Supporting Information

Photoinduced Radical Selective *O*-Alkenylation of Phenols and Naphthols with Terminal Alkynes

V. Praveen Kumar[a,b], C. S Athira[a,b], B. Mohan[a,b] , S. Priya[b,c], and B. S. Sasidhar*[,a,b]

[a] *Chemical Sciences and Technology Division,, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram-695019, Kerala, India.*

[b] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India*

[c] *Agro-processing and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram-695019, Kerala, India.*

drsasidharbs@niist.res.in and drsasidharbs@gmail.com

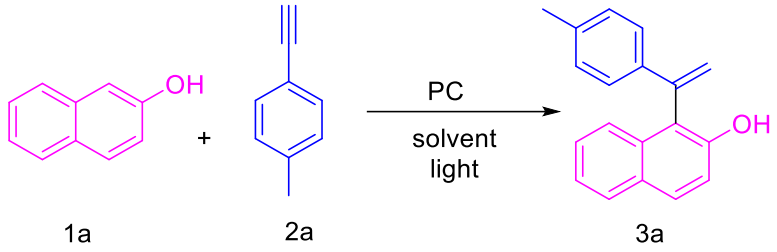
CONTENT

1. General Methods

1.1 General Experimental Methods

All the reactions are performed with commercially available best-grade chemicals without further purification. All of the solvents used are reagent-grade and commercially available. Column chromatography was performed using 100−200 mesh silica gel, and mixtures of hexane−ethyl acetate were used for the elution of the products. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 500 spectrometer ($CDCl_3$ as solvent). Chemical shifts for ^{1} H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.25, singlet) Multiplicities are given as s (singlet); d (doublet); t (triplet); *q* (quartet); dd (doublet of doublet); dt (doublet of triplet); m (multiplet). Coupling constants are reported as *J* values in Hz. Carbon nuclear magnetic resonance spectra $^{13}C\{^{1}H\}$ NMR are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.03, triplet). The mass spectra were recorded under EI/HRMS at 60,000 resolutions using a Thermo Scientific Exactive mass spectrometer.

Table S1: optimisation of reaction conditions[a]



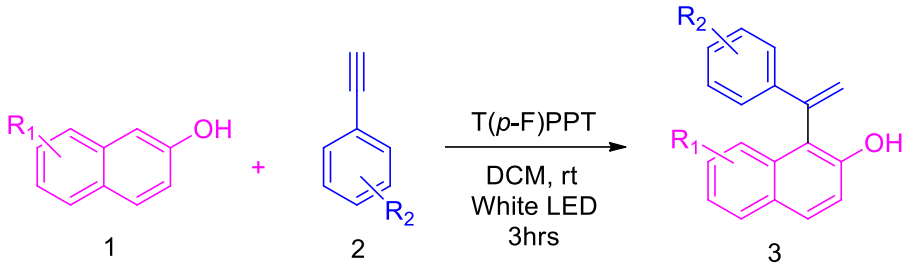
entry	1a (equiv.)	2a (equiv.)	photocatalyst	Additive (oxidant)	solvent	Light source	yield (%)
1	1	1.2	T(*p*-F)PPT	-	DCM	White LED	40
2	1	2	T(*p*-F)PPT	-	DCE	White LED	15
3	1	2	T(*p*-F)PPT	-	CH_3CN	White LED	N.D
4	1	2	T(*p*-F)PPT	-	MeOH	White LED	N.D
5	1	2	T(*p*-F)PPT	-	HFIP	White LED	N.D
6	1	2	T(*p*-F)PPT	-	TFE	White LED	N.D
7	1	2	T(*p*-F)PPT	-	DCM	White LED	89
8	1	2.5	T(*p*-F)PPT	-	DCM	White LED	70
9	1	3	T(*p*-F)PPT	-	DCM	White LED	69
10	1	2	$MesAcr^+BF_4^-$,	-	DCM	White LED	N.D
11	1	2	Eosin Y	-	DCM	White LED	N.D
12	1	2	Rose bengal	-	DCM	White LED	N.D

13	1	2	TPPT	-	DCM	White LED	N.D
14	1	2	T(*p*-Cl)PPT	-	DCM	White LED	15
15	1	2	T(*p*-Me)PPT	-	DCM	White LED	N.D
16	1	2	T(*p*-OMe)PPT	-	DCM	White LED	trace
17	1	2	T(*p*-F)PPT	-	TFE	White LED	18
18	1	2	T(*p*-Br)PPT	-	DCM	White LED	5
19	1	2	T(*p*-F)PPT	-	DCM	White LED	80[b]
20	1	2	T(*p*-F)PPT	-	DCM	White LED	78[c]
21	1	2	T(*p*-F)PPT	$K_2S_2O_8$	DCM	White LED	ND
22	1	2	T(*p*-F)PPT	$(NH_4)_2S_2O_8$	DCM	White LED	trace
23	1	2	T(*p*-F)PPT	$Na_2S_2O_8$	DCM	White LED	trace
24	1	2	No catalyst	-	DCM	White LED	ND
25	1	2	T(*p*-F)PPT	-	DCM	No light	ND
26	1	2	T(*p*-F)PPT	-	DCM	Green LED	ND
27	1	2	T(*p*-F)PPT	-	DCM	Red LED	ND

[a]unless otherwise mentioned **1a** (0.3468 mmol), **2a** (2 equiv.) and 5 mol% catalysts in 1 mL of solvent. [b]10 mol% catalyst added. [c]15 mol% catalyst added. ND: Not detected

2. Experimental procedures

2.1 General procedure for preparation of 2-hydroxy styrenes



1 2 3

To a 5 dram glass vial equipped with a magnetic stir bar **1** (0.3468 mmol), **2** (0.6936 mmol), 1 mL of DCM solvent and photocatalyst T(*p*-F)PPT (5 mol%) were sequentially added. The solution was stirred at a distance of ~3 cm from 20 W white LED at room temperature. After the completion of the reaction monitored by TLC, the solvent was removed in *vacuo* and extracted with ethyl acetate (3x10 ml), organic layers were dried over Na_2SO_4 and evaporated in vacuo and purified by column chromatography using 100–200 mesh silica gel with ethyl acetate/hexane (1:9) as the eluent to afford the corresponding hydroarylated compounds as the product.

2.1.1 Procedure for the gram scale preparation of 2-hydroxy styrenes

To a 5 dram glass vial equipped with a magnetic stir bar **1** (0.010 mol), **2** (0.020 mol) DCM solvent and photocatalyst T(*p*-F)PPT (5 mol%) were sequentially added. The solution was stirred at a distance of ~3 cm from 20 W white LED at room temperature. After the completion of the reaction monitored by TLC, the solvent was removed in *vacuo* and extracted with ethyl acetate (3x10 ml), organic layers were dried over Na_2SO_4 and evaporated in vacuo and purified by column chromatography using 100–200 mesh silica gel with ethyl acetate / hexane (1:9) as the eluent to afford the corresponding hydroarylated compounds as products.

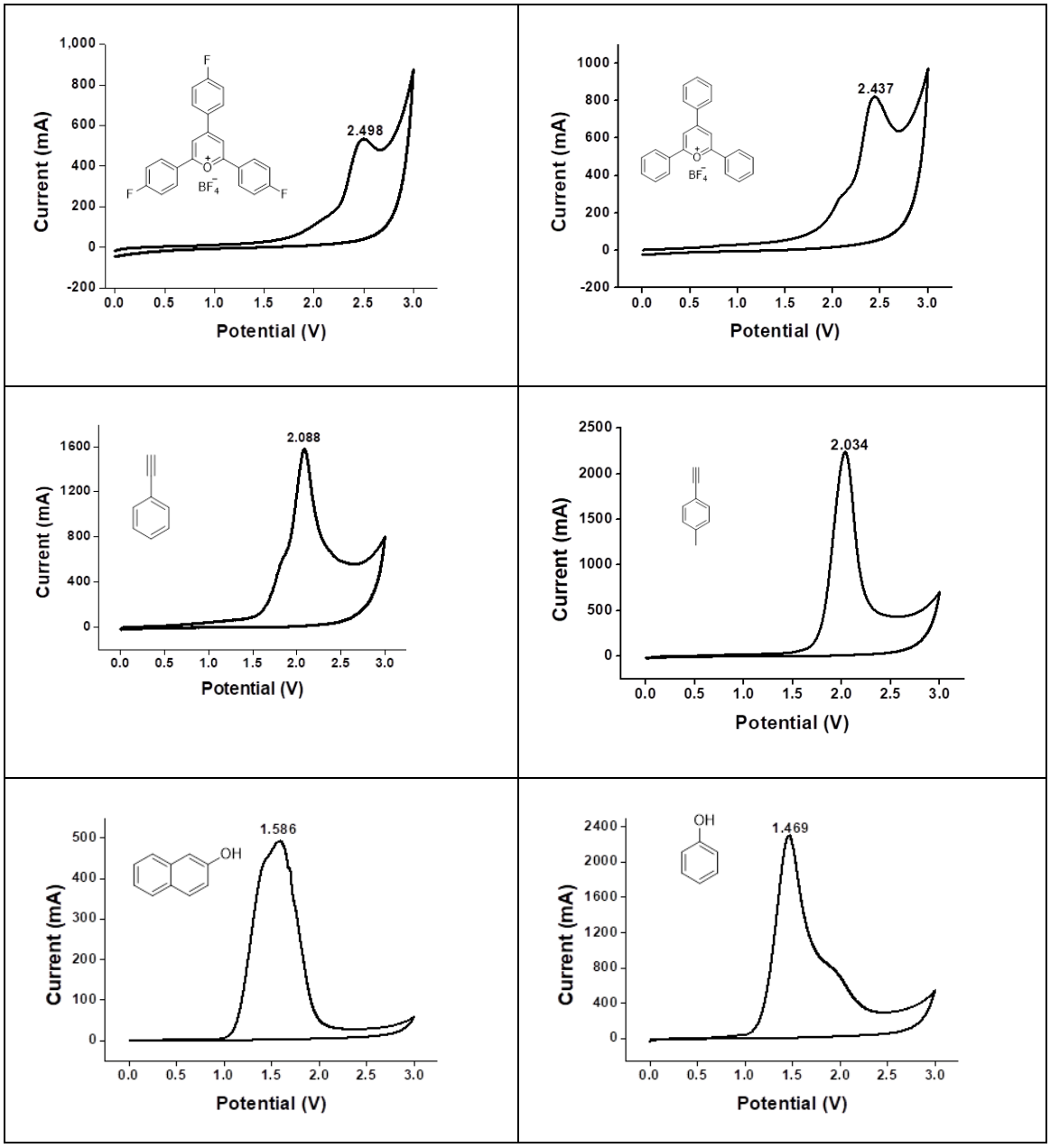


Figure S1. Cyclic voltammetry (CV) measurements

2.2 Control experiments

To a 5 dram glass vial equipped with a magnetic stir bar **1** (0.3468 mmol), **2** (0.6936 mmol), 1 mL of DCM solvent and photocatalyst T(*p*-F)PPT (5 mol%) and TEMPO were sequentially added. The solution was stirred at a distance of ~3 cm from 20W white LED at room temperature. After the completion of the reaction monitored by TLC, the solvent was removed in *vacuo* and extracted with ethyl acetate (3x10 ml), organic layers were dried over Na_2SO_4 and evaporated in vacuo and purified by column chromatography using 100–200

mesh silica gel with ethyl acetate / hexane (1:9) as the eluent to afford the corresponding hydroarylated compounds as products.

No hydroarylated products were formed in the presence of the TEMPO reagent instead TEMPO adduct of the 2-Naphthol 1a was detected in LCMS **Figure S2**. Which indicates the involvement of the radical pathway.

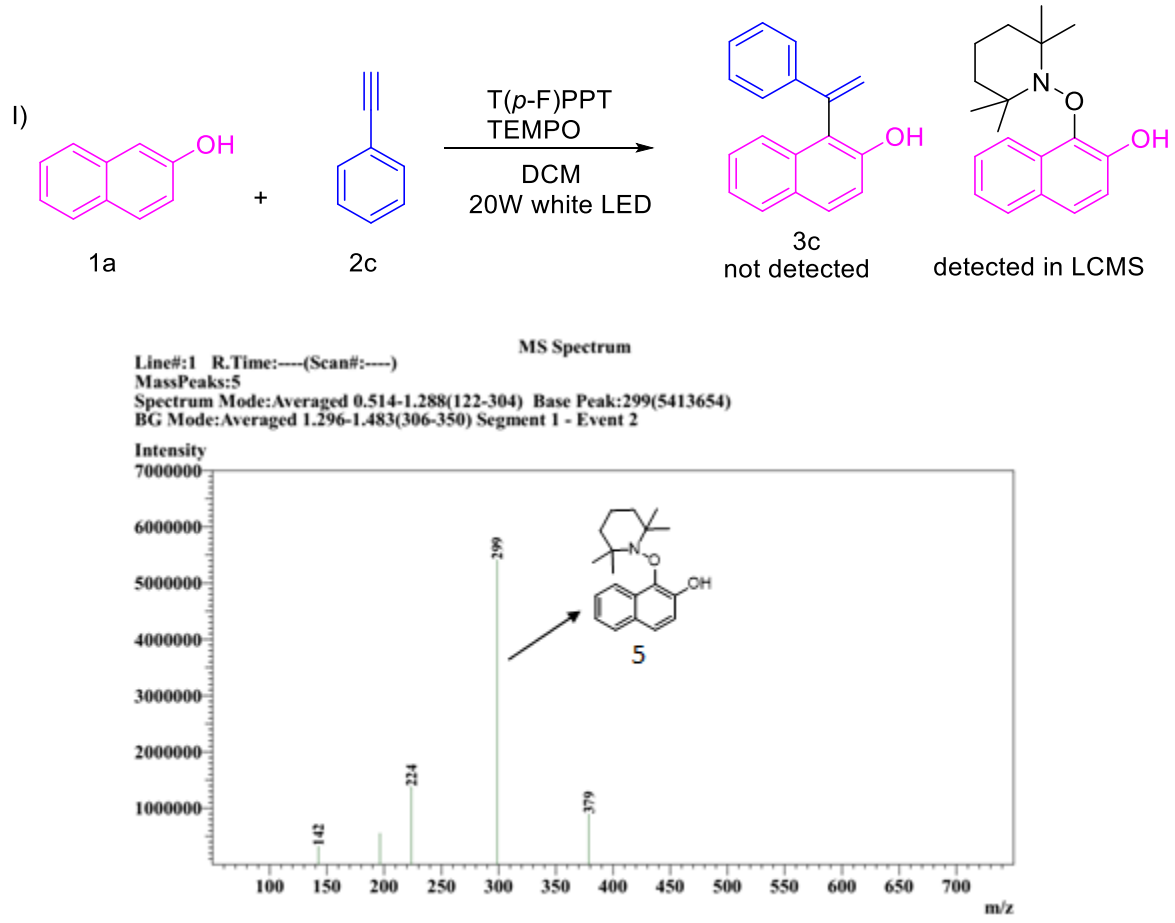
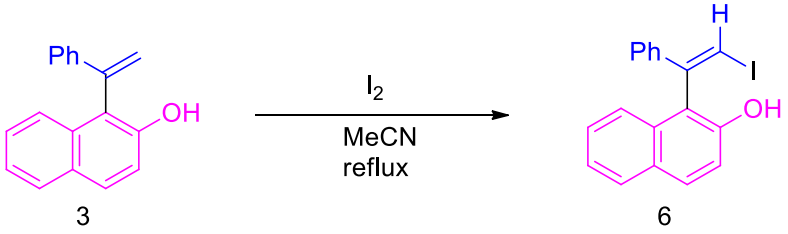


Figure S2. LCMS spectrum of TEMPO adduct 5

2.3 Product transformations

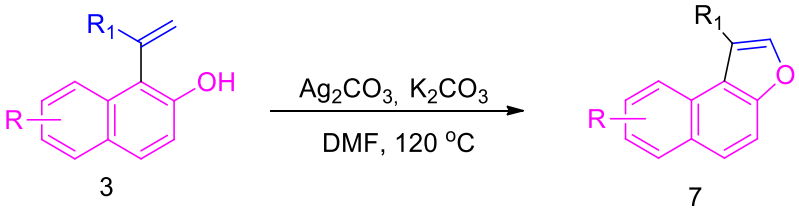
2.3.1. General procedure for one pot synthesis of vinyl iodide[1]



To a round bottom flask equipped with a magnetic stir bar **1** (0.3468 mmol), **2** (0.6936 mmol), 2 mL of DCM solvent and photocatalyst T(*p*-F)PPT (5 mol%) were sequentially added. The solution was stirred at a distance of ~3 cm from 20W white LED at room temperature. After the completion of the reaction monitored by TLC the solvent was removed in *vacuo* then to this crude I_2 (128.8 mg, 2.5 mmol), and MeCN (2mL) was added. The reaction mixture was refluxed for 4 h. allowed the reaction to cool at room temperature and quenched with $Na_2S_2O_3$ solution, then extracted with Ethyl acetate (2 x 10mL). The combined organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to afford the crude product. The residue was purified by column chromatography using 100–200 mesh silica gel with hexane /ethyl acetate (10 : 2, v/v) to afford the product **6** (96 mg, 74% yield). The NMR chemical shifts of **6** match with the previously reported values.

1. P. Kaswan, G. M. Shelke, V. K. Rao, A. Kumar, *Synlett* **2016**, *27*, 2553-2556

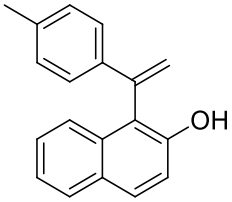
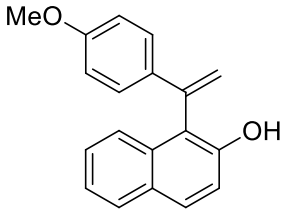
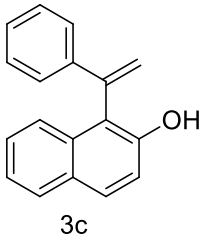
2.3.2. General procedure for one pot synthesis of naphthofuran derivatives[2]

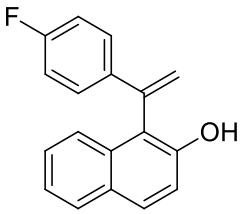
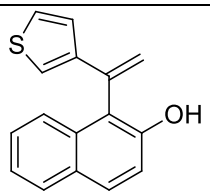
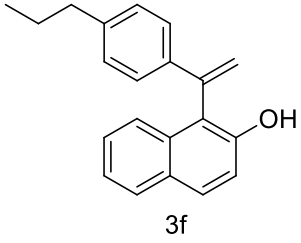


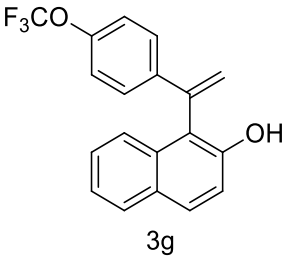
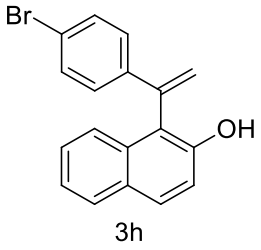
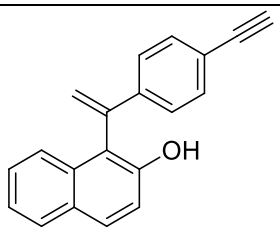
To a round bottom flask equipped with a magnetic stir bar **1** (0.3468 mmol), **2** (0.6936 mmol), 2 mL of DCM solvent and photocatalyst T(*p*-F)PPT (5 mol%) were sequentially added. The solution was stirred at a distance of ~ 3cm from 20W white LED at room temperature. After the completion of reaction monitored by TLC the solvent was removed in *vacuo* then to this crude K_2CO_3 (67.8mg, 0.4912 mmol) and $AgCO_3$ (90.3mg, 0.3274 mmol) DMF (2 mL), was added under Ar atmosphere, and stirred at 120 ℃ for 20 h. allow the reaction mixture to cool down and add 5mL of water into the reaction mixture and then extracted with ethyl acetate (EA) (3x15mL).). The combined organic layer was dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography using 100–200 mesh silica gel with hexane /ethyl acetate (10 : 1, v/v) to afford the product **7.**

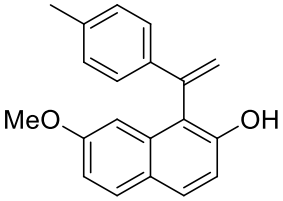
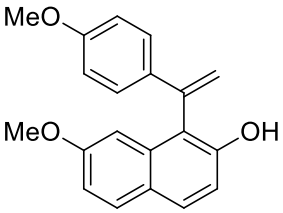
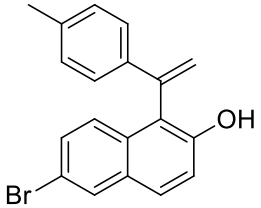
2. W. Wang, J. Huang, R. Zhou, Z.-J. Jiang, H.-Y. Fu, X.-L. Zheng, H. Chen, R.-X. Li, *Adv.Synth. Catal.* **2015**, *357*, 2442-2446

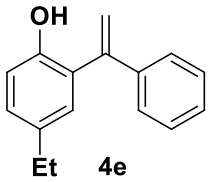
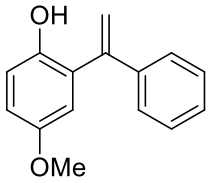
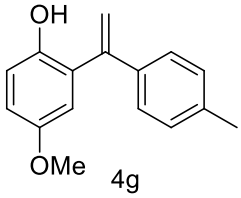
3. Characterisation of synthesised compounds

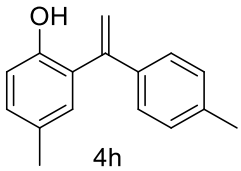
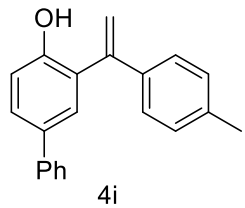
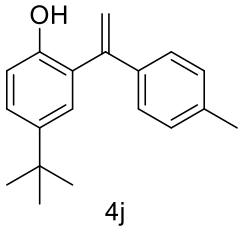
1	 3a **1-(1-(*p*-tolyl)vinyl)naphthalen-2-ol**	Pale yellow liquid (80.34mg, 89% Yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 - 7.71 (m, 2H), 7.43 -7.44 (m, 3H), 7.20 – 7.22 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 3H), 6.99 (d, *J* = 10.0 Hz, 2H), 620 (s, 1H), 5.56 (s, 1H), 5.37 (s, 1H), 2.23 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 150.4, 142.3, 138.6, 135.92, 132.8, 129.5, 129.4, 128.9, 128.0, 126.5, 126.2, 124.9, 123.3, 120.2, 117.9, 117.3, 21.2. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{19}H_{16}O([M+H]^+)$ 261.1279 ;found 261.1275
2	 3b **1-(1-(4-methoxyphenyl) vinyl)naphthalen-2-ol**	White solid (86.30 mg, 90% Yield); Mp: 82-84 ^{o}C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.63-7.67 (m, 2H), 7.41 – 7.42 (m, 1H), 7.14 – 7.19 (m, 5H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.08 (s, 1H), 5.58 (s, 1H), 5.26 (s, 1H), 3.62 (s, 3H). **^{13}C{^{1}H}** NMR **(125 MHz, $CDCl_3$)** δ 159.9, 150.4, 141.8, 132.87, 131.2, 129.5, 128.9, 128.0, 127.7, 126.5, 125.0, 123.3, 120.3, 117.3, 116.7, 114.1, 55.3. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{19}H_{16}O_2$ ($[M+H]^+$) 277.1228; found 277.1228
3	 3c **1-(1-phenylvinyl) naphthalen-2-ol**	Pale yellow solid (71mg, 83% Yield); Mp: 112-113 ^{o}C ; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 -7.73 (m,2H), 7.43 – 7.45 (m, 1H), 7.28 – 7.30 (m, 2H), 7.18 - 7.23 (m, 6H), 6.26 (s, 1H), 5.55 (s, 1H), 5.44 (s, 1H). **^{13}C{^{1}H}** NMR **(125 MHz, $CDCl_3$)** δ 150.4, 142.5, 138.7, 132.79, 129.6, 128.9, 128.7, 128.5, 128.0, 126.5, 126.3, 124.9, 123.3, 120.0, 118.9, 117.3, 77.2, 77.0, 76.7. **HRMS (ESI-Orbitrap) m/z:** Calcd for $C_{18}H_{14}O([M+H]^+)$ 247.1122; found 247.1122

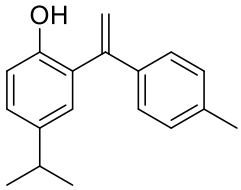
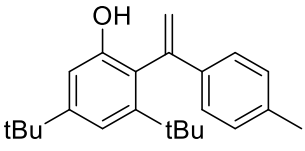
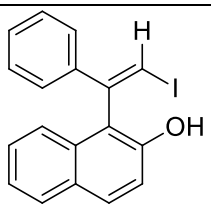
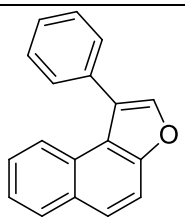
4	 3d **1-(1-(4-fluorophenyl)vinyl) naphthalen-2-ol**	Yellow viscous liquid (70mg, 76% Yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 – 7.73 (m,, 2H), 7.39 7.40 (m, 1H), 7.18 – 7.25 (m, 5H), 6.88(t, *J* = 8.0 Hz, 2H), 6.19 (s, 1H), 5.50 (s, 1H), 5.41 (s, 1H). **^{13}C{^{1}H}** NMR **(125 MHz, $CDCl_3$)** δ 163.9, 161.9, 150.4, 141.57, 134.9, 134.8, 132.6, 129.8, 128.9, 128.1, 128.1, 128.0, 126.6, 124.7, 123.4, 119.7, 118.5, 117.3, 115.7, 115.5. **^{19}F NMR (371 MHz, Chloroform-*d*) δ** -113.11 (s, 1F) **HRMS (ESI) m/z:** Calcd. for $C_{18}H_{13}FO([M+H]^+)$ 265.1028; found 265.1039
5	 3e **1-(1-(thiophen-3-yl)vinyl)naphthalen-2-ol**	Pale yellow liquid (61mg, 75% Yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.22 – 7.28 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.74 (s, 1H), 6.16 (s, 1H), 5.48 (s, 1H), 5.35 (s, 1H). **^{13}C{^{1}H}** NMR **(125 MHz, $CDCl_3$)** δ 150.0, 140.9, 137.3, 132.71, 129.6, 128.8, 128.0, 126.5, 125.1, 124.8, 124.2, 123.3, 120.2, 117.7, 117.3. **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{16}H_{12}OS([M+H]^+)$ 253.0687; found 253.0695
6	 3f **1-(1-(4-propylphenyl) vinyl)naphthalen-2-ol**	yellow liquid (95mg,95% Yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.70 – 7.72 (m, 2H), 7.45 – 7.46 (m, 1H), 7.17 -7.23 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.22 (s, 1H), 5.54 (s, 1H), 5.38 (s, 1H), 2.47 (t, J = 7.5 Hz, 2H), 2.05 (sext, 2H), 0.84 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 150.3, 143.4, 142.3, 136.0, 132.85, 129.5, 128.9, 128.8, 128.0, 126.5, 126.2, 124.9, 123.2, 120.2, 118.0, 117.3, 37.7, 24.4, 13.8. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{21}H_{20}O([M+H]^+)$ 289.1592; found 289.1593

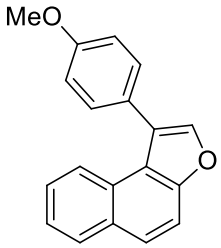
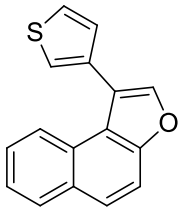
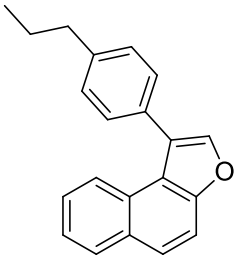
7	 3g **1-(1-(4-(trifluoromethoxy) phenyl)vinyl)naphthalen-2-ol**	Yellow viscous liquid (80.30mg, 70% Yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 – 7.74 (m, 2H), 7.38 – 7.40 (m, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.25 (m, 2H), 7.18 – 7.21 (m, 1H), 7.03 - 7.05 (d, *J* = 8.5 Hz, 2H), 6.25 (s, 1H), 5.50 (s,1H),5.48 (s,1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 150.4, 149.3, 141.3, 137.38, 132.5, 129.9, 128.9, 128.1, 127.7, 126.7, 124.6, 123.4, 121.0, 119.6, 119.4, 117.3. **^{19}F NMR (371 MHz, Chloroform-*d*) δ** -58.84 (s, 3F) **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{19}H_{13}F_3O_2$([M+H]$^+$) 331.0945, found 331.0948.
8	 3h **1-(1-(4-bromophenyl)vinyl) naphthalen-2-ol**	Pale yellow oil (82mg, 74% Yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.69 - 7.72 (m, 2H), 7.35 - 7.37 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.16 -7.24 (m,3H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.23 (s, 1H), 5.51 (s, 1H), 5.45 (s, 1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 150.4, 141.6, 137.7, 132.63, 131.8, 129.9, 128.9, 128.1, 127.9, 126.7, 124.7, 123.4, 122.7, 119.4, 119.3, 117.3, **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{18}H_{13}BrO$([M+H]$^+$) 325.0228; found 327.0173.
9	 3i **1-(1-(4-ethynylphenyl) vinyl)naphthalen-2-ol**	Yellow oil (76mg, 80% Yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.72 – 7.74 (m, 2H), 7.36 – 7.38 (m, 1H), 7.32 – 7.33 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.24 (m, 4H), 7.18 (d, *J* = 2.5 Hz, 1H), 6.28 (s, 1H), 5.49 - 5.50 (d, *J* = 6.5 Hz, 2H), 3.02 (s, 2H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 150.4, 141.9, 139.1, 132.6, 132.5, 129.8, 128.9, 128.1, 126.6, 126.2, 124.7, 123.4, 122.2, 119.8, 119.4, 117.3, 83.3, 78.2. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{20}H_{14}O$([M+Na]$^+$) 293.0942 ; found 292.0861.

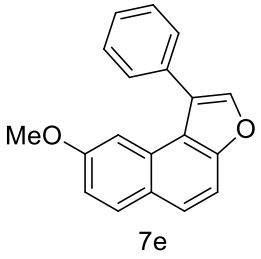
10	 4b **7-methoxy-1-(1-(*p*-tolyl)vinyl)naphthalen-2-ol**	Dark brown liquid (73mg, 88% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 (dd, *J* = 18.0 Hz, 9.0 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 1H), 6.99 -7.02 (m, 2H), 6.86 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.73 (d, *J* = 2.0 Hz, 1H), 6.17 (s, 1H), 5.56 (s, 1H), .5.39 (s, 1H), 3.57 (s, 1H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 158.1, 151.0, 142.7, 138.53, 136.0, 134.0, 129.5, 129.4, 129.2, 126.3, 124.3, 119.5, 117.9, 115.5, 114.7, 104.0, 55.0, 21.1. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{20}H_{18}O_2$([M+H]$^+$) 291.1385; found 291.1380.
11	 4c **7-methoxy-1-(1-(4-methoxyphenyl)vinyl)naphthalen-2-ol**	White solid (84mg,95% yield); Mp: 119-120 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.60 (dd, *J* = 16.0, 9.0 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.86 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 3H), 6.10 (s, 1H), 5.62 (s, 1H), 5.32 (s, 1H), 3.68 (s, 3H), 3.57 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 159.9, 158.1, 151.0, 142.19, 134.0, 131.3, 129.5, 129.2, 127.7, 124.2, 119.5, 116.7, 115.5, 114.7, 114.0, 104.0, 55.3, 55.0. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{20}H_{18}O_3$([M+H]$^+$)307.1334; found 307.1338.
12	 4d **6-bromo-1-(1-(*p*-tolyl)vinyl)naphthalen-2-ol**	Yellow oil (64 mg, 85% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (s, 1H), 7.60 – 7.61 (d, *J* = 9.0 Hz, 1H), 7.25 -7.31 (m, 2H), 7.19 – 7.21 (d, *J* = 9.0 Hz, 1H), 7.12 - 7.13 (d, *J* = 8.5 Hz, 2H), 6.99 - 7.01 (d, *J* = 8.0 Hz, 2H), 6.20 (s, 1H), 5.58 (s, 1H), 5.36 (s, 1H), 2.23 (s, 3H).**^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 150.7, 141.8, 138.8, 135.60, 131.3, 130.0, 129.9, 129.7, 129.5, 128.6, 126.8, 126.1, 120.4, 118.5, 118.2, 117.1, 21.2. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{19}H_{15}BrO$([M+Na]$^+$) 361.0204 ; found 362.1155

13	 4e **4-ethyl-2-(1-phenylvinyl)phenol**	Colourless liquid (55 mg, 51% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.21 - 7.23 *(*m, 2H), 7.09 - 7.10 (d, *J* = 8.0 Hz, 2H), 7.02 - 7.04 (m, 1H), 6.91 (s, 1H), 6.81 - 6.82 (d, *J* = 8.0 Hz, 1H), 5.76 (s, 1H), 5.30 (s, 1H), 4.96 (s, 1H), 2.47 - 2.51 (q, 2H), 2.30 (s, 3H), 1.12 - 1.15 (t, *J* = 7.5 Hz, 3H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ 151.04, 145.29, 138.60, 136.59, 136.12, 129.57, 129.42, 128.73, 127.41, 127.00, 115.70, 115.58, 77.28, 77.03, 76.78, 27.96, 21.21, 15.85. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{16}H_{16}O([M+Na]^+)$ 225.1279 ; found 225.1283.
14	 4f **4-methoxy-2-(1-phenylvinyl)phenol**	Viscous liquid (46 mg, 50% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33 – 7.38 (m, 5H), 6.87 (d, *J* = 9.0Hz 1H), 6.81-6.84 (m, 1H), 6.639(d, *J* = 2.5 Hz, 1H), 5.86 (s, 1H), 5.42 (s, 1H), 4.78 (s, 1H), 3.74 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 153.3, 147.1, 145.3, 139.1, 128.7, 128.6, 128.1, 127.0, 116.7, 116.5, 115.3, 115.1, 55.7. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{15}H_{14}O_2([M+H]^+)$ 227.1072; found 227.1068.
15	 4g **4-methoxy-2-(1-(p-tolyl)vinyl)phenol**	Viscous liquid (53mg, 55% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.17 – 7.20 (d, *J* = 3.0 Hz, 2H), 7.06 - 7.07 (d, *J* = 8.0 Hz, 2H), 6.78 – 6.80 (d, *J* = 4.0 Hz, 2H), 6.73 – 6.75 (dd, *J* = 7.0, 3.0 Hz, 1H), 6.25 – 6.31 (d, J = 3.0 Hz, 1H) 5.73 (s, 1H), 5.28 (s, 1H), 4.73 (s, 1H), 3.69 (s, 3H), 2.27 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 153.3, 147.1, 145.1, 138.69, 136.2, 129.4, 128.2, 126.9, 116.5, 115.9, 115.2, 115.0, 55.7, 21.2. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{16}H_{16}O_2([M+H]^+)$
16		Colourless liquid (53 mg, 51% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.18 – 7.20 (d, *J* = 7.5 Hz, 2H), 7.06 – 7.08 (d, *J* = 8.0 Hz, 2H), 6.96 - 6.98 (dd, *J* = 8.5 Hz, 3 Hz, 1H), 6.87 (s,

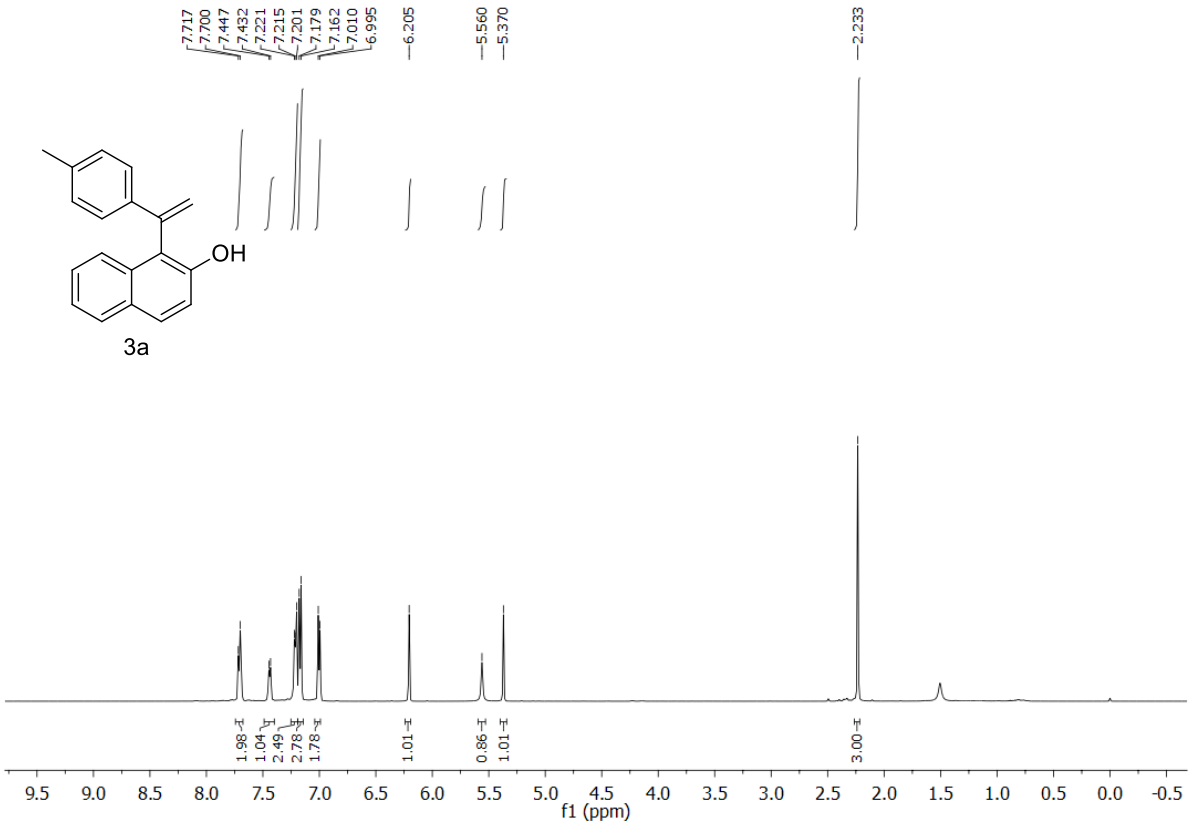
	 4h **4-methyl-2-(1-(*p*-tolyl)vinyl)phenol**	1H), 6.76 - 6.77 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 5.27 (s, 1H), 4.93 (s, 1H), 2.28 (s, 3H), 2.20 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 150.8, 145.2, 138.5, 136.6, 130.6, 129.9, 129.5, 129.4, 127.4, 126.99, 115.7, 115.5, 21.1, 20.4. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{16}H_{16}O([M+H]^+)$ 225.1279 ; found 225.1279.
17	 4i **3-(1-(p-tolyl)vinyl)-[1,1'-biphenyl]-4-ol**	Colourless liquid (59 mg, 50% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 - 7.48 (d, *J* = 7.5 Hz, 2H), 7.42 - 7.43 (d, *J* = 8.5 Hz, 1H), 7.30 - 7.33 (m, 3H), 7.21 - 7.24 (m, 2H), 7.18 (s, 1H), 7.08 -7.09 (d, *J* = 7.5 Hz), 6.94 - 6.95 (d, *J* = 8.0 Hz, 1H), 5.79 (s, 1H), 5.35 (s, 1H), 5.13(s, 1H), 2.28 (s, 3H); **^{13}C NMR (125 MHz, DMSO)** δ 152.76, 145.03, 140.60, 138.79, 136.31, 133.61, 129.51, 129.00, 128.72, 128.08, 127.02, 126.74, 116.23, 116.08, 77.28, 77.03, 76.78, 21.21. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{21}H_{18}O([M+H]^+)$ 287.1436 ; found 287.1441.
18	 4j **4-(tert-butyl)-2-(1-(*p*-tolyl)vinyl)phenol**	Pale yellow liquid (46 mg, 52% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.19 – 7.20 (m, 3H), 7.06 – 7.08 (m, 3H), 6.78 - 6.80 (d, *J* = 8.5 Hz, 1H), 5.74 (s, 1H), 5.27 (s, 1H), 4.93 (s, 1H), 2.28 (s, 3H), 1.21 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 150.78, 145.49, 143.11, 138.59, 136.49, 129.42, 127.22, 126.96, 126.30, 115.64, 115.18, 34.10, 31.55, 21.21. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{19}H_{22}O([M+H]^+)$ 267.1748; found 267.1753
19		Colourless liquid (51 mg, 55% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.19 – 7.21 (m, 2H), 7.07 - 7.09 (d, *J* = 8.0 Hz, 2H), 7.04 – 7.06 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.79 - 6.80 (d, *J* = 8.0 Hz, 1H), 5.75 (s, 1H), 5.29 (s,

	 4k **4-isopropyl-2-(1-(*p*-tolyl)vinyl)phenol**	1H), 4.94 (s, 1H), 2.72 - 2.80 (sept, 1H), 2.29 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 151.0, 145.3, 140.7, 138.59, 136.5, 129.4, 128.2, 127.3, 127.2, 126.9, 115.6, 115.5, 33.2, 24.2, 21.2. **HRMS (ESI-Orbitrap) m/z:** Calcd. for $C_{18}H_{20}OH([M+H]^+)$ 253.1592**;** found 253.1588
20	 4k **3,5-di-tert-butyl-2-(1-(*p*-tolyl)vinyl)phenol**	Viscous liquid (46 mg, 60% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.21 - 7.22 (d, *J* = 8.0 Hz, 2H), 7.09 - 7.12 (m, 3H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.21 (s, 1H), 5.38 – 5.39 (d, *J* = 4.5 Hz, 1H), 2.32 (s, 3H), 1.34 (s, 9H), 1.32 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 152.6, 151.4, 148.1, 145.18, 138.2, 136.5, 129.3, 126.1, 123.2, 118.1, 116.3, 109.8, 77.2, 77.0, 76.7, 37.1, 34.8, 32.3, 31.3, 21.1. **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{23}H_{30}OH([M+H]^+)$ 323.2374; found 323.2374
21	 6a **(*E*)-1-(2-iodo-1-phenylvinyl)naphthalen-2-ol**	Viscous liquid (96 mg, 74% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29-7.78 (m, 2H), 7.36 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.5-7.28(m, 7H), 5.18 (s, 1H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 149.4, 146.8, 138.6, 131.5, 130.4, 129.1, 128.9, 128.8, 128.2, 127.0, 126.4, 124.0, 123.7, 121.1, 117.6, 86.0. **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{18}H_{13}IO([M+H]^+)$ 373.0089; found 373.0091
22	 7a **1-phenylnaphtho[2,1-b]furan**	Colourless liquid (55 mg, 65% yield); **^{1}H NMR (500 MHz, $CDCl^3$)** δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.33 -7.76 (m, 2H), 7.67 (d, *J* =7.5 Hz, 2H), 7.52-7.58 (m, 3H), 7.47 7.50 (m, 1H), 7.40 (t,*J* = 7.5 Hz, 1H) **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 153.1, 141.7, 133.1, 130.8, 129.8, 128.9, 128.6, 128.3, 127.8, 125.9, 125.9, 124.4, 124.3, 123.3, 120.7, 112.6. **HRMS**

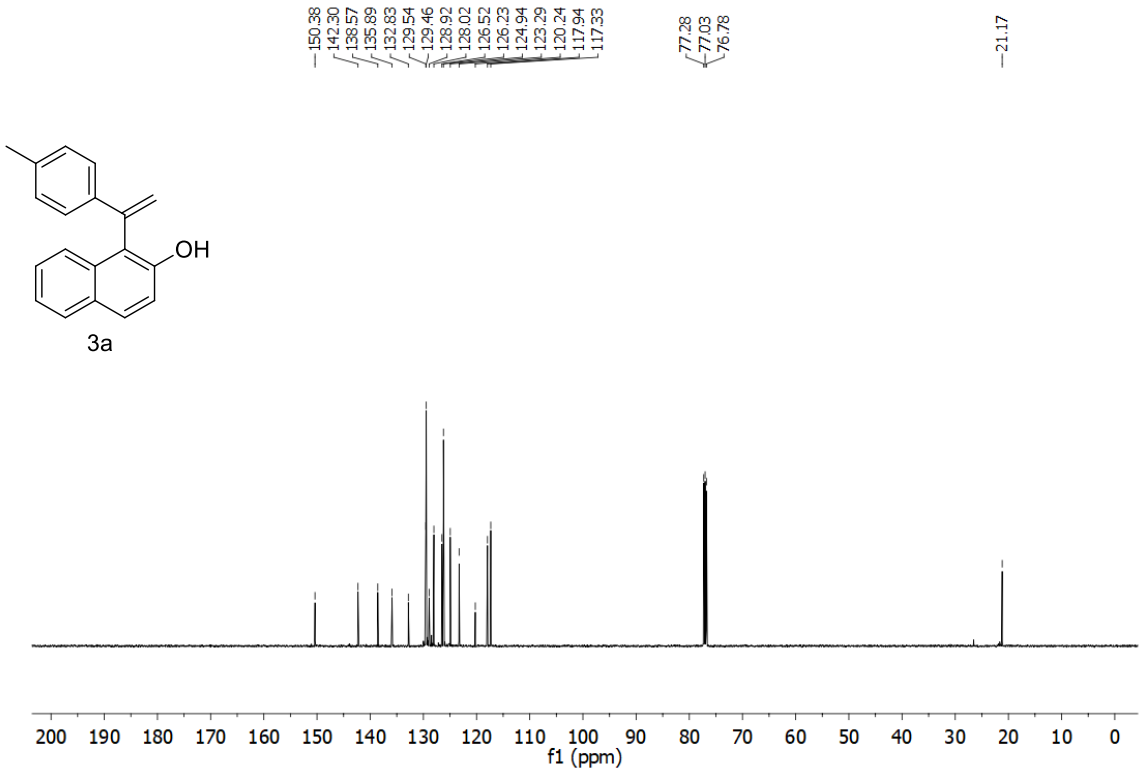
		(ESI-Orbitrap) m/z: Calcd. for $C_{18}H_{12}O([M+H]^+)$ 245.0966; found 245.0968
23	 7b **1-(4-methoxyphenyl)naphtho[2,1-b]furan**	Yellow liquid (65 mg, 68% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (d, *J* **=** 8.0 Hz, 1H), 7.81 (d *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.53 (s, 1H), 7.39 (d, *J* = 7.5 Hz), 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 3.78 (s, 3H**). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 159.3, 153.0, 141.5, 133.5, 130.9, 130.7, 128.8, 128.3, 125.9, 125.8, 125.1, 124.2, 123.9, 123.3, 120.9, 114.0, 112.6, 55.3. **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{19}H_{14}O_2([M+H]^+)$ 275.1072; found 272.1072
24	 7c **1-(thiophen-3-yl)naphtho[2,1-b]furan**	Pale yellow liquid (54 mg, 62% yield); **^{1}H NMR (500 MHz, $CDCl_3$) δ** 8.10 (d, *J* = 8.0 Hz), 7.97 (d, *J* = 8.0 Hz, 1H0, 7.79 (d, *J* = 9.0 Hz, 1H), 7.70 – 7.73 (m, 2H), 7.42 – 7.54 (m, 4H), 7.37 (d, *J* = 5.0 Hz, 1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ** 153.0, 141.8, 132.7, 130.7, 129.3, 128.8, 128.3, 126.1, 126.0, 125.9, 124.4, 123.8, 123.3, 120.9, 119.0, 112.6, **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{18}H_{10}OS([M+H]^+)$ 251.0530; found 251.0525
25	 7d **1-(4-propylphenyl)naphtho[2,1-b]furan**	Colourless liquid (68 mg, 68% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 (d, *J* = Hz,1H), 9.97 (d, *J* = 8.0 Hz), 7.95 (d, *J* = 9.0 Hz), 7.69 -7.73 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.44 -7.47 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 1.75 -1.82 (sext, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 153.1, 142.4, 141.6, 130.8, 130.2, 129.7, 128.8, 128.6, 128.4, 125.9, 125.8, 124.4, 124.3, 123.4, 120.8, 112.6, 37.9, 24.5, 13.9. **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{21}H_{18}O([M+H]^+)$ 287.1435; found 287.1444

26	 7e **8-methoxy-1-phenylnaphtho[2,1-b]furan**	Yellow liquid (59 mg, 62% yield); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84(d, *J* = 10 Hz, 1H), 7.71 (d, *J* = 10 Hz, 2H), 7.64(d, *J* = 5 Hz, 2H), 7.51 – 7.57 (m,3H), 7.45 – 7.48 (m, 1H), 7.30 (s, 1H), 7.08 (d, *J* = 10 Hz, 1H), 3.57 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 157.74, 153.62, 141.13, 133.13, 130.26, 130.09, 129.46, 128.41, 127.88, 125.70, 125.66, 124.22, 120.11, 116.35, 110.12, 102.87, 54.86. **HRMS (ESI-Orbitrap) m/z**: Calcd. for $C_{19}H_{14}O_2$([M+H]$^+$) 275.1072; found 275.1075

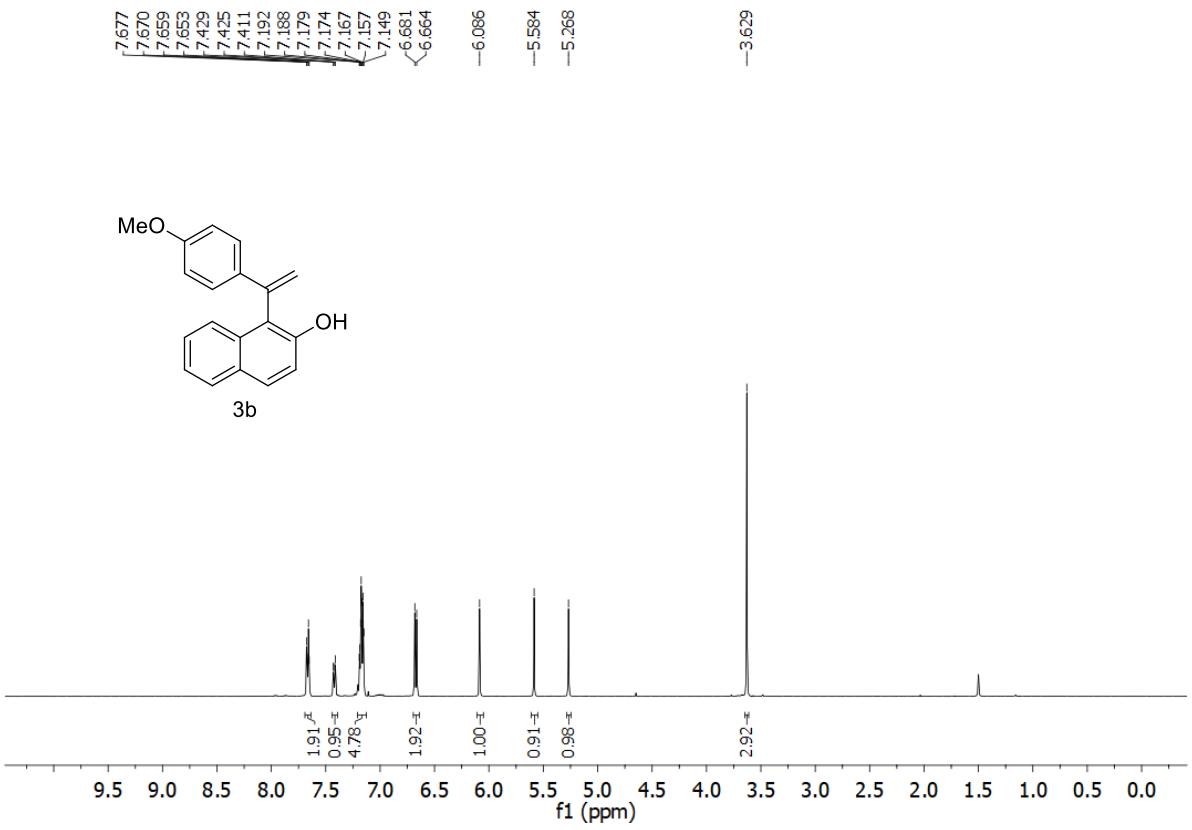
4. ^{1}H and $^{13}C\{^{1}H\}$ spectrum of synthesised compounds



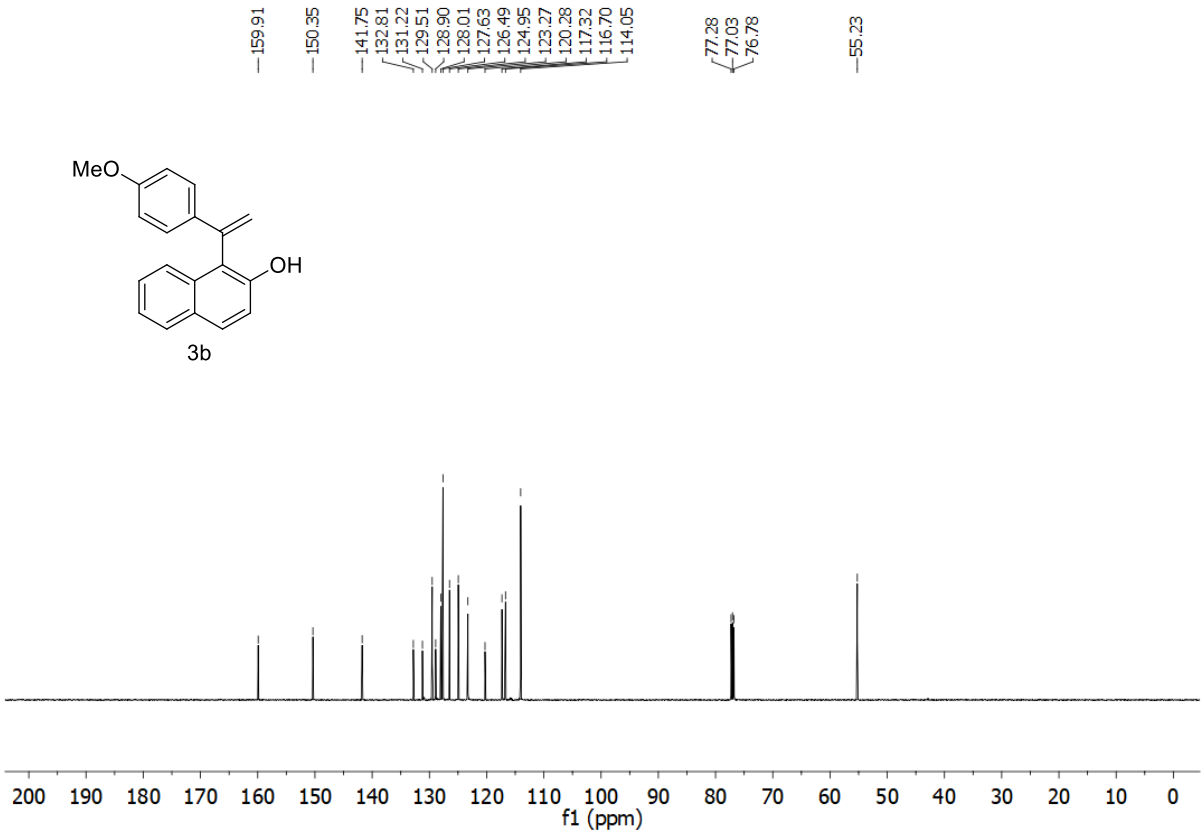
^{1}H NMR of 3a in $CDCl_3$



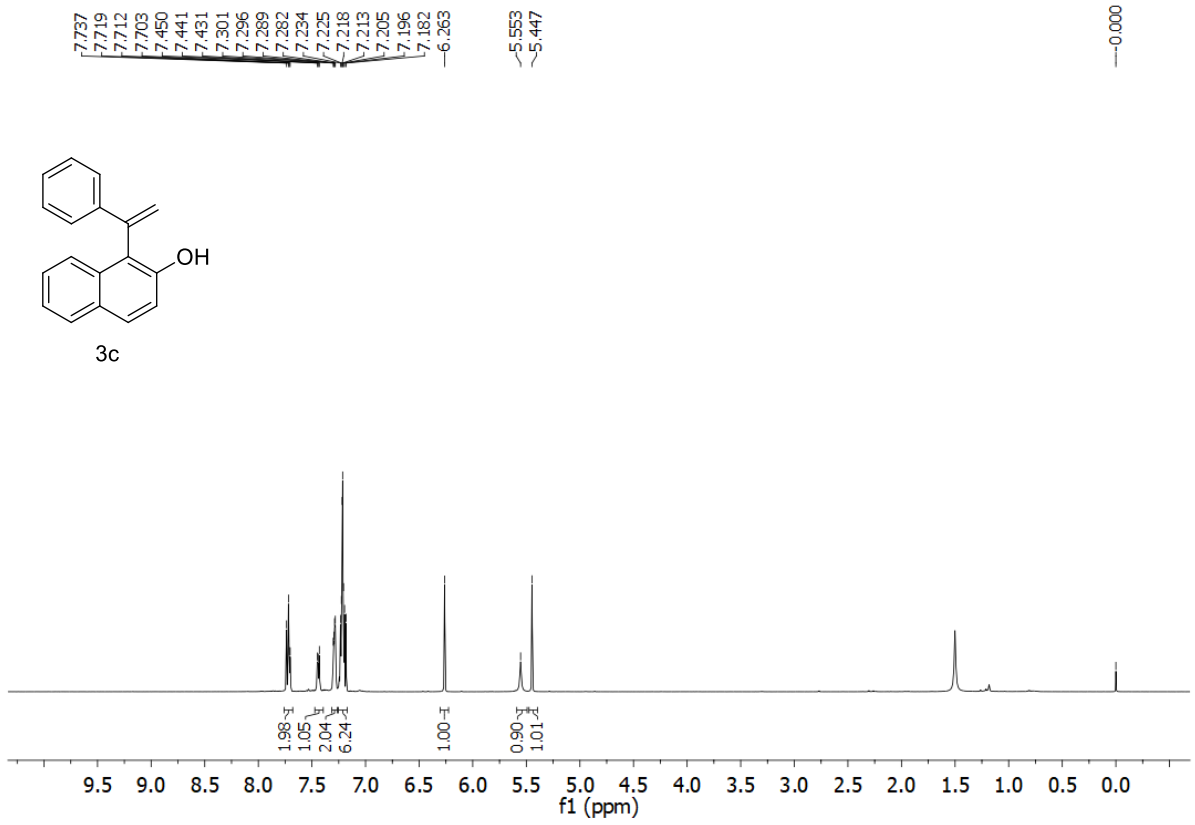
$^{13}C\{^{1}H\}$ NMR of 3a in $CDCl_3$



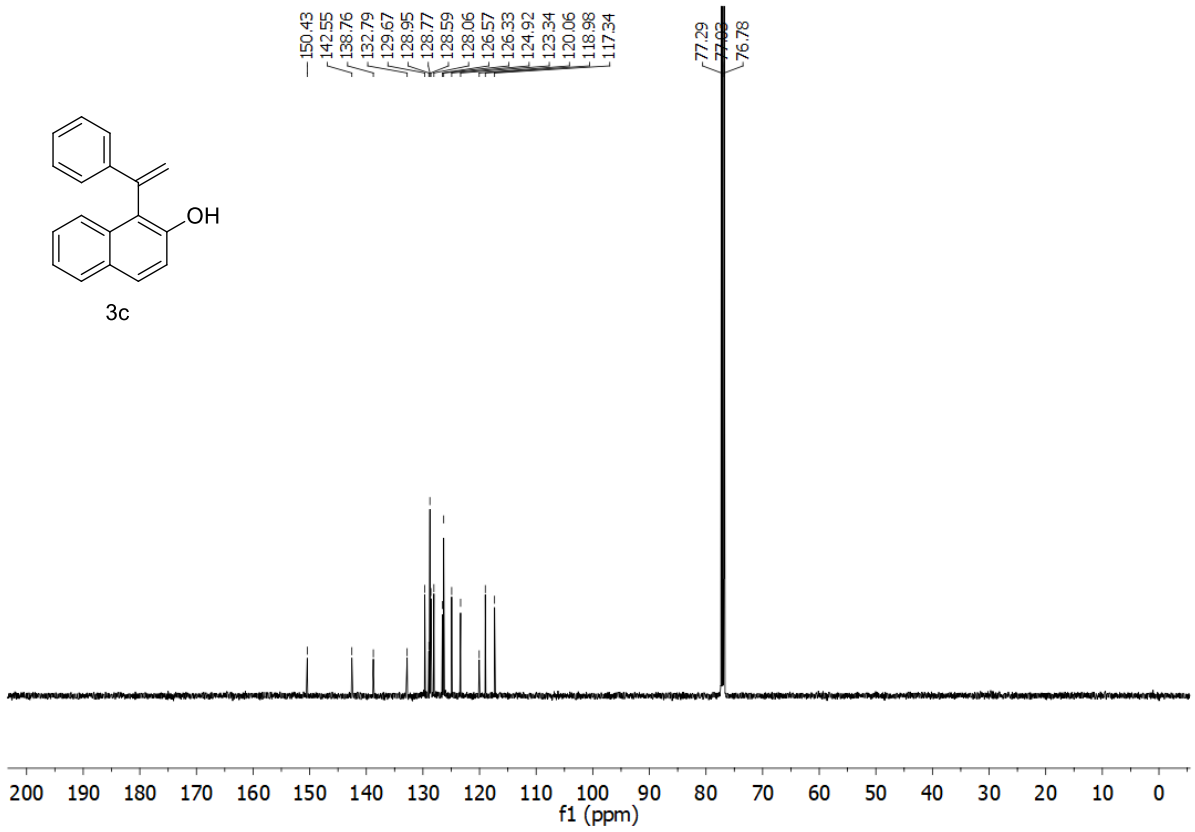
^{1}H NMR of 3b in $CDCl_3$



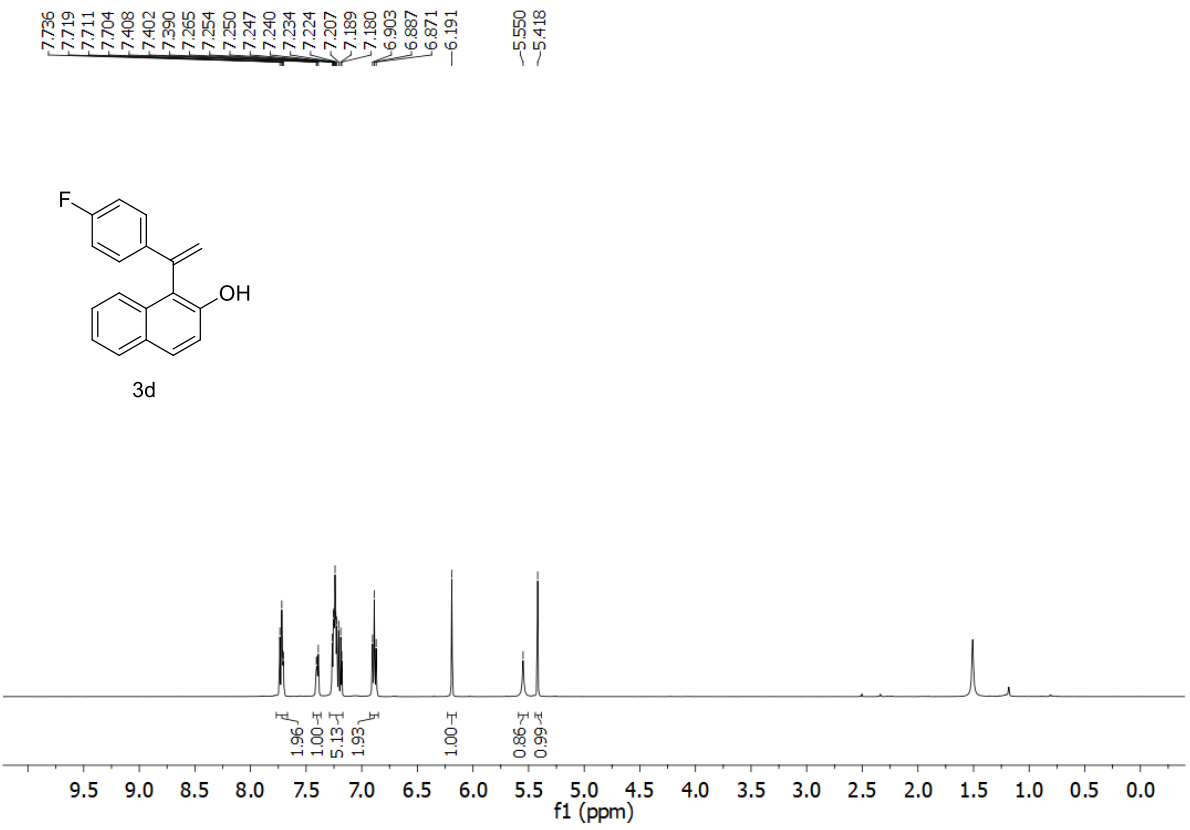
^{13}C{^{1}H} NMR of 3b in $CDCl_3$



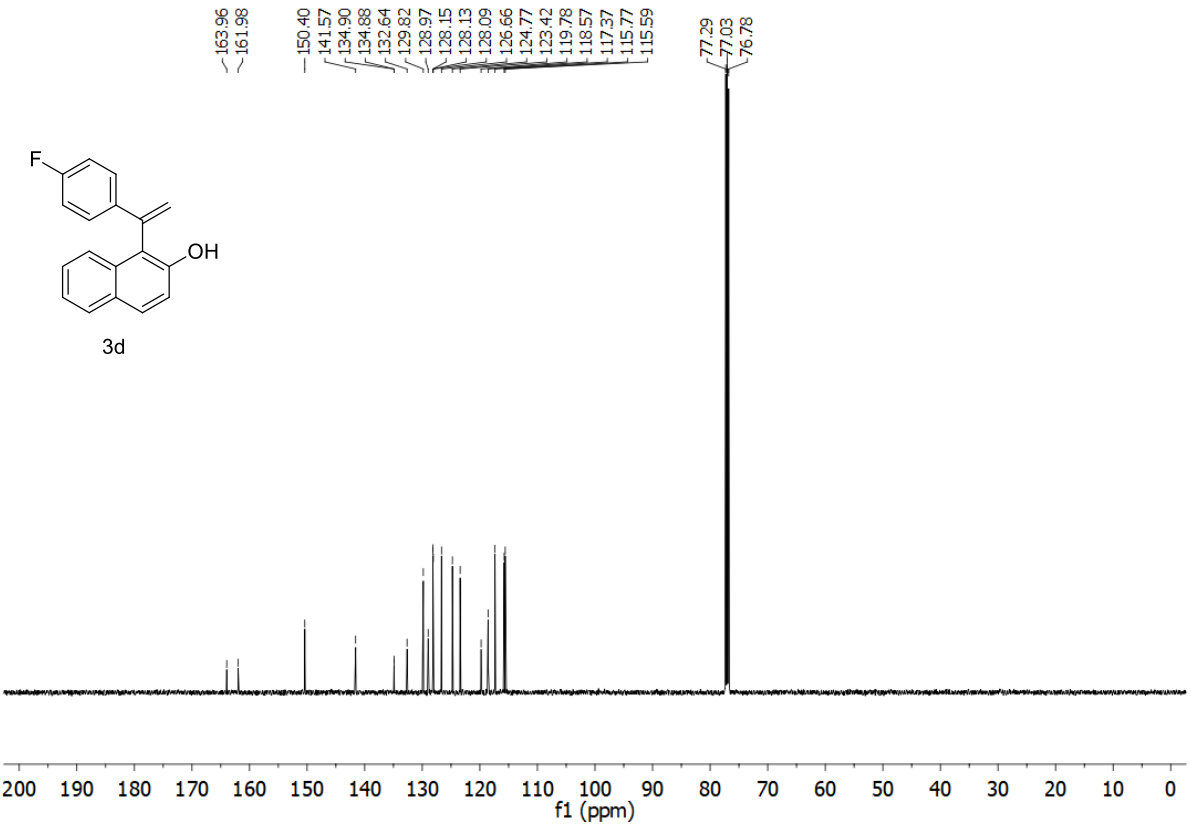
^{1}H NMR of 3c in $CDCl_3$



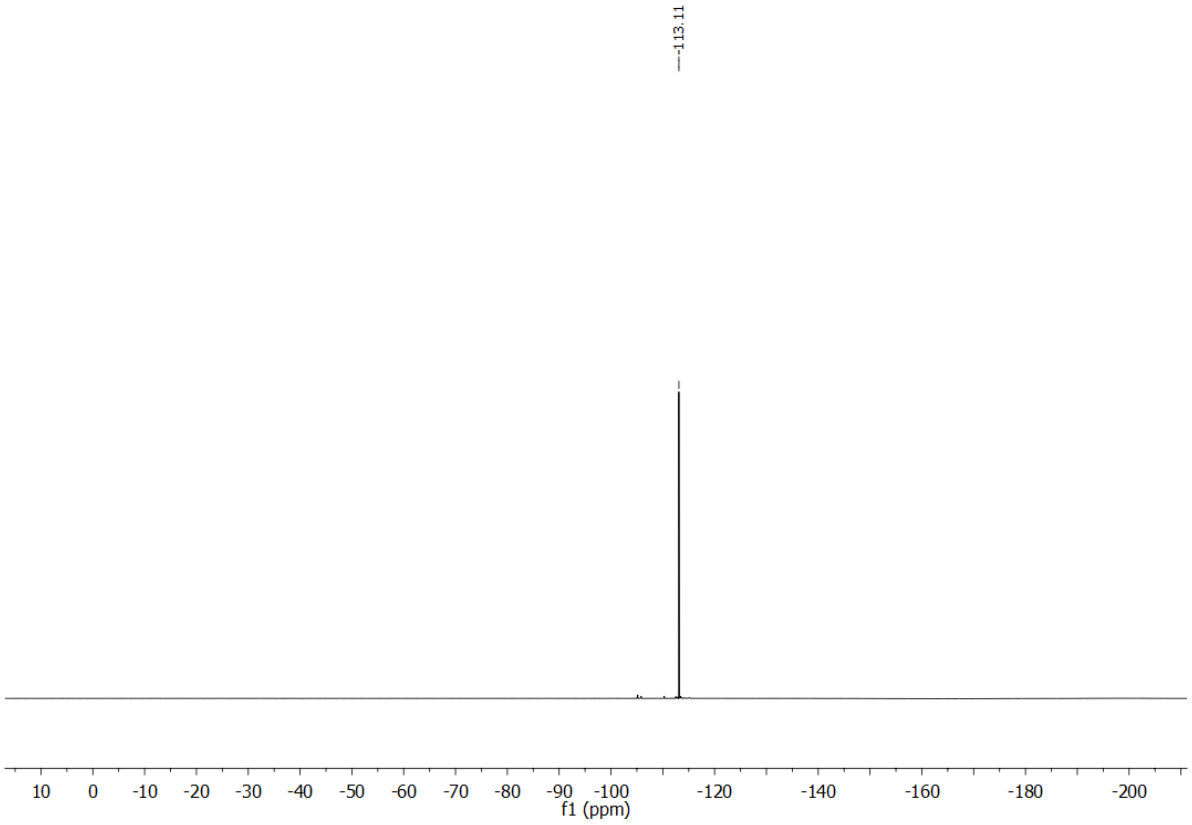
^{13}C{^{1}H} NMR of 3c in $CDCl_3$



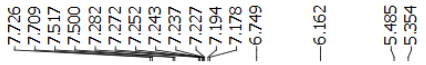
^{1}H NMR of 3d in $CDCl_3$

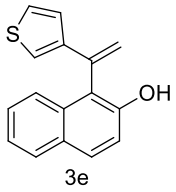


^{13}C{^{1}H} NMR of 3d in $CDCl_3$

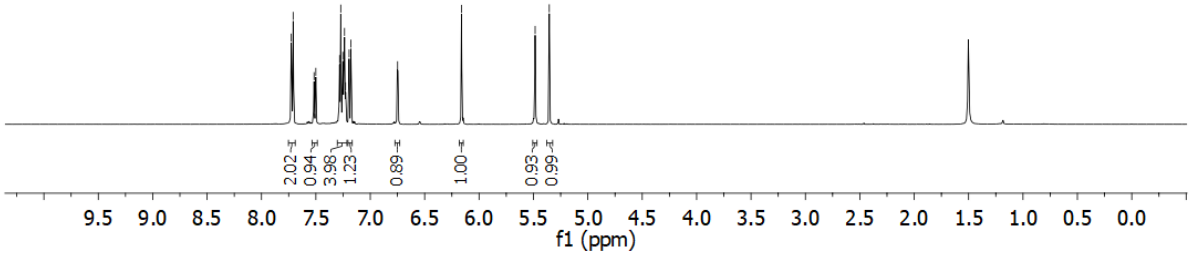


^{19}F NMR of 3d in $CDCl_3$

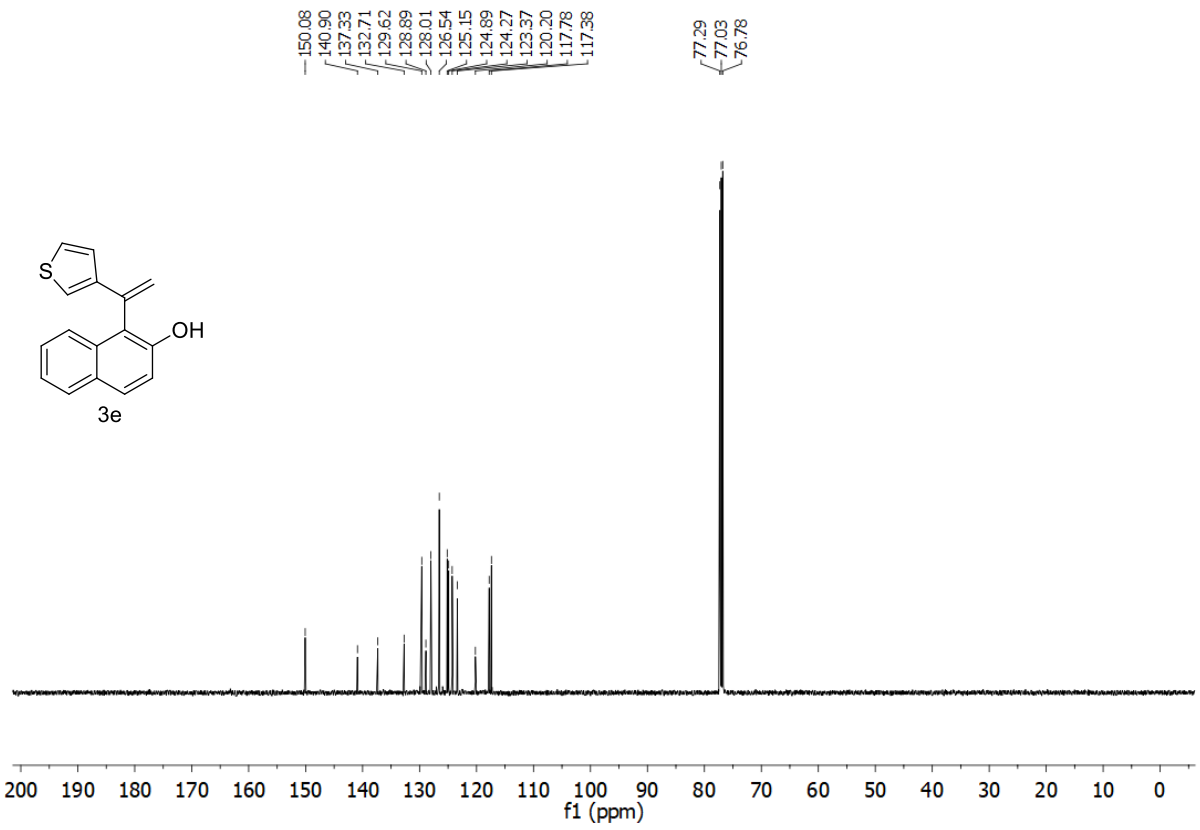




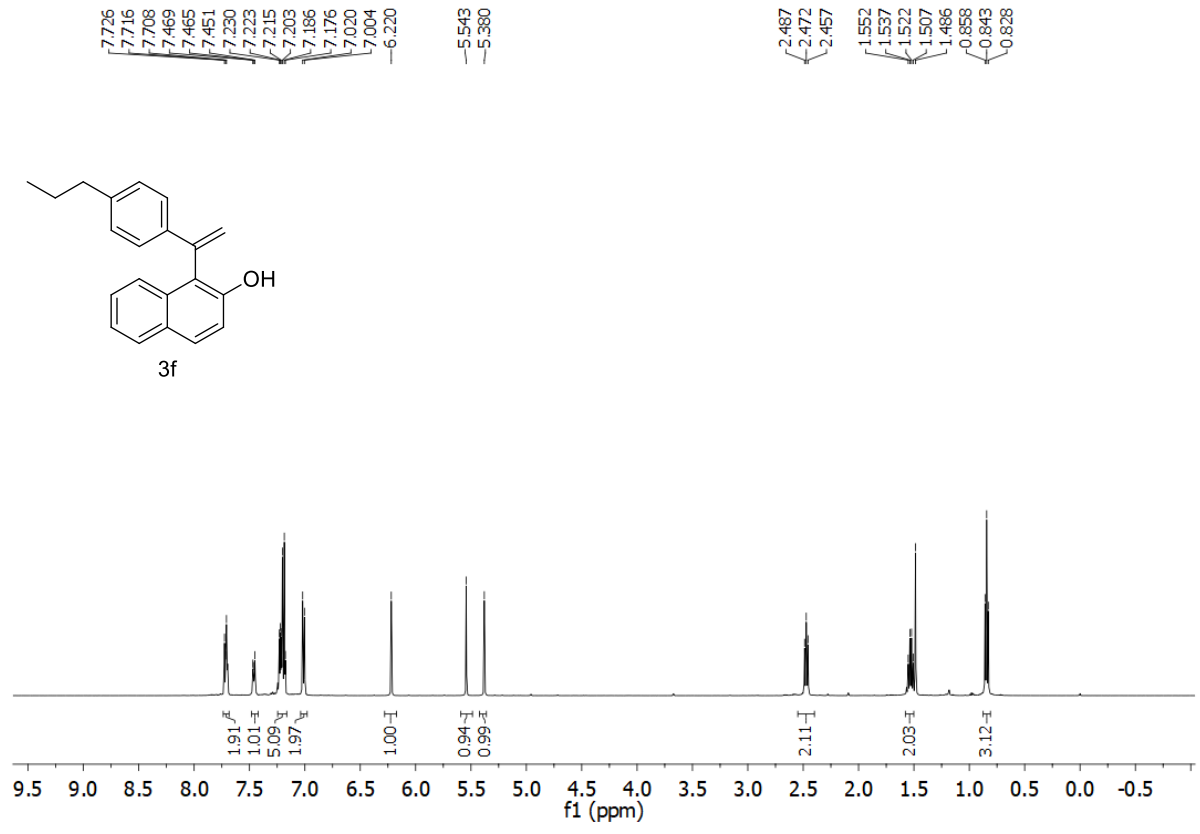
3e



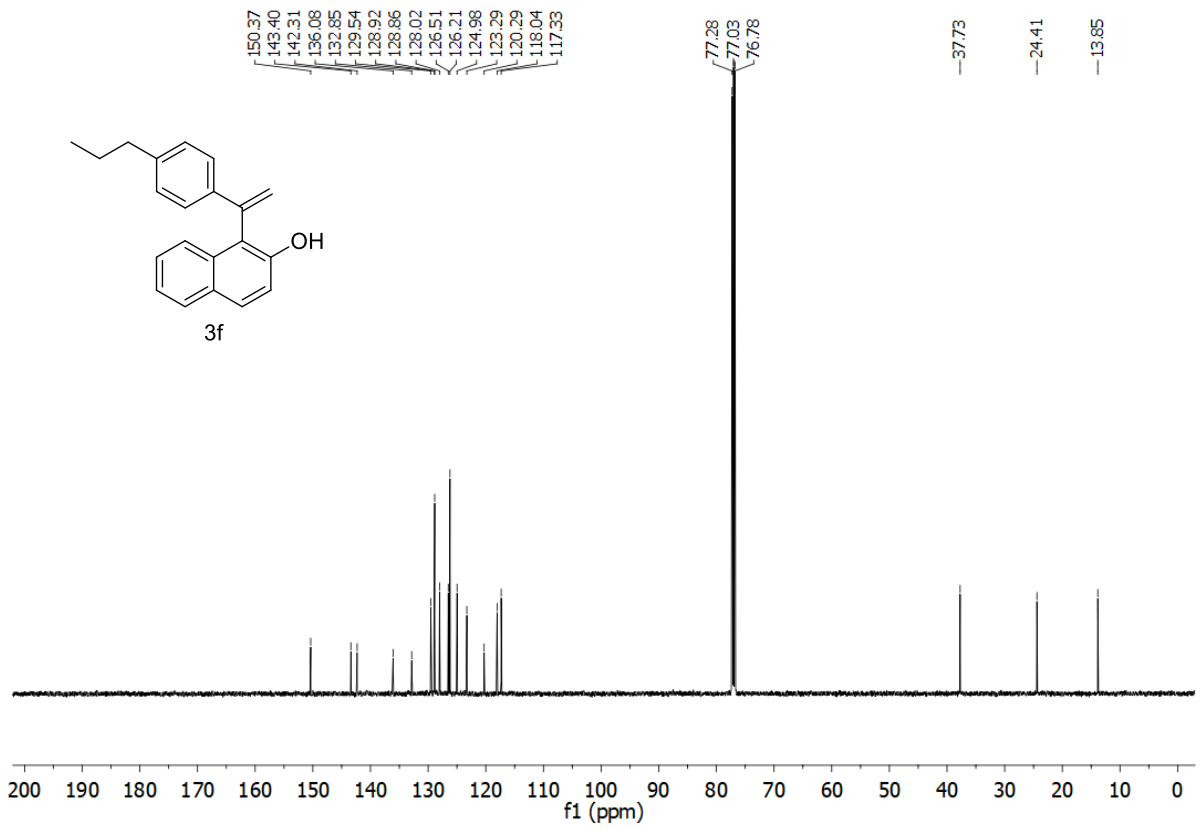
^{1}H NMR of 3e in $CDCl_3$



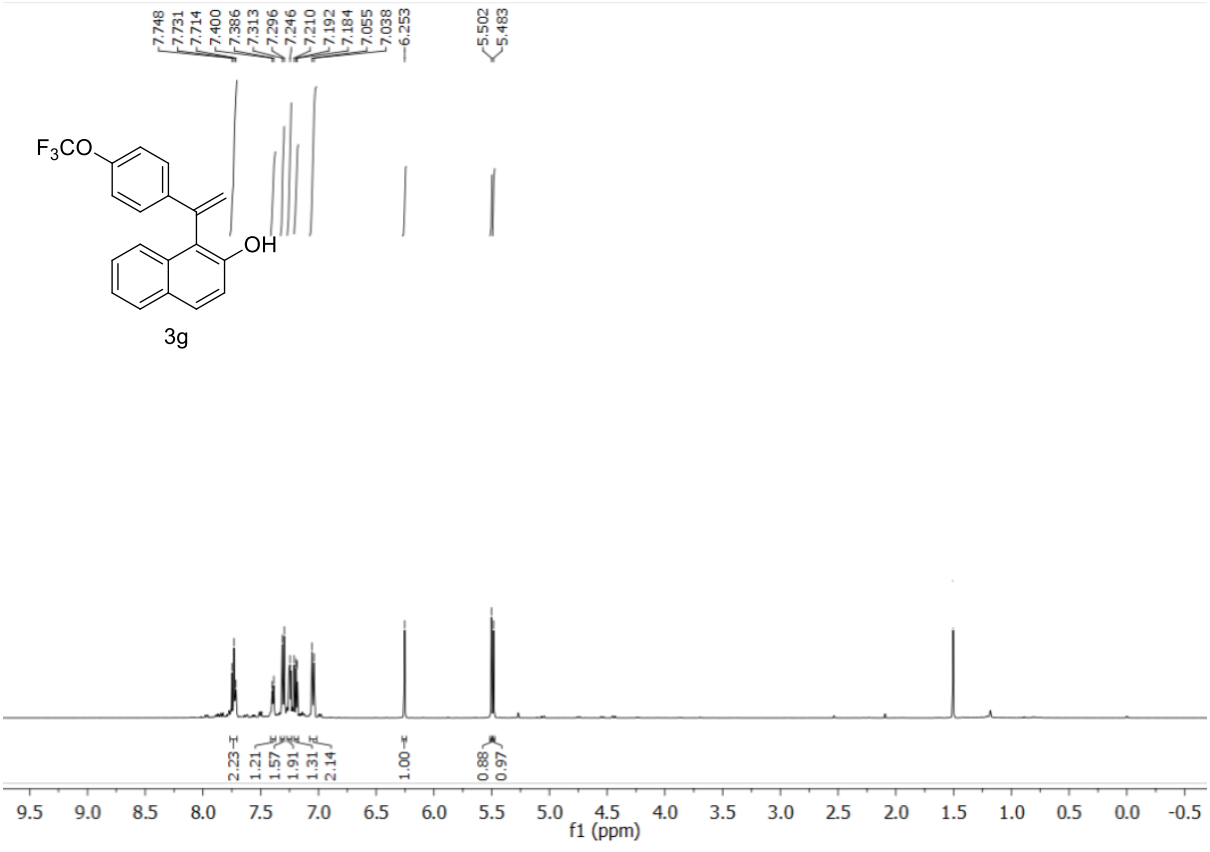
$^{13}C\{^{1}H\}$ NMR of 3e in $CDCl_3$



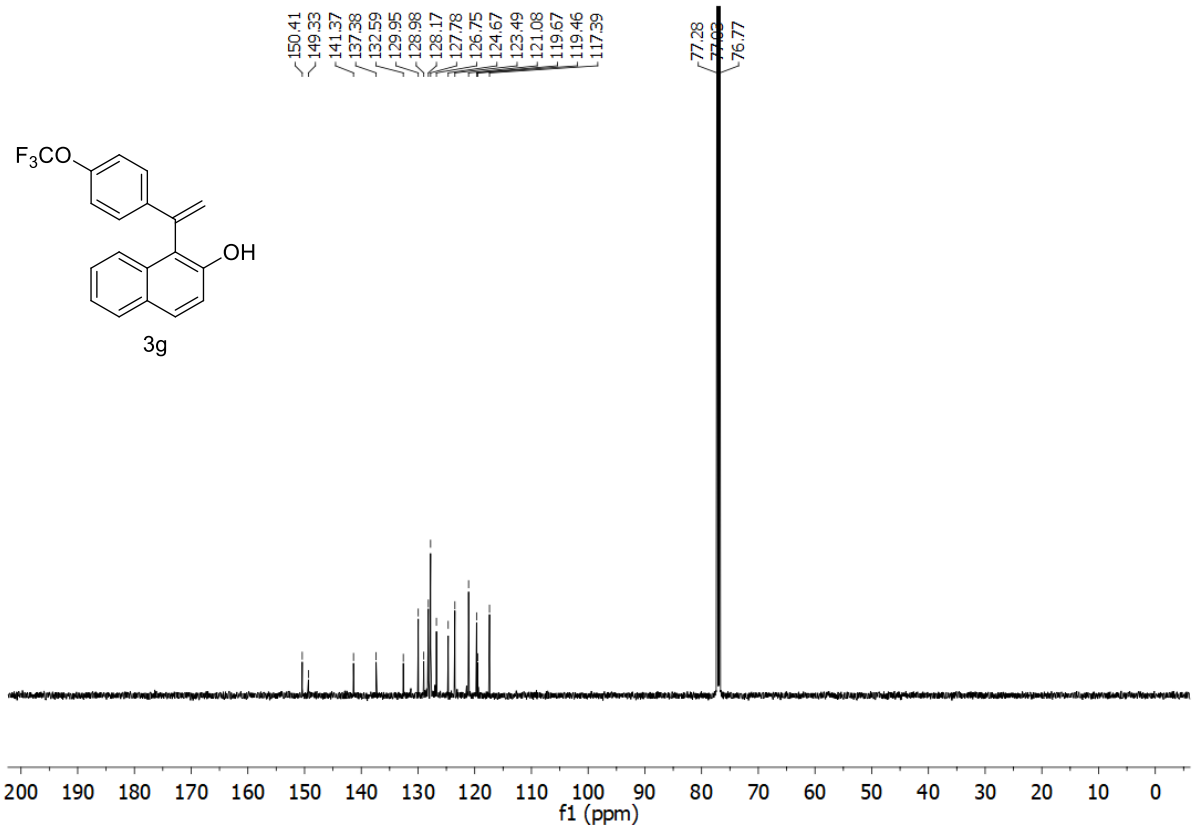
^{1}H NMR of 3f in $CDCl_3$



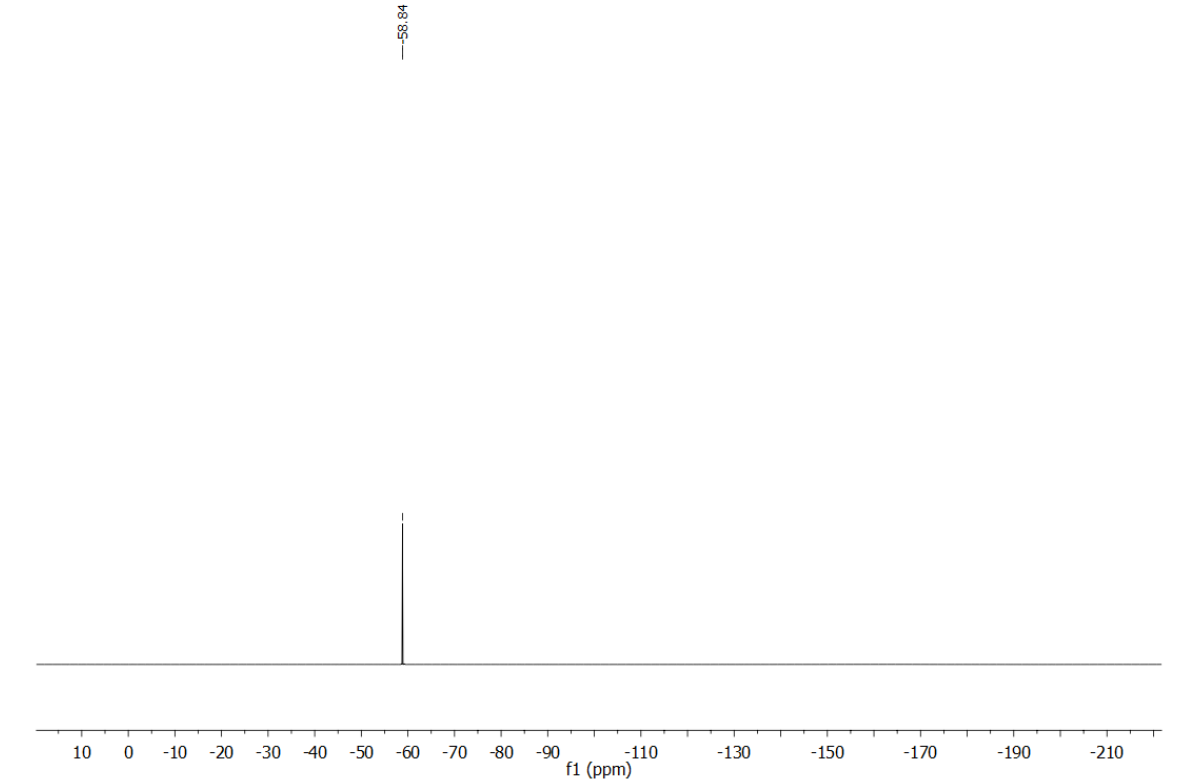
$^{13}C\{^{1}H\}$ NMR of 3f in $CDCl_3$



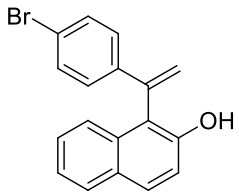
^{1}H NMR of 3g in $CDCl_3$



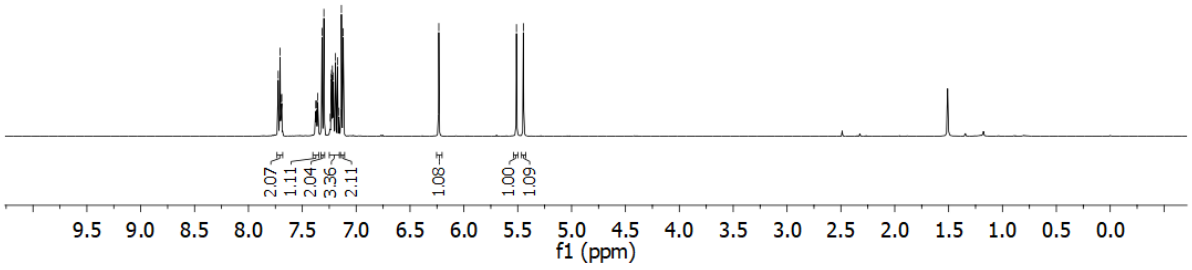
$^{13}C\{^{1}H\}$ NMR of 3g in $CDCl_3$



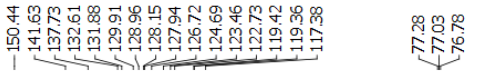
^{19}F NMR of 3g in $CDCl_3$

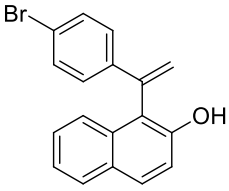


3h

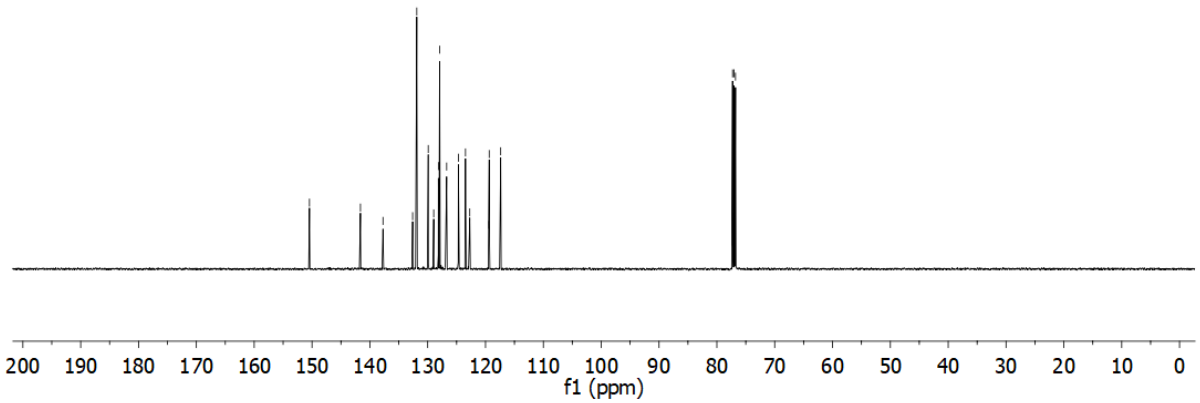


^{1}H NMR of 3h in $CDCl_3$

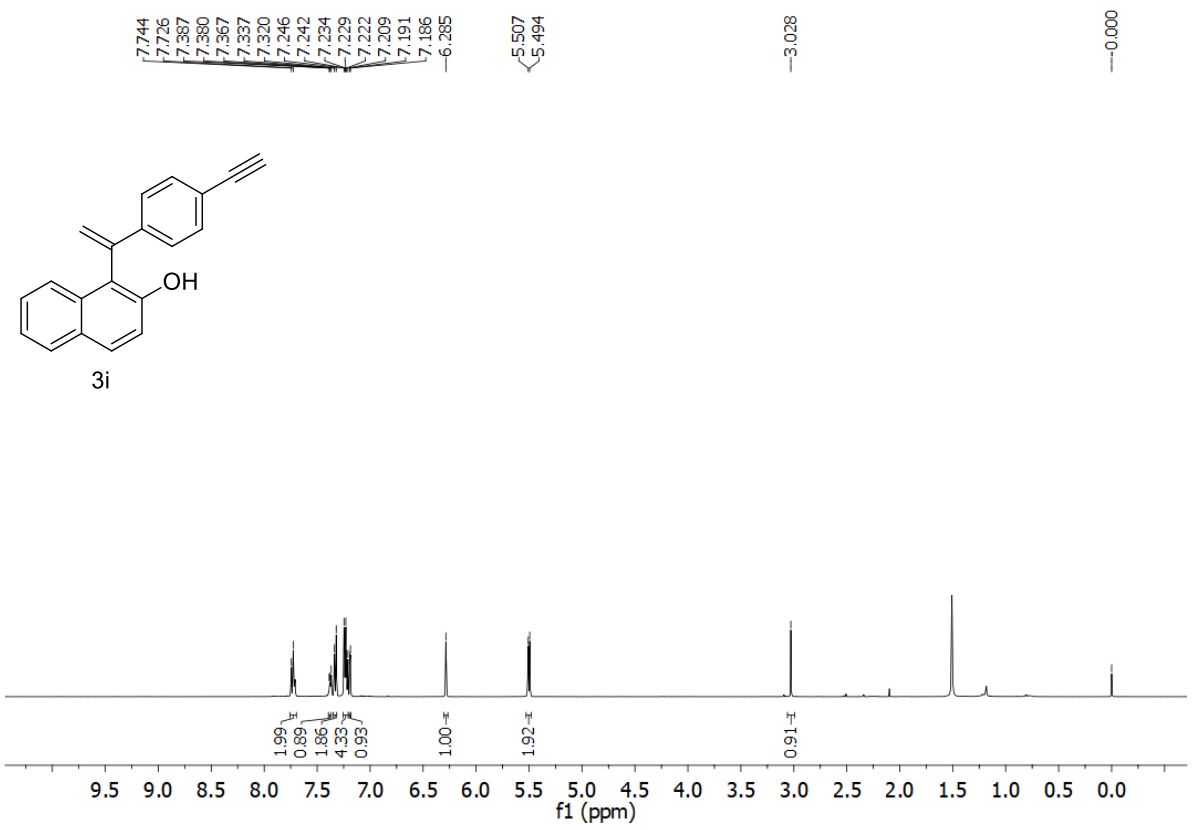




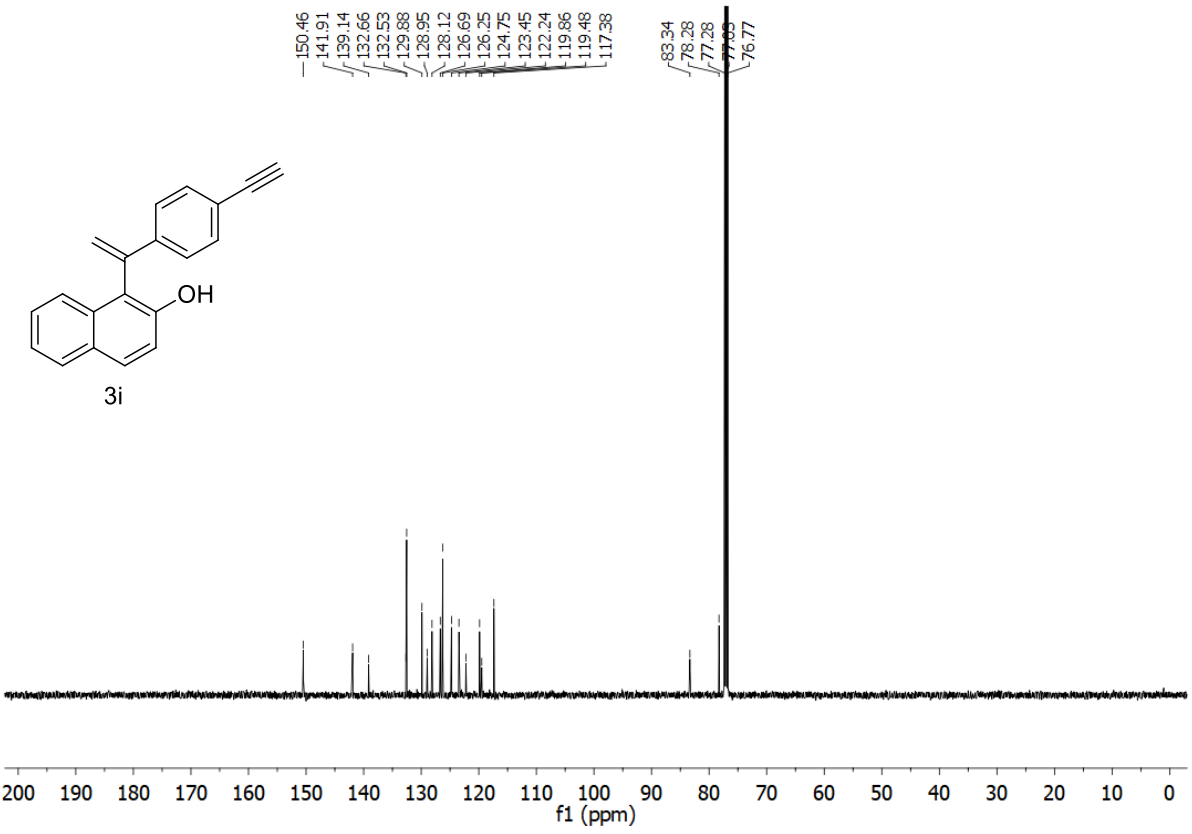
3h



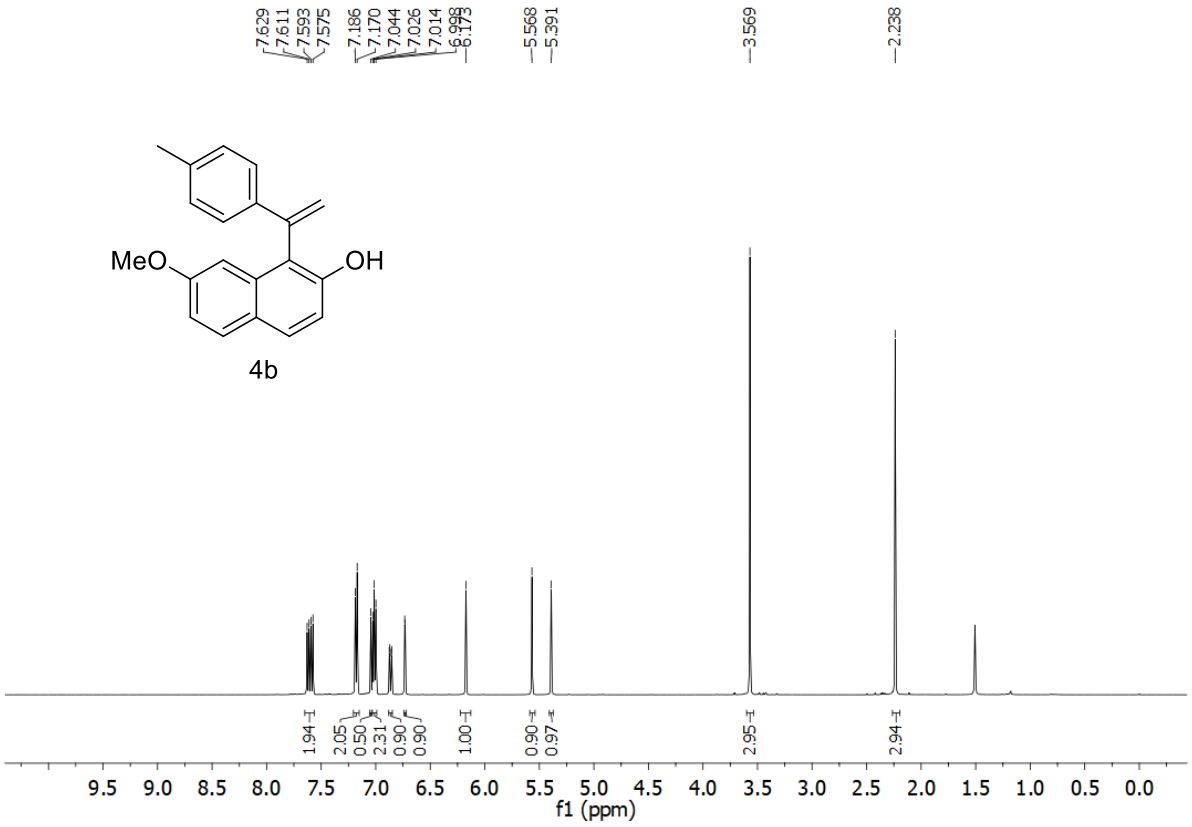
^{13}C{^{1}H} NMR of 3h in $CDCl_3$



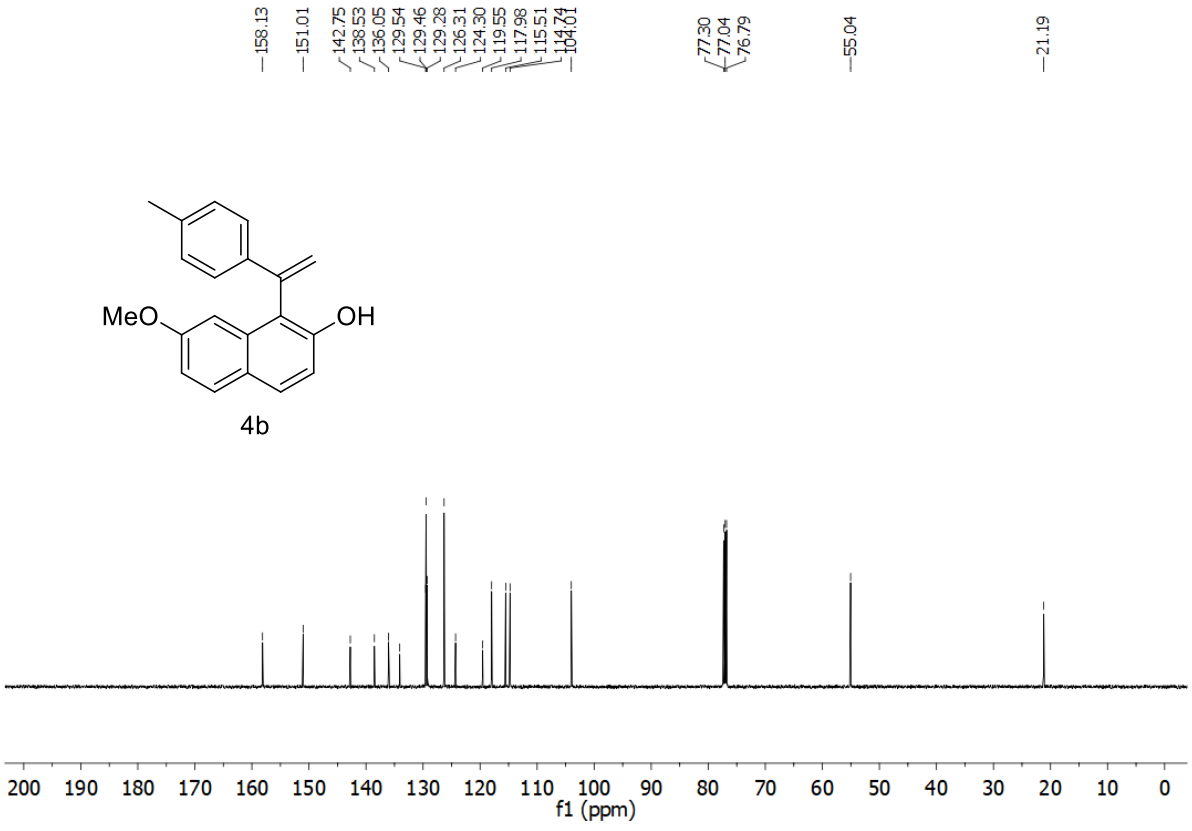
^{1}H NMR of 3i in $CDCl_3$



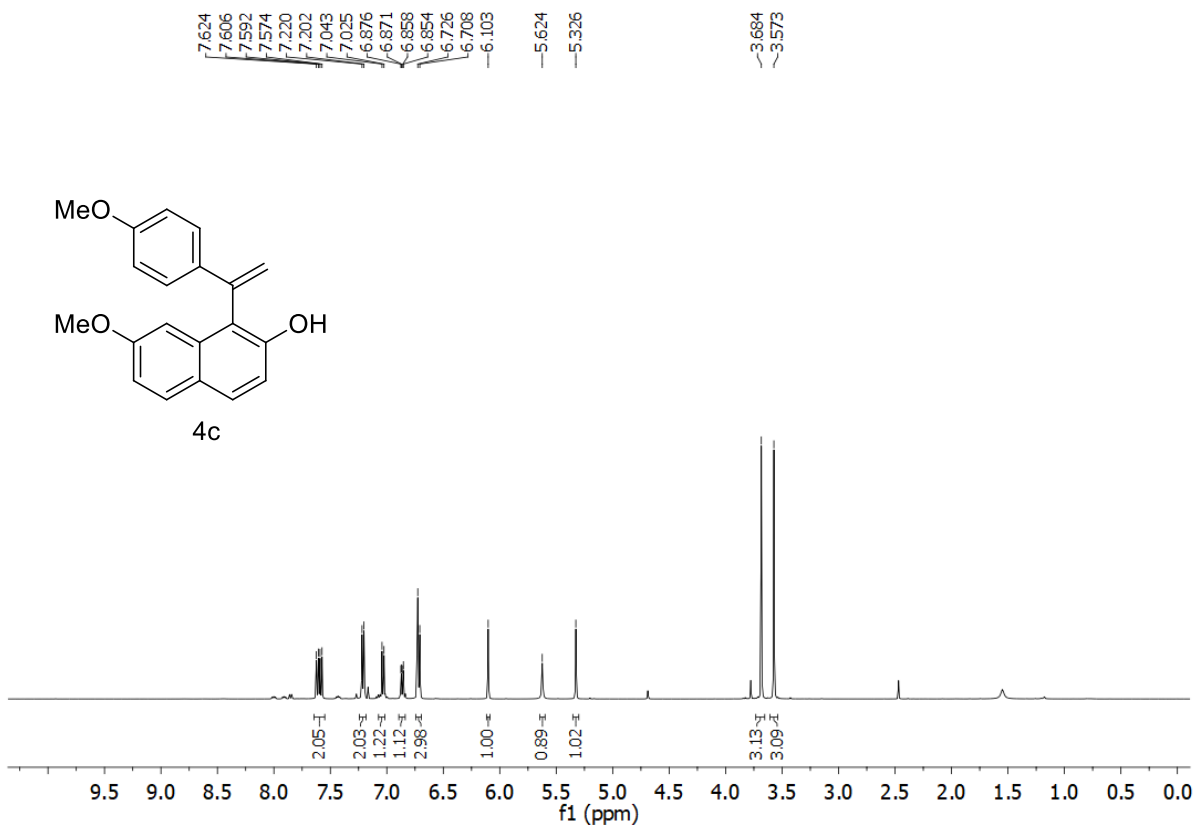
$^{13}C\{^{1}H\}$ NMR of 3i in $CDCl_3$



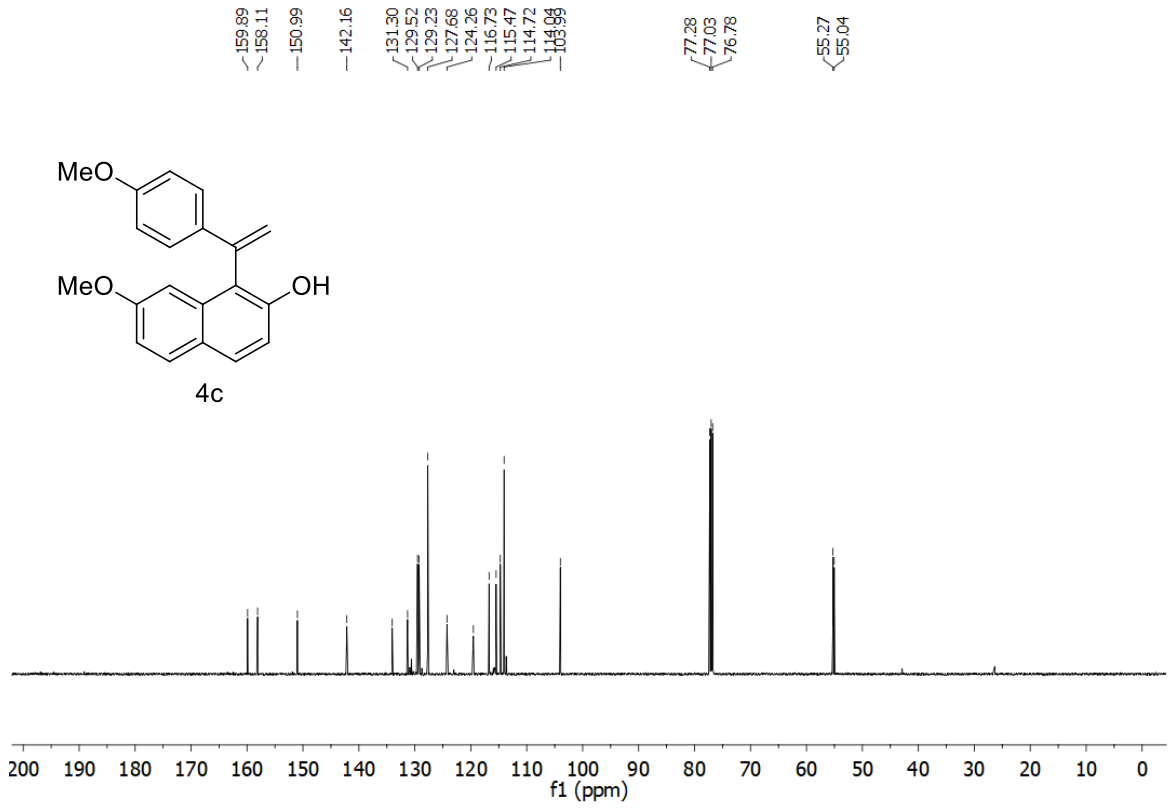
^{1}H NMR of 4b in $CDCl_3$



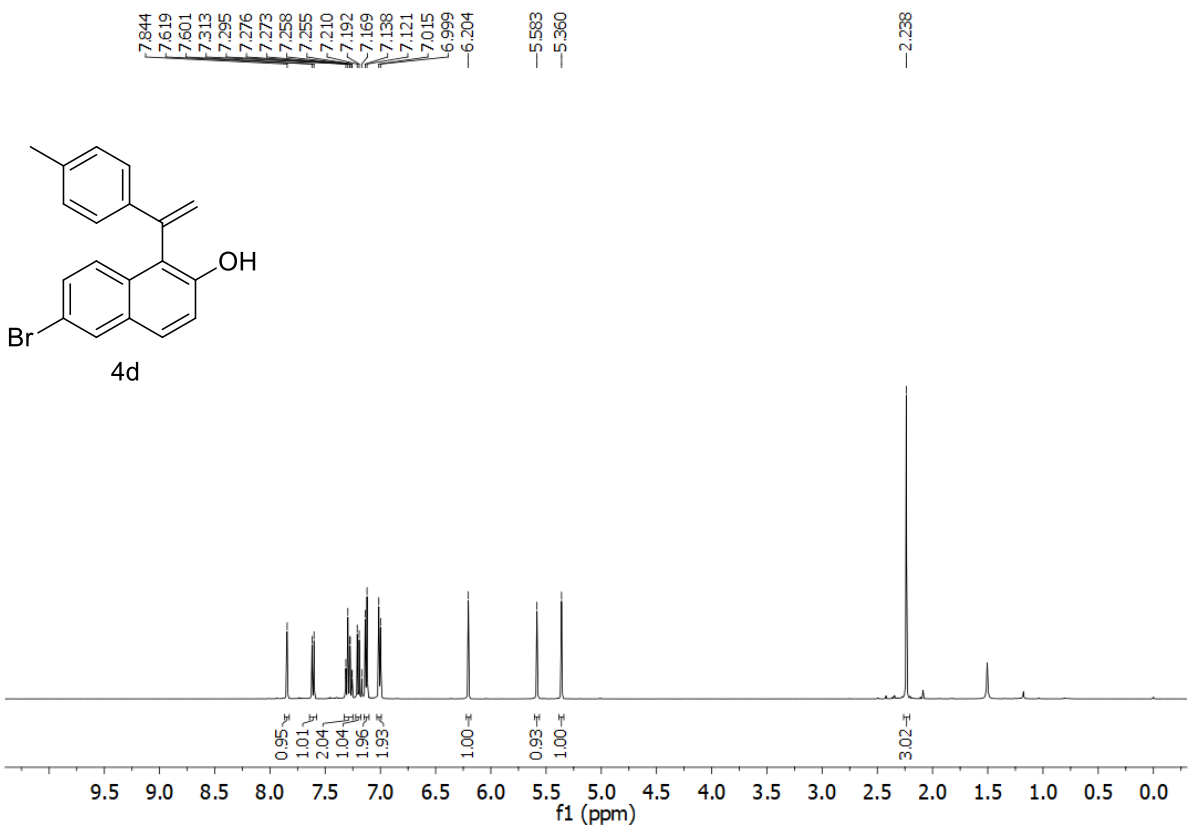
^{13}C{^{1}H} NMR of 4b in $CDCl_3$



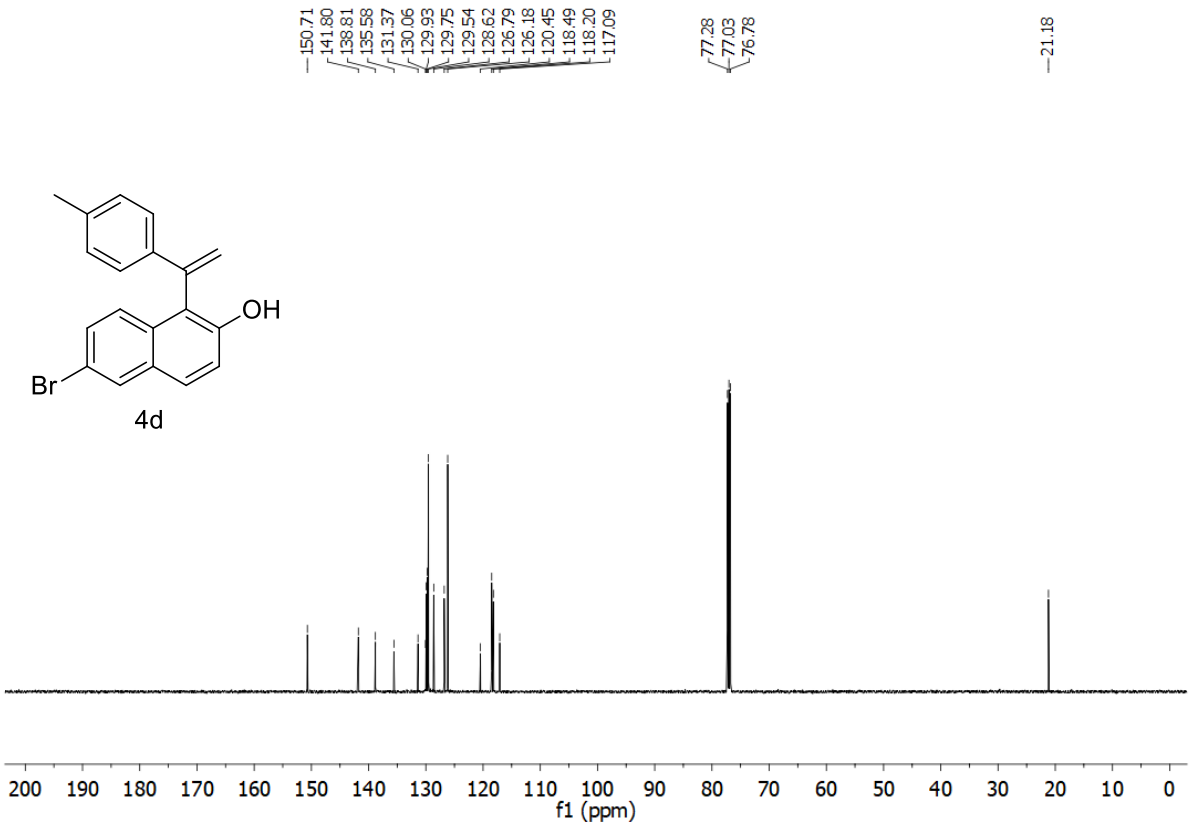
^{1}H NMR of 4c in $CDCl_3$



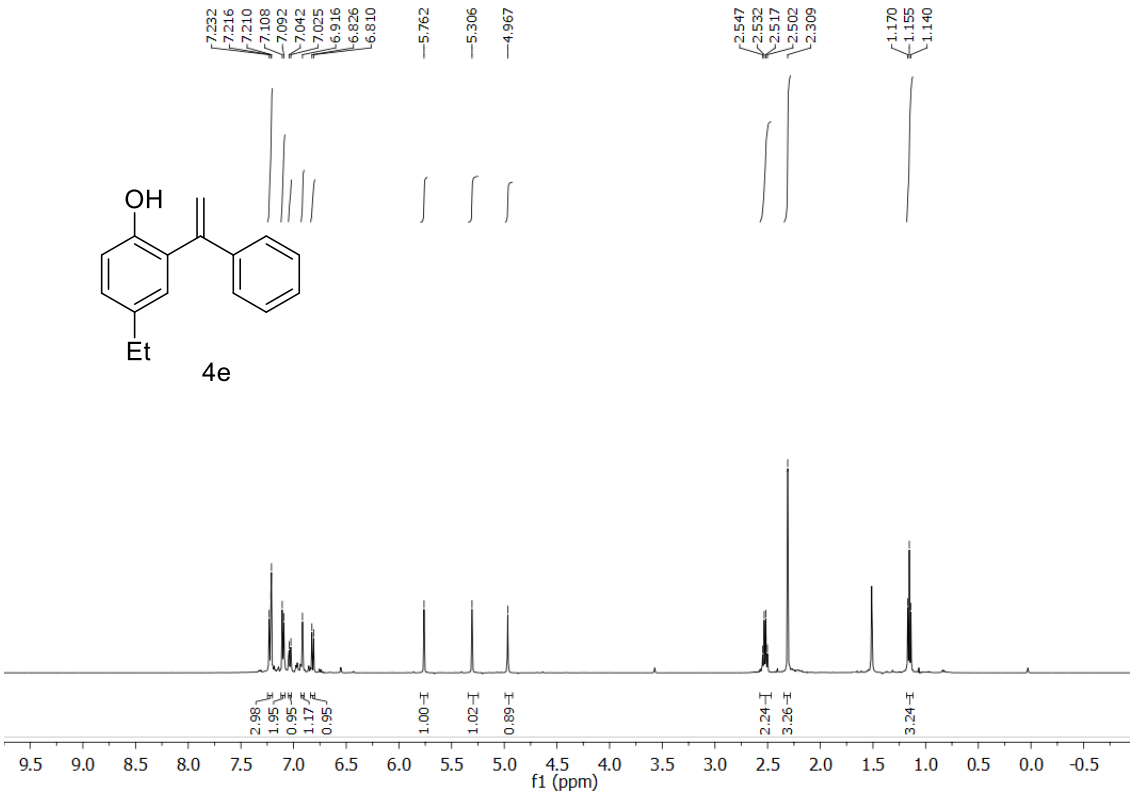
^{13}C{^{1}H} NMR of 4c in $CDCl_3$



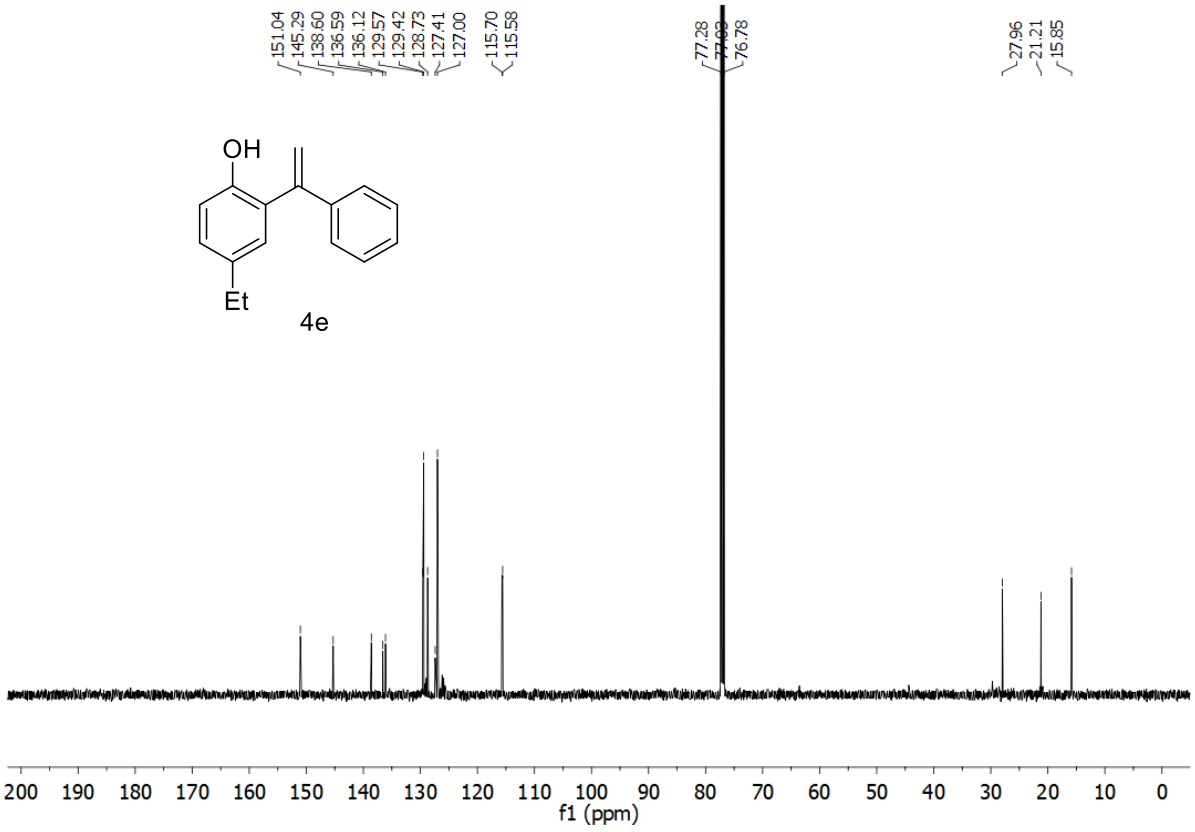
^{1}H NMR of 4d in $CDCl_3$



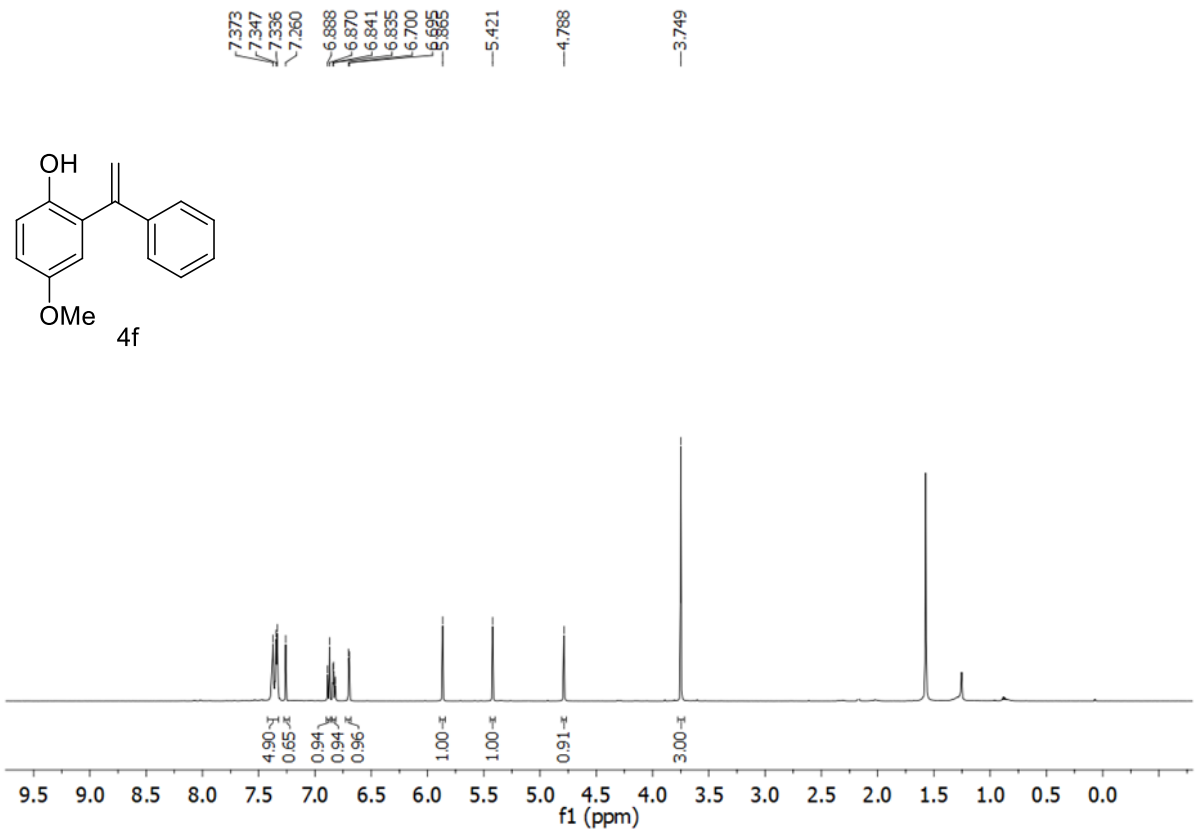
^{13}C{^{1}H} NMR of 4d in $CDCl_3$



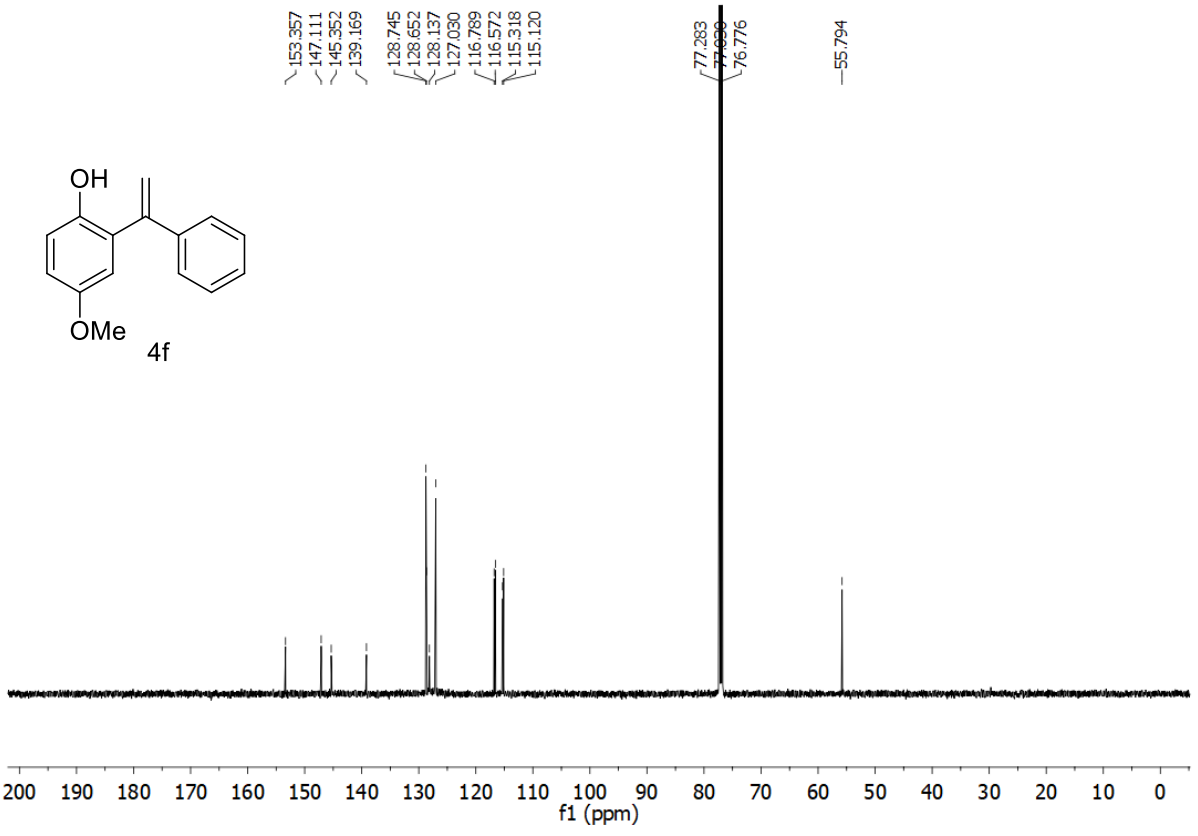
^{1}H NMR of 4e in $CDCl_3$



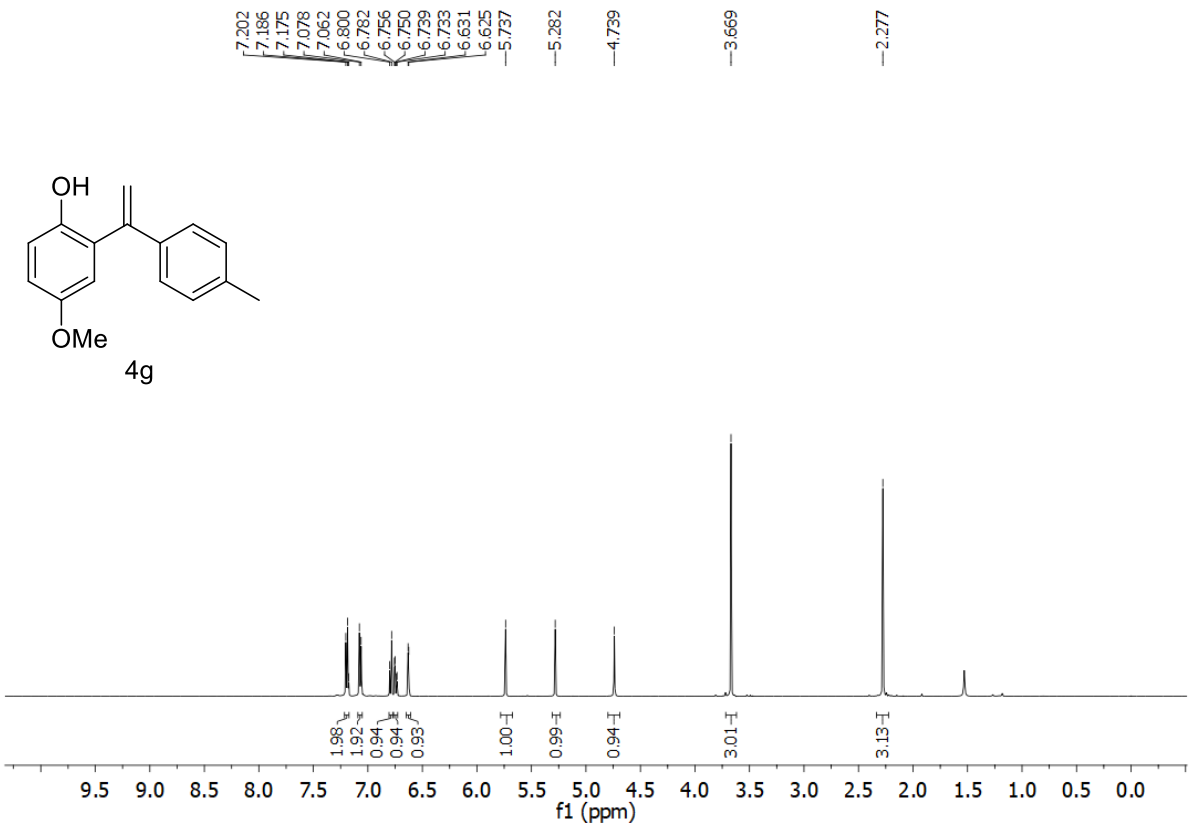
^{13}C{^{1}H} NMR of 4e in $CDCl_3$



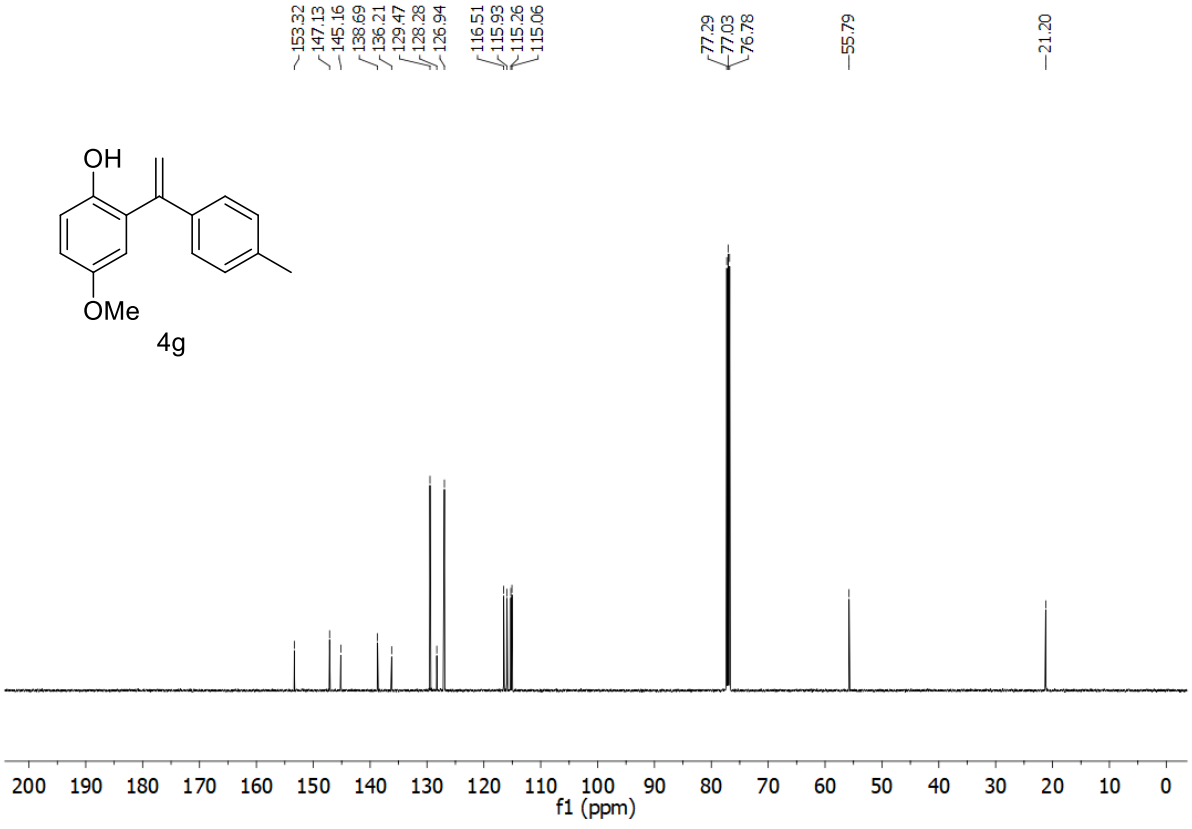
^{1}H NMR of 4f in $CDCl_3$



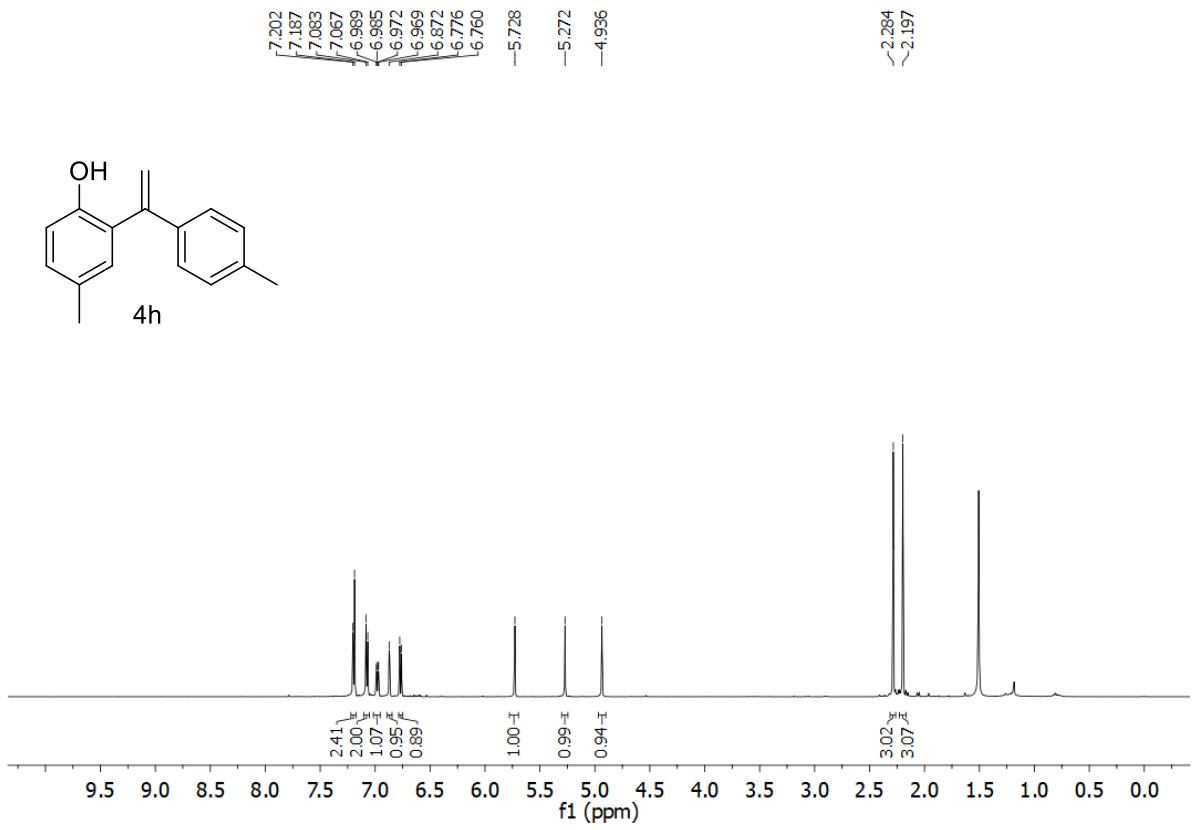
^{13}C{^{1}H} NMR of 4f in $CDCl_3$



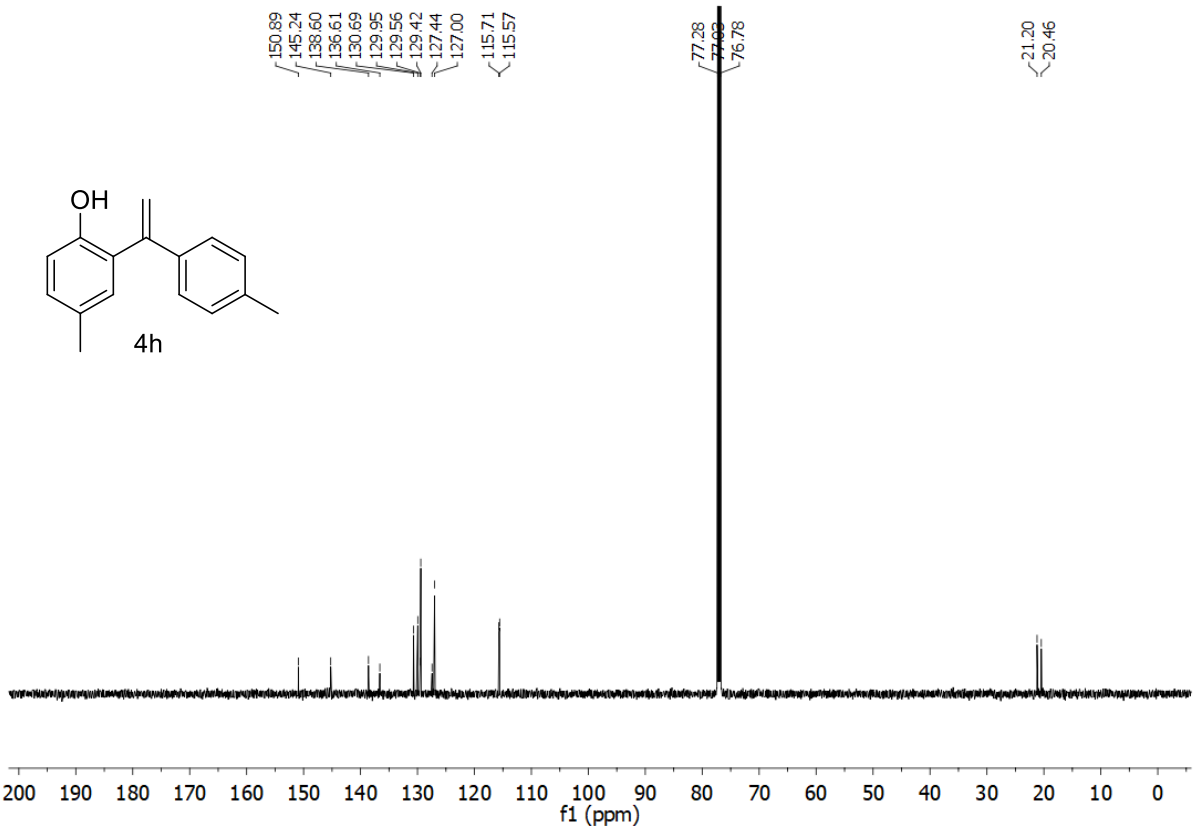
^{1}H NMR of 4g in $CDCl_3$



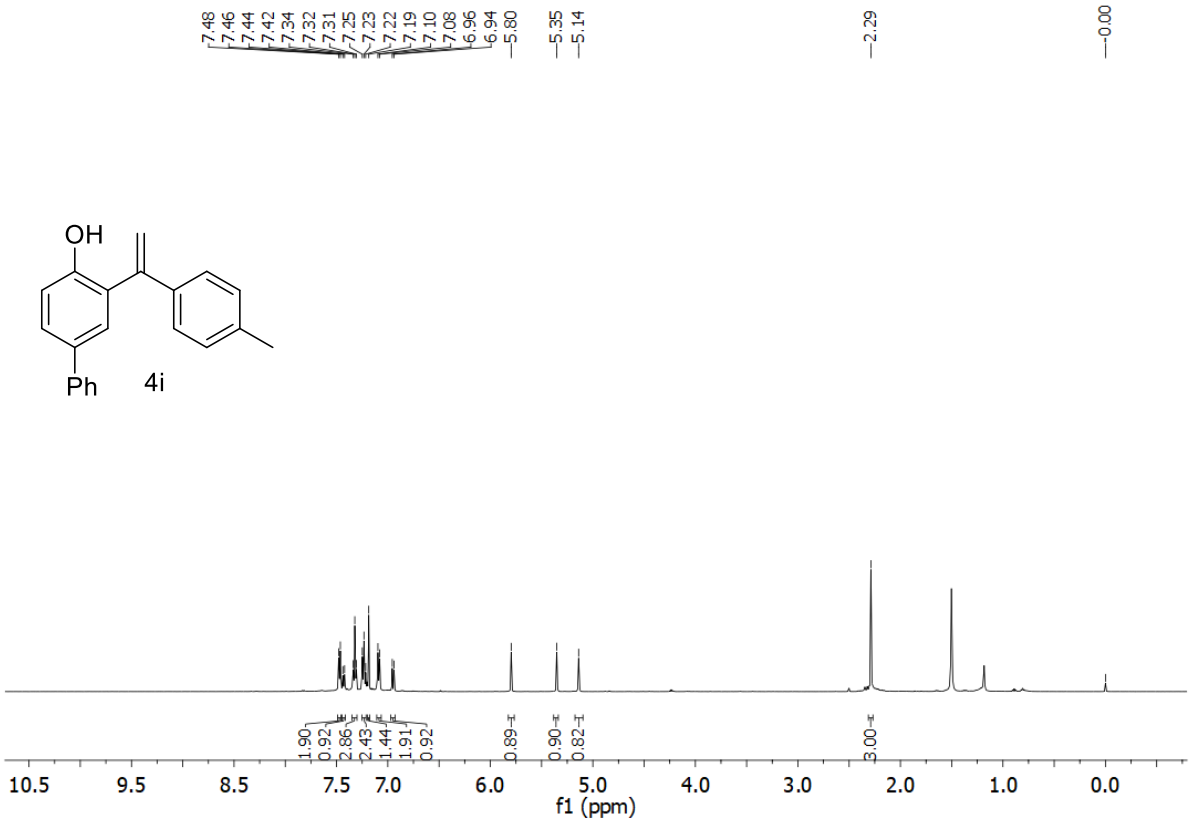
^{13}C{^{1}H} NMR of 4g in $CDCl_3$



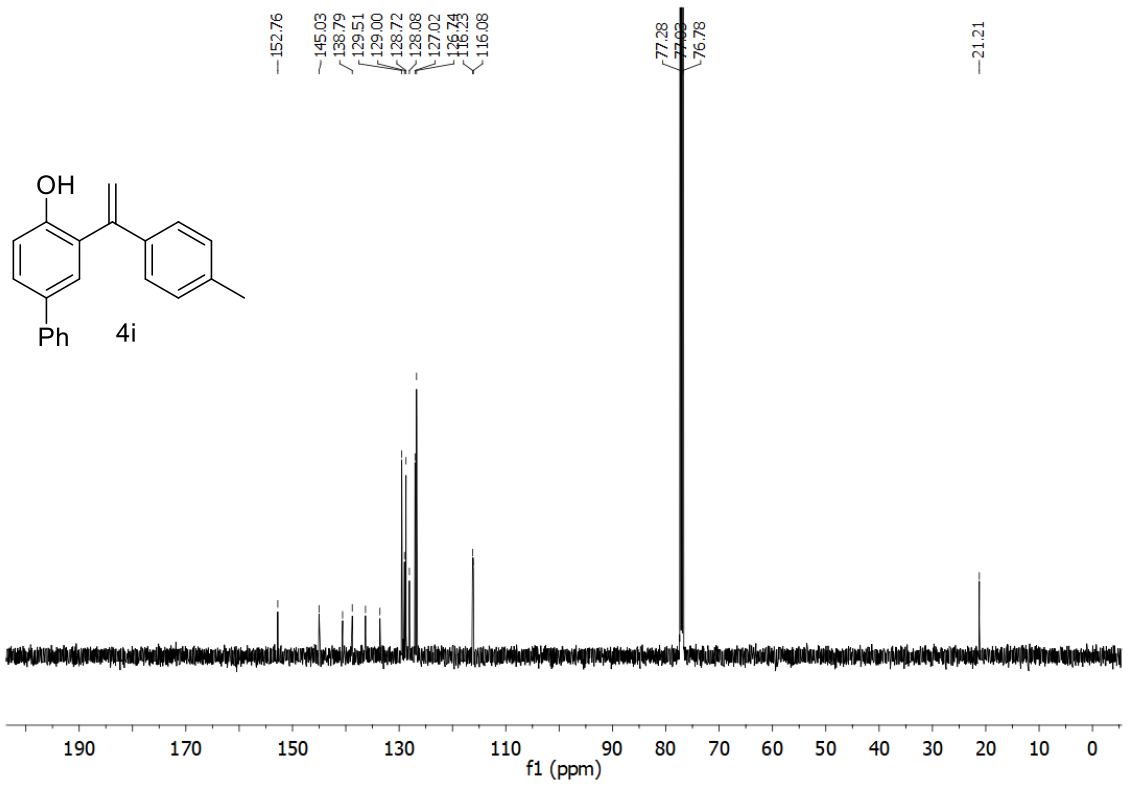
^{1}H NMR of 4h in $CDCl_3$



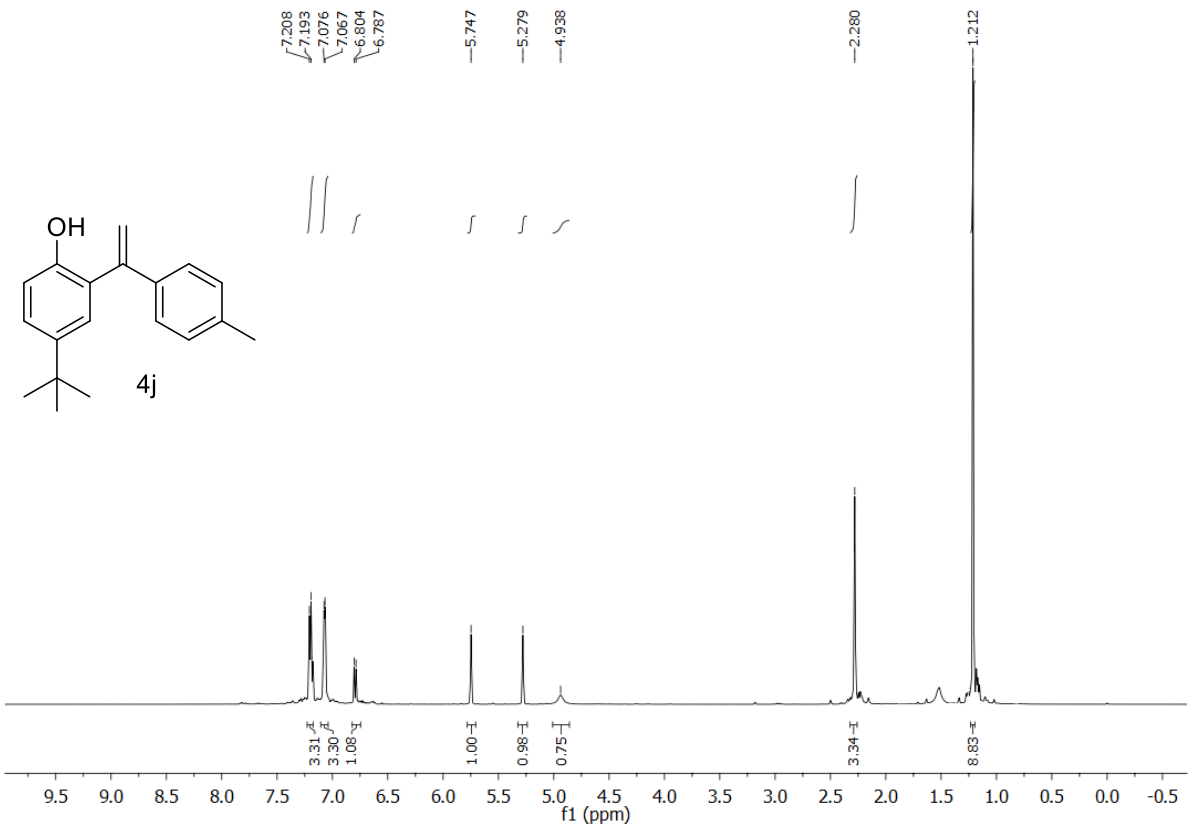
^{13}C{^{1}H} NMR of 4h in $CDCl_3$



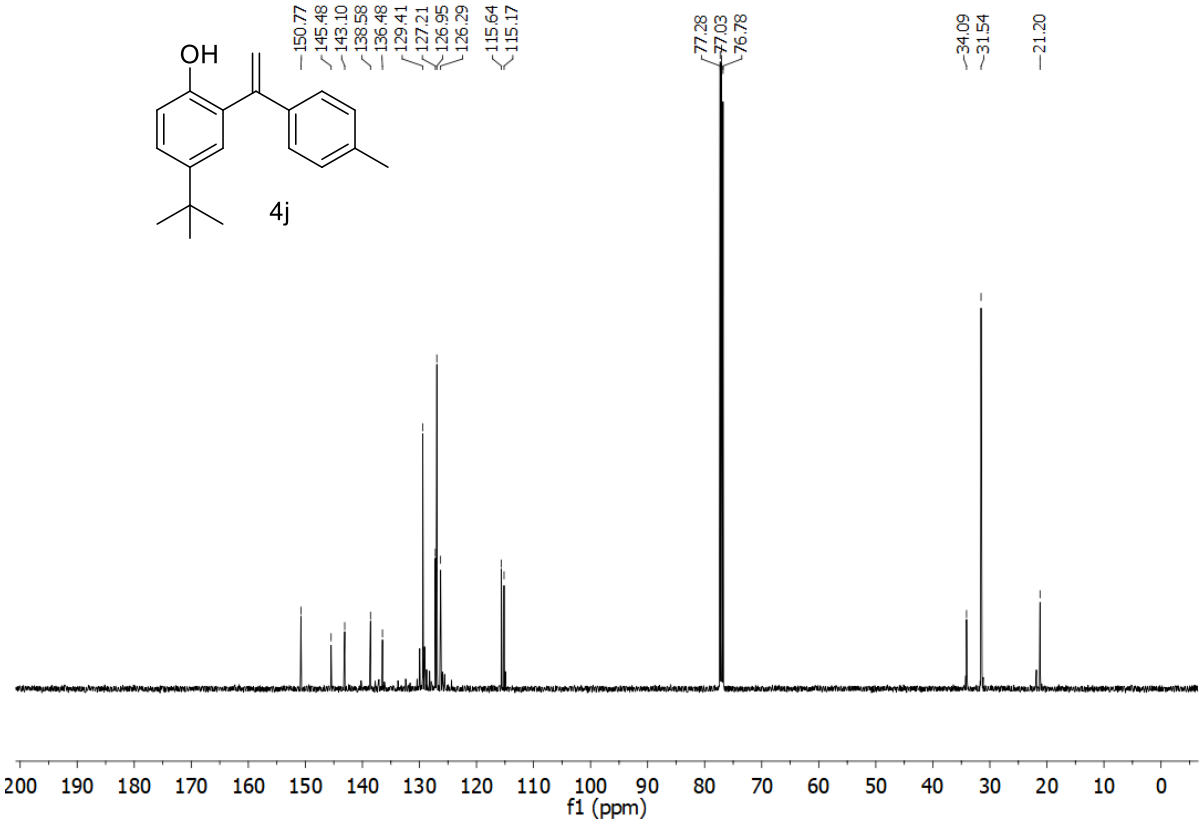
^{1}H NMR of 4i in $CDCl_3$



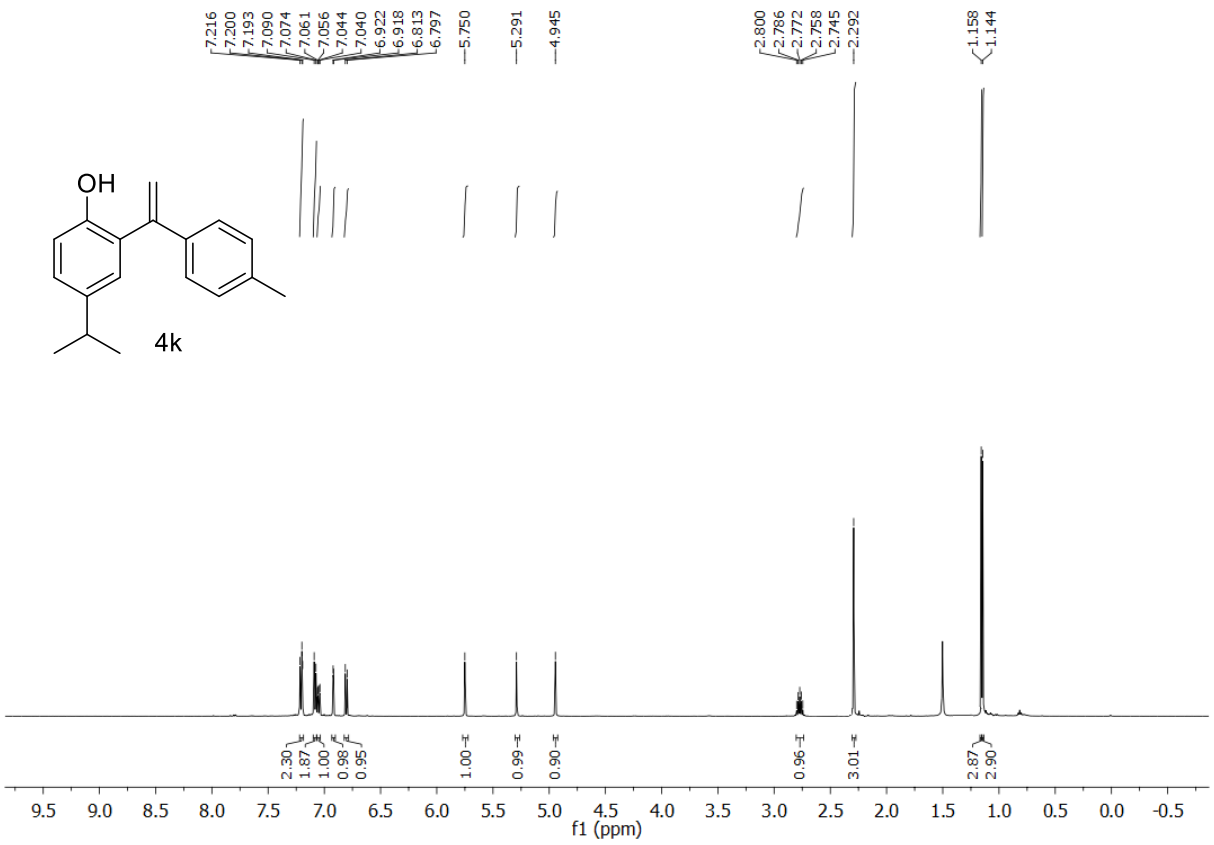
^{13}C{^{1}H} NMR of 4i in $CDCl_3$



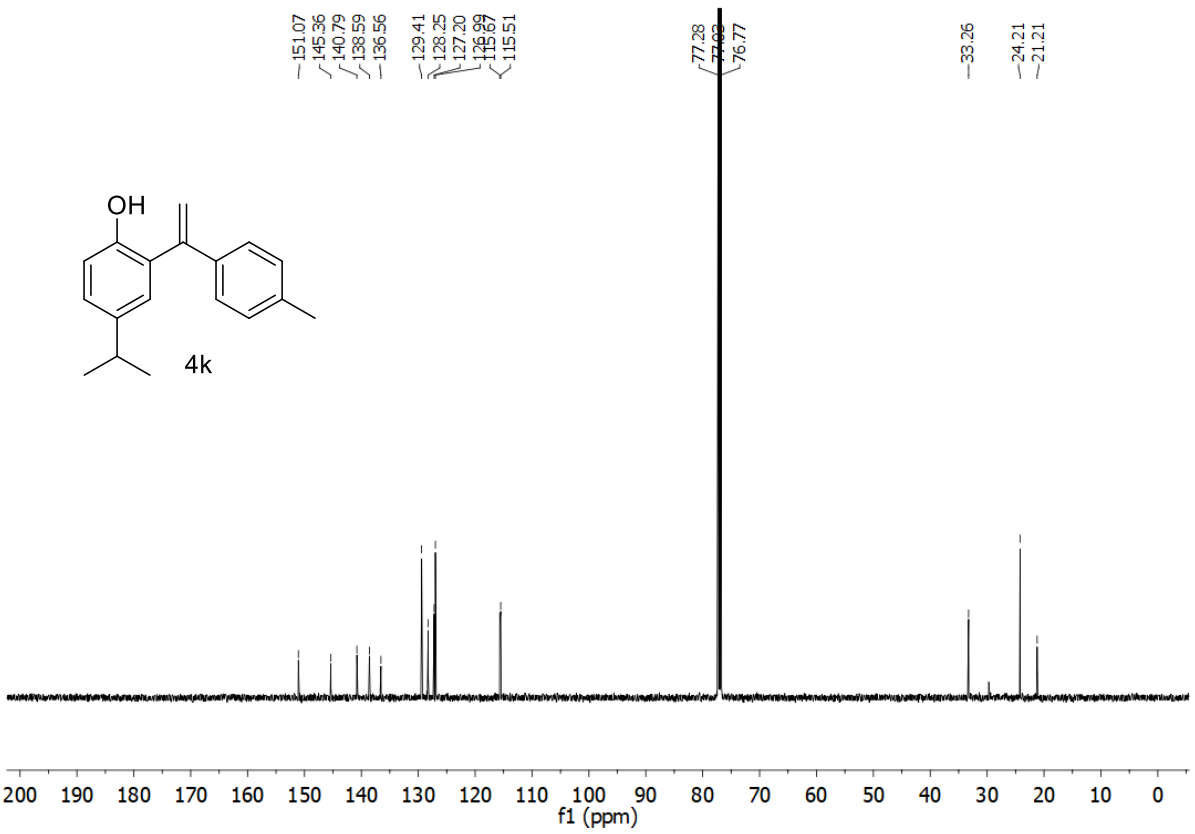
^{1}H NMR of 4j in $CDCl_3$



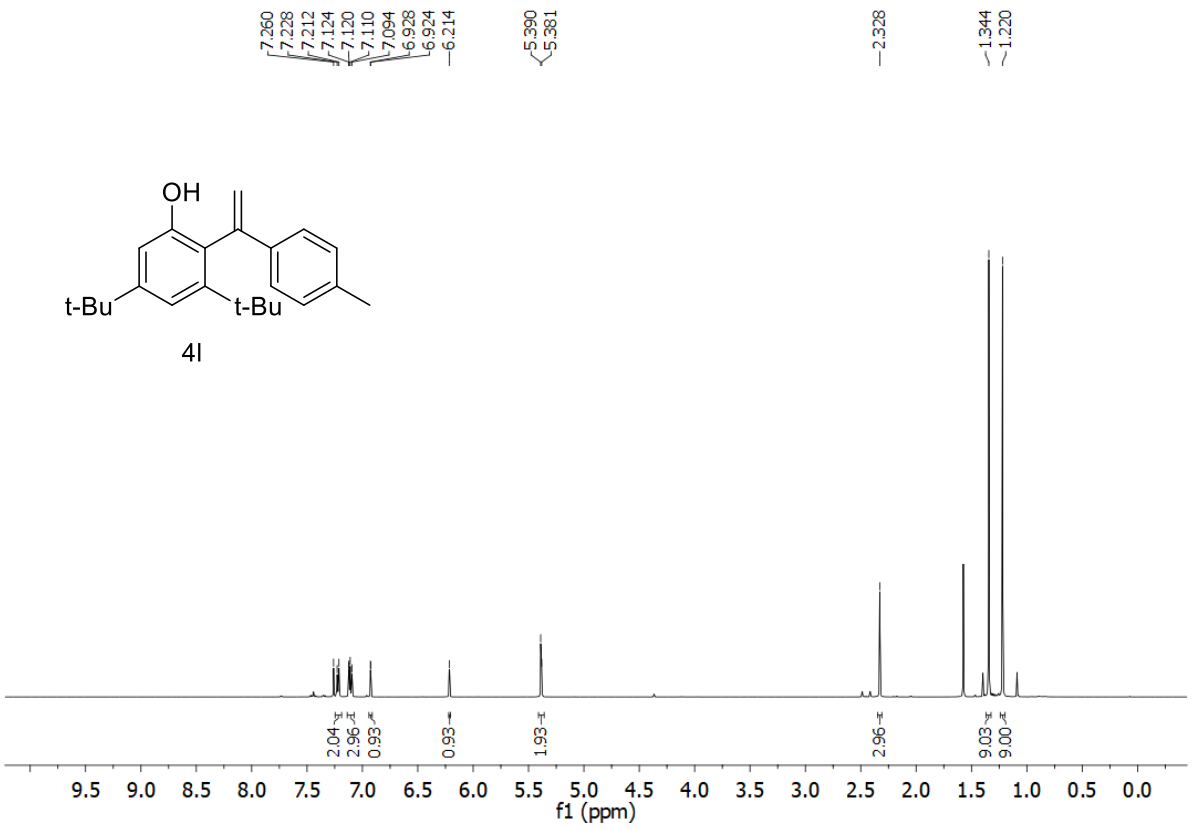
$^{13}C\{^{1}H\}$ NMR of 4j in $CDCl_3$



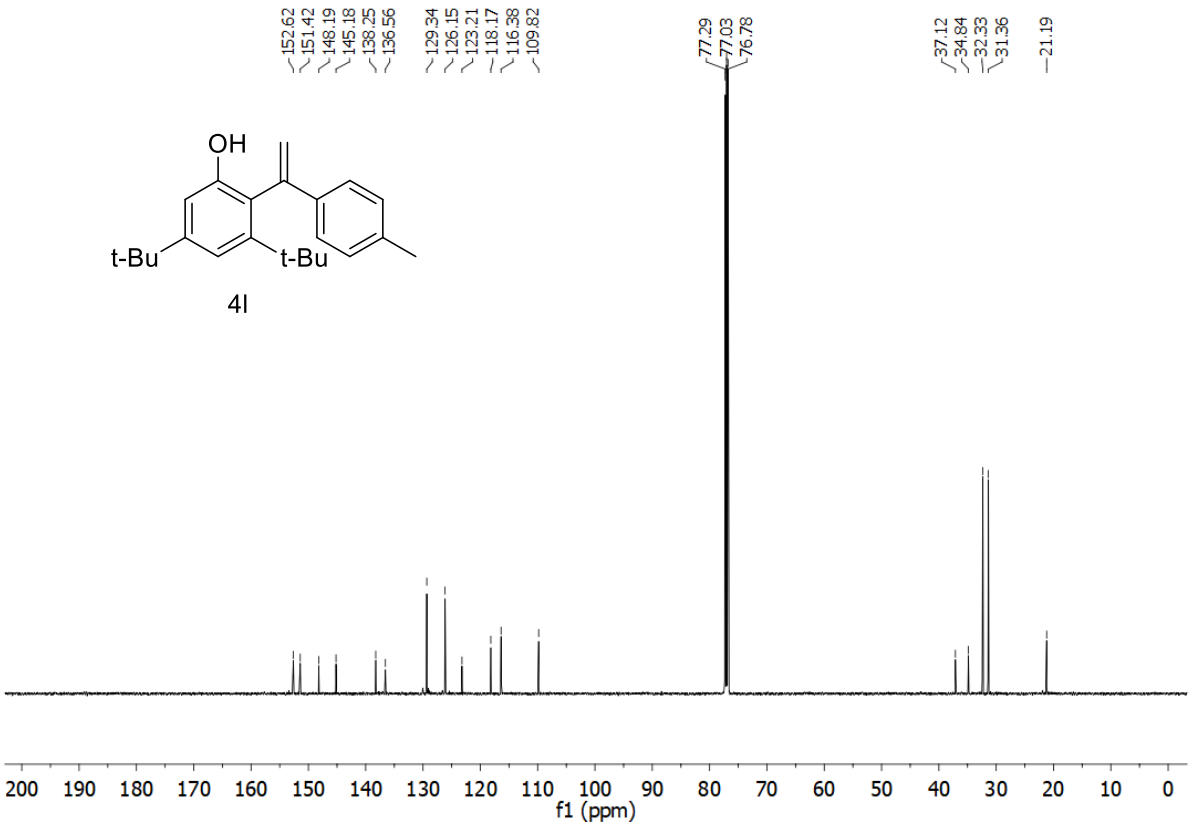
^{1}H NMR of 4k in $CDCl_3$



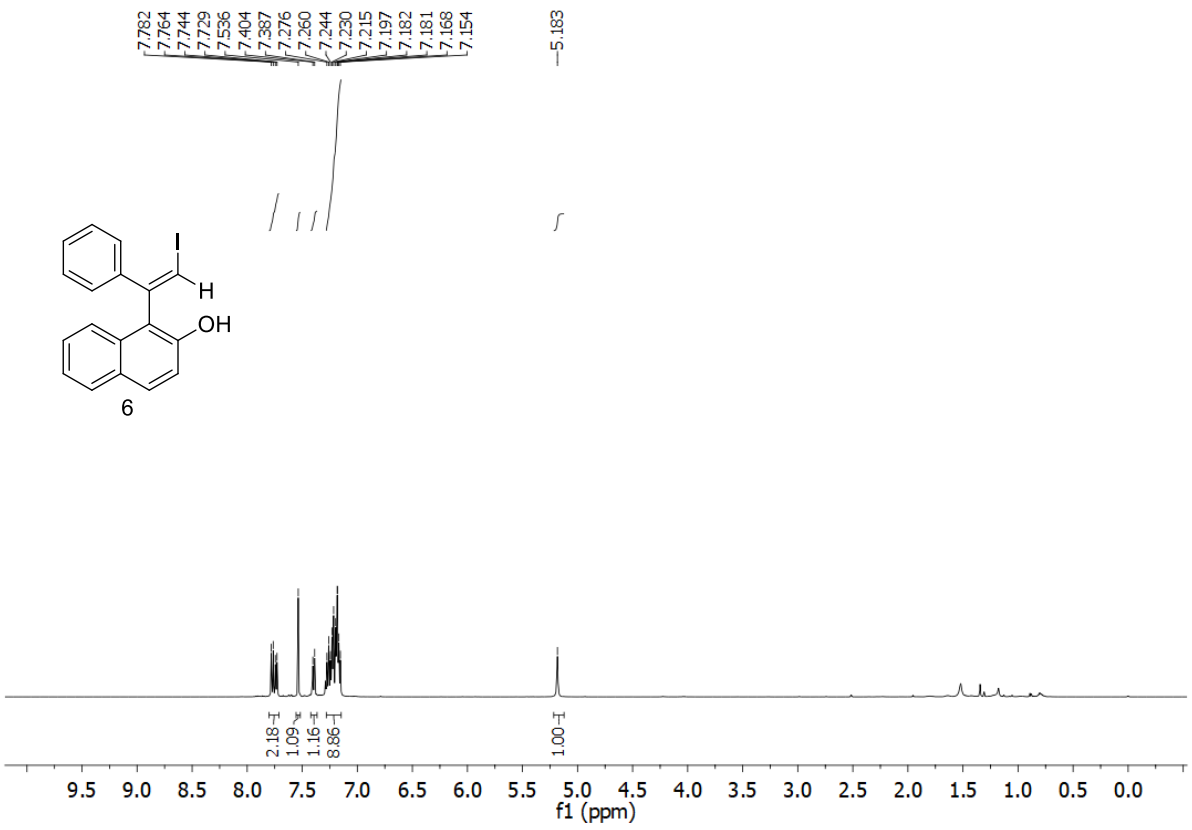
^{13}C{^{1}H} NMR of 4k in $CDCl_3$



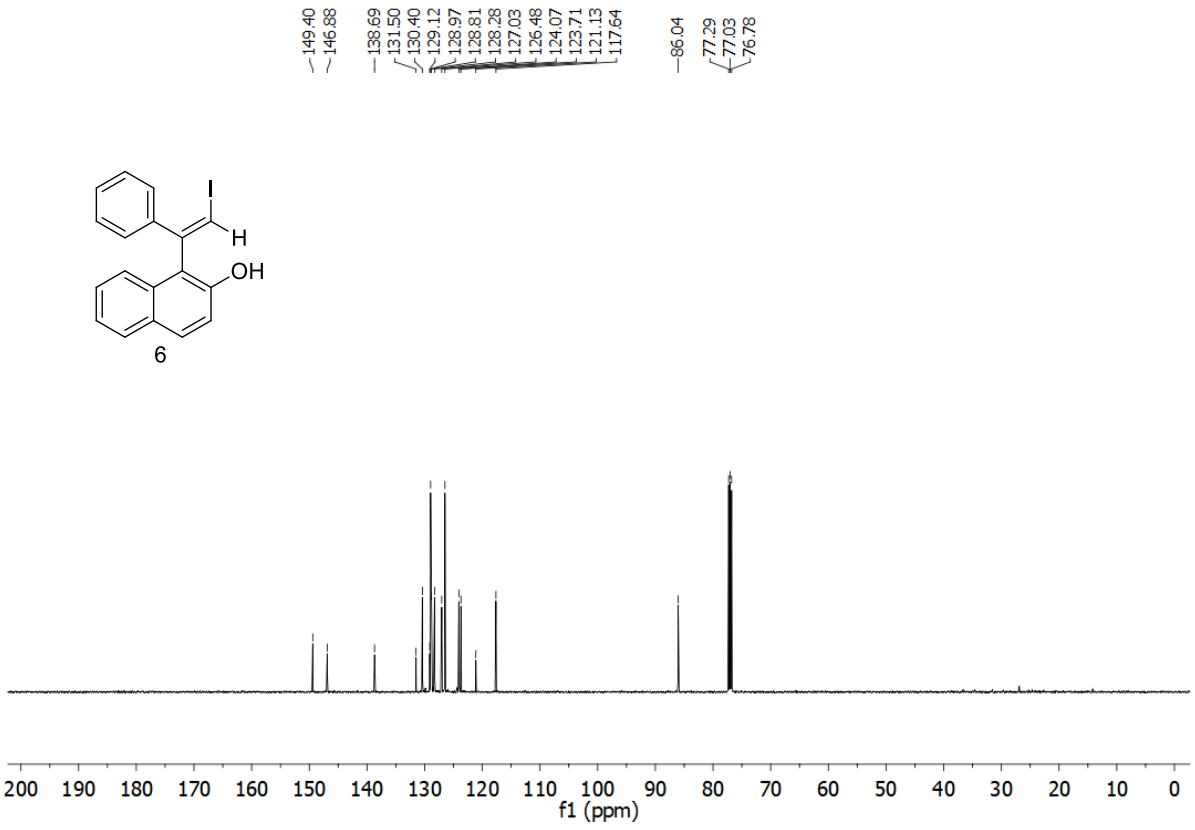
^{1}H NMR of 4l in $CDCl_3$



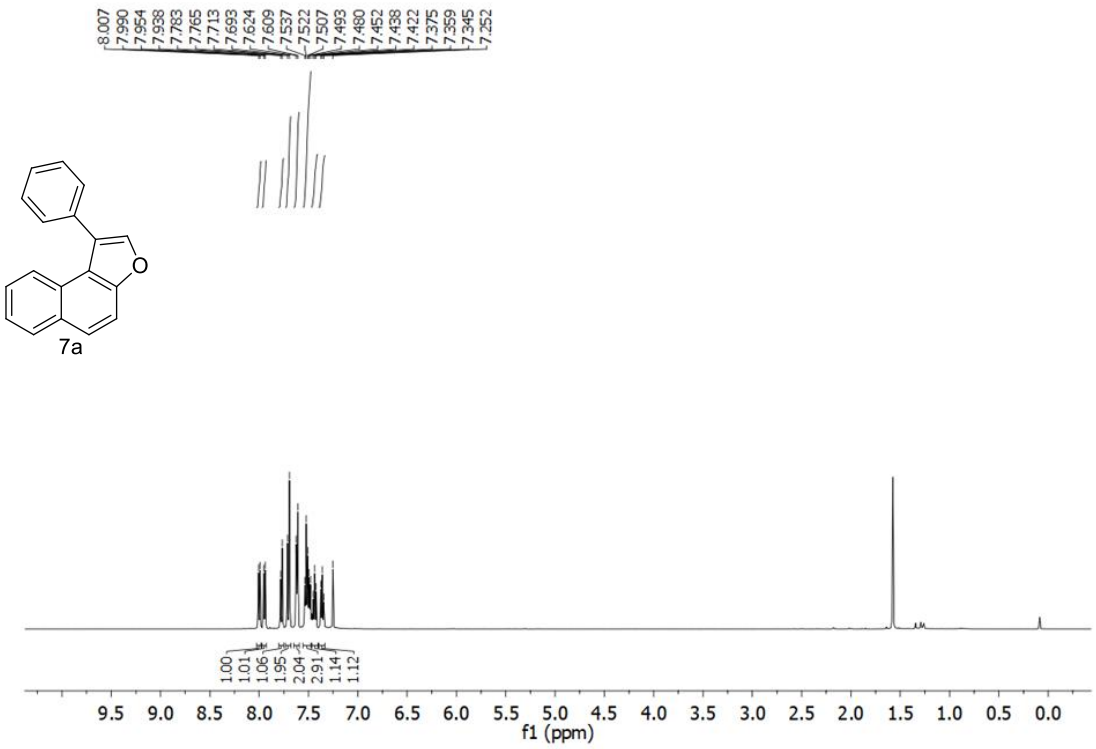
$^{13}C\{^{1}H\}$ NMR of 4l in $CDCl_3$



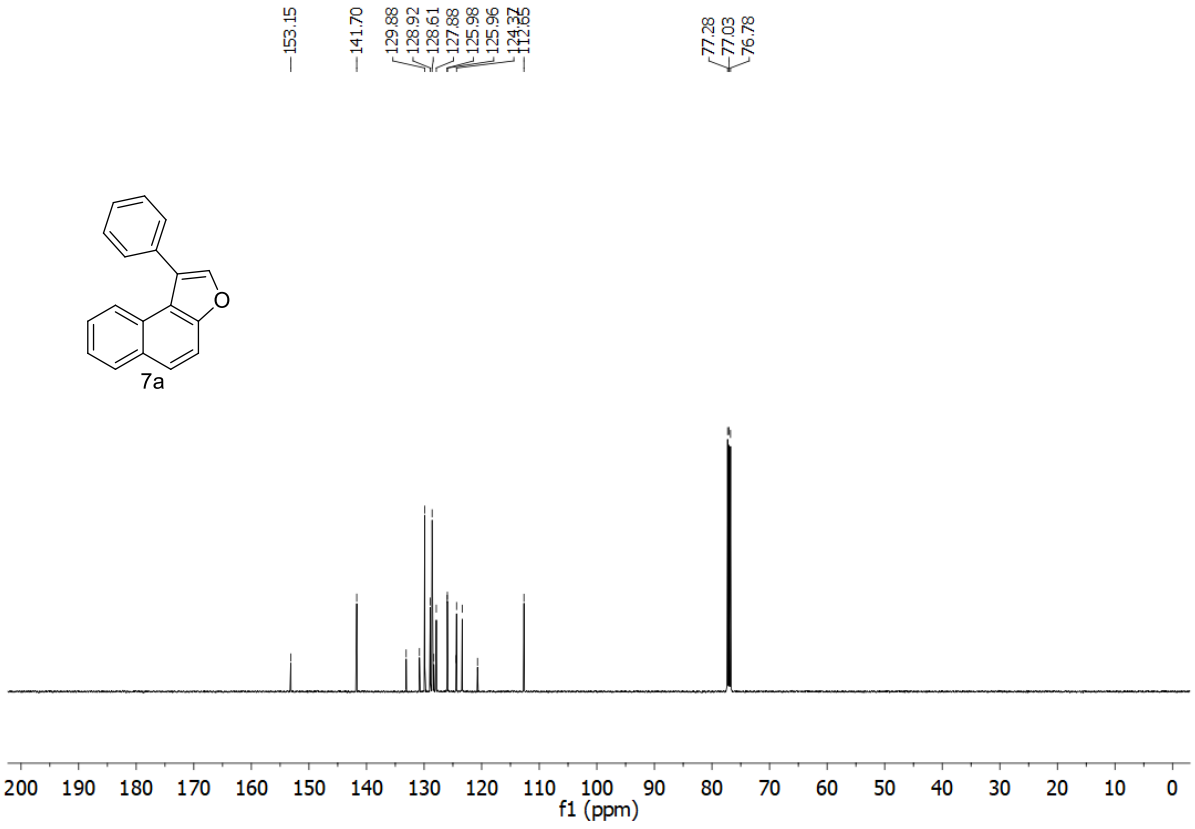
^{1}H NMR of 6 in $CDCl_3$



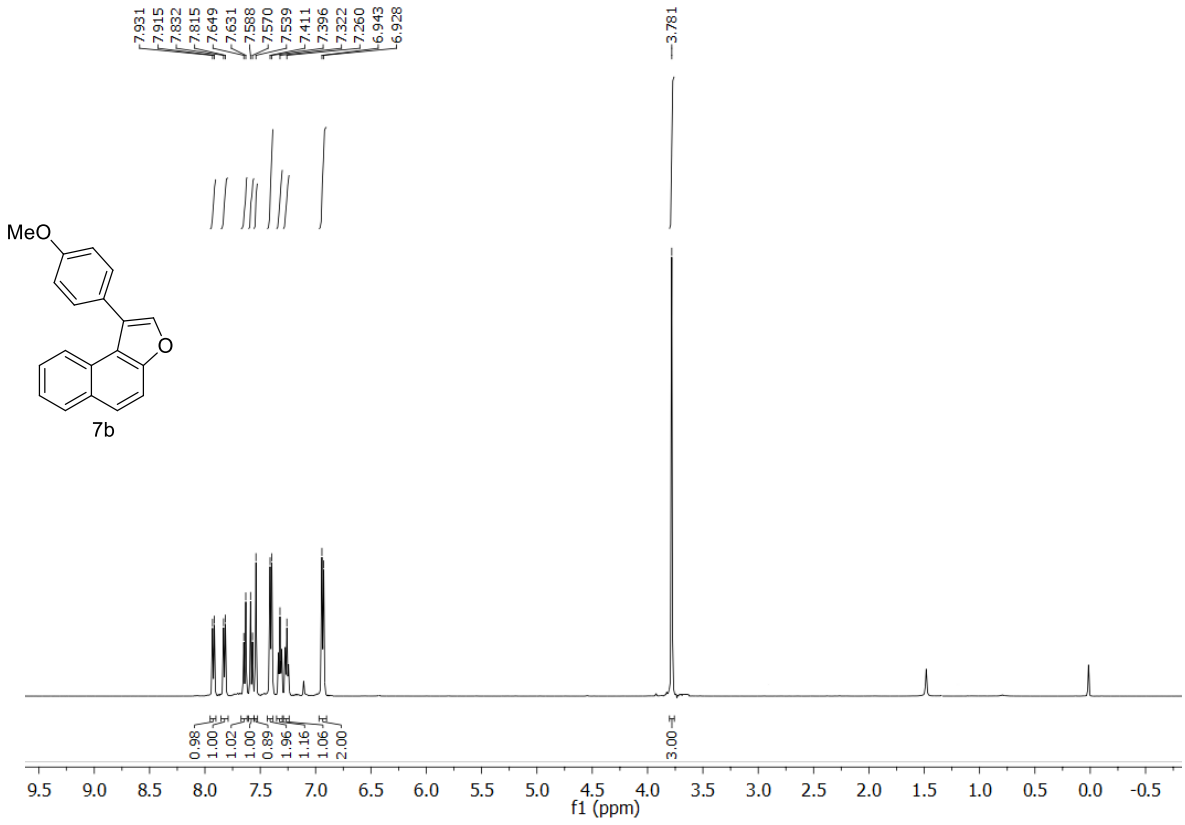
^{13}C{^{1}H} NMR of 6 in $CDCl_3$



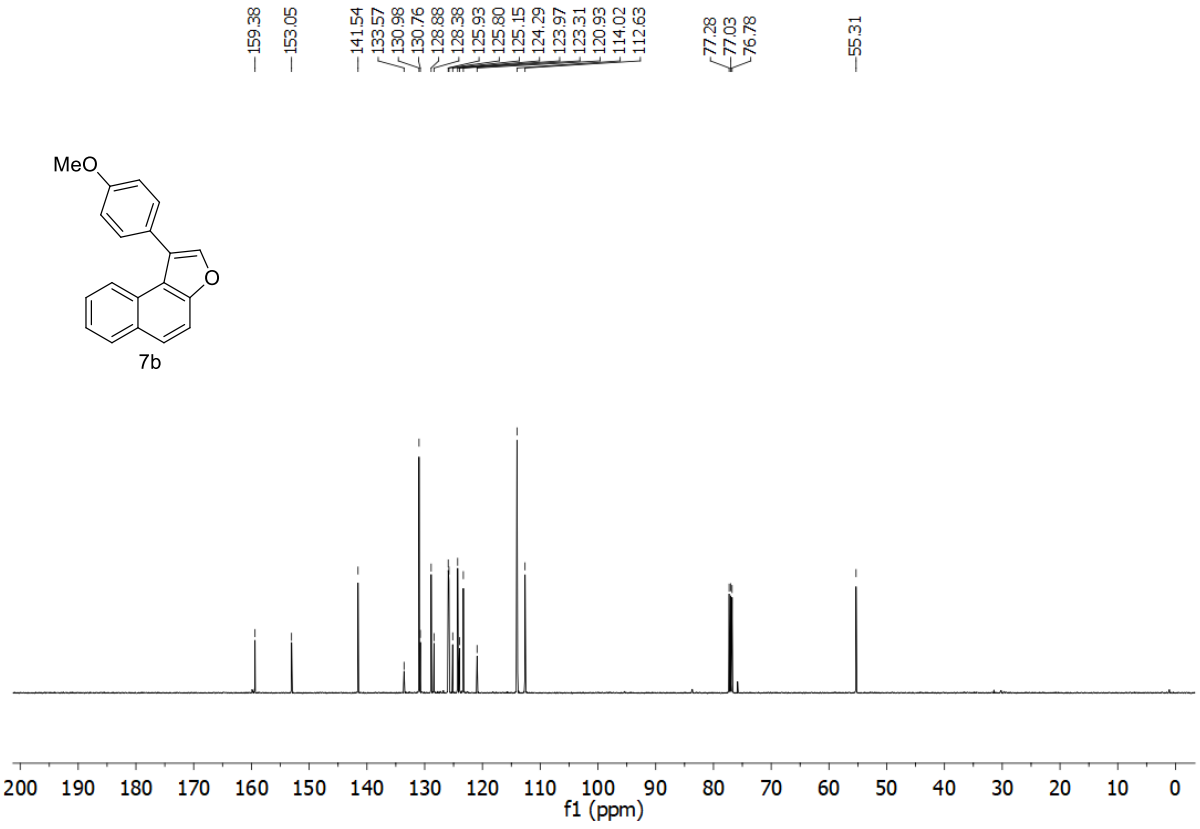
^{1}H NMR of 7a in $CDCl_3$



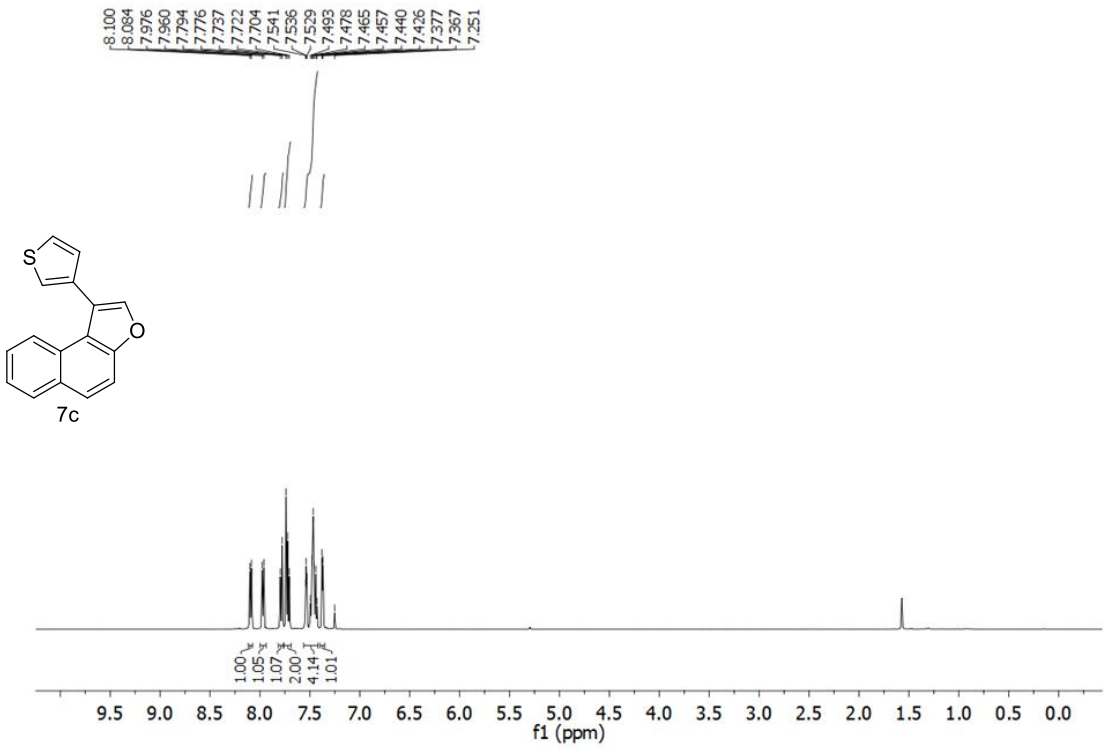
^{13}C{^{1}H} NMR of 7a in $CDCl_3$



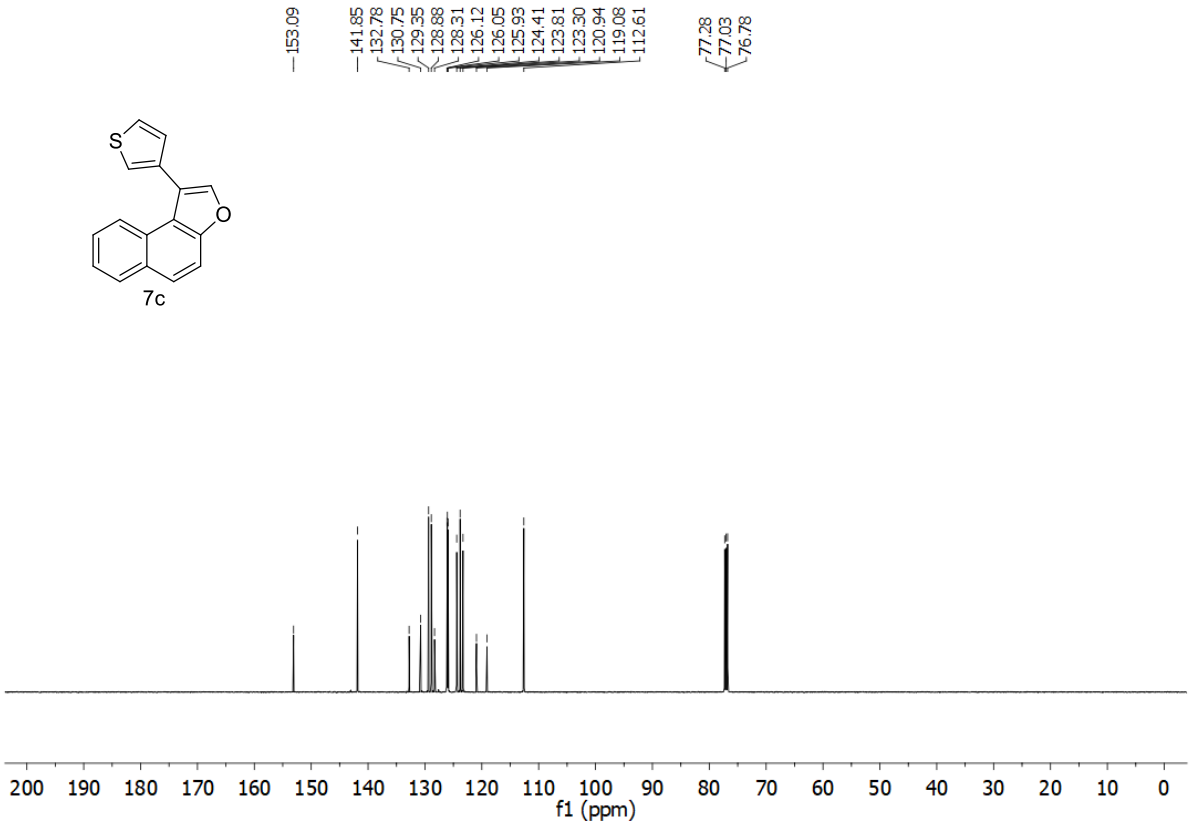
^{1}H NMR of 7b in $CDCl_3$



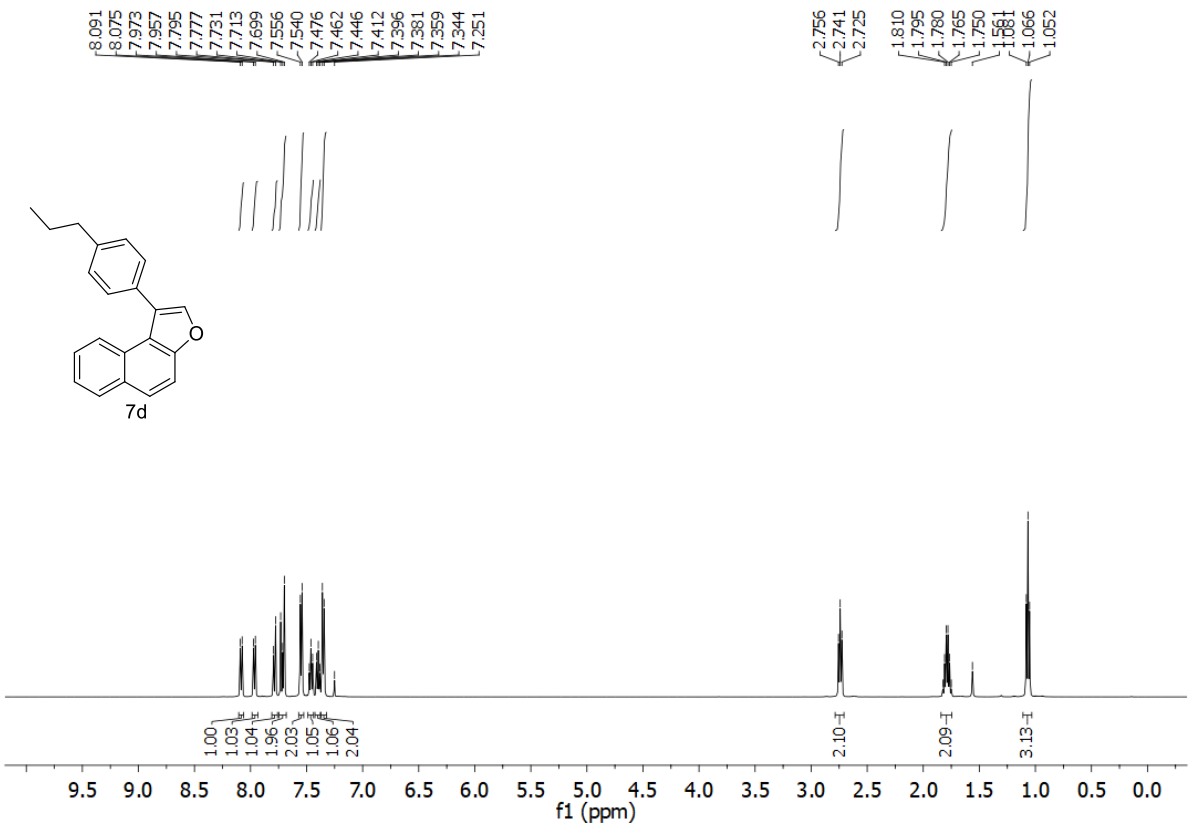
^{13}C{^{1}H} NMR of 7b in $CDCl_3$



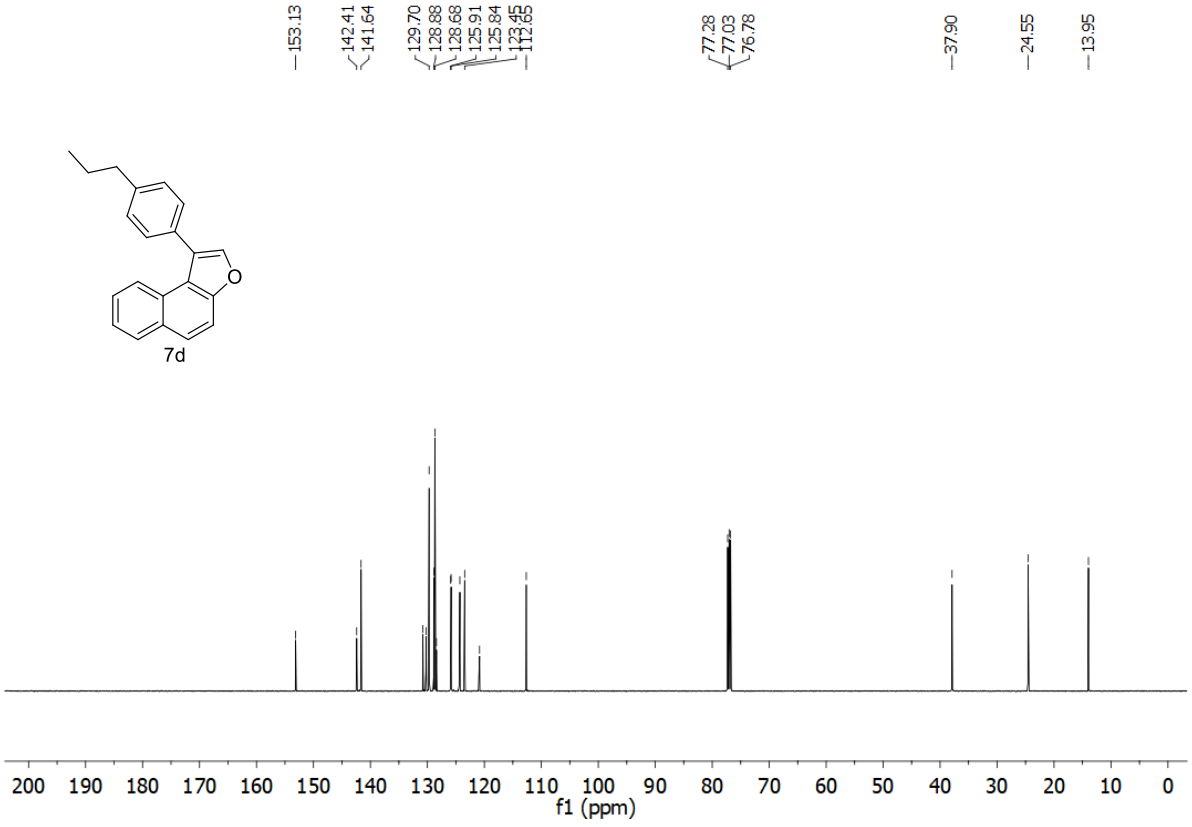
^{1}H NMR of 7c in $CDCl_3$



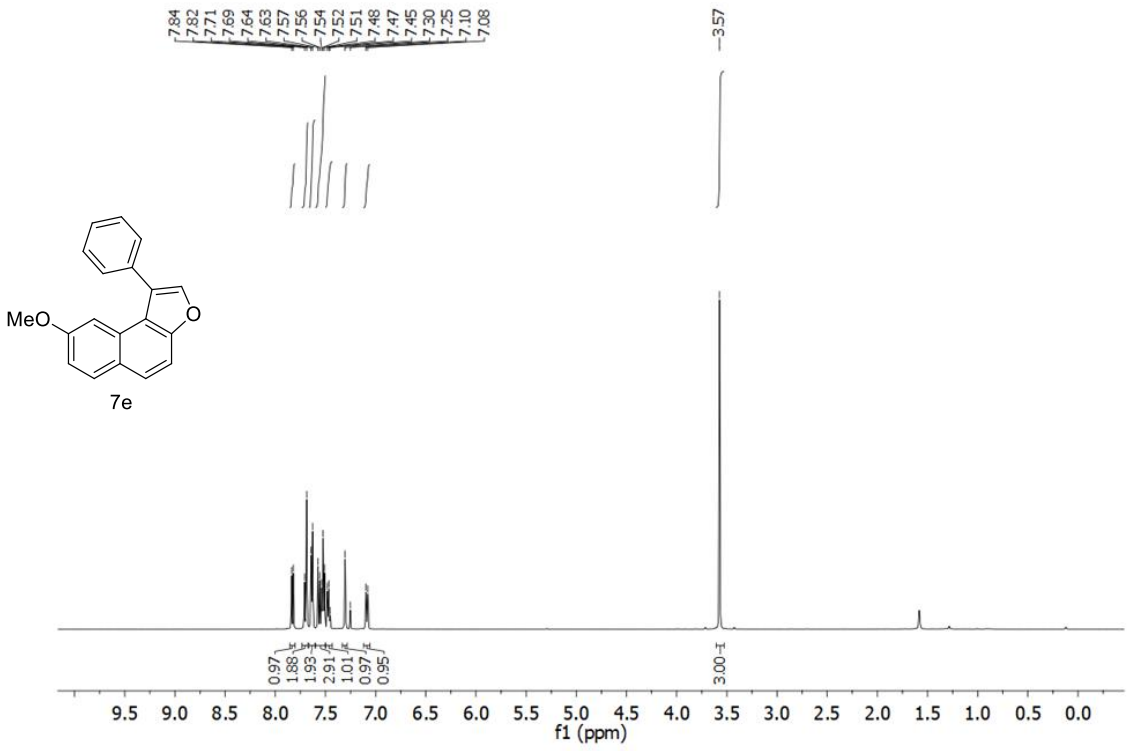
^{13}C{^{1}H} NMR of 7c in $CDCl_3$



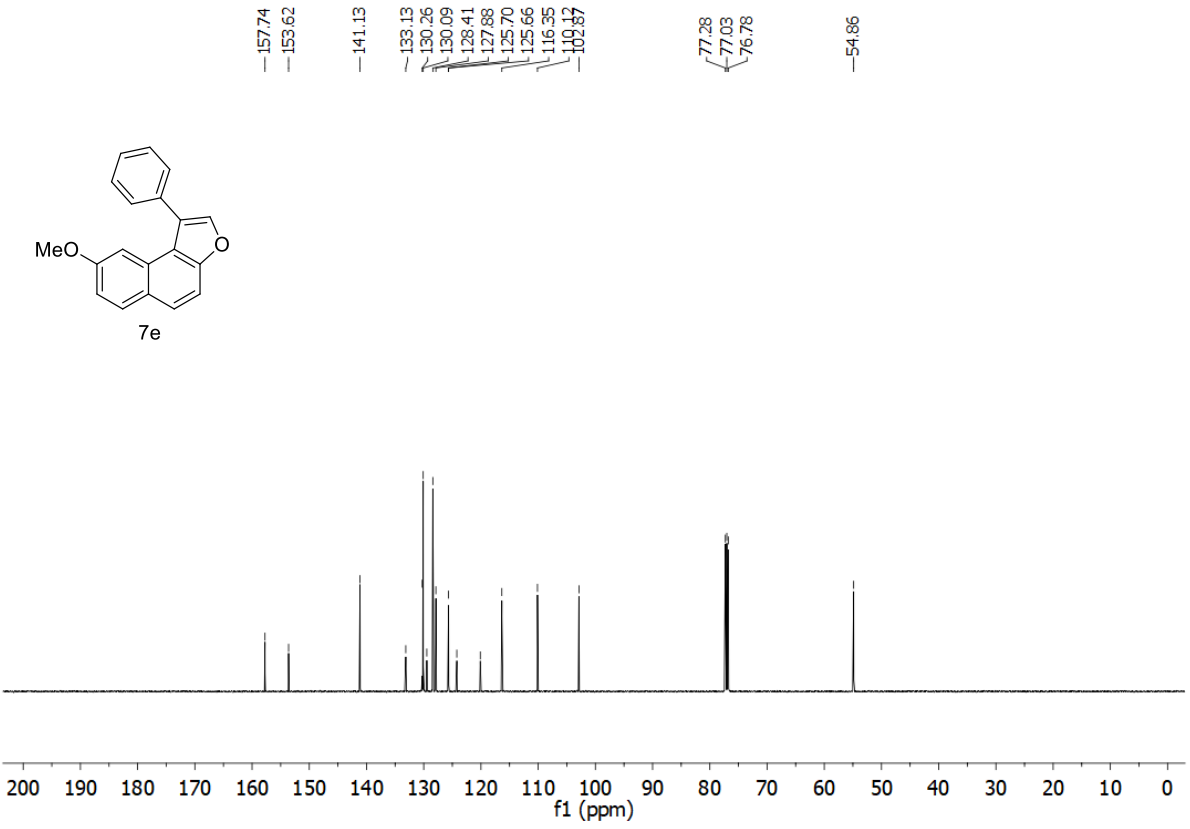
^{1}H NMR of 7d in $CDCl_3$



^{13}C{^{1}H} NMR of 7d in $CDCl_3$



^{1}H NMR of 7e in $CDCl_3$



^{13}C{^{1}H} NMR of 7e in $CDCl_3$