Halogen-bond-assisted radical remote difunctionalization of bicyclo[1.1.1]butane skeleton

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1. General Information

All commercially available compounds were used as received unless otherwise noted. Anhydrous solvents, purchased from J&K Scientific and Adamas-beta®, were used as received. Reaction temperatures are reported as the temperature of the medium surrounding the vessel.

The photocatalytic reactions were performed on a commercial photochemical-reactor with blue LEDs (455 nm, 10 W) and cooling water. The reaction temperature was measured to be between 18 °C and 23 °C using this setup. The employed photocatalysts were purchased from Shanghai Bidepharm.

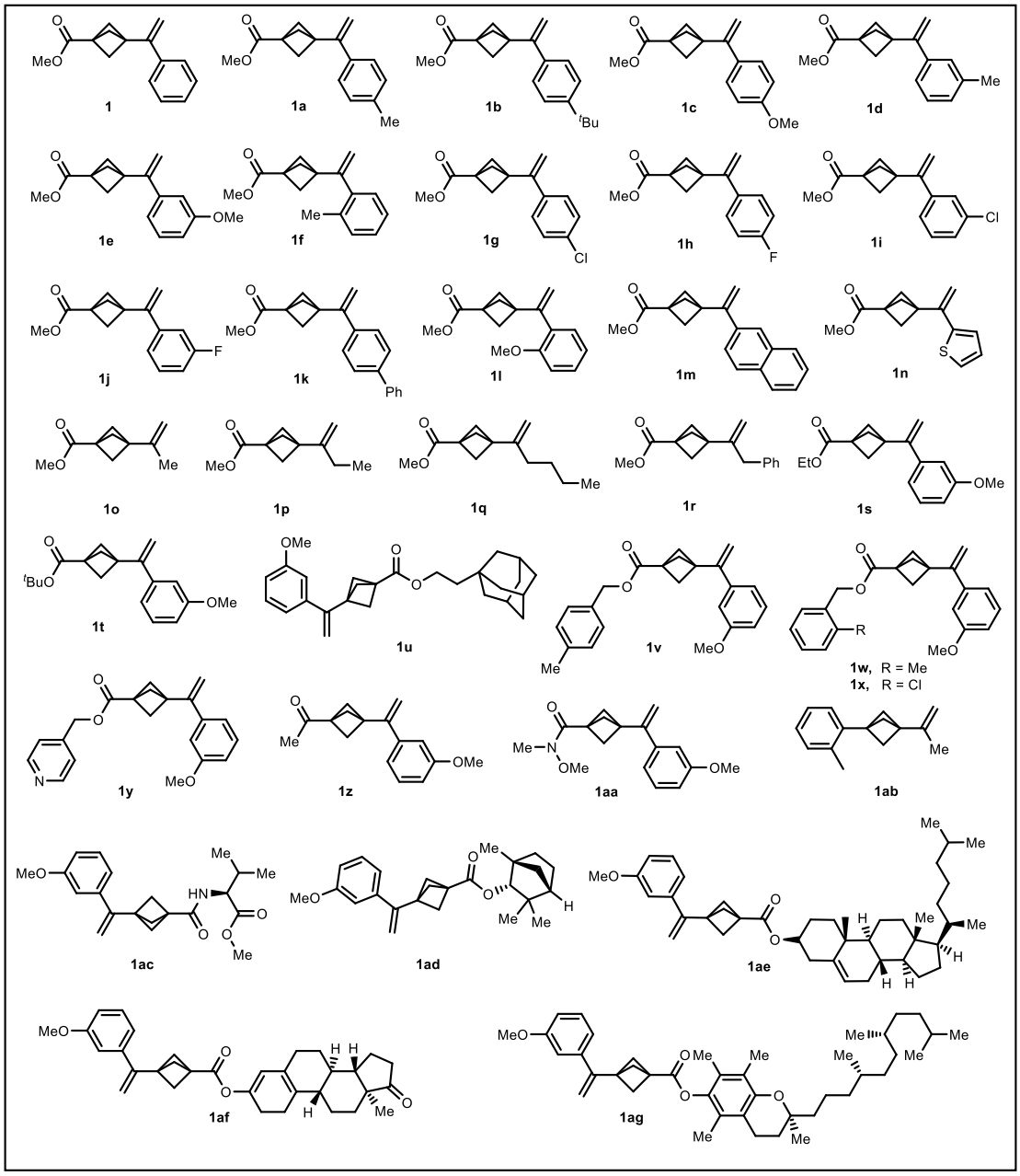
NMR spectra were recorded at room temperature on a Bruker Avance Neo 400 instrument. The chemical shifts (δ) are given in ppm. Residual solvent signal tetramethylsilane (δ = 0.0 ppm) was used as internal reference for ^{1}H and ^{13}C NMR. ^{19}F NMR spectra were not calibrated by an internal reference. All ^{13}C and ^{19}F NMR spectra were recorded with complete proton decoupling. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. All the NMRs were processed using Mestrenova 12 applying standard phase and baseline corrections. Coupling constants (*J*) are quoted in Hz. High-resolution mass spectra (HRMS) were recorded on Bruker impact HD (ESI) mass spectrometers. Melting point detector: binocular microscope XT4A melting point apparatus (without correct).

Analytical thin layer chromatography (TLC) was performed on XINNUO silica gel GF254 plates and visualized by exposure to ultraviolet light (254 nm). Column chromatography was carried out using XINNUO silica gel (200-300 mesh) eluting with solvent purchased from General-reagent® without further purification.

2. Experimental Procedures and Characterization Data

2.1 Starting Material Synthesis

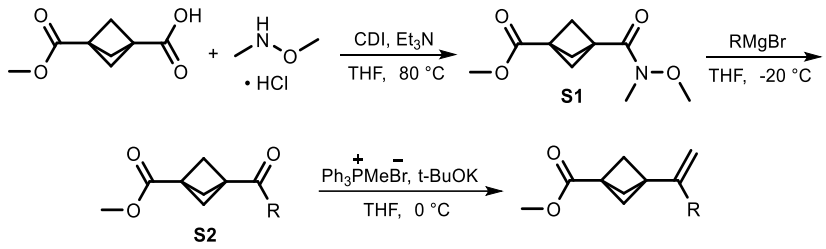
*Vinylbicyclo[1.1.1]pentanes (**VBCPs**):*



Note: Compound **1ab** was literature known and the characterization data were in accord with the reported.

Preparation of vinylbicyclo[1.1.1]pentanes:

General Procedure A for the synthesis of vinylbicyclo[1.1.1]pentanes (GP-A):[1][2]

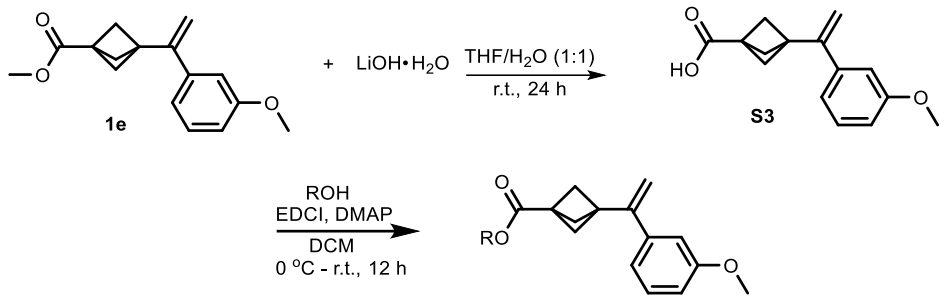


Step 1: To a 250 mL round bottom flask were added 1,1'-carbonyldiimidazole (CDI) (8.92 g, 55 mmol, 1.1 equiv), 3-(methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic acid (8.51 g, 50 mmol 1.0 equiv) and THF (50 ml, 1.0 M), and then the reaction mixture was heated to 70 ℃ for 30 min. To another 50 mL round bottom flask were added *N*, *O*-dimethylhydroxylamine hydrochloride (5.36 g, 55 mmol 1.1 equiv), Et_3N (7.7 ml, 55 mmol 1.1 equiv), and the reaction mixture was stirred for 10 min. Then, the solution of *N*, *O*-dimethylhydroxylamine hydrochloride in THF was added into the above THF solution of the acid and CDI in a 250 mL round bottom flask. Next, the reaction mixture was stirred at 80 ℃ for 5 hours. After that, Then the reaction was quenched with 3M HCl (100 ml) and extracted with DCM (50 ml × 3). The combined organic layer was dried over anhydrous Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by a column chromatography (eluent: PE : EtOAc = 1 : 1) to give the desired Weinreb amide **S1** as a white solid in 94% yield.

Step 2: The Weinreb amide **S1** (1.0 equiv) was dissolved in anhydrous THF (1M) under nitrogen atmosphere and then the solution was cooled to -20 ℃. Then RMgBr (1.0 equiv) was added dropwise at -20 ℃. Then the mixture was stirred at this temperature overnight. After the reaction completion, the mixture was quenched with sat. NH_4Cl aq. and the mixture was extracted with ethyl acetate. The organic layers were dried by Na_2SO_4, then filtered and removed under vacuum to give the crude product which was then purified by silica gel column chromatography (eluent: PE : EtOAc = 10 : 1) to provide the product **S2**.

Step 3: Under nitrogen atmosphere, a solution of methyl triphenylphosphonium bromide (2.0 equiv) in anhydrous THF was cooled to 0 °C, followed by addition of t-BuOK (2.0 equiv). The reaction mixture was stirred at 0 °C for 1 h, and then a solution of the ketone **S2** (1.0 equiv) in anhydrous THF was added dropwise. The resulting mixture was warmed gradually to room temperature and kept stirring for 12 h. The resultant reaction solution was quenched with sat. NH_4Cl aq. and the mixture was extracted with EtOAc. The organic layers were dried by Na_2SO_4, then filtered and removed under vacuum to yield a residue, which was further purified over silica gel flash column chromatography (eluent: PE : EtOAc = 15 : 1) to afford the product.

General Procedure B for the synthesis of vinylbicyclo[1.1.1]pentanes (GP-B):[3]



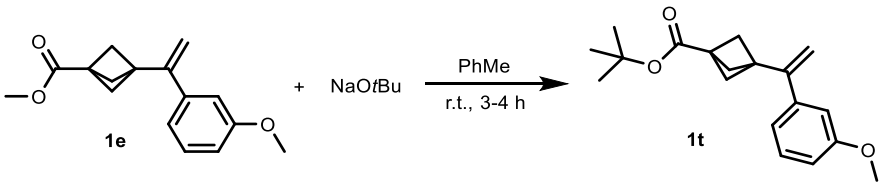
Step 1: To a flask equipped with a stir bar was added the **1e** (5.16 g, 20 mmol, 1.0 equiv) and $LiOH·H_2O$ (1.68 g, 40 mmol, 2.0 equiv). THF (50 mL) and water (50 mL) were added, and the mixture was stirred for 12 h at room temperature. After that time, the reaction was acidified with 1M HCl (100 mL), extracted with EtOAc (50 mL × 3). The combined organic layer was washed brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo.* giving the crude product as a white solid. The acquired acid was used in next step directly without further purification.

Step 2: To a flask equipped with a stir bar was added the acid **S3** (1 mmol, 1.0 equiv) and anhydrous DCM (5 mL, 0.2M), then the solution was cooled to 0 ℃. DMAP (0.1 mmol, 10 mol%) and EDCI (1.3 mmol,1.3 equiv) was added to the solution and the mixture was stirred at this temperature for 10 min. The alcohol (1.2 mmol, 1.2 equiv) was added into the reaction mixture, which was stirred for 3 h. The reaction was

quenched with saturated sodium bicarbonate, extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: PE : EtOAc = 10 : 1) to afford the product.

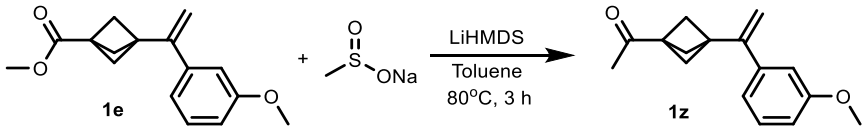
Note: Compounds **1, 1a-1r** were prepared according to **GP-A**. Compounds **1s-1y, 1ad-1ag** were prepared according to **GP-B** .

Synthesis of vinylbicyclo[1.1.1]pentane 1t:(4)



To a stirred suspension of NaO*t*Bu (0.12 g, 1.25 mmol, 2.5 equiv) in toluene (2.5 mL), ester **1e** (0.13 g, 0.5 mmol, 1.0 equiv) was added. The mixture was stirred at room temperature for 3-4 h. The reaction mixture was quenched with 5% HCl solution and extracted with diethyl ether (10 mL × 2). The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by silica gel column chromatography (eluent: PE : EtOAc = 20 : 1) to give the product **1t** as a white solid in 63% yield.

Synthesis of vinylbicyclo[1.1.1]pentane 1z:(5)



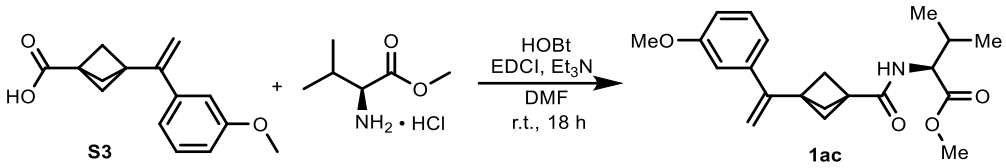
Into a 20 mL vial was added ester **1e** (0.258 g, 1.00 mmol, 1.0 equiv.), sodium methanesulfinate (0.306 g, 3.0 mmol, 3.0 equiv.), and lithium bis(trimethylsilyl)amide 1.0 M in toluene (3.0 mL, 3.0 mmol, 3.0 equiv.). The resulting mixture was stirred vigorously at 80 ℃ on a heating block for 3 hours. The reaction was quenched with sat. NH_4Cl aq., extracted with EtOAc (5 mL × 3). The combined organic layer was

concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: PE : EtOAc = 10 : 1) to give the product as a yellow oil in 61% yield.

Synthesis of vinylbicyclo[1.1.1]pentane 1aa:(3)

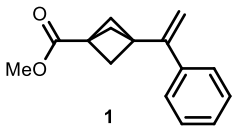
To a flask equipped with a stir bar containing the acid **S3** (0.25g, 1 mmol, 1.0 equiv) dissolved in anhydrous DCM (3.4 mL, 0.3M) was added EDCI (0.25 g, 1.3 mmol, 1.3 equiv), and the mixture was stirred for 10 min. HOBt (0.015 g, 0.2 mmol, 20 mol%), DIPEA (0.45 g, 3.5 mmol, 3.5 equiv) and *N*, *O*-dimethylhydroxylamine hydrochloride (0.20 g, 2 mmol, 2 equiv) were subsequently added, and the reaction mixture was stirred at rt for 16 h. The reaction mixture was washed with saturated sodium bicarbonate, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (eluent: PE : EtOAc = 5 : 1) to afford **1aa** (0.15 g, 51%) as a colorless oil.

Synthesis of vinylbicyclo[1.1.1]pentane 1ac:(6)



To a solution of the acid **S3** (0.37 g, 1.5 mmol, 1.0 equiv) in anhydrous DMF (5 mL), was added EDCI (0.43g, 2.25 mmol, 1.5 equiv), HOBt (0.17g, 2.25 mmol, 1.5 equiv), triethylamine (0.30g, 3 mmol, 2.0 equiv) and L-Valine Methyl Ester Hydrochloride (0.25g, 1.5 mmol, 1.0 equiv). The reaction mixture was stirred for 18h under argon atmosphere at room temperature. The reaction mixture was washed with water and extracted thrice with ethyl acetate. The organics were dried over sodium sulphate and concentrated in vacuo to obtain the crude reaction mixture. The crude reaction mixture

was purified by silica gel flash column chromatography (eluent: PE : EtOAc = 5 : 1) to afford the desired product (**1ac**) as a yellow oil in 33% yield.



1

white solid; m.p.: 37-39 ℃.

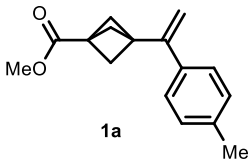
Compound was prepared according to GP-A, 35% yields over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.21 (m, 5H), 5.22 (d, *J* = 1.6 Hz, 1H), 5.09 (d, *J* = 1.6 Hz, 1H), 3.65 (s, 3H), 2.23 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.4, 147.2, 139.8, 128.0, 127.3, 126.8, 114.2, 53.1, 51.4, 42.8, 37.2.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{15}H_{17}O_2^+$ $[M+H]^+$ 229.1223, found 229.1224.



1a

white solid; m.p.: 44-47 ℃.

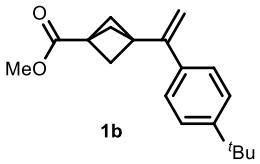
Compound was prepared according to GP-A, 32% yields over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.21 (m, 2H), 7.12 (d, *J* = 1.6 Hz, 2H), 5.22 (d, *J* = 1.6 Hz, 1H), 5.06 (d, *J* = 1.6 Hz, 1H), 3.68 (s, 3H), 2.34 (s, 3H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.9, 147.2, 137.3, 137.1, 129.0, 127.0, 113.9, 53.4, 51.8, 43.1, 37.5, 21.3.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{16}H_{19}O_2^+$ $[M+H]^+$ 243.1380, found 243.1378.



1b

orange solid; m.p.: 31-32 ℃.

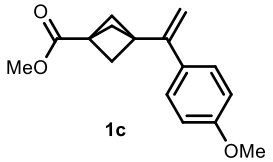
Compound was prepared according to GP-A, 22% yields over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 4H), 5.26 (d, *J* = 1.6 Hz, 1H), 5.07 (d, *J* = 1.6 Hz, 1H), 3.69 (s, 3H), 2.26 (s, 6H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.9, 150.5, 147.0, 137.0, 126.7, 125.2, 113.9, 53.5, 51.8, 43.1, 34.6, 31.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{19}H_{25}O_2^+$ $[M+H]^+$ 285.1849, found 285.1848.



1c

white solid; m.p.: 54-56 ℃.

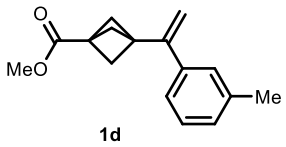
Compound was prepared according to GP-A, 58% yields over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 6.89 – 6.83 (m, 2H), 5.19 (d, *J* = 1.6 Hz, 1H), 5.03 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.8, 159.1, 146.7, 132.5, 128.1, 113.6, 113.2, 55.3, 53.4, 51.7, 43.1, 37.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{16}H_{19}O_3^+$ $[M+H]^+$ 259.1329, found 259.1327.



1d

yellow oil;

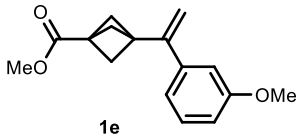
Compound was prepared according to GP-A, 32% yields over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.08 (m, 3H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.10 (d, *J* = 1.6 Hz, 1H), 3.70 (s, 3H), 2.36 (s, 3H), 2.26 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.8, 147.5, 140.0, 137.8, 128.3, 128.2, 127.9, 124.2, 114.3, 53.4, 51.7, 43.1, 37.5, 21.6.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{16}H_{19}O_2^+$ $[M+H]^+$ 243.1380, found 243.1379.



1e

colorless oil;

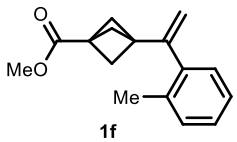
Compound was prepared according to GP-A, 48% yields over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 1H), 6.94 – 6.90 (m, 1H), 6.89 – 6.86 (m, 1H), 6.83 (dd, *J* = 7.9, 2.6 Hz, 1H), 5.25 (d, *J* = 1.2 Hz, 1H), 5.11 (d, *J* = 1.2 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.7, 159.5, 147.3, 141.4, 129.2, 119.6, 114.6, 113.0, 112.8, 55.3, 53.4, 51.7, 43.0, 37.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{16}H_{19}O_3^+$ $[M+H]^+$ 259.1329, found 259.1329.



1f

yellow oil;

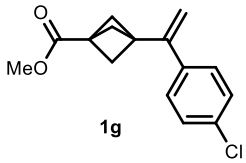
Compound was prepared according to GP-A, 38% yields over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.20 – 7.11 (m, 3H), 6.99 – 6.95 (m, 1H), 5.23 (d, *J* = 2.0 Hz, 1H), 4.93 (d, *J* = 2.0 Hz, 1H), 3.66 (s, 3H), 2.23 (s, 3H), 2.09 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.9, 147.8, 139.7, 135.27, 130.1, 128.6, 127.1, 125.3, 114.7, 52.5, 51.7, 43.8, 37.3, 19.9.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{16}H_{19}O_2^+$ $[M+H]^+$ 243.1380, found 243.1381.



1g

white solid; m.p.: 57-59 ℃.

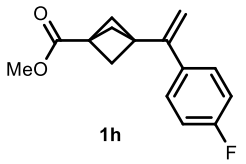
Compound was prepared according to GP-A, 35% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.22 (m, 4H), 5.22 (d, *J* = 1.6 Hz, 1H), 5.12 (d, *J* = 1.6 Hz, 1H), 3.68 (s, 3H), 2.23 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.6, 146.3, 138.4, 133.4, 128.5, 115.0, 53.3, 51.8, 42.9, 37.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{15}H_{16}ClO_2^+$ $[M+H]^+$ 263.0833, found 263.0829.



1h

yellow solid; m.p.: 57-59 ℃.

Compound was prepared according to GP-A, 26% yield over the last two steps.

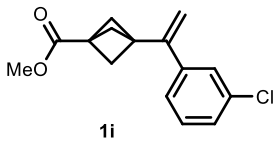
R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.04 – 6.97 (m, 2H), 5.19 (d, *J* = 1.2 Hz, 1H), 5.09 (d, *J* = 1.6 Hz, 1H), 3.69 (s, 3H), 2.23 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 162.4 (d, *J* = 247.5 Hz), 146.7, 136.1 (d, *J* = 3.0 Hz), 128.7 (d, *J* = 7.1 Hz), 115.2 (d, *J* = 22.2 Hz), 114.6, 53.3, 51.8, 43.0, 37.5.

^{19}F NMR (376 MHz, Chloroform-d) δ -115.02 (s, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{15}H_{16}FO_2^+$ $[M+H]^+$ 247.1129, found 247.1127.



1i

yellow oil;

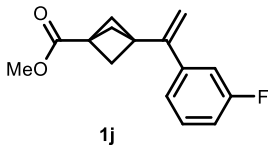
Compound was prepared according to GP-A, 29% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.22 (m, 1H), 7.19 – 7.16 (m, 2H), 7.15 – 7.10 (m, 1H), 5.17 (d, *J* = 1.6 Hz, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 3.61 (s, 3H), 2.16 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.6, 146.3, 141.8, 134.2, 129.6, 127.6, 127.3, 125.3, 115.5, 53.3, 51.8, 42.8, 37.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{15}H_{16}ClO_2^+$ $[M+H]^+$ 263.0833, found 263.0833.



1j

pink oil;

Compound was prepared according to GP-A, 54% yield over the last two steps.

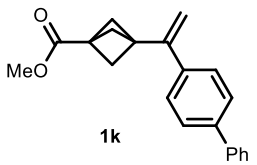
R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.23 (m, 1H), 7.12 – 7.07 (m, 1H), 7.04 – 6.99 (m, 1H), 6.99 – 6.93 (m, 1H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 3.68 (s, 3H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.6, 162.7 (d, J = 246.5 Hz), 146.3 (d, J = 2.0 Hz), 142.2 (d, *J* = 7.1 Hz), 129.7 (d, *J* = 8.1 Hz), 122.8 (d, *J* = 2.8 Hz), 114.3 (d, *J* = 21.2 Hz), 114.0 (d, *J* = 21.2 Hz), 53.3, 51.7, 42.8, 37.5.

^{19}F NMR (376 MHz, Chloroform-d) δ -113.20 (s, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{15}H_{16}FO_2^+$ $[M+H]^+$ 247.1129, found 247.1129.



1k

white solid; m.p.: 102-104 ℃.

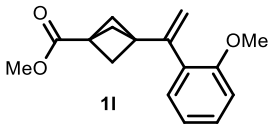
Compound was prepared according to GP-A, 30% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.64 – 7.54 (m, 4H), 7.48 – 7.41 (m, 4H), 7.39 – 7.33 (m, 1H), 5.33 (d, *J* = 1.3 Hz, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 3.71 (s, 3H), 2.30 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.8, 146.9, 140.8, 140.4, 139.0, 128.9, 127.5, 127.4, 127.1, 127.0, 114.6, 53.5, 51.8, 43.1, 37.6.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{21}H_{21}O_2^+$ $[M+H]^+$ 305.1536, found 305.1536.



1l

colorless oil;

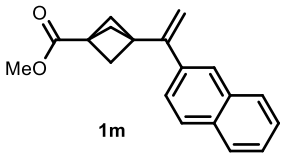
Compound was prepared according to GP-A, 18% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 1H), 7.06 – 7.01 (m, 1H), 6.95 – 6.84 (m, 2H), 5.20 (d, *J* = 2.0 Hz, 1H), 5.06 (d, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 3.66 (s, 3H), 2.10 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 171.2, 156.6, 146.9, 130.3, 129.6, 128.8, 120.5, 115.3, 110.5, 55.3, 53.2, 51.7, 43.2, 36.9.

HRMS (ESI^+) *m*/*z* Calcd for $C_{16}H_{19}O_3^+$ $[M+H]^+$ 259.1329, found 259.1328.



1m

white solid; m.p.: 84-86 ℃.

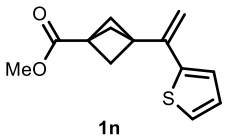
Compound was prepared according to GP-A, 50% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.77 (m, 4H), 7.51 – 7.42 (m, 3H), 5.38 (d, *J* = 1.6 Hz, 1H), 5.21 (d, *J* = 1.2 Hz, 1H), 3.70 (s, 3H), 2.32 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.8, 147.3, 137.5, 133.4, 132.8, 128.2, 127.9, 127.7, 126.4, 126.1, 125.9, 125.5, 115.0, 53.6, 51.8, 43.2, 37.6.

HRMS (ESI^+) *m*/*z* Calcd for $C_{19}H_{19}O_2^+$ $[M+H]^+$ 279.1380, found 279.1383.



1n

yellow oil;

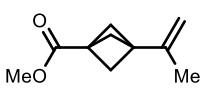
Compound was prepared according to GP-A, 50% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 5.2 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 7.02 – 6.96 (m, 1H), 5.44 (s, 1H), 4.99 (s, 1H), 3.71 (s, 3H), 2.32 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.7, 142.4, 140.1, 127.4, 124.7, 124.6, 113.1, 53.4, 51.9, 42.8, 37.4.

HRMS (ESI^+) *m*/*z* Calcd for $C_{13}H_{15}O_2S^+$ $[M+H]^+$ 235.0787, found.



1o

yellow oil;

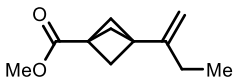
Compound was prepared according to GP-A, 49% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.78 (t, *J* = 2.2 Hz, 1H), 4.72 – 4.69 (m, 1H), 3.68 (s, 3H), 2.06 (s, 6H), 1.68 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 171.1, 143.6, 111.0, 52.0, 51.8, 43.6, 36.7, 18.9.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{10}H_{15}O_2^+$ $[M+H]^+$ 167.1067, found 167.1067.



1p

yellow oil;

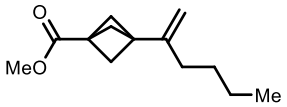
Compound was prepared according to GP-A, 21% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.77 (q, *J* = 1.6 Hz, 1H), 4.75 (t, *J* = 1.2 Hz, 1H), 3.66 (s, 3H), 2.07 (s, 6H), 2.02 – 1.95 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.8, 149.0, 108.7, 52.3, 51.5, 43.4, 36.6, 25.1, 12.2.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{11}H_{17}O_2^+$ $[M+H]^+$ 181.1223, found 181.1225.



1q

yellow oil;

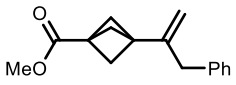
Compound was prepared according to GP-A, 17% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.80 – 4.73 (m, 2H), 3.67 (s, 3H), 2.08 (s, 6H), 2.02 – 1.95 (m, 2H), 1.43 – 1.28 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 171.1, 147.8, 110.0, 52.6, 51.7, 43.6, 36.8, 32.5, 30.3, 22.6, 14.1.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{13}H_{21}O_2^+$ $[M+H]^+$ 209.1536, found 209.1536.



1r

white solid; m.p.: 29-31 ℃.

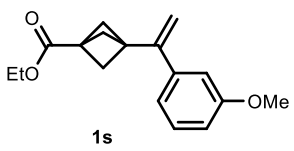
Compound was prepared according to GP-A, 30% yield over the last two steps.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 4.89 (d, *J* = 1.6 Hz, 1H), 4.79 – 4.75 (m, 1H), 3.64 (s, 3H), 3.35 (s, 2H), 1.98 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.7, 146.5, 139.1, 128.9, 128.2, 126.2, 112.7, 52.5, 51.5, 43.1, 39.9, 36.8.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{16}H_{19}O_2^+$ $[M+H]^+$ 243.1380, found 243.1384.



1s

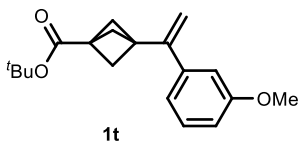
colorless oil, 98% yield.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 1H), 6.94 – 6.90 (m, 1H), 6.89 – 6.81 (m, 2H), 5.25 (d, *J* = 1.2 Hz, 1H), 5.10 (d, *J* = 1.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.24 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.5, 159.5, 147.4, 141.5, 129.3, 119.6, 114.6, 113.0, 112.8, 60.6, 55.3, 53.4, 42.9, 37.7, 14.3.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{17}H_{21}O_3^+$ [M+H]$^+$ 273.1485, found 273.1485.



1t

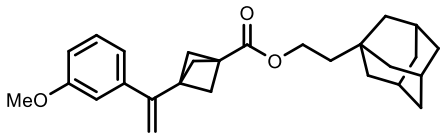
white solid, 63% yield. m.p.: 58-60 ℃.

R_f (PE : EtOAc = 20 : 1) = 0.4;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 8.0 Hz, 1H), 6.94 – 6.90 (m, 1H), 6.89 – 6.86 (m, 1H), 6.85 – 6.80 (m, 1H), 5.23 (d, *J* = 2.0 Hz, 1H), 5.09 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 2.19 (s, 6H), 1.45 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.0, 159.5, 147.6, 141.6, 129.2, 119.7, 114.4, 113.0, 112.8, 80.6, 55.3, 53.2, 42.5, 38.5, 28.2.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{19}H_{25}O_3^+$ [M+H]$^+$ 301.1798, found 301.1798.



1u

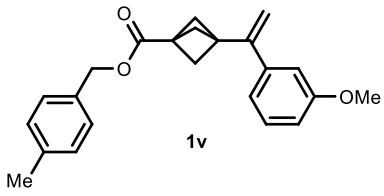
colorless oil, 96% yield.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.20 (m, 1H), 6.94 – 6.90 (m, 1H), 6.89 – 6.86 (m, 1H), 6.85 – 6.80 (m, 1H), 5.25 (d, *J* = 1.6 Hz, 1H), 5.10 (d, *J* = 1.6 Hz, 1H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.24 (s, 6H), 1.95 (s, 3H), 1.74 – 1.60 (m, 6H), 1.53 (s, 6H), 1.43 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.5, 159.4, 147.4, 141.5, 129.2, 119.6, 114.5, 113.0, 112.8, 61.1, 55.3, 53.3, 42.9, 42.6, 42.5, 37.7, 37.1, 31.9, 28.7.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{27}H_{35}O_3^+$ [M+H]$^+$ 407.2581, found 407.2580.



1v

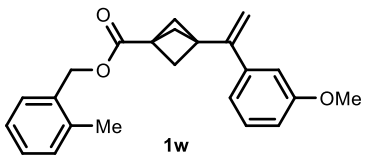
colorless oil, 91% yield.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.87 – 6.84 (m, 1H), 6.84 – 6.79 (m, 1H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.09 (d, *J* = 1.6 Hz, 1H), 5.08 (s, 2H), 3.80 (s, 3H), 2.35 (s, 3H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.3, 159.5, 147.3, 141.5, 138.1, 133.1, 129.3, 129.3, 128.3, 119.6, 114.6, 113.0, 112.8, 66.2, 55.3, 53.4, 43.0, 37.6, 21.3.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{23}H_{25}O_3^+$ $[M+H]^+$ 349.1798, found 349.1797.



1w

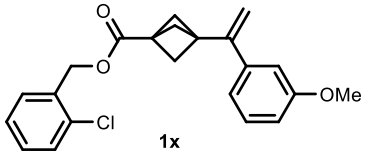
colorless oil, 97% yield.

R*f* (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 6.8 Hz, 1H), 7.26 – 7.16 (m, 4H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.87 – 6.80 (m, 2H), 5.24 (s, 1H), 5.13 (s, 2H), 5.09 (s, 1H), 3.80 (s, 3H), 2.33 (s, 3H), 2.26 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.2, 159.5, 147.3, 141.5, 137.1, 134.0, 130.5, 129.3, 129.1, 128.6, 126.1, 119.6, 114.6, 113.0, 112.8, 64.9, 55.3, 53.4, 43.1, 37.6, 19.0.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{23}H_{25}O_2^+$ $[M+H]^+$ 349.1798, found 349.1802.



1x

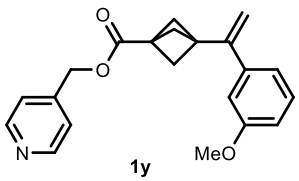
colorless oil, 98% yield.

R*f* (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.39 (m, 2H), 7.35 – 7.27 (m, 3H), 6.98 – 6.93 (m, 1H), 6.93 – 6.83 (m, 2H), 5.29 (d, *J* = 1.6 Hz, 1H), 5.27 (s, 2H), 5.15 (d, *J* = 1.6 Hz, 1H), 3.85 (s, 3H), 2.33 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 169.9, 159.5, 147.3, 141.5, 133.8, 133.6, 129.7, 129.5, 129.3, 127.0, 119.7, 114.7, 113.1, 112.8, 63.6, 55.3, 53.5, 43.1, 37.6.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{22}H_{22}ClO_3^+$ $[M+H]^+$ 369.1252, found 369.1252.



1y

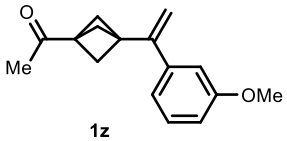
colorless oil, 90% yield

R*f* (PE : EtOAc = 2 : 1) = 0.3;

^{1}H NMR (400 MHz, Chloroform-d) δ 8.50 (d, *J* = 5.4 Hz, 2H), 7.18 – 7.10 (m, 3H), 6.88 – 6.70 (m, 3H), 5.17 (d, *J* = 1.2 Hz, 1H), 5.04 (s, 2H), 5.03 (d, 1H), 3.71 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 169.6, 159.4, 150.0, 147.0, 144.9, 141.2, 129.2, 121.7, 119.5, 114.7, 113.0, 112.7, 64.0, 55.2, 53.3, 43.1, 37.3.

MS (EI, m/z): 336 (M^+, 0.6), 243 (10.2), 197 (16.0), 108 (61.8), 93 (100.0), 65 (14.3).



1z

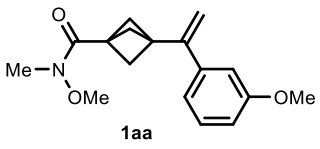
colorless oil, 61% yield.

R*f* (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.88 – 6.81 (m, 2H), 5.26 – 5.23 (m, 1H), 5.11 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 2.21 (s, 6H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 206.8, 159.5, 147.5, 141.5, 129.3, 119.6, 114.6, 113.1, 112.8, 55.3, 53.0, 44.1, 42.4, 26.4.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{16}H_{19}O_2^+$ $[M+H]^+$ 243.1380, found 243.1380.



1aa

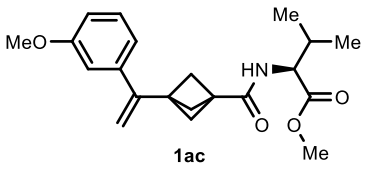
colorless oil, 51% yield.

R_f (PE : EtOAc = 5 : 1) = 0.2;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.90 – 6.87 (m, 1H), 6.83 (dd, *J* = 8.2, 1.8 Hz, 1H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.11 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 3.67 (s, 3H), 3.20 (s, 3H), 2.30 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 159.5, 147.7, 141.7, 129.3, 119.7, 114.4, 113.0, 112.8, 55.3, 54.0, 43.6, 38.7.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{17}H_{22}O_3^+$ $[M+H]^+$ 288.1594, found 288.1593.



1ac

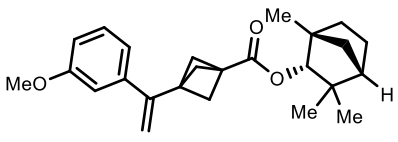
white solid, 33% yield. m.p.: 36-38 ℃.

R_f (PE : EtOAc = 10 : 1) = 0.2;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.21 (m, 1H), 6.94 – 6.89 (m, 1H), 6.88 – 6.81 (m, 2H), 6.01 (d, *J* = 8.8 Hz, 1H), 5.25 (d, *J* = 1.2 Hz, 1H), 5.12 (d, *J* = 1.6 Hz, 1H), 4.58 – 4.52 (m, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.23 (s, 6H), 2.19 – 2.10 (m, 1H), 0.94 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-d) δ 172.6, 170.1, 159.5, 147.3, 141.5, 129.3, 119.7, 114.6, 113.1, 112.8, 56.7, 55.3, 52.8, 52.3, 42.1, 39.1, 31.6, 19.0, 17.9.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{21}H_{28}NO_4^+$ $[M+H]^+$ 358.2013, found 358.2013.



1ad

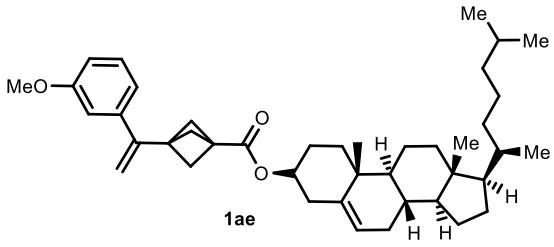
colorless oil, 46% yield.

R_f (PE : EtOAc = 10 : 1) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.22 (m, 2H), 6.93-6.90 (m, 1H), 6.88 – 6.85 (m, 1H), 6.85 – 6.81 (m, 1H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.11 (d, *J* = 1.6 Hz, 1H), 4.35 (d, *J* = 2.0 Hz, 1H), 3.82 (s, 3H), 2.25 (s, 6H), 1.76 – 1.65 (m, 3H), 1.60 – 1.55 (m, 2H), 1.48 – 1.40 (m, 1H), 1.20 – 1.16 (m, 1H), 1.09 (s, 3H), 1.02 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.8, 159.5, 147.5, 141.6, 129.3, 119.7, 114.5, 113.1, 112.7, 85.9, 55.4, 53.4, 48.5, 48.4, 43.0, 41.5, 39.6, 37.8, 29.8, 26.7, 26.0, 20.1, 19.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{25}H_{33}O_3^+$ $[M+H]^+$ 381.2424, found 381.2422.



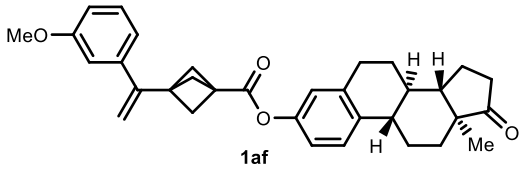
yellow solid, 21% yield. m.p.: 86-88 ℃.

R_f (PE : EtOAc = 10 : 1) = 0.4;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.94 – 6.90 (m, 1H), 6.89 – 6.86 (m, 1H), 6.84 – 6.80 (m, 1H), 5.37 (d, *J* = 4.0 Hz, 1H), 5.24 (d, *J* = 1.6 Hz, 1H), 5.10 (d, *J* = 1.6 Hz, 1H), 4.67 – 4.55 (m, 1H), 3.81 (s, 3H), 2.31 (d, *J* = 7.6 Hz, 2H), 2.23 (s, 6H), 2.03 – 1.93 (m, 2H), 1.90 – 1.78 (m, 3H), 1.57 – 0.89 (m, 27H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.68 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 170.0, 159.5, 147.5, 141.6, 139.8, 129.3, 122.8, 119.7, 114.5, 113.0, 112.8, 74.2, 56.8, 56.3, 55.3, 53.3, 50.2, 42.8, 42.5, 39.9, 39.7, 38.2, 37.8, 37.1, 36.7, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 27.9, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{42}H_{61}O_3^+$ $[M+H]^+$ 613.4615, found 613.4611.



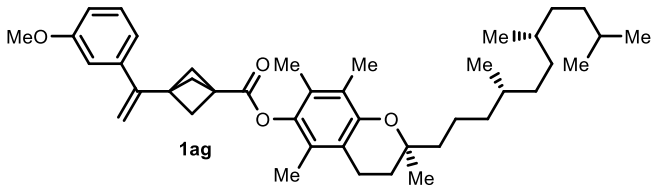
white solid, 73% yield. m.p.: 102-104 ℃.

R_f (PE : EtOAc = 5 : 1) = 0.3;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.88 – 6.80 (m, 3H), 5.28 (d, *J* = 1.6 Hz, 1H), 5.14 (d, *J* = 1.6 Hz, 1H), 3.83 (s, 3H), 2.94 – 2.88 (m, 2H), 2.55 – 2.46 (m, 1H), 2.44 – 2.39 (m, 1H), 2.37 (s, 6H), 2.32 – 2.25 (m, 1H), 2.19 – 2.10 (m, 1H), 2.08 – 1.93 (m, 3H), 1.68 – 1.58 (m, 2H), 1.57 – 1.41 (m, 4H), 0.91 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 168.9, 159.5, 148.6, 147.2, 141.4, 138.1, 137.5, 129.3, 126.5, 121.6, 119.7, 118.8, 114.8, 113.1, 112.8, 55.4, 53.6, 50.6, 48.1, 44.3, 43.2, 38.1, 37.7, 36.0, 31.7, 29.5, 26.5, 25.9, 21.7, 14.0.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{33}H_{37}O_4^+$ $[M+H]^+$ 497.2684, found 497.2686.



yellow oil, 93% yield.

R_f (PE : EtOAc = 10 : 1) = 0.3;

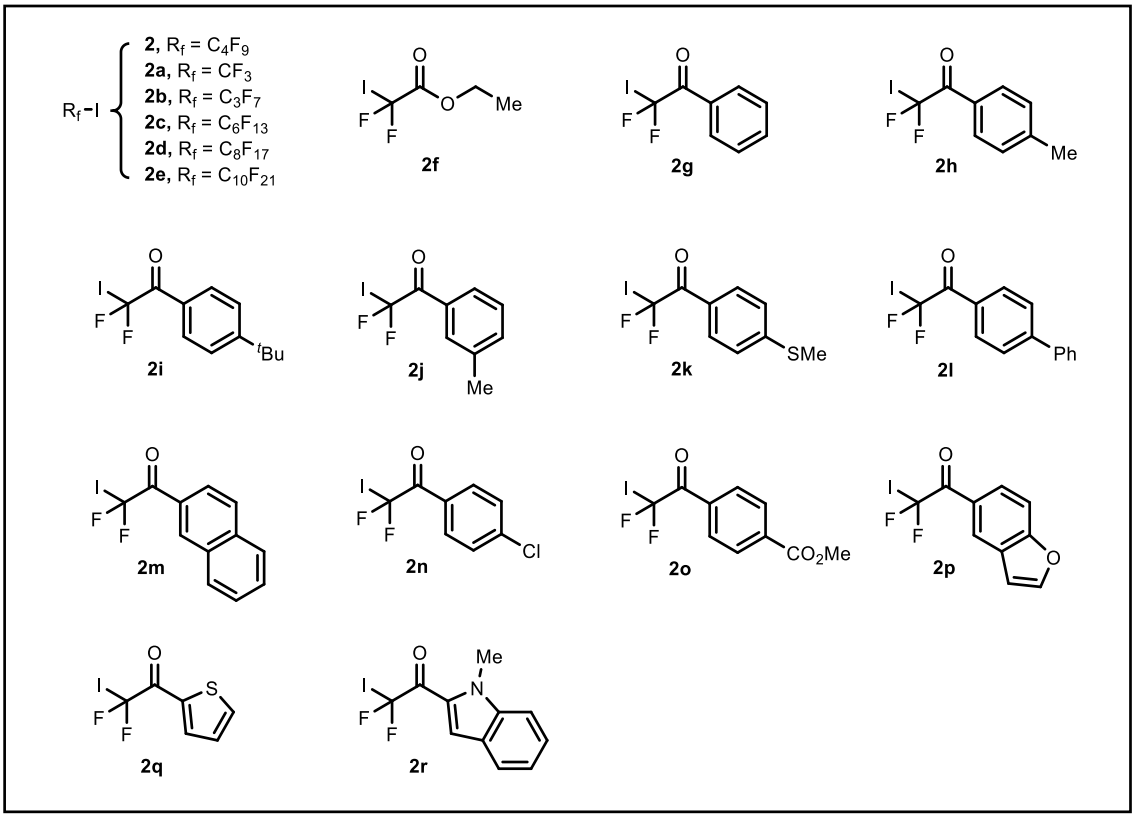
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 2H), 6.97 – 6.94 (m, 1H), 6.91 – 6.89 (m, 1H), 6.86 – 6.83 (m, 1H), 5.29 (d, *J* = 1.6 Hz, 1H), 5.16 (d, *J* = 1.2 Hz, 1H), 3.83 (s, 3H), 2.58 (t, *J* = 6.6 Hz, 2H), 2.42 (s, 6H), 2.09 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.84 – 1.72 (m, 2H), 1.56 – 1.48 (m, 3H), 1.40 – 1.05 (m, 21H), 0.88-0.83 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-d) δ 168.8, 159.5, 149.5, 147.3, 141.5, 140.2, 129.3, 126.8, 125.0, 123.2, 119.7, 117.6, 114.7, 113.1, 112.8, 75.2, 55.4, 53.6, 43.3, 39.5, 37.7,

37.6, 37.6, 37.6, 37.4, 32.9, 32.8, 28.1, 25.0, 24.6, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 12.9, 12.1, 12.0.

HRMS (ESI^+) *m*/*z* Calcd for $C_{44}H_{65}O_4^+$ $[M+H]^+$ 657.4877, found 657.4879.

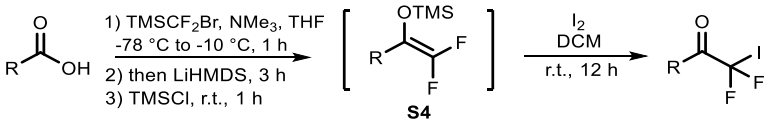
Polyfluoroalkyliodides:



Note: **2**, **2a-2f** are commercially available solvents; compound **2g-2r** were prepared according to **GP-C** in this work. Compound **2g-2h**, **2j, 2l-2o**, **2q** are literature known and the characterization data were in accord with those reported.

Preparation of polyfluoroalkyliodides:

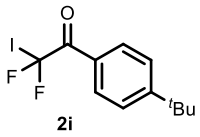
General Procedure C for the synthesis of polyfluoroalkyliodides (**GP-C**):[7]



Step 1: Under argon atmosphere, a solution of aldehyde (2 mmol, 1.0 equiv), $TMSCF_2Br$ (2.6 mmol, 1.3 equiv) and NMe_3 (2 M in THF, 4 mmol, 2.0 equiv) in THF (20 mL) was stirred at -78 ℃ to -10 ℃ for 1 hour. Then LiHMDS (1.0 M in THF, 5 mmol, 2.5 equiv) was added dropwise, and the resulting solution was stirred at -10 ℃ for 3 hours. Thereafter, TMSCl (4 mmol, 2.0 equiv) was added, and the mixture was stirred at room temperature for 1 hour. Volatile components were evaporated and the

solid residue was dissolved in DCM (5 mL) and filtered under argon atmosphere.

Step 2：To the filtrate of **S4** in situ generated under standard conditions was added I_2 (1.0 mmol, 2.0 equiv) under argon atmosphere. The resulting solution was stirred at room temperature for 12.0 hours. The mixture was quenched with water, and extracted with DCM for three times. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography using petroleum ether/ethyl acetate to afford product. (The purification process should be very careful and completed in a dark room as soon as possible!)



2i

yellow solid, 74% yield. m.p.: 37-39 ℃.

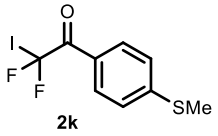
R_f (PE) = 0.5;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.09 (m, 2H), 7.58 – 7.51 (m, 2H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.1 (t, *J* = 23.2 Hz), 159.4, 131.0 (t, *J* = 3.0 Hz), 126.1, 125.77, 95.9 (t, *J* = 327.2 Hz), 35.5, 31.1.

^{19}F NMR (376 MHz, Chloroform-d) δ -53.8 (s, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{12}H_{14}F_2IO^+$ $[M+H]^+$ 339.0052, found 339.0051.



2k

brownish red solid, 36% yield. m.p.: 27-29 ℃.

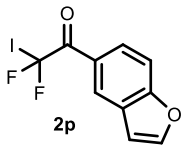
R_f (PE) = 0.2;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.03 (m, 2H), 7.33 – 7.27 (m, 2H), 2.54 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 181.6 (t, *J* = 23.2 Hz), 149.6, 131.2, 125.0, 124.2, 95.8 (t, *J* = 327.2 Hz), 14.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -53.76 (S, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_9H_8F_2IOS^+$ $[M+H]^+$ 328.9303, found.



2p

brownish red solid, 93% yield. m.p.: 39-41 ℃.

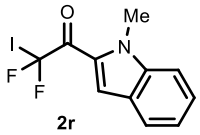
R_f (PE) = 0.25;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 1.2, 1.0 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.2 (t, *J* = 22.9 Hz), 158.4, 147.2, 128.0, 127.6 (t, *J* = 2.8 Hz), 125.8 (t, *J* = 3.5 Hz), 123.6, 112.3, 107.6, 96.0 (t, *J* = 327.2 Hz).

^{19}F NMR (376 MHz, Chloroform-d) δ -53.2 (s, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{10}H_6F_2IO_2^+$ $[M+H]^+$ 322.9375, found 322.9375.



2r

yellow solid, 25% yield. m.p.: 136-138 ℃.

R*f* (PE) = 0.25;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 – 8.36 (m, 1H), 7.98 (t, *J* = 2.2 Hz, 1H), 7.42 – 7.36 (m, 3H), 3.91 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 178.6 (t, *J* = 23.6 Hz), 138.1 (t, *J* = 8.0 Hz), 137.4, 127.6, 124.6, 123.9, 123.0, 110.2, 106.2, 97.3 (t, *J* = 327.4 Hz), 34.2.

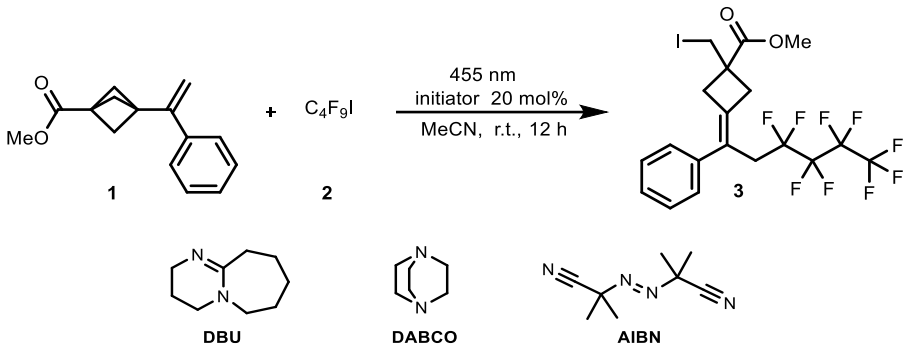
^{19}F NMR (376 MHz, Chloroform-d) δ -52.2 (s, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{11}H_9F_2NIO^+$ $[M+H]^+$ 335.9691, found 335.9690.

2.2 Optimization Studies

In a N_2-filled glovebox, methyl 3-(1-phenylvinyl)bicyclo[1.1.1]pentane-1-carboxylate (**1**) and initiator were dissolved in 1 mL solvent in a 10 mL Schlenk tube, C_4F_9I (**2**) was then added. The mixture was stirred under irradiation with blue LEDs (455nm, 10 W). Later, the solvent was removed *in vacuo*. The mixture was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.

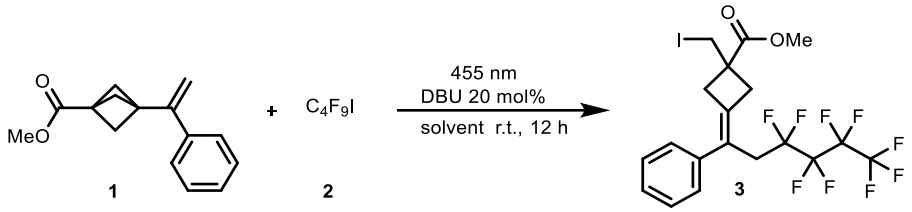
Table S1. Investigating the effect of initiators



Entry[a]	initiator (20 mol%)	Yield (%)
1	PPh_3	87
2	DBU	95
3	DABCO	88
4	Cs_2CO_3	25
5	AIBN	50
6	Et_3B	85
7	none	20

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.1 mmol), initiator (20 mol%) in MeCN (1.0 mL), under 455 nm blue LEDs at r.t. for 12 h. n.d. = not detected.

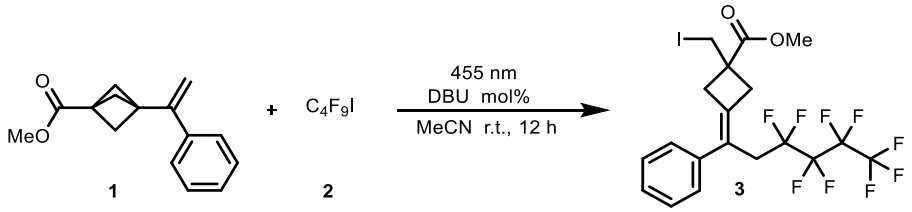
Table S2. Investigating the effect of solvents



Entry[a]	Solvent	Yield (%)
1	MeCN	95
2	DCM	91
3	THF	88
4	MeOH	50
5	$PhCF_3$	93
6	DMF	95

[a]Reaction conditions: **1** (0.1 mmol), **2** (0.1 mmol), DBU (20 mol%) in solvent (1.0 mL), under 455 nm blue LEDs at r.t. for 12 h.

Table S3. Investigating the effect of initiators loading

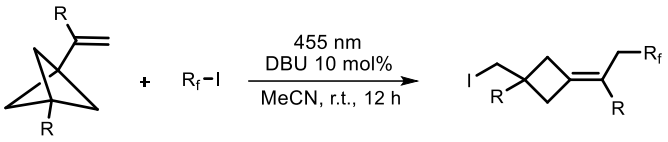


Entry [a]	Load of DBU(mol%)	Yield (%)
1	3	71
2	5	87
3	10	97/93[b]
4	15	98
5	20	95

[a]Reaction conditions: 1 (0.1 mmol), 2 (0.1 mmol), different loading of DBU in MeCN (1.0 mL), under 455 nm blue LEDs at r.t. for 12 h. [b]Reaction under white light LEDs at r.t. for 12 h.

2.3 Substrate Scope

General Procedure D (**GP-D**):



In a N_2-filled glovebox, VBCP (0.1 mmol) and MeCN (1.0 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and R_fI (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and stirred at room temperature under blue LEDs (455 nm, 10W) for approximately 12 h. Then the mixture was concentrated and purified by column chromatography on silica gel or preparative thin-layer chromatography to give the pure product.

Note: Compounds **17, 28, 34** were prepared according to **GP-D** for approximately 36 h**;** compound **37** was prepared according to **GP-D** with R_fI (1.5 equiv).

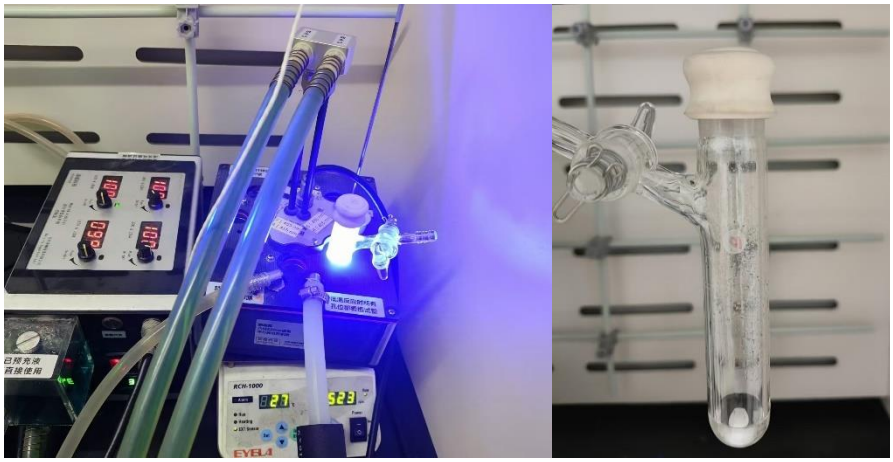
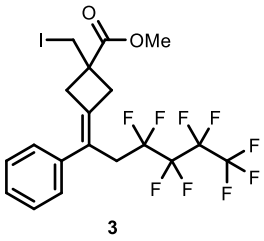


Figure S1. Reaction setup.

Characterization of Products

Note: Due to the complex carbon fluorine coupling effect, the carbon signal of $CF_3(CF_2)_x$ in the related compounds is relatively weak and cannot be identified in the carbon spectrum.



3

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

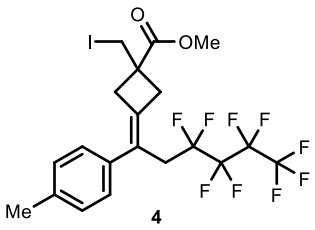
yield: 96% (49 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 7.17 – 7.12 (m, 2H), 3.70 (s, 3H), 3.49 (s, 2H), 3.34 – 3.25 (m, 2H), 3.17 – 2.97 (m, 2H), 2.75 – 2.63 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-d) δ 173.7, 138.5, 136.3, 128.6, 127.4, 127.1, 123.8, 52.8, 45.2, 41.5, 40.6, 32.8 (t, *J* = 22.3 Hz), 12.1. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.7 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{19}H_{17}F_9IO_2^+$ $[M+H]^+$ 575.0124, found 575.0123.



4

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

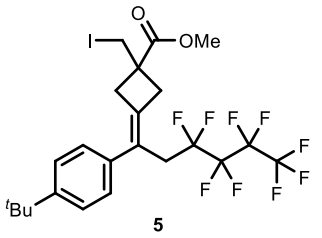
yield: 91% (54 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.09 (m, 4H), 3.78 (s, 3H), 3.56 (s, 2H), 3.40 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.35 (dd, *J* = 6.4, 3.2 Hz, 1H),, 3.21 – 3.01 (m, 2H), 2.81 – 2.70 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.8, 137.2, 135.6, 135.5, 129.3, 127.0, 123.5, 52.8, 45.2, 41.5, 40.6, 32.7 (t, *J* = 22.3 Hz), 21.3, 12.2. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.8 – -112.0 (m, 2F), -124.1 – -124.3 (m, 2F), -125.8 – -126.1 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{20}H_{19}F_9IO_2^+$ $[M+H]^+$ 589.0281, found 589.0284.



5

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

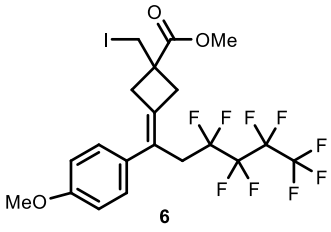
yield: 94% (59 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 2H), 7.18 – 7.14 (m, 2H), 3.77 (s, 3H), 3.56 (s, 2H), 3.39 (td, *J* = 17.1, 2.8 Hz, 2H), 3.23 – 3.02 (m, 2H), 2.84 – 2.73 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.8, 150.2, 135.6, 135.5, 126.7, 125.5, 123.4, 52.8, 45.3, 41.7, 40.7, 34.7, 32.5 (t, *J* = 22.2 Hz), 31.4, 12.2. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.1 – -81.1 (m, 3F), -111.8 – -111.9 (m, 2F), -124.1 – -124.6 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{23}H_{25}F_9IO_2^+$ $[M+H]^+$ 631.0750, found 631.0756.



6

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

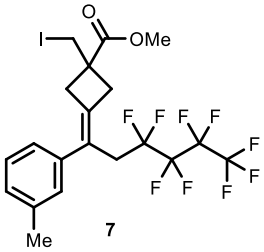
yield: 90% (54 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.12 (m, 2H), 6.91 – 6.85 (m, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.56 (s, 2H), 3.36 (ddd, *J* = 16.4, 8.0, 2.8 Hz, 2H), 3.22 – 2.99 (m, 2H), 2.82 – 2.68 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.8, 158.8, 134.8, 130.9, 128.3, 123.2, 114.0, 55.4, 52.8, 45.2, 41.5, 40.6, 32.8 (t, *J* = 22.2 Hz), 12.2. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.8 – -111.9 (m, 2F), -124.1 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{20}H_{19}F_9IO_3^+$ $[M+H]^+$ 605.0230, found 605.0234.



7

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

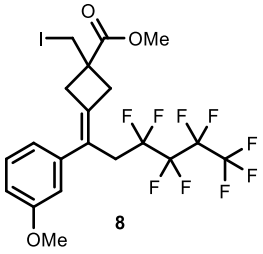
yield: 92% (54 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.20 (m, 1H), 7.10 – 7.05 (m, 1H), 7.04 – 7.00 (m, 2H), 3.78 (s, 3H), 3.56 (s, 2H), 3.38 (dt, *J* = 16.8, 3.2 Hz, 2H), 3.25 – 3.03 (m, 2H), 2.81 – 2.70 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 138.5, 138.2, 136.0, 128.5, 128.2, 127.8, 124.3, 123.8, 52.8, 45.2, 41.0, 40.6, 32.8 (t, *J* = 22.2 Hz), 21.6, 12.1. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.8 – -111.9 (m, 2F), -123.9 – -124.4 (m, 2F), -125.9 – -125.9 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{20}H_{19}F_9IO_2^+$ $[M+H]^+$ 589.0281, found 589.0278.



8

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

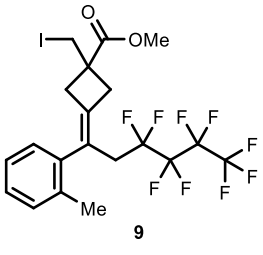
yield: 92% (56 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 8.0 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.76 – 6.72 (m, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.56 (s, 2H), 3.37 (dt, *J* = 16.8, 3.6 Hz, 2H), 3.23 – 3.01 (m, 2H), 2.80 – 2.71 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 159.7, 140.0, 136.6, 129.6, 123.6, 119.6, 113.4, 112.4, 55.4, 52.8, 45.2, 41.6, 40.6, 32.8 (t, *J* = 22.7 Hz), 12.1. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.2 (m, 3F), -111.8 – -111.9 (m, 2F), -124.1 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{20}H_{19}F_9IO_3^+$ $[M+H]^+$ 605.0230, found 605.0230.



9

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

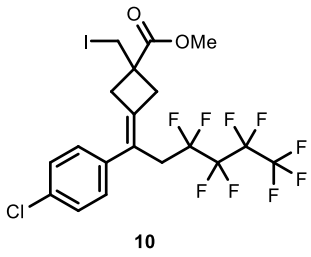
yield: 76% (45 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.11 (m, 3H), 7.08 – 7.02 (m, 1H), 3.77 (s, 3H), 3.56 (s, 2H), 3.35 (dd, *J* = 16.3, 3.1 Hz, 1H), 3.08 – 2.91 (m, 3H), 2.82 – 2.73 (m, 1H), 2.39 (d, *J* = 15.7 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.62, 138.20, 136.56, 130.35, 128.72, 127.51, 125.85, 123.93, 52.62, 44.43, 40.49, 39.89, 33.95 (t, *J* = 22.0 Hz), 19.29, 12.02. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.2 (m, 3F), -112.4 (d, *J* = 86.5 Hz, 2F), -124.1 – -124.4 (m, 2F), -125.8 – -126.01 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{20}H_{19}F_9IO_2^+$ $[M+H]^+$ 589.0281, found 589.0282.



10

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

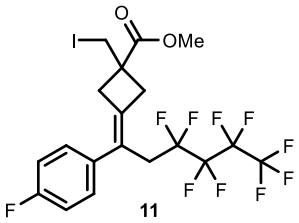
yield: 89% (54 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 2H), 7.18 – 7.11 (m, 2H), 3.77 (s, 3H), 3.55 (s, 2H), 3.35 (ddd, *J* = 16.9, 5.6, 3.2 Hz, 2H), 3.11 (td, *J* = 18.4, 4.6 Hz, 2H), 2.81 – 2.67 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 137.2, 136.2, 133.2, 128.8, 128.8, 122.8, 52.9, 45.1, 41.4, 40.62, 32.9 (t, *J* = 22.2 Hz), 11.9. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.7 – -111.8 (m, 2F), -124.0 – -124.2 (m, 2F), -125.9 – -126.0 (m, 2F).

HRMS (ESI^+) *m/z* Calcd for $C_{19}H_{16}ClF_9IO_2^+$ $[M+H]^+$ 608.9734, found 608.9736.



11

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

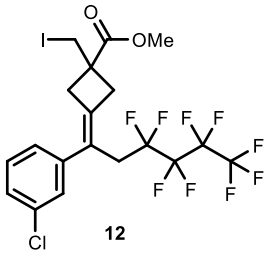
yield: 81% (48 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.15 (m, 2H), 7.06 – 7.00 (m, 2H), 3.80 – 3.75 (m, 3H), 3.56 (s, 2H), 3.34 (ddd, *J* = 16.4, 8.4, 3.2 Hz, 2H), 3.18 – 3.03 (m, 2H), 2.81 – 2.66 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 162.0 (d, *J* = 248.5 Hz), 136.4, 134.5 (d, *J* = 4.0 Hz), 128.9 (d, *J* = 8.1 Hz), 122.9, 115.6 (d, *J* = 21.2 Hz), 52.9, 451, 41.3, 40.6, 33.1 (t, *J* = 22.5 Hz), 12.0. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.5 – -81.6 (m, 3F), -111.2 – -112.4 (m, 2F), -114.6, -123.5 – -124.7 (m, 2F), -125.9 – -126.0 (m, 2F).

HRMS (ESI^+) *m/z* Calcd for $C_{19}H_{16}F_{10}IO_2^+$ $[M+H]^+$ 593.0030, found 593.0030.



12

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

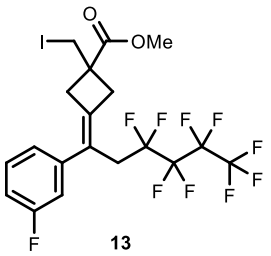
yield: 91% (55 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.25 – 7.22 (m, 1H), 7.19 (t, *J* = 1.8 Hz, 1H), 7.09 (dt, *J* = 7.4, 1.6 Hz, 1H), 3.78 (s, 3H), 3.56 (s, 2H), 3.36 (dt, *J* = 16.7, 4.0 Hz, 2H), 3.20 – 3.02 (m, 2H), 2.81 – 2.70 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.5, 140.3, 137.9, 134.6, 129.9, 127.6, 127.3, 125.4, 122.7, 52.9, 45.1, 41.4, 40.6, 32.9 (t, *J* = 22.2 Hz), 11.8. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.7 – -111.8 (m, 2F), -124.0 – -124.1 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{19}H_{16}ClF_9IO_2^+$ $[M+H]^+$ 608.9734, found 608.9732.



13

colorless oil.

R$_f$ (DCM : PE = 1 : 2) = 0.4;

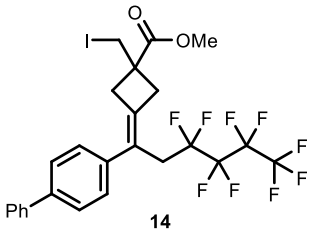
yield:90% (53 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 1H), 7.03 – 6.88 (m, 3H), 3.81 – 3.74 (m, 3H), 3.56 (s, 2H), 3.37 (dd, *J* = 16.9, 2.5 Hz, 2H), 3.20 – 3.04 (m, 2H), 2.83 – 2.71 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.5, 162.9 (d, *J* = 246.4 Hz), 140.7 (d, *J* = 7.7 Hz), 137.7, 130.1 (d, *J* = 8.1 Hz), 122.9 (d, *J* = 3.0 Hz), 122.8 (d, *J* = 2.0 Hz), 114.4 (d, *J* = 13.1 Hz), 114.1 (d, *J* = 14.1 Hz), 52.8, 45.1, 41.5, 40.6, 32.8 (t, *J* = 22.2 Hz), 11.8. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.1 – -81.2 (m, 3F), -111.7 – -111.9 (m, 2F), -112.8 (s, 1F), -124.06 – -124.2 (m, 2F), -125.9 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{19}H_{16}F_{10}IO_2^+$ $[M+H]^+$ 593.0030, found 593.0027.



14

colorless oil.

R$_f$ (DCM : PE = 1 : 2) = 0.4;

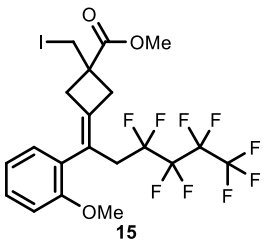
yield: 82% (53mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 4H), 7.48 – 7.42 (m, 2H), 7.39 – 7.33 (m, 1H), 7.33 – 7.28 (m, 2H), 3.79 (s, 3H), 3.59 (s, 2H), 3.43 (td, *J* = 17.2, 2.4 Hz, 2H), 3.29 – 3.09 (m, 2H), 2.87 – 2.76 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 140.6, 140.1, 137.4, 136.6, 128.9, 127.6, 127.5, 127.3, 127.1, 123.3, 52.8, 45.2, 41.7, 40.7, 32.6 (t, *J* = 22.2 Hz), 12.1. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.1 (m, 3F), -111.7 – -111.8 (m, 2F), -124.00 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{25}H_{21}F_9IO_2^+$ $[M+H]^+$ 651.0437, found 651.0438.



15

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

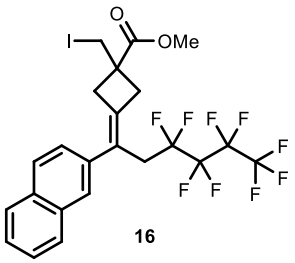
yield: 86% (54 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.22 (m, 1H), 7.11 – 7.07 (m, 1H), 6.93 – 6.87 (m, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 3.57 (s, 2H), 3.35 (dd, *J* = 16.2, 3.0 Hz, 1H), 3.27 – 3.06 (m, 3H), 2.75 (dt, *J* = 16.4, 2.5 Hz, 1H), 2.52 (dt, *J* = 16.5, 2.6 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.9, 156.5, 136.3, 130.6, 129.0, 127.2, 122.7, 120.7, 111.0, 55.4, 52.7, 44.7, 40.5, 40.0, 32.5 (t, *J* = 22.2 Hz), 12.4. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.2 (m), -112.2 – -112.3 (m), -124.2 – -124.3 (m), -125.9 – -126.1 (m).

HRMS (ESI^+) *m/z* Calcd for $C_{20}H_{19}F_9IO_3^+$ $[M+H]^+$ 605.0230, found 605.0232.



16

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

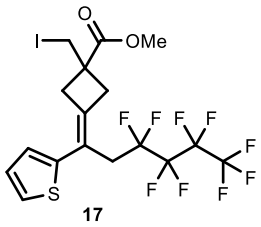
yield: 77% (48 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.80 (m, 3H), 7.68 – 7.66 (m, 1H), 7.52 – 7.45 (m, 2H), 7.36 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.79 (s, 3H), 3.59 (s, 2H), 3.44 (dt, *J* = 16.4, 3.6 Hz, 2H), 3.36 – 3.16 (m, 2H), 2.87 – 2.74 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 136.9, 136.0, 133.4, 132.6, 128.3, 128.1, 127.8, 126.5, 126.3, 126.2, 125.2, 123.8, 52.8, 45.2, 41.6, 40.7, 32.9 (t, *J* = 22.2 Hz), 12.1. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.6 – -111.8 (m, 2F), -124.0 – -124.1 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI^+) *m/z* Calcd for $C_{23}H_{19}F_9IO_2^+$ $[M+H]^+$ 625.0281, found 625.0276.



17

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

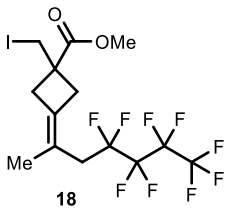
yield: 71% (41 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 1H), 7.05 – 7.00 (m, 1H), 6.97 – 6.92 (m, 1H), 3.79 (s, 3H), 3.59 (d, *J* = 1.6 Hz, 2H), 3.52 (dd, *J* = 17.6, 3.6 Hz, 1H), 3.38 (dd, *J* = 17.2, 3.6 Hz, 1H), 3.16 (t, *J* = 18.8 Hz, 2H), 2.99 (dd, *J* = 17.4, 3.0 Hz, 1H), 2.80 (dd, *J* = 17.2, 3.2 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 142.0, 135.7, 127.1, 125.3, 124.3, 124.2, 117.9, 52.9, 44.9, 42.5, 40.6, 32.5 (t, *J* = 22.2 Hz), 12.1. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.1 (m, 3F), -111.7 – -111.9 (m, 2F), -124.2 – -124.4 (m, 2F), -125.7 – -125.9 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{17}H_{15}F_9IO_2S^+$ $[M+H]^+$ 580.9688, found 580.9687.



18

colorless oil.

R*f* (DCM : PE = 1 : 2) = 0.4;

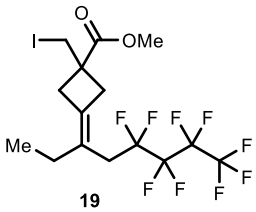
yield: 90% (46 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.76 (s, 3H), 3.59 – 3.51 (m, 2H), 3.15 (t, *J* = 15.1 Hz, 3H), 2.73 – 2.52 (m, 4H), 1.67 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 131.7, 119.1, 52.7, 44.1, 39.4, 39.2, 33.9 (t, *J* = 22.2 Hz), 18.1, 12.6. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.03 – -81.18 (m, 3F), -112.30 – -112.47 (m, 2F), -124.26 – -124.42 (m, 2F), -125.87 – -126.04 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{14}H_{14}F_9IO_2^+$ $[M+H]^+$ 512.9968, found 512.9970.



19

colorless oil.

R*f* (DCM : PE = 1 : 2) = 0.4;

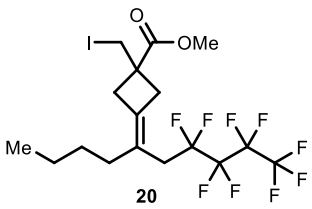
yield: 78% (46 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.76 (s, 3H), 3.54 (s, 2H), 3.23 – 3.09 (m, 2H), 2.73 – 2.53 (m, 4H), 2.06 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 131.7, 124.8, 52.7, 44.3, 39.4, 39.3, 30.6 (t, *J* = 22.5 Hz), 24.8, 12.6, 12.2. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.00 – -81.3 (m, 3F), -112.3 – -112.6 (m, 2F), -124.2 – -124.5 (m, 2F), -125.9 – -126.0 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{15}H_{17}F_9IO_2^+$ $[M+H]^+$ 527.0124, found 527.0119.



20

colorless oil.

R*f* (DCM : PE = 1 : 2) = 0.4;

yield: 81% (45 mg);

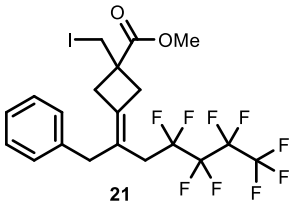
^{1}H NMR (400 MHz, Chloroform-d) δ 3.76 (s, 3H), 3.54 (s, 2H), 3.16 (t, *J* = 17.0 Hz, 2H), 2.63 (q, *J* = 19.0, 18.1 Hz, 4H), 2.04 (t, *J* = 7.3 Hz, 2H),

1.38 – 1.24 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 174.0, 132.2, 123.5, 52.7, 44.3, 39.5, 39.4, 31.3, 30.9 (t, *J* = 22.6 Hz), 29.7, 22.5, 14.0, 12.6. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-d) δ -81.0 – -81.1 (m, 3F), -112.3 – -112.4 (m, 2F), -124.2 – -124.4 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{17}H_{21}F_9IO_2^+$ $[M+H]^+$ 555.0437, found 555.0439.



21

colorless oil.

R$_f$ (DCM : PE = 1 : 2) = 0.4;

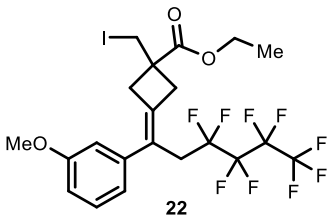
yield: 84% (49 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.20 (m, 1H), 7.16 – 7.11 (m, 2H), 3.79 (s, 3H), 3.59 (s, 2H), 3.42 – 3.27 (m, 3H), 3.21 (d, *J* = 16.4 Hz, 1H), 2.75 (d, *J* = 16.2 Hz, 1H), 2.66 (d, *J* = 16.4 Hz, 1H), 2.53 (t, *J* = 19.5 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.8, 138.6, 133.7, 128.9, 128.8, 126.7, 122.6, 52.8, 44.3, 39.8, 39.5, 37.8, 30.5 (t, *J* = 22.3 Hz), 12.3. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.2 (m, 3F), -111.8 – -112.0 (m, 2F), -124.2 – -124.4 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{20}H_{19}F_9IO_2^+$ $[M+H]^+$ 589.0281, found 589.0284.



22

colorless oil.

R$_f$ (DCM : PE = 1 : 2) = 0.4;

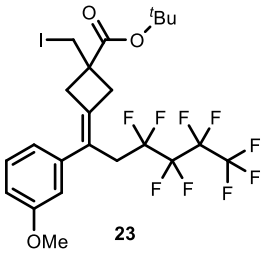
yield: 90% (56 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 8.0 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.79 – 6.75 (m, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 3.58 (s, 2H), 3.38 (dt, *J* = 16.4, 3.6 Hz, 2H), 3.25 – 3.04 (m, 2H), 2.82 – 2.73 (m, 2H), 1.32 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.2, 159.7, 140.0, 136.7, 129.6, 123.5, 119.6, 113.4, 112.4, 61.7, 55.3, 45.0, 41.5, 40.5, 32.8 (t, *J* = 22.2 Hz), 14.3, 12.2. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.2 (m, 3F), -111.7 – -112.0 (m, 2F), -124.02 – -124.2 (m, 2F), -125.8 – -126.1 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{21}H_{21}F_9IO_3^+$ $[M+H]^+$ 619.0386, found 619.0382.



23

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

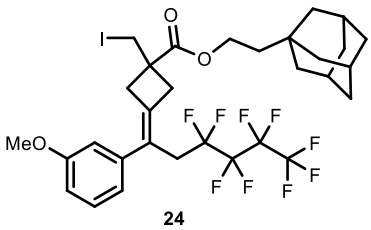
yield: 84% (54 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 8.0 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.77 – 6.73 (m, 1H), 3.81 (s, 3H), 3.52 (s, 2H), 3.35 – 3.27 (m, 2H), 3.20 – 3.03 (m, 2H), 2.74 – 2.65 (m, 2H), 1.49 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.3, 159.7, 140.1, 137.1, 129.6, 123.3, 119.6, 113.4, 112.4, 81.9, 55.4, 45.5, 41.3, 40.3, 32.8 (t, *J* = 22.2 Hz), 28.0, 12.8. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.8 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI^+) *m/z* Calcd for $C_{23}H_{25}F_9IO_3^+$ $[M+H]^+$ 647.0699, found 647.0703.



24

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

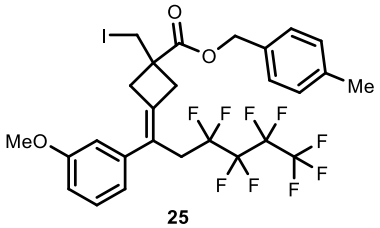
yield: 75% (57 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 1H), 6.83 – 6.77 (m, 2H), 6.76 – 6.73 (m, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.55 (s, 2H), 3.40 – 3.31 (m, 2H), 3.23 – 3.01 (m, 2H), 2.80 – 2.70 (m, 2H), 1.95 (s, 3H), 1.74 – 1.60 (m, 6H), 1.54 (d, *J* = 2.4 Hz, 6H), 1.46 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 159.7, 140.0, 136.7, 129.6, 123.5, 119.6, 113.3, 112.4, 62.3, 55.3, 45.1, 42.7, 42.5, 41.5, 40.5, 37.1, 32.8 (t, *J* = 22.0 Hz), 32.0, 28.7, 12.3. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.8 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI^+) *m/z* Calcd for $C_{31}H_{35}F_9IO_3^+$ $[M+H]^+$ 753.1482, found 753.1483.



25

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

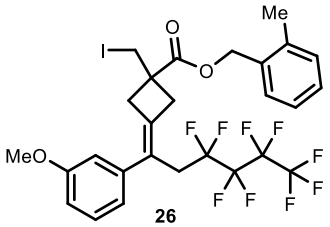
yield: 81% (55 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 3H), 7.23 – 7.18 (m, 2H), 6.85 – 6.79 (m, 2H), 6.77 – 6.74 (m, 1H), 5.18 (s, 2H), 3.82 (s, 3H), 3.59 (s, 2H), 3.38 (dd, *J* = 16.6, 3.4 Hz, 2H), 3.23 – 3.04 (m, 2H), 2.82 – 2.74 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 159.7, 140.0, 138.4, 136.5, 132.6, 129.6, 129.4, 128.6, 123.6, 119.6, 113.3, 112.4, 67.5, 55.3, 45.2, 41.5, 40.6, 32.8 (t, *J* = 22.4 Hz), 21.3, 12.0. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.8 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{27}H_{25}F_9IO_3^+$ $[M+H]^+$ 695.0699, found 695.0698.



26

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

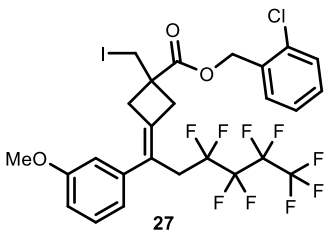
yield: 83% (57 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 1H), 7.29 – 7.23 (m, 2H), 7.22 – 7.16 (m, 2H), 6.82 – 6.75 (m, 2H), 6.75 – 6.70 (m, 1H), 5.20 (s, 2H), 3.79 (s, 3H), 3.56 (s, 2H), 3.35 (dd, *J* = 16.9, 2.7 Hz, 2H), 3.21 – 3.00 (m, 2H), 2.81 – 2.72 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.07, 159.68, 139.94, 137.24, 136.43, 133.49, 130.54, 129.59, 128.87, 126.17, 123.66, 119.59, 113.32, 112.43, 66.00, 55.32, 45.31, 41.57, 40.63, 32.85 (t, *J* = 22.2 Hz), 19.19, 11.93. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.96 – -81.11 (m), -111.73 – -111.90 (m), -124.01 – -124.17 (m), -125.80 – -125.99 (m).

HRMS (ESI^+) *m*/*z* Calcd for $C_{27}H_{25}F_9IO_3^+$ $[M+H]^+$ 695.0699, found 695.0699.



27

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

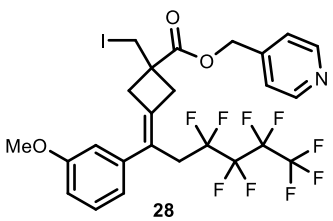
yield: 88% (63 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.32 – 7.22 (m, 3H), 6.82 – 6.76 (m, 2H), 6.75 – 6.71 (m, 1H), 5.30 (s, 2H), 3.79 (s, 3H), 3.58 (s, 2H), 3.42 – 3.34 (m, 2H), 3.23 – 3.01 (m, 2H), 2.85 – 2.74 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.9, 159.7, 140.0, 136.4, 133.3, 130.4, 129.9, 129.8, 129.6, 127.0, 123.7, 119.6, 113.3, 112.4, 64.9, 55.3, 45.3, 41.6, 40.7, 32.9 (t, *J* = 22.2 Hz), 11.8. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.7 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{26}H_{22}ClF_9IO_3^+$ $[M+H]^+$ 715.0153, found 705.0151.



28

colorless oil.

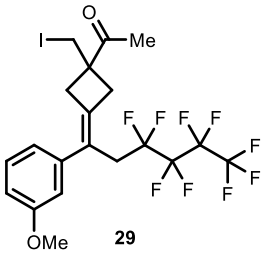
R_f (PE : EA = 2 : 1) = 0.4;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 – 8.46 (m, 2H), 7.23 – 7.17 (m, 3H), 6.77 – 6.70 (m, 2H), 6.68 – 6.65 (m, 1H), 5.14 (s, 2H), 3.73 (s, 3H), 3.53 (s, 2H), 3.36 – 3.27 (m, 2H), 3.04 (t, *J* = 20.5, 10.1 Hz, 2H), 2.78 – 2.70 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.8, 159.7, 150.2, 144.5, 139.8, 135.9, 129.7, 124.0, 122.3, 119.7, 113.4, 112.4, 65.4, 55.4, 45.3, 41.7, 40.7, 32.9, 32.7, 11.5. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.09 (m, 3F), -111.75 – -111.91 (m, 2F), -124.00 – -124.17 (m, 2F), -125.80 – -126.00 (m, 2F).

MS (EI, m/z): 461 (4.8), 417 (30.8), 320 (8.8), 109 (52.1), 93 (100.0), 65 (20.3).



29

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

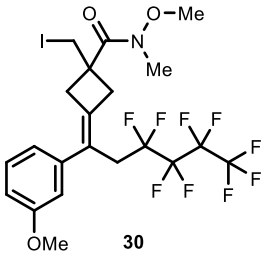
yield: 86% (51 mg);

^{1}H NMR (400 MHz, Chloroform-d) δ 7.26 (t, *J* = 7.6 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.76 – 6.72 (m, 1H), 3.80 (s, 3H), 3.55 (s, 2H), 3.31 – 3.22 (m, 2H), 3.20 – 3.03 (m, 2H), 2.75 – 2.65 (m, 2H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 206.6, 159.7, 139.9, 135.8, 129.6, 124.1, 119.6, 113.4, 112.4, 55.4, 50.5, 40.3, 39.2, 32.9 (t, *J* = 22.2 Hz), 24.4, 11.4. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-d) δ -81.0 – -81.1 (m), -111.8 – -111.9 (m), -124.0 – -124.2 (m), -125.8 – -126.0 (m).

HRMS (ESI^+) *m/z* Calcd for $C_{20}H_{19}F_9IO_2^+$ $[M+H]^+$ 589.0281, found 589.0278.



30

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

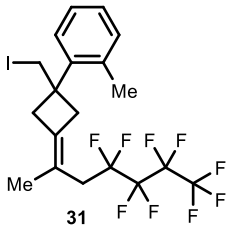
yield: 91% (58 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.8 Hz 1H), 6.82 – 6.78 (m, 2H), 6.76 – 6.74 (m, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.60 (s, 2H), 3.49 – 3.38 (m, 2H), 3.25 (s, 3H), 3.21 – 3.01 (m, 2H), 2.77 – 2.65 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 159.7, 140.2, 138.2, 129.5, 123.2, 119.6, 113.3, 112.3, 61.0, 55.3, 45.3, 41.4, 40.6, 33.3, 32.9 (t, *J* = 22.2 Hz), 11.8. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.7 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{21}H_{22}F_9INO_3^+$ $[M+H]^+$ 634.0495, found 634.0496.



31

colorless oil.

R_f (PE) = 0.4;

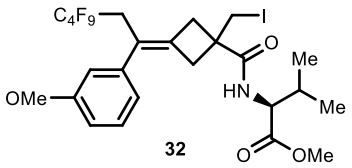
yield: 91% (50 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.08 (m, 4H), 3.68 (s, 2H), 3.29 – 3.15 (m, 2H), 3.06 – 2.91 (m, 2H), 2.82 – 2.61 (m, 2H), 2.31 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.5, 135.3, 134.9, 131.7, 128.9, 127.2, 125.4, 117.5, 42.9, 42.0, 41.8, 34.1 (t, *J* = 22.2 Hz), 21.2, 20.2, 18.2. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -112.2 – -112.4 (m, 2F), -124.1 – -124.3 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{19}H_{19}F_9I^+$ $[M+H]^+$ 545.0382, found 545.0386.



32

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

yield: 79% (56 mg);

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (m, 1H), 7.31 – 7.23 (m, 1H), 6.93 – 6.80 (m, 3H), 4.24 – 4.13 (m, 1H), 3.85 – 3.80 (m, 1H), 3.75 (s, 3H), 3.71 – 3.66 (m, 1H), 3.64 (s, 2H), 3.62 (s, 2H), 3.43 – 3.37 (m, 1H), 3.34 – 3.25 (m, 2H), 3.23 – 3.11 (m, 1H), 2.90 – 2.77 (m, 1H), 2.71 – 2.60 (m, 1H), 2.16 – 2.01 (m, 1H), 0.95 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 173.14 / 173.13, 172.58 /172.54, 159.61, 140.31 / 140.27, 138.43, 129.79 / 129.77, 122.47 – 121.99 (m), 119.81 / 119.77, 113.24 / 113.21, 112.66 / 112.63, 58.44 / 58.42, 55.49, 52.08 / 52.06, 45.22 / 45.10, 41.64, 41.26 / 40.40, 40.19, 32.37 – 31.97 (m), 30.16, 19.68, 19.22 / 19.19, 15.88 / 15.75. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, DMSO-d_6) δ -80.5 – -80.7 (m, 3F), -110.8 (s, 2F), -123.5 – -123.8 (m, 2F), -125.5 – -125.8 (m, 2F).

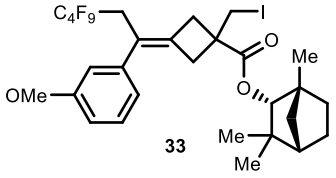
^{1}H NMR (400 MHz, DMSO-d_6, 80 ℃) δ 7.84 – 7.72 (m, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 6.93 – 6.80 (m, 3H), 4.22 (t, *J* = 7.6 Hz, 1H), 3.84 – 3.78 (m, 1H), 3.77 (s, 3H), 3.73 – 3.67 (m, 1H), 3.65 (s, 1.57H) / 3.63(s, 1.43H), 3.38 – 3.16 (m, 4H), 2.86 – 2.64 (m, 2H), 2.16 – 2.05 (m, 1H), 0.93 (t, *J* = 6.3 Hz, 6H).

^{13}C NMR (100 MHz, DMSO-d_6, DMSO-d_6, 80 ℃) δ 172.96 / 172.94, 172.25 / 172.22,

159.84, 140.48 /140.47, 138.33 / 138.31, 129.72, 122.44 / 122.41, 119.9 / 119.91, 113.53, 112.93, 58.57, 55.63, 51.86, 51.84, 45.22 / 45.13, 41.70, 41.47 / 40.59, 40.49, 32.69 (t, J = 22.2 Hz) / 32.69 (t, J = 22.2 Hz), 30.22 / 30.21, 19.56, 19.10 / 19.08, 15.65 / 15.58. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, DMSO-d_6, 80 ℃) δ -80.3 – -80.6 (m, 3F), -110.1 (s, 2F), -123.2 – -123.4 (m, 2F), -125.1 (t, J = 12.0 Hz, 2F).

HRMS (ESI$^+$) m/z Calcd for $C_{25}H_{28}F_9INO_4^+$ $[M+H]^+$ 704.0914, found 704.0915.



33

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

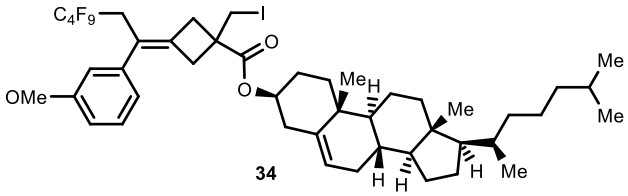
yield: 58% (42 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 1H), 6.83 – 6.77 (m, 2H), 6.76 – 6.72 (m, 1H), 4.43 – 4.40 (m, 1H), 3.81 (s, 1.5H) / 3.80 (s, 1.5H), 3.66 – 3.53 (m, 2H), 3.41 – 3.24 (m, 2H), 3.19 – 3.05 (m, 2H), 2.86 – 2.74 (m, 2H), 1.77 – 1.66 (m, 3H), 1.63 – 1.58 (m, 1H), 1.54 – 1.44 (m, 1H), 1.23 – 1.18 (m, 1H), 1.12 (s, 3H), 1.11 – 1.03 (m, 4H), 0.81 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.53 / 173.51, 159.67, 140.06 / 140.02, 136.61, 129.60, 123.53, 119.66, 113.34 / 113.32, 112.49 / 112.43, 87.37, 55.35, 48.72, 48.41, 45.57, 45.52, 41.89, 41.73, 41.45, 40.94, 40.80, 39.77 / 39.75, 32.95(t, J = 22.5 Hz), 29.77, 26.78 / 26.77, 25.93, 20.59, 19.72 / 19.71, 12.19. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.7 – -111.8 (m, 2F), -124.0 – -124.12 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) m/z Calcd for $C_{29}H_{33}F_9IO_3^+$ $[M+H]^+$ 727.1325, found 727.1321.



34

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

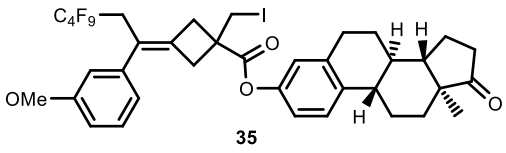
yield: 71% (68 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (t, J = 7.6 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.70 – 6.65 (m, 1H), 5.32 (s, 1H), 4.67 – 4.56 (m, 1H), 3.73 (s, 3H), 3.48 (s, 2H), 3.27 (dt, J = 17.2, 2.7 Hz, 2H), 3.15 – 2.94 (m, 2H), 2.75 – 2.61 (m, 2H), 2.29 (t, J = 6.4 Hz, 2H), 1.98 – 1.72 (m, 6H), 1.52 – 1.21 (m, 12H), 1.13 – 0.98 (m, 8H), 0.92 – 0.88 (m, 2H), 0.87 – 0.82 (m, 4H), 0.79 (dd, J = 6.6, 1.8 Hz, 6H), 0.61 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.6, 159.7, 140.0, 139.5, 136.8, 129.6, 123.5, 123.1, 119.6, 113.4, 112.4, 75.3, 56.8, 56.3, 55.3, 50.1, 45.0, 42.5, 41.4, 40.5, 39.9, 39.7, 38.1, 37.1, 36.7, 36.3, 35.9, 32.8 (t, J = 22.2 Hz), 32.1, 32.0, 28.4, 28.2, 27.8, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.4, 12.0. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.1 (m, 3F), -111.7 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{46}H_{61}F_9IO_3^+$ $[M+H]^+$ 959.3516, found 959.3521.



35

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.2;

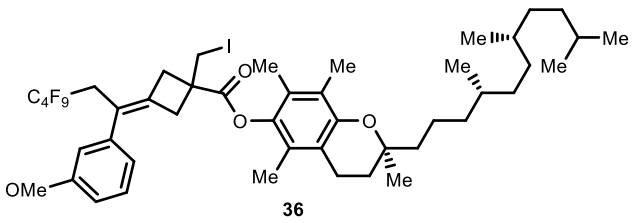
yield: 83% (70 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.88 – 6.85 (m, 1H), 6.85 – 6.79 (m, 2H), 6.79 – 6.75 (m, 1H), 3.82 (s, 3H), 3.69 (s, 2H), 3.51 (dt, *J* = 16.4, 3.6 Hz, 2H), 3.26 – 3.05 (m, 2H), 2.95 – 2.87 (m, 3H), 2.85 (s, 1H), 2.56 – 2.47 (m, 1H), 2.45 – 2.38 (m, 1H), 2.34 – 2.26 (m, 1H), 2.21 – 2.10 (m, 1H), 2.08 – 1.93 (m, 3H), 1.63 – 1.42 (m, 6H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.7, 148.6, 139.9, 138.3, 137.9, 136.1, 129.6, 126.6, 124.0, 121.4, 119.6, 118.6, 113.4, 112.4, 55.4, 50.6, 48.1, 45.4, 44.3, 41.6, 40.6, 38.1, 36.0, 32.9 (t, *J* = 21.2 Hz), 31.7, 29.5, 26.4, 25.9, 21.7, 14.0, 11.7. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.1 (m, 3F), -111.7 – -111.9 (m, 2F), -124.0 – -124.2 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{37}H_{37}F_9IO_4^+$ $[M+H]^+$ 843.1587, found 843.1587.



36

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.3;

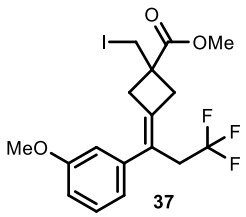
yield: 63% (63 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 1H), 6.85 – 6.80 (m, 2H), 6.79 – 6.76 (m, 1H), 3.82 (s, 3H), 3.76 (s, 2H), 3.57 (dt, *J* = 17.2, 3.6 Hz, 2H), 3.26 – 3.06 (m, 2H), 2.99 – 2.91 (m, 2H), 2.60 (t, *J* = 6.6 Hz, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.86 – 1.73 (m, 2H), 1.56 – 1.49 (m, 3H), 1.41 – 1.05 (m, 21H), 0.89 – 0.84 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 159.7, 149.7, 140.4, 140.0, 136.3, 129.7, 126.8, 125.1, 123.8, 123.4, 119.7, 117.7, 113.4, 112.5, 75.3, 55.4, 45.6, 42.3, 41.4, 39.5, 37.6, 37.4, 33.0, 32.9, 32.9, 28.1, 24.9, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.5, 12.7, 12.0, 11.9. ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.1 (m, 3F), -111.7 – -111.9 (m, 2F), -123.9 – -124.1 (m, 2F), -125.8 – -126.0 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{48}H_{65}F_9IO_4^+$ $[M+H]^+$ 1003.3778, found 1003.3779.



37

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

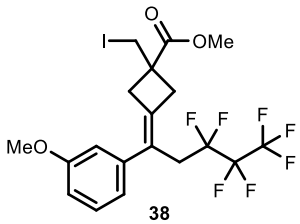
yield: 74% (34 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.23 (m, 1H), 6.82 – 6.78 (m, 2H), 6.76 – 6.73 (m, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.57 – 3.54 (m, 2H), 3.37 (dt, *J* = 16.4, 2.6 Hz, 2H), 3.19 – 3.05 (m, 2H), 2.83 – 2.70 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.8, 159.7, 139.6, 135.8, 129.6, 126.1 (q, *J* = 278.8 Hz), 124.6 (q, *J* = 3.0 Hz), 119.6, 113.3, 112.5, 55.4, 52.8, 45.2, 41.4, 40.5, 36.1 (q, *J* = 30.3 Hz), 12.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.1 (s, 3F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{17}H_{19}F_3IO_3^+$ $[M+H]^+$ 455.0325, found 455.0324.



38

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

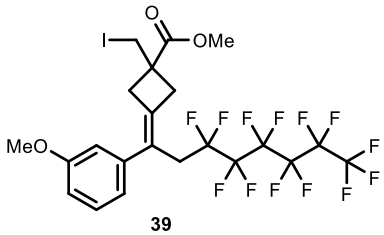
yield: 71% (39 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 1H), 6.83 – 6.78 (m, 2H), 6.75 – 6.72 (m, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.56 (s, 2H), 3.37 (dt, *J* = 16.8, 3.2 Hz, 2H), 3.21 – 3.01 (m, 2H), 2.80 – 2.71 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 159.7, 140.0, 136.5, 129.6, 123.6, 119.6, 113.4, 112.4, 55.4, 52.8, 45.2, 41.5, 40.6, 32.7 (t, *J* = 22.7 Hz), 12.1. ($CF_3(CF_2)_2$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.4 (t, *J* = 11.3 Hz, 3F), -112.4 – -112.5 (m, 2F), -127.4 – -127.5 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{19}H_{19}F_7IO_3^+$ $[M+H]^+$ 555.0262, found 555.0258.



39

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

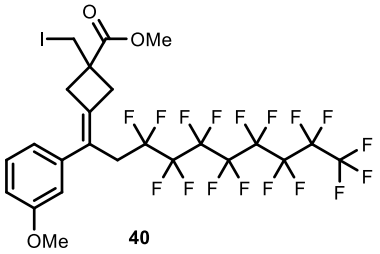
yield: 95% (67 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.8 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.70 – 6.65 (m, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.49 (s, 2H), 3.30 (dt, *J* = 16.4, 3.6 Hz, 2H), 3.15 – 2.95 (m, 2H), 2.73 – 2.64 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 159.7, 140.0, 136.5, 129.6, 123.7, 119.6, 113.3, 112.4, 55.4, 52.8, 45.2, 41.6, 40.6, 32.9 (t, *J* = 22.7 Hz), 12.1. ($CF_3(CF_2)_5$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.7 – -80.9 (m, 3F), -111.5 – -111.7 (m, 2F), -121.7 – -121.9 (m, 2F), -122.8 – -123.0 (m, 2F), -123.1 – -123.3 (m, 2F), -126.0 – -126.3 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{22}H_{19}F_{13}IO_3^+$ $[M+H]^+$ 705.0166, found 705.0163.



40

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

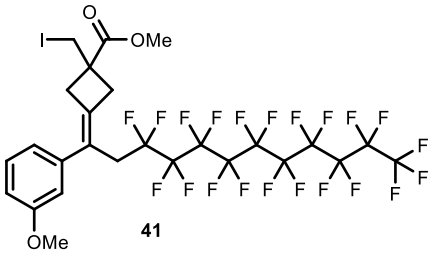
yield: 94% (75 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 8.0 Hz, 1H), 6.75 – 6.71 (m, 2H), 6.69 – 6.66 (m, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.48 (s, 2H), 3.34 – 3.26 (m, 2H), 3.17 – 2.93 (m, 2H), 2.74 – 2.64 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.71, 159.70, 139.97, 136.55, 129.60, 123.68, 119.59, 113.34, 112.43, 55.33, 52.79, 45.18, 41.56, 40.60, 32.93 (t, *J* = 22.7 Hz), 12.04. ($CF_3(CF_2)_7$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.83 (t, *J* = 11.3 Hz, 3F), -111.64 (t, *J* = 15.0 Hz, 2F), -121.5 – -121.8 (m, 2F), -121.8 – -122.1 (m, 4F), -122.8 (s, 2F), -123.0 – -123.4 (m, 2F), -125.9 – -126.4 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{24}H_{19}F_{17}IO_3^+$ $[M+H]^+$ 805.0102, found 805.0103.



41

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

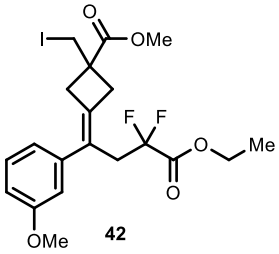
yield: 82% (74 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 8.0 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.77 – 6.72 (m, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.56 (s, 2H), 3.43 – 3.32 (m, 2H), 3.24 – 3.01 (m, 2H), 2.81 – 2.71 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 159.7, 140.0, 136.5, 129.6, 123.7, 119.6, 113.3, 112.4, 55.3, 52.8, 45.2, 41.6, 40.6, 32.9 (t, *J* = 22.2 Hz), 12.1. ($CF_3(CF_2)_9$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.8 (t, *J* = 9.4 Hz, 3F), -111.7 (t, *J* = 13.2 Hz, 2F), -121.3 – -122.2 (m, 10F), -122.7 (s, 2F), -123.2 (s, 2F), -125.8 – -126.5 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{26}H_{19}F_{21}IO_3^+$ $[M+H]^+$ 905.0038, found 905.0040.



42

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

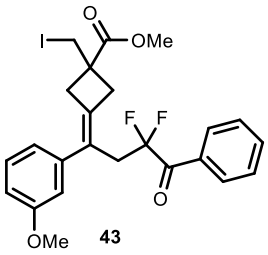
yield: 73% (37 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 1H), 6.80 – 6.74 (m, 2H), 6.71 – 6.68 (m, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.54 (s, 2H), 3.35 (td, *J* = 16.5, 3.2 Hz, 2H), 3.13 (td, *J* = 16.4F, 7.6 Hz, 2H), 2.78 (dt, *J* = 16.4, 2.4 Hz, 1H), 2.69 (dt, *J* = 16.8, 2.4 Hz, 1H), 1.14 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.8, 163.9 (t, *J* = 32.8 Hz), 159.6, 139.5, 135.75, 129.4, 125.1 (t, *J* = 4.5 Hz), 120.0, 115.3 (t, *J* = 253.5 Hz), 113.4, 112.6, 62.9, 55.4, 52.7, 45.2, 41.4, 40.7, 37.1 (t, *J* = 24.7 Hz), 13.8, 12.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.8 (d, *J* = 251.9 Hz, 1F), -103.6 (d *J* = 251.9 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{20}H_{24}F_2IO_5^+$ $[M+H]^+$ 509.0631, found 509.0631.



43

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

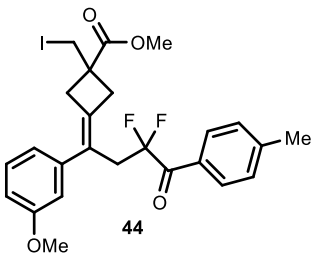
yield: 73% (40 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.55 (m, 1H), 7.47 – 7.39 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.78 – 6.71 (m, 2H), 6.70 – 6.64 (m, 1H), 3.76 (s, 6H), 3.53 (s, 2H), 3.38 – 3.20 (m, 4H), 2.77 – 2.65 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.49 (t, *J* = 30.3 Hz), 173.82, 159.50, 140.15, 135.23, 134.31, 132.21 (t, *J* = 2.0 Hz), 130.12 (t, *J* = 3.0 Hz), 129.33, 128.70, 125.58 (t, *J* = 3.3 Hz), 119.89, 118.99 (t, *J* = 255.5 Hz), 113.26, 112.43, 55.27, 52.71, 45.14, 41.40, 40.73, 36.28 (t, *J* = 23.5 Hz), 12.36.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.3 (d, *J* = 278.2 Hz, 1F), -98.1 (d, *J* = 278.2 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{24}H_{24}F_2IO_4^+$ $[M+H]^+$ 541.0682, found 541.0687.



44

colorless oil.

R_f (PE : EtOAc = 10 : 1) = 0.2;

yield: 90% (50 mg);

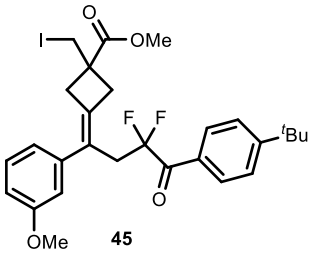
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.16 (m, 3H), 6.79 – 6.72 (m, 2H), 6.70 – 6.65

(m, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.52 (S, Hz, 2H), 3.36 – 3.19 (m, 4H), 2.76 – 2.65 (m, 2H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.1 (t, *J* = 30.3 Hz), 173.8, 159.5, 145.5, 140.2, 135.1, 130.3 (t, *J* = 3.0 Hz), 129.7 (t, *J* = 2.2 Hz), 129.4, 1293, 125.7 (t, *J* = 3.0 Hz), 119.9, 119.1 (t, *J* = 256.0 Hz), 113.3, 112.4, 55.3, 52.7, 36.3 (t, *J* = 23.7 Hz), 21.9, 12.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.3 (d, *J* = 274.5 Hz, 1F), -98.1 (d, *J* = 278.2 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{25}H_{26}F_2IO_4^+$ $[M+H]^+$ 555.0838, found 555.0835.



45

colorless oil.

R_f (PE : EtOAc = 10 : 1) = 0.2;

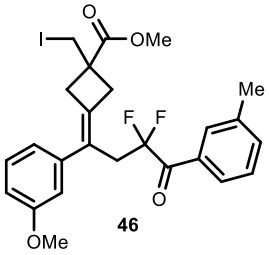
yield: 85% (51 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.69 – 6.66 (m, 1H), 3.75 (s, 6H), 3.53 (d, *J* = 1.6 Hz, 2H), 3.37 – 3.20 (m, 4H), 2.76 – 2.66 (m, 2H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.1 (t, *J* = 30.3 Hz), 173.8, 159.5, 158.3, 140.2, 135.1, 130.2 (t, *J* = 3.4 Hz), 129.6 (t, *J* = 2.0 Hz), 129.3, 125.7, 119.9, 119.1 (t, *J* = 256.5Hz), 113.2, 112.4, 55.3, 52.7, 45.2, 41.4, 40.7, 36.4 (t, *J* = 23.2 Hz), 35.4, 31.1, 12.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.3 (d, *J* = 274.5 Hz, 1F), -98.1 (d, *J* = 274.5 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{28}H_{32}F_2IO_4^+$ $[M+H]^+$ 597.1308, found 597.1308.



46

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

yield: 78% (43 mg);

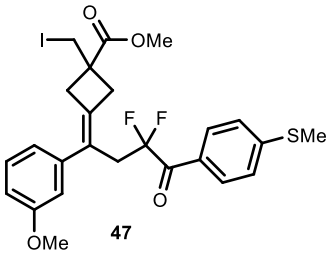
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.43 – 7.37 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.68 – 6.65 (m, 1H), 3.76 (s, 6H), 3.53 (s, 2H), 3.35 – 3.20 (m, 4H), 2.76 – 2.66 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.6 (t, *J* = 30.3 Hz), 173.7, 159.4, 140.1, 138.4, 135.1, 135.0, 132.2 (t, *J* = 2.0 Hz), 130.5 (t, *J* = 3.0 Hz), 129.2, 128.4, 127.2 (t, *J* = 3.5 Hz), 125.5 (t, *J* = 3.0 Hz), 119.8, 118.9 (t, *J* = 256.0 Hz), 113.2, 112.3, 55.2, 52.6, 45.1, 41.3, 40.6, 36.3 (t, *J* = 23.2 Hz), 21.3, 12.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.3 (d, J = 278.2 Hz, 1F), -98.1 (d, J = 274.5

Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{25}H_{26}F_2IO_4^+$ $[M+H]^+$ 555.0838, found 555.0838.



47

colorless oil.

R$_f$ (PE : EtOAc = 10 : 1) = 0.2;

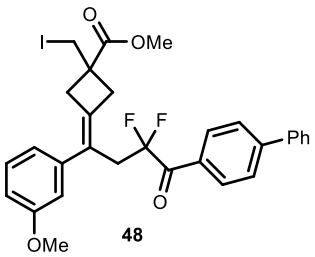
yield: 76% (46 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.23 – 7.16 (m, 3H), 6.77 – 6.72 (m, 2H), 6.68 – 6.65 (m, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.53 (s, 2H), 3.37 – 3.19 (m, 4H), 2.76 – 2.66 (m, 2H), 2.51 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.4 (t, *J* = 30.3 Hz), 173.8, 159.5, 148.1, 140.2, 135.2, 130.4 (t, *J* = 3.5 Hz), 129.3, 128.2 (t, *J* = 2.0 Hz), 125.6 (t, *J* = 3.0 Hz), 124.8, 119.9, 119.1 (t, *J* = 256.0 Hz), 113.3, 112.4, 55.3, 52.7, 45.1, 41.4, 40.7, 36.3 (t, *J* = 23.7 Hz), 14.7, 12.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.2 (d, *J* = 278.2 Hz, 1F), -98.0 (d, *J* = 278.2 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{25}H_{26}F_2IO_4S^+$ $[M+H]^+$ 587.0559, found 587.0559.



48

colorless oil.

R$_f$ (DCM : PE = 1 : 2) = 0.4;

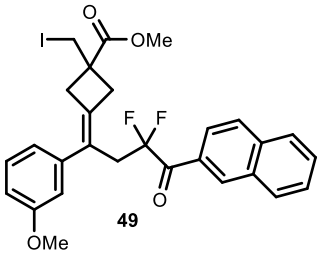
yield: 77% (48 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.61 (m, 4H), 7.51 – 7.46 (m, 2H), 7.44 – 7.39 (m, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 6.78 – 6.73 (m, 2H), 6.70 – 6.66 (m, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.54 (s, 2H), 3.39 – 3.24 (m, 4H), 2.79 – 2.67 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.1 (t, *J* = 30.3 Hz), 173.8, 159.5, 146.9, 1402, 139.6, 135.3, 130.9 (t, *J* =2.0 Hz), 130.8 (t, *J* = 3.0 Hz), 129.3, 129.1, 128.7, 127.4, 127.3, 125.6 (t, *J* = 3.0 Hz), 119.9, 119.1 (t, *J* = 256.0 Hz), 113.3, 112.4, 55.3, 52.7, 45.2, 41.4, 40.8, 36.4 (t, *J* = 23.7 Hz), 12.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.3 (d, *J* = 278.2 Hz, 1F), -98.1 (d, *J* = 278.2 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{30}H_{28}F_2IO_4^+$ $[M+H]^+$ 617.0995, found 617.0994.



49

colorless oil.

R_f (PE : EtOAc = 10 : 1) = 0.25;

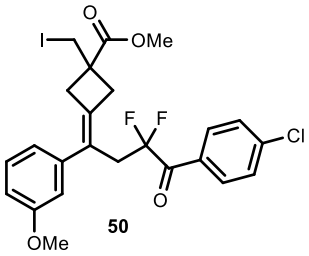
yield: 83% (49 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 7.97 – 7.89 (m, 2H), 7.88 – 7.84 (m, 2H), 7.66 – 7.60 (m, 1H), 7.58 – 7.53 (m, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.79 – 6.72 (m, 2H), 6.70 – 6.66 (m, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.54 – 3.50 (m, 2H), 3.40 – 3.27 (m, 4H), 2.81 – 2.66 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.5 (t, *J* = 29.8 Hz), 173.8, 159.5, 140.2, 136.0, 135.3, 132.9 (t, *J* = 5.0 Hz), 132.3, 130.2, 129.5, 129.4, 129.4, 128.6, 127.9, 127.1, 125.6 (t, *J* = 3.0 Hz), 124.8 (t, *J* = 2.0 Hz), 119.9, 119.3 (t, *J* = 256.5 Hz), 113.3, 112.4, 55.2, 52.7, 45.2, 41.4, 40.8, 36.5 (t, *J* = 23.7 Hz), 12.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.7 (d, *J* = 274.5 Hz, 1F), -97.5 (d, *J* = 274.5 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{28}H_{26}F_2IO_4^+$ $[M+H]^+$ 591.0838, found 591.084



50

colorless oil.

R_f (PE : EtOAc = 10 : 1) = 0.2;

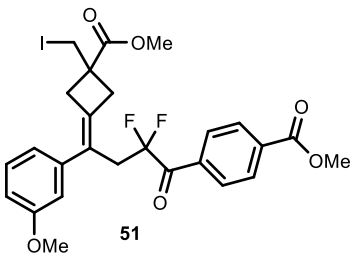
yield: 80% (46 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.78 – 6.69 (m, 2H), 6.66 – 6.60 (m, 1H), 3.76 (s, 3H), 3.76 (s, 3H), 3.54 (s, 2H), 3.37 – 3.18 (m, 4H), 2.79 – 2.65 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.3 (t, *J* = 31.3 Hz), 173.7, 159.4, 140.9, 139.9, 135.3, 131.4 (t, *J* = 3.4 Hz), 130.4 (t, *J* = 2.0 Hz), 129.3, 129.0, 125.3 (t, *J* = 3.4 Hz), 119.8, 118.8 (t, *J* = 256.0 Hz), 113.3, 112.3, 55.2, 52.6, 45.1, 41.3, 40.6, 36.1 (t, *J* = 23.2 Hz), 12.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.3 (d, *J* = 282.0 Hz, 1F), -98.1 (d, *J* = 278.2 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{28}H_{32}F_2IO_4^+$ $[M+H]^+$ 597.1308, found 597.1308.



51

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

yield: 64% (38 mg);

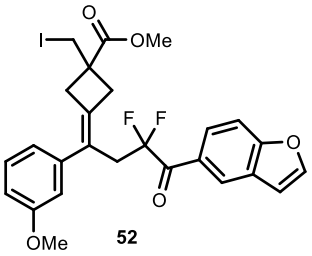
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.04 (m, 2H), 7.99 – 7.95 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.75 – 6.69

(m, 2H), 6.65 – 6.61 (m, 1H), 3.94 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.53 (s, 2H), 3.37 – 3.21 (m, 4H), 2.78 – 2.65 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.2 (t, *J* = 30.3 Hz), 173.8, 166.1, 159.5, 139.9, 135.5, 135.5 (t, *J* = 2.0 Hz), 134.8, 130.0 (t, *J* = 3.5 Hz), 129.7, 129.4, 125.3 (t, *J* = 3.5 Hz), 119.9, 118.8 (t, *J* = 256.0 Hz), 113.4, 112.4, 55.3, 52.8, 52.7, 45.2, 41.4, 40.7, 36.2 (t, *J* = 23.7 Hz), 12.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -97.4 (d, *J* = 282.0 Hz, 1F), -98.2 (d, *J* = 282.0 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{26}H_{26}F_2IO_6^+$ $[M+H]^+$ 599.0737, found 599.0735.



52

colorless oil.

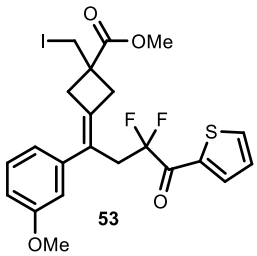
R_f (DCM : PE = 1 : 2) = 0.4;

yield: 62% (36 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.98 – 7.93 (m, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.78 – 6.72 (m, 2H), 6.68 – 6.65 (m, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.53 (s, 2H), 3.36 – 3.24 (m, 4H), 2.77 – 2.66 (m, 2H).**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 189.0 (t, *J* = 29.8 Hz), 173.9, 159.5, 158.0, 146.8, 140.3, 135.2, 129.3, 127.7, 127.6 (t, *J* = 2.0 Hz), 126.8 (t, *J* = 3.0 Hz), 125.7 (t, *J* = 3.0 Hz), 125.0 (t, *J* = 4.5 Hz), 119.9, 119.3 (t, *J* = 256.5 Hz), 113.3, 112.4, 111.9, 107.5, 55.3, 52.7, 45.2, 41.4, 40.8, 36.4 (t, *J* = 23.2 Hz), 12.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -96.4 (d, *J* = 278.2 Hz, 1F), -97.2 (d, *J* = 274.5 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{26}H_{24}F_2IO_5^+$ $[M+H]^+$ 581.0631, found 581.0634.



53

colorless oil.

R_f (PE : EtOAc = 10 : 1) = 0.2;

yield: 76% (42mg);

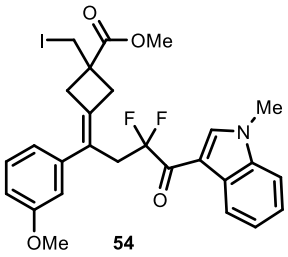
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 1H), 7.77 – 7.73 (m, 1H), 7.21 – 7.11 (m, 2H), 6.77 – 6.70 (m, 2H), 6.66 – 6.63 (m, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.56 – 3.49 (m, 2H), 3.35 – 3.19 (m, 4H), 2.77 – 2.64 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 183.0 (t, *J* = 31.3 Hz), 173.8, 159.5, 139.9, 138.54 (t, *J* = 2.5 Hz), 136.6, 135.9 (t, *J* = 5.6 Hz), 135.4, 129.3, 128.8, 125.4 (t, *J* = 3.5 Hz), 119.9, 118.6 (t, *J* = 256.5 Hz), 113.2, 112.5, 55.3, 52.7, 45.1, 41.4, 40.7, 36.5 (t, *J* = 23.7 Hz), 12.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -98.6 (d, *J* = 267.0 Hz, 1F), -99.5 (d, *J* = 263.2

Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{22}H_{22}F_2IO_4S^+$ $[M+H]^+$ 547.0246, found 547.0245.



54

colorless oil.

R*f* (PE : EtOAc = 10 : 1) = 0.1;

yield: 92% (55 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.41 – 8.35 (m, 1H), 7.76 – 7.72 (m, 1H), 7.37 – 7.31 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.78 – 6.74 (m, 1H), 6.74 – 6.70 (m, 1H), 6.68 – 6.64 (m, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.48 (d, *J* = 9.6 Hz, 1H), 3.42 (d, *J* = 9.6 Hz, 1H), 3.35 – 3.21 (m, 4H), 2.76 (dt, *J* = 16.6, 2.6 Hz, 1H), 2.62 (dt, *J* = 16.6, 2.6 Hz, 1H).

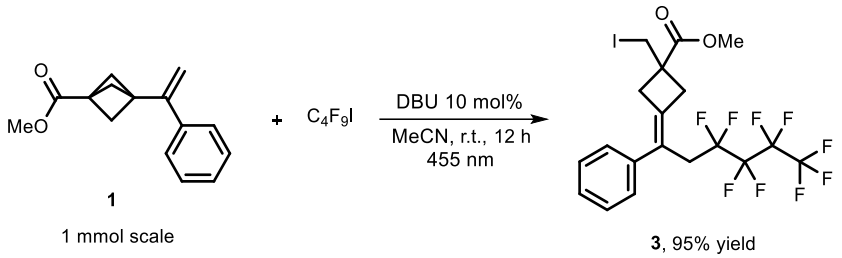
^{13}C NMR (100 MHz, Chloroform-*d*) δ 184.7 (t, *J* = 29.3 Hz), 173.8, 159.4, 140.4, 138.5 (t, *J* = 10.1 Hz), 137.0, 134.9, 129.2, 127.4, 125.9 (t, *J* = 3.5 Hz), 124.1, 123.5, 122.7, 119.9, 119.4 (t, *J* = 256.0 Hz), 113.5, 112.0, 110.9 (t, *J* = 2.0 Hz), 109.9, 55.2, 52.6, 45.0, 41.3, 40.8, 36.4 (t, *J* = 24.7 Hz), 33.8, 12.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -98.2 (d, *J* = 259.4 Hz, 1F), -99.2 (d, *J* = 263.2 Hz, 1F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{27}H_{27}F_2INO_4^+$ $[M+H]^+$ 594.0947, found 594.0947.

2.4 Product Diversification

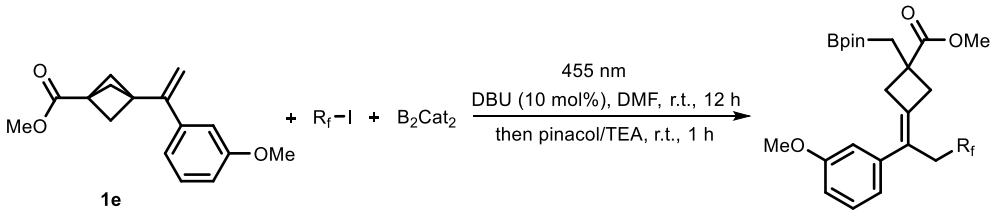
Large scale reaction:



In a N_2-filled glovebox, VBCP **1** (1 mmol) and MeCN (10 mL) were added to a 25 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9I (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and stirred at room temperature under blue LEDs (455 nm, 40W) for approximately 12 h. Then the mixture was concentrated and purified by column chromatography on silica gel (eluent: PE : EtOAc = 20 : 1) to give the product.

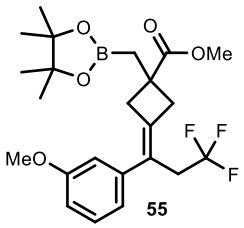
Three-component remote perfluorocarboborylation:

General Procedure E for the synthesis of 55-60 *(*GP-E*)*:[8]



In a N_2-filled glovebox, B_2Cat_2(0.3 mmol, 3.0 equiv) and DMF (1 mL) were added to a 10 mL Schlenk tube. Subsequently, VBCP **1e** (0.1 mmol, 1.0 equiv), DBU (10 mol%) and R_fI (0.11 mmol, 1.1 equiv) were added. The Schlenk tube was removed from the glovebox and stirred at room temperature under blue LEDs (455 nm, 10W) for approximately 12 h. Then a solution of pinacol (0.9 mmol, 9.0 equiv) in triethylamine (1 mL) was added to the mixture. After 1 hour, water (5 mL) was added and the aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The product was purified by

flash column chromatography on silica gel (eluent: PE : EtOAc = 5 : 1) to give the product.



55

colorless oil.

R_f (PE : EtOAc = 5 : 1) = 0.4;

yield: 39% (18 mg);

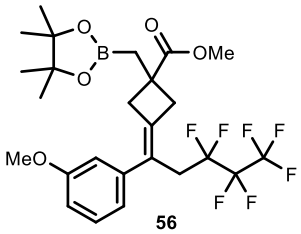
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.14 (m, 1H), 6.77 – 6.73 (m, 1H), 6.70 (d, *J* = 6.8 Hz, 2H), 3.73 (s, 3H), 3.62 (s, 3H), 3.34 – 3.23 (m, 2H), 3.11 – 2.98 (m, 2H), 2.75 – 2.60 (m, 2H), 1.23 (s, 2H), 1.13 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.3, 159.6, 140.2, 140.0, 129.4, 126.4 (q, *J* = 279.8 Hz), 123.1 (q, *J* = 3.0 Hz), 119.8, 113.3, 112.2, 83.3, 55.3, 52.2, 43.3, 42.2, 41.0, 35.9 (q, *J* = 29.3 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.1 (s, 3F).

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{23}H_{31}BF_3O_5^+$ $[M+H]^+$ 455.2211, found 455.2210.



56

colorless oil.

R_f (PE : EtOAc = 5 : 1) = 0.4;

yield: 49% (27 mg);

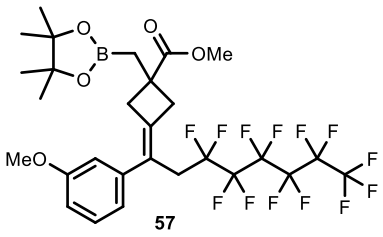
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.14 (m, 1H), 6.77 – 6.67 (m, 3H), 3.73 (s, 3H), 3.62 (s, 3H), 3.35 – 3.22 (m, 2H), 3.14 – 2.95 (m, 2H), 2.72 – 2.62 (m, 2H), 1.23 (s, 2H), 1.14 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.3, 159.6, 140.6, 129.4, 122.1, 119.7, 113.3, 112.2, 83.3, 55.3, 52.2, 43.3, 42.3, 41.0, 32.4 (t, *J* = 22.2 Hz), 24.9. ($CF_3(CF_2)_2$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.4 (t, *J* = 9.7 Hz, 3F), -112.4 – -112.6 (m, 2F), -127.4 – -127.5 (m, 2F).

^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.7.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{25}H_{31}BF_7O_5^+$ $[M+H]^+$ 555.2147, found 555.2147.



57

colorless oil.

R_f (PE : EtOAc = 5 : 1) = 0.4;

yield: 56% (39 mg);

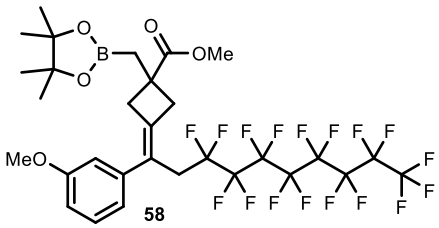
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 1H), 6.79 – 6.75 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 3.35 (td, *J* = 16.8, 3.2 Hz, 2H), 3.19 – 3.04 (m, 2H), 2.80 – 2.69 (m, 2H), 1.30 (s, 2H), 1.20 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.3, 159.6, 140.7, 140.5, 129.4, 122.1, 119.7, 113.3, 112.2, 83.3, 55.3, 52.2, 43.3, 42.3, 41.0, 32.7 (t, *J* = 22.2 Hz), 25.0, 24.9. ($CF_3(CF_2)_5$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) -80.6 – -81.0 (m, 3F), -111.5 – -111.8 (m, 2F), -121.8 (s, 2F), -122.9 (s, 2F), -123.0 – -123.4 (m, 2F), -126.0 – -126.3 (m, 2F).

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.5.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{28}H_{31}BF_{13}O_5^+$ $[M+H]^+$ 705.2051, found 705.2051.



58

colorless oil.

R_f (PE : EtOAc = 5 : 1) = 0.4;

yield: 52% (42mg);

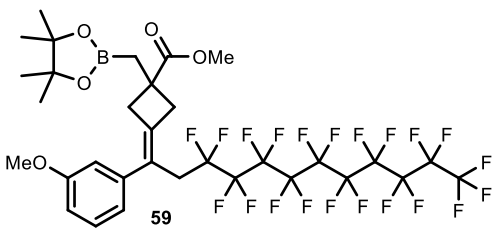
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 1H), 6.77 – 6.73 (m, 1H), 6.73 – 6.68 (m, 2H), 3.73 (s, 3H), 3.62 (s, 3H), 3.28 (td, *J* = 17.0, 3.2 Hz, 2H), 3.15 – 2.97 (m, 2H), 2.74 – 2.61 (m, 2H), 1.23 (s, 2H), 1.13 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.3, 159.6, 140.7, 140.5, 129.4, 122.1, 119.7, 113.3, 112.2, 83.3, 55.3, 52.1, 43.3, 42.3, 41.0, 32.7 (t, *J* = 22.7 Hz), 24.9. ($CF_3(CF_2)_7$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.8 (t, *J* = 9.4 Hz, 3F), -111.6 (t, *J* = 14.1 Hz, 2F), -121.5 – -121.8 (m, 2F), -121.8 – -122.1 (m, 4F), -122.7 (s, 2F), -123.0 – -123.4 (m, 2F), -125.9 – -126.4 (m, 2F).

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.2.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{30}H_{31}BF_{17}O_5^+$ $[M+H]^+$ 805.1988, found 805.1989.



59

colorless oil.

R_f (PE : EtOAc = 5 : 1) = 0.4;

yield: 52% (47 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 –

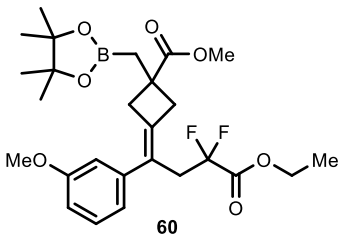
7.21 (m, 1H), 6.84 – 6.80 (m, 1H), 6.80 – 6.75 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 3.41 – 3.30 (m, 2H), 3.19 – 3.04 (m, 2H), 2.79 – 2.69 (m, 2H), 1.30 (s, 2H), 1.20 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.3, 159.6, 140.7, 140.5, 129.4, 122.1, 119.7, 113.3, 112.2, 83.3, 55.3, 52.1, 43.3, 42.3, 41.0, 32.7 (t, *J* = 22.2 Hz), 24.9. ($CF_3(CF_2)_9$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.8 (t, *J* = 9.6 Hz, 3F), -111.7 (t, *J* = 12.6 Hz, 2F), -121.4 – -122.2 (m, 10F), -122.7 (s, 2F), -123.2 (s, 2F), -126.0 – -126.3 (m, 2F).

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.4.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{32}H_{31}BF_{21}O_5^+$ $[M+H]^+$ 905.1924, found 905.1924.



60

colorless oil.

R_f (DCM : PE = 1 : 2) = 0.4;

yield: 48% (25 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 8.0 Hz, 1H), 6.80 – 6.69 (m, 3H), 3.92 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.68 (s, 3H), 3.33 (dd, *J* = 16.4, 2.4 Hz, 2H), 3.22 – 3.04 (m, 2H), 2.81 – 2.71 (m, 1H), 2.69 – 2.60 (m, 1H), 1.27 (s, 2H), 1.19 (s, 12H), 1.15 (t, *J* = 7.2 Hz, 3H).

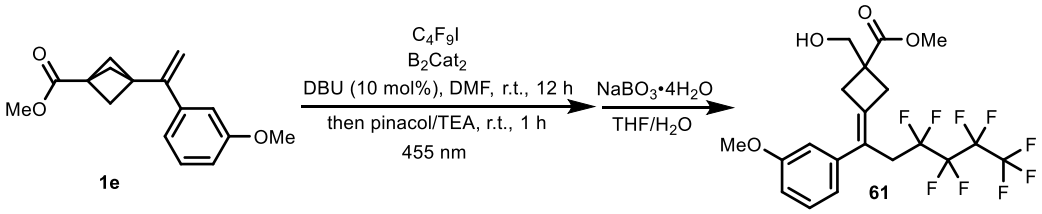
^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.3, 164.1 (t, *J* = 32.8 Hz), 159.4, 140.0, 139.8, 129.2, 123.6 (t, *J* = 4.5 Hz), 120.1, 115.6 (t, *J* = 253.5 Hz), 113.4, 112.3, 83.3, 62.8, 55.3, 52.1, 43.2, 42.4, 41.0, 36.9 (t, *J* = 24.7 Hz), 24.9, 13.8.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.8 (d, *J* = 251.9 Hz, 1F), -103.5 (d, *J* = 251.9 Hz, 1F).

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.6.

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{26}H_{36}BF_2O_7^+$ $[M+H]^+$ 509.2517, found 509.2518.

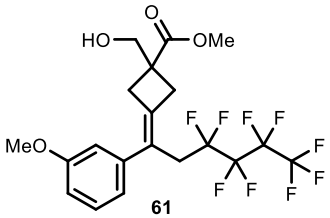
Procedure for the synthesis of 61:



1e **61**

In a N_2-filled glovebox, B_2Cat_2(0.3 mmol, 3.0 equiv) and DMF (1 mL) were added to a 10 mL Schlenk tube. Subsequently, VBCP **1e** (0.1 mmol, 1.0 equiv), DBU (10 mol%)

and C_4F_9I (0.11 mmol, 1.1 equiv) were added. The Schlenk tube was removed from the glovebox and stirred at room temperature under blue LEDs (455 nm, 10W) for approximately 12 h. Then a solution of pinacol (0.9 mmol, 9.0 equiv) in triethylamine (1 mL) was added to the mixture. After 1 hour, water (5 mL) was added and the aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. Then, the crude product and $NaBO_3$ •$4H_2O$ (0.5 mmol, 5.0 equiv) was added to a 10 mL Schlenk tube. Subsequently, THF/H_2O (5ml/5ml) were added. The reaction was stirred at room temperature for 6 h. The solution was extracted with ethyl acetate (3 × 5 mL) and dried over anhydrous Na_2SO_4, filtered and concentrated. The product was purified by flash column chromatography on silica gel (eluent: PE : EtOAc = 5 : 1) to give the product.



61

colorless oil.

R_f (PE : EtOAc = 5 : 1) = 0.4;

yield: 55% (27 mg);

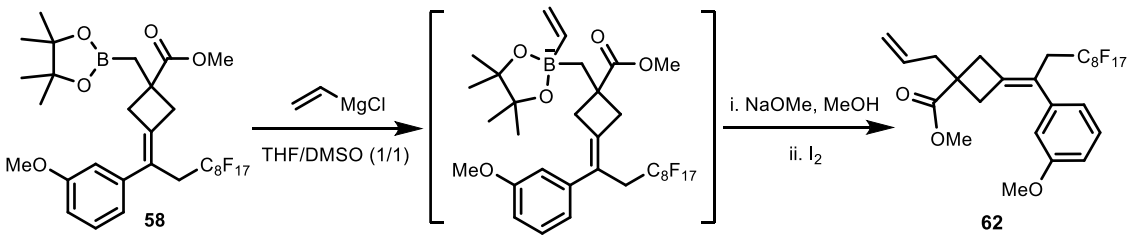
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.15 (m, 1H), 6.76 – 6.70 (m, 2H), 6.70 – 6.67 (m, 1H), 3.72 (d, *J* = 3.3 Hz, 5H), 3.70 (s, 3H), 3.24 – 3.13 (m, 2H), 3.05 (td, *J* = 19.2, 9.4 Hz, 2H), 2.75 – 2.63 (m, 2H), 2.07 (brs, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.9, 159.6, 140.0, 139.2, 129.5, 123.3, 119.6, 113.3, 112.3, 66.5, 55.3, 52.5, 44.2, 38.2, 37.3, 32.6 (t, *J* = 22.3 Hz). ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.8 – -112.0 (m, 2F), -124.1 – -124.3 (m, 2F), -125.8 – -126.0 (m, 2F).

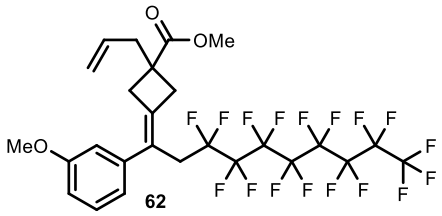
HRMS (ESI^+) *m*/*z* Calcd for $C_{20}H_{20}F_9IO_4^+$ $[M+H]^+$ 495.1212, found 495.1209.

Procedure for the synthesis of 62:



58 **62**

A stirred solution of boronic ester **58** (0.15 mmol) in THF (0.5 mL) and DMSO (0.5 mL) was cooled to 0 °C and a solution of Grignard reagent (0.2 mmol) was added dropwise [upon addition of the Grignard reagent, a white precipitate was observed]. The resulting mixture was stirred at room temperature for 30 min and then cooled to 0 °C. A suspension of NaOMe (3 M in MeOH, 0.15 mL, 0.45 mmol) was added in a single portion, followed by dropwise addition of a solution of I_2 (0.5 M in MeOH, 0.36 mL, 0.18 mmol). The resulting mixture was stirred at 0 °C for 30 min and then saturated aqueous sodium thiosulfate and dichloromethane were added. The organic phase was separated and the aqueous phase was extracted twice with dichloromethane. The combined organic extracts were washed with water twice, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The product was purified by flash column chromatography on silica gel (eluent: PE : EtOAc = 15 : 1) to give the product.



colorless oil.

R_f (PE : EtOAc = 10 : 1) = 0.5;

yield: 64% (68 mg);

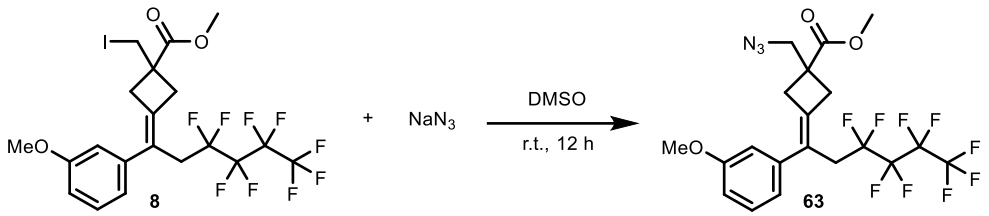
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (t, *J* = 8.0 Hz, 1H), 6.77 – 6.66 (m, 3H), 5.68 – 5.55 (m, 1H), 5.03 – 5.00 (m, 1H), 4.98 (s, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.24 – 3.14 (m, 2H), 3.11 – 2.95 (m, 2H), 2.70 – 2.60 (m, 2H), 2.45 (d, *J* = 7.0 Hz, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.1, 159.6, 140.3, 139.5, 133.4, 129.5, 122.7, 119.6, 118.3, 113.3, 112.2, 55.3, 52.2, 43.0, 41.6, 40.4, 39.3, 32.8 (t, *J* = 22.0 Hz). ($CF_3(CF_2)_7$ signals are not assigned.)

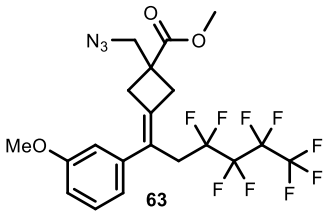
^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.8 (t, *J* = 9.9 Hz, 3F), -111.6 (t, *J* = 13.9 Hz, 2F), -121.4 – -121.8 (m, 2F), -121.8 – -122.1 (m, 4F), -122.8 (s, 2F), -123.0 – -123.4 (m, 2F), -125.9 – -126.4 (m, 2F).

HRMS (ESI$^+$) *m*/*z* Calcd for $C_{26}H_{22}F_{17}O_3^+$ $[M+H]^+$ 705.1292, found 705.1286.

Procedure for the synthesis of 63:



The iodide **8** (0.2 mmol), DMSO (1 mL), and sodium azide (0.3 mmol) were added into an 8 mL screw-capped vial. Then the reaction was stirred at room temperature for 12 h. The solution was extracted with diethyl ether (3 × 5 mL), and the combine organic layers were washed with water (2 × 5 mL), dried over anhydrous magnesium sulfate and evaporate to dryness in vacuo. The product was purified by flash column chromatography on silica gel (eluent: DCM : PE = 1 : 2) to give the product.



colorless oil.

R_f (DCM : PE = 1 : 2) = 0.25;

yield: 92% (96 mg);

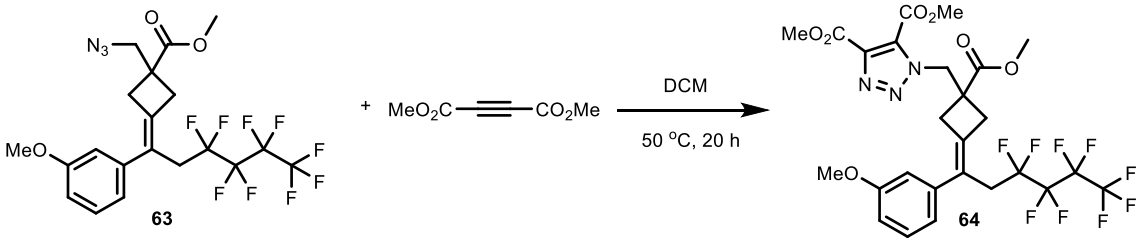
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.13 (m, 1H), 6.76 – 6.69 (m, 2H), 6.67 (s, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.59 – 3.54 (m, 2H), 3.29 – 3.18 (m, 2H), 3.12 – 2.96 (m, 2H), 2.74 – 2.63 (m, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.3, 159.7, 139.9, 137.9, 129.6, 123.6, 119.6, 113.3, 112.4, 56.2, 55.3, 52.7, 43.4, 39.1, 38.0, 32.7 (t, J = 22.4 Hz). ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.9 – -81.2 (m, 3F), -111.8 – -112.0 (m, 2F), -124.1 – -124.3 (m, 2F), -125.8 – -126.1 (m, 2F).

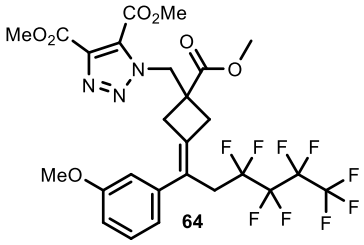
HRMS (ESI^+) *m/z* Calcd for $C_{20}H_{19}F_9N_3O_3^+$ $[M+H]^+$ 520.1277, found 520.1276.

Procedure for the synthesis of 64:



The azide compound **63** (0.2 mmol) was added into an 8 mL screw-capped vial with 1

mL of DCM. Dimethyl acetylenedicarboxylate (0.4 mmol) was added, and the mixture was stirred at 50 °C for 20 h. The volatiles were evaporated in vacuo, affording a crude yellow oil. The product was purified by flash column chromatography on silica gel (eluent: PE : EtOAc = 2 : 1) to give the product.



colorless oil.

R_f (PE : EtOAc = 2 : 1) = 0.5;

yield: 82% (108 mg);

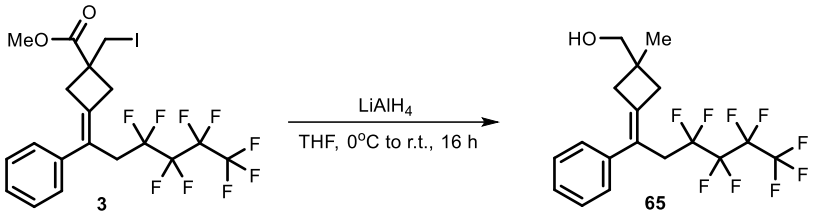
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.14 (m, 1H), 6.76 – 6.68 (m, 2H), 6.68 – 6.63 (m, 1H), 4.91 – 4.83 (m, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.72 (s, 3H), 3.61 (s, 3H), 3.37 – 3.23 (m, 2H), 3.13 – 2.93 (m, 3H), 2.93 – 2.84 (m, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.5, 160.4, 159.7, 159.2, 139.6, 139.6, 136.78, 131.0, 129.5, 123.9, 119.6, 113.3, 112.5, 55.3, 53.8, 53.5, 52.8, 52.8, 43.80, 39.6, 38.6, 32.7 (t, J = 22.2 Hz). ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.2 (m, 3F), -111.8 – -112.0 (m, 2F), -124.1 – -124.2 (m, 2F), -125.8 – -126.1 (m, 2F).

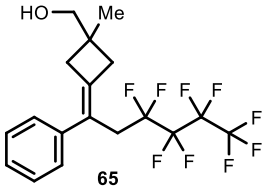
HRMS (ESI^+) *m*/*z* Calcd for $C_{26}H_{25}F_9N_3O_7^+$ $[M+H]^+$ 662.1543, found 662.1541.

Procedure for the synthesis of 65:



To a flask equipped with a stir bar was added the VBCP ester (**3**, 0.1 mmol, 25.8 mg) and THF (1 mL). The solution was cooled to 0 °C and $LiAlH_4$ (15.2 mg, 0.4 mmol, 4.0 equiv) was added portion-wise. The reaction mixture was stirred for 3 h at the temperature. The reaction was quenched with water (0.02 mL) and 10% NaOH aq. (0.02 mL). The mixture was extracted with EtOAc (5 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was

purified by silica gel column chromatography (PE : EtOAc = 5 : 1, R_f = 0.5) to give the product **65** (25.7 mg, 73%) as a yellow solid.



yellow solid. m.p.: 65-67 ℃.

R_f (PE : EtOAc = 5 : 1) = 0.5;

yield: 73% (25.7 mg);

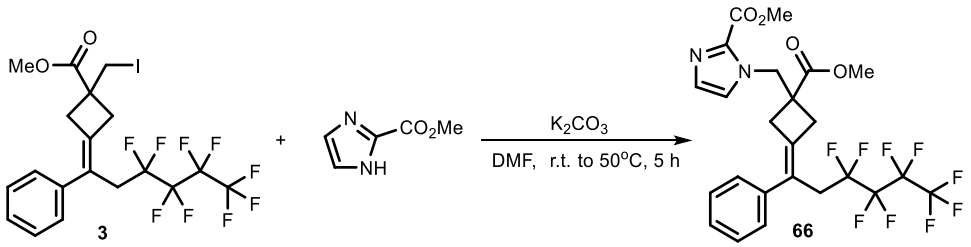
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.25 – 7.20 (m, 3H), 3.54 (s, 2H), 3.14 (t, *J* = 18.8 Hz, 2H), 2.71 (dt, *J* = 15.7, 3.2 Hz, 2H), 2.55 – 2.44 (m, 2H), 1.22 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.3, 139.3, 128.4, 127.2, 126.9, 122.1, 70.4, 40.5, 39.6, 36.1, 32.6 (t, *J* = 22.1 Hz), 23.6. ($CF_3(CF_2)_3$ signals are not assigned.)

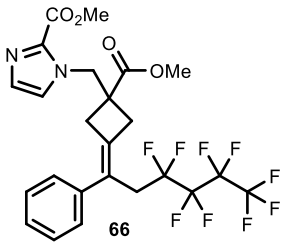
^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.0 – -81.1 (m, 3F), -111.9 – -112.0 (m, 2F), -124.2 – -124.3 (m, 2F), -125.9 – -126.0 (m, 2F).

HRMS (ESI^+) *m/z* Calcd for $C_{18}H_{18}F_9O^+$ $[M+H]^+$ 421.1208, found 421.1209.

Procedure for the synthesis of 66:(9)



To a mixture of **3** (51.6 mg, 0.2 mmol) and K_2CO_3 (33 mg, 0.24 mmol) in DMF (5 mL) was added Methyl 1H-Pyrrole-2-Carboxylate (30 mg, 0.24 mmol) at room temperature. After being stirred at 50 °C for 5 h, the solid was removed by filtration. Water was added to the filtrate and the mixture was extracted with EtOAc. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude mixture was purified by silica gel column chromatography to give the product to give 85 mg (74%) of **66** as a colorless oil.



66

colorless oil.

(PE : EtOAc = 2 : 1) = 0.5;

yield: 74% (85 mg);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 7.10 (s, 1H), 7.04 (s, 1H), 4.94 (dd, 2H), 3.84 (s, 3H), 3.72 (s, 3H), 3.27 (ddd, *J* = 16.1, 6.7, 2.6 Hz, 2H), 3.21 – 3.00 (m, 2H), 2.88 – 2.70 (m, 2H).

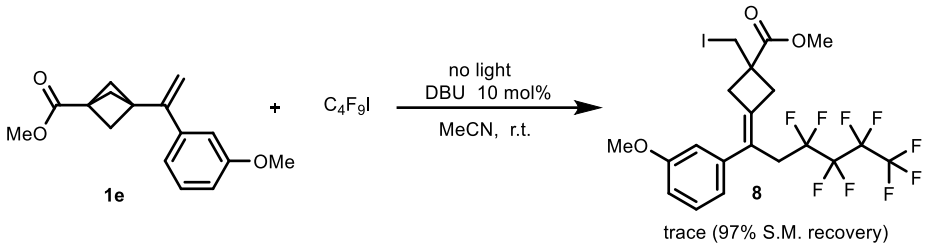
^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.40, 159.85, 138.42, 136.84, 136.59, 130.02, 128.46, 127.30, 127.17, 125.01, 123.78, 52.74, 52.34, 51.37, 44.81, 39.30, 38.10, 32.70 (t, *J* = 22.2 Hz). ($CF_3(CF_2)_3$ signals are not assigned.)

^{19}F NMR (376 MHz, Chloroform-*d*) δ -81.04 – -81.20 (m, 3F), -111.80 – -111.98 (m, 2F), -124.11 – -124.29 (m, 2F), -125.89 – -126.06 (m, 2F).

HRMS (ESI^+) *m*/*z* Calcd for $C_{24}H_{22}F_9N_2O_4^+$ $[M+H]^+$ 573.1430, found 574.1431.

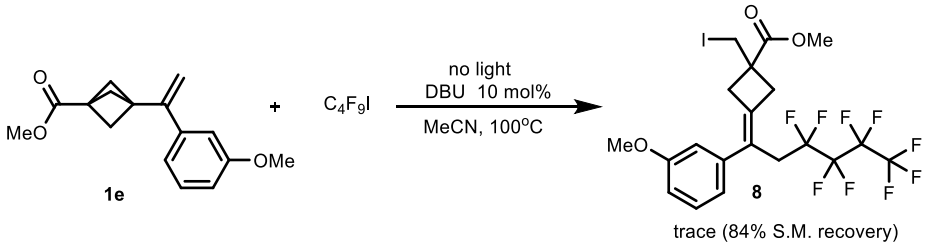
3. Mechanistic Analysis

3.1 Control Experiments



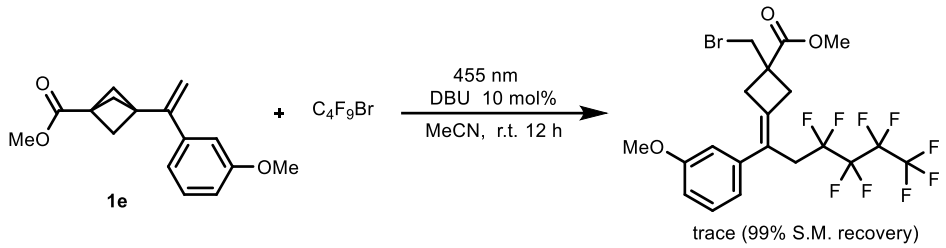
trace (97% S.M. recovery)

In a N_2-filled glovebox, VBCP **1e** (0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9I (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and the mixture was stirred in the dark at room temperature for 12 h. Then the solvent was removed *in vacuo*. The mixture was analyzed by ^1H NMR with 1,3,5-Trimethoxybenzene (16.8 mg) as an internal standard. No desired product was observed. The substrate **1e** can be recovered in 97% ^1H NMR yield.

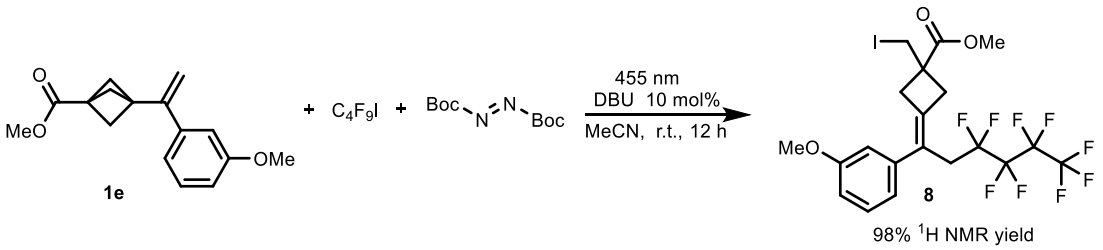


trace (84% S.M. recovery)

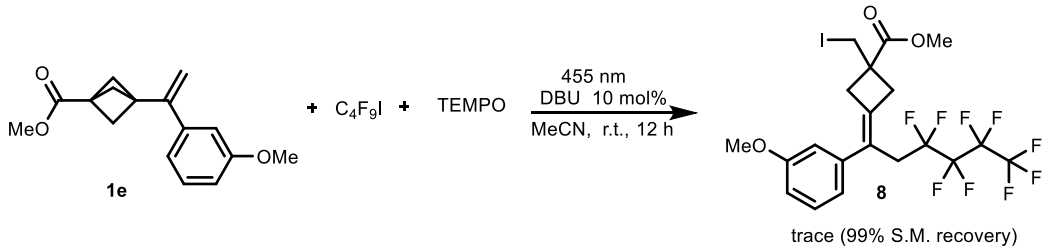
In a N_2-filled glovebox, VBCP **1e** (0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9I (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and the mixture was stirred in the dark at 100 ℃ for 12 h. Then the solvent was removed *in vacuo*. The mixture was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene (16.8 mg) as an internal standard. The desired product was obtained in 13% ^1H NMR yield. The substrate **1e** can be recovered in 84% ^1H NMR yield.



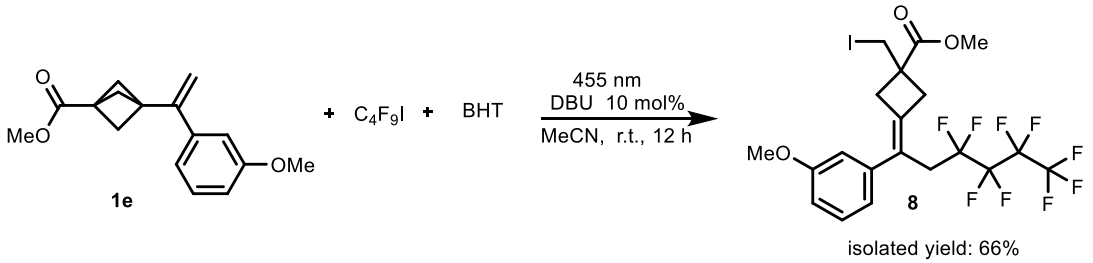
In a N_2-filled glovebox, VBCP **1e** (0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9Br (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and the mixture was stirred at room temperature under blue LEDs (455 nm, 10W) for 12 h. No product was observed. Then the solvent was removed *in vacuo*. The mixture was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene (16.8 mg) as an internal standard. The substrate **1e** was recovered in 99% ^1H NMR yield.



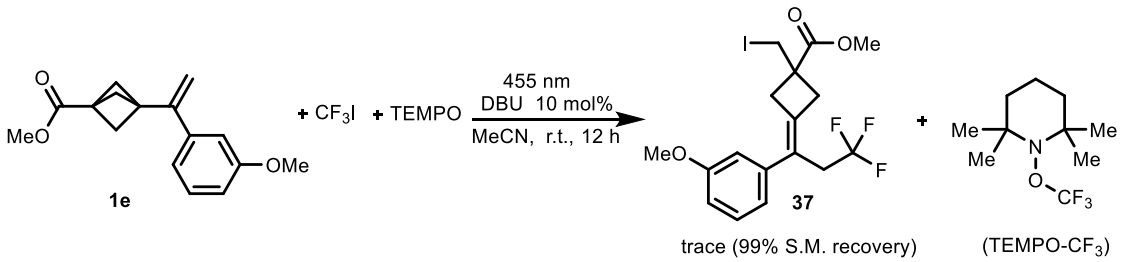
In a N_2-filled glovebox, di-*tert*-butyl azodicarboxylate(0.1 mmol), VBCP **1e**(0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9I (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and the mixture was stirred at room temperature under blue LEDs (455 nm, 10W) for 12 h. Then the solvent was removed *in vacuo*. The mixture was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene (16.8 mg) as an internal standard. The product **8** was obtained in 98% ^1H NMR yield.



In a N_2-filled glovebox, TEMPO (0.5 mmol), VBCP **1e** (0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9I (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and the mixture was stirred at room temperature under blue LEDs (455 nm, 10W) for 12 h. Then the solvent was removed *in vacuo*. The mixture was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene (16.8 mg) as an internal standard. The substrate **1e** was recovered in 99% ^1H NMR yield.



In a N_2-filled glovebox, BHT (0.25 mmol), VBCP **1e** (0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9I (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and the mixture was stirred at room temperature under blue LEDs (455 nm, 10W) for 12 h. Then the solvent was removed *in vacuo*. The mixture was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene (16.8 mg) as an internal standard. The substrate **1e** was recovered in 21% ^1H NMR yield, and the crude mixture was purified by silica gel column chromatography (DCM : PE = 2 : 1) to give the product **8** in 66% yield.



In a N_2-filled glovebox, TEMPO (0.5 mmol), VBCP **1e** (0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and CF_3I (0.15

mmol) were added. The Schlenk tube was removed from the glovebox and the mixture was stirred at room temperature under blue LEDs (455 nm, 10W) for 12 h. Then the solvent was removed *in vacuo*. The mixture was analyzed by ^{19}F NMR with fluorobenzene (0.2 mmol) as an internal standard. In the fluoride spectrum, we did not detect the fluoride signal of product **37**, but detected the fluoride signal of species TEMPO-CF_3(2.3% ^{19}F NMR yield), which confirms the involvement of CF_3 • free radicals. The GC-MS detection results also support the above conclusion.(10)

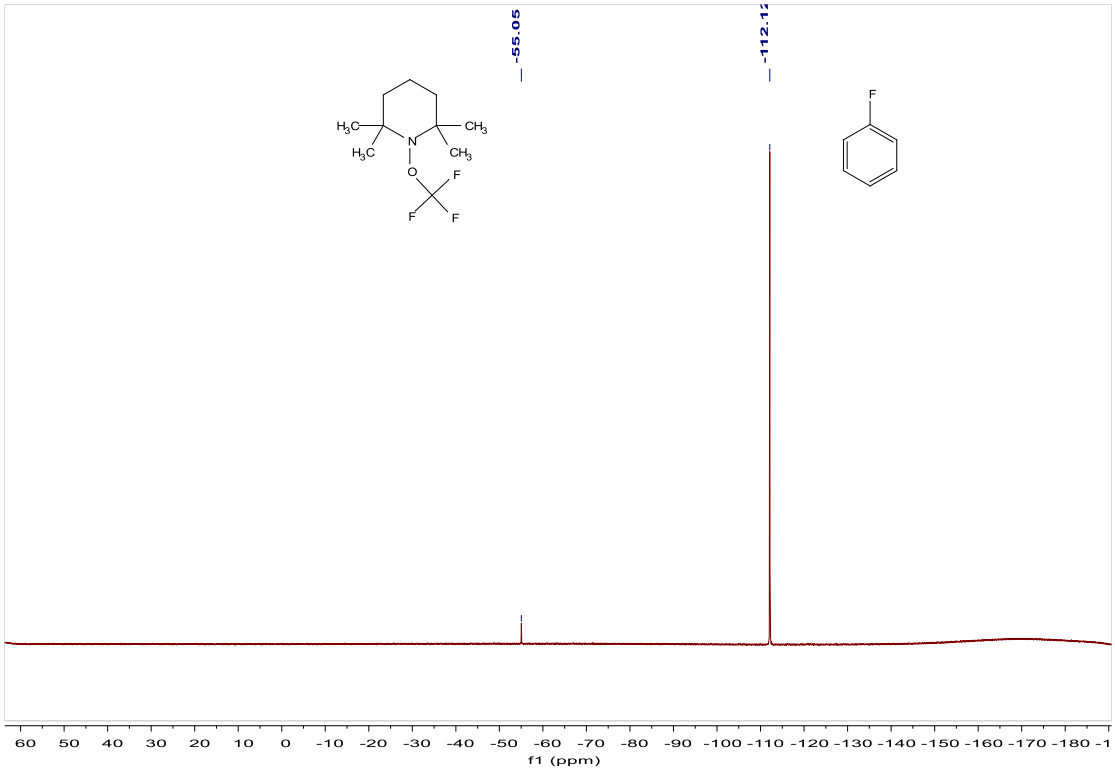


Figure S2. ^{19}F NMR spectra of the radical trapping TEMPO-CF_3 adduct.

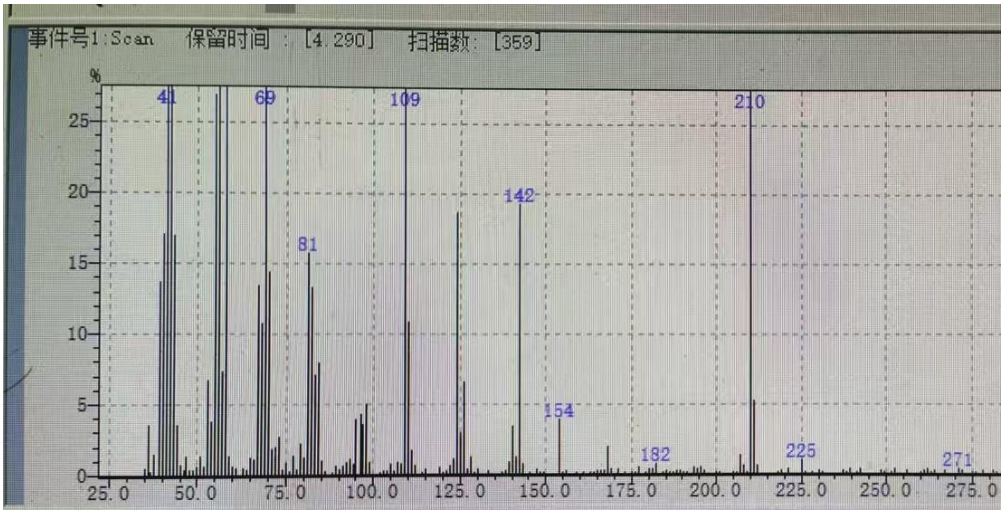


Figure S3. GC-MS spectra of the radical trapping TEMPO-CF_3 adduct.

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3.2 UV/Vis Absorption Spectroscopy

UV/Vis absorption spectra were recorded on a Hitachi UH5300 spectrophotometer at room temperature. The samples were measured in in quartz absorption cells (chamber volume = 3.5 mL, H × W × D = 45 mm × 12.5 mm, 12.5 mm).

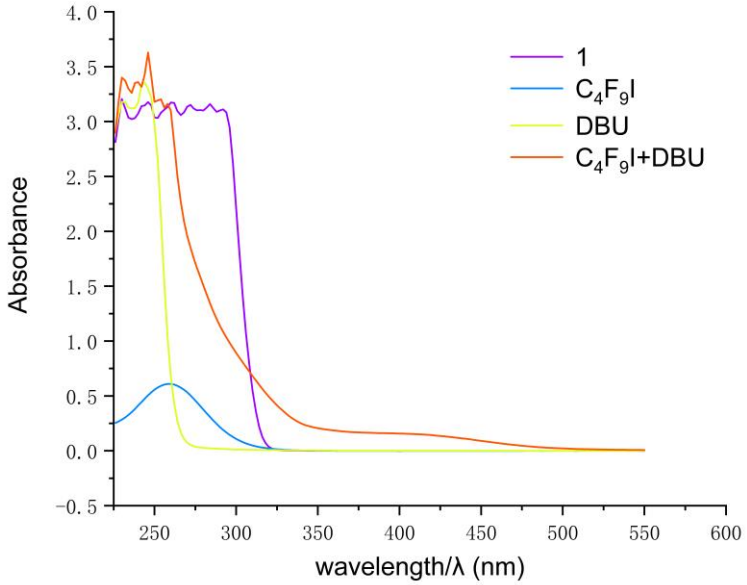


Figure S4. UV/Vis Absorption spectra of solutions: 1) 1 was VBCP **1e** (0.1 mol) in CH_3CN (30 ml); 2) C_4F_9I (0.1 mol) in CH_3CN (30 ml); 3) DBU (0.1 mol) in CH_3CN (30 ml); 4) DBU (0.1 mol) and C_4F_9I (0.1 mol) in CH_3CN (30 ml).

3.3 Quantum Yield Determination[11], [12]

a) Determination of Photon Flux using Ferrioxalate Actinometry

Standard ferrioxalate actinometry was used to determine the photon flux of the spectrophotometer at 455 nm.

Preparation of solutions: Two stock solutions of H_2SO_4 (0.05 M and 0.5 M) were prepared in volumetric flasks. A 0.15 M solution of ferrioxalate (Solution A) was prepared by dissolving potassium ferrioxalate hydrate (2.21 g, 4.5 mmol) in 30 mL of 0.05 M aq. H_2SO_4 in a volumetric flask wrapped in aluminum foil. A buffered solution of phenanthroline (Solution B) was prepared by dissolving phenanthroline (0.05 g, 0.28 mmol) and NaOAc (11.25 g, 0.14 mmol) in 50 mL of 0.5 M aq. H_2SO_4 in a volumetric flask wrapped in aluminum foil. Both solutions were stored in the dark. Absorbance of

non-irradiated sample: In a dark room, 2.0 mL of Solution A and 0.35 mL of Solution B were added via syringes to a vial. The vial was capped and allowed to sit in the dark for 1 h, after which time it was transferred to a cuvette, and the absorbance at 510 nm measured.

Absorbance of the irradiate sample: In a dark room, 2.0 mL of Solution A was placed in a vial and irradiated for 90.0 seconds at λ = 455 nm. After irradiation, 0.35 mL of Solution B was added to the vial. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline, after which time it was transferred to a cuvette, and the absorbance at 510 nm measured.

Calculation of photon flux: The following equations were used to calculate the photon flux.

$$mol\ Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon}$$

Where V is the total volume of the solution, ΔA is the difference in absorption between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,110 L mol^{-1} cm^{-1}).

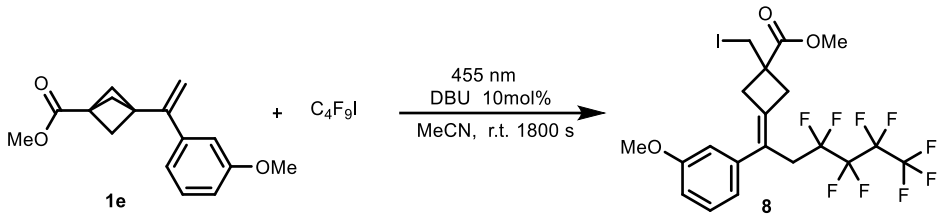
$$photon\ flux = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.845 for a 0.15 M solution at λ = 457 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 455nm.

$$\text{mol } Fe^{2+} = \frac{0.00235\text{L} \cdot 1.5862}{1\text{ cm} \cdot 11100\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}} = 3.36 \times 10^{-7}\text{ mol}$$

$$photon\ flux = \frac{3.56 \times 10^{-7}}{0.845 \cdot 90\text{ s} \cdot 0.9633} = 4.58 \times 10^{-9}\text{ einstein} \cdot \text{s}^{-1}$$

b) Measurement of quantum yield



In a N_2-filled glovebox, BCP **1e** (0.1 mmol) and MeCN (1 mL) were added to a 10 mL Schlenk tube. Subsequently, DBU (10 mol%) and C_4F_9I (0.1 mmol) were added. The Schlenk tube was removed from the glovebox and stirred at room temperature under blue LEDs (455 nm, 10W) for 1800 s. Then the solvent was removed *in vacuo*. After irradiation, the reaction was transferred to a foil lined flask and concentrated under reduced pressure to give a yellow oil. The yield of **3** was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene (16.8 mg) as a standard.

$$\Phi = \frac{\text{moles of product}}{\text{moles of absorbed photons}} = \frac{\text{moles of product}}{\text{flux} \cdot t \cdot f}$$

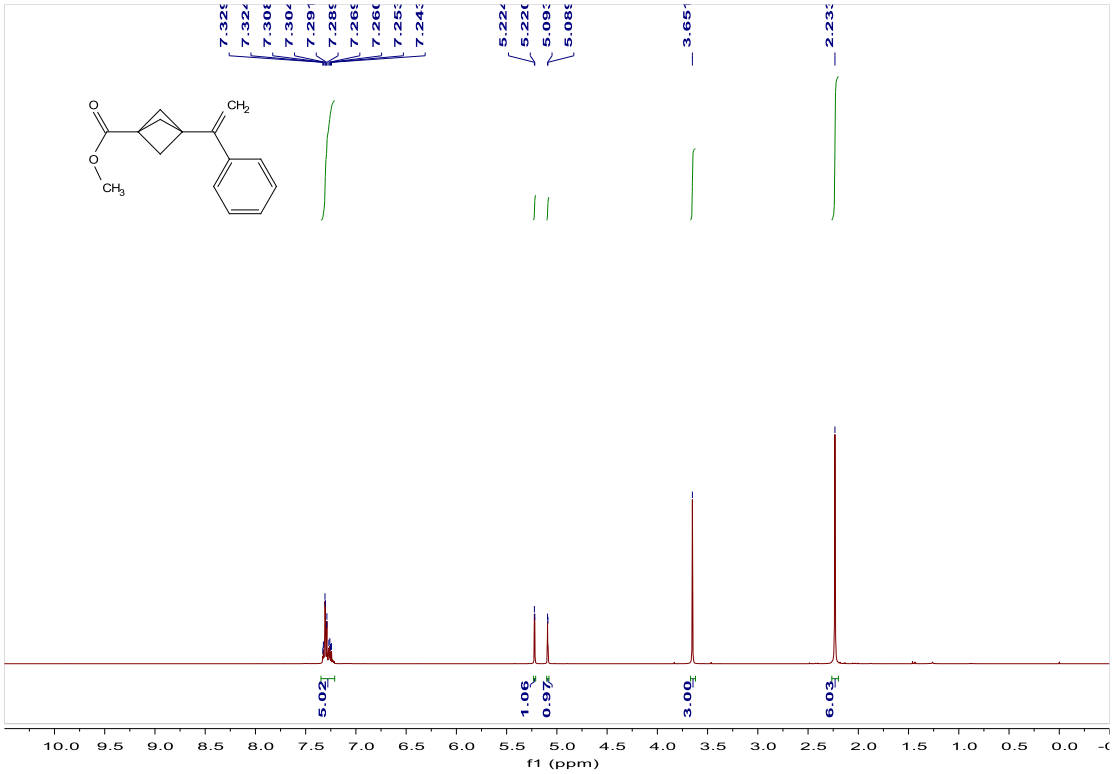
Where flux is the photon flux determined by ferrioxalate actinometry (4.58×10^{-9} einstein s^{-1}), t is the time (1800 s), and f is the fraction of light absorbed by reaction system at 455 nm.

The absorbance of the solution at 455 nm was calculated: $f = 1 - 10^{-A}$. Where A is the absorbance of the solution at 455 nm, which was found to be 0.161. ($f = 1 - 10^{-0.161} = 0.309$.)

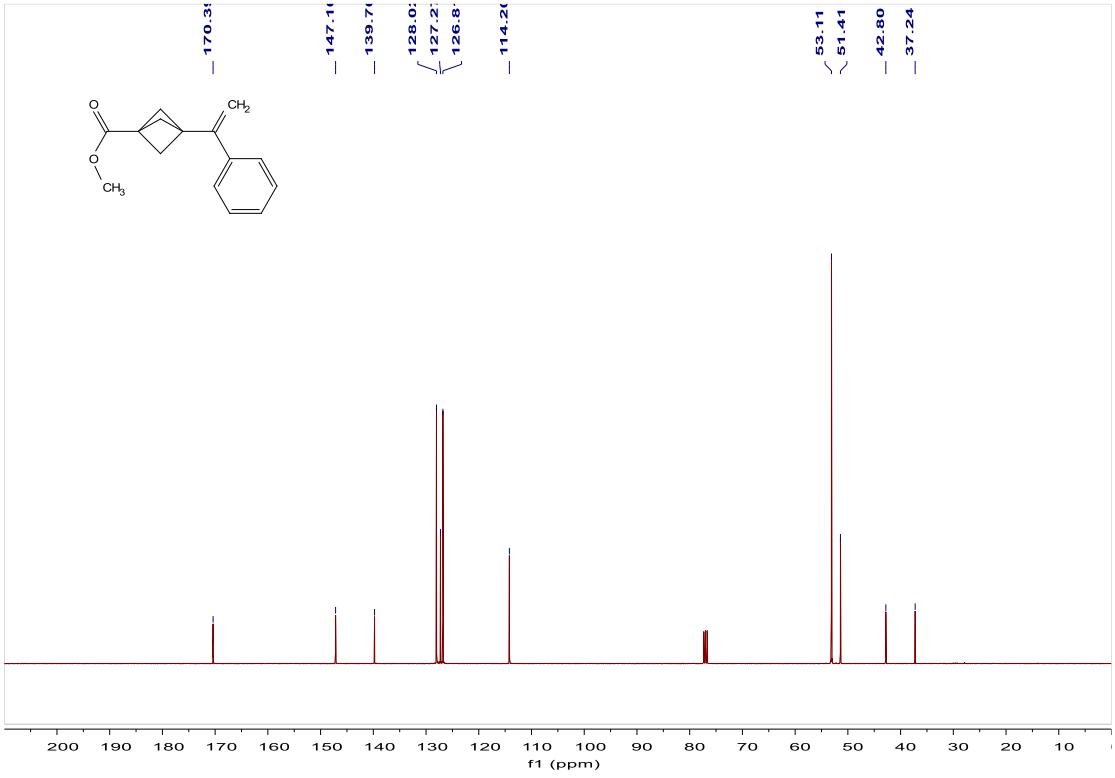
$$\Phi = \frac{4\times10^{-5}}{4.58 \times 10^{-9}\text{einstein}\cdot\text{s}^{-1} \cdot 1800\ \text{s} \cdot 0.309} = 15.67$$

4. NMR spectra

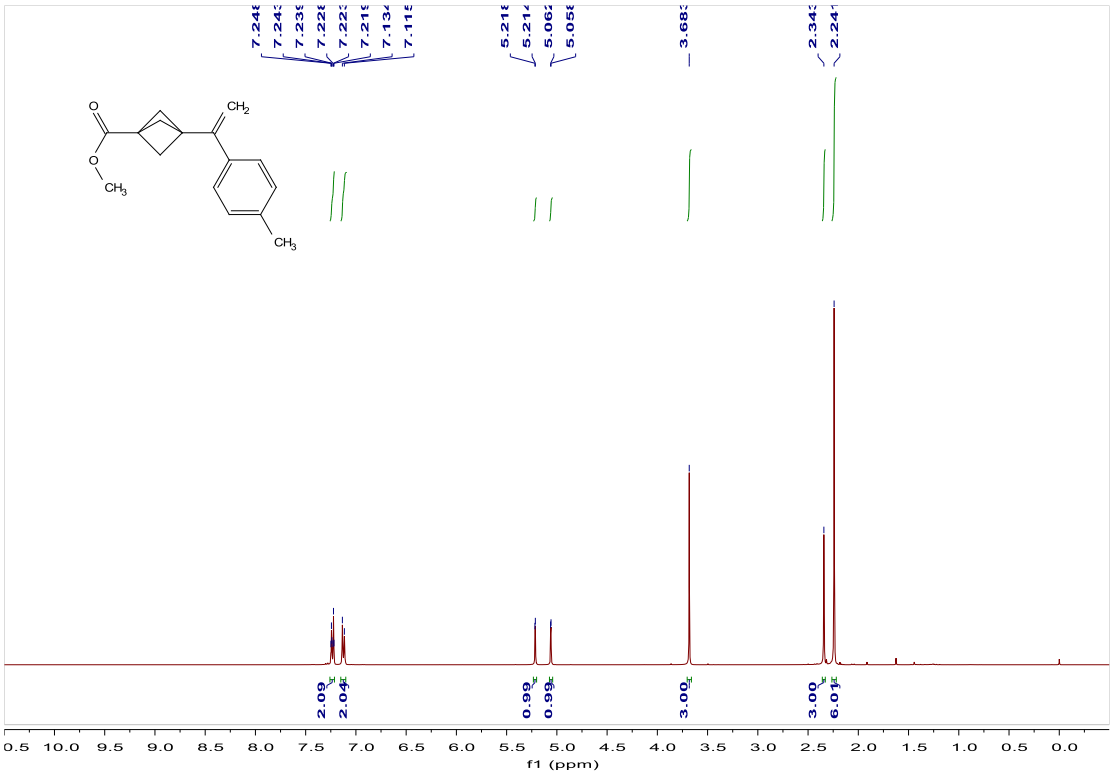
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**



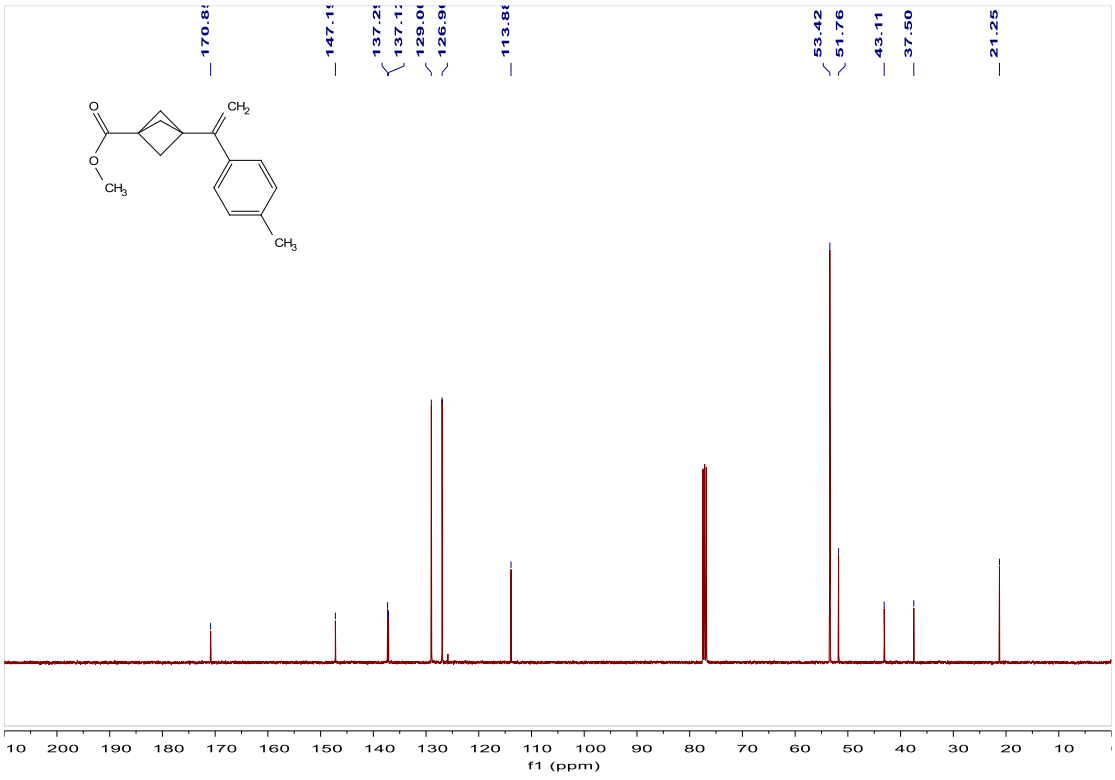
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1**



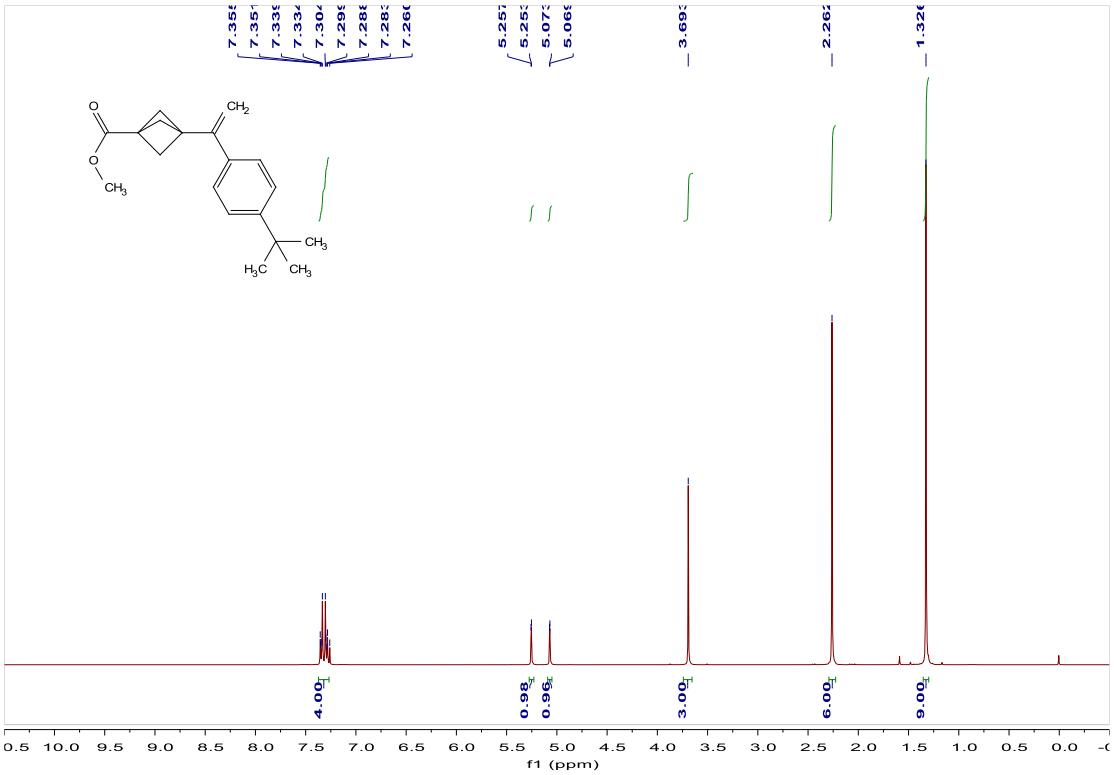
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1a**



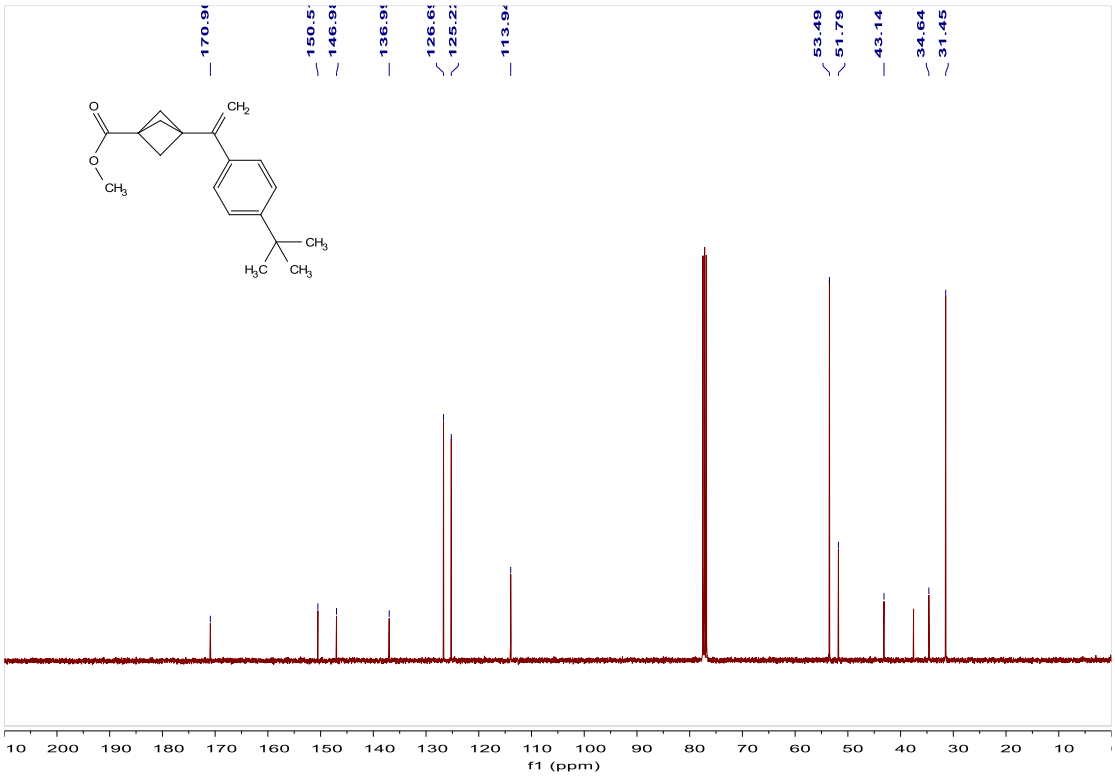
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1a**



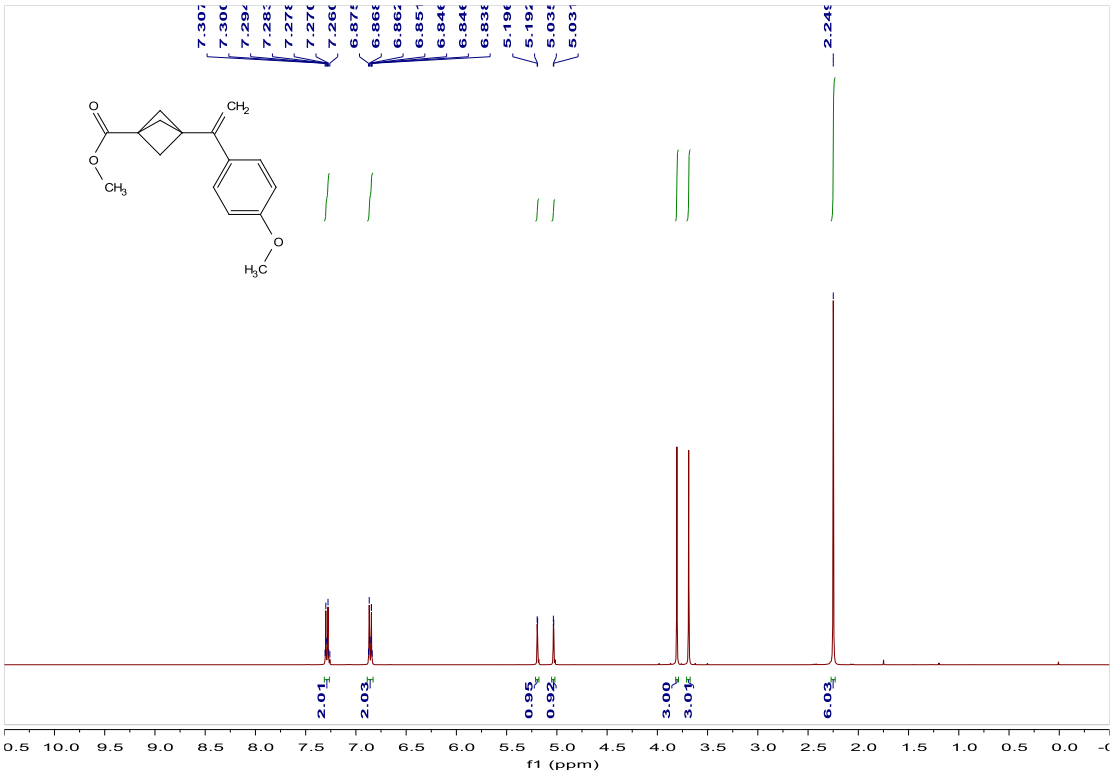
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b**



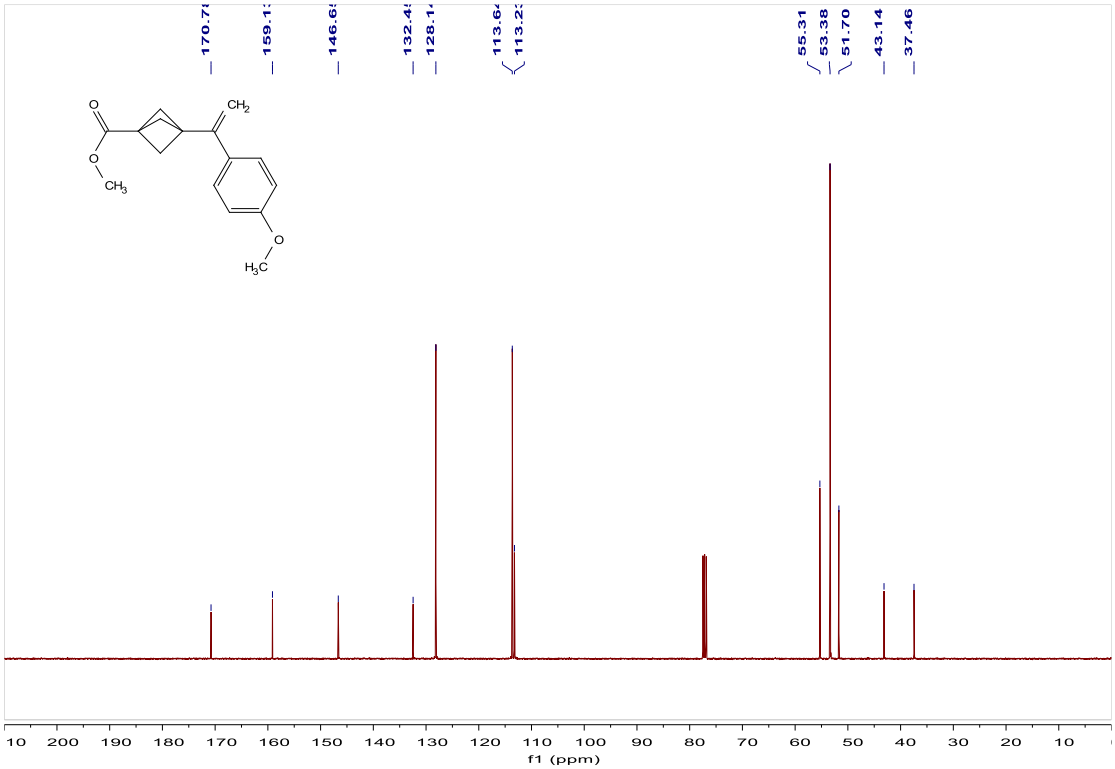
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1b**



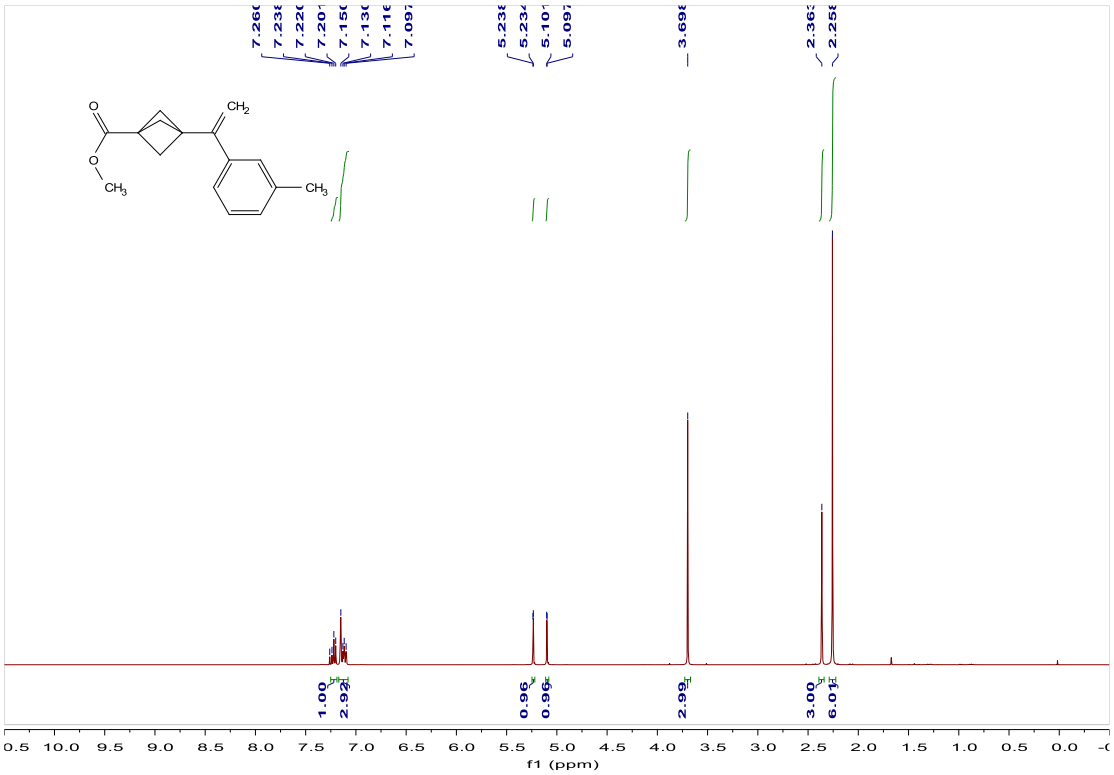
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c**



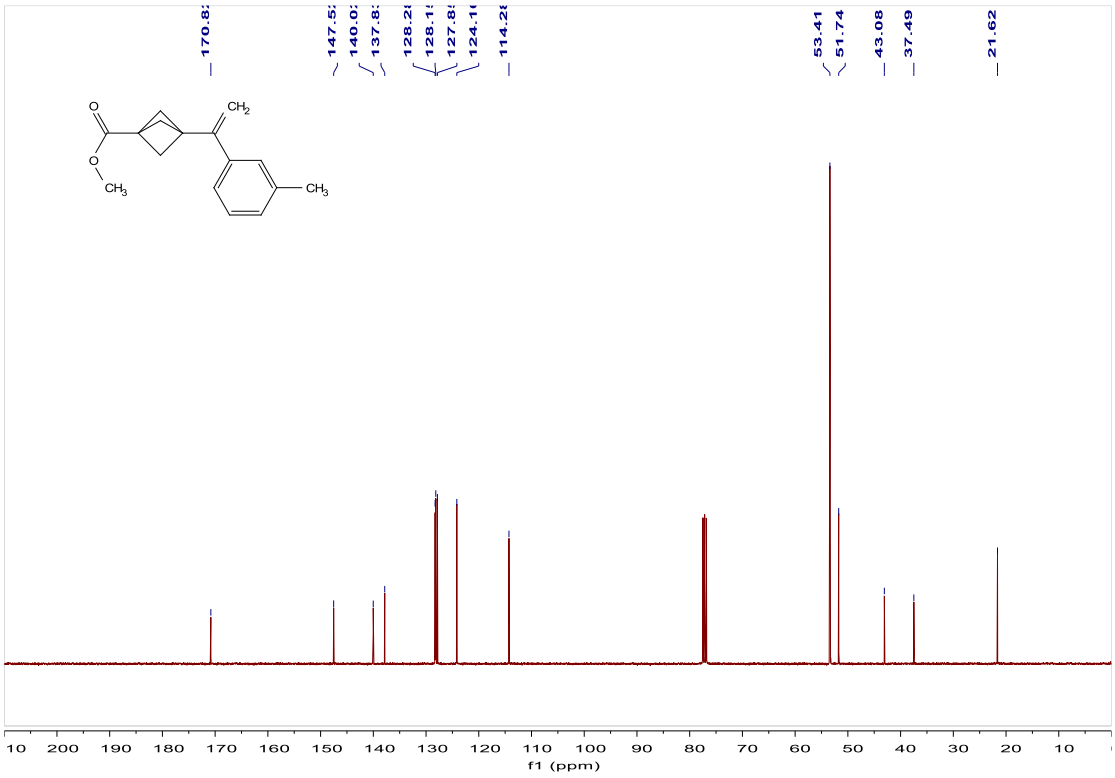
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1c**



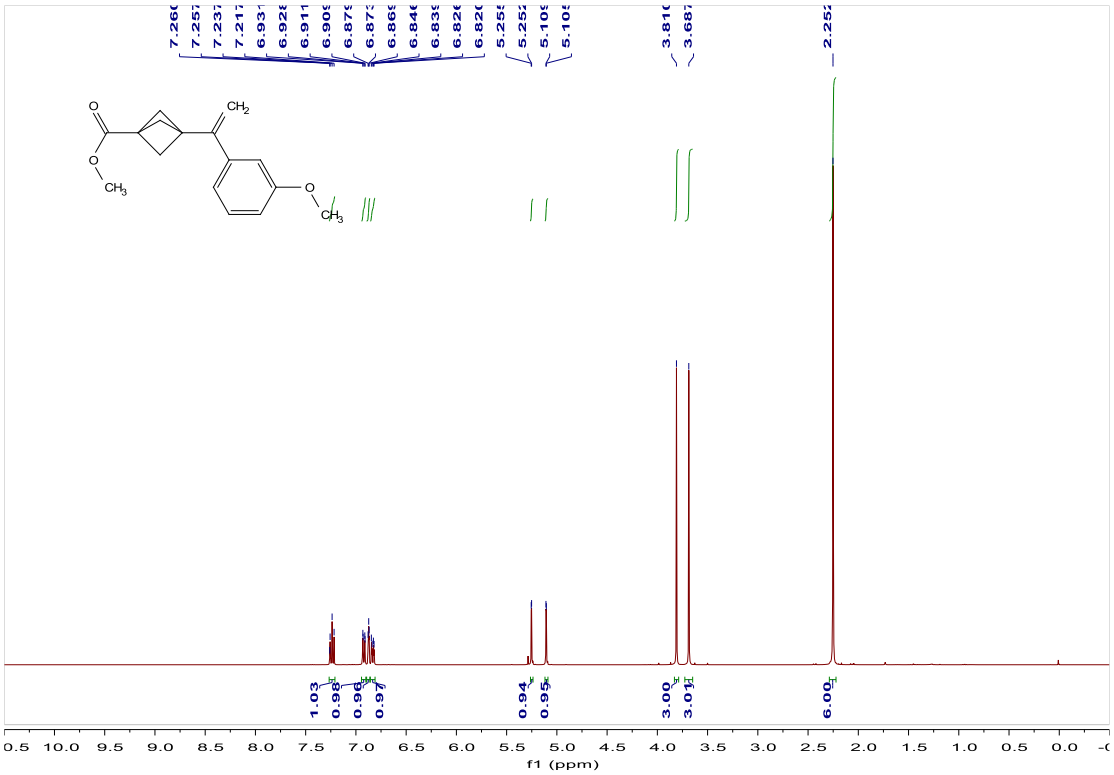
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1d**



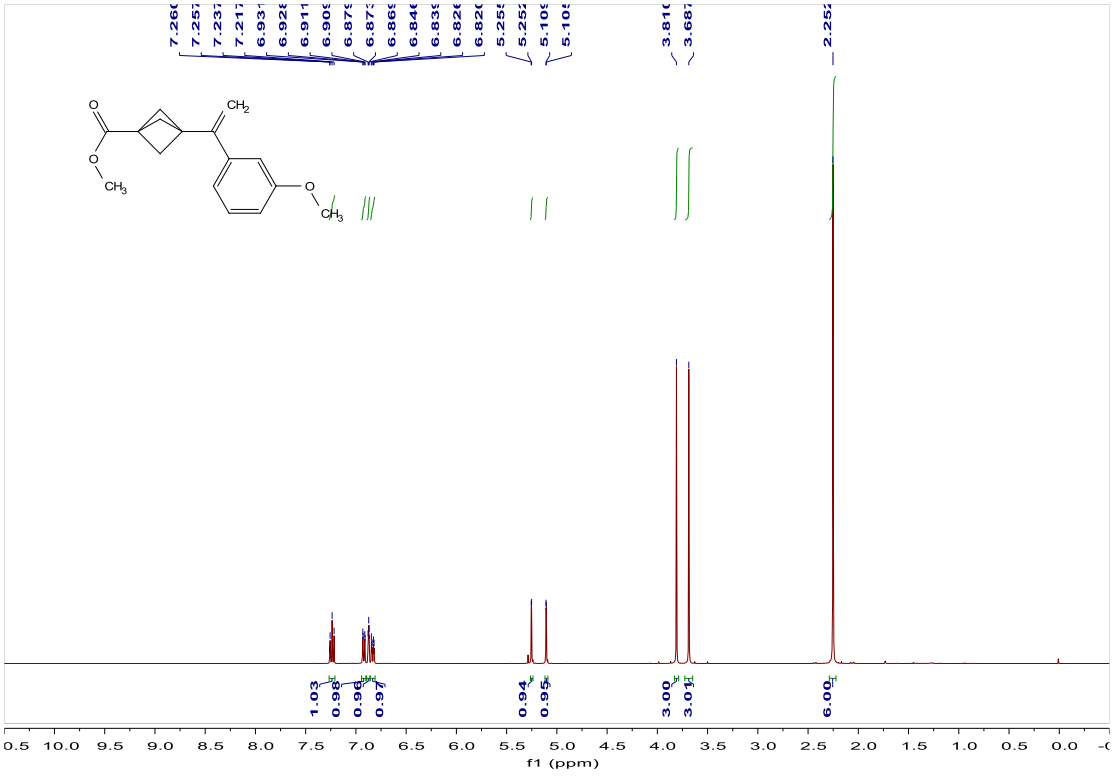
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1d**



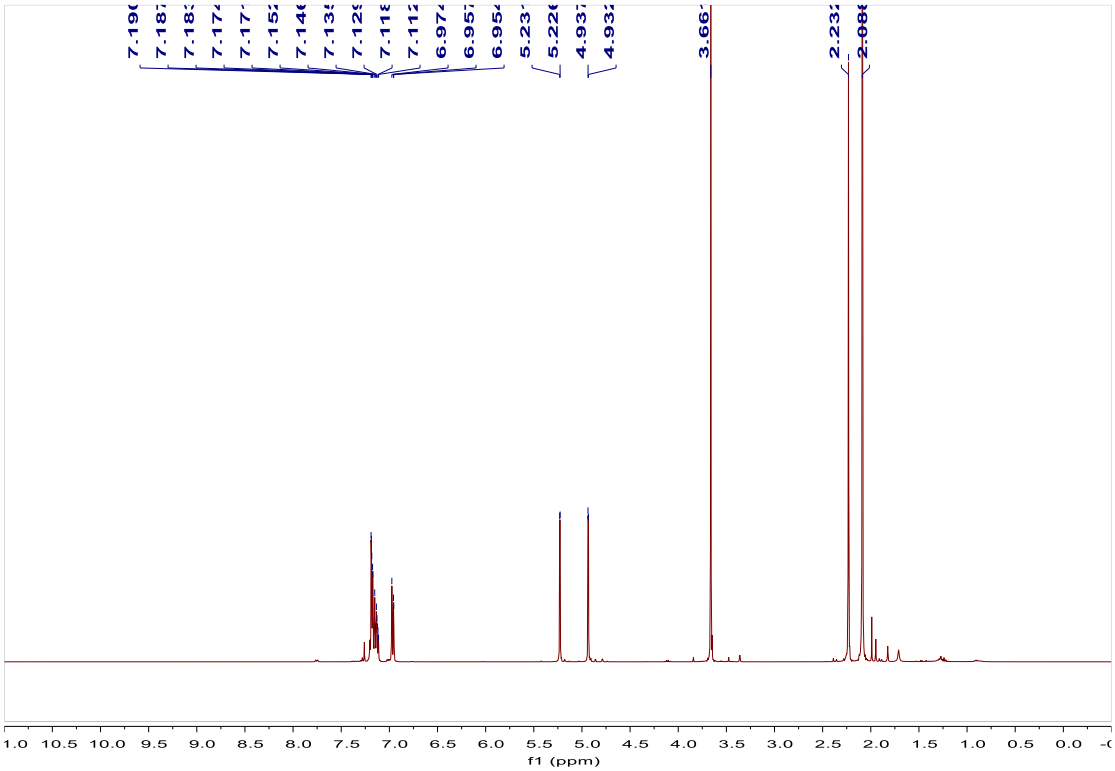
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1e**



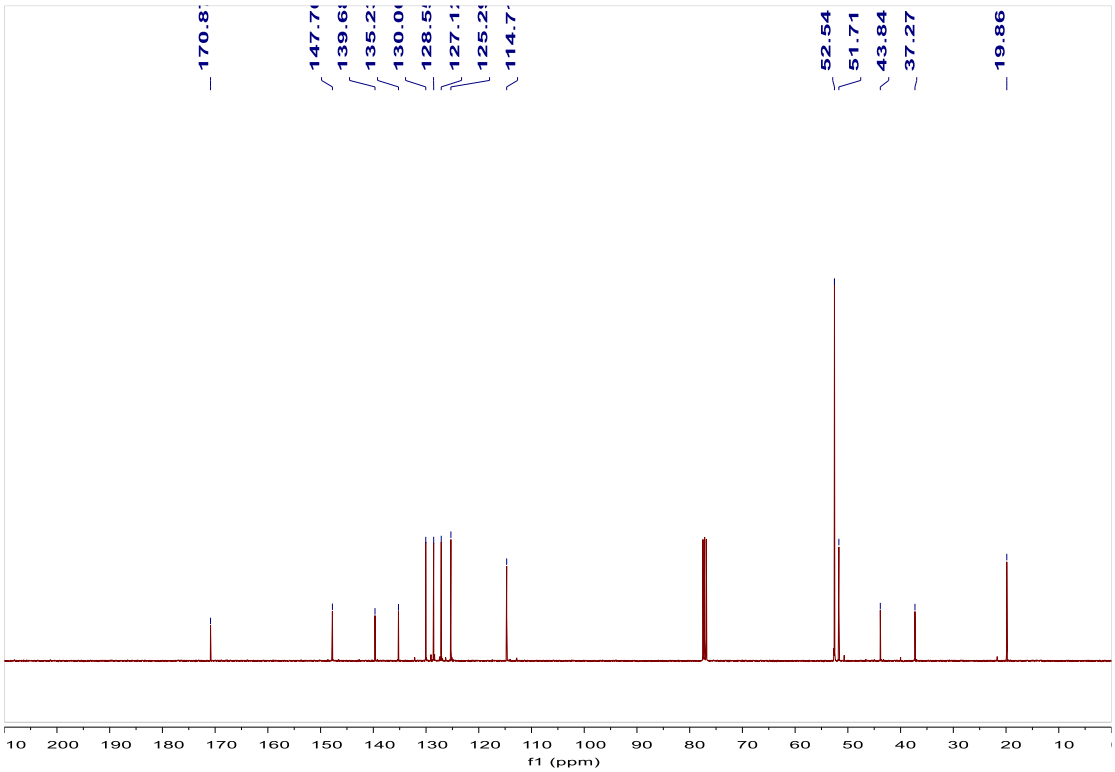
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1e**



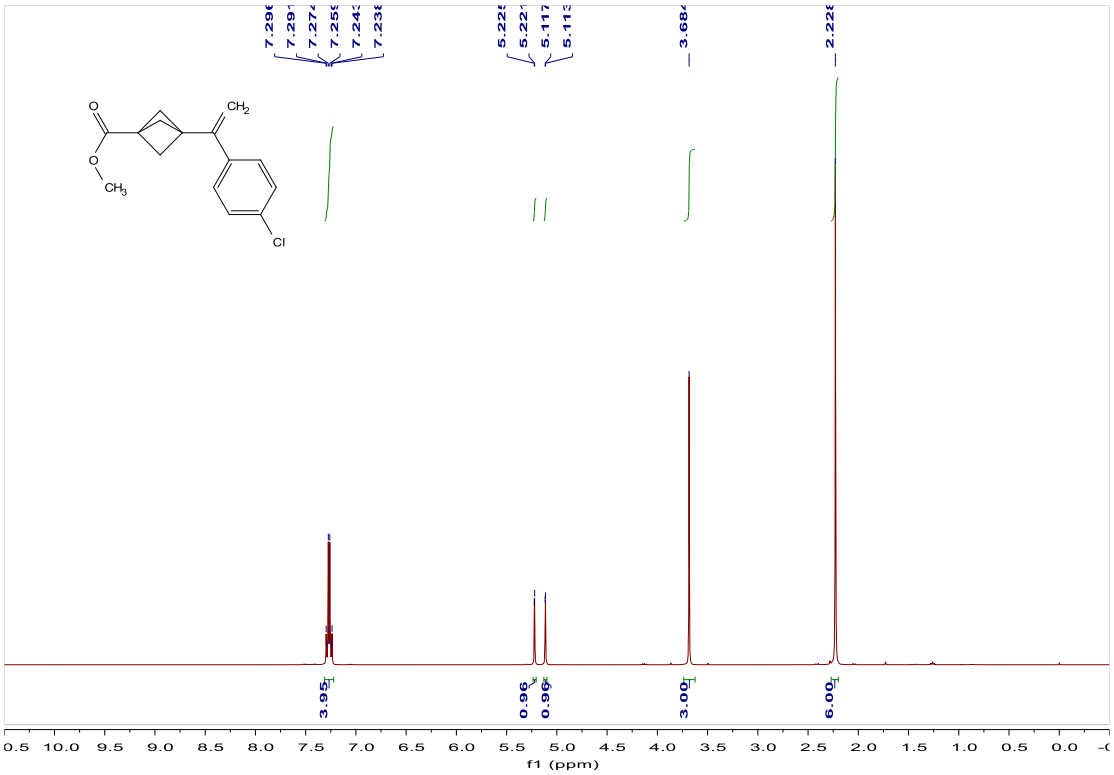
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f**



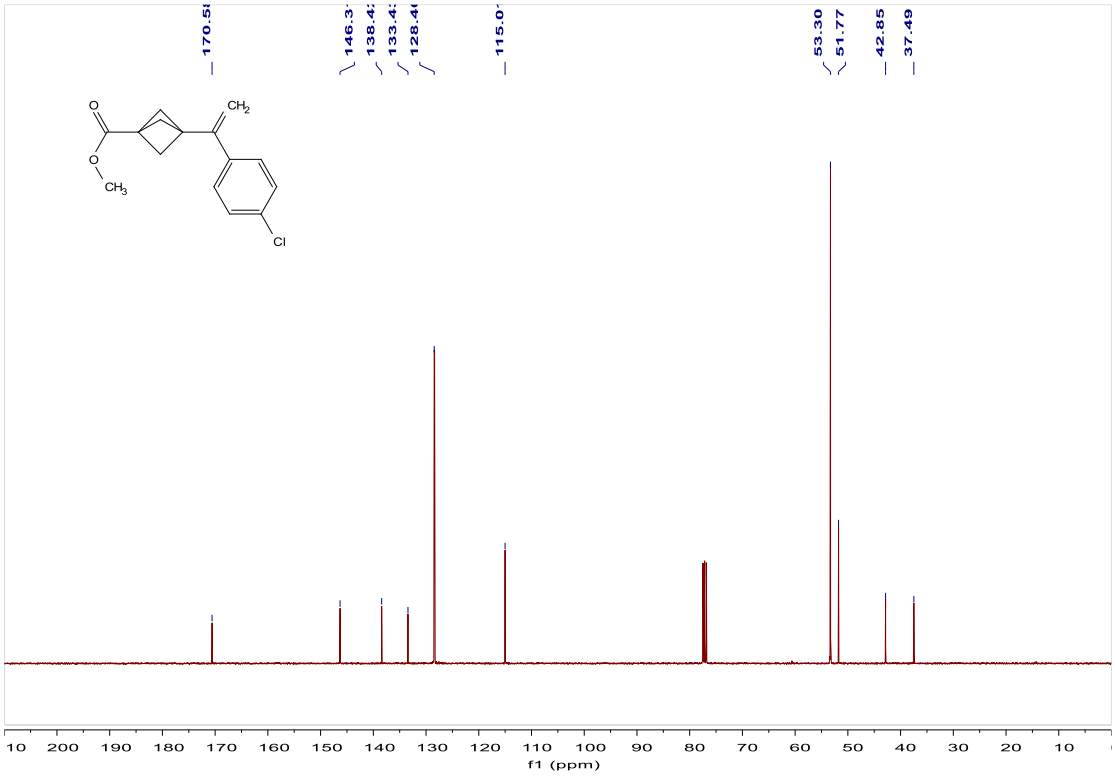
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1f**



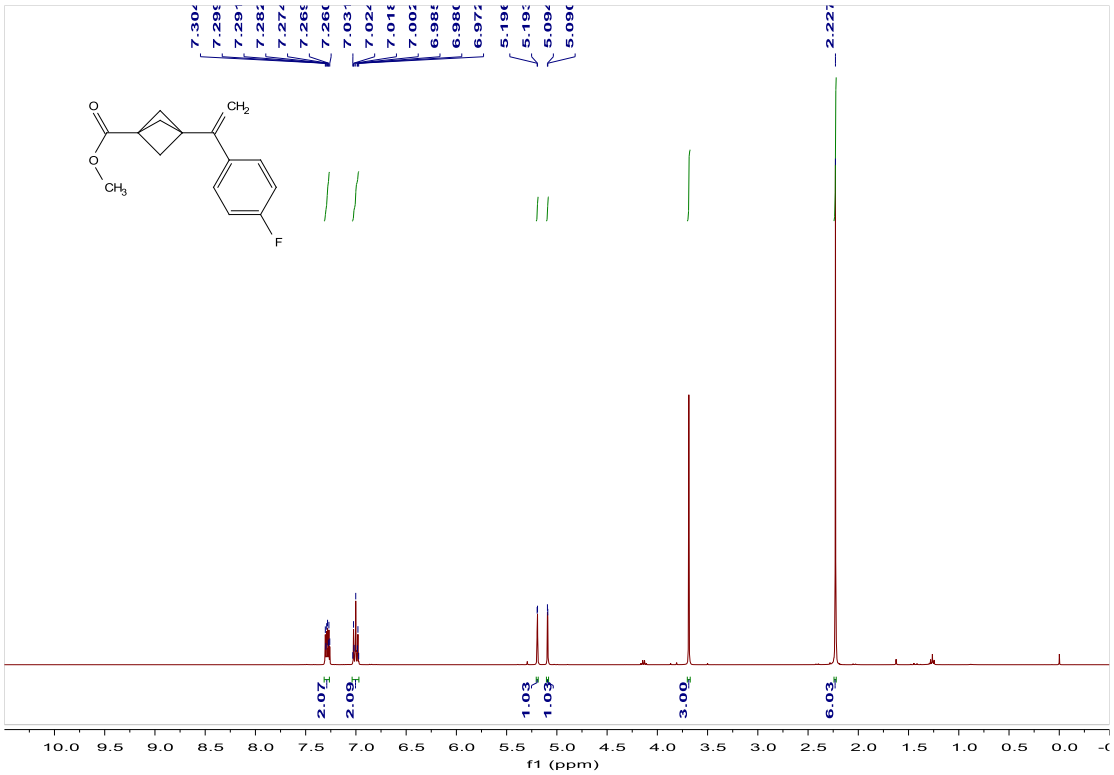
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1g**



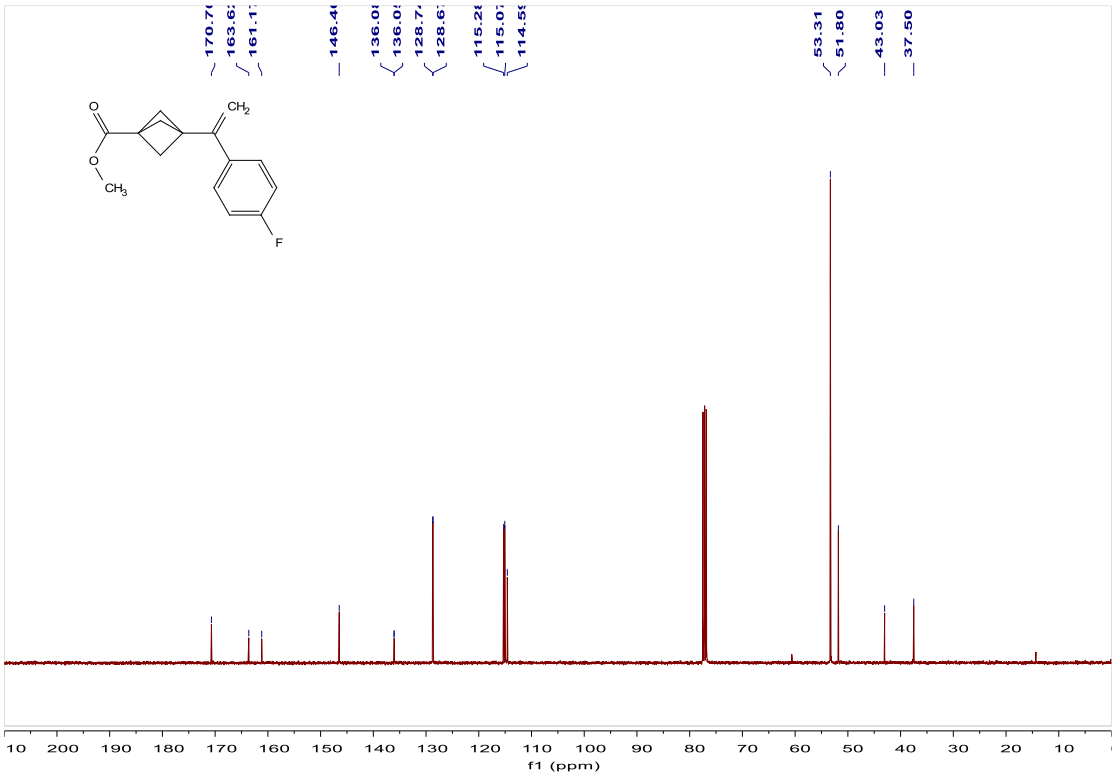
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1g**



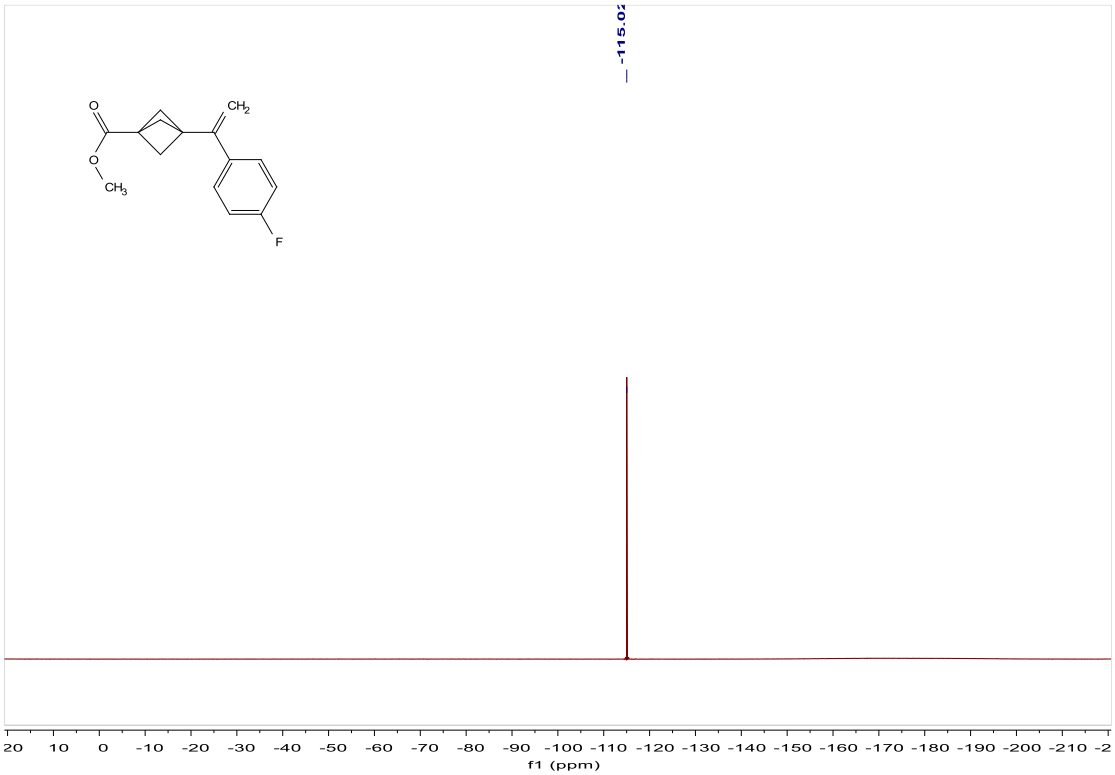
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1h**



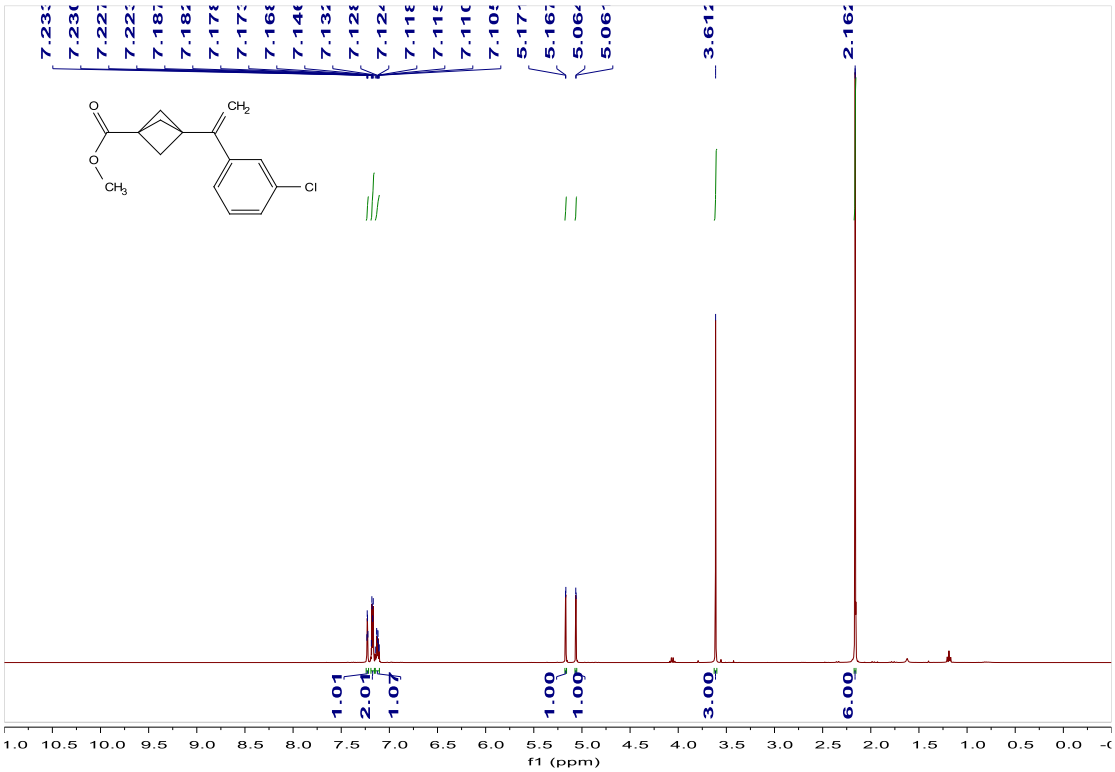
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1h**



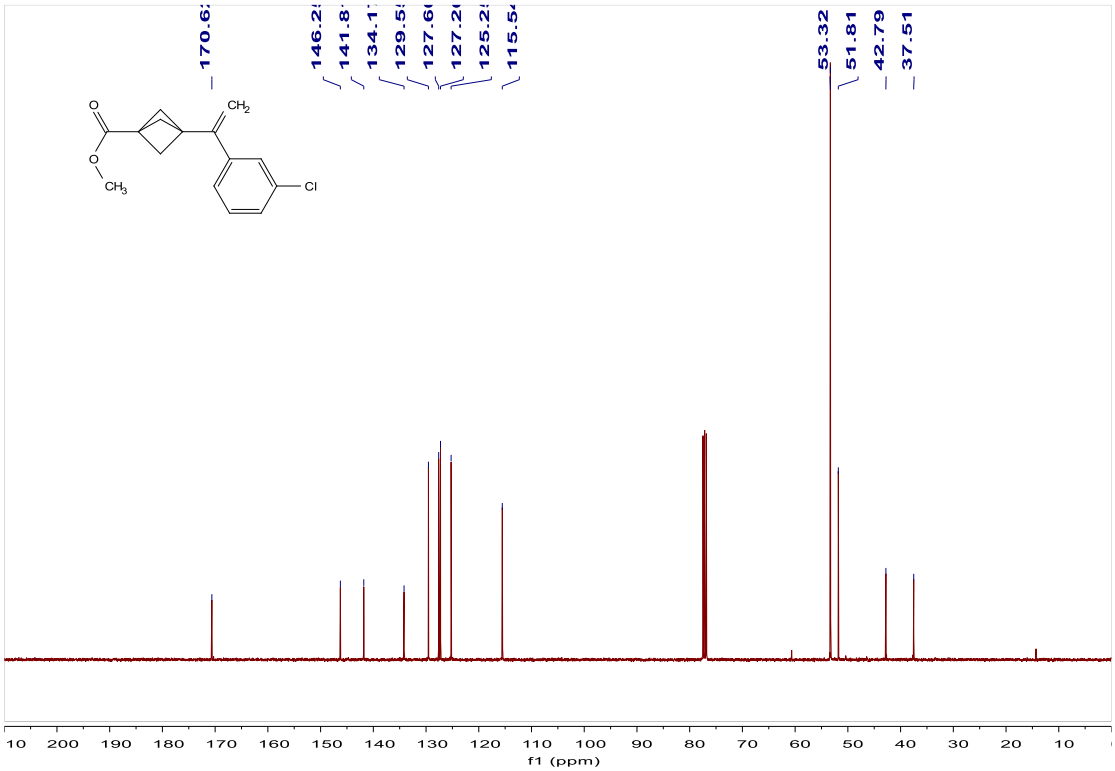
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **1h**



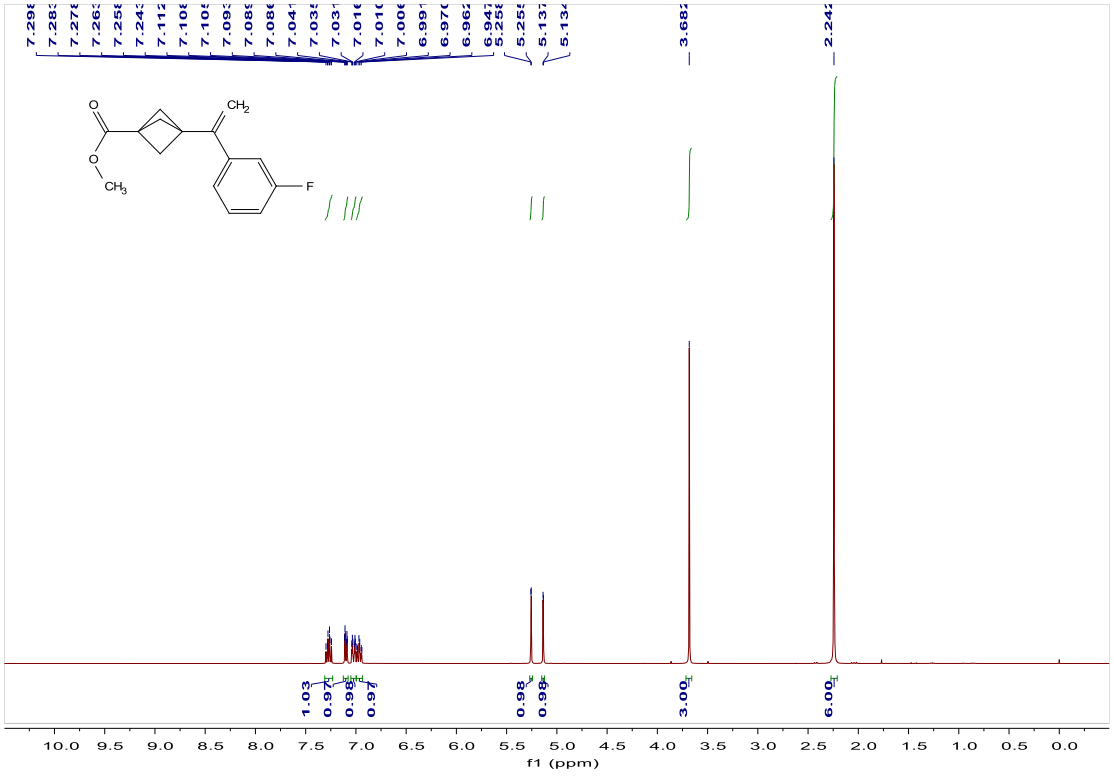
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i**



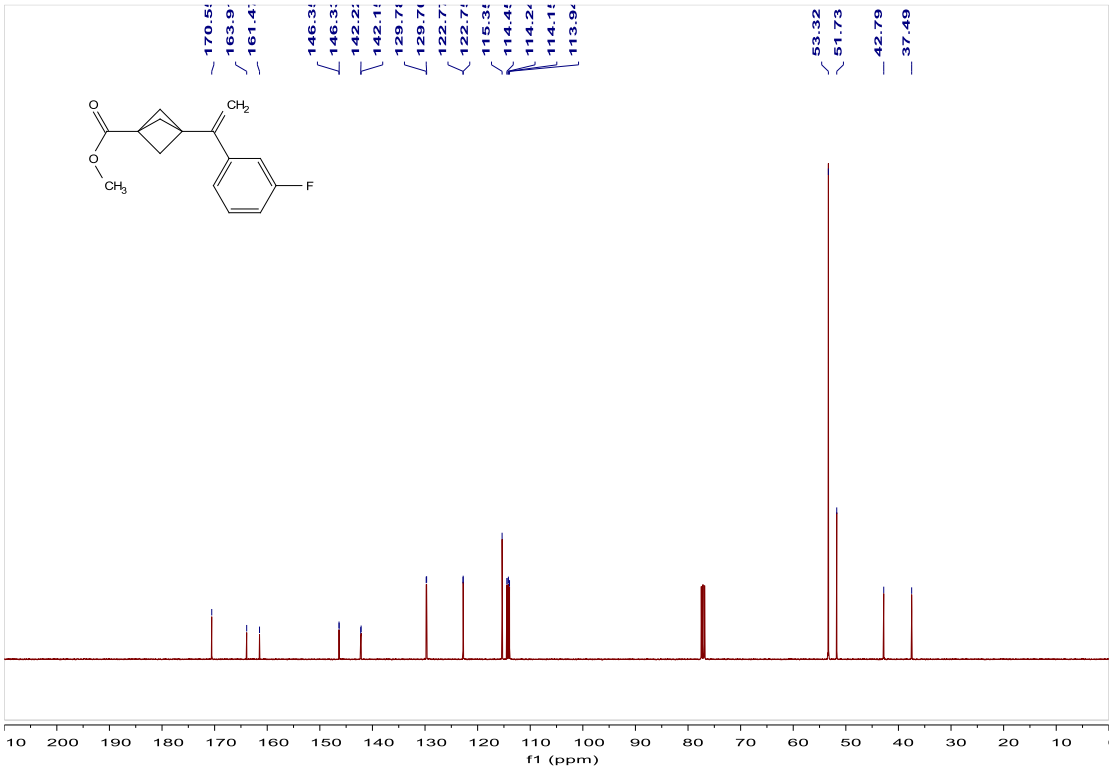
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1i**



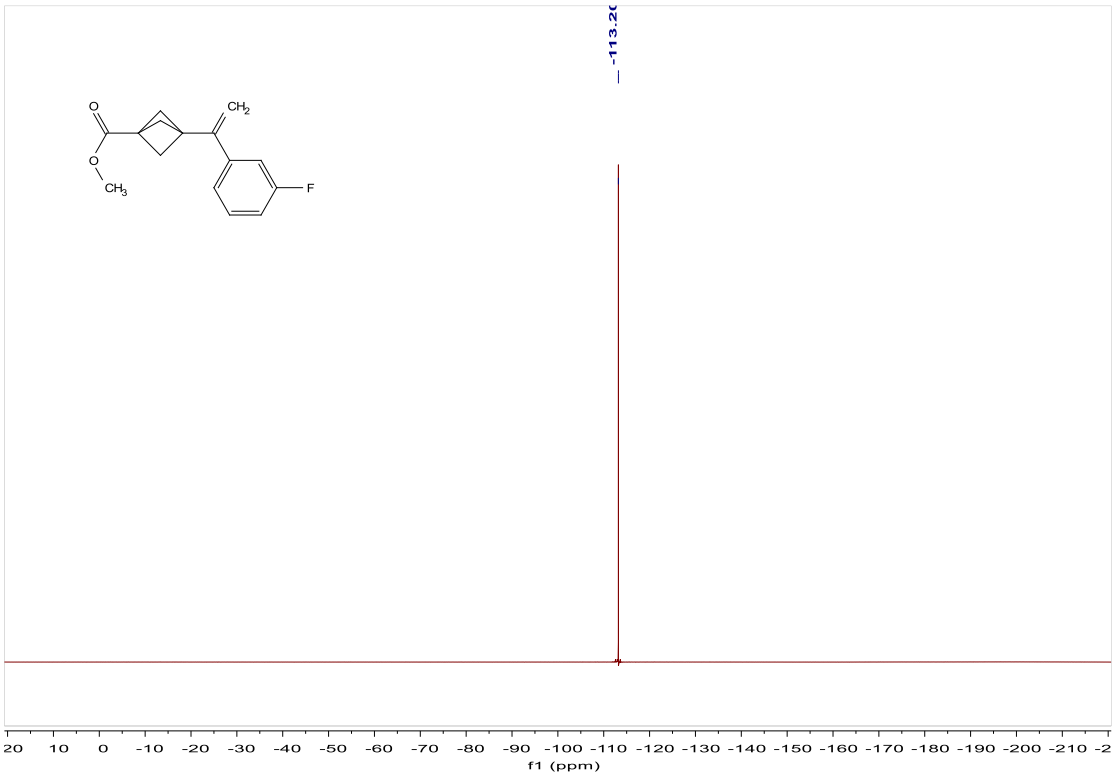
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1j**



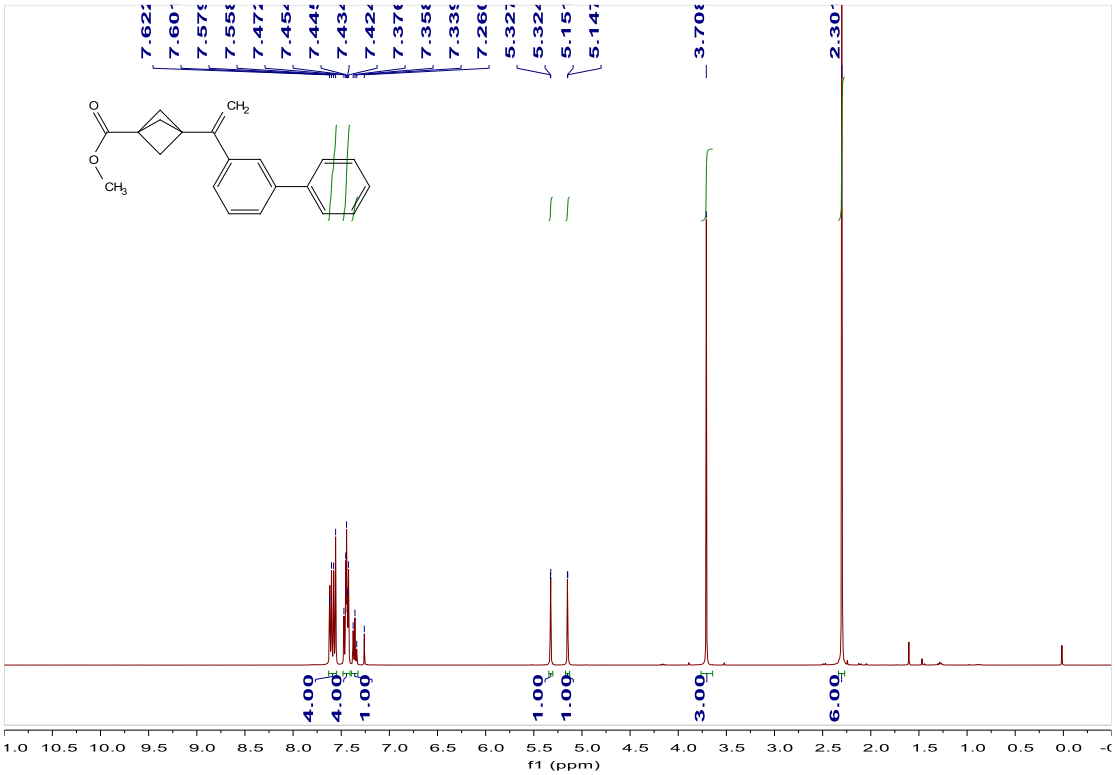
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1j**



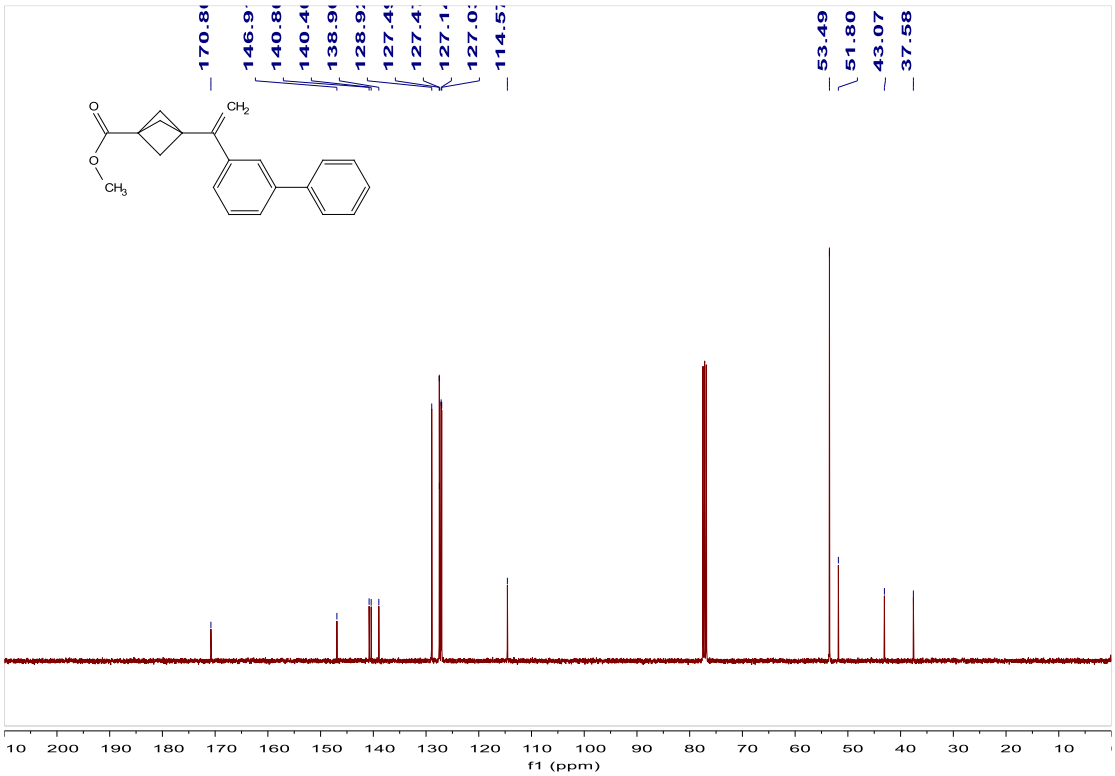
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **1j**



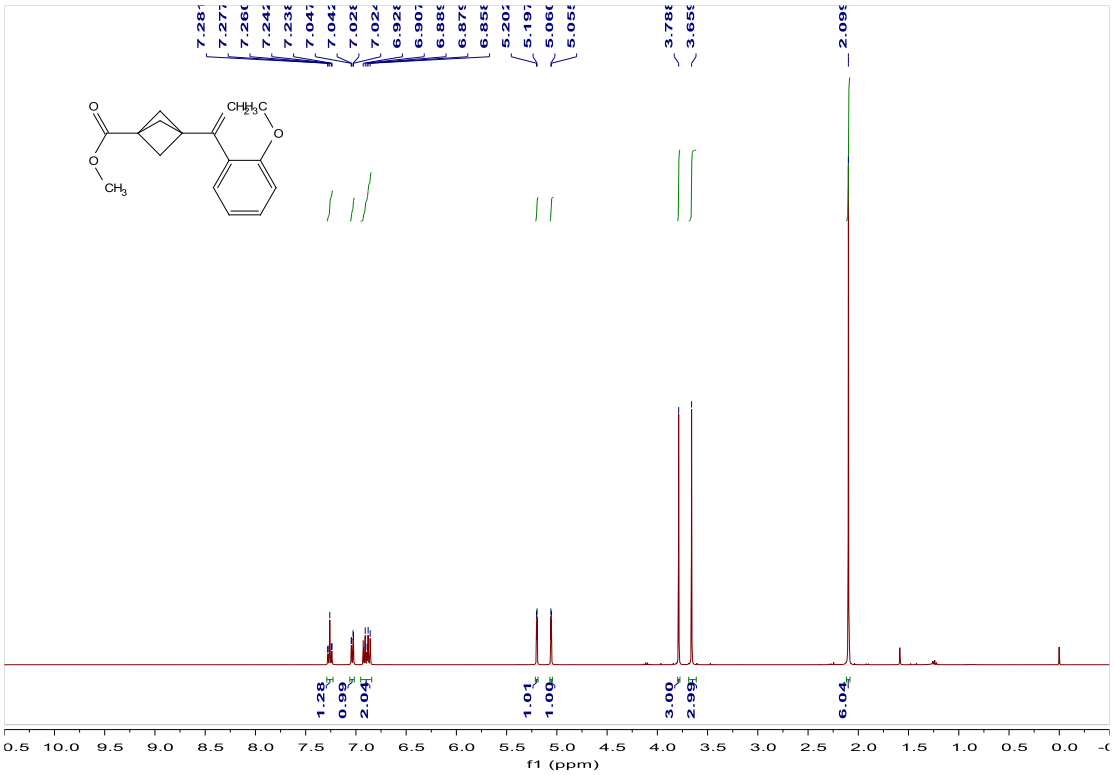
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1k**



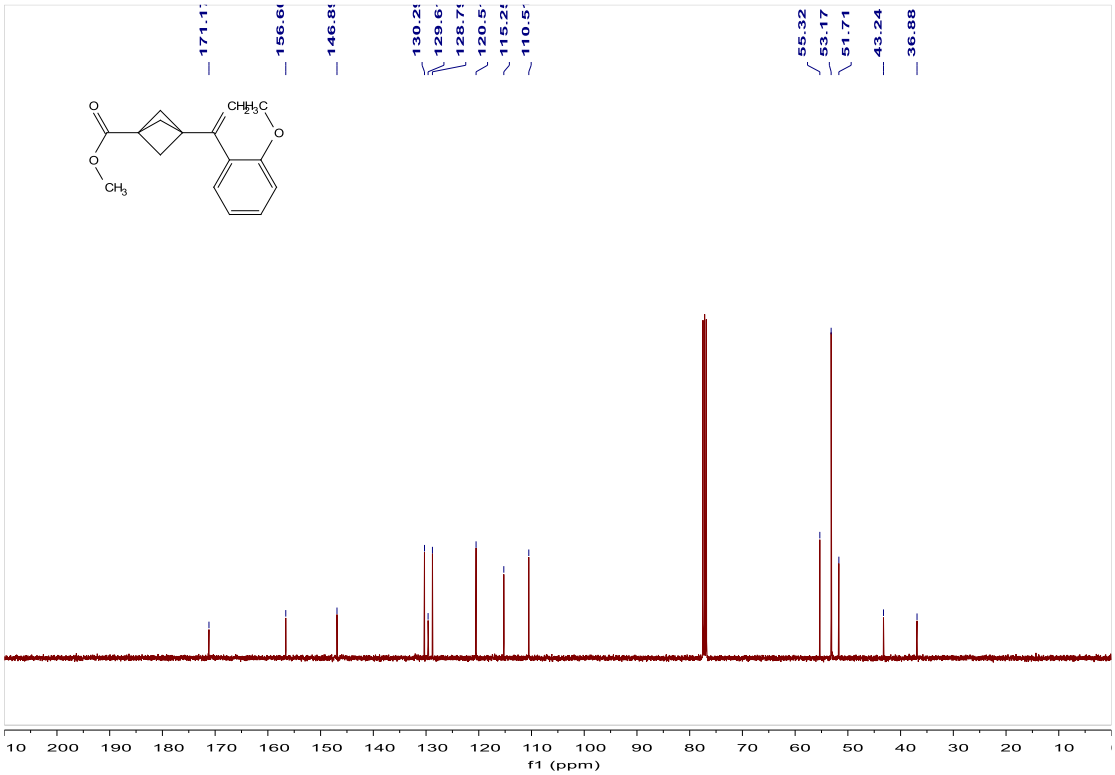
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1k**



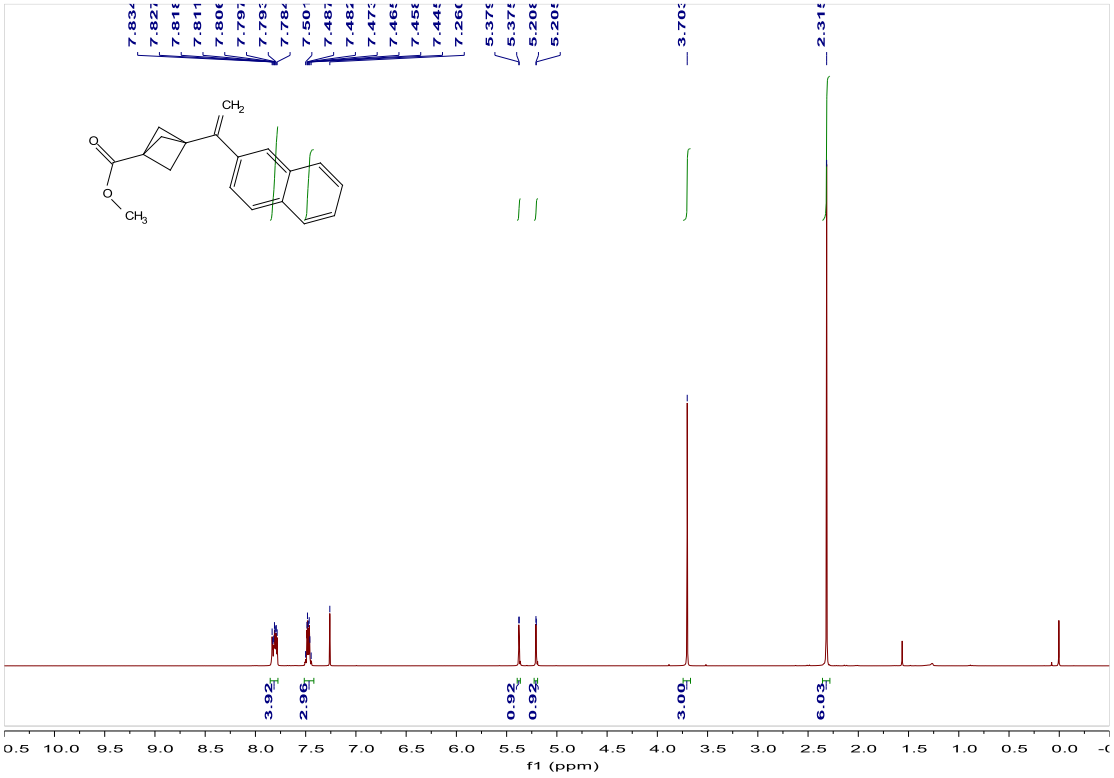
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1l**



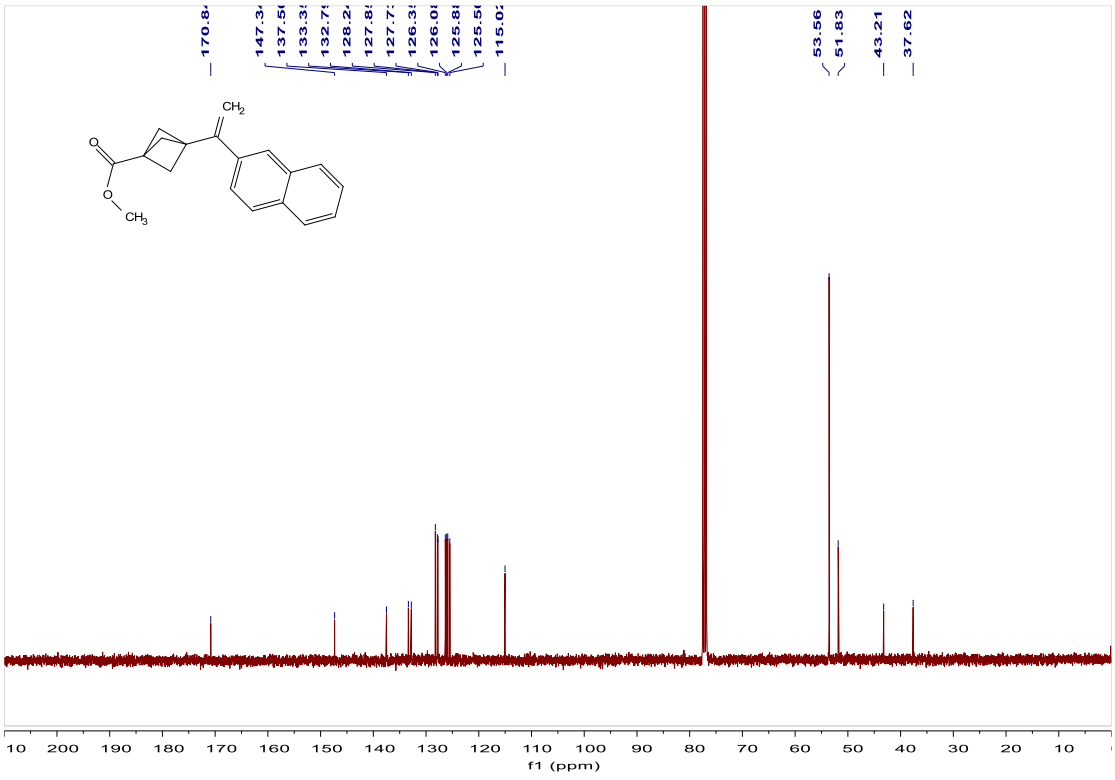
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1l**



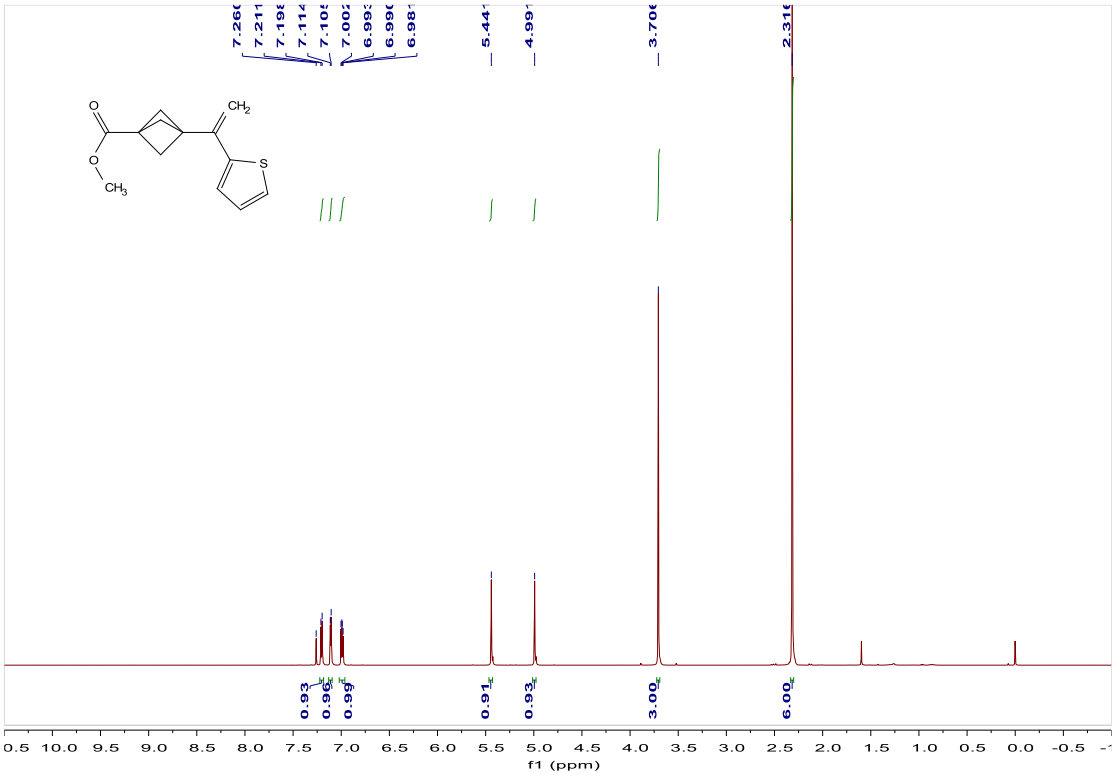
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1m**



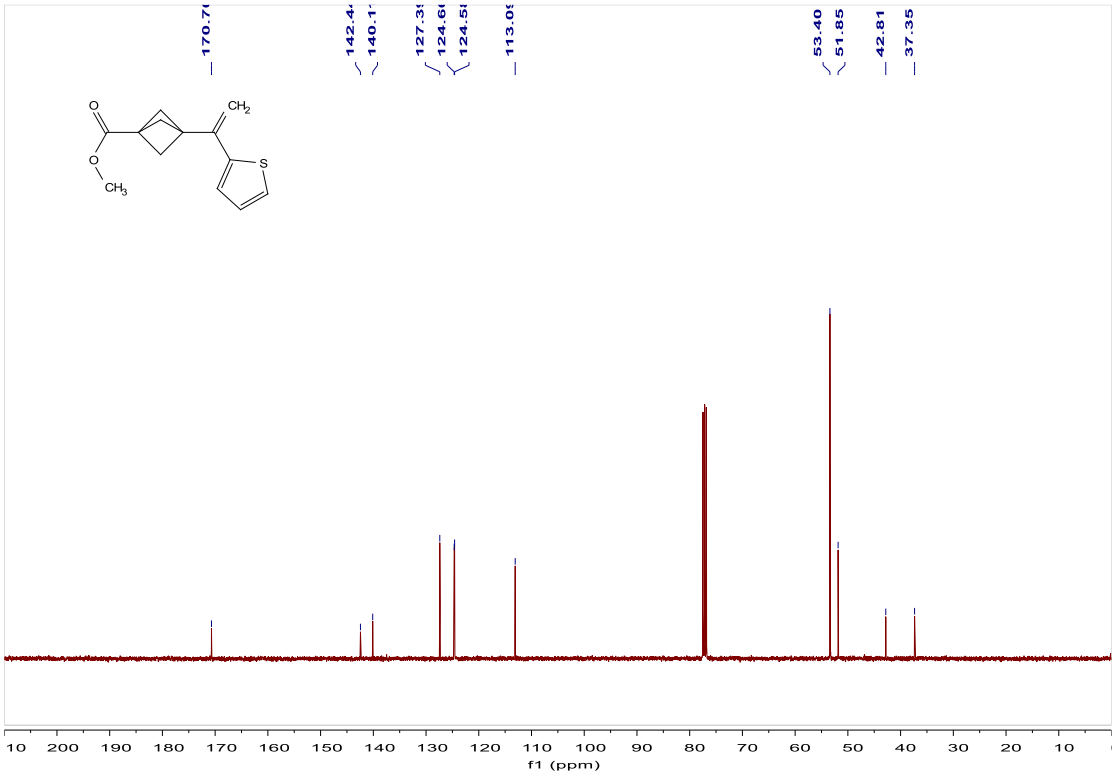
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1m**



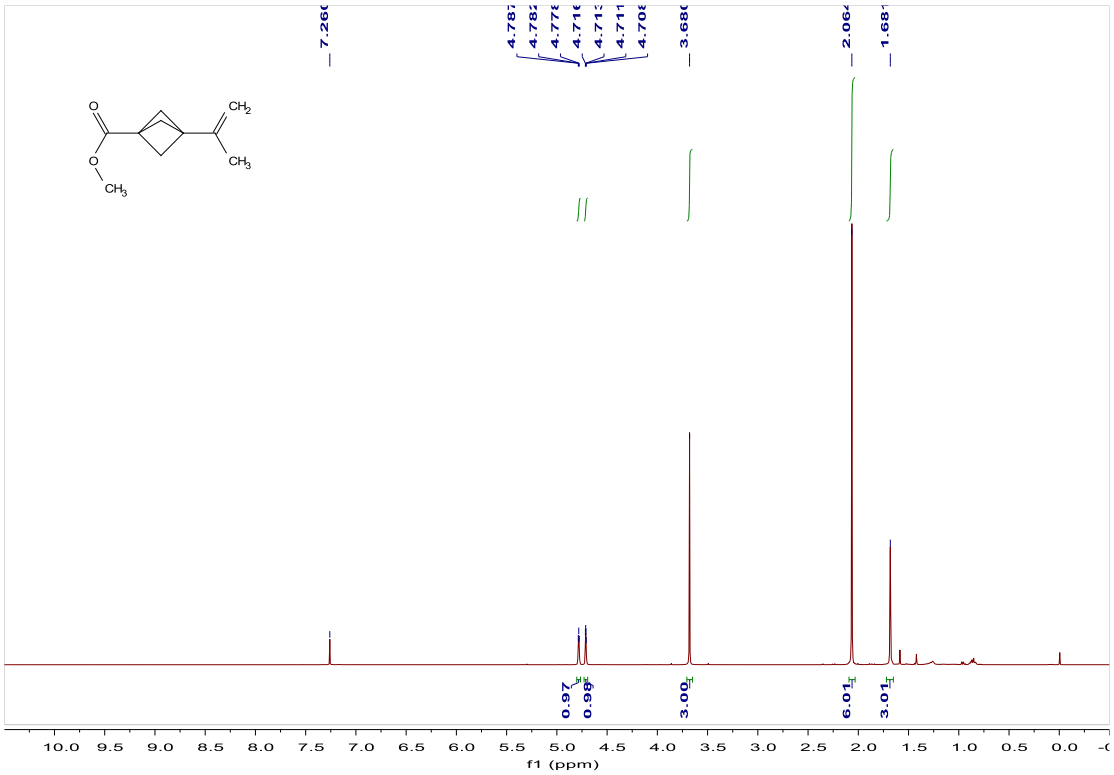
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1n**



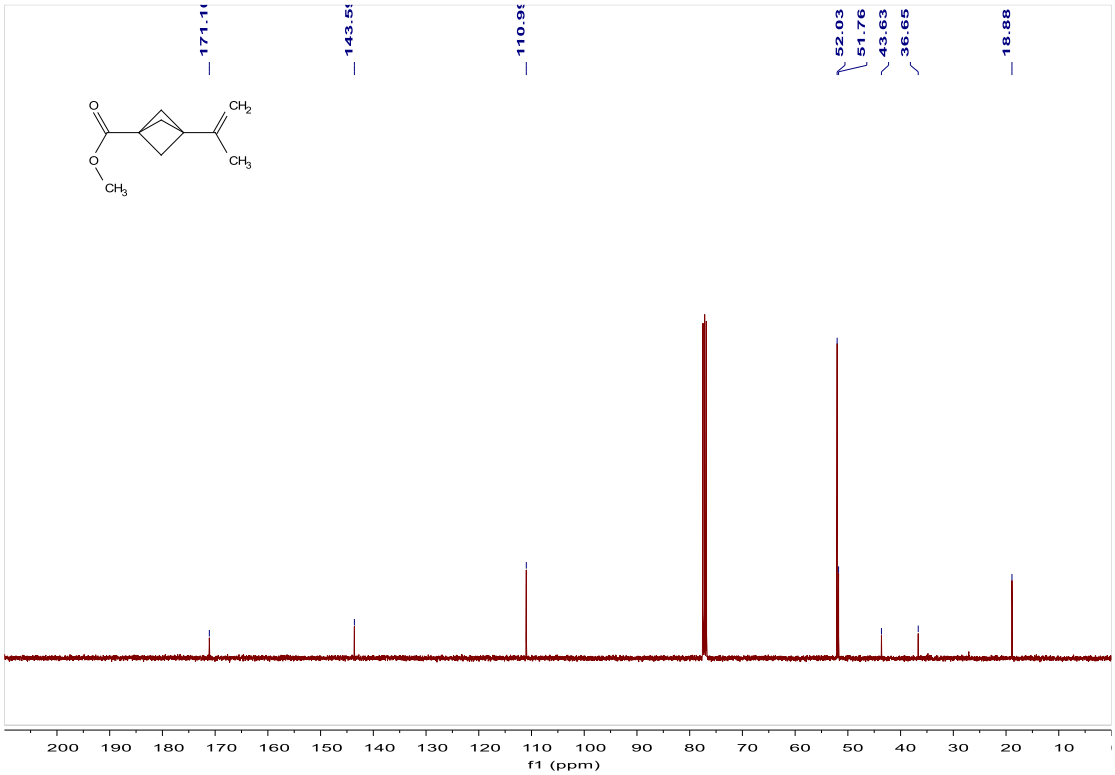
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1n**



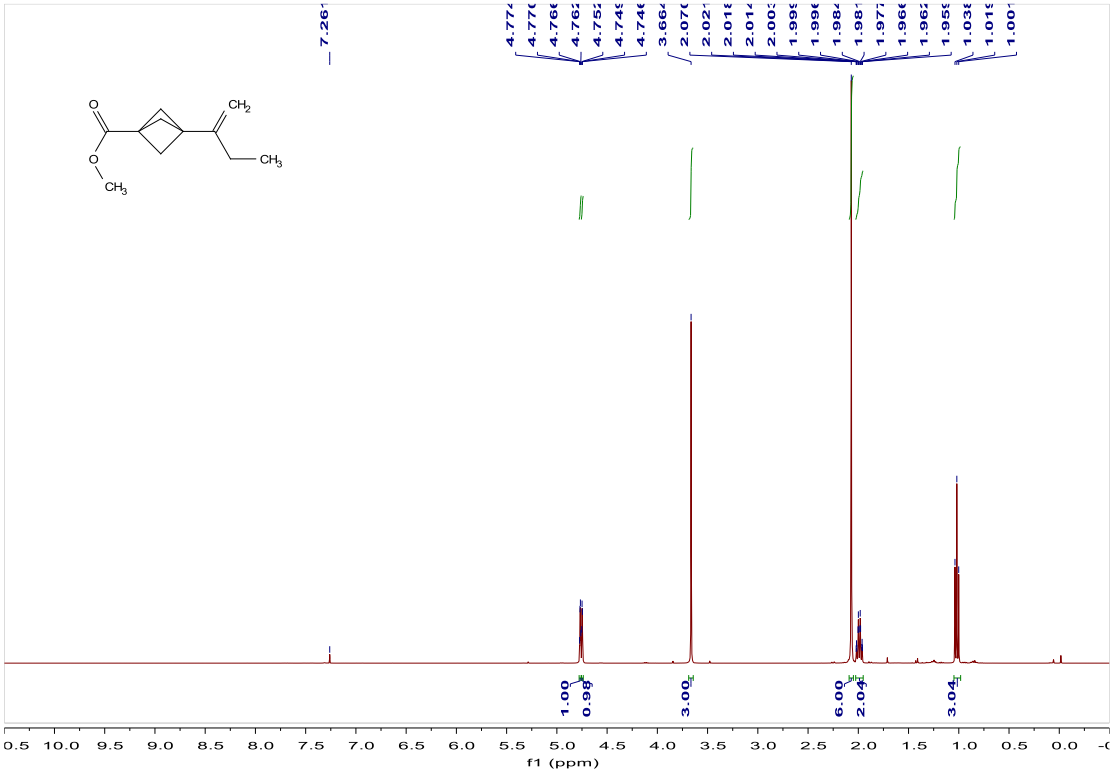
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1o**



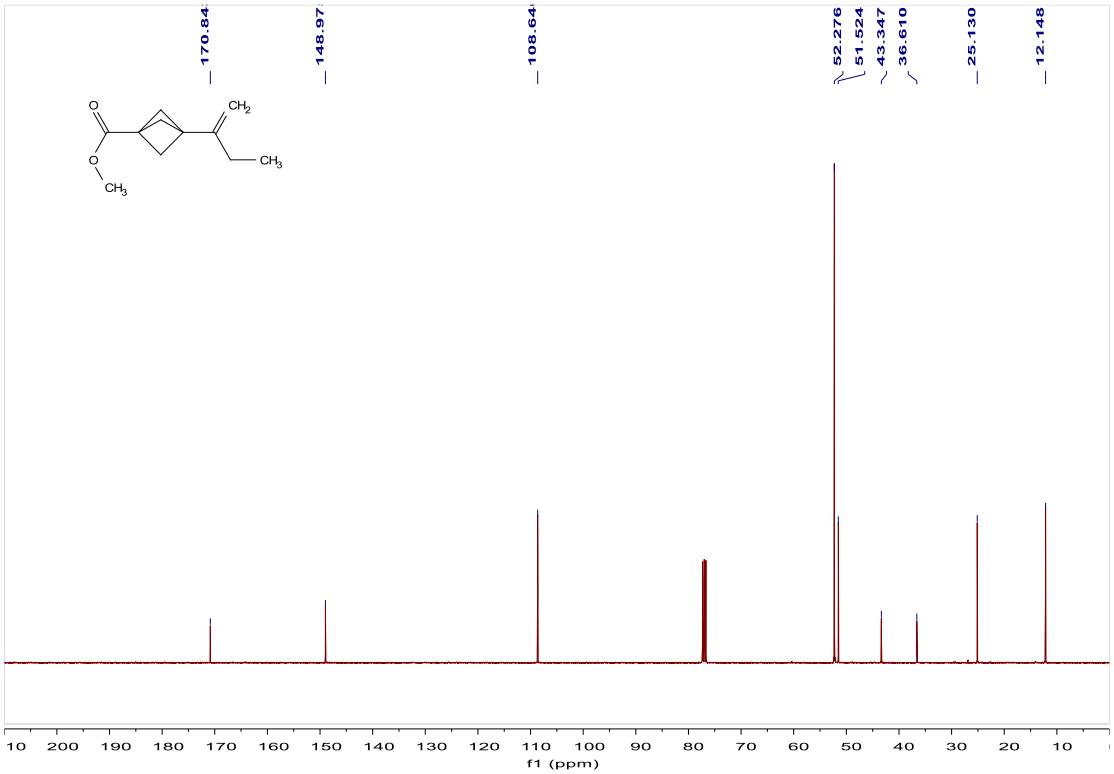
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1o**



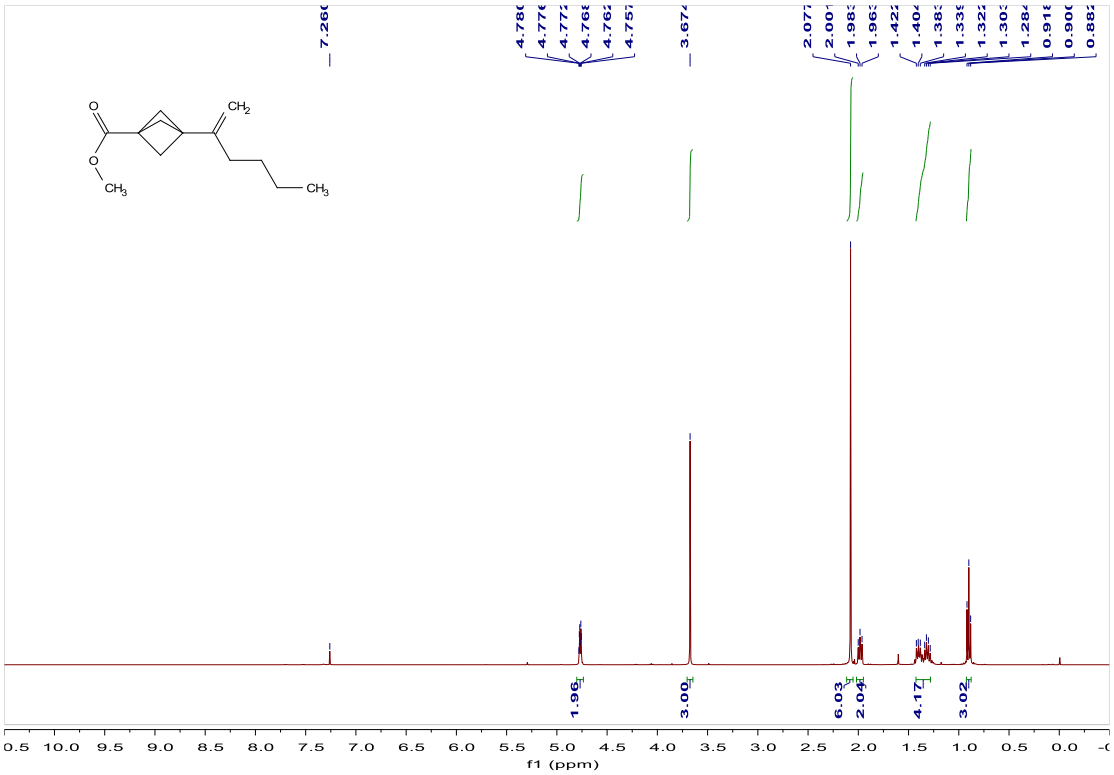
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1p**



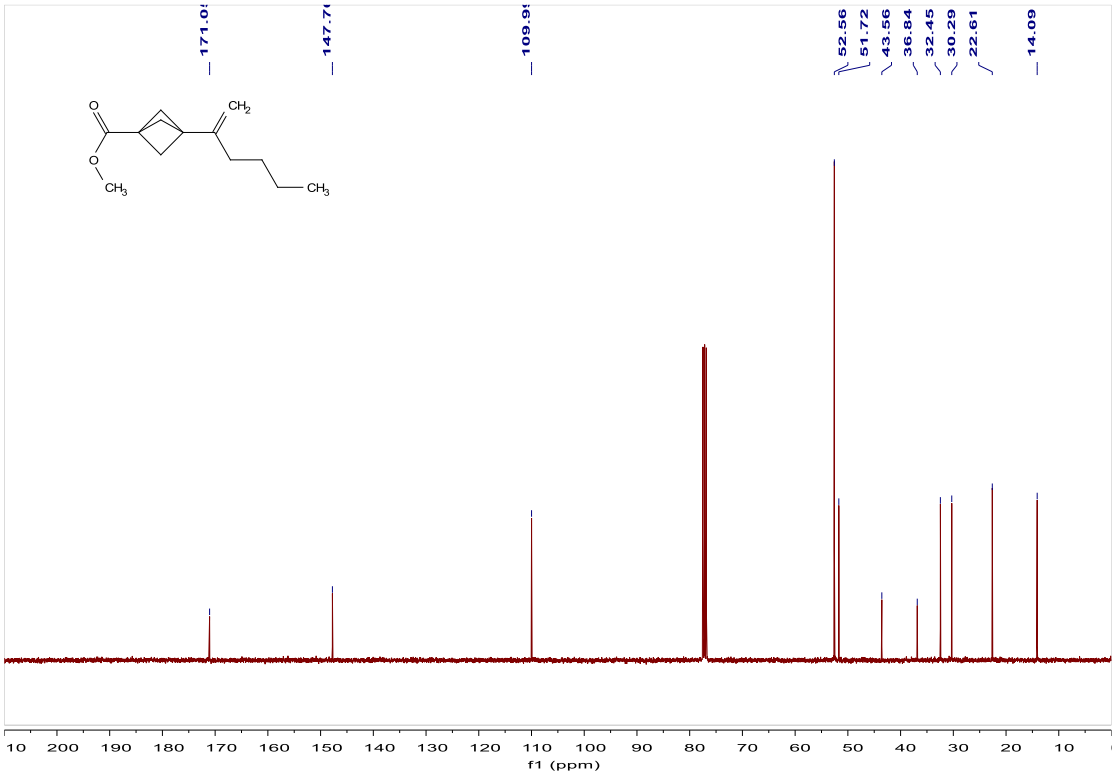
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1p**



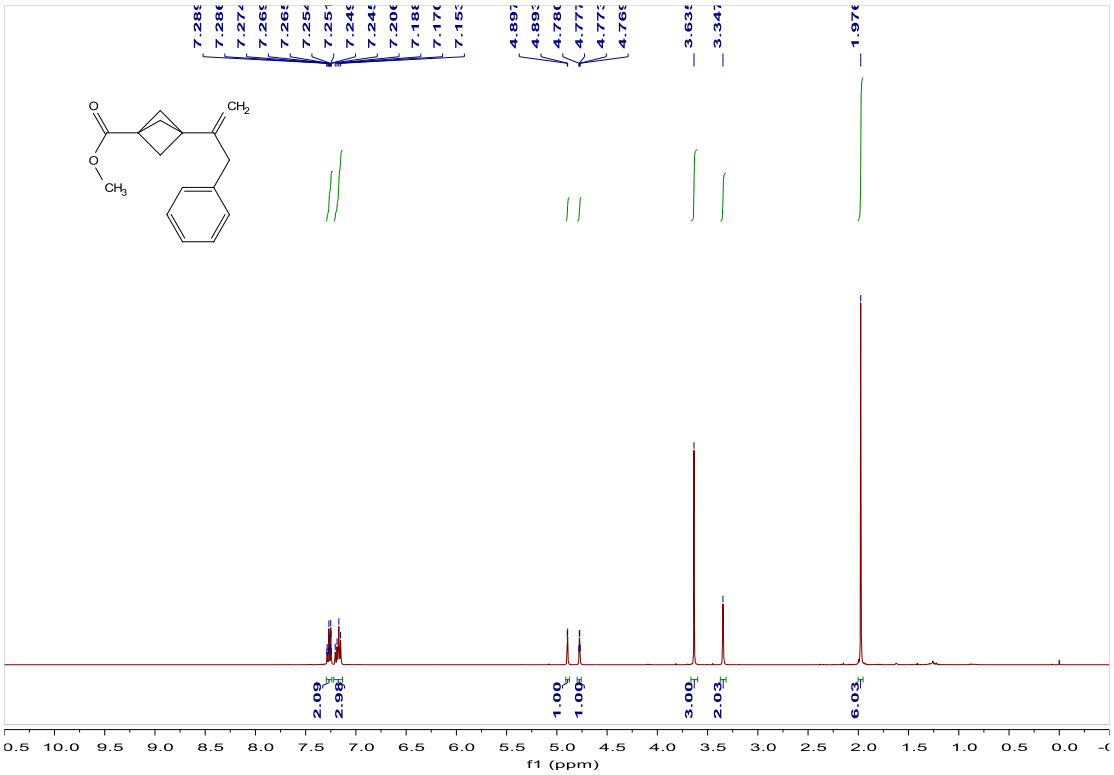
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1q**



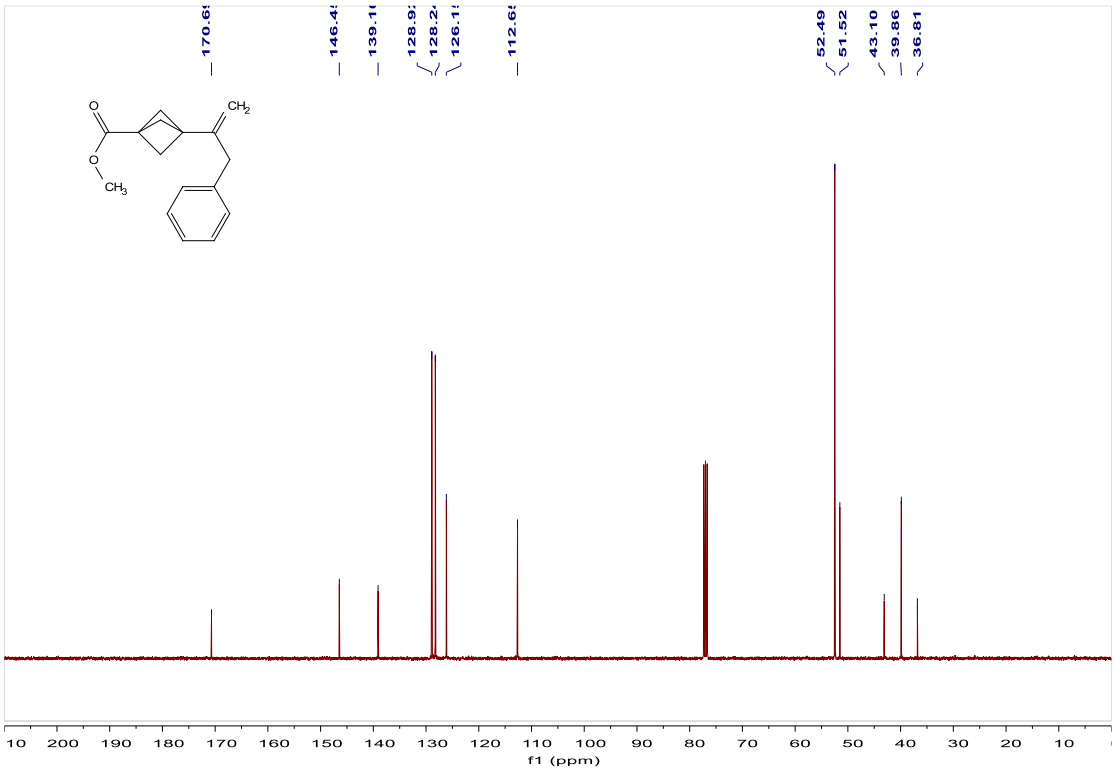
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1q**



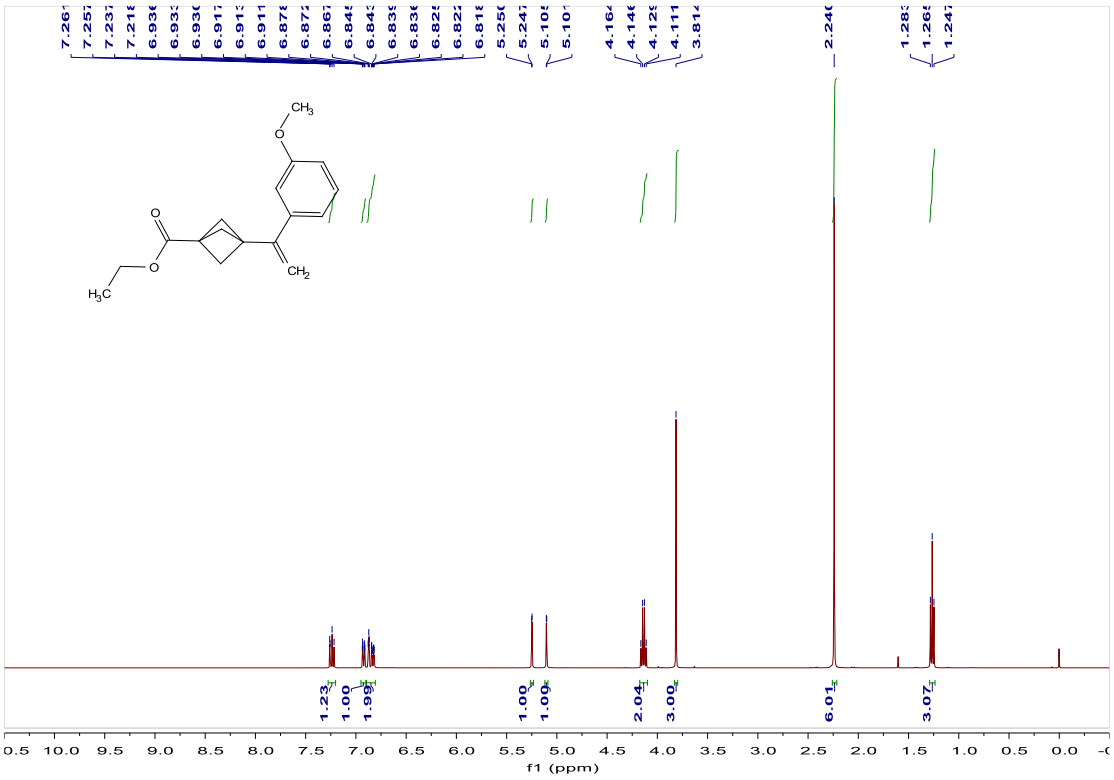
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1r**



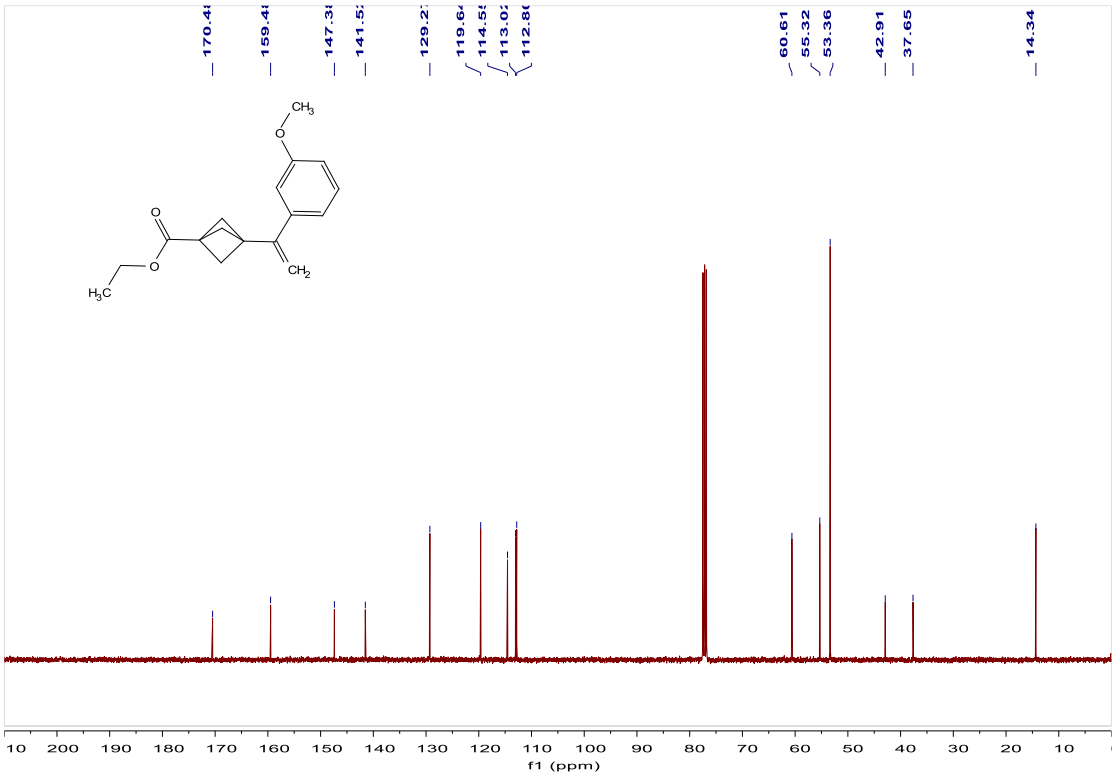
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1r**



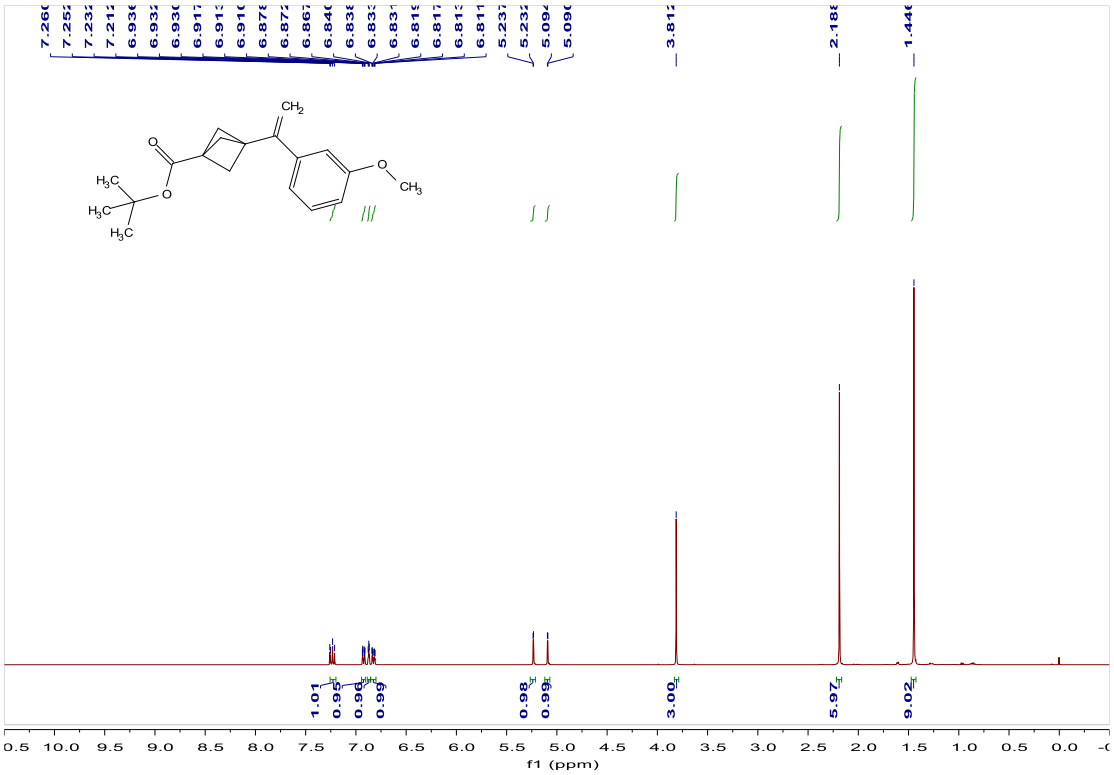
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1s**



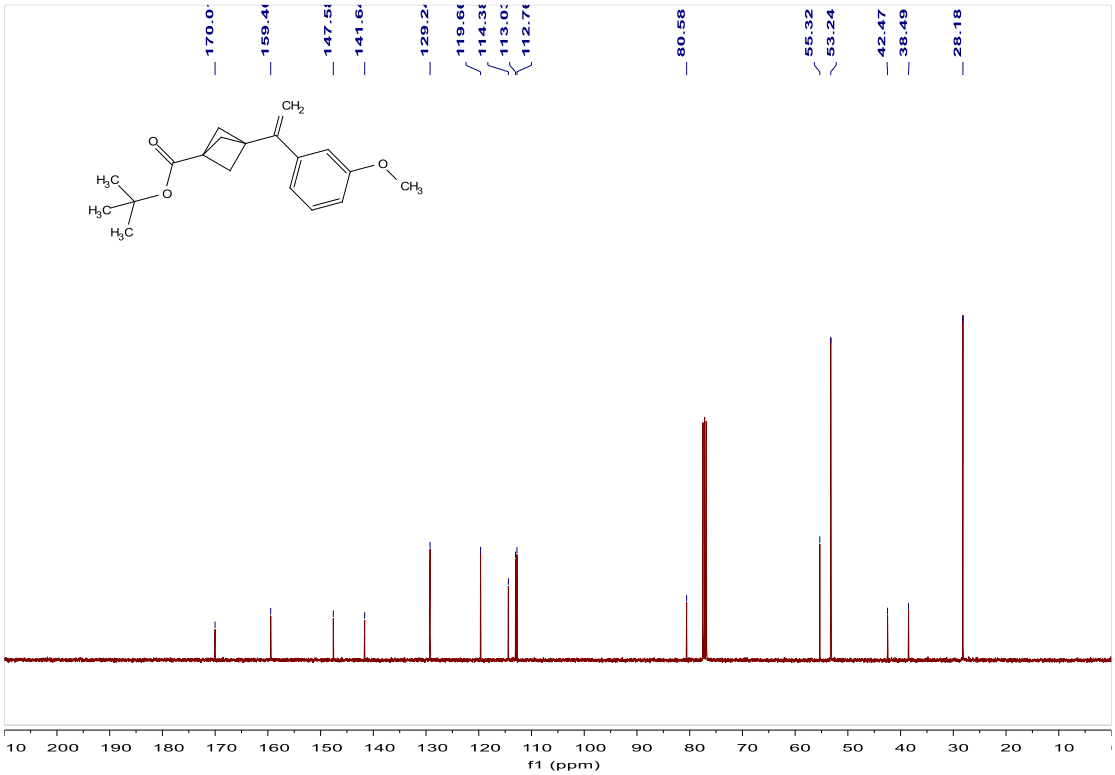
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1s**



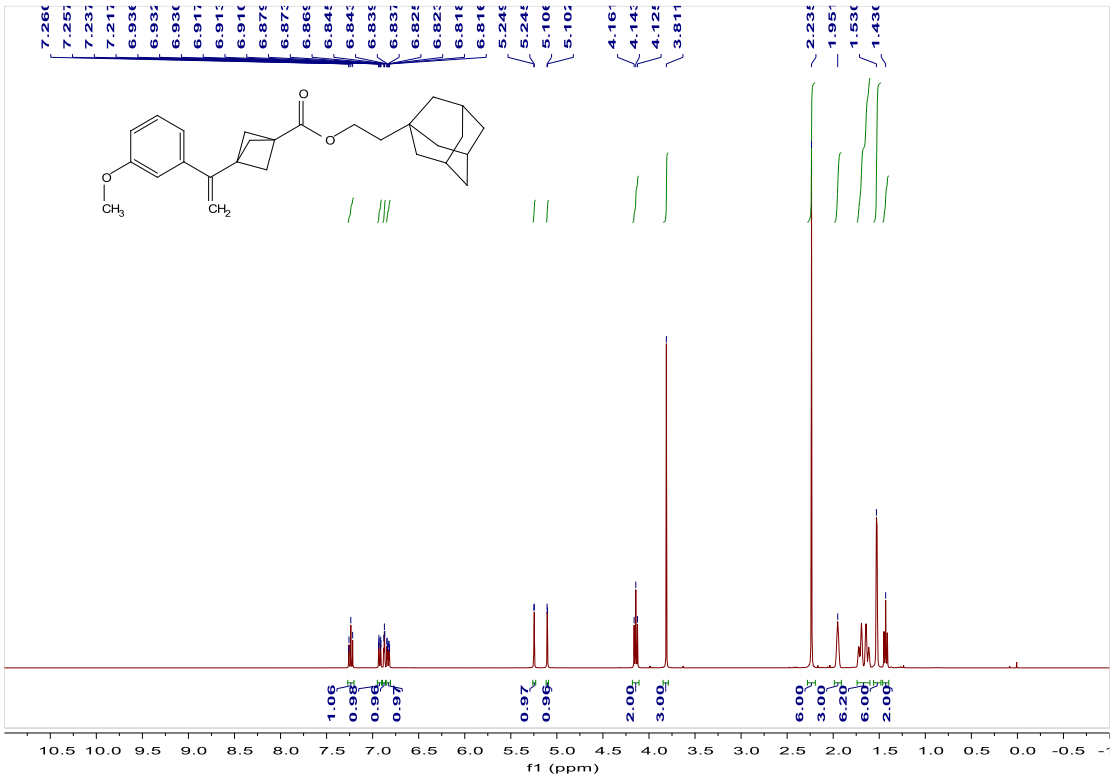
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1t**



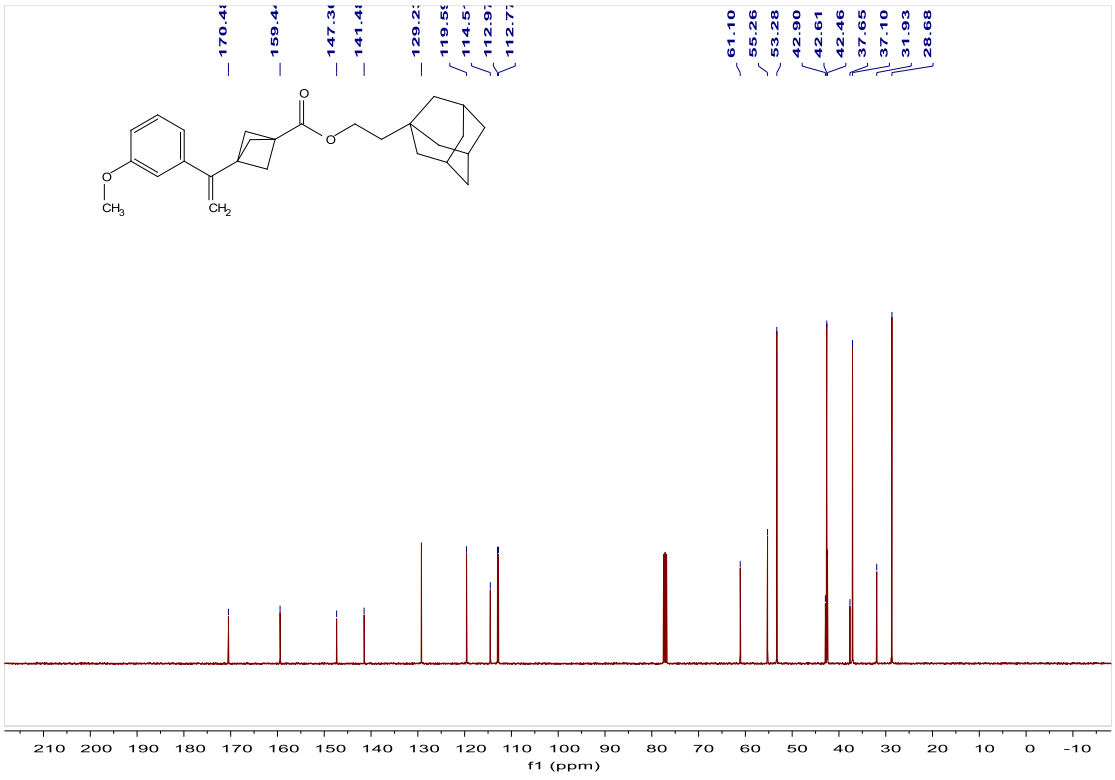
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1t**



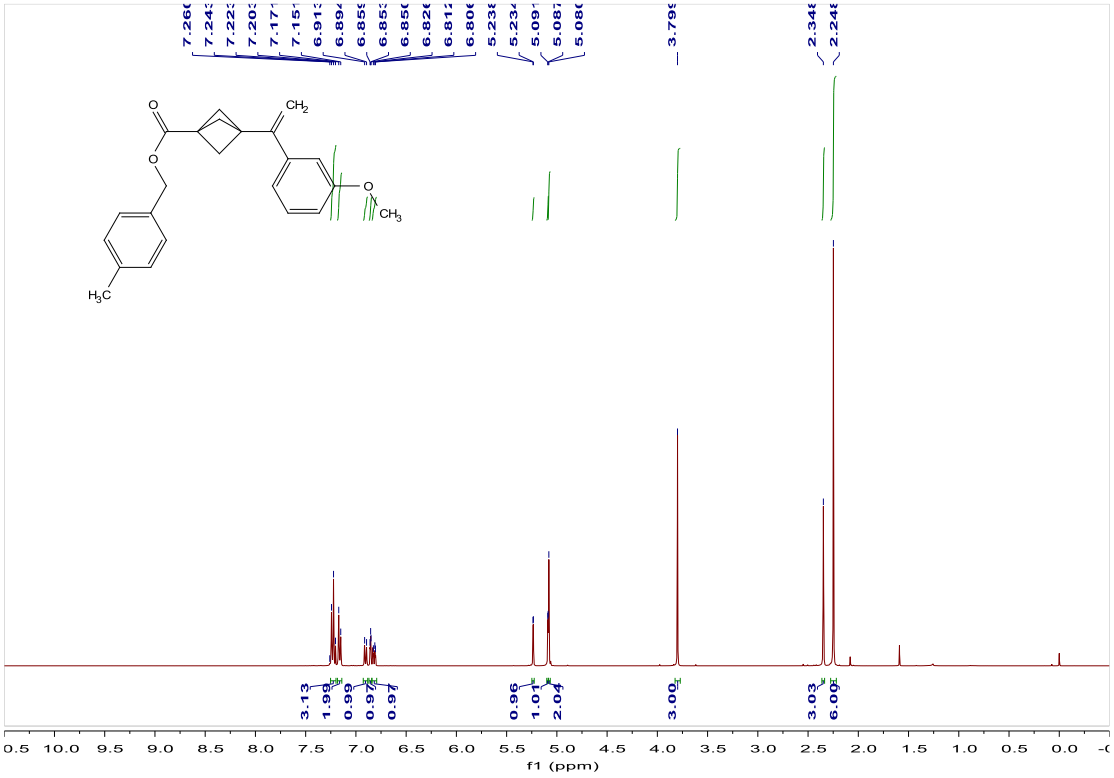
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1u**



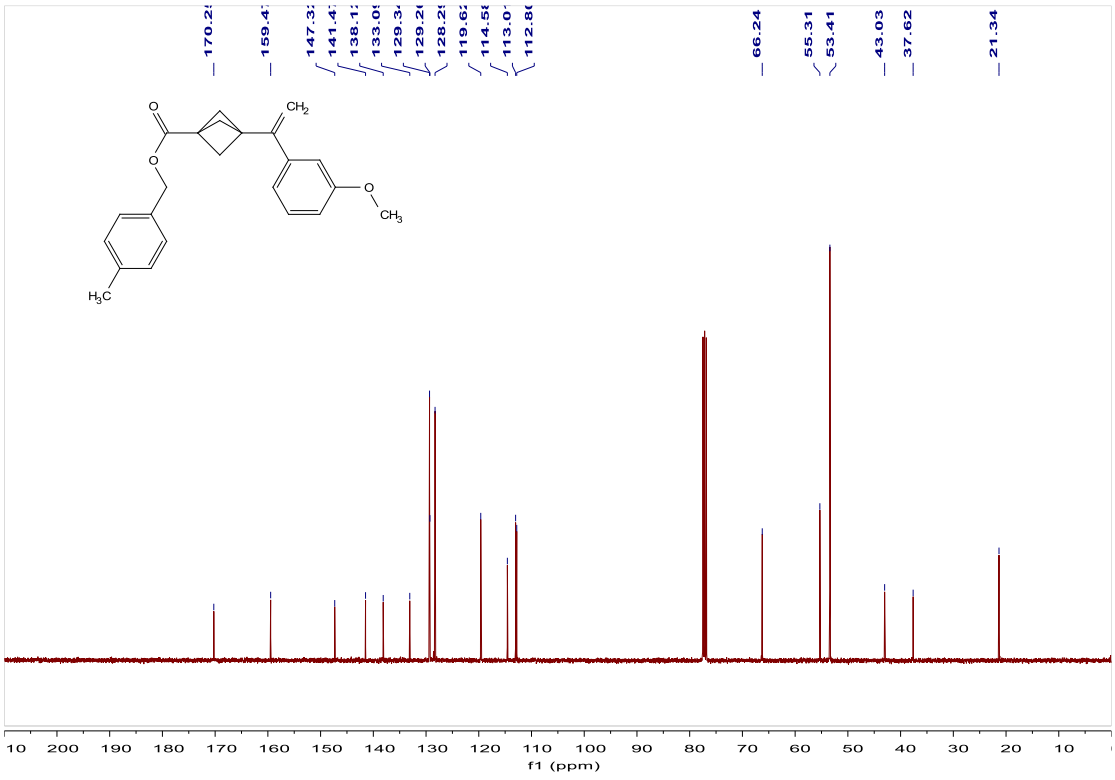
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1u**



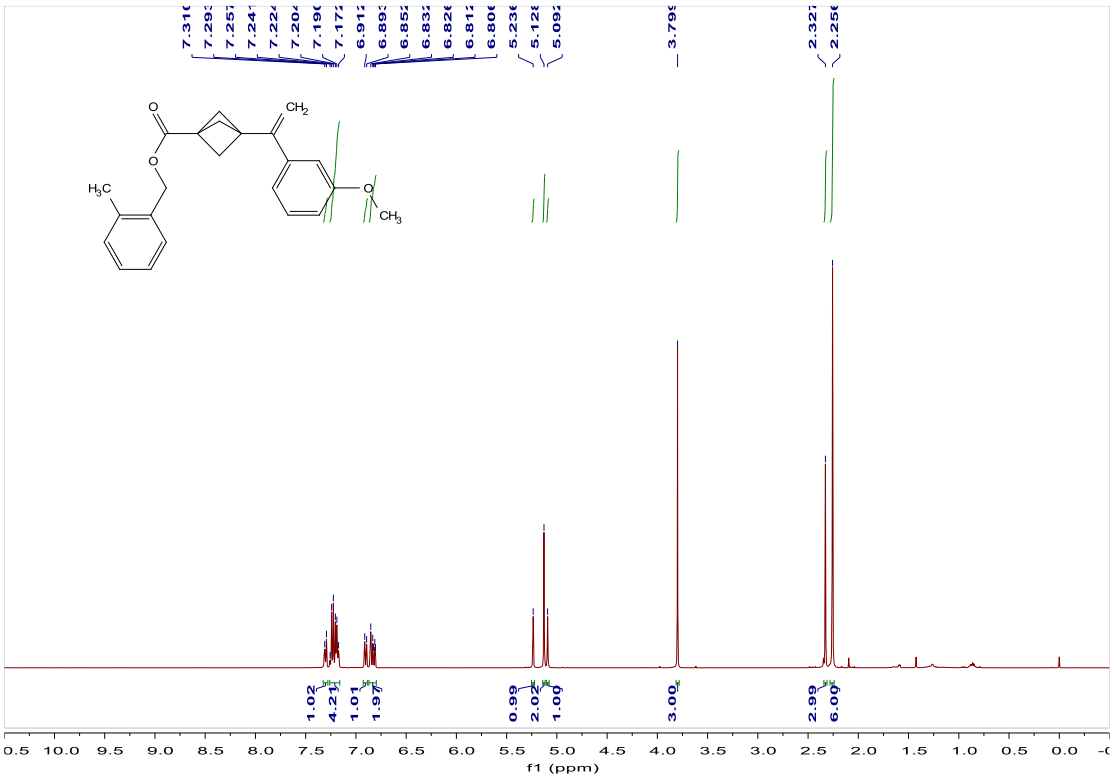
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1v**



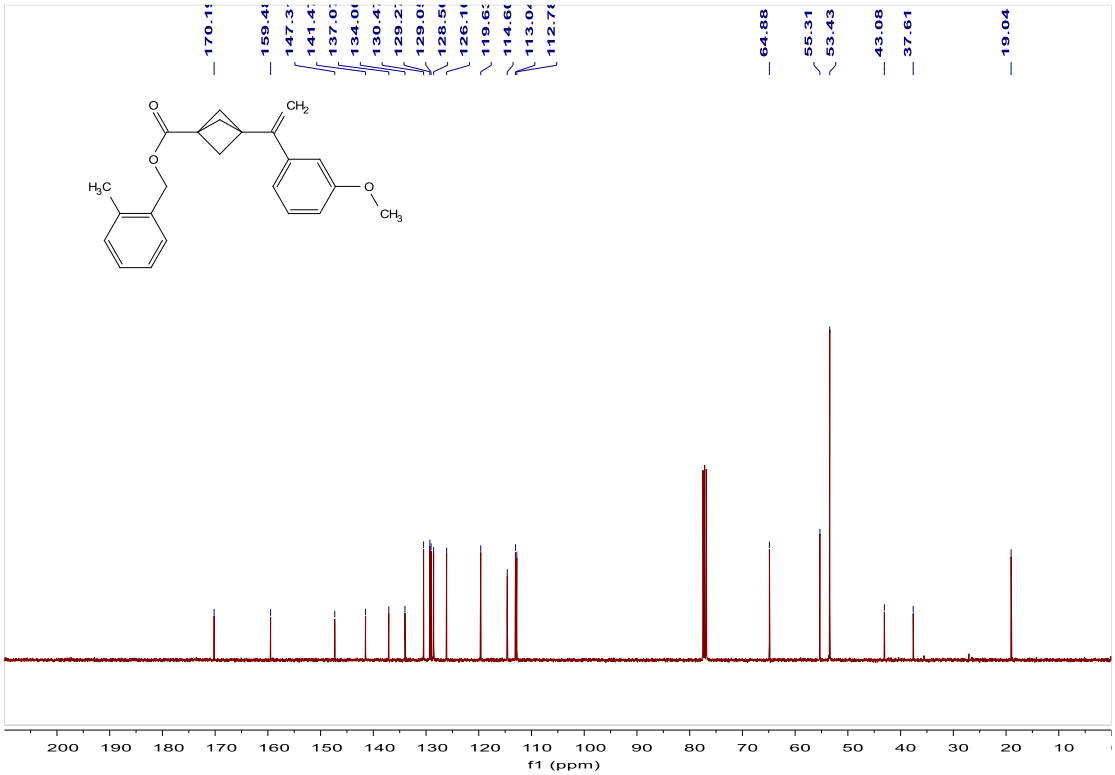
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1v**



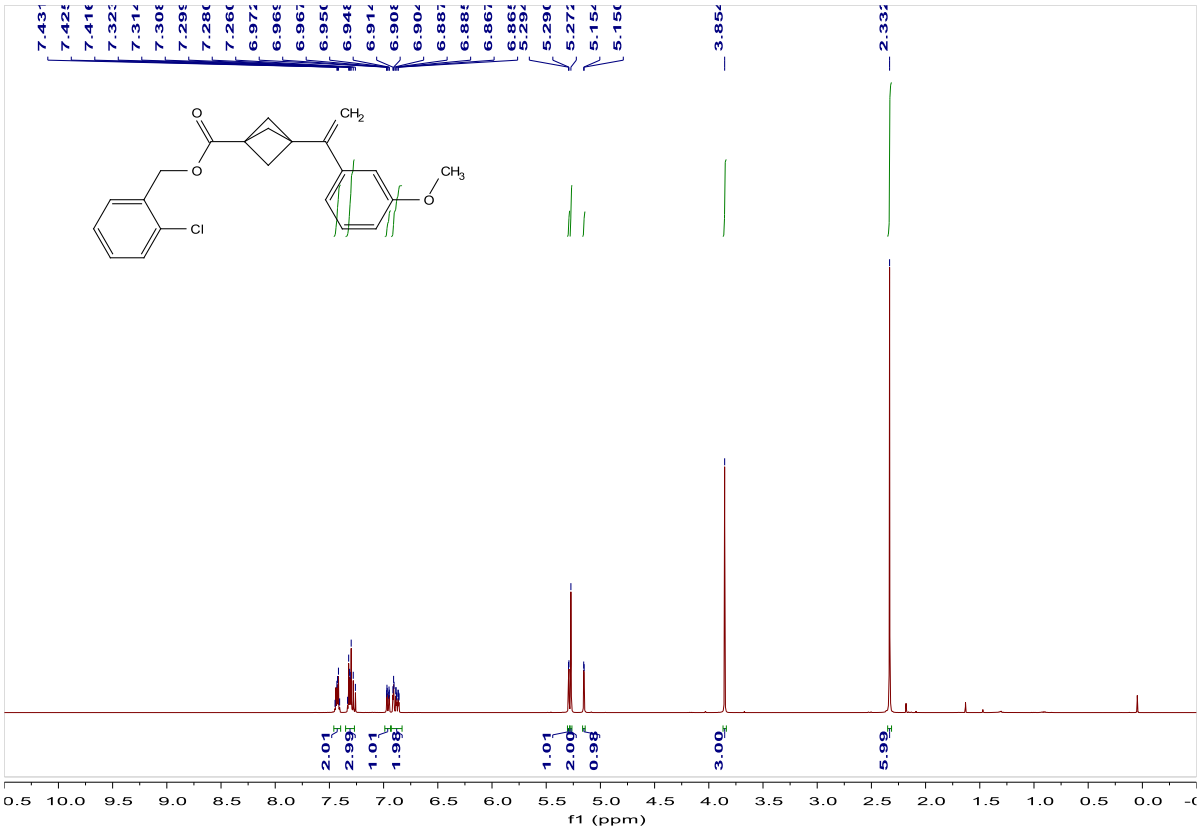
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1w**



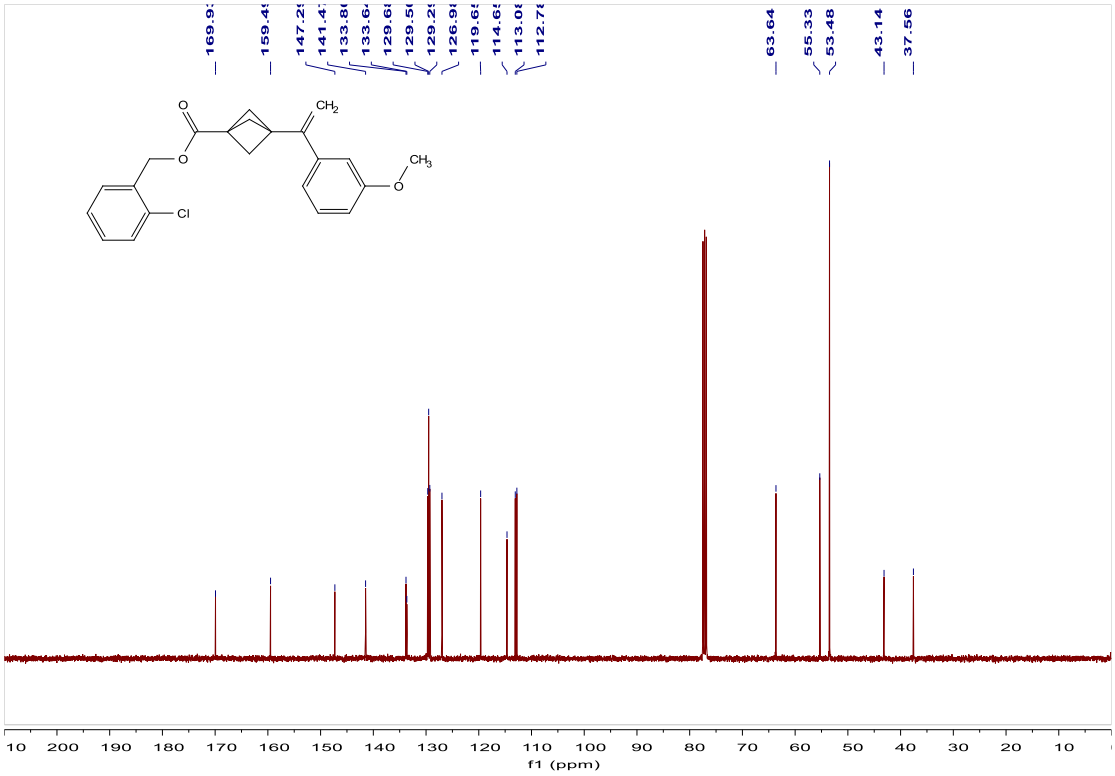
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1w**



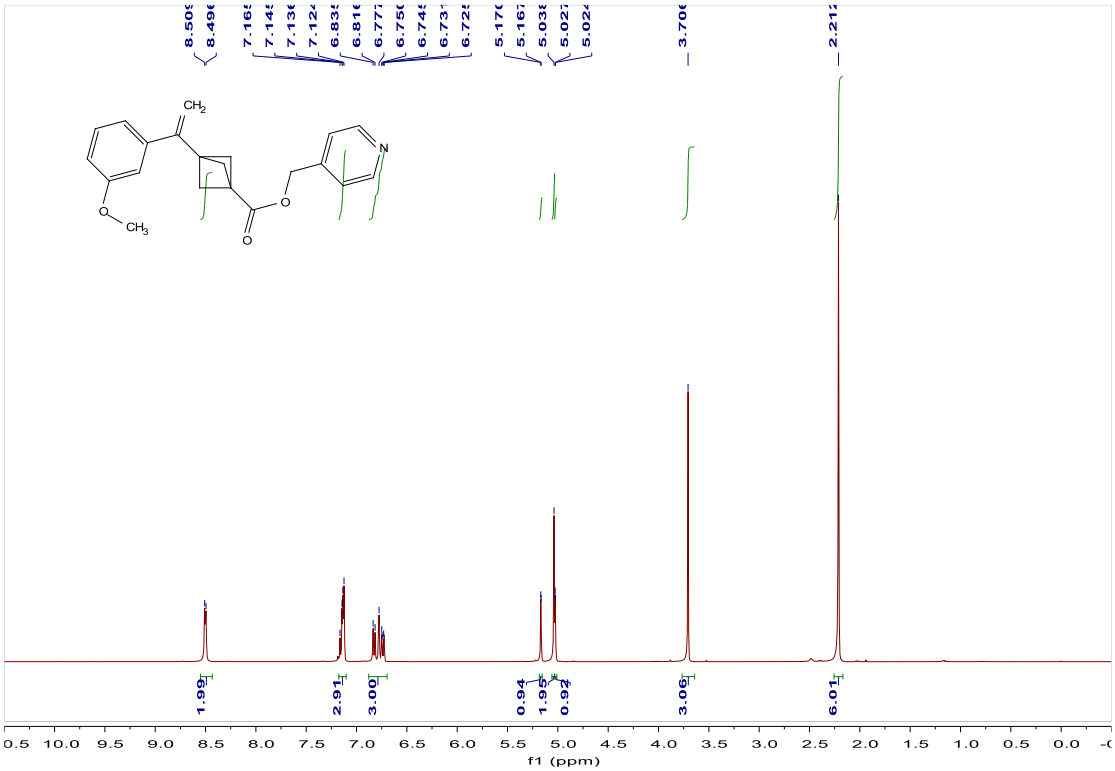
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1x**



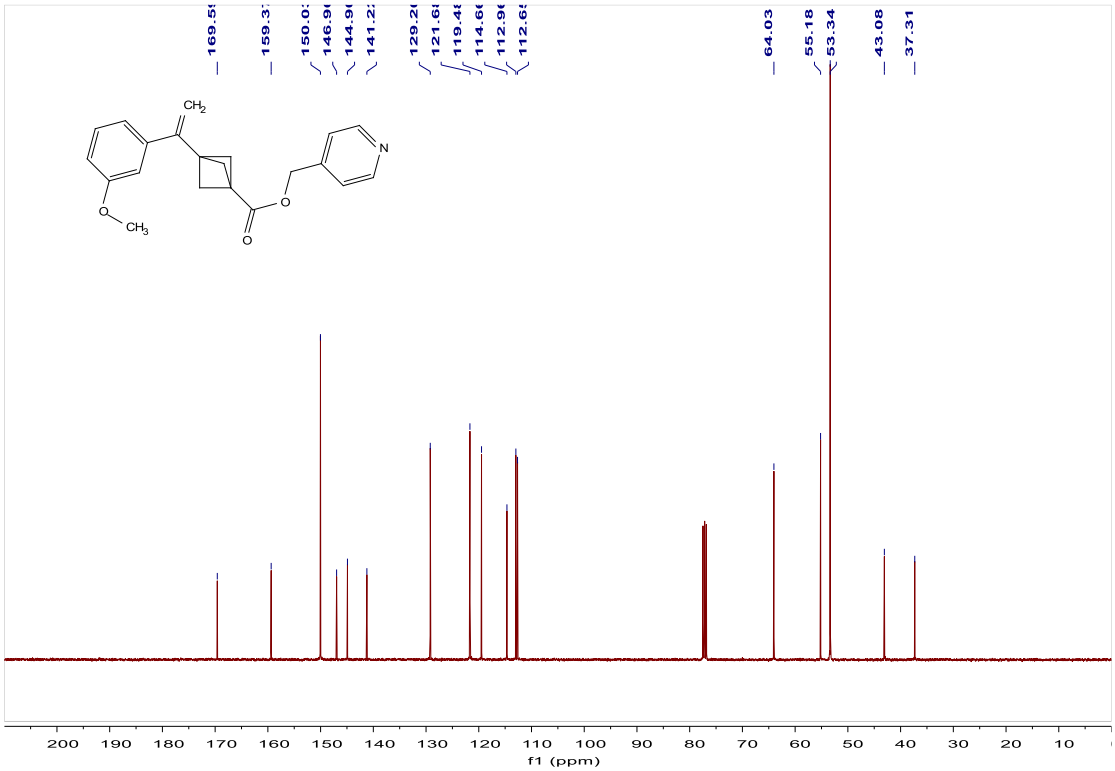
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1x**



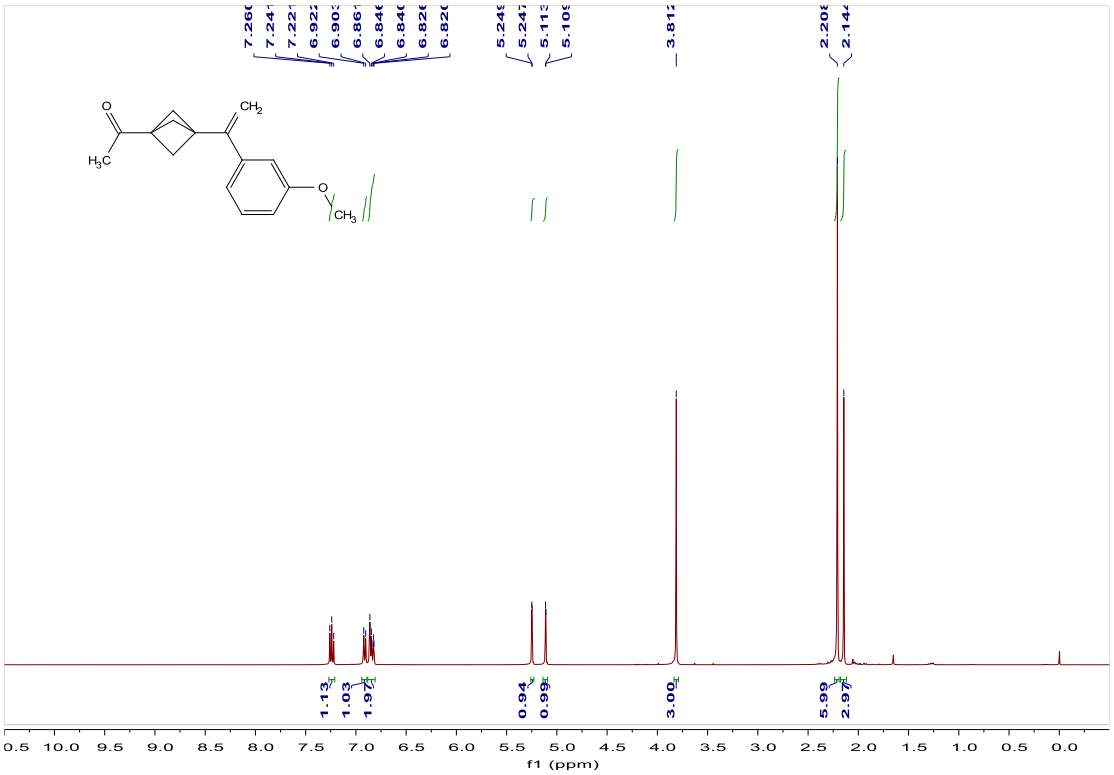
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1y**



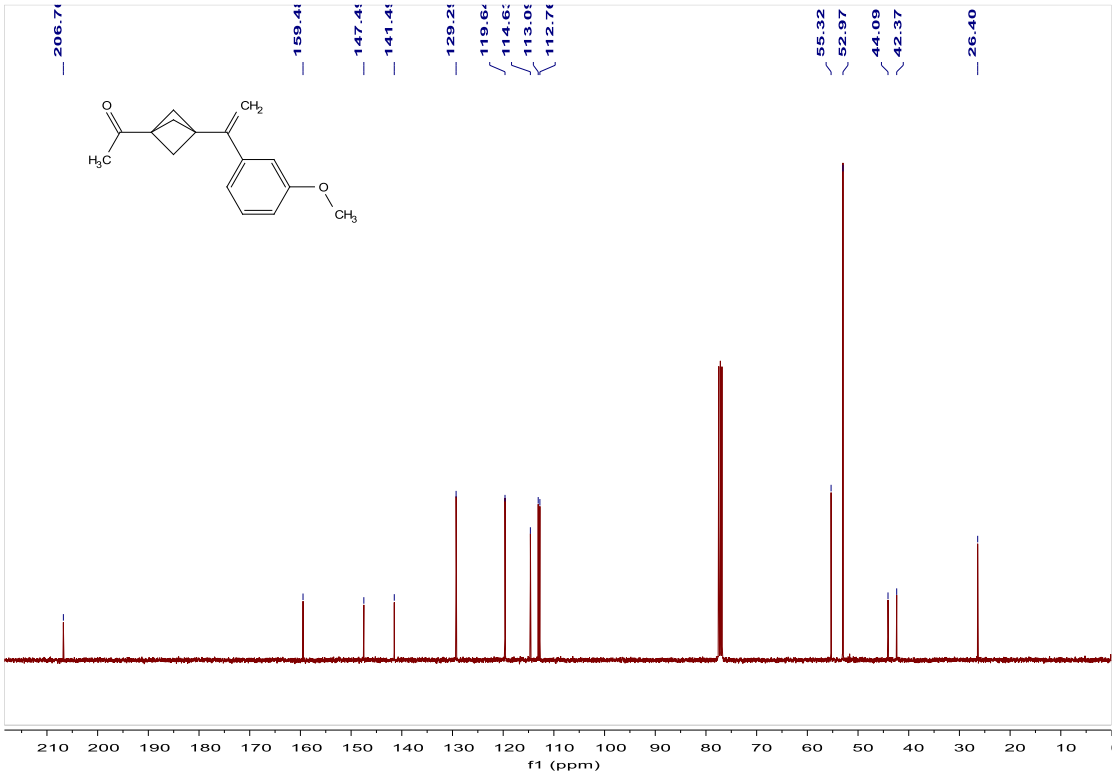
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1y**



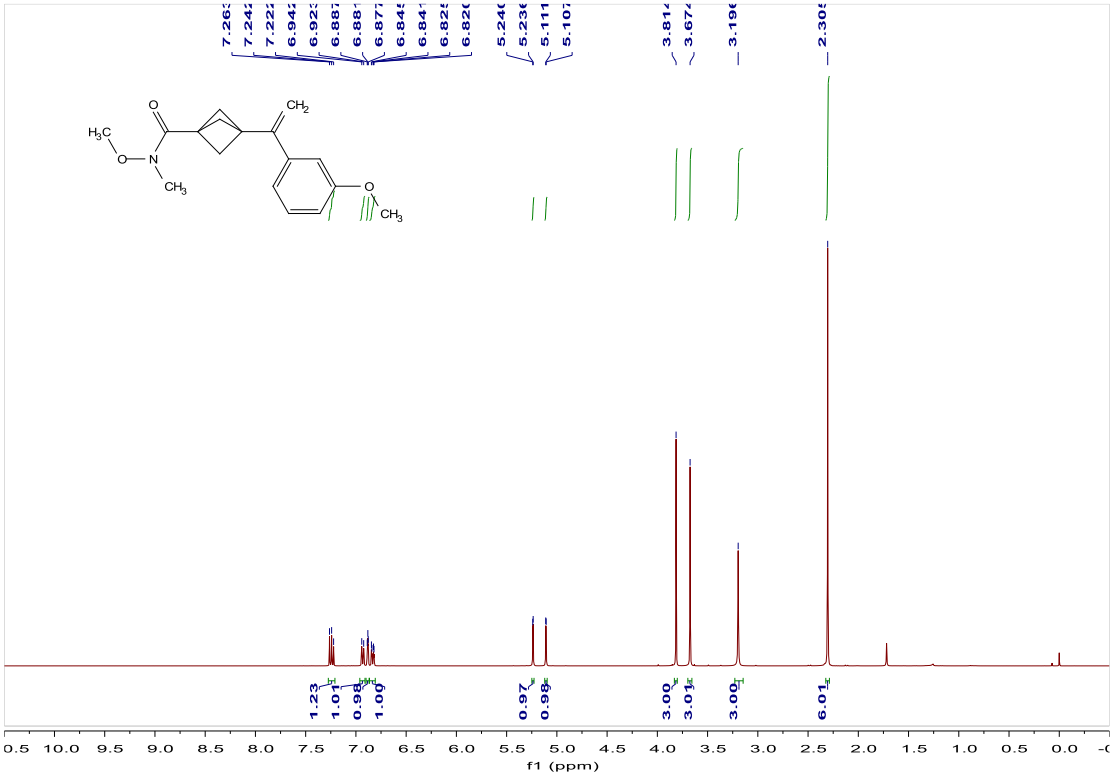
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1z**



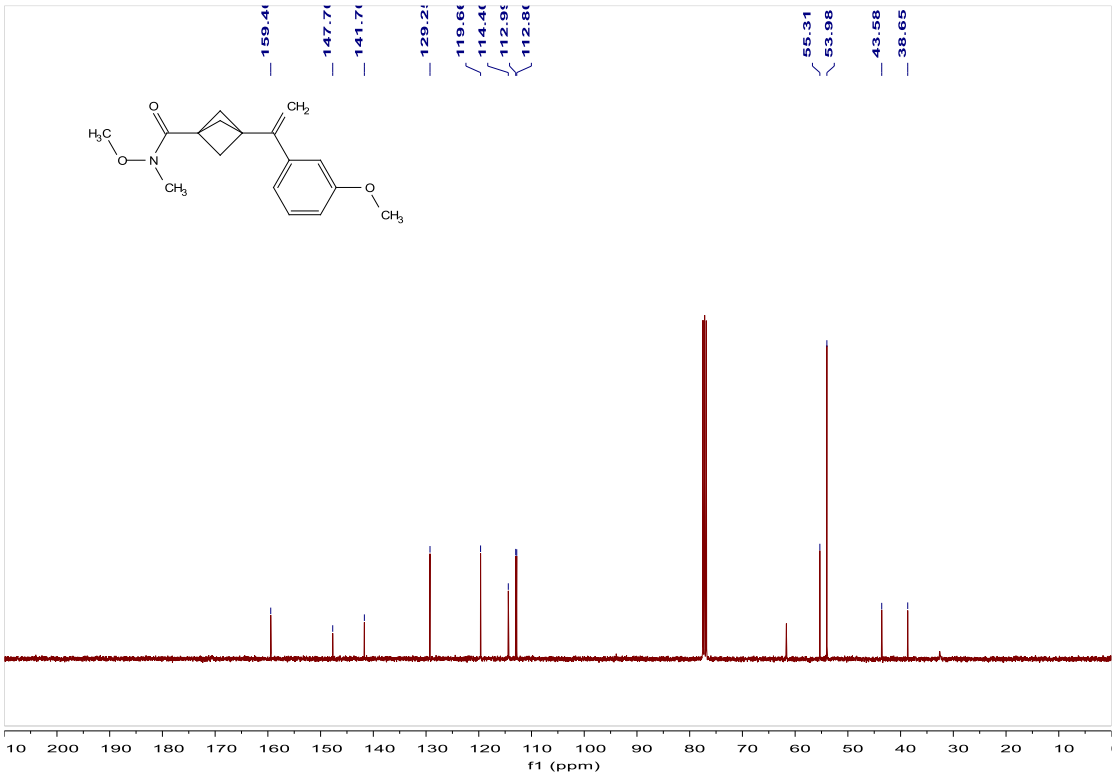
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1z**



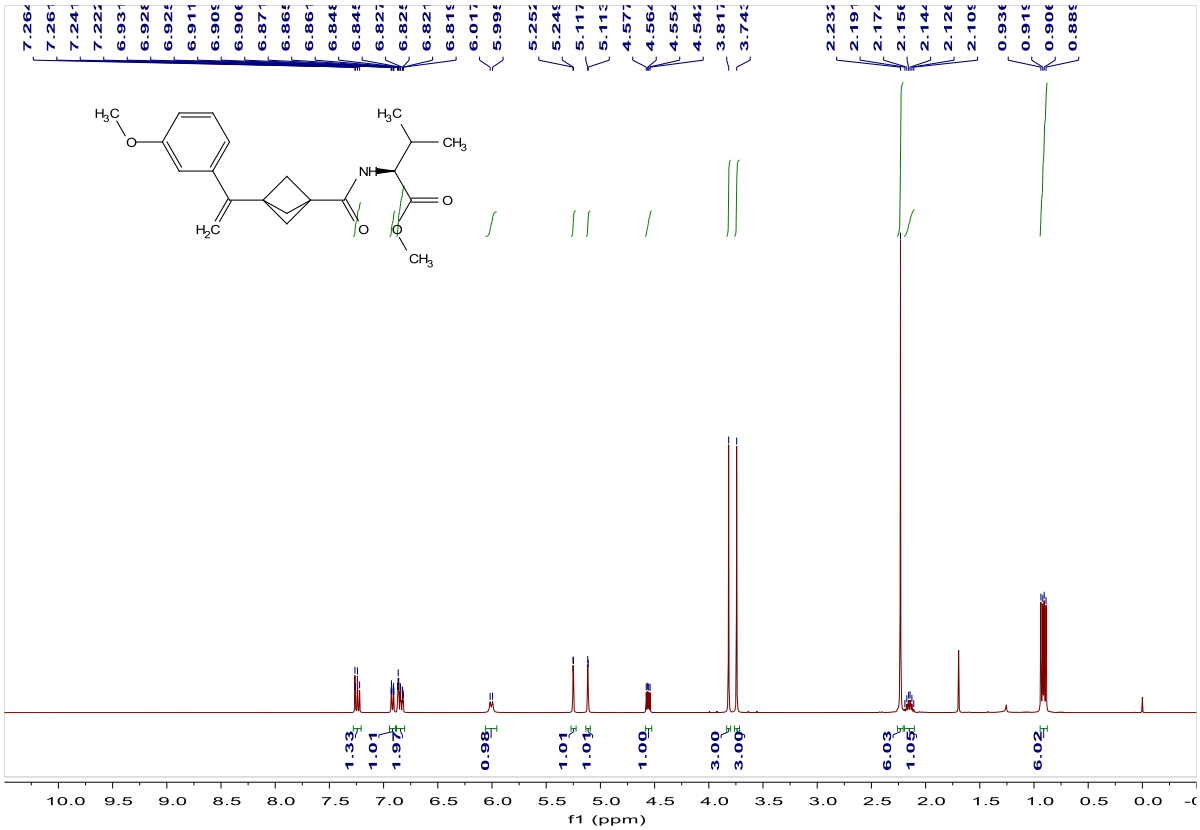
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1aa**



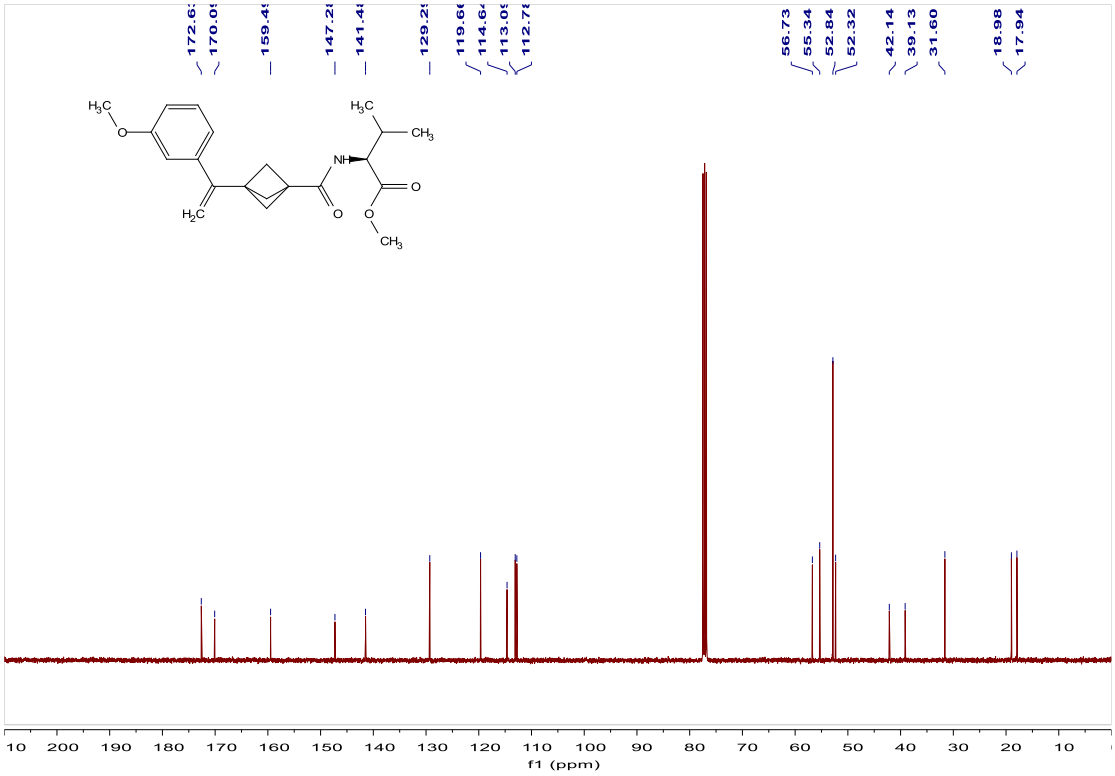
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1aa**



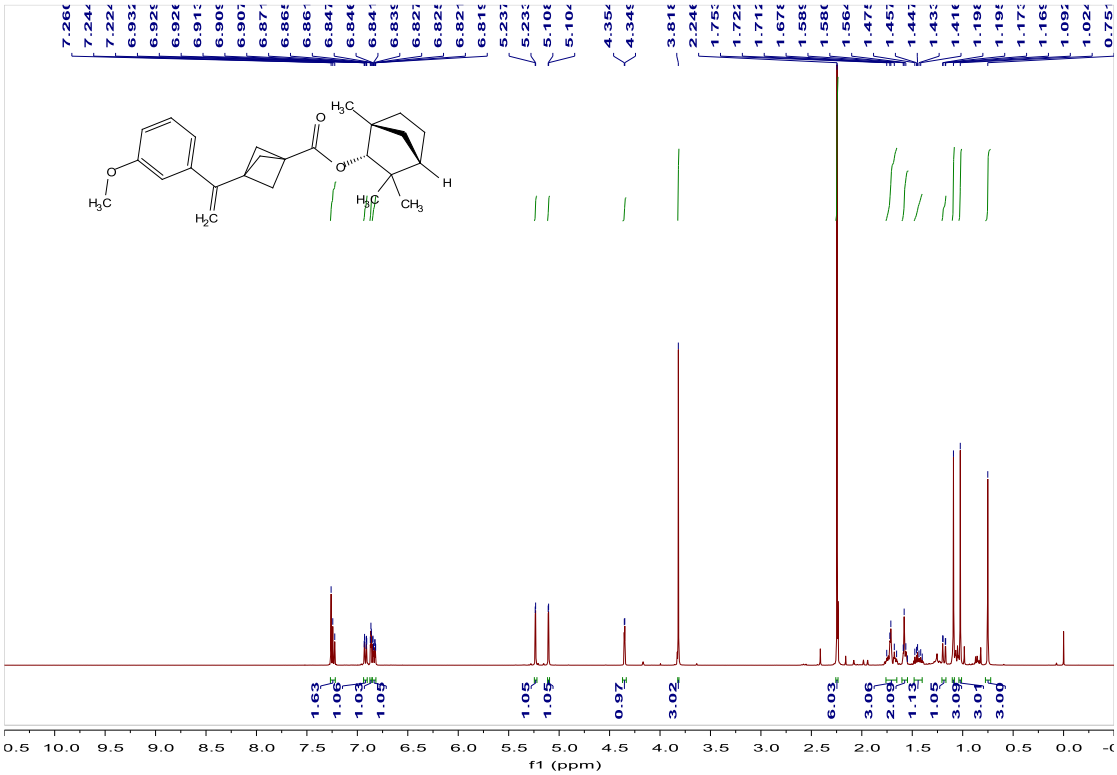
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ac**



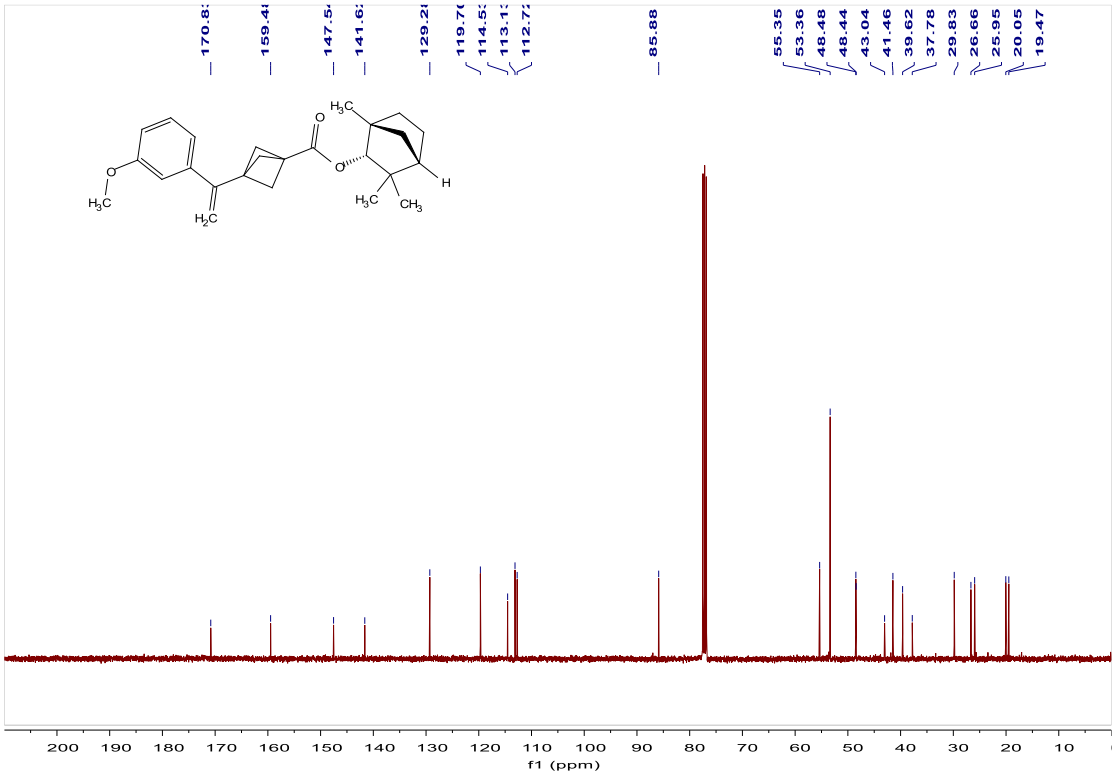
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ac**



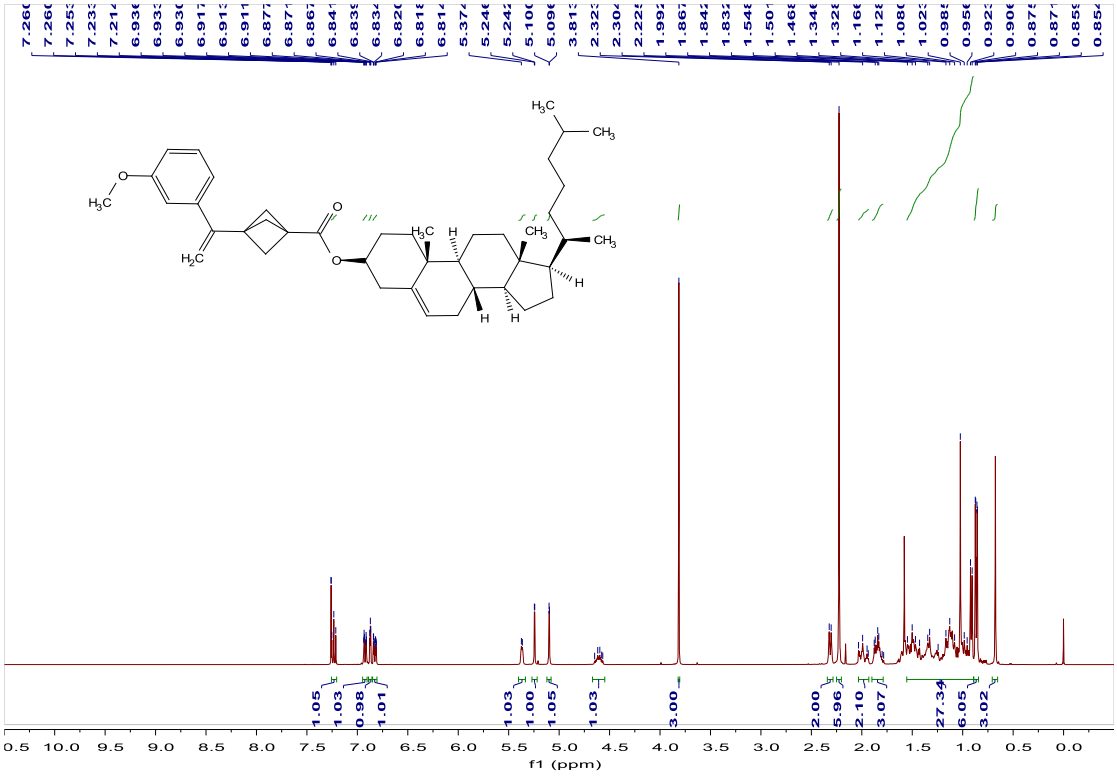
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ad**



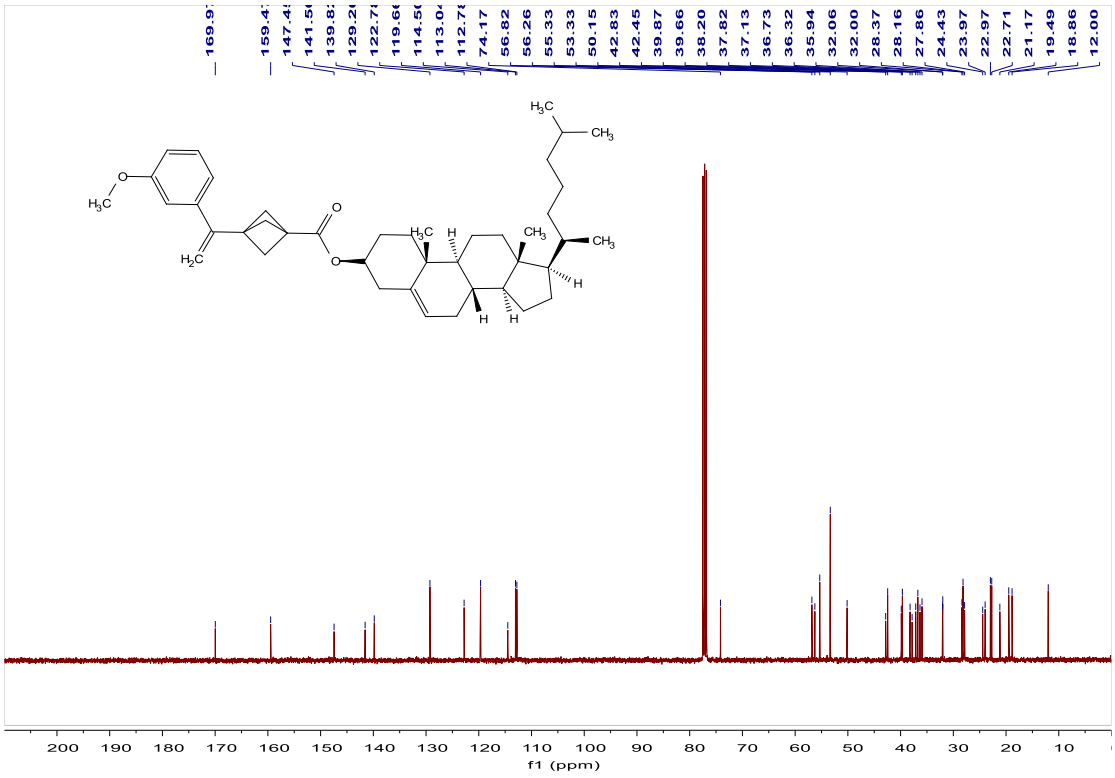
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ad**



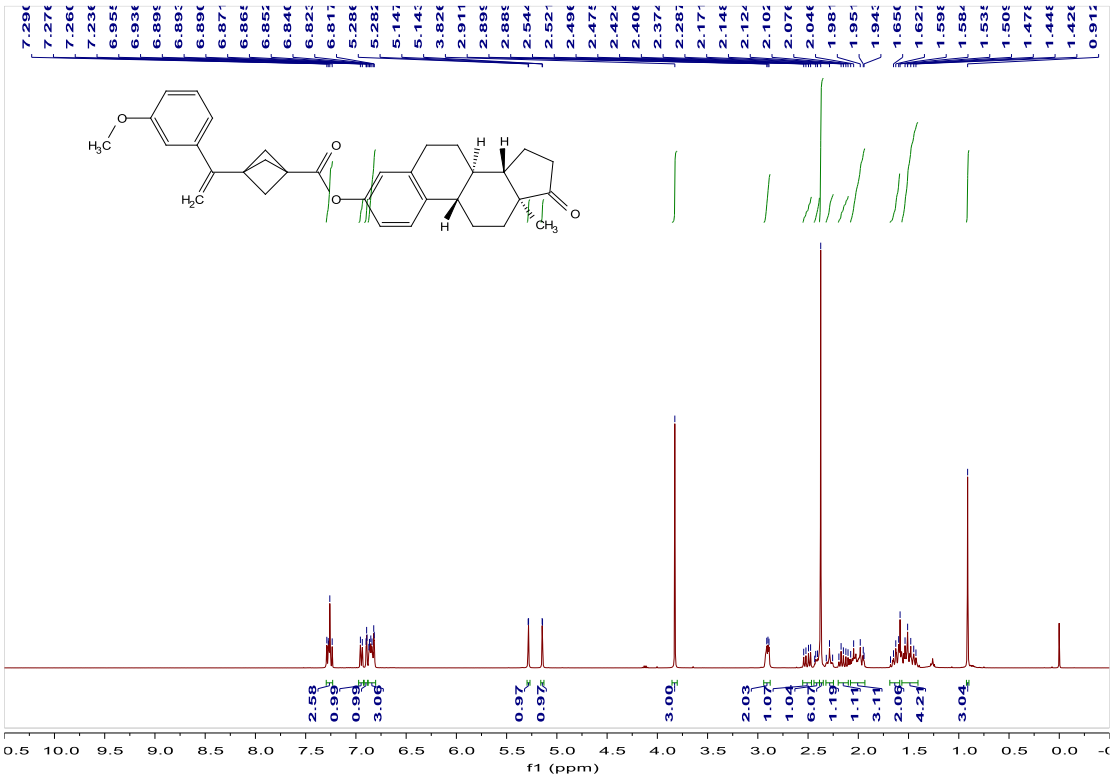
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ae**



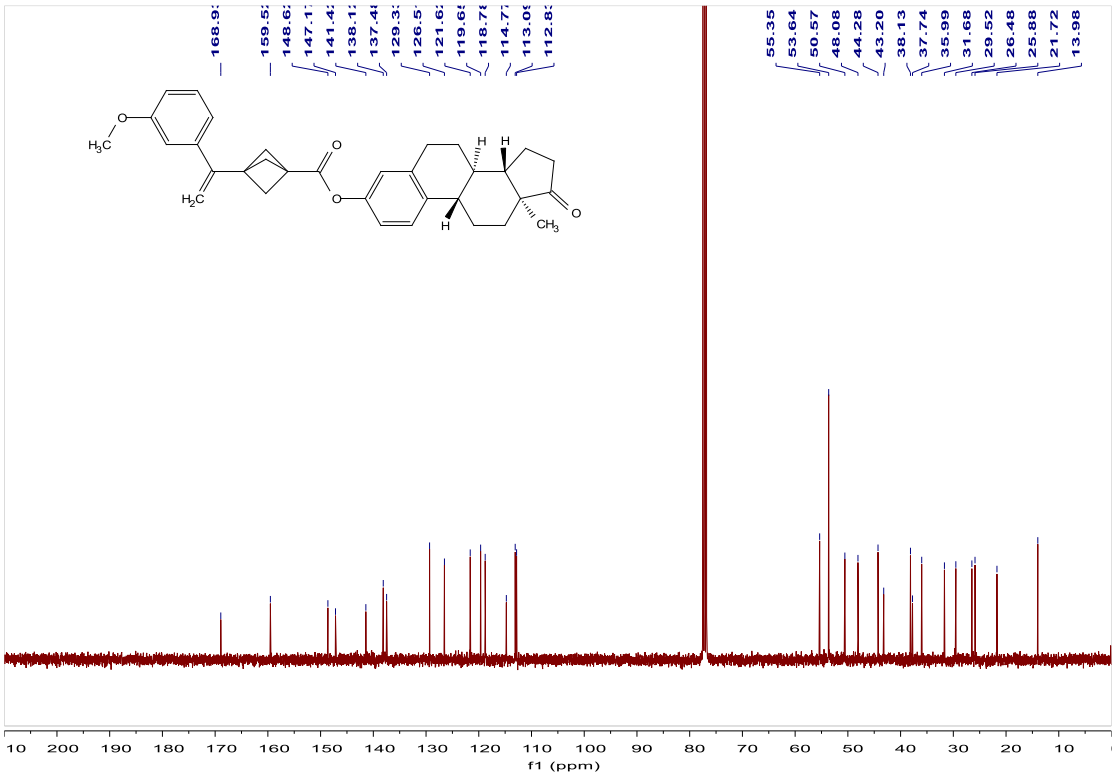
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ae**



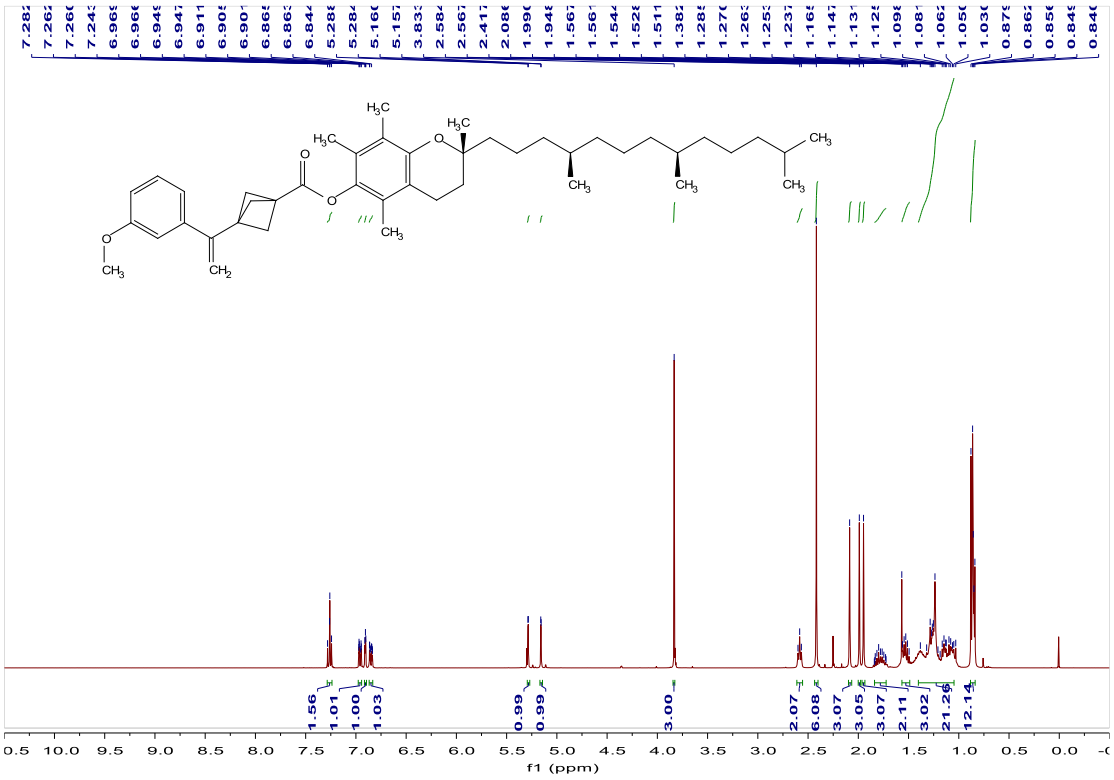
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1af**



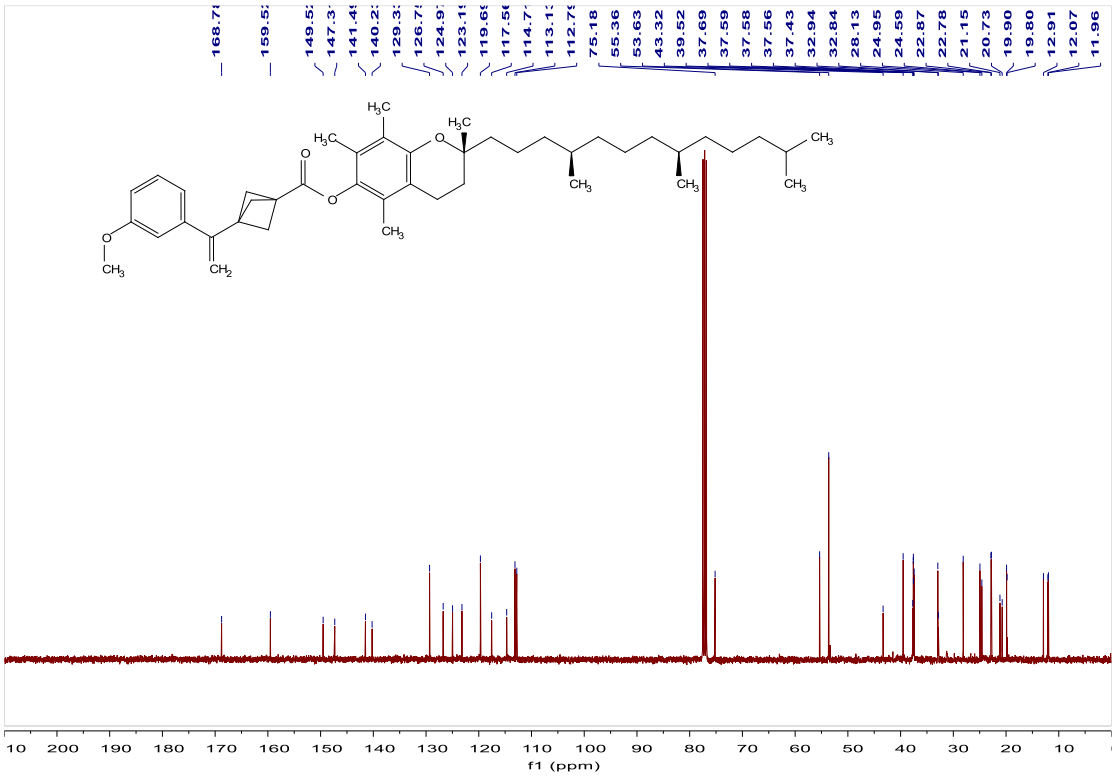
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1af**



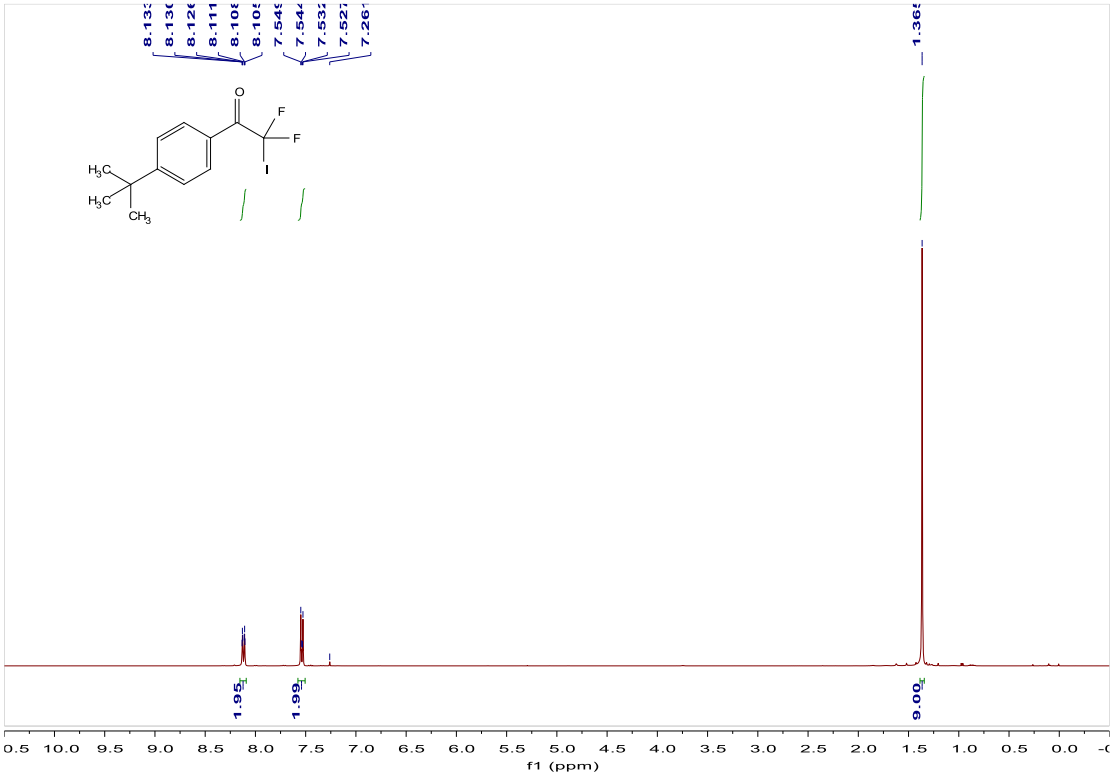
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1ag**



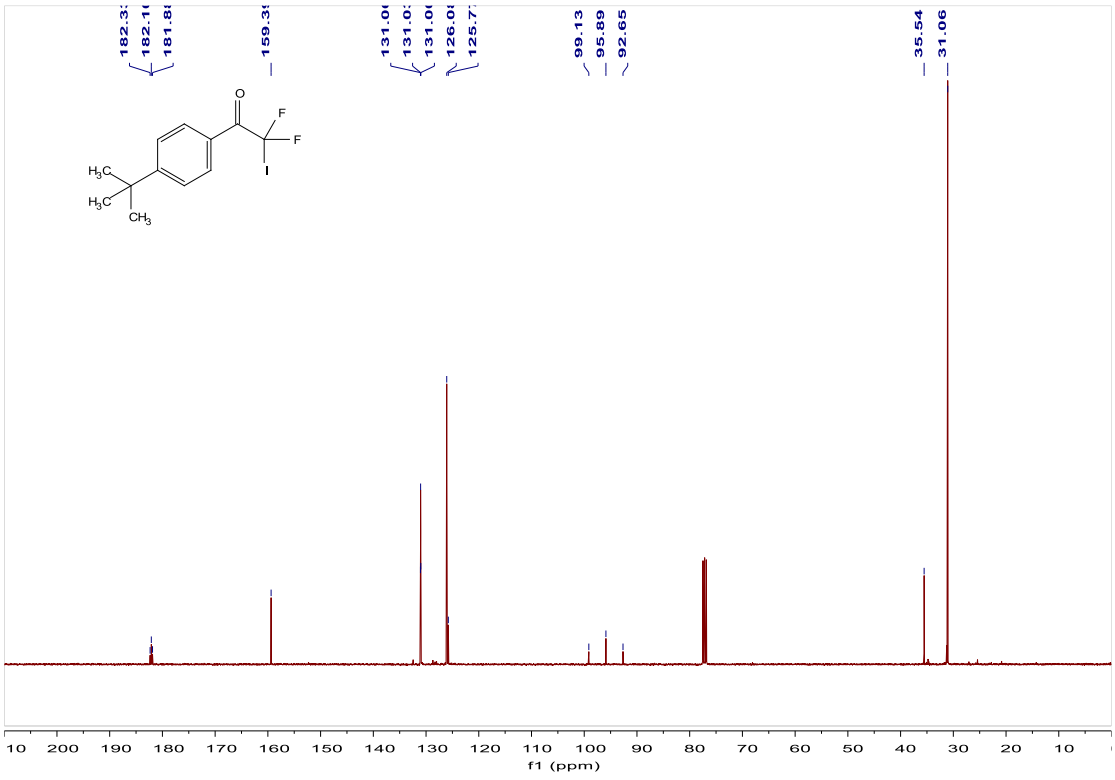
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1ag**



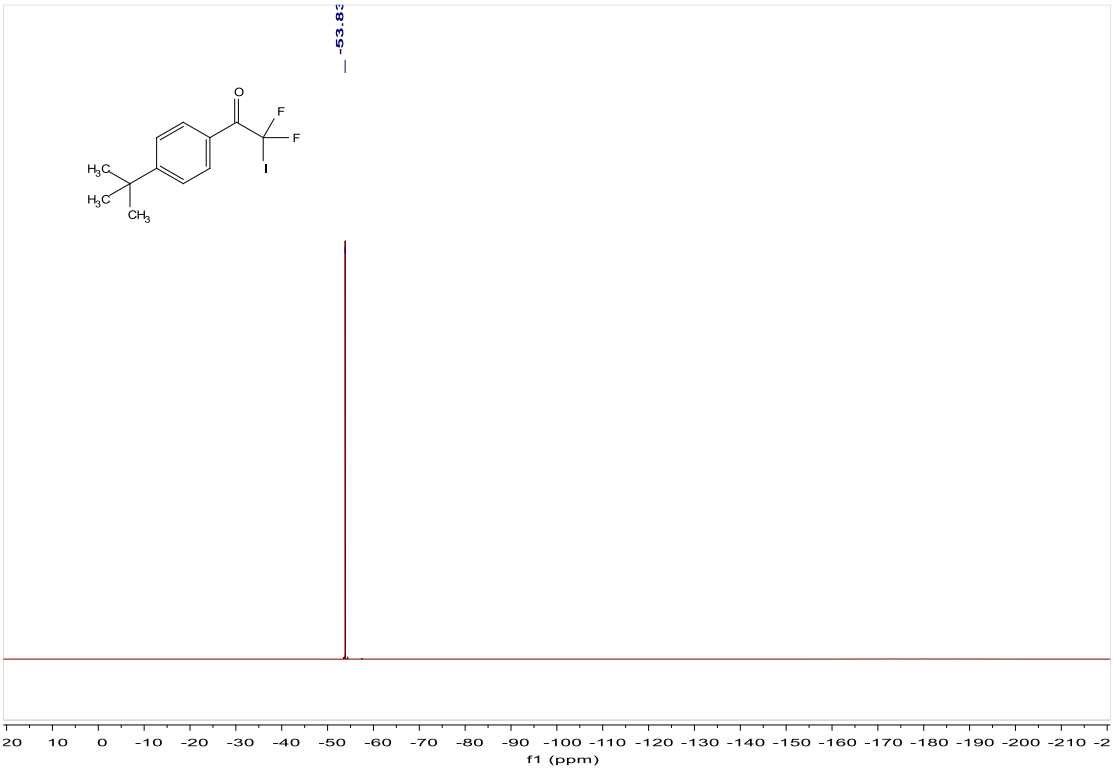
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2i**



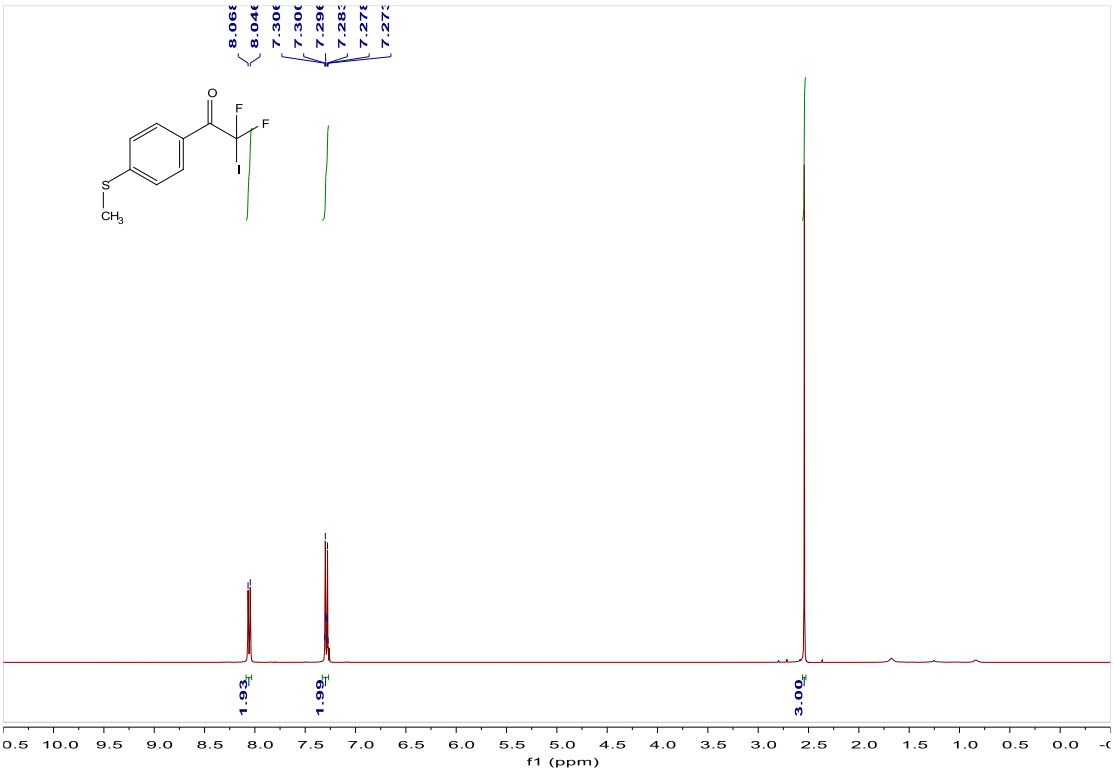
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2i**



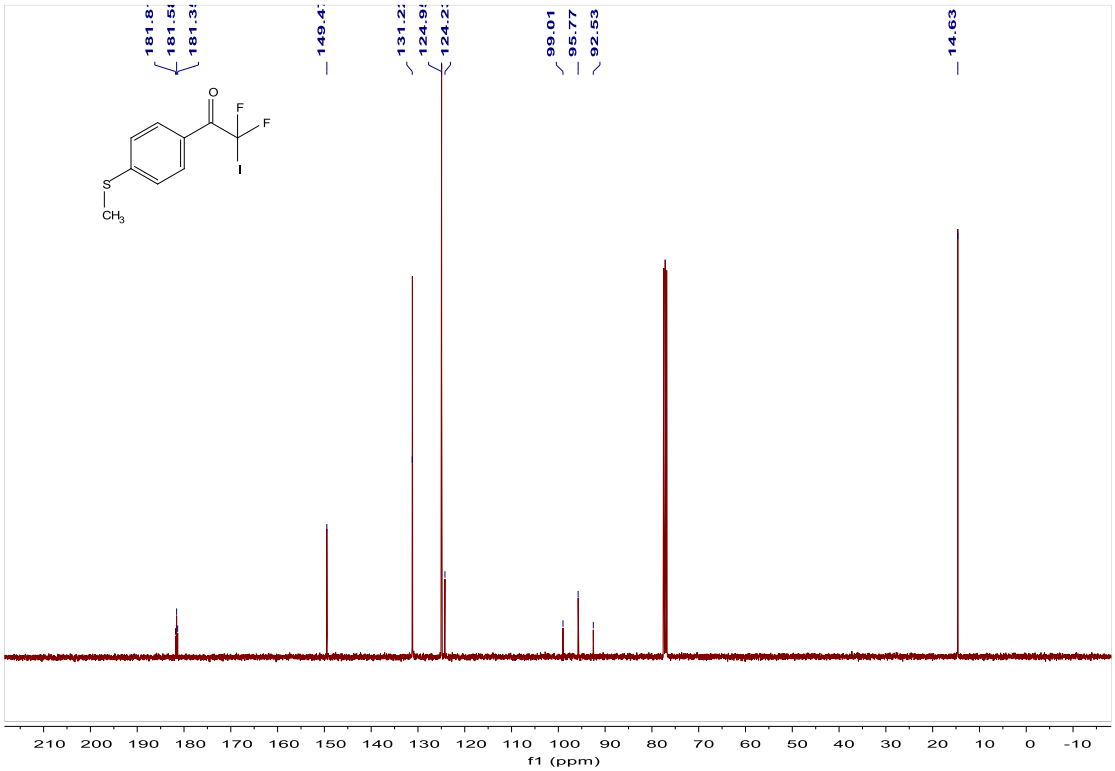
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2i**



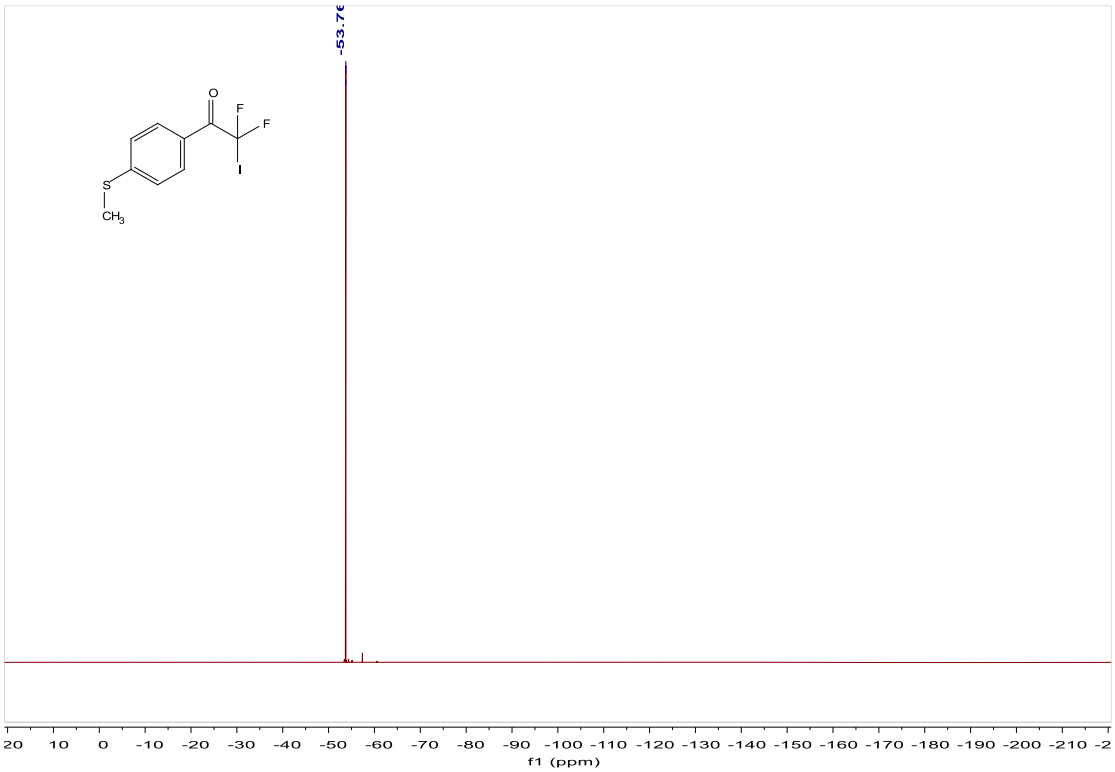
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2k**



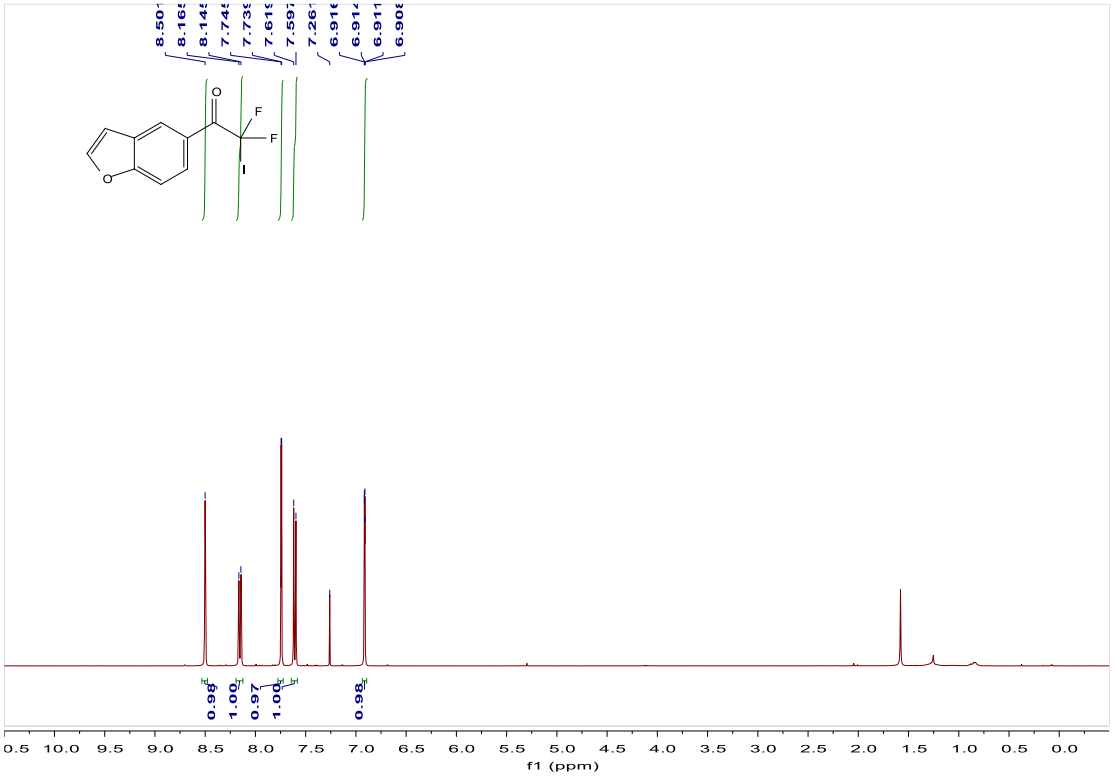
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2k**



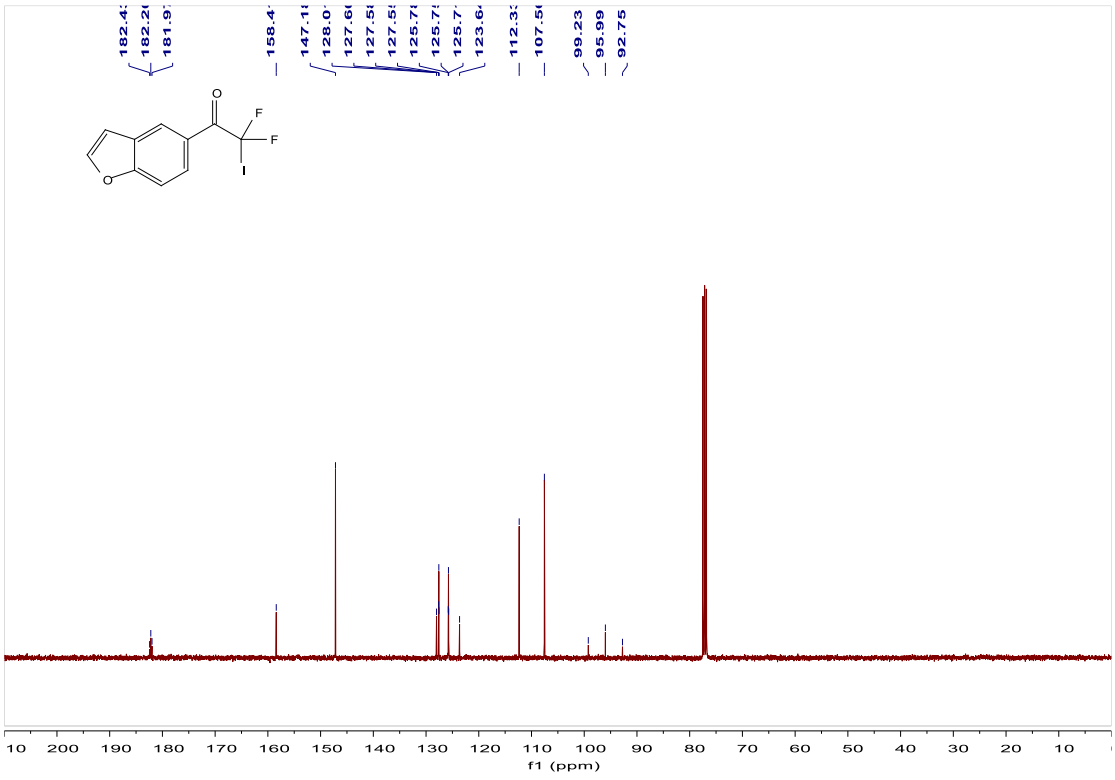
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2k**



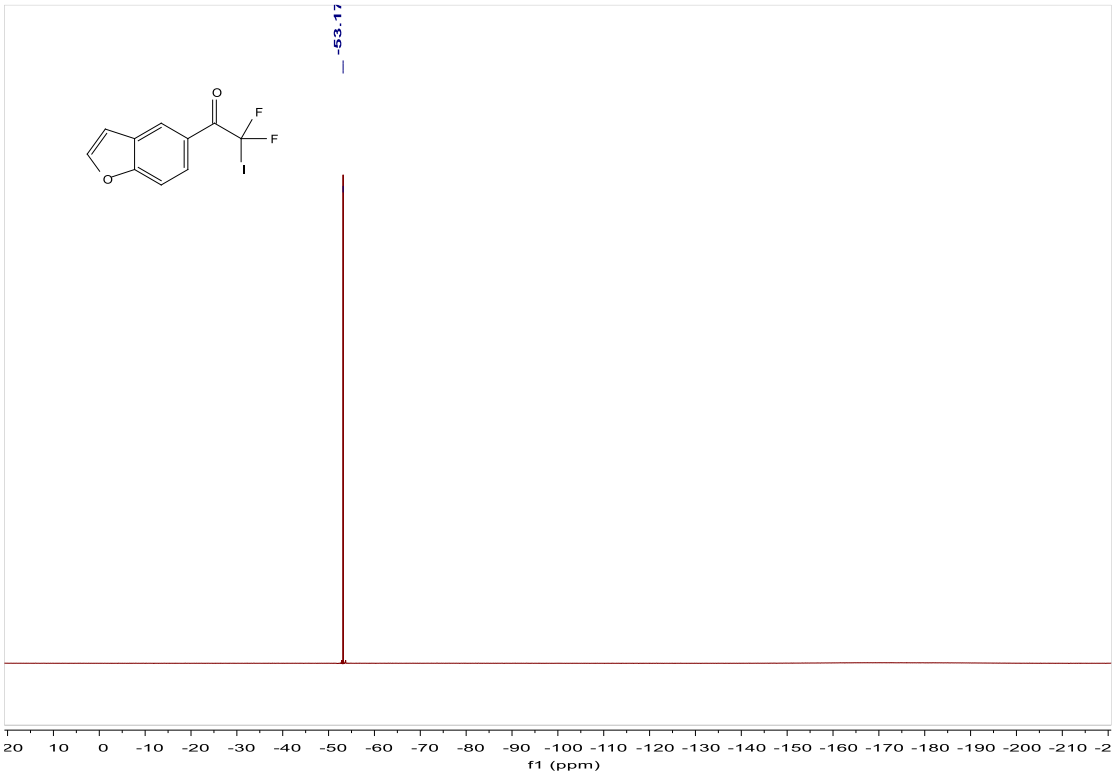
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2p**



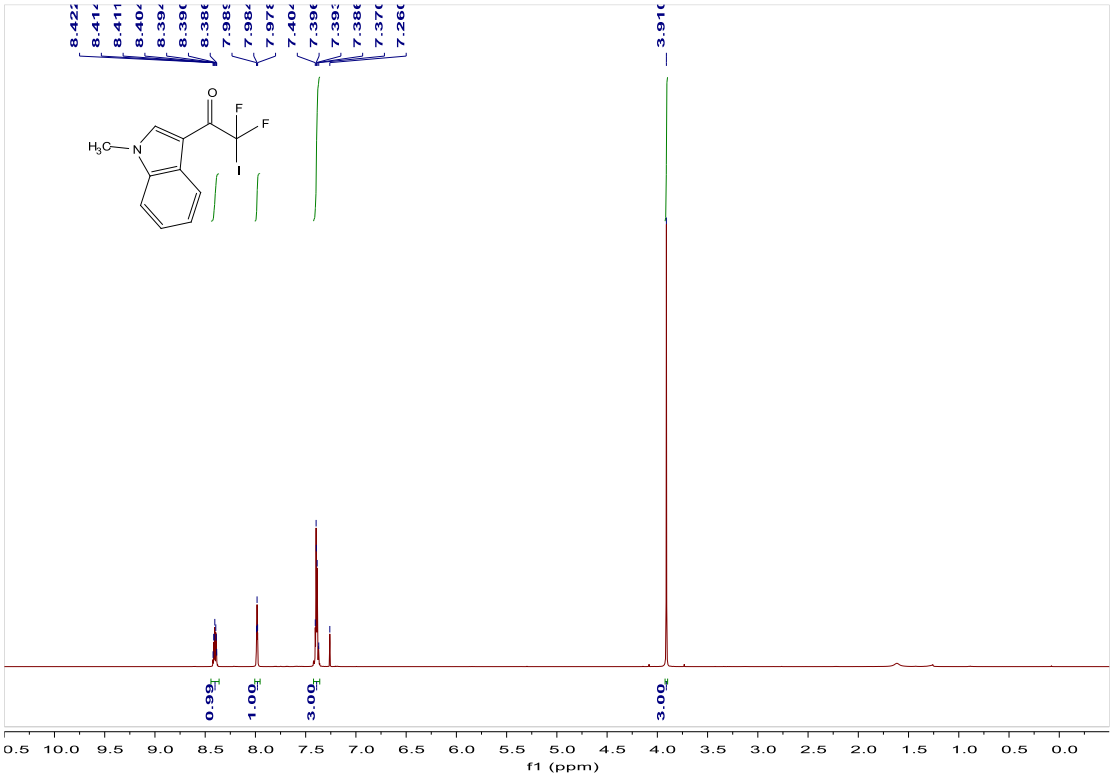
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2p**



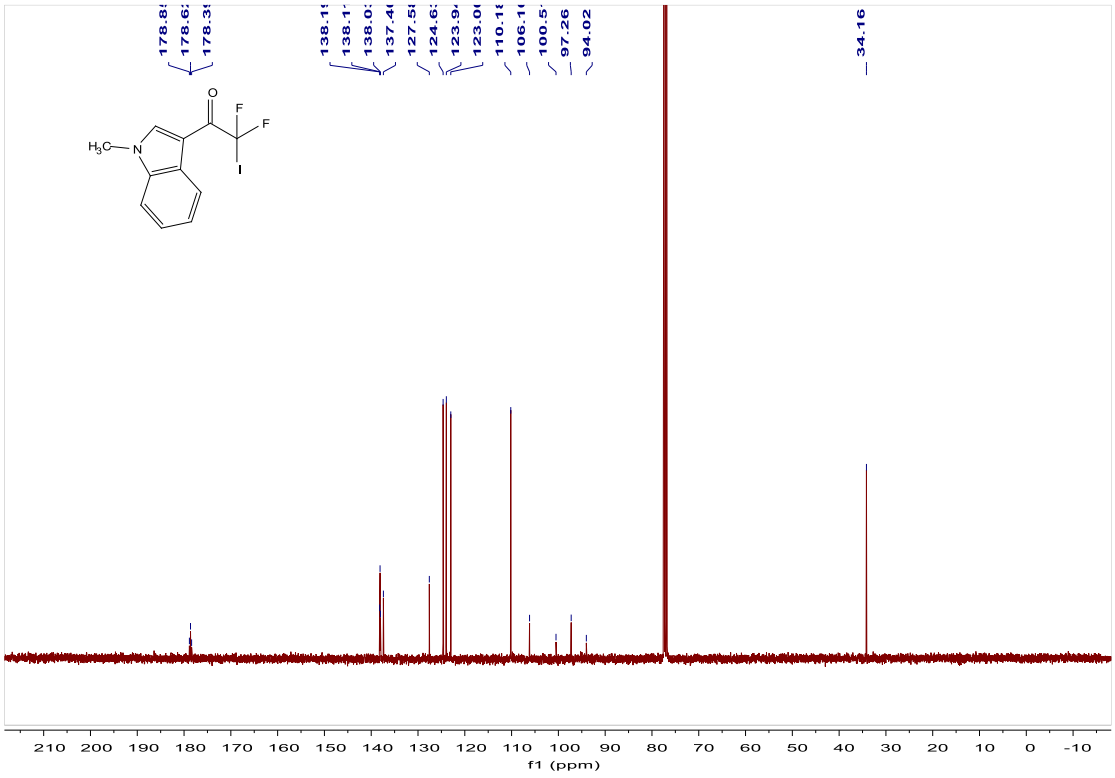
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2p**



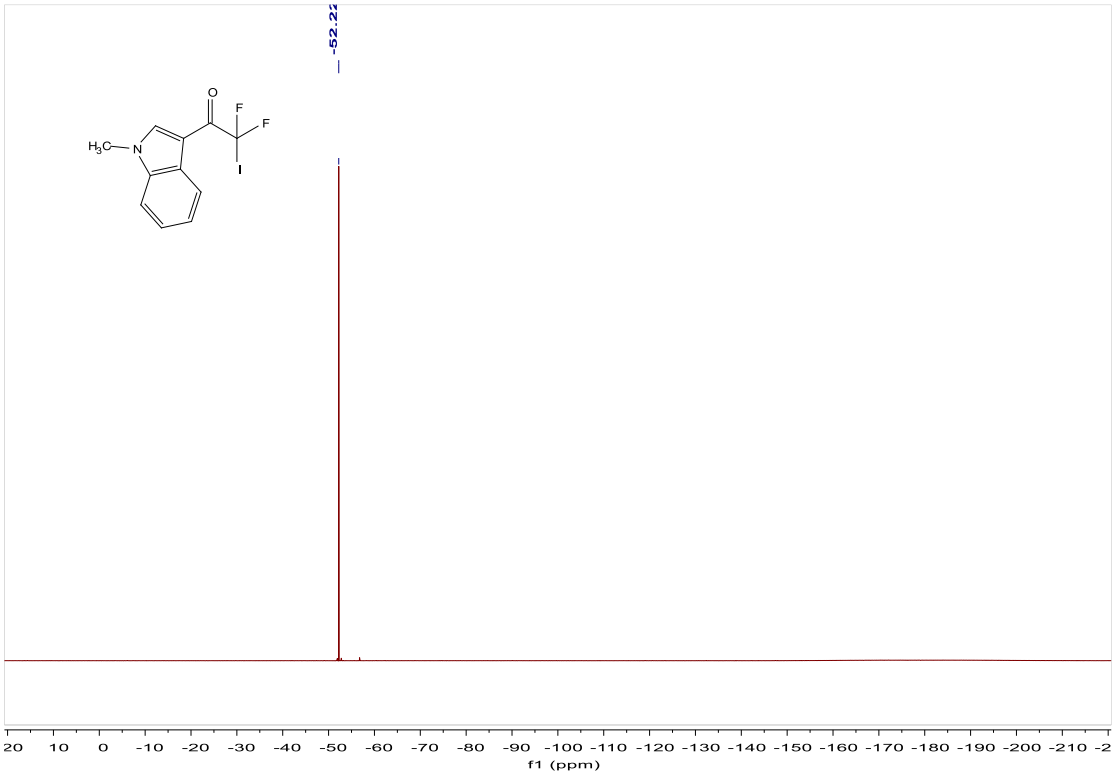
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2r**



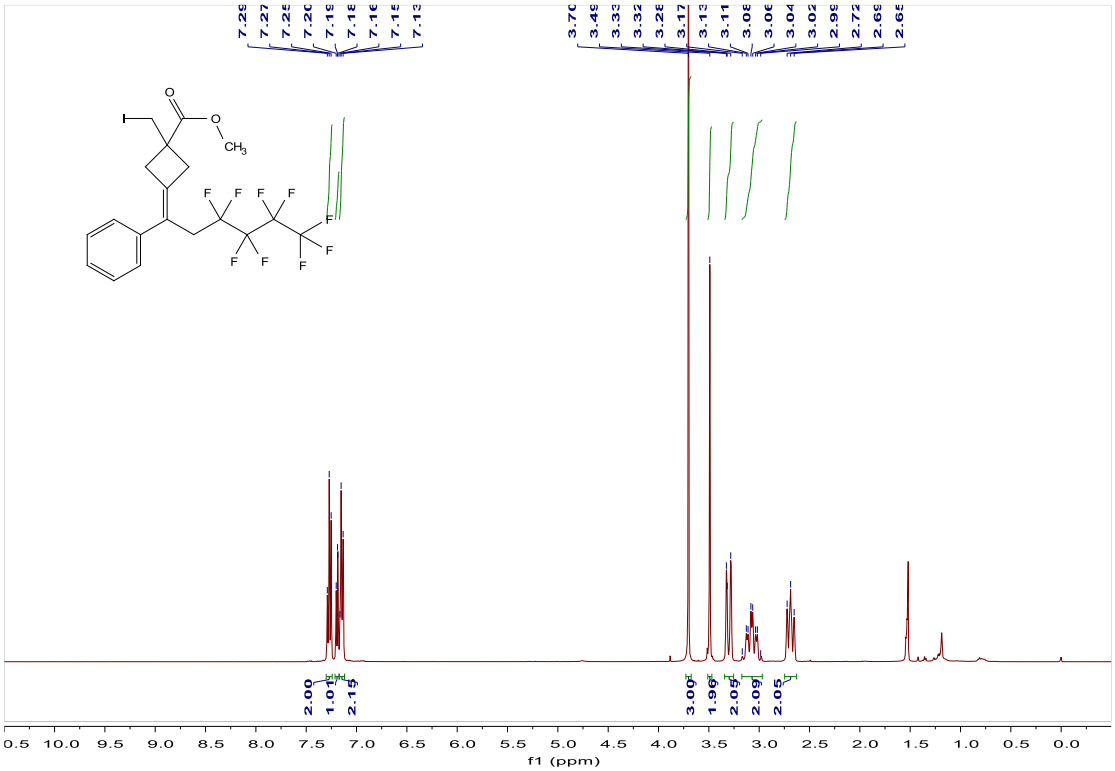
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2r**



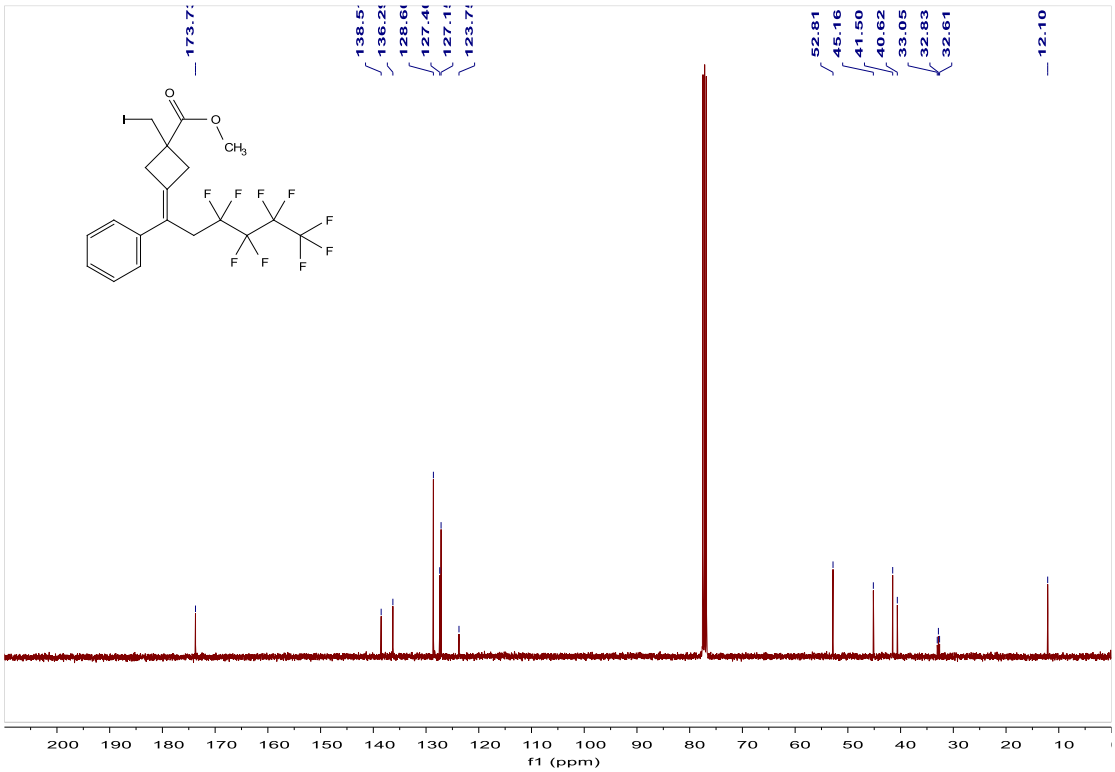
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2r**



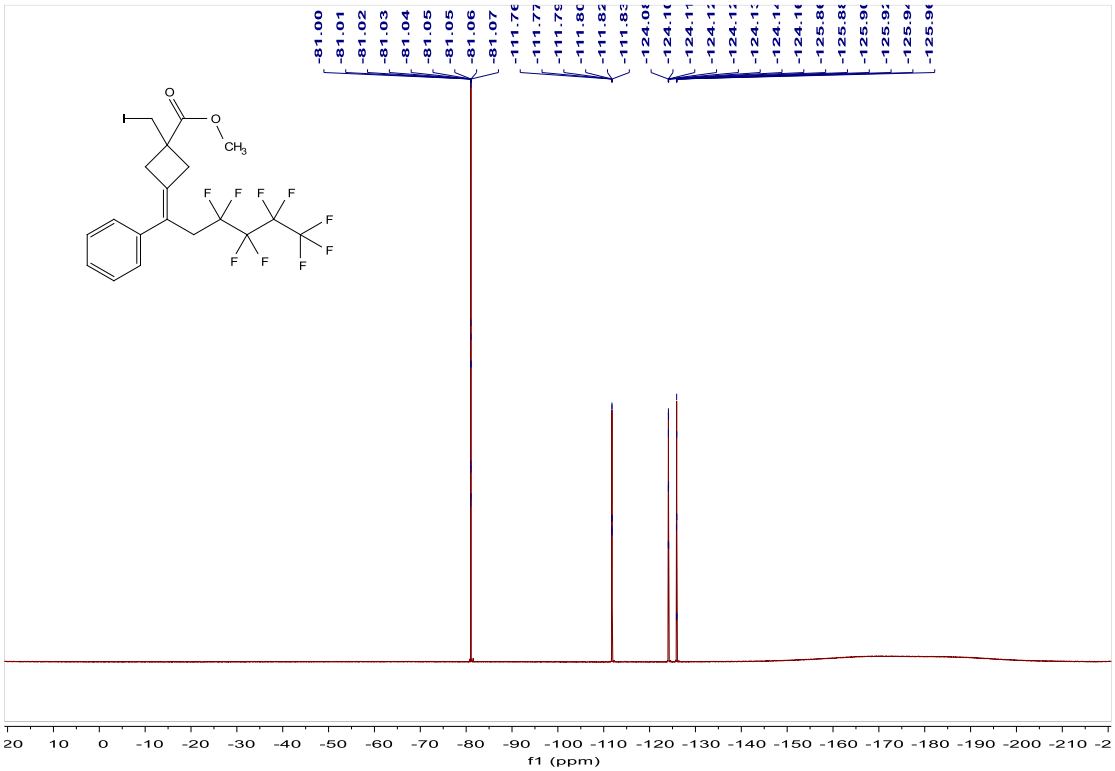
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**



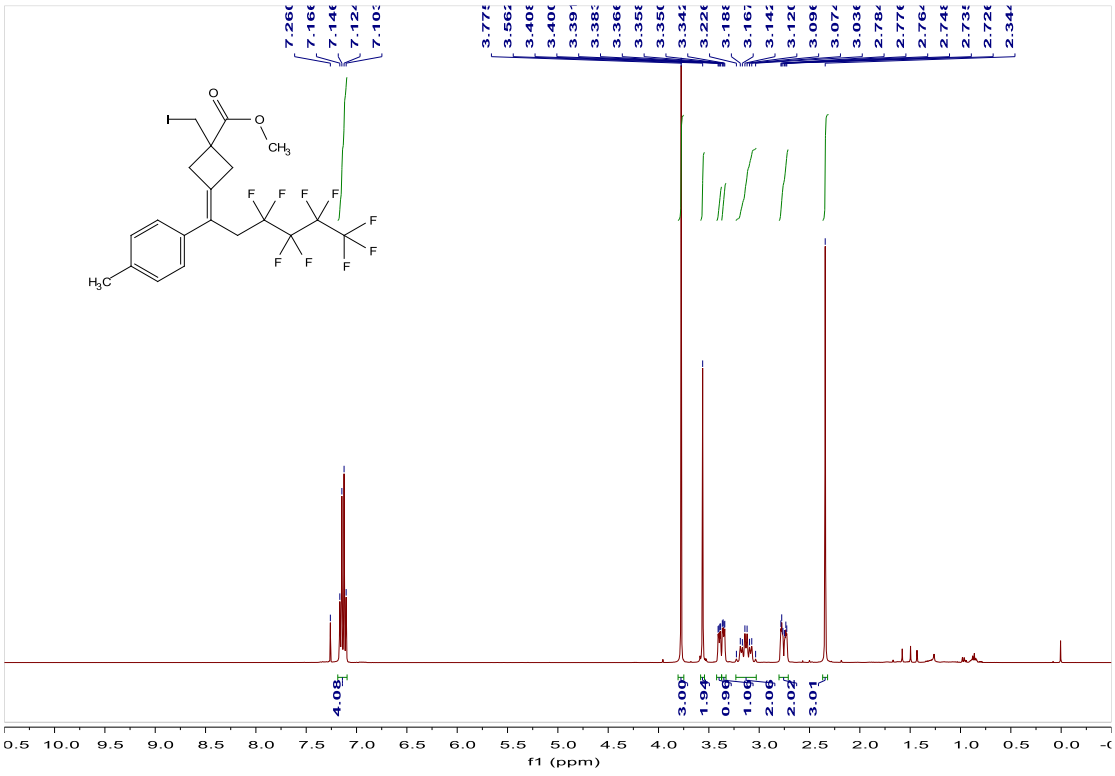
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**



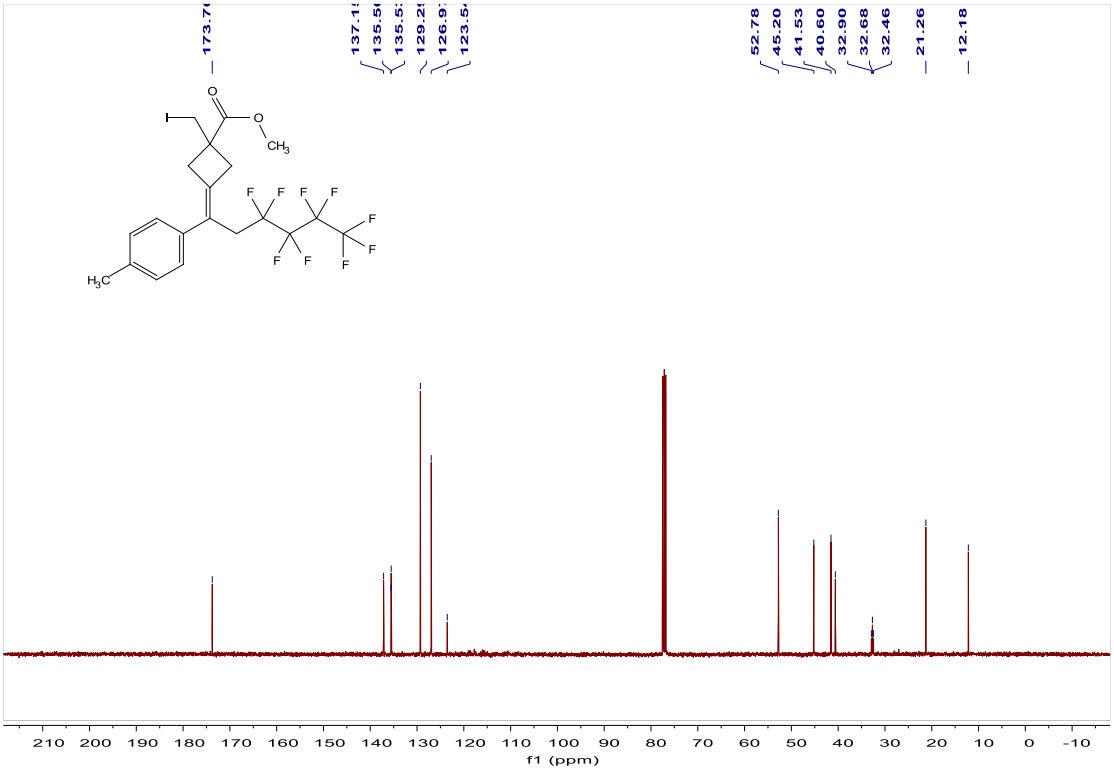
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **3**



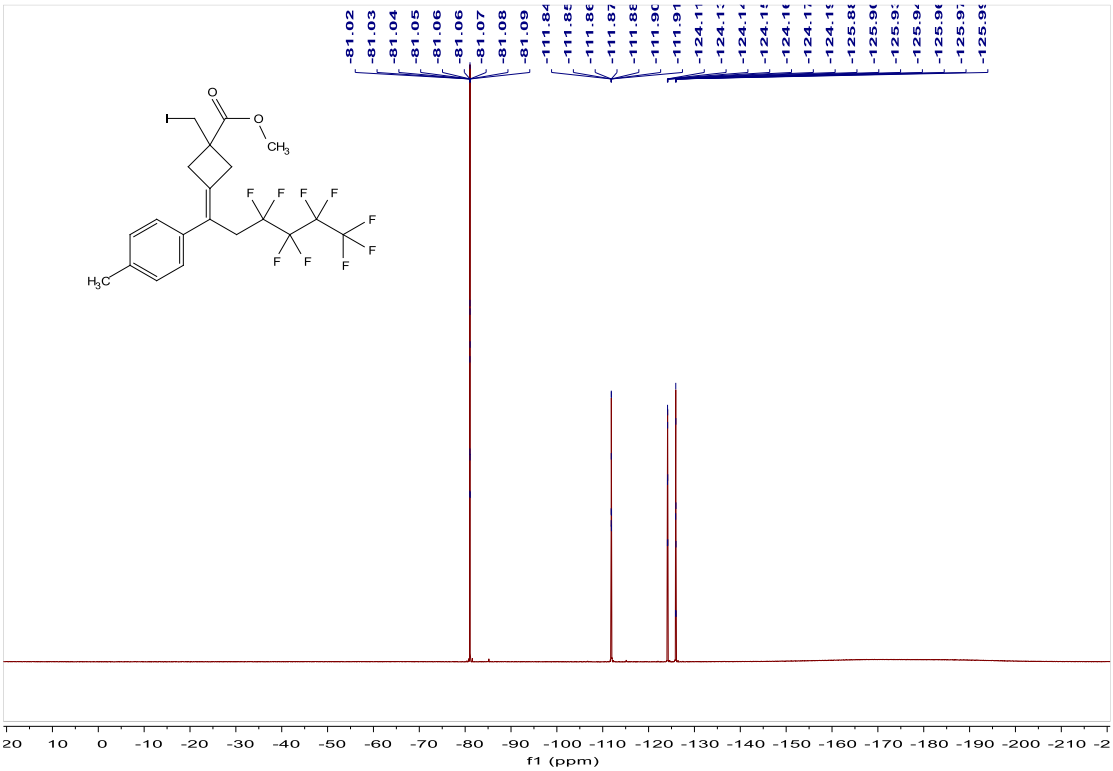
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**



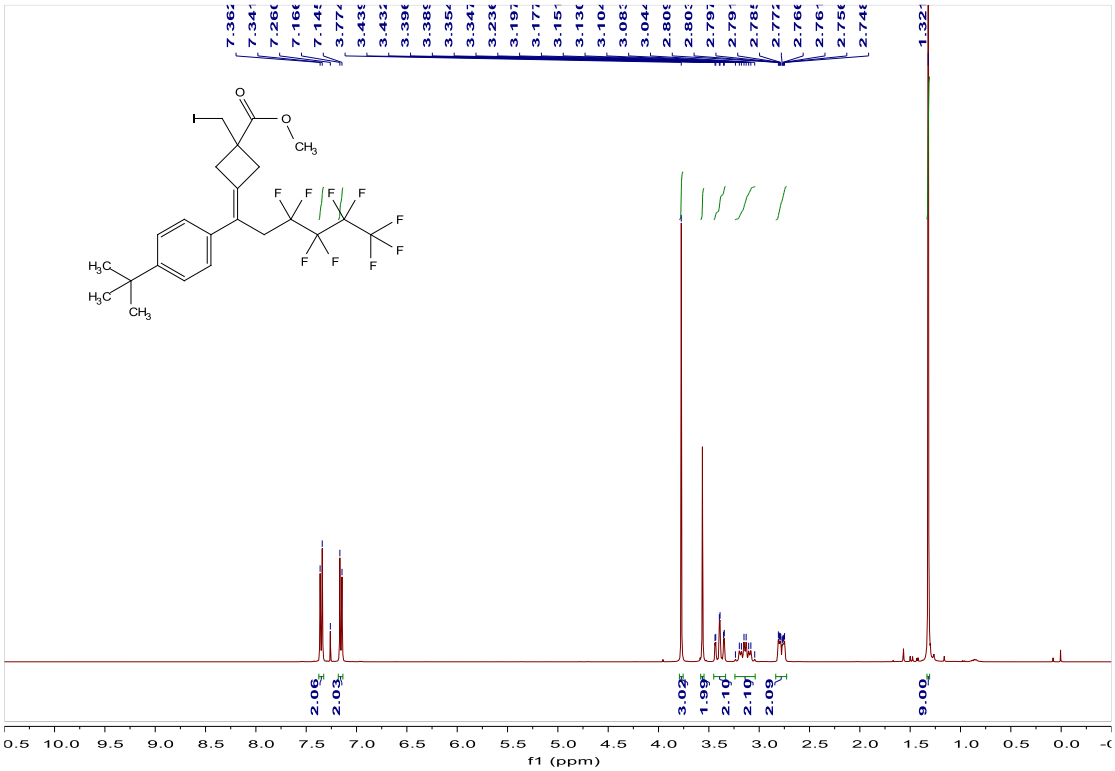
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4**



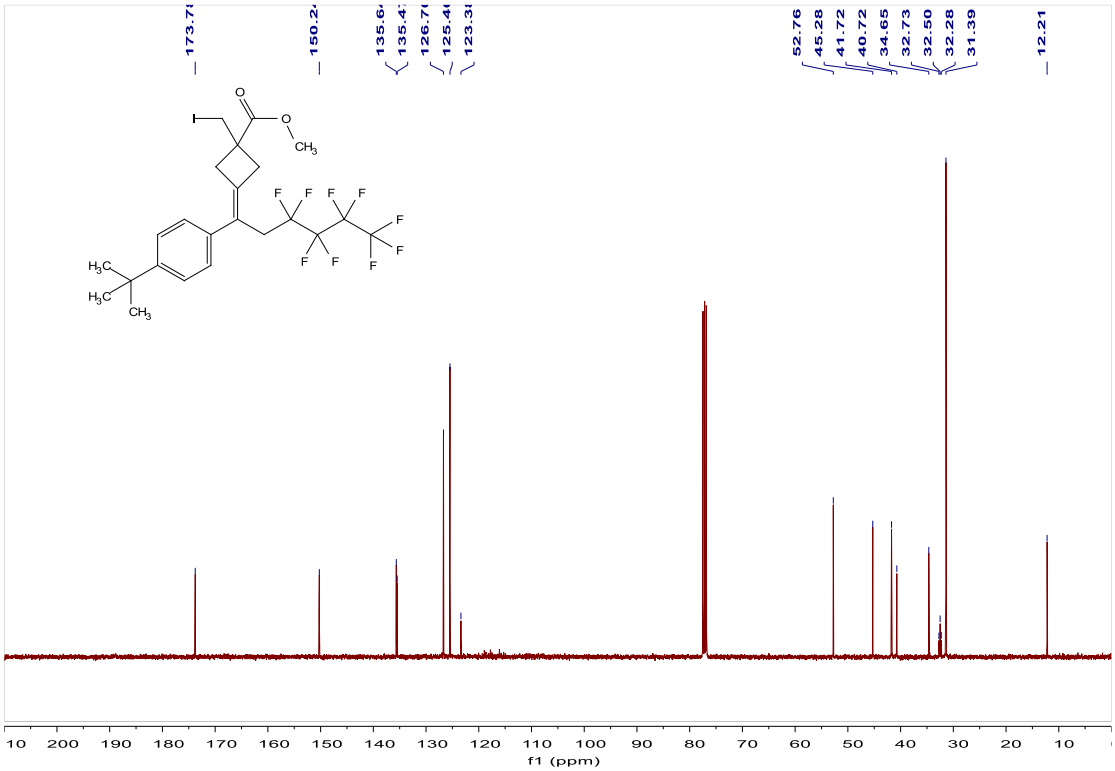
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4**



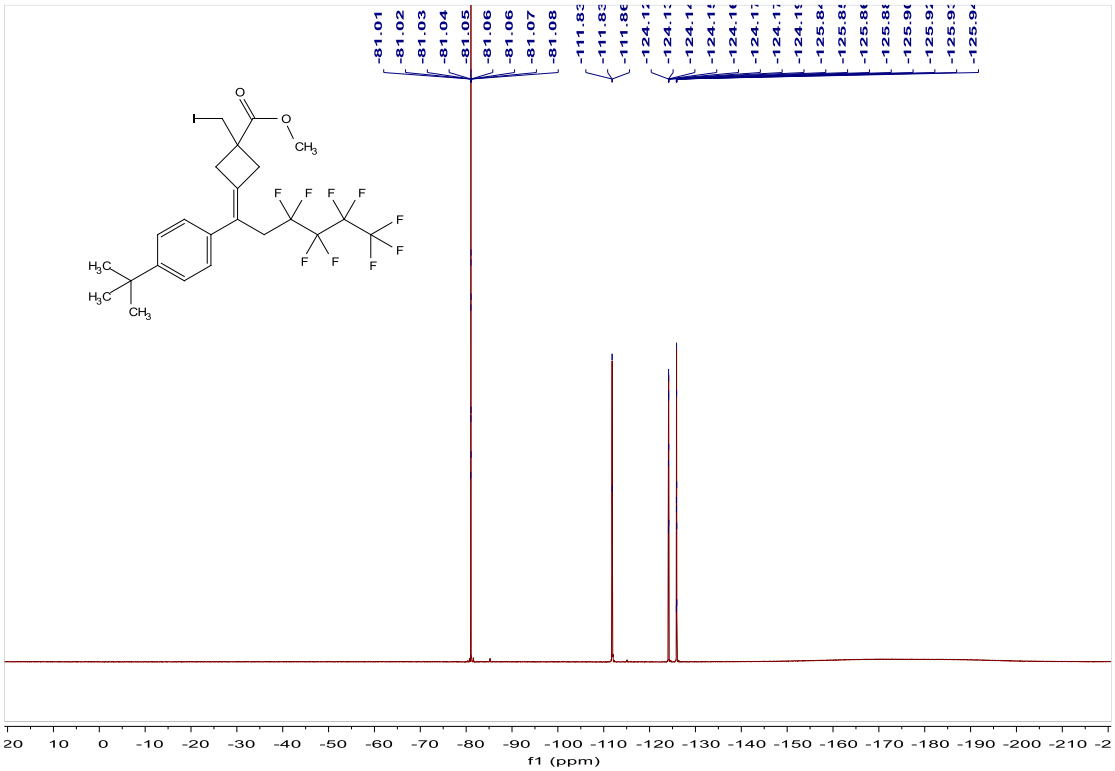
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**



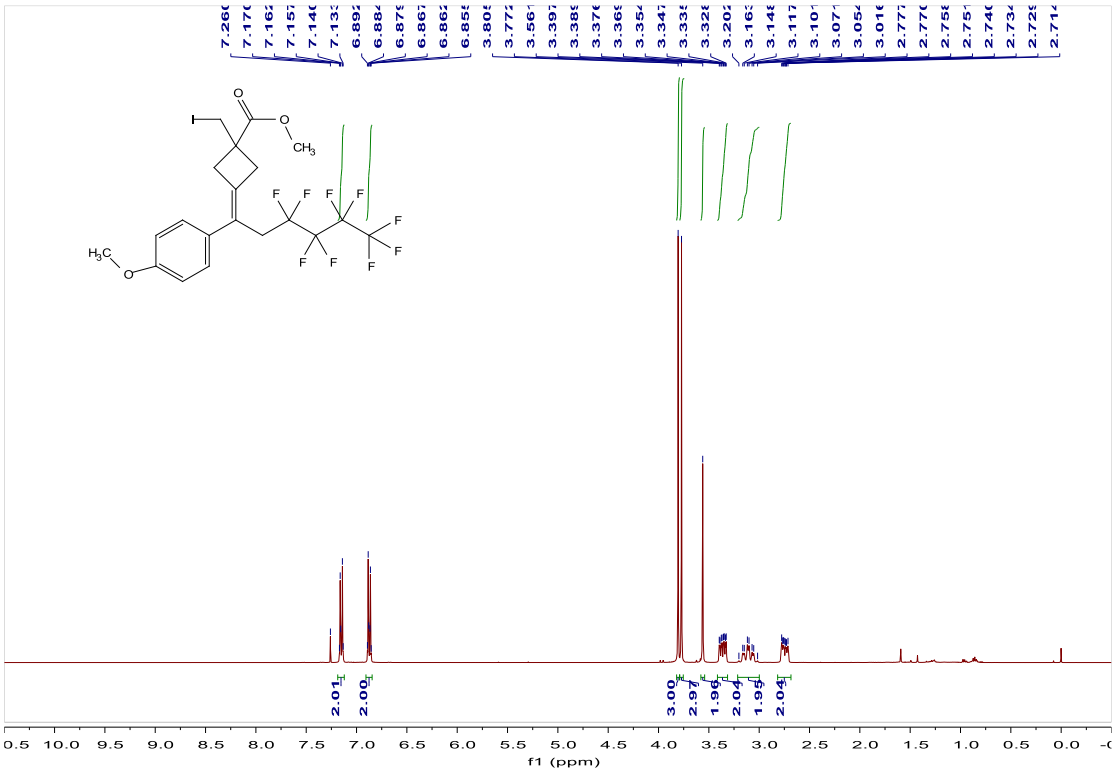
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5**



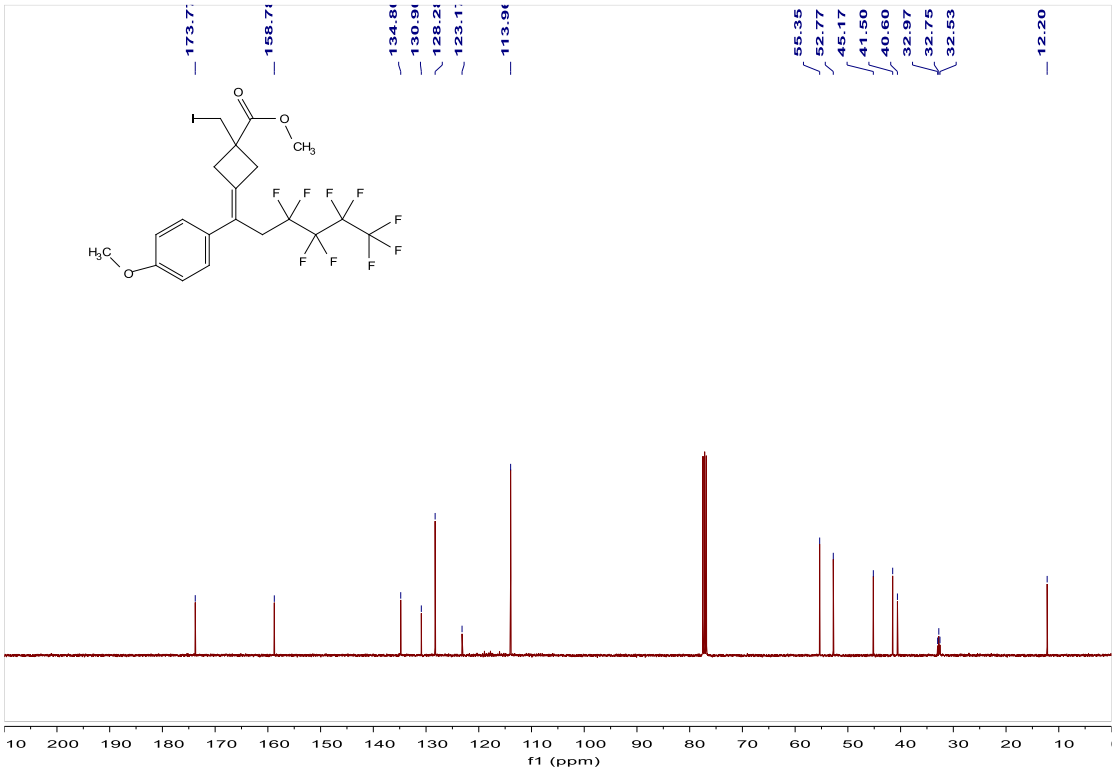
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5**



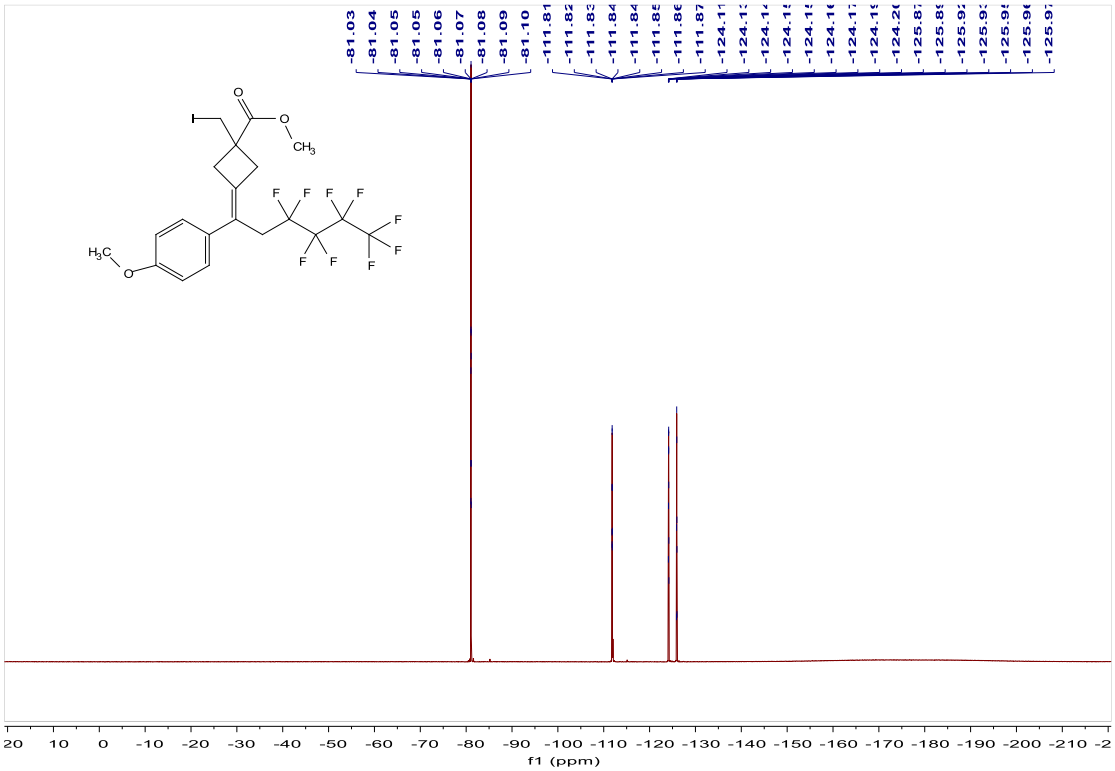
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**



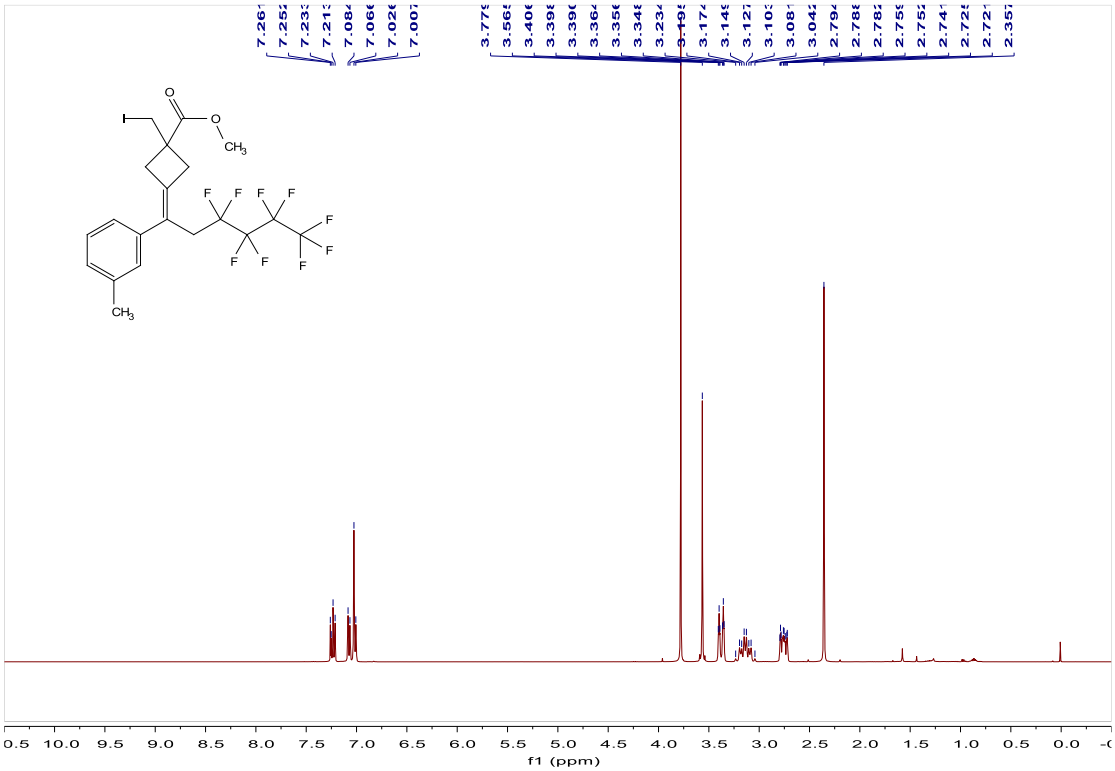
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6**



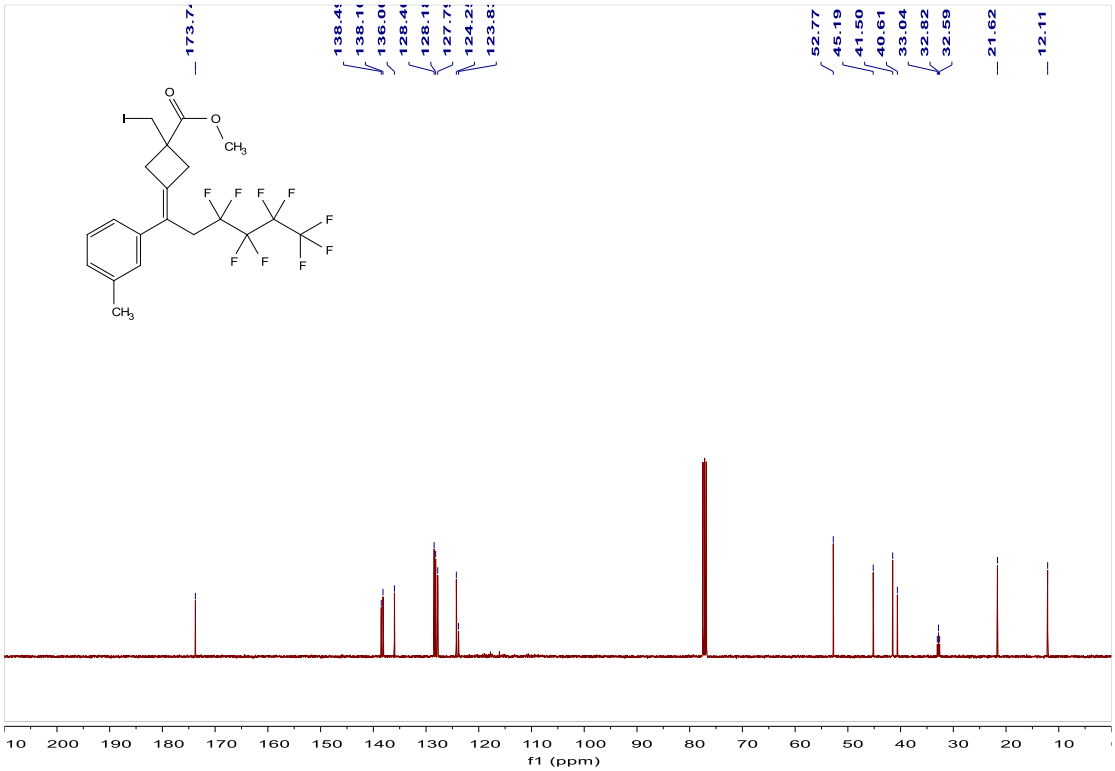
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **6**



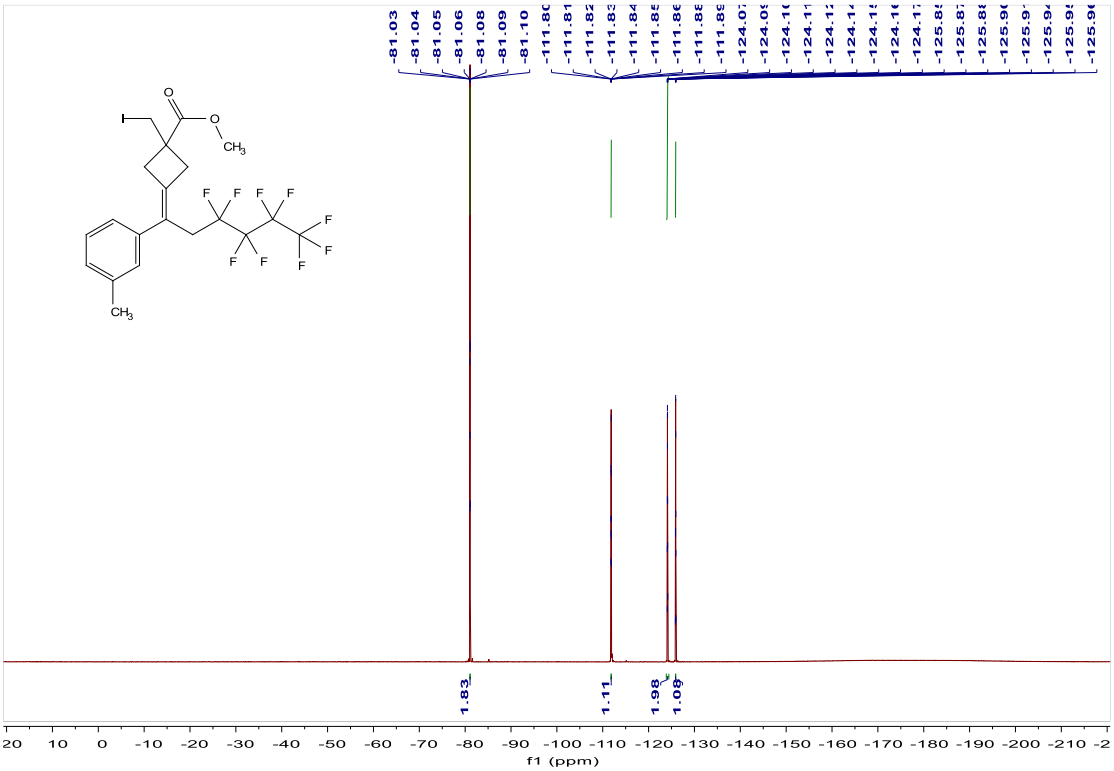
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**



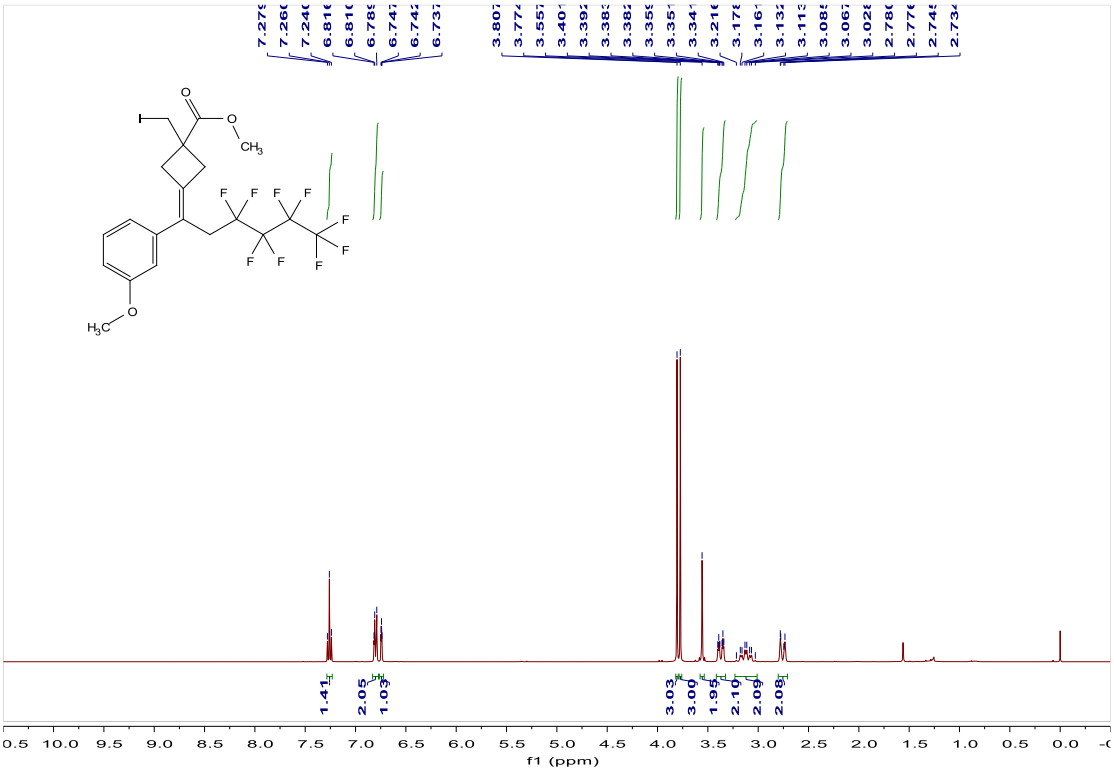
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7**



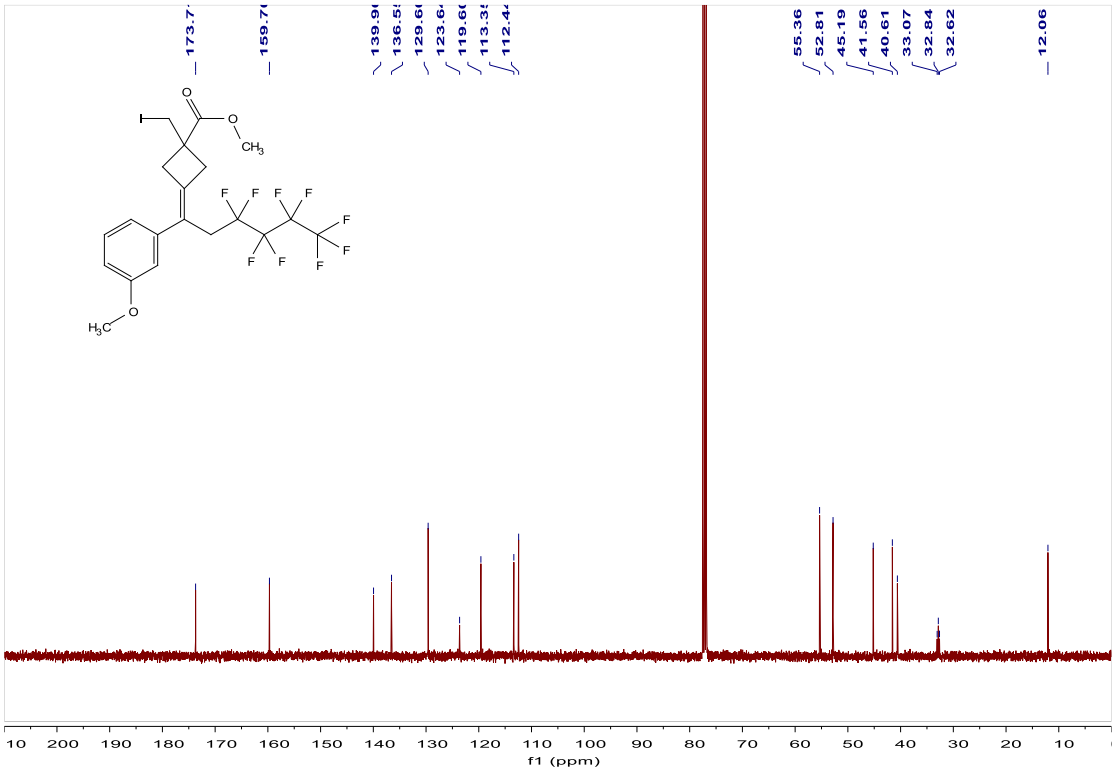
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **7**



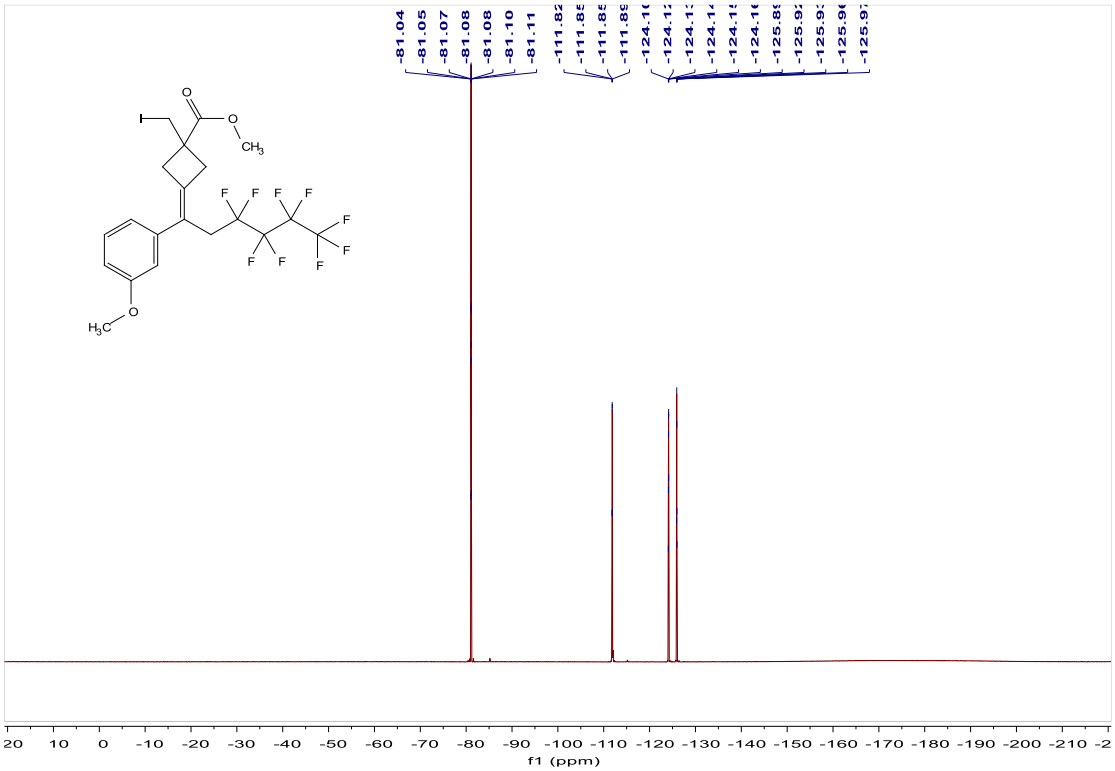
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**



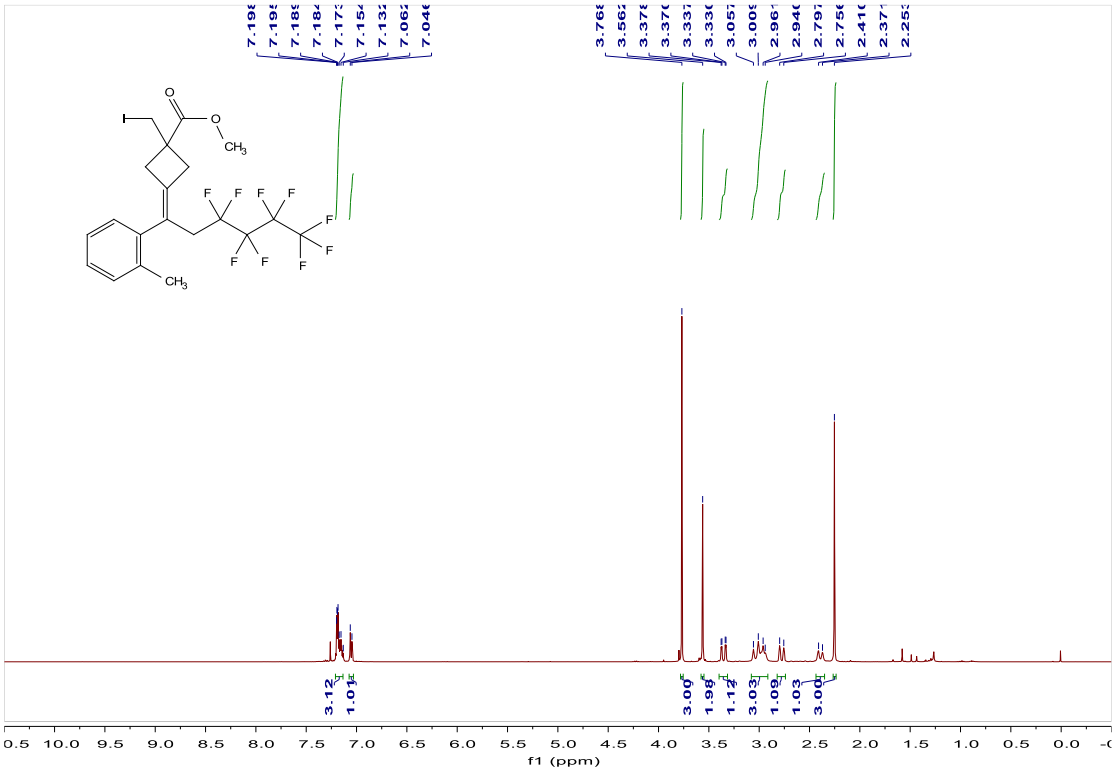
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8**



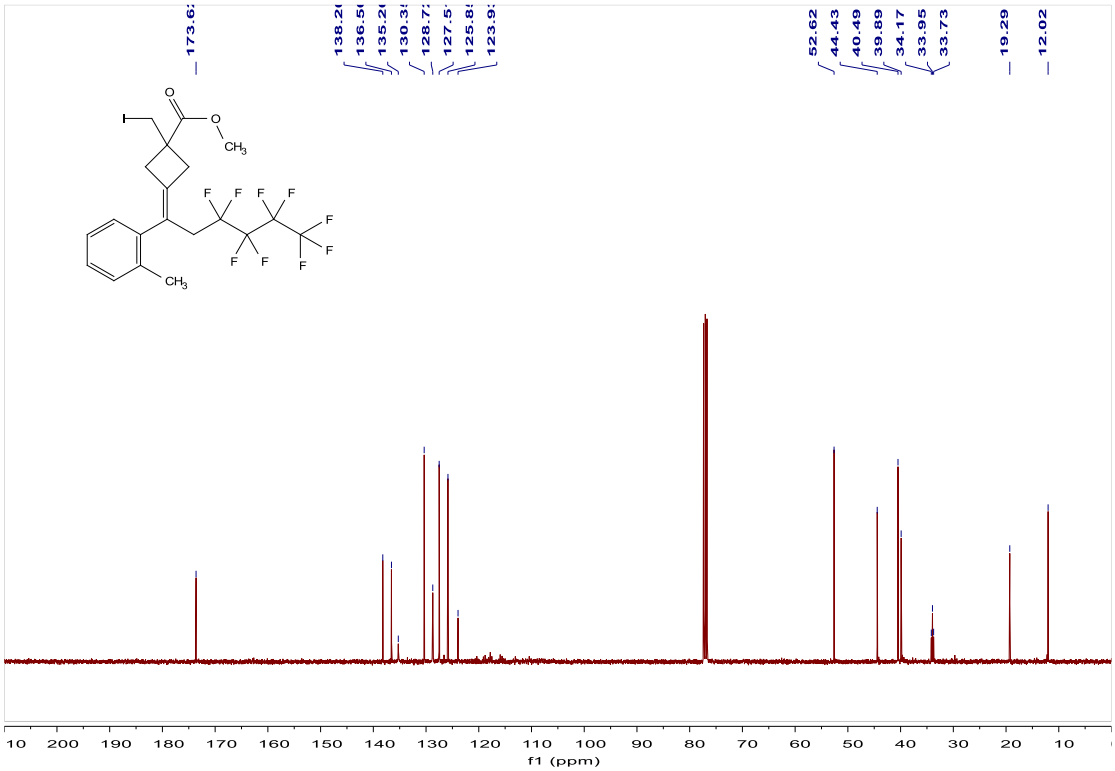
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **8**



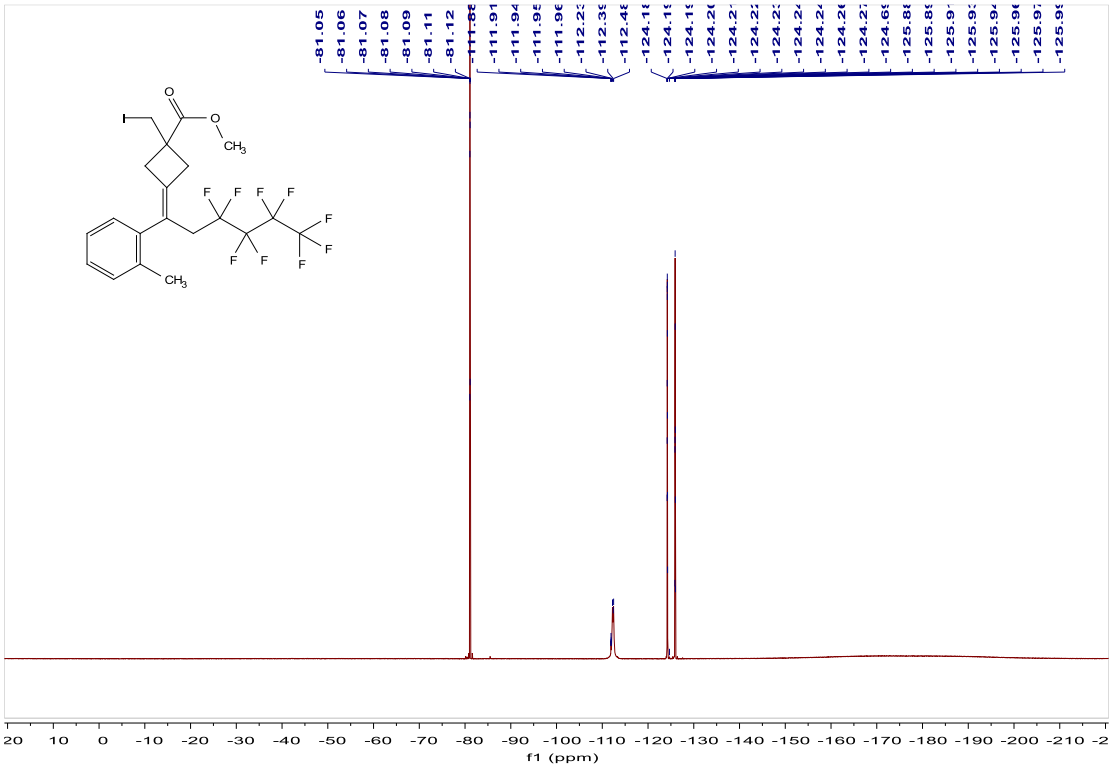
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**



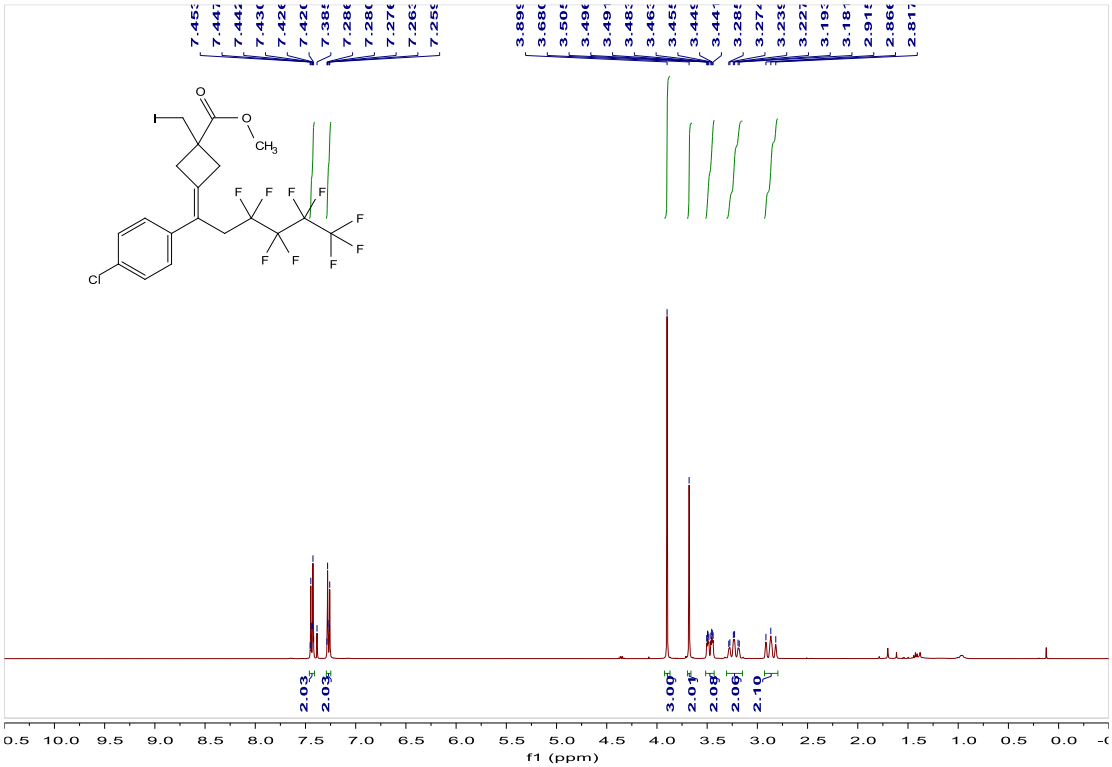
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9**



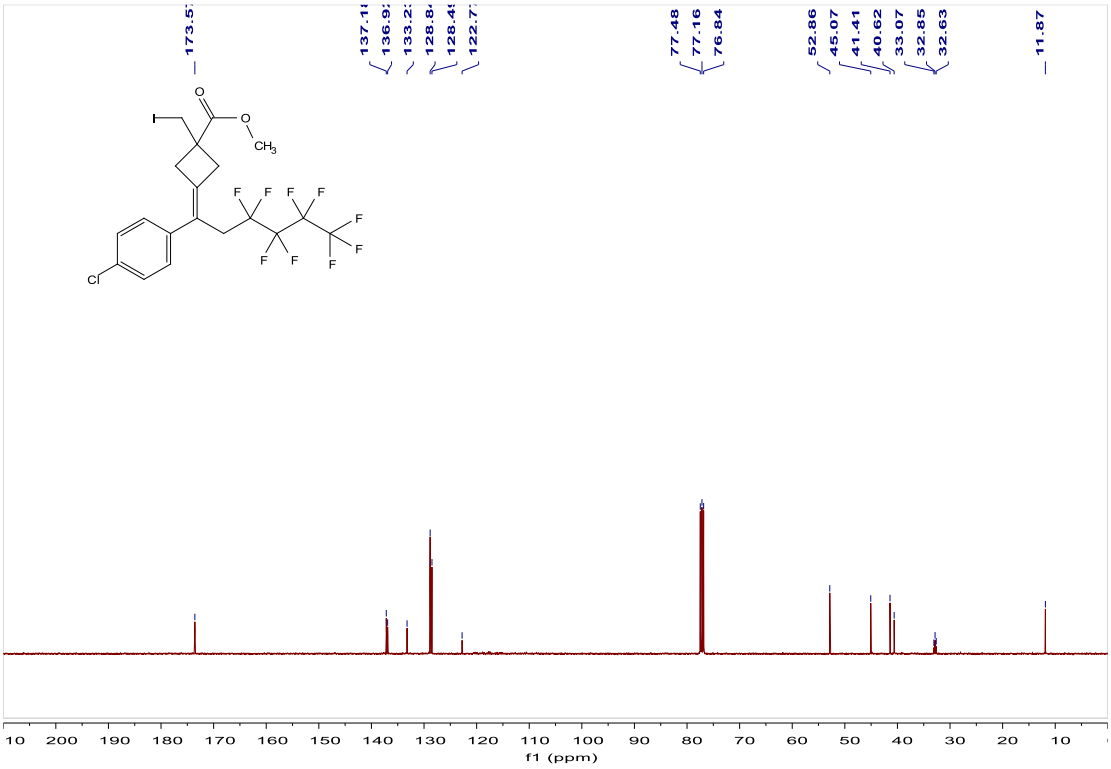
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **9**



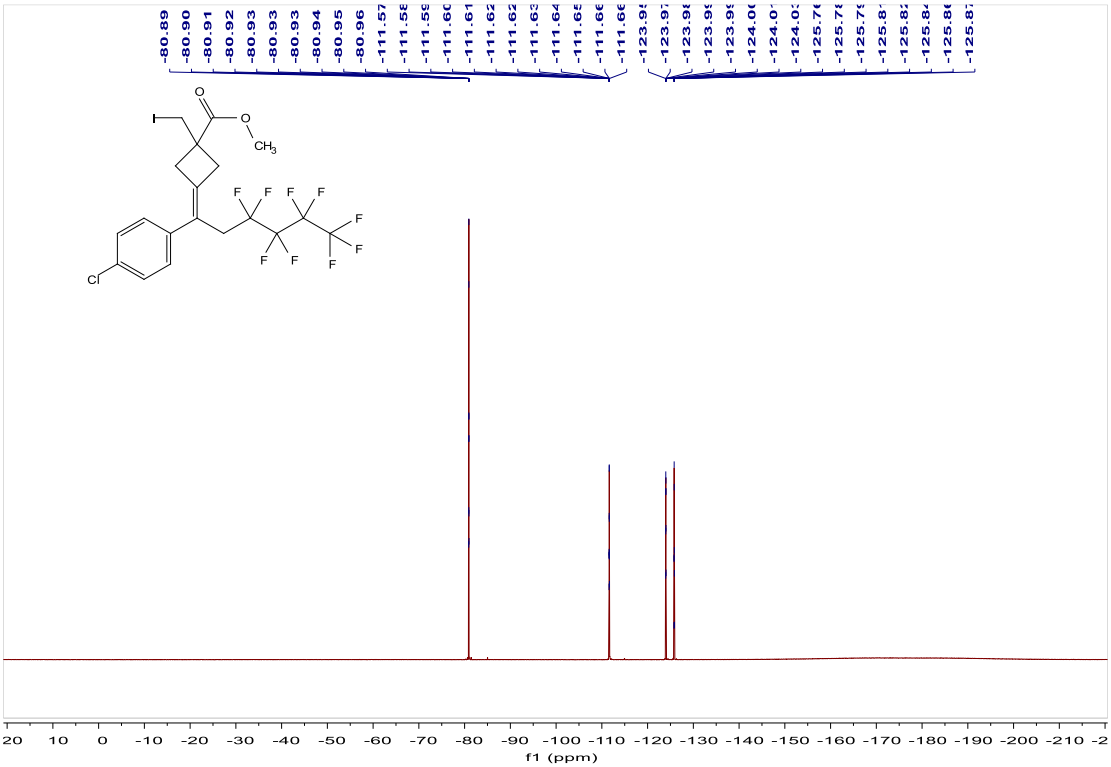
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**



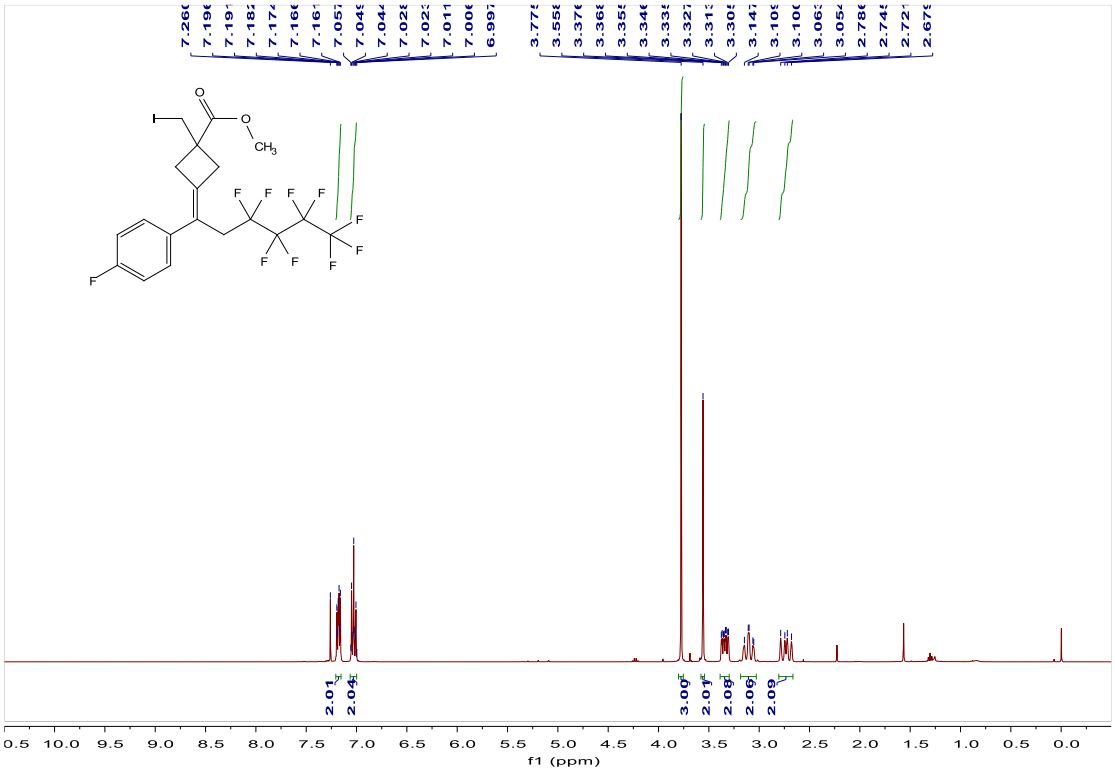
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**



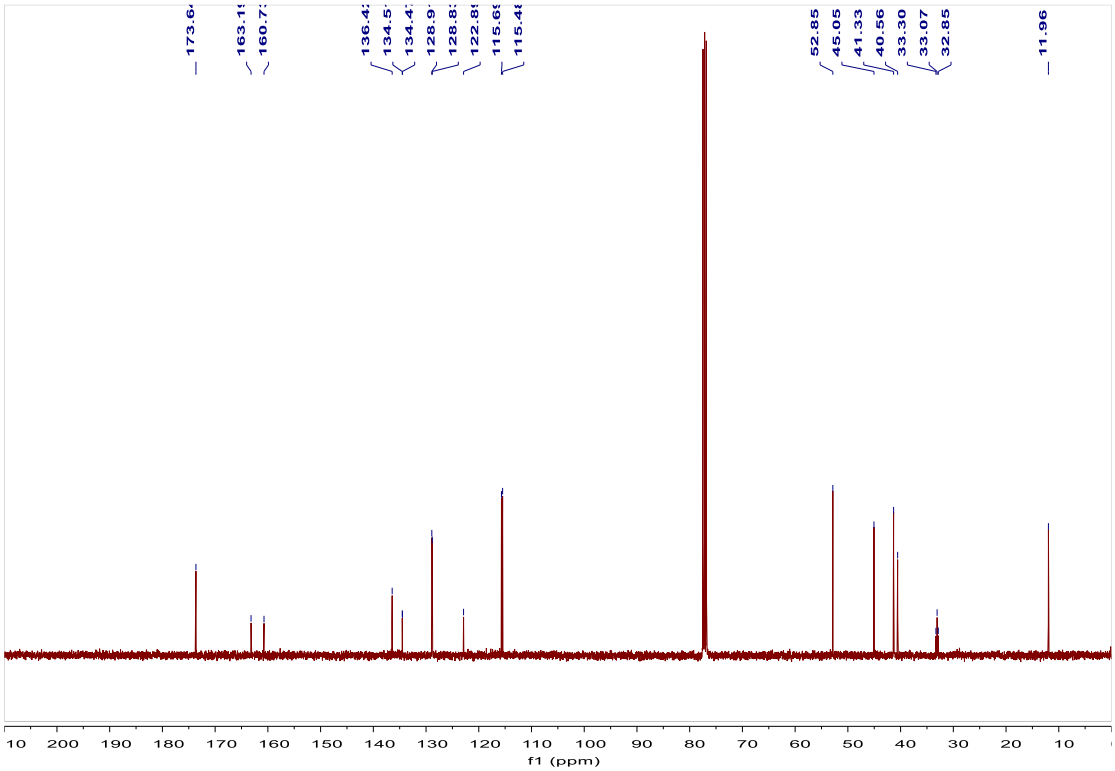
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **10**



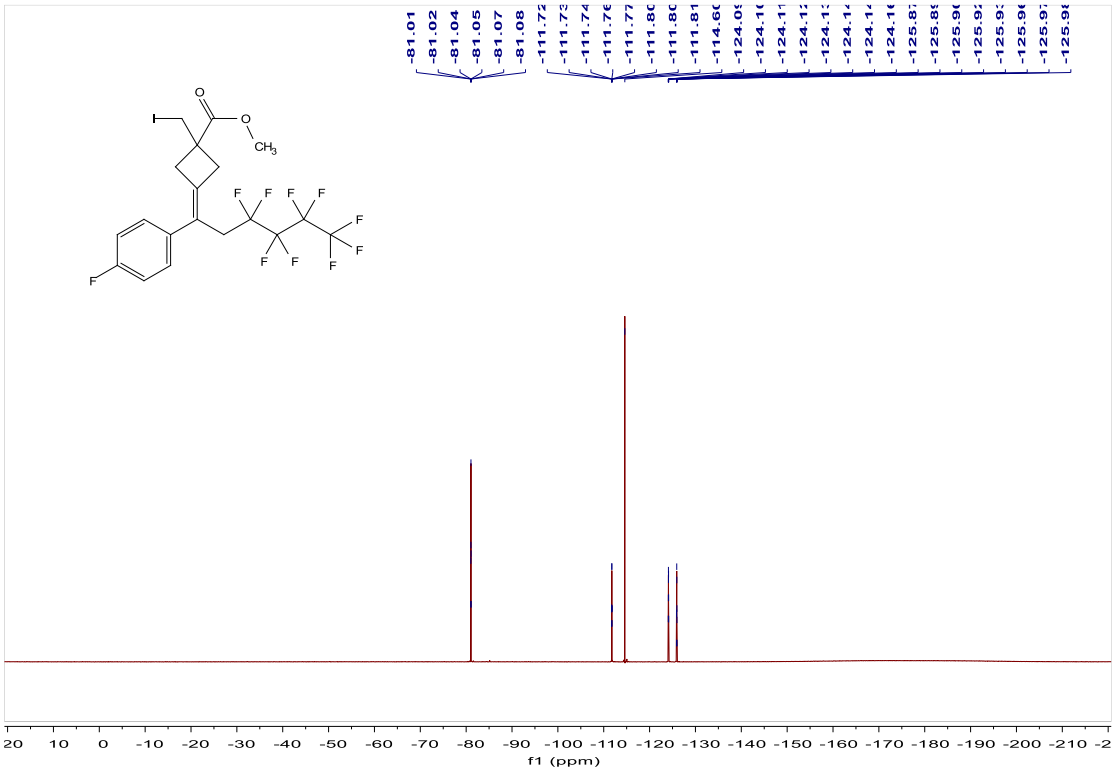
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**



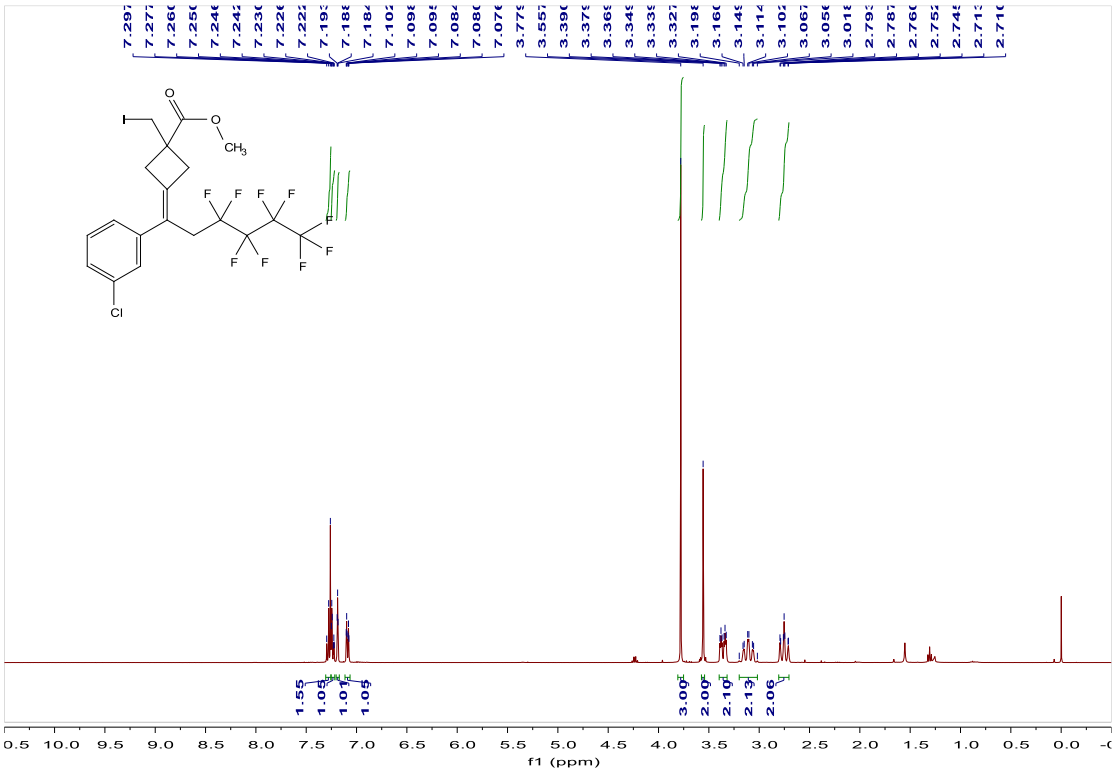
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11**



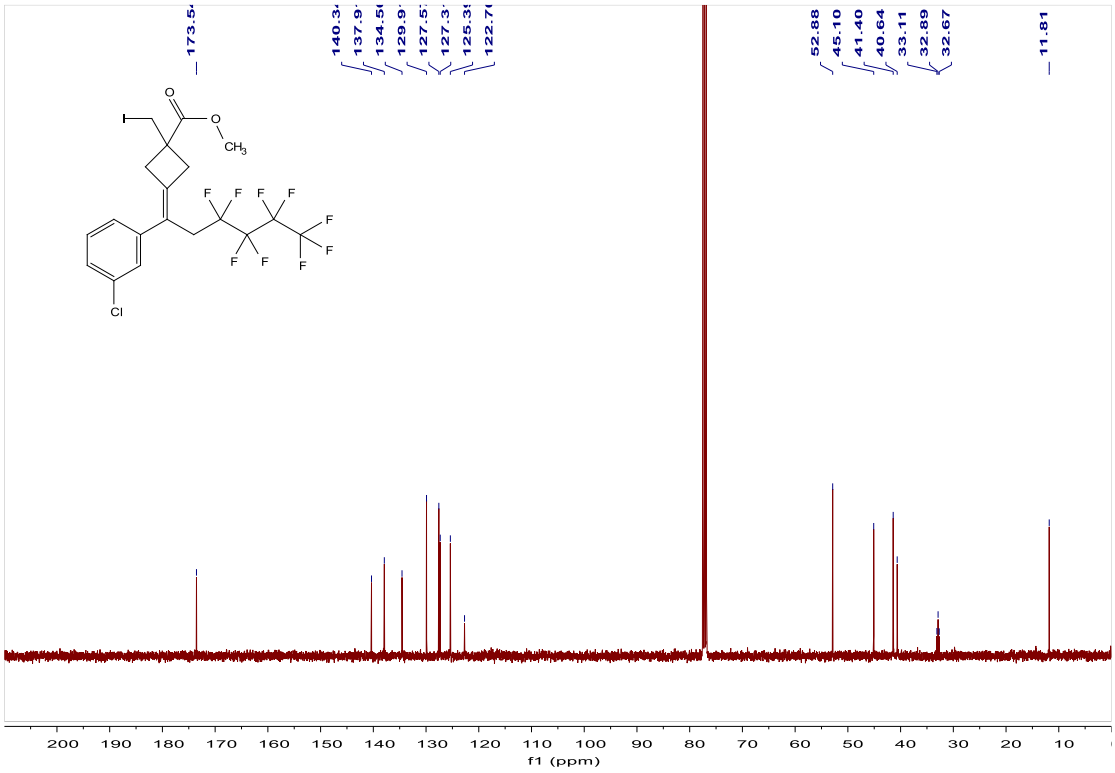
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **11**



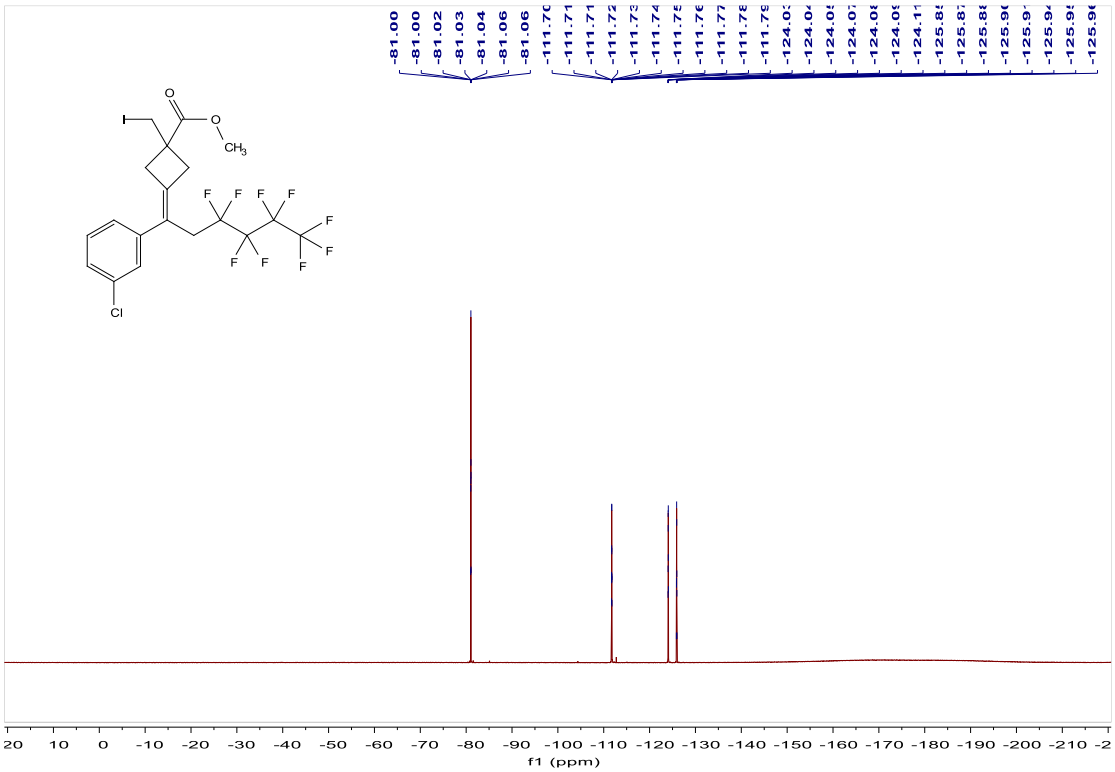
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**



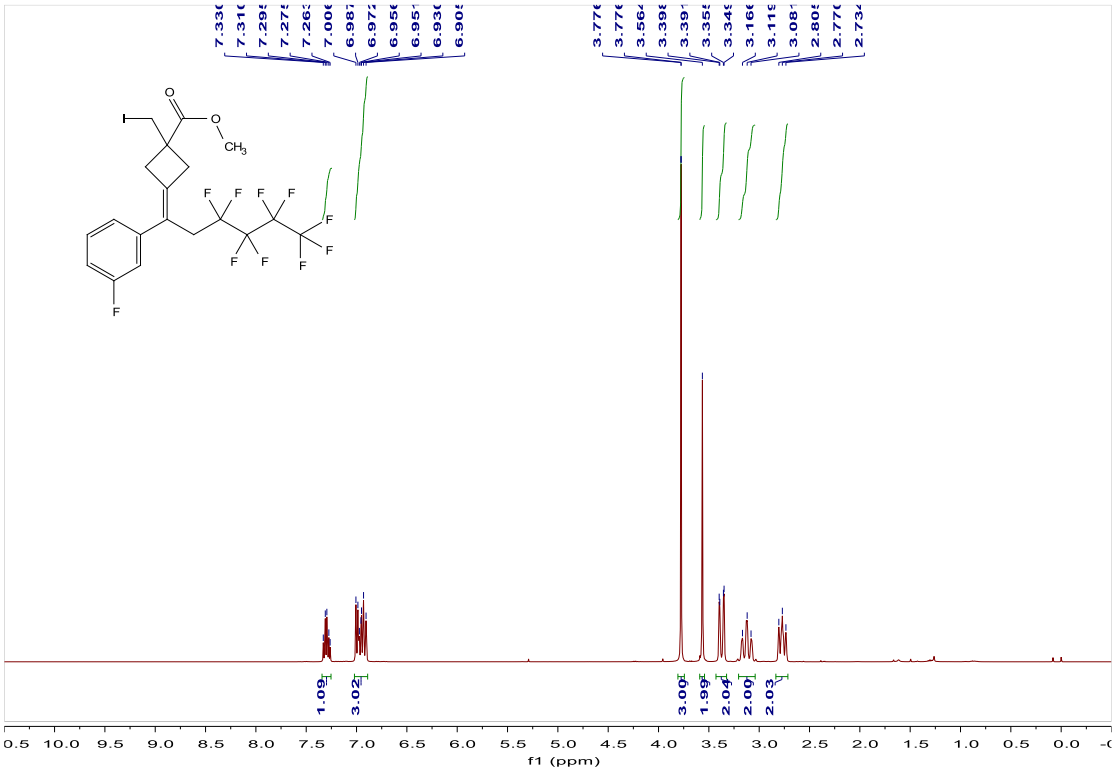
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **12**



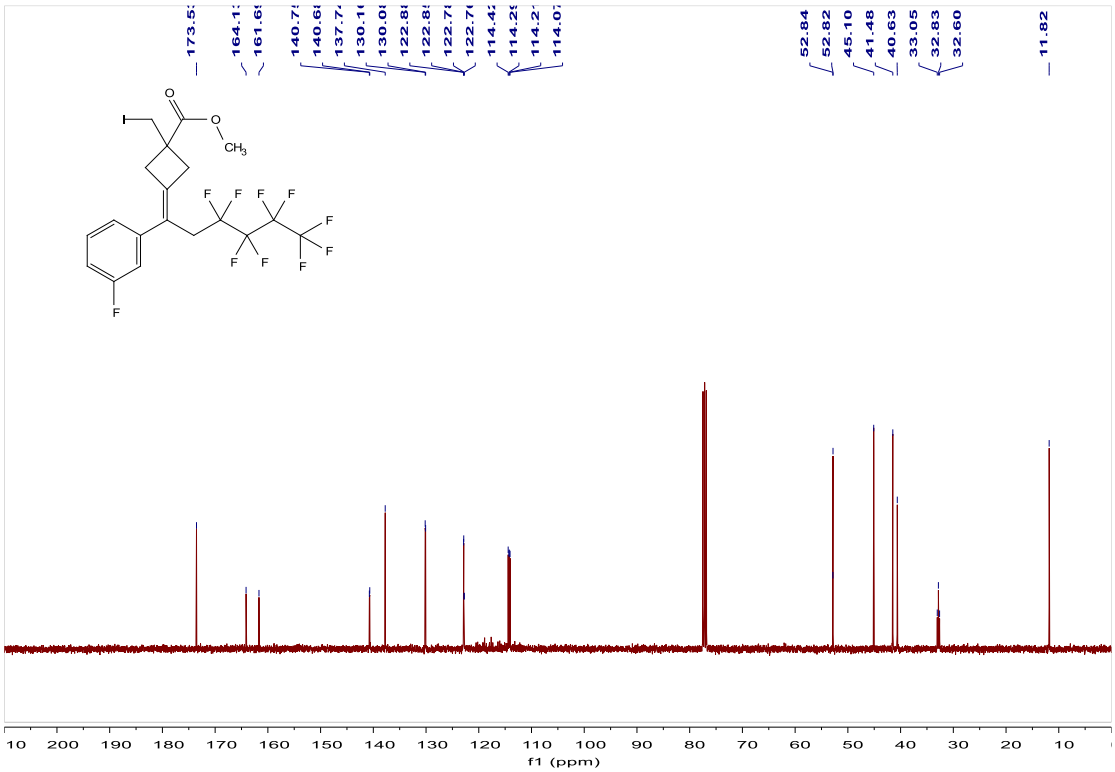
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **12**



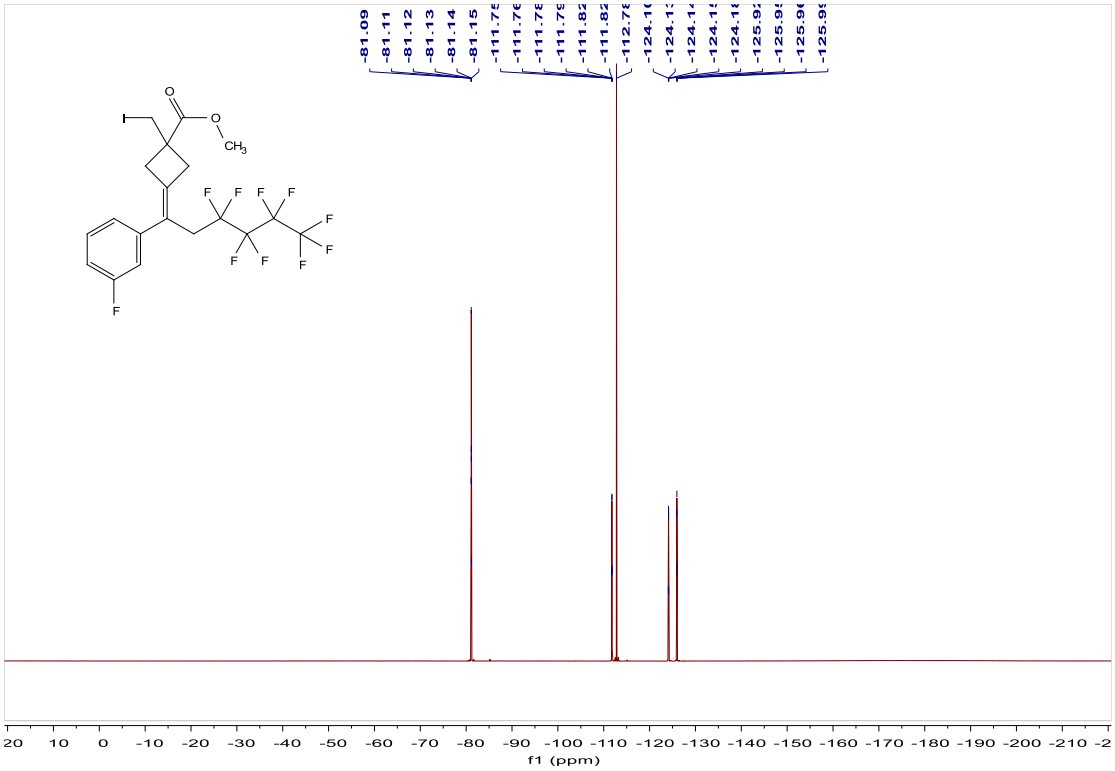
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**



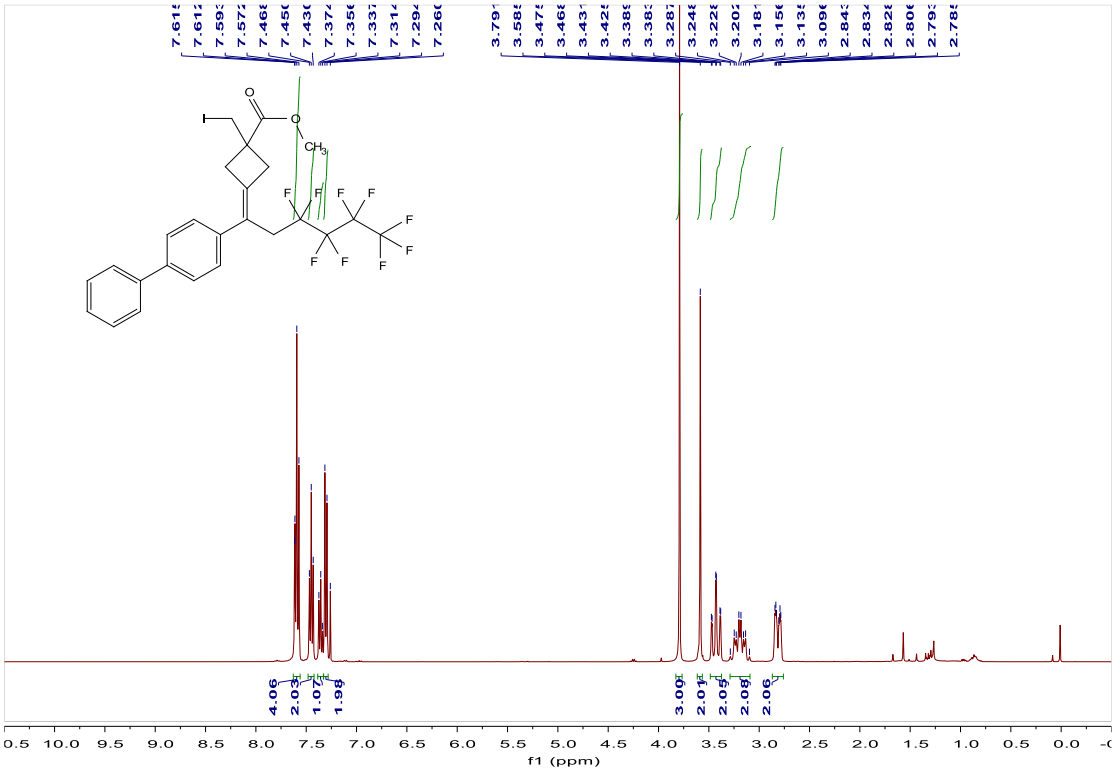
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13**



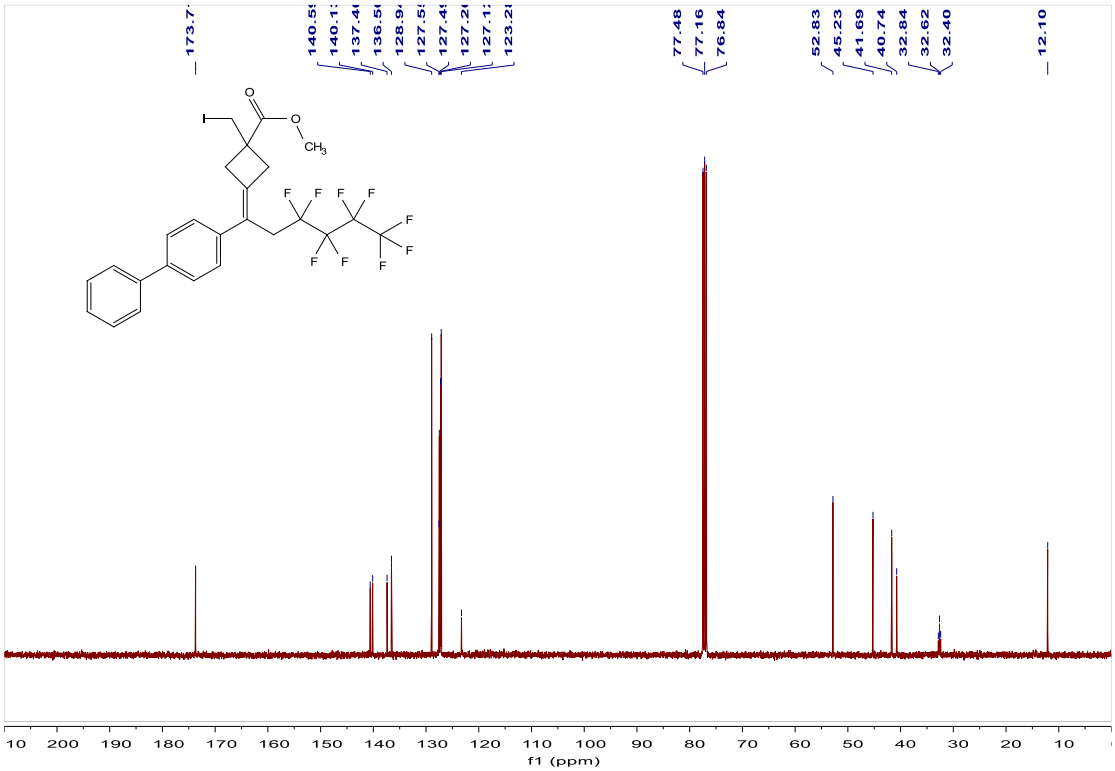
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **13**



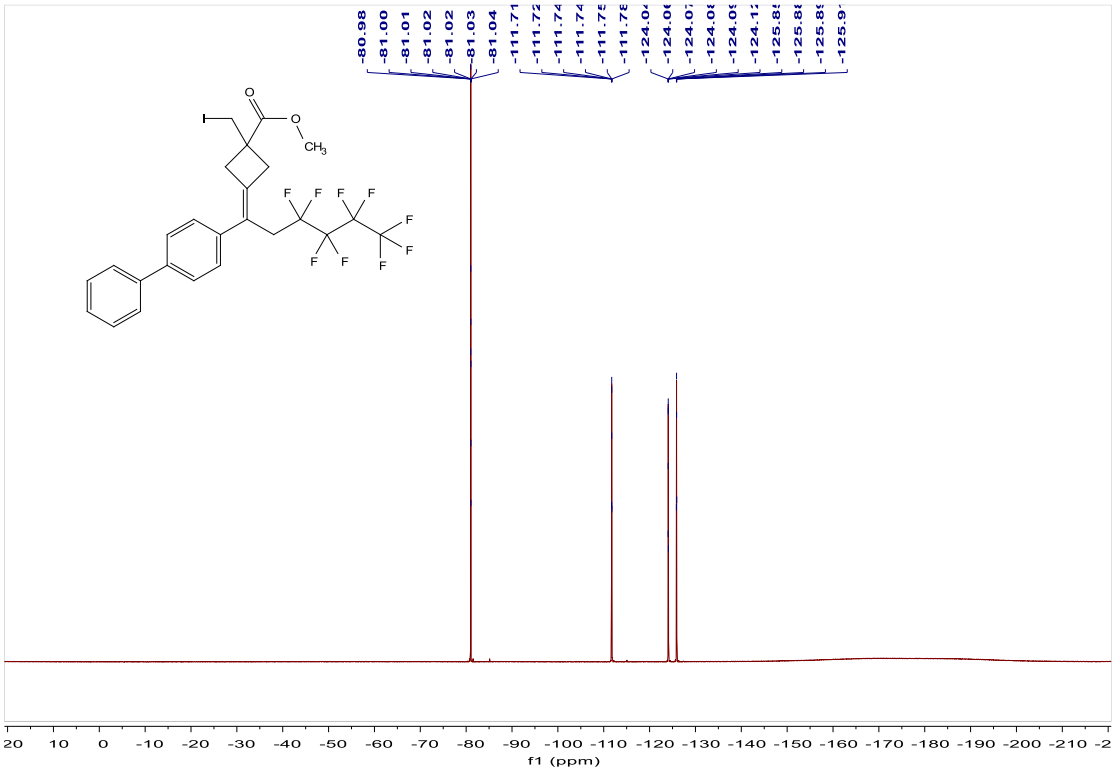
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14**



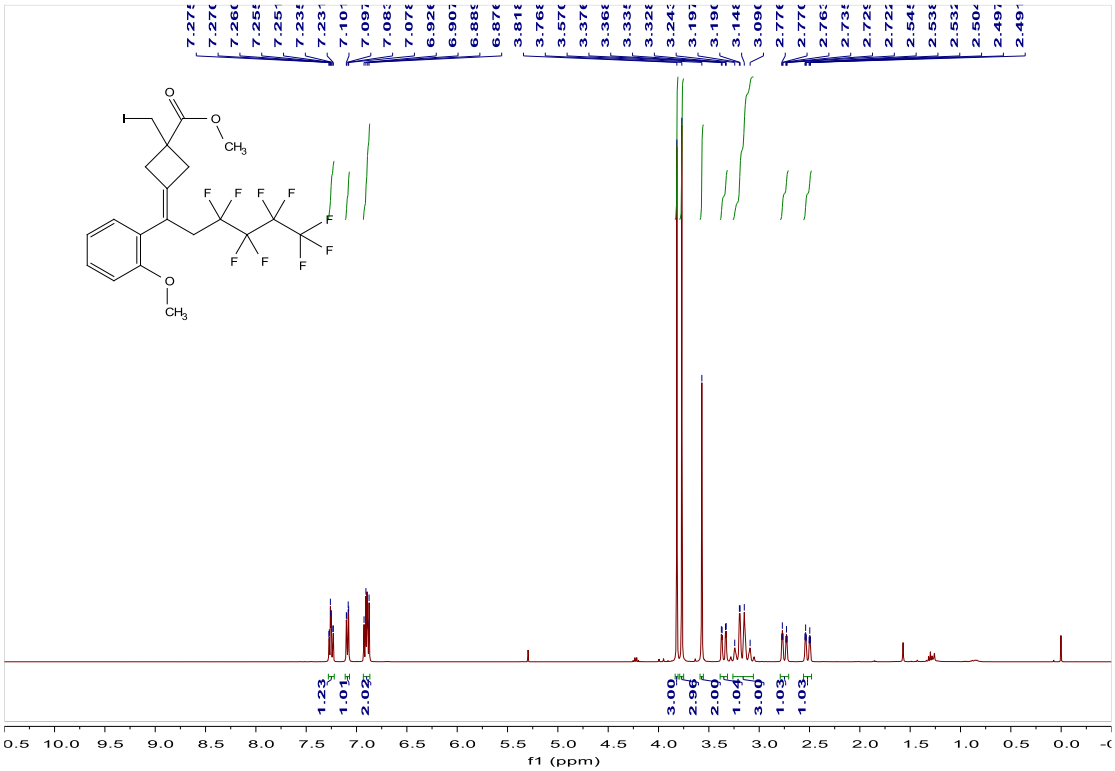
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **14**



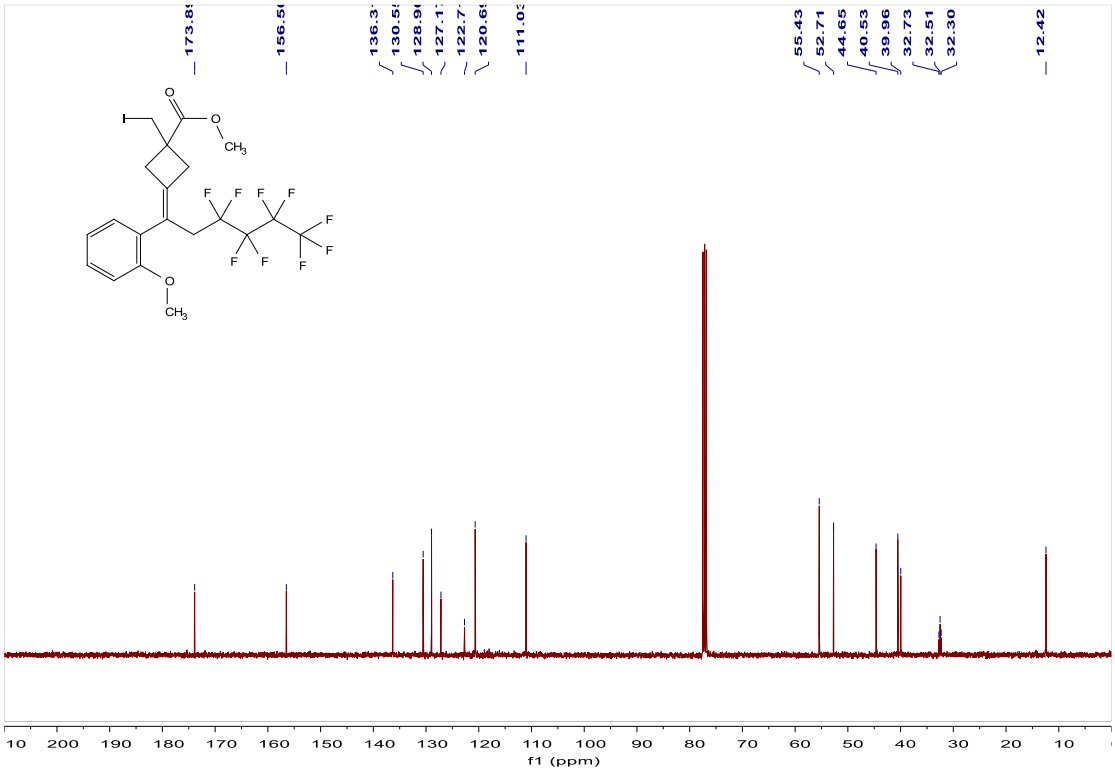
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **14**



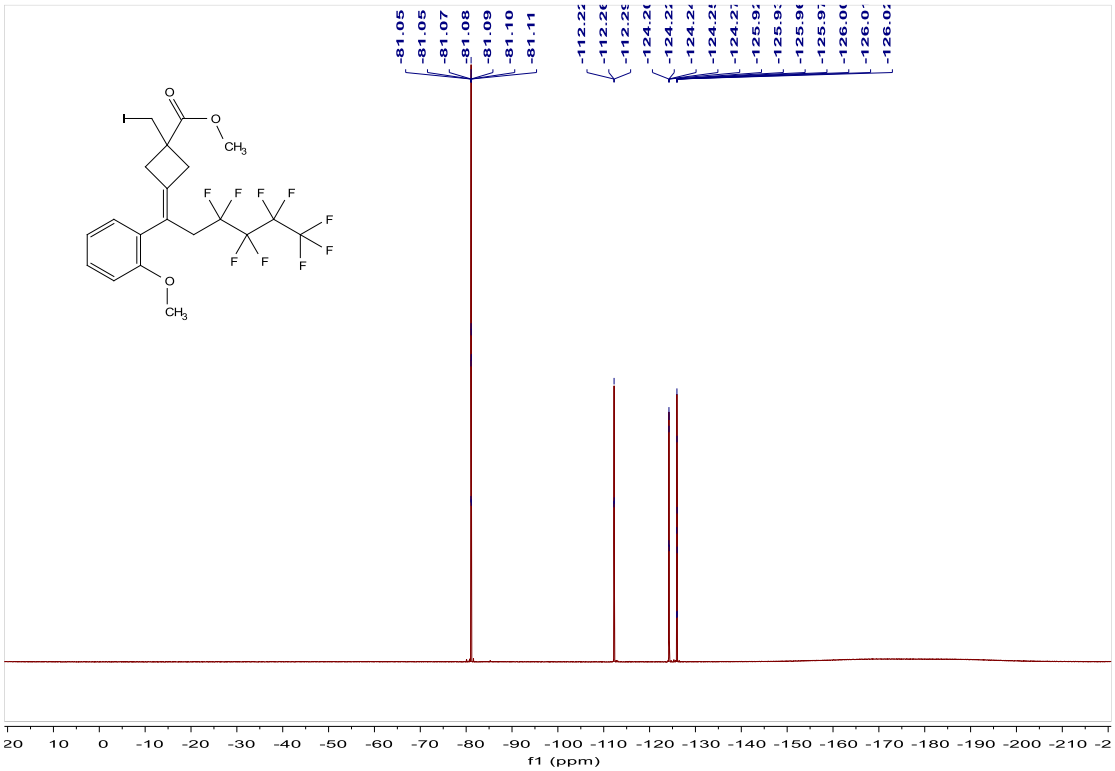
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **15**



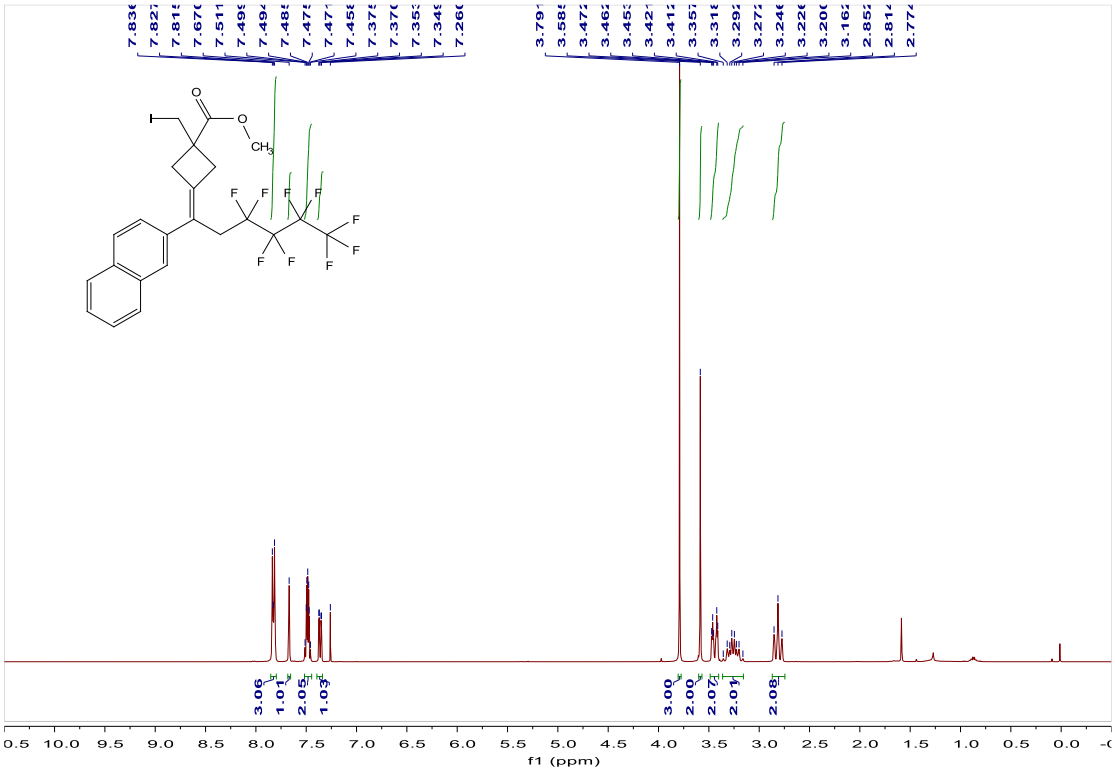
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **15**



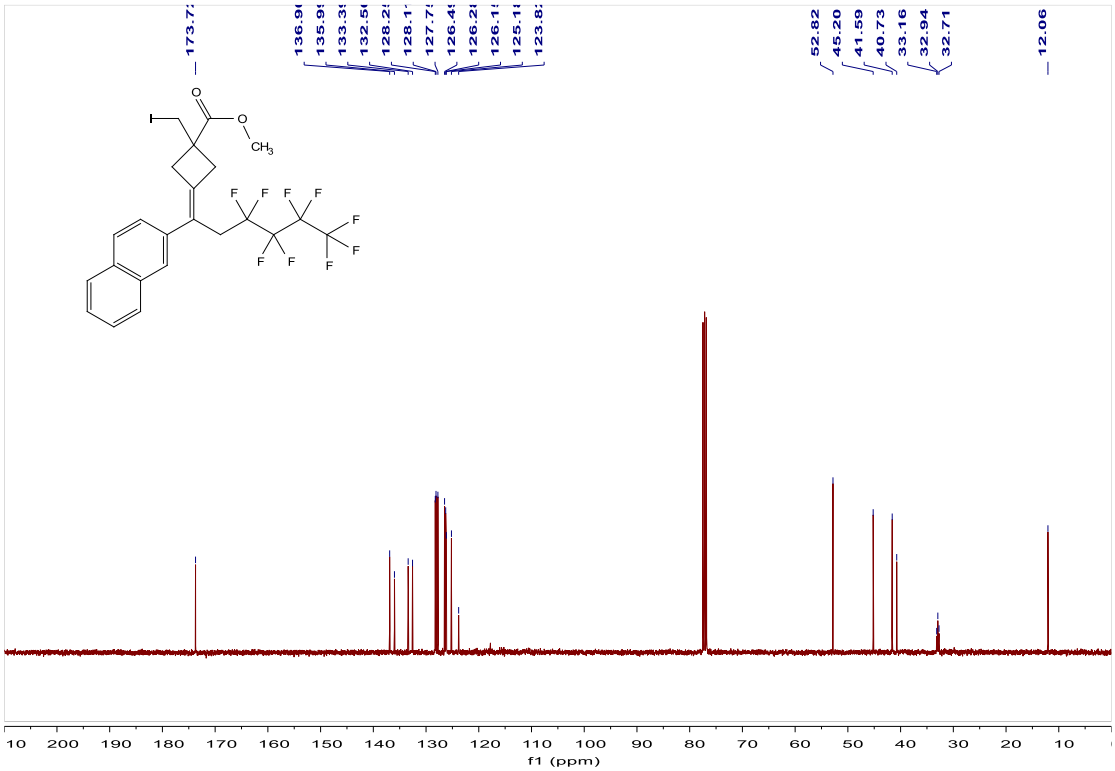
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **15**



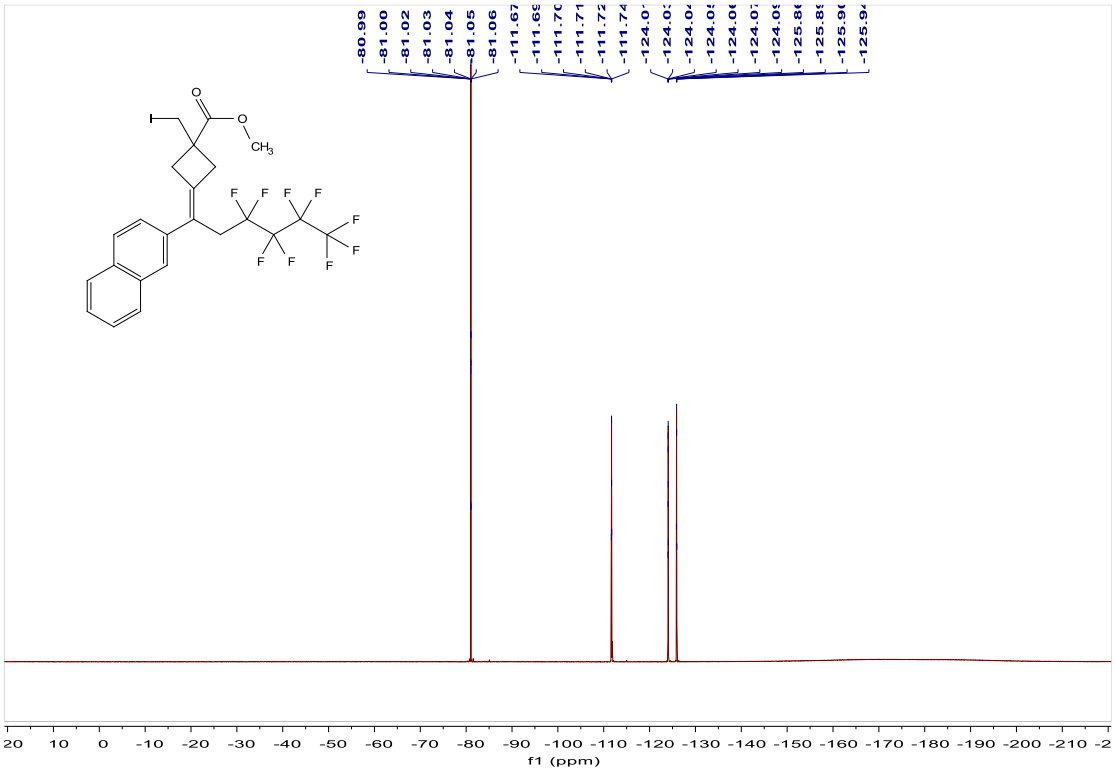
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16**



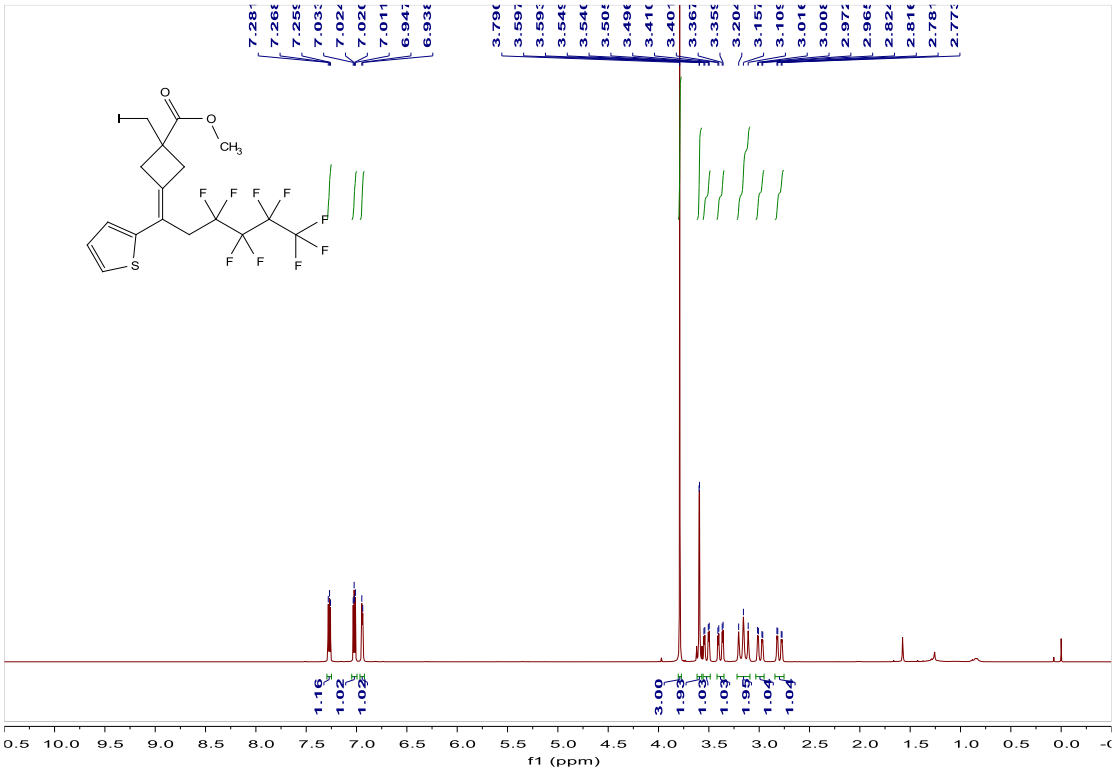
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16**



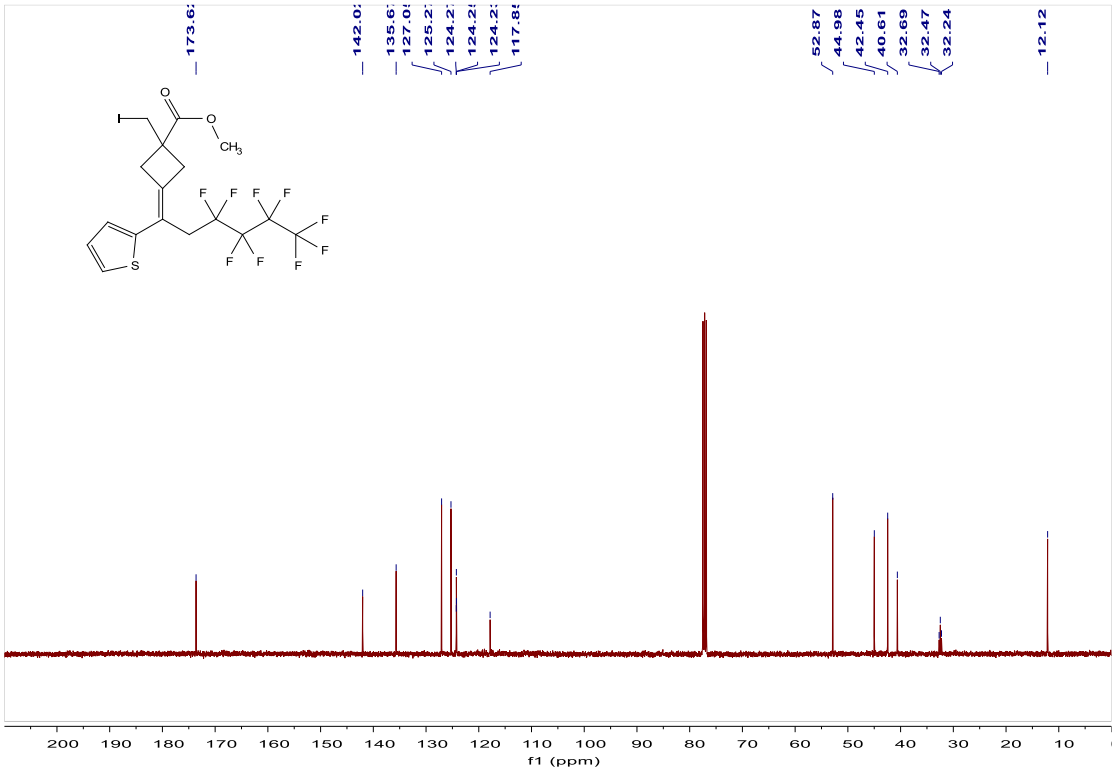
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **16**



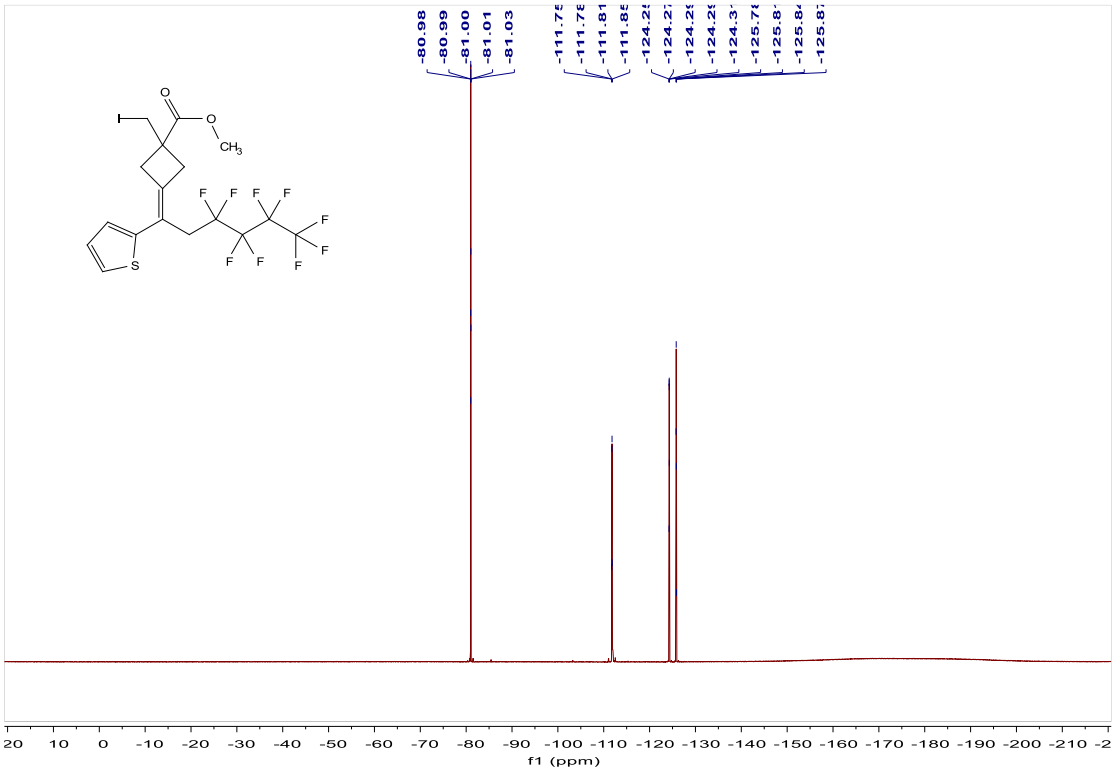
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **17**



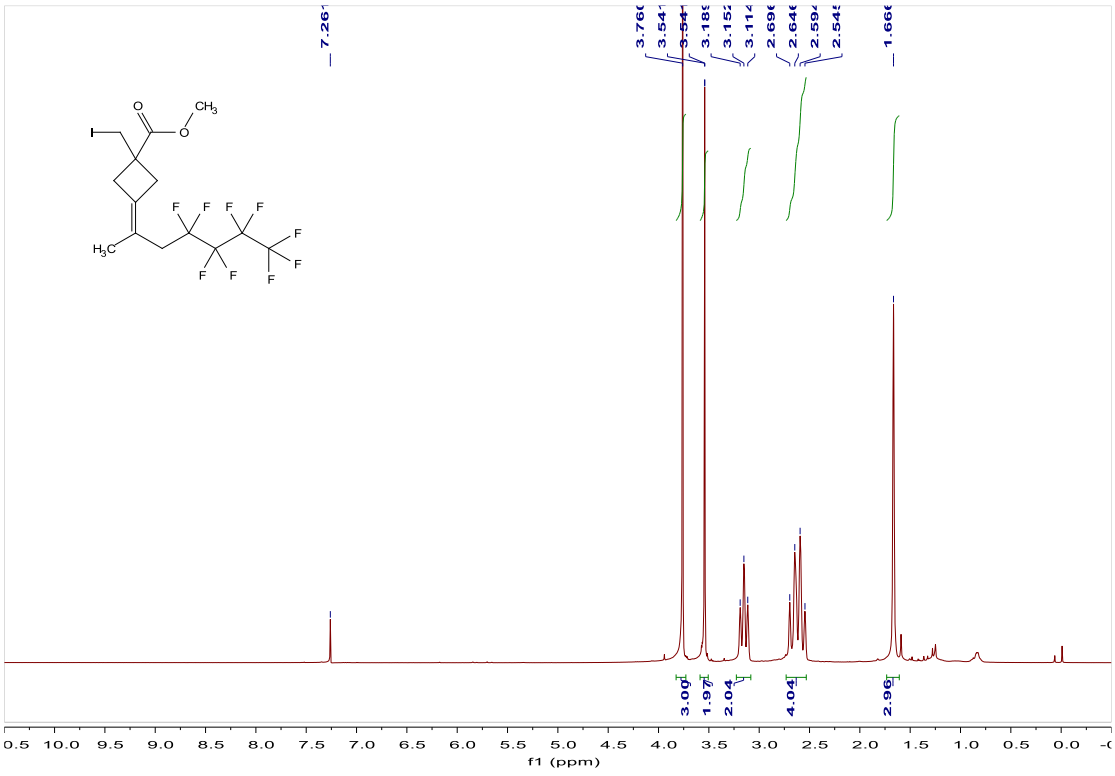
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **17**



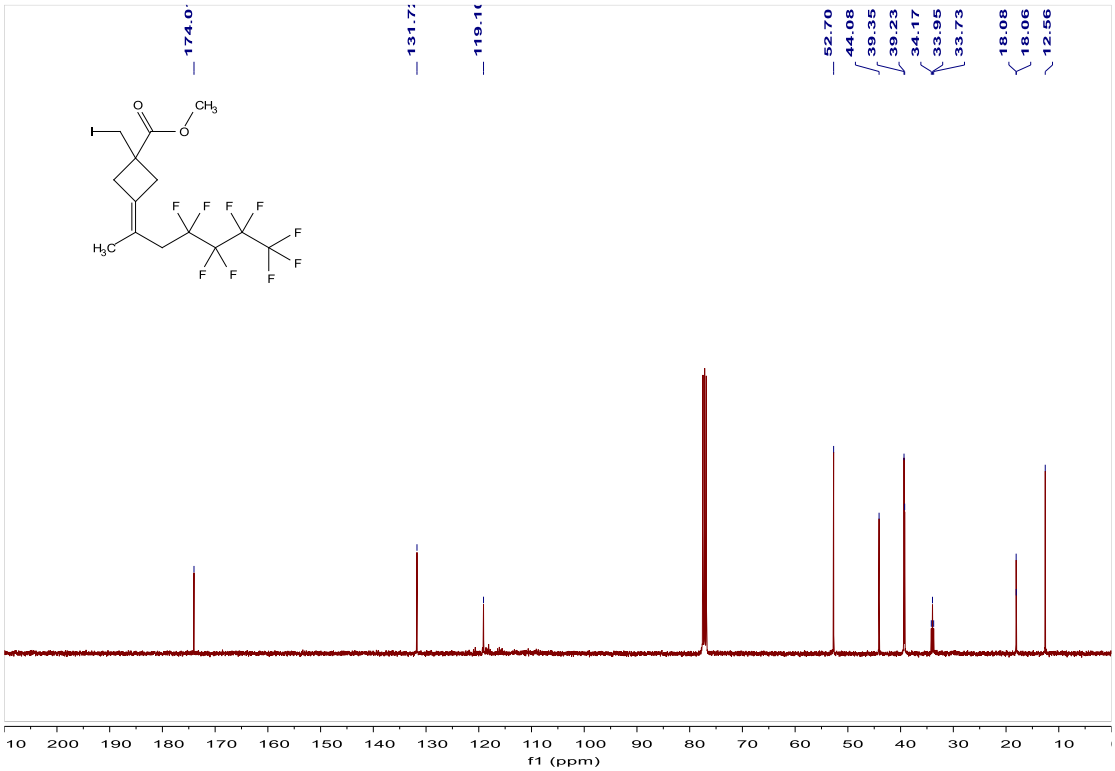
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **17**



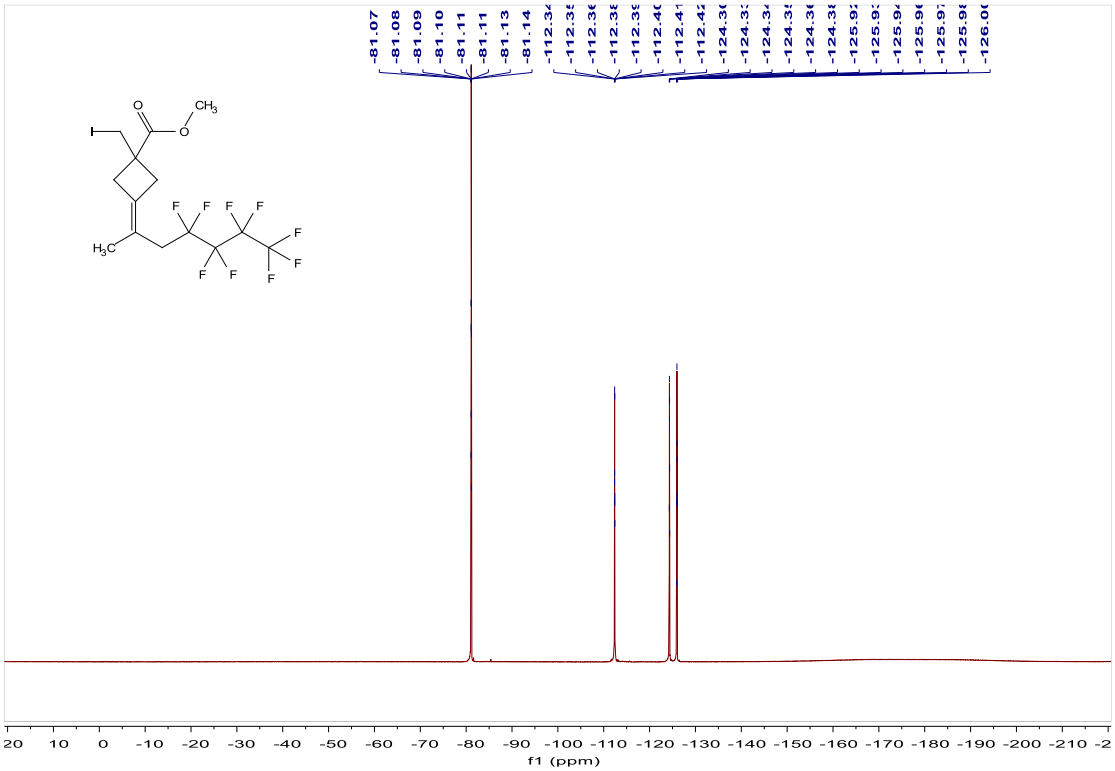
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18**



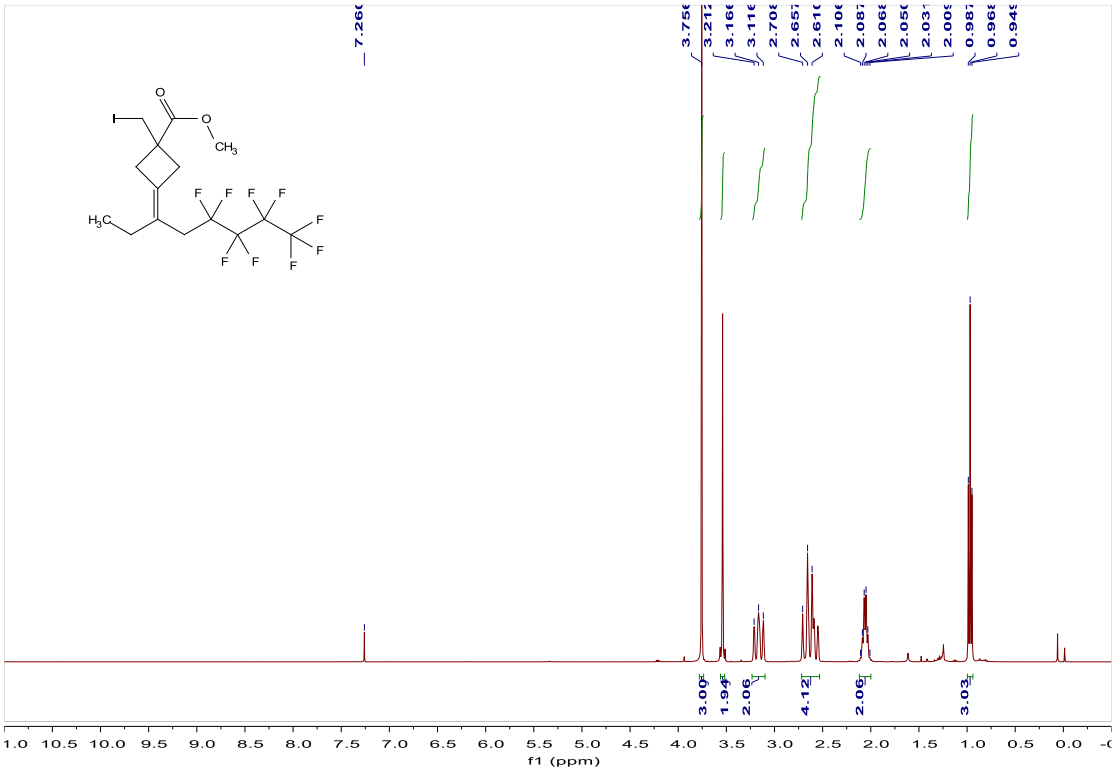
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **18**



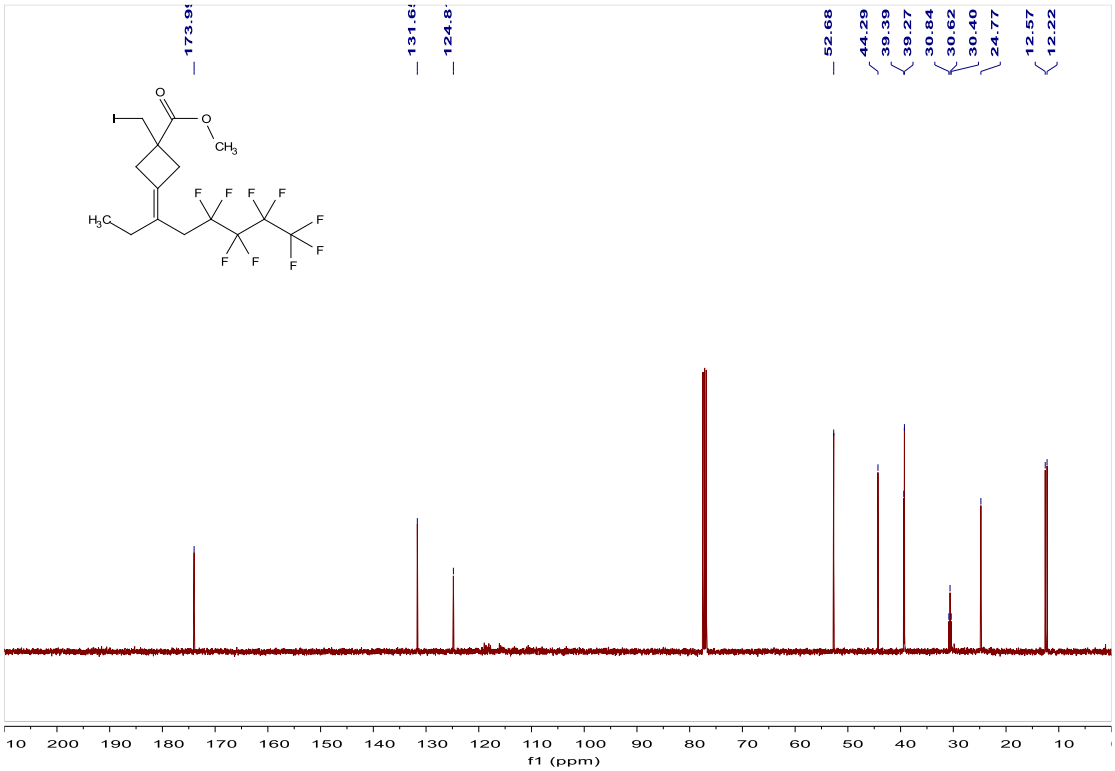
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **18**



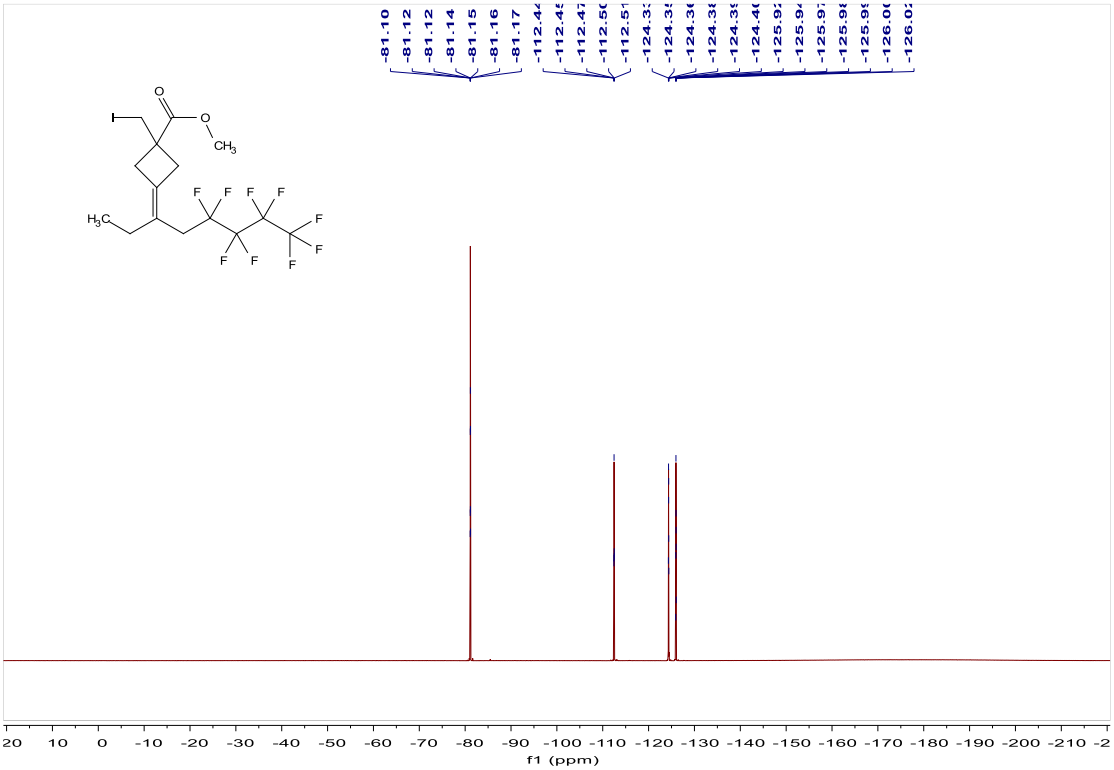
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**



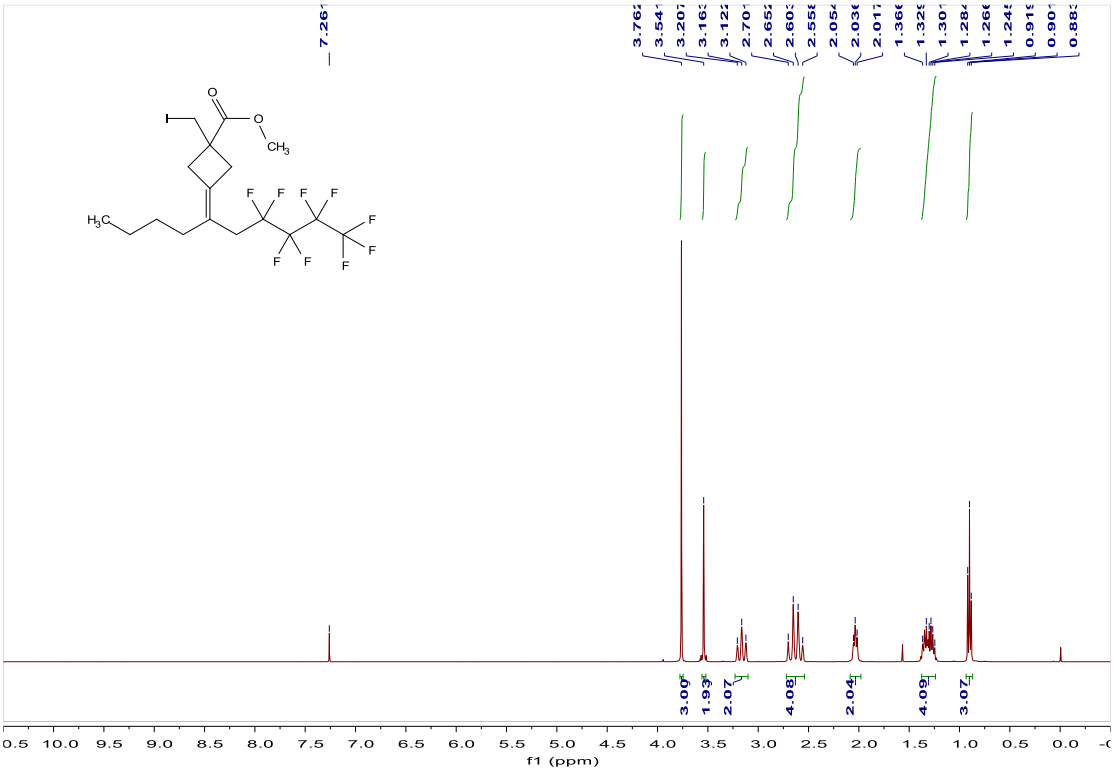
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **19**



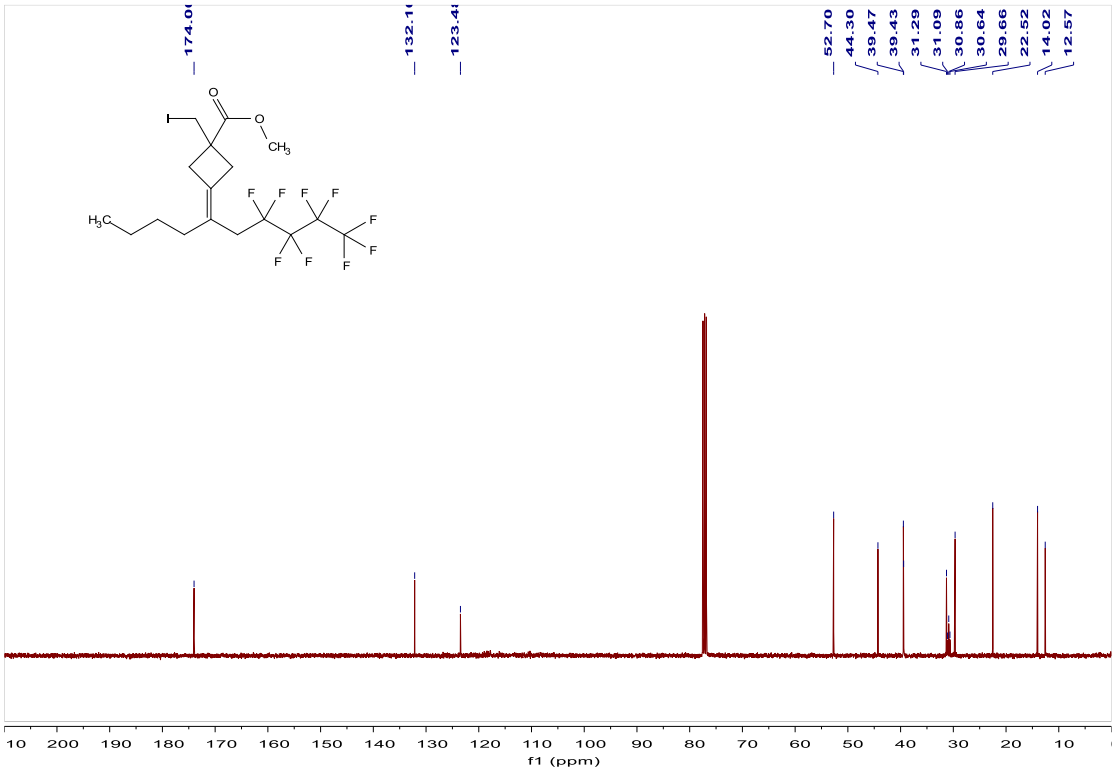
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **19**



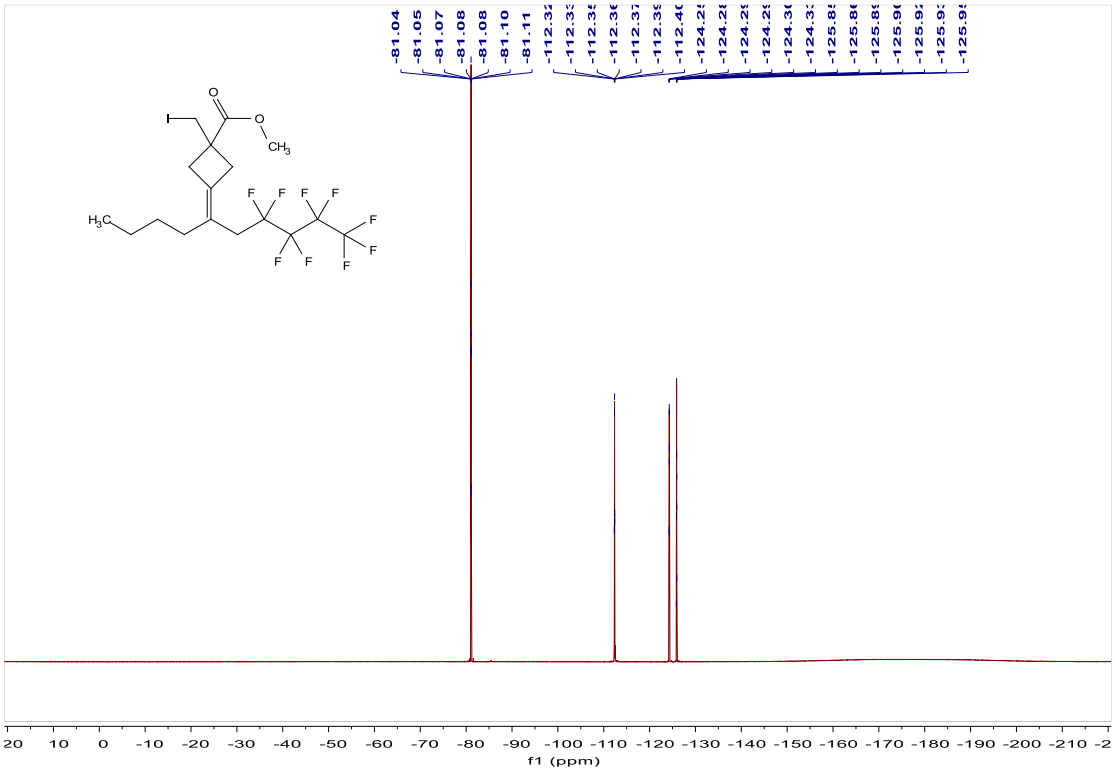
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **20**



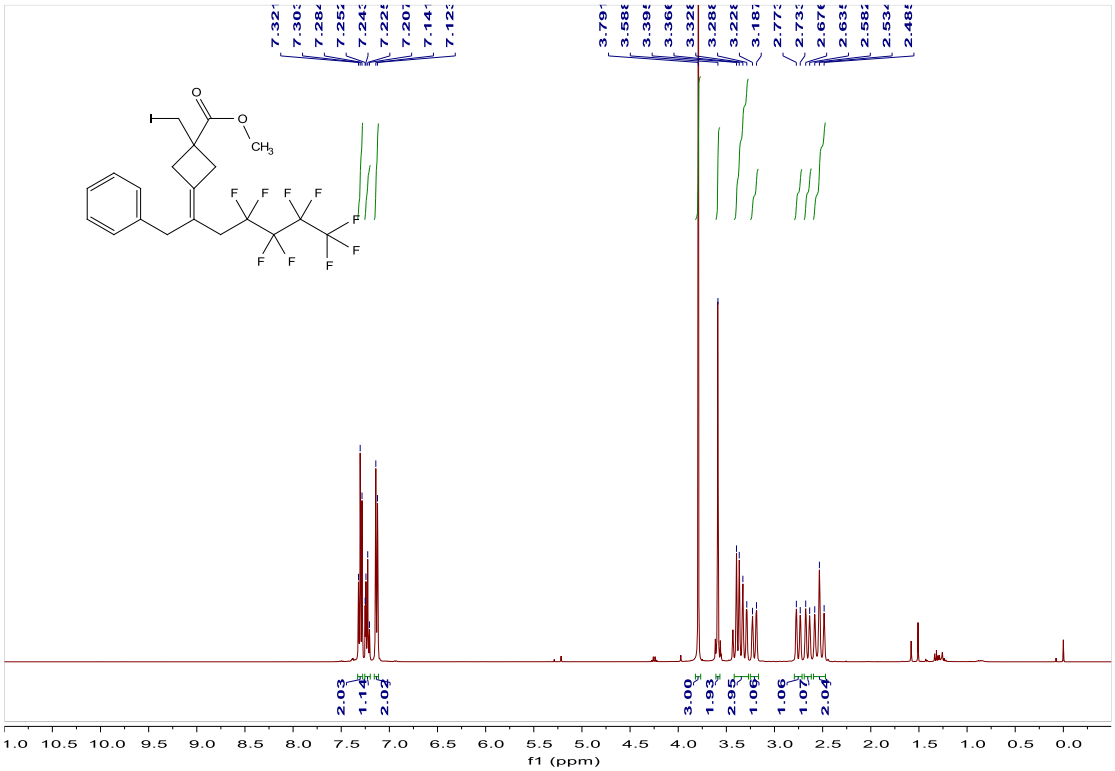
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **20**



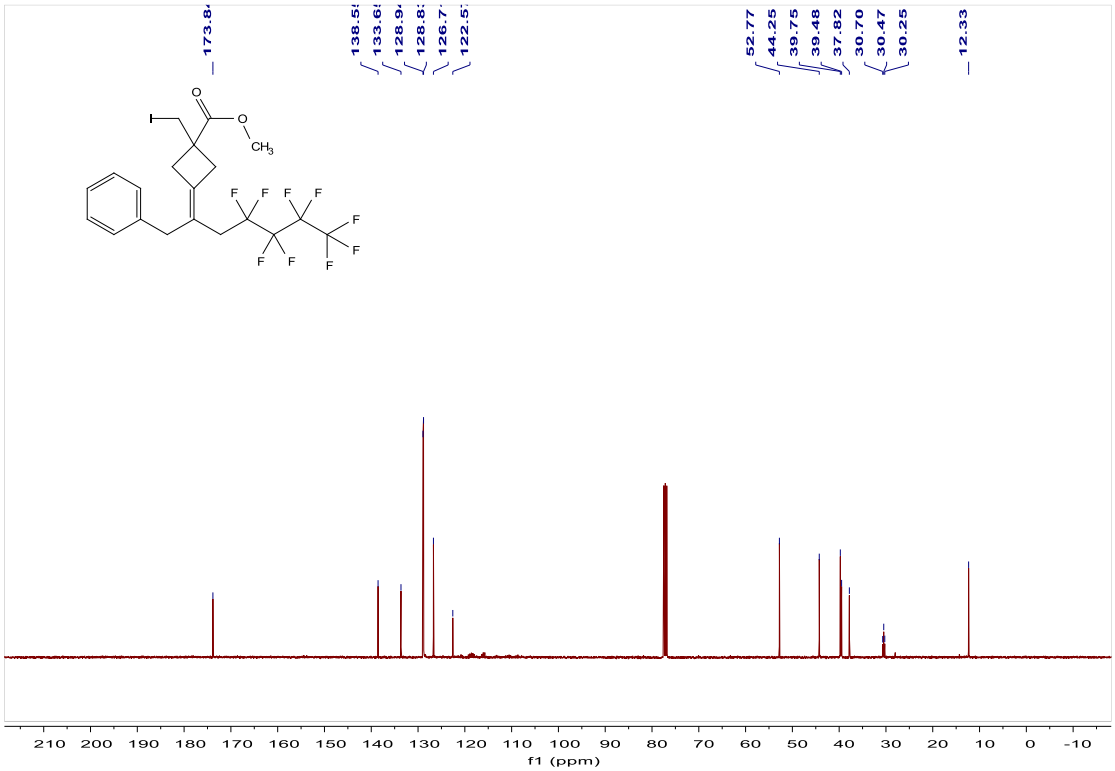
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **20**



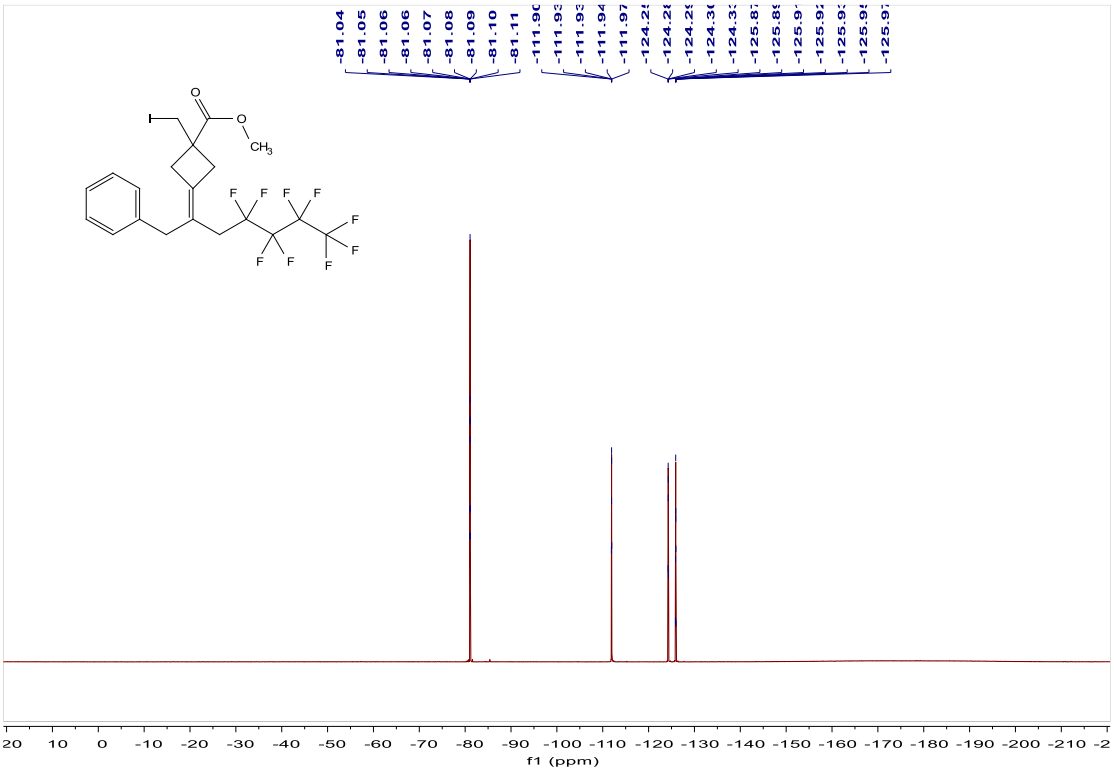
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **21**



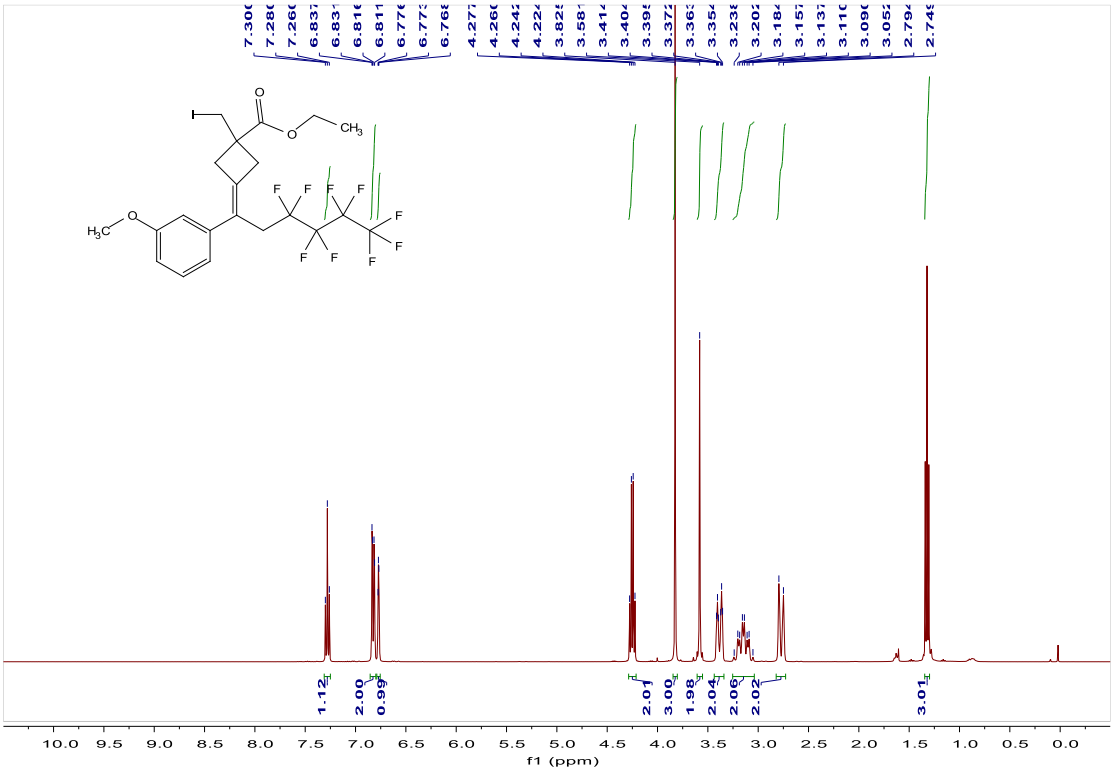
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **21**



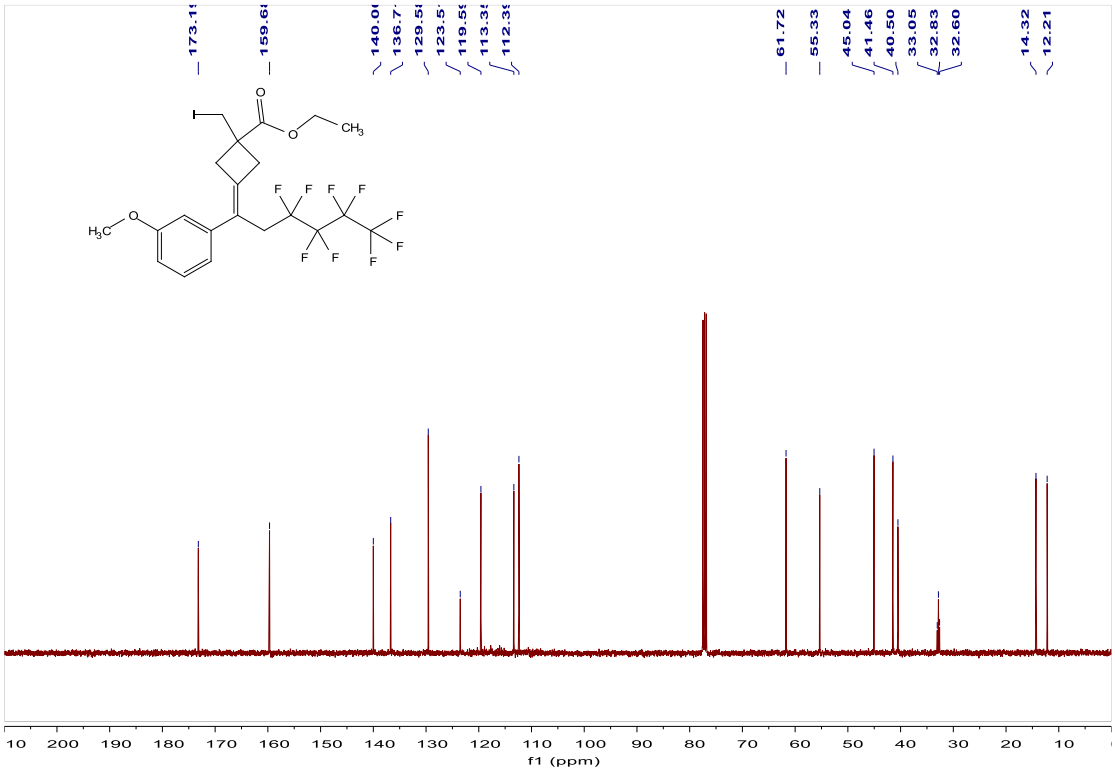
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **21**



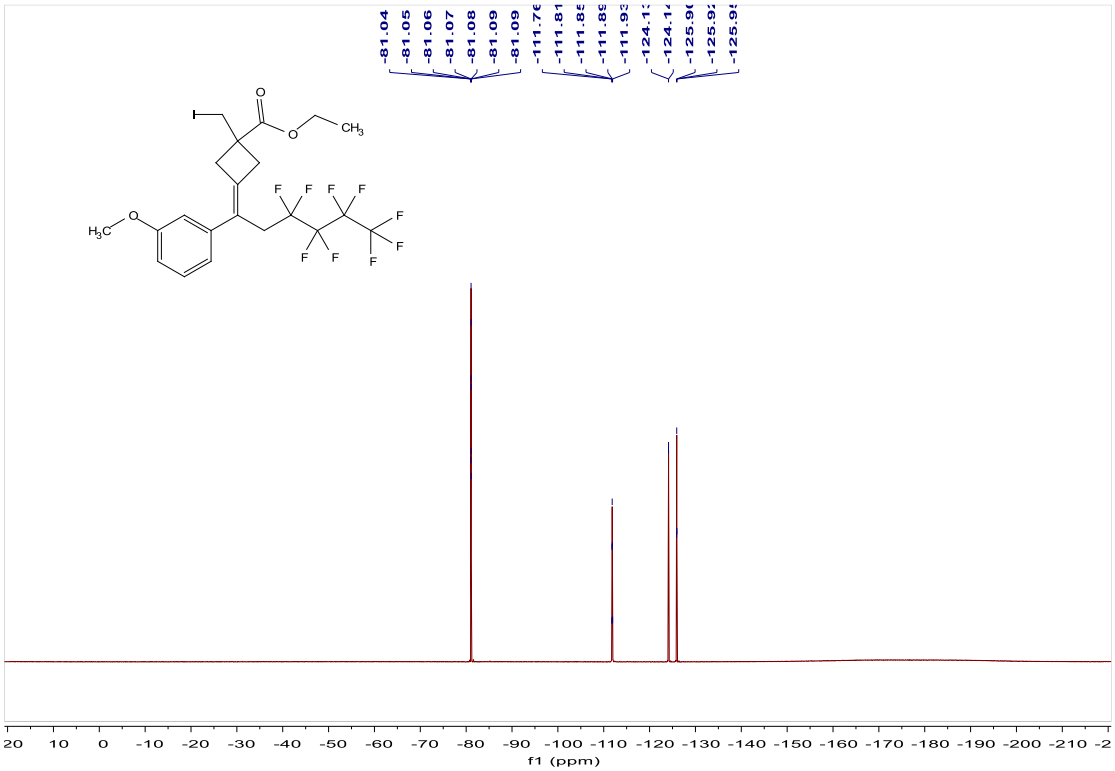
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **22**



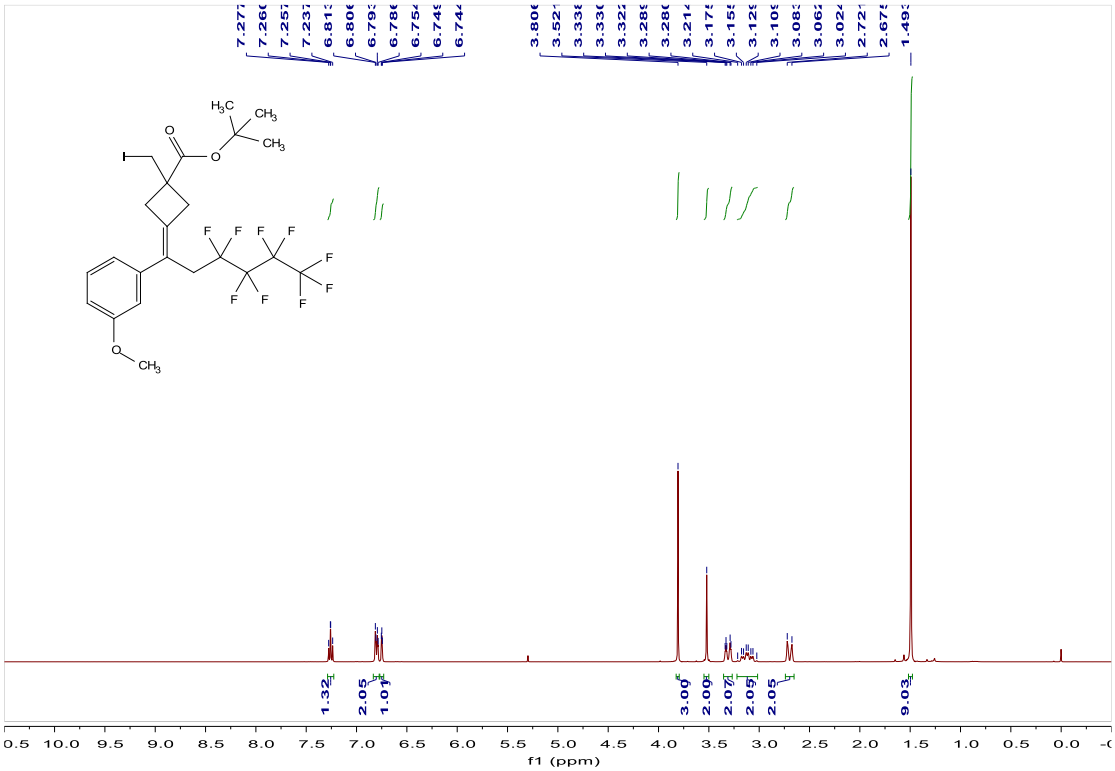
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **22**



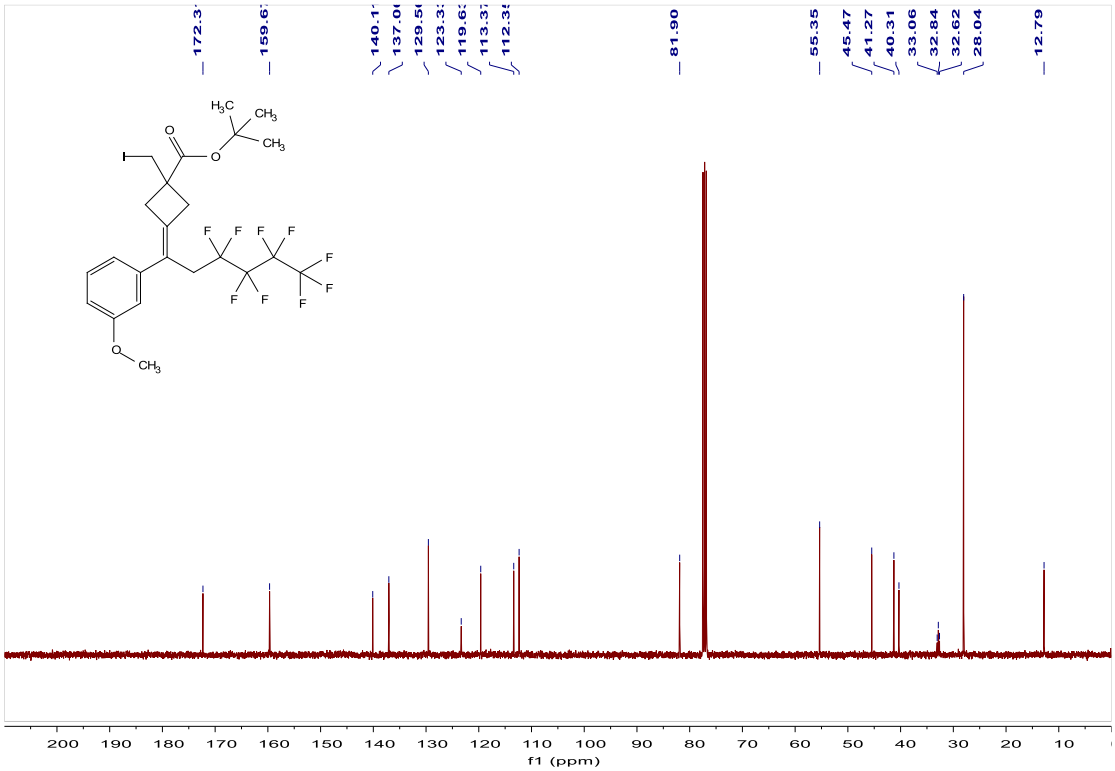
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **22**



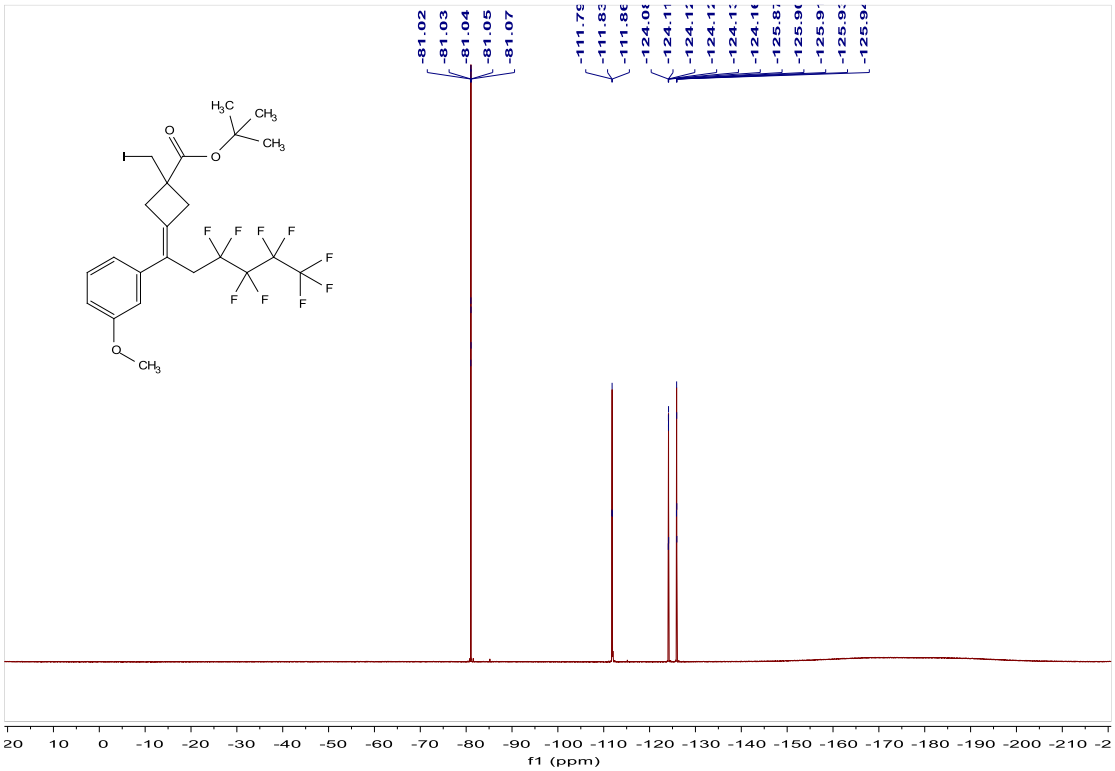
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **23**



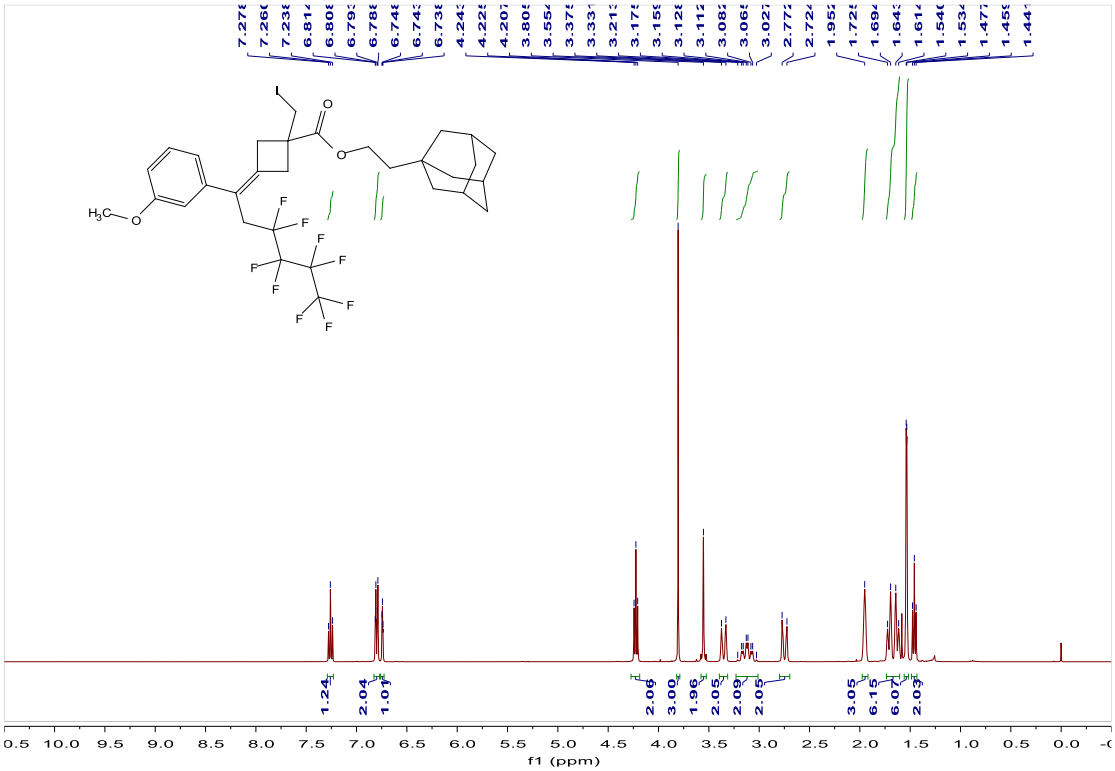
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **23**



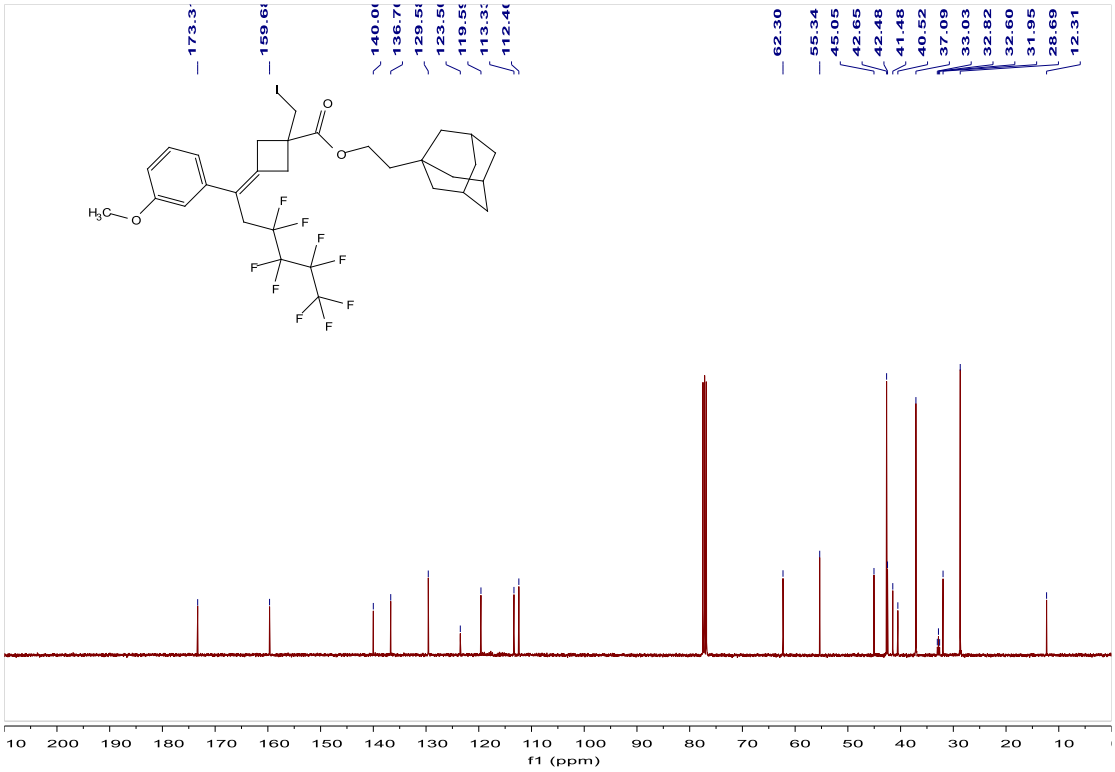
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **23**



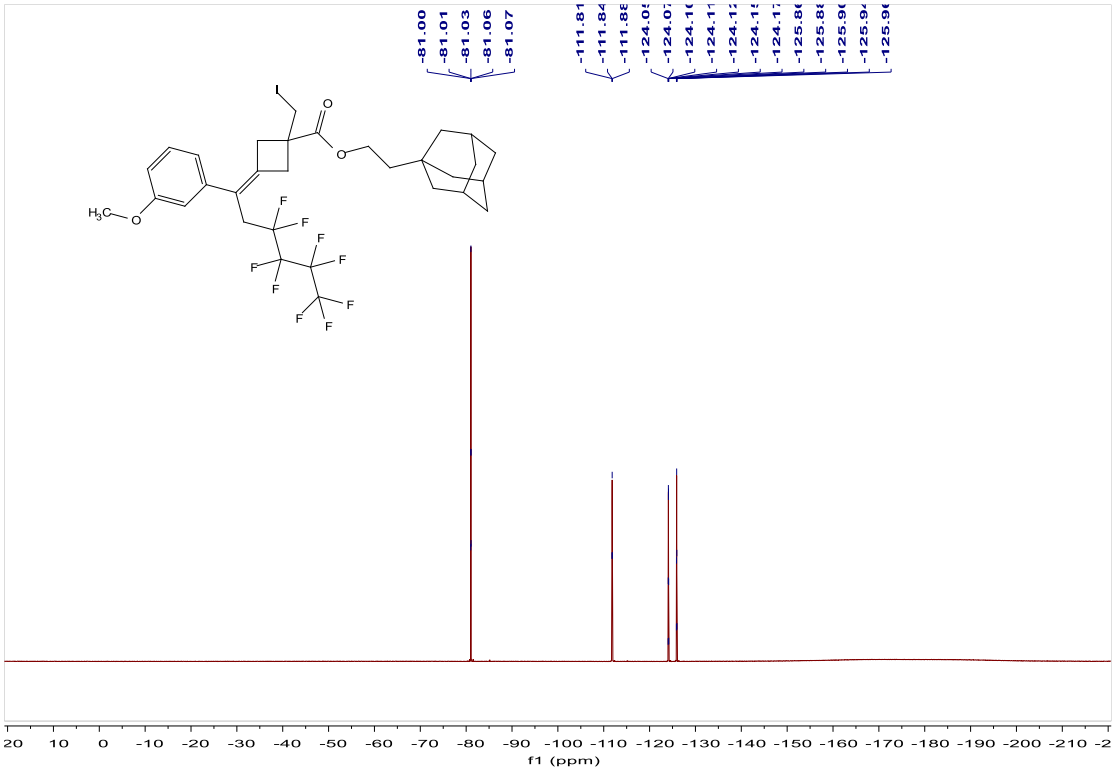
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **24**



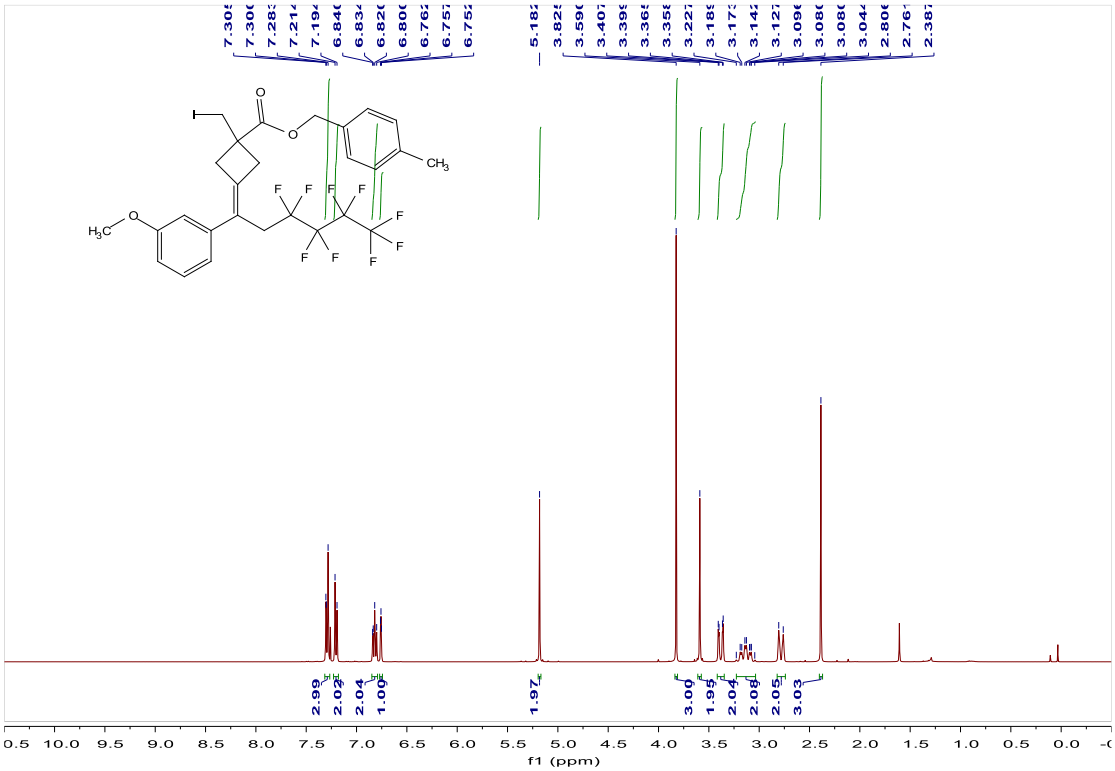
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **24**



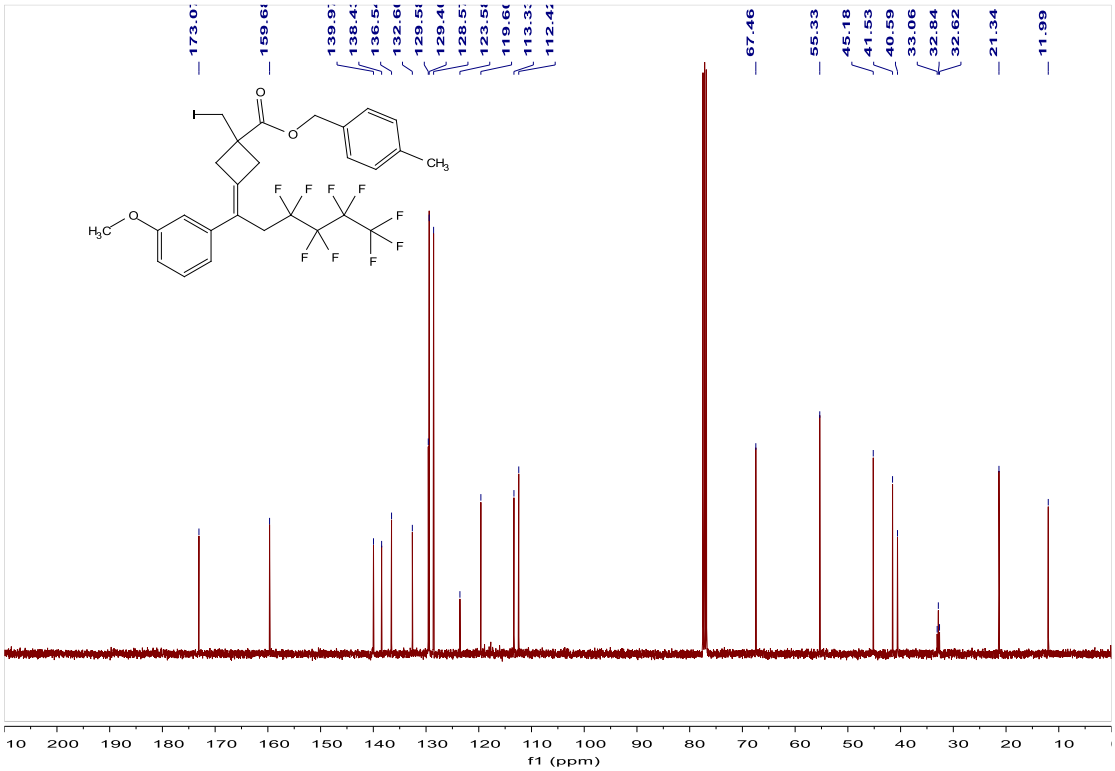
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **24**



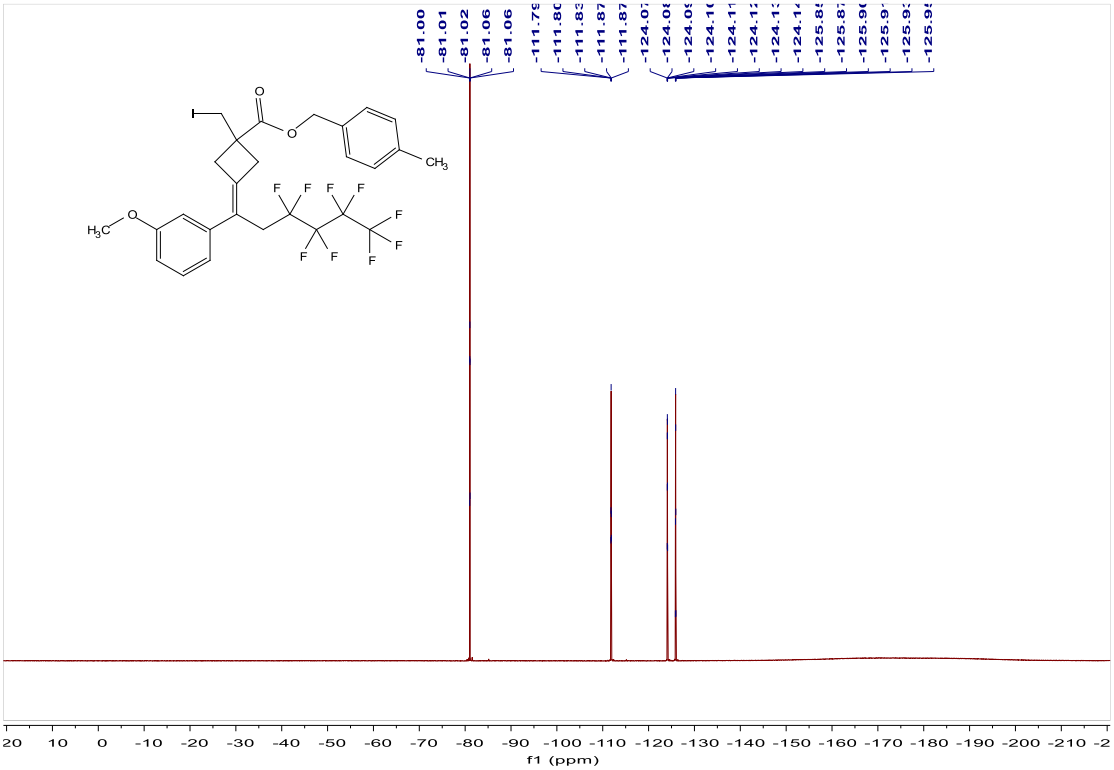
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **25**



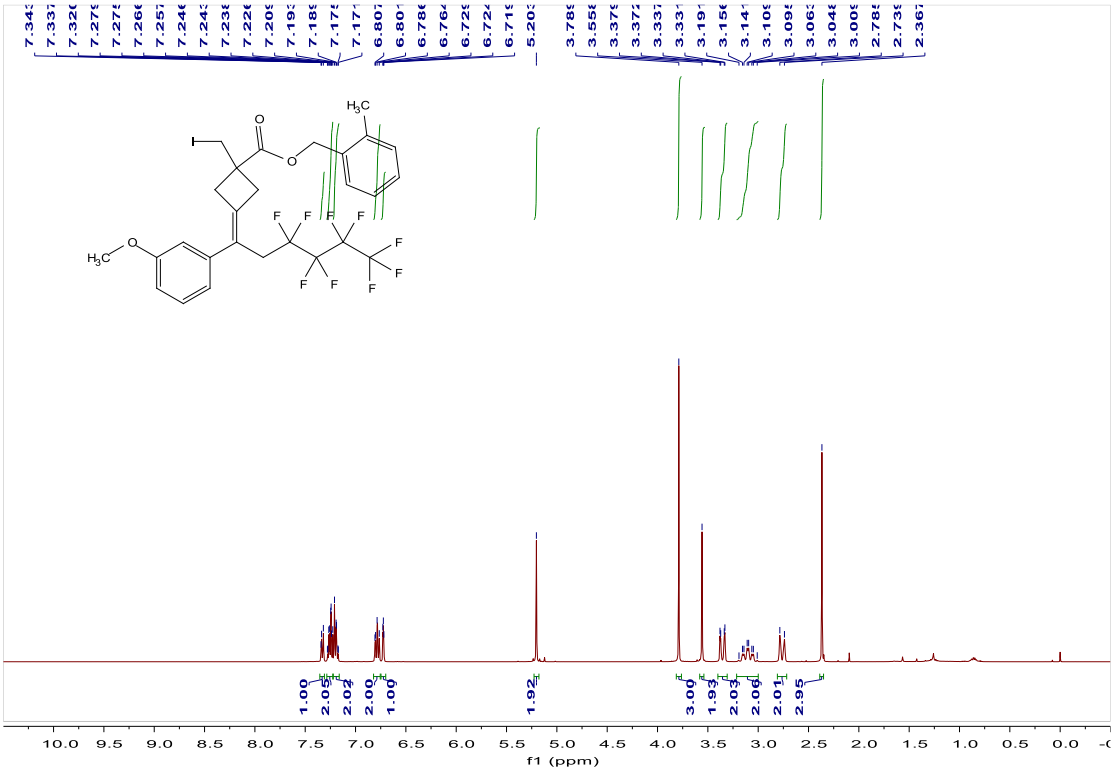
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **25**



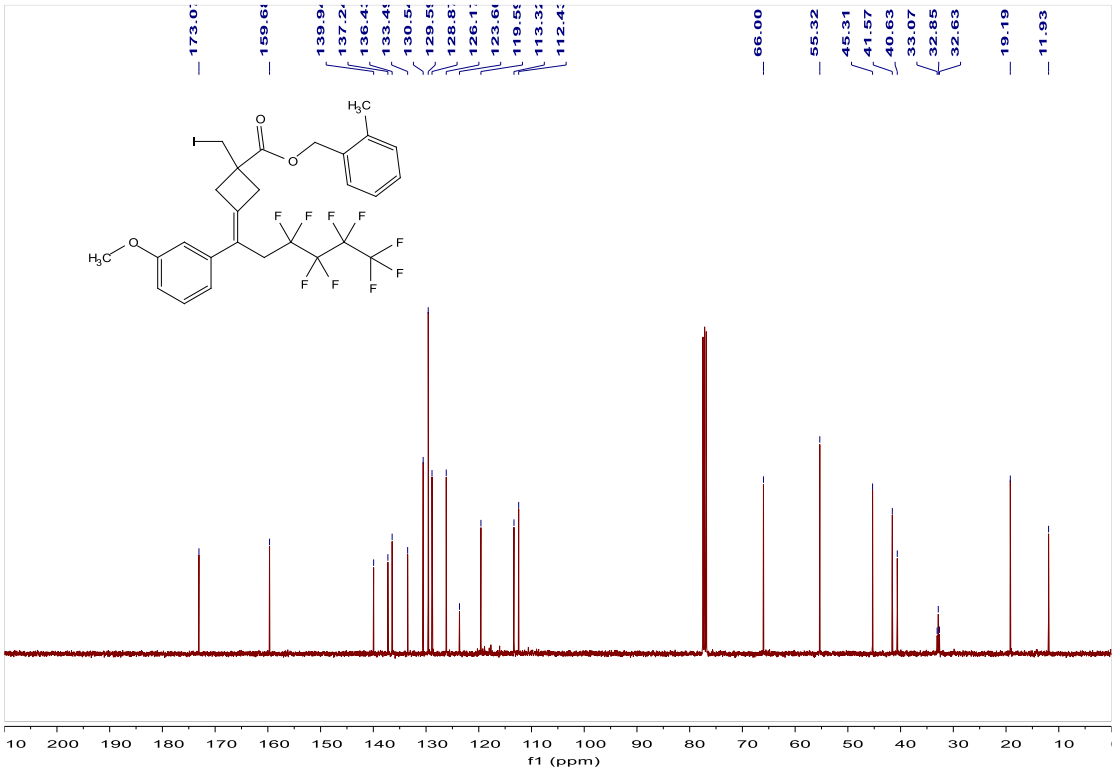
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **25**



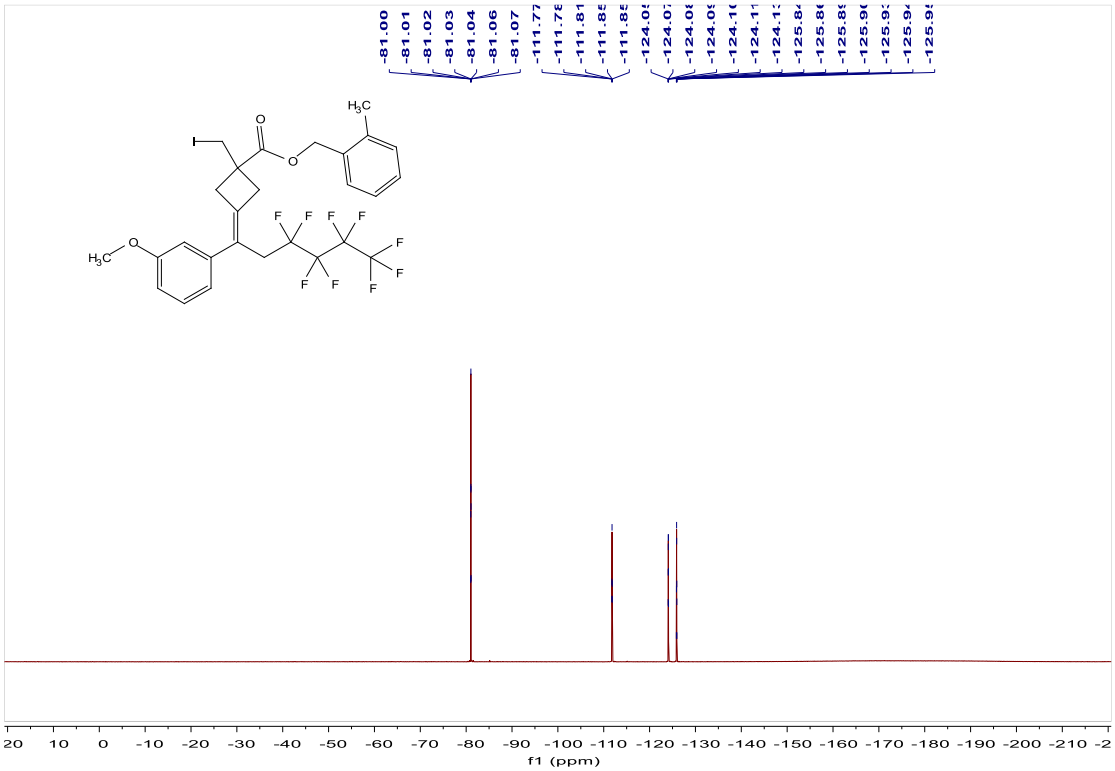
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **26**



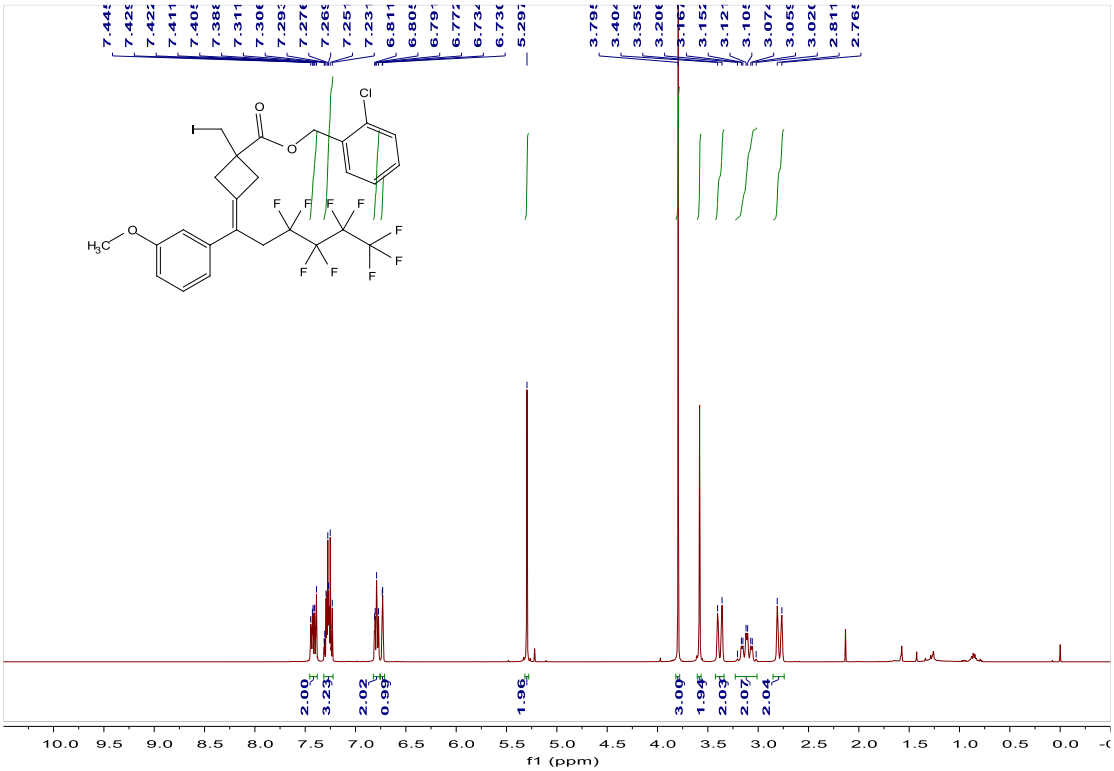
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **26**



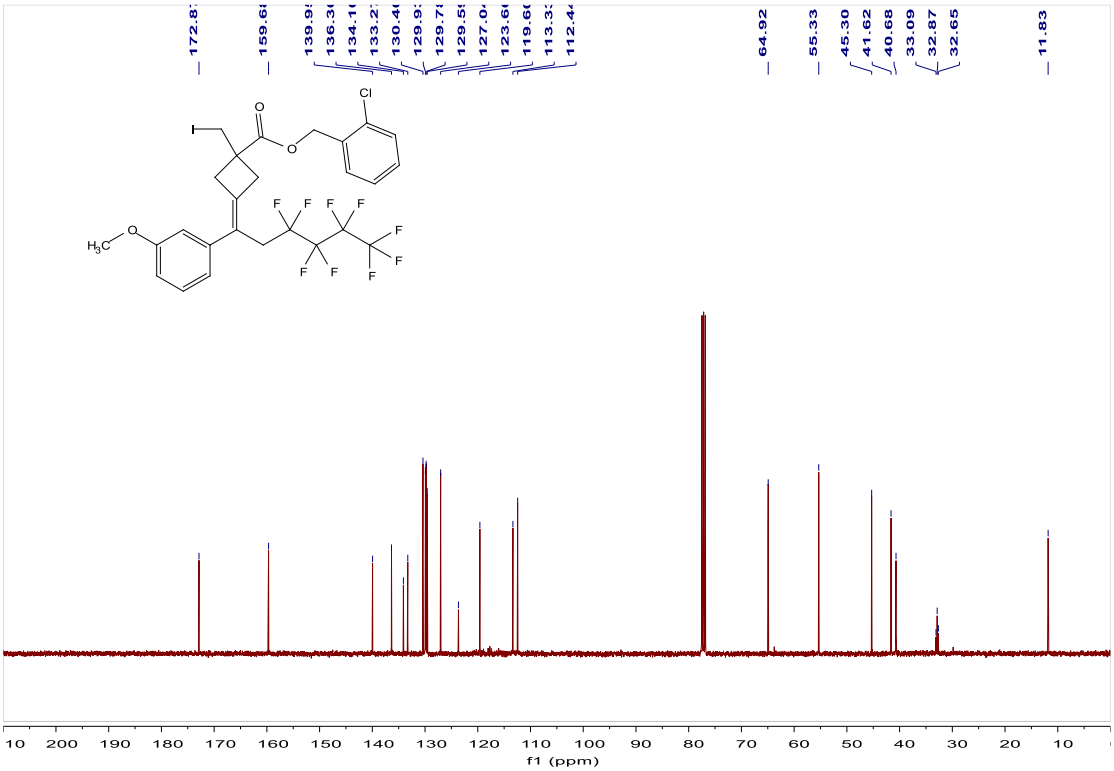
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **26**



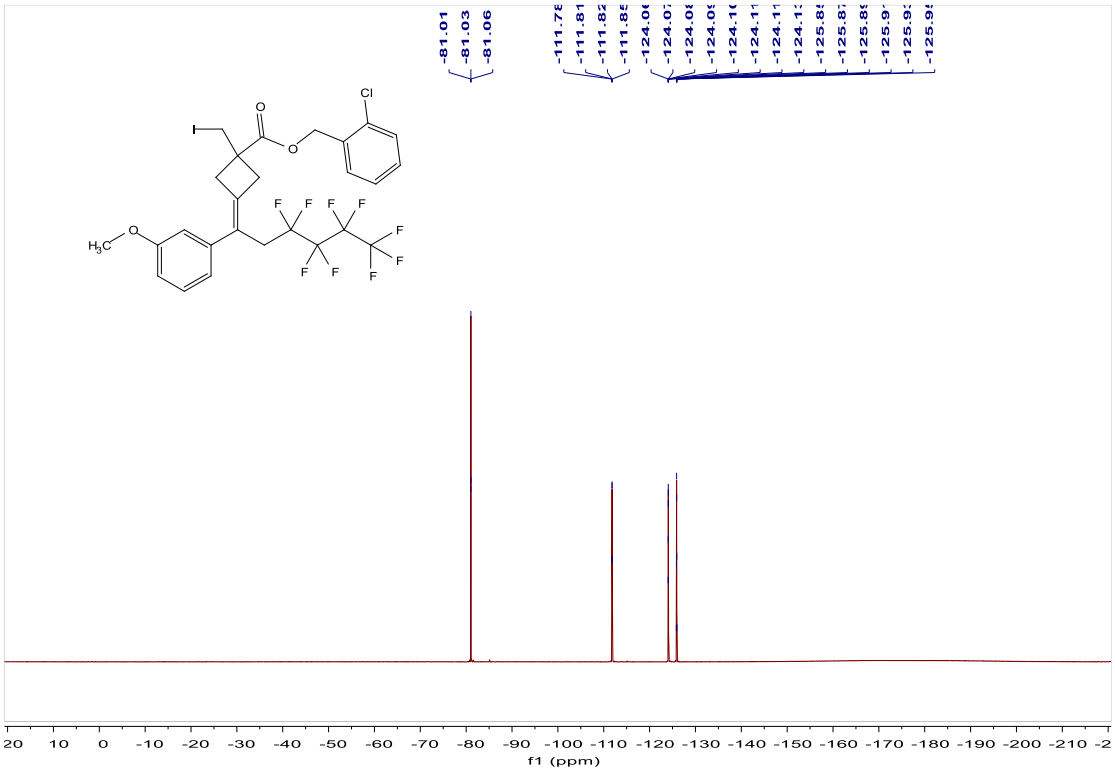
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **27**



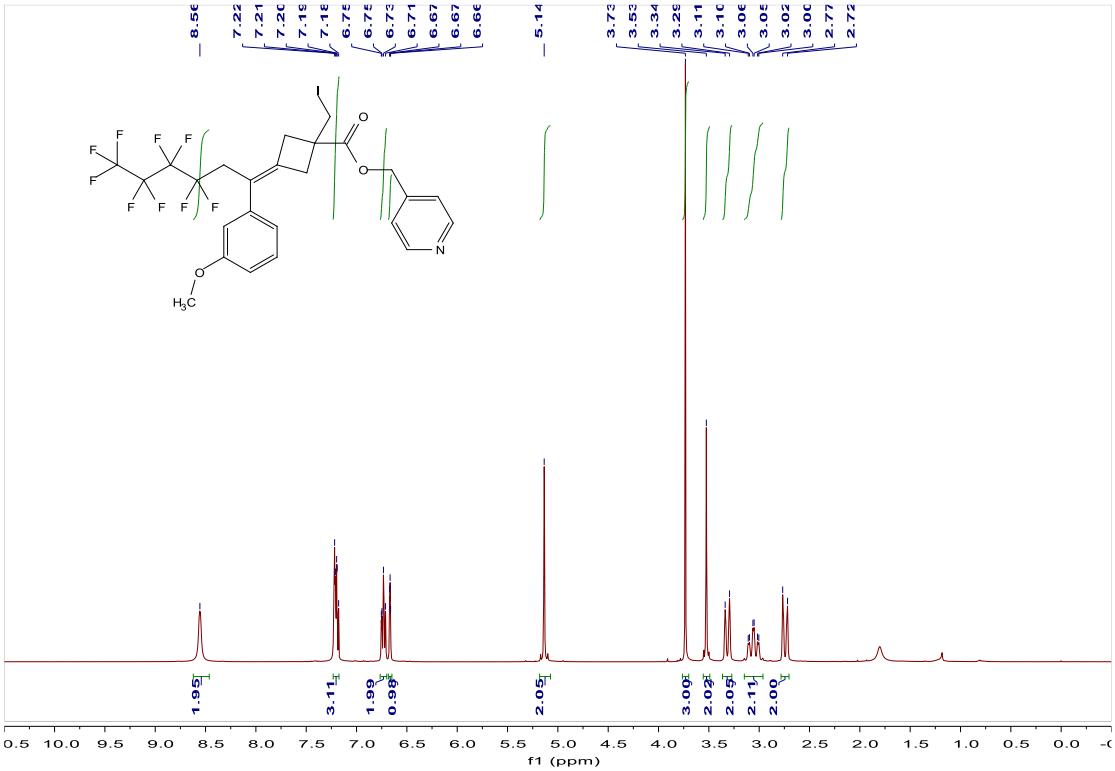
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **27**



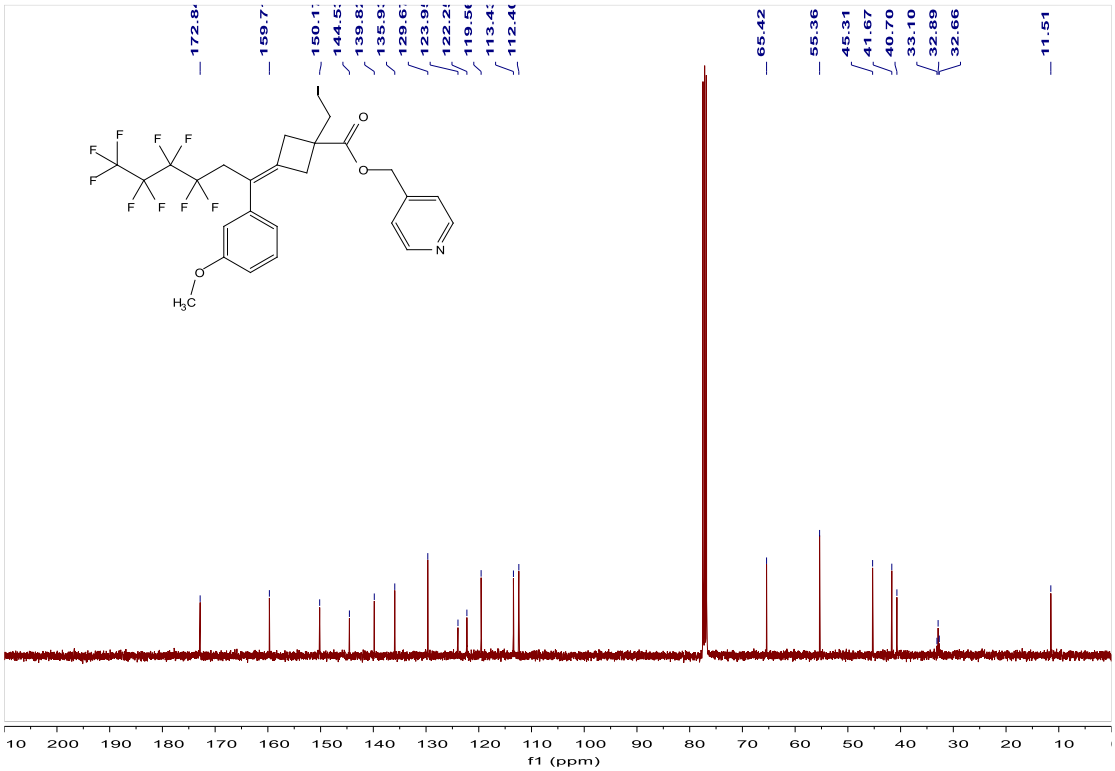
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **27**



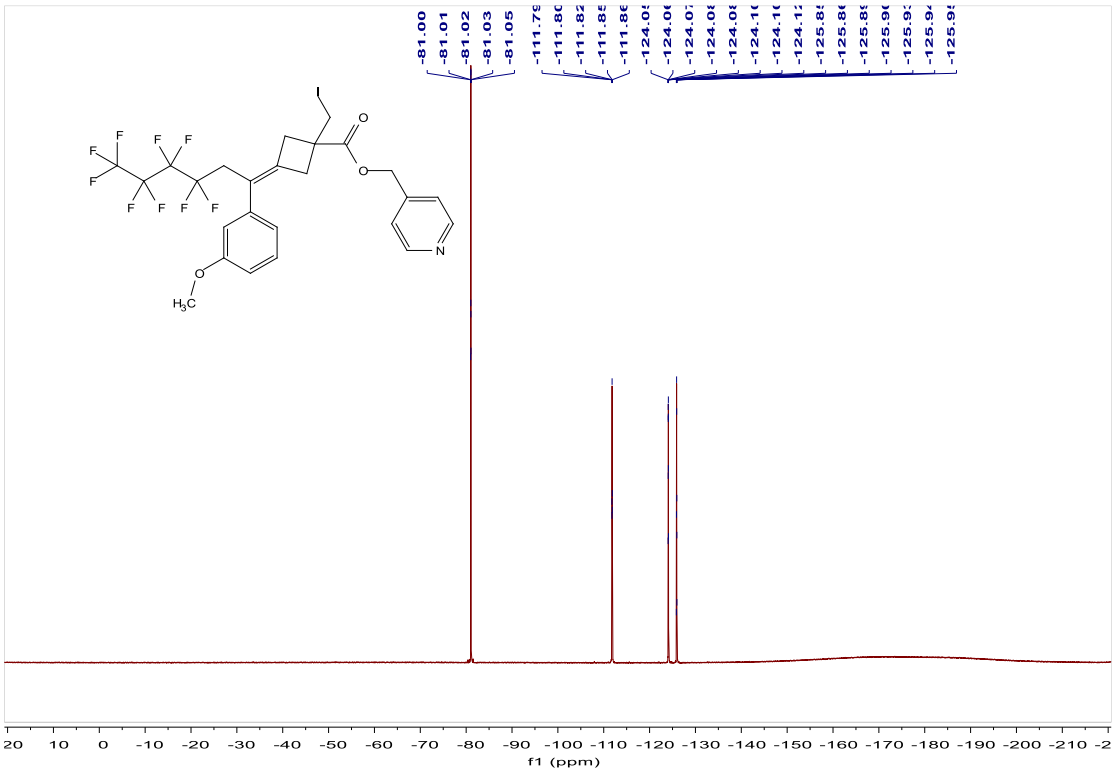
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **28**



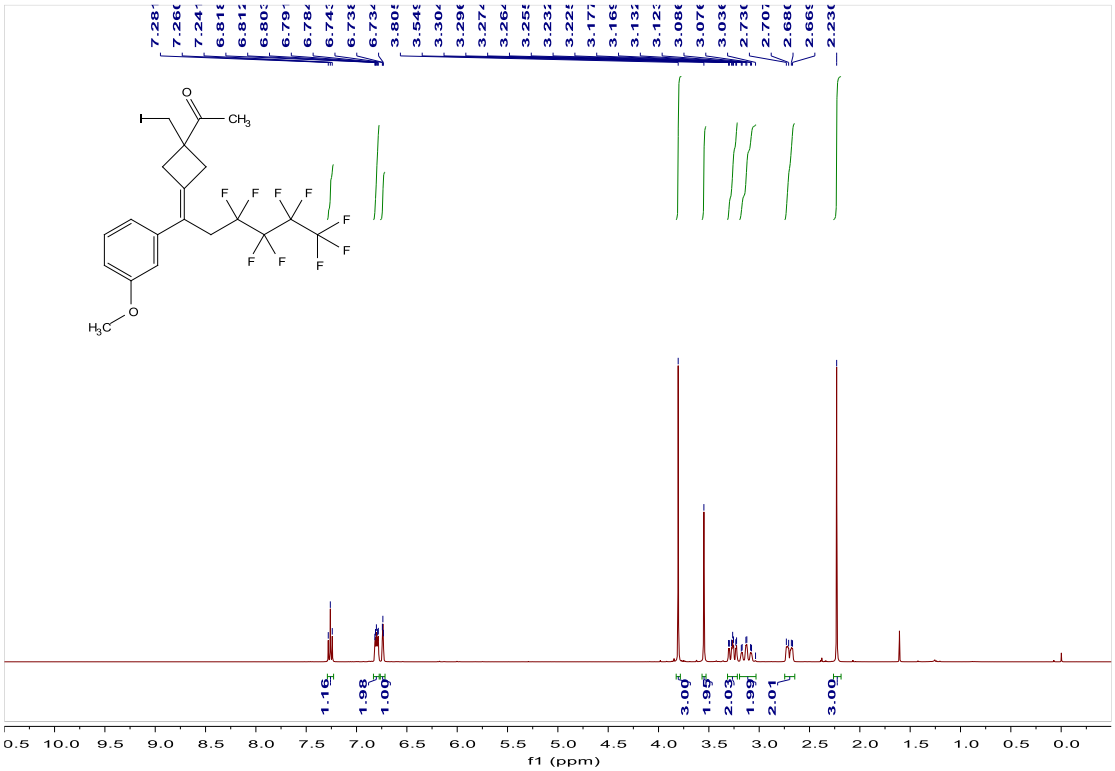
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **28**



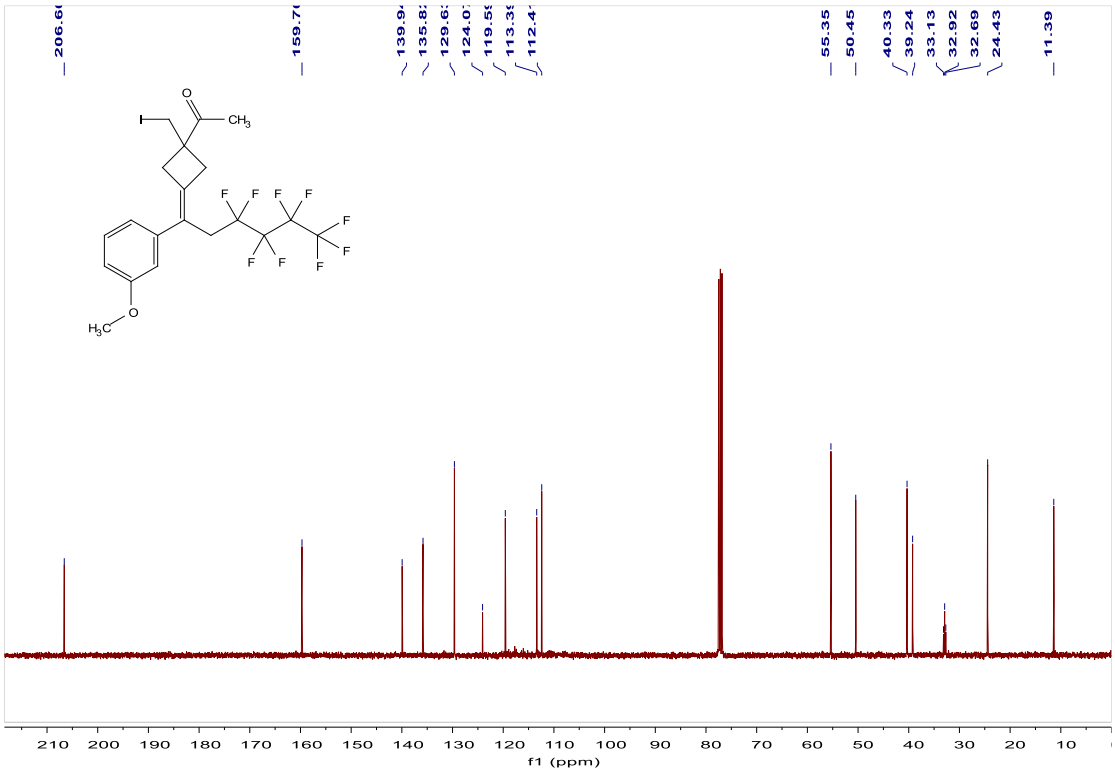
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **28**



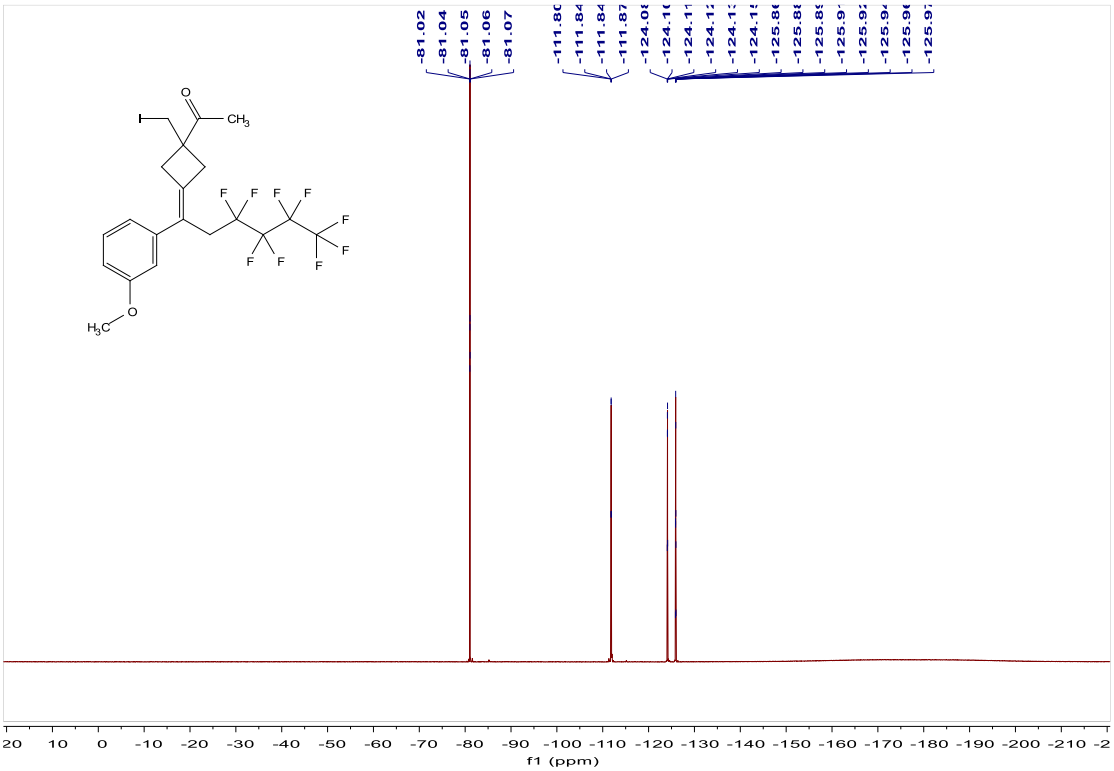
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **29**



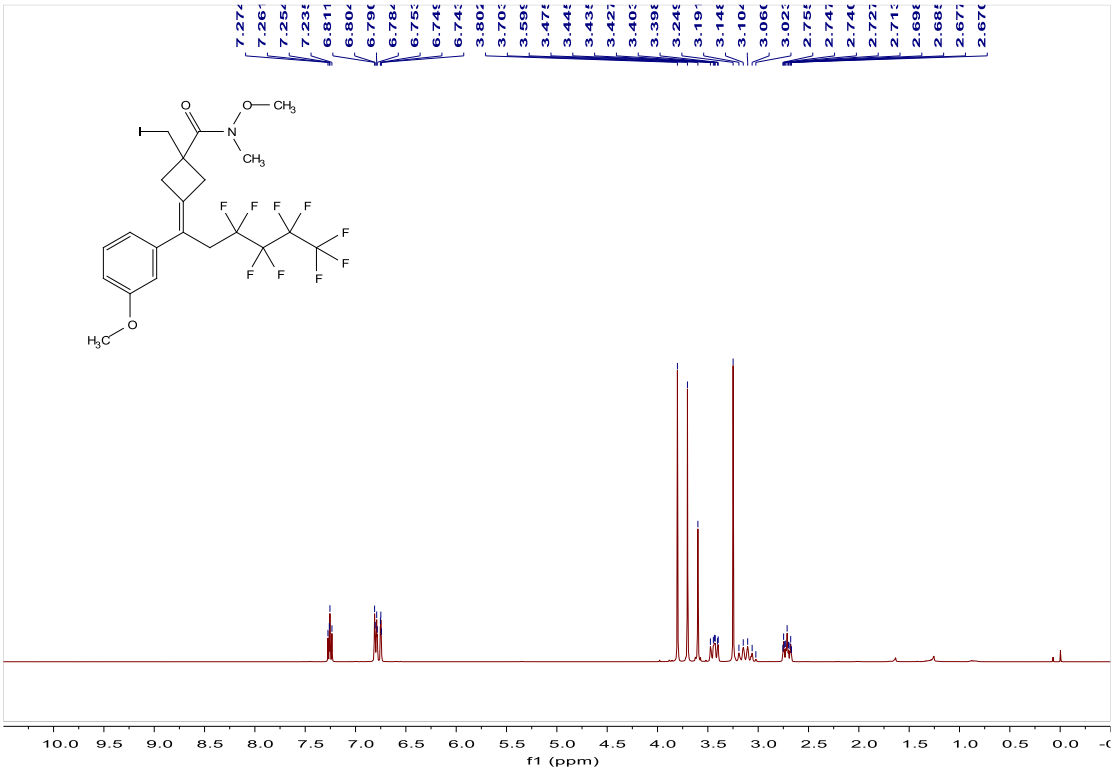
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **29**



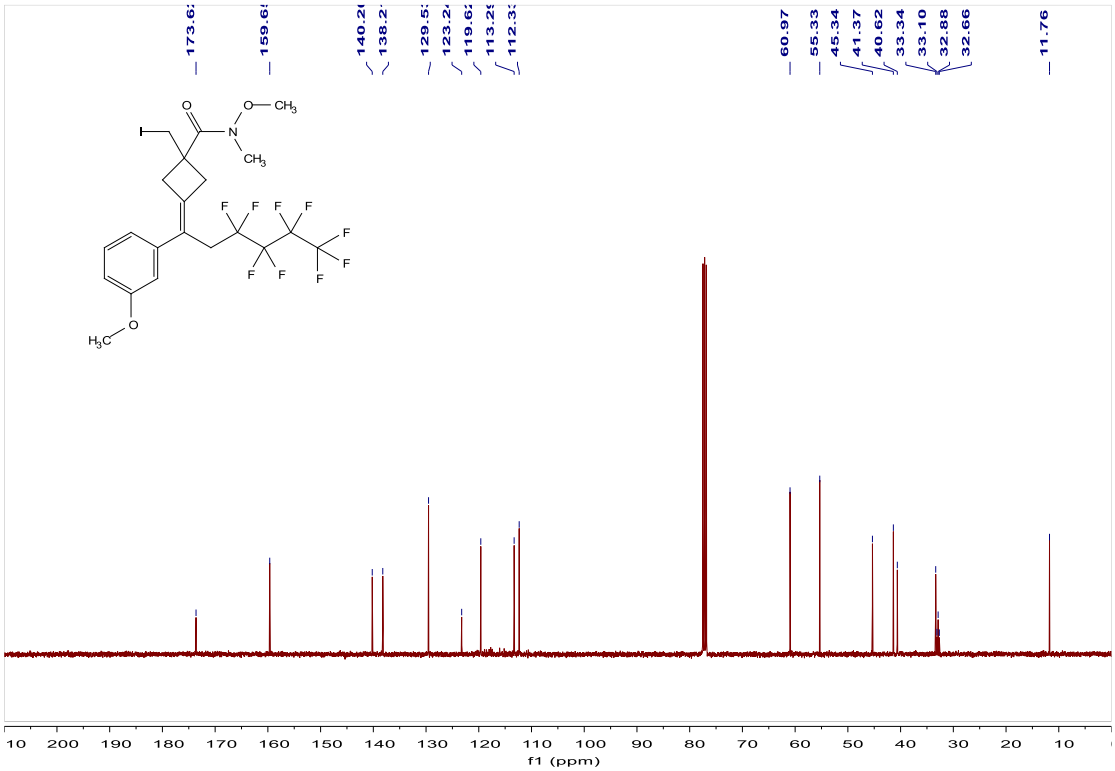
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **29**



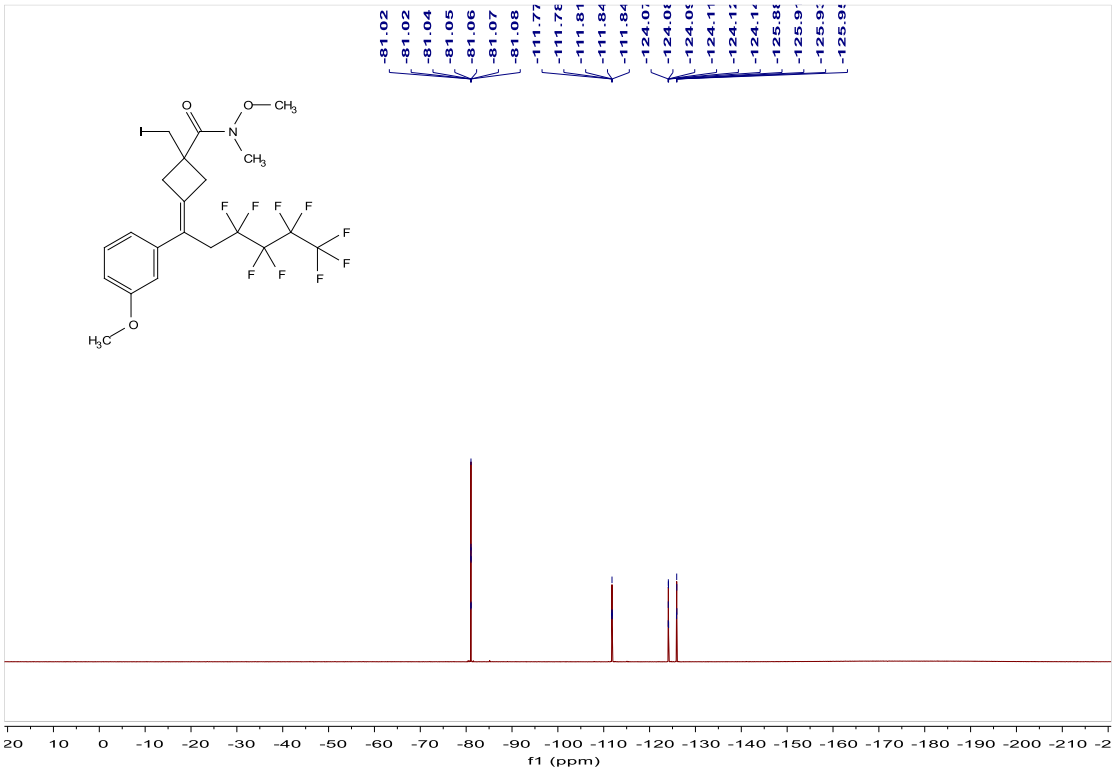
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **30**



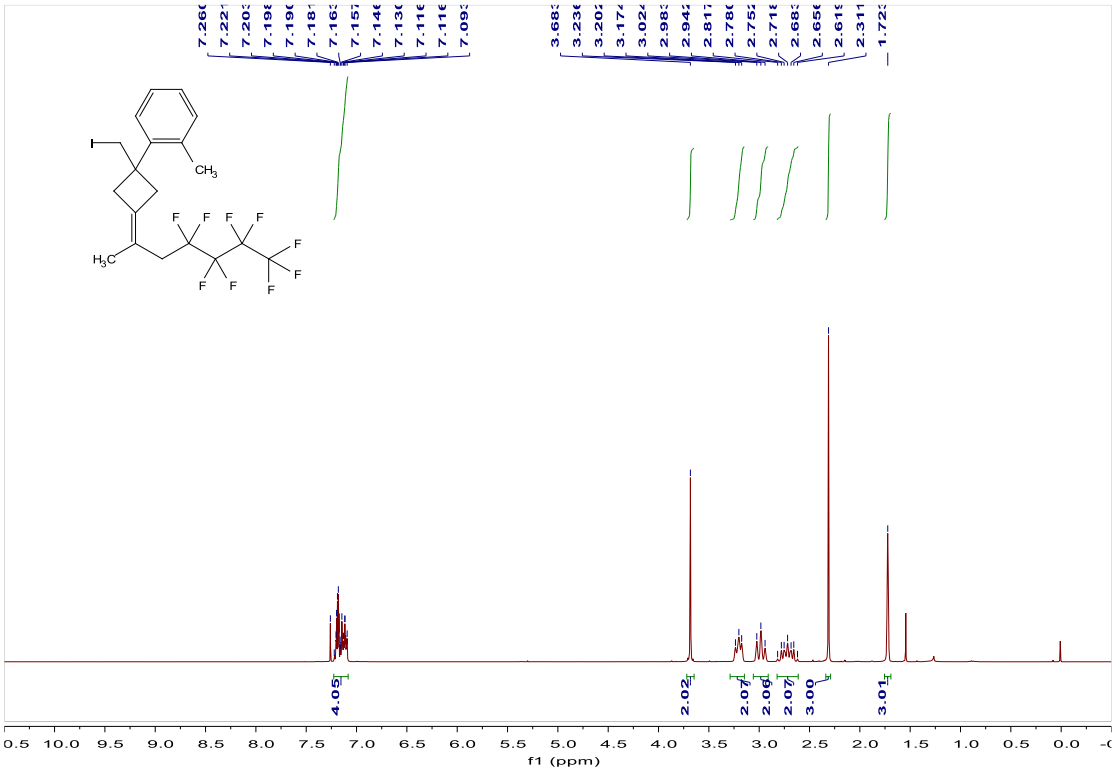
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **30**



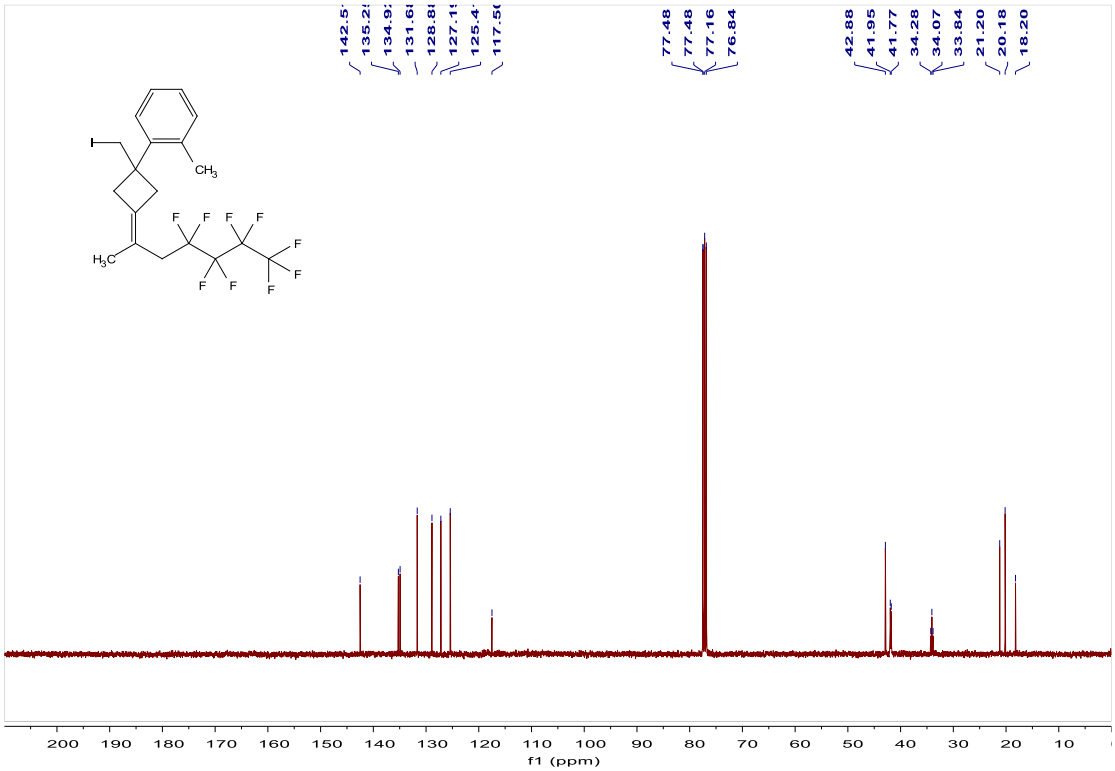
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **30**



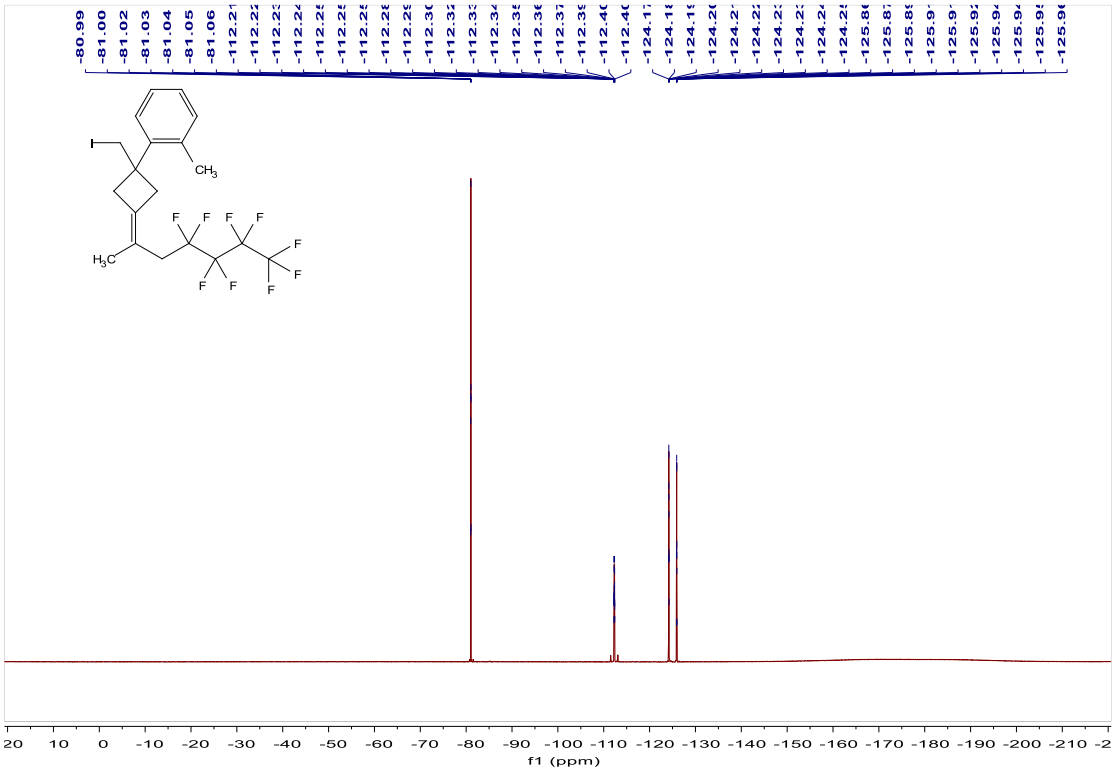
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **31**



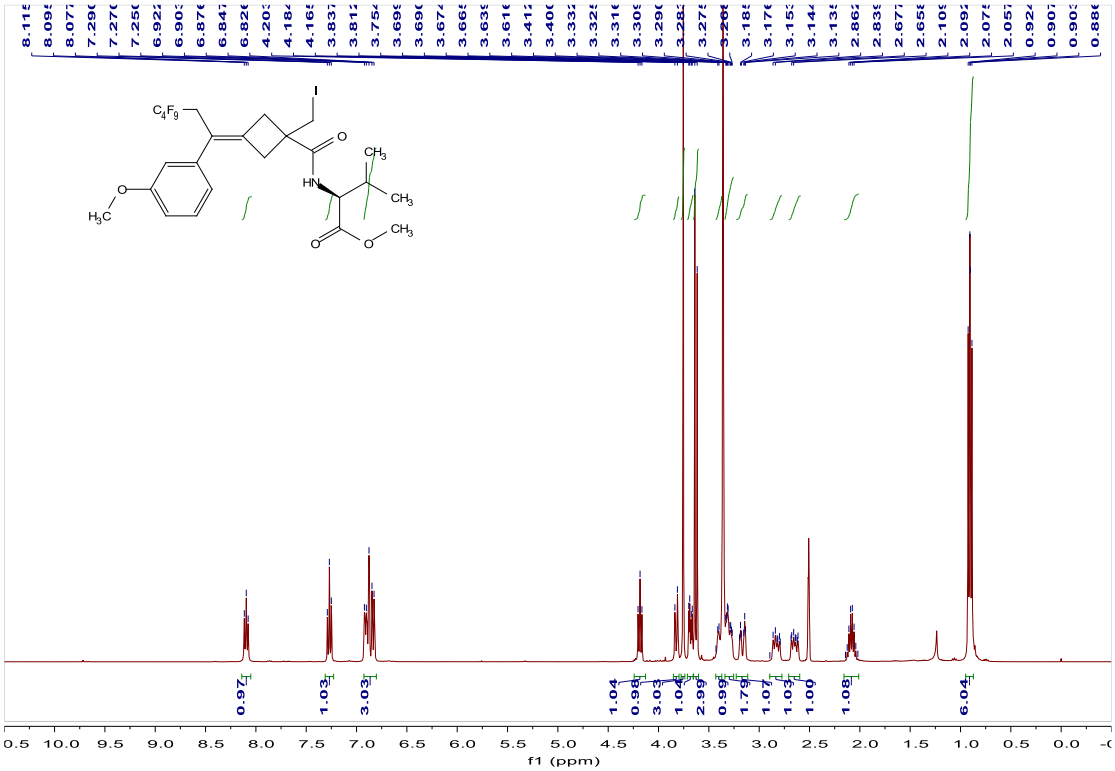
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **31**



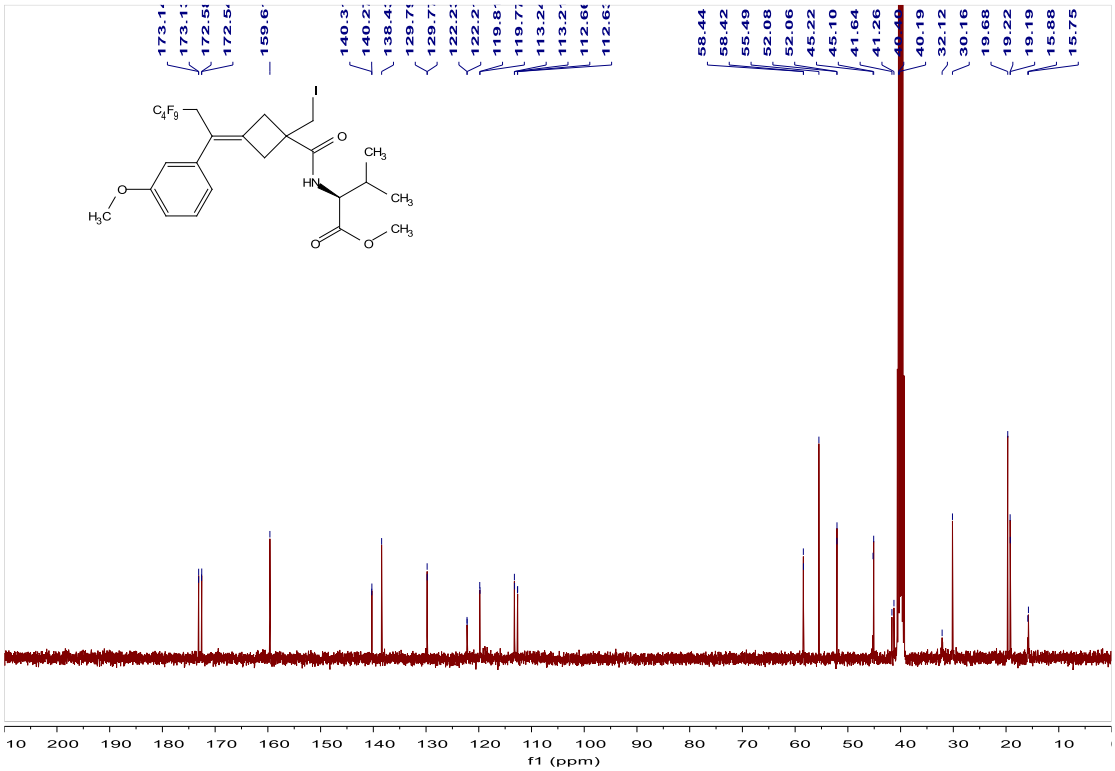
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **31**



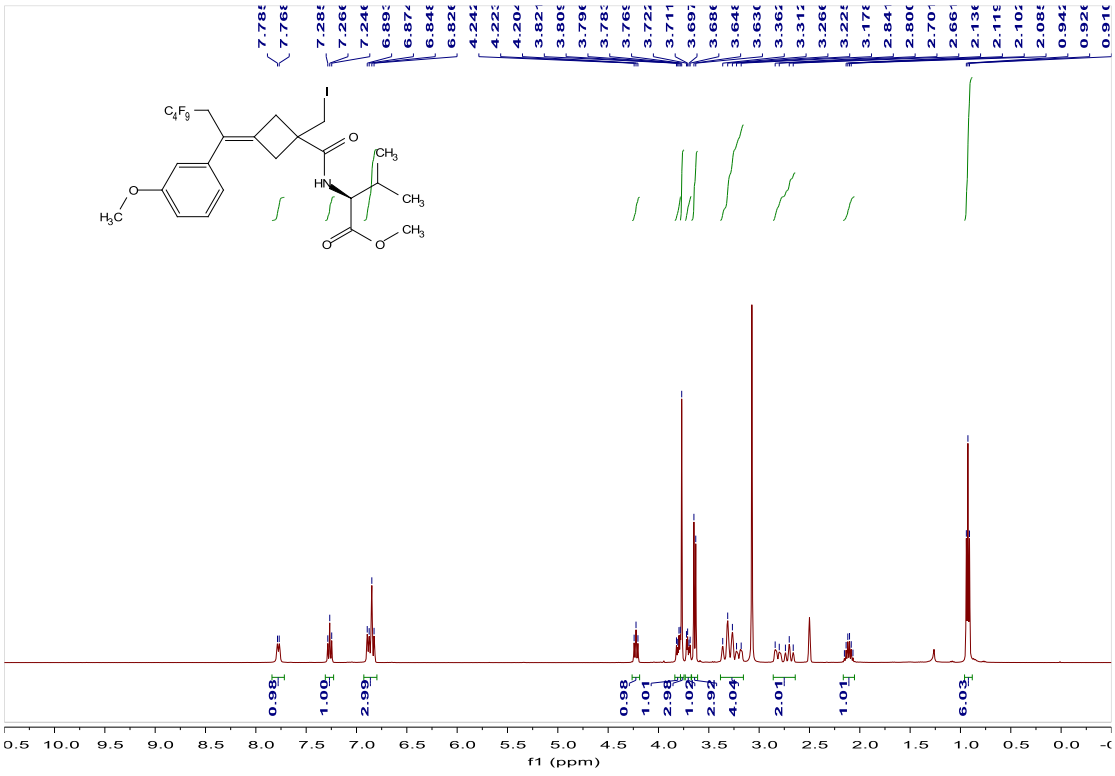
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **32**



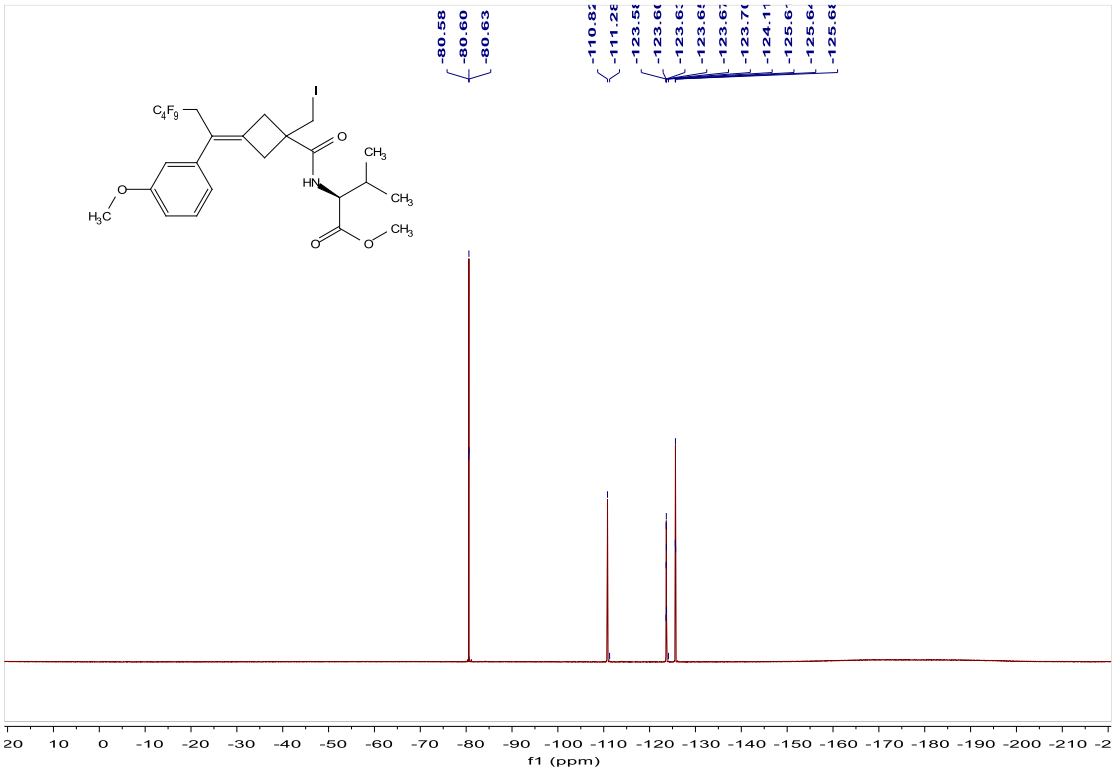
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **32**



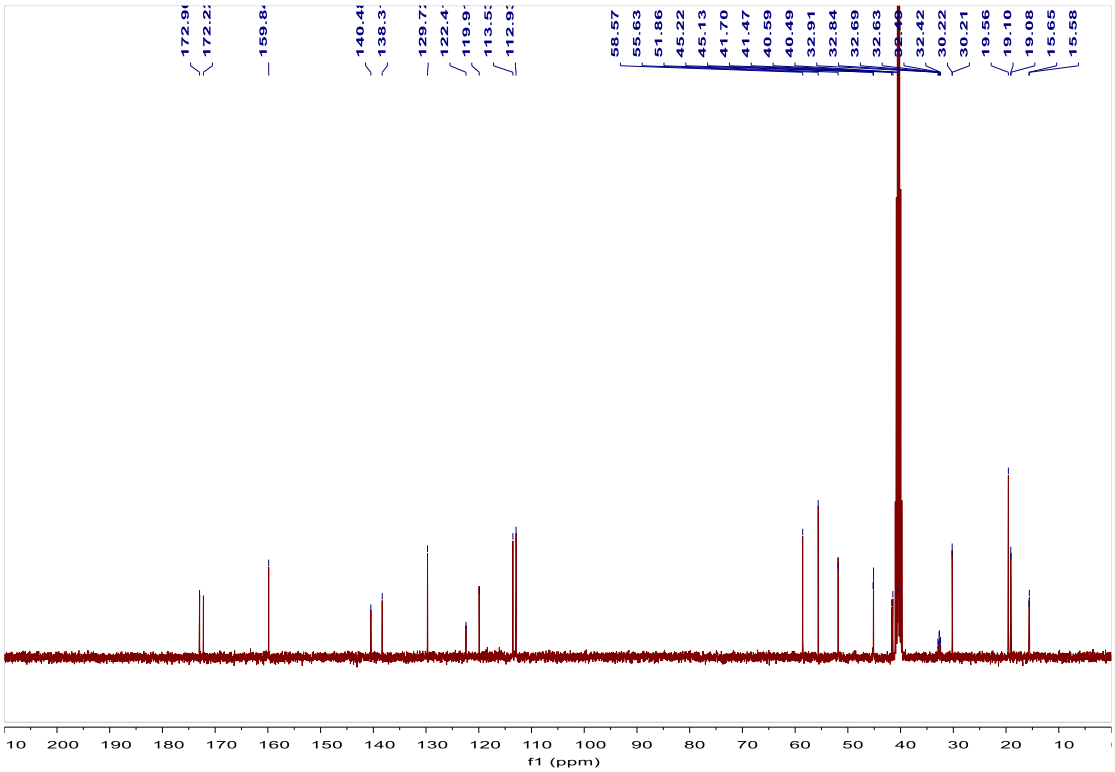
^{1}H NMR (400 MHz, DMSO-d_6, 80 ℃) spectrum of **32**



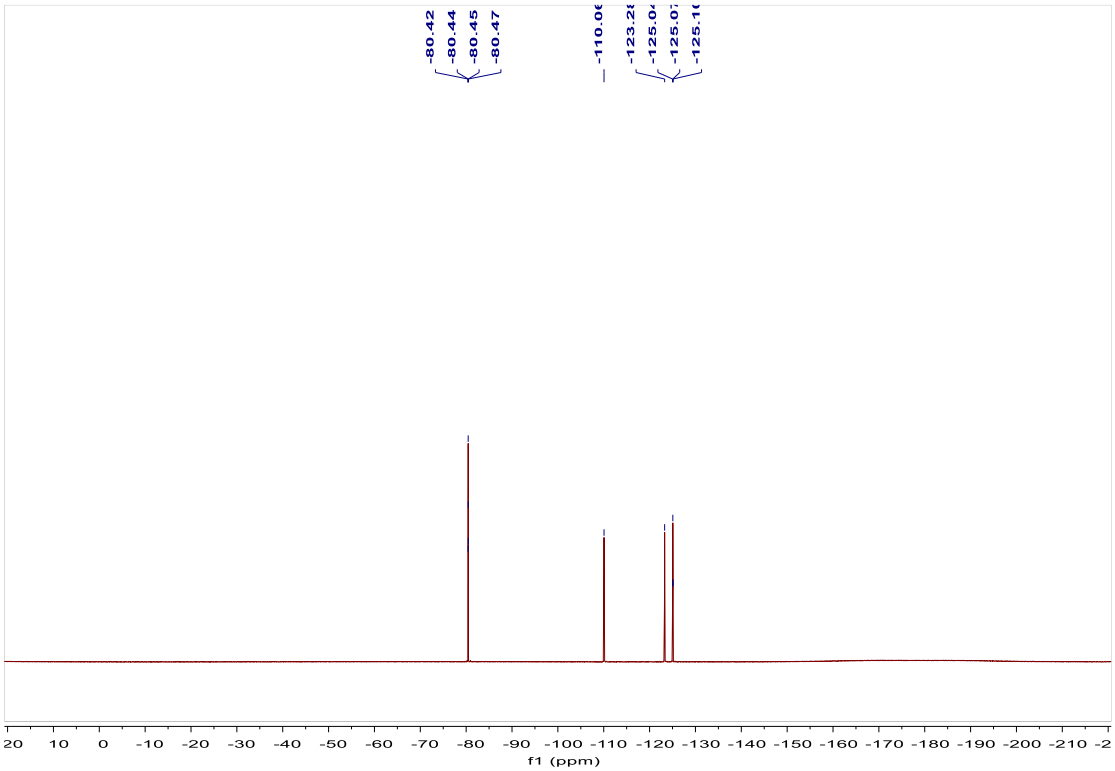
^{19}F NMR (376 MHz, DMSO-d_6) spectrum of **32**



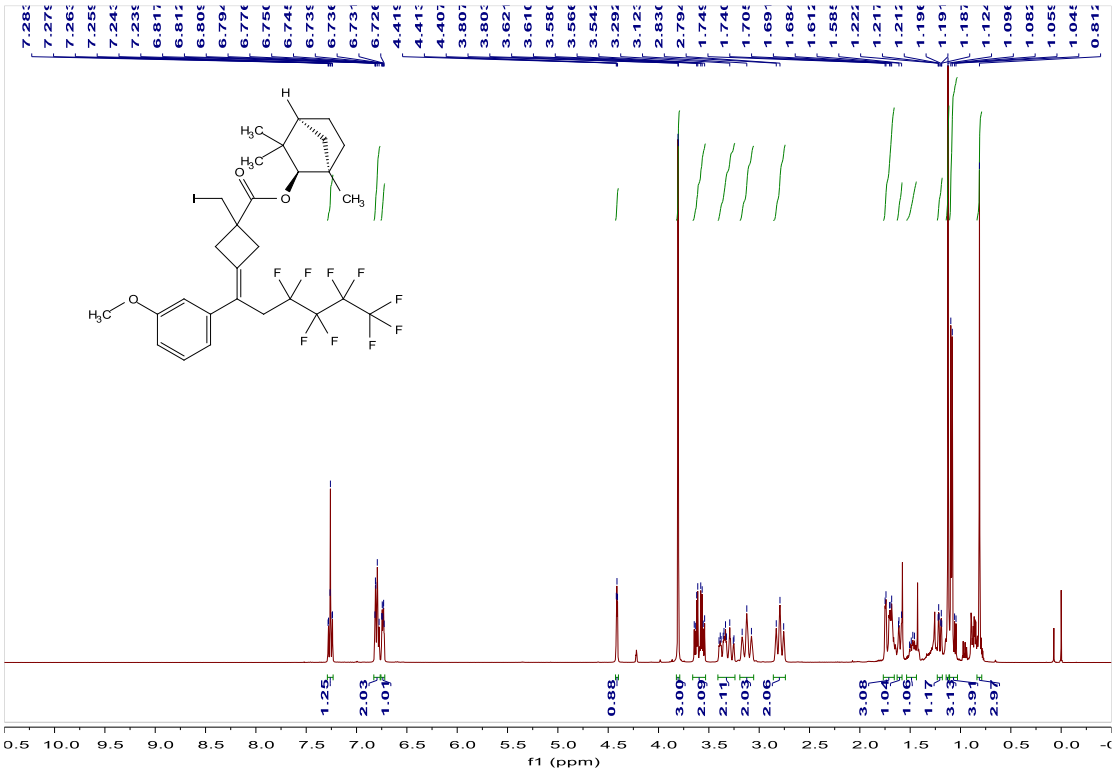
^{13}C NMR (100 MHz, DMSO-d_6, 80 ℃) spectrum of **32**



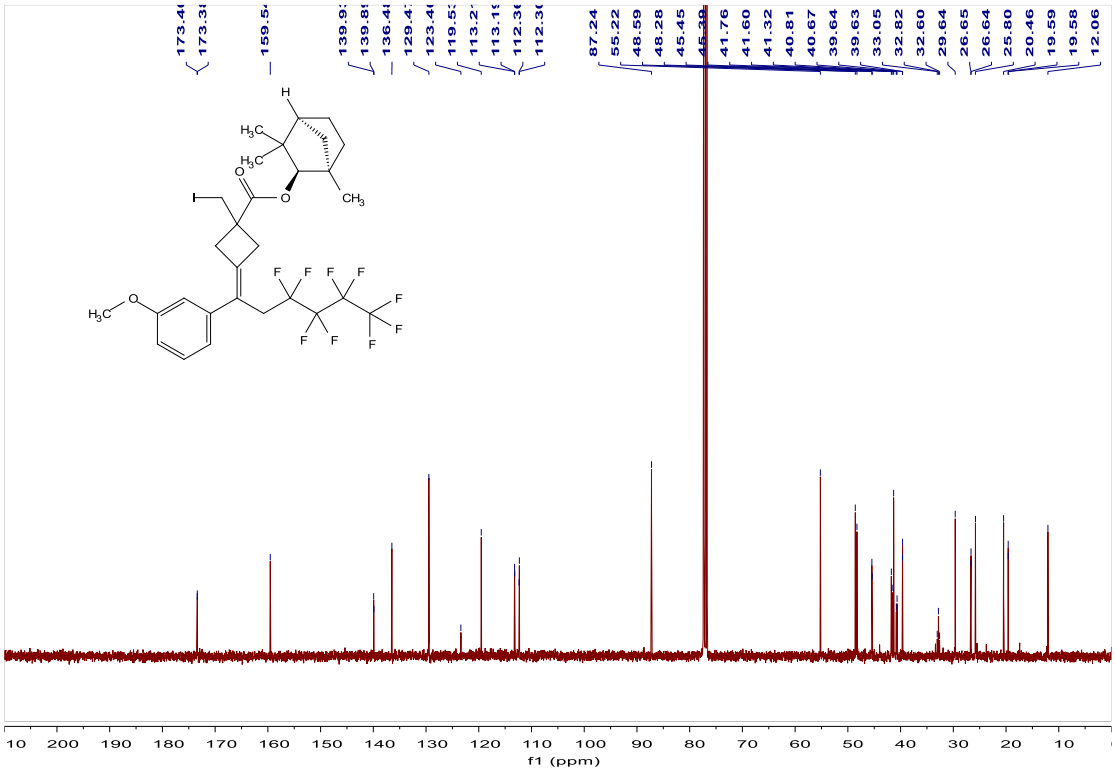
^{19}F NMR (376 MHz, DMSO-d_6, 80 ℃) spectrum of **32**



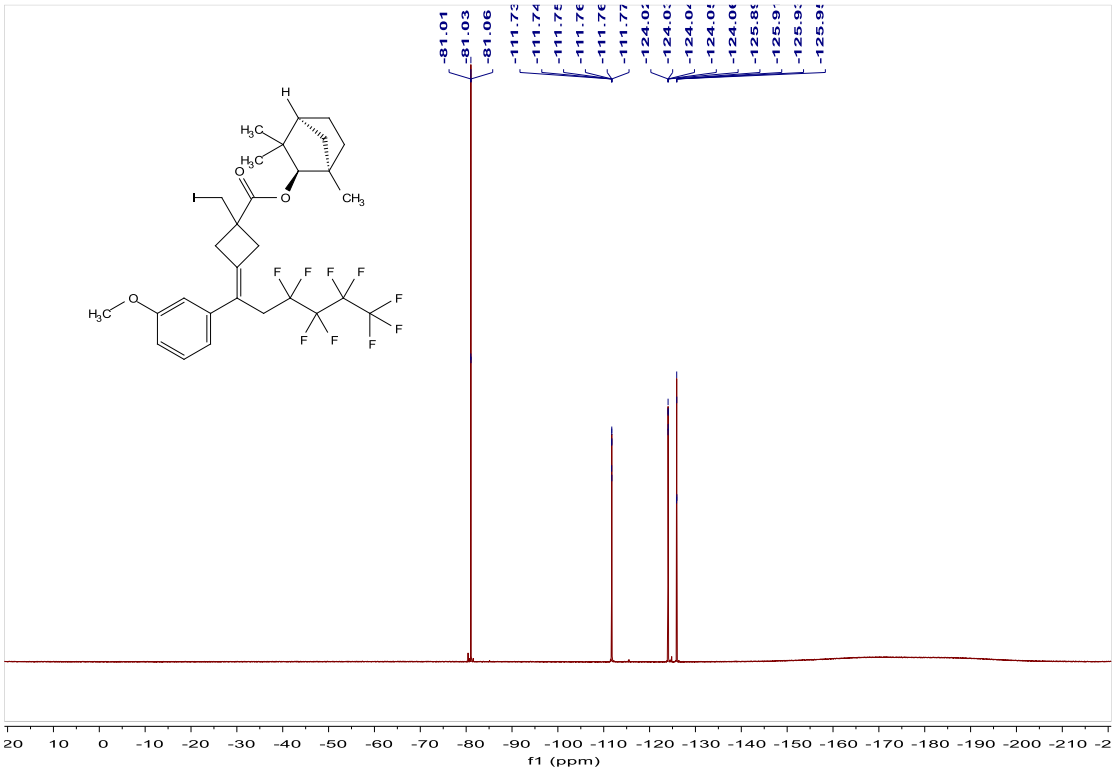
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **33**



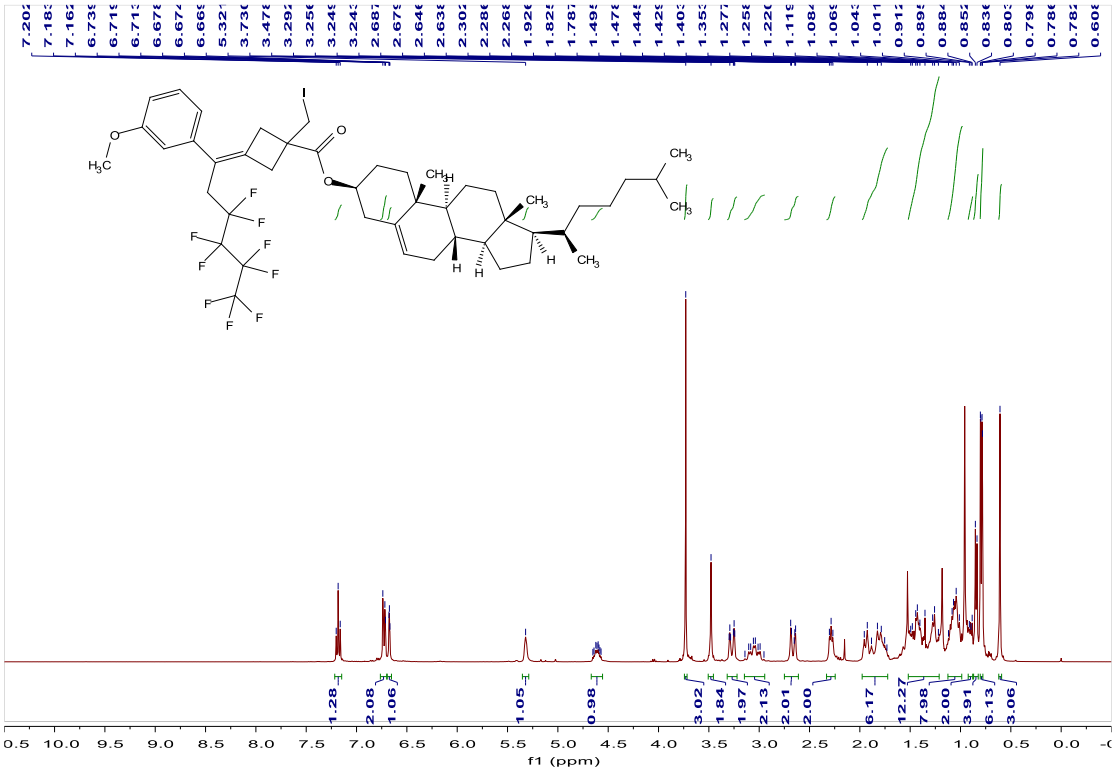
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **33**



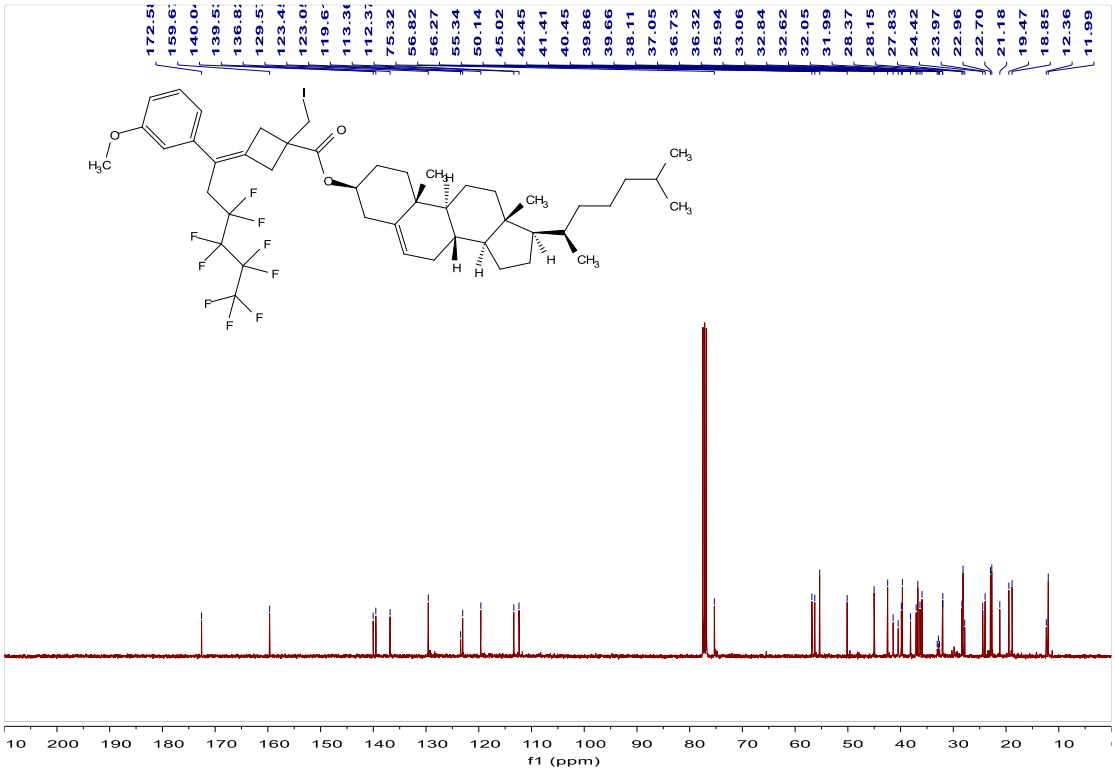
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **33**



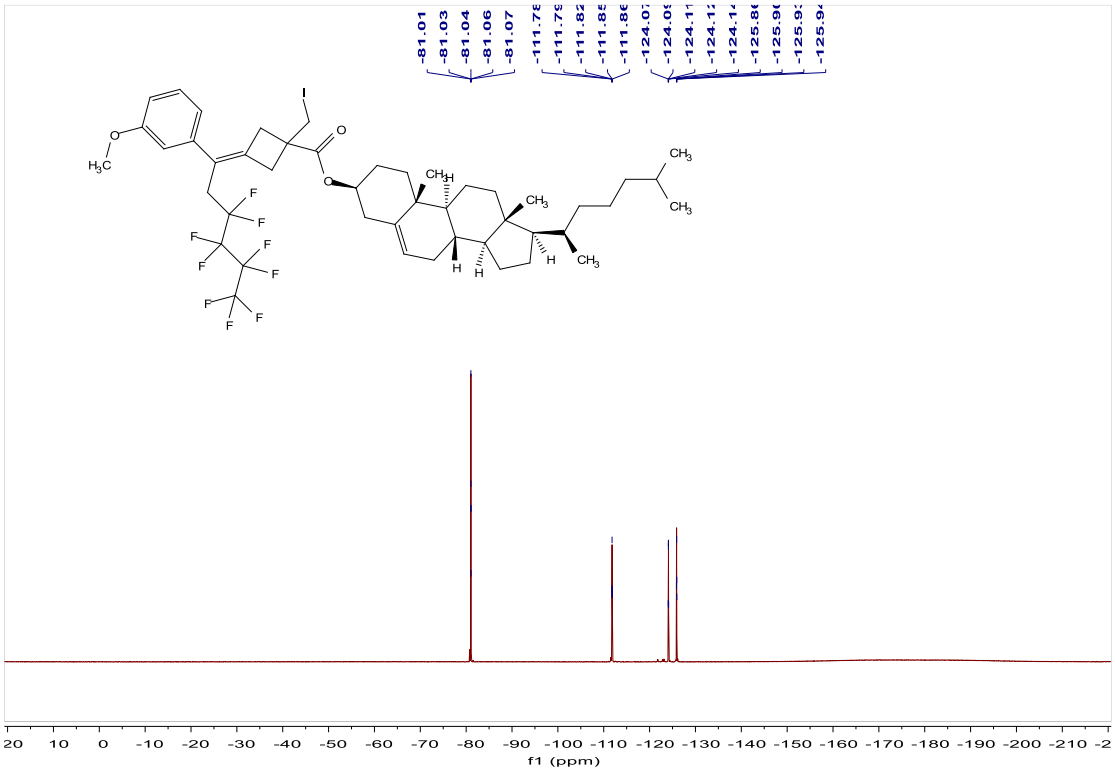
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **34**



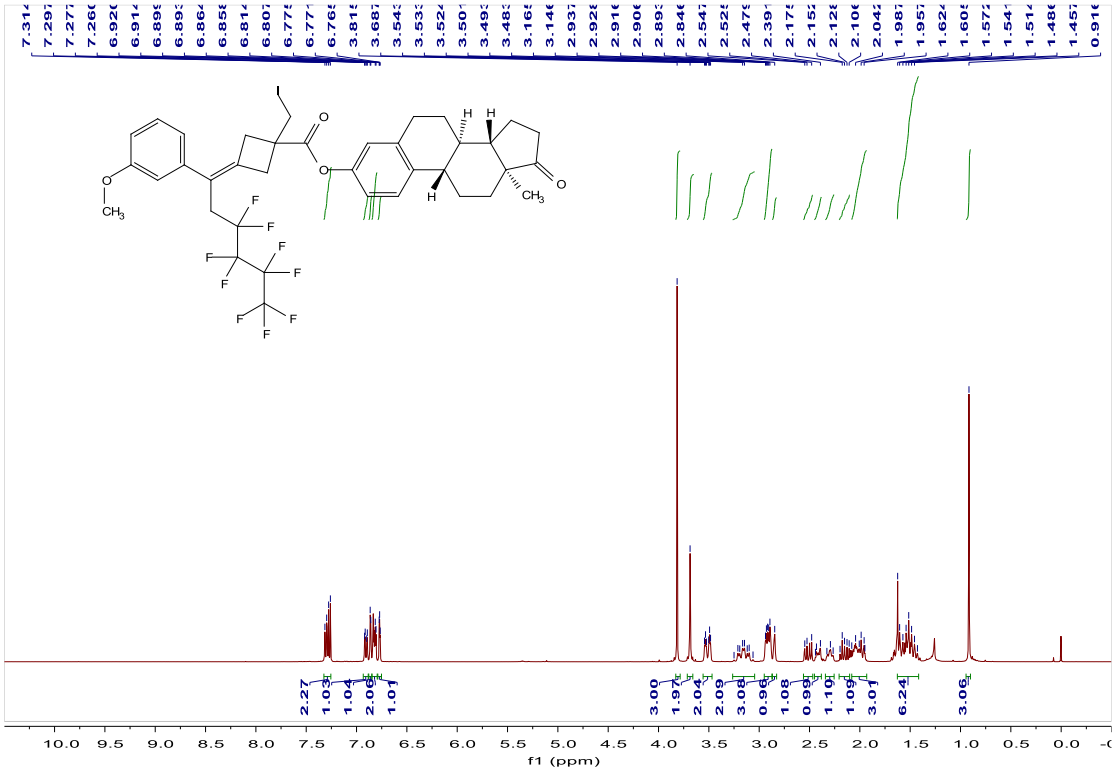
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **34**



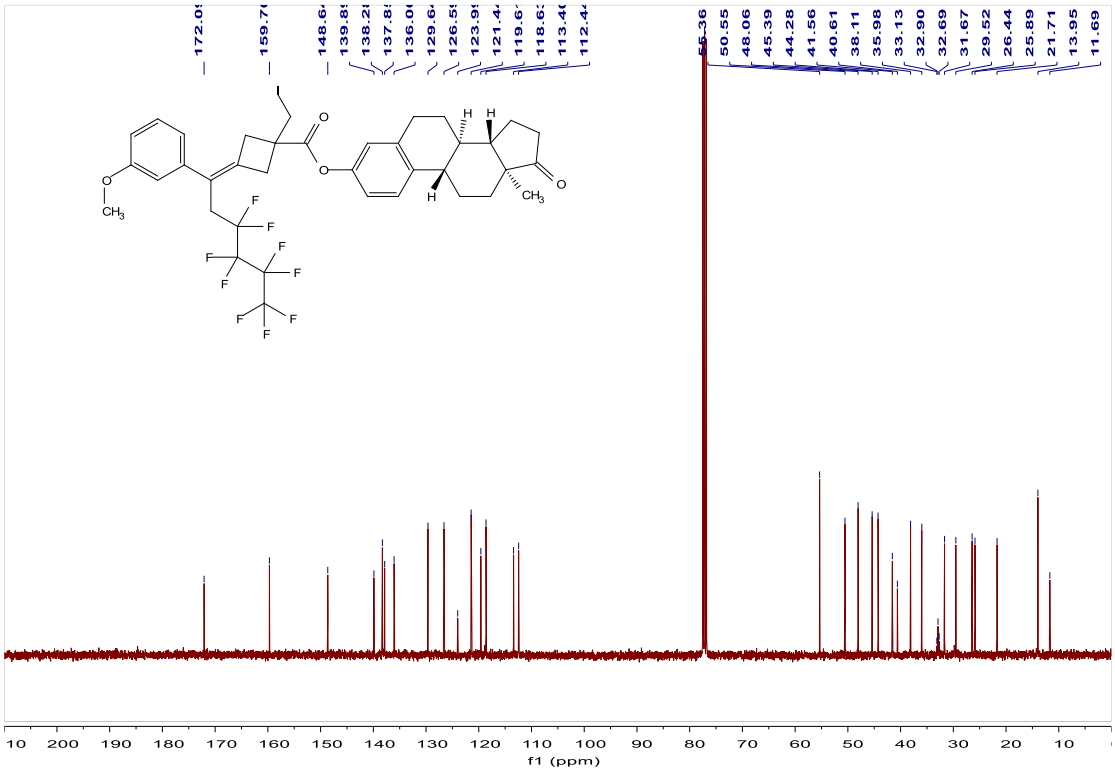
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **34**



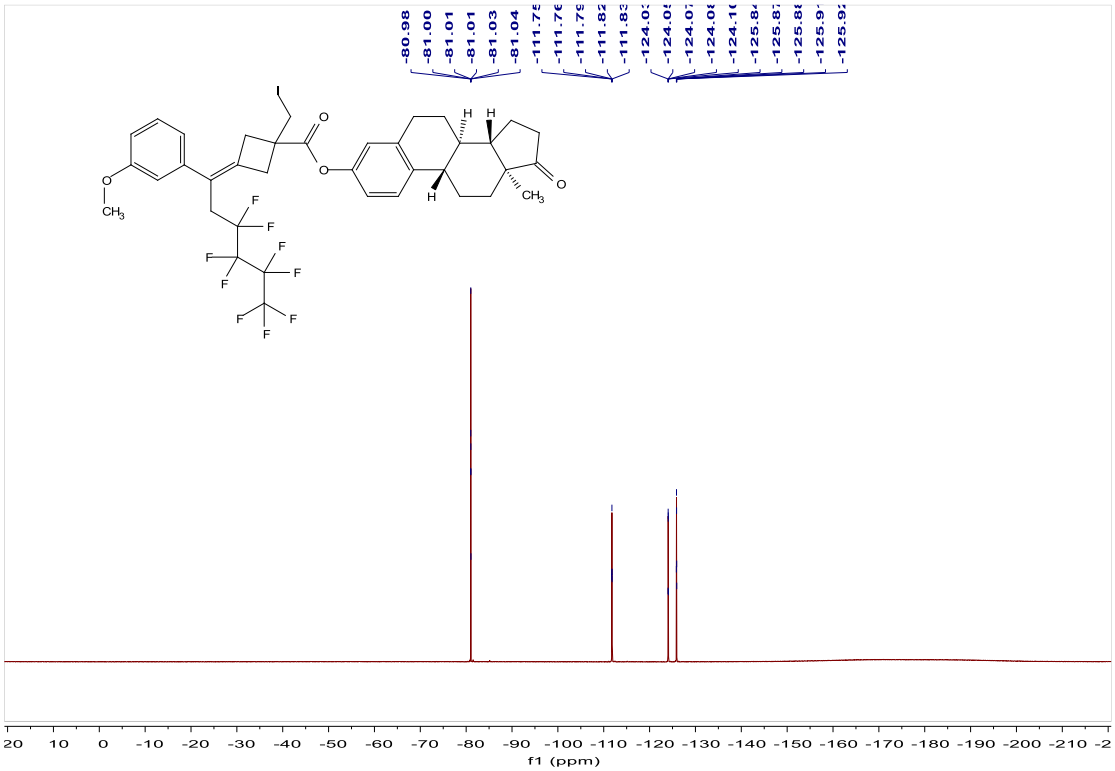
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **35**



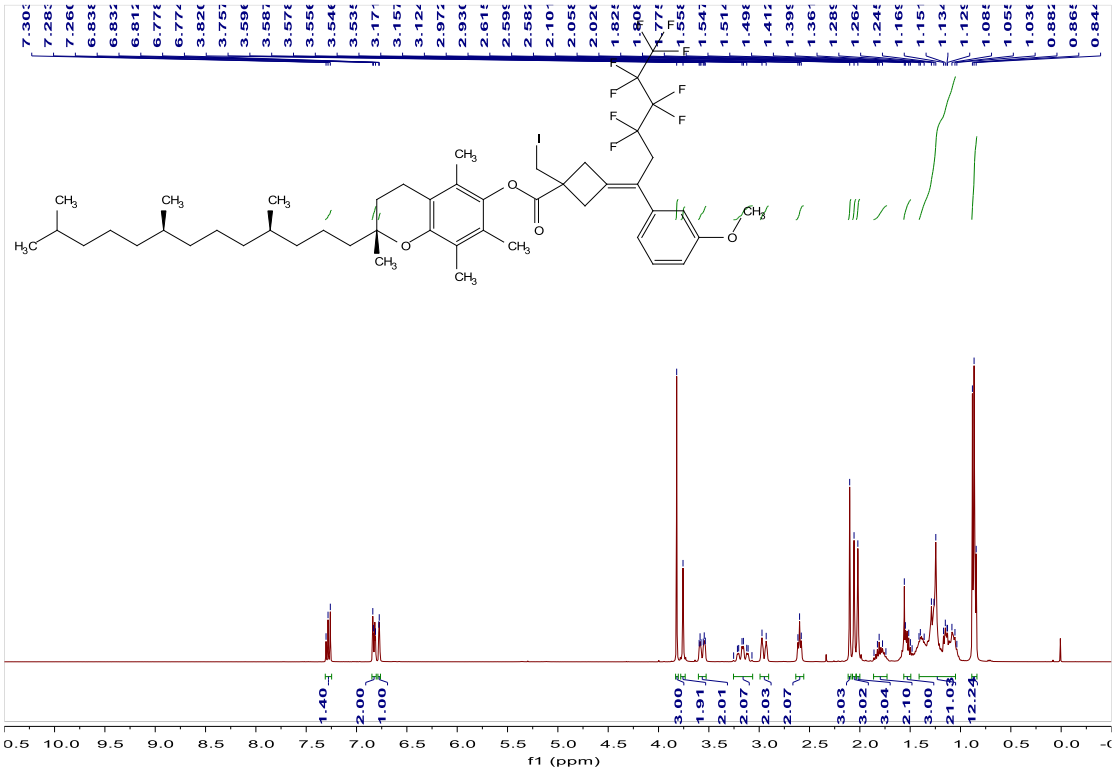
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **35**



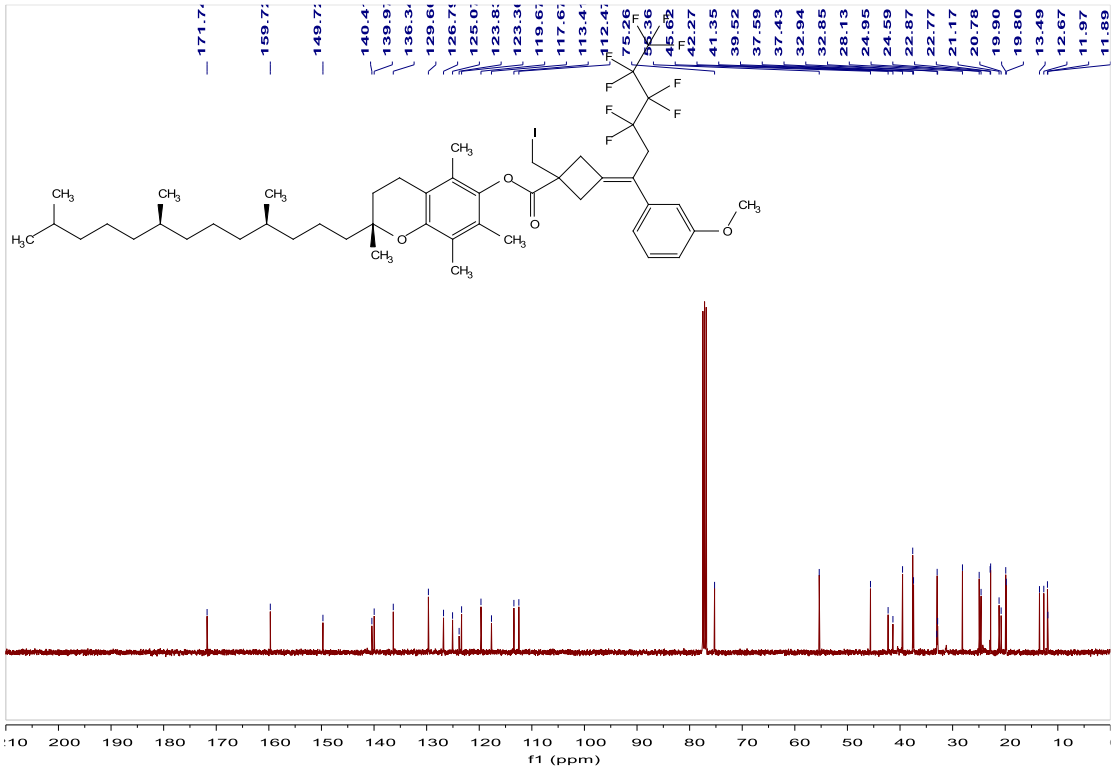
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **35**



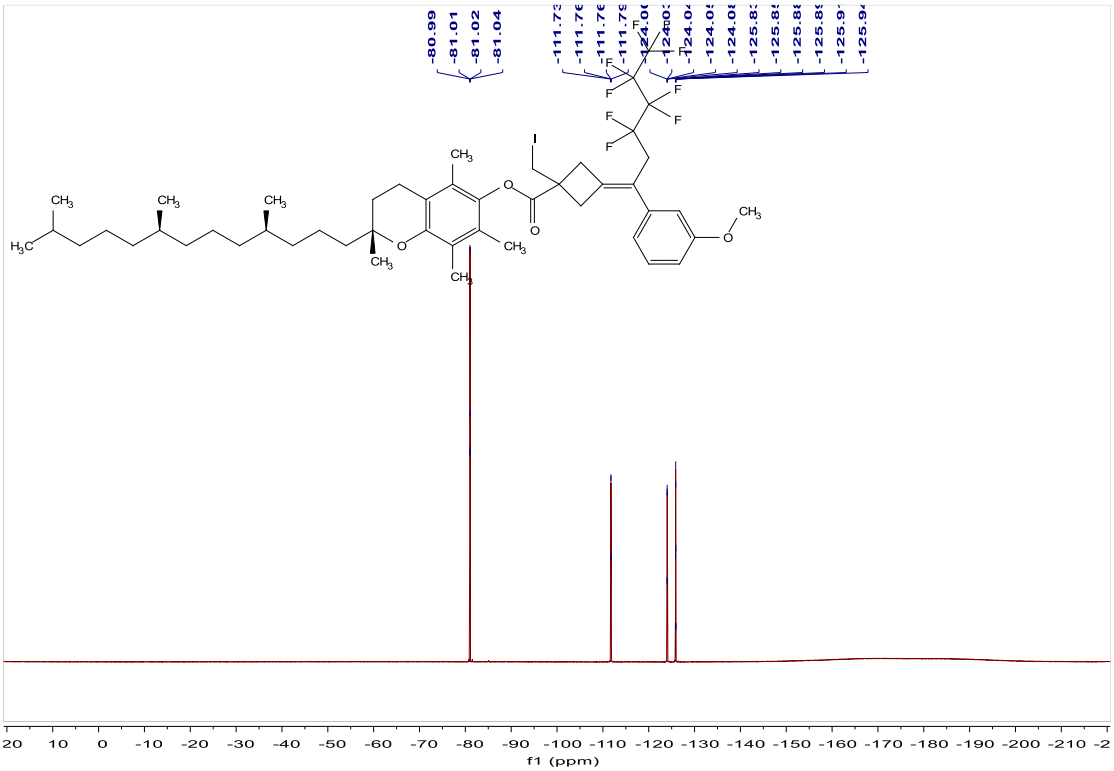
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **36**



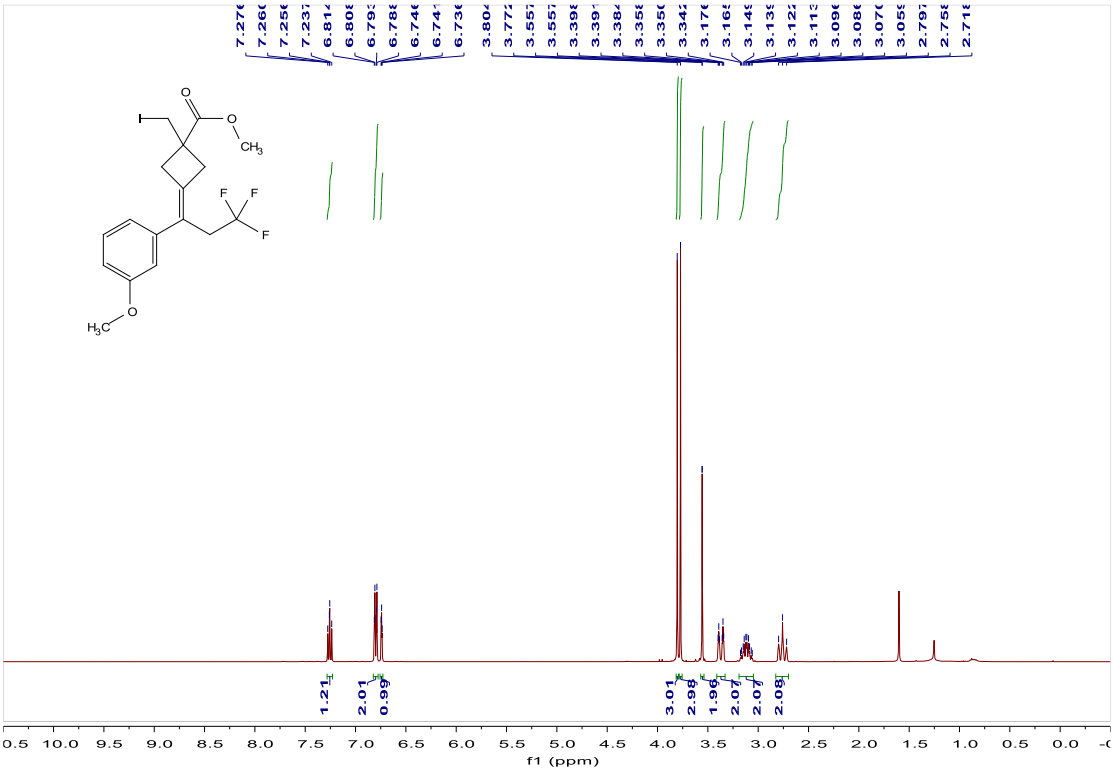
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **36**



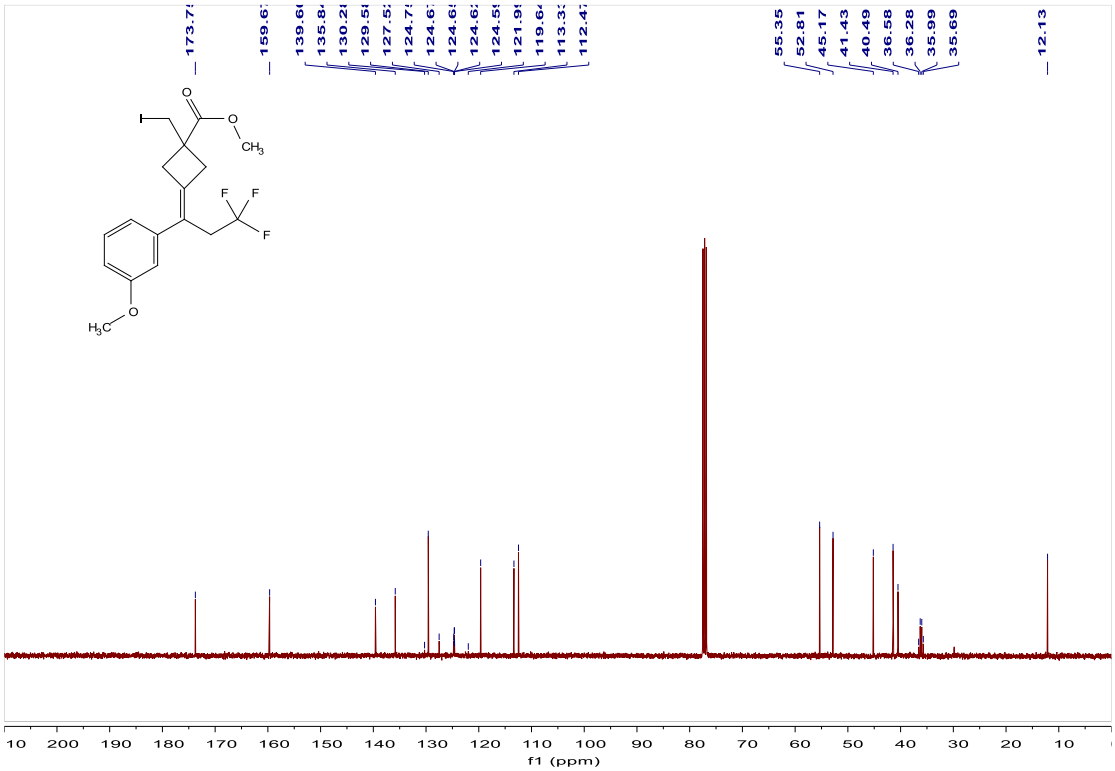
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **36**



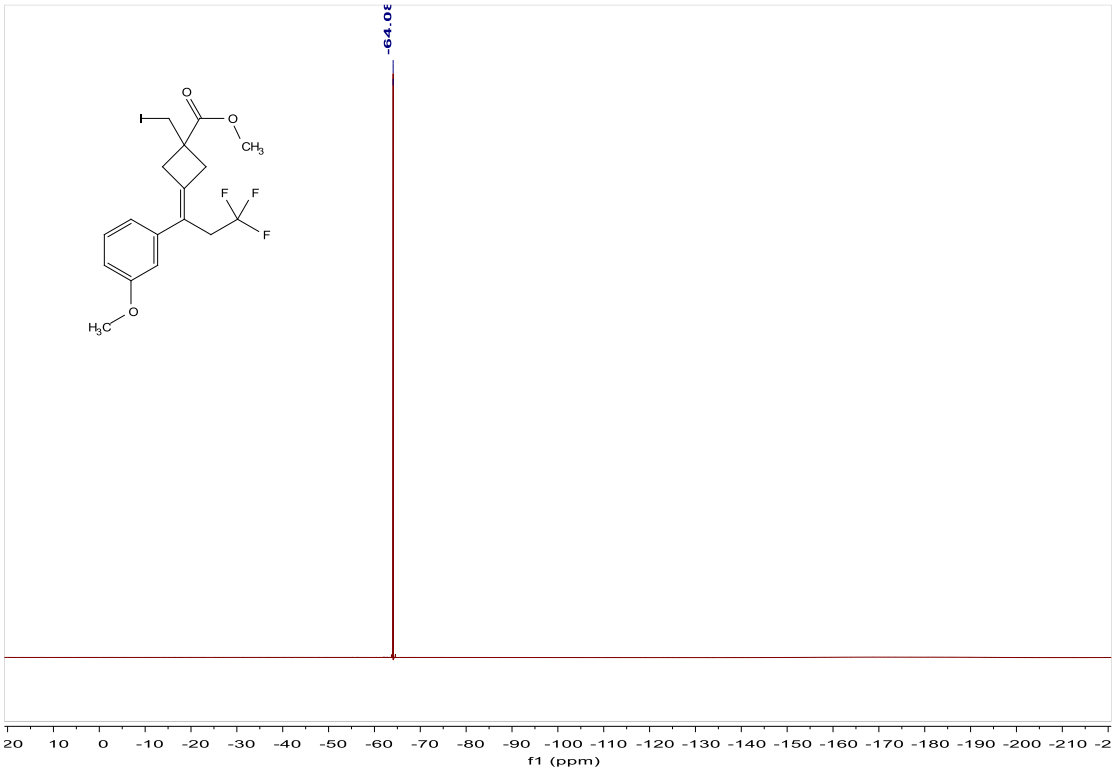
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **37**



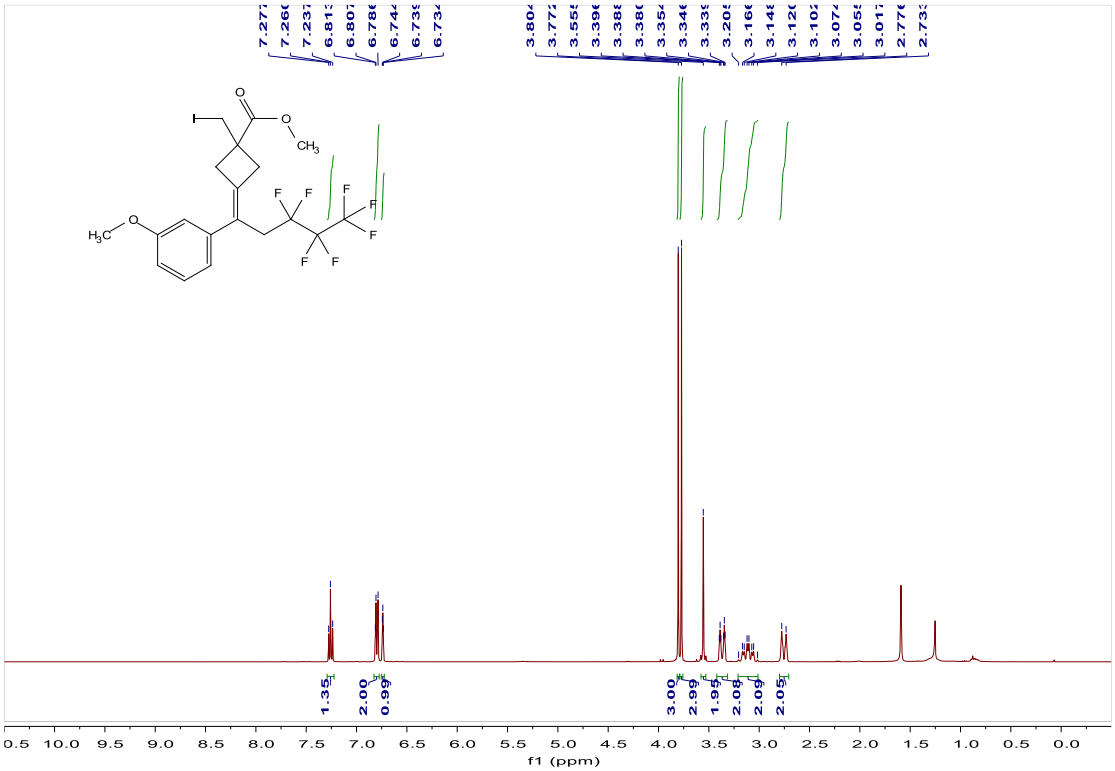
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **37**



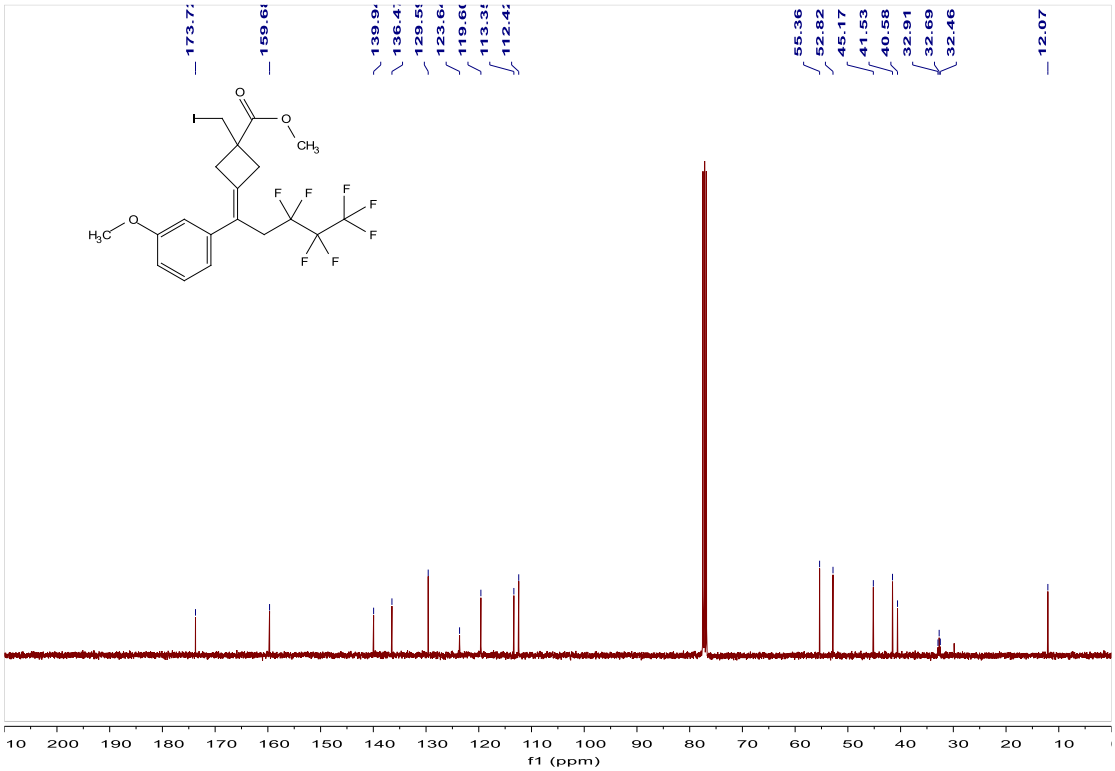
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **37**



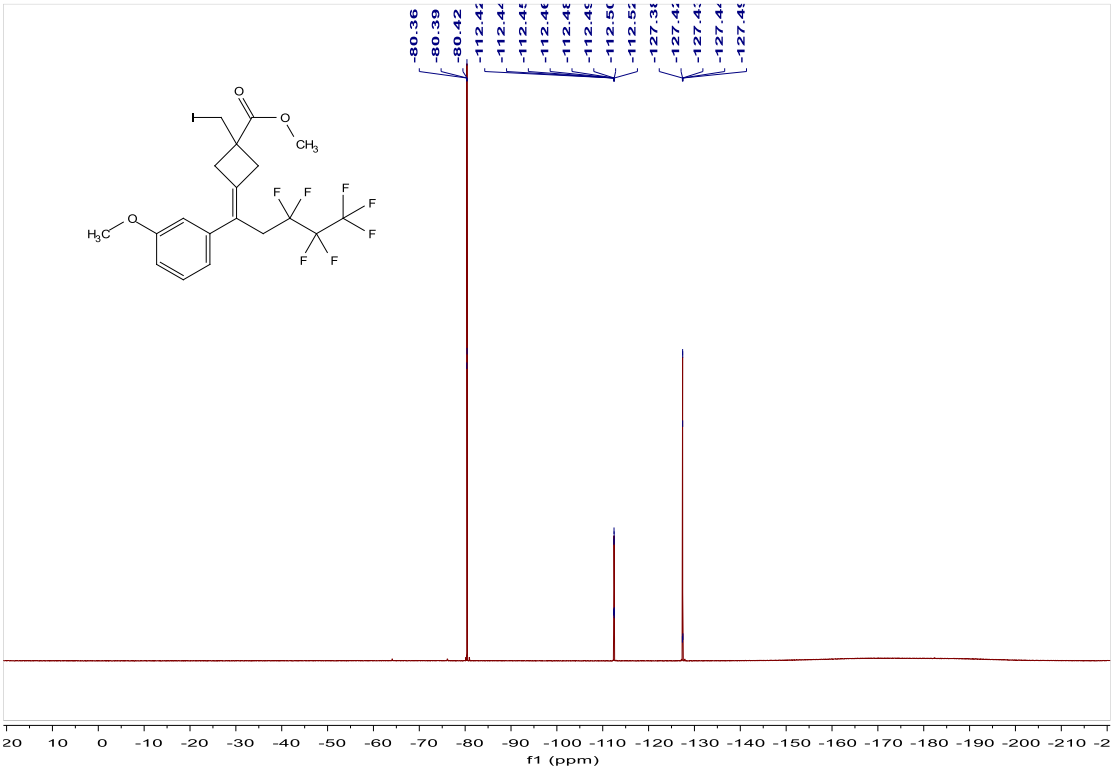
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **38**



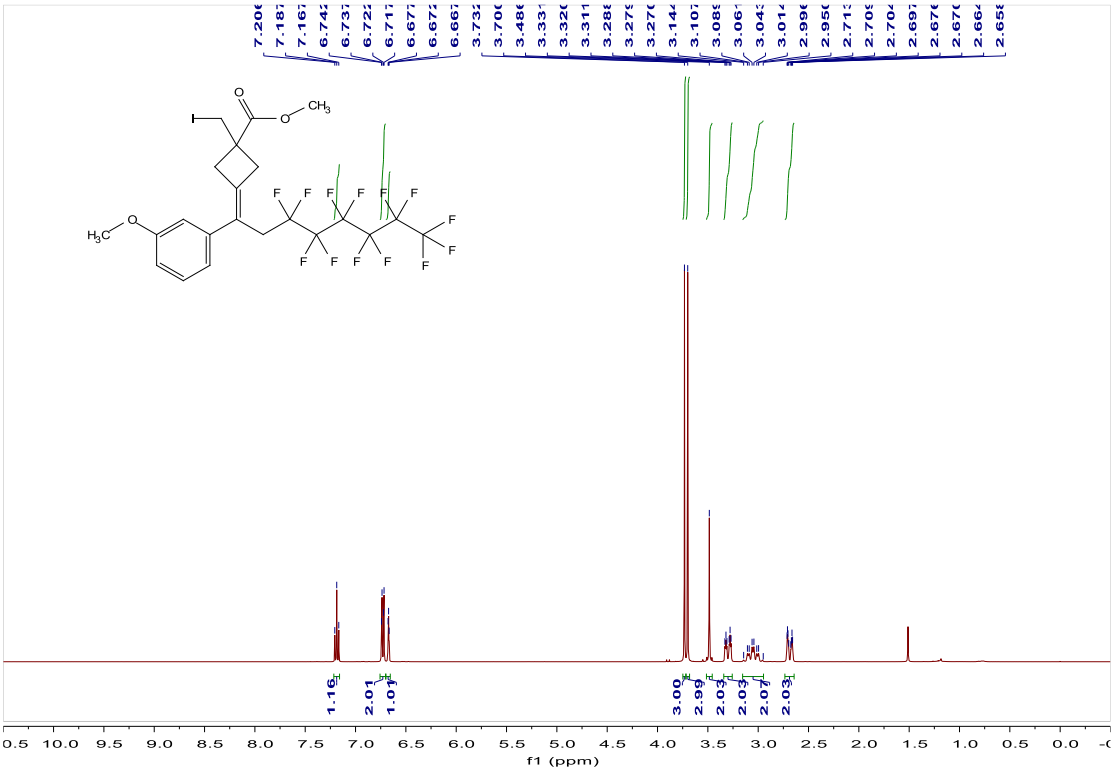
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **38**



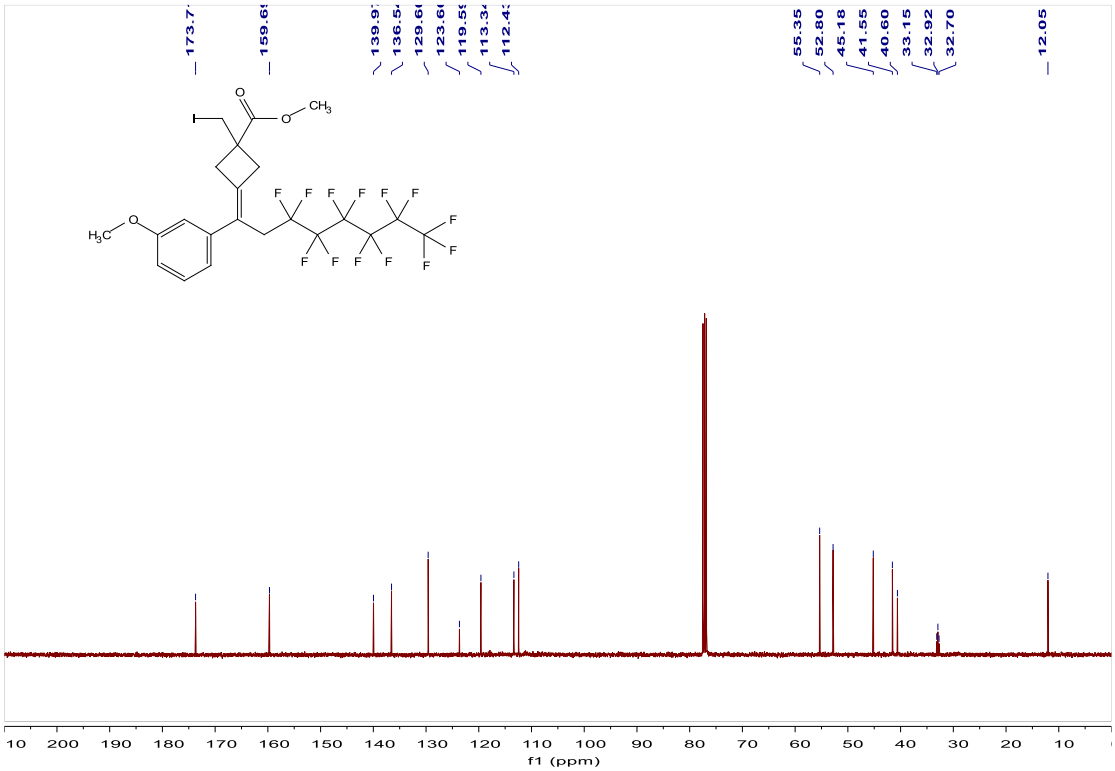
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **38**



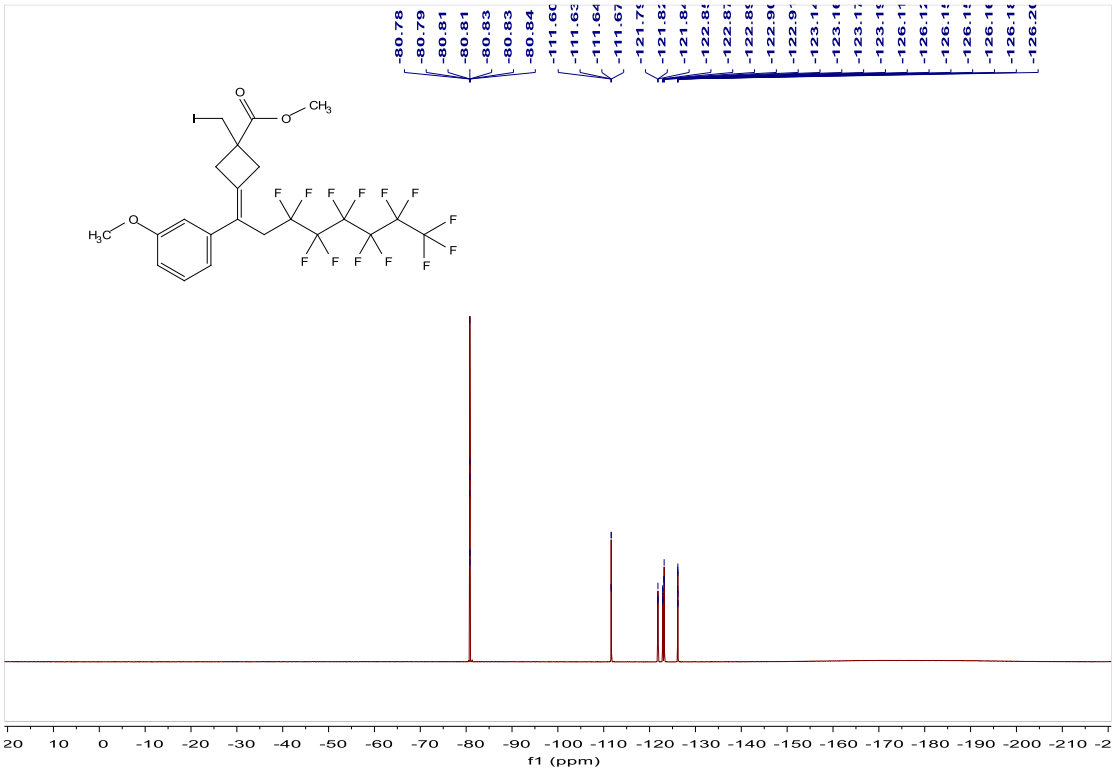
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **39**



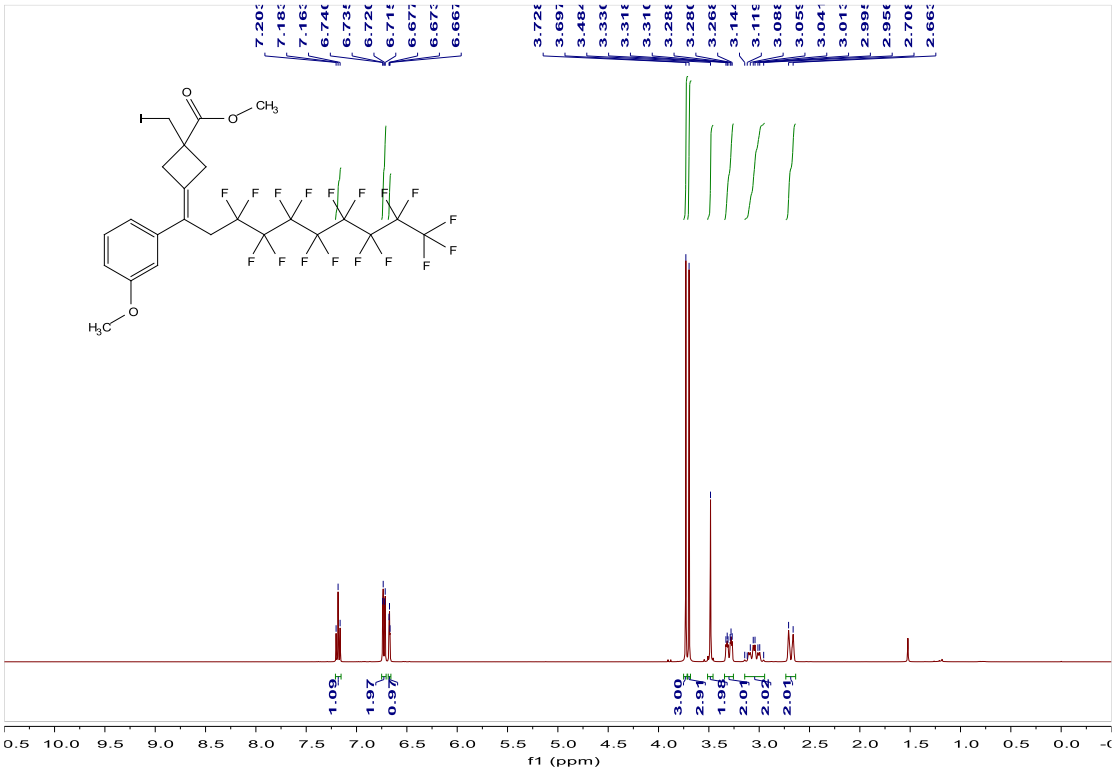
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **39**



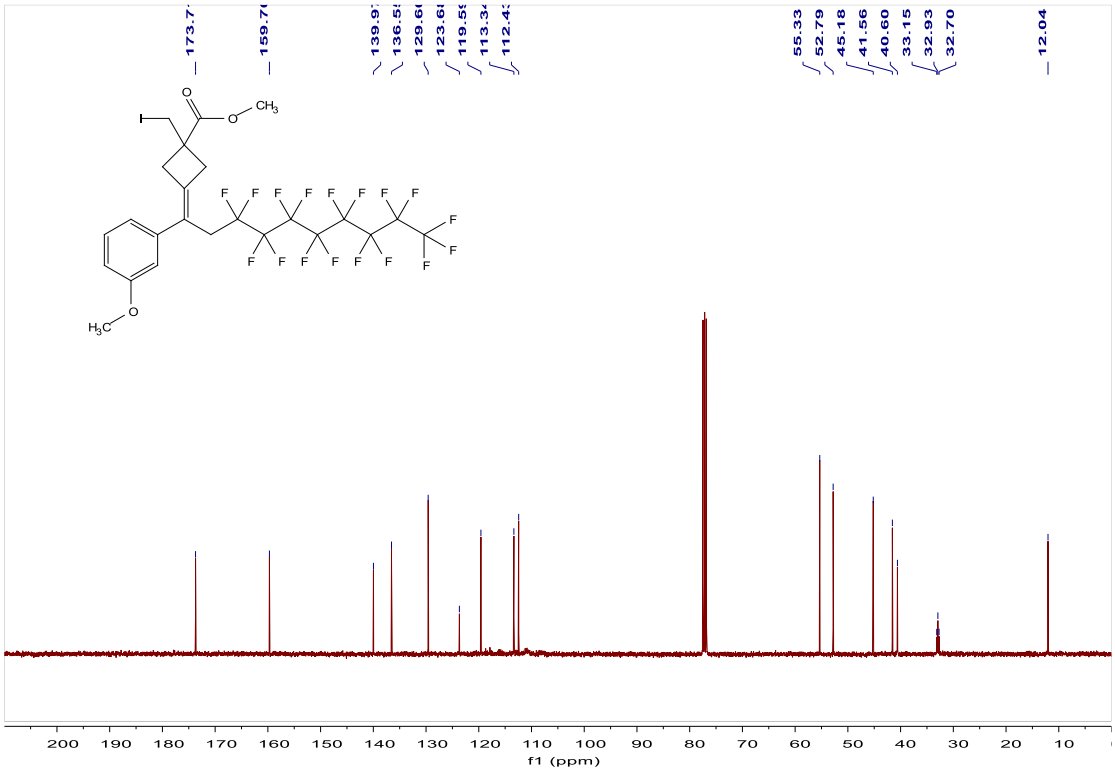
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **39**



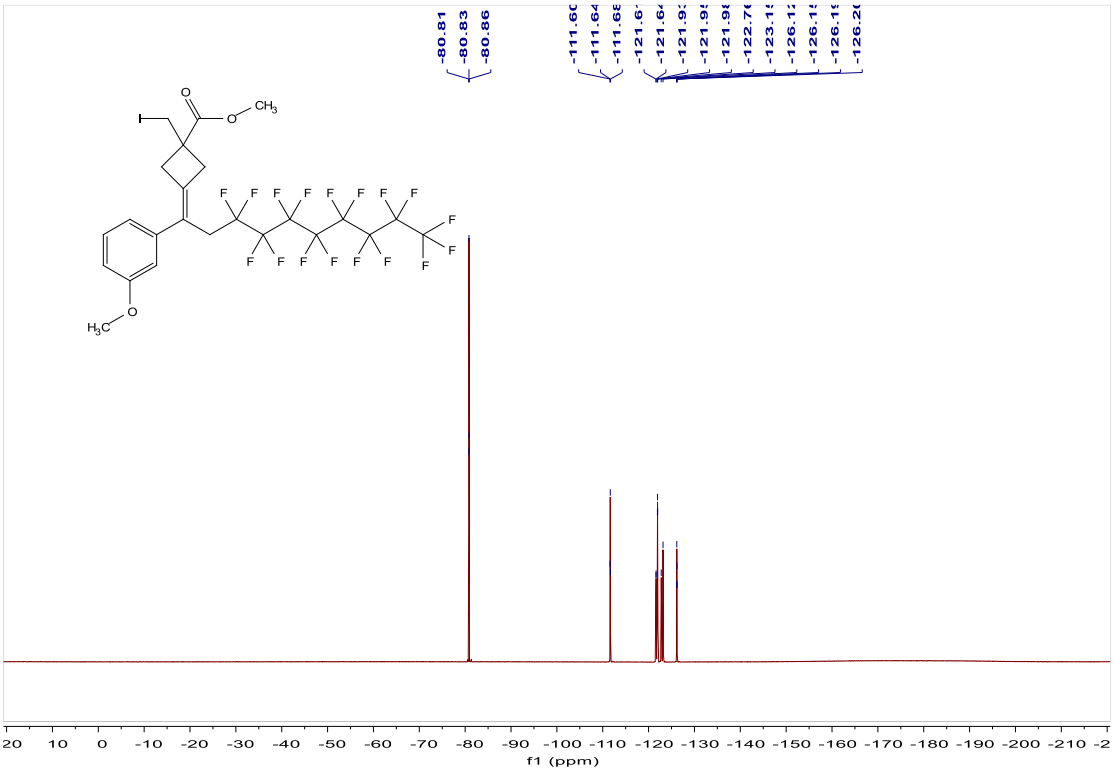
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **40**



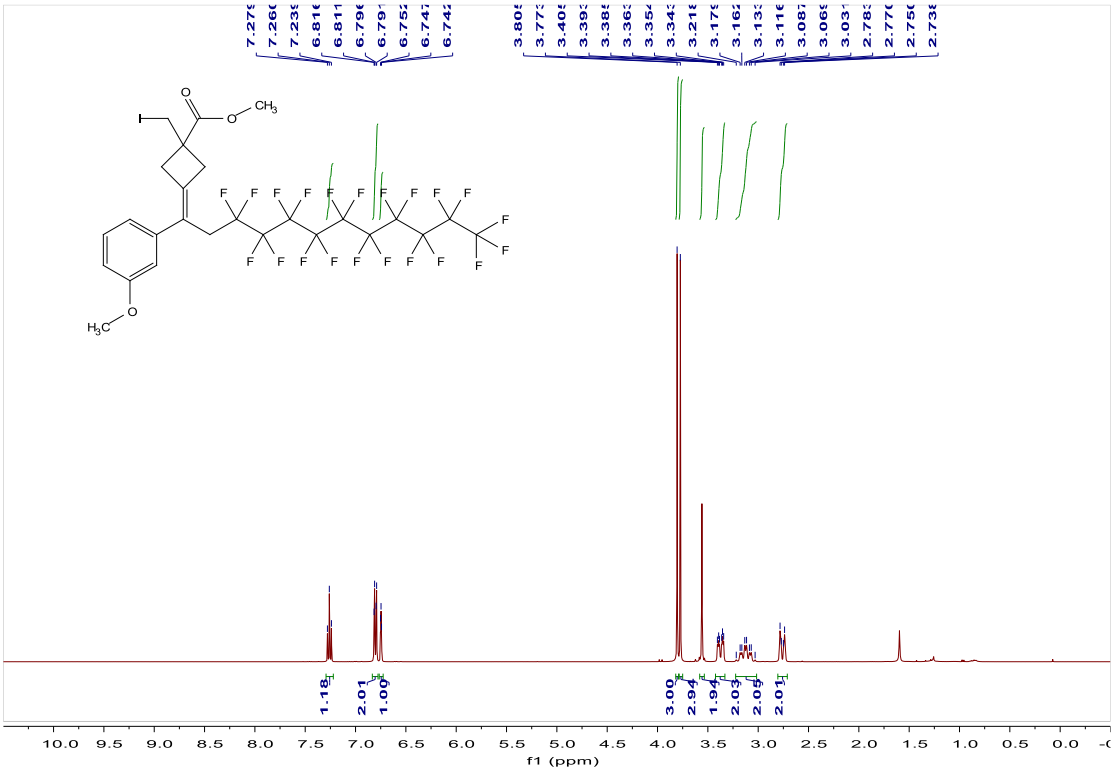
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **40**



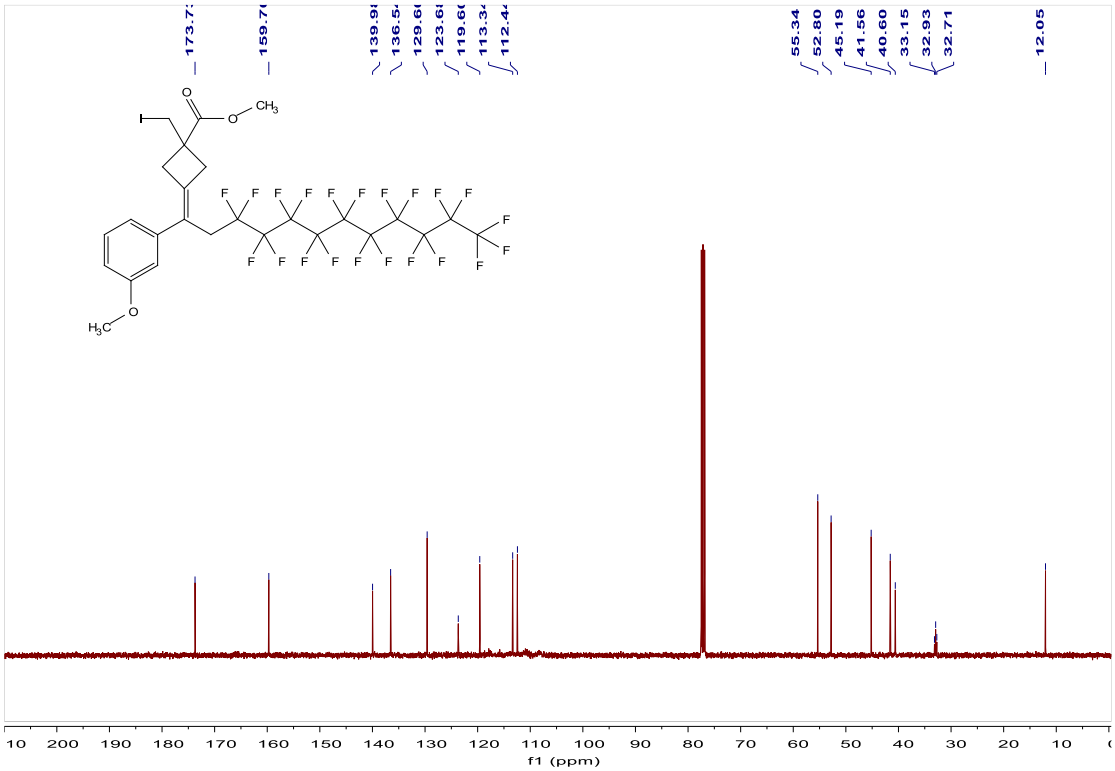
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **40**



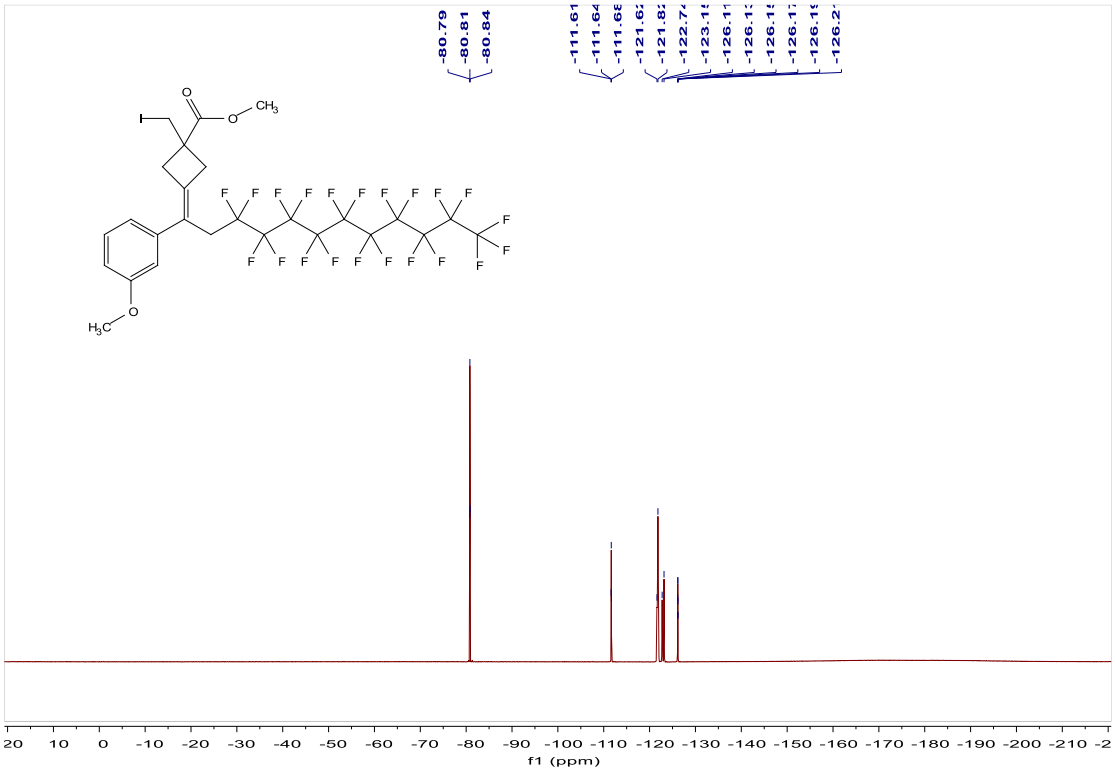
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **41**



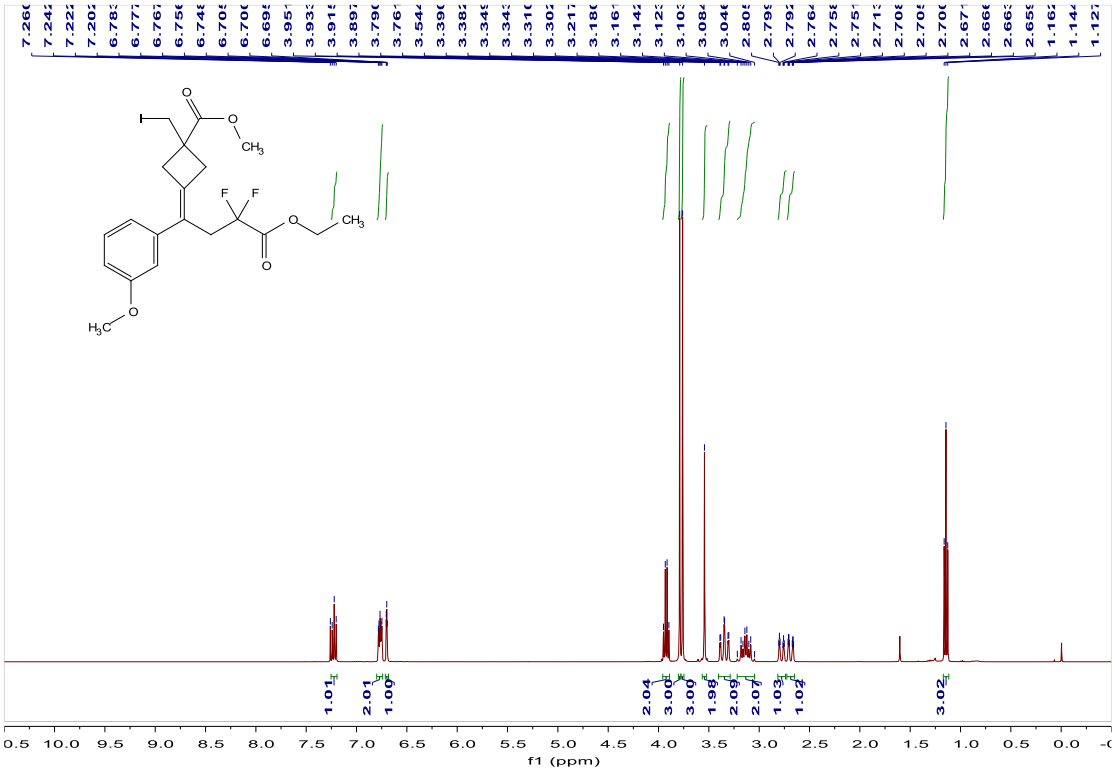
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **41**



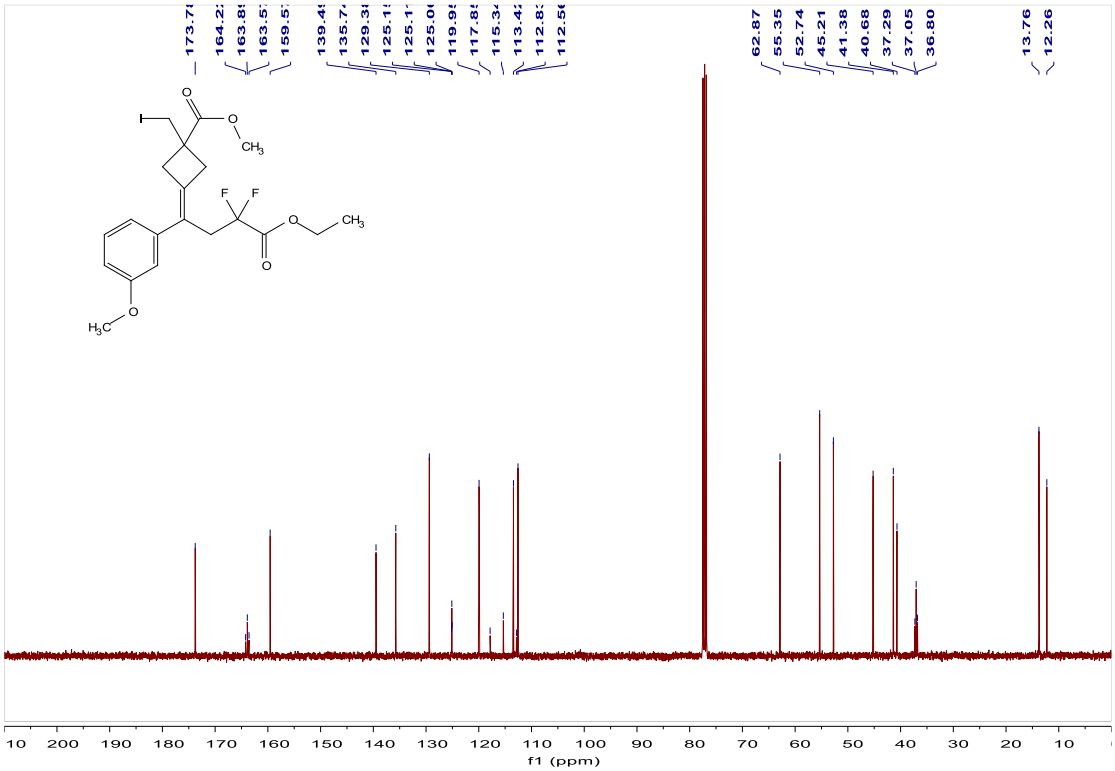
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **41**



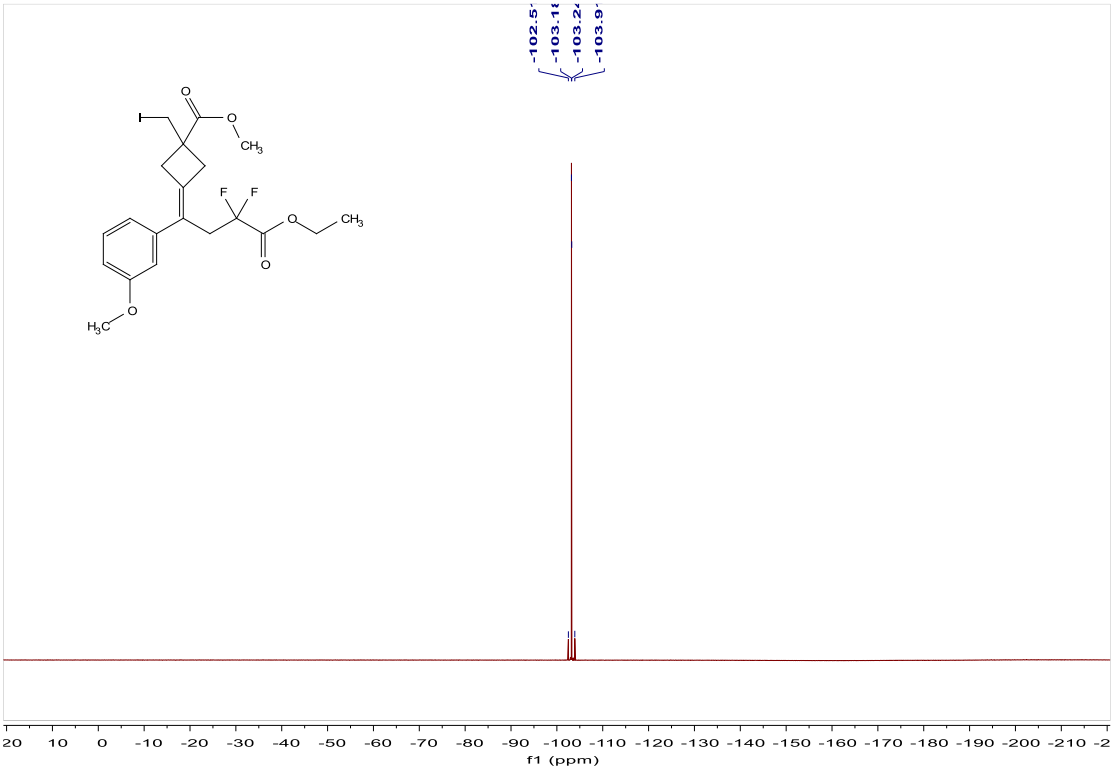
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **42**



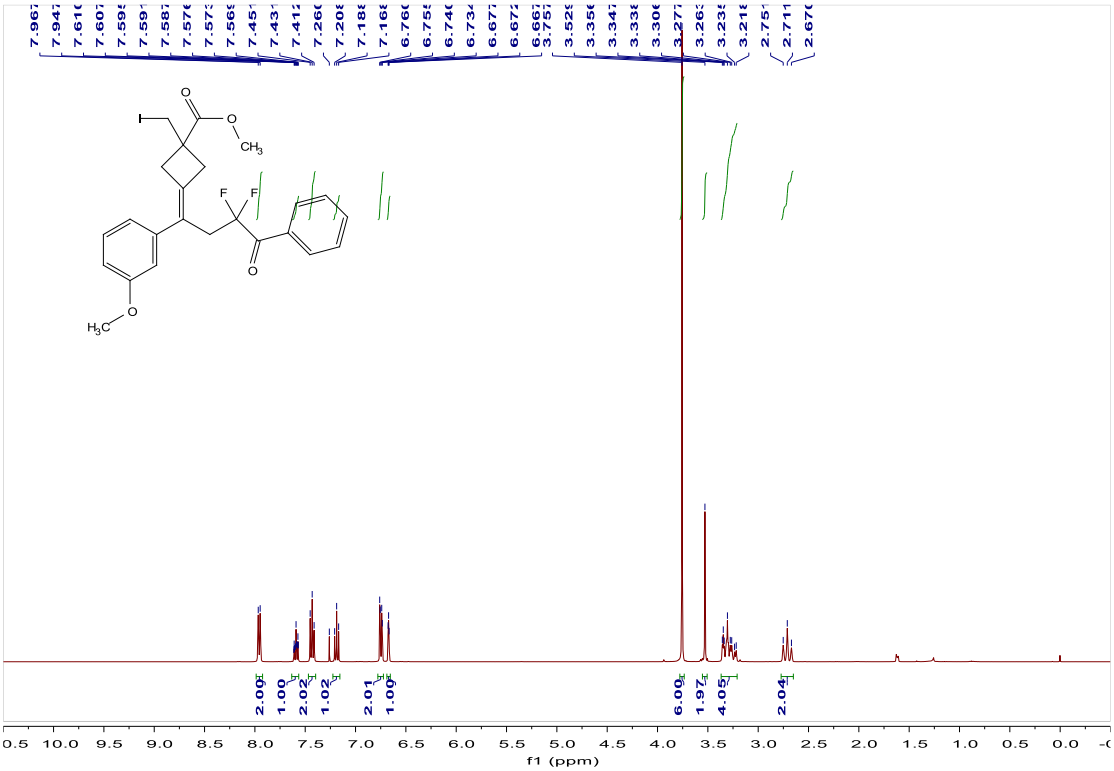
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **42**



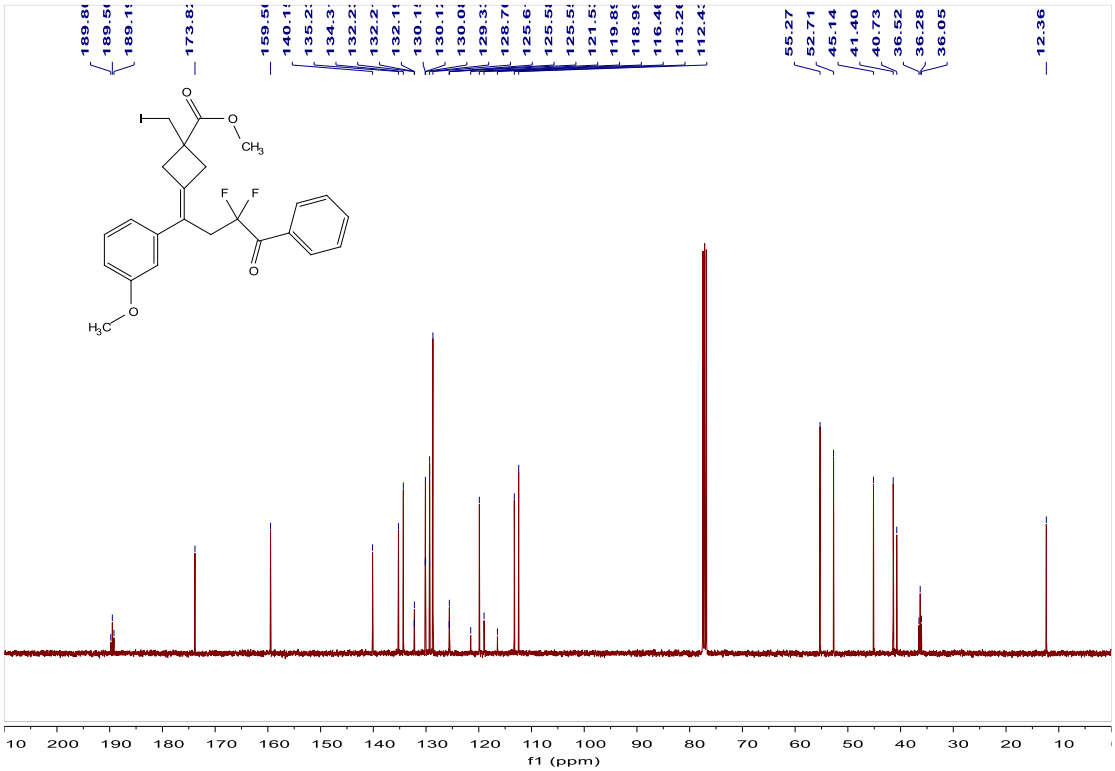
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **42**



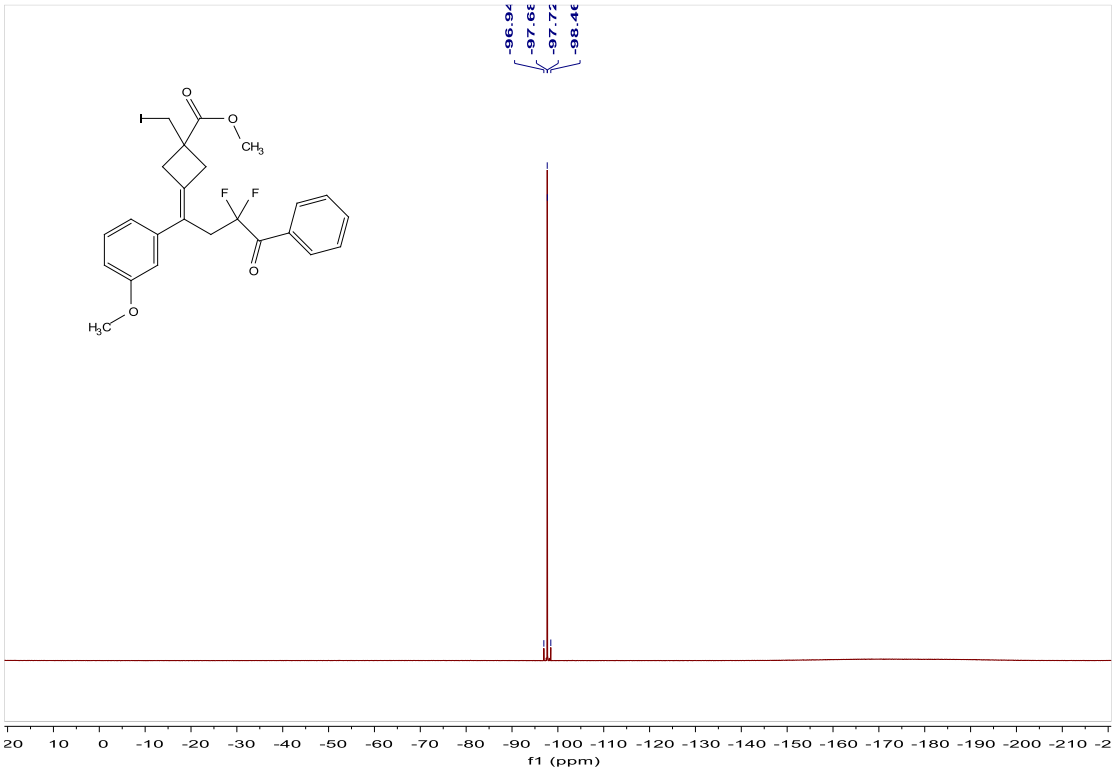
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **43**



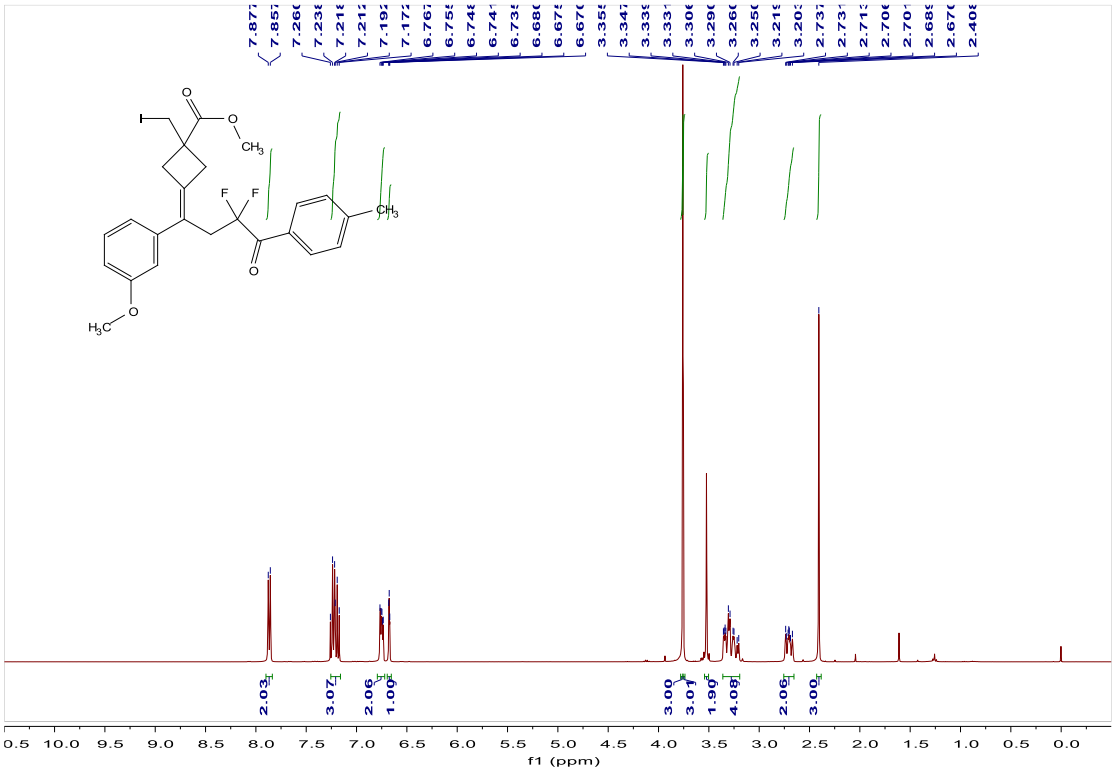
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **43**



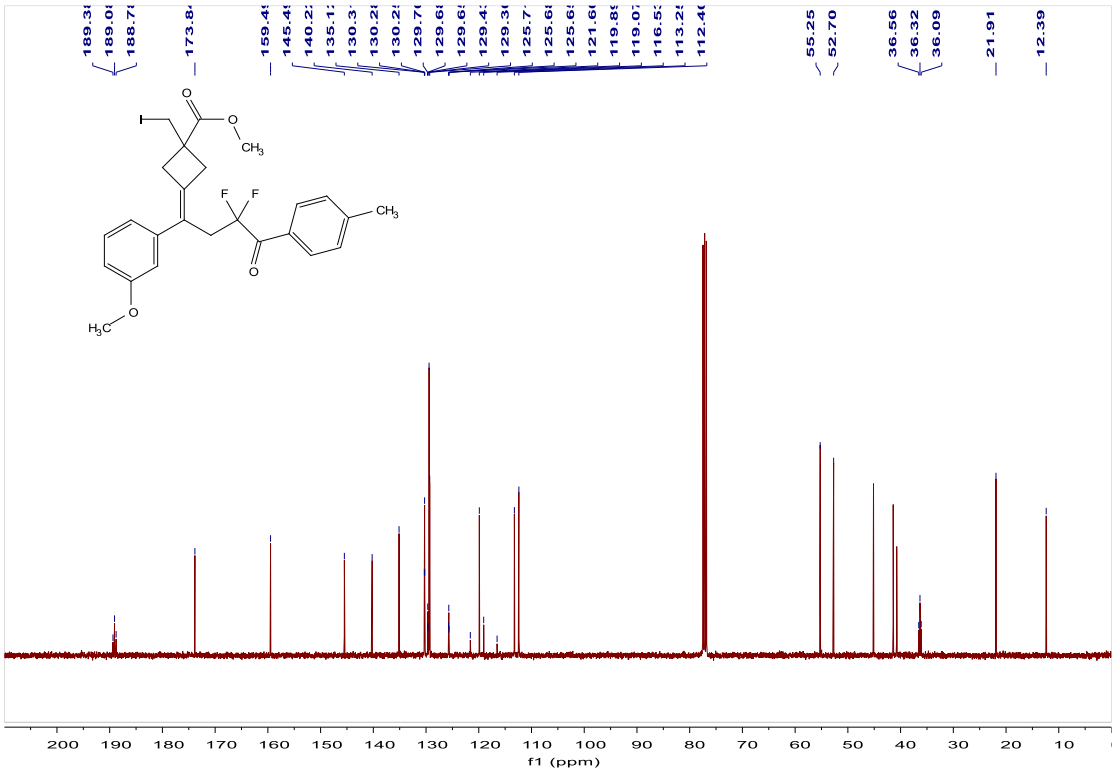
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **43**



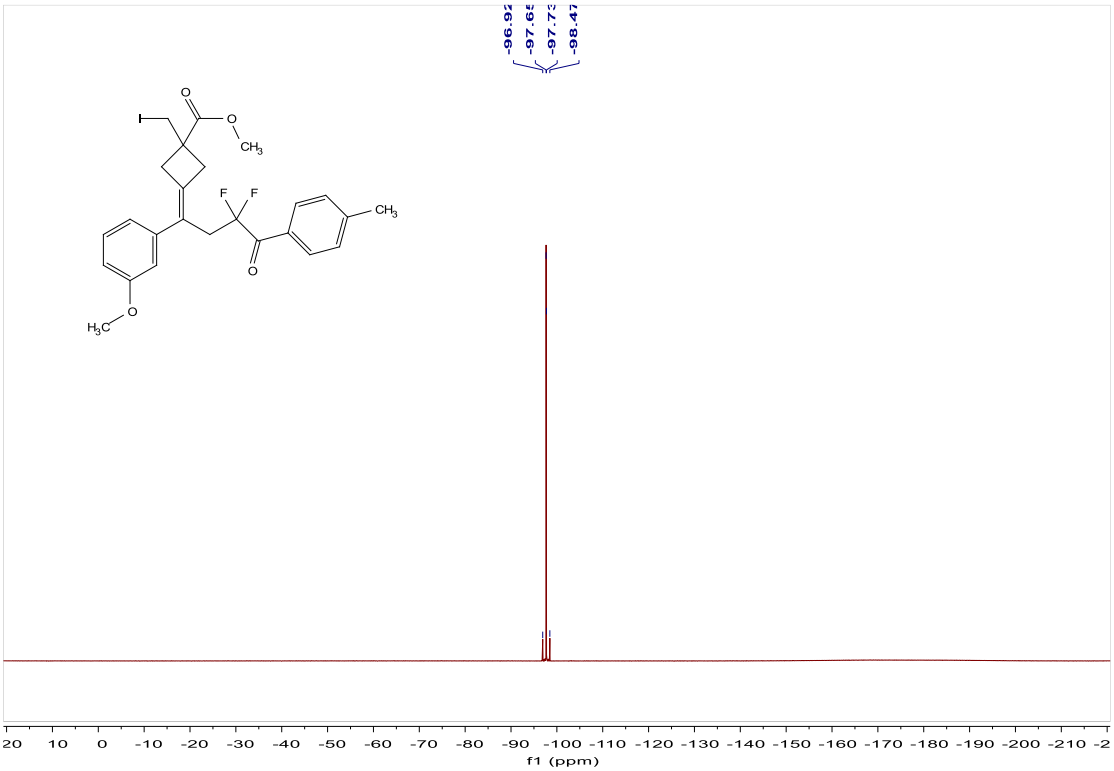
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **44**



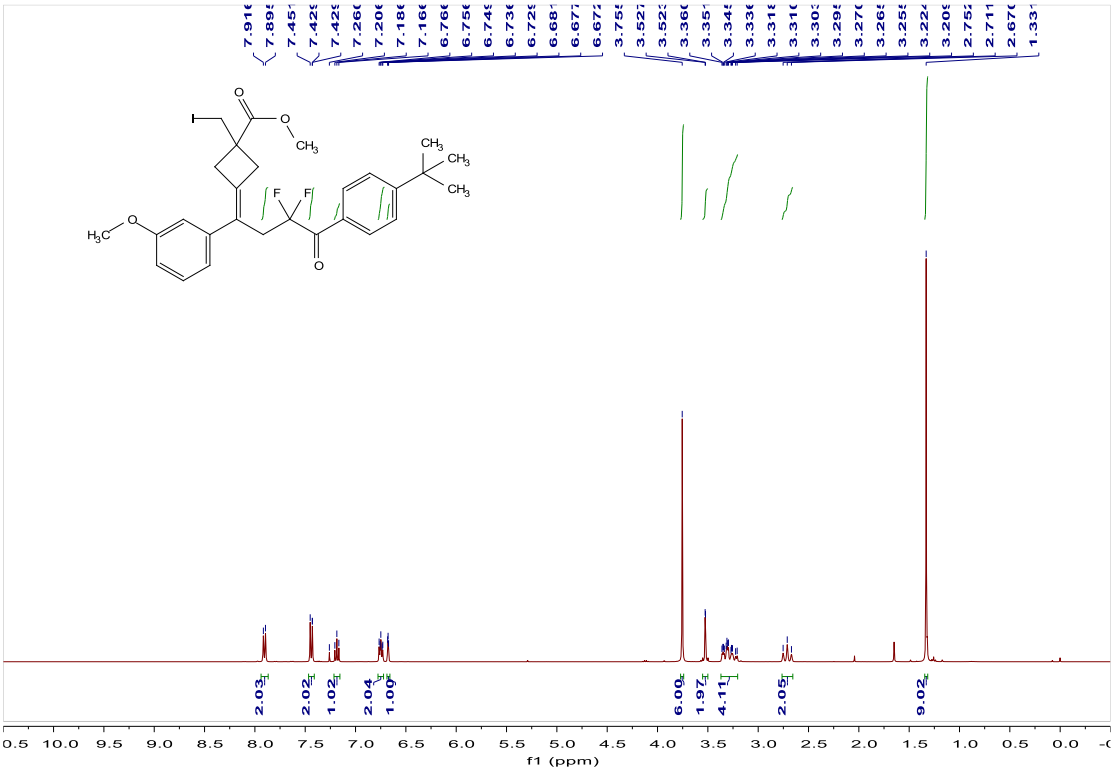
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **44**



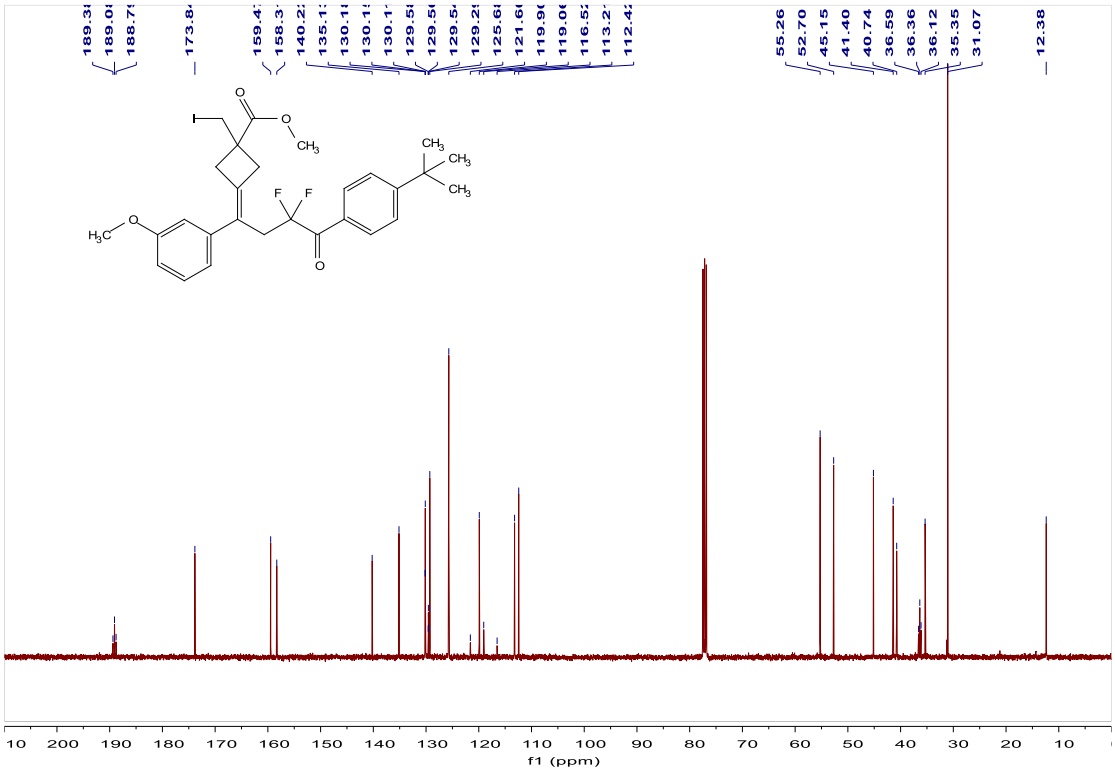
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **44**



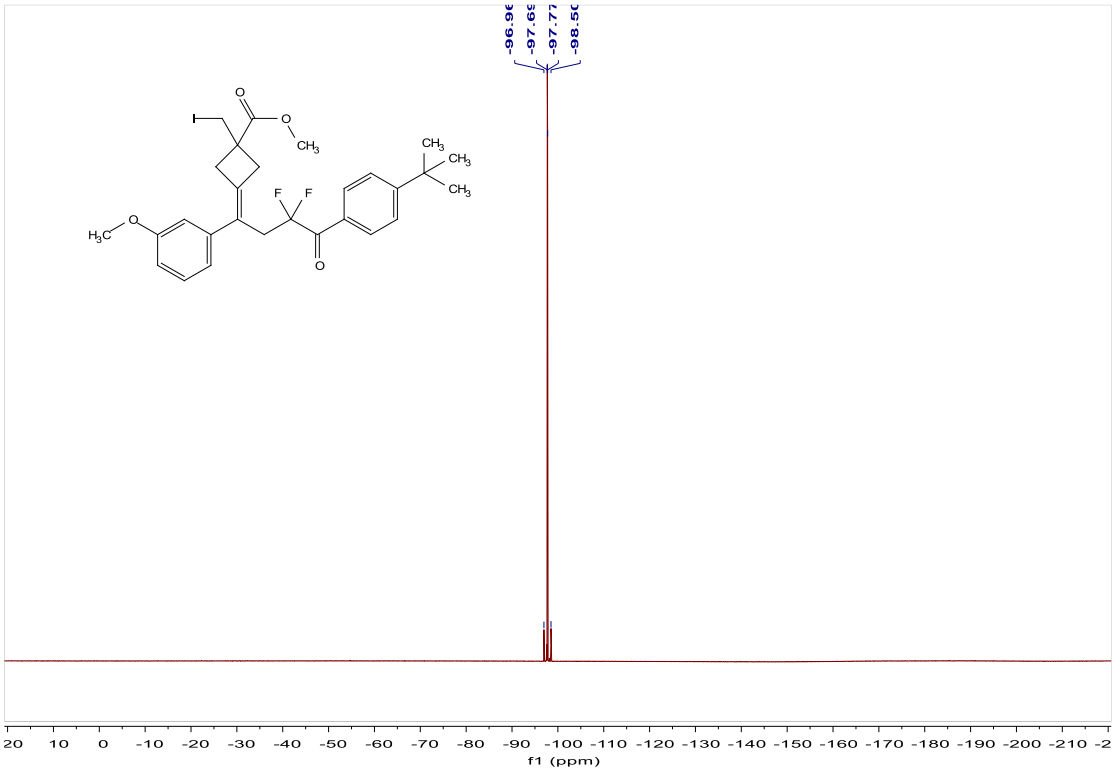
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **45**



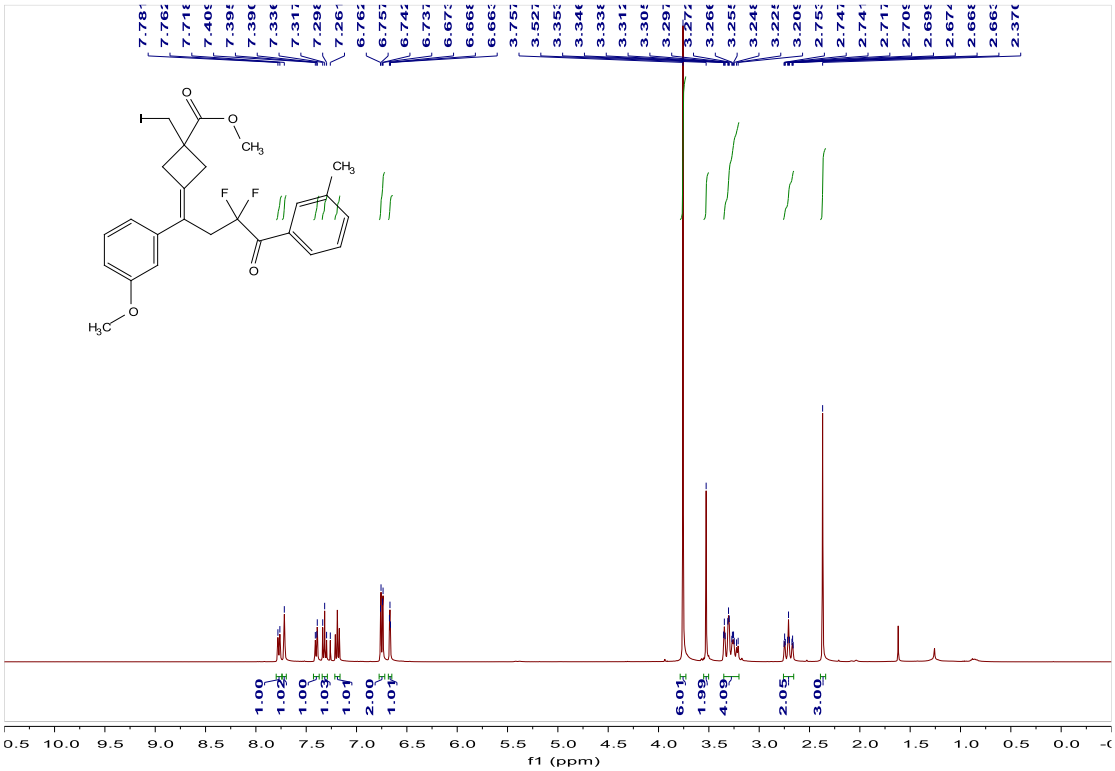
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **45**



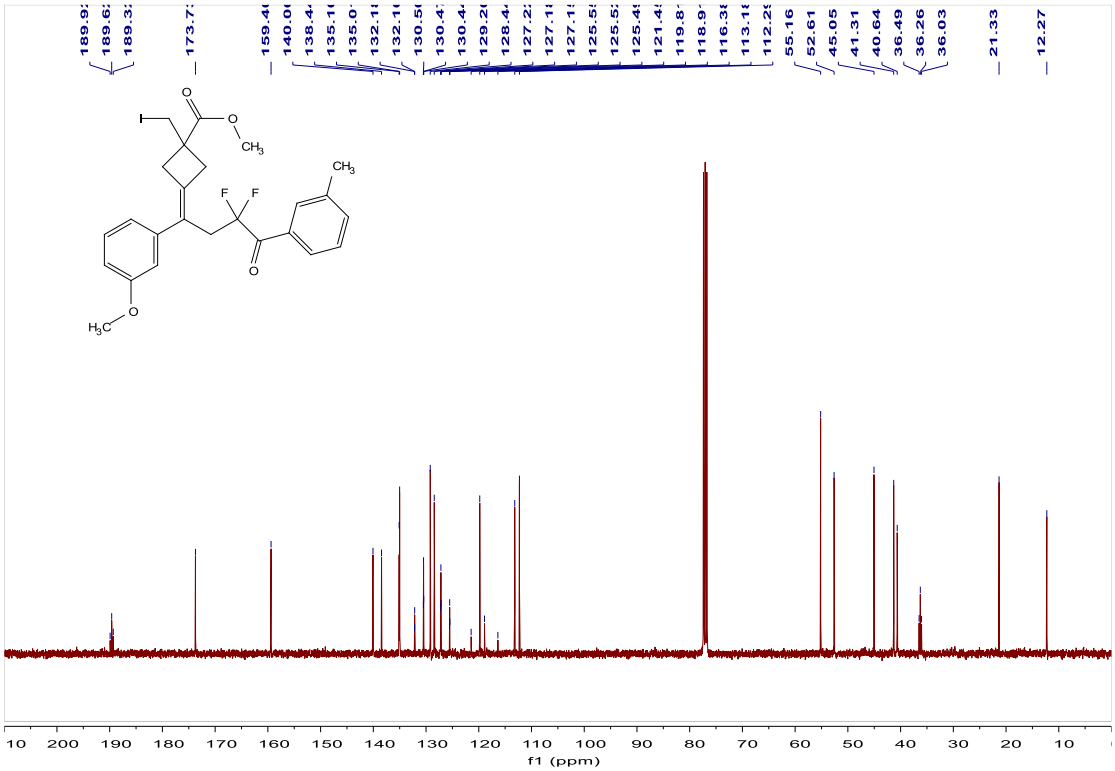
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **45**



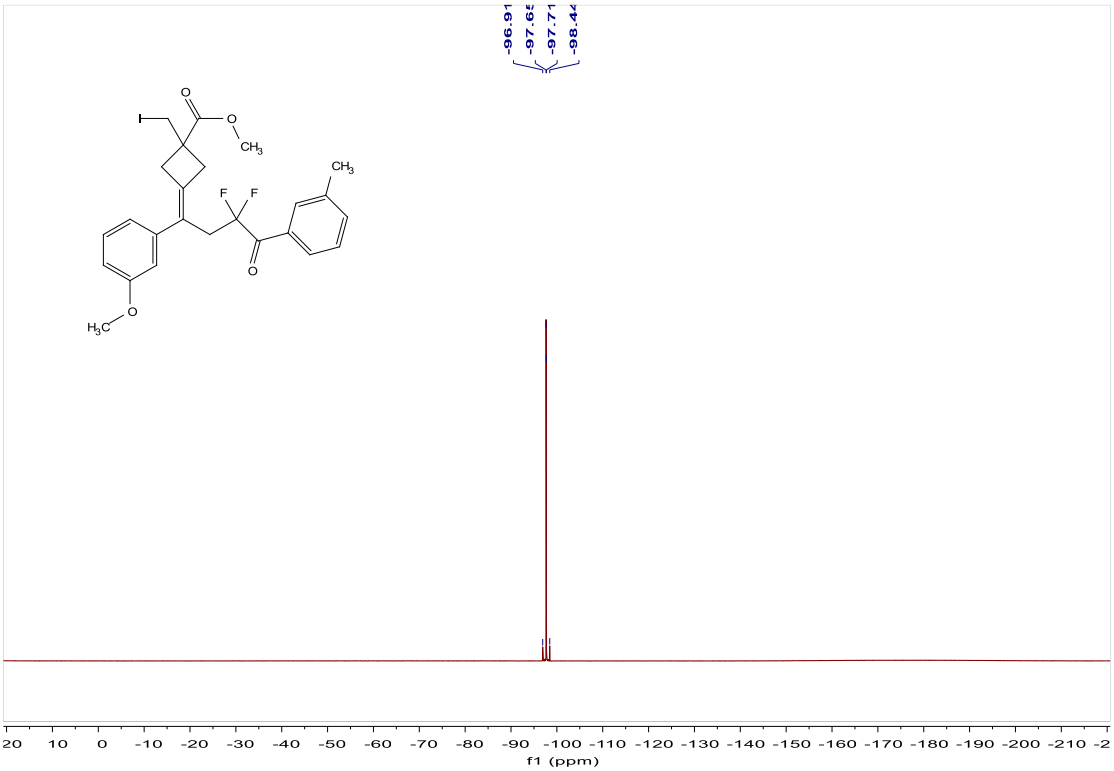
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **46**



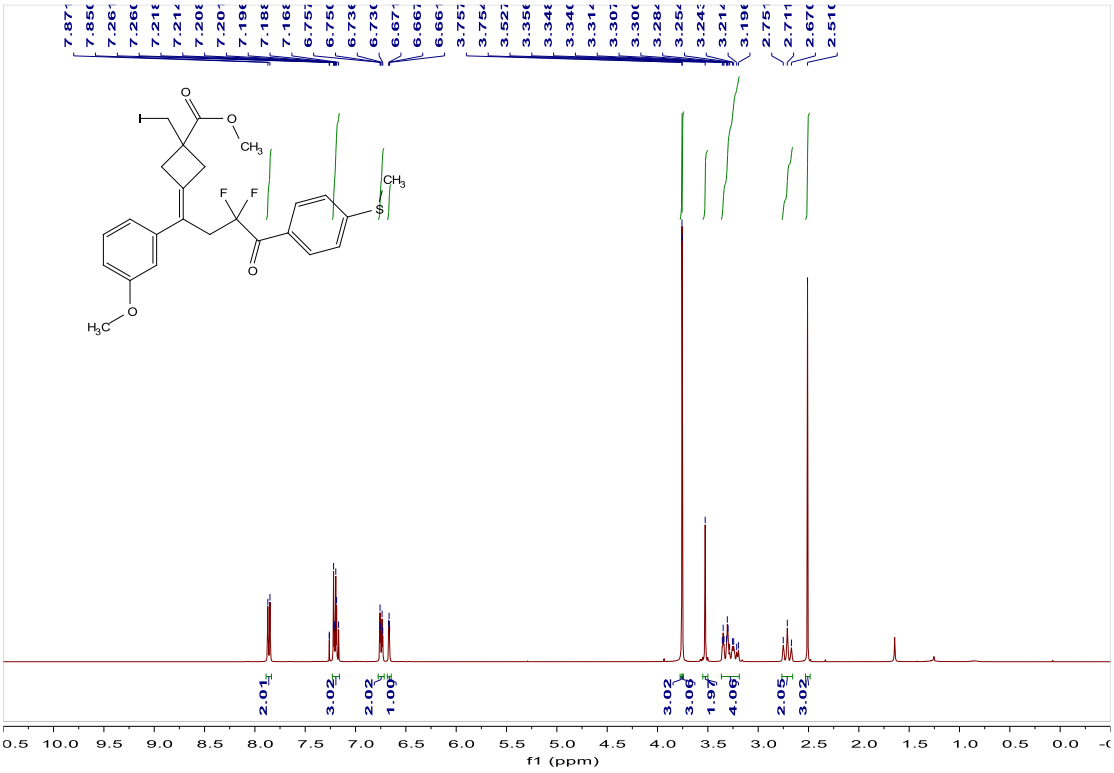
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **46**



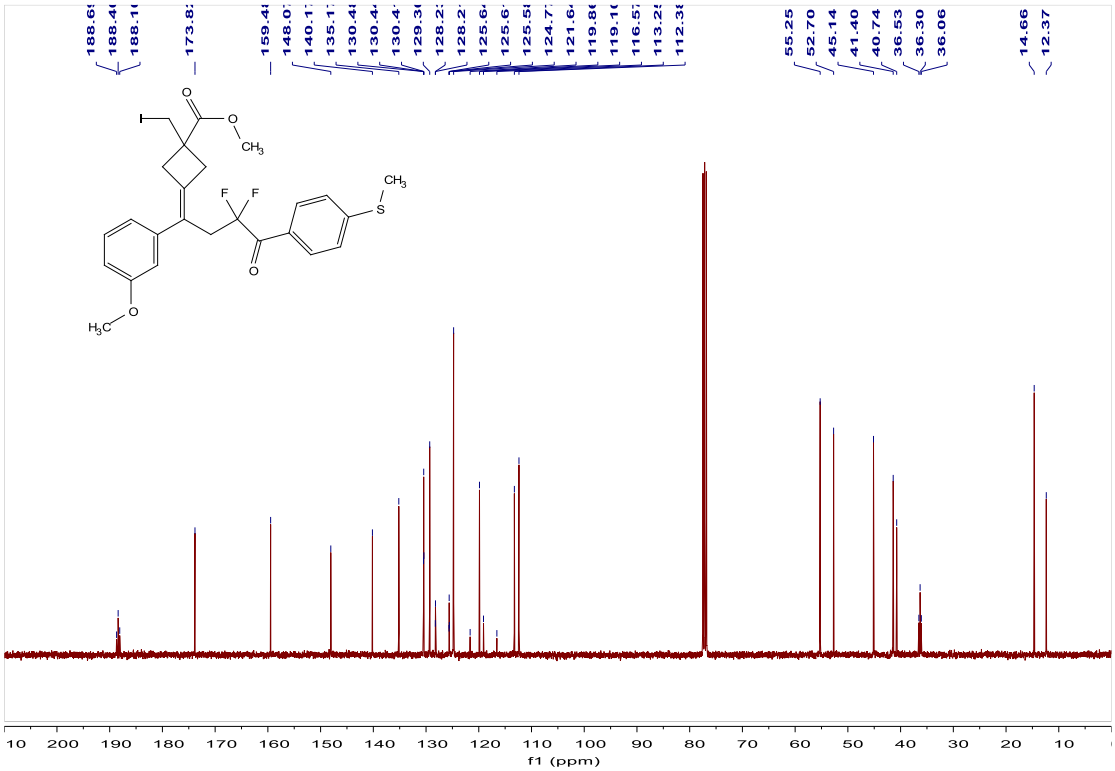
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **46**



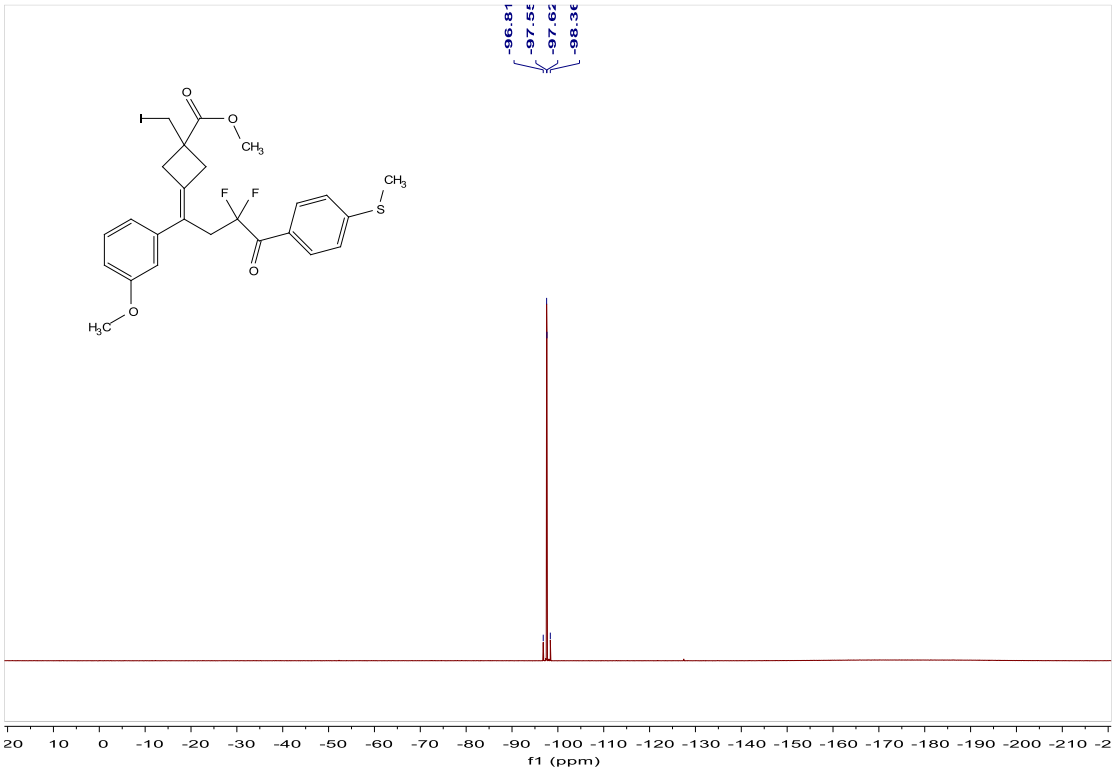
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **47**



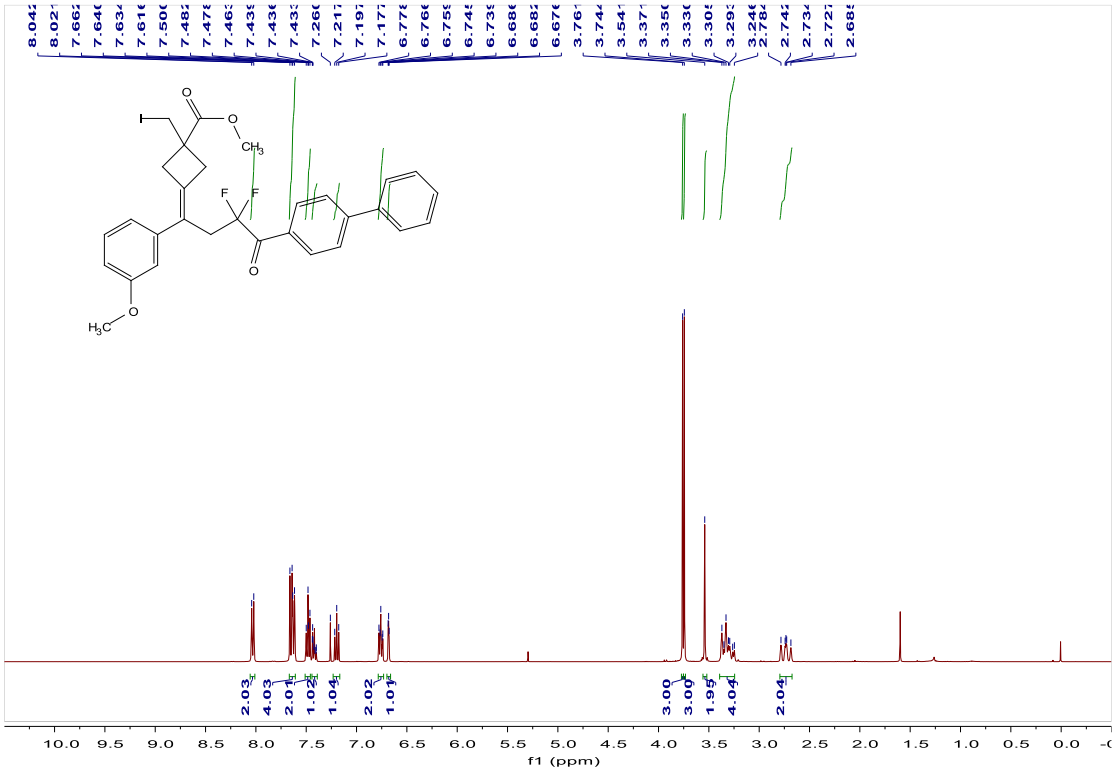
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **47**



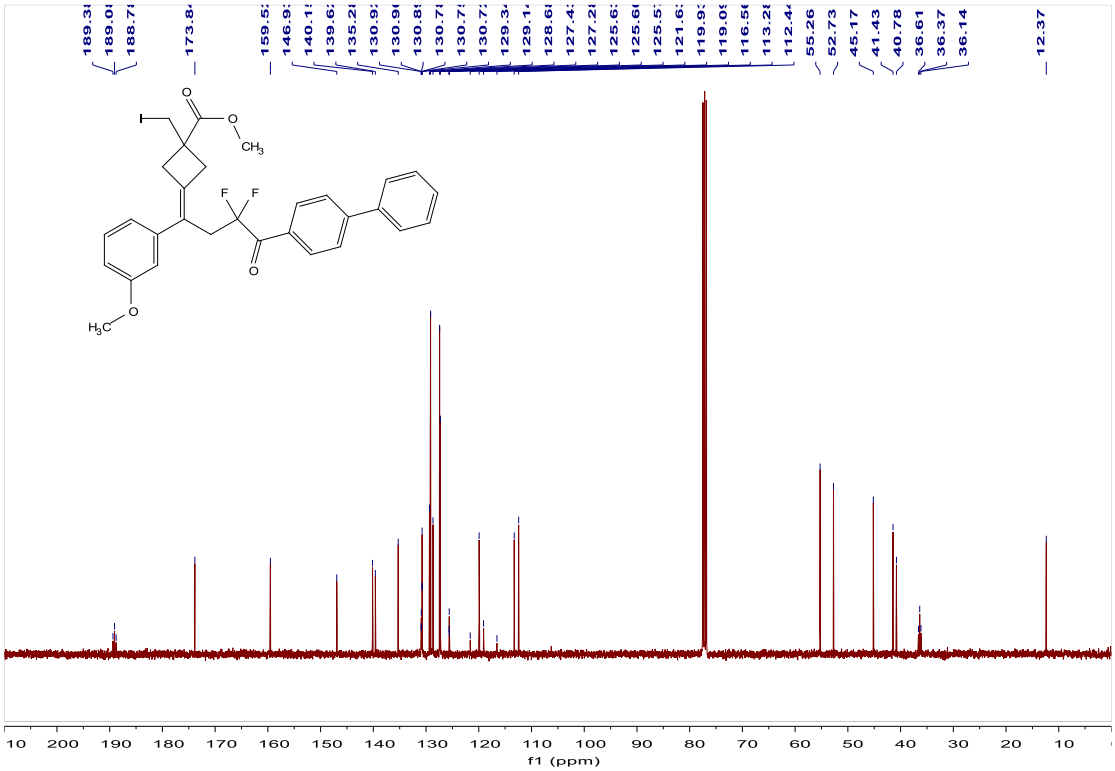
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **47**



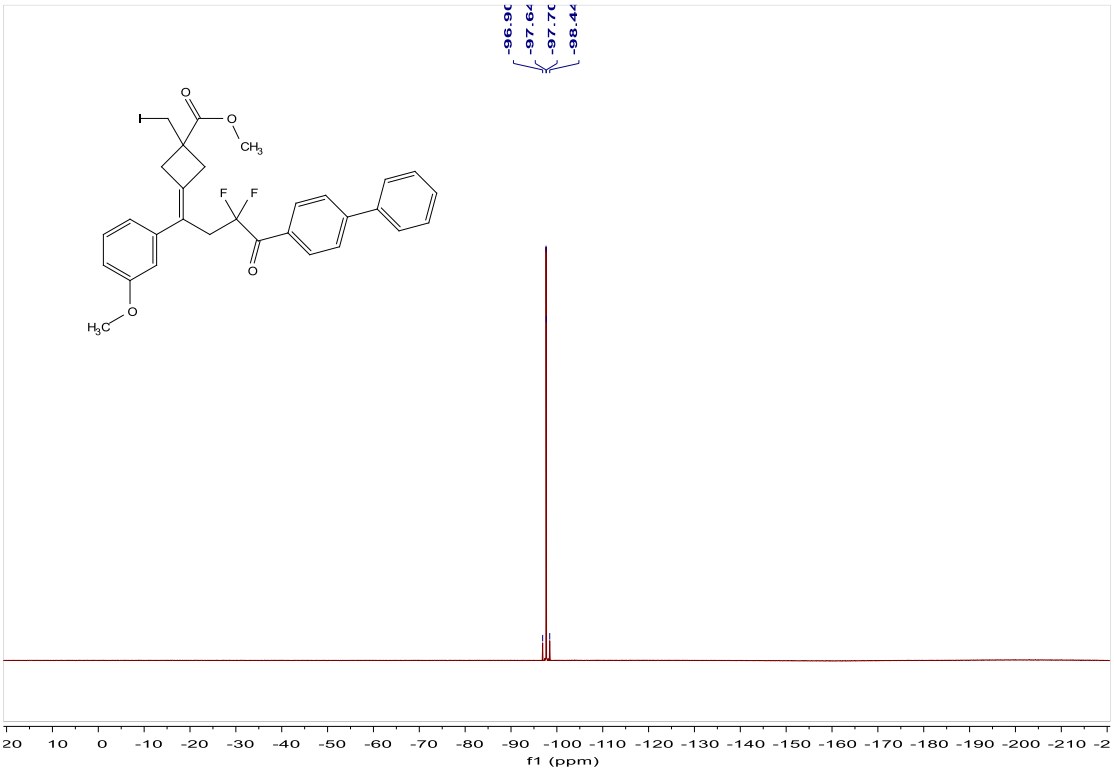
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **48**



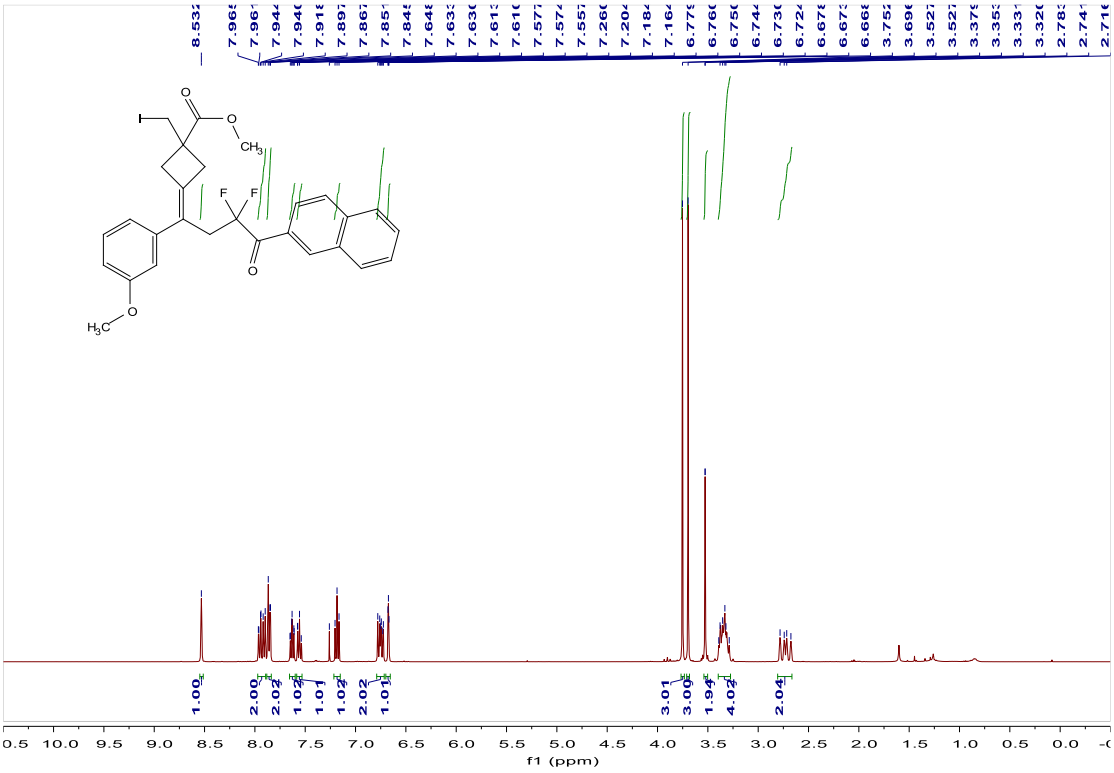
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **48**



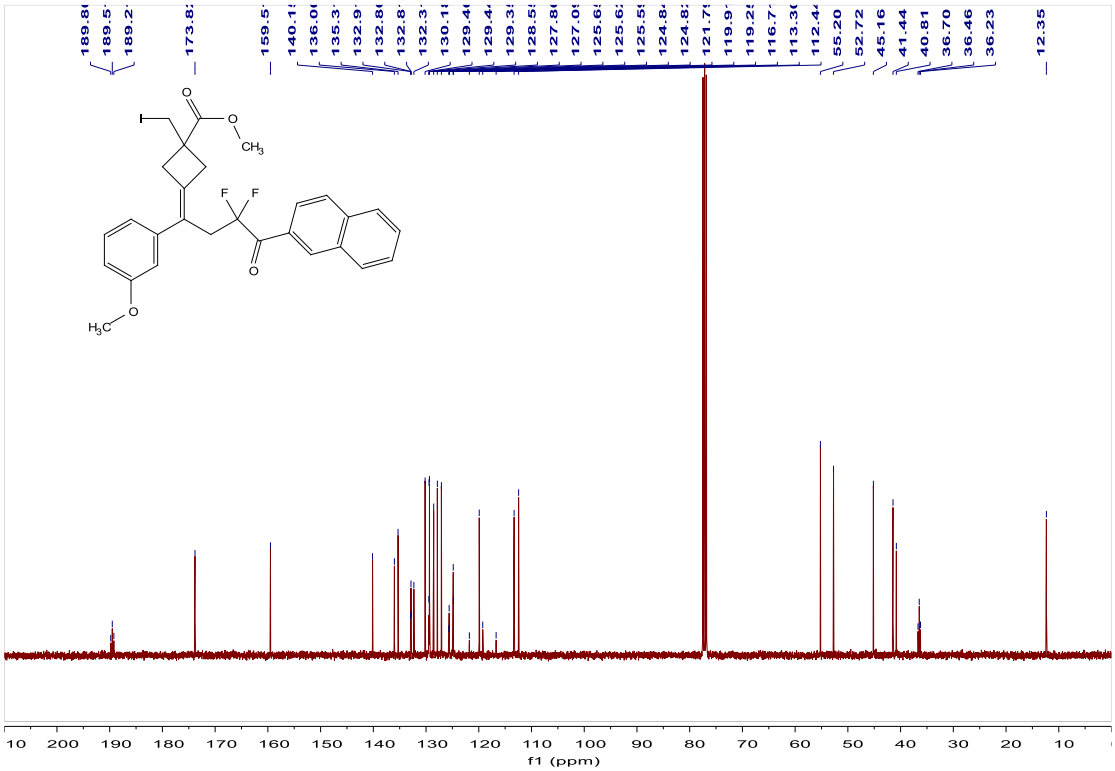
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **48**



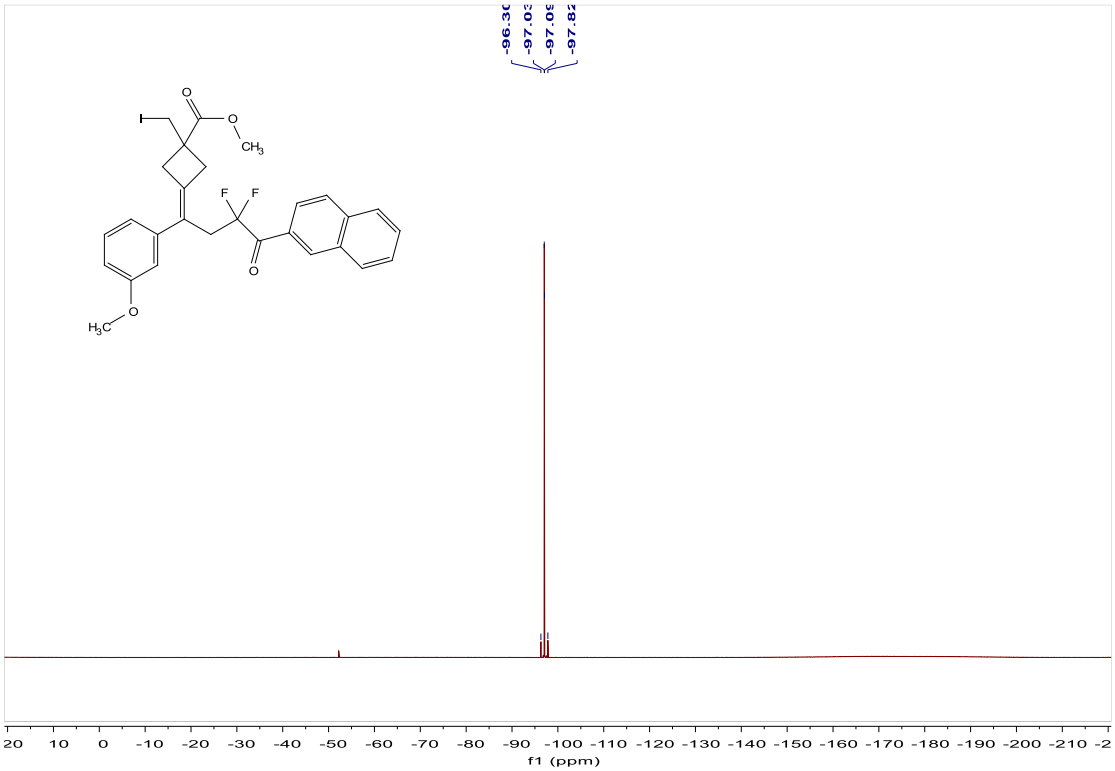
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **49**



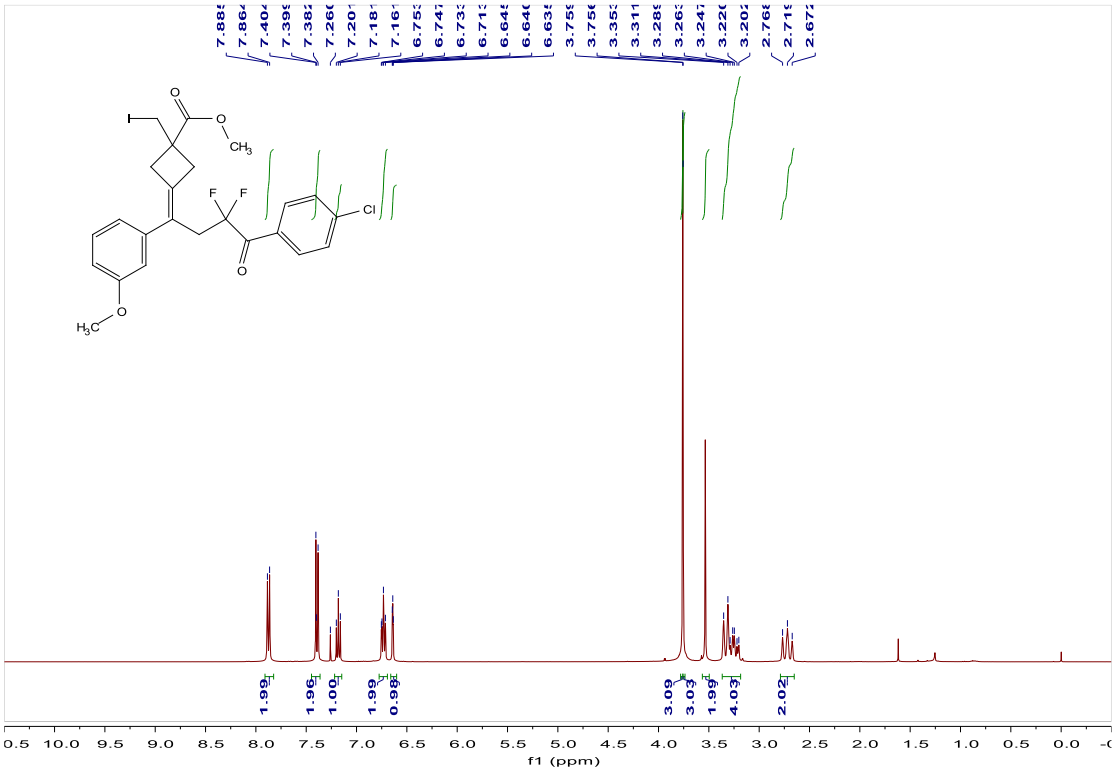
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **49**



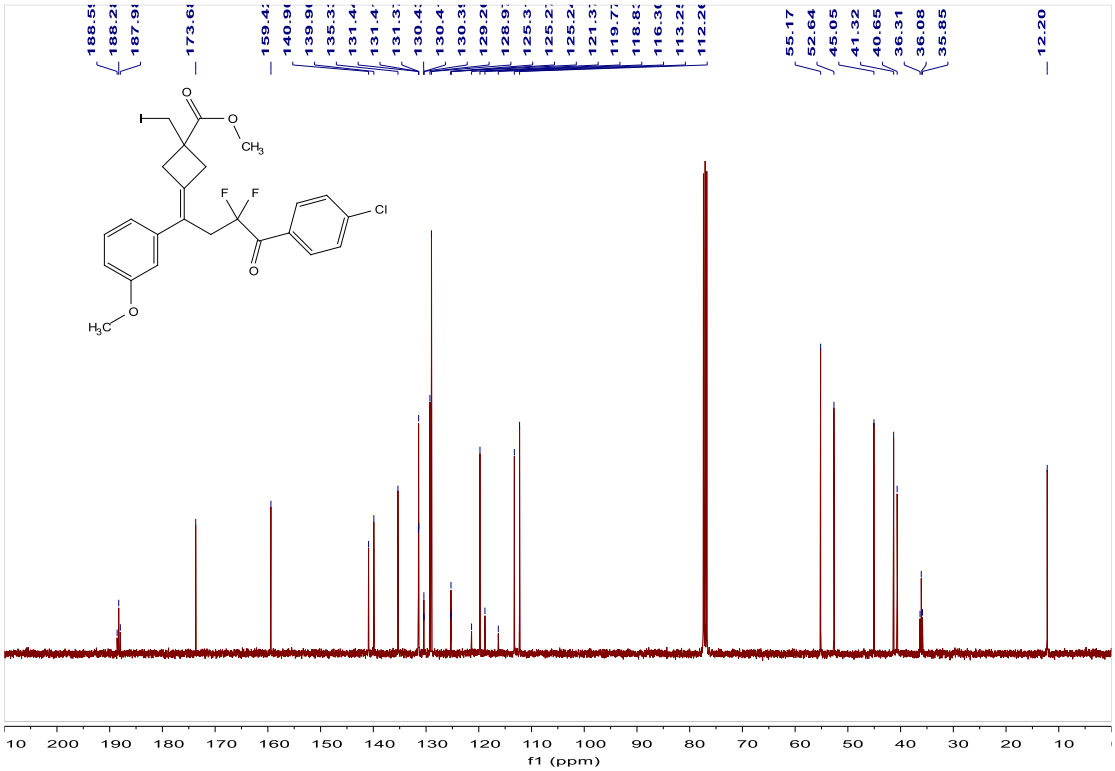
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **49**



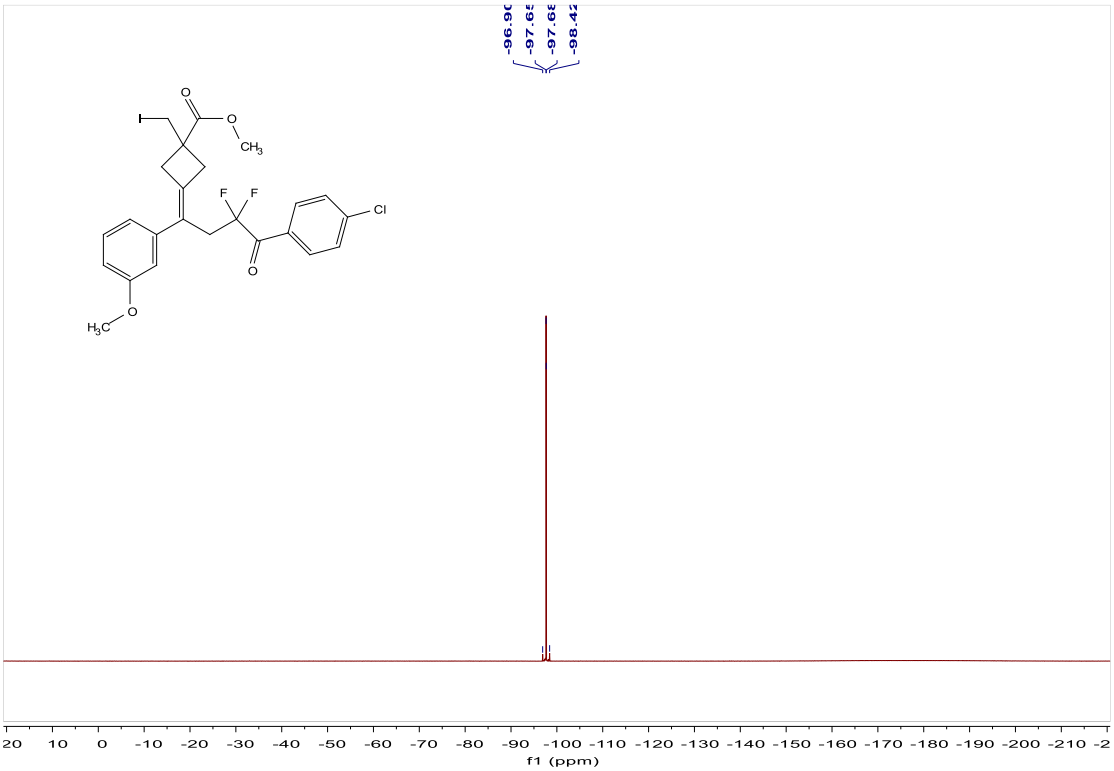
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **50**



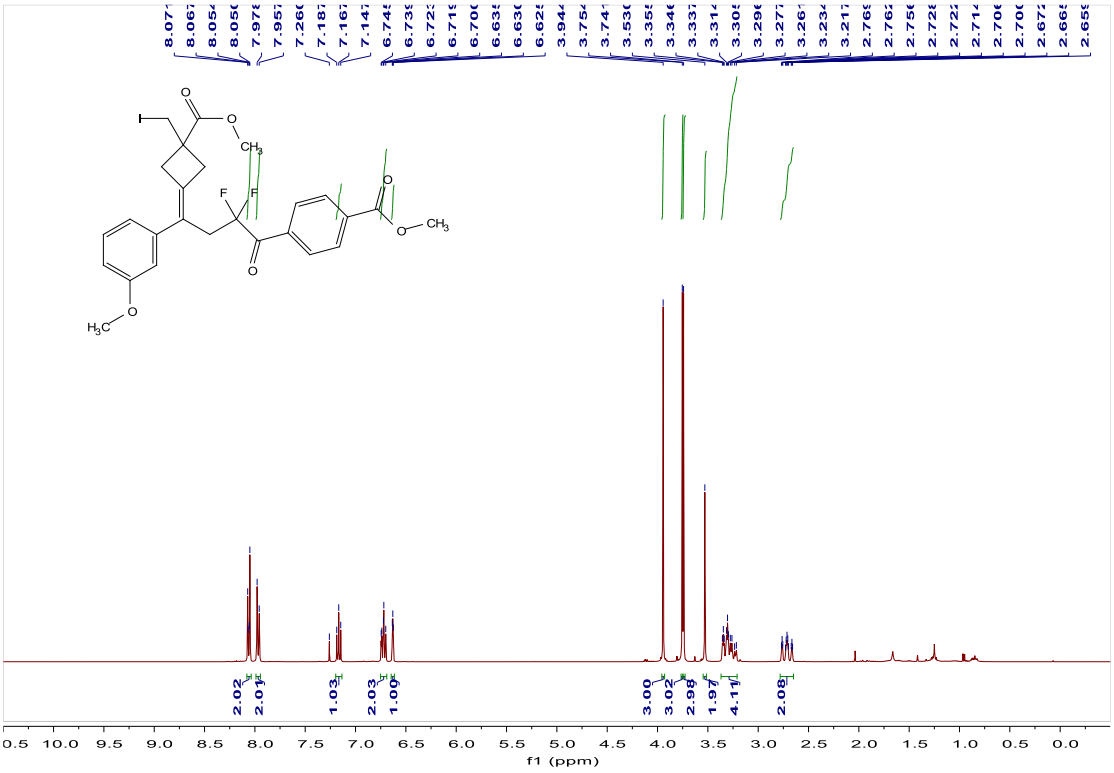
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **50**



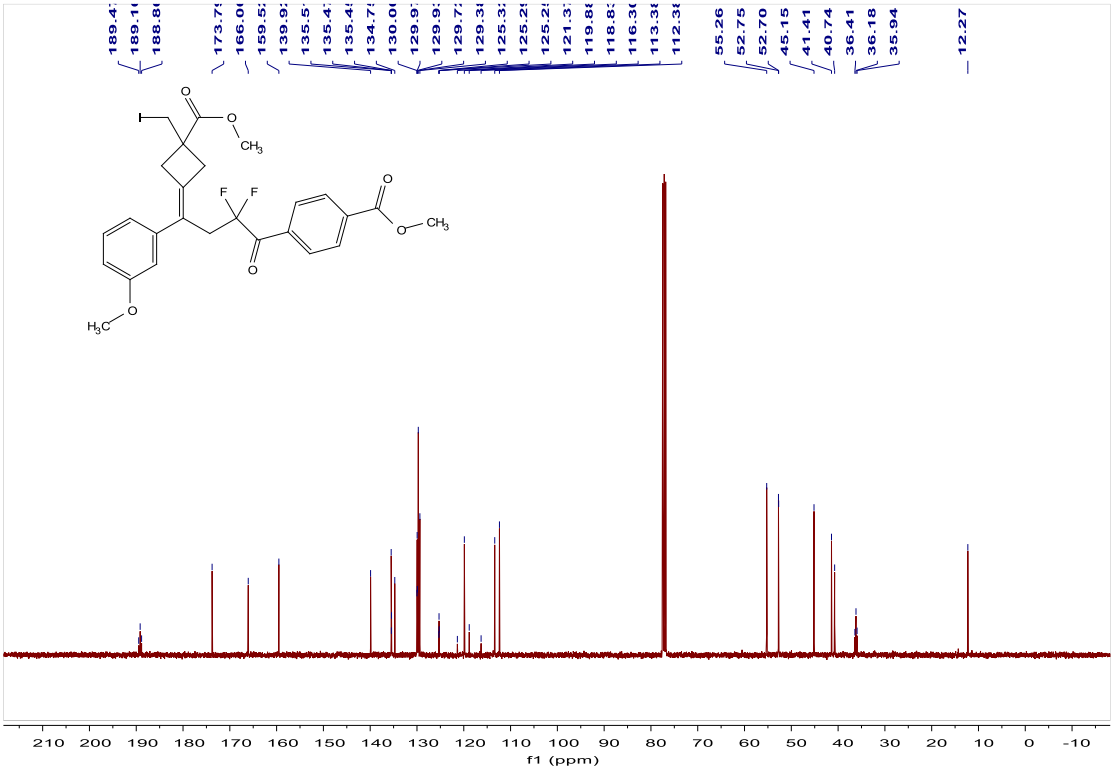
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **50**



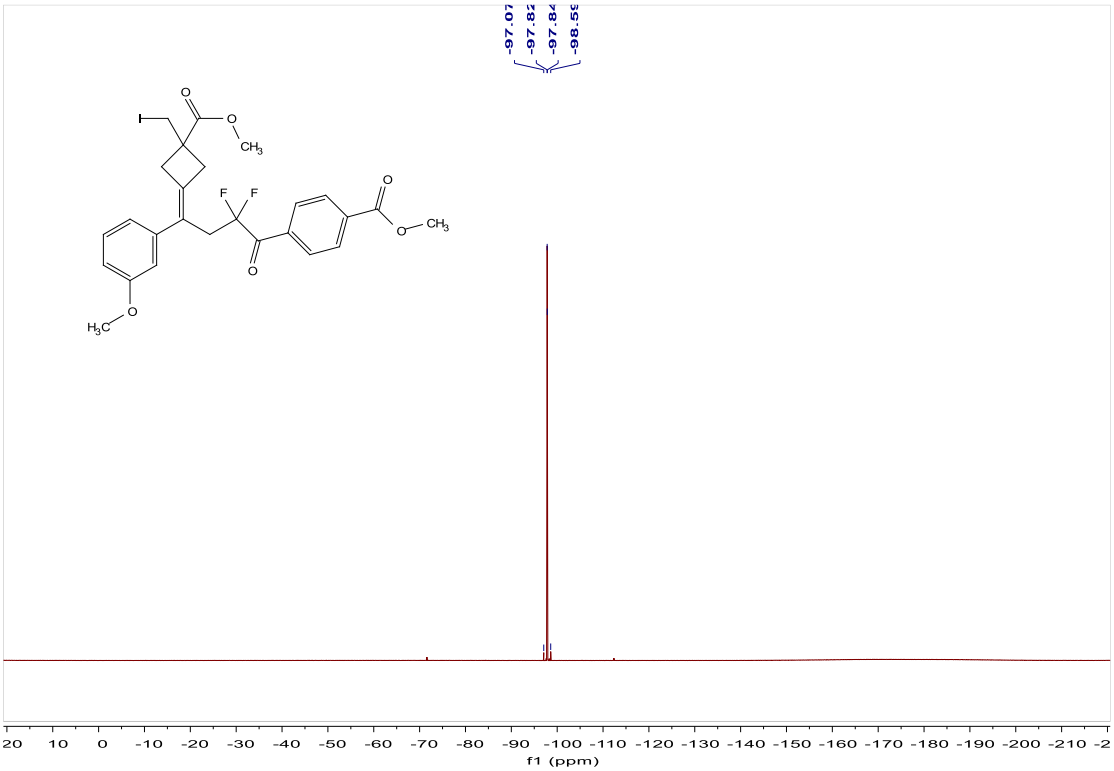
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **51**



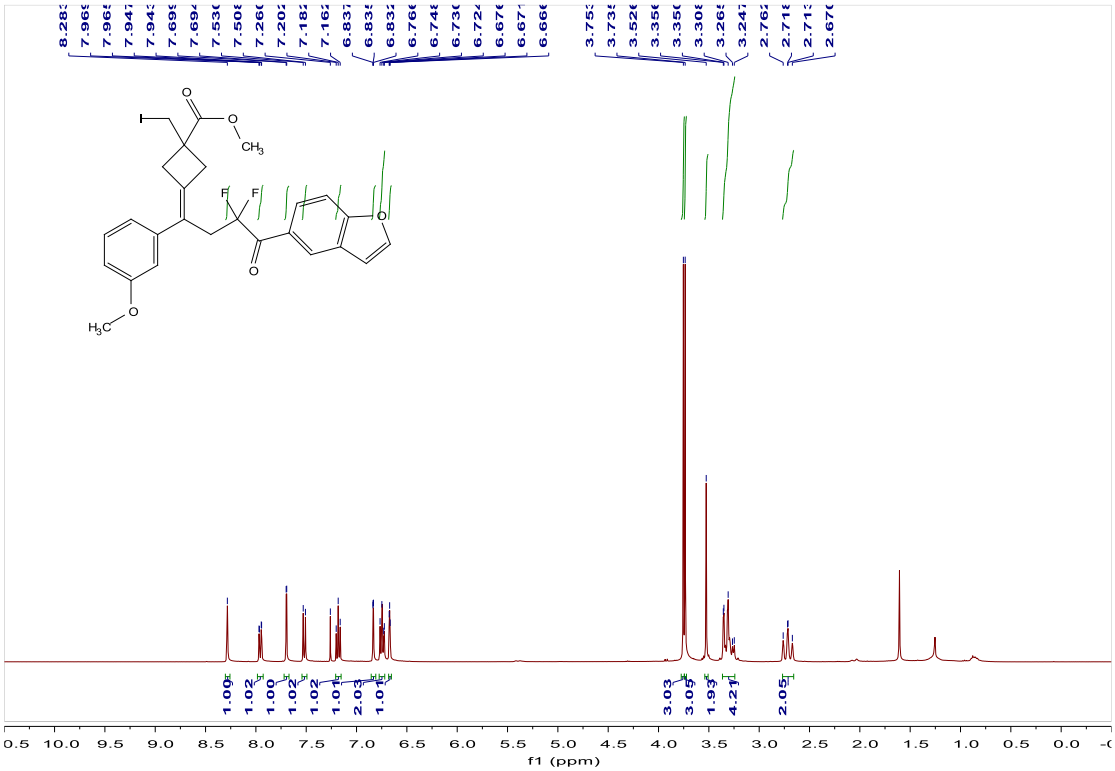
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **51**



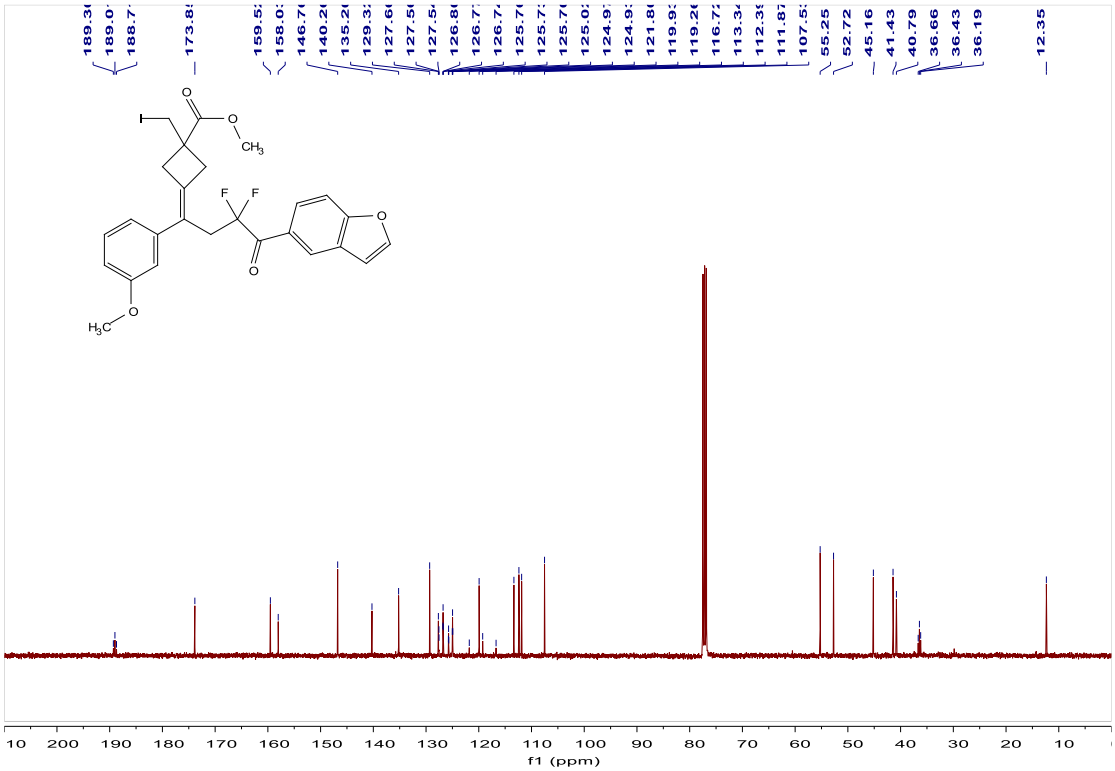
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **51**



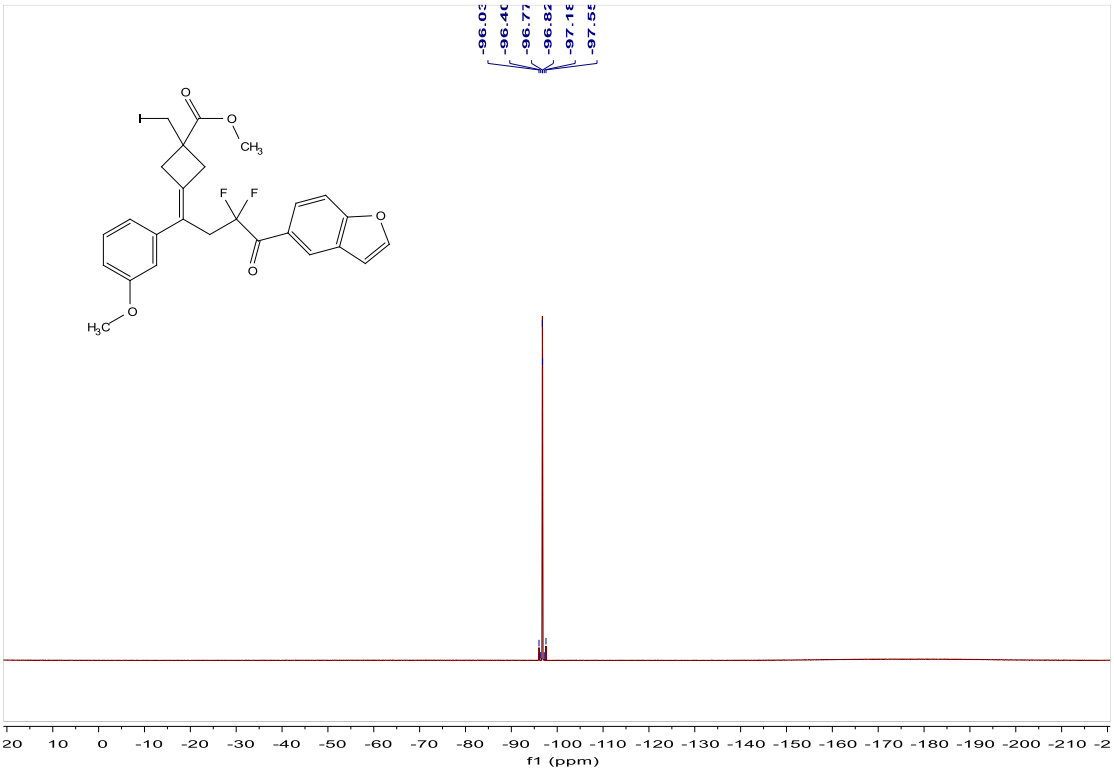
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **52**



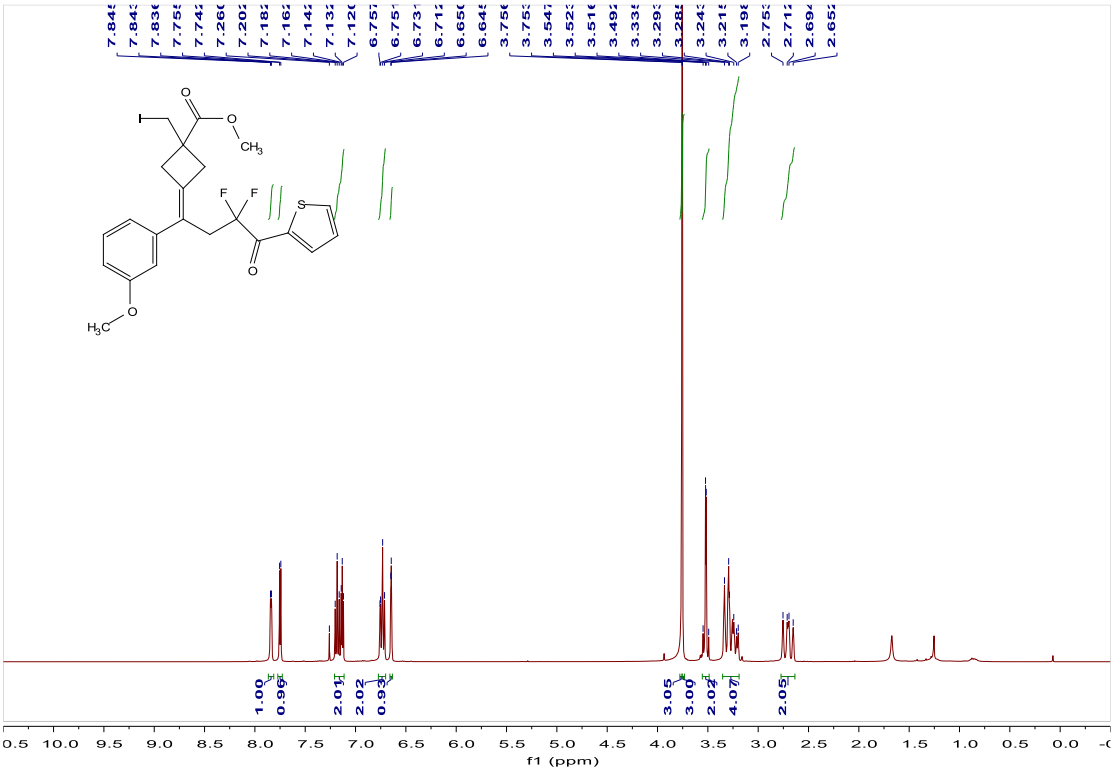
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **52**



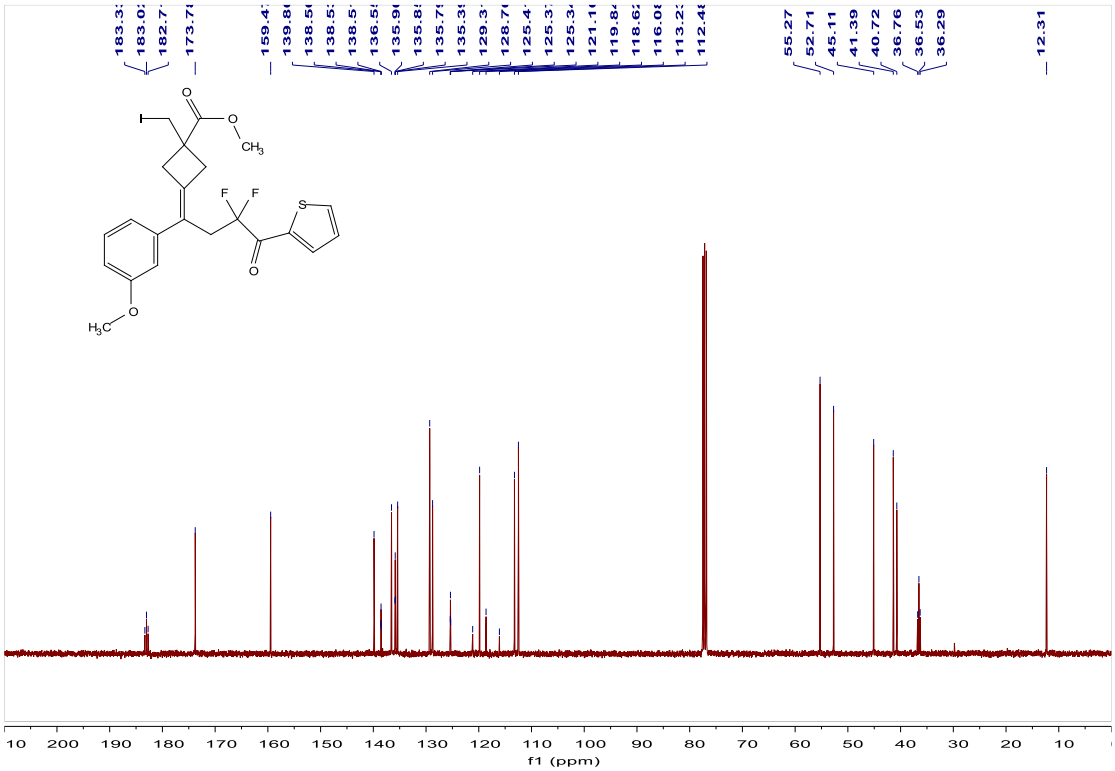
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **52**



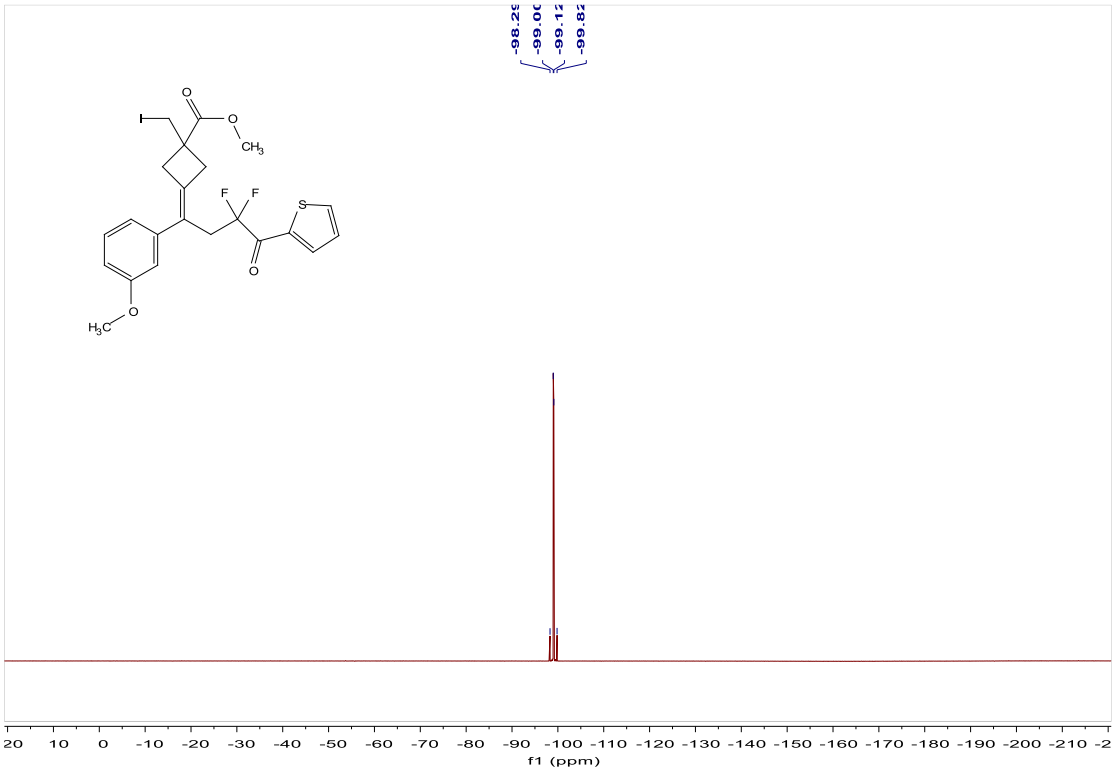
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **53**



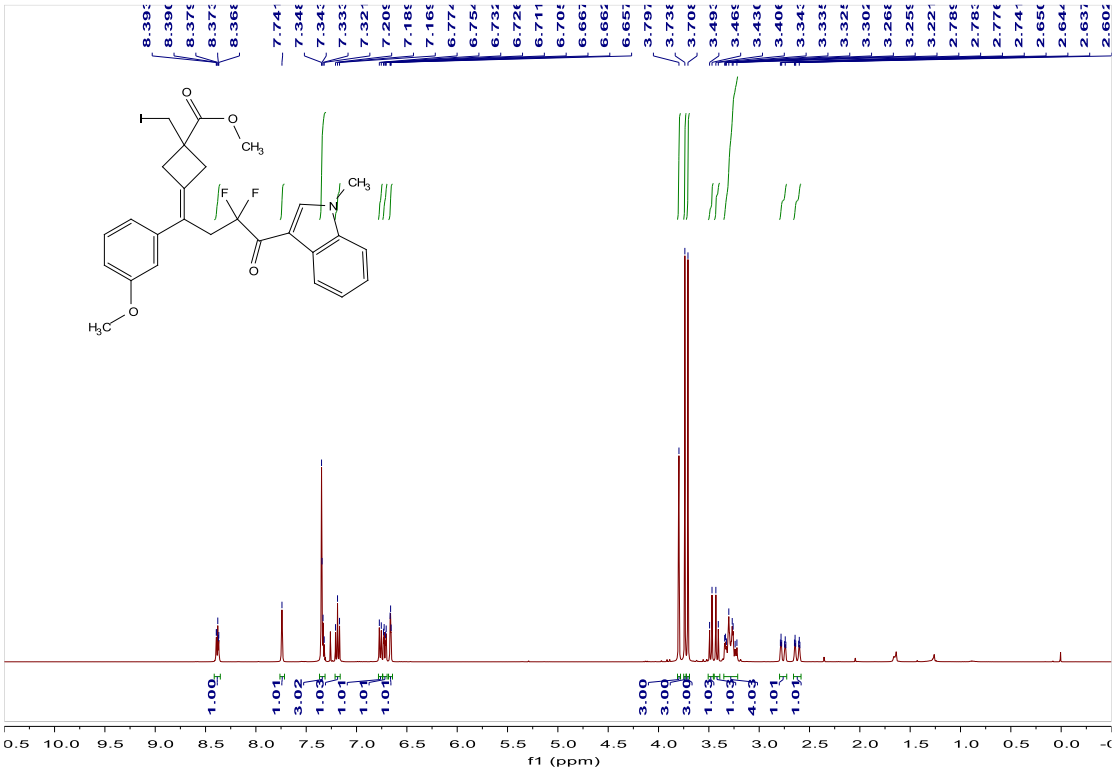
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **53**



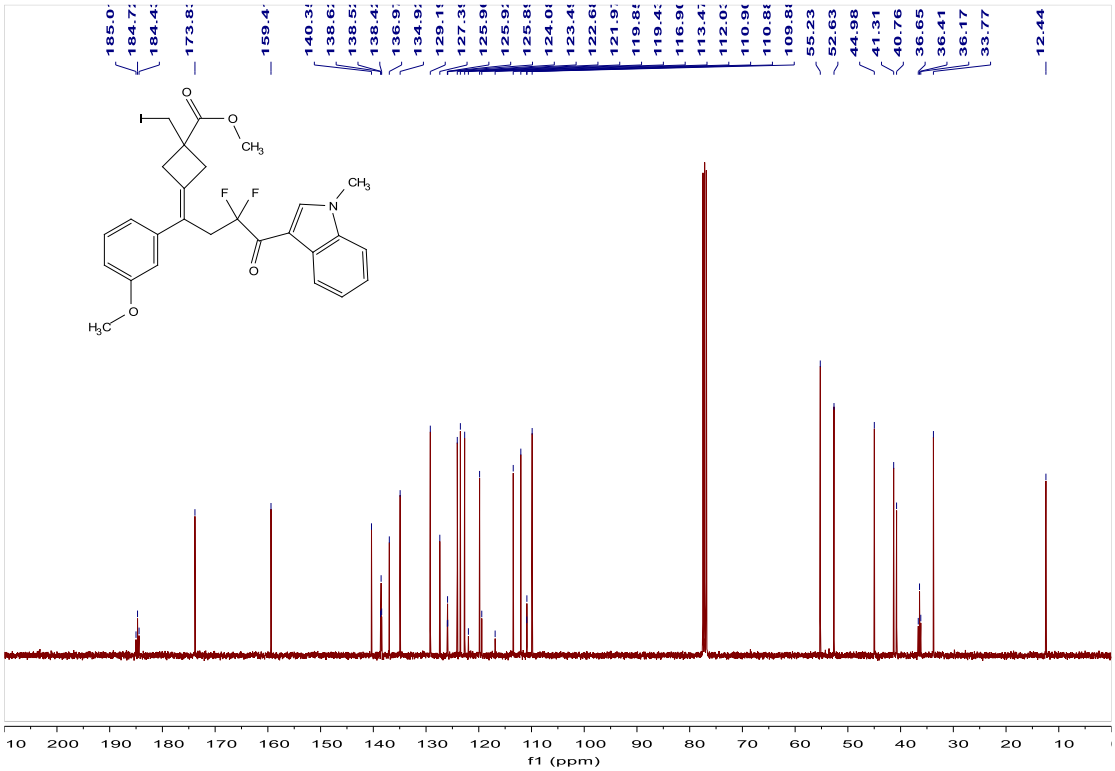
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **53**



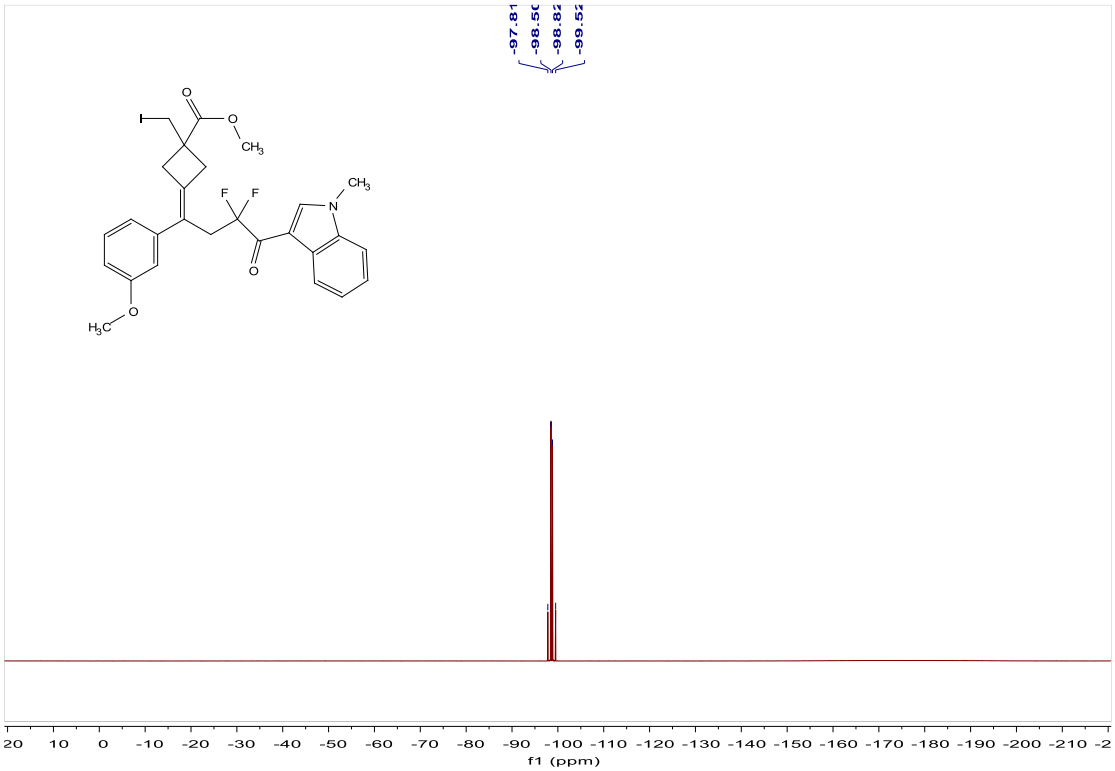
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **54**



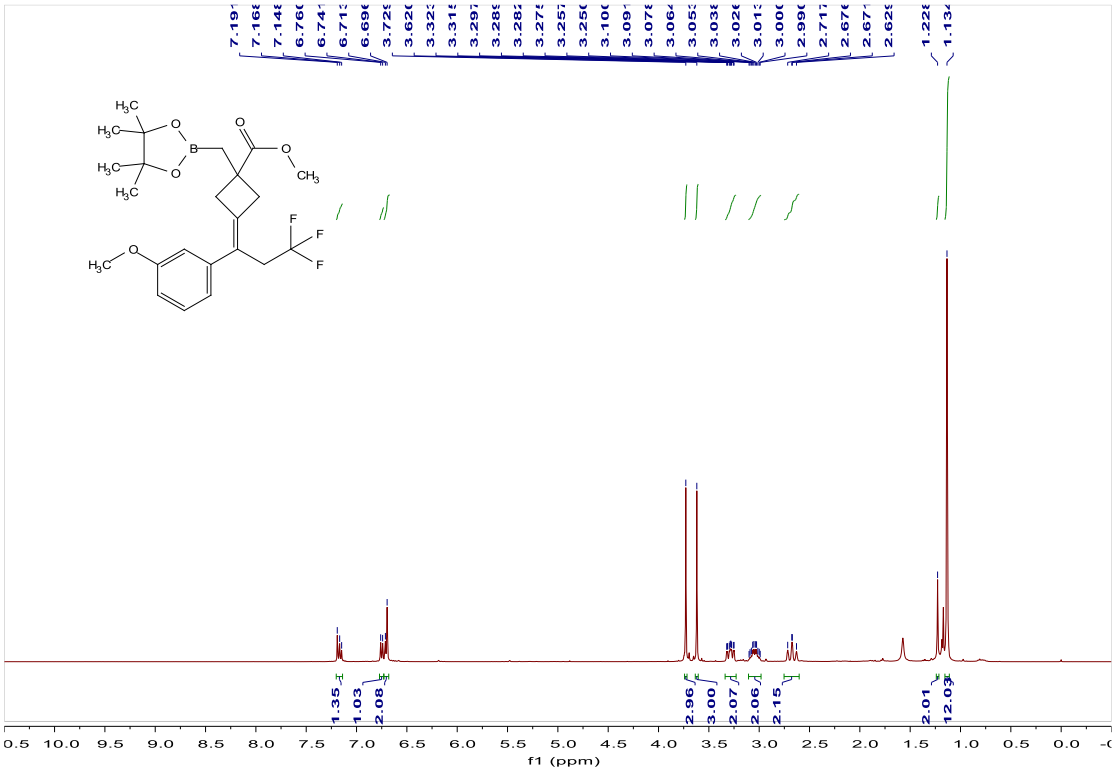
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **54**



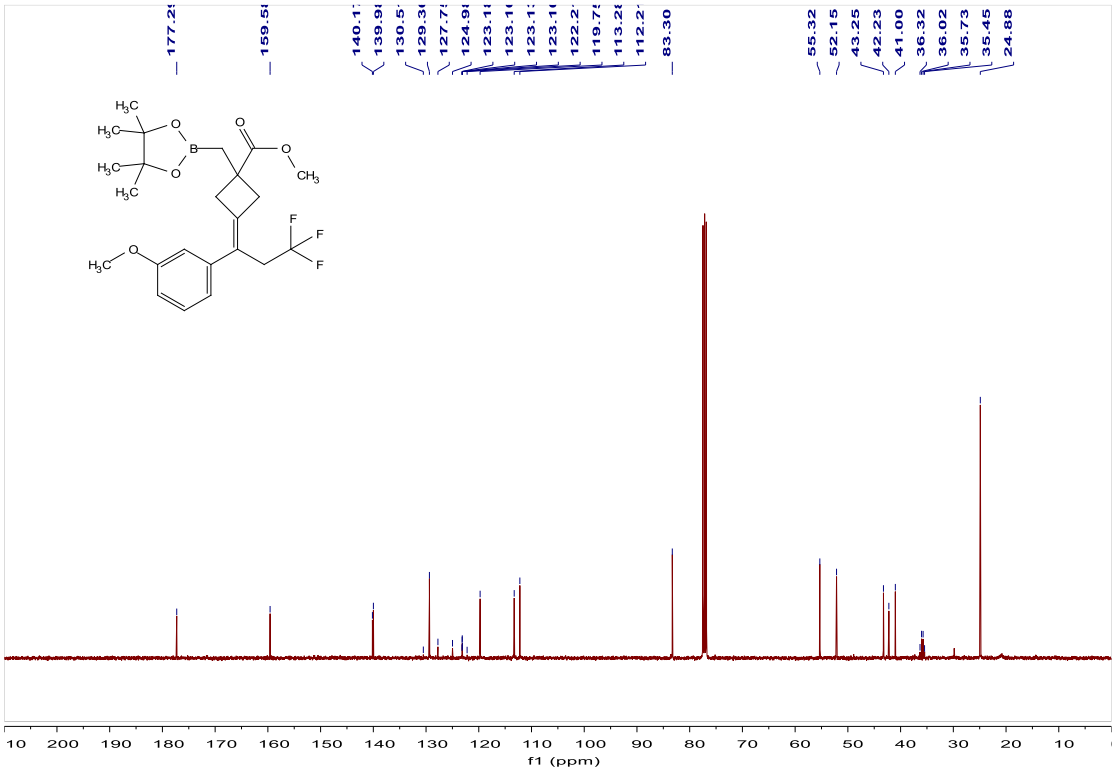
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **54**



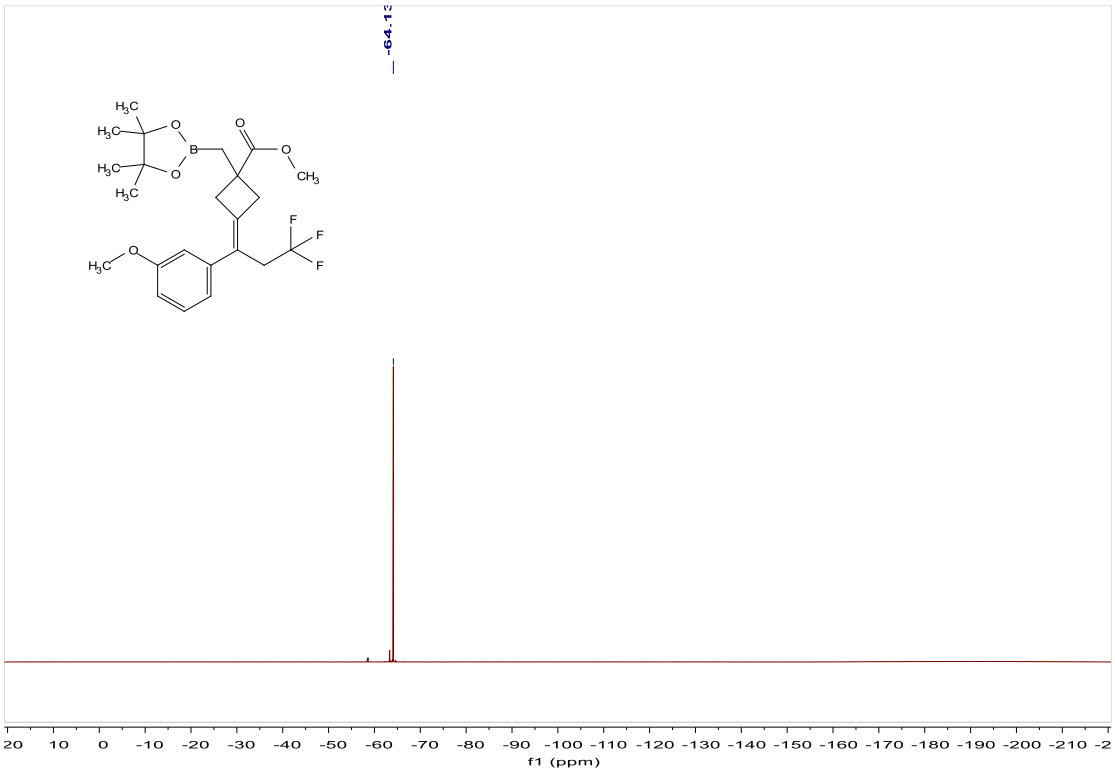
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **55**



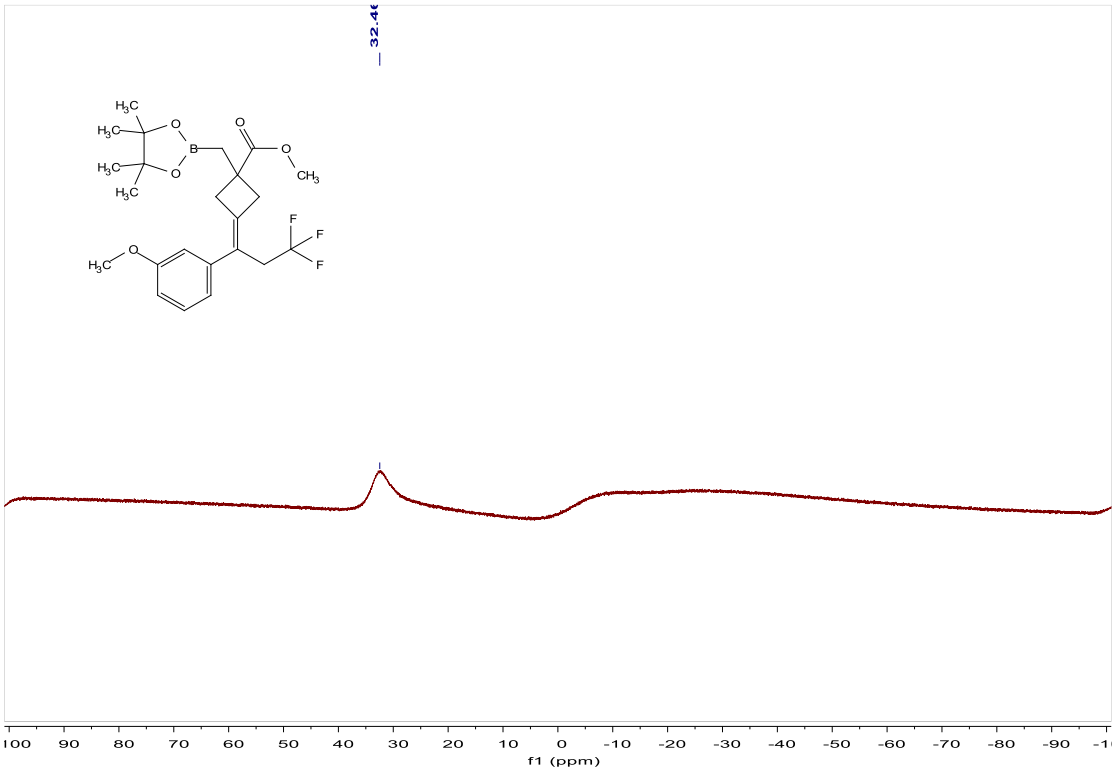
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **55**



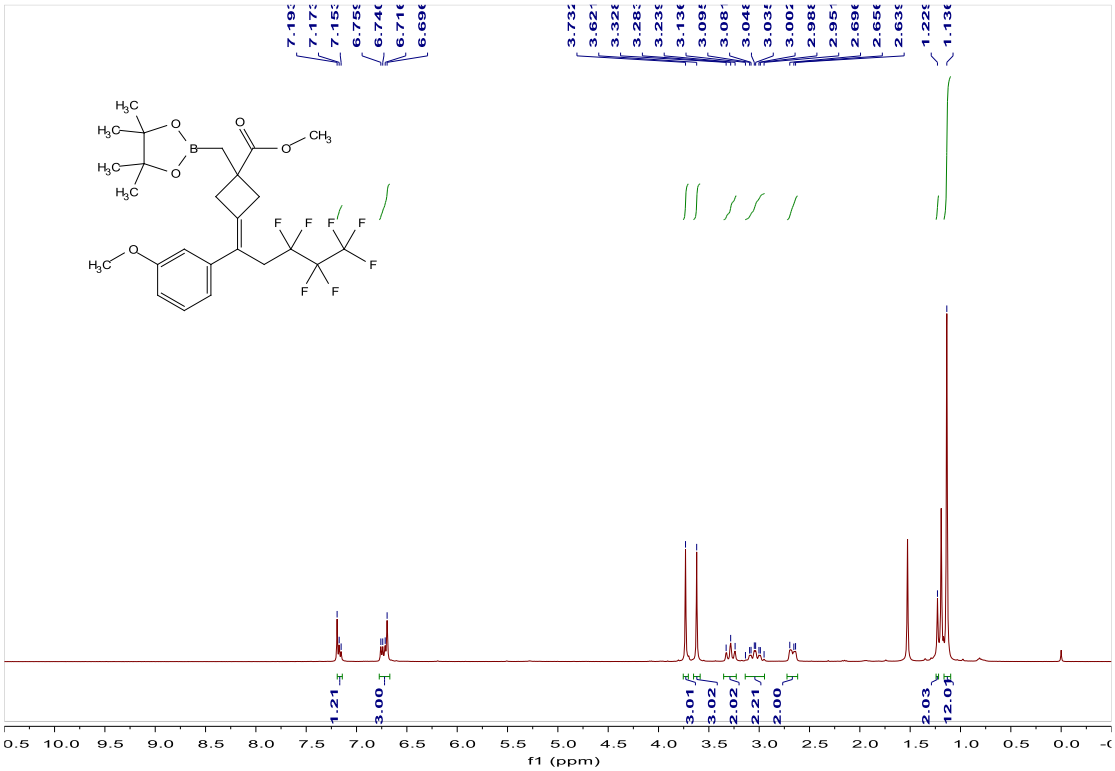
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **55**



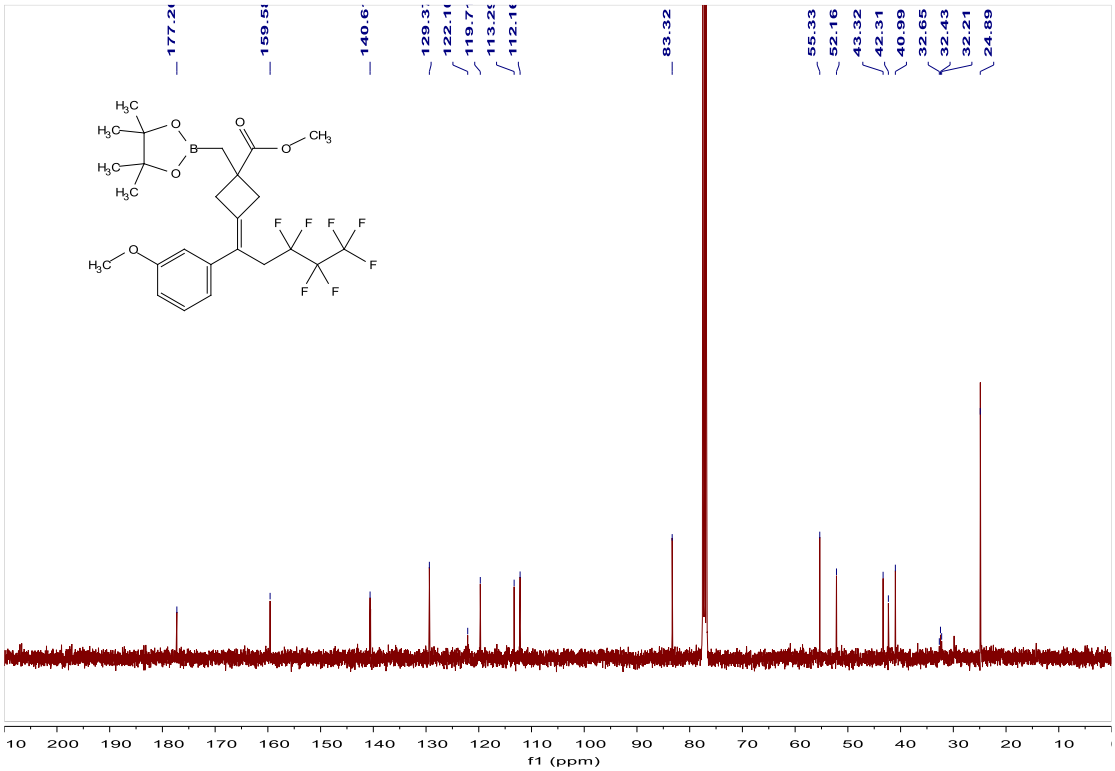
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of **55**



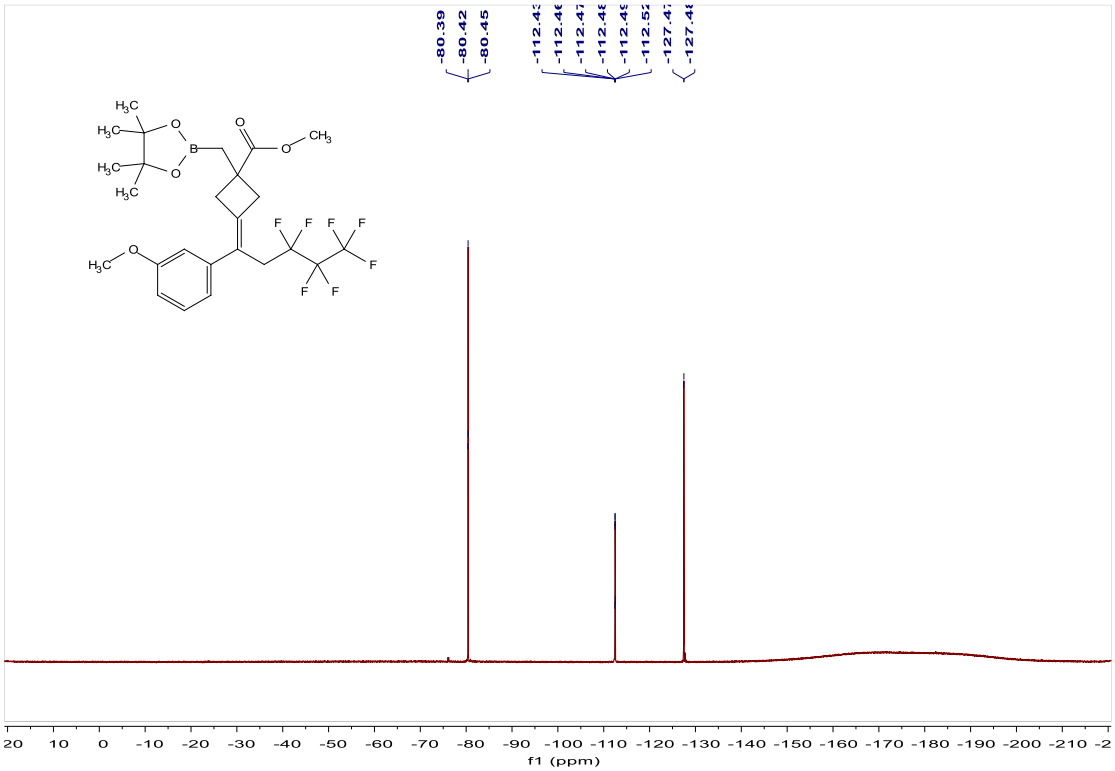
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **56**



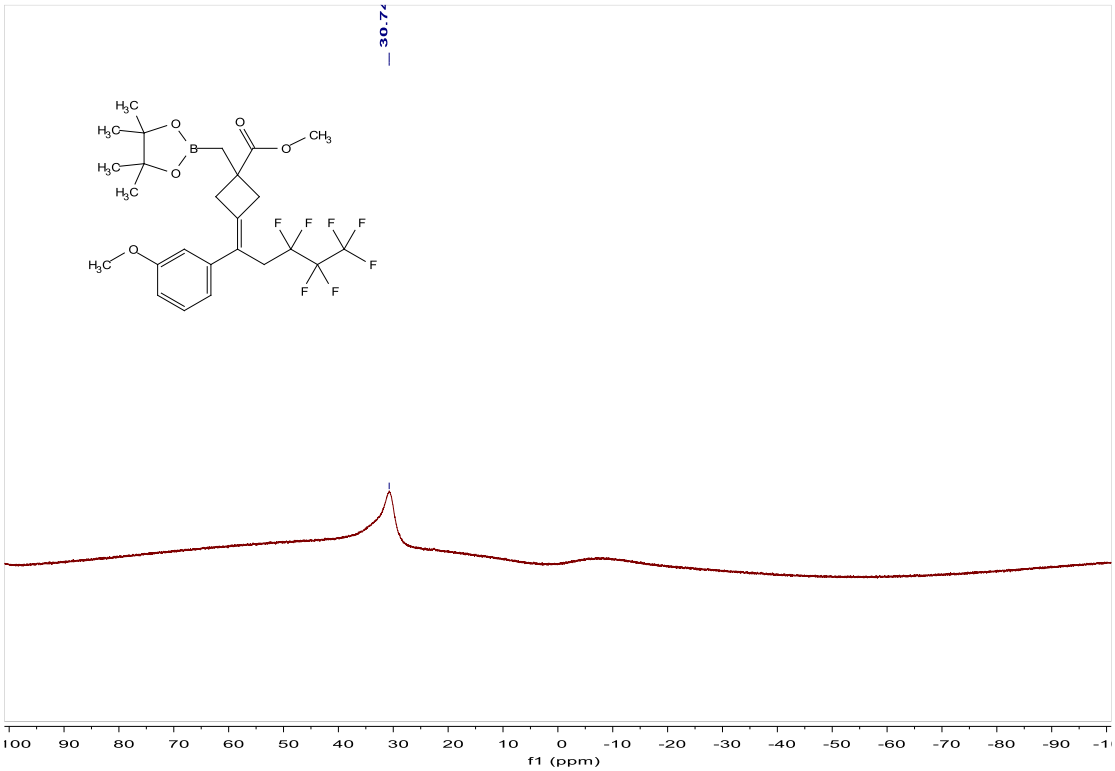
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **56**



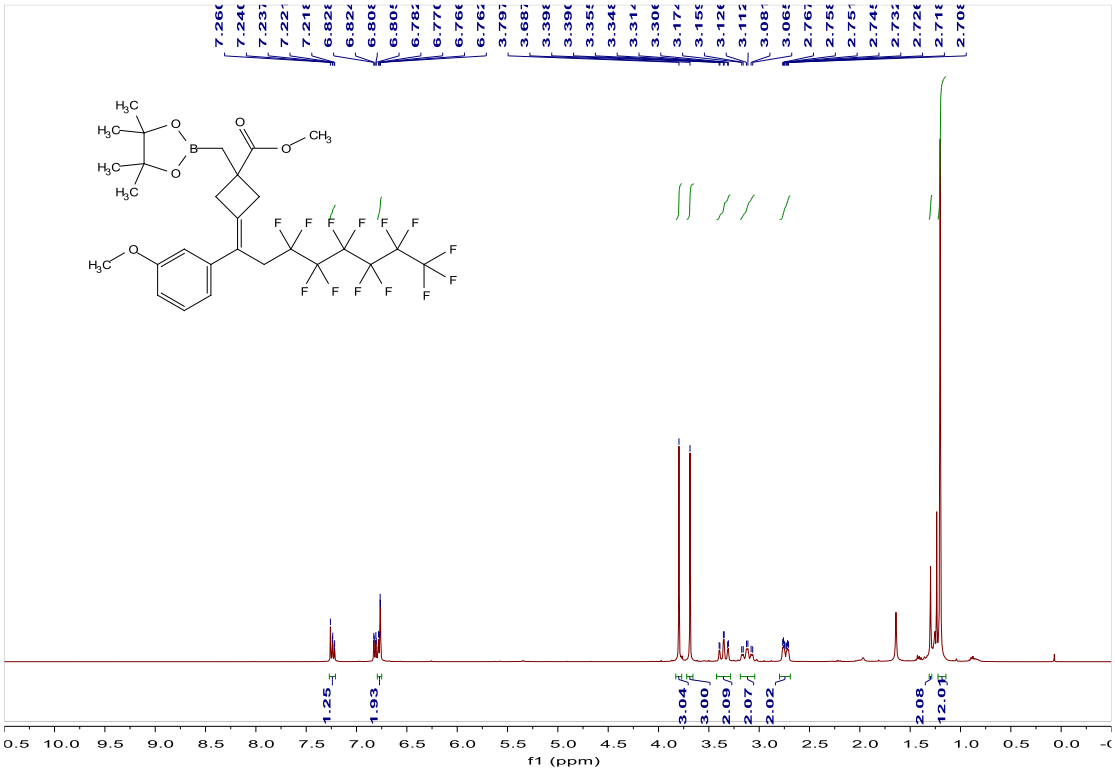
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **56**



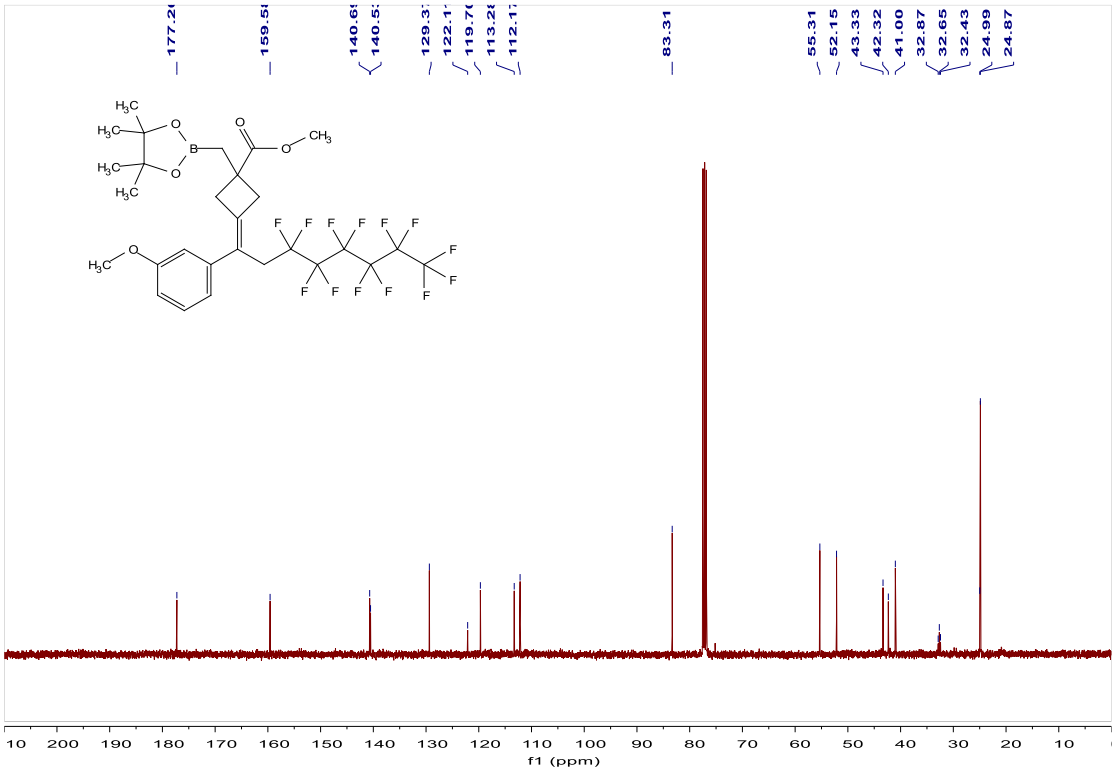
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of **56**



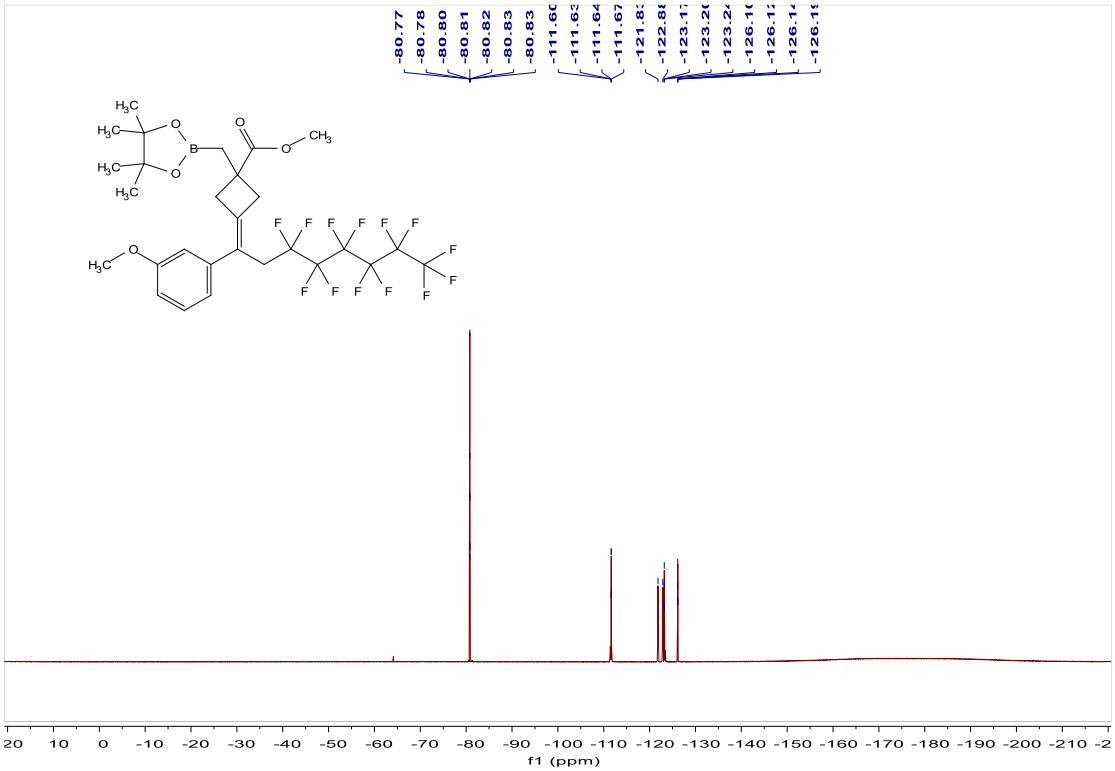
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **57**



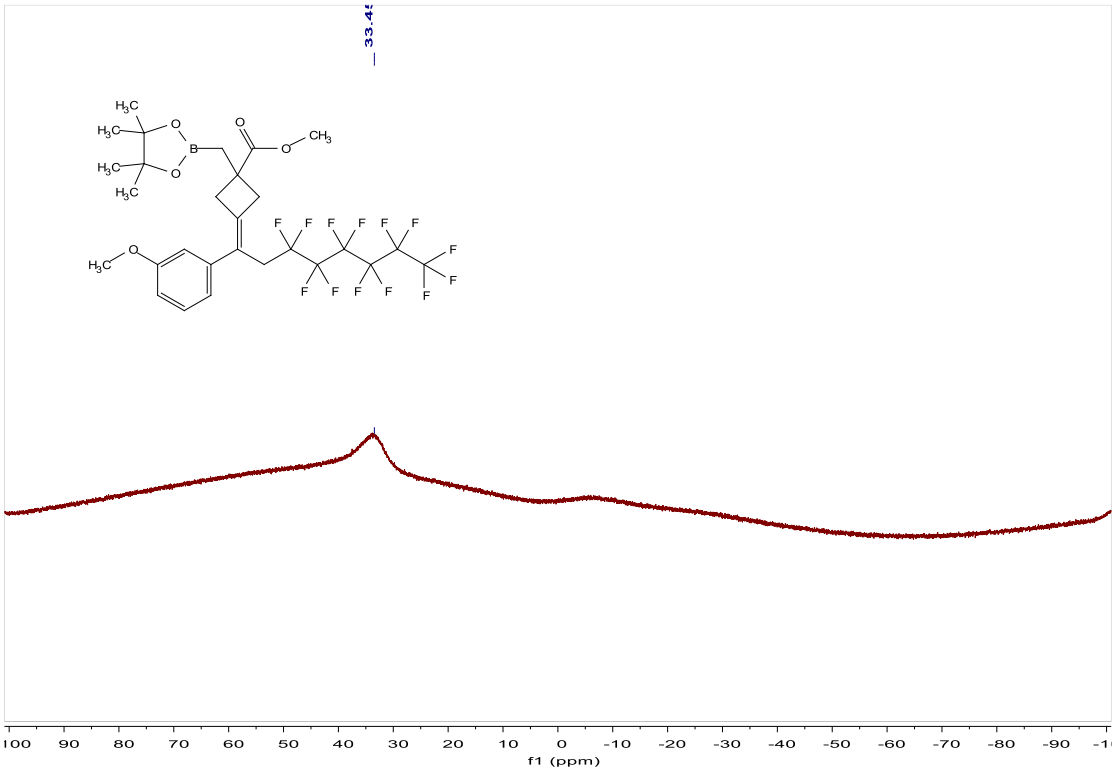
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **57**



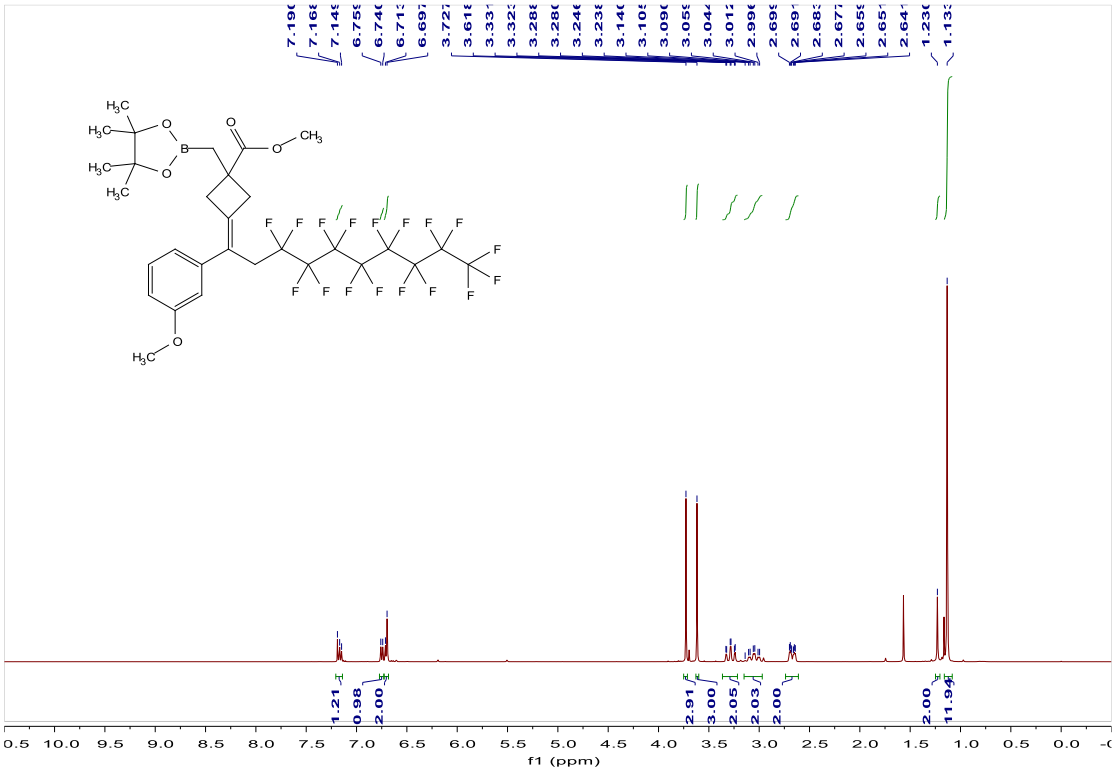
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **57**



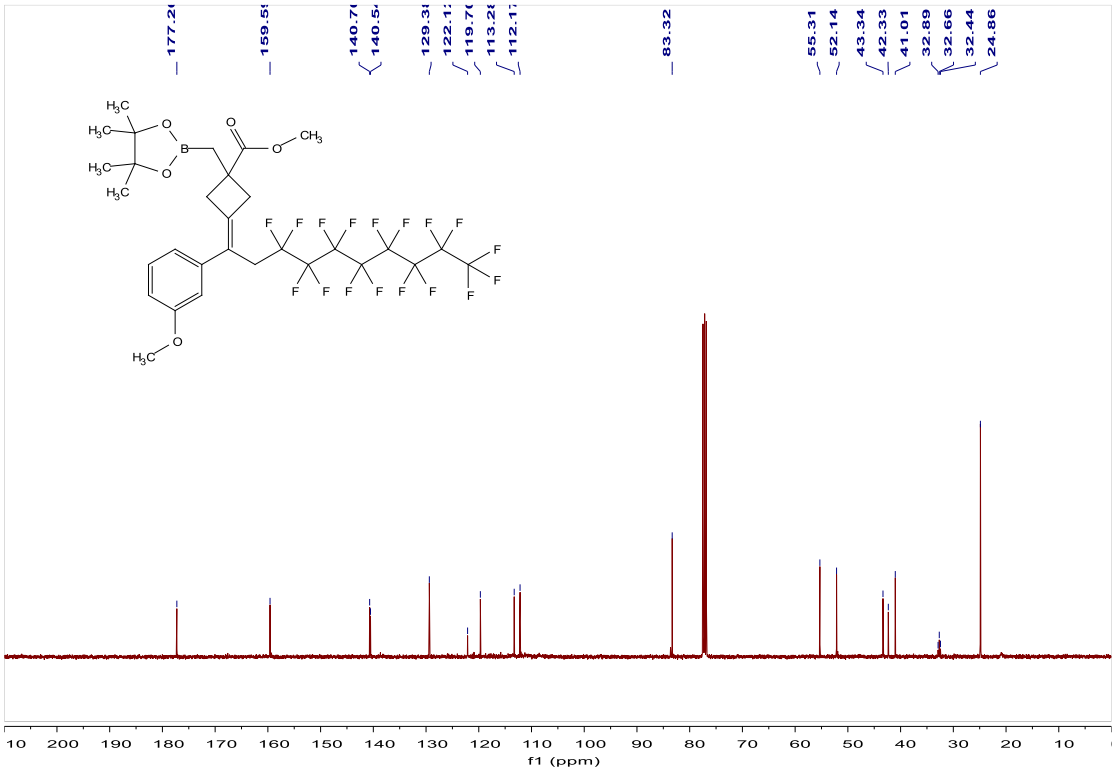
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of **57**



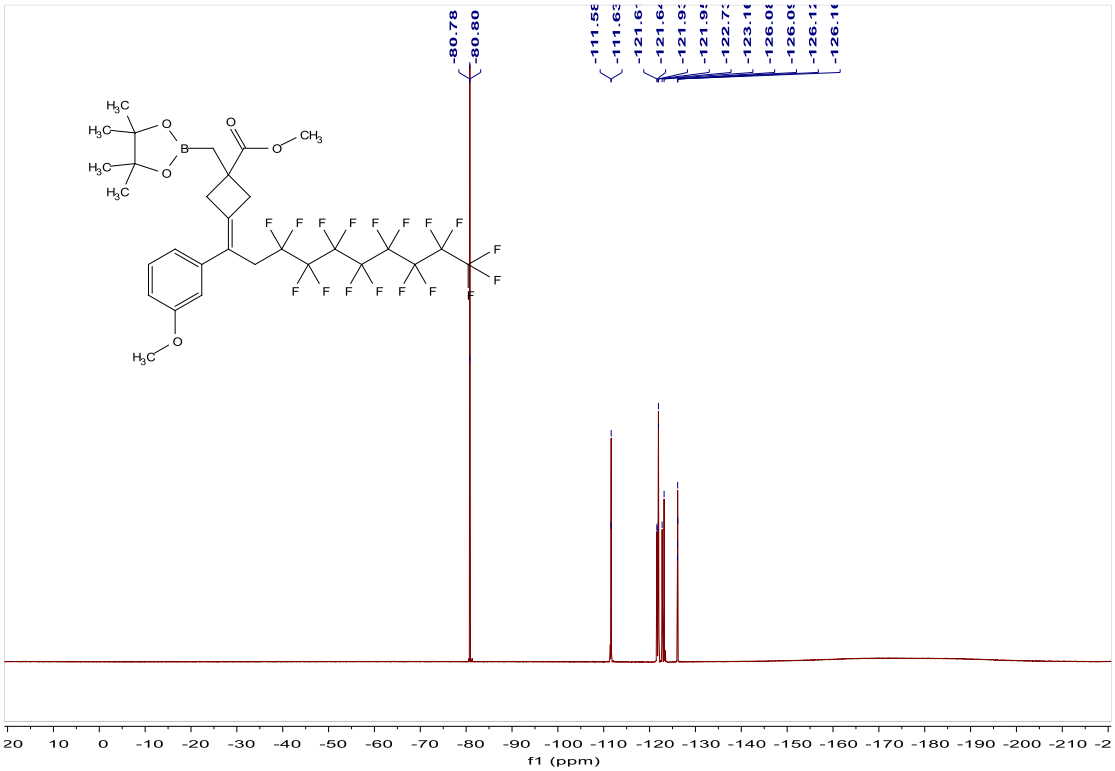
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **58**



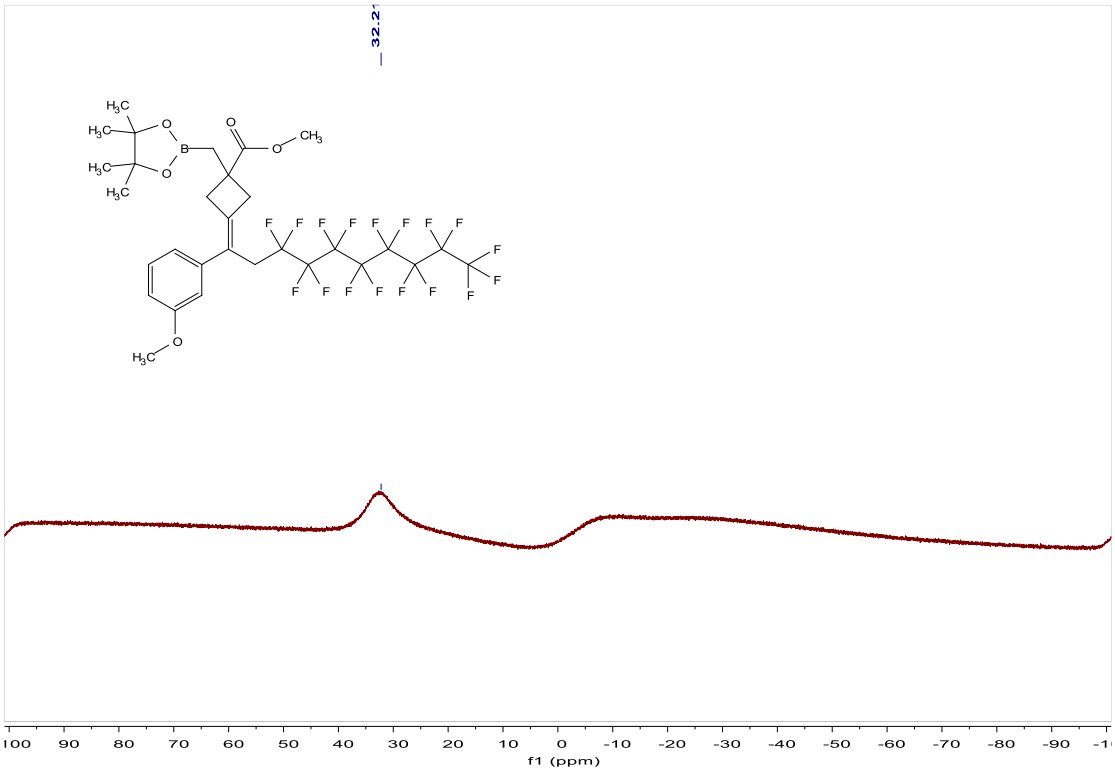
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **58**



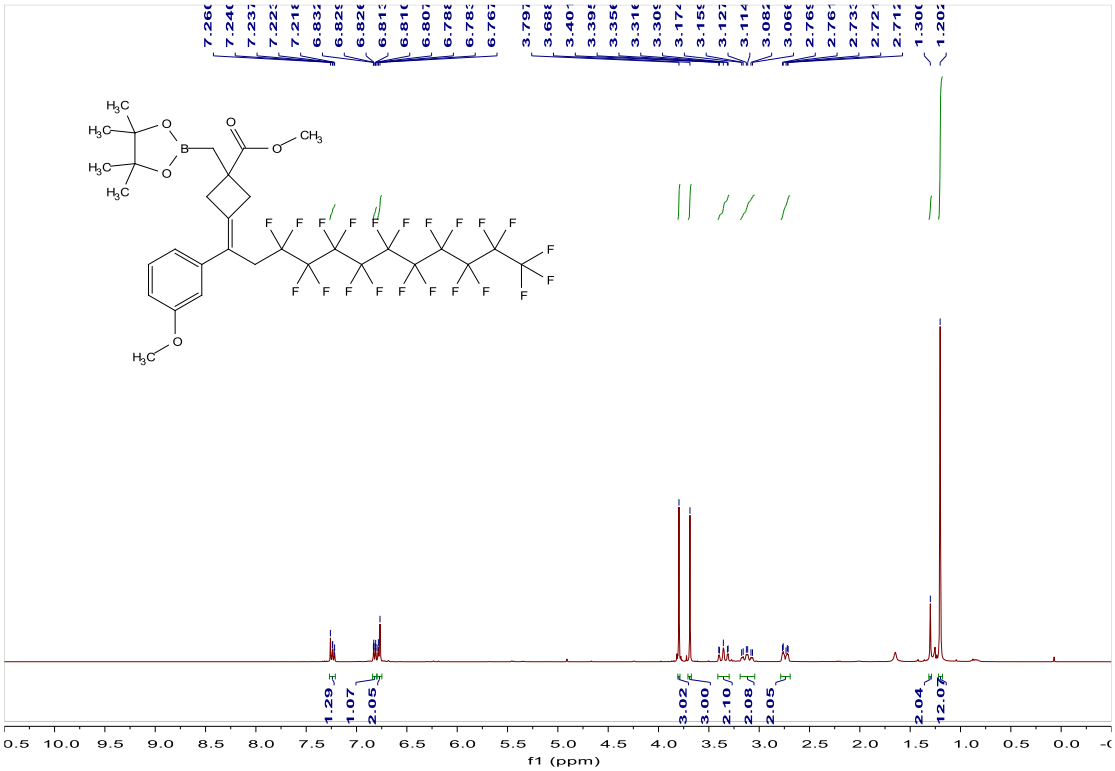
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **58**



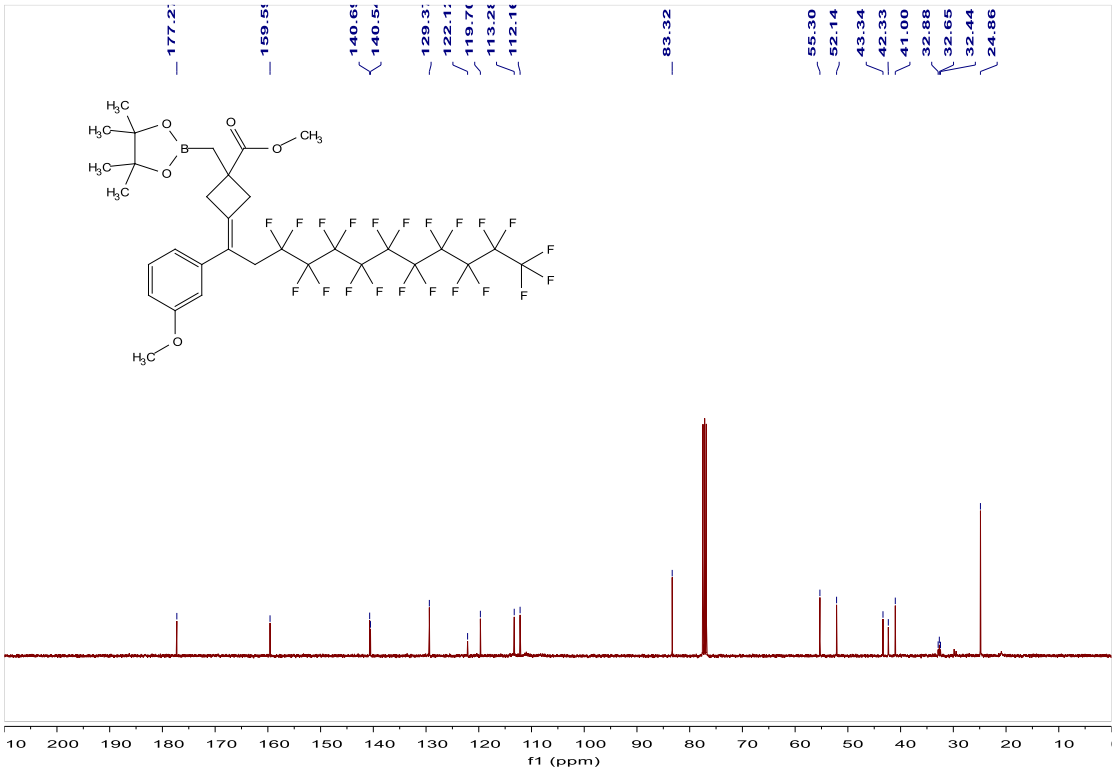
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of **58**



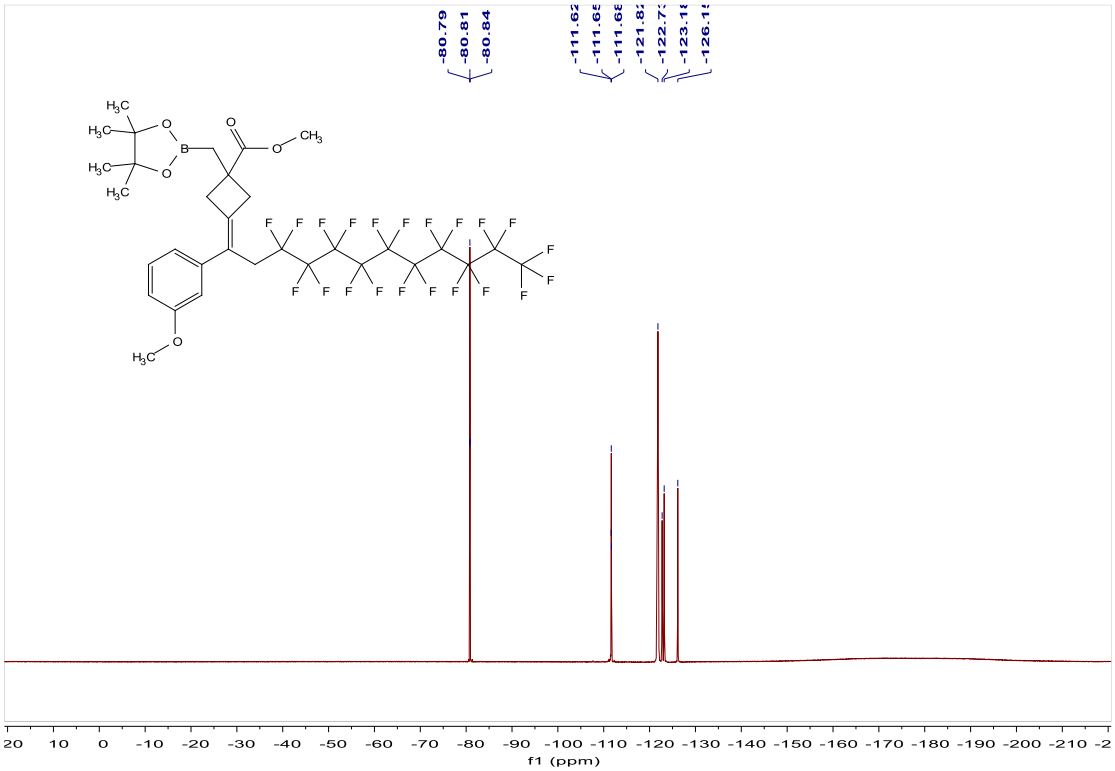
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **59**



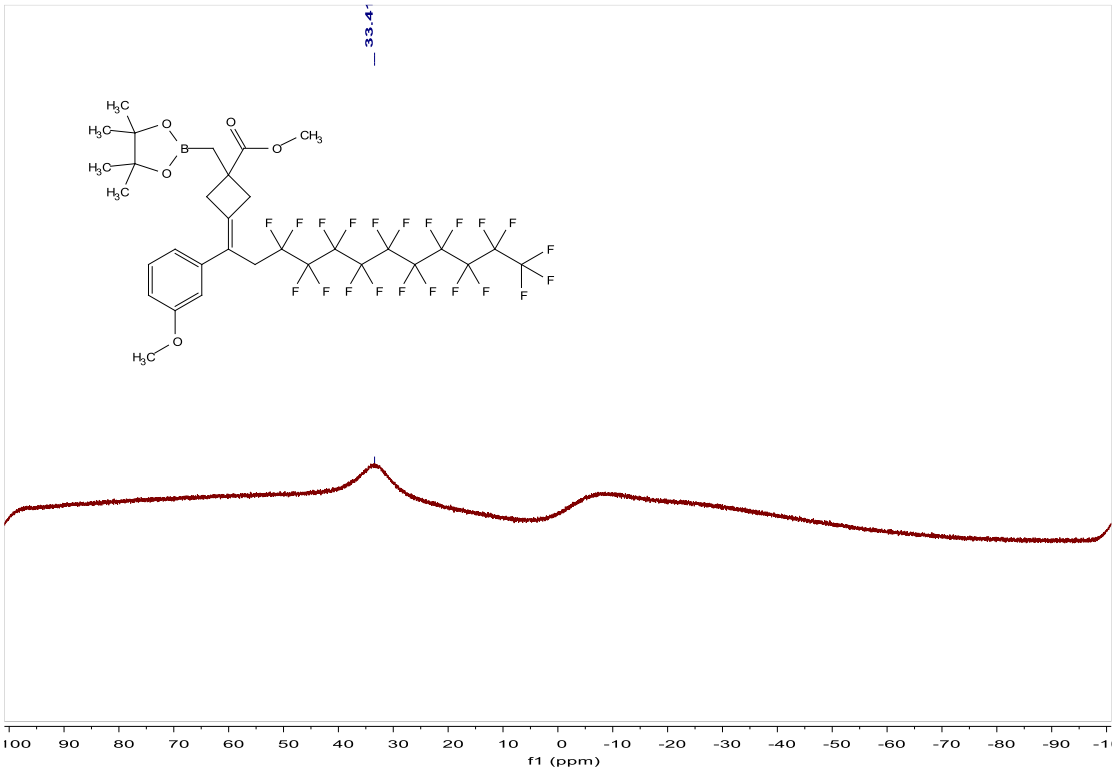
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **59**



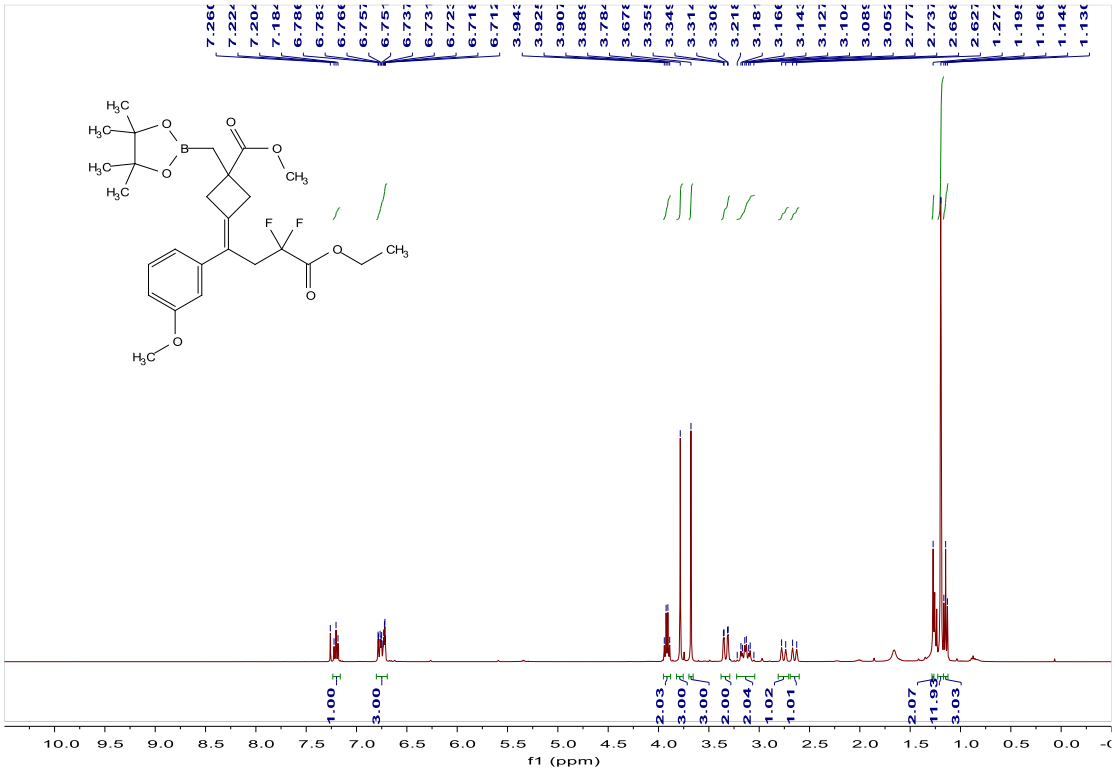
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **59**



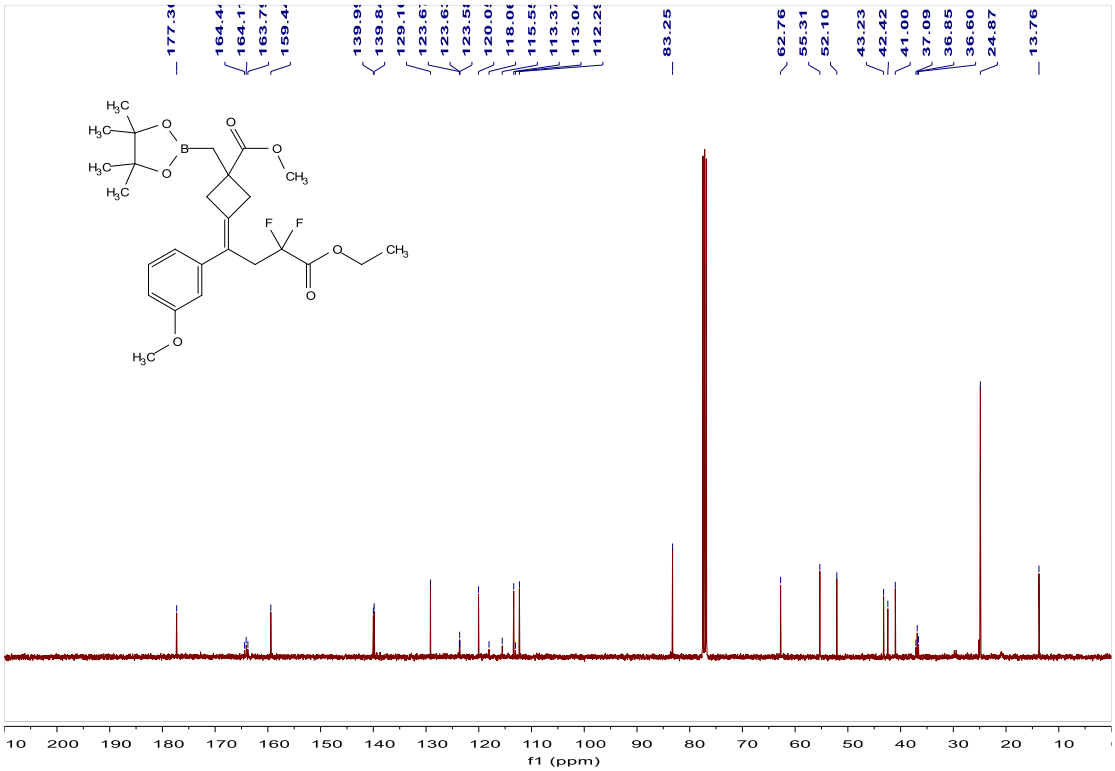
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of **59**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **60**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **60**



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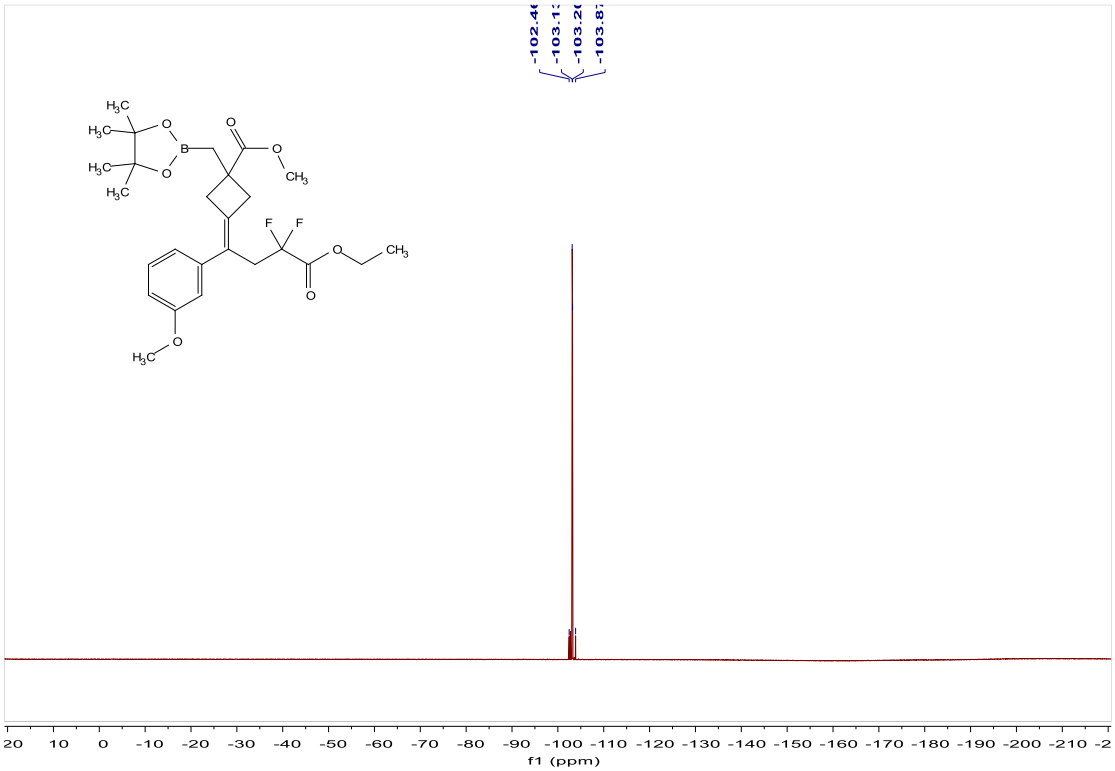

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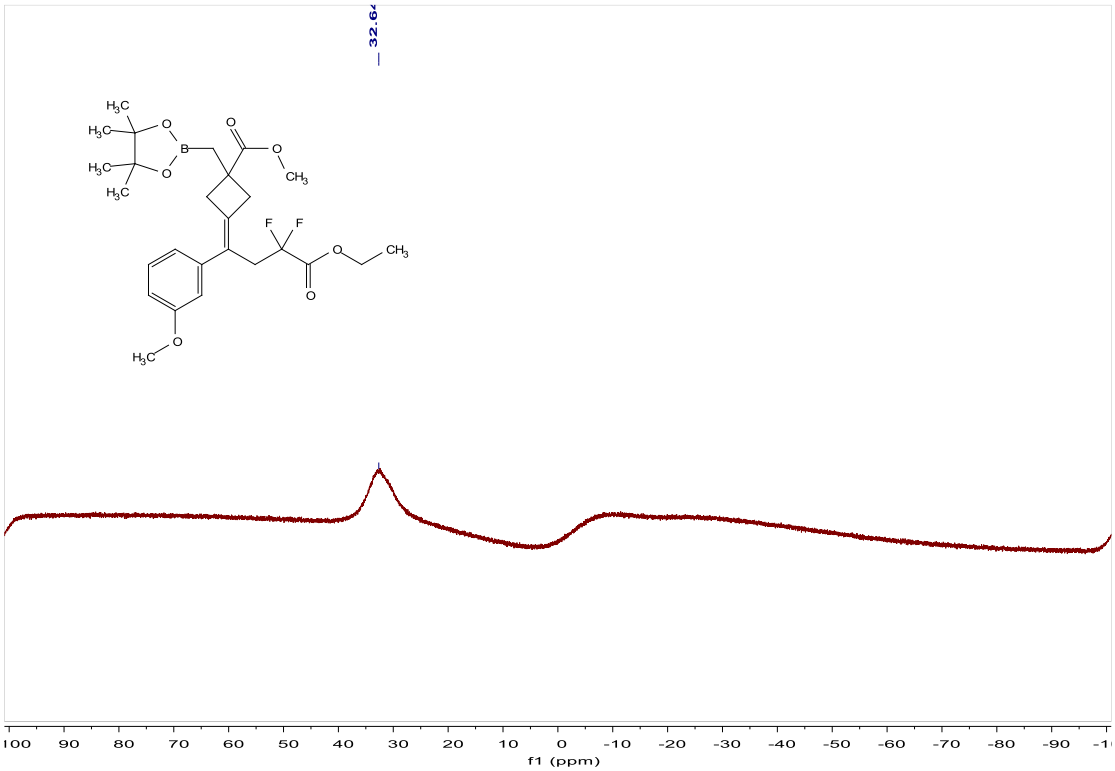
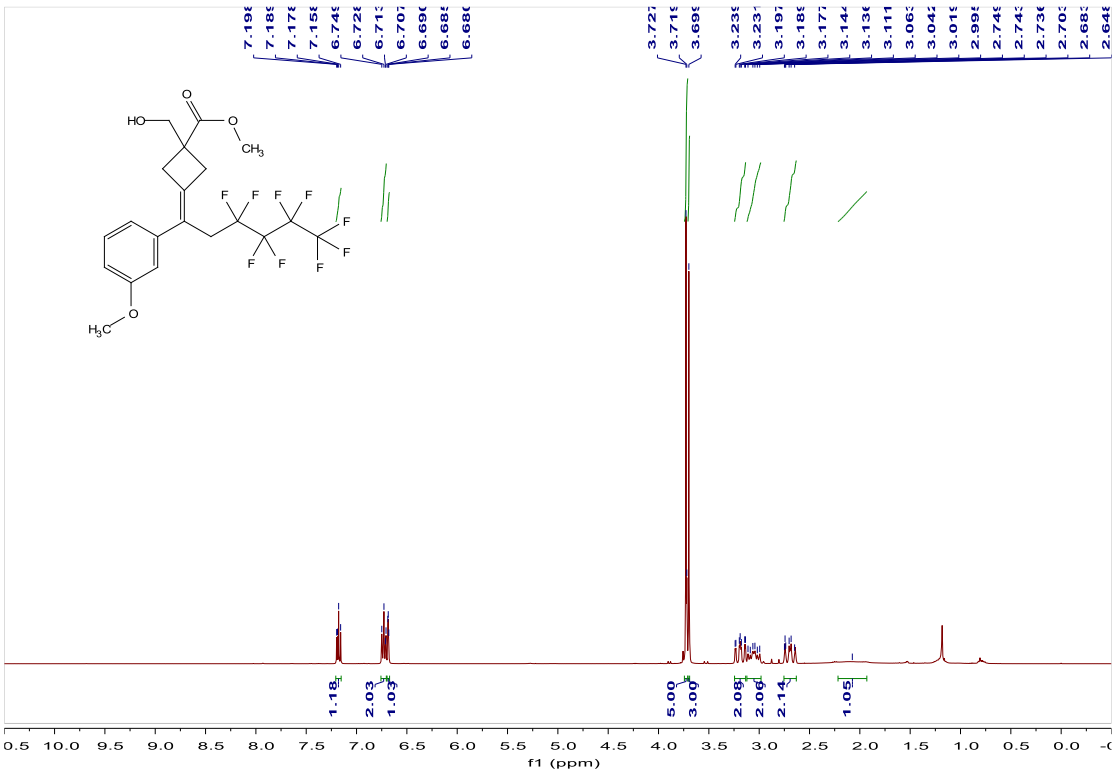
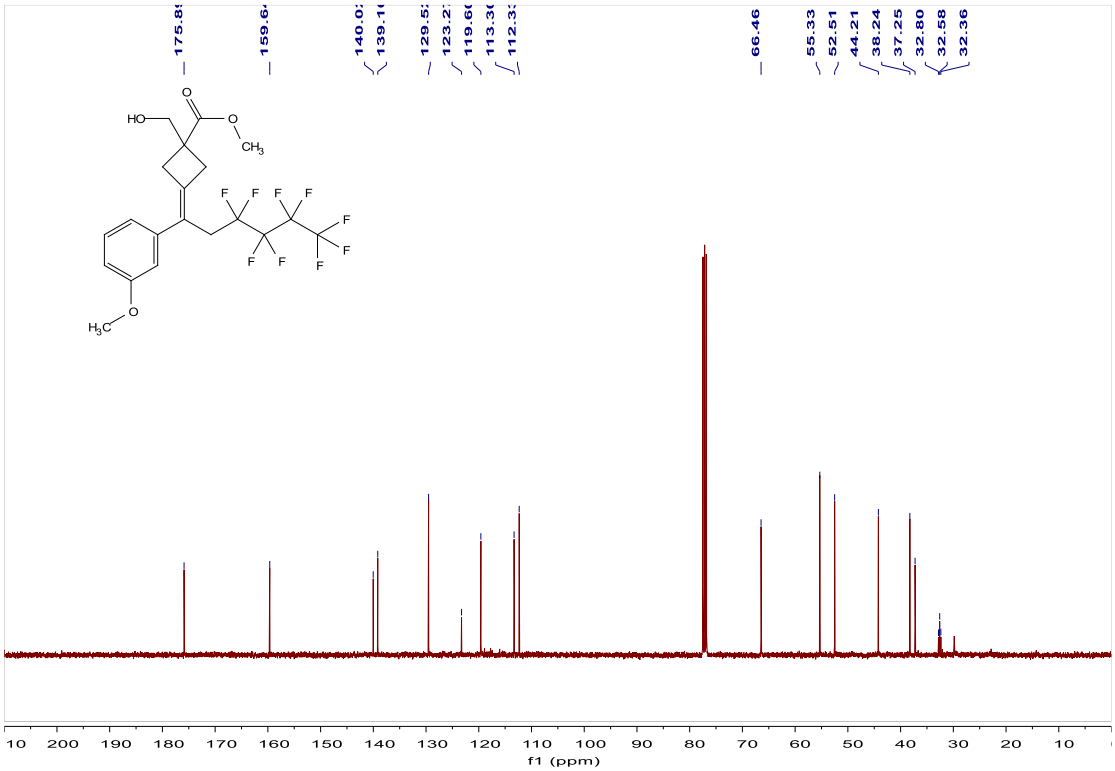


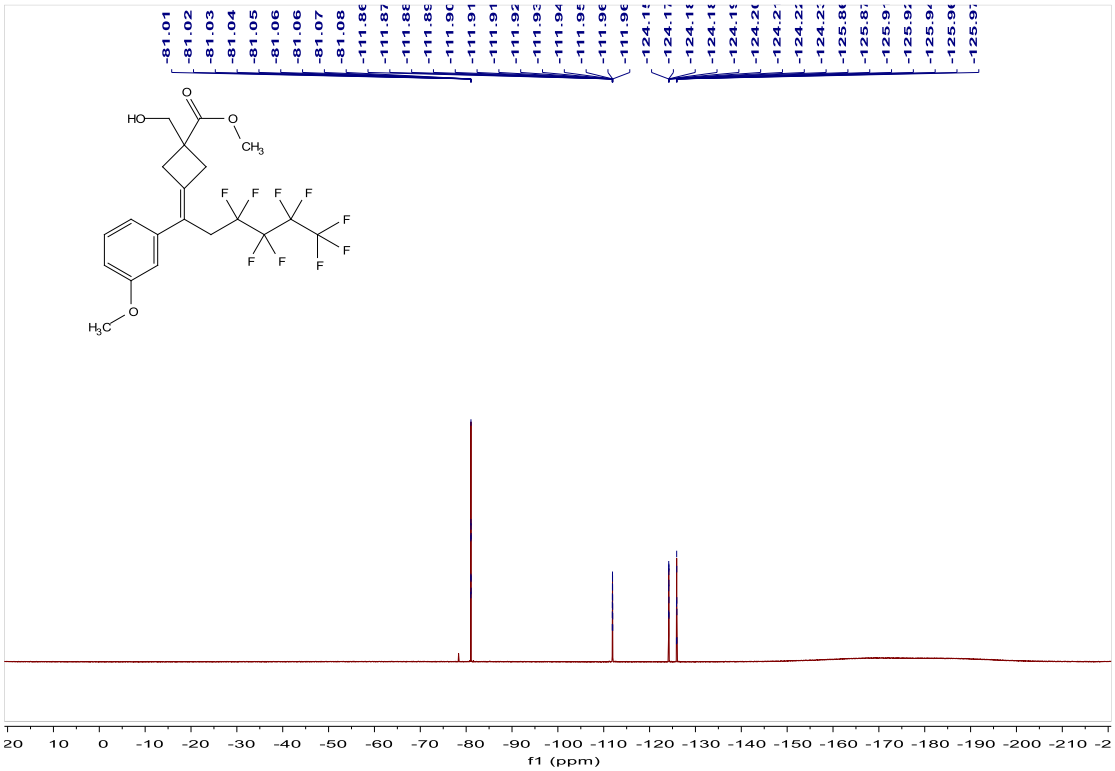
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **61**



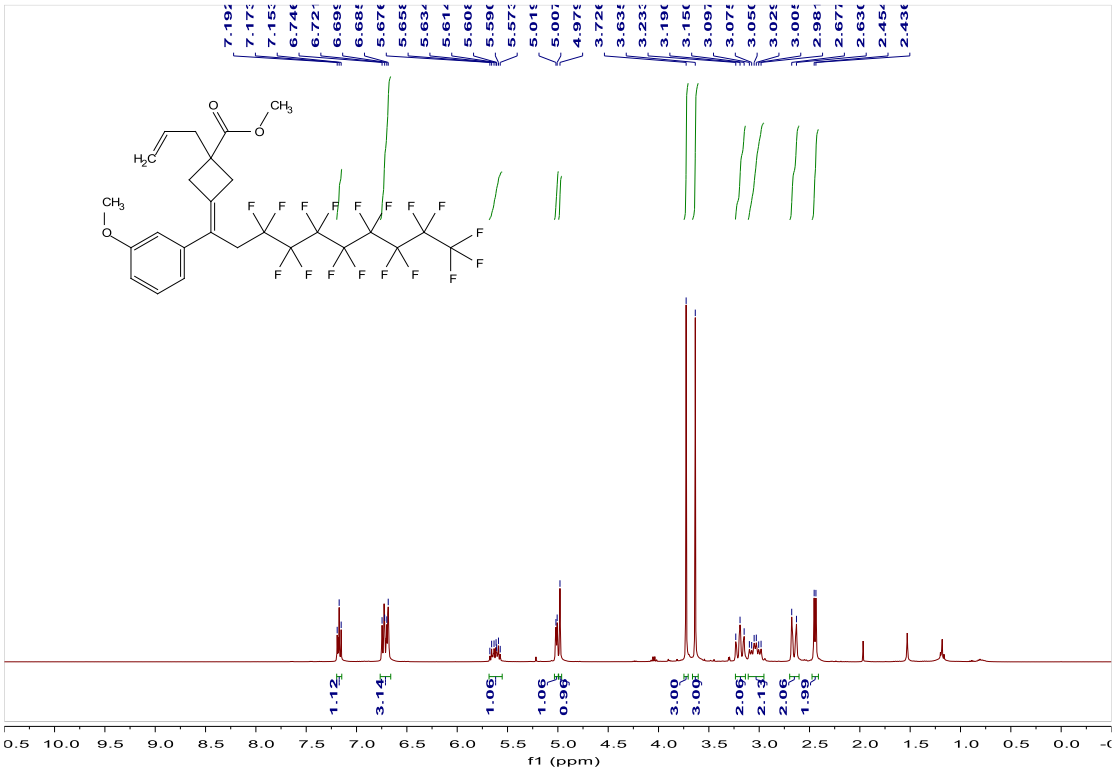
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **61**



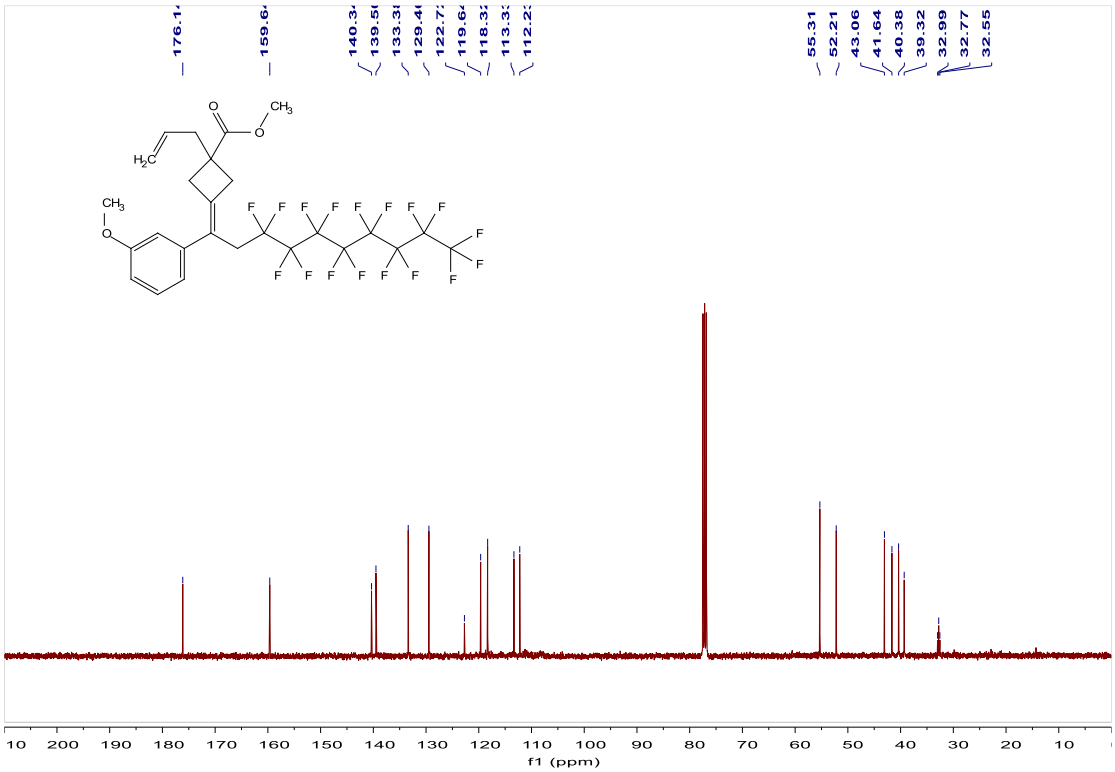
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **61**



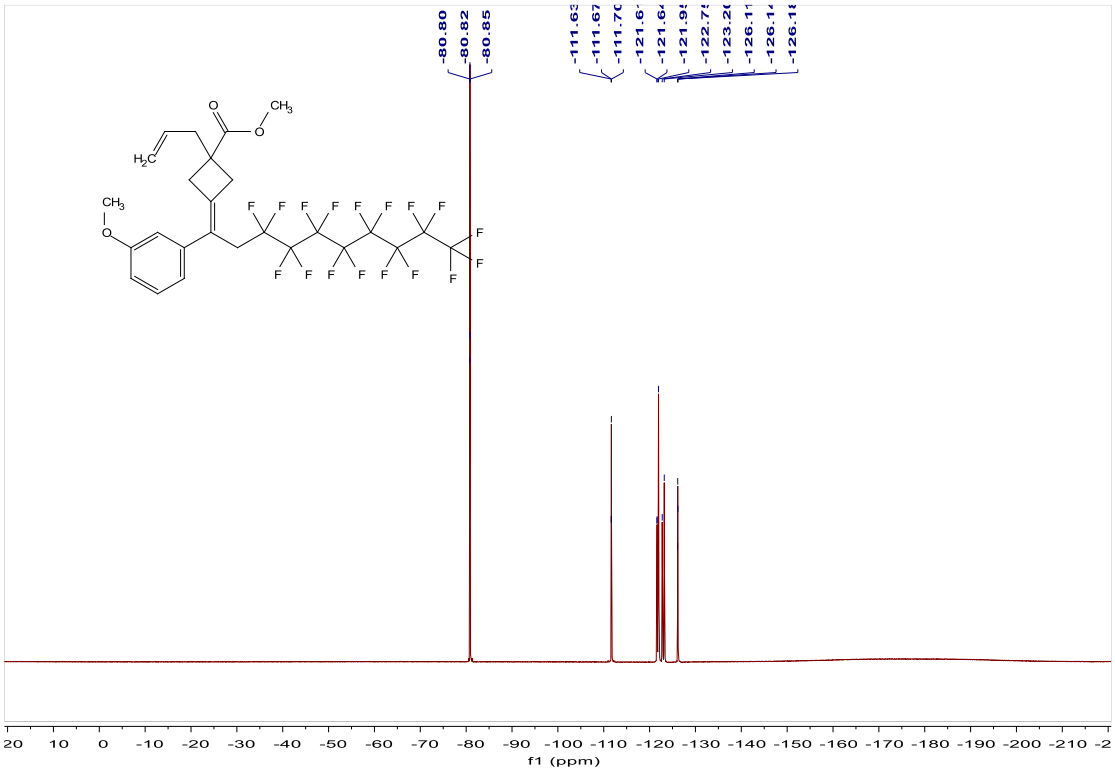
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **62**



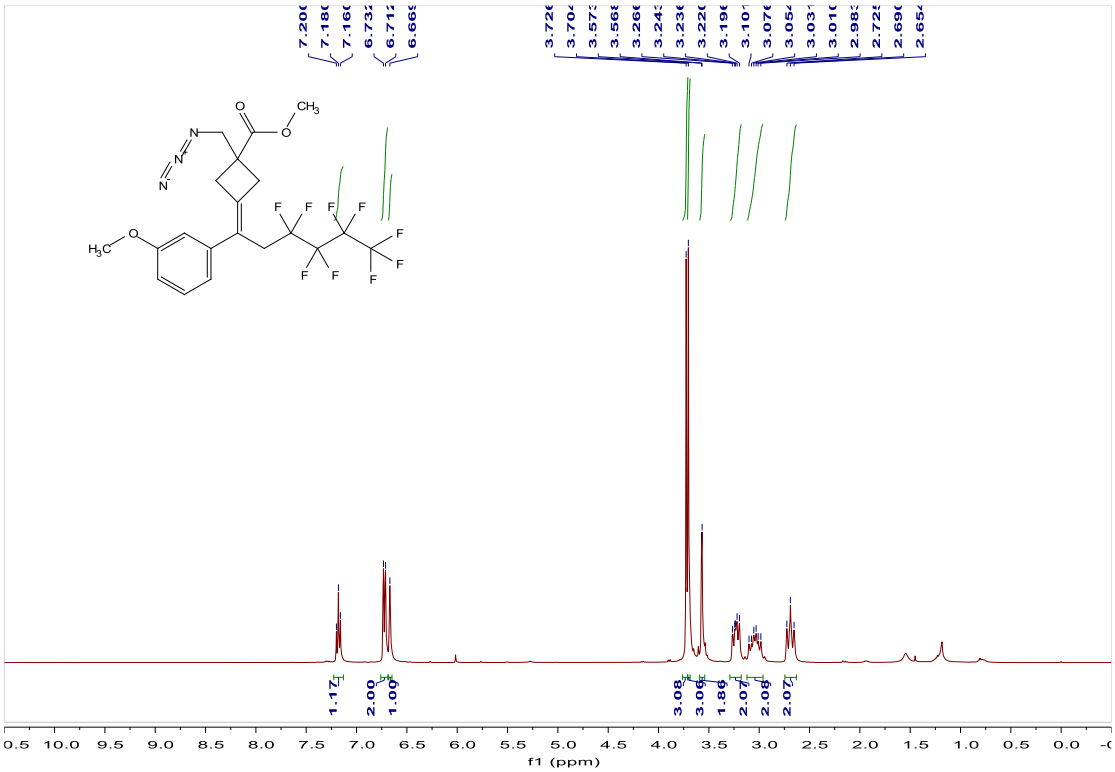
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **62**



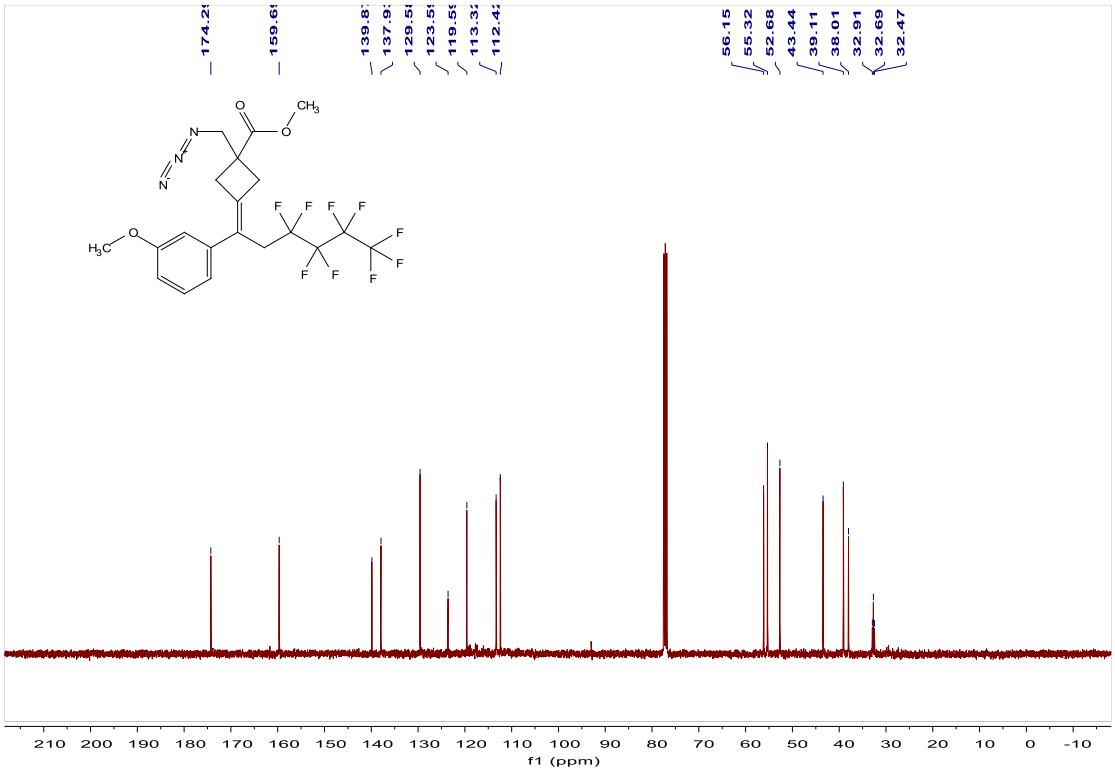
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **62**



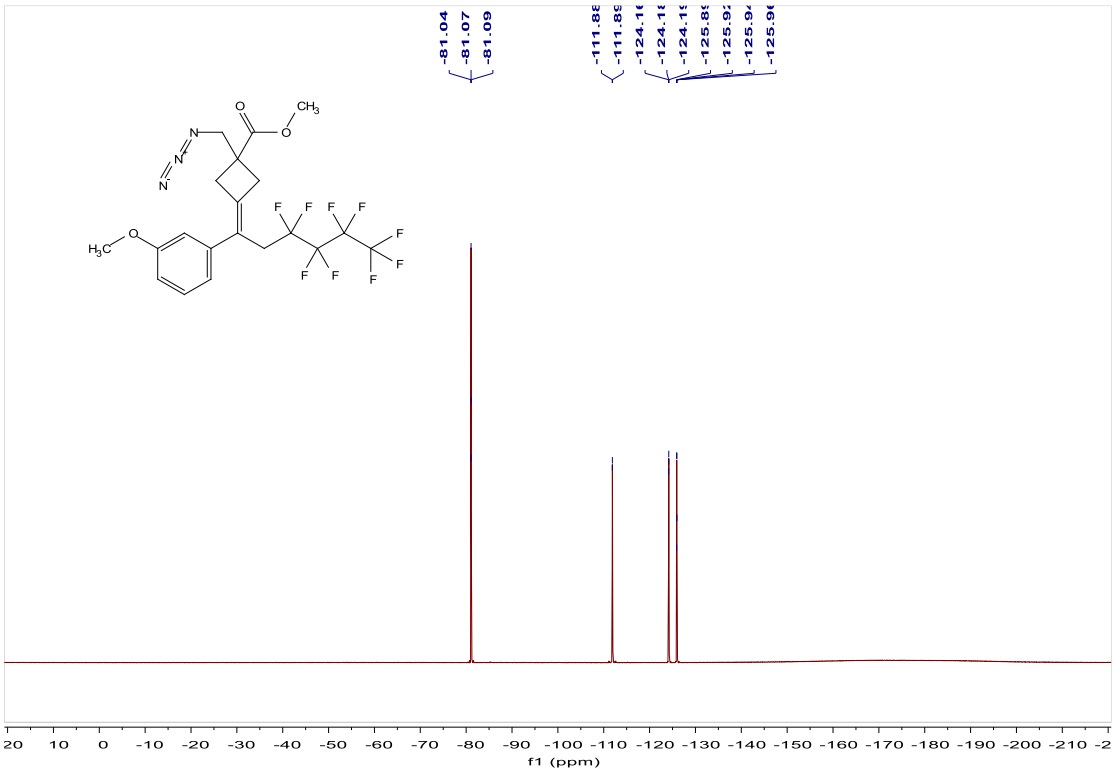
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **63**



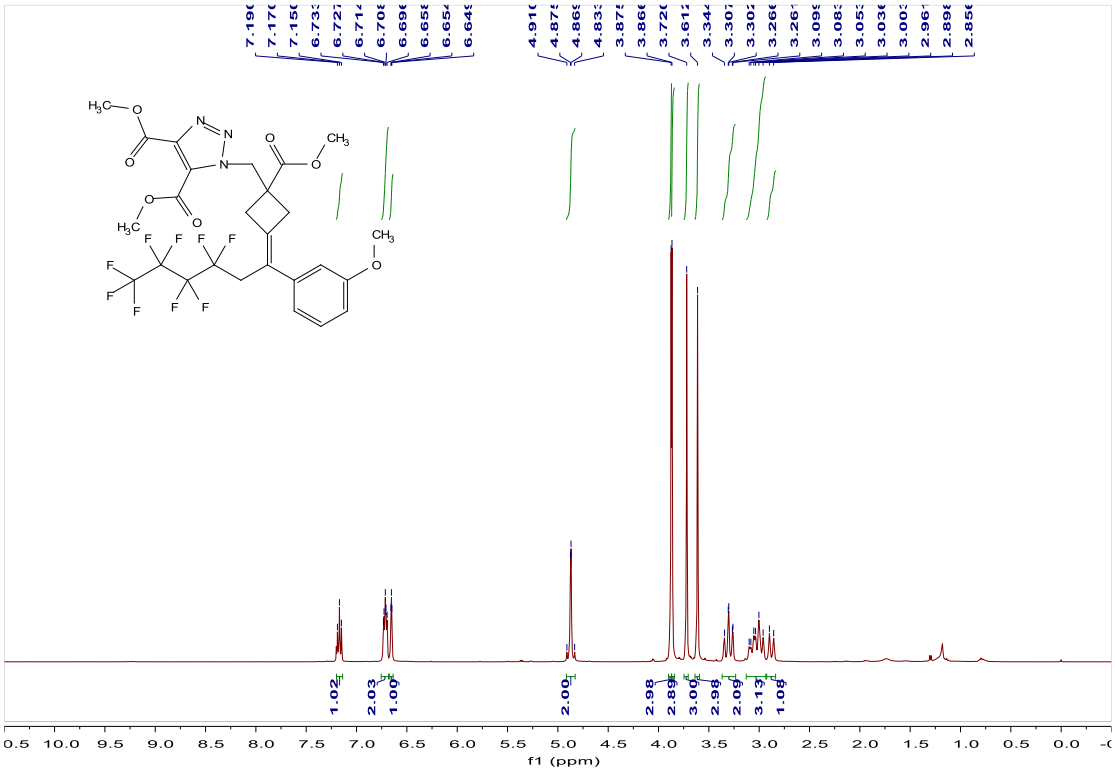
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **63**



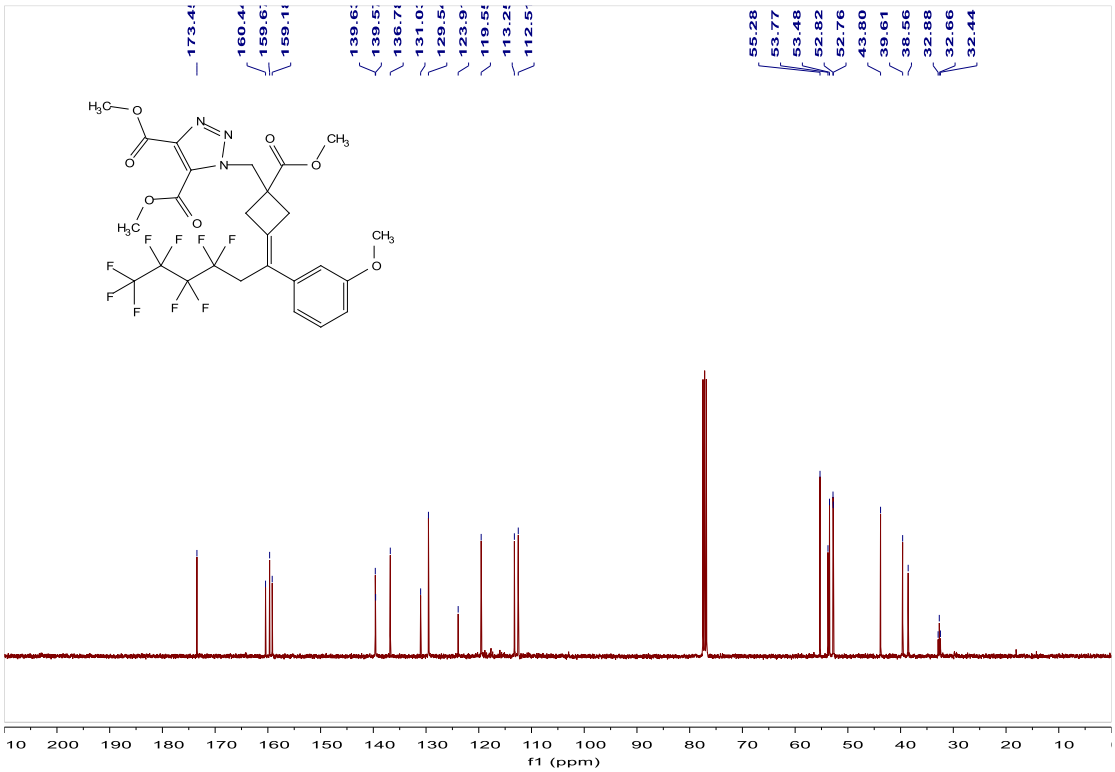
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **63**



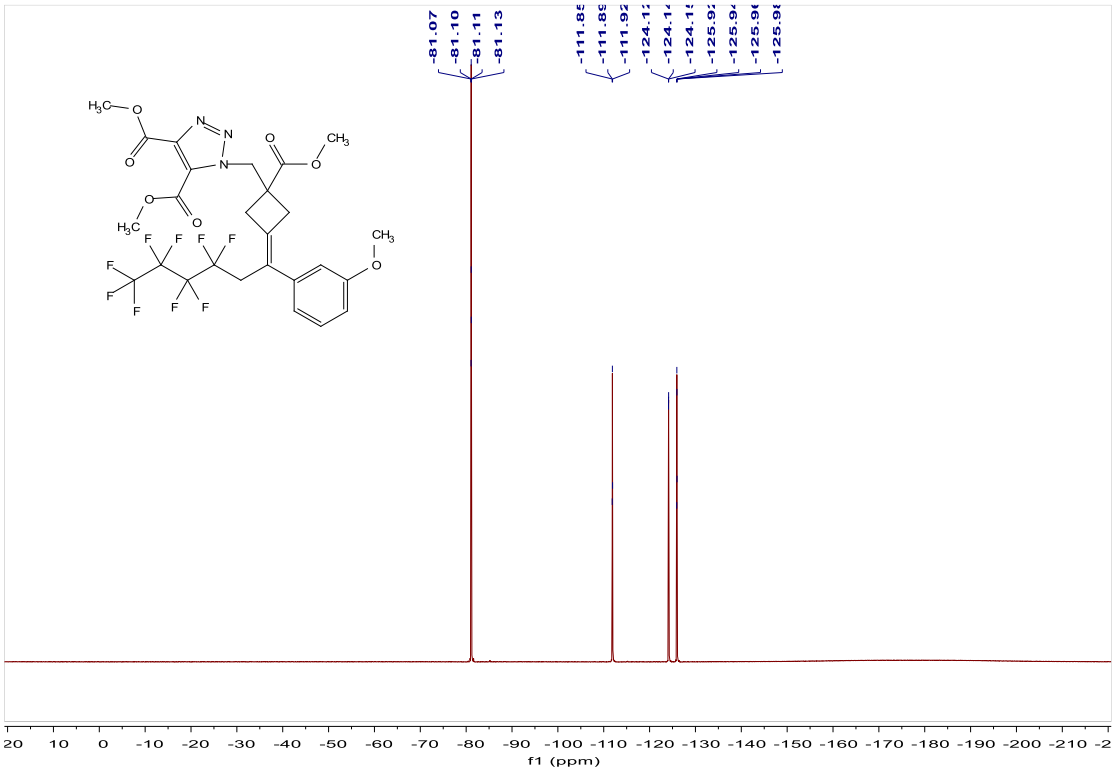
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **64**



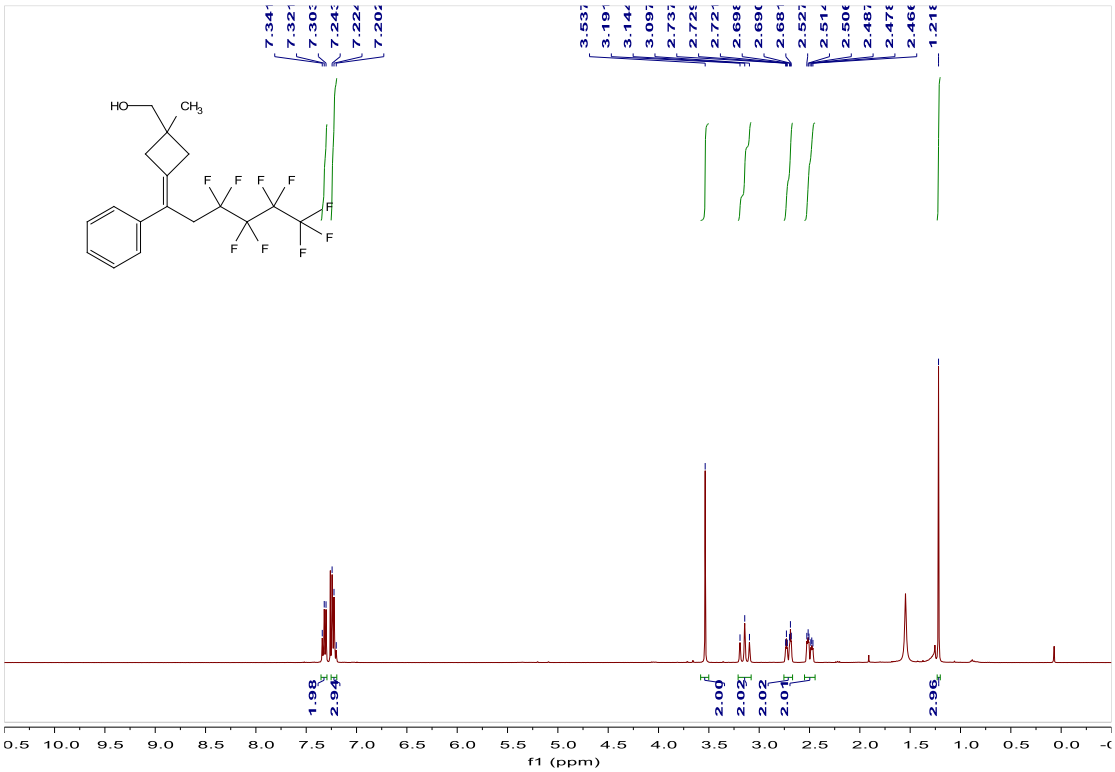
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **64**



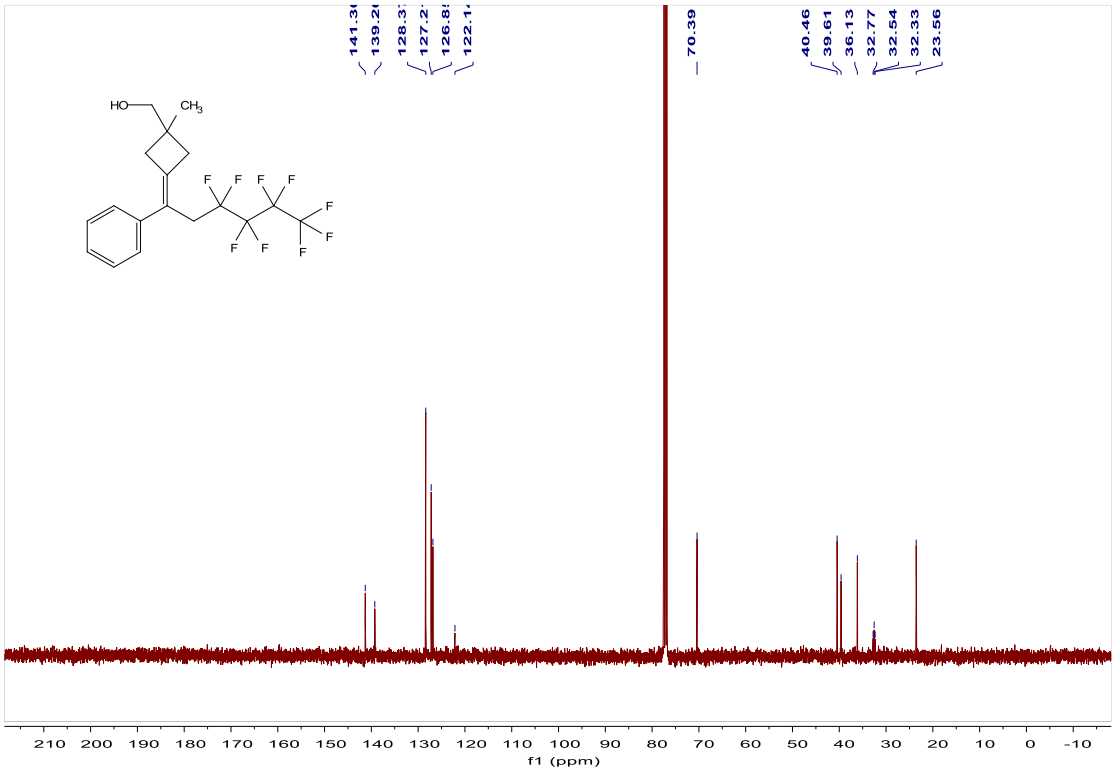
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **64**



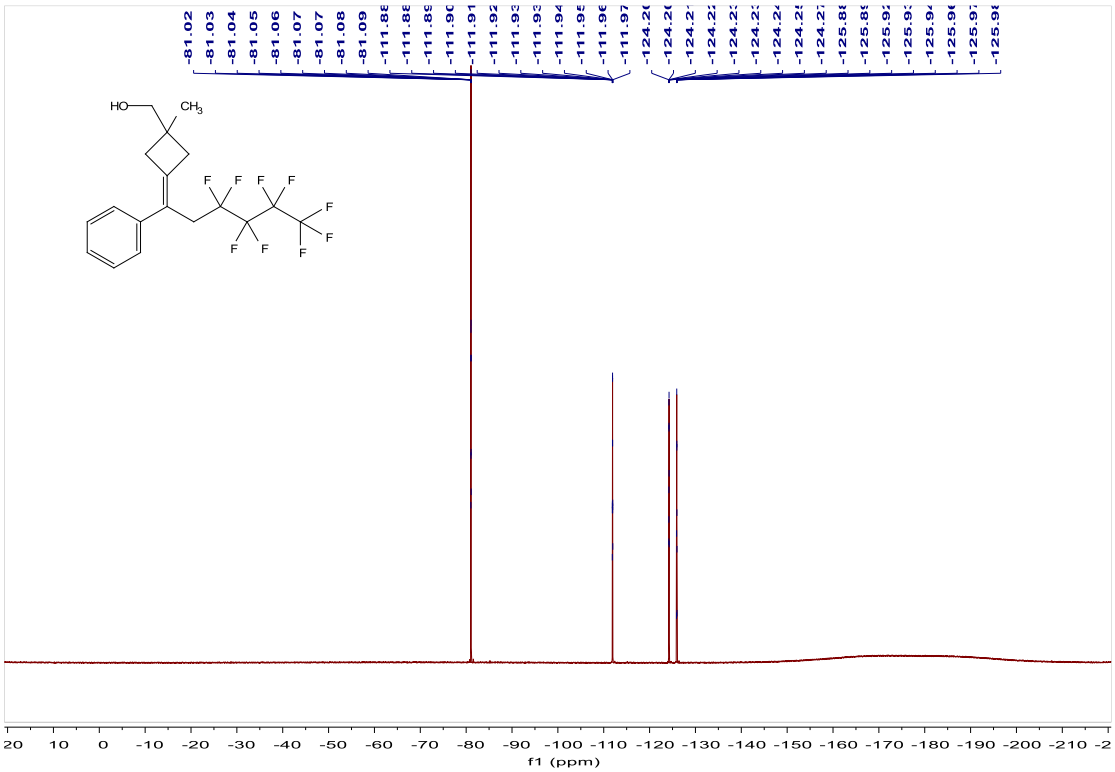
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **65**



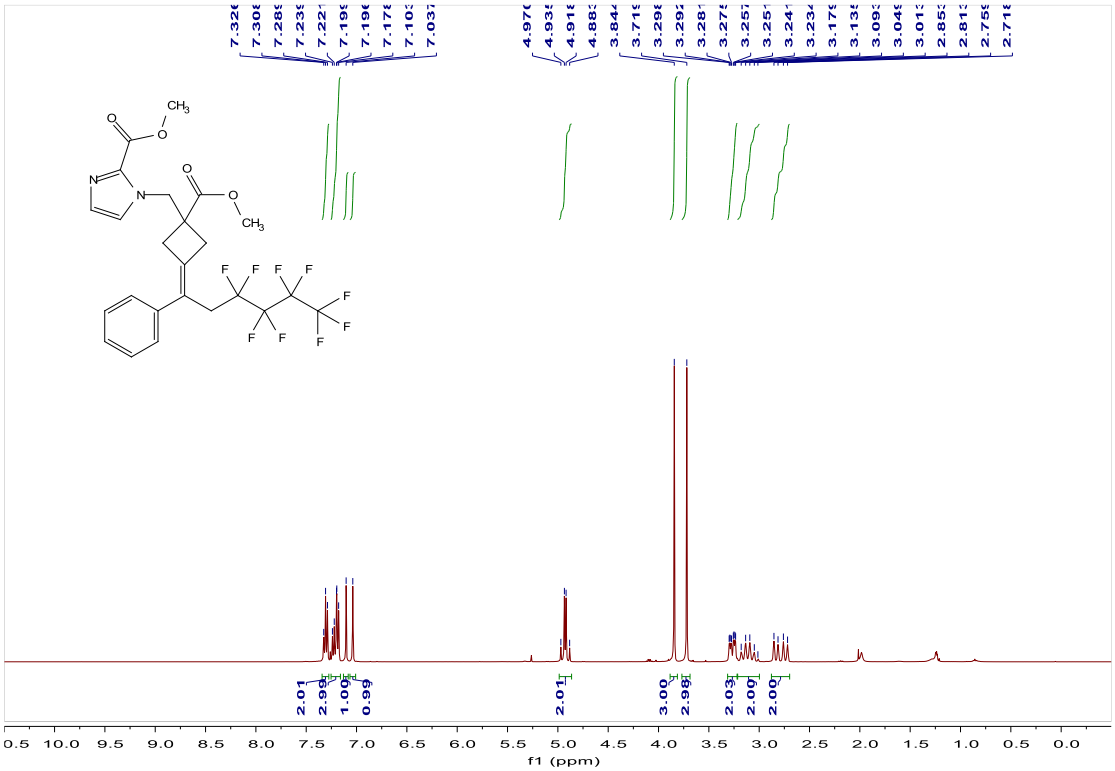
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **65**



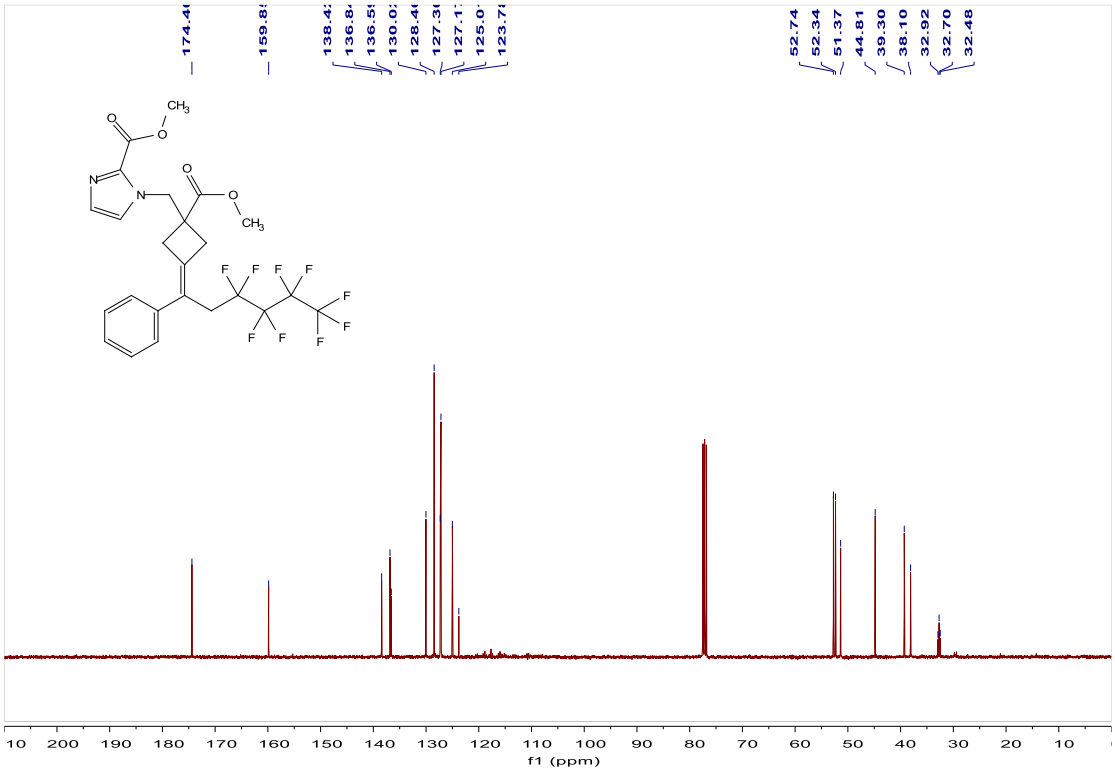
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **65**



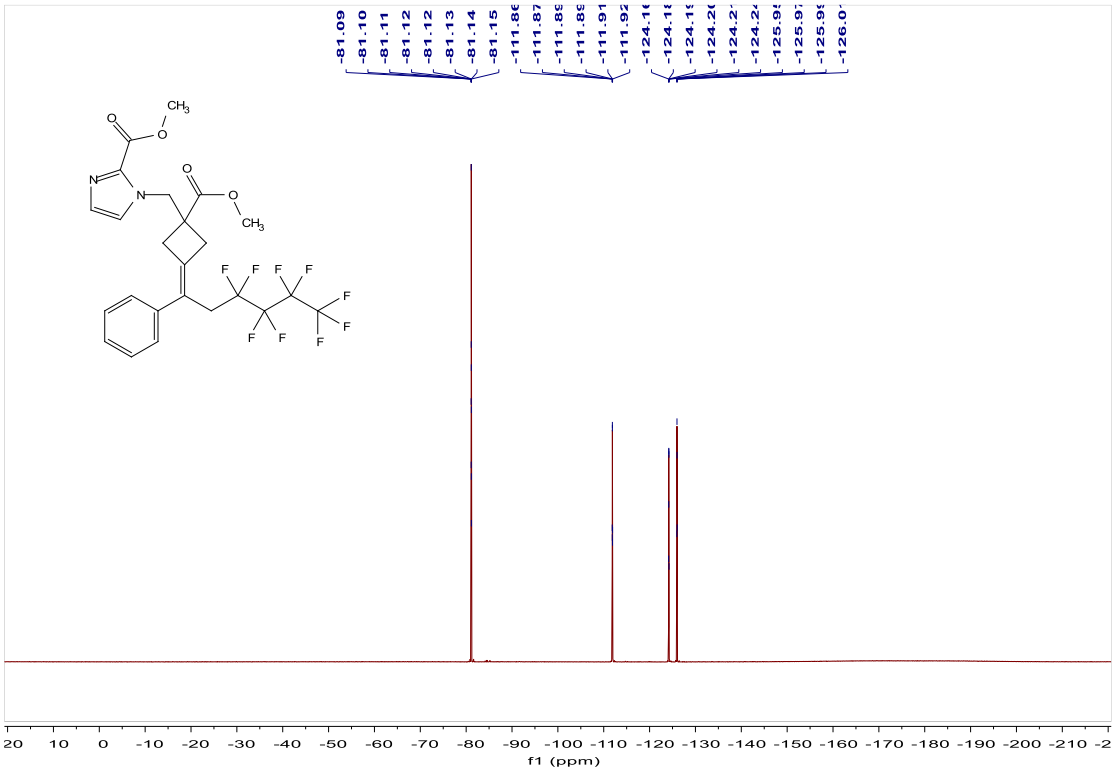
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **66**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **66**



^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **66**



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