Orthogonal Selectivity with Cinnamic Acids in 3-substituted Benzofuran Synthesis through C-H Olefination of Phenols

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Supporting Information

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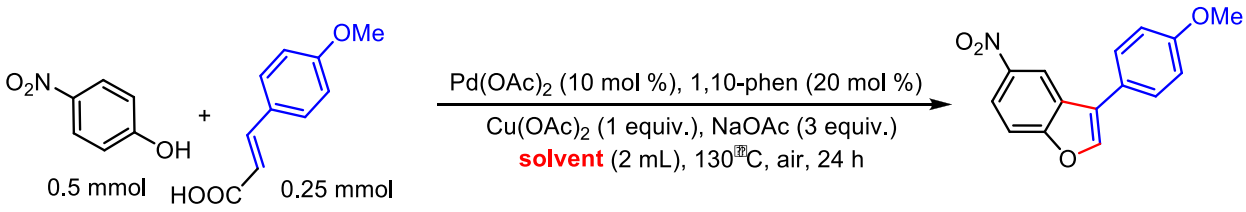
General Consideration:

Reagent Information: Unless otherwise stated, all reactions were carried out under oxygen (O_2) atmosphere in screw cap reaction tubes. All the solvents were bought from Aldrich in sure-seal bottle and were used as received. Palladium acetate was obtained as generous gift from Johnson Matthey. All the cinnamic acids and phenols were bought from Aldrich and Alfa-Aesar. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using pet ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$).

Analytical Information: All isolated compounds are characterized by ^{1}H NMR,^{13}C NMR spectroscopy, gas chromatography mass spectra (GC-MS). In addition, new compounds are further characterized by HRMS. Copies of the ^{1}H NMR, ^{13}C NMR can be found in the supporting information. Nuclear magnetic resonance spectra were recorded on Bruker 400 MHz, 500 MHz or Varian 400 MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuteron chloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. All GC analyses were performed on Agilent 7890A GC system with an FID detector using a J & W DB–1 column (10 m, 0.1 mm I.D.) with *n*-decane as the internal standard. All GCMS analysis was done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector).

Optimization Details:

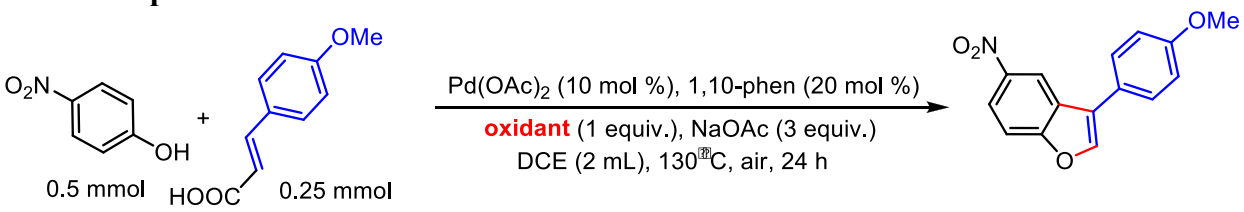
Table S1.Optimization of Solvent



entry	solvent	GC yield (%)
1	**$ClCH_2CH_2Cl$**	**36**
2	cyclohexane	5
3	toluene	9
4	CH_3CN	9
5	TFT	6
6	1,2,3-trichloropropane	27
7	DMA	4
8	1,4-dioxane	9
9	NMP	11
10	isobutylbenzene	10
11	*m*-xylene	8
12	benzene	21
13	anisole	23
14	decalin	12
15	THF	9
16	DMSO	21
17	pivalic acid	24
18	butyronitrile	16
19	DMF	12

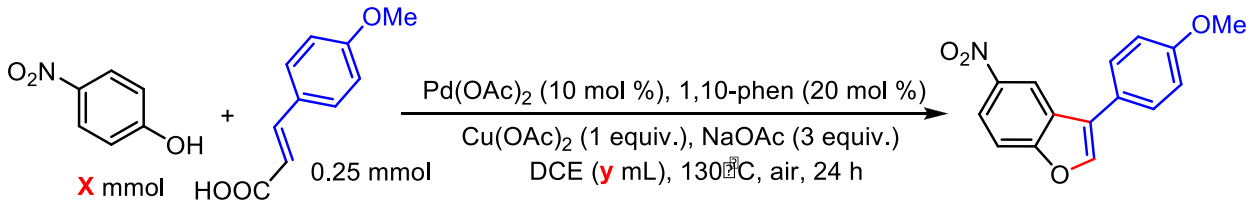
20	mesitylene	9

Table S2.Optimization of Oxidant



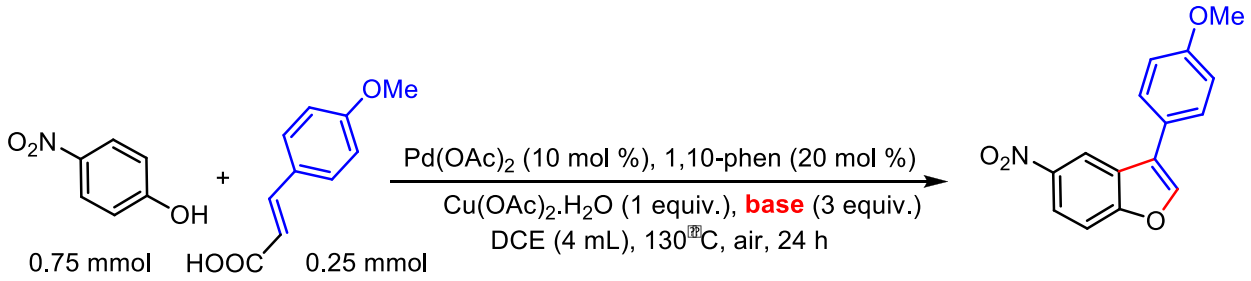
entry	solvent	GC yield (%)
1	**$Cu(OAc)_2$**	**36**
2	$CuSO_4.5H_2O$	34
3	CuF_2	32
4	CuBr	23
5	CuI	25
6	$Cu(NO_3)_2$	18
7	CuCN	14
8	CuO	26
9	$Cu(acac)_2$	10
10	$Cu(CF_3O_3SNa)$	26
11	$Cu(BF_4)_2$	31
12	$CuCl_2$	33
13	AgI	9
14	AgOAc	15
15	Ag_2CO_3	34
16	Ag_2SO_4	10
17	AgOTf	4
18	$K_2S_2O_8$	6
19	$Na_2S_2O_8$	20
20	$(NH_4)_2S_2O_8$	25
21	*m*-CPBA	22
22	DTBP	11
23	1,4-benzoquinone	20
24	oxone	23

Table S3. Optimization of Solvent volume and ratio of coupling partner



Entry	Solvent volume (mL)	4-nitrophenol (mmol)	GC yield (%)
1	2	0.5	36
2	3	0.5	39
3	4	0.5	44
4	5	0.5	44
5	4	0.25	22
6	**4**	**0.75**	**56**
7	4	1.0	49

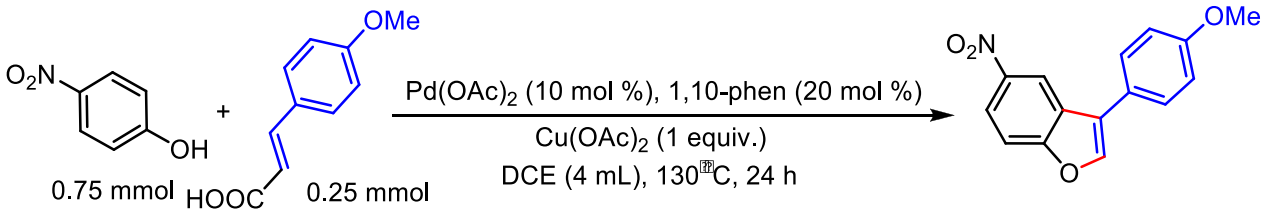
Table S4. Optimization of Base



entry	base	GC yield (%)
1	**-**	**61**
2	NaOAc	56
3	$BaCO_3$	13
4	Na_2CO_3	34
5	K_2CO_3	16

6	Cs_2CO_3	32
7	$NaHCO_3$	29
8	K_3PO_4	9
9	KO^tBu	33
10	KOAc	30
11	LiO^tBu	6

Table S5. Optimization of different reaction environment



entry	atmosphere	GC yield (%)
1	**O_2**	**77**
2	air	61
3	N_2	50

Table S6. Optimization of Ligand

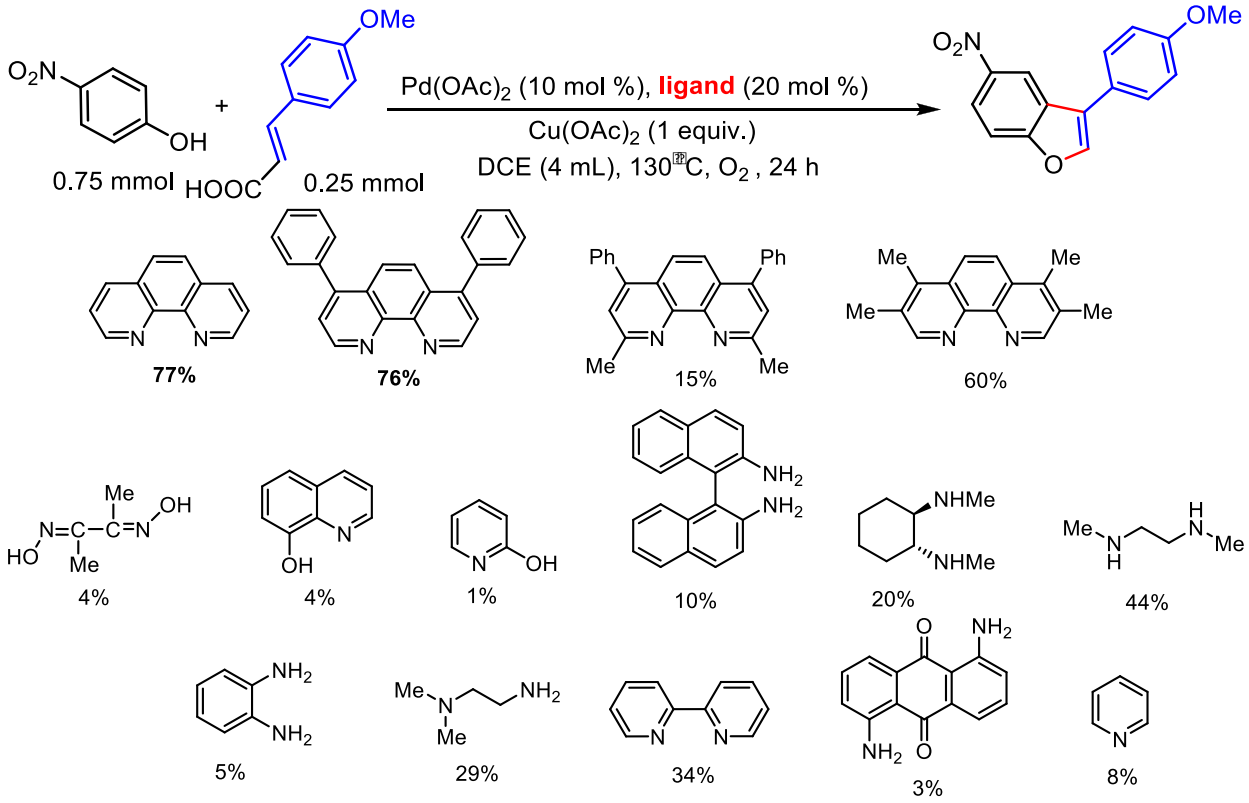
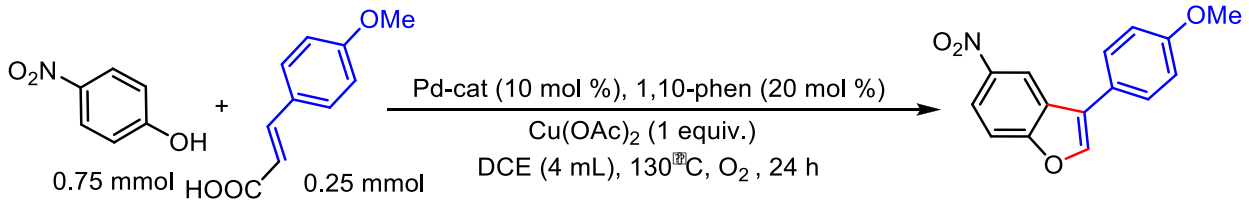


Table S7. Optimization of Catalyst



entry	catalyst	GC yield (%)
1	**$Pd(OAc)_2$**	**77**
2	$Pd_2(dba)_3$	41
3	$Pd(PhCN)_2Cl_2$	43
4	$Pd(PPh_3)_2Cl_2$	29
5	$Pd(NCCH_3)_2Cl_2$	30
6	$[C_3H_5PdCl]_2$	28
7	$Pd(COD)Cl_2$	49

General Procedure (A) for Pd-Catalyzed Benzofuran Synthesis from Corresponding Phenols and cinnamic acids:

To an oven-dried screw cap reaction tube charged with a magnetic stir-bar, $Pd(OAc)_2$ (10 mol%, 0.025 mmol, 5.6 mg), 1,10-phenonthroline monohydrate (20 mol%, 0.05 mmol, 10 mg) or bathophenanthroline[a] (20 mol%, 0.05mmol, 16.62 mg), $Cu(OAc)_2.H_2O$ (0.25 mmol, 50 mg) were added. Depending on the physical state of the phenol (0.75 mmol) and cinnamic acid (0.25 mmol), solid compounds were weighed before the other reagents, whereas liquid phenols were added by micro-litre syringe and laboratory syringe under air atmosphere. In the reaction tube 4 mL DCE ($ClCH_2CH_2Cl$) was added and O_2 was purged in the reaction mixture for 15 min. Then the reaction mixture was vigorously stirred (700 rpm on Heidolph MR Hei-Standard stirrer) in a preheated oil bath at 130 ºC for 24h. After completion, reaction mixture was filtered through a celite pad with ethyl acetate as the washing solvent. The ethyl acetate layer was washed with brine solution and dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography using silica gel (100-200 mesh size) and petroleum-ether / ethyl acetate as the eluent.

Characterization Data

3-(naphthalen-1-yl)-5-nitrobenzofuran (Table 1, entry 3a) was synthesized by general procedure A. Desired product was obtained as yellow solid in 82% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.53 – 7.63 (m, 3H), 7.70 (dd, *J* = 8.9, 0.7 Hz, 1H), 7.82 – 7.88 (m, 1H), 7.94 – 8.01 (m, 3H), 8.28 – 8.36 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 112.40, 117.80, 120.80, 121.98, 125.31, 125.73, 126.58, 126.96, 127.40, 128.16, 128.90, 129.14, 129.40, 132.09, 134.14, 144.62, 145.80, 158.22.

HRMS (ESI) calculated for $C_{18}H_{11}NNaO_3$ is 312.0631 and found 312.0632.

GC-MS (*m/z*): 289.2 $[M]^+$.**m.p.**115 ºC

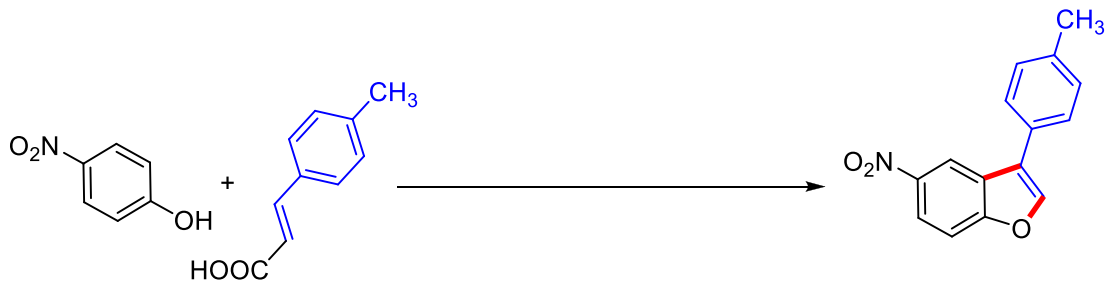
3-(naphthalen-2-yl)benzofuran-5-carbonitrile (Table 1; entry 3b) was synthesized by general procedure A. Desired product was obtained as white solid in 50% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 97:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.53 – 7.59 (m, 2H), 7.66 – 7.70 (m, 3H), 7.93 (ddd, *J* = 8.2, 6.7, 5.4 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 8.07 (dd, *J* = 1.6, 0.8 Hz, 1H), 8.29 (t, *J* = 1.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 107.41, 113.31, 119.62, 122.69, 125.60, 126.09, 126.52, 126.73, 127.04, 127.67, 128.06, 128.23, 128.54, 129.32, 133.20, 133.87, 133.97, 143.72, 157.69.

HRMS (ESI) calculated for $C_{19}H_{11}NNaO$ 292.0733, found 292.0732.

GC-MS (*m/z*): 269.1 $[M]^+$.



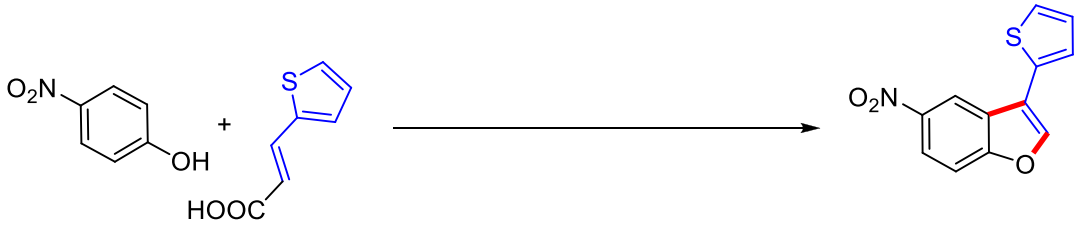
5-nitro-3-p-tolylbenzofuran (Table 1; entry 3c) was synthesized by general procedure A. Desired product was obtained as white solid in 75% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 7.32 – 7.35 (m, 2H), 7.50 – 7.54 (m, 2H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.90(s, 1H), 8.28 (dd, *J* = 9.1, 2.4 Hz, 1H), 8.73 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 21.49, 112.33, 117.47, 120.62, 123.50, 125.44, 127.42, 127.62, 130.18, 138.51, 143.88, 144.57, 158.68.

GC-MS (*m/z*): 253.0 $[M]^+$.

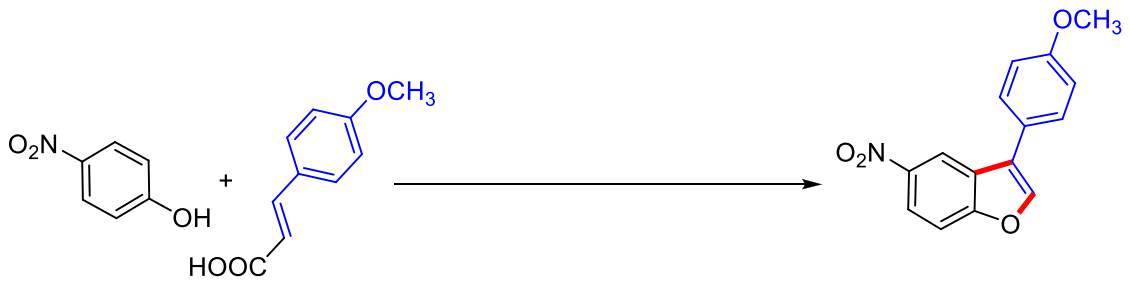
Structure of the compound was further confirmed by X-ray crystallography.



5-nitro-3-(thiophen-2-yl)benzofuran (Table 1; entry 3d) was synthesized by general procedure A. Desired product was obtained as light yellow solid in 45% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.78 (d, *J* = 2.3 Hz, 1H), 8.29 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.97 (s, 1H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.19 (dd, *J* = 5.1, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.38, 144.66, 143.91, 131.26, 128.23, 126.82, 125.60, 125.52, 120.97, 117.54, 117.49, 112.40.



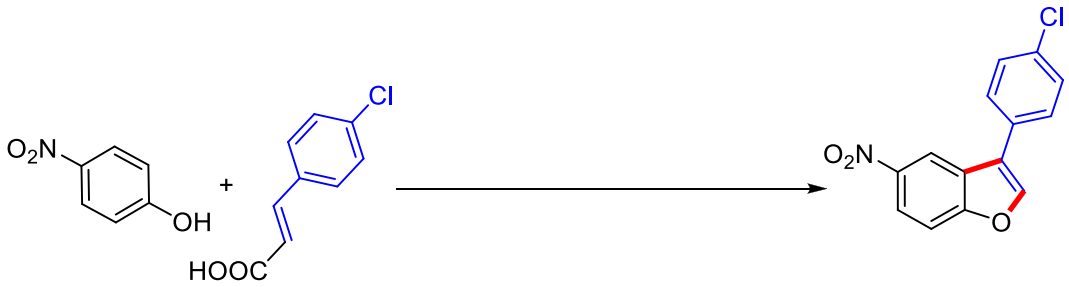
3-(4-methoxyphenyl)-5-nitrobenzofuran (Table 1, entry 3e) was synthesized by general procedure A. Desired product was obtained as light yellow solid in 70% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 97: 3).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.89 (s, 3H), 7.04 – 7.08 (m, 2H), 7.53 – 7.58 (m, 2H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.87 (s, 1H), 8.28 (dd, *J* = 9.1, 2.3 Hz, 1H), 8.73 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 55.66, 112.35, 115.02, 117.44, 120.63, 122.75, 123.26, 127.56, 128.99, 143.56, 144.61, 158.69, 159.98.

HRMS (ESI) calculated for $C_{15}H_{11}NNaO_4$is 292.0580 and found 292.0578.

GC-MS (*m/z*): 269.0 $[M]^+$.



3-(4-chlorophenyl)-5-nitrobenzofuran (Table 1, entry 3f) was synthesized by general procedure A. Desired product was obtained as yellow solid in 69% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98: 2).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 – 7.52 (m, 2H), 7.55 – 7.58 (m, 2H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.93 (s, 1H), 8.31 (dd, *J* = 9.1, 2.3 Hz, 1H), 8.69 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 112.56, 117.21, 120.93, 122.63, 126.73, 127.03, 128.99, 129.80, 134.61, 144.32, 144.78, 158.68

GC-MS (*m/z*): 273.1 $[M]^+$. **m.p.**181 ºC

3-(2-fluorophenyl)-5-nitrobenzofuran (Table 1, entry 3g) was synthesized by general procedure A. Desired product was obtained as white solid in 42% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.70 (dd, *J* = 2.4, 1.3 Hz, 1H), 8.30 (dd, *J* = 9.1, 2.3 Hz, 1H), 8.05 (d, *J* = 1.9 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.43 (dddd, *J* = 8.2, 7.1, 5.2, 1.8 Hz, 1H), 7.32 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 – 7.22 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 160.01 (d, *J* = 248.22 Hz), 158.26, 146.4 (d, *J* = 7.56 Hz), 144.65, 130.12 (d, *J* = 7.56), 129.95 (d, *J* = 3.78), 127.24, 125.03 (d, *J* = 3.78), 120.76, 118.3 (d, *J* = 15.12), 117.86 (d, *J* = 2.52), 117.09, 116.62 (d, *J* = 22.68), 112.40.

HRMS (ESI) calculated for $C_{14}H_8FNNaO_3$ is 280.0380 and found 280.0382.

GC-MS (*m/z*): 257.2 $[M]^+$. **m.p.**117-119 ºC

3-(4-bromophenyl)-5-nitrobenzofuran (Table1, entry 3h) was synthesized by general procedure A. Desired product was obtained as light yellow solid in 49%[a] yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99: 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 – 7.52 (m, 2H), 7.63 – 7.69 (m, 3H), 7.94(s, 1H), 8.31 (dd, *J* = 9.1, 2.4 Hz, 1H), 8.69 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 112.57, 117.21, 120.75, 120.95, 122.68, 126.97, 129.28, 129.40, 132.76, 144.31, 144.80, 158.70

GC-MS (*m/z*): 316.9 $[M]^+$. **m.p.**198 ºC

3-(4-methoxyphenyl)benzofuran-5-carbonitrile (Table1; entry 3i) was synthesized by general procedure A. Desired product was obtained as light yellow solid in 57% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 97:3)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.87 (s, 3H), 7.02 – 7.07 (m, 2H), 7.49 – 7.54 (m, 2H), 7.62 (d, *J* = 1.2 Hz, 2H), 7.83(s, 1H), 8.14 (t, *J* = 1.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 55.63, 107.11, 113.16, 114.94, 119.65, 122.26, 122.91, 125.91, 127.80, 128.31, 128.95, 142.73, 157.52, 159.86.

HRMS (ESI) calculated for $C_{16}H_{11}NNaO_2[M\text{-}Na]^+$, 272.0682found 272.0680.

GC-MS (*m/z*): 249.1 $[M]^+$. **m.p.**144 ºC

3-phenylbenzofuran (Table 1; entry 3j) was synthesized by general procedure A. Desired product was obtained as light yellow liquid in 35% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether). Intermediate 2-(1-phenylvinyl) phenol (***Scheme 3; compound 6***) in standard condition was also gave this compound in 33% yield. (reference 1)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 – 7.40 (m, 3H), 7.48 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.55 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.64 – 7.67 (m, 2H), 7.79 (s, 1H), 7.83 – 7.86 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 111.99, 120.61, 122.48, 123.19, 124.76, 126.68, 127.67, 127.73, 129.18, 132.28, 141.51, 156.01

GC-MS (*m/z*): 194.1 $[M]^+$.

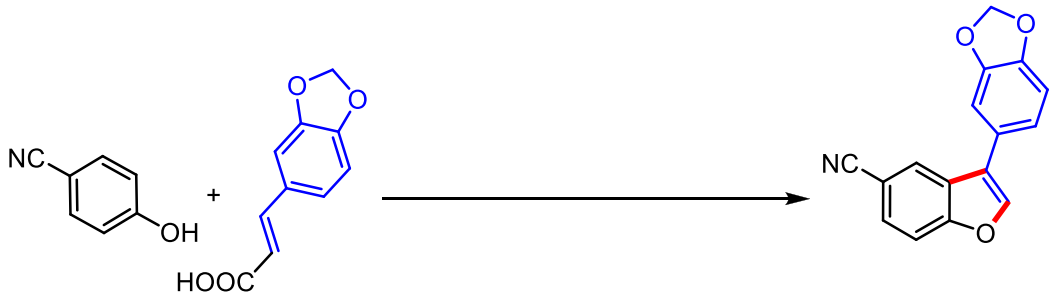
5-(5-nitrobenzofuran-3-yl)benzo[d][1,3]dioxole (Table 1; entry 3k) was synthesized by general procedure A. Desired product was obtained as light yellow solid in 81% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98: 2).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.05(s, 2H), 6.96 (d, *J* = 7.9 Hz, 1H), 7.04 – 7.13 (m, 2H), 7.61 (d, *J* = 9.1 Hz, 1H), 7.85 (s, 1H), 8.28 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.70 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 101.64, 108.19, 109.35, 112.41, 117.34, 120.72, 121.44, 124.07, 127.39, 134.88, 143.77, 144.60, 148.03, 148.67, 158.61.

HRMS (ESI) calculated for $C_{15}H_9NNaO_5$306.0373, found 306.0377.

GC-MS (*m/z*): 283.1 $[M]^+$. **m.p.**165-167 ºC



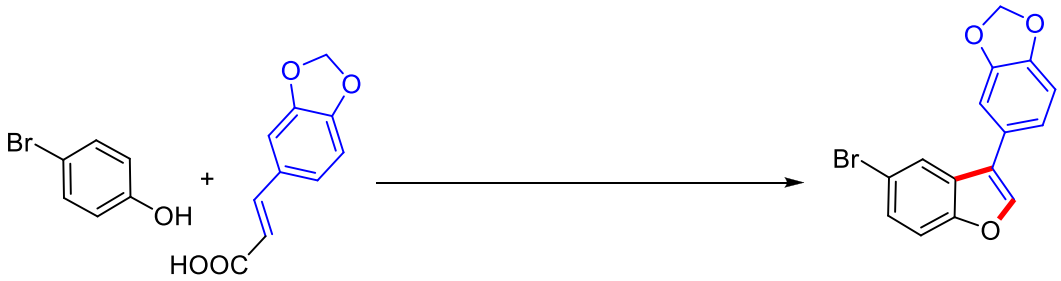
3-(benzo[d][1,3]dioxol-5-yl)benzofuran-5-carbonitrile (Table 1; entry 3l) was synthesized by general procedure A. Desired product was obtained as white solid in 72%[a] yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.04(s, 2H), 6.95 (d, *J* = 7.9 Hz, 1H), 7.02 – 7.08 (m, 2H), 7.60 – 7.64 (m, 2H), 7.82(s, 1H), 8.12 (t, *J* = 1.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 101.62, 101.78, 107.24, 108.19, 109.31, 113.21, 119.58, 121.39, 124.30, 125.84, 127.67, 128.42, 142.96, 147.96, 148.67, 157.49.

HRMS (ESI) calculated for $C_{16}H_9NNaO_3$ 286.0475, found 286.0471.

GC-MS (*m/z*): 263.0 $[M]^+$. **m.p.**184 ºC



5-(5-bromobenzofuran-3-yl)benzo[d][1,3]dioxole (Table 1, entry 3m) was synthesized by general procedure A. Desired product was obtained as brown solid in 51%[a] yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.02 (d, *J* = 3.0 Hz, 2H), 6.92 (dd, *J* = 7.8, 2.6 Hz, 1H), 7.01 – 7.11 (m, 2H), 7.36 – 7.47 (m, 2H), 7.70 (d, *J* = 3.3 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)δ:101.48, 108.17, 109.15, 113.43, 116.36, 121.23, 121.95, 123.21, 125.16, 127.70, 128.78, 142.17, 147.54, 148.44, 154.62

GC-MS (*m/z*): 315.9 $[M]^+$.**m.p.**93-95 ºC

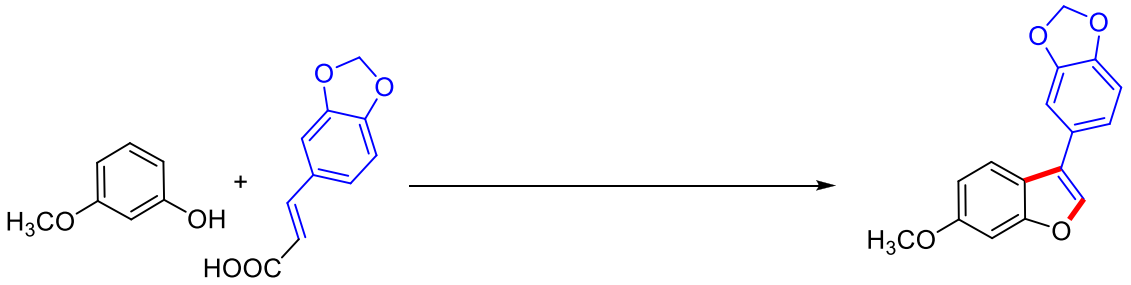
methyl 3-(benzo[d][1,3]dioxol-5-yl)benzofuran-5-carboxylate (Table 1; entry 3n) was synthesized by general procedure A. Desired product was obtained as white solid in 56% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.95 (s, 3H), 6.04 (s, 2H), 6.94 (dd, *J* = 7.9, 0.5 Hz, 1H), 7.05 – 7.17 (m, 2H), 7.55 (dd, *J* = 8.7, 0.6 Hz, 1H), 7.77 (s, 1H), 8.07 (dd, *J* = 8.7, 1.7 Hz, 1H), 8.51 (dd, *J* = 1.7, 0.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 52.38, 101.49, 108.33, 109.21, 111.86, 121.43, 122.86, 123.06, 125.15, 125.62, 126.57, 126.91, 142.23, 147.64, 148.48, 158.45, 167.45

ESI-MS calculated for $C_{17}H_{12}NaO_5$ 319.0577, found 319.0574.

GC-MS (*m/z*): 296.1 $[M]^+$.



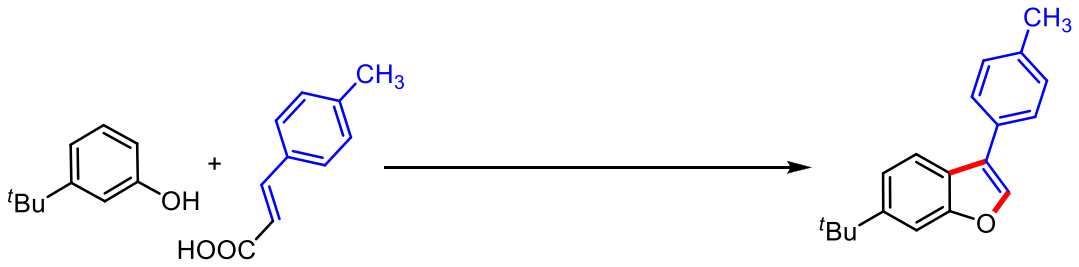
5-(6-methoxybenzofuran-3-yl)benzo[d][1,3]dioxole (Table 1, entry 3o) was synthesized by general procedure A. Desired product was obtained as light white solid in 38% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 98:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 8.7 Hz, 2H), 7.12 – 7.07 (m, 2H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.01 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.41, 156.97, 148.35, 147.24, 140.11, 126.24, 122.13, 121.02, 120.61, 120.13, 112.25, 109.04, 108.13, 101.36, 96.42, 55.97.

HRMS (ESI) calculated for $C_{16}H_{12}NaO_4$ 291.0628, found 291.0627.

GC-MS (*m/z*): 268.2 $[M]^+$.



6-tert-butyl-3-p-tolylbenzofuran (Table 1, entry 3p) was synthesized by general procedure A. Desired product was obtained as colorless liquid in 32% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.4 Hz, 1H), 7.75 (s, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 1.9 Hz, 1H), 7.39 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.29 (dt, *J* = 7.7, 0.7 Hz, 2H), 2.43 (s, 3H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.37, 148.68, 141.00, 137.29, 129.82, 129.55, 127.45, 124.16, 122.09, 120.97, 119.92, 108.59, 35.16, 31.90, 21.46.

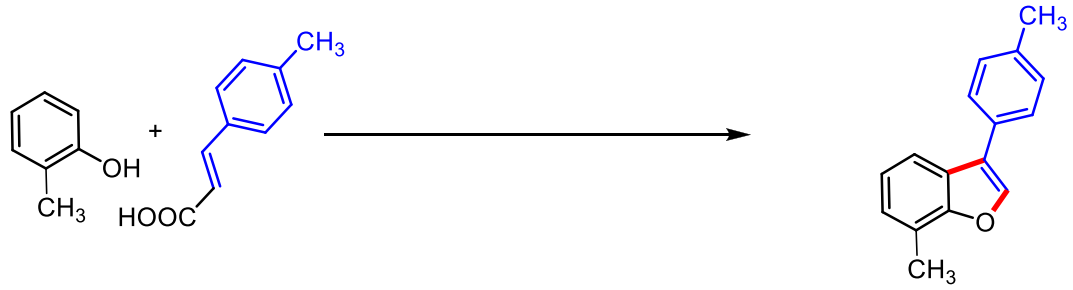
GC-MS (*m/z*): 264.1 $[M]^+$.

5-tert-butyl-3-p-tolylbenzofuran (Table 1, entry 3q) was synthesized by general procedure A. Desired product was obtained as colorless liquid in 26% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 2.2 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.56 – 7.52 (m, 2H), 7.47 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.42 (dt, *J* = 8.8, 2.2 Hz, 1H), 7.34 – 7.29 (m, 2H), 2.44 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.18, 146.23, 141.47, 137.36, 129.89, 129.53, 127.70, 126.43, 122.64, 122.51, 116.54, 111.20, 35.04, 32.12, 21.48.

GC-MS (*m/z*): 264.1 $[M]^+$.



7-methyl-3-p-tolylbenzofuran (Table 1, entry 3r) was synthesized by general procedure A. Desired product was obtained as colorless liquid 34% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (s, 1H), 7.67 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.57 – 7.54 (m, 2H), 7.31 – 7.28 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.16 (dt, *J* = 7.1, 1.1 Hz, 1H), 2.57 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.01, 140.98, 137.34, 129.82, 129.53, 127.59, 126.27, 125.52, 123.16, 122.57, 122.16, 118.08, 21.46, 15.24.

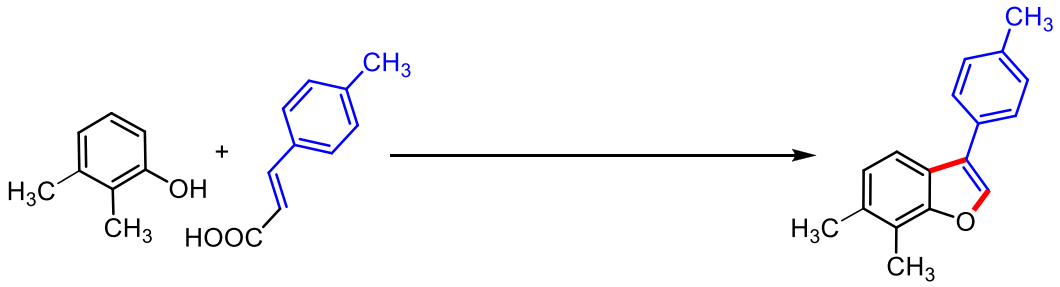
GC-MS (*m/z*): 222.1 $[M]^+$.

5-(6-tert-butylbenzofuran-3-yl)benzo[d][1,3]dioxole (Table 1, entry 3s) was synthesized by general procedure A. Desired product was obtained as white solid in 36%[a] yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.3 Hz, 1H), 7.69 (s, 1H), 7.56 (d, *J* = 1.7 Hz, 1H), 7.38 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.94 – 6.90 (m, 1H), 6.02 (s, 2H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.32, 148.80, 148.33, 147.18, 140.83, 126.36, 124.11, 122.01, 121.01, 119.75, 109.04, 108.62, 108.13, 101.34, 35.17, 31.89.

GC-MS (*m/z*): 294.1 $[M]^+$.

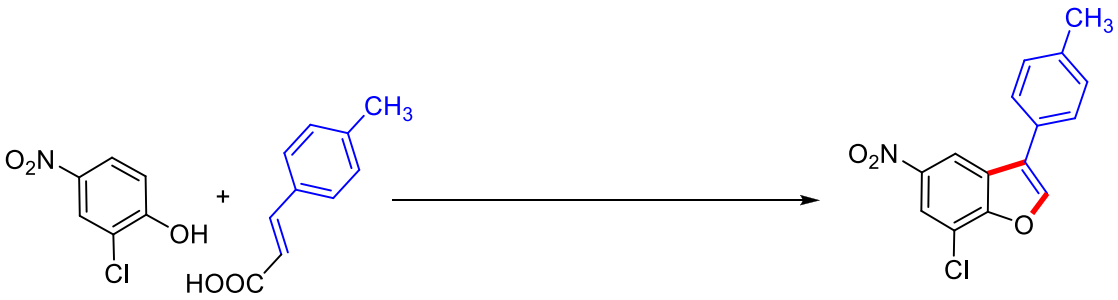


6,7-dimethyl-3-p-tolylbenzofuran (Table 1, entry 3t) was synthesized by general procedure A. Desired product was obtained as white solid in 31% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (s, 1H), 7.59 (dd, *J* = 8.0, 4.1 Hz, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H), 2.45 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.50, 140.52, 137.19, 133.00, 129.78, 129.72, 127.45, 125.21, 124.11, 122.48, 120.42, 117.15, 21.44, 19.32, 11.84.

GC-MS (*m/z*): 236.1 $[M]^+$.



7-chloro-5-nitro-3-p-tolylbenzofuran (Table 1, entry 3u) was synthesized by general procedure A. Desired product was obtained as yellow solid in 50% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (d, *J* = 2.1 Hz, 1H), 8.31 (d, *J* = 2.1 Hz, 1H), 7.95 (s, 1H), 7.51 – 7.47 (m, 2H), 7.35 – 7.32 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.60, 144.75, 144.37, 138.94, 130.29, 128.44, 127.71, 126.80, 124.48, 120.62, 118.31, 115.93, 21.52.

GC-MS (*m/z*): 287.0 $[M]^+$.

5-(4,7-dichlorobenzofuran-3-yl)benzo[d][1,3]dioxole (Table 1; entry 3v) was synthesized by general procedure A. Desired product was obtained as white solid in 47% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (s, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 1.7 Hz, 1H), 6.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.02 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 151.78, 147.82, 147.41, 143.94, 126.09, 125.50, 125.25, 125.07, 124.15, 123.83, 123.51, 116.20, 111.32, 108.06, 101.44.

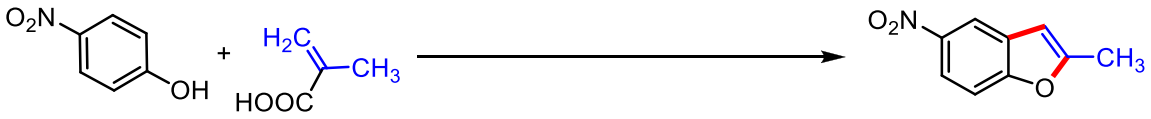
GC-MS (*m/z*): 306 $[M]^+$. **m.p.**122 ºC

2-methyl-5-nitro-3-phenylbenzofuran (Table 2; entry 5a) was synthesized by general procedure A. Desired product was obtained as yellow solid in 41%[a] yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether: ethyl acetate 99:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.59 (s, 3H), 7.41 – 7.45 (m, 1H), 7.47 – 7.56 (m, 5H), 8.20 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.46 (d, *J* = 2.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 13.17, 111.30, 116.22, 118.15, 119.87, 128.05, 129.07, 129.35, 129.63, 131.27, 144.46, 155.00, 157.17.

GC-MS (*m/z*): 253.1 $[M]^+$.



2-methyl-5-nitrobenzofuran (Table 2; entry 5b) was synthesized by general procedure A. Desired product was obtained as white amorphous solid in 44% yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.50 (d, *J* = 1.1 Hz, 3H), 6.52 (q, *J* = 1.1 Hz, 1H), 7.46 (dd, *J* = 8.9, 0.7 Hz, 1H), 8.15 (dd, *J* = 9.0, 2.4 Hz, 1H), 8.39 (d, *J* = 2.4 Hz, 1H).

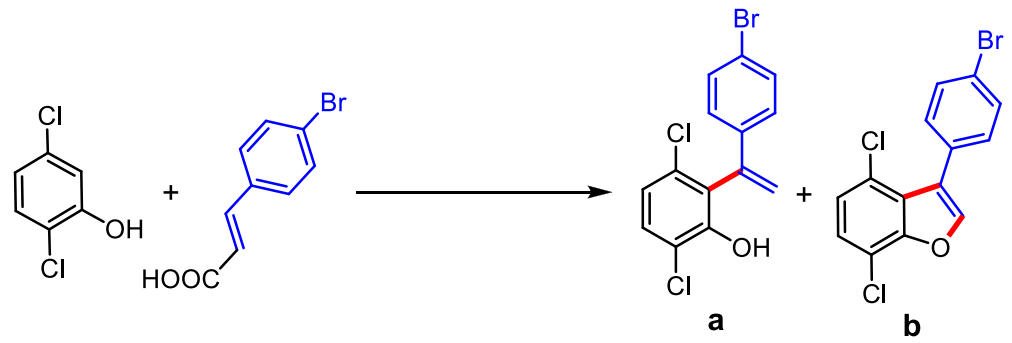
^{13}C NMR (126 MHz, $CDCl_3$) δ: 14.52, 103.80, 111.17, 116.87, 119.52, 129.89, 144.30, 157.96, 159.45.

HRMS (ESI) calculated for $C_9H_7NNaO_3$ $[M\text{-}Na]^+$, 200.0318, found 200.0311.

GC-MS (*m/z*): 177 $[M]^+$.

Mechanistic Study

***Isolation of Intermediate*:**



Pdt-(a) ***2-(1-(4-bromophenyl)vinyl)-3,6-dichlorophenol (Scheme 4; compound 8)*** was synthesized by general procedure A. Desired product was obtained as colorless liquid in32%yield after column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.38 (s, 1H), 5.70 (s, 1H), 6.09 (s, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 7.16 – 7.20 (m, 2H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.46 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 118.93, 119.14, 122.19, 122.65, 127.80, 128.07, 129.33, 131.95, 133.17, 137.23, 141.05, 150.14.

GC-MS (*m/z*): 341.9 $[M]^+$.

Structure of the compound was further confirmed by 1D (DEPT-135).

Pdt-(b) ***3-(4-bromophenyl)-4,7-dichlorobenzofuran(Scheme 4; compound 9)***was synthesized by general procedure A. Desired product was obtained as white solid in 15%yield. Intermediate 2-(1-(4-bromophenyl)vinyl)-3,6-dichlorophenol (***Scheme 4; compound 8***) in standard condition was also produced this compound in 30% yield. Compound was purified by column chromatography of the crude reaction mixture (silica gel, mesh 100-200; petroleum ether)

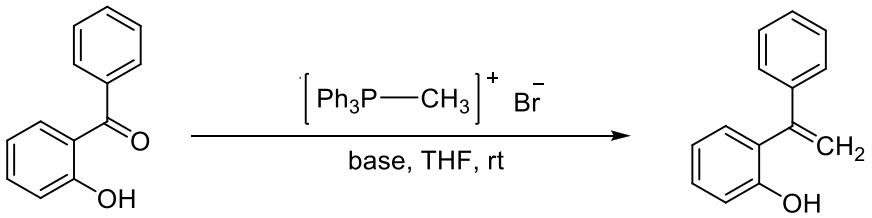
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67 (s, 1H), 7.57 – 7.54 (m, 2H), 7.38 – 7.35 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 151.89, 143.99, 138.33, 132.25, 131.31, 129.34, 125.50, 125.44, 125.21, 122.87, 122.60, 116.33.

GC-MS (*m/z*): 340 $[M]^+$.

Intermediate synthesis:

(a) General Procedure for Synthesis of 2-(1-phenylvinyl) phenol by Wittig reaction *(Scheme 3; compound 6)*:



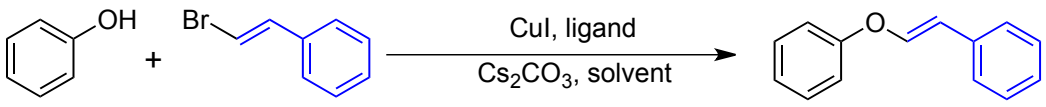
To an oven-dried round bottom flusk already charged with a magnetic stir-bar wittig salt (5.0 mmol, 1.78 g) was added. Then the round bottom flusk was kept inside the glove box. Inside the glove box 5 mL dry THF was added in the round bottom flusk. KO^{t}Bu (10.0 mmol,1.12 g) was added in the reaction mixture and stirred it in room temperature until deep yellow color appears.Once deep yellow color appear 2-hydroxy benzophenone (1.0 mmol,198.2µL) was added in the reaction mixture followed by 10 mL of dry THF and stirred it in room temperature for 6 h. Then the round bottom flusk was removed from glove box. 10 mL of $H_2O$was added and the mixture was extracted with EtOAc (3 × 10 mL).The combined organic layer dried over Na_2SO_4, filtered and evaporated in vacuum and purified by column chromatography (silica gel, 100-120 mesh size; elutant, petroleum-ether)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.20(s, 1H), 5.45 (d, *J* = 1.2 Hz, 1H), 5.90 (d, *J* = 1.2 Hz, 1H), 6.98 (qd, *J* = 7.6, 1.2 Hz, 2H), 7.17 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.25 – 7.34 (m, 1H), 7.35 – 7.43 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 116.02, 116.96, 120.67, 127.26, 127.74, 128.82, 128.90, 129.69, 130.64, 139.59, 145.40, 153.28.

GC-MS (*m/z*): 196.1 $[M]^+$.

(b) General Procedure for Synthesis of (*E*)-(2-phenoxyvinyl)benzene *(Scheme 3; compound 7)*: (reference 3)



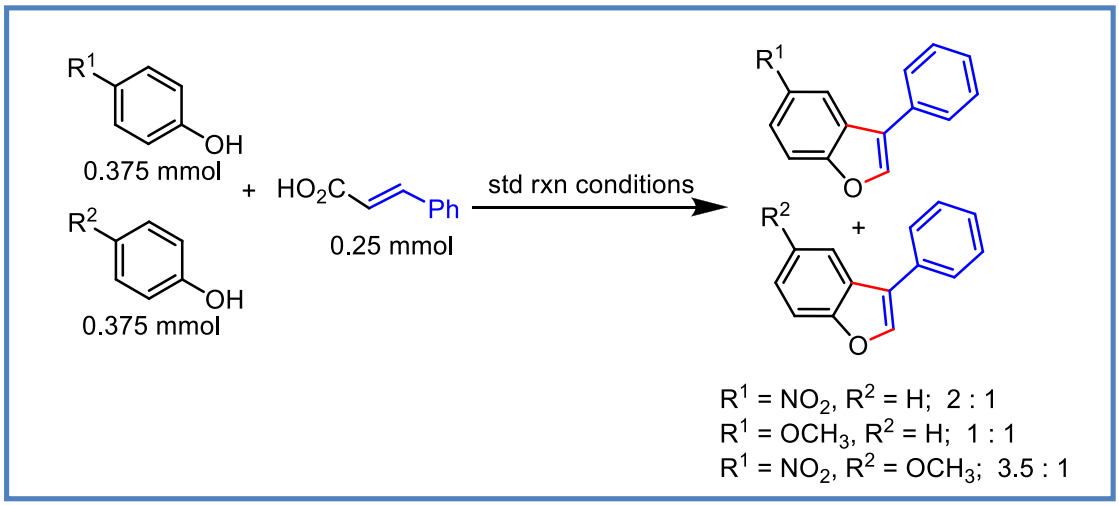
An oven-dried Schlenk tube was back-filled with N_2 and charged with Cs_2CO_3 (325 mg, 1.0 mmol), CuI (15 mg, 0.075 mmol, 15 mol%), ethyl 2-oxocyclohexanecarboxylate (25 mg,

0.15mmol, 30 mol%), (E)-β-bromostyrene (0.5mmol, 64.2 μL), and phenol (1.2 mmol, 53 μL). Then NMP solvent (2 mL) was added under continuous flow of N_2. Then the reaction tube was kept for vigorous stirring in a preheated oil bath at 60°C for 24h. After completion, the cooled reaction mixture was dissolved in H_2O and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuum and purified by column chromatography (silica gel, 100-120 mesh size; elutant, petroleum-ether)

^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.35 (d, J = 12.4 Hz, 1H), 7.06 – 7.13 (m, 3H), 7.18 (d, J = 12.4 Hz, 1H), 7.22 (dt, J = 5.8, 3.0 Hz, 1H), 7.28 – 7.33 (m, 4H), 7.35 (tt, J = 8.0, 2.1 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ: 113.83, 117.17, 123.47, 125.87, 126.86, 128.90, 129.94, 135.35, 143.66, 157.36.
GC-MS (*m/z*): 196.0 $[M]^+$.

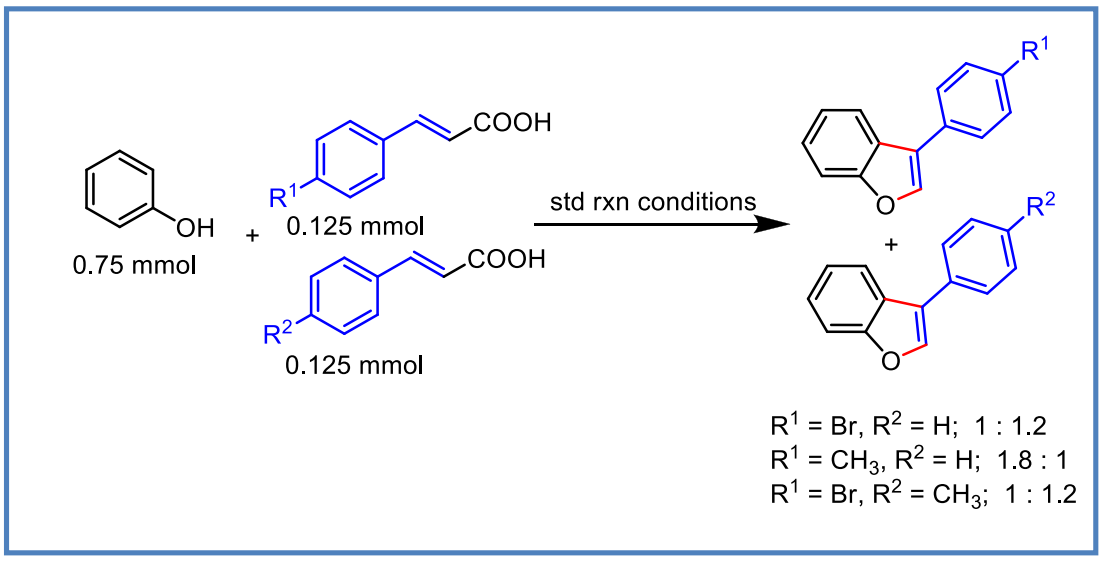
***Competition Experiment*:**

Experiment-(a):



Three competition experiment were carried out with cinnamic acid (0.25 mmol, 37 mg) and different combination of phenols [**experiment 1**: phenol (0.375 mmol, 33 μL) and 4-nitrophenol (0.375 mmol, 52.16mg); **experiment 2**: phenol (0.375 mmol, 33 μL) and 4-methoxyphenol (0.375 mmol, 46.55 mg); **experiment 3**: 4-nitrophenol (0.375 mmol, 52.16 mg) and 4-methoxyphenol (0.375 mmol, 46.55 mg)] under standard reaction condition. For each case the ratio is determined by GC-MS analysis of the reaction mixture.

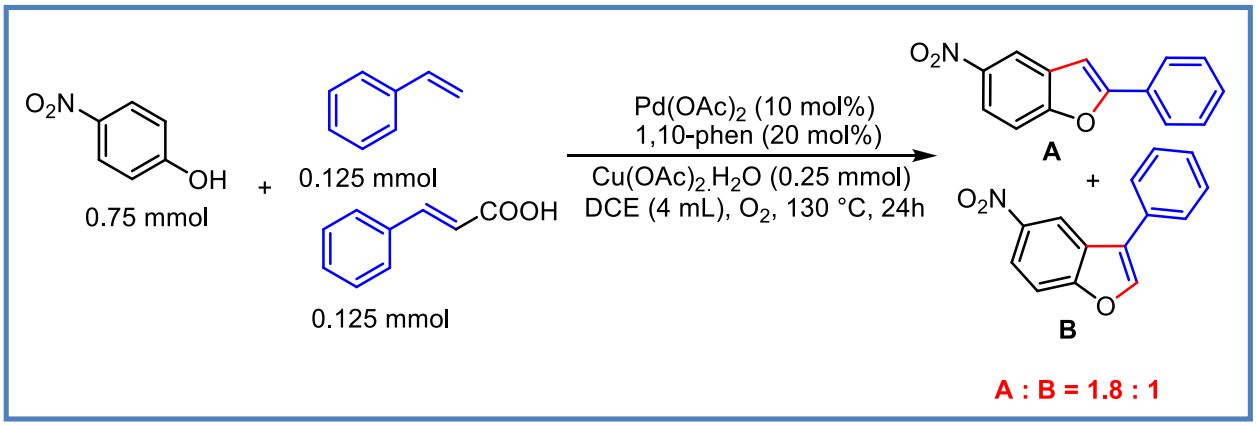
Experiment-(b):



Three competition experiments were carried out with phenol (0.75 mmol, 66 μL) and different combination of cinnamic acids [**experiment 1**: 4-bromo cinnamic acid (0.125 mmol, 28.4 mg) and cinnamic acid (0.125 mmol, 18.5 mg); **experiment 2**: 4-methyl cinnamic acid (0.125 mmol, 20.3 mg) and cinnamic acid (0.125 mmol, 18.5 mg); **experiment 3**: 4-bromo cinnamic acid (0.125 mmol, 28.4 mg) and 4-methyl cinnamic acid (0.125 mmol, 20.3 mg)] under standard reaction condition. For each case the ratio is determined by GC-MS analysis of the reaction mixture.

Competition experiment between styrene and cinnamic acid:

***Procedure*:** To an oven-dried screw cap reaction tube charged with a magnetic stir-bar, cinnamic acid (18.5 mg, 0.125 mmol),$Pd(OAc)_2$(10 mol%, 5.6 mg), 1,10-phenonthrolinemonohydrate (20 mol%, 10 mg), $Cu(OAc)_2.H_2O$(0.25 mmol, 50 mg) were added. In this tube4-nitrophenol (0.75mmol, 104.33) and styrene (0.125mmol, 14.3 µL) were added by micro-litre syringe under air atmosphere. Then 4 mL of DCE (fully O_2 purged) was added in the reaction tube and closed it with screw cap and kept it for vigorous stirring in a preheated oil bath at 130 ^oC for 24h. After completion, reaction mixture was filtered through a celite pad with ethylacetate as the washing solvent. The ethylacetate layer was washed with brine solution and dried over anhydrous Na_2SO_4. Then the ratio of two products was determined from GC and GC-MS analysis.



Experimental Details for Kinetic Study:

Kinetic study was performed by taking the standard reaction of 4-nitrophenol and 4-methoxycinnamic acid. All the reactions were done by following the standard reaction protocol. Amount of product and reactant in each reaction was measured by gas chromatography using *n*-decane as internal standard.

Now, both phenol and cinnamic acid were involved in the reaction. We can assume that rate of the reaction is only dependent on the concentration of phenol and cinnamic acid.

So, Rate = $k.[phenol]^x[acid]^y$ ……..(1)

[x = order with respect to phenol; y = order with respect to cinnamic acid; k = rate constant]

Determination of order with respect to cinnamic acid:

run	4-methoxycinnamic acid(mmol)	4-nitrophenol (mmol)	$Pd(OAc)_2$ (mmol)	1,10-phen (mmol)	$Cu(OAc)_2.H_2O$ (mmol)	DCE (mL)
1	0.35	0.75	10 mol%	20 mol%	0.35	4
2	0.5	0.75	10 mol%	20 mol%	0.35	4

From the different set of experiment (**run 1** and **run 2**) the following product formation plot was observed:

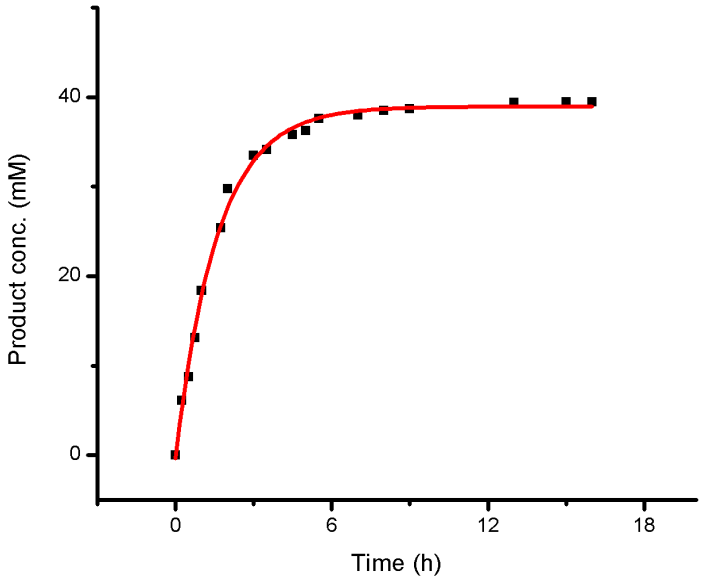


Figure 1. Product formation plot in **run 1 (acid = 0.35 mmol and phenol 0.75 mmol).**

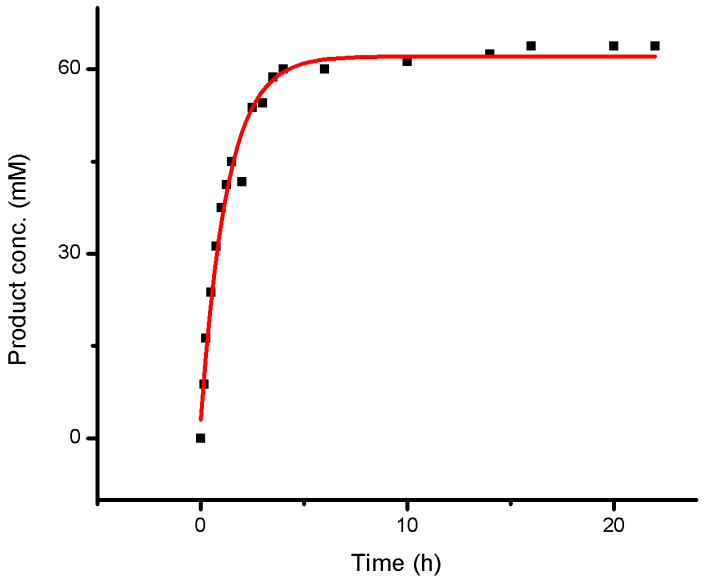


Figure 2. Product formation plot in **run 2 (acid = 0.5 mmol and phenol 0.75 mmol).**

From the equation (1) we got, Rate = k. $[phenol]^x[acid]^y$

For **run 1** initial rate = Rate 1

So, Rate 1 = k. $[phenol]^x[acid]^y$

or, $20.88 = k.[0.75]^x[0.35]^y$ ……(2)

For **run 2**initial rate = Rate 2

So, Rate 2= k. $[phenol]^x[acid]^y$

or, $31.033 = k.[0.75]^x[0.5]^y$ …….(3)

Hence,from equation (2) and (3) we get, $[Rate\ 1/Rate\ 2] = [0.35/0.5]^y$

or, y = [log(Rate 1) - log(Rate 2)] / [log(0.35) - log(0.5)]

or, y = [log(20.88) – log(31.033)] / [log(0.35) – log(0.5)]

or, y = 1.12~ 1.0

So, order with respect to cinnamic acid derivatives is ~ **1.0**

Determination of order with respect to phenol:

run	4-methoxycinnamic acid(mmol)	4-nitrophenol (mmol)	$Pd(OAc)_2$ (mmol)	1,10-phen (mmol)	$Cu(OAc)_2.H_2O$ (mmol)	DCE (mL)
3	0.25	1.0	10 mol%	20 mol%	0.25	4
4	0.25	0.5	10 mol%	20 mol%	0.25	4

From the different set of experiment (**run 3** and **run 4**) the following product formation plot was observed:

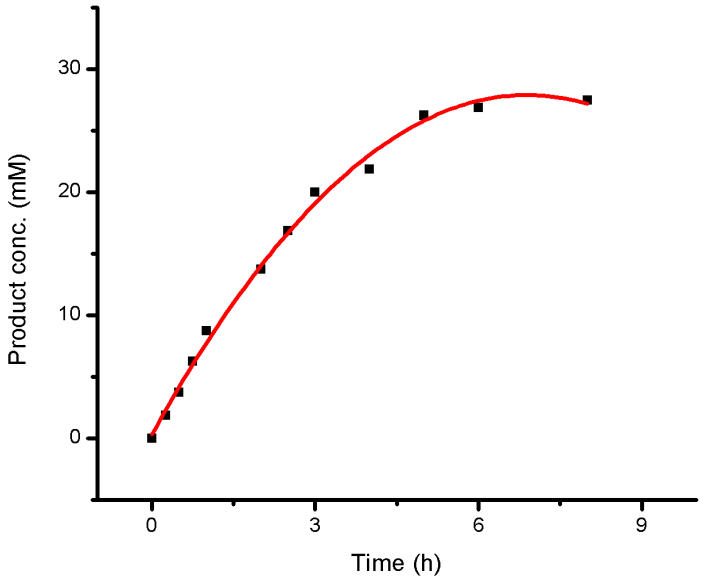


Figure 3. Product formation plot in **run 3 (acid = 0.25 mmol and phenol 1.0mmol).**

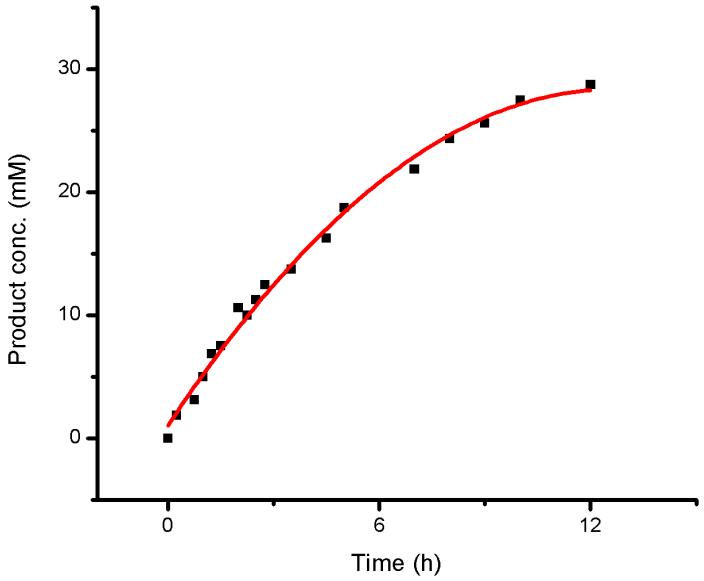


Figure 4. Product formation plot in **run 4 (acid = 0.25 mmol and phenol 0.5mmol).**

From the equation (1) we got, Rate = k. $[phenol]^x[acid]^y$

For **run 3**initial rate = Rate 3

So, Rate 3= k. $[phenol]^x[acid]^y$

or, 9.31 = k. $[1.0]^x[0.25]^y$ ……(4)

For **run 4** initial rate = Rate 4

So, Rate 4= k. $[phenol]^x[acid]^y$

or, 4.41 = k. $[0.5]^x[0.25]^y$ …….(5)

Hence, from equation (4) and (5) we get, $[\text{Rate 3}/\text{Rate 4}] = [1.0/0.5]^x$

or, x = [log(Rate 3) - log(Rate 4)] / [log(1.0) - log(0.5)]

or, x= [log(9.31) – log(4.41)] / [log(1.0) – log(0.5)]

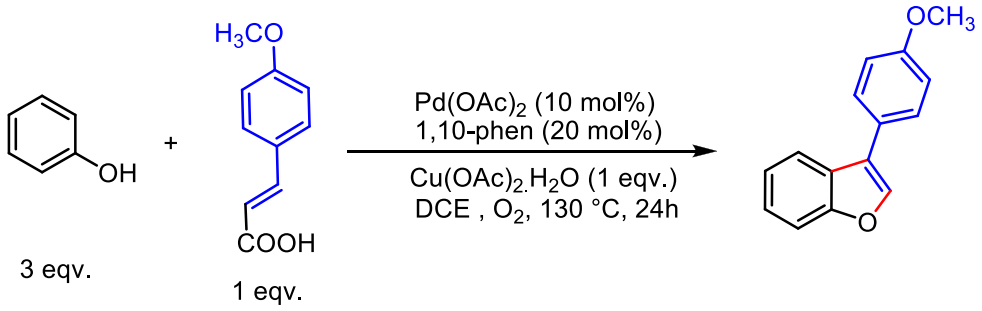
or, x = 1.07~ 1.0

So, order with respect to phenol derivatives is ~ **1.0**

Kinetic isotope effect: determination of k_H/k_D

Kinetic isotope effect study was done by monitoring the reaction of phenol with 4-methoxycinnamic acid and deuterated phenol with 4-methoxycinnamic acid. All the reactions were done by following the standard reaction protocol. Amount of product and reactant in each reaction was measured by gas chromatography using *n*-decane as internal standard.

Set 1:



$$\text{So, Rate } (R_H) = k_H.[\text{PhOH}]^x[\text{acid}]^y \quad \text{……..(1)}$$

[x = order with respect to phenol; y = order with respect to cinnamic acid; k_H = rate constant]

Following product formation plot was observed for this case:

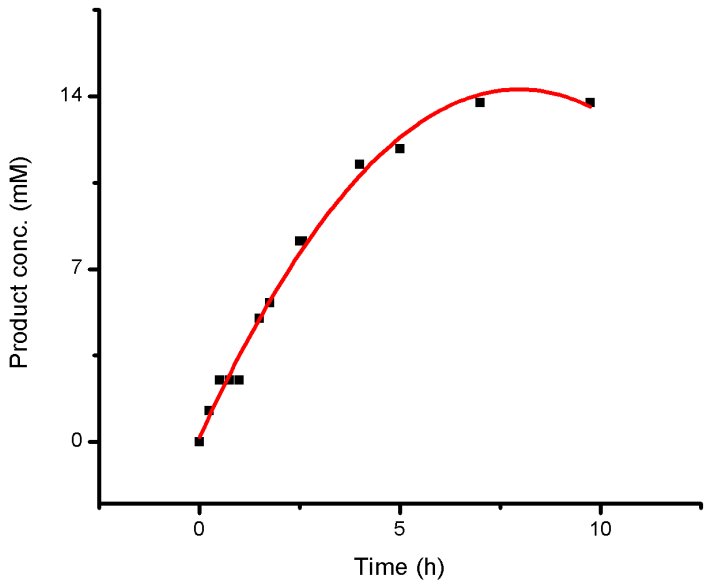
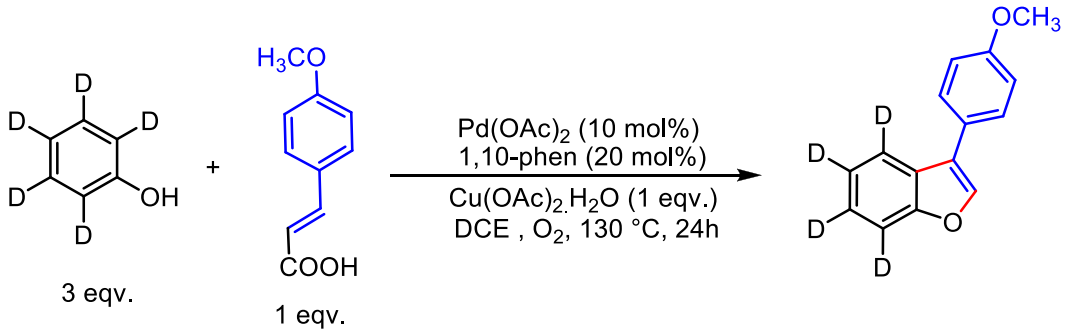


Figure 1. Product formation plot in **Set 1**

$$\text{So,}\quad R_H = k_H.\,[PhOH]^x[acid]^y$$

$$\text{or,}\quad 8.45 = k_H.[0.3]^x[0.1]^y \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Set 2:



$$\text{So, Rate } (R_D) = k_D.[d_5\text{-PhOH}]^x[acid]^y \quad \ldots\ldots\ldots..(3)$$

[x = order with respect to phenol; y = order with respect to cinnamic acid; k_D = rate constant for d_5-PhOH reaction]

Following product formation plot was observed for this case:

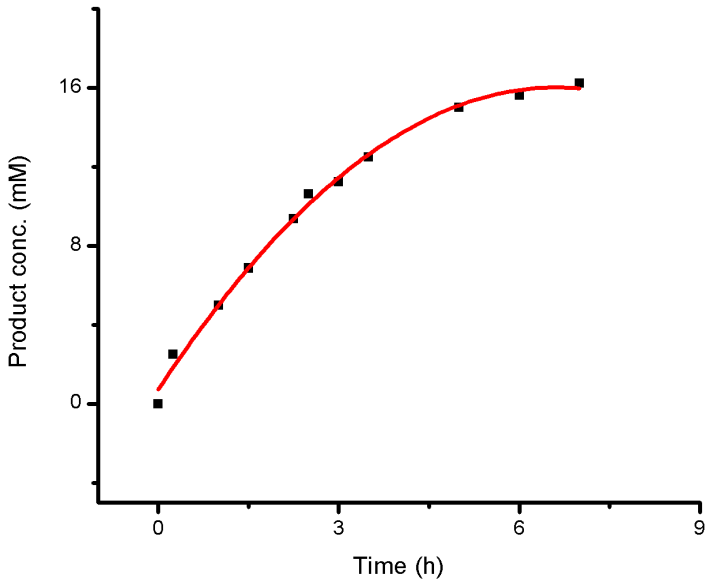


Figure 2. Product formation plot in **Set 2**

$$\text{So,}\quad R_D = k_D.\,[d_5\text{-PhOH}]^x[\text{acid}]^y$$

$$\text{or,}\quad 7.46 = k_D.[0.3]^x[0.1]^y \quad \ldots\ldots\ldots\ldots\ldots(4)$$

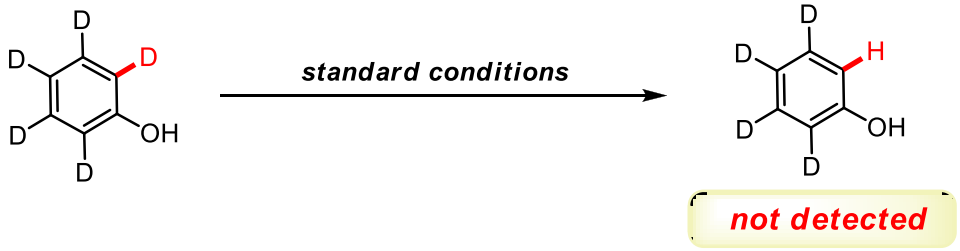
Hence, from equation (2) and (4) we get, $[8.45/7.46] = (k_H/k_D)$

$$\textbf{So, } (k_H/k_D) = \textbf{1.13}$$

H/D exchange experiment:

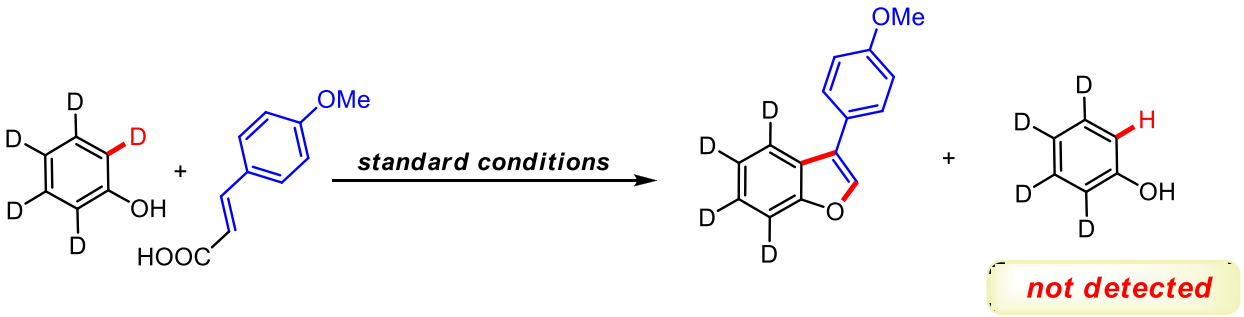
***Procedure*:**

Experiment 1: To an oven-dried screw cap reaction tube charged with a magnetic stir-bar, $Pd(OAc)_2$ (10 mol%, 5.6 mg), 1,10-phenonthrolinemonohydrate (20 mol%, 10 mg), $Cu(OAc)_2.H_2O$ (0.25 mmol, 50 mg) were added. In this tube d_5-PhOH (0.75mmol, 65.9 µL) was added by micro-litre syringe under air atmosphere. Then 4 mL of DCE (fully O_2 purged) was added in the reaction tube and closed it with screw cap and kept it for vigorous stirring in a preheated oil bath at 130 ^oC for 24h. After completion, reaction mixture was filtered through a celite pad with ethylacetate as the washing solvent. The ethylacetate layer was washed with brine solution and dried over anhydrous Na_2SO_4. Then the ratio of two products was determined from GC and GC-MS analysis.



Experiment 2: To an oven-dried screw cap reaction tube charged with a magnetic stir-bar, 4-methoxy cinnamicacid (0.25 mmol, 44.5 mg), $Pd(OAc)_2$ (10 mol%, 5.6 mg), 1,10-phenonthrolinemonohydrate (20 mol%, 10 mg), $Cu(OAc)_2.H_2O$ (0.25 mmol, 50 mg) were added. In this tube d_5-PhOH (0.75mmol, 65.9 µL) was added by micro-litre syringe under air atmosphere. Then 4 mL of DCE (fully O_2 purged) was added in the reaction tube and closed it with screw cap and kept it for vigorous stirring in a preheated oil bath at 130 ^oC for 24h. After completion, reaction mixture was filtered through a celite pad with ethylacetate as the washing

solvent. The ethylacetate layer was washed with brine solution and dried over anhydrous Na_2SO_4. Then the ratio of two products was determined from GC and GC-MS analysis.

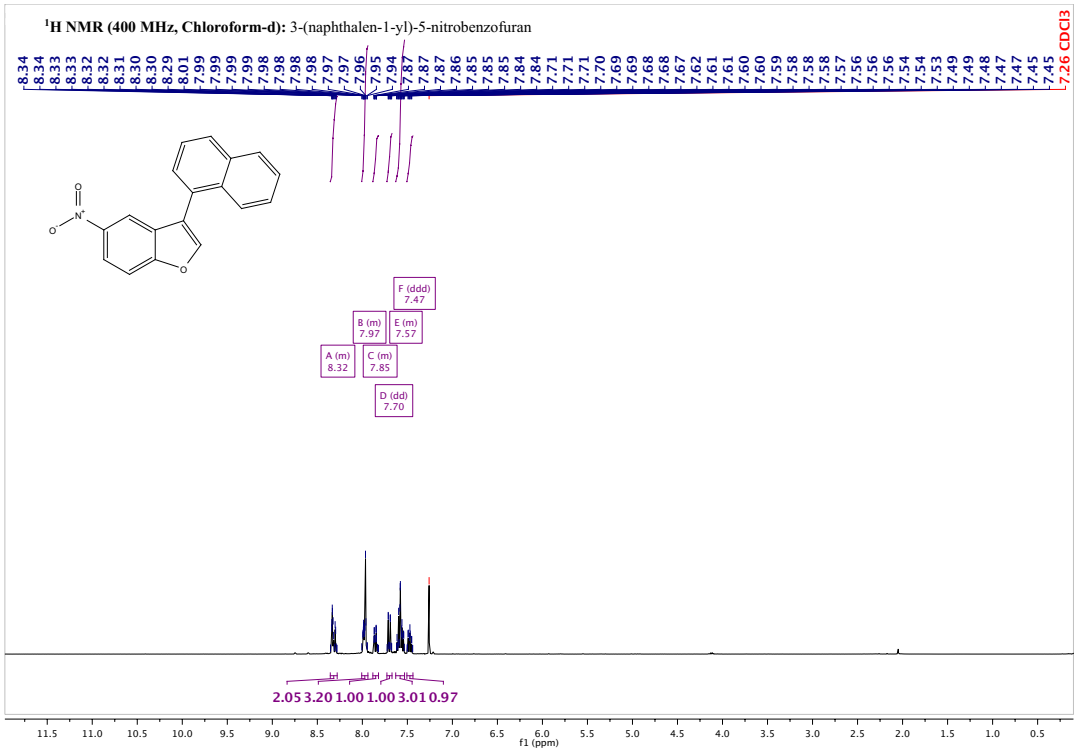


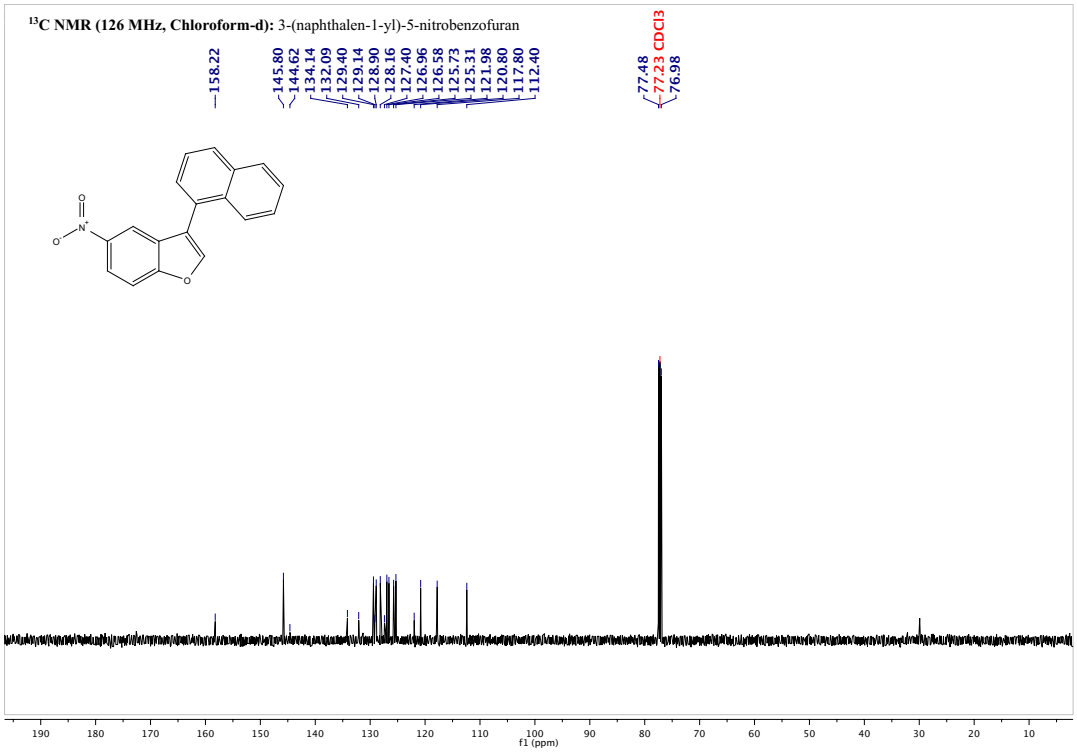
References:

1. Moure, M. J.; SanMartin, R.; Dominguez, E. *Angew. Chem. Int. Ed.* **2012**, *51*, 3220
2. Liu, Y.; Lv, X.; Bao, W. *Synthesis.* **2008,** *12,* 1911-1917.

Supporting Information (NMR Files)

Table 1, Entry 3a:





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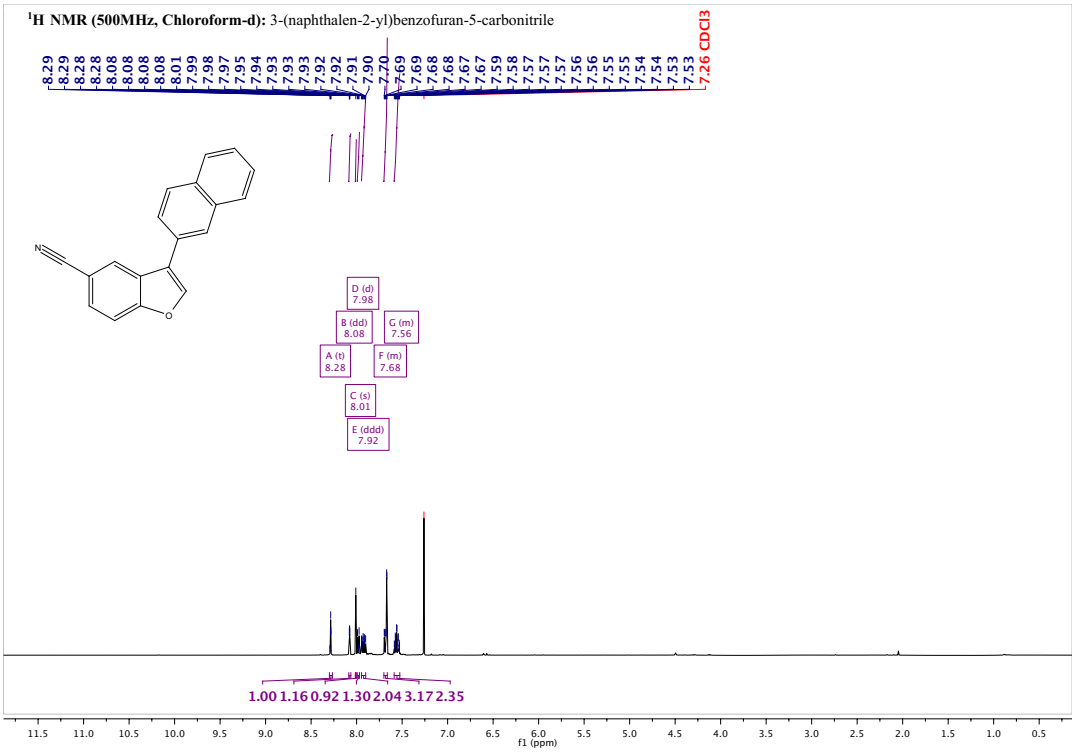

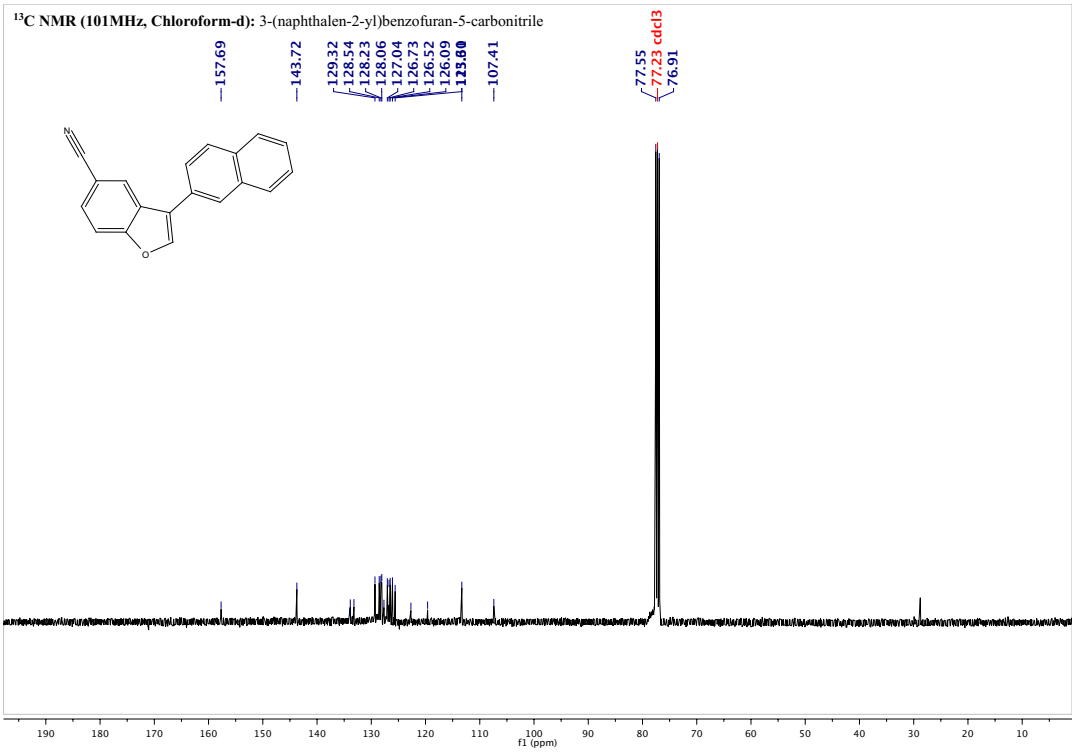

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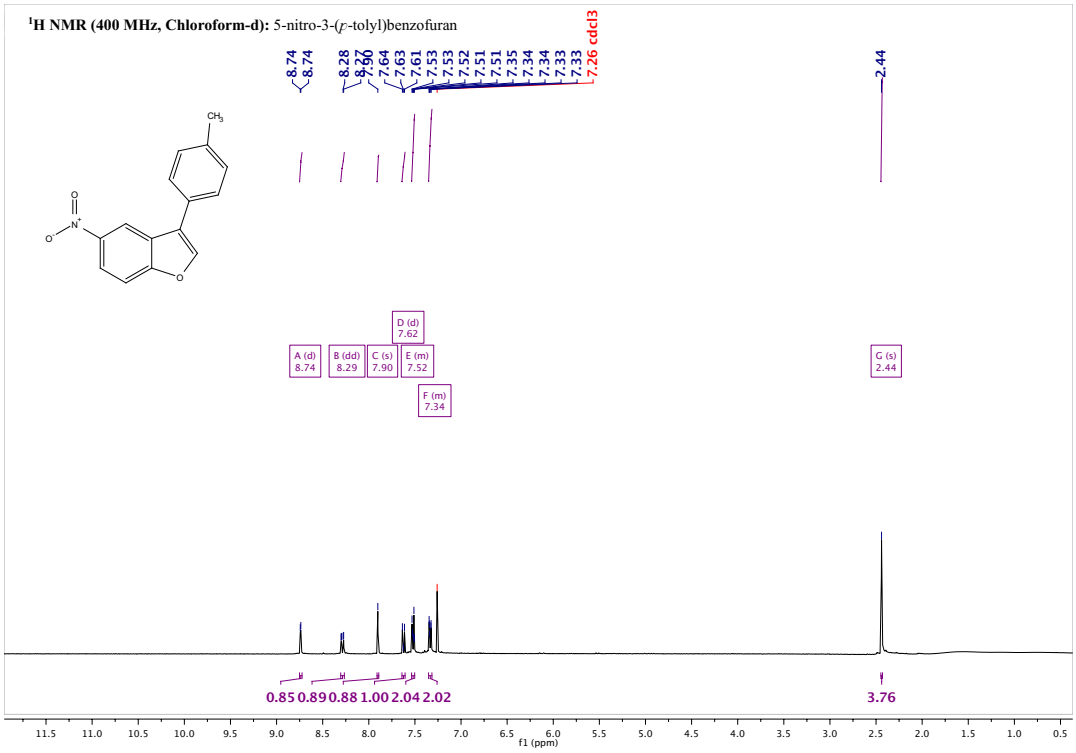

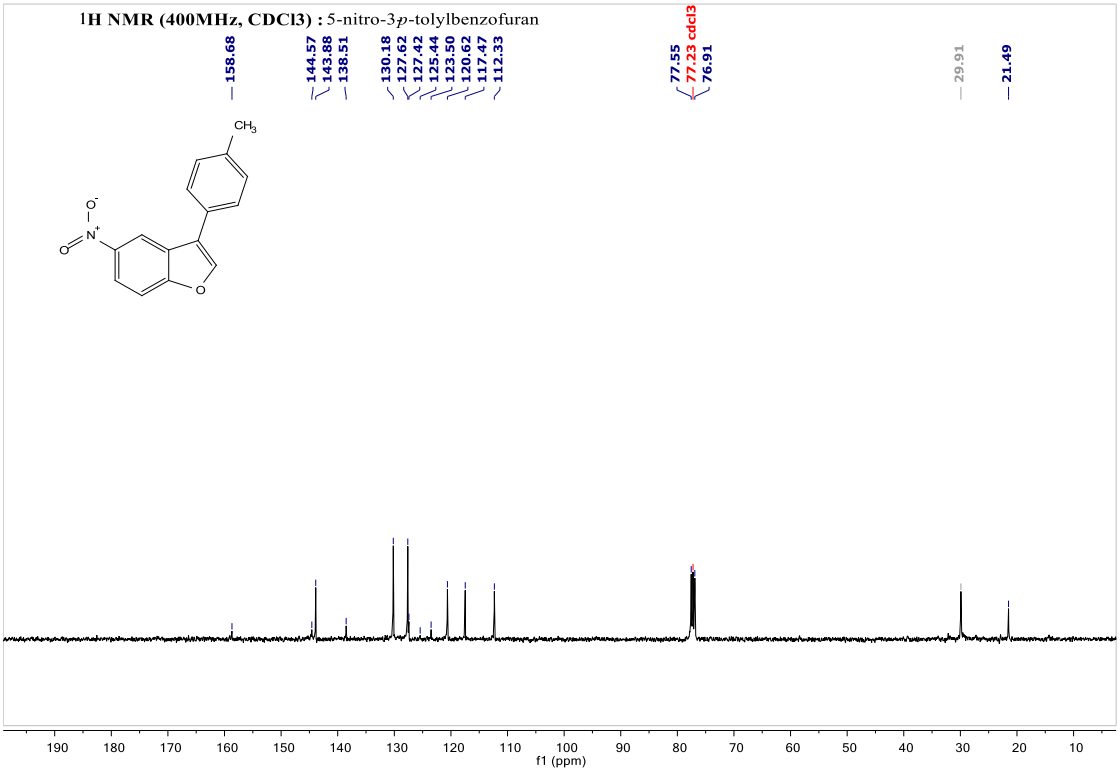

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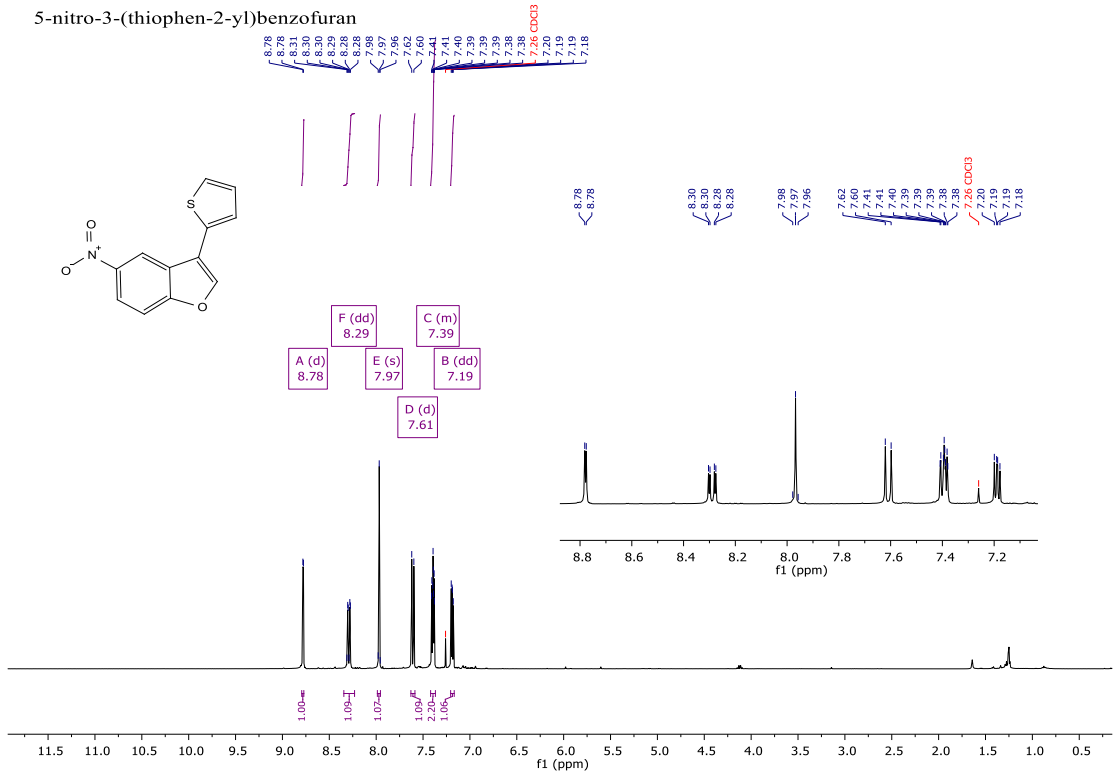

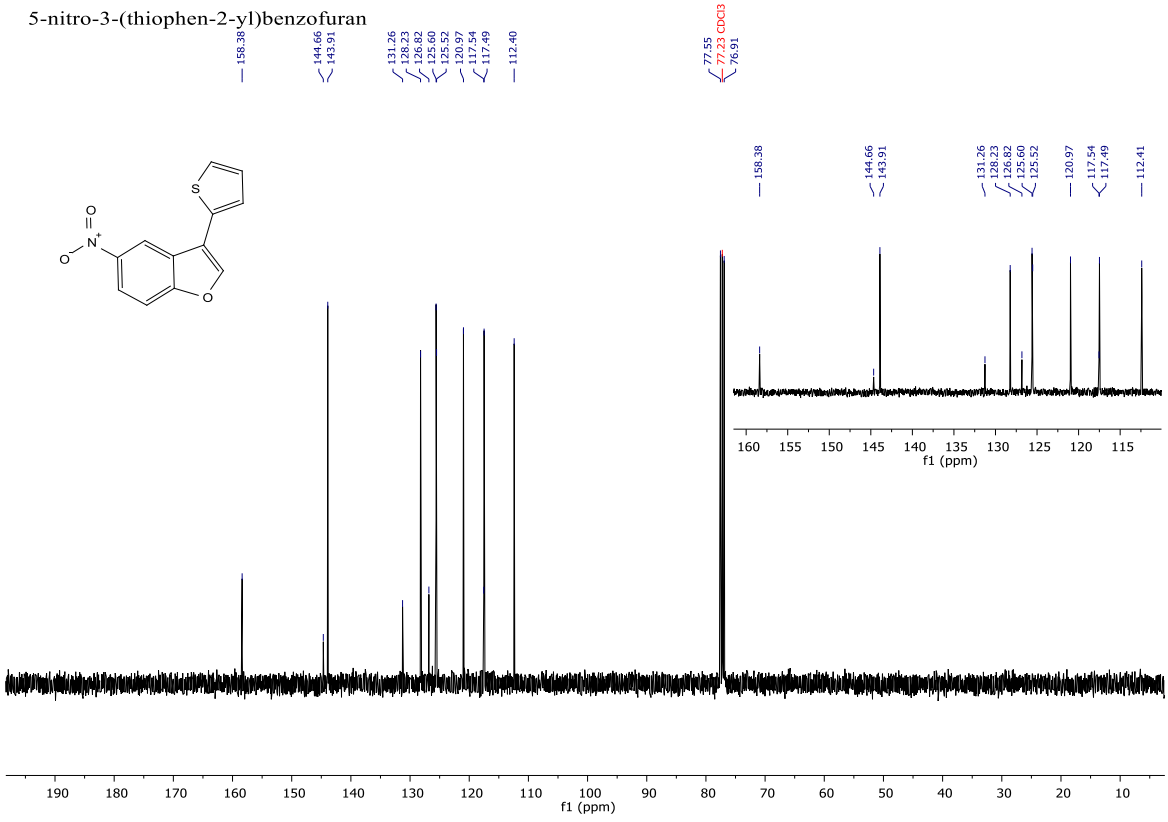

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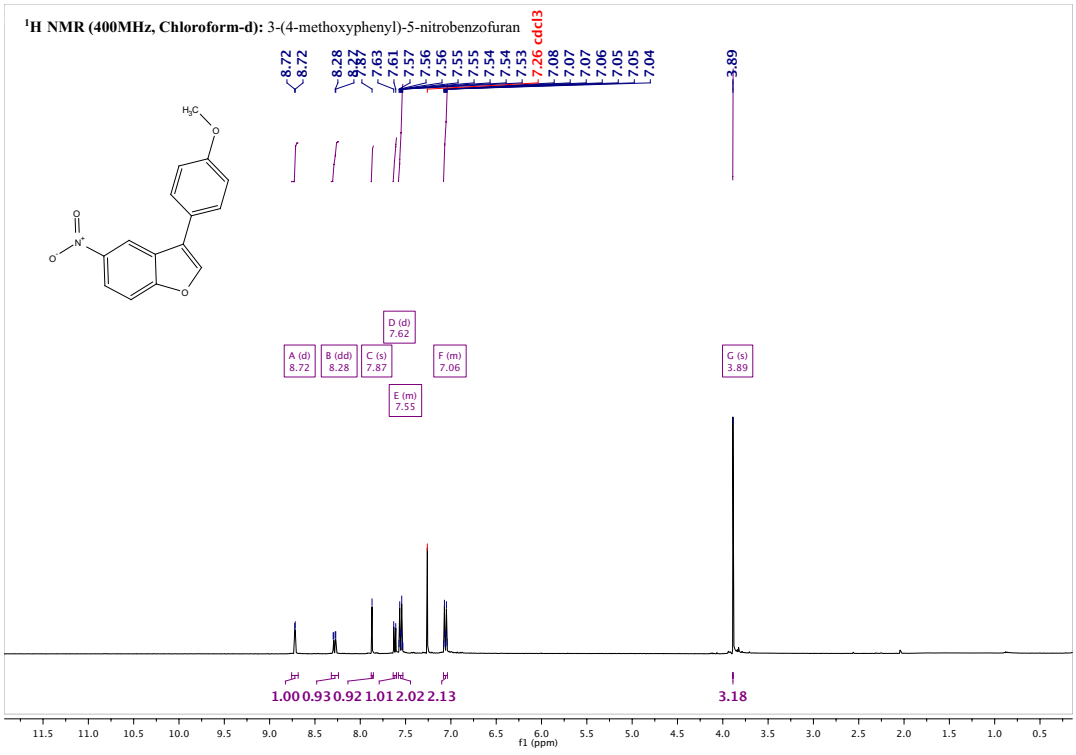

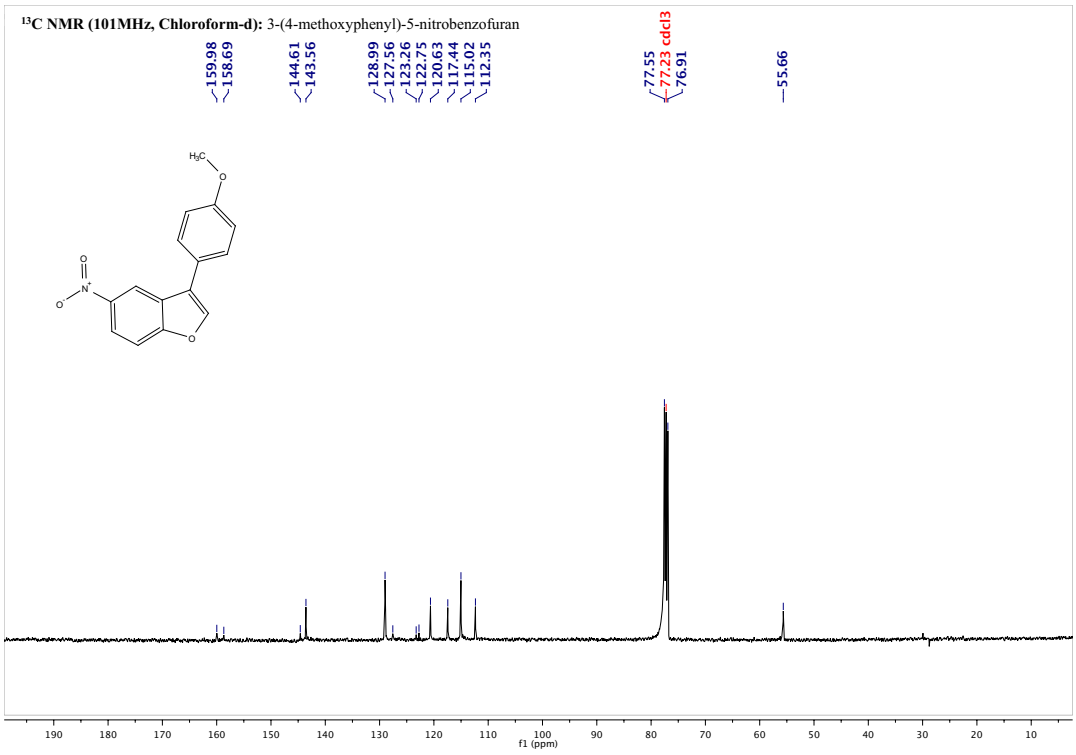

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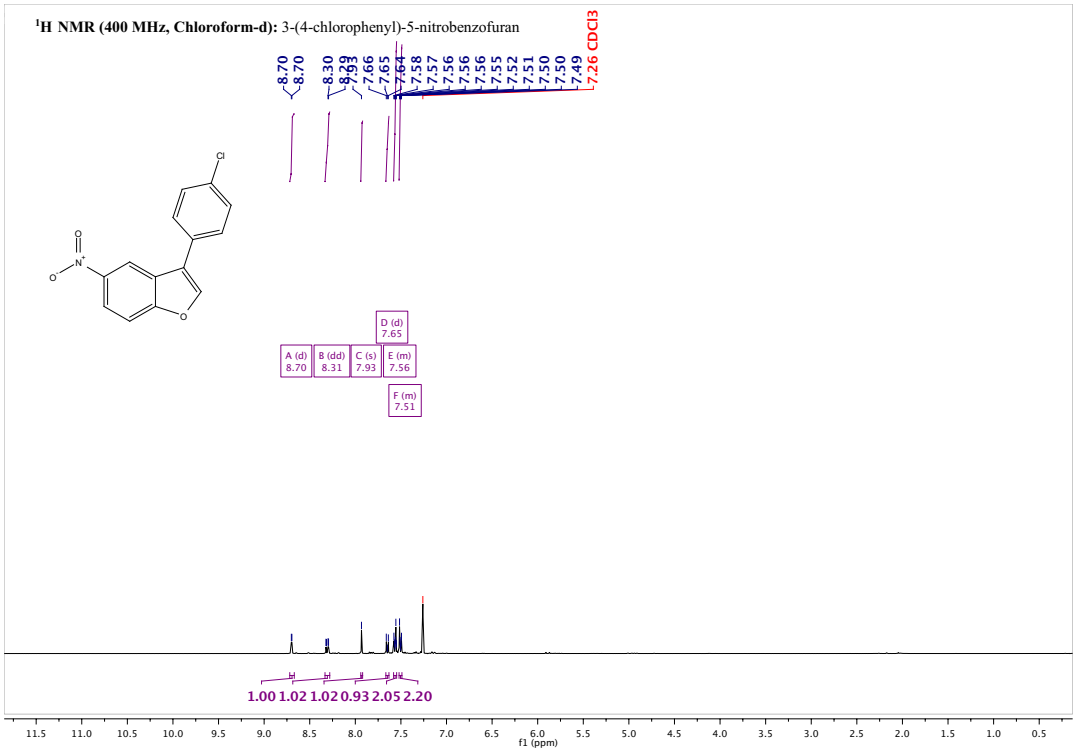

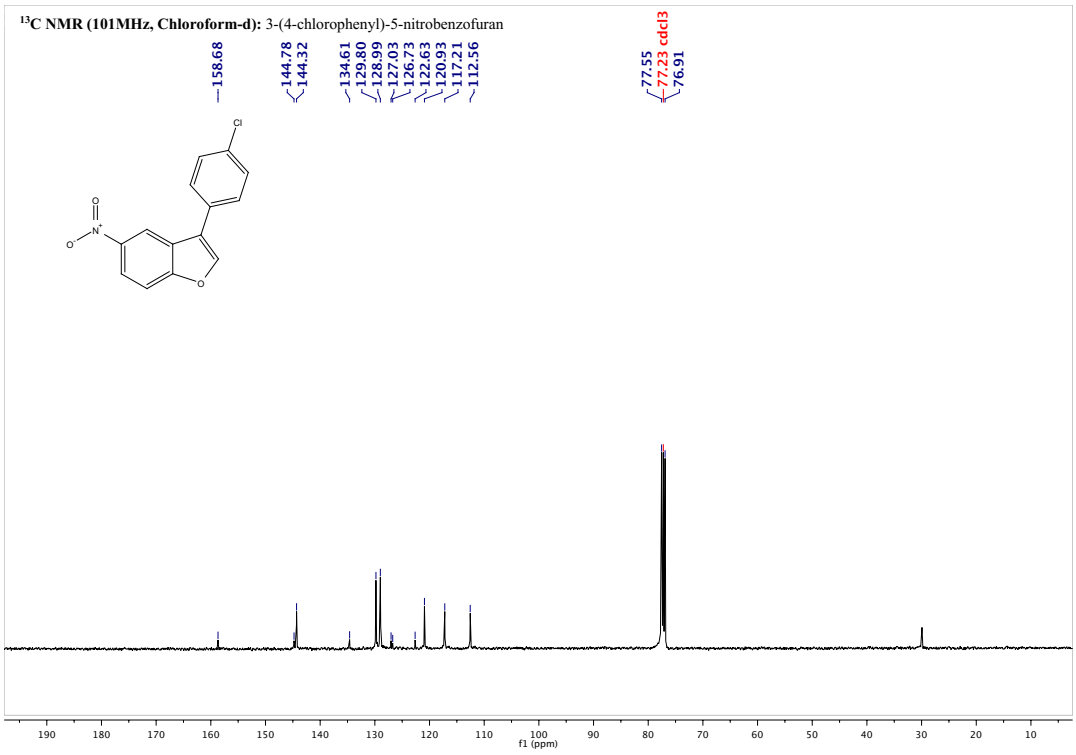

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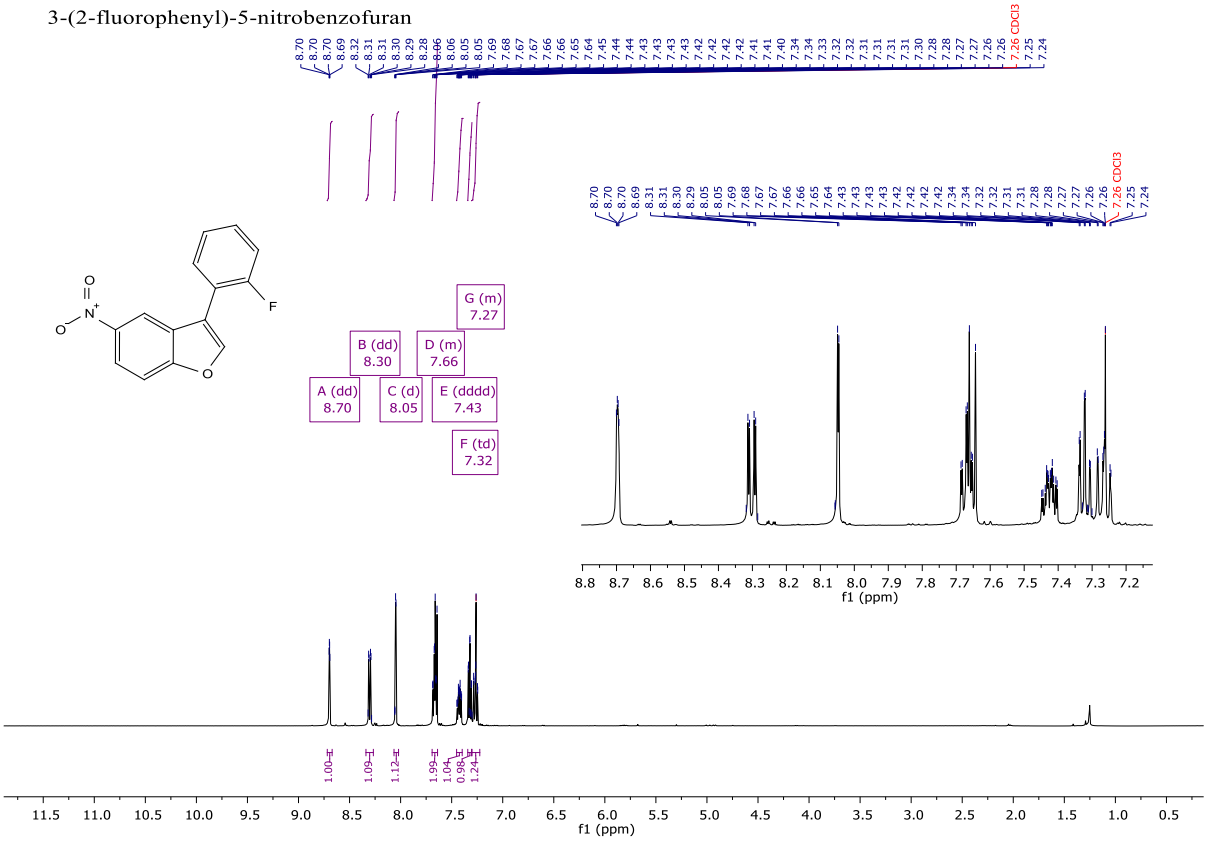

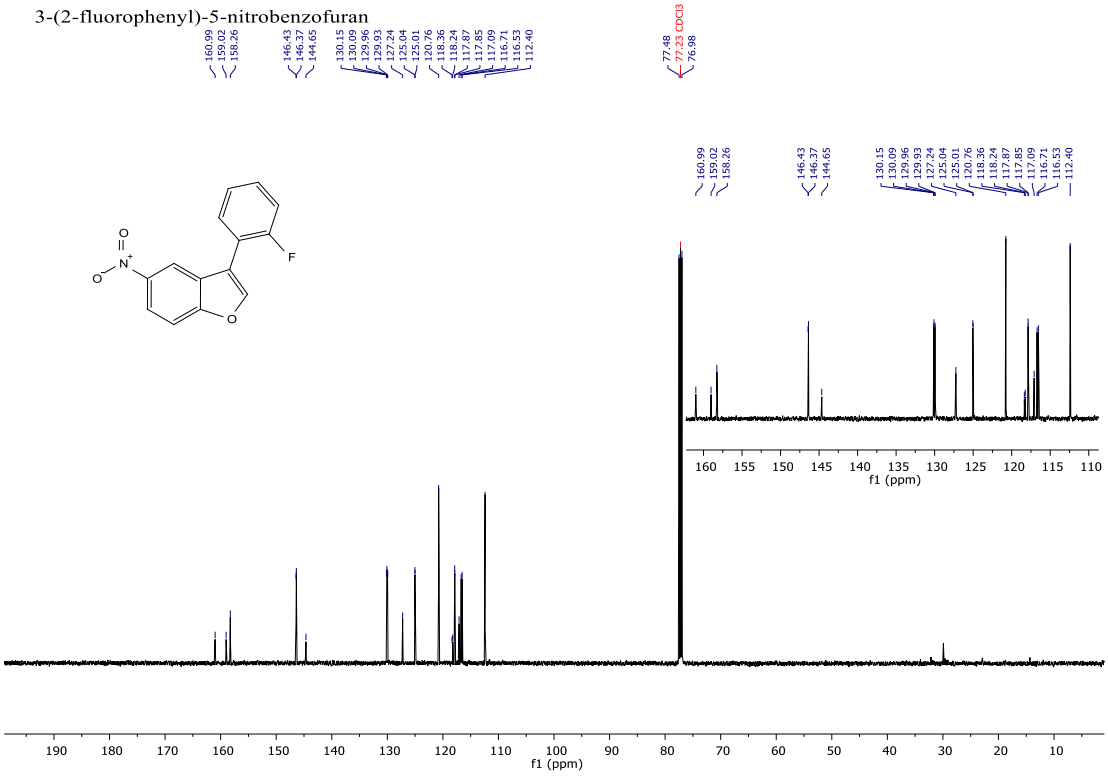

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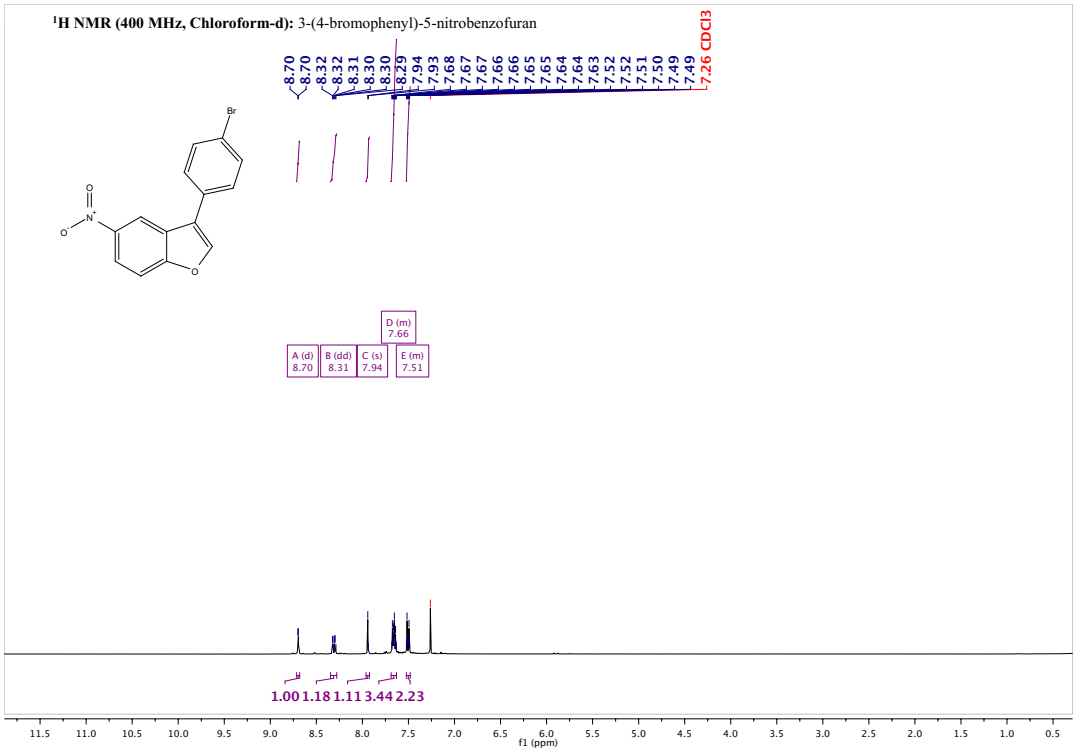

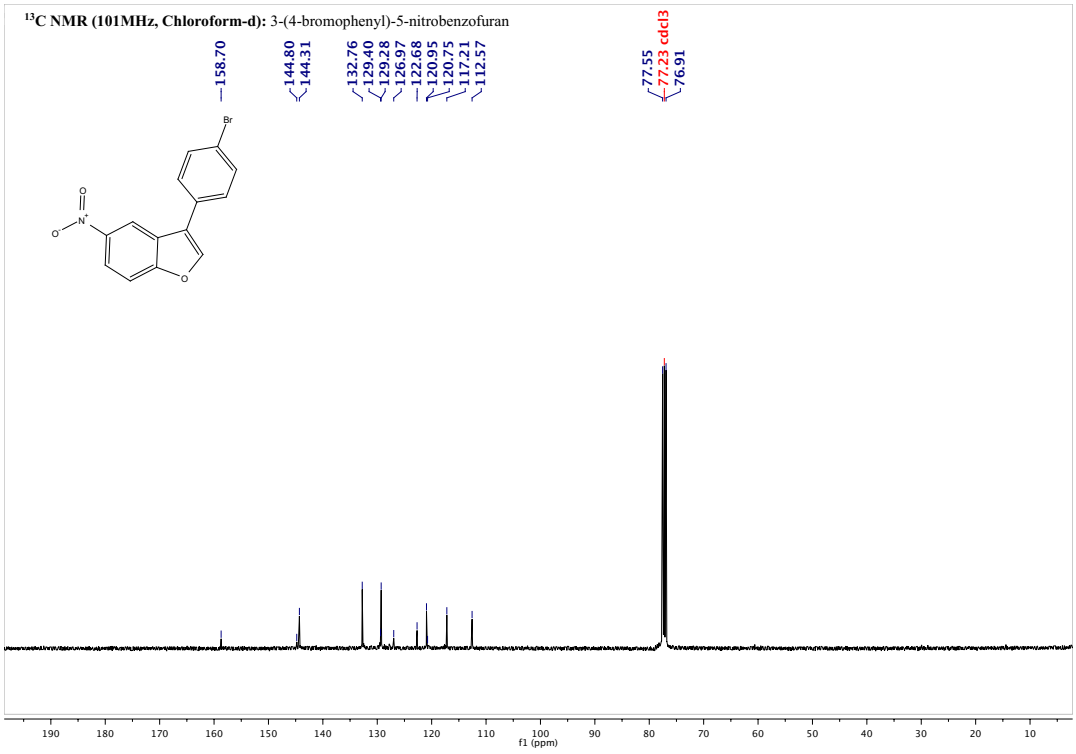

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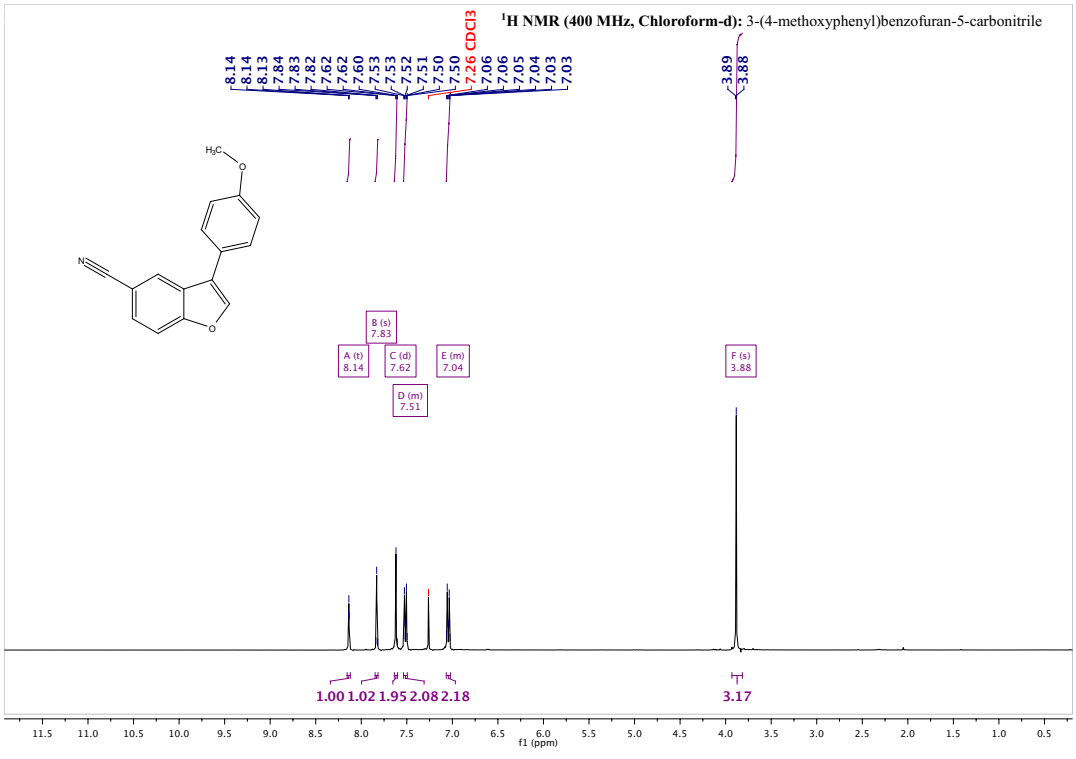

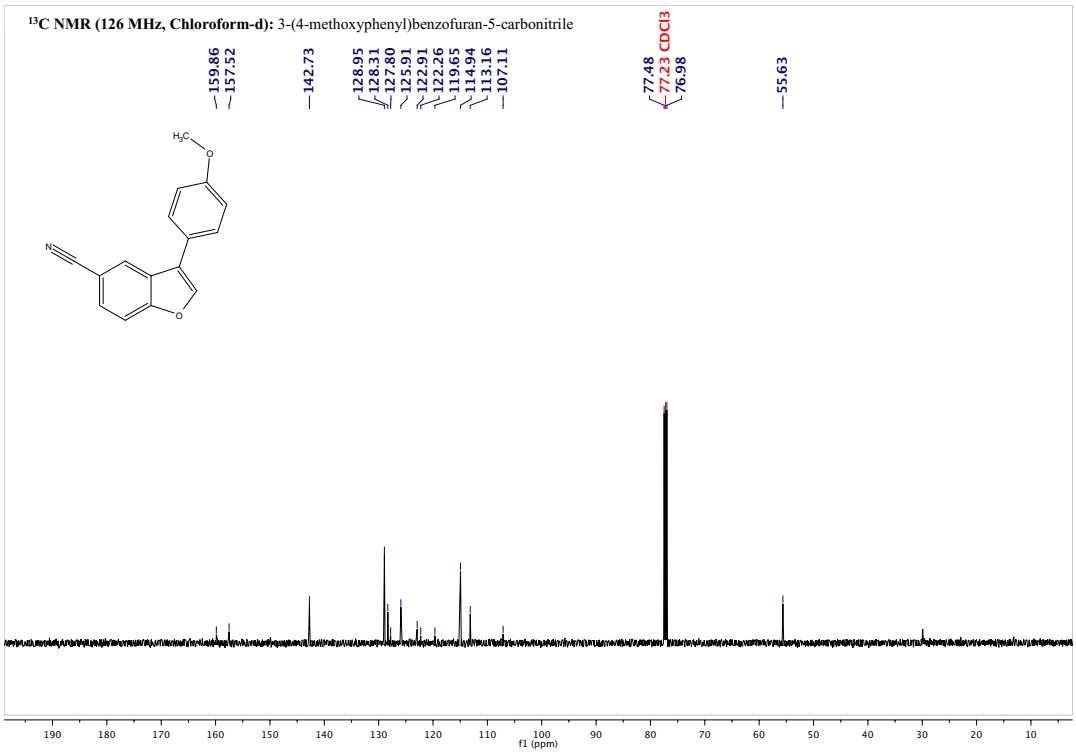

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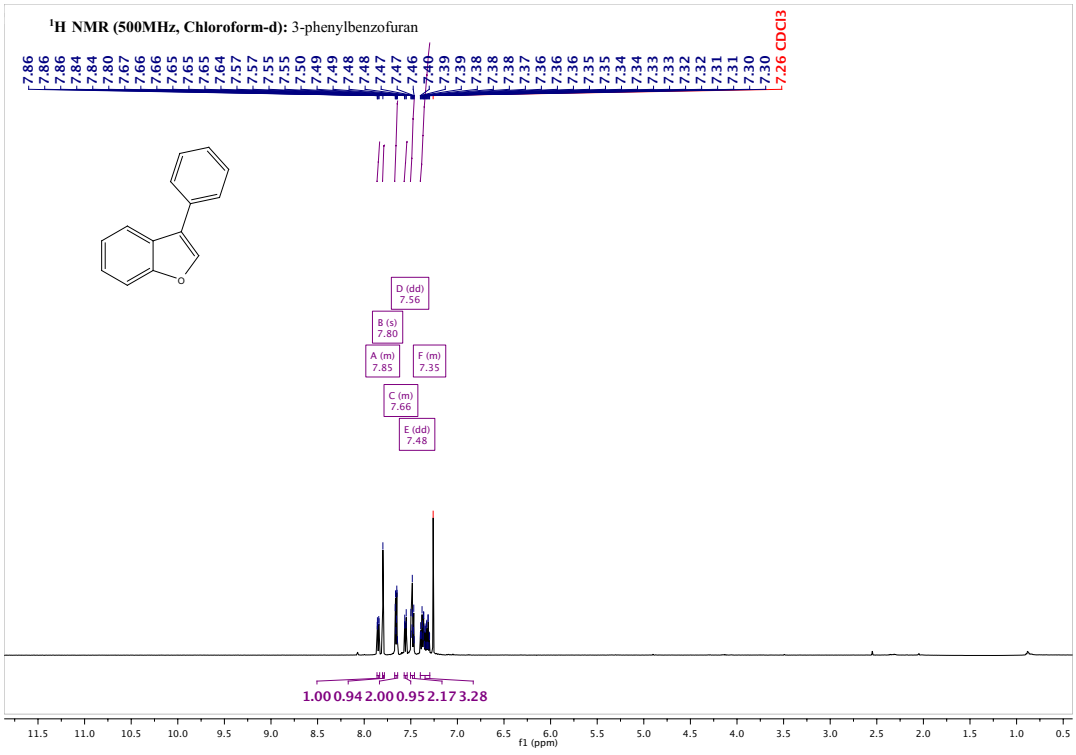

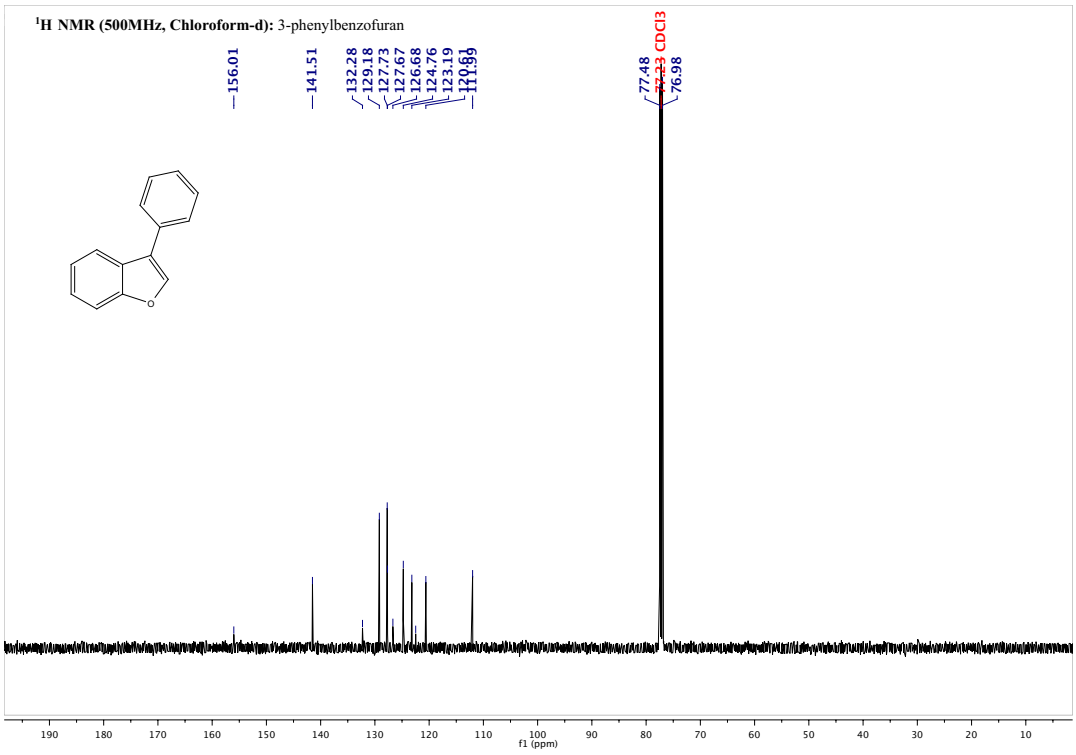

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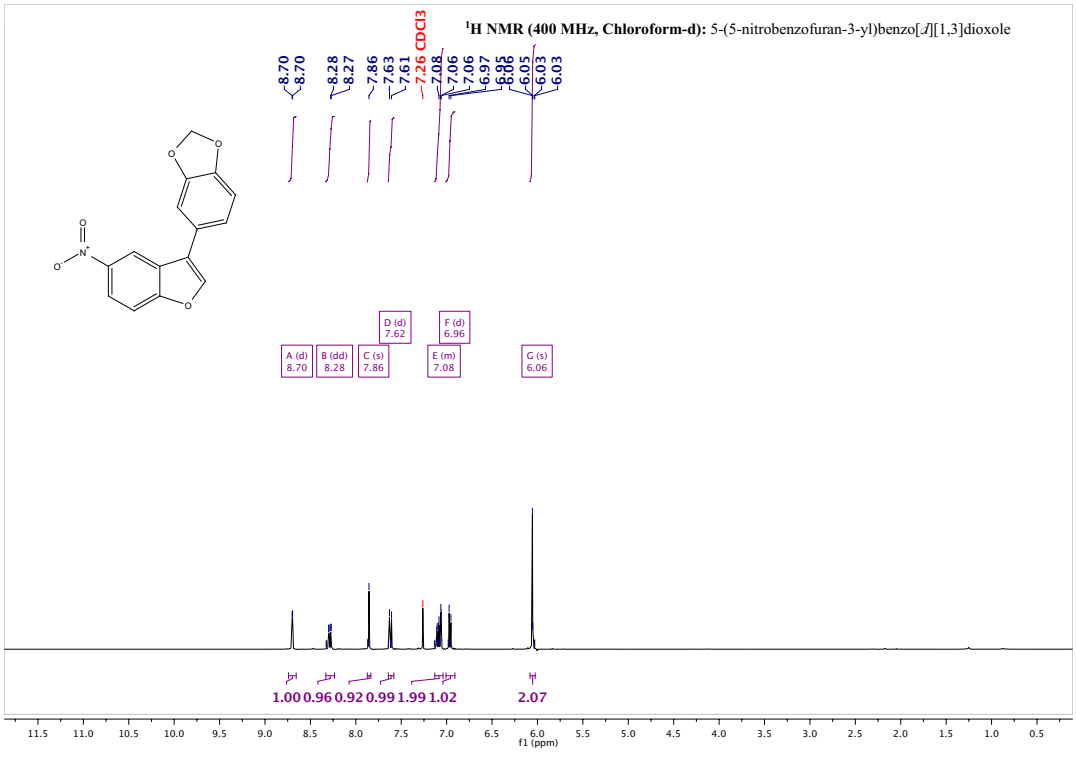

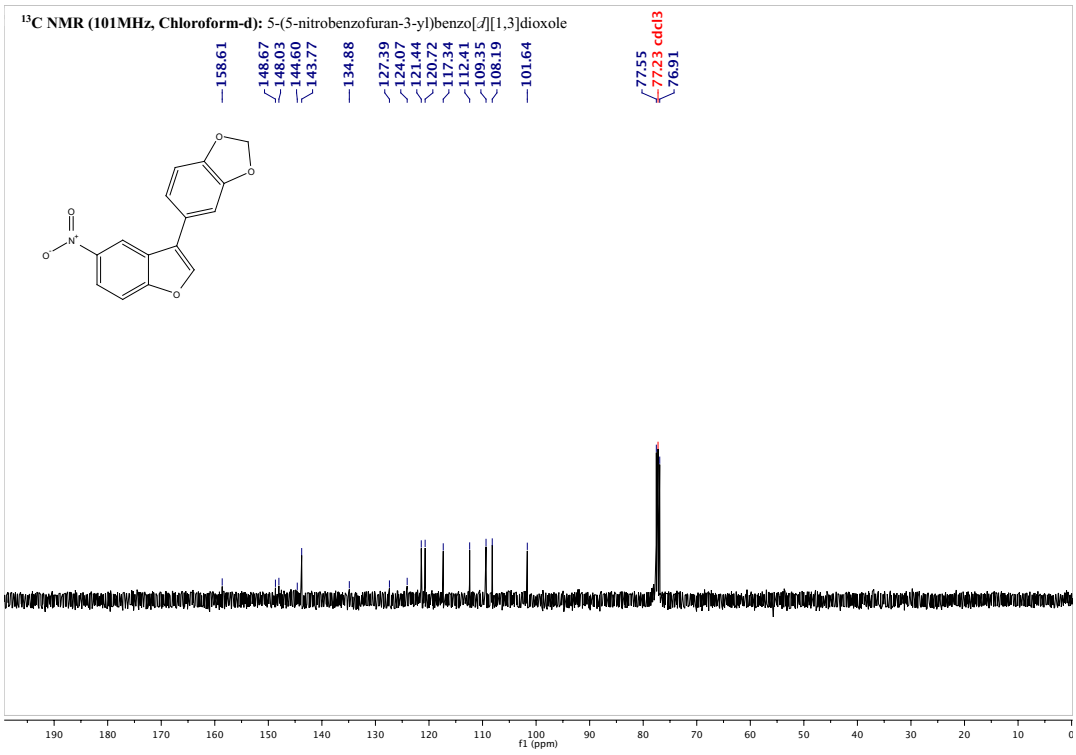

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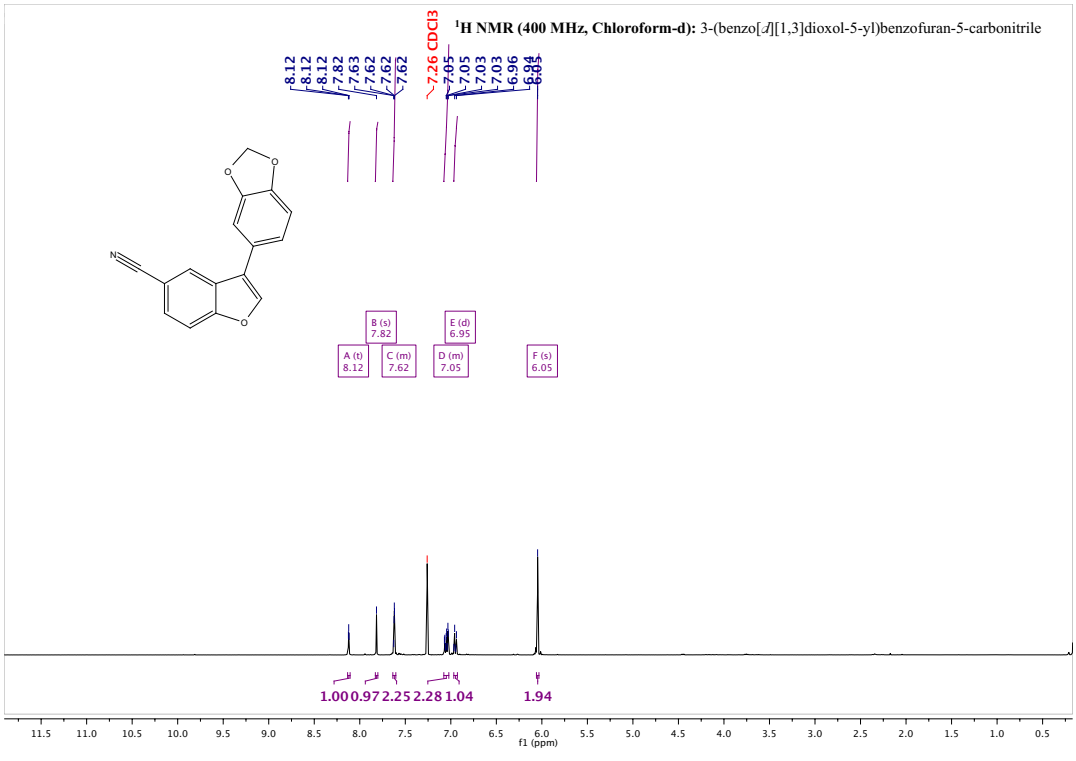

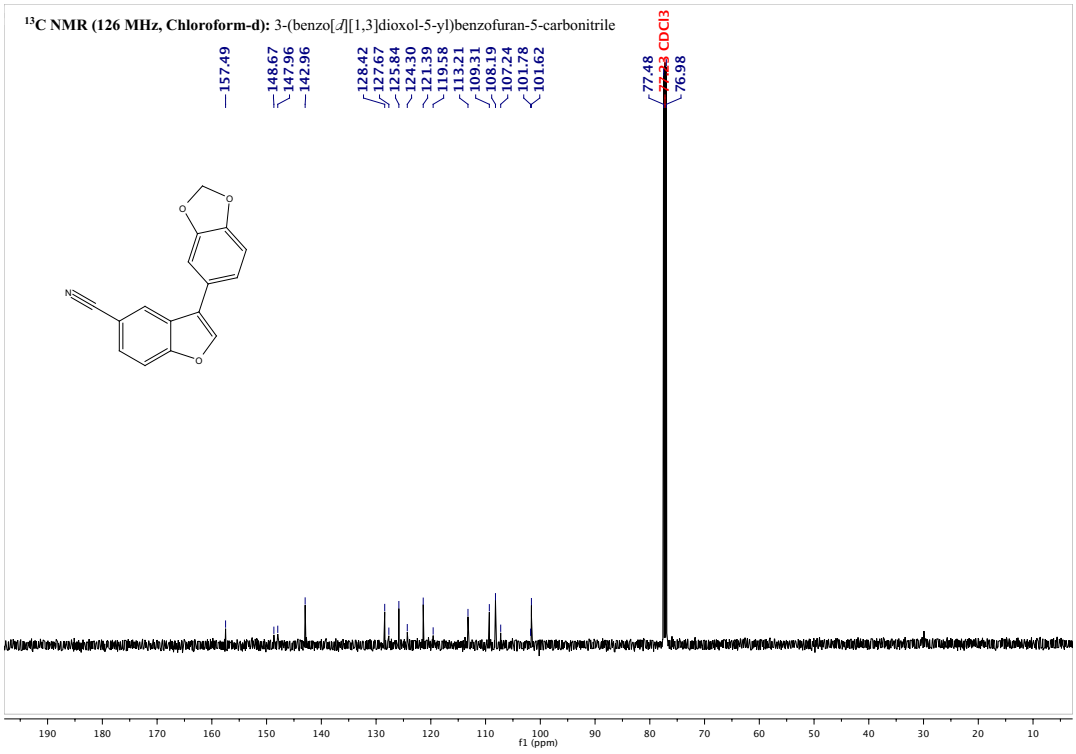

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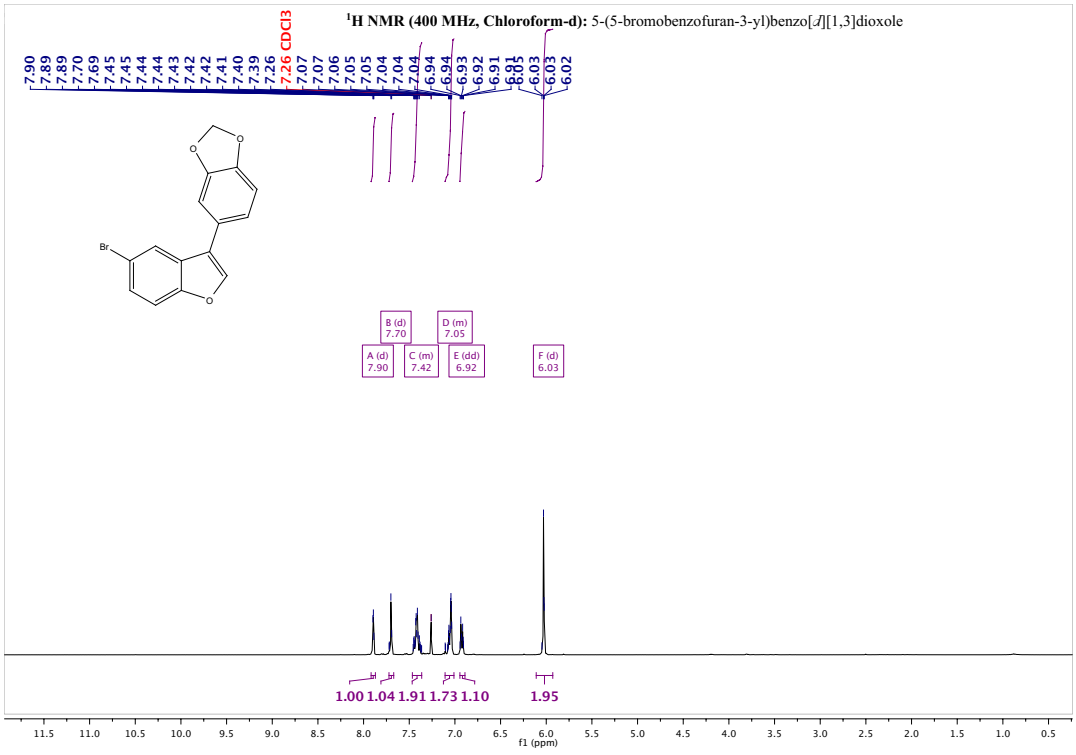

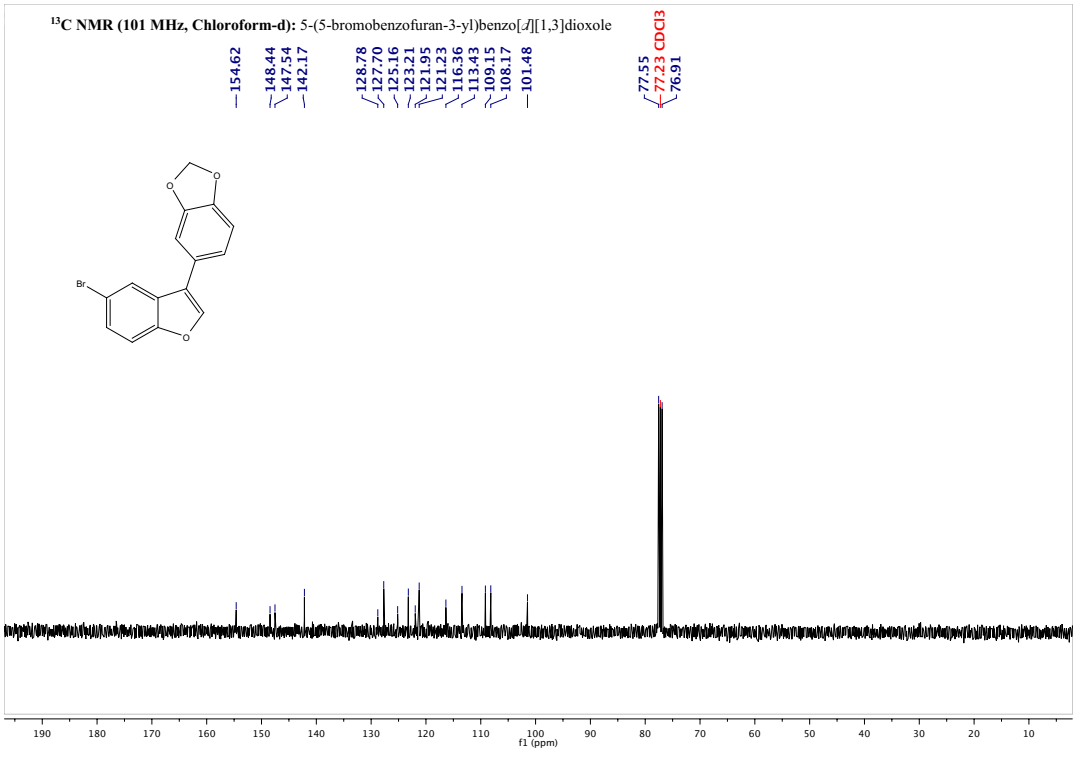

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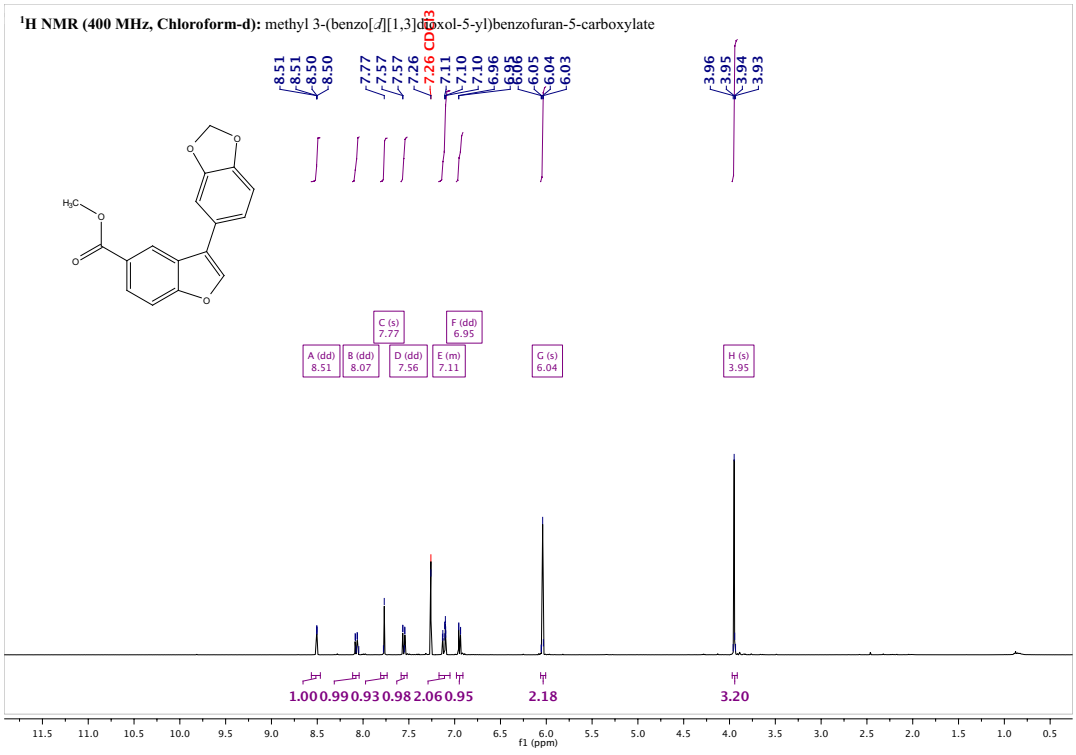

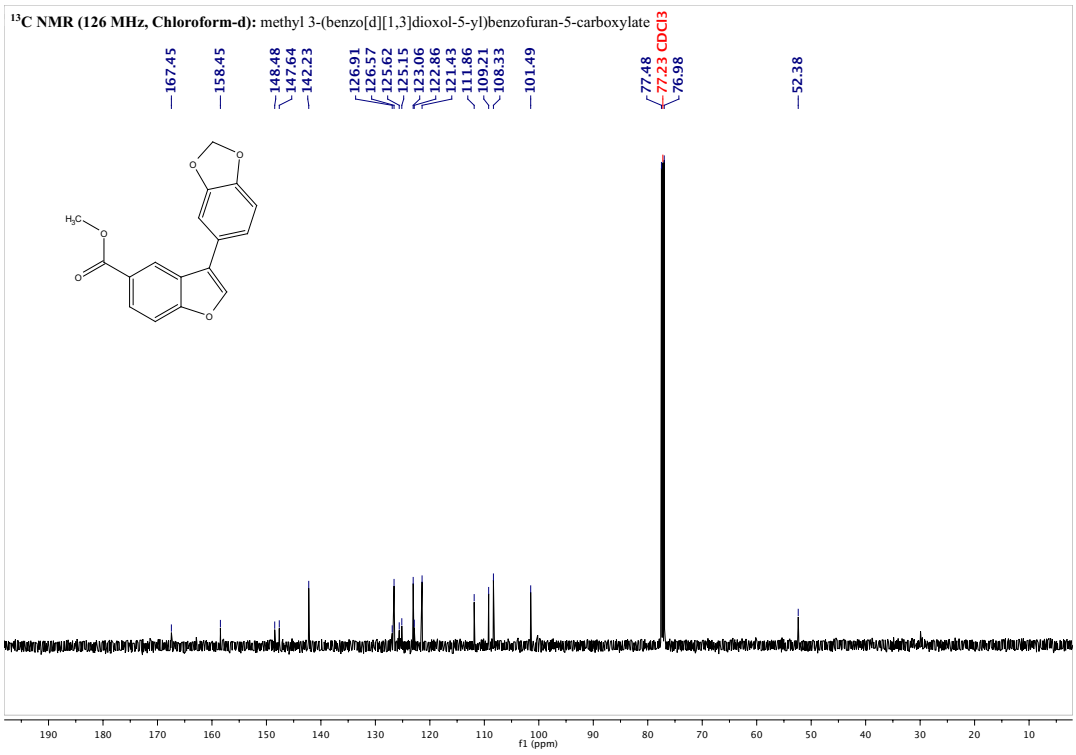

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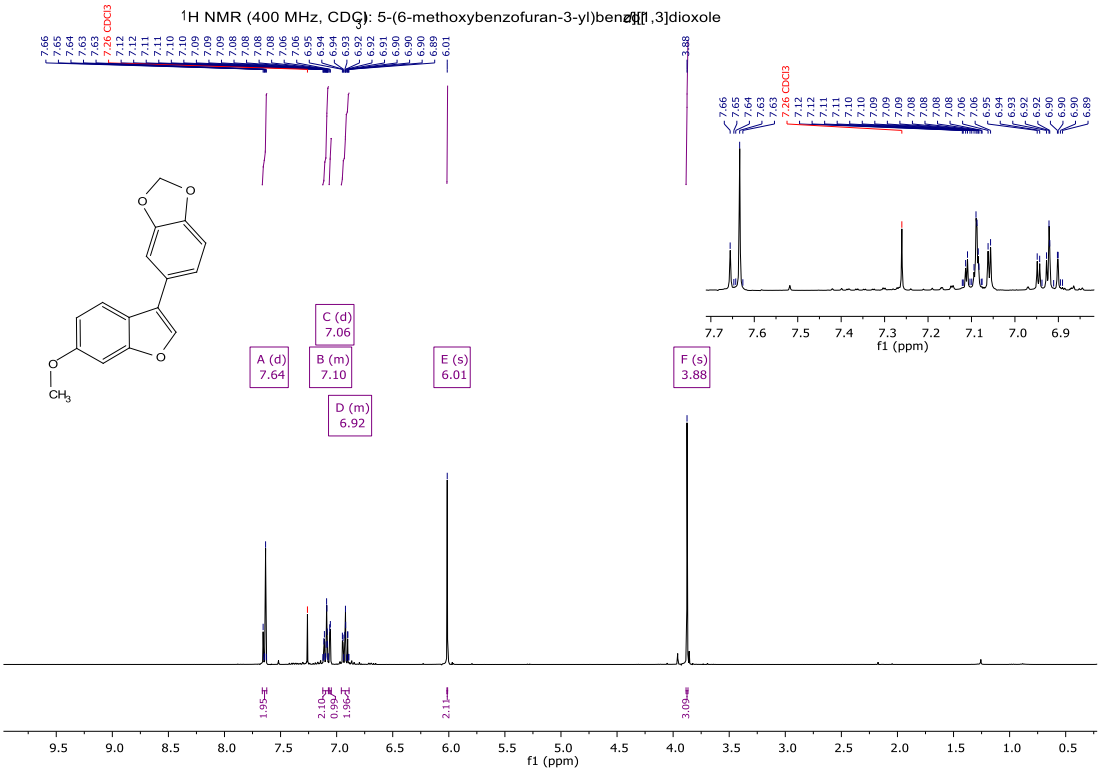

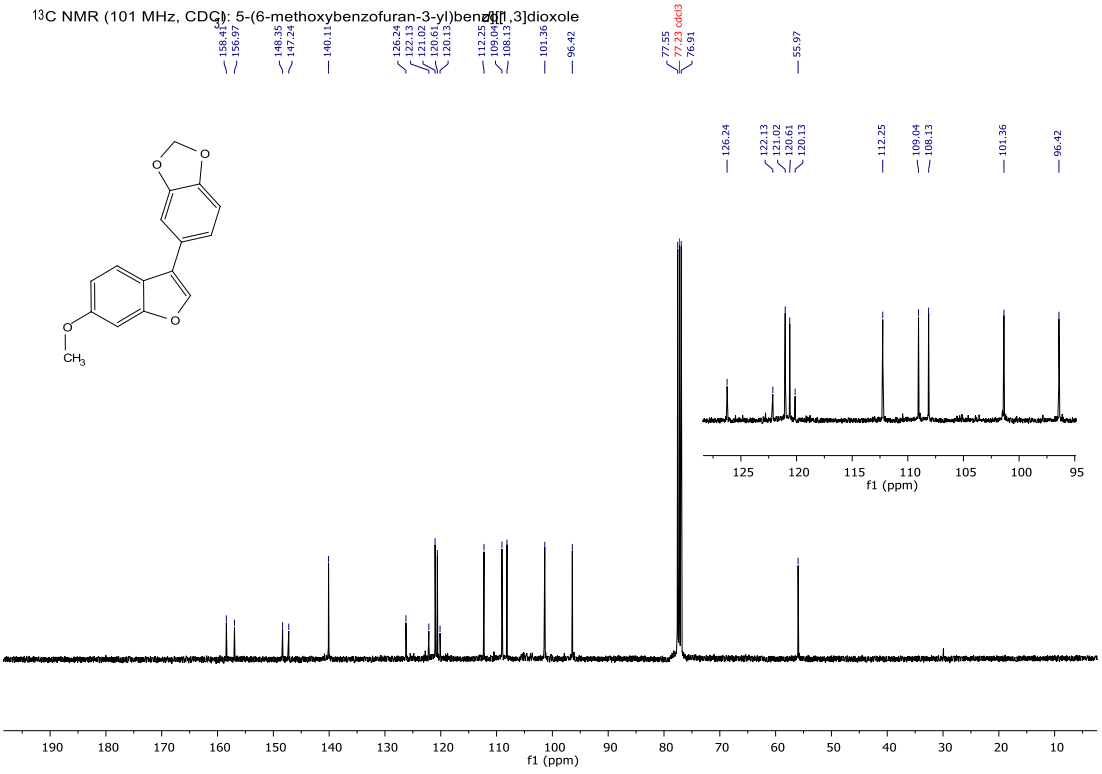

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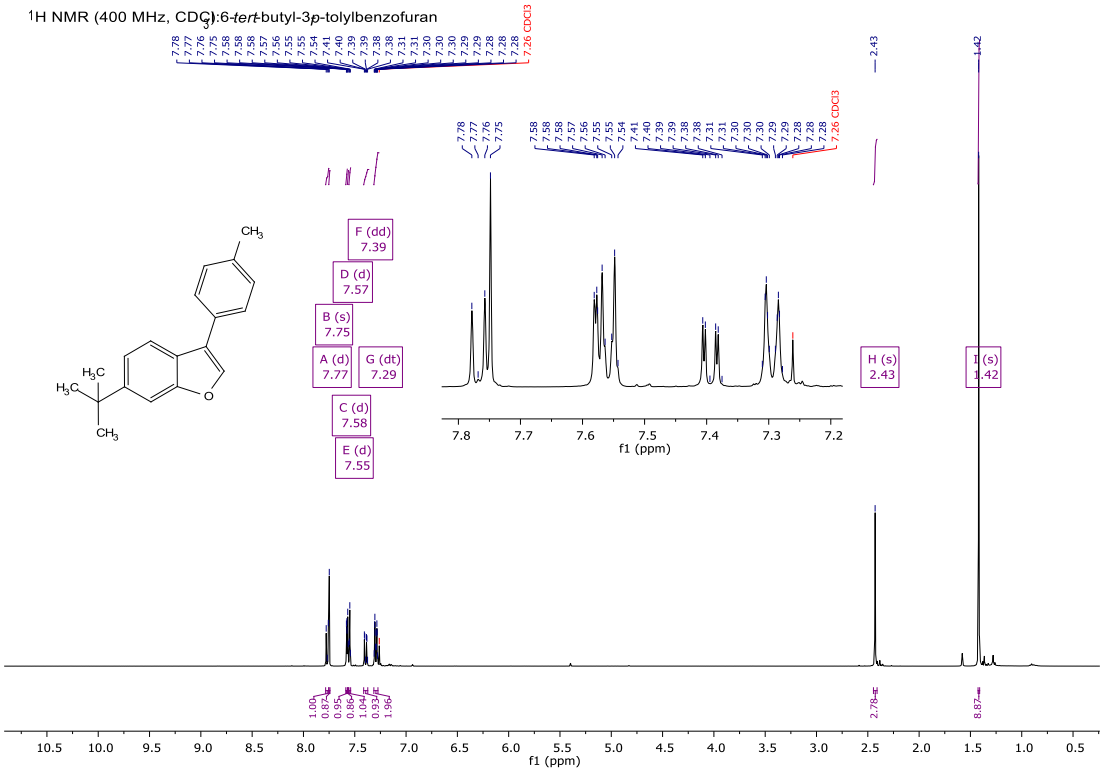

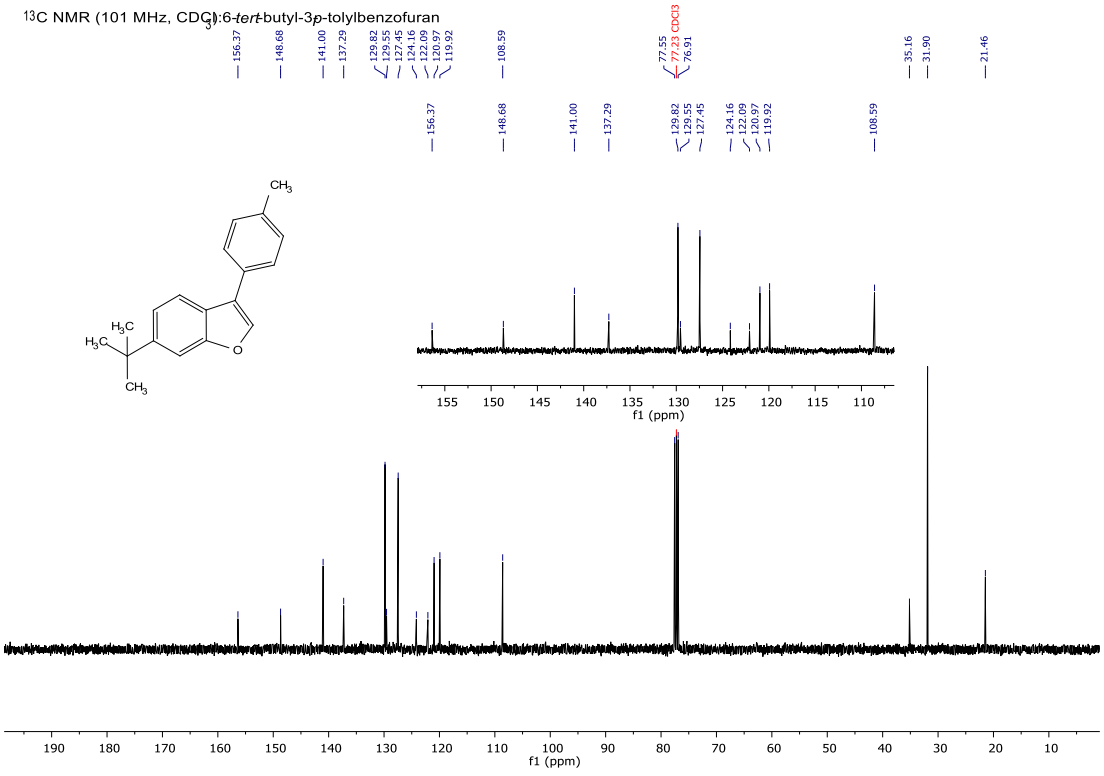

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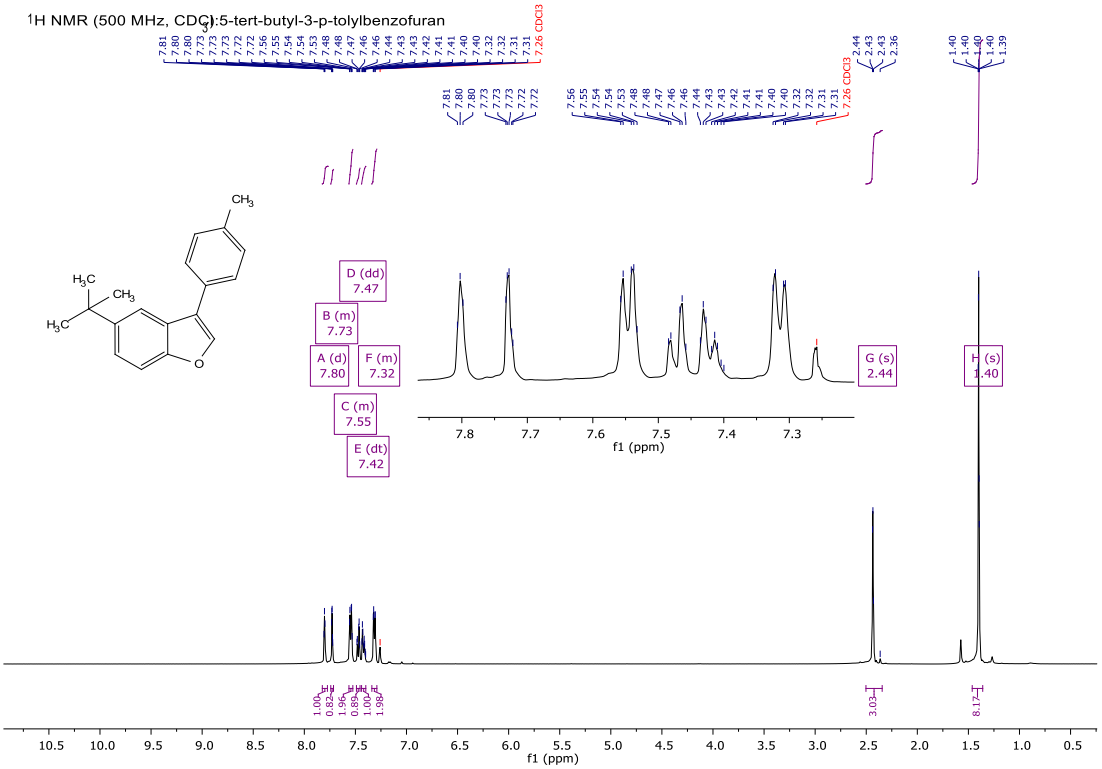

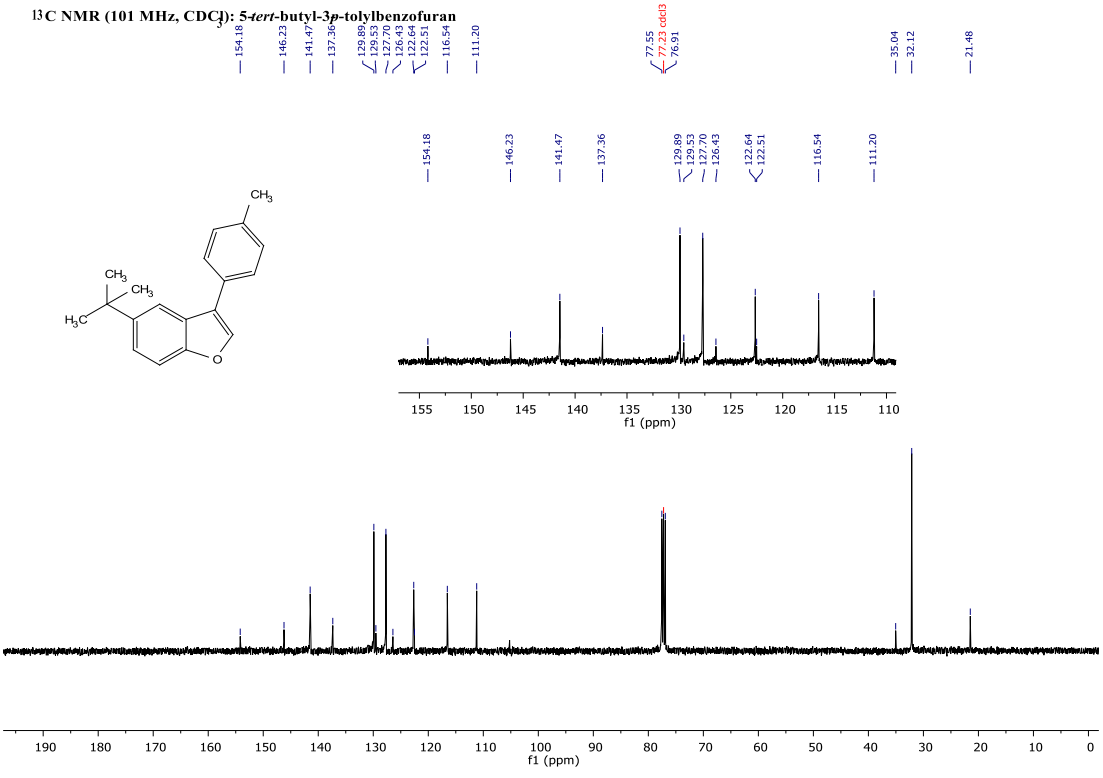

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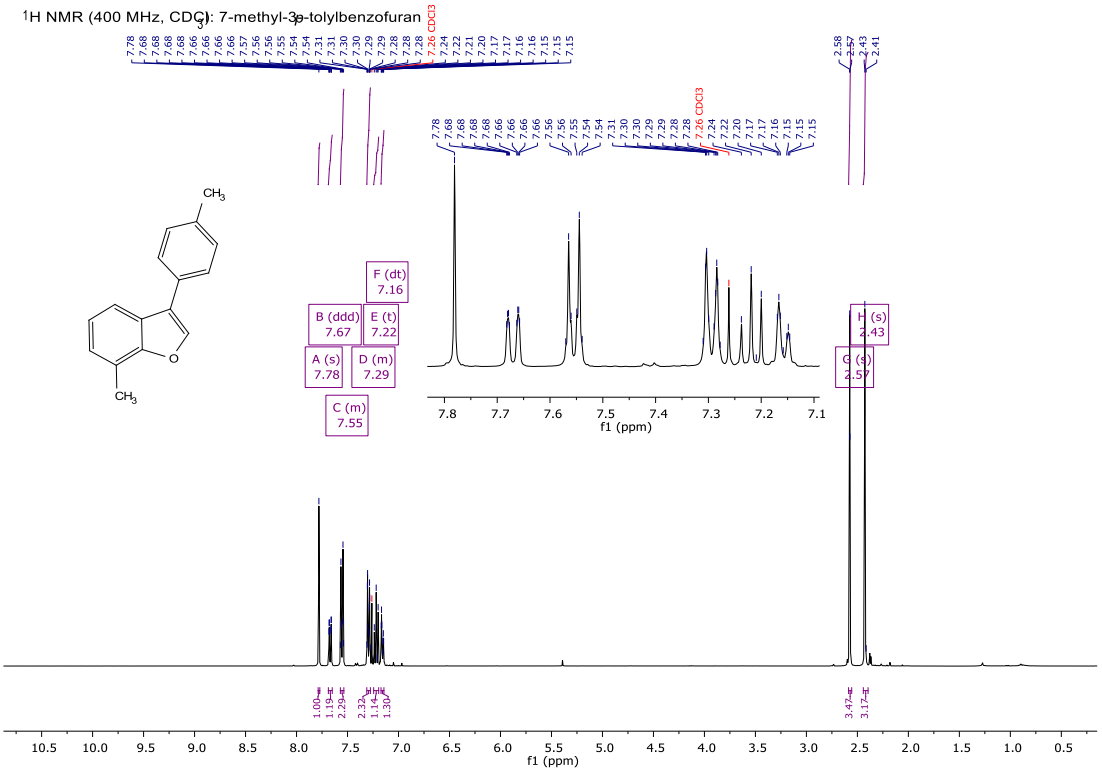

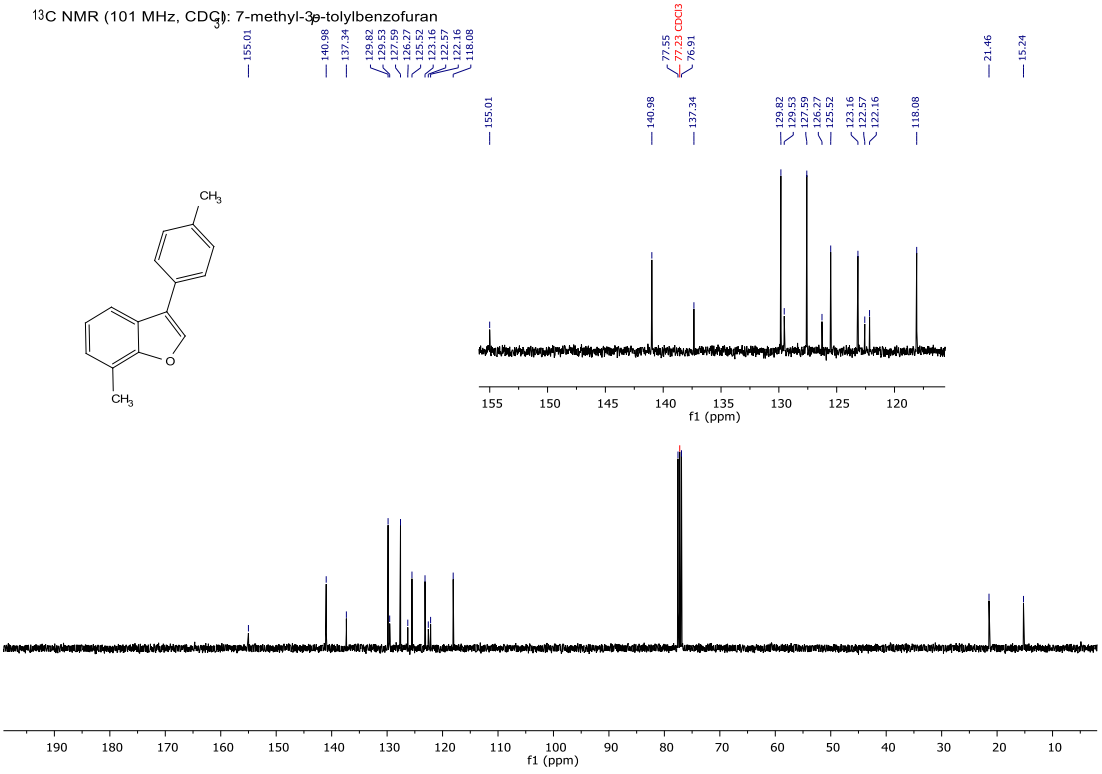

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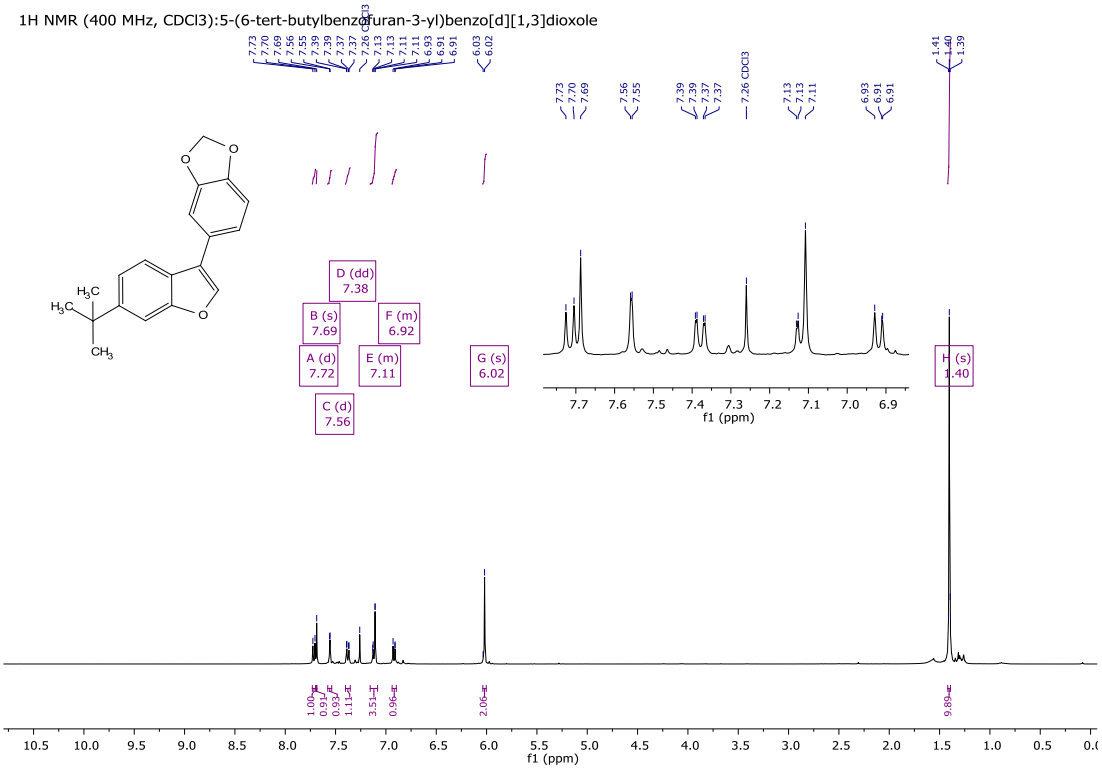

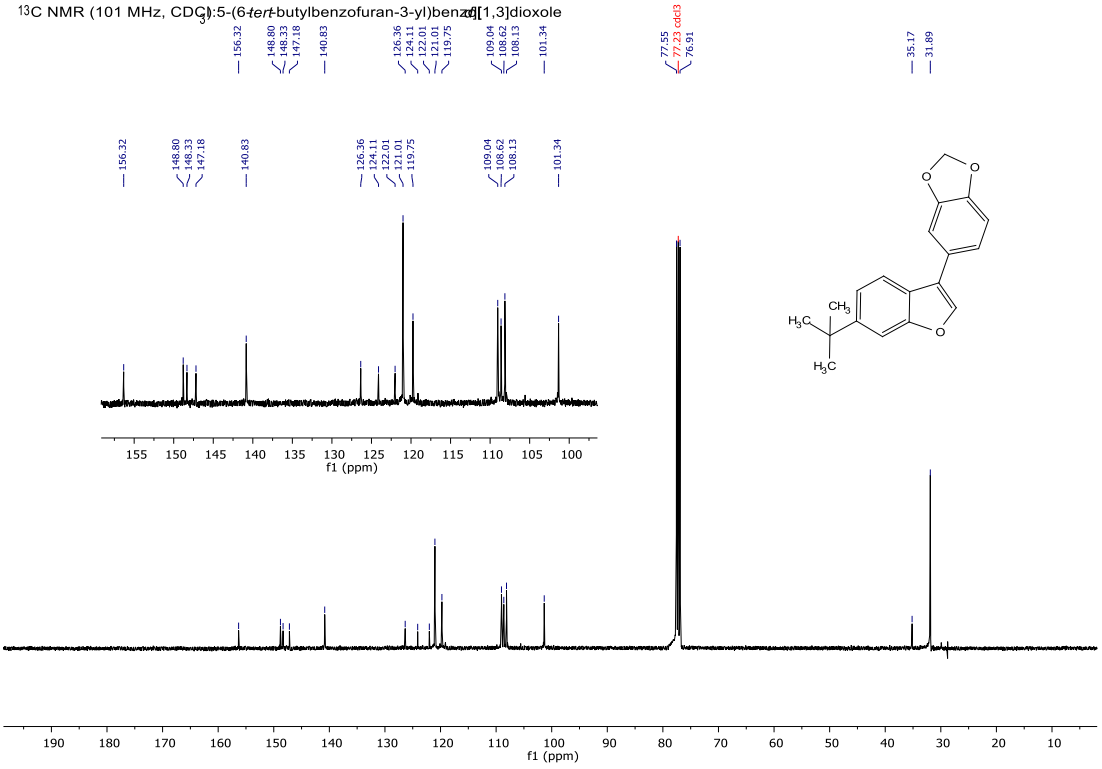

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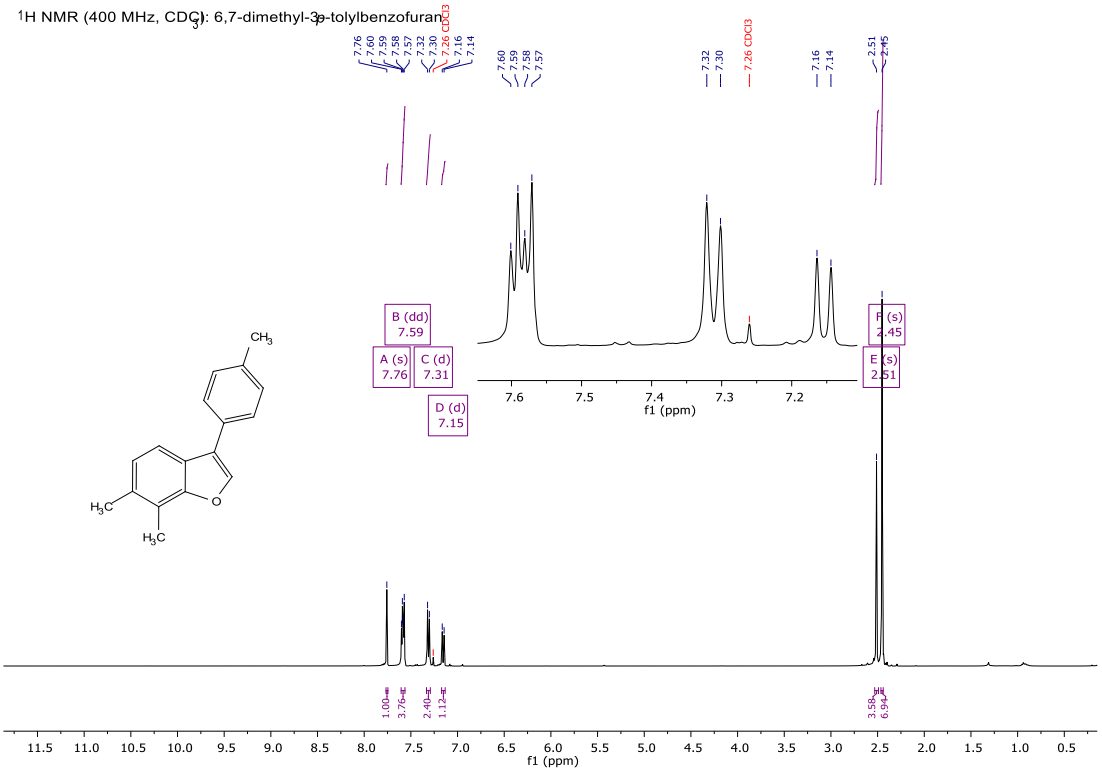

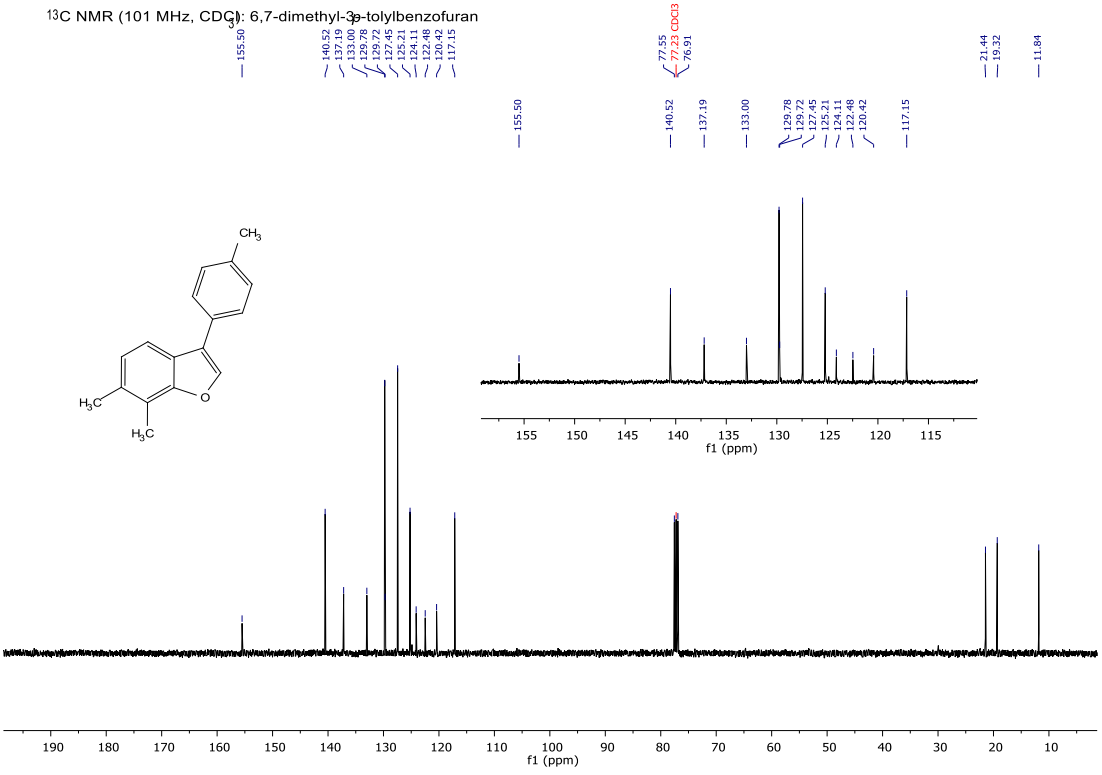

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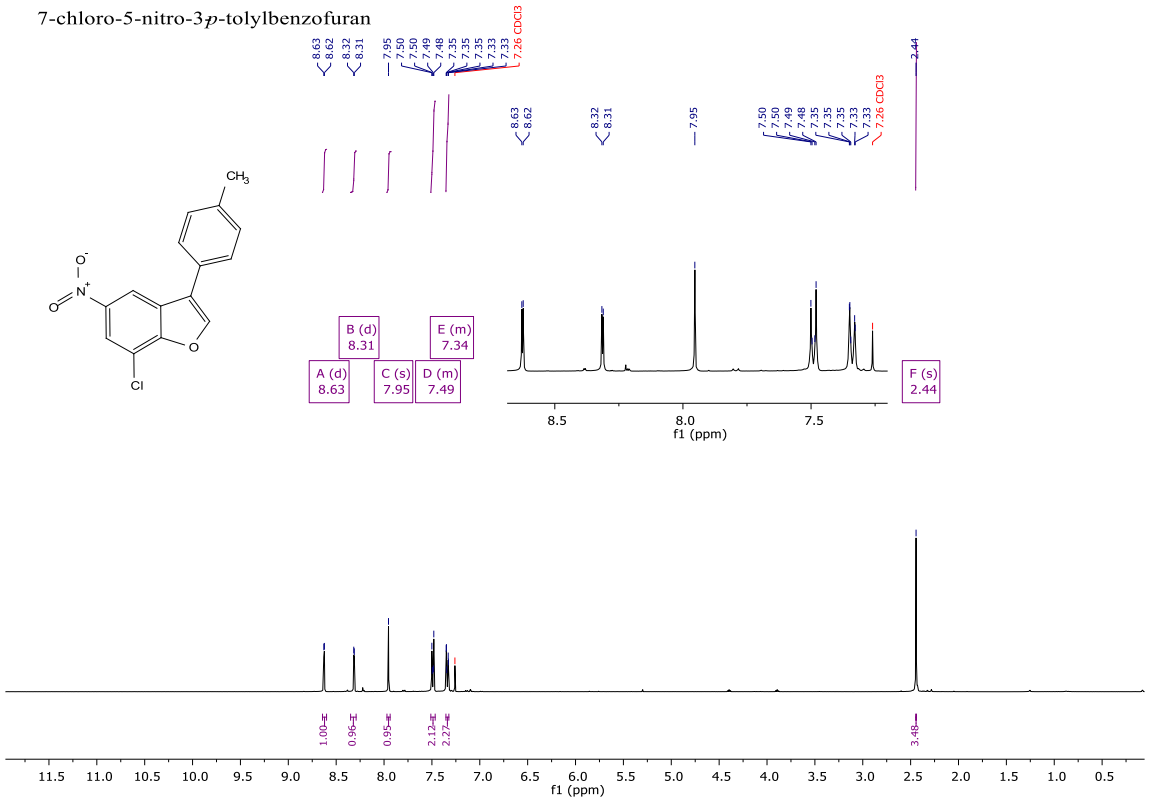

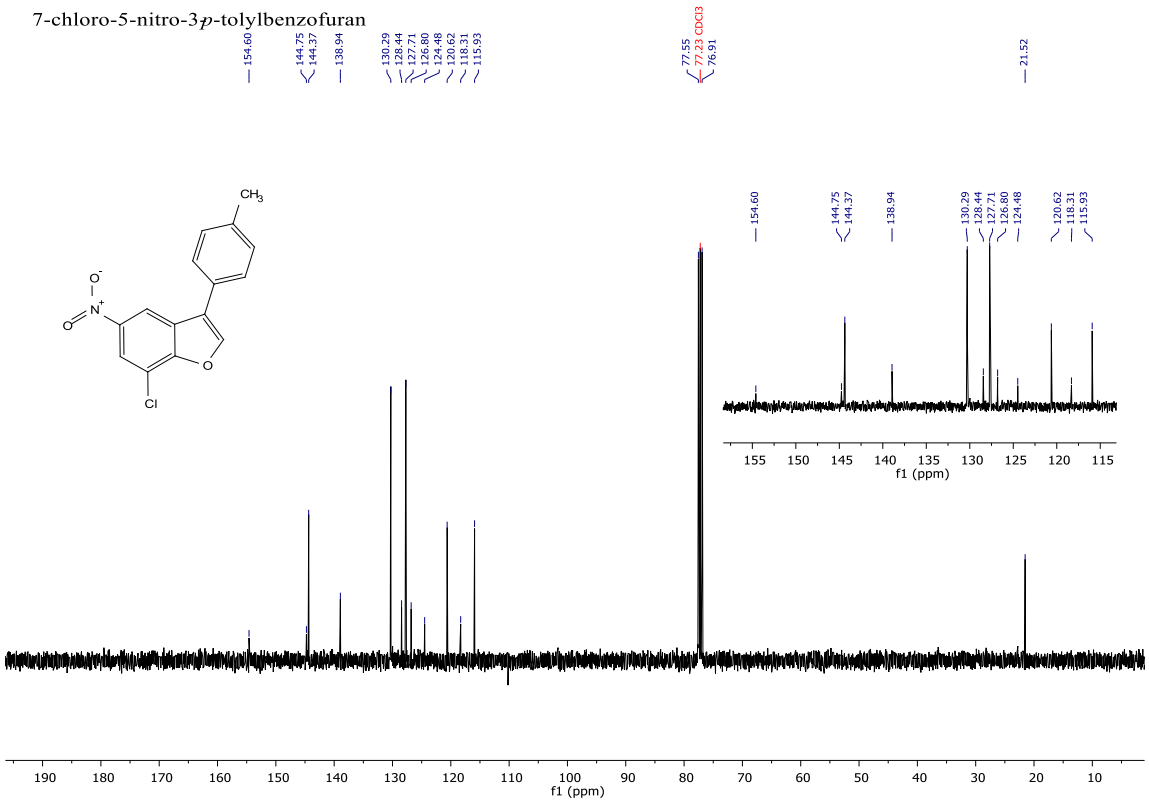

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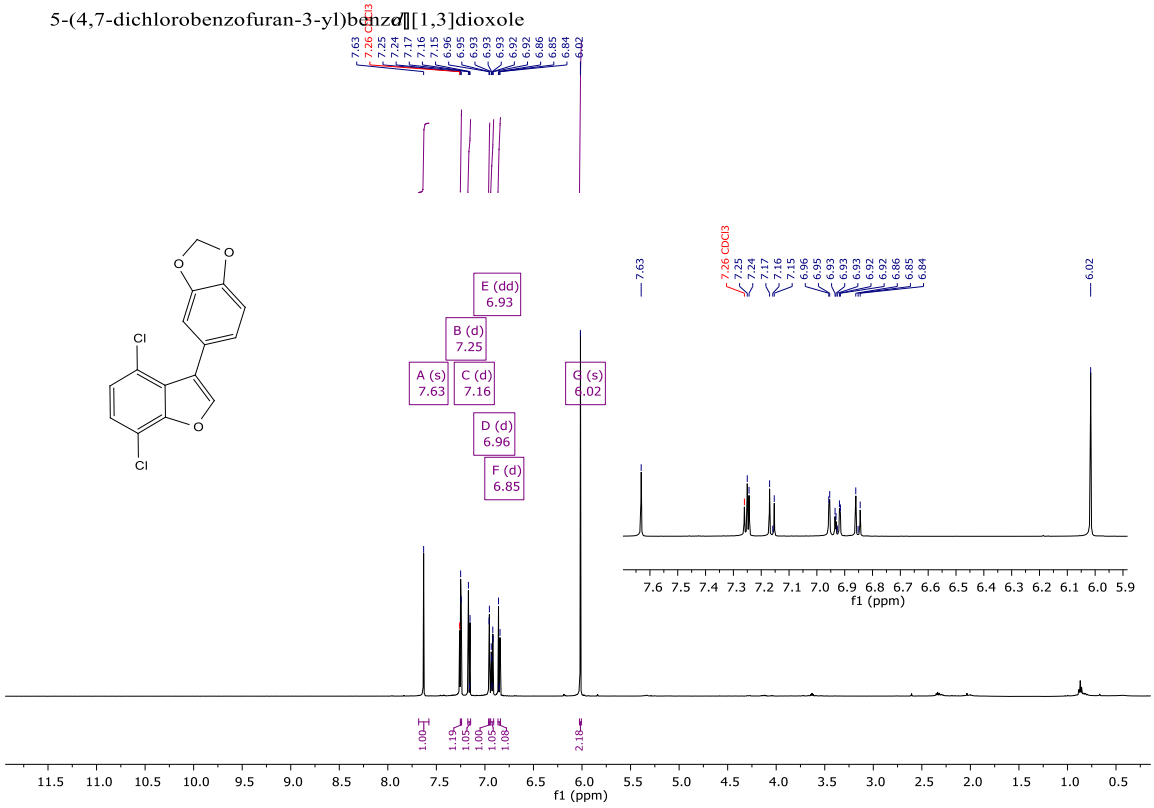


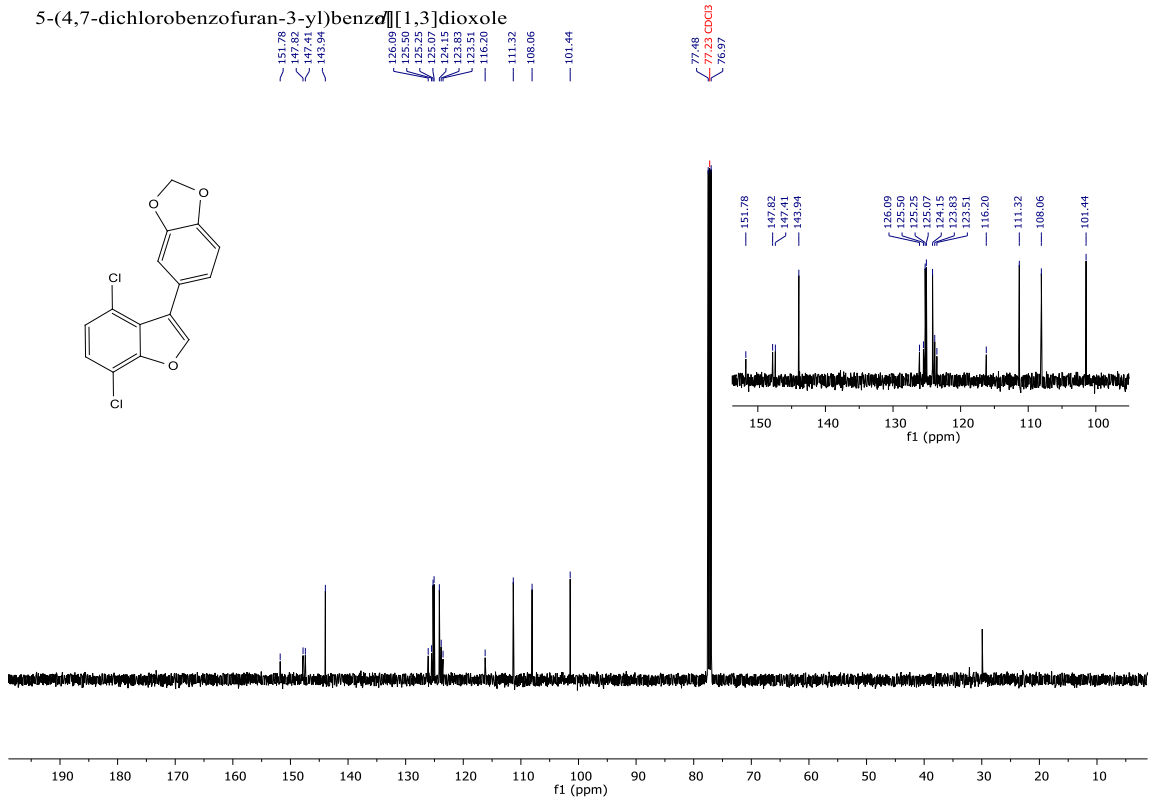
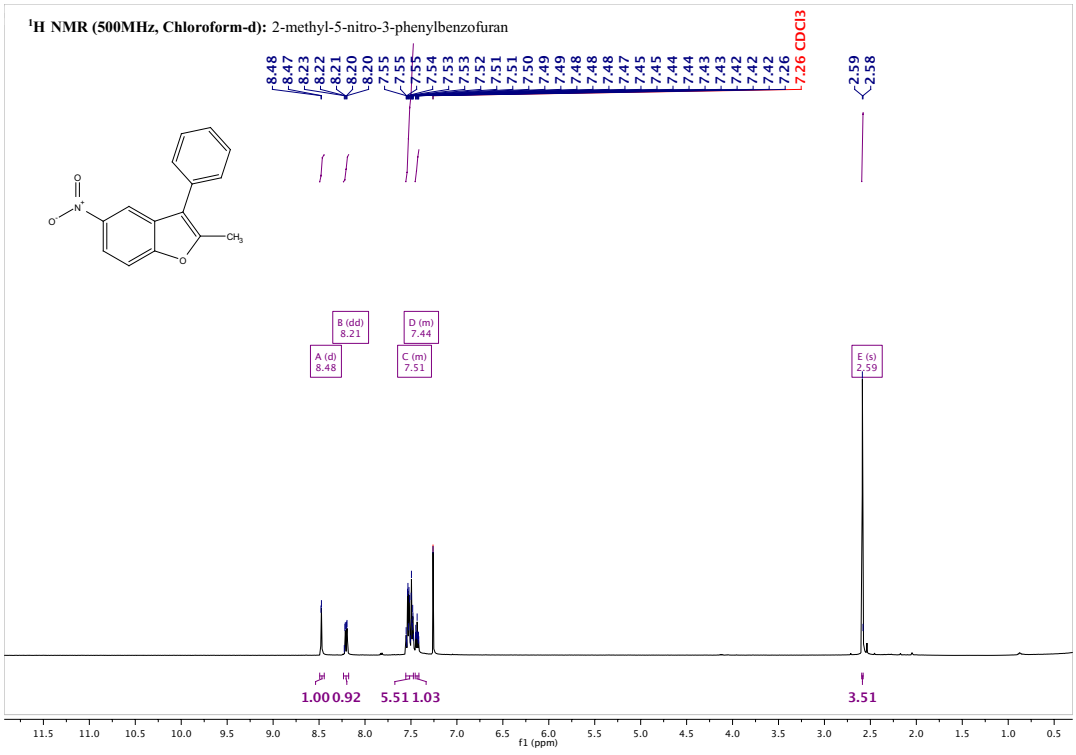


Table 2, Entry 5a:



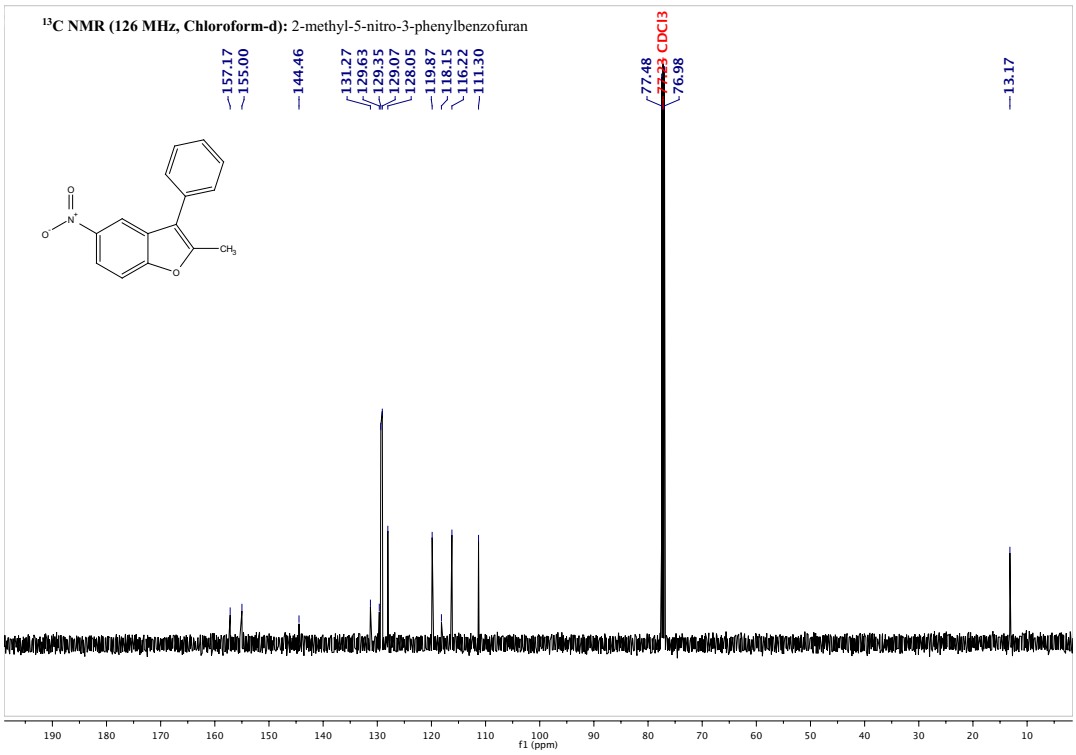
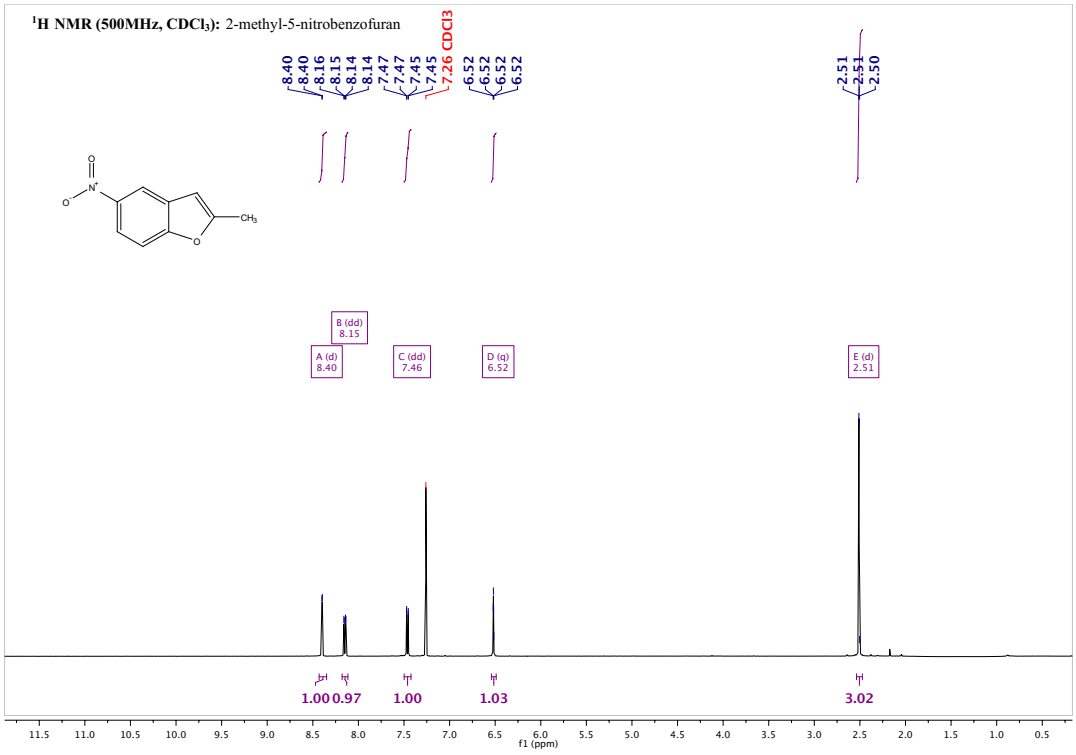
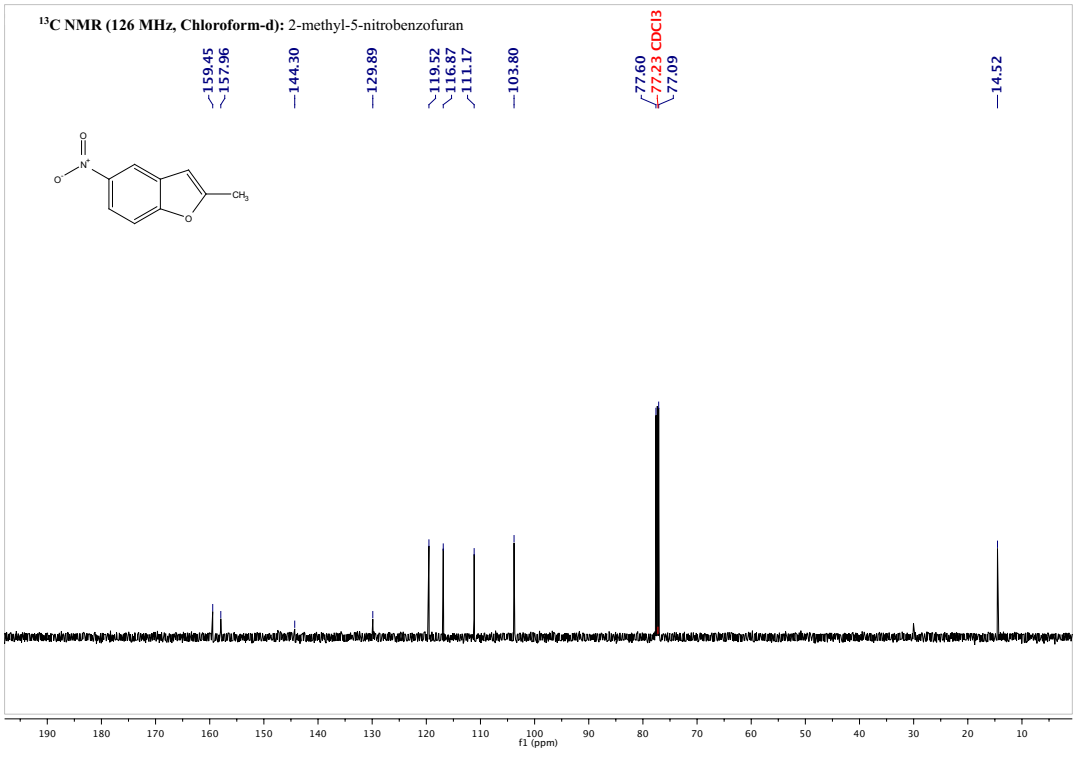
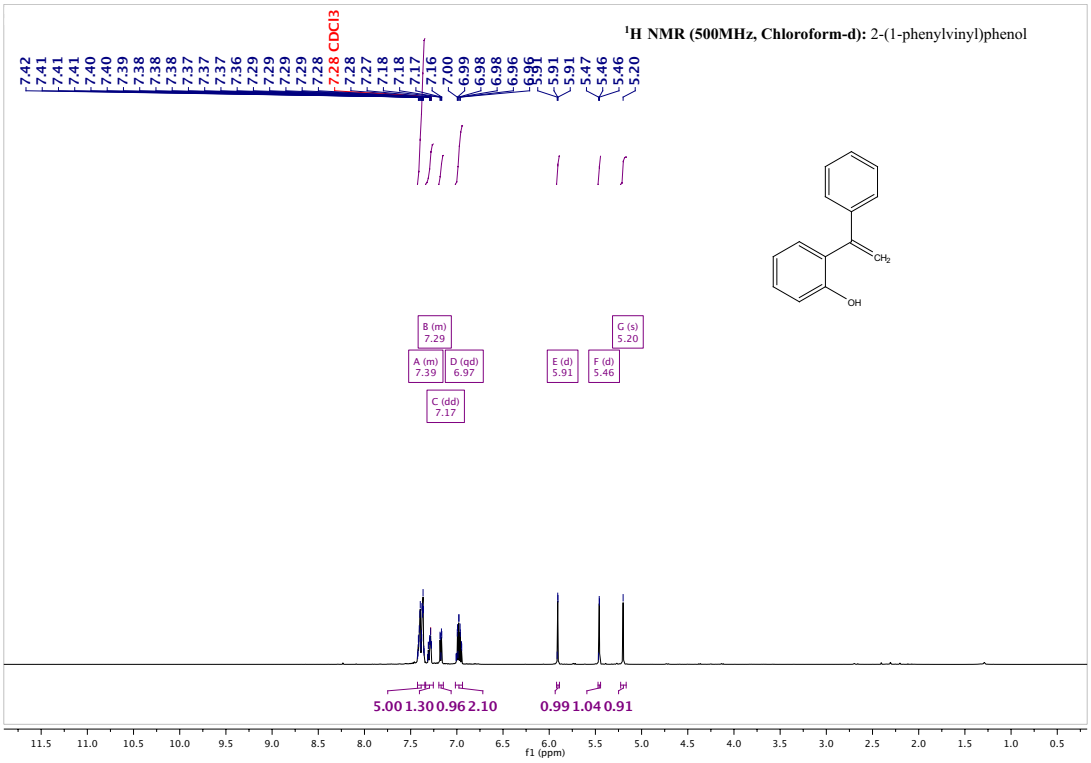


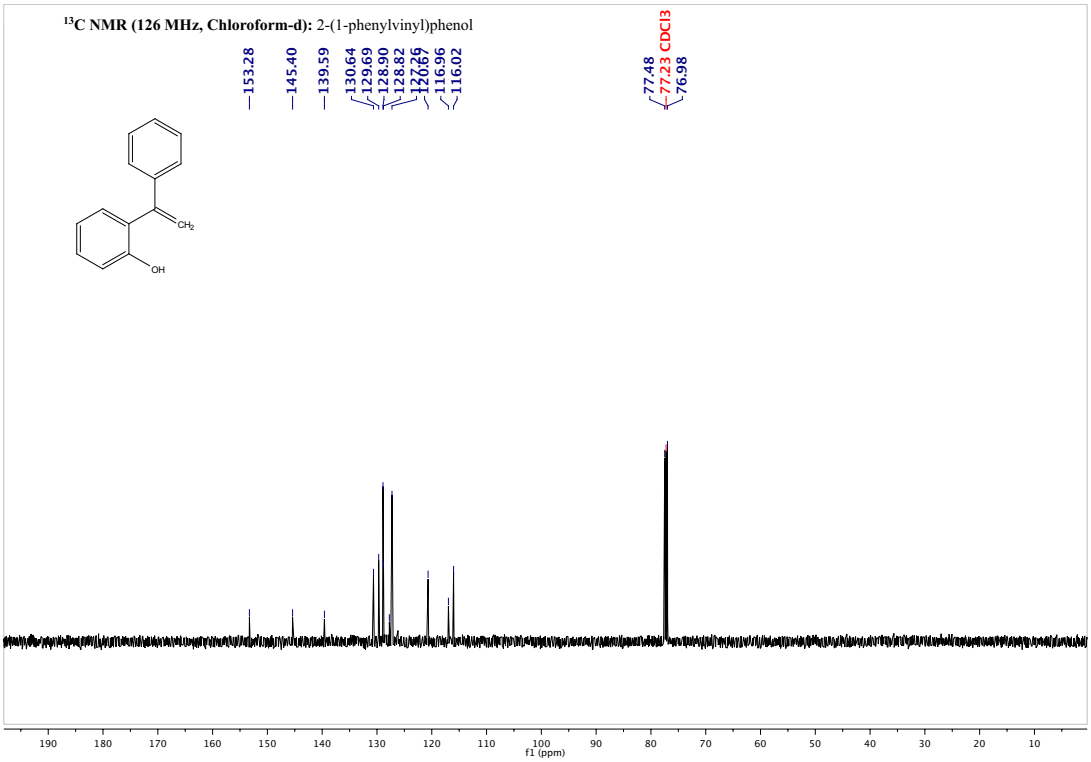
Table 2, Entry 5b:



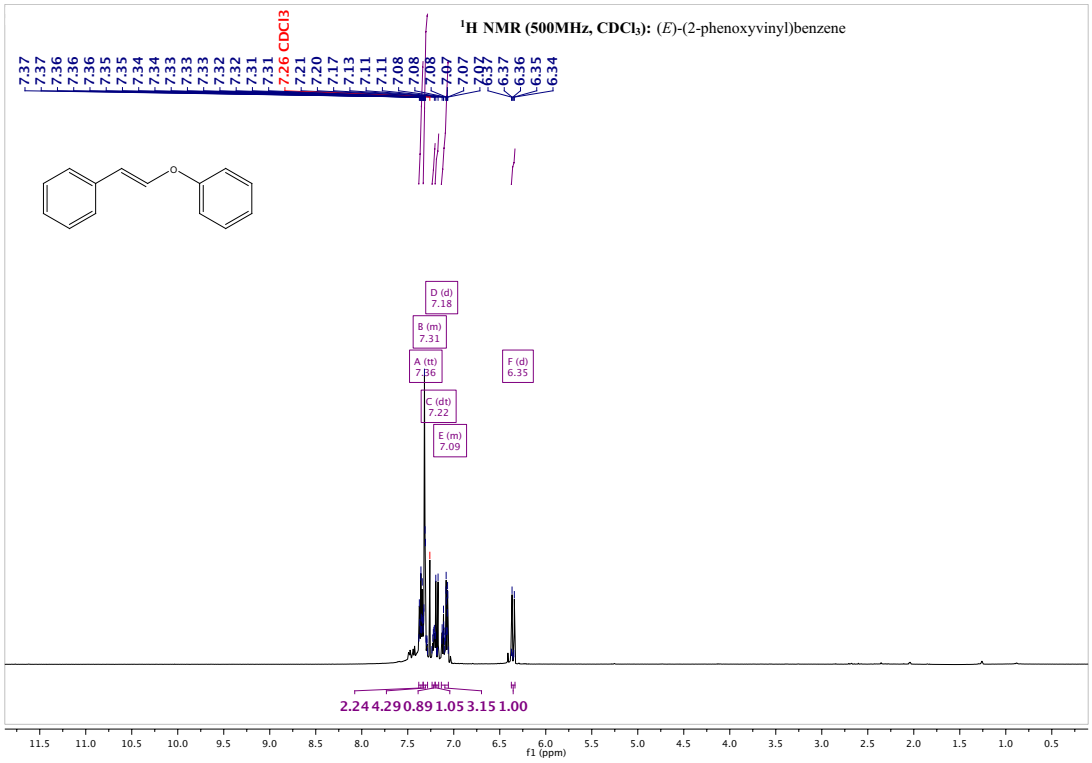


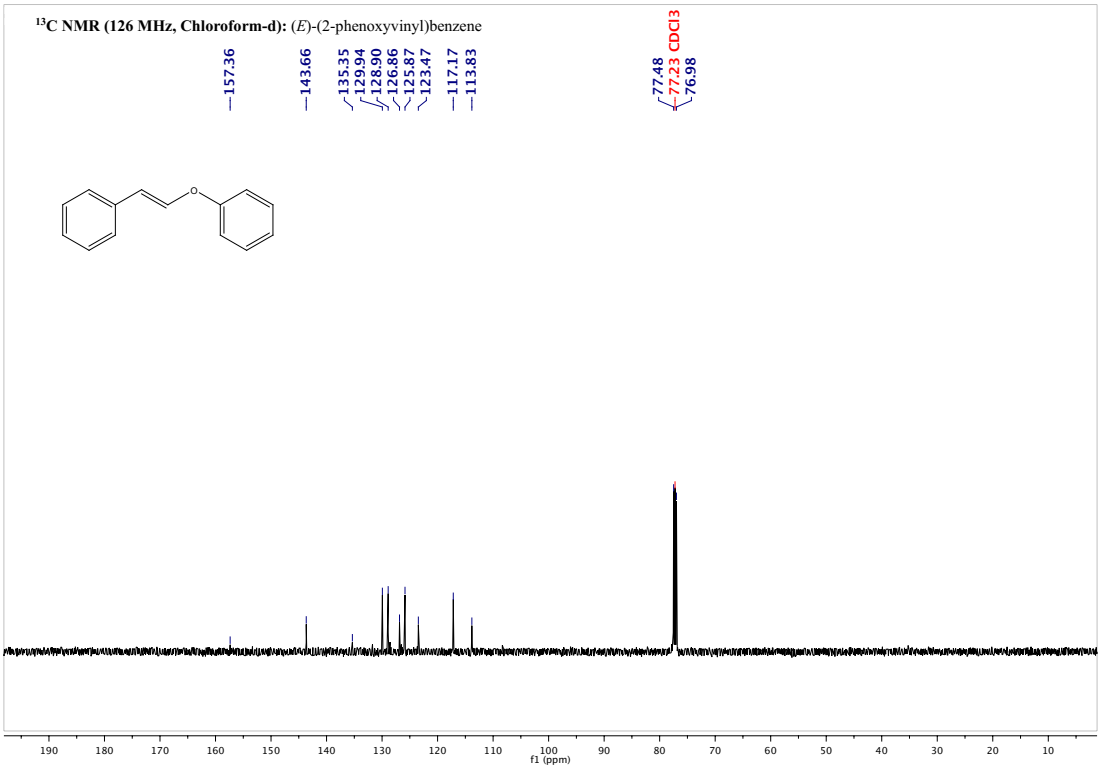
Scheme 3, Compound 6:



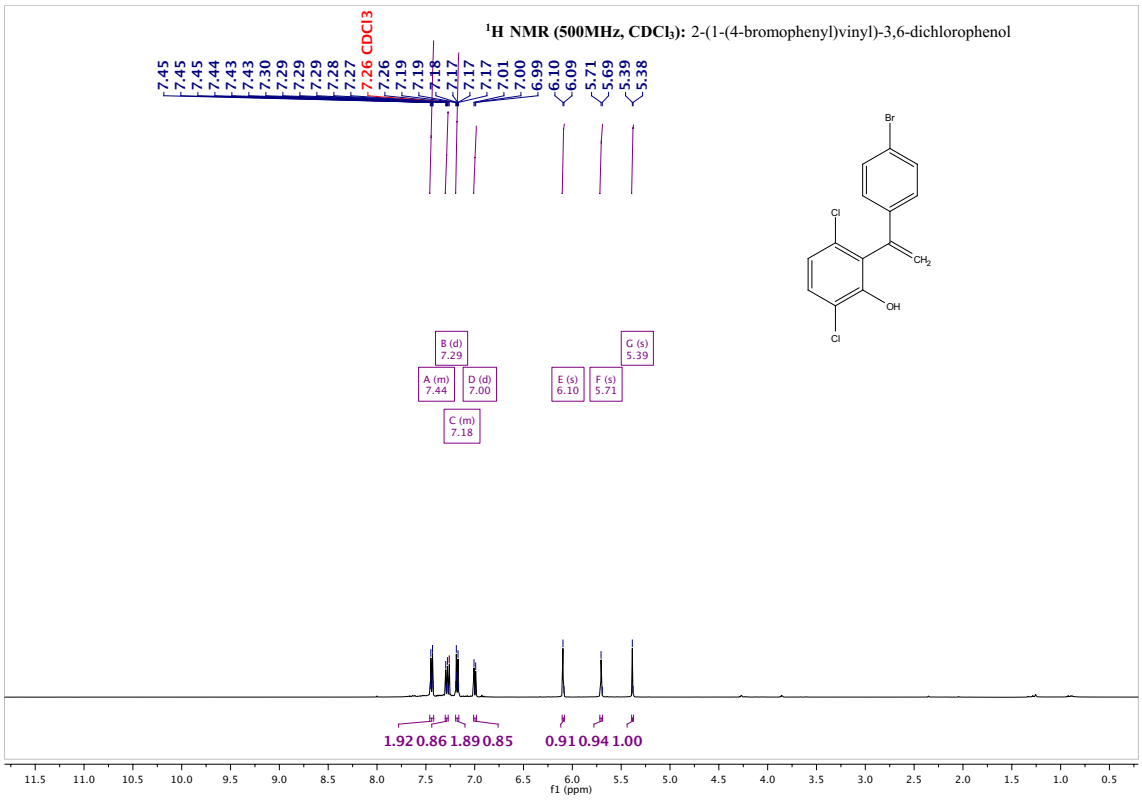


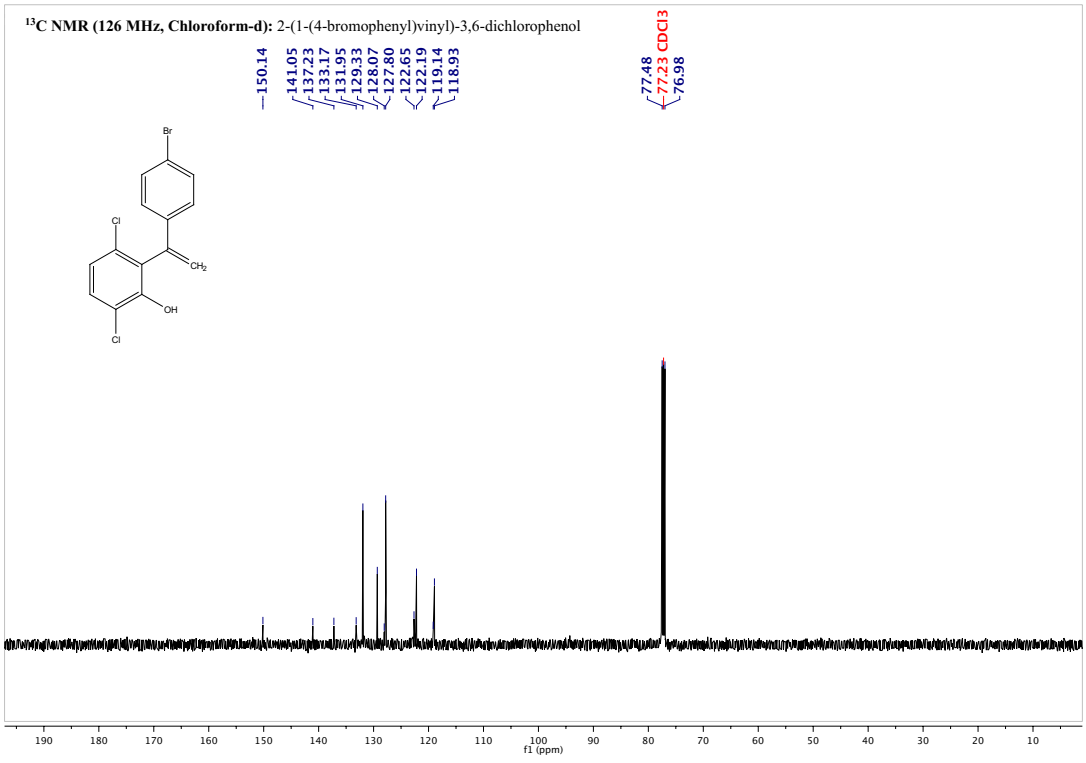
Scheme 3, Compound 7:

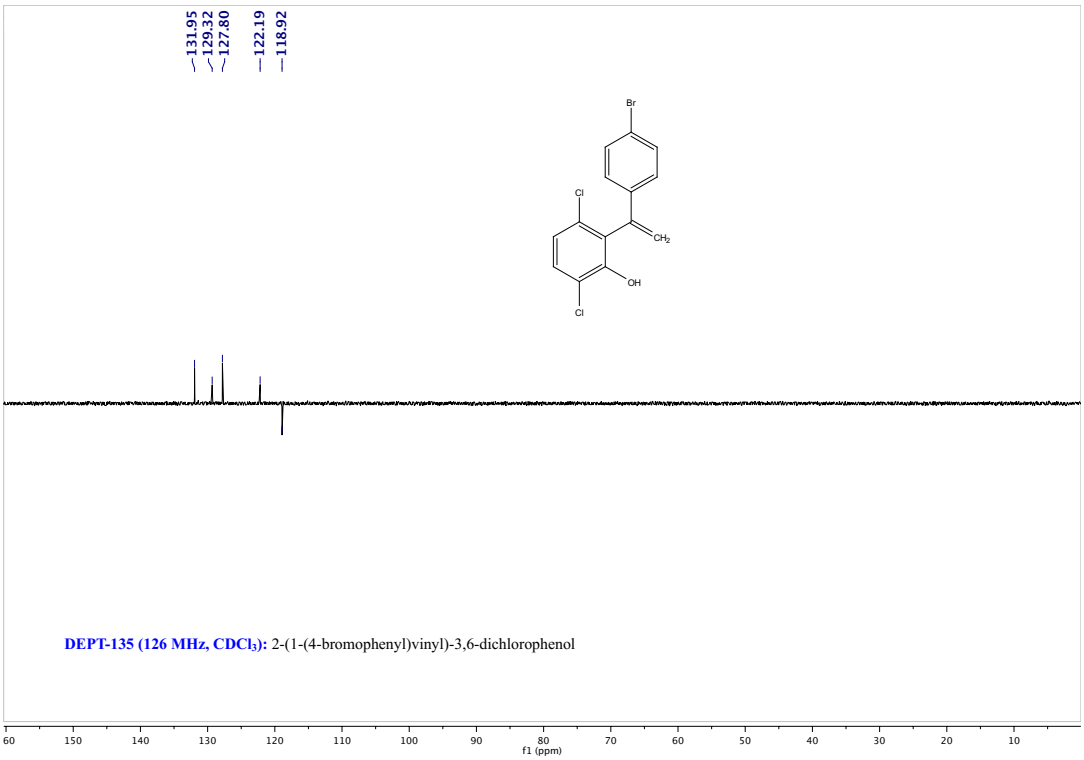




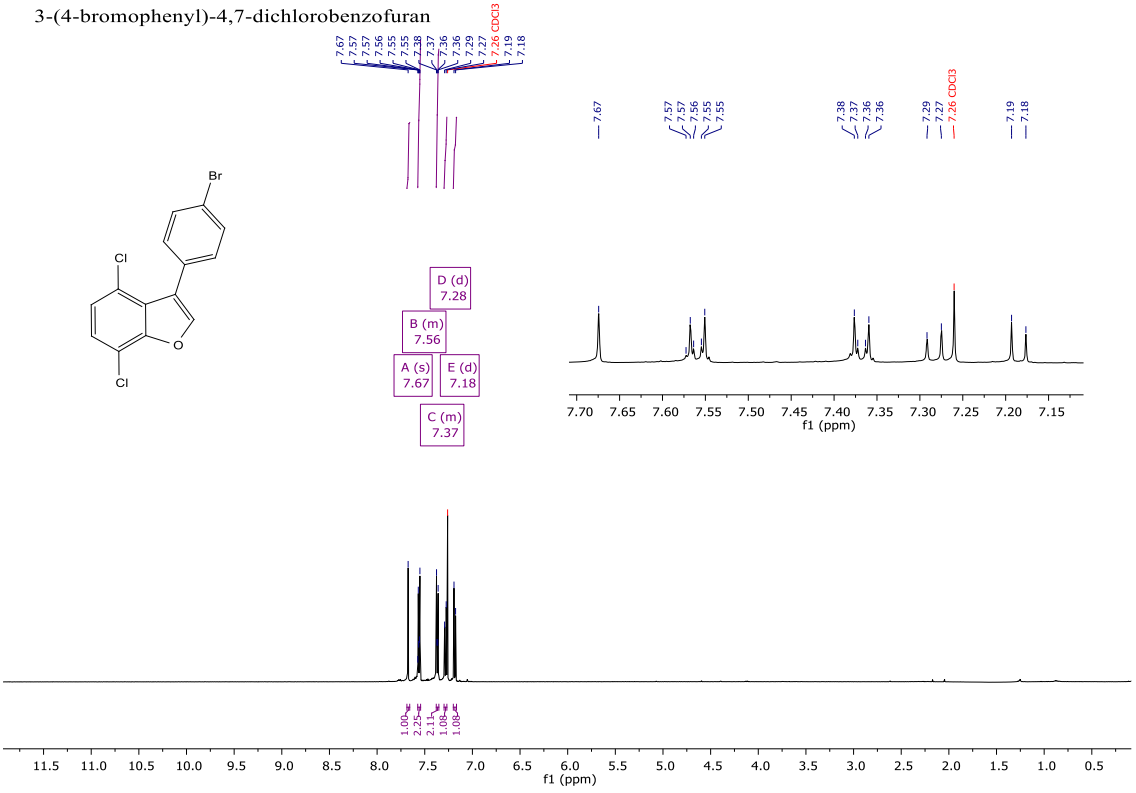
Scheme 4, Compound 8:



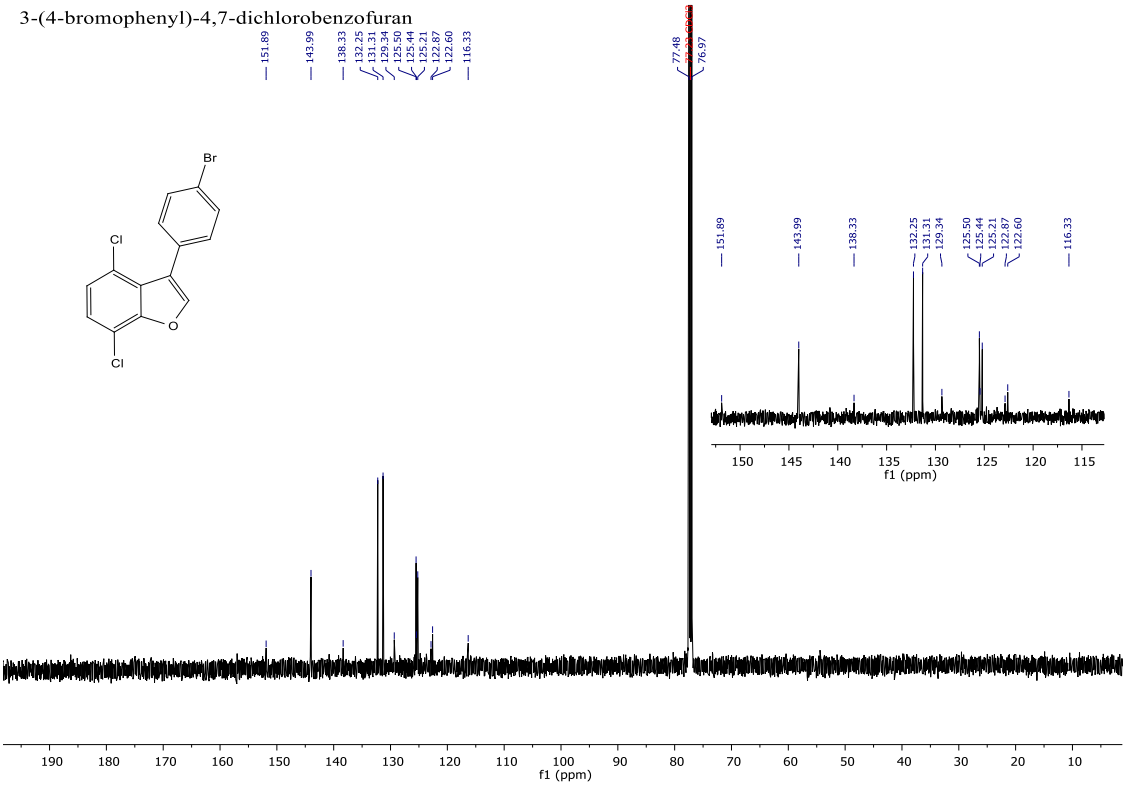


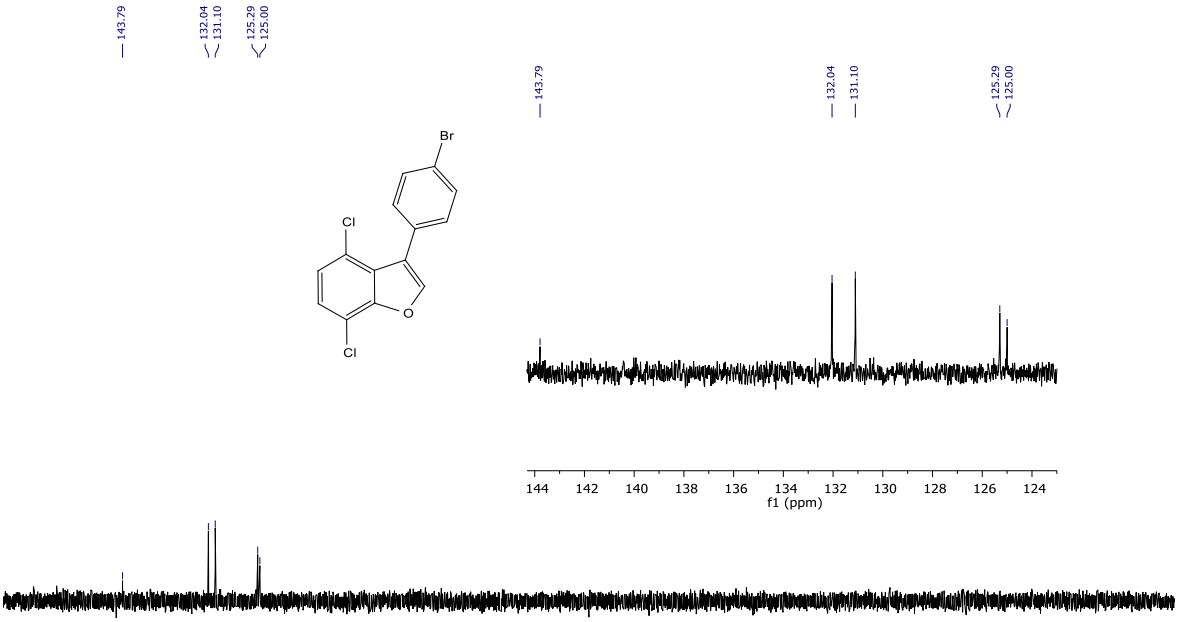


Scheme 4, Compound 9:



3-(4-bromophenyl)-4,7-dichlorobenzofuran





DEPT-135 (126 MHz, CDCl3): 3-(4-bromophenyl)-4,7-dichlorobenzofuran