Supporting Information

Photoinduced halogen anion-mediated arene C–H functionalization through arylsulfonium salts *via* electron donor-acceptor complexs

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1. General Information

1.1 Analytical Methods

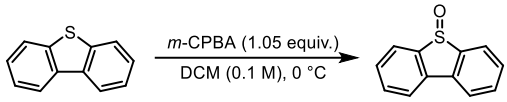
The NMR spectra were recorded on Bruker 400 or 600 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR were reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of NMR solvent: $CDCl_3$ (7.26 ppm). Coupling 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 565 MHz. ^{31}P NMR spectra were recorded at 162 or 243 MHz. ^{11}B NMR spectra were recorded at 193 MHz. The absorption spectra in solution were recorded on a UNIC 4802 UV/VIS double beam spectrophotometer in a 1.0 cm or 0.1 cm length quartz cell and measured at room temperature. 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. GC chromatograms were recorded on Shimadzu GC-2014.

1.2 Materials

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity ≥ 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 were accomplished using forced-flow chromatography on silica gel (200-300 mesh). The LED lamps were purchased from Kessil (427 nm, 440 nm), HepatoChem (450 nm), Anhui Kemi Instrument Co., Ltd. (365 nm, 390 nm, 420 nm, 455 nm) and ROGER (425 nm, 455 nm). The photo-reaction setup was purchased from HepatoChem.

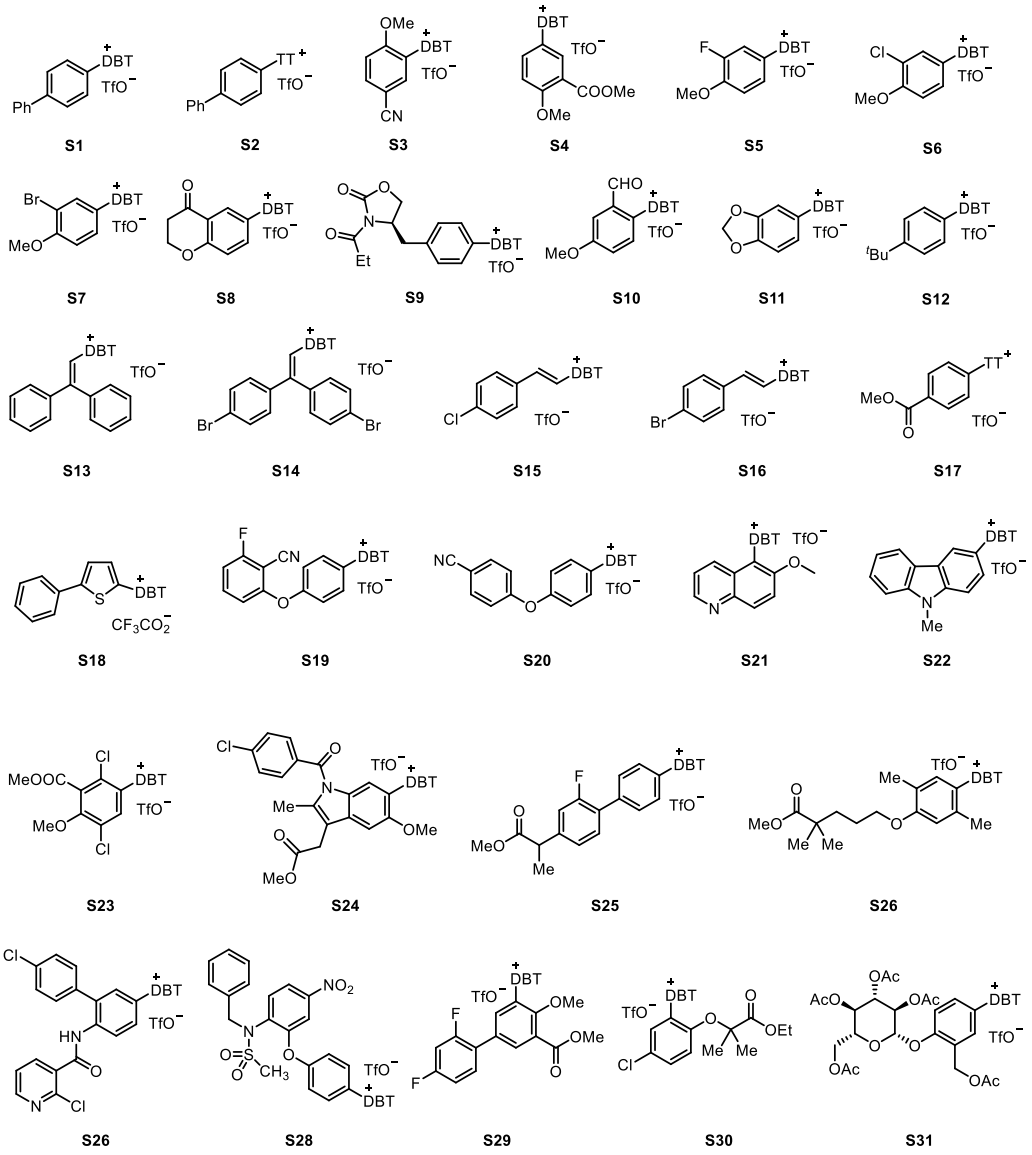
2. General procedure for preparation of substrates

2.1 General procedure for preparation of sulfoxides[1]

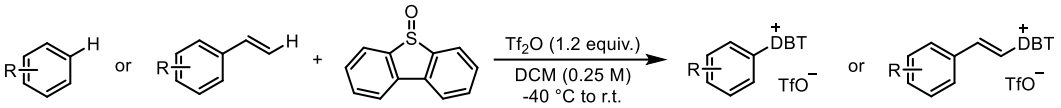


Sulfide (1.0 equiv.), was dissolved in DCM (0.1 M) and cooled to 0 °C. *m*-CPBA (1.05 equiv.) was added portion wise over 30 minutes at 0 °C and the resulting suspension stirred for 2 h. The mixture was diluted with DCM, washed with brine, and dried over anhydrous Na_2SO_4. Upon filtration, the organic layers were combined and concentrated on rotary evaporator. The residue was purified by silica gel column chromatography to give the product.

2.2 General procedure for preparation of sulfonium salts from arenes and styrenes[2-4]

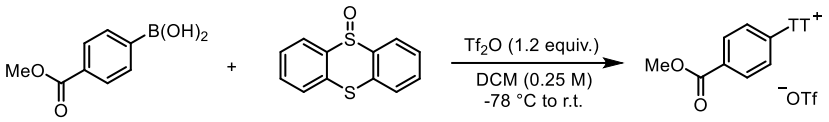


A. Preparation of substrates S1-S16



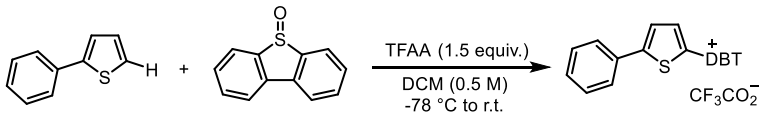
Under an argon atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 4.8 mmol, 1.2 equiv.) was added to a solution of arene or styrene (4.0 mmol, 1.0 equiv.) and dibenzo[*b,d*]thiophene 5-oxide (4.4 mmol, 1.1 equiv.) in DCM (0.25 M) at -40 ℃ with stirring. The mixture was reacted at -40 ℃ for 1 h, then at room temperature for another 1 h. After stirring for 2 h, the solution was diluted with DCM, and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel to give the product.

B. Preparation of substrate S17



Under an argon atmosphere, trifluoromethanesulfonic anhydride (Tf_2O, 1.2 mmol, 1.2 equiv.) was slowly added to a stirred solution of the (4-(methoxycarbonyl)phenyl)boronic acid (1.0 mmol, 1.0 equiv.) and dibenzo[*b,d*]thiophene 5-oxide (1.0 mmol, 1.0 equiv.) in DCM (0.25 M) at -78 ℃ with stirring. The mixture was reacted at -78 ℃ for 1 h, then at room temperature for another 1 h. After stirring for 2 h, the reaction was quenched with the addition of methanol which removed the dark colour of the reaction mixture. At this point, the solvent was removed under vacuum while keeping the water bath at 30 °C. The residue was purified by silica gel column chromatography to give the product. **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 8.86 (d, *J* = 7.5 Hz, 2H), 8.05 – 7.98 (m, 2H), 7.90 – 7.74 (m, 6H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 164.9, 136.8, 136.4, 135.0, 134.1, 131.1, 130.3, 130.3, 129.2, 128.2, 119.1, 52.8. **HRMS** (ESI) calcd. for $C_{20}H_{15}O_2S_2$ $[M\text{-}CF_3O_3S]^+$: 351.0508, found: 351.0505.

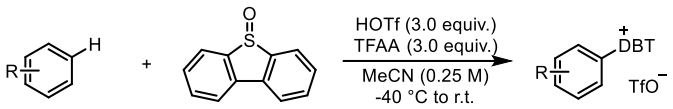
C. Preparation of substrate S18



Under an argon atmosphere, trifluoroacetic anhydride (TFAA, 6 mmol, 1.5 equiv.) was added to a solution of (hetero)arene (4.0 mmol, 1.0 equiv.) and dibenzo[b,d]thiophene 5-oxide (4.4 mmol, 1.1 equiv.) in MeCN (0.5 M) at -78 ℃ with stirring. The mixture was slowly warmed to room temperature, reacted at room temperature for 1 h. Then, the solution was diluted with DCM, and neutralized by a saturated aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to

dryness under reduced pressure. The crude product was purified by column chromatography on silica gel to give the product.

D. Preparation of substrates S19-S31

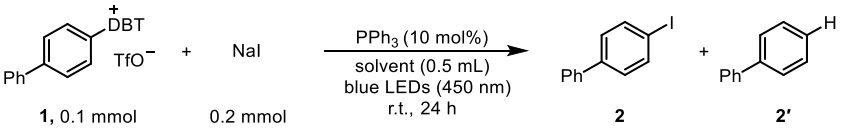


Under an argon atmosphere, trifluoroacetic anhydride (TFAA, 12.0 mmol, 3.0 equiv.) and trifluoromethanesulfonic acid (TfOH, 12.0 mmol, 3.0 equiv.) were successively added to a solution of arene (4.0 mmol, 1.0 equiv.) in MeCN (0.25 M) at -40 ℃ with stirring. Then, dibenzo[*b,d*]thiophene 5-oxide (6 mmol, 1.5 equiv.) was slowly added. The mixture was reacted at -40 ℃ for 1 h, then at room temperature for another 1 h. After stirring for 2 h, the solution was diluted with DCM, neutralized by a saturated aqueous $NaHCO_3$ solution and washed with aqueous NaOTf solution (5% (w/w)). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel to give the product.

3. Investigation of the key reaction parameters

3.1 Investigation of the key reaction parameters for iodination

Table S1. Screening of different solvents

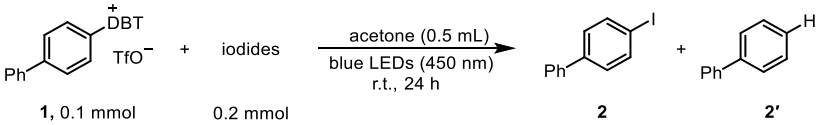


1, 0.1 mmol 0.2 mmol **2** **2′**

entry	solvent	yield of **2** (%)	yield of **2′**(%)
1	DMF	51	34
2	DMA	55	31
3	Acetone	73	8
[a]4	Acetone	76	trace
5	DME	60	25
6	THF	59	28
7	Dioxane	68	19
8	Diglyme	59	26
9	Toluene	56	7
10	DMSO	59	8
11	MeCN	44	5
12	DCE	67	16

The yield was determined by GC using benzophenone as internal standard. [a]no PPh_3.

Table S2. Screening of different iodides

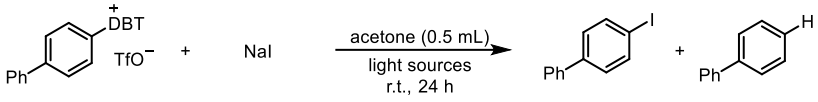


1, 0.1 mmol 0.2 mmol **2** **2′**

entry	iodides	yield of **2** (%)	yield of **2′** (%)
1	LiI	37	trace
2	NaI	76	trace
3	KI	74	trace
4	CsI	37	trace
5	*n*-Bu_4NI	75	5

The yield was determined by GC using benzophenone as internal standard.

Table S3. Screening of different light sources

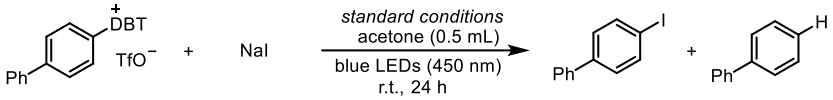


1, 0.1 mmol 0.2 mmol **2** **2′**

entry	slight sources	yield of **2** (%)	yield of **2′** (%)
1	455 nm	61	trace
2	450 nm	76	trace
3	440 nm	66	trace
4	427 nm	72	trace
5	420 nm	73	trace
6	390 nm	73	trace
7	365 nm	75	trace

The yield was determined by GC using benzophenone as internal standard.

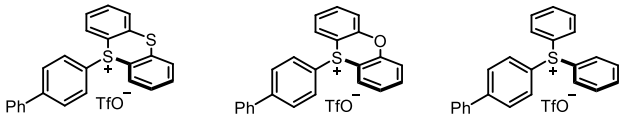
Table S4: Control experiments



1, 0.1 mmol 0.2 mmol **2** **2′**

entry	Variation from conditions	yield of **2** (%)	yield of **2′** (%)
1	none	76 (70)	trace
2	0.3 mmol NaI	68	trace
3	acetone (0.1 M)	63	5
4	0.2 mmol I_2 instead of 0.2 mmol NaI	trace	trace
5	0.1 mmol I_2 was added	5	trace
6	**1a** instead of **1**	21	5
7	**1b** instead of **1**	47	10
8	**1c** instead of **1**	18	trace
9	no light (60 °C)	trace	n.d.

The yield was determined by GC using benzophenone as internal standard. Isolated yield in parentheses.



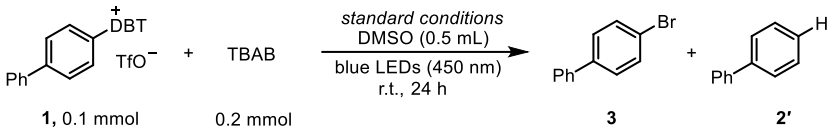
1a **1b** **1c**

The phenomena of model reaction mixture (TS4 entry 1)

Figure S1. Left: before the reaction; **Right:** after the reaction

3.2 Investigation of the key reaction parameters for bromination

Table S5. control experiments

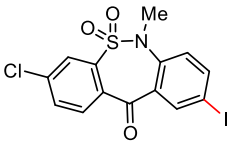


1, 0.1 mmol 0.2 mmol **3** **2′**

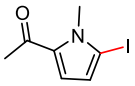
entry	Variation from conditions	yield of **3** (%)	yield of **2′** (%)
1	none	74 (71)	9
2	0.1 mmol TBAB	57	11
3	0.3 mmol TBAB	74	9
4	DMSO (0.1 M)	72	13
5	455 nm	43	5
6	**1a** instead of **1**	14	trace
7	**1b** instead of **1**	17	trace
8	no light (50 °C)	trace	trace

The yield was determined by GC using benzophenone as internal standard. Isolated yield in parentheses.

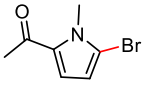
3.3 Unsuccessful examples



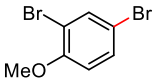
20%



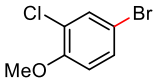
28%



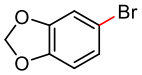
trace



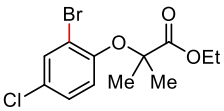
trace



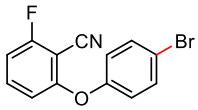
trace



25%



trace



trace

4. General procedure and spectral data

4.1 General procedure A for iodination

Sulfonium salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 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, acetone (0.5 mL) was added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs (18 W), maintained at approximately room temperature. After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The residue was purified via flash column chromatography on silica gel to give the product (Eluent: petroleum ether/ethyl acetate).

4.2 General procedure B for bromination

Sulfonium salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 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, DMSO (0.5 mL) was added using a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs (18 W), maintained at approximately room temperature. 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).

4.3 General procedure C for phosphonylation

Sulfonium salts (0.1 mmol, 1.0 equiv.), NaBr (0.2 mmol, 2.0 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, acetone (0.5 mL) and the corresponding radical trap reagent (0.5 mmol, 5.0 equiv.) were added using gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 455 nm blue LEDs (15 W), maintained at approximately room temperature. After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The residue was purified via flash column chromatography on silica gel to give the product (Eluent: petroleum ether/ethyl acetate).

4.4 General procedure D for (hetero)arylation

Sulfonium salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.) and the corresponding radical trap reagent (if solid, 20 mmol, 20.0 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, DMSO (0.5 mL) and the corresponding radical trap reagent (if liquid, 20 mmol, 20.0 equiv.) were added using gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 455 nm blue LEDs (15 W), maintained at approximately room temperature. 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

Halogenation was conducted using HepatoChem (Figure S2-a), phosphonylation and (hetero)arylation were conducted using ROGER (Figure S2-b).

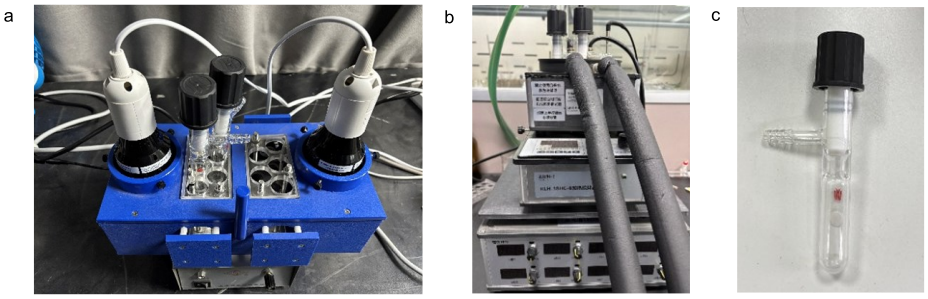
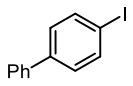


Figure S2. (a) Photoreactor of halogenation. (b) Photoreactor of phosphonylation and (hetero)arylation. (c) Reaction tube

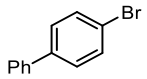
4.5 Characterization data for the products



4-iodo-1,1'-biphenyl (2)[5]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 70% yield as white solid (19.6 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 – 7.75 (m, 2H), 7.57 – 7.54 (m, 2H), 7.46 – 7.42 (m, 2H), 7.39 – 7.32 (m, 3H).

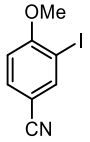
^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.7, 140.0, 137.8, 129.0, 128.9, 127.7, 126.9, 93.0.



4-bromo-1,1'-biphenyl (3)[6]: Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 71% yield as white solid (16.5 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 4H), 7.49 – 7.44 (m, 4H), 7.41 – 7.36 (m, 1H).

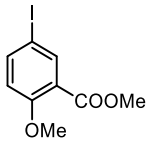
^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.1, 140.0, 131.8, 128.9, 128.7, 127.6, 126.9, 121.5.



3-iodo-4-methoxybenzonitrile (4)[7]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 92% yield as white solid (23.8 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H).

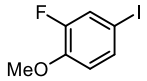
^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.5, 142.7, 134.1, 117.6, 110.7, 105.8, 86.0, 56.7.



methyl 5-iodo-2-methoxybenzoate (5)[8]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 78% yield as white solid (22.8 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 1.3 Hz, 1H), 7.72 (dd, *J* = 8.8, 1.4 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 3.87 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.1, 158.9, 142.0, 140.0, 122.0, 114.3, 81.7, 56.1, 52.3.

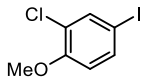


2-fluoro-4-iodo-1-methoxybenzene (6)[9]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 71% yield as colorless oil (17.9 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.37 (m, 1H), 7.37 (s, 1H), 6.73 – 6.68 (m, 1H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.3 (d, *J* = 251.4 Hz), 147.9 (d, *J* = 10.4 Hz), 133.3 (d, *J* = 4.0 Hz), 125.1 (d, *J* = 20.6 Hz), 115.2 (d, *J* = 2.1 Hz), 80.9 (d, *J* = 7.1 Hz), 56.3.

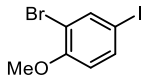
^{19}F NMR (565 MHz, Chloroform-*d*) δ -132.29.



2-chloro-4-iodo-1-methoxybenzene (7)[10]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 75% yield as white solid (20.1 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 2.1 Hz, 1H), 7.50 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 3H).

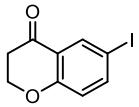
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.1, 138.2, 136.5, 123.8, 113.9, 81.9, 56.2.



2-bromo-4-iodo-1-methoxybenzene (8)[11]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 84% yield as white solid (26.2 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 3.86 (s, 3H).

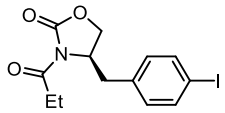
^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.9, 140.9, 137.2, 113.8, 112.9, 82.4, 56.3.



6-iodochroman-4-one (9)[12]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 51% yield as white solid (13.9 mg, Eluent: petroleum ether/ethyl acetate = 10/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 2.3 Hz, 1H), 7.71 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 4.53 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 6.5 Hz, 2H).

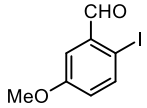
^{13}C NMR (151 MHz, Chloroform-*d*) δ 190.3, 161.4, 144.2, 135.8, 123.1, 120.3, 83.7, 67.0, 37.3.



(*R*)-4-(4-iodobenzyl)-3-propionyloxazolidin-2-one (10)[5]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 64% yield as white solid (22.9 mg, Eluent: petroleum ether/ethyl acetate = 8/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 4.67 – 4.58 (m, 1H), 4.21 (t, *J* = 8.5 Hz, 1H), 4.11 (dd, *J* = 9.1, 2.6 Hz, 1H), 3.23 (dd, *J* = 13.5, 3.1 Hz, 1H), 3.03 – 2.86 (m, 2H), 2.72 (dd, *J* = 13.5, 9.6 Hz, 1H), 1.19 (t, *J* = 7.3 Hz, 3H).

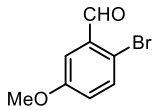
^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.0, 153.3, 138.0, 134.9, 131.3, 92.8, 66.1, 54.9, 37.5, 29.2, 8.3.



2-iodo-5-methoxybenzaldehyde (11)[13]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 52% yield as white solid (13.6 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.01 (s, 1H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 3.1 Hz, 1H), 6.91 (dd, *J* = 8.7, 3.2 Hz, 1H), 3.84 (s, 3H).

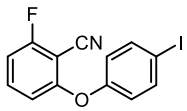
^{13}C NMR (151 MHz, Chloroform-*d*) δ 195.7, 160.2, 141.0, 135.6, 123.5, 113.5, 89.9, 55.6.



2-bromo-5-methoxybenzaldehyde (12)[14]: Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 51% yield as white solid (10.9 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.31 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 3.2 Hz, 1H), 7.03 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.8, 159.2, 134.5, 133.9, 123.1, 118.0, 112.6, 55.7.

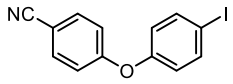


2-fluoro-6-(4-iodophenoxy)benzonitrile (13)[5]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 65% yield as white solid (22.1 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 2H), 7.49 – 7.41 (m, 1H), 6.94 – 6.85 (m, 3H), 6.62 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.9, 163.2, 160.4 (d, *J* = 4.1 Hz), 154.5, 139.3, 135.0 (d, *J* = 10.3 Hz), 122.4, 112.0 (d, *J* = 3.4 Hz), 110.9, 110.2 (d, *J* = 19.6 Hz), 89.2.

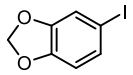
^{19}F NMR (565 MHz, Chloroform-*d*) δ -104.17.



4-(4-iodophenoxy)benzonitrile (14)[15]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 70% yield as white solid (22.4 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H).

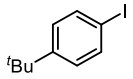
^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.0, 154.9, 139.2, 134.2, 122.4, 118.7, 118.1, 106.4, 88.5.



5-iodobenzo[*d*][1,3]dioxole (15)[16]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 50% yield as colorless oil (12.4 mg, Eluent: petroleum ether/ethyl acetate = 30/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.14 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.12 (d, *J* = 1.7 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 2H).

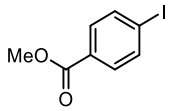
^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.7, 147.8, 130.6, 117.7, 110.5, 101.4, 82.2.



1-(*tert*-butyl)-4-iodobenzene (16)[17]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 73% yield as colorless oil (18.9 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 1.29 (s, 9H).

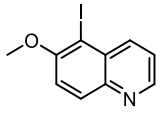
^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.8, 137.0, 127.6, 90.6, 34.6, 31.2.



methyl 4-iodobenzoate (17)[18]: Following the general procedure A, using corresponding TT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 82% yield as white solid (21.5 mg, Eluent: petroleum ether/ethyl acetate = 30/1).

^{1}H NMR (600 MHz, Chloroform-d) δ 7.82 – 7.77 (m, 2H), 7.76 – 7.71 (m, 2H), 3.90 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 166.6, 137.7, 131.0, 129.6, 100.7, 52.3.

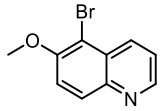


5-iodo-6-methoxyquinoline (18): Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 71% yield as white solid (20.2 mg, Eluent: petroleum ether/ethyl acetate = 5/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 4.0 Hz, 1H), 8.42 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 9.2 Hz, 1H), 7.44 – 7.40 (m, 2H), 4.03 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.8, 148.8, 144.6, 139.4, 131.4, 131.3, 122.9, 115.8, 86.3, 57.3.

HRMS (ESI) calcd. for $C_{10}H_9INO$ $[M+H]^+$: 285.9723, found: 285.9718.

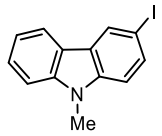


5-bromo-6-methoxyquinoline (19): Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 55% yield as white solid (13 mg, Eluent: petroleum ether/ethyl acetate = 5/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.82 (d, *J* = 4.1 Hz, 1H), 8.54 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 7.53 (d, *J* = 9.2 Hz, 1H), 7.48 (dd, *J* = 8.6, 4.2 Hz, 1H), 4.07 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.0, 148.7, 144.3, 134.6, 130.3, 128.7, 122.4, 116.5, 107.3, 57.1.

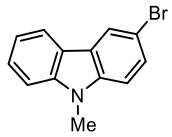
HRMS (ESI) calcd. for $C_{10}H_9BrNO$ $[M+H]^+$: 237.9862, found: 237.9863.



3-iodo-9-methyl-9*H*-carbazole (20)[19]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 43% yield as white solid (13.2 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 1.7 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.71 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.17 (m, 2H), 3.82 (s, 3H).

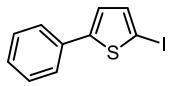
^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.9, 140.1, 133.8, 129.1, 126.4, 125.2, 121.5, 120.4, 119.4, 110.5, 108.6, 81.3, 29.1.



3-bromo-9-methyl-9*H*-carbazole (21)[20]: Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 31% yield as white solid (8.1 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 2.1 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.56 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.29 – 7.24 (m, 2H), 3.84 (s, 3H).

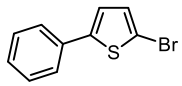
^{13}C NMR (151 MHz, Chloroform-*d*) δ 141.2, 139.6, 128.3, 126.4, 124.4, 123.0, 121.7, 120.5, 119.3, 111.6, 109.9, 108.7, 29.2.



2-iodo-5-phenylthiophene (22)[21]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 72% yield as white solid (20.6 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 2H), 7.41 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 7.22 (d, J = 3.7 Hz, 1H), 6.98 (d, J = 3.8 Hz, 1H).

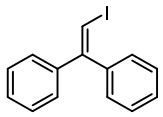
^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.4, 137.9, 133.6, 129.0, 127.9, 125.8, 124.5, 72.4.



2-bromo-5-phenylthiophene (23)[21]: Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 55% yield as white solid (13 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 – 7.48 (m, 2H), 7.40 – 7.35 (m, 2H), 7.32 – 7.28 (m, 1H), 7.07 – 7.02 (m, 2H).

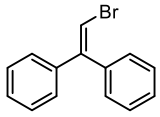
^{13}C NMR (151 MHz, Chloroform-*d*) δ 145.9, 133.6, 130.8, 129.0, 127.9, 125.6, 123.2, 111.4.



(2-iodoethene-1,1-diyl)dibenzene (24)[22]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 76% yield as colorless oil (23.2 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 – 7.36 (m, 3H), 7.31 – 7.25 (m, 5H), 7.25 – 7.20 (m, 2H), 6.94 (s, 1H).

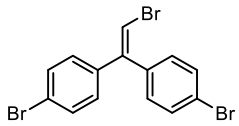
^{13}C NMR (151 MHz, Chloroform-*d*) δ 152.7, 141.8, 141.1, 129.4, 128.4, 128.3, 128.1, 128.0, 127.6, 79.0.



(2-bromoethene-1,1-diyl)dibenzene (25)[23]: Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 64% yield as white solid (16.5 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.19 (m, 10H), 6.77 (s, 1H).

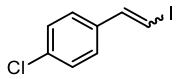
^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.9, 140.8, 139.1, 129.7, 128.5, 128.3, 128.2, 128.0, 127.7, 105.2.



4,4'-(2-bromoethene-1,1-diyl)bis(bromobenzene) (26)[24]: Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 80% yield as colorless oil (33.1 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.79 (s, 1H).

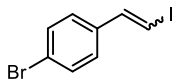
^{13}C NMR (151 MHz, Chloroform-*d*) δ 144.8, 139.2, 137.4, 131.7, 131.7, 131.4, 129.2, 122.6, 122.5, 106.2.



1-chloro-4-(2-iodovinyl)benzene (27)[25]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 83% yield as white solid (21.9 mg, Z/E = 2/1, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 4H), 7.40 – 7.33 (m, 4.5H), 7.32 – 7.24 (m, 4.5H), 7.24 – 7.19 (m, 2H), 6.84 (d, J = 15.0 Hz, 1H), 6.61 (d, J = 8.7 Hz, 2H).

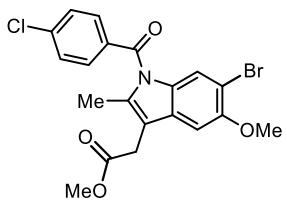
^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.7, 137.4, 136.1, 135.1, 134.1, 129.7, 128.9, 128.4, 127.1, 80.3, 77.4.



1-bromo-4-(2-iodovinyl)benzene (28)[26, 27]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 86% yield as white solid (26.5 mg, Z/E = 2.3/1, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, J = 1.7 Hz, 10H), 7.46 – 7.43 (m, 2H), 7.36 (d, J = 15.0 Hz, 1H), 7.25 (d, J = 8.9 Hz, 3H), 7.15 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 15.0 Hz, 1H), 6.62 (d, J = 8.7 Hz, 2.3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.8, 137.5, 136.5, 135.6, 131.9, 131.4, 129.9, 127.4, 122.4, 122.3, 80.4, 77.6.

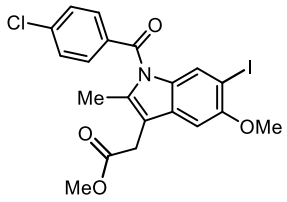


methyl 2-(6-bromo-1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (29): Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL DMF, 425 nm blue LEDs, obtained in 63% yield as white solid (28.3 mg, Eluent: petroleum ether/ethyl acetate = 5/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 2H), 7.54 – 7.46 (m, 2H), 7.36 (s, 1H), 6.97 (s, 1H), 3.93 (s, 3H), 3.70 (s, 3H), 3.66 (s, 2H), 2.28 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.1, 168.1, 152.3, 139.7, 135.8, 133.4, 131.2, 130.9, 129.7, 129.3, 118.8, 112.3, 108.0, 100.5, 56.6, 52.2, 30.2, 13.5.

HRMS (ESI) calcd. for $C_{20}H_{17}BrClNNaO_4$ $[M+Na]^+$: 471.9922, found: 471.9919.

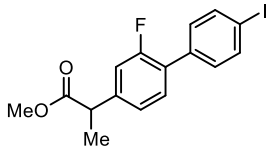


methyl 2-(1-(4-chlorobenzoyl)-6-iodo-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (30): Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 81% yield as white solid (40.2 mg, Eluent: petroleum ether/ethyl acetate = 5/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.90 (s, 1H), 3.91 (s, 3H), 3.69 (s, 3H), 3.65 (s, 2H), 2.27 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.1, 168.0, 154.2, 139.6, 135.8, 133.4, 131.7, 131.2, 130.7, 129.2, 124.7, 112.3, 99.3, 81.1, 56.7, 52.2, 30.1, 13.5.

HRMS (ESI) calcd. for $C_{20}H_{17}ClINNaO_4$ $[M+Na]^+$: 519.9783, found: 519.9792.



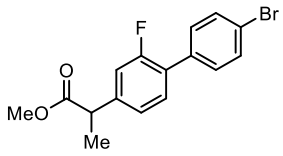
methyl 2-(2-fluoro-4'-iodo-[1,1'-biphenyl]-4-yl)propanoate (31): Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 81% yield as colorless oil (31.1 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 2H), 7.38 – 7.32 (m, 1H), 7.29 – 7.24 (m, 2H), 7.17 – 7.09 (m, 2H), 3.76 (q, *J* = 7.3 Hz, 1H), 3.70 (s, 3H), 1.53 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.3, 159.5 (d, *J* = 248.9 Hz), 142.3 (d, *J* = 7.7 Hz), 137.6, 134.9, 130.7 (d, *J* = 3.0 Hz), 130.5 (d, *J* = 3.6 Hz), 126.7 (d, *J* = 13.5 Hz), 123.7 (d, *J* = 3.3 Hz), 115.4 (d, *J* = 23.6 Hz), 93.6, 52.3, 44.9 (d, *J* = 2.4 Hz), 18.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.32.

HRMS (ESI) calcd. for $C_{16}H_{14}FINaO_2$ $[M+Na]^+$: 406.9915, found: 406.9911.



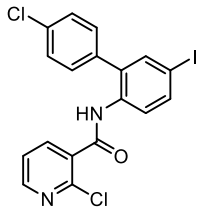
methyl 2-(4'-bromo-2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (32): Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL DMF, 425 nm blue LEDs, obtained in 67% yield as colorless oil (22.5 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 – 7.54 (m, 2H), 7.42 – 7.38 (m, 2H), 7.38 – 7.34 (m, 1H), 7.16 – 7.10 (m, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.3, 159.6 (d, *J* = 248.7 Hz), 142.3 (d, *J* = 7.7 Hz), 134.4, 131.6, 130.5 (d, *J* = 3.1 Hz) (2C), 126.7 (d, *J* = 13.3 Hz), 123.7 (d, *J* = 3.3 Hz), 122.0, 115.4 (d, *J* = 23.5 Hz), 52.3, 44.9, 18.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.39.

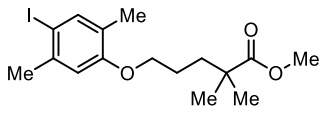
HRMS (ESI) calcd. for $C_{16}H_{14}BrFNaO_2$ $[M+Na]^+$: 359.0053, found: 359.0052.



2-chloro-*N*-(4'-chloro-5-iodo-[1,1'-biphenyl]-2-yl)nicotinamide (33)[5]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 71% yield as white solid (33.2 mg, Eluent: petroleum ether/ethyl acetate = 5/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.44 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 8.19 (s, 1H), 8.15 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.74 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.35 (dd, *J* = 7.6, 4.7 Hz, 1H), 7.32 – 7.28 (m, 2H).

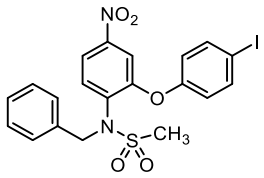
^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.3, 151.5, 146.5, 140.4, 138.7, 137.7, 135.0, 134.6, 134.3, 133.9, 130.7, 129.5, 123.4, 123.0, 88.9. (one carbon signal was overlapped)



methyl 5-(4-iodo-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (34)[28]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 61% yield as brown oil (23.8 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 6.67 (s, 1H), 3.88 (t, *J* = 5.7 Hz, 2H), 3.66 (s, 3H), 2.36 (s, 3H), 2.13 (s, 3H), 1.73 – 1.70 (m, 4H), 1.21 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.2, 157.3, 139.9, 139.3, 126.5, 112.7, 89.0, 68.0, 51.8, 42.1, 37.0, 28.0, 25.2, 25.1, 15.3.

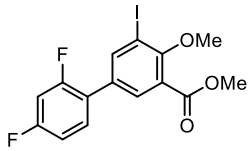


***N*-benzyl-*N*-(2-(4-iodophenoxy)-4-nitrophenyl)methanesulfonamide (35):** Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 75% yield as colorless oil (39.3 mg, Eluent: petroleum ether/ethyl acetate = 4/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.31 – 7.24 (m, 5H), 6.83 – 6.80 (m, 2H), 4.88 (s, 2H), 3.06 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.9, 154.3, 147.9, 139.7, 135.1, 134.6, 134.1, 128.7, 128.7, 128.3, 121.9, 118.2, 112.4, 89.4, 54.1, 40.5.

HRMS (ESI) calcd. for $C_{20}H_{18}IN_2O_5S$ $[M+H]^+$: 524.9976, found: 524.9982.



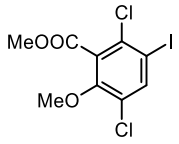
methyl 2',4'-difluoro-5-iodo-4-methoxy-[1,1'-biphenyl]-3-carboxylate (36): Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 66% yield as colorless oil (26.7 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 – 8.03 (m, 1H), 7.94 – 7.88 (m, 1H), 7.39 – 7.34 (m, 1H), 6.97 – 6.89 (m, 2H), 3.94 (s, 3H), 3.93 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.4, 162.7 (dd, *J* = 250.5, 11.9 Hz), 159.6 (dd, *J* = 251.1, 12.0 Hz). 158.8, 143.4 (d, *J* = 3.2 Hz), 132.5, 132.3 (d, *J* = 2.9 Hz), 131.3 (dd, *J* = 9.5, 4.5 Hz), 125.4, 122.5 (dd, *J* = 13.7, 4.0 Hz), 111.9 (dd, *J* = 21.5, 3.8 Hz), 104.6 (t, *J* = 25.8 Hz), 94.1, 62.4, 52.6.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -109.76 (d, *J* = 8.1 Hz), -113.12 (d, *J* = 7.8 Hz).

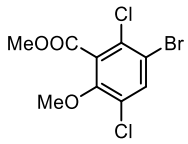
HRMS (ESI) calcd. for $C_{15}H_{11}F_2INaO_3$ $[M+Na]^+$: 426.9613, found: 426.9616.



methyl 2,5-dichloro-3-iodo-6-methoxybenzoate (37)[29]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 75% yield as colorless oil (27 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 3.96 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.5, 153.8, 141.0, 133.9, 130.7, 127.3, 92.5, 62.3, 53.2.

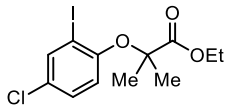


methyl 3-bromo-2,5-dichloro-6-methoxybenzoate (38): Following the general procedure B, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL DMF, 425 nm blue LEDs, obtained in 45% yield as colorless oil (14 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 3.97 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.4, 152.9, 134.9, 131.5, 130.1, 127.4, 118.1, 62.3, 53.2.

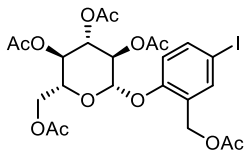
HRMS (ESI) calcd. for $C_9H_7BrCl_2NaO_3$ $[M+Na]^+$: 334.8848, found: 334.8845.



ethyl 2-(4-chloro-2-iodophenoxy)-2-methylpropanoate (39)[5]: Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, 390 nm blue LEDs, obtained in 60% yield as colorless oil (22.1 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 2.5 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.63 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.8, 153.9, 138.7, 128.8, 127.9, 118.0, 91.4, 81.2, 61.7, 25.3, 14.1.

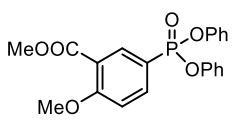


(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(2-(acetoxymethyl)-4-iodophenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (40): Following the general procedure A, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 72% yield as colorless oil (44.8 mg, Eluent: petroleum ether/ethyl acetate = 3/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 2.3 Hz, 1H), 7.54 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 5.28 – 5.25 (m, 2H), 5.17 – 5.13 (m, 1H), 5.05 – 5.00 (m, 2H), 4.95 (d, *J* = 13.4 Hz, 1H), 4.24 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.16 (dd, *J* = 12.3, 2.5 Hz, 1H), 3.83 (ddd, *J* = 10.2, 5.4, 2.5 Hz, 1H)., 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 170.4, 170.1, 169.3, 169.2, 154.2, 138.1, 137.8, 128.8, 118.0, 99.2, 86.5, 72.4, 72.1, 70.9, 68.1, 61.8, 60.1, 20.9, 20.7, 20.6 (3C).

HRMS (ESI) calcd. for $C_{23}H_{27}INaO_{12}$ $[M+Na]^+$: 645.0439, found: 645.0436.

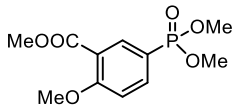


methyl 5-(diphenoxyphosphoryl)-2-methoxybenzoate (41)[30]: Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), triphenyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 48% yield as colorless oil (19.1 mg, Eluent: petroleum ether/ethyl acetate = 1/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.40 (dd, *J* = 13.8, 2.1 Hz, 1H), 8.03 (ddd, *J* = 13.1, 8.6, 2.1 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.21 – 7.11 (m, 6H), 7.06 (dd, *J* = 8.7, 3.5 Hz, 1H), 3.96 (s, 3H), 3.90 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.4 (d, *J* = 1.7 Hz), 162.6 (d, *J* = 3.2 Hz), 150.2 (d, *J* = 7.5 Hz), 137.8 (d, *J* = 11.9 Hz), 136.2 (d, *J* = 12.7 Hz), 129.8, 125.2, 120.6 (d, *J* = 4.5 Hz), 120.4, 117.9 (d, *J* = 202.2 Hz), 112.1 (d, *J* = 16.7 Hz), 56.3, 52.3.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 11.0.

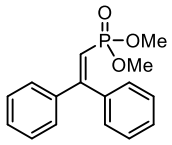


methyl 5-(dimethoxyphosphoryl)-2-methoxybenzoate (42)[30]: Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), trimethyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 91% yield as colorless oil (24.9 mg, 23% yield without NaBr, Eluent: petroleum ether/ethyl acetate = 1/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 13.4, 2.0 Hz, 1H), 7.89 (ddd, *J* = 12.6, 8.5, 2.1 Hz, 1H), 7.04 (dd, *J* = 8.6, 3.2 Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.5, 162.2 (d, *J* = 3.4 Hz), 137.4 (d, *J* = 11.4 Hz), 135.7 (d, *J* = 12.1 Hz), 120.4 (d, *J* = 15.4 Hz), 118.0 (d, *J* = 197.3 Hz), 112.0 (d, *J* = 15.6 Hz), 56.2, 52.7 (d, *J* = 5.3 Hz), 52.2.

^{31}P NMR (243 MHz, Chloroform-*d*) δ 20.8.

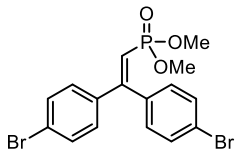


dimethyl (2,2-diphenylvinyl)phosphonate (43)[31]: Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), trimethyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 97% yield as colorless oil (27.9 mg, Eluent: petroleum ether/ethyl acetate = 2/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 10H), 6.17 (d, *J* = 15.6 Hz, 1H), 3.49 (s, 3H), 3.47 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 160.7 (d, *J* = 6.4 Hz), 141.2 (d, *J* = 22.5 Hz), 138.8 (d, *J* = 7.6 Hz), 129.6 (d, *J* = 2.1 Hz), 129.5, 128.8, 128.4, 128.2, 127.9, 113.5 (d, *J* = 194.2 Hz), 52.2 (d, *J* = 6.1 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 19.5.



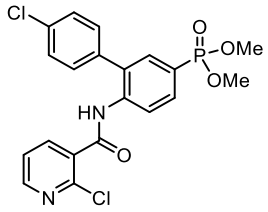
dimethyl (2,2-bis(4-bromophenyl)vinyl)phosphonate (44): Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), trimethyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 85% yield as colorless oil (37.7 mg, Eluent: petroleum ether/ethyl acetate = 2/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.15 (d, *J* = 14.6 Hz, 1H), 3.54 (s, 3H), 3.52 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.2 (d, *J* = 6.5 Hz), 139.7 (d, *J* = 22.3 Hz), 137.1 (d, *J* = 7.6 Hz), 131.7, 131.3, 131.3, 129.7, 124.3, 123.4, 114.8 (d, *J* = 193.9 Hz), 52.3 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 18.4.

HRMS (ESI) calcd. for $C_{16}H_{16}Br_2O_3P$ $[M+H]^+$: 444.9198, found: 444.9193.



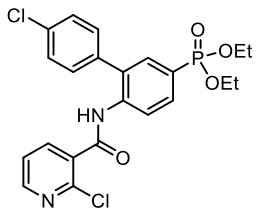
dimethyl (4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)phosphonate (45): Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), trimethyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 88% yield as white solid (39.6 mg, Eluent: petroleum ether/ethyl acetate = 1/3).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.63 (dd, *J* = 8.6, 3.6 Hz, 1H), 8.46 (s, 1H), 8.43 (dd, *J* = 4.7, 1.9 Hz, 1H), 8.14 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.69 (dd, *J* = 13.3, 1.8 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.36 – 7.31 (m, 3H), 3.77 (s, 3H), 3.75 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.6, 151.6, 146.6, 140.4, 138.4 (d, *J* = 3.8 Hz), 135.1, 134.9, 133.9 (d, *J* = 11.1 Hz), 132.6 (d, *J* = 9.9 Hz), 131.7 (d, *J* = 15.5 Hz), 130.8, 130.6, 129.6, 123.1 (d, *J* = 193.0 Hz).123.0, 121.2 (d, *J* = 15.1 Hz), 52.8 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 20.6.

HRMS (ESI) calcd. for $C_{20}H_{17}Cl_2N_2NaO_4P$ $[M+Na]^+$: 473.0195, found: 473.0193.



diethyl (4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)phosphonate (46): Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), triethyl phosphite (0.5 mmol,

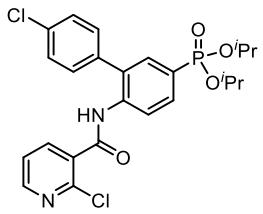
5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 63% yield as white solid (30.1 mg, Eluent: petroleum ether/ethyl acetate = 1/3).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.62 (dd, *J* = 8.6, 3.8 Hz, 1H), 8.49 – 8.37 (m, 2H), 8.15 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.89 – 7.79 (m, 1H), 7.70 (dd, *J* = 13.2, 1.7 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.40 – 7.30 (m, 3H), 4.18 – 4.05 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.6, 151.6, 146.5, 140.4, 138.1 (d, *J* = 3.8 Hz), 135.0, 134.9, 133.8 (d, *J* = 11.1 Hz), 132.4 (d, *J* = 9.9 Hz), 131.5 (d, *J* = 15.7 Hz), 130.8, 130.6, 129.5, 124.6 (d, *J* = 193.3 Hz), 123.0, 121.1 (d, *J* = 15.0 Hz), 62.3 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 6.4 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 17.8.

HRMS (ESI) calcd. for $C_{22}H_{22}Cl_2N_2O_4P$ $[M+H]^+$: 479.0689, found: 479.0693.



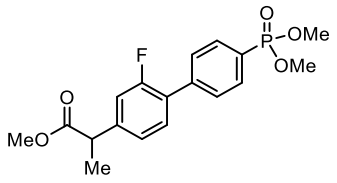
diisopropyl (4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)phosphonate (47): Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), triisopropyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 43% yield as white solid (21.7 mg, Eluent: petroleum ether/ethyl acetate = 1/3).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.62 (dd, *J* = 8.5, 3.7 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.39 (s, 1H), 8.16 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.85 (ddd, *J* = 12.9, 8.3, 1.8 Hz, 1H), 7.71 (dd, *J* = 13.2, 1.8 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.37 – 7.32 (m, 3H), 4.73 – 4.67 (m, 2H), 1.37 (d, *J* = 6.2 Hz, 6H), 1.24 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.5, 151.6, 146.5, 140.4, 137.8 (d, *J* = 3.7 Hz), 135.0, 133.7 (d, *J* = 11.3 Hz), 132.4 (d, *J* = 10.1 Hz), 131.3 (d, *J* = 15.8 Hz), 130.8, 130.6, 129.5, 126.2 (d, *J* = 192.3 Hz), 123.0, 120.8 (d, *J* = 14.9 Hz), 70.9 (d, *J* = 5.7 Hz), 24.1 (d, *J* = 3.8 Hz), 23.9 (d, *J* = 4.7 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 15.6.

HRMS (ESI) calcd. for $C_{24}H_{26}Cl_2N_2O_4P$ $[M+H]^+$: 507.1002, found: 507.1002.



methyl 2-(4'-(dimethoxyphosphoryl)-2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (48): Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), trimethyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 82% yield as colorless oil (30 mg, Eluent: petroleum ether/ethyl acetate = 1/2).

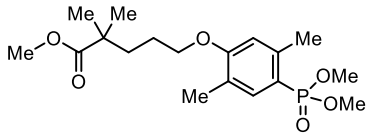
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 13.0, 7.9 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.41 – 7.36 (m, 1H), 7.19 – 7.08 (m, 2H), 3.79 (s, 3H), 3.78 – 3.73 (m, 4H), 3.69 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.3, 159.7 (d, *J* = 249.6 Hz), 142.9 (d, *J* = 7.7 Hz), 139.9 (d, *J* = 3.3 Hz), 132.1 (d, *J* = 10.0 Hz), 130.7 (d, *J* = 3.7 Hz), 129.1 (dd, *J* = 15.2, 3.1 Hz), 126.6 (d, *J* = 13.8 Hz), 126.0 (d, *J* = 189.3 Hz).123.8 (d, *J* = 3.2 Hz), 115.5 (d, *J* = 23.5 Hz), 52.8 (d, *J* = 5.6 Hz), 52.3, 44.9, 18.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.18.

^{31}P NMR (243 MHz, Chloroform-*d*) δ 21.4.

HRMS (ESI) calcd. for $C_{18}H_{21}FO_5P$ $[M+H]^+$: 367.1105, found: 367.1100.



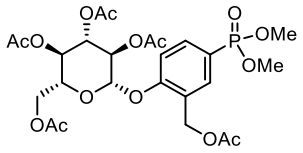
methyl 5-(4-(dimethoxyphosphoryl)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (49): Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), trimethyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 40% yield as colorless oil (14.9 mg, Eluent: petroleum ether/ethyl acetate = 1/2).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 13.3 Hz, 1H), 6.64 (d, *J* = 4.1 Hz, 1H), 3.95 (t, *J* = 5.8 Hz, 2H), 3.72 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 2.48 (s, 3H), 2.17 (s, 3H), 1.76 – 1.66 (m, 4H), 1.21 (s, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 178.2, 160.4 (d, *J* = 3.4 Hz), 141.6 (d, *J* = 11.4 Hz), 136.5 (d, *J* = 11.6 Hz), 123.8 (d, *J* = 15.7 Hz), 115.6 (d, *J* = 190.7 Hz), 113.5 (d, *J* = 16.6 Hz), 68.0, 52.2 (d, *J* = 5.2 Hz), 51.8, 42.1, 37.0, 25.2, 25.0, 21.2 (d, *J* = 3.5 Hz), 15.5.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.0.

HRMS (ESI) calcd. for $C_{18}H_{30}O_6P$ $[M+H]^+$: 373.1775, found: 373.1772.



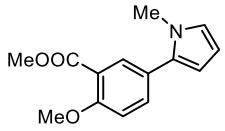
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(2-(acetoxymethyl)-4-(dimethoxyphosphoryl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (50): Following the general procedure C, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), trimethyl phosphite (0.5 mmol, 5.0 equiv.), NaBr (0.2 mmol, 2.0 equiv.), 0.5 mL acetone, obtained in 62% yield as colorless oil (37.4 mg, Eluent: petroleum ether/ethyl acetate = 1/4).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.68 (m, 2H), 7.11 (dd, *J* = 8.3, 2.8 Hz, 1H), 5.32 – 5.26 (m, 2H), 5.20 – 5.12 (m, 2H), 5.11 – 4.99 (m, 2H), 4.24 (dd, *J* = 12.4, 5.4 Hz, 1H), 4.16 (dd, *J* = 12.4, 2.4 Hz, 1H), 3.90 (ddd, *J* = 10.4, 5.4, 2.4 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.5, 170.4, 170.1, 169.3, 169.2, 157.5 (d, *J* = 3.5 Hz), 133.7 (d, *J* = 11.0 Hz), 133.0 (d, *J* = 11.4 Hz), 126.6 (d, *J* = 15.5 Hz), 121.5 (d, *J* = 194.4 Hz), 114.8 (d, *J* = 16.0 Hz), 98.5, 72.4, 72.3, 70.8, 68.1, 61.8, 60.5, 52.7 (d, *J* = 5.5 Hz), 20.9, 20.6, 20.6 (2C), 20.6.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 21.1.

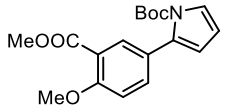
HRMS (ESI) calcd. for $C_{25}H_{33}NaO_{15}P$ $[M+Na]^+$: 627.1449, found: 627.1448.



methyl 2-methoxy-5-(1-methyl-1*H*-pyrrol-2-yl)benzoate (51)[32]: Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1-methyl-1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 70% yield as white solid (17.2 mg, 35% yield without TBAB, Eluent: petroleum ether/ethyl acetate = 10/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 2.4 Hz, 1H), 7.49 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.71 – 6.68 (m, 1H), 6.21 – 6.16 (m, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.63 (s, 3H).

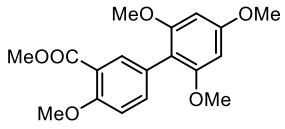
^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.5, 158.0, 133.7, 133.2, 131.9, 125.6, 123.4, 119.9, 112.1, 108.5, 107.7, 56.1, 52.1, 34.9.



***tert*-butyl 2-(4-methoxy-3-(methoxycarbonyl)phenyl)-1*H*-pyrrole-1-carboxylate (52)[32]:** Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), *tert*-butyl 1*H*-pyrrole-1-carboxylate (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 48% yield as colorless oil (15.9 mg, Eluent: petroleum ether/ethyl acetate = 7/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 2.4 Hz, 1H), 7.46 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.35 – 7.33 (m, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.22 – 6.20 (m, 1H), 6.17 – 6.15 (m, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 1.37 (s, 9H).

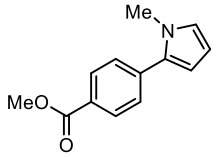
^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.4, 158.4, 149.3, 134.2, 133.5, 132.8, 126.5, 122.5, 118.9, 114.5, 111.2, 110.6, 83.8, 56.1, 52.0, 27.6.



methyl 2',4,4',6'-tetramethoxy-[1,1'-biphenyl]-3-carboxylate (53)[32]: Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1,3,5-trimethoxybenzene (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 33% yield as white solid (10.9 mg, Eluent: petroleum ether/ethyl acetate = 5/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 2.2 Hz, 1H), 7.44 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.22 (s, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.72 (s, 6H).

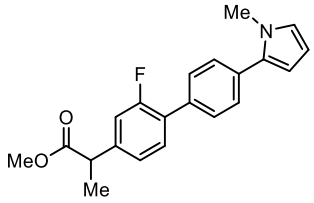
^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.9, 160.6, 158.4, 157.8, 136.4, 134.6, 126.0, 119.2, 111.5, 111.0, 90.9, 56.0, 55.9, 55.4, 51.9.



methyl 4-(1-methyl-1*H*-pyrrol-2-yl)benzoate (54)[33]: Following the general procedure D, using corresponding TT salts (0.1 mmol, 1.0 equiv.), 1-methyl-1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 42% yield as white solid (9 mg, Eluent: petroleum ether/ethyl acetate = 10/1).

^{1}H NMR (600 MHz, Chloroform-d) δ 8.06 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.79 – 6.73 (m, 1H), 6.34 (dd, J = 3.7, 1.8 Hz, 1H), 6.25 – 6.19 (m, 1H), 3.93 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 167.0, 137.7, 133.5, 129.7, 127.9, 127.9, 125.1, 110.0, 108.3, 52.1, 35.4.

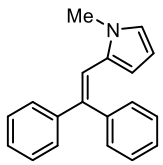


methyl 2-(2-fluoro-4'-(1-methyl-1*H*-pyrrol-2-yl)-[1,1'-biphenyl]-4-yl)propanoate (55)[34]: Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1-methyl-1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 61% yield as colorless oil (20.6 mg, Eluent: petroleum ether/ethyl acetate = 20/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H), 7.51 – 7.41 (m, 3H), 7.19 – 7.12 (m, 2H), 6.79 – 6.73 (m, 1H), 6.29 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.26 – 6.20 (m, 1H), 3.78 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.72 (s, 3H), 1.55 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.4, 159.7 (d, *J* = 248.4 Hz), 141.8 (d, *J* = 7.7 Hz), 134.1, 133.7, 132.7, 130.7 (d, *J* = 3.9 Hz), 128.9 (d, *J* = 3.0 Hz), 128.5, 127.4 (d, *J* = 13.3 Hz), 124.0, 123.6 (d, *J* = 3.3 Hz), 115.3 (d, *J* = 23.6 Hz), 109.0, 107.9, 52.3, 44.9, 35.2, 18.4.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -117.39.



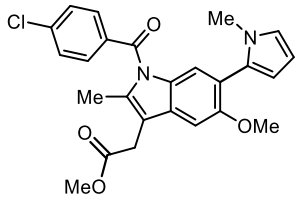
2-(2,2-diphenylvinyl)-1-methyl-1*H*-pyrrole (56): Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1-methyl-1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB

(0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 35% yield as yellow oil (9.1 mg, Eluent: petroleum ether).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 7.39 – 7.35 (m, 1H), 7.33 – 7.24 (m, 7H), 6.88 (s, 1H), 6.56 (s, 1H), 5.93 – 5.86 (m, 1H), 5.26 (d, J = 3.8 Hz, 1H), 3.68 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.0, 141.0, 138.4, 130.8, 130.0, 129.0, 128.3, 127.3, 127.0, 126.8, 122.9, 115.8, 110.1, 107.9, 34.2.

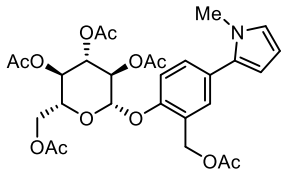
HRMS (ESI) (m/z): $[M+H]^+$ Calcd for $C_{19}H_{18}N^+$, 260.1434; found: 260.1437.



methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-6-(1-methyl-1*H*-pyrrol-2-yl)-1*H*-indol-3-yl)acetate (57)[35]: Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1-methyl-1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 52% yield as yellow oil (23.4 mg, Eluent: petroleum ether/ethyl acetate = 5/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.01 (s, 1H), 6.96 (s, 1H), 6.70 – 6.65 (m, 1H), 6.18 – 6.13 (m, 1H), 5.94 (dd, *J* = 3.5, 1.6 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 3.72 (s, 2H), 3.41 (s, 3H), 2.40 (s, 3H).

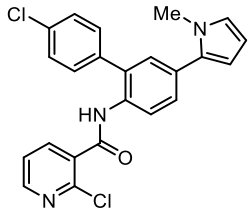
^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 168.2, 154.1, 139.5, 136.0, 133.6, 131.4, 131.3, 130.4, 130.1, 129.1, 122.4, 118.7, 117.6, 112.2, 109.1, 107.4, 99.3, 55.8, 52.2, 34.5, 30.2, 13.3.



(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(2-(acetoxymethyl)-4-(1-methyl-1*H*-pyrrol-2-yl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (58)[32]: Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1-methyl-1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 50% yield as colorless oil (28.8 mg, Eluent: petroleum ether/ethyl acetate = 2/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 2.4 Hz, 1H), 7.29 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.73 – 6.67 (m, 1H), 6.20 – 6.15 (m, 2H), 5.35 – 5.29 (m, 2H), 5.21 – 5.05 (m, 4H), 4.29 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.20 (dd, *J* = 12.4, 2.6 Hz, 1H), 3.88 (ddd, *J* = 10.1, 5.3, 2.5 Hz, 1H), 3.61 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H).

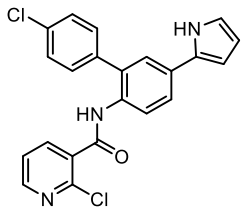
^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.6, 170.5, 170.2, 169.4, 169.3, 153.3, 133.5, 129.7, 129.6, 128.8, 126.1, 123.6, 115.7, 108.6, 107.7, 99.3, 72.6, 72.0, 71.0, 68.3, 61.9, 60.9, 34.9, 21.0, 20.7, 20.6 (2C), 20.6.



2-chloro-*N*-(4'-chloro-5-(1-methyl-1*H*-pyrrol-2-yl)-[1,1'-biphenyl]-2-yl)nicotinamide (59)[32]: Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1-methyl-1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 51% yield as white solid (21.5 mg, Eluent: petroleum ether/ethyl acetate = 3/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.48 – 8.42 (m, 2H), 8.22 (s, 1H), 8.15 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.40 – 7.34 (m, 3H), 7.32 (d, *J* = 2.2 Hz, 1H), 6.74 – 6.72 (m, 1H), 6.26 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.22 – 6.19 (m, 1H), 3.70 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.5, 151.4, 146.7, 140.2, 136.0, 134.6, 133.5, 132.9, 132.3, 131.0, 130.8, 130.4, 130.2, 129.4, 128.7, 124.1, 122.9, 122.0, 109.0, 108.0, 35.2.

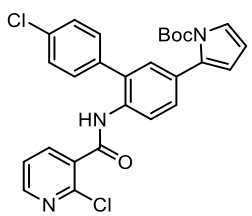


2-chloro-*N*-(4'-chloro-5-(1*H*-pyrrol-2-yl)-[1,1'-biphenyl]-2-yl)nicotinamide (60): Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), 1*H*-pyrrole (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 47% yield as white solid (19.1 mg, Eluent: petroleum ether/ethyl acetate = 2/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.69 (s, 1H), 8.44 (dd, *J* = 4.8, 2.0 Hz, 1H), 8.41 (d, *J* = 8.6 Hz, 1H), 8.18 (s, 1H), 8.14 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.55 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.39 – 7.33 (m, 4H), 6.87 – 6.84 (m, 1H), 6.54 – 6.52 (m, 1H), 6.32 – 6.28 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.4, 151.4, 146.7, 140.2, 136.1, 134.7, 132.8, 132.4, 131.1, 131.0, 130.8, 130.0, 129.4, 125.6, 123.9, 123.0, 122.6, 119.3, 110.3, 106.4.

HRMS (ESI) calcd. for $C_{22}H_{16}Cl_2N_3O$ $[M+H]^+$: 408.0665, found: 408.0656.



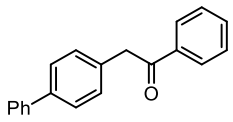
***tert*-butyl 2-(4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)-1*H*-pyrrole-1-carboxylate (61):** Following the general procedure D, using corresponding DBT salts (0.1 mmol, 1.0 equiv.), *tert*-

butyl 1*H*-pyrrole-1-carboxylate (2.0 mmol, 20.0 equiv.), TBAB (0.2 mmol, 2.0 equiv.), 0.5 mL DMSO, obtained in 36% yield as white solid (18.3 mg, Eluent: petroleum ether/ethyl acetate = 4/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.46 – 8.41 (m, 2H), 8.19 (s, 1H), 8.14 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.44 (dd, *J* = 8.0, 6.1 Hz, 3H), 7.39 – 7.32 (m, 4H), 7.27 (d, *J* = 2.1 Hz, 1H), 6.28 – 6.20 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.2, 146.1, 144.0, 141.5, 135.0, 130.9, 129.3, 128.8, 128.1, 126.1, 126.1, 125.9, 125.6, 125.6, 124.3, 124.2, 117.7, 117.6, 116.0, 109.6, 105.5, 78.6, 22.6.

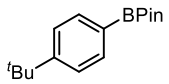
HRMS (ESI) calcd. for $C_{27}H_{23}Cl_2N_3NaO_3$ $[M+Na]^+$: 530.1009, found: 530.1011.



2-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-one (62)[36]: Using corresponding TT salts (0.1 mmol, 1.0 equiv.), trimethyl((1-phenylvinyl)oxy)silane (0.3 mmol, 3.0 equiv.), NaI (0.2 mmol, 2.0 equiv.), 1 mL DMSO, 420 nm LEDs (20 W), obtained in 65% yield as white solid (17.7 mg, Eluent: petroleum ether/ethyl acetate = 50/1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 – 8.04 (m, 2H), 7.61 – 7.56 (m, 5H), 7.51 – 7.47 (m, 2H), 7.47 – 7.42 (m, 2H), 7.38 – 7.33 (m, 3H), 4.35 (s, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.6, 140.8, 139.9, 136.6, 133.6, 133.3, 130.0, 128.8, 128.7, 128.6, 127.5, 127.3, 127.1, 45.1.



2-(4-(*tert*-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (63)[37]: Using corresponding DBT salts (0.1 mmol, 1.0 equiv.), B_2Pin_2 (0.3 mmol, 3.0 equiv.), NaBr (50 mol%), 0.5 mL acetone, 425 nm LEDs (15 W), obtained in 62% yield as white solid (16.1 mg, Eluent: petroleum ether/ethyl acetate = 50/1).

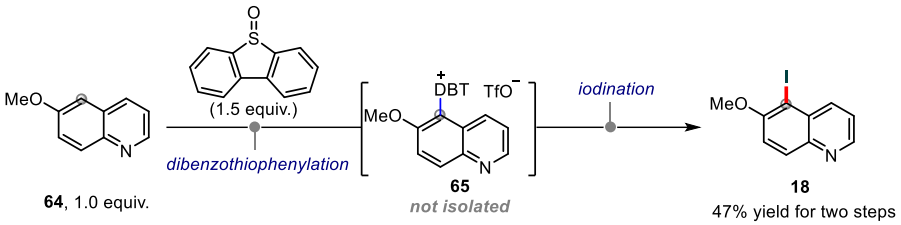
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 1.33 (s, 12H), 1.32 (s, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.5, 134.7, 124.7, 83.6, 34.9, 31.2, 24.8.

^{11}B NMR (193 MHz, Chloroform-*d*) δ 31.0.

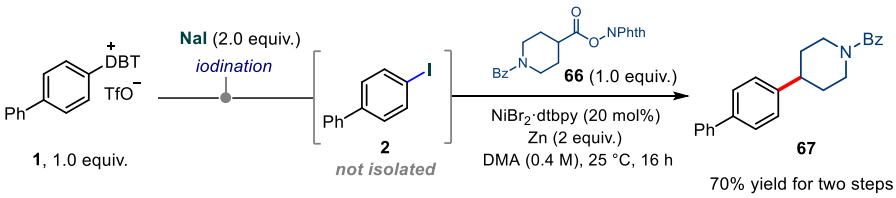
5. Synthetic applications

5.1 Two-step one-pot for arene C–H iodination

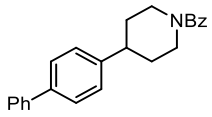


Under an argon atmosphere, trifluoroacetic anhydride (TFAA, 1.5 mmol, 3.0 equiv.) and trifluoromethanesulfonic acid (TfOH, 1.5 mmol, 3.0 equiv.) were successively added to a solution of 6-methoxyquinoline (0.5 mmol, 1.0 equiv.) in MeCN (0.25 M) at -40 ℃ with stirring. Then, dibenzo[*b,d*]thiophene 5-oxide (0.75 mmol, 1.5 equiv.) was slowly added. The mixture was reacted at -40 ℃ for 1 h, then at room temperature for another 1 h. After stirring for 2 h, TLC analysis showed complete consumption of the arene starting material, at which point the solvent was removed in vacuo. NaI (1.0 mmol, 2.0 equiv.) was then added to the reaction vial, followed by evacuating and filling with argon (repeated for three times). Acetone (2.5 mL) was added under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs, maintained at approximately room temperature. After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The product was purified via flash column chromatography on silica gel to give the product **18** (47%, 67 mg, petroleum ether/ethyl acetate = 5/1).

5.2 Two-step one-pot for C(sp^2)–C(sp^3) bond formation with redox-active ester[38]



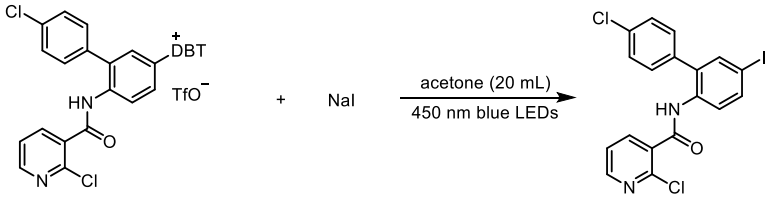
1 (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, acetone (0.5 mL) was added under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs, maintained at approximately room temperature. After 24 h, the solvent was removed in vacuo. **66** (0.1 mmol, 1.0 equiv.), $NiBr_2$·dtbpy (20 mol%), Zn power (0.2 mmol, 2.0 equiv.) were then added to the reaction vial, followed by evacuating and filling with argon (repeated for three times). DMA (0.25 mL) was added under argon atmosphere. The mixture was stirred and maintained at approximately room temperature. After 16 h, ethyl acetate (5 mL) was added to the reaction mixture. The resulting solution was washed with aqueous solution of HCl (1 M) and brine, 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 **67** as white solid (70%, 23.8 mg, petroleum ether/ethyl acetate = 3/1).



(4-([1,1'-biphenyl]-4-yl)piperidin-1-yl)(phenyl)methanone (67): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 4H), 7.51 – 7.39 (m, 7H), 7.37 – 7.28 (m, 3H), 4.93 (br s, 1H), 3.92 (br s, 1H), 3.15 (br s, 1H), 2.96 – 2.78 (m, 2H), 2.02 (br s, 1H), 1.84 (br s, 2H), 1.68 (br s, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 170.4, 144.2, 140.8, 139.5, 136.2, 129.6, 128.8, 128.5, 127.3, 127.2, 127.2, 127.0, 126.9, 48.4, 42.9, 42.5, 34.0, 33.0. **HRMS** (ESI) calcd. for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1852, found: 342.1847.

5.3 Gram scale reactions for arene C–H iodination and phosphonylation

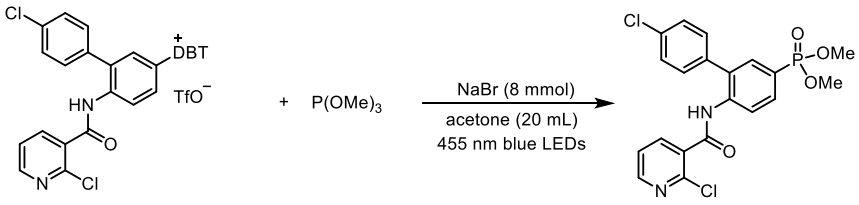
A. Synthesis of 2-chloro-*N*-(4'-chloro-5-iodo-[1,1'-biphenyl]-2-yl)nicotinamide



68, 4 mmol 8 mmol **33**, 60%, 1.12 g

68 (4 mmol, 1.0 equiv.), NaI (8 mmol, 2.0 equiv.) were added in 100 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, acetone (20 mL) was added under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs, maintained at approximately room temperature. After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The residue was purified via flash column chromatography on silica gel to give the product **33** (60%, 1.12 g, petroleum ether/ethyl acetate = 3/1).

B. Synthesis of dimethyl (4'-chloro-6-(2-chloronicotinamido)-[1,1'-biphenyl]-3-yl)phosphonate

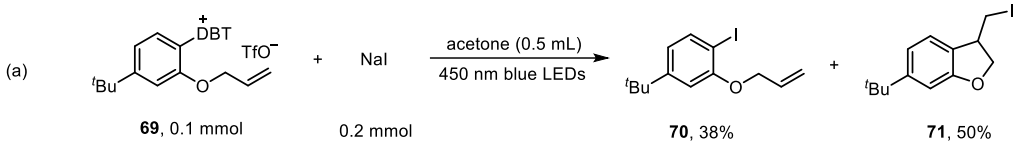


68, 4 mmol 20 mmol **45**, 71%, 1.27 g

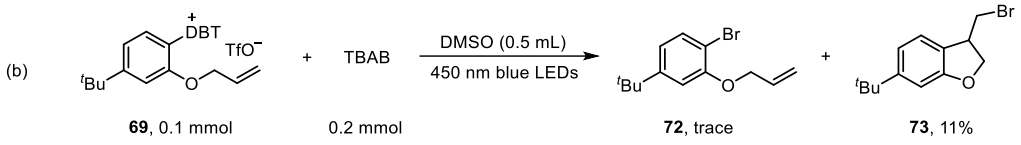
68 (4 mmol, 1.0 equiv.), NaBr (8 mmol, 2.0 equiv.) were added in 100 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, acetone (20 mL) and trimethyl phosphite (20 mmol, 5.0 equiv.) were added added under argon atmosphere. The reaction mixture was stirred under irradiation with 455 nm blue LEDs (40 W, Kemi), maintained at approximately room temperature. After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The residue was purified via flash column chromatography on silica gel to give the product **45** (71%, 1.27 g, petroleum ether/ethyl acetate = 3/1).

6. Preliminary mechanistic studies

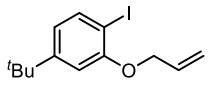
6.1 Radical clock experiment



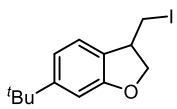
69 (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 equiv.) were added in 10 mL Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To this solid, acetone (0.5 mL) was added under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs, maintained at approximately room temperature. After 24 h, the mixture was transferred to a round bottom flask and concentrated on rotary evaporator. The residue was purified via flash column chromatography on silica gel to give the product **70** as colorless oil (38%, 12 mg, petroleum ether/ethyl acetate = 30/1) and **71** as white solid (50%, 15.8 mg, petroleum ether/ethyl acetate = 30/1).



69 (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 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, DMSO (0.5 mL) was added under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs, maintained at approximately room temperature. 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 **73** as white solid (11%, 3 mg, petroleum ether/ethyl acetate = 30/1).

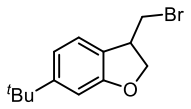


2-(allyloxy)-4-(*tert*-butyl)-1-iodobenzene (70): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.78 – 6.73 (m, 1H), 6.13 – 6.02 (m, 1H), 5.56 – 5.49 (m, 1H), 5.34 – 5.29 (m, 1H), 4.61 (d, *J* = 4.8 Hz, 2H), 1.29 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 156.9, 153.3, 138.8, 132.9, 120.1, 117.6, 110.5, 83.0, 69.8, 34.9, 31.2. **HRMS** (ESI) calcd. for $C_{13}H_{18}IO$ $[M+H]^+$: 317.0397, found: 317.0404.



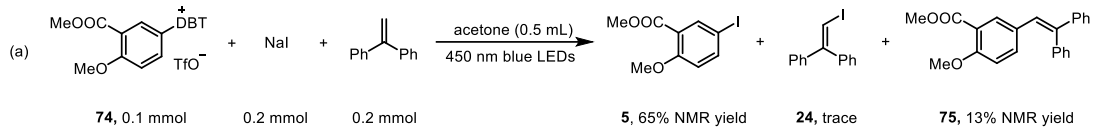
6-(*tert*-butyl)-3-(iodomethyl)-2,3-dihydrobenzofuran (71): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 7.8 Hz, 1H), 6.94 – 6.91 (m, 1H), 6.85 (d, *J* = 1.9 Hz, 1H), 4.65 (t, *J* = 9.0 Hz, 1H), 4.33 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.86 – 3.79 (m, 1H), 3.45 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.19 (t, *J* = 10.0 Hz, 1H), 1.29

(s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 160.4, 153.4, 125.8, 123.7, 117.8, 107.5, 78.0, 44.9, 35.0, 31.4, 9.0. **HRMS** (ESI) calcd. for $C_{13}H_{18}IO$ $[M+H]^+$: 317.0397, found: 317.0396.

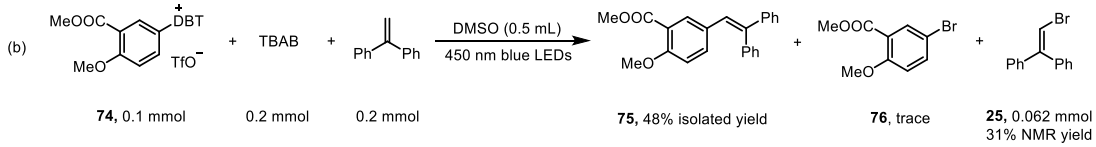


3-(bromomethyl)-6-(*tert*-butyl)-2,3-dihydrobenzofuran (73): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 7.8 Hz, 1H), 6.92 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.87 (d, *J* = 1.8 Hz, 1H), 4.66 (t, *J* = 9.0 Hz, 1H), 4.45 (dd, *J* = 9.4, 5.3 Hz, 1H), 3.87 – 3.81 (m, 1H), 3.65 – 3.60 (m, 1H), 3.40 (t, *J* = 10.0 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 160.4, 153.5, 124.5, 123.9, 117.7, 107.4, 76.2, 44.7, 35.1, 34.9, 31.4. **HRMS** (ESI) calcd. for $C_{13}H_{18}BrO$ $[M+H]^+$: 269.0536, found: 269.0535.

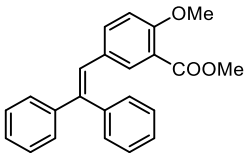
6.2 Radical trap experiment



74 (0.1 mmol, 1.0 equiv.), NaI (0.2 mmol, 2.0 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, acetone (0.5 mL) and ethene-1,1-diyldibenzene (0.2 mmol, 2.0 equiv.) were added under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs, maintained at approximately room temperature. After 24 h, the reaction mixture was sent for ^{1}H NMR and GC-MS analysis, the compounds **5** (65%, 0.065 mmol) and **75** (13%, 0.013 mmol) were detected by ^{1}H NMR and compounds **24** was detected by GC-MS.



74 (0.1 mmol, 1.0 equiv.), TBAB (0.2 mmol, 2.0 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, DMSO (0.5 mL) and ethene-1,1-diyldibenzene (0.2 mmol, 2.0 equiv.) were added under argon atmosphere. The reaction mixture was stirred under irradiation with 450 nm blue LEDs, maintained at approximately room temperature. After 24 h, the reaction mixture was sent for ^{1}H NMR and GC-MS analysis, the compounds **25** (31%, 0.062 mmol) was detected by ^{1}H NMR, **76** was detected by GC-MS, and **75** (48%, 0.048 mmol, 16.5 mg, petroleum ether/ethyl acetate = 10/1) was purified by flash column chromatography on silica gel as white solid.



methyl 5-(2,2-diphenylvinyl)-2-methoxybenzoate (75)[39]: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 2.4 Hz, 1H), 7.39 – 7.26 (m, 8H), 7.23 – 7.20 (m, 2H), 7.04 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.92 (s, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 166.4, 157.8, 143.1, 141.9, 140.2, 134.2, 133.3, 130.3, 129.6, 128.9, 128.3, 127.5, 127.5, 127.4, 126.5, 119.5, 111.6, 56.0, 51.9.

6.3 UV-vis absorption spectra

The absorption spectra in solution were recorded on a UNIC 4802 UV/VIS double beam spectrophotometer in a 1 cm length quartz cell. All solutions were prepared in the presence of air using acetone as solvent and measured at approximately room temperature.

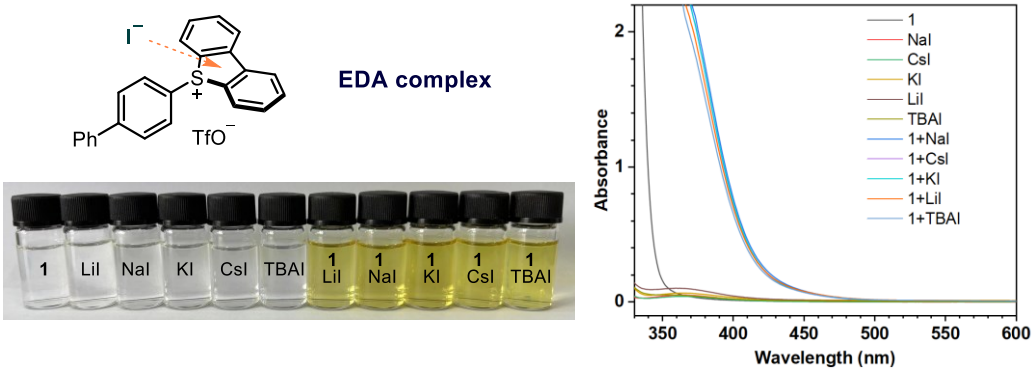


Figure S3. Left: [**1**] = 0.01 M, [iodine salts] = 0.02 M, the mixture was filtered through membrane. **Right:** [**1**] = 0.004 M, [iodine salts] = 0.008 M.

The absorption spectra in solution were recorded on a UNIC 4802 UV/VIS double beam spectrophotometer in a 0.1 cm length quartz cell. All solutions were prepared using DMSO as solvent under nitrogen, left overnight and measured at approximately room temperature.

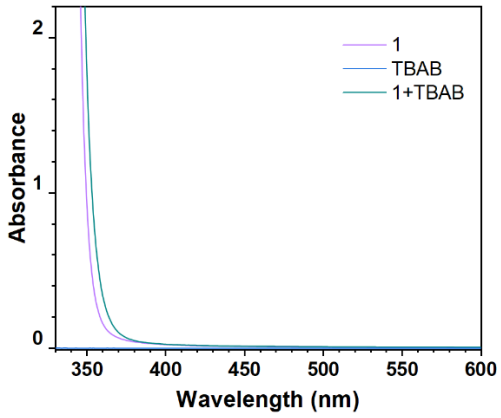
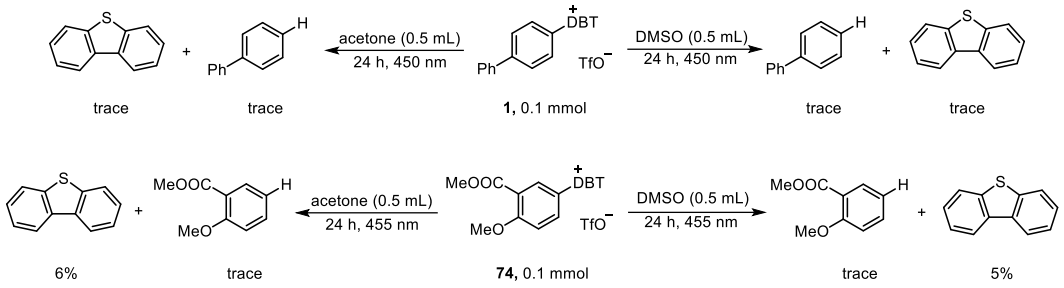


Figure S4. [**1**] = 0.4 M, [TBAB] = 0.8 M.

6.4 Experiments for the cleavage of C–S bonds under blue LEDs irradiation



Only a small amount of protonation products and dibenzothiophene were detected by GC analysis of the reaction mixture using benzophenone as an external standards.

6.5 ^{1}H NMR spectrometry of titration experiments

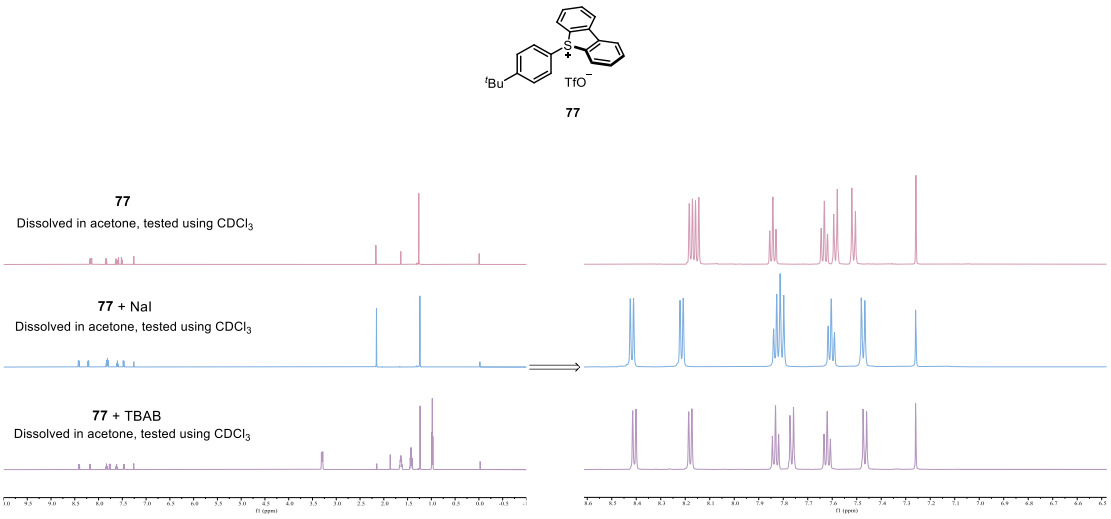


Figure S5. ^{1}H NMR spectrometry of titration experiments. The compounds were dissolved in acetone. [**77**] = 0.2 M, [NaI] = 0.4 M. [TBAB] = 0.4 M. After 10 minutes, the solvent was removed in vacuo. The solid residue was dissolved in chloroform-*d* for testing.

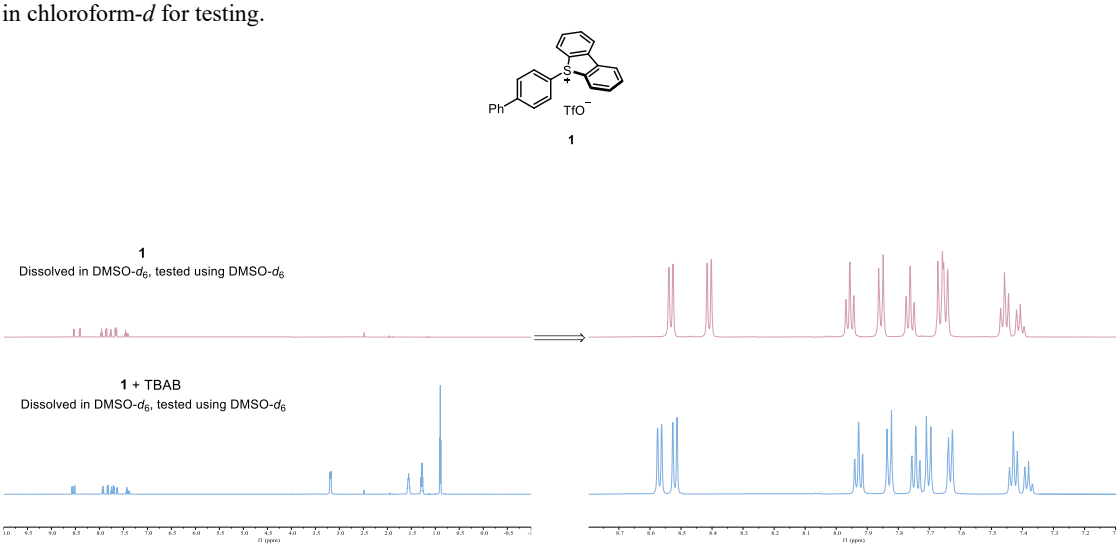


Figure S6. ^{1}H NMR spectrometry of titration experiments. The compounds were dissolved in DMSO-d_6. [**1**] = 0.2 M, [TBAB] = 0.4 M. After 12 h, the solution was sent for ^{1}H NMR testing.

7. DFT calculations

Computational Methods

The Gaussian 16 program was adopted to perform all calculations in this study[40]. For solution phase geometry optimization in solvent acetonitrile, the B3LYP[41, 42]/GEN1 method (GEN: 6-31g* for C, H, O, P, S, LANL2DZ for Br, I) combined with the SMD model[43] were used. The frequency analysis was conducted at the same level with optimization (zero imaginary frequency for local minima). Frontier orbital analysis is performed on the optimized structure.

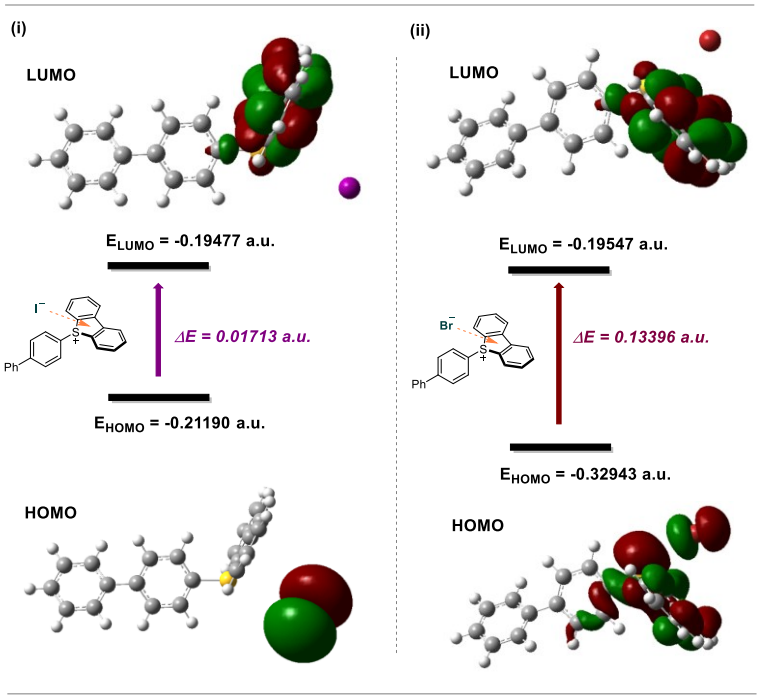


Figure S7. Frontier orbital analysis of arylsulfonium-I and arylsulfonium-Br complexes.

Cartesian coordinates of related compounds

arylsulfonium-I

C	2.14650800	2.22404100	3.39487200
C	1.55788500	0.99383200	3.71094600
C	1.05273600	0.16846800	2.70161700
C	1.14696500	0.63472000	1.39792000
C	1.72931300	1.86443500	1.04640000
C	2.24003800	2.66446800	2.07298800
H	2.54102500	2.84778300	4.19141800
H	1.49659800	0.66993700	4.74509900
H	0.60101800	-0.79024500	2.93455500
H	2.70454300	3.61804500	1.84115100
C	1.11636900	1.08205400	-1.13603800
C	0.98472800	1.09186100	-2.51749300
C	1.46144400	2.21887400	-3.19416900

C	2.05665200	3.27206100	-2.48967700
C	2.18691000	3.23240900	-1.09979600
C	1.70879200	2.12118600	-0.39845800
H	0.52674900	0.26681400	-3.05359500
H	1.37146200	2.26948300	-4.27470000
H	2.42650700	4.13648000	-3.03301600
H	2.65376100	4.05427200	-0.56589200
S	0.62189700	-0.27485700	-0.06304600
C	-1.17652200	-0.27940000	-0.04606100
C	-1.92146900	0.88210300	0.18017900
C	-1.78911400	-1.51341200	-0.27670200
C	-3.30787300	0.79391700	0.17269300
H	-1.43491400	1.83357700	0.36854500
C	-3.18110100	-1.57901100	-0.28295300
H	-1.20061500	-2.40746600	-0.45934500
C	-3.96408600	-0.43323800	-0.05948200
H	-3.88897900	1.68836400	0.37242700
H	-3.65828800	-2.53191900	-0.48663300
C	-5.44646200	-0.51219300	-0.06777600
C	-6.22245700	0.55400800	-0.55817000
C	-6.10829100	-1.65725000	0.41200700
C	-7.61504200	0.47517900	-0.57096800
H	-5.73479700	1.43912600	-0.95631800
C	-7.50100500	-1.73224400	0.40245600
H	-5.53183900	-2.48394400	0.81714300
C	-8.26007600	-0.66725700	-0.08995900
H	-8.19592300	1.30556400	-0.96339500
H	-7.99318800	-2.62185000	0.78623300
H	-9.34503100	-0.72721700	-0.09882800
I	4.62910400	-1.95409000	-0.32796900

arylsulfonium-Br

C	2.68924100	-1.65065300	3.34766900
C	2.06309300	-2.62763000	2.56450200
C	1.56066900	-2.30841500	1.29883000
C	1.70513000	-0.99763800	0.86937700
C	2.32194900	0.00702700	1.63318400
C	2.82310300	-0.33711200	2.89247400
H	3.07784800	-1.91696800	4.32624300

H	1.96810000	-3.64353300	2.93552500
H	1.07929500	-3.06032800	0.68169500
H	3.31078200	0.41192800	3.50900400
C	1.73606700	1.28286400	-0.30743500
C	1.62721700	2.39489700	-1.12905200
C	2.15307900	3.59952000	-0.65100700
C	2.76772900	3.65790800	0.60550400
C	2.86625100	2.52366500	1.41437200
C	2.34035400	1.30991200	0.96067000
H	1.15580600	2.33860100	-2.10490300
H	2.08619700	4.49205000	-1.26555400
H	3.17524600	4.60053500	0.95886200
H	3.34586500	2.58111800	2.38685800
S	1.13724000	-0.36424200	-0.71766300
C	-0.66201800	-0.22129400	-0.47448900
C	-1.24658000	0.40110300	0.63281600
C	-1.44560600	-0.78974000	-1.48086400
C	-2.63310400	0.44640100	0.72442600
H	-0.63833200	0.83731100	1.41851200
C	-2.83505200	-0.73434000	-1.37463900
H	-0.98617800	-1.26370400	-2.34348500
C	-3.45350700	-0.11905900	-0.27355100
H	-3.08553100	0.90826600	1.59630600
H	-3.43929300	-1.15693400	-2.17097200
C	-4.93329700	-0.06511200	-0.16010000
C	-5.57091500	1.04519800	0.42269300
C	-5.73123100	-1.12369200	-0.63110200
C	-6.96092600	1.09498300	0.52969900
H	-4.97786200	1.88529000	0.77259300
C	-7.12090600	-1.07371300	-0.52051600
H	-5.26128400	-2.00211300	-1.06403000
C	-7.74172400	0.03565800	0.05972800
H	-7.43410500	1.96583300	0.97557300
H	-7.71841200	-1.90640700	-0.88208500
H	-8.82434600	0.07414800	0.14524100
Br	4.20160800	-0.96633300	-1.83176900

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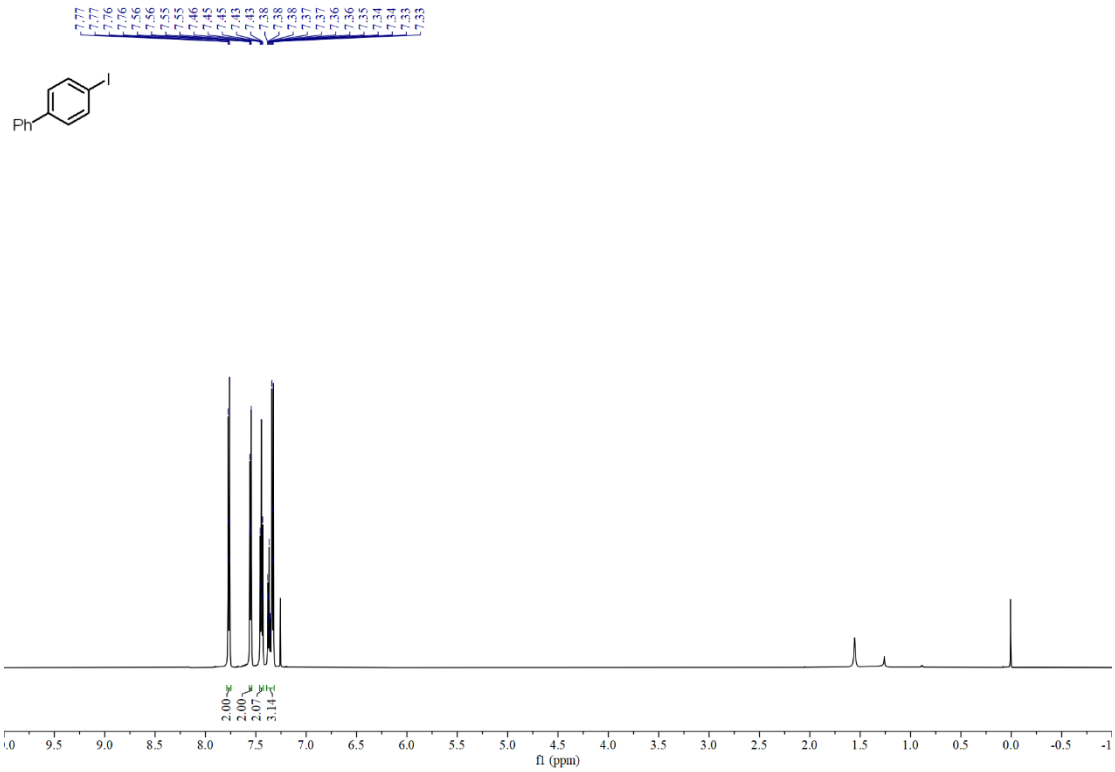
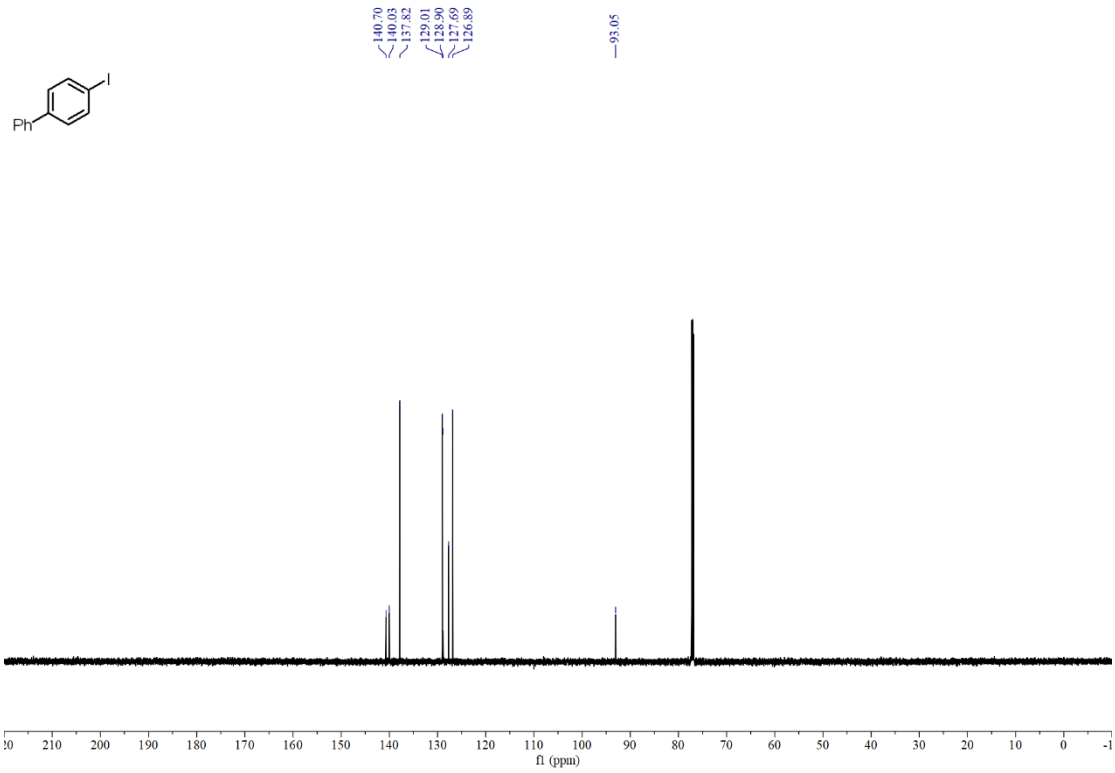
9. NMR spectra

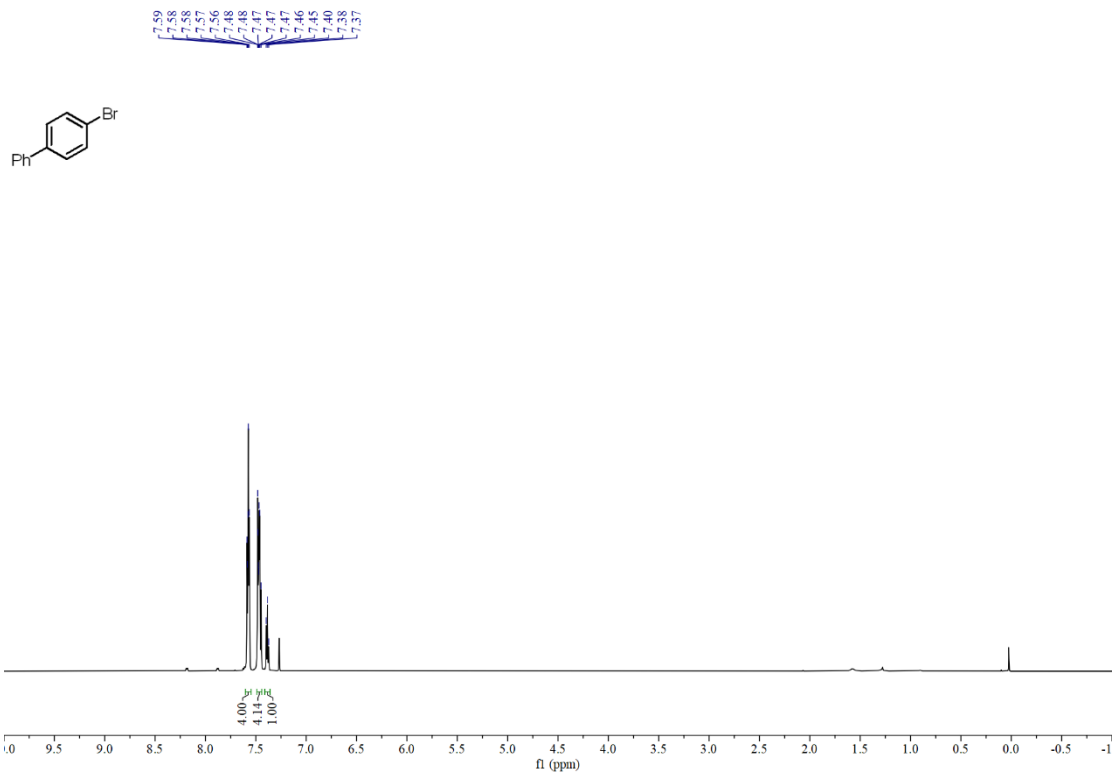
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 2



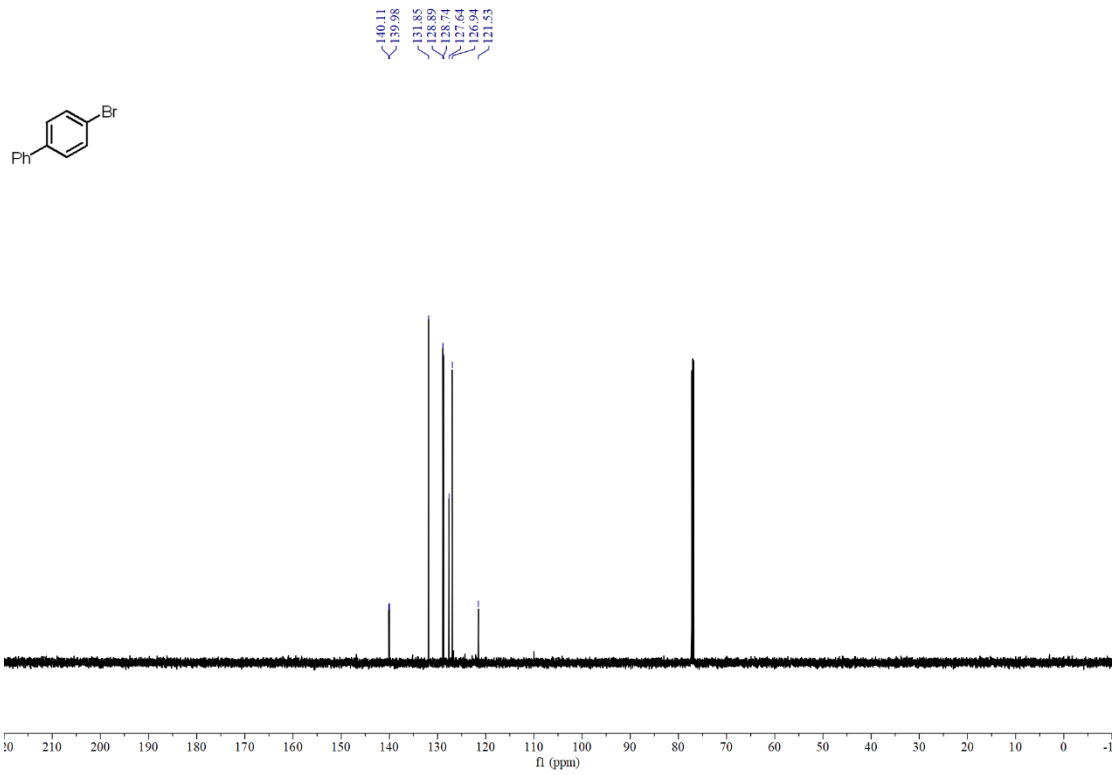
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 2



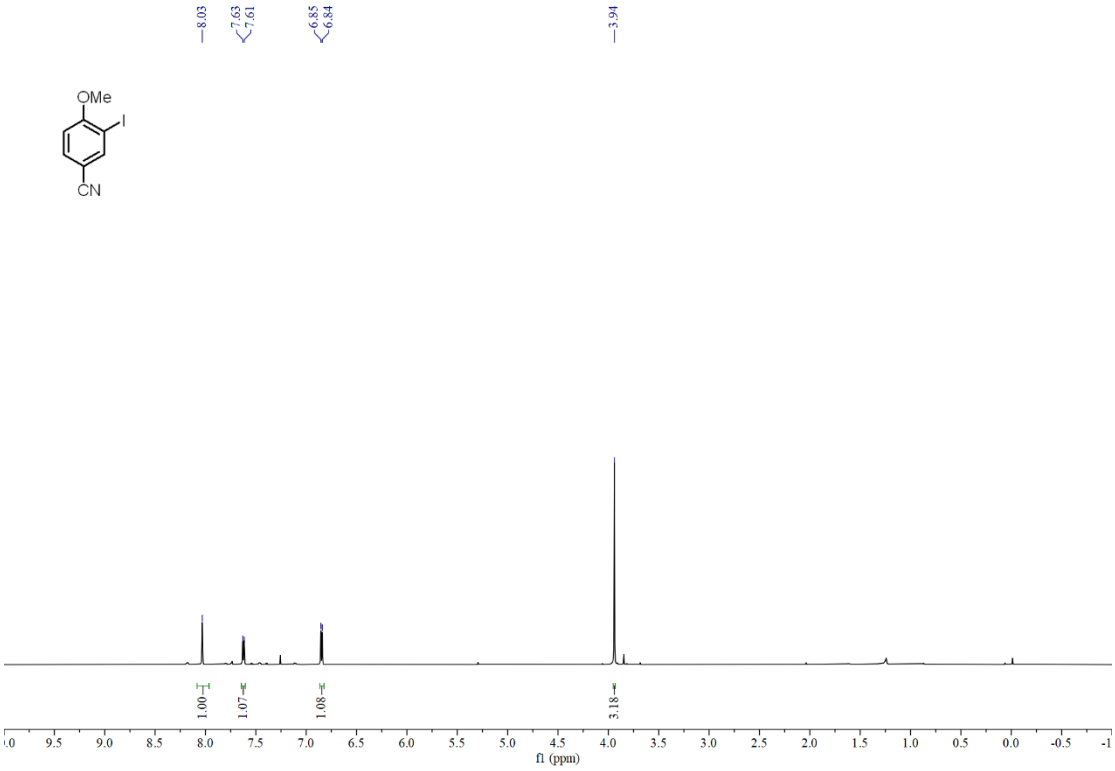
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 3



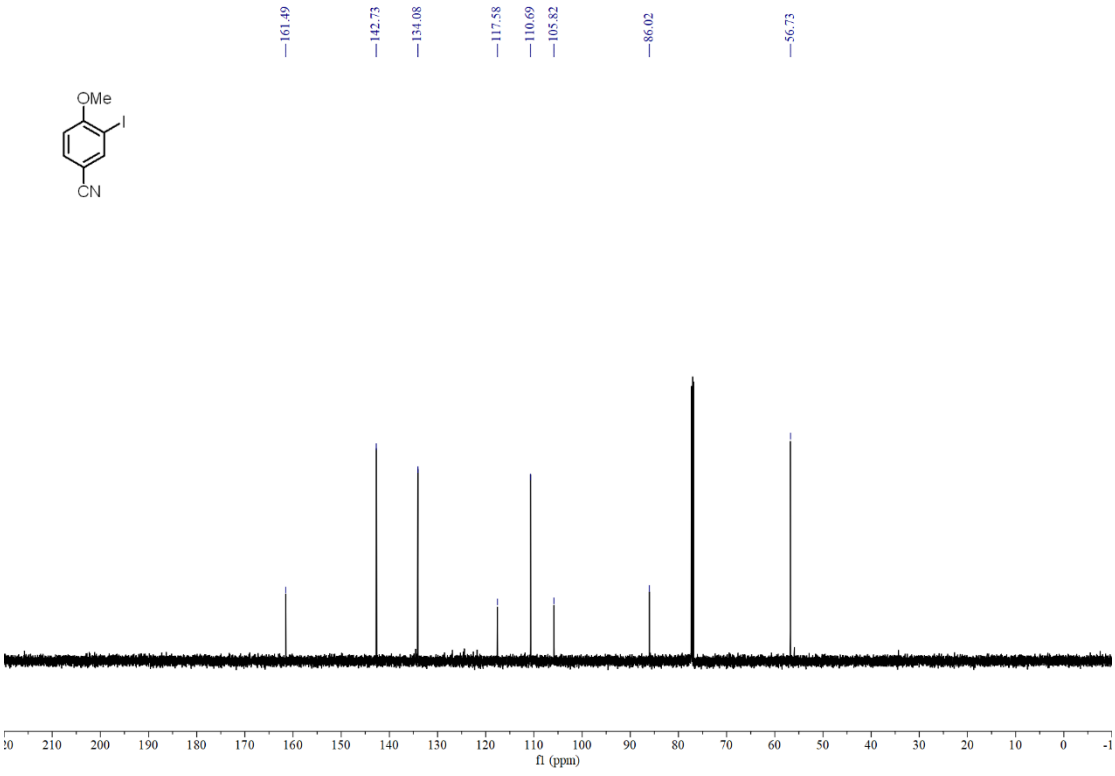
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 3



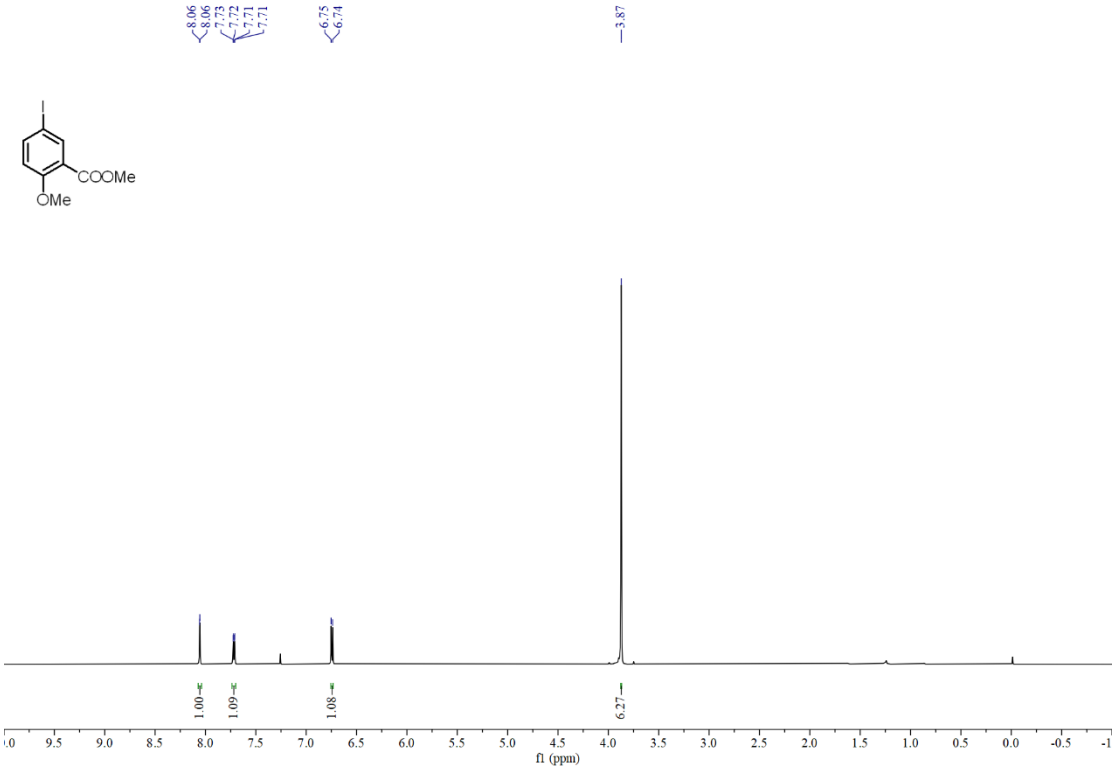
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 4



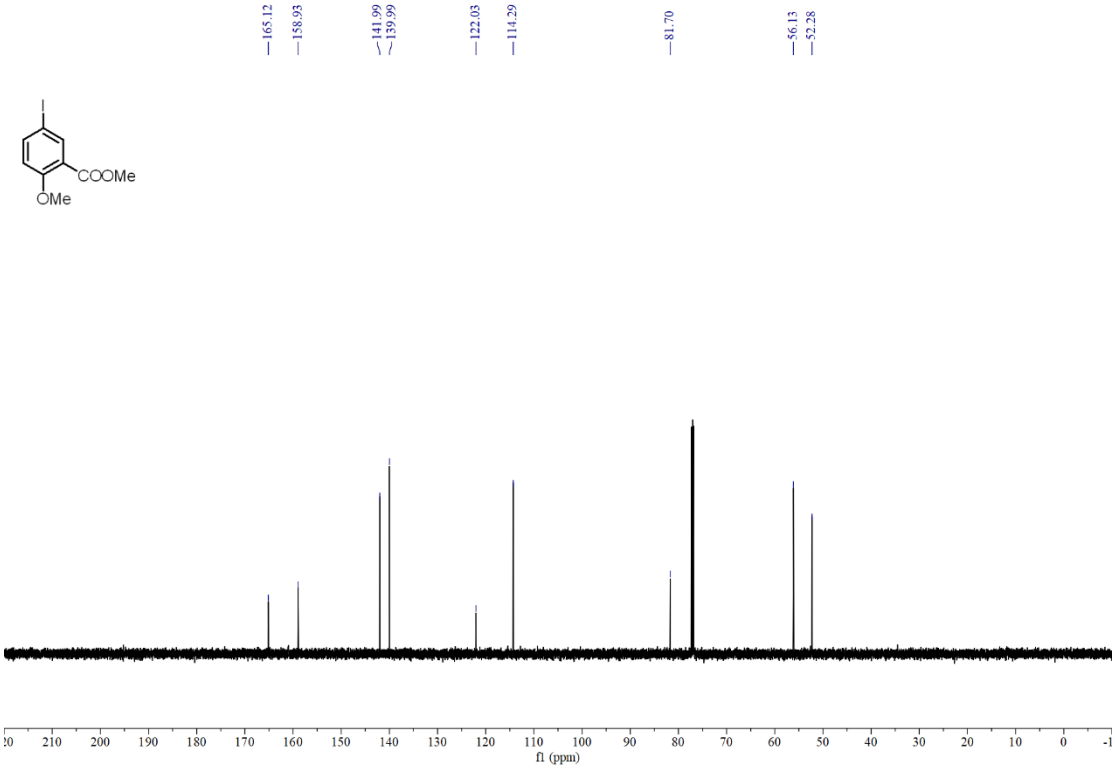
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 4



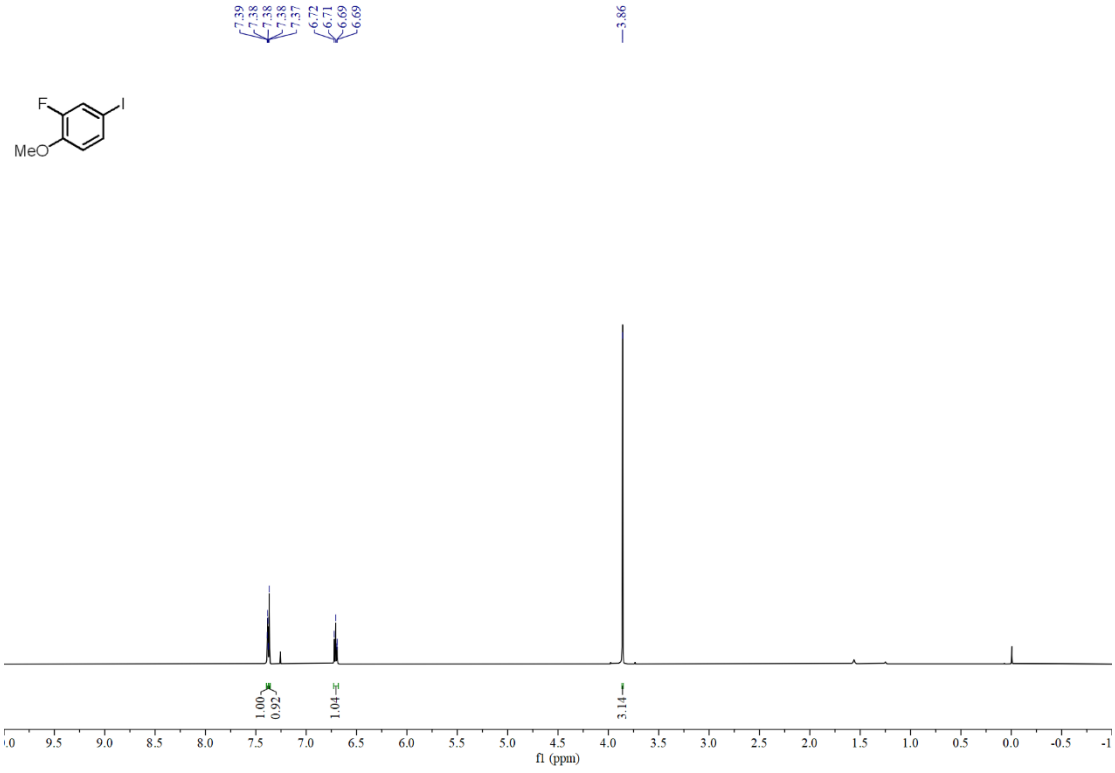
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 5



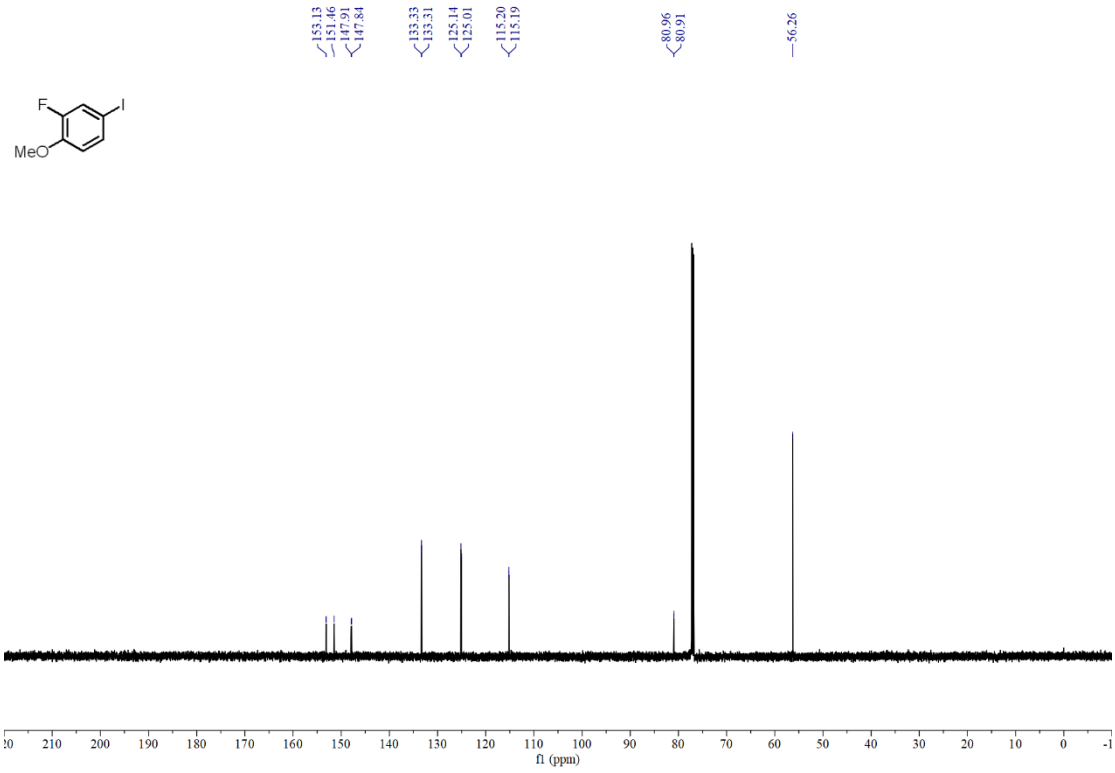
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 5



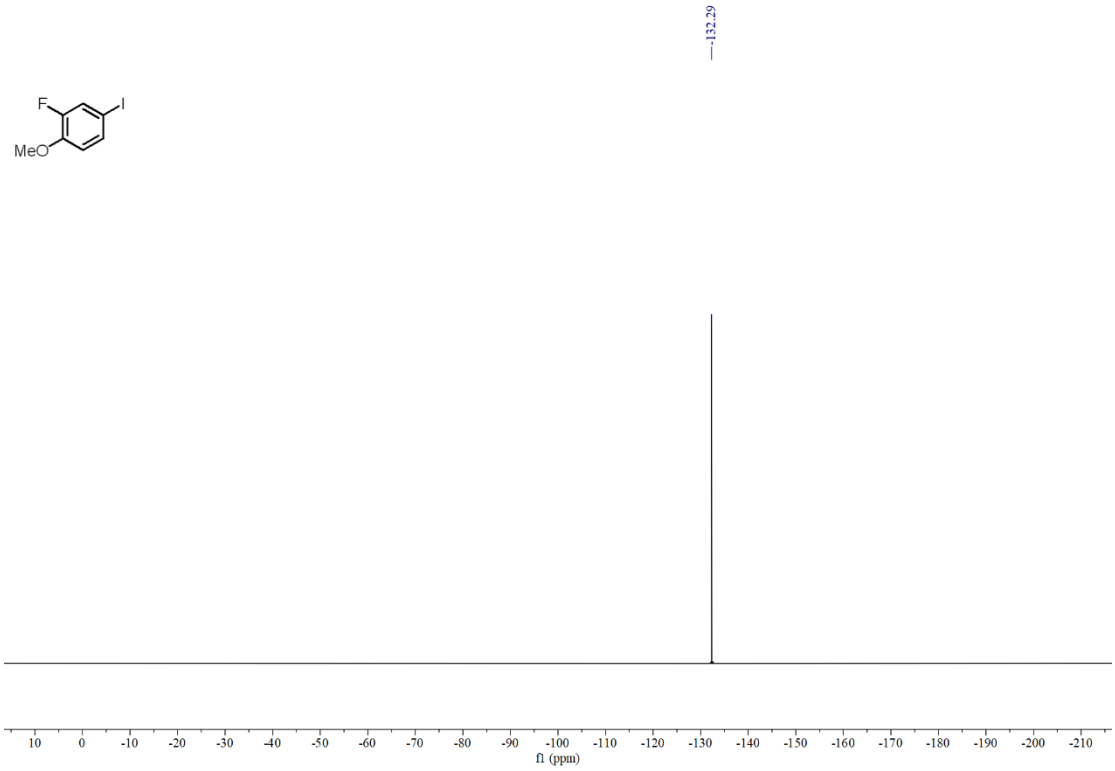
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 6



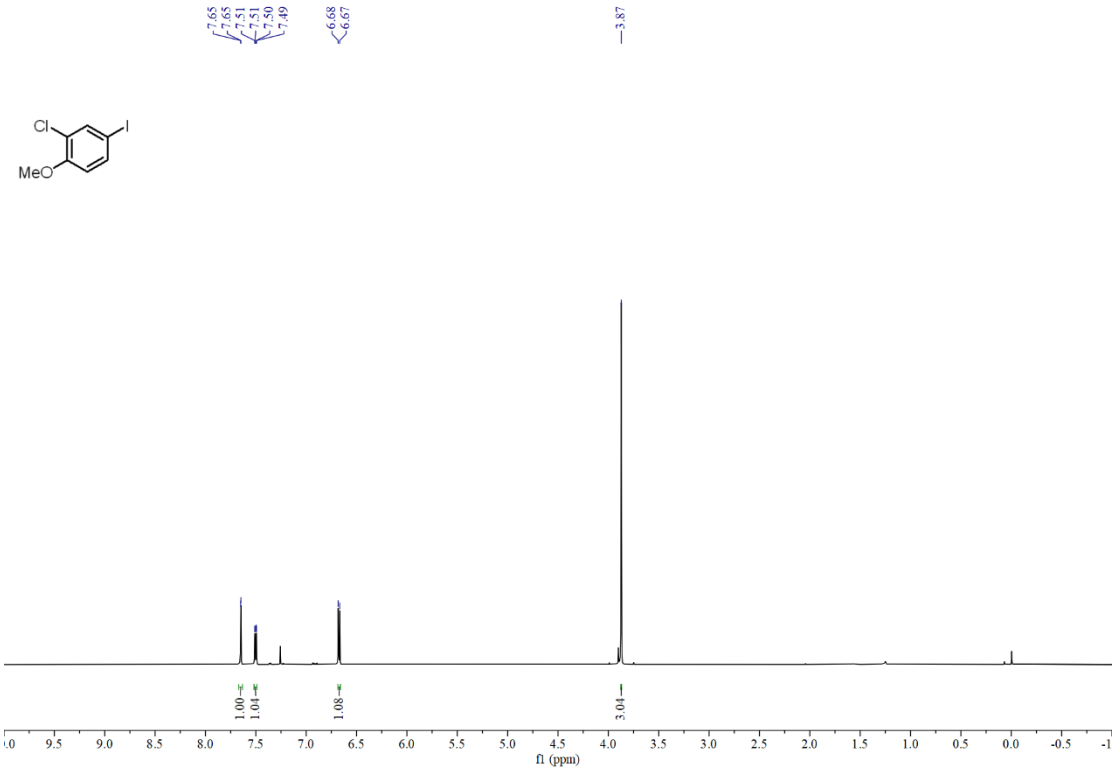
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 6



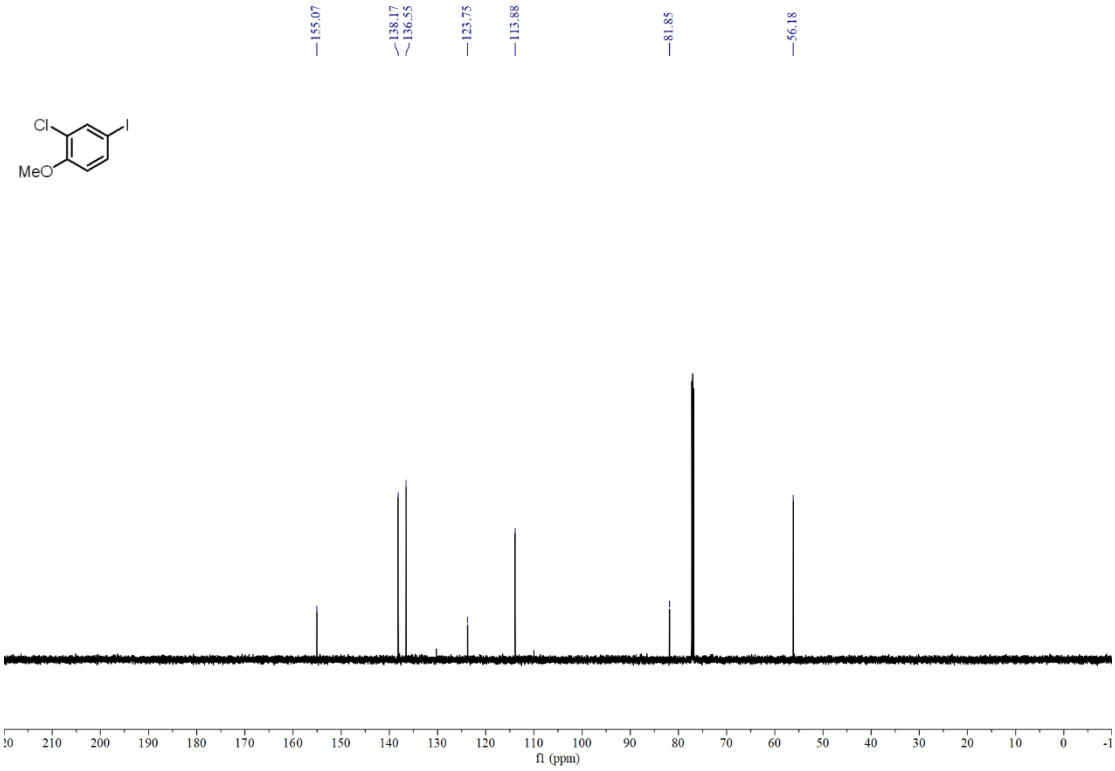
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 6



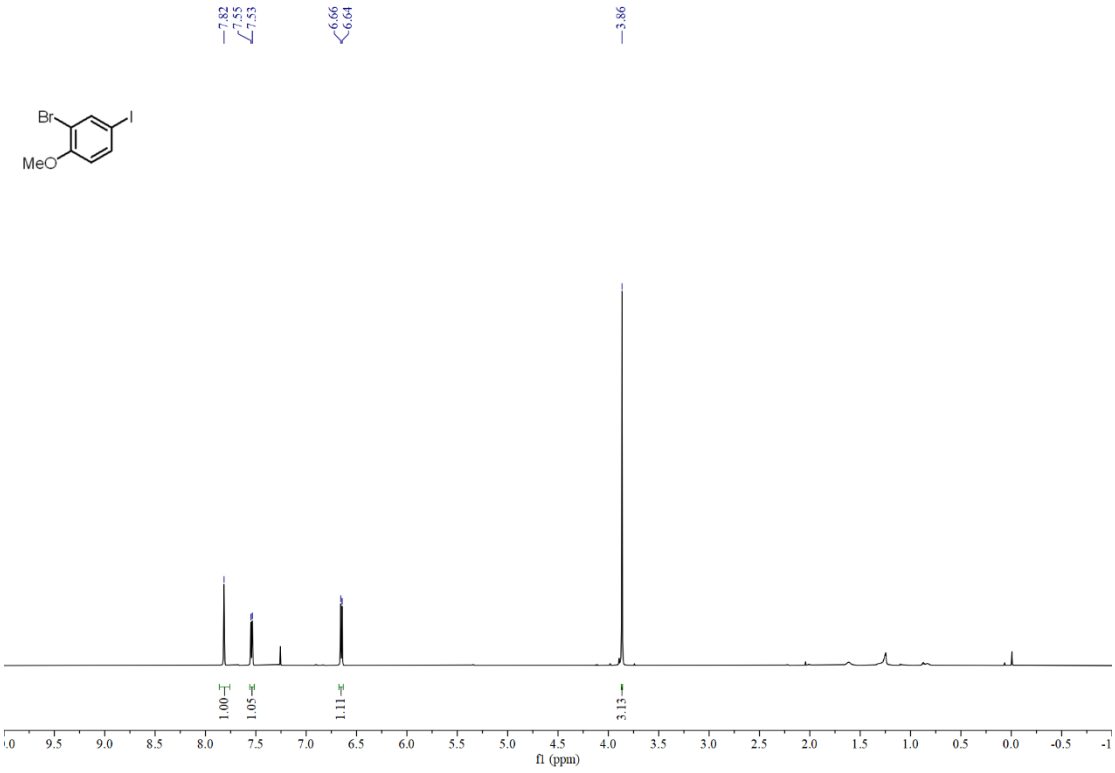
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 7



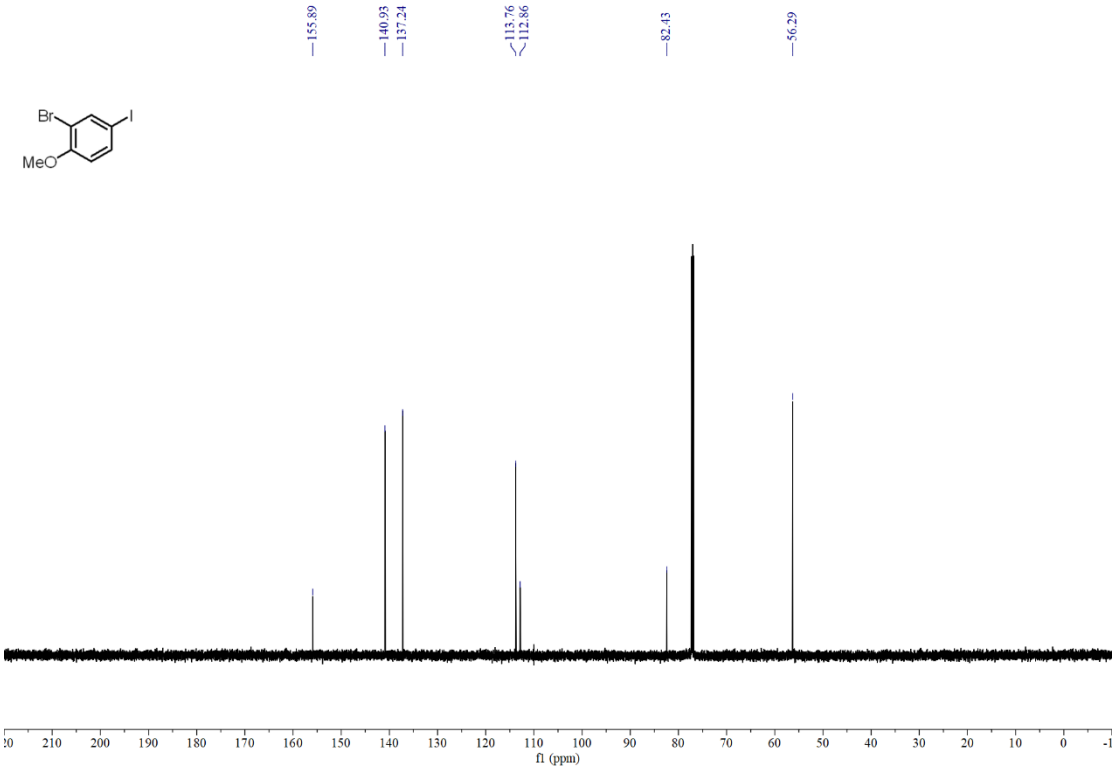
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 7



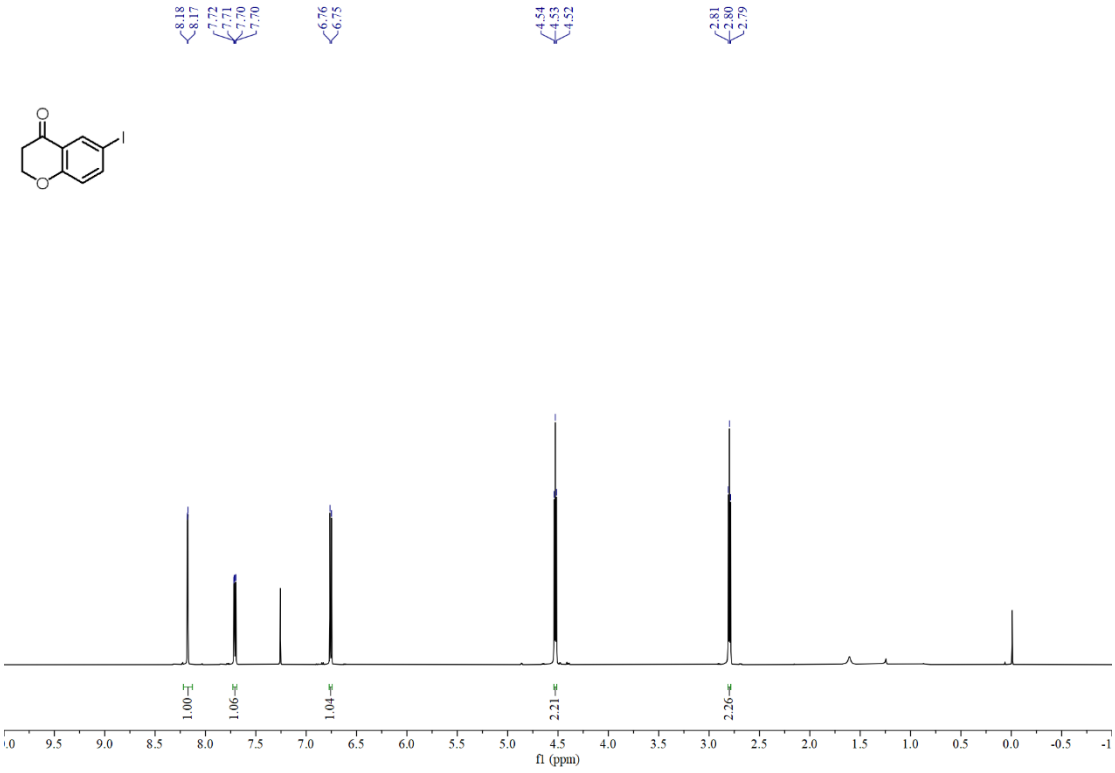
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 8



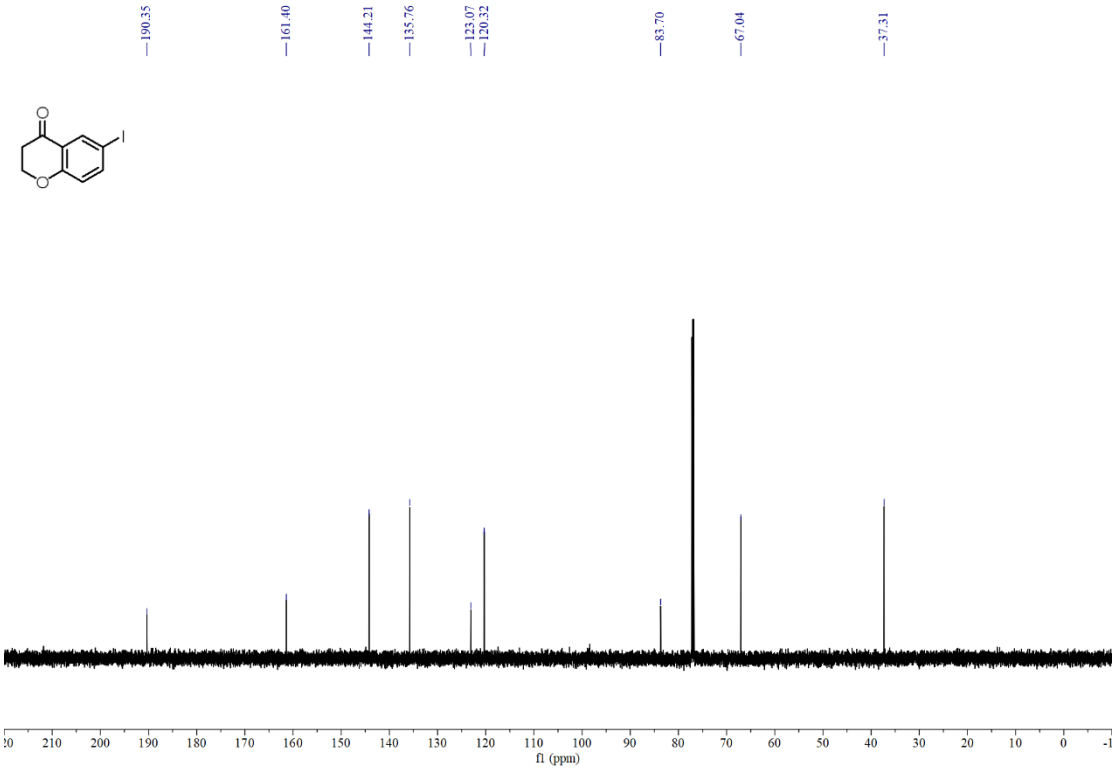
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 8



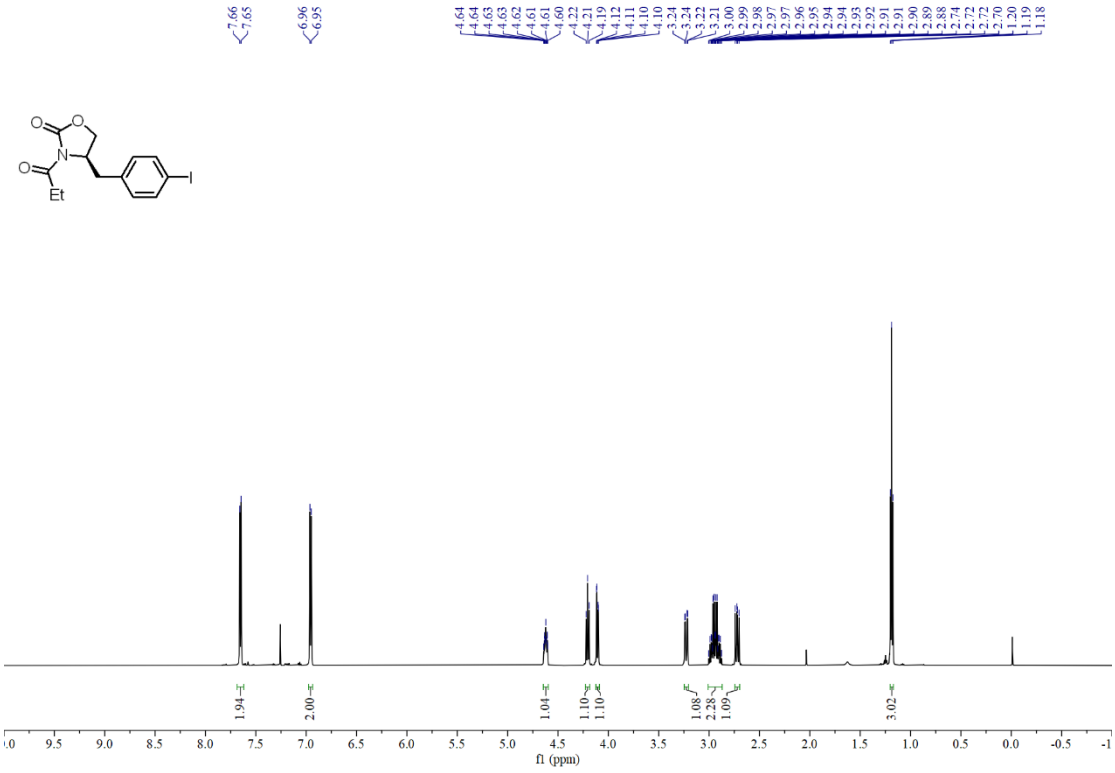
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 9



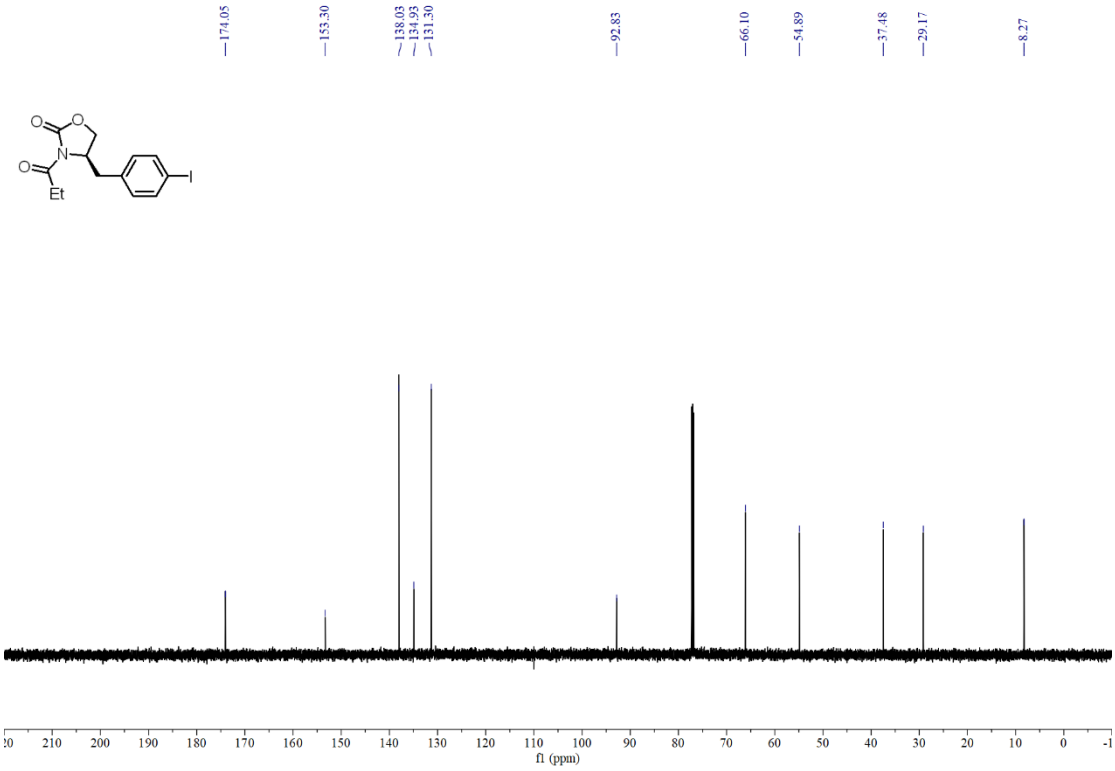
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 9



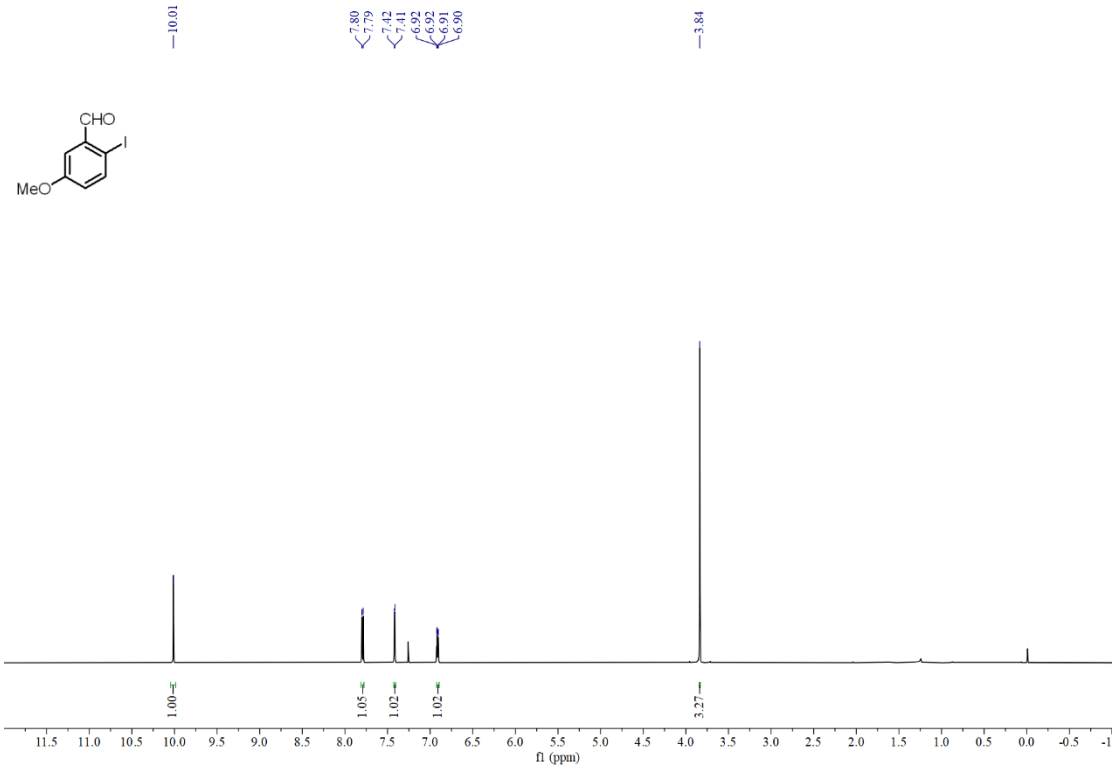
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 10



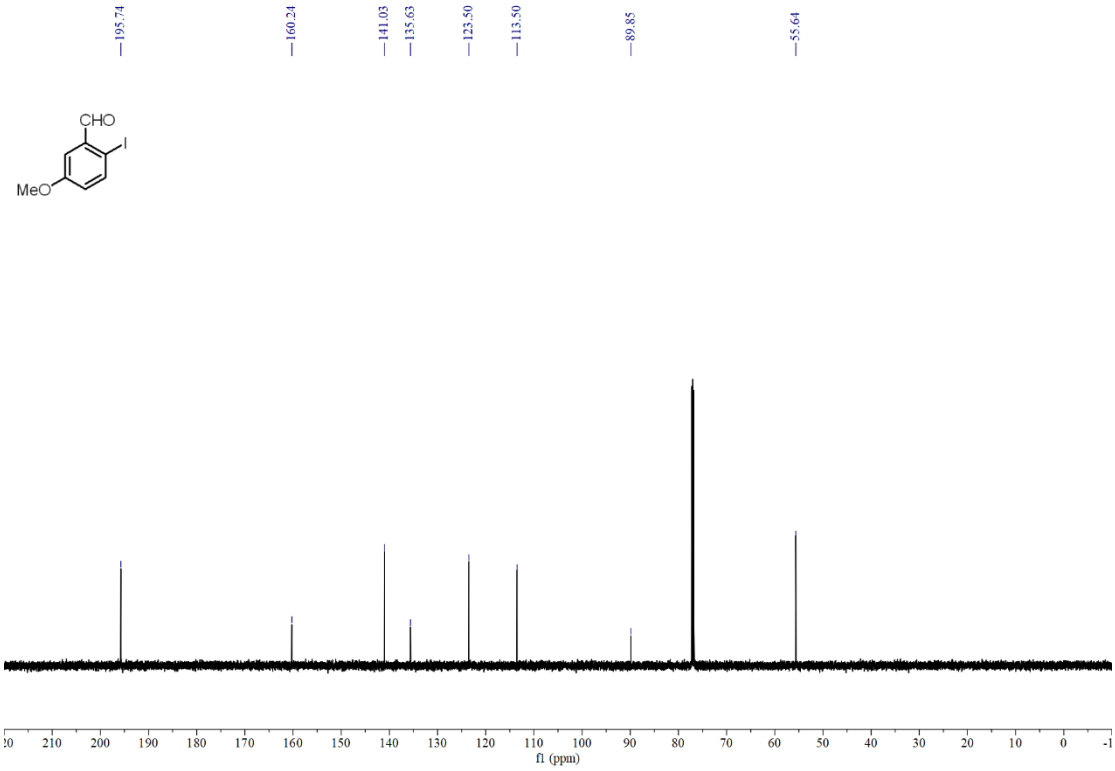
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 10



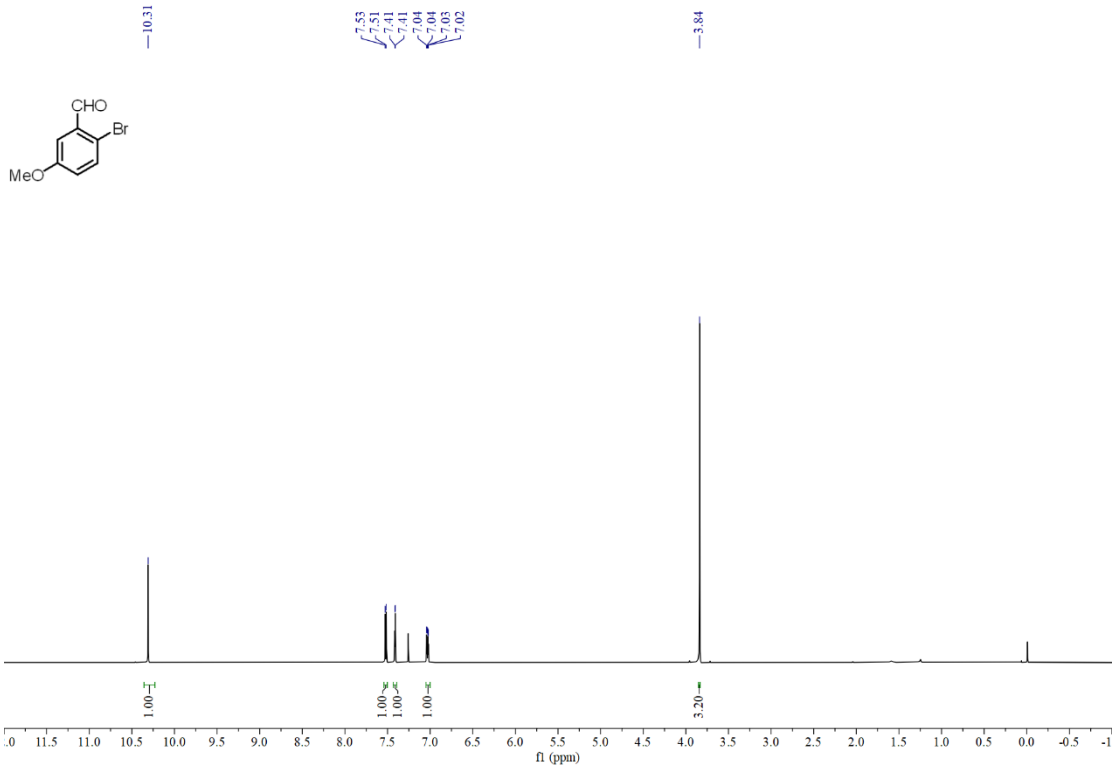
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 11



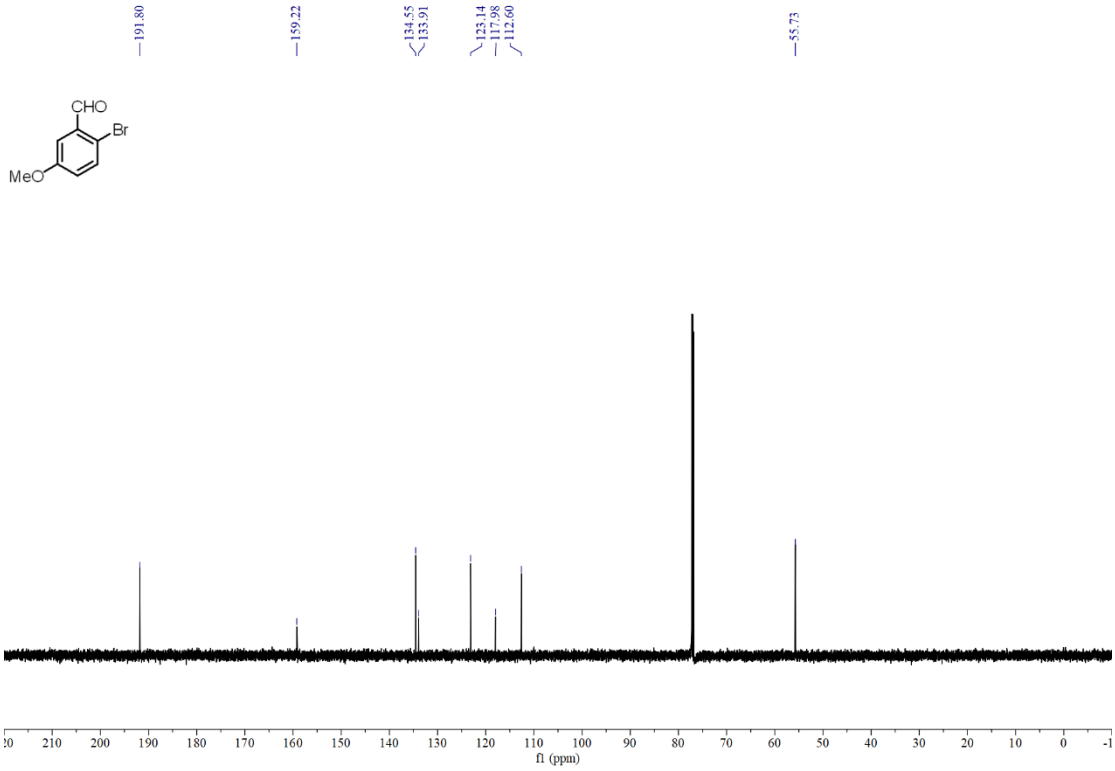
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 11



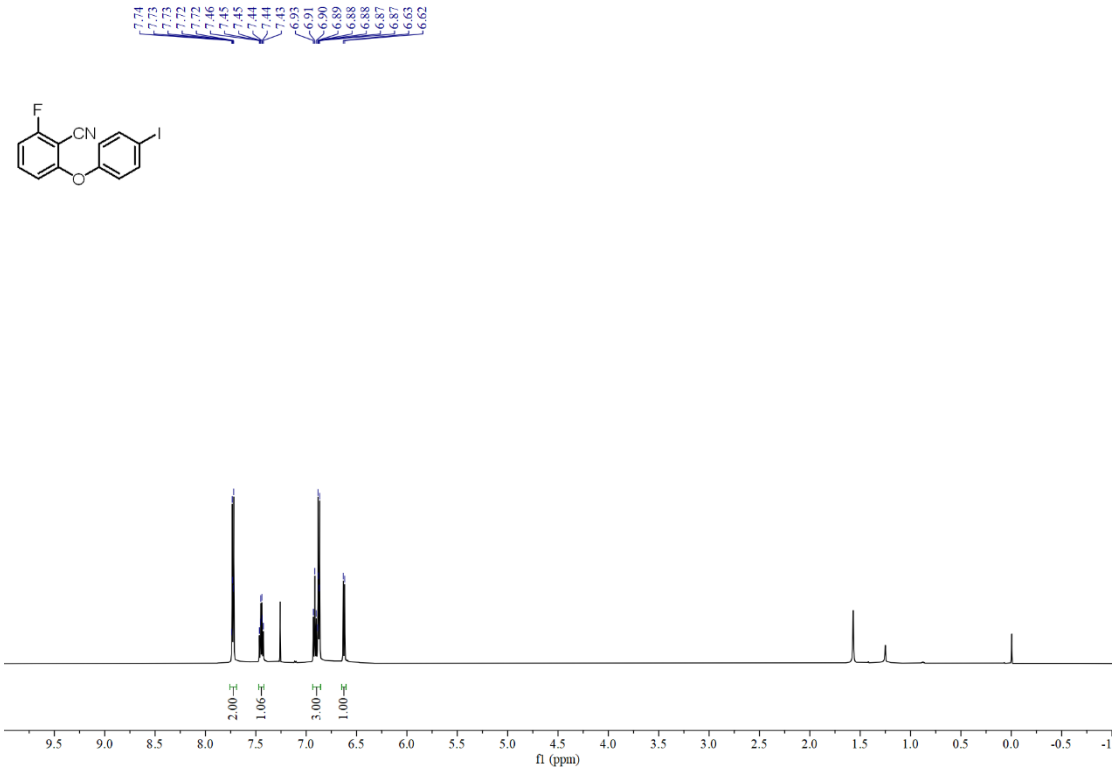
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 12



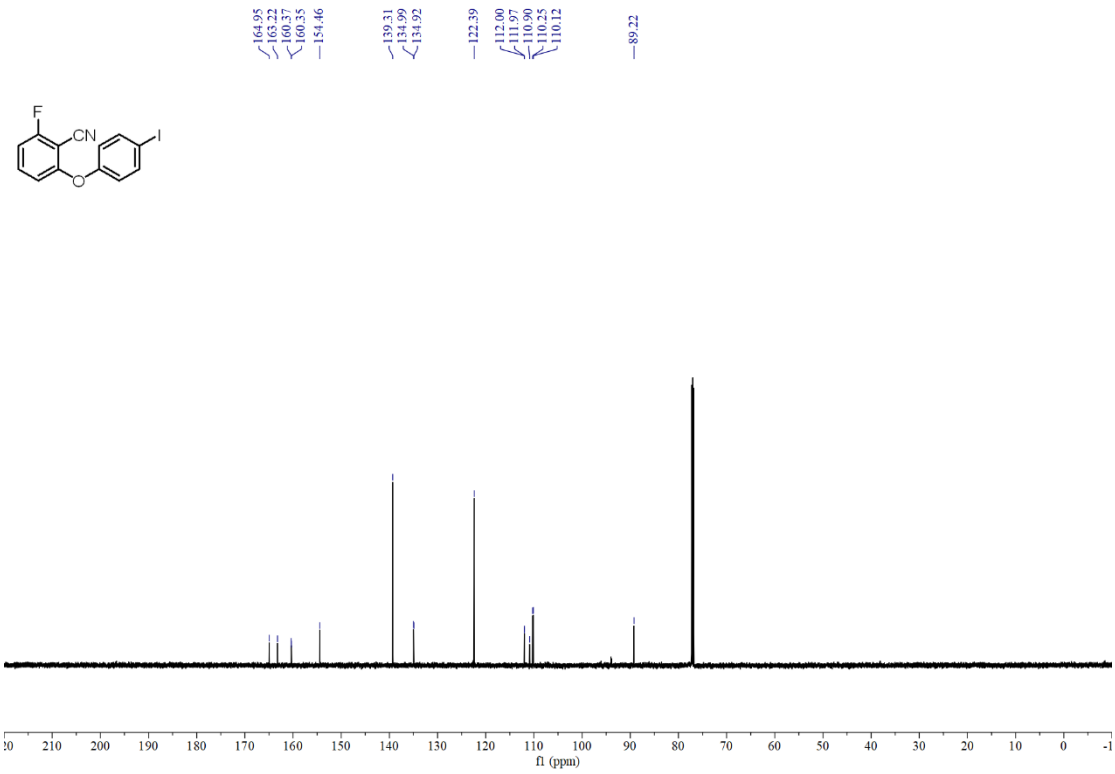
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 12



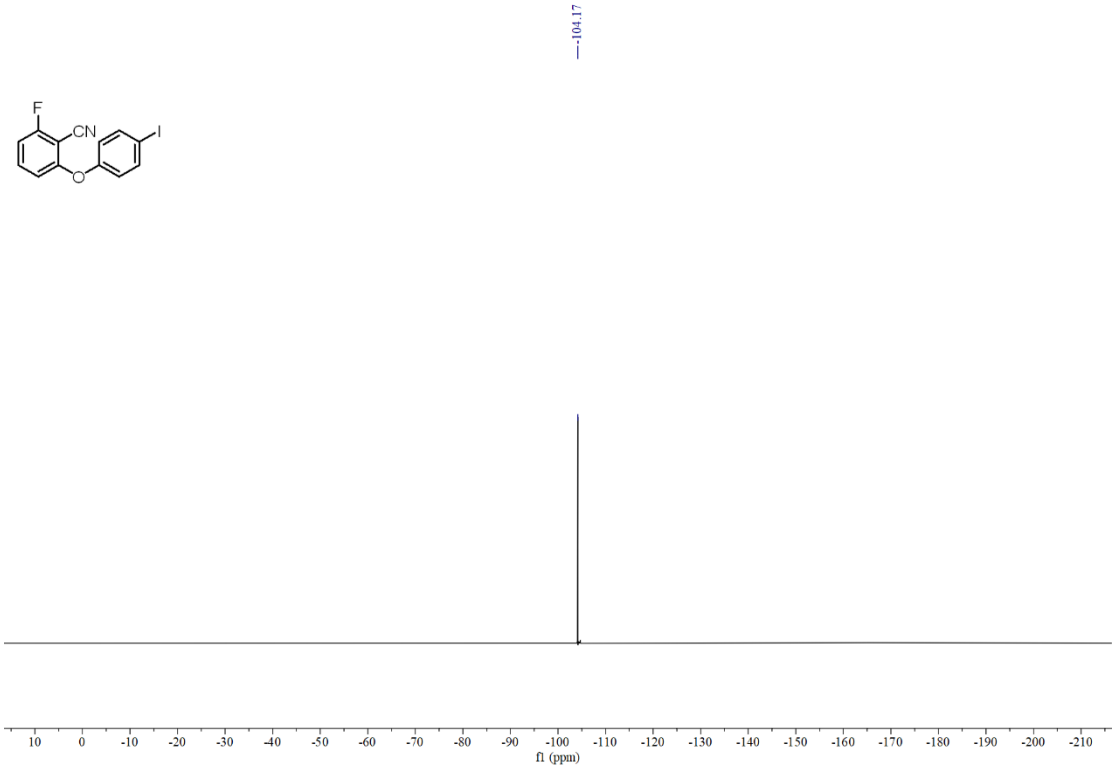
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 13



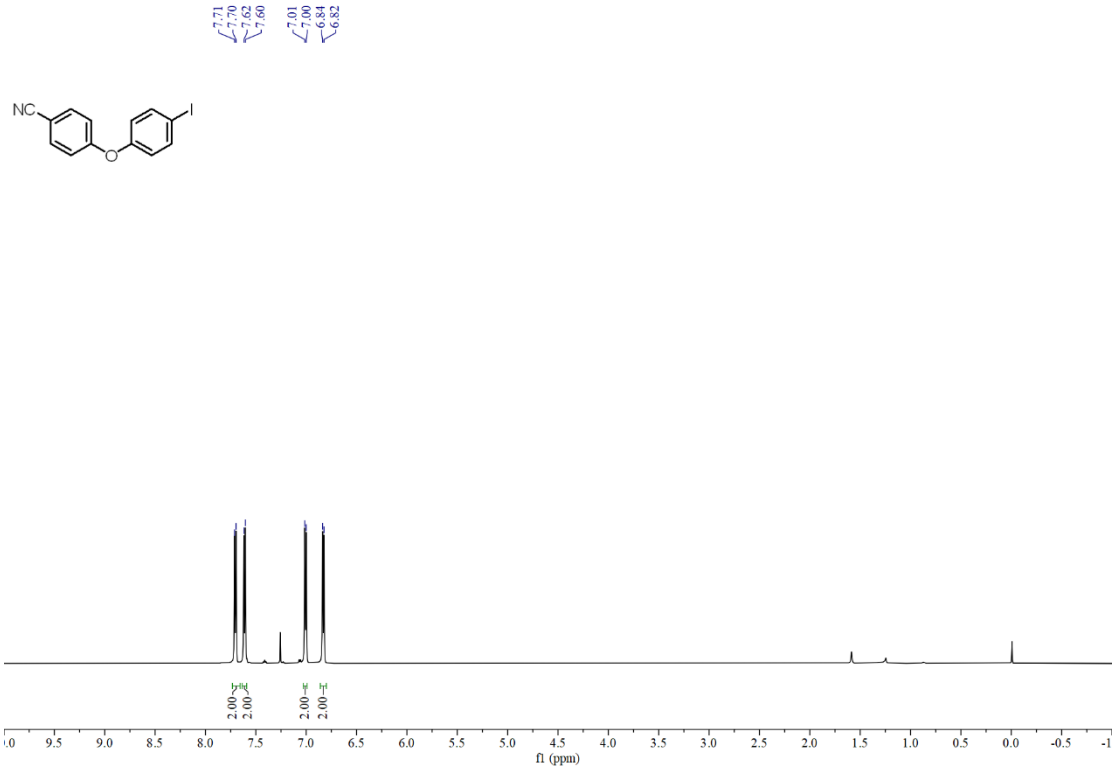
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 13



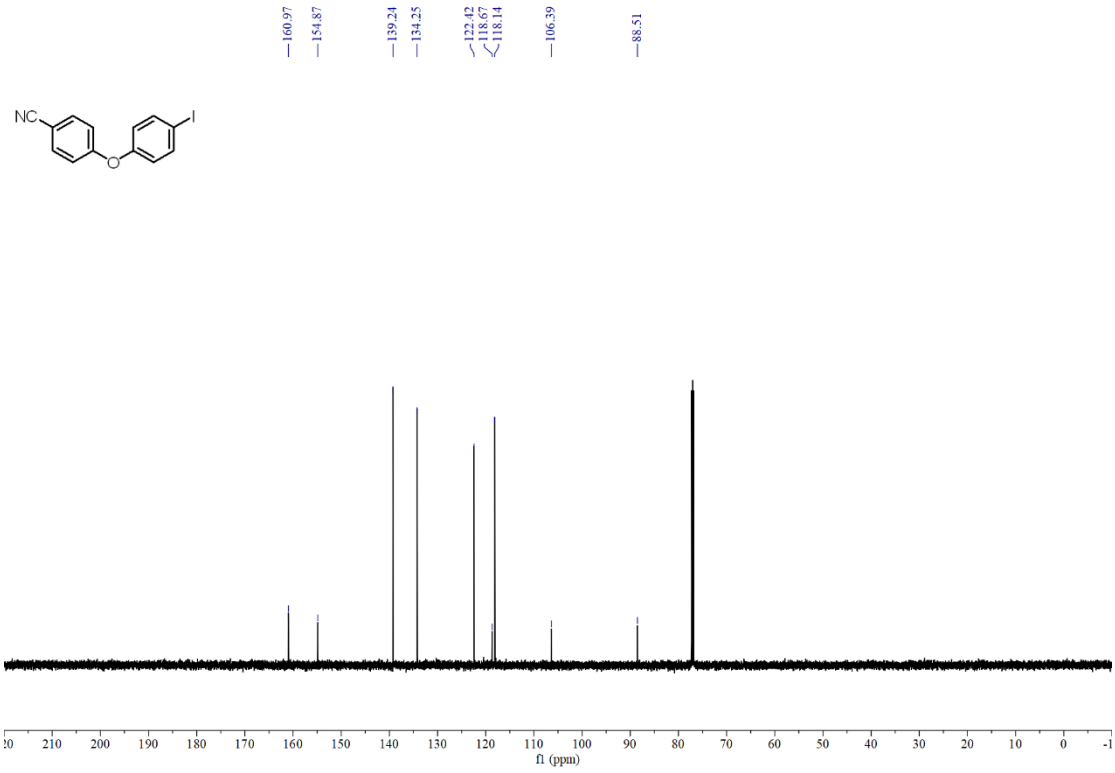
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 13



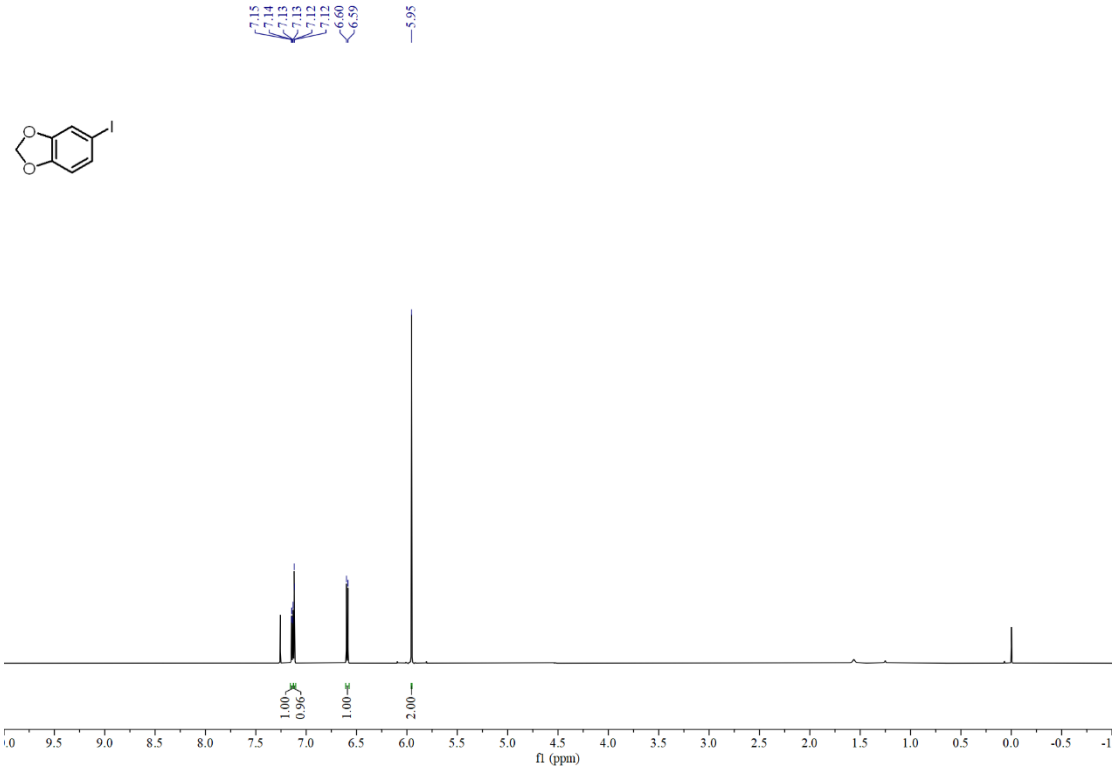
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 14



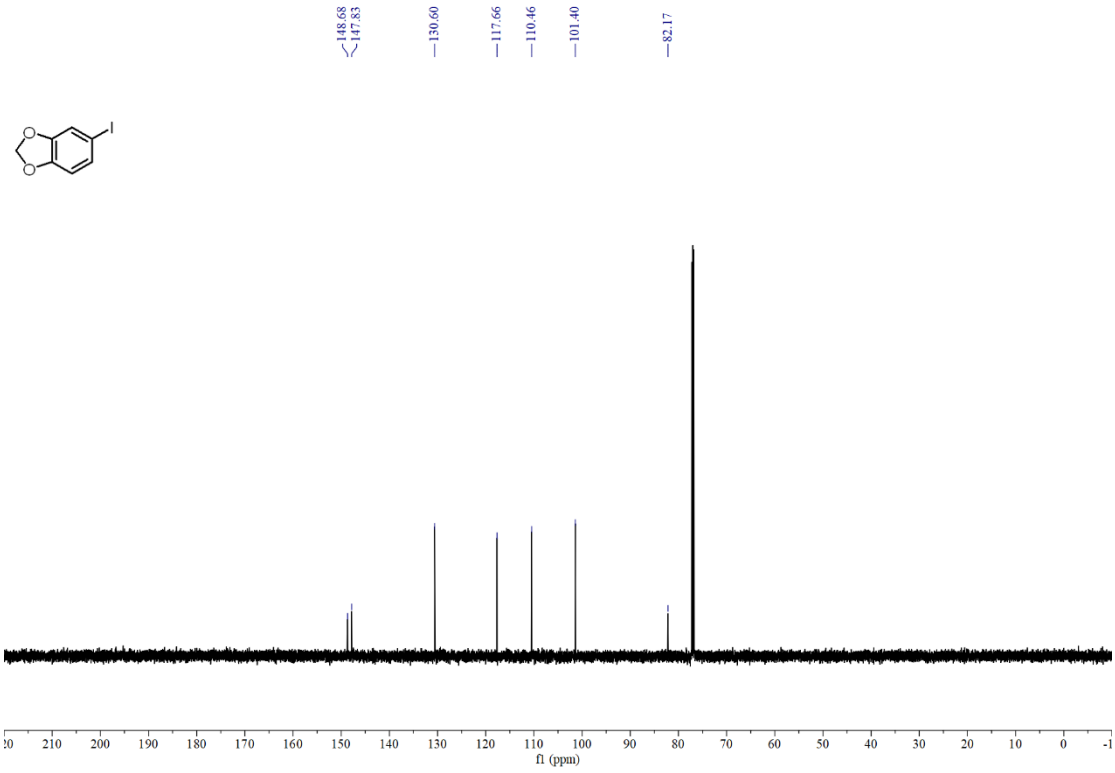
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 14



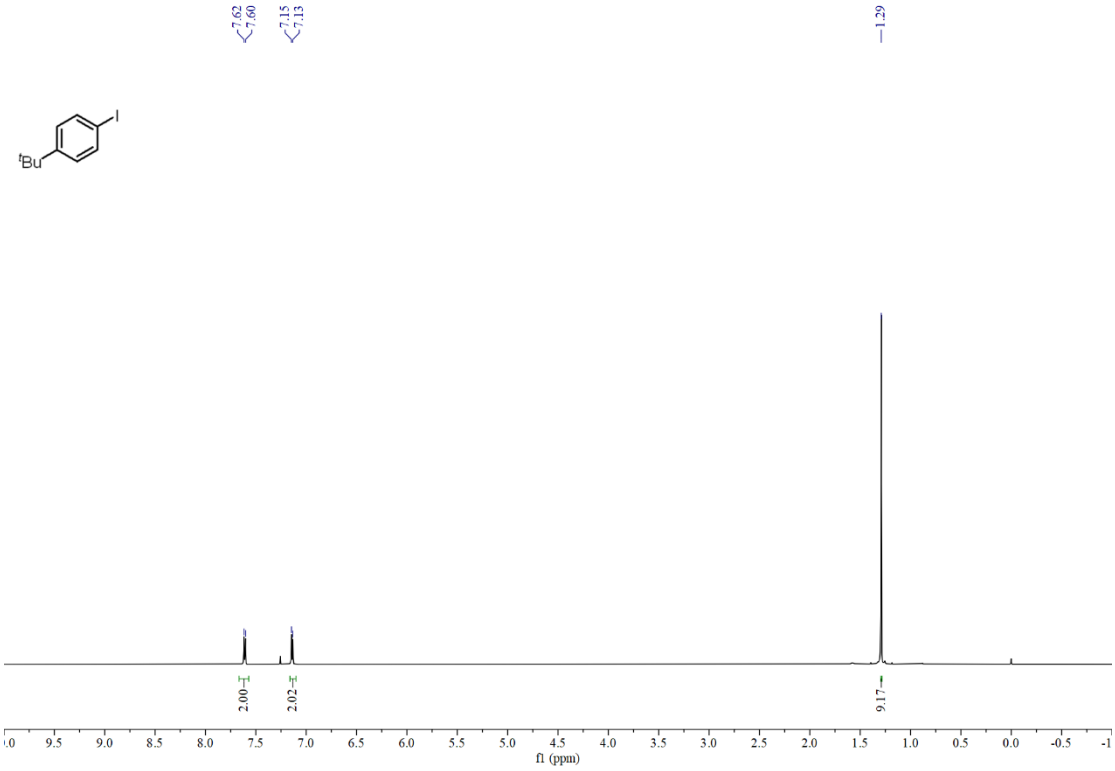
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 15



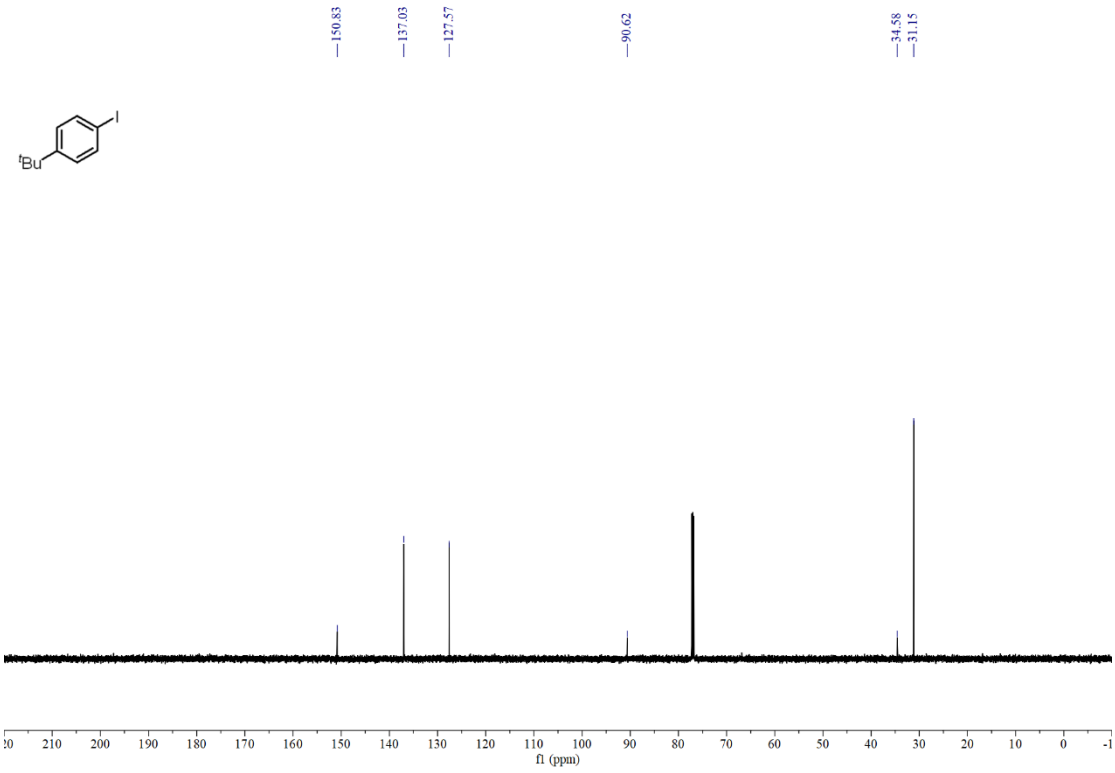
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 15



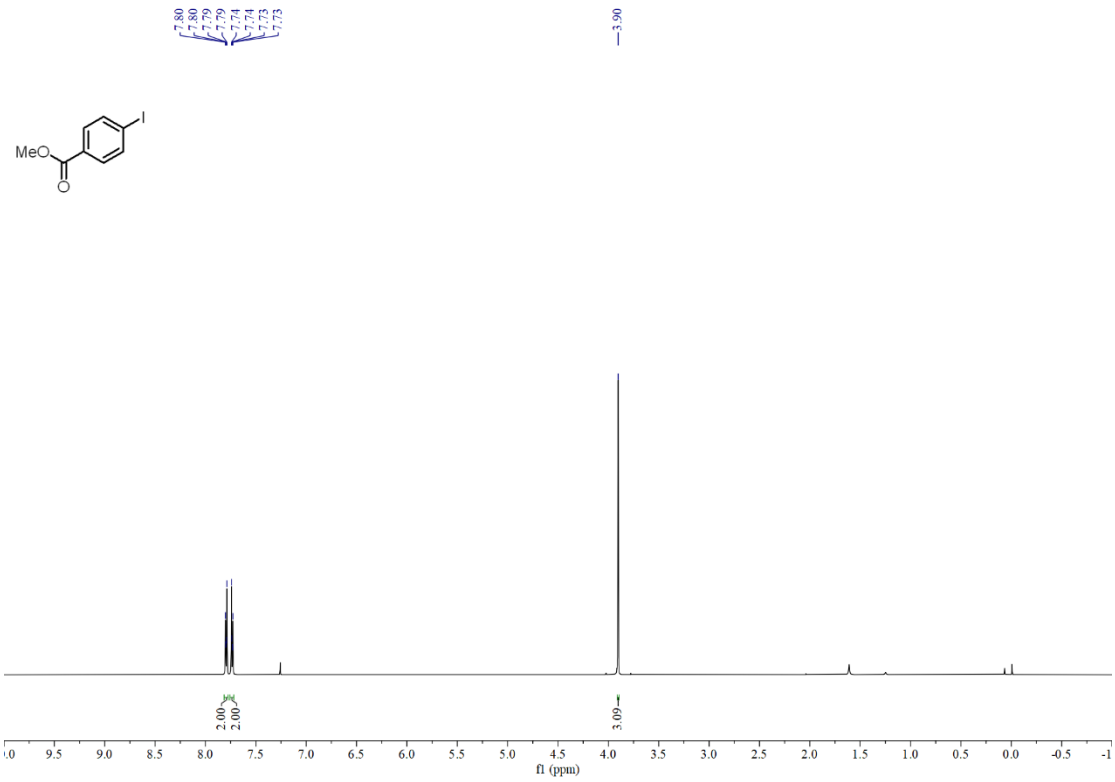
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 16



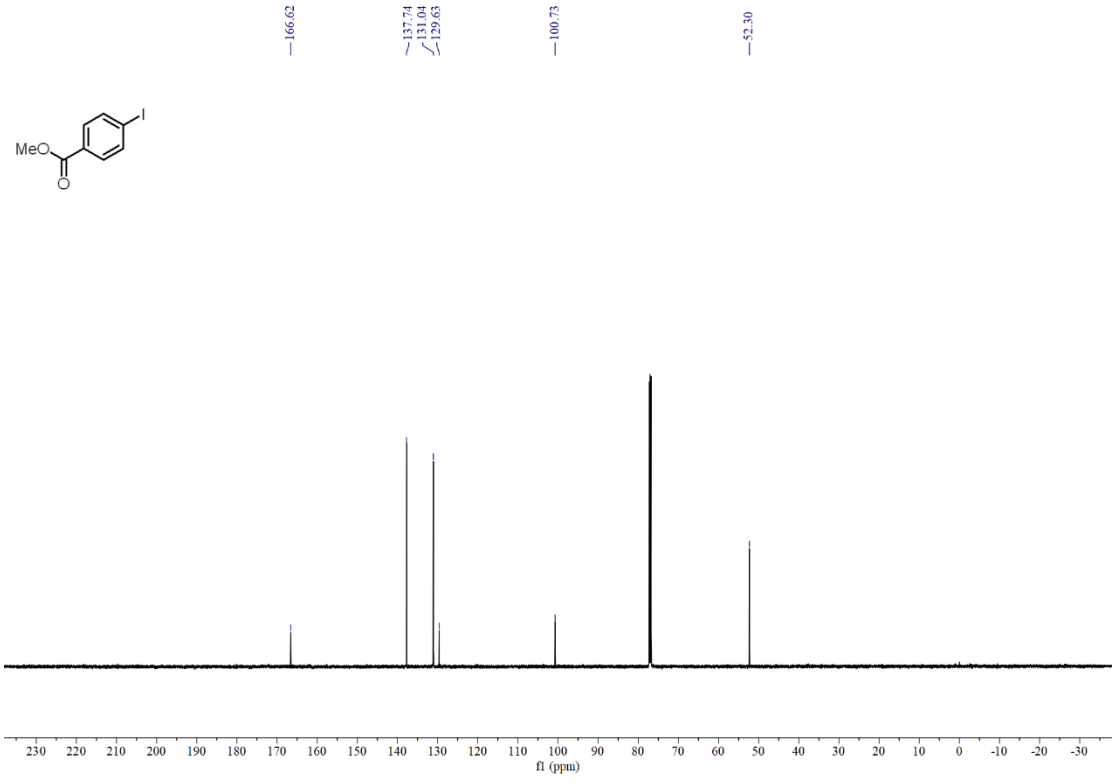
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 16



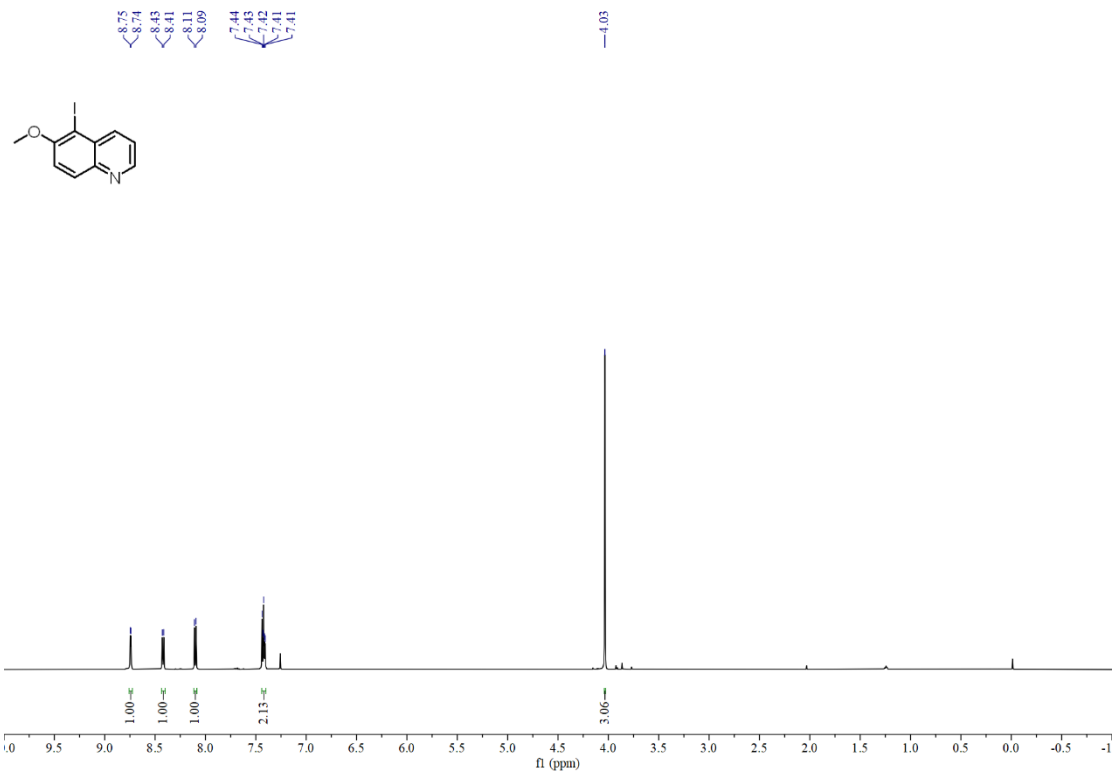
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 17



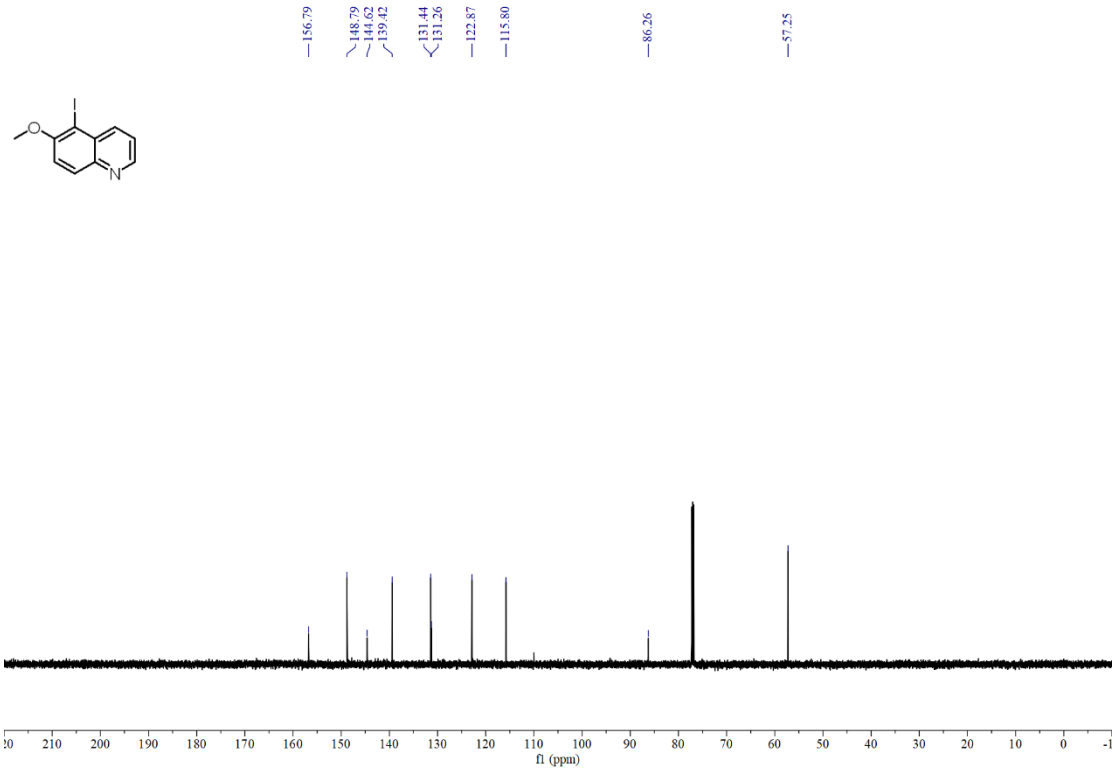
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 17



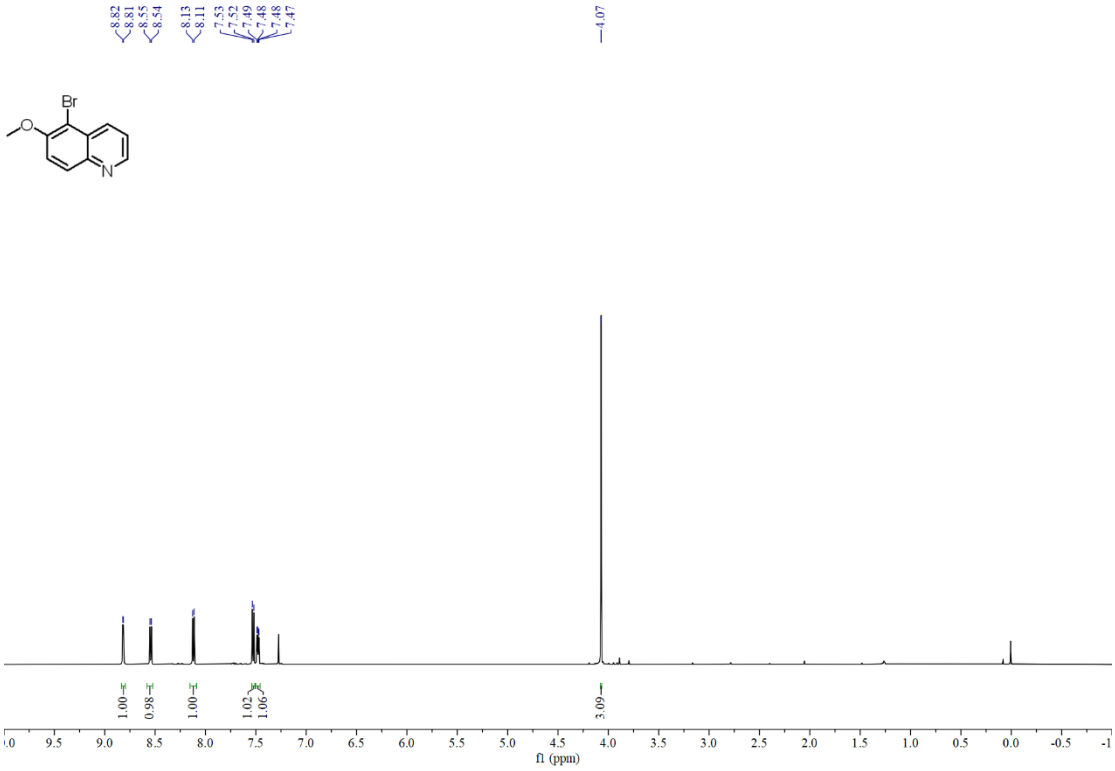
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 18



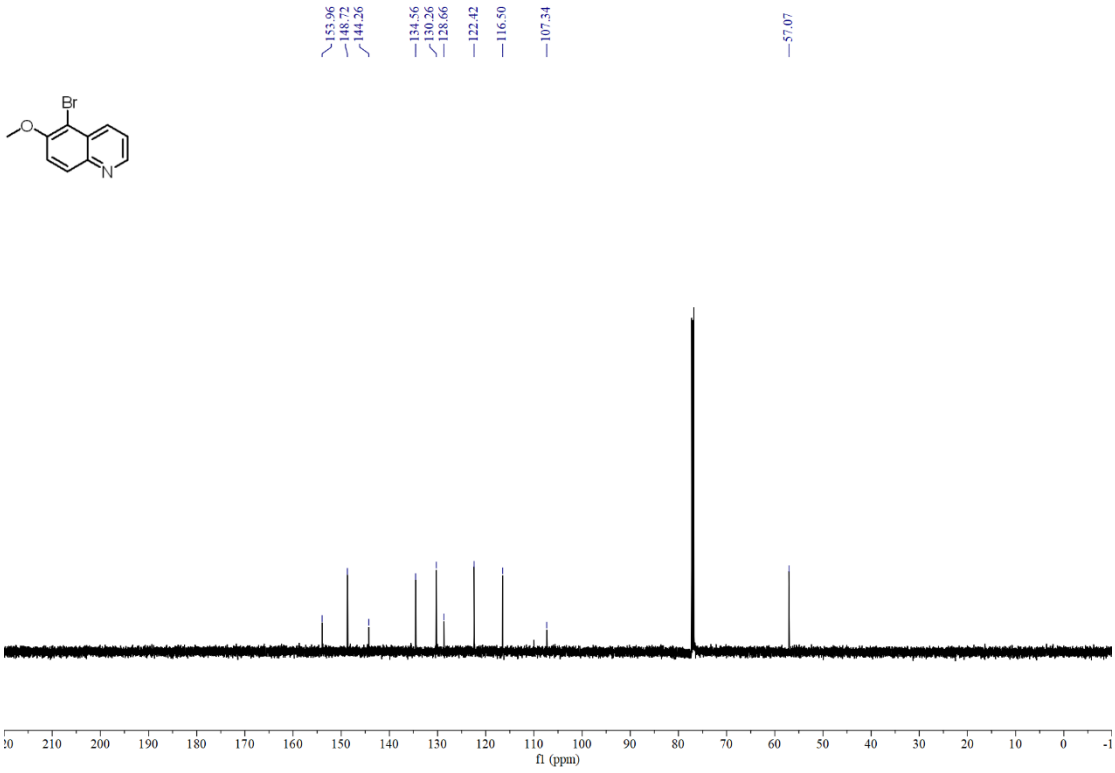
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 18



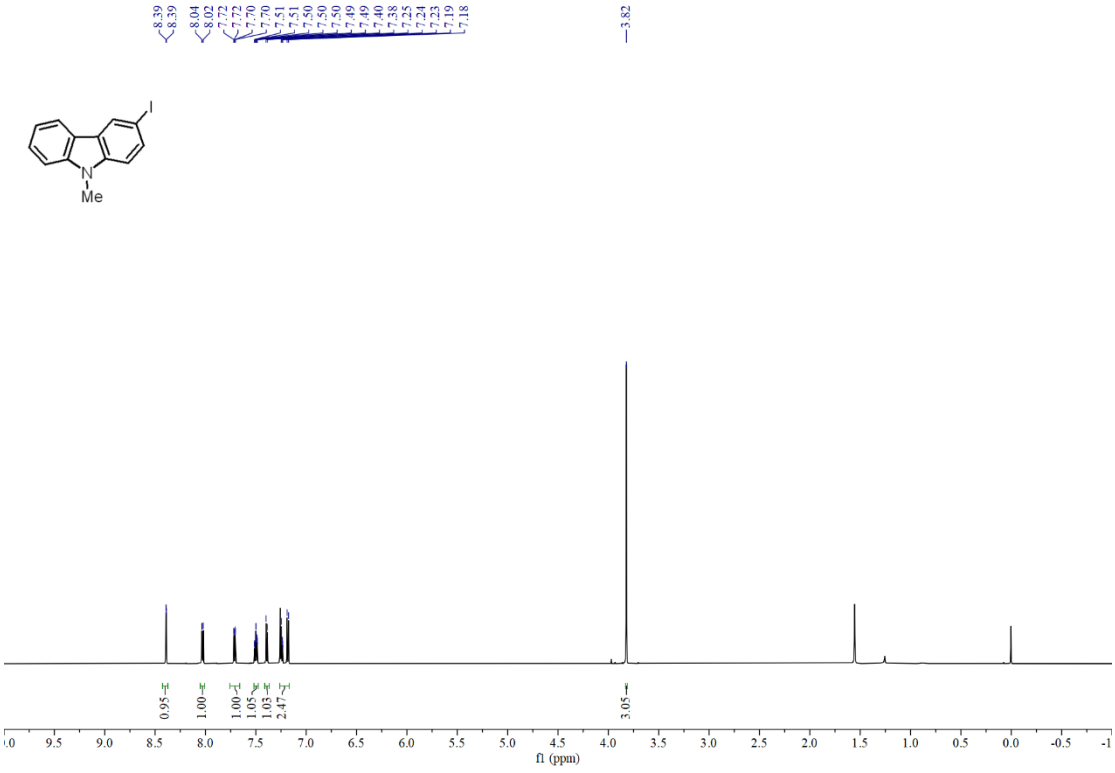
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 19



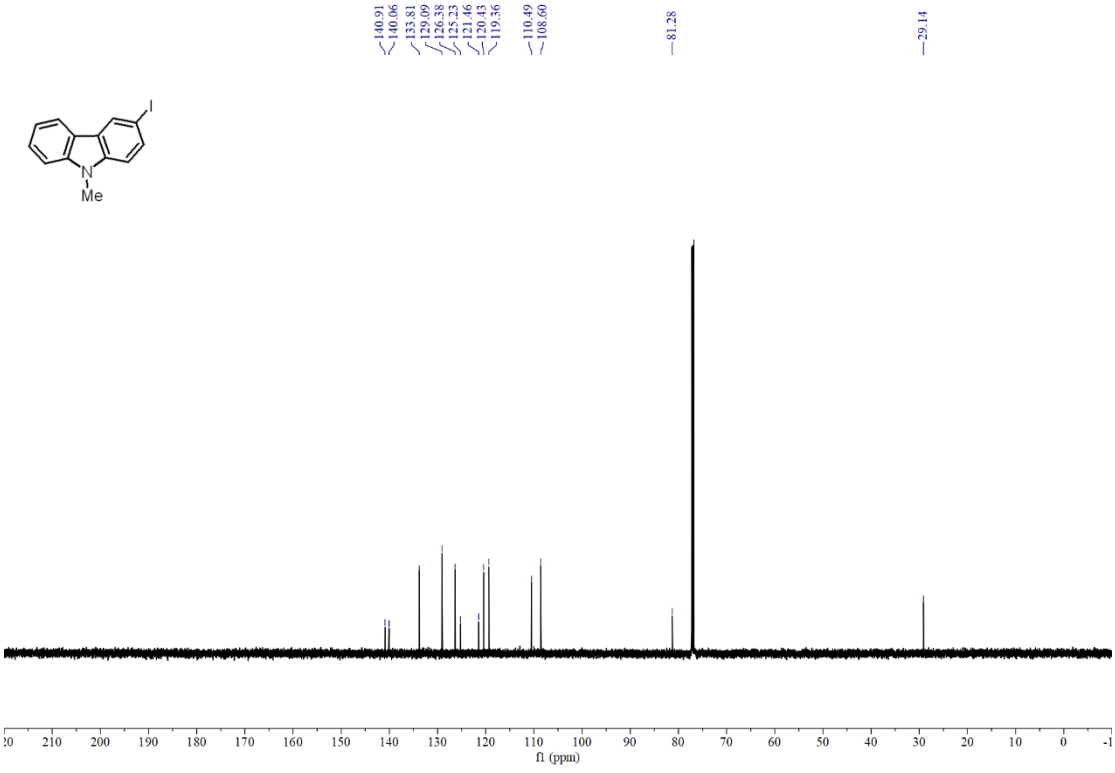
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 19



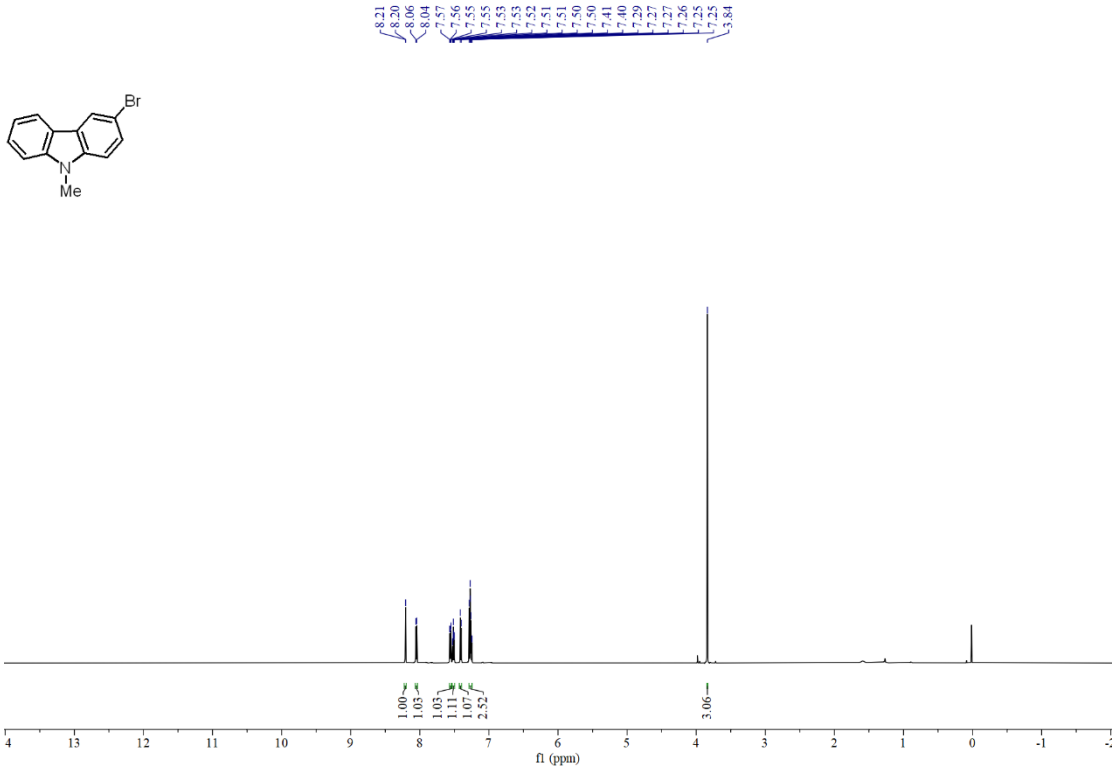
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 20



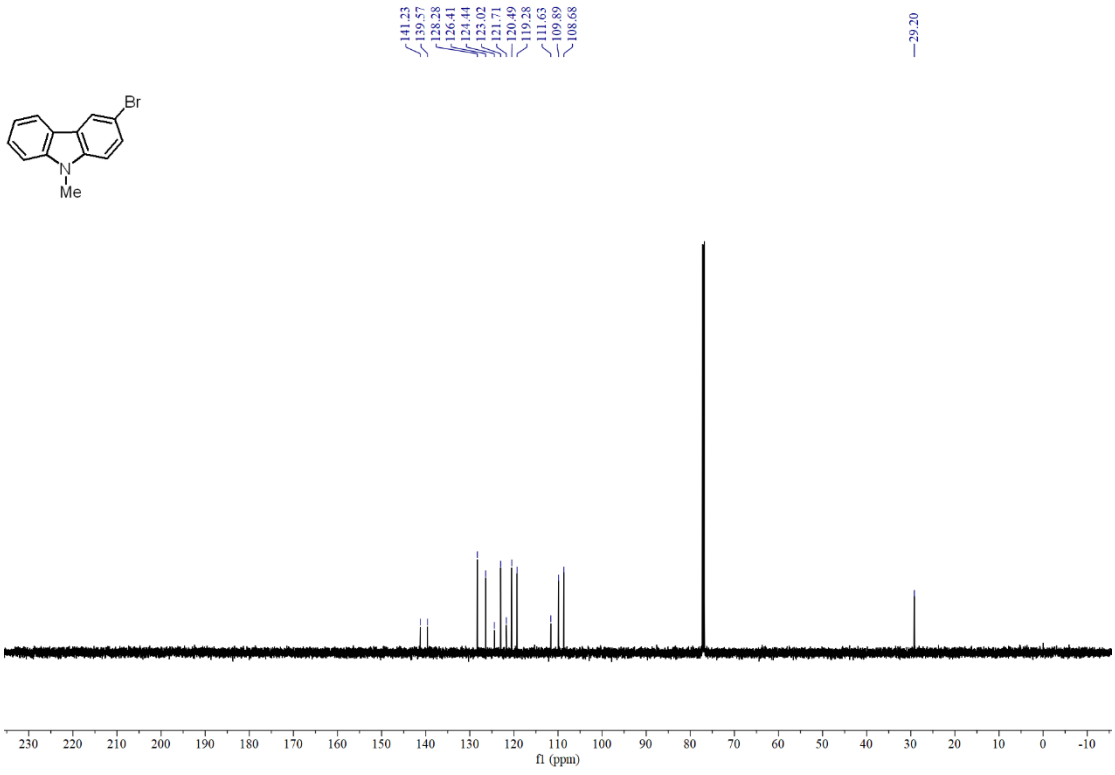
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 20



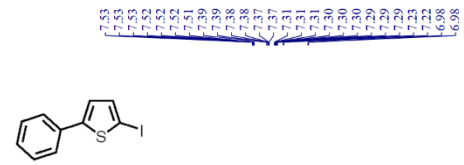
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 21

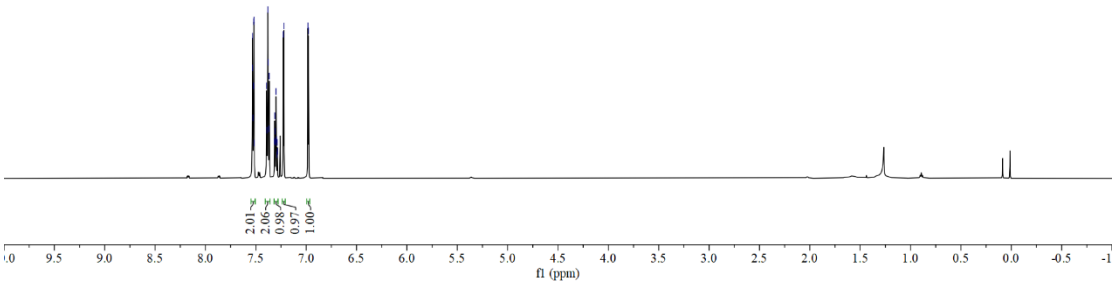


^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 21

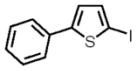


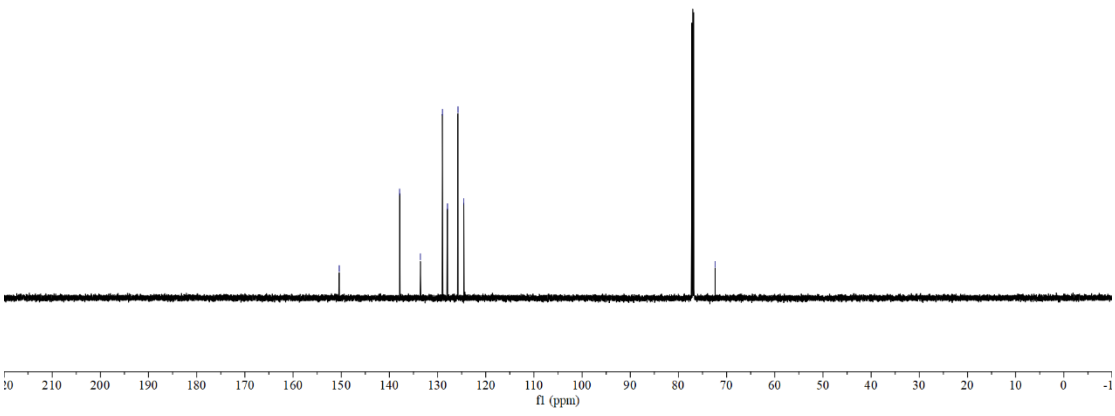
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 22



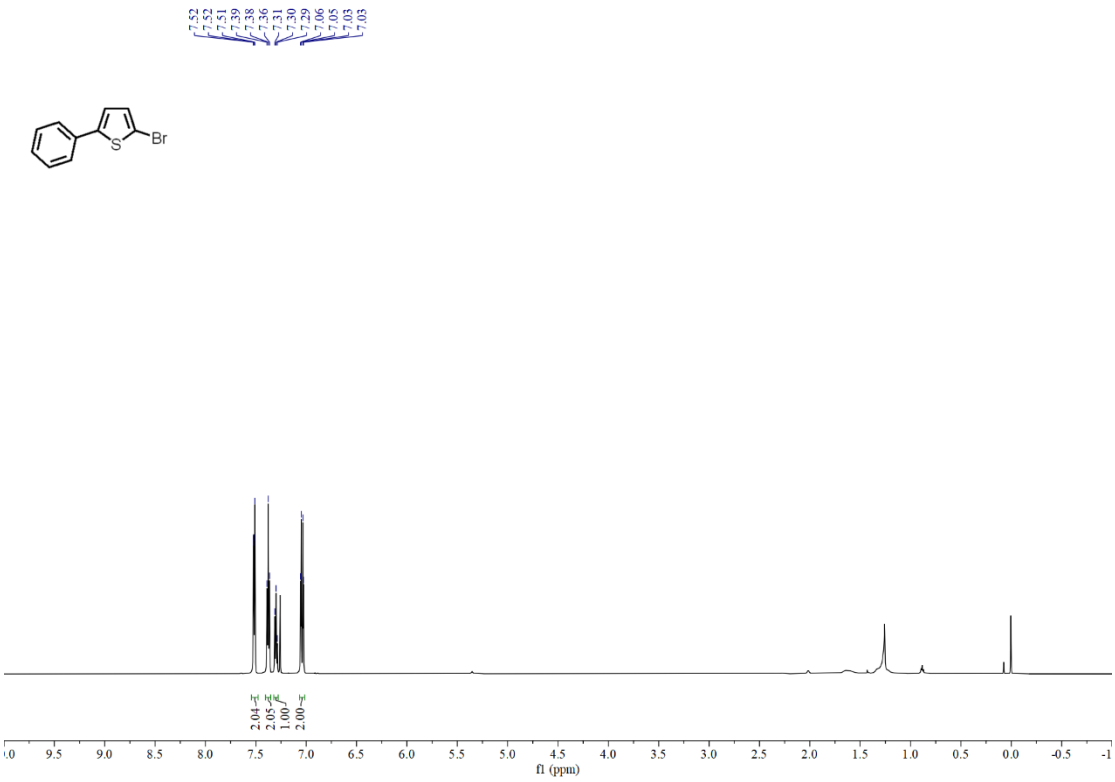


^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 22

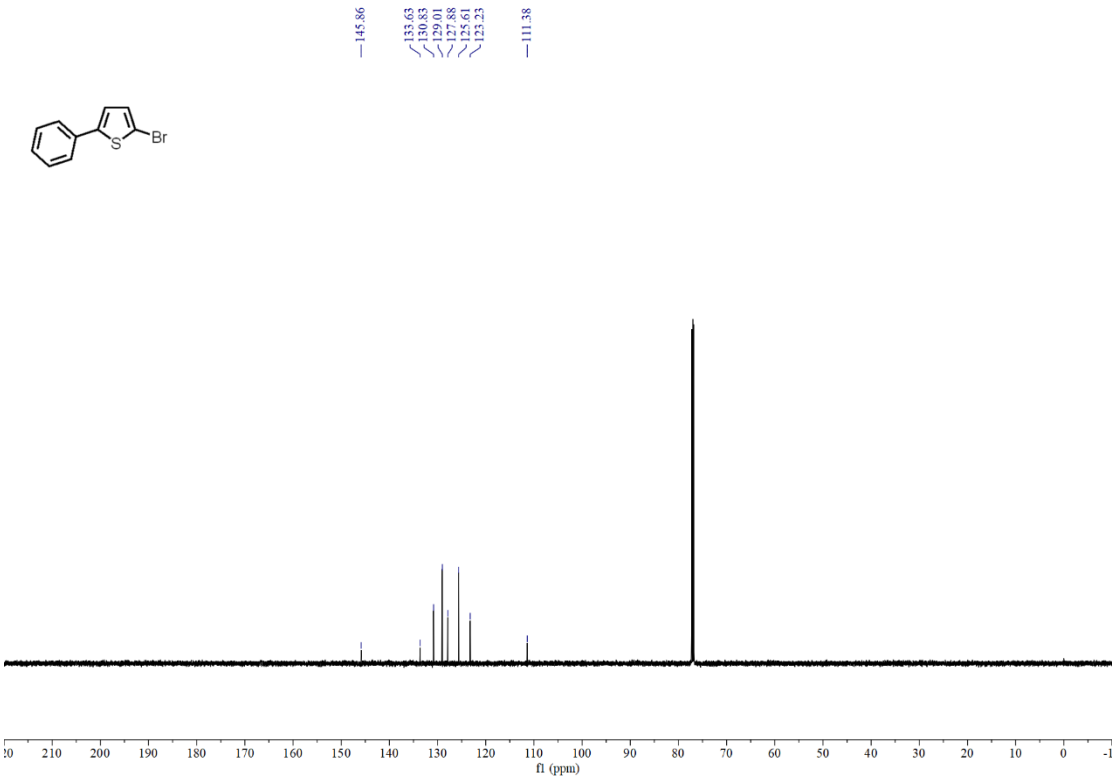




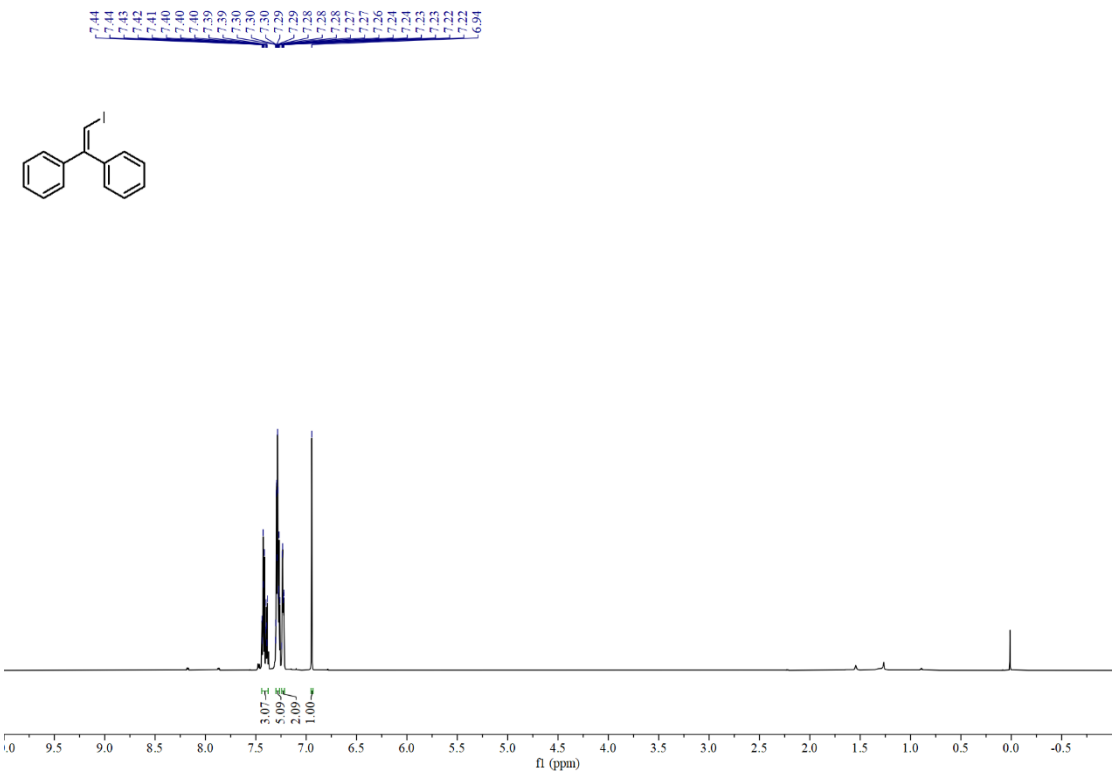
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 23



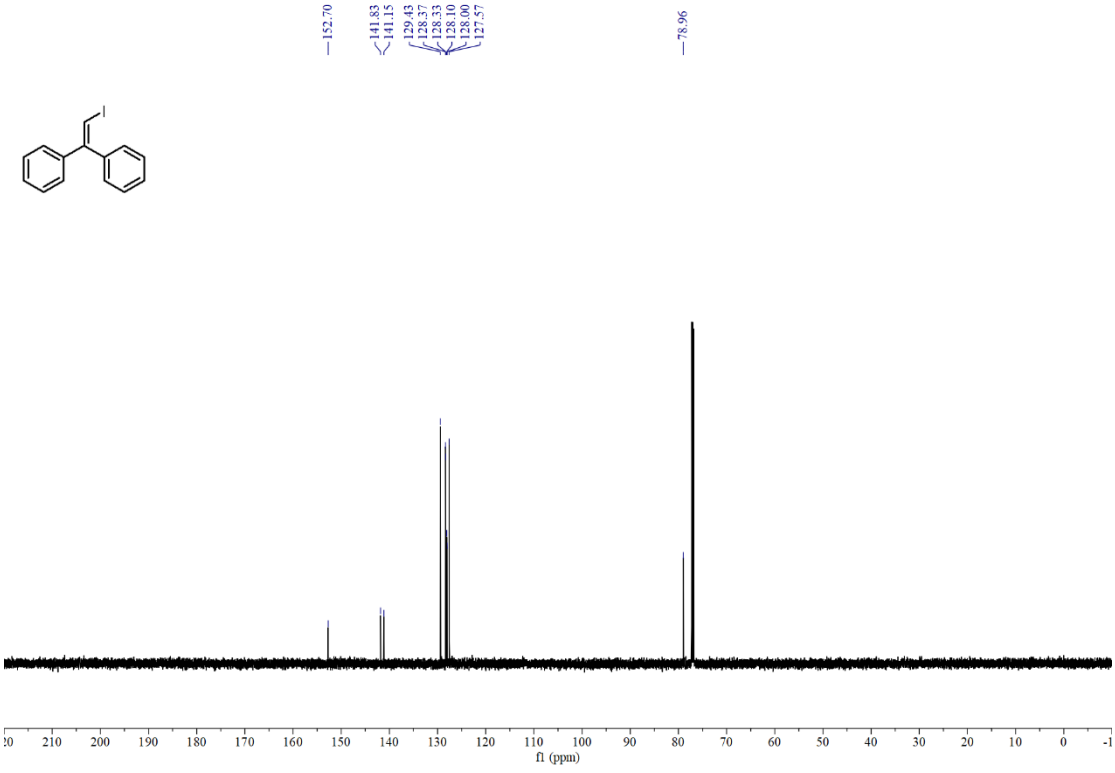
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 23



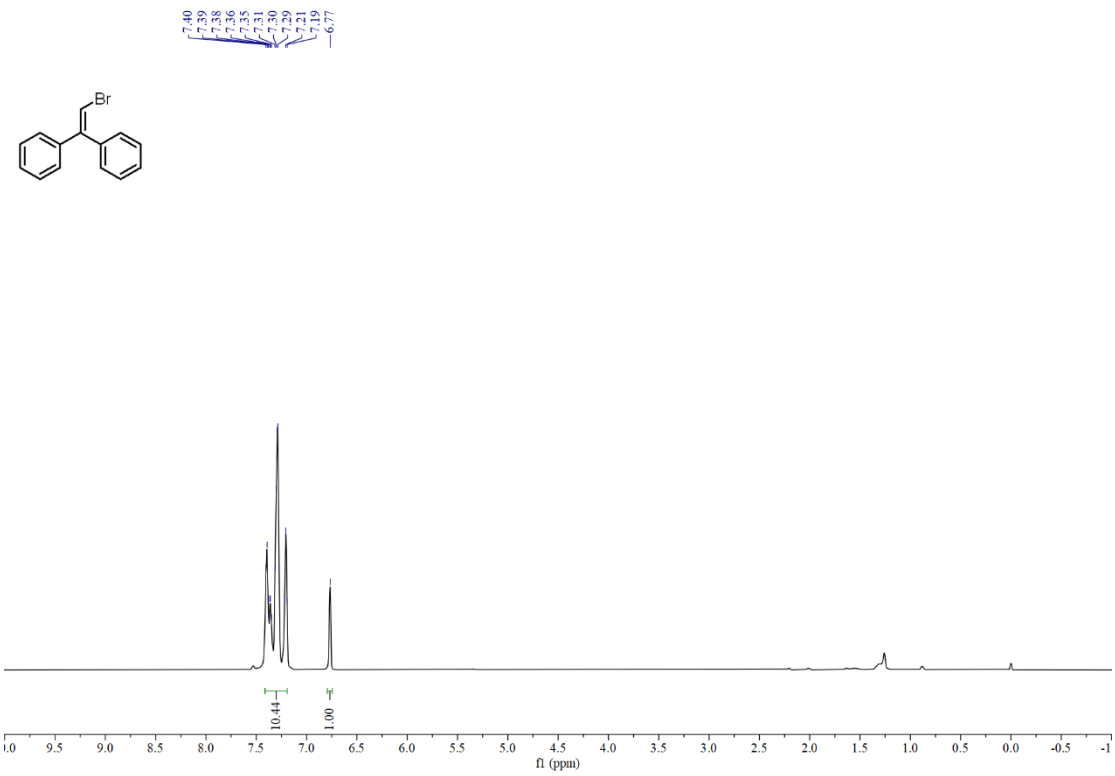
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 24



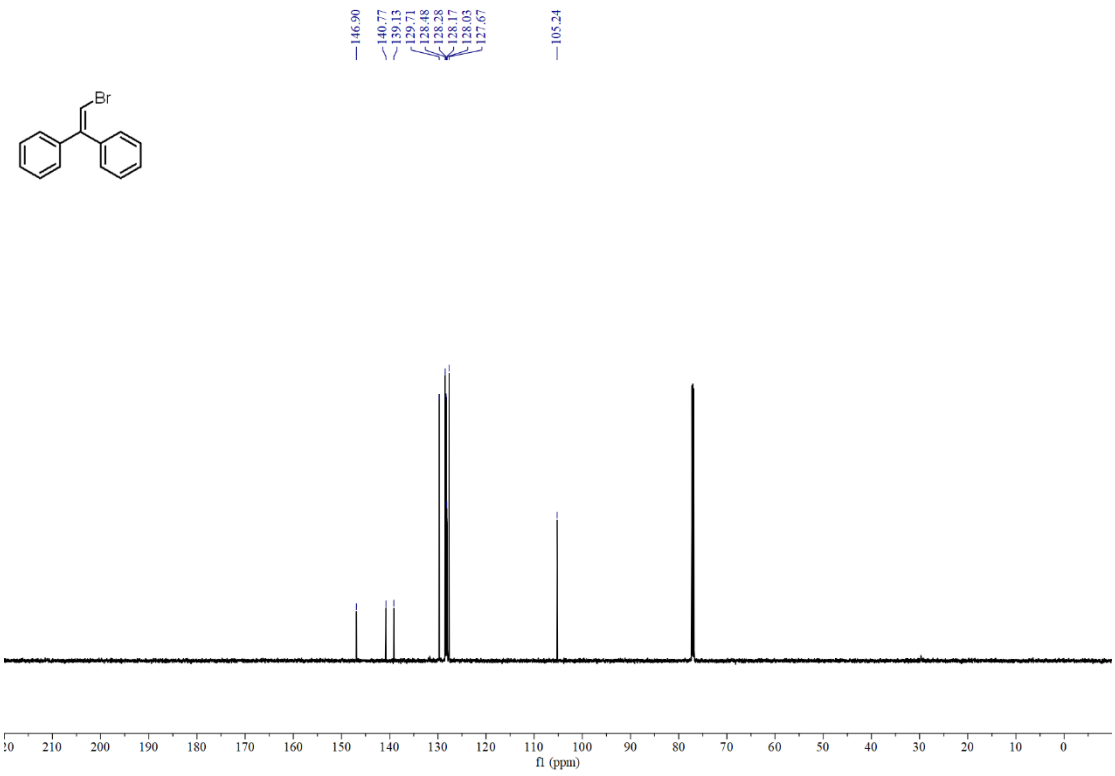
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 24



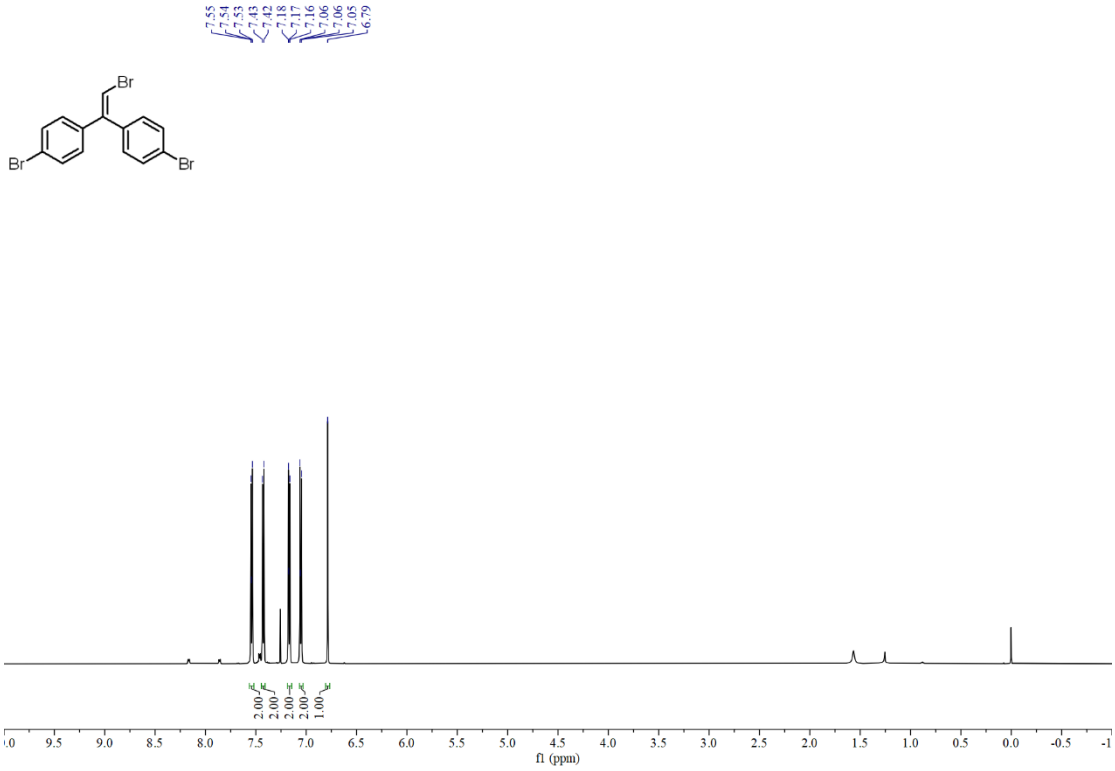
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 25



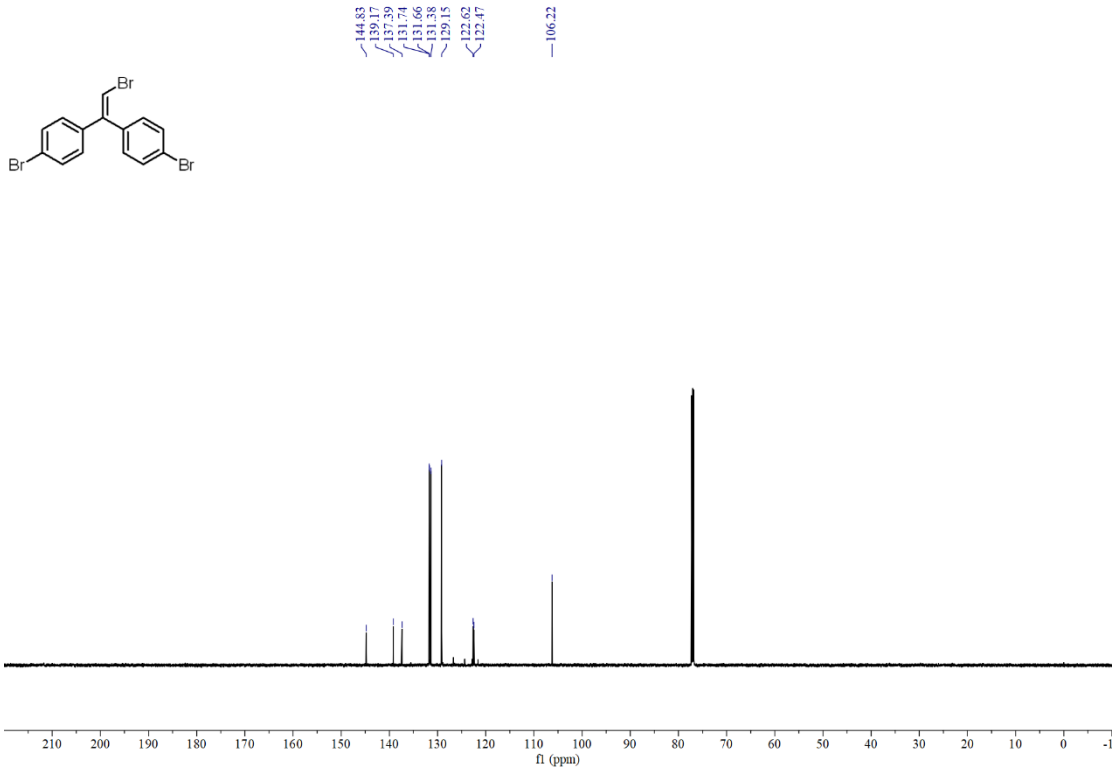
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 25



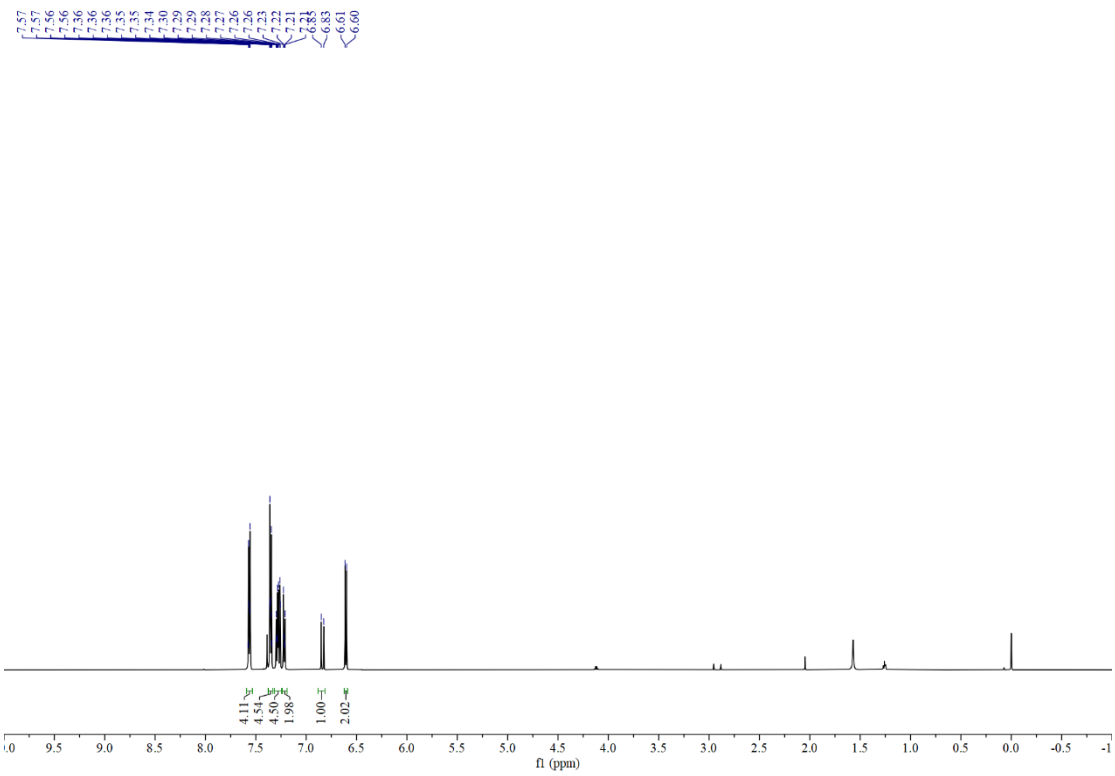
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 26



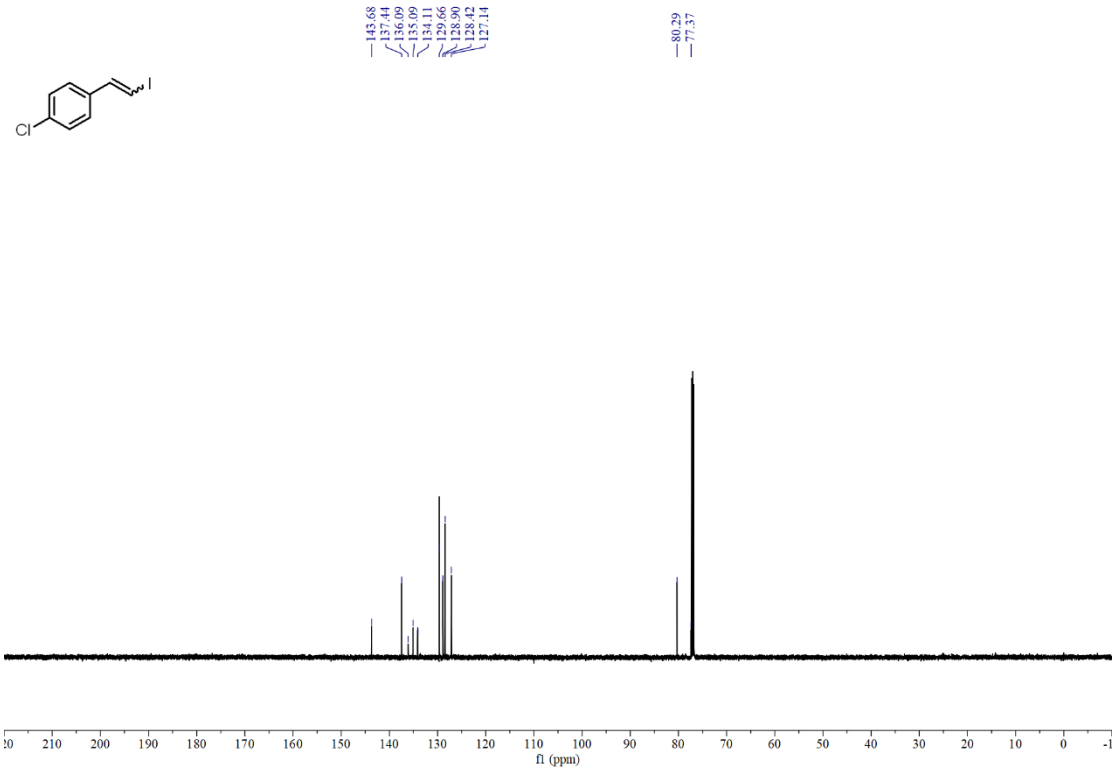
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 26



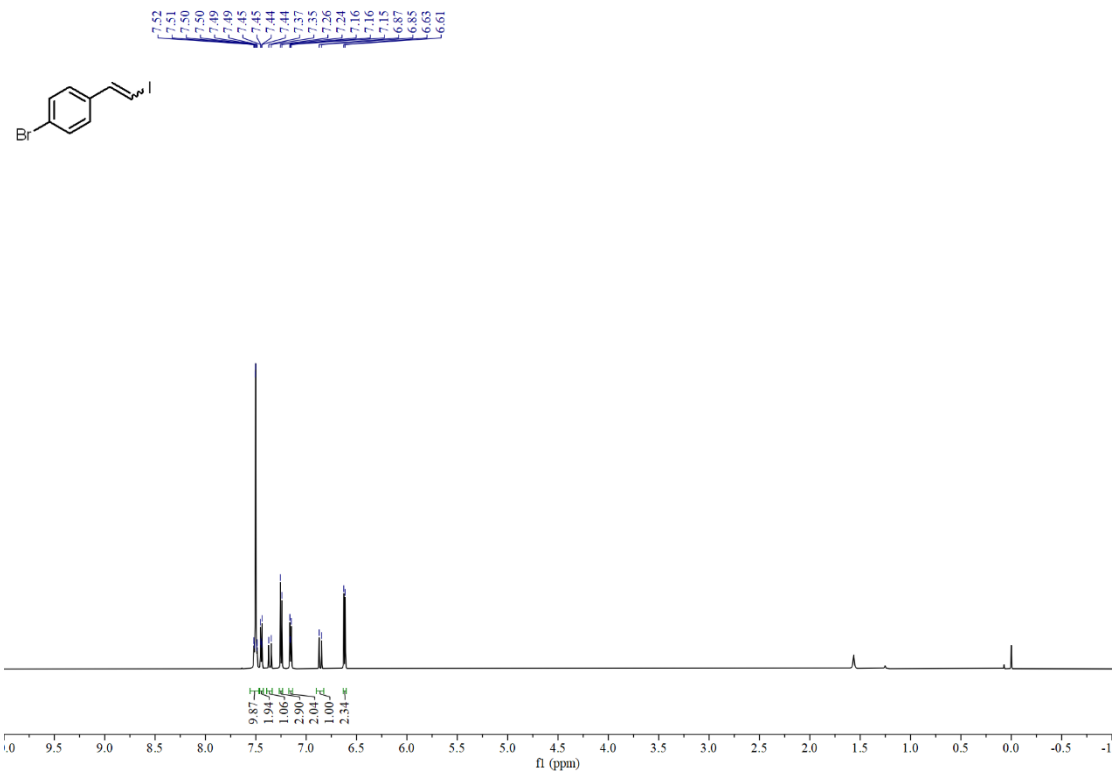
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 27



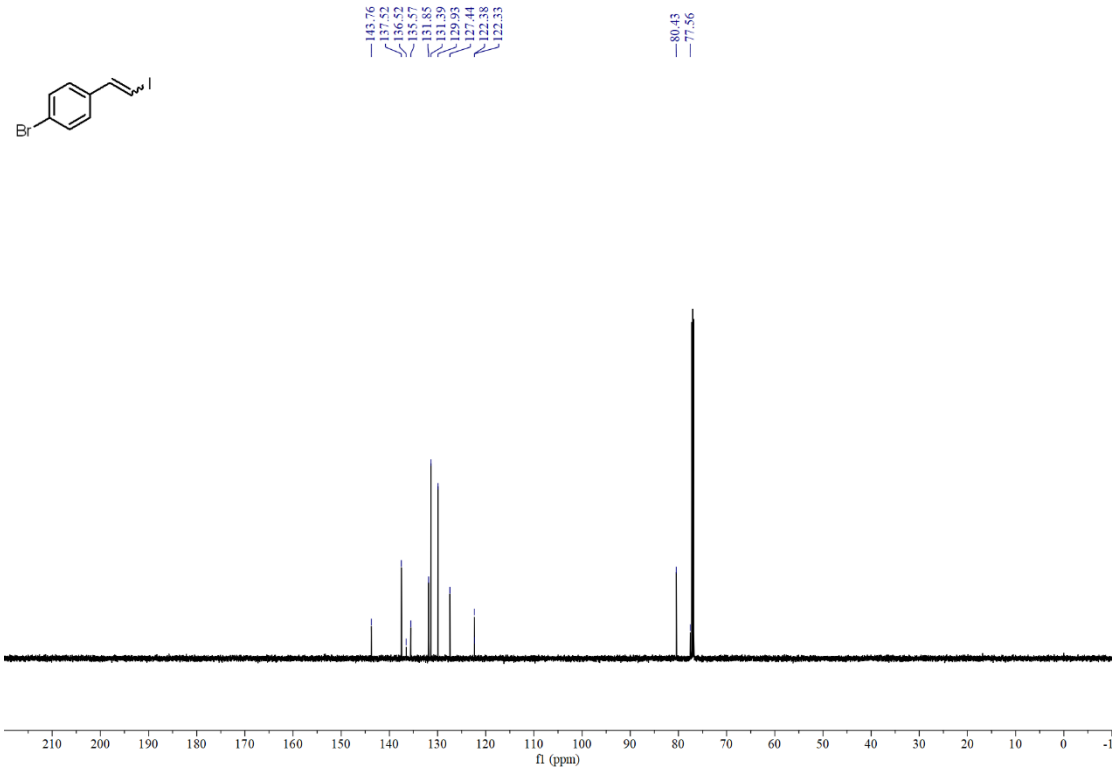
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 27



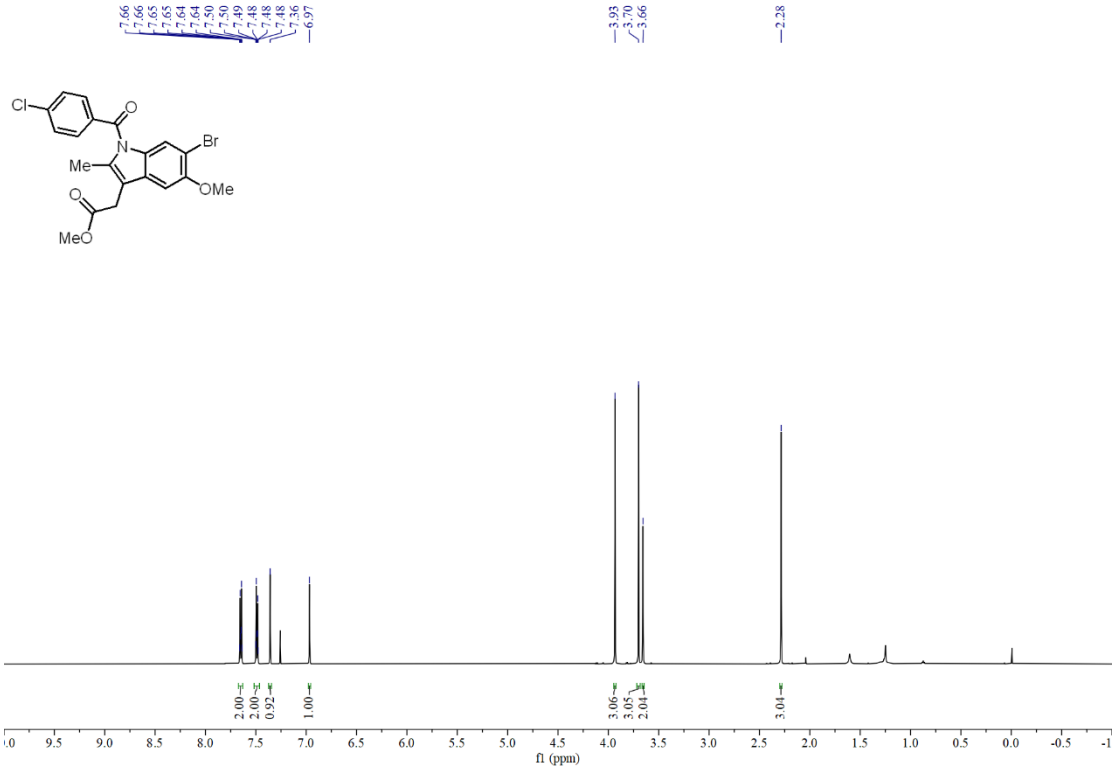
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 28



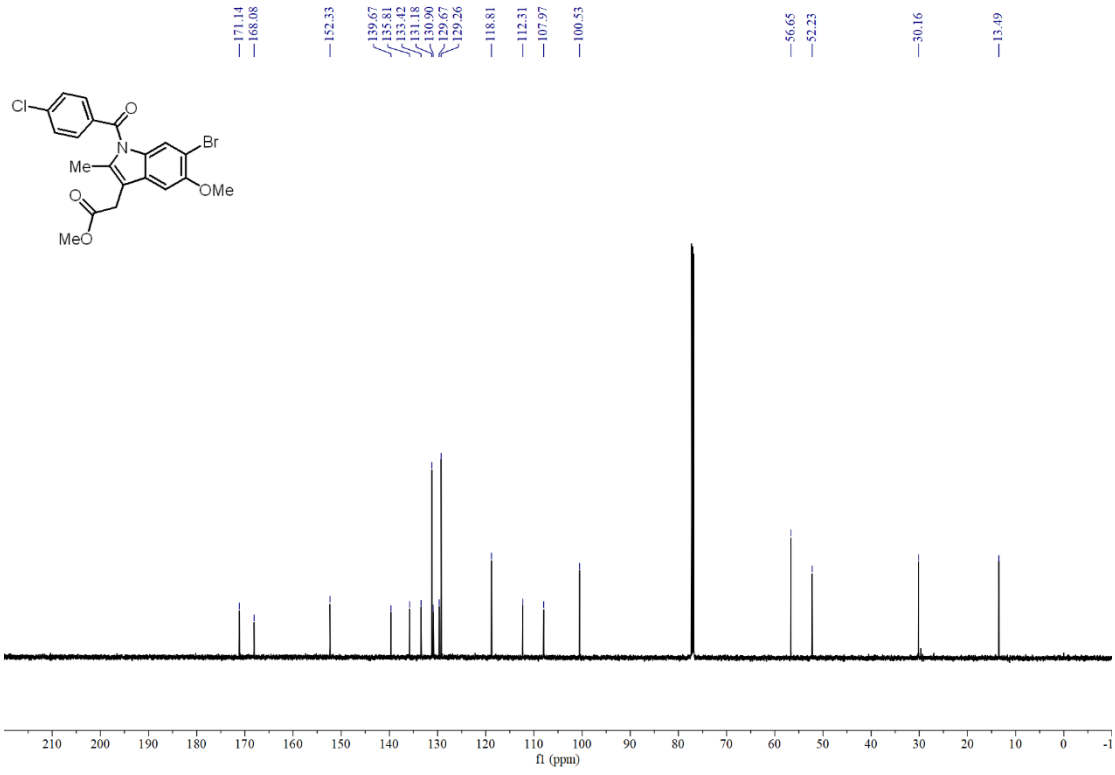
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 28



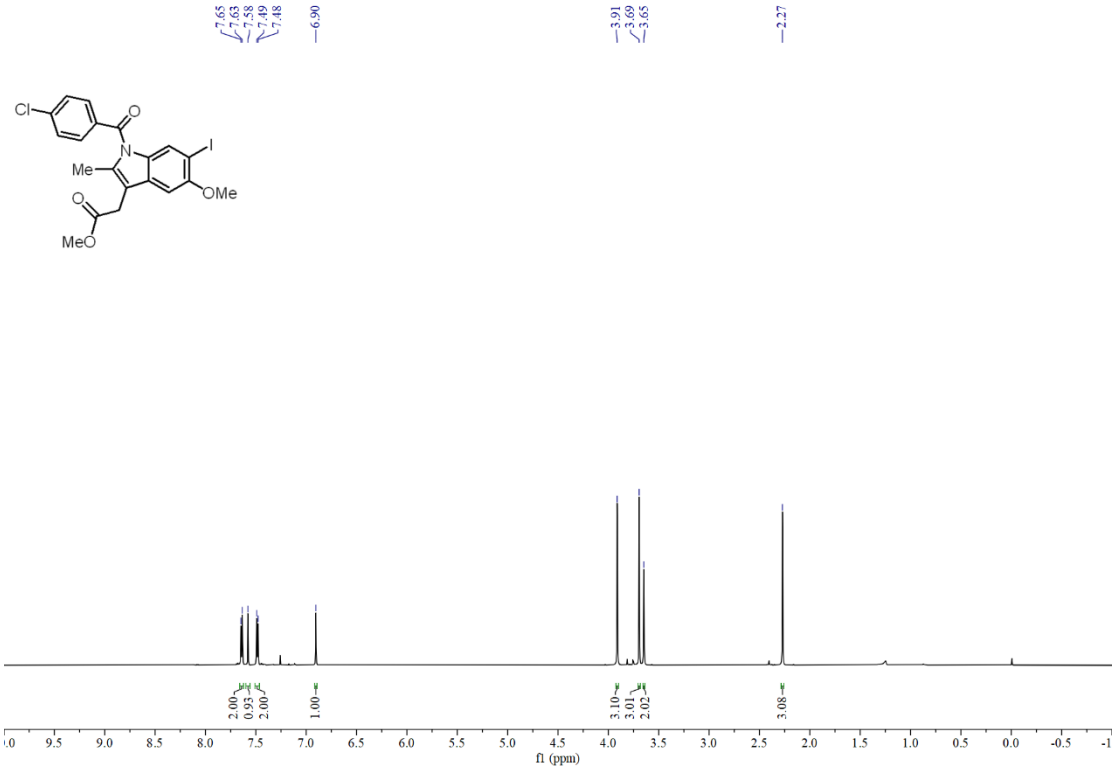
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 29



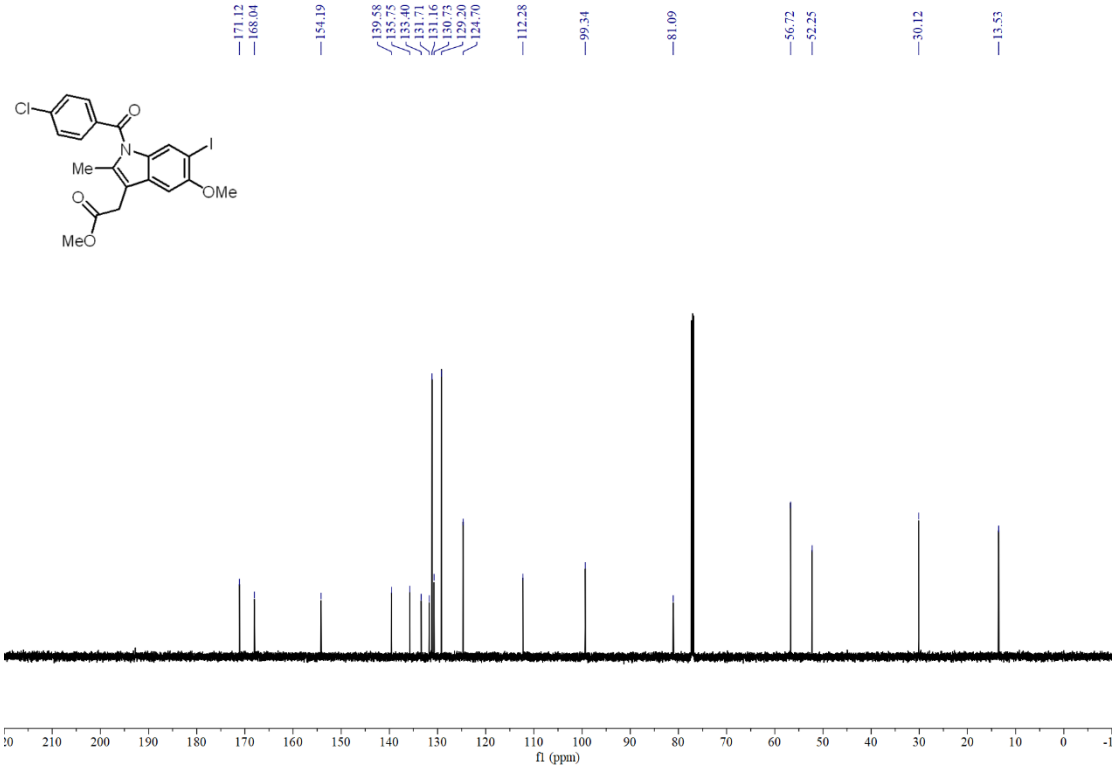
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 29



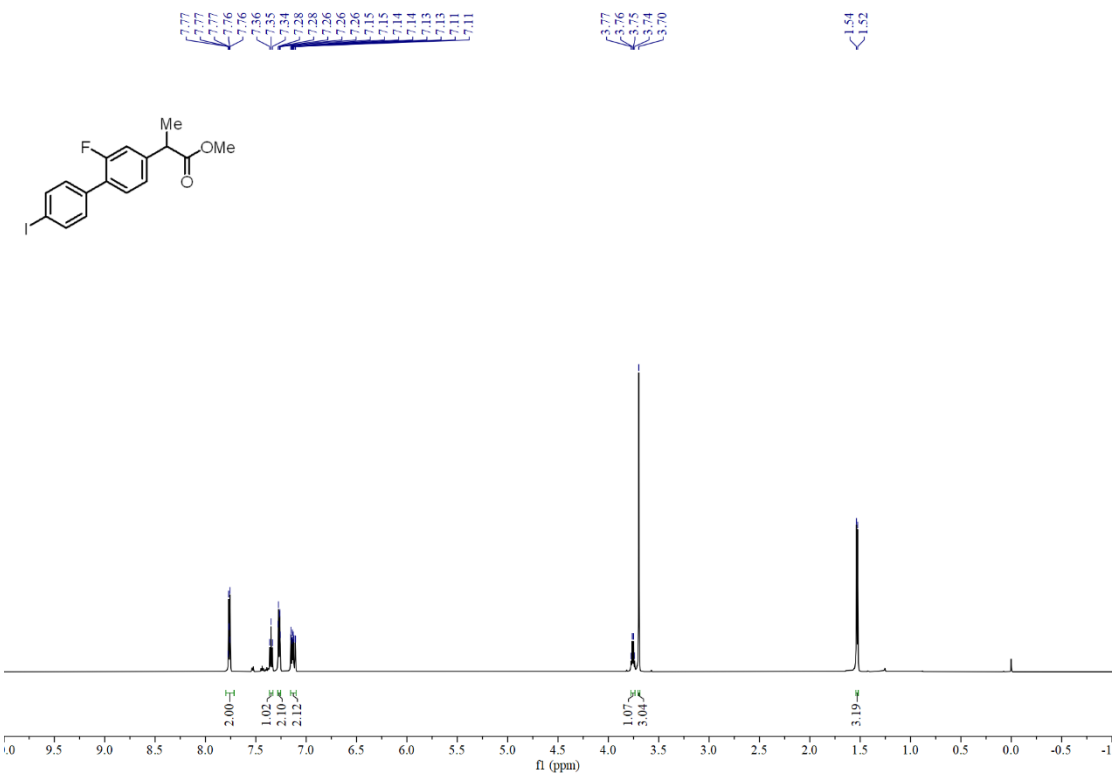
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 30



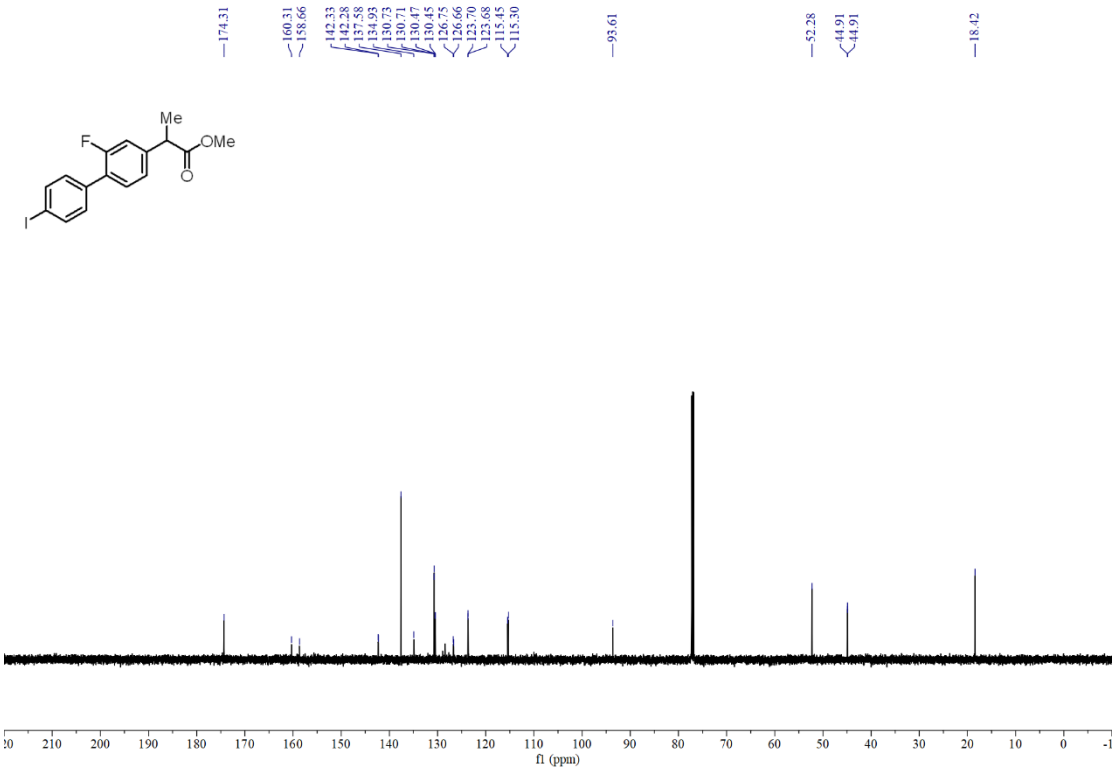
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 30



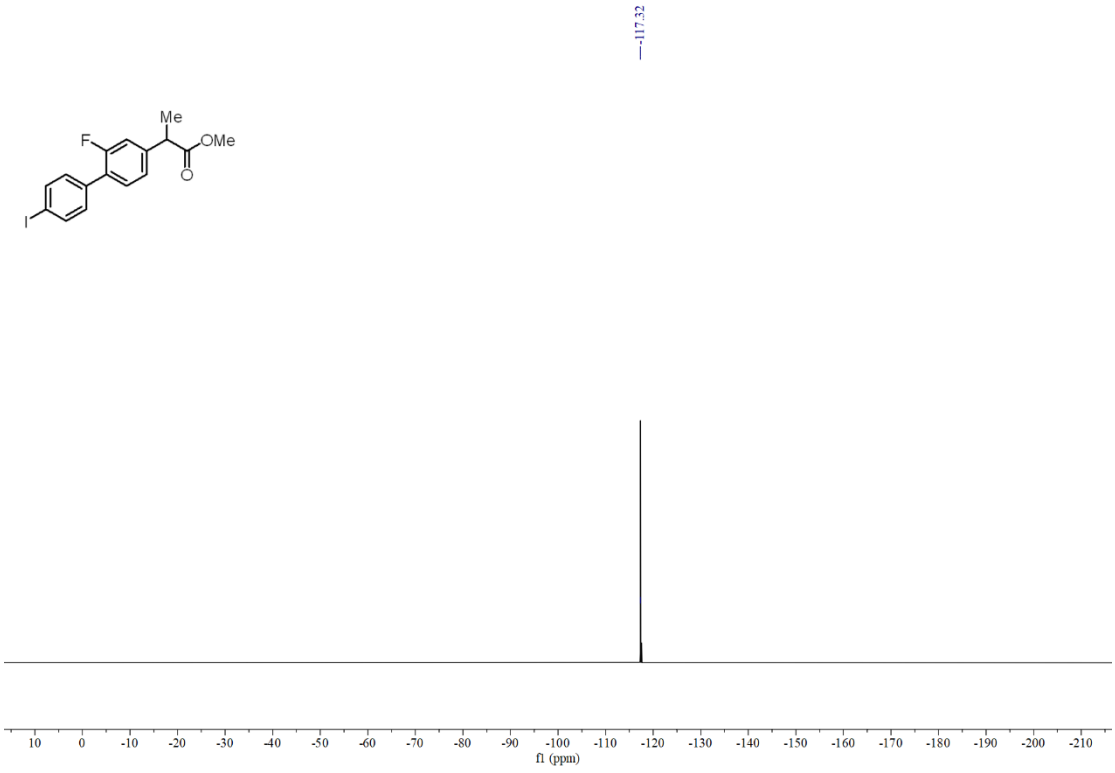
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 31



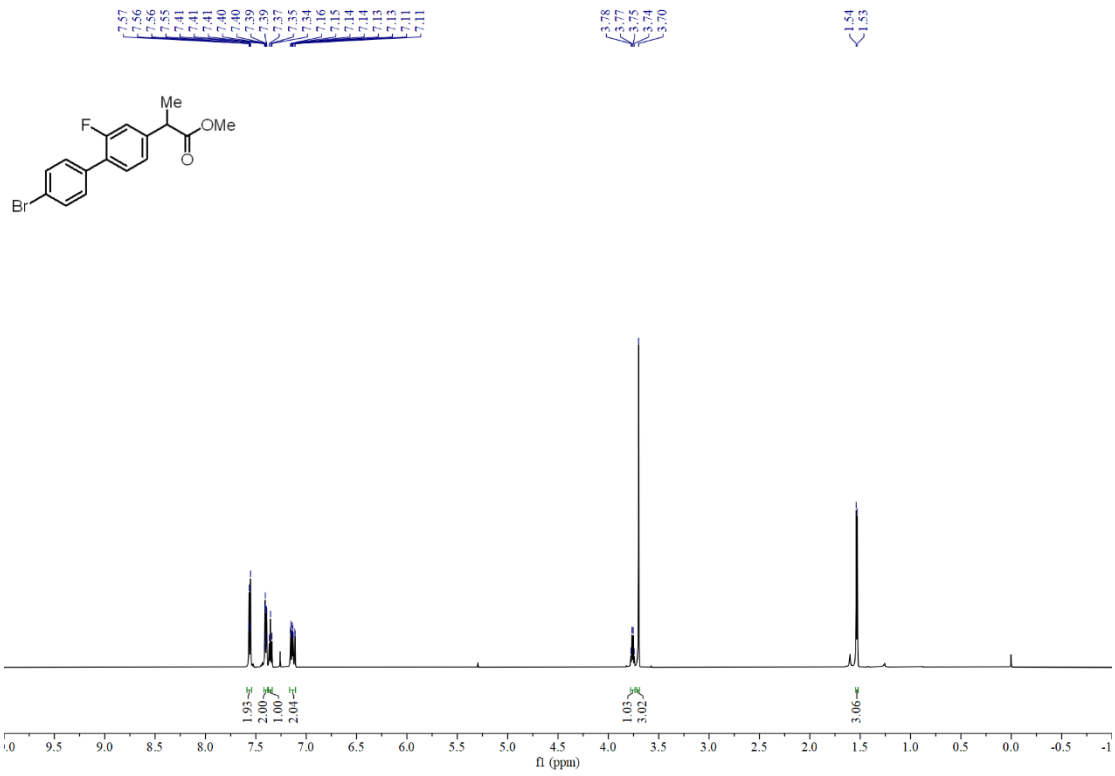
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 31



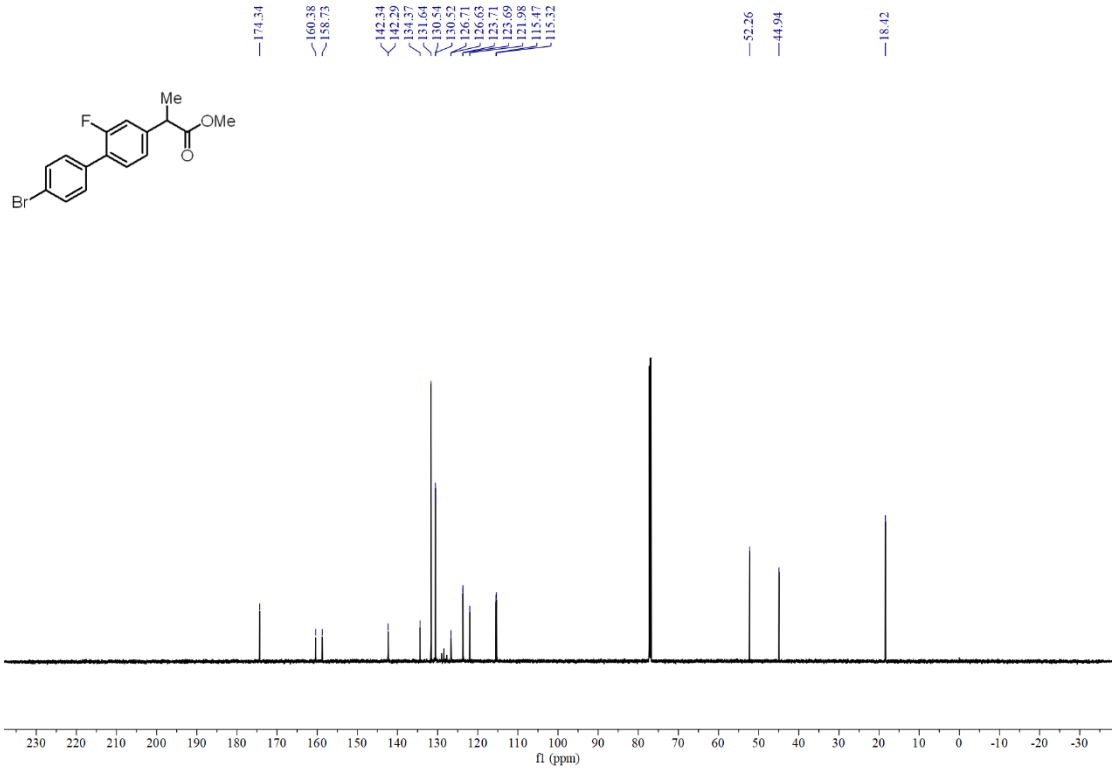
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 31



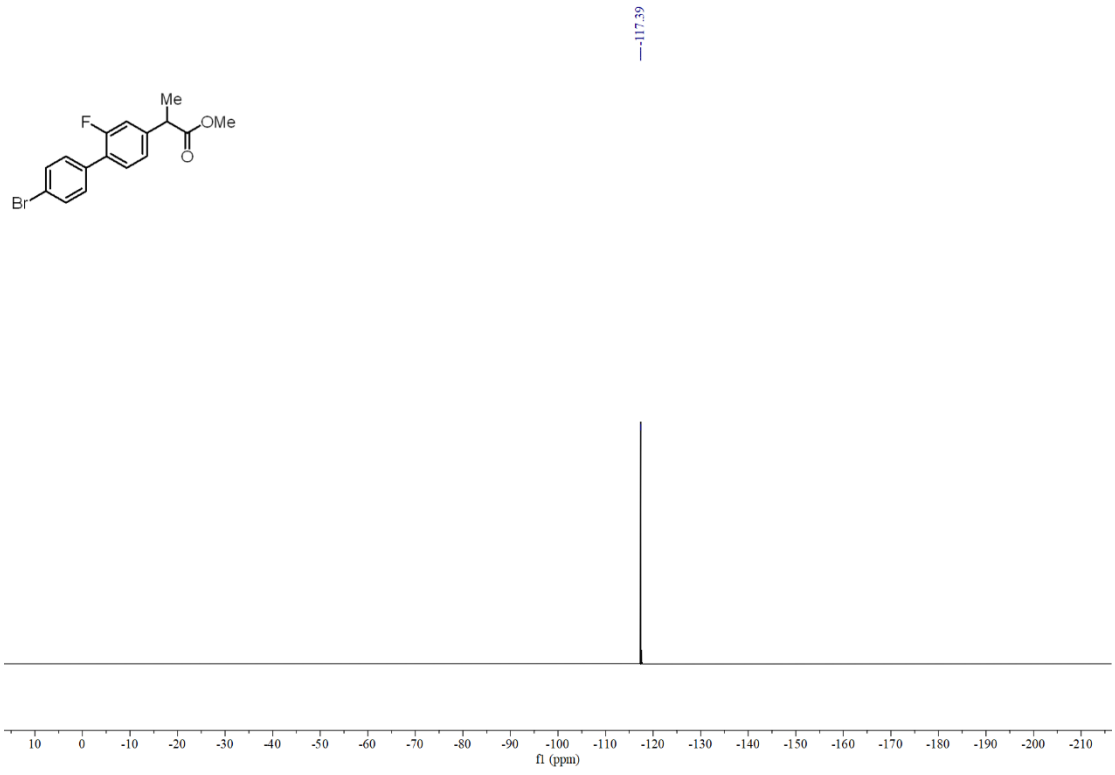
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 32



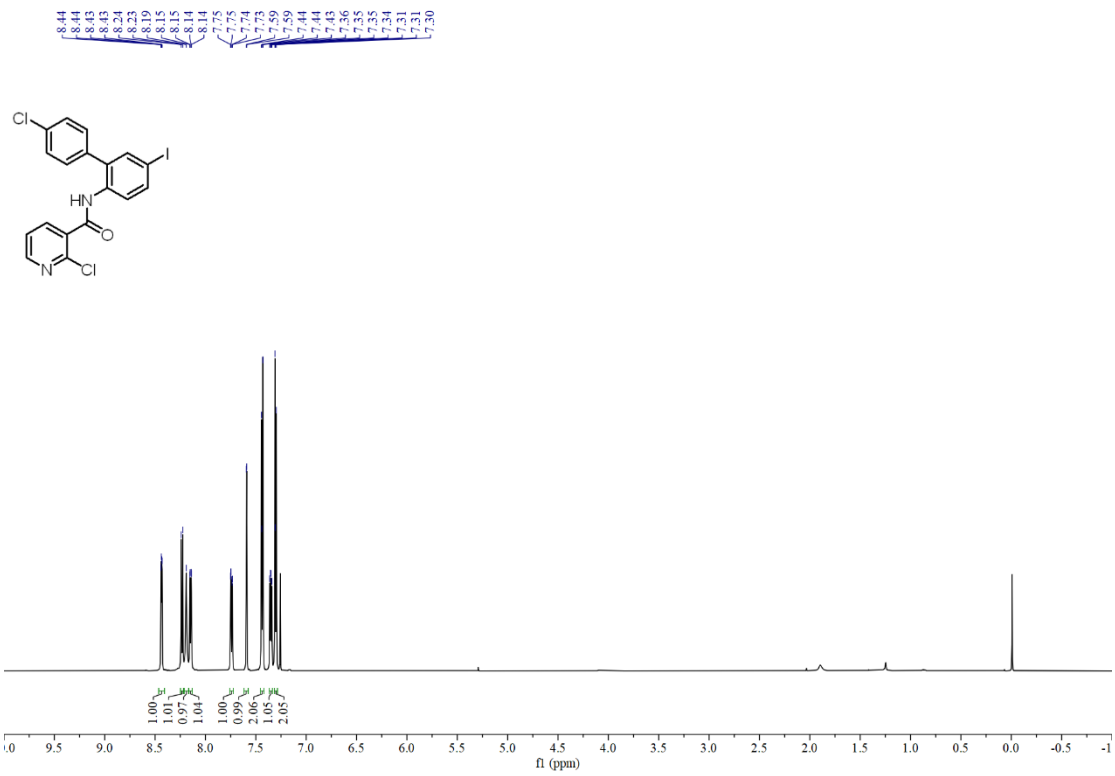
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 32



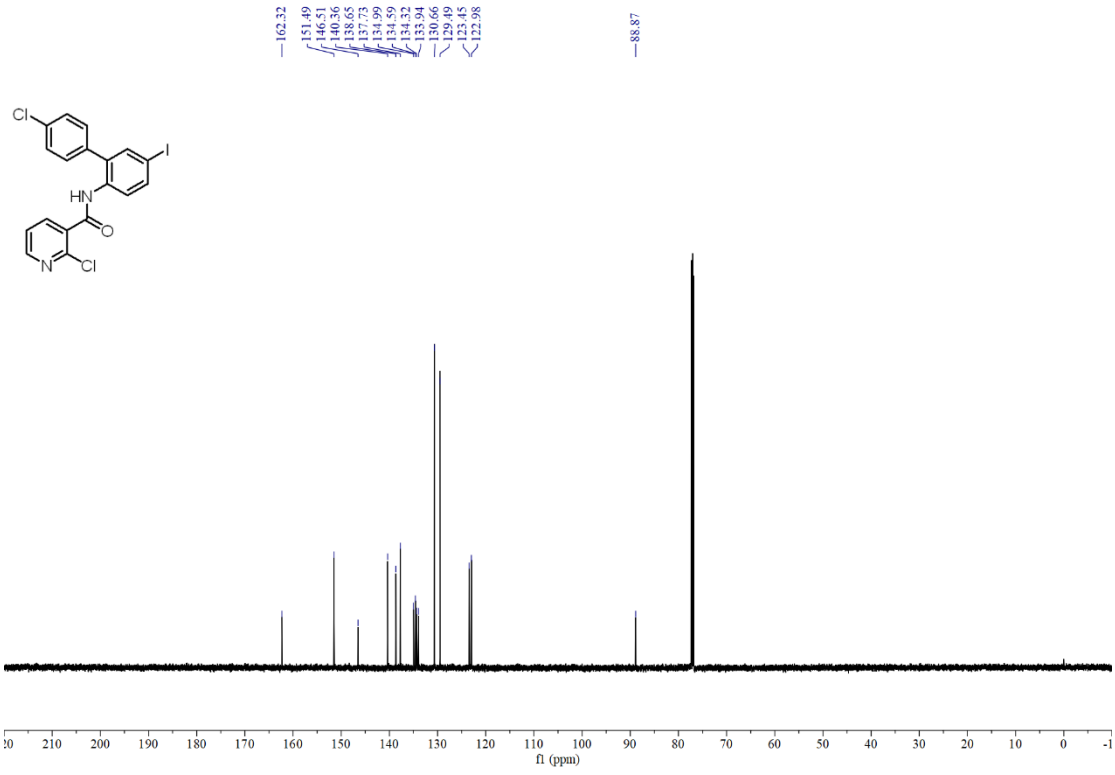
^{19}F NMR (565 MHz, Chloroform-d) spectrum of compound 32



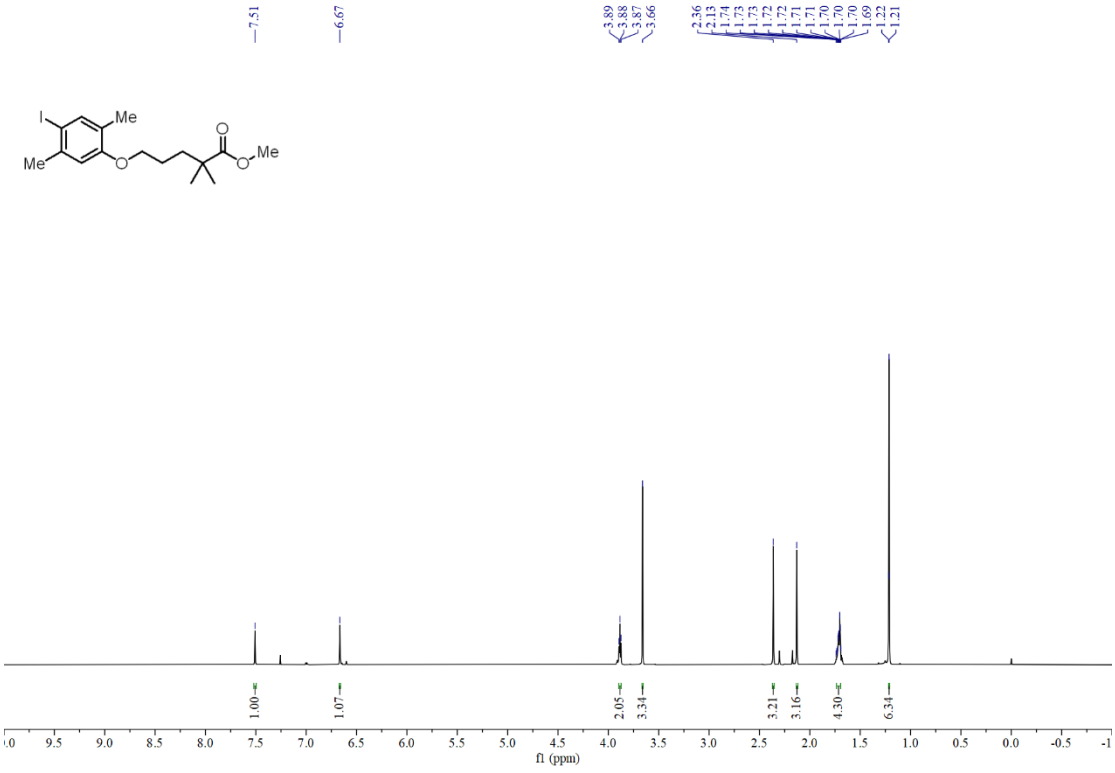
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 33



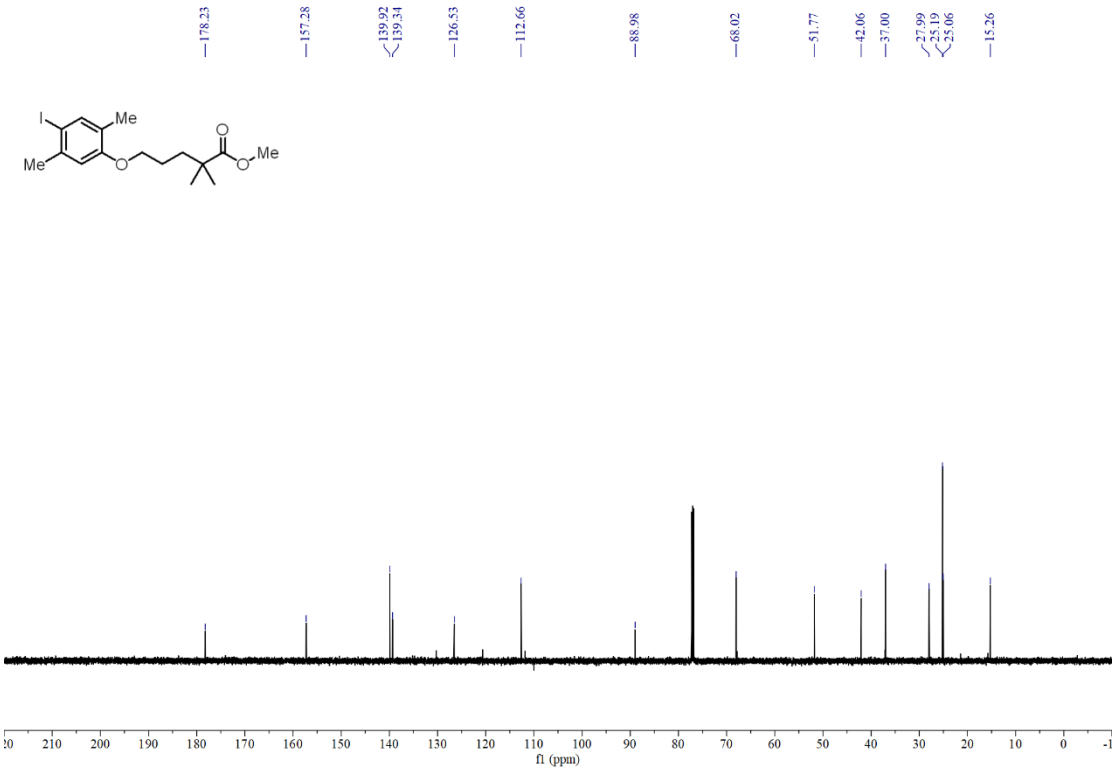
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 33



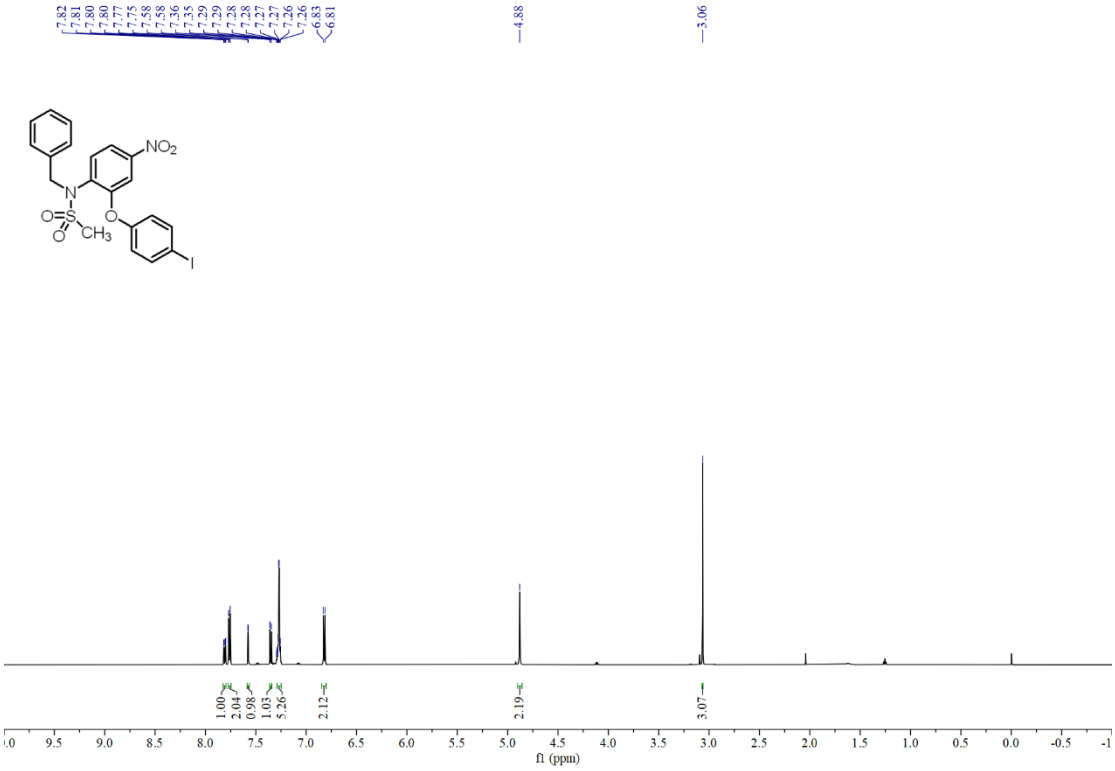
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 34



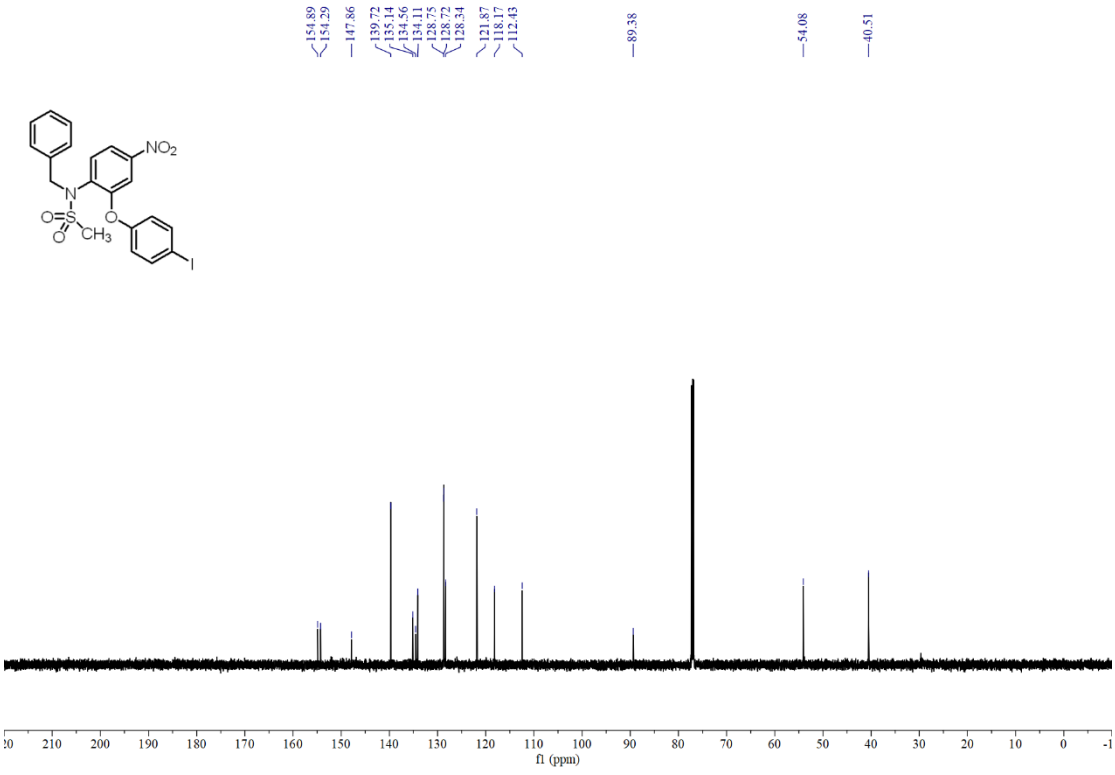
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 34



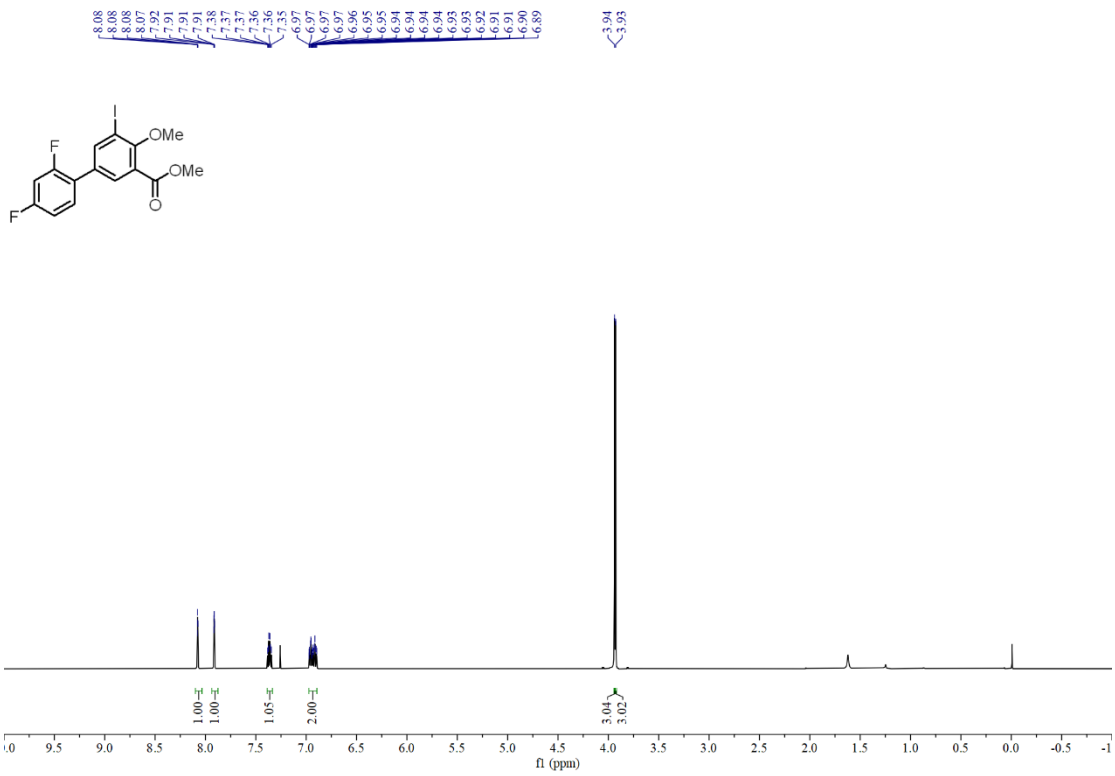
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 35



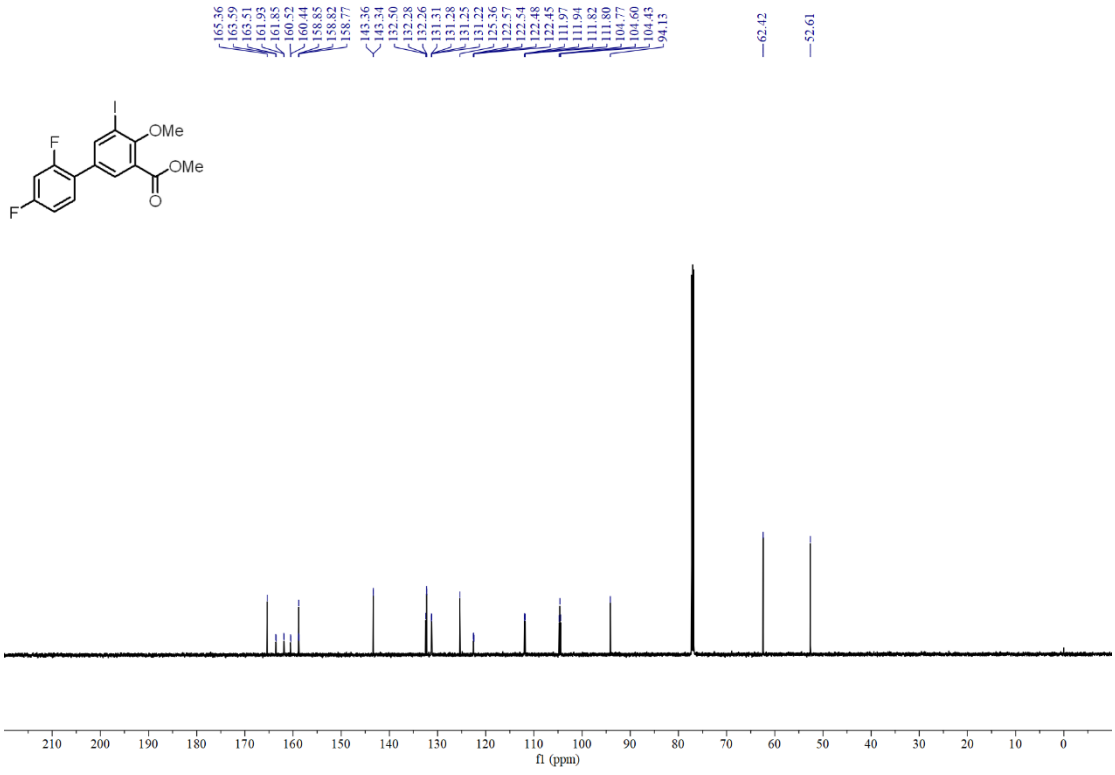
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 35



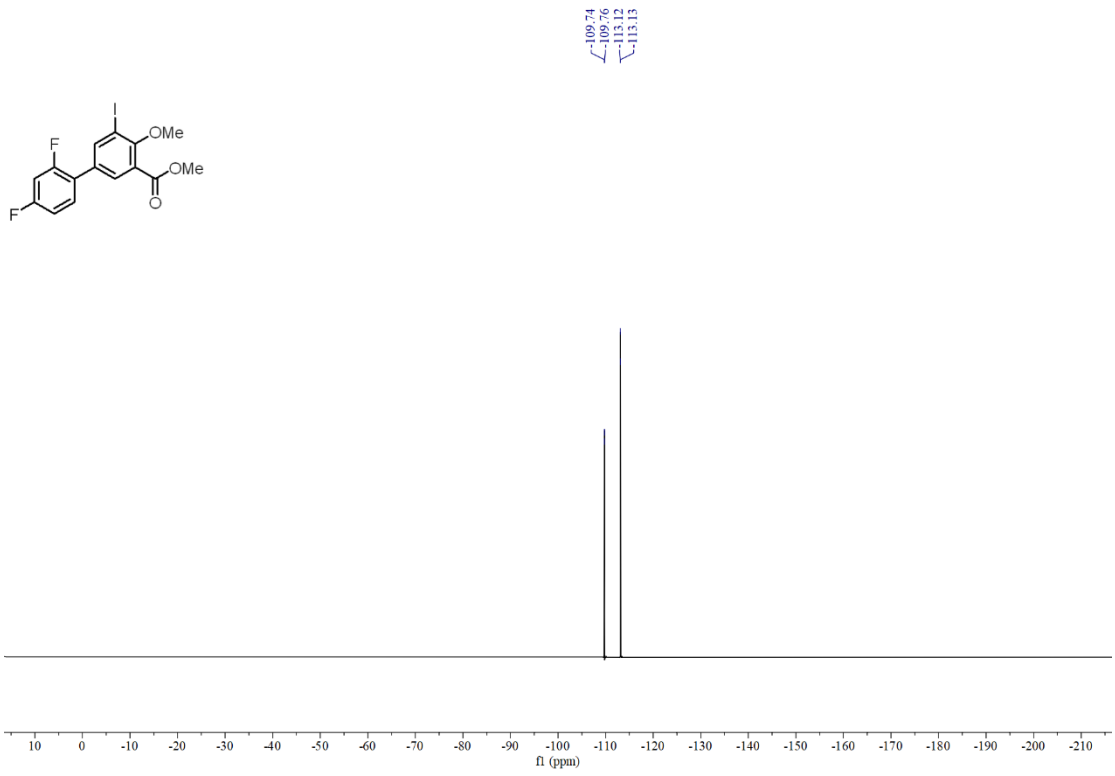
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 36



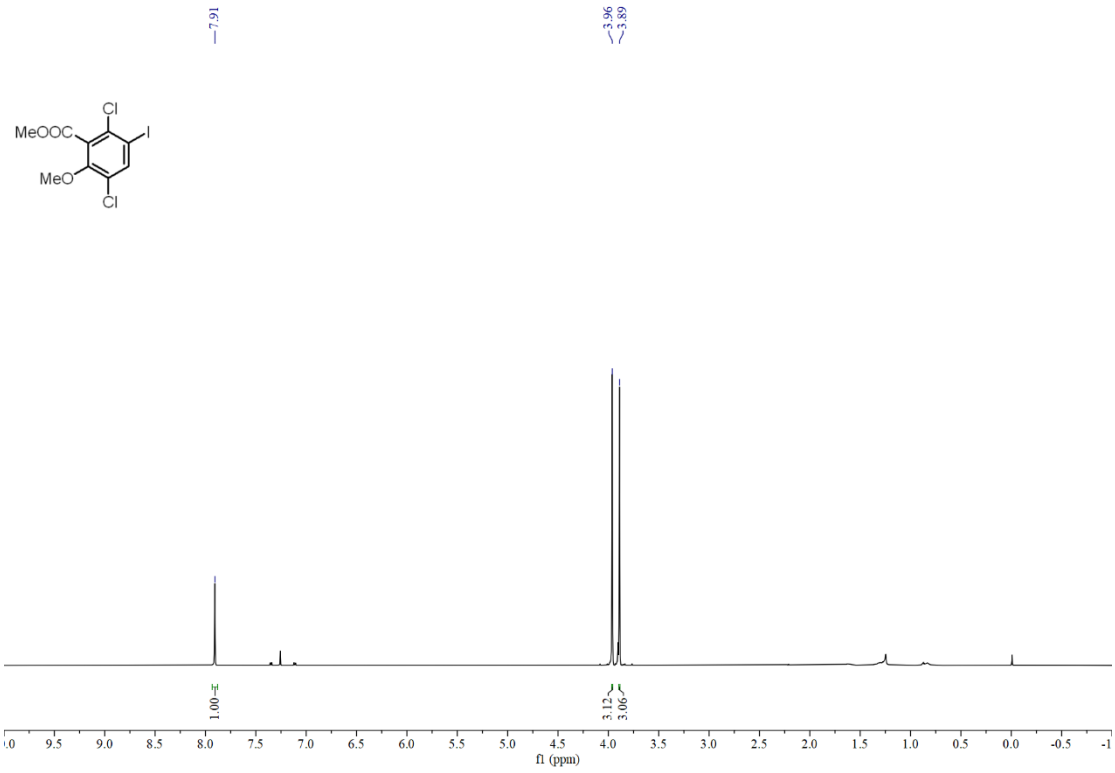
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 36



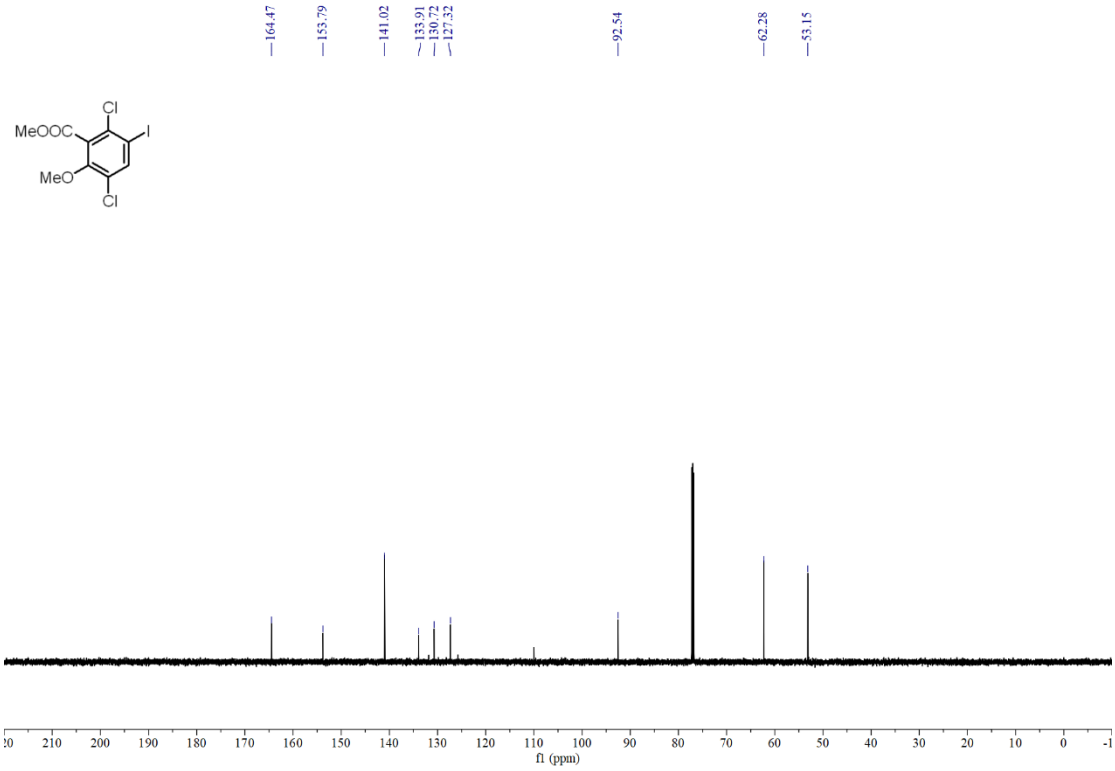
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 36



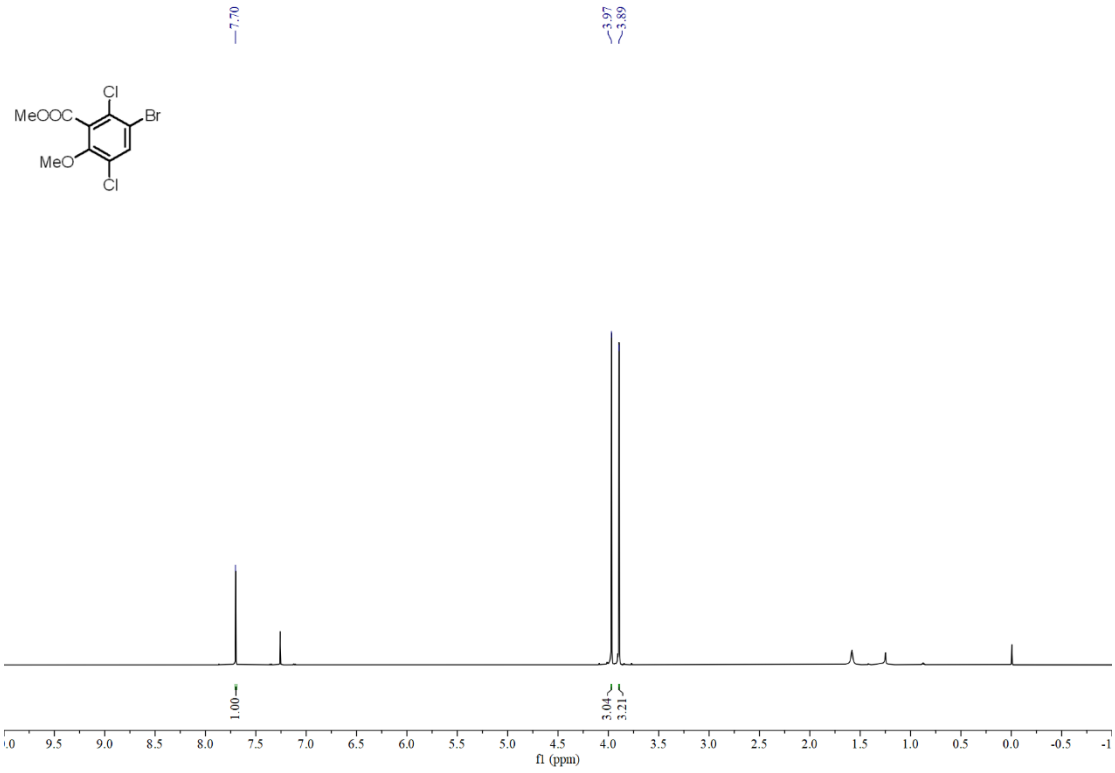
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 37



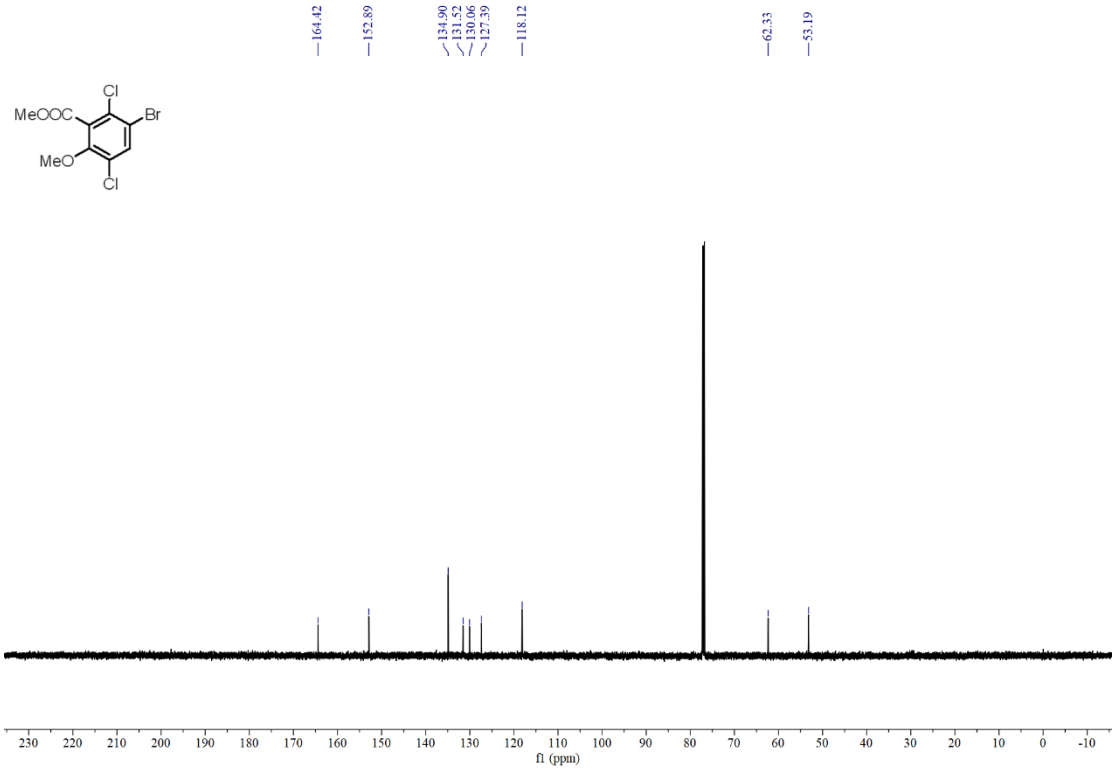
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 37



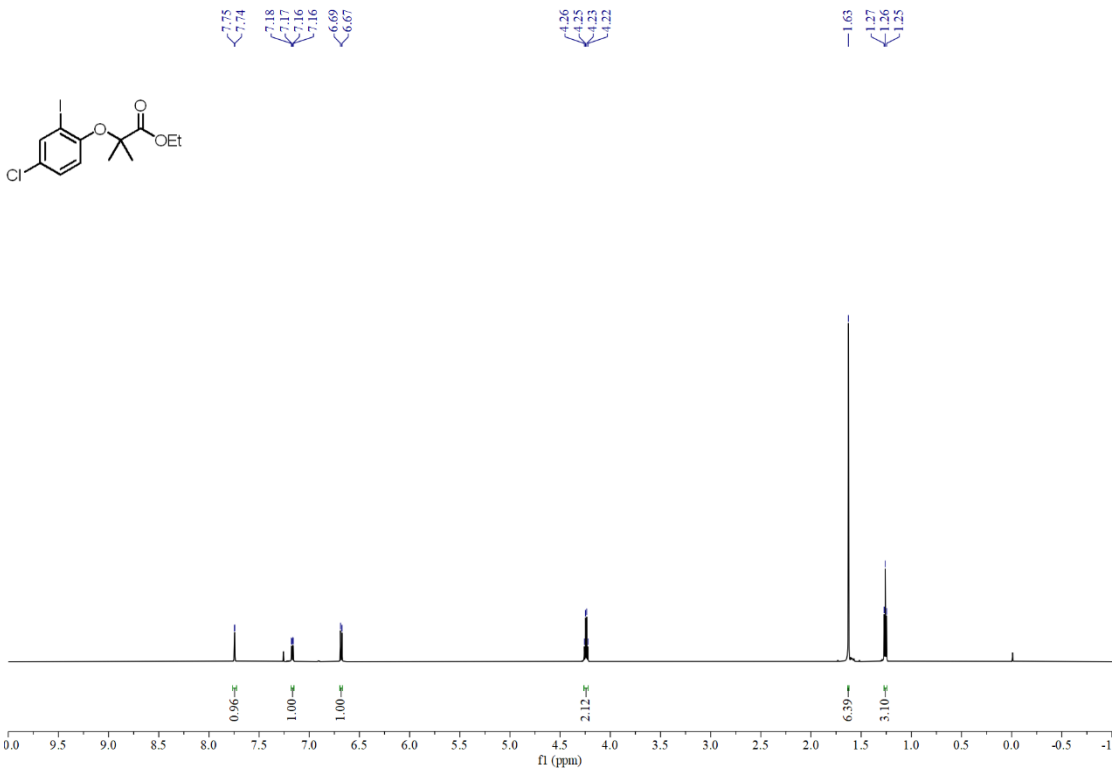
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 38



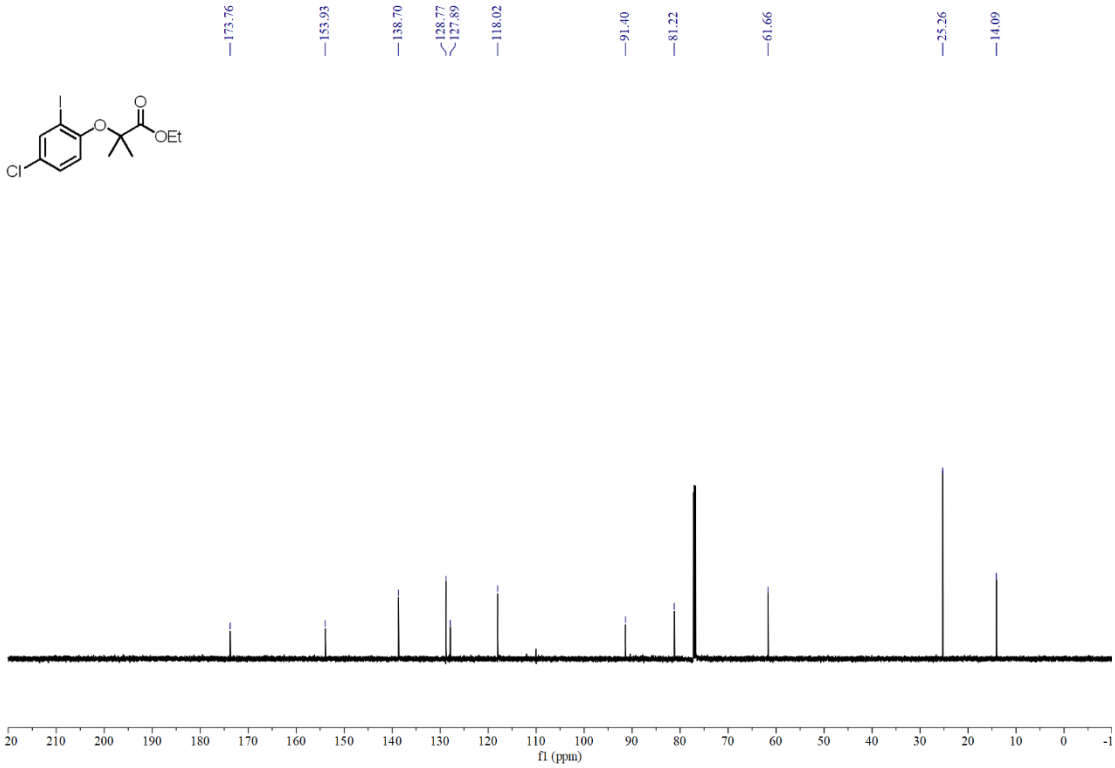
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 38



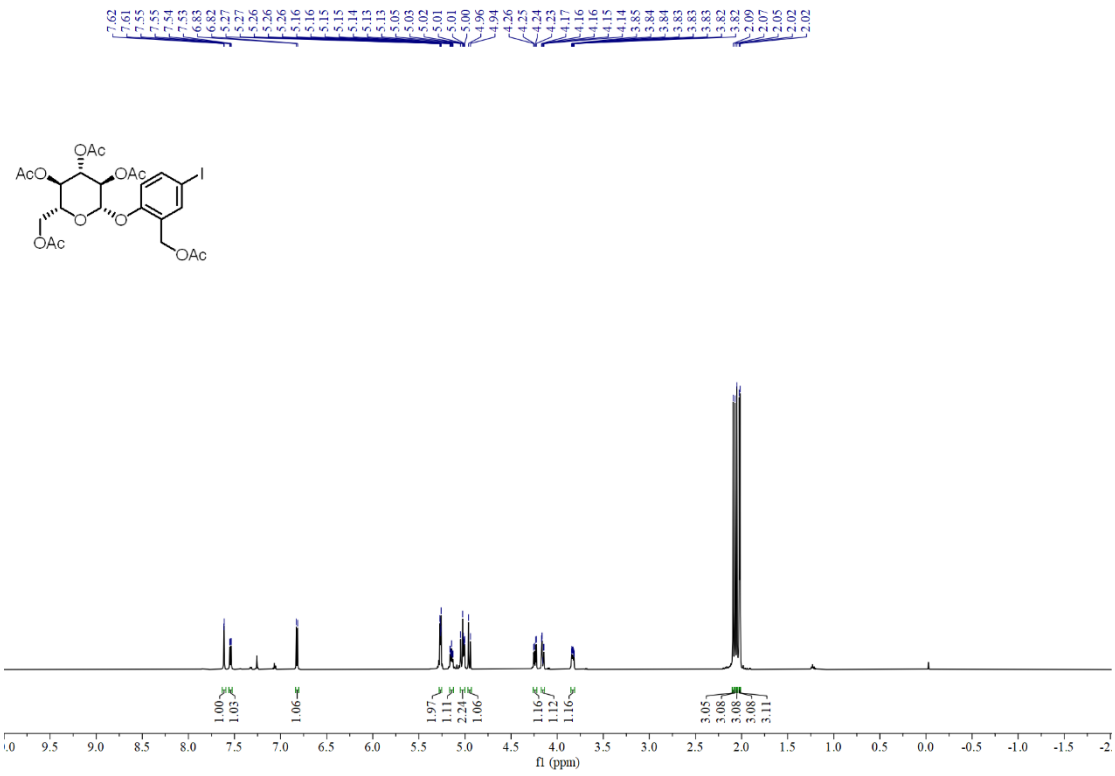
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 39



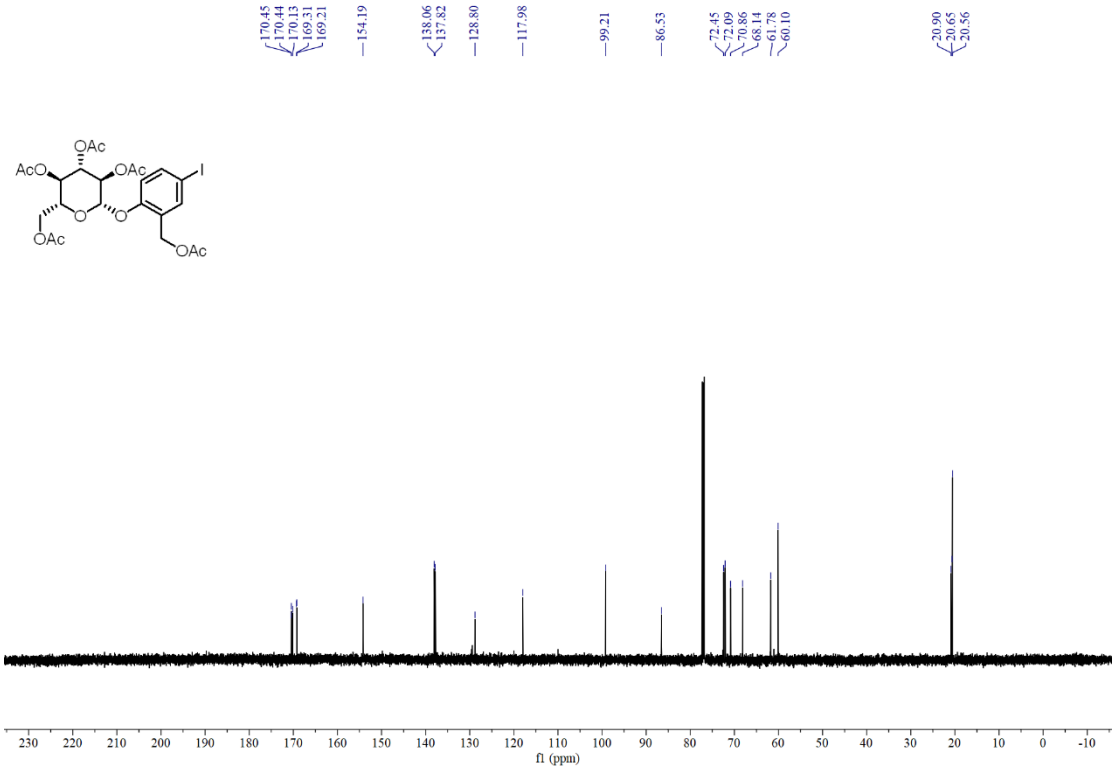
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 39



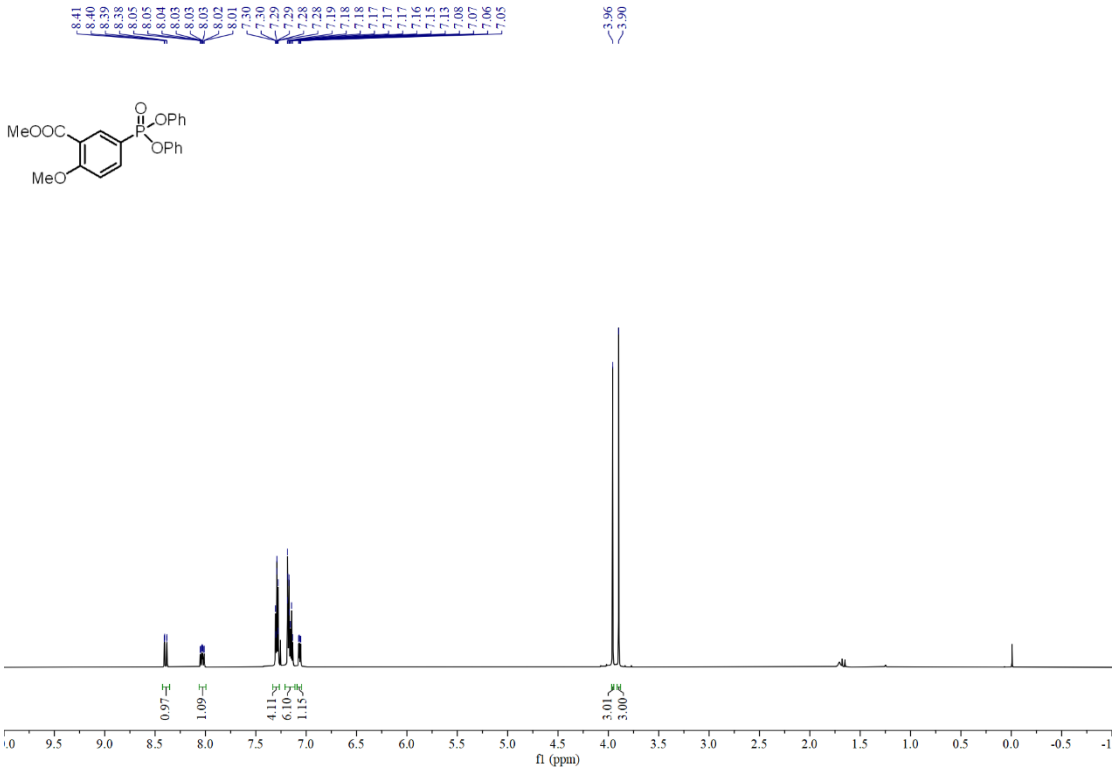
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 40



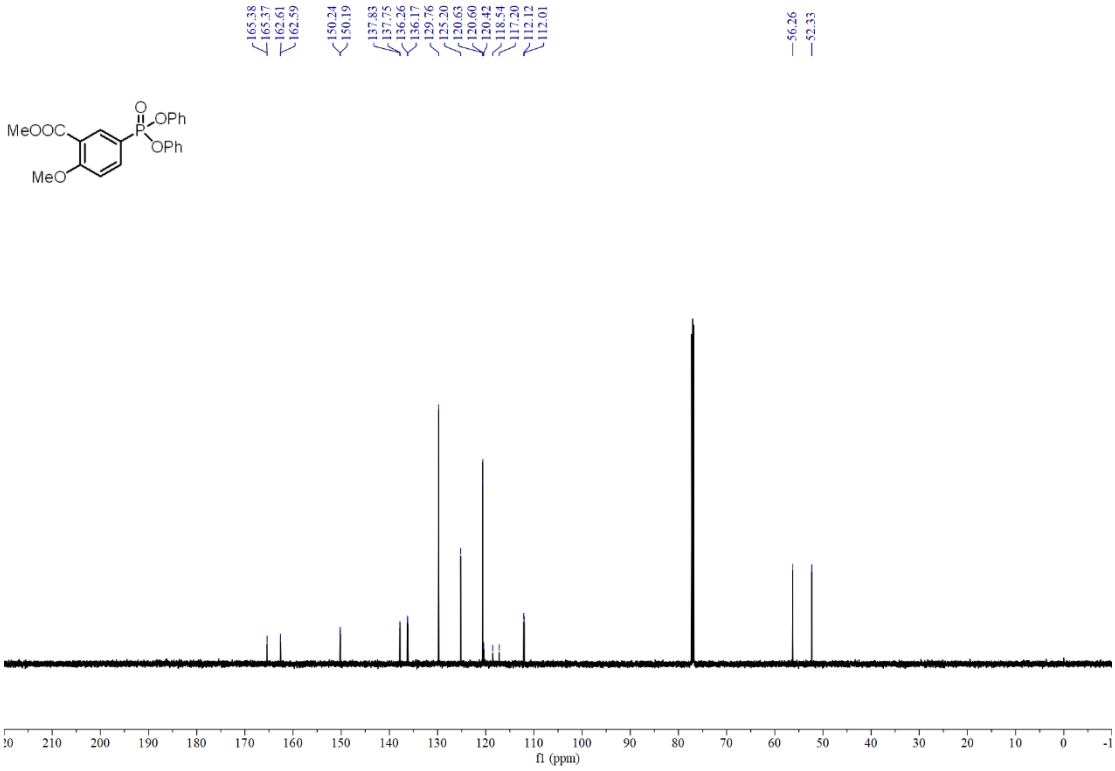
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 40



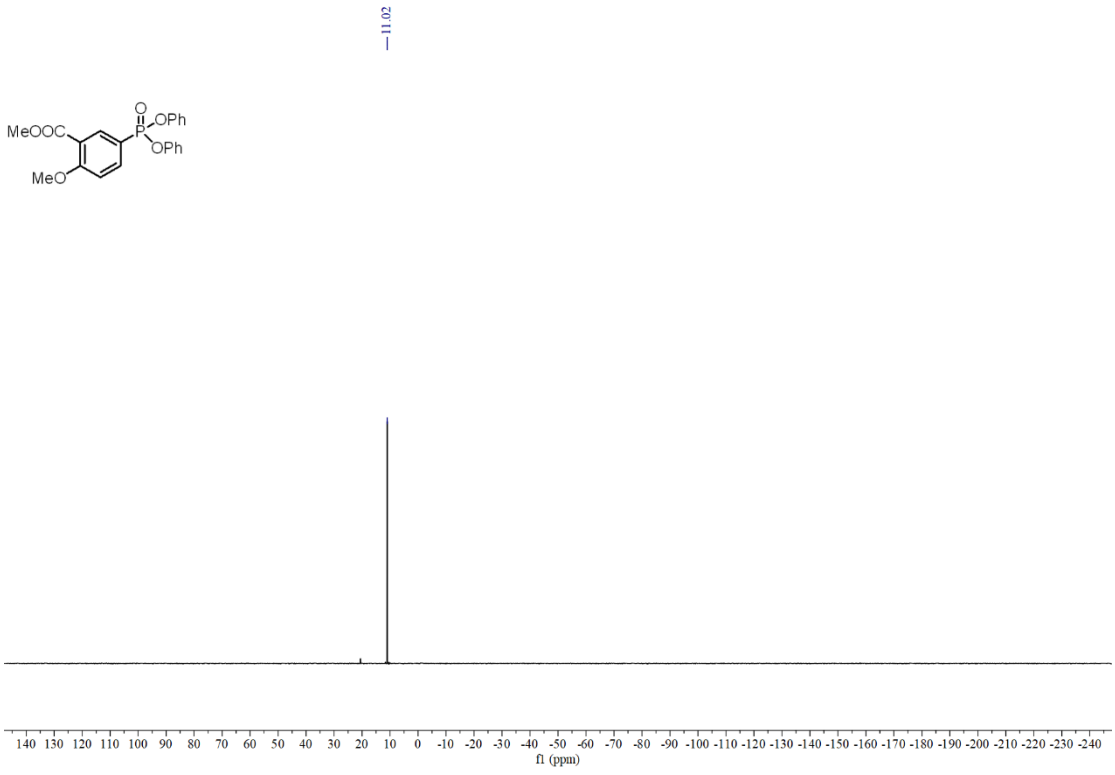
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 41



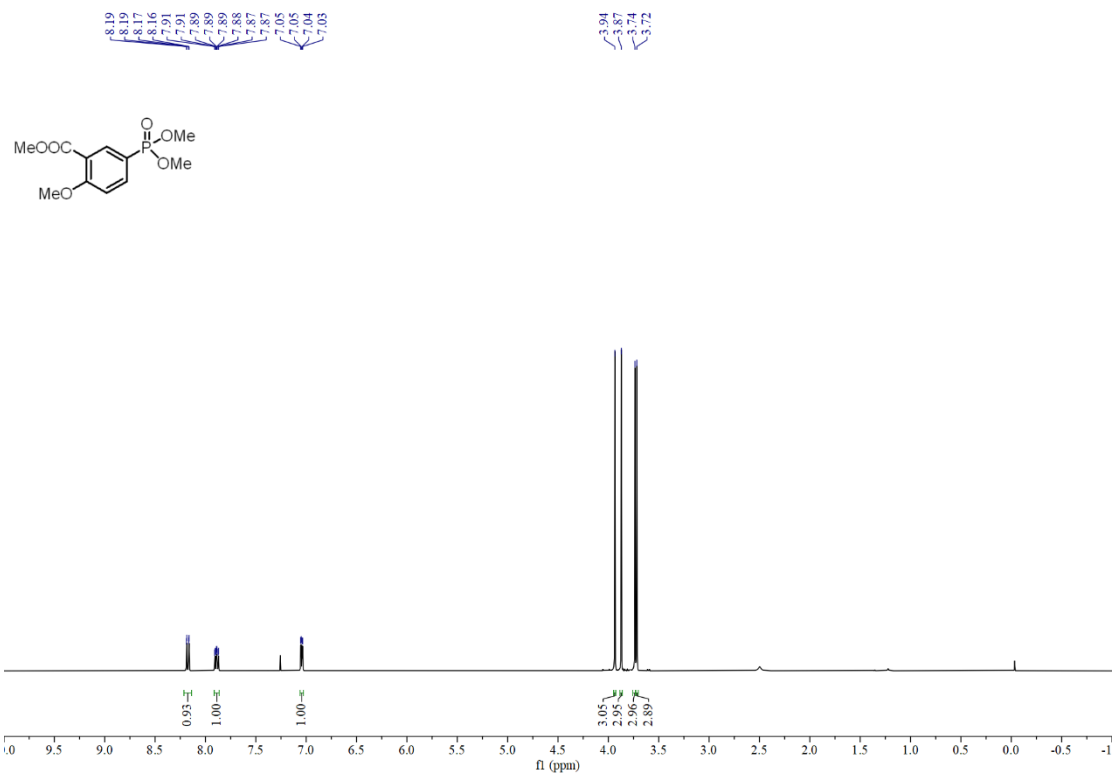
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 41



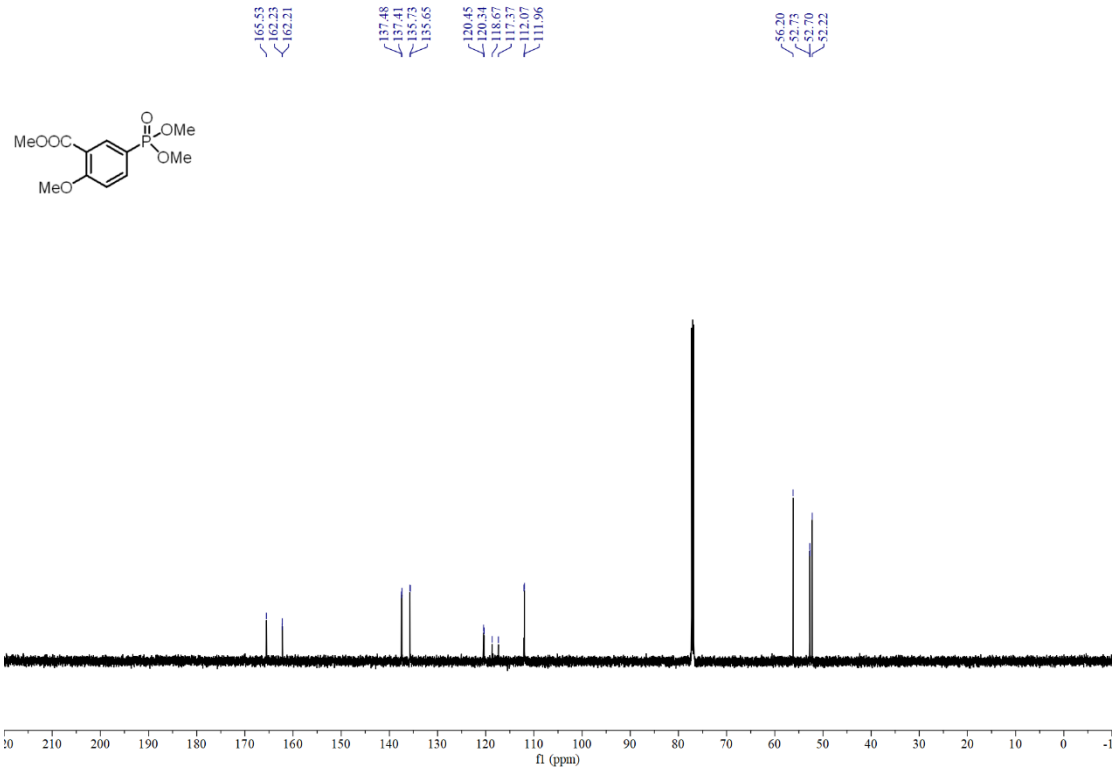
^{31}P NMR (162 MHz, Chloroform-d) spectrum of compound 41



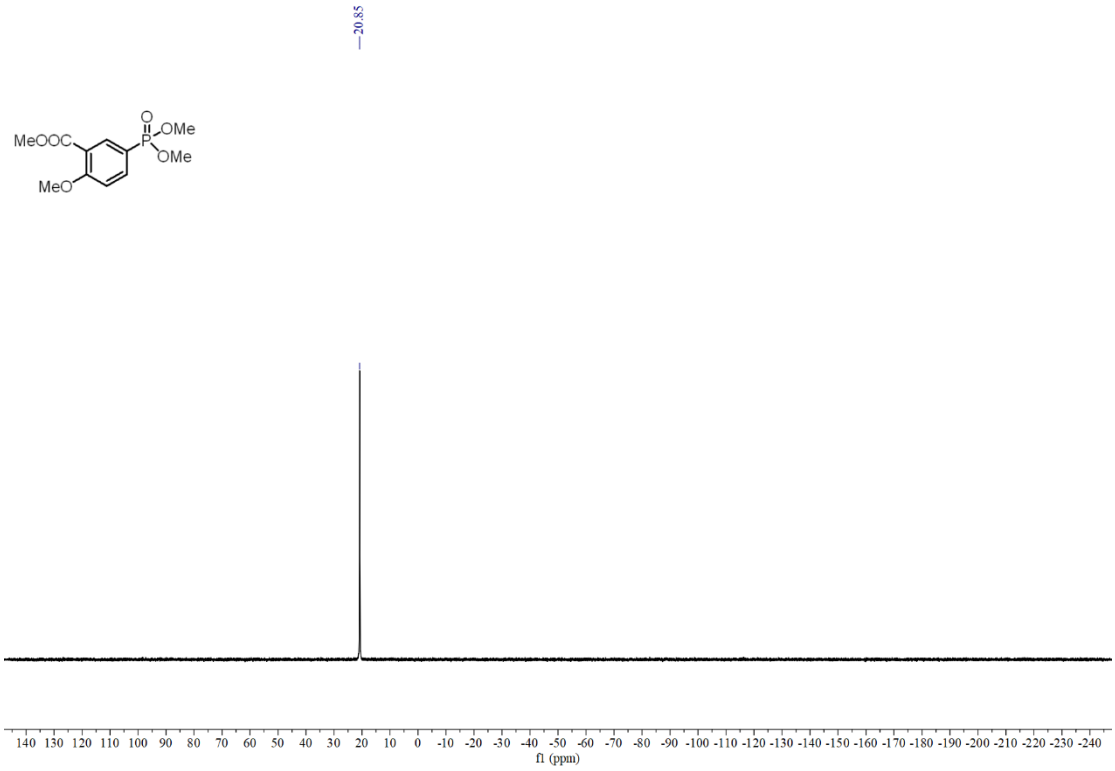
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 42



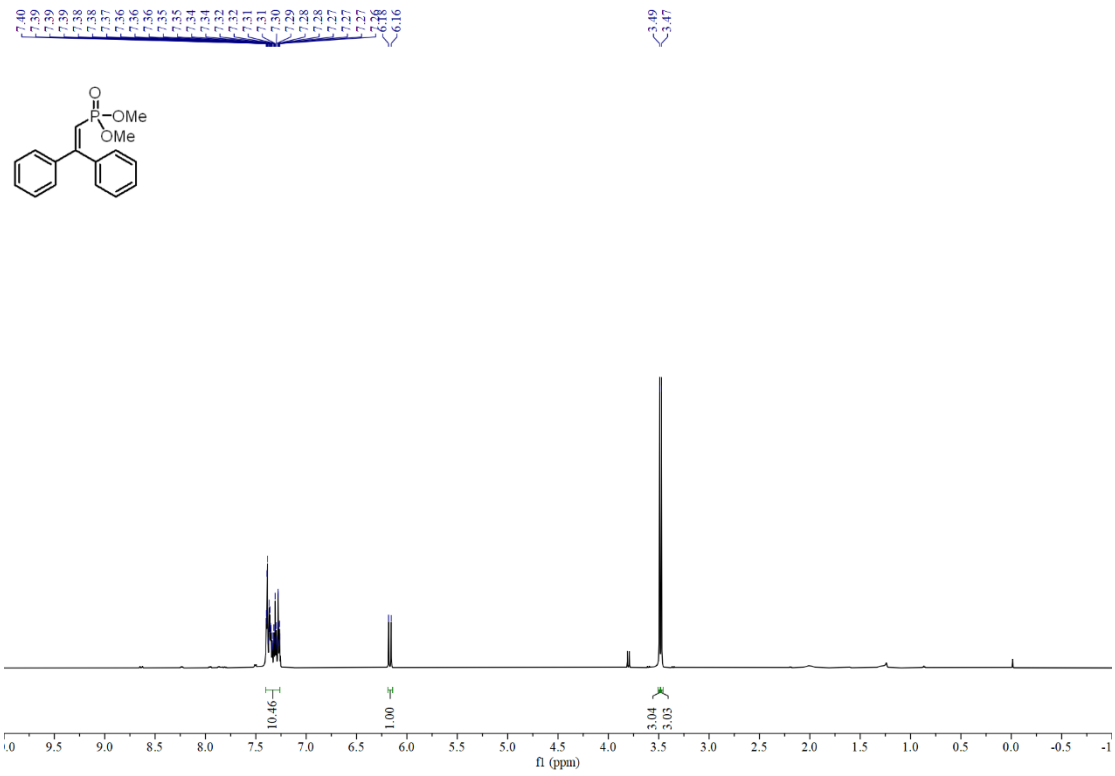
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 42



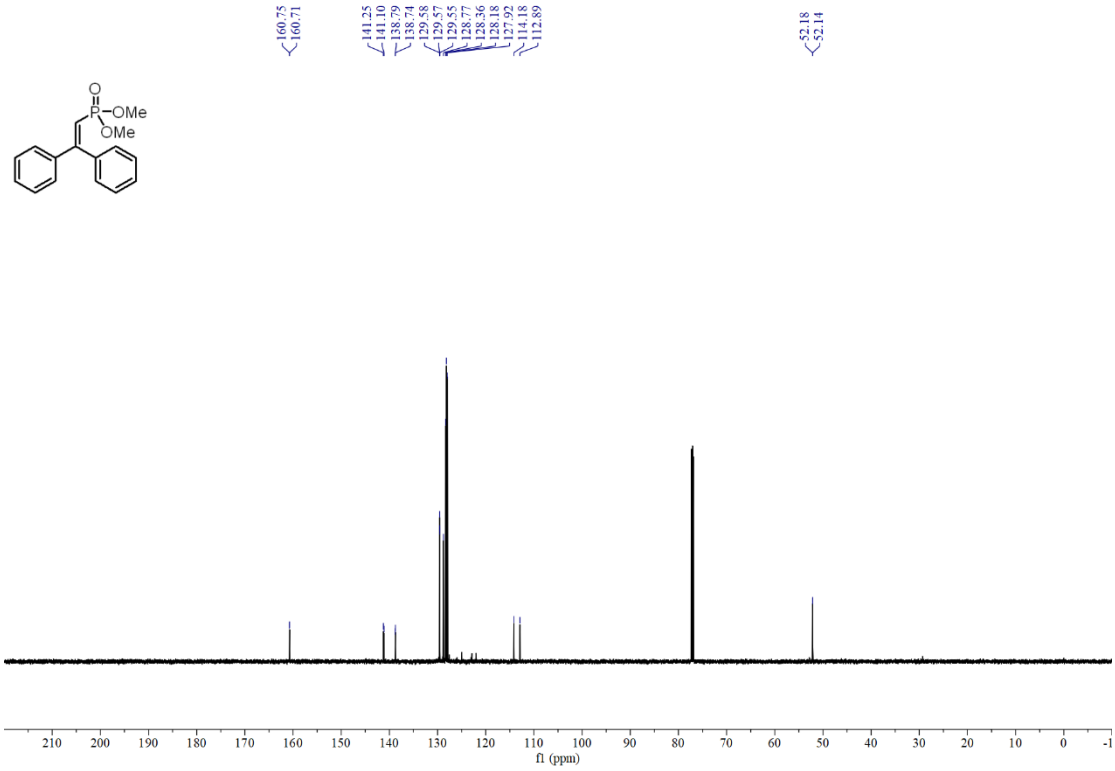
^{31}P NMR (243 MHz, Chloroform-d) spectrum of compound 42



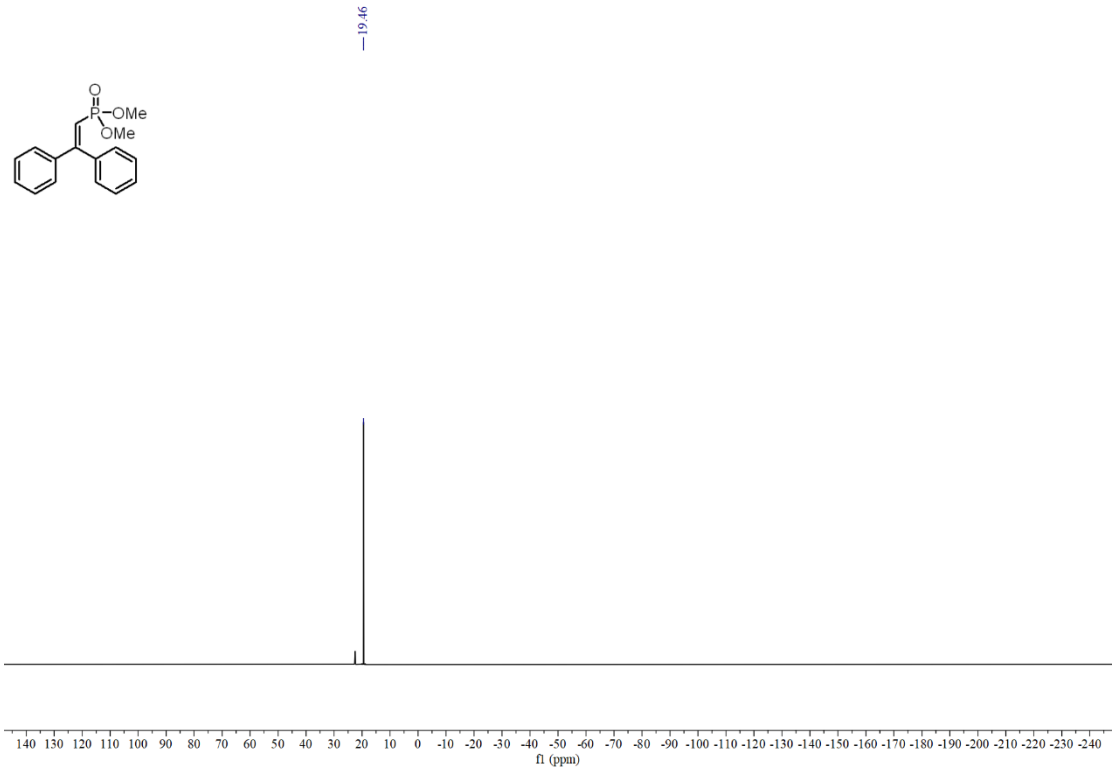
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 43



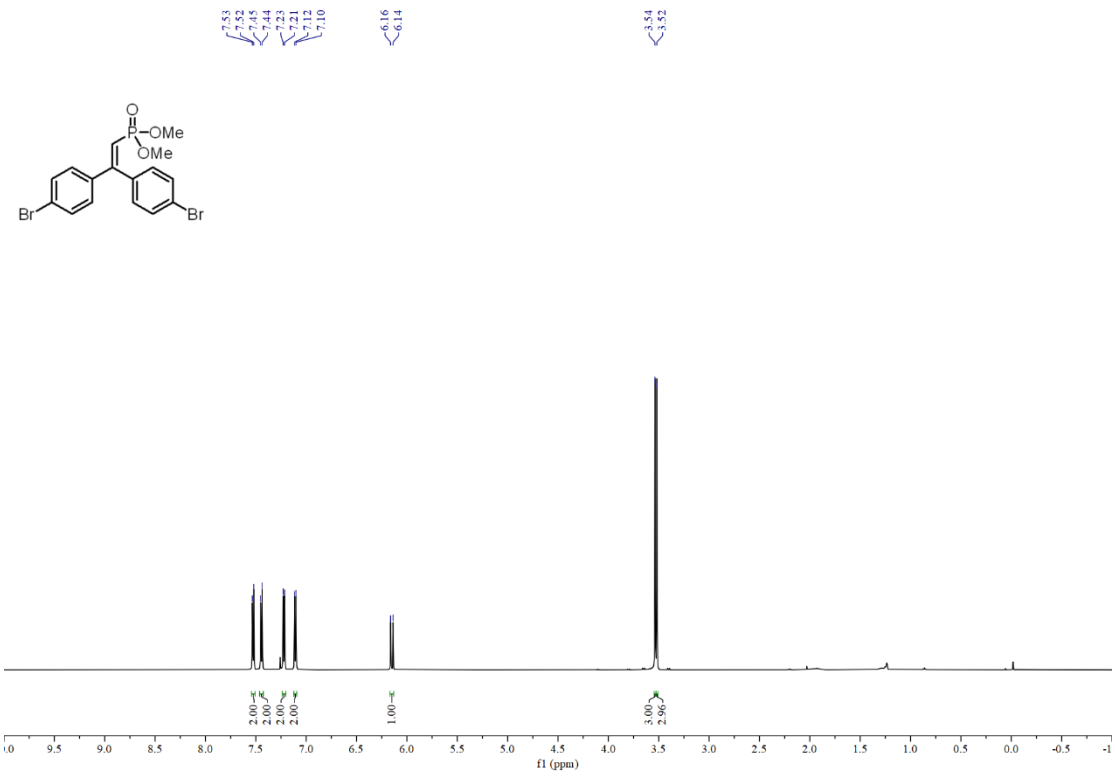
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 43



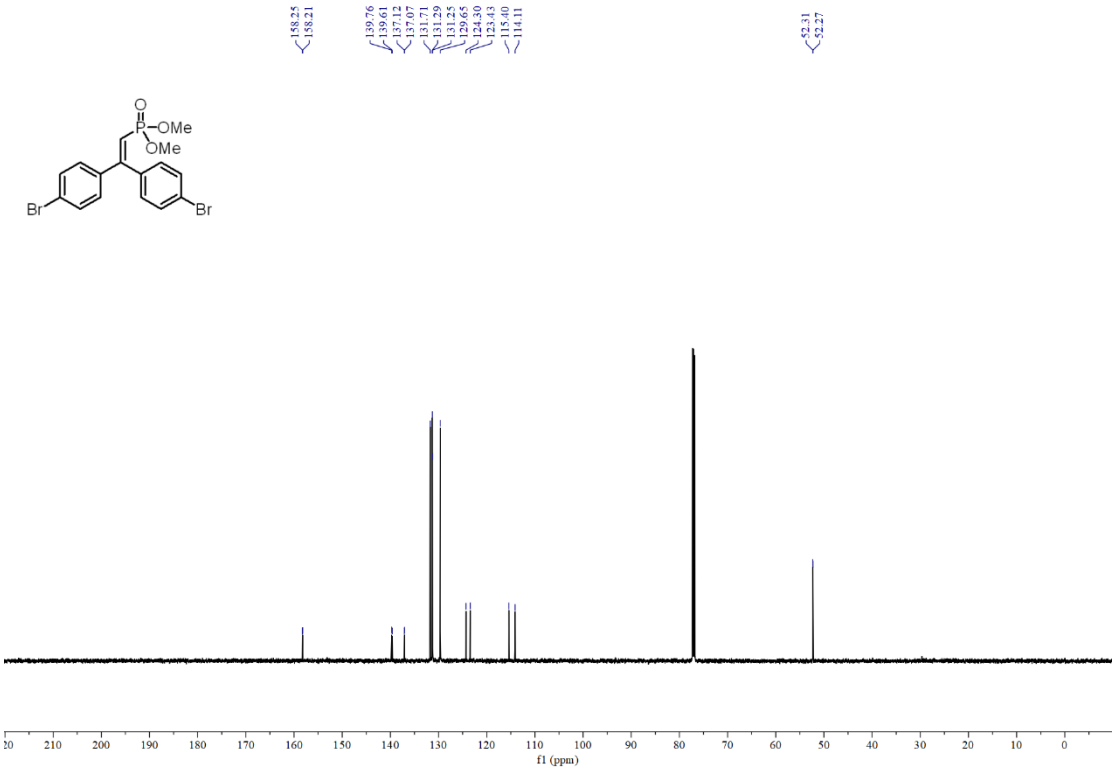
^{31}P NMR (162 MHz, Chloroform-*d*) spectrum of compound 43



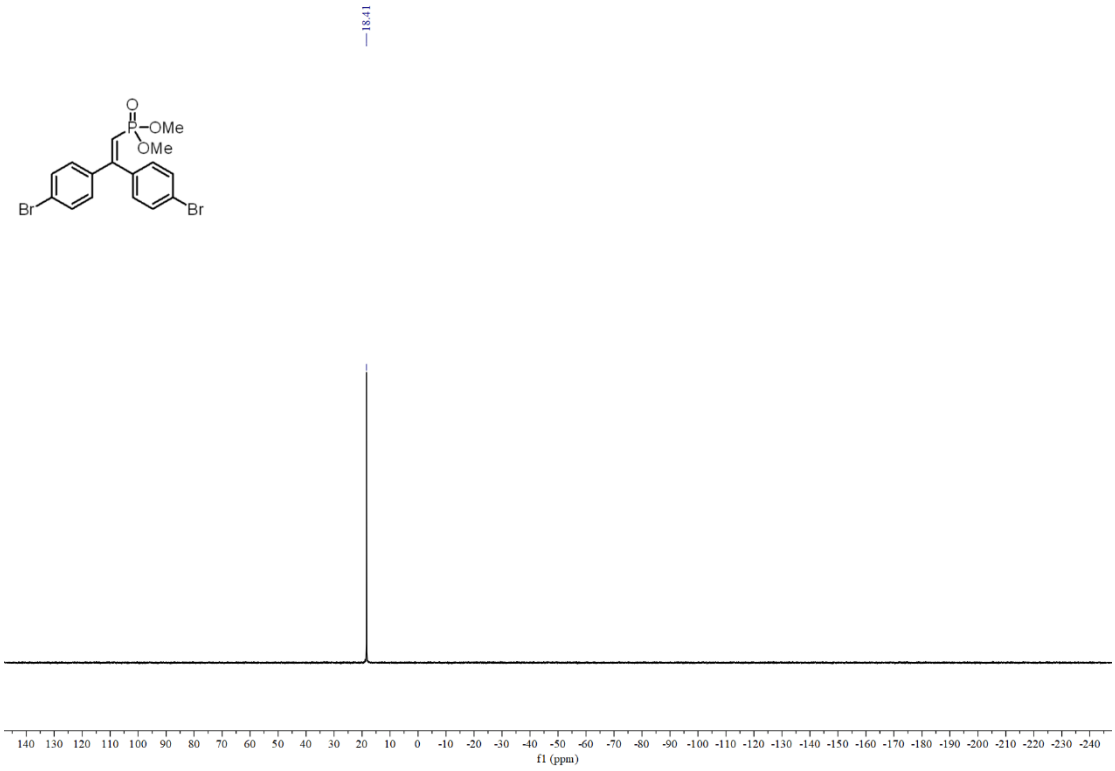
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 44



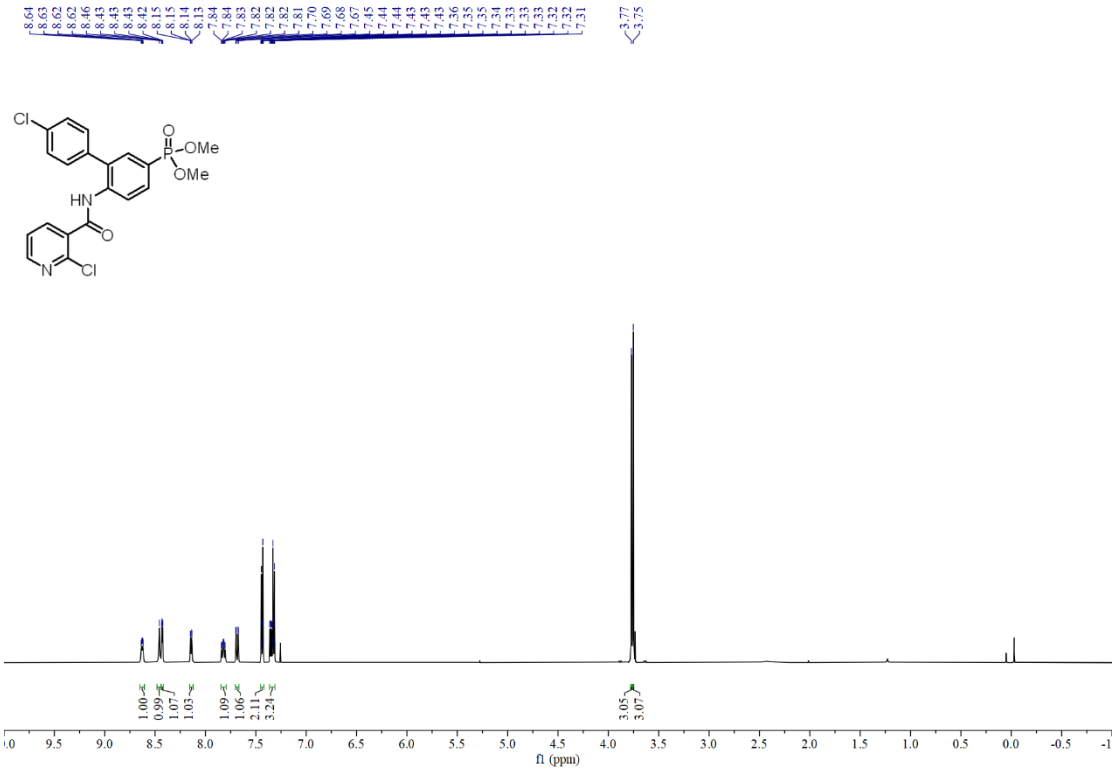
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 44



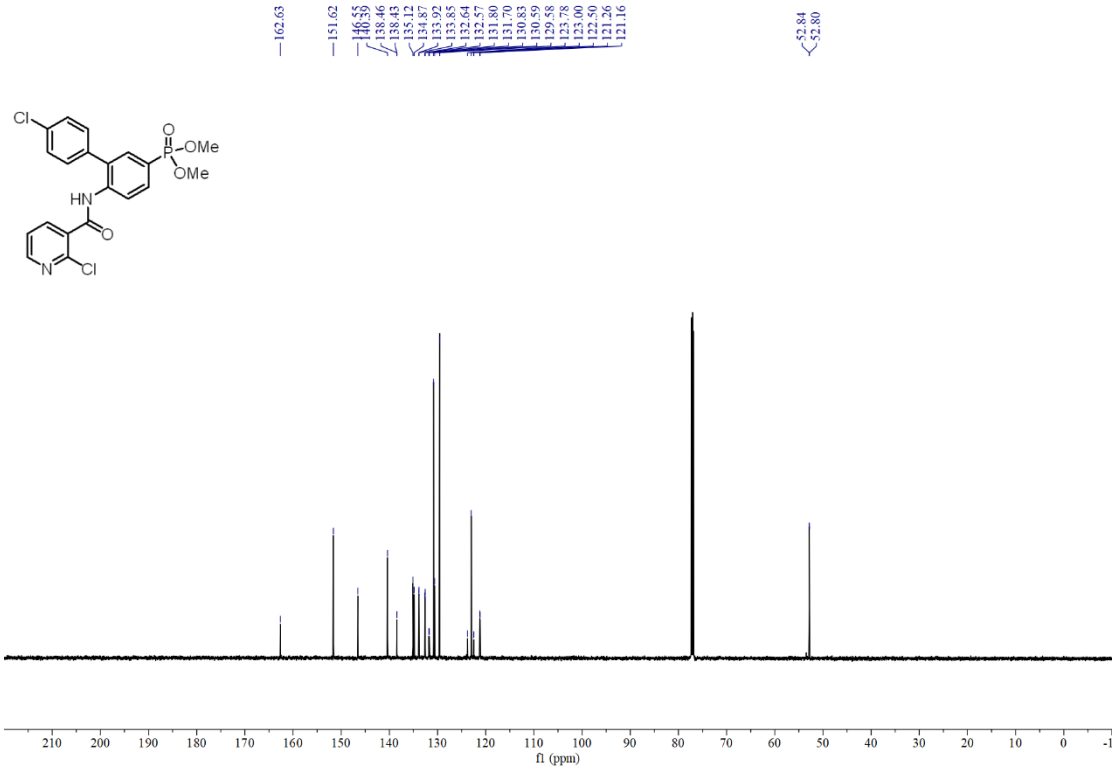
^{31}P NMR (162 MHz, Chloroform-*d*) spectrum of compound 44



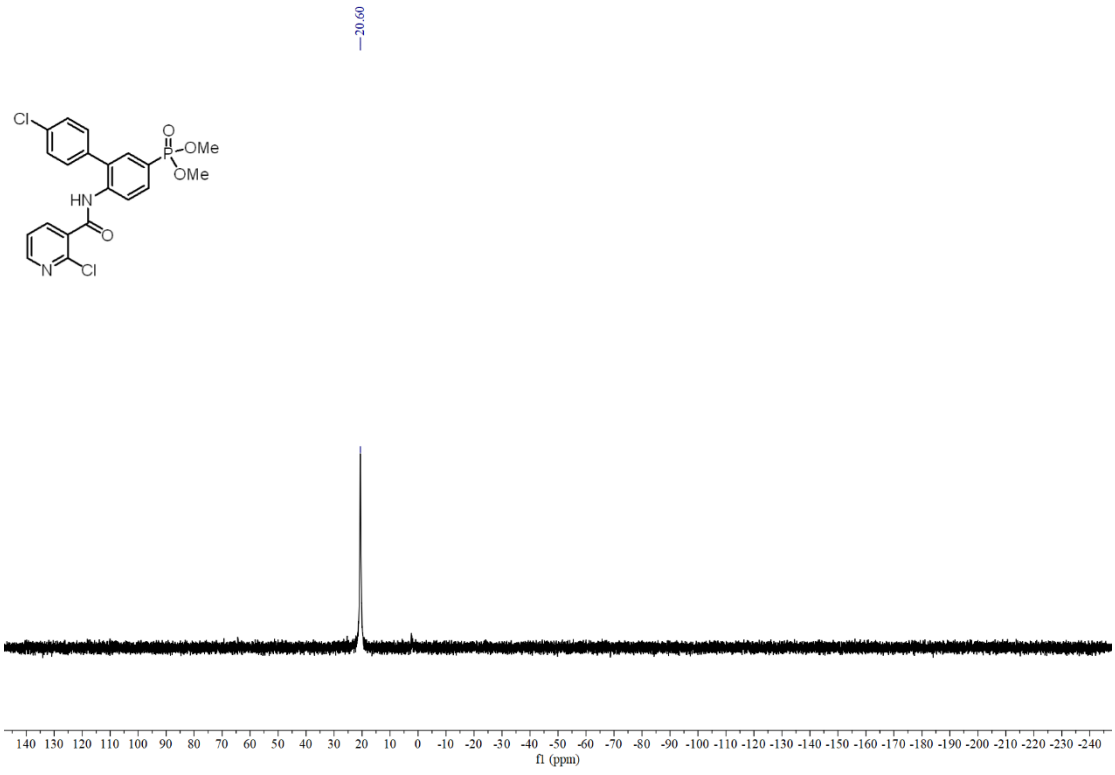
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 45



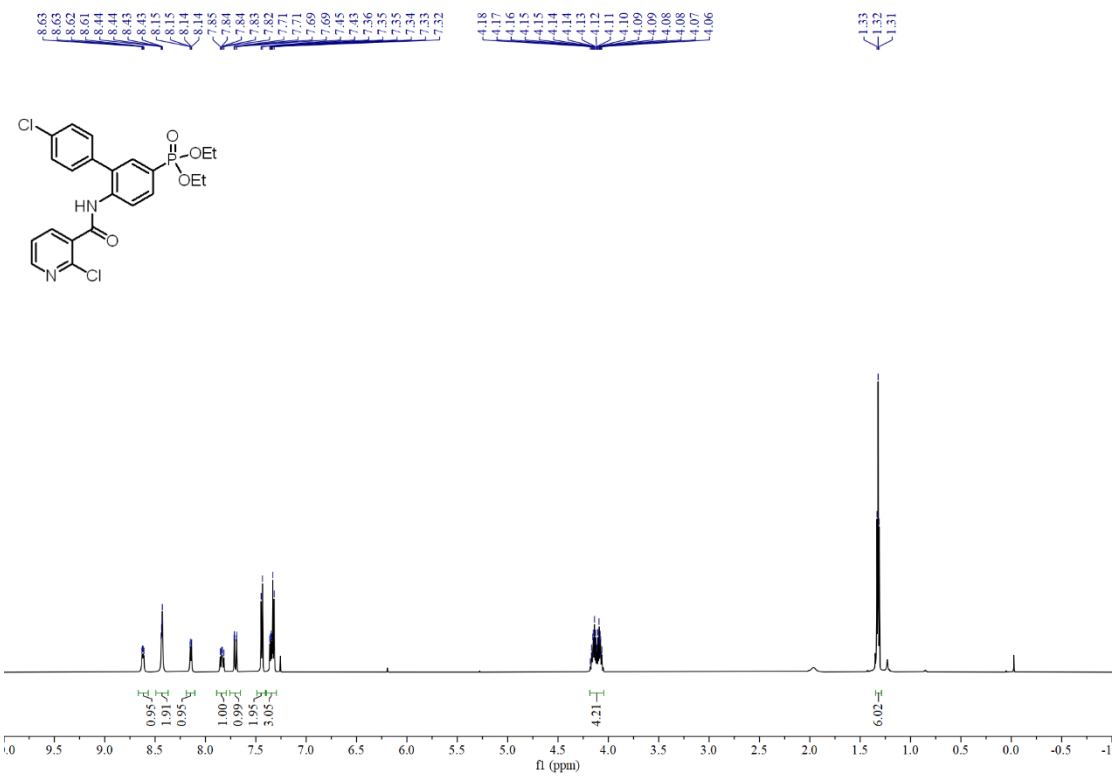
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 45



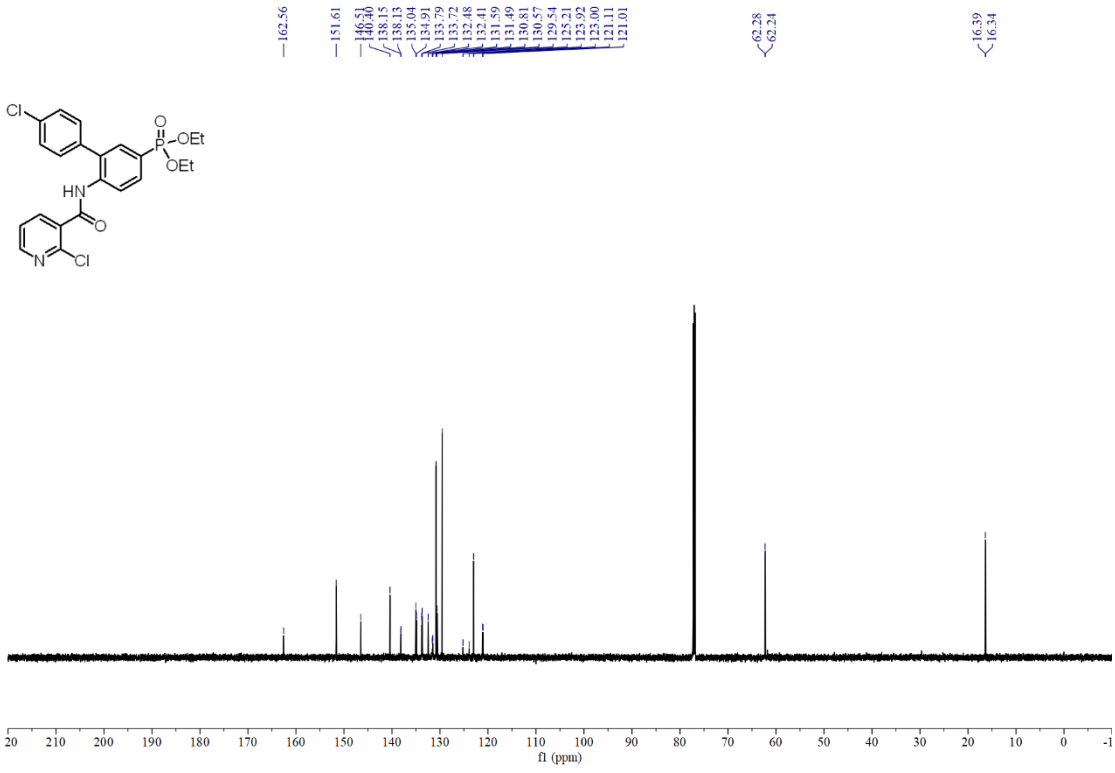
^{31}P NMR (162 MHz, Chloroform-*d*) spectrum of compound 45



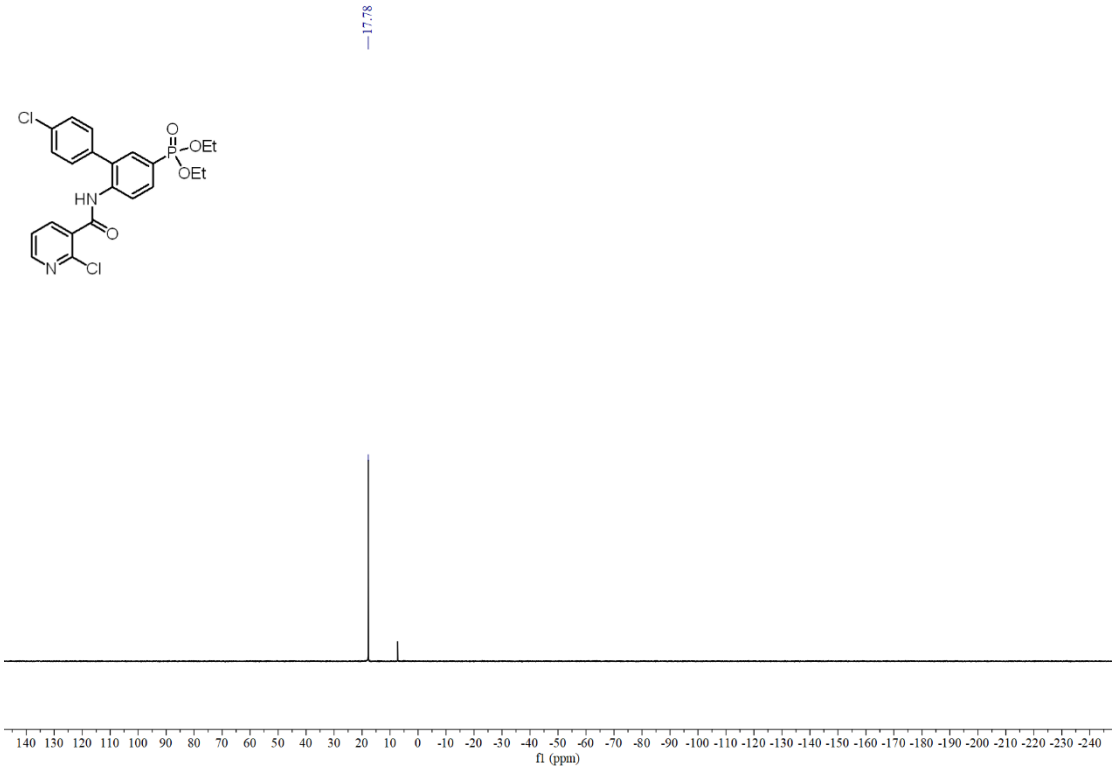
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 46



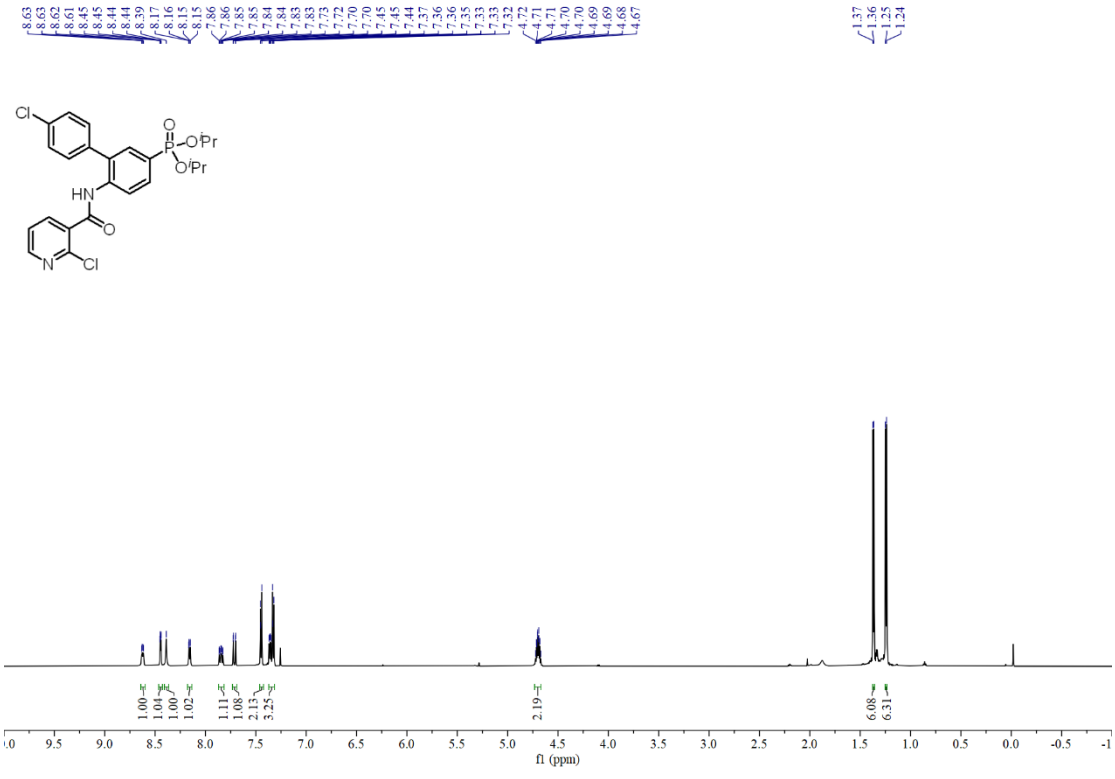
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 46



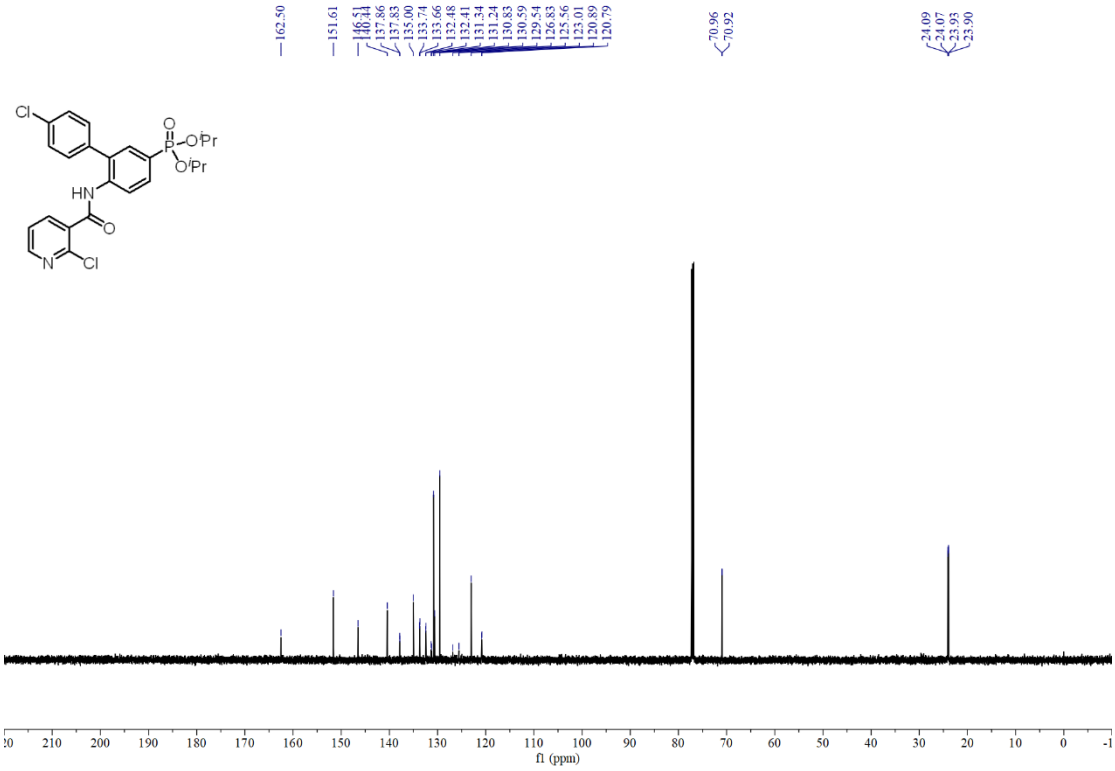
^{31}P NMR (162 MHz, Chloroform-*d*) spectrum of compound 46



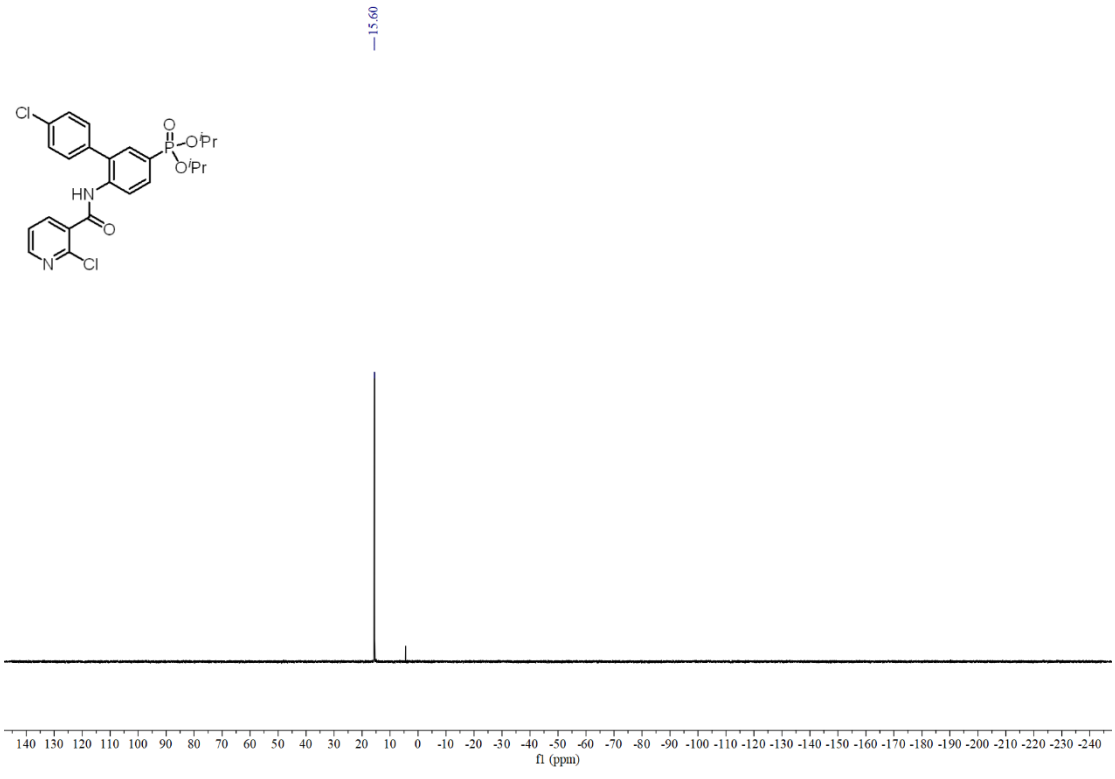
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 47



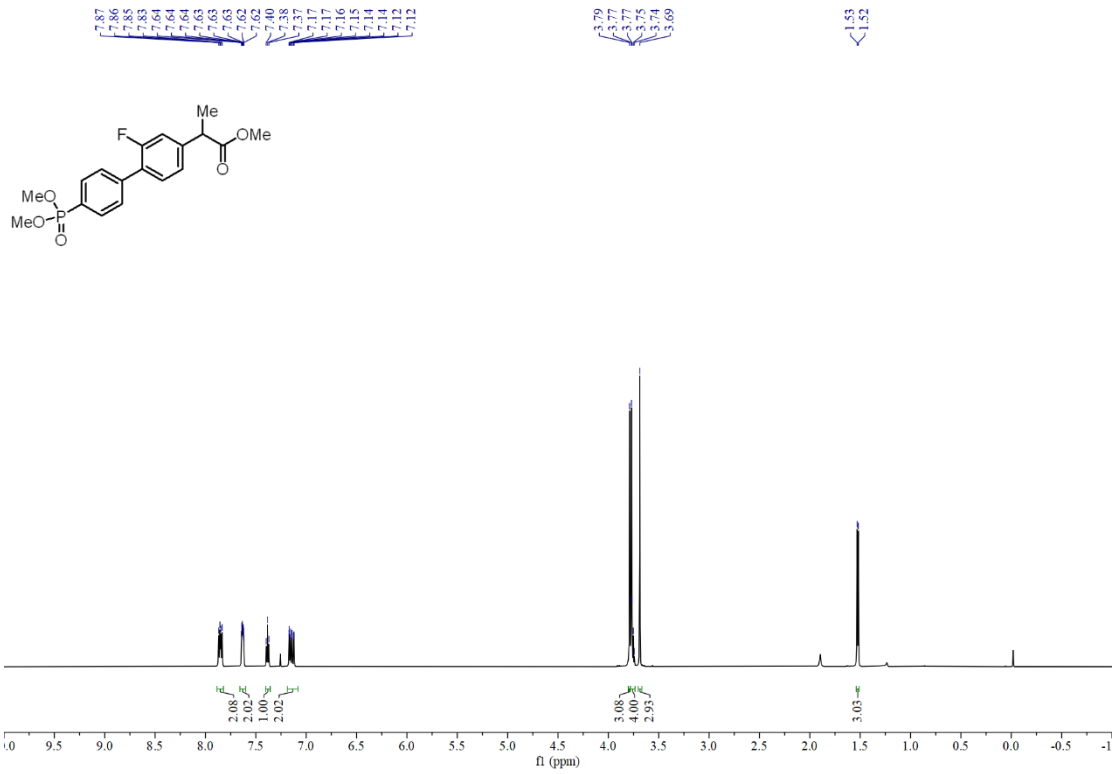
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 47



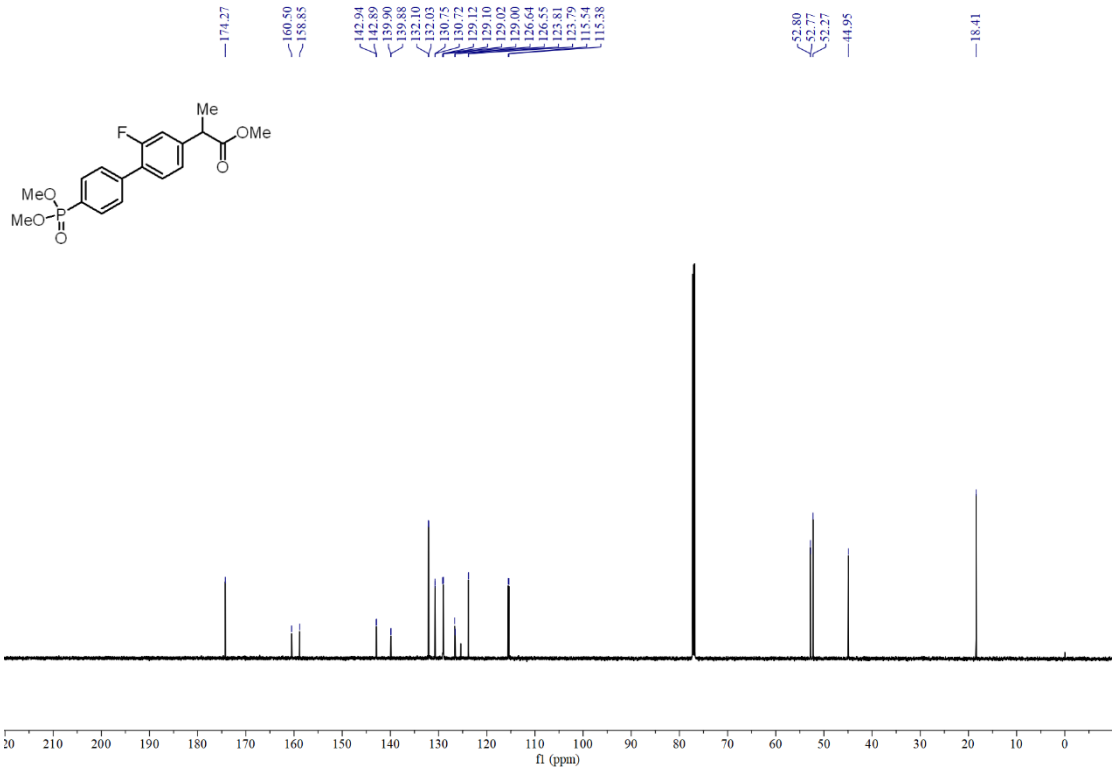
^{31}P NMR (162 MHz, Chloroform-*d*) spectrum of compound 47



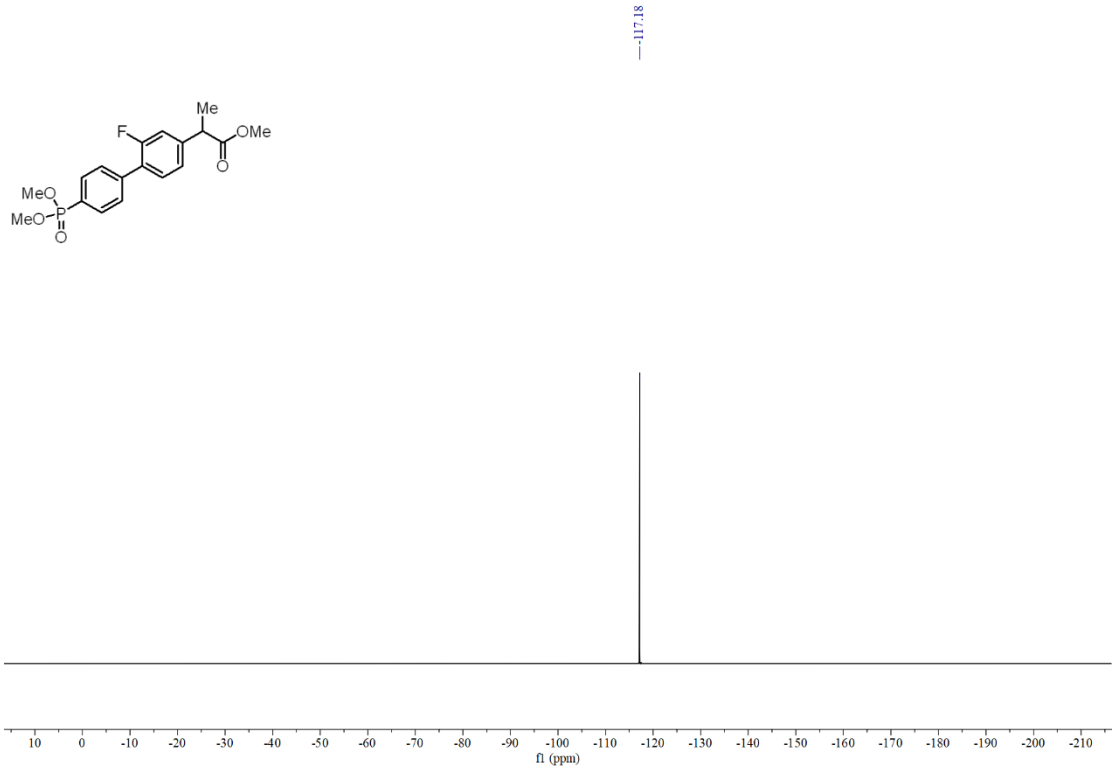
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 48



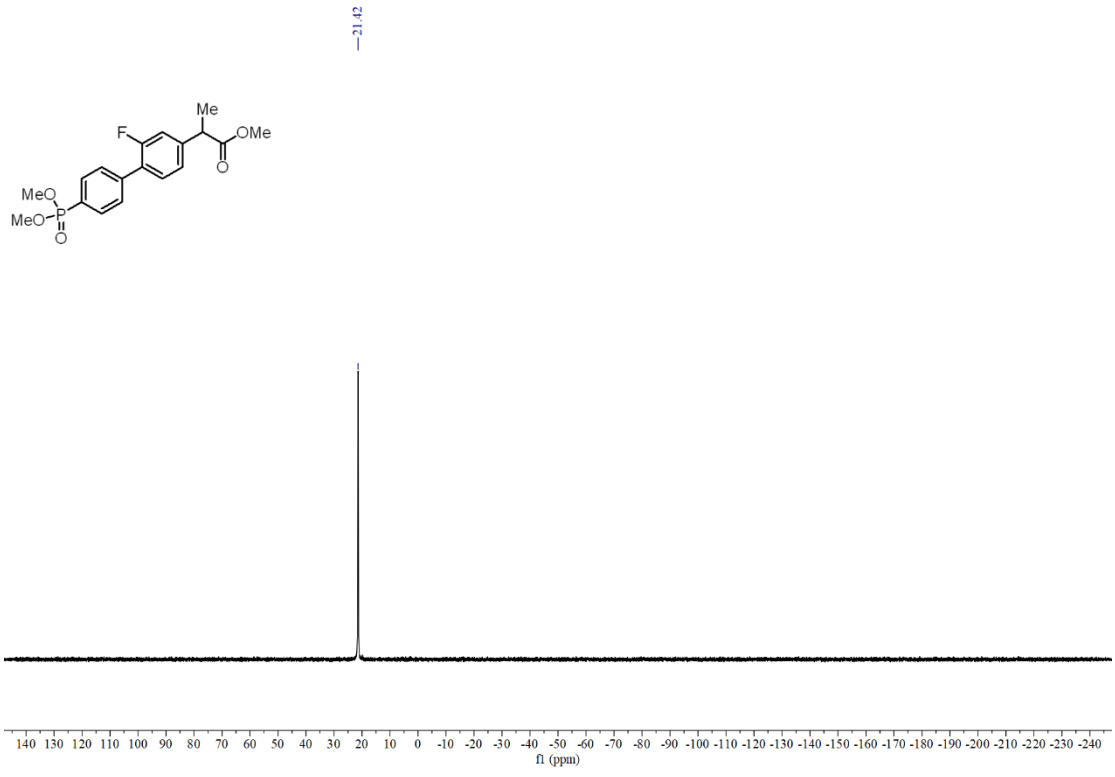
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 48



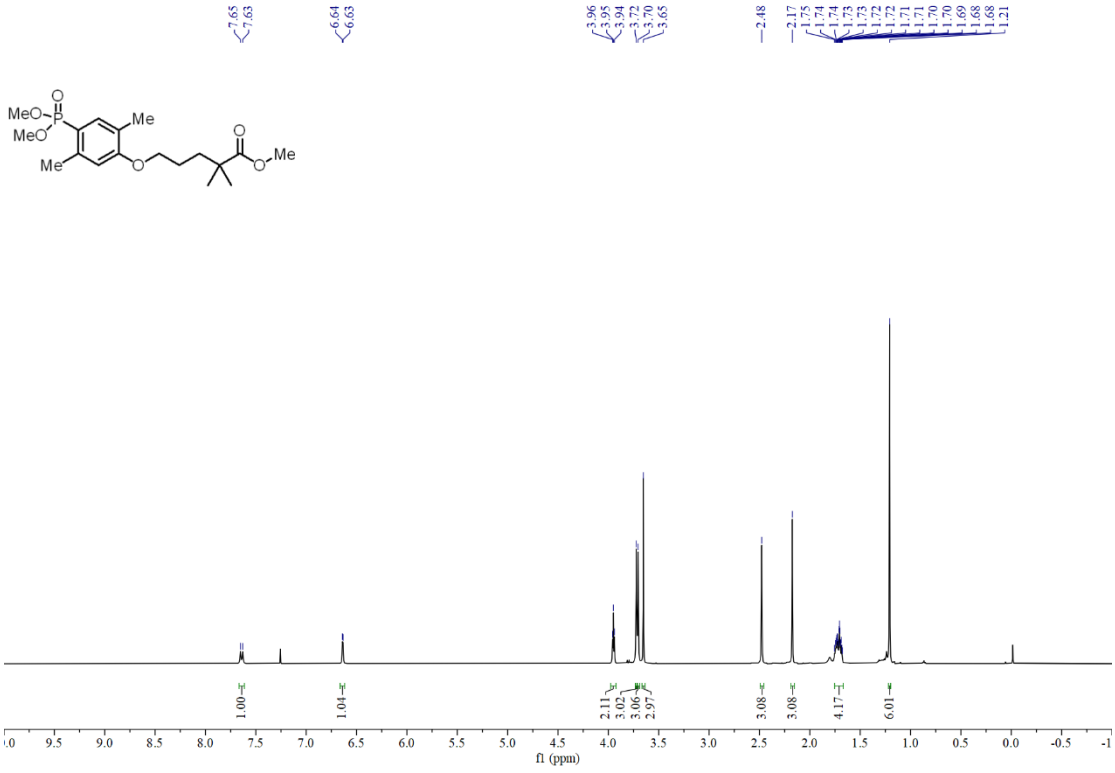
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 48



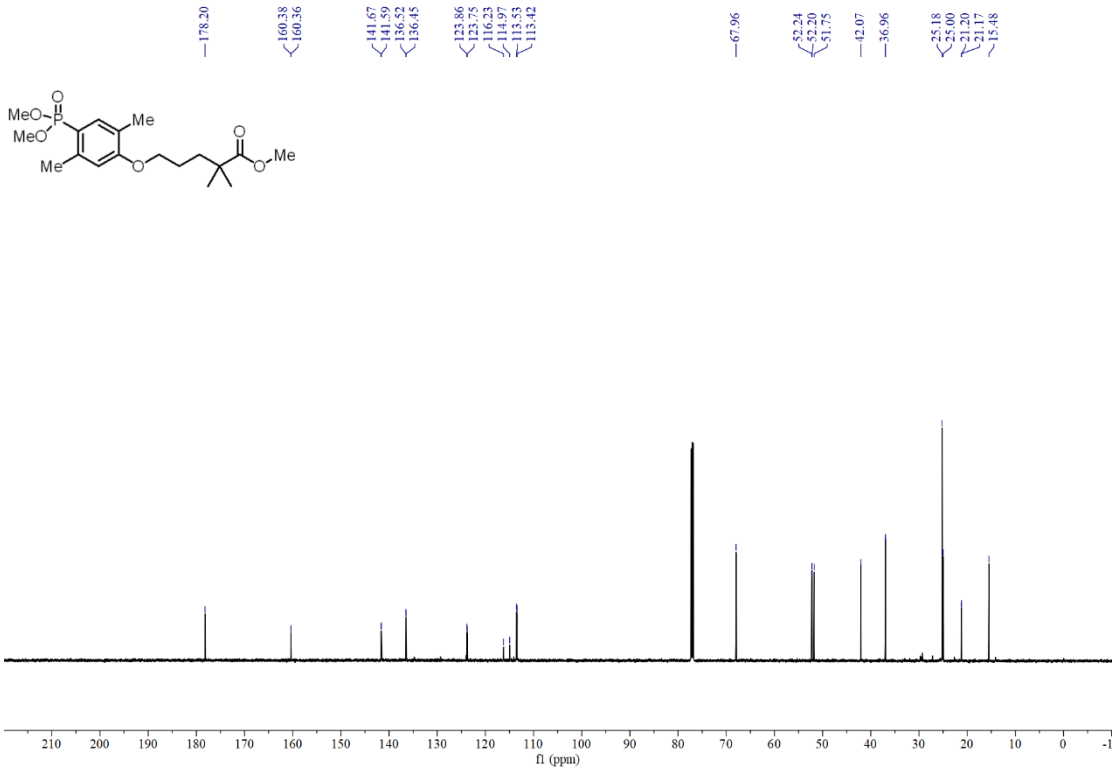
^{31}P NMR (243 MHz, Chloroform-*d*) spectrum of compound 48



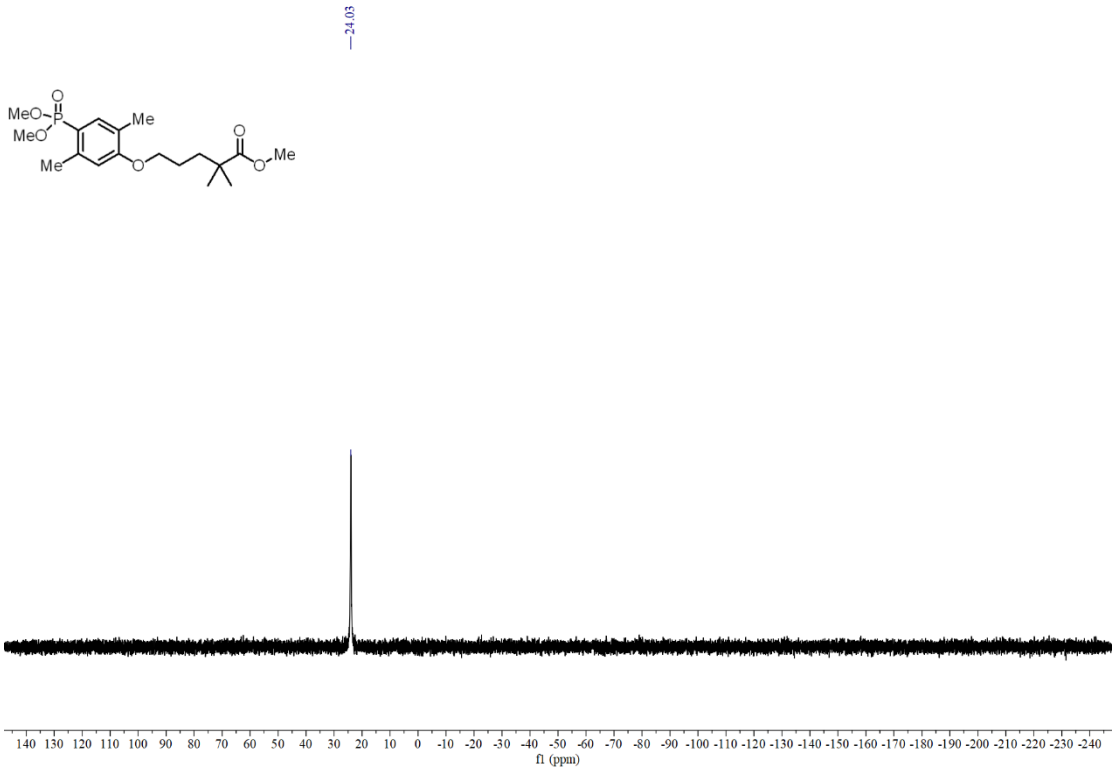
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 49



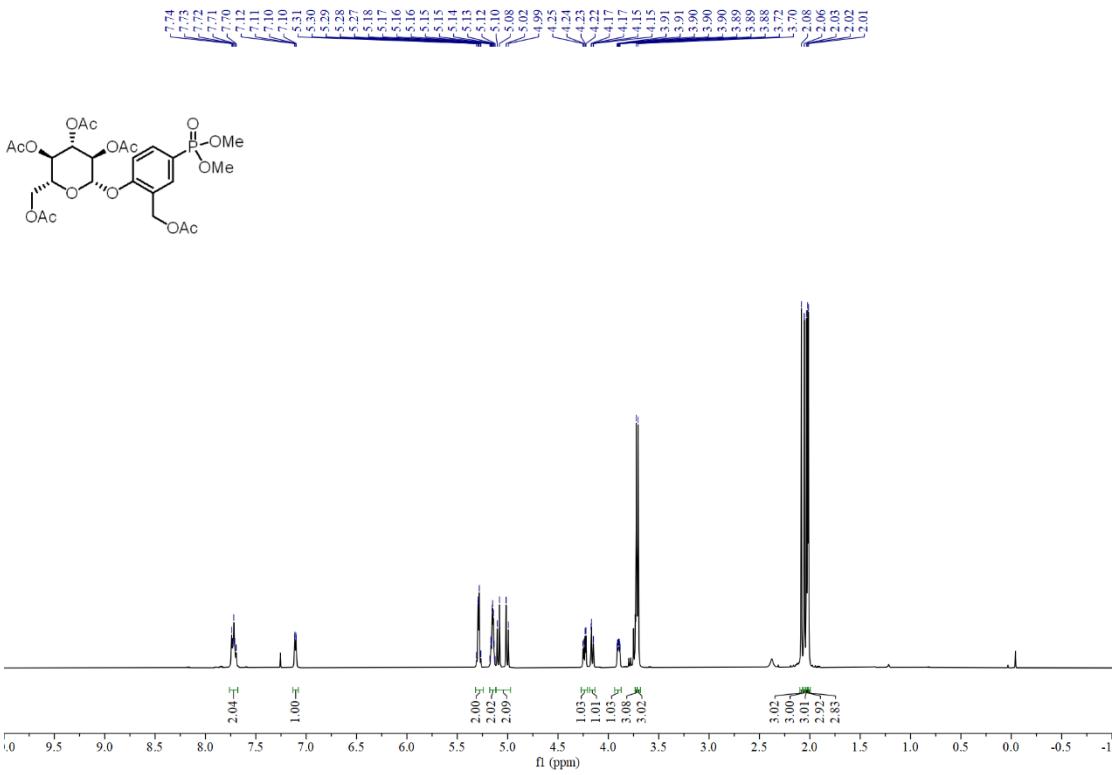
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 49



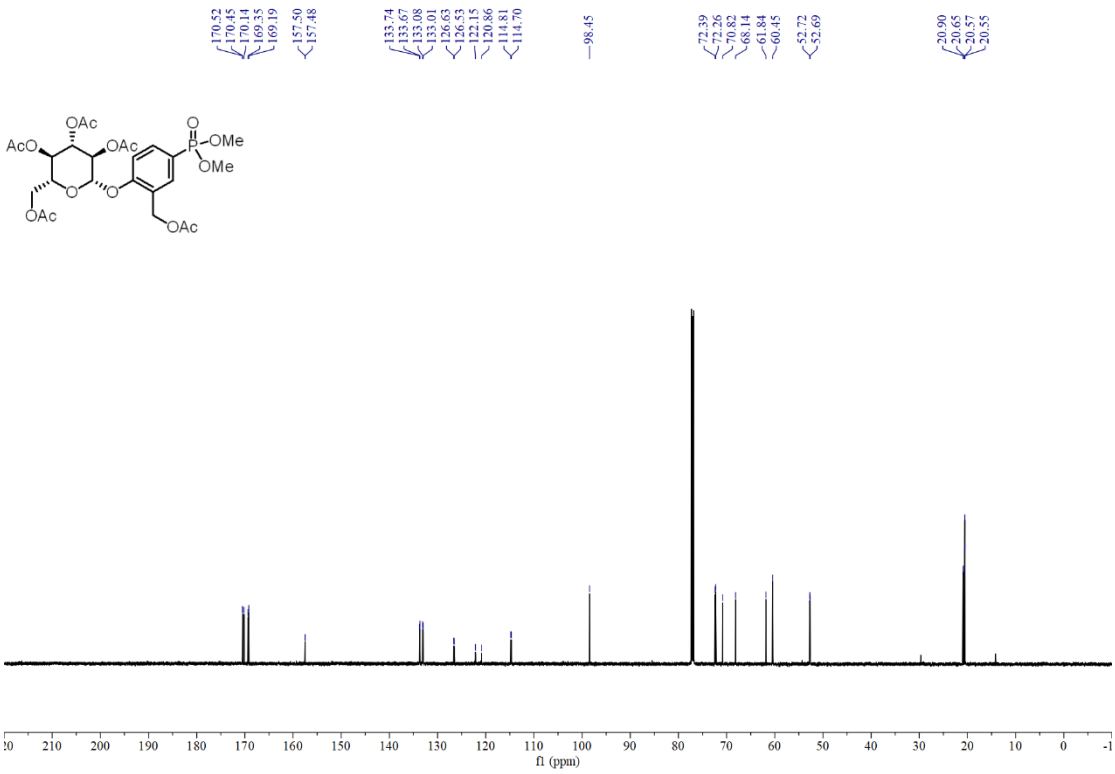
^{31}P NMR (162 MHz, Chloroform-*d*) spectrum of compound 49



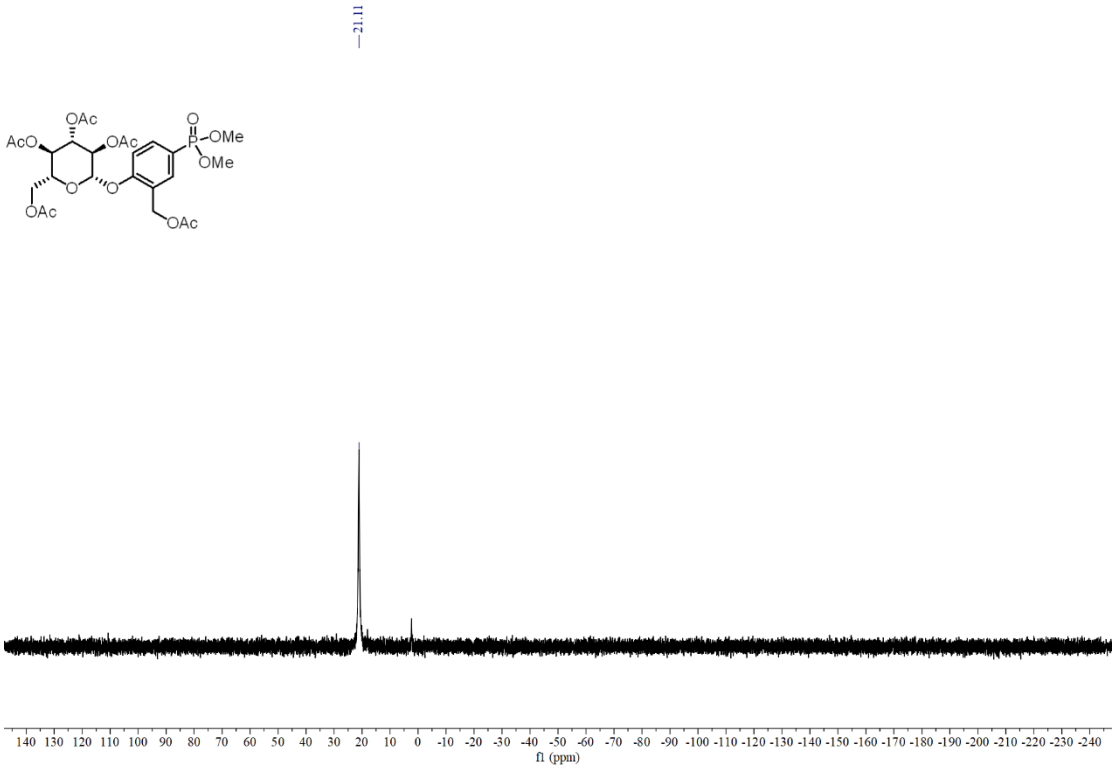
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 50



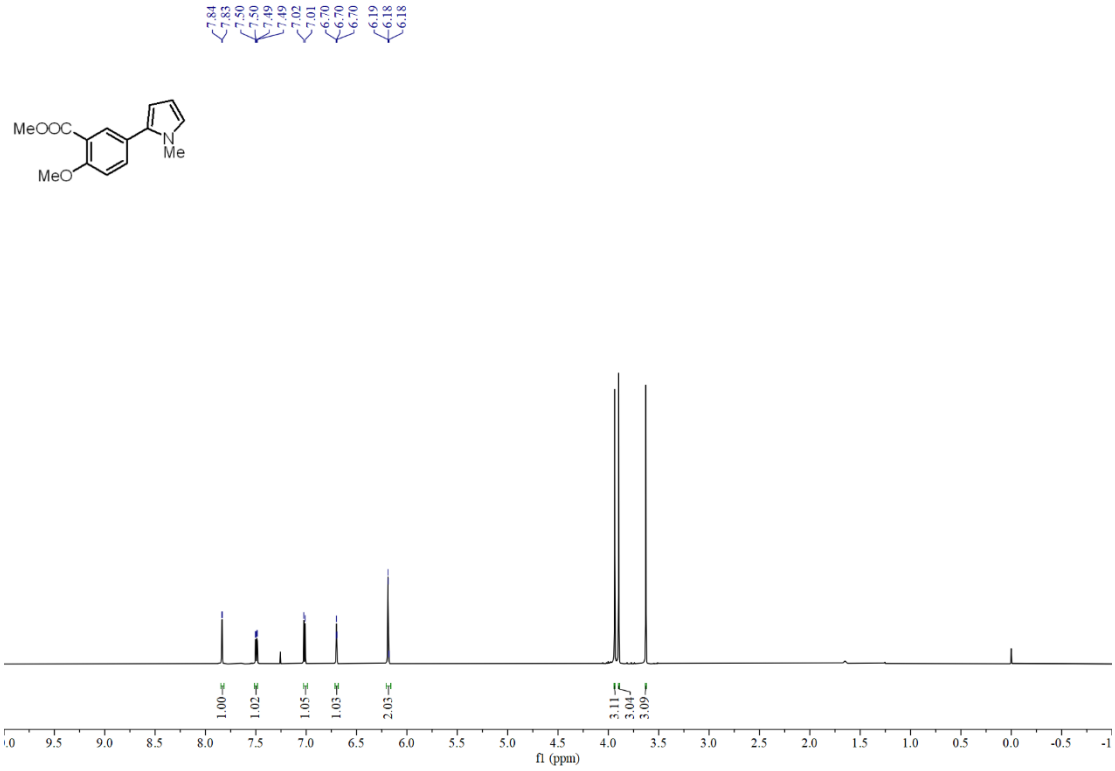
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 50



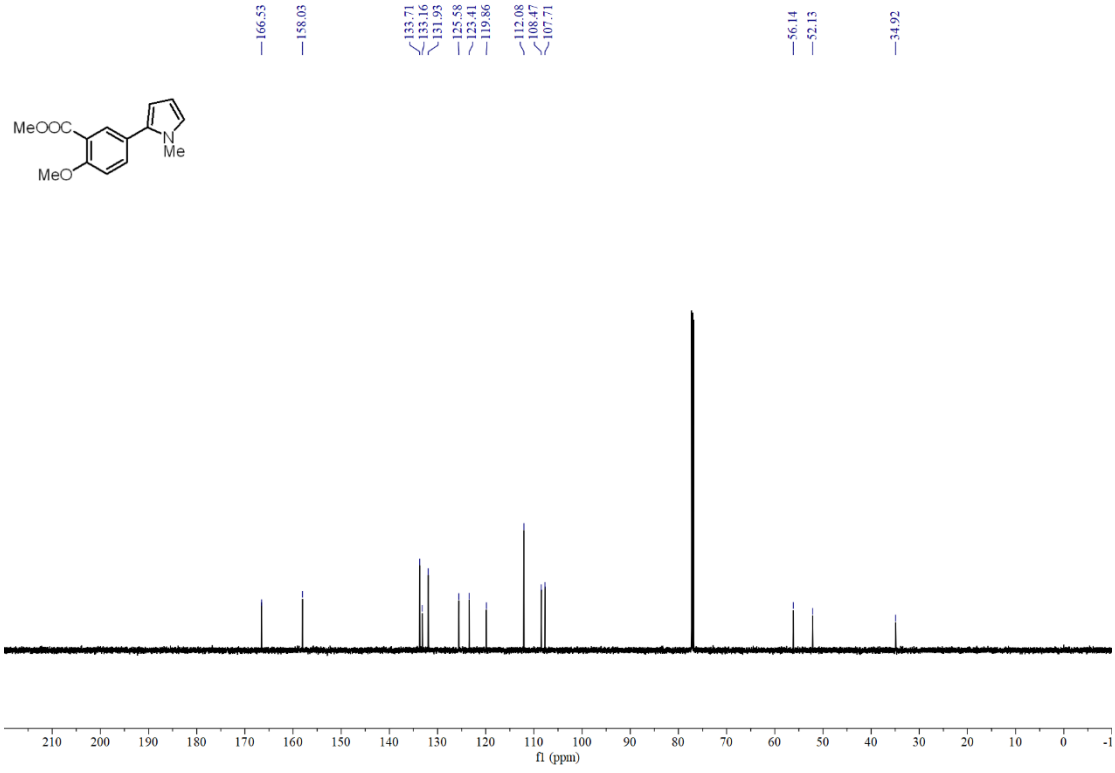
^{31}P NMR (162 MHz, Chloroform-*d*) spectrum of compound 50



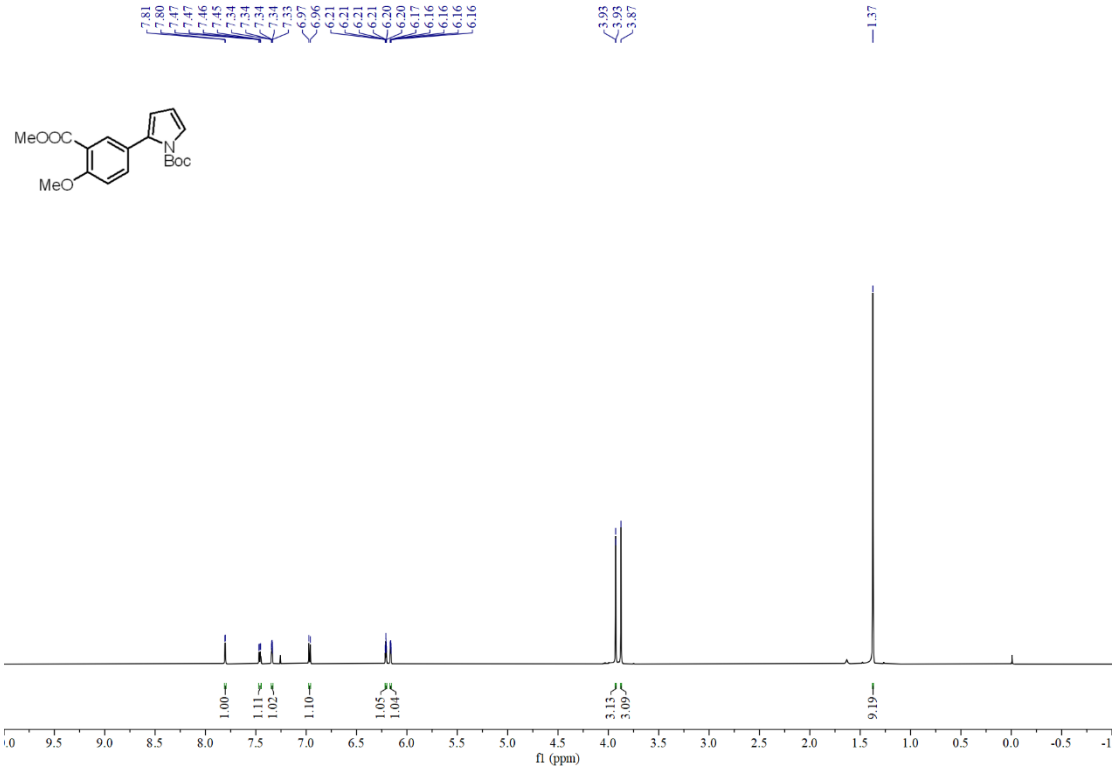
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 51



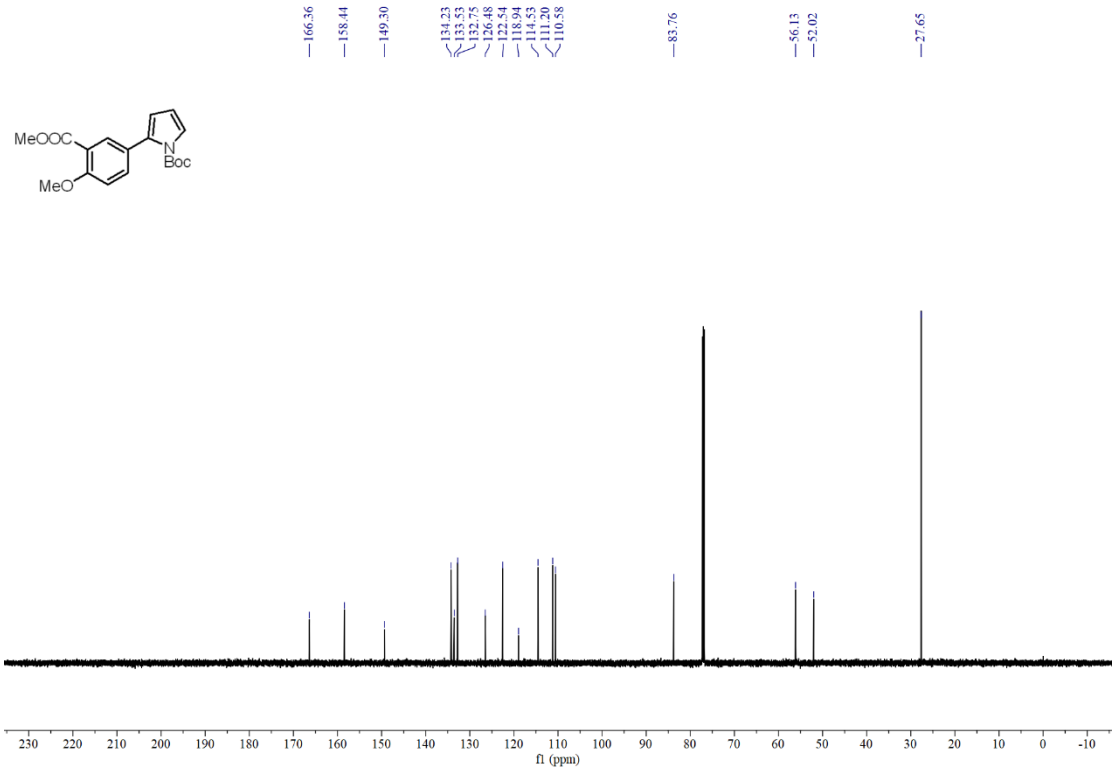
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 51



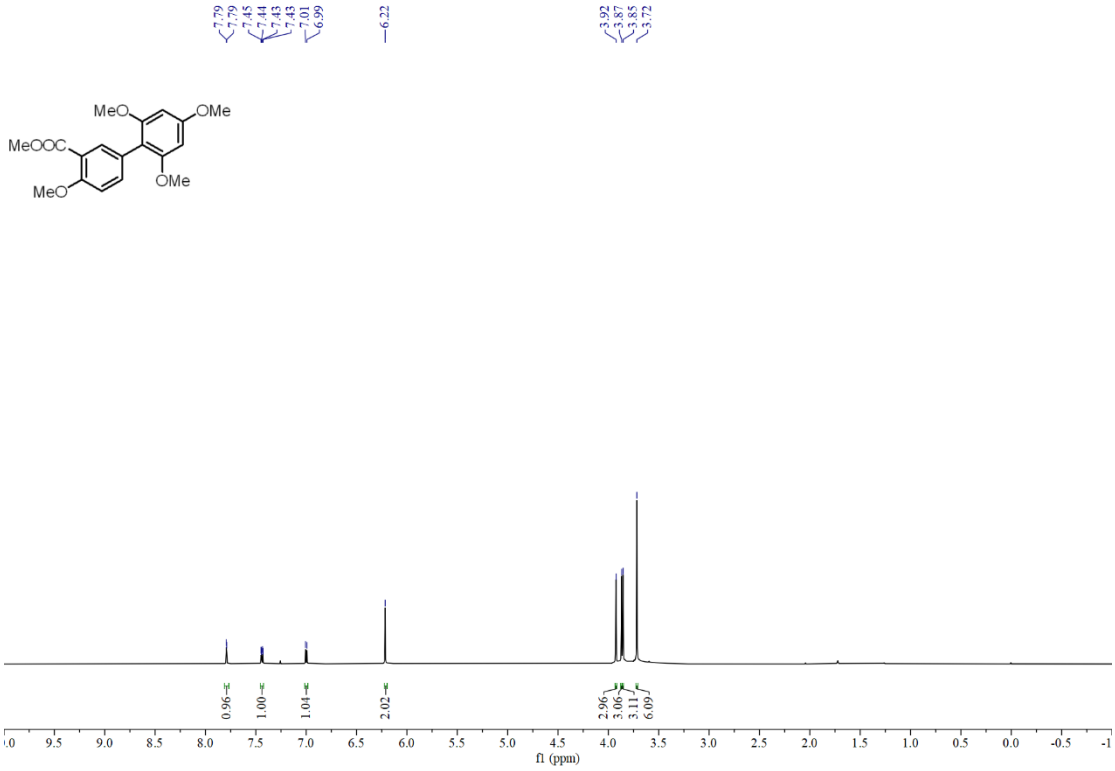
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 52



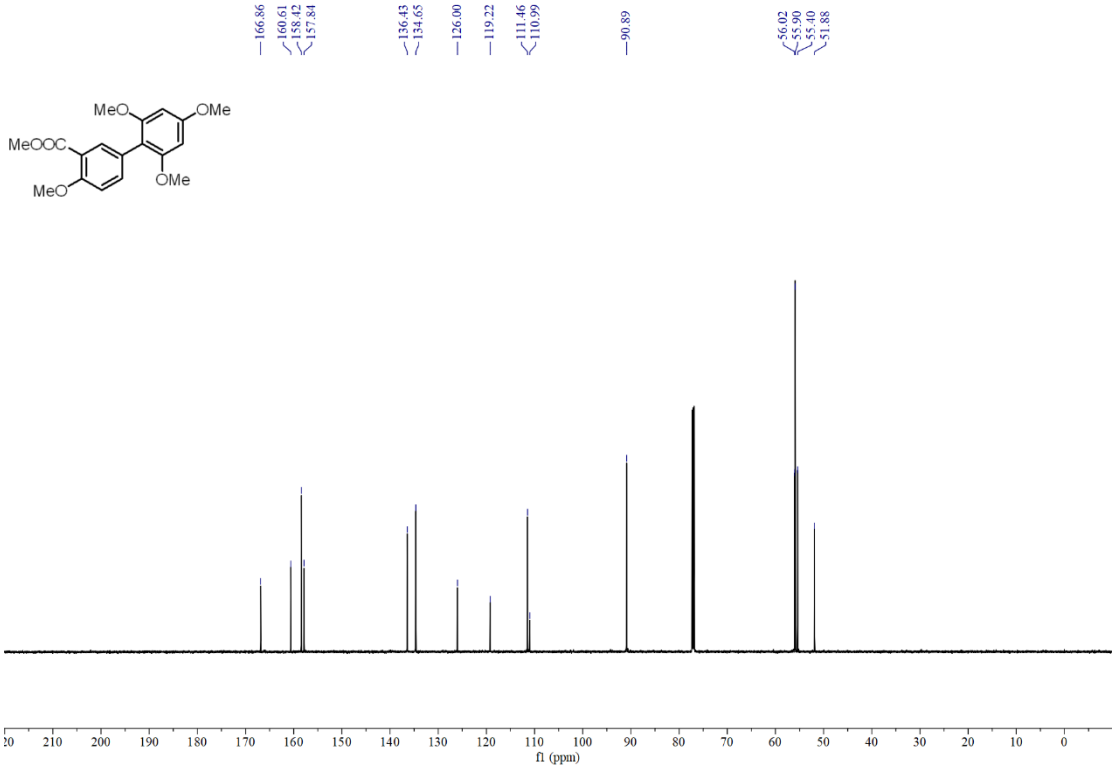
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 52



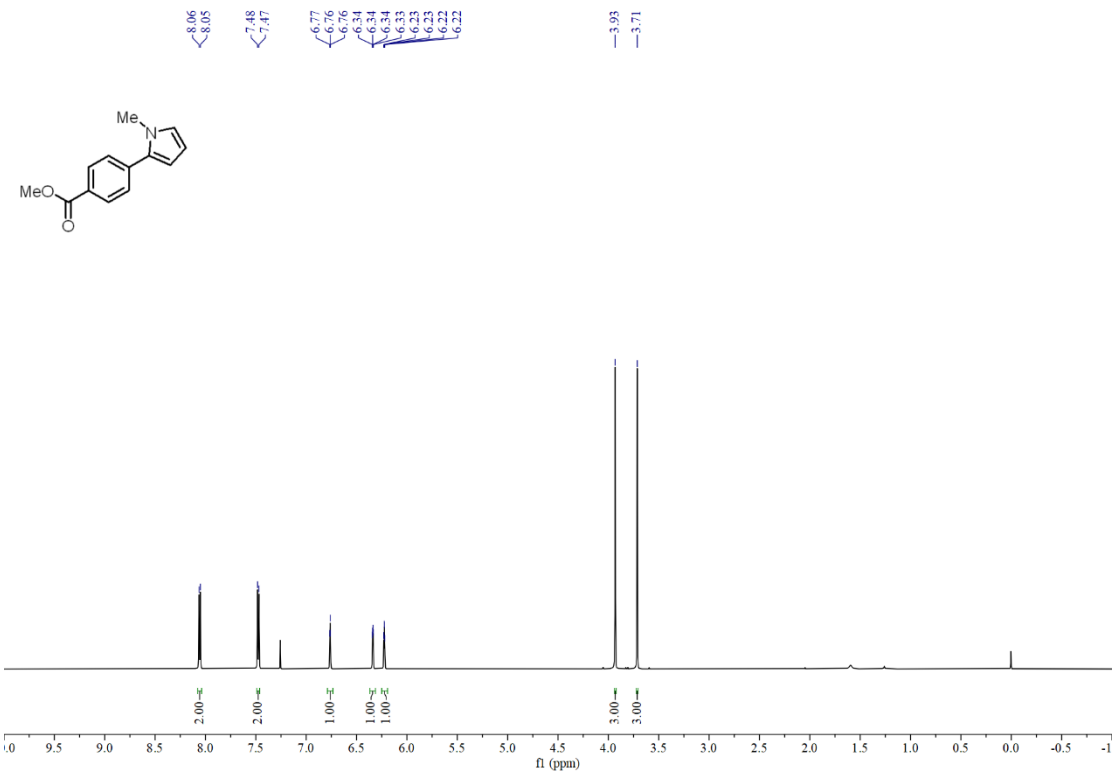
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 53



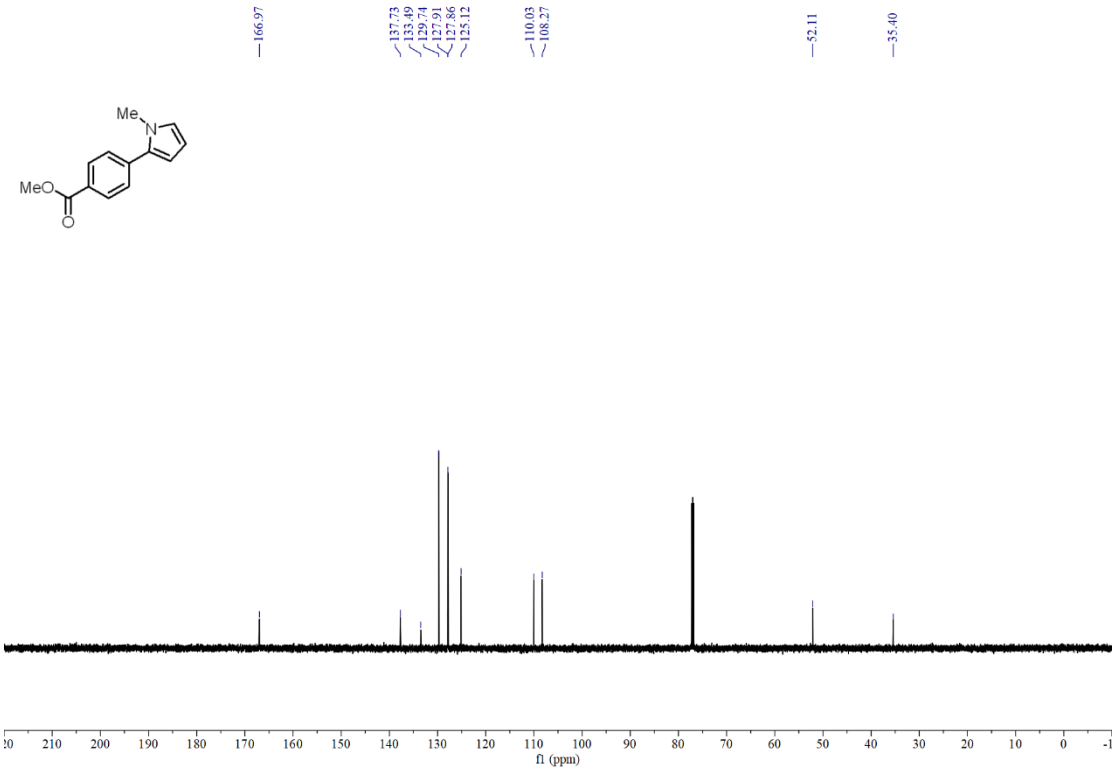
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 53



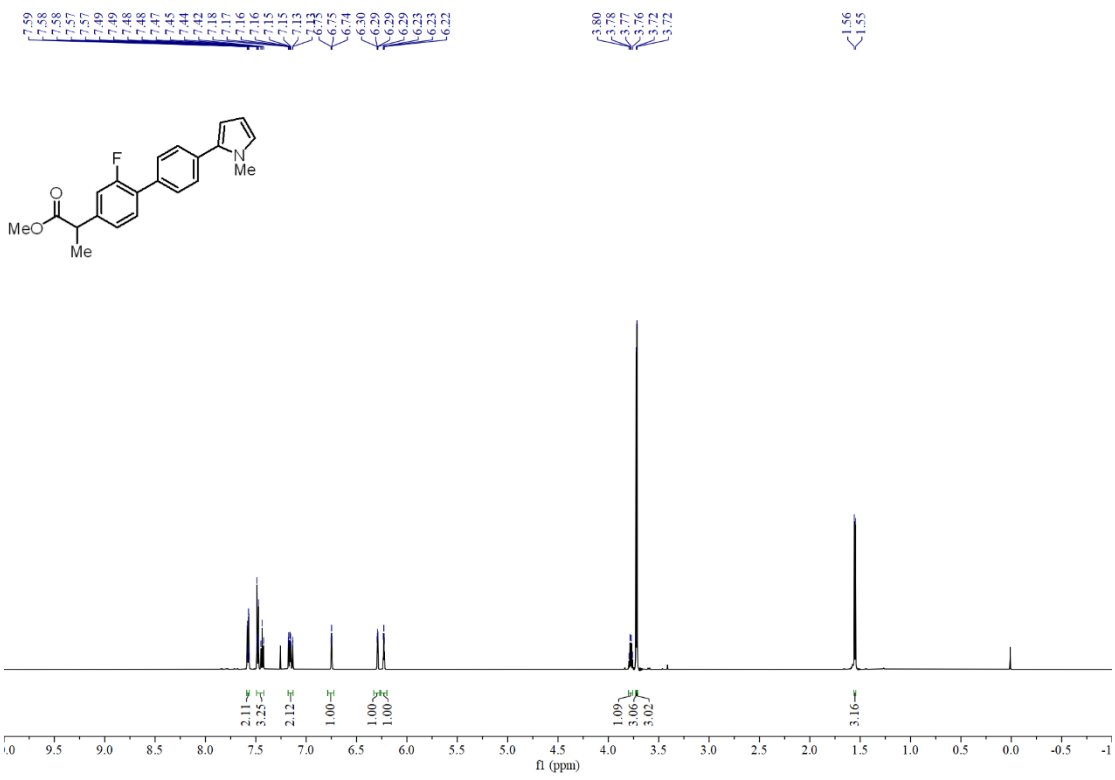
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 54



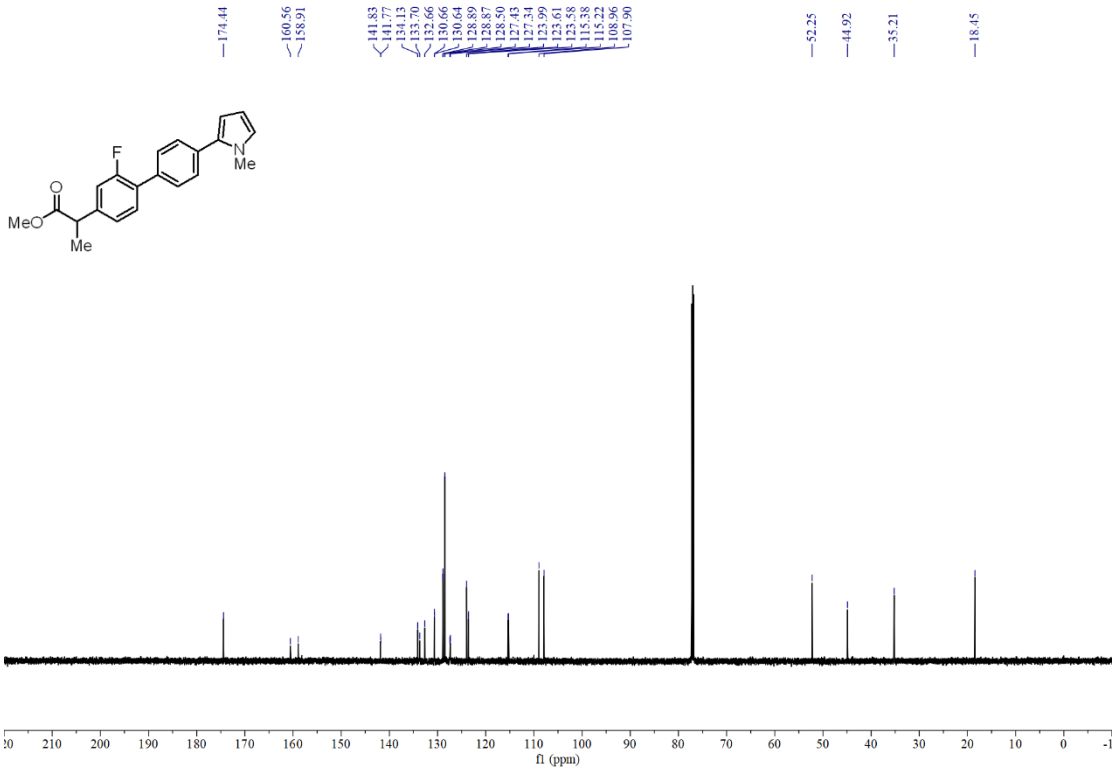
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 54



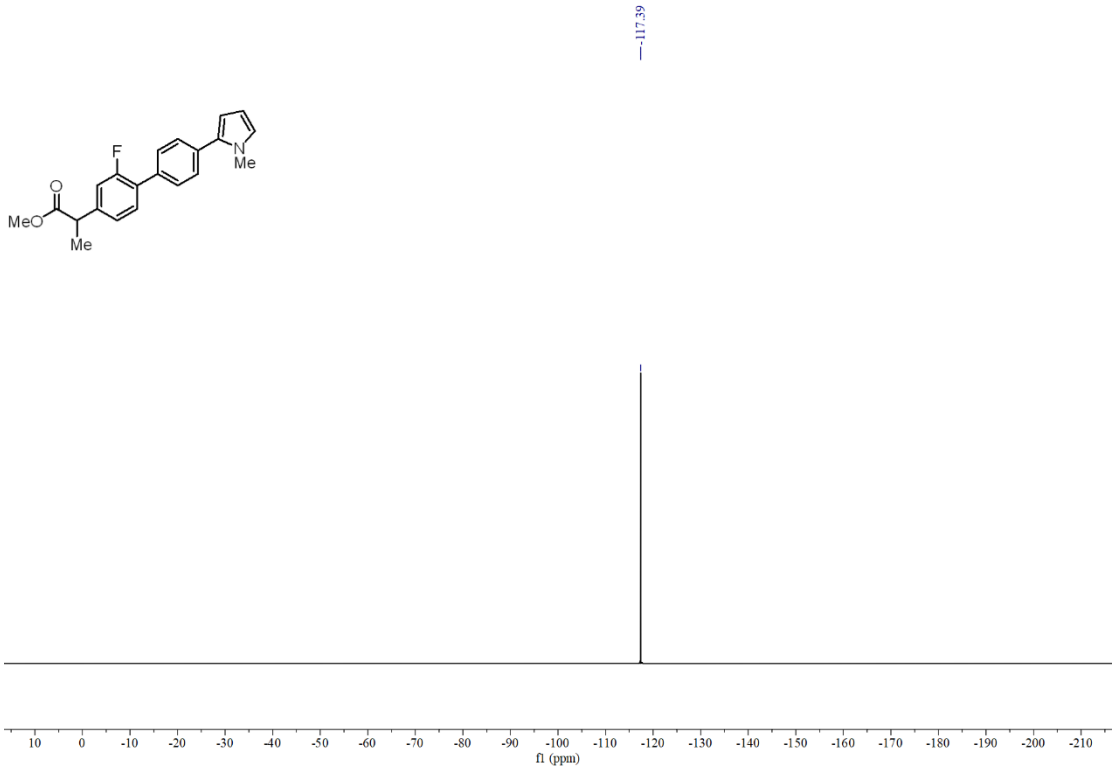
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 55



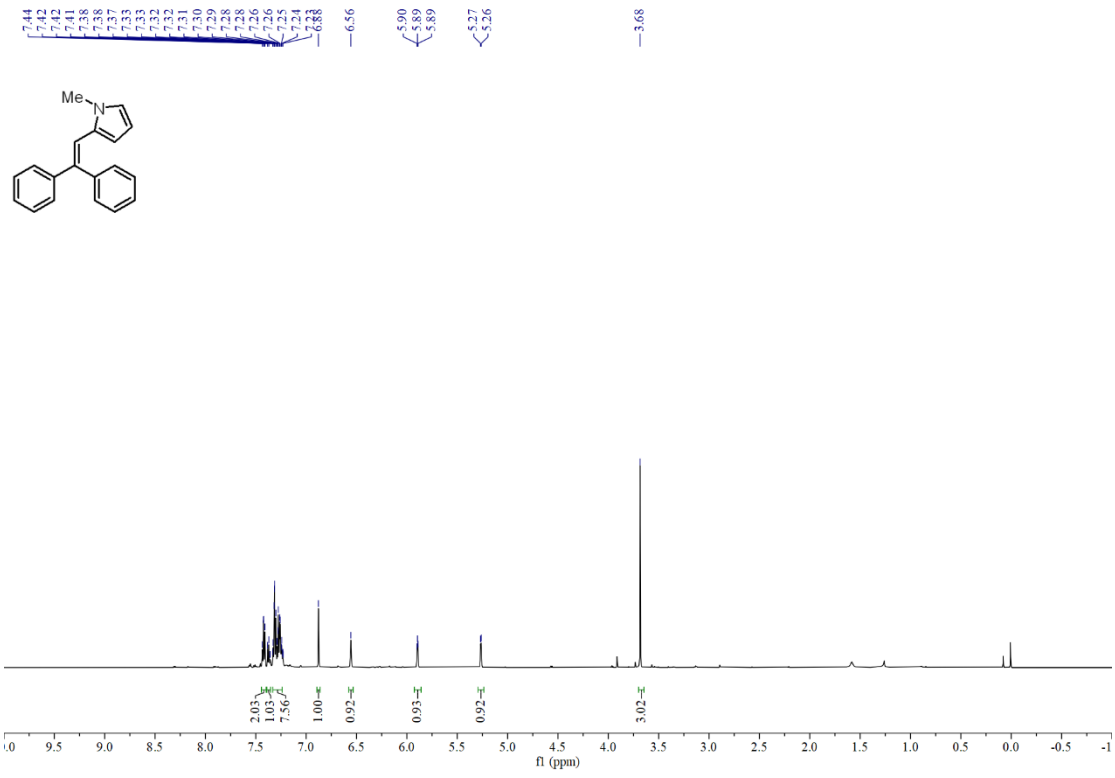
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 55



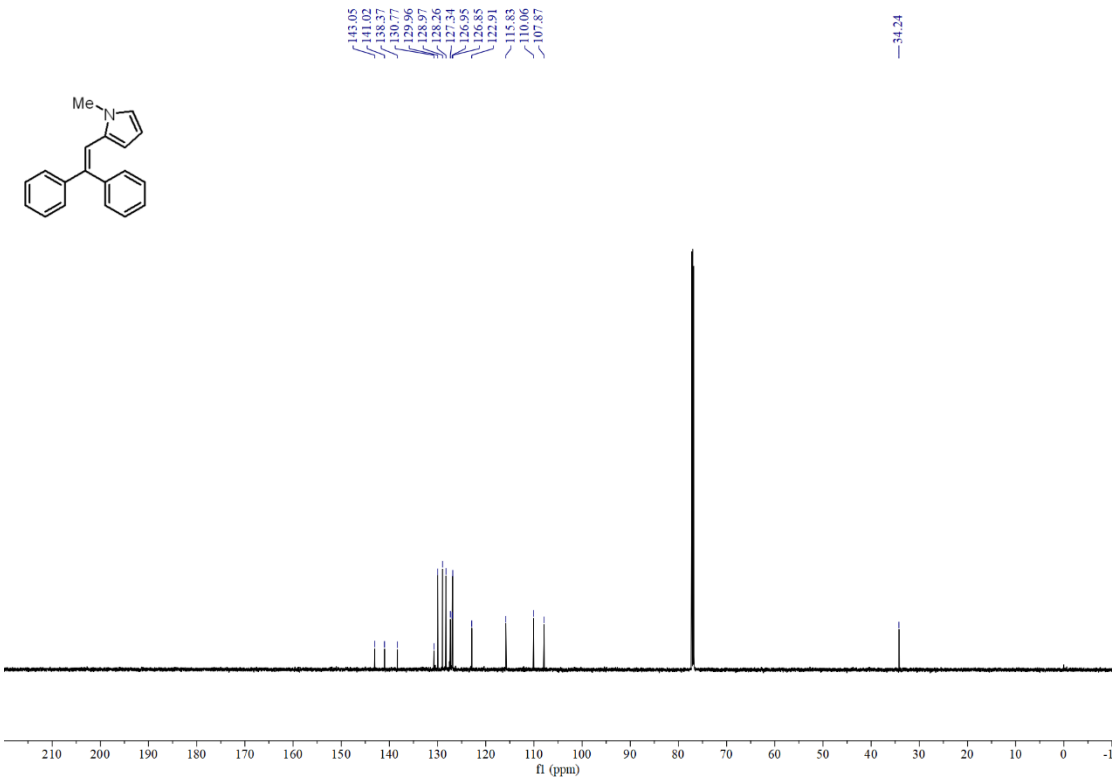
^{19}F NMR (565 MHz, Chloroform-*d*) spectrum of compound 55



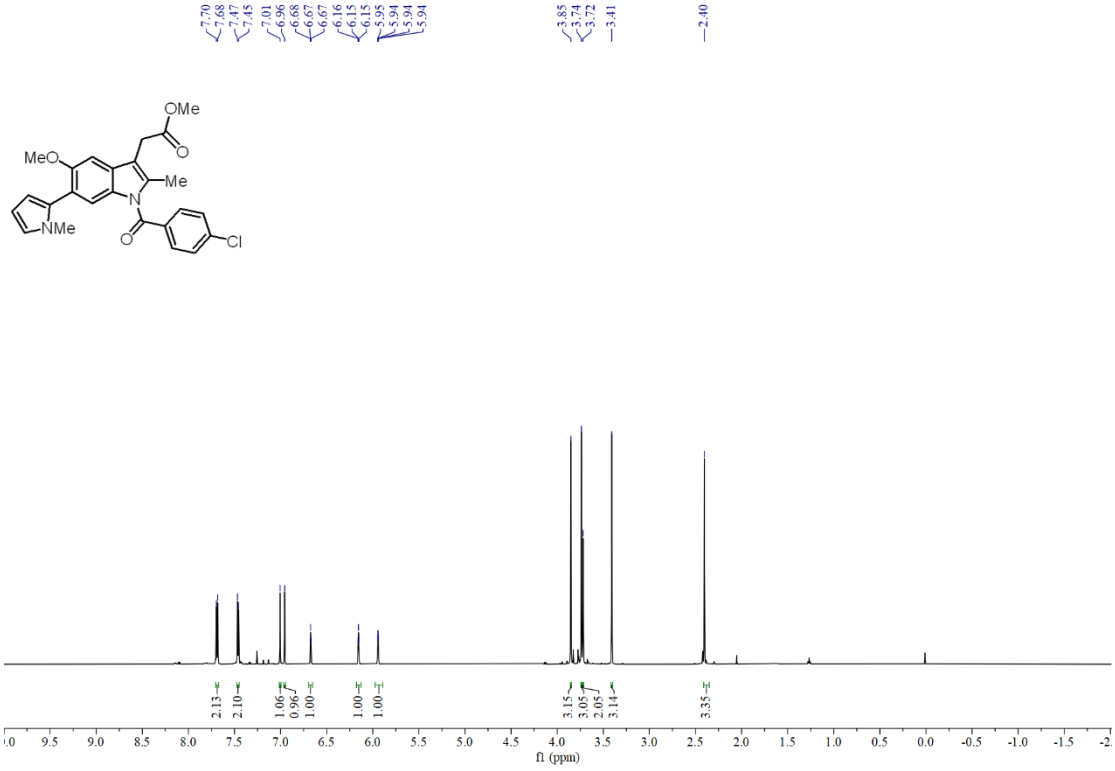
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 56



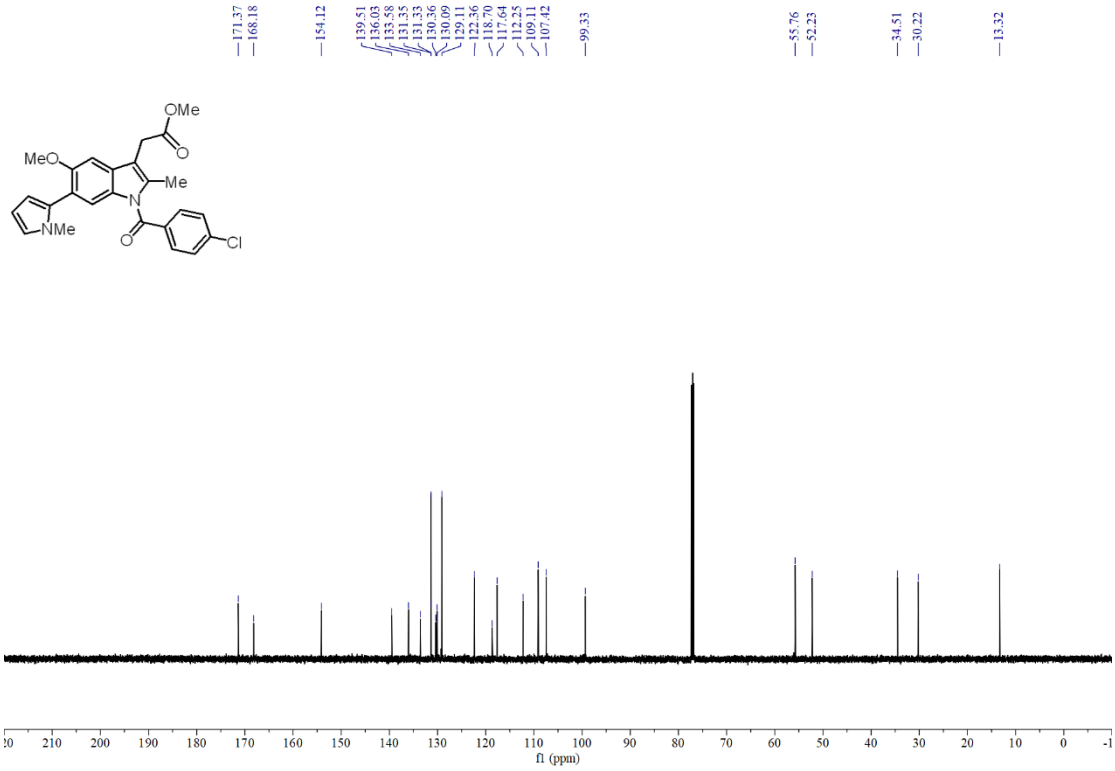
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 56



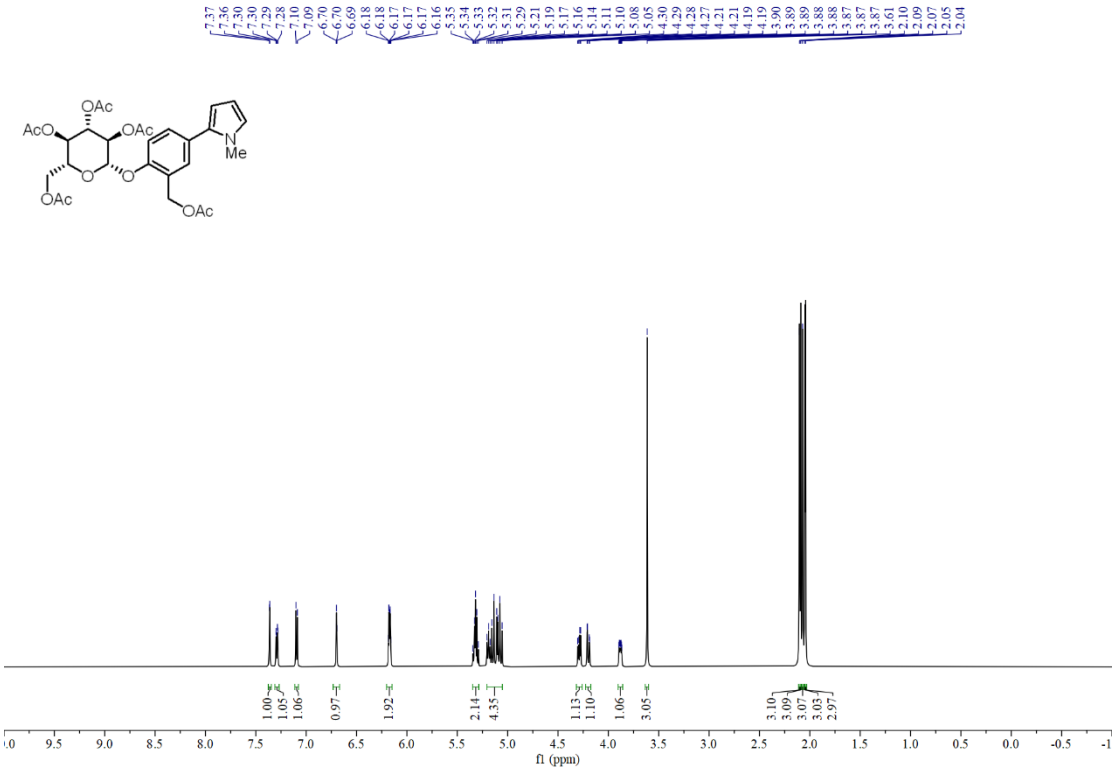
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 57



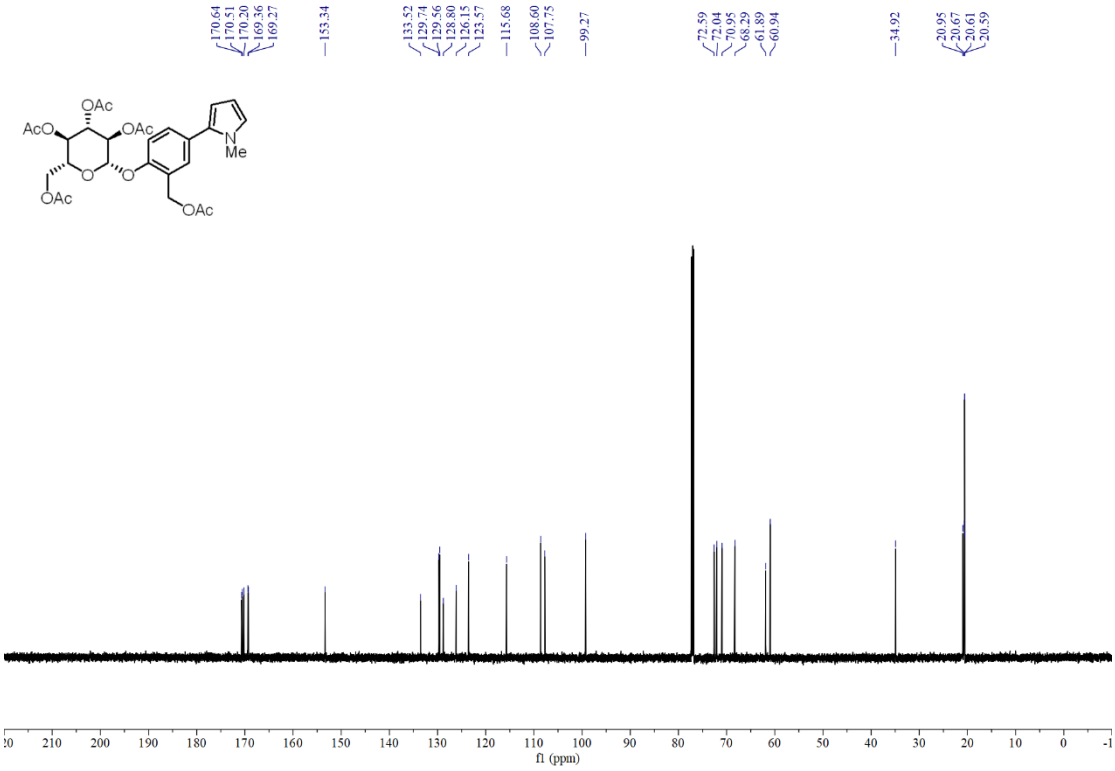
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 57



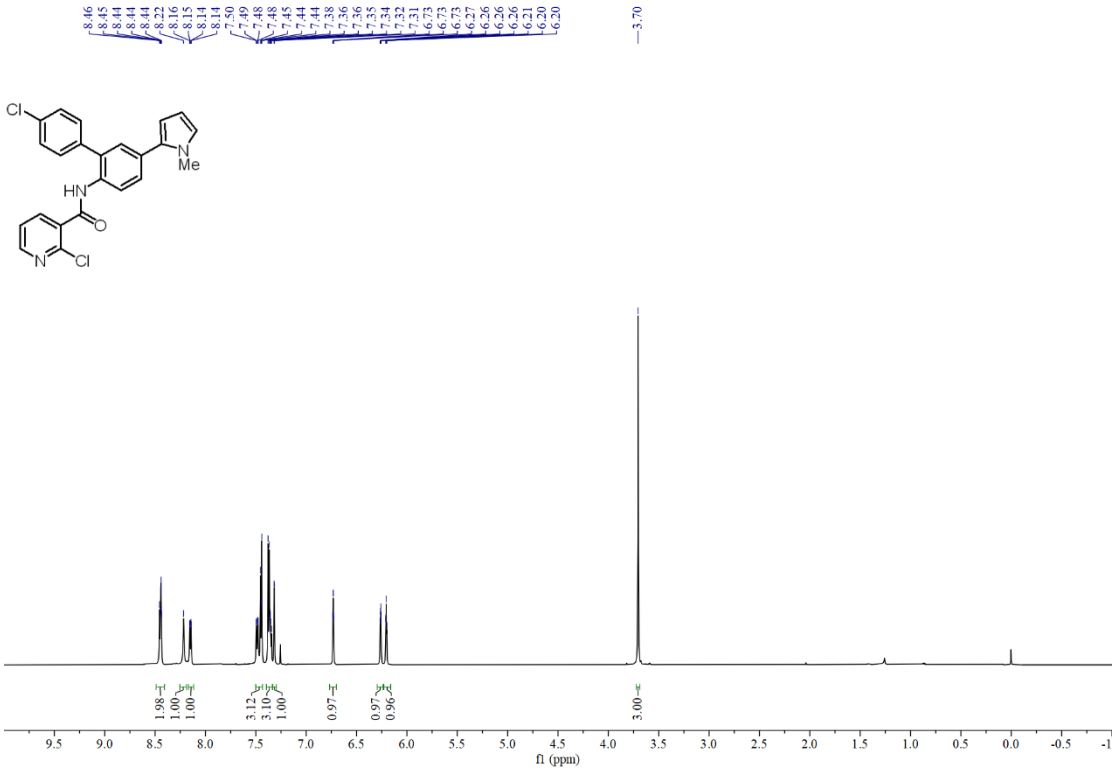
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 58



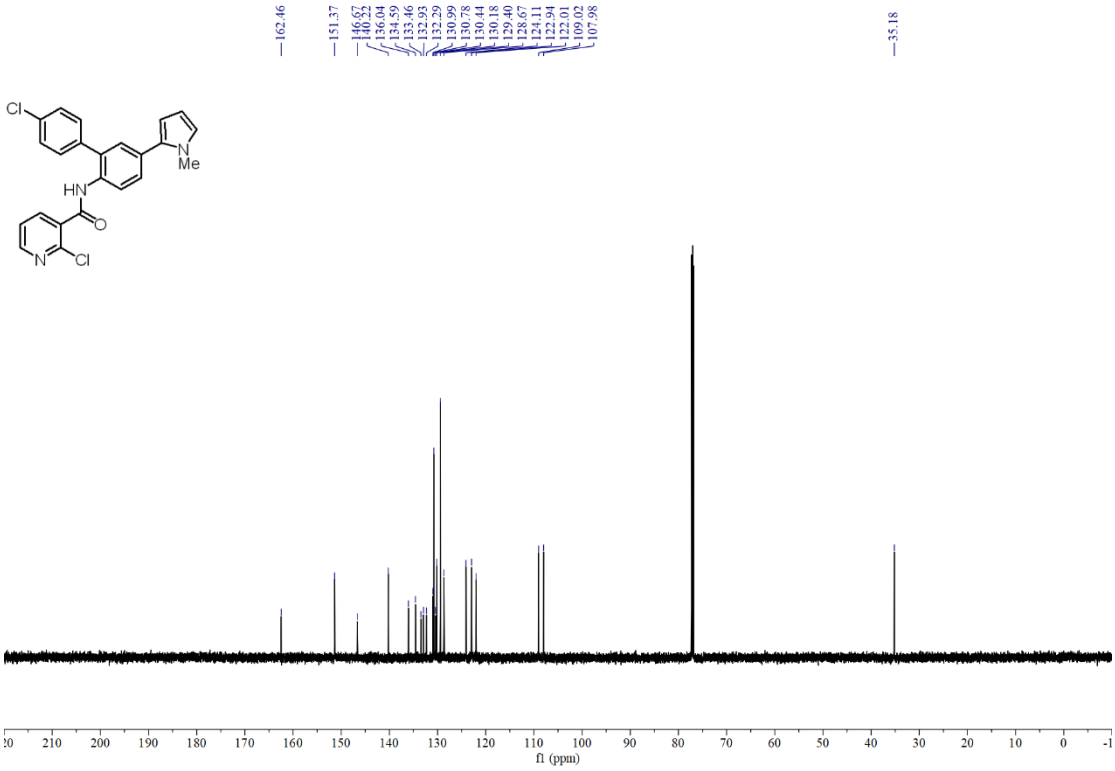
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 58



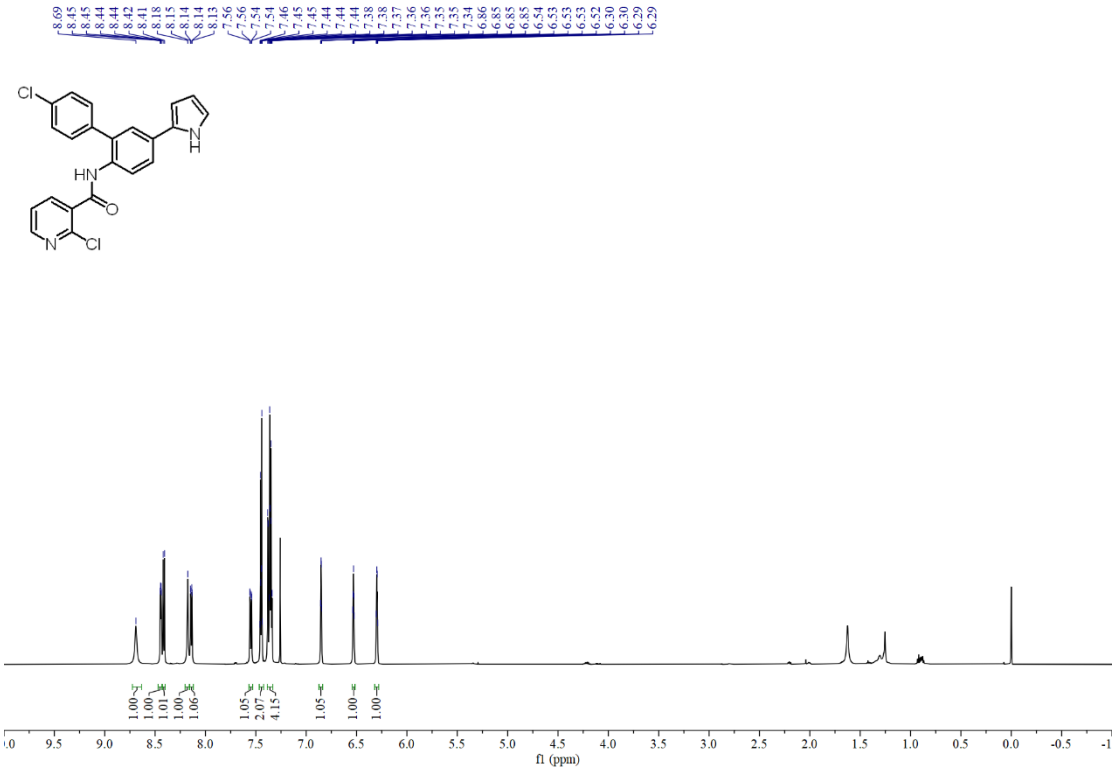
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 59



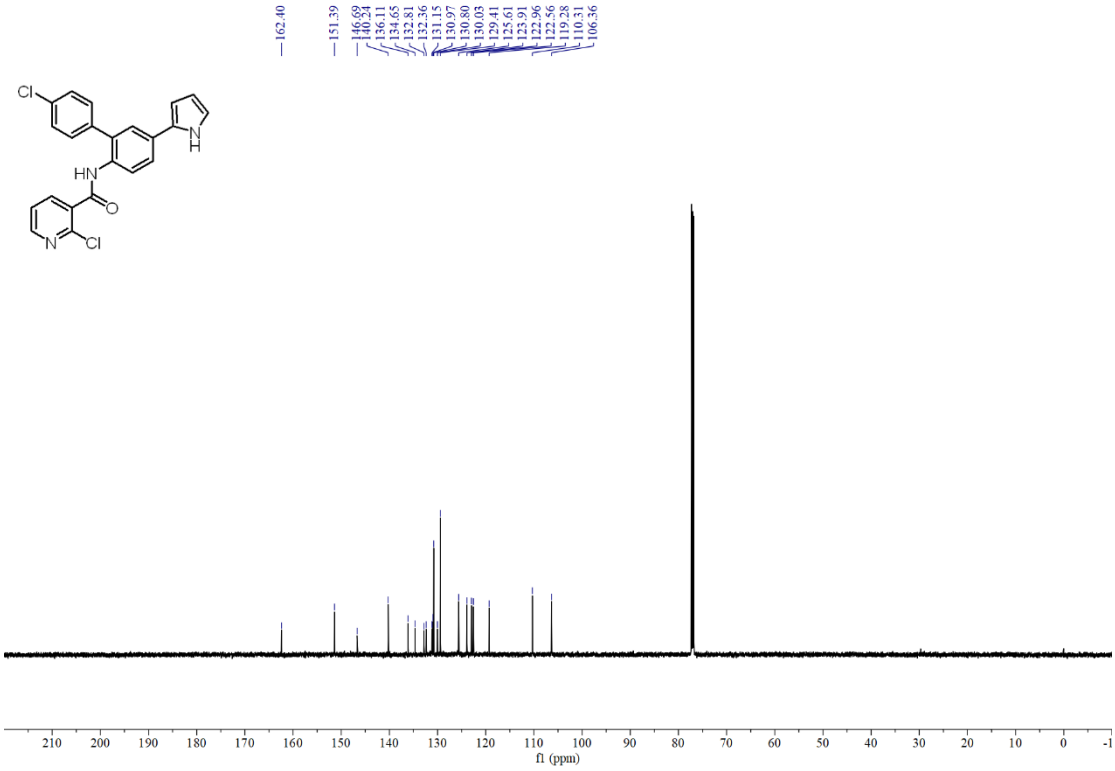
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 59



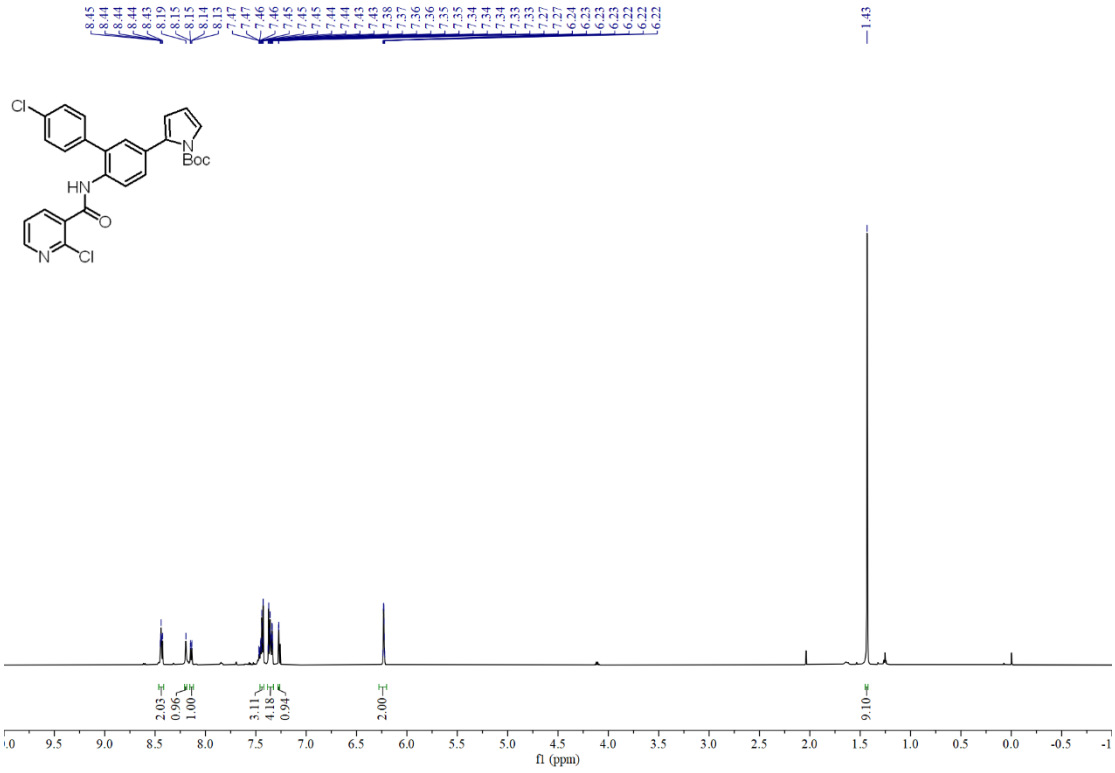
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 60



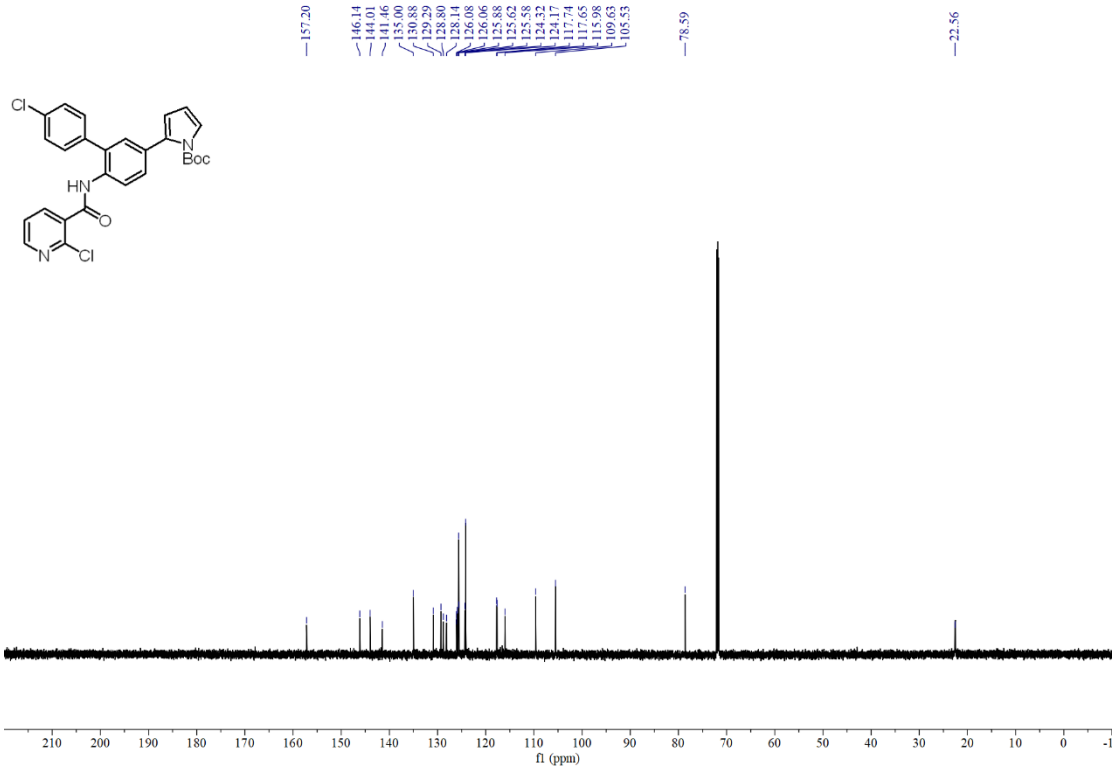
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 60



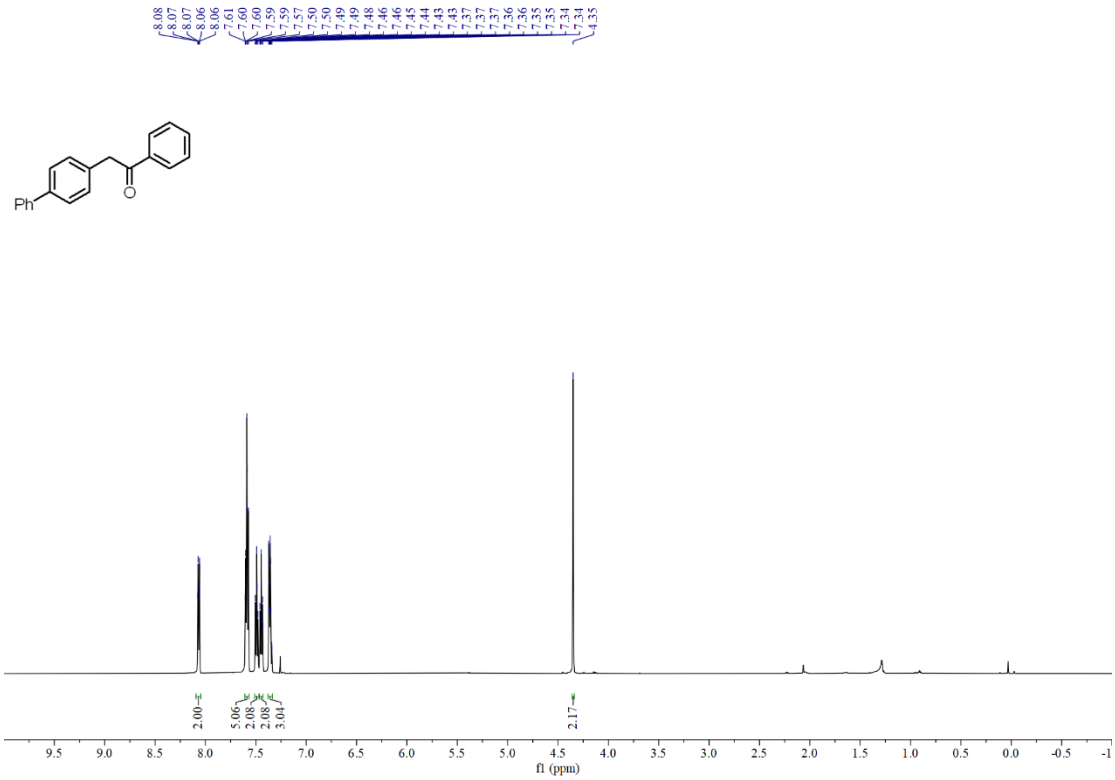
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 61



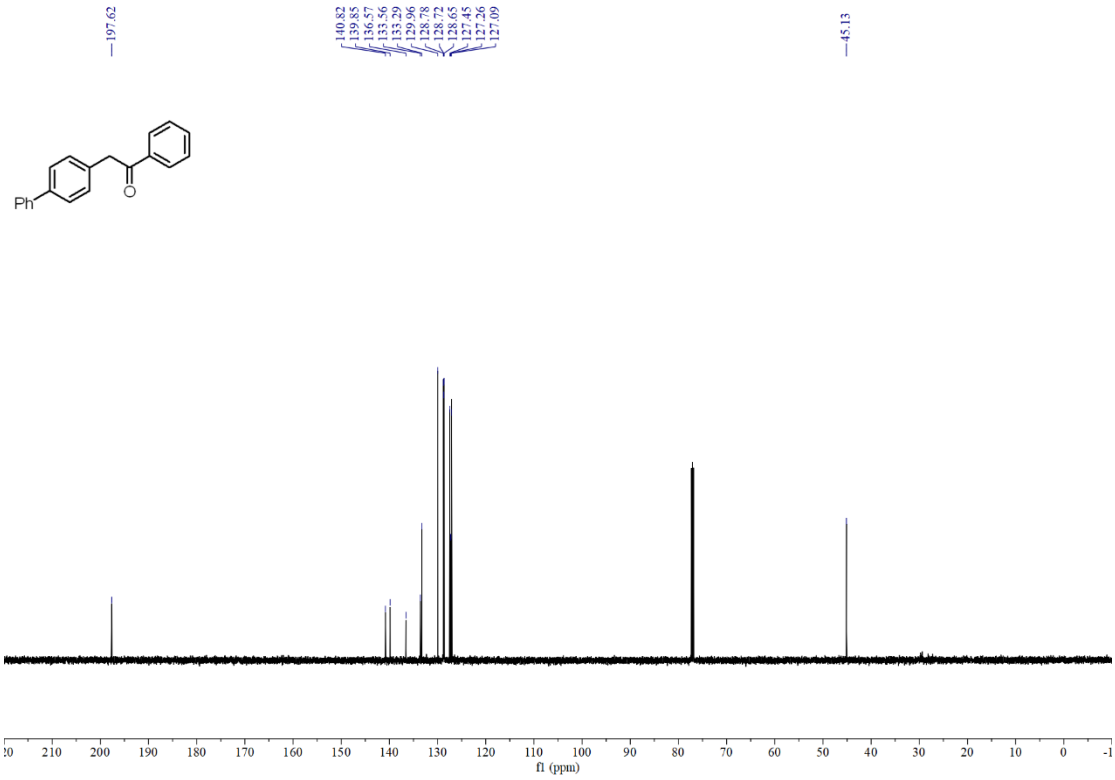
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 61



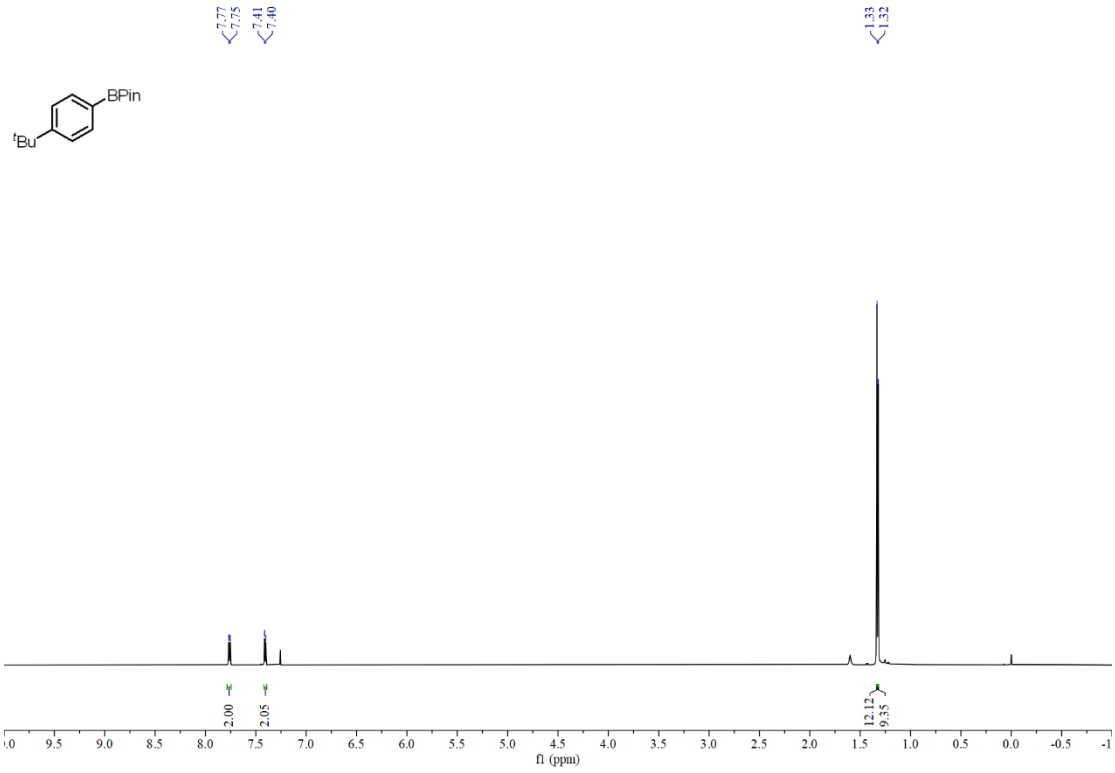
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 62



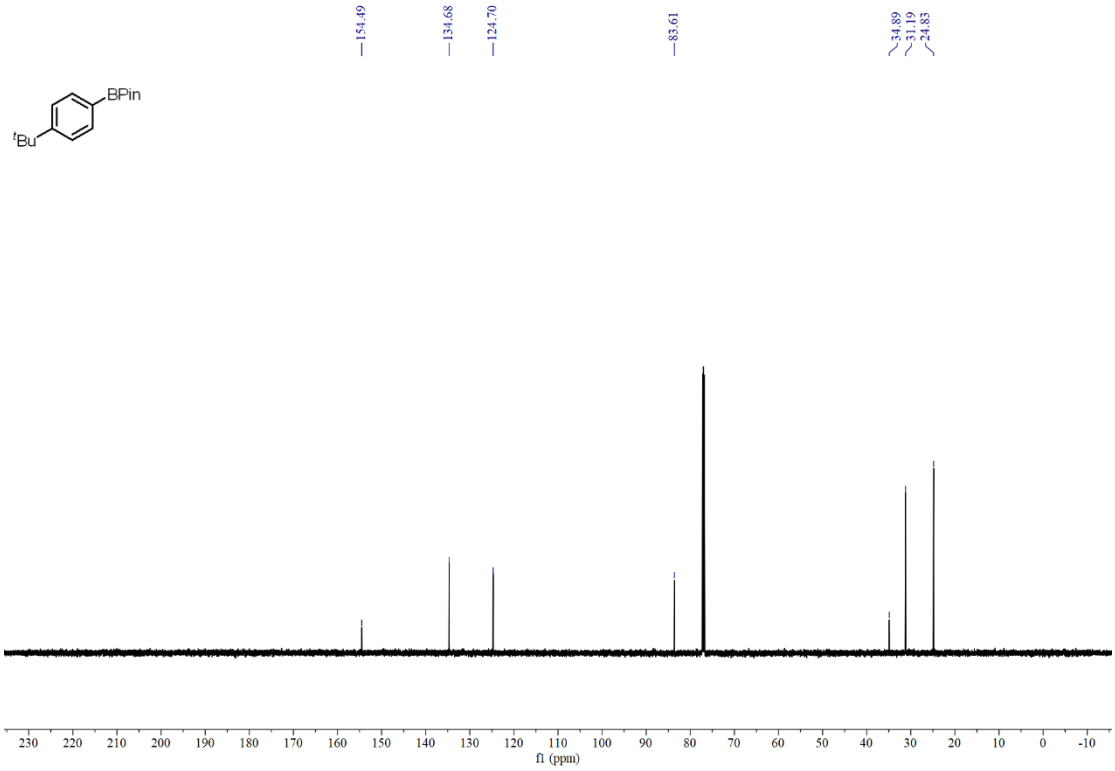
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 62



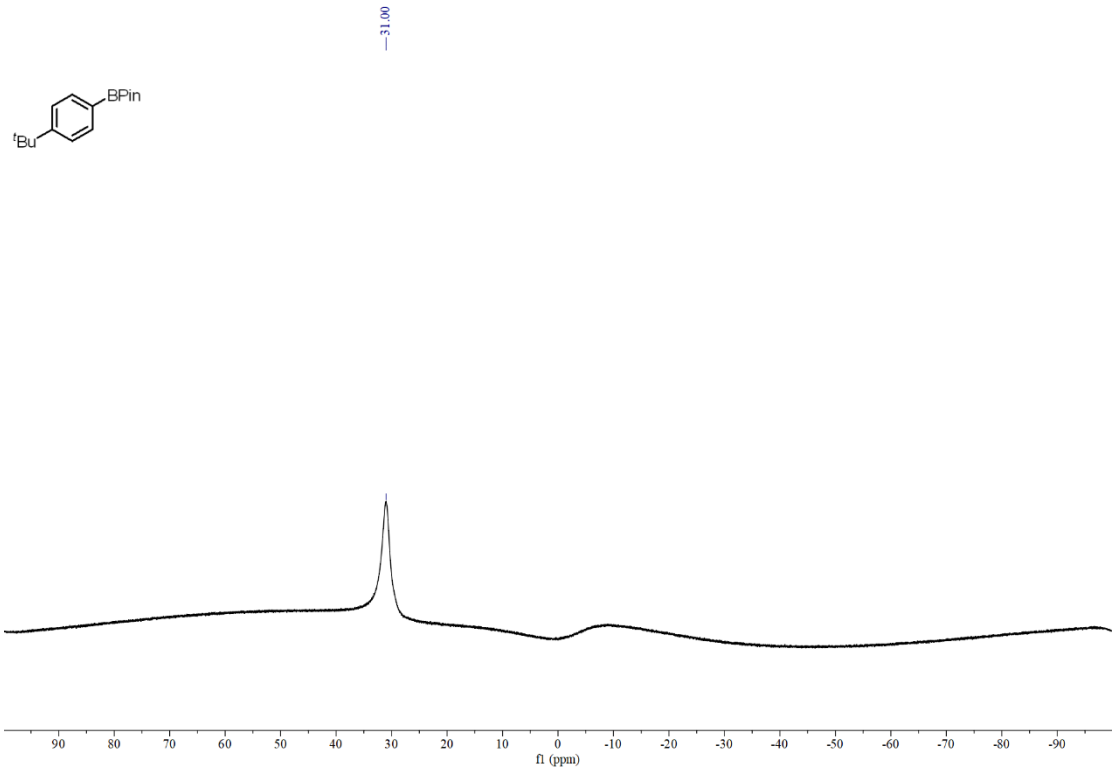
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 63



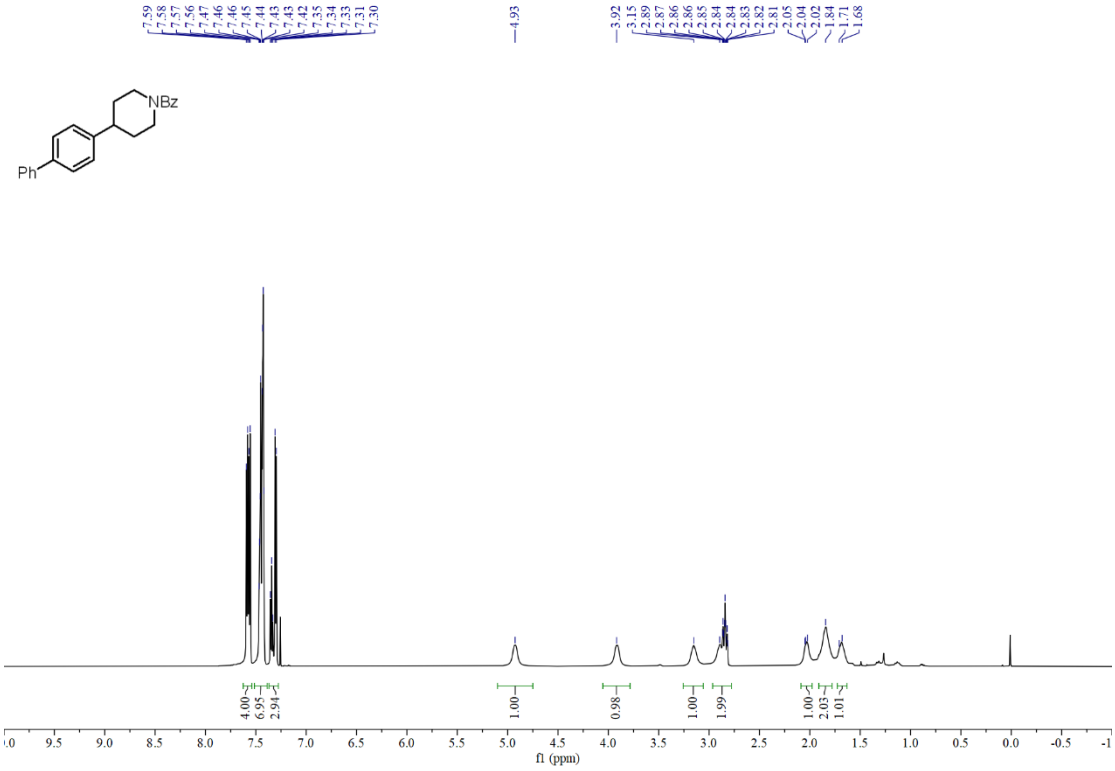
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 63



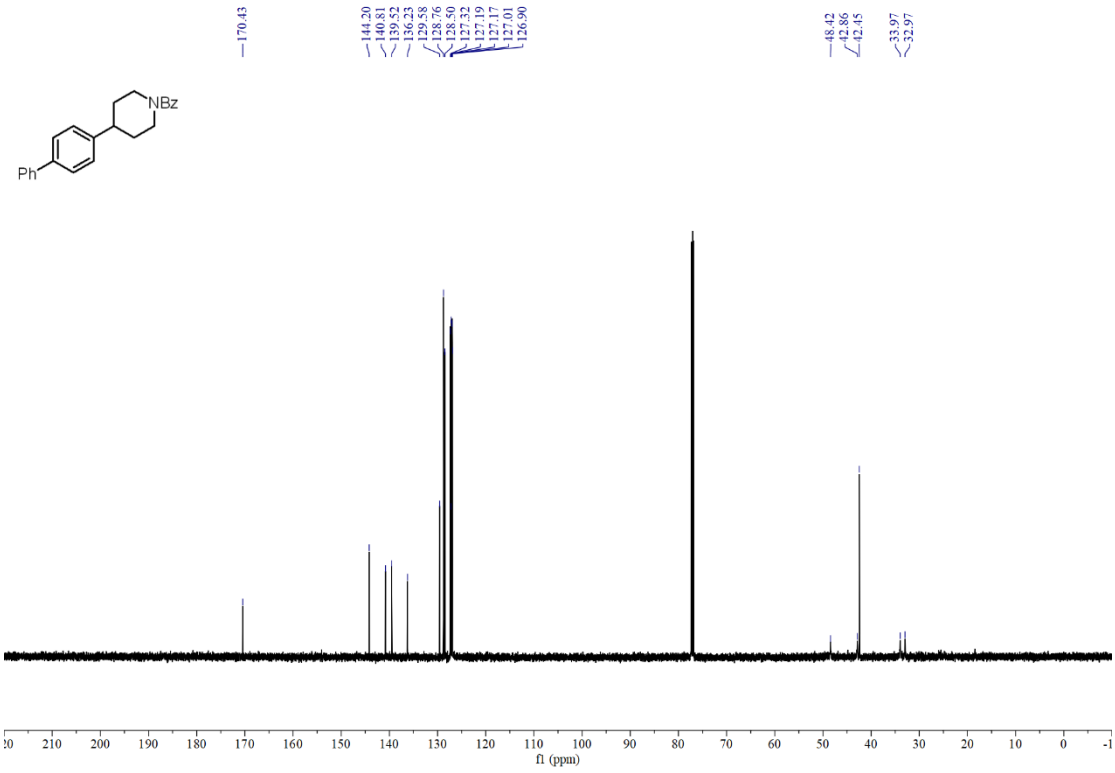
^{11}B NMR (193 MHz, Chloroform-*d*) spectrum of compound 63



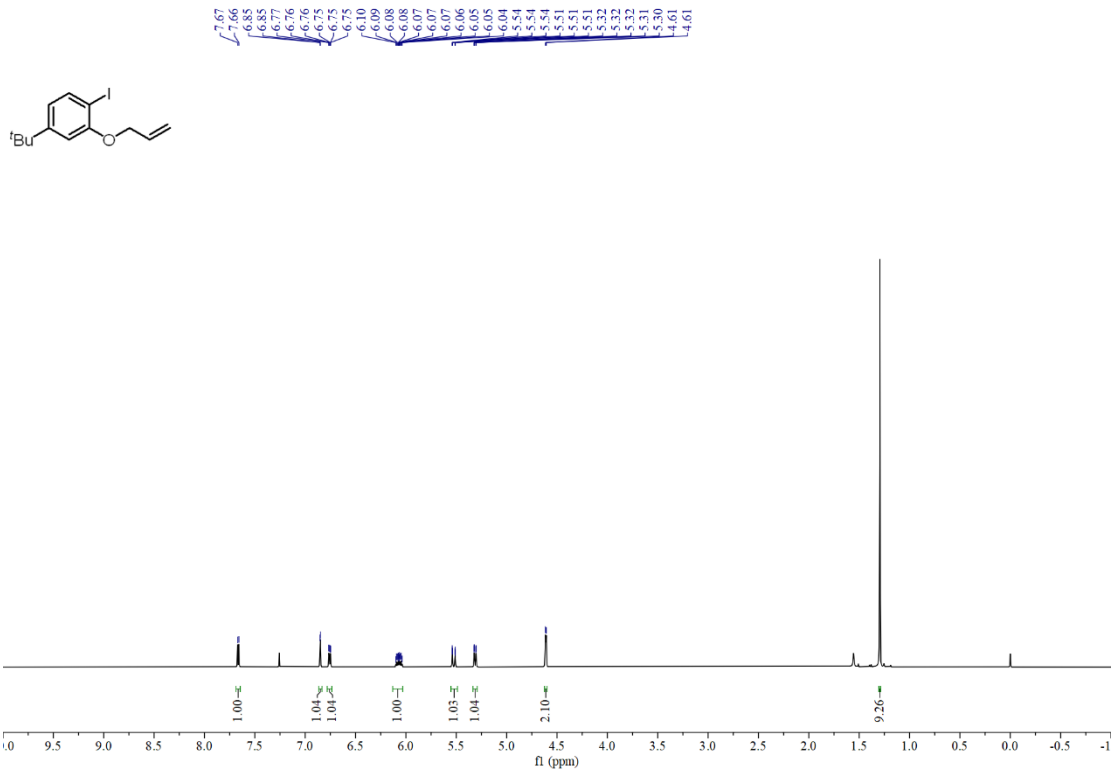
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 67



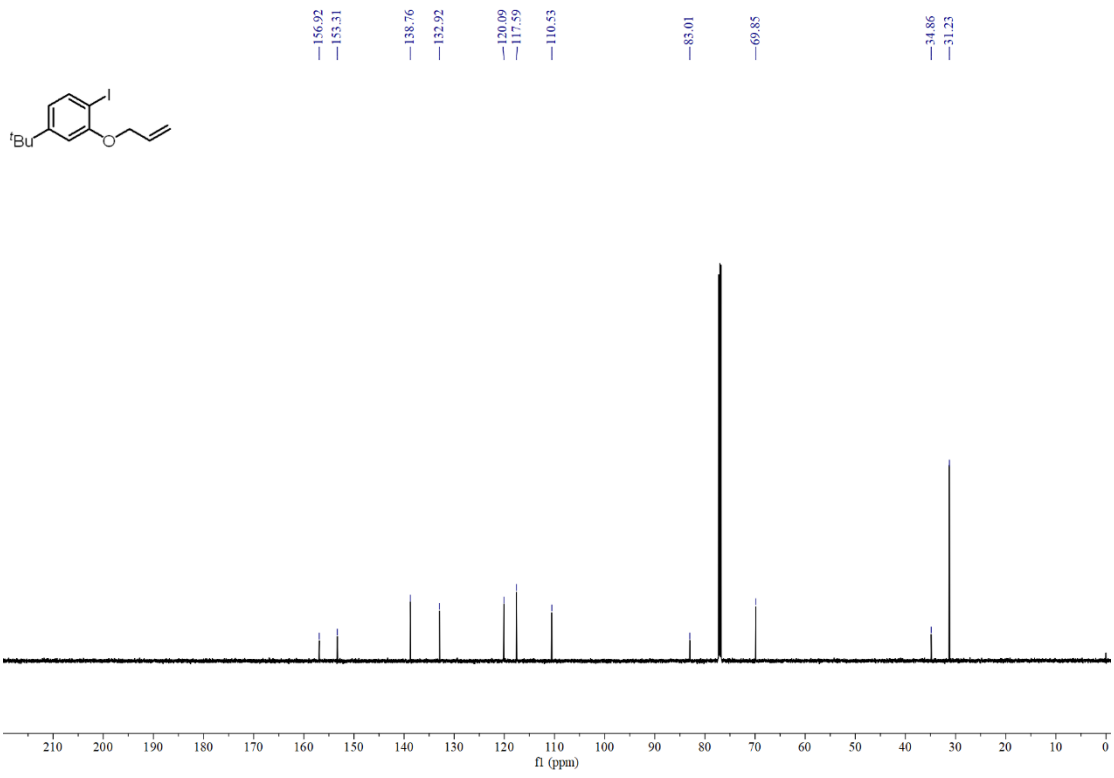
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 67



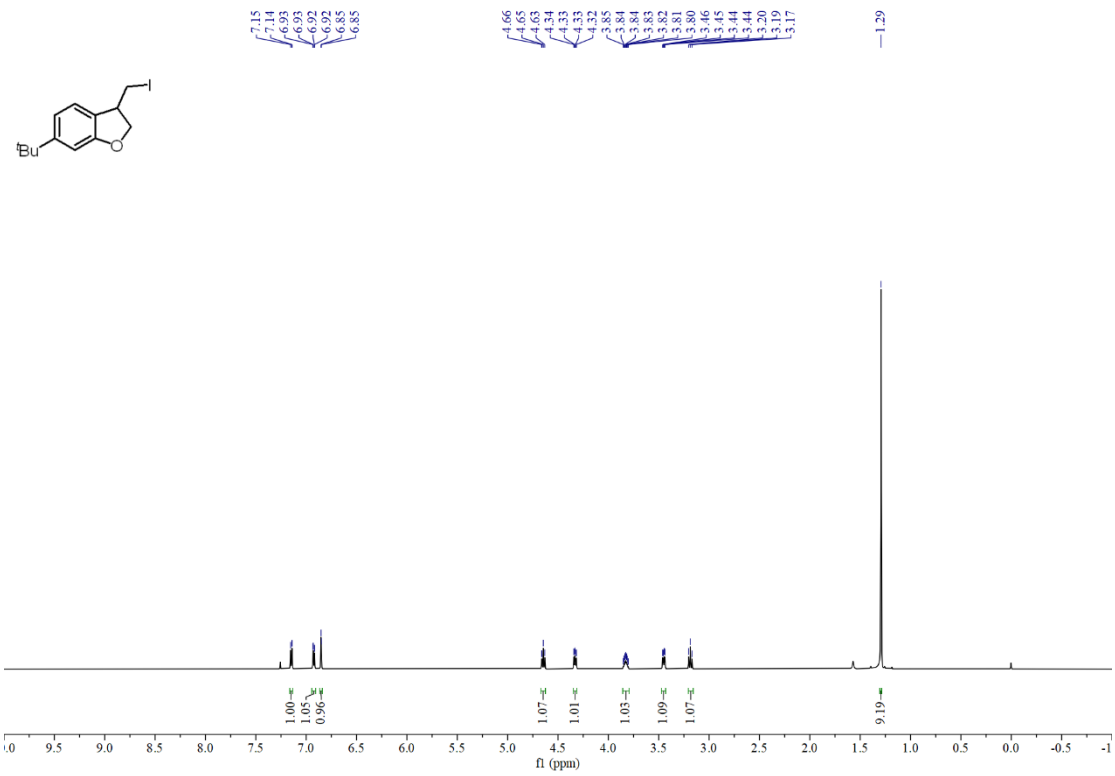
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 70



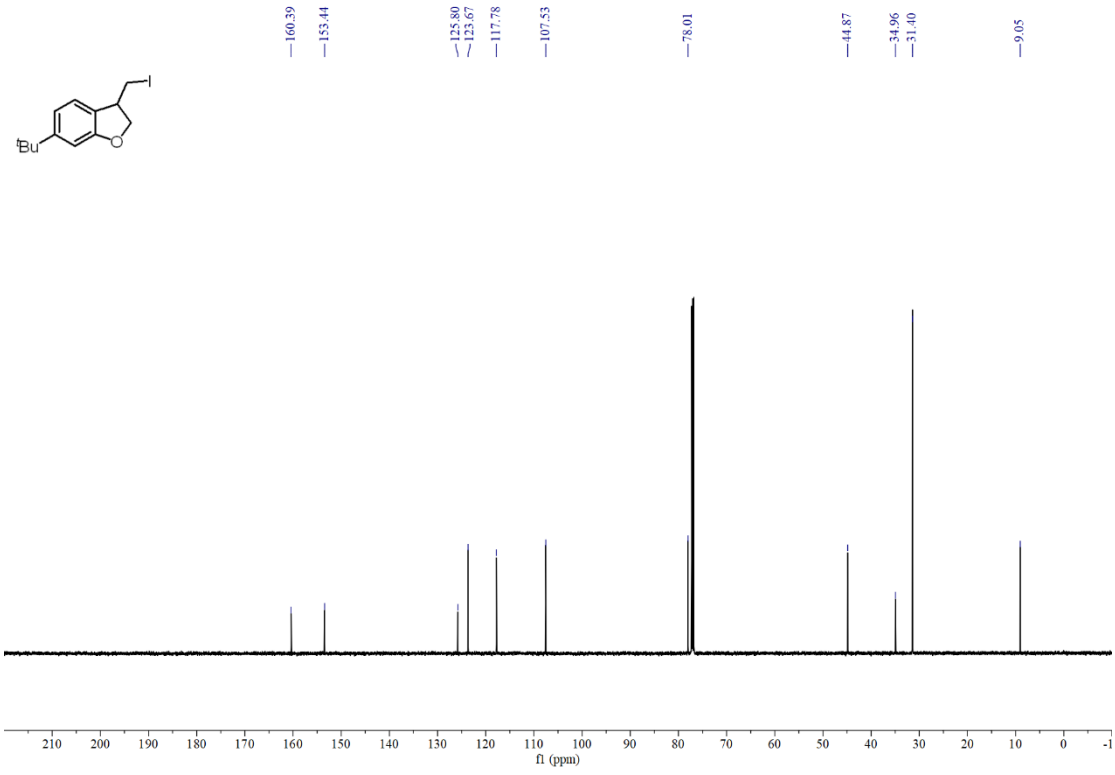
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 70



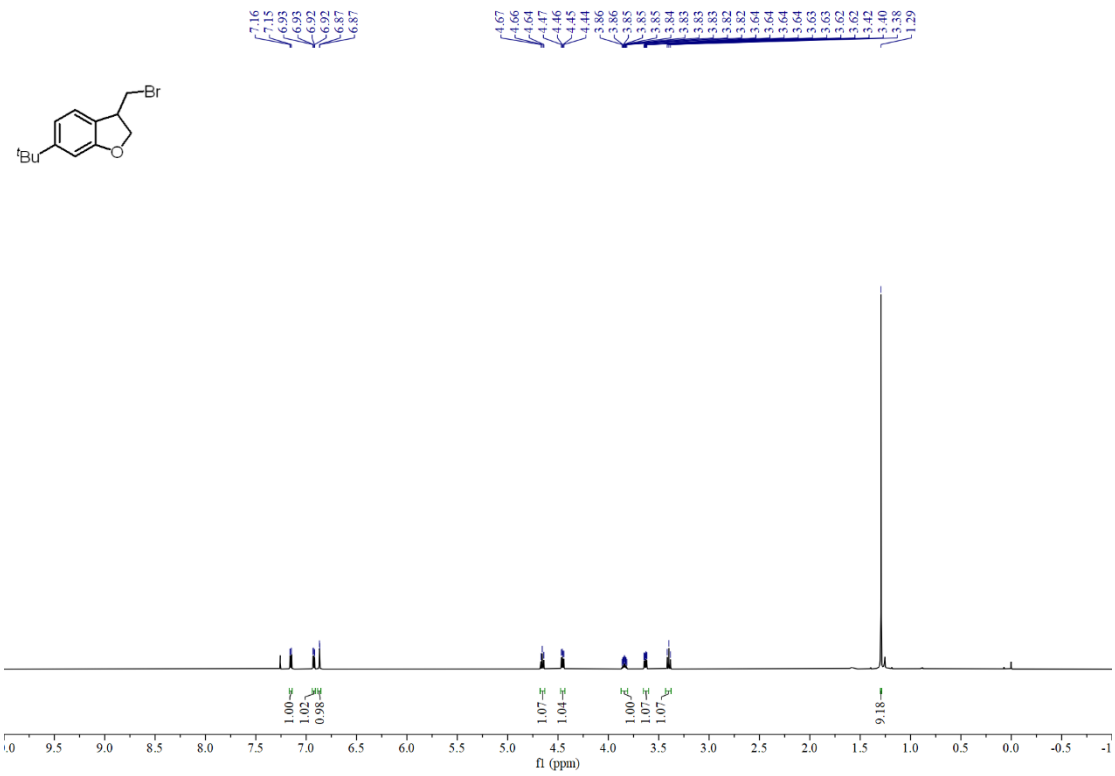
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 71



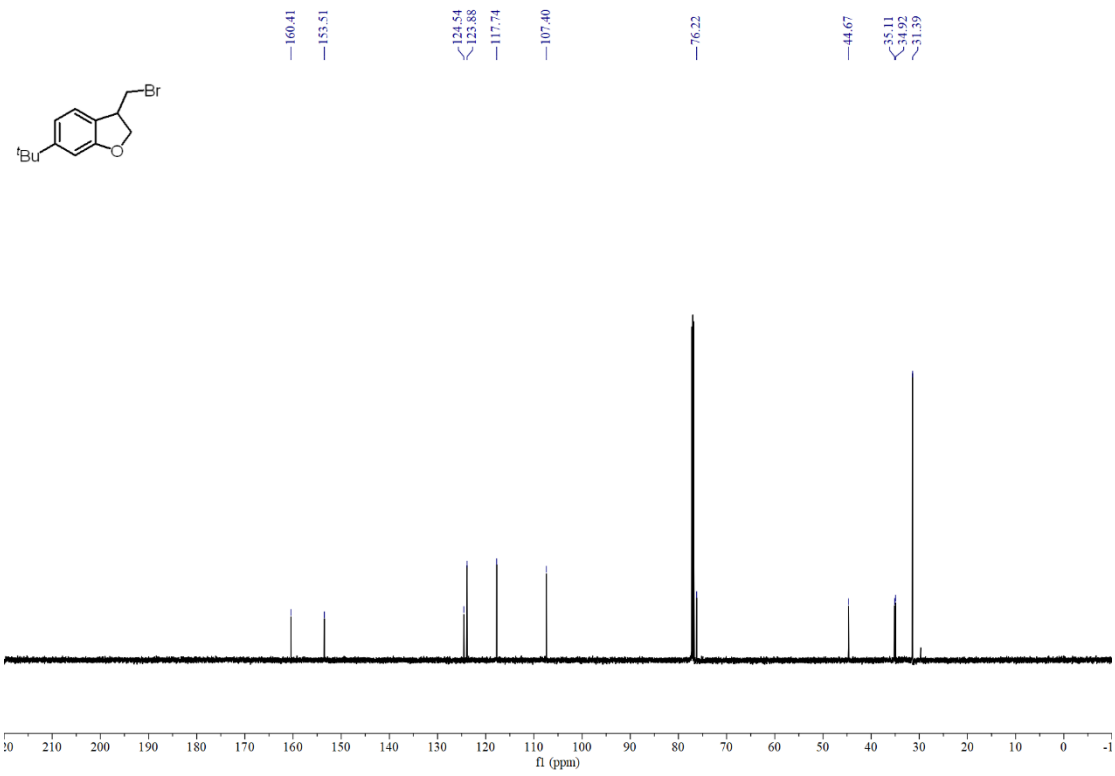
^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 71



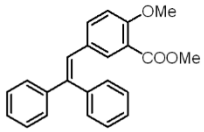
^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 73

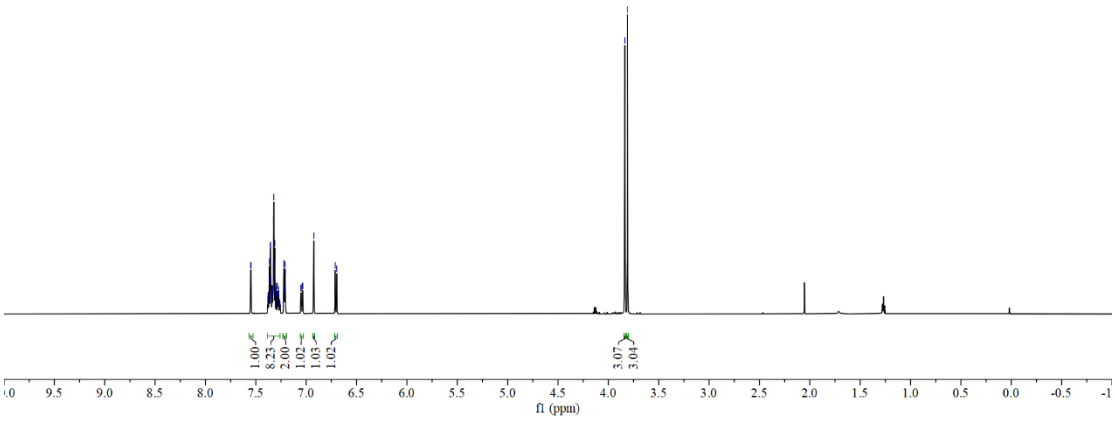


^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 73



^{1}H NMR (600 MHz, Chloroform-*d*) spectrum of compound 75





^{13}C NMR (151 MHz, Chloroform-*d*) spectrum of compound 75