Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of 2-arylbenzofuran-3-carbaldehydes *via* an organocatalytic [3+2] annulation/oxidative aromatization reaction

Huiwen Zhang, Chunmei Ma, Ziwei Zheng, Rengwei Sun, Xinhong Yu* and Jianhong Zhao*

State Key Laboratory of Bioengineering Reactors and Shanghai Key Laboratory of New Drug Design, School of Pharmacy, East China University of Science and Technology, Shanghai 200237, China

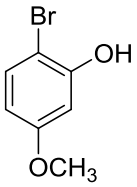
Table of Contents

1. General Remarks

Commercial reagents were used as received without further purification unless otherwise noted. Solvents, unless otherwise specified, were reagent grade and distilled once prior to use. ^{1}H and ^{13}C NMR ^{19}F NMR spectra were recorded on Bruke Avance-400 (400 MHz, 100 MHz, and 376 MHz, respectively). Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26, dimethyl sulfoxide δ 2.50), carbon (chloroform δ 77.00, dimethyl sulfoxide δ 39.52) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets). Coupling constants (*J*) in Hertz (Hz), integration. Melting points were determined in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. High resolution mass spectrometry (HRMS) were carried out using Micromass GCTTM gas chromatograph-mass spectrometer. Flash chromatography was carried out with silica gel (300-400 mesh) using mixtures of petroleum ether (b.p. 60-90 ℃) and ethyl acetate as eluents.

2. Synthesis of Starting Materials

2-bromo-5-methoxyphenol (1a)

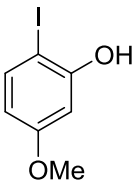


To a solution of 3-methoxyphenol (2.48 g, 20.0 mmol) in technical grade CH_2Cl_2 (500 mL) was added *N*-bromosuccinimide (3.56 g, 20.0 mmol) in one portion. The reaction mixture was stirred at room temperature for 2 h, and then quenched with water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) to afford 2-bromo-5-methoxyphenol as a colorless oil (2.42 g, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.9 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.42 (dd, *J* = 8.9, 2.8 Hz, 1H), 5.50 (s, 1H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 153.0, 131.9, 108.4, 101.7, 100.9, 55.5.

Physical and spectral data were found to be consistent with the reported literature[1]

2-iodo-5-methoxyphenol (S1)



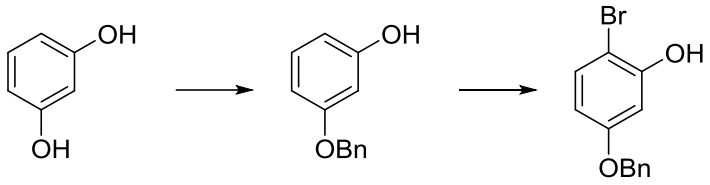
To a solution of 3-methoxyphenol (0.25 g, 2 mmol) in $CHCl_3$ (10 mL) was added $Ag(CO_2CF_3)_2$ (0.45 g, 2 mmol). A solution of I_2 (0.51 g, 2 mmol) in $CHCl_3$ (1 mL) was added dropwise over a

period of approximately 30 min and the mixture was stirred at room temperature overnight. Then the reaction was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) to afford 2-iodo-5-methoxyphenol as a white solid (0.38 g, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.33 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.35 (s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 155.6, 138.0, 109.4, 100.9, 74.4, 55.4.

Physical and spectral data were found to be consistent with the reported literature[2]

5-benzyloxy-2-bromophenol (1b)



S2 **1b**

Benzyl bromide (1.71 g, 10 mmol) was added dropwise to a stirred suspension of resorcinol (2.2 g, 20 mmol) and K_2CO_3 (1.38 g, 10 mmol) in acetone (20 mL) under argon atmosphere. The mixture was heated under reflux overnight, filtered and washed with water (10 mL), dried over Na_2SO_4, subjected to filtration, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20:1) to afford 3-benzyloxyphenol as a brown oil (1.4 g, 70%).

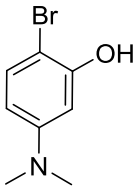
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 7.12 (t, *J* = 8.1 Hz, 1H), 6.56 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.48 (t, *J* = 2.3 Hz, 1H), 6.43 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.02 (s, 2H), 4.62 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 156.7, 136.8, 130.2, 128.6 (2C), 128.0, 127.5 (2C), 108.1, 107.3, 102.5, 70.0.

To a solution of 3-benzyloxyphenol (1.0 g, 5 mmol) in CH_2Cl_2 (200 mL) was added *N*-bromosuccinimide (0.89 g, 5 mmol) under ice bath. The reaction mixture was stirred at room temperature for 2 h, then washed with water (20 mL), dried over Na_2SO_4, subjected to filtration, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) to afford 2-bromo-5-(benzyloxy)phenol as a yellow oil (1.13 g, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 5H), 7.31 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 2.8 Hz, 1H), 6.48 (dd, *J* = 8.8, 2.9 Hz, 1H), 5.39 (s, 1H), 5.01 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 153.0, 136.5, 132.0, 128.7 (2C), 128.1, 127.5 (2C), 109.3, 102.7, 101.2, 70.3.

Physical and spectral data were found to be consistent with those reported literature[3]

2-bromo-5-dimethylaminophenol (1c)



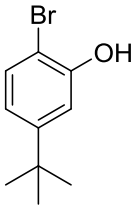
To a solution of 3-dimethylaminophenol (0.69 g, 5 mmol) in AcOH (10 mL) was added bromine (0.80 g, 5 mmol) in AcOH (5 mL) dropwise at room temperature. The reaction mixture

was stirred at room temperature for 7 h, then quenched with saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) to afford 2-bromo-5-dimethylaminophenol as a white solid (0.81 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.9 Hz, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 6.24 (dd, *J* = 8.9, 2.9 Hz, 1H), 5.52 (s, 1H), 2.92 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 151.2, 131.8, 107.0, 100.2, 97.2, 40.8 (2C).

Physical and spectral data were found to be consistent with the reported literature[4]

2-bromo-5-*tert*-butylphenol (1d)

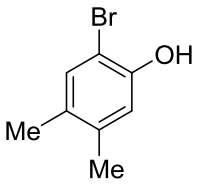


To a solution of 3-*tert*-butylphenol (0.75 g, 5 mmol) in CH_2Cl_2 (20 mL) was added bromine (0.80 g, 5 mmol) in CH_2Cl_2 (5 mL) dropwise under nitrogen atomsphere. After the addition was completed, the reaction was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) to afford 2-bromo-5-*tert*-butylphenol as a colorless oil (1.03 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.49 (s, 1H), 1.27 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 151.8, 131.4, 119.2, 113.5, 106.9, 34.7, 31.2 (3C).

Physical and spectral data were found to be consistent with those reported literature[5]

2-bromo-4,5-dimethylphenol (1f)

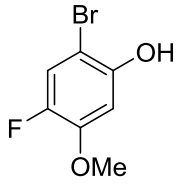


To a solution of 3,4-dimethylphenol (0.61 g, 5 mmol) in CH_2Cl_2 (100 mL) and Et_2O (10 mL) was added a solution of bromine (0.80 g, 5 mmol) in CH_2Cl_2 (10 mL) dropwise at 0 °C. After the addition was completed, the reaction was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) to afford 2-bromo-4,5-dimethylphenol as a white solid (0.69 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 6.81 (s, 1H), 5.28 (s, 1H), 2.17 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 137.9, 132.2, 130.2, 117.1, 106.5, 19.6, 18.7.

Physical and spectral data were found to be consistent with the reported literature[6]

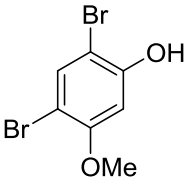
2-bromo-4-fluoro-5-methoxyphenol (1g)



To a solution of 4-fluoro-3-methyoxyphenol (0.43 g, 3 mmol) in CH_2Cl_2 (50 mL) was added *N*-bromosuccinimide (0.54 g, 3 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 2 h, and then quenched with water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 30:1) to afford 2-bromo-4-fluoro-5-methoxyphenol as a white solid (0.49 g, 74%, mp 76-77 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 10.2 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 5.26 (s, 1H), 3.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0 (d, *J* = 2.8 Hz), 148.3 (d, *J* = 11.7 Hz), 146.5 (d, *J* = 242.5 Hz), 118.4 (d, *J* = 22.6 Hz), 101.3 (d, *J* = 1.6 Hz), 98.2 (d, *J* = 8.9 Hz), 56.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -143.12 (dd, *J* = 10.2, 7.6 Hz, 1F).

2,4-dibromo-5-methoxyphenol (1h)

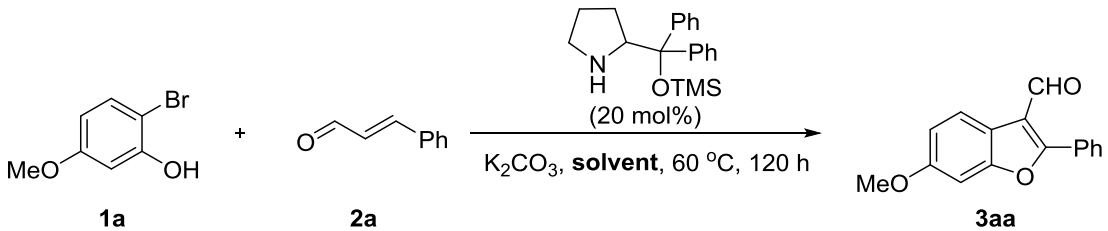


To a solution of 4-bromo-3-methyoxyphenol (0.61 g, 3 mmol) in CH_2Cl_2 (50 mL) was added *N*-bromosuccinimide (0.54 g, 3 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 2 h, and then quenched with water. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 30:1) to afford 2,4-dibromo-5-methoxyphenol as a white solid (0.74 g, 88%, mp 70-71 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 6.53 (s, 1H), 5.40 (s, 1H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 152.6, 134.5, 102.6, 100.6, 100.4, 56.5.

3. Optimization of Reaction Conditions

Table S1. Solvent optimization study[a]



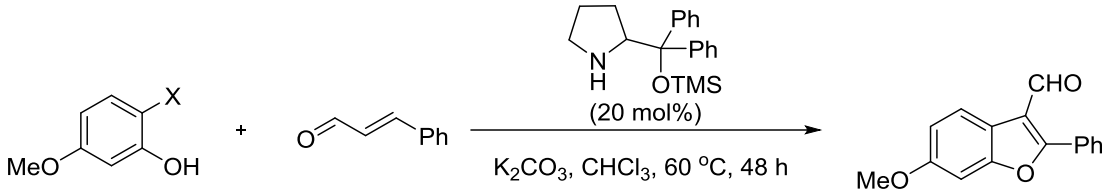
1a **2a** **3aa**

entry	solvent	yield[b] (%)

1	CH_2Cl_2	n.r.
2	$CHCl_3$	35
3	toluene	15
4	CH_3CN	16
5	DMF	n.r.
6	Et_2O	n.r.
7	DMSO	trace
8	THF	trace
9	acetone	n.r.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), K_2CO_3 (0.5 mmol) and catalyst (0.02 mmol) in solvent (2.0 mL) at 60 °C for 5 days. [b]Determined by ^{1}H NMR analysis with dibromomethane as an internal standard. n.r. = no reaction.

Table S2. Leaving groups (C−X) optimization study[a]



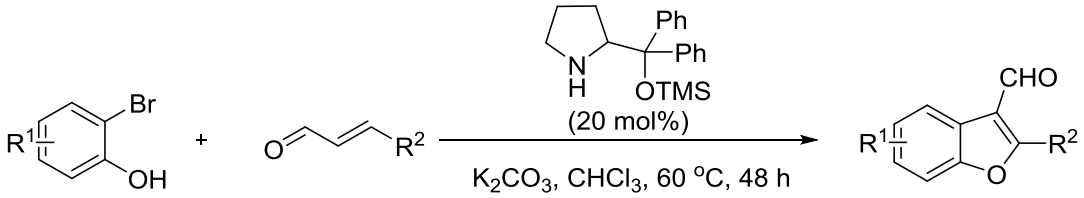
1a **2a** **3aa**

entry	X	C-X (kal/mol)[7]	yield[b] (%)
1	H	96-99	n.r.
2	Cl	79	n.r.
3	Br	66	85[c]
4	I	52	38

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.1 mmol), K_2CO_3 (0.5 mmol) and catalyst (0.02 mmol) in chloroform (2.0 mL) at 60 °C for 48 h. [b]Determined by ^{1}H NMR analysis with dibromomethane as an internal standard. [c]Isolated yield. n.r. = no reaction.

4. General Synthetic Procedure and Compound Characterization

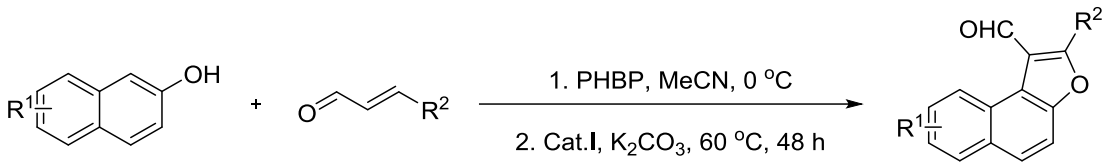
4.1 General procedure for the synthesis of 2,3-disubstituted benzofurans



To a 10 mL tube was added 2-bromophenol derivatives (0.6 mmol), α,β-unsaturated aldehydes (0.1 mmol), potassium carbonate (69 mg, 0.5 mmol), diphenylprolinol TMS ether (7 mg, 0.02 mmol) and chloroform (2.0 mL), then the reaction mixture was stirred at 60 °C until TLC showed complete consumption of aldehydes. The mixture was cooled to ambient temperature and filtered through the Celite pad. The solvent was removed under reduced pressure and the crude

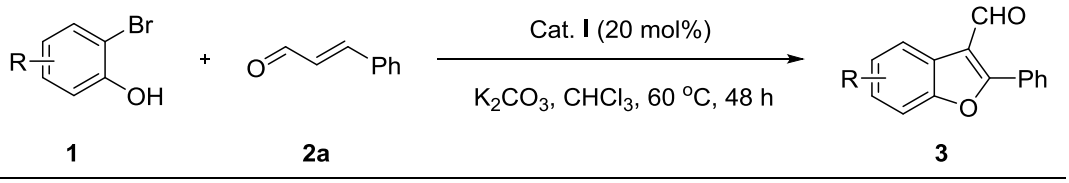
product was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) to afford the desired products.

4.2 General procedure for the synthesis of 2,3-disubstituted naphthofurans

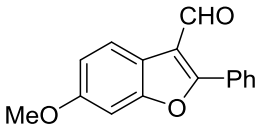


β-naphthols (1.2 mmol) in MeCN (10 mL) was added pyridine hydrobromide perbromide (0.38 g, 1.2 mmol) at 0 °C, after the bromination reaction was completed, a solution of *α,β*-unsaturated aldehydes (1.0 mmol), potassium carbonate (0.69 g, 5.0 mmol) and diphenylprolinol TMS ether (70 mg, 0.2 mmol) were added, then the reaction was stirred at 60 °C until TLC showed complete consumption of aldehydes. The mixture was cooled to ambient temperature and filtered through the Celite pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) to afford the desired products.

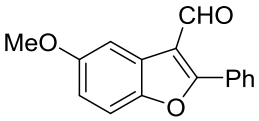
Table S3. Unreactive substrates[a]



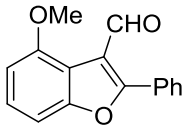
1 **2a** **3**



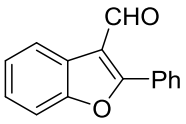
85% yield[b]



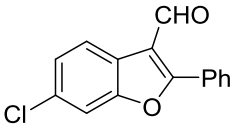
0% yield[c]



<10% yield[d]



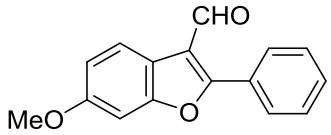
0% yield[c]



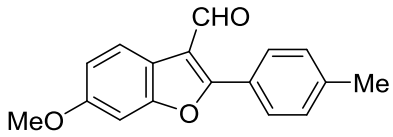
0% yield[c]

[a]Reaction conditions: **1** (0.6 mmol) **2a** (0.1 mmol), K_2CO_3 (0.5 mmol) and catalyst **I** (0.02 mmol) in chloroform (2.0 mL) at 60 °C for 48 h. [b]Isolated yield. [c]Reaction was run for 7 days. [d]Determined by ^1H NMR analysis with dibromomethane as an internal standard.

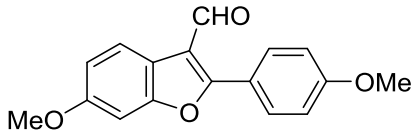
4.3 Analytical data of products



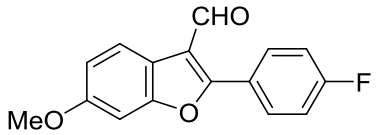
6-methoxy-2-phenylbenzofuran-3-carbaldehyde (3aa): Yellow solid (21.4 mg, 85%); mp 117-118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.59 – 7.53 (m, 3H), 7.08 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 164.6, 159.1, 155.2, 130.8, 129.1 (2C), 128.9 (2C), 128.8, 122.9, 118.6, 117.6, 113.5, 95.8, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{12}O_3$ (M^+): 252.0786; found: 252.0787.



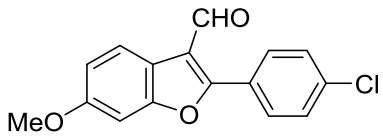
6-methoxy-2-(*p*-tolyl)benzofuran-3-carbaldehyde (3ab): Yellow solid (22.8 mg, 86%); mp 103-105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.91 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.80 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 165.0, 159.0, 155.1, 141.4, 129.9 (2C), 128.8 (2C), 126.0, 122.8, 118.7, 117.2, 113.3, 95.8, 55.8, 21.6. **HRMS** (EI) m/z Calcd for $C_{17}H_{14}O_3$ (M^+): 266.0943; found: 266.0944.



6-methoxy-2-(4-methoxyphenyl)benzofuran-3-carbaldehyde (3ac): Yellow solid (26.7 mg, 95%); mp 104-105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.05 – 6.96 (m, 3H), 6.92 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.6, 164.9, 161.8, 158.9, 154.9, 130.4 (2C), 122.7, 121.3, 118.8, 116.7, 114.6 (2C), 113.1, 95.8, 55.8, 55.5. **HRMS** (EI) m/z Calcd for $C_{17}H_{14}O_4$ (M^+): 282.0892; found: 282.0894.

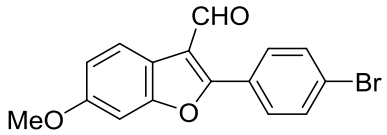


2-(4-fluorophenyl)-6-methoxybenzofuran-3-carbaldehyde (3ad): Yellow solid (20.5 mg, 76%); mp 126-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.25 (t, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.2, 164.2 (d, *J* = 252.8 Hz), 163.3, 159.2, 155.1, 130.9, 130.8, 125.0 (d, *J* = 3.3 Hz), 122.8, 118.5, 117.5, 116.6, 116.3, 113.5, 95.8, 55.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.24 (ddd, *J* = 13.5, 8.5, 5.1 Hz, 1F). **HRMS** (EI) m/z Calcd for $C_{16}H_{11}FO_3$ (M^+): 270.0692; found: 270.0694.

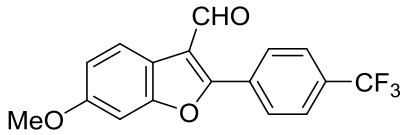


2-(4-chlorophenyl)-6-methoxybenzofuran-3-carbaldehyde (3ae): Yellow solid (22.8 mg, 80%); mp 128-129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.48 – 7.43 (m, 2H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.81 (s,

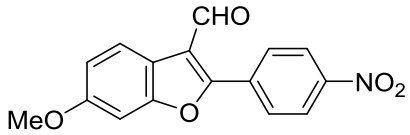
3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.1, 162.9, 159.3, 155.2, 137.1, 129.9 (2C), 129.5 (2C), 127.2, 122.9, 118.5, 117.8, 113.7, 95.7, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{11}ClO_3$ (M^+): 286.0397; found: 286.0400.



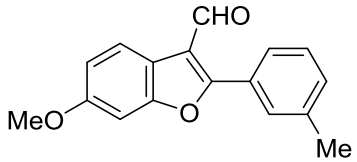
2-(4-bromophenyl)-6-methoxybenzofuran-3-carbaldehyde (3af): Yellow solid (26.0 mg, 79%); mp 119-120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 1.1 Hz, 4H), 7.06 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.1, 162.9, 159.3, 155.2, 132.4 (2C), 130.1 (2C), 127.6, 125.5, 122.9, 118.5, 117.8, 113.7, 95.7, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{11}BrO_3$ (M^+): 329.9892; found: 329.9890.



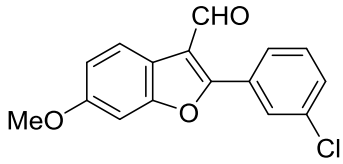
6-methoxy-2-(4-(trifluoromethyl)phenyl)benzofuran-3-carbaldehyde (3ag): Yellow solid (26.2 mg, 82%); mp 126-127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.99 – 7.95 (m, 2H), 7.84 – 7.79 (m, 2H), 7.09 (d, *J* = 2.2 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9, 161.8, 159.6, 155.4, 132.3 (q, *J* = 33.0 Hz), 132.1, 132.1 (q, *J* = 41.4 Hz), 129.0 (2C), 126.1 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.6 Hz), 123.1, 118.6, 118.4, 114.0, 95.7, 55.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.92. **HRMS** (EI) m/z Calcd for $C_{17}H_{11}F_3O_3$ (M^+): 320.0660; found: 320.0664.



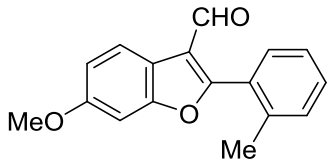
6-methoxy-2-(4-nitrophenyl)benzofuran-3-carbaldehyde (3ah): Yellow solid (22.8 mg, 77%); mp 184-186 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 8.45 – 8.38 (m, 2H), 8.14 (d, *J* = 8.6 Hz, 1H), 8.09 – 8.04 (m, 2H), 7.11 (d, *J* = 2.2 Hz, 1H), 7.05 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.5, 160.0, 159.9, 155.6, 148.6, 134.6, 129.3 (2C), 124.3 (2C), 123.2, 119.3, 118.5, 114.4, 95.7, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{11}NO_5$ (M^+): 297.0637; found: 297.0640.



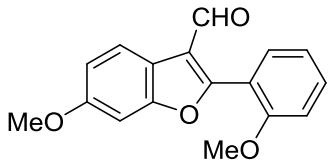
6-methoxy-2-(*m*-tolyl)benzofuran-3-carbaldehyde (3ai): Yellow solid (17.5 mg, 66%); mp 99-100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.81 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9, 165.0, 159.1, 155.1, 139.0, 131.7, 129.4, 129.0, 128.7, 126.1, 122.9, 118.6, 117.5, 113.4, 95.8, 55.8, 21.5. **HRMS** (EI) m/z Calcd for $C_{17}H_{14}O_3$ (M^+): 266.0943; found: 266.0944.



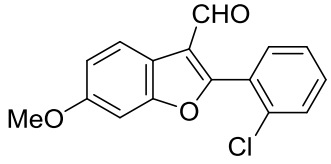
2-(3-chlorophenyl)-6-methoxybenzofuran-3-carbaldehyde (3aj): Yellow solid (18.0 mg, 63%); mp 105-107 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.77 (t, *J* = 1.9 Hz, 1H), 7.64 (dt, *J* = 7.0, 1.7 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.94 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.2, 162.3, 159.4, 155.2, 135.3, 130.7, 130.4, 130.4, 128.6, 126.9, 123.0, 118.4, 118.2, 113.8, 95.7, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{11}ClO_3$ (M^+): 286.0397; found: 286.0400.



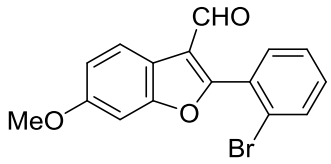
6-methoxy-2-(*o*-tolyl)benzofuran-3-carbaldehyde (3ak): Yellow solid (13.5 mg, 51%); mp 129-130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.40 – 7.31 (m, 2H), 7.07 (d, *J* = 2.2 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.88 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.0, 166.6, 159.0, 155.4, 138.4, 131.8, 131.1, 130.8, 127.7, 125.9, 122.7, 118.9, 117.7, 113.4, 95.9, 55.8, 20.4. **HRMS** (EI) m/z Calcd for $C_{17}H_{14}O_3$ (M^+): 266.0943; found: 266.0944.



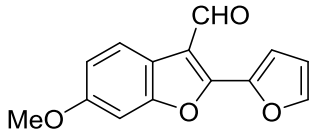
6-methoxy-2-(2-methoxyphenyl)benzofuran-3-carbaldehyde (3al): Yellow solid (16.0 mg, 57%); mp 115-117 °C; **^{1}H NMR** (400 MHz, CDCl3) δ 10.07 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.99 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 160.8, 157.7, 156.2, 154.6, 131.3, 130.7, 121.7, 119.8, 117.3, 117.2, 116.8, 112.1, 110.6, 94.8, 54.7 (2C). **HRMS** (EI) m/z Calcd for $C_{17}H_{14}O_4$ (M^+): 282.0892; found: 282.0894.



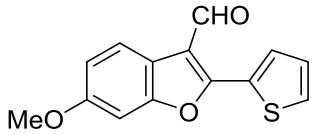
2-(2-chlorophenyl)-6-methoxybenzofuran-3-carbaldehyde (3am): Yellow solid (12.6 mg, 45%); mp 82-84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.44 (td, *J* = 7.7, 1.8 Hz, 1H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 1H), 6.96 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.5, 162.1, 159.3, 155.8, 134.3, 132.8, 132.0, 130.7, 127.7, 127.0, 122.9, 119.3, 117.6, 113.8, 95.8, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{11}ClO_3$ (M^+): 286.0397; found: 286.0400.



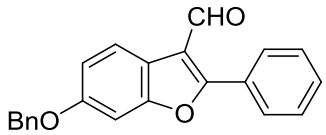
2-(2-bromophenyl)-6-methoxybenzofuran-3-carbaldehyde (3an): Yellow solid (13.0 mg, 40%); mp 91-93 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 1H), 7.79 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.57 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.43 (td, *J* = 7.9, 1.9 Hz, 1H), 7.10 (d, *J* = 2.2 Hz, 1H), 7.04 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.5, 163.6, 159.3, 155.7, 133.9, 133.0, 132.1, 129.8, 127.5, 123.8, 122.9, 119.2, 117.5, 113.8, 95.8, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{11}BrO_3$ (M^+): 329.9892; found: 329.9890.



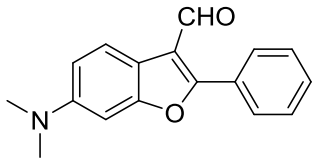
2-(furan-2-yl)-6-methoxybenzofuran-3-carbaldehyde (3ao): Yellow solid (20.0 mg, 83%); mp 163-164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.67 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.12 (dd, *J* = 3.5, 0.7 Hz, 1H), 7.03 (d, *J* = 2.2 Hz, 1H), 6.98 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.64 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9, 159.2, 155.2, 153.6, 145.7, 145.5, 123.1, 118.2, 116.5, 113.4, 112.8, 112.3, 95.7, 55.8. **HRMS** (EI) m/z Calcd for $C_{14}H_{10}O_4$ (M^+): 242.0579; found: 242.0577.



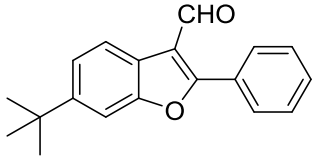
6-methoxy-2-(thiophen-2-yl)benzofuran-3-carbaldehyde (3ap): Yellow solid (20.0 mg, 78%); mp 138-140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.69 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.53 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.16 (dd, *J* = 5.1, 3.8 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 6.91 (dd, *J* = 8.6, 2.2 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.4, 159.2, 158.2, 154.9, 130.5, 129.9, 129.5, 128.3, 122.6, 118.6, 116.5, 113.5, 95.7, 55.8. **HRMS** (EI) m/z Calcd for $C_{14}H_{10}SO_3$ (M^+): 258.0351; found: 258.0352.



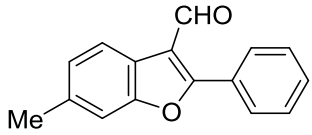
6-(benzyloxy)-2-phenylbenzofuran-3-carbaldehyde (3ba): Yellow solid (22.5 mg, 69%); mp 118-120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.58 – 7.53 (m, 3H), 7.50 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.31 (m, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 7.09 (dd, *J* = 8.6, 2.2 Hz, 1H), 5.14 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 164.7, 158.2, 155.0, 136.6, 130.8, 129.1 (2C), 128.9 (2C), 128.7, 128.7 (2C), 128.1, 127.5 (2C), 123.0, 118.9, 117.6, 114.2, 97.0, 70.6. **HRMS** (EI) m/z Calcd for $C_{22}H_{16}O_3$ (M^+): 328.1099; found: 328.1102.



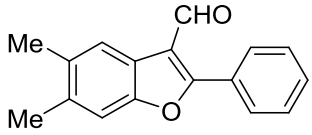
6-(dimethylamino)-2-phenylbenzofuran-3-carbaldehyde (3ca): Yellow solid (12.4 mg, 47%); mp 100-102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.54 (m, 3H), 6.90 (d, *J* = 9.1 Hz, 2H), 3.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9, 163.7, 155.9, 149.5, 130.5, 130.4, 129.1 (2C), 129.0, 128.8 (2C), 122.8, 117.8, 111.9, 94.9, 41.5 (2C). **HRMS** (EI) m/z Calcd for $C_{17}H_{15}NO_2$ (M^+): 265.1103; found: 265.1104.



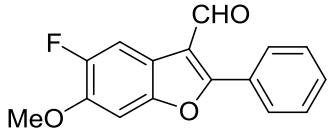
6-(*tert*-butyl)-2-phenylbenzofuran-3-carbaldehyde (3da): Yellow oil (10.4 mg, 38%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.21 – 8.14 (m, 1H), 7.85 (ddd, *J* = 5.6, 3.0, 1.7 Hz, 2H), 7.60 – 7.58 (m, 1H), 7.58 – 7.54 (m, 3H)., 7.46 (dd, *J* = 8.3, 1.6 Hz, 1H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 165.2, 154.5, 150.3, 130.9, 129.1 (2C), 129.0 (2C), 128.8, 122.7, 122.7, 122.0, 117.5, 107.8, 35.2, 31.6 (3C). **HRMS** (EI) m/z Calcd for $C_{19}H_{18}O_2$ (M^+): 278.1307; found: 278.1308.



6-methyl-2-phenylbenzofuran-3-carbaldehyde (3ea): Yellow solid (7.3 mg, 31%); mp 87-88 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.61 – 7.52 (m, 3H), 7.37 (s, 1H), 7.22 (dd, *J* = 7.9, 1.3 Hz, 1H), 2.5JZ1 (Fs, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ186.8, 164.9, 154.5, 136.6, 130.9, 129.1 (2C), 129.1 (2C), 128.8, 126.2, 122.9, 122.1, 117.6, 111.3, 21.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{12}O_2$ (M^+): 236.0837; found: 236.0836.

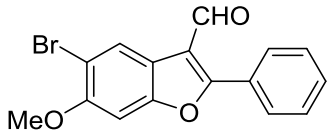


5,6-dimethyl-2-phenylbenzofuran-3-carbaldehyde (3fa): Yellow solid (10.5 mg, 42%); mp 130-132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.02 (s, 1H), 7.85 – 7.80 (m, 2H), 7.57 – 7.52 (m, 3H), 7.32 (s, 1H), 2.38 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 164.8, 153.0, 135.4, 133.7, 130.8, 129.1 (2C), 129.0 (2C), 128.9, 123.1, 122.6, 117.5, 111.5, 20.6, 20.0. **HRMS** (EI) m/z Calcd for $C_{17}H_{14}O_2$ (M^+): 250.0994; found: 250.0992.

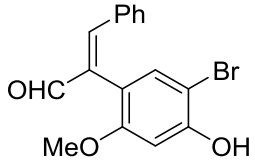


5-fluoro-6-methoxy-2-phenylbenzofuran-3-carbaldehyde (3ga): Yellow solid (19.9 mg, 74%); mp 155-157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.94 (d, *J* = 10.6 Hz, 1H), 7.86 – 7.76 (m, 2H), 7.61 – 7.52FZ (m, 3H), 7.15 (d, *J* = 6.7 Hz, 1H), 3.96 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.4, 165.0, 151.1 (d, *J* = 242.8 Hz), 150.3 (d, *J* = 1.4 Hz), 147.5 (d, *J* = 13.6 Hz), 131.0, 129.2 (2C),

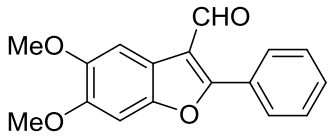
128.8 (2C), 128.5, 117.7 (d, *J* = 3.6 Hz), 117.4 (d, *J* = 10.3 Hz), 108.7 (d, *J* = 23.0 Hz), 96.2 (d, *J* = 2.1 Hz), 56.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.52 (dd, *J* = 10.6, 6.6 Hz, 1F). **HRMS** (EI) m/z Calcd for $C_{16}H_{11}FO_3$ (M^+): 270.0692; found: 270.0694.



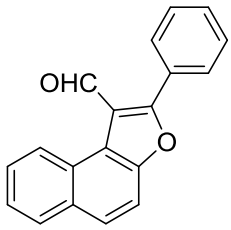
5-bromo-6-methoxy-2-phenylbenzofuran-3-carbaldehyde (3ha): White solid (29.6 mg, 45%); mp 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.45 (s, 1H), 7.85 – 7.80 (m, 2H), 7.60 – 7.55 (m, 3H), 7.11 (s, 1H), 3.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.3, 164.9, 154.8, 154.1, 131.1, 129.2 (2C), 128.8 (2C), 128.4, 126.3, 119.4, 116.9, 109.3, 95.2, 56.6. **HRMS** (EI) m/z Calcd for $C_{16}H_{11}BrO_3$ (M^+): 329.9892; found: 329.9891.



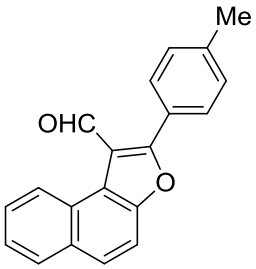
2-(5-bromo-4-hydroxy-2-methoxyphenyl)-3-phenylacrylaldehyde (3ha'): *E*/*Z* = 10:1, Yellow solid (20.0 mg, 30%); mp 153-155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.45 (s, 1H), 7.35 – 7.24 (m, 5H), 7.12 (s, 1H), 6.66 (s, 1H), 5.82 (s, 1H), 3.61 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 157.9, 153.6, 151.0, 137.1, 134.3, 132.8, 130.4, 130.3 (2C), 128.6 (2C), 116.4, 100.8, 100.1, 55.8. **HRMS** (EI) m/z Calcd for $C_{16}H_{13}BrO_3$ (M^+): 332.0048; found: 332.0046.



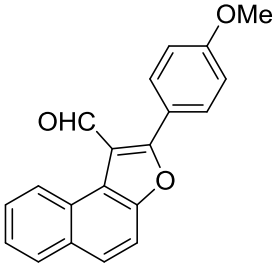
5,6-dimethoxy-2-phenylbenzofuran-3-carbaldehyde (3ia): Yellow solid (26.1 mg, 93%); mp 123-125 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 7.79 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.70 (s, 1H), 7.55 (dt, *J* = 4.8, 3.0 Hz, 3H), 7.08 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9, 164.3, 149.1, 148.8, 147.9, 130.6, 129.1 (2C), 128.9, 128.7 (2C), 117.8, 117.4, 103.2, 94.8, 56.4, 56.3. **HRMS** (EI) m/z Calcd for $C_{17}H_{14}O_4$ (M^+): 282.0892; found: 282.0891.



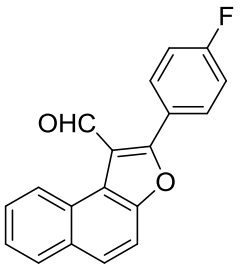
2-phenylnaphtho[2,1-*b*]furan-1-carbaldehyde (5aa): Yellow solid (204 mg, 75%); mp 126-127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 9.54 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.93 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.70 – 7.64 (m, 2H), 7.59 – 7.52 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.8, 166.2, 151.6, 130.4, 129.8, 128.9 (2C), 128.0 (2C), 127.7, 127.6, 127.4, 127.2, 126.8, 125.9, 124.5, 119.4, 119.2, 110.7. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{12}O_2$ (M^+): 272.0837; found: 272.0838.



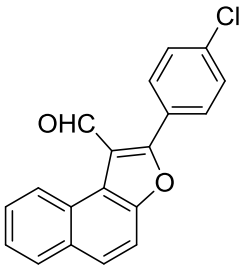
2-(*p*-tolyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ab): Yellow solid (217 mg, 76%); mp 154-155 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 9.54 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 1H), 7.66 (td, *J* = 7.4, 6.7, 1.7 Hz, 4H), 7.53 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 167.5, 152.4, 141.4, 131.4, 129.8 (2C), 129.7 (2C), 128.6, 128.5, 128.0, 127.9, 126.8, 125.8, 125.4, 120.2, 120.0, 111.7, 21.6. **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{14}O_2$ (M^+): 286.0994; found: 286.0995.



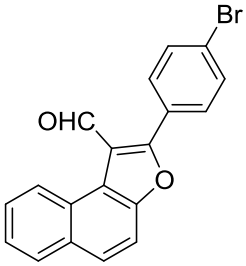
2-(4-methoxyphenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ac): Yellow solid (241 mg, 80%); mp 132-134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 9.56 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.69 (dd, *J* = 11.0, 8.3 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 167.4, 161.8, 152.3, 131.5 (2C), 131.4, 128.6, 128.5, 127.9, 127.9, 126.8, 125.4, 121.1, 120.3, 119.6, 114.5 (2C), 111.6, 55.5. **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{14}O_3$ (M^+): 302.0943; found: 302.0942.



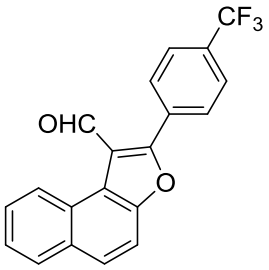
2-(4-fluorophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ad): Yellow solid (208 mg, 72%); mp 157-158 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 9.51 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.69 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 8.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.4, 165.9, 164.3 (d, *J* = 253.0 Hz), 152.5, 132.0, 131.9, 131.5, 128.7, 128.4, 128.4, 127.7, 127.0, 125.6, 124.9 (d, *J* = 3.5 Hz), 120.4, 120.1, 116.5, 116.3, 111.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.17 (ddd, *J* = 13.4, 8.4, 5.1 Hz, 1F). **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}FO_2$ (M^+): 290.0743; found: 290.0745.



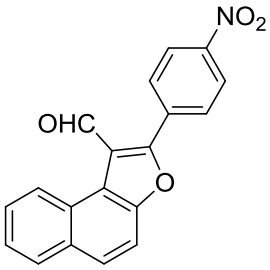
2-(4-chlorophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ae): Yellow solid (226 mg, 74%); mp 165-166 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 9.49 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.71 – 7.66 (m, 2H), 7.59 – 7.53 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.2, 165.4, 152.7, 137.3, 131.5, 131.0 (2C), 129.4 (2C), 128.7, 128.5, 128.4, 127.7, 127.1, 127.0, 125.6, 120.7, 120.1, 111.6. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}ClO_2$ (M^+): 306.0448; found: 306.0450.



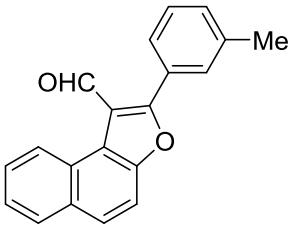
2-(4-bromophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5af): Yellow solid (254 mg, 73%); mp 170-171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.50 (d, *J* = 8.3 Hz, 1H), 7.99 – 7.94 (m, 1H), 7.88 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.70 (q, *J* = 5.5, 5.0 Hz, 6H), 7.59 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ186.2, 165.4, 152.7, 132.3 (2C), 131.5, 131.1 (2C), 128.7, 128.5, 128.4, 127.7, 127.6, 127.0, 125.7, 125.6, 120.7, 120.2, 111.6. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}BrO_2$ (M^+): 349.9942; found: 349.9943.



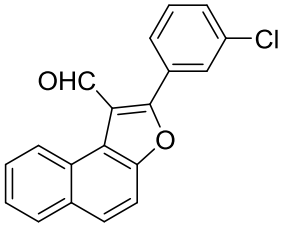
2-(4-(trifluoromethyl)phenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ag): Yellow solid (244 mg, 72%); mp 153-154 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 9.41 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.91 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.61 (m, 2H), 7.54 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.0, 164.2, 152.9, 132.4 (q, *J* = 32.9 Hz), 132.2 (q, *J* = 41.4 Hz), 131.5, 130.0 (2C), 128.8, 128.7, 128.3, 128.3, 127.6, 127.1, 125.9 (q, *J*= 3.7 Hz), 125.7, 123.7 (q, *J* = 272.6 Hz), 121.3, 120.0, 111.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.86. **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{11}F_3O_2$ (M^+): 340.0711; found: 340.0712.



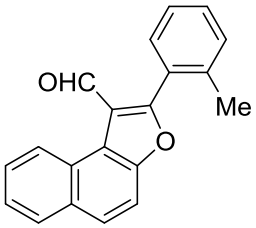
2-(4-nitrophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ah): Yellow solid (212 mg, 67%); mp 210-211 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 9.41 (d, *J* = 8.5 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.60 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.7, 162.5, 153.3, 148.8, 134.5, 131.6, 130.4 (2C), 129.4, 128.9, 128.3, 127.4 (2C), 125.9, 124.2 (2C), 122.1, 120.2, 111.6. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}NO_4$ (M^+): 317.0688; found: 317.0687.



2-(*m*-tolyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ai): Yellow solid (185 mg, 65%); mp 122-124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 9.56 (d, *J* = 8.4 Hz, 1H), 7.99 – 7.91 (m, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.65 – 7.57 (m, 2H), 7.56 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.43 – 7.35 (m, 1H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.9, 167.5, 152.5, 138.9, 131.7, 131.4, 130.4, 128.9, 128.6, 128.6, 128.4, 128.1, 127.8, 127.2, 126.8, 125.4, 120.3, 120.2, 111.7, 21.4. **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{14}O_2$ (M^+): 286.0994; found: 286.0995.

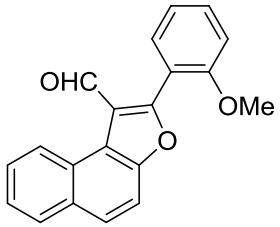


2-(3-chlorophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5aj): Yellow solid (183 mg, 60%); mp 160-162 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 9.48 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.90 – 7.79 (m, 2H), 7.72 – 7.65 (m, 3H), 7.59 – 7.47 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.2, 164.8, 152.7, 135.2, 131.5, 130.8, 130.3, 130.2, 129.6, 128.7, 128.7, 128.4, 128.0, 127.7, 127.1, 125.6, 120.9, 120.1, 111.6. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}ClO_2$ (M^+): 306.0448; found: 306.0450.

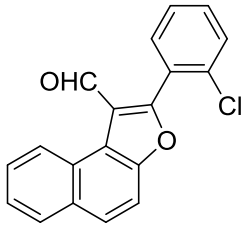


2-(*o*-tolyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ak): Yellow solid (163 mg, 57%); mp

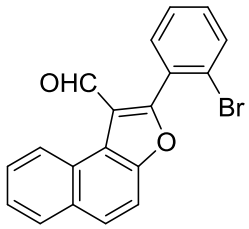
139-141 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 9.59 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.61 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 – 7.27 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 168.7, 152.8, 138.7, 132.2, 131.5, 131.0, 131.0, 128.7, 128.5, 128.1, 128.0, 128.0, 127.0, 125.9, 125.6, 121.7, 119.6, 111.8, 20.4. . **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{14}O_2$ (M^+): 286.0994; found: 286.0995.



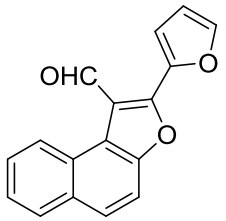
2-(2-methoxyphenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5al): Yellow solid (184 mg, 61%); mp 132-134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 9.57 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.69 (dd, *J* = 10.9, 8.2 Hz, 2H), 7.61 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.2, 164.6, 157.7, 153.1, 132.5, 132.2, 131.4, 128.5, 128.4, 127.9, 127.7, 126.8, 125.3, 121.1, 120.8, 120.0, 117.8, 111.8, 111.6, 55.8. **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{14}O_3$ (M^+): 302.0943; found: 302.0942.



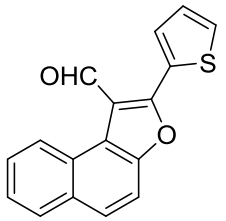
2-(2-chlorophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5am): Yellow solid (159 mg, 52%); mp 144-145 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 9.54 (d, *J* = 8.4 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.63 – 7.53 (m, 3H), 7.50 (td, *J* = 7.8, 1.8 Hz, 1H), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.1, 164.6, 153.2, 134.8, 133.1, 132.2, 131.5, 130.5, 128.6, 128.4, 128.4, 127.9, 127.9, 127.1, 126.9, 125.6, 122.1, 119.5, 111.8. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}ClO_2$ (M^+): 306.0448; found:306.0450.



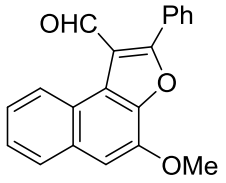
2-(2-bromophenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5an): Yellow solid (164 mg, 47%); mp 149-151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 9.55 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.34 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.1, 166.0, 153.1, 133.6, 133.3, 132.3, 131.5, 130.0, 128.7, 128.5, 128.5, 127.9, 127.5, 127.1, 125.6, 124.4, 122.0, 119.4, 111.8. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}BrO_2$ (M^+): 349.9942; found: 349.9943.



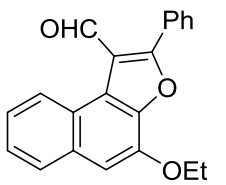
2-(furan-2-yl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ao): Yellow solid (183 mg, 70%); mp 172-173 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 9.51 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.70 – 7.68 (m, 1H), 7.65 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 6.64 (dd, *J* = 3.5, 1.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.5, 155.5, 152.5, 145.9, 145.2, 131.5, 128.6, 128.5, 128.3, 127.9, 126.9, 125.5, 120.0, 119.9, 113.8, 112.4, 111.5. **HRMS** (EI) *m/z* Calcd. for $C_{17}H_{10}O_3$ (M^+): 262.0630; found: 262.0631.



2-(thiophen-2-yl)naphtho[2,1-*b*]furan-1-carbaldehyde (5ap): Yellow solid (189 mg, 68%); mp 164-165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 9.41 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.90 (m, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.74 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.72 – 7.61 (m, 3H), 7.55 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.28 – 7.21 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.5, 160.1, 152.3, 131.5, 130.8, 130.4, 130.2, 128.7, 128.4, 128.3, 128.2, 127.5, 127.0, 125.5, 120.3, 119.7, 111.5. **HRMS** (EI) *m/z* Calcd. for $C_{17}H_{10}SO_2$ (M^+): 278.0402; found: 278.0403.

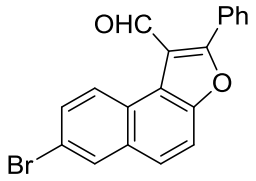


4-methoxy-2-phenylnaphtho[2,1-*b*]furan-1-carbaldehyde (5ba): Yellow solid (220 mg, 73%); mp 206-207 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 9.44 (d, *J* = 7.4 Hz, 1H), 7.82 (dd, *J* = 6.8, 2.9 Hz, 3H), 7.60 – 7.48 (m, 5H), 7.15 (s, 1H), 4.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 167.4, 144.9, 144.3, 132.5, 130.9, 130.1 (2C), 129.0 (2C), 128.5, 127.5, 127.3, 125.9, 124.6, 123.9, 122.0, 120.5, 105.5, 56.0. **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{14}O_3$ (M^+): 302.0943; found: 302.0942.

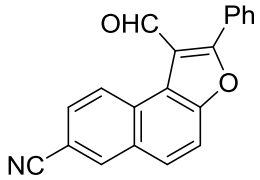


4-ethoxy-2-phenylnaphtho[2,1-*b*]furan-1-carbaldehyde (5ca): Yellow solid (224 mg, 71%); mp 172-174 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 9.43 (d, *J* = 7.2, 1H), 7.82 – 7.76 (m, 3H), 7.57 – 7.47 (m, 5H), 7.13 (s, 1H), 4.33 (q, *J* = 7.0 Hz, 2H), 1.57 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.8, 167.3, 144.5, 144.2, 132.5, 130.9, 130.1 (2C), 128.9 (2C), 128.6, 127.5, 127.3,

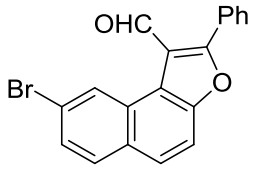
125.8, 124.5, 123.8, 122.0, 120.5, 106.3, 64.5, 14.8. **HRMS** (EI) *m/z* Calcd. for $C_{21}H_{16}O_3$ (M^+): 316.1099; found: 316.1100.



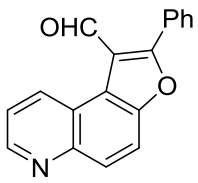
7-bromo-2-phenylnaphtho[2,1-*b*]furan-1-carbaldehyde (5da): Yellow solid (147 mg, 42%); mp 179-180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 9.45 (d, *J* = 9.0 Hz, 1H), 8.08 (d, *J* = 2.1 Hz, 1H), 7.84 – 7.76 (m, 2H), 7.78 – 7.67 (m, 3H), 7.59 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.7, 167.6, 152.5, 132.7, 131.1, 130.5, 130.0, 129.9 (2C), 129.8, 129.1 (2C), 128.4, 127.2, 126.9, 120.3, 120.1, 119.4, 112.8. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}BrO_2$ (M^+): 349.9942; found: 349.9943.



1-formyl-2-phenylnaphtho[2,1-*b*]furan-7-carbonitrile (5ea): Yellow solid (118 mg, 40%); mp 218-220 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 9.74 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 2.1 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.85 – 7.79 (m, 3H), 7.63 (dd, *J* = 5.3, 1.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.5, 168.1, 153.8, 134.3, 131.4, 130.4, 130.3, 130.0 (2C), 129.3, 129.2 (2C), 128.3, 128.1, 127.5, 120.5, 120.0, 119.2, 113.7, 109.0. **HRMS** (EI) *m/z* Calcd. for $C_{20}H_{11}NO_2$ (M^+): 297.0790; found: 297.0791.



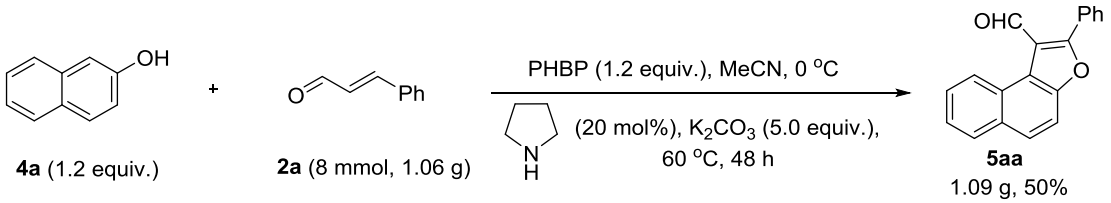
8-bromo-2-phenylnaphtho[2,1-*b*]furan-1-carbaldehyde (5fa): Yellow solid (136 mg, 39%); mp 209-211 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 9.79 (d, *J* = 1.9 Hz, 1H), 7.85 – 7.76 (m, 4H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.66 – 7.57 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.6, 167.4, 153.0, 131.1, 130.2, 130.1, 129.9 (2C), 129.9, 129.5, 129.1 (2C), 128.9, 128.5, 128.0, 121.3, 120.1, 119.7, 112.1. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{11}BrO_2$ (M^+): 349.9942; found: 349.9944.



2-phenylfuro[3,2-*f*]quinoline-1-carbaldehyde (5ga): Yellow solid (131 mg, 24%); mp 192-194 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 9.77 (d, *J* = 8.5 Hz, 1H), 8.87 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 9.1 Hz, 1H), 7.73 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.53 (dd, *J* = 5.2, 1.8 Hz, 3H), 7.45 (dd, *J* = 8.6, 4.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.2, 162.6, 146.6, 144.0, 141.3, 130.9, 125.9, 124.6 (2C), 124.0, 123.8 (2C), 123.0, 118.5, 116.0, 115.1, 114.6, 109.7. **HRMS** (EI) *m/z* Calcd. for $C_{18}H_{11}NO_2$ (M^+): 273.0790; found: 273.0787.

5. Gram-scale Reaction and Further Synthetic Applications

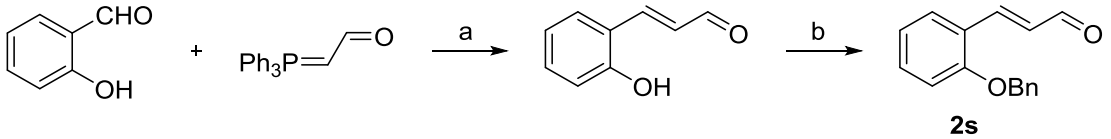
5.1 Gram-scale Reaction



β-naphthol **4a** (1.38 g, 9.6 mmol) in MeCN (30 mL) was added pyridine hydrobromide perbromide (3.07 g, 9.6 mmol) at 0 °C, after the bromination reaction was completed, **2a** (1.06 g, 8 mmol), K_2CO_3 (5.52 g, 40 mmol) and pyrrolidine (0.12 g, 1.6 mmol) were added, then the reaction was stirred at 60 °C for 48 h. The mixture was cooled to ambient temperature and filtered through the Celite pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) to afford **5aa** in a yellow solid (1.09 g, 50% yield).

5.2 Further synthetic applications

(*E*)-3-(2-(benzyloxy)phenyl)acrylaldehyde (2s)



Reagents and conditions: a) aldehyde (5 mmol), Ph_3P=CHCHO (1.2 equiv), toluene, 60 °C, 8 h, N_2; b) BnCl (1.1 equiv), K_2CO_3 (1.1 equiv), KI (0.05 equiv), EtOH, reflux, 5 h.

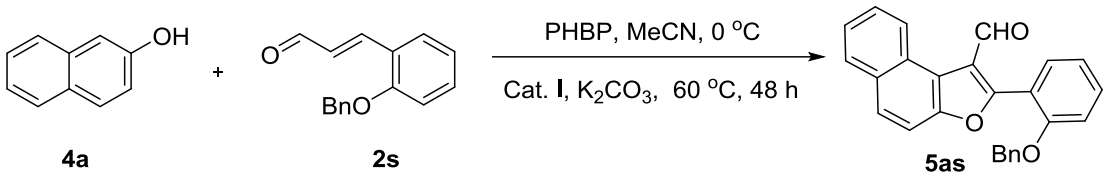
A mixture of 2-hydroxybenzaldehyde (0.61 g, 5 mmol) with Ph_3P=CHCHO (1.83 g, 6 mmol) in toluene (10 mL) was stirred at 60 °C for 8 h under nitrogen. The solvent was removed in vacuo and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20:1 to 5:1) to afford (*E*)-3-(2-hydroxyphenyl)acrylaldehyde as a yellow solid. (0.37 g, 50%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 16.0 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.32 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.06 (dd, *J* = 16.0, 8.1 Hz, 1H), 6.98 (td, *J* = 7.6, 1.1 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.86 (s, 1H).

The data for this compound matched that reported in the literature[8]

Benzyl chloride (0.28 g, 2.2 mmol) was added to a mixture of (*E*)-3-(2-hydroxyphenyl)acrylaldehyde (0.30 g, 2 mmol), and K_2CO_3 (0.30 g, 2.2 mmol) and KI (17 mg, 0.1 mmol) in ethanol (10 mL). The reaction mixture was heated at reflux and stirred for 5 h. After the completion of reaction monitored by TLC analysis, the mixture was filtered and the solid filter cake was washed with CH_2Cl_2 (10 mL). The combined organic fractions were evaporated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1) to afford **2s** as a yellow solid.

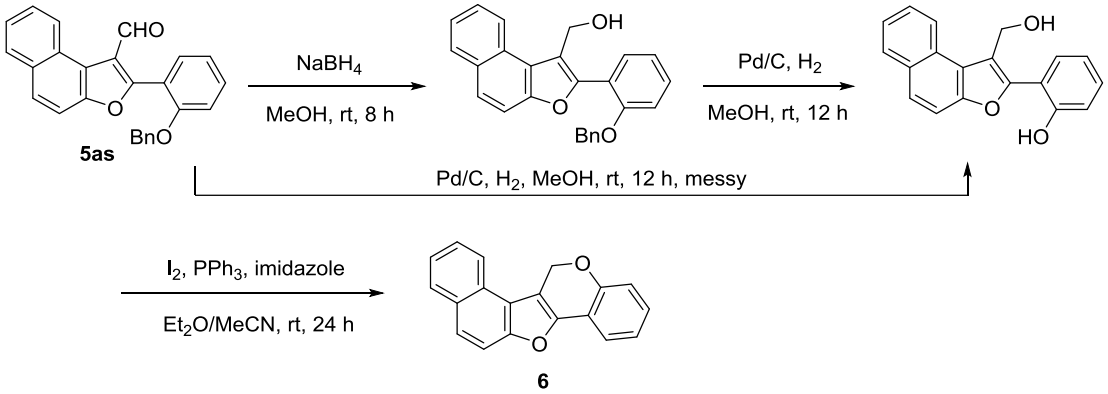
2-(2-(benzyloxy)phenyl)naphtho[2,1-*b*]furan-1-carbaldehyde (5as)



β-naphthol **4a** (0.17 g, 1.2 mmol) in MeCN (10 mL) was added pyridine hydrobromide perbromide (0.38 g, 1.2 mmol) at 0 °C, after the bromination reaction was completed, **2s** (0.24 g, 1 mmol), K_2CO_3 (0.69 g, 5 mmol) and diphenylprolinol TMS ether (70 mg, 0.2 mmol) were added, then the reaction was stirred at 60 °C for 48 h. The mixture was cooled to ambient temperature and filtered through the Celite pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) to afford **5as** in a yellow solid (0.21 g, 56% yield, mp 133-135 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 9.57 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.61 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.28 (tdd, *J* = 9.4, 7.6, 5.9 Hz, 5H), 7.18 – 7.11 (m, 2H), 5.16 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.1, 164.9, 157.0, 153.1, 136.1, 132.5, 132.5, 131.4, 128.6 (2C), 128.5, 128.4, 128.0, 128.0, 127.8, 127.0 (2C), 126.8, 125.4, 121.3, 121.2, 119.9, 118.4, 113.6, 111.8, 70.8. **HRMS** (EI) *m/z* Calcd. for $C_{26}H_{18}O_3$ (M^+): 378.1256; found: 378.1258.

6*H*-naphtho[1',2':4,5]furo[3,2-*c*]chromene (6)



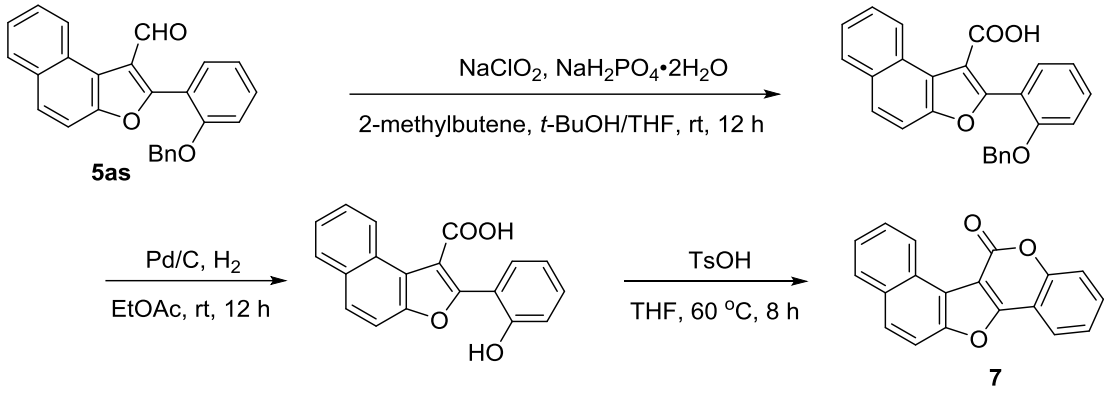
To a solution of **5as** (76 mg, 0.2 mmol) in CH_3OH (4 mL) was added sodium borohydride (12 mg, 0.3 mmol), and the reaction mixture stirred at ambient temperature for 8 h. The solvent was reduced in vacuo and the crude product was used directly in the next reaction. To a solution of the crude alcohol in CH_3OH (4 mL) was added 10% Pd/C (10 mg), and the reaction was stirred under atmosphere of H_2 for 12 h. The reaction mixture was filtered through Celite then concentrated under reduced pressure to give the crude product that was used in the next step without further purification.

To a solution of the crude phenol derivative in CH_3CN (2 mL), and Et_2O (3 mL) was added PPh_3 (79 mg, 0.3 mmol), I_2 (152 mg, 0.6 mmol), and imidazole (20 mg, 0.3 mmol) at 0 °C, and the residue was stirred at the same temperature for 10 min. Then the mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with water and brine then dried over Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by

flash chromatography (petroleum ether/ethyl acetate = 20:1) to afford the corresponding product **6** as a white solid (41 mg, 75% over three steps, mp 168-170 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.80 (dq, *J* = 8.2, 0.8 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.57 – 7.51 (m, 2H), 7.46 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.17 (ddd, *J* = 8.1, 7.5, 1.7 Hz, 1H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.99 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 153.0, 146.8, 130.8, 129.5, 129.0, 127.6, 126.5, 125.3, 124.7, 123.8, 121.6, 120.6, 120.4, 116.2, 116.1, 112.4, 110.0, 66.5. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{12}O_2$ (M^+): 272.0837; found: 272.0834.

6*H*-naphtho[1',2':4,5]furo[3,2-*c*]chromen-6-one (7)



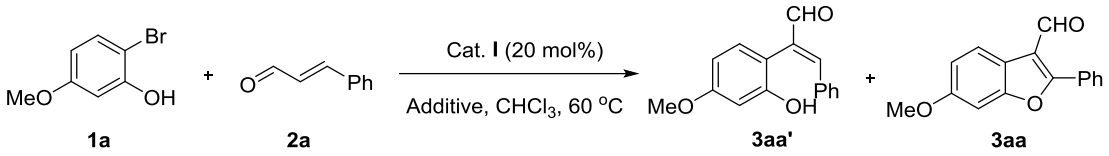
The aldehyde **5as** (76 mg, 0.2 mmol) was dissolved in 4 mL of *tert*-butyl alcohol:THF (1:1) and 2-methylbutene (0.2 mL, 2 mmol). A solution of sodium chlorite (55 mg, 0.6 mmol) and sodium dihydrogenphosphate (156 mg, 1 mmol) in 1 mL of water was added dropwise over a 10 minute period. The reaction mixture was stirred at ambient temperature for 12 h, then diluted with water and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuo and the crude acid was used in the next step without further purification.

To a solution of the crude acid in EtOAc (6 mL) was added 10% Pd/C (10 mg), and the reaction was stirred under atmosphere of H_2 for 12 h. The reaction mixture was filtered through Celite then concentrated under reduced pressure to give the crude product that was used directly in the next step without further purification. This mixture product was dissolved in THF (4 mL), added $TsOH{\cdot}H_2O$ (57 mg, 0.3 mmol). The reaction was stirred at 60 °C for 8 h. The solvent was reduced in vacuo and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 50:1) to afford the corresponding product **7** as a white solid (40 mg, 69% over three steps, mp >250 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 8.4 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.71 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 158.4, 153.4, 153.3, 131.5, 131.4, 128.8, 128.5, 127.9, 127.4, 127.3, 125.8, 124.6, 121.6, 119.2, 117.1, 112.6, 111.7, 107.8.. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{10}O_3$ (M^+): 286.0630; found: 286.0627.

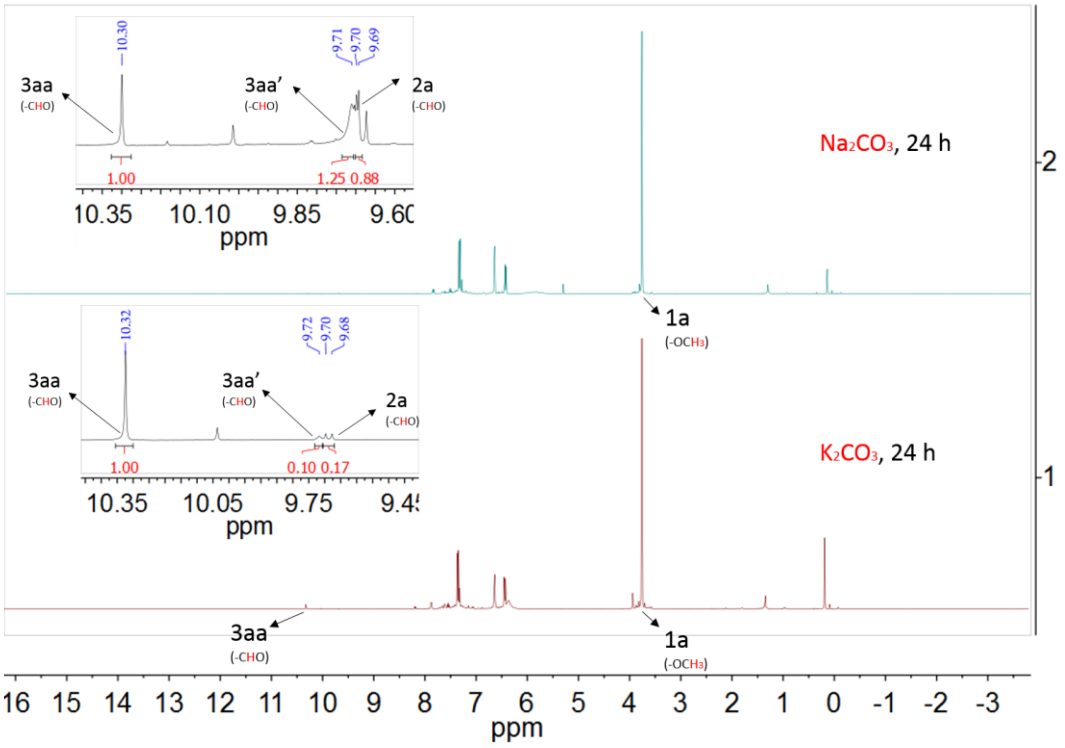
6. Mechanistic Study

Table S4. Capturing the proposed intermediate 3aa'[a]

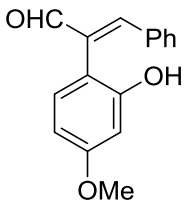


entry	additive (5.0 equiv.)	time	ratio (**3aa'**:**3aa**)[b]	yield **3aa'**	yield **3aa**
1	Na_2CO_3	24 h	1.25:1	-[c]	-[d]
2	K_2CO_3	24 h	0.10:1	-[d]	74%[e]

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.1 mmol), additive (0.5 mmol) and diphenylprolinol TMS ether (0.02 mmol) in chloroform (2.0 mL) at 60 °C for 24 h. [b]Determined by ^{1}H NMR analysis of crude reaction mixtures. [c]Failed to obtain a pure sample, crude ^{1}H NMR is offered. [d]Not isolated. [e]Isolated yield.



The intermediate 3aa'

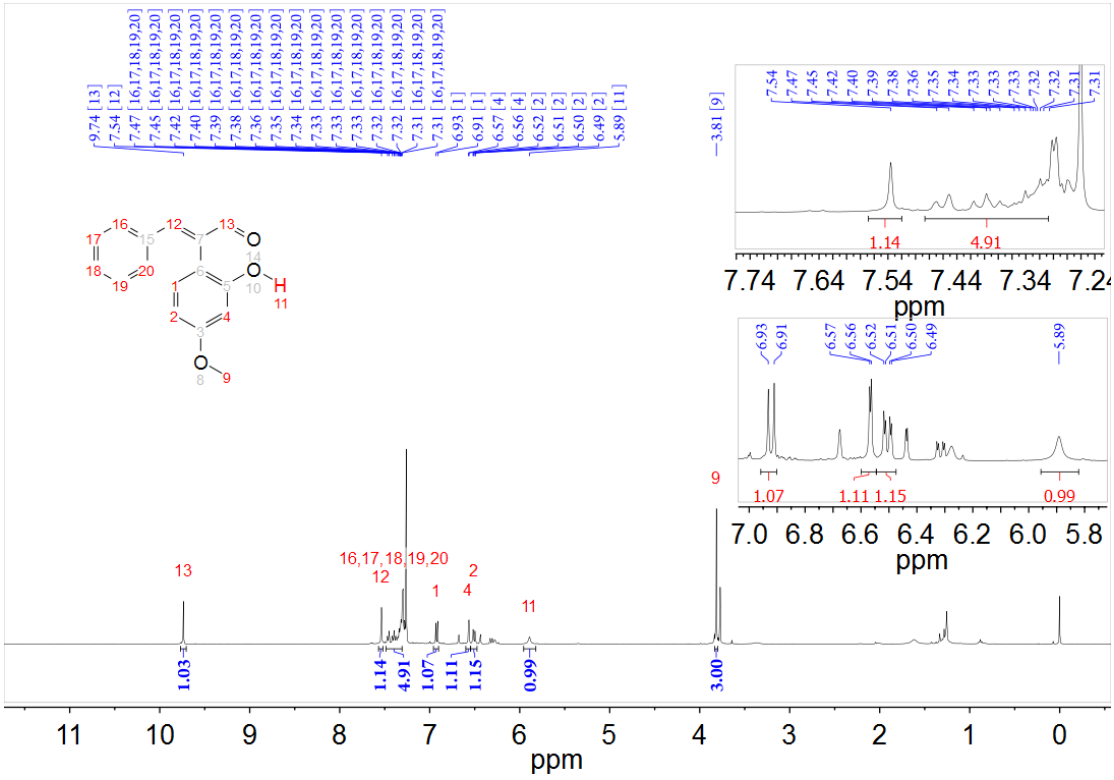


To a 10 mL tube was added 2-bromo-5-methyoxyphenol **1a** (6.0 equiv.), α,β-unsaturated aldehydes **2a** (0.5 mmol, 1.0 equiv.), Na_2CO_3 (5.0 equiv.), diphenylprolinol TMS ether (0.2 equiv.) and chloroform (5.0 mL), then the reaction mixture was stirred at 60 °C for 24 h. The mixture was cooled to ambient temperature and filtered through the Celite pad. The solvent was removed under

reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1 to 2:1) to afford the intermediate **3aa'** (failed to obtain a pure sample, crude ^{1}H NMR is offered).

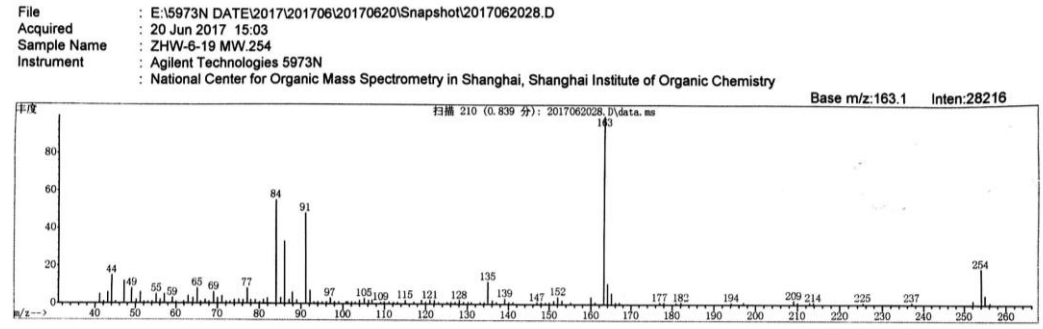
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.54 (s, 1H), 7.47 – 7.31 (m, 5H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.56 (d, *J* = 2.5 Hz, 1H), 6.50 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.89 (s, 1H), 3.81 (s, 3H).

^{1}H NMR Spectrum of 3aa'



MS (EI)

m/z Calcd. for $C_{16}H_{14}O_3$ (M+): 254.0943; found: 254.

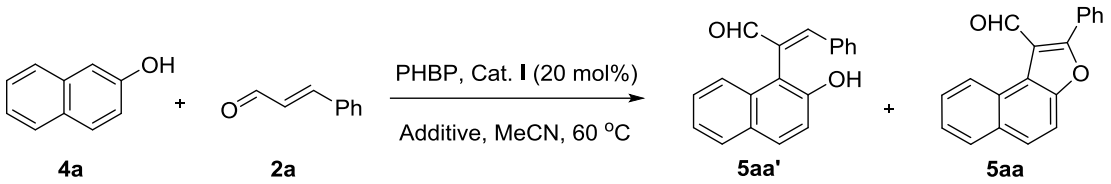


m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
41	4.58	42	1.32	43	5.68	44	15.26	45	0.77	47	11.63	49	8.22	50	1.95	51	6.19
52	0.82	53	1.43	54	0.85	55	4.96	56	1.97	57	5.37	59	2.5	60	0.55	62	1.29
63	3.51	64	2.62	65	8.43	66	1.07	67	1.6	68	0.8	69	5.65	70	3.28	71	3.55
72	1.2	73	1.02	74	1.5	75	1.76	76	2.06	77	8.34	78	1.5	79	2.48	80	0.58
81	1.9	82	3.17	84	54.85	85	3.33	86	33.25	87	1.55	88	5.95	89	1.94	91	47.68
92	7.33	93	1.43	94	0.77	95	0.87	96	0.97	97	3.04	98	0.98	99	1.23	101	0.54
101	0.63	102	1.13	103	1	104	1.59	105	2.99	106	1.76	107	1.77	109	0.7	110	0.87
111	0.91	112	0.94	113	0.87	115	2.48	117	1.19	119	1.64	120	1.35	121	1.85	122	1.68
123	0.63	125	1.1	126	1.35	127	1.41	128	2.01	129	1.02	130	0.97	131	0.75	133	1.18
134	1.29	135	12.31	136	1.76	137	0.63	139	2.69	140	0.87	141	0.89	147	0.65	148	0.87
149	1.12	150	0.87	151	1.79	152	4.22	153	1.99	155	0.73	160	3.6	161	1.18	163	100
164	11.18	165	6.12	166	1.37	167	0.6	177	0.71	178	1.26	181	1.42	182	0.91	194	0.64
197	0.79	209	1.82	210	0.67	213	0.68	214	0.85	225	0.8	237	1.41	252	2	254	18.91
255	4.53	256	0.82														

8 Peak Value:

163	100	84	54.85	91	47.68	86	33.25	254	18.91	44	15.26	135	12.31	47	11.63		

Table S5. Capturing the proposed intermediate 5aa'[a]

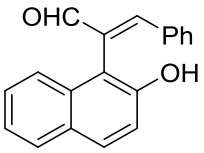


4a 2a 5aa' 5aa

entry	additive (5.0 equiv.)	time	yield[b] 5aa'	yield[b] 5aa
1	Na_2CO_3	24 h	32%	23%
2	K_2CO_3	24 h	trace	57%

[a]Reaction conditions: 0 °C, **4a** (1.2 mmol) in acetonitrile (10 mL) was added pyridine hydrobromide perbromide (1.2 mmol), followed by addition of **2a** (1.0 mmol), additive (5.0 mmol) and diphenylprolinol TMS ether (0.2 mmol), then the reaction was stirred at 60 °C for 24 h.. [b]Isolated yields.

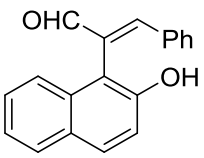
The intermediate 5aa'

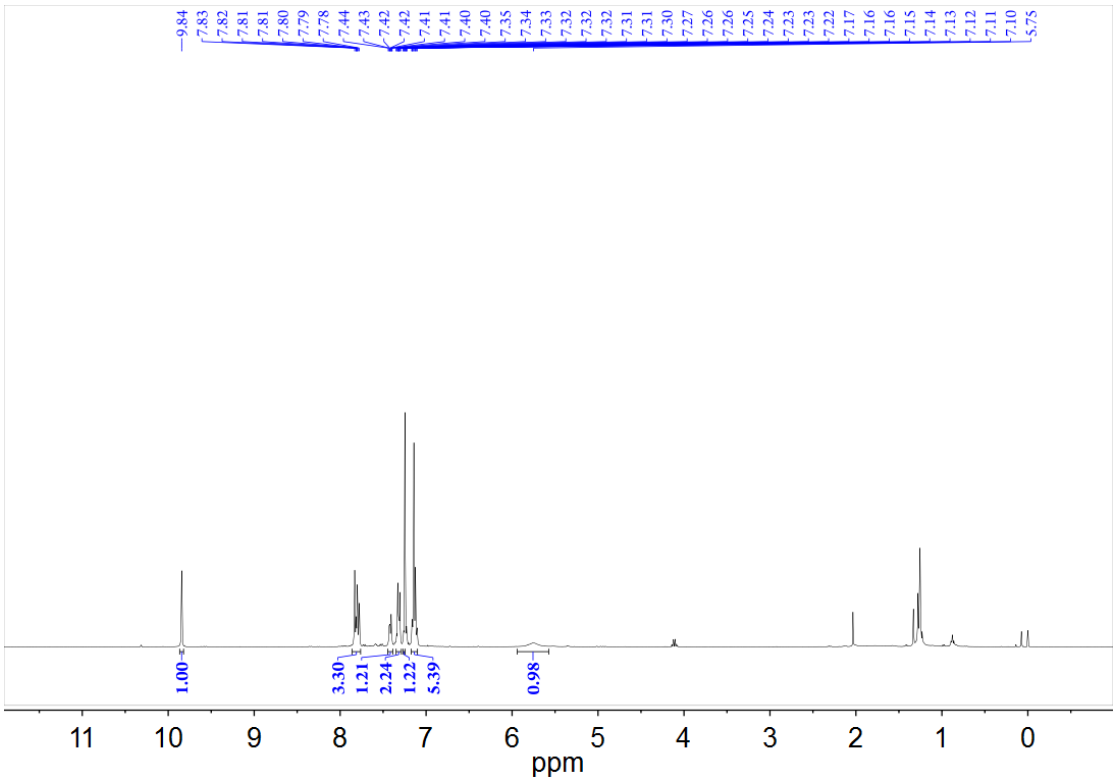


β-naphthol **4a** (0.17 g, 1.2 mmol) in MeCN (10 mL) was added pyridine hydrobromide perbromide (0.38 g, 1.2 mmol) at 0 °C, after the bromination reaction was completed, **2a** (0.13 g, 1.0 mmol), Na_2CO_3 (0.53 g, 5.0 mmol) and diphenylprolinol TMS ether (70 mg, 0.2 mmol) were added, then the reaction mixture was stirred at 60 °C for 24 h. After cooling to ambient temperature, the mixture was filtered through the Celite pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1 to 2:1) to afford the intermediate **5aa'** as a yellow solid (88 mg, 32 %, mp 181-182 °C).

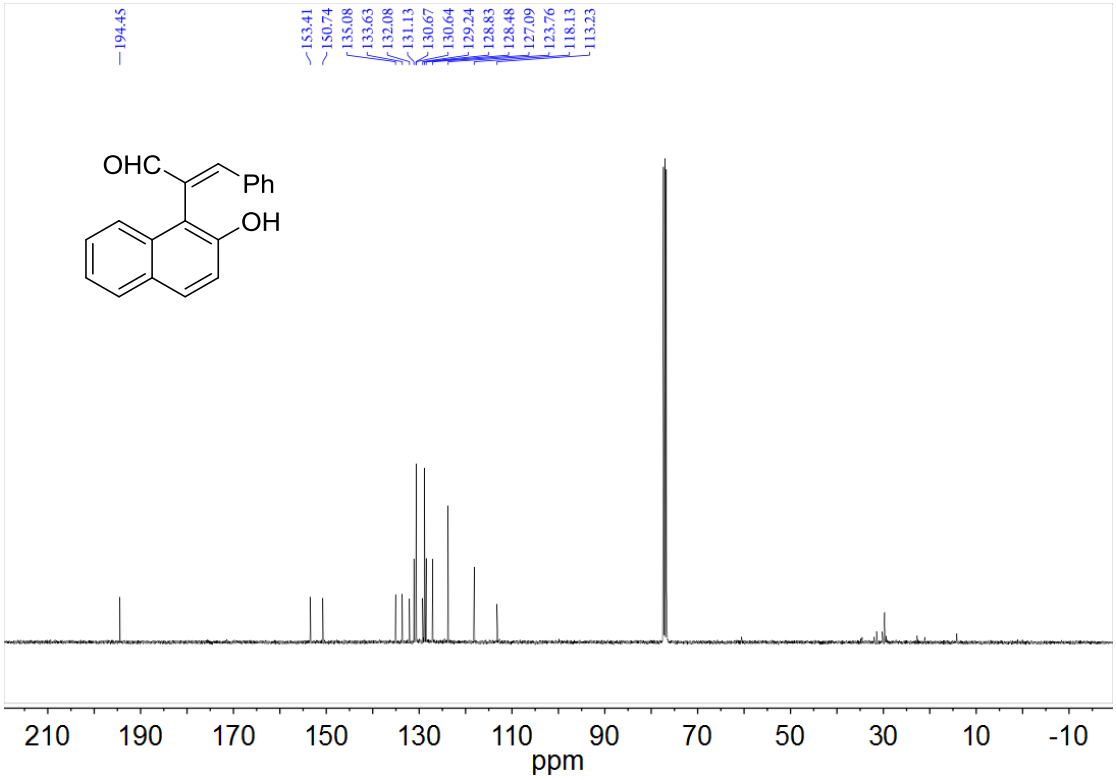
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.86 – 7.74 (m, 3H), 7.47 – 7.37 (m, 1H), 7.37 – 7.27 (m, 2H), 7.27 – 7.27 (m, 1H), 7.19 – 7.08 (m, 5H), 5.75 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.5, 153.4, 150.7, 135.1, 133.6, 132.1, 131.1, 130.7, 130.6 (2C), 129.2, 128.8 (2C), 128.5, 127.1, 123.8 (2C), 118.1, 113.2. **HRMS** (EI) *m/z* Calcd. for $C_{19}H_{14}O_2$ (M^+): 274.0994; found: 274.0995.

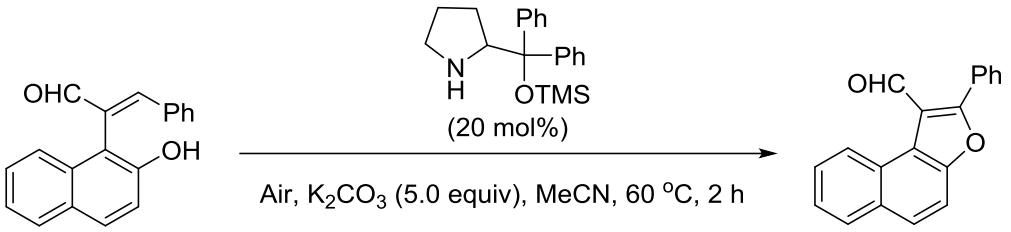
^{1}H NMR Spectrum of Compound 5aa'





^{13}C NMR Spectrum of Compound 5aa'





5aa' **5aa**

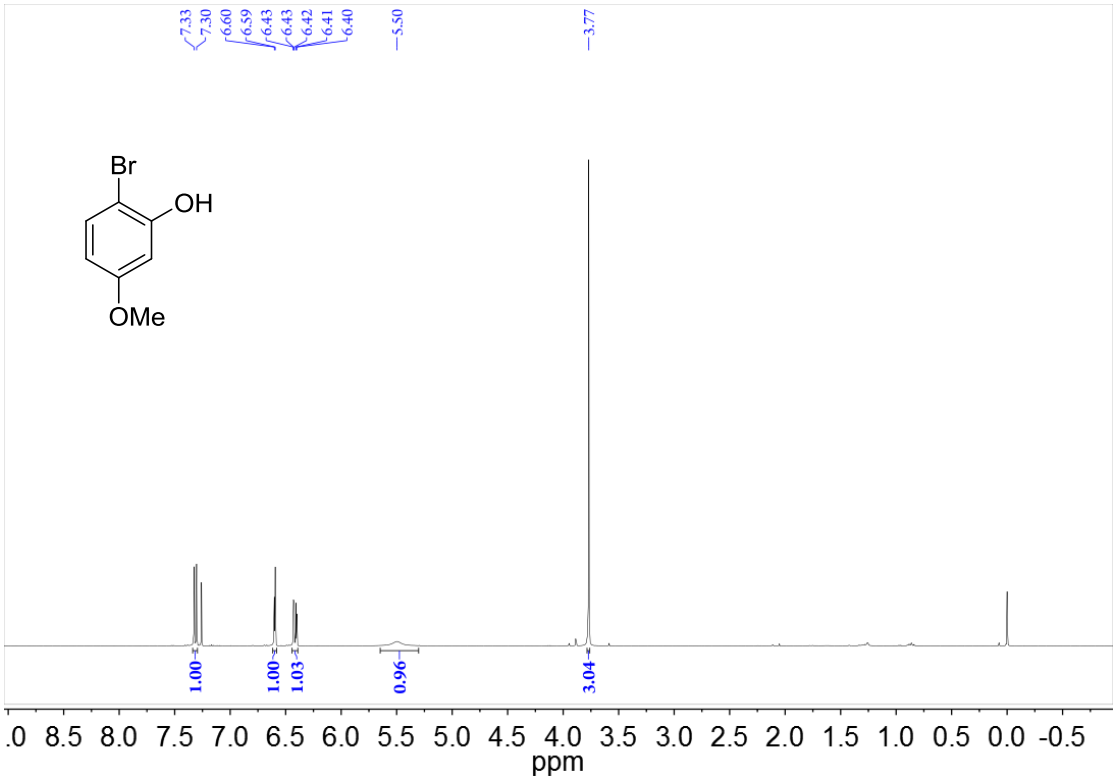
To a solution of **5aa'** (18 mg) in MeCN (1 mL) was added potassium carbonate (46 mg) and diphenylprolinol TMS ether (5 mg), then the reaction mixture was stirred at 60 °C for 2 h. After cooling to ambient temperature, the mixture was filtered through the Celite pad. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 200:1) to afford the desired product **5aa** as a yellow solid (17 mg, 97%).

7. References

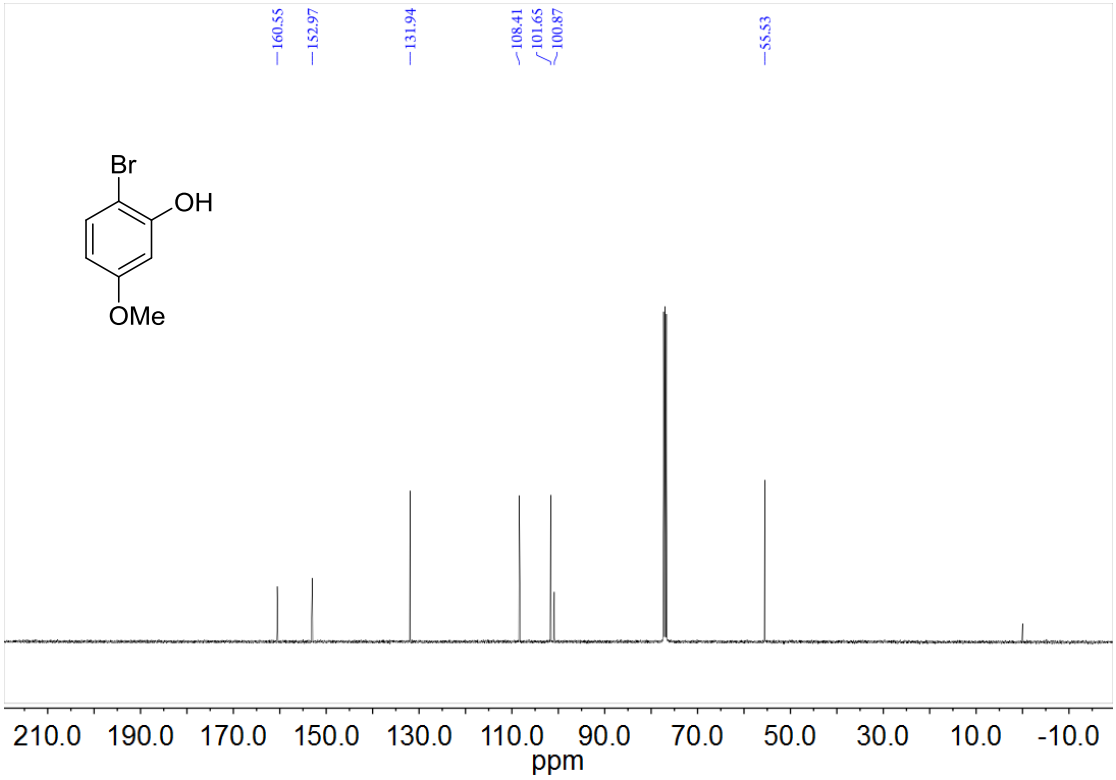
1. M. O. Kitching, T. E. Hurst and V. Snieckus, *Angew. Chem. Int. Ed.*, 2012, **51**, 2925.
2. M. W. Carson, M. W. Giese and M. J. Coghlan, *Org. Lett.*, 2008, **10**, 2701.
3. (a) R. Frlan, S. Gobec and D. Kikelj, *Tetrahedron*, 2007, **63**, 10698; (b) S. Balamurugan, P. Kannan, M. T. Chuang and S. L. Wu, *Ind. Eng. Chem. Res.*, 2010, **49**, 7121; (c) V. Sandgren, M. Back, I. Kvarnstrom and A. Dahlgren, *Open Med. Chem. J.*, 2013, **7**, 1.
4. H. Kajita and A. Togni, *ChemistrySelect*, 2017, **2**, 1117.
5. (a) G. Hermann, M. Annis, P. Edwards, M. Corrales, L. Díaz and R. Goodnow, *Synthesis*, 2008, **2008**, 221; (b) L. Shu, P. Wang, W. Liu and C. Gu, *Org. Process Res. Dev.*, 2012, **16**, 1866.
6. Y. Ueta, K. Mikami and S. Ito, *Angew. Chem. Int. Ed.*, 2016, **55**, 7525.
7. E. G. Lovering and K. J. Laidler, *Can. J. Chem.*, 1960, **38**, 2367.
8. L. Zu, S. Zhang, H. Xie and W. Wang, *Org. Lett.*, 2009, **11**, 1627.

8. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

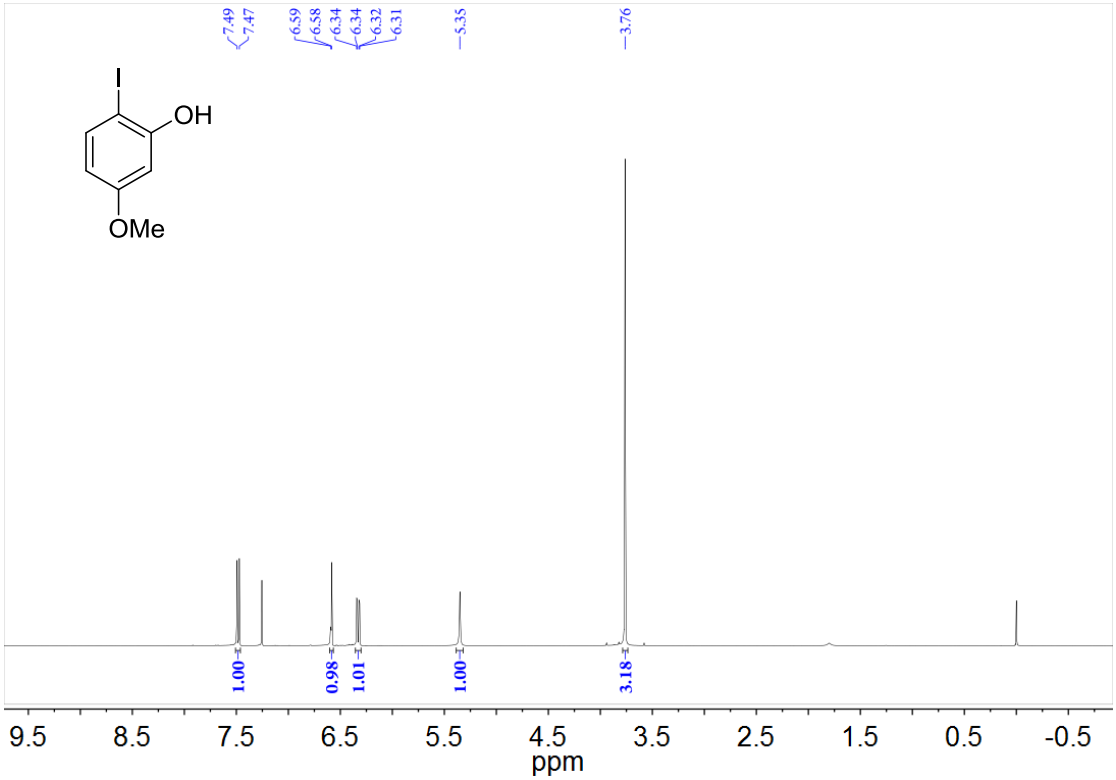
^{1}H NMR Spectrum of Compound 1a



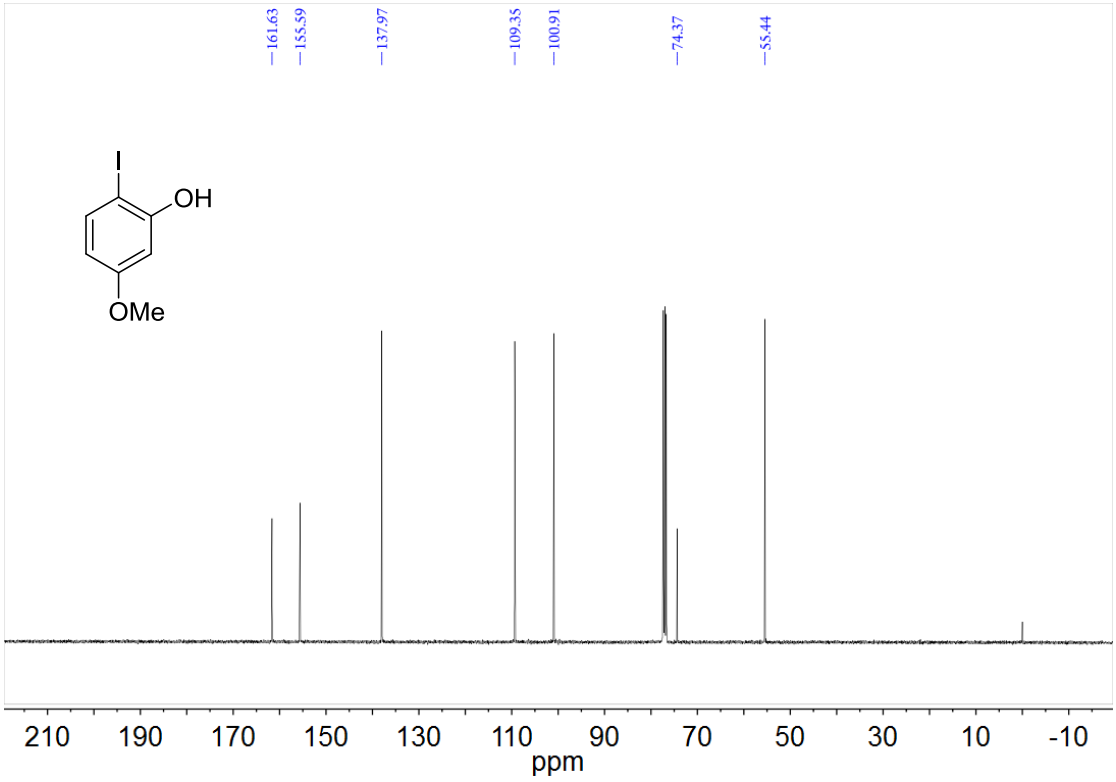
^{13}C NMR Spectrum of Compound 1a



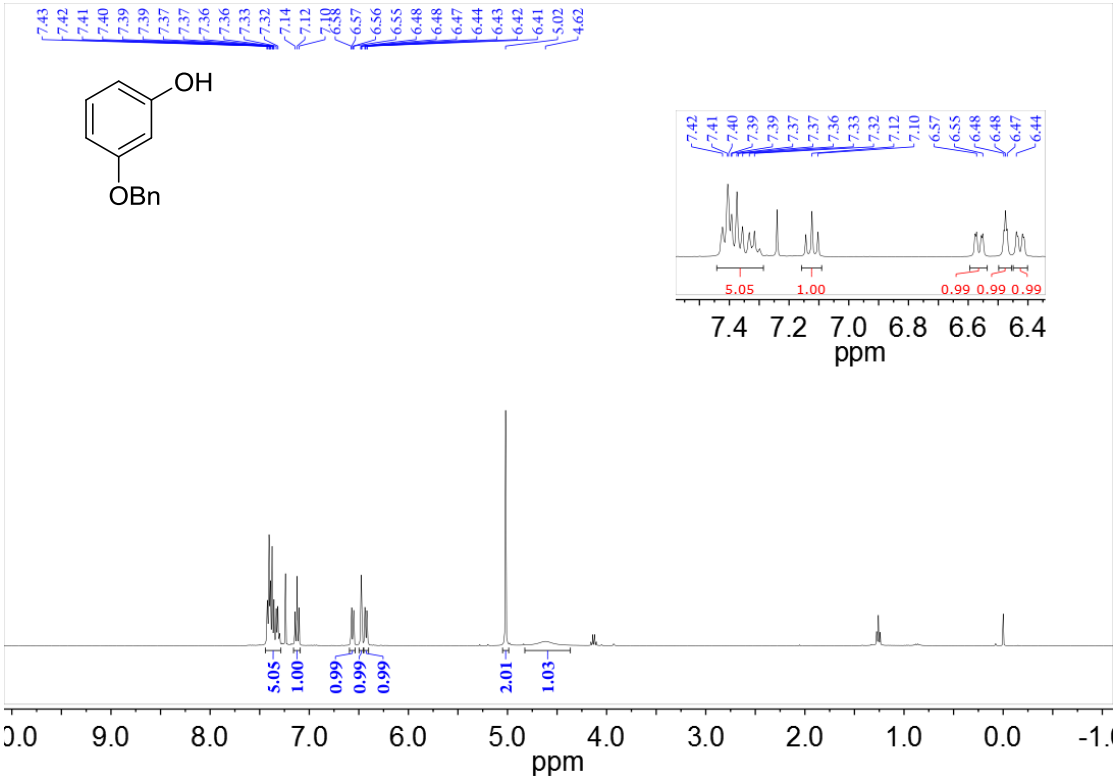
^{1}H NMR Spectrum of Compound S1



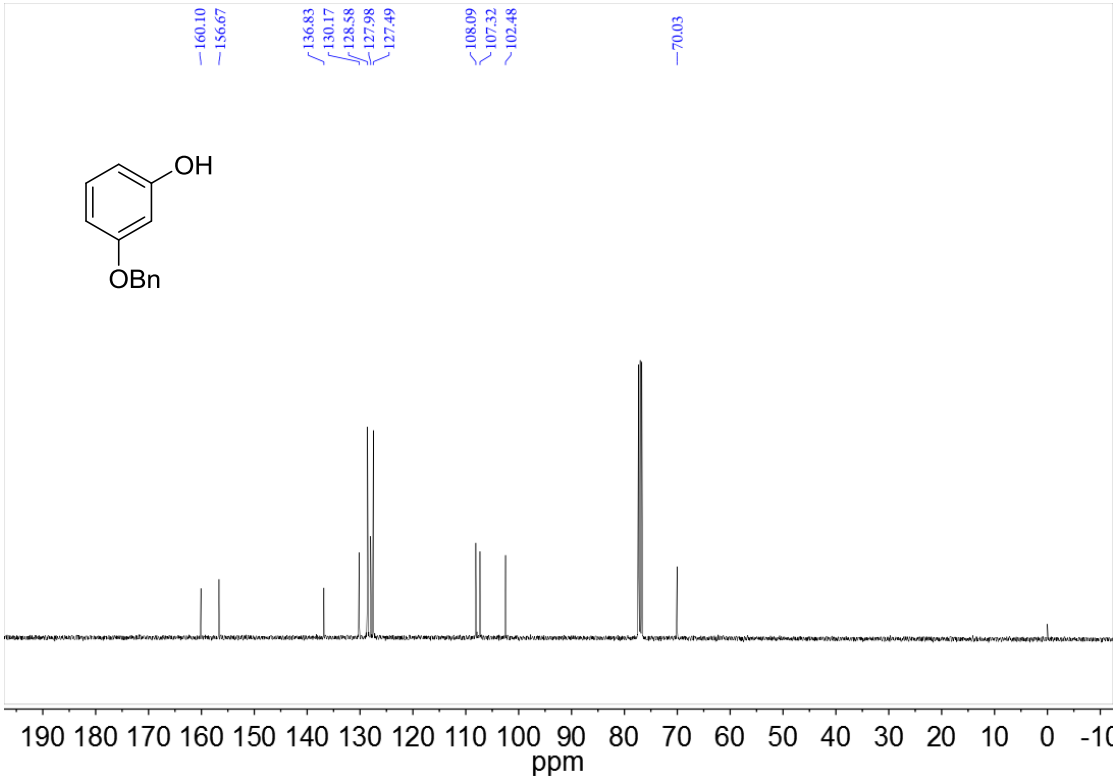
^{13}C NMR Spectrum of Compound S1



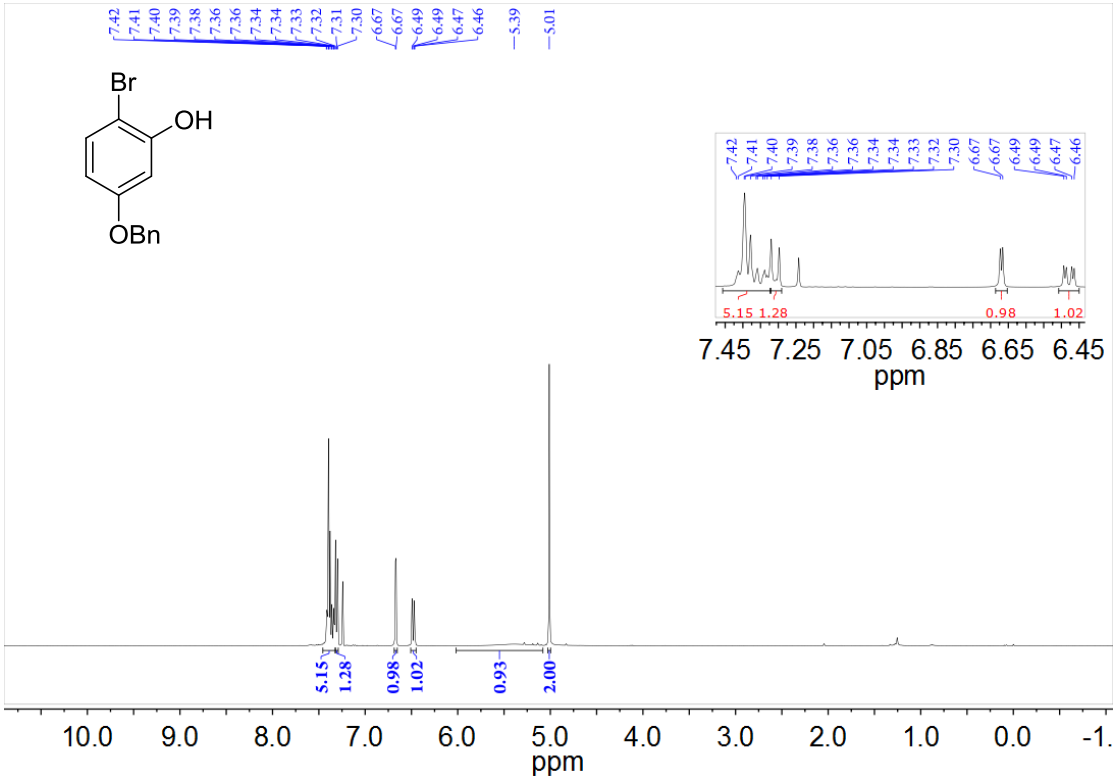
^{1}H NMR Spectrum of Compound S2



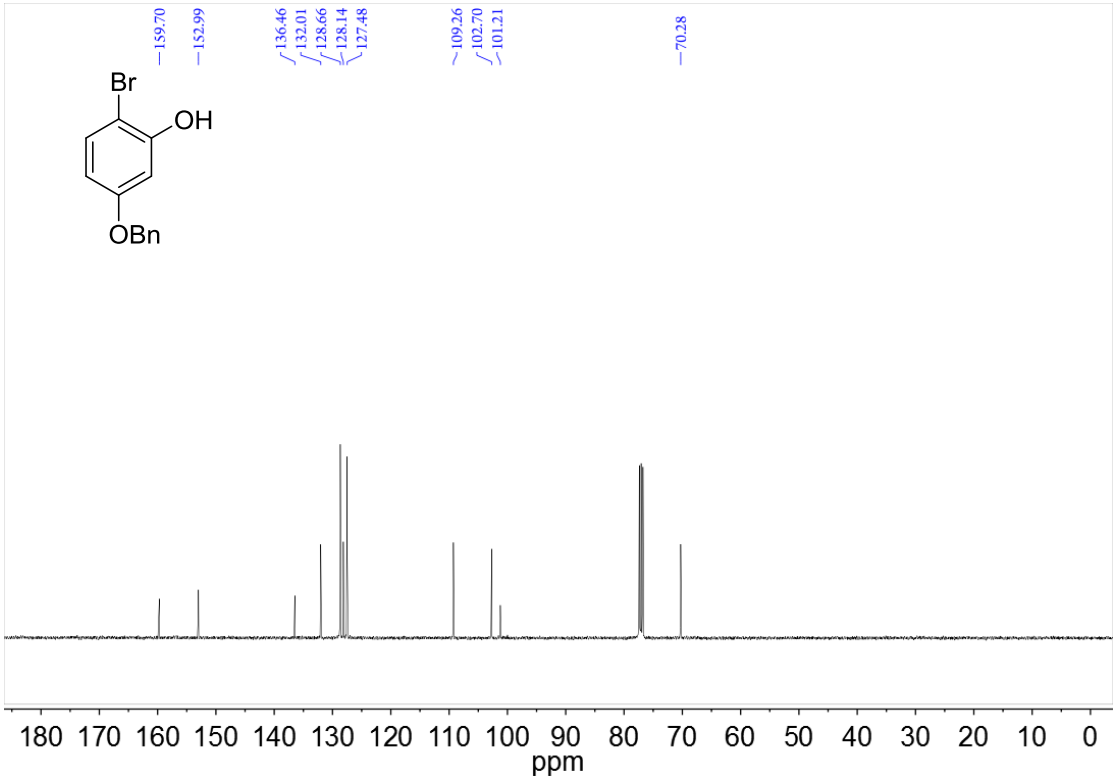
^{13}C NMR Spectrum of Compound S2



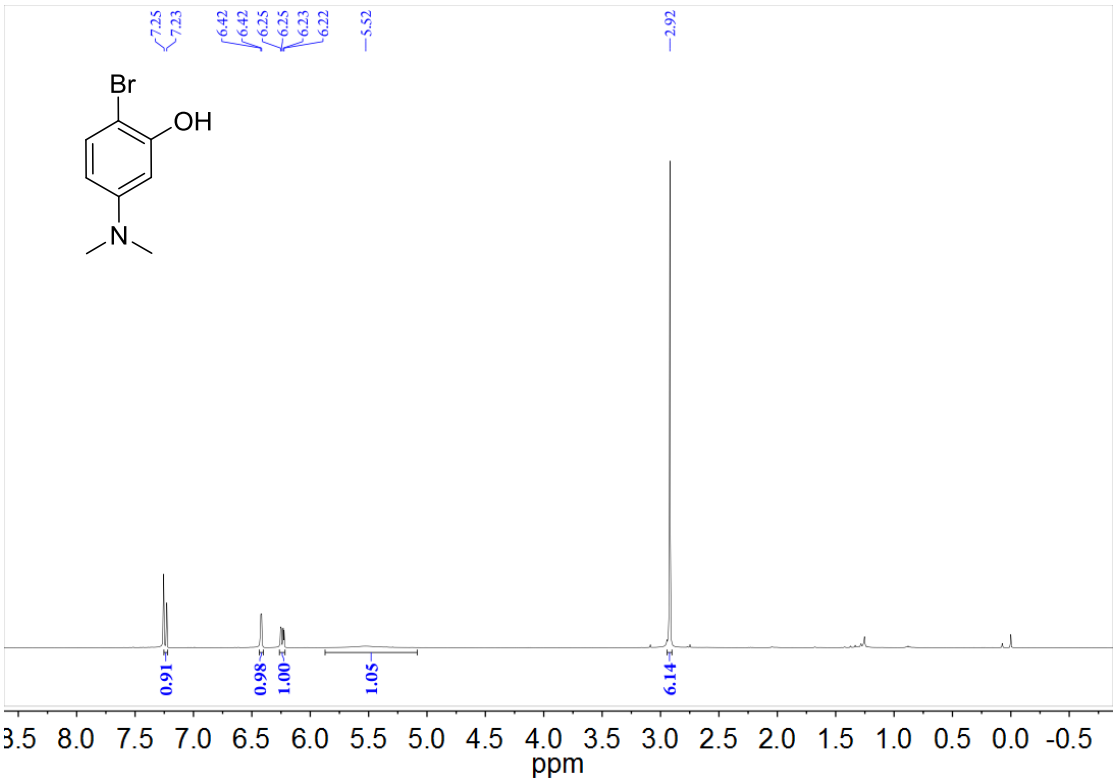
^{1}H NMR Spectrum of Compound 1b



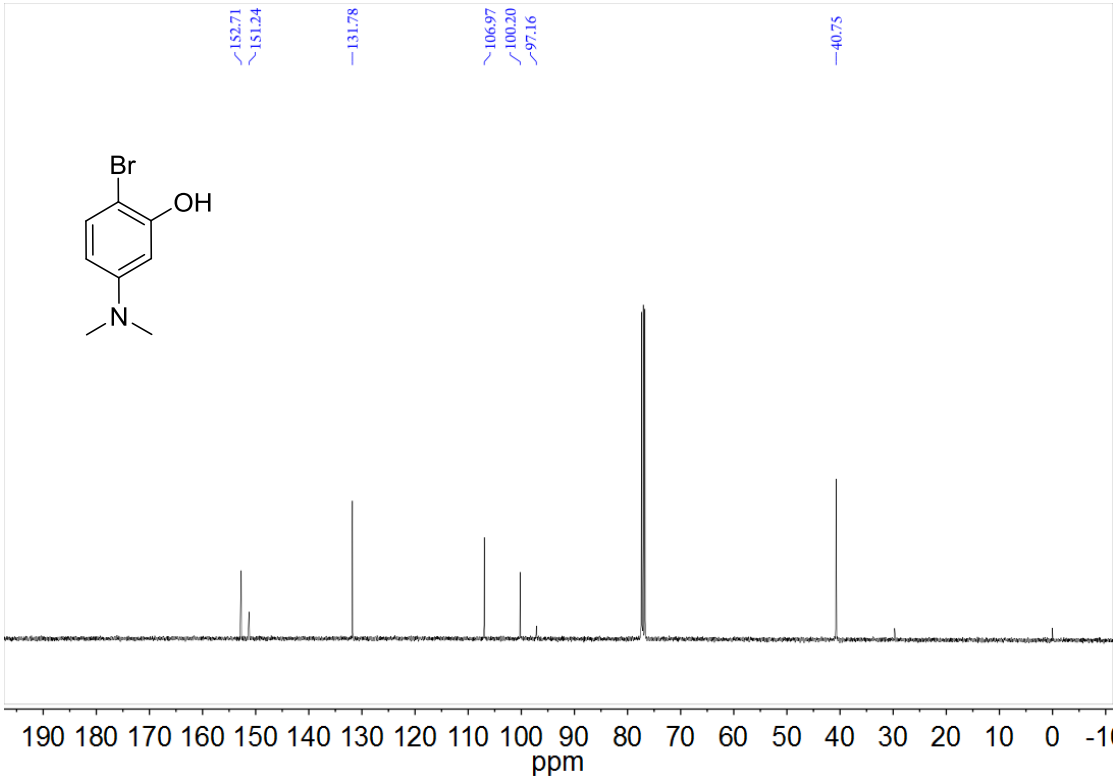
^{13}C NMR Spectrum of Compound 1b



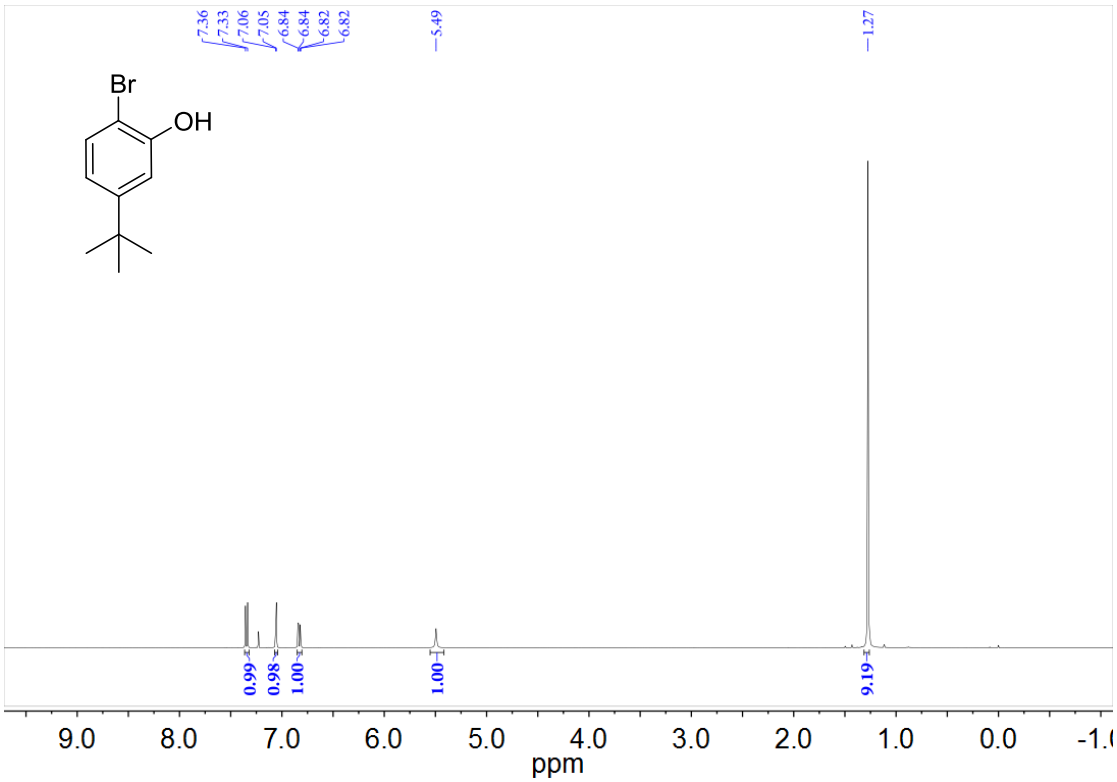
^{1}H NMR Spectrum of Compound 1c



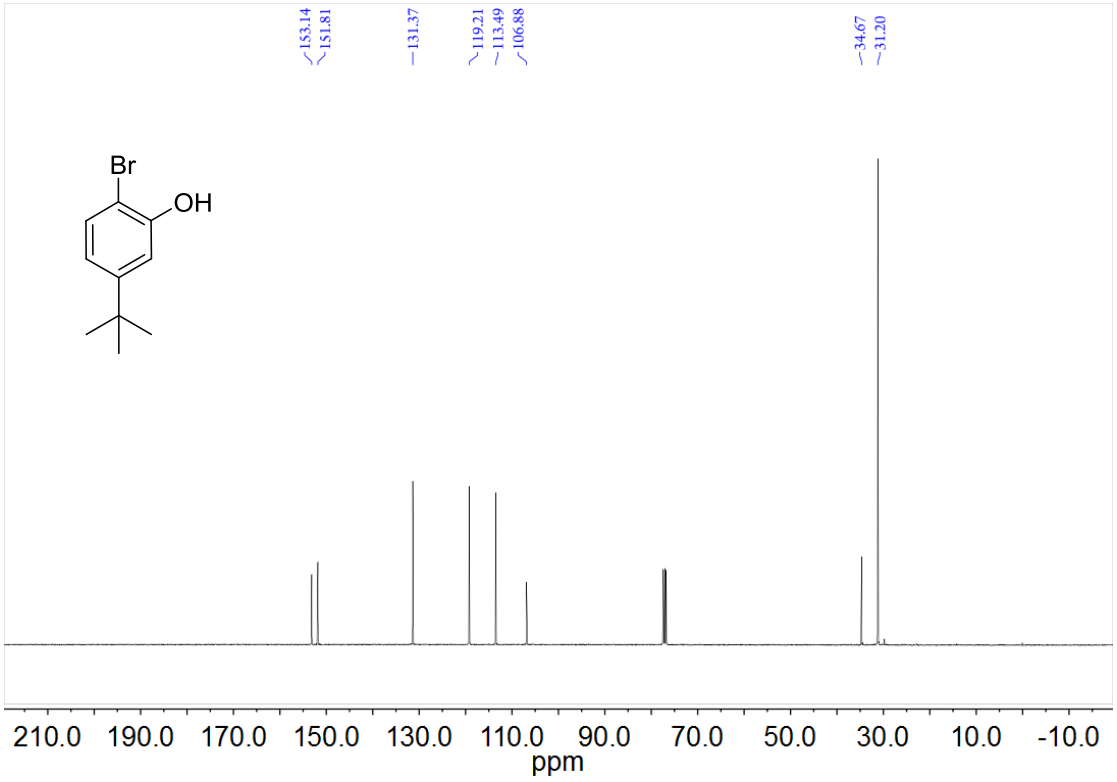
^{13}C NMR Spectrum of Compound 1c



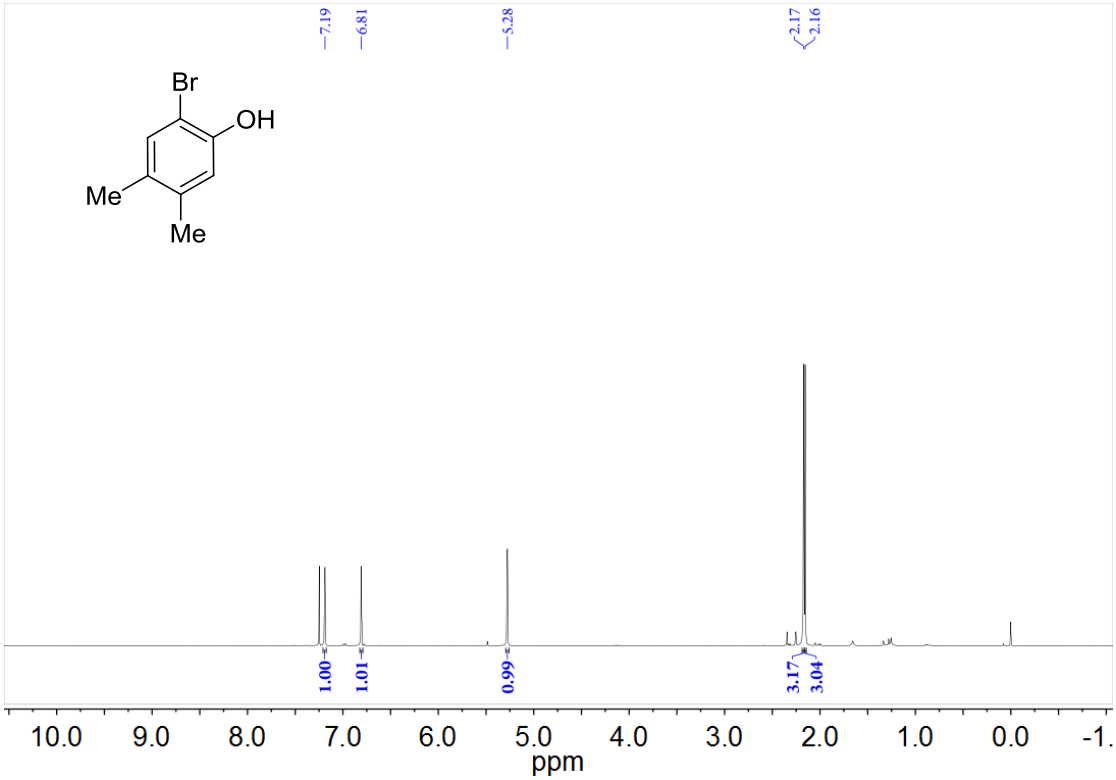
^{1}H NMR Spectrum of Compound 1d



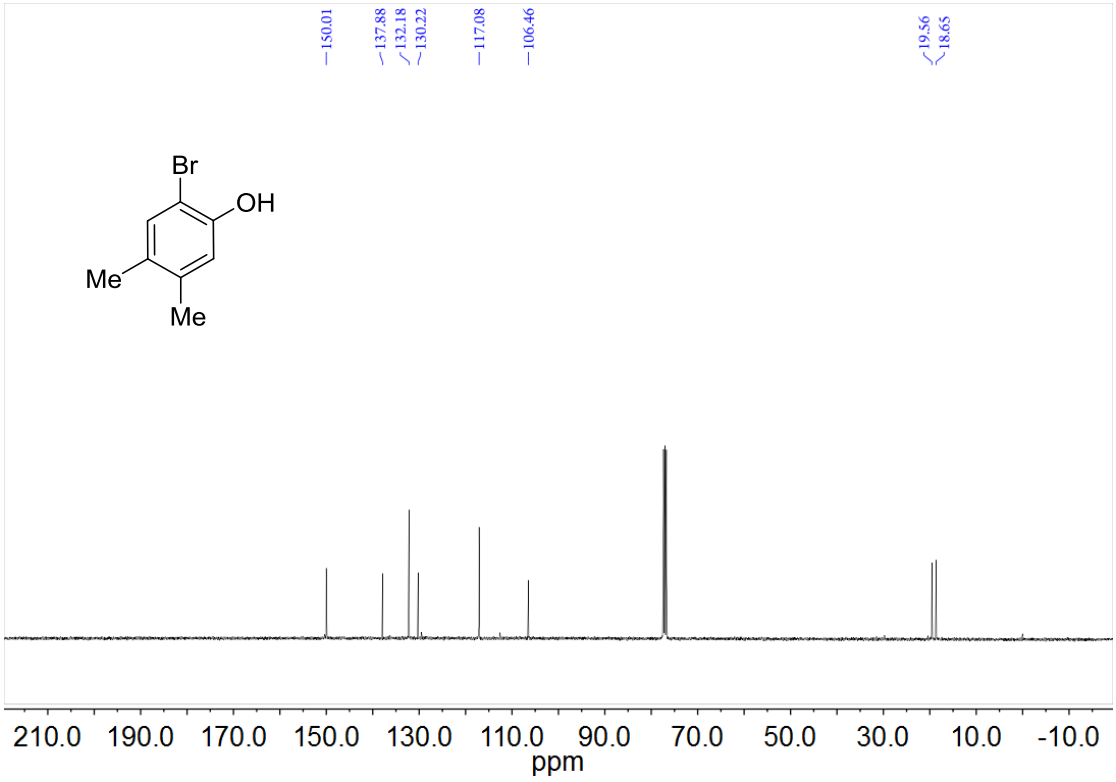
^{13}C NMR Spectrum of Compound 1d



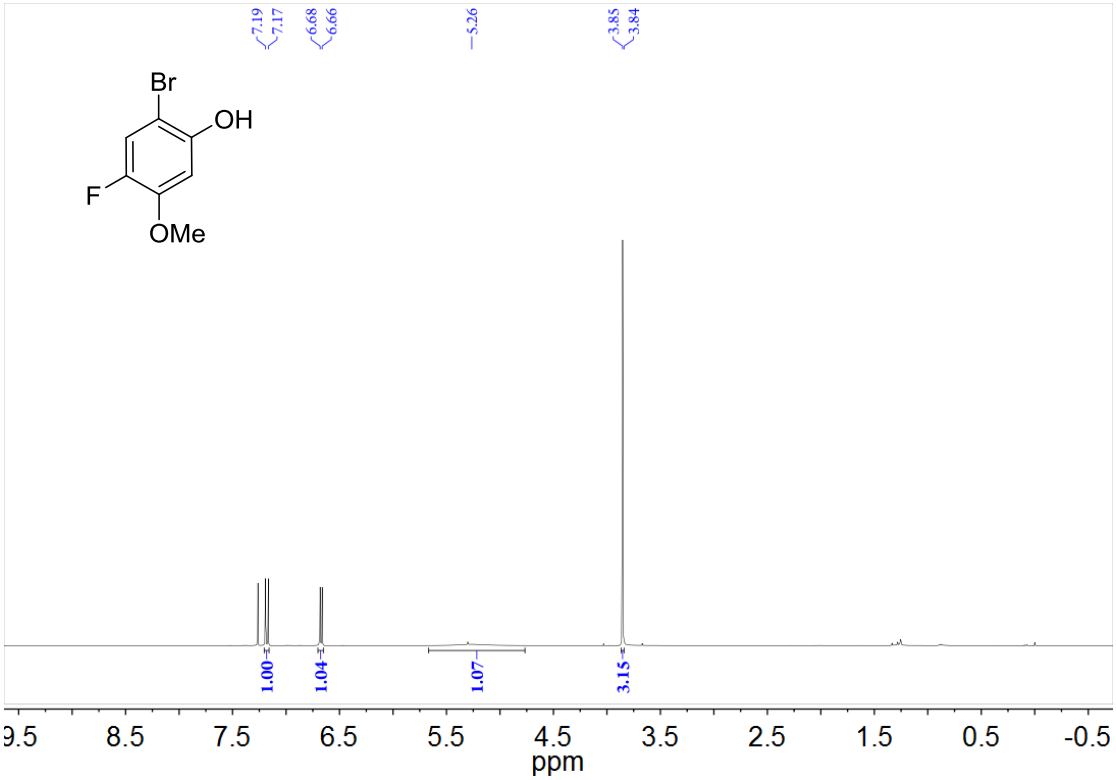
^{1}H NMR Spectrum of Compound 1f



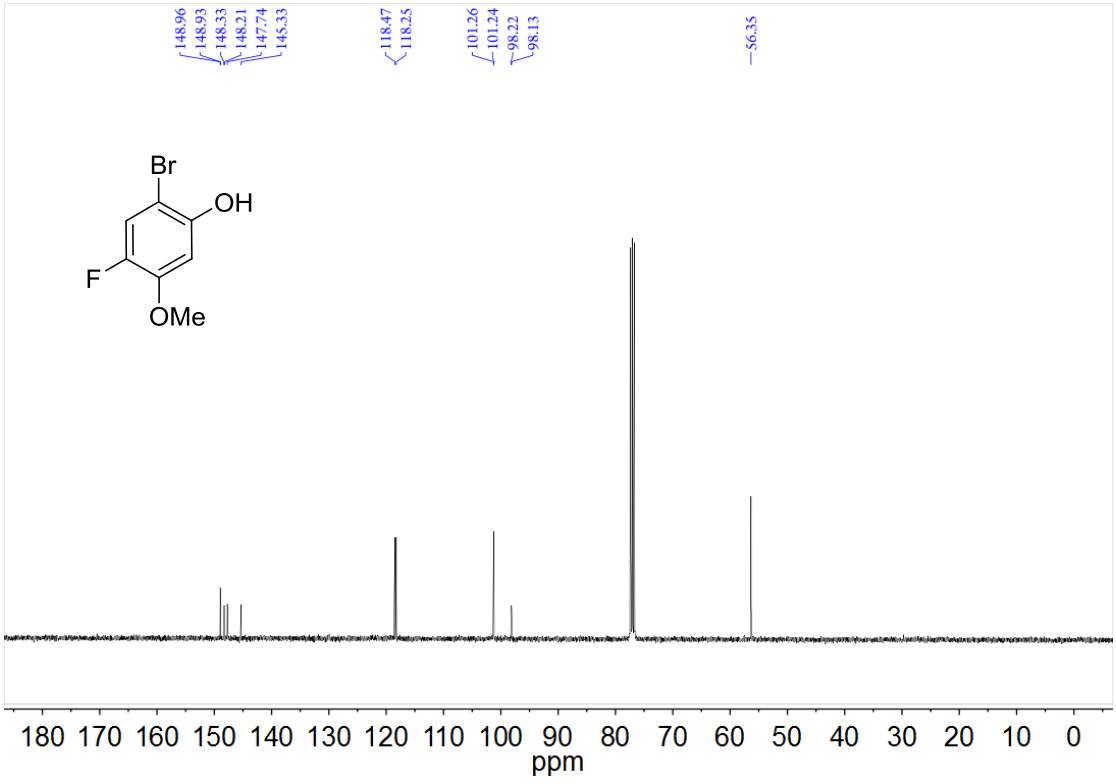
^{13}C NMR Spectrum of Compound 1f



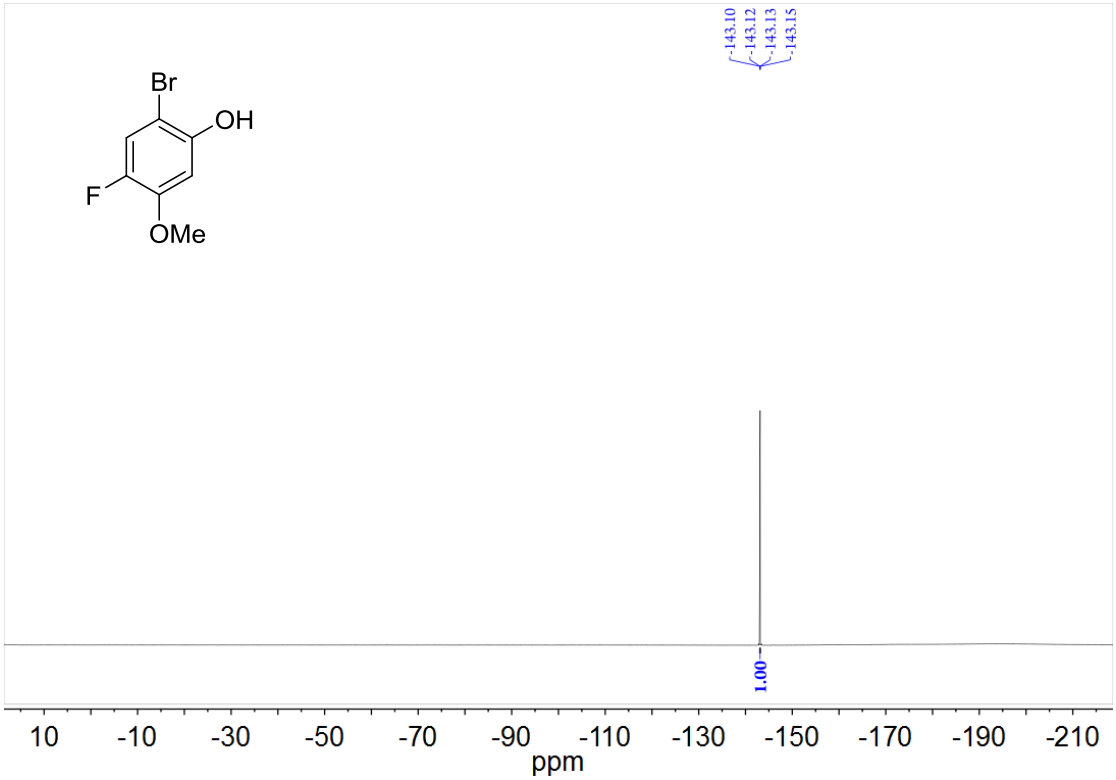
^{1}H NMR Spectrum of Compound 1g



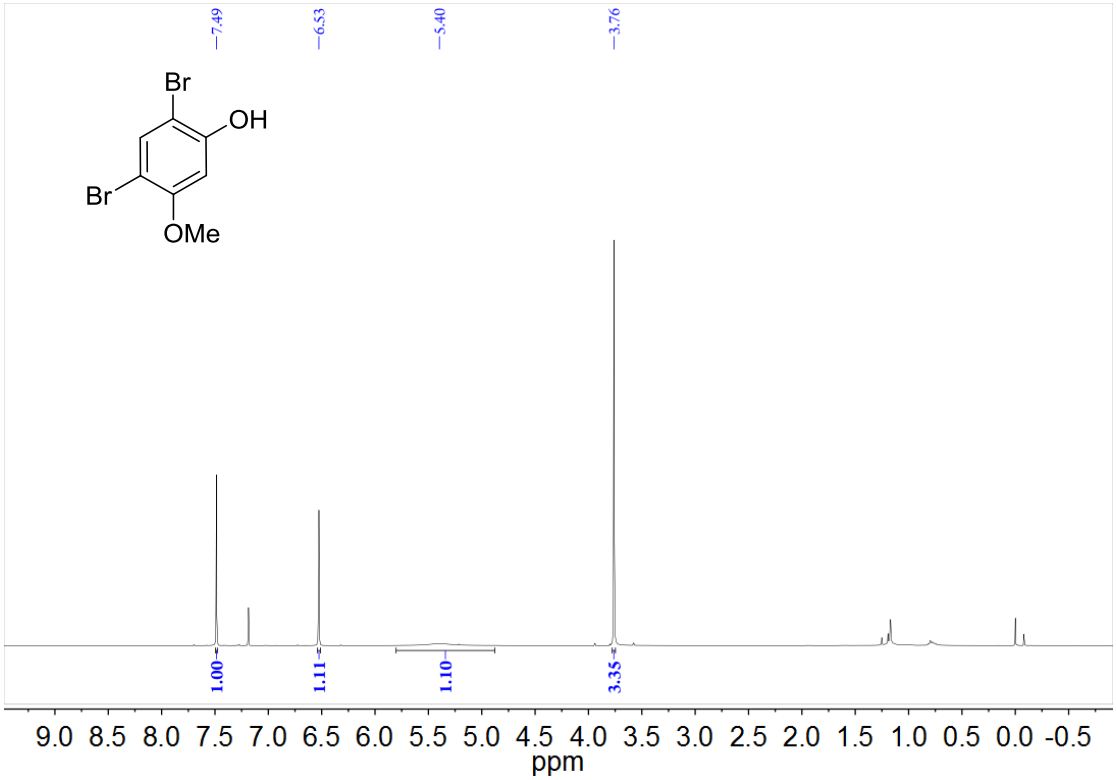
^{13}C NMR Spectrum of Compound 1g



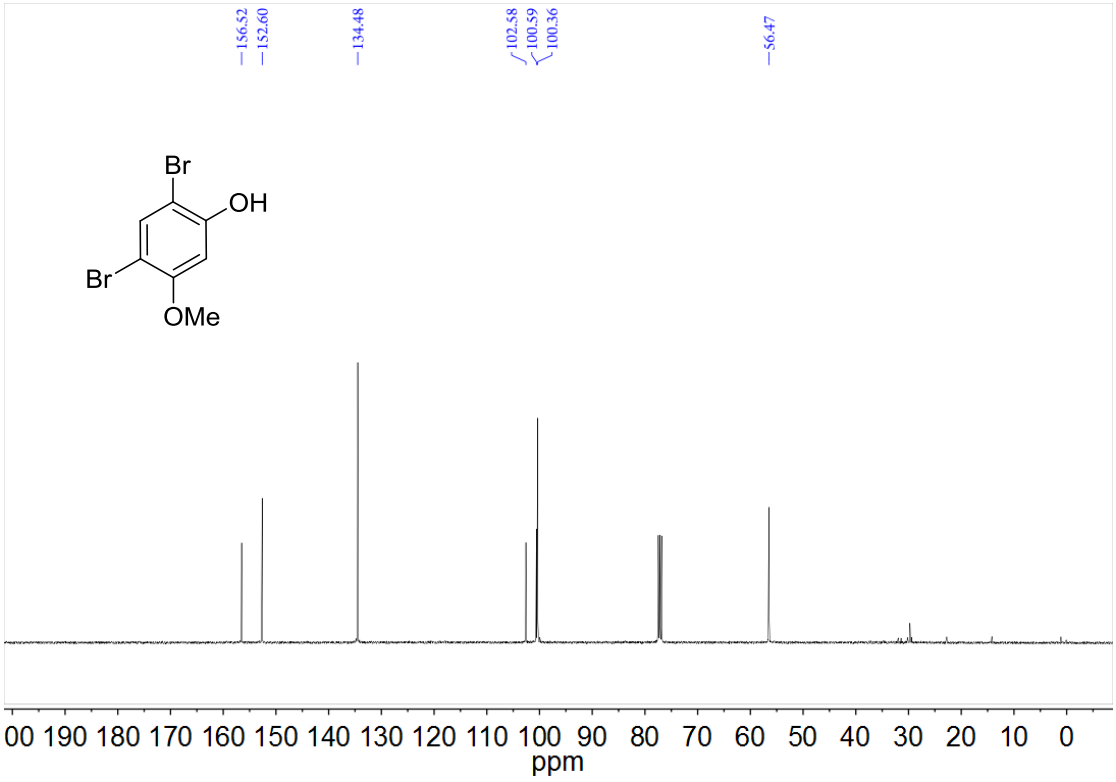
^{19}F NMR Spectrum of Compound 1g



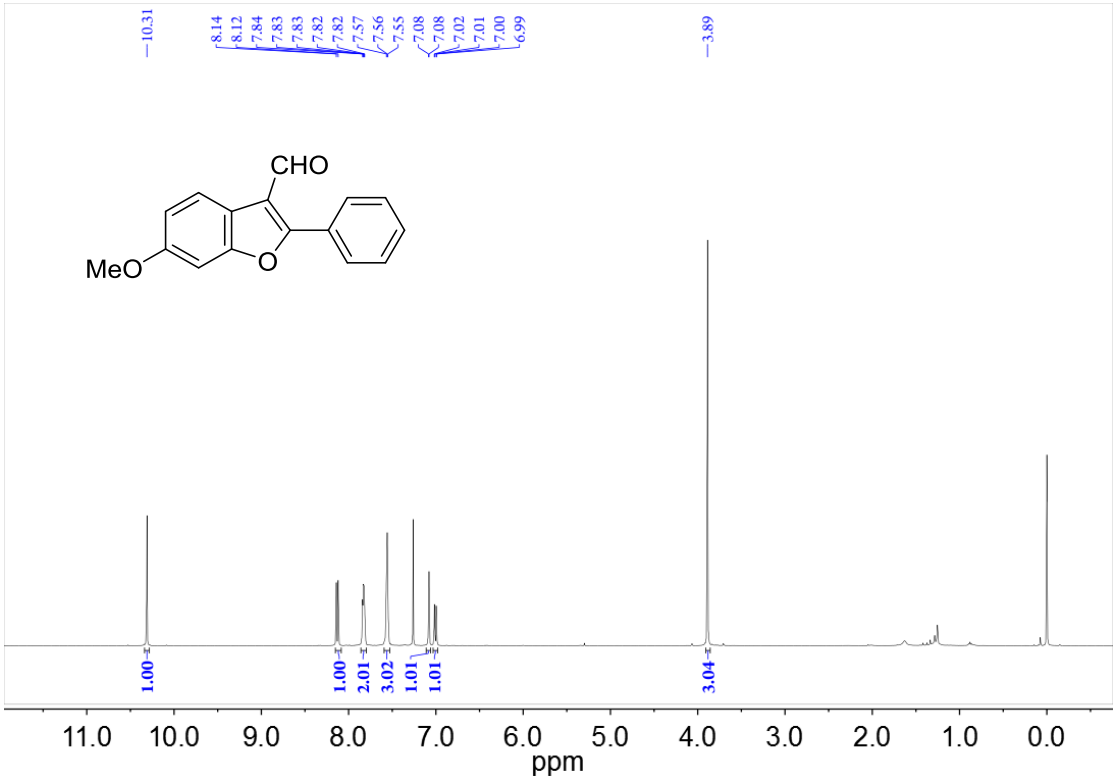
^{1}H NMR Spectrum of Compound 1h



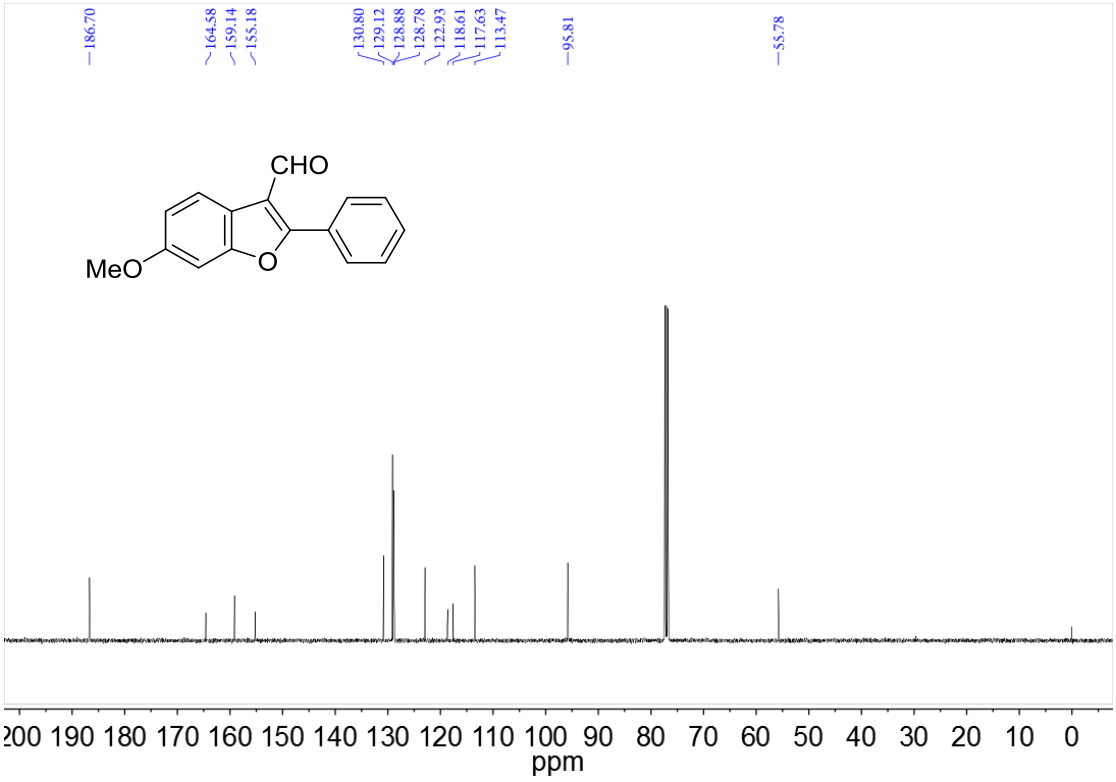
^{13}C NMR Spectrum of Compound 1h



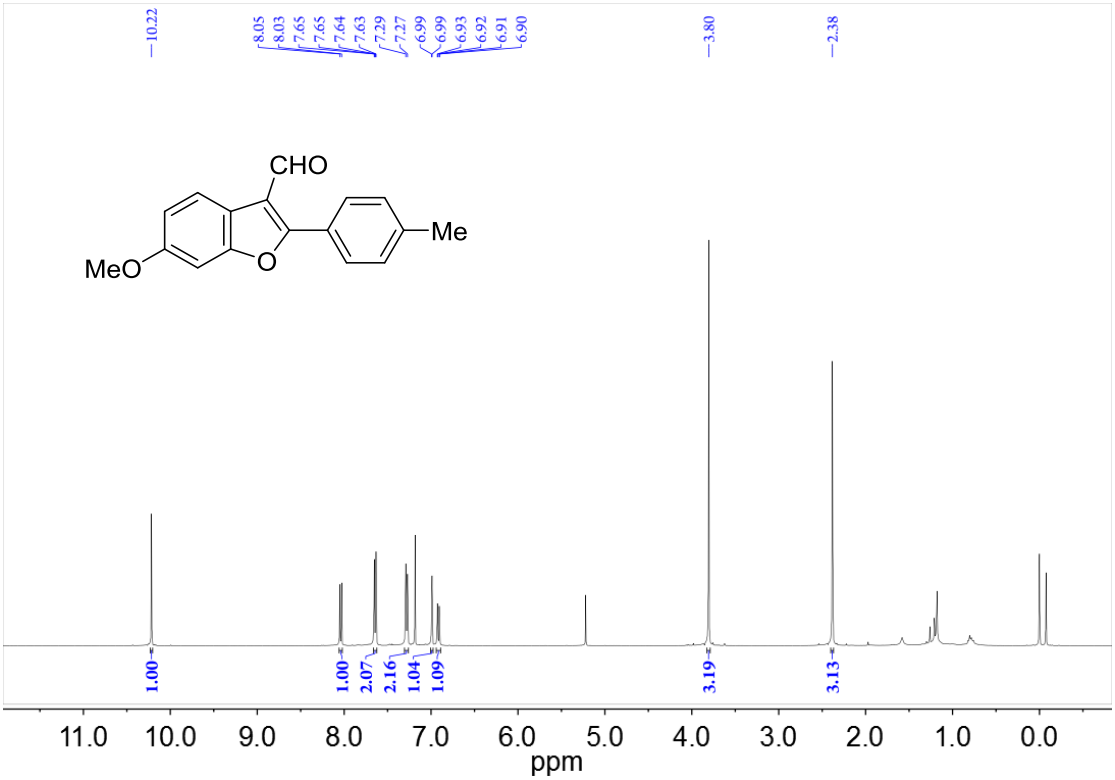
^{1}H NMR Spectrum of Compound 3aa



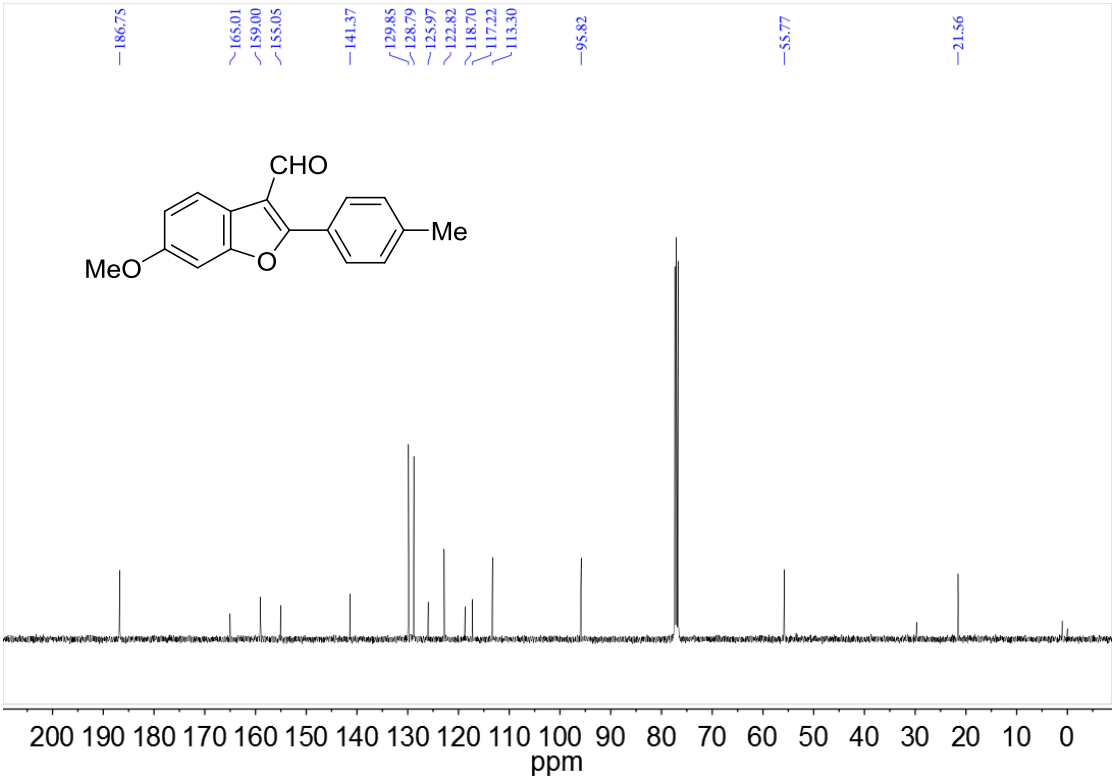
^{13}C NMR Spectrum of Compound 3aa



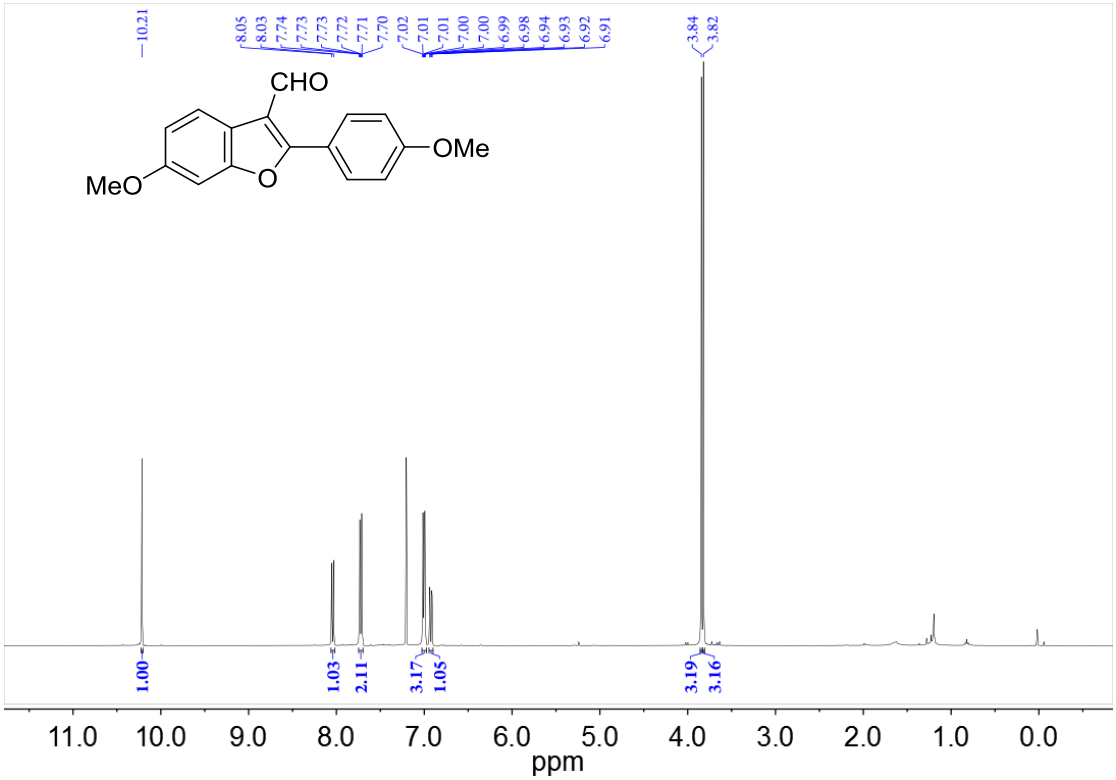
^{1}H NMR Spectrum of Compound 3ab



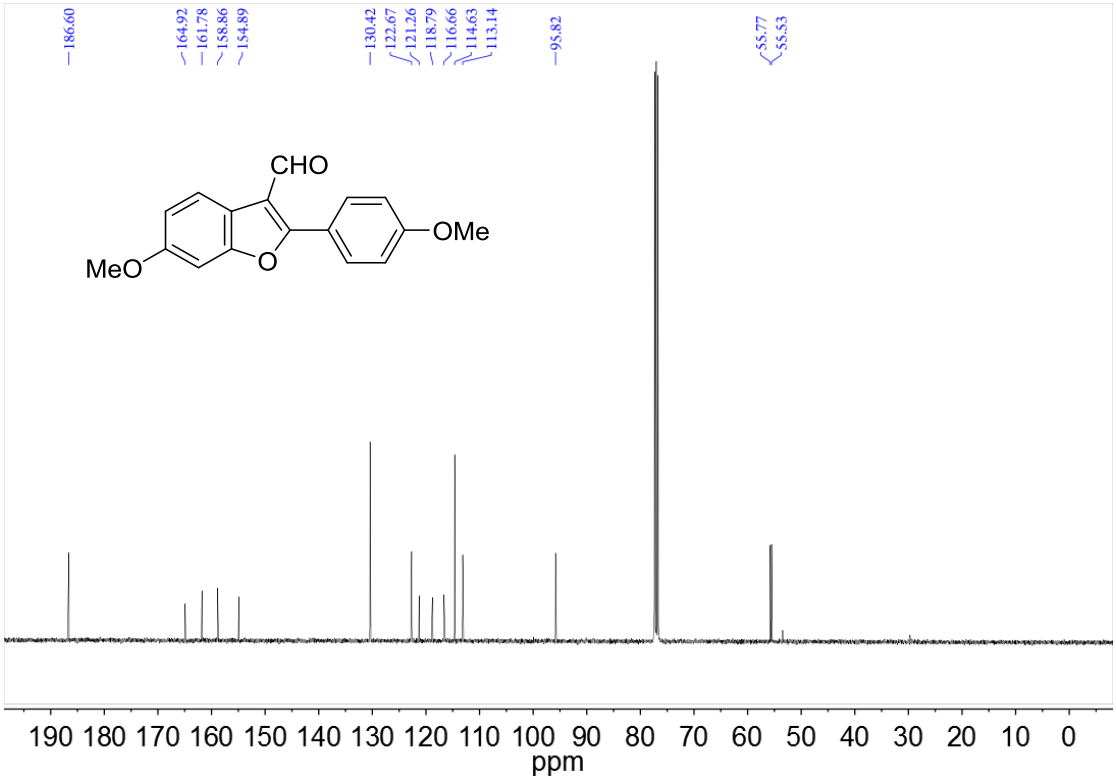
^{13}C NMR Spectrum of Compound 3ab



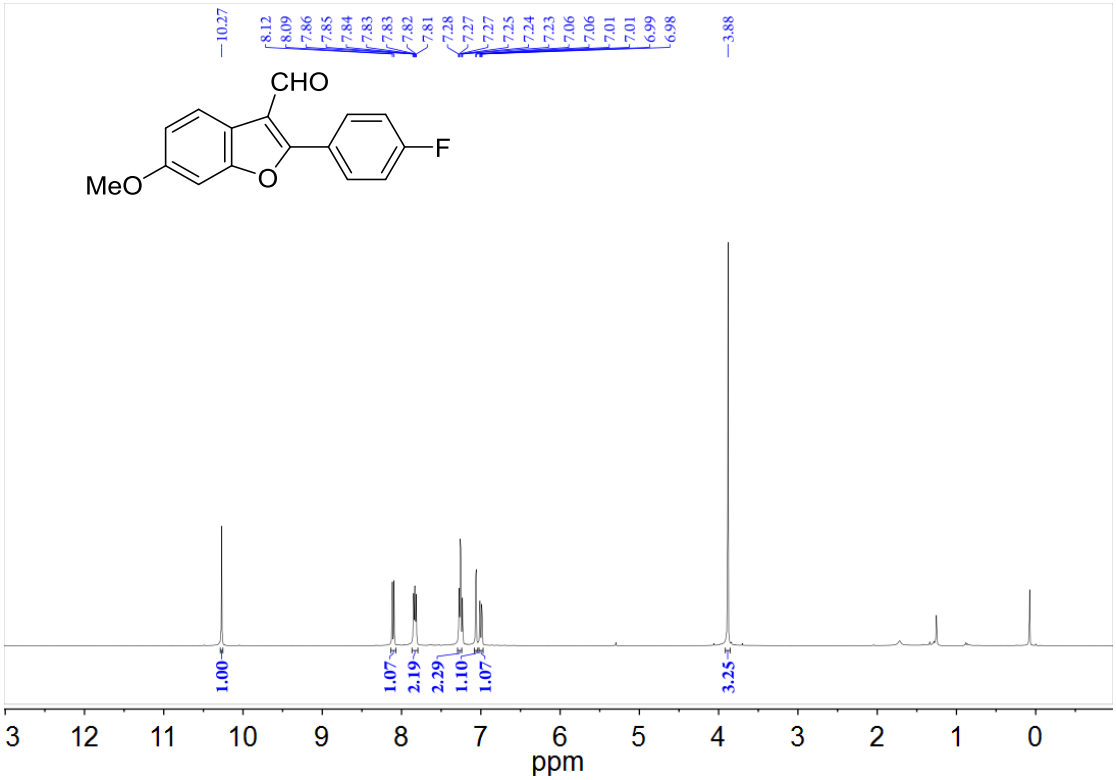
^{1}H NMR Spectrum of Compound 3ac



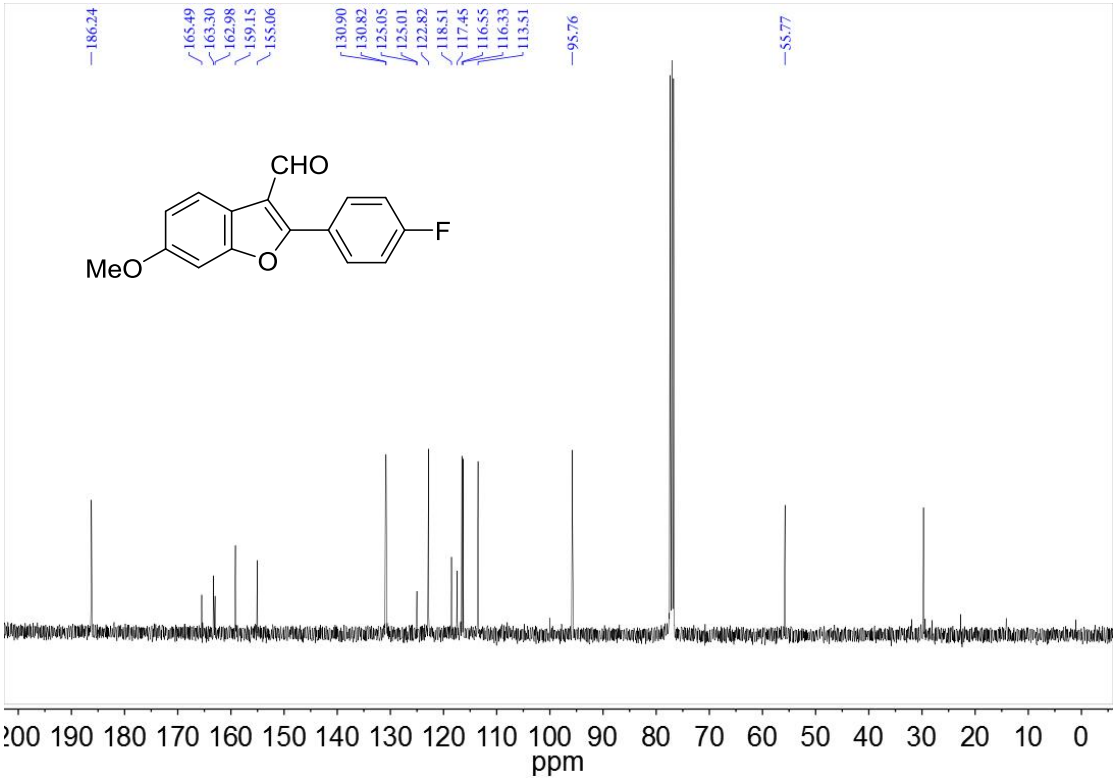
^{13}C NMR Spectrum of Compound 3ac



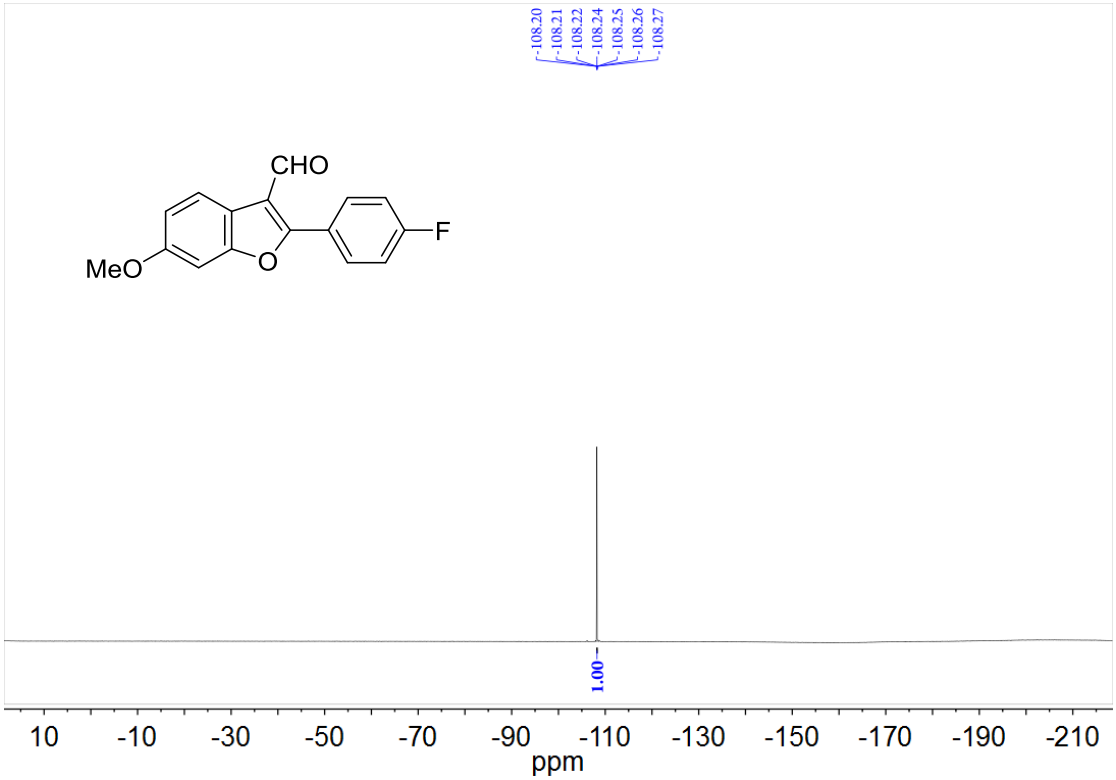
^{1}H NMR Spectrum of Compound 3ad



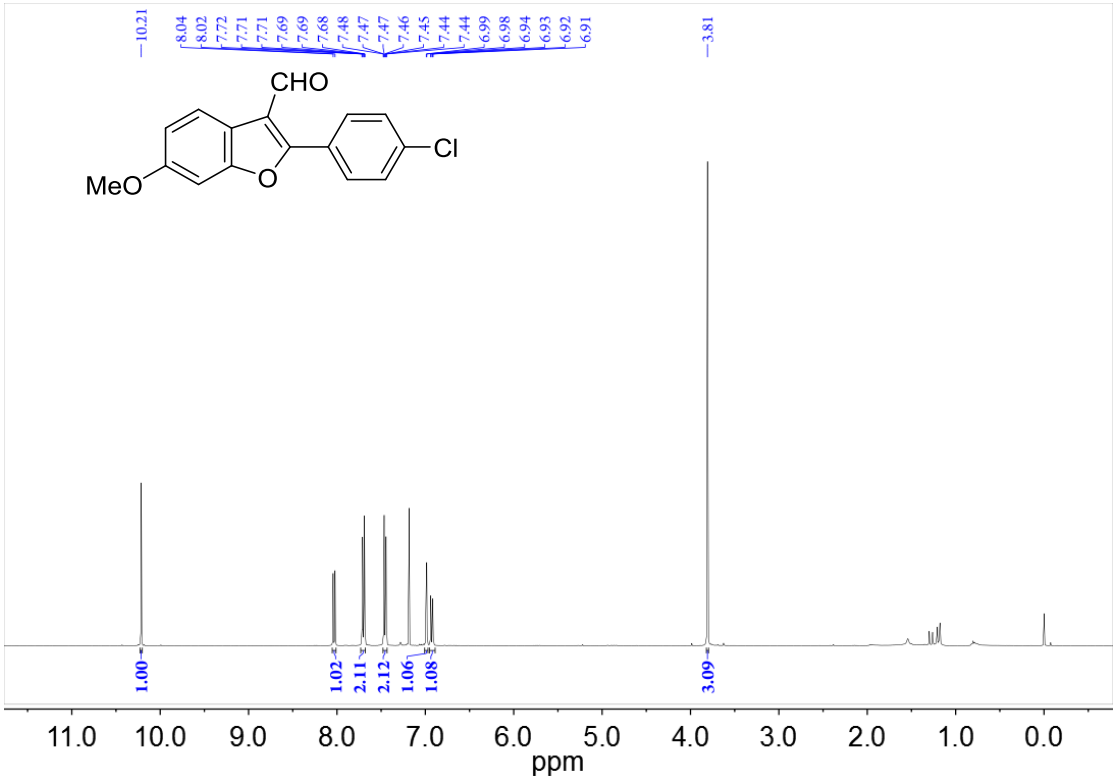
^{13}C NMR Spectrum of Compound 3ad



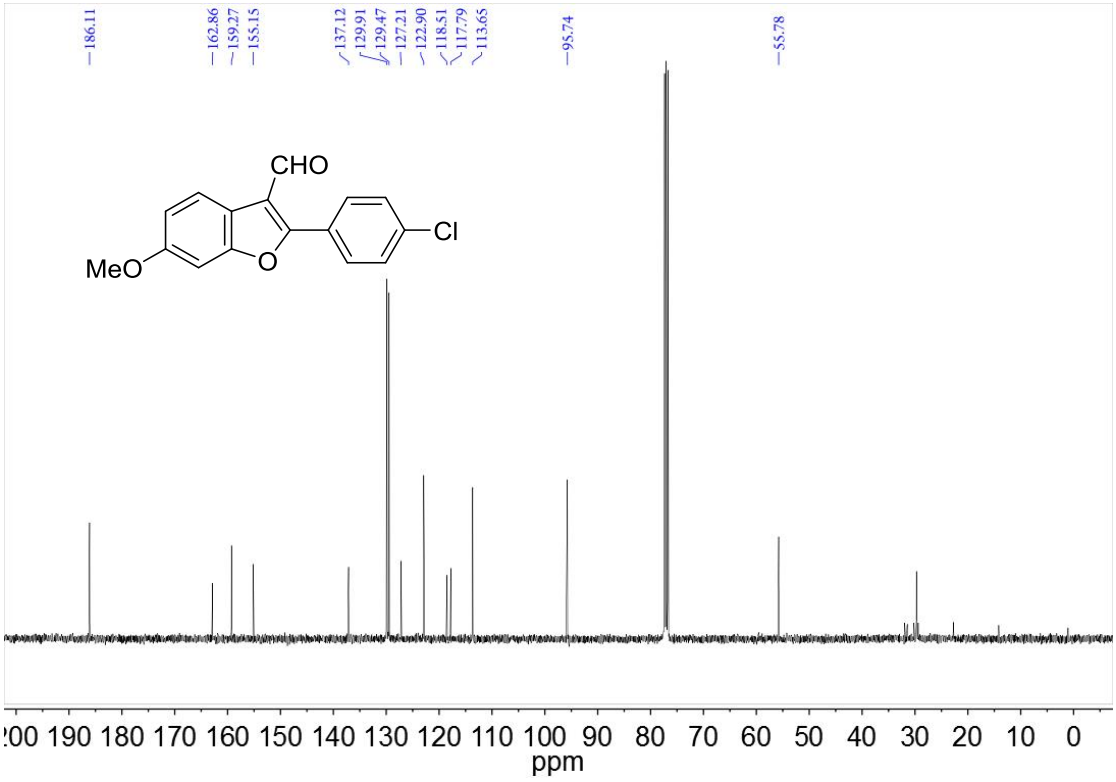
^{19}F NMR Spectrum of Compound 3ad



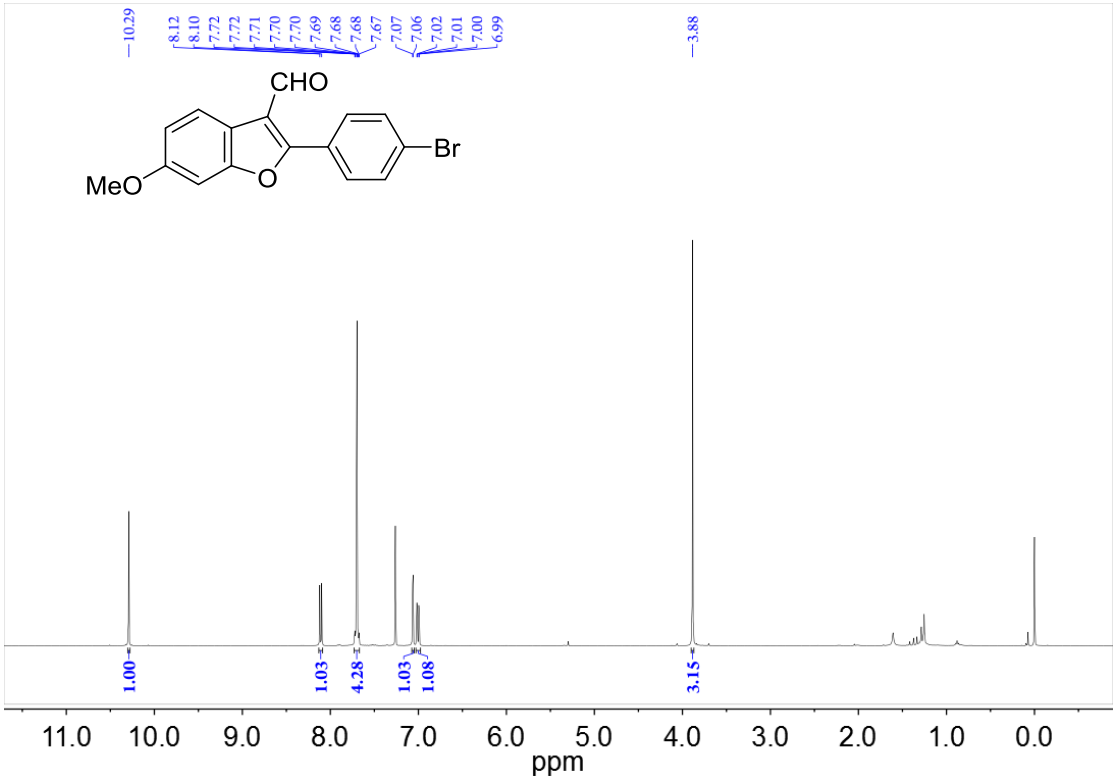
^{1}H NMR Spectrum of Compound 3ae



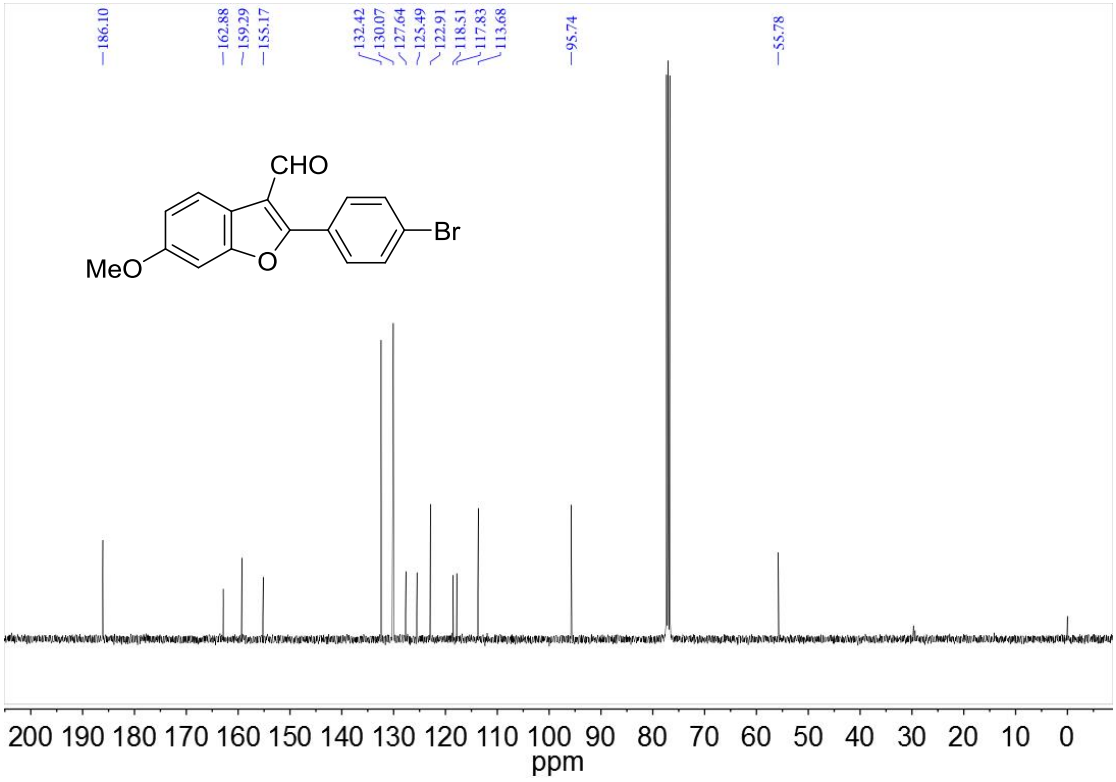
^{13}C NMR Spectrum of Compound 3ae



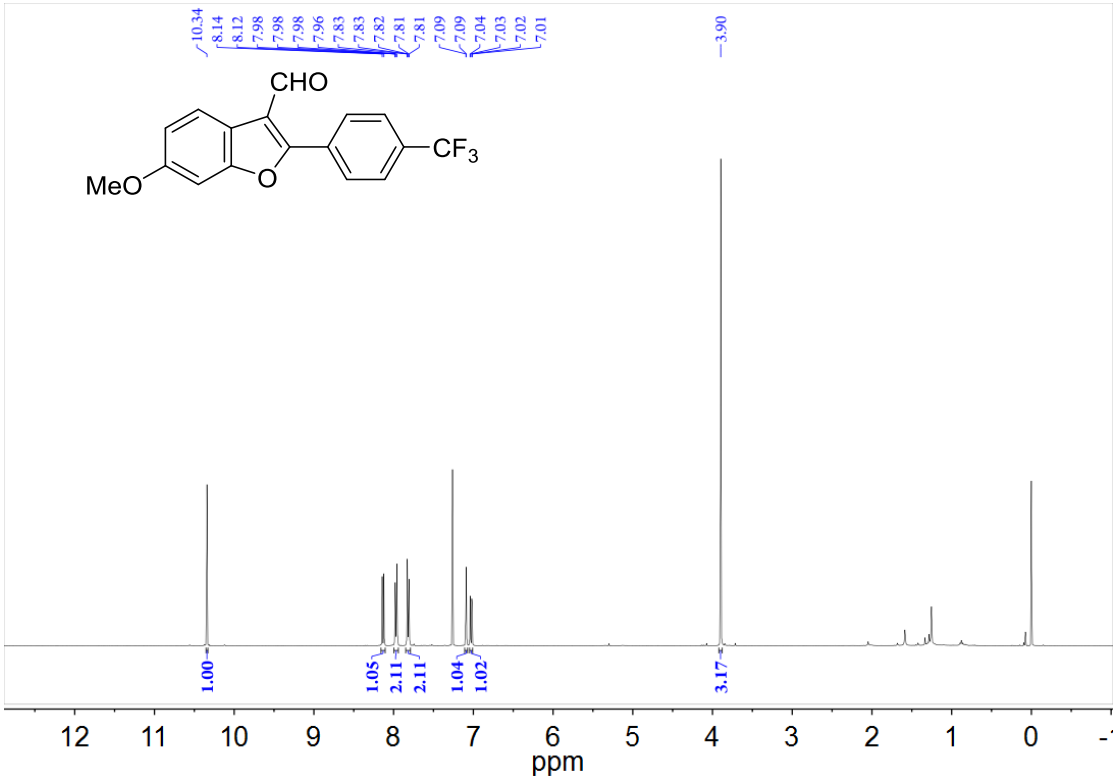
^{1}H NMR Spectrum of Compound 3af



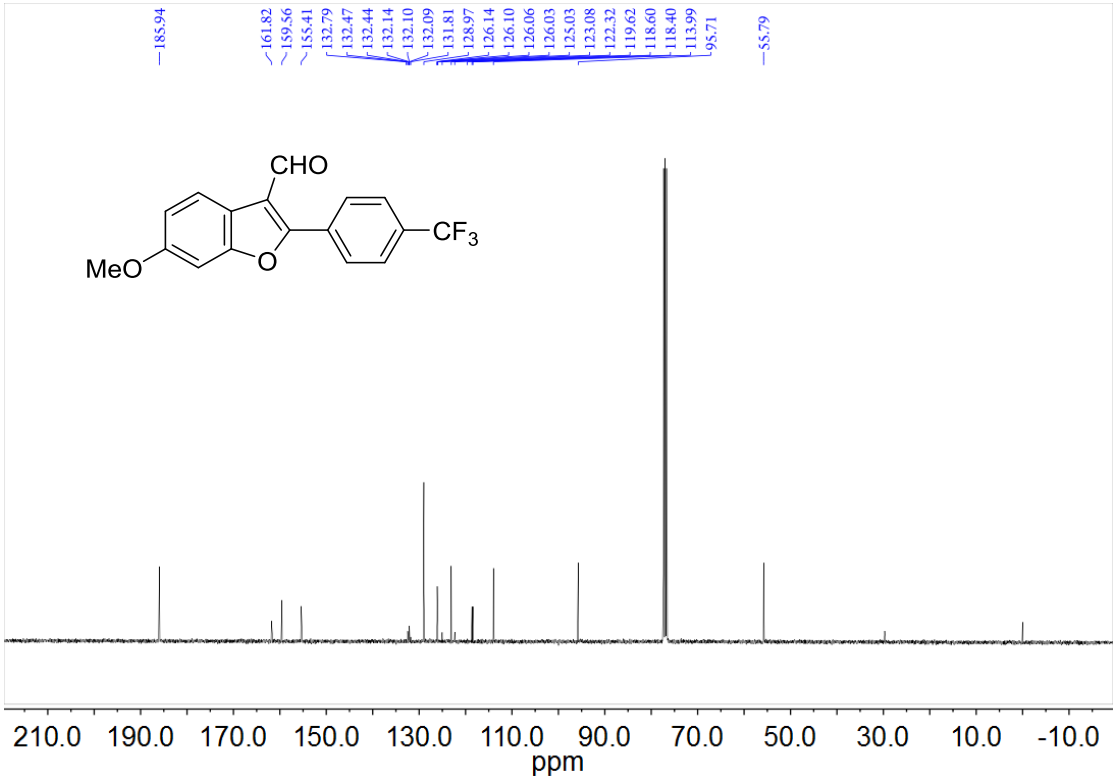
^{13}C NMR Spectrum of Compound 3af



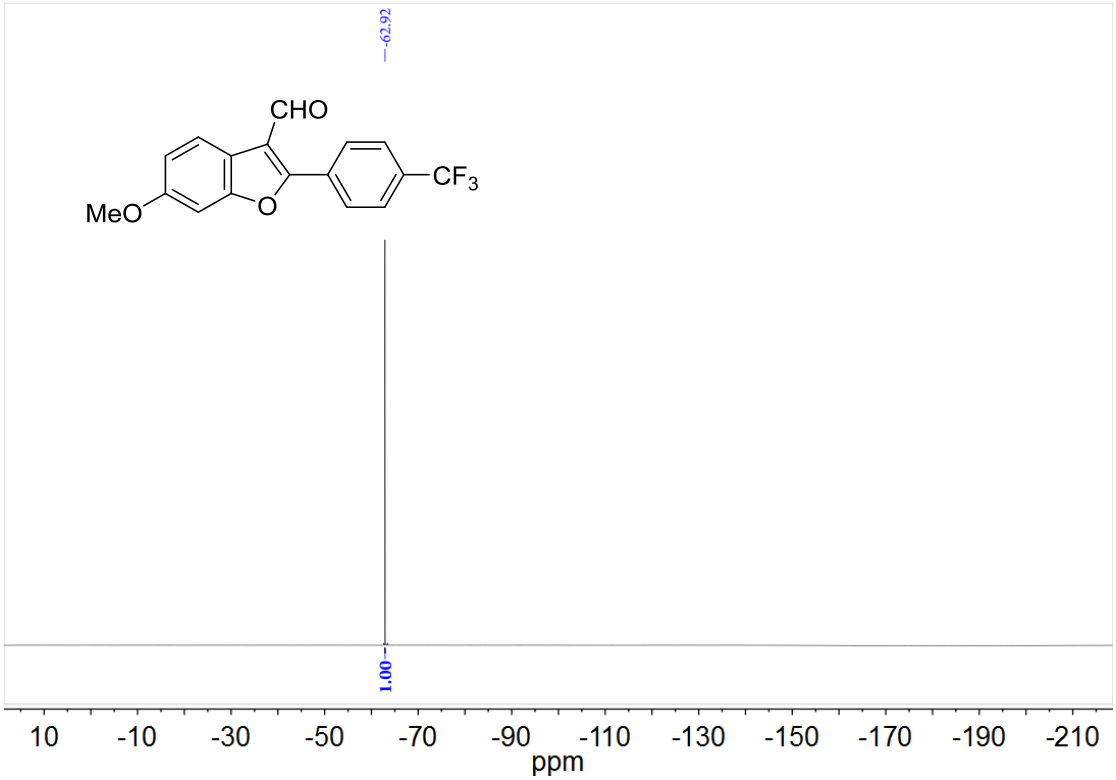
^{1}H NMR Spectrum of Compound 3ag



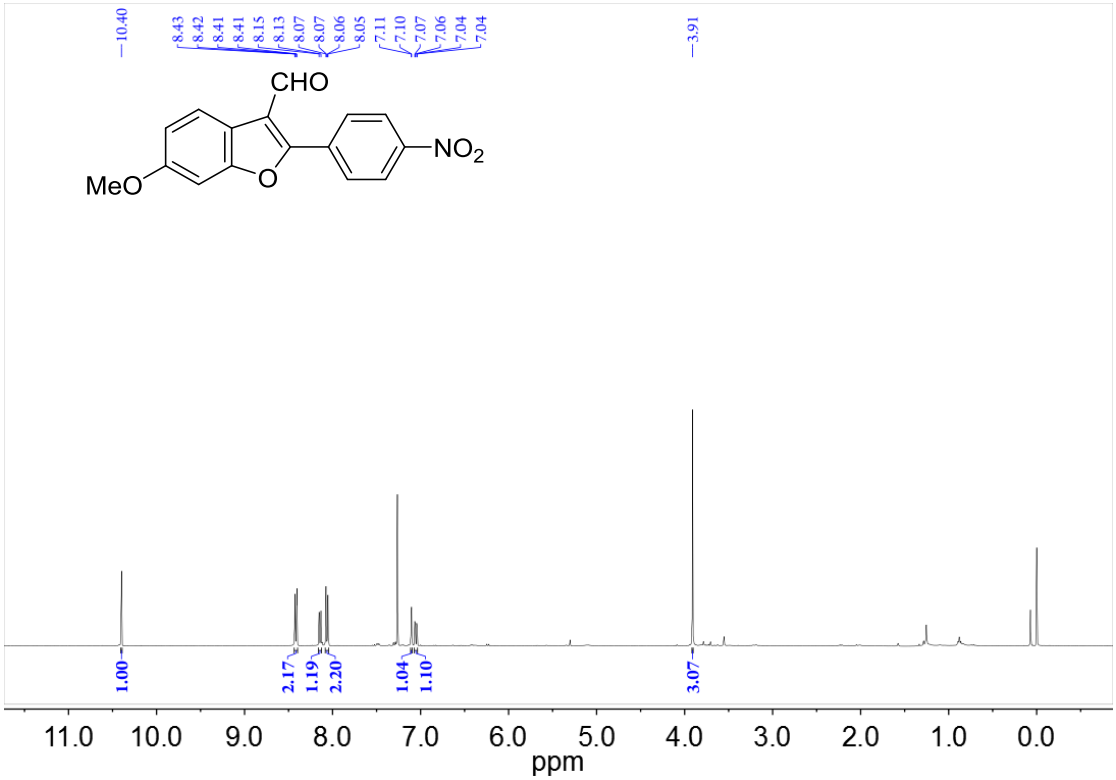
^{13}C NMR Spectrum of Compound 3ag



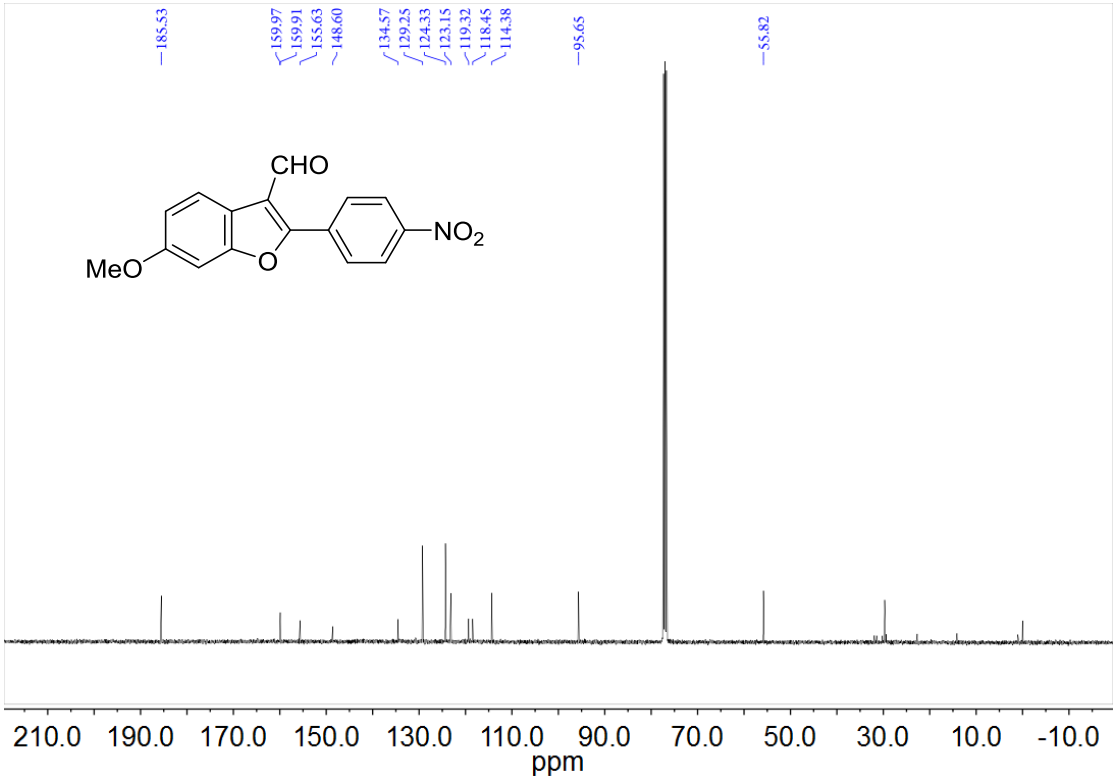
^{19}F NMR Spectrum of Compound 3ag



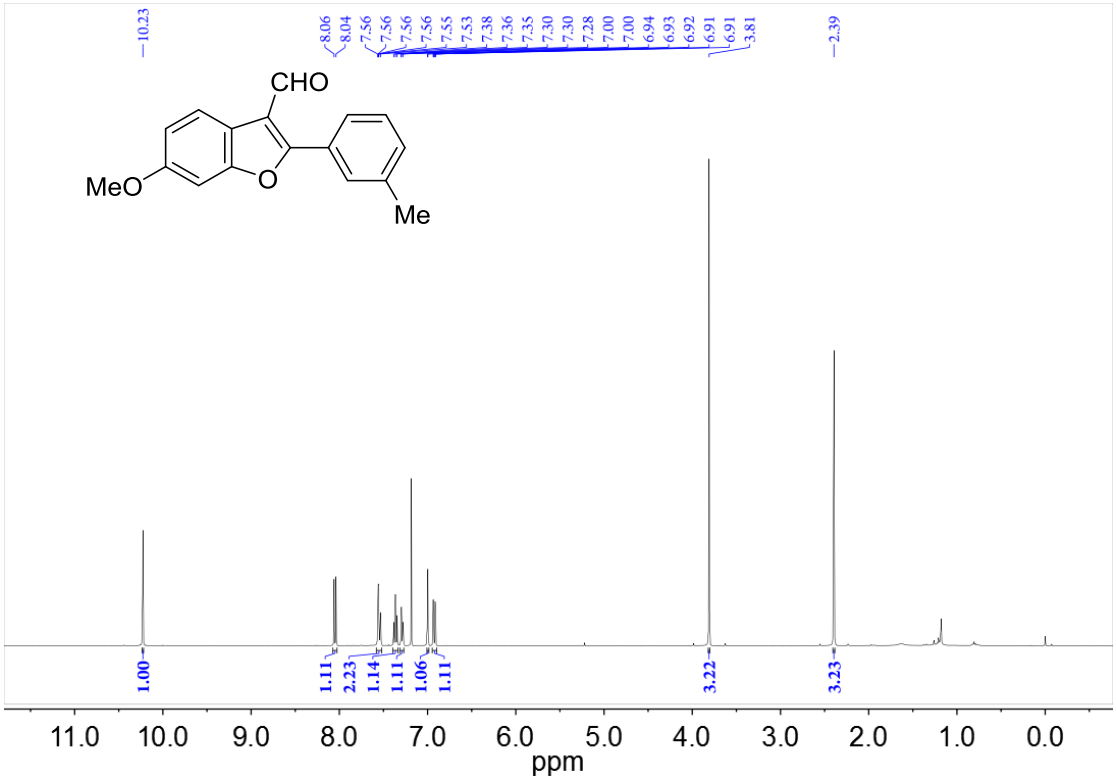
^{1}H NMR Spectrum of Compound 3ah



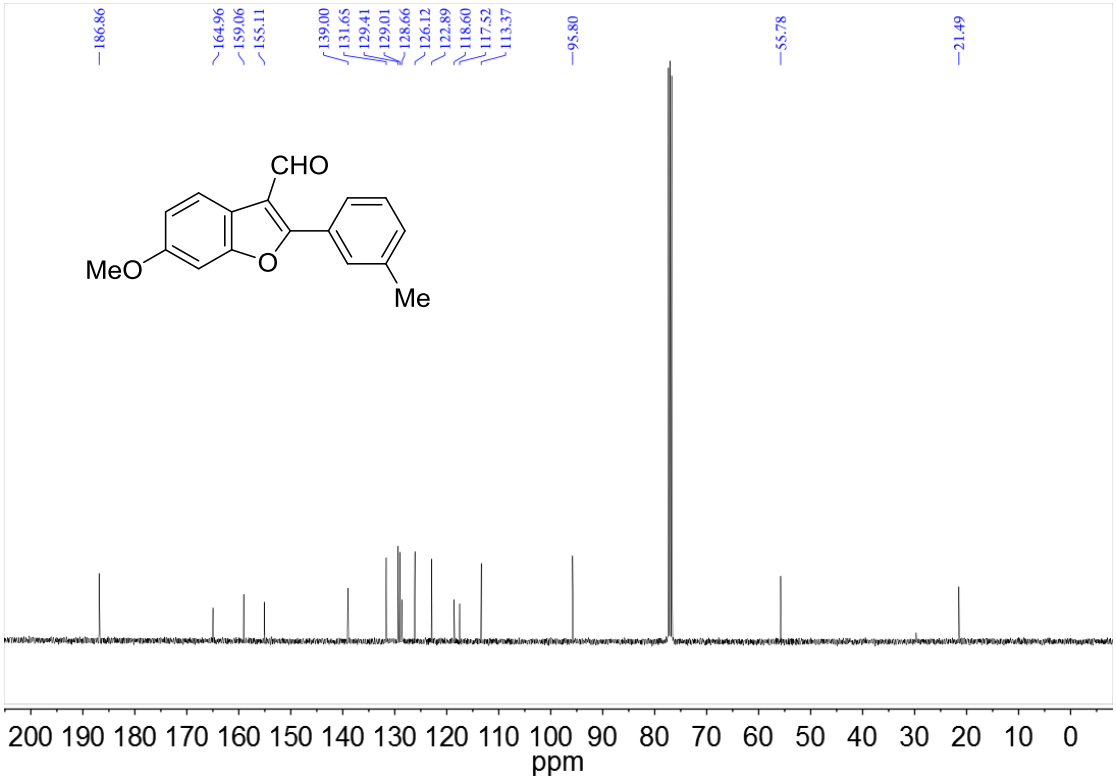
^{13}C NMR Spectrum of Compound 3ah



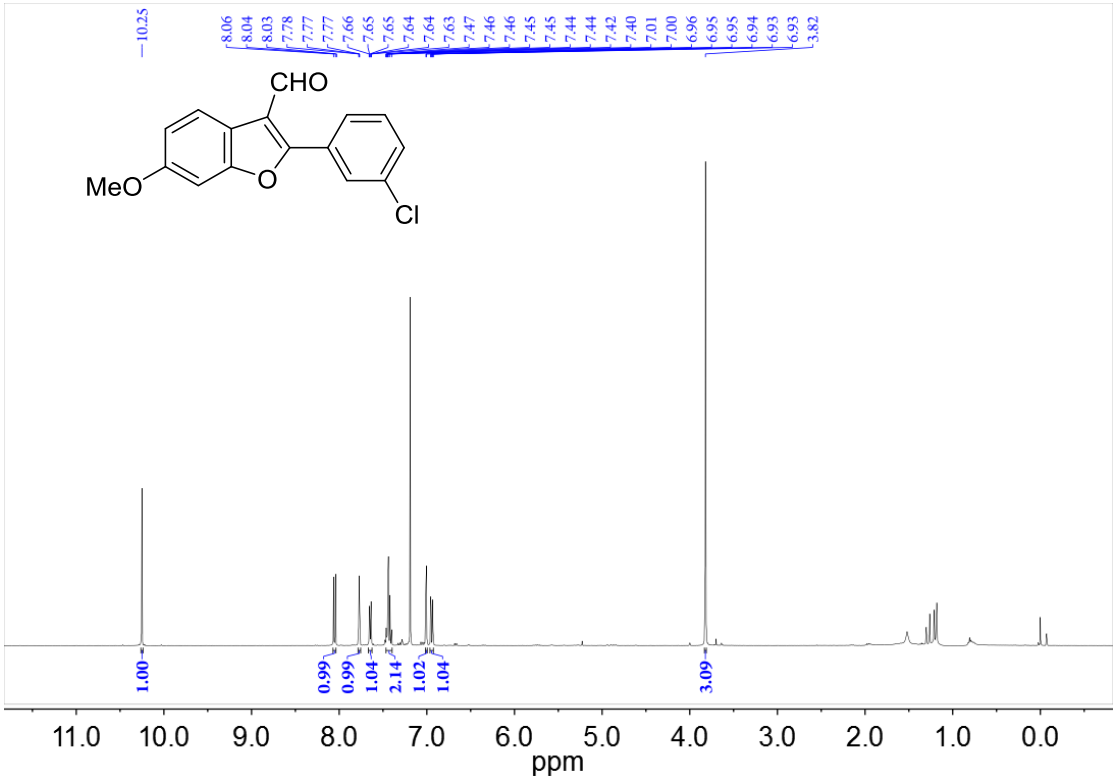
^{1}H NMR Spectrum of Compound 3ai



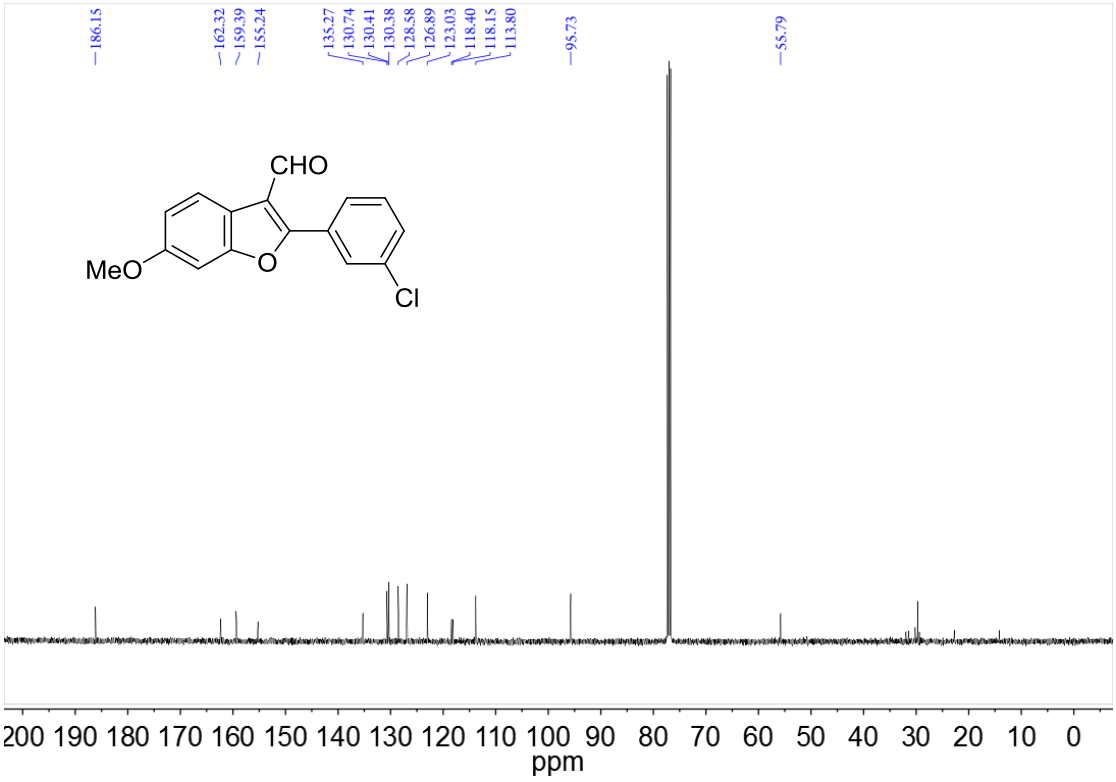
^{13}C NMR Spectrum of Compound 3ai



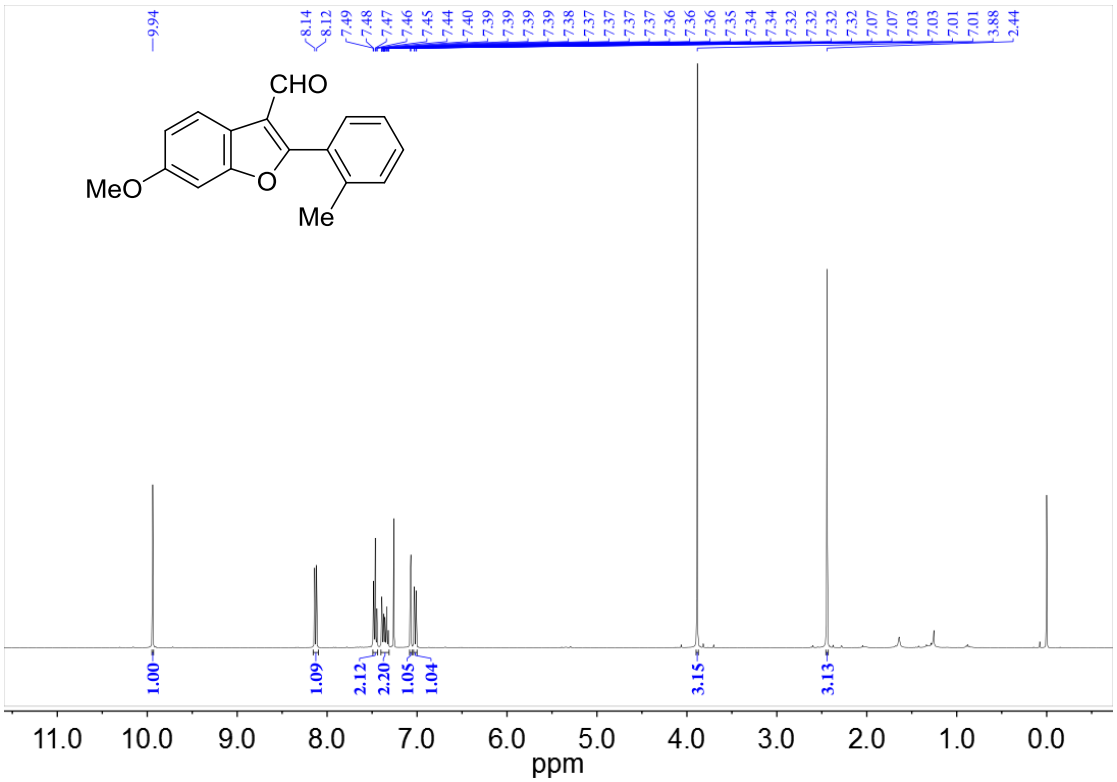
^{1}H NMR Spectrum of Compound 3aj



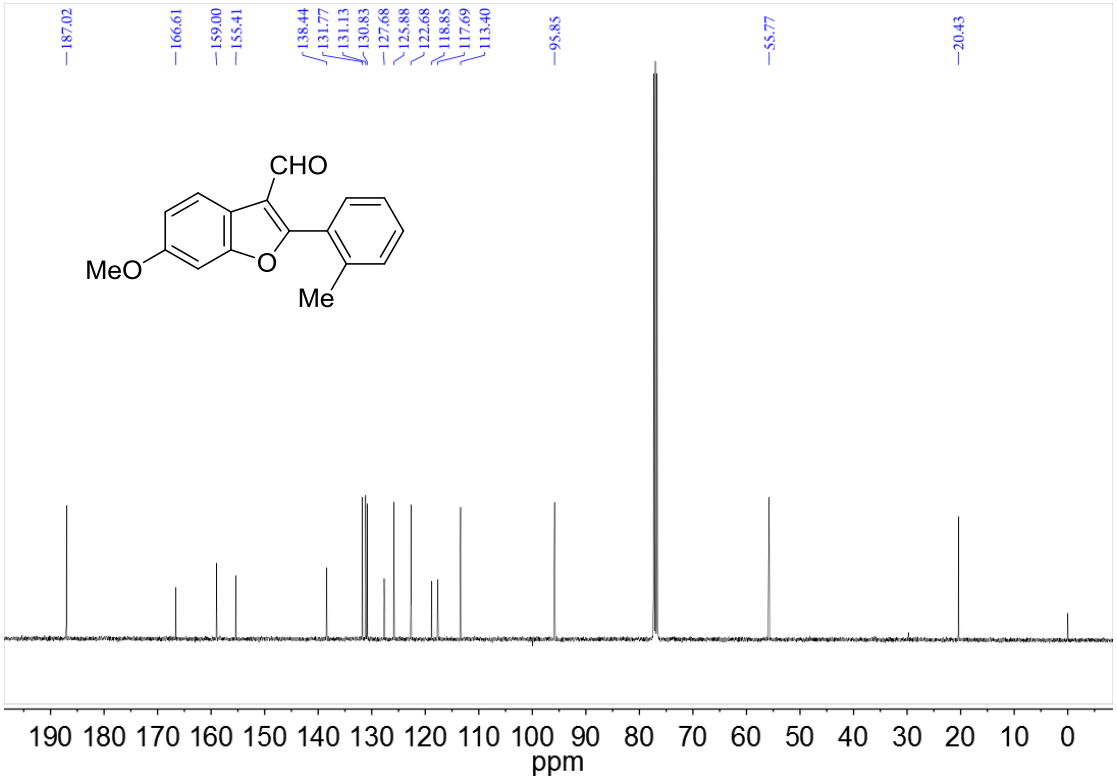
^{13}C NMR Spectrum of Compound 3aj



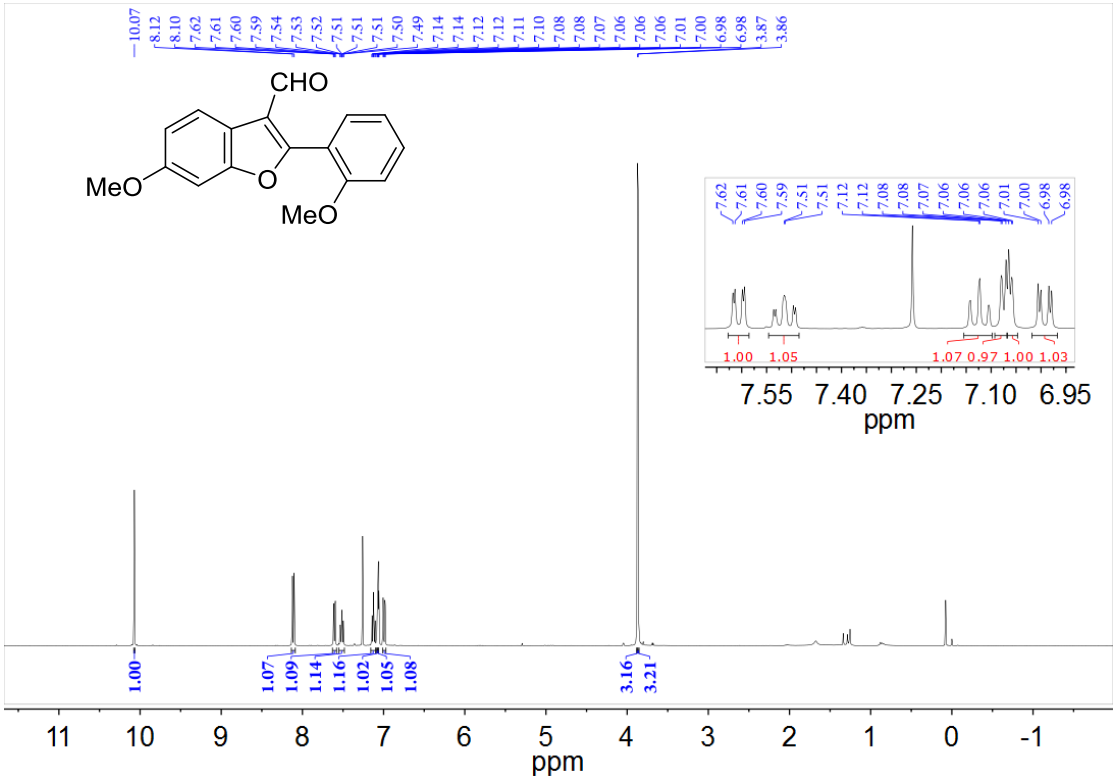
^{1}H NMR Spectrum of Compound 3ak



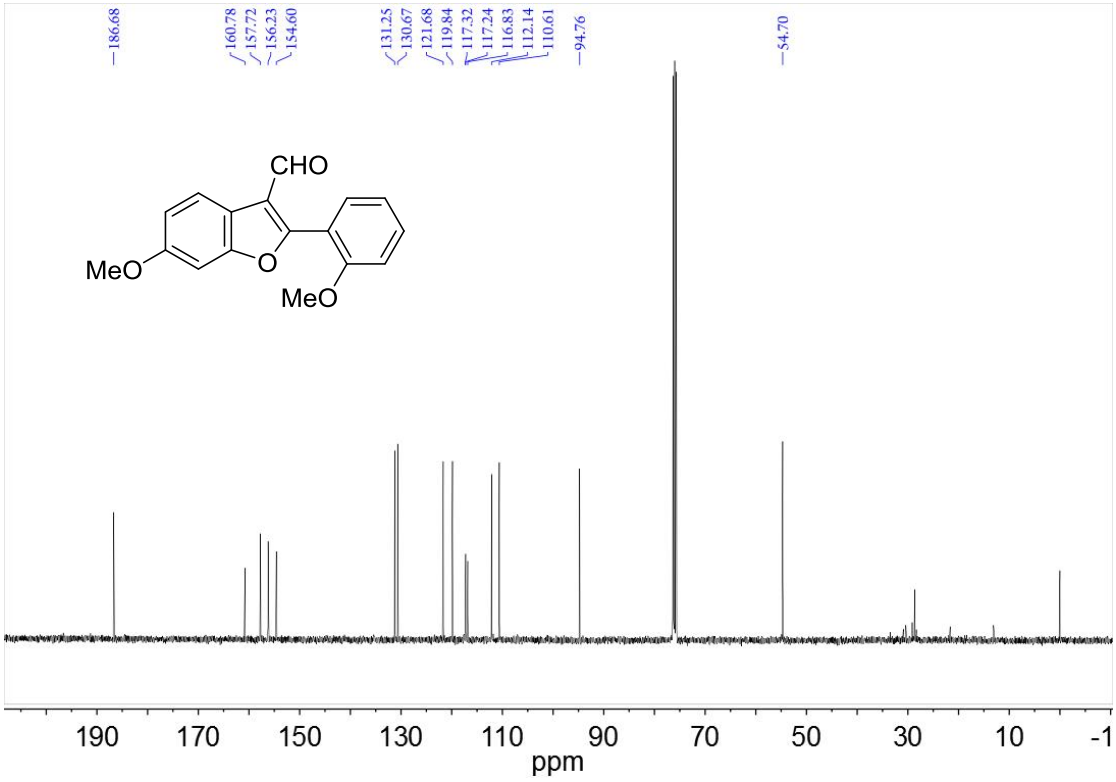
^{13}C NMR Spectrum of Compound 3ak



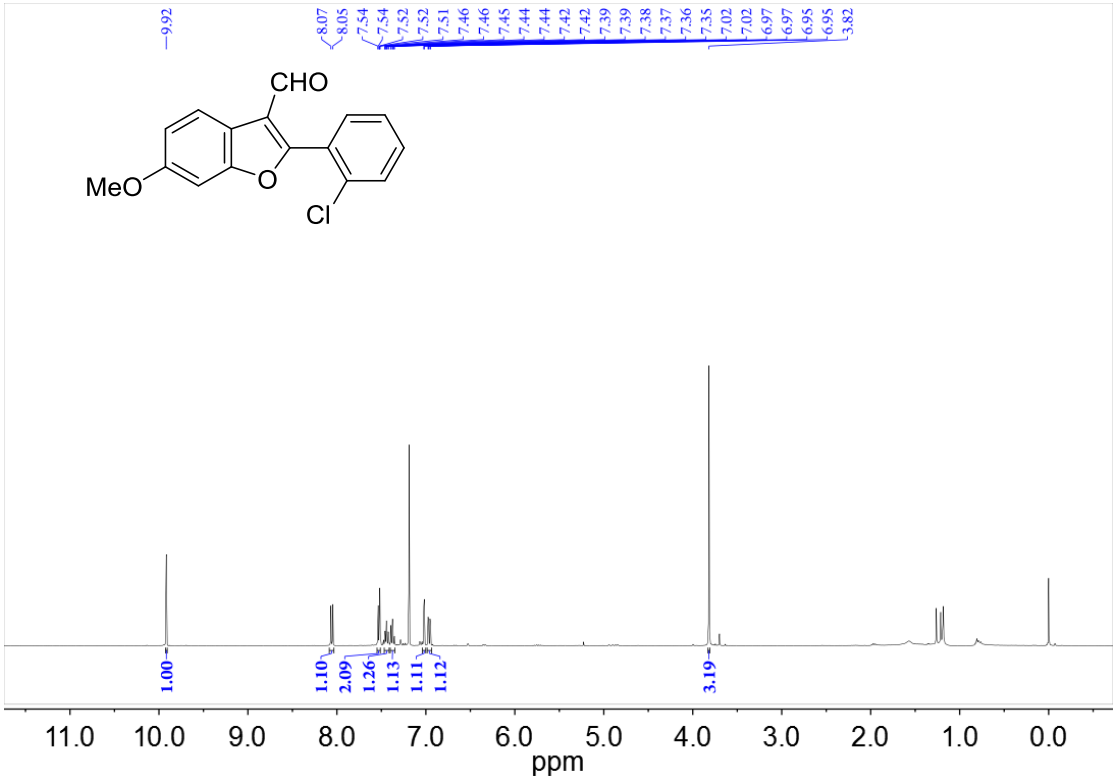
^{1}H NMR Spectrum of Compound 3al



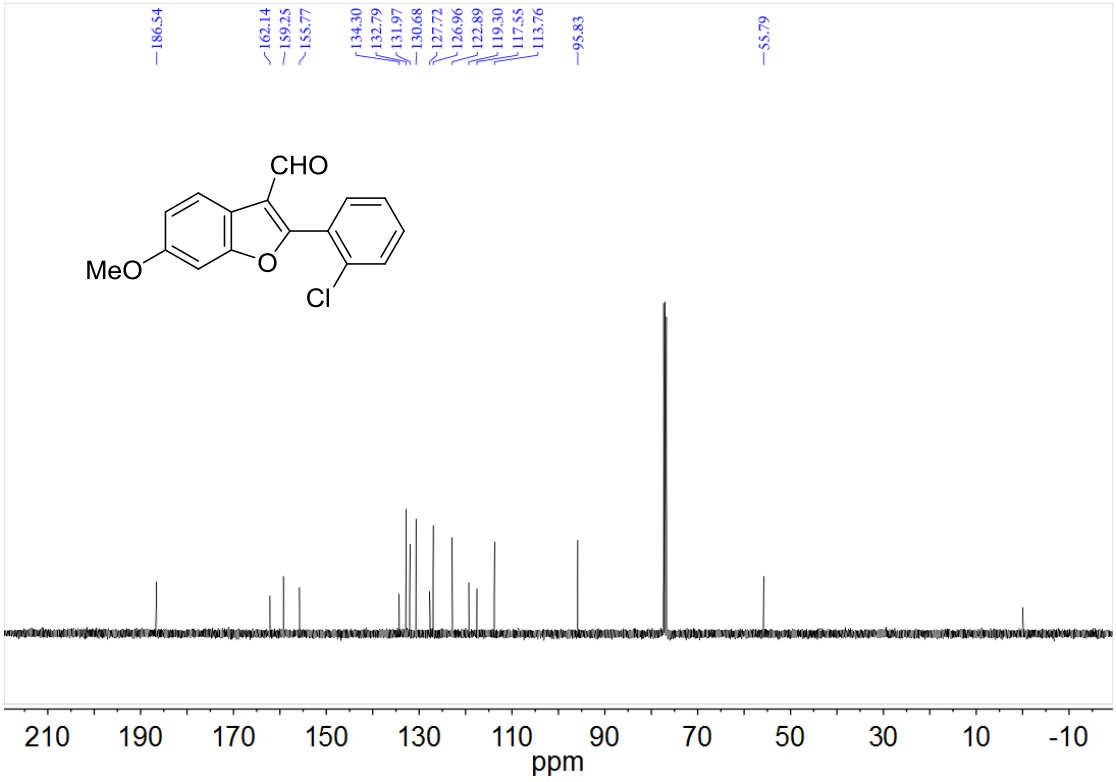
^{13}C NMR Spectrum of Compound 3al



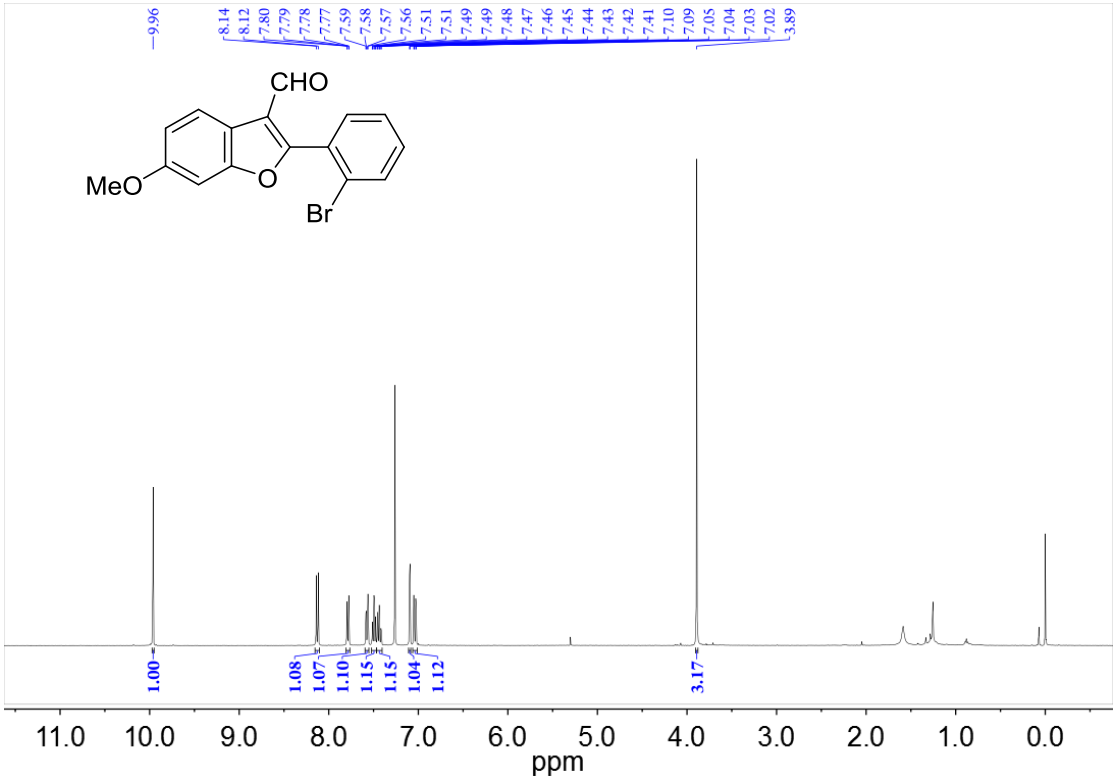
^{1}H NMR Spectrum of Compound 3am



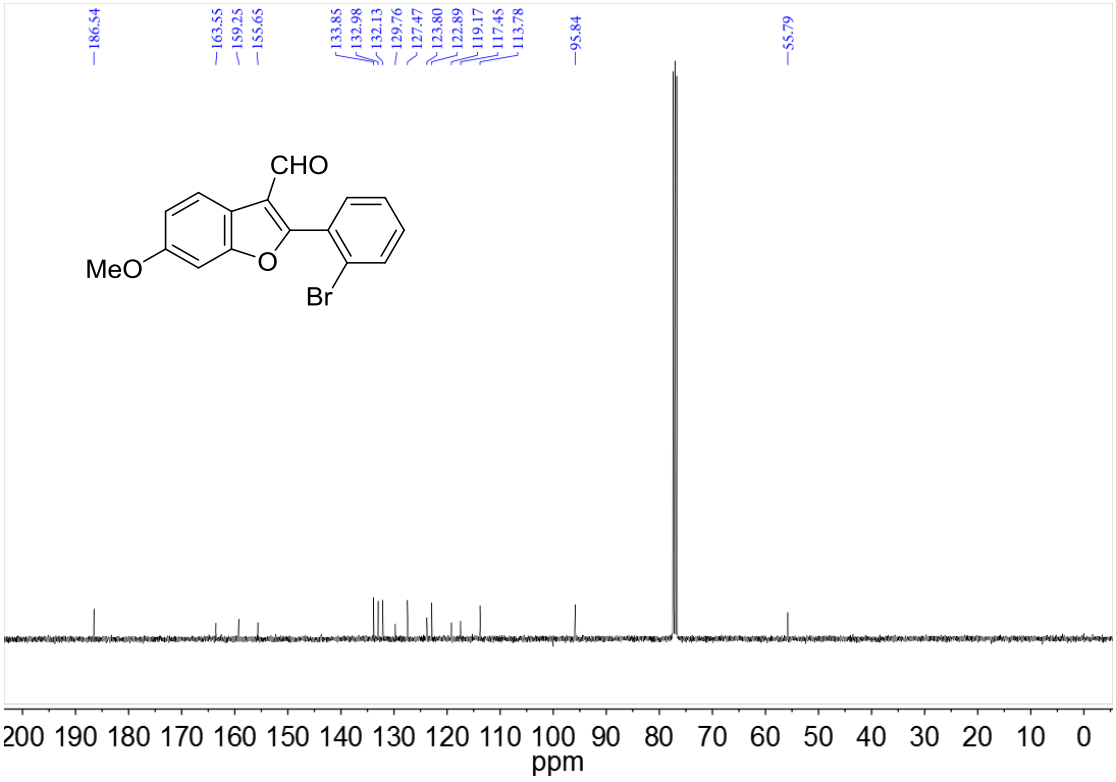
^{13}C NMR Spectrum of Compound 3am



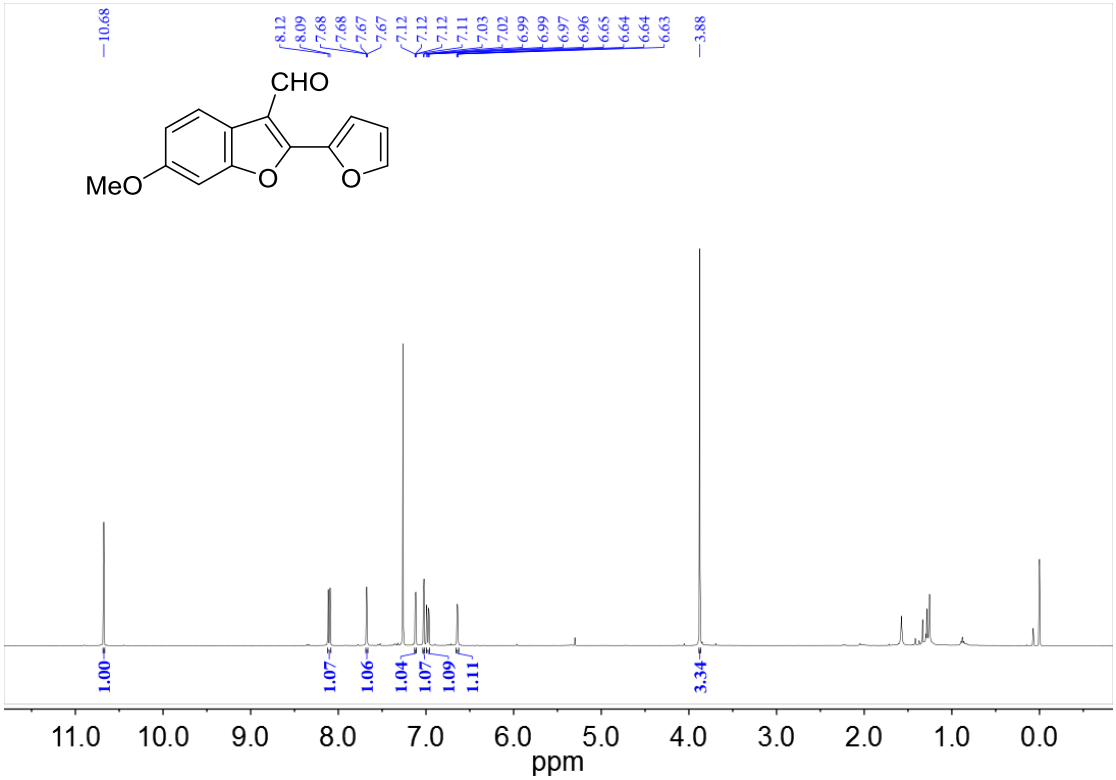
^{1}H NMR Spectrum of Compound 3an



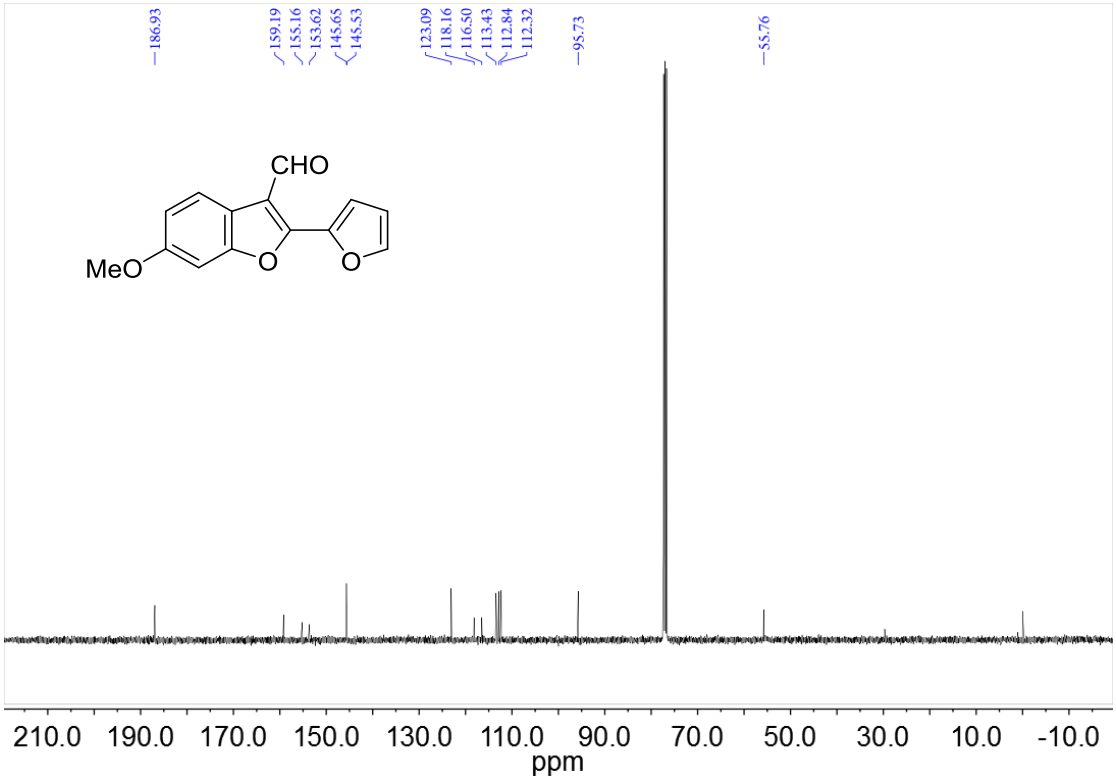
^{13}C NMR Spectrum of Compound 3an



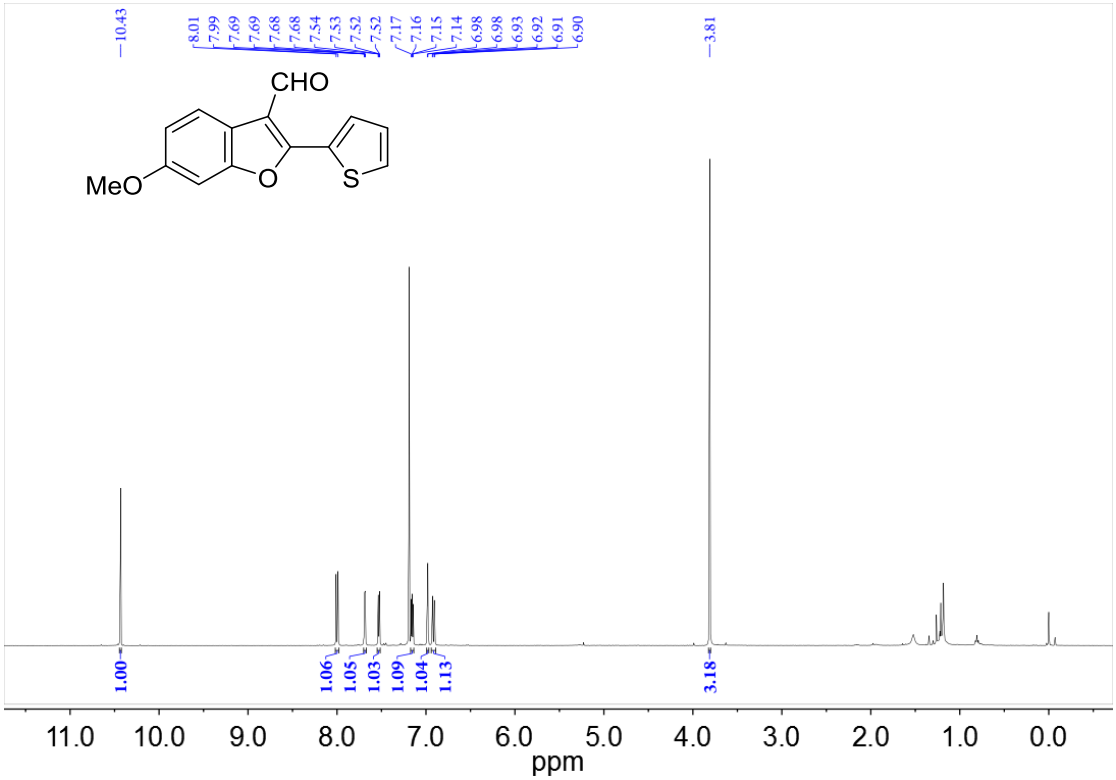
^{1}H NMR Spectrum of Compound 3ao



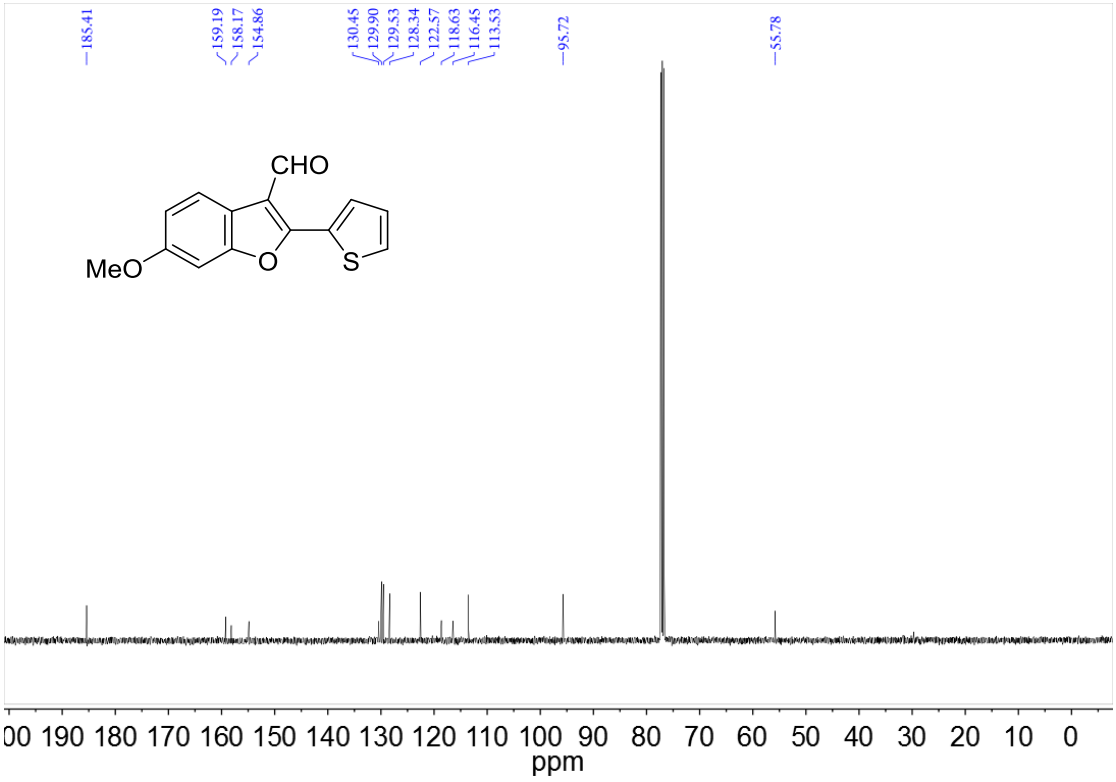
^{13}C NMR Spectrum of Compound 3ao



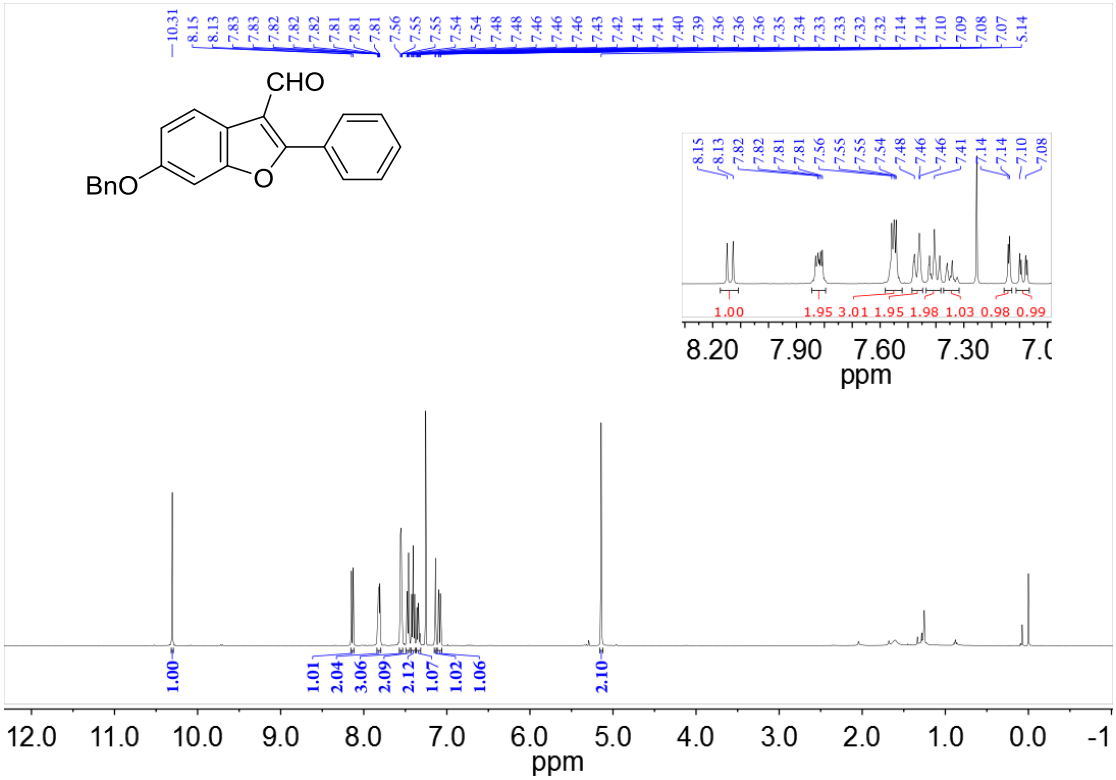
^{1}H NMR Spectrum of Compound 3ap



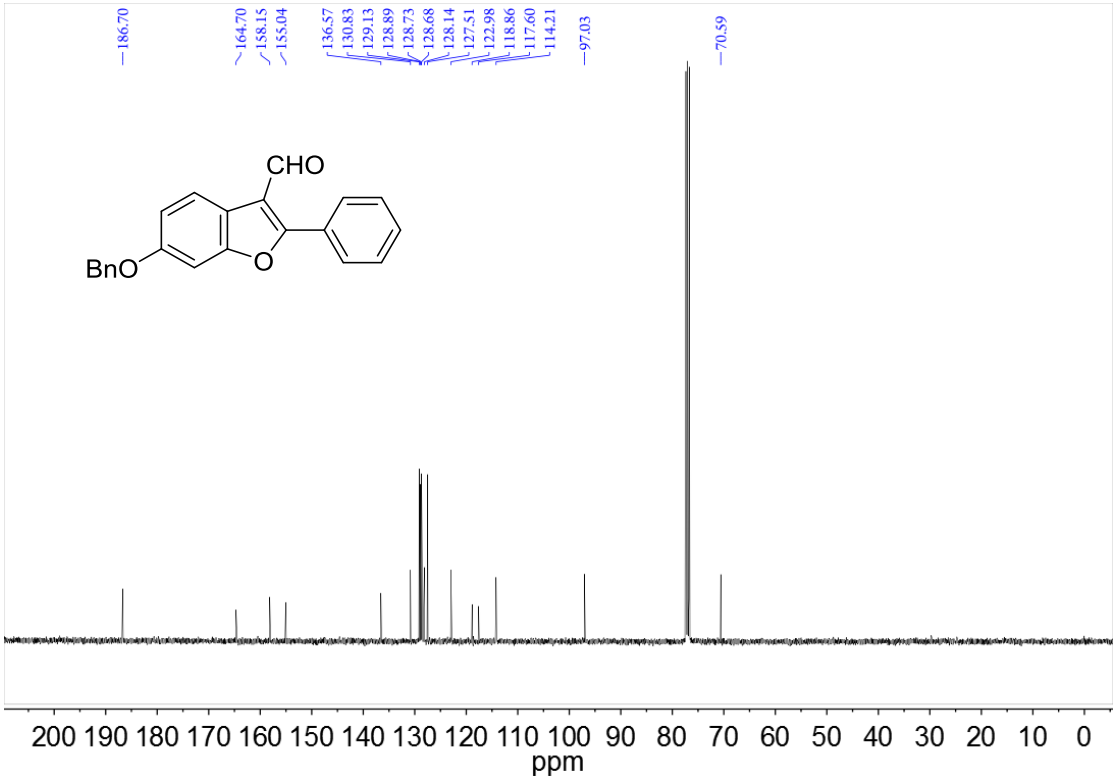
^{13}C NMR Spectrum of Compound 3ap



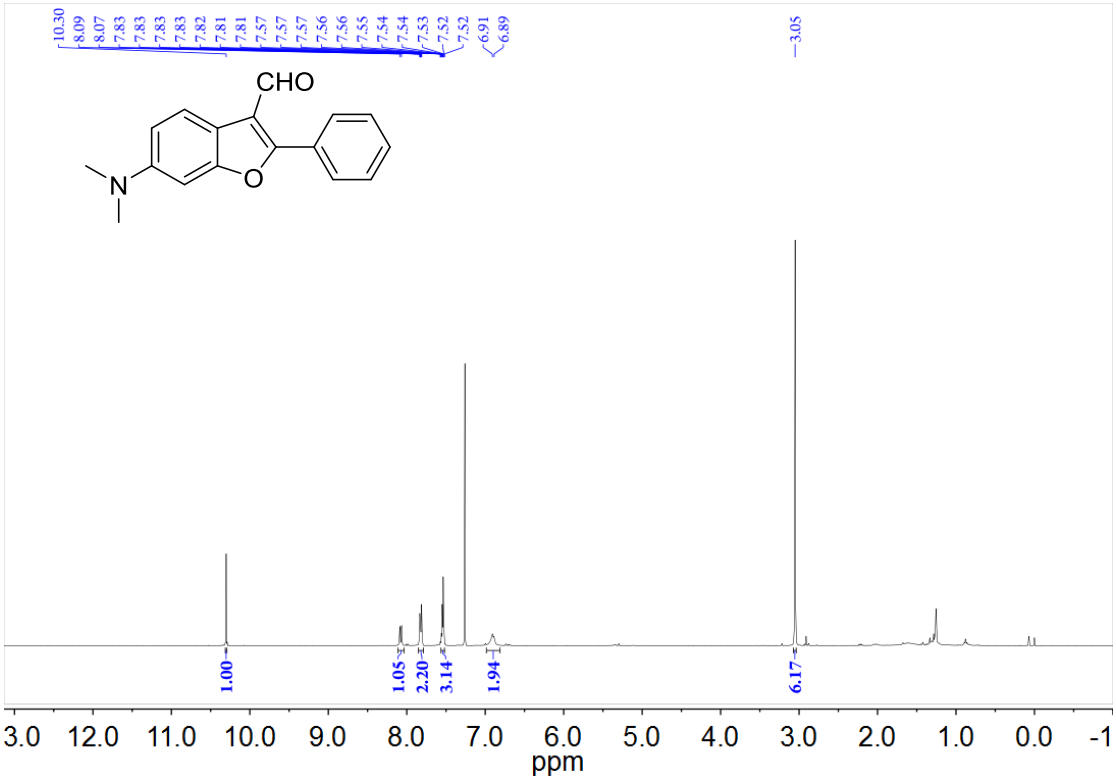
^{1}H NMR Spectrum of Compound 3ba



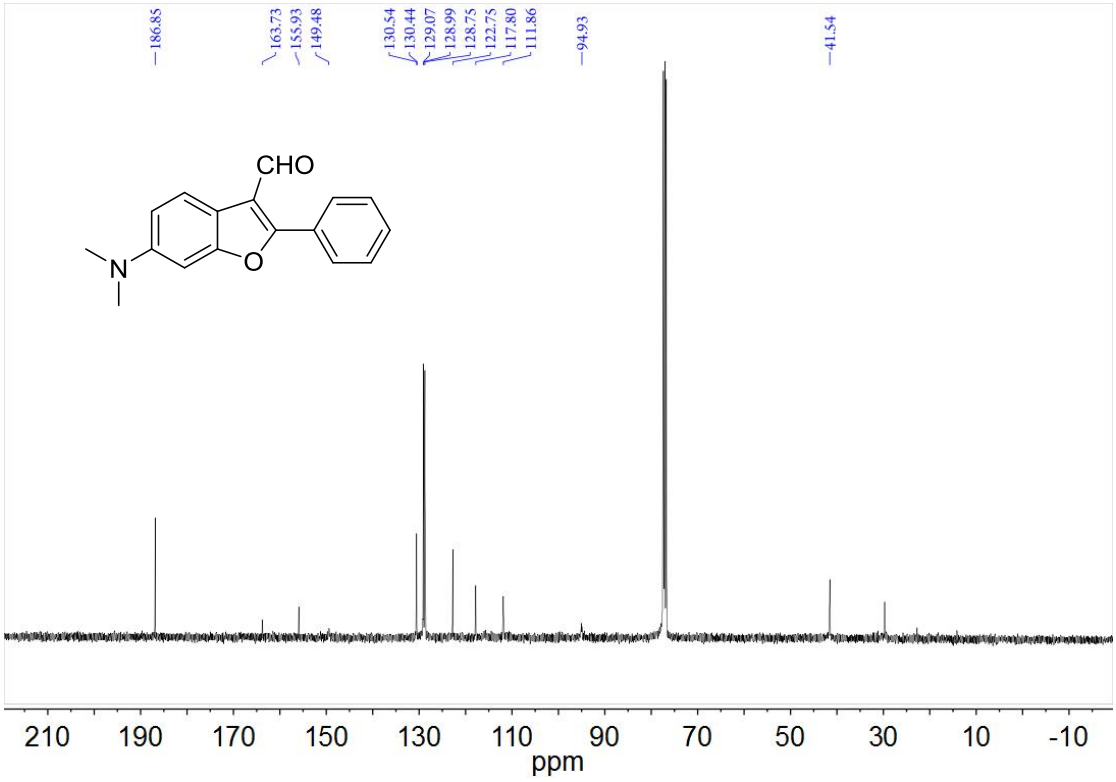
^{13}C NMR Spectrum of Compound 3ba



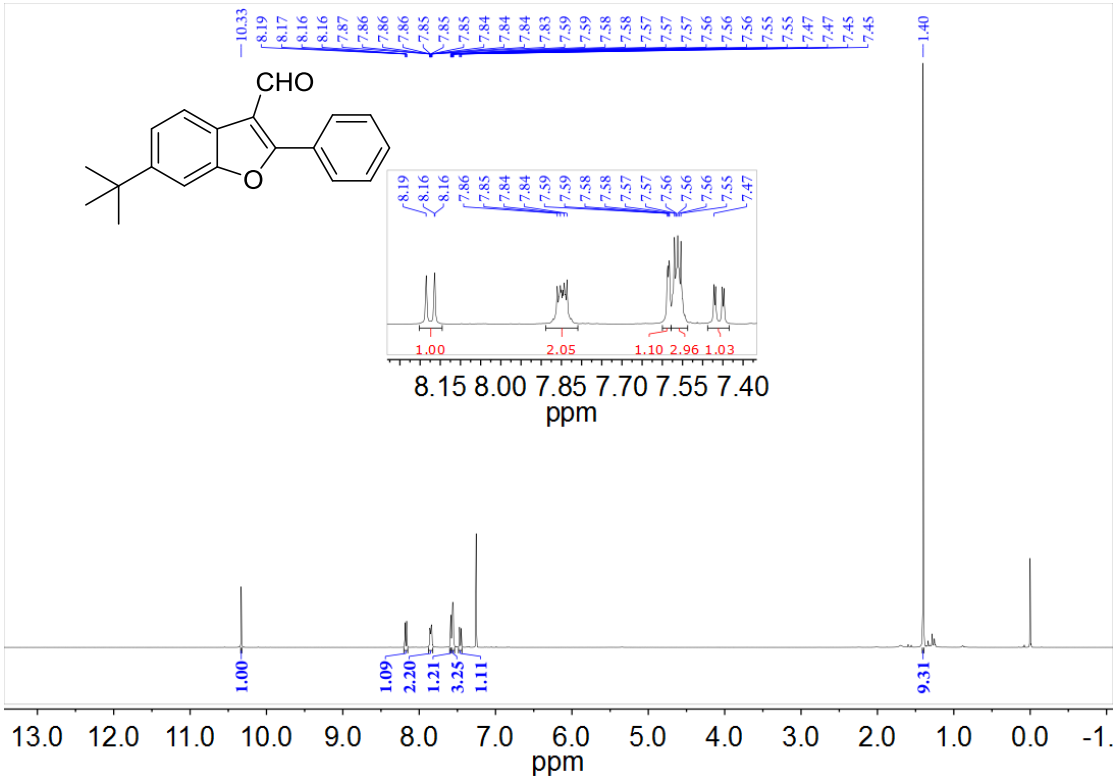
^{1}H NMR Spectrum of Compound 3ca



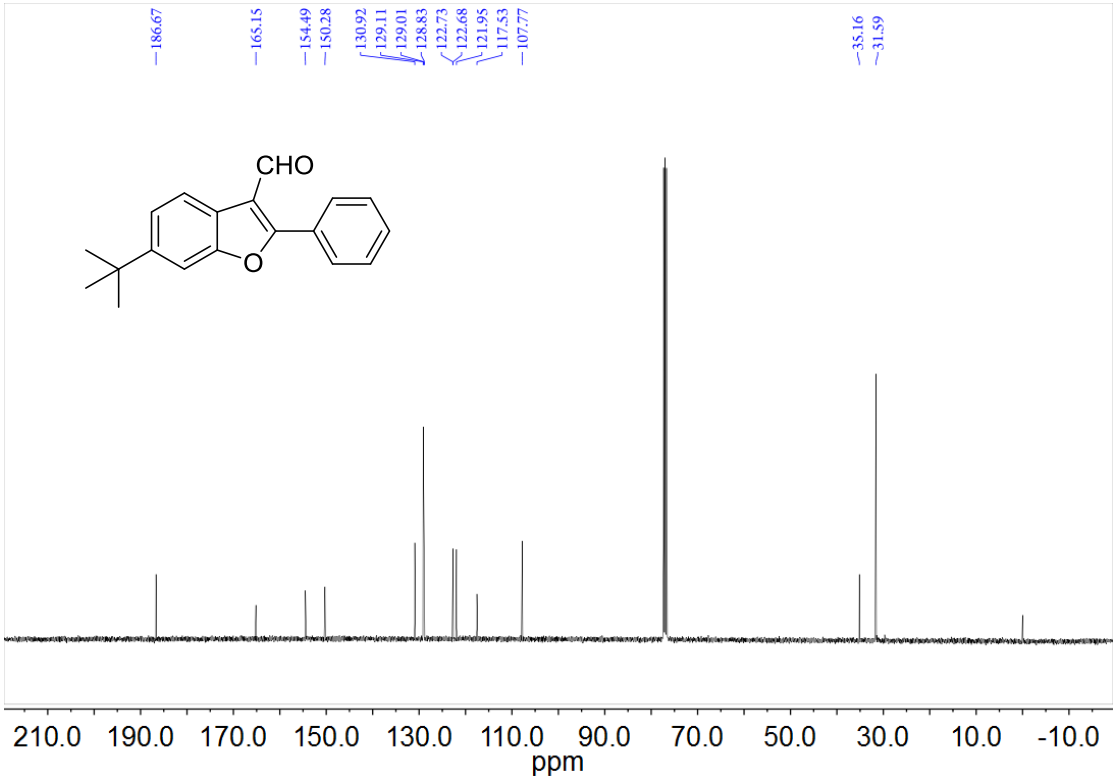
^{13}C NMR Spectrum of Compound 3ca



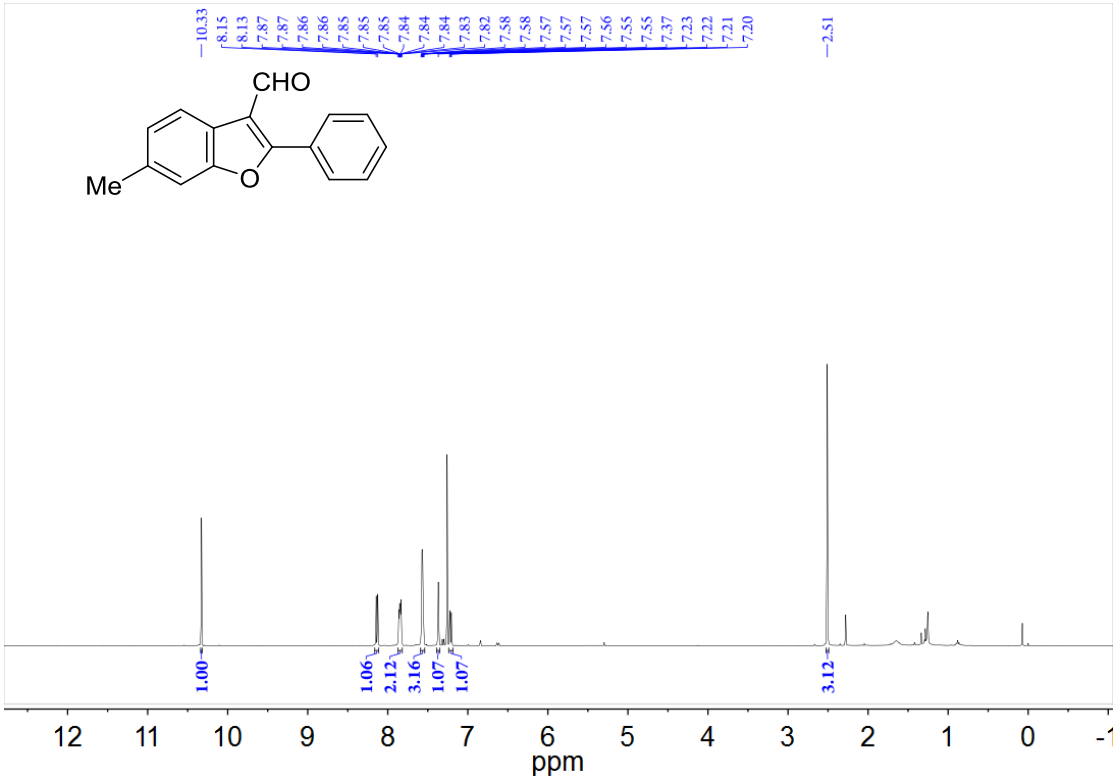
^{1}H NMR Spectrum of Compound 3da



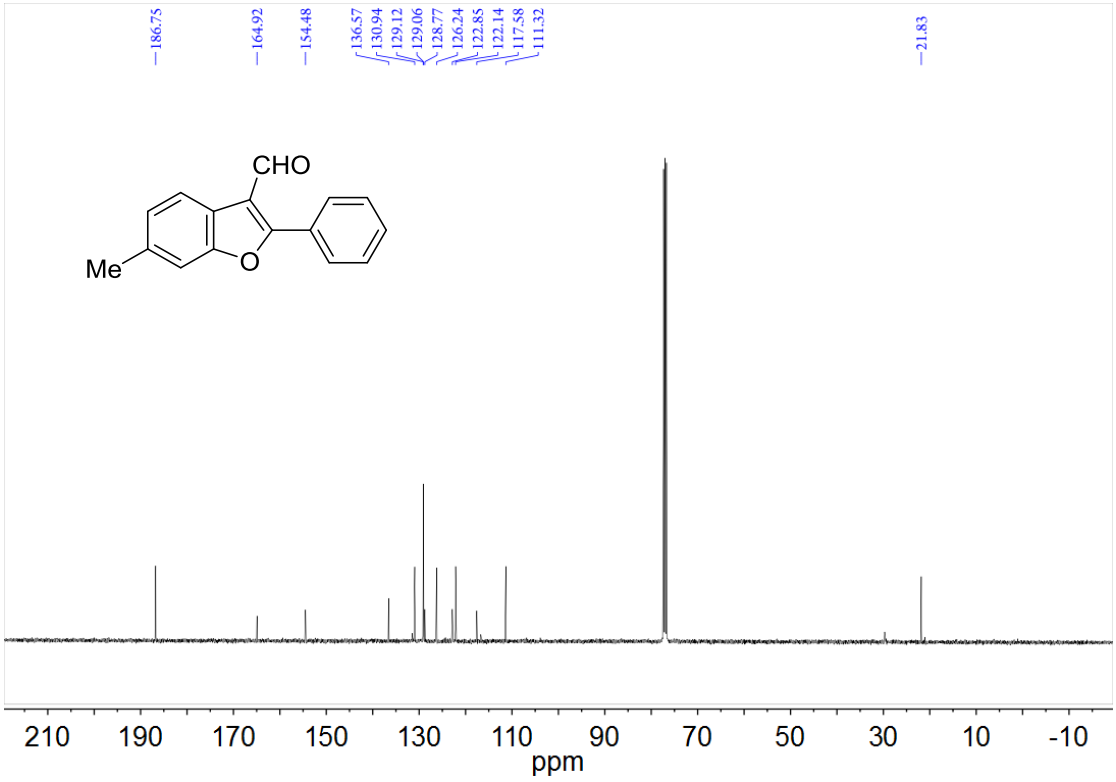
^{13}C NMR Spectrum of Compound 3da



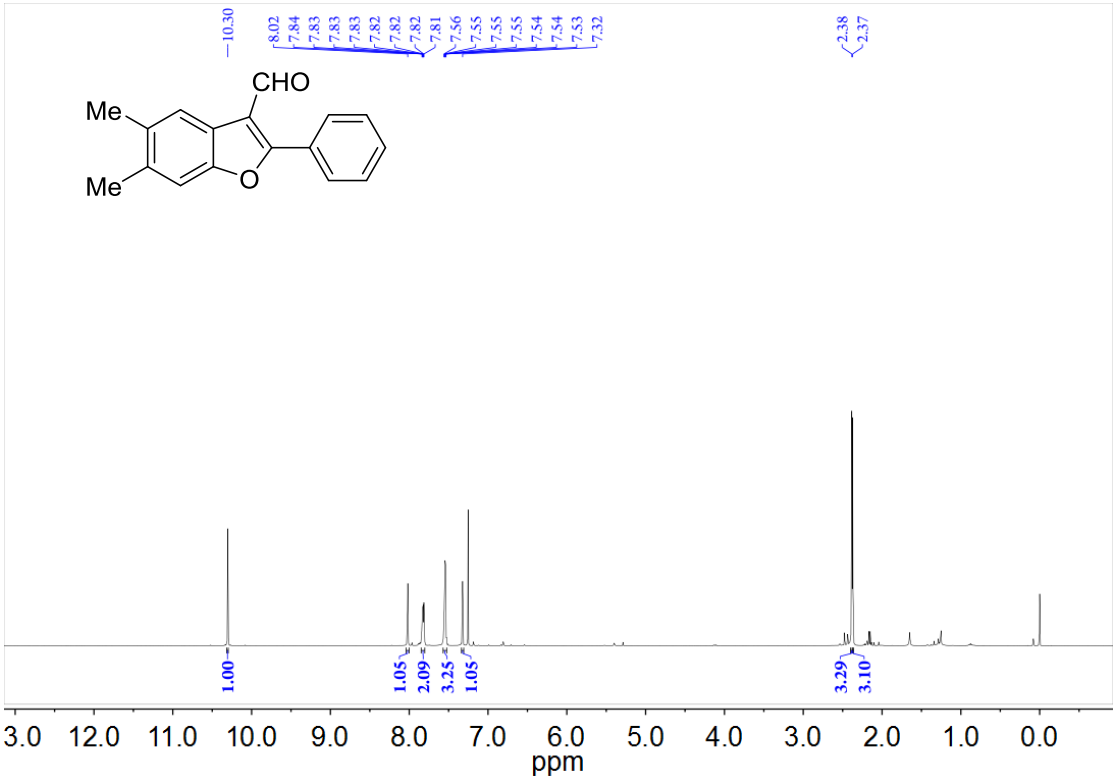
^{1}H NMR Spectrum of Compound 3ea



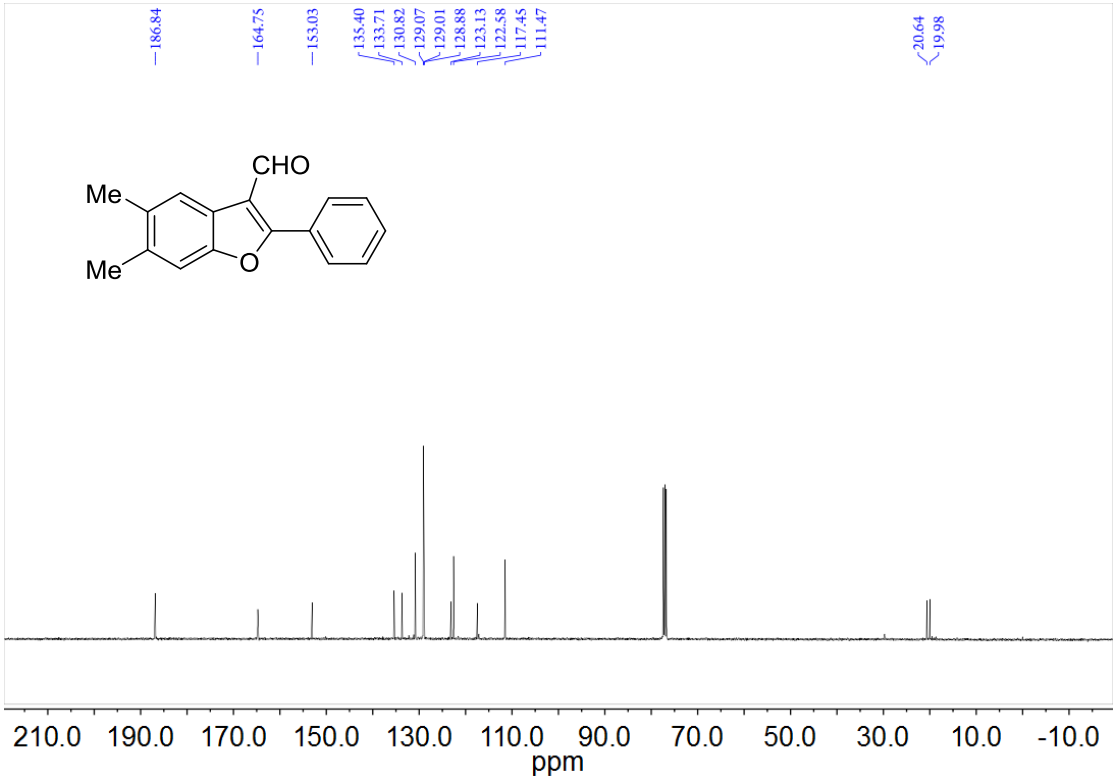
^{13}C NMR Spectrum of Compound 3ea



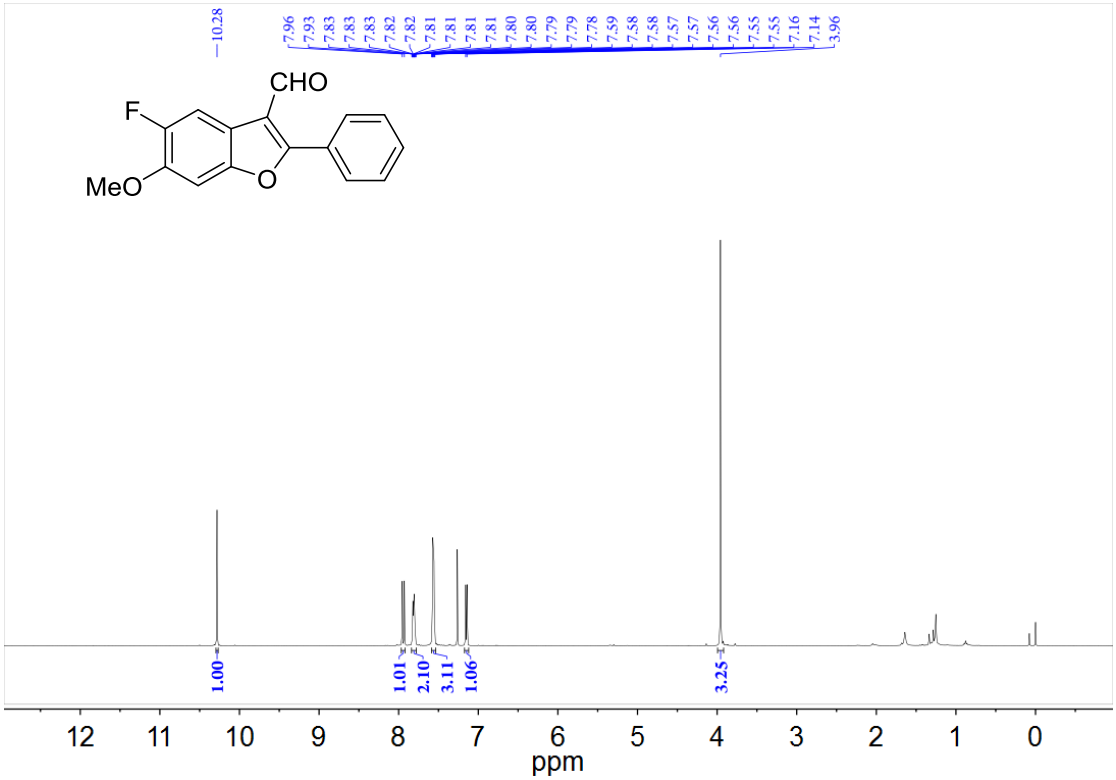
^{1}H NMR Spectrum of Compound 3fa



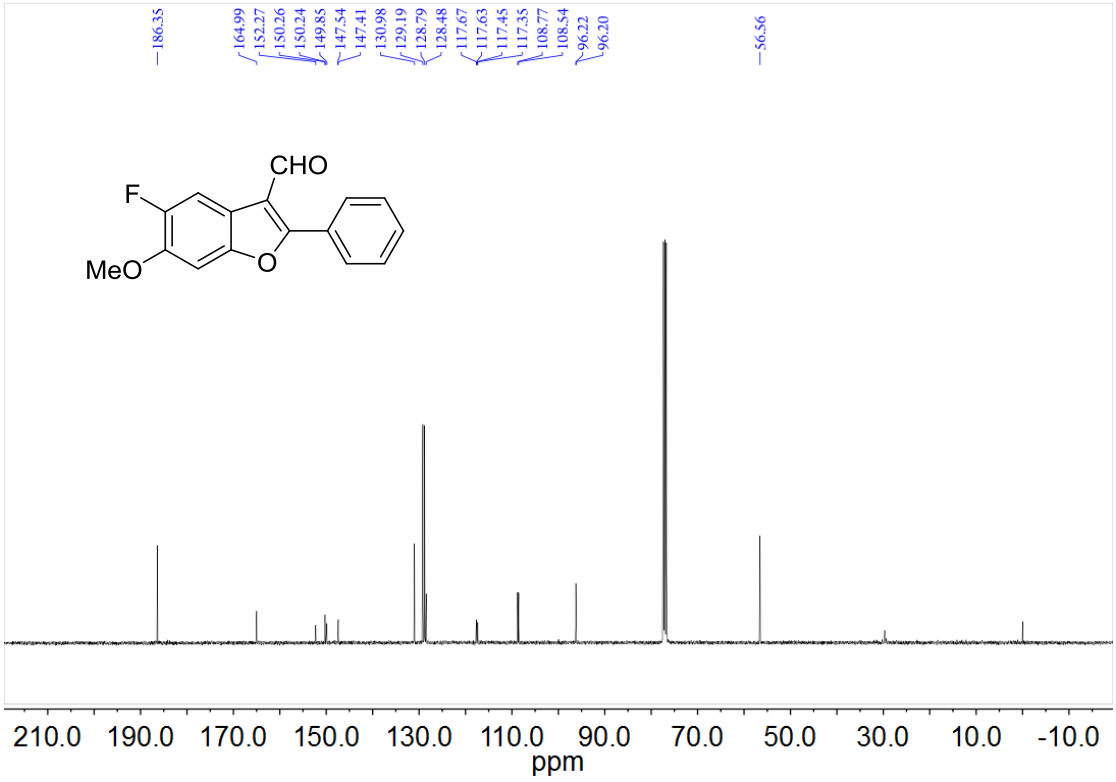
^{13}C NMR Spectrum of Compound 3fa



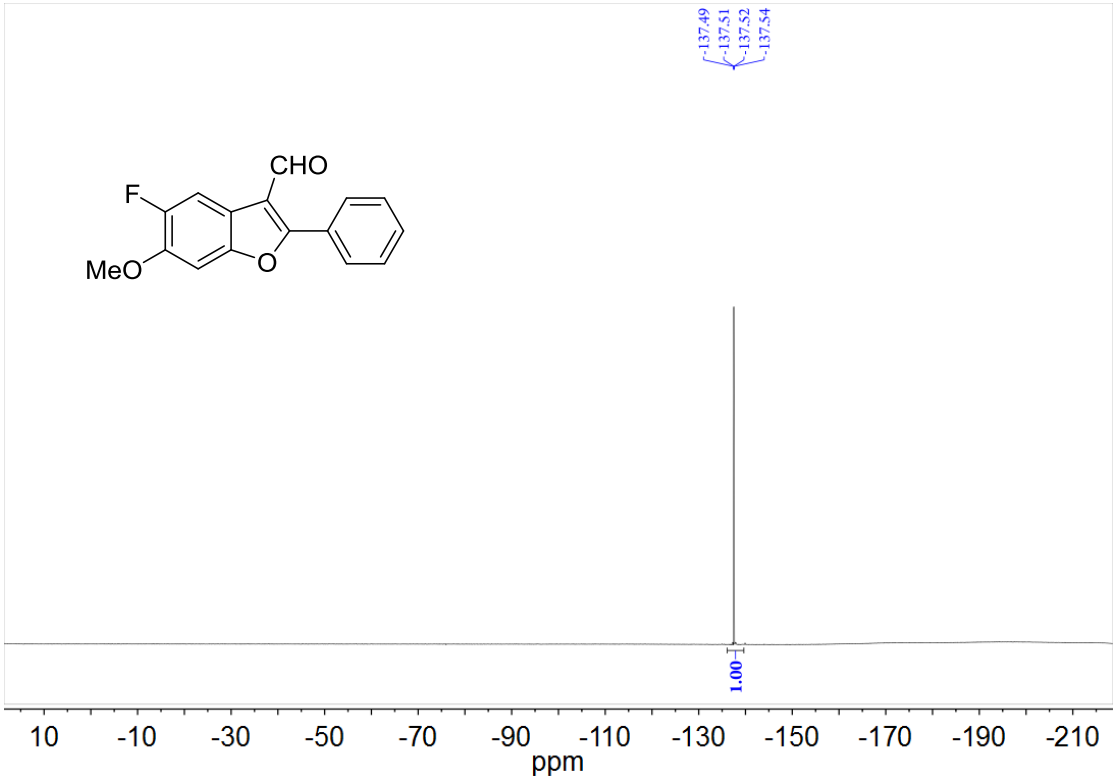
^{1}H NMR Spectrum of Compound 3ga



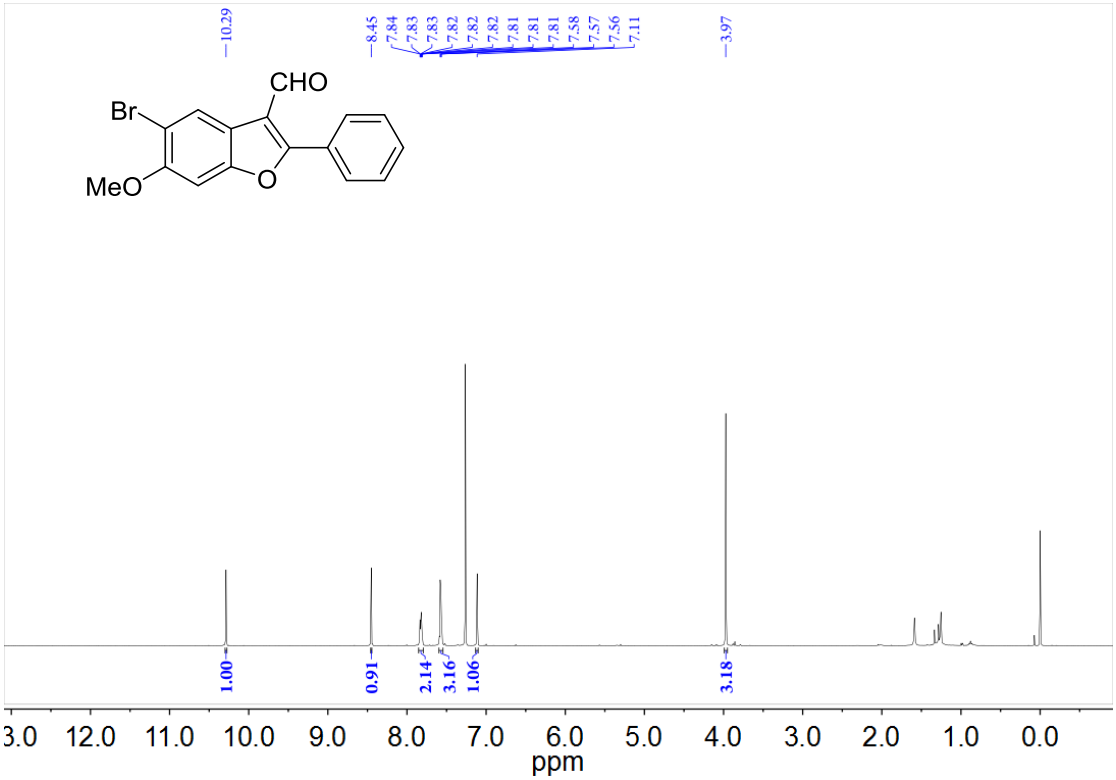
^{13}C NMR Spectrum of Compound 3ga



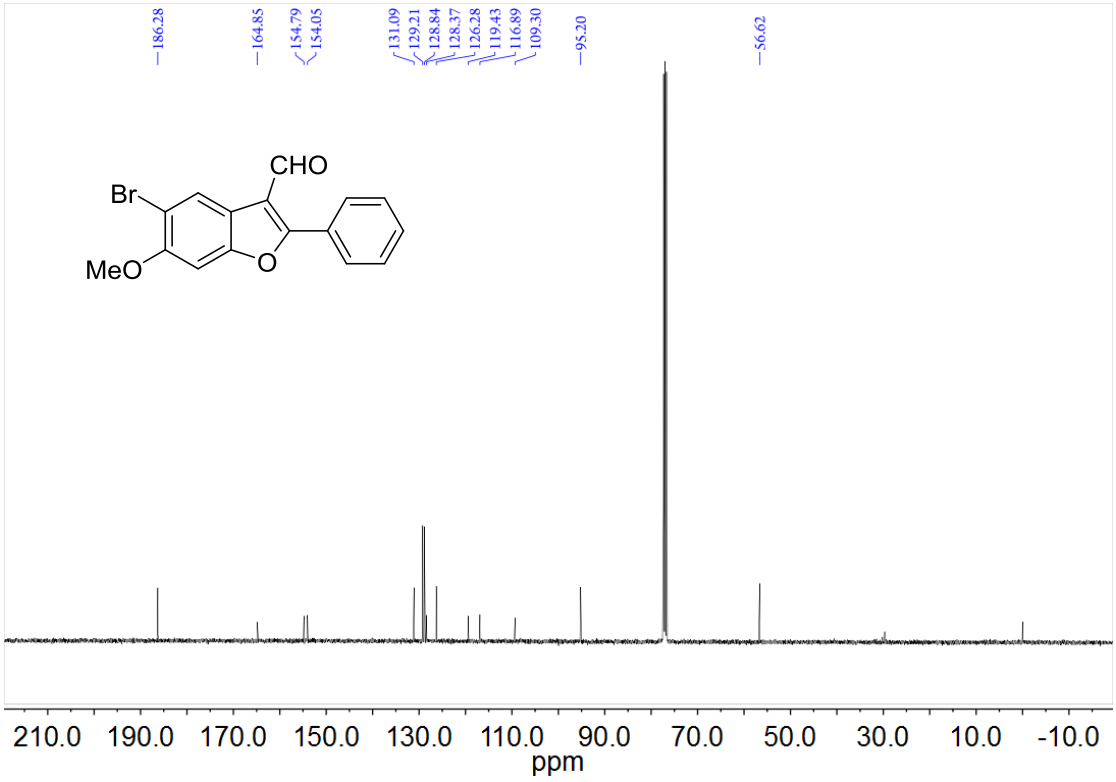
^{19}F NMR Spectrum of Compound 3ga



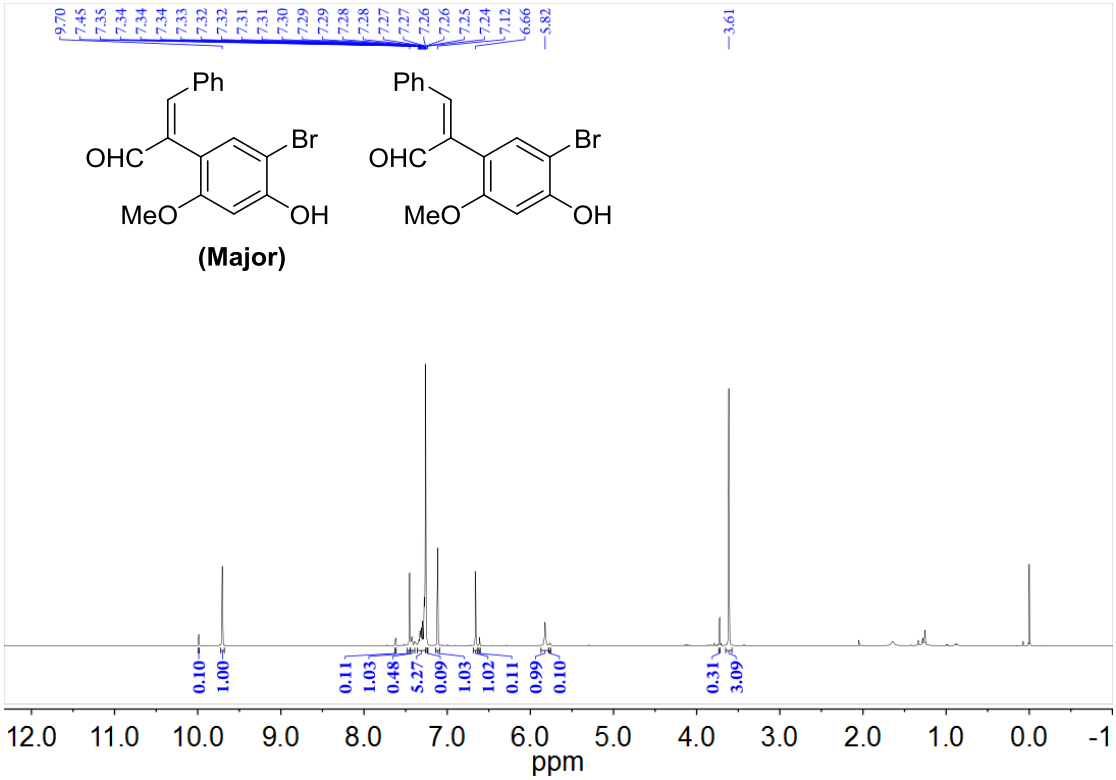
^{1}H NMR Spectrum of Compound 3ha



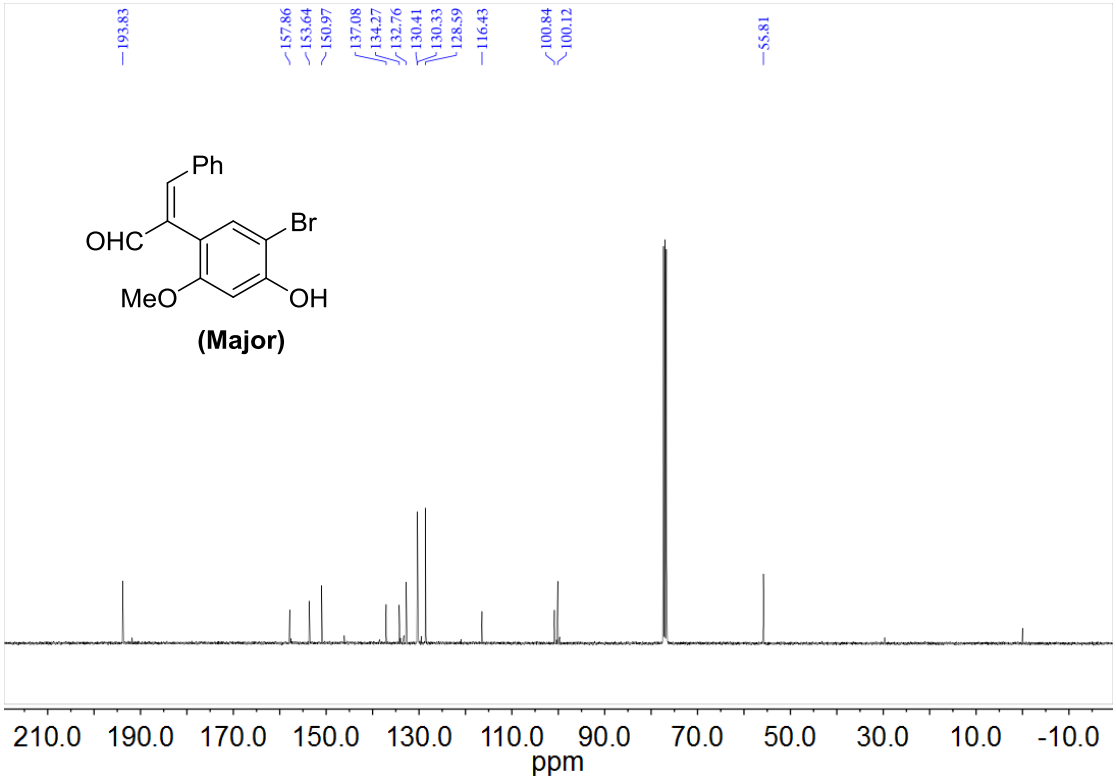
^{13}C NMR Spectrum of Compound 3ha



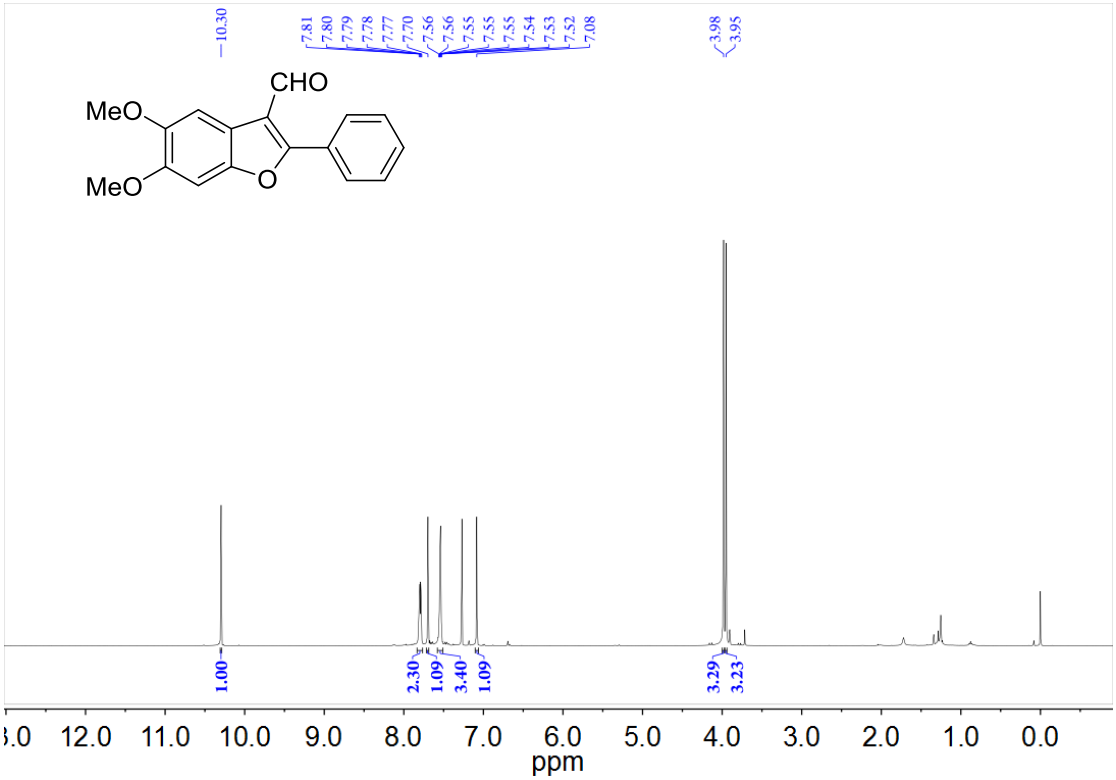
^{1}H NMR Spectrum of Compound 3ha'



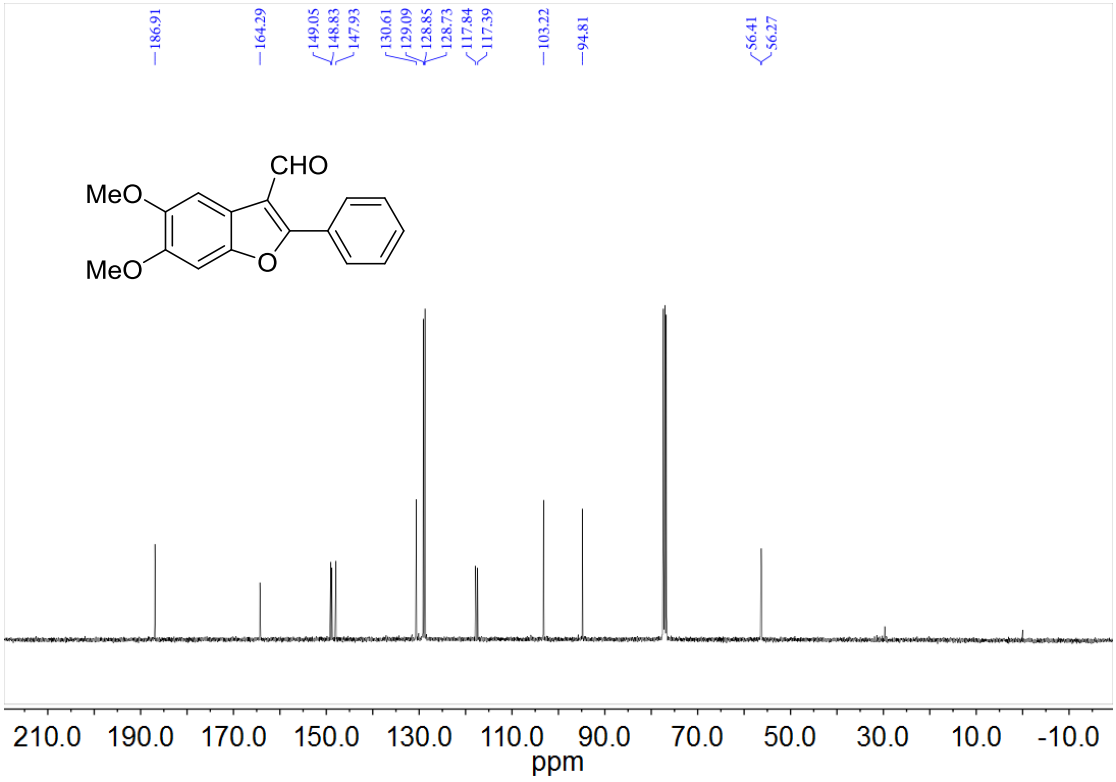
^{13}C NMR Spectrum of Compound 3ha'



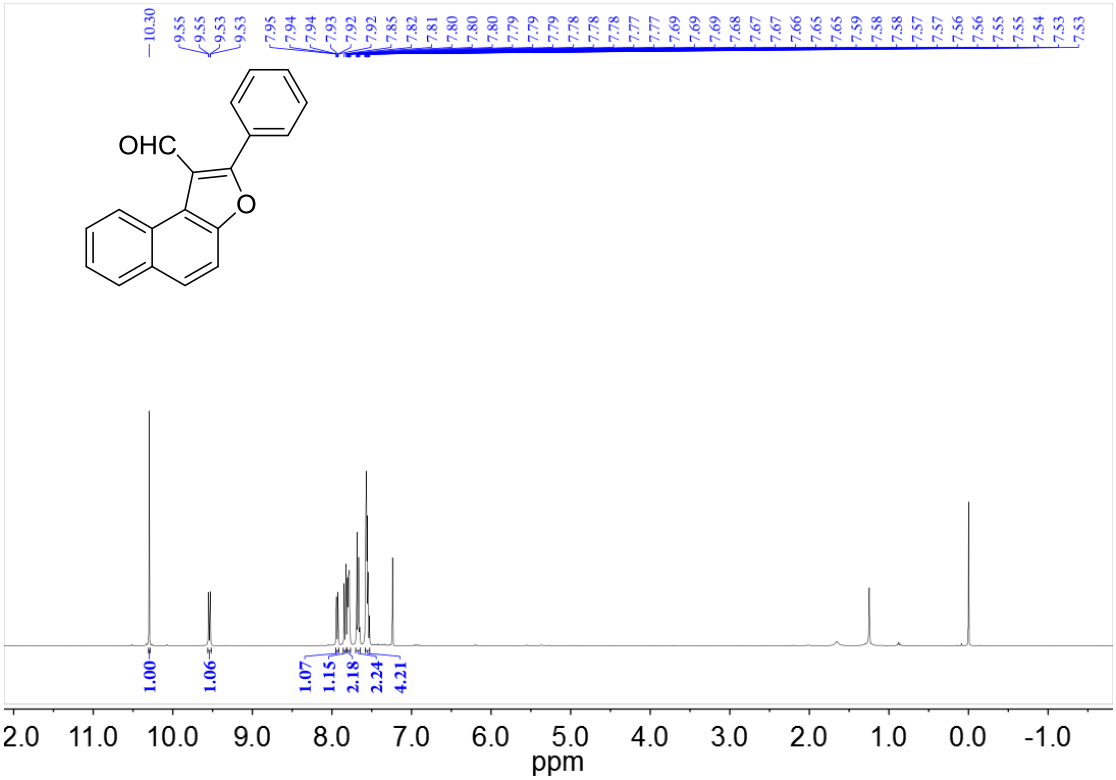
^{1}H NMR Spectrum of Compound 3ia



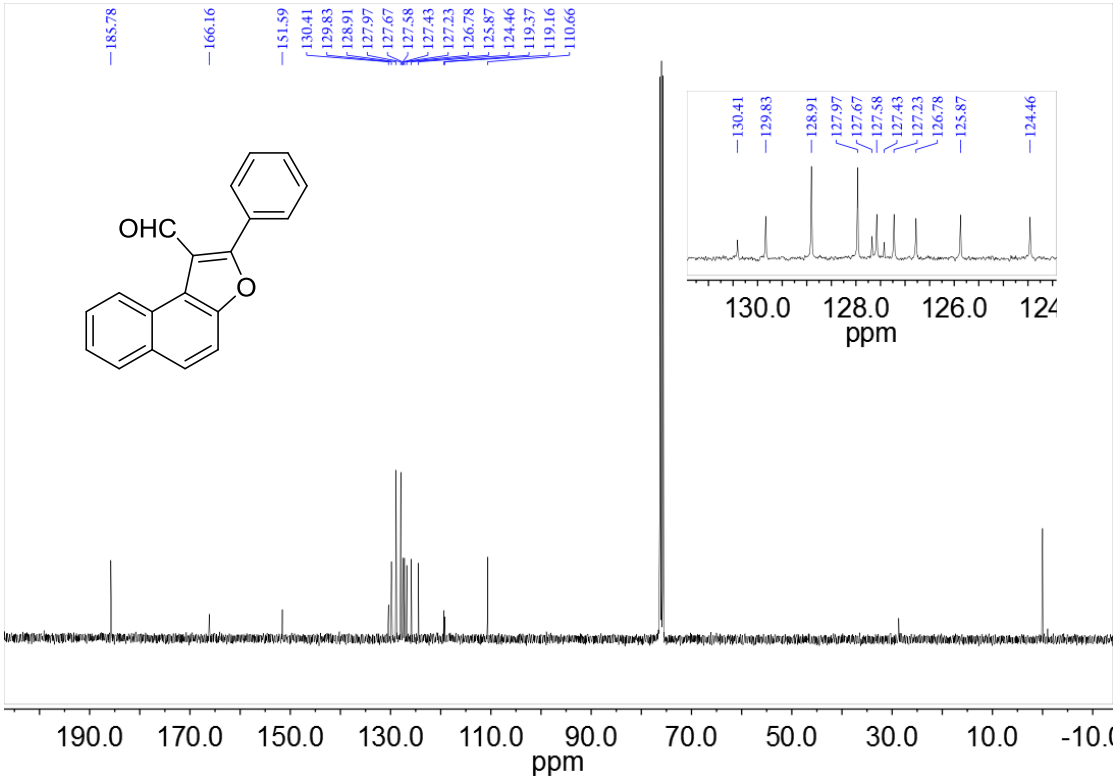
^{13}C NMR Spectrum of Compound 3ia



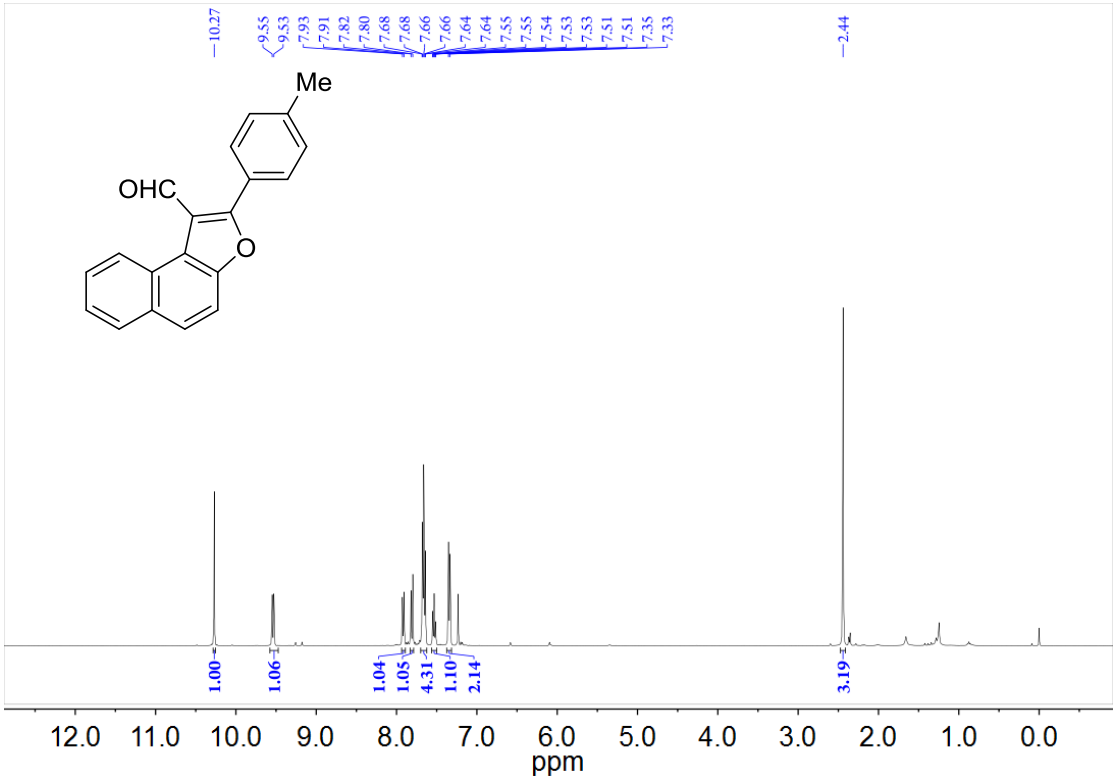
^{1}H NMR Spectrum of Compound 5aa



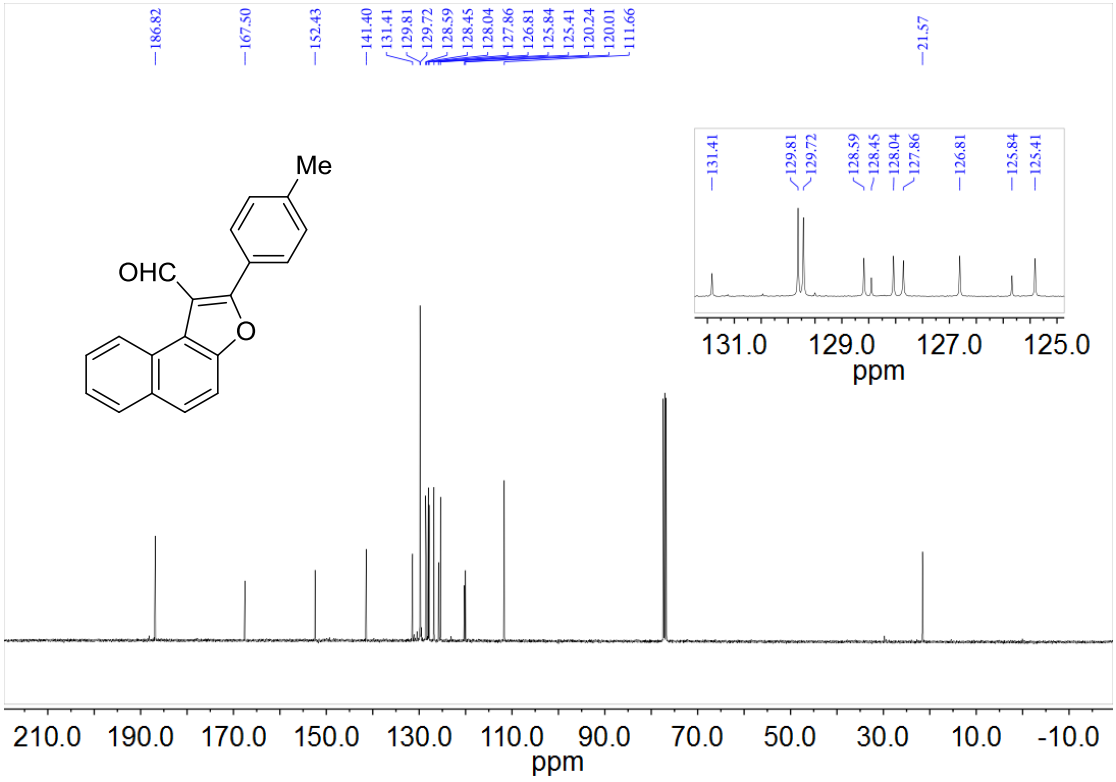
^{13}C NMR Spectrum of Compound 5aa



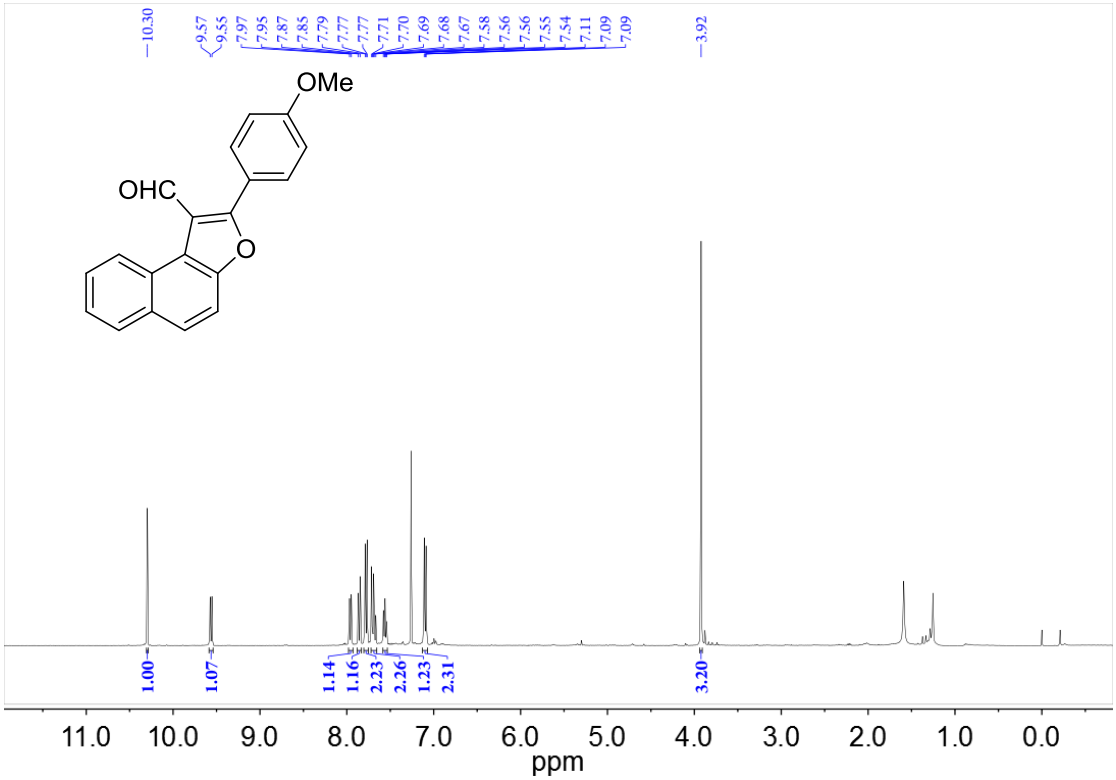
^{1}H NMR Spectrum of Compound 5ab



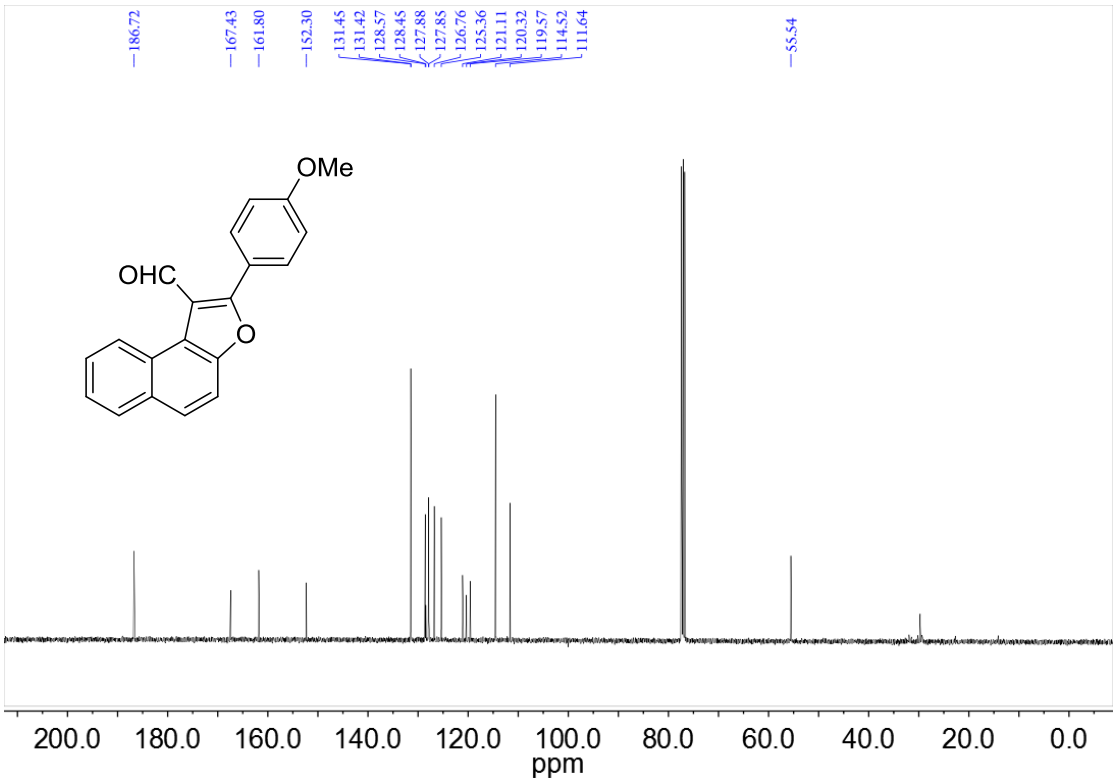
^{13}C NMR Spectrum of Compound 5ab



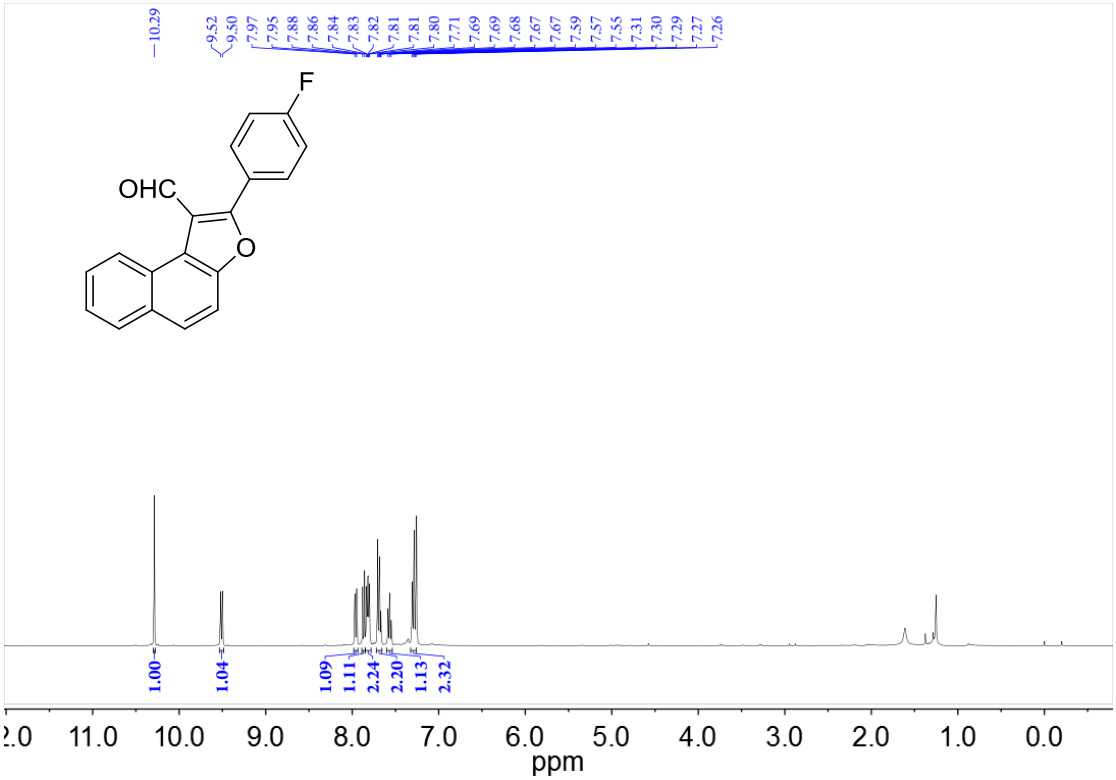
^{1}H NMR Spectrum of Compound 5ac



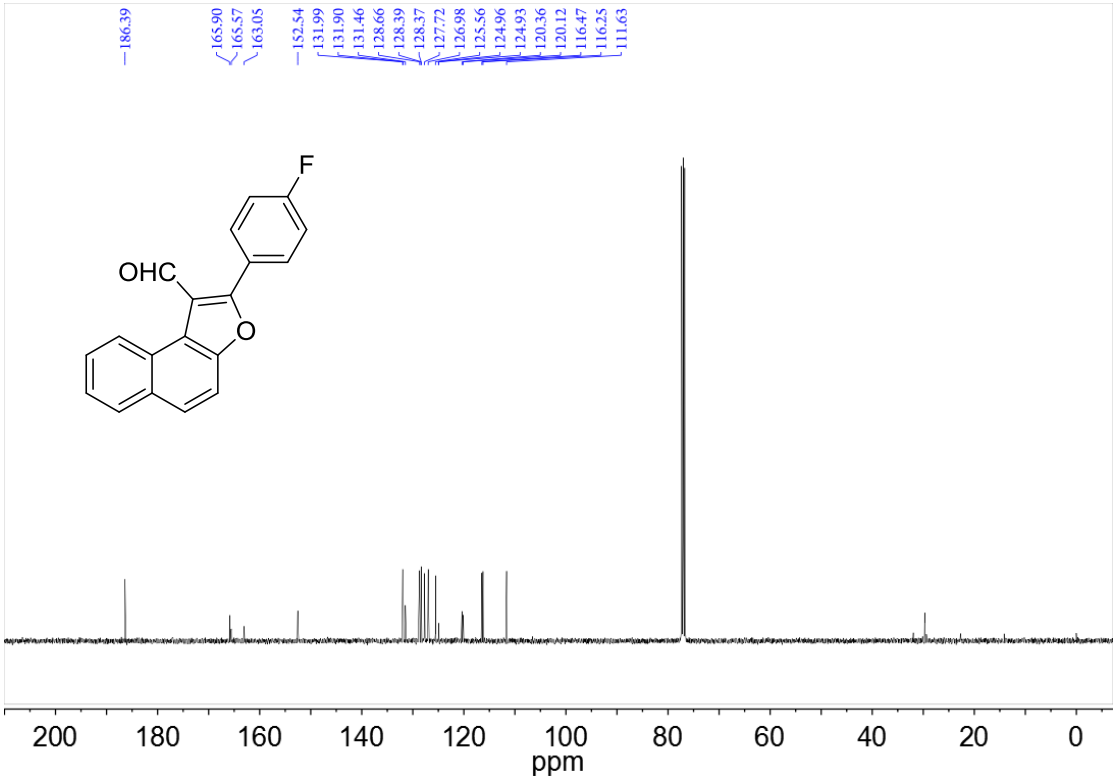
^{13}C NMR Spectrum of Compound 5ac



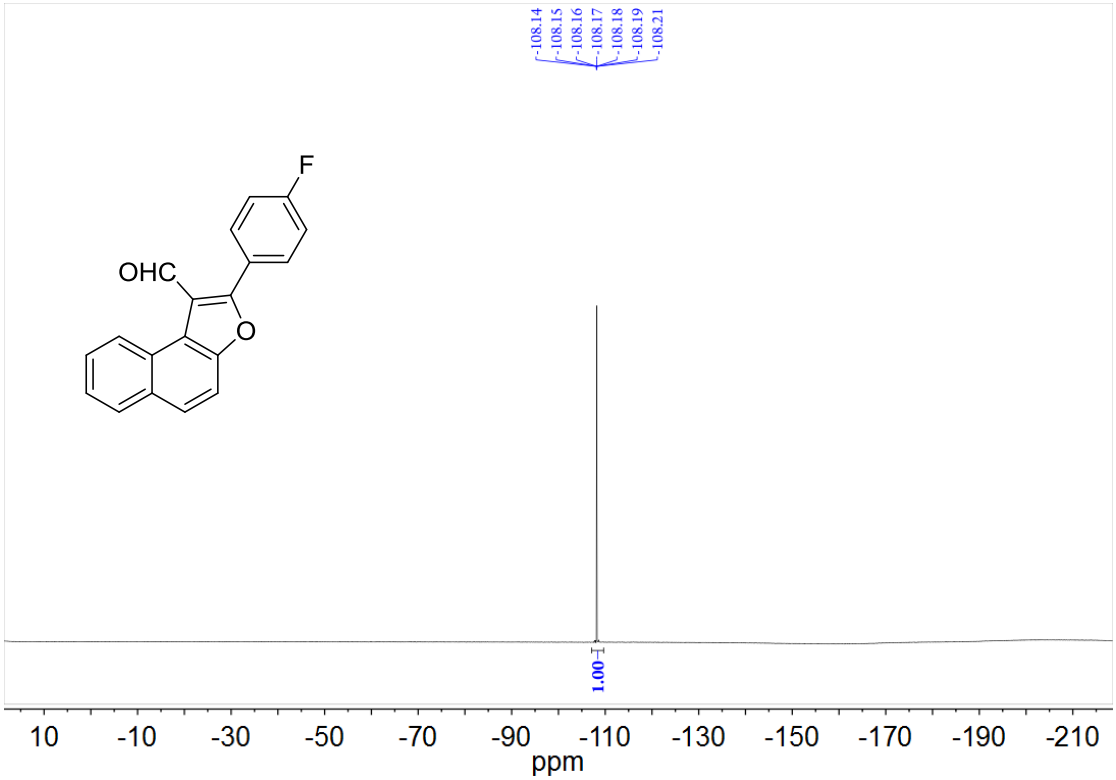
^{1}H NMR Spectrum of Compound 5ad



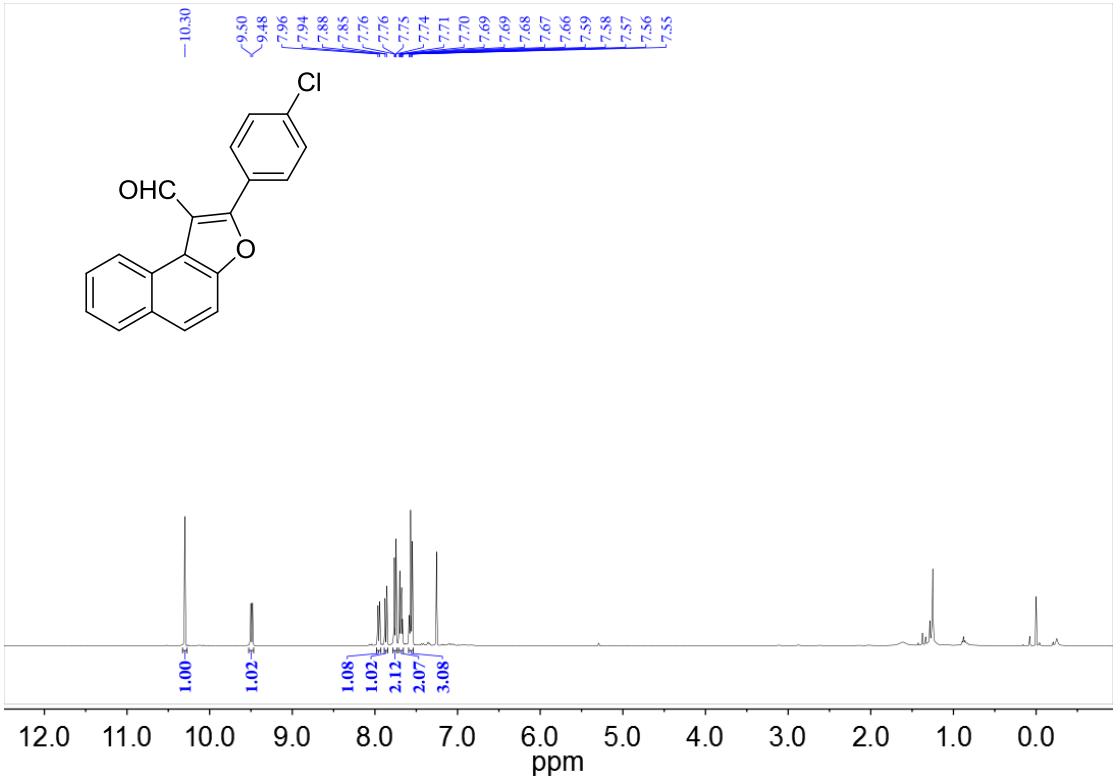
^{13}C NMR Spectrum of Compound 5ad



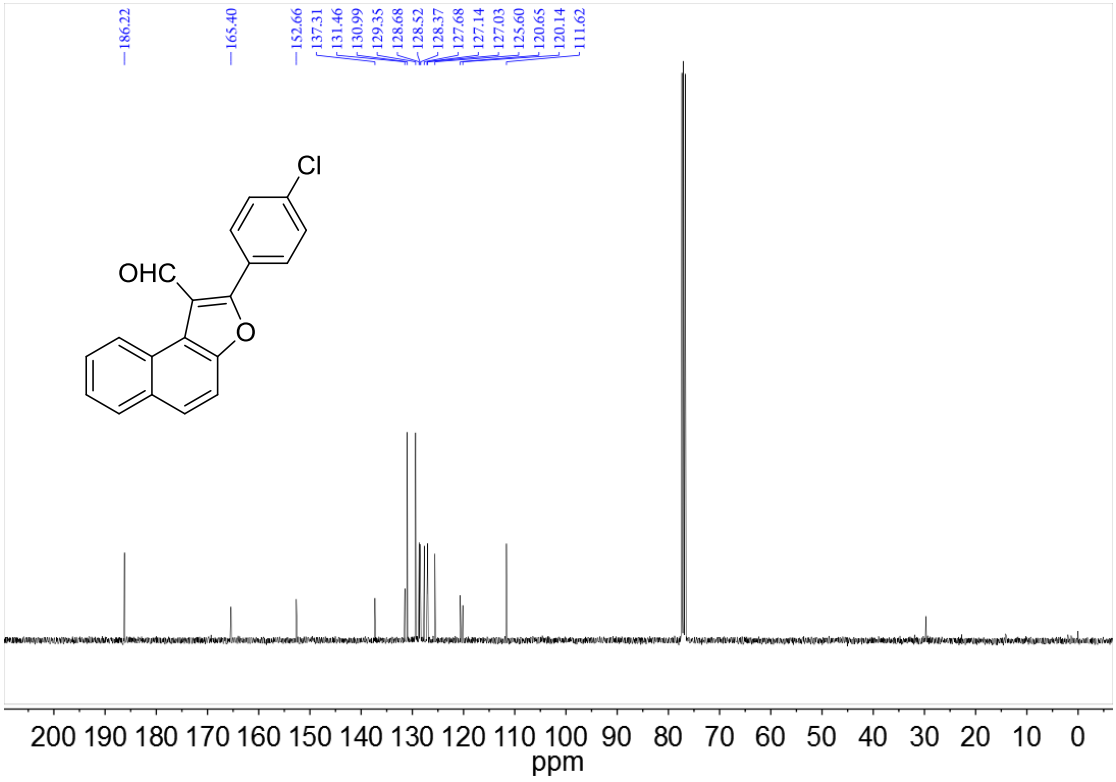
^{19}F NMR Spectrum of Compound 5ad



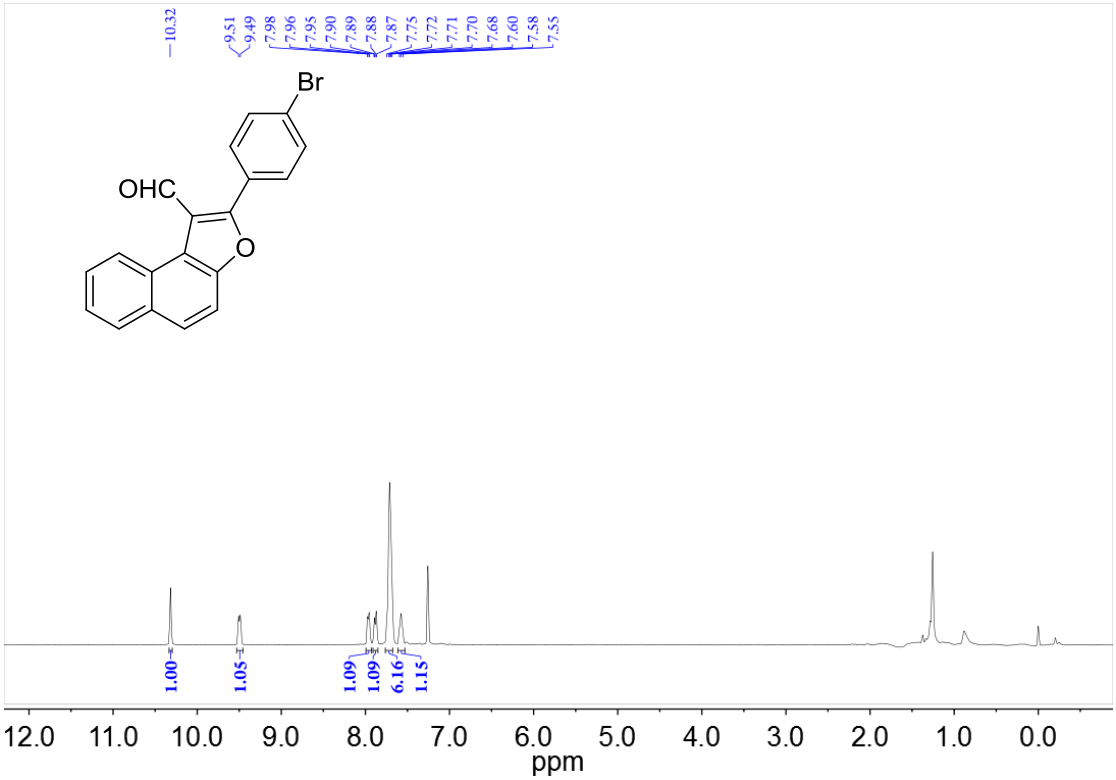
^{1}H NMR Spectrum of Compound 5ae



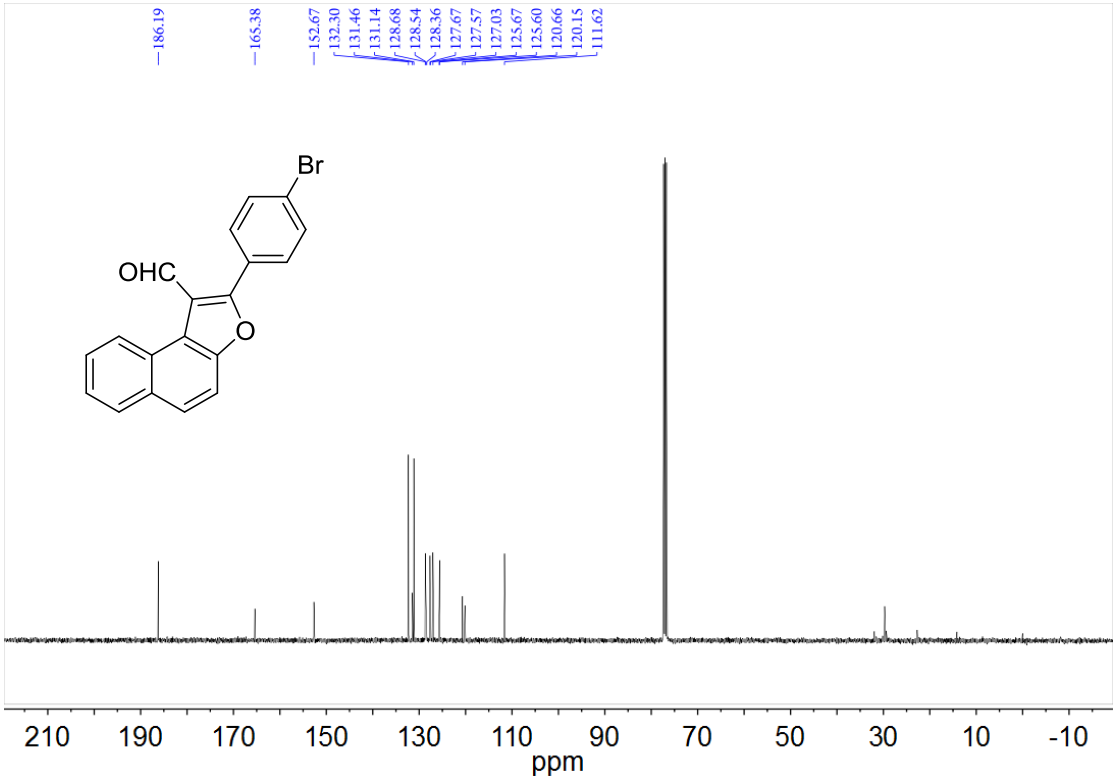
^{13}C NMR Spectrum of Compound 5ae



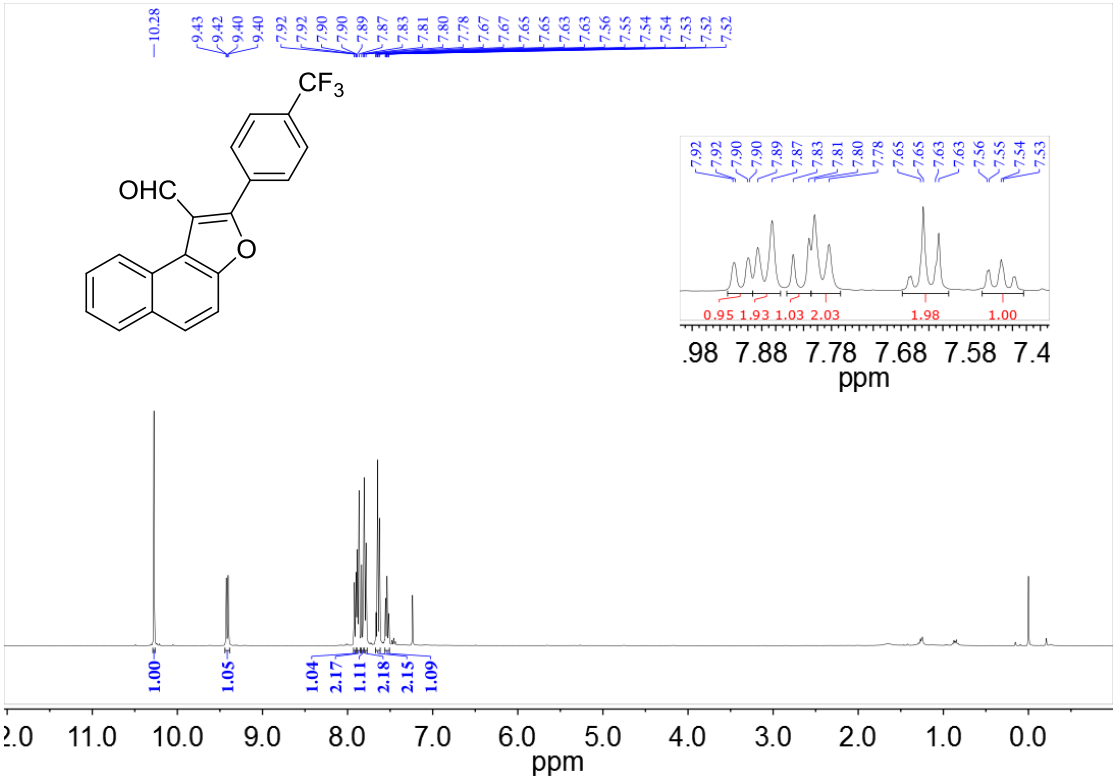
^{1}H NMR Spectrum of Compound 5af



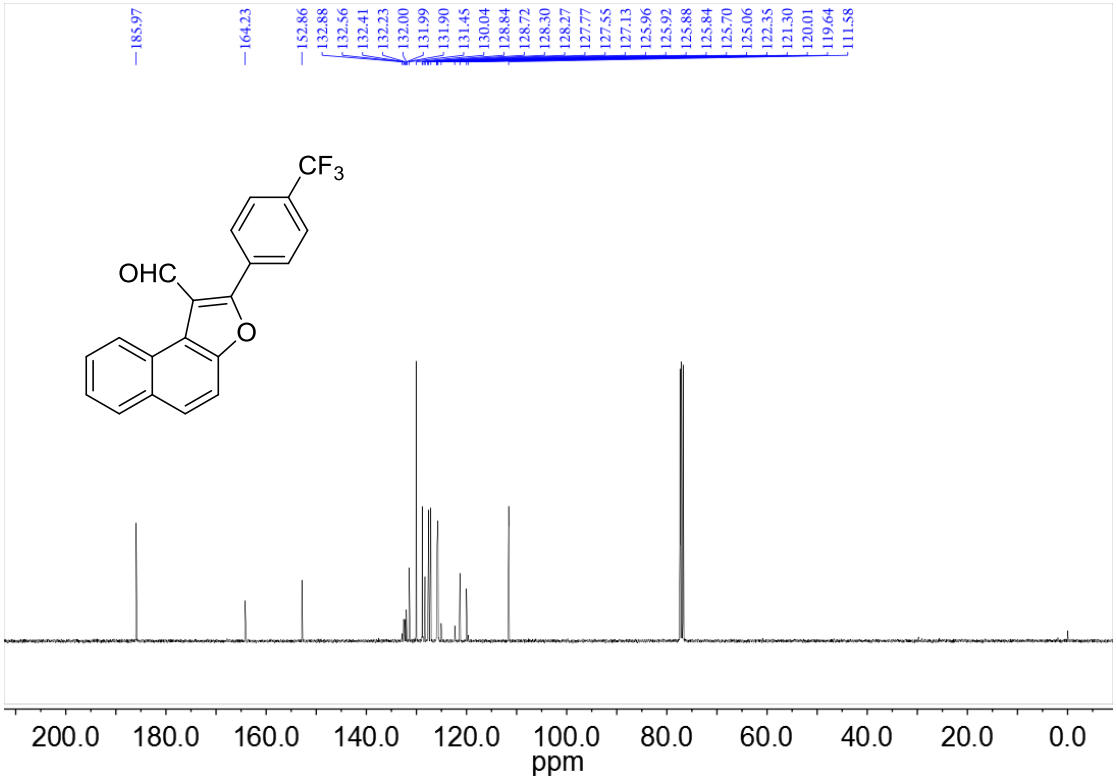
^{13}C NMR Spectrum of Compound 5af



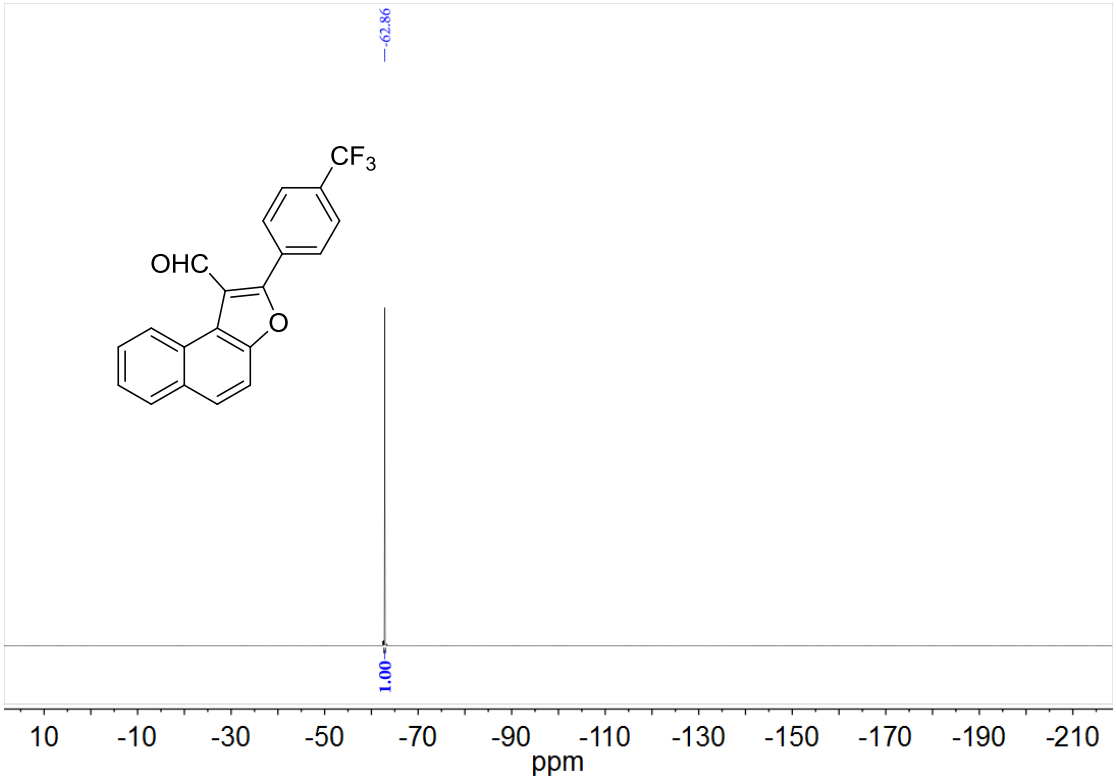
^{1}H NMR Spectrum of Compound 5ag



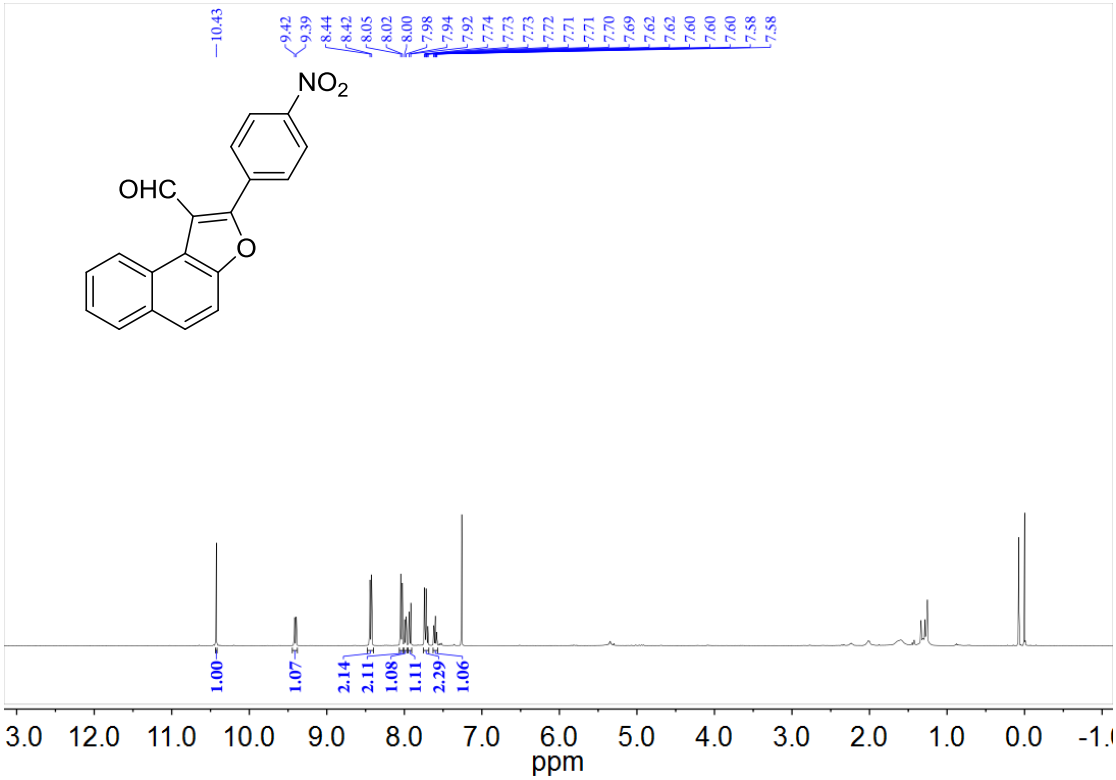
^{13}C NMR Spectrum of Compound 5ag



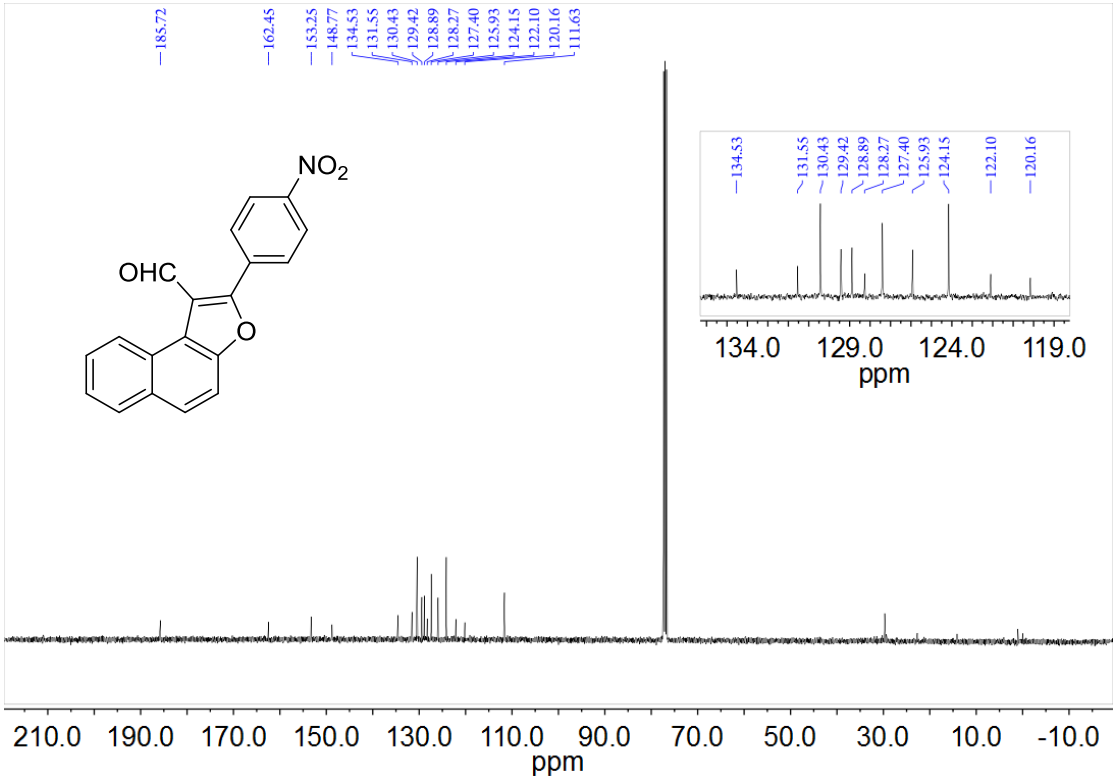
^{19}F NMR Spectrum of Compound 5ag



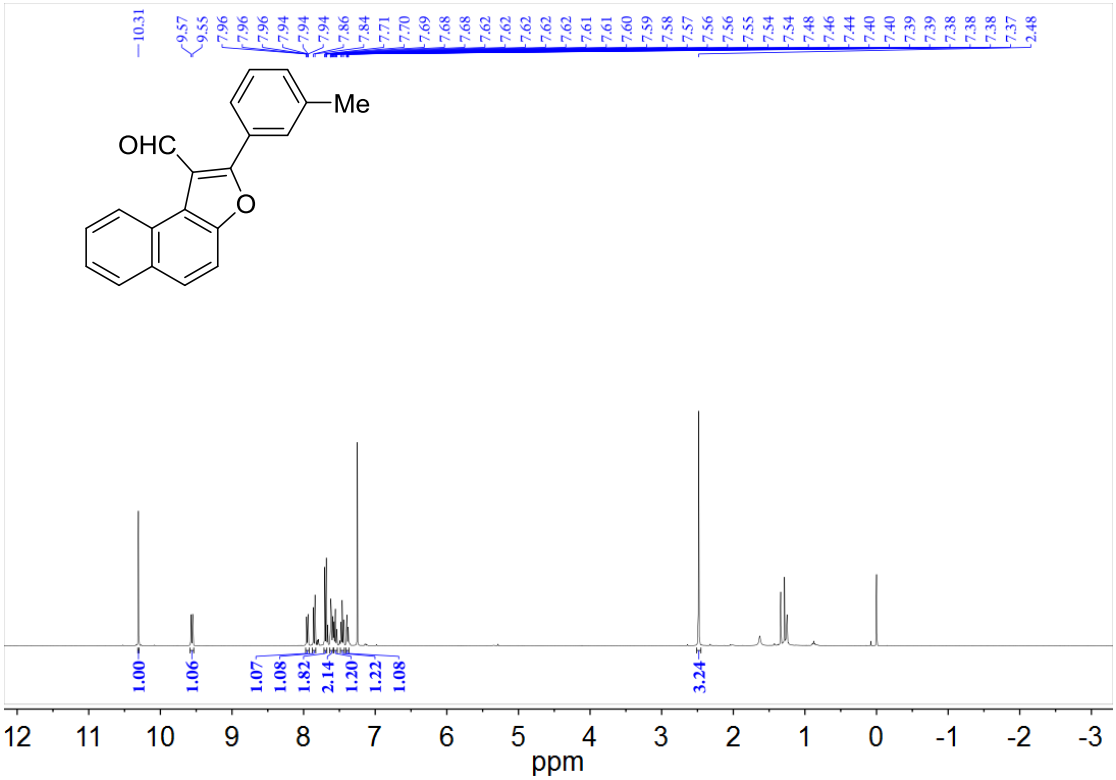
^{1}H NMR Spectrum of Compound 5ah



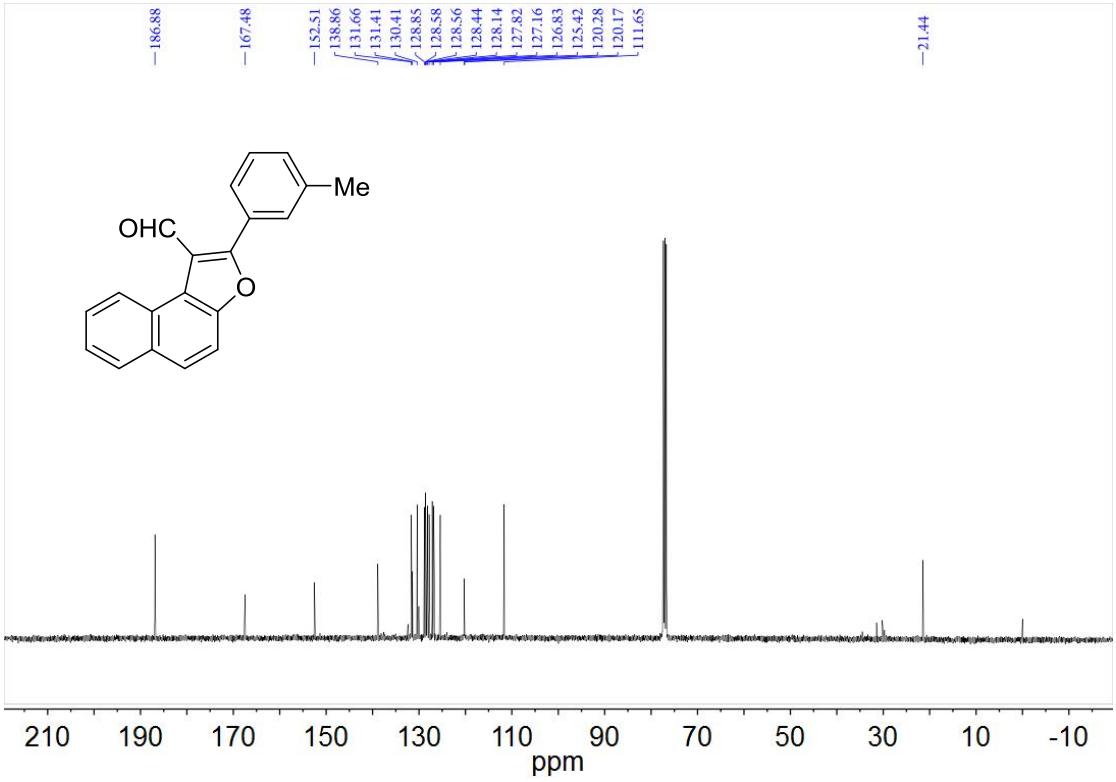
^{13}C NMR Spectrum of Compound 5ah



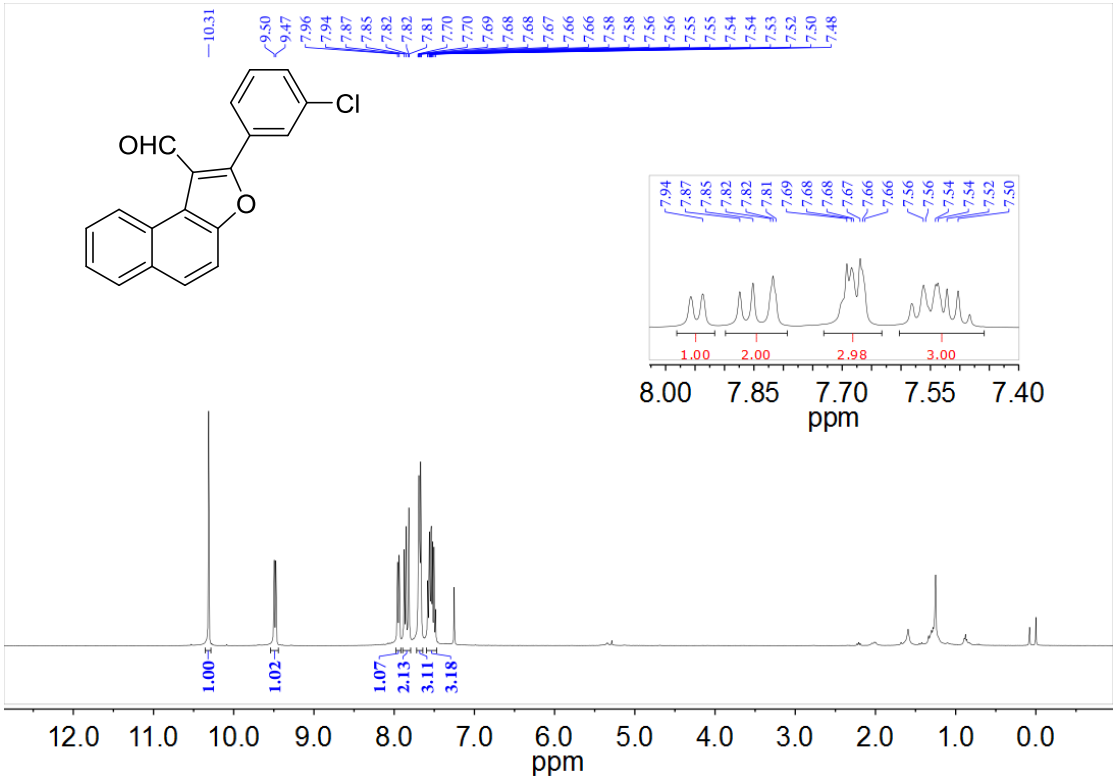
^{1}H NMR Spectrum of Compound 5ai



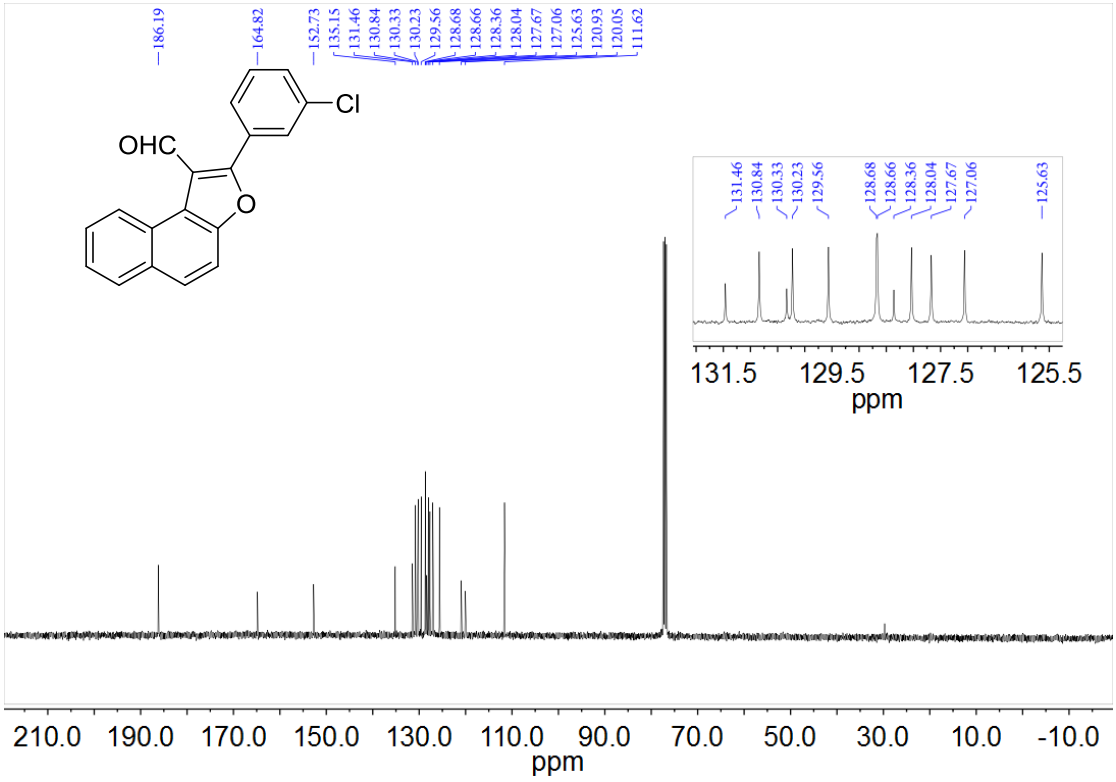
^{13}C NMR Spectrum of Compound 5ai



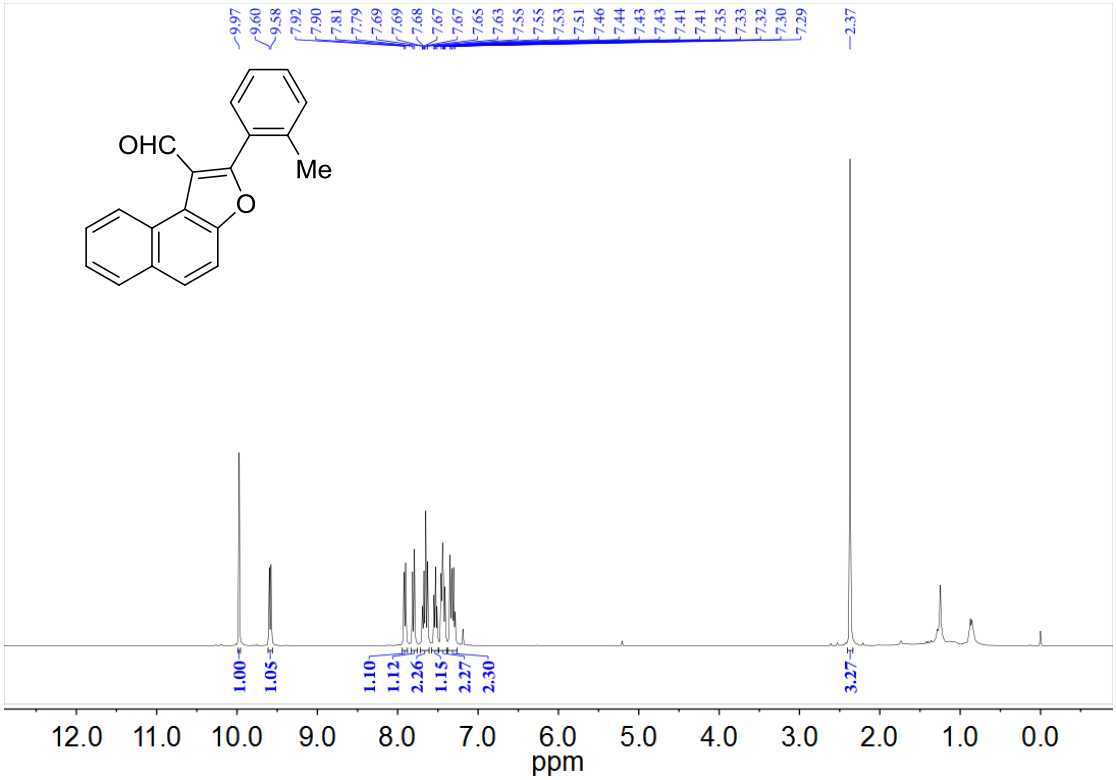
^{1}H NMR Spectrum of Compound 5aj



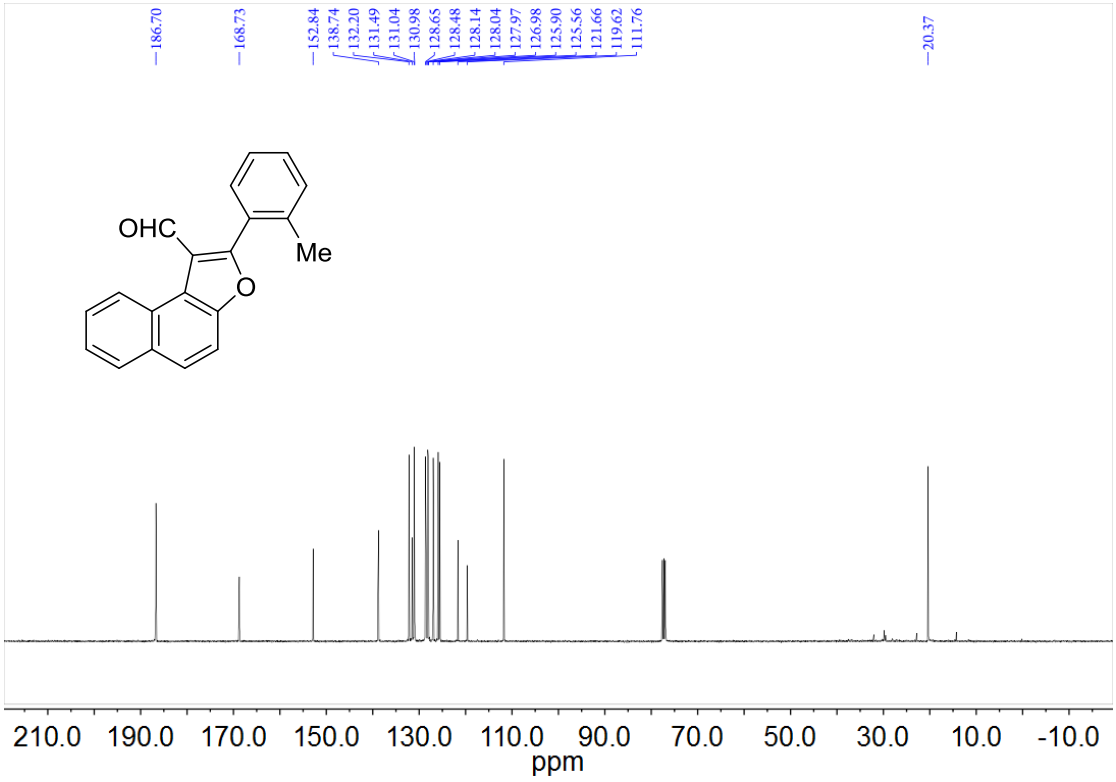
^{13}C NMR Spectrum of Compound 5aj



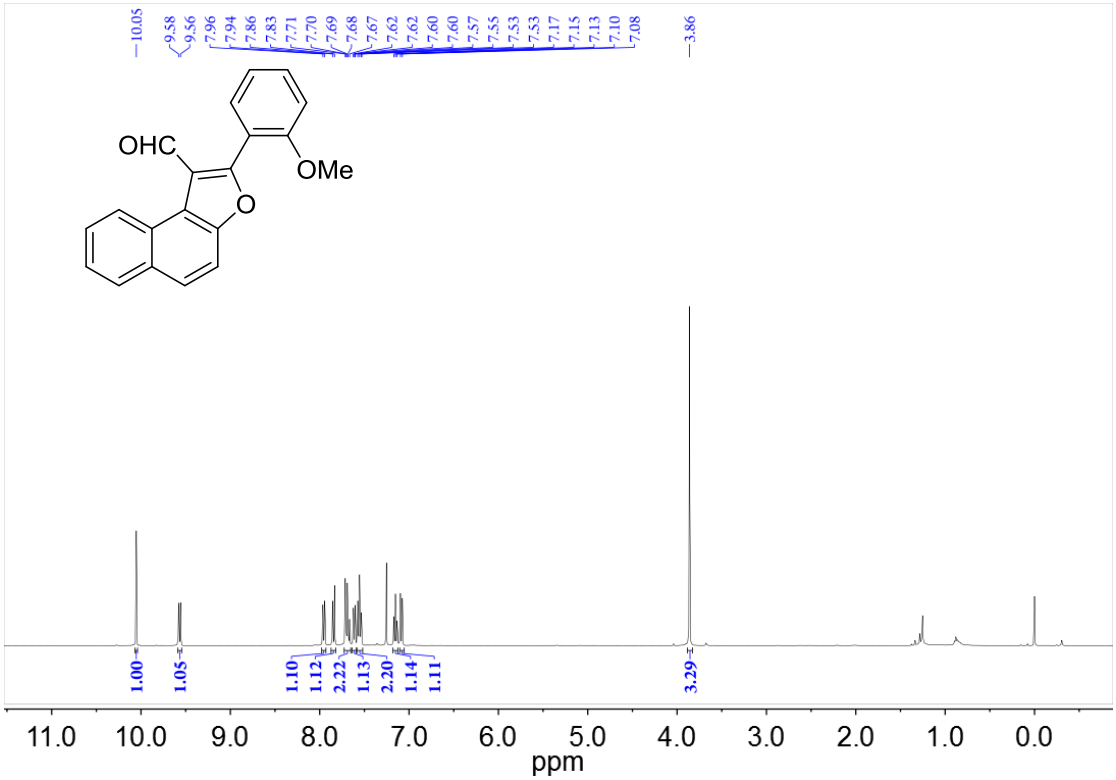
^{1}H NMR Spectrum of Compound 5ak



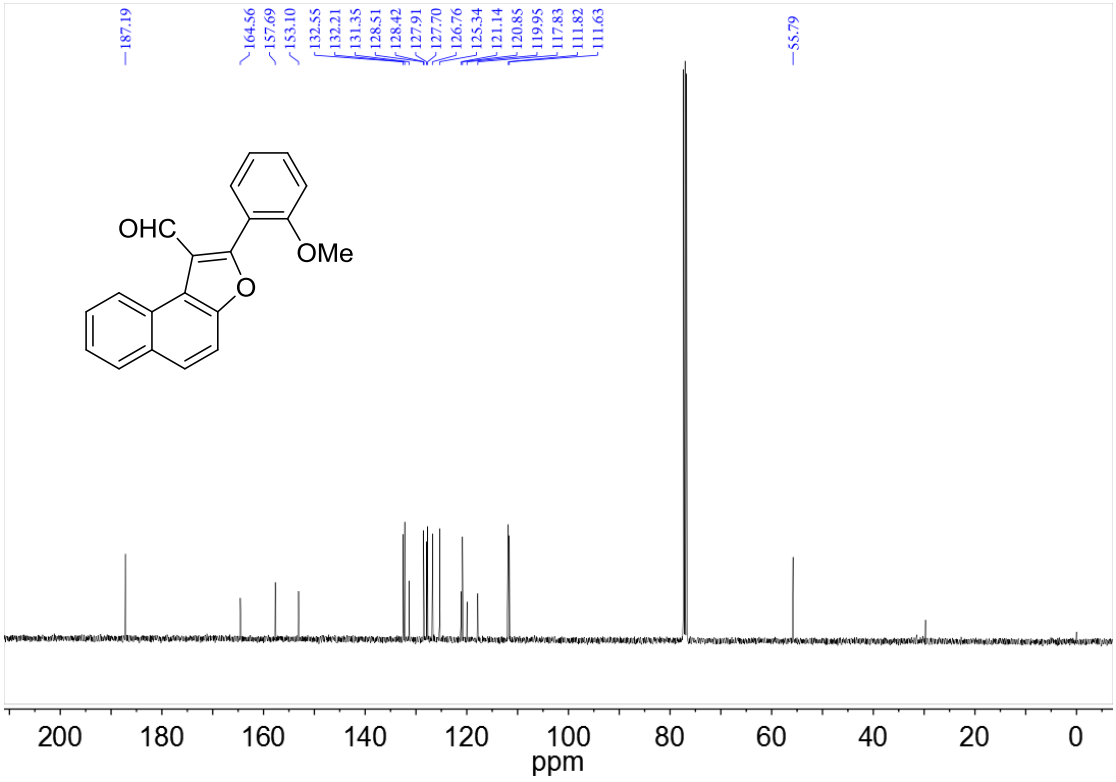
^{13}C NMR Spectrum of Compound 5ak



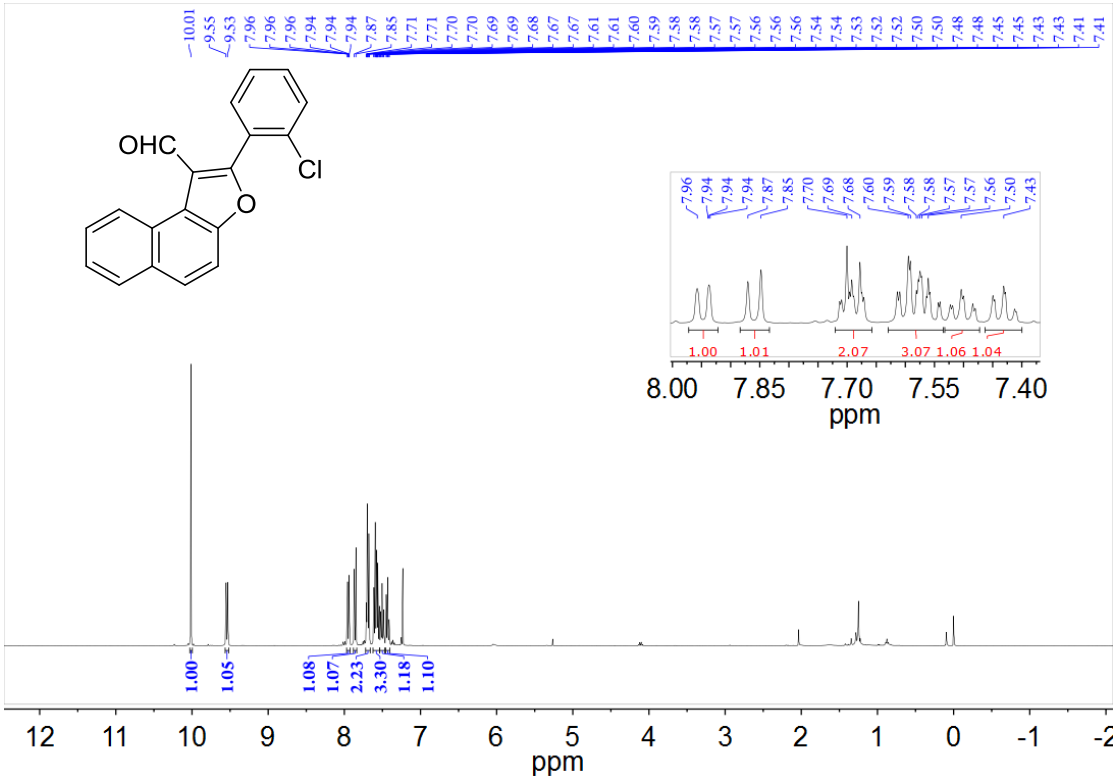
^{1}H NMR Spectrum of Compound 5al



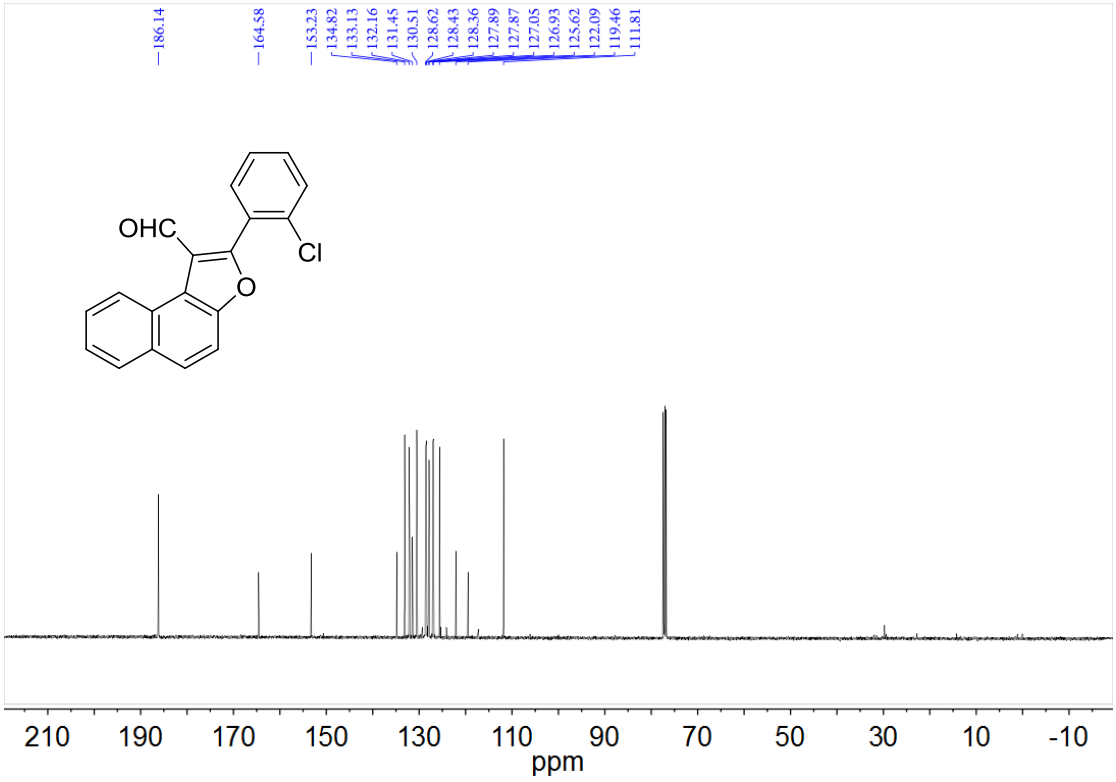
^{13}C NMR Spectrum of Compound 5al



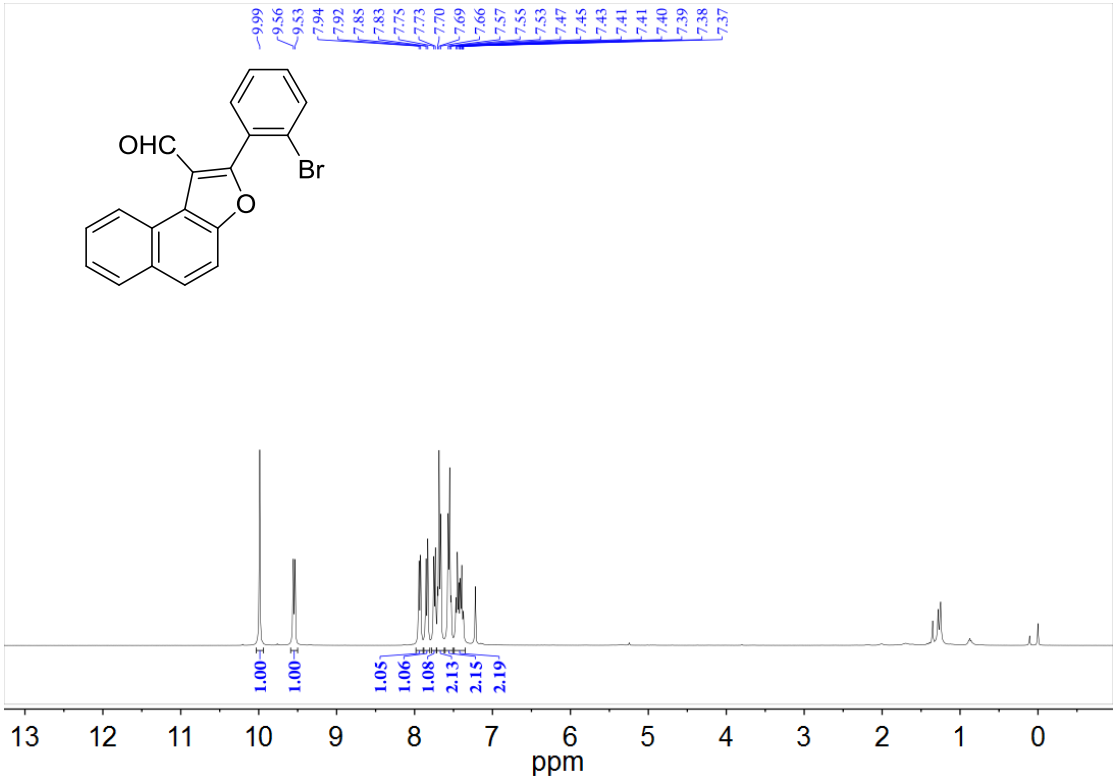
^{1}H NMR Spectrum of Compound 5am



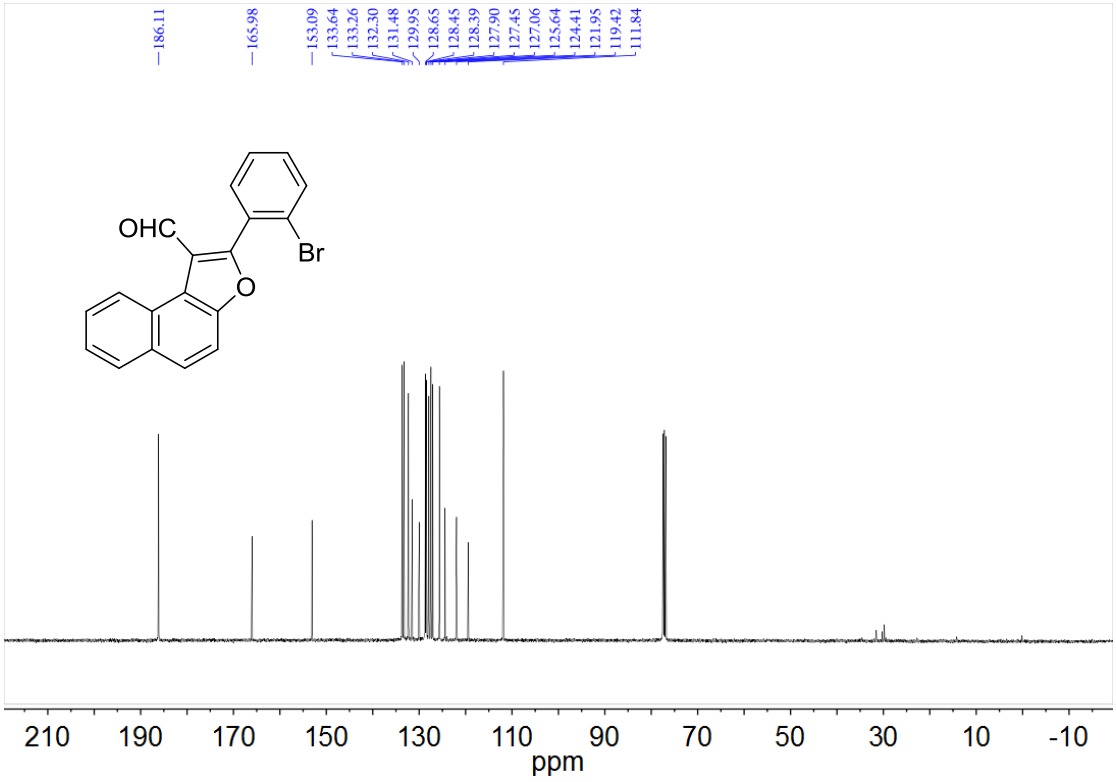
^{13}C NMR Spectrum of Compound 5am



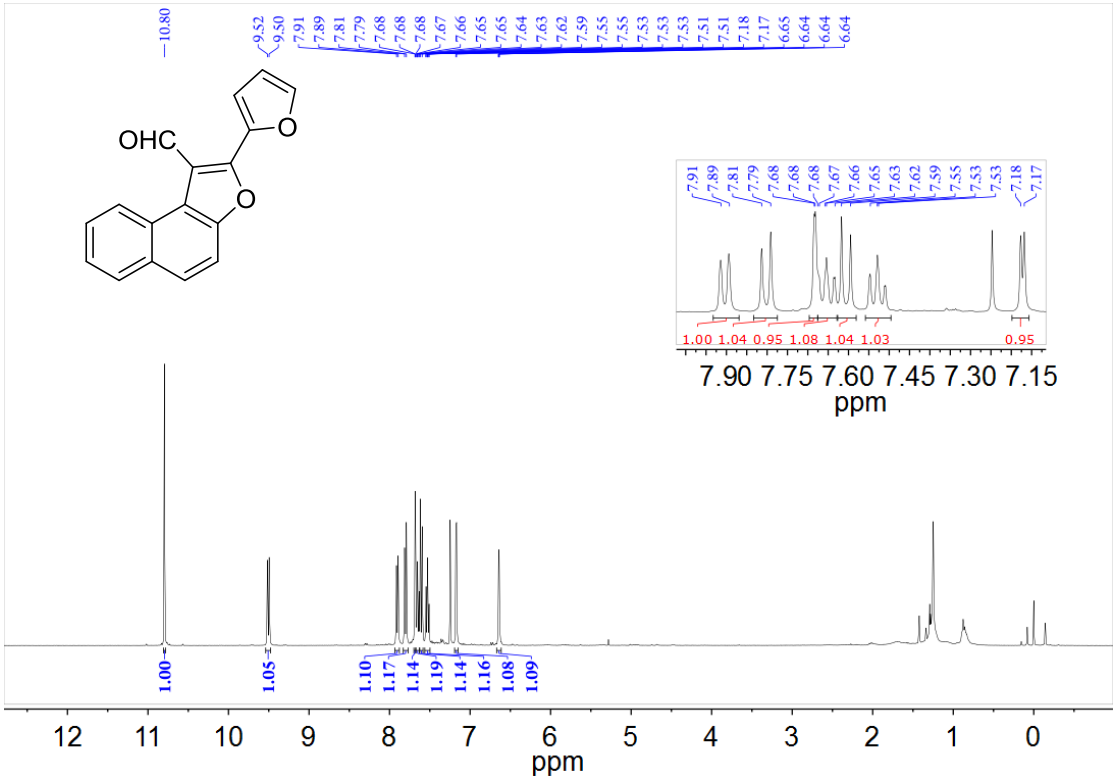
^{1}H NMR Spectrum of Compound 5an



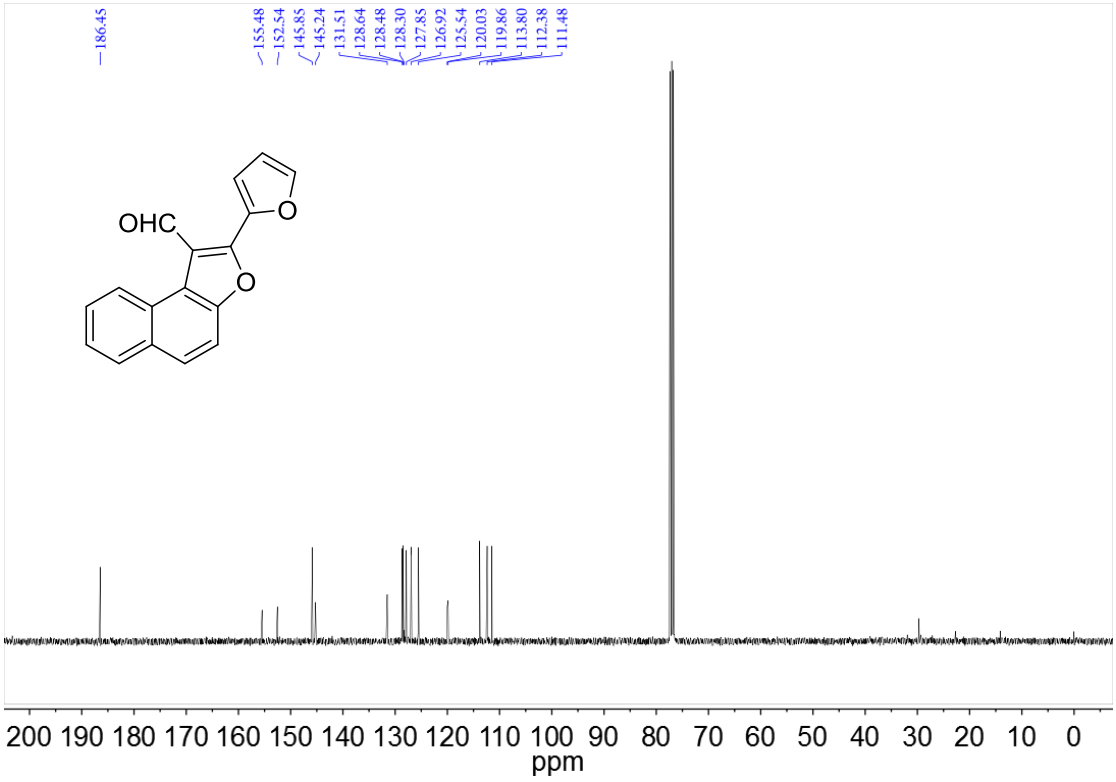
^{13}C NMR Spectrum of Compound 5an



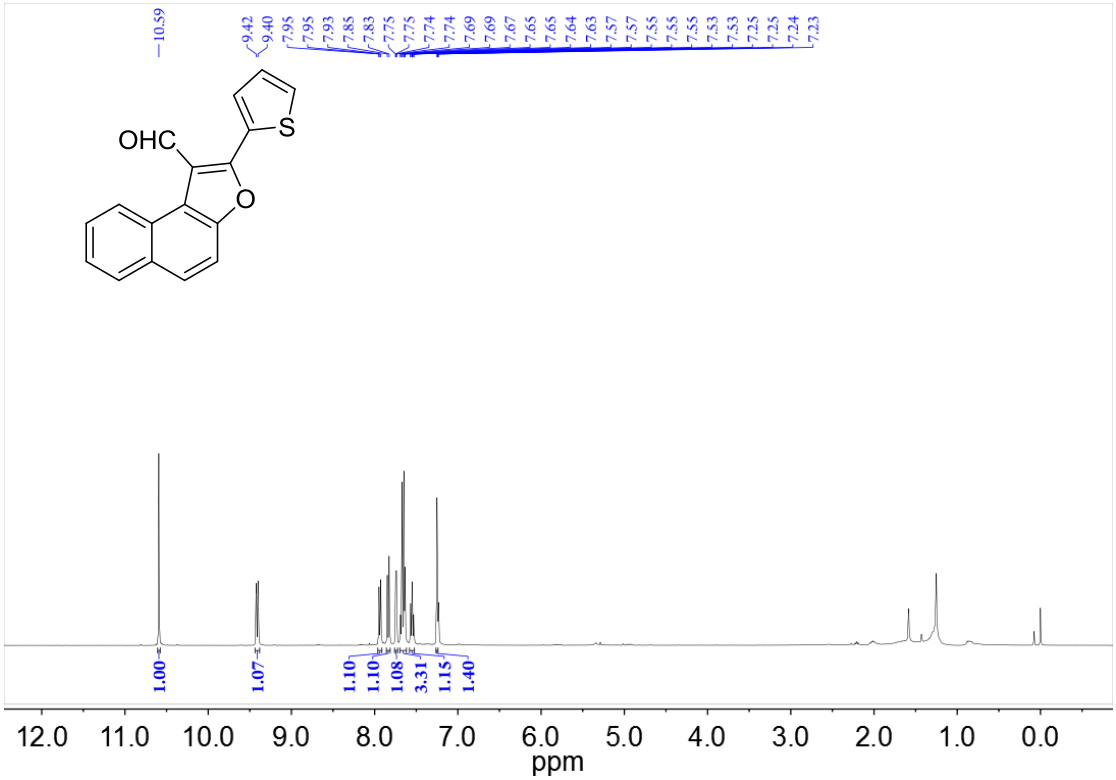
^{1}H NMR Spectrum of Compound 5ao



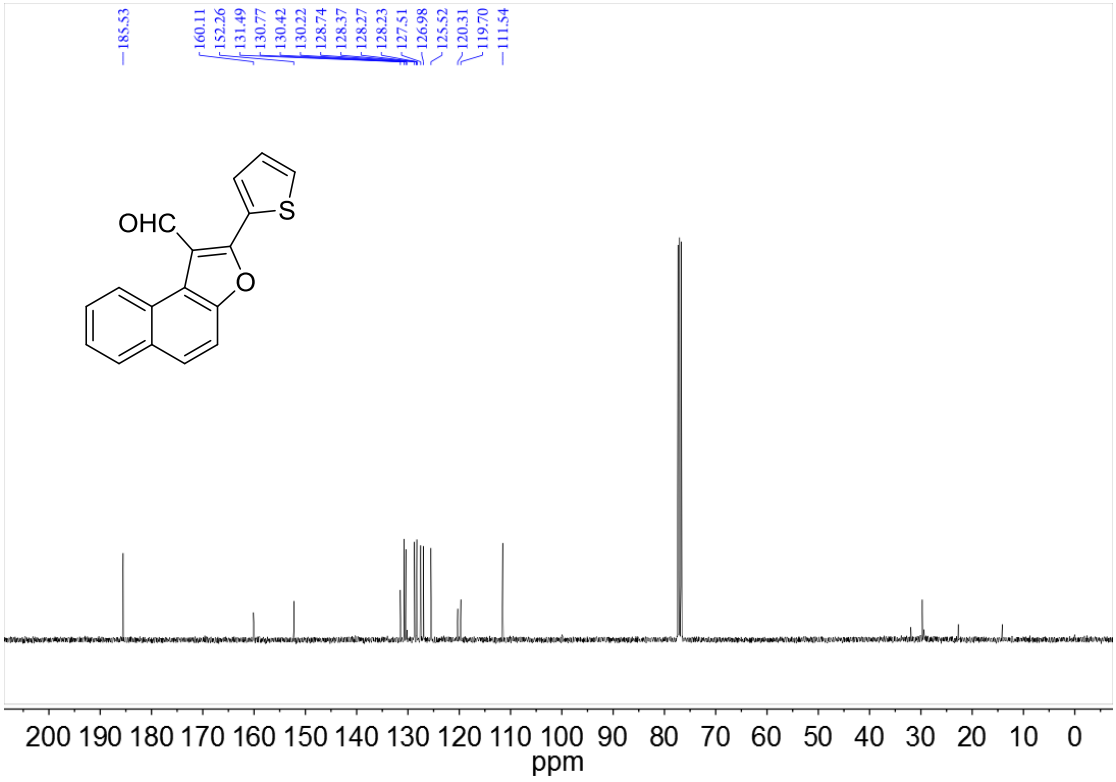
^{13}C NMR Spectrum of Compound 5ao



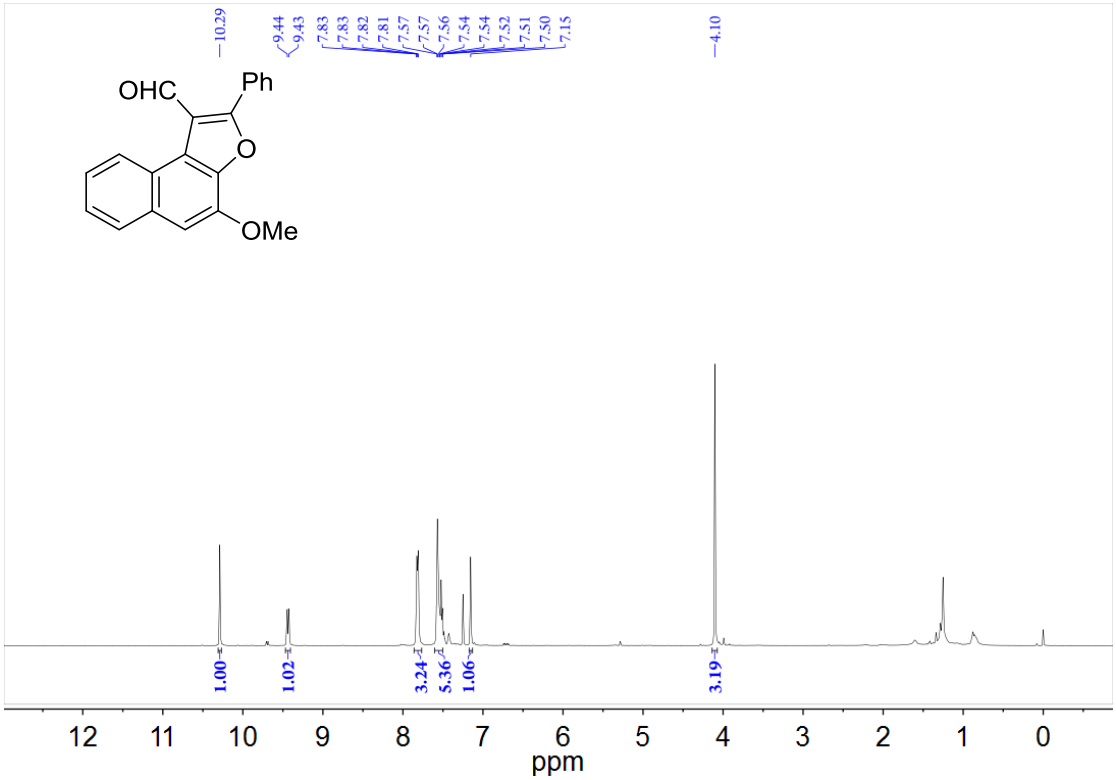
^{1}H NMR Spectrum of Compound 5ap



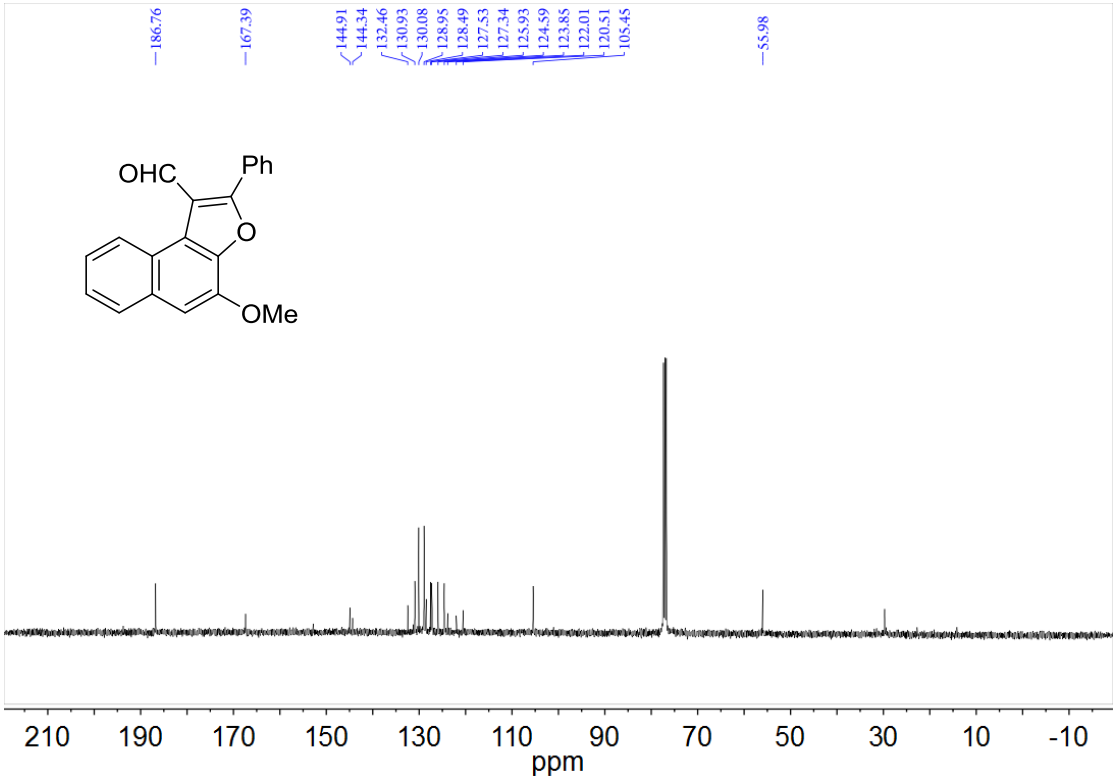
^{13}C NMR Spectrum of Compound 5ap



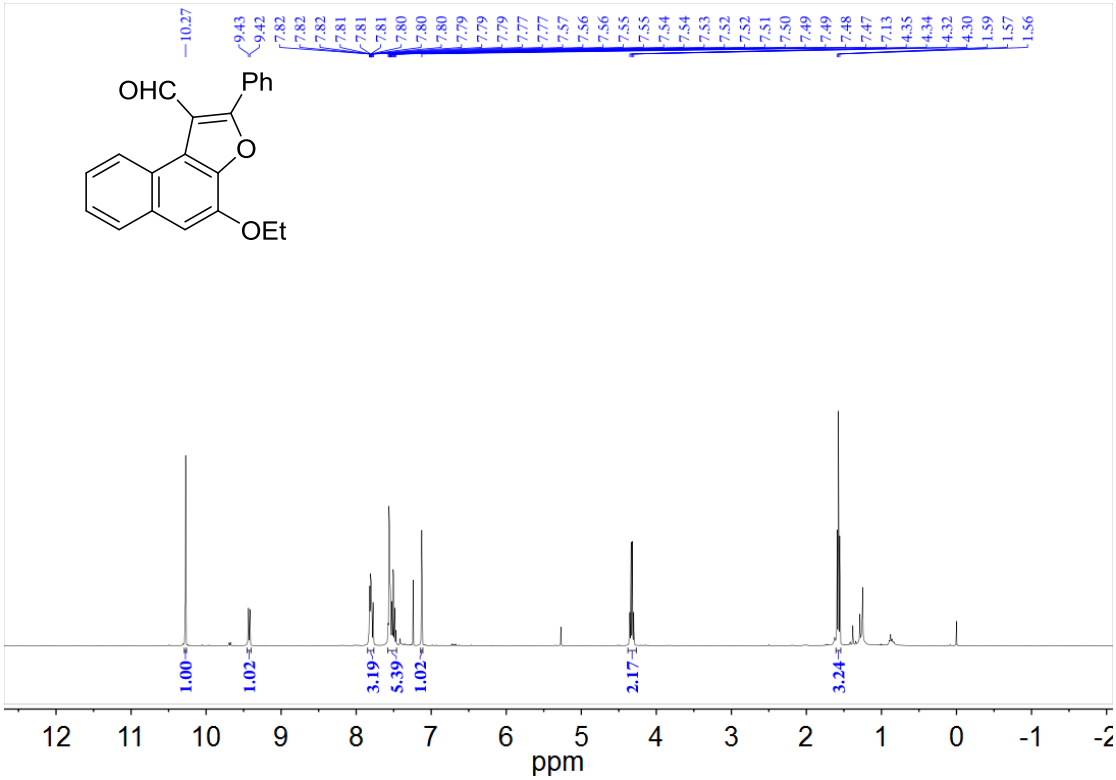
^{1}H NMR Spectrum of Compound 5ba



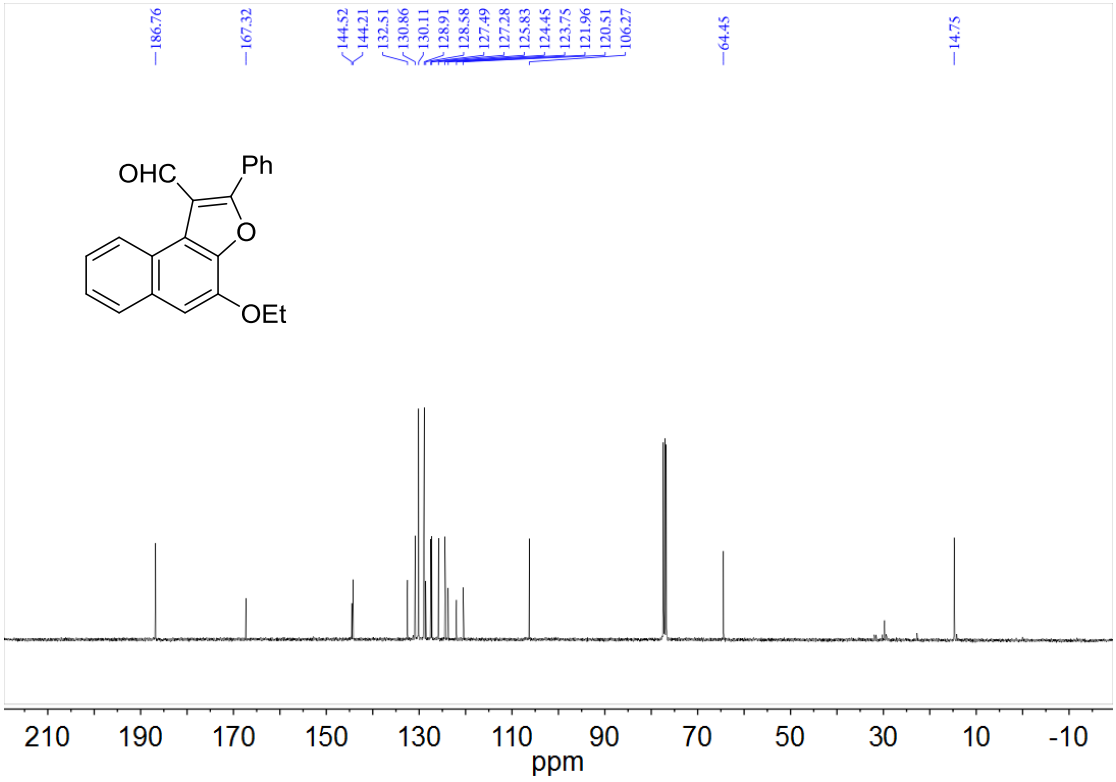
^{13}C NMR Spectrum of Compound 5ba



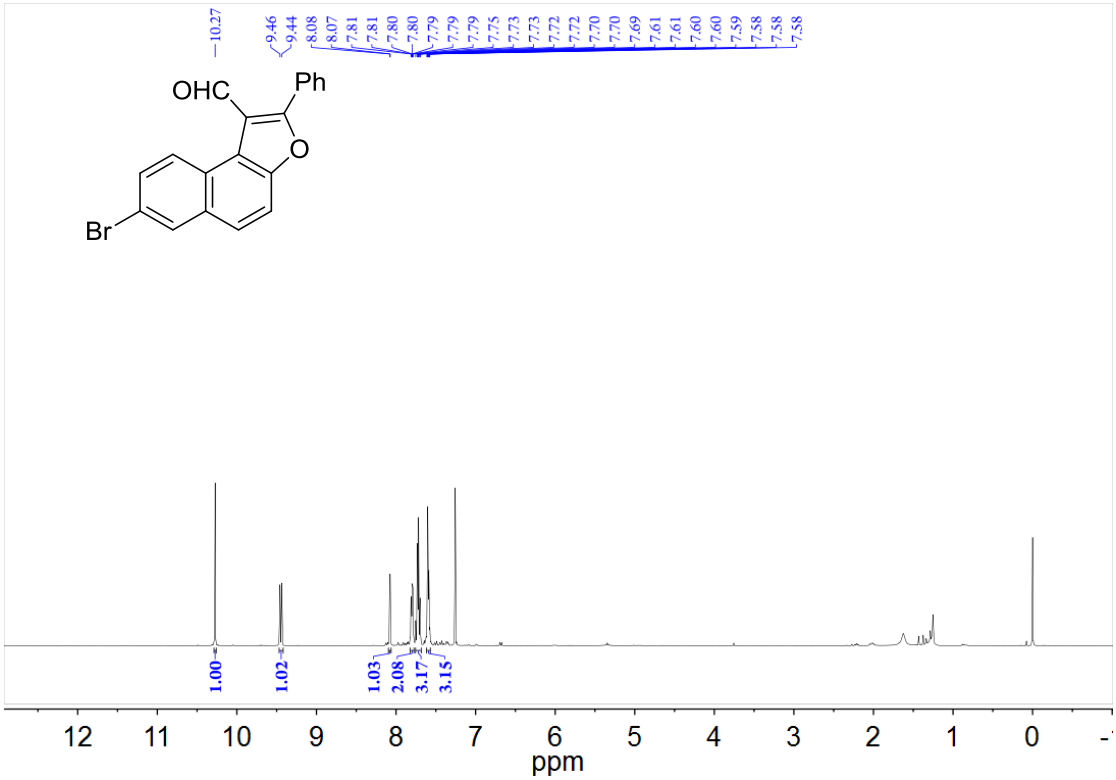
^{1}H NMR Spectrum of Compound 5ca



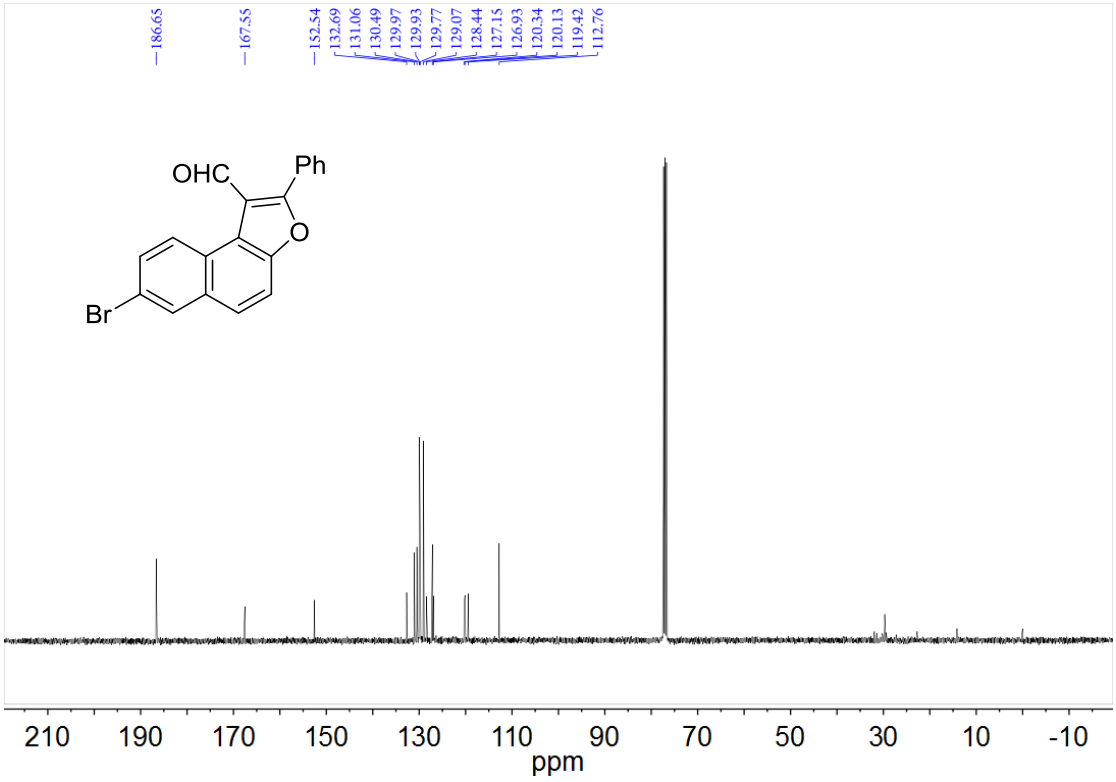
^{13}C NMR Spectrum of Compound 5ca



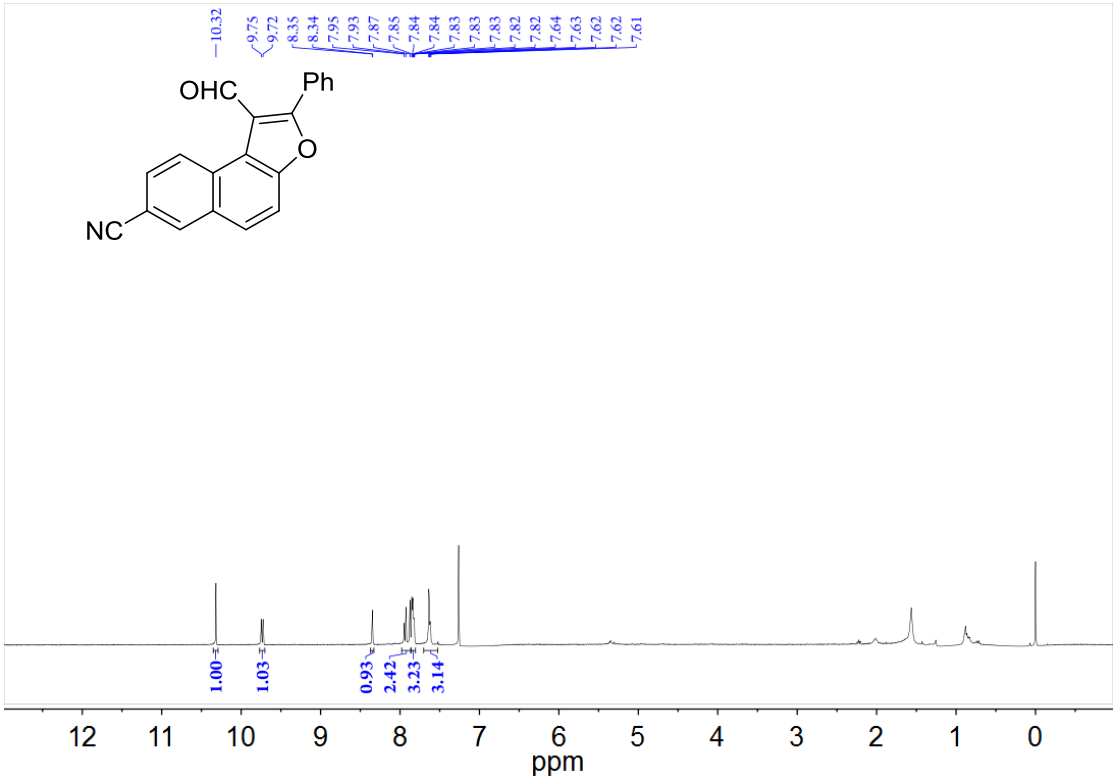
^{1}H NMR Spectrum of Compound 5da



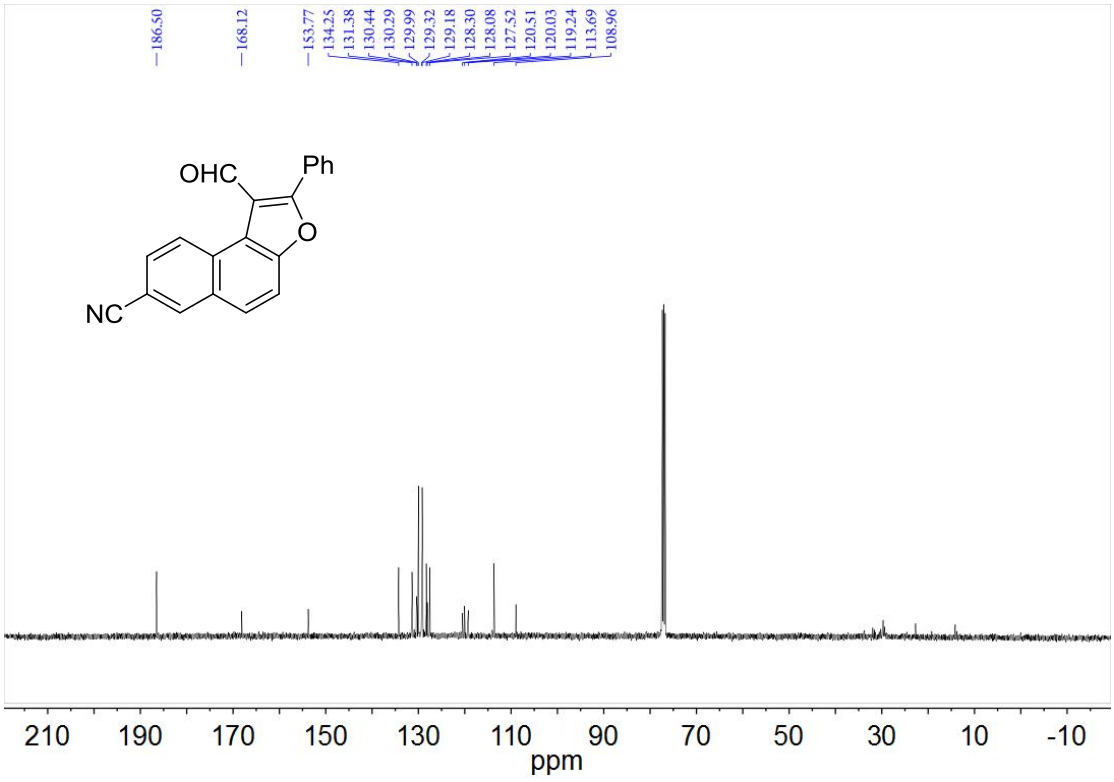
^{13}C NMR Spectrum of Compound 5da



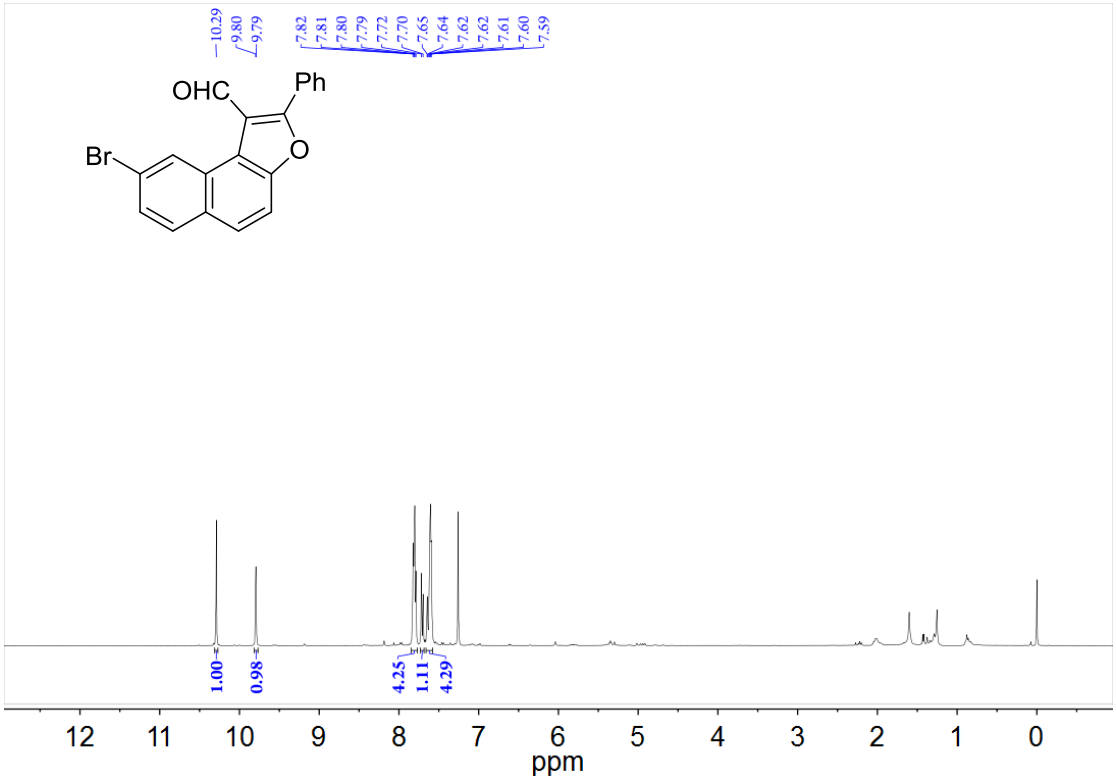
^{1}H NMR Spectrum of Compound 5ea



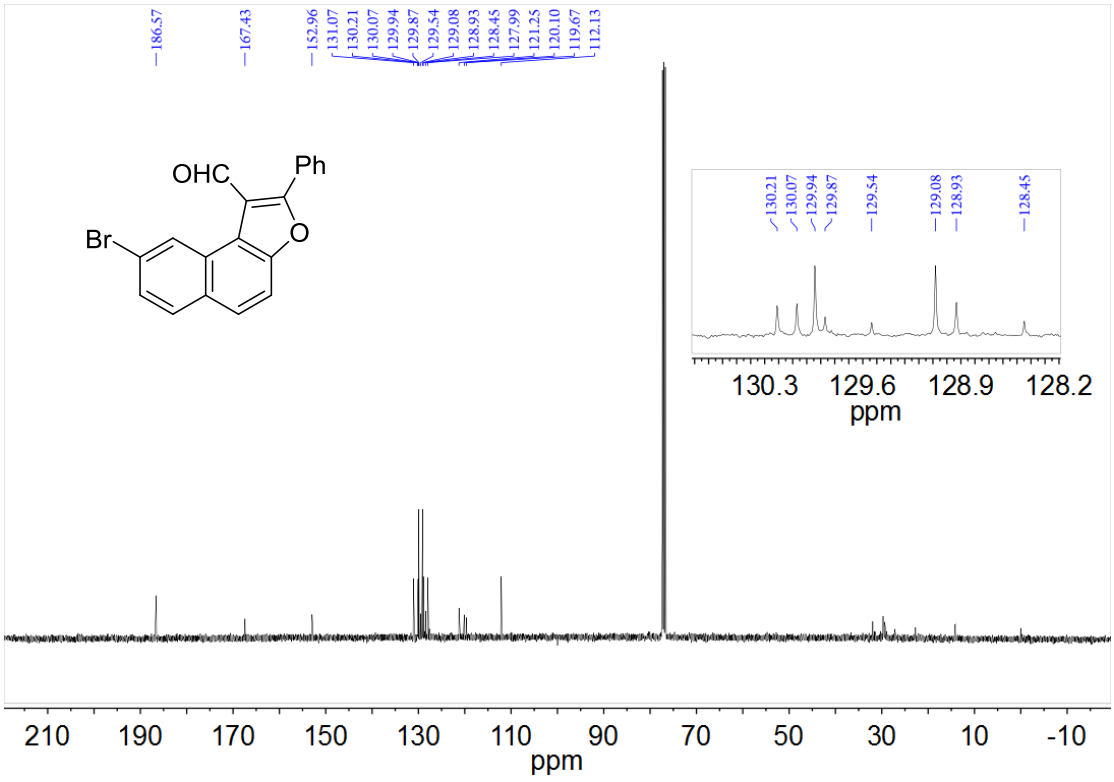
^{13}C NMR Spectrum of Compound 5ea



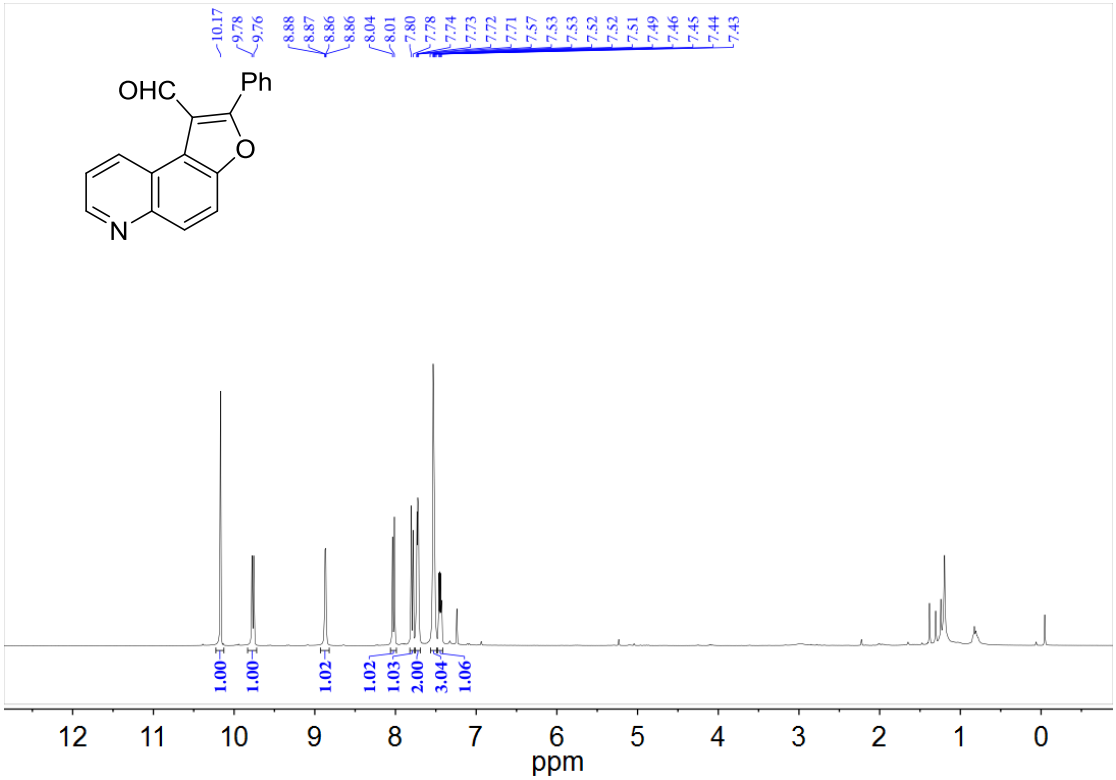
^{1}H NMR Spectrum of Compound 5fa



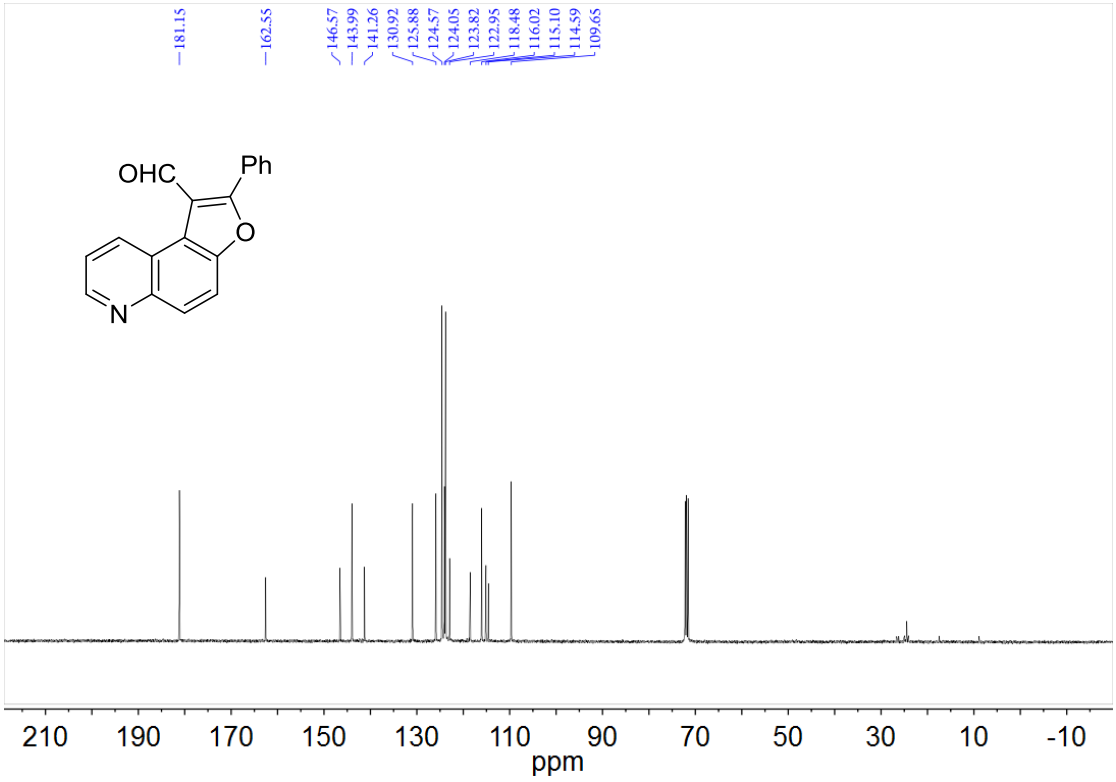
^{13}C NMR Spectrum of Compound 5fa



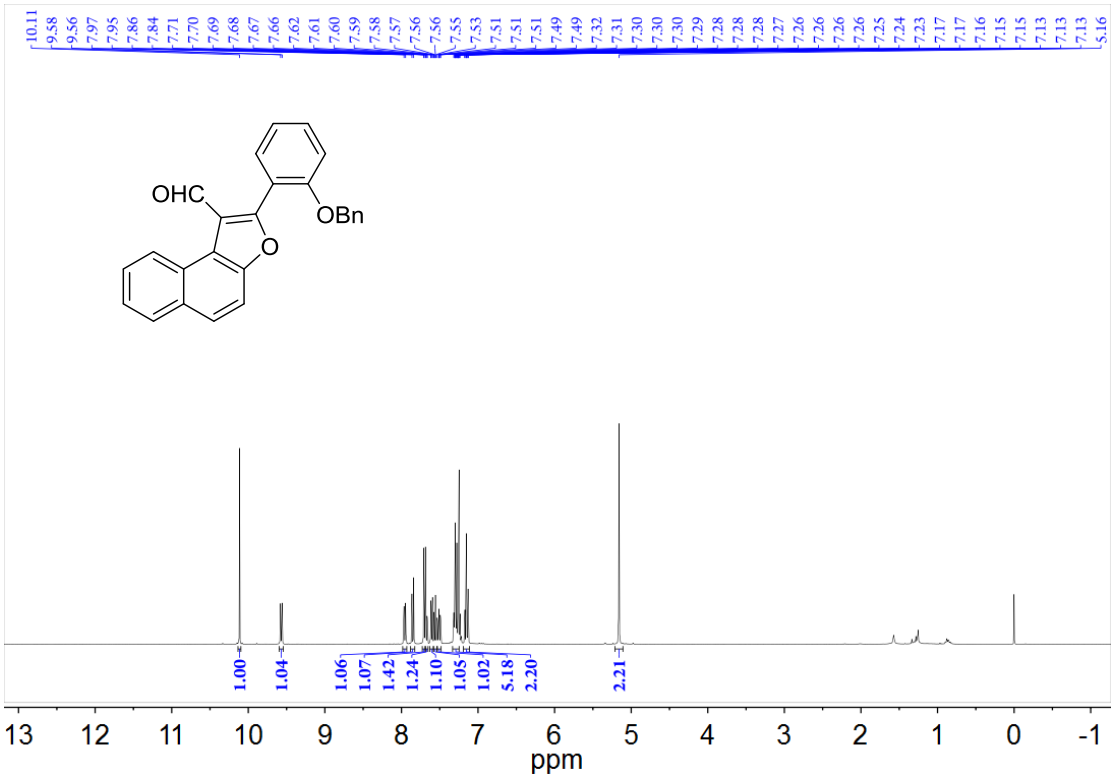
^{1}H NMR Spectrum of Compound 5ga



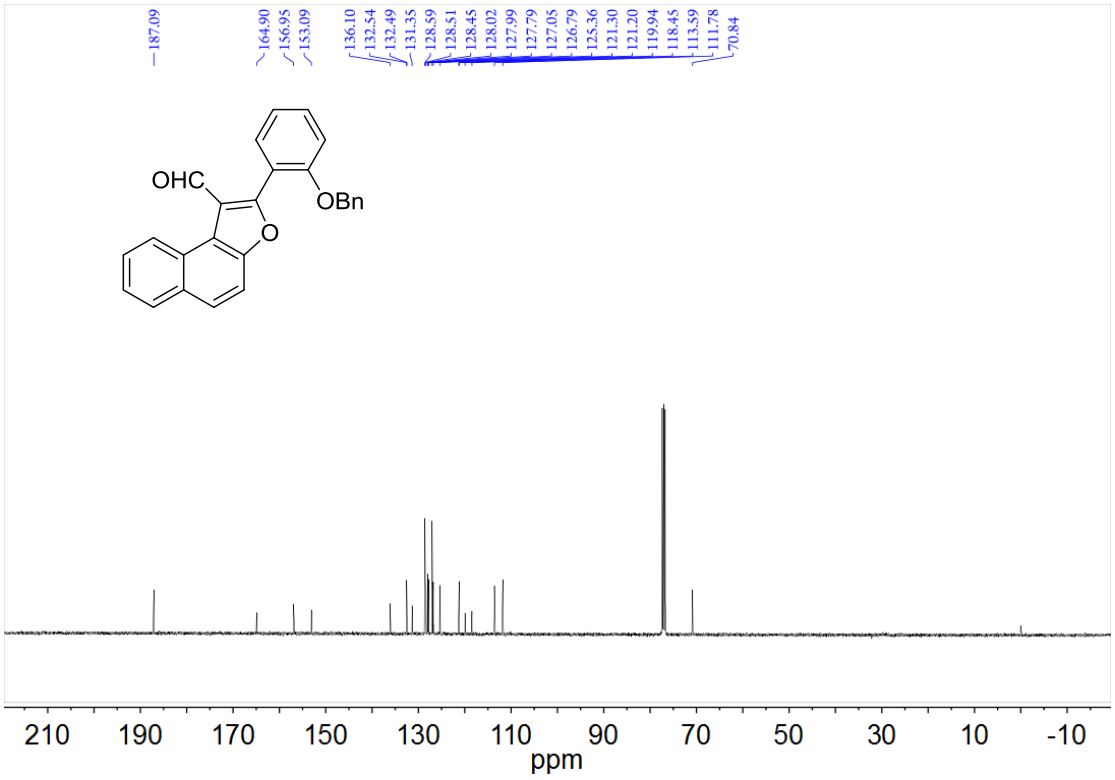
^{13}C NMR Spectrum of Compound 5ga



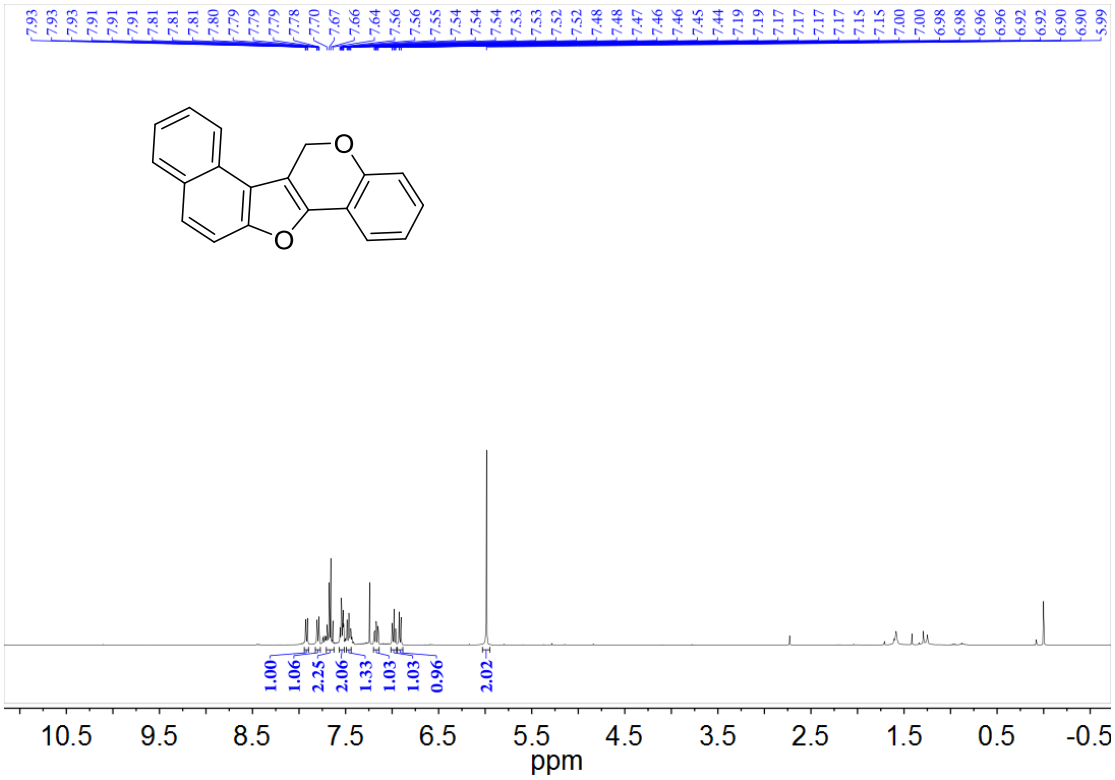
^{1}H NMR Spectrum of Compound 5as



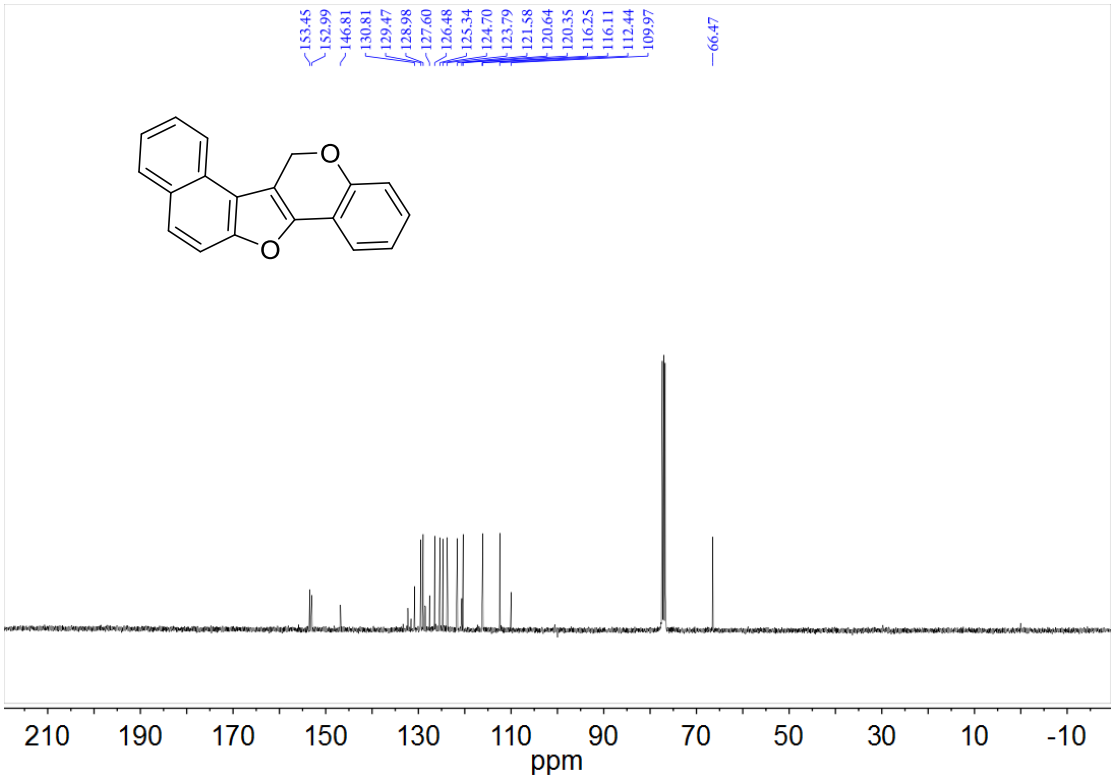
^{13}C NMR Spectrum of Compound 5as



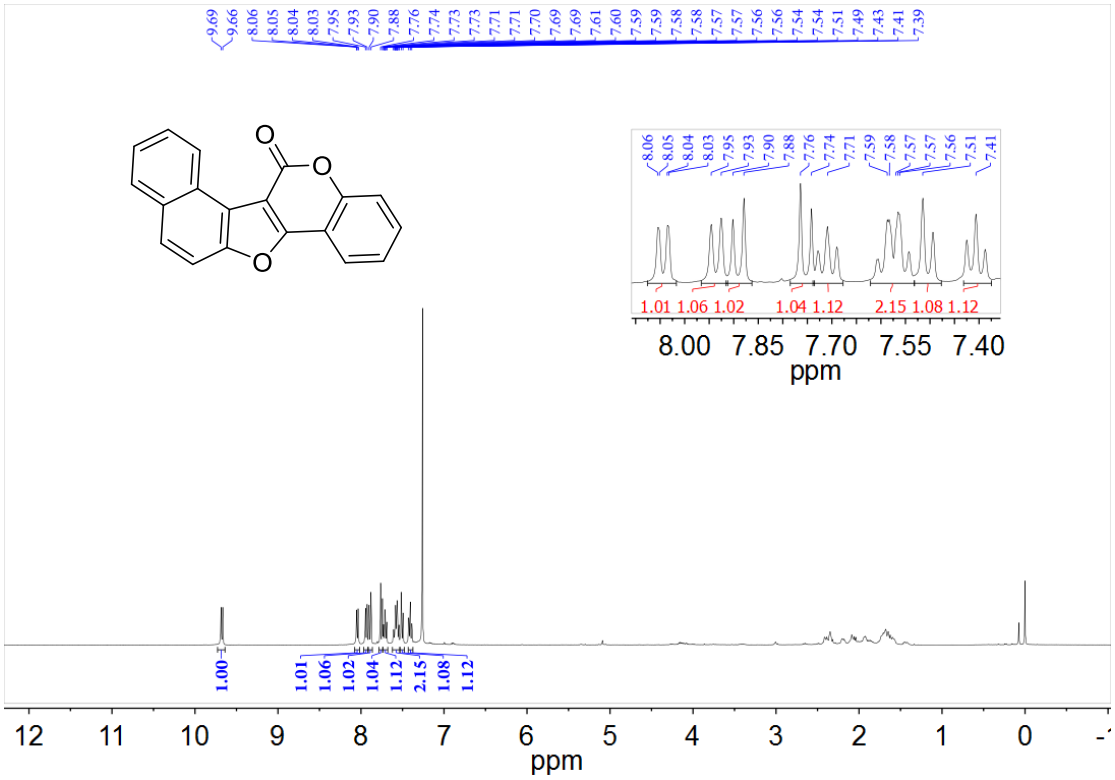
^{1}H NMR Spectrum of Compound 6



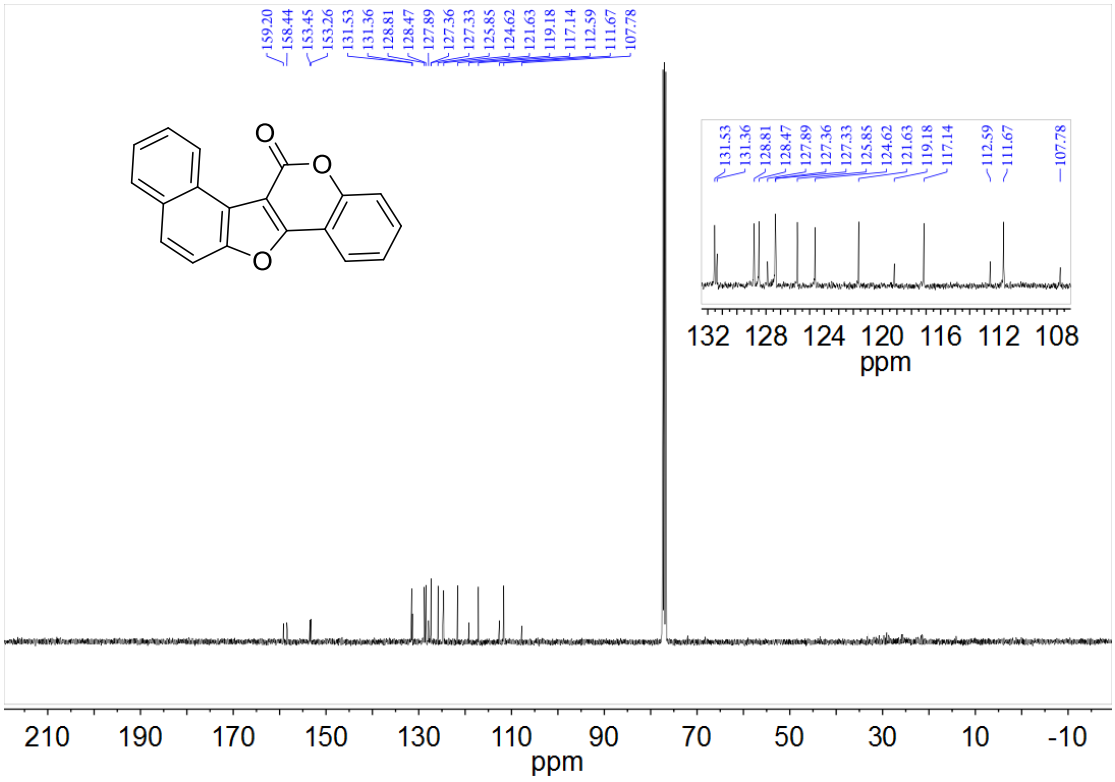
^{13}C NMR Spectrum of Compound 6



^{1}H NMR Spectrum of Compound 7

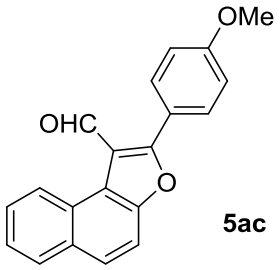


^{13}C NMR Spectrum of Compound 7



9. Crystallographic Data for Compound 5ac

The crystallographic data are provided free of charge by The Cambridge Crystallographic Data Centre with CCDC deposition number 1557770.



5ac

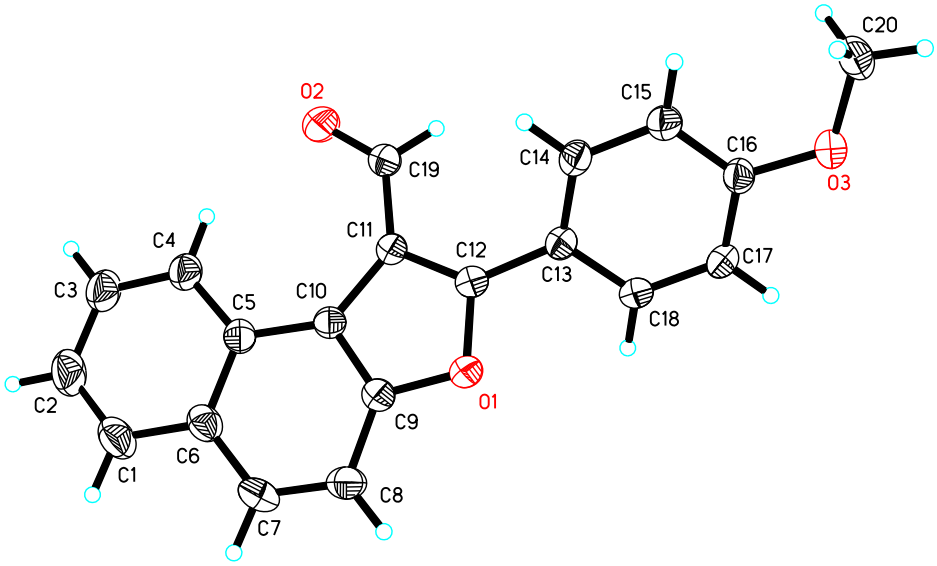


Table 1. Crystal data and structure refinement for cd16106.

Identification code	cd16106	
Empirical formula	C20 H14 O3	
Formula weight	302.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 7.2027(13) Å	α= 90 °.
	b = 18.296(3) Å	β= 90 °.
	c = 22.189(4) Å	γ = 90 °.
Volume	2924.1(9) $Å^3$	
Z	8	
Density (calculated)	1.373 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	1264	
Crystal size	0.200 x 0.160 x 0.130 mm^3	
Theta range for data collection	1.836 to 25.999 °.	
Index ranges	-8<=h<=8, -21<=k<=22, -27<=l<=25	
Reflections collected	16358	
Independent reflections	2868 [R(int) = 0.0416]	
Completeness to theta = 25.242 °	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6522	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2868 / 0 / 210	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1150	
R indices (all data)	R1 = 0.0614, wR2 = 0.1256	
Extinction coefficient	0.0048(10)	
Largest diff. peak and hole	0.169 and -0.160 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cd16106. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	452(2)	10123(1)	3595(1)	49(1)
O(2)	-738(2)	8323(1)	2186(1)	78(1)
O(3)	-1(2)	7872(1)	5687(1)	55(1)
C(1)	840(3)	11202(1)	1293(1)	70(1)
C(2)	492(3)	10760(1)	816(1)	78(1)
C(3)	40(3)	10035(1)	906(1)	70(1)
C(4)	-29(3)	9751(1)	1471(1)	56(1)
C(5)	315(2)	10189(1)	1979(1)	44(1)
C(6)	749(3)	10939(1)	1887(1)	53(1)
C(7)	1046(3)	11412(1)	2383(1)	60(1)
C(8)	934(3)	11178(1)	2958(1)	57(1)
C(9)	545(2)	10441(1)	3037(1)	45(1)
C(10)	256(2)	9940(1)	2589(1)	41(1)
C(11)	-48(2)	9254(1)	2901(1)	42(1)
C(12)	127(2)	9401(1)	3503(1)	44(1)
C(13)	93(2)	8966(1)	4055(1)	44(1)
C(14)	919(2)	8285(1)	4098(1)	48(1)
C(15)	910(3)	7899(1)	4632(1)	49(1)
C(16)	99(2)	8198(1)	5137(1)	43(1)
C(17)	-714(3)	8884(1)	5102(1)	49(1)
C(18)	-709(3)	9260(1)	4572(1)	48(1)
C(19)	-595(3)	8535(1)	2696(1)	54(1)
C(20)	787(3)	7170(1)	5758(1)	62(1)

Table 3. Bond lengths [Å] and angles [ ] for cd16106.

O(1)-C(12)	1.3570(18)
O(1)-C(9)	1.3689(19)
O(2)-C(19)	1.2022(19)
O(3)-C(16)	1.3598(18)
O(3)-C(20)	1.414(2)
C(1)-C(2)	1.355(3)
C(1)-C(6)	1.405(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.381(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.358(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.405(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.421(2)
C(5)-C(10)	1.429(2)
C(6)-C(7)	1.415(3)
C(7)-C(8)	1.348(2)
C(7)-H(7)	0.9300
C(8)-C(9)	1.389(2)
C(8)-H(8)	0.9300
C(9)-C(10)	1.368(2)
C(10)-C(11)	1.450(2)
C(11)-C(12)	1.367(2)
C(11)-C(19)	1.446(2)
C(12)-C(13)	1.461(2)
C(13)-C(14)	1.384(2)
C(13)-C(18)	1.392(2)
C(14)-C(15)	1.380(2)
C(14)-H(14)	0.9300
C(15)-C(16)	1.379(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.386(2)
C(17)-C(18)	1.364(2)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300

C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600

C(12)-O(1)-C(9)	106.61(12)
C(16)-O(3)-C(20)	118.56(13)
C(2)-C(1)-C(6)	121.36(19)
C(2)-C(1)-H(1)	119.3
C(6)-C(1)-H(1)	119.3
C(1)-C(2)-C(3)	120.23(19)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(4)-C(3)-C(2)	120.6(2)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	121.08(18)
C(3)-C(4)-H(4)	119.5
C(5)-C(4)-H(4)	119.5
C(4)-C(5)-C(6)	118.29(15)
C(4)-C(5)-C(10)	124.88(15)
C(6)-C(5)-C(10)	116.83(15)
C(1)-C(6)-C(7)	120.88(17)
C(1)-C(6)-C(5)	118.38(17)
C(7)-C(6)-C(5)	120.73(15)
C(8)-C(7)-C(6)	122.20(16)
C(8)-C(7)-H(7)	118.9
C(6)-C(7)-H(7)	118.9
C(7)-C(8)-C(9)	116.07(16)
C(7)-C(8)-H(8)	122.0
C(9)-C(8)-H(8)	122.0
C(10)-C(9)-O(1)	111.40(13)
C(10)-C(9)-C(8)	126.13(15)
O(1)-C(9)-C(8)	122.45(14)
C(9)-C(10)-C(5)	118.00(14)
C(9)-C(10)-C(11)	104.81(14)
C(5)-C(10)-C(11)	137.20(14)
C(12)-C(11)-C(19)	120.73(14)

C(12)-C(11)-C(10)	106.40(13)
C(19)-C(11)-C(10)	132.66(15)
O(1)-C(12)-C(11)	110.74(13)
O(1)-C(12)-C(13)	113.97(13)
C(11)-C(12)-C(13)	135.26(14)
C(14)-C(13)-C(18)	117.99(15)
C(14)-C(13)-C(12)	122.71(14)
C(18)-C(13)-C(12)	119.21(14)
C(15)-C(14)-C(13)	121.20(15)
C(15)-C(14)-H(14)	119.4
C(13)-C(14)-H(14)	119.4
C(16)-C(15)-C(14)	119.84(15)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
O(3)-C(16)-C(15)	125.34(15)
O(3)-C(16)-C(17)	115.10(14)
C(15)-C(16)-C(17)	119.56(14)
C(18)-C(17)-C(16)	120.20(15)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(17)-C(18)-C(13)	121.21(15)
C(17)-C(18)-H(18)	119.4
C(13)-C(18)-H(18)	119.4
O(2)-C(19)-C(11)	127.87(16)
O(2)-C(19)-H(19)	116.1
C(11)-C(19)-H(19)	116.1
O(3)-C(20)-H(20A)	109.5
O(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cd16106. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	66(1)	41(1)	40(1)	-4(1)	-2(1)	-2(1)
O(2)	138(2)	52(1)	45(1)	-9(1)	-5(1)	-9(1)
O(3)	73(1)	53(1)	38(1)	4(1)	2(1)	1(1)
C(1)	83(2)	61(1)	66(1)	24(1)	4(1)	3(1)
C(2)	102(2)	84(2)	48(1)	21(1)	5(1)	15(1)
C(3)	93(2)	74(1)	43(1)	3(1)	0(1)	14(1)
C(4)	68(1)	56(1)	43(1)	3(1)	2(1)	10(1)
C(5)	43(1)	46(1)	43(1)	4(1)	3(1)	9(1)
C(6)	54(1)	49(1)	54(1)	12(1)	1(1)	6(1)
C(7)	71(1)	40(1)	71(1)	11(1)	0(1)	-5(1)
C(8)	70(1)	41(1)	59(1)	-4(1)	-4(1)	-3(1)
C(9)	51(1)	41(1)	43(1)	2(1)	0(1)	2(1)
C(10)	42(1)	40(1)	42(1)	1(1)	1(1)	4(1)
C(11)	51(1)	39(1)	37(1)	-1(1)	1(1)	3(1)
C(12)	50(1)	39(1)	42(1)	-2(1)	1(1)	-1(1)
C(13)	53(1)	43(1)	36(1)	-3(1)	-1(1)	-3(1)
C(14)	55(1)	50(1)	39(1)	-2(1)	6(1)	7(1)
C(15)	56(1)	46(1)	44(1)	-1(1)	0(1)	7(1)
C(16)	50(1)	45(1)	35(1)	1(1)	-3(1)	-6(1)
C(17)	64(1)	47(1)	37(1)	-9(1)	4(1)	-2(1)
C(18)	65(1)	37(1)	44(1)	-4(1)	0(1)	1(1)
C(19)	79(1)	42(1)	41(1)	0(1)	-2(1)	-2(1)
C(20)	72(1)	63(1)	51(1)	16(1)	2(1)	8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for cd16106.

	x	y	z	U(eq)
H(1)	1146	11689	1225	84
H(2)	557	10946	426	93
H(3)	-219	9737	577	84
H(4)	-309	9259	1523	67
H(7)	1328	11900	2309	73
H(8)	1108	11492	3283	68
H(14)	1491	8085	3760	58
H(15)	1449	7438	4650	58
H(17)	-1265	9088	5442	59
H(18)	-1252	9720	4555	58
H(19)	-869	8196	2995	65
H(20A)	181	6832	5492	94
H(20B)	627	7011	6168	94
H(20C)	2087	7189	5664	94

Table 6. Torsion angles [°] for cd16106.

C(6)-C(1)-C(2)-C(3)	-0.2(3)
C(1)-C(2)-C(3)-C(4)	-1.2(4)
C(2)-C(3)-C(4)-C(5)	1.4(3)
C(3)-C(4)-C(5)-C(6)	-0.3(3)
C(3)-C(4)-C(5)-C(10)	179.40(17)
C(2)-C(1)-C(6)-C(7)	-177.6(2)
C(2)-C(1)-C(6)-C(5)	1.2(3)
C(4)-C(5)-C(6)-C(1)	-1.0(2)
C(10)-C(5)-C(6)-C(1)	179.29(16)
C(4)-C(5)-C(6)-C(7)	177.83(17)
C(10)-C(5)-C(6)-C(7)	-1.9(2)
C(1)-C(6)-C(7)-C(8)	178.78(19)
C(5)-C(6)-C(7)-C(8)	0.0(3)
C(6)-C(7)-C(8)-C(9)	1.2(3)
C(12)-O(1)-C(9)-C(10)	0.97(18)
C(12)-O(1)-C(9)-C(8)	-177.52(16)
C(7)-C(8)-C(9)-C(10)	-0.5(3)
C(7)-C(8)-C(9)-O(1)	177.75(17)
O(1)-C(9)-C(10)-C(5)	-179.83(13)
C(8)-C(9)-C(10)-C(5)	-1.4(3)
O(1)-C(9)-C(10)-C(11)	0.23(18)
C(8)-C(9)-C(10)-C(11)	178.65(17)
C(4)-C(5)-C(10)-C(9)	-177.20(16)
C(6)-C(5)-C(10)-C(9)	2.5(2)
C(4)-C(5)-C(10)-C(11)	2.7(3)
C(6)-C(5)-C(10)-C(11)	-177.57(18)
C(9)-C(10)-C(11)-C(12)	-1.33(17)
C(5)-C(10)-C(11)-C(12)	178.74(18)
C(9)-C(10)-C(11)-C(19)	173.30(19)
C(5)-C(10)-C(11)-C(19)	-6.6(3)
C(9)-O(1)-C(12)-C(11)	-1.87(18)
C(9)-O(1)-C(12)-C(13)	176.61(13)
C(19)-C(11)-C(12)-O(1)	-173.40(15)
C(10)-C(11)-C(12)-O(1)	2.01(18)
C(19)-C(11)-C(12)-C(13)	8.6(3)
C(10)-C(11)-C(12)-C(13)	-176.02(17)

O(1)-C(12)-C(13)-C(14)	-138.08(16)
C(11)-C(12)-C(13)-C(14)	39.9(3)
O(1)-C(12)-C(13)-C(18)	38.3(2)
C(11)-C(12)-C(13)-C(18)	-143.7(2)
C(18)-C(13)-C(14)-C(15)	1.6(2)
C(12)-C(13)-C(14)-C(15)	178.04(16)
C(13)-C(14)-C(15)-C(16)	-1.3(3)
C(20)-O(3)-C(16)-C(15)	0.3(2)
C(20)-O(3)-C(16)-C(17)	179.63(16)
C(14)-C(15)-C(16)-O(3)	179.89(15)
C(14)-C(15)-C(16)-C(17)	0.5(3)
O(3)-C(16)-C(17)-C(18)	-179.51(15)
C(15)-C(16)-C(17)-C(18)	-0.1(3)
C(16)-C(17)-C(18)-C(13)	0.4(3)
C(14)-C(13)-C(18)-C(17)	-1.2(3)
C(12)-C(13)-C(18)-C(17)	-177.72(16)
C(12)-C(11)-C(19)-O(2)	-177.11(19)
C(10)-C(11)-C(19)-O(2)	8.9(3)

Symmetry transformations used to generate equivalent atoms: