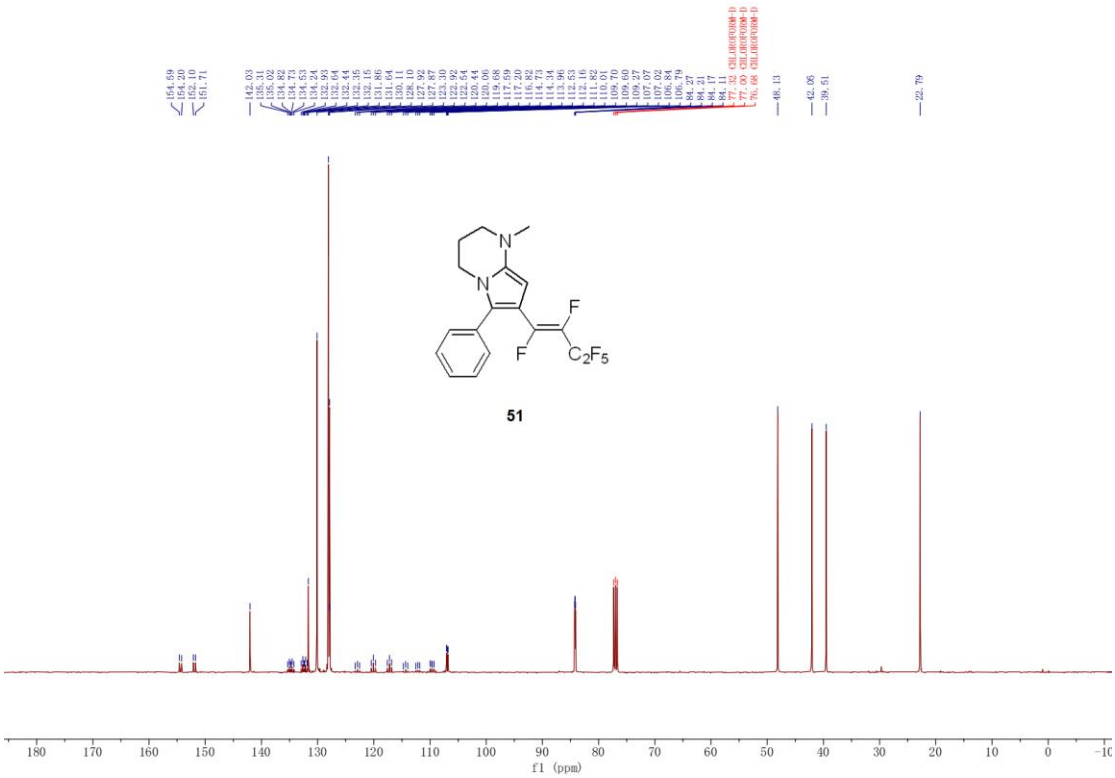
^{1}H NMR spectra of the product **51** (400 MHz, $CDCl_3$):



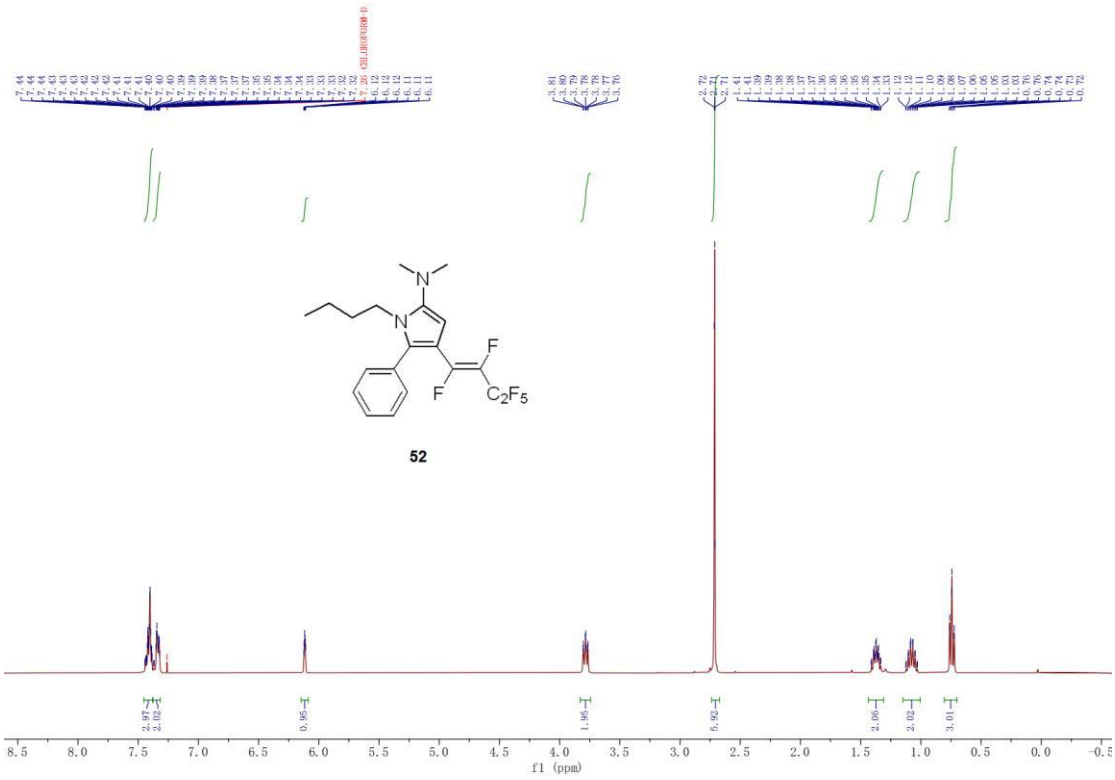
^{19}F NMR spectra of the product **51** (376 MHz, $CDCl_3$):



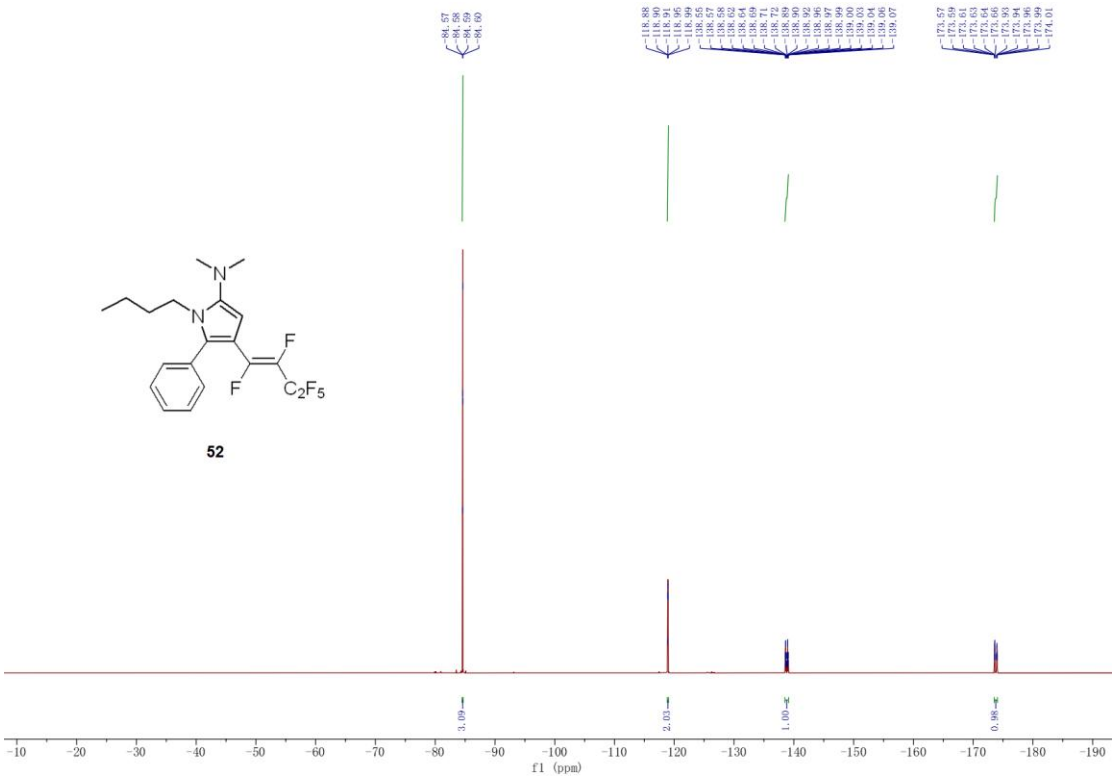
^{13}C NMR spectra of the product **51** (101 MHz, $CDCl_3$):



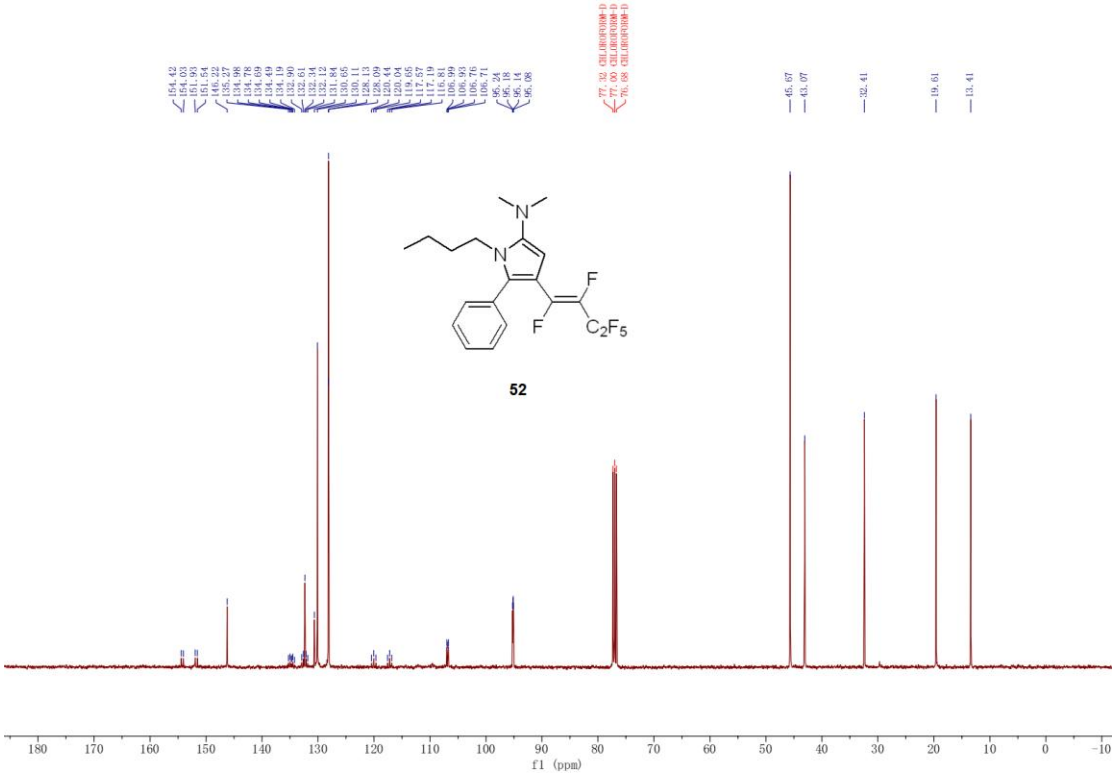
^{1}H NMR spectra of the product **52** (400 MHz, $CDCl_3$):



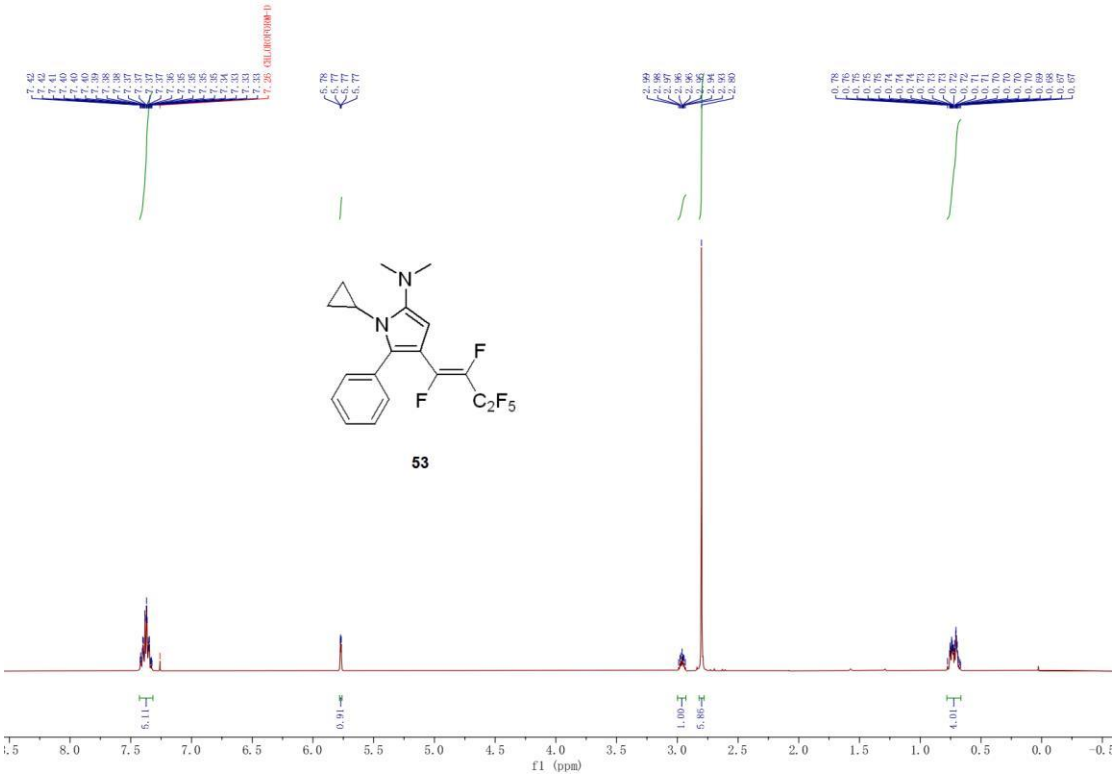
^{19}F NMR spectra of the product **52** (376 MHz, $CDCl_3$):



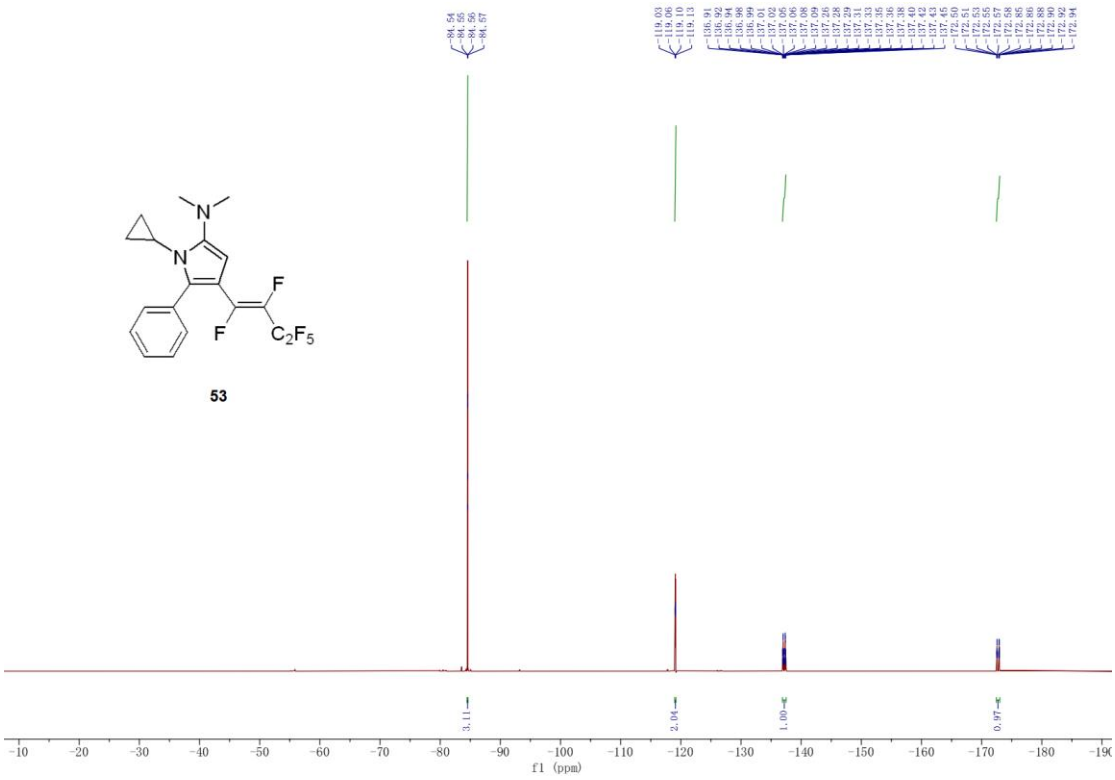
^{13}C NMR spectra of the product **52** (101 MHz, $CDCl_3$):



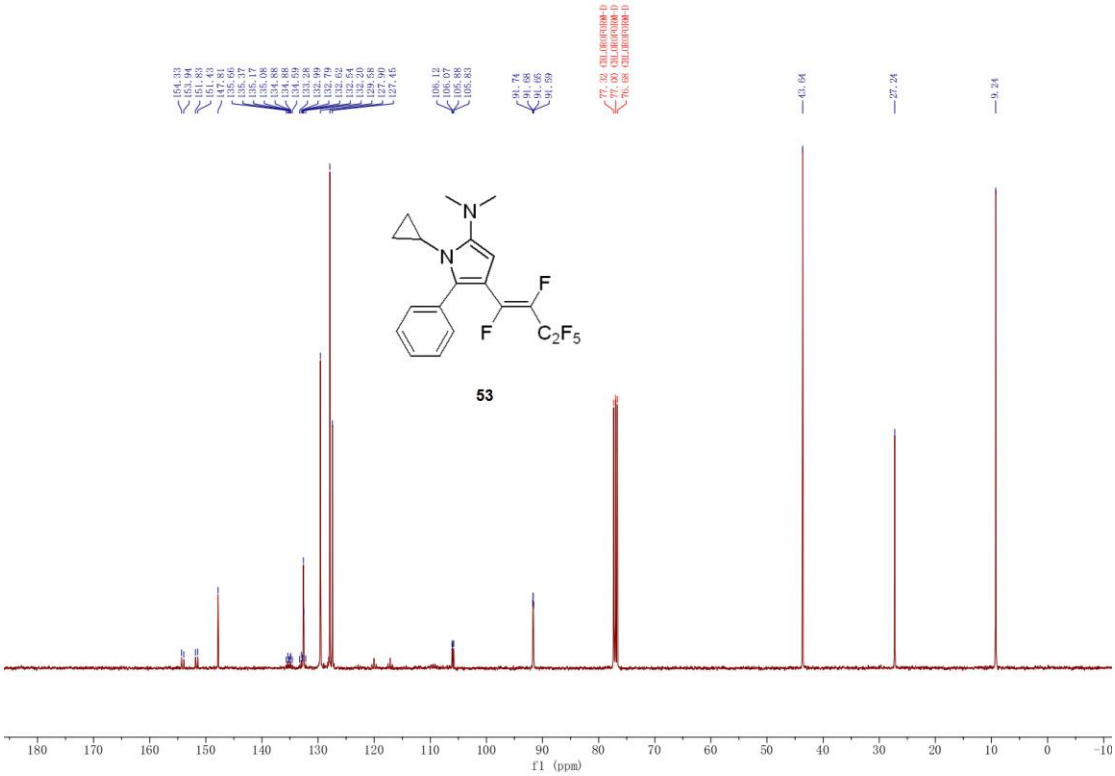
^{1}H NMR spectra of the product **53** (400 MHz, $CDCl_3$):



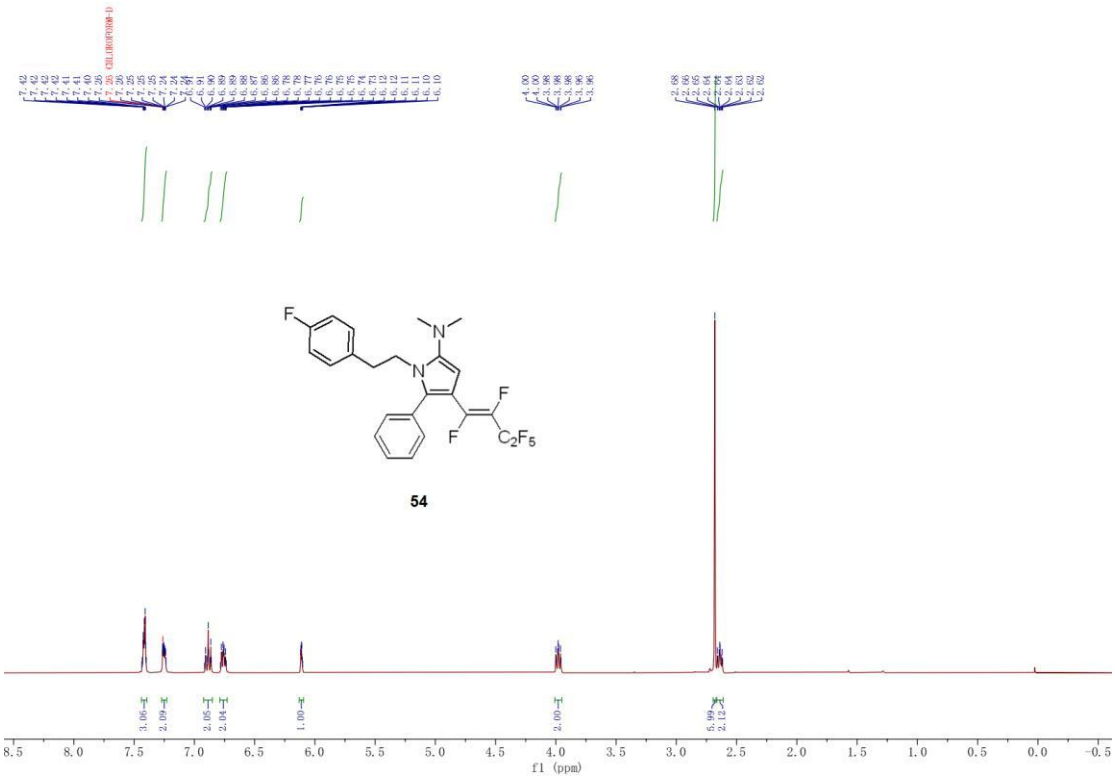
^{19}F NMR spectra of the product **53** (376 MHz, $CDCl_3$):



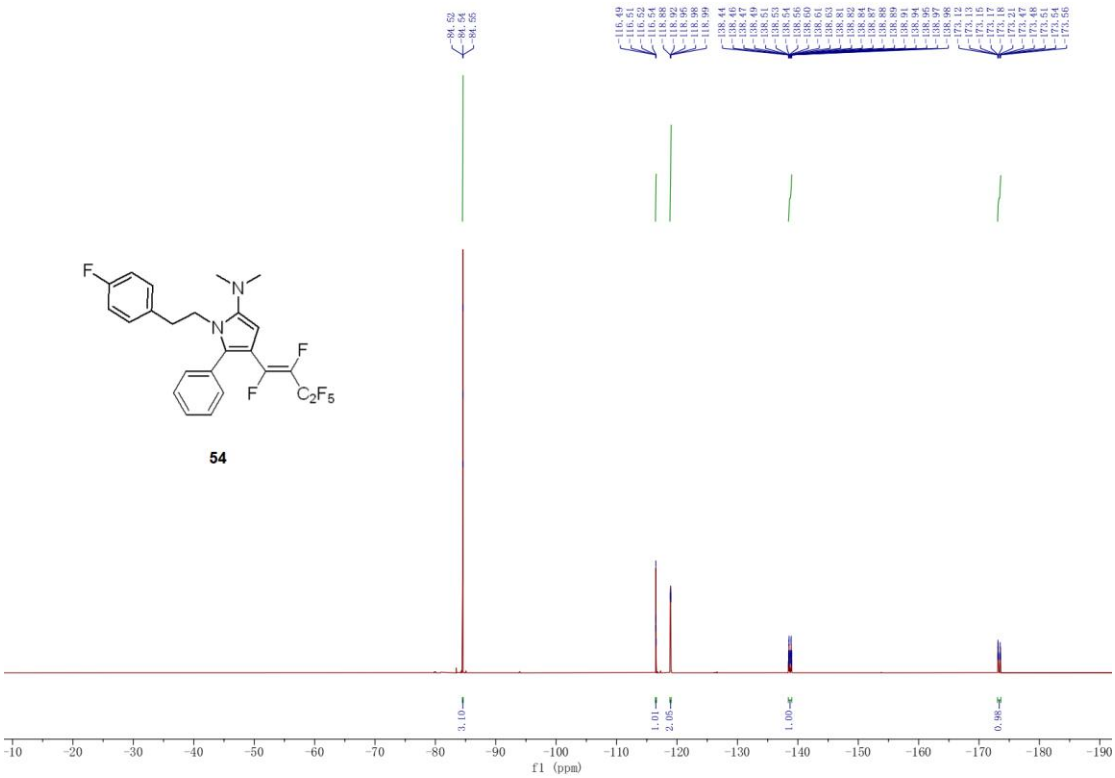
^{13}C NMR spectra of the product **53** (101 MHz, $CDCl_3$):



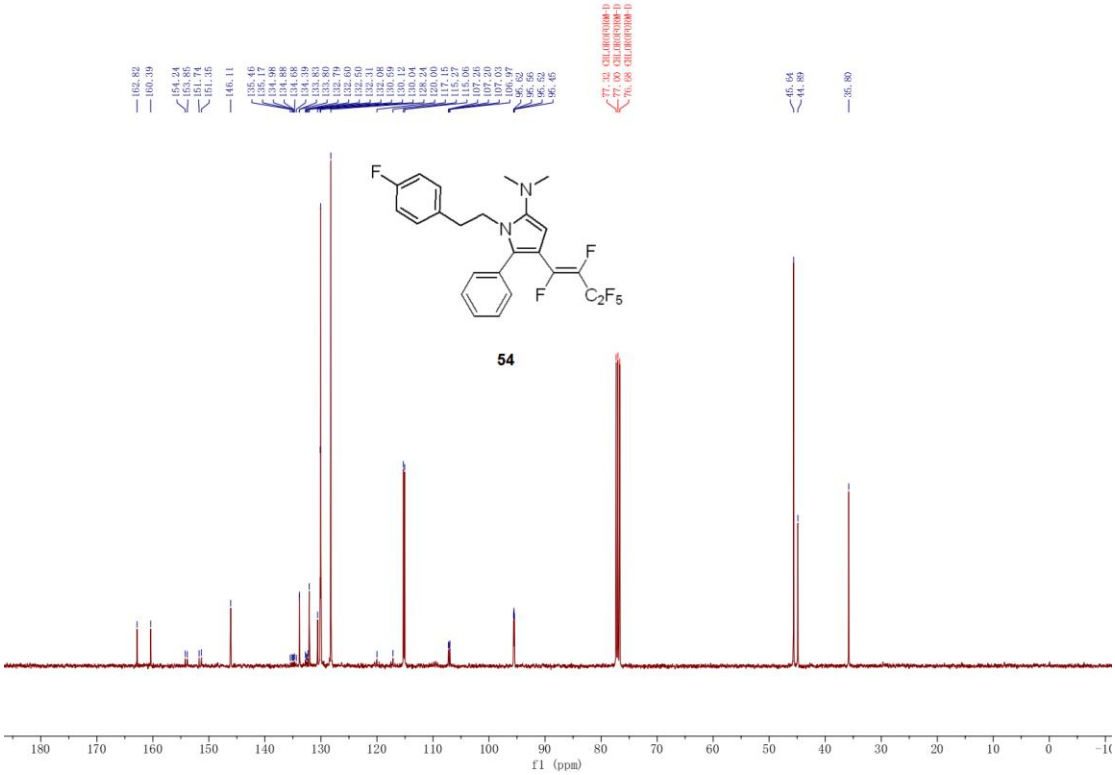
^{1}H NMR spectra of the product **54** (400 MHz, $CDCl_3$):



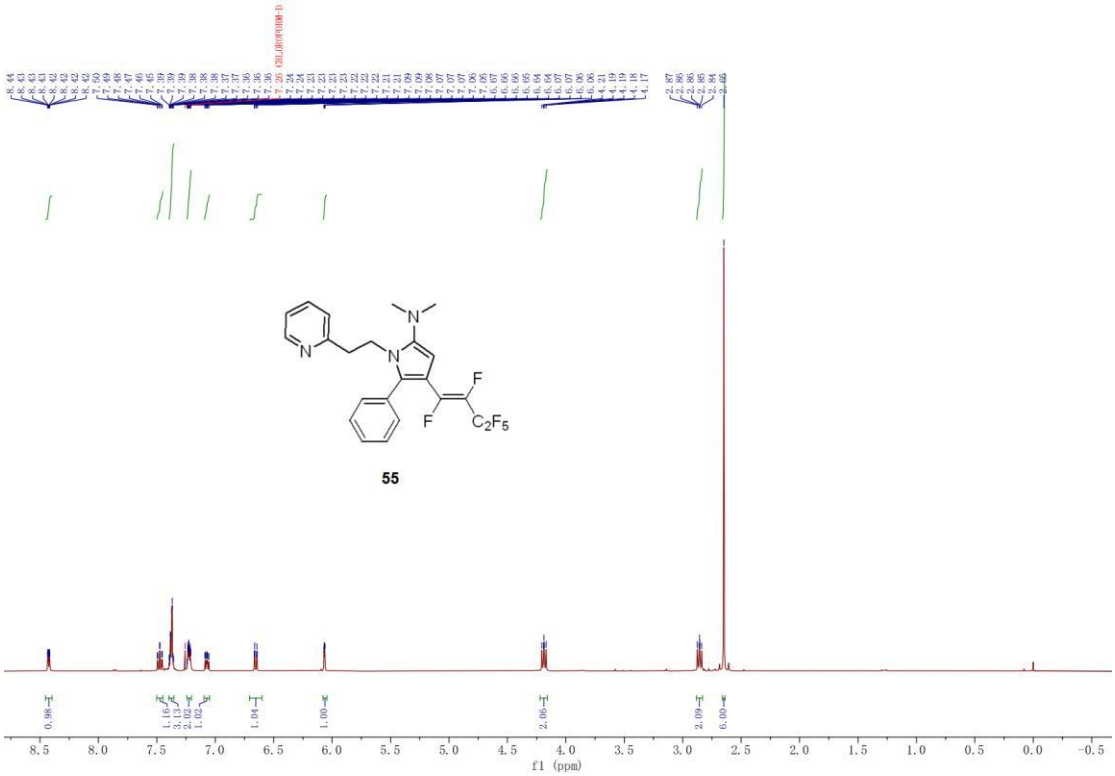
^{19}F NMR spectra of the product **54** (376 MHz, $CDCl_3$):



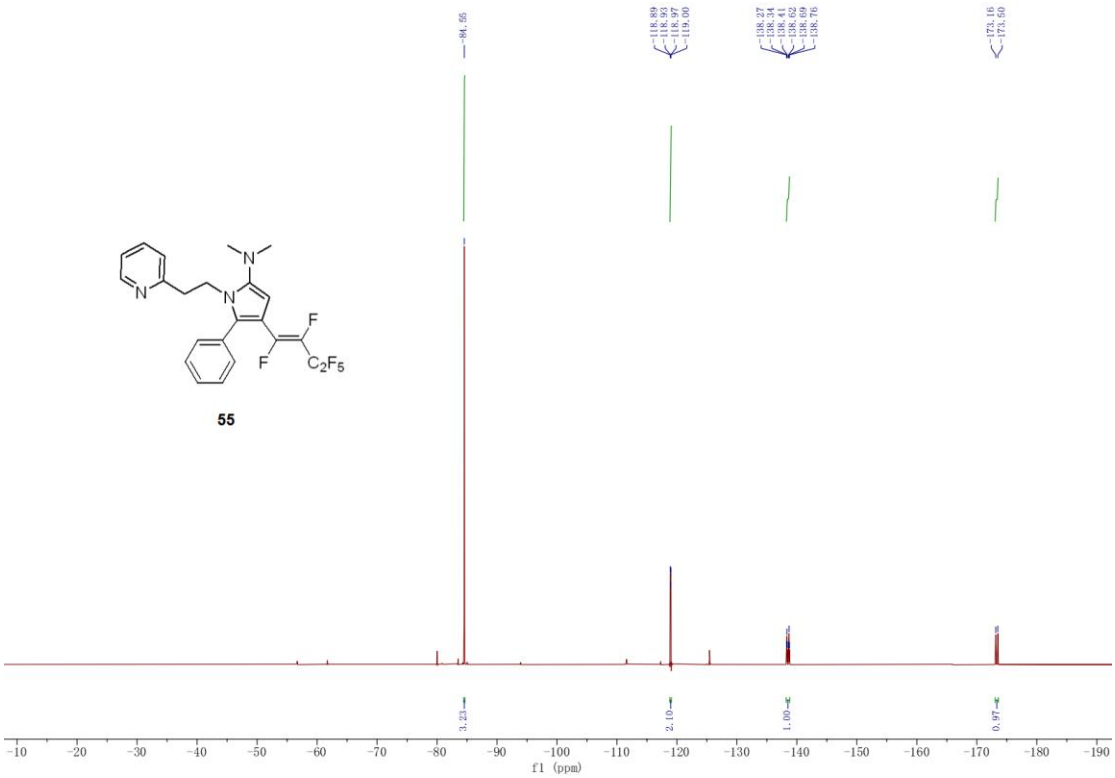
^{13}C NMR spectra of the product **54** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **55** (400 MHz, $CDCl_3$):

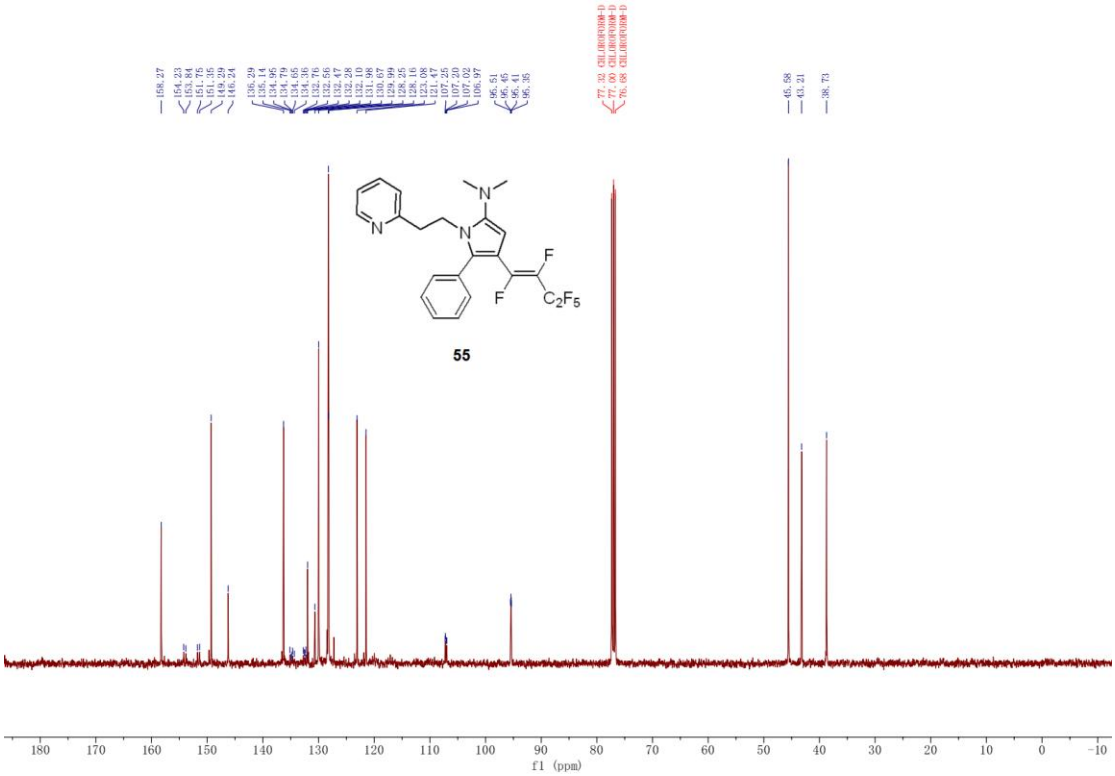


^{19}F NMR spectra of the product **55** (376 MHz, $CDCl_3$):



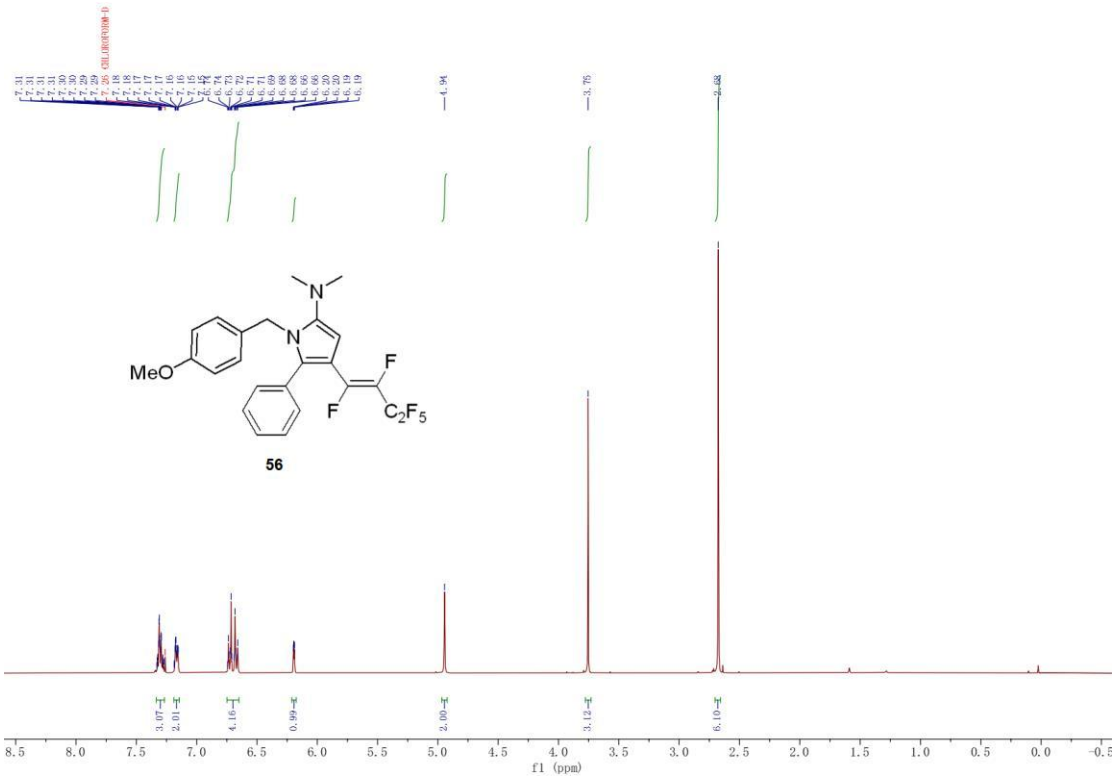
55

^{13}C NMR spectra of the product **55** (101 MHz, $CDCl_3$):

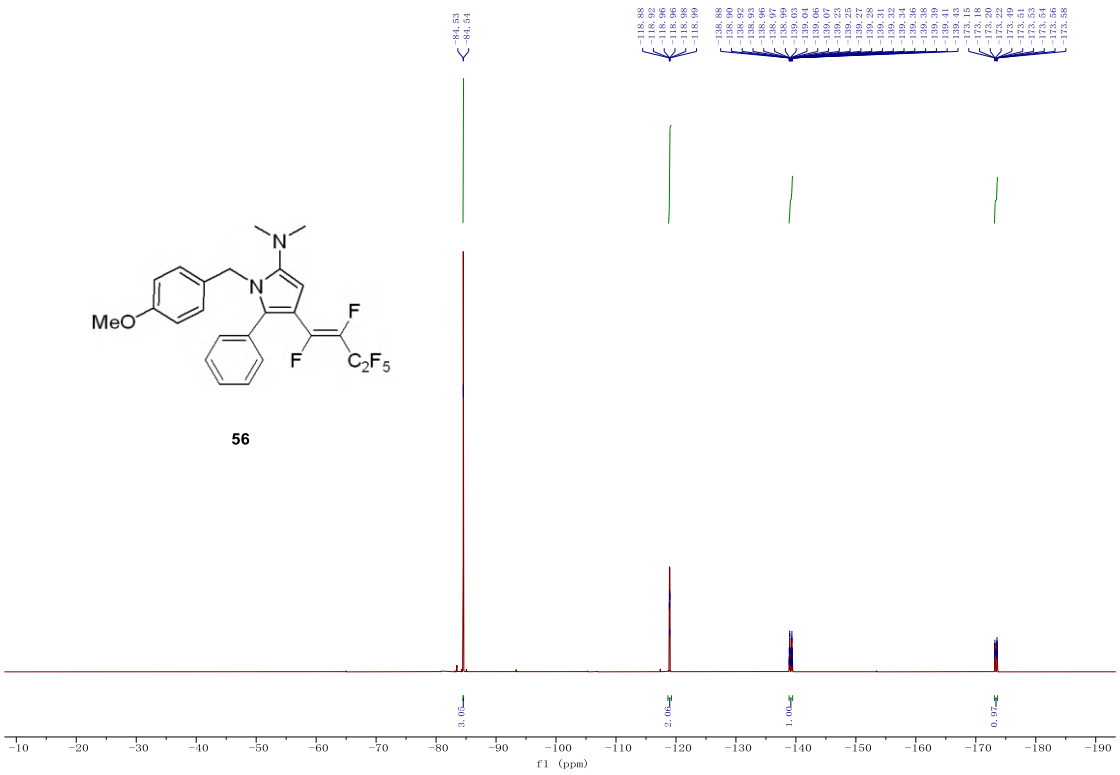


55

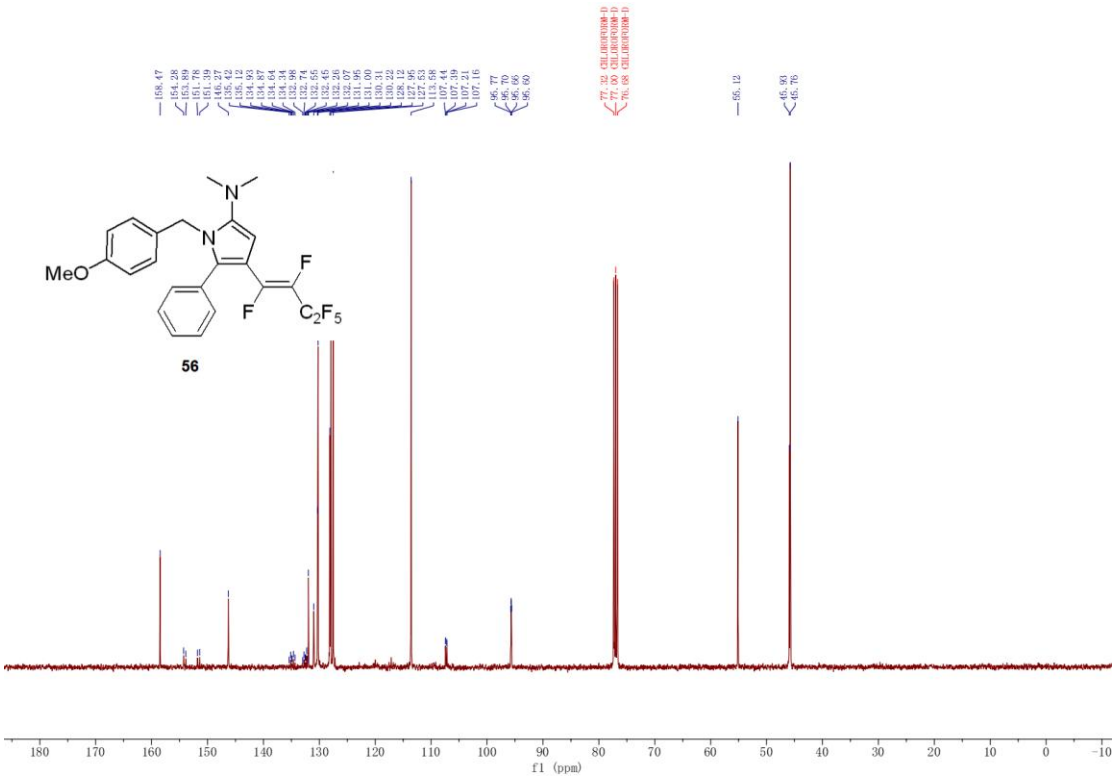
^{1}H NMR spectra of the product **56** (400 MHz, $CDCl_3$):



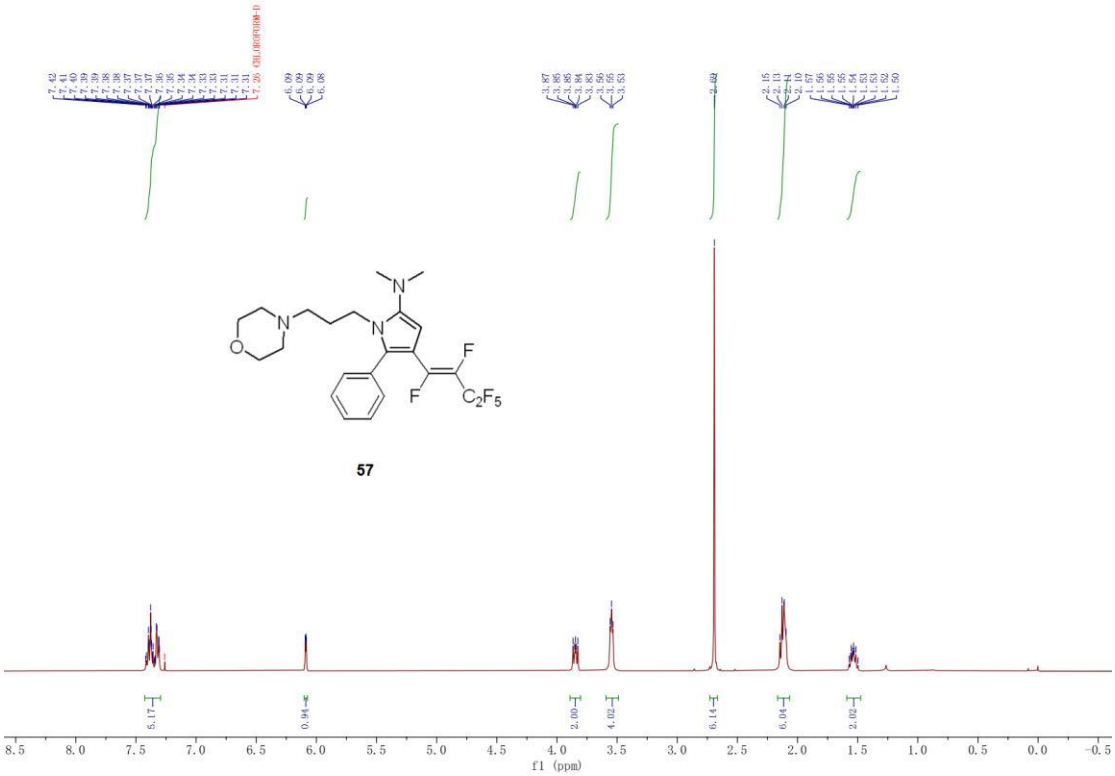
^{19}F NMR spectra of the product **56** (376 MHz, $CDCl_3$):



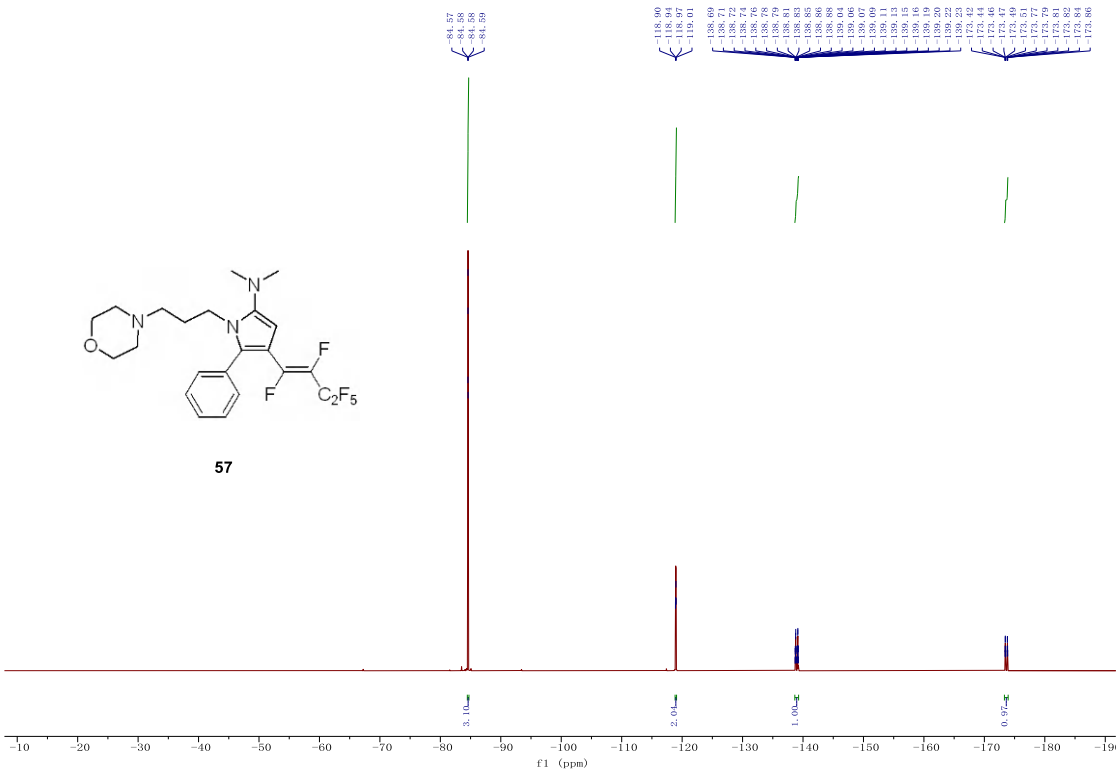
^{13}C NMR spectra of the product **56** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **57** (400 MHz, $CDCl_3$):

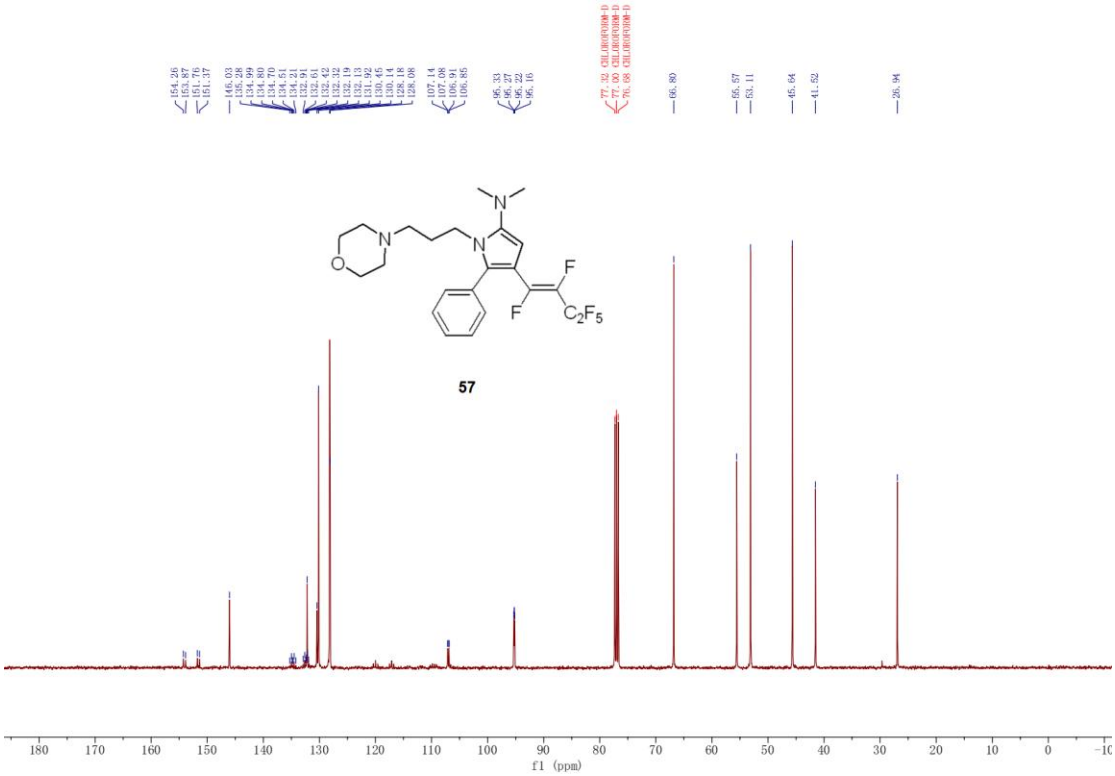


^{19}F NMR spectra of the product **57** (376 MHz, $CDCl_3$):



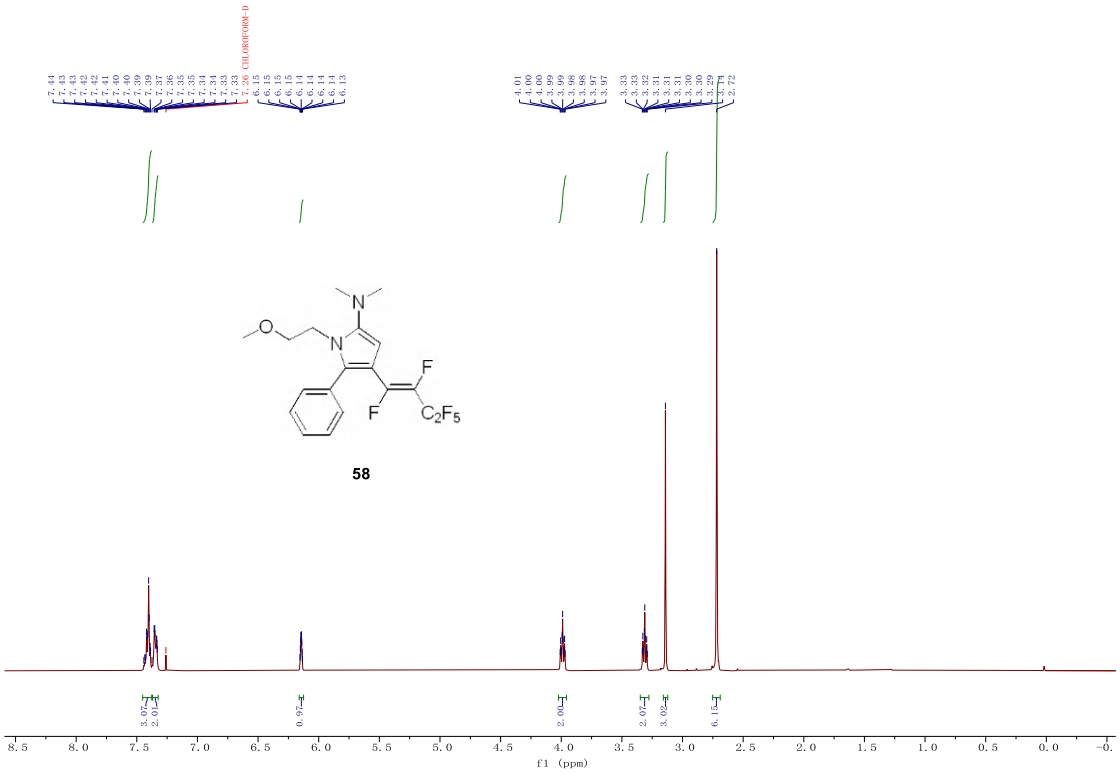
57

^{13}C NMR spectra of the product **57** (101 MHz, $CDCl_3$):

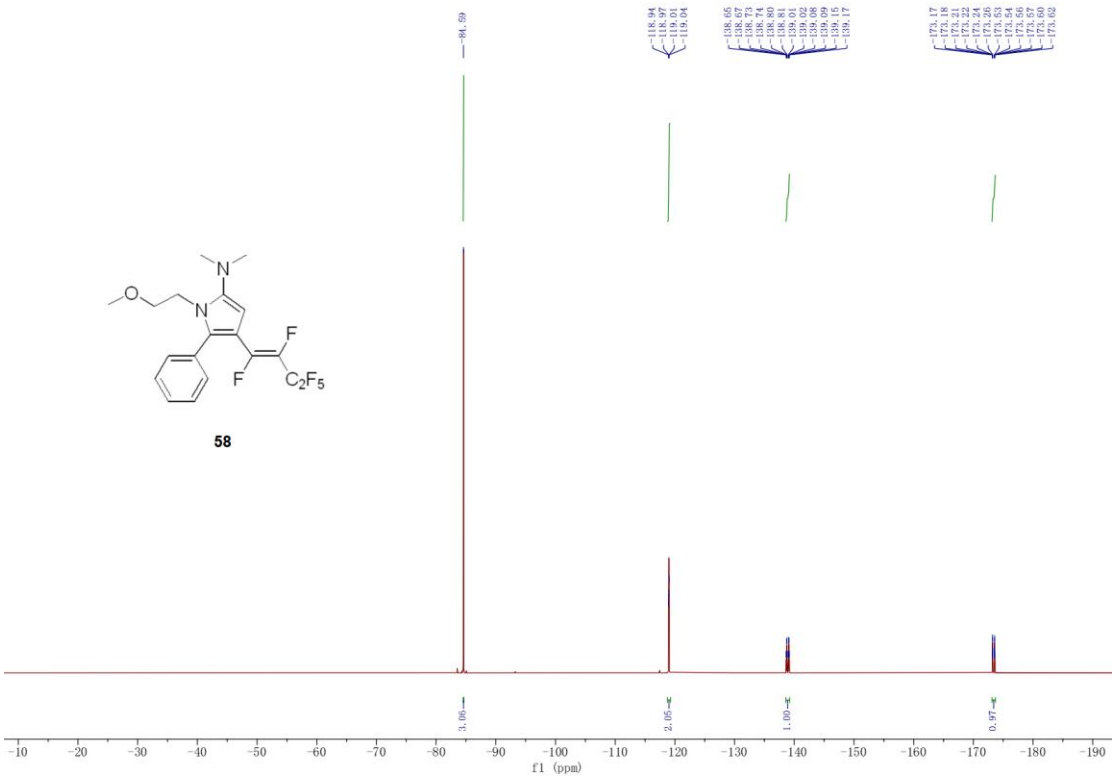


57

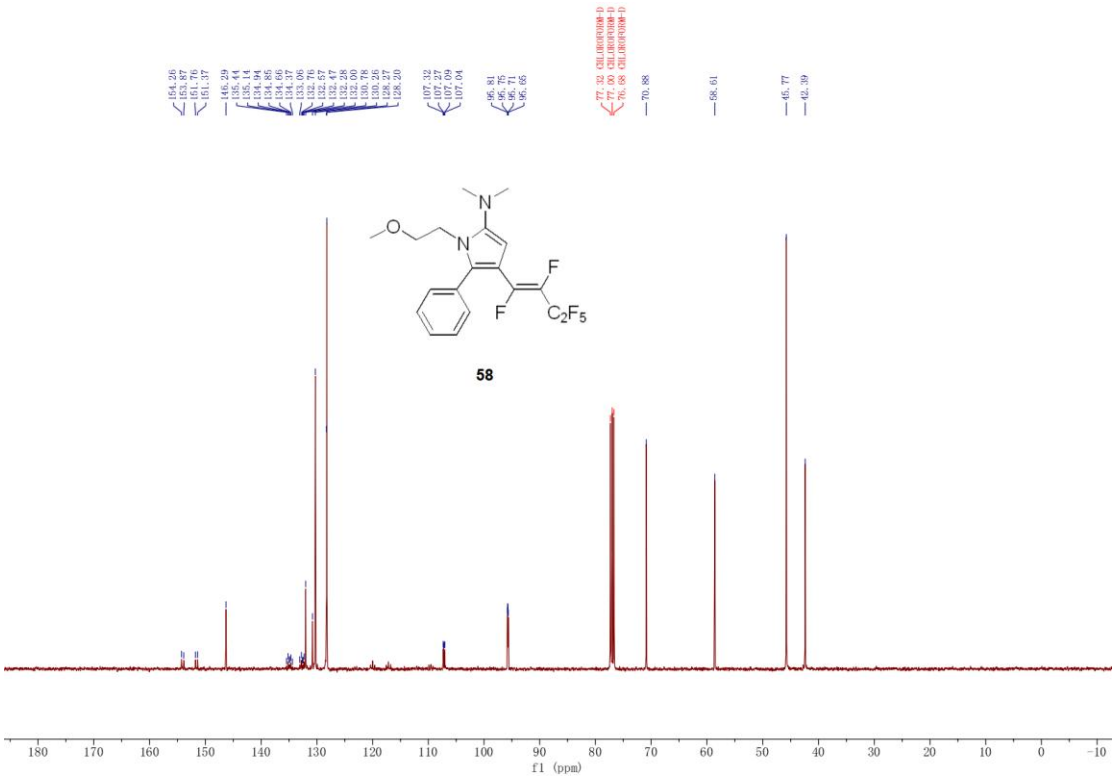
^{1}H NMR spectra of the product **58** (400 MHz, $CDCl_3$):



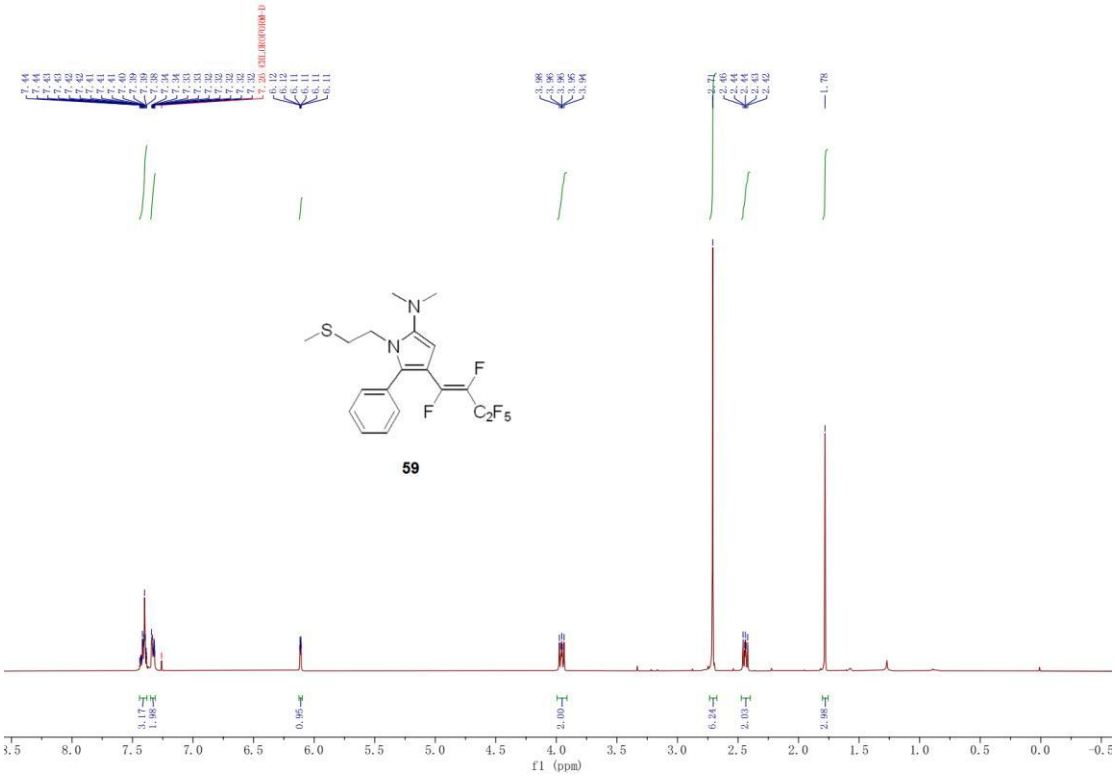
^{19}F NMR spectra of the product **58** (376 MHz, $CDCl_3$):



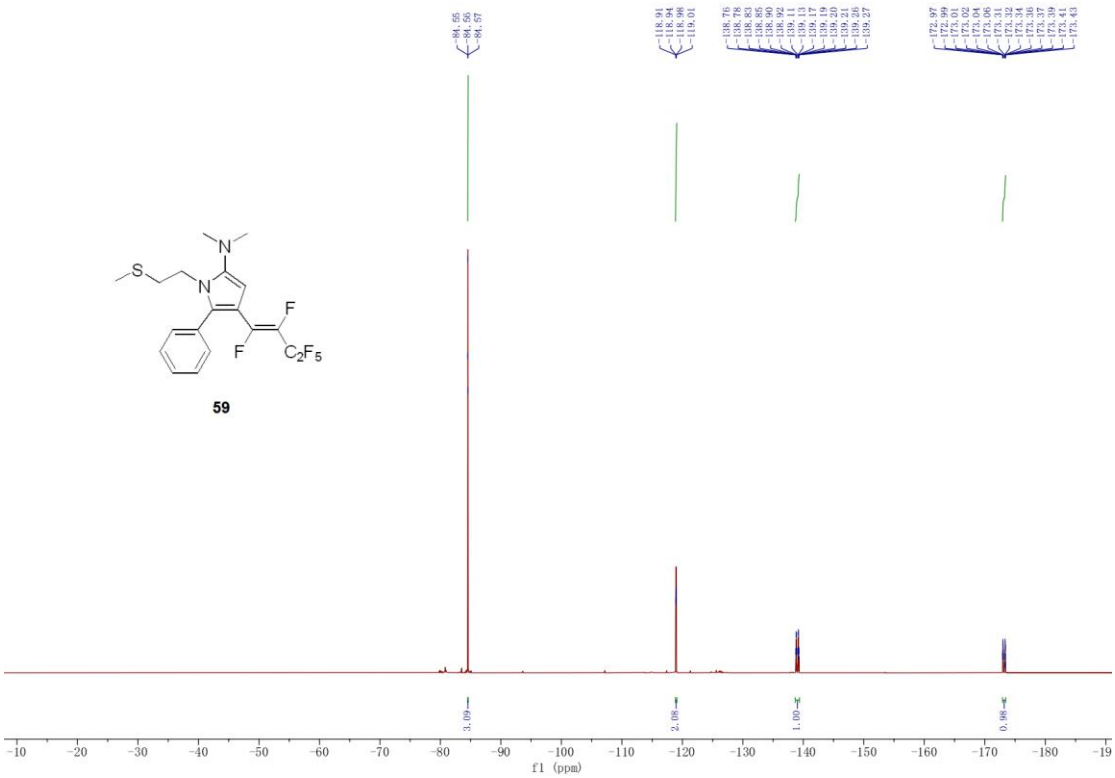
^{13}C NMR spectra of the product **58** (101 MHz, $CDCl_3$):



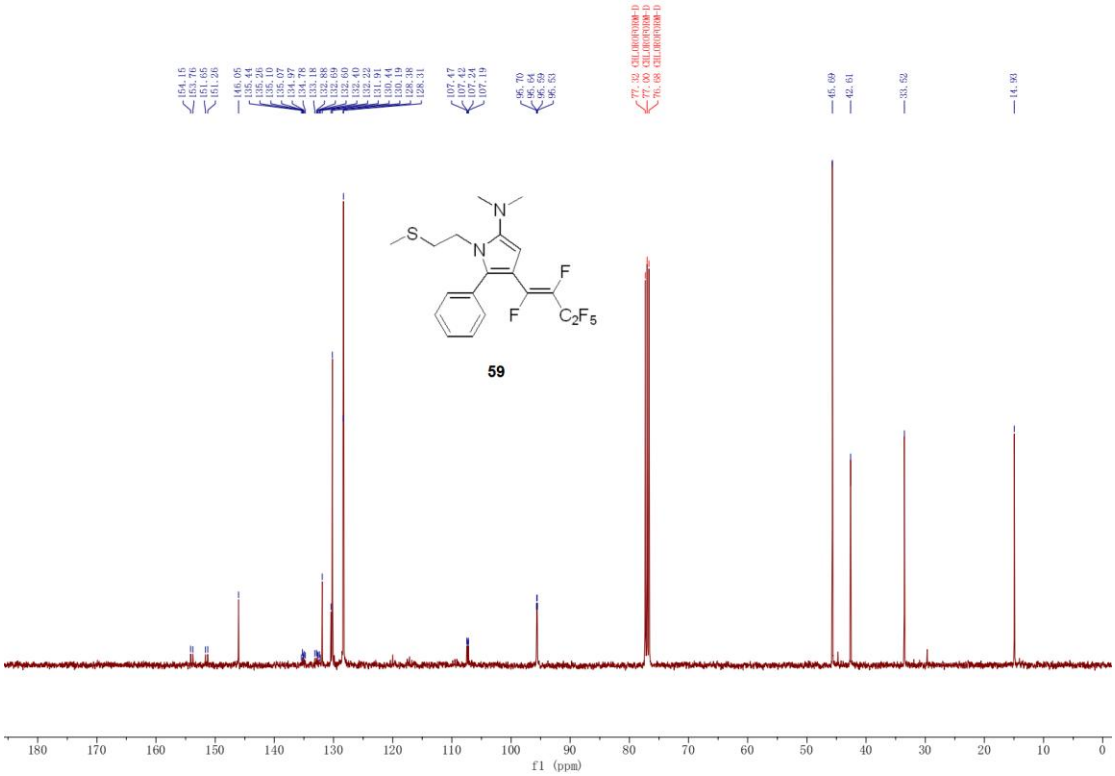
^{1}H NMR spectra of the product **59** (400 MHz, $CDCl_3$):



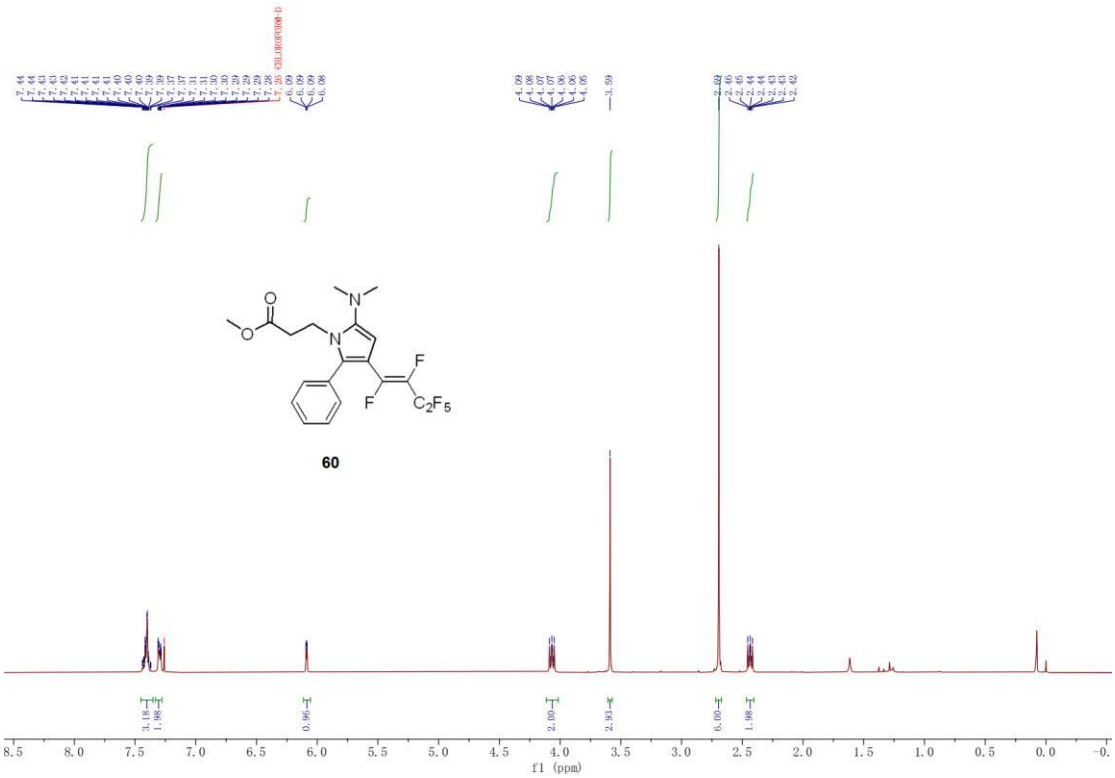
^{19}F NMR spectra of the product **59** (376 MHz, $CDCl_3$):



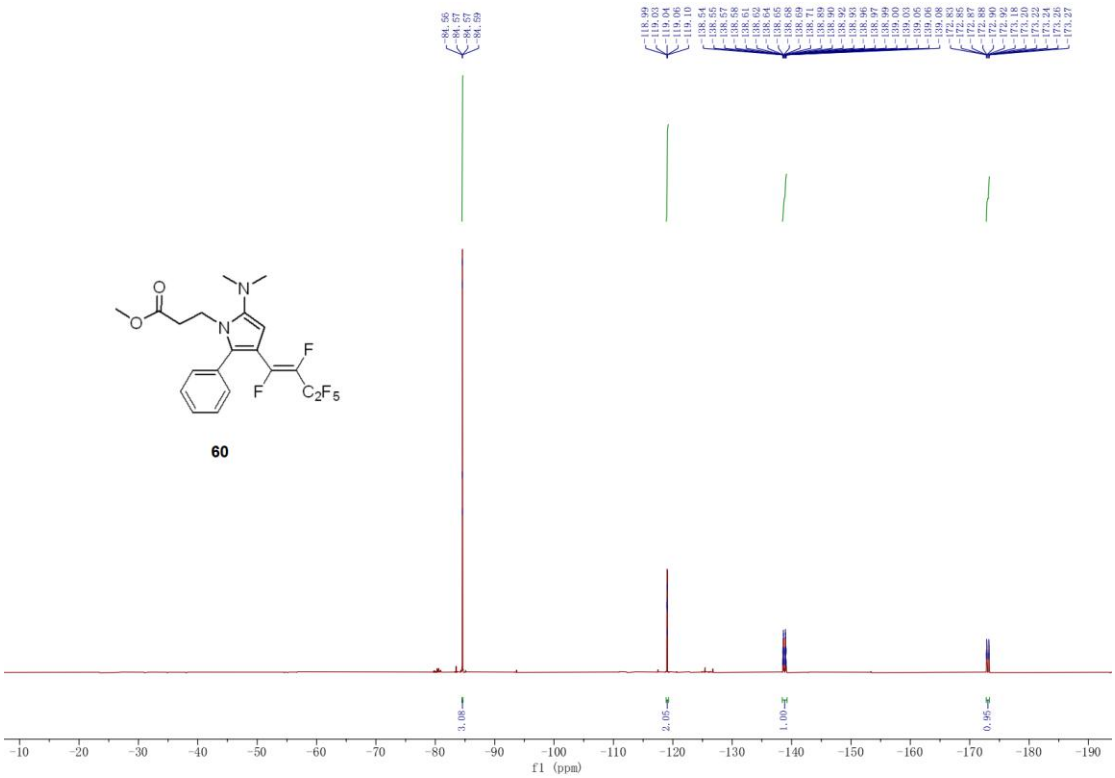
^{13}C NMR spectra of the product **59** (101 MHz, $CDCl_3$):



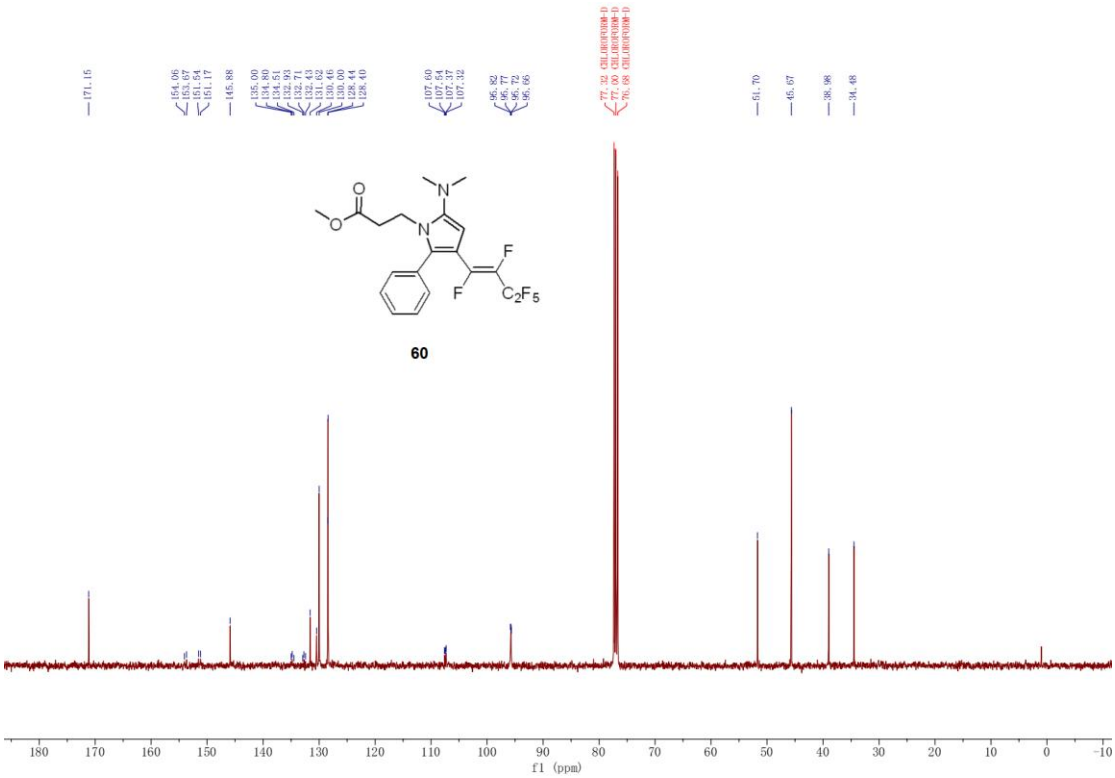
^{1}H NMR spectra of the product **60** (400 MHz, $CDCl_3$):



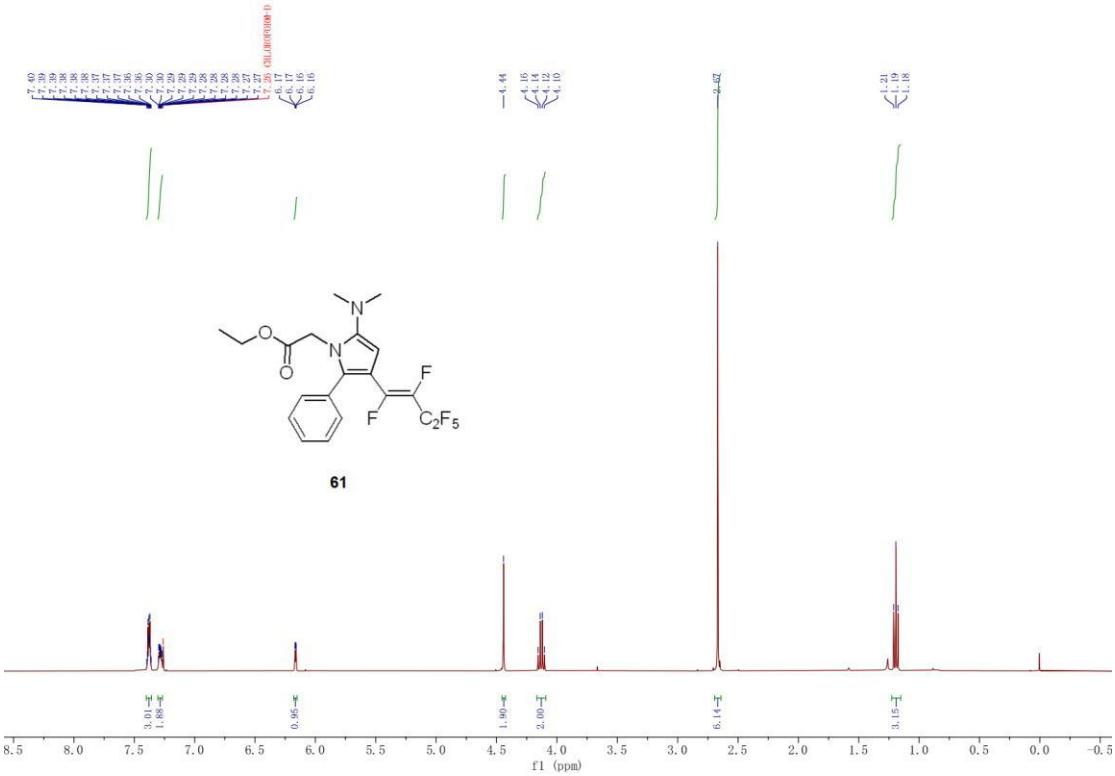
^{19}F NMR spectra of the product **60** (376 MHz, $CDCl_3$):



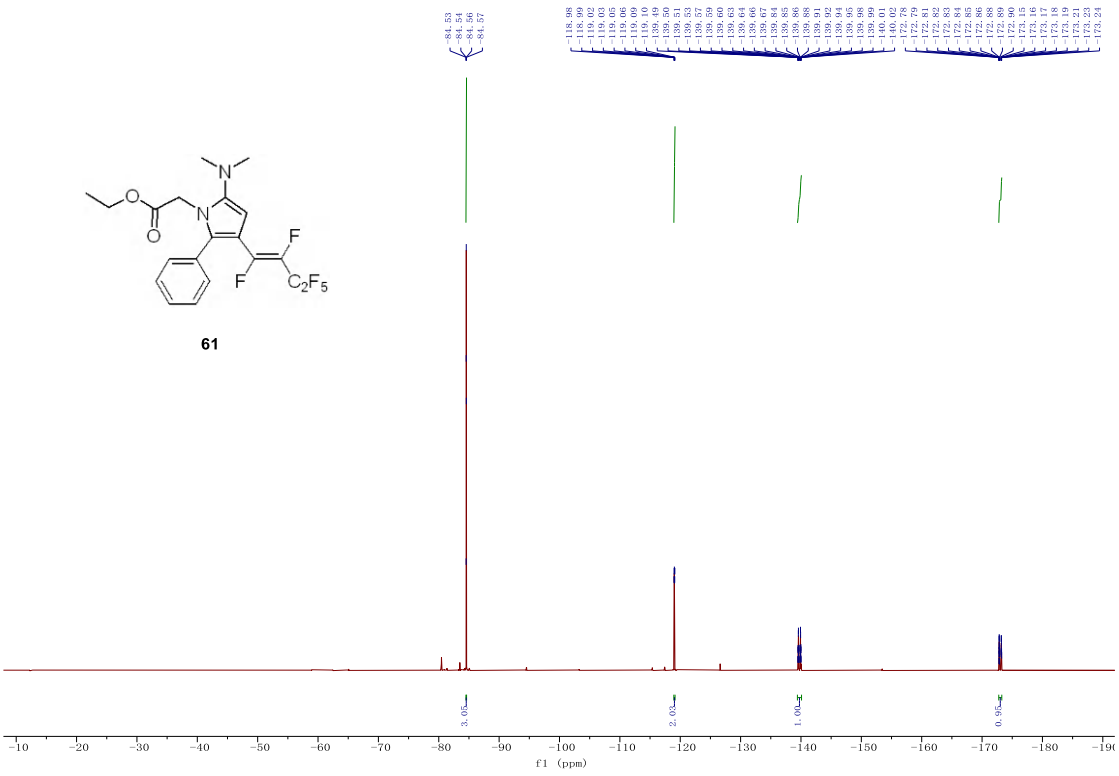
^{13}C NMR spectra of the product **60** (101 MHz, $CDCl_3$):



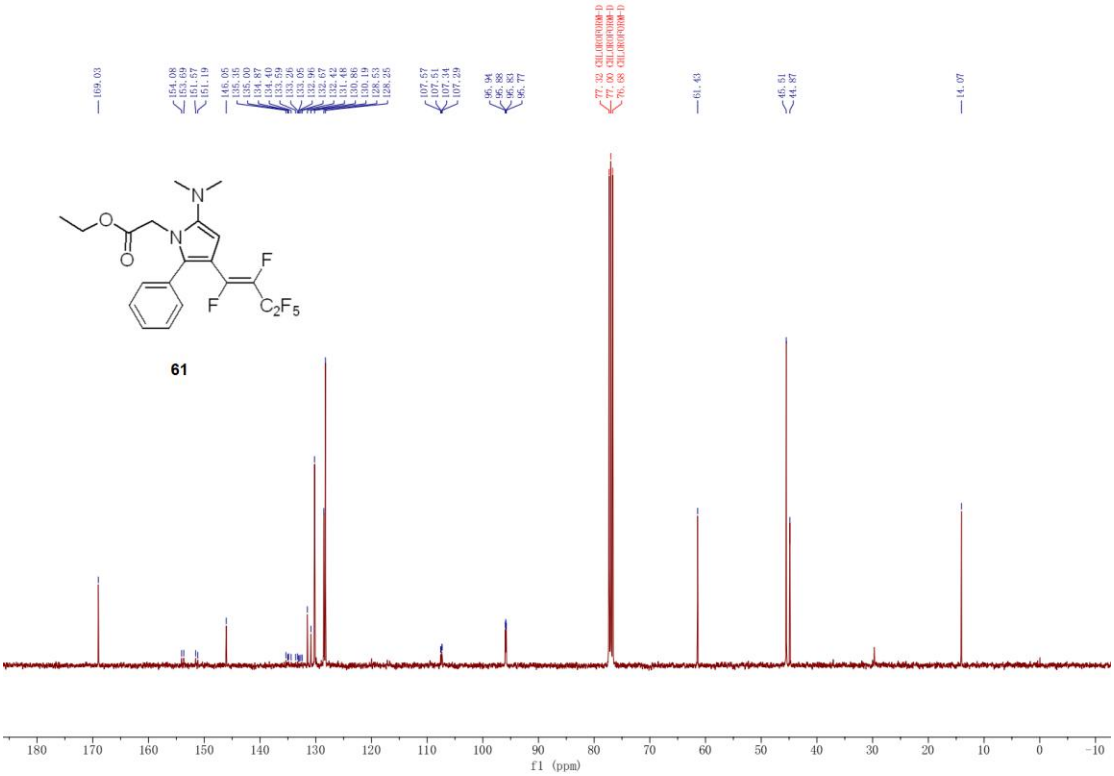
^{1}H NMR spectra of the product **61** (400 MHz, $CDCl_3$):



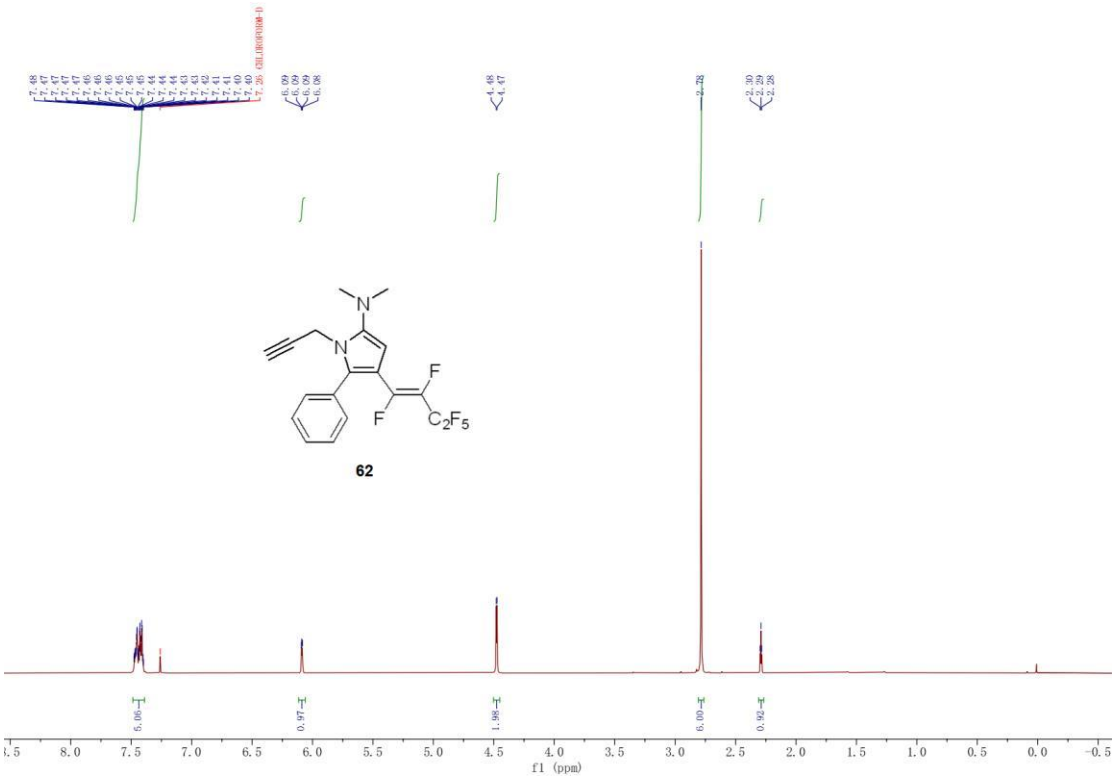
^{19}F NMR spectra of the product **61** (376 MHz, $CDCl_3$):



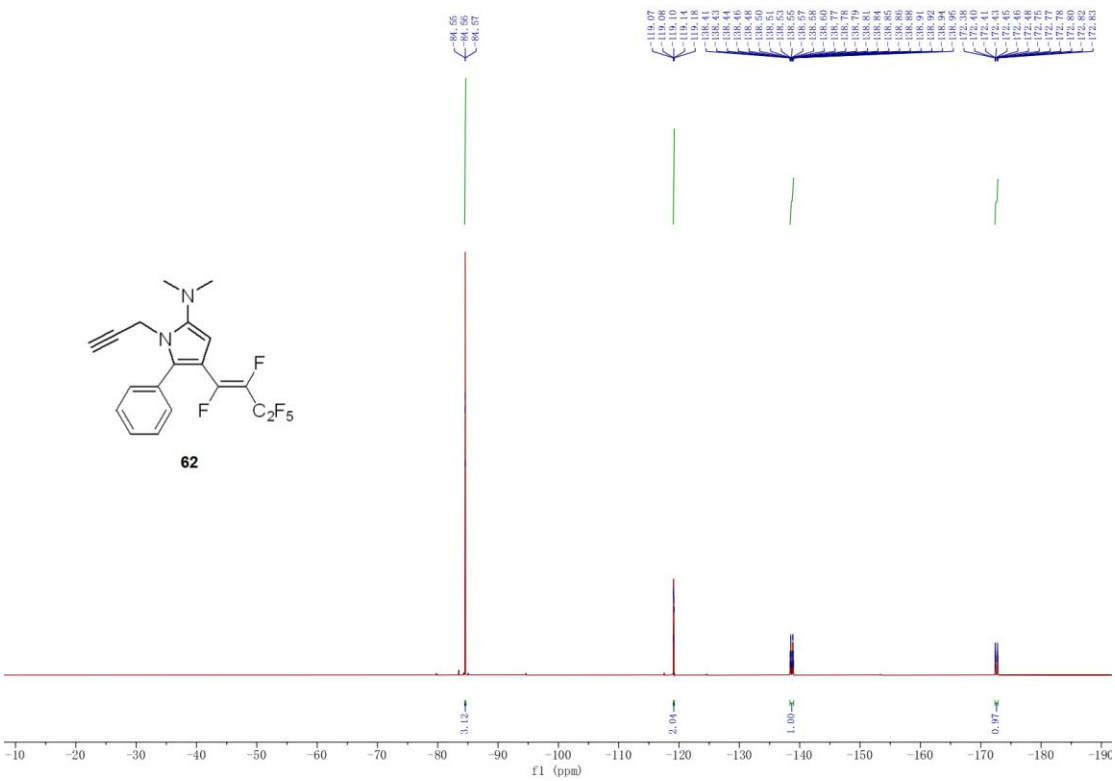
^{13}C NMR spectra of the product **61** (101 MHz, $CDCl_3$):



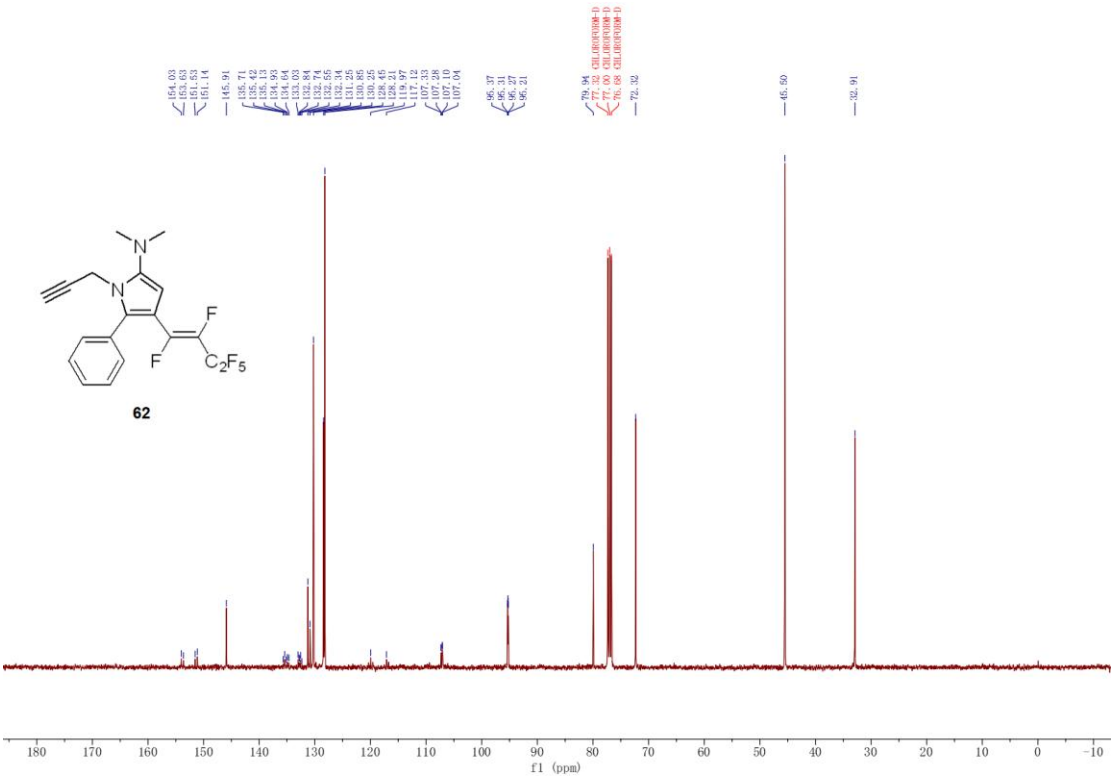
^{1}H NMR spectra of the product **62** (400 MHz, $CDCl_3$):



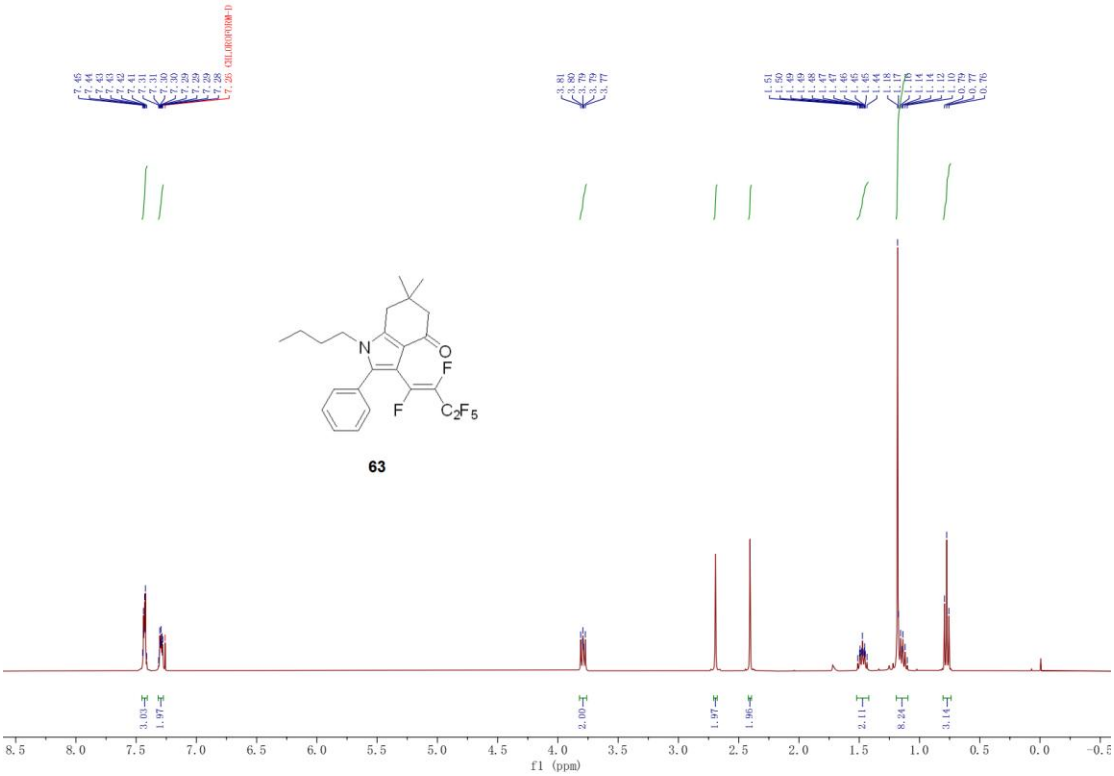
^{19}F NMR spectra of the product **62** (376 MHz, $CDCl_3$):



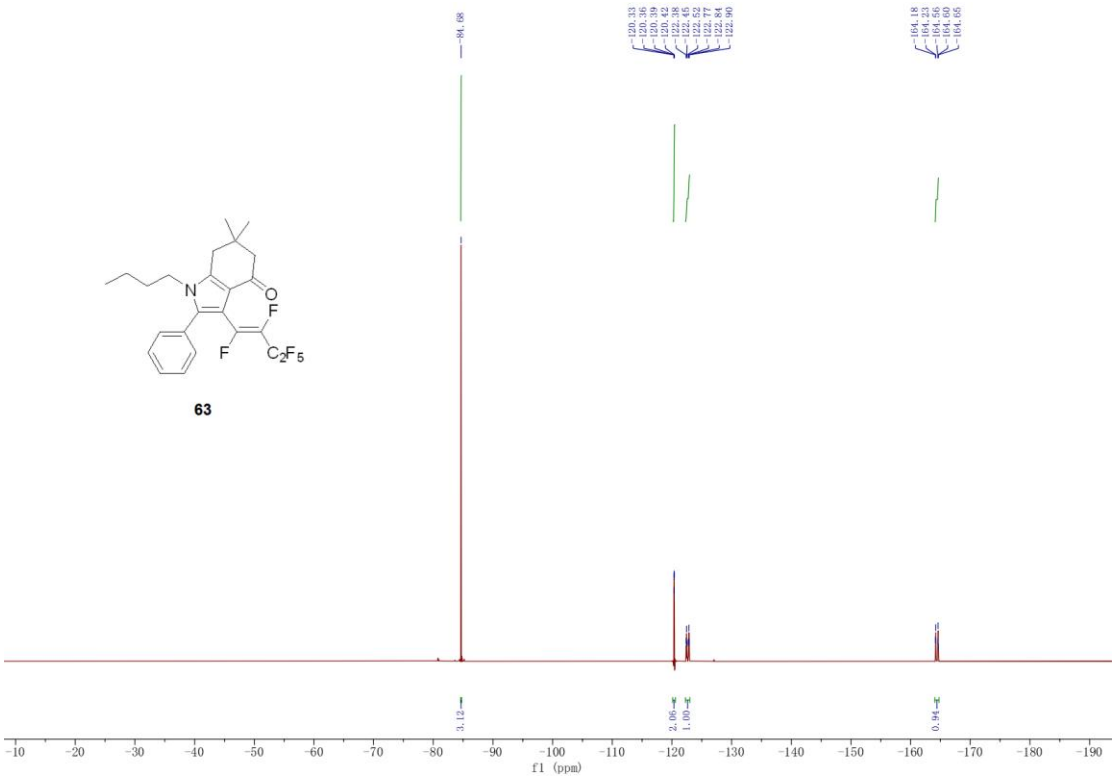
^{13}C NMR spectra of the product **62** (101 MHz, $CDCl_3$):



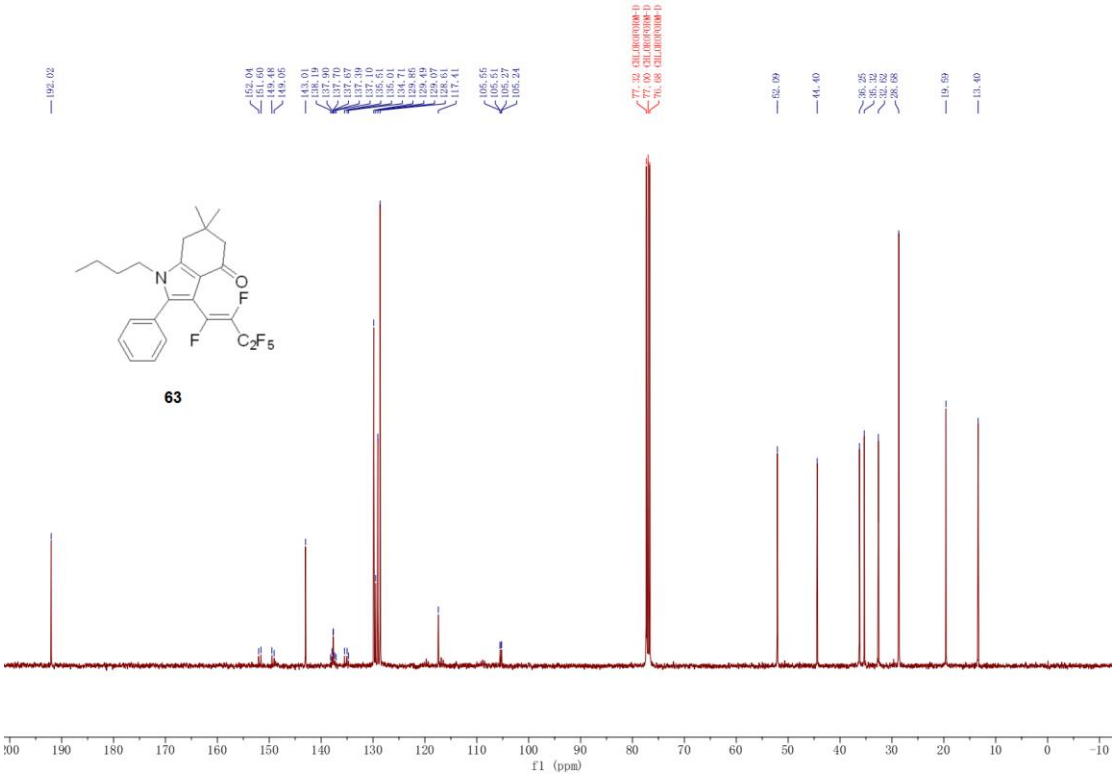
^{1}H NMR spectra of the product **63** (400 MHz, $CDCl_3$):



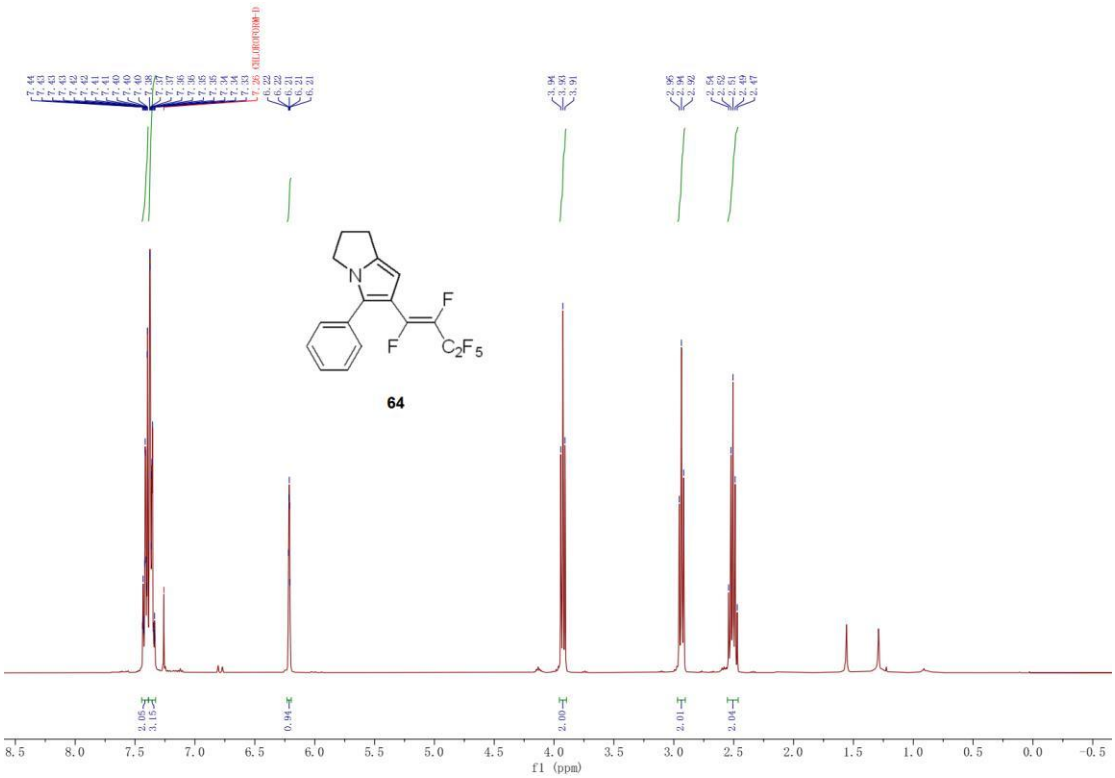
^{19}F NMR spectra of the product **63** (376 MHz, $CDCl_3$):



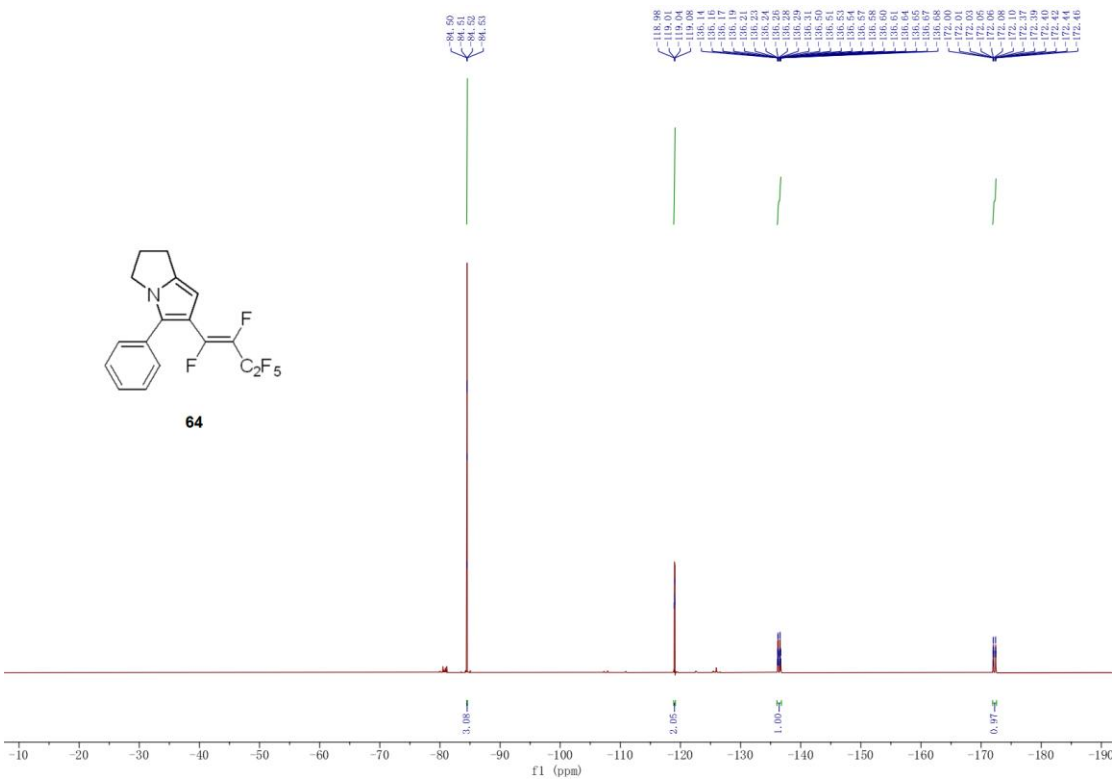
^{13}C NMR spectra of the product **63** (101 MHz, $CDCl_3$):



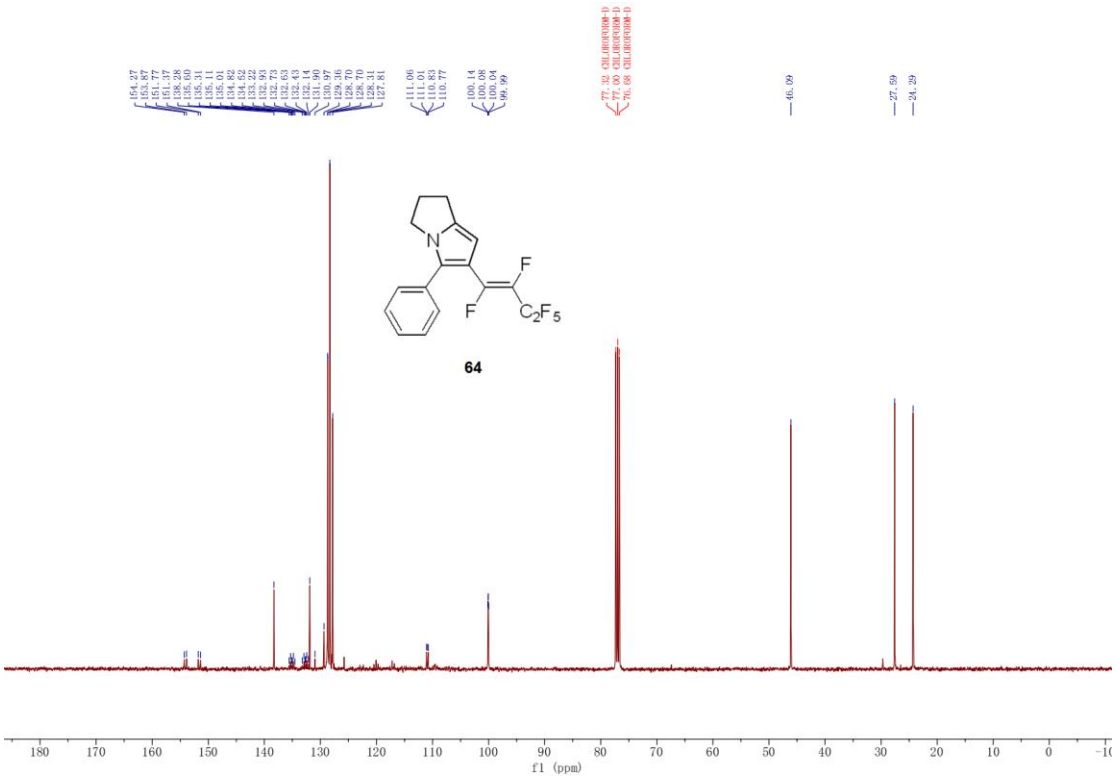
^{1}H NMR spectra of the product **64** (400 MHz, $CDCl_3$):



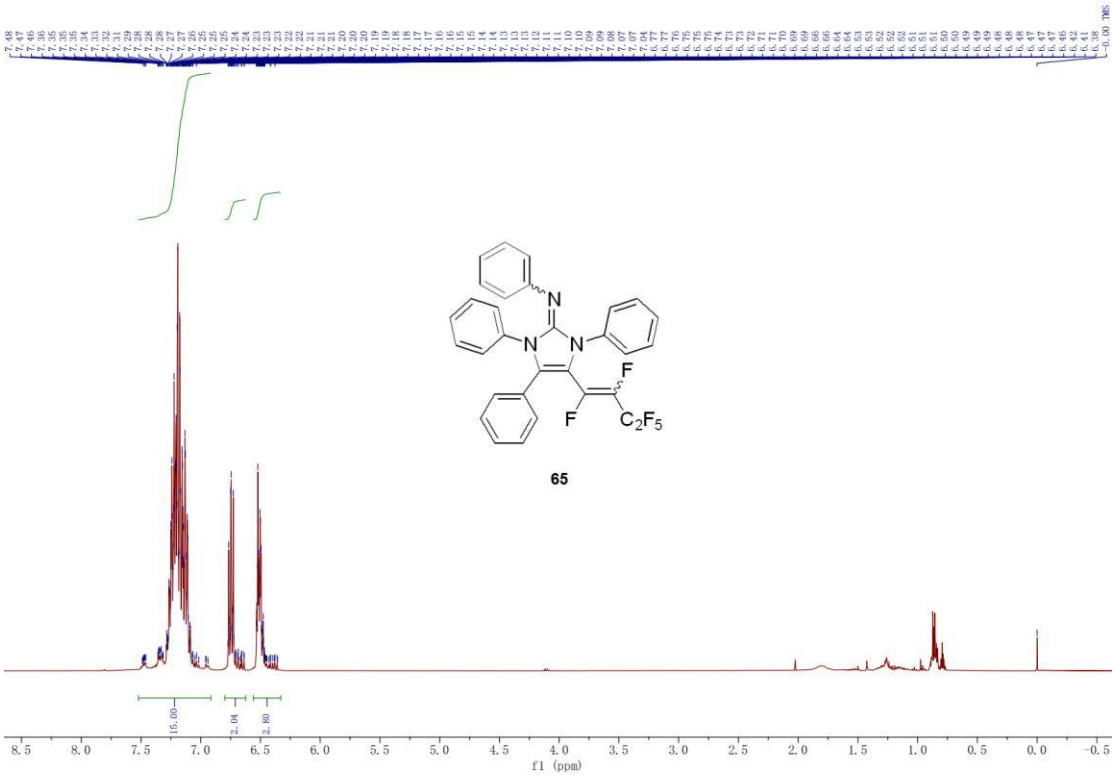
^{19}F NMR spectra of the product **64** (376 MHz, $CDCl_3$):



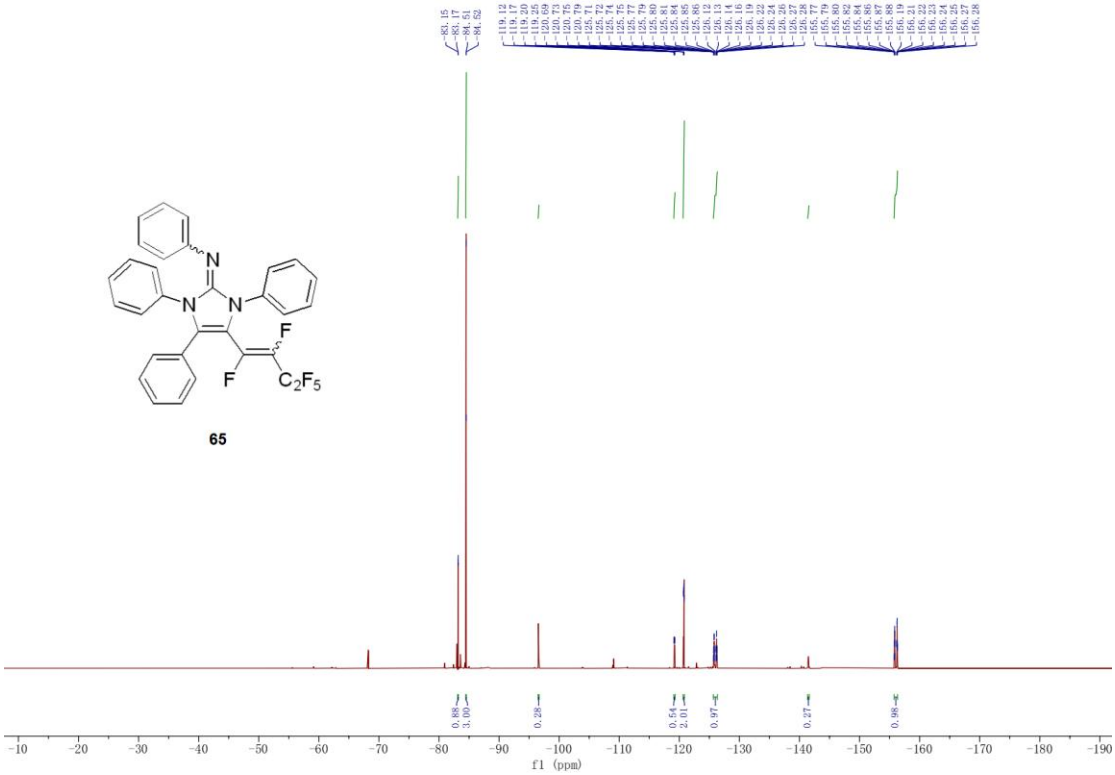
^{13}C NMR spectra of the product **64** (101 MHz, $CDCl_3$):



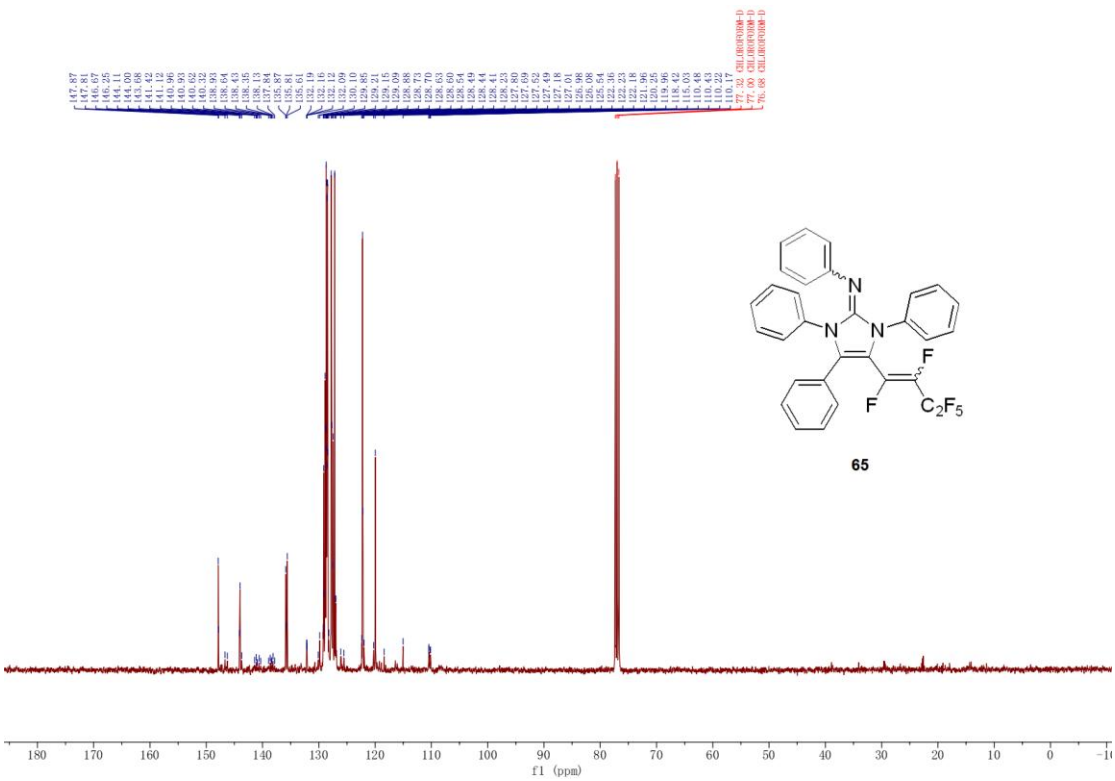
^{1}H NMR spectra of the product **65** (400 MHz, $CDCl_3$):



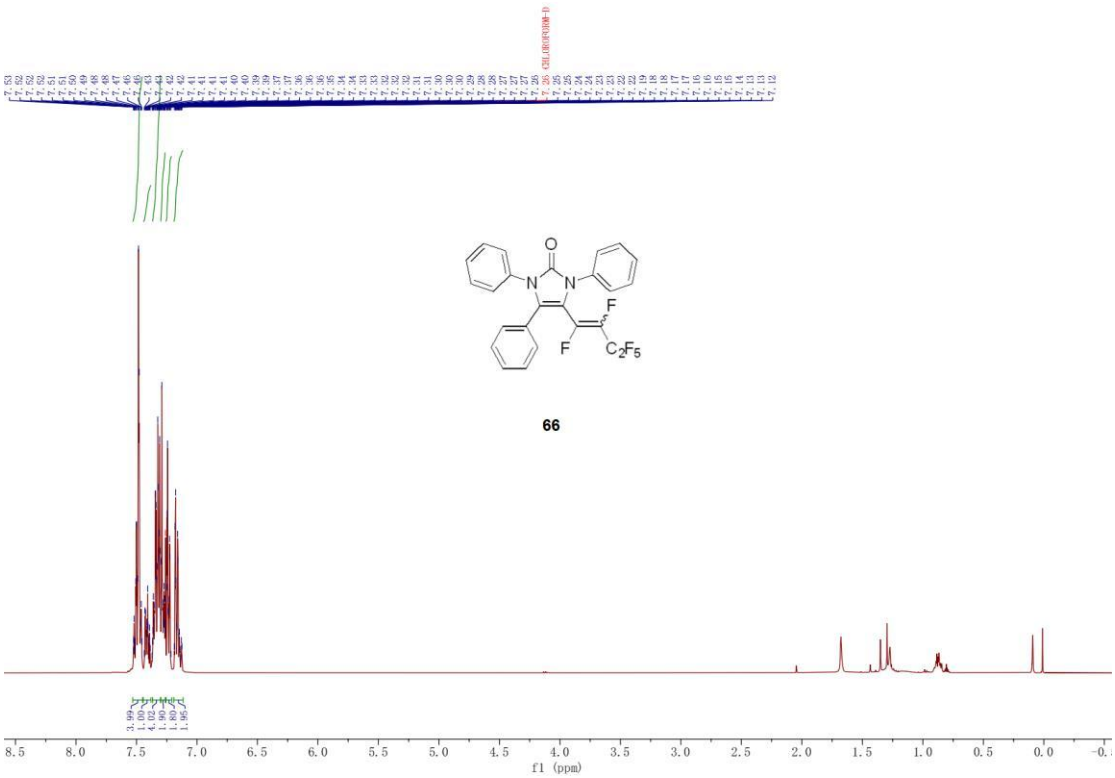
^{19}F NMR spectra of the product **65** (376 MHz, $CDCl_3$):



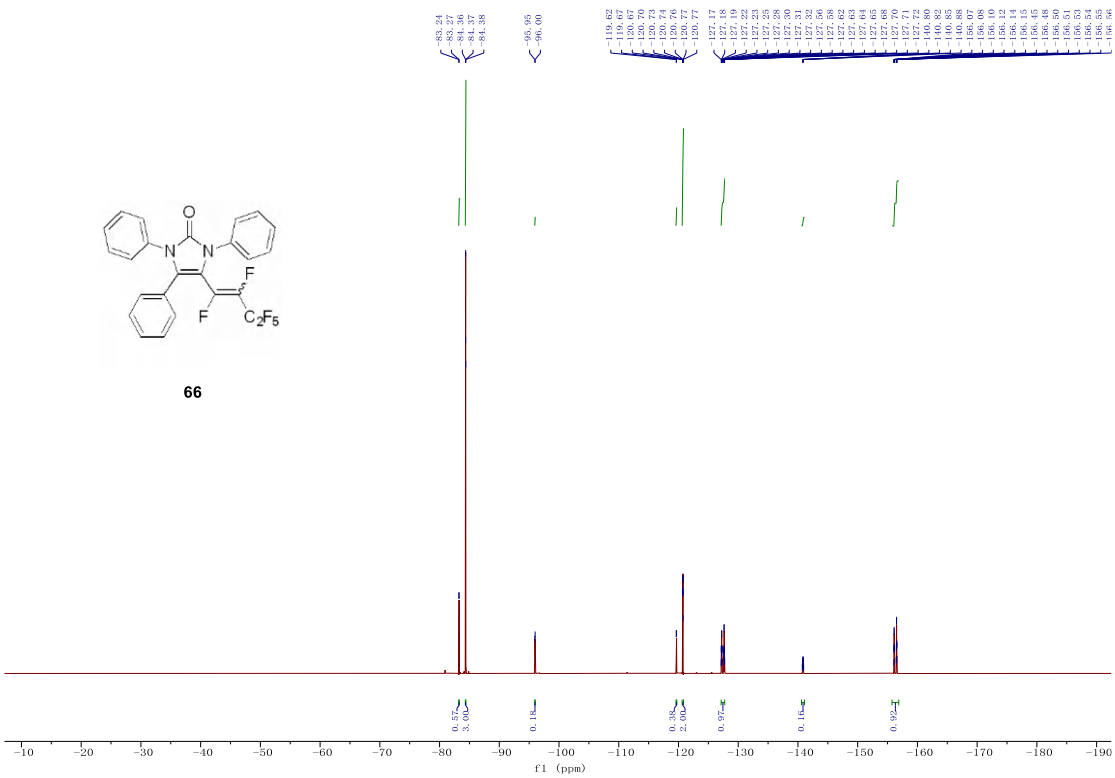
^{13}C NMR spectra of the product **65** (101 MHz, $CDCl_3$):



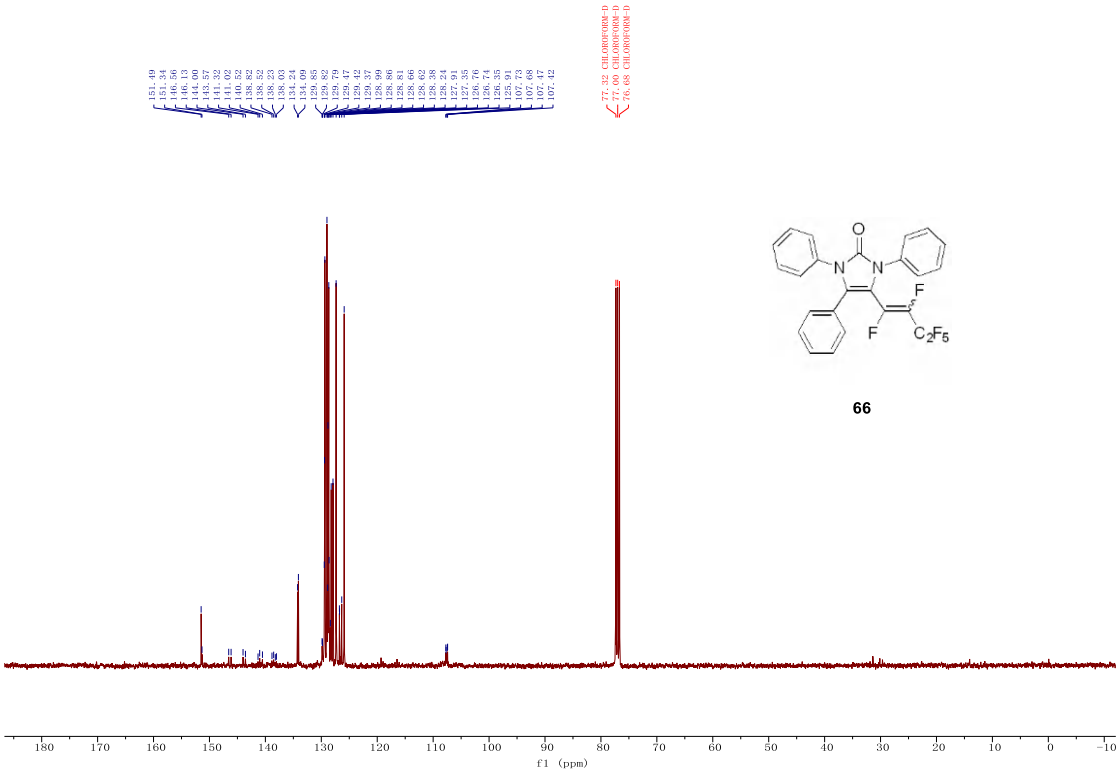
^{1}H NMR spectra of the product **66** (400 MHz, $CDCl_3$):



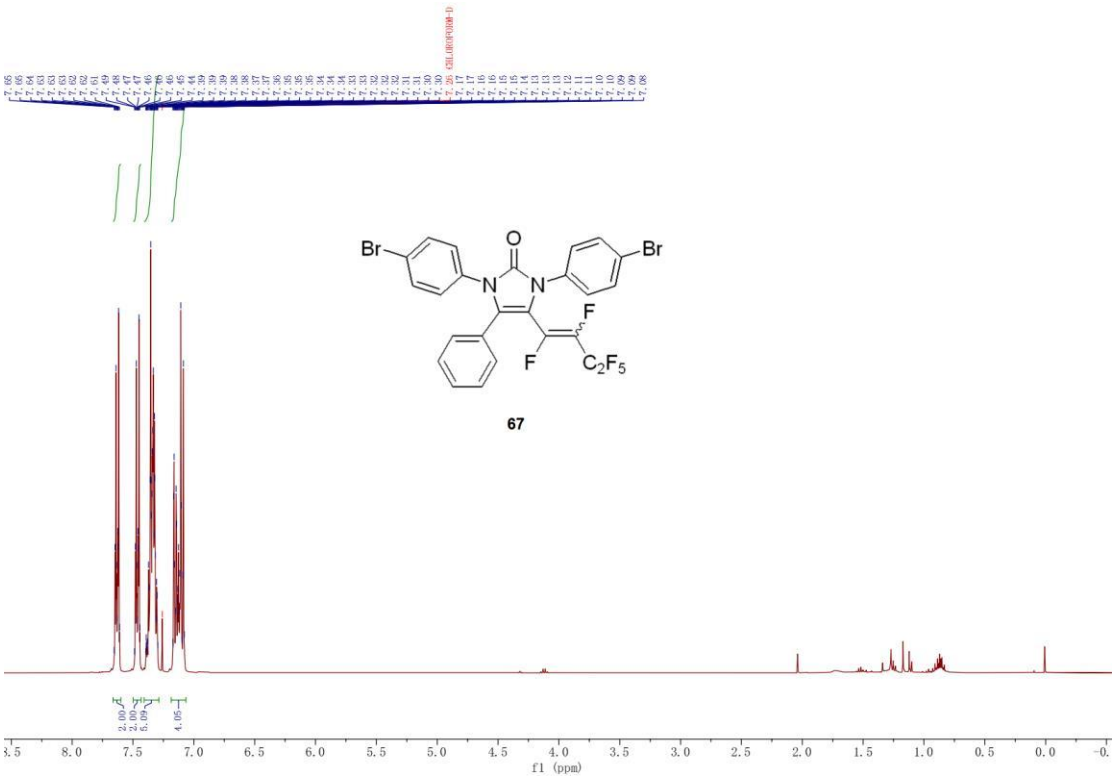
^{19}F NMR spectra of the product **66** (376 MHz, $CDCl_3$):



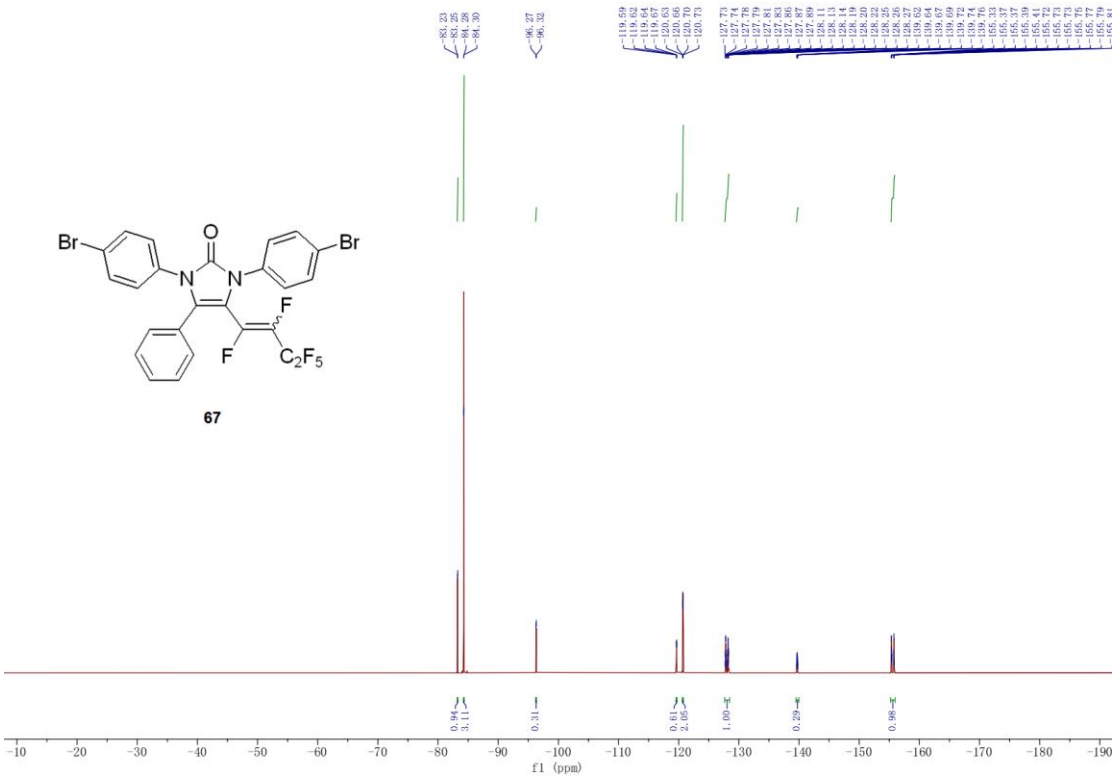
^{13}C NMR spectra of the product **66** (101 MHz, $CDCl_3$):



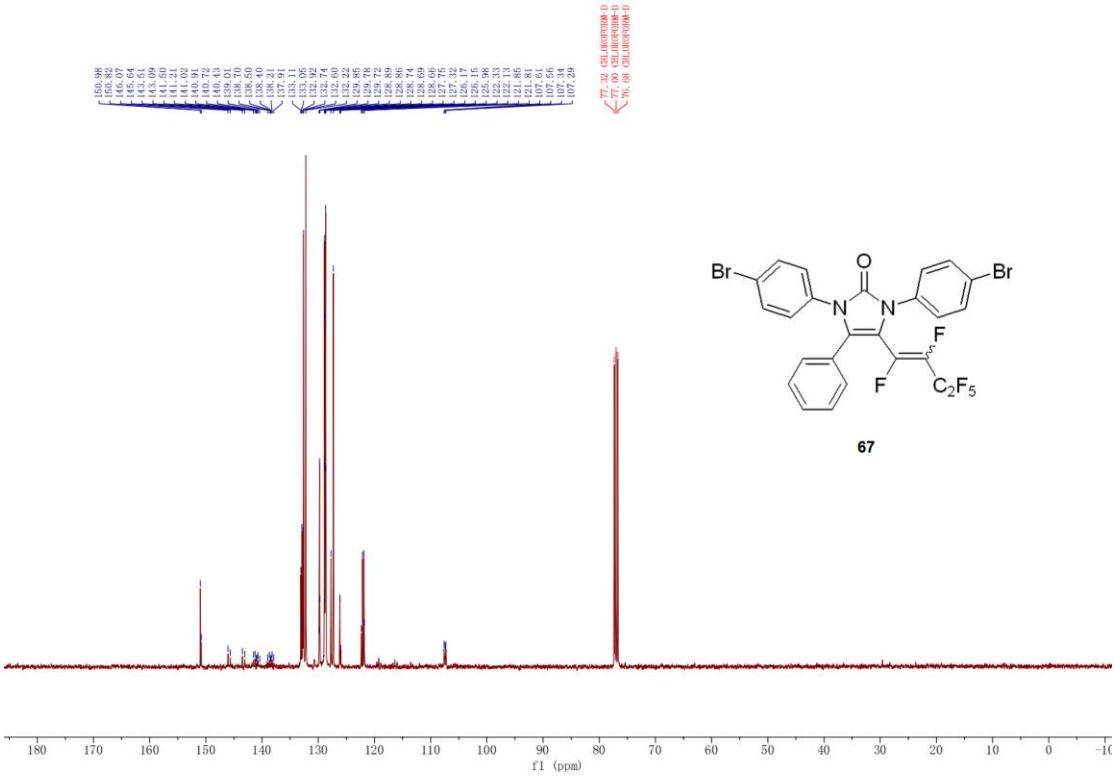
^{1}H NMR spectra of the product **67** (400 MHz, $CDCl_3$):



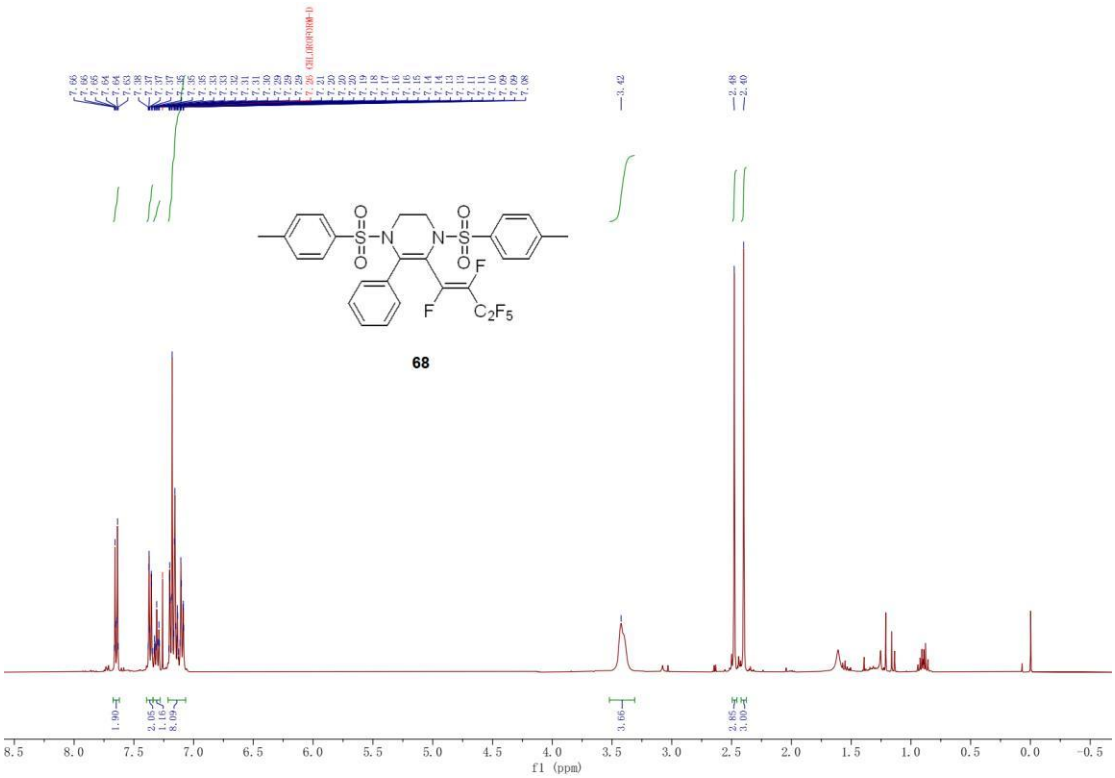
^{19}F NMR spectra of the product **67** (376 MHz, $CDCl_3$):



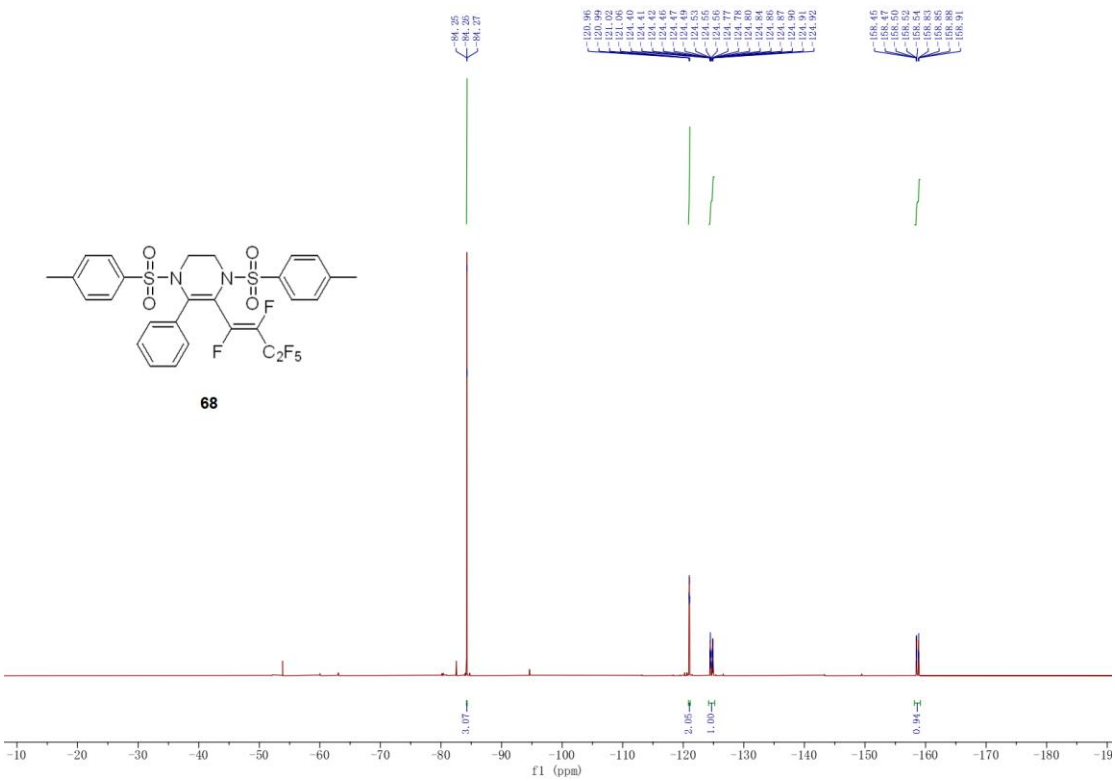
^{13}C NMR spectra of the product **67** (101 MHz, $CDCl_3$):



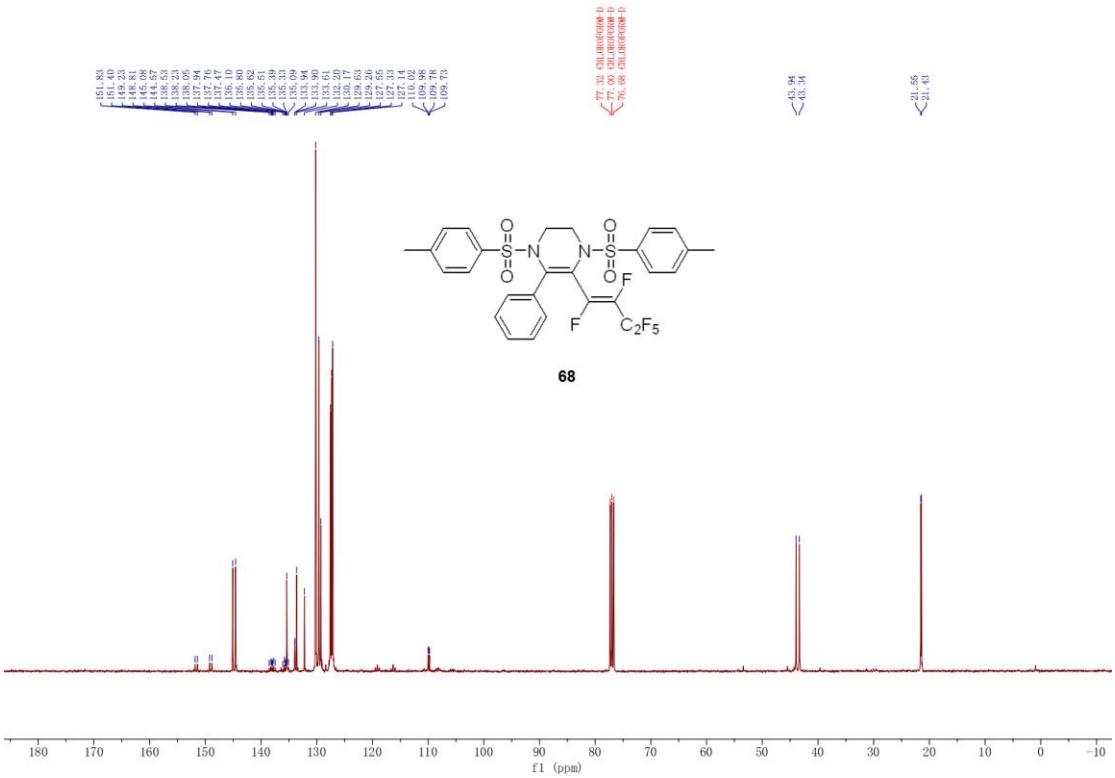
^{1}H NMR spectra of the product **68** (400 MHz, $CDCl_3$):



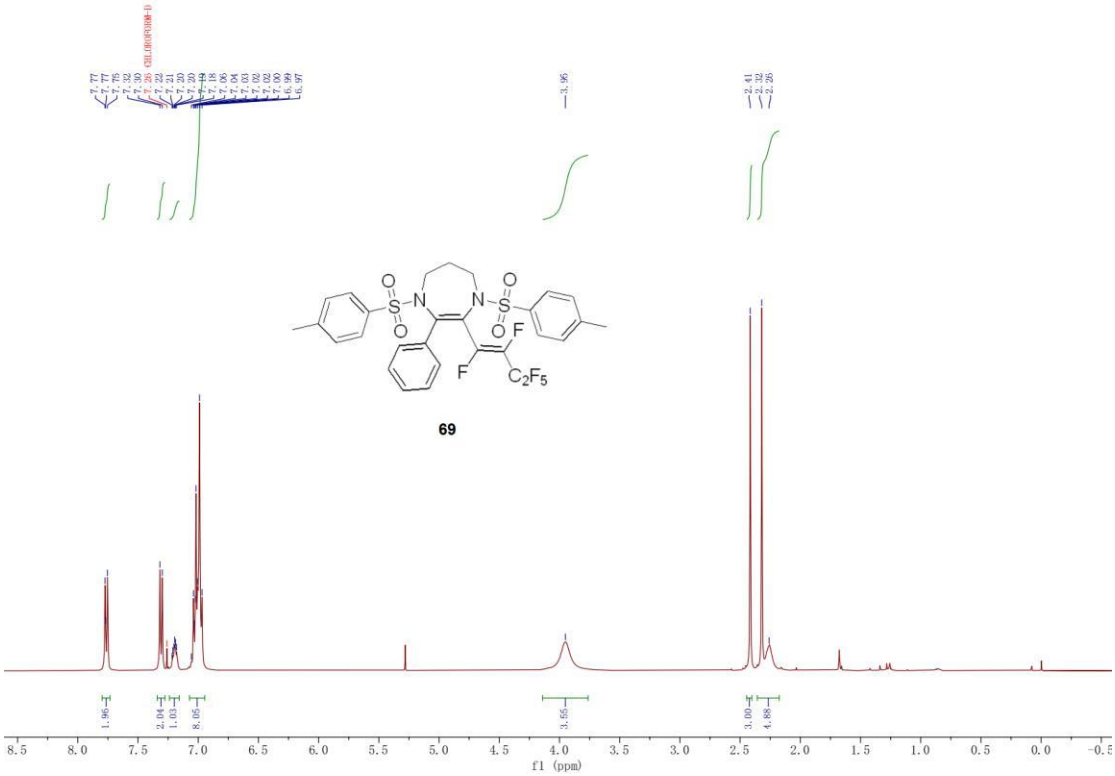
^{19}F NMR spectra of the product **68** (376 MHz, $CDCl_3$):



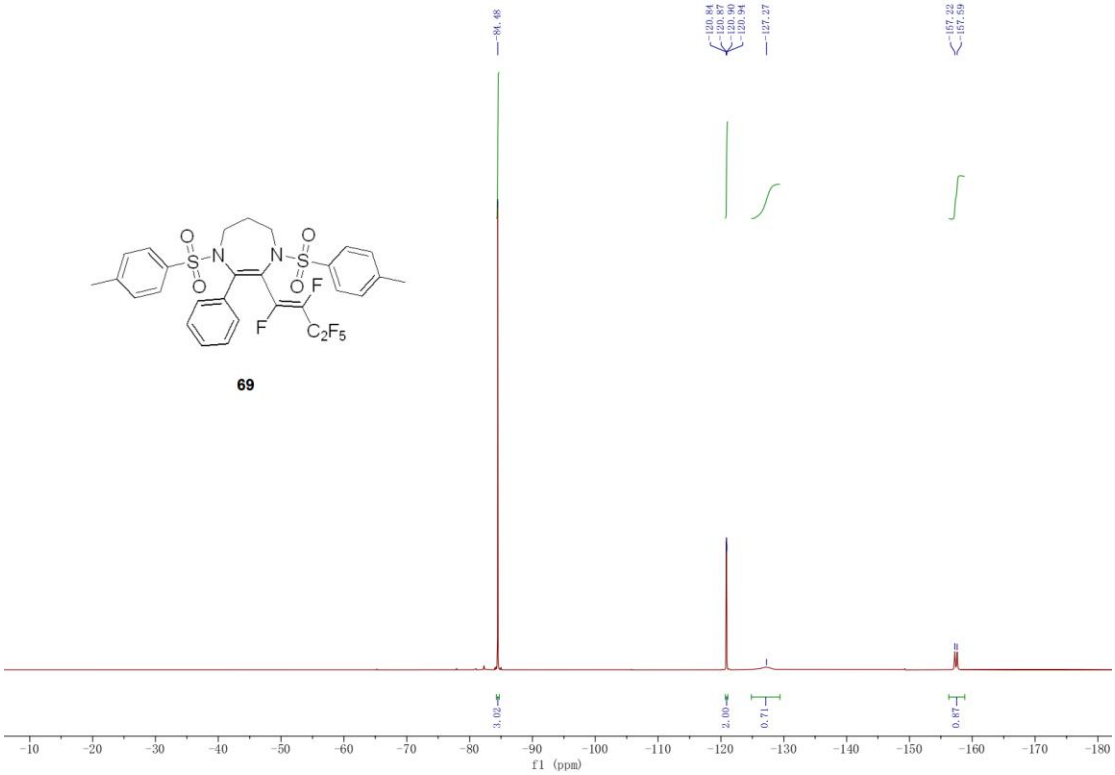
^{13}C NMR spectra of the product **68** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **69** (400 MHz, $CDCl_3$):

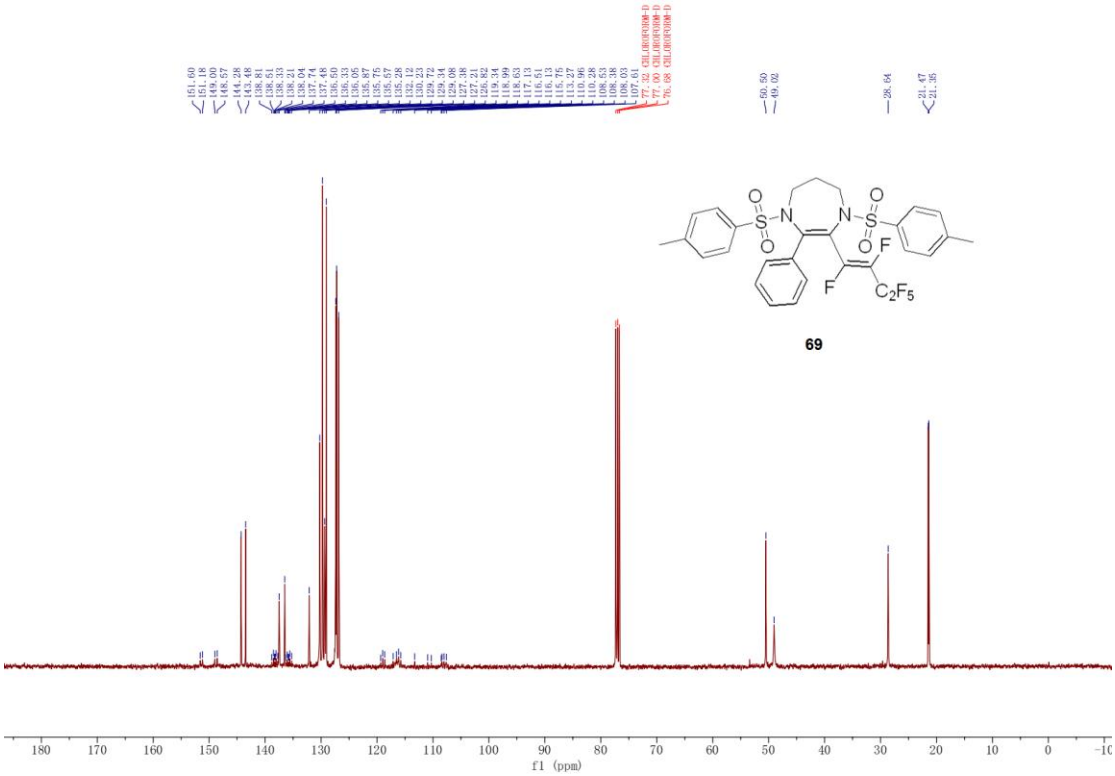


^{19}F NMR spectra of the product **69** (376 MHz, $CDCl_3$):



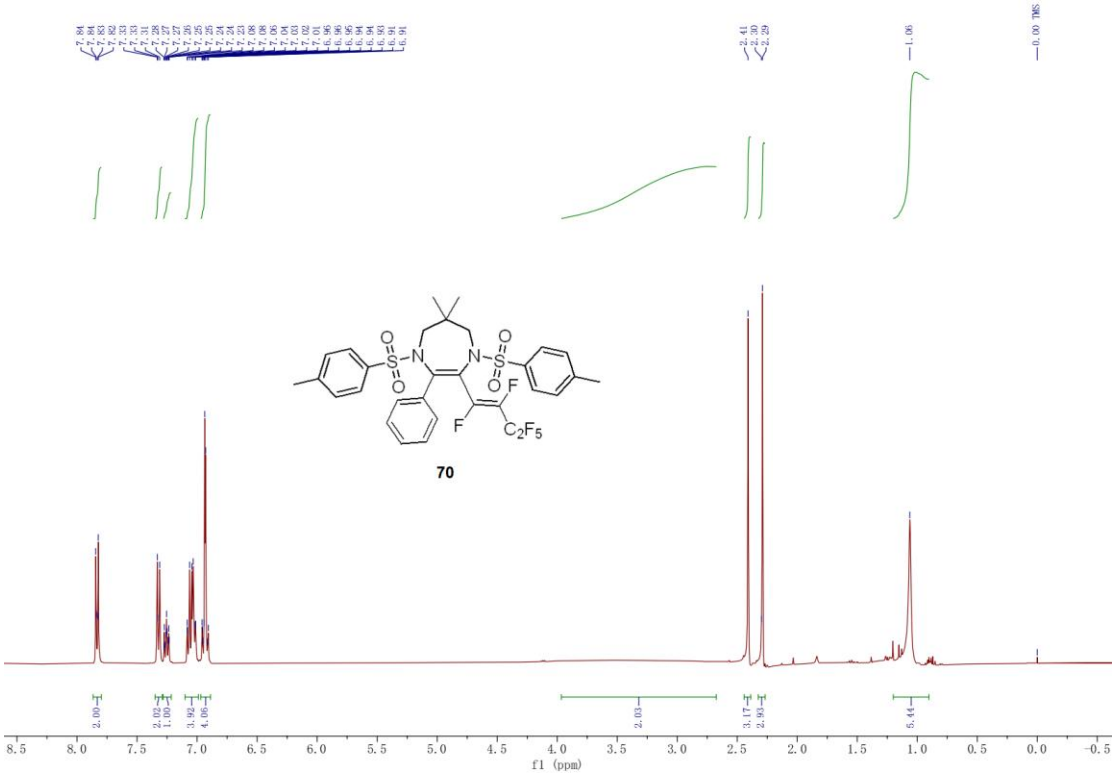
69

^{13}C NMR spectra of the product **69** (101 MHz, $CDCl_3$):

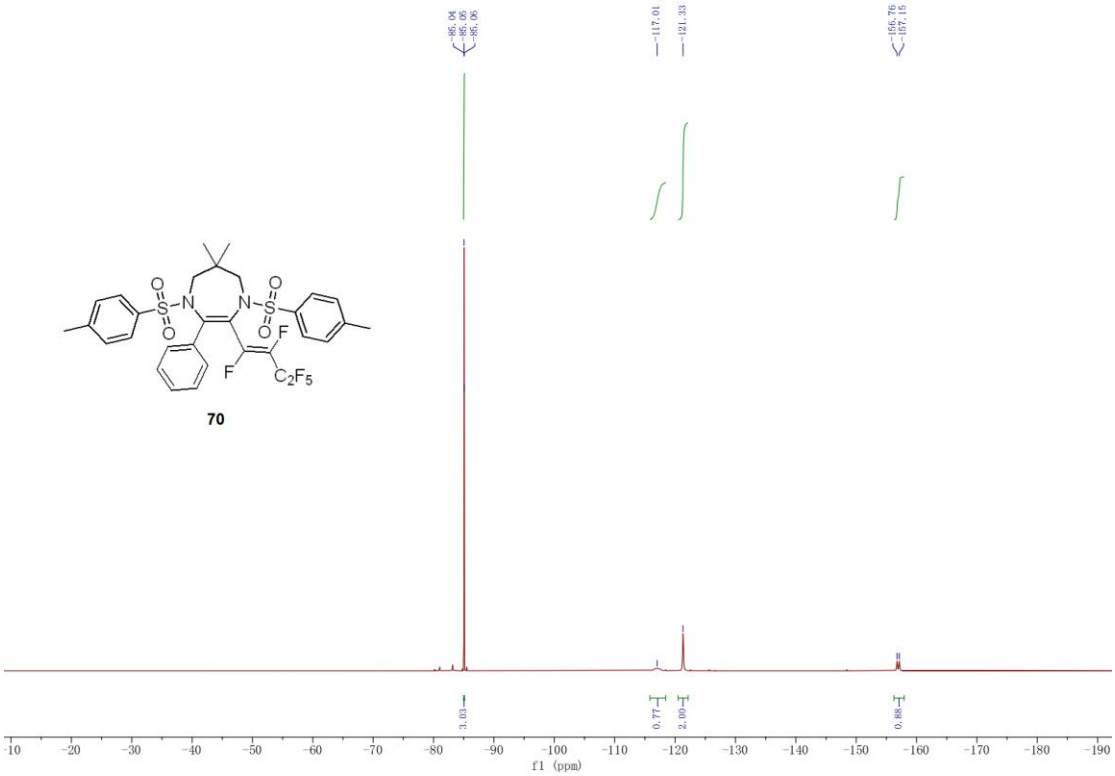


69

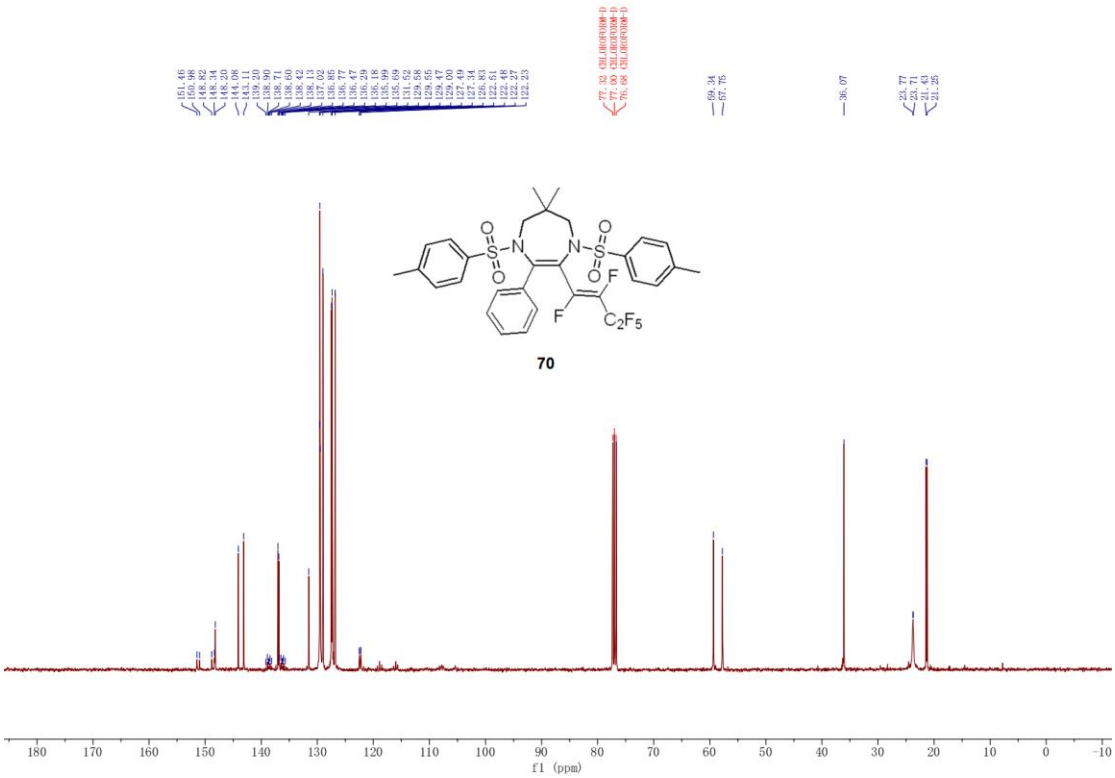
^{1}H NMR spectra of the product **70** (400 MHz, $CDCl_3$):



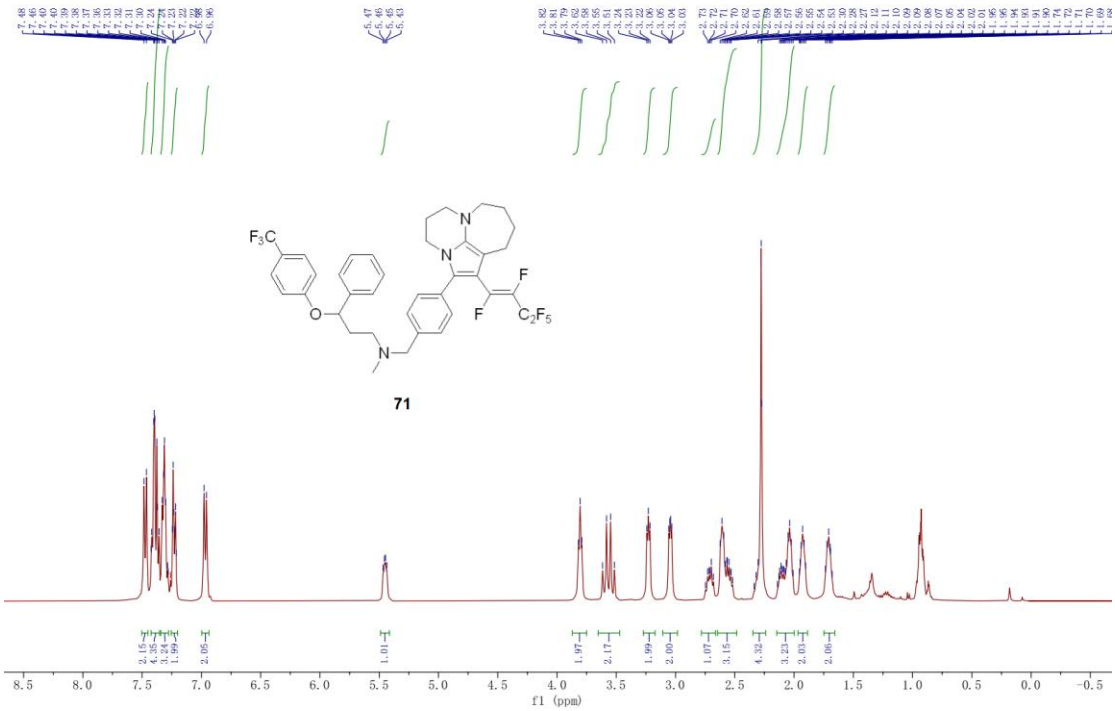
^{19}F NMR spectra of the product **70** (376 MHz, $CDCl_3$):



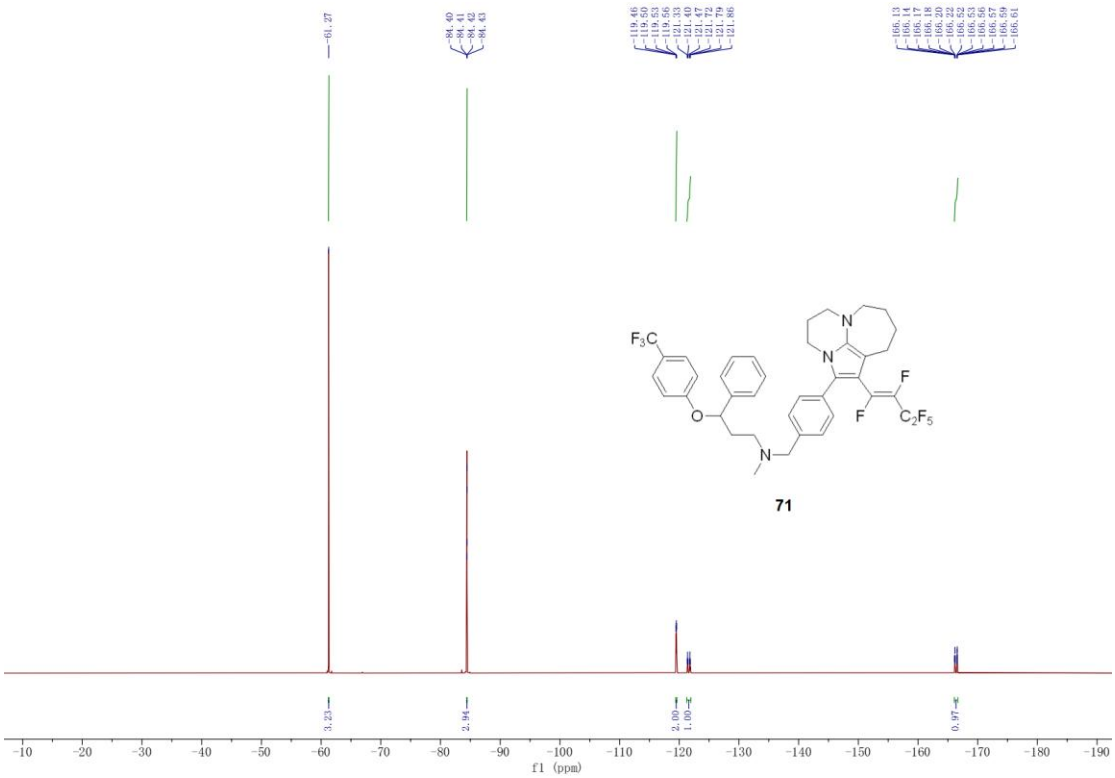
^{13}C NMR spectra of the product **70** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **71** (400 MHz, $CDCl_3$):

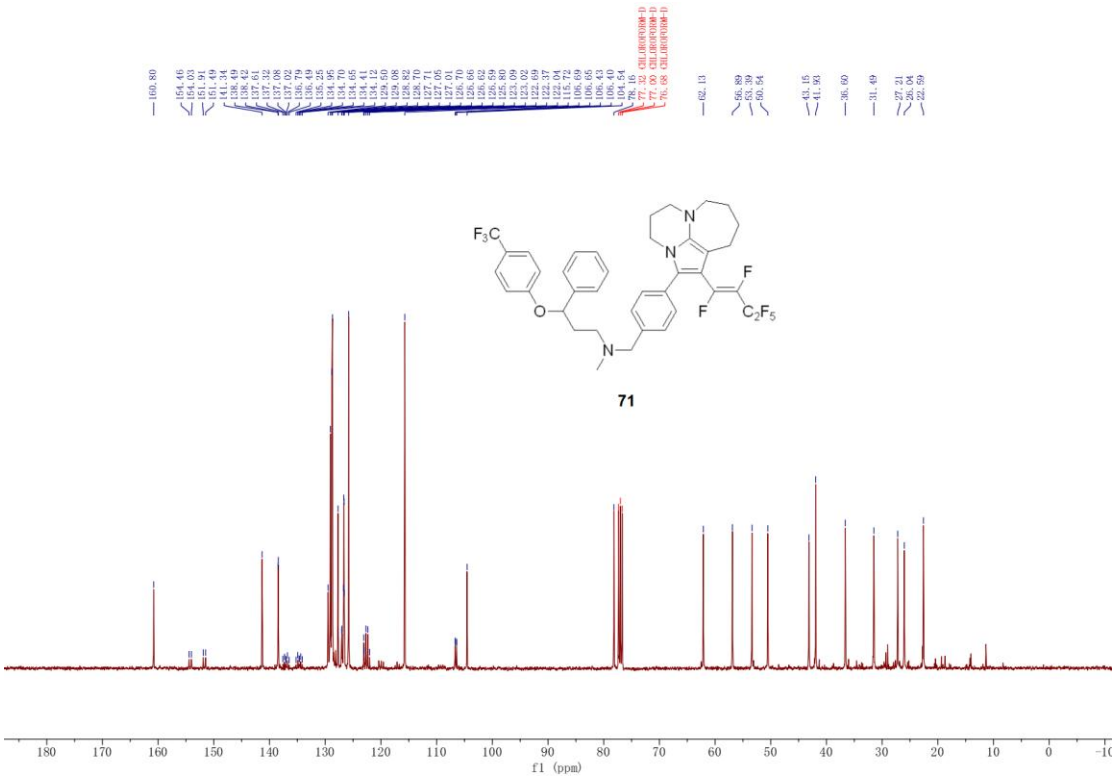


^{19}F NMR spectra of the product **71** (376 MHz, $CDCl_3$):



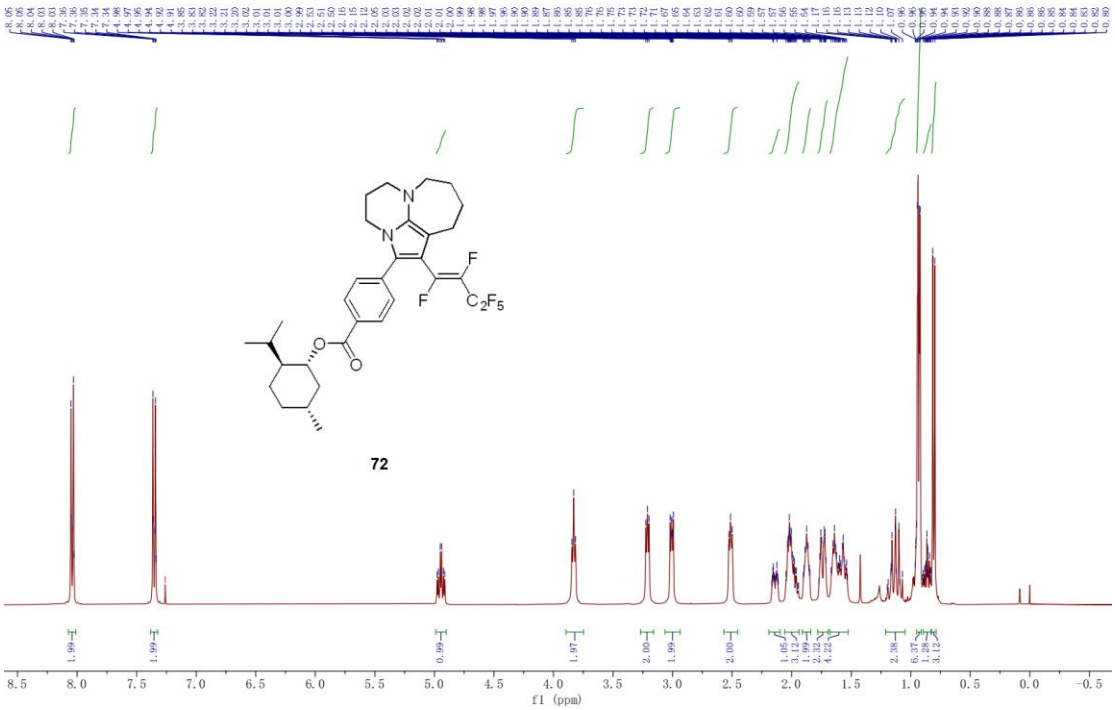
71

^{13}C NMR spectra of the product **71** (101 MHz, $CDCl_3$):

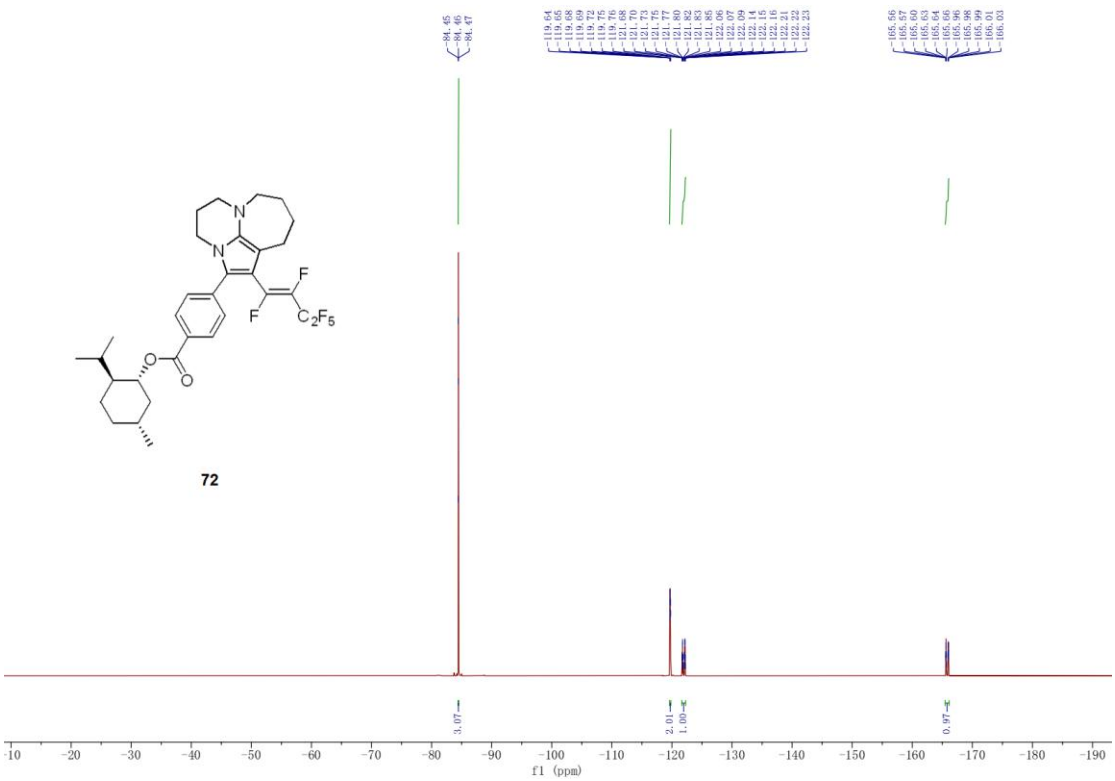


71

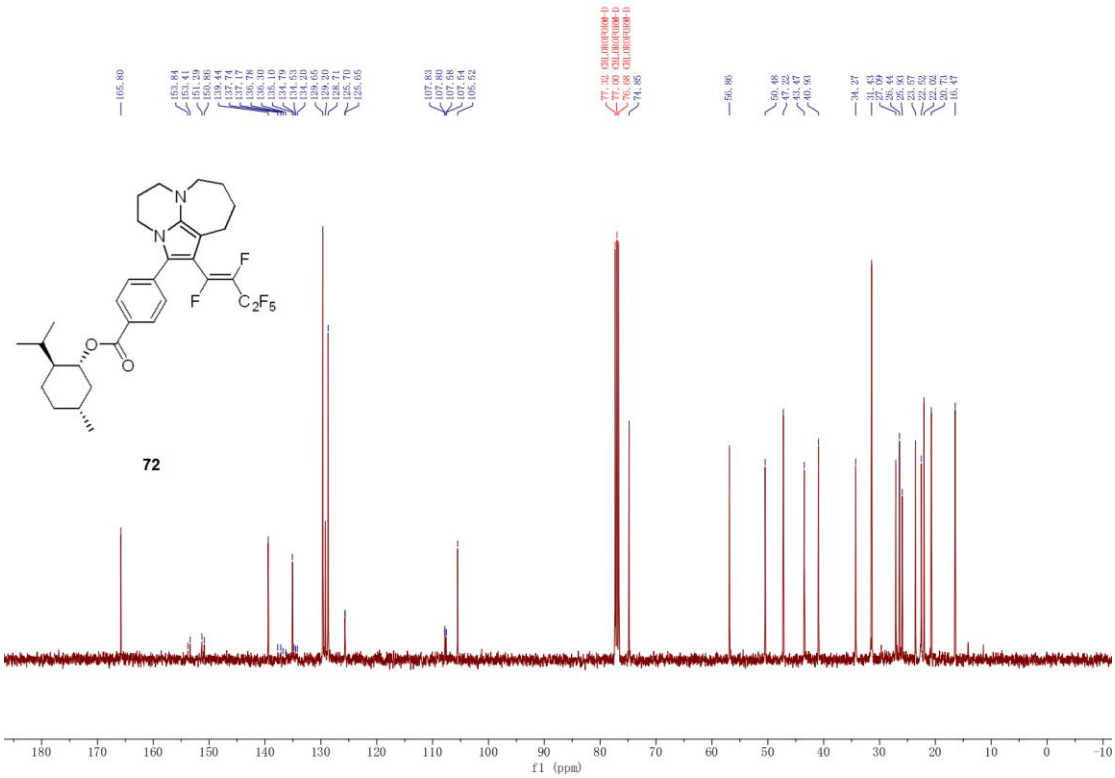
^{1}H NMR spectra of the product **72** (400 MHz, $CDCl_3$):



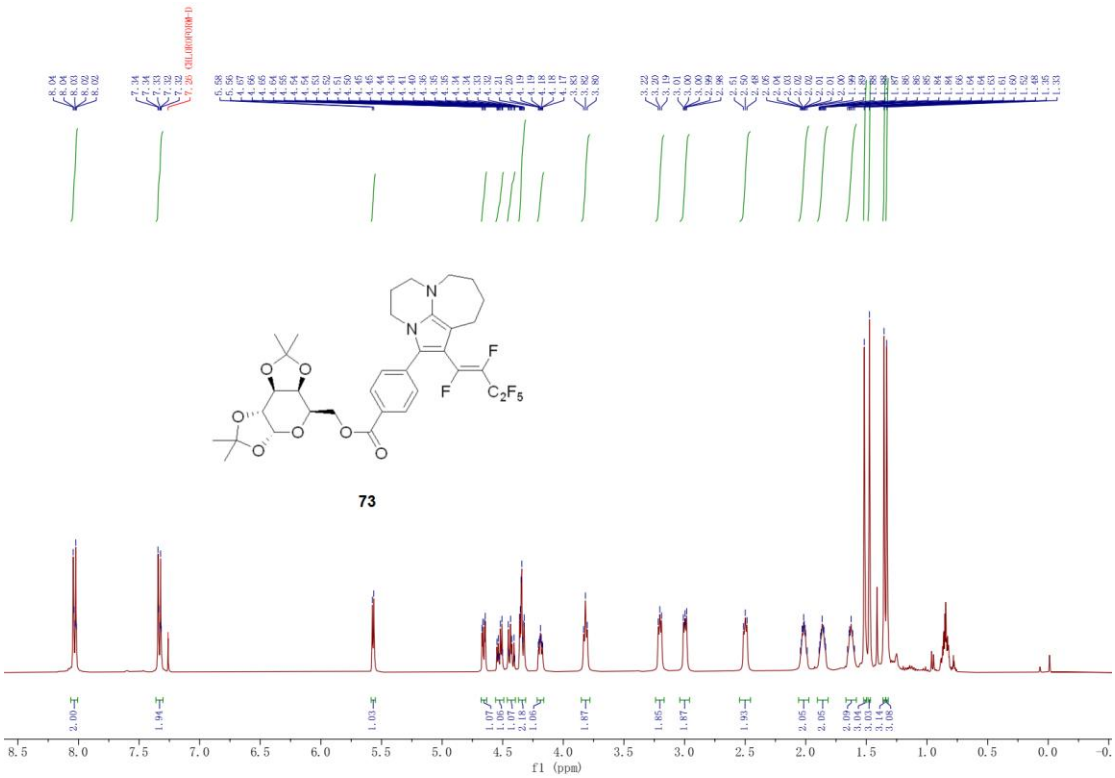
^{19}F NMR spectra of the product **72** (376 MHz, $CDCl_3$):



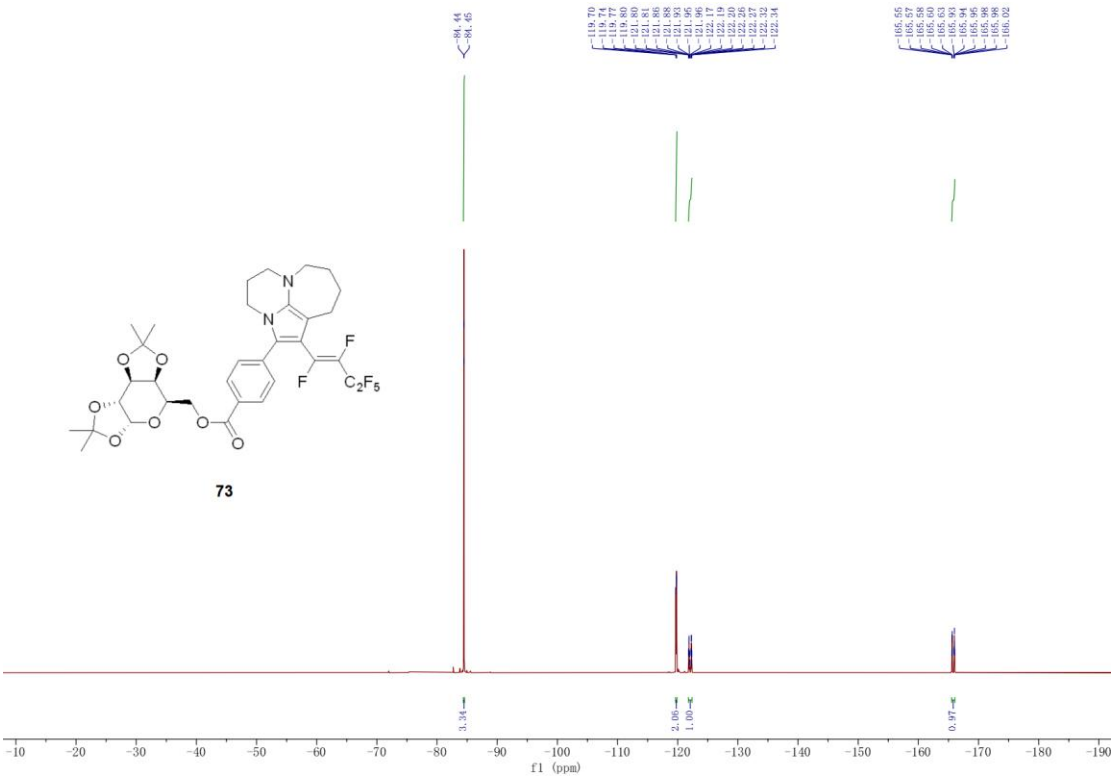
^{13}C NMR spectra of the product **72** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **73** (400 MHz, $CDCl_3$):

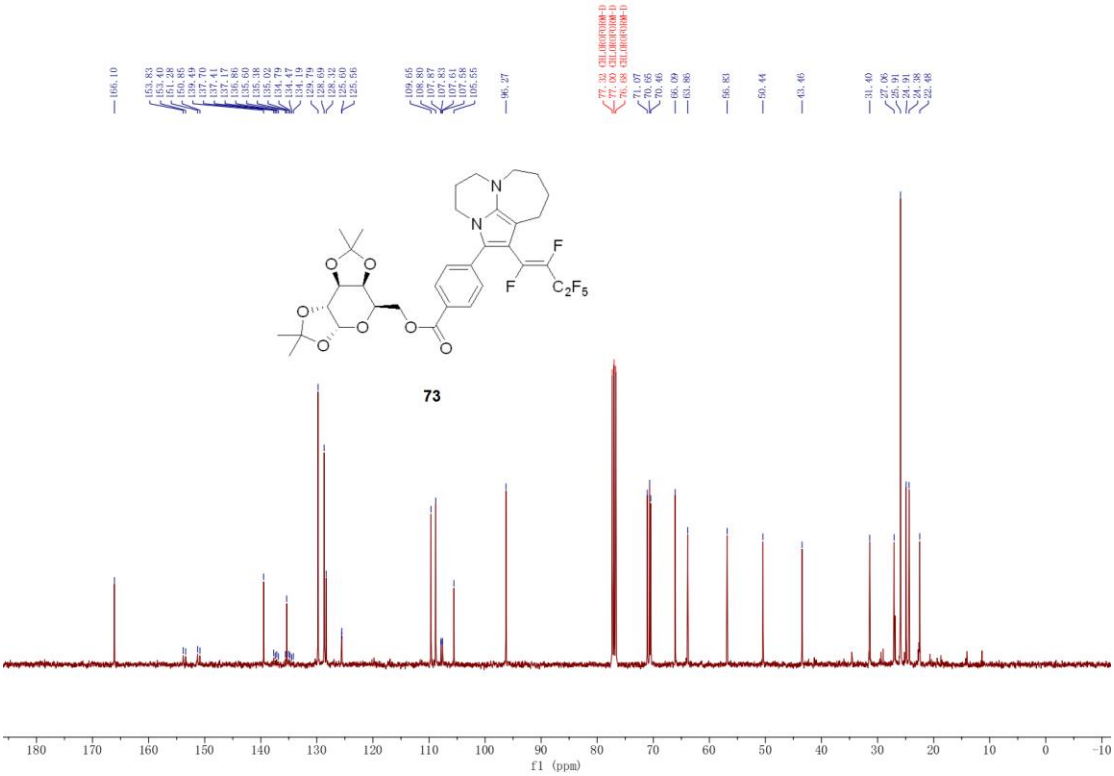


^{19}F NMR spectra of the product **73** (376 MHz, $CDCl_3$):



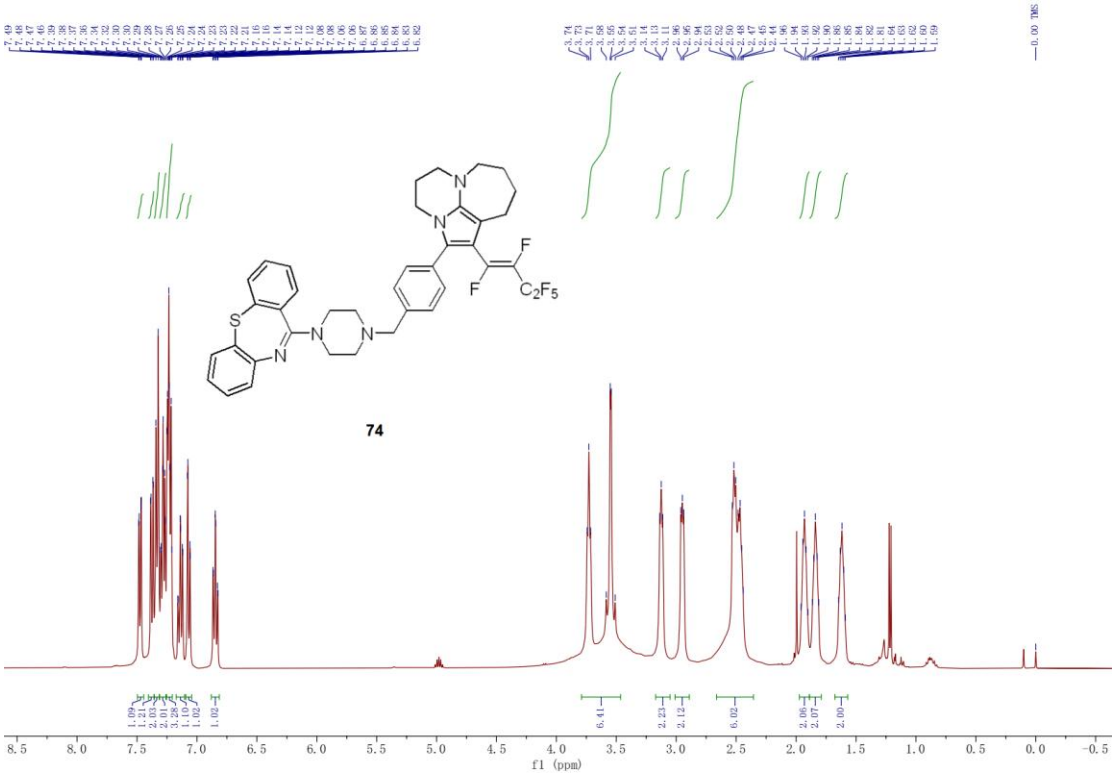
73

^{13}C NMR spectra of the product **73** (101 MHz, $CDCl_3$):

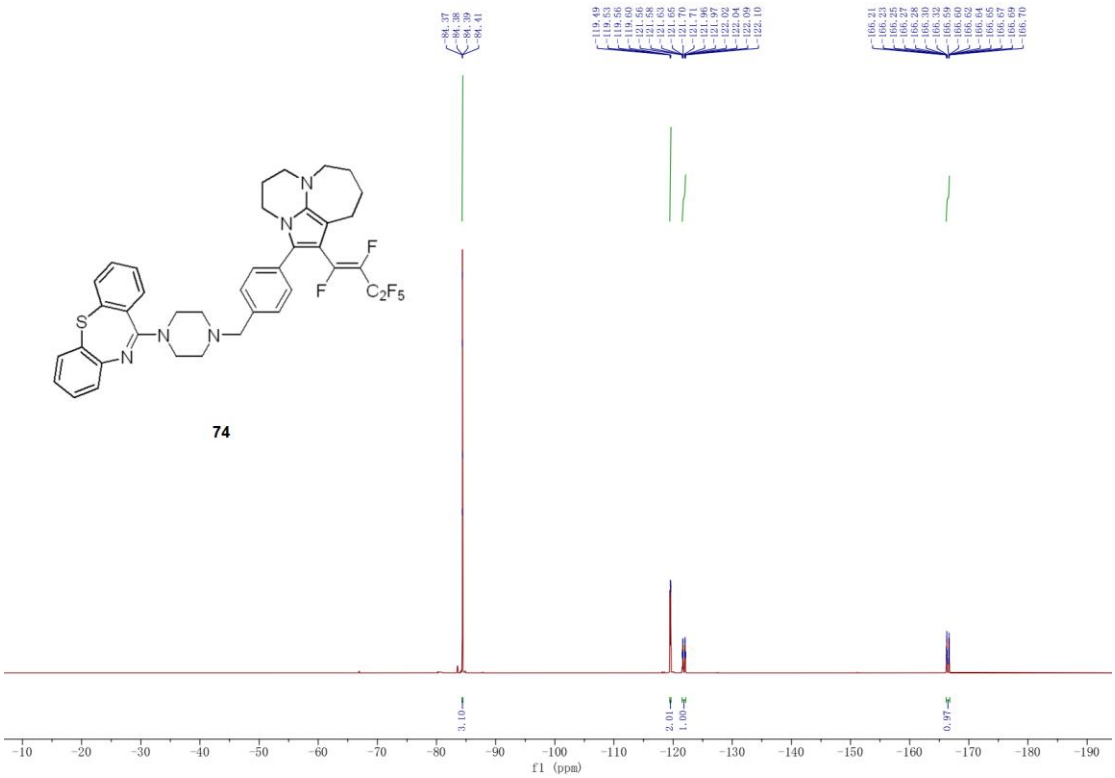


73

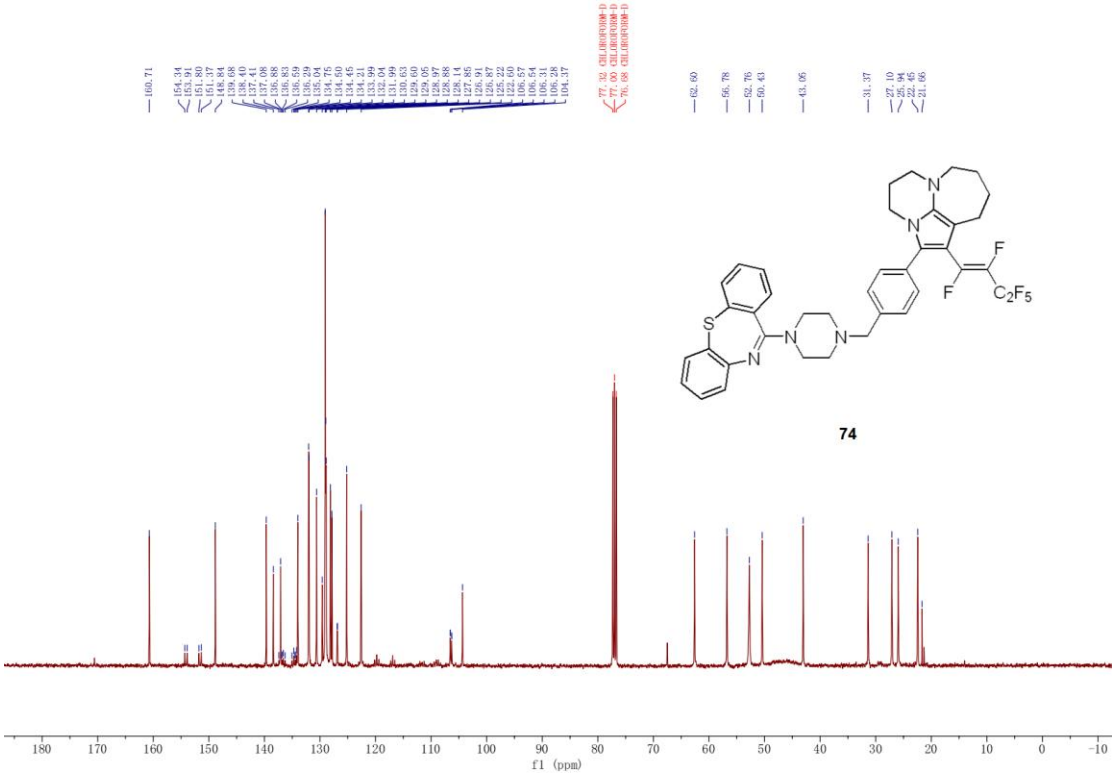
^{1}H NMR spectra of the product **74** (400 MHz, $CDCl_3$):



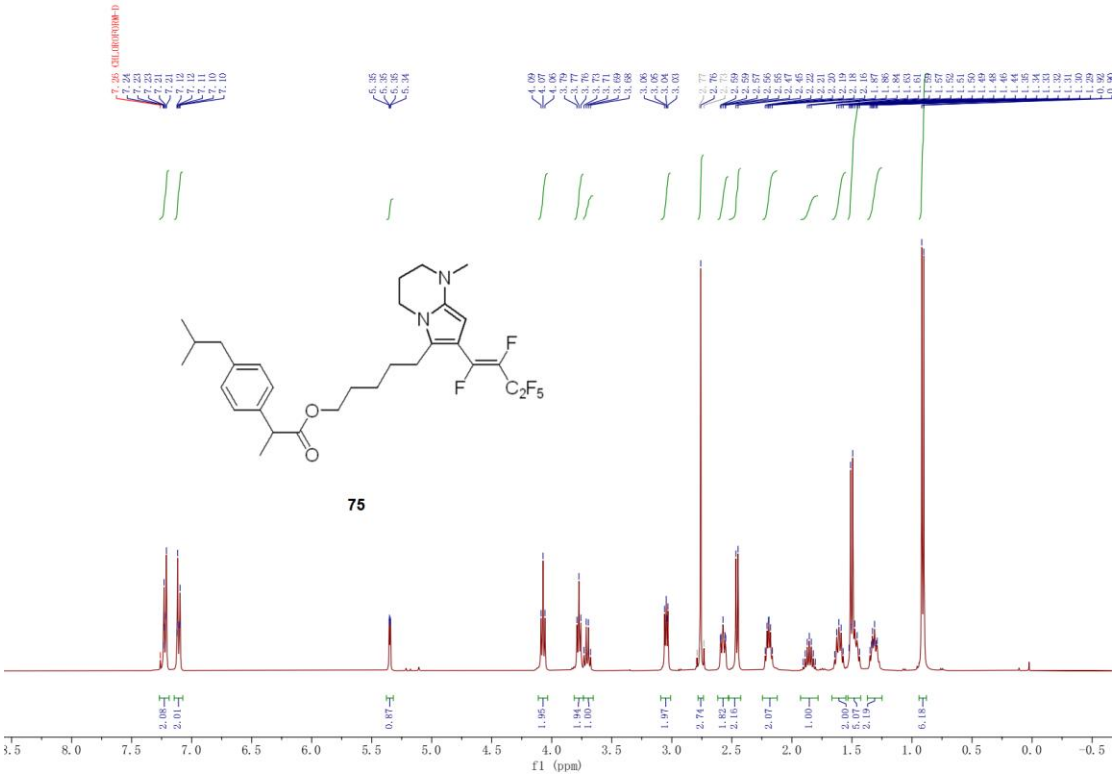
^{19}F NMR spectra of the product **74** (376 MHz, $CDCl_3$):



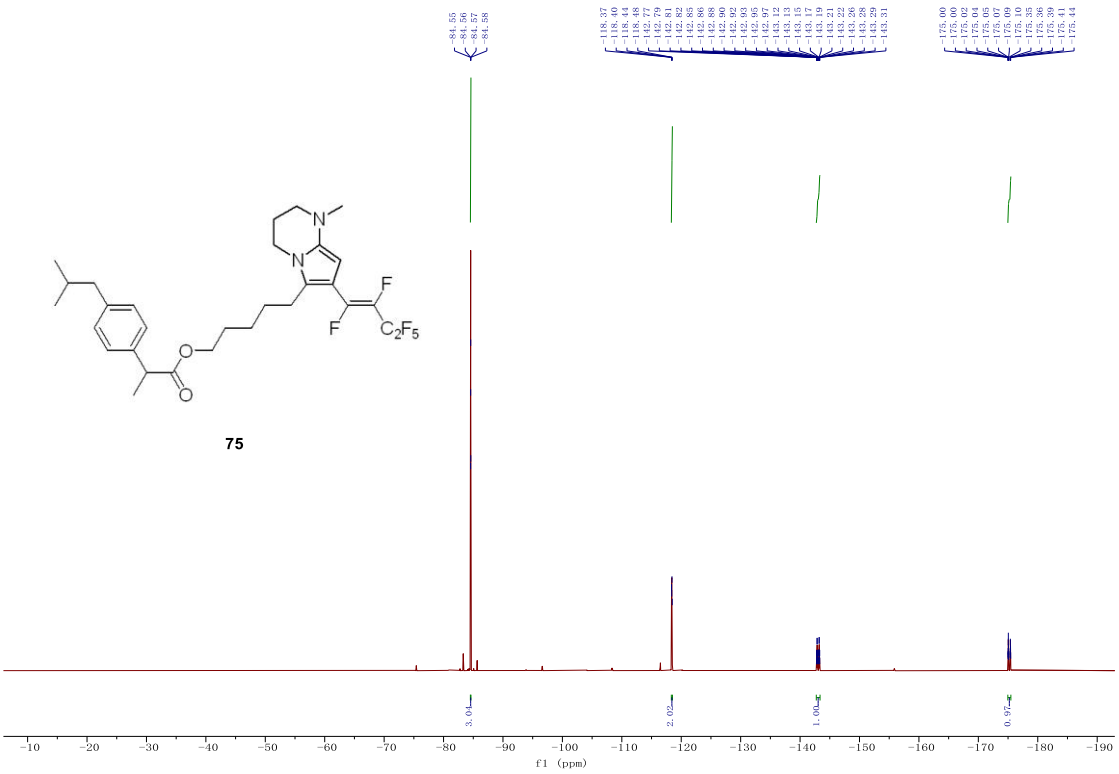
^{13}C NMR spectra of the product **74** (101 MHz, $CDCl_3$):



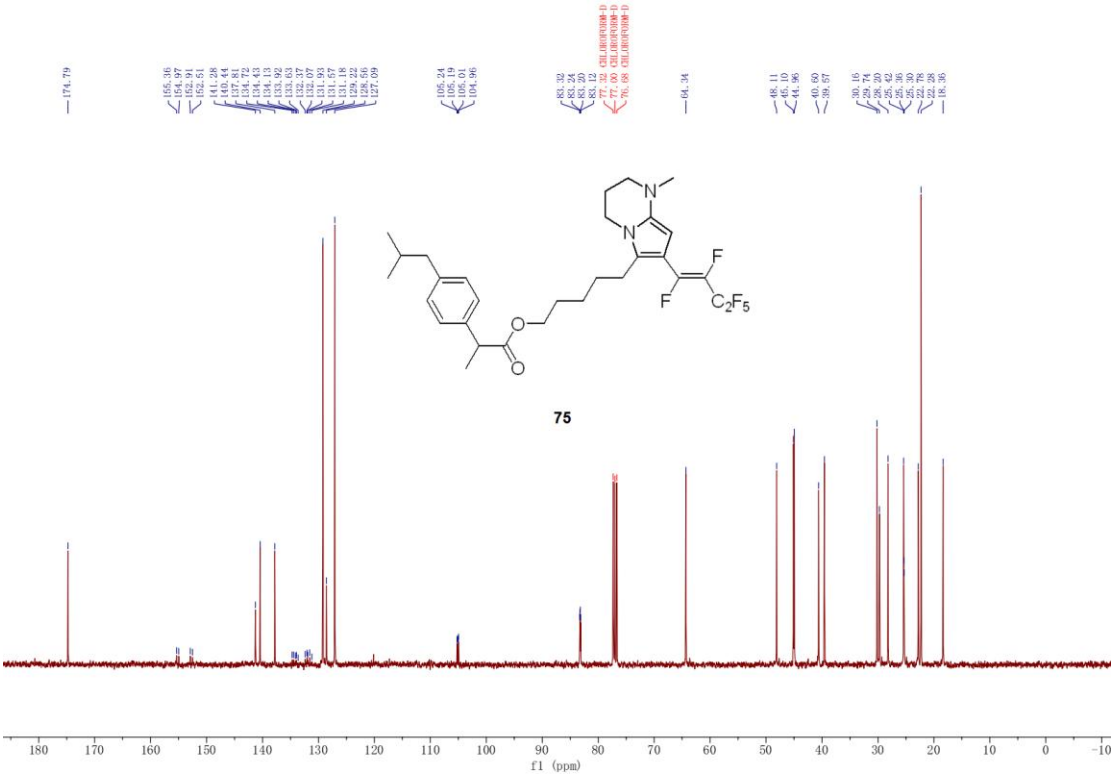
^{1}H NMR spectra of the product **75** (400 MHz, $CDCl_3$):



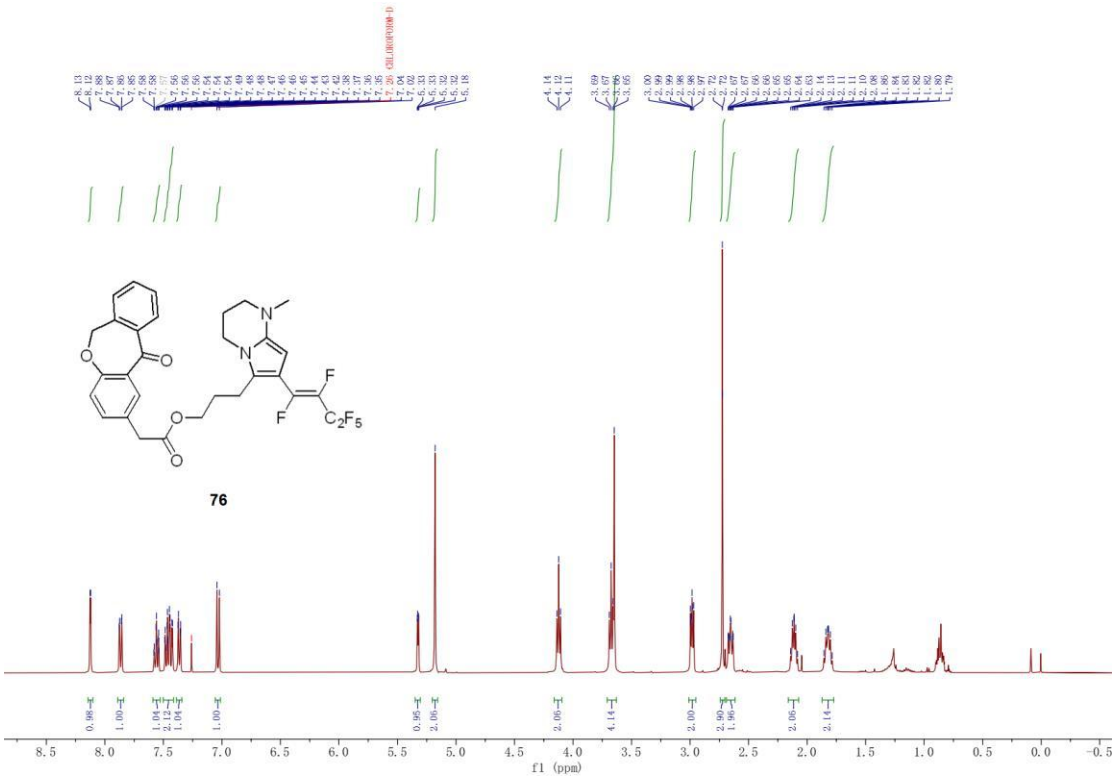
^{19}F NMR spectra of the product **75** (376 MHz, $CDCl_3$):



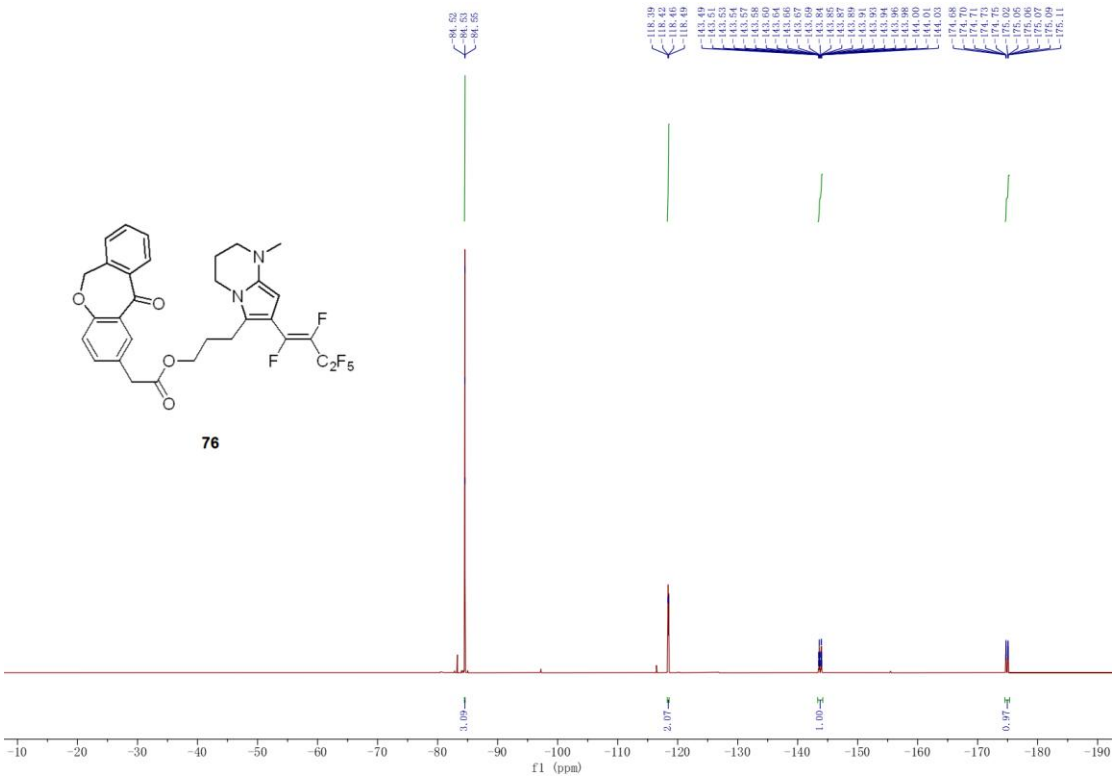
^{13}C NMR spectra of the product **75** (101 MHz, $CDCl_3$):



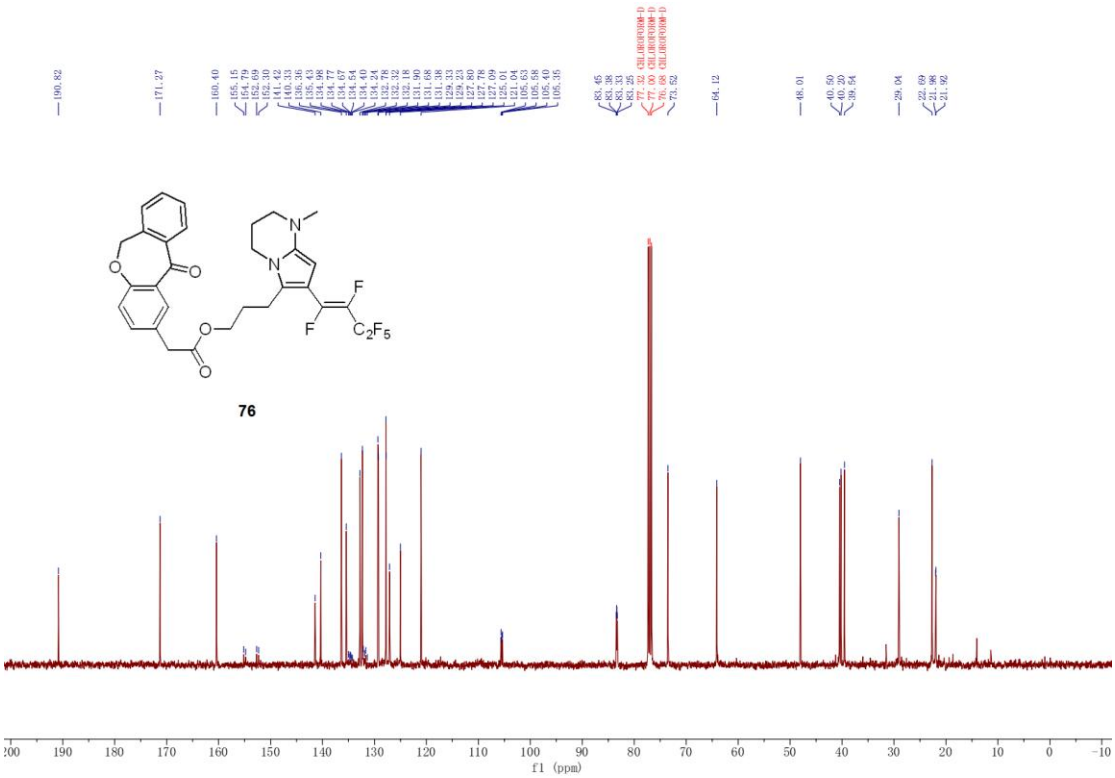
^{1}H NMR spectra of the product **76** (400 MHz, $CDCl_3$):



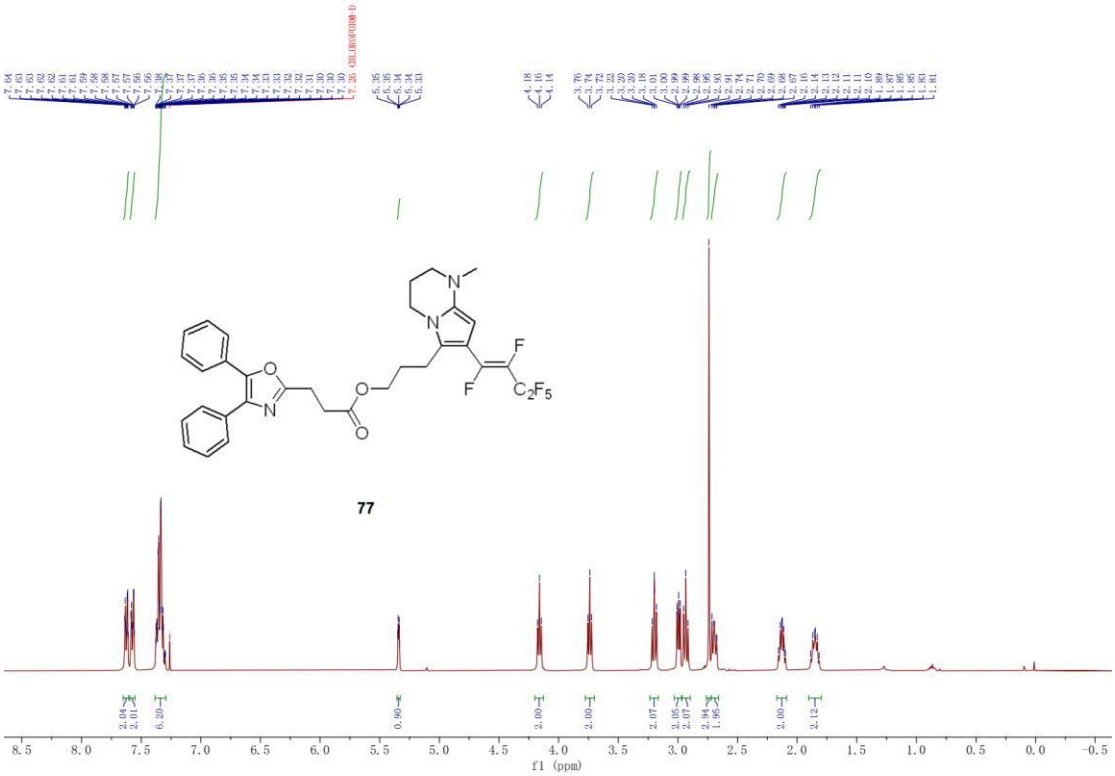
^{19}F NMR spectra of the product **76** (376 MHz, $CDCl_3$):



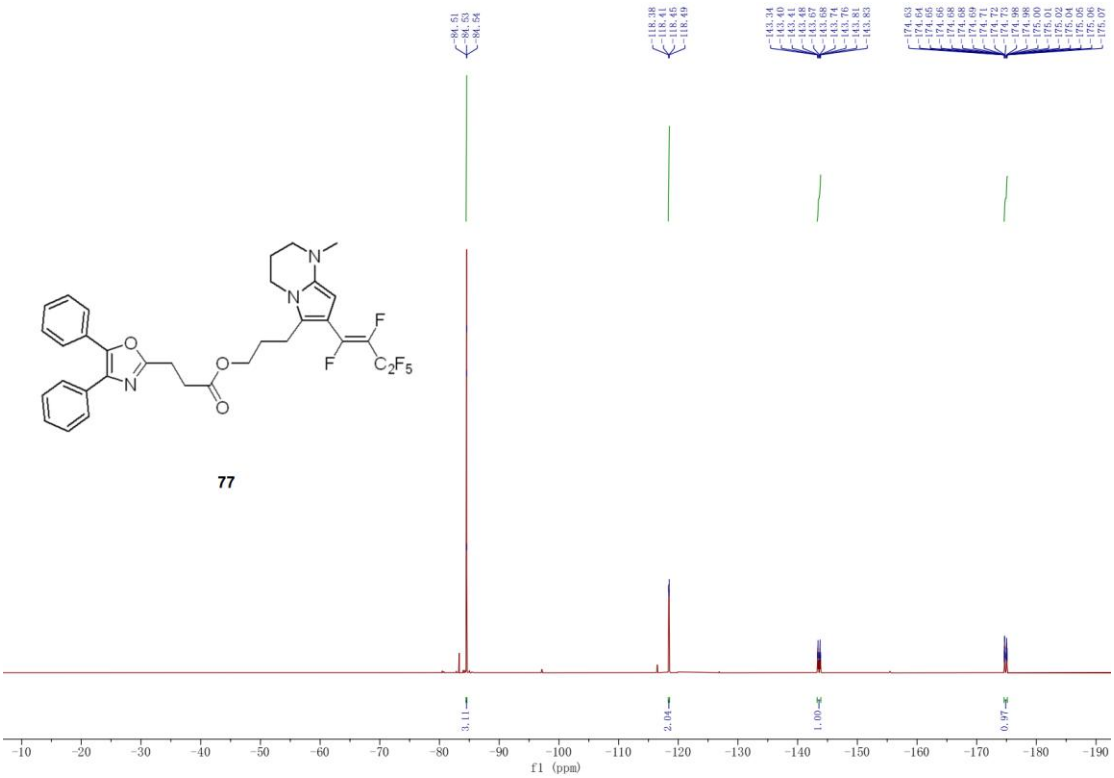
^{13}C NMR spectra of the product **76** (101 MHz, $CDCl_3$):



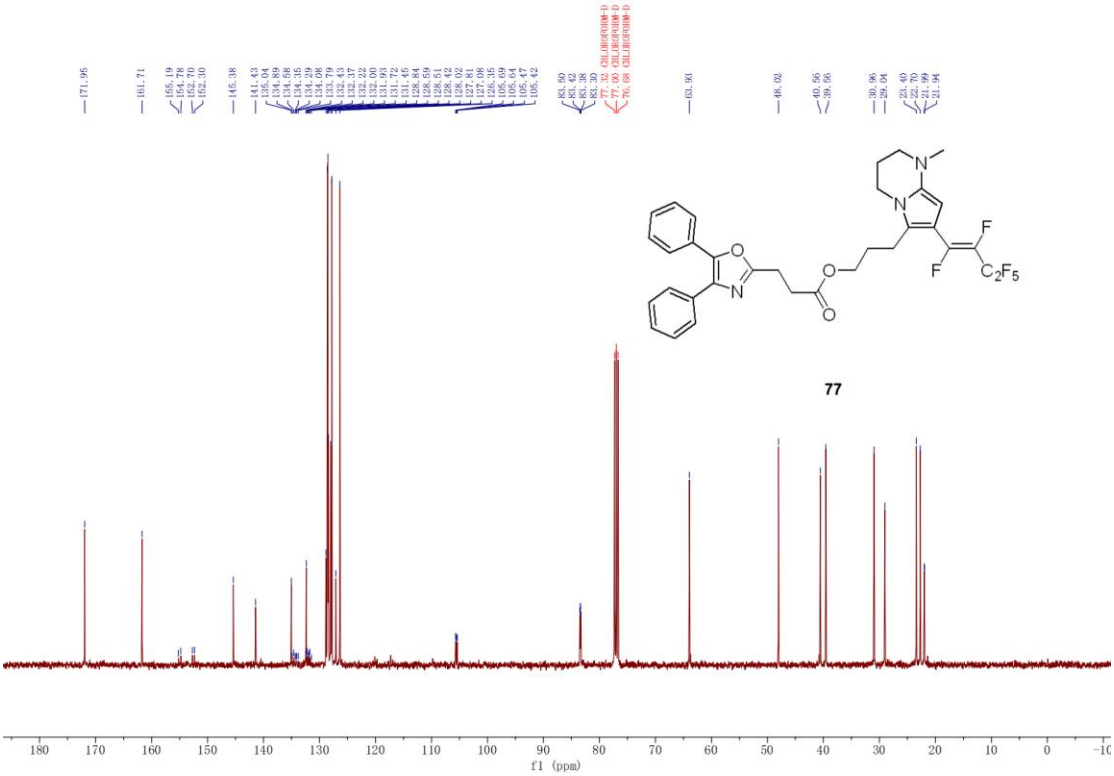
^{1}H NMR spectra of the product **77** (400 MHz, $CDCl_3$):



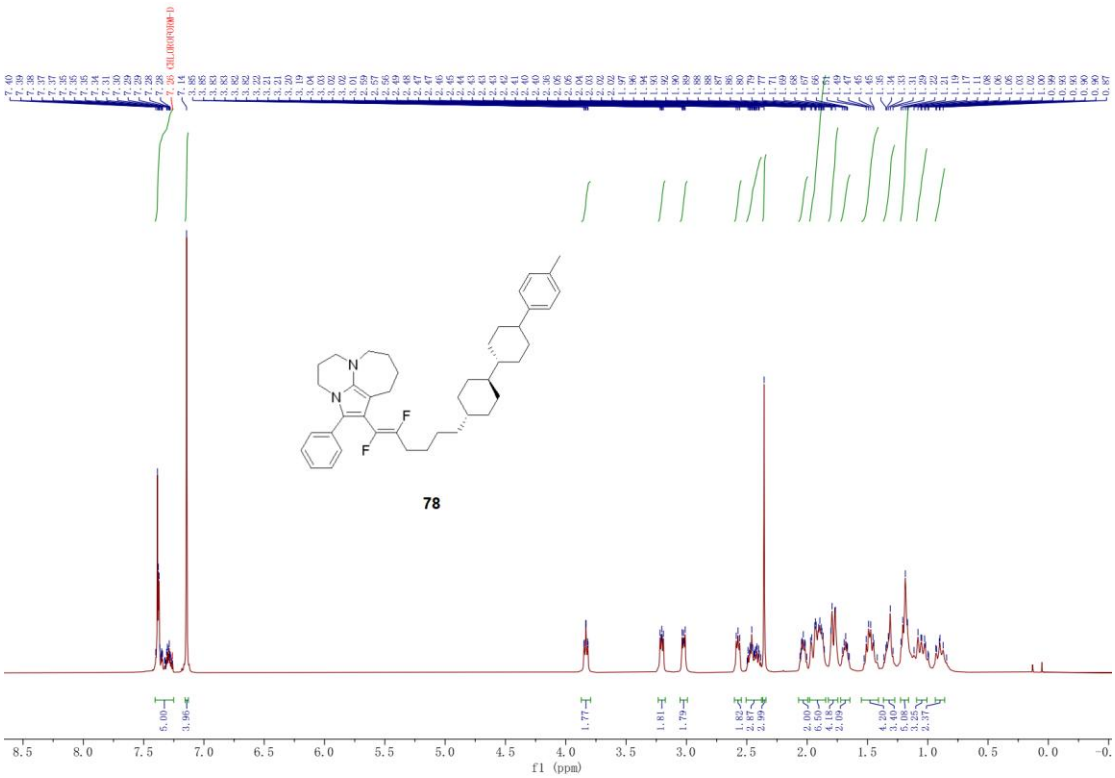
^{19}F NMR spectra of the product **77** (376 MHz, $CDCl_3$):



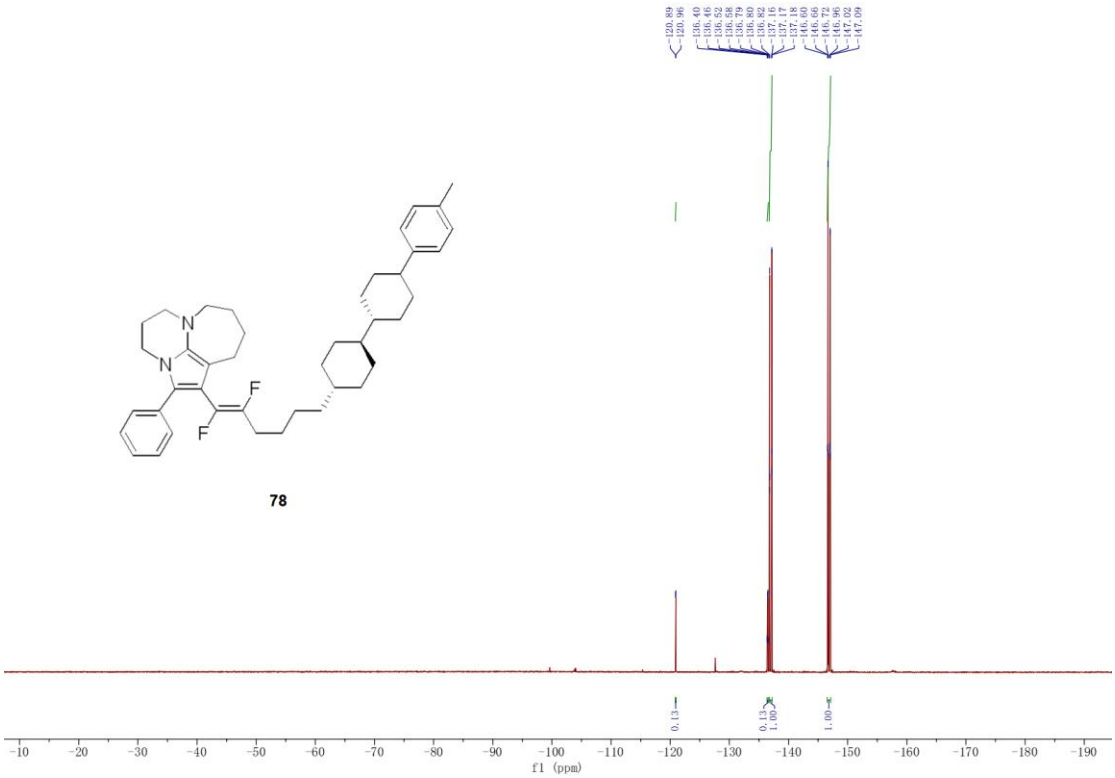
^{13}C NMR spectra of the product **77** (101 MHz, $CDCl_3$):



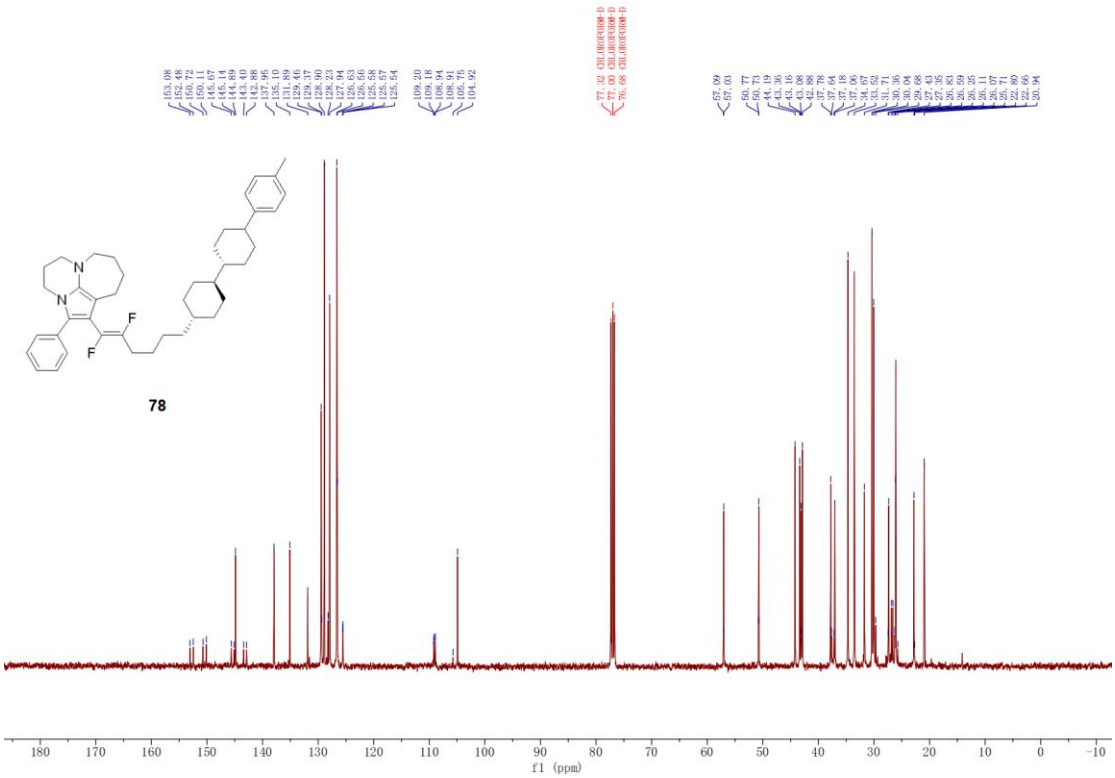
^{1}H NMR spectra of the product **78** (400 MHz, $CDCl_3$):



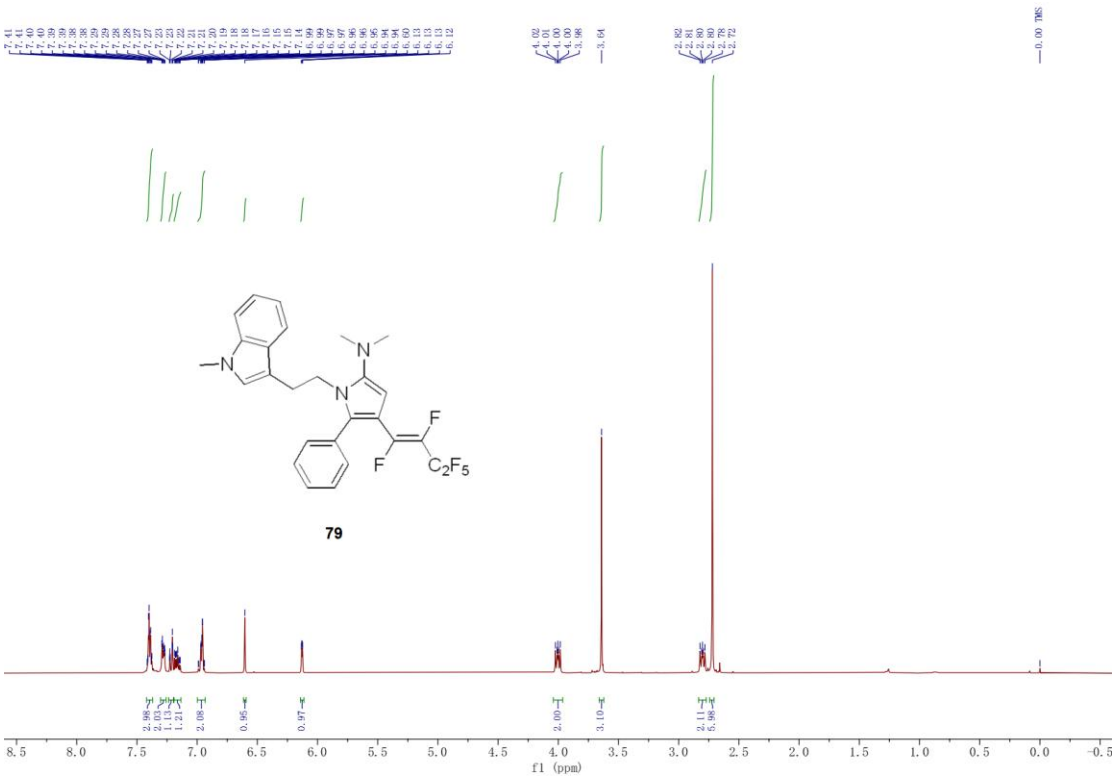
^{19}F NMR spectra of the product **78** (376 MHz, $CDCl_3$):



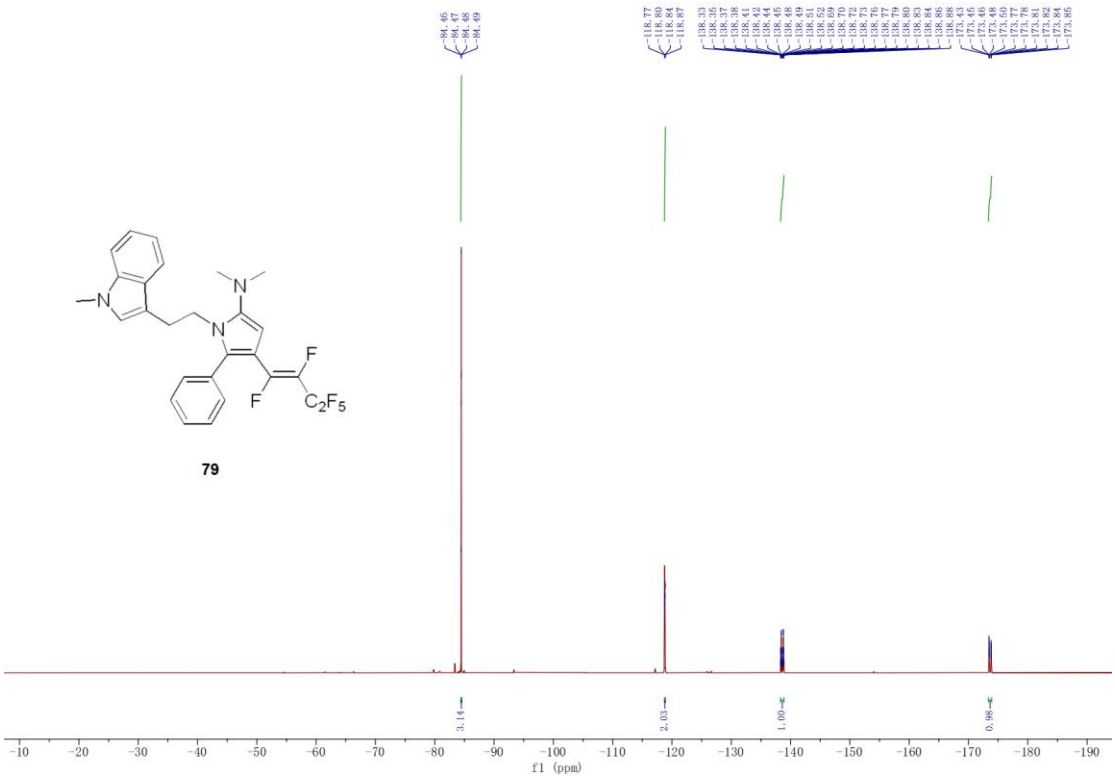
^{13}C NMR spectra of the product **78** (101 MHz, $CDCl_3$):



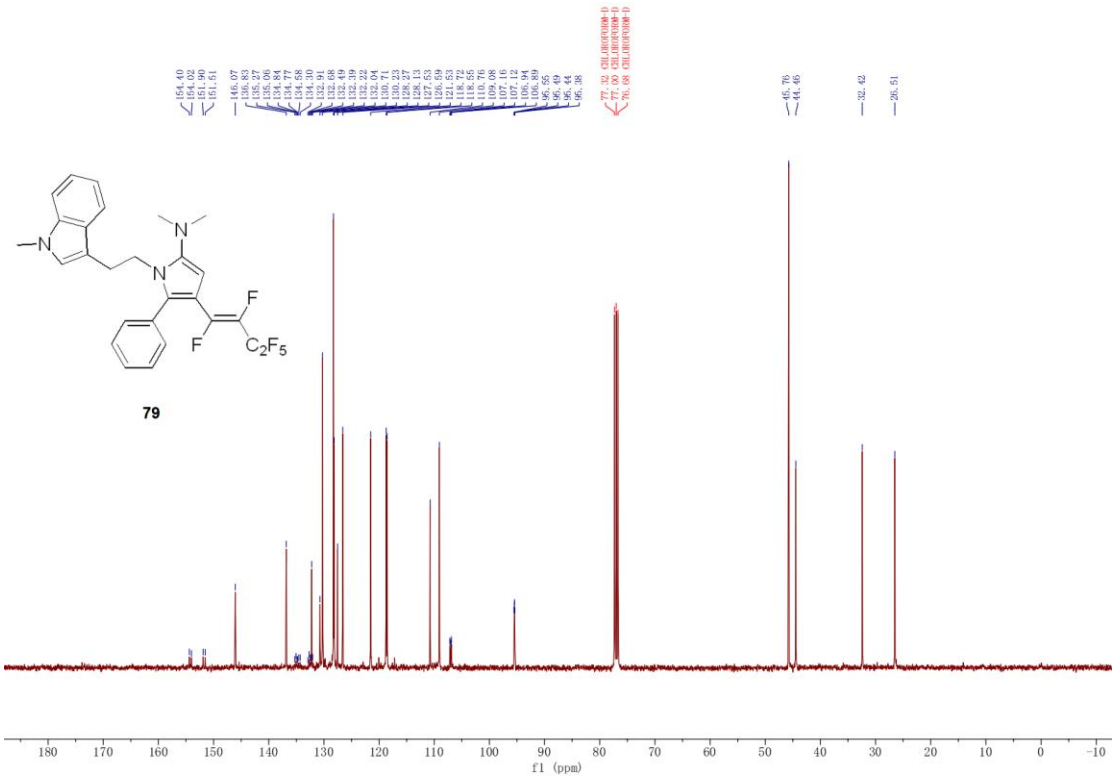
^{1}H NMR spectra of the product **79** (400 MHz, $CDCl_3$):



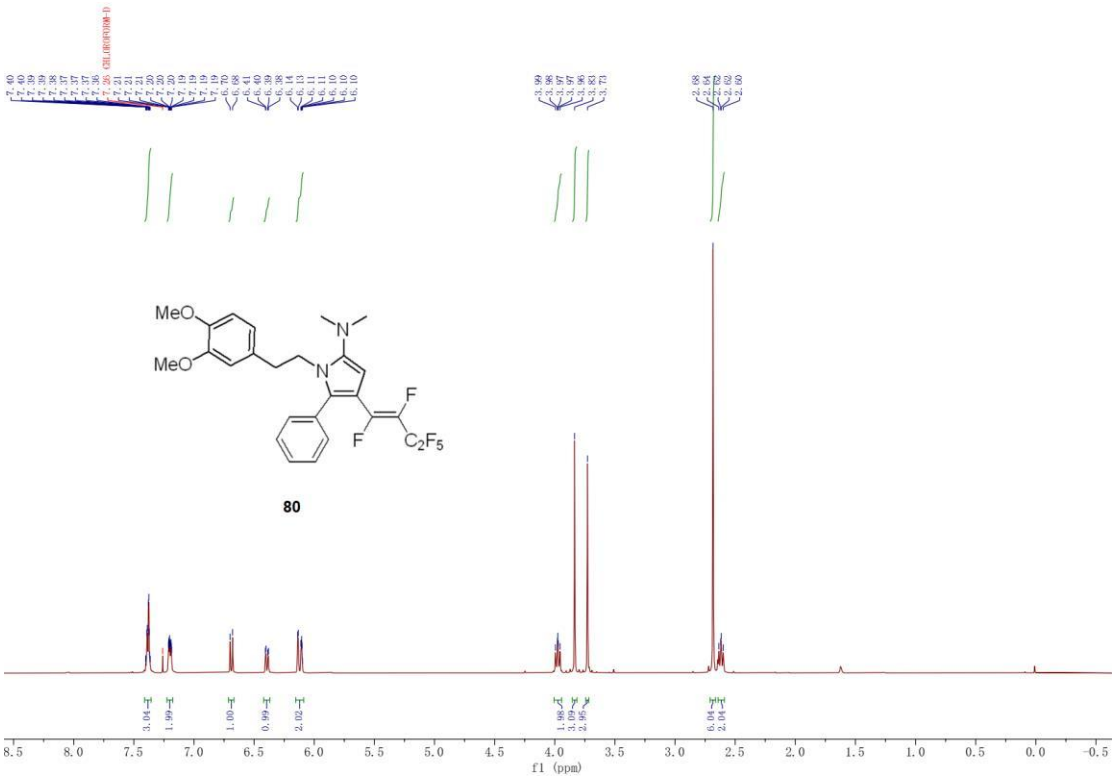
^{19}F NMR spectra of the product **79** (376 MHz, $CDCl_3$):



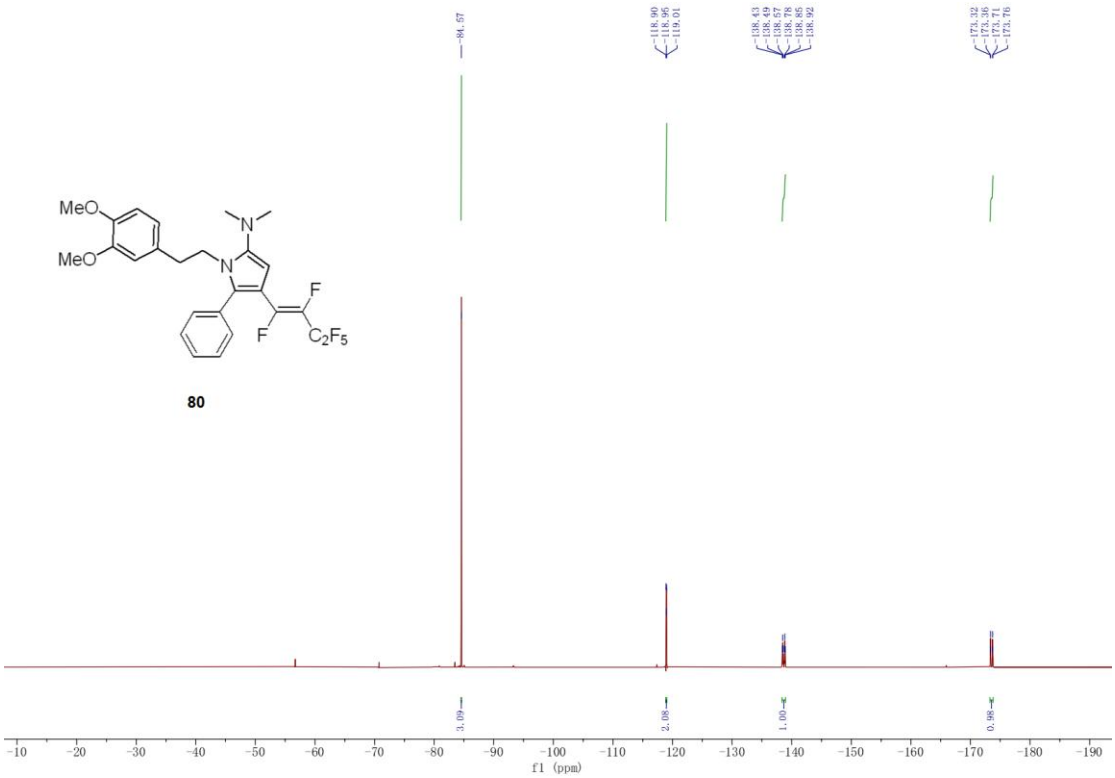
^{13}C NMR spectra of the product **79** (101 MHz, $CDCl_3$):



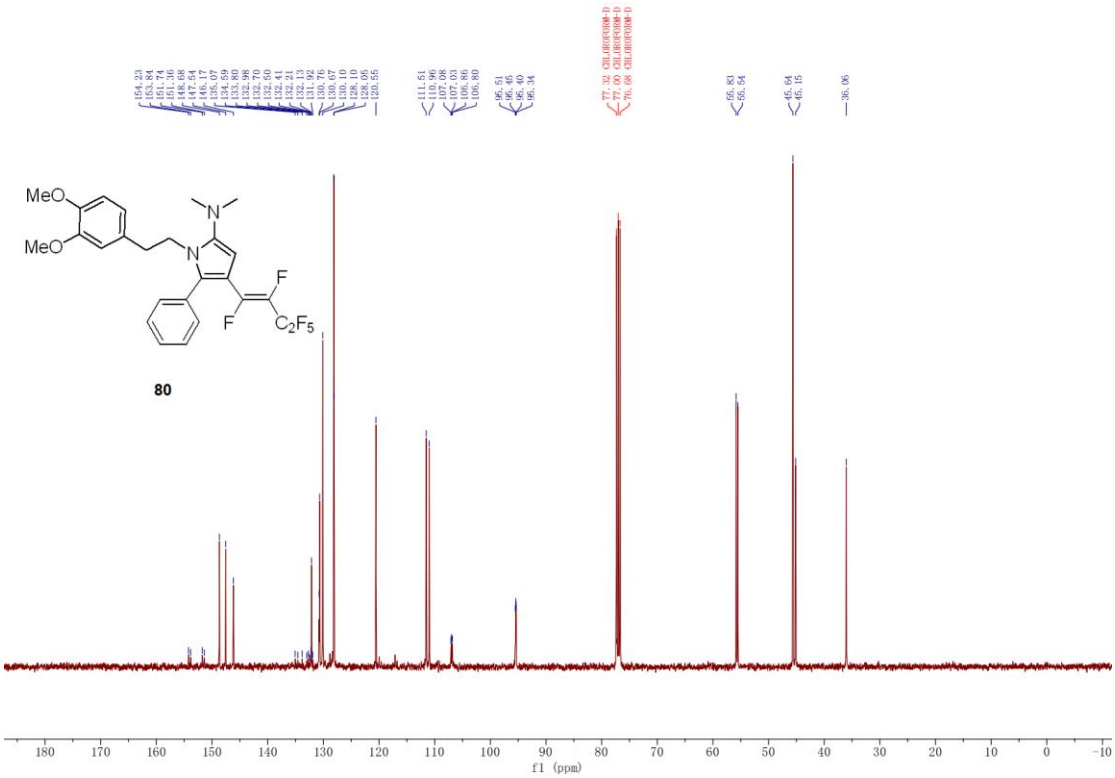
^{1}H NMR spectra of the product **80** (400 MHz, $CDCl_3$):



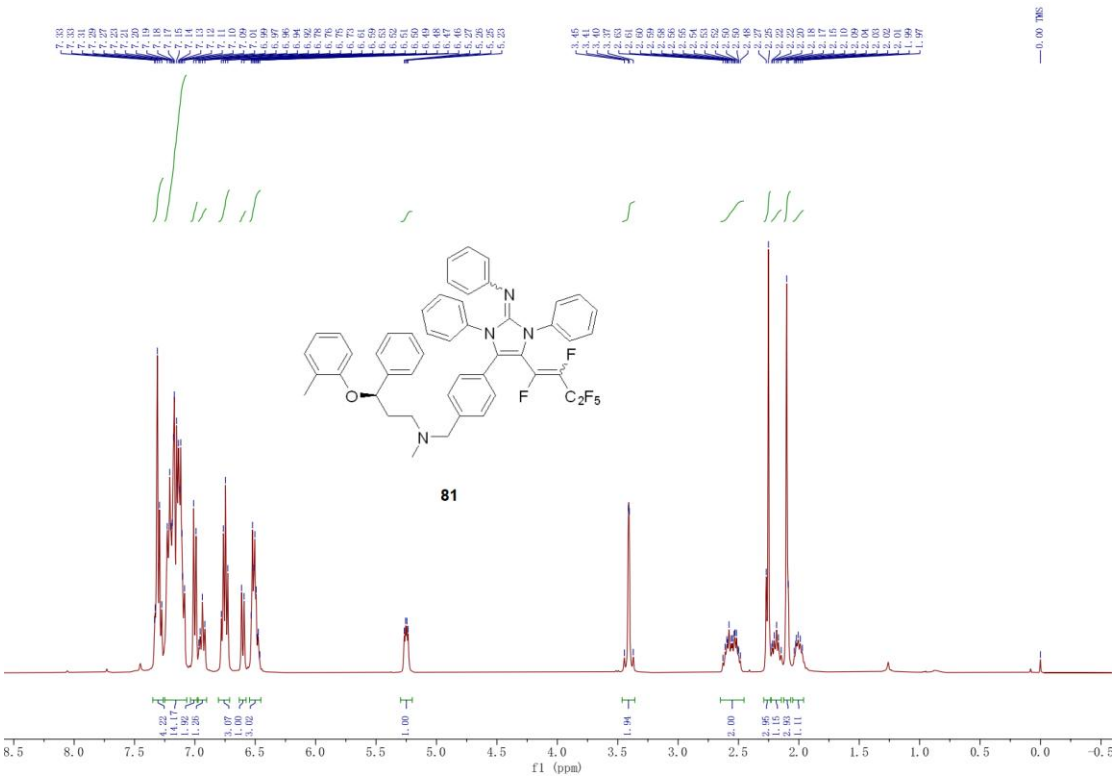
^{19}F NMR spectra of the product **80** (376 MHz, $CDCl_3$):



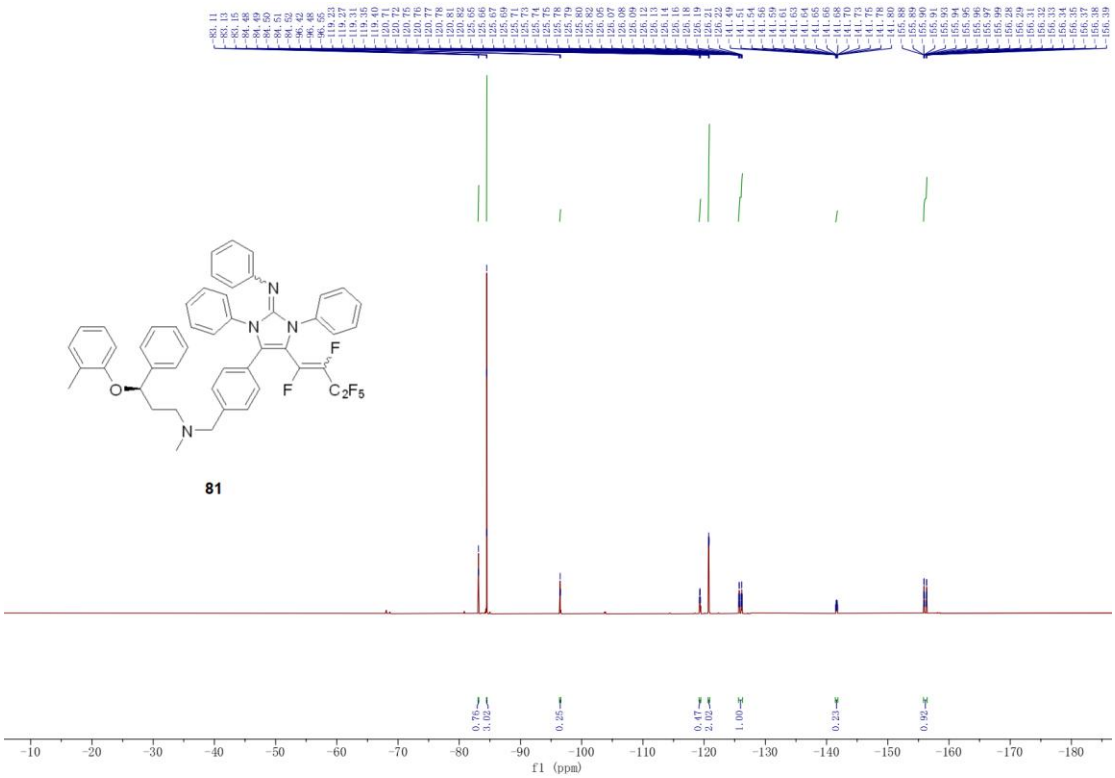
^{13}C NMR spectra of the product **80** (101 MHz, $CDCl_3$):



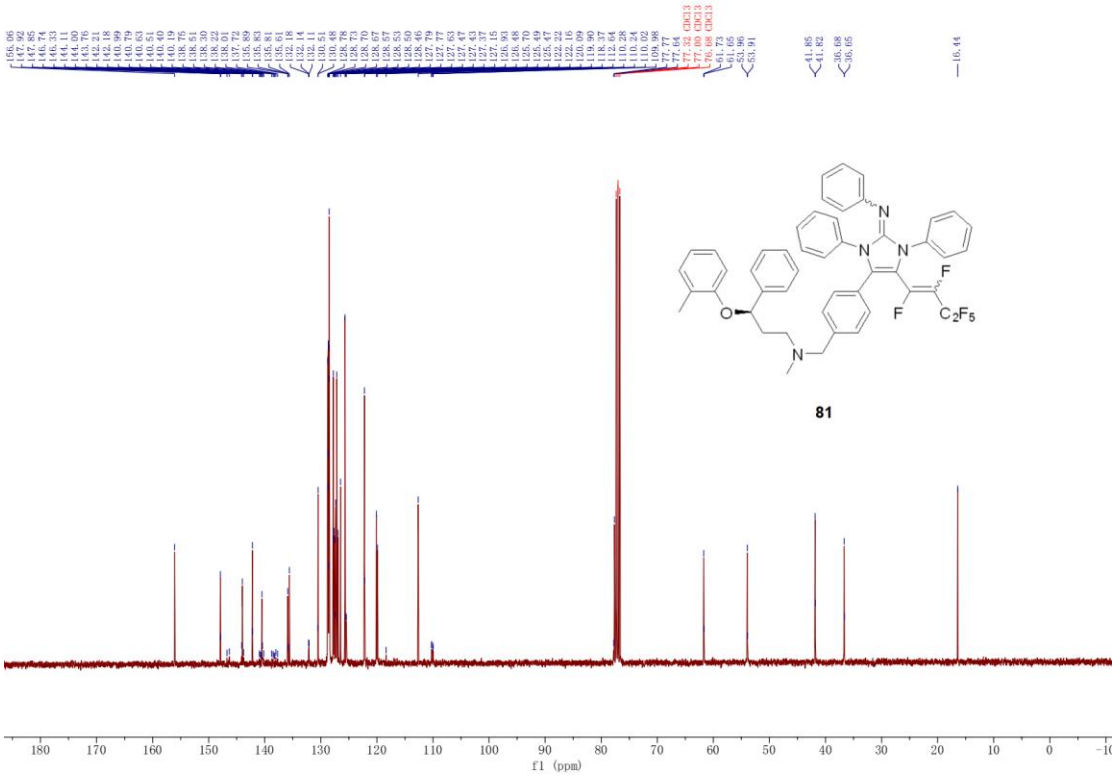
^{1}H NMR spectra of the product **81** (400 MHz, $CDCl_3$):



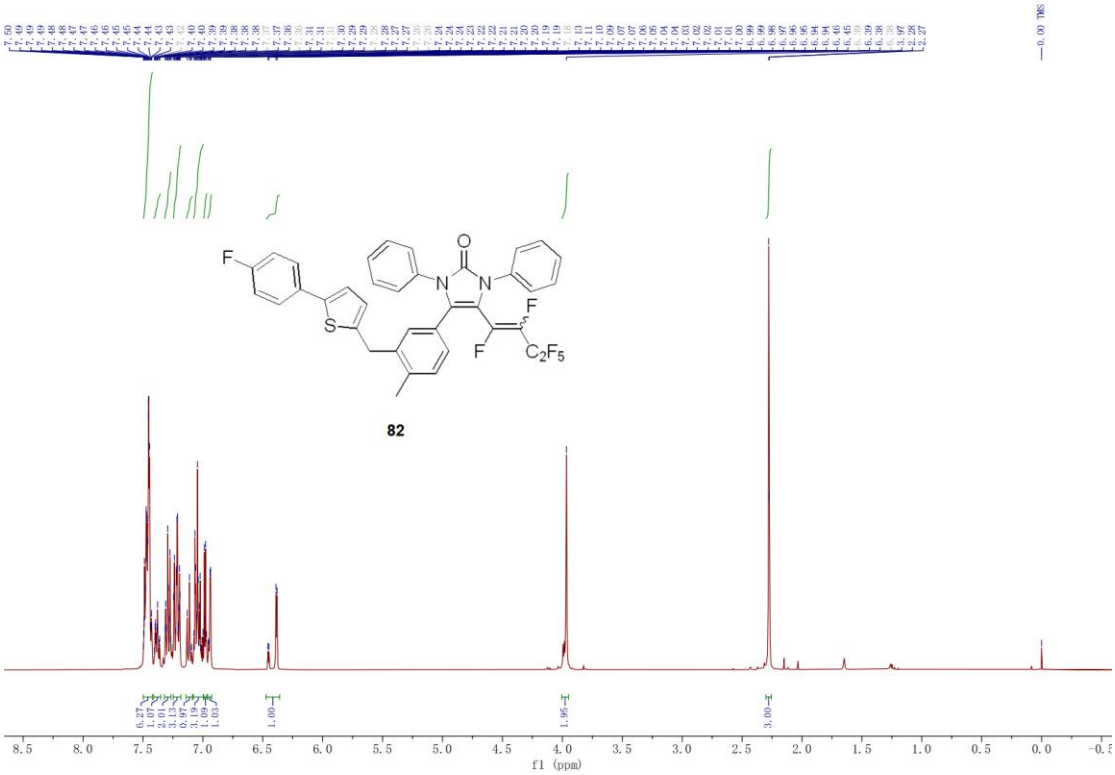
^{19}F NMR spectra of the product **81** (376 MHz, $CDCl_3$):



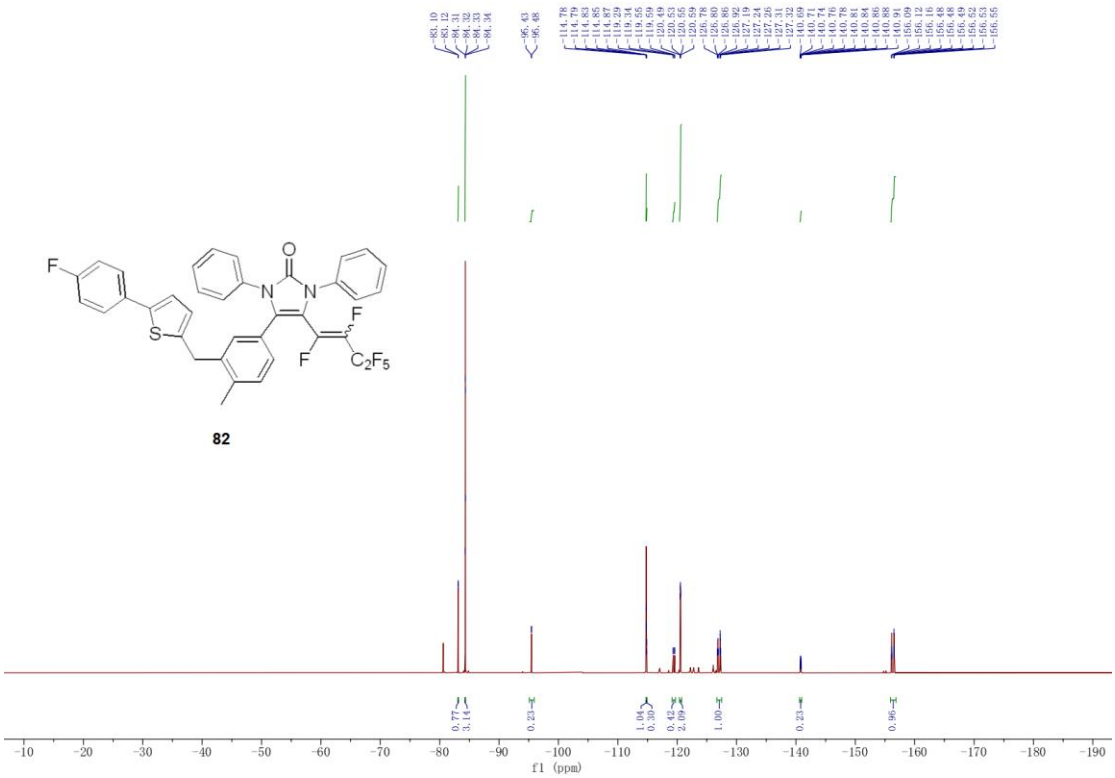
^{13}C NMR spectra of the product **81** (101 MHz, $CDCl_3$):



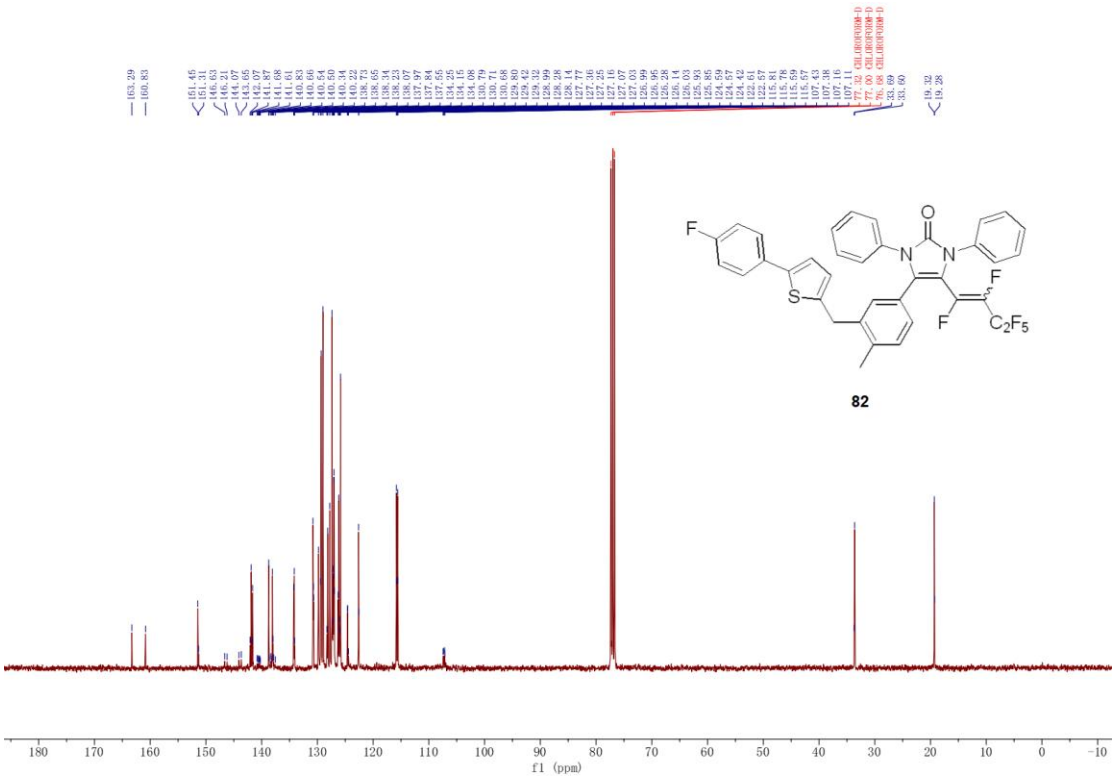
^{1}H NMR spectra of the product **82** (400 MHz, $CDCl_3$):



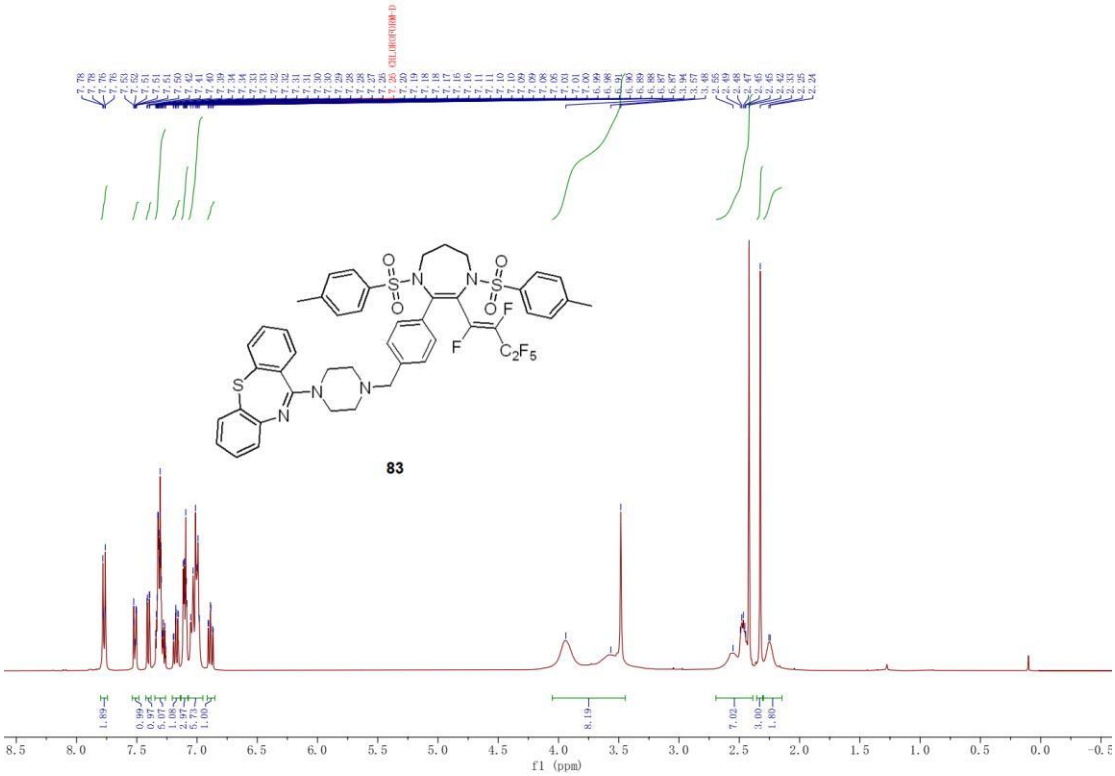
^{19}F NMR spectra of the product **82** (376 MHz, $CDCl_3$):



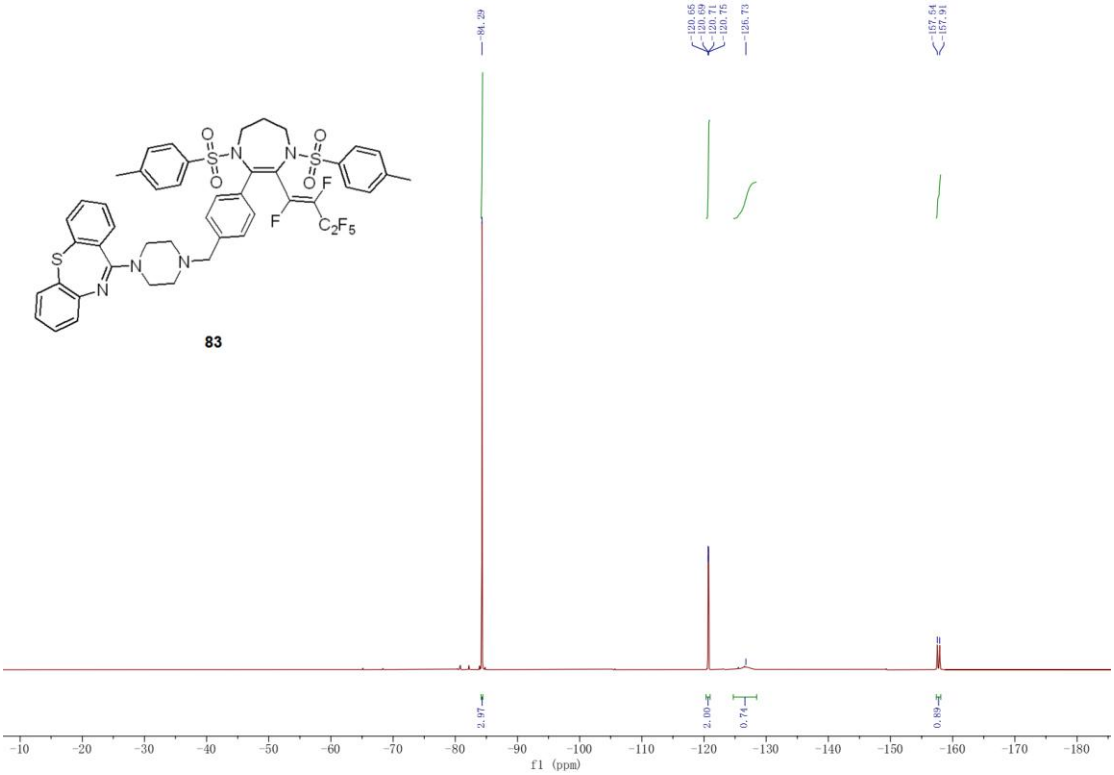
^{13}C NMR spectra of the product **82** (101 MHz, $CDCl_3$):



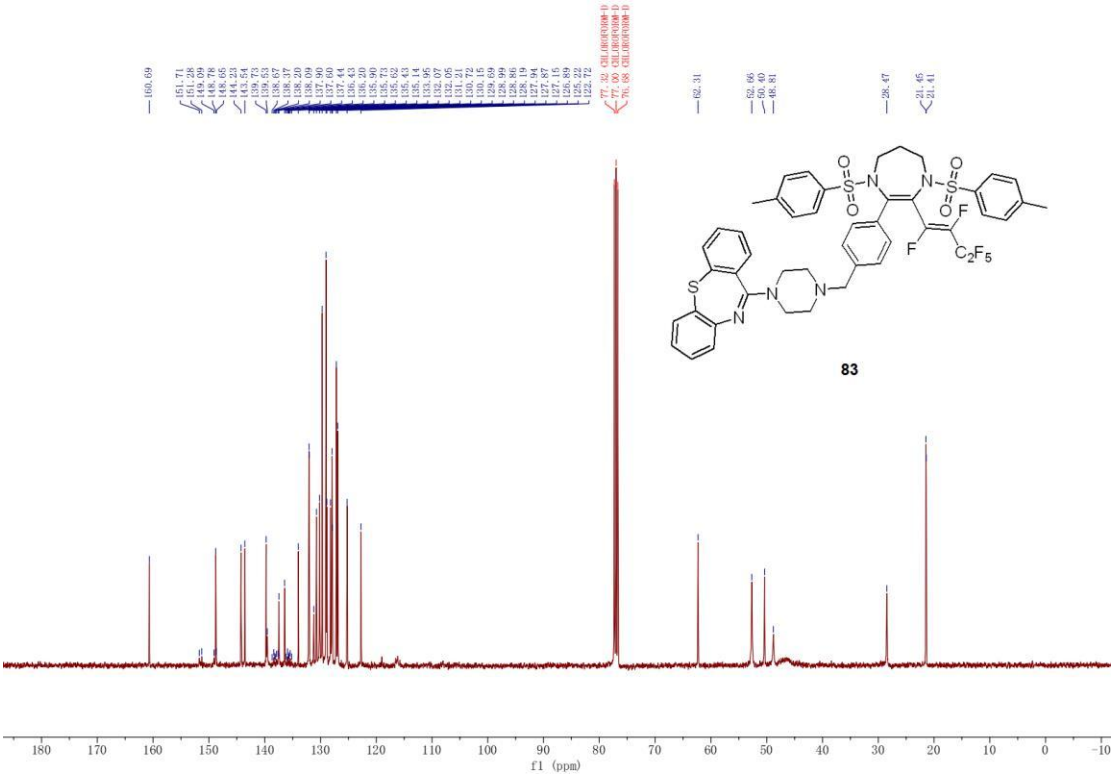
^{1}H NMR spectra of the product **83** (400 MHz, $CDCl_3$):



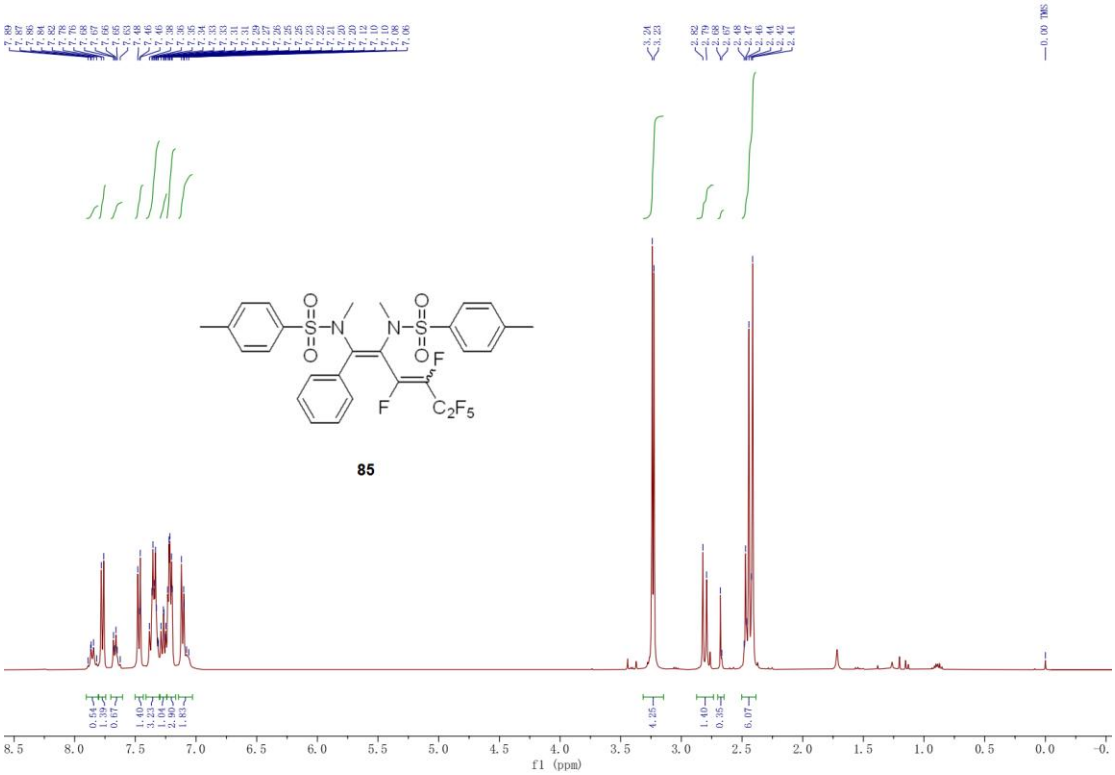
^{19}F NMR spectra of the product **83** (376 MHz, $CDCl_3$):



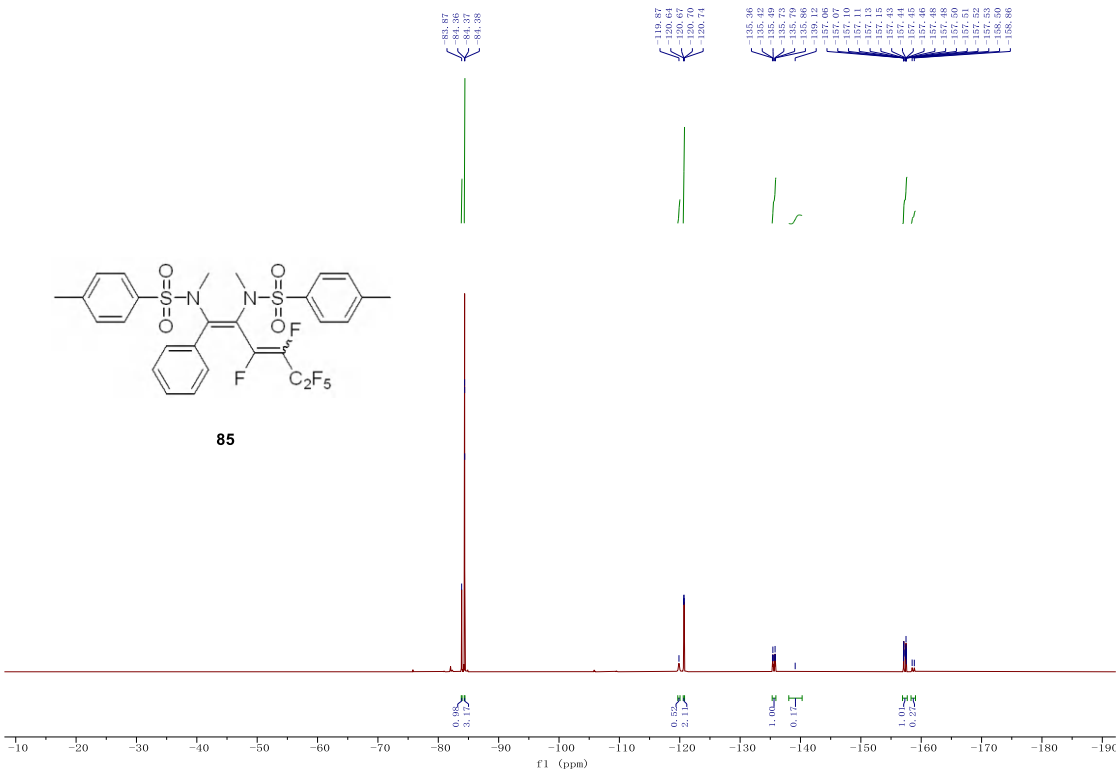
^{13}C NMR spectra of the product **83** (101 MHz, $CDCl_3$):



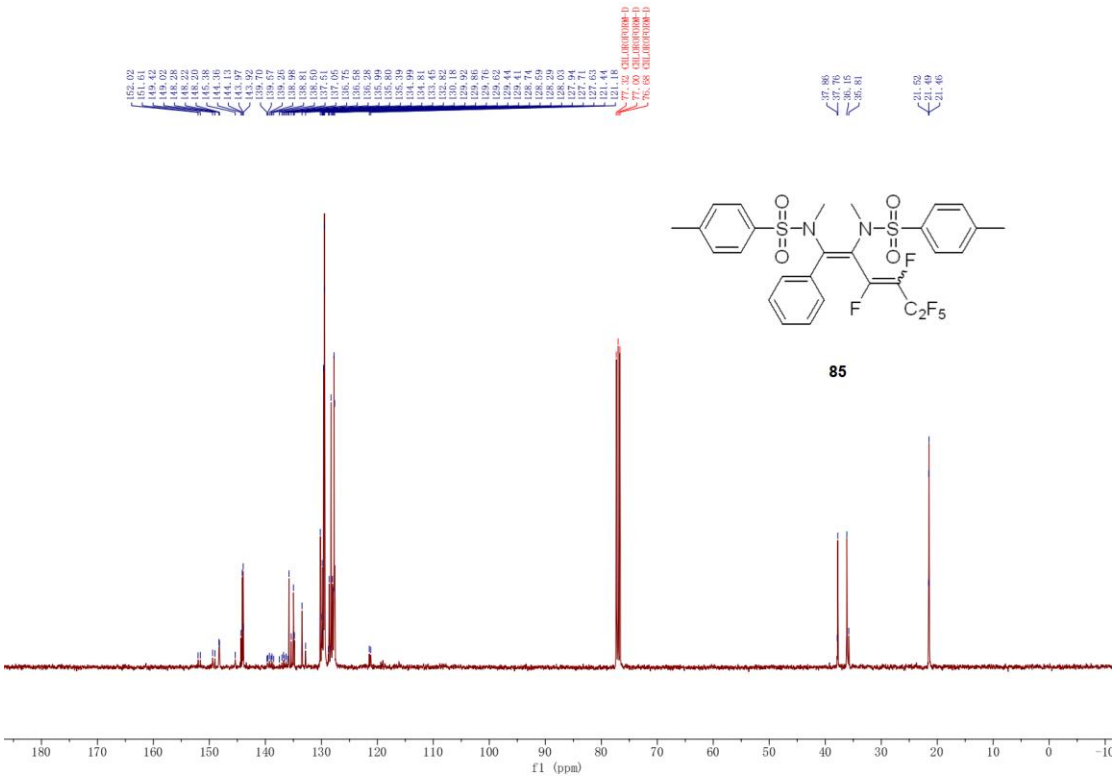
^{1}H NMR spectra of the product **85** (400 MHz, $CDCl_3$):



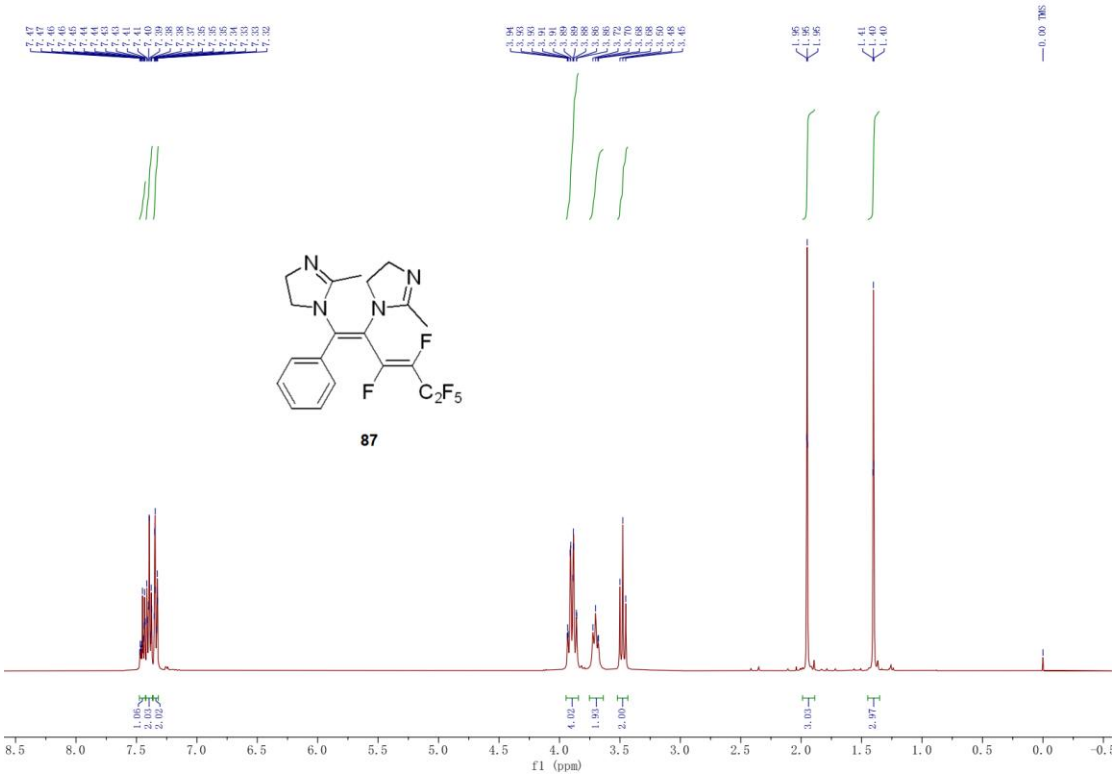
^{19}F NMR spectra of the product **85** (376 MHz, $CDCl_3$):



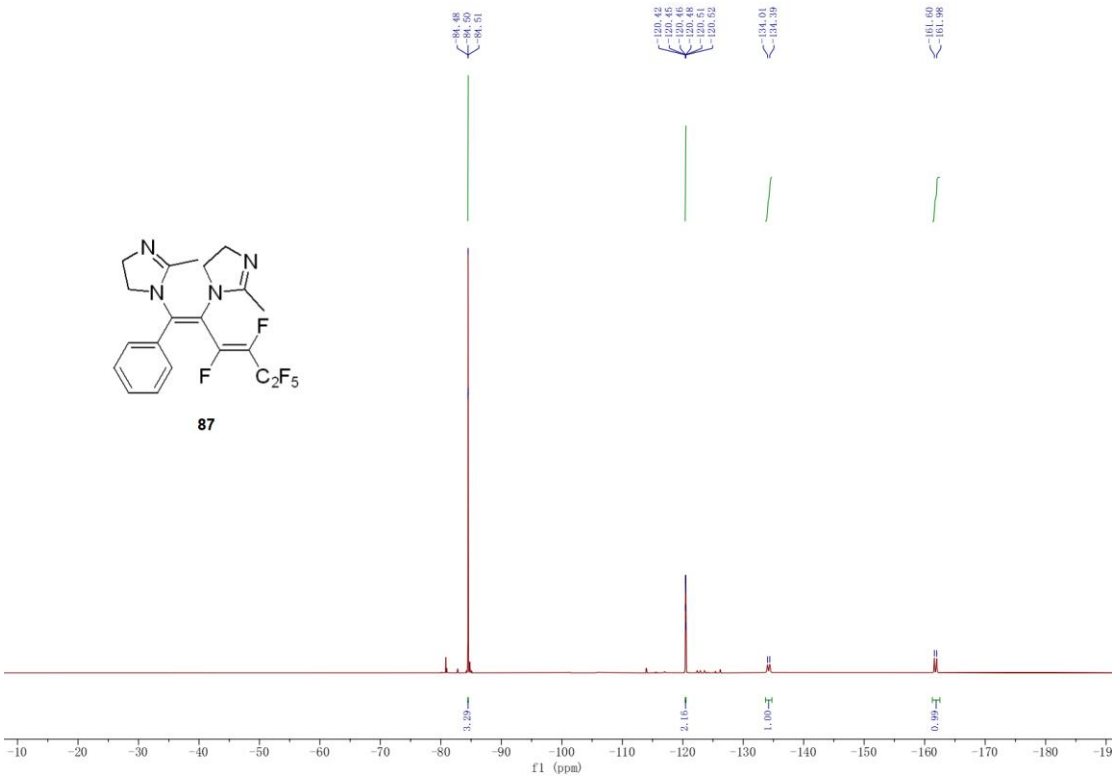
^{13}C NMR spectra of the product **85** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **87** (400 MHz, $CDCl_3$):

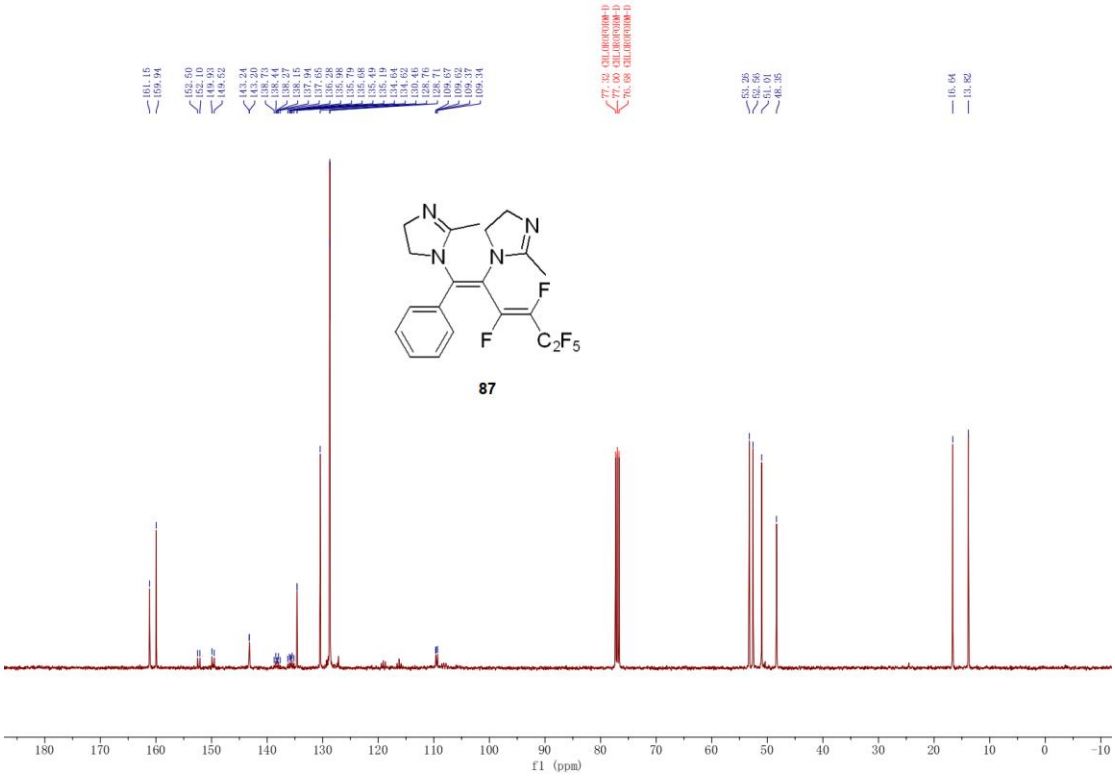


^{19}F NMR spectra of the product **87** (376 MHz, $CDCl_3$):



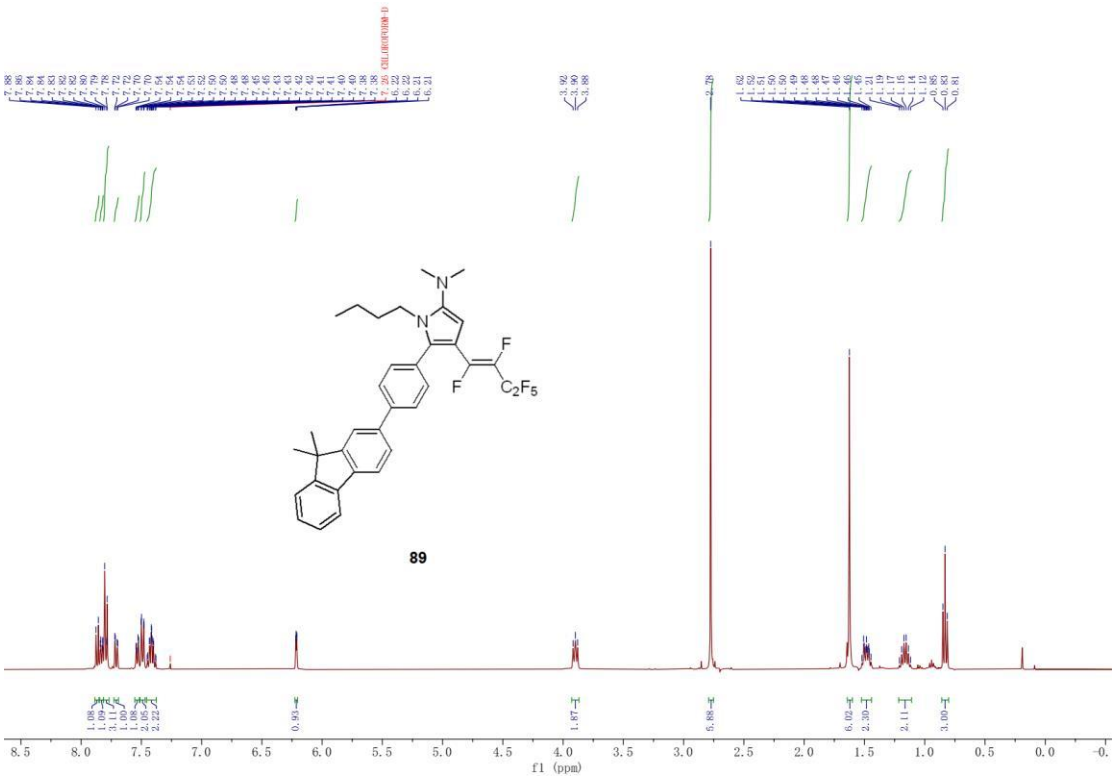
87

^{13}C NMR spectra of the product **87** (101 MHz, $CDCl_3$):

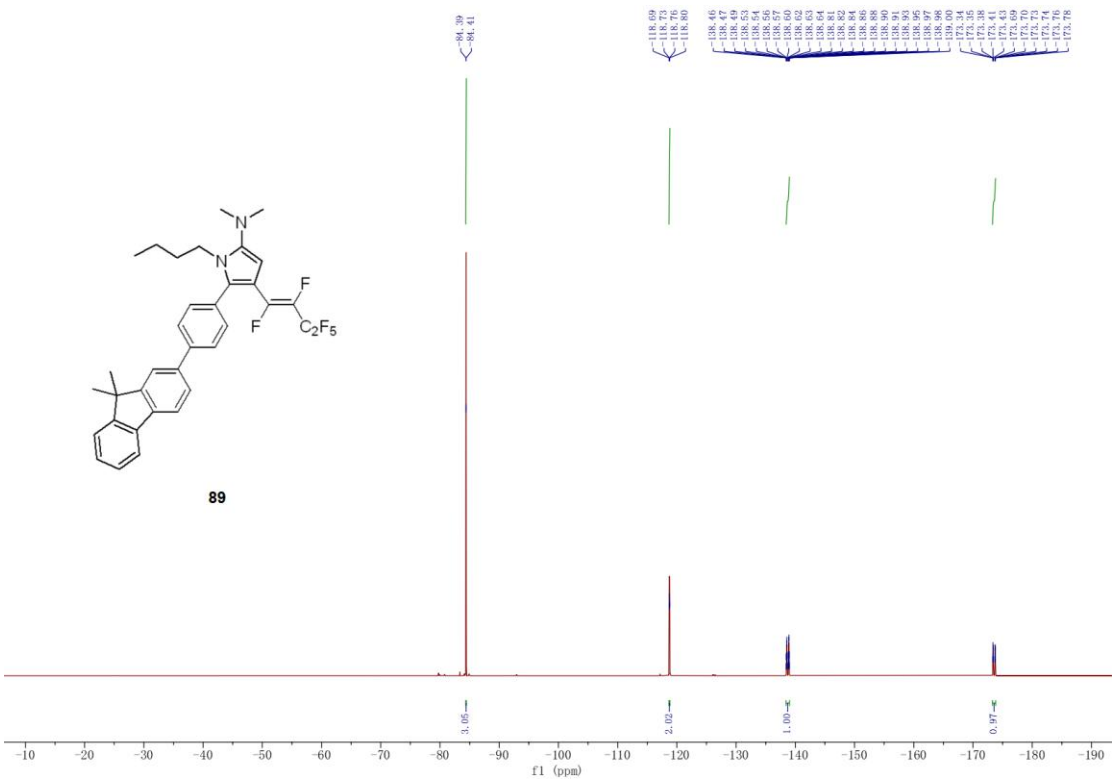


87

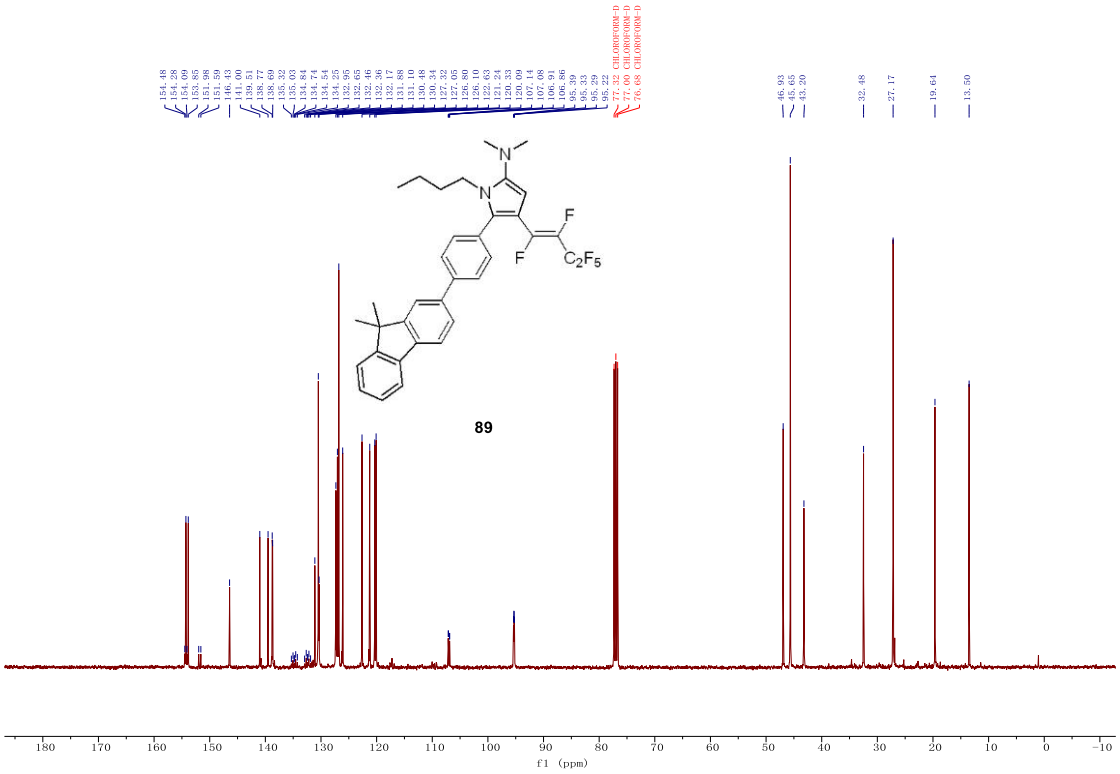
^{1}H NMR spectra of the product **89** (400 MHz, $CDCl_3$):



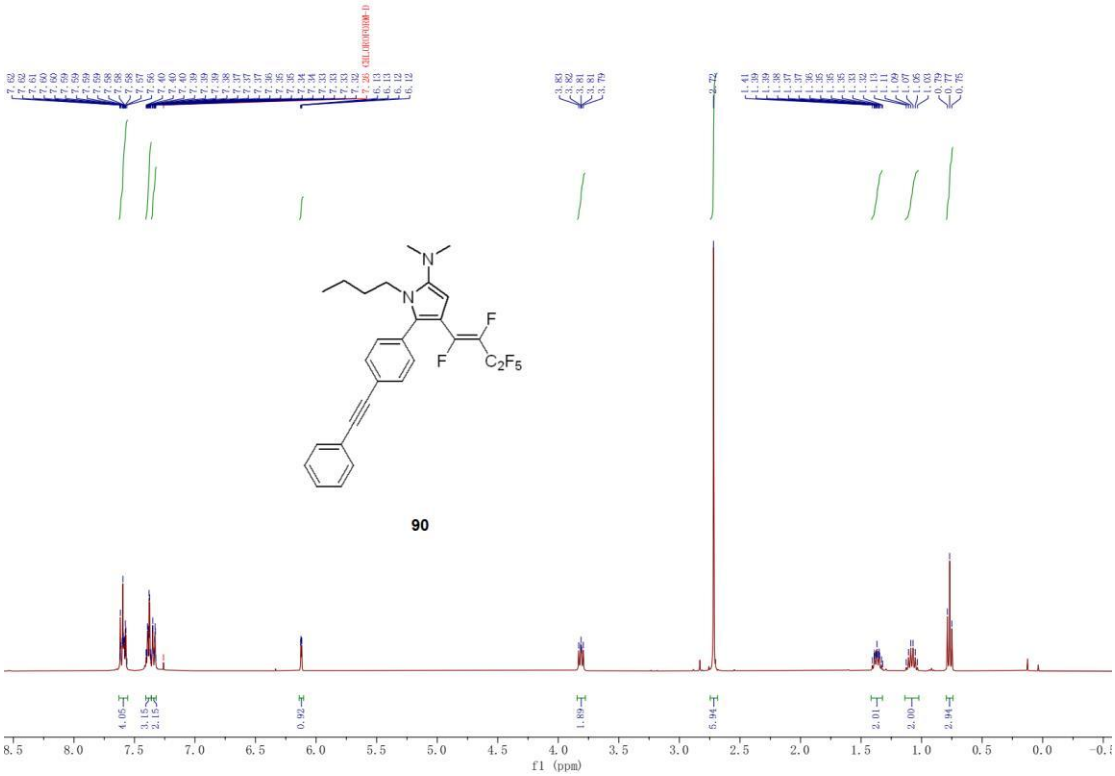
^{19}F NMR spectra of the product **89** (376 MHz, $CDCl_3$):



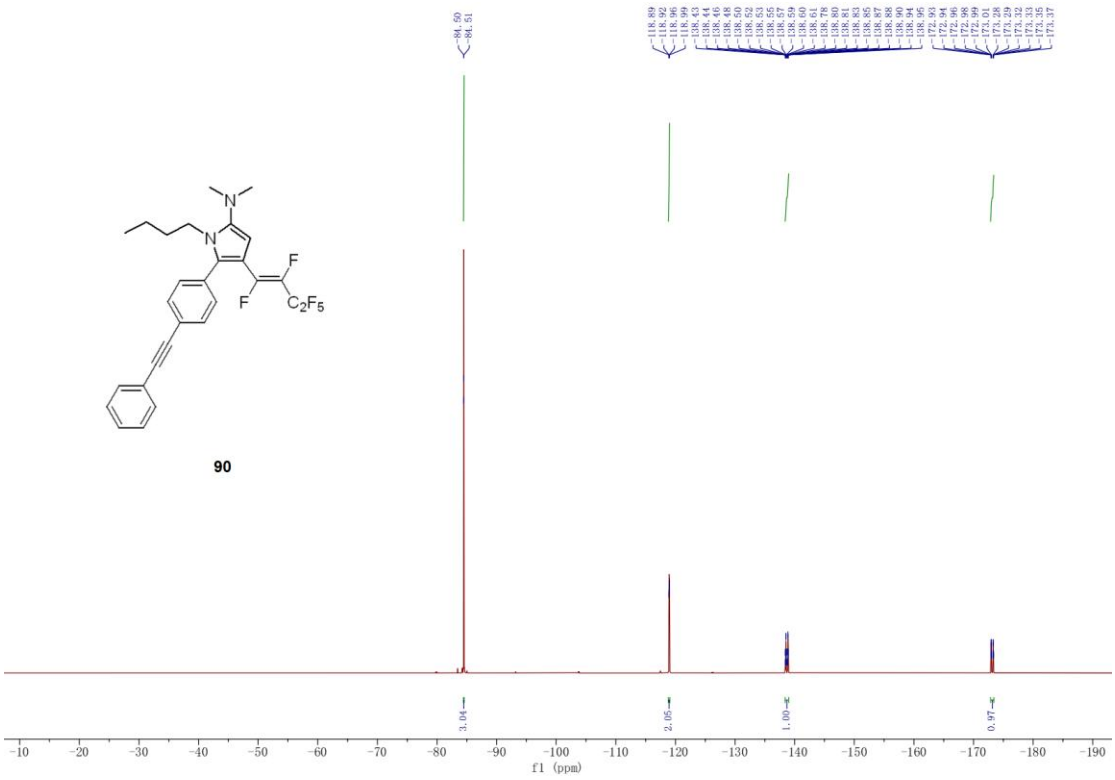
^{13}C NMR spectra of the product **89** (101 MHz, $CDCl_3$):



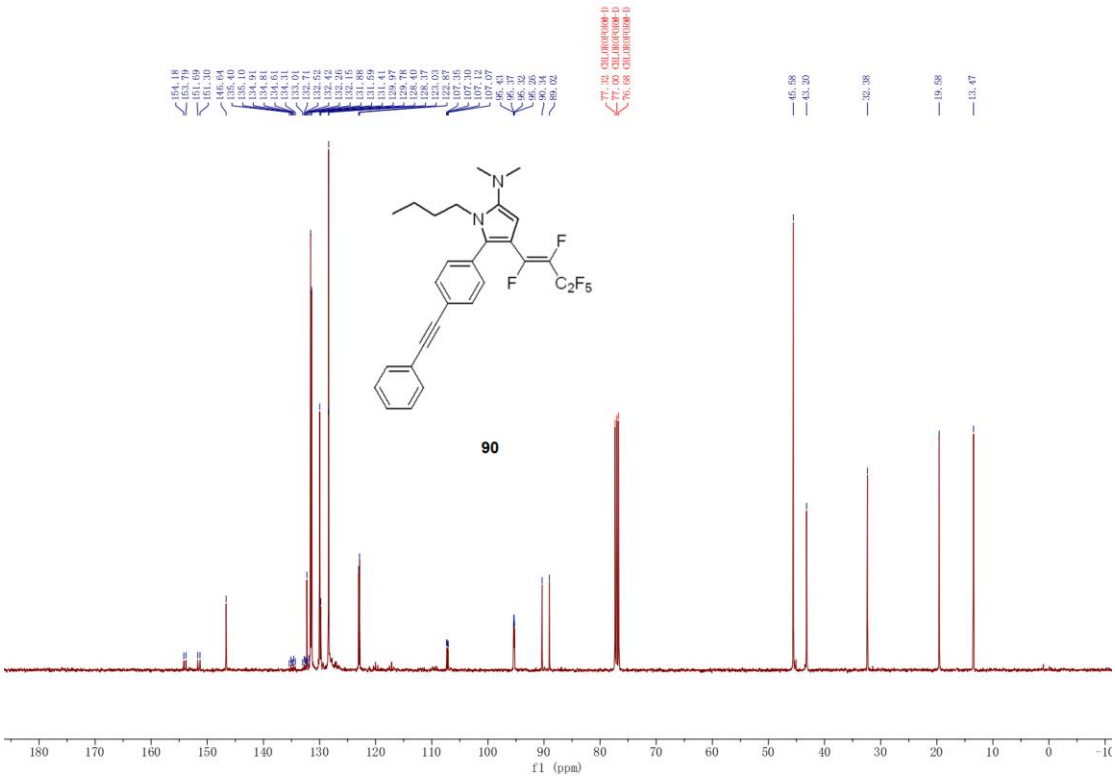
^{1}H NMR spectra of the product **90** (400 MHz, $CDCl_3$):



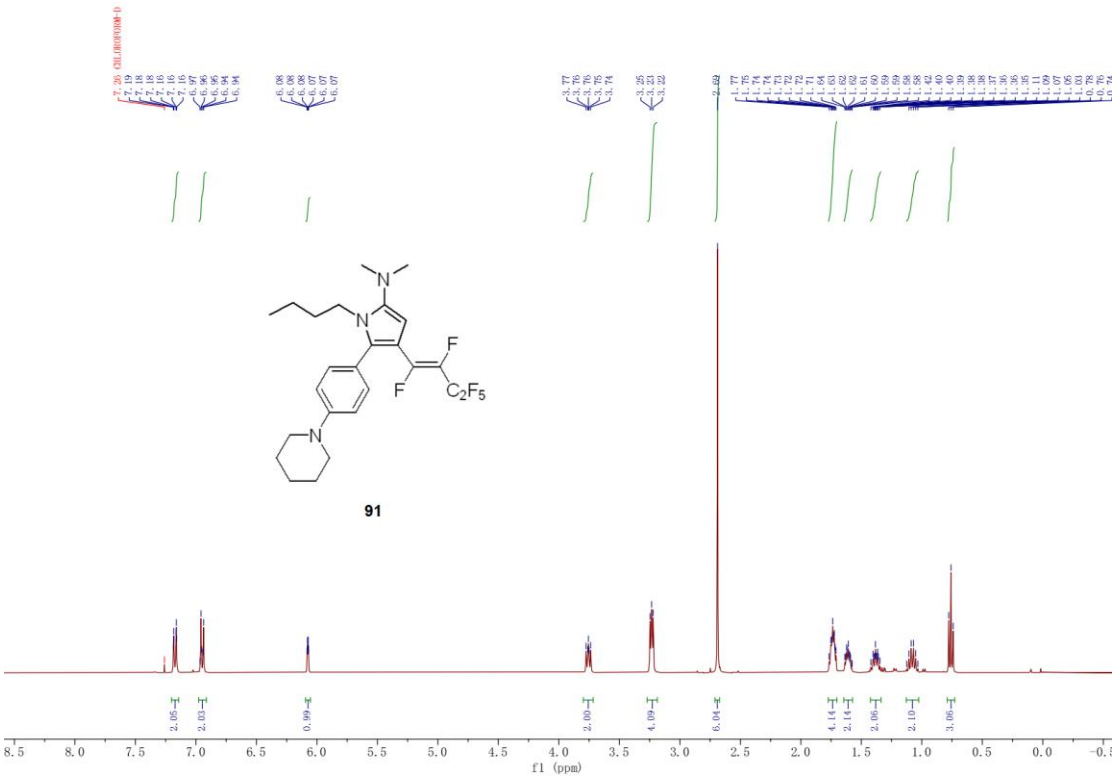
^{19}F NMR spectra of the product **90** (376 MHz, $CDCl_3$):



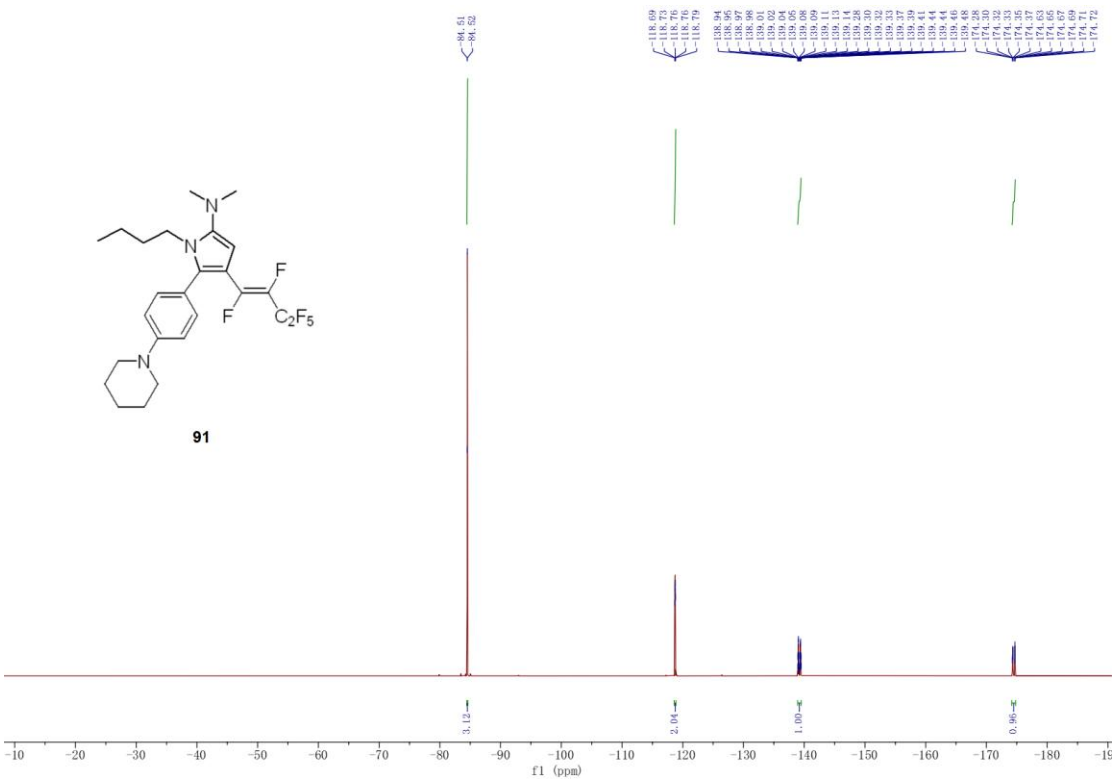
^{13}C NMR spectra of the product **90** (101 MHz, $CDCl_3$):



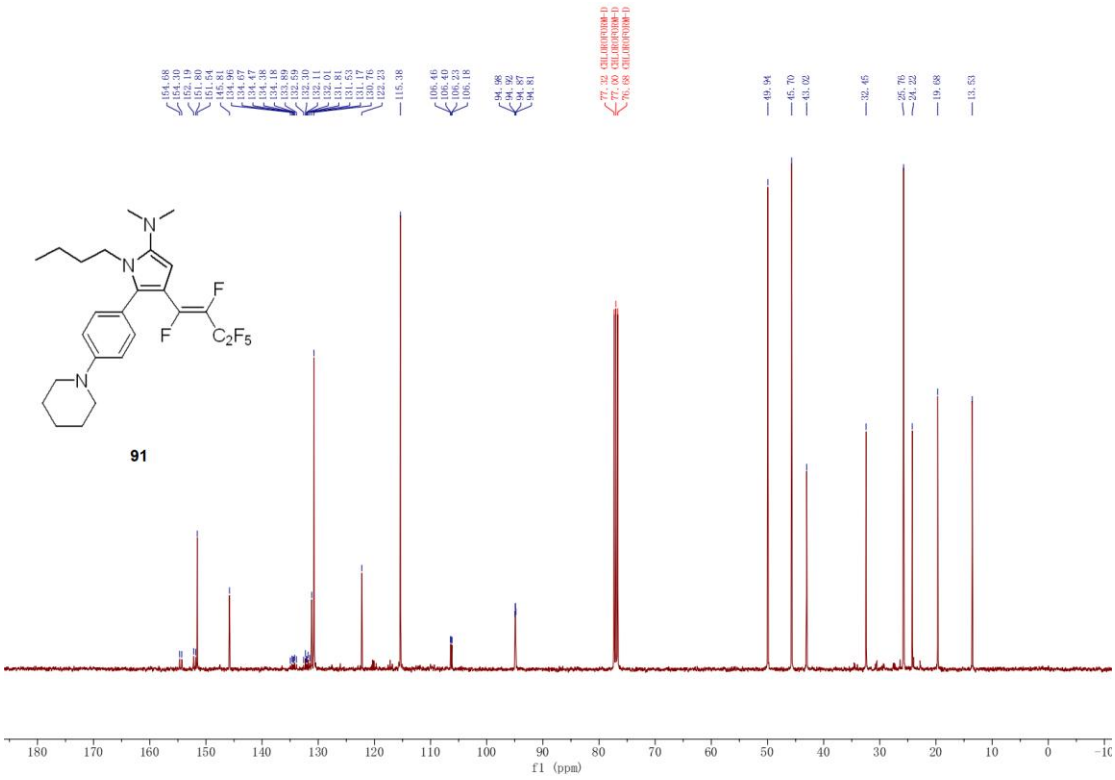
^{1}H NMR spectra of the product **91** (400 MHz, $CDCl_3$):



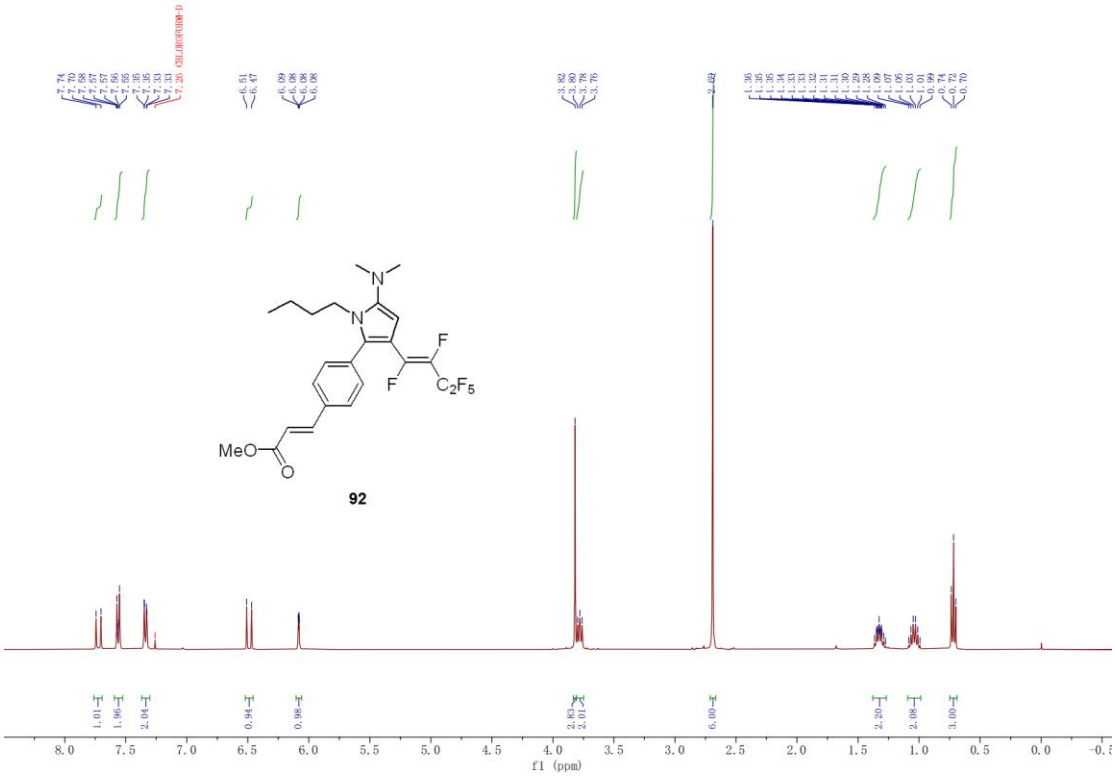
^{19}F NMR spectra of the product **91** (376 MHz, $CDCl_3$):



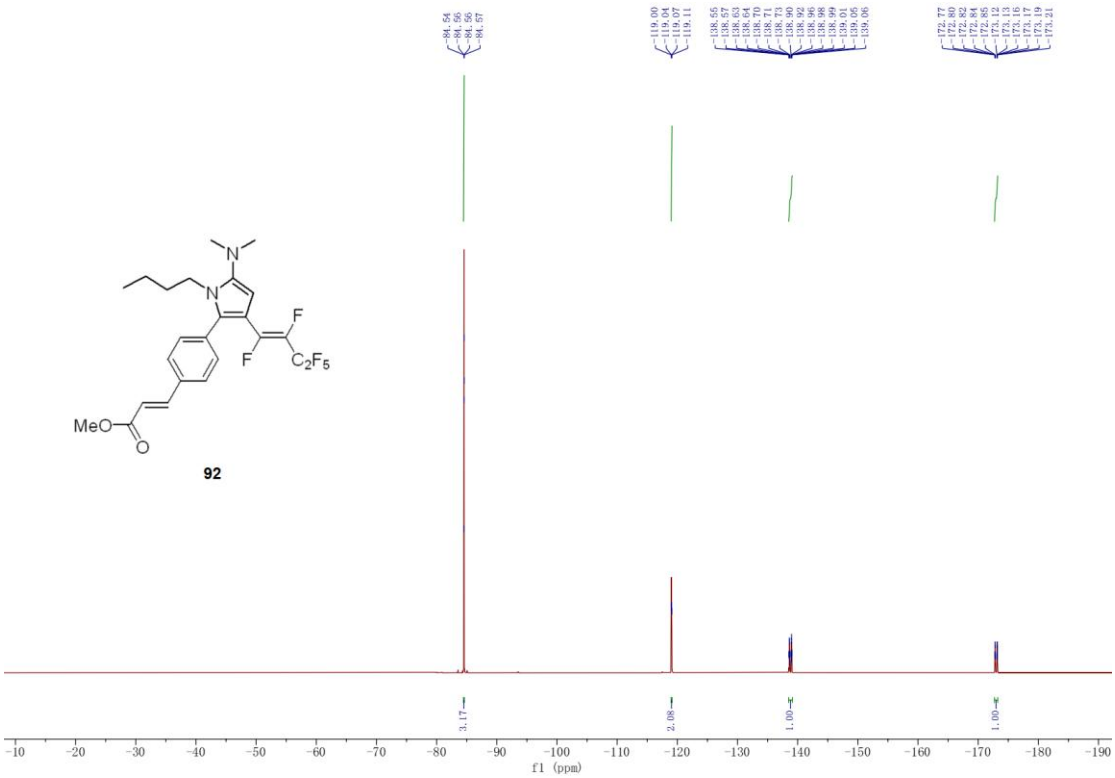
^{13}C NMR spectra of the product **91** (101 MHz, $CDCl_3$):



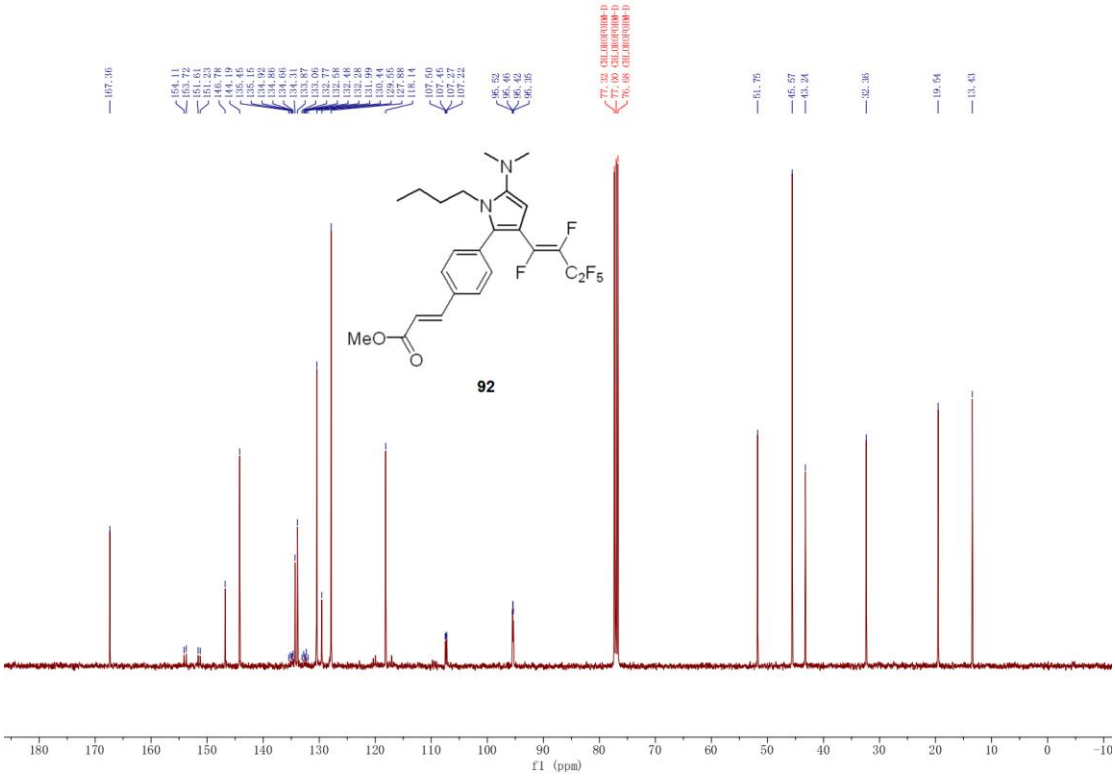
^{1}H NMR spectra of the product **92** (400 MHz, $CDCl_3$):



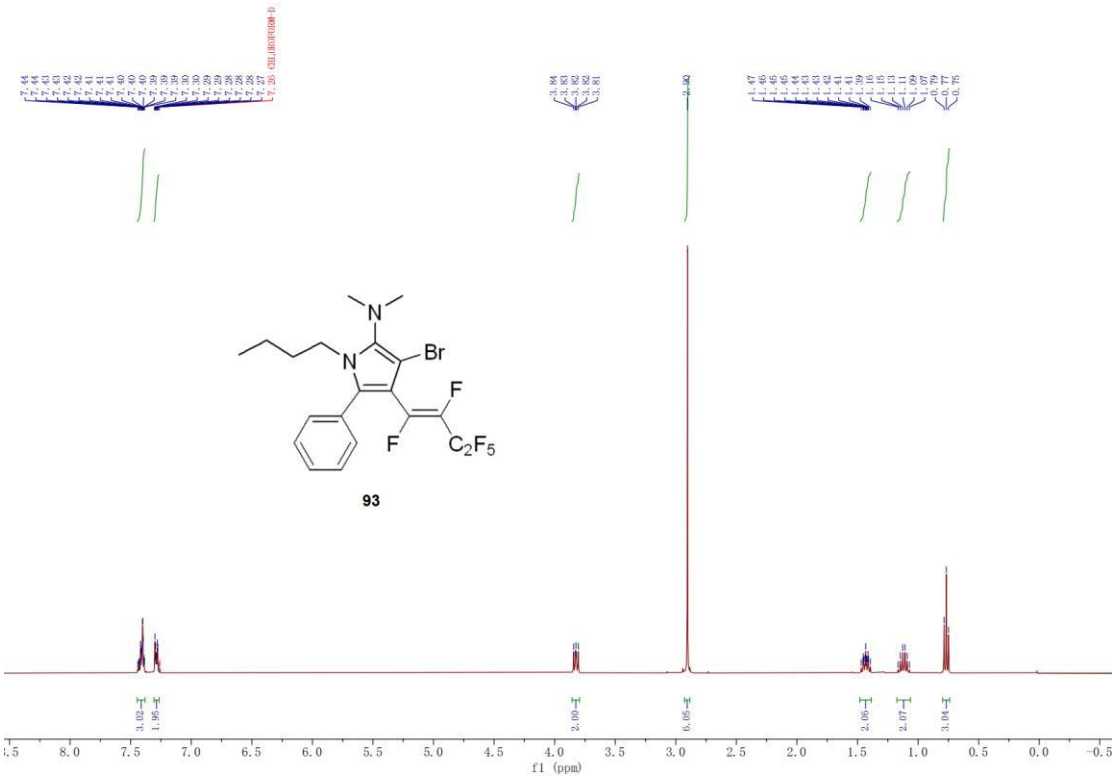
^{19}F NMR spectra of the product **92** (376 MHz, $CDCl_3$):



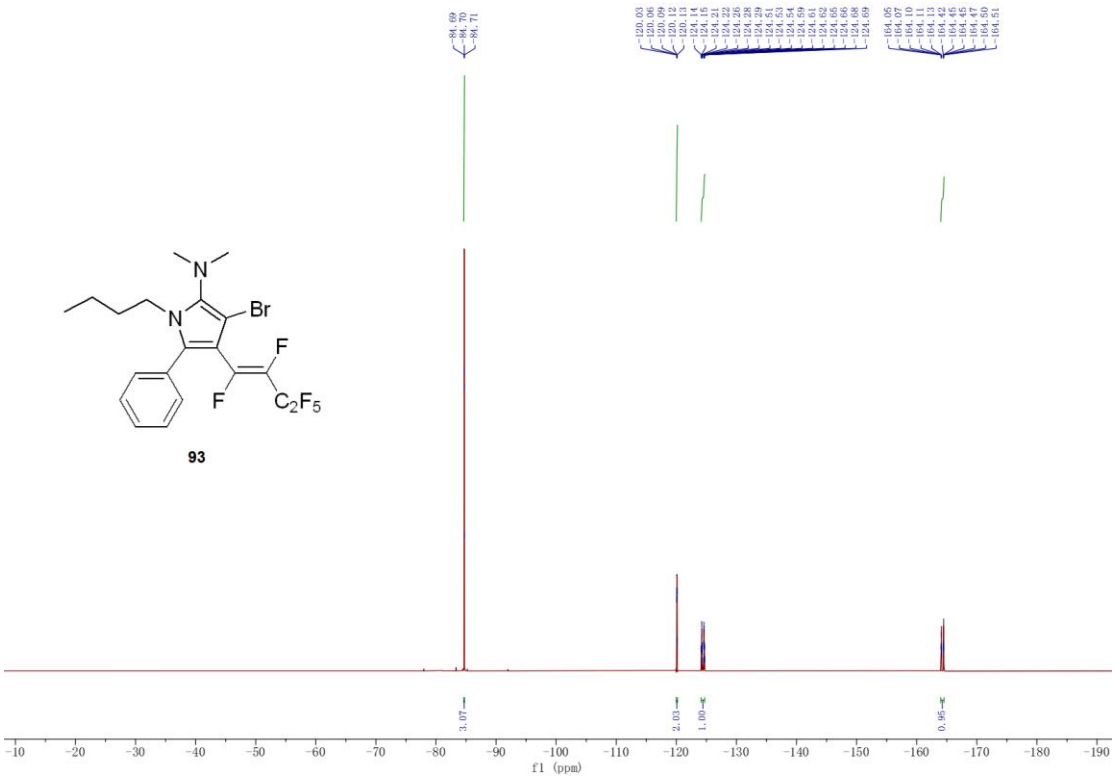
^{13}C NMR spectra of the product **92** (101 MHz, $CDCl_3$):



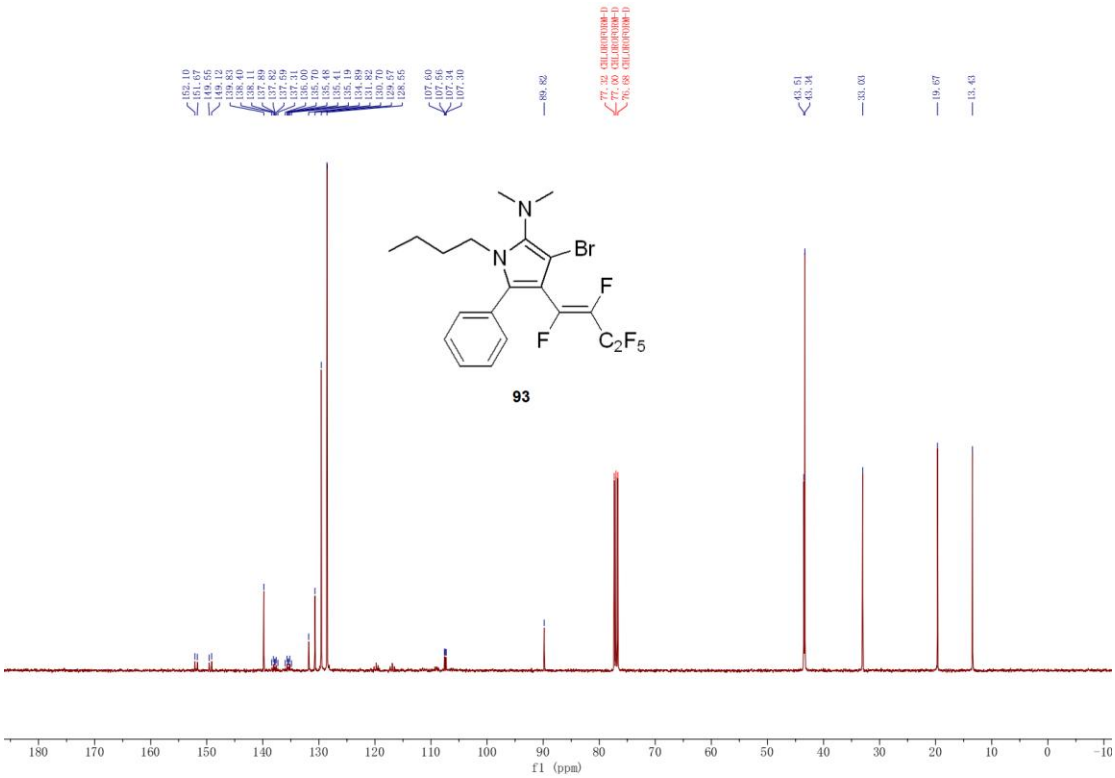
^{1}H NMR spectra of the product **93** (400 MHz, $CDCl_3$):



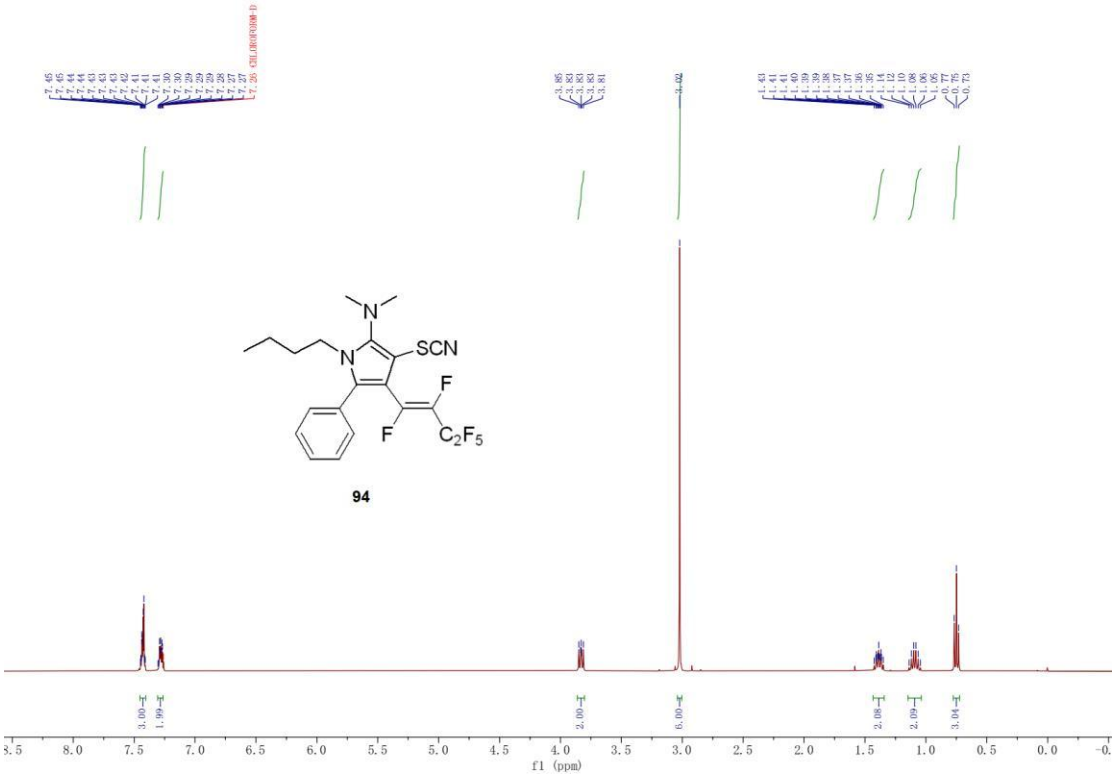
^{19}F NMR spectra of the product **93** (376 MHz, $CDCl_3$):



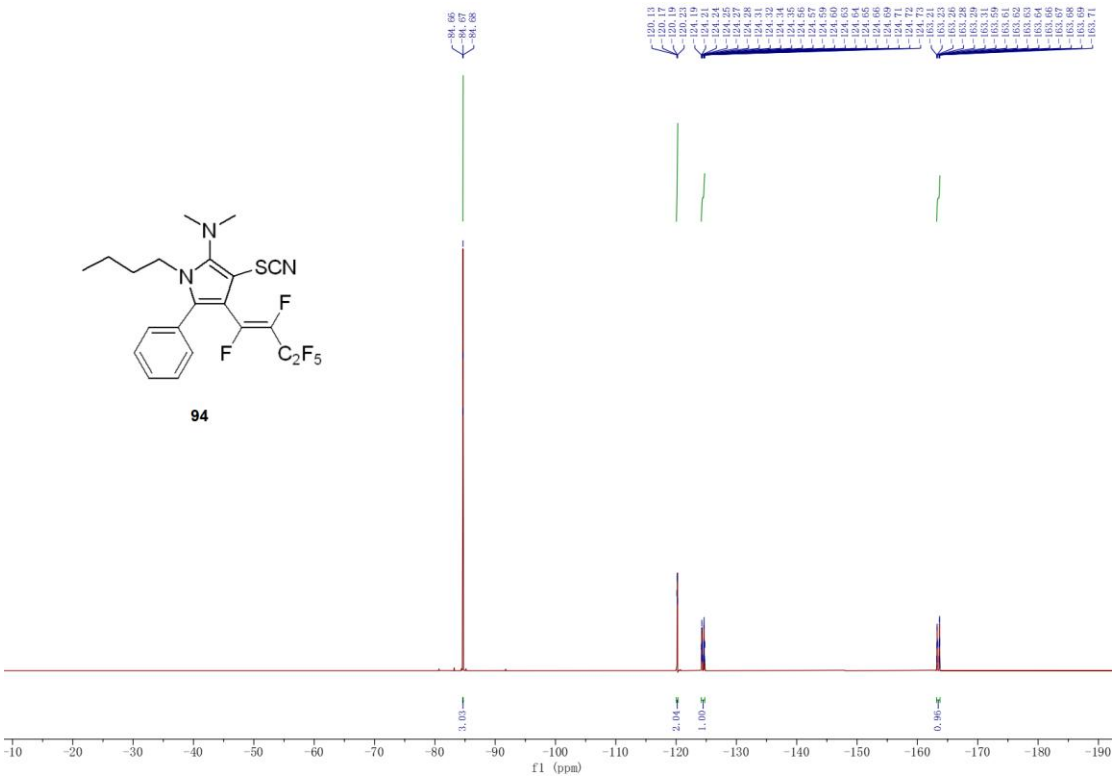
^{13}C NMR spectra of the product **93** (101 MHz, $CDCl_3$):



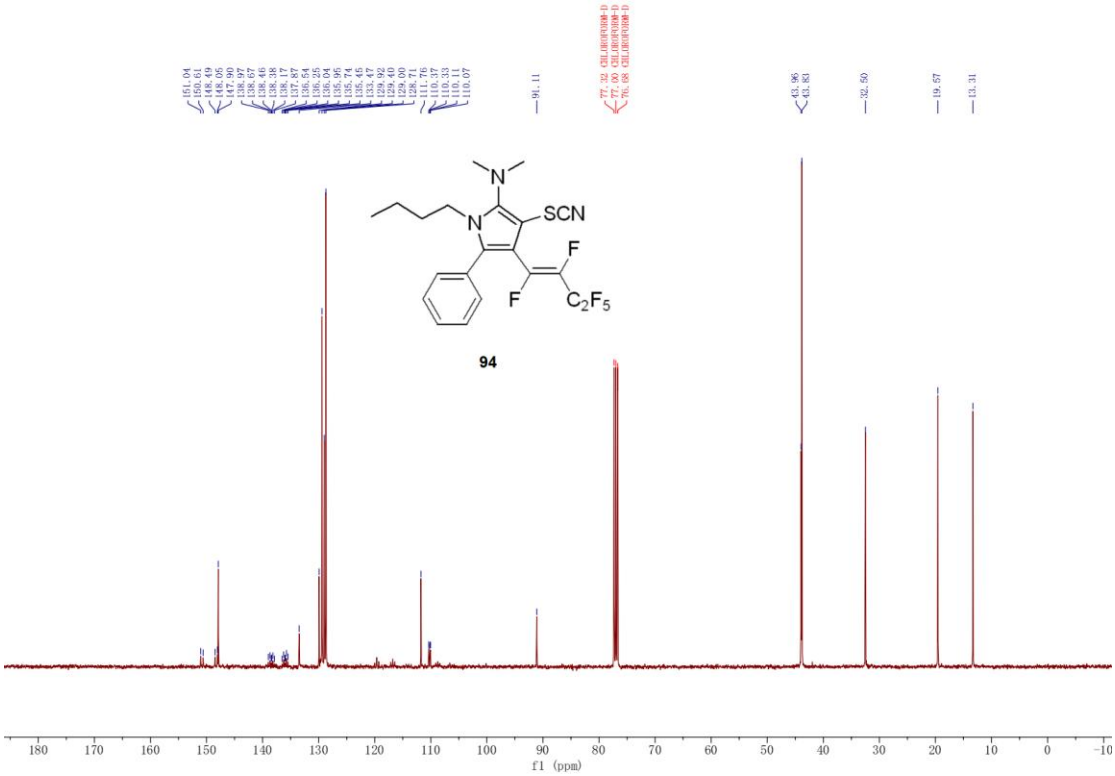
^{1}H NMR spectra of the product **94** (400 MHz, $CDCl_3$):



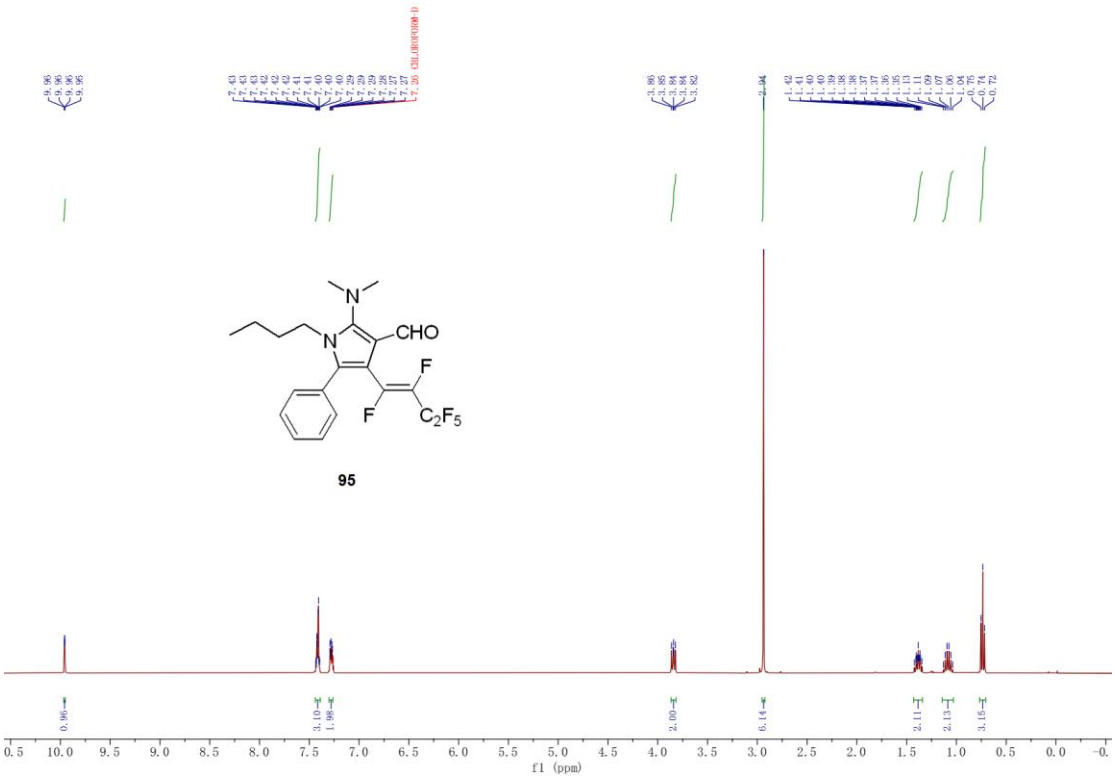
^{19}F NMR spectra of the product **94** (376 MHz, $CDCl_3$):



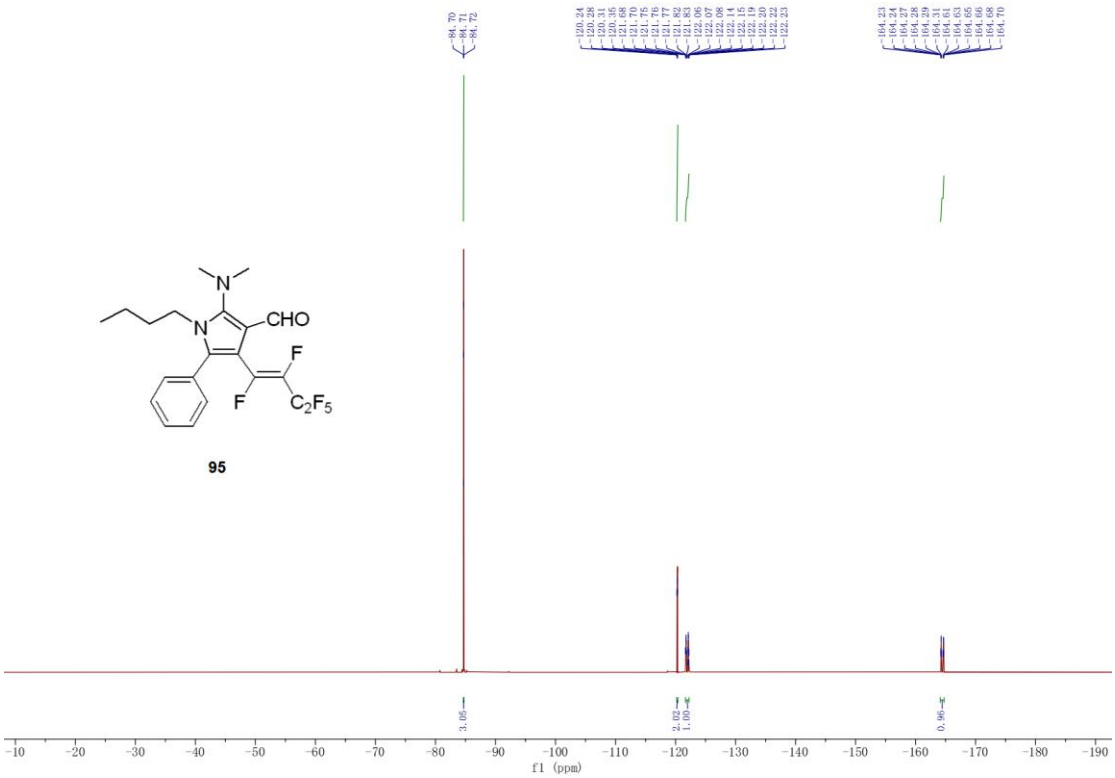
^{13}C NMR spectra of the product **94** (101 MHz, $CDCl_3$):



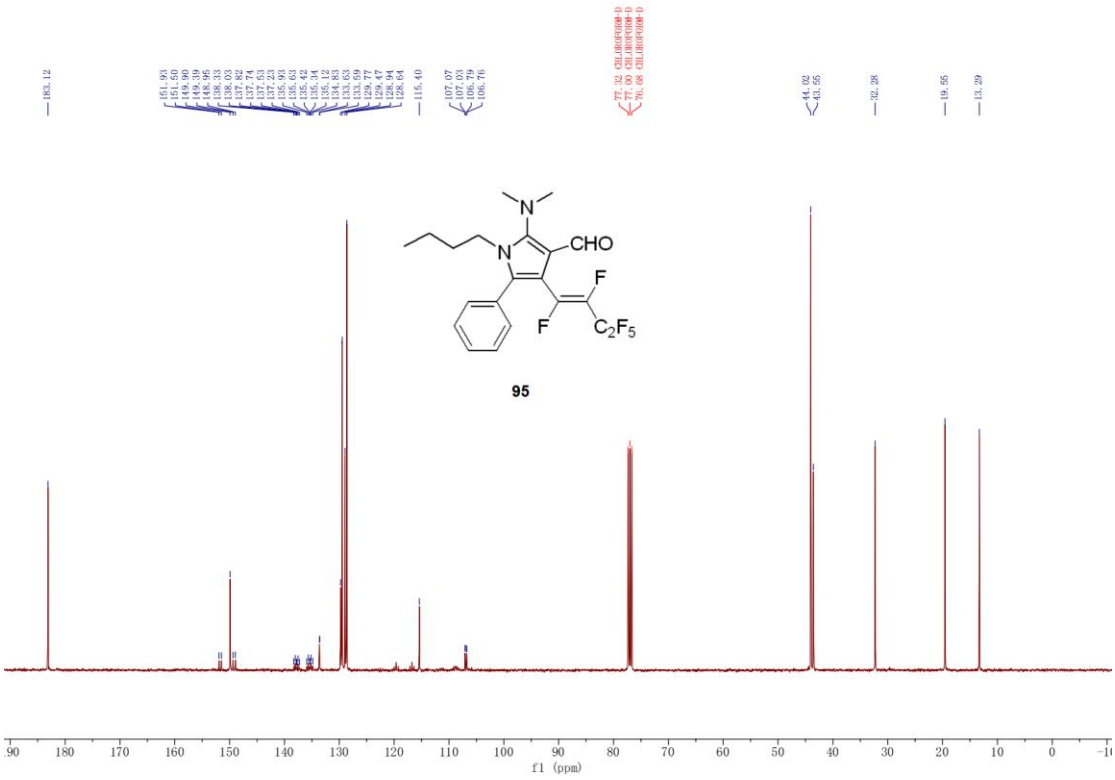
^{1}H NMR spectra of the product **95** (400 MHz, $CDCl_3$):



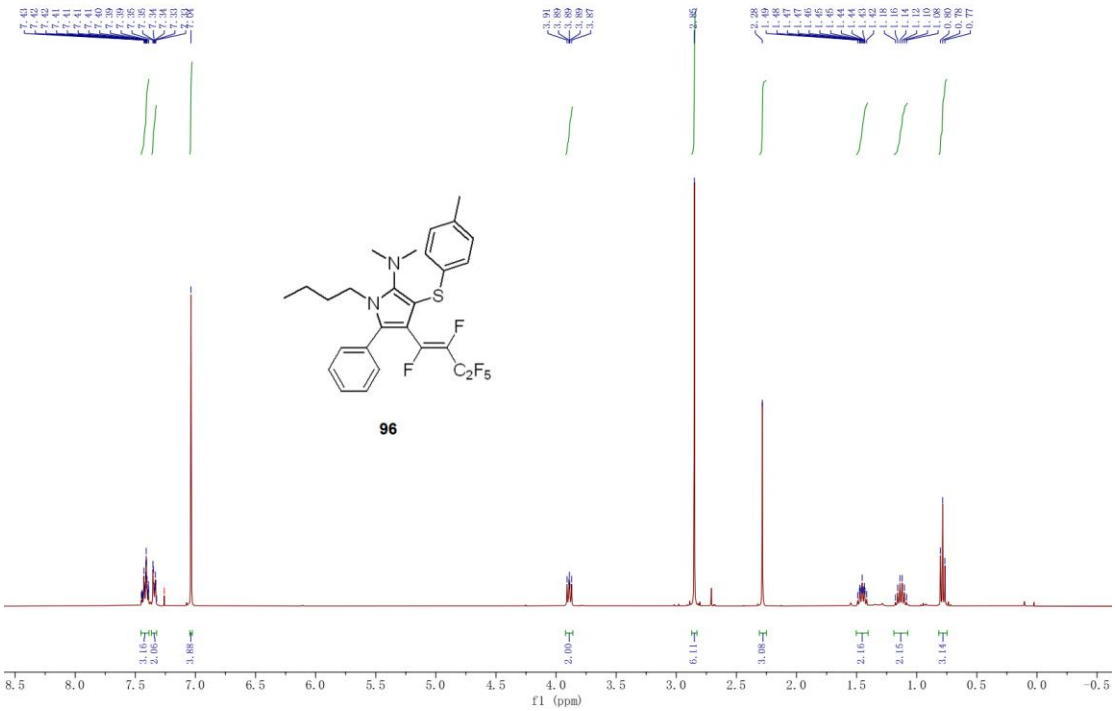
^{19}F NMR spectra of the product **95** (376 MHz, $CDCl_3$):



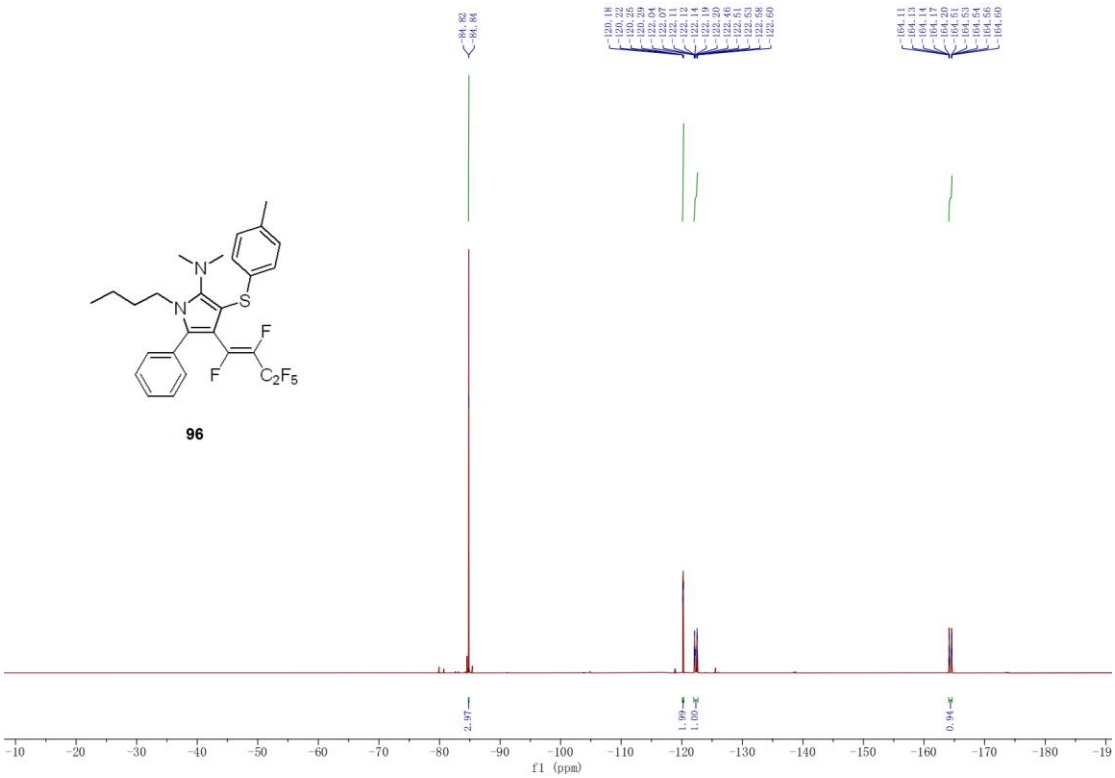
^{13}C NMR spectra of the product **95** (101 MHz, $CDCl_3$):



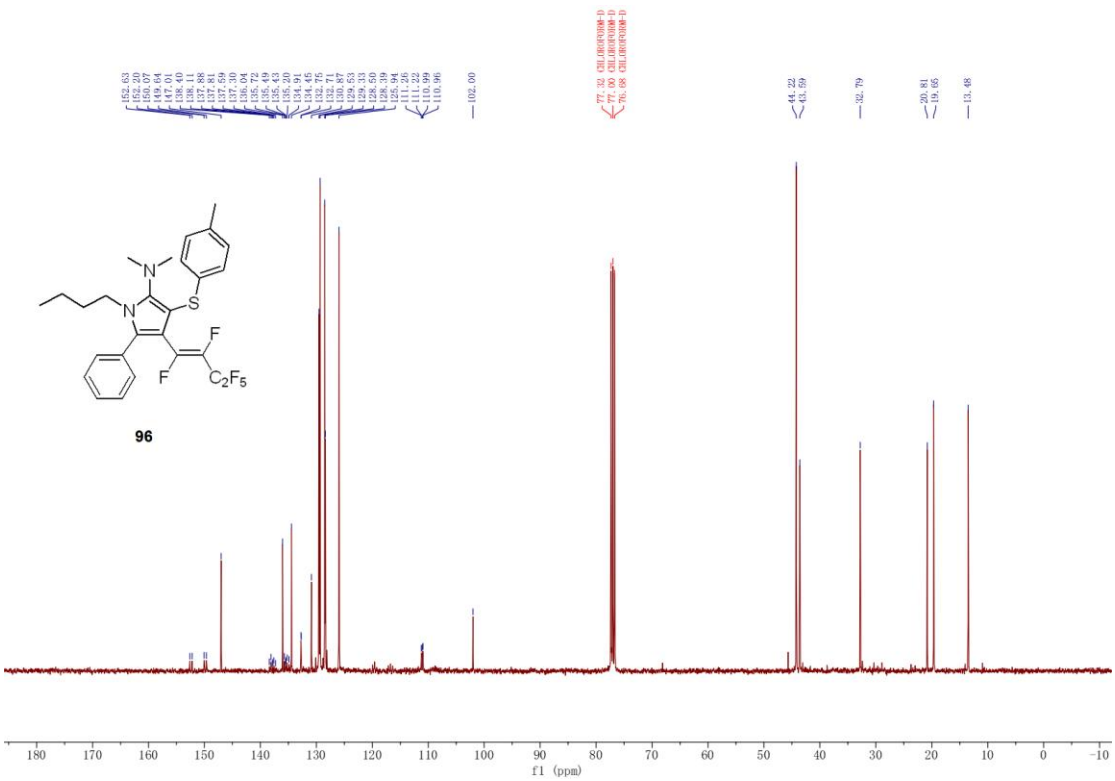
^{1}H NMR spectra of the product **96** (400 MHz, $CDCl_3$):



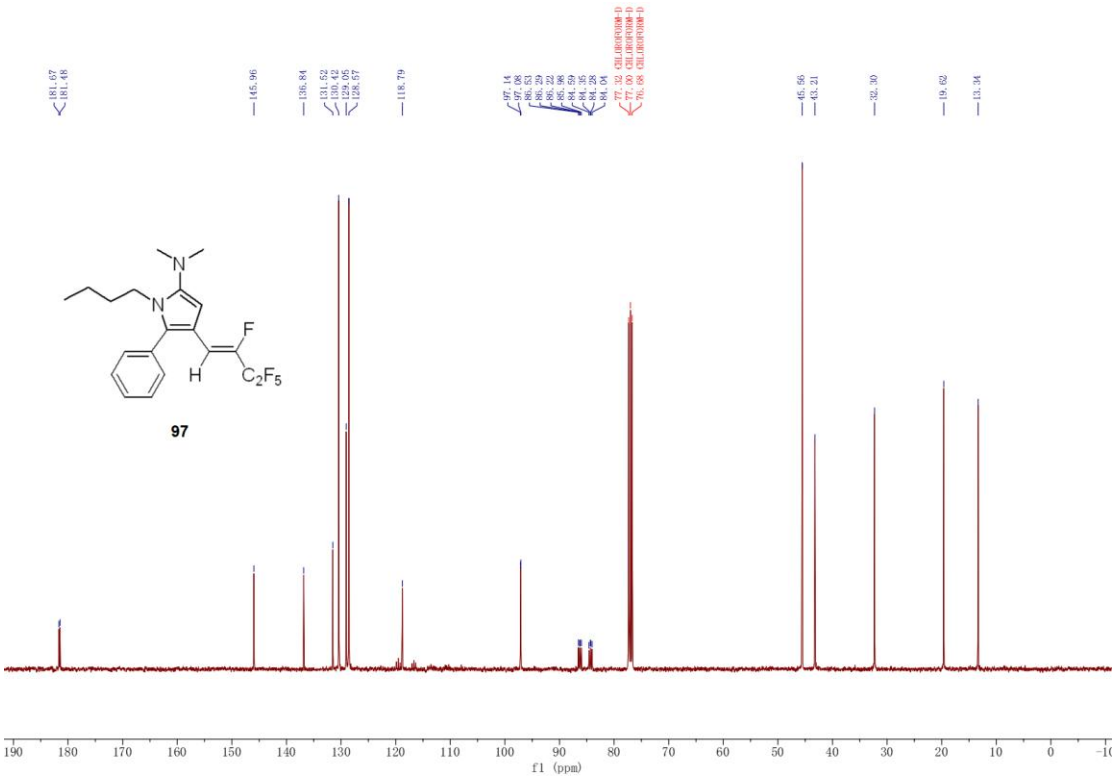
^{19}F NMR spectra of the product **96** (376 MHz, $CDCl_3$):



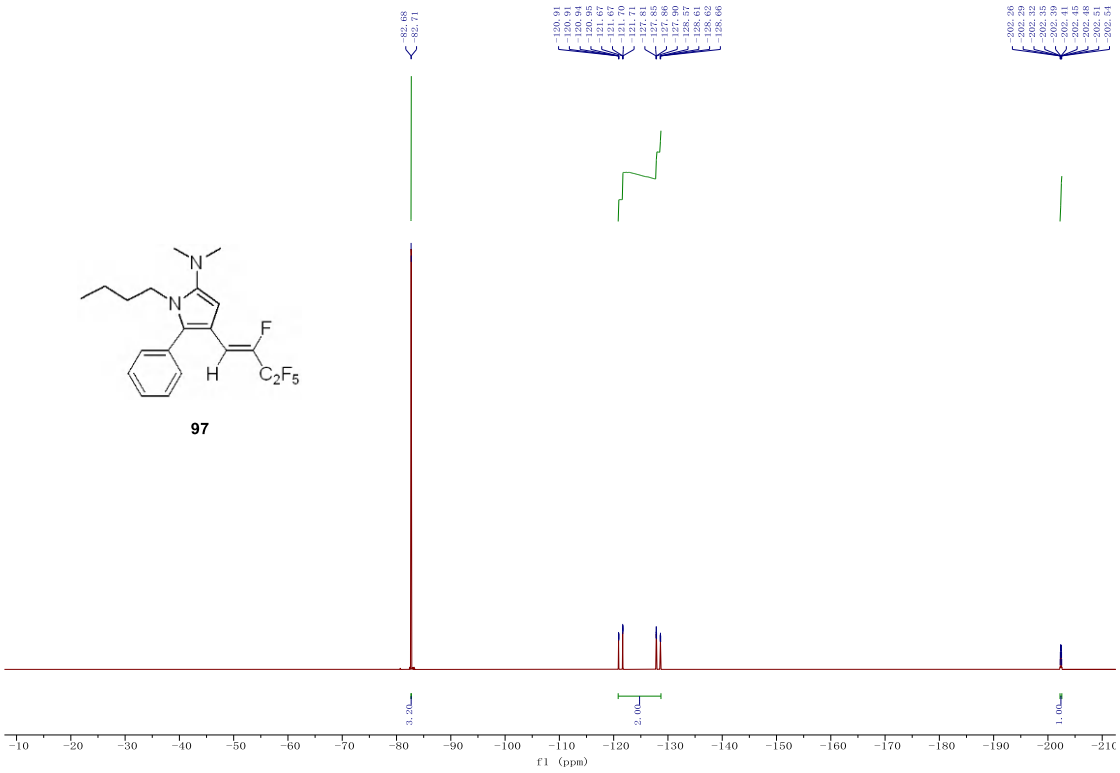
^{13}C NMR spectra of the product **96** (101 MHz, $CDCl_3$):



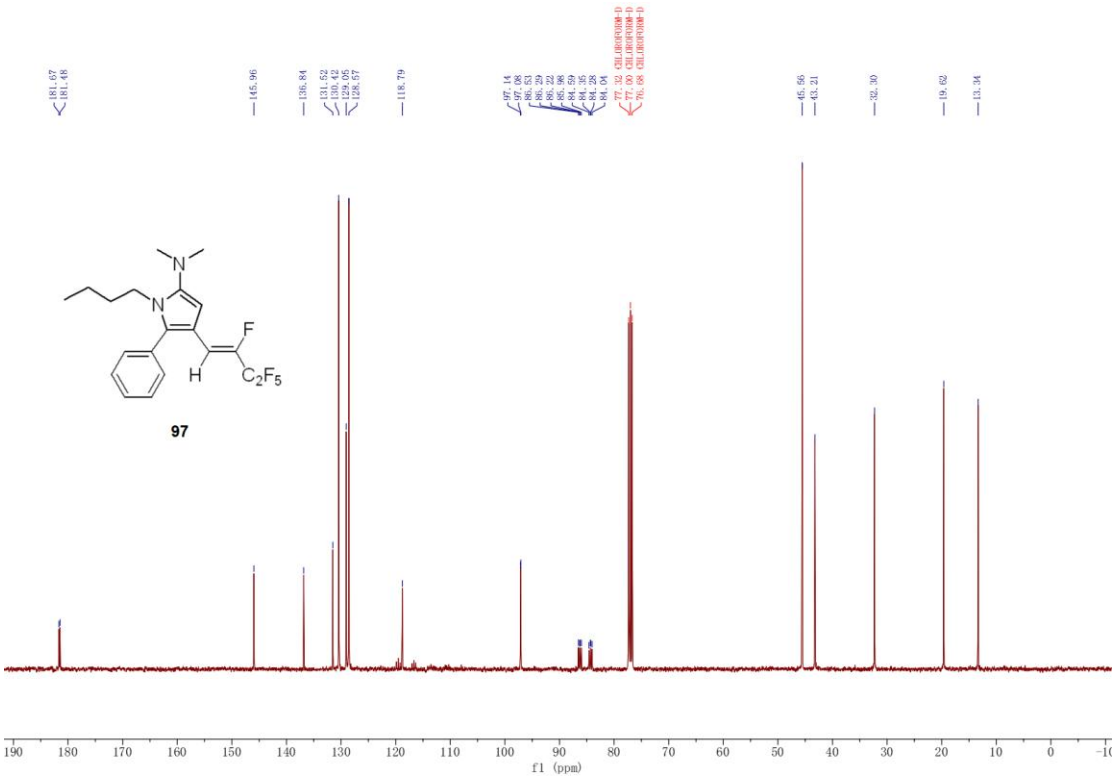
^{1}H NMR spectra of the product **97** (400 MHz, $CDCl_3$):



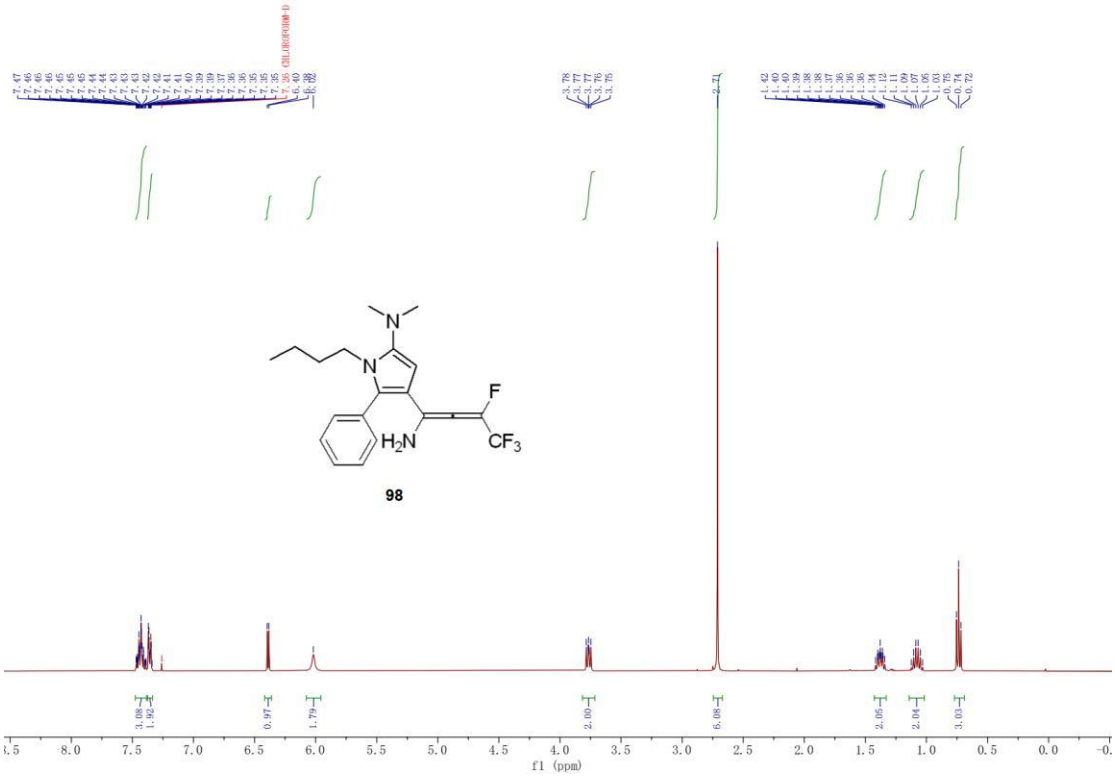
^{19}F NMR spectra of the product **97** (376 MHz, $CDCl_3$):



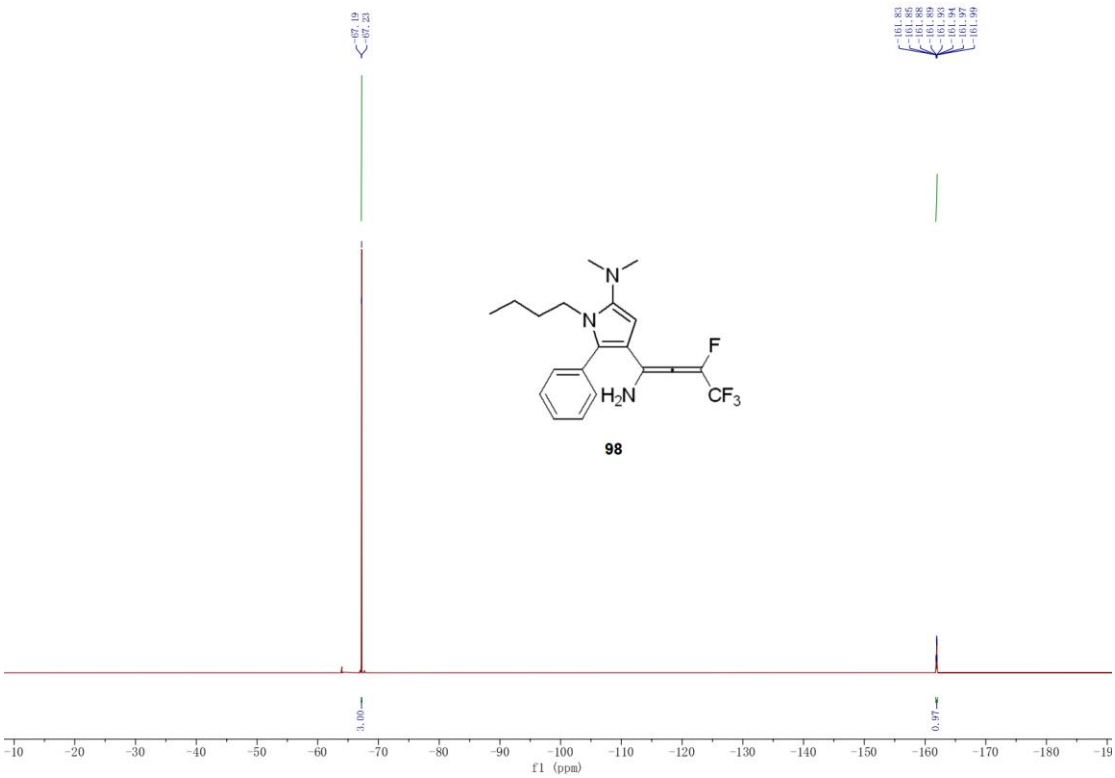
^{13}C NMR spectra of the product **97** (101 MHz, $CDCl_3$):



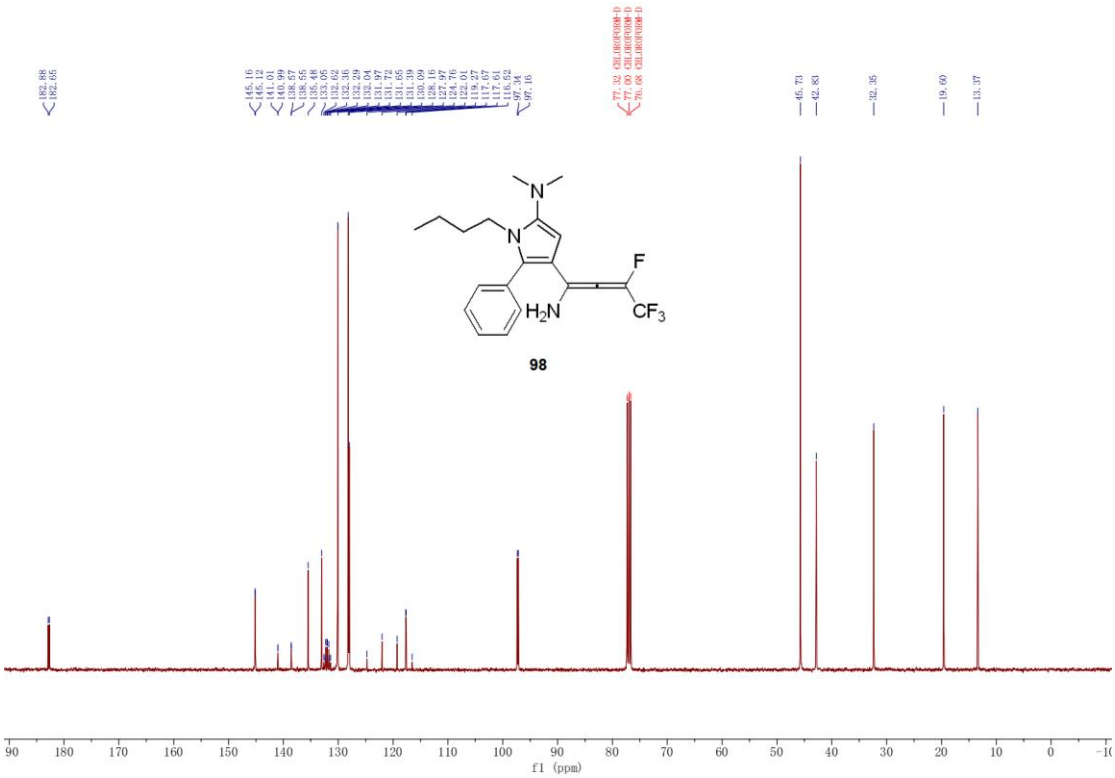
^{1}H NMR spectra of the product **98** (400 MHz, $CDCl_3$):



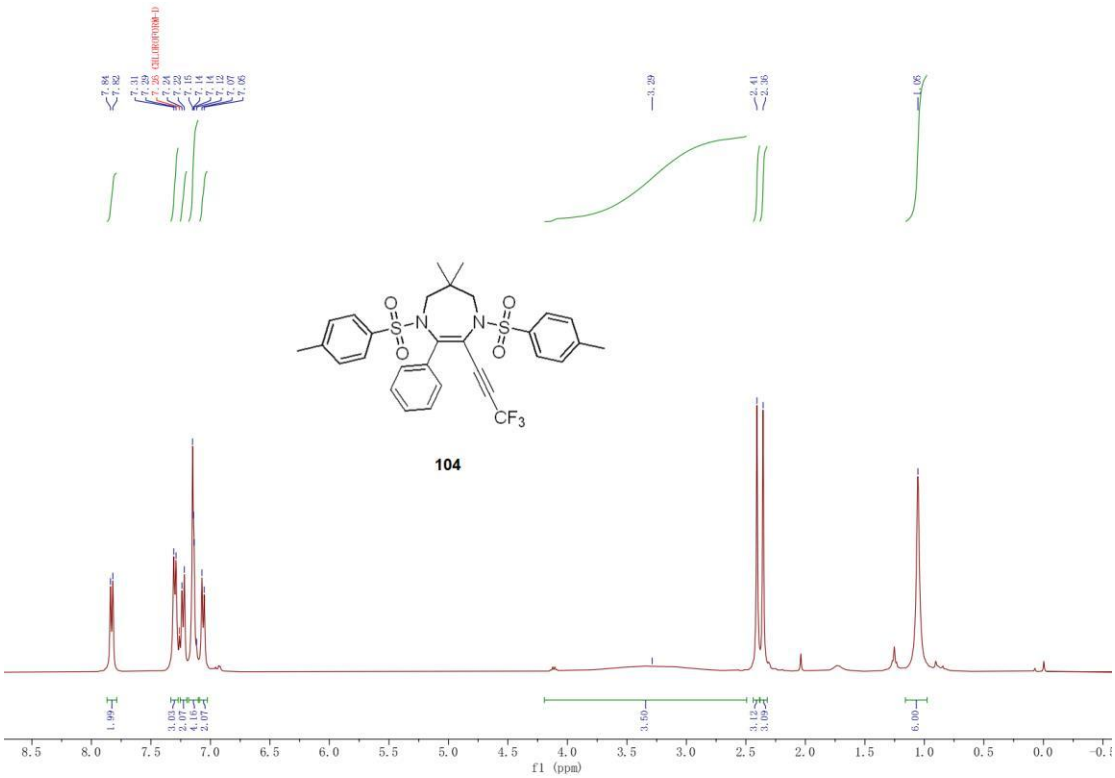
^{19}F NMR spectra of the product **98** (376 MHz, $CDCl_3$):



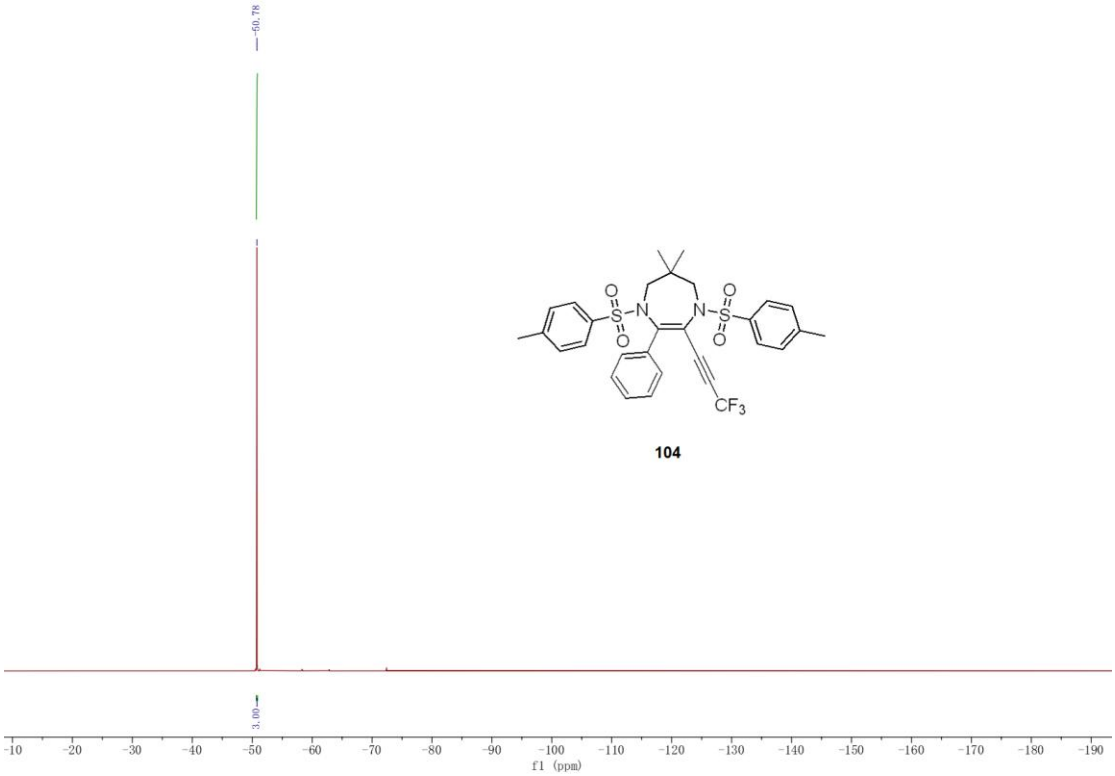
^{13}C NMR spectra of the product **98** (101 MHz, $CDCl_3$):



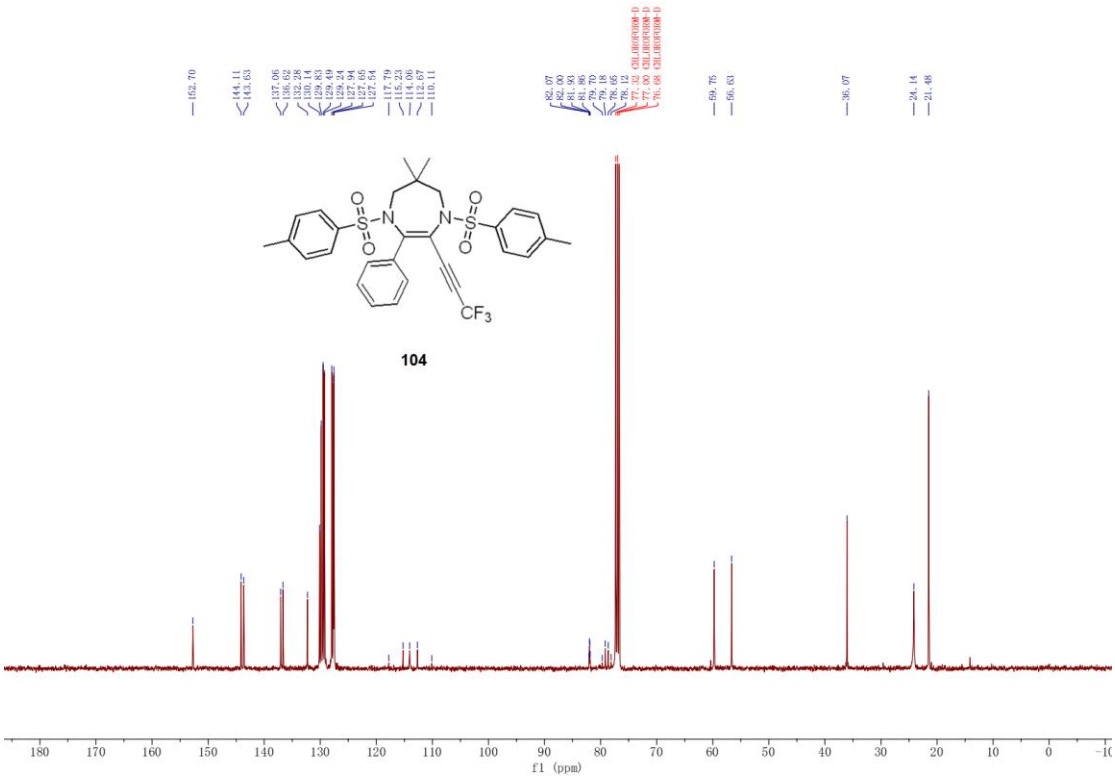
^{1}H NMR spectra of the product **104** (400 MHz, $CDCl_3$):



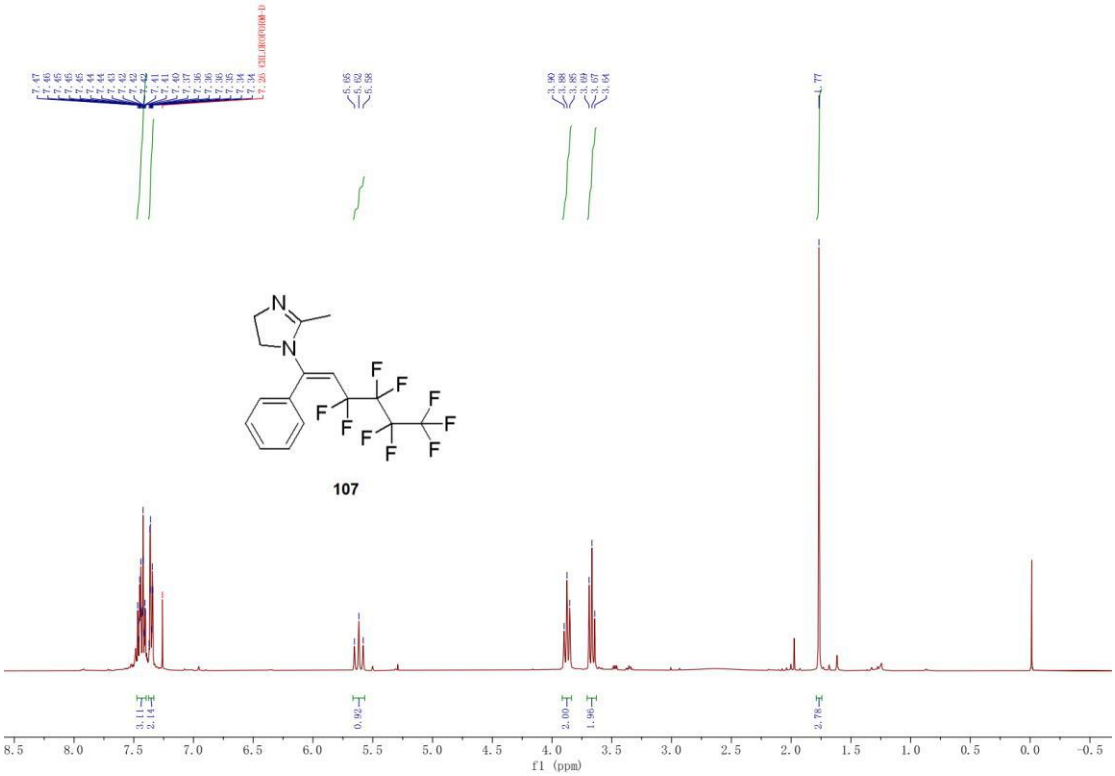
^{19}F NMR spectra of the product **104** (376 MHz, $CDCl_3$):



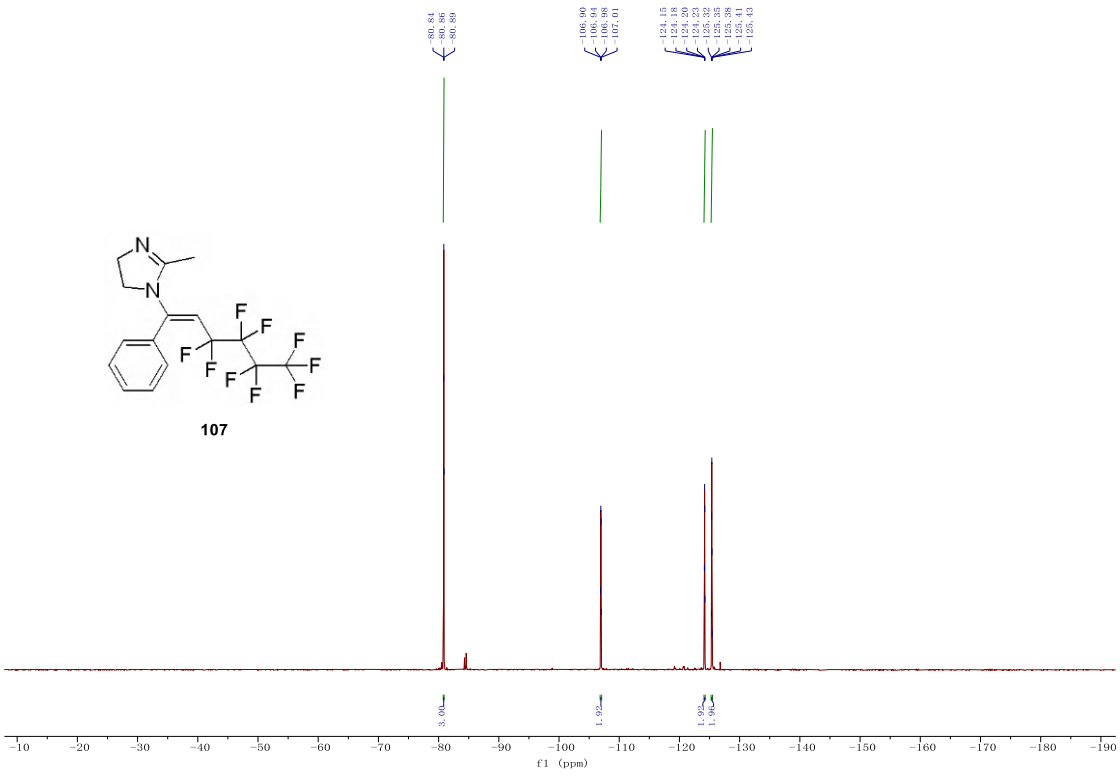
^{13}C NMR spectra of the product **104** (101 MHz, $CDCl_3$):



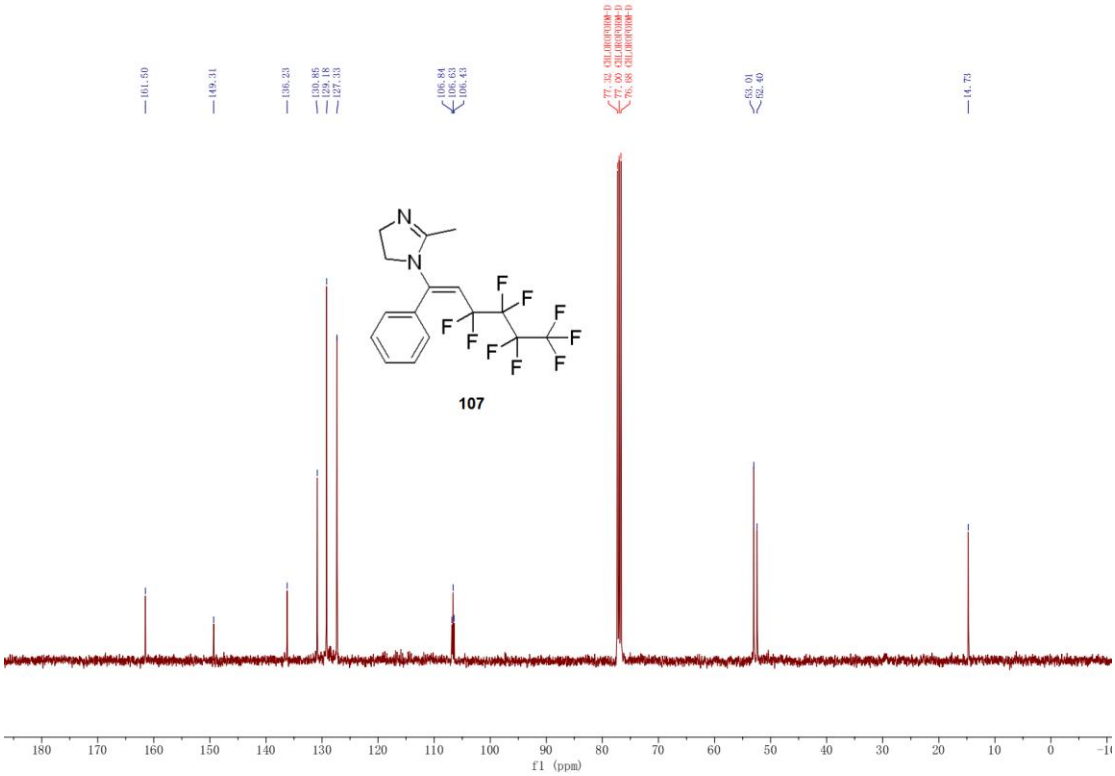
^{1}H NMR spectra of the product **107** (400 MHz, $CDCl_3$):



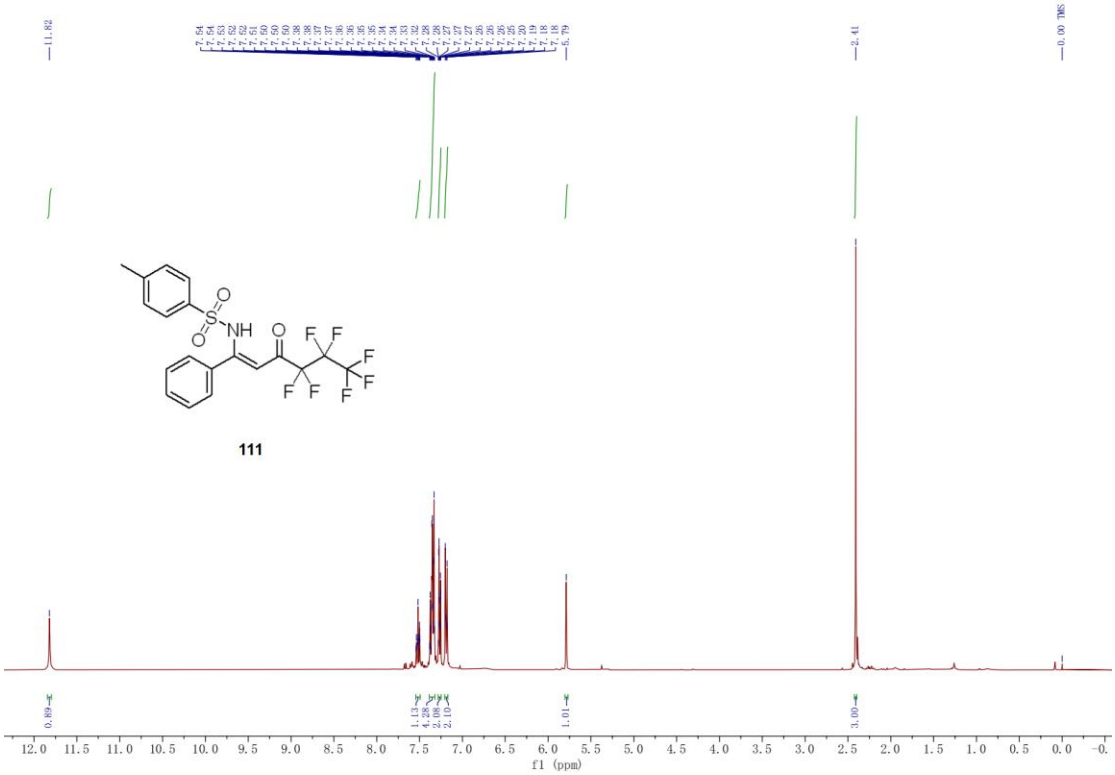
^{19}F NMR spectra of the product **107** (376 MHz, $CDCl_3$):



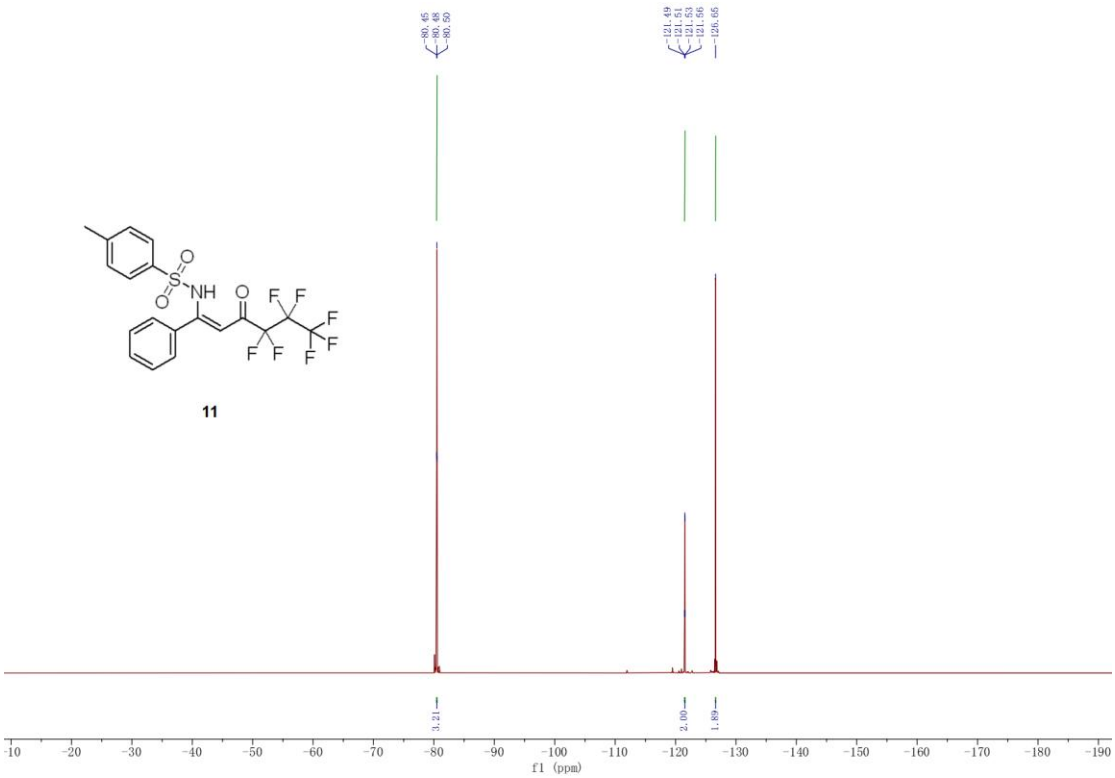
^{13}C NMR spectra of the product **107** (101 MHz, $CDCl_3$):



^{1}H NMR spectra of the product **111** (400 MHz, $CDCl_3$):



^{19}F NMR spectra of the product **111** (376 MHz, $CDCl_3$):



^{13}C NMR spectra of the product **111** (101 MHz, $CDCl_3$):