Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Photoinduced Defluorinative Alkylation of Trifluorome-thyl alkenes with Carbonyl Derivatives by C–C Bond Scission

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1. General Information

1.1 Analytical Methods

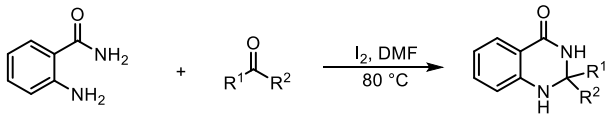
The NMR spectra were recorded on a Bruker 600 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR were reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of NMR solvent: $CDCl_3$ (7.26 ppm). Coupling constants (J) are expressed in hertz. ^{13}C NMR spectra were recorded at 151 MHz, and the chemical shifts (δ) were reported in ppm relative to $CDCl_3$ (77.10 ppm). ^{19}F NMR spectra were recorded at 564 MHz. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data was acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software.

1.2 Materials

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity $\geq$ 99.99%) unless otherwise mentioned. Other Commercial reagents were purchased from Adamas-beta, Energy Chemical, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on silica gel (200-300 mesh). The Photo Reaction Setup was purchased from Anhui kemi machinery technology Co., Ltd.

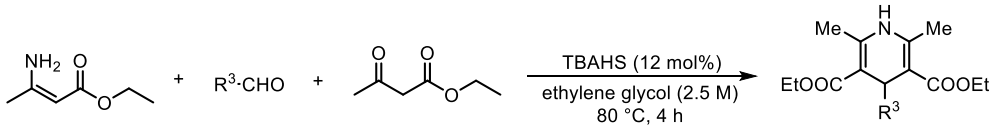
2. Procedure for the Synthesis of Substrates

2.1 Preparation of ketone derived dihydroquinazolinones[1]



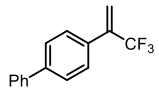
A dry round-bottom flask was charged with 2-aminobenzamides (1.0 equiv.), ketone (1.05 equiv.), I_2 (5 mol%) and DMF (0.67 M). The reaction mixture was stirred at 80 ℃ for 18 h. After completion of the reaction, as indicated by TLC, and then cooled down to room temperature. Water was added to the mixture, and the generated solid was filtered off. The crude products were washed with water and purified by recrystallization from EtOH to give the desired product.

2.2 Preparation of aldehyde-derived 1,4-dihydropyridines (DHPs)[2]



A dry round-bottom flask was charged with ethyl 3-aminocrotonate (1.0 equiv.) and ethylene glycol (2.5 M). Next, ethyl acetoacetate (1.0 equiv.) was added, followed by the aldehyde (1.0 equiv.). Finally, TBAHS (12 mol %) was added in one portion. The flask was closed with a septum and heated at 80 ℃ for 4 h. At this time, the reaction was cooled to room temperature and diluted with EtOAc. The solution was poured into a separatory funnel containing brine and extracted three times with EtOAc. After drying over anhydrous Na_2SO_4, it was filtered and taken to dryness. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired product.

2.3 Preparation of trifluoromethyl alkenes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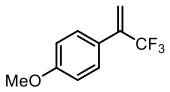
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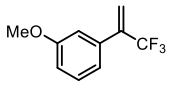
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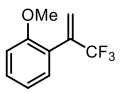
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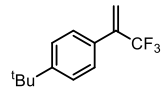
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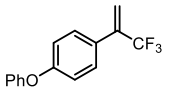
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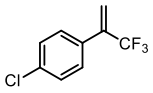
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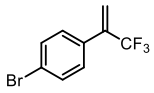
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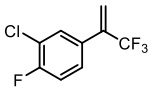
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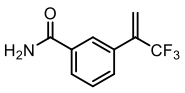
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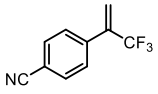
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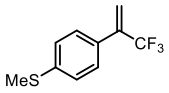
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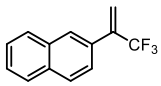
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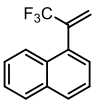
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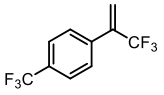
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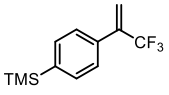
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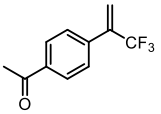
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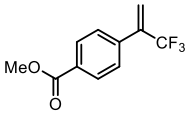
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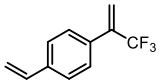
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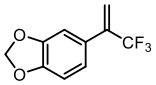
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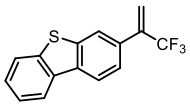
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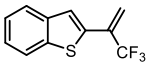
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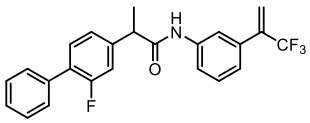
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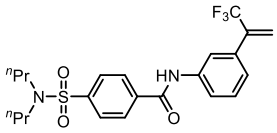
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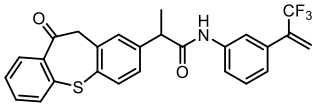
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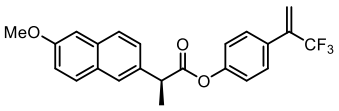
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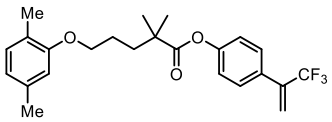
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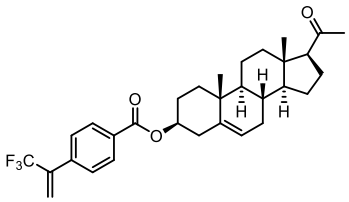
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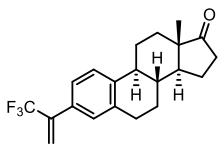
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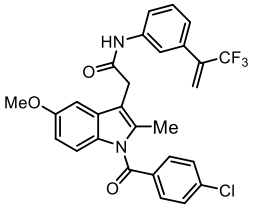
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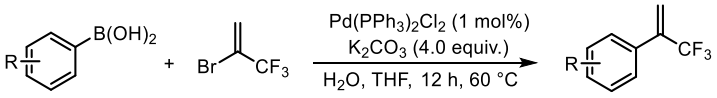
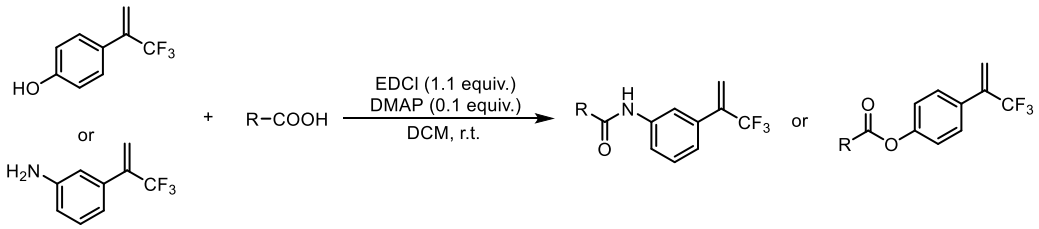
1) Preparation of substrates S1-S22[3]



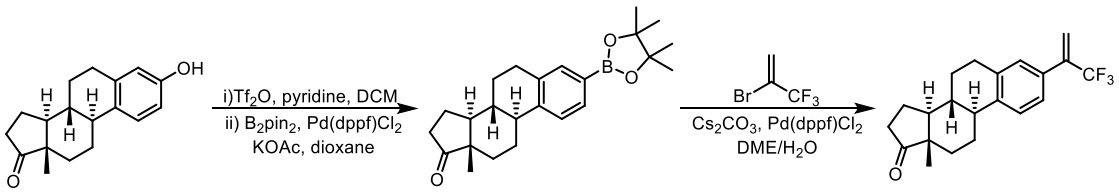
To a Schlenk tube equipped a magnetic stir bar, boronic acid (10 mmol, 1.0 equiv.) and $Pd(PPh_3)_2Cl_2$ (70.2 mg, 1 mol%) were added. The vessel was evacuated and filled with argon (three times), and then THF (30 mL) and aqueous K_2CO_3 (20 mL) were added. After the addition of 2-bromo-3,3,3-trifluoropropene (2 mL, 20 mmol, 2.0 equiv.), the reaction mixture was stirred at 60 ℃ for 12 h under argon atmosphere. The resultant mixture was cooled to room temperature, quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (3 × 30 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired trifluoromethyl alkene.

2) Preparation of substrates S23-S28[3]



A dry round-bottom flask was charged with carboxylic acid (1.1 equiv.), DMAP (0.1 equiv.) and 4-(3,3,3-trifluoroprop-1-en-2-yl)phenol or 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (1.0 equiv.), followed by the addition of DCM (0.4 M) and EDCI (1.1 equiv.). The reaction mixture was stirred at room temperature for 12 h (TLC tracking detection). Once complete, the reaction was quenched by water. The organic layer was then separated, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The mixture was purified by column chromatography (petroleum ether/ethyl acetate) to afford the corresponding trifluoromethyl alkenes.

3) Preparation of substrates S29[4]



Step I

To a 50 mL of sealed tube was added estrone (2.7 g, 10 mmol, 1.0 equiv.), which was dissolved in DCM (25 mL). After cooling to 0 ℃, Tf_2O (2.2 mL, 13 mmol, 1.3 equiv.) was added, followed by the addition of pyridine (2.8 mL, 20 mmol, 2.0 equiv.). The mixture was stirred at 0 ℃ for 1h, slowly warmed to room temperature and quenched by water. The layers were separated and the aqueous layer was extracted with DCM, combined organic layers were dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure. The crude mixture was purified by

column chromatography on silica gel (petroleum ether/ethyl acetate = 10:3) to give estrone trifluoromethanesulfonic ester (2.8 g, yield: 70%) which was used in the next step.

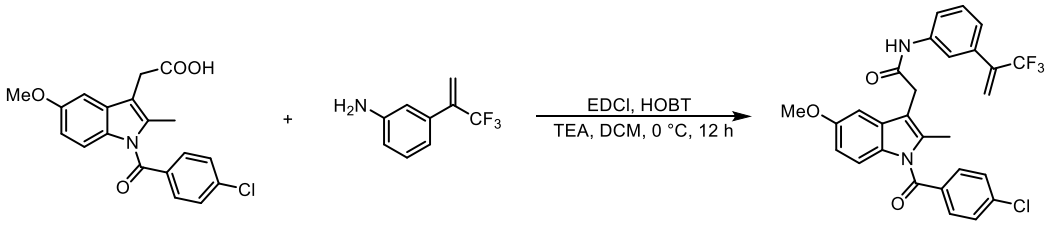
Step II

To a 50 mL Schlenk tube equipped a magnetic stir bar, estrone trifluoromethanesulfonic ester (2.8 g, 7 mmol, 1.0 equiv.), bis(pinacolato)diboron (3.6 g, 14 mmol, 2.0 equiv.), KOAc (2.0 g, 21 mmol, 3.0 equiv.), and Pd(dppf)Cl_2 (205 mg, 4 mol%) were added, the vessel was evacuated and filled with argon (three times), and then dioxane (30 mL) was added. The tube was heated to 120 ℃ (oil bath). After stirring for 8 h, the reaction mixture was cooled to room temperature and diluted with THF, dried over anhydrous Na_2SO_4, then filtered and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the desired boronate pinacol (2.3 g, yield: 86%) which was used in the next step.

Step III

To a 50 mL Schlenk tube equipped a magnetic stir bar, boronate pinacol (2.3 g, 6 mmol, 1.0 equiv.), Cs_2CO_3 (2.4 g, 7.2 mmol, 1.2 equiv.), and Pd(dppf)Cl_2 (440 mg, 0.6 mmol, 0.1 equiv.) were added, the vessel was evacuated and filled with argon (three times), and then degassed DME (23.4 mL), degassed, deionized H_2O (7 mL) and 2-bromo-3,3,3- trifluoroprop-1-ene (1.24 mL, 12 mmol, 2.0 equiv.) were added. The tube was heated to 80 ℃ (oil bath) for 24 hours. Once completed, the reaction was cooled to room temperature and diluted with EtOAc (50 mL). The resultant crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give the desired trifluoromethyl alkene (1.33 g, yield: 63%).

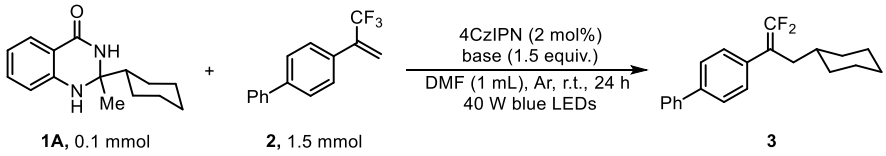
4) Preparation of substrates S30[5]



A dry round-bottom flask was charged with 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetic acid (1.0 equiv.), 3-(3,3,3-trifluoroprop-1-en-2-yl)aniline (1.0 equiv.) and HOBT (1.2 equiv.), followed by the addition of DCM (0.25 M), TEA (2.0 equiv.) and EDCI (1.2 equiv.). The reaction mixture was stirred at 0 ℃ for 12 h (TLC tracking detection). Once complete, the reaction was quenched by water. The organic layer was then separated, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The mixture was purified by column chromatography (petroleum ether/ethyl acetate = 3:1) to afford the corresponding trifluoromethyl alkene.

3. Investigation of the Key Reaction Parameters

Table S1. Screening of bases

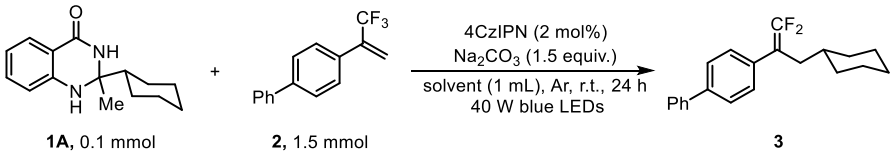


1A, 0.1 mmol **2**, 1.5 mmol **3**

entry	base	yield (%)
1	KOAc	23
2	K_2HPO_4	trace
3	Na_2HPO_4	trace
4	K_2CO_3	85
5	Na_2CO_3	92
6	Cs_2CO_3	60
7	2,4,6-collidine	trace
8	DIPEA	n.d.

Reaction conditions: **1A** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.), 4CzIPN (2 mol%), base (0.15 mmol, 1.5 equiv.), DMF (1 mL), stirred at room temperature for 24 h under 40 W blue LEDs irradiation. Isolated yield. n.d. = not detected.

Table S2. Screening of solvents

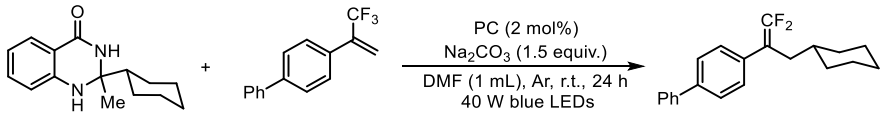


1A, 0.1 mmol **2**, 1.5 mmol **3**

entry	solvent	yield (%)
1	DMSO	73
2	DMA	58
3	MeCN	trace
4	THF	trace
5	acetone	trace
6	EA	n.d.
7	dioxane	n.d.
8	toluene	n.d.
9	DMF	92

Reaction conditions: **1A** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.), 4CzIPN (2 mol%), Na_2CO_3 (0.15 mmol, 1.5 equiv.), solvent (1 mL), stirred at room temperature for 24 h under 40 W blue LEDs irradiation. Isolated yield. n.d. = not detected.

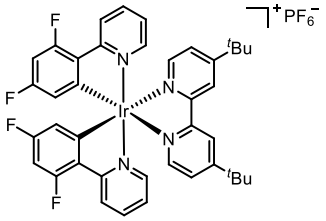
Table S3. Screening of catalyst



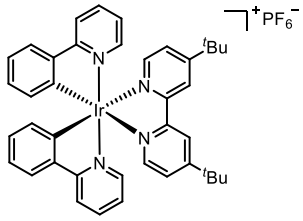
1A, 0.1 mmol **2,** 1.5 mmol **3**

entry	catalyst	yield (%)
1	$[Ir(dFppy)_2(dtbbpy)]PF_6$	70
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	70
3	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	83
4	$Ir(ppy)_3$	n.d.
5	4DPAIPN	52
6	3DPA2FBN	trace
7	4CzIPN	92
8	Eosin Y	8

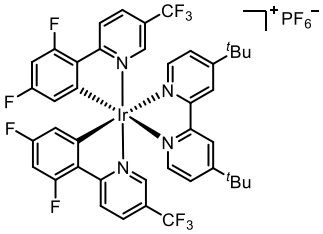
Reaction conditions: **1A** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.), PC (2 mol%), Na_2CO_3 (0.15 mmol, 1.5 equiv.), DMF (1 mL), stirred at room temperature for 24 h under 40 W blue LEDs irradiation. Isolated yield. n.d. = not detected.



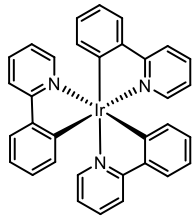
$[Ir(dFppy)_2(dtbbpy)]PF_6$



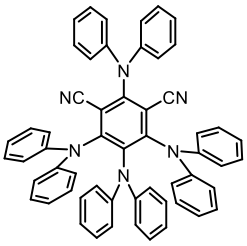
$[Ir(dtbbpy)(ppy)_2]PF_6$



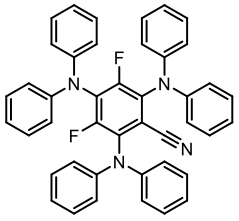
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$



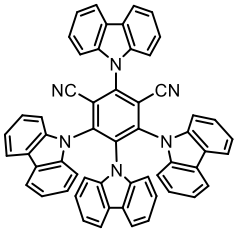
$Ir(ppy)_3$



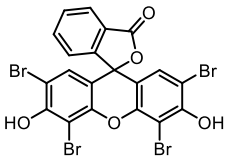
4DPAIPN



3DPA2FBN

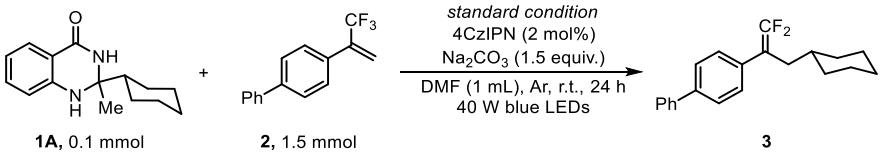


4CzIPN



Eosin Y

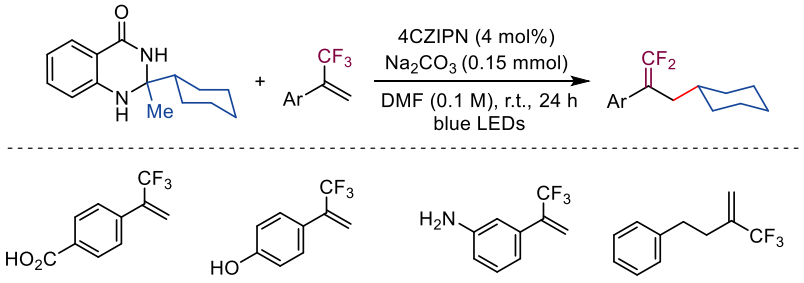
Table S4. Control experiments



1A, 0.1 mmol **2**, 1.5 mmol **3**

entry	variation from standard conditions	yield (%)
1	390 nm blue LEDs	30
2	420 nm blue LEDs	74
3	450 nm blue LEDs	82
4	without light	n.d.
5	without base	8
6	without PC	n.d.
7	reaction time: 15 h	53
8	0.1 mmol Na_2CO_3	57
9	0.2 mmol Na_2CO_3	81
10	**1B** instead of **1A**	56
11	**1B**, Eosin Y instead of **1A**, 4CzIPN	83

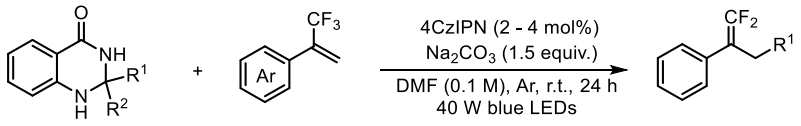
Standard conditions: **1A** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 1.5 equiv.), 4CzIPN (2 mol%), Na_2CO_3 (0.15 mmol, 1.5 equiv.), in DMF (1 mL), stirred at room temperature for 24 h under 40 W blue LEDs irradiation. Isolated yield. n.d. = not detected.



Scheme S1. Failed substrates

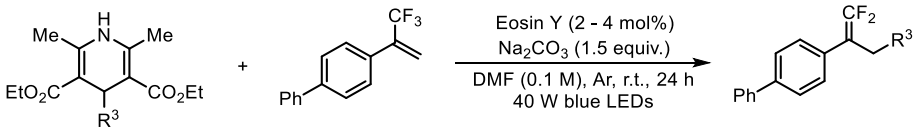
4. General Procedure and Spectral Data

4.1 General Procedure A



Dihydroquinazolinones (0.1 mmol, 1.0 equiv.), trifluoromethyl alkenes (0.15 mmol, 1.5 equiv.) (if solid), 4CzIPN (2 - 4 mol%), Na_2CO_3 (0.15 mmol, 1.5 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, trifluoromethyl alkenes (1.5 mmol, 1.5 equiv.) (if liquid) and anhydrous DMF (1 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40 W blue LEDs, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 24 h, ethyl acetate (5 mL) was added to the reaction mixture. The resulting solution was washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. The organic layers were combined and concentrated on rotary evaporator. The residue was purified by flash column chromatography on silica gel to give the product (Eluent: petroleum ether/ethyl acetate).

4.2 General Procedure B



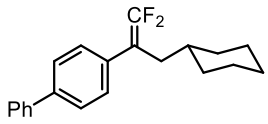
1,4-dihydropyridines (0.1 mmol, 1.0 equiv.) (if solid), 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (0.15 mmol, 1.5 equiv.), Eosin Y (2 - 4 mol%), Na_2CO_3 (0.15 mmol, 1.5 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, 1,4-dihydropyridines (1.0 equiv., 0.1 mmol) (if liquid) and anhydrous DMF (1 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40 W blue LEDs, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 24 h, ethyl acetate (5 mL) was added to the reaction mixture. The resulting solution was washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. The organic layers were combined and concentrated on rotary evaporator. The residue was purified by flash column chromatography on silica gel to give the product (Eluent: petroleum ether/ethyl acetate).

Reaction Setup

Figure S1 Photo-reaction setup and reaction tube

4.3 Characterization data for the products

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (3)[6]



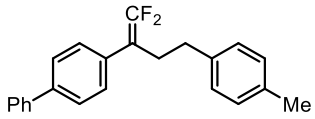
The substrate was prepared following the general procedure A using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24.4 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (1.6 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **3** was isolated using flash column chromatography on silica gel (petroleum ether) as a white solid (28.7 mg, 92%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 4H), 7.49 – 7.33 (m, 5H), 2.36 – 2.27 (m, 2H), 1.77 – 1.61 (m, 5H), 1.38 – 1.29 (m, 1H), 1.22 – 1.10 (m, 3H), 1.02 – 0.87 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.06 (dd, *J* = 290.7, 286.2 Hz), 140.58, 139.83, 133.06 (dd, *J* = 4.6, 3.3 Hz), 128.78, 128.59 (t, *J* = 3.3 Hz), 127.34, 127.03, 126.99, 90.77 (dd, *J* = 22.1, 12.2 Hz), 35.73, 35.11, 32.89, 26.41, 26.06.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.72 (d, *J* = 43.2 Hz, 1F), -91.27 (d, *J* = 43.3 Hz, 1F).

4-(1,1-difluoro-4-(*p*-tolyl)but-1-en-2-yl)-1,1'-biphenyl (4)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-methyl-2-(4-methylbenzyl)-2,3-dihydroquinazolin-4(1*H*)-one (53.2 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **4** was isolated using flash column chromatography on silica gel (petroleum ether) as a white solid (23.7 mg, 71%).

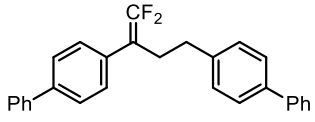
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 4H), 7.50 – 7.35 (m, 5H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 2.77 – 2.71 (m, 2H), 2.71 – 2.66 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.81 (dd, *J* = 291.2, 287.2 Hz), 140.55, 140.06, 137.92, 135.56, 132.49 – 132.41 (m), 129.06, 128.81, 128.61 (t, *J* = 3.4 Hz), 128.27, 127.40, 127.16, 127.02, 91.63 (dd, *J* = 21.9, 13.0 Hz), 36.67 (t, *J* = 1.51 Hz**),** 29.69 (d, *J* = 1.3 Hz), 21.03.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.51 (d, *J* = 41.8 Hz, 1F), -90.99 (d, *J* = 41.8 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{23}H_{20}F_2Na^+$, 357.1425; found: 357.1429.

4,4''-(4,4-difluorobut-3-ene-1,3-diyl)di-1,1'-biphenyl (5)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-([1,1'-biphenyl]-4-ylmethyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (65.6 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **5** was isolated using flash column chromatography on silica gel (petroleum ether) as a white solid (32.9 mg, 83%).

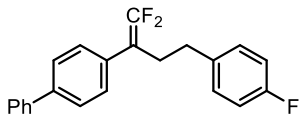
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 6H), 7.57 – 7.42 (m, 8H), 7.42 – 7.33 (m, 2H), 7.28 – 7.22 (m, 2H), 2.85 – 2.73 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.86 (dd, *J* = 291.4, 287.4 Hz), 141.00, 140.54, 140.13, 140.10, 139.08, 132.39 (dd, *J* = 4.3, 3.6 Hz), 128.85, 128.83, 128.74, 128.64 (t, *J* = 3.3 Hz), 127.44, 127.21, 127.12, 127.09, 127.04, 127.01, 91.60 (dd, *J* = 21.9, 13.1 Hz), 33.77 (t, *J* = 3.02 Hz**)**, 29.54 (d, *J* = 1.1 Hz).

^{19}F NMR (564 MHz, $CDCl_3$) δ -86.17 (d, *J* = 41.5 Hz, 1F), -86.66 (d, *J* = 41.5 Hz, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{28}H_{23}F_2^+$, 397.1762; found: 397.1755.

4-(1,1-difluoro-4-(4-fluorophenyl)but-1-en-2-yl)-1,1'-biphenyl (6)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-(4-fluorobenzyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (54.0 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **6** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (26.4 mg, 78%).

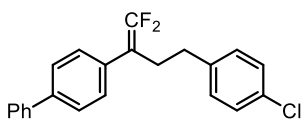
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.58 (m, 4H), 7.49 – 7.35 (m, 5H), 7.14 – 7.06 (m, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 2.77 – 2.64 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.41 (d, *J* = 243.8 Hz), 153.85 (dd, *J* = 291.5, 287.4 Hz), 140.48, 140.16, 136.52 (d, *J* = 3.3 Hz), 132.23 (dd, *J* = 4.3, 3.6 Hz), 129.80 (d, *J* = 7.9 Hz), 128.83, 128.59 (t, *J* = 3.3 Hz), 127.45, 127.21, 127.01, 115.11 (d, *J* = 21.2 Hz), 91.31 (dd, *J* = 21.8, 13.1 Hz), 33.18 (t, *J* = 2.2 Hz), 29.59.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.42 (d, *J* = 41.4 Hz, 1F), -90.82 (d, *J* = 41.4 Hz, 1F), -116.02 – -118.66 (m, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{22}H_{17}F_3Na^+$, 361.1175; found: 361.1171.

4-(4-(4-chlorophenyl)-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (7)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-(4-chlorobenzyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (57.2 mg, 0.2 mmol, 2.0

equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **7** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (24.8 mg, 70%).

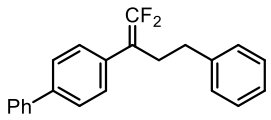
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 4H), 7.51 – 7.34 (m, 5H), 7.27 – 7.23 (m, 2H), 7.12 – 7.04 (m, 2H), 2.76 – 2.71 (m, 2H), 2.70 – 2.65 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.83 (dd, *J* = 291.5, 287.4 Hz), 140.46, 140.19, 139.32, 132.17 – 132.09 (m), 131.85, 129.79, 128.83, 128.58 (t, *J* = 3.3 Hz), 128.46, 127.46, 127.22, 127.01, 91.24 (dd, *J* = 21.8, 13.3 Hz), 33.32 (t, *J* = 3.02**)**, 29.35.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.31 (d, *J* = 41.2 Hz, 1F), -90.73 (d, *J* = 41.2 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{22}H_{17}ClF_2Na^+$, 377.0879; found: 377.0885.

4-(1,1-difluoro-4-phenylbut-1-en-2-yl)-1,1'-biphenyl (8)[7]



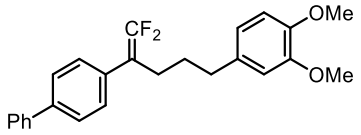
The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-benzyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (62.8 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **8** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (20.5 mg, 64%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 4H), 7.51 – 7.45 (m, 2H), 7.44 – 7.36 (m, 3H), 7.34 – 7.28 (m, 2H), 7.24 – 7.15 (m, 3H), 2.80 – 2.70 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.83 (dd, *J* = 291.3, 287.3 Hz), 141.00, 140.54, 140.09, 132.43 – 132.36 (m), 128.82, 128.61 (t, *J* = 3.4 Hz), 128.42, 128.39, 127.42, 127.19, 127.02, 126.11, 91.55 (dd, *J* = 21.9, 13.0 Hz), 34.10 (t, *J* = 2.6 Hz), 29.58 (d, *J* = 1.4 Hz).

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.45 (d, *J* = 41.6 Hz), -90.92 (d, *J* = 41.6 Hz).

4-(5-(3,4-dimethoxyphenyl)-1,1-difluoropent-1-en-2-yl)-1,1'-biphenyl (9)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-(3,4-dimethoxyphenethyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (48.9 mg, 0.15 mmol, 1.5 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **9** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (18.9 mg, 48%).

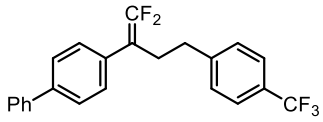
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 4H), 7.48 – 7.32 (m, 5H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.70 – 6.62 (m, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.49 – 2.45 (m, 2H), 1.76 – 1.69 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.65 (dd, *J* = 290.8, 287.0 Hz), 148.75, 147.14, 140.50, 140.01, 134.40, 132.52 (dd, *J* = 4.0, 3.1 Hz), 128.80, 128.57 (t, *J* = 3.3 Hz), 127.40, 127.08, 126.97, 120.17, 111.58, 111.12, 91.91 (dd, *J* = 21.6, 13.0 Hz), 55.91, 55.75, 34.74, 29.52 (t, *J* = 2.2 Hz), 27.00.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.84 (d, *J* = 43.0 Hz, 1F), -91.03 (d, *J* = 43.0 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{25}H_{24}F_2NaO_2^+$, 417.1637; found: 417.1631.

4-(1,1-difluoro-4-(4-(trifluoromethyl)phenyl)but-1-en-2-yl)-1,1'-biphenyl (10)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-methyl-2-(4-(trifluoromethyl)benzyl)-2,3-dihydroquinazolin-4(1*H*)-one (64.0 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **10** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (27.5 mg, 71%).

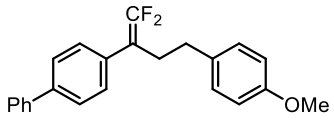
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 4H), 7.47 (t, *J* = 7.7 Hz, 3H), 7.43 – 7.32 (m, 6H), 2.78 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.87 (dd, *J* = 291.6, 287.7 Hz), 141.71, 140.46, 140.28, 132.04 – 131.96 (m), 131.86 (d, *J* = 0.9 Hz), 130.63 (q, *J* = 32.0 Hz), 128.84, 128.79, 128.60 (t, *J* = 3.3 Hz), 127.48, 127.27, 127.02, 125.22 (q, *J* = 3.8 Hz), 123.04 (q, *J* = 3.9 Hz), 91.14 (dd, *J* = 21.7, 13.5 Hz), 33.77 (t, *J* = 2.3 Hz), 29.21 (d, *J* = 1.3 Hz).

^{19}F NMR (564 MHz, $CDCl_3$) δ -62.59 (s, 3F), -90.29 (d, *J* = 41.0 Hz, 1F), -90.68 (d, *J* = 40.7 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{23}H_{17}F_5Na^+$, 411.1143; found: 411.1149.

4-(1,1-difluoro-4-(4-methoxyphenyl)but-1-en-2-yl)-1,1'-biphenyl (11)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-(4-methoxybenzyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (56.4 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **11** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (17.5 mg, 50%).

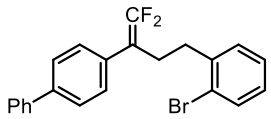
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 4H), 7.42 (m, 5H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 2.99 – 2.49 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.93, 153.81 (dd, *J* = 291.3, 287.3 Hz), 140.53, 140.04, 133.06, 132.47 – 132.39 (m), 129.34, 128.82, 128.61 (t, *J* = 3.3 Hz), 127.41, 127.16, 127.02, 113.76, 91.54 (dd, *J* = 22.1, 12.8 Hz), 55.25, 33.15 (t, *J* = 3.02 Hz), 29.77.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.83 (d, *J* = 43.6 Hz, 1F), -91.24 (d, *J* = 43.5 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{23}H_{20}F_2NaO^+$, 373.1374; found: 373.1365.

4-(4-(2-bromophenyl)-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (12)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-(2-bromobenzyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (66.0 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **12** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (21.5 mg, 54%).

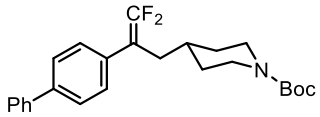
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 4H), 7.55 – 7.43 (m, 5H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 6.4 Hz, 1H), 7.09 – 7.05 (m, 1H), 2.90 – 2.71 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.95 (dd, *J* = 292.0, 287.9 Hz), 140.52, 140.27, 140.07, 132.86, 132.27 – 132.18 (m), 130.59, 128.81, 128.56 (t, *J* = 3.5 Hz), 127.93, 127.43, 127.41, 127.14, 127.00, 124.31, 91.38 (dd, *J* = 21.9, 12.9 Hz), 34.78 (dd, *J* = 3.0, 2.2 Hz), 27.82 (d, *J* = 1.5 Hz).

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.74 (d, *J* = 40.3 Hz, 1F), -90.47 (d, *J* = 40.3 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{22}H_{17}BrF_2Na^+$, 421.0374; found: 421.0378.

***tert*-butyl 4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)piperidine-1-carboxylate (13)[6]**

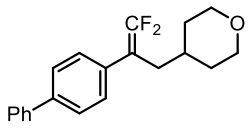


The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (51.8 mg, 0.15 mmol, 1.5 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **13** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (29.7 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.49 – 7.41 (m, 2H), 7.41 – 7.34 (m, 3H), 4.05 (s, 2H), 2.59 (t, *J* = 12.3 Hz, 2H), 2.38 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.73 – 1.59 (m, 2H), 1.53 – 1.42 (m, 10H), 1.20 – 1.08 (m, 2H).

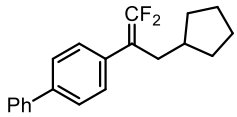
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.77, 154.25 (dd, J = 291.4, 286.9 Hz), 140.42, 140.11, 132.53 (dd, *J* = 4.3, 3.6 Hz), 128.81, 128.51 (t, *J* = 3.3 Hz), 127.44, 127.18, 126.98, 90.21 (dd, *J* = 22.1, 12.9 Hz), 79.28, 43.84, 34.28 (t, *J* = 2.2 Hz), 31.73, 28.45. (one carbon signal was overlapped).
^{19}F NMR (564 MHz, $CDCl_3$) δ -90.09 (d, *J* = 41.8 Hz, 1F), -90.56 (d, *J* = 41.8 Hz, 1F).

4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)tetrahydro-2*H*-pyran (14)[6]



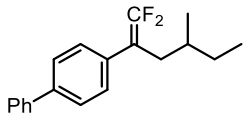
The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-methyl-2-(tetrahydro-2*H*-pyran-4-yl)-2,3-dihydroquinazolin-4(1*H*)-one (49.2 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **14** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a yellow solid (15.7 mg, 50%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.49 – 7.33 (m, 5H), 3.96 – 3.87 (m, 2H), 3.32 – 3.24 (m, 2H), 2.47 – 2.33 (m, 2H), 1.62 – 1.52 (m, 3H), 1.38 – 1.29 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.15 (dd, *J* = 291.2, 286.9 Hz), 140.43, 140.09, 132.57 (dd, *J* = 5.1, 2.6 Hz), 128.81, 128.52 (t, *J* = 3.3 Hz), 127.44, 127.17, 126.98, 90.05 (dd, *J* = 22.1, 12.9 Hz), 67.79, 34.60, 33.24 (t, *J* = 2.4 Hz), 32.63.
^{19}F NMR (564 MHz, $CDCl_3$) δ -90.17 (d, *J* = 41.5 Hz, 1F), -90.59 (d, *J* = 42.2 Hz, 1F).

4-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (15)[6]



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-cyclopentyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (46.0 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **15** was isolated using flash column chromatography on silica gel (petroleum ether) as a white solid (20.1 mg, 67%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.47 – 7.33 (m, 5H), 2.43 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.94 – 1.80 (m, 1H), 1.77 – 1.66 (m, 2H), 1.65 – 1.59 (m, 2H), 1.53 – 1.42 (m, 2H), 1.23 – 1.10 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.93 (dd, *J* = 290.1, 286.1 Hz), 140.59, 139.90, 132.95 (dd, *J* = 4.5, 3.1 Hz), 128.77, 128.68 (t, *J* = 3.2 Hz), 127.33, 127.02, 127.00, 92.03 (dd, *J* = 22.0, 12.3 Hz), 38.26 (t, *J* = 2.3 Hz), 33.46, 32.15, 24.98.
^{19}F NMR (564 MHz, $CDCl_3$) δ -91.57 (d, *J* = 44.4 Hz, 1F), -91.98 (d, *J* = 44.4 Hz, 1F).

4-(1,1-difluoro-4-methylhex-1-en-2-yl)-1,1'-biphenyl (16)[6]



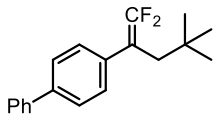
The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-(*sec*-butyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (32.7 mg, 0.15 mmol, 1.5 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **16** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (21.7 mg, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.48 – 7.42 (m, 2H), 7.42 – 7.33 (m, 3H), 2.47 – 2.41 (m, 1H), 2.27 – 2.21 (m, 1H), 1.45 – 1.36 (m, 2H), 1.23 – 1.13 (m, 1H), 0.90 – 0.85 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.04 (dd, *J* = 290.4, 286.3 Hz), 140.57, 139.87, 132.90 (dd, *J* = 4.3, 3.5 Hz), 128.78, 128.62 (t, *J* = 3.2 Hz), 127.34, 127.04, 127.00, 91.25 (dd, *J* = 22.0, 12.4 Hz), 34.49, 32.65 (t, *J* = 2.2 Hz), 29.07, 18.62, 11.27.

^{19}F NMR (564 MHz, $CDCl_3$) δ -91.05 (d, *J* = 43.6 Hz, 1F), -91.37 (d, *J* = 43.6 Hz, 1F).

4-(1,1-difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl (17)[8]



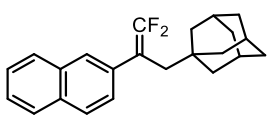
The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-(*tert*-butyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (43.6 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **17** was isolated using flash column chromatography on silica gel (petroleum ether) as a white solid (17.4 mg, 61%).

^{1}H NMR **(600 MHz, $CDCl_3$)** δ 7.59 (dd, *J* = 20.8, 7.8 Hz, 4H), 7.48 – 7.32 (m, 5H), 2.38 (s, 2H), 0.84 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.43 (dd, *J* = 290.3, 287.8 Hz), 140.54, 139.66, 134.55 (dd, *J* = 4.6, 2.9 Hz), 128.77, 128.75, 127.31, 126.96, 126.89, 90.81 (dd, *J* = 21.5, 12.6 Hz), 41.03, 32.77 (t, *J* = 2.5 Hz), 29.77.

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.32 (d, *J* = 40.3 Hz, 1F), -91.99 (d, *J* = 40.3 Hz, 1F).

(3*r*,5*r*,7*r*)-1-(3,3-difluoro-2-(naphthalen-2-yl)allyl)adamantane (18)[9]



The substrate was prepared following the general procedure A using **S13** (33.3 mg, 0.15 mmol, 1.5 equiv.), 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (29.6 mg, 0.1

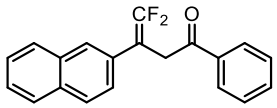
mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **18** was isolated using flash column chromatography on silica gel (petroleum ether) as a white solid (28.4 mg, 84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.76 (m, 4H), 7.55 – 7.41 (m, 3H), 2.32 (t, 2H), 1.85 (br s, 3H), 1.64 – 1.50 (m, 6H), 1.44 – 1.38 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.58 (dd, *J* = 291.0, 287.6 Hz), 133.37 (dd, *J* = 4.7, 3.1 Hz), 133.21, 132.28, 127.88, 127.77, 127.58, 127.19 (t, *J* = 3.0 Hz), 126.48 (t, *J* = 2.8 Hz), 126.12, 125.90, 89.83 (dd, *J* = 22.0, 12.3 Hz), 42.67, 41.99, 36.83, 34.71, 28.57.

^{19}F NMR (564 MHz, $CDCl_3$) δ -88.48 (d, *J* = 39.9 Hz, 1F), -91.80 (d, *J* = 39.8 Hz, 1F).

4,4-difluoro-3-(naphthalen-2-yl)-1-phenylbut-3-en-1-one (19)



The substrate was prepared following the general procedure A using **S13** (22.2 mg, 0.1 mmol, 1.0 equiv.), 2-benzoyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (53.2 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **19** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a white solid (19.4 mg, 63%).

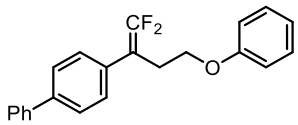
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.83 – 7.75 (m, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.43 (m, 5H), 4.17 (t, *J* = 1.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.34 (dd, *J* = 3.3, 2.3 Hz), 154.92 (dd, *J* = 292.6, 288.6 Hz), 136.28, 133.46, 133.17, 132.47, 130.89 (t, *J* = 4.0 Hz), 128.73, 128.16, 128.15, 127.97, 127.55, 127.10 (t, *J* = 3.5 Hz), 126.26, 126.19, 125.80 (dd, *J* = 4.1, 2.6 Hz), 87.33 (dd, *J* = 22.0, 17.3 Hz), 38.49 (d, *J* = 2.5 Hz).

^{19}F NMR (564 MHz, $CDCl_3$) δ -87.62 (d, *J* = 35.6 Hz, 1F), -88.80 (d, *J* = 35.9 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{20}H_{14}F_2NaO^+$, 331.0905; found: 331.0901.

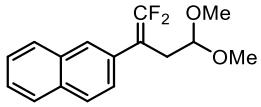
4-(1,1-difluoro-4-phenoxybut-1-en-2-yl)-1,1'-biphenyl (20)



The substrate was prepared following the general procedure A using **S1** (24.8 mg, 0.1 mmol, 1.0 equiv.), 2-methyl-2-(phenoxymethyl)-2,3-dihydroquinazolin-4(1*H*)-one (53.6 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **20** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (26.9 mg, 80%).

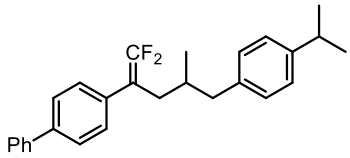
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.50 – 7.33 (m, 5H), 7.30 – 7.22 (m, 2H), 6.97 – 6.90 (m, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.02 (t, *J* = 6.9 Hz, 2H), 2.93 (dd, *J* = 9.4, 4.2 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.58, 154.31 (dd, *J* = 291.4, 288.7 Hz), 140.47, 140.29, 132.13 – 132.03 (m), 129.43, 128.82, 128.63 (t, *J* = 3.3 Hz), 127.46, 127.22, 127.02, 120.85, 114.53, 88.98 (dd, *J* = 21.6, 15.0 Hz), 65.37 (t, *J* = 3.02 Hz), 28.10 (d, *J* = 1.4 Hz).
^{19}F NMR (564 MHz, $CDCl_3$) δ -89.09 (d, *J* = 39.0 Hz, 1F), -89.42 (d, *J* = 39.0 Hz, 1F).
HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{22}H_{18}F_2NaO^+$, 359.1218; found: 359.1223.

2-(1,1-difluoro-4,4-dimethoxybut-1-en-2-yl)naphthalene (21)



The substrate was prepared following the general procedure A using **S13** (33.3 mg, 0.15 mmol, 1.5 equiv.), 2-(dimethoxymethyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (23.6 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **21** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (26.1 mg, 94%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 4H), 7.52 – 7.45 (m, 3H), 4.37 (t, *J* = 5.8 Hz, 1H), 3.29 (d, *J* = 1.1 Hz, 6H), 2.80 (dd, *J* = 3.9, 1.5 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.53 (dd, *J* = 290.4, 288.6 Hz), 133.22, 132.50, 130.81 (dd, *J* = 4.1, 3.1 Hz), 128.11, 127.95, 127.59, 127.47 (t, *J* = 3.2 Hz), 126.29, 126.21 – 126.14 (m), 102.38 (dd, *J* = 3.7, 2.8 Hz), 88.75 (dd, *J* = 21.5, 16.3 Hz), 53.09, 31.88 (d, *J* = 1.5 Hz). (one carbon signal was overlapped).
^{19}F NMR (564 MHz, $CDCl_3$) δ -89.82 (d, *J* = 39.4 Hz, 1F), -90.02 (d, *J* = 39.2 Hz, 1F).
HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{16}H_{16}F_2NaO_2^+$, 301.1011; found: 301.1016.

4-(1,1-difluoro-5-(4-isopropylphenyl)-4-methylpent-1-en-2-yl)-1,1'-biphenyl (22)



The substrate was prepared following the general procedure B using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-(1-(4-isopropylphenyl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (41.3 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **22** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (29.3 mg, 75%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 4H), 7.49 – 7.29 (m, 5H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 2.93 – 2.83 (m, 1H), 2.65 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.55 – 2.46 (m, 1H),

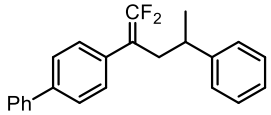
2.41 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.36 – 2.24 (m, 1H), 1.83 – 1.74 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 0.89 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.07 (dd, *J* = 290.8, 286.5 Hz), 146.37, 140.58, 139.93, 138.09, 132.61 – 132.53 (m), 128.99, 128.80, 128.60 (t, *J* = 3.2 Hz), 127.37, 127.04, 127.01, 126.18, 91.15 (dd, *J* = 21.9, 12.6 Hz), 42.74, 34.37, 33.69, 33.27 (t, *J* = 2.2 Hz), 24.09, 19.16.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.64 (d, *J* = 42.9 Hz, 1F), -90.94 (d, *J* = 43.0 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{27}H_{28}F_2Na^+$, 413.2051; found: 413.2054.

4-(1,1-difluoro-4-phenylpent-1-en-2-yl)-1,1'-biphenyl (23)



The substrate was prepared following the general procedure B using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), diethyl 2,6-dimethyl-4-(1-phenylethyl)-1,4-dihydropyridine-3,5-dicarboxylate (35.7 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **23** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (22.4 mg, 67%).

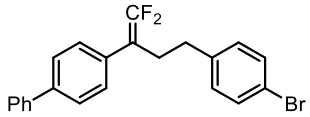
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 4H), 7.50 – 7.32 (m, 5H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 2.79 – 2.63 (m, 3H), 1.27 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.13 (dd, *J* = 290.8, 287.0 Hz), 146.16, 140.54, 140.02, 132.43 (dd, *J* = 4.5, 3.2 Hz), 128.80, 128.71 (t, *J* = 3.1 Hz), 128.34, 127.39, 127.10, 127.00, 126.94, 126.23, 90.98 (dd, *J* = 21.8, 13.2 Hz), 37.74 (t, *J* = 2.3 Hz), 36.22 (d, *J* = 1.0 Hz), 21.10.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.59 (d, *J* = 41.8 Hz, 1F), -91.28 (d, *J* = 41.8 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{23}H_{20}F_2Na^+$, 357.1425; found: 357.1421.

4-(4-(4-bromophenyl)-1,1-difluorobut-1-en-2-yl)-1,1'-biphenyl (24)



The substrate was prepared following the general procedure B using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-(4-bromobenzyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.1 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **24** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (27.9 mg, 70%).

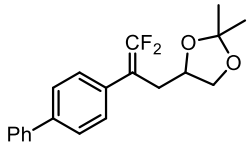
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 4H), 7.50 – 7.35 (m, 7H), 7.03 (d, *J* = 8.3 Hz, 2H), 2.76 – 2.65 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.83 (dd, *J* = 291.5, 287.4 Hz), 140.46, 140.20, 139.84, 132.15 – 132.07 (m), 131.43, 130.21, 128.84, 128.59 (t, *J* = 3.3 Hz), 127.47, 127.23, 127.02, 119.90, 91.24 (dd, *J* = 21.8, 13.2 Hz), 33.39 (t, *J* = 3.02 Hz), 29.28 (d, *J* = 1.5 Hz).

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.30 (d, *J* = 41.2 Hz, 1F), -90.71 (d, *J* = 41.2 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{22}H_{17}BrF_2Na^+$, 421.0374; found: 421.0379.

4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2,2-dimethyl-1,3-dioxolane (25)



The substrate was prepared following the general procedure B using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-(4,4-dimethyl-1,3-dioxolan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (35.3 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **25** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (27.4 mg, 83%).

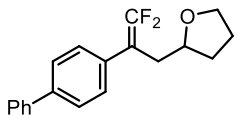
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 4H), 7.47 – 7.34 (m, 5H), 4.18 – 4.06 (m, 1H), 3.96 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.59 (dd, *J* = 8.0, 6.6 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.67 – 2.56 (m, 1H), 1.42 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.34 (t, *J* = 12.08 Hz), 140.40, 140.36, 131.99 (d, *J* = 1.1 Hz), 128.81, 128.63 (t, *J* = 3.2 Hz), 127.47, 127.22, 127.00, 109.19, 88.85 (dd, *J* = 19.2, 17.5 Hz), 74.00 (t, *J* = 3.1 Hz), 68.88, 32.43, 26.89, 25.61.

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.31 (s, 2F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{20}H_{20}F_2NaO_2^+$, 353.1324; found: 353.1321.

2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)tetrahydrofuran (26)[8]



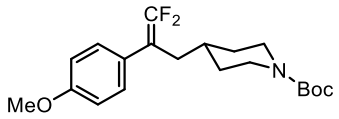
The substrate was prepared following the general procedure B using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), diethyl 2,6-dimethyl-4-(tetrahydrofuran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (32.3 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **26** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a white solid (24.3 mg, 81%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 4H), 7.50 – 7.41 (m, 4H), 7.37 – 7.33 (m, 1H), 3.93 – 3.81 (m, 2H), 3.78 – 3.64 (m, 1H), 2.83 – 2.69 (m, 1H), 2.64 – 2.48 (m, 1H), 2.00 – 1.74 (m, 3H), 1.57 – 1.45 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.34 (t, *J* = 12.08 Hz), 140.52, 140.09, 132.47 (d, *J* = 1.6 Hz), 128.78, 128.67 (t, *J* = 3.3 Hz), 127.38, 127.11, 126.99, 89.79 (dd, *J* = 19.2, 16.8 Hz), 77.05, 67.81, 33.76, 30.95, 25.58.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.15 (s, 2F).

***tert*-butyl 4-(3,3-difluoro-2-(4-methoxyphenyl)allyl)piperidine-1-carboxylate (27)[10]**



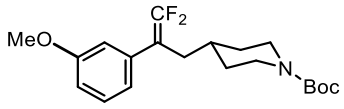
The substrate was prepared following the general procedure A using **S2** (30.3 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **27** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (31.6 mg, 86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.03 (d, *J* = 12.4 Hz, 2H), 3.81 (s, 3H), 2.56 (t, *J* = 12.2 Hz, 2H), 2.29 (d, *J* = 7.2 Hz, 2H), 1.60 (d, *J* = 12.9 Hz, 2H), 1.43 (s, 9H), 1.42 – 1.36 (m, 1H), 1.16 – 1.06 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.67, 154.75, 154.06 (dd, *J* = 289.9, 286.9 Hz), 129.28 (t, *J* = 3.2 Hz), 125.68 (dd, *J* = 4.1, 3.1 Hz), 113.93, 89.89 (dd, *J* = 21.9, 13.6 Hz), 79.25, 55.23, 43.35, 34.45, 34.17 (t, *J* = 2.4 Hz), 31.68, 28.43.

^{19}F NMR (564 MHz, $CDCl_3$) δ -91.76 (d, *J* = 45.3 Hz, 1F), -92.10 (d, *J* = 45.2 Hz, 1F).

***tert*-butyl 4-(3,3-difluoro-2-(3-methoxyphenyl)allyl)piperidine-1-carboxylate (28)[10]**



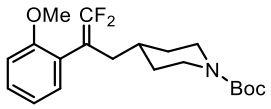
The substrate was prepared following the general procedure A using **S3** (30.3 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **28** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (29.4 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 1H), 6.91 – 6.80 (m, 3H), 4.03 (d, *J* = 11.9 Hz, 2H), 3.81 (s, 3H), 2.57 (t, *J* = 12.1 Hz, 2H), 2.31 (dt, *J* = 7.1, 2.0 Hz, 2H), 1.61 (d, *J* = 14.1 Hz, 2H), 1.44 (s, 9H), 1.42 – 1.38 (m, 1H), 1.16 – 1.05 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.56, 154.75, 154.18 (dd, *J* = 291.4, 286.9 Hz), 135.02 (dd, *J* = 3.4, 2.2 Hz), 129.46, 120.62 (t, *J* = 3.1 Hz), 114.41 (t, *J* = 3.3 Hz), 112.32, 90.43 (dd, *J* = 20.9, 14.2 Hz), 79.25, 55.22, 43.70, 34.40, 34.23 (t, *J* = 2.5 Hz), 31.69, 28.43.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.44 (d, *J* = 42.0 Hz, 1F), -90.55 (d, *J* = 42.1 Hz, 1F).

***tert*-butyl 4-(3,3-difluoro-2-(2-methoxyphenyl)allyl)piperidine-1-carboxylate (29)[10]**



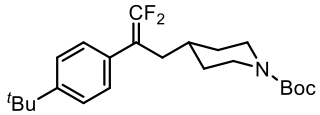
The substrate was prepared following the general procedure A using **S4** (30.3 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **29** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (27.5 mg, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.86 (m, 2H), 4.02 (s, 2H), 3.81 (s, 3H), 2.58 (t, *J* = 12.1 Hz, 2H), 2.27 (d, *J* = 7.1 Hz, 2H), 1.64 (d, *J* = 11.6 Hz, 2H), 1.44 (s, 9H), 1.37 – 1.27 (m, 1H), 1.15 – 1.05 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.26 (d, *J* = 2.0 Hz), 154.81, 153.46 (t, *J* = 287.20 Hz), 130.84 – 130.78 (m), 129.11, 122.66 (dd, *J* = 5.1, 1.6 Hz), 120.46, 111.03, 87.22 (dd, *J* = 23.9, 16.6 Hz), 79.18, 55.4, 43.52, 34.81, 34.23 (t, *J* = 2.5 Hz), 31.75, 28.44.

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.43 (d, *J* = 43.0 Hz, 1F), -93.40 (d, *J* = 43.0 Hz, 1F).

***tert*-butyl 4-(2-(4-(*tert*-butyl)phenyl)-3,3-difluoroallyl)piperidine-1-carboxylate (30)[10]**



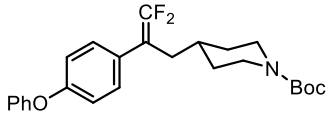
The substrate was prepared following the general procedure A using **S5** (34.2 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **30** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (32.6 mg, 83%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 4.04 (s, 2H), 2.58 (t, *J* = 12.3 Hz, 2H), 2.34 – 2.29 (m, 2H), 1.62 (d, *J* = 12.4 Hz, 2H), 1.44 (s, 9H), 1.43 – 1.40 (m, 1H), 1.32 (s, 9H), 1.17 – 1.06 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.77, 154.19 (dd, *J* = 291.4, 286.9 Hz), 150.19, 130.52 – 130.40 (m), 127.70 (t, *J* = 3.3 Hz), 125.39, 90.15 (dd, *J* = 21.7, 12.9 Hz), 79.24, 43.73, 34.51, 34.29, 34.18 (t, *J* = 2.4 Hz), 31.71, 31.26, 28.44.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.55 (d, *J* = 41.8 Hz, 1F), -91.00 (d, *J* = 41.8 Hz, 1F).

***tert*-butyl 4-(3,3-difluoro-2-(4-phenoxyphenyl)allyl)piperidine-1-carboxylate (31)**



The substrate was prepared following the general procedure A using **S6** (39.6 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **31** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (33.5 mg, 78%).

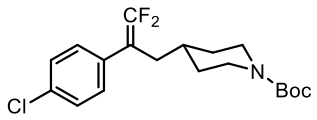
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 4.05 (s, 2H), 2.59 (s, 2H), 2.31 (d, *J* = 7.1 Hz, 2H), 1.62 (d, *J* = 12.5 Hz, 2H), 1.47 – 1.39 (m, 10H), 1.12 (dd, *J* = 21.0, 10.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.66, 156.60, 154.76, 154.16 (dd, *J* = 291.4, 286.9 Hz), 129.80, 129.50 (t, *J* = 3.2 Hz), 128.18 (dd, *J* = 4.2, 3.3 Hz), 123.61, 119.25, 118.46, 89.89 (dd, *J* = 22.2, 13.2 Hz), 79.29, 43.68, 34.42, 34.23 (t, *J* = 2.3 Hz), 31.69, 28.44.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.97 (d, *J* = 43.4 Hz, 1F), -91.30 (d, *J* = 38.2 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{25}H_{29}F_2NNaO_3^+$, 452.2008; found: 452.2012.

***tert*-butyl 4-(2-(4-chlorophenyl)-3,3-difluoroallyl)piperidine-1-carboxylate (32)**



The substrate was prepared following the general procedure A using **S7** (30.9 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **32** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (29.7 mg, 80%).

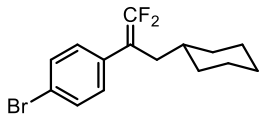
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.03 (s, 2H), 2.56 (t, *J* = 12.3 Hz, 2H), 2.33 – 2.28 (m, 2H), 1.58 (d, *J* = 12.7 Hz, 2H), 1.43 (s, 9H), 1.41 – 1.34 (m, 1H), 1.15 – 1.06 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.72, 154.16 (dd, *J* = 291.4, 286.9 Hz), 133.16, 132.05 (dd, *J* = 4.4, 3.6 Hz), 129.47 (t, *J* = 3.3 Hz), 128.76, 89.74 (dd, *J* = 22.7, 13.0 Hz), 79.31, 43.55, 34.23 (t, *J* = 2.1 Hz), 31.65, 28.43. (one carbon signal was overlapped).

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.86 (d, *J* = 41.0 Hz, 1F), -90.34 (d, *J* = 40.9 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{19}H_{24}ClF_2NNaO_2^+$, 394.1356; found: 394.1353.

1-bromo-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (33)[11]



The substrate was prepared following the general procedure B using **S8** (37.5 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (33.5 mg, 0.1

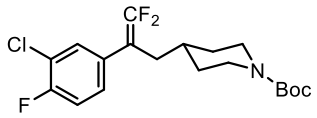
mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **33** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (23.6 mg, 75%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 2.24 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.71 – 1.58 (m, 5H), 1.30 – 1.04 (m, 4H), 0.97 – 0.85 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.88 (dd, *J* = 290.8, 286.7 Hz), 133.05 (dd, *J* = 4.7, 3.4 Hz), 131.54, 129.89 (t, *J* = 3.3 Hz), 120.99, 90.36 (dd, *J* = 22.9, 12.4 Hz), 35.66 (t, *J* = 1.9 Hz), 35.00, 32.80, 26.33, 26.00.

^{19}F NMR (564 MHz, $CDCl_3$) δ -95.17 (d, *J* = 42.2 Hz, 1F), -95.72 (d, *J* = 42.2 Hz, 1F).

***tert*-butyl 4-(2-(3-chloro-4-fluorophenyl)-3,3-difluoroallyl)piperidine-1-carboxylate (34)**



The substrate was prepared following the general procedure A using **S9** (33.6 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **34** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (29.6 mg, 76%).

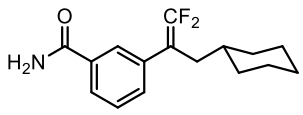
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 6.9, 1.6 Hz, 1H), 7.19 – 7.10 (m, 2H), 4.04 (d, *J* = 10.7 Hz, 2H), 2.58 (t, *J* = 12.4 Hz, 2H), 2.35 – 2.21 (m, 2H), 1.59 (d, *J* = 12.9 Hz, 2H), 1.43 (s, 9H), 1.40 – 1.34 (m, 1H), 1.16 – 1.06 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.17 (d, *J* = 250.1 Hz), 154.71, 154.26 (dd, *J* = 291.4, 289.9 Hz), 130.73 (dd, *J* = 8.0, 4.1 Hz), 130.30 (t, *J* = 3.4 Hz), 128.11 – 127.84 (m), 121.19 (d, *J* = 18.0 Hz), 116.70 (d, *J* = 21.2 Hz), 89.13 (dd, *J* = 23.4, 13.0 Hz), 79.35, 43.46, 34.33, 34.19 (t, *J* = 2.3 Hz), 31.63, 28.42.

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.46 (d, *J* = 40.1 Hz, 1F), -89.94 (d, *J* = 40.1 Hz, 1F), -116.57 (s, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{19}H_{24}ClF_3NO_2^+$, 390.1442; found: 390.1440.

3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzamide (35)



The substrate was prepared following the general procedure A using **S10** (34.8 mg, 0.15 mmol, 1.5 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24.4 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The

product **35** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) as a white solid (17.0 mg, 61%).

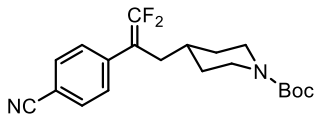
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.44 (dt, J = 15.3, 7.5 Hz, 2H), 6.21 (s, 2H), 2.32 – 2.26 (m, 2H), 1.71 – 1.59 (m, 5H), 1.23 – 1.16 (m, 1H), 1.15 – 1.05 (m, 3H), 0.94 – 0.84 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.41, 154.10 (dd, J = 290.8, 287.1 Hz), 134.88 (dd, J = 4.8, 3.2 Hz), 133.61, 131.89 (t, J = 3.1 Hz), 128.69, 127.39 (t, J = 3.2 Hz), 125.86, 90.64 (dd, J = 22.8, 12.1 Hz), 35.66, 35.07, 32.80, 26.31, 25.99.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.27 (d, J = 41.9 Hz, 1F), -91.01 (d, J = 41.9 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{16}H_{19}F_2NNaO^+$, 302.1327; found: 302.1322.

***tert*-butyl 4-(2-(4-cyanophenyl)-3,3-difluoroallyl)piperidine-1-carboxylate (36)**



The substrate was prepared following the general procedure A using **S11** (29.6 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **36** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) as a colorless oil (25.7 mg, 71%).

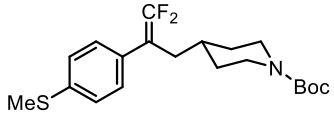
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 4.04 (d, *J* = 9.1 Hz, 2H), 2.56 (t, *J* = 12.5 Hz, 2H), 2.36 (d, *J* = 7.1 Hz, 2H), 1.58 (d, *J* = 13.2 Hz, 2H), 1.43 (s, 9H), 1.39 – 1.34 (m, 1H), 1.17 – 1.06 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.68, 154.46 (dd, *J* = 294.5, 289.9 Hz), 138.71 – 138.61 (m), 132.33, 128.76 (t, *J* = 3.5 Hz), 118.50, 111.10, 89.99 (dd, *J* = 23.3, 12.1 Hz), 79.40, 43.59, 34.43 (t, *J* = 2.3 Hz), 33.87, 31.65, 28.41.

^{19}F NMR (564 MHz, $CDCl_3$) δ -86.92 (d, *J* = 34.8 Hz, 1F), -87.89 (d, *J* = 34.8 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{20}H_{24}F_2N_2NaO_2^+$, 385.1698; found: 385.1707.

***tert*-butyl 4-(3,3-difluoro-2-(4-(methylthio)phenyl)allyl)piperidine-1-carboxylate (37)**



The substrate was prepared following the general procedure A using **S12** (32.7 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **37** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (26.1 mg, 68%).

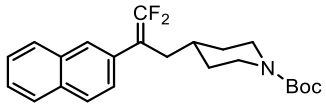
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 4H), 4.03 (s, 2H), 2.56 (t, *J* = 11.9 Hz, 2H), 2.49 (s, 3H), 2.31 (d, *J* = 7.2 Hz, 2H), 1.59 (d, *J* = 12.8 Hz, 2H), 1.43 (s, 9H), 1.42 – 1.36 (m, 1H), 1.15 – 1.04 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.74, 154.15 (dd, *J* = 291.4, 286.9 Hz), 137.66, 130.22 – 130.13 (m), 128.52 (t, *J* = 3.3 Hz), 126.40, 90.01 (dd, *J* = 22.1, 13.0 Hz), 79.28, 43.67, 34.30 – 34.14 (m), 31.68, 28.43, 15.59. (one carbon signal was overlapped).

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.51 (d, *J* = 42.6 Hz, 1F), -90.88 (d, *J* = 42.6 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{20}H_{27}F_2NNaO_2S^+$, 406.1623; found: 406.1620.

***tert*-butyl 4-(3,3-difluoro-2-(naphthalen-2-yl)allyl)piperidine-1-carboxylate (38)[12]**



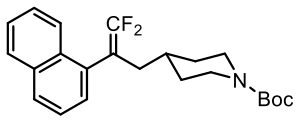
The substrate was prepared following the general procedure A using **S13** (33.3 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **38** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a white solid (34.8 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (t, *J* = 7.8 Hz, 3H), 7.76 (s, 1H), 7.54 – 7.47 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 4.03 (s, 2H), 2.54 (t, *J* = 12.4 Hz, 2H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.65 (d, *J* = 12.8 Hz, 2H), 1.49 – 1.37 (m, 10H), 1.21 – 1.03 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.74, 154.35 (dd, J = 291.4, 288.41 Hz), 133.23, 132.46, 131.04 (dd, *J* = 4.4, 3.2 Hz), 128.16, 127.88, 127.61, 127.27 (t, *J* = 3.3 Hz), 126.35, 126.20, 126.01 (t, *J* = 3.0 Hz), 90.65 (dd, *J* = 22.0, 13.1 Hz), 79.27, 43.96, 34.46 (d, *J* = 0.9 Hz), 34.29 (t, *J* = 2.4 Hz), 31.72, 28.44.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.27 (d, *J* = 41.9 Hz, 1F), -90.88 (d, *J* = 41.9 Hz, 1F).

***tert*-butyl 4-(3,3-difluoro-2-(naphthalen-1-yl)allyl)piperidine-1-carboxylate (39)**



The substrate was prepared following the general procedure A using **S14** (33.3 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **39** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (28.6 mg, 74%).

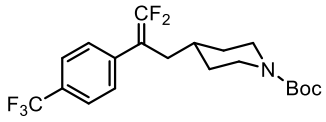
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.80 (m, 3H), 7.57 – 7.38 (m, 3H), 7.33 (d, *J* = 7.0 Hz, 1H), 4.04 (s, 2H), 2.57 (s, 2H), 2.40 (s, 2H), 1.82 – 1.57 (m, 2H), 1.44 (s, 9H), 1.41 – 1.35 (m, 1H), 1.16 (d, *J* = 10.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.77, 154.01 (dd, *J* = 288.4, 286.9 Hz), 133.86, 131.45 (d, *J* = 2.3 Hz), 131.40 – 131.33 (m), 128.66, 128.41, 127.35 – 127.29 (m), 126.39, 125.99, 125.28, 124.76, 88.50 (dd, *J* = 22.4, 17.1 Hz), 79.27, 43.77, 36.32, 34.27 (t, *J* = 2.6 Hz), 31.78, 28.44.

^{19}F NMR (564 MHz, $CDCl_3$) δ -87.70 (d, *J* = 41.7 Hz, 1F), -92.21 (d, *J* = 42.1 Hz, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{23}H_{28}F_2NO_2^+$, 388.2083; found: 388.2088.

***tert*-butyl 4-(3,3-difluoro-2-(4-(trifluoromethyl)phenyl)allyl)piperidine-1-carboxylate (40)**



The substrate was prepared following the general procedure A using **S15** (36.0 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **40** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (36.8 mg, 91%).

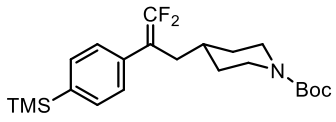
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.04 (d, *J* = 13.3 Hz, 2H), 2.61 – 2.54 (m, 2H), 2.39 – 2.34 (m, 2H), 1.60 (d, *J* = 12.4 Hz, 2H), 1.43 (s, 9H), 1.42 – 1.35 (m, 1H), 1.17 – 1.07 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.71, 154.38 (dd, *J* = 292.9, 288.4 Hz), 137.52 – 137.42 (m), 129.34 (dd, *J* = 36.7, 28.7 Hz), 128.46 (t, *J* = 3.3 Hz), 125.49 (q, *J* = 3.8 Hz), 124.72 (q, *J* = 271.8 Hz), 89.95 (dd, *J* = 23.0, 12.6 Hz), 79.34, 43.63, 34.29 (t, *J* = 2.4 Hz), 34.14, 31.65, 28.41.

^{19}F NMR (564 MHz, $CDCl_3$) δ -62.70 (s, 3F), -88.53 (d, *J* = 38.1 Hz, 1F), -89.32 (d, *J* = 38.1 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{20}H_{24}F_5NNaO_2^+$, 428.1619; found: 428.1613.

***tert*-butyl 4-(3,3-difluoro-2-(4-(trimethylsilyl)phenyl)allyl)piperidine-1-carboxylate (41)**



The substrate was prepared following the general procedure A using **S16** (36.6 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **41** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (26.6 mg, 65%).

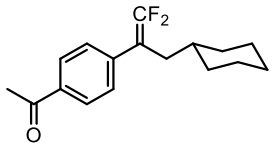
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 4.03 (s, 2H), 2.58 (t, *J* = 11.8 Hz, 2H), 2.34 (d, *J* = 7.2 Hz, 2H), 1.62 (d, *J* = 10.3 Hz, 2H), 1.48 – 1.37 (m, 10H), 1.18 – 1.08 (m, 2H), 0.27 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.76, 154.23 (dd, *J* = 291.4, 286.9 Hz), 139.59, 133.99 – 133.90 (m), 133.47, 127.36 (t, *J* = 3.2 Hz), 90.45 (dd, *J* = 21.8, 12.8 Hz), 79.25, 43.69, 34.25 (d, *J* = 0.8 Hz), 34.20 (t, *J* = 2.4 Hz), 31.70, 28.43, -1.17.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.26 (d, *J* = 42.0 Hz, 1F), -90.72 (d, *J* = 41.8 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{22}H_{33}F_2NNaO_2Si^+$, 432.2141; found: 432.2144.

1-(4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)ethan-1-one (42)[13]



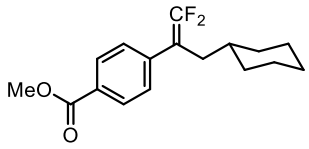
The substrate was prepared following the general procedure B using **S17** (32.1 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (33.5 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **42** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) as a colorless oil (22.8 mg, 82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 2.60 (s, 3H), 2.31 (dt, *J* = 7.2, 2.3 Hz, 2H), 1.67 – 1.59 (m, 5H), 1.26 – 1.18 (m, 1H), 1.15 – 1.04 (m, 3H), 0.91 (dd, *J* = 22.1, 12.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.54, 154.19 (dd, *J* = 292.6, 287.7 Hz), 139.22 (dd, *J* = 4.9, 3.7 Hz), 135.69, 128.42, 128.34 (t, *J* = 3.02 Hz), 90.84 (dd, *J* = 23.0, 11.7 Hz), 35.83, 34.80, 32.80, 26.56, 26.30, 25.99.

^{19}F NMR (564 MHz, $CDCl_3$) δ -88.77 (d, *J* = 38.6 Hz, 1F), -89.51 (d, *J* = 38.6 Hz, 1F).

methyl 4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzoate (43)[13]



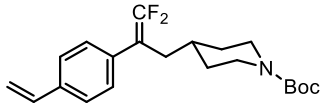
The substrate was prepared following the general procedure B using **S18** (34.5 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (33.5 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **43** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (17.9 mg, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 3.91 (s, 3H), 2.30 (dt, 2H), 1.69 – 1.60 (m, 5H), 1.25 – 1.18 (m, 1H), 1.14 – 1.04 (m, 3H), 0.91 (dd, *J* = 22.3, 12.2 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.75, 154.15 (dd, *J* = 292.3, 287.6 Hz), 139.02 (dd, *J* = 4.8, 3.6 Hz), 129.62, 128.74, 128.17 (t, *J* = 3.4 Hz), 90.85 (dd, *J* = 22.8, 11.8 Hz), 52.11, 35.81, 34.84, 32.80, 26.31, 25.99.

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.05 (d, *J* = 39.1 Hz, 1F), -89.72 (d, *J* = 39.1 Hz, 1F).

***tert*-butyl 4-(3,3-difluoro-2-(4-vinylphenyl)allyl)piperidine-1-carboxylate (44)**



The substrate was prepared following the general procedure A using **S19** (29.7 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **44** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (19.6 mg, 54%).

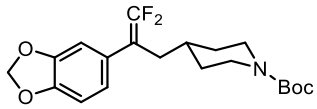
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.9, 4.6 Hz, 2H), 7.29 – 7.24 (m, 2H), 6.76 – 6.60 (m, 1H), 5.76 (dd, *J* = 17.6, 4.4 Hz, 1H), 5.26 (dd, *J* = 10.9, 4.4 Hz, 1H), 4.02 (s, 2H), 2.56 (s, 2H), 2.33 (s, 2H), 1.60 (d, *J* = 12.2 Hz, 2H), 1.50 – 1.34 (m, 10H), 1.11 (d, *J* = 11.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.76, 154.20 (dd, *J* = 291.4, 286.9 Hz), 136.58, 136.17, 132.98 (dd, *J* = 4.3, 3.3 Hz), 128.26 (t, *J* = 3.3 Hz), 126.31, 114.21, 90.28 (dd, *J* = 22.0, 13.0 Hz), 79.31, 43.57, 34.26 (t, *J* = 2.4 Hz), 34.18 (d, *J* = 0.8 Hz), 31.68, 28.43.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.24 (d, *J* = 41.8 Hz, 1F), -90.57 (d, *J* = 41.8 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{21}H_{27}F_2NNaO_2^+$, 386.1902; found: 386.1894.

***ootert*-butyl 4-(2-(benzo[*d*][1,3]dioxol-5-yl)-3,3-difluoroallyl)piperidine-1-carboxylate (45)[10]**



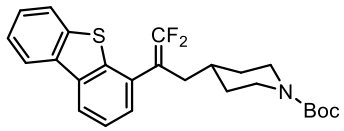
The substrate was prepared following the general procedure A using **S20** (32.4 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **45** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (27.1 mg, 71%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 – 6.73 (m, 3H), 5.97 (s, 2H), 4.03 (s, 2H), 2.58 (t, *J* = 12.1 Hz, 2H), 2.26 (d, *J* = 7.2 Hz, 2H), 1.59 (d, *J* = 12.7 Hz, 2H), 1.44 (s, 9H), 1.42 – 1.37 (m, 1H), 1.15 – 1.05 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.75, 154.11 (dd, *J* = 289.9, 287.6 Hz), 147.74, 146.75, 127.21 (d, *J* = 2.3 Hz), 121.72 (t, *J* = 3.2 Hz), 108.68 (t, *J* = 3.3 Hz), 108.34, 101.15, 90.22 (dd, *J* = 20.1, 15.8 Hz), 79.26, 43.81, 34.65, 34.15 (t, *J* = 2.4 Hz), 31.66, 28.43.

^{19}F NMR (564 MHz, $CDCl_3$) δ -91.37 (d, *J* = 44.8 Hz, 1F), -91.45 (d, *J* = 44.4 Hz, 1F).

***tert*-butyl 4-(2-(dibenzo[*b*,*d*]thiophen-4-yl)-3,3-difluoroallyl)piperidine-1-carboxylate (46)**



The substrate was prepared following the general procedure A using **S21** (41.7 mg, 0.15 mmol, 1.5 equiv.), *tert*-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (34.5 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **46** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (38.9 mg, 88%).

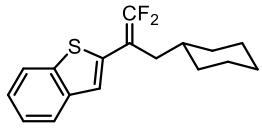
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 – 8.10 (m, 2H), 7.86 (dd, *J* = 5.1, 3.7 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.31 (d, *J* = 7.3 Hz, 1H), 4.04 (d, *J* = 12.7 Hz, 2H), 2.56 (t, *J* = 12.0 Hz, 2H), 2.46 (d, *J* = 7.0 Hz, 2H), 1.71 (d, *J* = 12.7 Hz, 2H), 1.44 (s, 9H), 1.39 – 1.32 (m, 1H), 1.22 – 1.12 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.76, 153.63 (t, *J* = 10.57 Hz), 139.70 (dd, *J* = 2.4, 1.2 Hz), 139.06, 136.08, 135.65, 128.83 (dd, *J* = 5.0, 1.4 Hz), 127.37 (d, *J* = 1.8 Hz), 127.02, 124.74, 124.52, 122.72, 121.74, 121.06, 89.70 (dd, *J* = 23.6, 15.8 Hz), 79.25, 43.61, 34.96, 34.43 (t, *J* = 2.5 Hz), 31.87, 28.44.

^{19}F NMR (564 MHz, $CDCl_3$) δ -85.94 (d, *J* = 37.4 Hz, 1F), -90.81 (d, *J* = 37.5 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{25}H_{27}F_2NNaO_2S^+$, 466.1623; found: 466.1627.

2-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzo[*b*]thiophene (47)

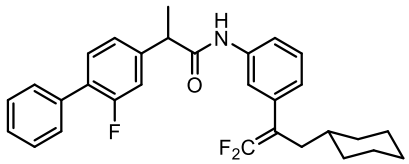


The substrate was prepared following the general procedure B using **S22** (34.2 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (33.5 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **47** was isolated using flash column chromatography on silica gel (petroleum ether) as a colorless oil (23.4 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.25 (s, 1H), 2.37 – 2.33 (m, 2H), 1.79 – 1.63 (m, 5H), 1.61 – 1.56 (m, 1H), 1.21 – 1.14 (m, 3H), 1.04 – 0.96 (m, 2H).

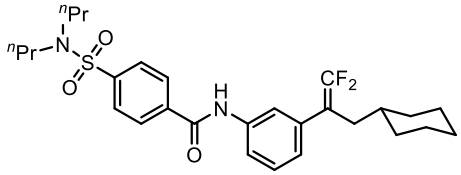
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.46 (dd, *J* = 297.0, 288.8 Hz), 139.58, 139.23 (dd, *J* = 5.2, 1.5 Hz), 136.72 (dd, *J* = 7.1, 4.3 Hz), 124.37, 124.21, 123.23, 121.92 – 121.82 (m), 87.57 (dd, *J* = 26.9, 11.2 Hz), 36.47 (t, *J* = 1.9 Hz), 35.25, 32.96, 26.35, 26.11. (one carbon signal was overlapped).
^{19}F NMR (564 MHz, $CDCl_3$) δ -83.55 (d, *J* = 30.4 Hz, 1F), -87.73 (d, *J* = 30.4 Hz, 1F).
HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{17}H_{18}F_2NaS^+$, 315.0989; found: 315.0994.

***N*-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propenamide (48)**



The substrate was prepared following the general procedure A using **S23** (41.3 mg, 0.1 mmol, 1.0 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (48.8 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **48** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) as a white solid (37.2 mg, 78%).
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.35 (m, 6H), 7.31 – 7.17 (m, 4H), 7.03 (d, *J* = 7.7 Hz, 1H), 3.73 (q, *J* = 7.0 Hz, 1H), 2.24 (d, *J* = 7.2 Hz, 2H), 1.70 – 1.60 (m, 8H), 1.26 – 1.19 (m, 1H), 1.15 – 1.06 (m, 3H), 0.94 – 0.85 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.56, 159.88 (d, *J* = 249.4 Hz), 153.95 (dd, *J* = 290.1, 286.4 Hz), 142.13 (d, *J* = 7.4 Hz), 137.79, 135.23, 135.08 (dd, *J* = 4.4, 3.3 Hz), 131.30 (d, *J* = 3.9 Hz), 128.95, 128.91 (d, *J* = 2.9 Hz), 128.49, 128.24 (d, *J* = 13.6 Hz), 127.80, 124.43 (t, *J* = 2.6 Hz), 123.61 (d, *J* = 3.3 Hz), 119.60 (t, *J* = 3.0 Hz), 118.67, 115.37 (d, *J* = 23.6 Hz), 90.86 (dd, *J* = 22.2, 12.5 Hz), 47.67, 35.64, 35.19, 32.81, 26.36, 26.01, 18.69.
^{19}F NMR (564 MHz, $CDCl_3$) δ -90.97 (d, *J* = 43.1 Hz, 1F), -91.19 (d, *J* = 42.9 Hz, 1F), -116.72 (s, 1F).
HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{30}H_{30}F_3NNaO^+$, 500.2172; found: 500.2176.

***N*-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-4-(*N*,*N*-dipropylsulfamoyl)benzamide (49)**



The substrate was prepared following the general procedure A using **S24** (45.4 mg, 0.1 mmol, 1.0 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (48.8 mg, 0.2 mmol, 2.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The

product **49** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) as a colorless oil (29.1 mg, 56%).

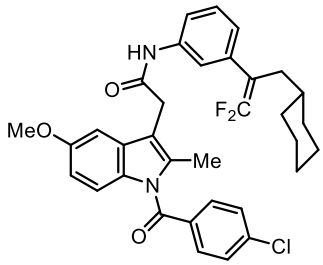
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.63 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 3.10 – 3.04 (m, 4H), 2.30 – 2.26 (m, 2H), 1.72 – 1.62 (m, 5H), 1.57 – 1.48 (m, 4H), 1.30 – 1.25 (m, 1H), 1.15 – 1.09 (m, 3H), 0.96 – 0.90 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.71, 154.01 (dd, *J* = 290.6, 286.5 Hz), 142.75, 138.73, 137.87, 135.15 (dd, *J* = 4.7, 3.2 Hz), 129.10, 127.93, 127.28, 124.81 (dd, *J* = 4.5, 2.7 Hz), 120.10 – 120.02 (m), 119.10, 90.90 (dd, *J* = 22.4, 12.5 Hz), 49.95, 35.68, 35.18, 32.83, 26.37, 26.03, 21.91, 11.13.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.84 (d, *J* = 42.7 Hz, 1F), -91.09 (d, *J* = 43.0 Hz, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{28}H_{37}F_2N_2O_3S^+$, 519.2487; found: 519.2484.

2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-*N*-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl) phenyl) acetamide (50)



The substrate was prepared following the general procedure A using **S30** (78.9 mg, 0.15 mmol, 1.5 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24.4 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **50** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) as a light yellow oil (30.7 mg, 52%).

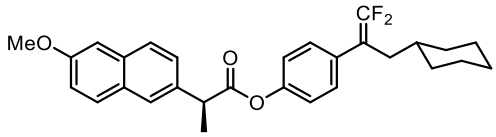
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 3H), 7.35 – 7.30 (m, 2H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.80 (d, *J* = 2.5 Hz, 5H), 2.44 (s, 3H), 2.24 – 2.18 (m, 2H), 1.67 – 1.54 (m, 5H), 1.23 – 1.17 (m, 1H), 1.12 – 1.04 (m, 3H), 0.92 – 0.84 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.33, 168.27, 156.39, 153.90 (dd, *J* = 290.1, 286.4 Hz), 139.64, 137.52, 136.68, 135.02 (dd, *J* = 4.6, 2.8 Hz), 133.44, 131.17, 130.94, 130.19, 129.21, 128.88, 124.59 (t, *J* = 2.7 Hz), 119.96 (t, *J* = 2.9 Hz), 119.05, 115.20, 112.43, 112.28, 100.76, 90.82 (dd, *J* = 22.1, 12.7 Hz), 55.75, 35.63, 35.16, 33.33, 32.79, 26.35, 26.00, 13.36.

^{19}F NMR (564 MHz, $CDCl_3$) δ -90.93 (d, *J* = 43.0 Hz, 1F), -91.15 (d, *J* = 43.0 Hz, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{34}H_{34}ClF_2N_2O_3^+$, 591.2221; found: 591.2219.

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (51)



The substrate was prepared following the general procedure A using **S26** (60.0 mg, 0.15 mmol, 1.5 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24.4 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **51** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) as a colorless oil (32.5 mg, 70%).

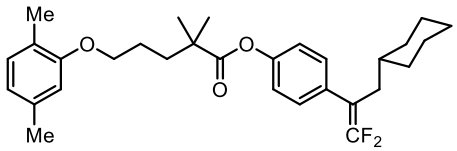
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 17.4, 7.9 Hz, 3H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.12 (m, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 2.22 (d, *J* = 7.2 Hz, 2H), 1.70 (d, *J* = 7.2 Hz, 3H), 1.66 – 1.57 (m, 5H), 1.25 – 1.18 (m, 1H), 1.12 – 1.05 (m, 3H), 0.94 – 0.84 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.13, 157.75, 153.96 (dd, *J* = 290.4, 286.0 Hz), 149.69, 135.04, 133.82, 131.57 (dd, *J* = 4.6, 3.1 Hz), 129.31, 129.20 (t, *J* = 3.2 Hz), 128.98, 127.37, 126.14, 126.08, 121.29, 119.12, 105.59, 90.39 (dd, *J* = 22.7, 12.5 Hz), 55.32, 45.58, 35.52, 35.20, 32.80, 26.36, 25.99, 18.46.

^{19}F NMR (564 MHz, $CDCl_3$) δ -91.09 (d, *J* = 43.6 Hz, 1F), -91.52 (d, *J* = 43.5 Hz, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{29}H_{31}F_2O_3^+$, 465.2236; found: 465.2232.

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (52)



The substrate was prepared following the general procedure A using **S27** (63.0 mg, 0.15 mmol, 1.5 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24.4 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **52** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (29.1 mg, 60%).

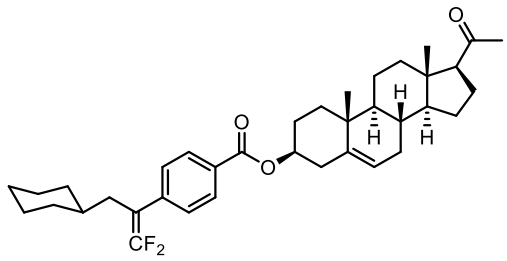
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.06 – 6.99 (m, 3H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 4.00 (d, *J* = 4.3 Hz, 2H), 2.31 (s, 3H), 2.28 – 2.24 (m, 2H), 2.19 (s, 3H), 1.91 – 1.85 (m, 4H), 1.70 – 1.59 (m, 5H), 1.38 (s, 6H), 1.32 – 1.22 (m, 1H), 1.18 – 1.08 (m, 3H), 0.98 – 0.87 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.30, 156.84, 153.99 (dd, *J* = 290.3, 286.0 Hz), 149.85, 136.47, 131.47 (dd, *J* = 4.7, 3.2 Hz), 130.34, 129.26 (t, *J* = 3.3 Hz), 123.60, 121.43, 120.75, 111.93, 90.43 (dd, *J* = 22.6, 12.6 Hz), 67.74, 42.46, 37.15, 35.56 (d, *J* = 1.9 Hz), 35.25, 32.83, 26.38, 26.02, 25.27, 25.14, 21.40, 15.80.

^{19}F NMR (564 MHz, $CDCl_3$) δ -86.90 (d, *J* = 43.7 Hz, 1F), -87.30 (d, *J* = 43.6 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{30}H_{38}F_2NaO_3^+$, 507.2681; found: 507.2688.

(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzoate (53)



The substrate was prepared following the general procedure B using **S28** (77.1 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (33.5 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (2.6 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **53** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) as a white solid (43.4 mg, 75%).

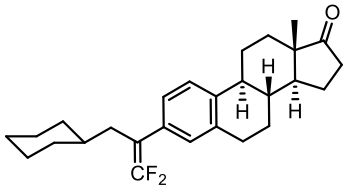
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 2H), 5.41 (d, *J* = 4.0 Hz, 1H), 4.88 – 4.82 (m, 1H), 2.54 (t, *J* = 9.0 Hz, 1H), 2.45 (d, *J* = 7.8 Hz, 2H), 2.32 – 2.27 (m, 2H), 2.21 – 2.14 (m, 1H), 2.12 (s, 3H), 2.07 – 1.97 (m, 3H), 1.92 (dt, *J* = 13.3, 3.4 Hz, 1H), 1.75 – 1.56 (m, 10H), 1.53 – 1.45 (m, 3H), 1.26 – 1.14 (m, 4H), 1.11 – 1.01 (m, 7H), 0.90 (dd, *J* = 23.0, 12.8 Hz, 2H), 0.63 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.58, 165.63, 154.11 (dd, *J* = 292.1, 287.5 Hz), 139.58, 138.88 – 138.79 (m), 129.59, 129.35, 128.11 (t, *J* = 3.2 Hz), 122.48, 90.87 (dd, *J* = 22.8, 11.8 Hz), 74.43, 63.66, 56.81, 49.87, 43.98, 38.77, 38.15, 37.01, 36.64, 35.78, 34.86, 32.80, 31.81, 31.77, 31.56, 27.83, 26.30, 25.99, 24.47, 22.80, 21.04, 19.35, 13.22.

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.22 (d, *J* = 39.4 Hz, 1F), -89.83 (d, *J* = 39.3 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{37}H_{48}F_2NaO_3^+$, 601.3464; found: 601.3468.

(8*R*,9*S*,13*S*,14*S*)-3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (54)[6]



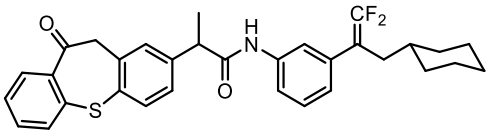
The substrate was prepared following the general procedure A using **S29** (52.2 mg, 0.15 mmol, 1.5 equiv.), 2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24.4 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **54** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a colorless oil (24.7 mg, 60%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.8 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.03 (s, 1H), 2.92 (dd, *J* = 8.6, 3.7 Hz, 2H), 2.56 – 2.38 (m, 2H), 2.31 (td, *J* = 11.2, 4.0 Hz, 1H), 2.24 (dt, *J* = 7.2, 2.4 Hz, 2H), 2.19 – 1.95 (m, 4H), 1.72 – 1.42 (m, 11H), 1.32 – 1.26 (m, 1H), 1.17 – 1.09 (m, 3H), 0.96 – 0.88 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 220.92, 153.94 (dd, *J* = 289.9, 285.8 Hz), 138.64, 136.39, 131.48 (dd, *J* = 3.8 Hz), 128.72 (t, *J* = 3.2 Hz), 125.60 (t, *J* = 3.1 Hz), 125.29, 90.68 (dd, *J* = 21.8, 12.4 Hz), 50.52, 47.99, 44.35, 38.04, 35.85, 35.57, 35.18, 32.85, 31.58, 29.41, 26.49, 26.41, 26.03, 25.58, 21.58, 13.85.

^{19}F NMR (564 MHz, $CDCl_3$) δ -91.52 (d, *J* = 45.1 Hz, 1F), -91.90 (d, *J* = 45.1 Hz, 1F).

***N*-(3-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)phenyl)-2-(10-oxo-10,11-dihydrodibenzo[*b*,*f*]thiepin-2-yl)propanamide (55)**



The substrate was prepared following the general procedure B using **S25** (46.7 mg, 0.1 mmol, 1.0 equiv.), diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (67.0 mg, 0.2 mmol, 2.0 equiv.), Eosin Y (2.6 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **55** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) as a colorless oil (31.3 mg, 59%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 14.3, 7.9 Hz, 2H), 7.46 – 7.37 (m, 4H), 7.34 – 7.21 (m, 4H), 7.00 (d, *J* = 7.6 Hz, 1H), 4.35 (dd, *J* = 35.3, 11.7 Hz, 2H), 3.66 (q, *J* = 7.0 Hz, 1H), 2.21 (d, *J* = 7.1 Hz, 2H), 1.65 – 1.55 (m, 5H), 1.53 (d, *J* = 7.0 Hz, 3H), 1.22 – 1.16 (m, 1H), 1.13 – 1.03 (m, 3H), 0.92 – 0.80 (m, 2H).

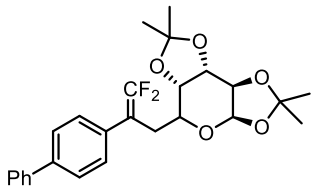
^{13}C NMR (151 MHz, $CDCl_3$) δ 191.42, 171.49, 153.91 (dd, *J* = 290.4, 286.3 Hz), 143.16, 140.09, 138.23, 137.82, 136.04, 135.01 (dd, *J* = 7.3, 3.0 Hz), 133.60, 132.61, 131.89, 131.49, 130.83, 128.89,

128.71, 126.88, 126.22, 124.35 (d, *J* = 2.7 Hz), 119.56 (t, *J* = 2.9 Hz), 118.64, 90.85 (dd, *J* = 22.0, 12.9 Hz), 51.00, 47.73, 35.61, 35.15, 32.78, 26.35, 25.98, 18.88.

^{19}F NMR (564 MHz, $CDCl_3$) δ -91.03 (d, *J* = 43.2 Hz, 1F), -91.23 (d, *J* = 43.0 Hz, 1F).

HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{32}H_{32}F_2NO_2S^+$, 532.2116; found: 532.2122.

(3*aR*,5*aS*,8*aS*,8*bR*)-5-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (56)



The substrate was prepared following the general procedure B using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), diethyl 2,6-dimethyl-4-((3*aR*,5*aS*,8*aS*,8*bR*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)-1,4-dihydropyridine-3,5-dicarboxylate (48.1 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **56** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a white solid (23.9 mg, 52%).

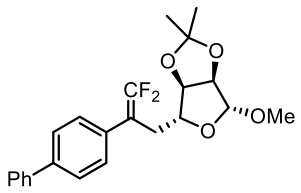
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 4H), 7.49 – 7.32 (m, 5H), 5.02 (d, *J* = 2.4 Hz, 1H), 4.49 (d, *J* = 5.3 Hz, 1H), 4.13 (d, *J* = 2.0 Hz, 1H), 3.93 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.14 (td, *J* = 9.4, 3.0 Hz, 1H), 2.90 – 2.82 (m, 1H), 2.63 – 2.56 (m, 1H), 1.52 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.36 (dd, *J* = 290.7, 288.0 Hz), 140.51, 140.03, 132.12 (t, *J* = 3.9 Hz), 128.78, 128.73 (t, *J* = 3.3 Hz), 127.39, 127.02, 126.98, 110.79, 108.79, 96.77 (d, *J* = 3.3 Hz), 88.70 (dd, *J* = 21.6, 15.0 Hz), 75.77, 74.29, 73.60, 70.54 (t, *J* = 2.2 Hz), 30.40 (d, *J* = 1.3 Hz), 27.90, 27.78, 25.95, 25.78.

^{19}F NMR (564 MHz, $CDCl_3$) δ -88.90 (d, *J* = 39.7 Hz, 1F), -89.58 (d, *J* = 39.6 Hz, 1F).

HRMS (ESI) (m/z): $[M+Na]^+$ Calcd for $C_{26}H_{28}F_2NaO_5^+$, 481.1797; found: 481.1796.

(3*aR*,4R,6*R*,6a*R*)-4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (57)[14]



The substrate was prepared following the general procedure B using **S1** (37.3 mg, 0.15 mmol, 1.5 equiv.), diethyl 4-((3*aR*,6*R*,6*aR*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (42.5 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (1.3

mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), anhydrous DMF (1 mL). The product **57** was isolated using flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) as a white solid (34.9 mg, 87%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 4H), 7.48 – 7.33 (m, 5H), 4.95 (s, 1H), 4.65 (d, *J* = 5.9 Hz, 1H), 4.57 (d, *J* = 5.9 Hz, 1H), 4.18 (t, *J* = 7.7 Hz, 1H), 3.35 (s, 3H), 2.81 – 2.64 (m, 2H), 1.42 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.32 (dd, *J* = 291.0, 288.3 Hz), 140.48, 140.42, 131.54 (dd, *J* = 4.0, 3.4 Hz), 128.86 – 128.78 (m), 127.44, 127.34, 127.02, 112.32, 109.93 (d, *J* = 1.5 Hz), 89.32 (dd, *J* = 21.2, 15.4 Hz), 85.58, 84.48 (t, *J* = 2.8 Hz), 83.54, 55.11, 33.28, 26.38, 24.90. (one carbon signal was overlapped).

^{19}F NMR (564 MHz, $CDCl_3$) δ -89.50 (d, *J* = 39.8 Hz, 1F), -90.06 (d, *J* = 39.8 Hz, 1F).

Crystals suitable for X-ray diffraction were prepared by recrystallization from petroleum ether and ethyl acetate at room temperature.

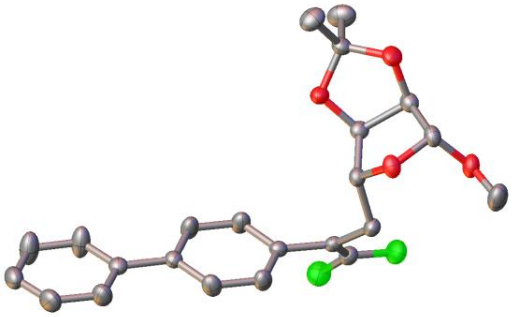


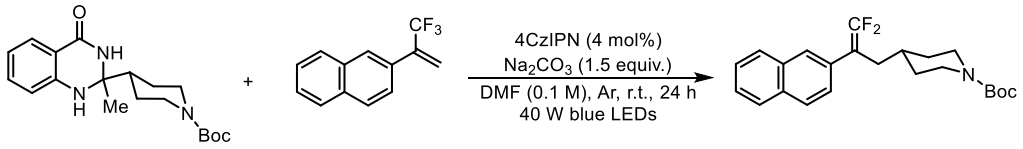
Figure S2 Crystal data and structure refinement for (3*aR*,4R,6*R*,6a*R*)-4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole

Empirical formula	$C_{23}H_{24}F_2O_4$	
Formula weight	402.42	
Temperature	248 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.97500(10) Å	α= 90°.
	b = 16.6014(4) Å	β= 90°.
	c = 20.4417(5) Å	γ = 90°.
Volume	2027.68(8) $Å^3$	
Z	4	
Density (calculated)	1.318 Mg/m^3	
Absorption coefficient	0.540 mm^{-1}	
F (000)	848	
Crystal size	0.07 x 0.07 x 0.05 mm^3	

Theta range for data collection	2.983 to 55.122°.
Index ranges	-6<=h<=7, -20<=k<=19, -24<=l<=24
Reflections collected	23095
Independent reflections	3868 [R(int) = 0.0414]
Completeness to theta = 53.594°	99.9 %
Absorption correction	Semi-empirical from eq.alents
Max. and min. transmission	0.7508 and 0.6240
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3868 / 0 / 265
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0984
R indices (all data)	R1 = 0.0544, wR2 = 0.1060
Absolute structure parameter	0.07(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.135 and -0.208 e.$Å^{-3}$

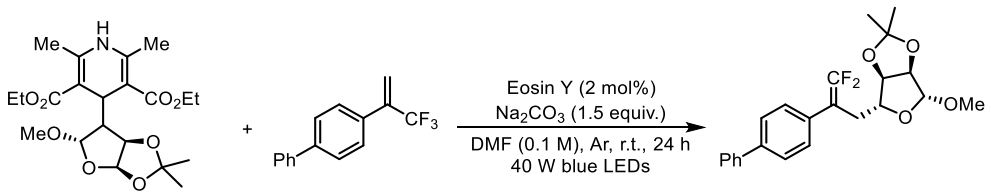
5. Scaling-up Reaction

A. Synthesis of *tert*-butyl 4-(3,3-difluoro-2-(naphthalen-2-yl)allyl)piperidine-1-carboxylate



Tert-butyl 4-(2-methyl-4-oxo-1,2,3,4-tetrahydroquinazolin-2-yl)piperidine-1-carboxylate (5 mmol, 1.0 equiv.), 4CzIPN (4 mol%), Na_2CO_3 (7.5 mmol, 1.5 equiv.) were added in a 100 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times), 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (7.5 mmol, 1.5 equiv.) and anhydrous DMF (50 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40 W blue LEDs, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 24 h, ethyl acetate (100 mL) was added to the reaction mixture. The resulting solution was washed with brine (3 × 50 mL) and dried over anhydrous Na_2SO_4. The organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product (white solid, 1.59 g, 82%, petroleum ether/ethyl acetate = 20:1).

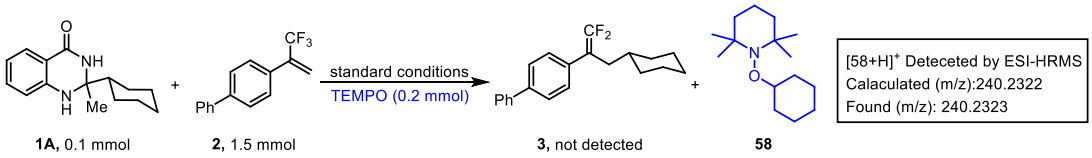
B. Synthesis of (3*aR*,4*R*,6*R*,6*aR*)-4-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole



Diethyl 4-((3*aR*,5*S*,6*aR*)-5-methoxy-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (4 mmol, 1.0 equiv.), 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (1.5 equiv., 6 mmol), Eosin Y (2 mol%), Na_2CO_3 (6 mmol, 1.5 equiv.) were added in a 100 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times), and anhydrous DMF (40 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40 W blue LEDs, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 24 h, ethyl acetate (80 mL) was added to the reaction mixture. The resulting solution was washed with brine (3 × 40 mL) and dried over anhydrous Na_2SO_4. The organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product (white solid, 1.0 g, 62%, petroleum ether/ethyl acetate = 20:1).

6. Preliminary Mechanistic Studies

6.1. Radical Trap Experiment



1A, 0.1 mmol **2**, 1.5 mmol **3**, not detected **58**

2-cyclohexyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24.4 mg, 0.1 mmol, 1.0 equiv.), 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-bipheny (37.3 mg, 0.15 mmol, 1.5 equiv.), 4CzIPN (1.6 mg, 2 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.), TEMPO (0.2 mmol) were added in a 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times), and anhydrous DMF (1 mL) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40 W blue LEDs, maintained at approximately room temperature in the air-conditioned room of 25 ℃ for 24 h. The reaction mixture was sent for HRMS analysis, the compounds **58** were detected by HRMS.

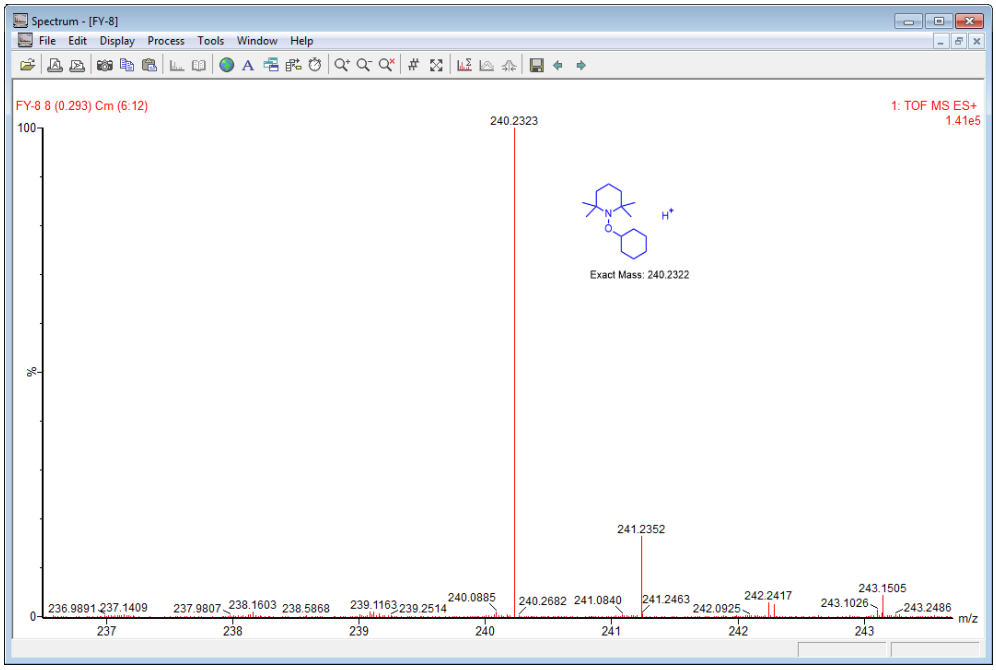
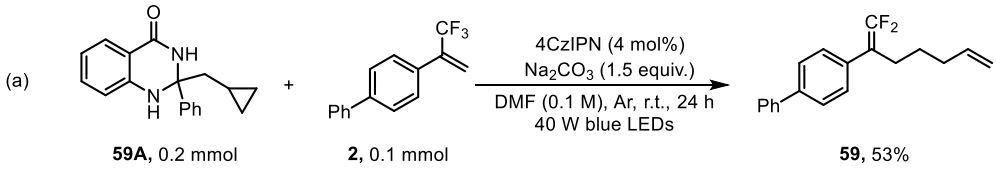


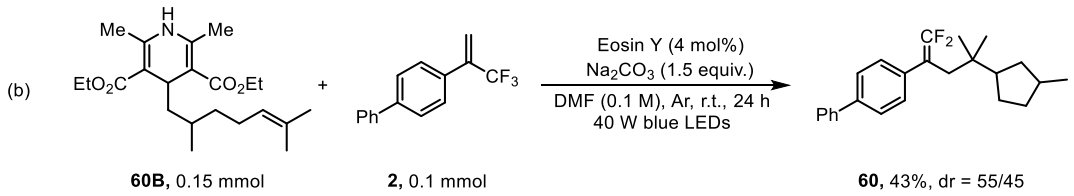
Figure S3 Radical trapping experiment

6.2. Radical Clock Experiment



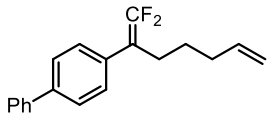
59A, 0.2 mmol **2**, 0.1 mmol **59**, 53%

2-(cyclopropylmethyl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (55.6 mg, 0.2 mmol, 2.0 equiv.), 4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (24.8 mg, 0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.) were added in a 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times), and anhydrous DMF (1 mL) was added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40 W blue LEDs, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 24 h, ethyl acetate (5 mL) was added to the reaction mixture. The resulting solution was washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. The organic layers were combined and concentrated on rotary evaporator. The residue was purified by flash column chromatography on silica gel (colorless oil, 15.1 mg, 53%, petroleum ether).



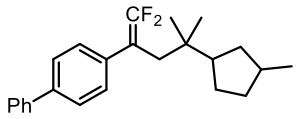
4-(3,3,3-trifluoroprop-1-en-2-yl)-1,1'-biphenyl (24.8 mg, 0.1 mmol, 1.0 equiv.), Eosin Y (2.6 mg, 4 mol%), Na_2CO_3 (15.9 mg, 0.15 mmol, 1.5 equiv.) were added in a 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times), then anhydrous DMF (1 mL) and diethyl 4-(2,6-dimethylhept-5-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (56.6 mg, 0.15 mmol, 1.5 equiv.) were added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40 W blue LEDs, maintained at approximately room temperature in the air-conditioned room of 25 ℃. After 24 h, ethyl acetate (5 mL) was added to the reaction mixture. The resulting solution was washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. The organic layers were combined and concentrated on rotary evaporator. The residue was purified by flash column chromatography on silica gel (colorless oil, 15.2 mg, 43%, petroleum ether).

4-(1,1-difluorohepta-1,6-dien-2-yl)-1,1'-biphenyl (59)[14]



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 4H), 7.47 – 7.38 (m, 4H), 7.37 – 7.34 (m, 1H), 5.84 – 5.72 (m, 1H), 5.05 – 4.94 (m, 2H), 2.48 – 2.43 (m, 2H), 2.12 – 2.05 (m, 2H), 1.55 – 1.48 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 153.65 (dd, J = 290.3, 287.3 Hz), 140.55, 139.98, 138.08, 132.70 – 132.57 (m), 128.78, 128.55 (t, J = 3.4 Hz), 127.36, 127.09, 126.99, 114.95, 91.92 (dd, J = 21.1, 13.5 Hz), 33.08, 27.01 (t, J = 2.4 Hz), 26.96.
^{19}F NMR (564 MHz, $CDCl_3$) δ -91.05 (d, *J* = 43.0 Hz, 1F), -91.18 (d, *J* = 43.1 Hz, 1F).

4-(1,1-difluoro-4-methyl-4-(3-methylcyclopentyl)pent-1-en-2-yl)-1,1'-biphenyl (60)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 4H), 7.46 – 7.33 (m, 5H), 2.37 (d, *J* = 2.2 Hz, 2H), 1.91 – 1.64 (m, 4H), 1.61 – 1.46 (m, 2H), 1.30 – 1.19 (m, 1H), 1.11 – 0.98 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 1.3H), 0.89 (d, *J* = 6.7 Hz, 1.7H), 0.71 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.38 – 152.14 (m), 140.60, 140.57, 139.65, 139.61, 134.86 – 134.77 (m), 128.83 (dd, *J* = 6.0, 2.9 Hz), 128.76, 127.30, 126.97, 126.96, 126.87, 126.85, 90.63 (dd, *J* = 21.6, 12.9 Hz), 50.37, 48.57, 38.48, 38.43, 37.27 (t, *J* = 2.2 Hz), 37.09 (t, *J* = 2.2 Hz), 36.77, 35.25, 34.90, 34.61, 34.10, 33.96, 27.70, 26.01, 24.62, 24.56, 24.33, 24.23, 21.10, 20.57.

^{19}F NMR (564 MHz, $CDCl_3$) δ -85.16 (d, *J* = 40.6 Hz), -87.46 (dd, *J* = 40.6, 17.8 Hz).

HRMS (ESI) (m/z): [M+Na]+ Calcd for $C_{24}H_{28}F_2Na^+$, 377.2051; Found 377.2056.

6.3 Light On-Off Experiments

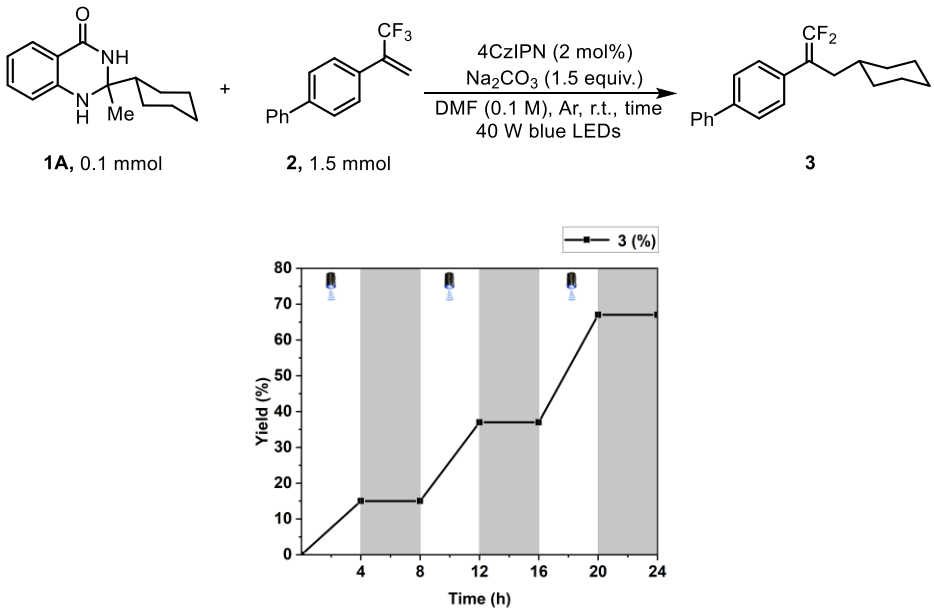


Figure S4 Light on-off experiments

To examine the impact of light, we conducted experiments under alternating periods of irradiation and darkness. These resulted in a total interruption of the reaction progress in the absence of light and recuperation of reactivity on further illumination, which allows precise temporal control over the entire reaction period. These results demonstrated that light is a necessary component of the reaction.

7. References

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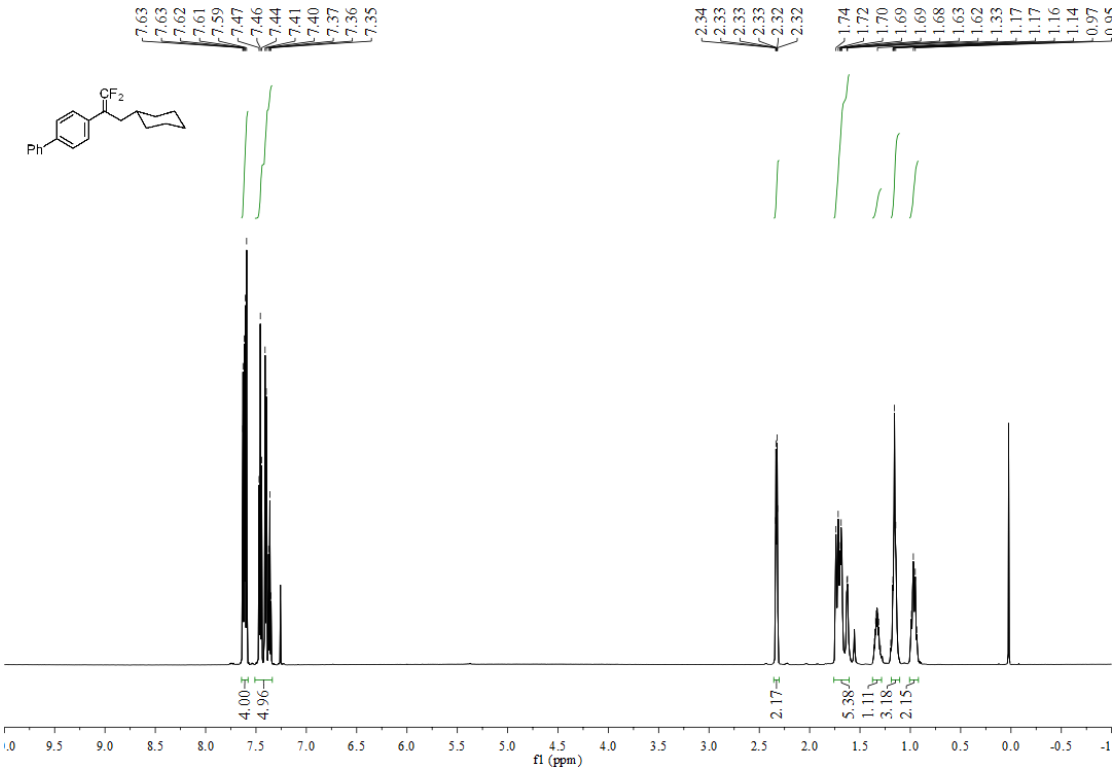
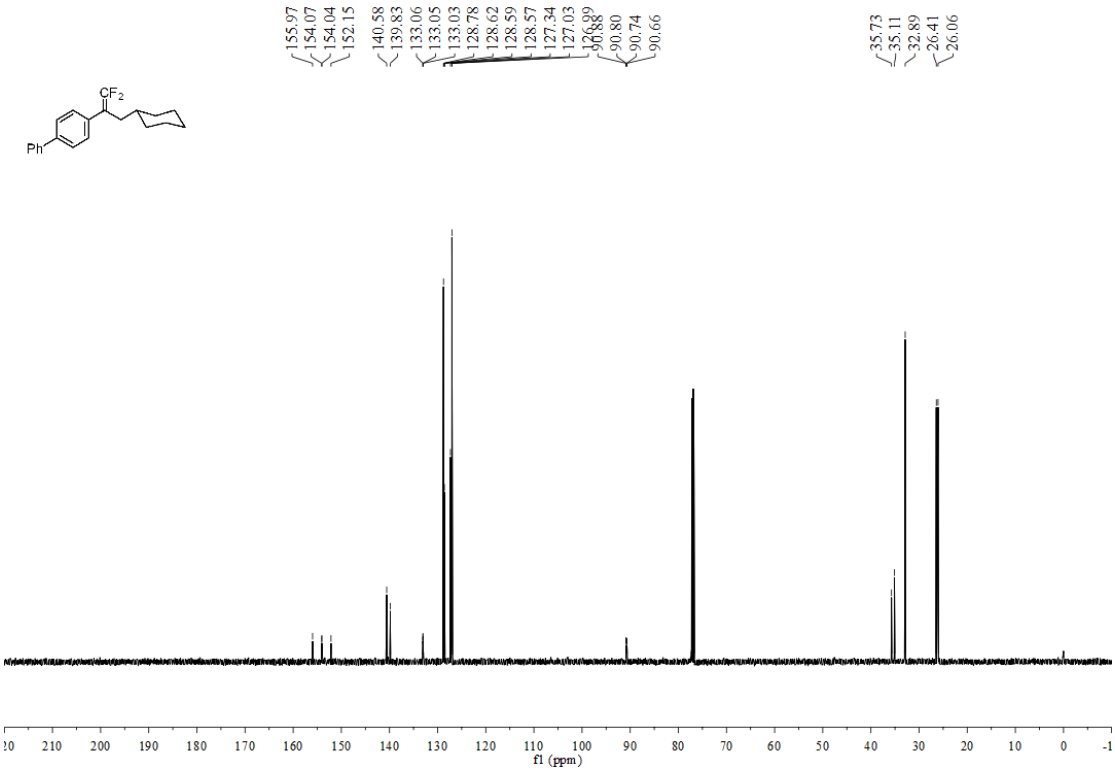
8. NMR Spectra

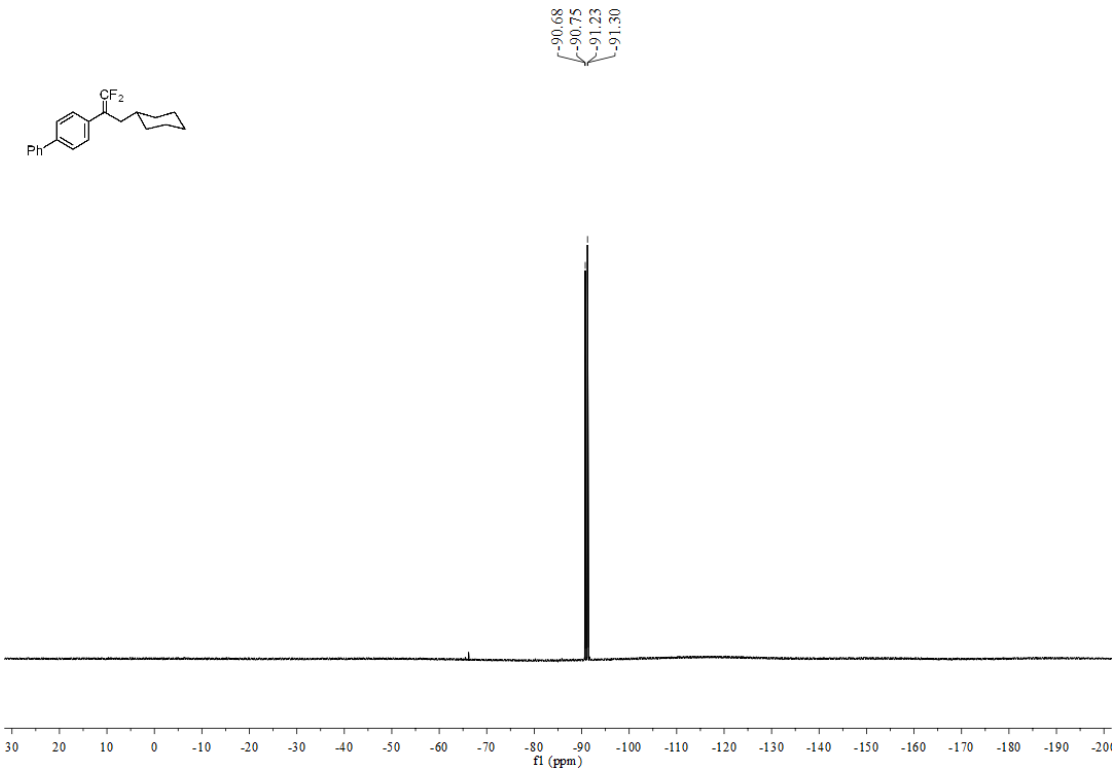
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 3



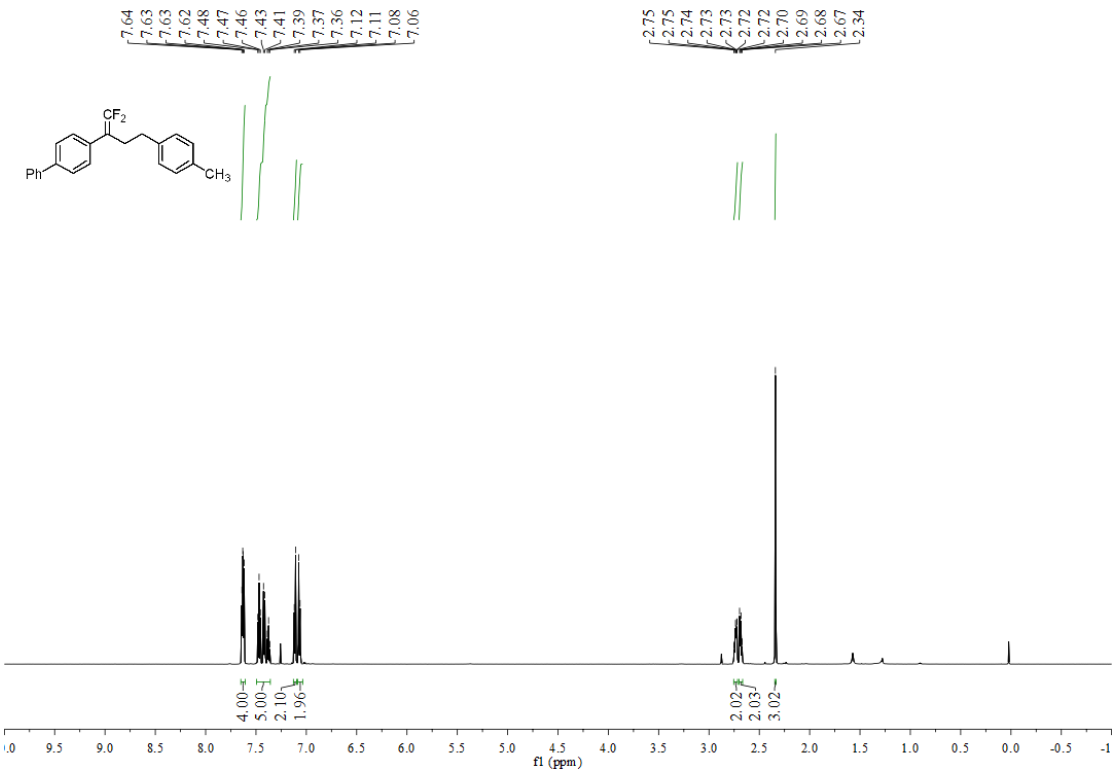
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 3



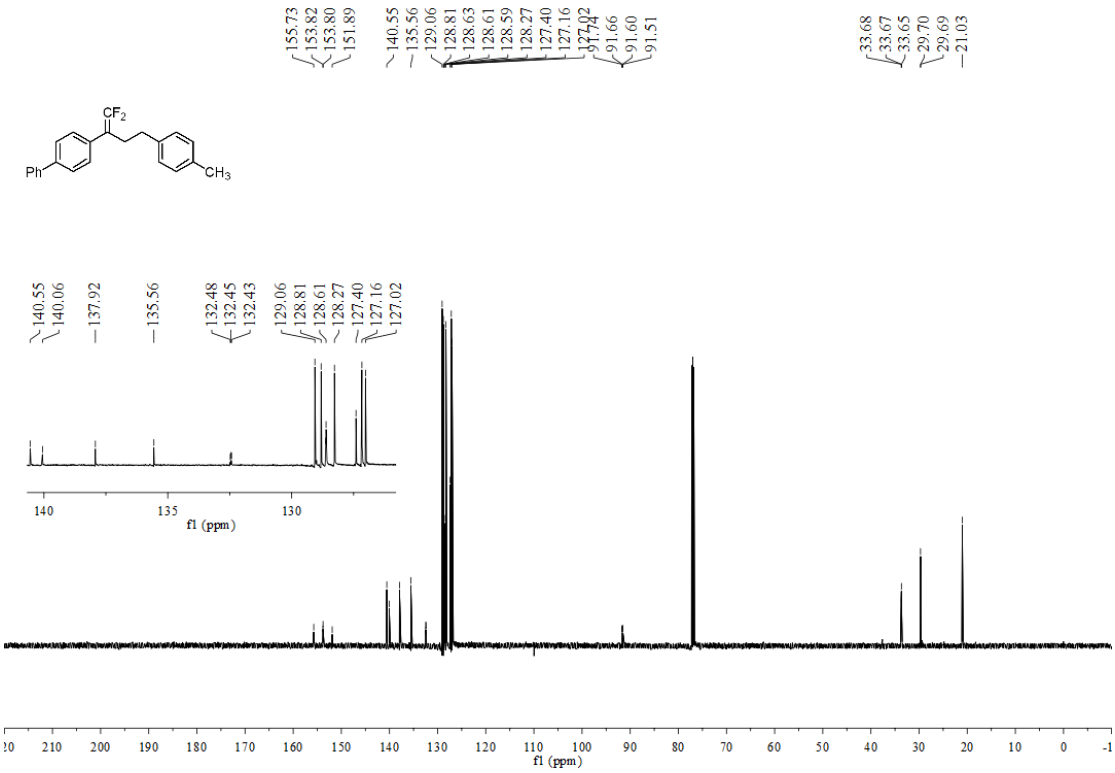
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 3



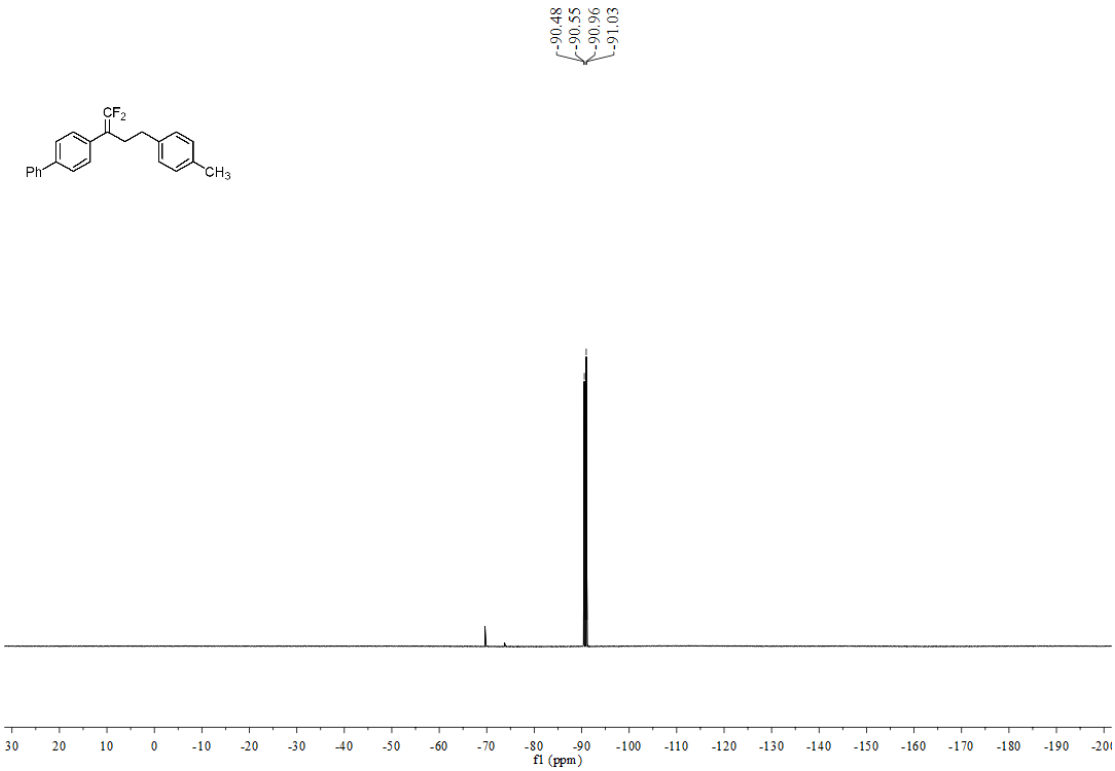
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 4



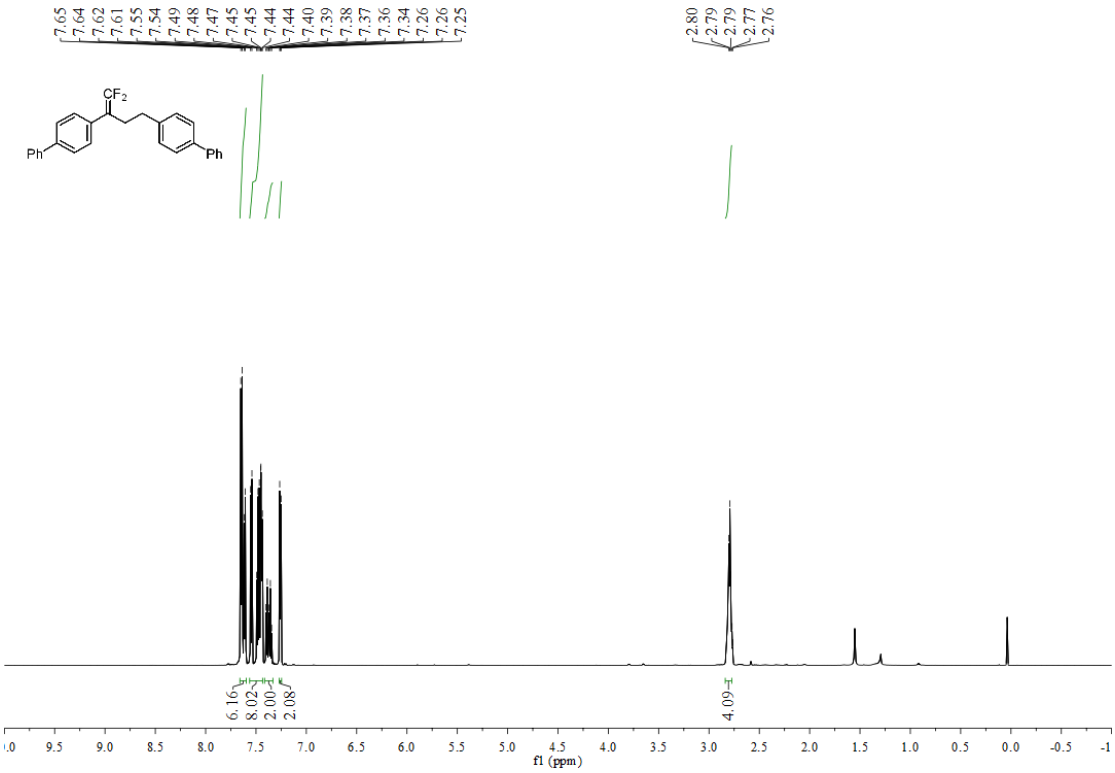
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 4



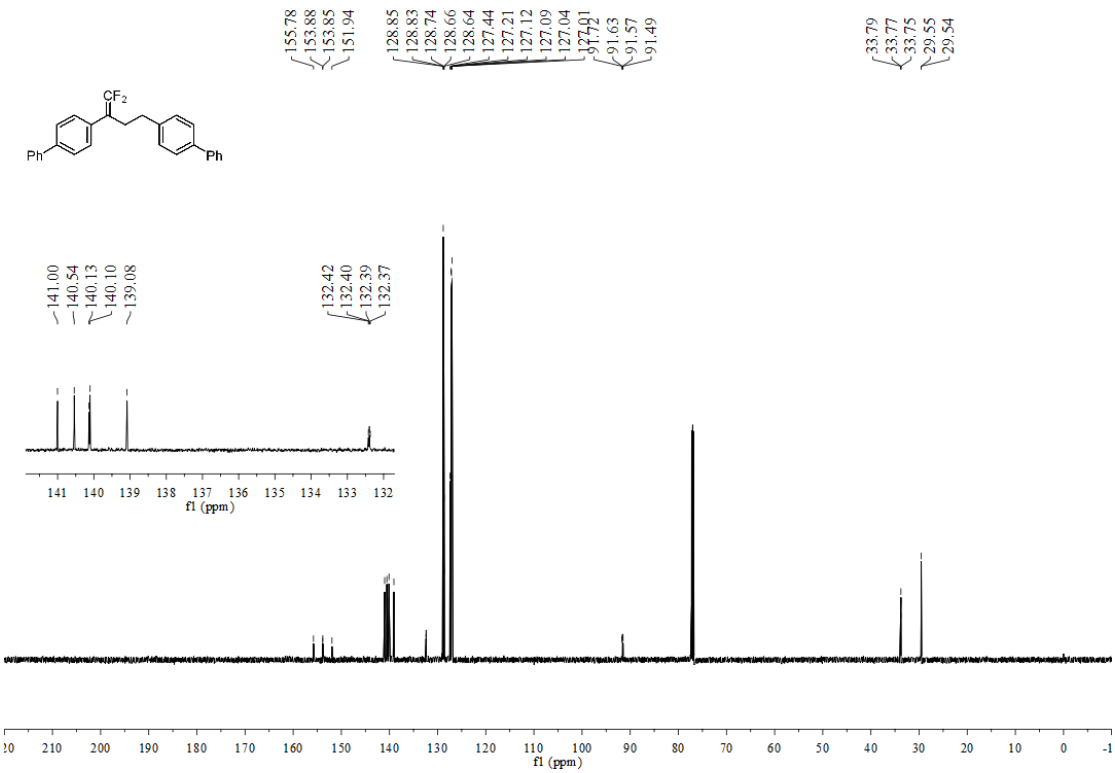
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 4



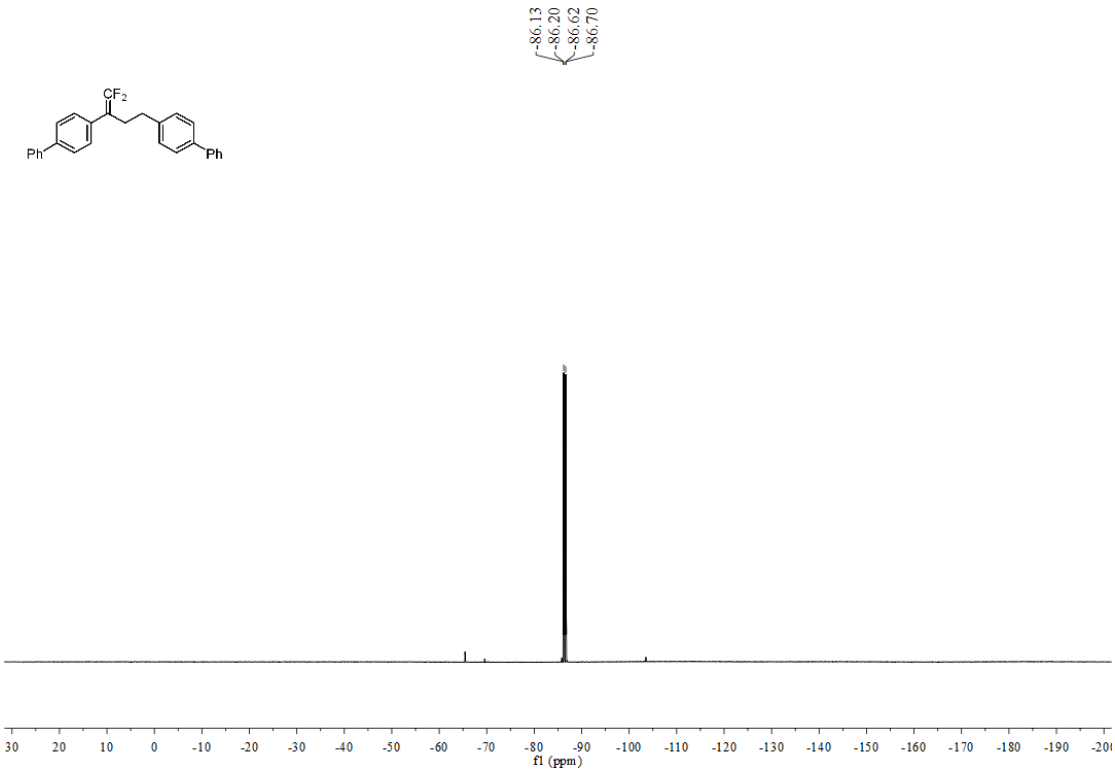
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 5



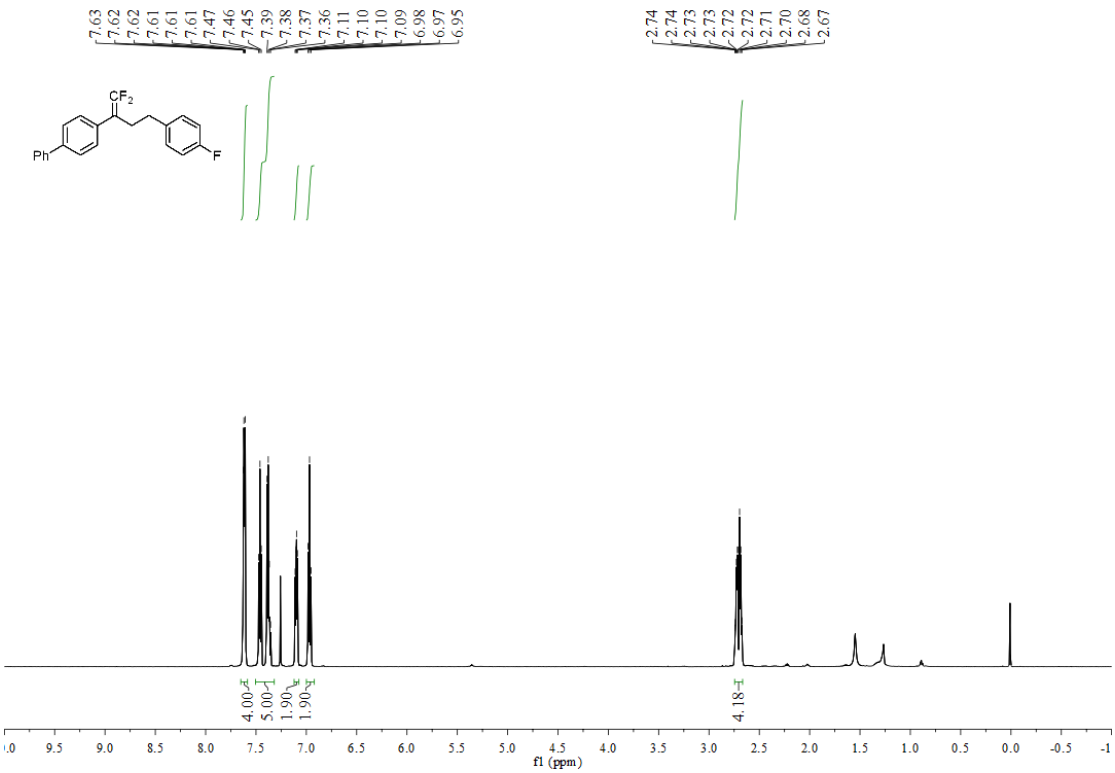
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 5



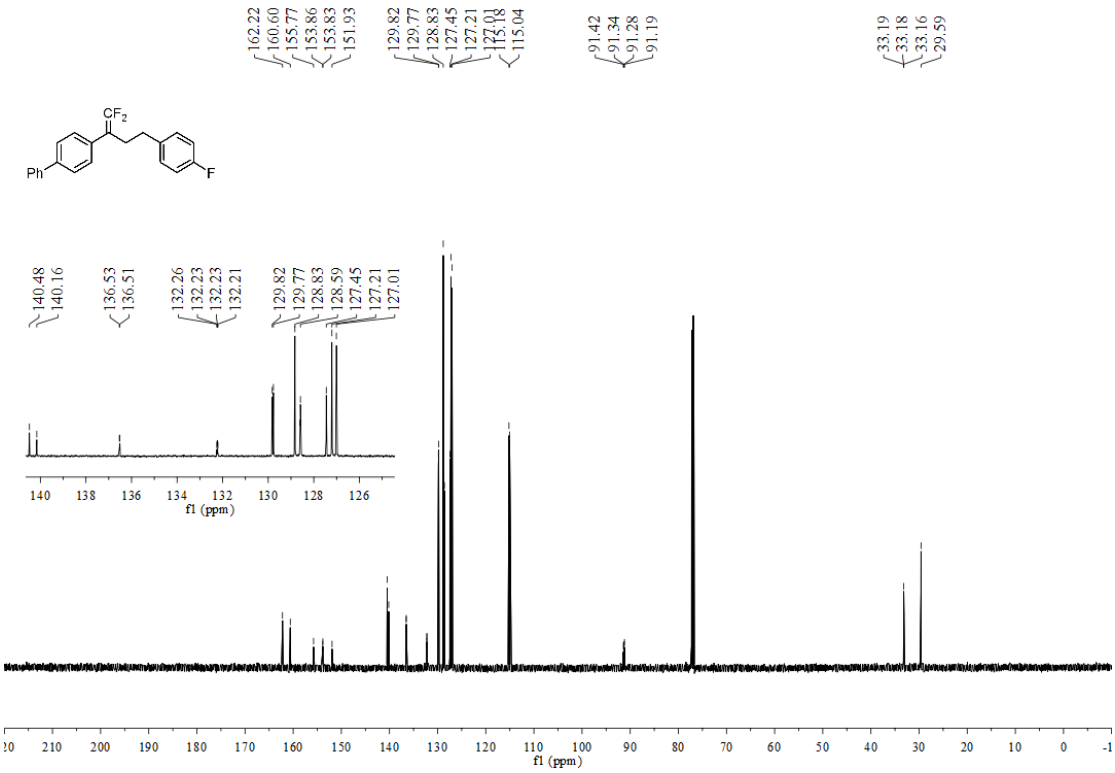
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 5



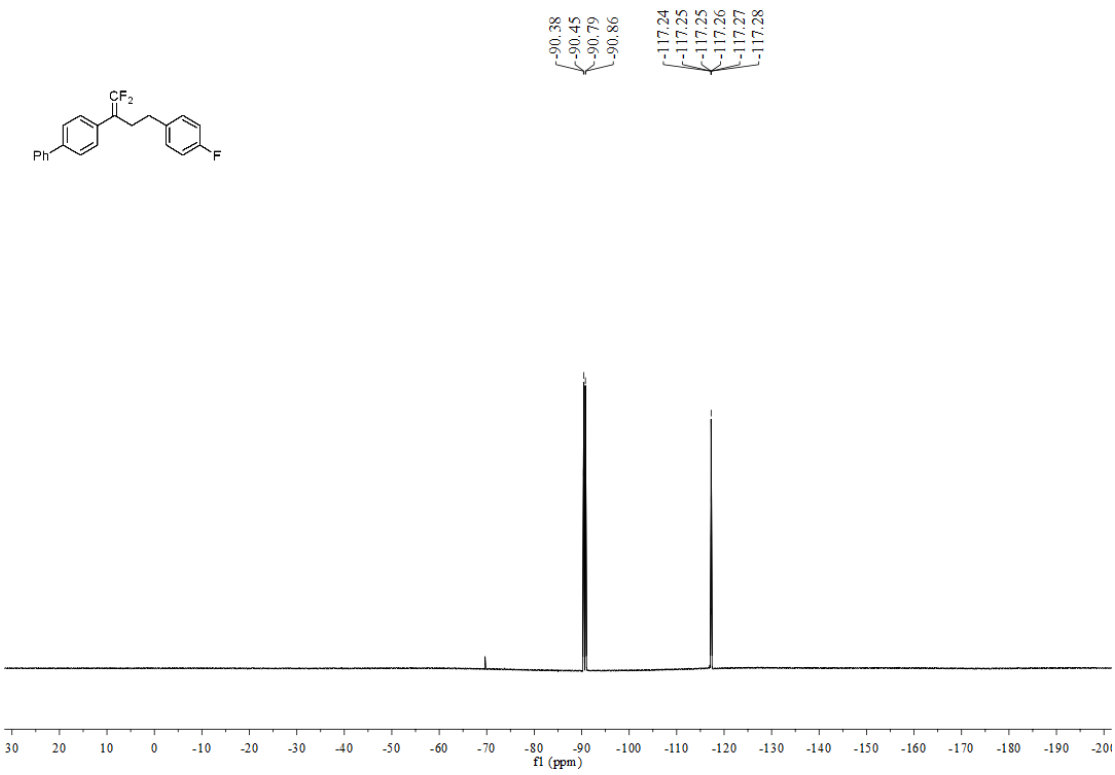
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 6



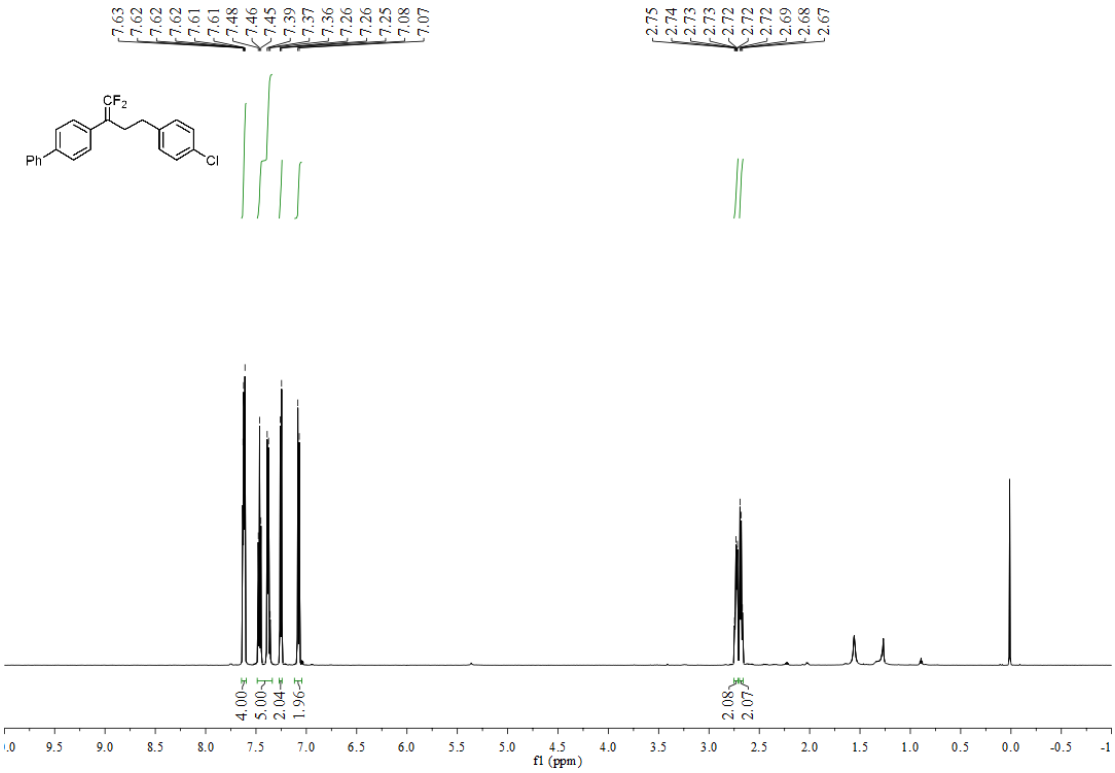
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 6



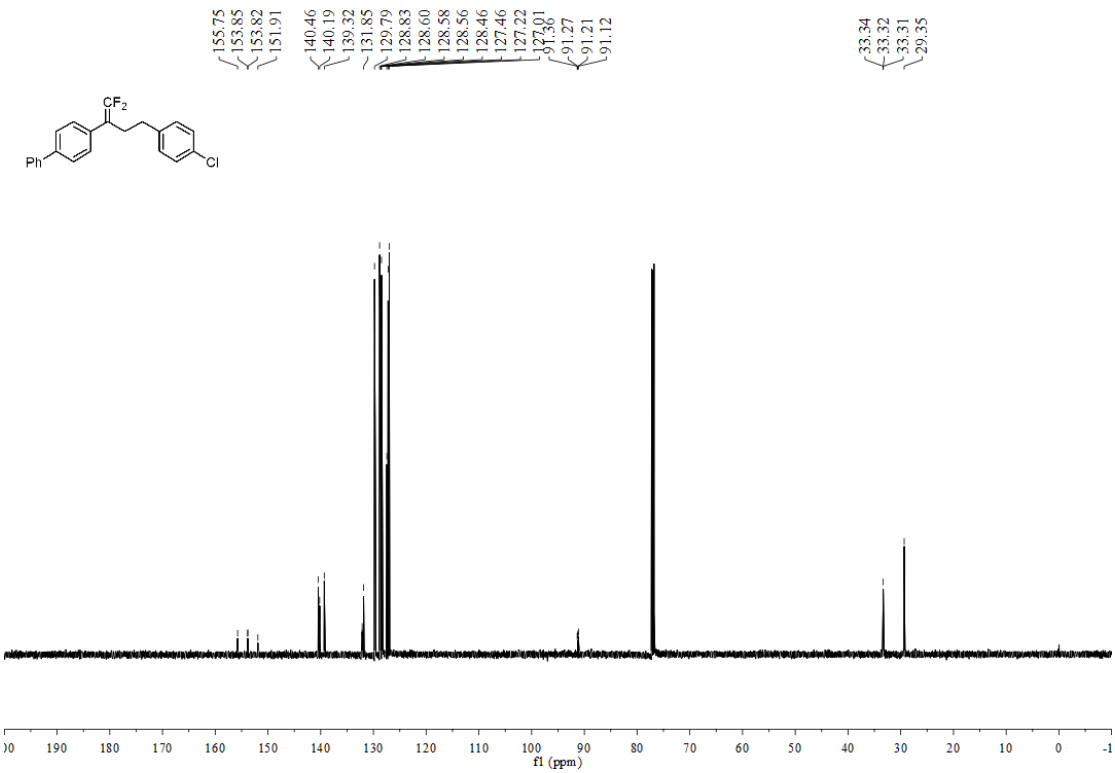
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 6



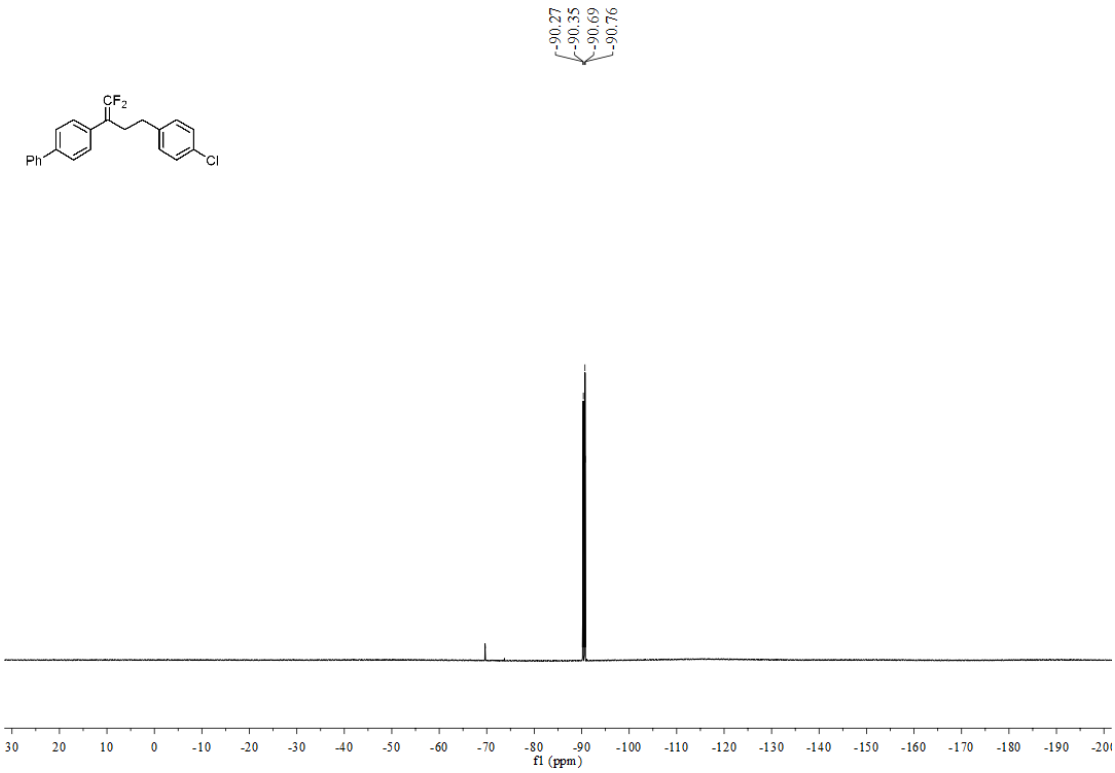
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 7



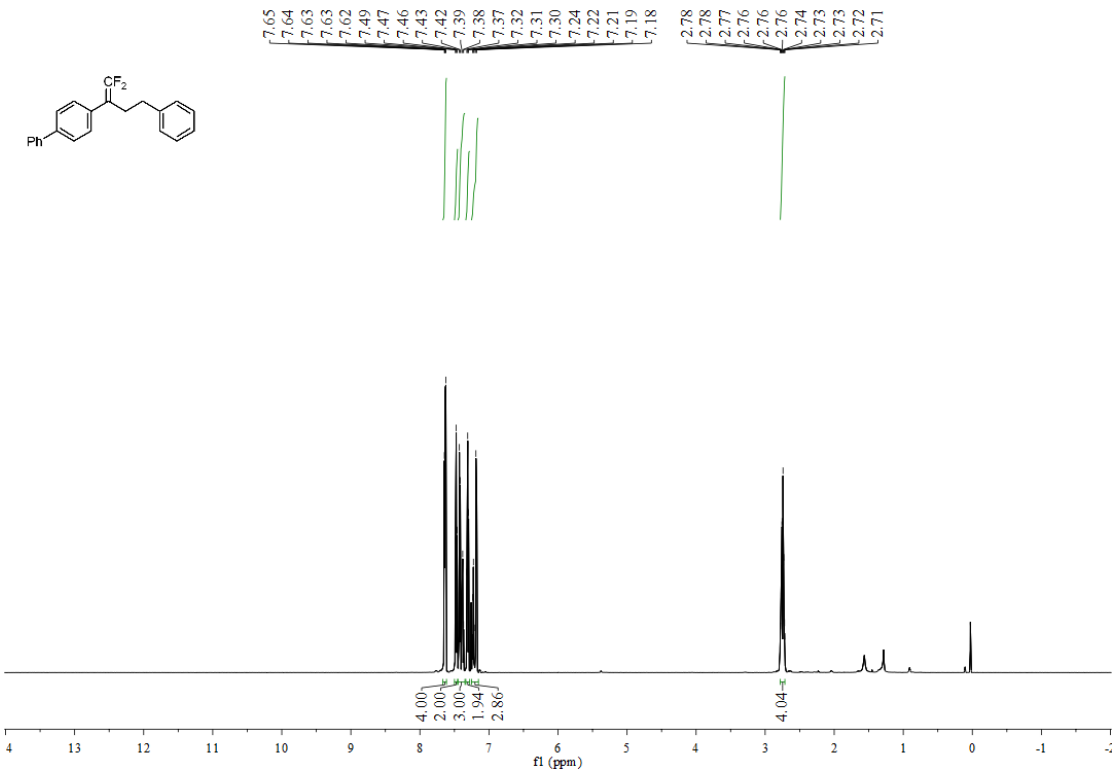
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 7



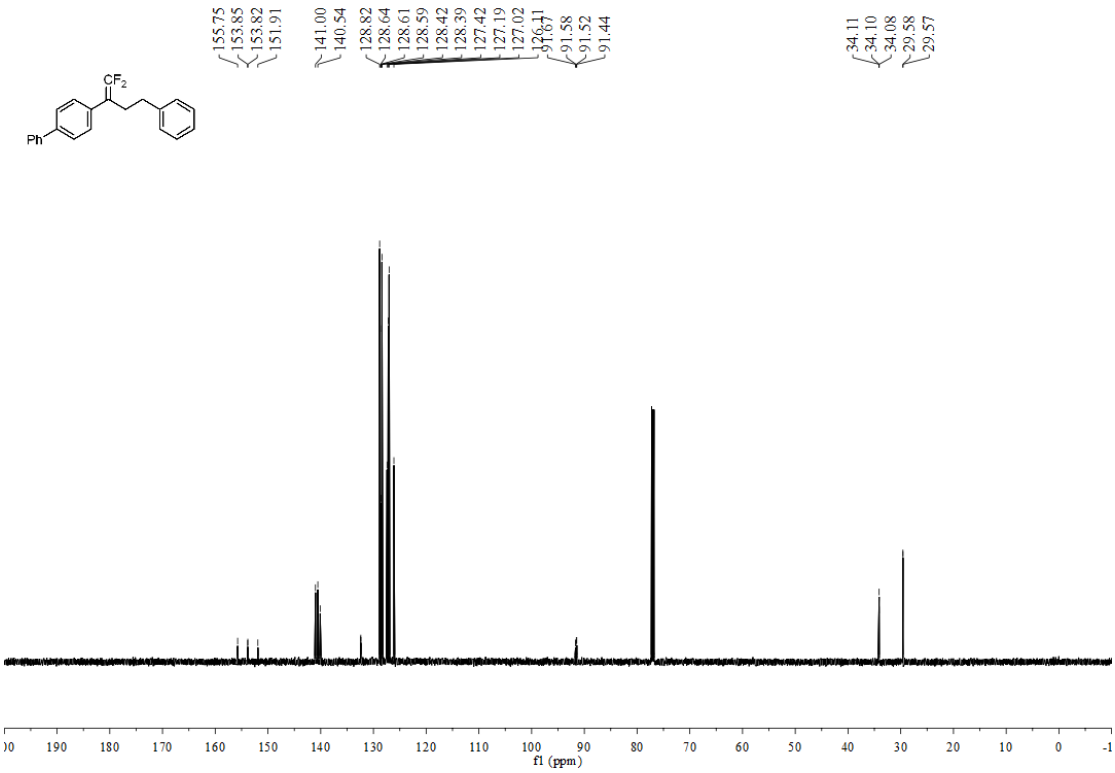
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 7



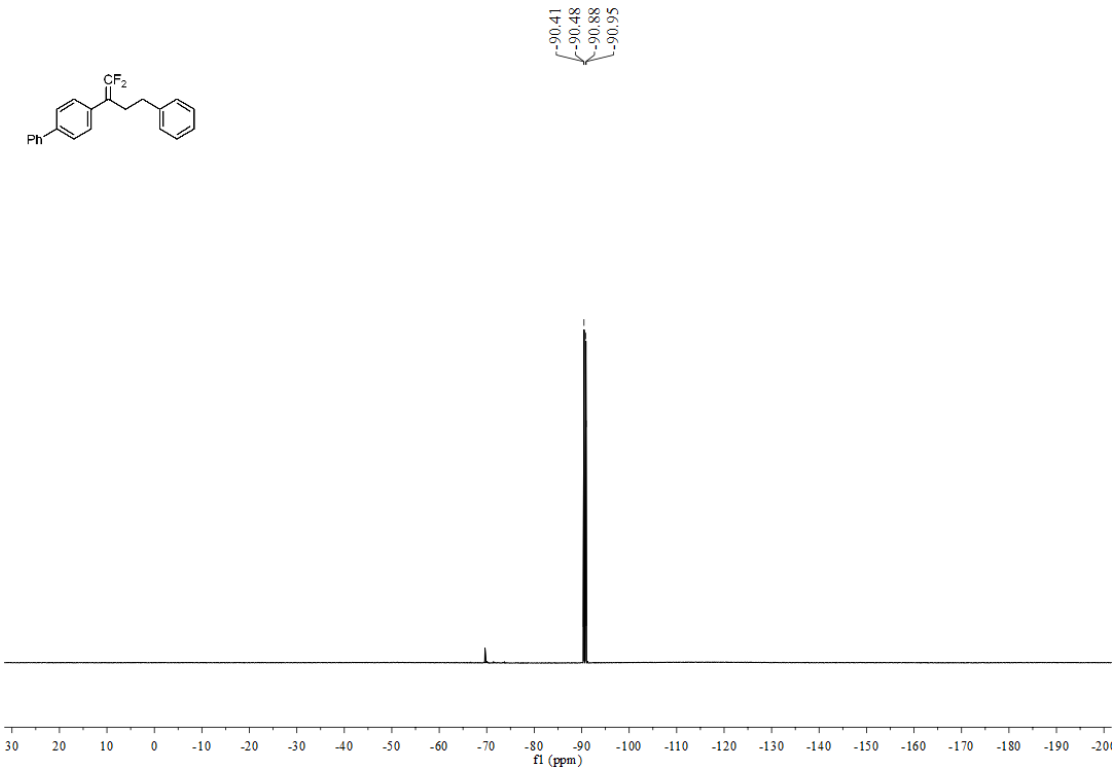
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 8



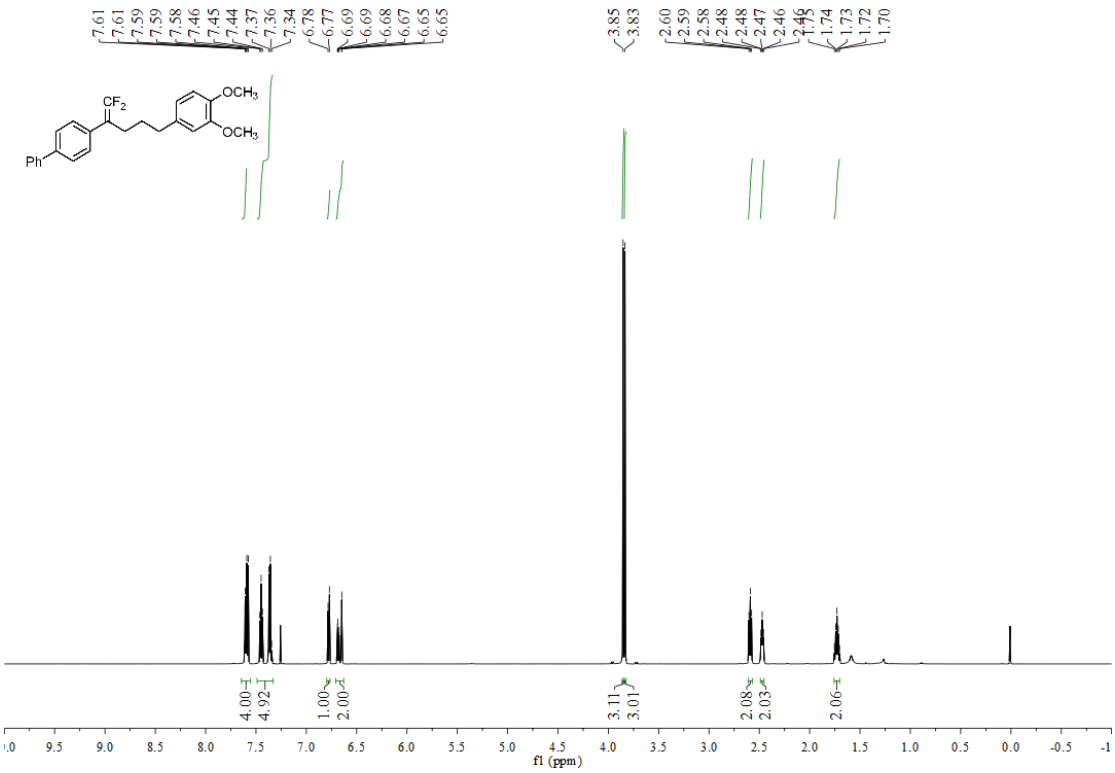
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 8



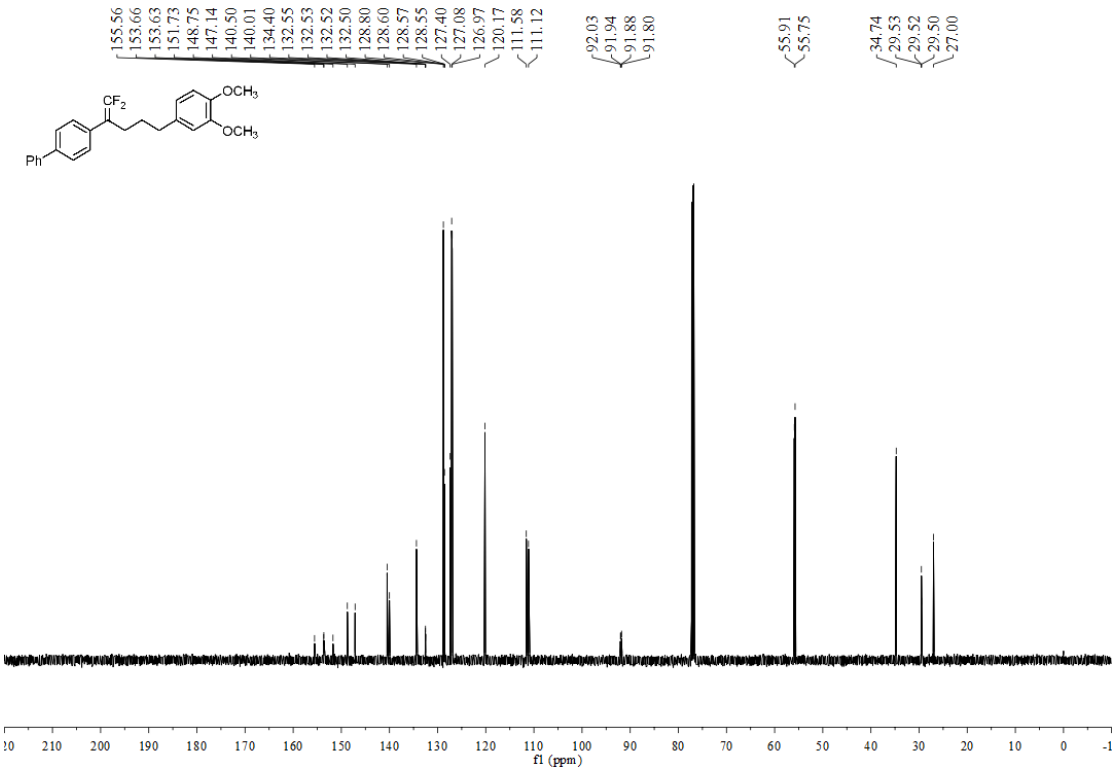
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 8



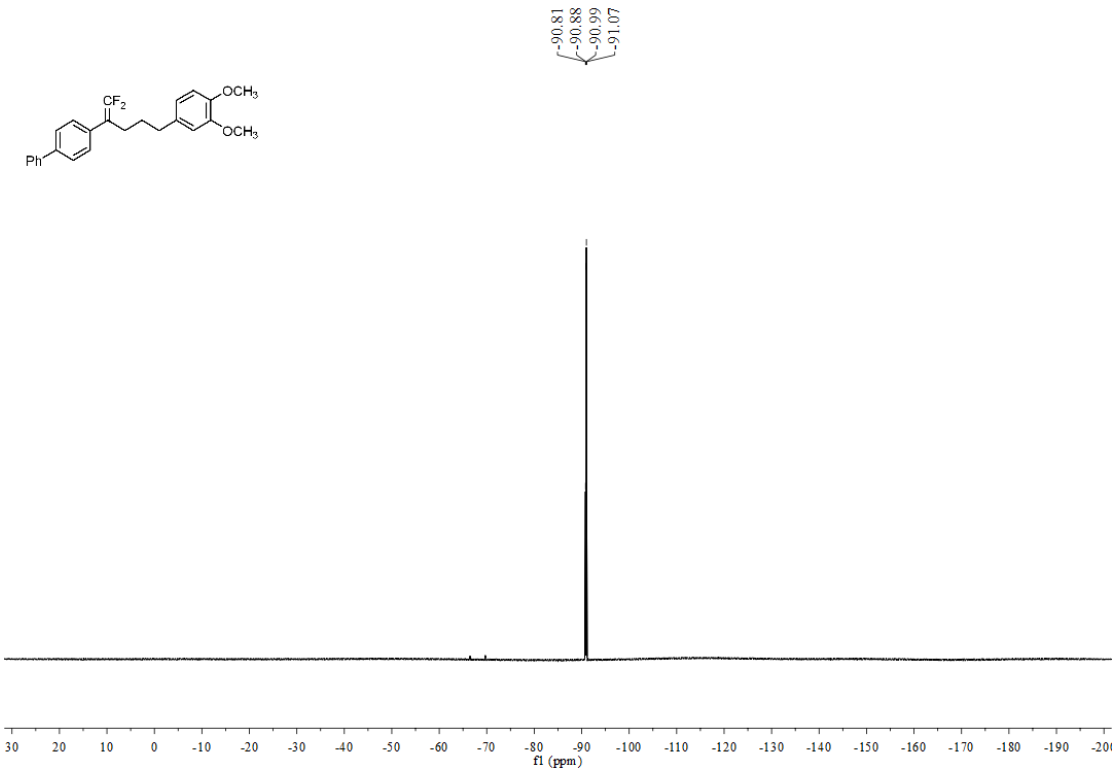
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 9



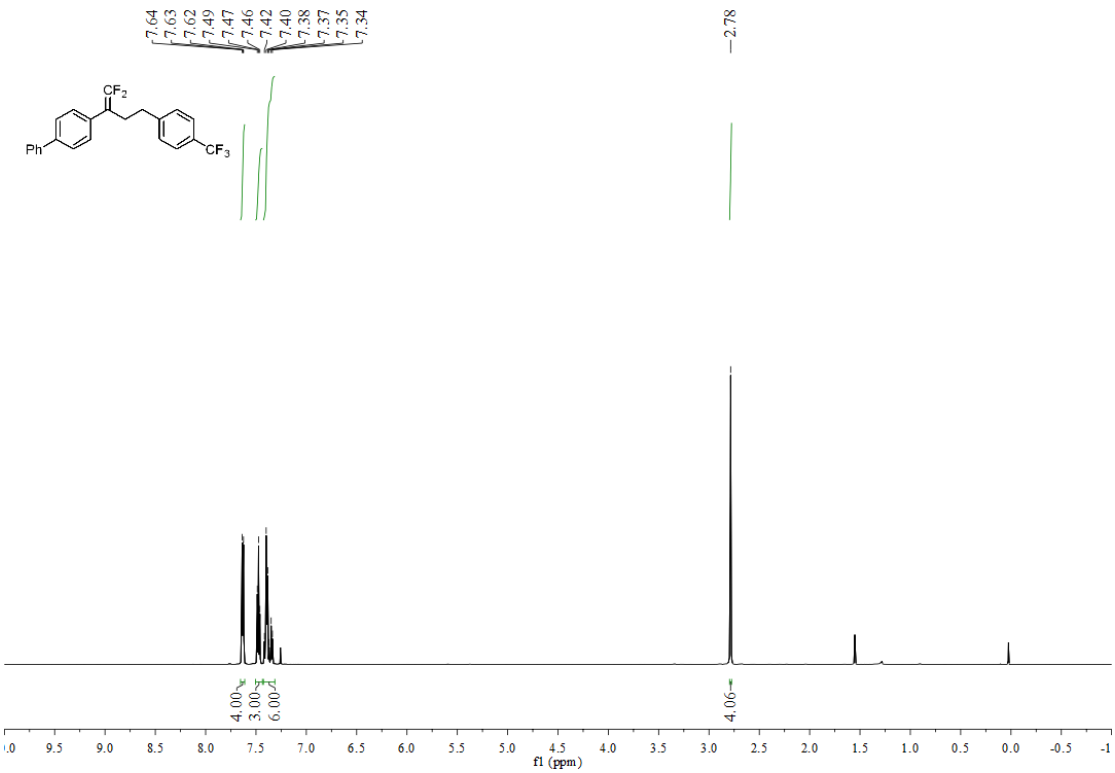
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 9



^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 9



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 10



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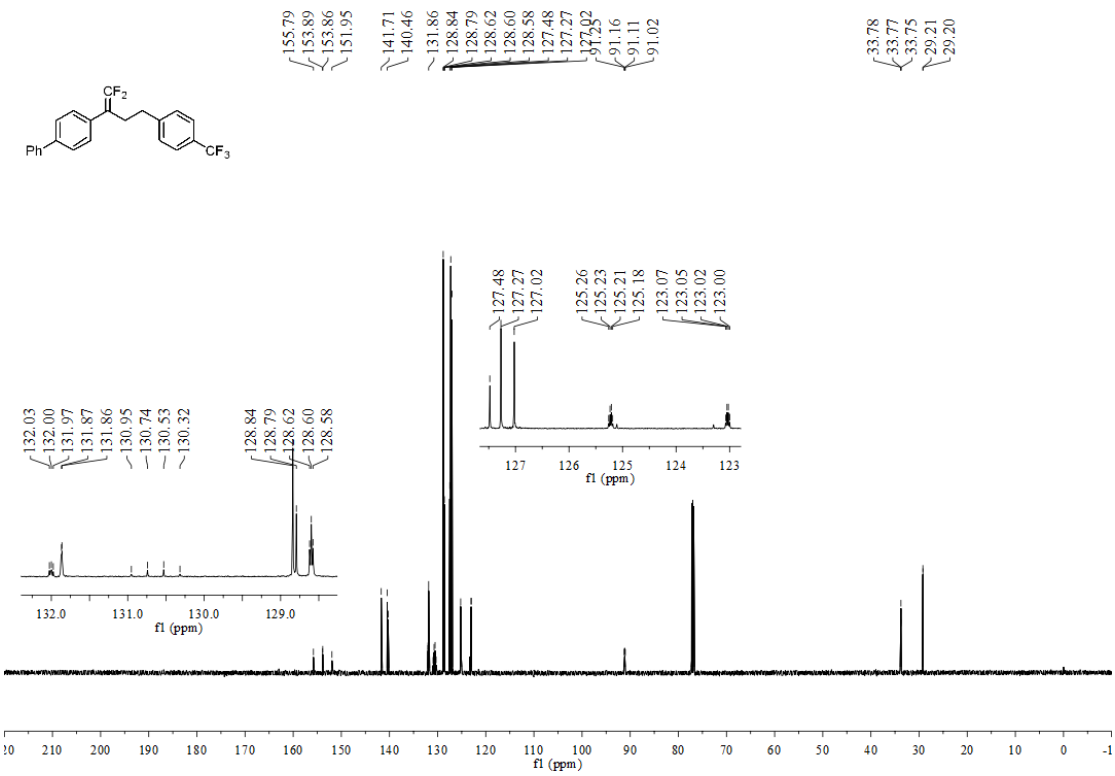
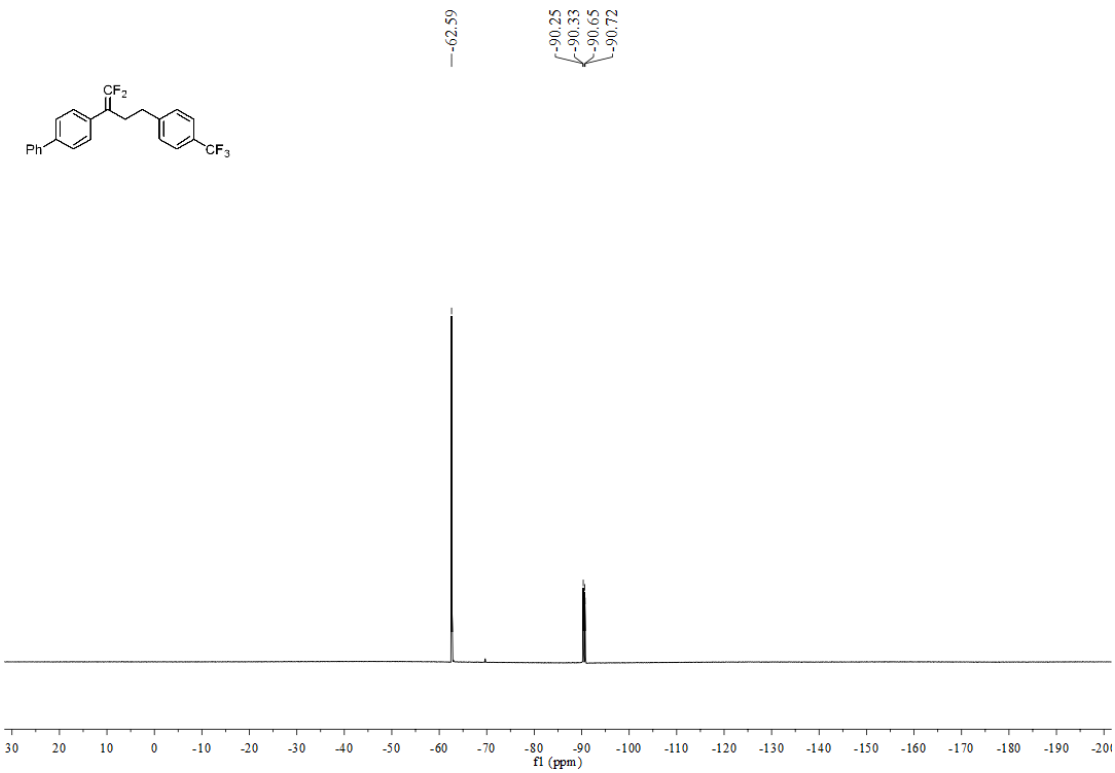
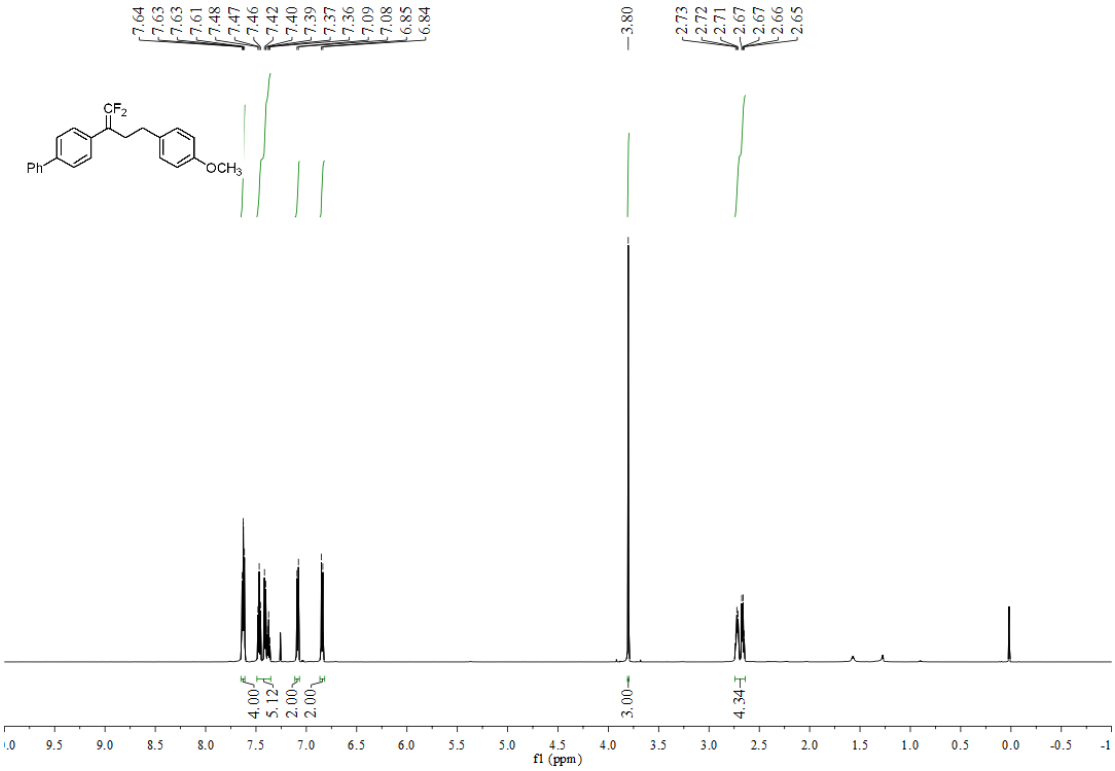


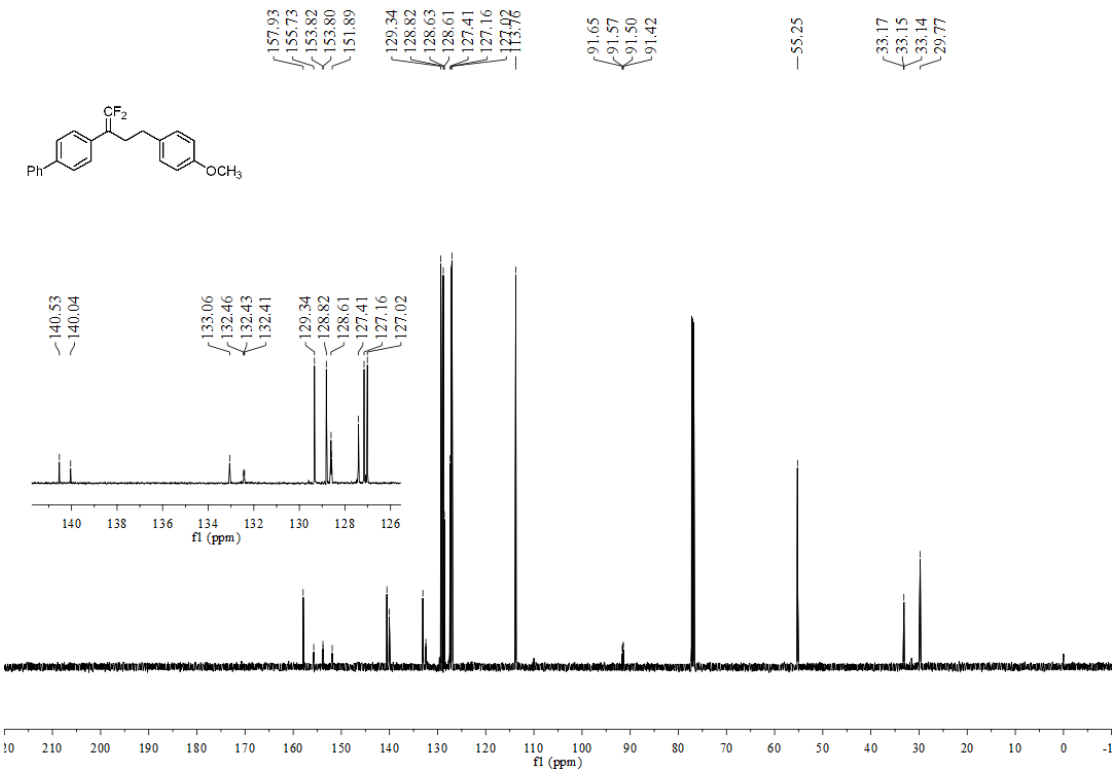
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 10



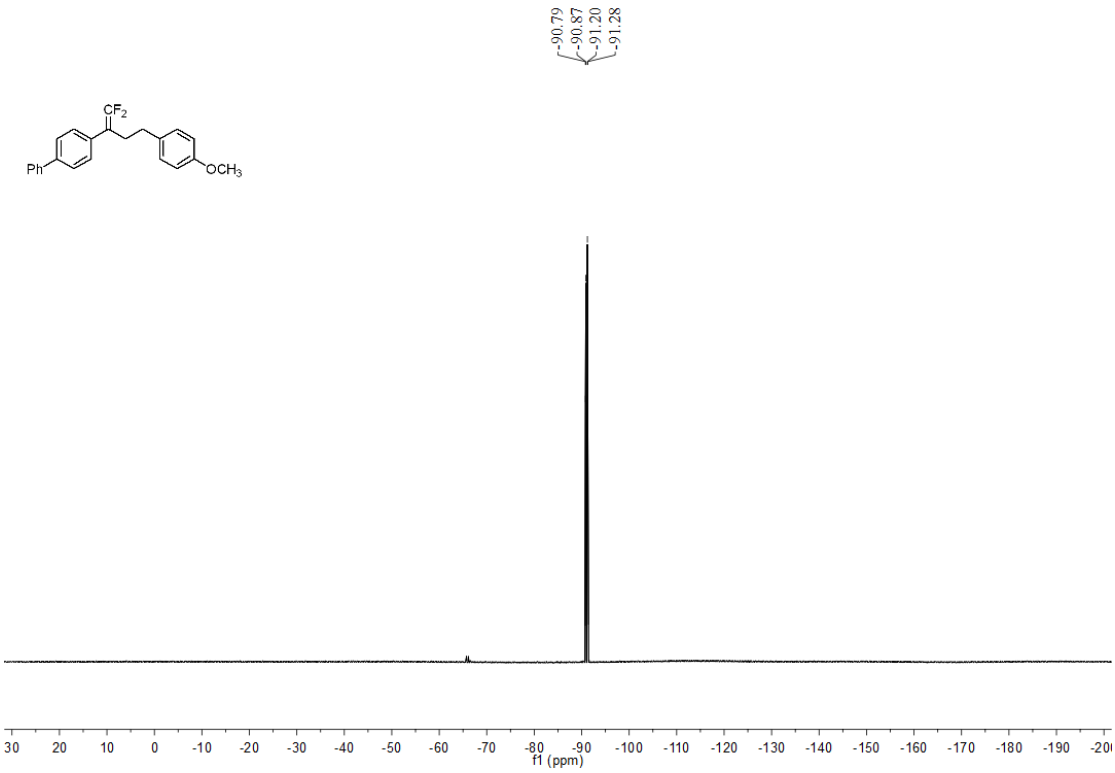
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 11



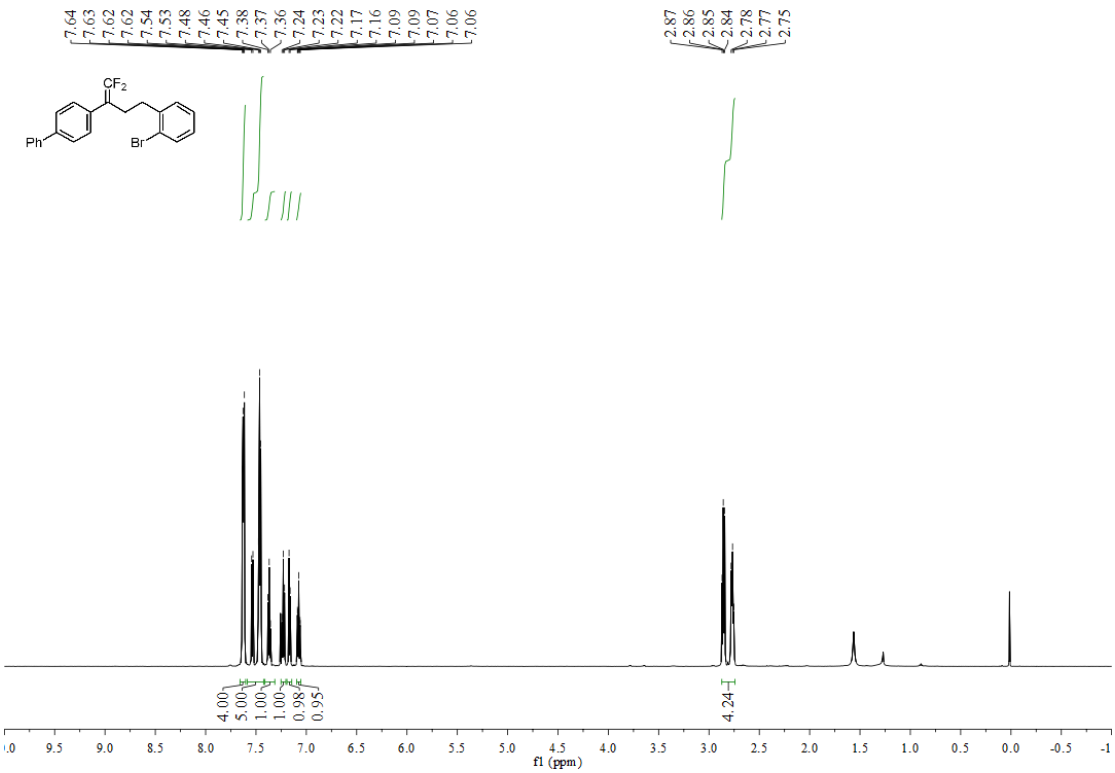
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 11



^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 11



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 12



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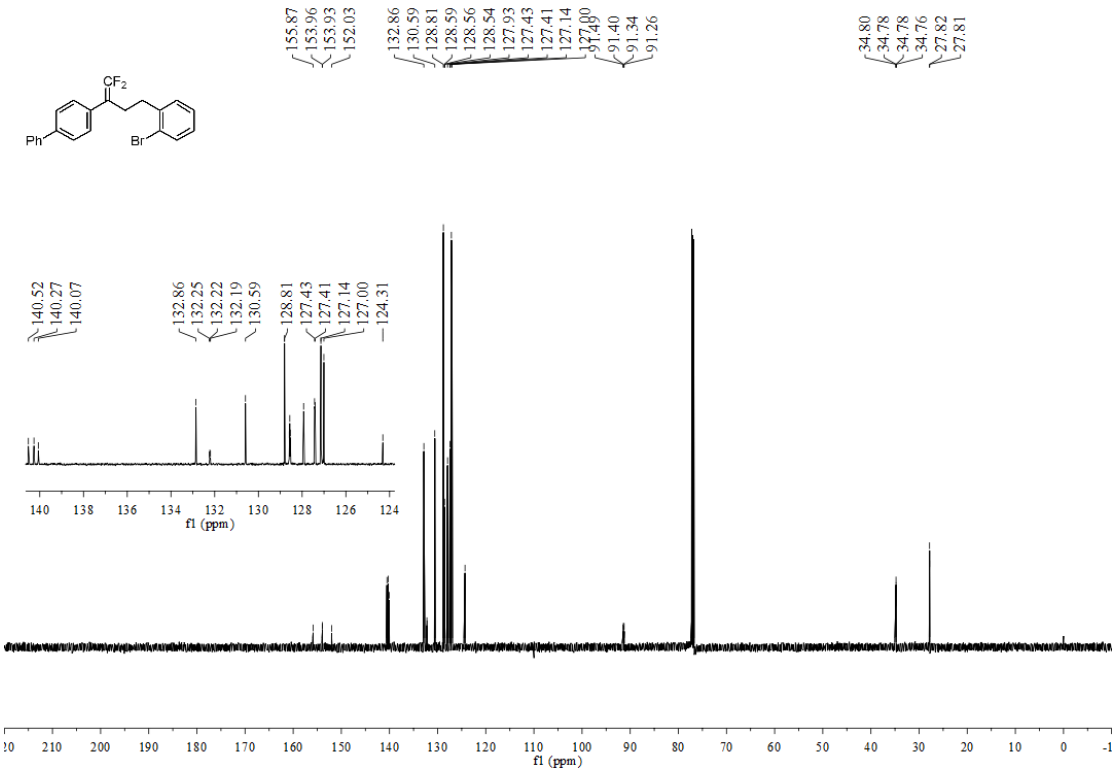

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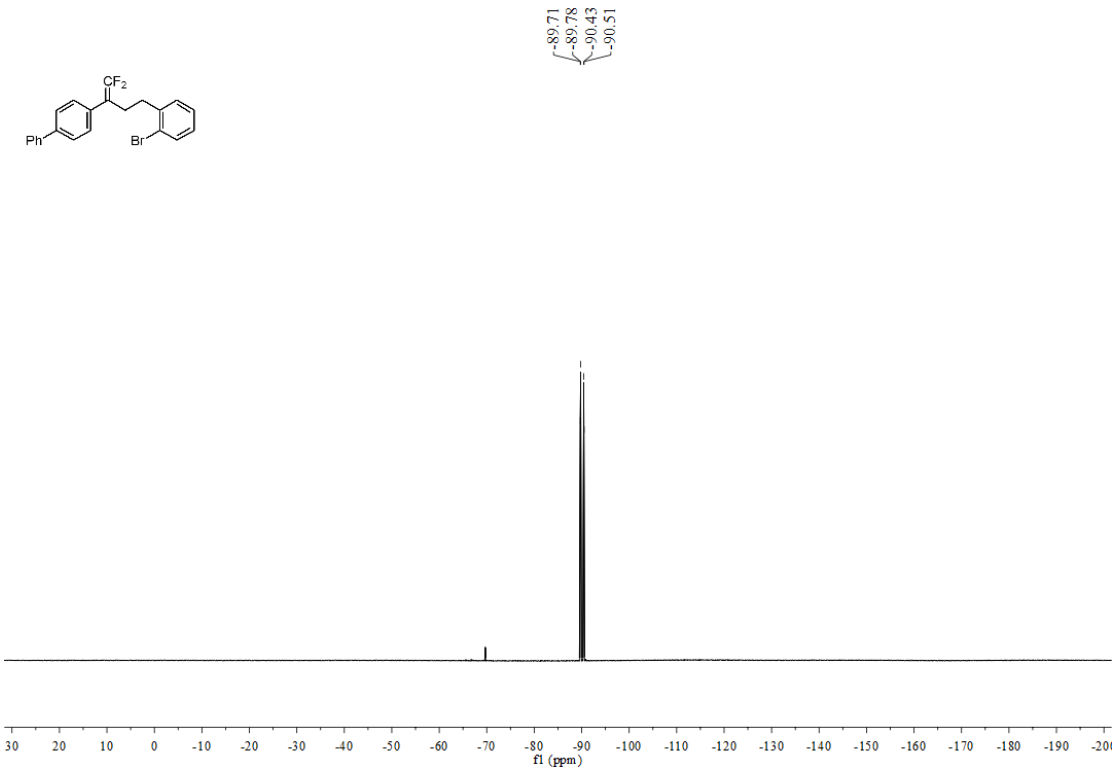
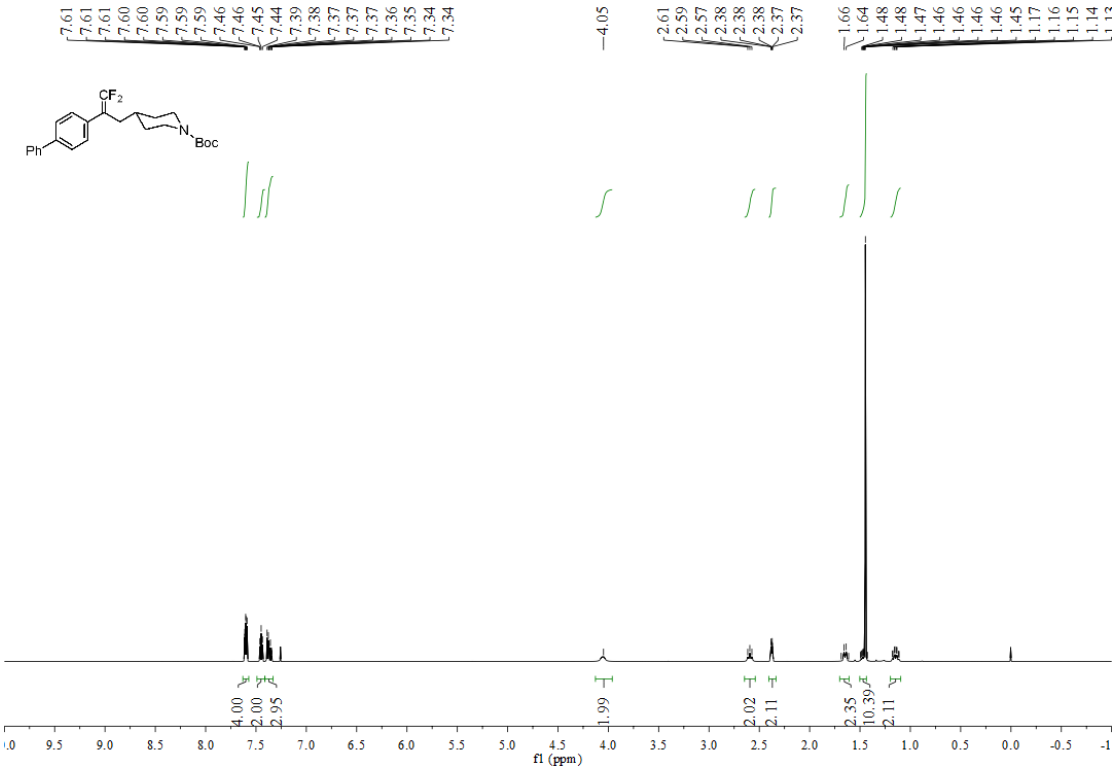
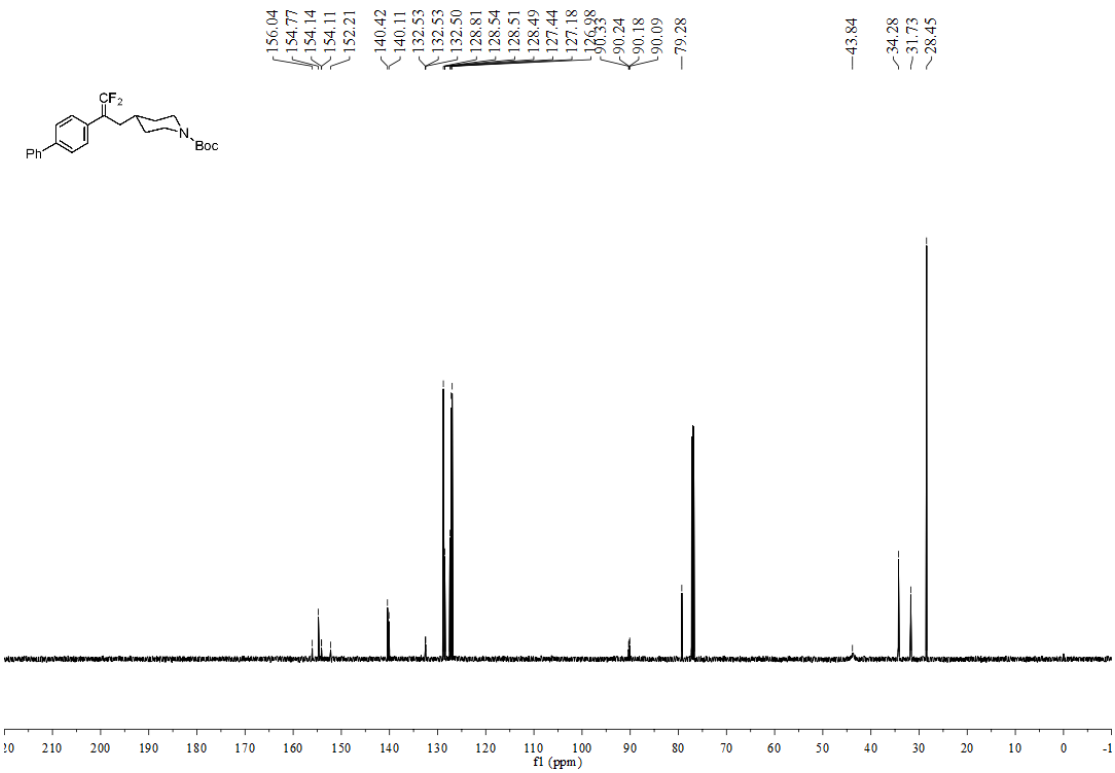


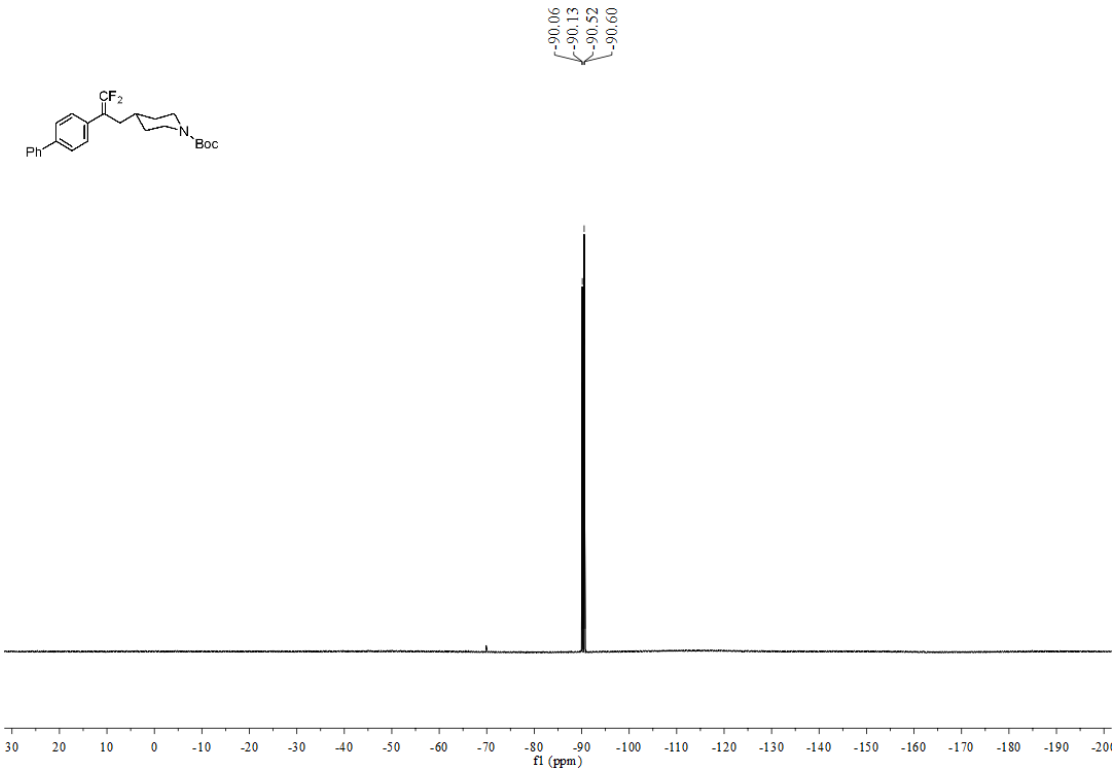
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 13



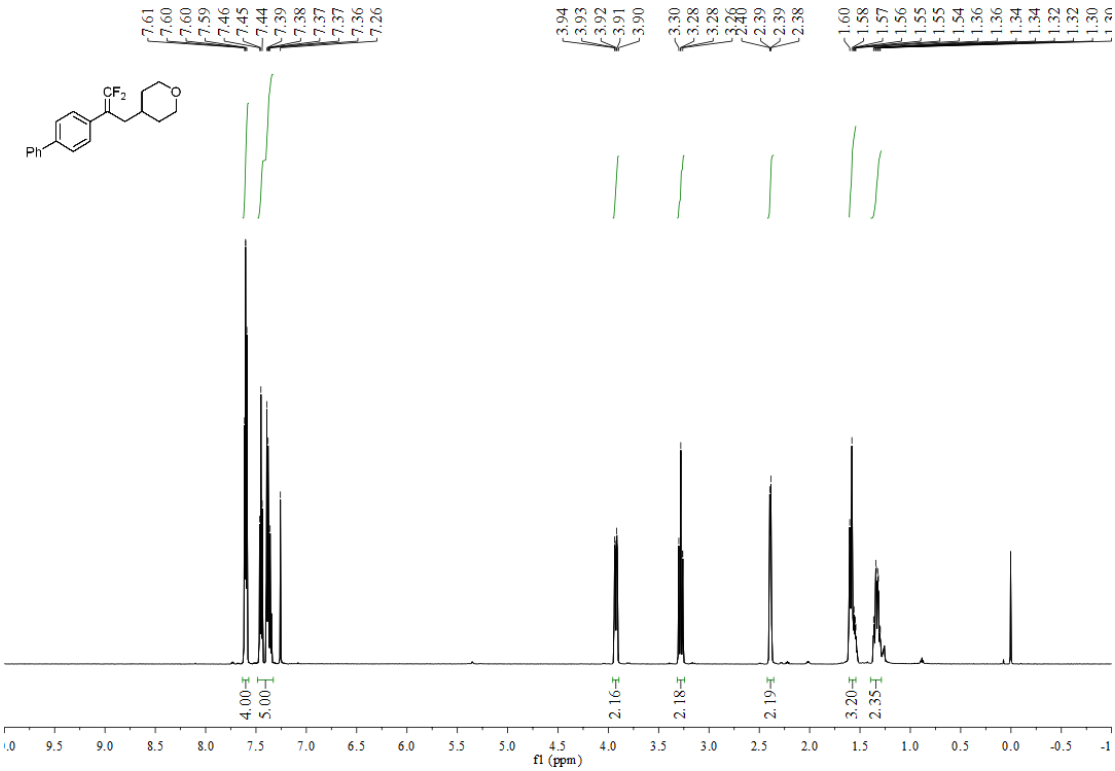
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 13



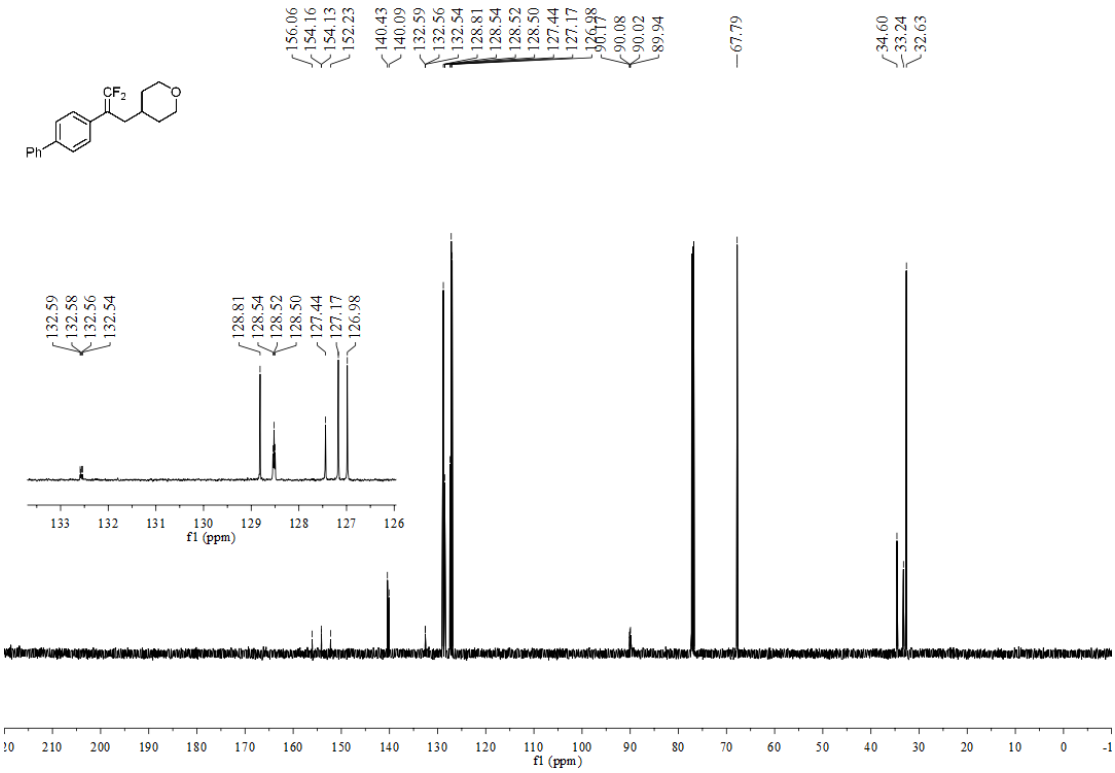
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 13



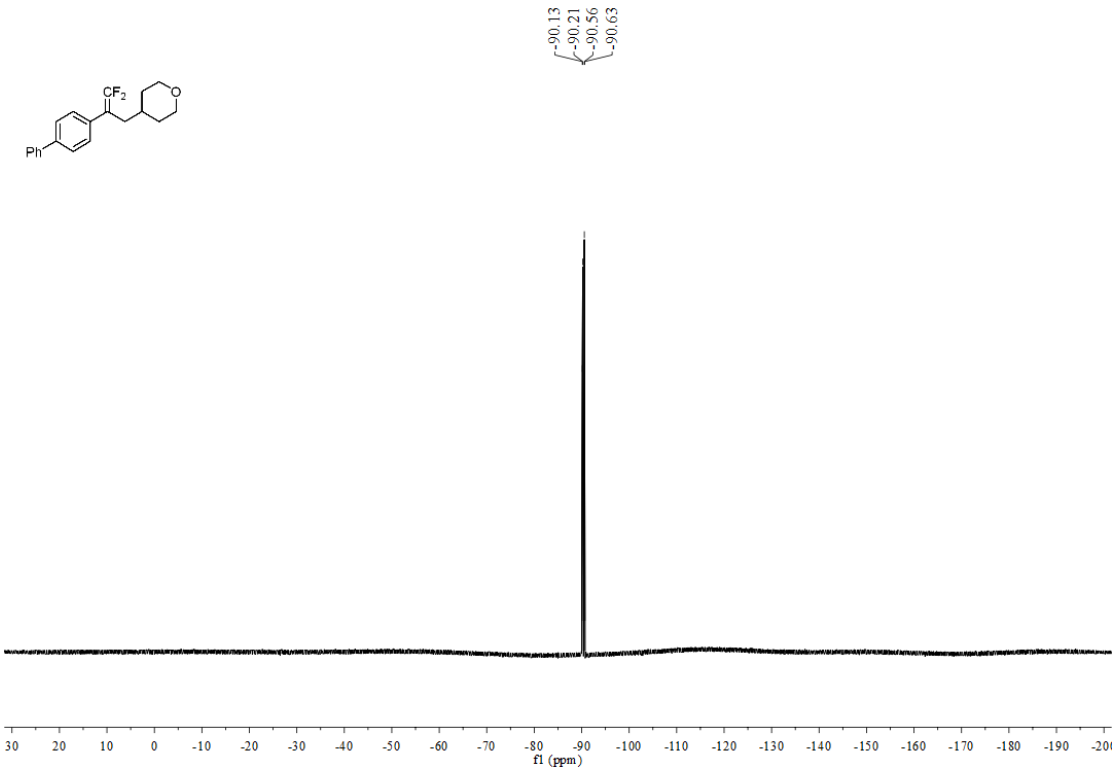
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 14



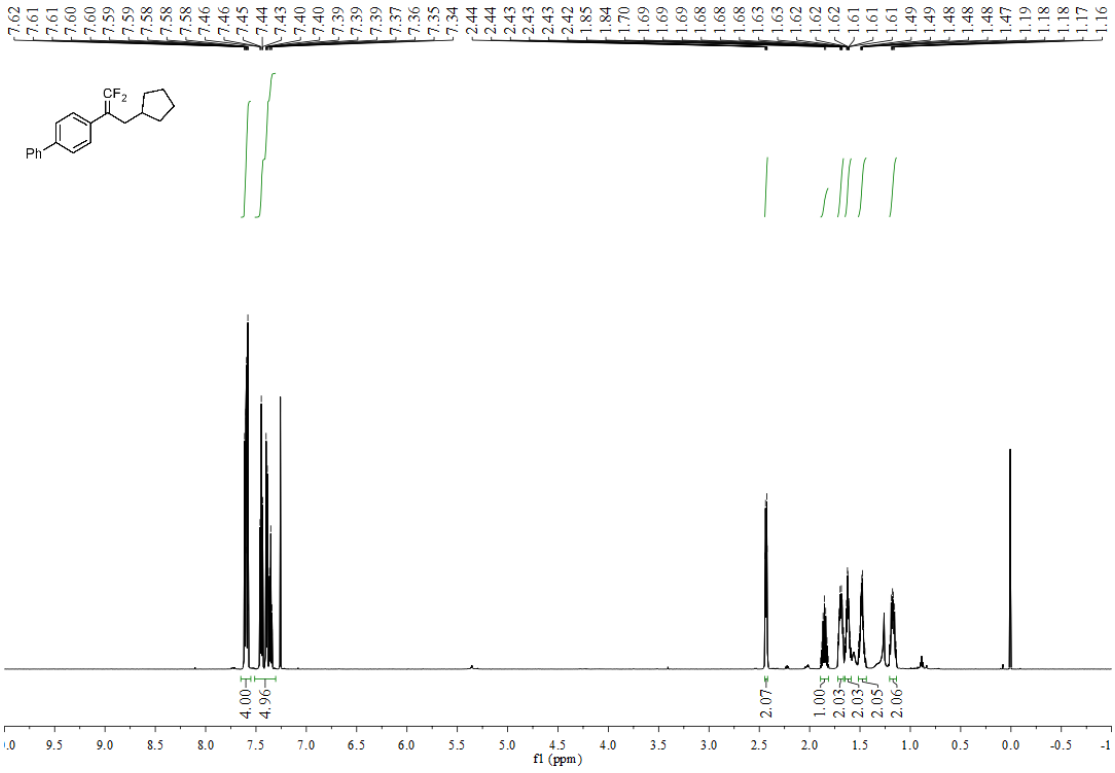
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 14



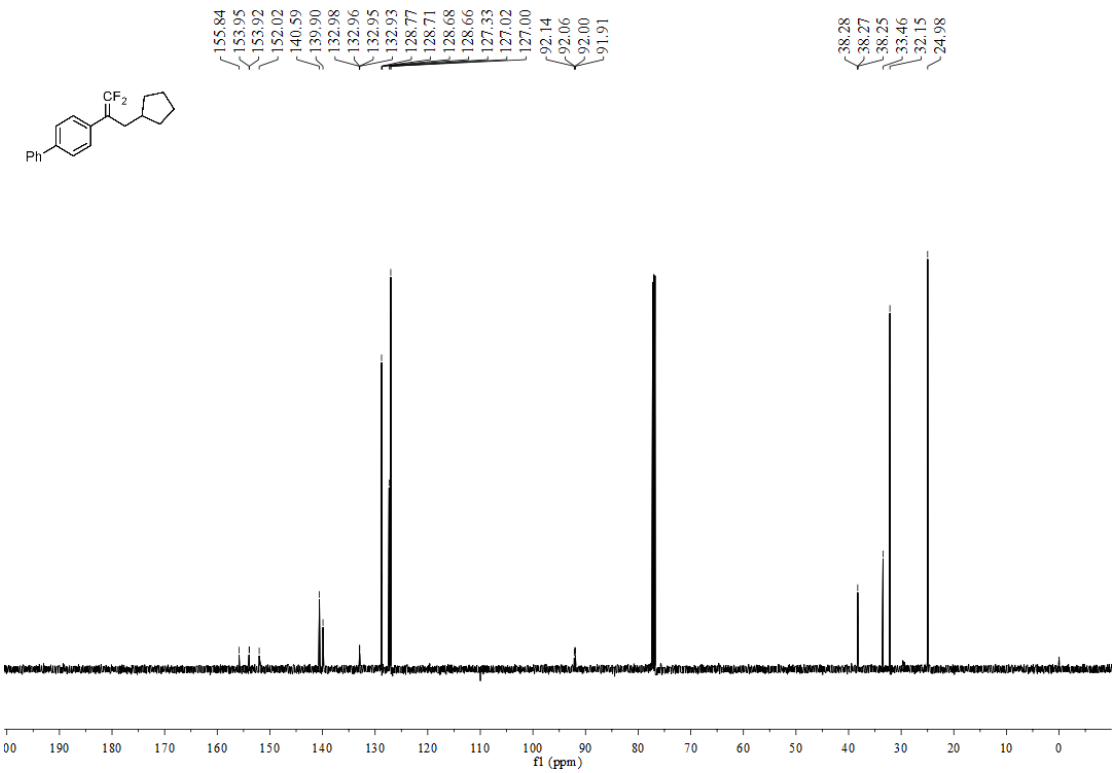
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 14



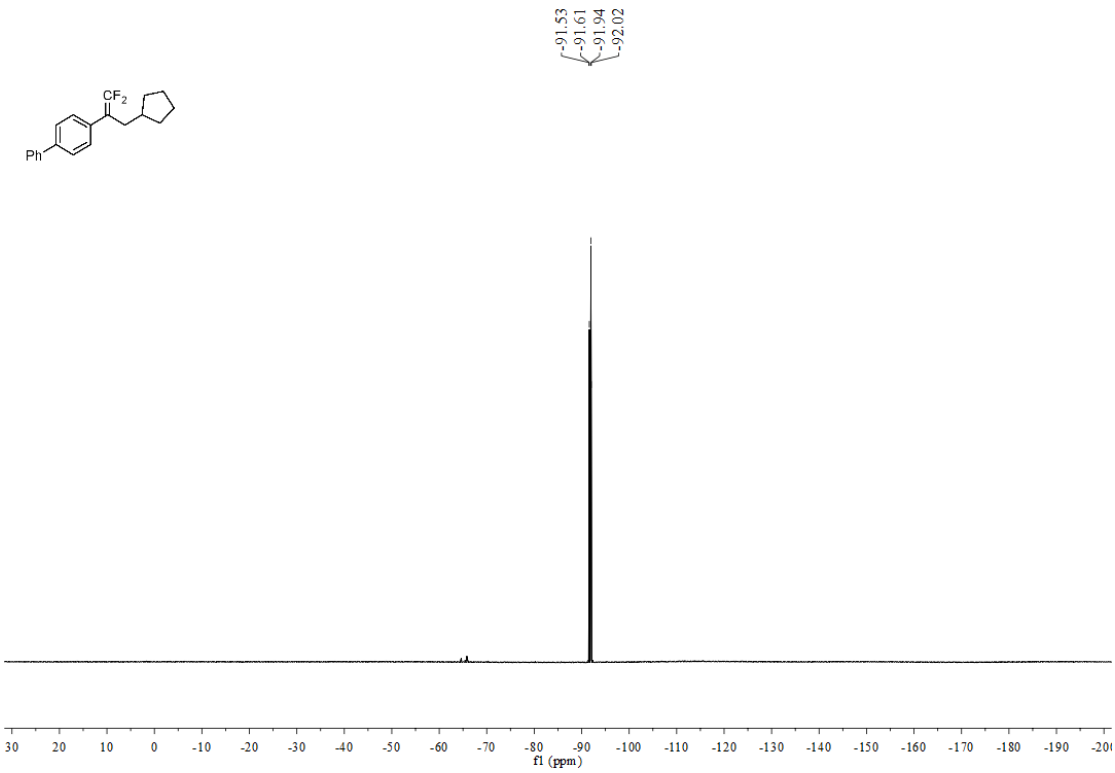
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 15



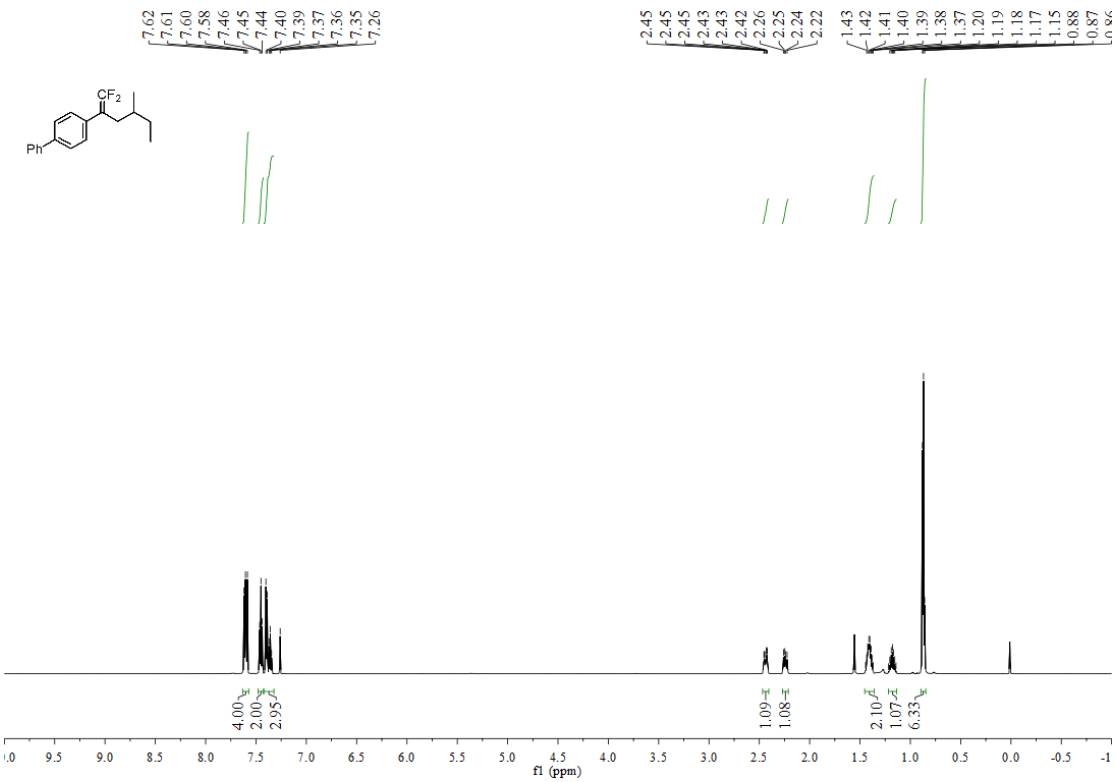
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 15



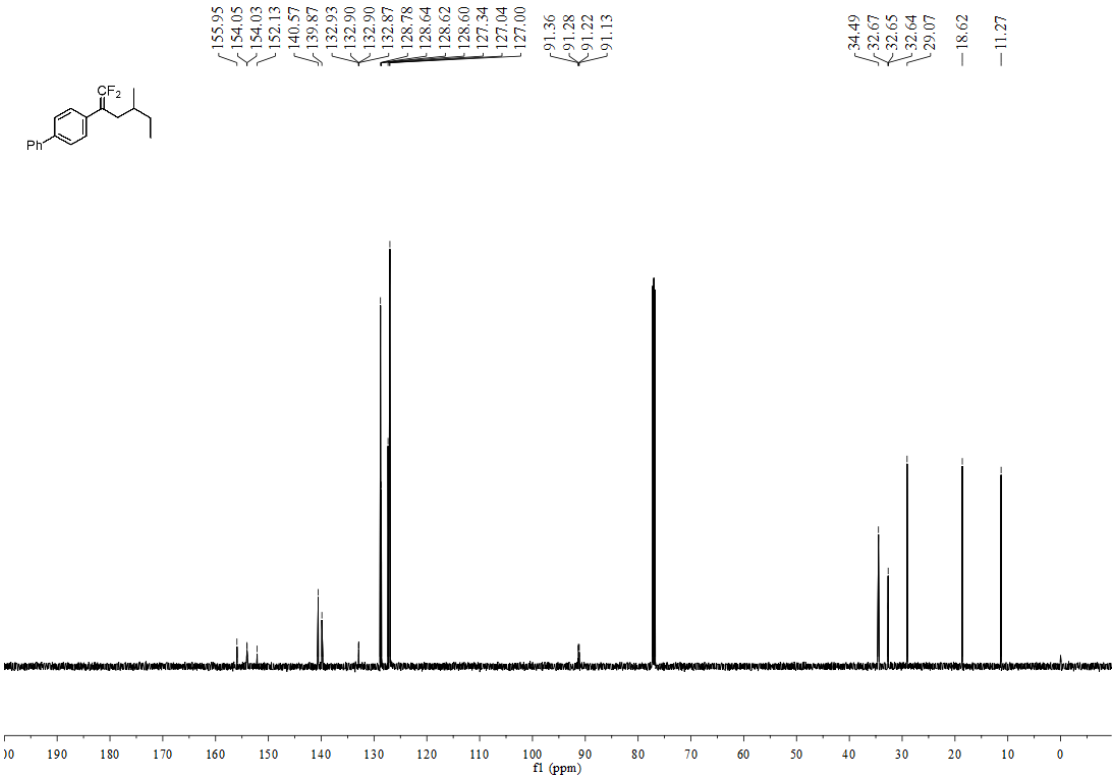
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 15



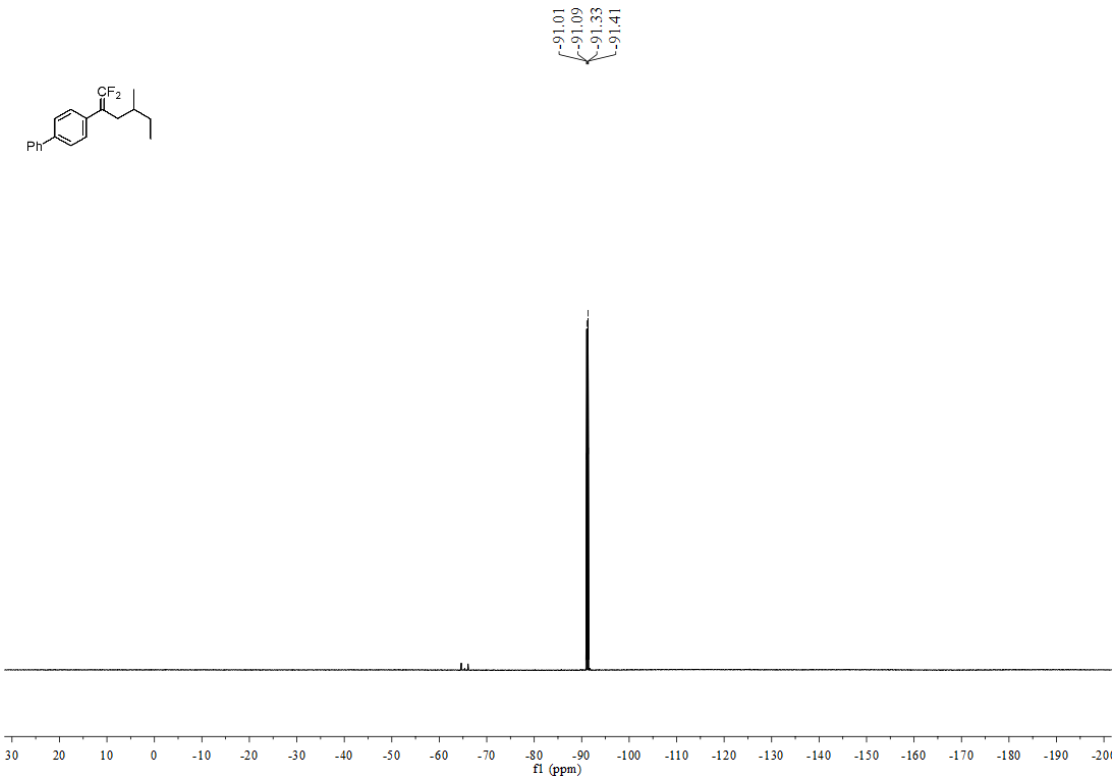
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 16



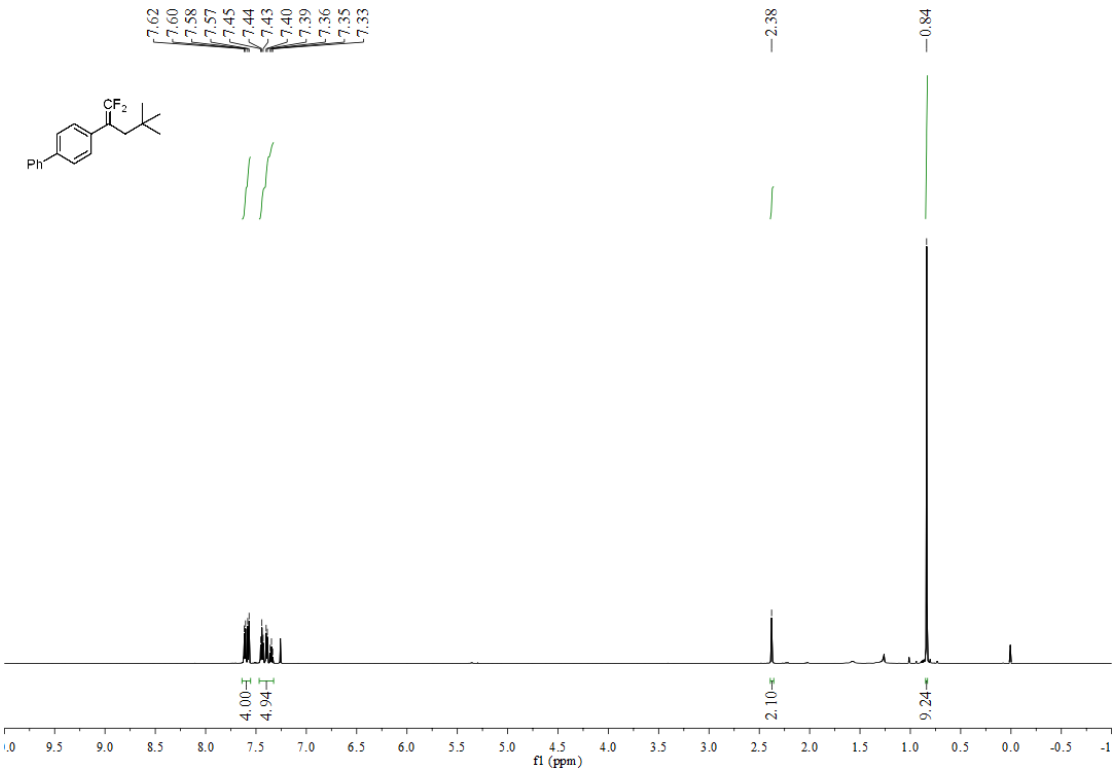
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 16



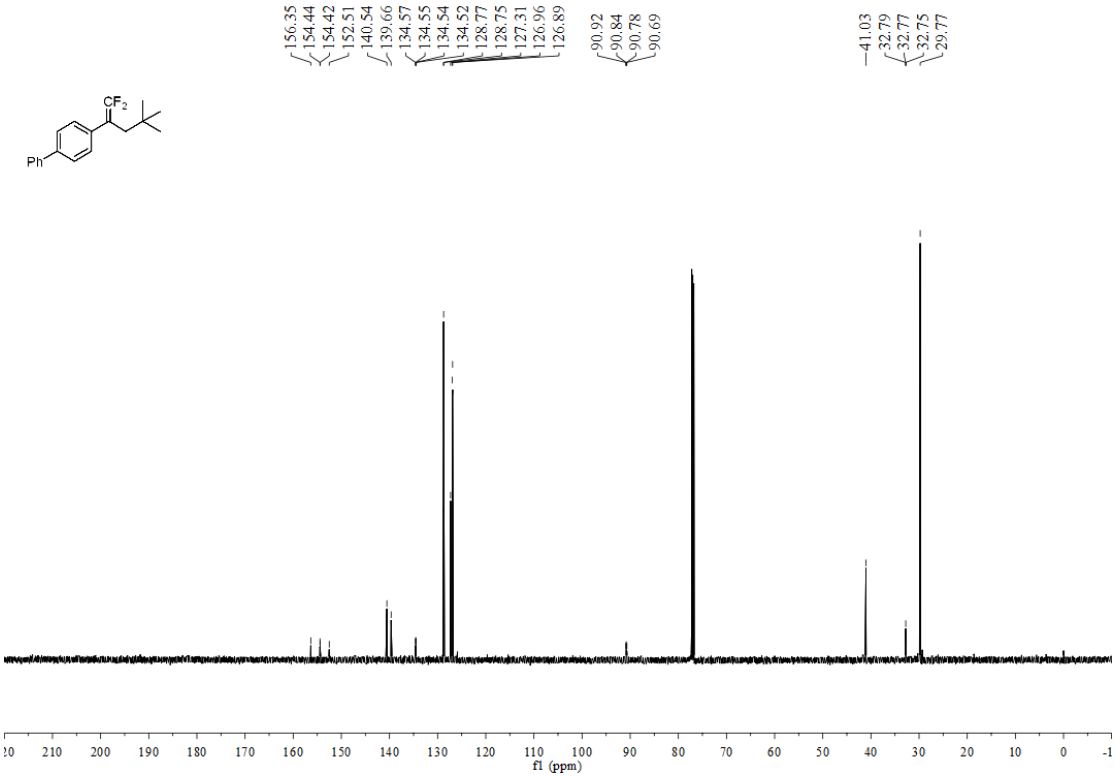
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 16



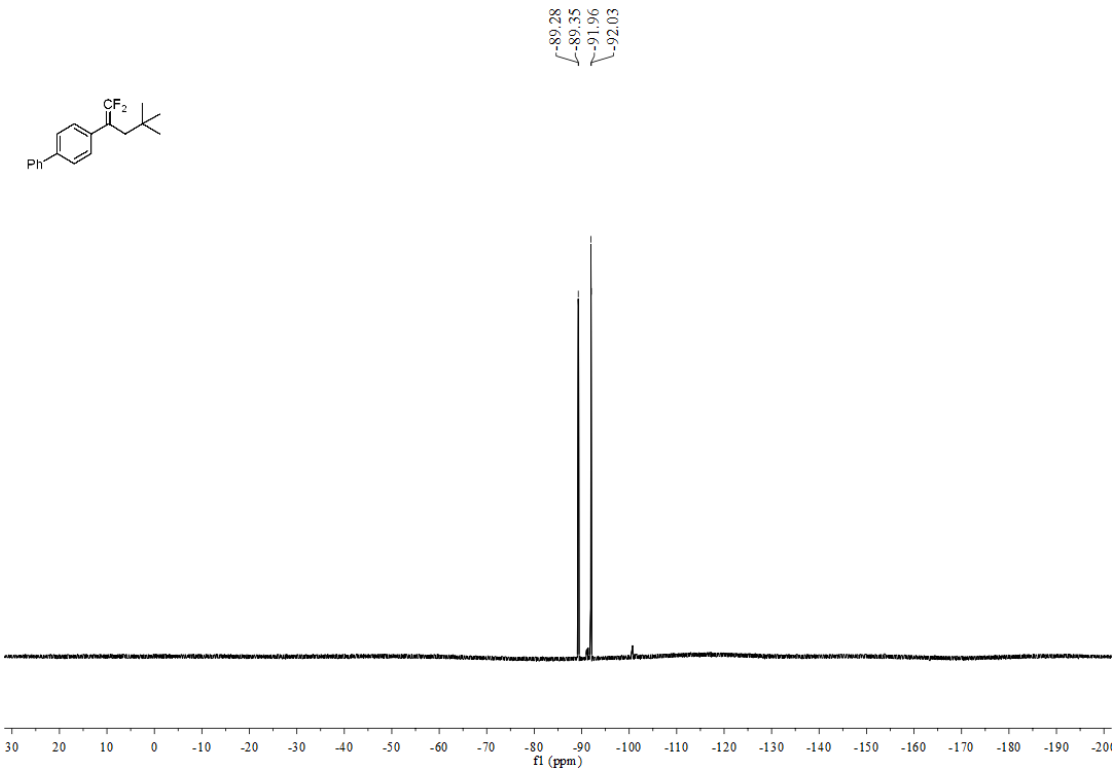
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 17



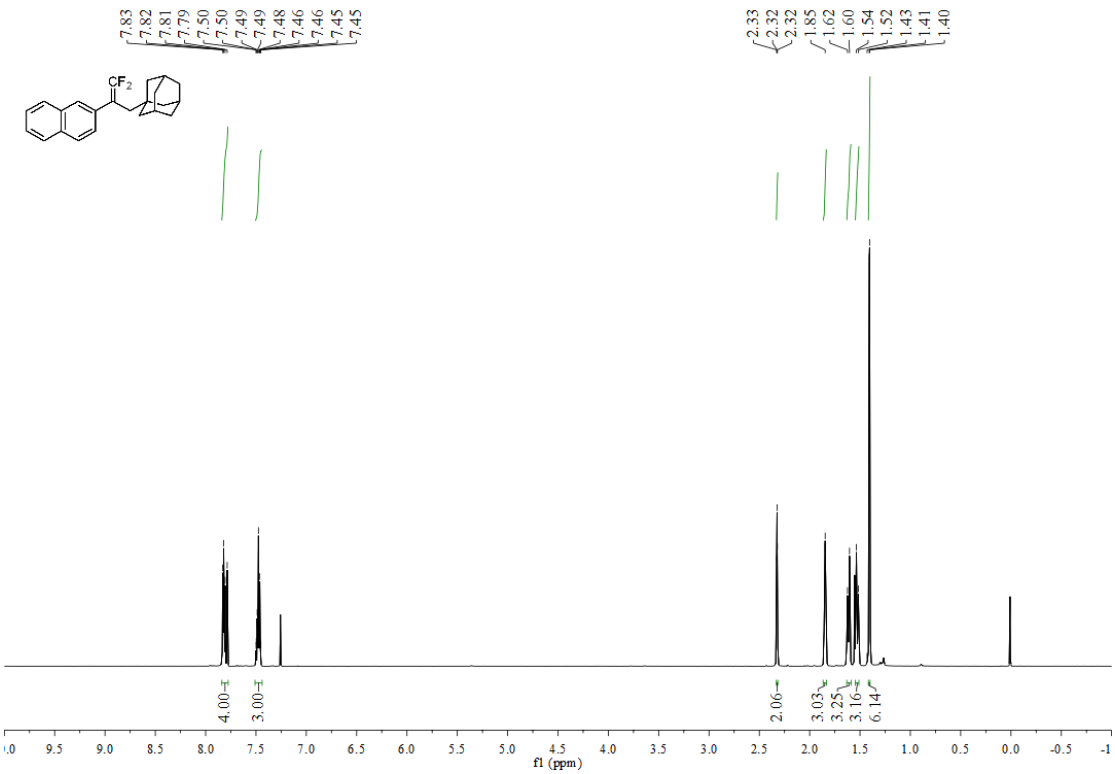
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 17



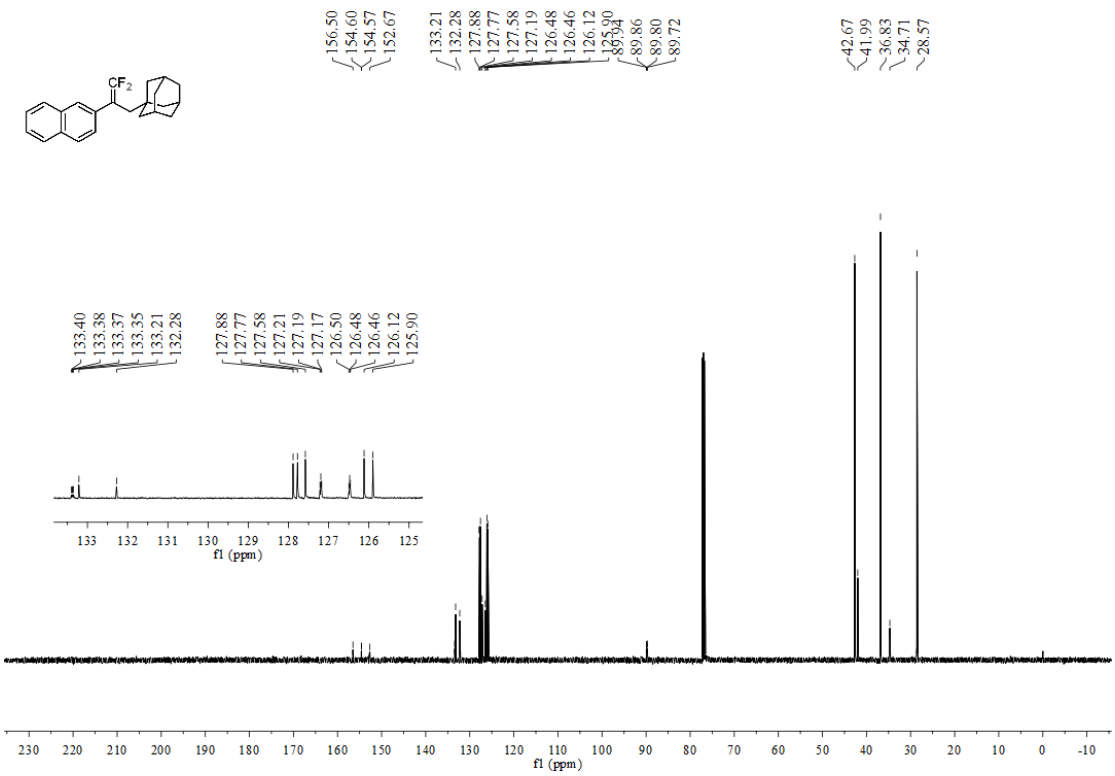
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 17



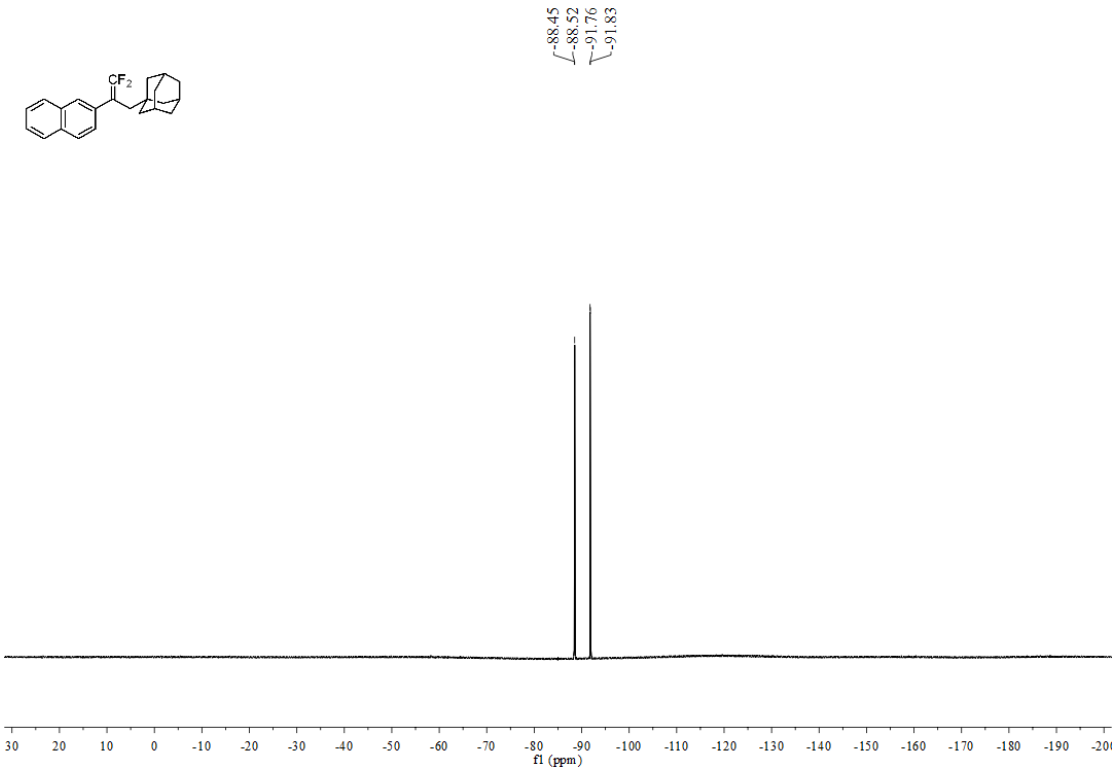
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 18



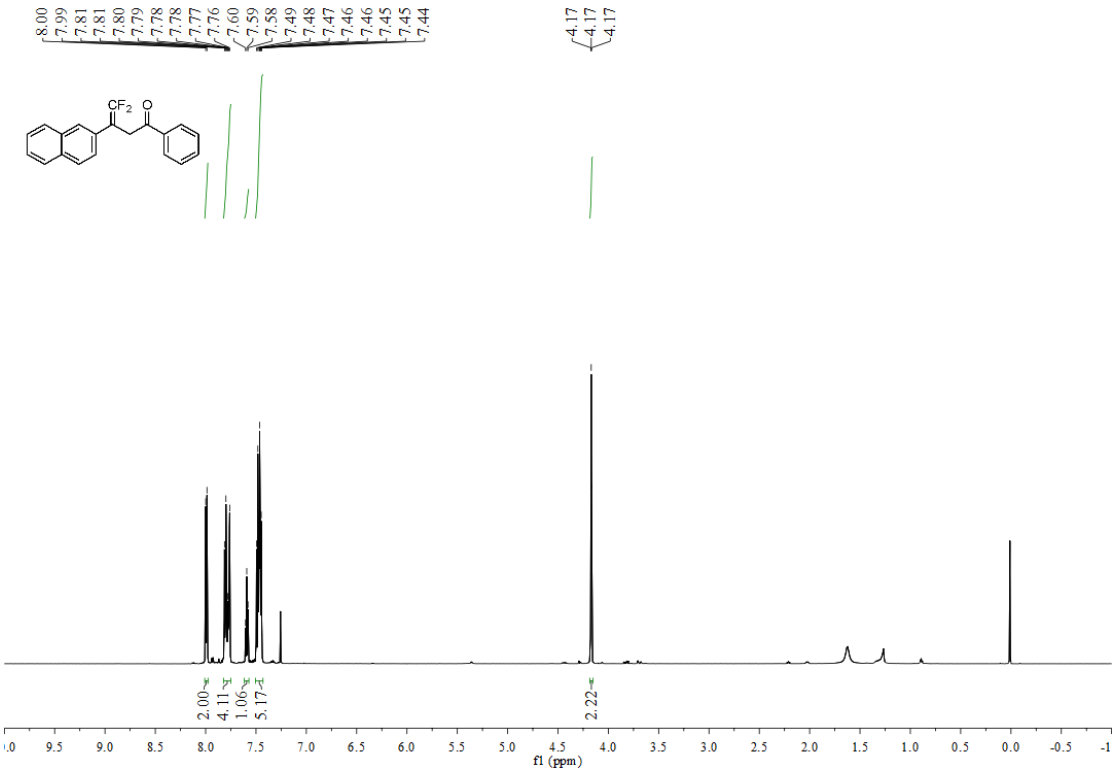
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 18



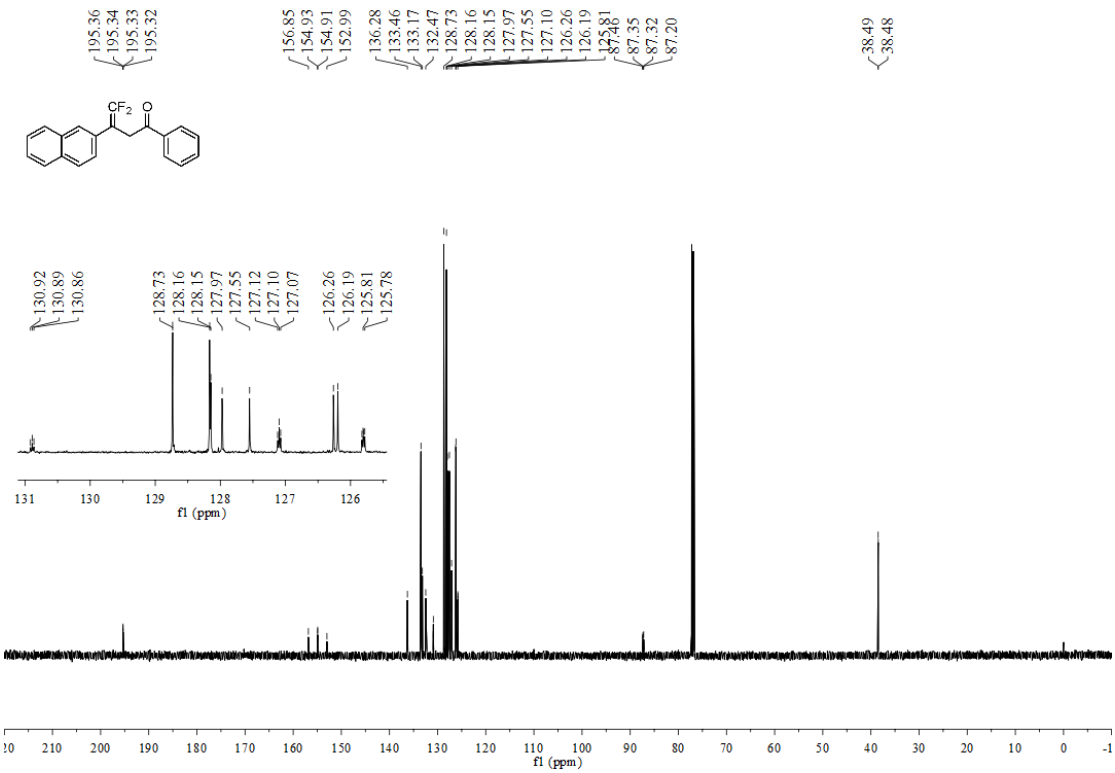
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 18



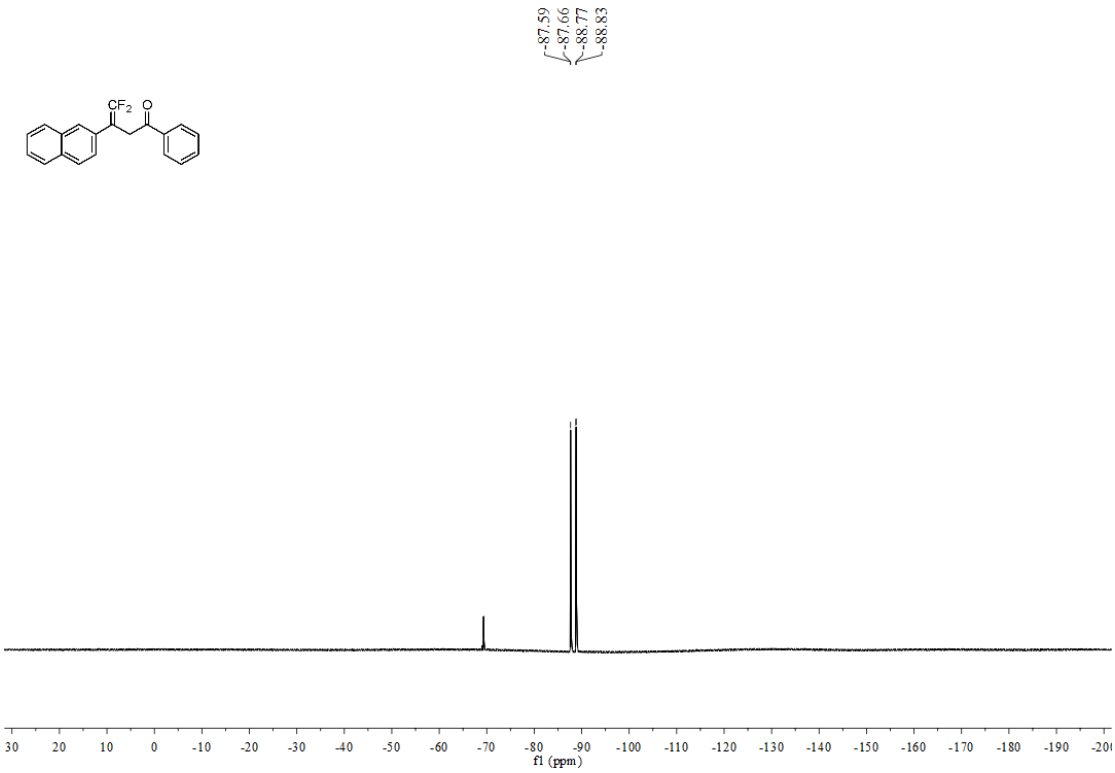
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 19



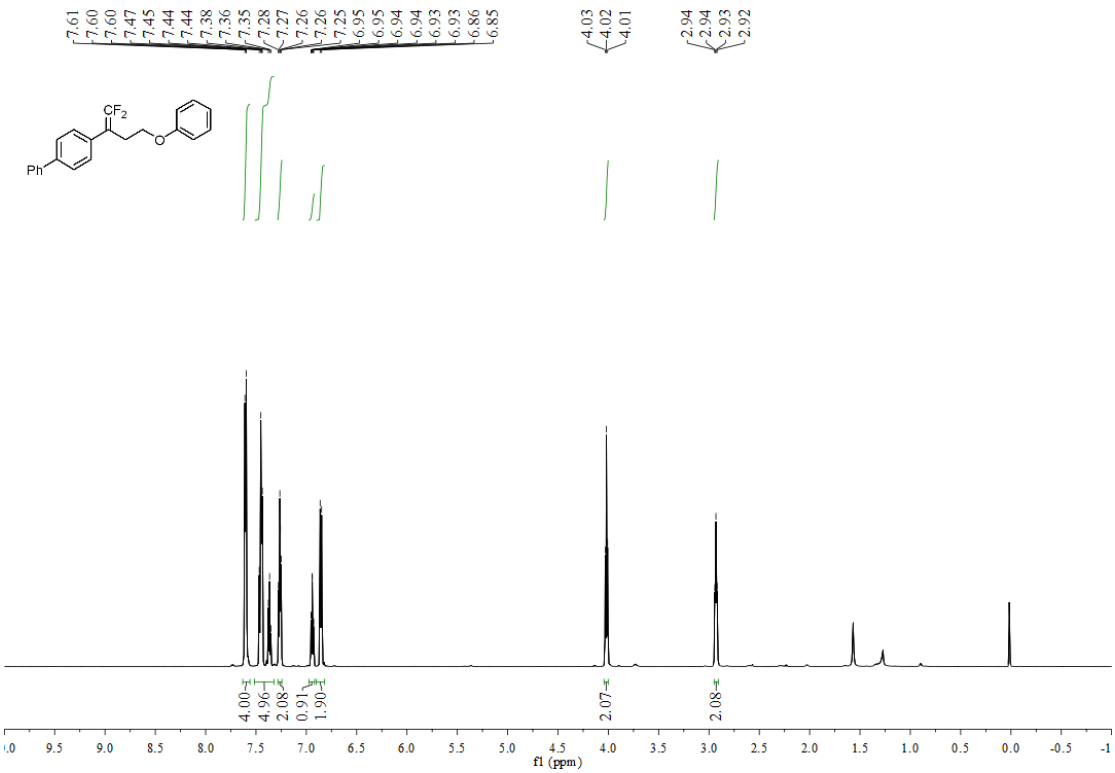
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 19



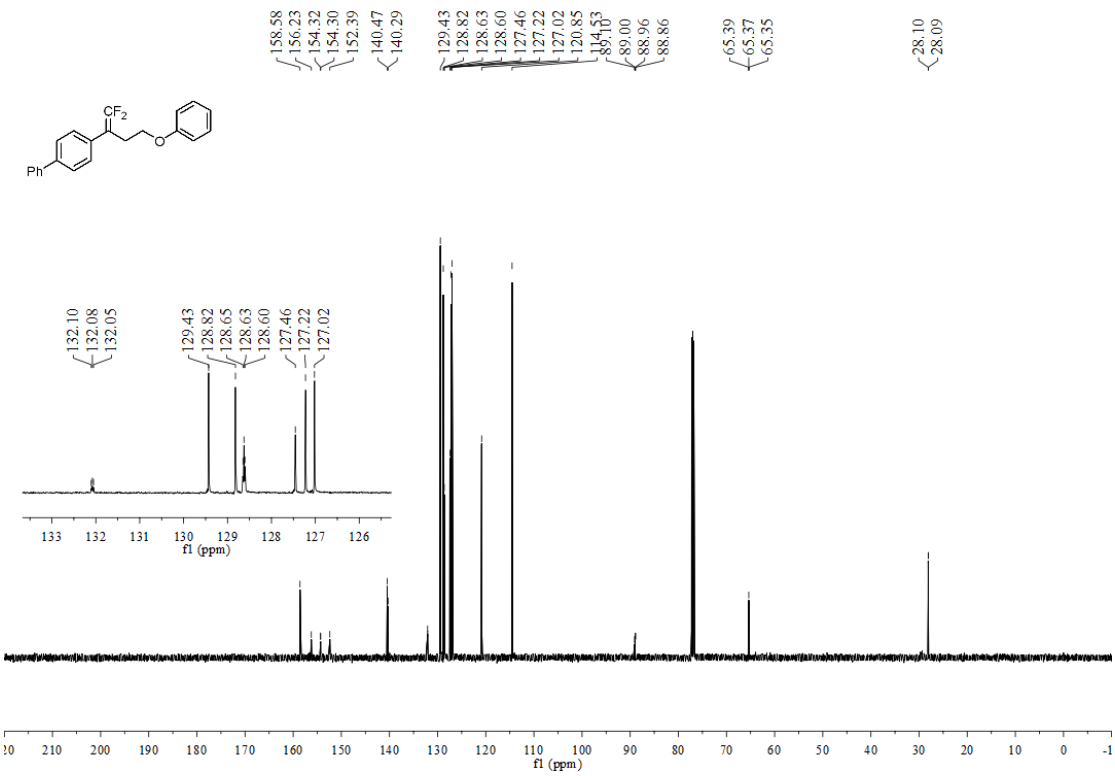
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 19



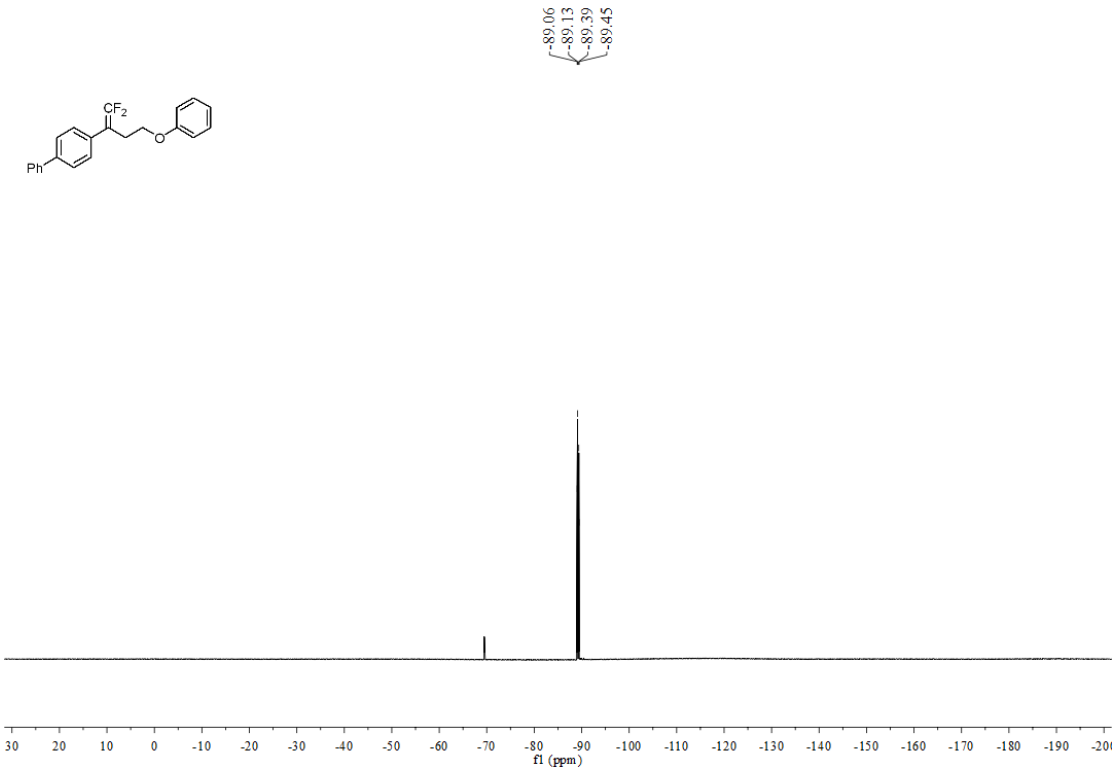
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 20



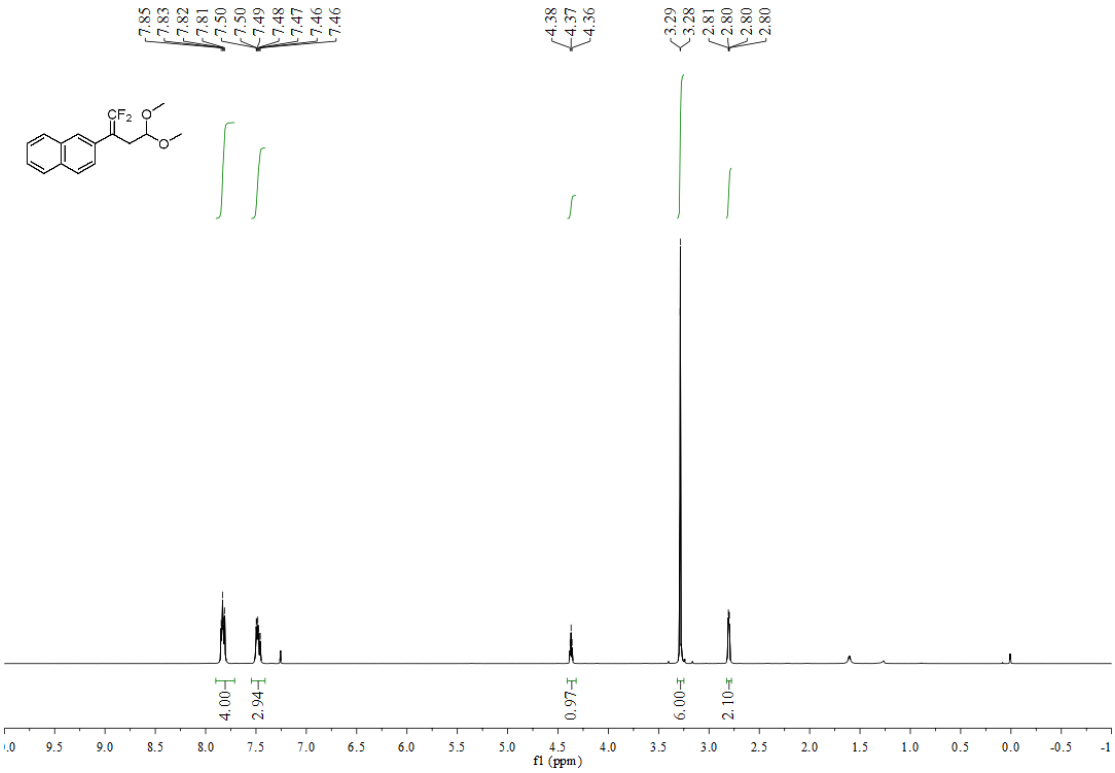
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 20



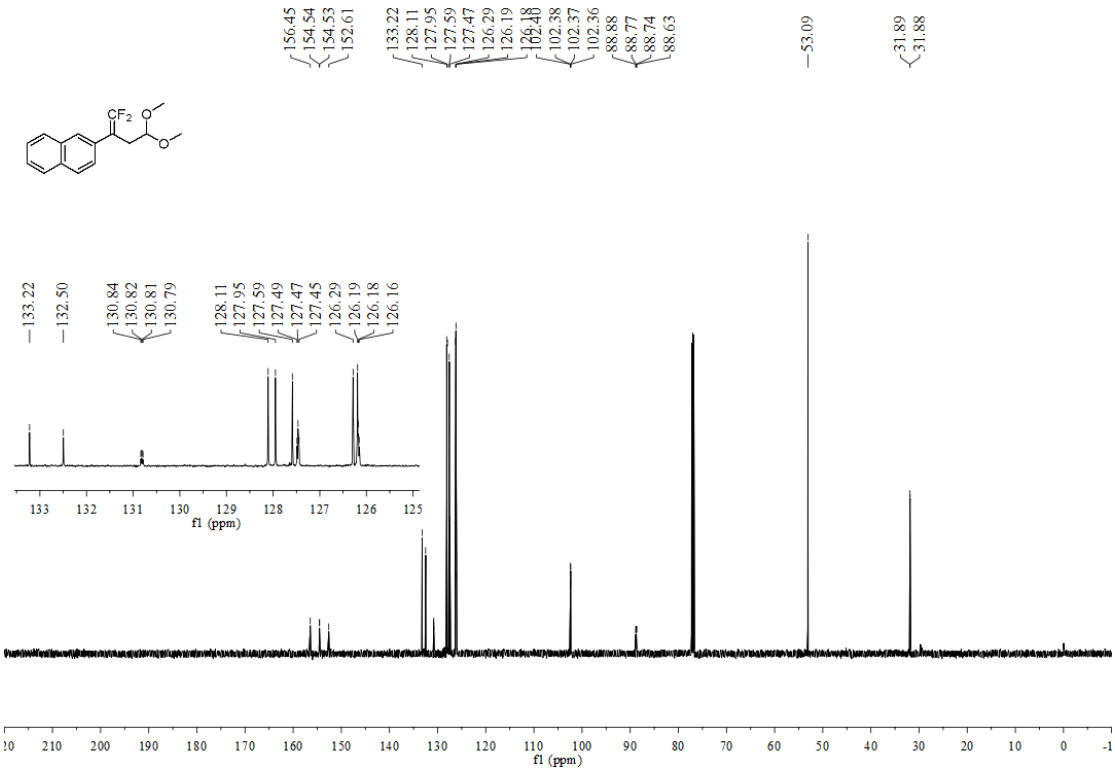
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 20



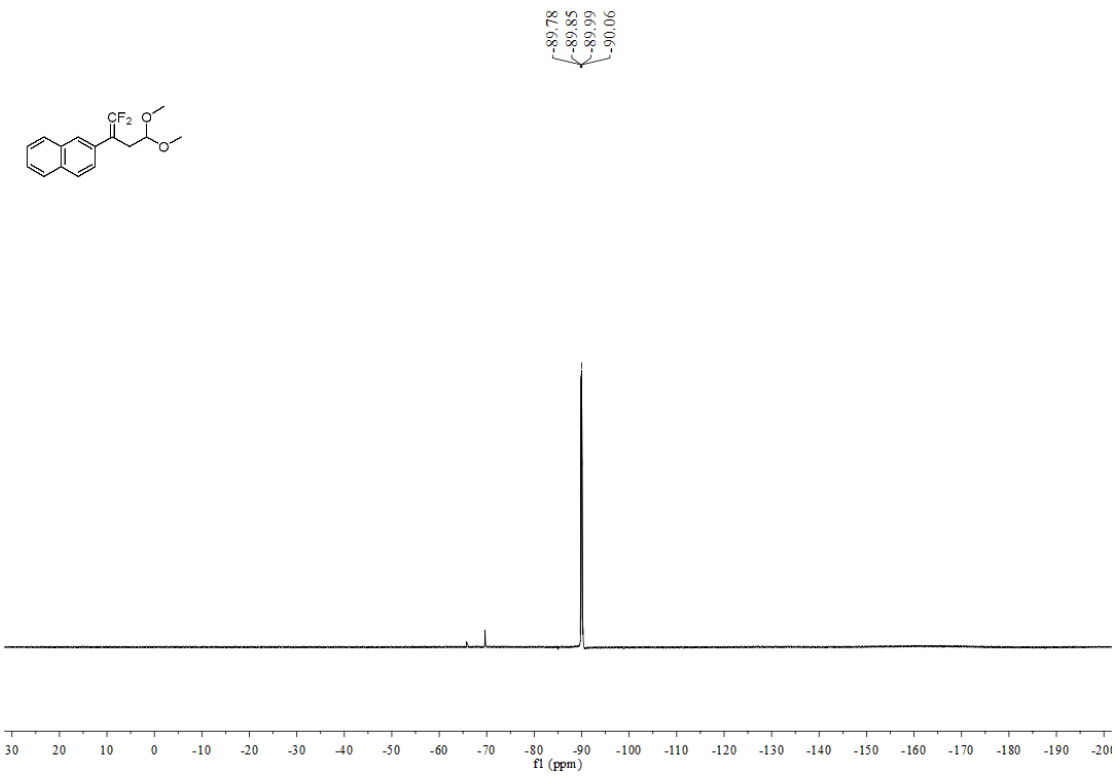
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 21



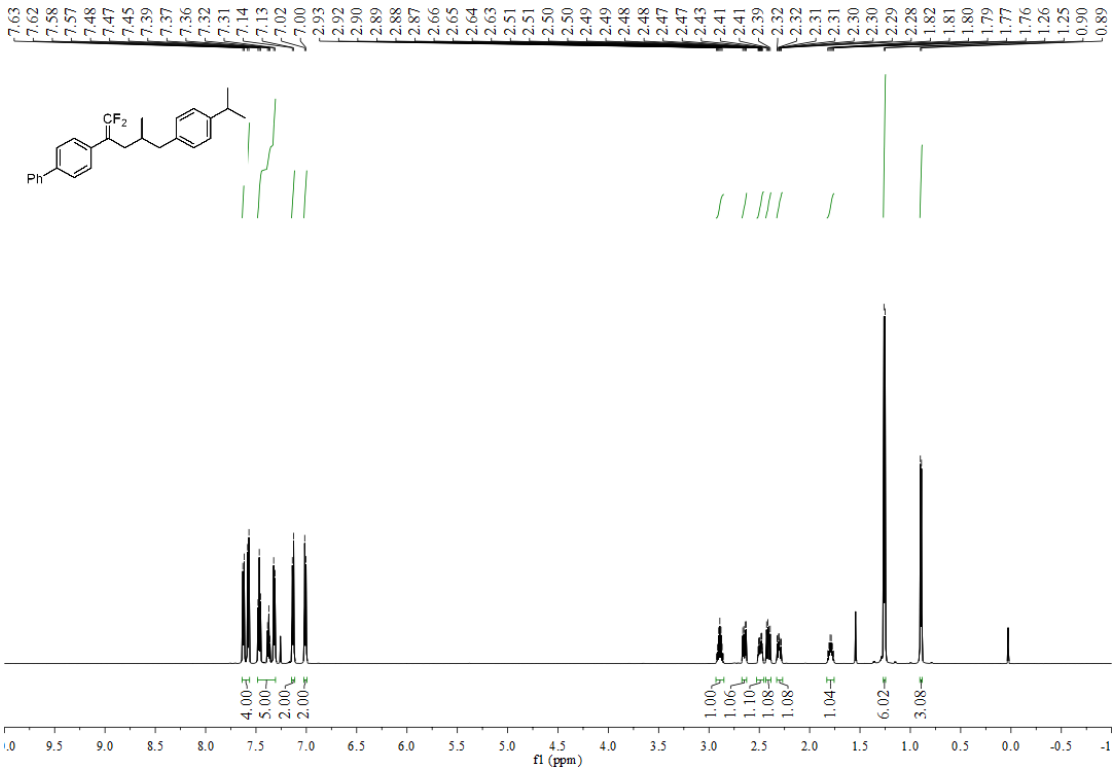
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 21



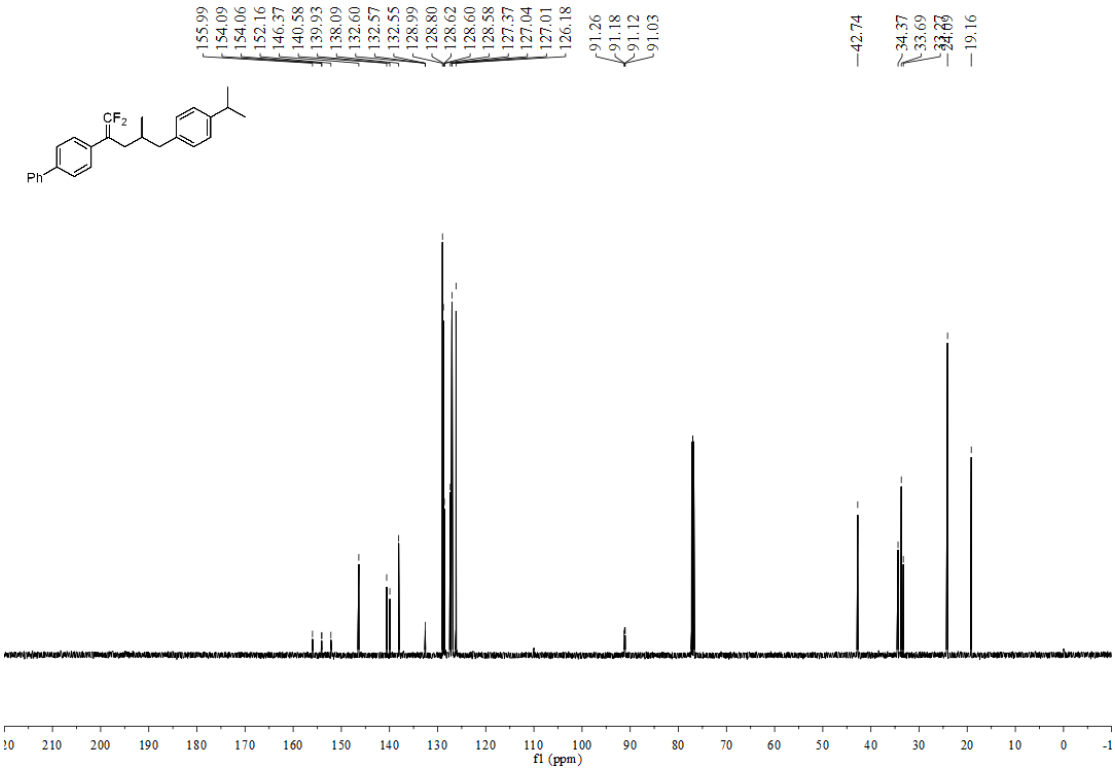
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 21



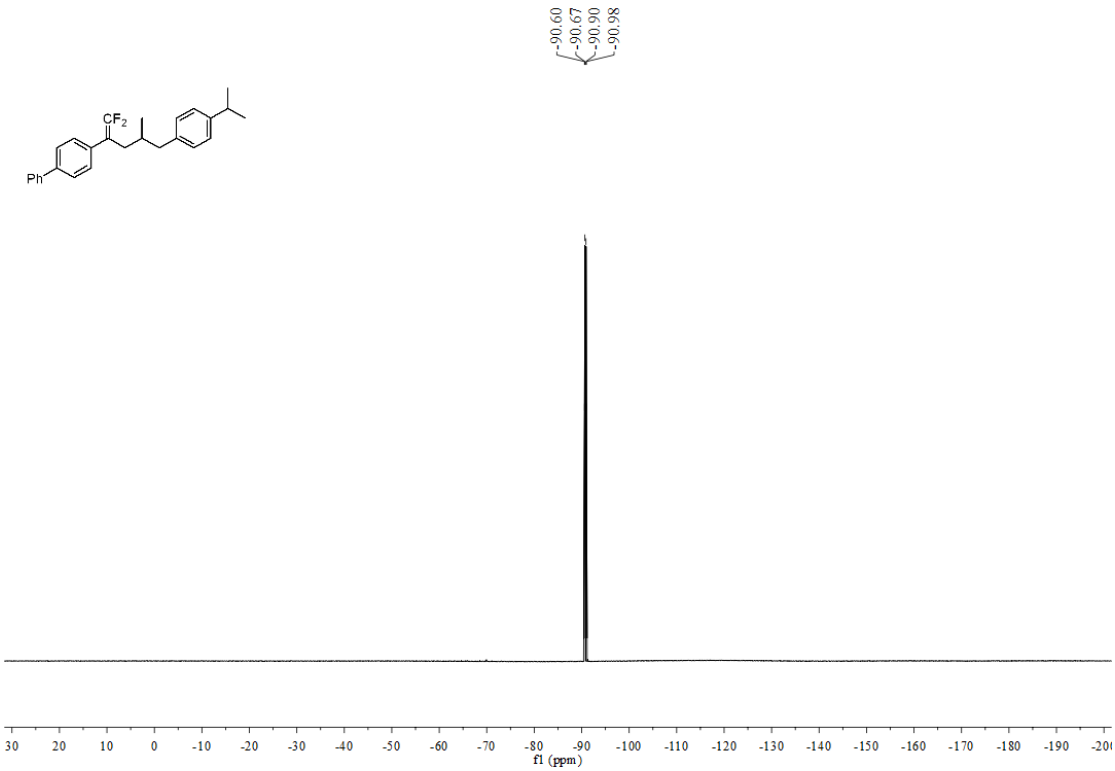
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 22



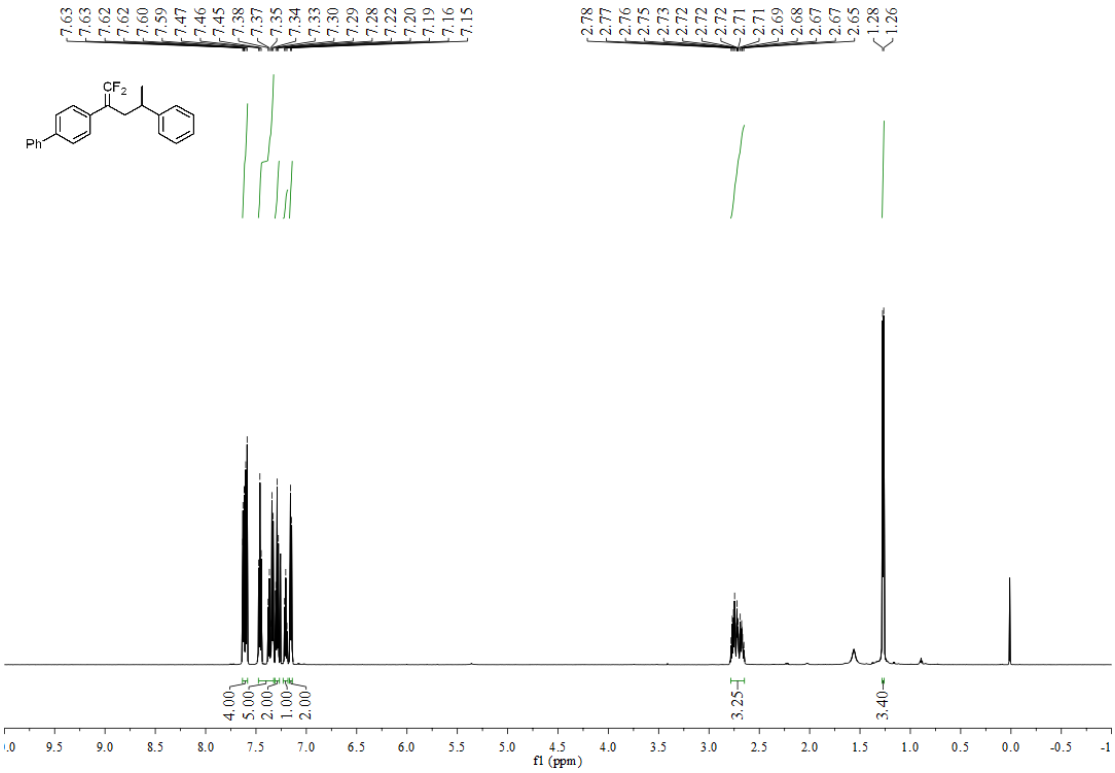
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 22



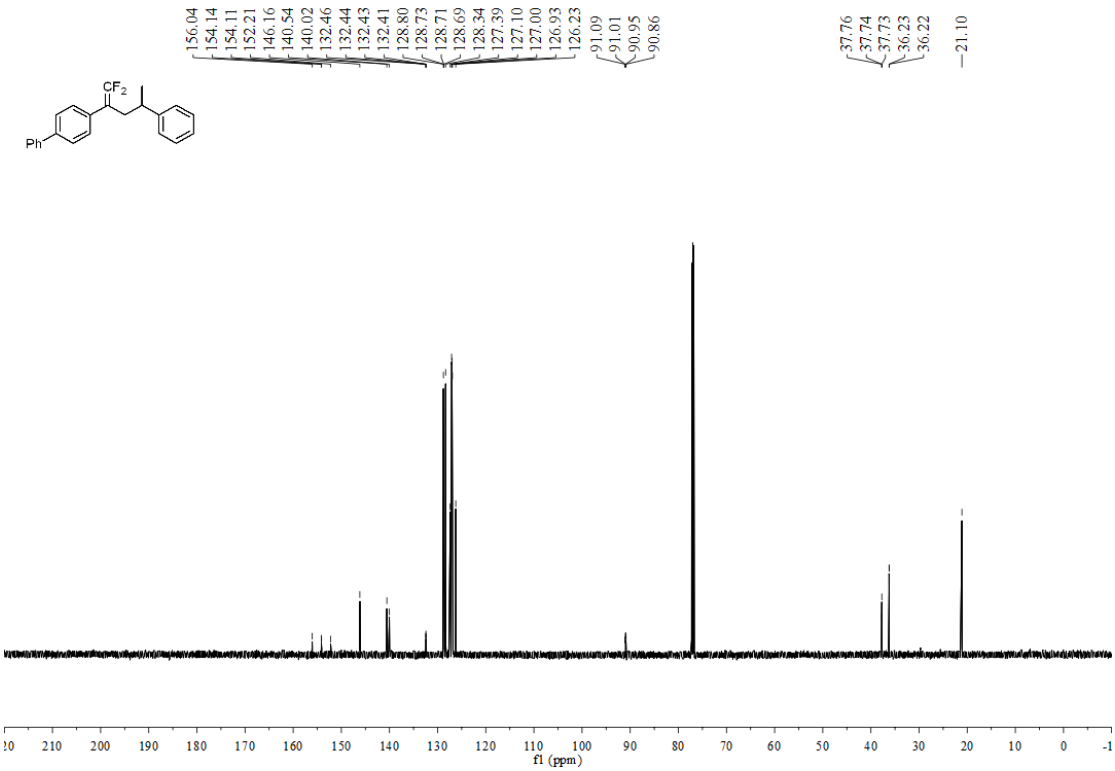
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 22



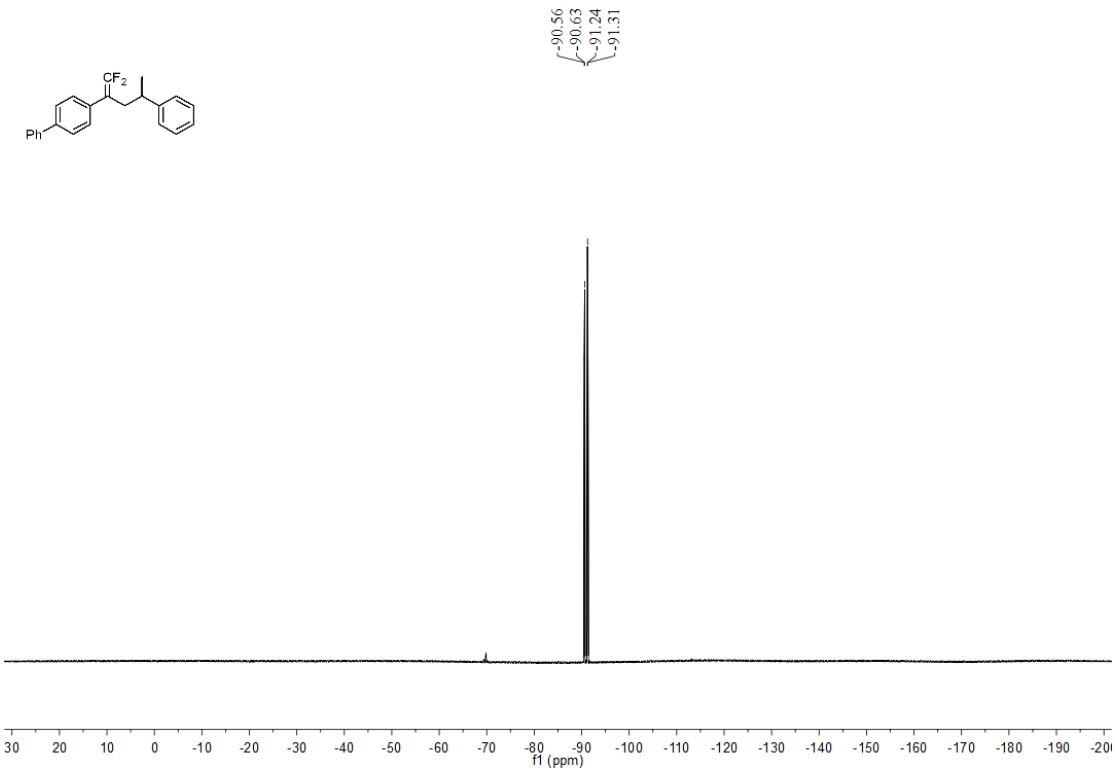
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 23



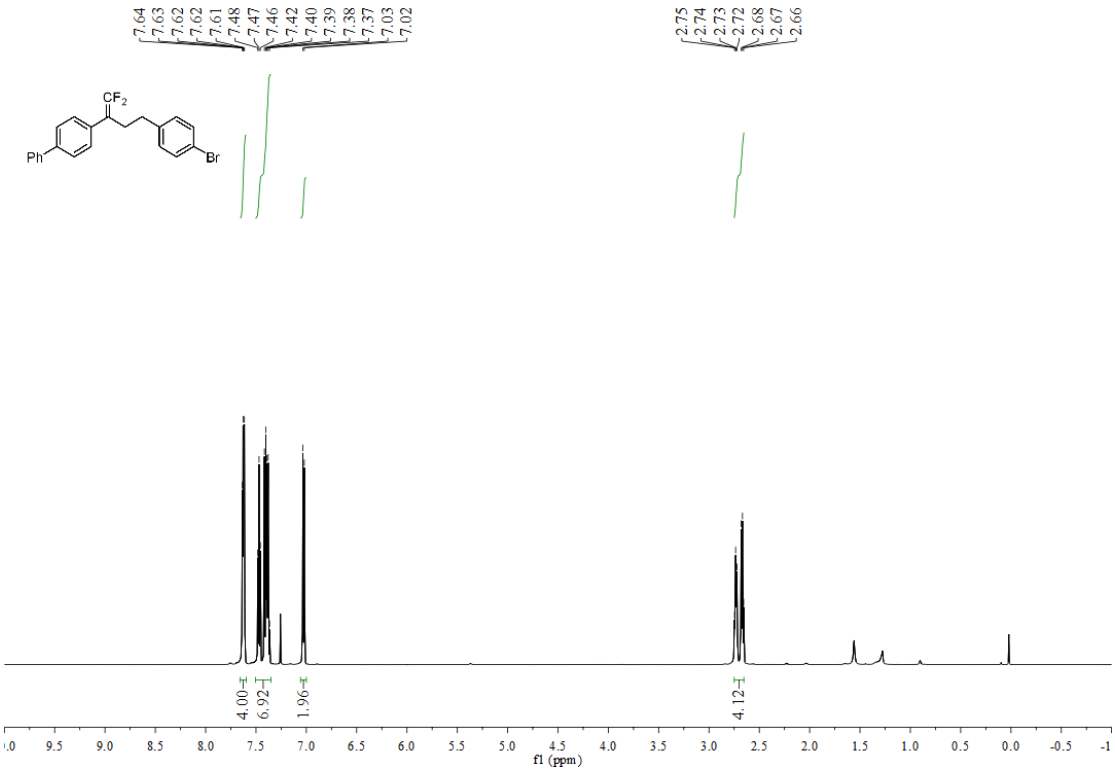
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 23



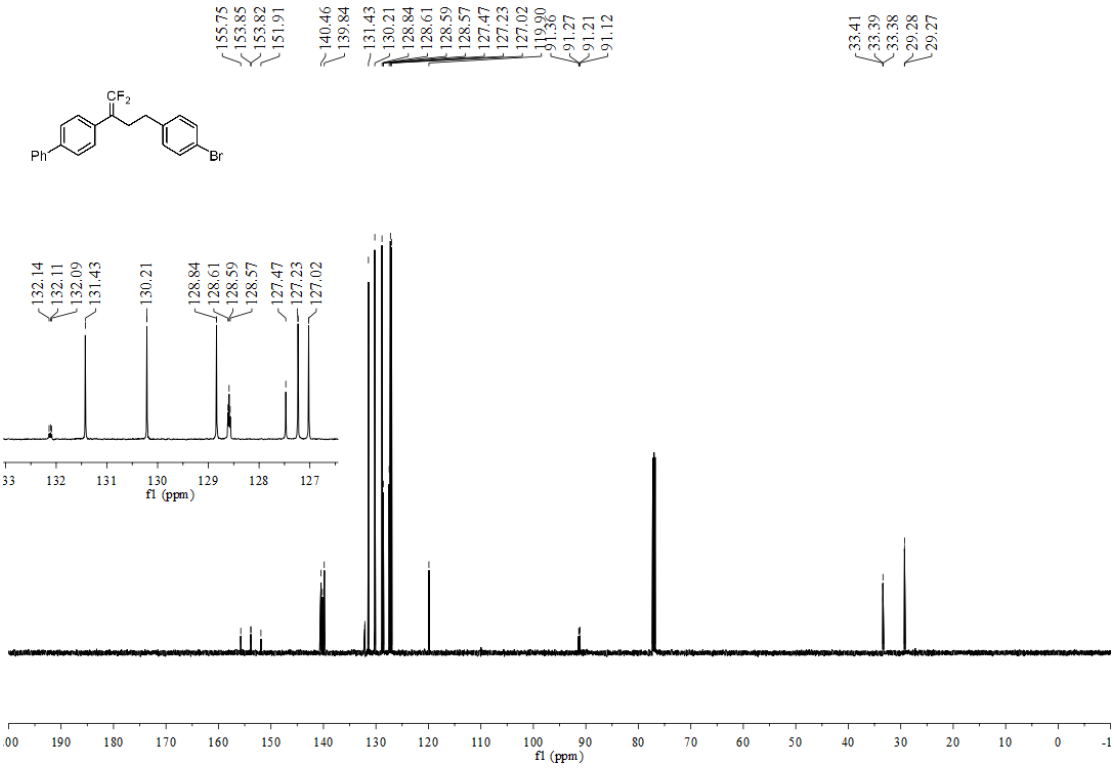
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 23



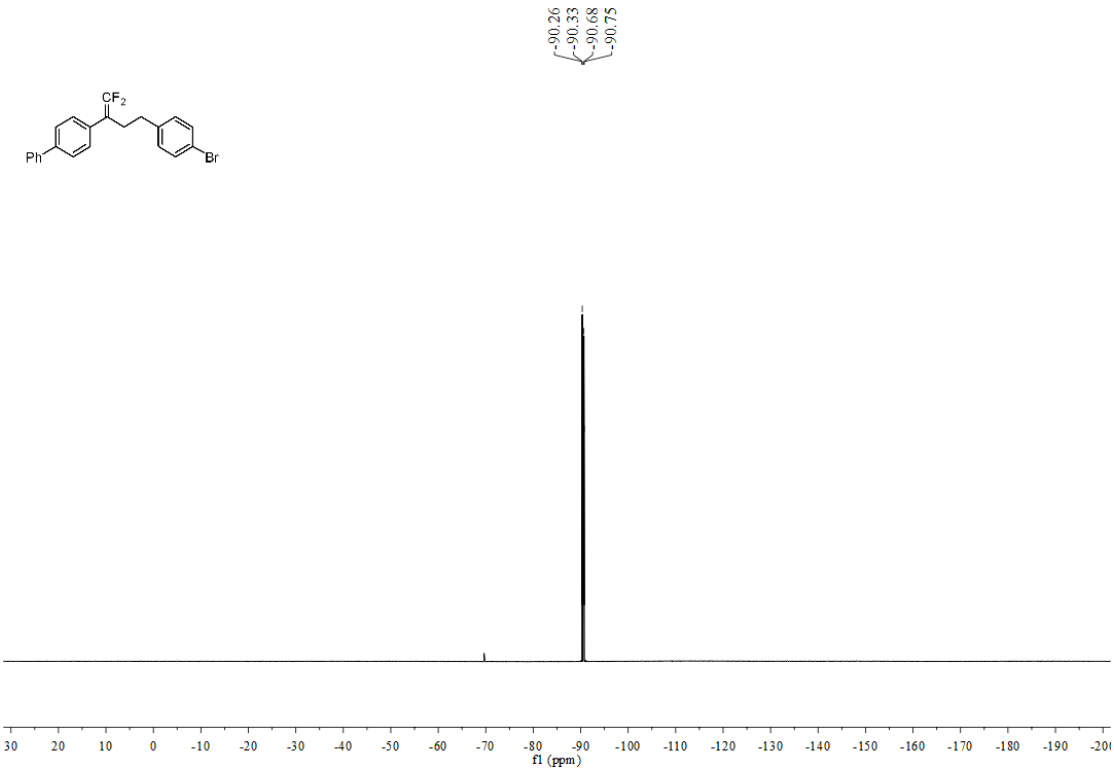
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 24



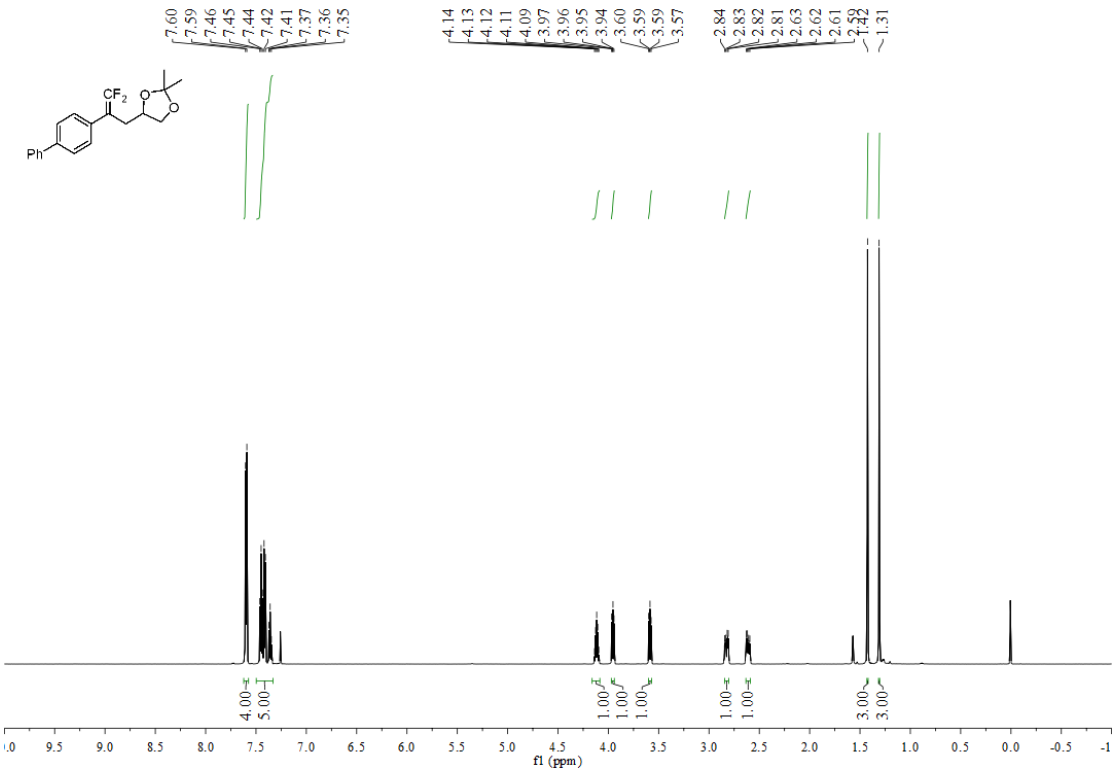
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 24



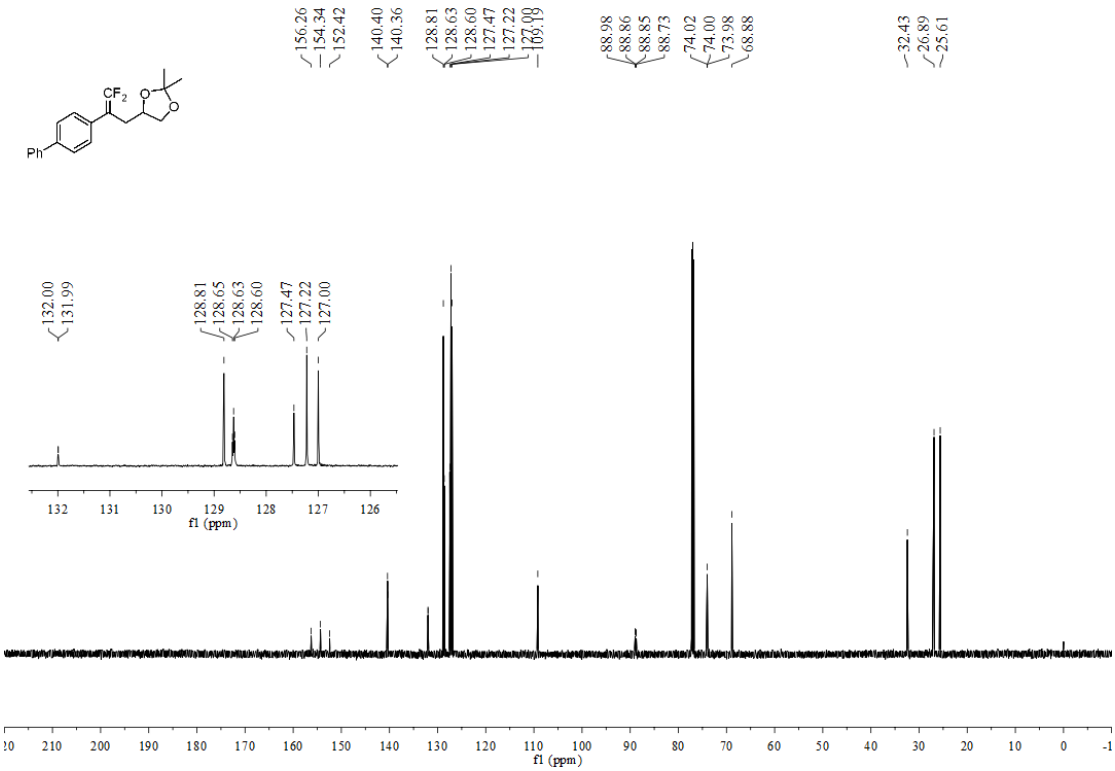
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 24



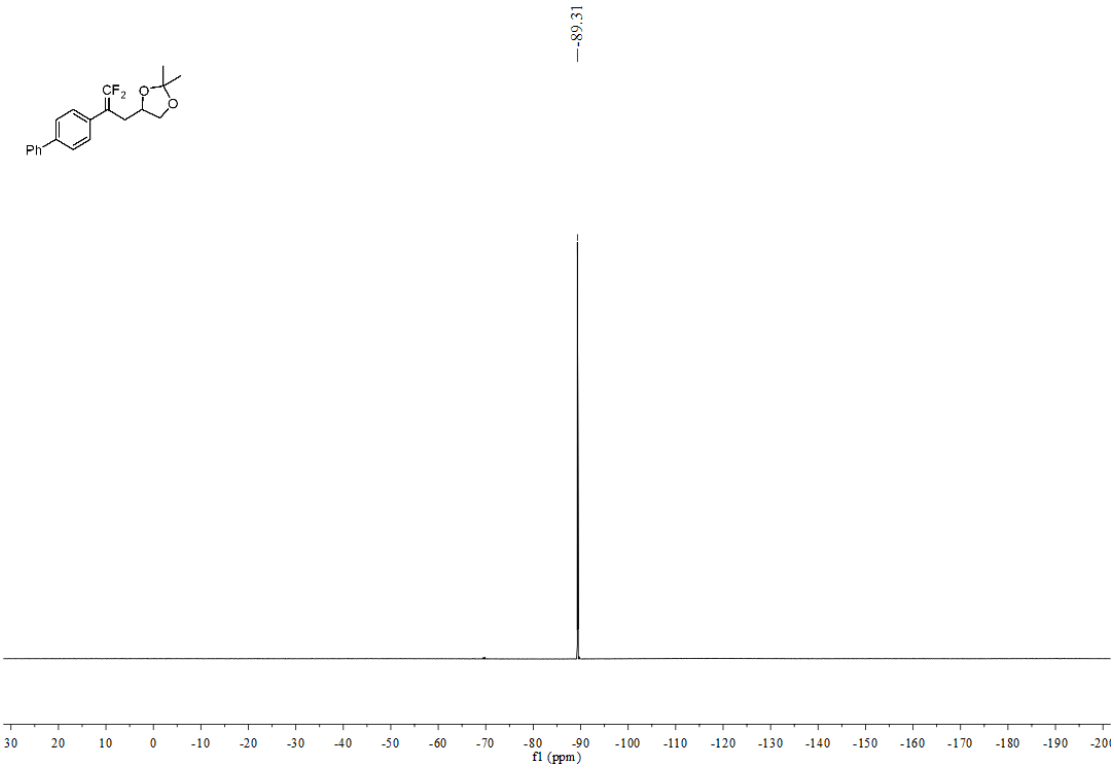
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 25



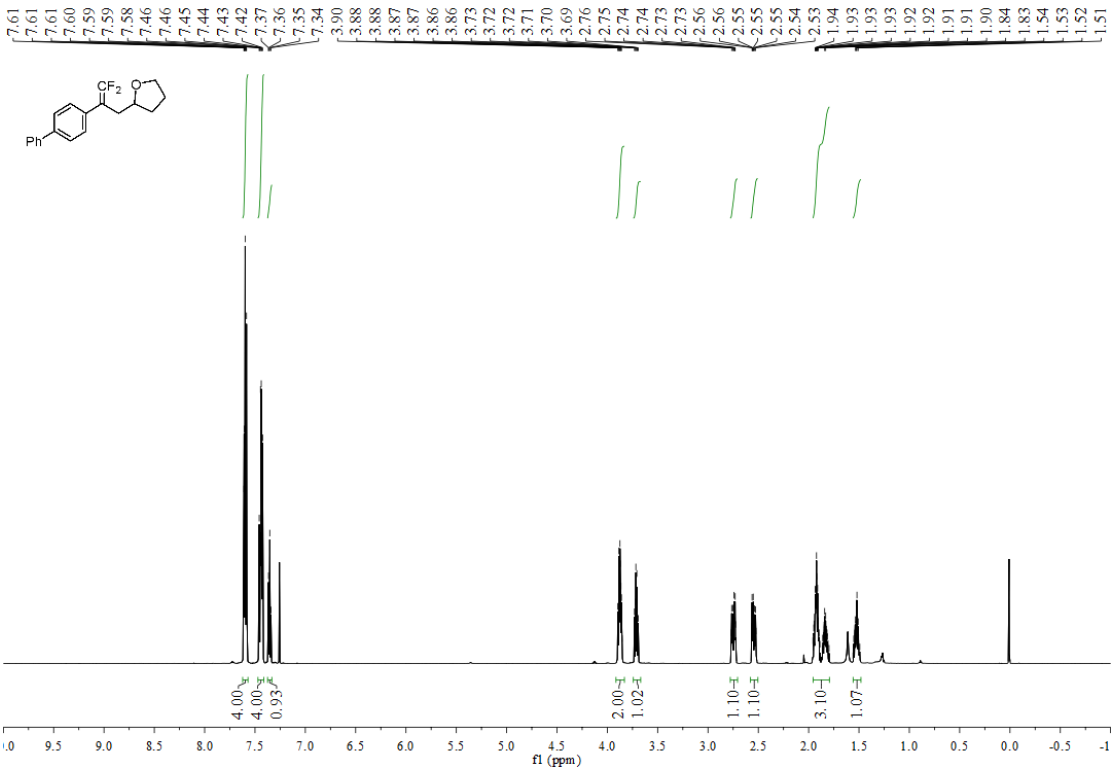
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 25



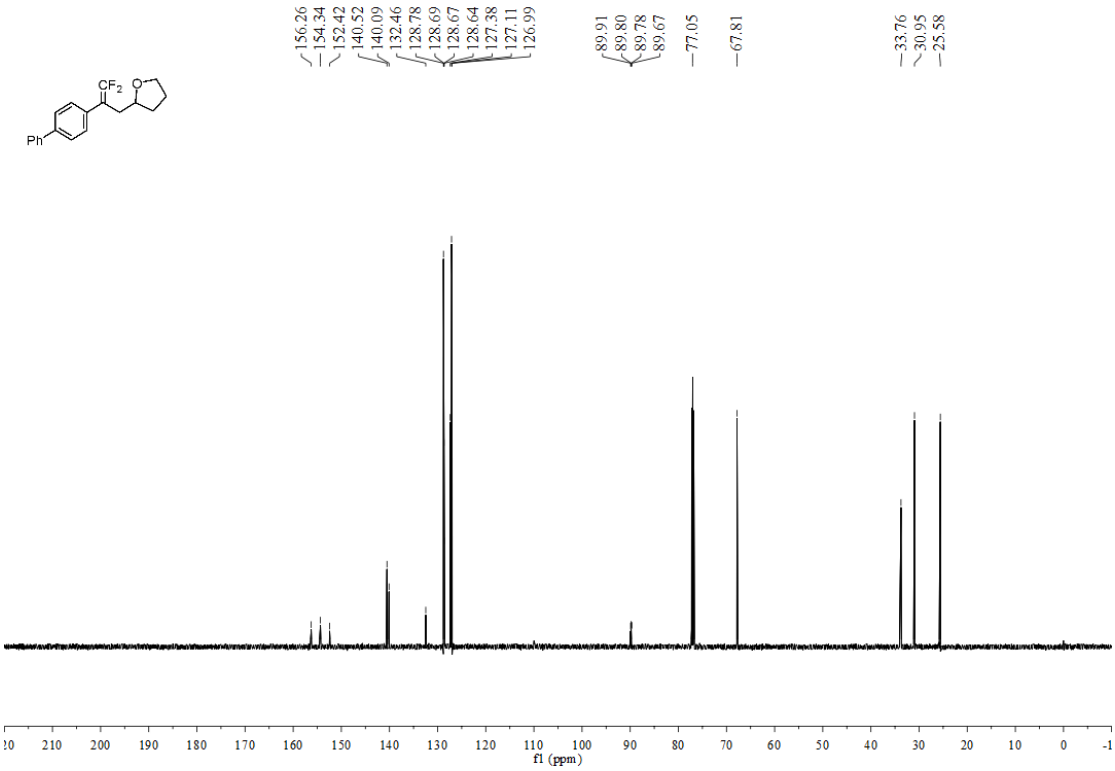
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 25



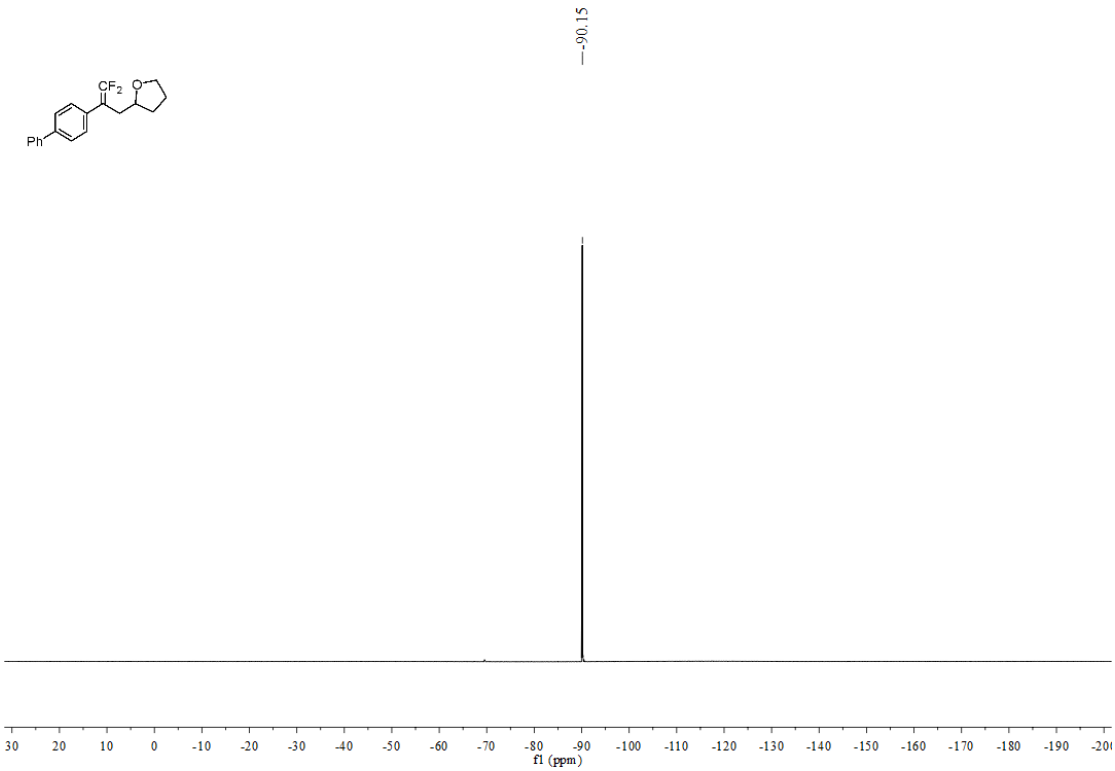
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 26



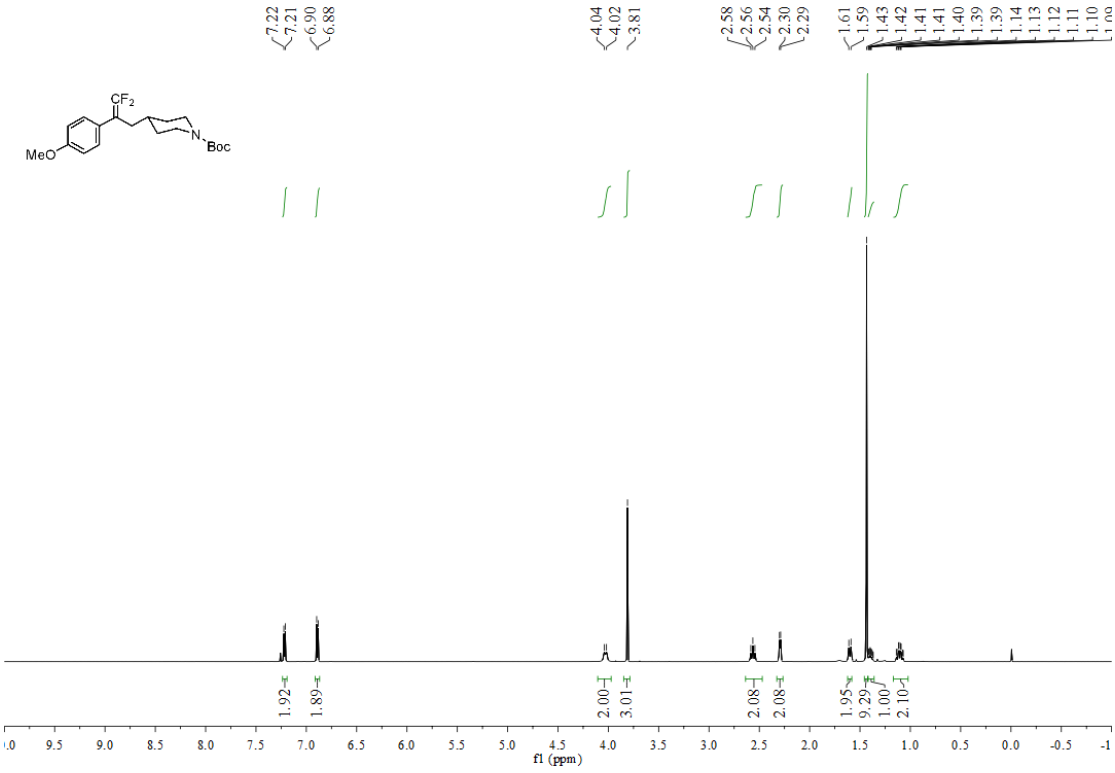
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 26



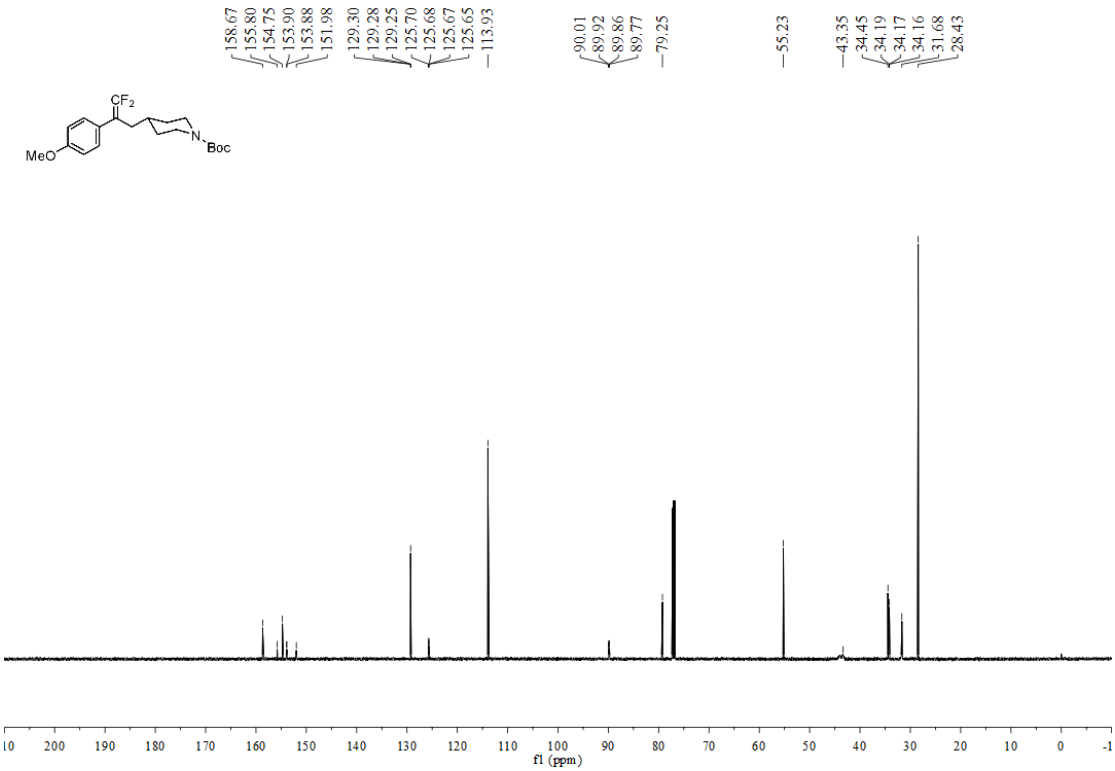
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 26



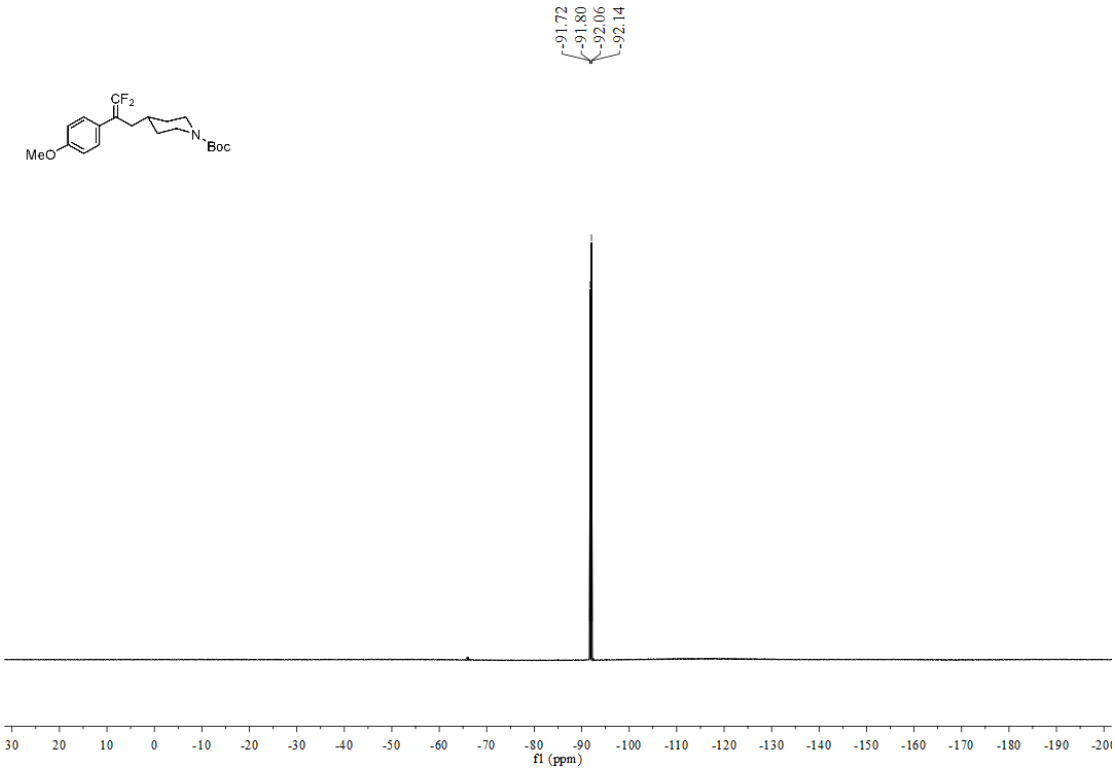
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 27



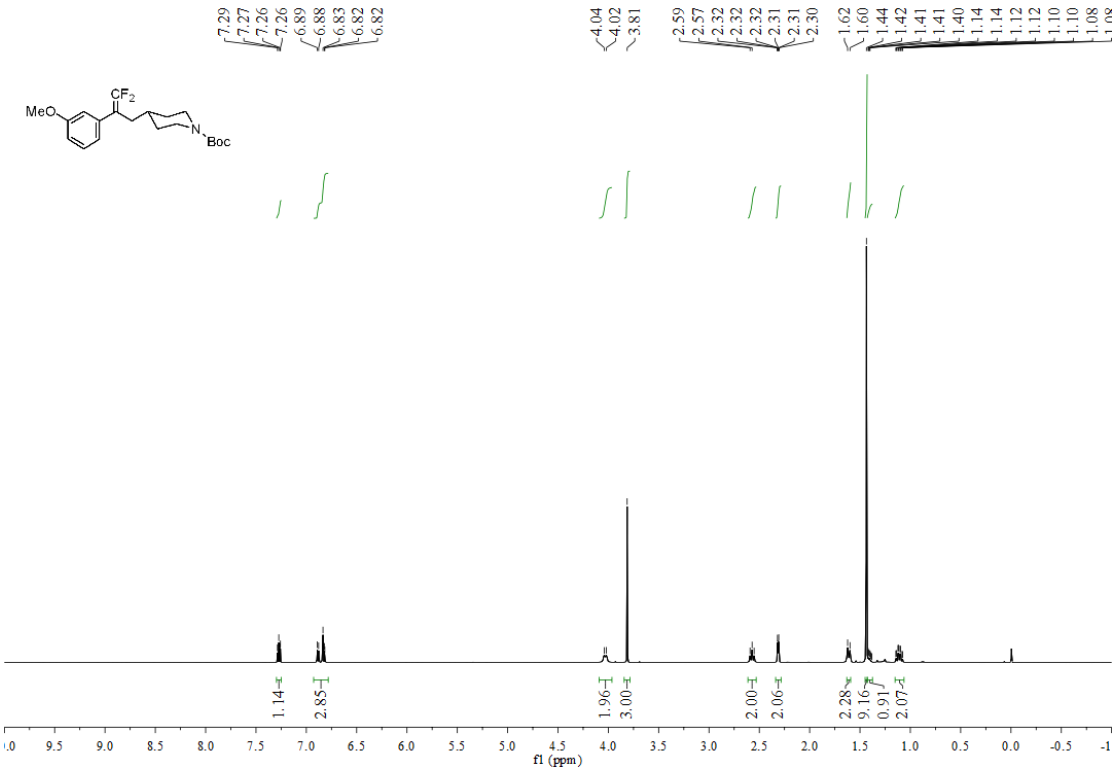
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 27



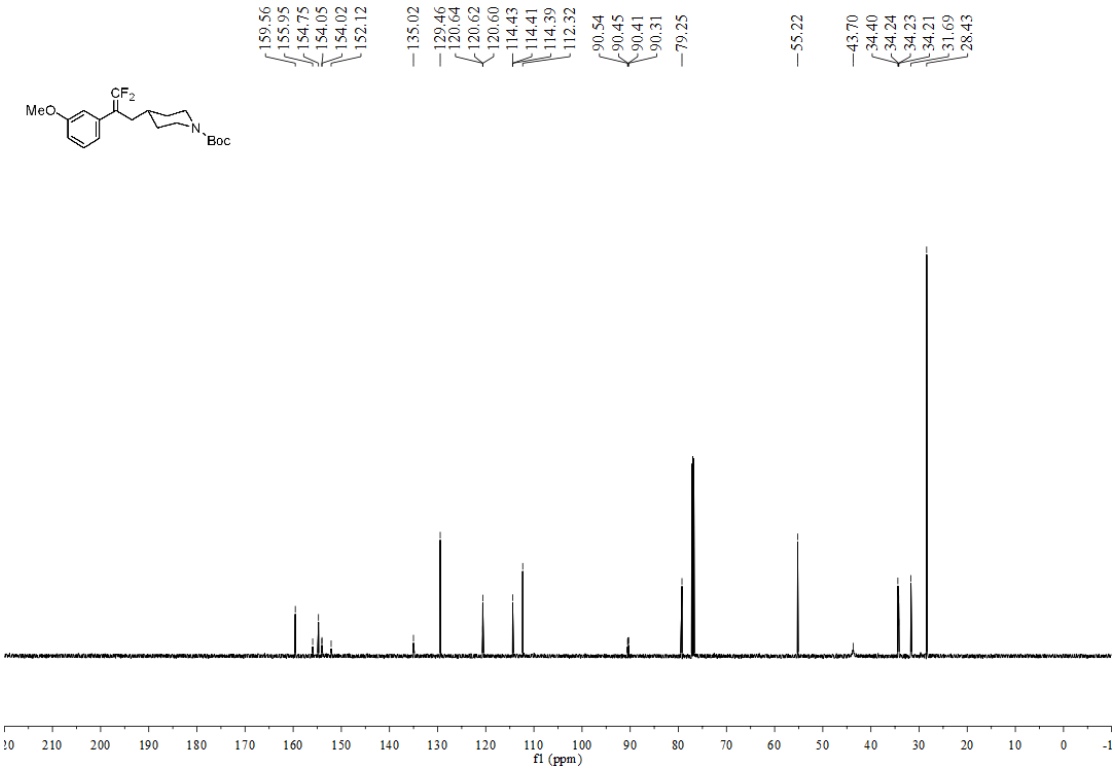
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 27



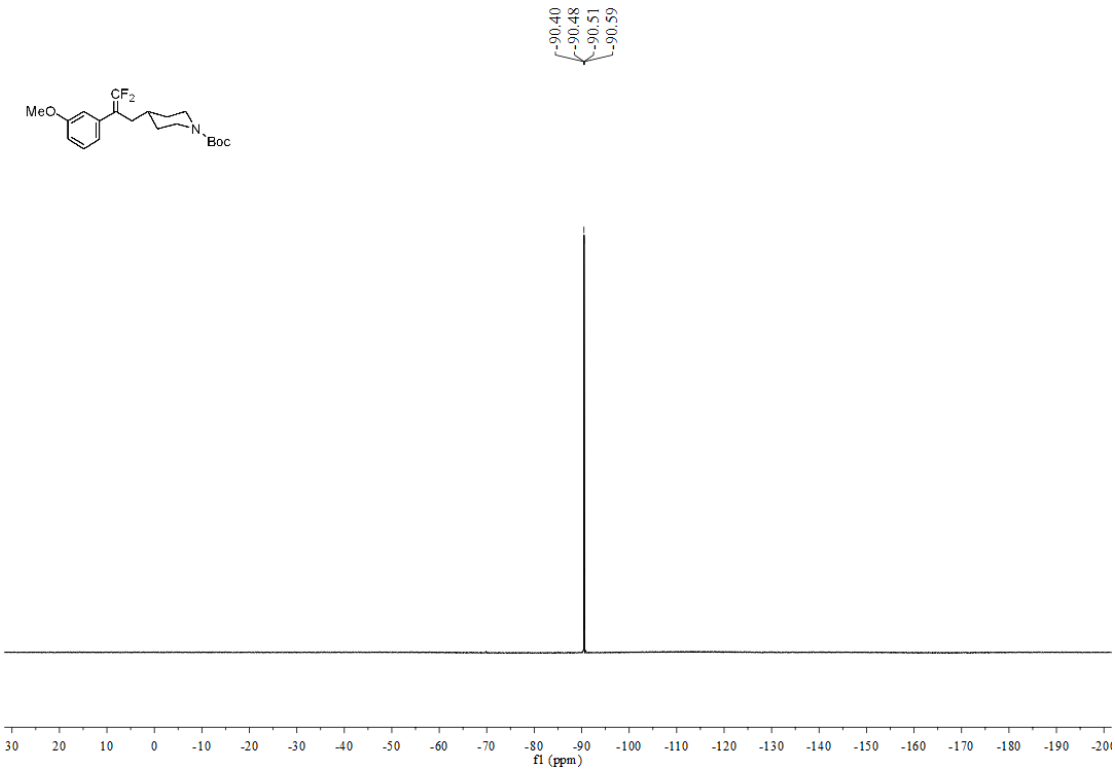
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 28



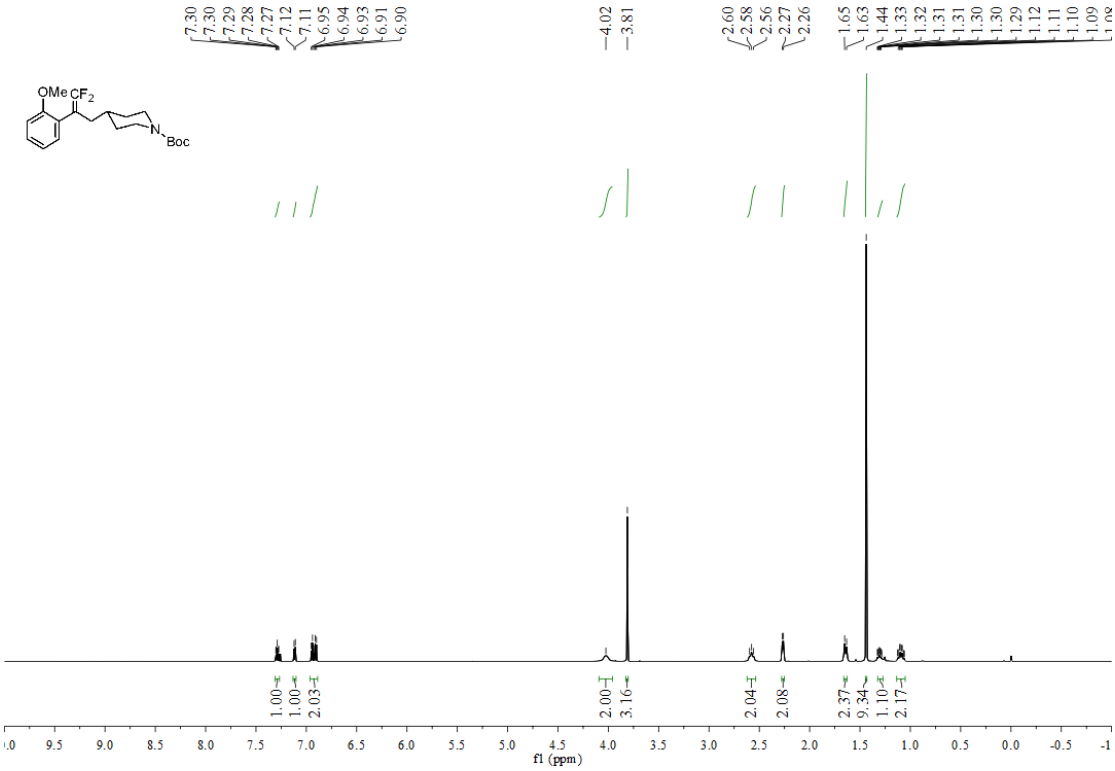
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 28



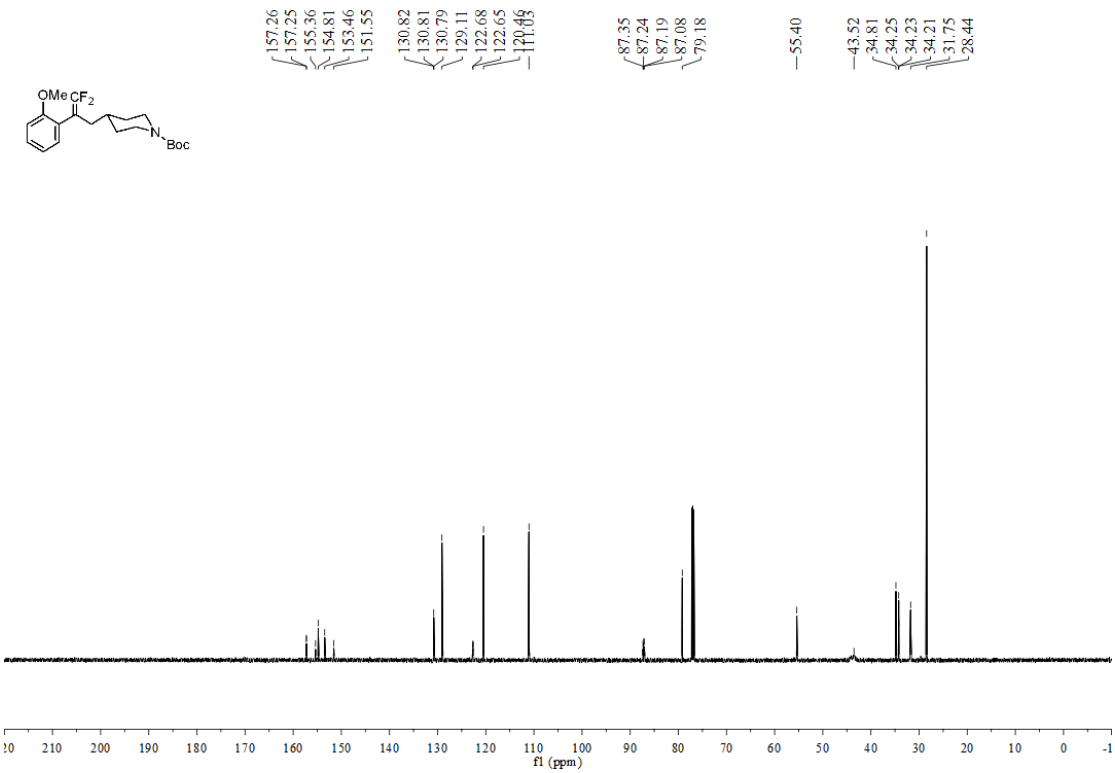
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 28



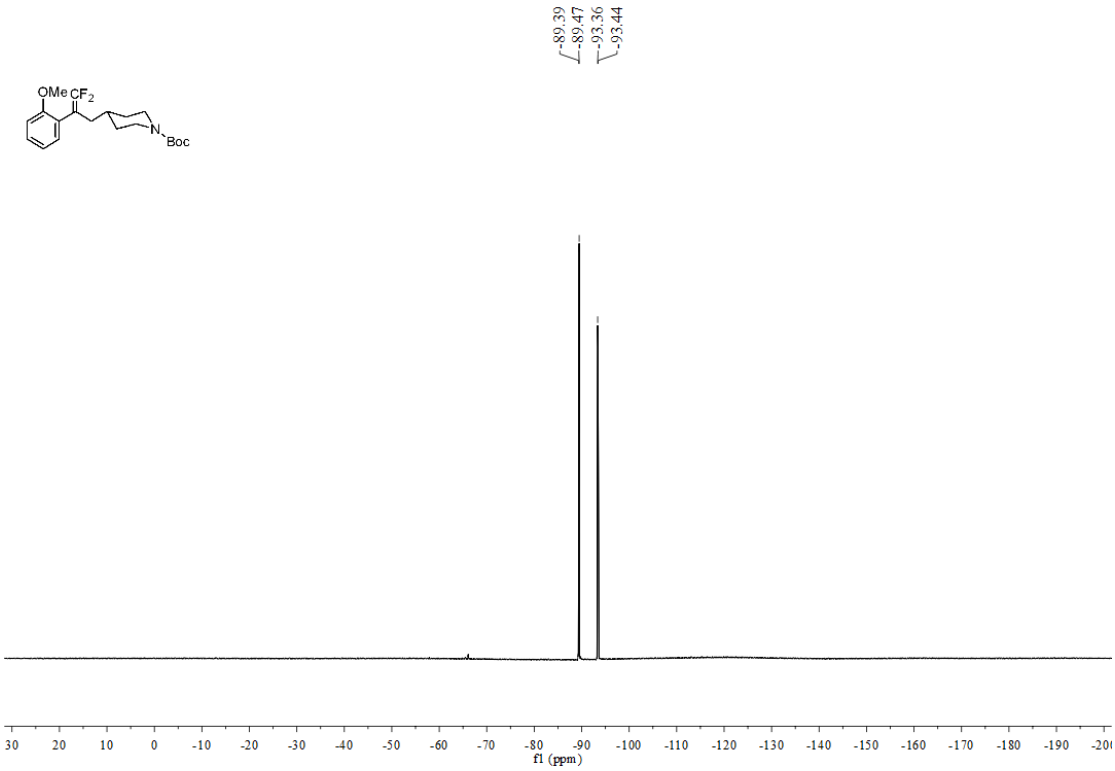
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 29



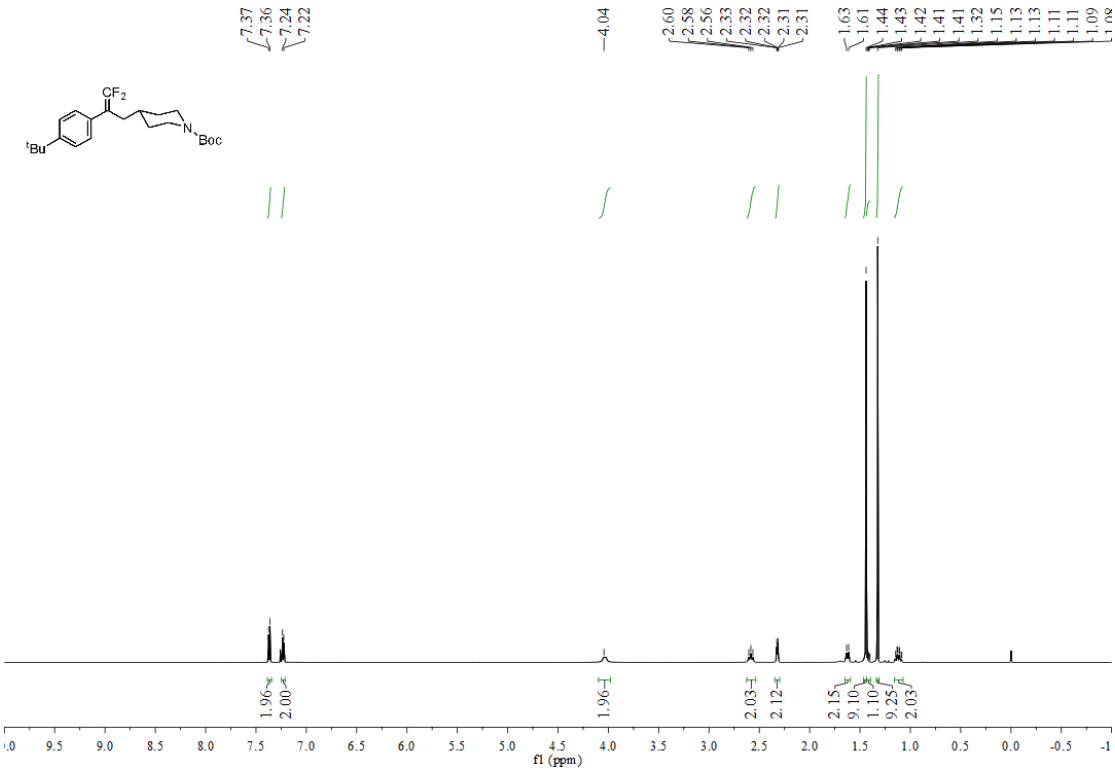
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 29



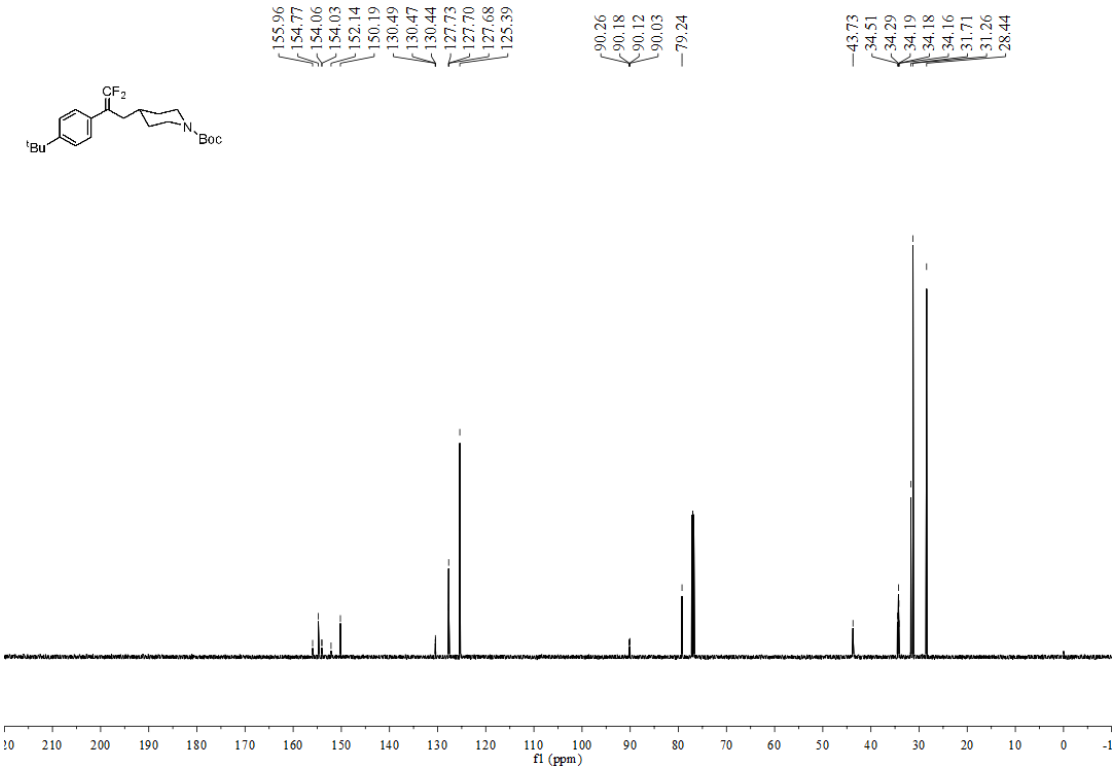
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 29



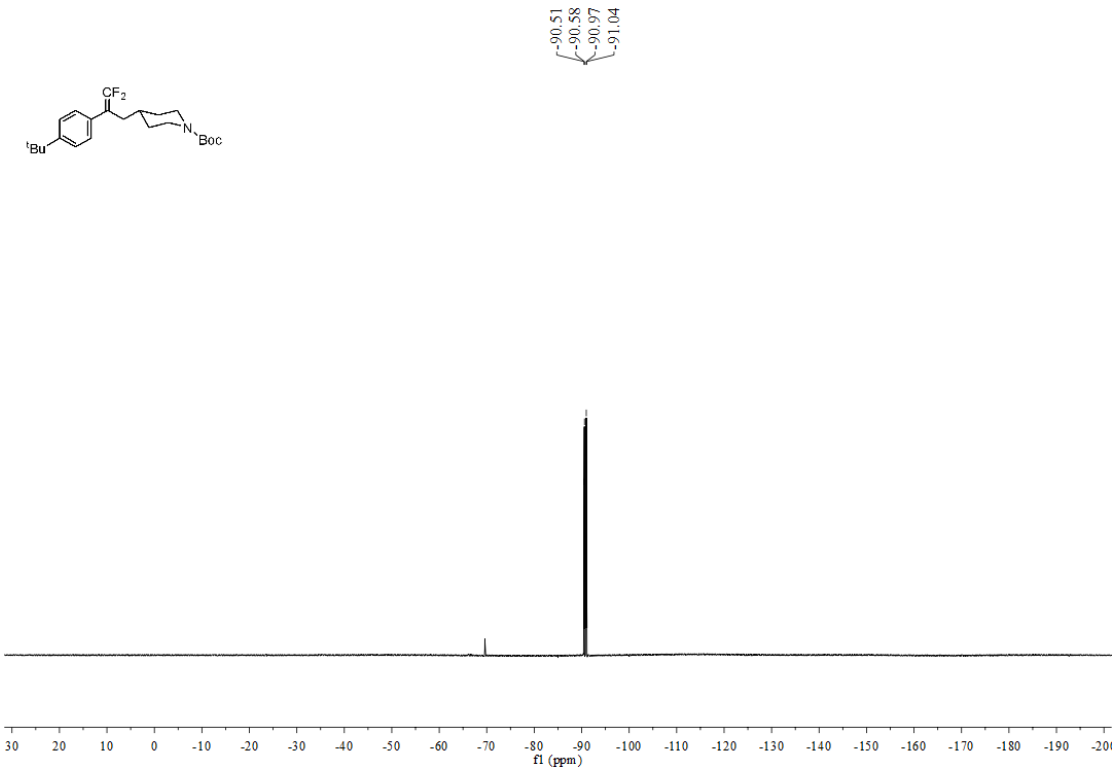
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 30



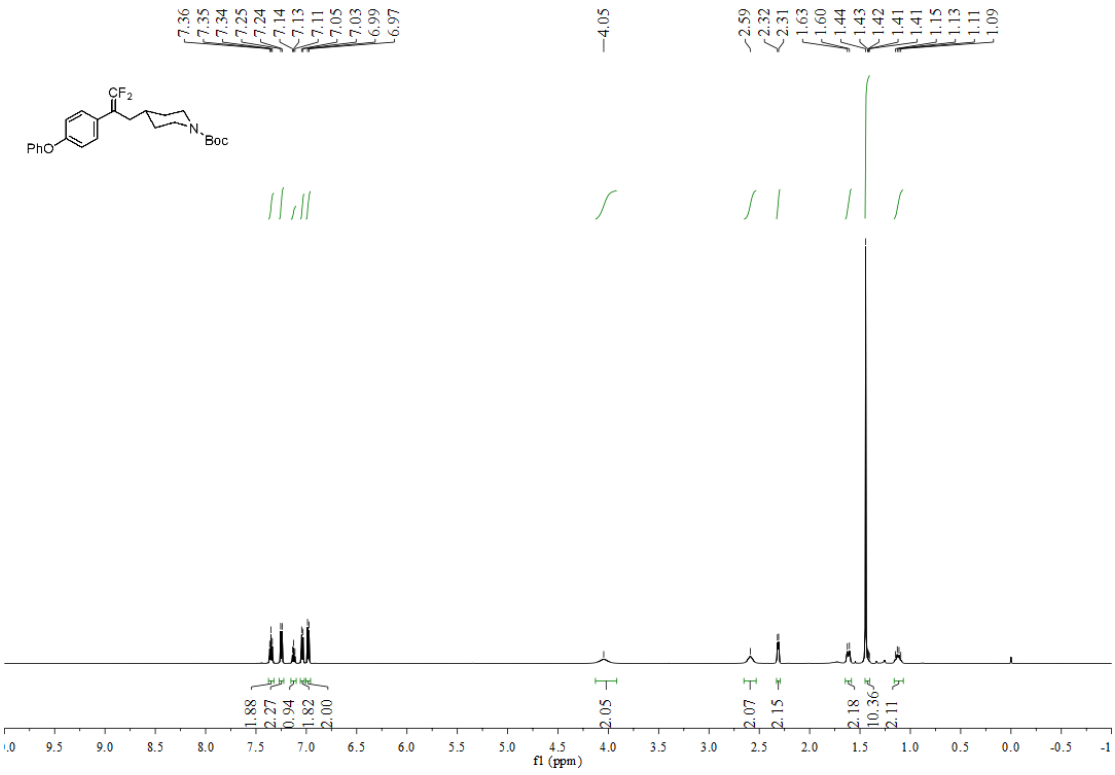
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 30



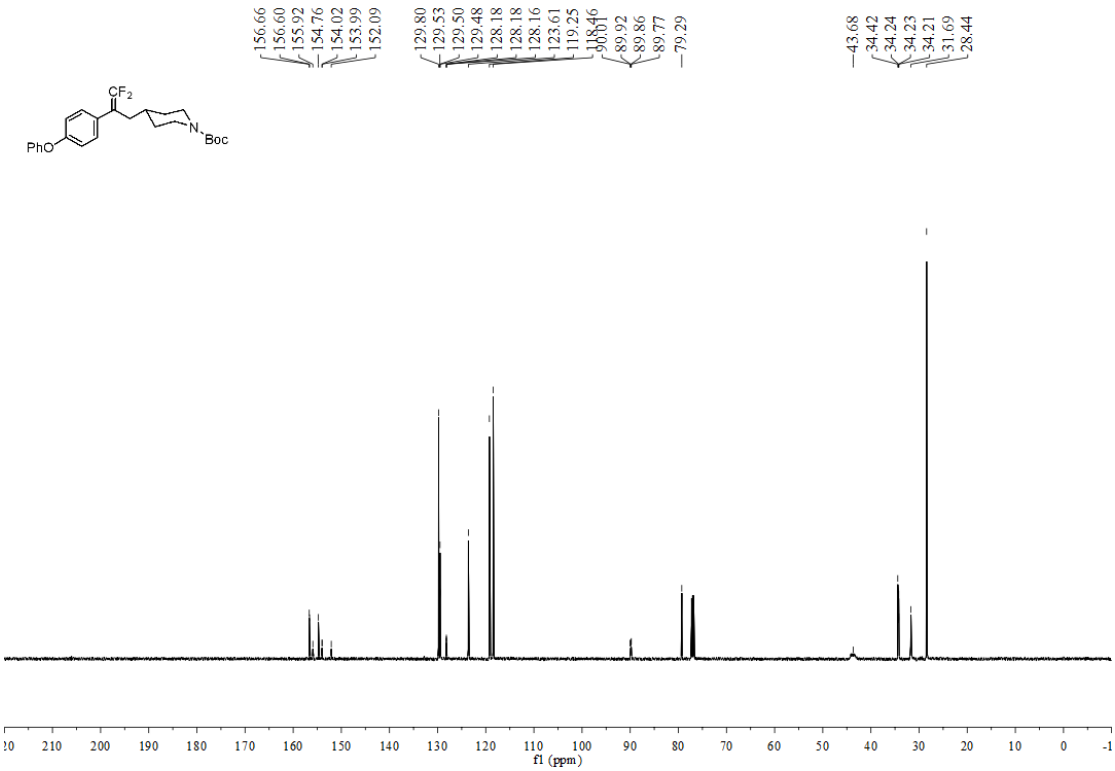
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 30



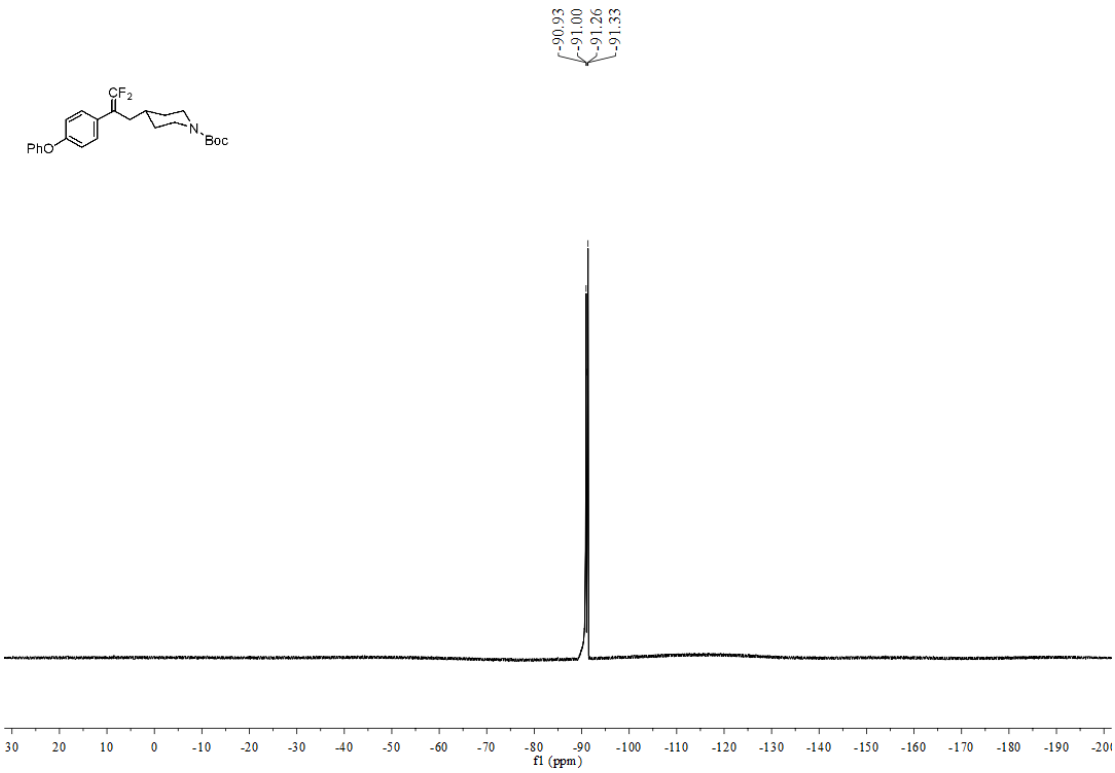
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 31



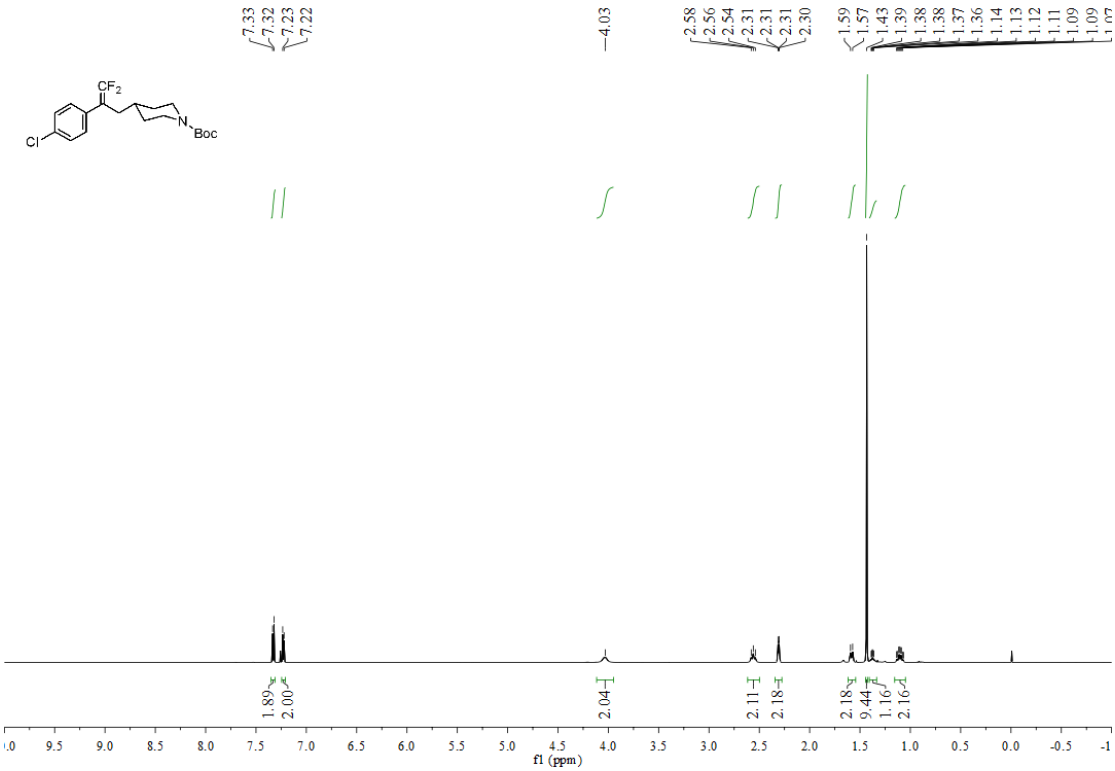
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 31



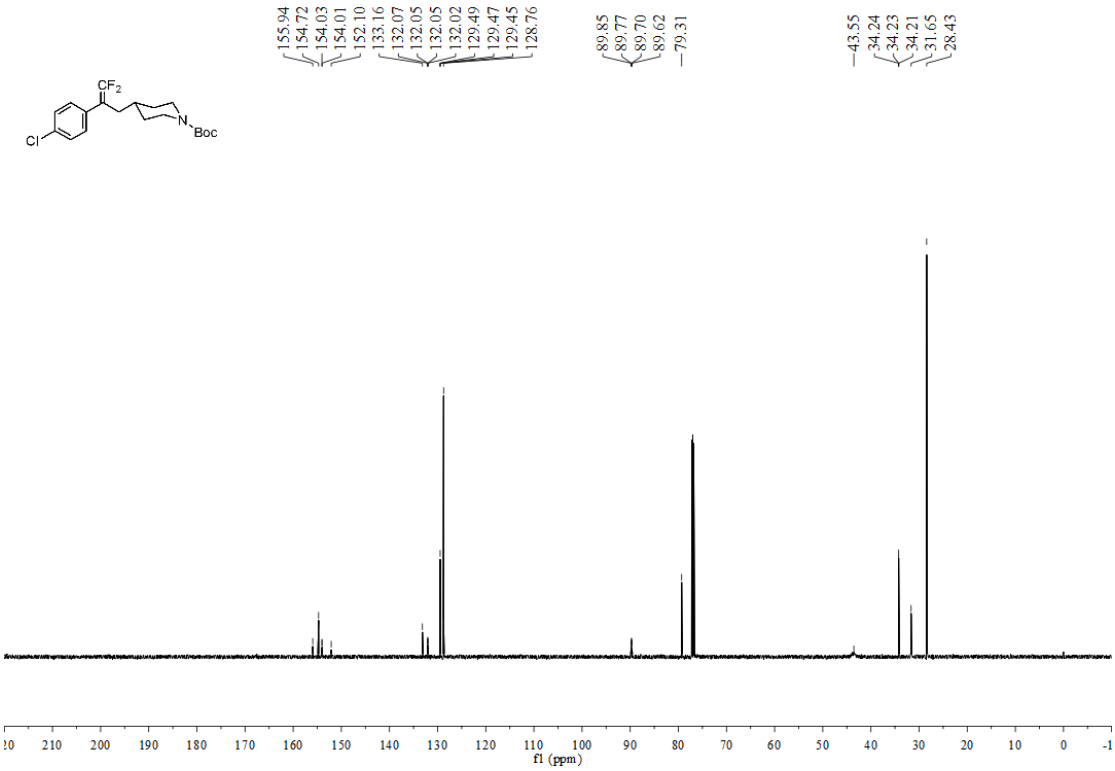
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 31



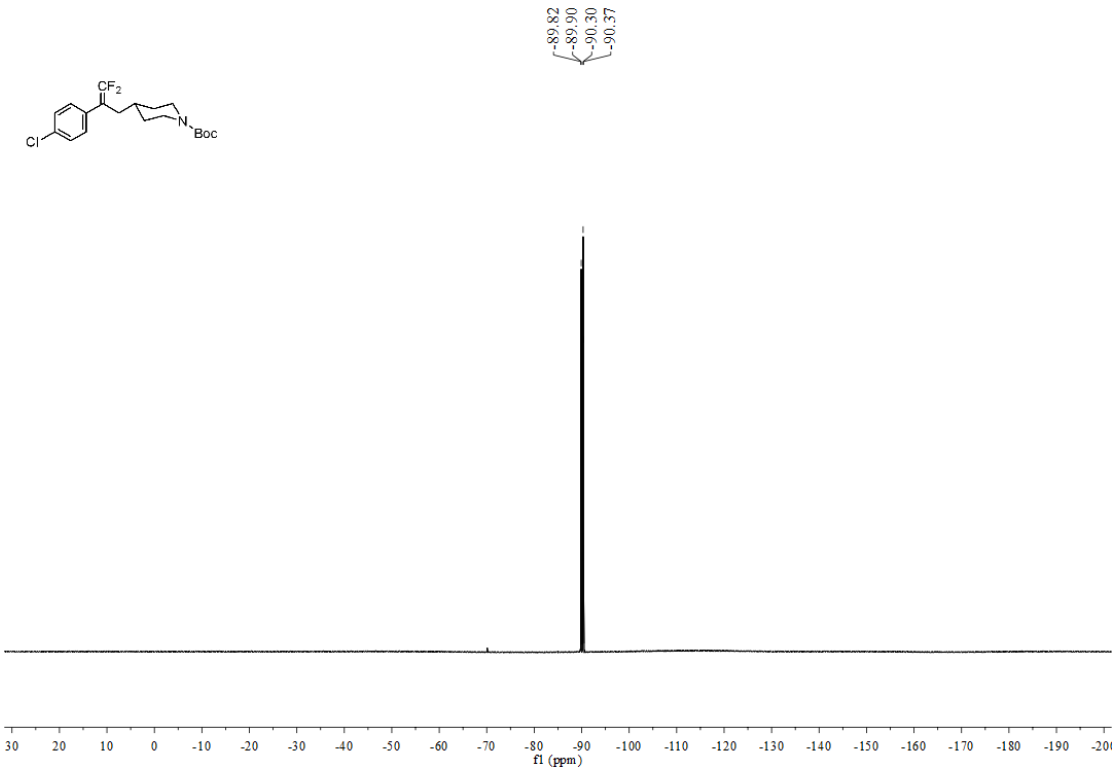
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 31



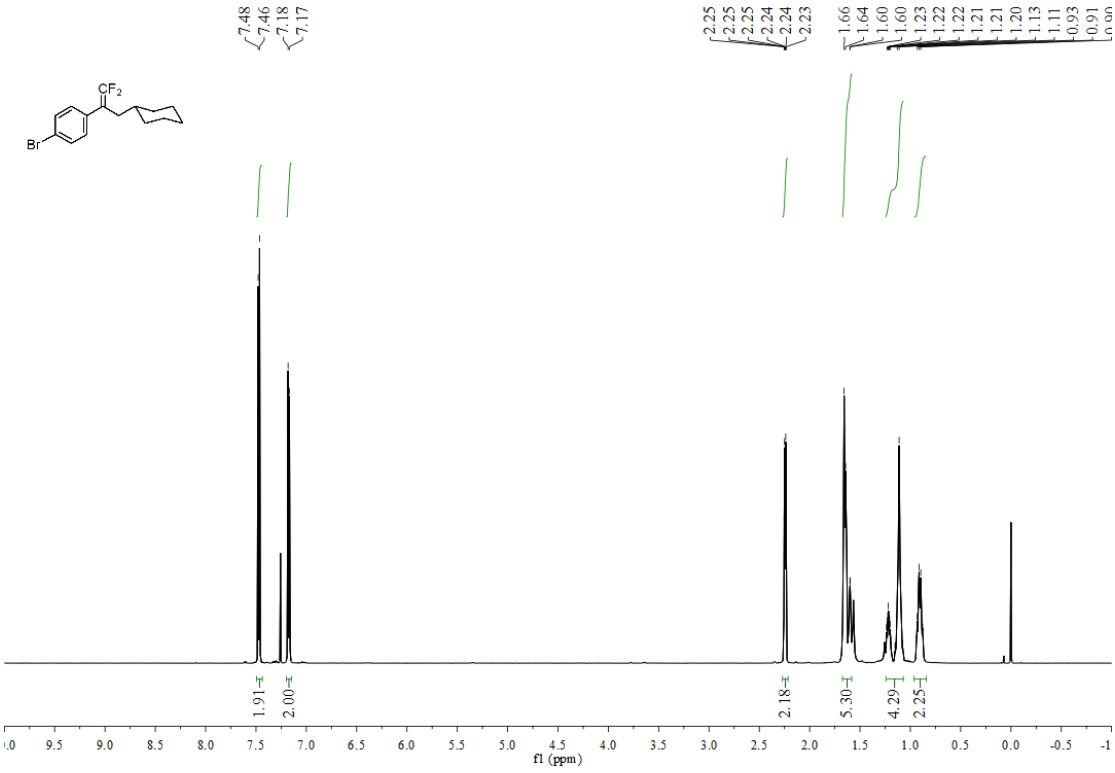
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 32



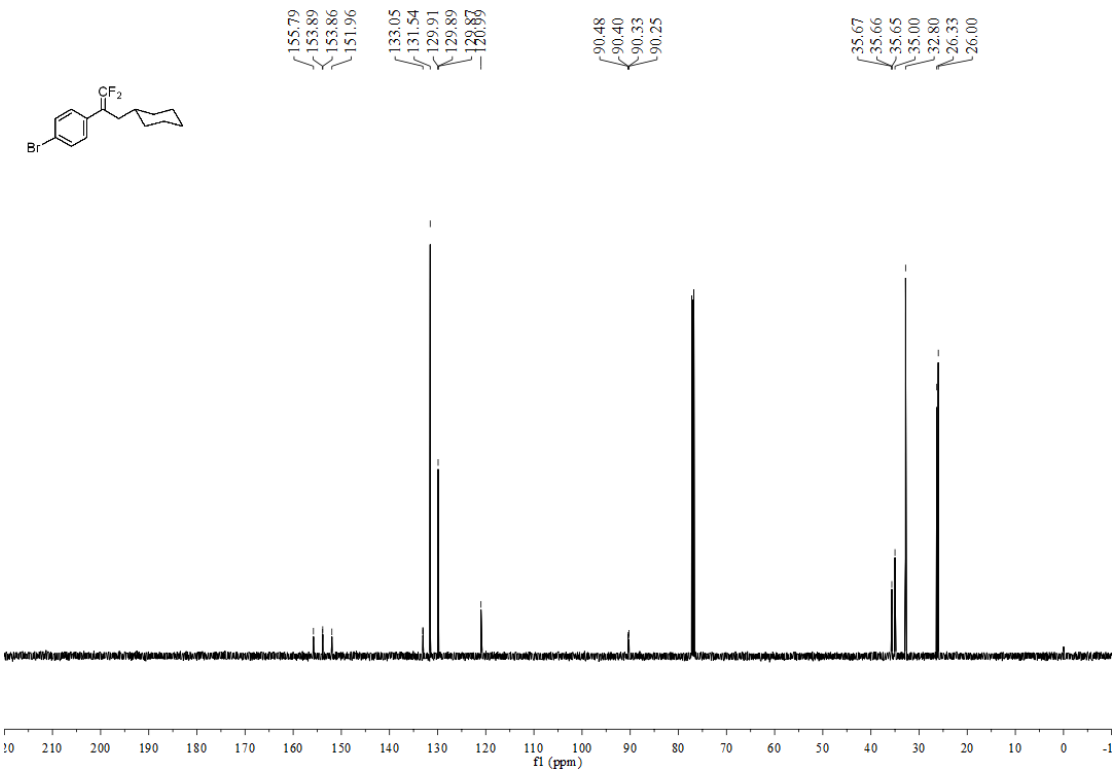
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 32



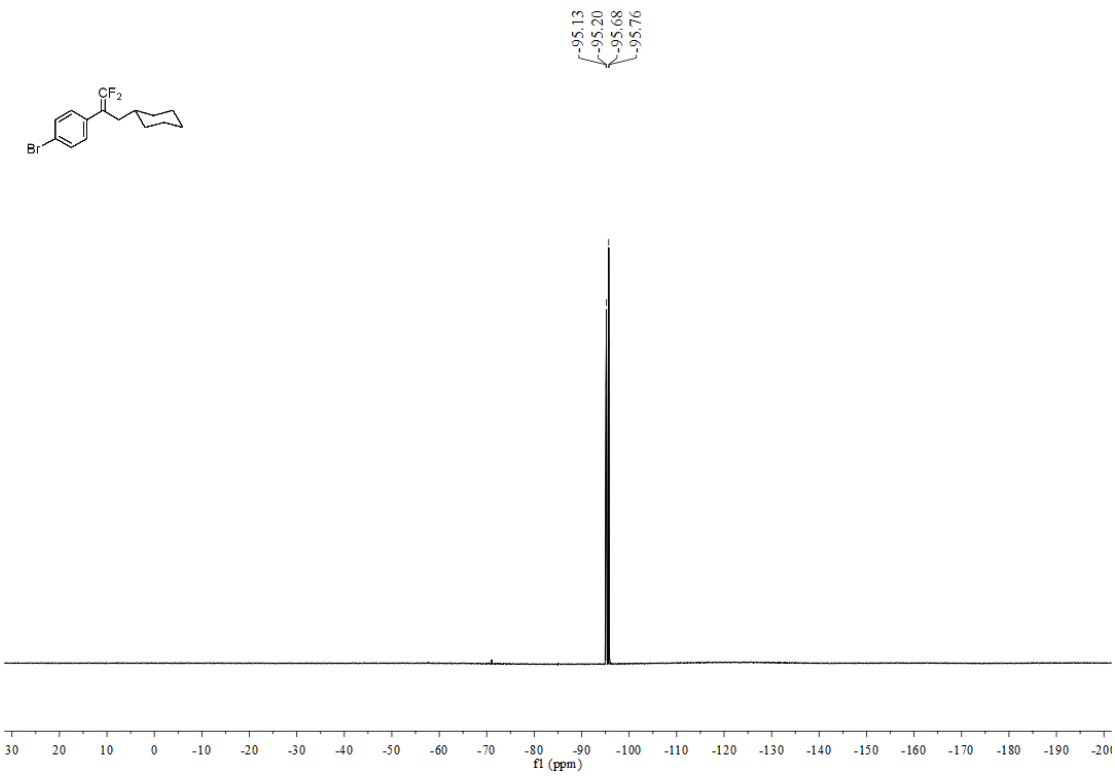
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 33



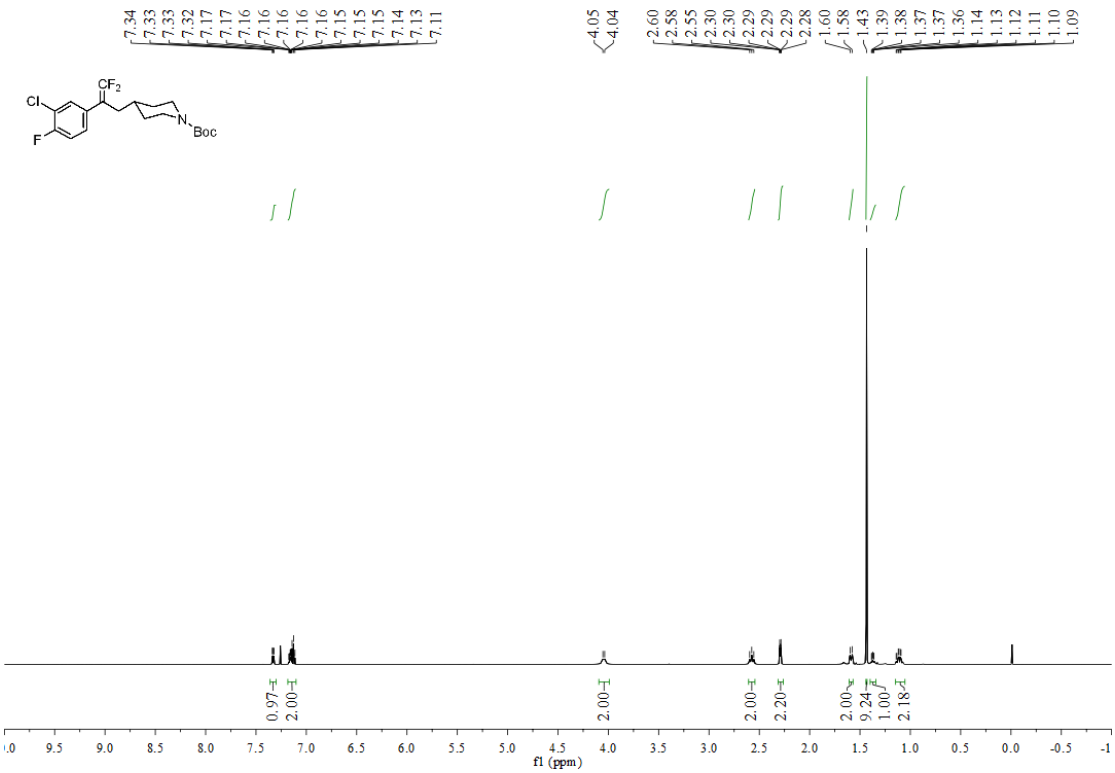
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 33



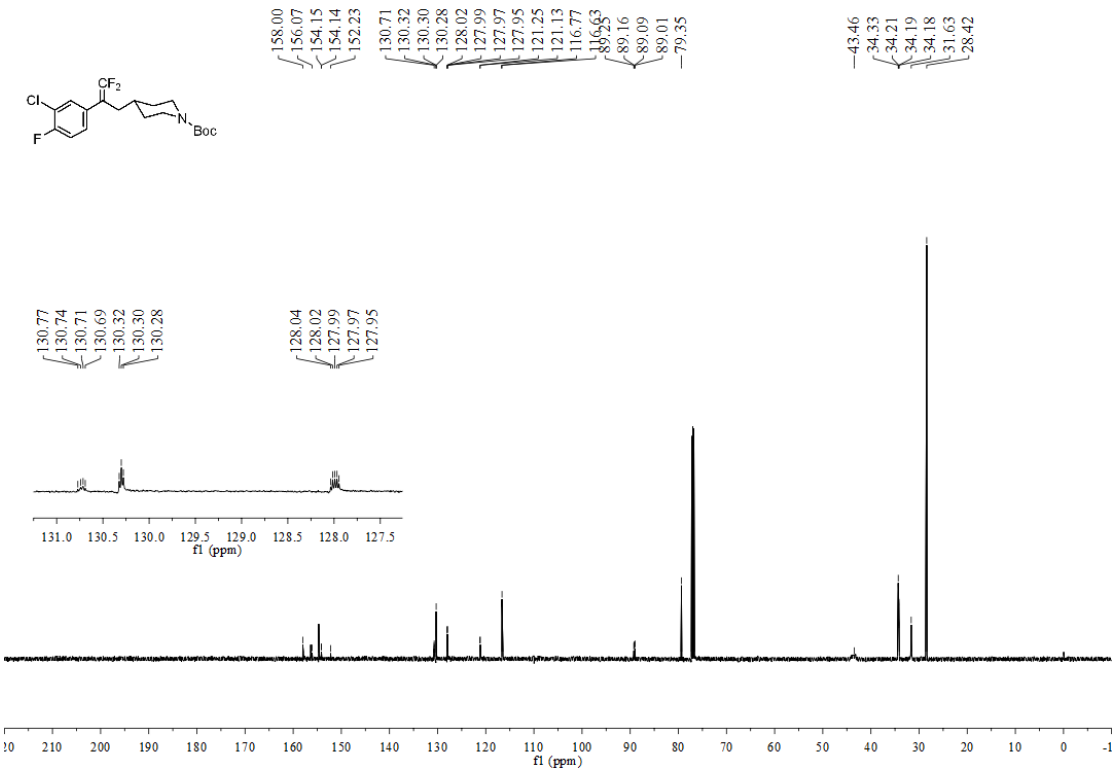
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 33



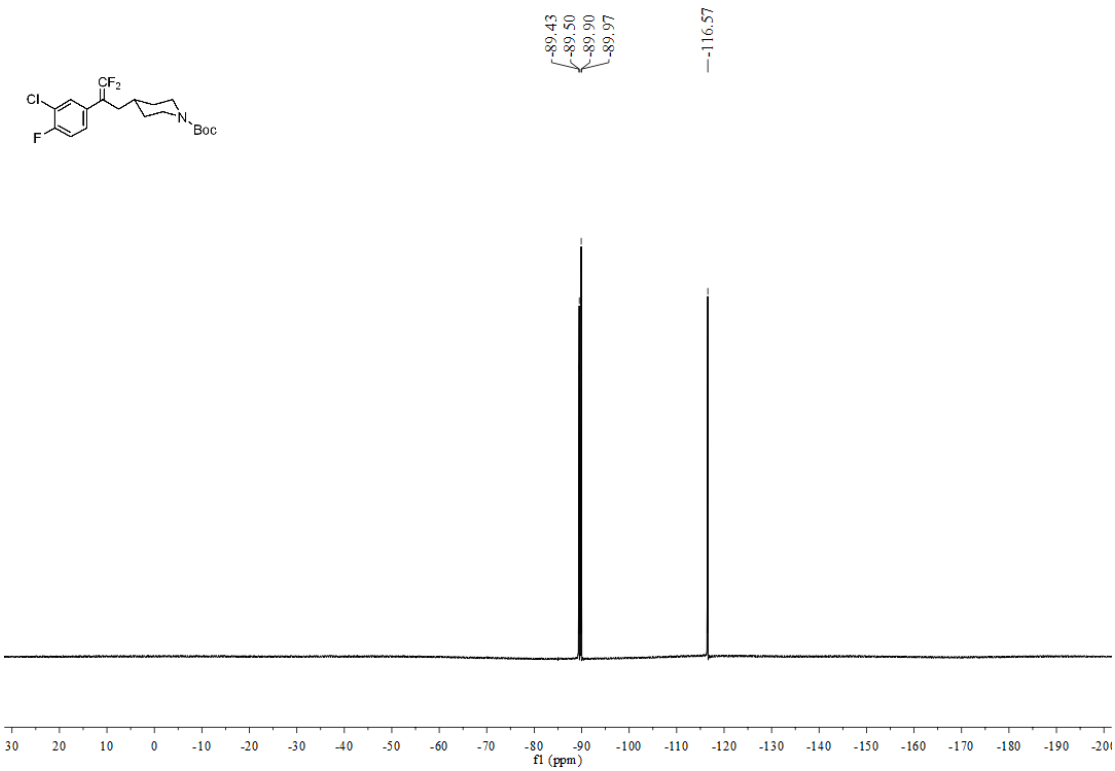
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 34



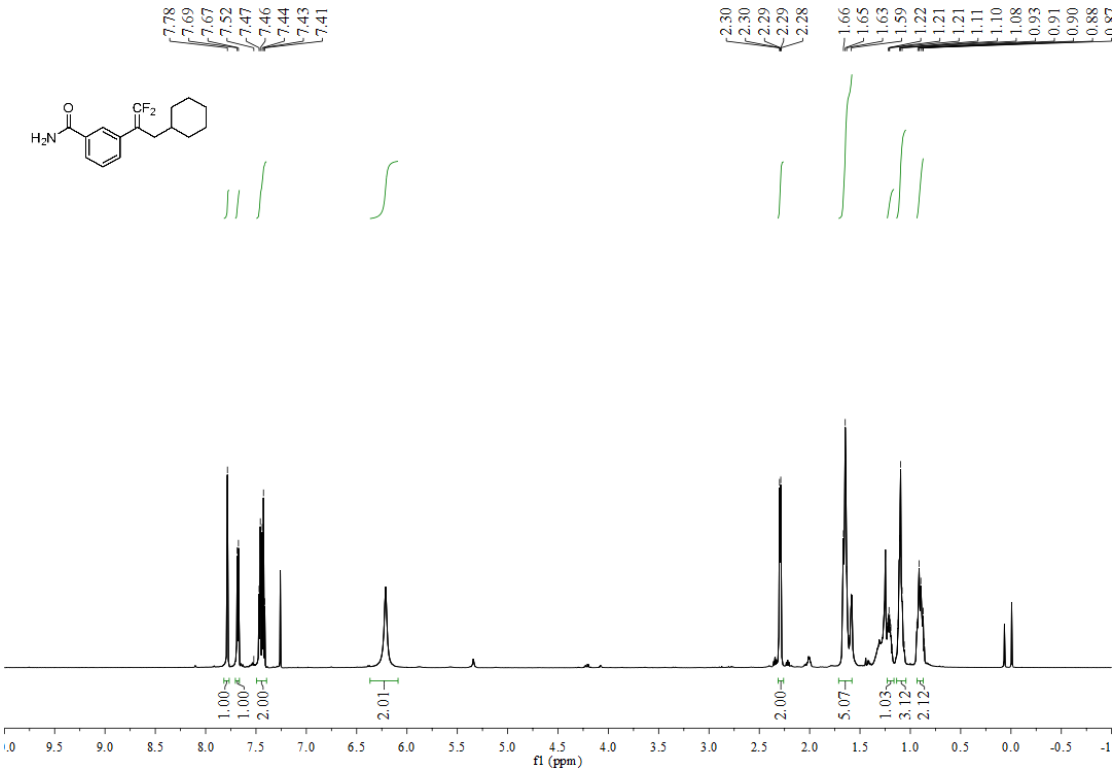
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 34



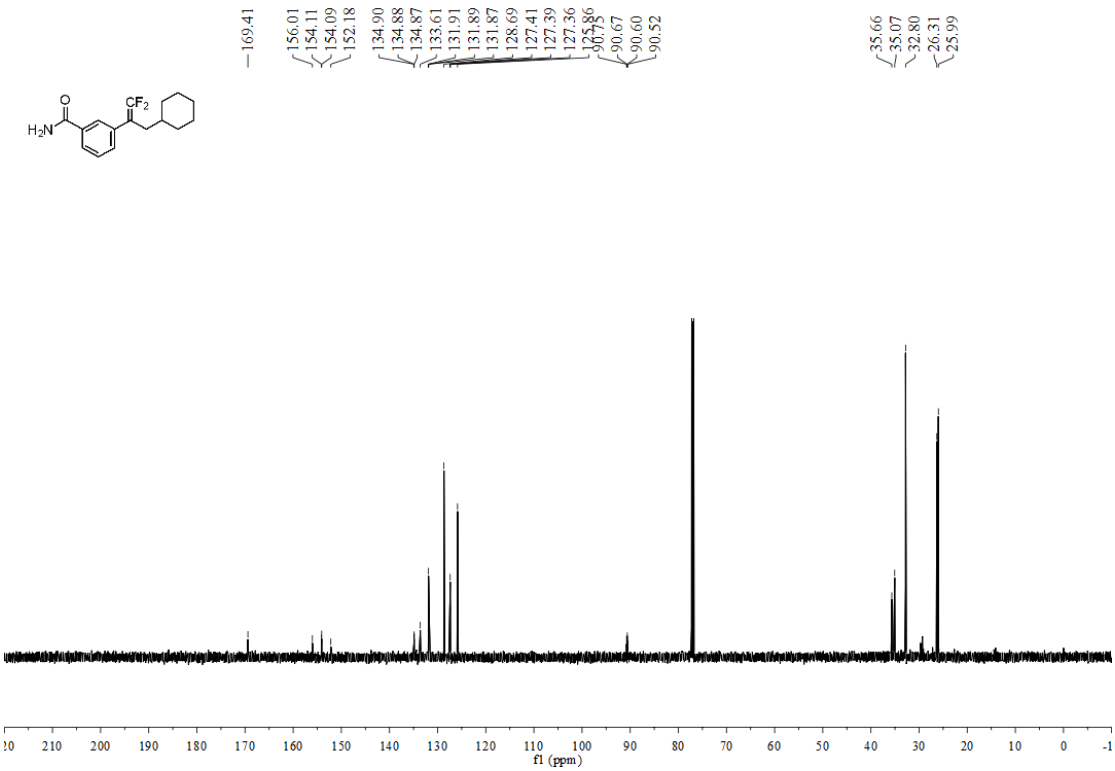
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 34



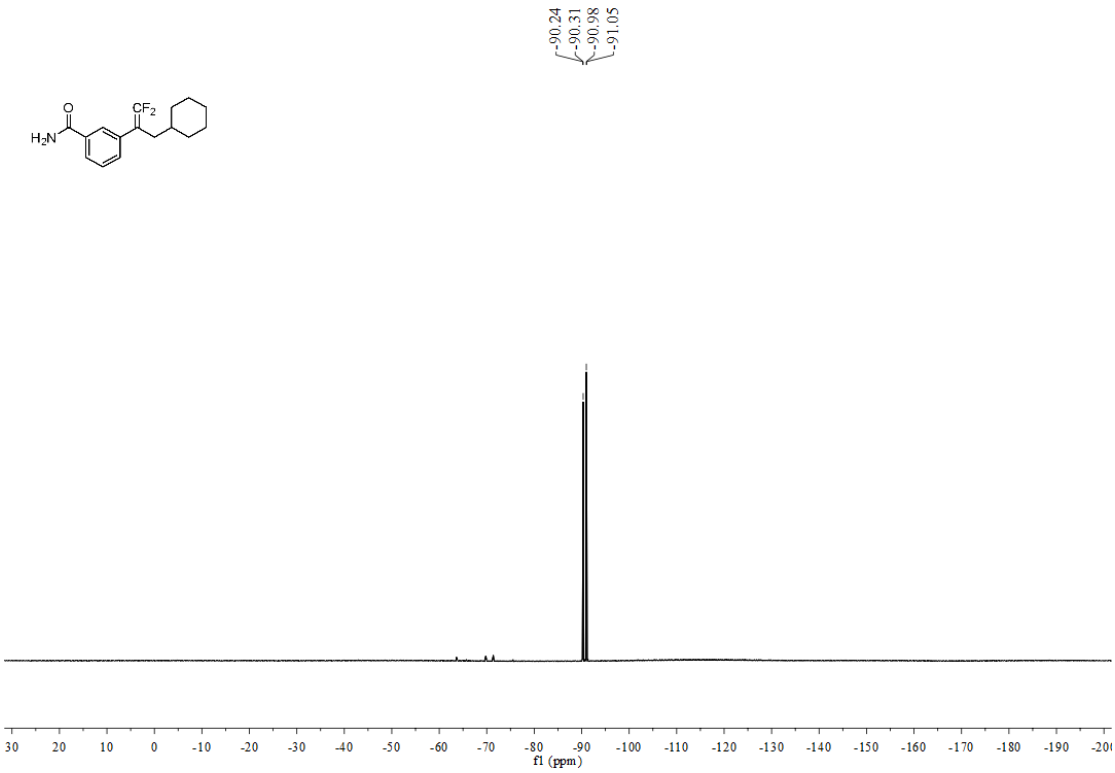
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 35



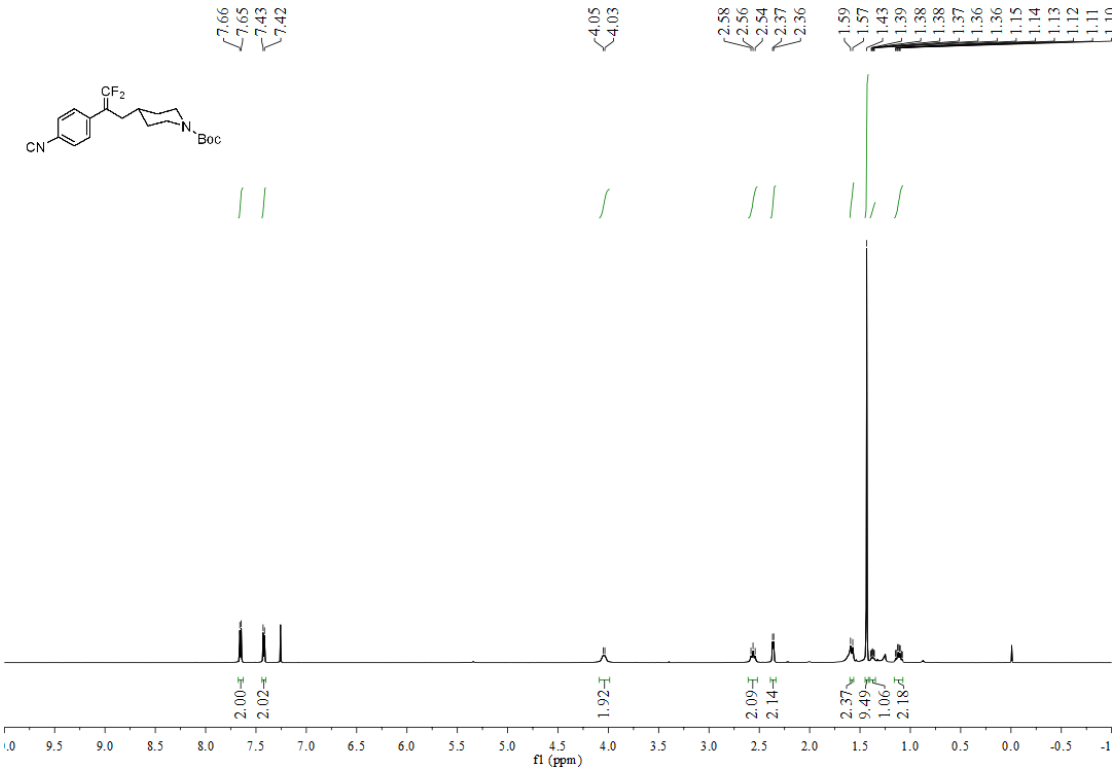
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 35



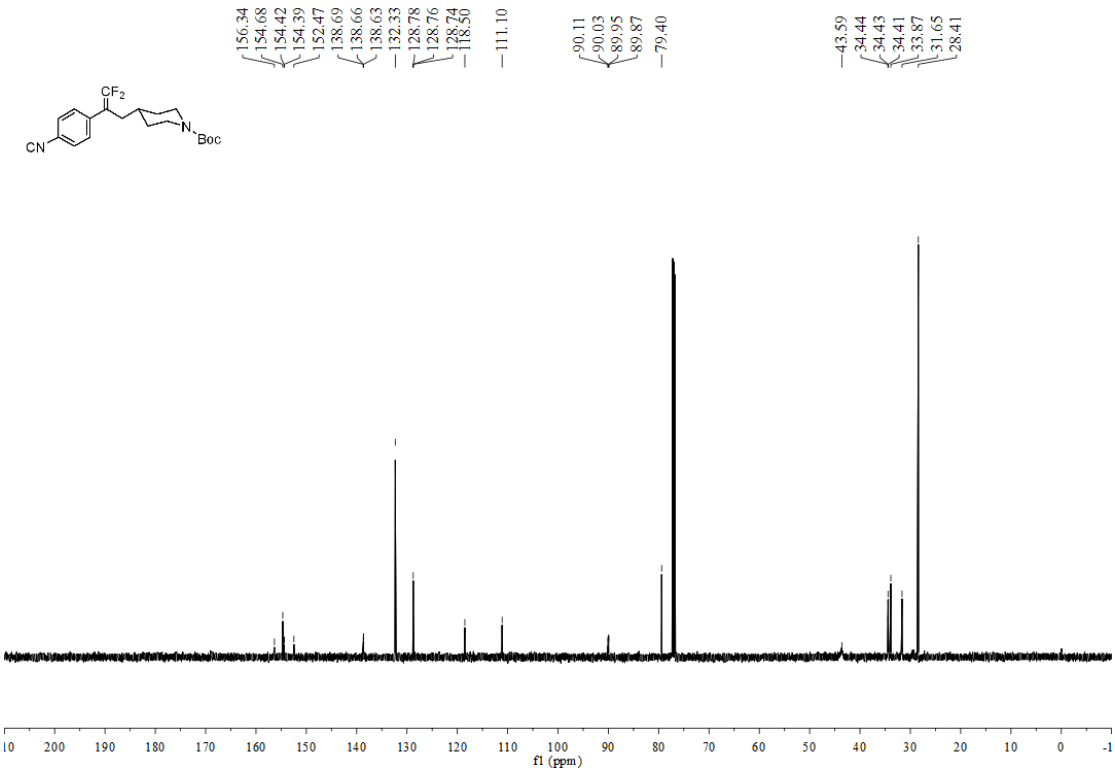
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 35



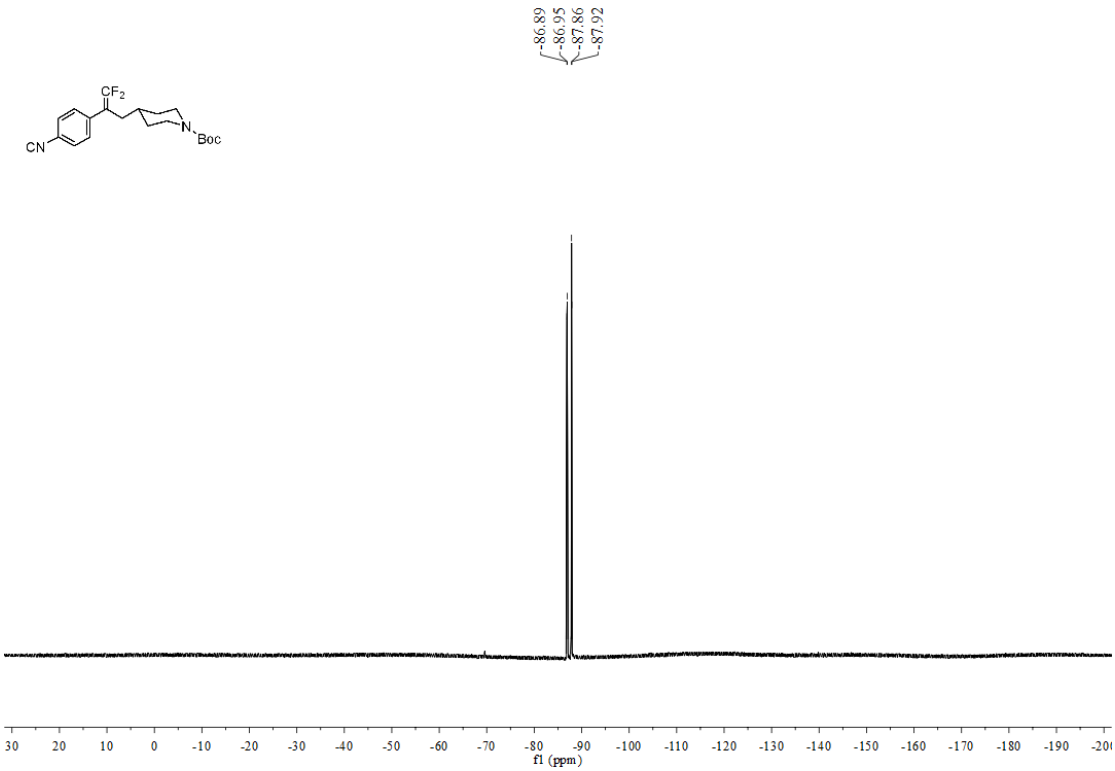
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 36



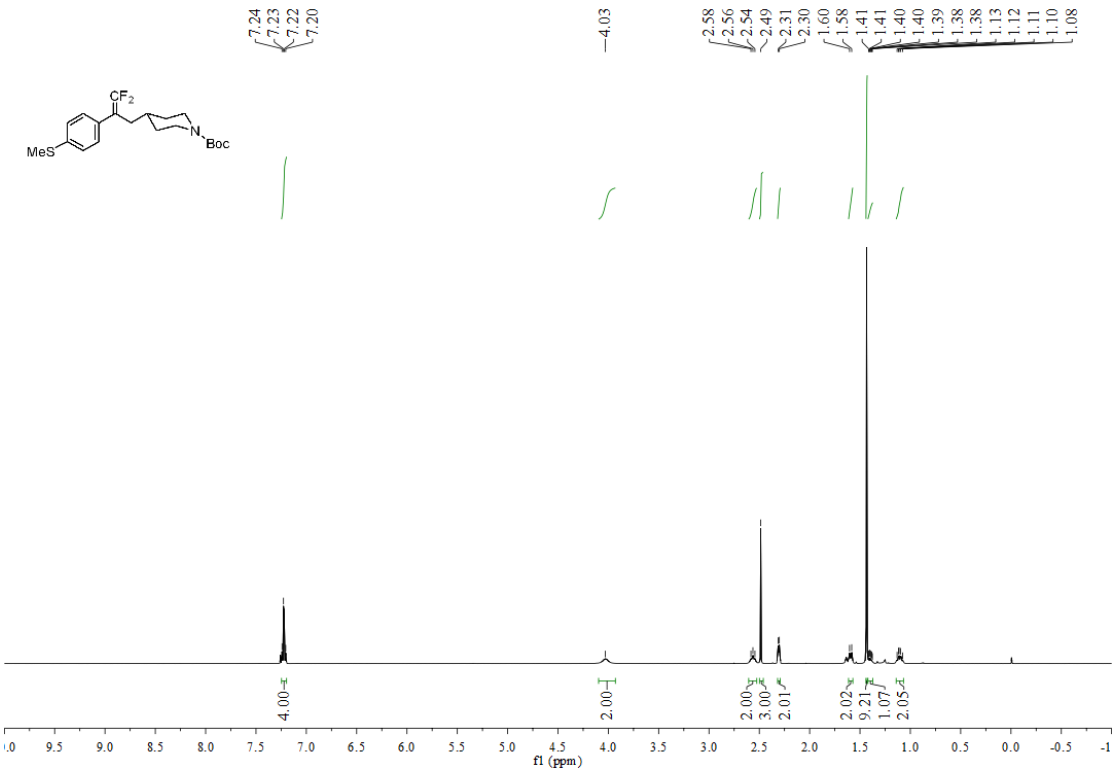
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 36



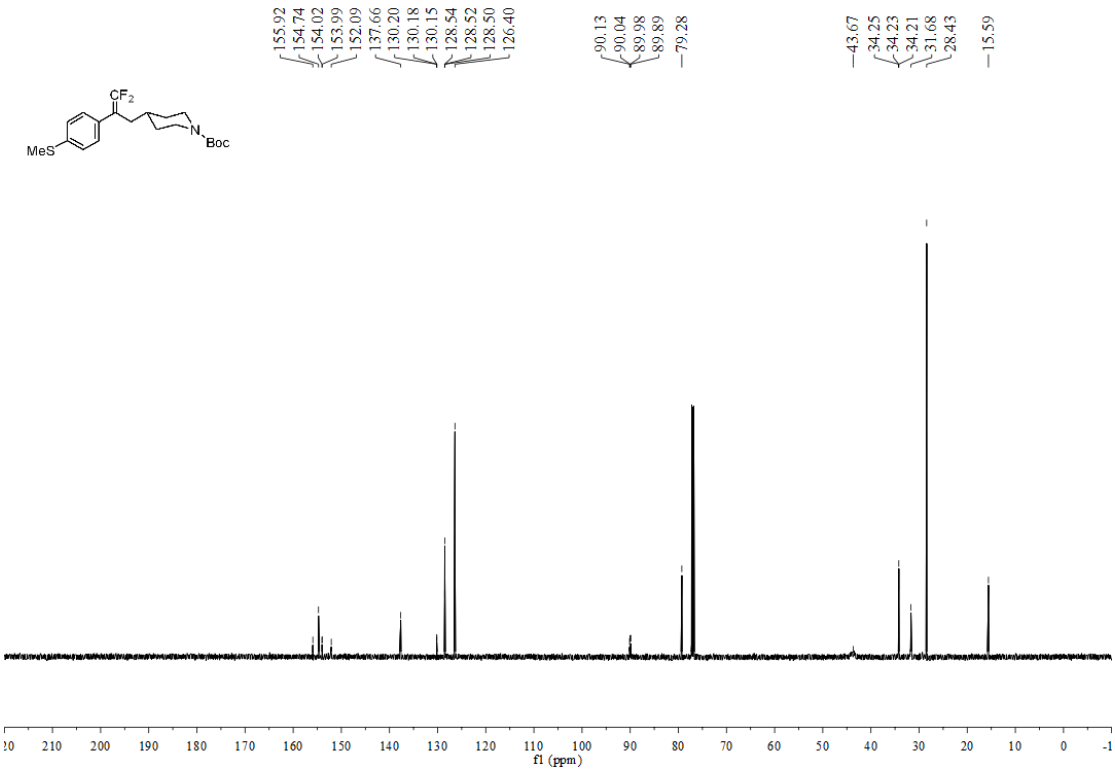
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 36



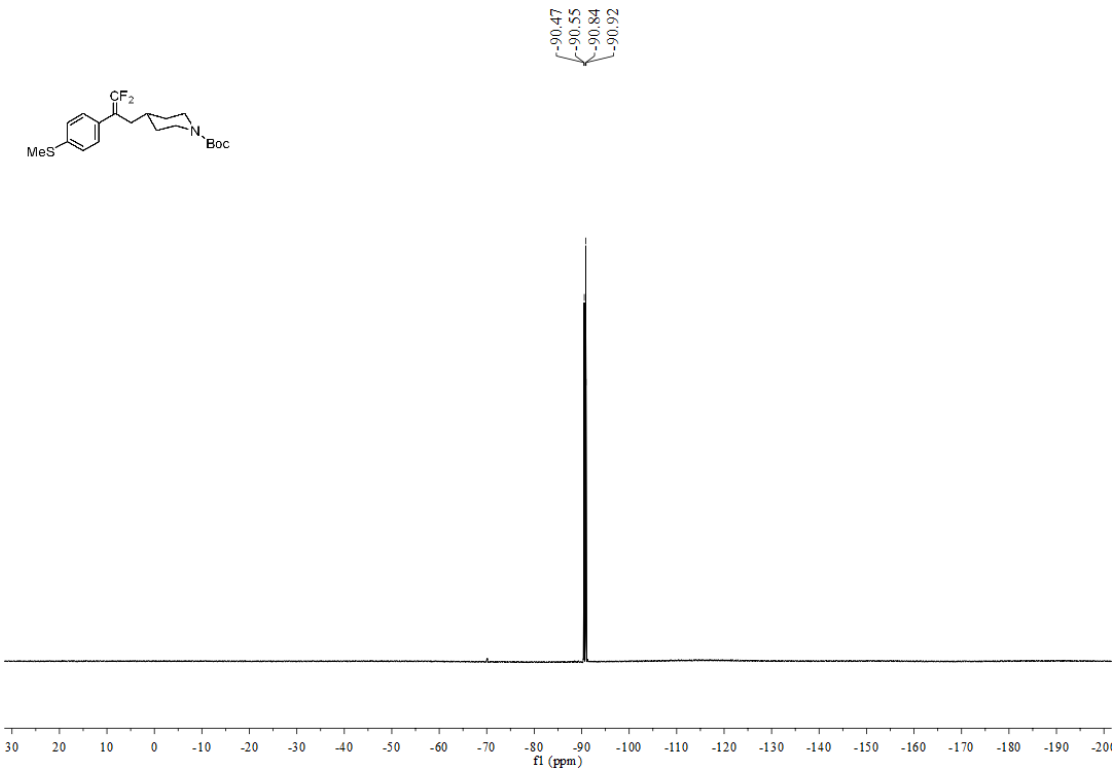
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 37



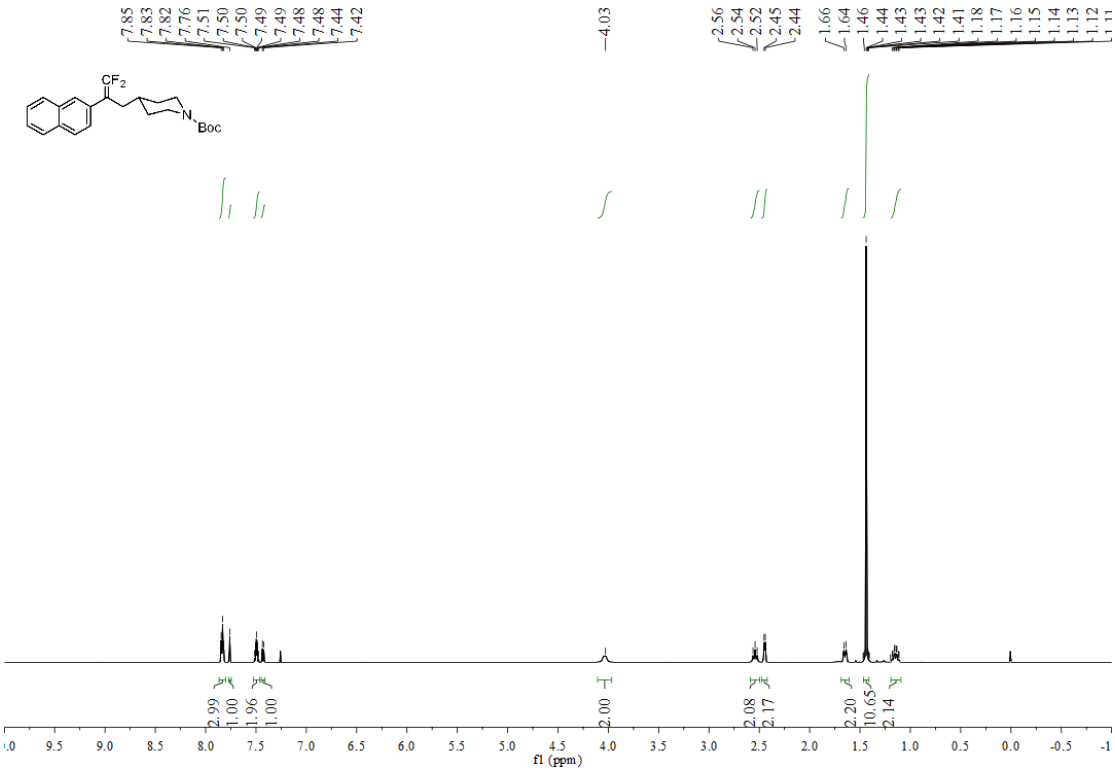
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 37



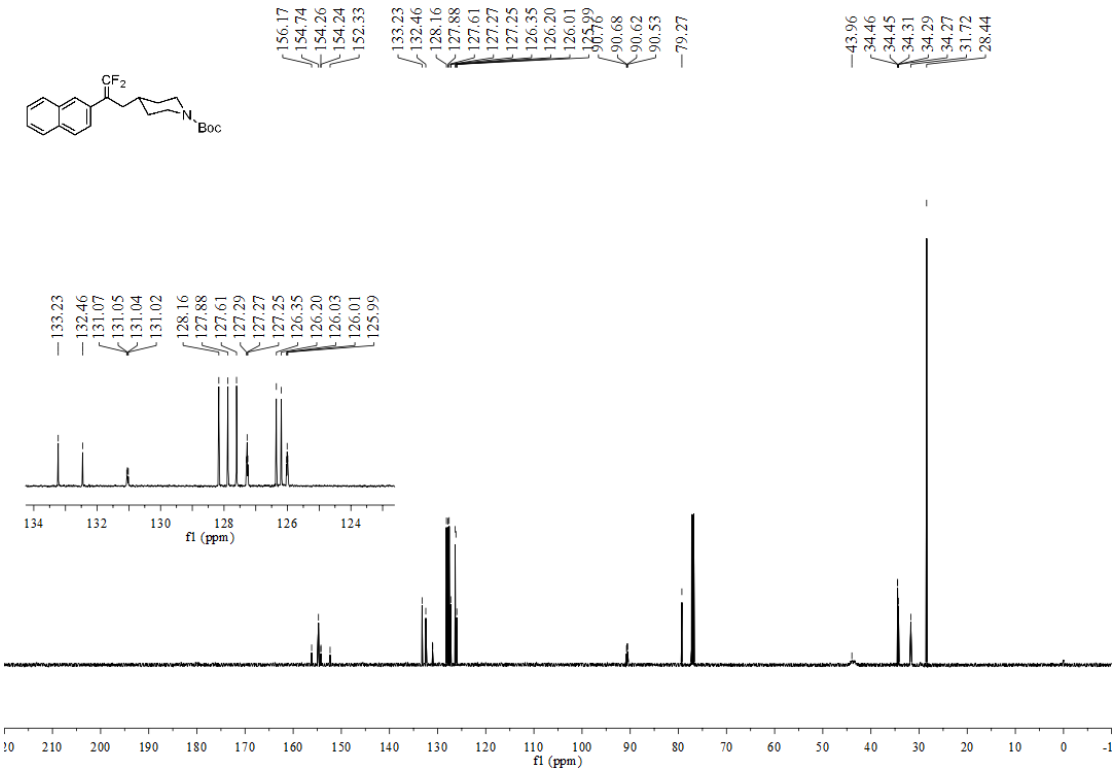
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 37



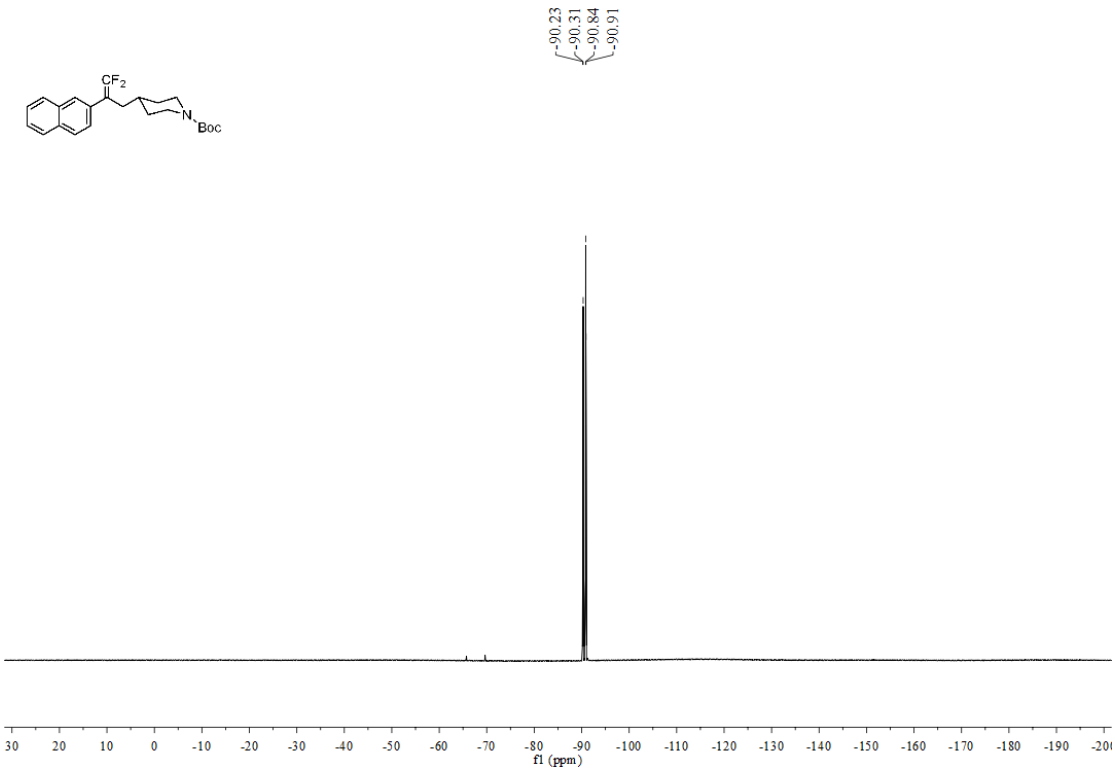
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 38



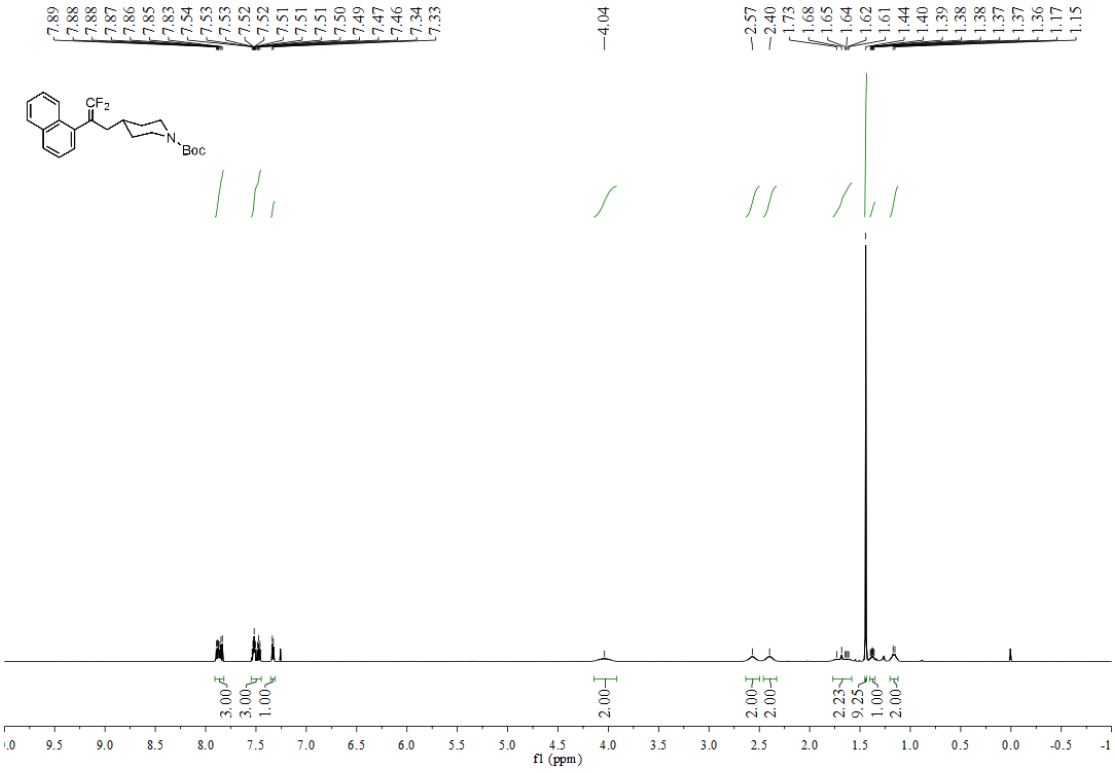
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 38



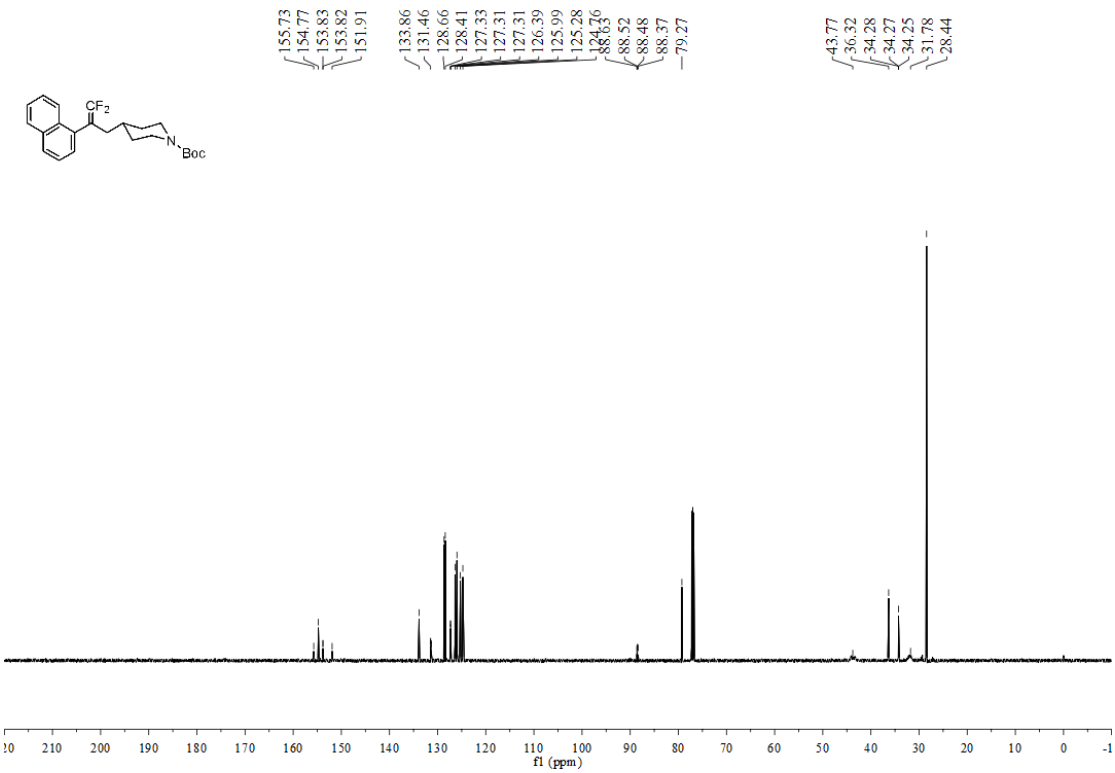
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 38



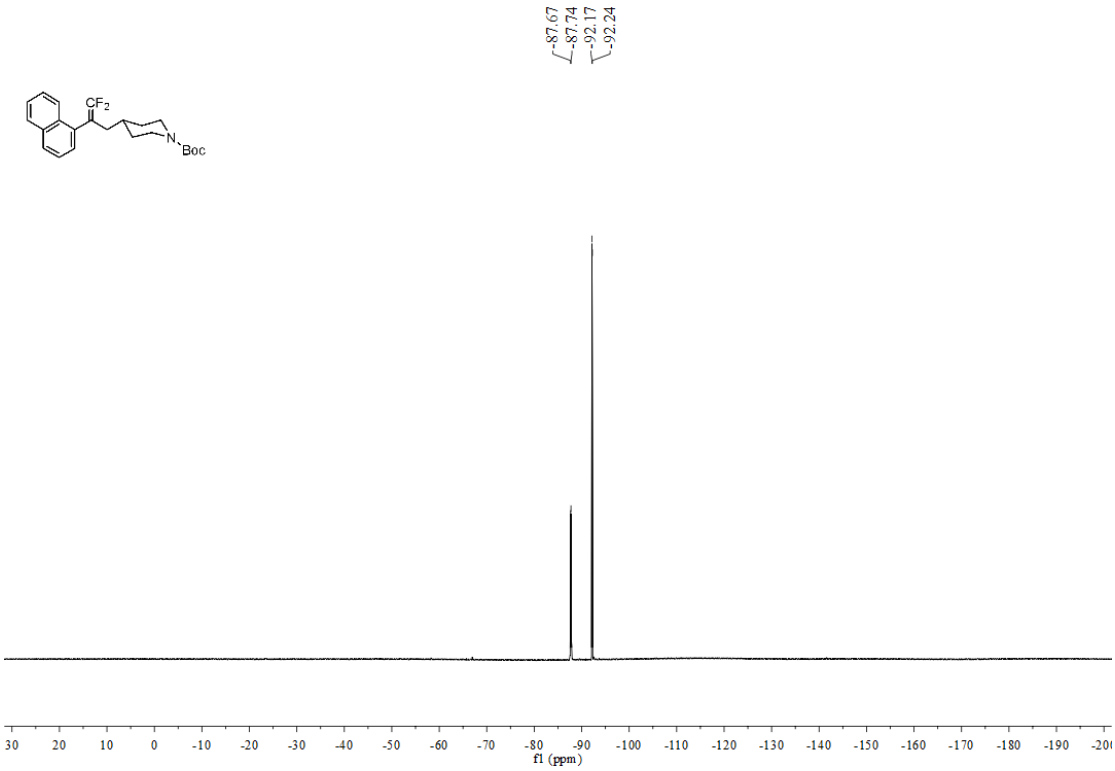
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 39



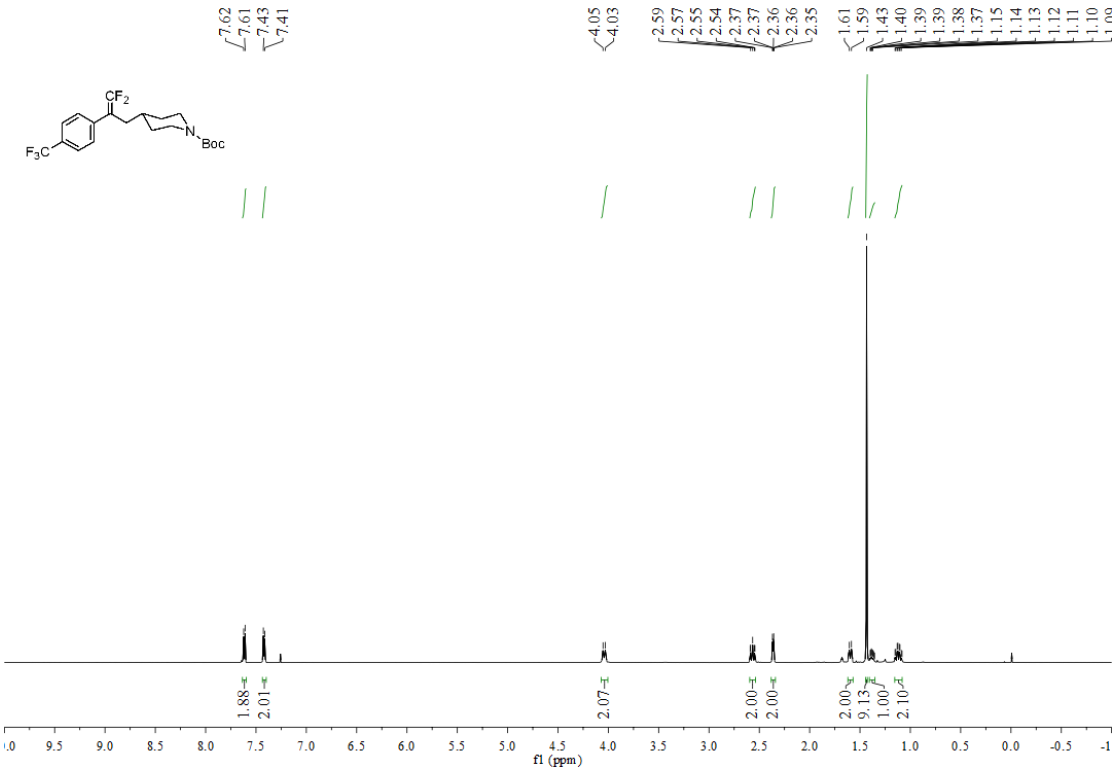
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 39



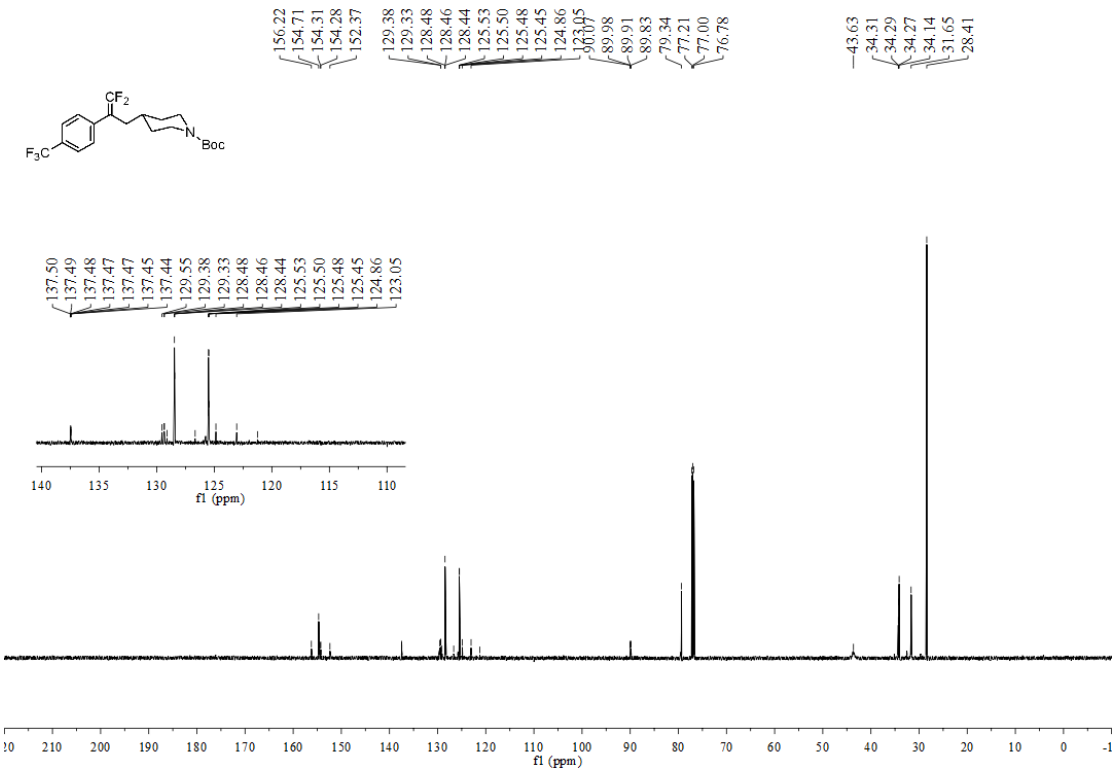
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 39



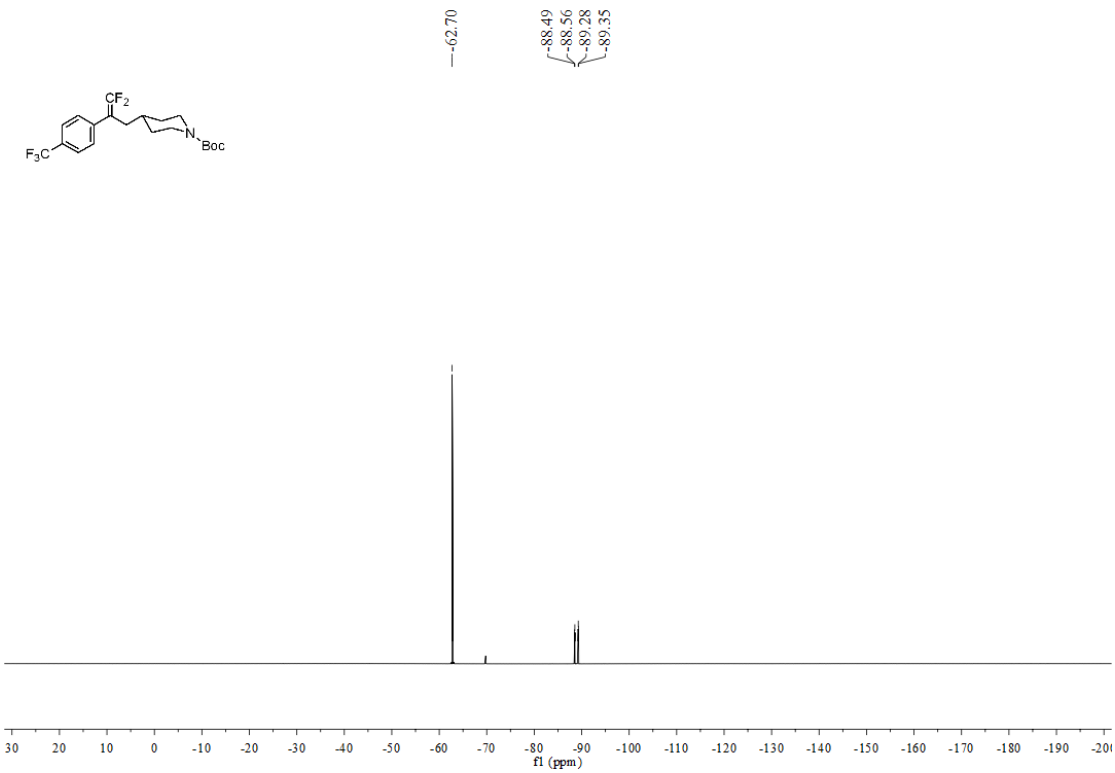
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 40



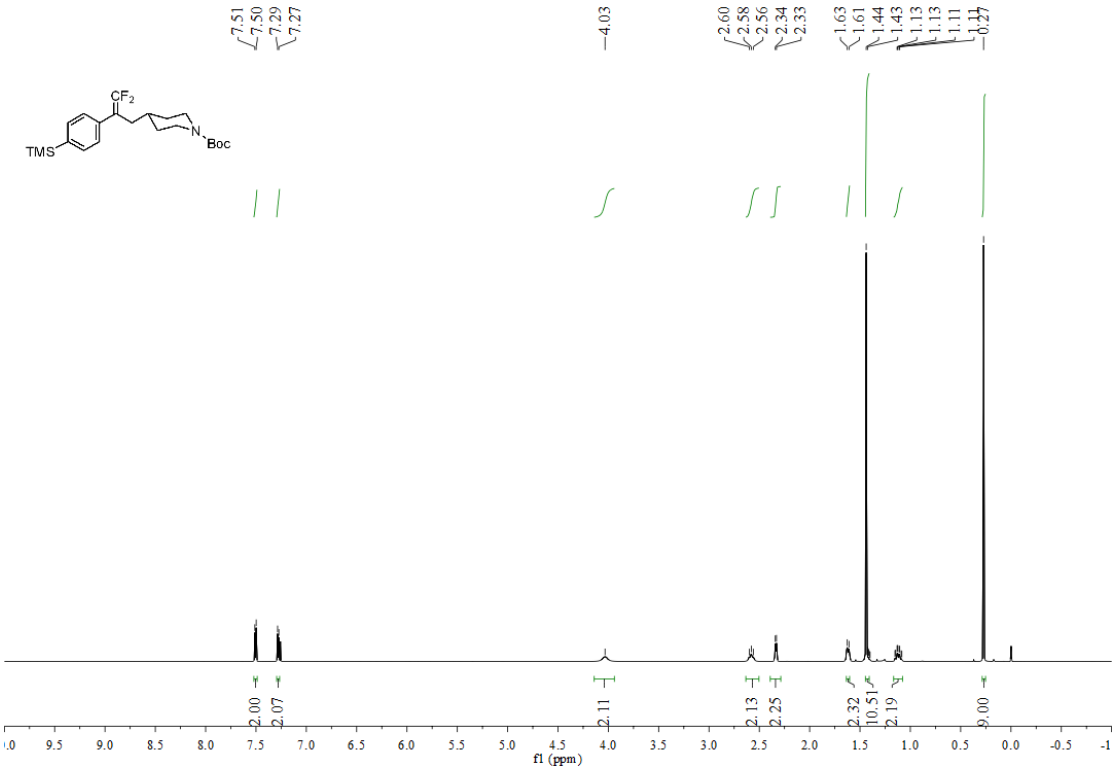
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 40



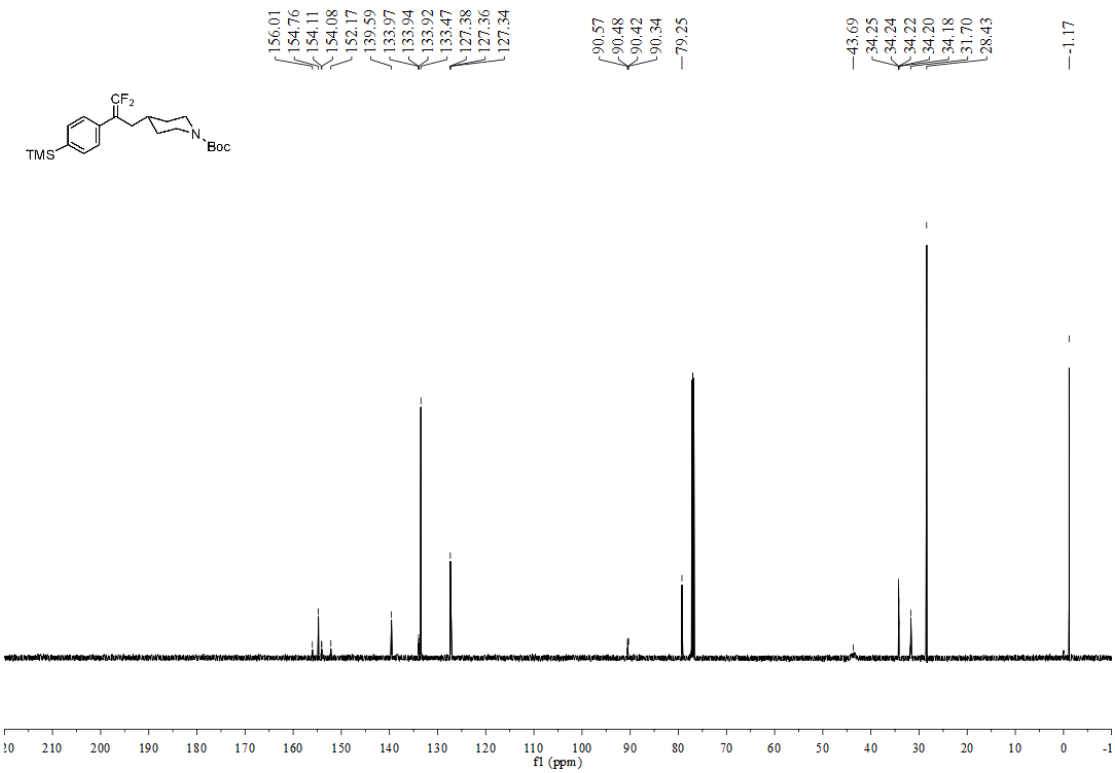
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 40



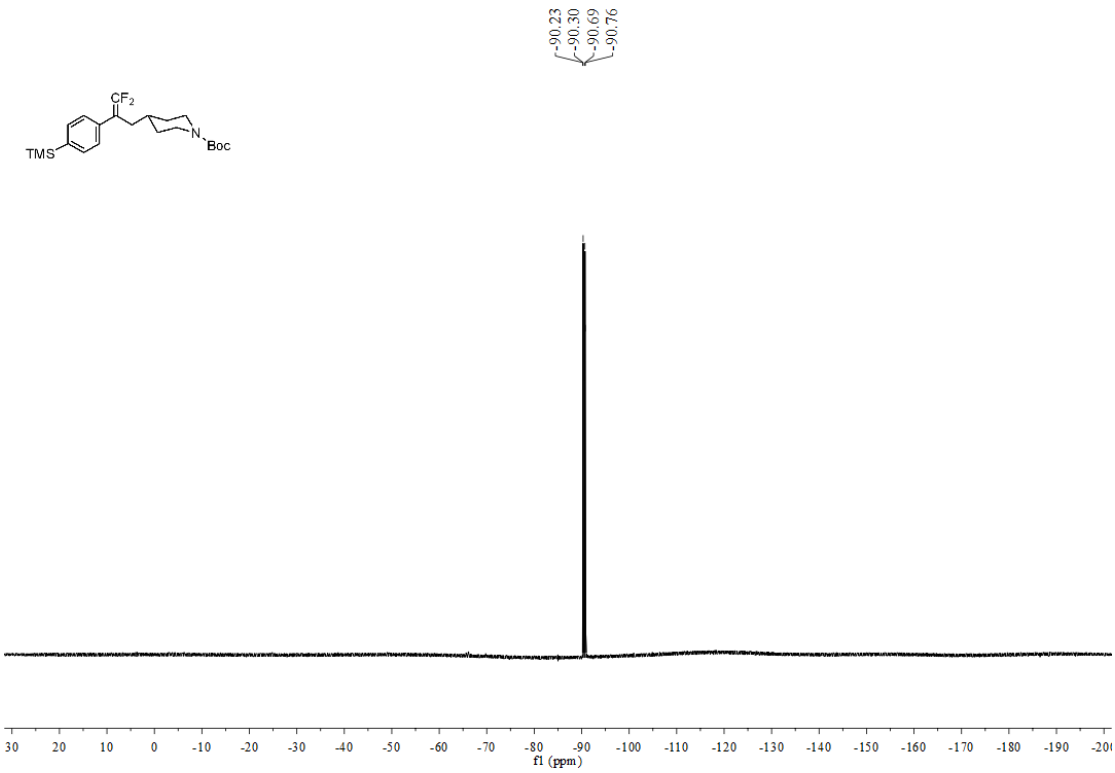
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 41



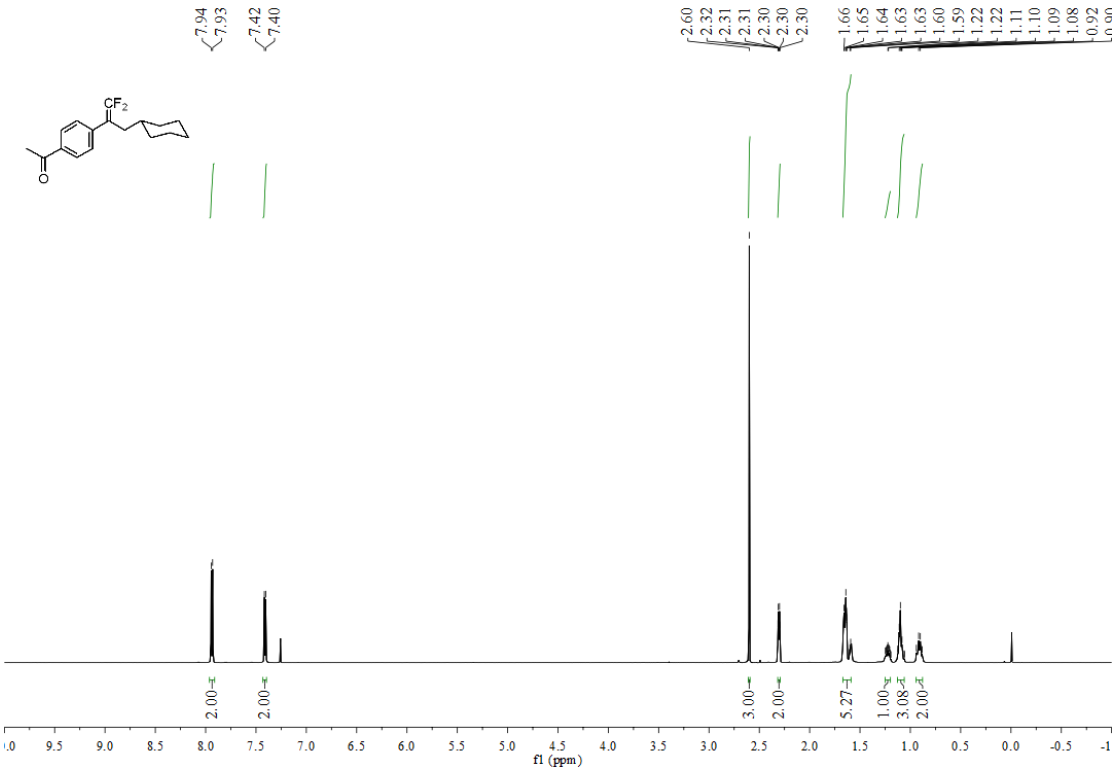
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 41



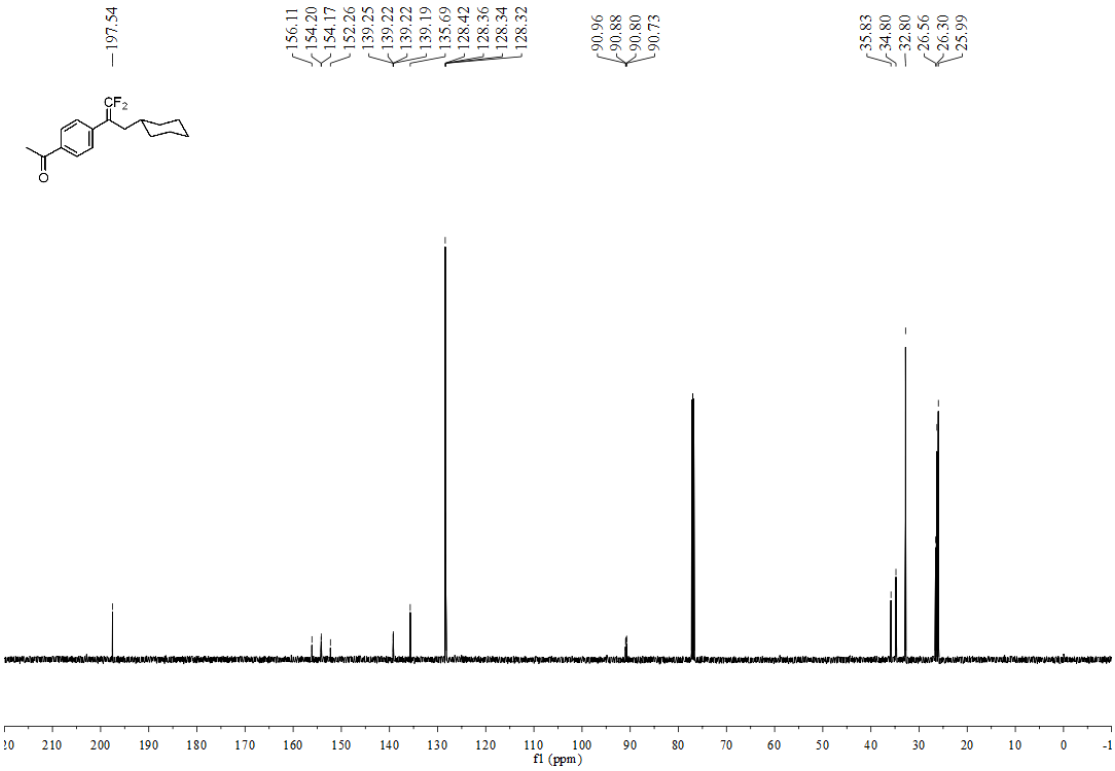
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 41



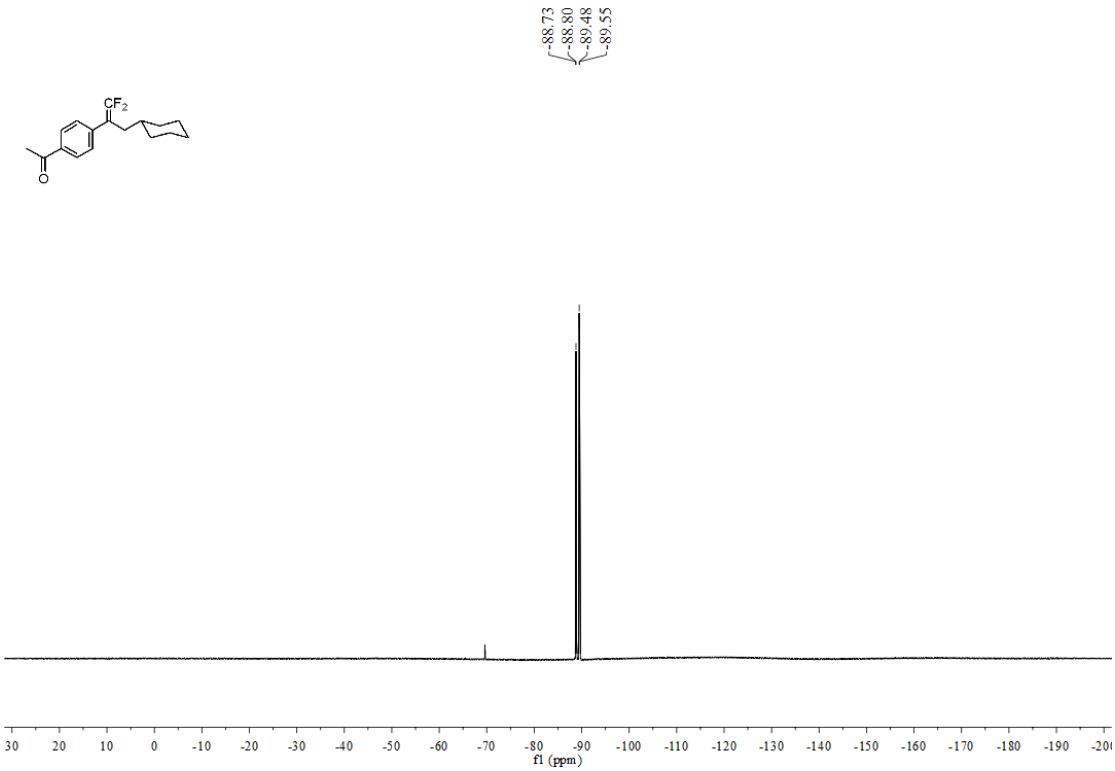
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 42



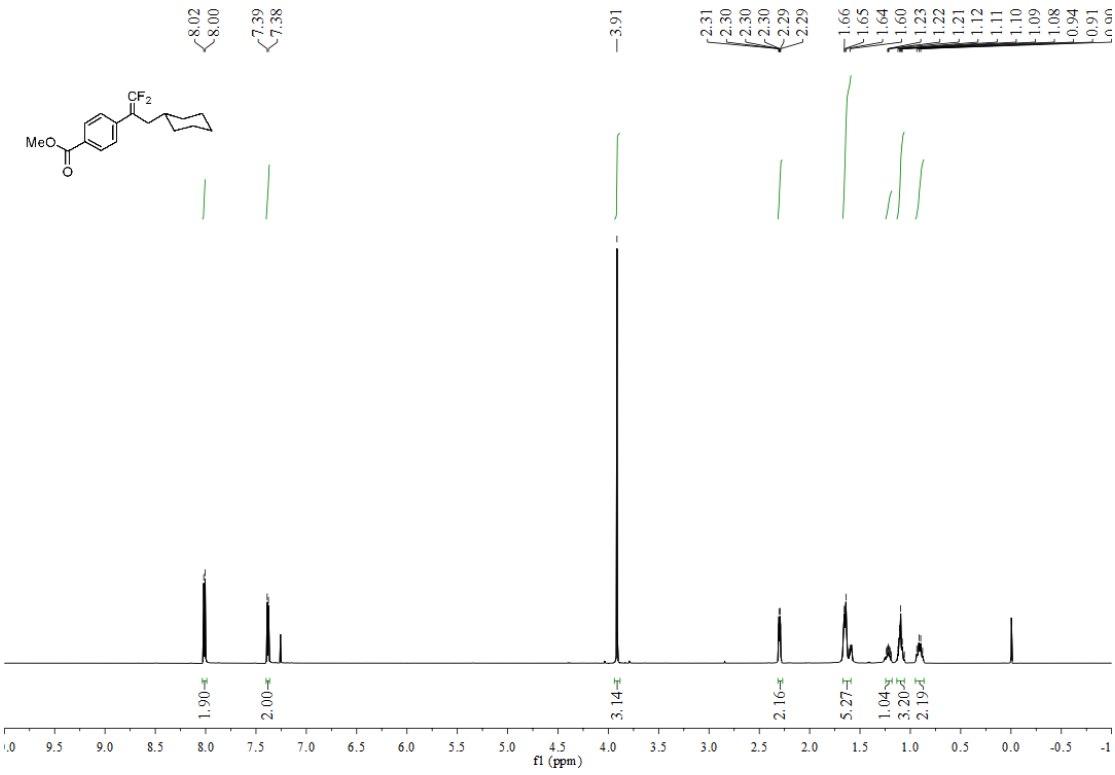
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 42



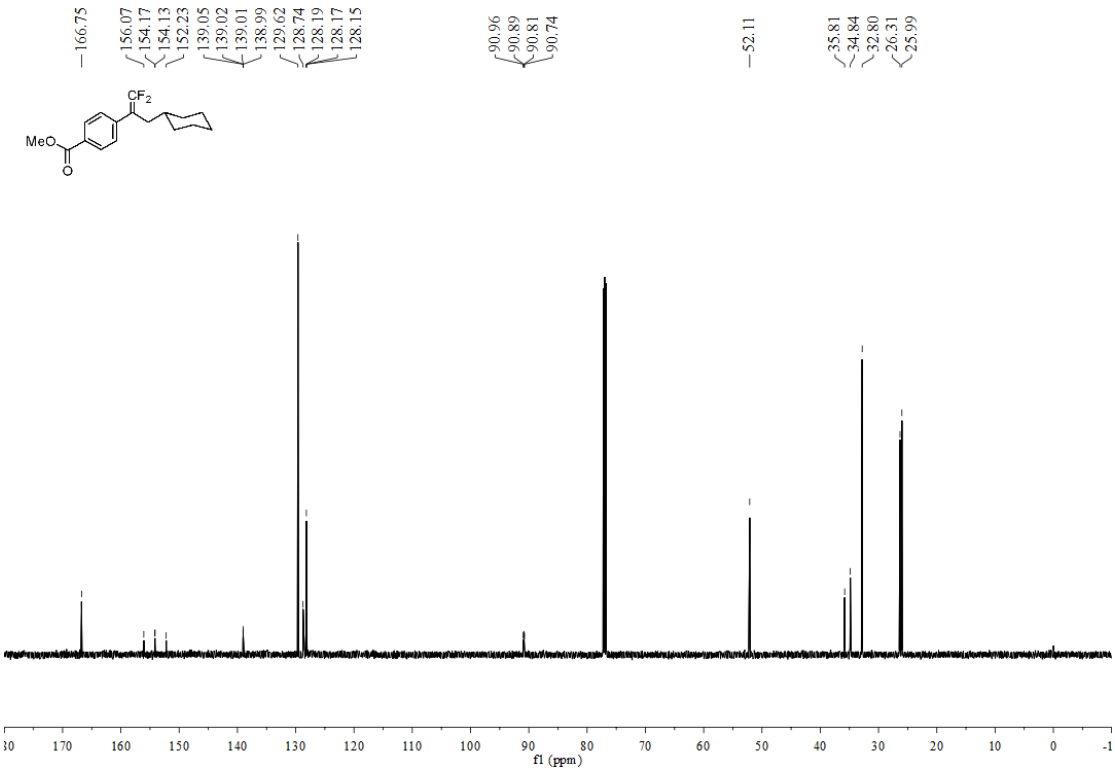
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 42



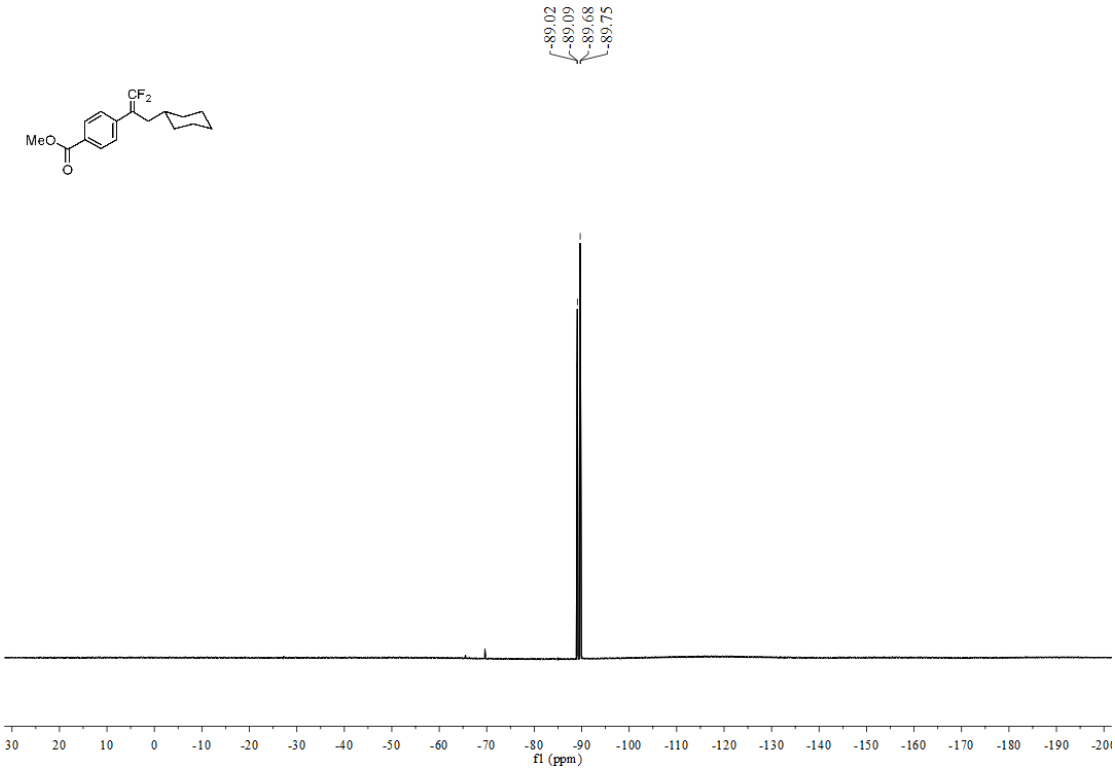
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 43



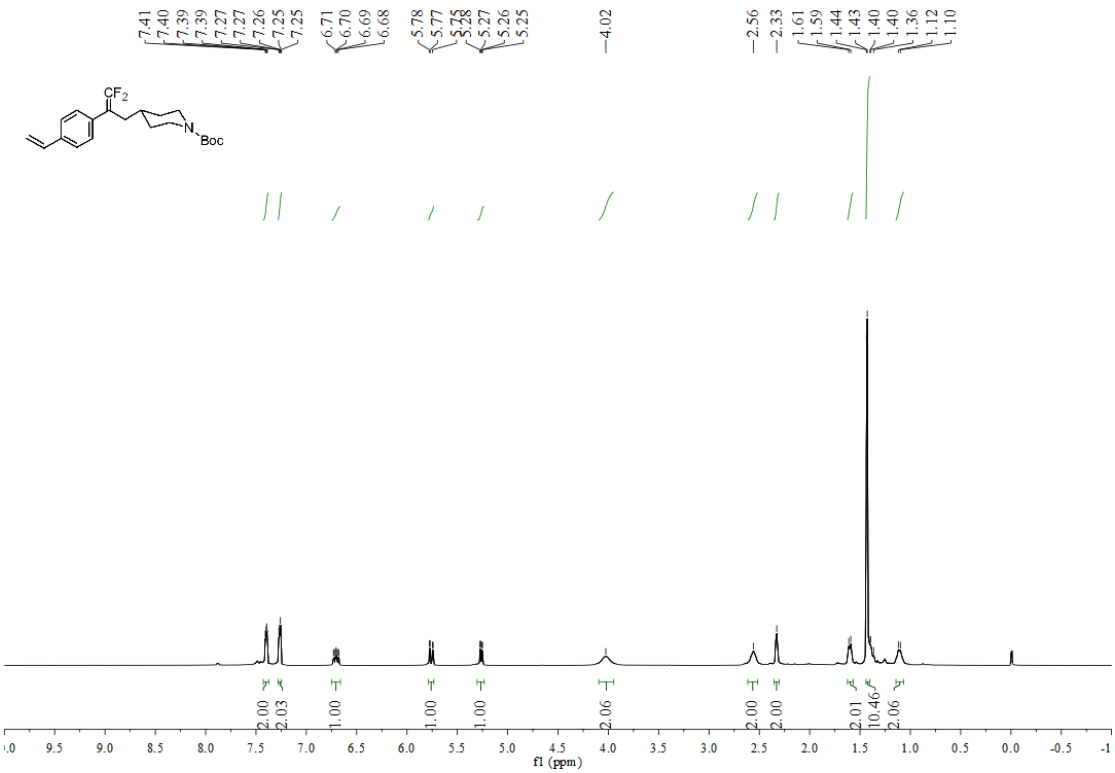
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 43



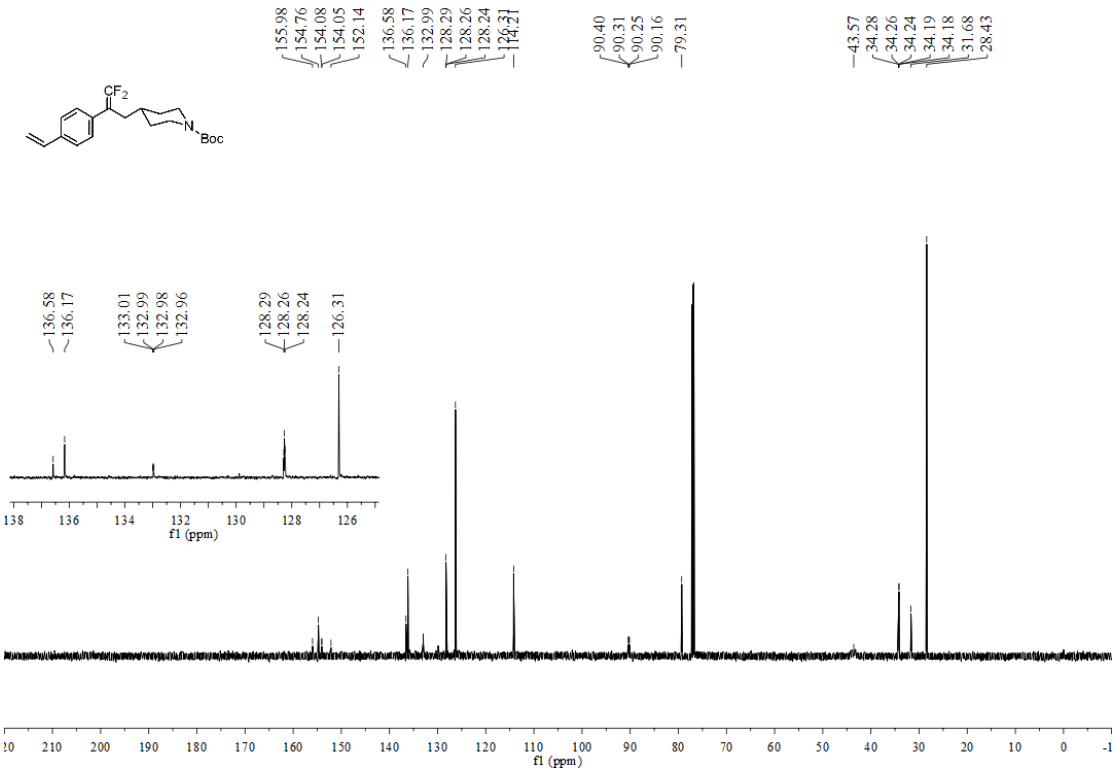
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 43



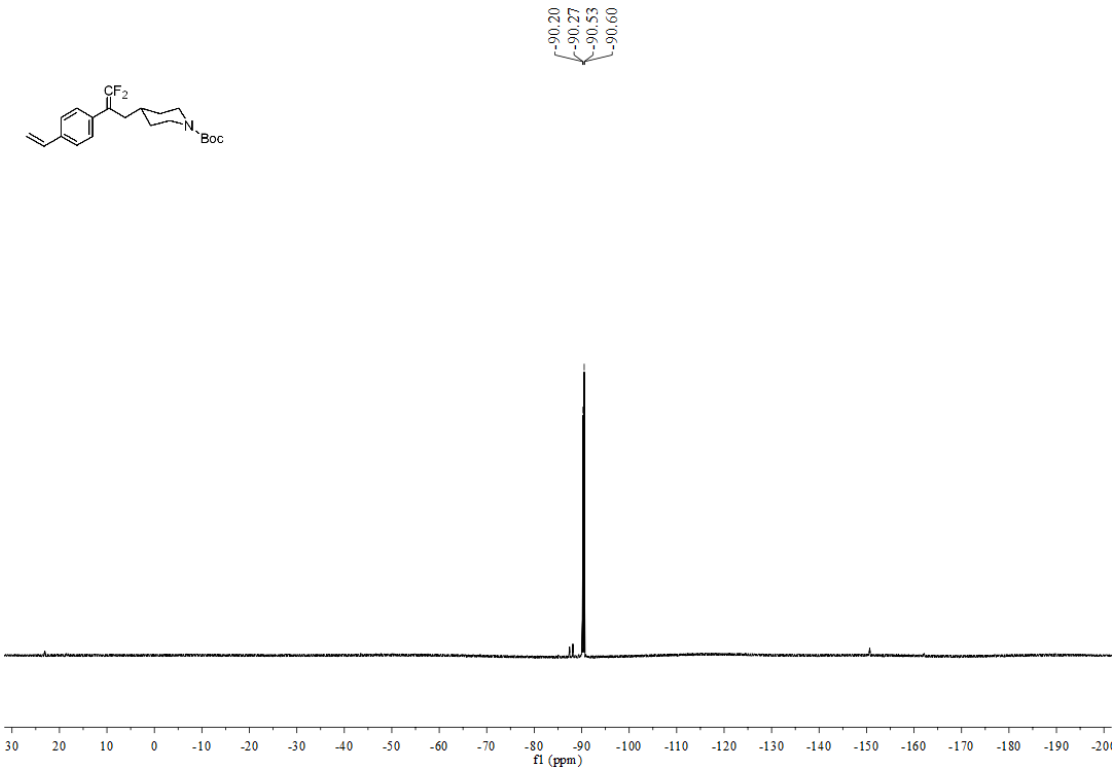
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 44



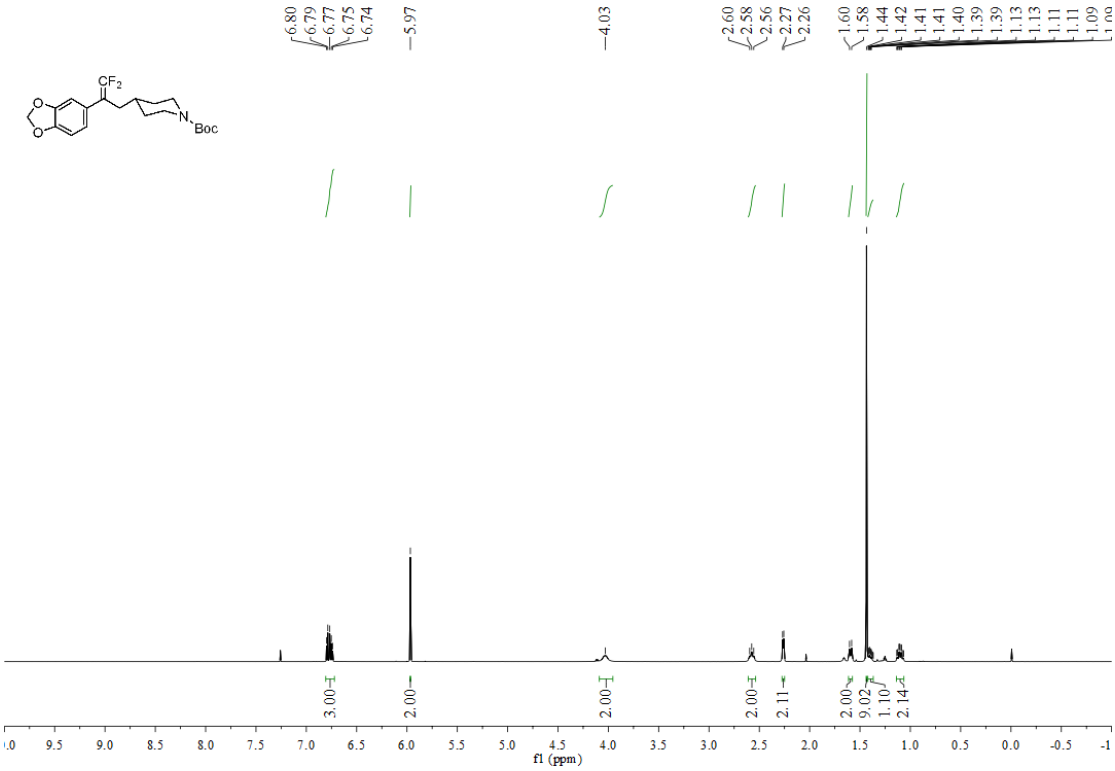
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 44



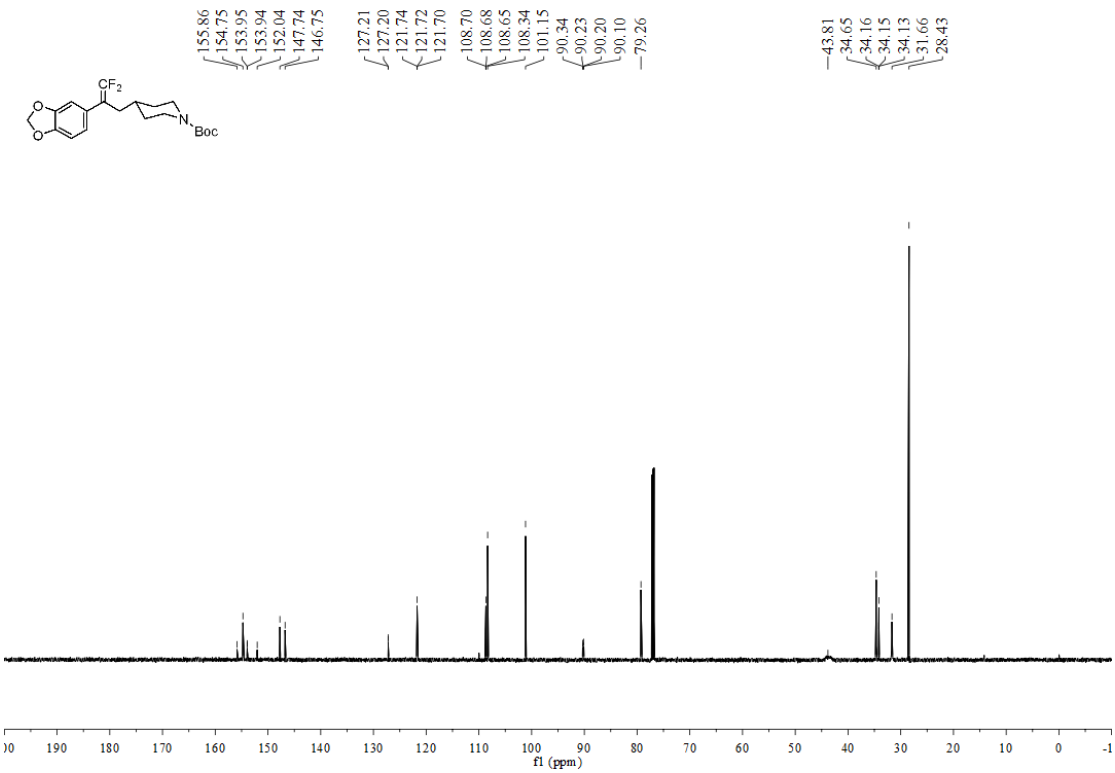
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 44



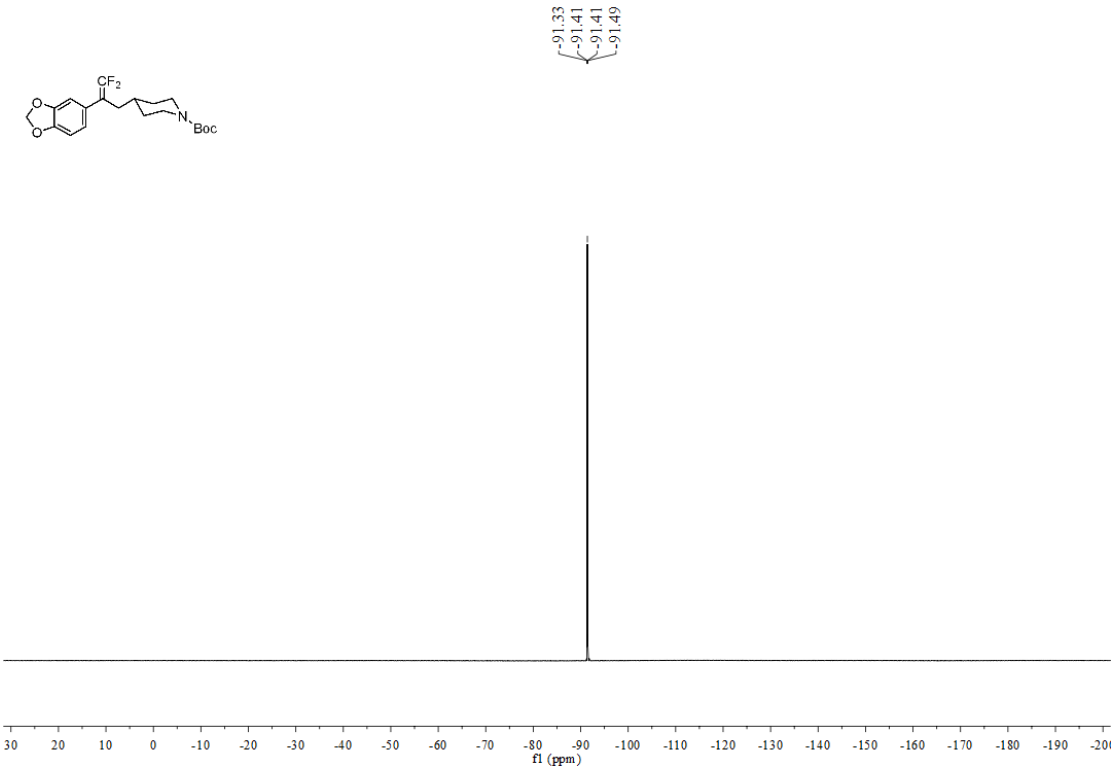
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 45



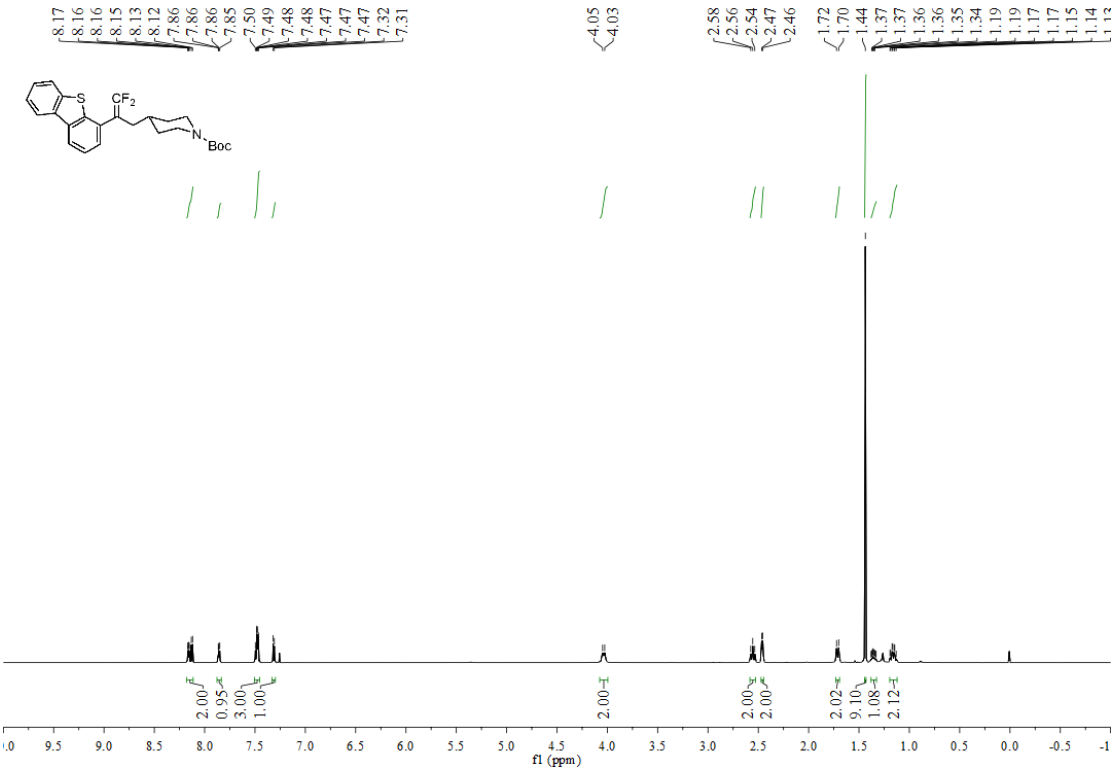
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 45



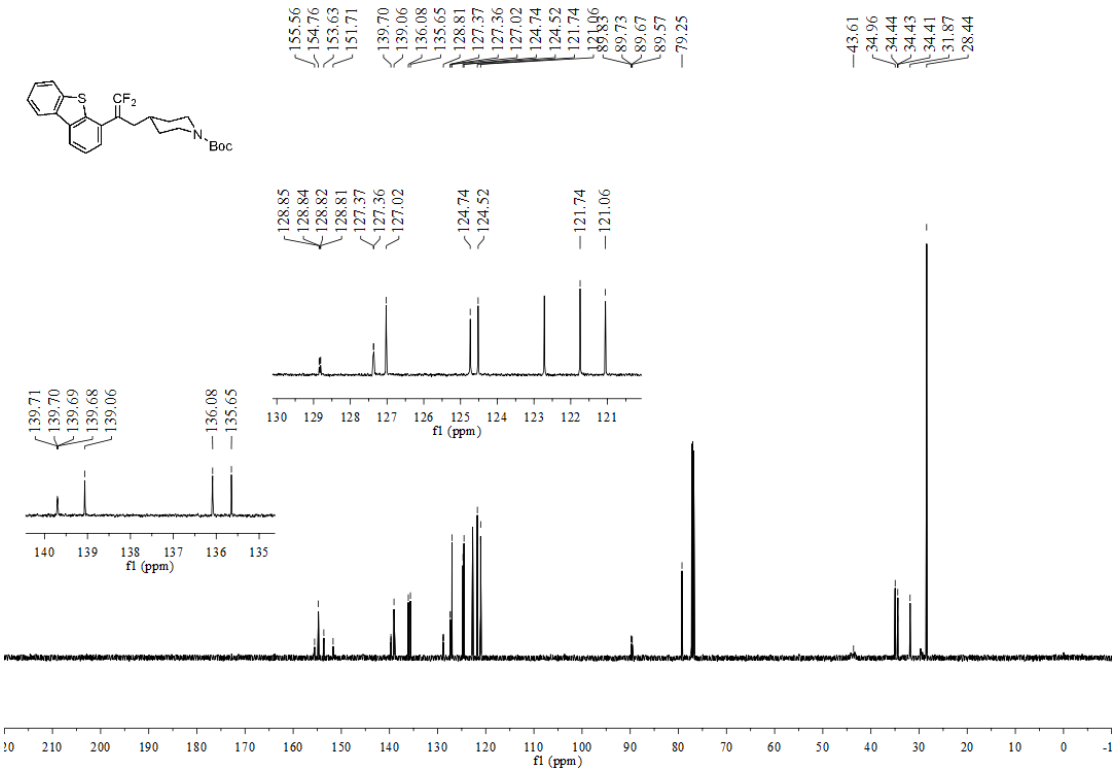
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 45



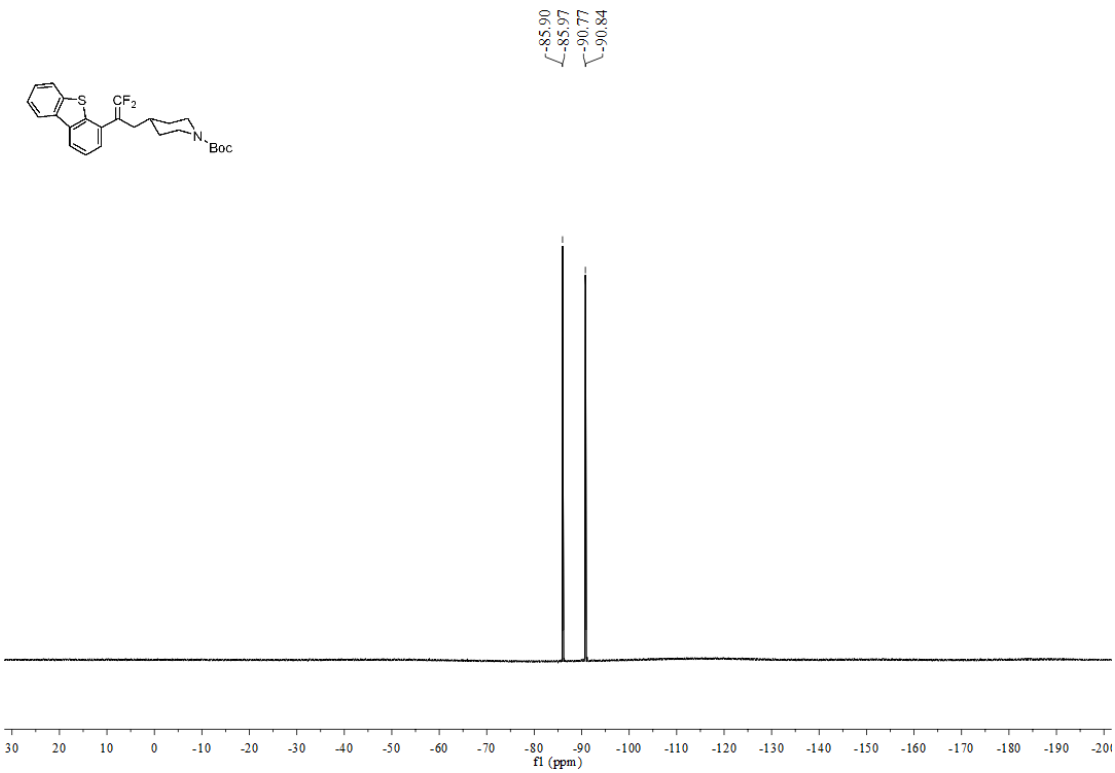
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 46



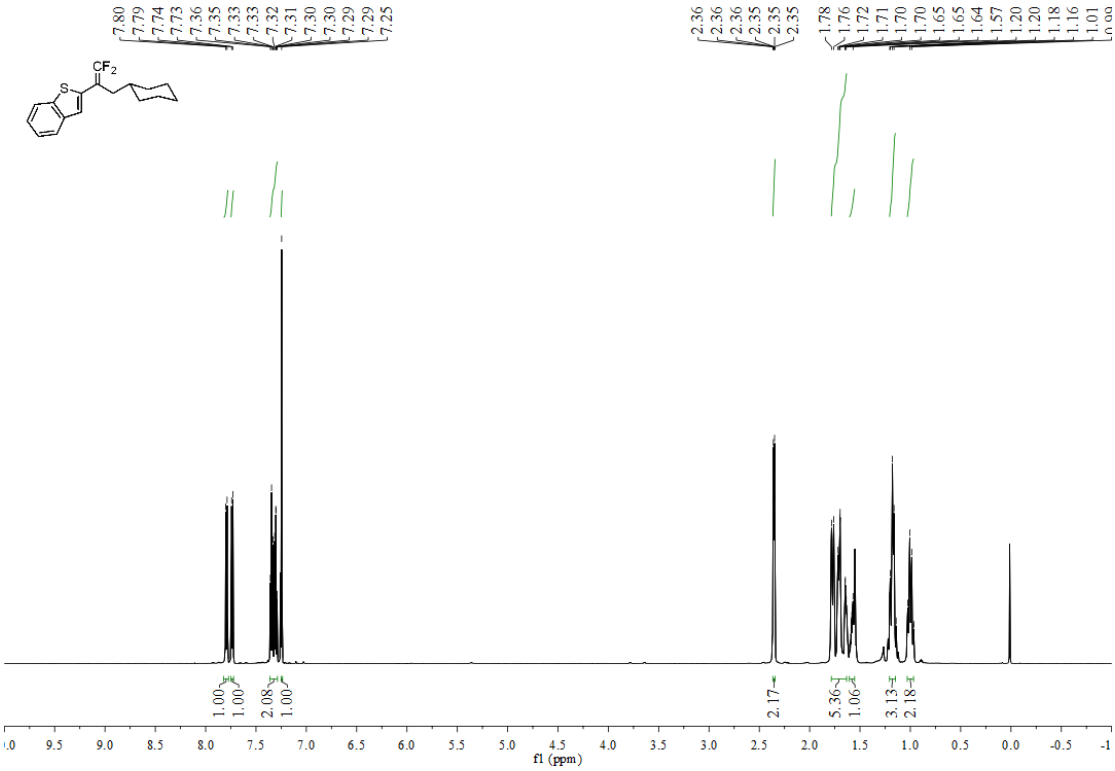
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 46



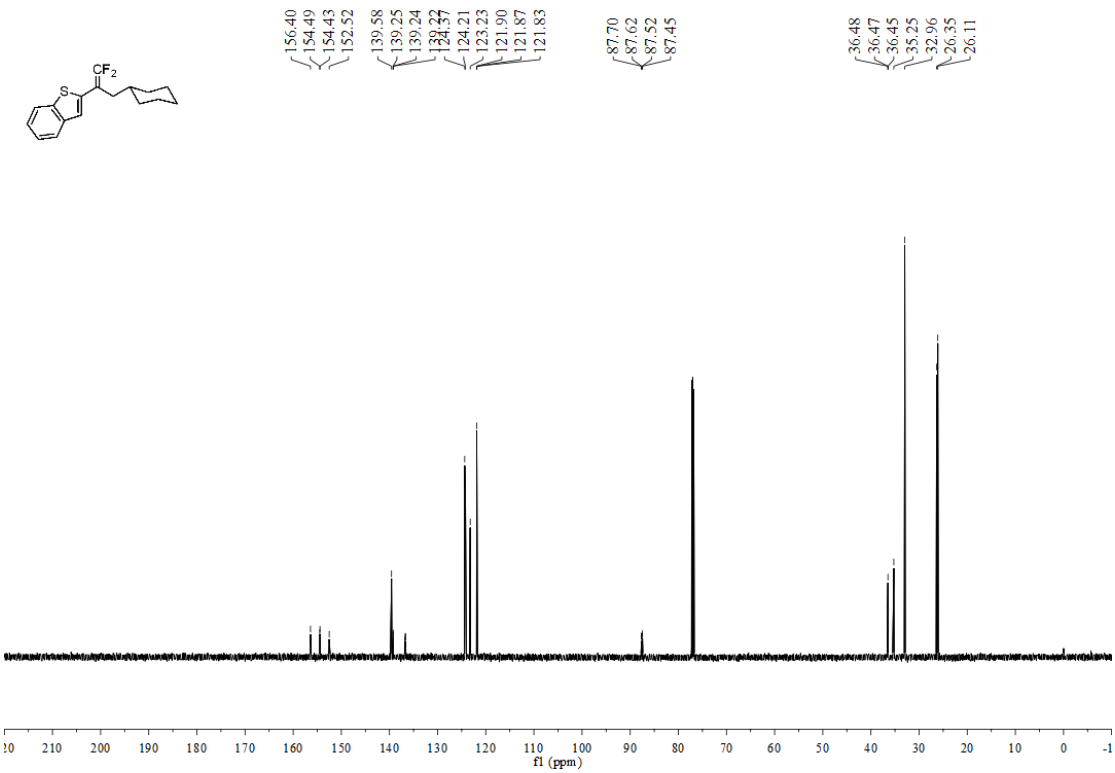
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 46



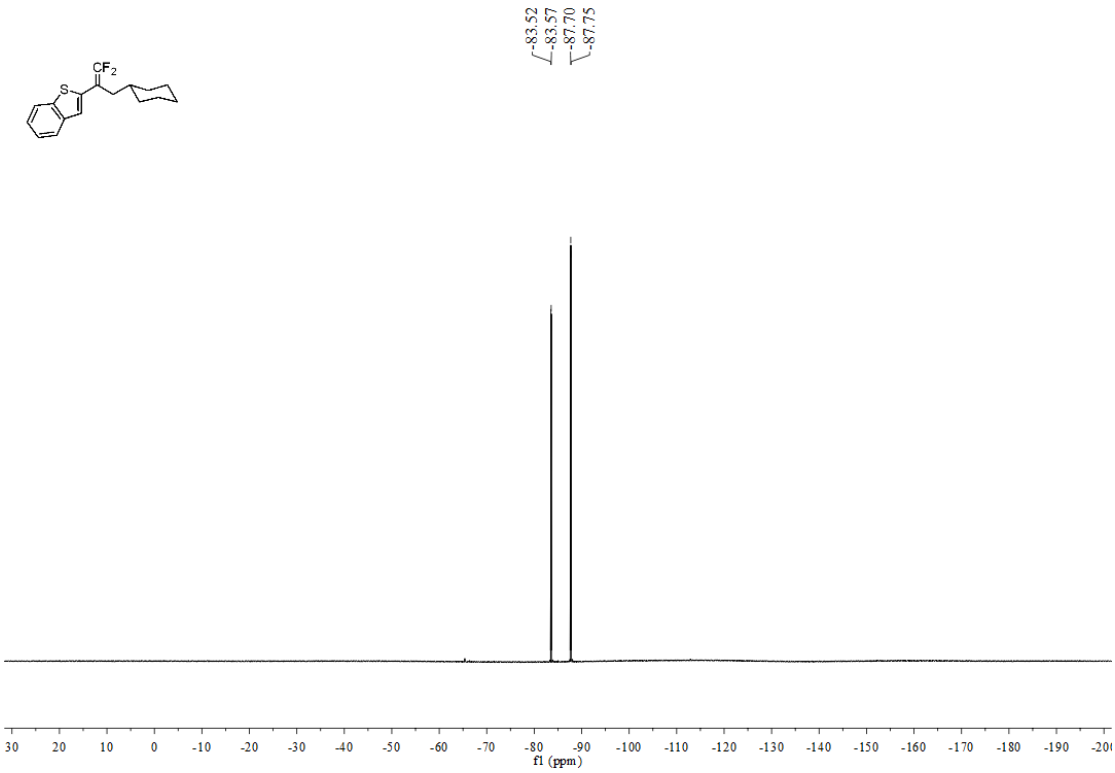
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 47



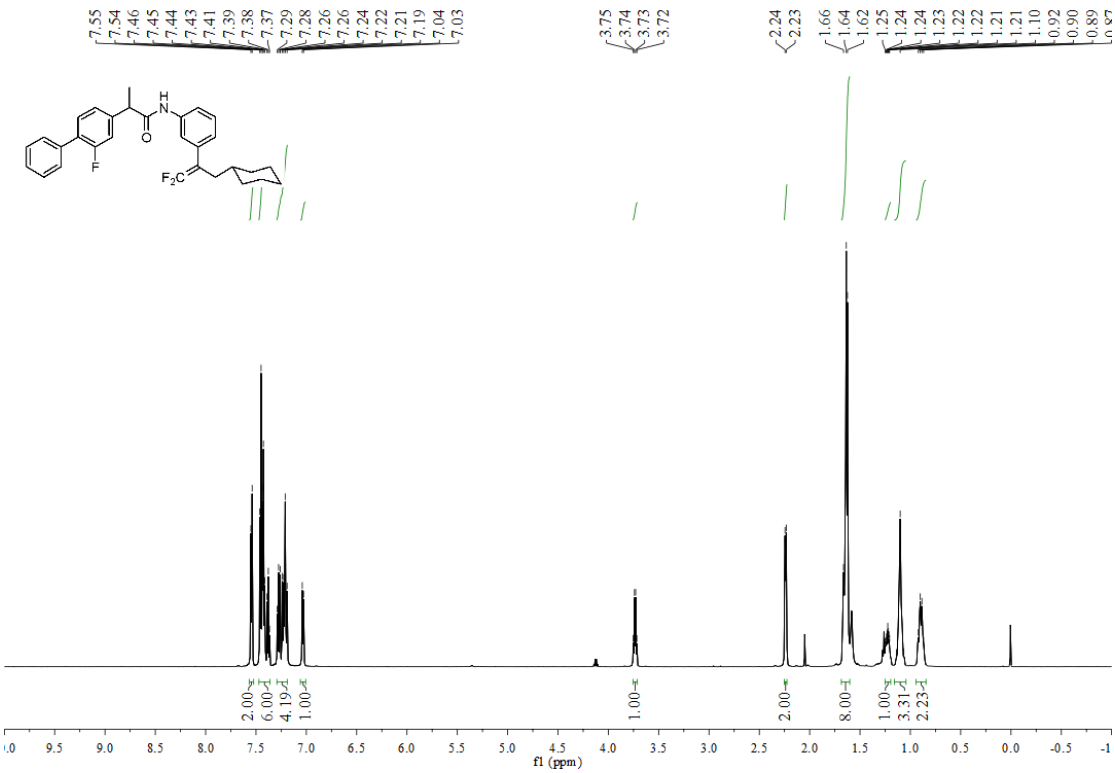
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 47



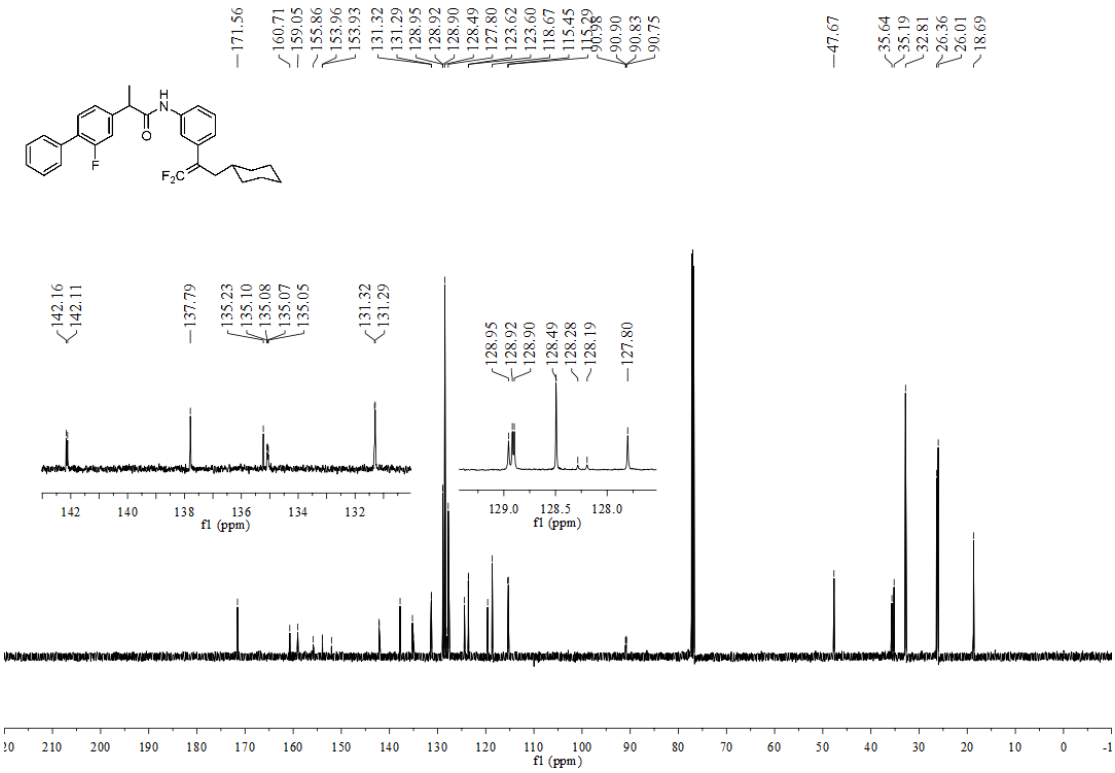
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 47



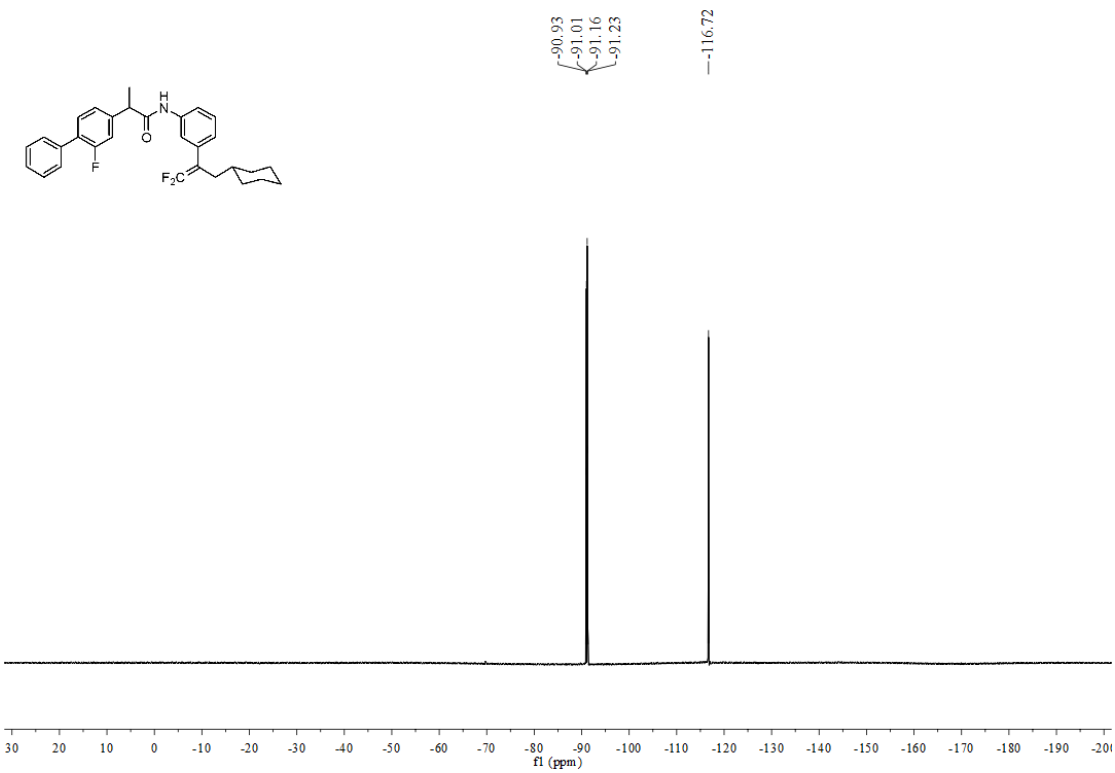
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 48



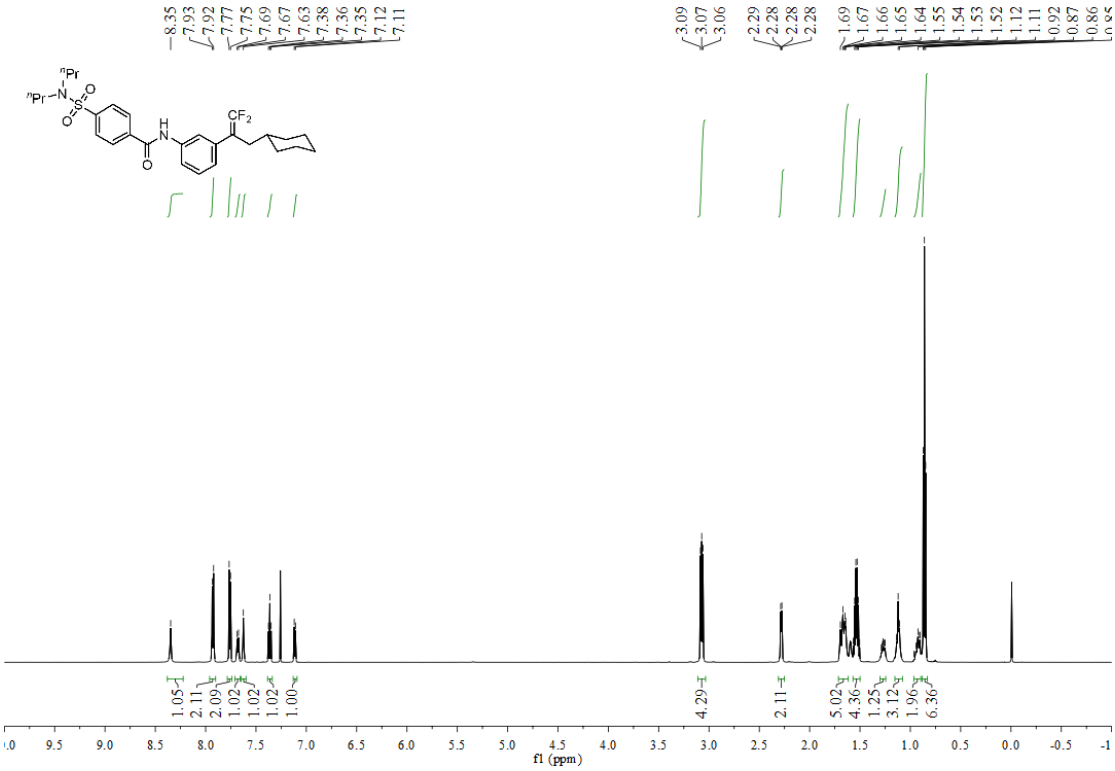
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 48



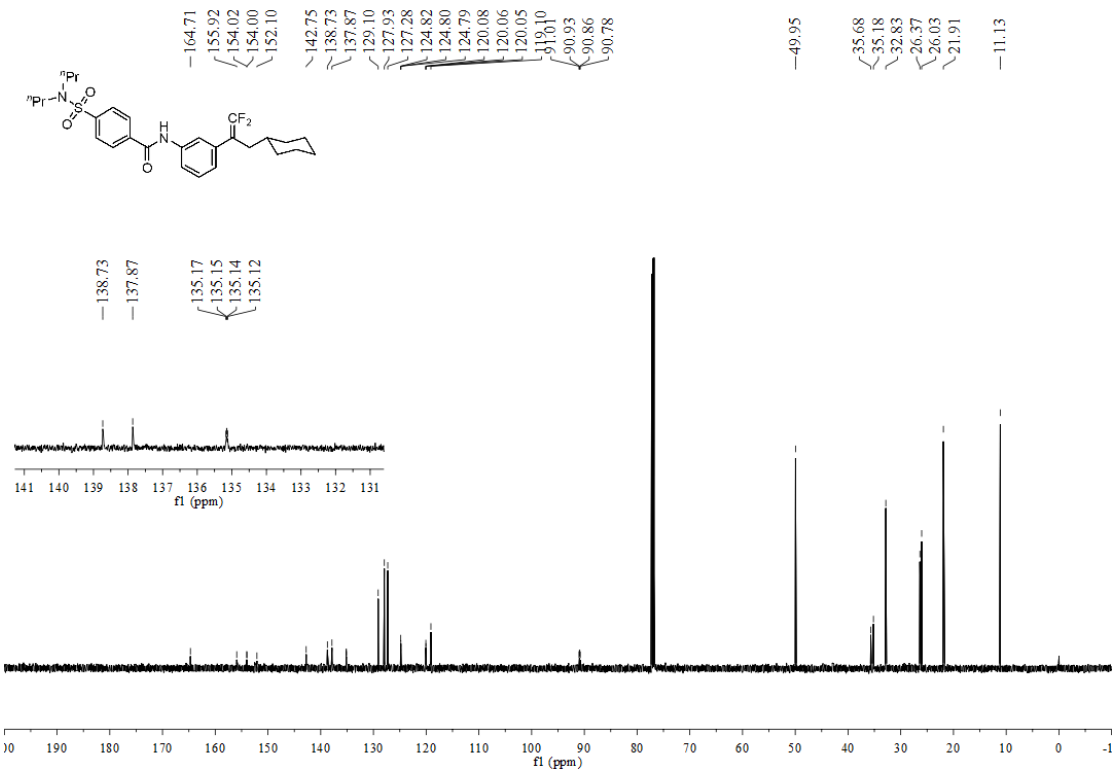
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 48



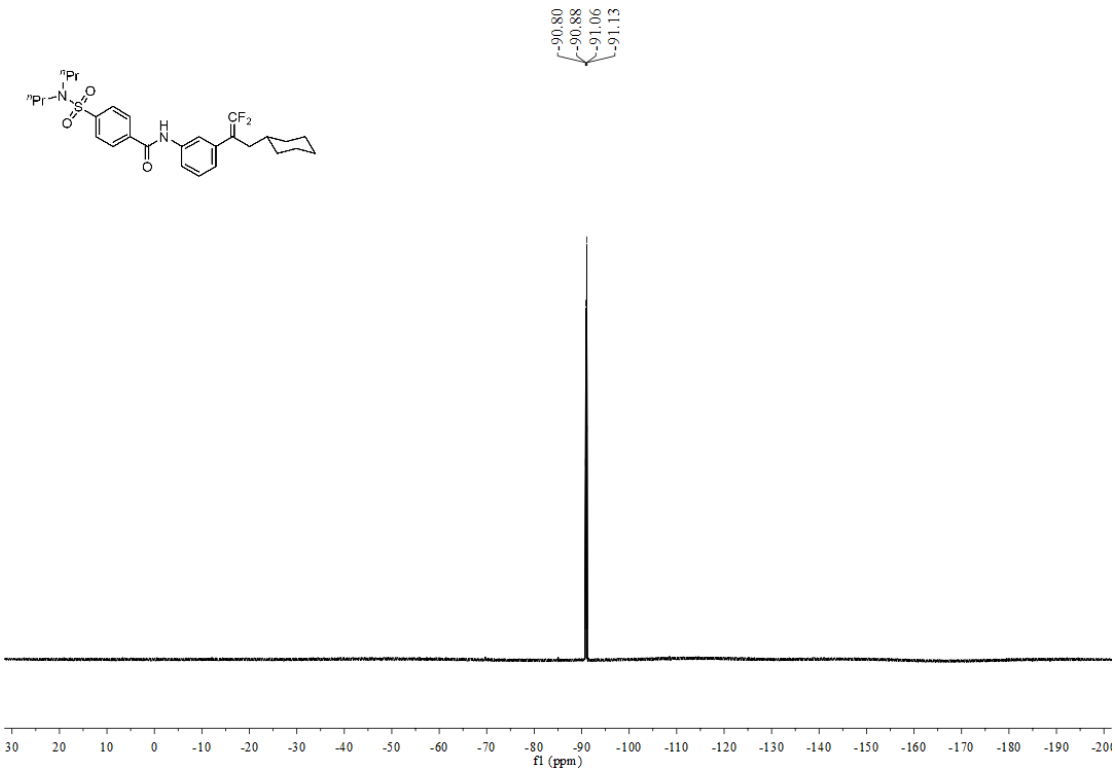
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 49



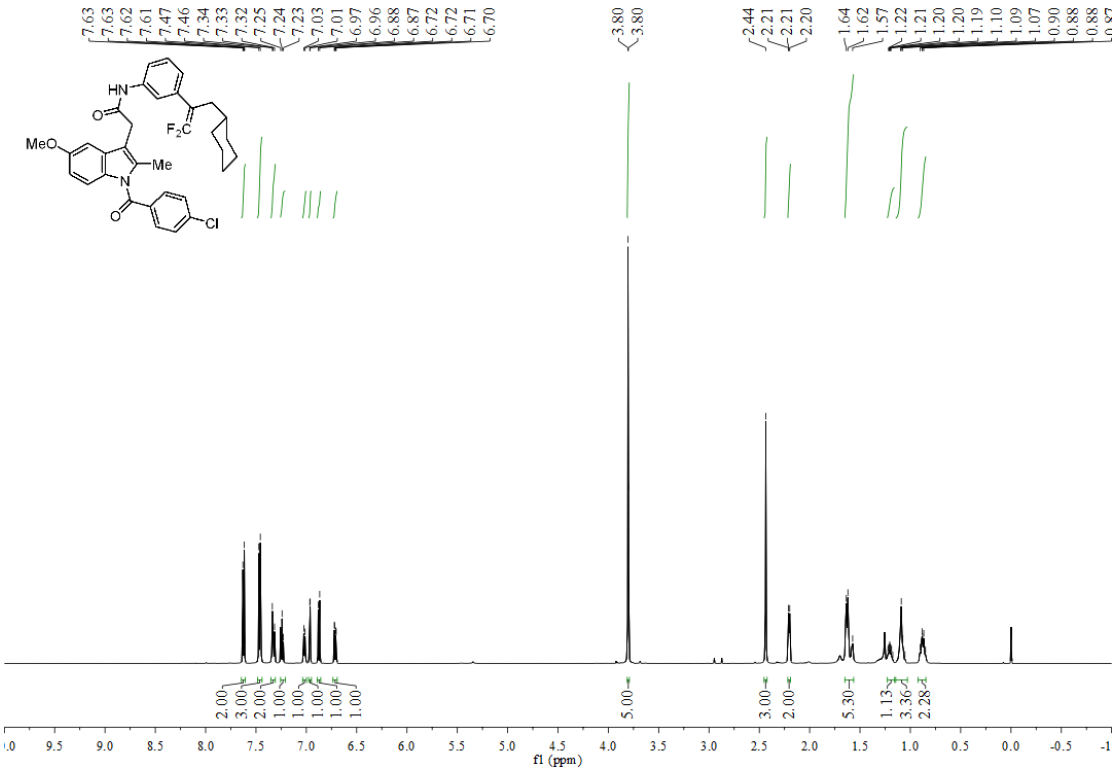
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 49



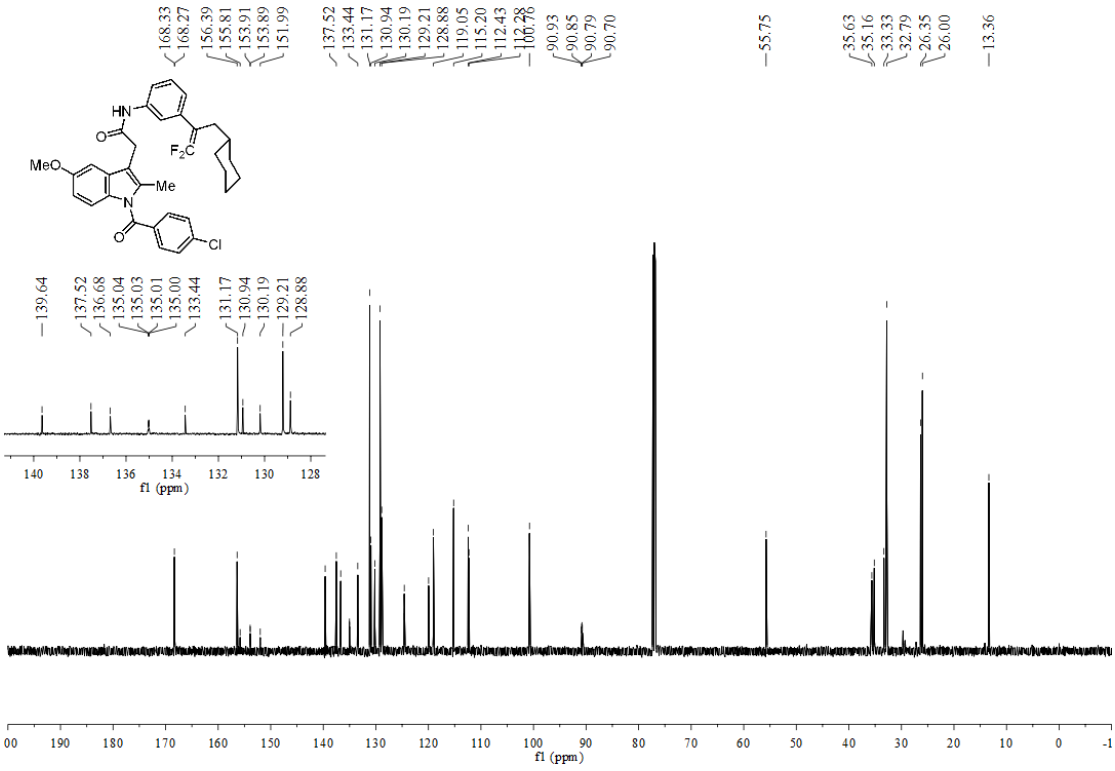
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 49



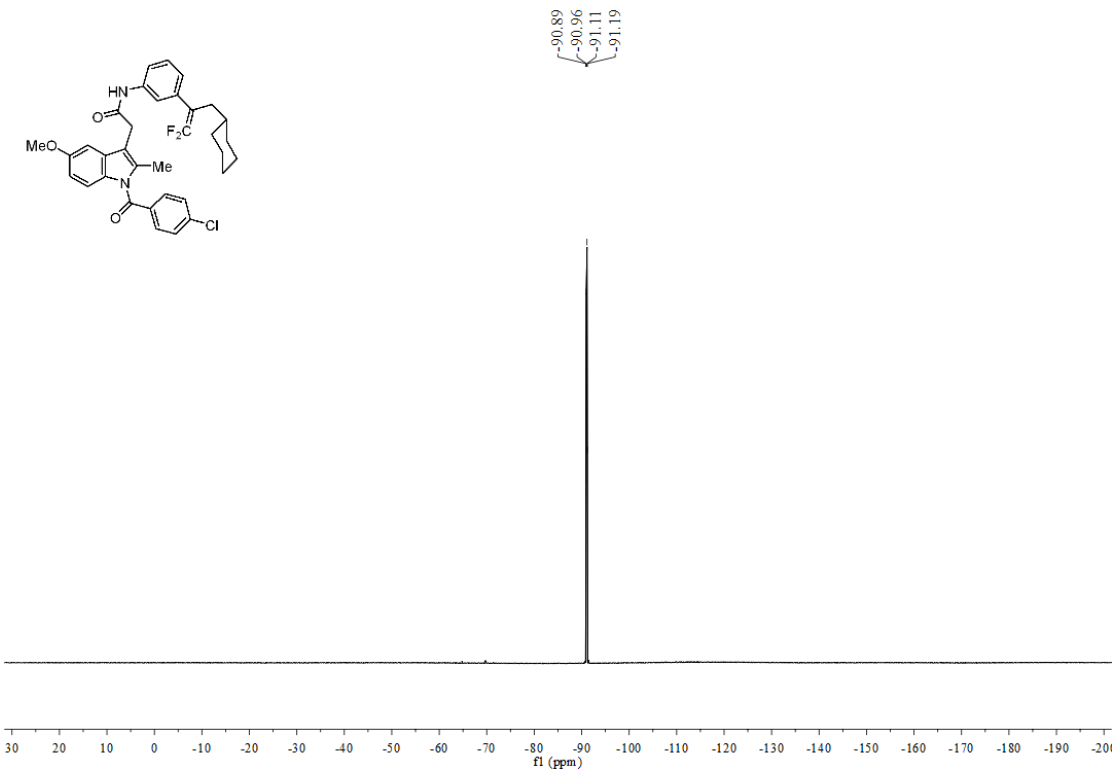
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 50



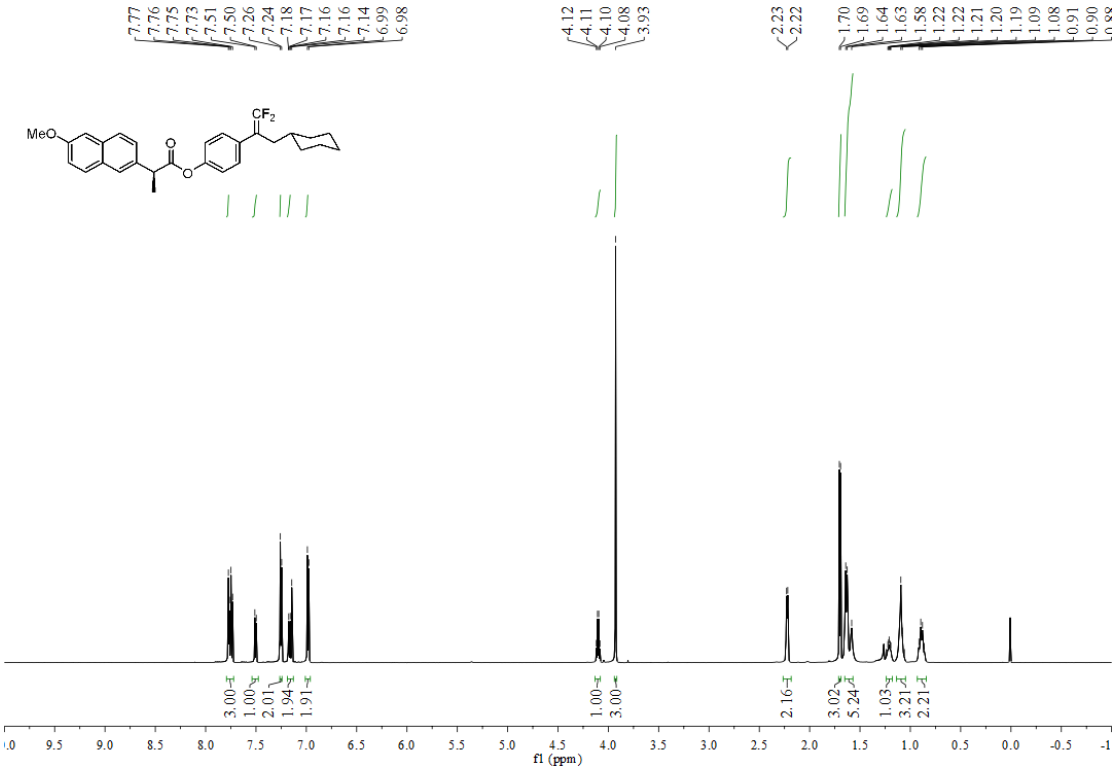
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 50



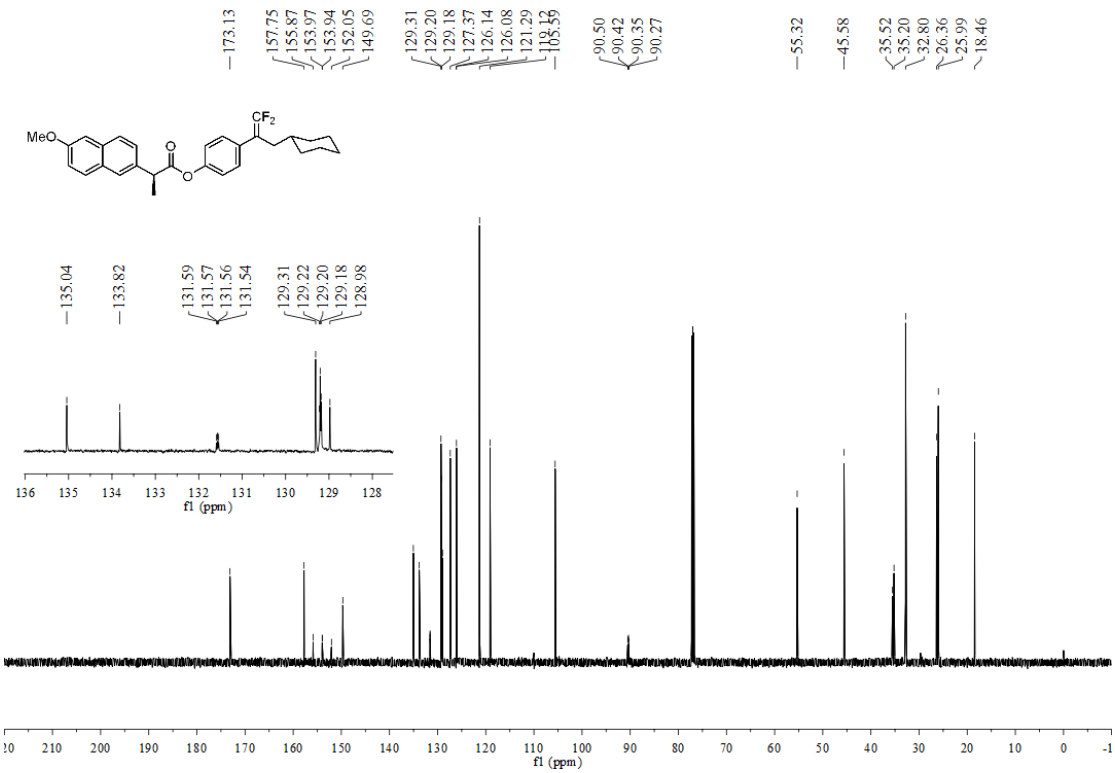
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 50



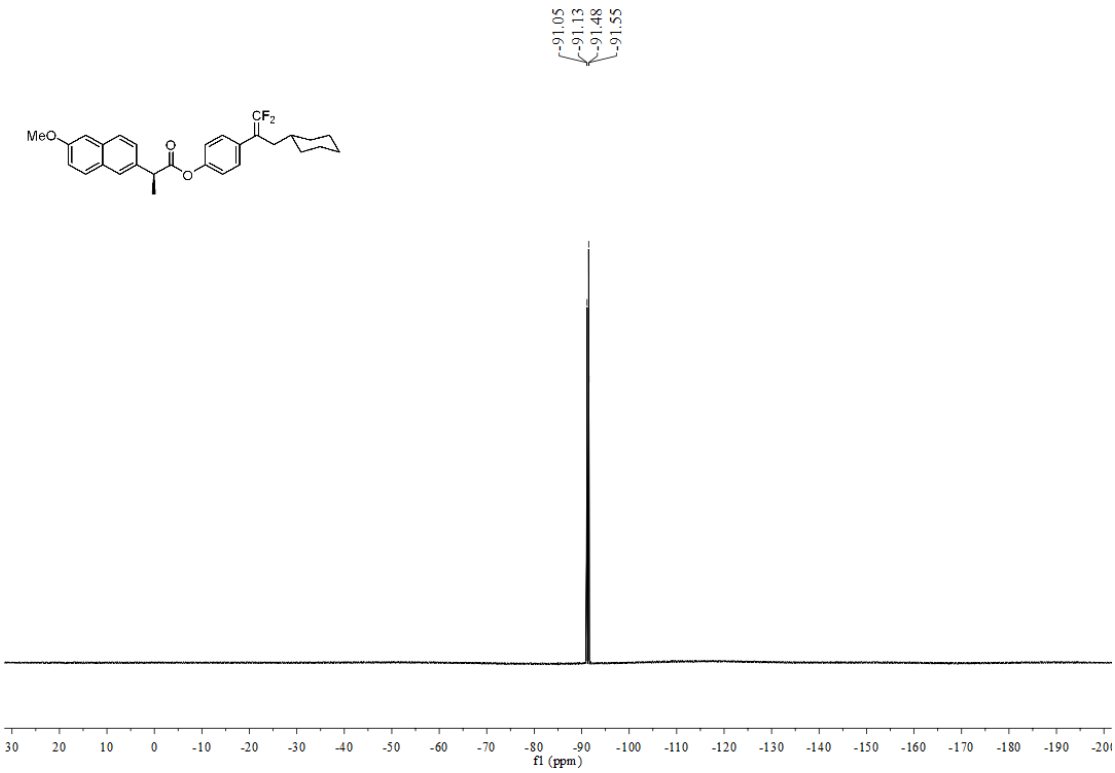
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 51



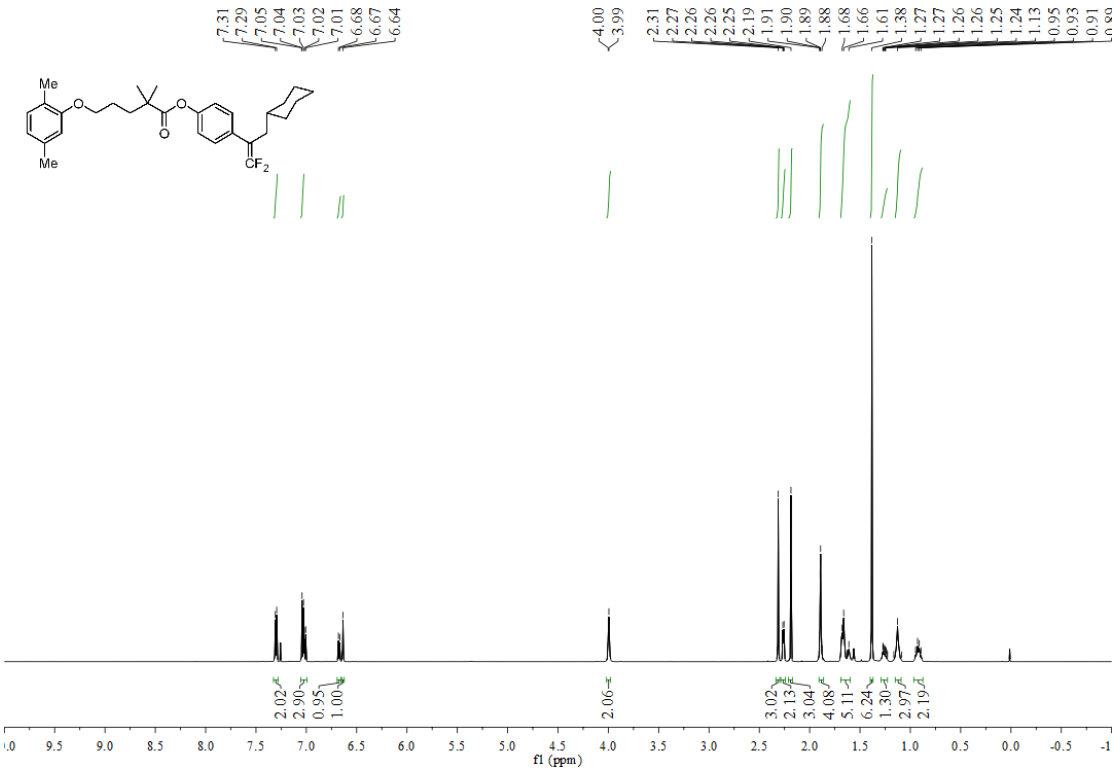
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 51



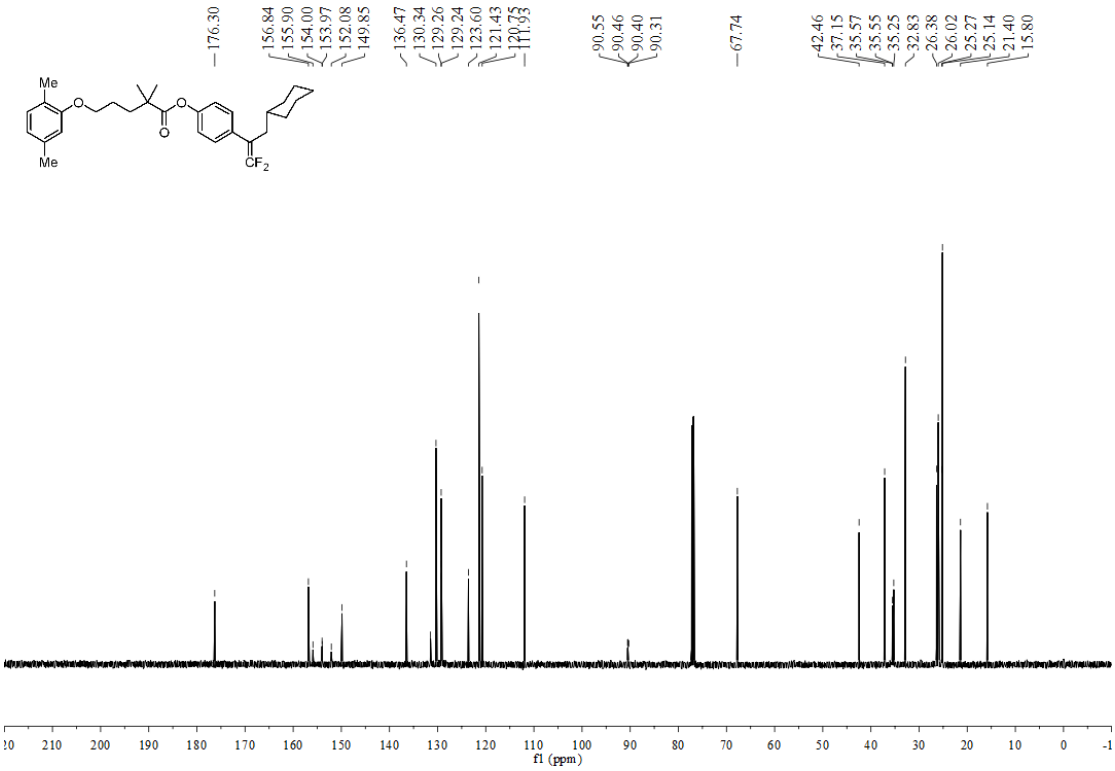
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 51



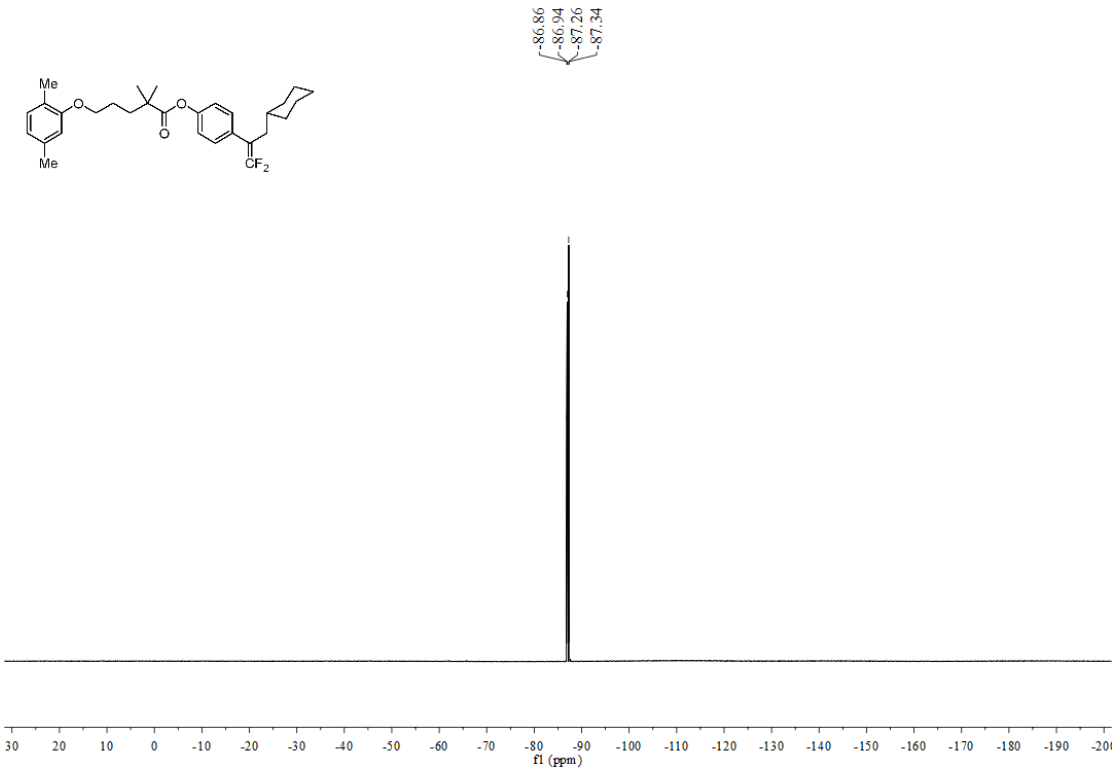
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 52



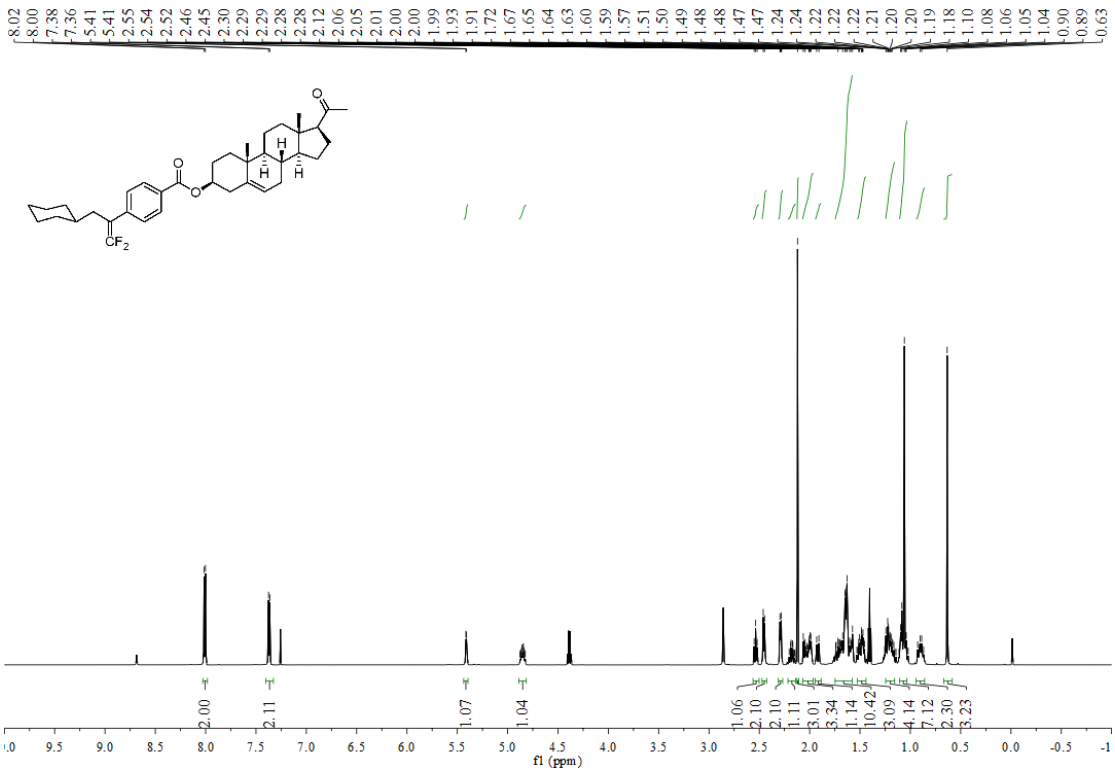
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 52



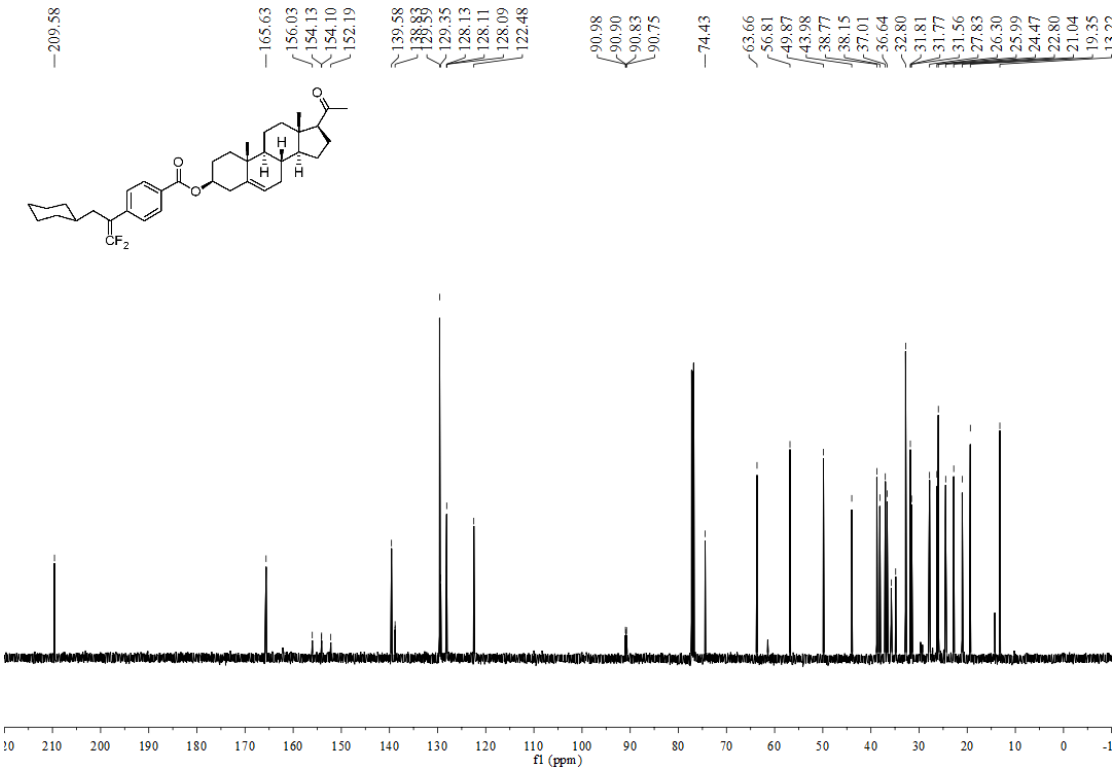
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 52



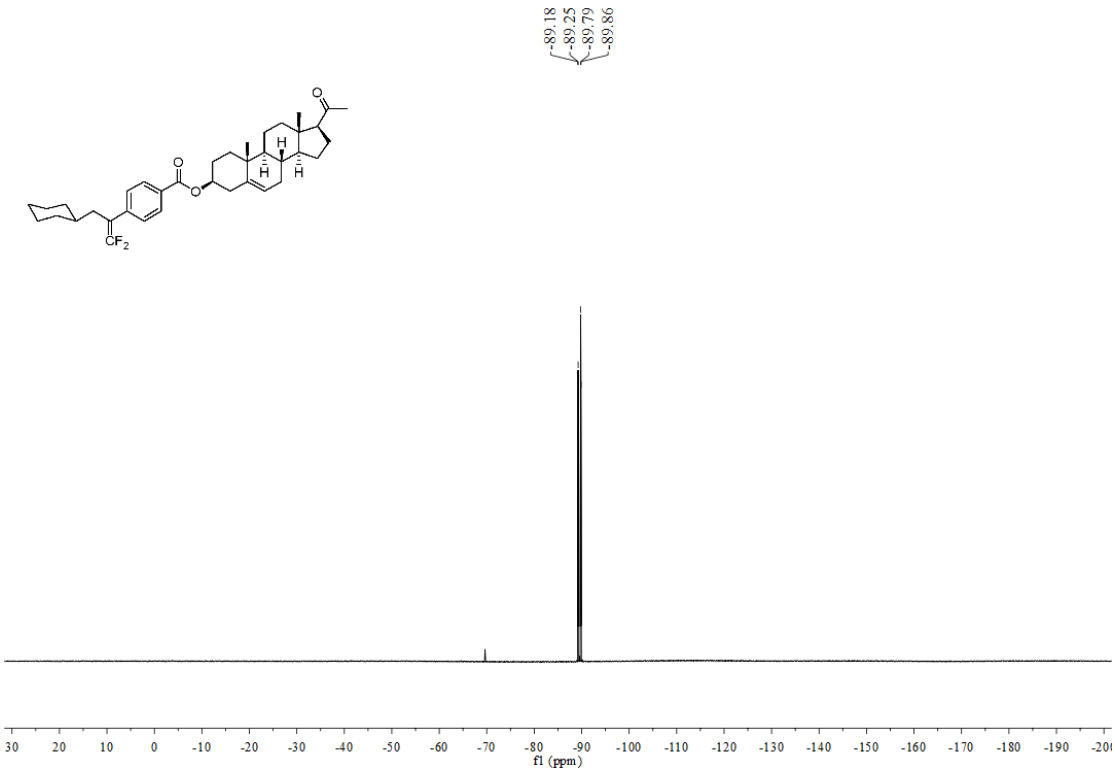
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 53



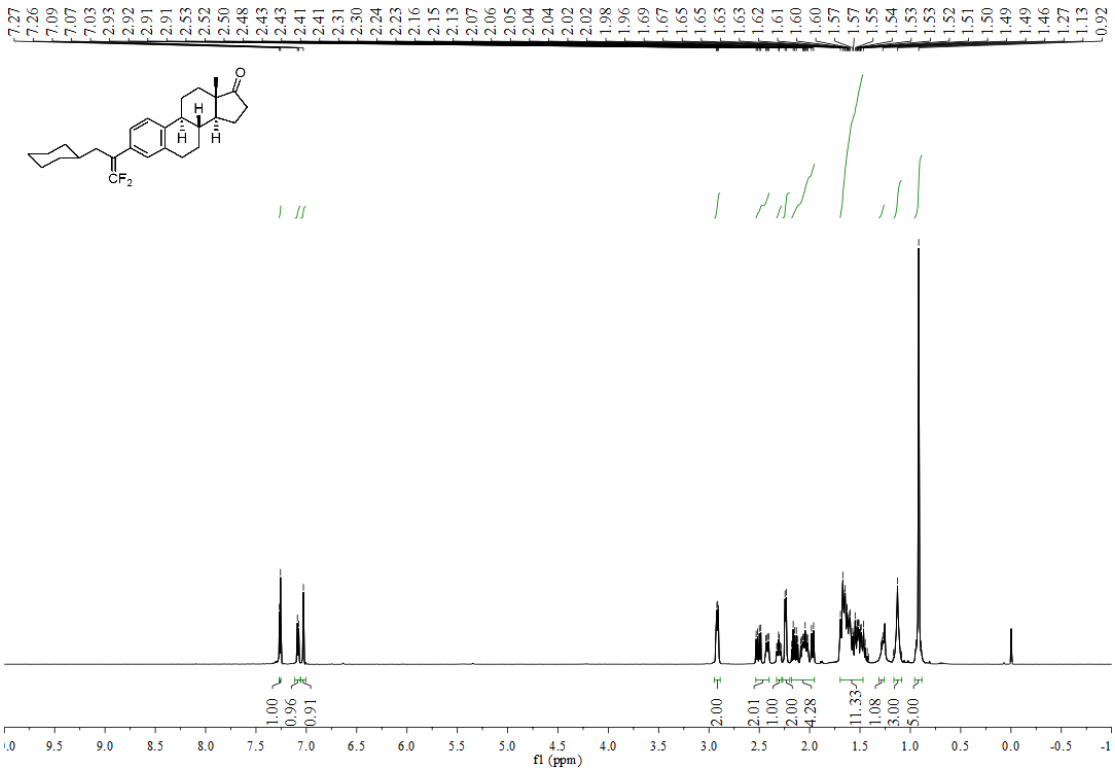
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 53



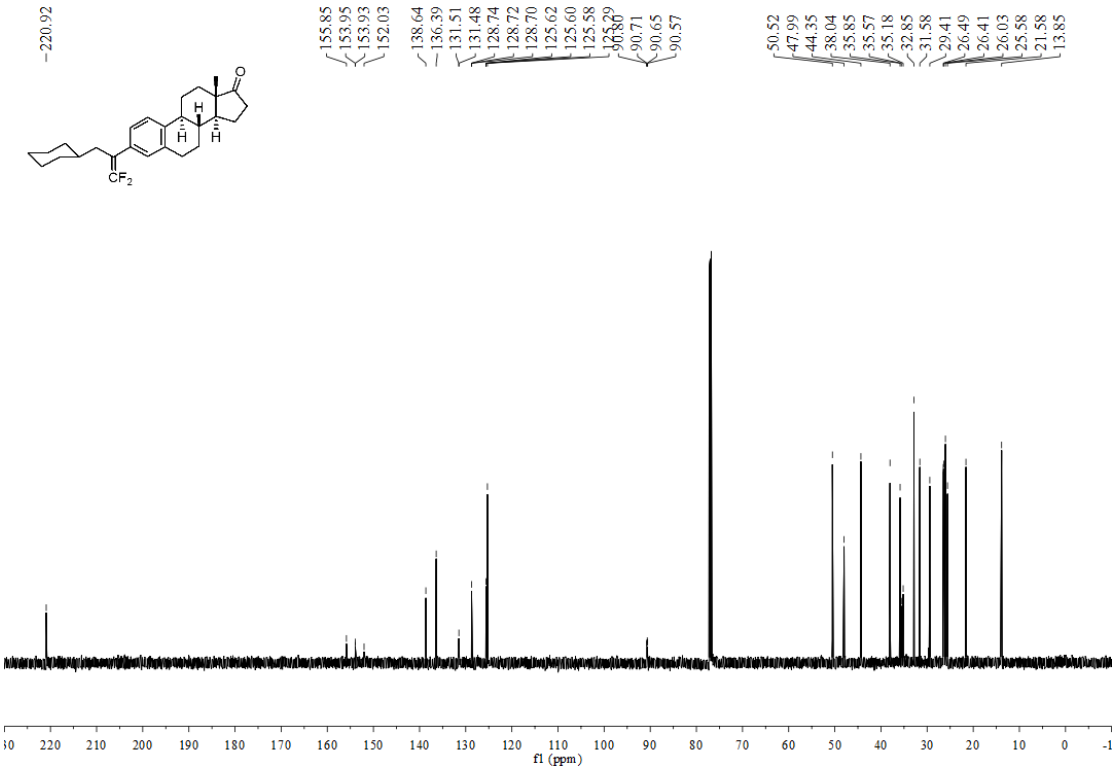
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 53



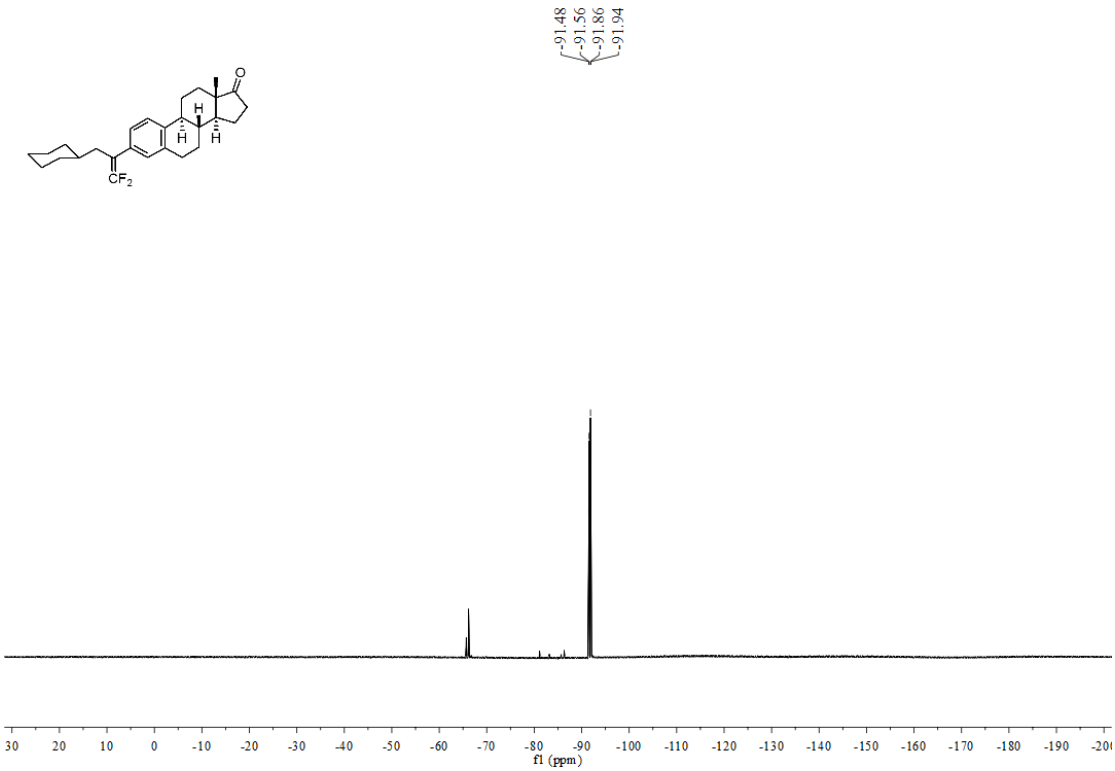
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 54



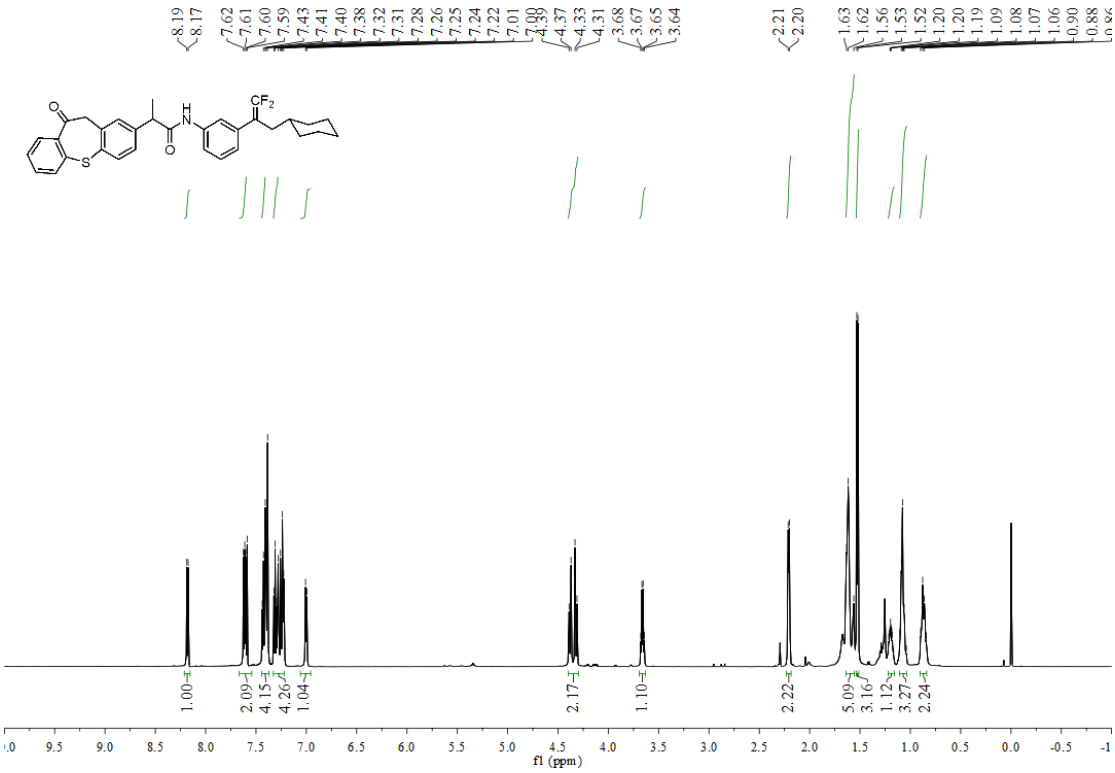
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 54



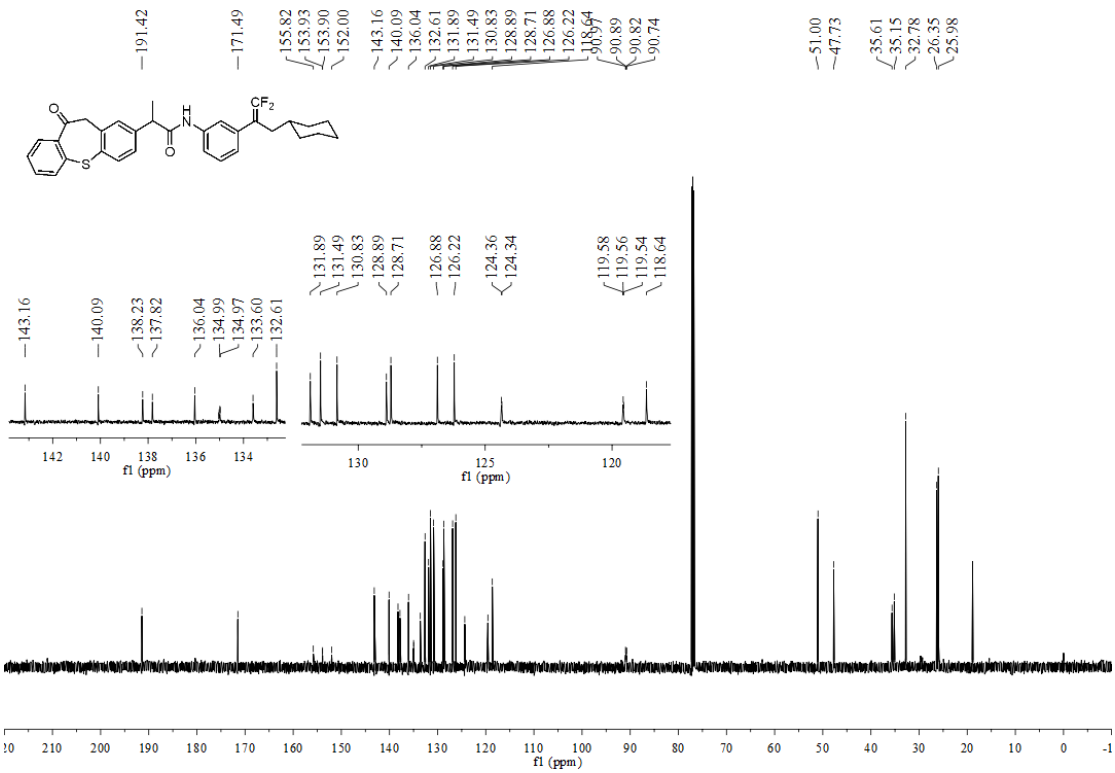
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 54



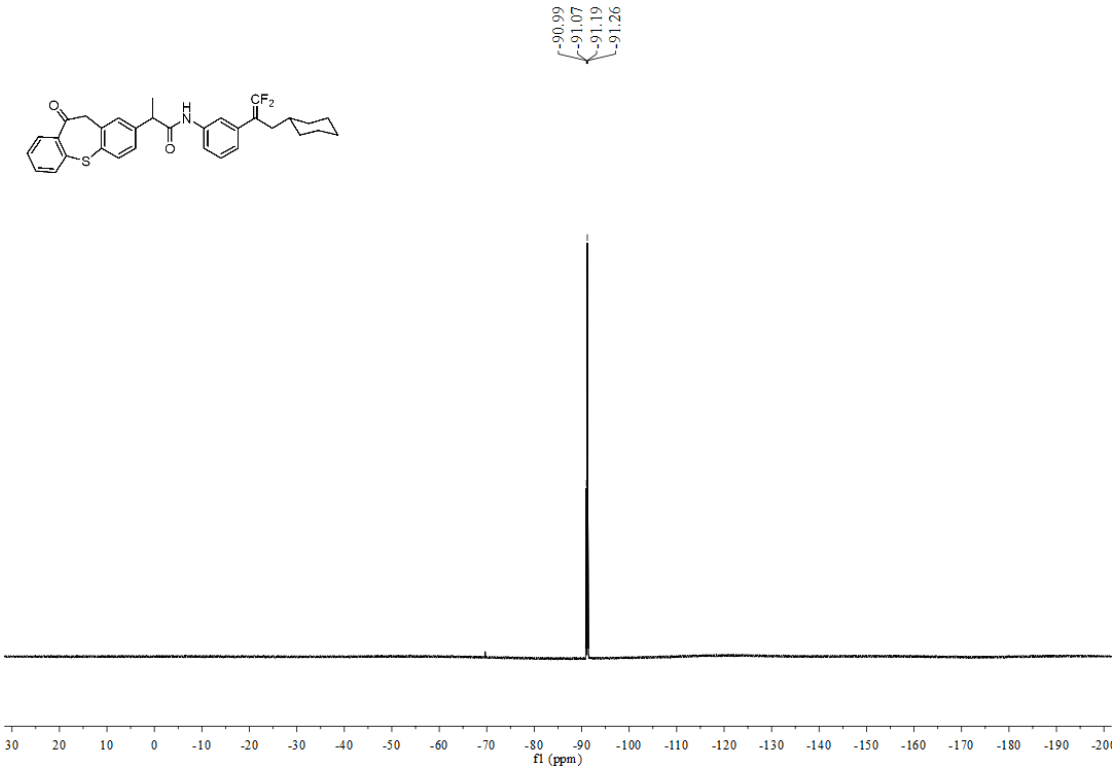
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 55



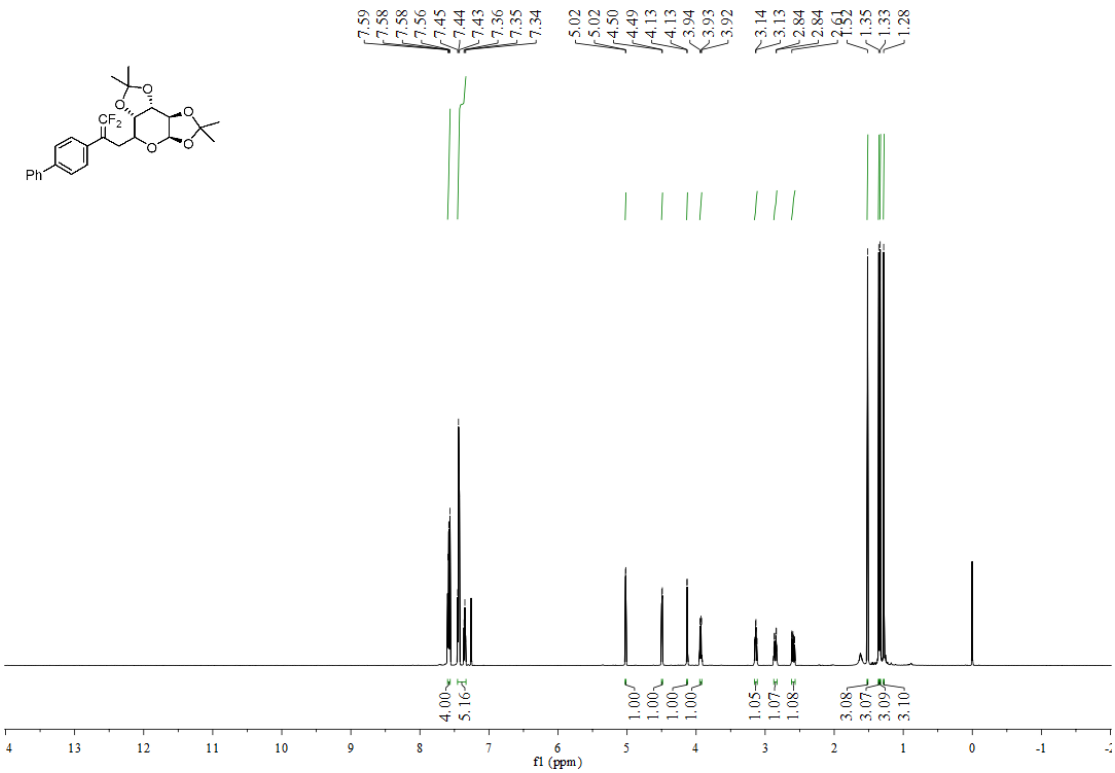
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 55



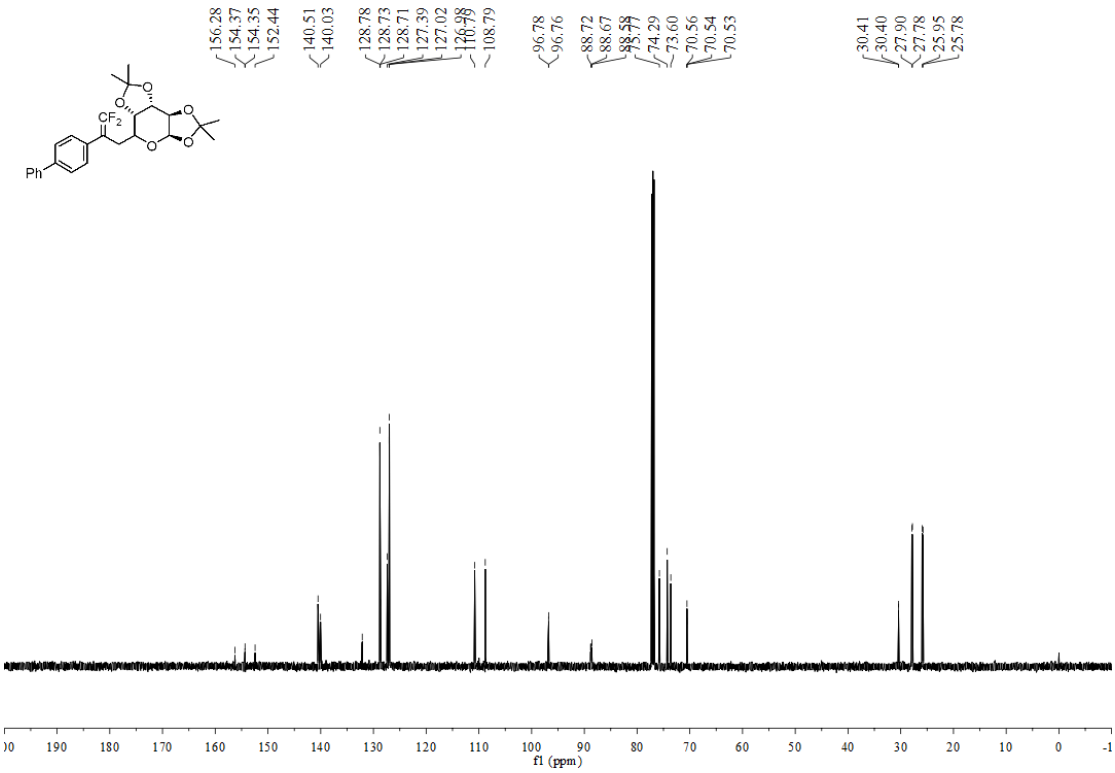
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 55



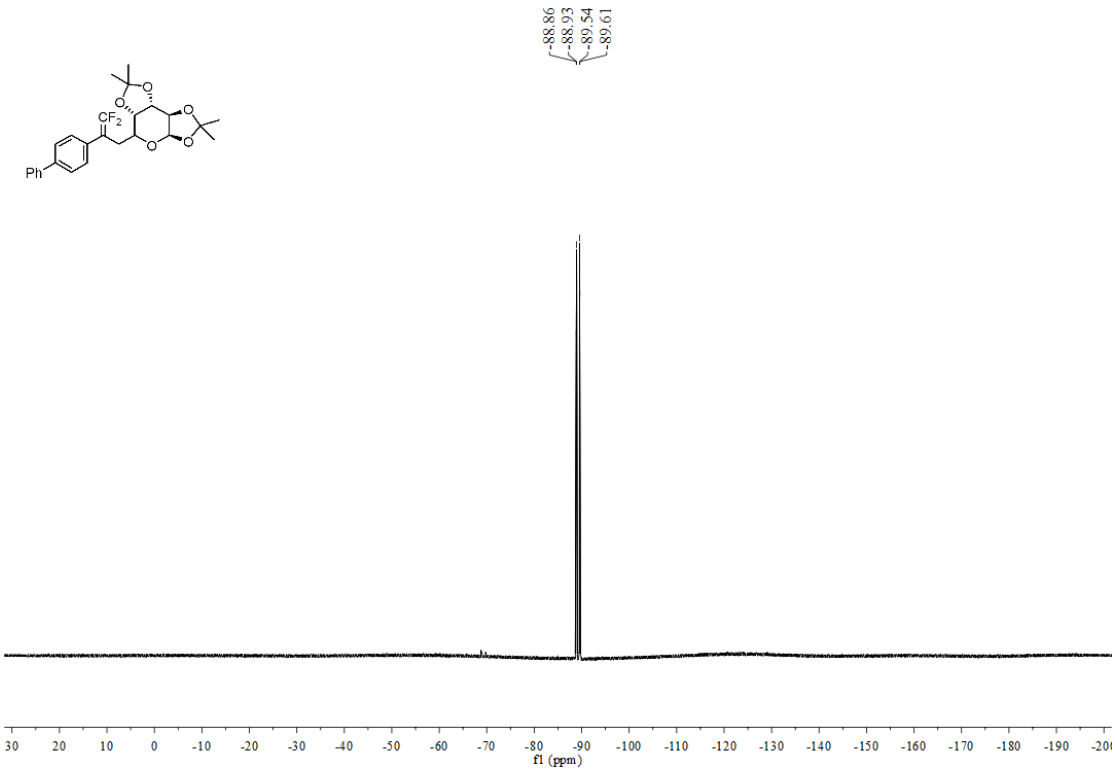
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 56



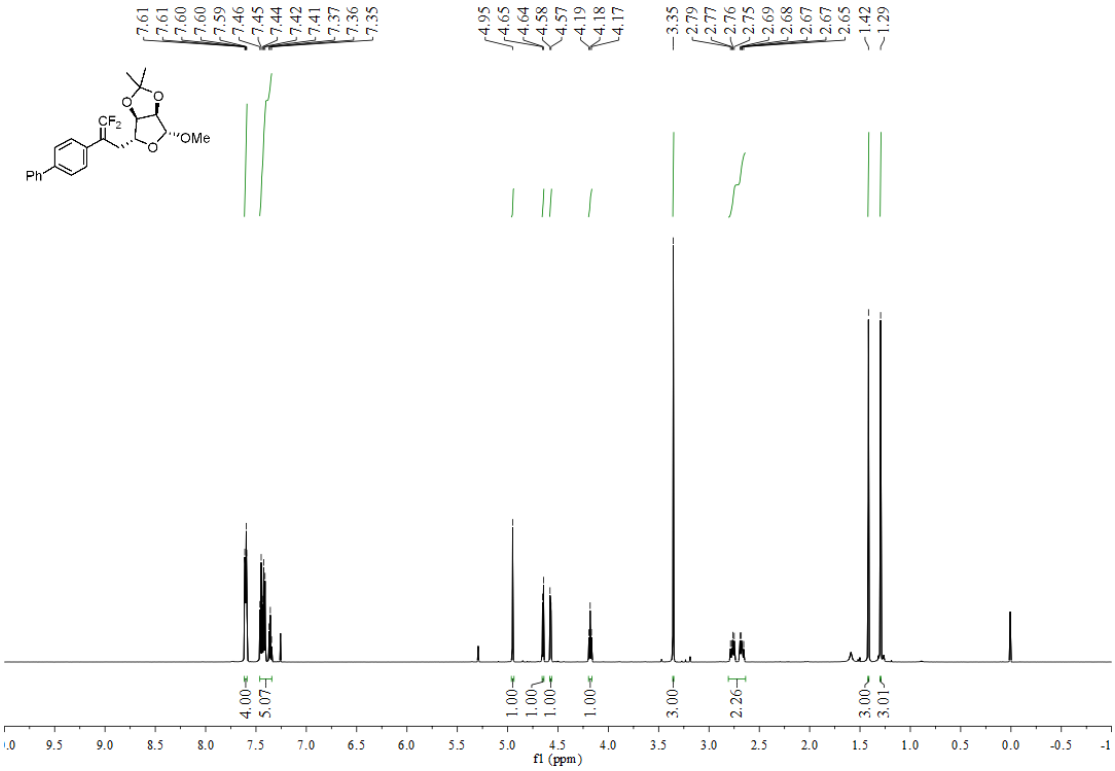
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 56



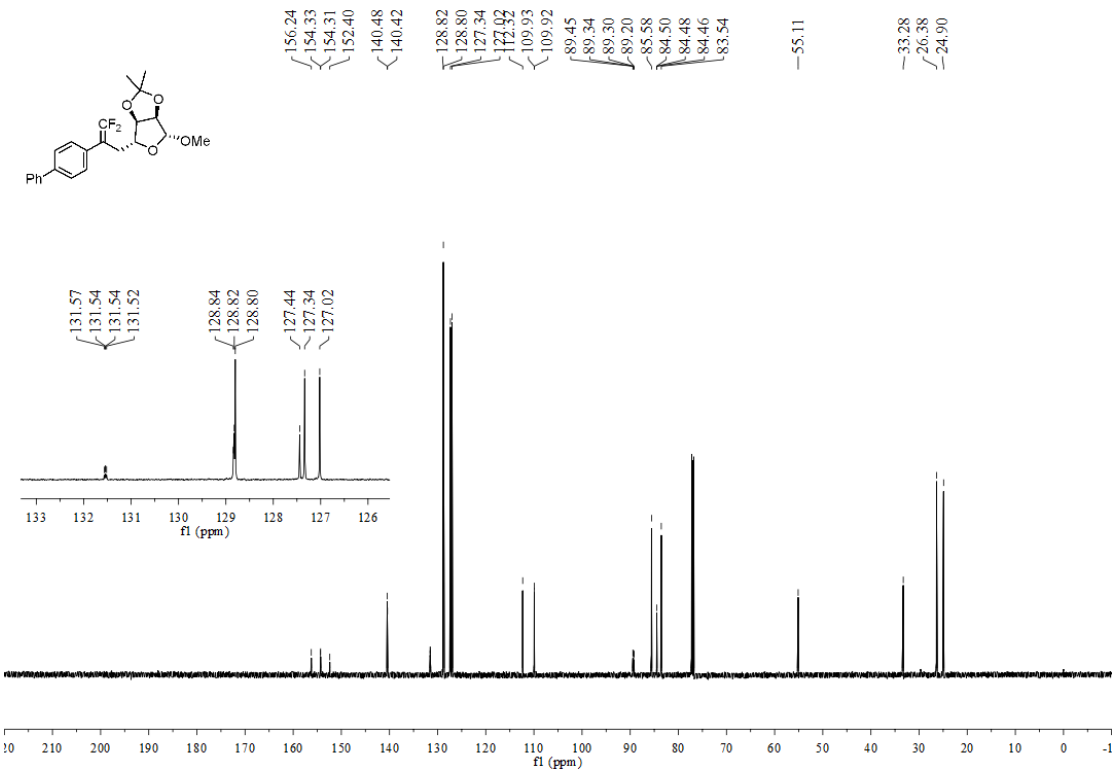
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 56



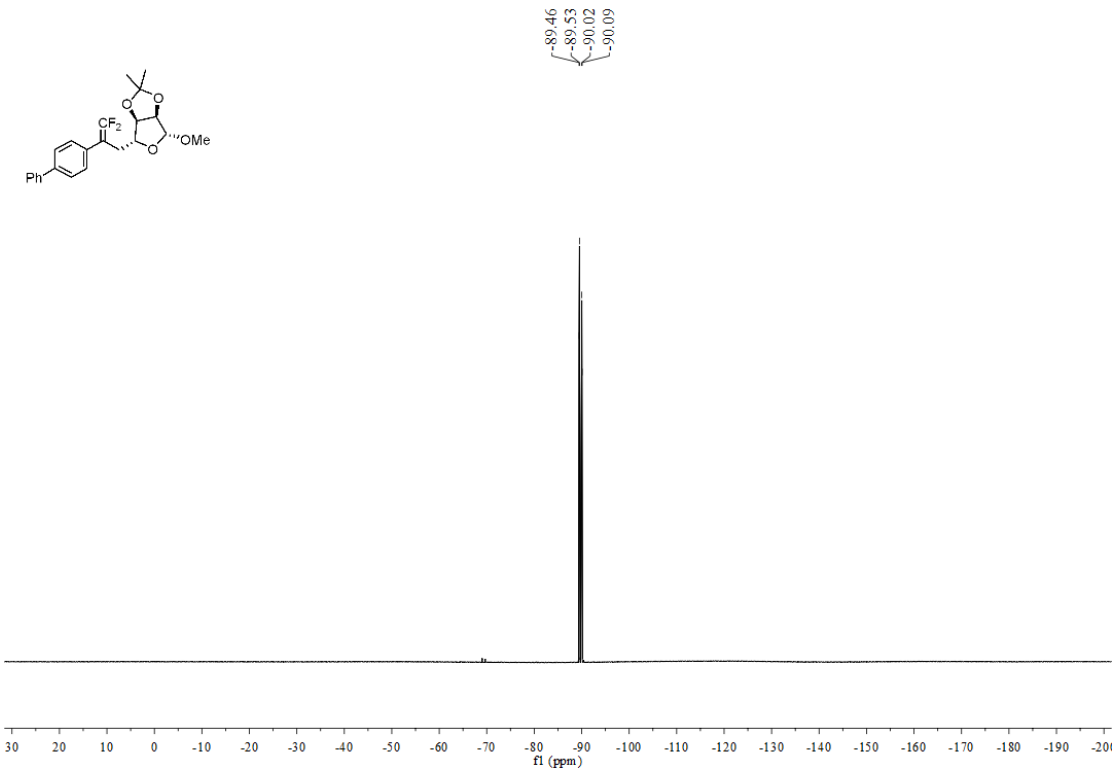
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 57



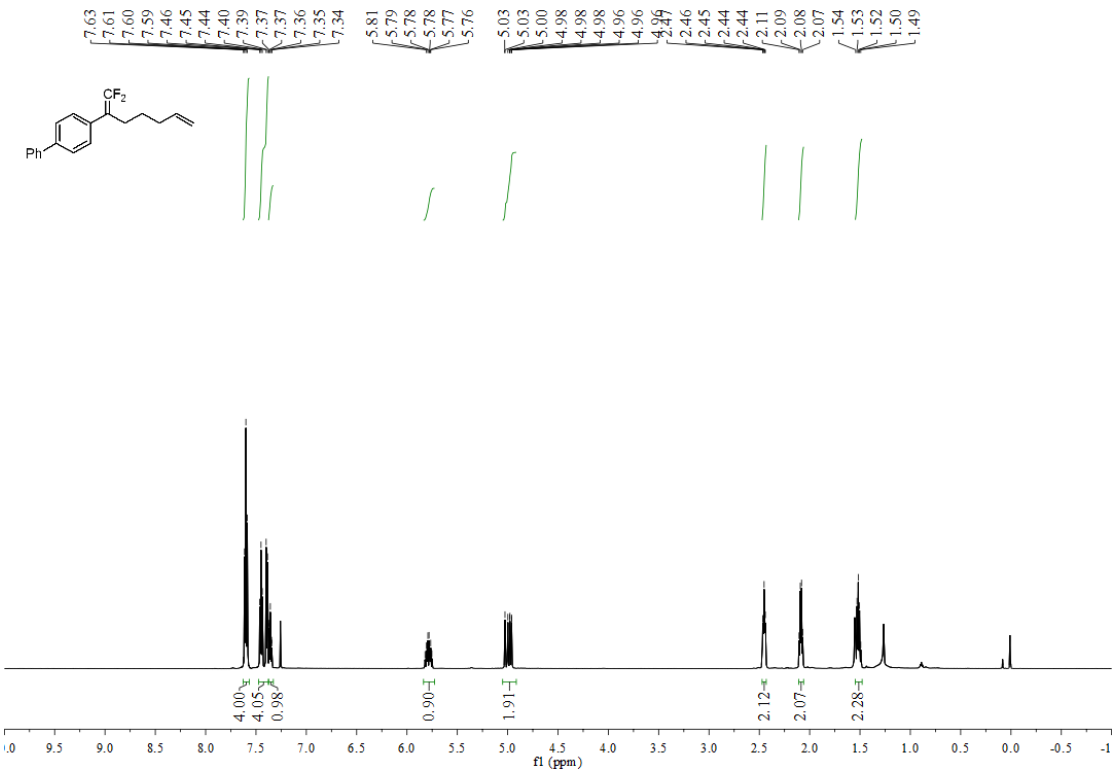
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 57



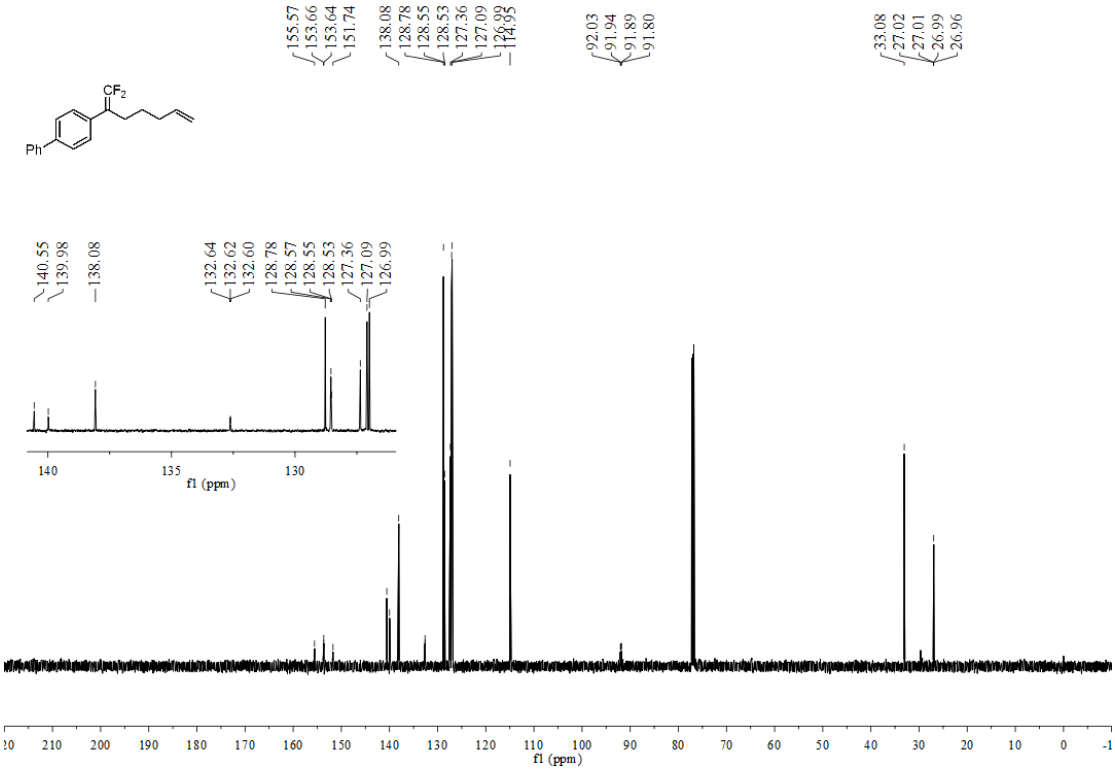
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 57



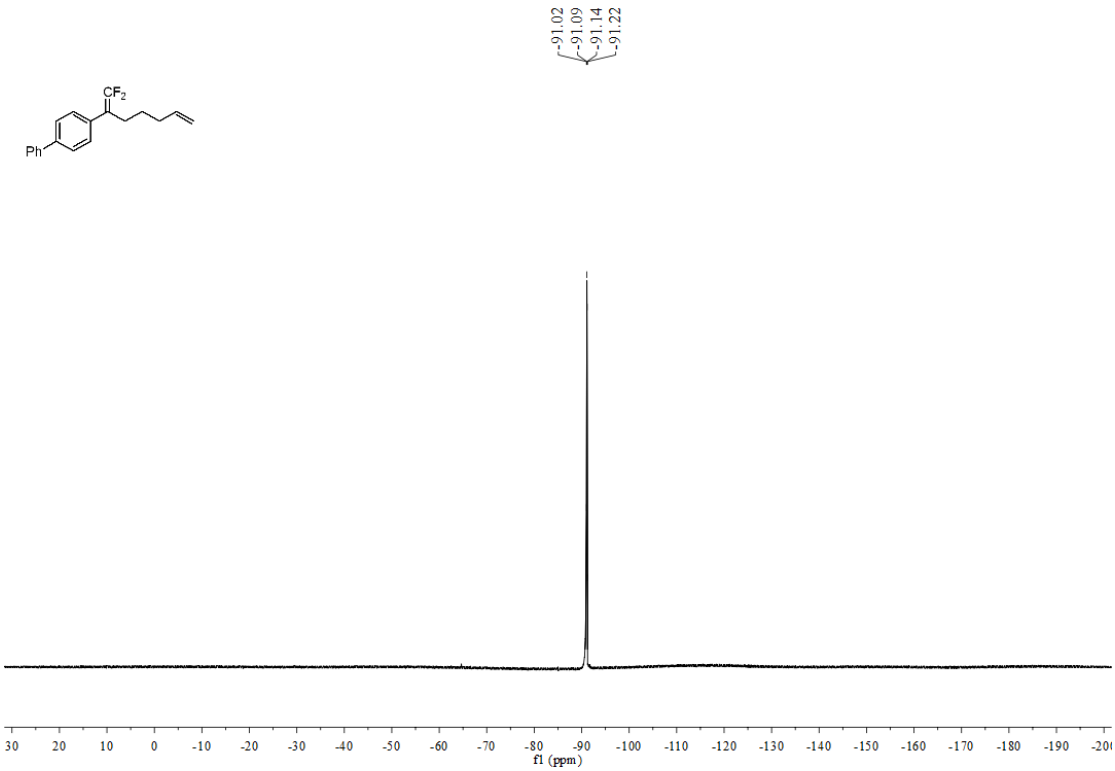
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 59



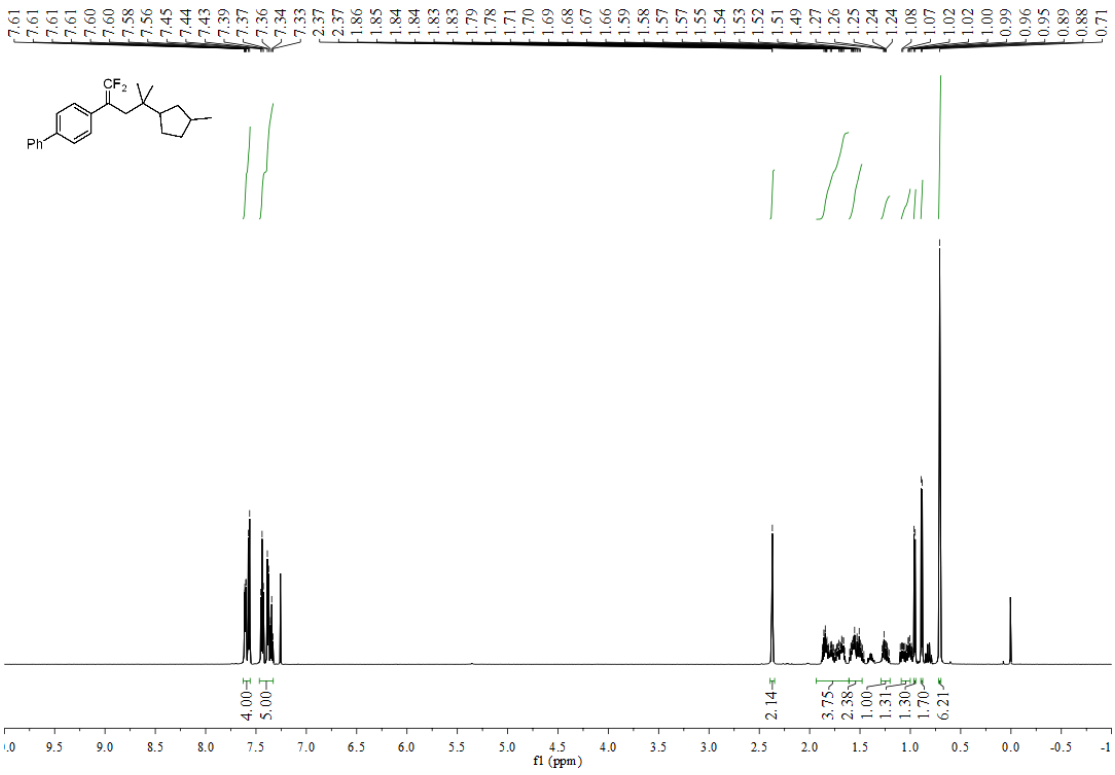
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 59



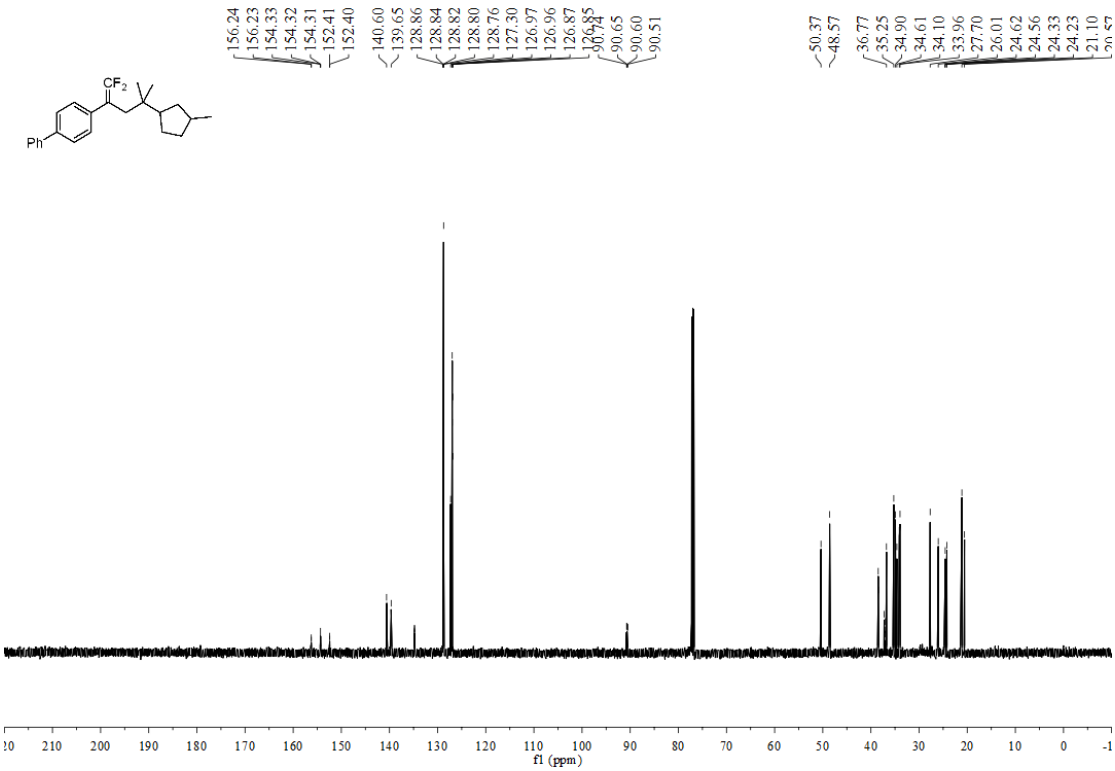
^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 59



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound 60



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound 60



^{19}F NMR (564 MHz, $CDCl_3$) spectrum of compound 60