Supporting Information

Photoredox radical annulation of aroyl sulfoxonium ylides and alkynes for 1-naphthol assembly

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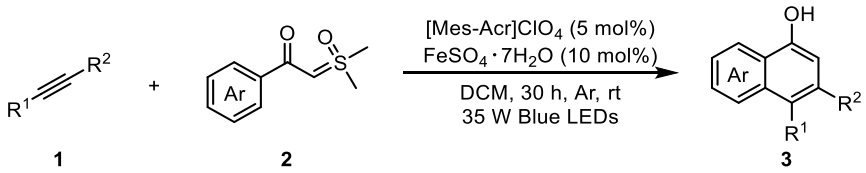
1. General information

The reactions via general procedure were carried out under an atmosphere of argon unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker-AV (400, 100 and 376 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and HRMS data with those in literature. A commercially available blue LED (35W, HIPAR30, luminous flux is not less than 3200 lm) was purchased from Shenzhen Jing Feng Times Lighting Technology Co., Ltd as the reaction light source. All irradiation reactions were carried out in borosilicate glass vessel. The distance from the light source to the irradiation vessel is around 4-5 cm. Unless otherwise noted, all photocatalysts and reagents were obtained from commercial suppliers and used without further purification.

2. General procedure of the reaction products

Reaction device diagram: Reaction set-up for irradiation of mixture with 35 W blue LEDs (λ_{max} = 415 nm) and a fan was used to maintain the reaction temperature at 25-35 °C.



1 2 3

General Procedure A: A 10 mL reaction vessel was charged with alkynes **1** (0.24 mmol, 1.2 equiv.), sulfoxonium ylides **2** (0.2 mmol, 1.0 equiv.), $FeSO_4{\cdot}7H_2O$ (5.6 mg, 10 mol%), and $[Mes\text{-}Acr]ClO_4$ (4.1 mg, 5 mol%). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was carried out three times). Then, DCM (2.0 mL) was added. The solution was stirred at a distance of 4-5 cm from a 35 W Blue LEDs at room temperature (25-35 °C) for 30 h. After completion of the reaction, the crude mixture was diluted with ethyl acetate, filtered, and concentrated under reduced pressure to remove volatile components. Column chromatography was performed using silica gel (200-300 mesh) to give the pure products **3**.

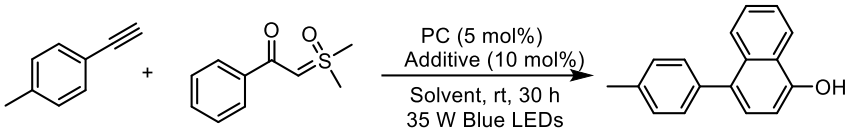
General Procedure B: A 10 mL reaction vessel was charged with alkynes **1** (0.24 mmol, 1.2 equiv.), sulfoxonium ylides **2** (0.2 mmol, 1.0 equiv.), $FeSO_4{\cdot}7H_2O$ (5.6 mg, 10 mol%), and $[Mes\text{-}Acr]ClO_4$ (4.1 mg, 5 mol%). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was carried out three times). Then, DCM (2.0 mL) was added. The solution was stirred at a distance of 4-5 cm from a 35 W Blue LEDs at room temperature (25-35 °C) for 48 h. After completion of the reaction, the crude mixture was diluted with ethyl acetate, filtered, and concentrated under reduced pressure to remove volatile components. Column chromatography was performed using silica gel (200-300 mesh) to give the pure products **3**.

Scaled-up reaction:

1a, 2.4 mmol **2a**, 2mmol **3a**, 52%, 244 mg

2 mmol scale reaction: A 50 mL reaction vessel was charged with alkyne **1a** (299 μL, 2.4 mmol, 1.0 equiv.), sulfoxonium ylide **2a** (392 mg, 2 mmol, 1.2 equiv.), $FeSO_4{\cdot}7H_2O$ (56 mg, 10 mol%), and [Mes-Acr]ClO_4 (41 mg, 5 mol%). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was carried out three times). Then, DCM (20 mL) was added. The solution was stirred at a distance of 4-5 cm from a 35 W Blue LEDs at room temperature (25-35 ^oC) for 48 h. After completion of the reaction, the crude mixture was diluted with ethyl acetate, filtered, and concentrated under reduced pressure to remove volatile components. Column chromatography was performed using silica gel (200-300 mesh) to give the pure product **3a** (52%, 244 mg).

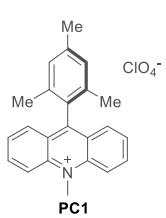
3. Optimization of reaction conditions[a]



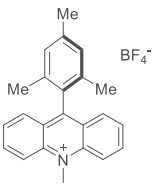
1a 2a 3a

Entry	PC	Solvent	Additive	Yield (%)[b]
1	PC1	DCM	$FeSO_4·7H_2O$	59
2	PC2	DCM	$FeSO_4·7H_2O$	53
3	PC3	DCM	$FeSO_4·7H_2O$	<10
4	PC4	DCM	$FeSO_4·7H_2O$	n.d.
5	PC5	DCM	$FeSO_4·7H_2O$	<10
6	PC6	DCM	$FeSO_4·7H_2O$	n.d.
7	PC7	DCM	$FeSO_4·7H_2O$	trace
8	PC8	DCM	$FeSO_4·7H_2O$	trace
9	PC9	DCM	$FeSO_4·7H_2O$	trace
10	PC1	DCE	$FeSO_4·7H_2O$	50
11	PC1	MeCN	$FeSO_4·7H_2O$	40
12	PC1	EA	$FeSO_4·7H_2O$	22
13	PC1	1,4-Dioxane	$FeSO_4·7H_2O$	31
14	PC1	Acetone	$FeSO_4·7H_2O$	45
15	PC1	DMSO	$FeSO_4·7H_2O$	17
16	PC1	THF	$FeSO_4·7H_2O$	29
17	PC1	DCM	$Fe(OAc)_2·4H_2O$	54
18	PC1	DCM	$K_4[Fe(CN)_6]$	48
19	PC1	DCM	$FeSO_4$	43
20	PC1	DCM	$FeCl_3$	39
21	PC1	DCM	FeF_2	52
22	PC1	DCM	Cp_2Fe	31
23	PC1	DCM	$Fe_2(SO_4)_3·xH_2O$	44
24	PC1	DCM	$Ni(NO_3)_2·6H_2O$	41
25	PC1	DCM	$Ni(OAc)_2·4H_2O$	35
26	PC1	DCM	$NiCO_3$	50
27	PC1	DCM	$Bi(OAc)_3$	41
28	PC1	DCM	$Co(OAc)_2·4H_2O$	53
29	PC1	DCM	$Cu(OAc)_2·H_2O$	30
30	PC1	DCM	CuI	36

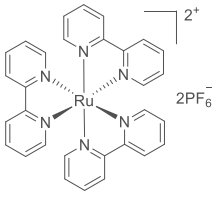
31	PC1	DCM	$Cu(CH_3CN)_4BF_4$	49
32	PC1	DCM	$Zn(OAc)_2$	54
33	PC1	DCM	$Mn(OAc)_2{\cdot}4H_2O$	45
34	PC1	DCM	NH_4OAc	18
35	PC1	DCM	CsOAc	n.d.
36	PC1	DCM	AgOAc	39
37	PC1	DCM	$AgSbPF_6$	18
38	PC1	DCM	$(PhS)_2$	51
39	PC1	DCM	LiBr	32
40	PC1	DCM	4-MePhSH	<10
41	PC1	DCM	$PhSiH_3$	46
42	PC1	DCM	$AlCl_3$	37
43[c]	PC1	DCM	$FeSO_4{\cdot}7H_2O$	58
44[d]	PC1	DCM	$FeSO_4{\cdot}7H_2O$	53
45[e]	PC1	DCM	$FeSO_4{\cdot}7H_2O$	55
46[f]	PC1	DCM	$FeSO_4{\cdot}7H_2O$	49
47[g]	PC1	DCM	$FeSO_4{\cdot}7H_2O$	36
48[h]	PC1	DCM	$FeSO_4{\cdot}7H_2O$	18
49	PC1	DCM	-	46
50	-	DCE	$FeSO_4{\cdot}7H_2O$	n.d.
51[i]	PC1	DCE	$FeSO_4{\cdot}7H_2O$	n.d.



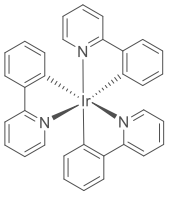
PC1



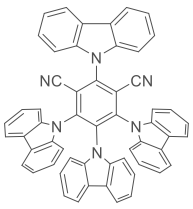
PC2



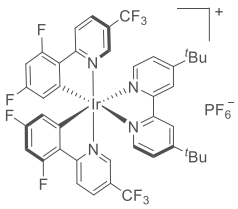
PC3



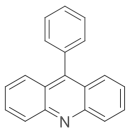
PC4



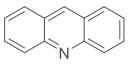
PC5



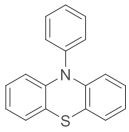
PC6



PC7



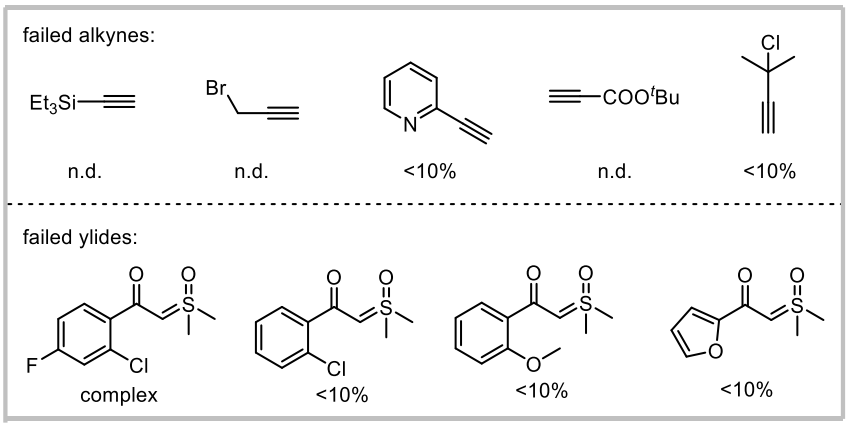
PC8



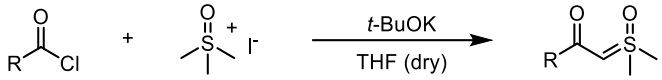
PC9

[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), photocatalyst (PC, 0.01 mmol), additive (10% mol) in solvent (2.0 mL) at 25-35 ℃ under argon and 35 W blue LEDs irradiation for 30 h. [b] Yields of isolated products. [c] $FeSO_4{\cdot}7H_2O$ (20% mol) was used. [d] $FeSO_4{\cdot}7H_2O$ (5% mol) was used. [e] **1a** :**2a** = 1:1.2. [f] **1a** :**2a** = 1:2. [g] 35W white light was used. [h] 9W purple light was used. [i] Without light.

Substrates failed or with low reactivity (General Procedure A):



4. Procedures for the preparation of sulfoxonium ylides

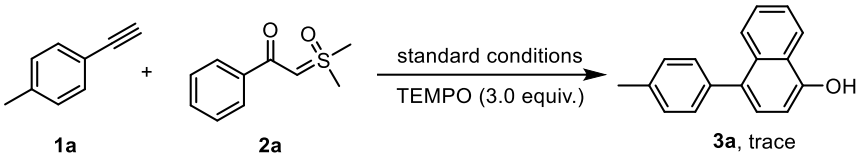


To a stirred solution of potassium tert-butoxide (3.0 g, 27.2 mmol) in anhydrous THF (30 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at rt. The resulting mixture is refluxed for 2 h. The reaction mixture is then cooled to 0 °C, followed by addition of acyl chlorides (7 mmol) in THF (7 mL). The reaction was allowed to rt and stirred for 3 h. Next, the solvent was evaporated and water (15 mL) and dichloromethane (20 mL) were added to the resulting slurry. The layers were separated and the aqueous layer was washed with dichloromethane (3×50 mL) and the organic layers were combined. The organic solution was dried over anhydrous sodium sulphate (Na_2SO_4), filtered over a sintered funnel and evaporated to dryness. The crude product was purified by flash chromatography over silica gel using DCM/MeOH (95:5) to afford the corresponding sulfoxonium ylides. [1]

5. Mechanistic studies

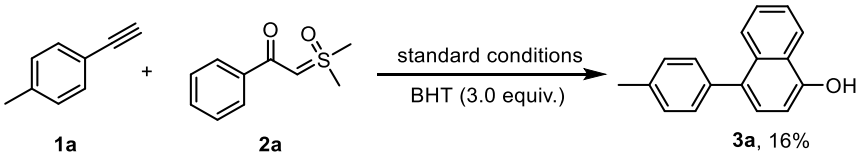
5.1 Radical trapping experiments

(a) The following reaction was carried out under standard conditions. A 10 mL reaction vessel was charged with *p*-methylphenylethyne **1a** (29.9 μL, 0.24 mmol, 1.2 equiv.), sulfoxonium ylide **2a** (39.2 mg, 0.2 mmol, 1.0 equiv.), $FeSO_4{\cdot}7H_2O$ (5.6 mg, 10 mol%), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (94 mg, 0.6 mmol), and [Mes-Acr]ClO_4 (4.1 mg, 5 mol%). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was carried out three times). Then, DCM (2 mL) was added. The solution was stirred at a distance of 4-5 cm from a 35 W Blue LEDs at room temperature (25-35 °C) for 30 h. After completion of the reaction, the crude mixture was diluted with ethyl acetate, filtered, and concentrated under reduced pressure to remove volatile components. The crude residues were analyzed by GC-MS. The product **3a** was completely suppressed.

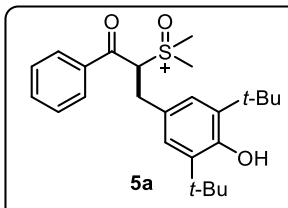


1a **2a** **3a**, trace

(b) The following reaction was carried out under standard conditions: A 10 mL reaction vessel was charged with *p*-methylphenylethyne **1a** (29.9 μL, 0.24 mmol, 1.2 equiv.), sulfoxonium ylide **2a** (39.2 mg, 0.2 mmol, 1.0 equiv.), $FeSO_4{\cdot}7H_2O$ (5.6 mg, 10 mol%), butylatedhy droxytoluene (BHT) (132 mg, 0.6 mmol), and [Mes-Acr]ClO_4 (4.1 mg, 5 mol%). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was carried out three times). Then, DCM (2 mL) was added. The solution was stirred at a distance of 4-5 cm from a 35 W Blue LEDs at room temperature (25-35 °C) for 30 h. After completion of the reaction, the crude mixture was diluted with ethyl acetate, filtered, and concentrated under reduced pressure to remove volatile components. The crude residues were analyzed by GC-MS and HRMS. BHT-trapped product **5a** was detected by HRMS and the formation of product **3a** was reduced to 16%.

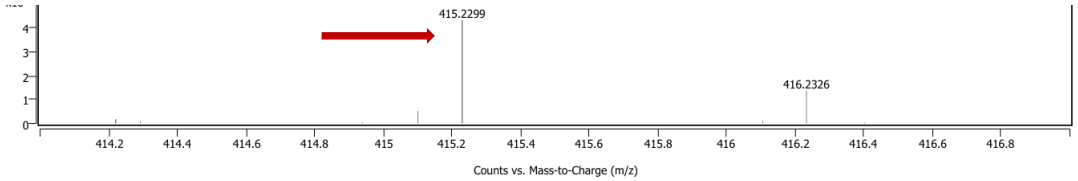


1a **2a** **3a**, 16%

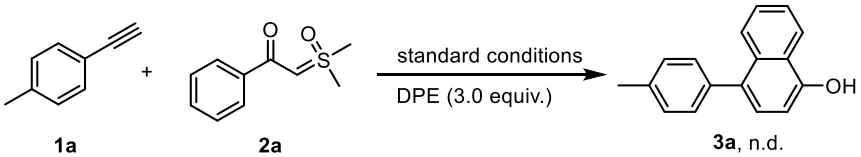


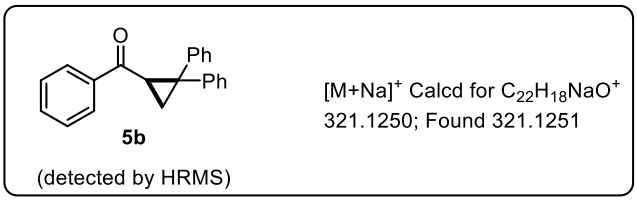
5a
(detected by HRMS)

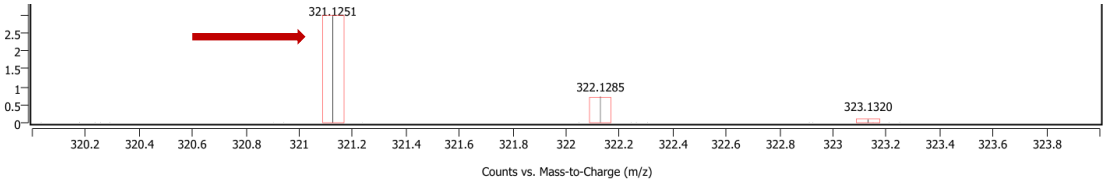
$[M]^+$ Calcd for $C_{25}H_{35}O_3S^+$
415.2301; Found 415.2299



(c) The following reaction was carried out under standard conditions: A 10 mL reaction vessel was charged with *p*-methylphenylethyne **1a** (29.9 μL, 0.24 mmol, 1.2 equiv.), sulfoxonium ylide **2a** (39.2 mg, 0.2 mmol, 1.0 equiv.), $FeSO_4{\cdot}7H_2O$ (5.6 mg, 10 mol%), 1,1-diphenylethylene (DPE) (106 μL, 0.6 mmol), and [Mes-Acr]ClO_4 (4.1 mg, 5 mol%). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was carried out three times). Then, DCM (2 mL) was added. The solution was stirred at a distance of 4-5 cm from a 35 W Blue LEDs at room temperature (25-35 °C) for 30 h. After completion of the reaction, the crude mixture was diluted with ethyl acetate, filtered, and concentrated under reduced pressure to remove volatile components. Cyclopropane product **5b** was detected by HRMS and the formation of product **3a** was completely suppressed.





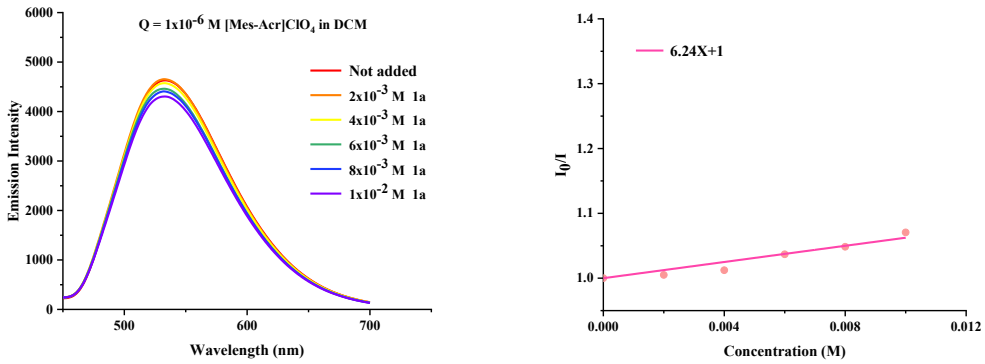


5.2 Stern-Volmer quenching

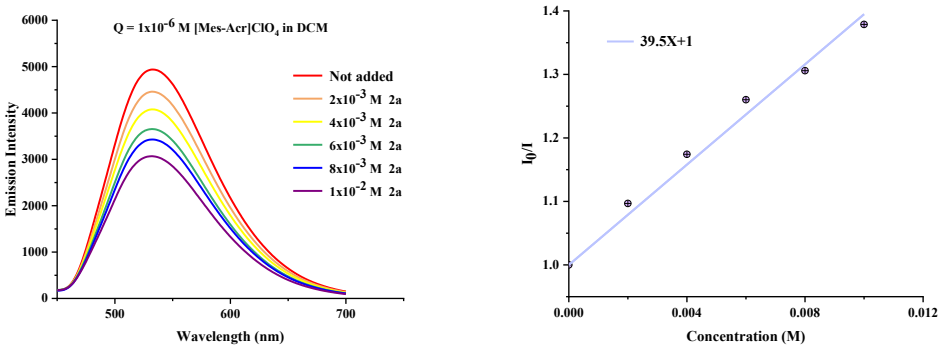
Formulation solution: *p*-Methylphenylethyne (**1a**, 299 μL) was dissolved in DCM in a 5 mL volumetric flask to set the concentration to be 0.2 M. Acetophenone sulfoxonium ylide (**2a**, 196 mg) was dissolved in DCM in a 5 mL volumetric flask to set the concentration to be 0.2 M. Photocatalyst [Mes-Acr]ClO_4 (**PC**, 1.1 mg) was dissolved in DCM (25.0 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 mM PC solution (20 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding DCM (2.0 mL) to prepare a 1.0 μM solution. The resulting mixture was sparged with argon for 2 minutes and then irradiated at 430 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 20.0 μL of a *p*-methylphenylethyne **1a** solution was

successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 2 minutes and irradiated at 430 nm. Fluorescence emission spectra of 0 μL, 20.0 μL, 40.0 μL, 60.0 μL, 80.0 μL, 100.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern-Volmer relationship in turn. The results were shown in the following figures.



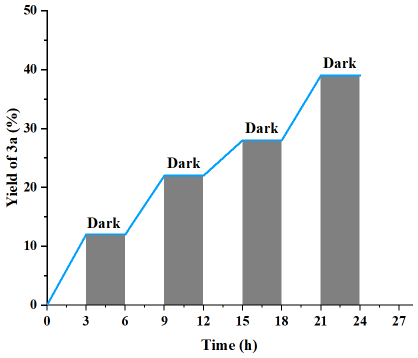
Emission quenching of [Mes-Acr]ClO_4 with *p*-methylphenylethyne (**1a**) in DCM



Emission quenching of [Mes-Acr]ClO_4 with acetophenone sulfoxonium ylide (**2a**) in DCM

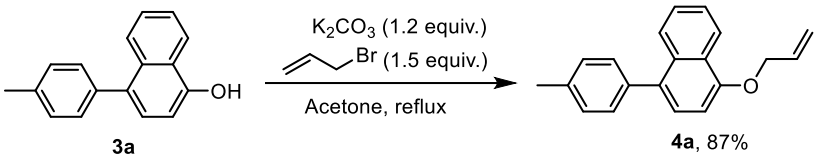
5.3 Light on/off experiment

Conducted the relationship of products with light on-off under standard conditions. Subsequent samples (each 20 μL) taken at regular time intervals and determined by GC with dodecane as the internal standard.



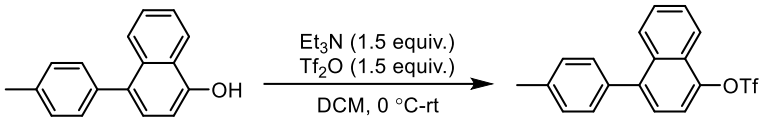
Plot of light on-off experiment

6. Late-stage derivation and application



3a **4a**, 87%

An oven- dried 10 mL reaction tube was equipped with naphthol **3a** (0.2 mmol, 46.8 mg) and K_2CO_3 (0.24 mmol, 1.2 equiv.) in acetone (2 mL) at room temperature. Allyl bromide (0.3 mmol, 1.5 equiv.) was added dropwise over 20 min, then it was heated to reflux for 7 h, after which time TLC showed that the reaction was complete. [2] The reaction was quenched with water (5 mL), and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1) to afford product **4a** (47.8 mg, 87% yield) a yellow solid (mp: 89-91 ℃).

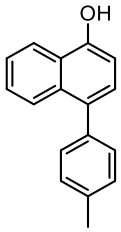


3a **4b**, 91%

Naphthol **3a** (46.8 mg, 0.2 mmol) was dissolved in DCM (1.0 mL) and then cooled to 0 ºC. Triethylamine (TEA, 0.3 mmol) was added, followed by addition of trifluoromethanesulfonic anhydride (Tf_2O, 0.3 mmol) within 5 minutes via a syringe. The mixture was gradually warmed to room temperature and stirred for 2 h until **3a** was completely consumed, as monitored by TLC. [3] The solvent was then removed under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1) to afford the alcohol product **4b** (66.6 mg, 91% yield) as a yellow solid (mp: 127-129 ℃).

7. Characterization data of all products

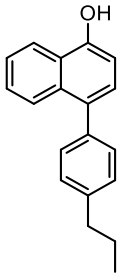
4-(*p*-tolyl)naphthalen-1-ol (3a) [4]



Following General Procedure A, product **3a** (27.6 mg, 59%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.10 (m, 7H), 6.75 (d, *J* = 7.7 Hz, 1H), 5.51 (s, 1H), 2.41 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 137.7, 136.5, 133.2, 132.7, 130.1, 128.9, 126.7, 126.4, 126.0, 125.1, 124.4, 121.7, 108.3, 21.2.

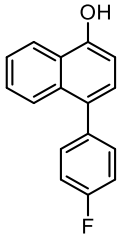
4-(4-propylphenyl)naphthalen-1-ol (3b)



Following General Procedure A, product **3b** (26.2 mg, 50%) as a gray solid (mp: 74-76 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.39 (m, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.19 (m, 3H), 6.83 (d, *J* = 7.7 Hz, 1H), 5.51 (s, 1H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.79 – 1.65 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 141.3, 138.0, 133.2, 132.7, 130.0, 128.3, 126.7, 126.4, 126.1, 125.1, 124.4, 121.8, 108.2, 37.8, 24.6, 14.0.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{19}H_{17}O^-$ 261.1285; Found 261.1304.

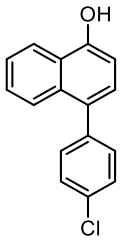
4-(4-fluorophenyl)naphthalen-1-ol (3c) [4]



Following General Procedure A, product **3c** (26.7 mg, 56%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.37 (m, 4H), 7.27 – 7.12 (m, 3H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.49 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 245.5 Hz), 151.0, 136.6 (d, *J* = 3.3 Hz), 132.7, 132.1, 131.7 (d, *J* = 8.0 Hz), 126.9, 126.7, 125.7, 125.2, 124.4, 121.9, 115.1 (d, *J* = 21.3 Hz), 108.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.9.

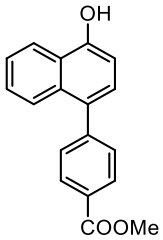
4-(4-chlorophenyl)naphthalen-1-ol (3d) [4]



Following General Procedure A, product **3d** (26.9 mg, 53%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.34 (m, 6H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 5.50 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 139.2, 132.9, 132.5, 131.8, 131.5, 128.4, 126.9, 126.8, 125.6, 125.3, 124.4, 121.9, 108.1.

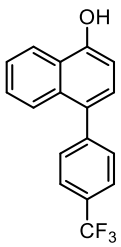
methyl 4-(4-hydroxynaphthalen-1-yl)benzoate (3e) [4]



Following General Procedure A, product **3e** (24.5 mg, 44%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.41 (m, 4H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.43 (s, 1H), 3.99 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 151.8, 145.9, 132.3, 131.7, 130.3, 129.6, 128.4, 127.1, 126.8, 125.4, 125.3, 124.5, 122.1, 108.1, 52.3.

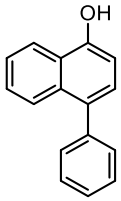
4-(4-(trifluoromethyl)phenyl)naphthalen-1-ol (3f) [4]



Following General Procedure A, product **3f** (27.7 mg, 48%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.60 – 7.43 (m, 4H), 7.24 (d, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 5.49 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 144.5, 132.3, 131.6, 130.5, 129.2, 128.9, 127.05, 127.96, 125.4, 125.2 (q, *J* = 3.7 Hz), 124.45, 124.36 (q, *J* = 272.0 Hz), 122.0, 108.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3.

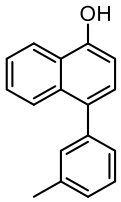
4-phenylnaphthalen-1-ol (3g) [4]



Following General Procedure A, product **3g** (22.5 mg, 51%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.38 (m, 7H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 5.52 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 140.7, 133.2, 132.6, 130.2, 128.2, 126.9, 126.8, 126.5, 125.9, 125.1, 124.4, 121.8, 108.1.

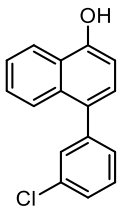
4-(*m*-tolyl)naphthalen-1-ol (3h) [4]



Following General Procedure A, product **3h** (24.4 mg, 52%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.20 (m, 4H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.44 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 140.7, 137.8, 133.3, 132.7, 131.0, 128.1, 127.6, 127.3, 126.7, 126.5, 126.0, 125.1, 124.4, 121.8, 108.1, 21.5.

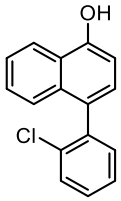
4-(3-chlorophenyl)naphthalen-1-ol (3i)



Following General Procedure A, product **3i** (27.4 mg, 54%) as a gray solid (mp: 89-91 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.41 – 7.30 (m, 3H), 7.22 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.56 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 142.6, 134.0, 132.4, 131.6, 130.2, 129.4, 128.4, 127.0, 126.9, 126.8, 125.5, 125.3, 124.4, 122.0, 108.0.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{16}H_{10}ClO^-$ 253.0426; Found 253.0420.

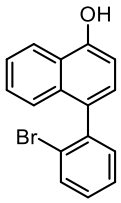
4-(2-chlorophenyl)naphthalen-1-ol (3j)



Following General Procedure A, product **3j** (29.5 mg, 58%) as a gray solid (mp: 110-112 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.47 – 7.41 (m, 2H), 7.39 – 7.31 (m, 3H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.52 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 139.2, 134.4, 132.7, 132.5, 130.2, 129.5, 128.8, 127.1, 126.7, 126.6, 125.8, 125.2, 124.2, 121.9.
HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{16}H_{11}ClKO^+$ 293.0130; Found 293.0148.

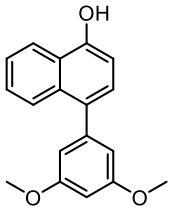
4-(2-bromophenyl)naphthalen-1-ol (3k)



Following General Procedure A, product **3k** (29.3 mg, 49%) as a gray solid (mp: 101-103 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.44 – 7.31 (m, 4H), 7.30 – 7.23 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 5.72 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 141.2, 132.6, 132.4, 131.9, 128.9, 127.1, 127.0, 126.6, 125.9, 125.2, 124.9, 124.2, 121.9, 107.9.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{16}H_{10}BrO^-$ 296.9921; Found 296.9911.

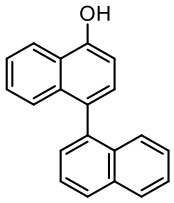
4-(3,5-dimethoxyphenyl)naphthalen-1-ol (3l) [4]



Following General Procedure A, product **3l** (31.4 mg, 56%) as a gray liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.40 (m, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 2.3 Hz, 2H), 6.53 (t, *J* = 2.3 Hz, 1H), 5.72 (s, 1H), 3.83 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 151.1, 142.8, 132.9, 132.5, 126.6, 126.5, 125.9, 125.1, 124.4, 121.8, 108.4, 107.9, 99.1, 55.4.

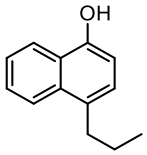
[1,1'-binaphthalen]-4-ol (3m) [4]



Following General Procedure A, product **3m** (20.0 mg, 37%) as a gray solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.40 (s, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.62 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.35 – 7.24 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 7.7 Hz, 1H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 153.6, 138.8, 133.8, 133.7, 133.1, 128.8, 128.7, 128.6, 128.5, 128.1, 126.9, 126.6, 126.5, 126.4, 126.2, 126.1, 125.1, 125.0, 122.9, 108.2.

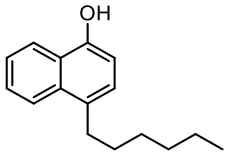
4-propylnaphthalen-1-ol (3n) [4]



Following General Procedure A, product **3n** (19.1 mg, 51%) as a brown liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.42 (m, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 5.69 (s, 1H), 2.98 – 2.89 (m, 2H), 1.79 – 1.65 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 132.8, 131.1, 126.1, 125.6, 124.73, 124.69, 123.9, 122.2, 108.1, 34.7, 24.0, 14.2.

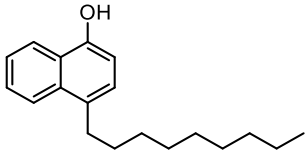
4-hexylnaphthalen-1-ol (3o)



Following General Procedure A, product **3o** (39.1 mg, 70%) as a brown liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 5.52 (s, 1H), 2.96 (t, *J* = 7.8 Hz, 2H), 1.69 (p, *J* = 7.7 Hz, 2H), 1.46 – 1.36 (m, 2H), 1.35 – 1.28 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 132.8, 131.5, 126.1, 125.4, 124.7, 123.9, 122.2, 108.1, 32.6, 31.8, 30.9, 29.4, 22.7, 14.1.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{16}H_{19}O^-$ 227.1441; Found 227.1438.

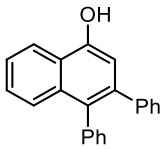
4-nonylnaphthalen-1-ol (3p)



Following General Procedure A, product **3p** (32.4 mg, 60%) as a gray solid (mp: 65-67 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.54 (dt, *J* = 18.5, 7.0 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.56 (s, 1H), 3.01 (t, *J* = 7.8 Hz, 2H), 1.74 (p, *J* = 7.5 Hz, 2H), 1.50 – 1.30 (m, 12H), 0.93 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 132.8, 131.5, 126.1, 125.4, 124.7, 124.0, 122.2, 108.2, 32.7, 31.9, 31.0, 29.8, 29.61, 29.56, 29.3, 22.7, 14.1.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{19}H_{25}O^-$ 269.1911; Found 269.1905.

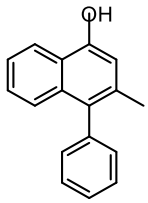
3,4-diphenylnaphthalen-1-ol (3q) [4]



Following General Procedure B, product **3q** (18.3 mg, 31%) as a brown solid was obtained after flash chromatography (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.44 – 7.38 (m, 1H), 7.29 – 7.22 (m, 3H), 7.18 – 7.09 (m, 7H), 6.90 (s, 1H), 5.62 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 141.8, 139.0, 138.4, 133.9, 131.9, 130.7, 130.0, 127.7, 127.6, 126.7, 126.5, 126.2, 125.0, 123.6, 121.5, 110.9.

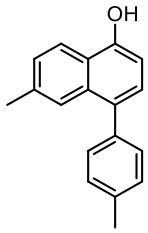
3-methyl-4-phenylnaphthalen-1-ol (3r)



Following General Procedure A, product **3r** (19.7 mg, 42%) as a yellow liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.34 (m, 6H), 7.29 – 7.24 (m, 2H), 6.78 (s, 1H), 5.42 (s, 1H), 2.18 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 139.7, 134.1, 133.4, 131.2, 130.7, 128.3, 126.8, 126.3, 126.1, 124.1, 122.7, 121.3, 111.1, 20.8.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{13}O^-$ 233.0972; Found 233.0965.

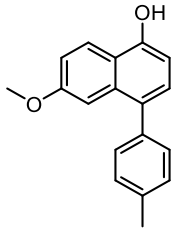
6-methyl-4-(*p*-tolyl)naphthalen-1-ol (3t)



Following General Procedure A, product **3t** (30.0 mg, 60%) as a gray solid (mp: 56-58 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 1H), 7.65 (s, 1H), 7.39 – 7.25 (m, 5H), 7.18 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.36 (s, 1H), 2.43 (d, *J* = 9.6 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 138.0, 136.4, 136.2, 132.9, 132.5, 130.1, 128.9, 127.3, 126.9, 124.9, 122.6, 121.7, 107.4, 21.9, 21.2.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{15}O^-$ 247.1128; Found 247.1120.

6-methoxy-4-(*p*-tolyl)naphthalen-1-ol (3u)

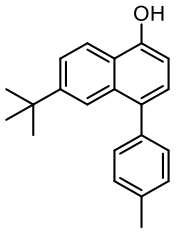


Following General Procedure A, product **3u** (26.5 mg, 59%) as a gray liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 12:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.1 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.22 – 7.13 (m, 2H), 6.71 (d, *J* = 7.7 Hz, 1H), 5.45 (s, 1H), 3.77 (s, 3H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 151.0, 138.1, 136.4, 134.2, 132.0, 129.9, 129.0, 127.6, 123.7, 119.7, 117.2, 106.3, 104.8, 55.2, 21.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}O_2^+$ 265.1223; Found 265.1226.

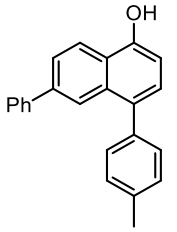
6-(tert-butyl)-4-(*p*-tolyl)naphthalen-1-ol (3v)



Following General Procedure A, product **3v** (36.6 mg, 63%) as a gray liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 18:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.41 (s, 1H), 2.44 (s, 3H), 1.32 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.1, 138.0, 136.3, 133.1, 132.6, 130.0, 128.9, 126.9, 123.9, 122.5, 121.5, 121.1, 107.7, 35.0, 31.1, 21.2.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O^+$ 291.1743; Found 291.1742.

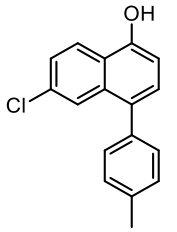
6-phenyl-4-(*p*-tolyl)naphthalen-1-ol (3w)



Following General Procedure A, product **3w** (35.3 mg, 57%) as a gray solid (mp: 153-155 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 1.8 Hz, 1H), 7.75 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 14.1, 7.7 Hz, 4H), 7.35 – 7.21 (m, 4H), 6.83 (d, *J* = 7.7 Hz, 1H), 5.51 (s, 1H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 141.2, 139.1, 137.7, 136.6, 133.4, 133.0, 130.1, 129.0, 128.7, 127.5, 127.3, 127.3, 124.7, 124.0, 123.5, 122.5, 108.3, 21.2.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{23}H_{17}O^-$ 309.1285; Found 309.1277.

6-chloro-4-(*p*-tolyl)naphthalen-1-ol (3x)

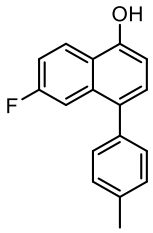


Following General Procedure A, product **3x** (26.3 mg, 49%) as a brown solid (mp: 121-123 ℃) was

obtained after flash chromatography (petroleum ether/ethyl acetate = 18:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.49 (d, J = 2.6 Hz, 1H), 8.24 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 2.1 Hz, 1H), 7.47 (dd, J = 8.9, 2.1 Hz, 1H), 7.35 – 7.25 (m, 5H), 6.97 (d, J = 7.8 Hz, 1H), 2.39 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 153.4, 137.3, 136.9, 133.4, 131.9, 130.3, 130.1, 129.8, 129.5, 125.6, 125.5, 124.2, 123.6, 108.9, 21.4.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{12}ClO^-$ 267.0582; Found 267.0574.

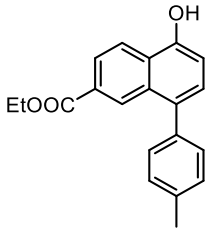
6-fluoro-4-(*p*-tolyl)naphthalen-1-ol (3y)



Following General Procedure A, product **3y** (28.3 mg, 56%) as a gray solid (mp: 97-99 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 18:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, J = 9.3, 5.8 Hz, 1H), 7.50 (dd, J = 11.5, 2.6 Hz, 1H), 7.38 – 7.20 (m, 6H), 6.78 (d, J = 7.7 Hz, 1H), 5.33 (s, 1H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 245.2 Hz), 150.9, 137.3, 136.8, 134.0 (d, J = 8.9 Hz), 132.7 (d, J = 5.4 Hz), 129.9, 129.1, 127.9, 124.8 (d, J = 9.1 Hz), 121.5, 115.2 (d, J = 25.3 Hz), 109.5 (d, J = 22.1 Hz), 107.4 (d, J = 2.2 Hz), 21.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{12}FO^-$ 251.0878; Found 251.0870.

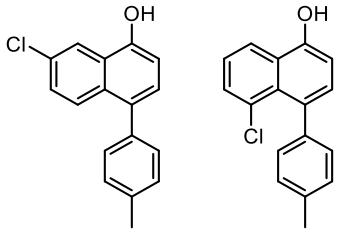
ethyl 5-hydroxy-8-(*p*-tolyl)-2-naphthoate (3z)



Following General Procedure A, product **3z** (25.1 mg, 41%) as a brown solid (mp: 134-136 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.54 (d, J = 2.1 Hz, 1H), 8.49 (s, 1H), 8.31 (d, J = 8.8 Hz, 1H), 7.95 (dd, J = 8.8, 1.7 Hz, 1H), 7.33 (s, 5H), 7.08 (d, J = 7.8 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 153.2, 137.4, 137.0, 132.1, 131.7, 130.4, 129.7, 129.0, 128.5, 128.0, 127.1, 123.9, 123.7, 110.8, 61.4, 21.4, 14.8.
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{18}NaO_3^+$ 329.1148; Found 329.1152.

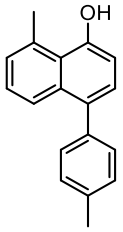
7-chloro-4-(*p*-tolyl)naphthalen-1-ol (3aa) + 5-chloro-4-(*p*-tolyl)naphthalen-1-ol (3aa')



Following General Procedure B, product **3aa + 3aa'** (26.3 mg, 49%) as a brown solid (mp: 66-68 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 10.0 Hz, 1H), 7.81 (d, *J* = 9.1 Hz, 0.5H), 7.52 (d, *J* = 7.4 Hz, 0.5H), 7.40 – 7.24 (m, 3H), 7.24 – 7.13 (m, 3H), 6.83 (t, *J* = 7.9 Hz, 1H), 5.66 (d, *J* = 25.0 Hz, 1H), 2.43 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.0, 140.7, 137.3, 136.8, 136.0, 133.1, 132.2, 131.4, 131.1, 131.0, 130.8, 130.0, 129.9, 129.7, 129.6, 129.0, 127.9, 127.8, 127.2, 126.9, 126.7, 125.2, 124.9, 121.6, 121.2, 109.1, 108.3, 21.3, 21.2.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{12}ClO^-$ 267.0582; Found 267.0575.

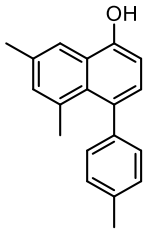
8-methyl-4-(*p*-tolyl)naphthalen-1-ol (3ab)



Following General Procedure B, product **3ab** (14.9 mg, 30%) as a yellow solid (mp: 73-75 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 18:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.15 (m, 7H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.30 (s, 1H), 2.99 (s, 3H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 138.6, 136.4, 135.1, 134.5, 133.7, 130.1, 128.9, 128.1, 126.6, 125.9, 124.5, 123.9, 109.7, 25.0, 21.2.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{15}O^-$ 247.1128; Found 247.1120.

5,7-dimethyl-4-(*p*-tolyl)naphthalen-1-ol (3ac)

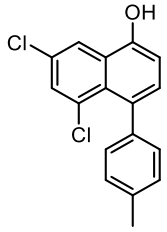


Following General Procedure A, product **3ac** (27.4 mg, 52%) as a gray solid (mp: 59-61 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.18 (t, *J* = 5.5 Hz, 5H), 7.09 (s, 1H), 7.03 (d, *J* = 7.6

Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 5.41 (s, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 1.99 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 142.2, 136.0, 135.2, 134.4, 133.2, 132.5, 130.4, 129.7, 128.2, 128.1, 125.6, 119.2, 107.4, 25.1, 21.4, 21.2.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{19}H_{17}O^-$ 261.1285; Found 261.1276.

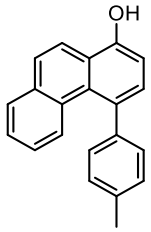
5,7-dichloro-4-(*p*-tolyl)naphthalen-1-ol (3ad)



Following General Procedure A, product **3ad** (32.8 mg, 54%) as a brown liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.3 Hz, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.17 (d, *J* = 10.8 Hz, 5H), 6.83 (d, *J* = 7.7 Hz, 1H), 5.76 (s, 1H), 2.41 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 140.0, 136.3, 132.5, 132.3, 131.0, 130.1, 130.0, 129.7, 128.1, 128.0, 126.9, 120.9, 109.2, 21.2.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{11}Cl_2O^-$ 301.0192; Found 301.0187.

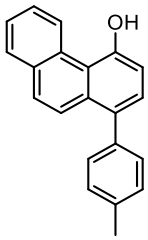
4-(*p*-tolyl)phenanthren-1-ol (3ae)



Following General Procedure A, product **3ae** (30.1 mg, 53%) as a brown solid (mp: 53-55 °C) was obtained after flash chromatography (petroleum ether/ethyl acetate = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 9.1 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.29 – 7.21 (m, 5H), 7.14 – 7.06 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 5.48 (s, 1H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 142.4, 136.3, 133.5, 133.3, 130.7, 130.2, 129.8, 129.6, 129.0, 128.4, 128.3, 126.8, 126.1, 124.7, 122.9, 120.0, 109.9, 21.3.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}O^+$ 285.1274; Found 285.1265.

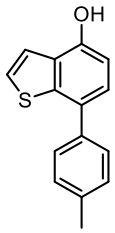
1-(*p*-tolyl)phenanthren-4-ol (3af)



Following General Procedure A, product **3af** (26.8 mg, 47%) as a gray liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 8:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 9.1 Hz, 1H), 7.68 – 7.56 (m, 3H), 7.38 – 7.27 (m, 5H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.82 (s, 1H), 2.45 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 138.4, 136.6, 133.8, 132.5, 132.3, 130.3, 128.9, 128.7, 128.0, 127.8, 127.7, 126.4, 126.1, 124.9, 119.4, 112.7, 21.2.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}O^+$ 285.1274; Found 285.1266.

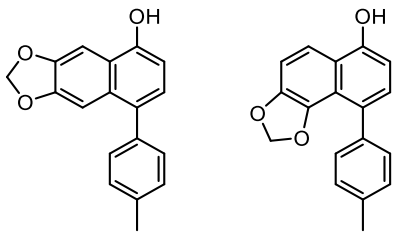
7-(*p*-tolyl)benzo[*b*]thiophen-4-ol (3ag)



Following General Procedure A, product **3ag** (23.1 mg, 48%) as a gray solid (mp: 95-97 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 8:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 7.72 (d, *J* = 5.5 Hz, 1H), 7.39 (d, *J* = 6.0 Hz, 3H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 2.36 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 152.0, 139.5, 138.2, 136.4, 129.7, 129.0, 128.9, 128.0, 128.0, 126.6, 123.8, 109.1, 21.3.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{11}OS^-$ 239.0536; Found 239.0529.

8-(*p*-tolyl)naphtho[2,3-*d*][1,3]dioxol-5-ol (3ah') + 9-(*p*-tolyl)naphtho[1,2-*d*][1,3]dioxol-6-ol (3ah)

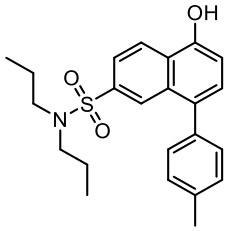


Following General Procedure A, product **3ah' + 3ah** (33.9 mg, 61%) as a gray solid (mp: 71-73 ℃) was obtained after flash chromatography (petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 0.2H), 10.08 (s, 0.8H), 7.87 (d, *J* = 8.9 Hz, 0.2H), 7.49

(s, 0.8H), 7.30 – 7.19 (m, 3.8H), 7.13 (d, *J* = 7.8 Hz, 0.4H), 7.08 – 6.99 (m, 1.8H), 6.82 (d, *J* = 7.8 Hz, 0.8H), 6.77 (d, *J* = 7.8 Hz, 0.2H), 6.08 (s, 1.6H), 5.90 (s, 0.4H), 2.35 (d, *J* = 10.5 Hz, 3H).
^{13}C ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.6, 152.6, 148.3, 146.8, 144.7, 141.3, 139.2, 138.4, 136.4, 135.7, 130.3, 130.14, 130.07, 129.7, 129.5, 128.2, 126.5, 126.4, 122.4, 121.4, 119.5, 117.5, 109.6, 107.6, 106.2, 101.9, 101.7, 100.9, 99.2, 21.32, 21.29.
HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{13}O_3^-$ 277.0870; Found 277.0864.

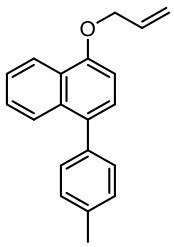
5-hydroxy-*N*,*N*-dipropyl-8-(*p*-tolyl)naphthalene-2-sulfonamide (3ai)



Following General Procedure A, product **3ai** (41.3 mg, 52%) as a brown liquid was obtained after flash chromatography (petroleum ether/ethyl acetate = 4:1).

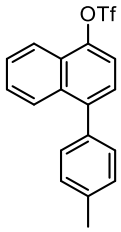
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.28 (m, 2H), 7.76 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.33 – 7.19 (m, 5H), 7.05 – 6.95 (m, 2H), 3.14 – 3.02 (m, 4H), 2.40 (s, 3H), 1.59 – 1.45 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 137.1, 137.0, 136.6, 133.7, 131.6, 129.8, 129.2, 128.5, 126.0, 125.9, 123.9, 121.2, 110.8, 49.9, 21.8, 21.1, 11.1.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO_3S^+$ 398.1784; Found 398.1782.

1-(allyloxy)-4-(*p*-tolyl)naphthalene (4a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.39 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.23 (m, 3H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.24 – 6.11 (m, 1H), 5.53 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.34 (dd, *J* = 10.5, 1.6 Hz, 1H), 4.72 (d, *J* = 5.3 Hz, 2H), 2.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 137.9, 136.5, 133.3, 132.8, 132.6, 130.1, 128.9, 126.7, 126.4, 125.8, 125.0, 122.3, 117.4, 104.7, 68.9, 21.2.
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}O^+$ 275.1430; Found 275.1425.

4-(*p*-tolyl)naphthalen-1-yl trifluoromethanesulfonate (4b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.44 (m, 2H), 7.41 – 7.25 (m, 5H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 141.2, 137.7, 136.3, 133.1, 129.8, 129.1, 127.6, 127.3, 126.7, 126.6, 125.9, 120.9, 118.8 (q, *J* = 320.3 Hz), 117.3, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.3.

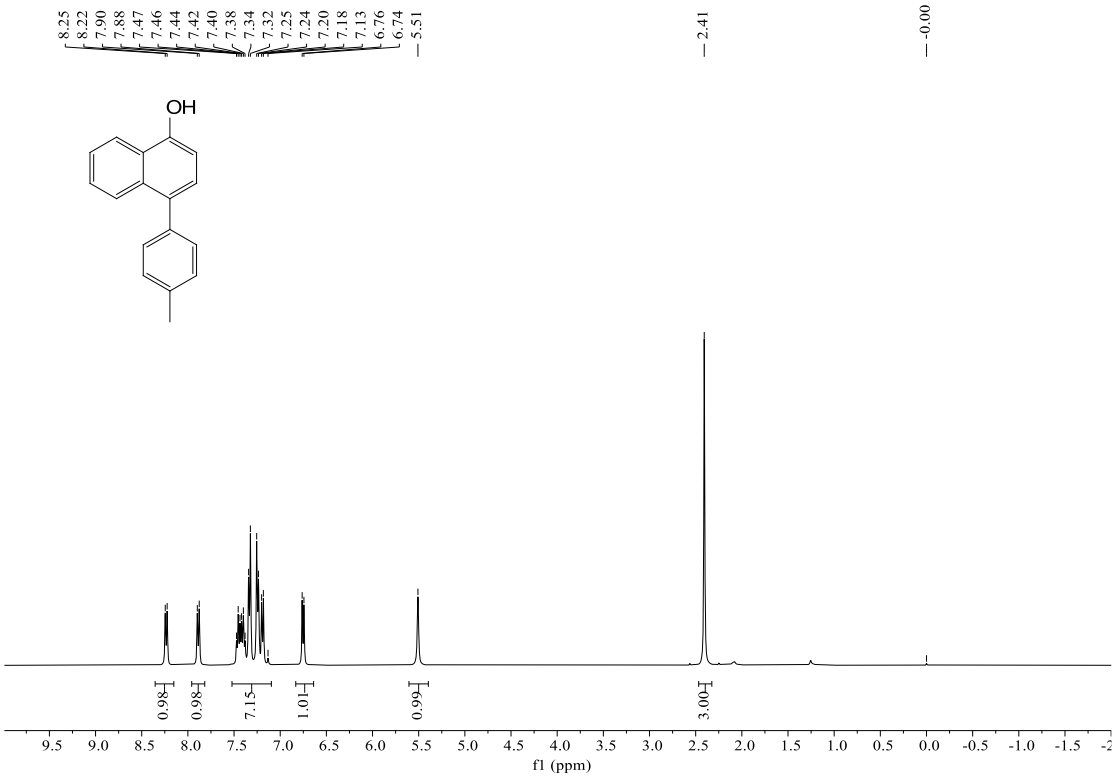
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}F_3O_3S^+$ 367.0610; Found 367.0602.

8. References

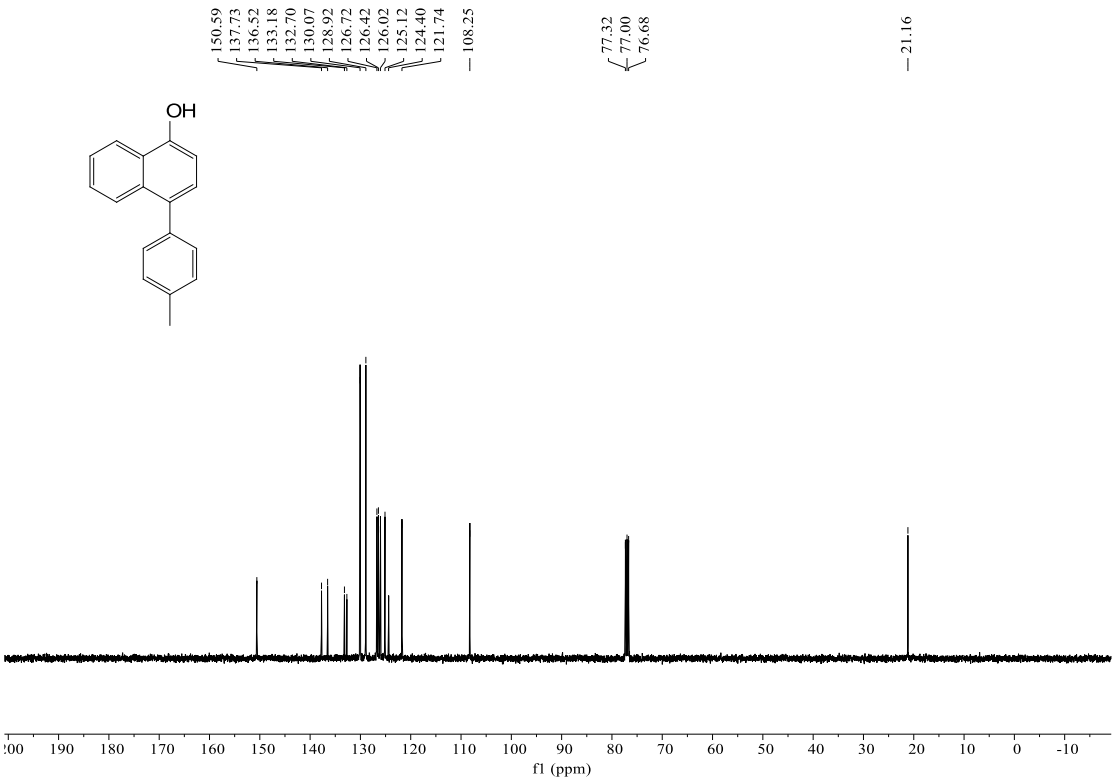
[1] (a) A. G. Talero, B. S. Martins and A. C. B. Burtoloso, *Org. Lett.,* 2018, **20**, 7206; (b) Y. Xu, Y. Gao, L. Su, H. Wu, H. Tian, M. Zeng, C. Xu, X. Zhu and K. Liao, *Angew. Chem. Int. Ed.,* 2023, **62**, e202313638.
[2] N. Jain and M. A. Ciufolini, *Synlett*., 2015, **26**, 631.
[3] Y. Xu, X. Yang, X. Zhou, L. Kong and X. Li, *Org. Lett.*, 2017, **19**, 4307.
[4] H. Huang, Y. Lu, M. Gui, N. Wang and H. Li, *Org. Lett.*, 2025, **27**, 13957.

9. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of all products

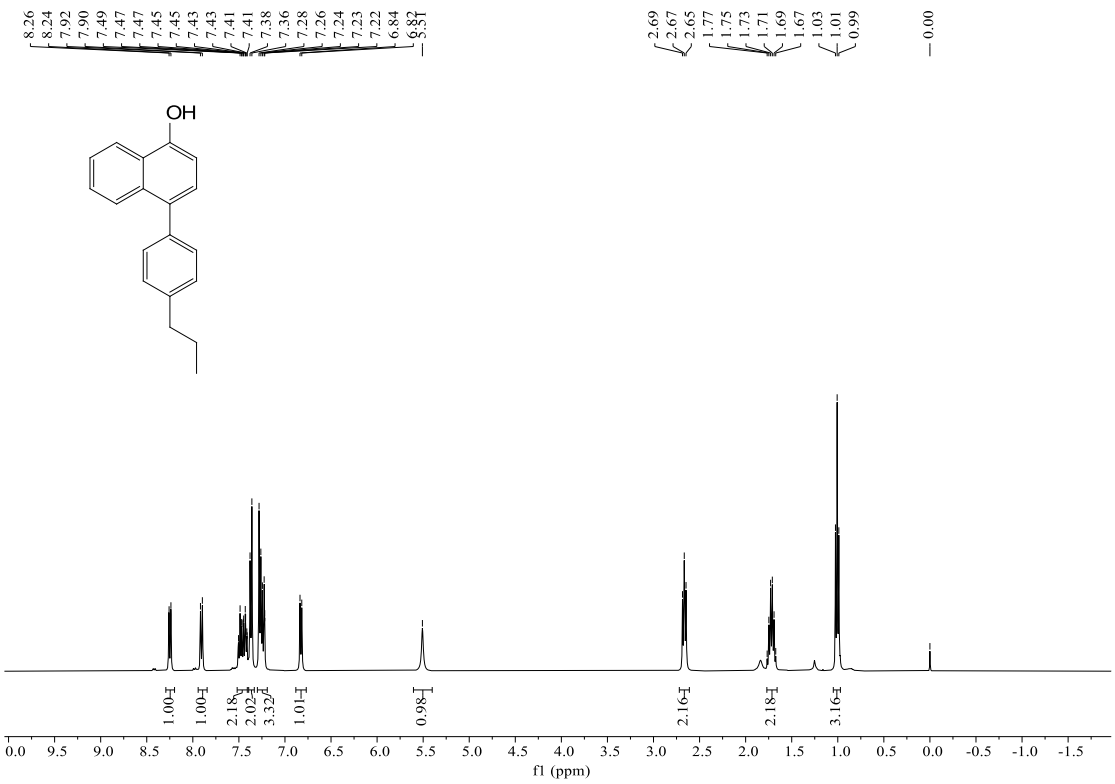
^{1}H NMR spectra of 3a (400 MHz, $CDCl_3$)



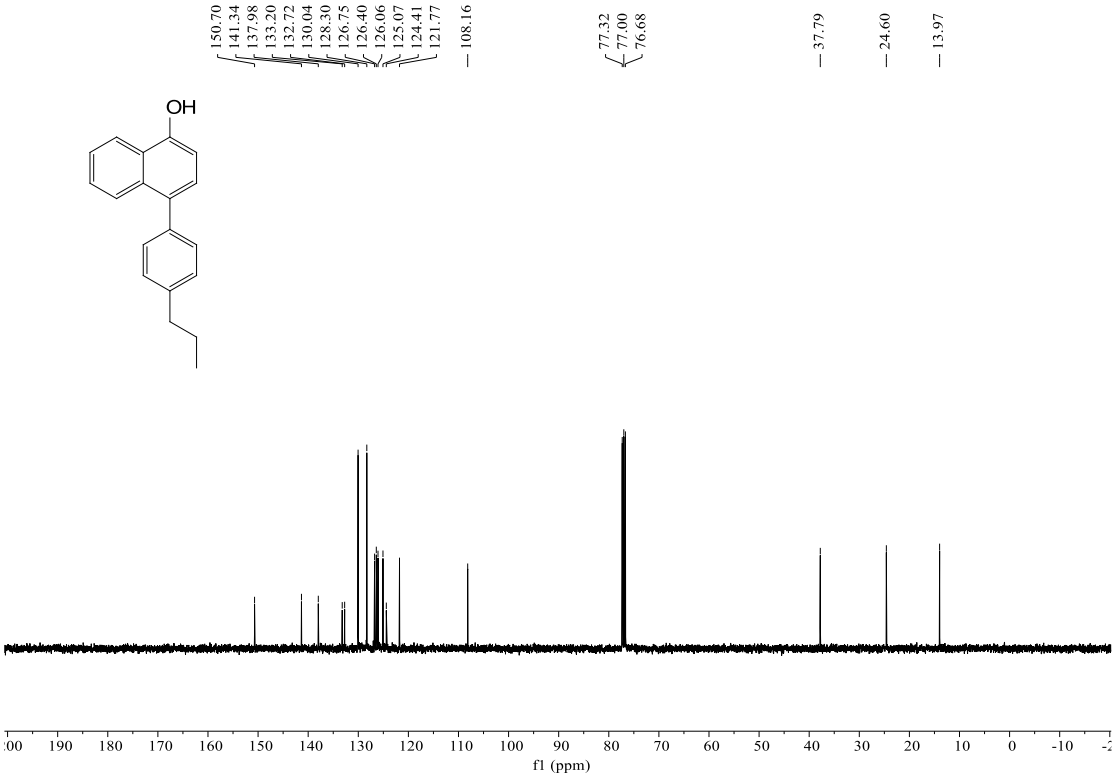
^{13}C NMR spectra of 3a (100 MHz, $CDCl_3$)



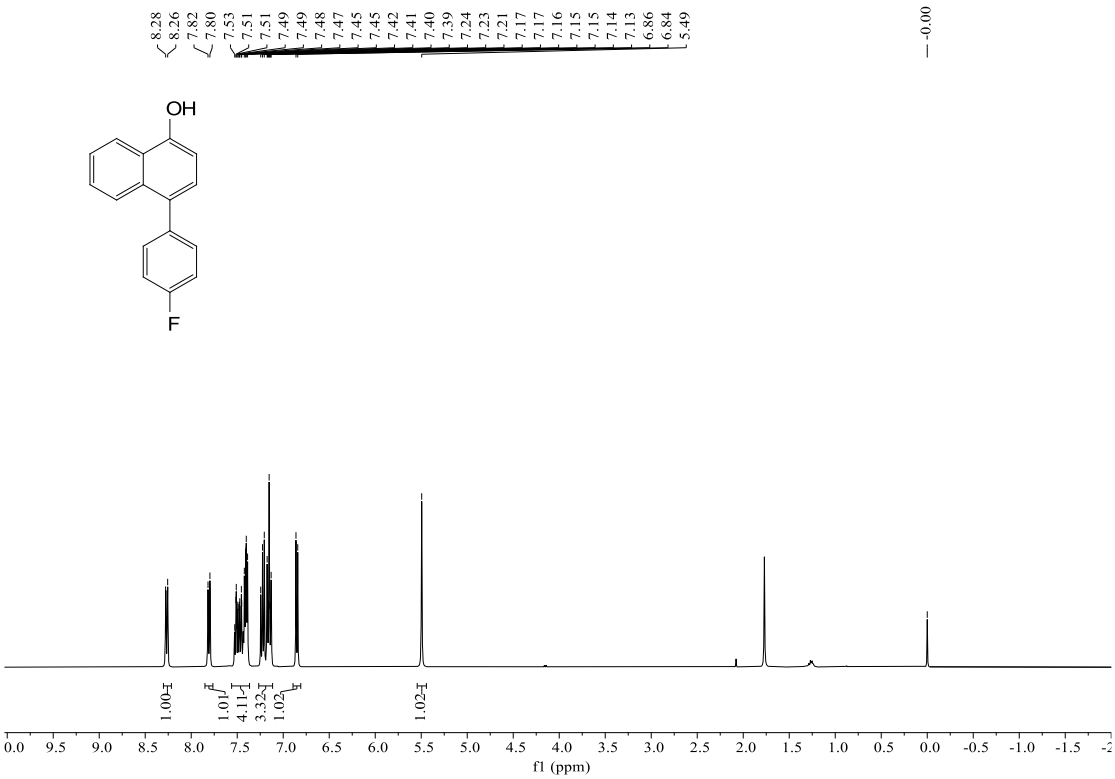
^{1}H NMR spectra of 3b (400 MHz, $CDCl_3$)



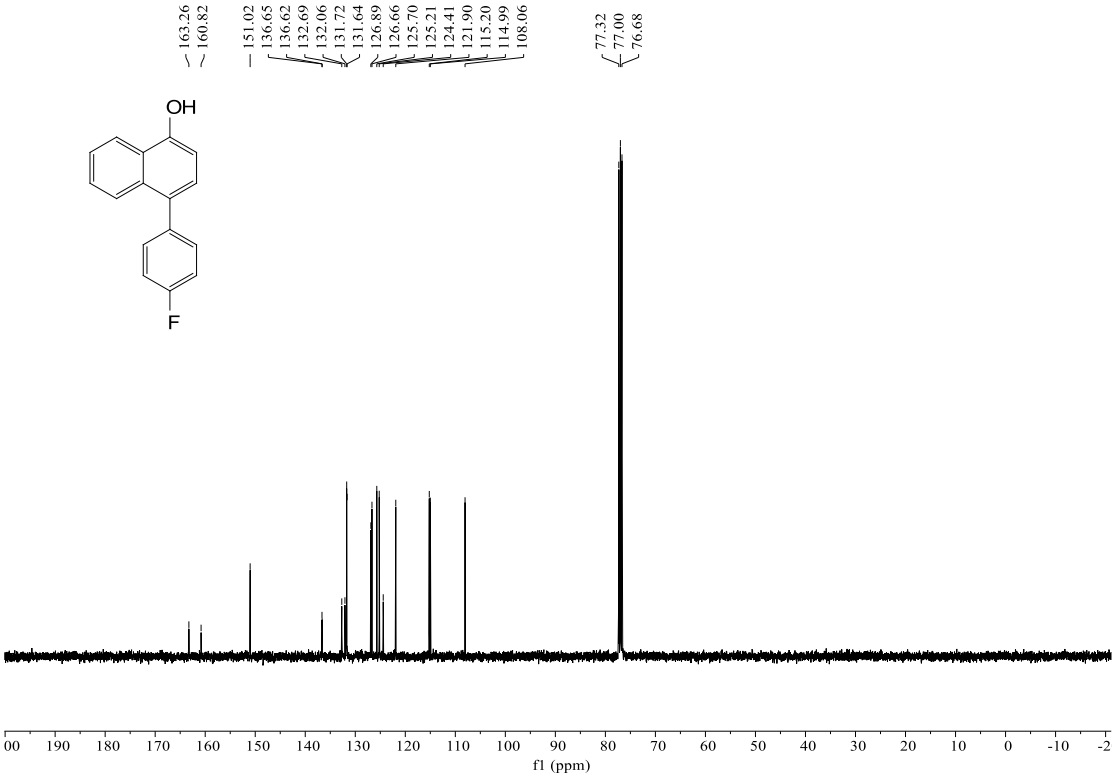
^{13}C NMR spectra of 3b (100 MHz, $CDCl_3$)



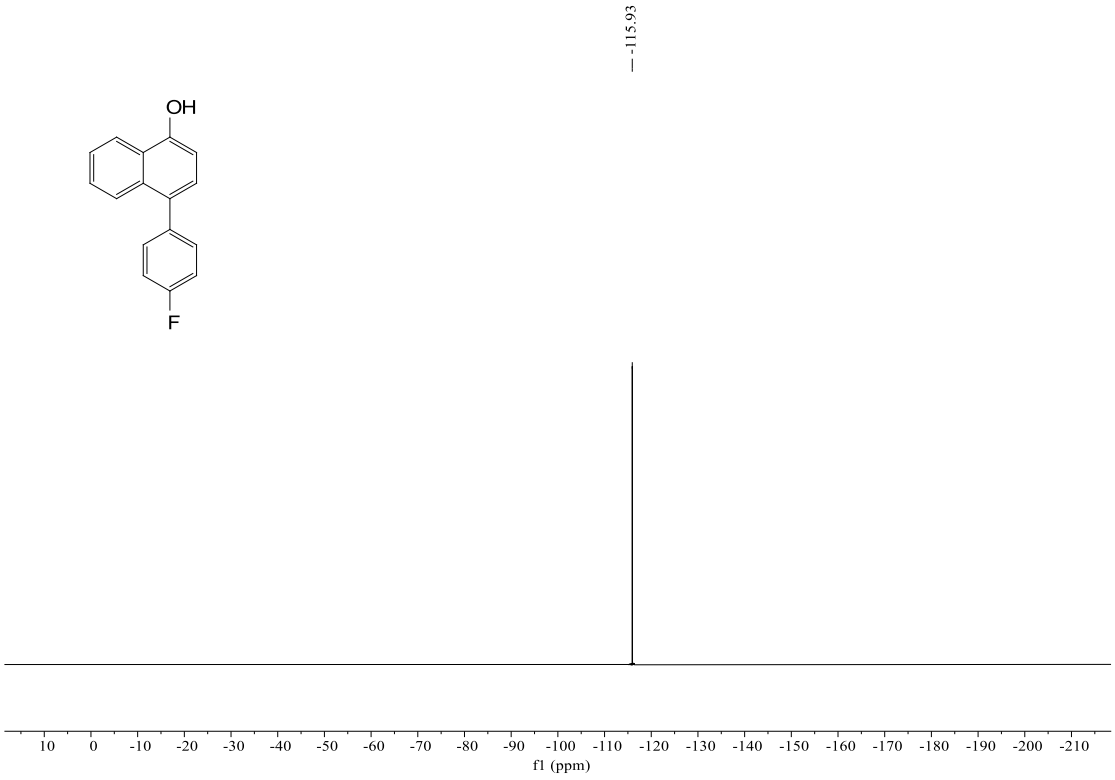
^{1}H NMR spectra of 3c (400 MHz, $CDCl_3$)



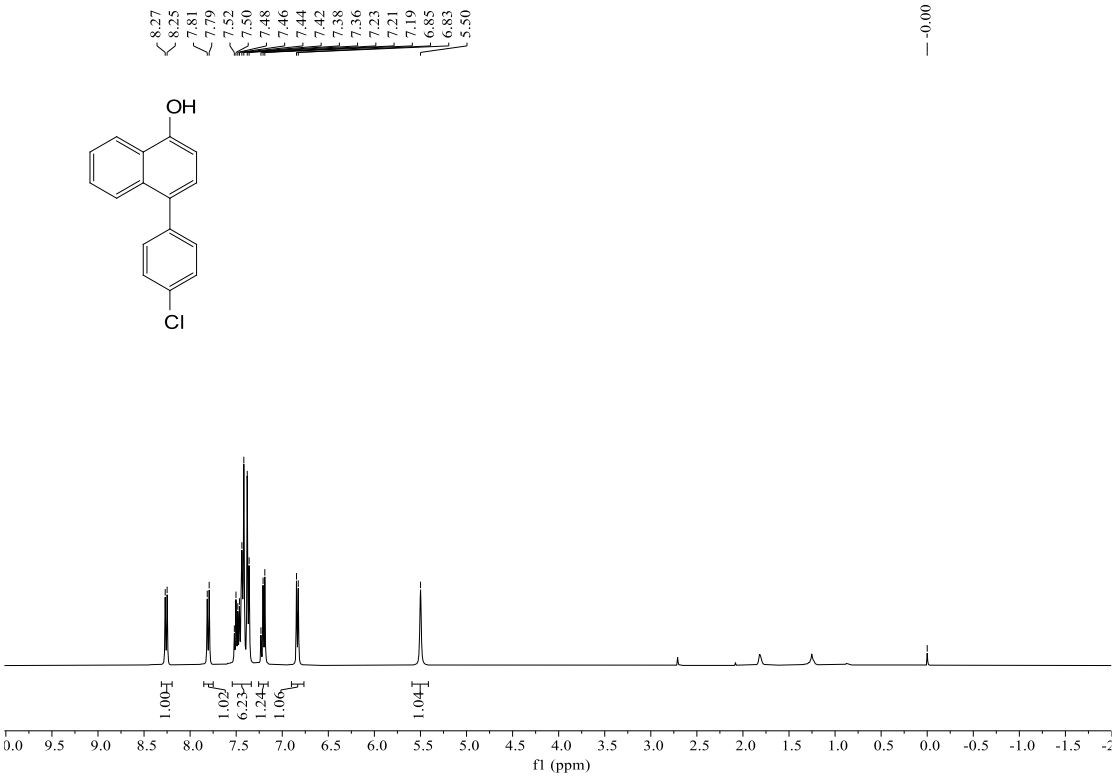
^{13}C NMR spectra of 3c (100 MHz, $CDCl_3$)



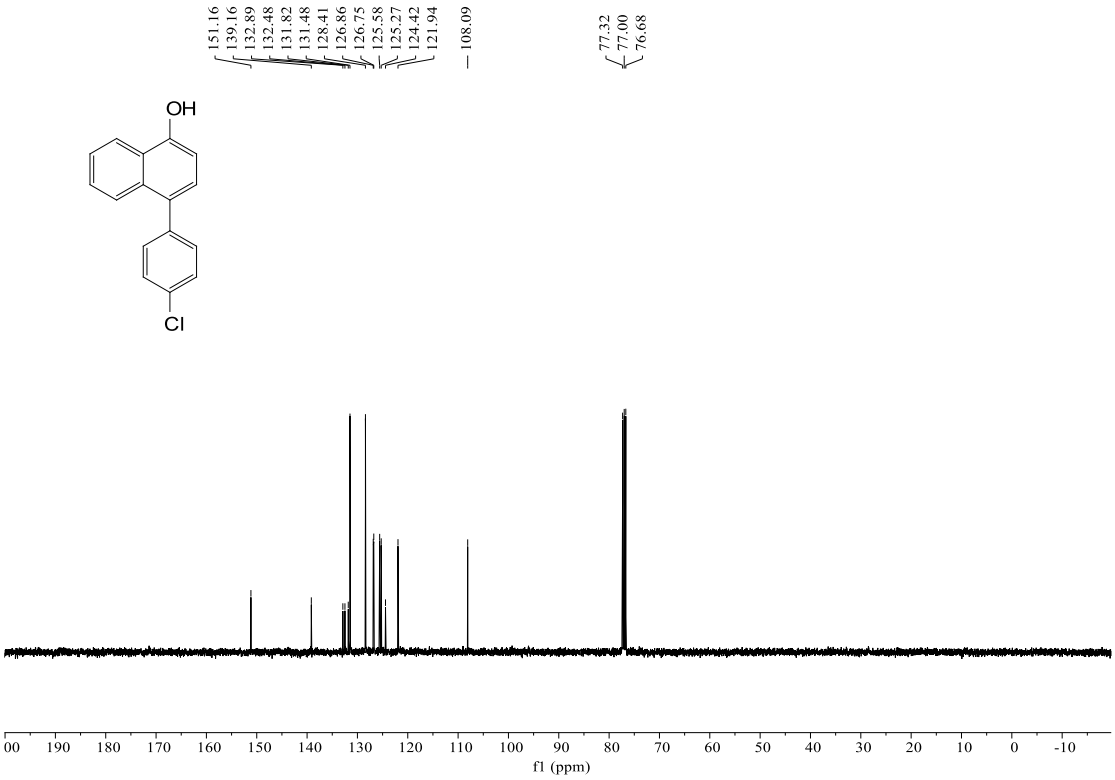
^{19}F NMR spectra of 3c (376 MHz, $CDCl_3$)



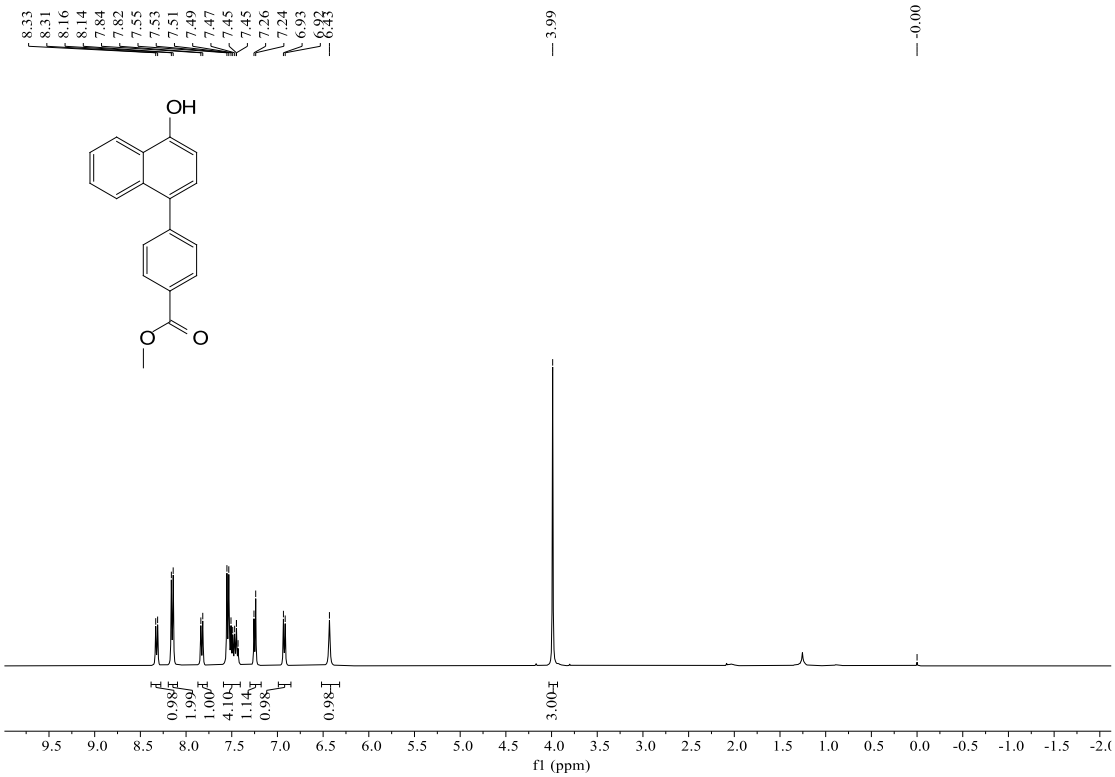
^{1}H NMR spectra of 3d (400 MHz, $CDCl_3$)



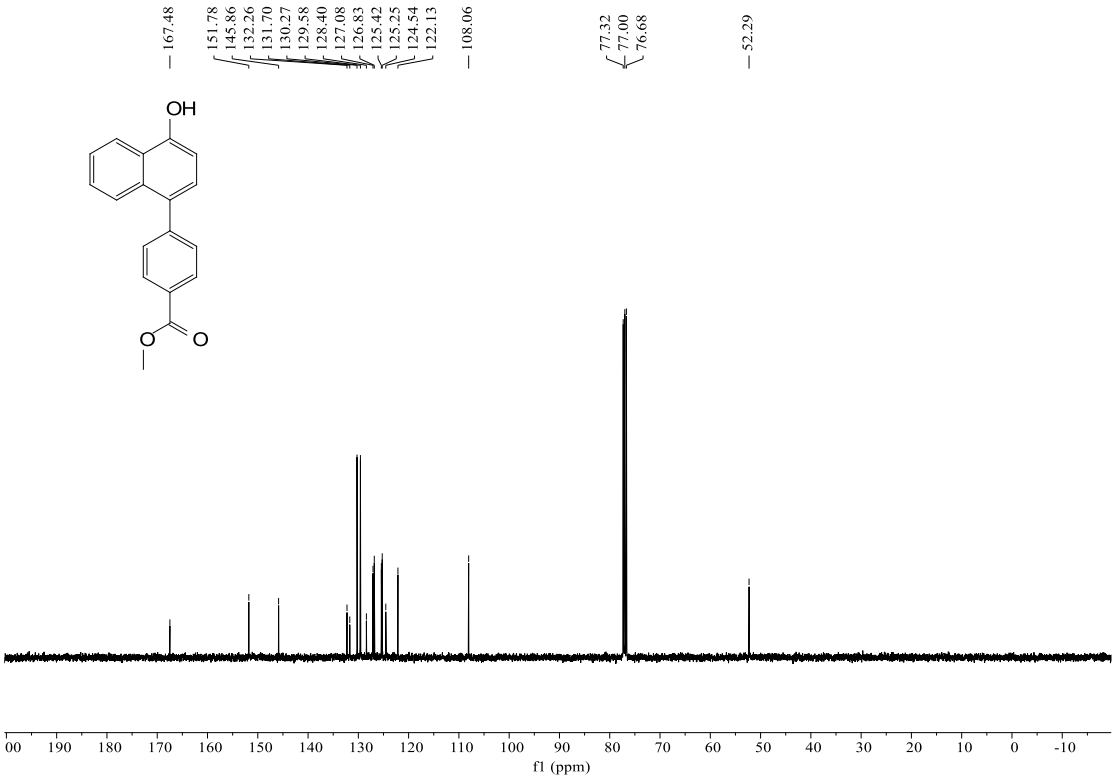
^{13}C NMR spectra of 3d (100 MHz, $CDCl_3$)



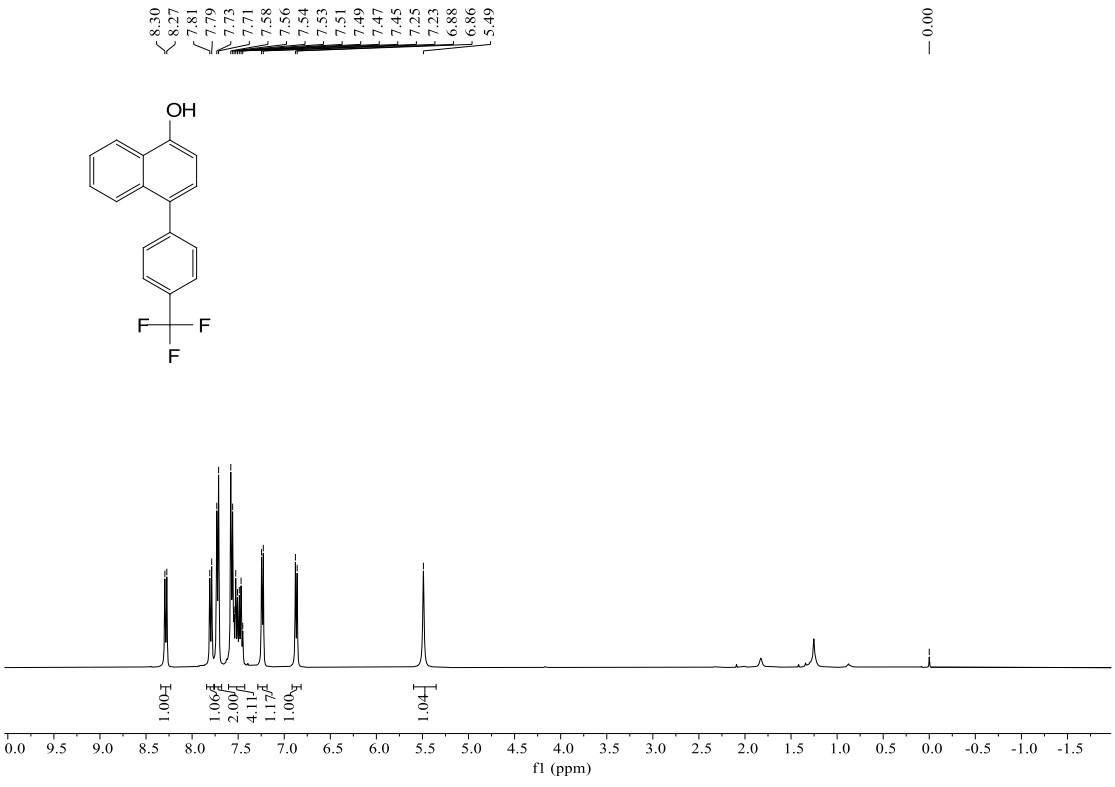
^{1}H NMR spectra of 3e (400 MHz, $CDCl_3$)



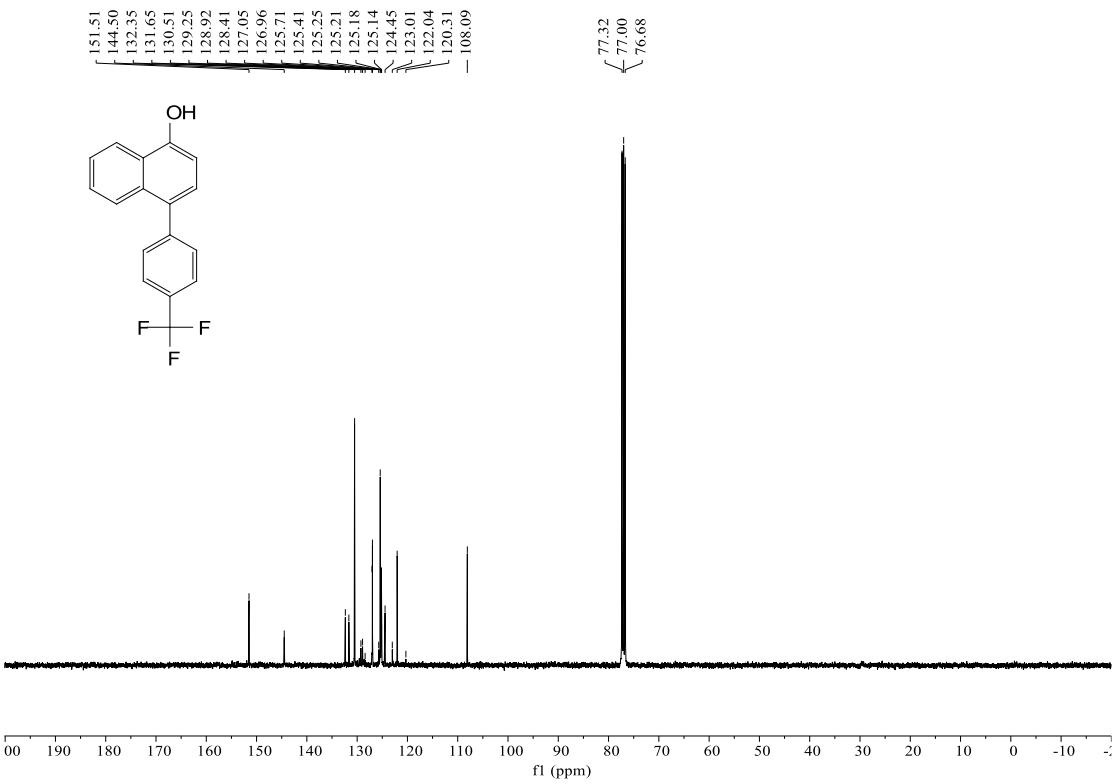
^{13}C NMR spectra of 3e (100 MHz, $CDCl_3$)



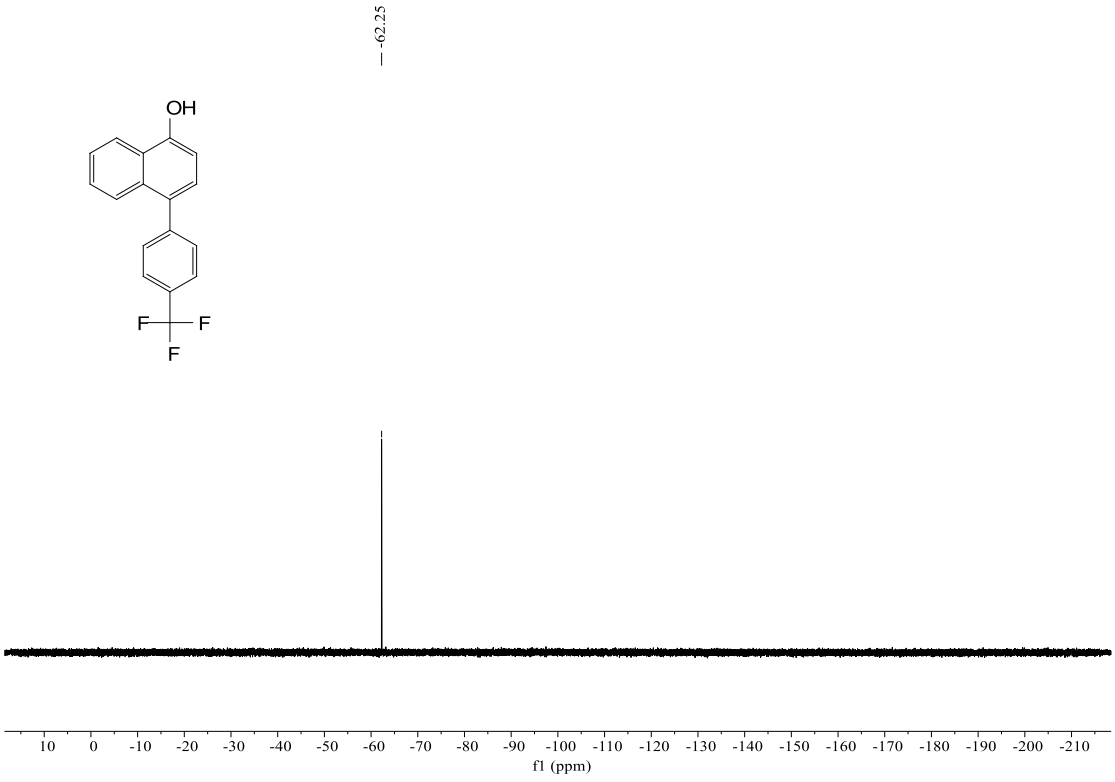
^{1}H NMR spectra of 3f (400 MHz, $CDCl_3$)



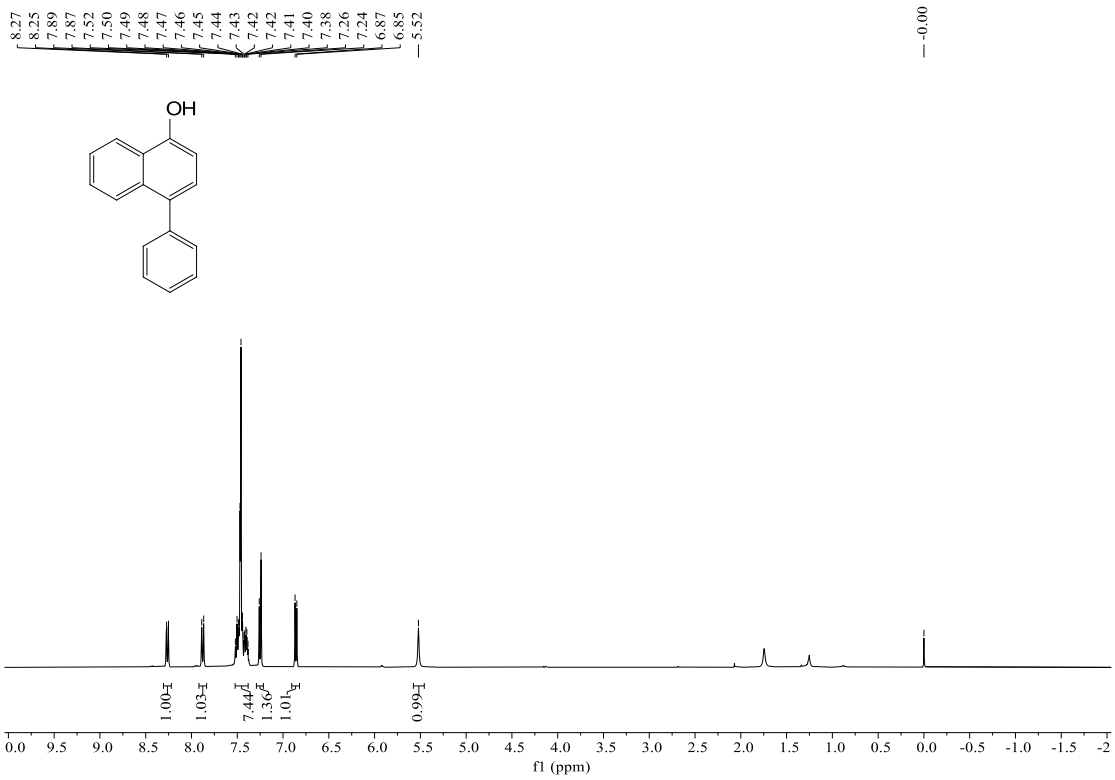
^{13}C NMR spectra of 3f (100 MHz, $CDCl_3$)



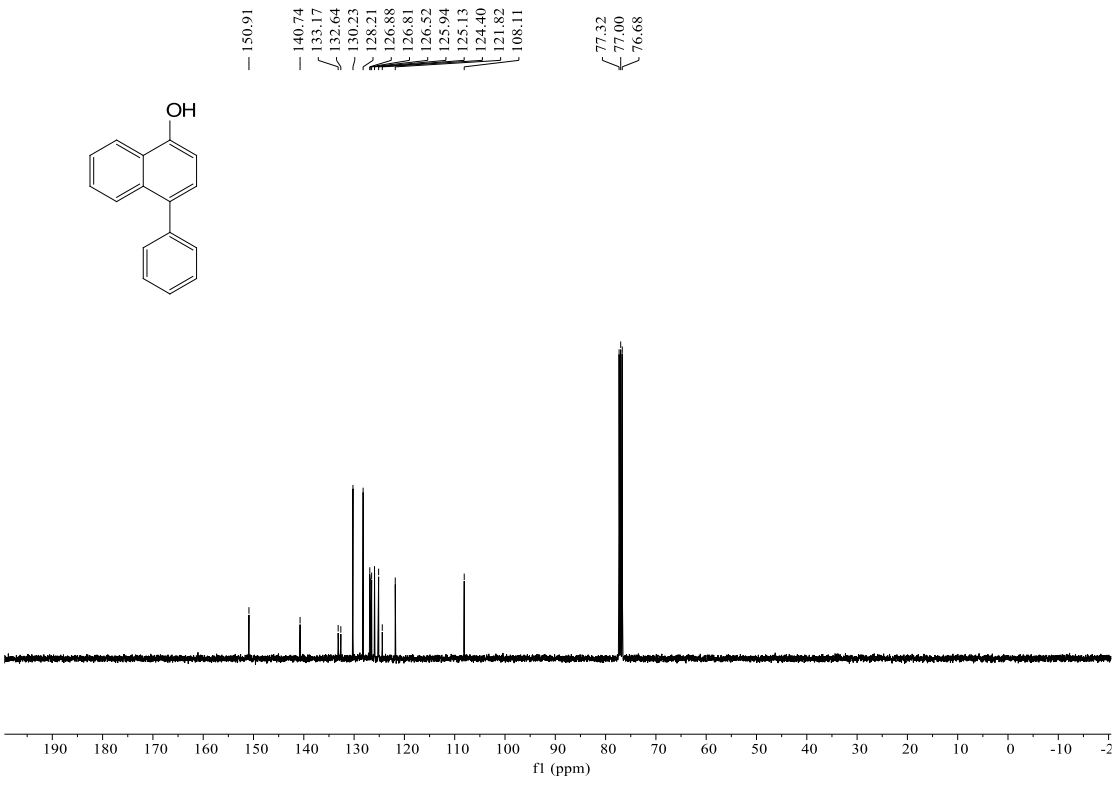
^{19}F NMR spectra of 3f (376 MHz, $CDCl_3$)



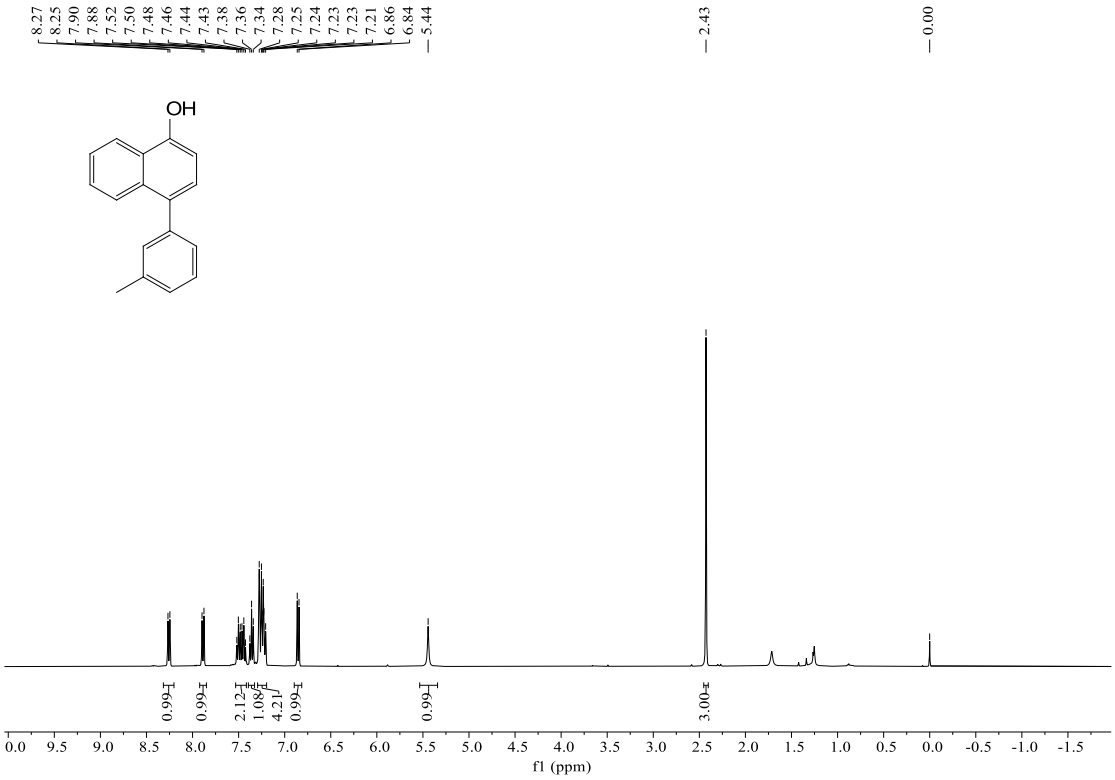
^{1}H NMR spectra of 3g (400 MHz, $CDCl_3$)



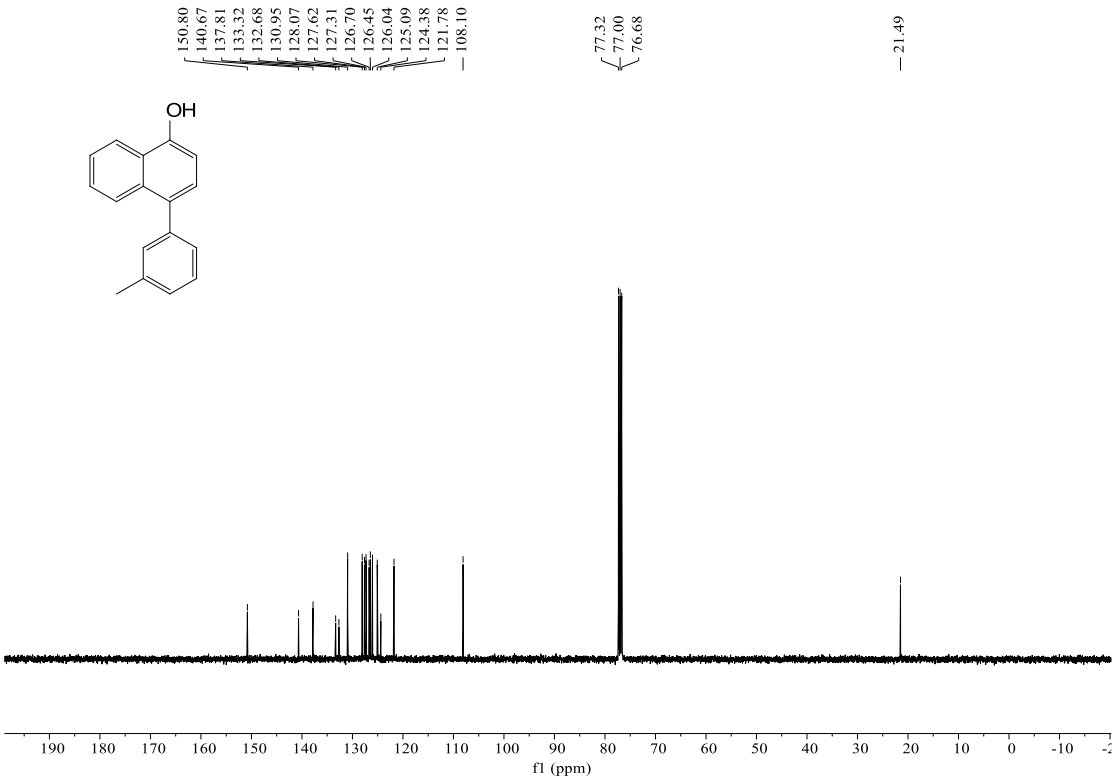
^{13}C NMR spectra of 3g (100 MHz, $CDCl_3$)



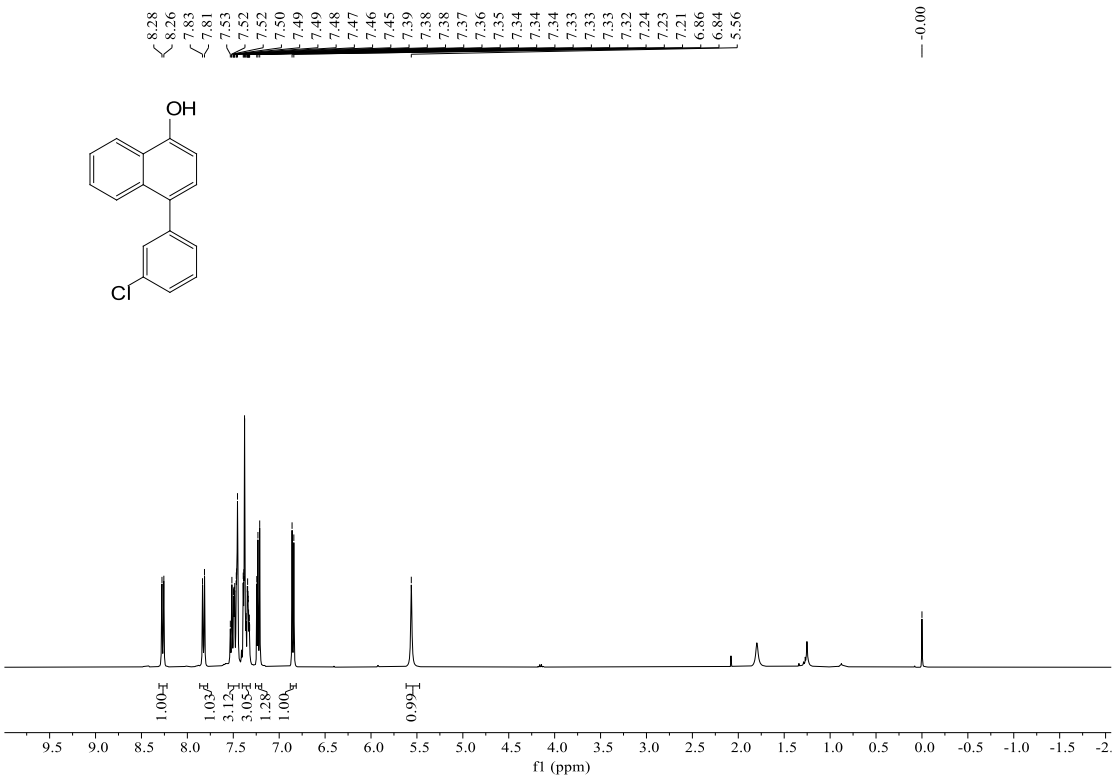
^{1}H NMR spectra of 3h (400 MHz, $CDCl_3$)



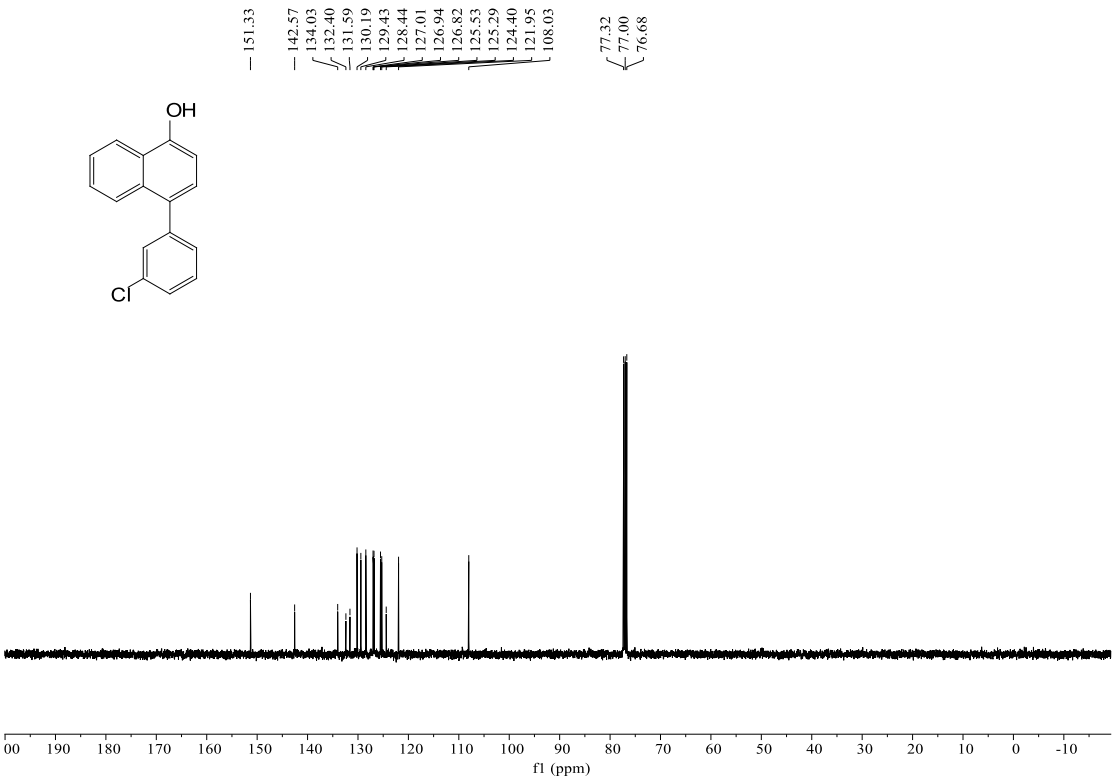
^{13}C NMR spectra of 3h (100 MHz, $CDCl_3$)



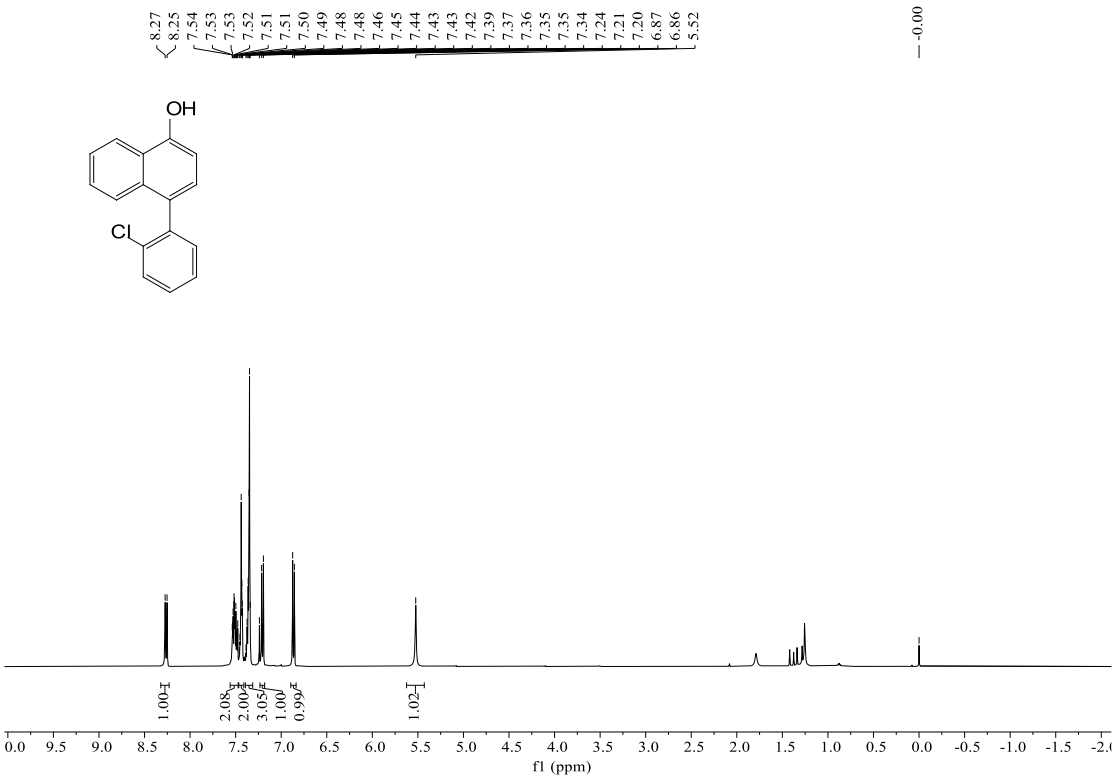
^{1}H NMR spectra of 3i (400 MHz, $CDCl_3$)



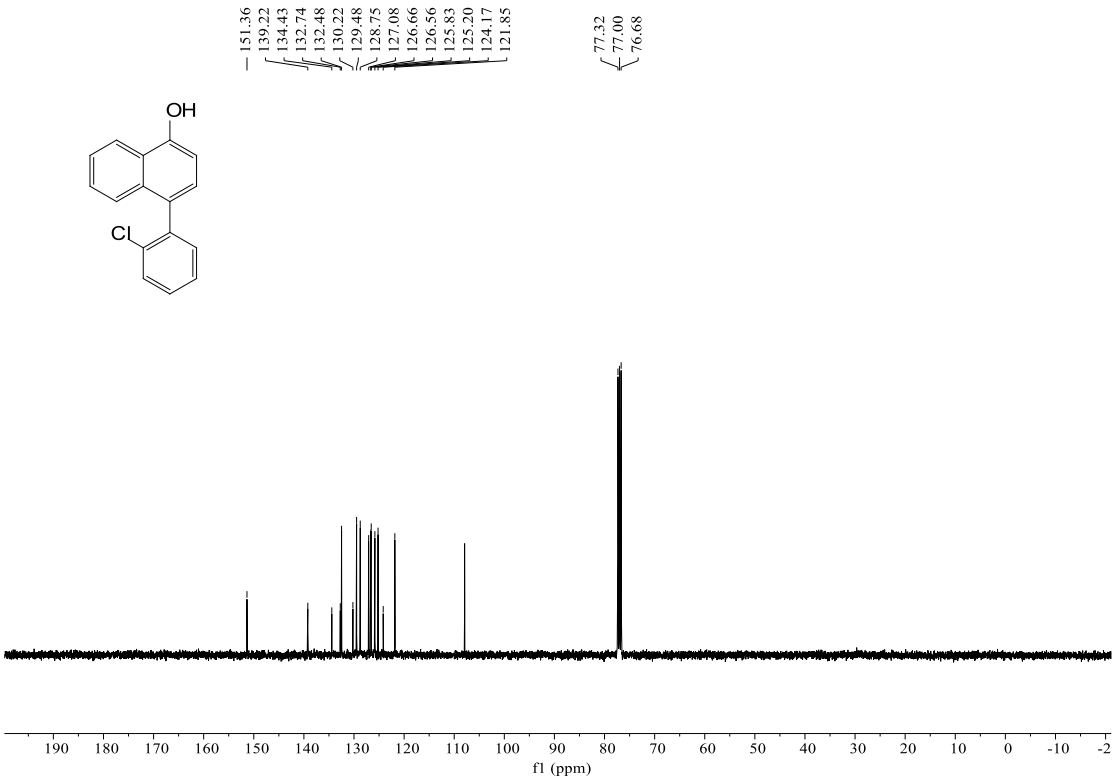
^{13}C NMR spectra of 3i (100 MHz, $CDCl_3$)



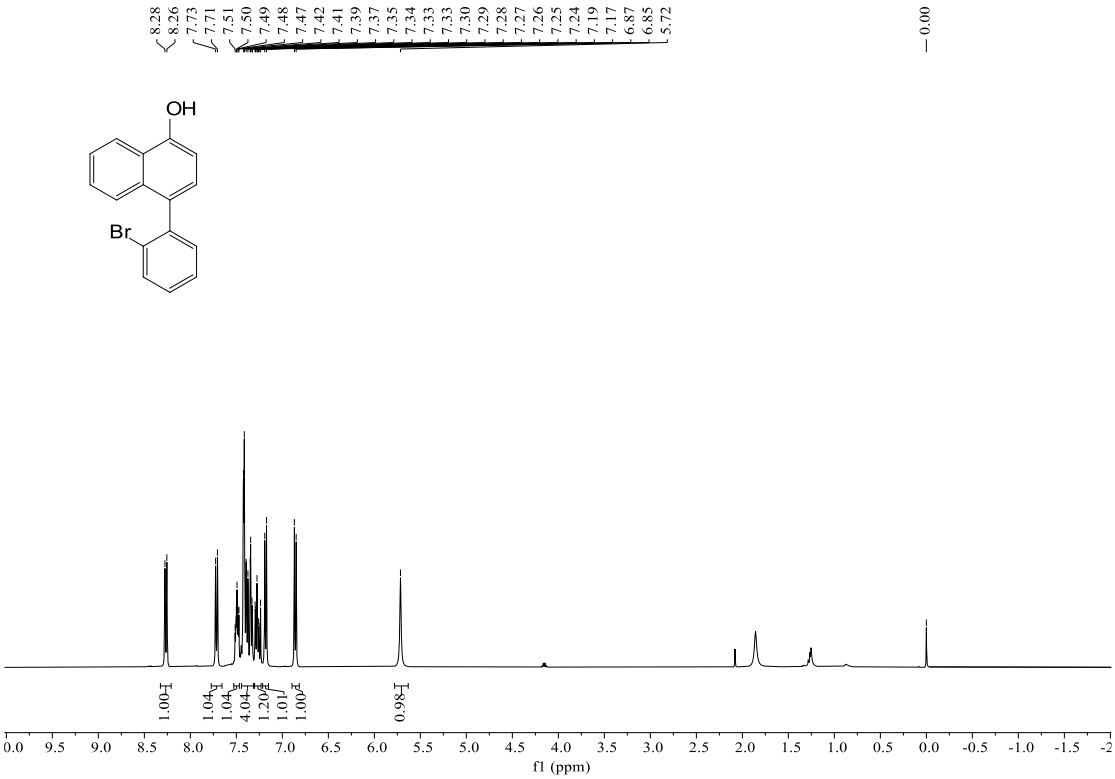
^{1}H NMR spectra of 3j (400 MHz, $CDCl_3$)



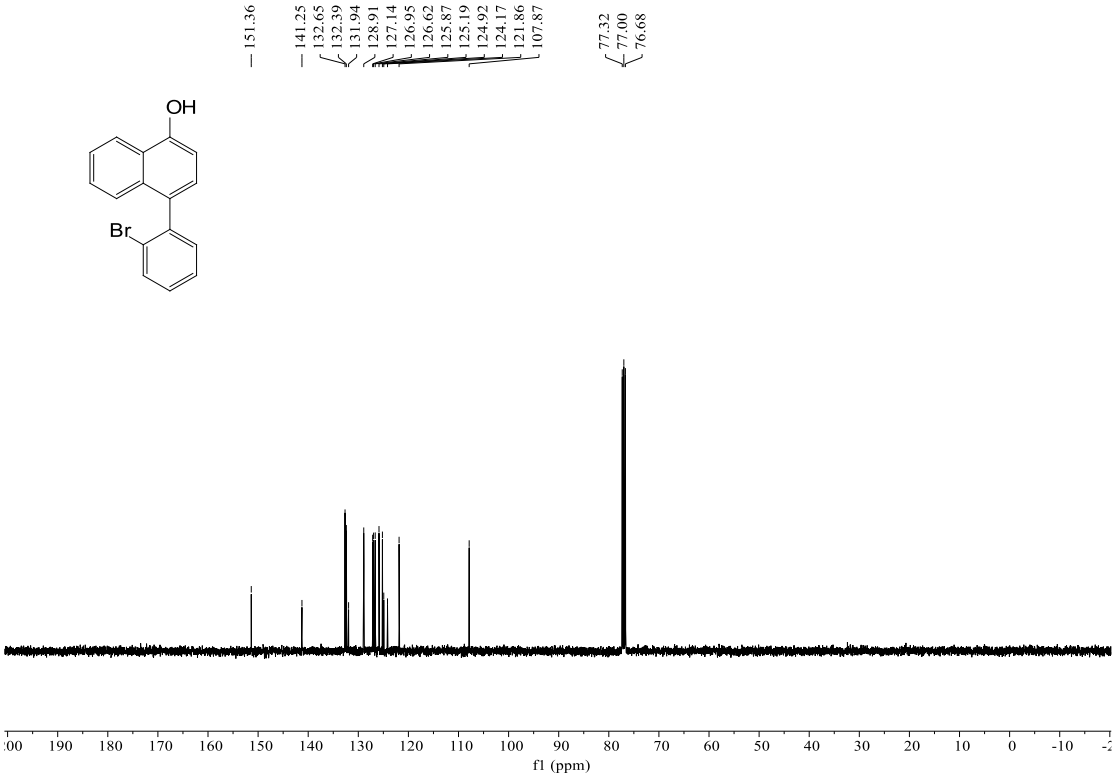
^{13}C NMR spectra of 3j (100 MHz, $CDCl_3$)



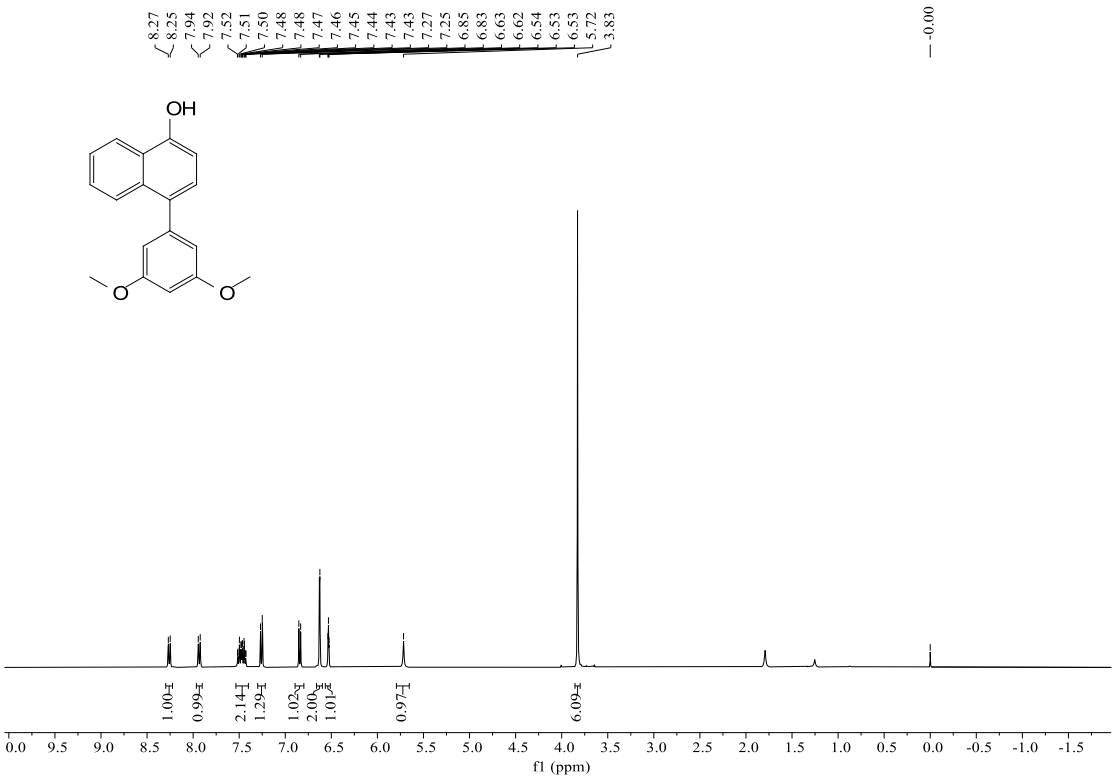
^{1}H NMR spectra of 3k (400 MHz, $CDCl_3$)



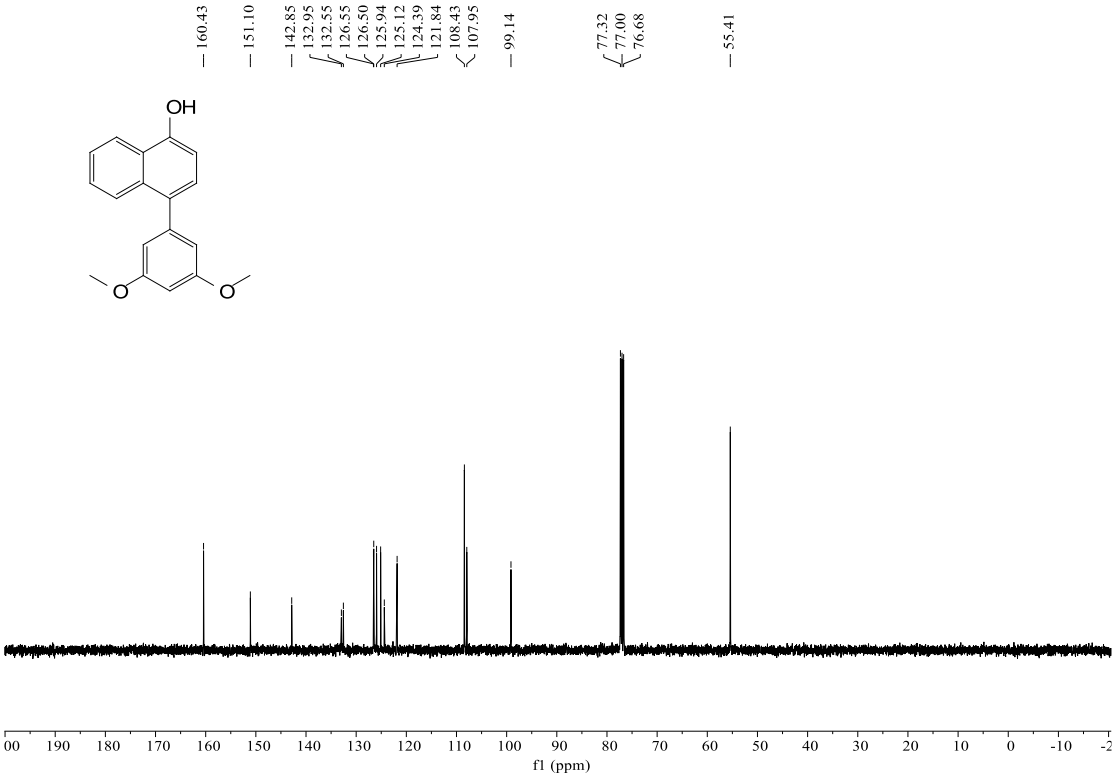
^{13}C NMR spectra of 3k (100 MHz, $CDCl_3$)



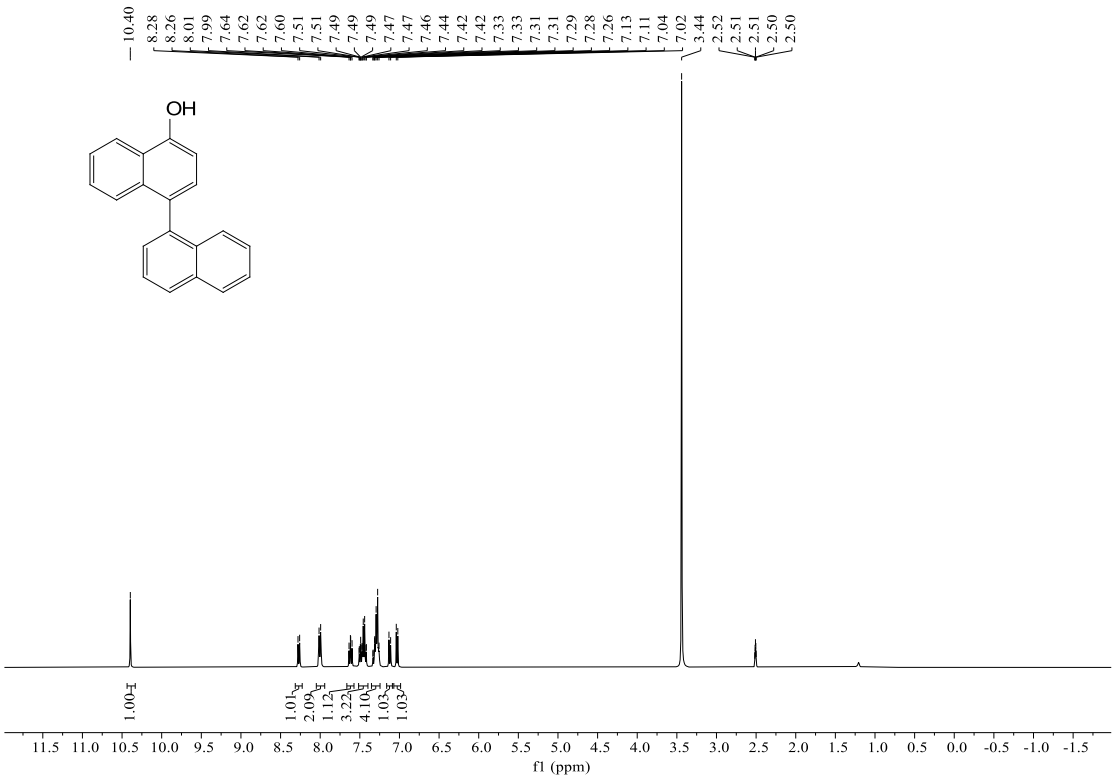
^{1}H NMR spectra of 3l (400 MHz, $CDCl_3$)



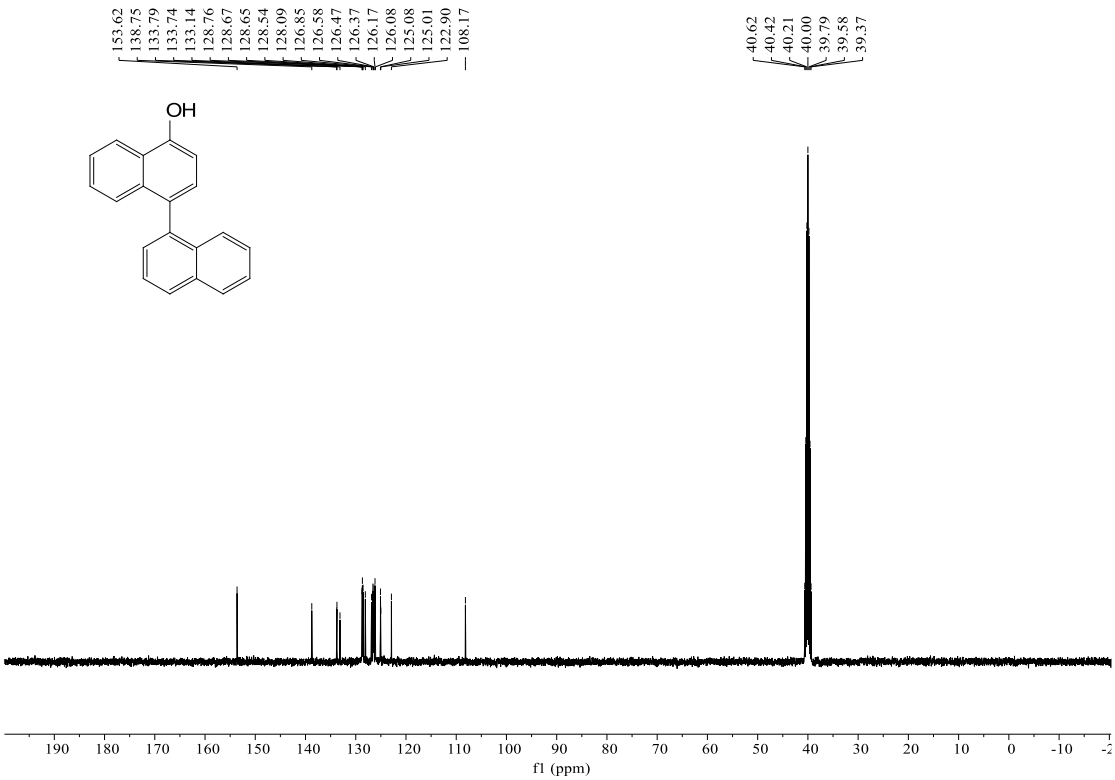
^{13}C NMR spectra of 3l (100 MHz, $CDCl_3$)



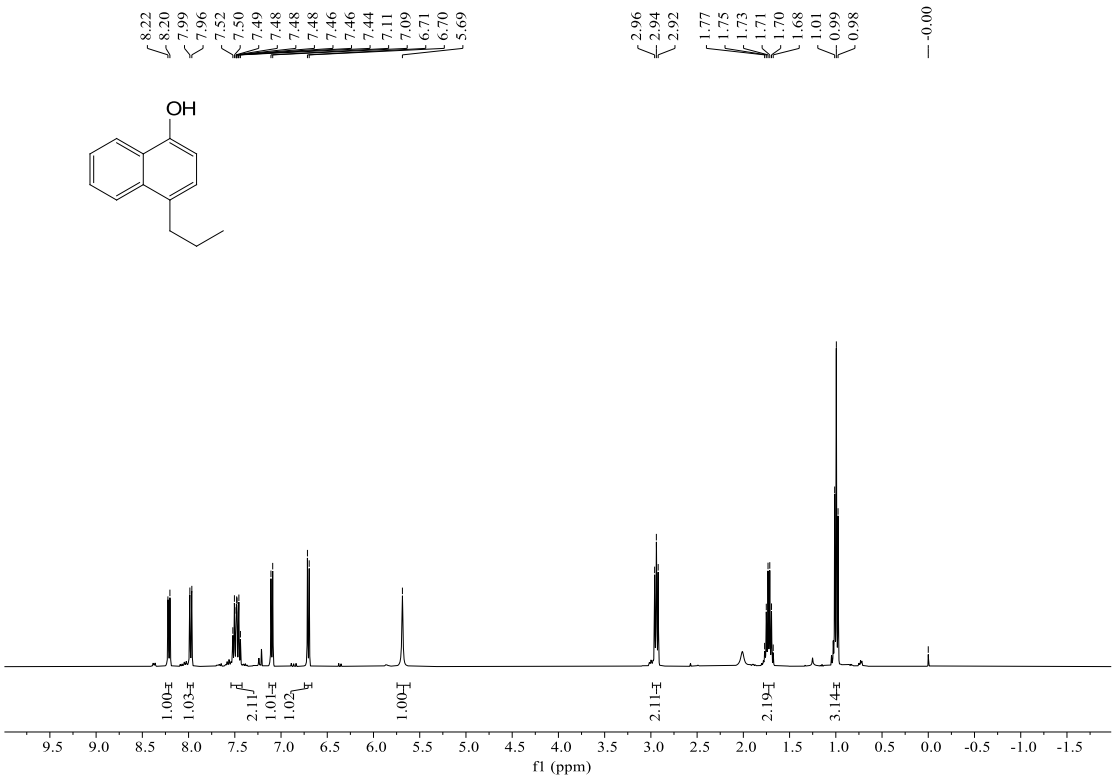
^{1}H NMR spectra of 3m (400 MHz, DMSO-d_6)



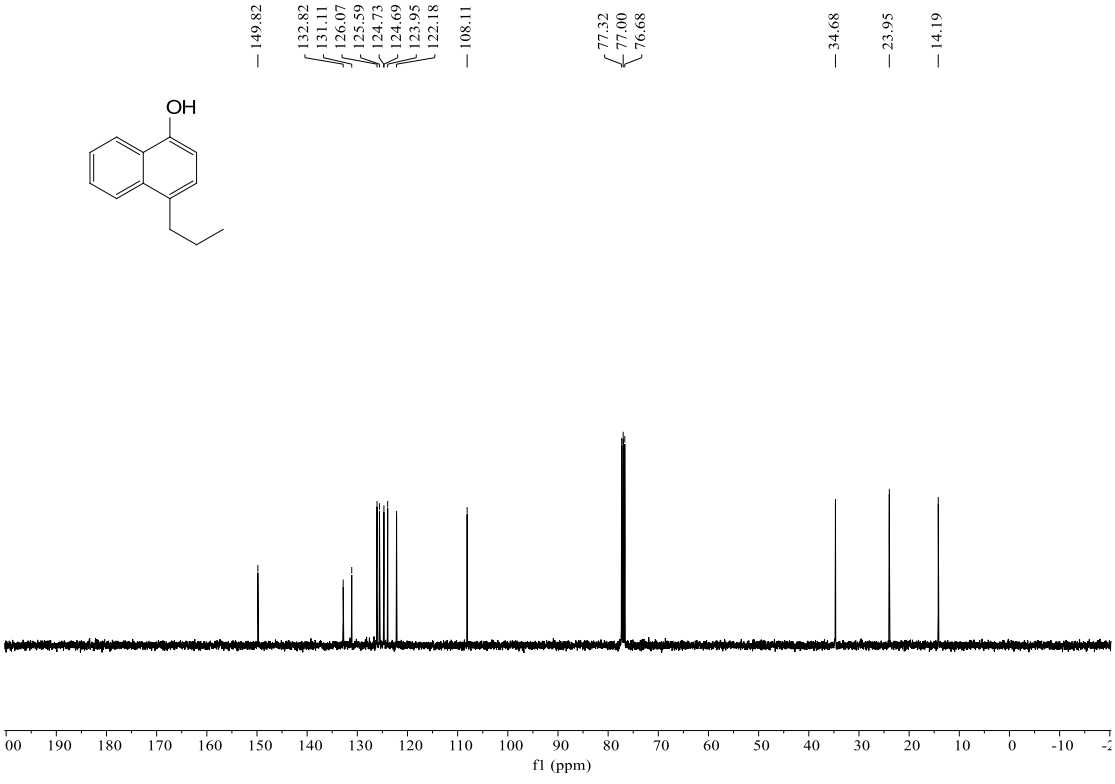
^{13}C NMR spectra of 3m (100 MHz, DMSO-d_6)



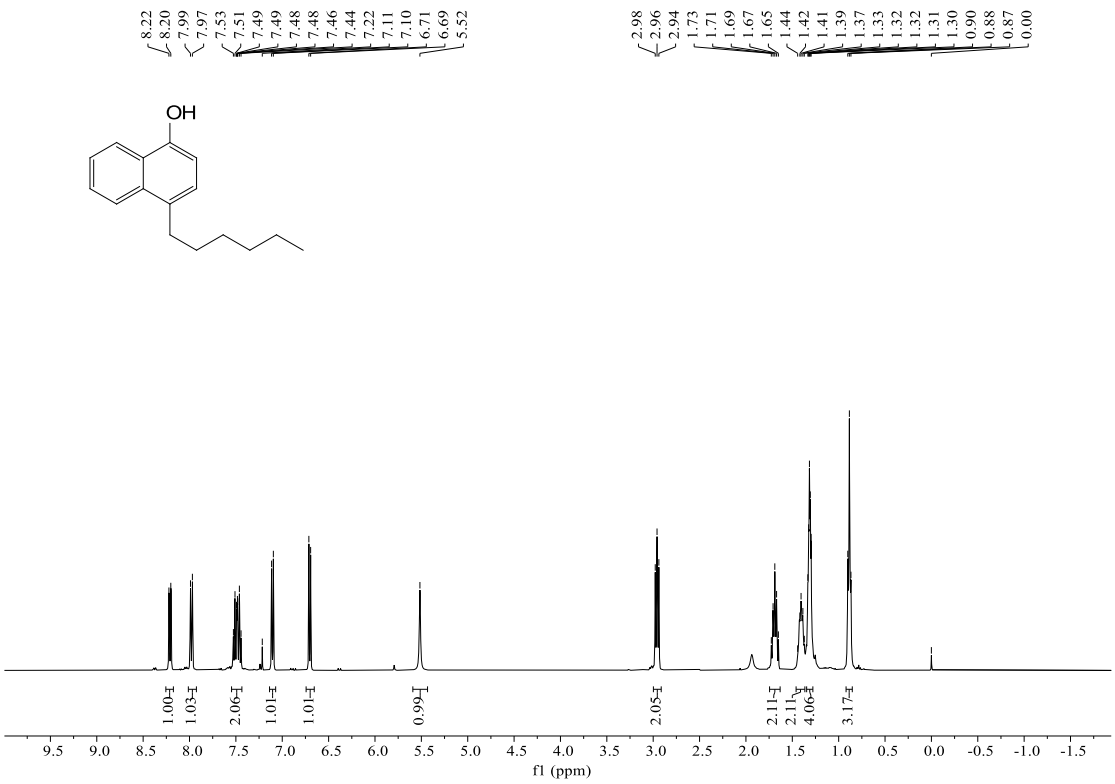
^{1}H NMR spectra of 3n (400 MHz, $CDCl_3$)



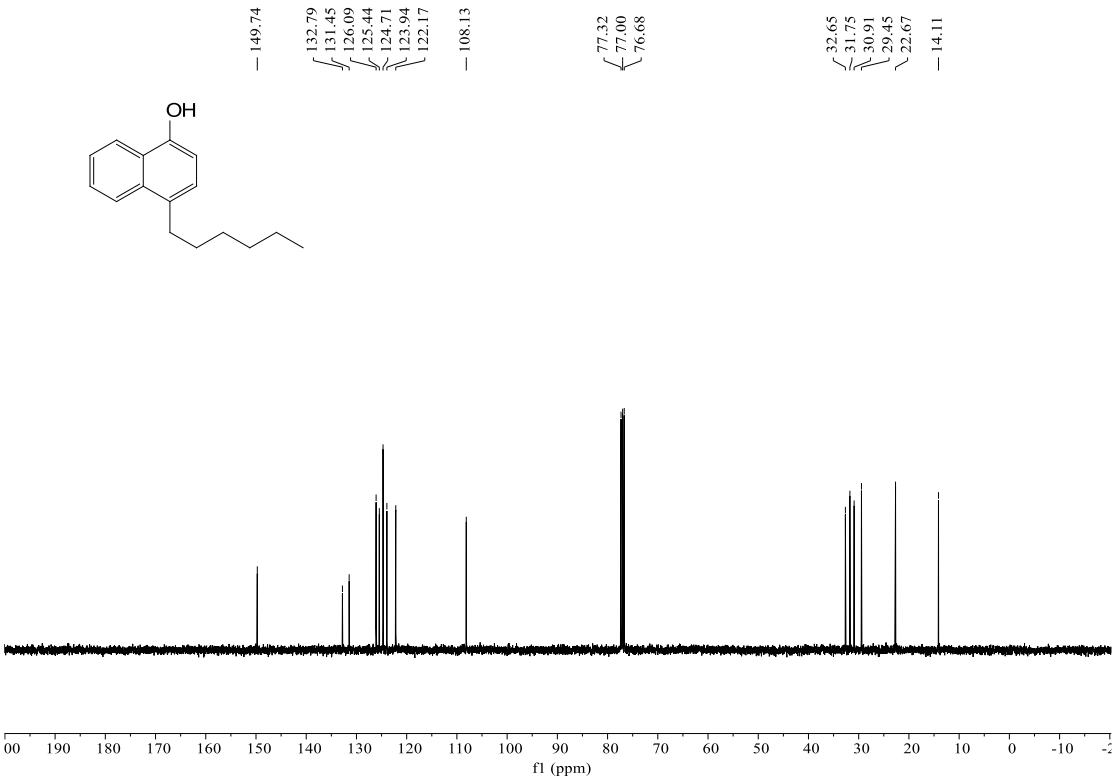
^{13}C NMR spectra of 3n (100 MHz, $CDCl_3$)



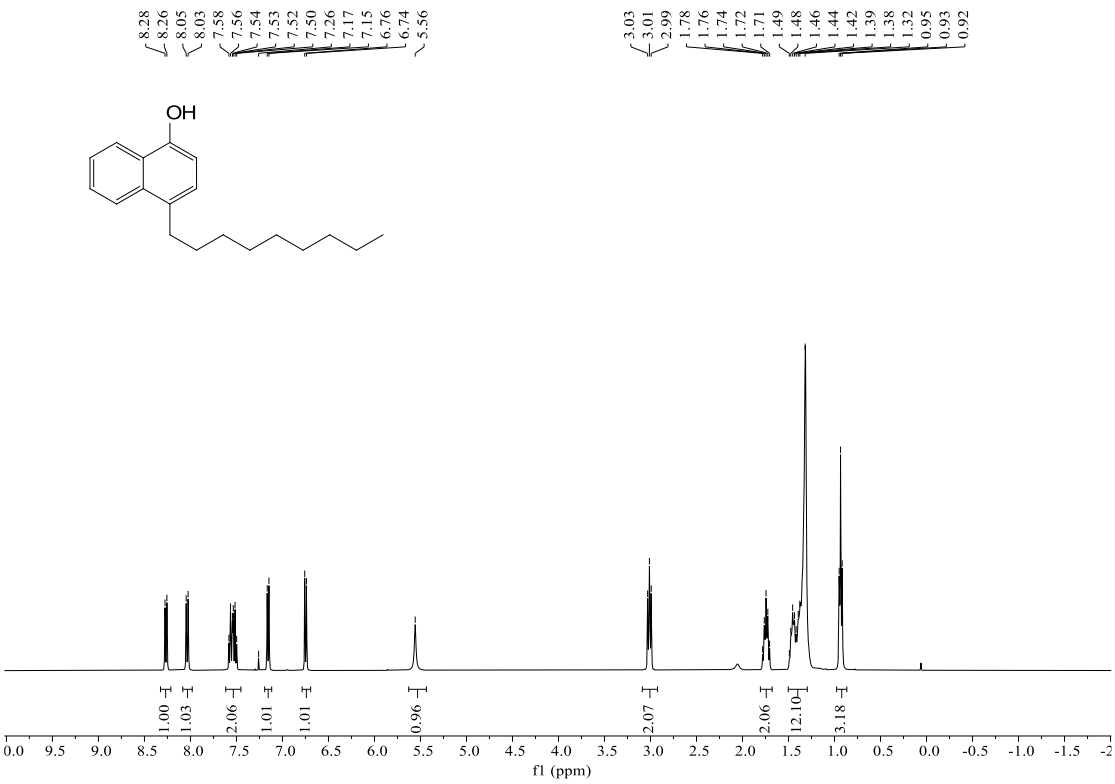
^{1}H NMR spectra of 3o (400 MHz, $CDCl_3$)



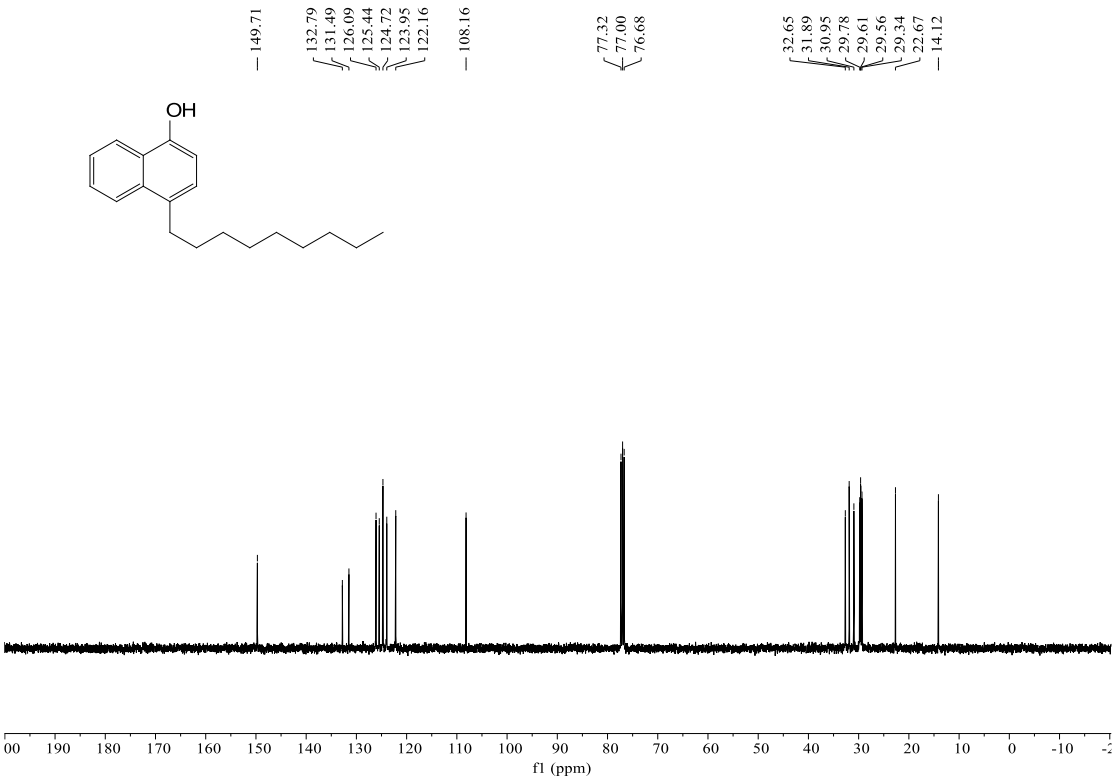
^{13}C NMR spectra of 3o (100 MHz, $CDCl_3$)



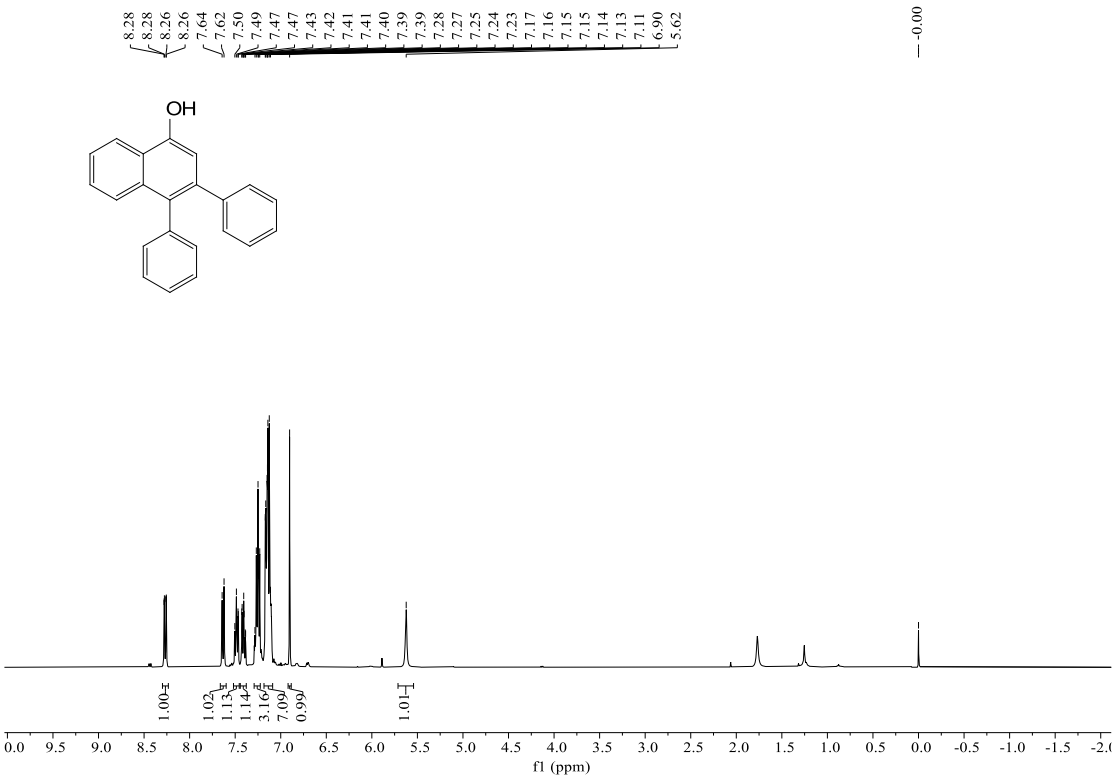
^{1}H NMR spectra of 3p (400 MHz, $CDCl_3$)



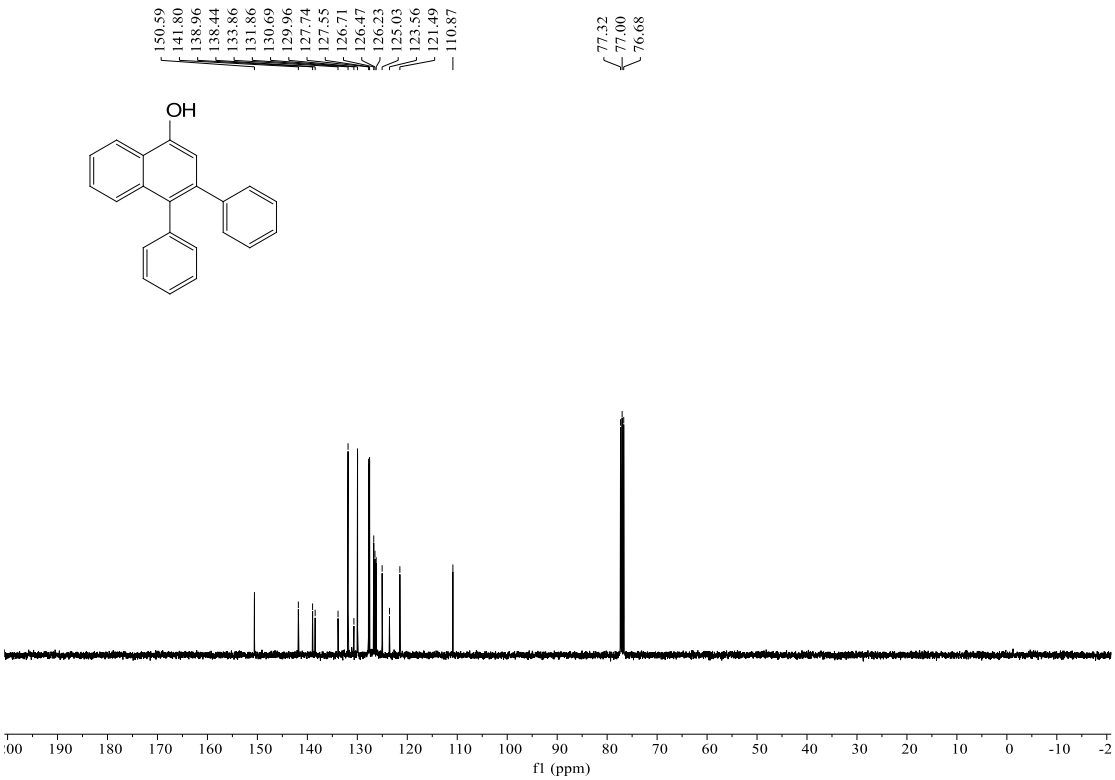
^{13}C NMR spectra of 3p (100 MHz, $CDCl_3$)



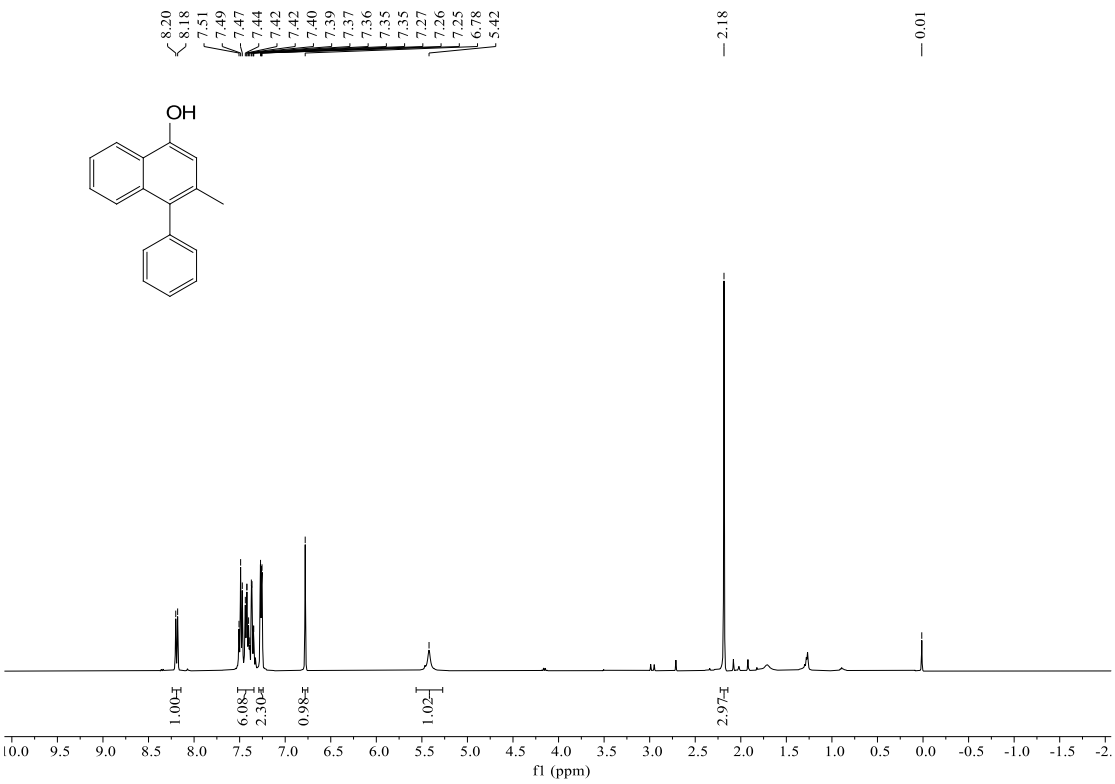
^{1}H NMR spectra of 3q (400 MHz, $CDCl_3$)



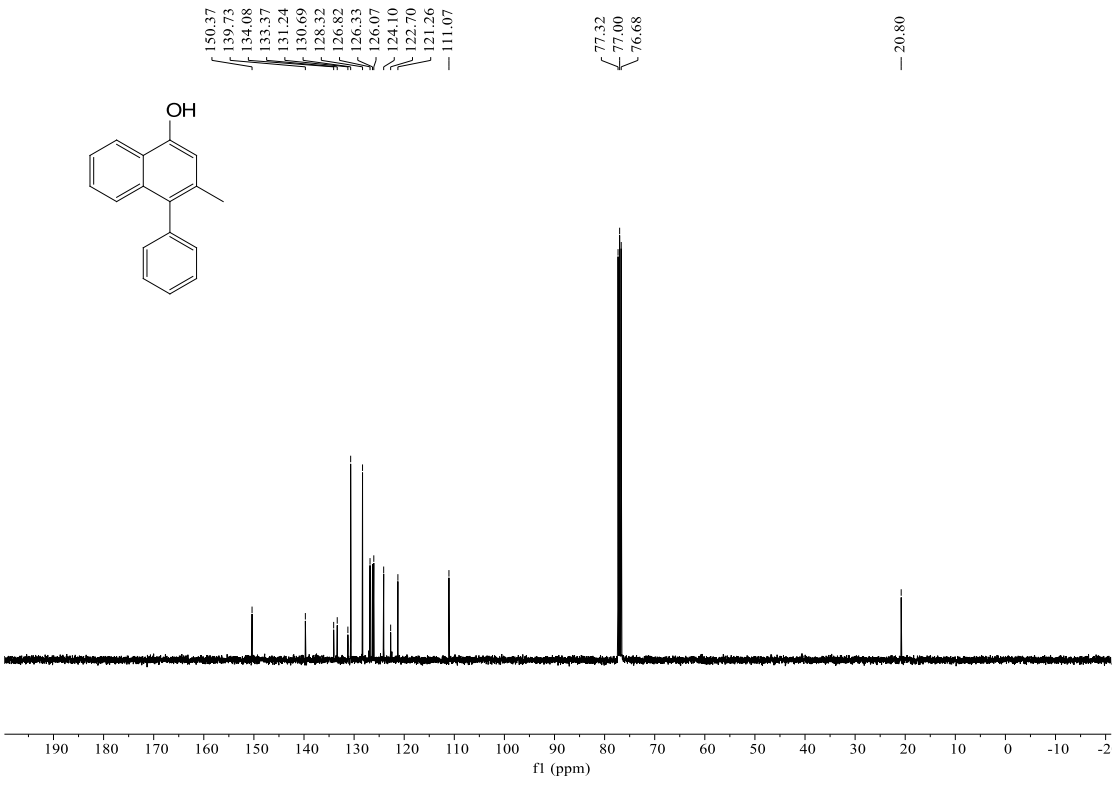
^{13}C NMR spectra of 3q (100 MHz, $CDCl_3$)



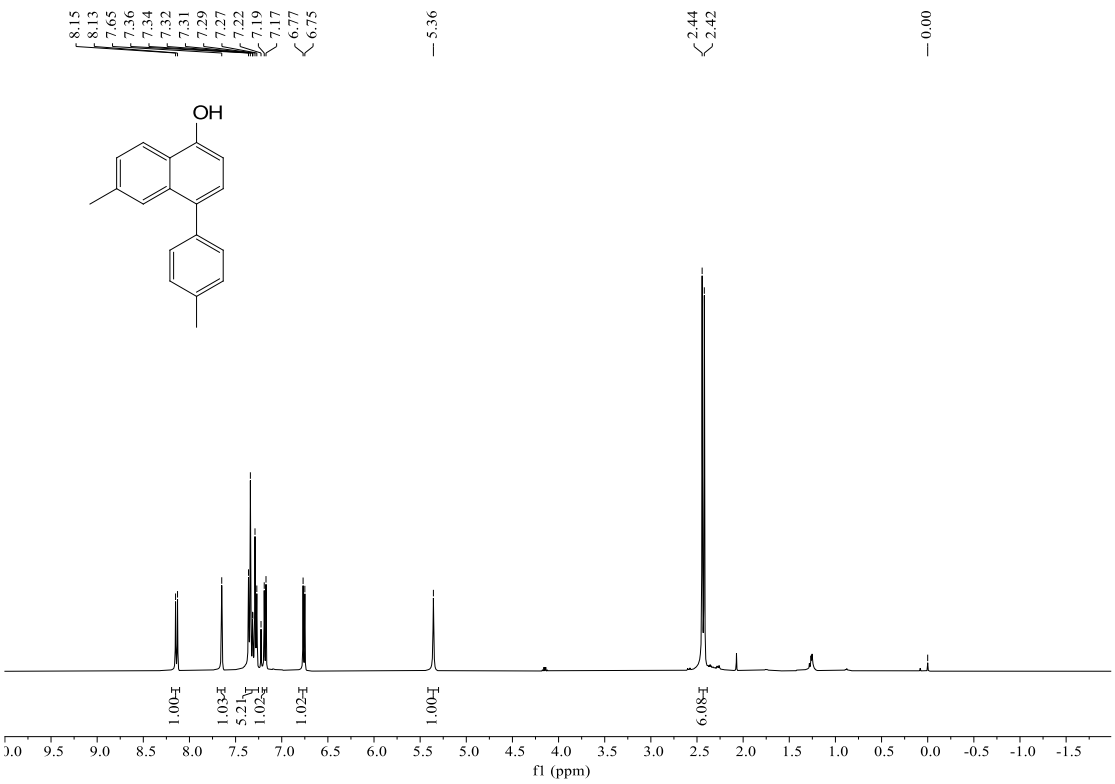
^{1}H NMR spectra of 3r (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 3r (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 3t (400 MHz, $CDCl_3$)



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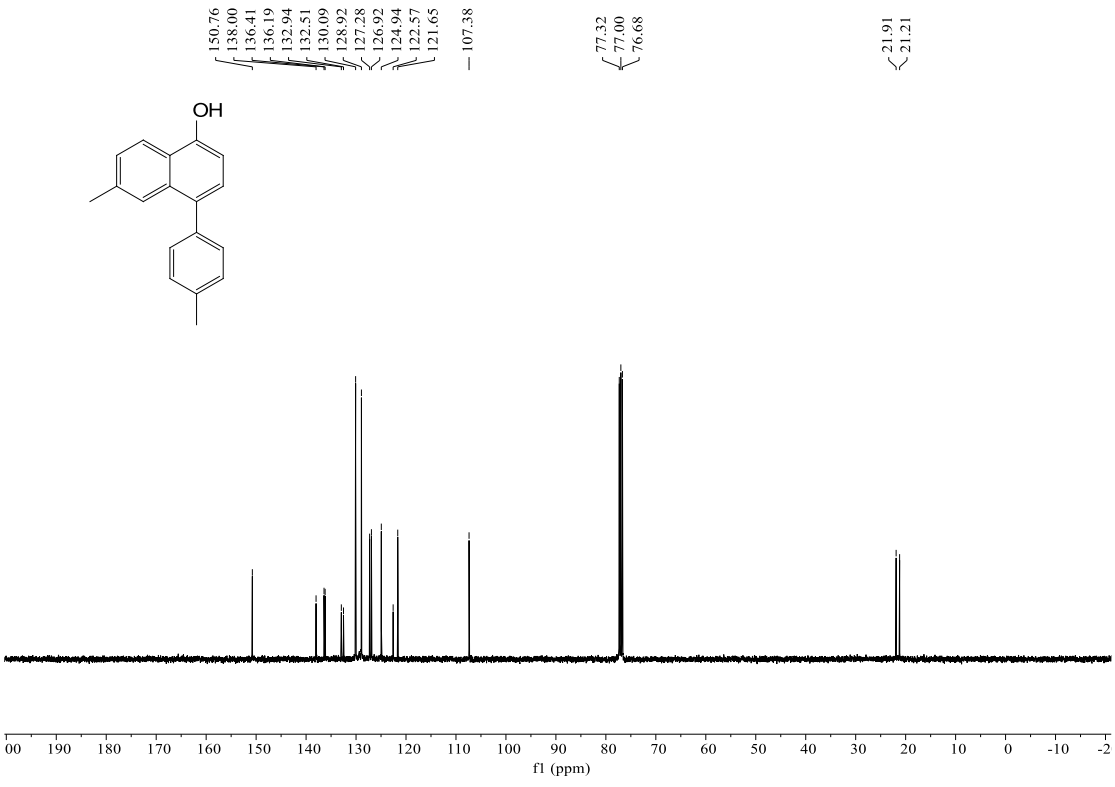
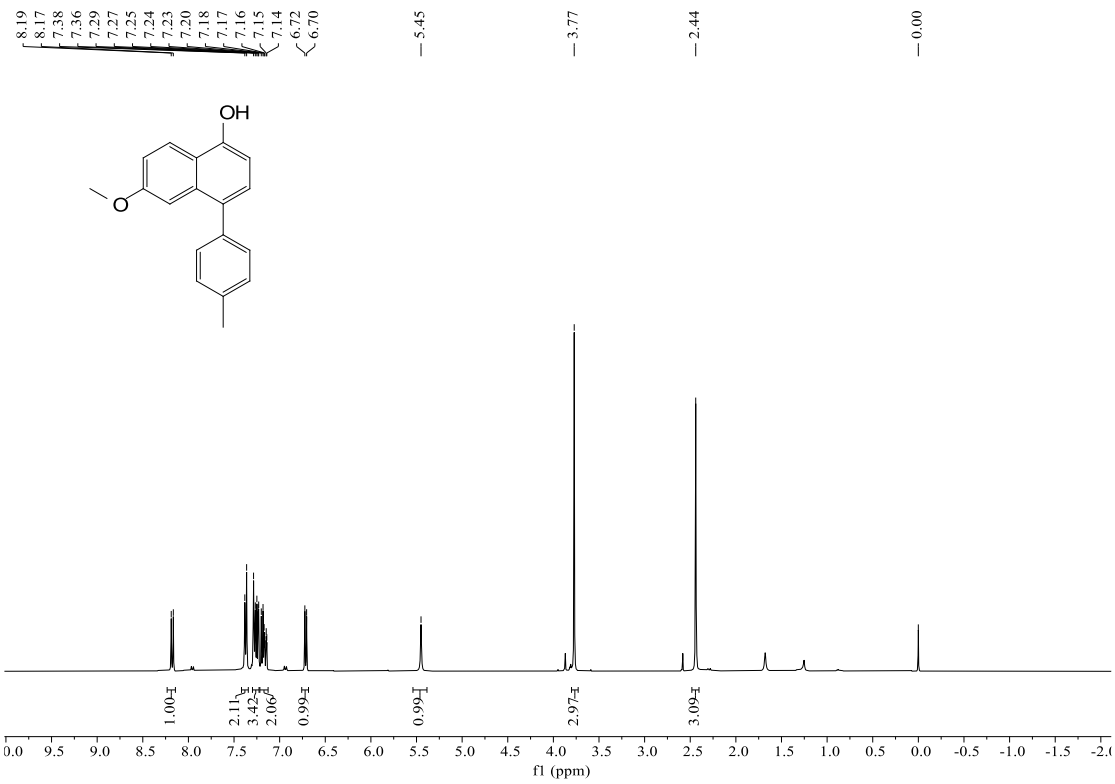
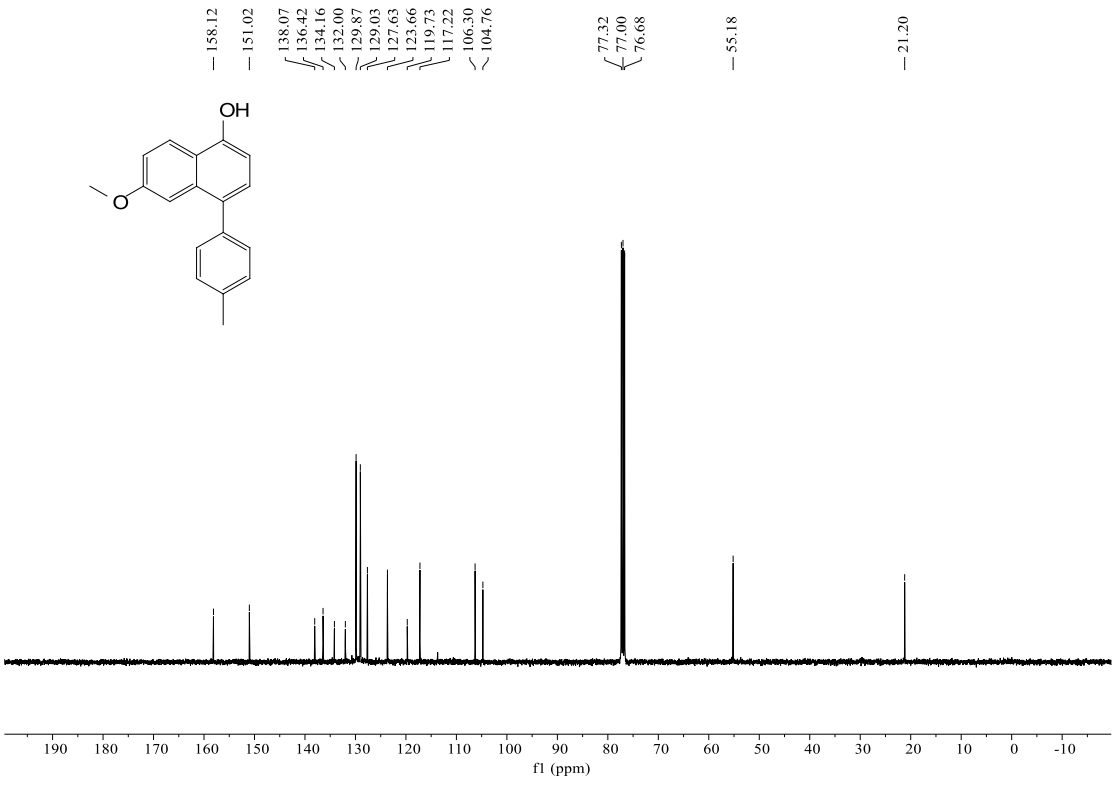


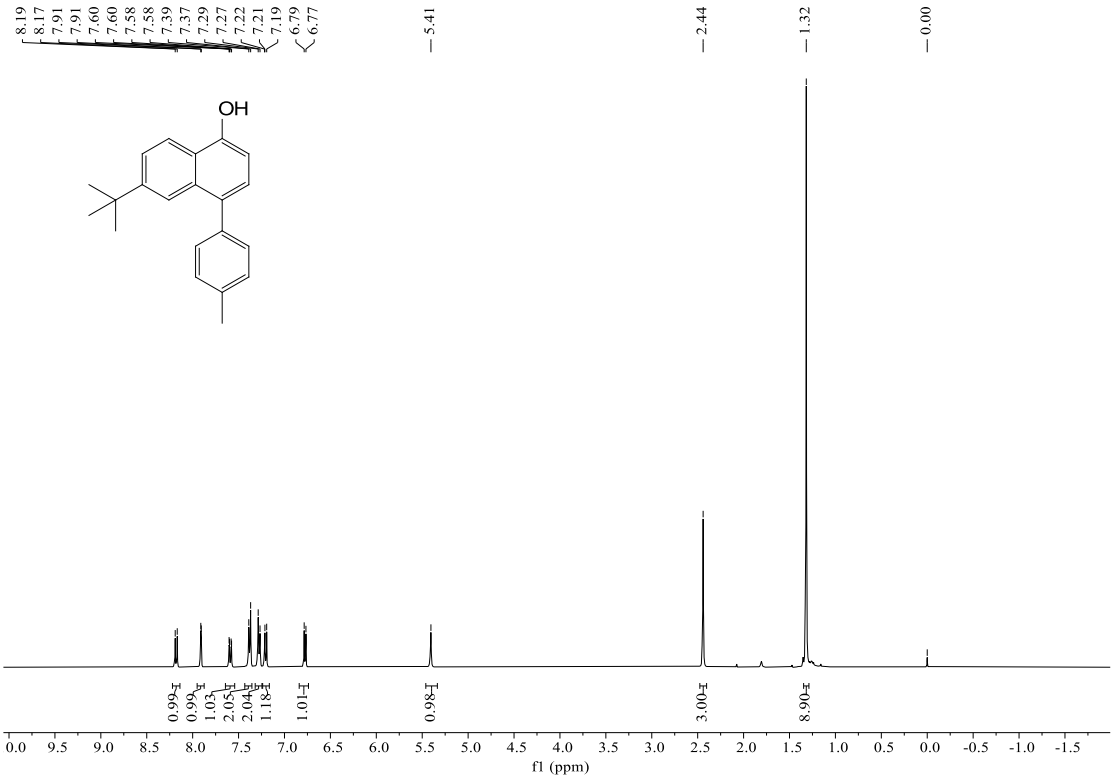
^{1}H NMR spectra of 3u (400 MHz, $CDCl_3$)



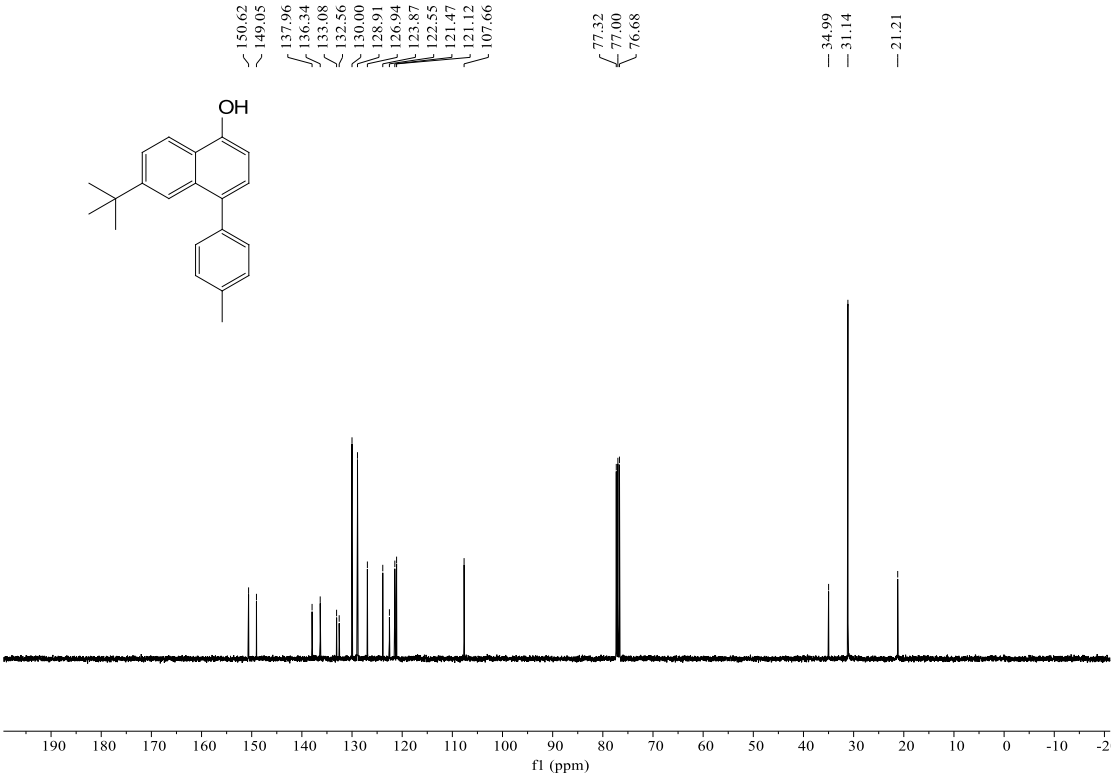
^{13}C NMR spectra of 3u (100 MHz, $CDCl_3$)



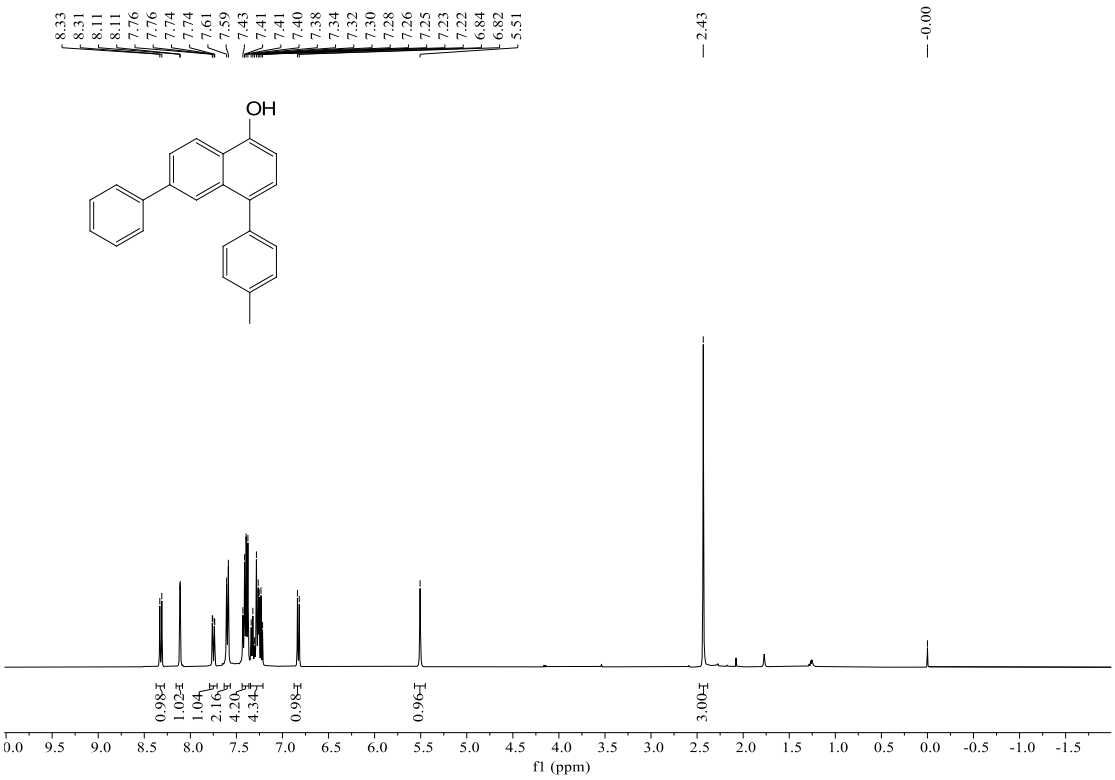
^{1}H NMR spectra of 3v (400 MHz, $CDCl_3$)



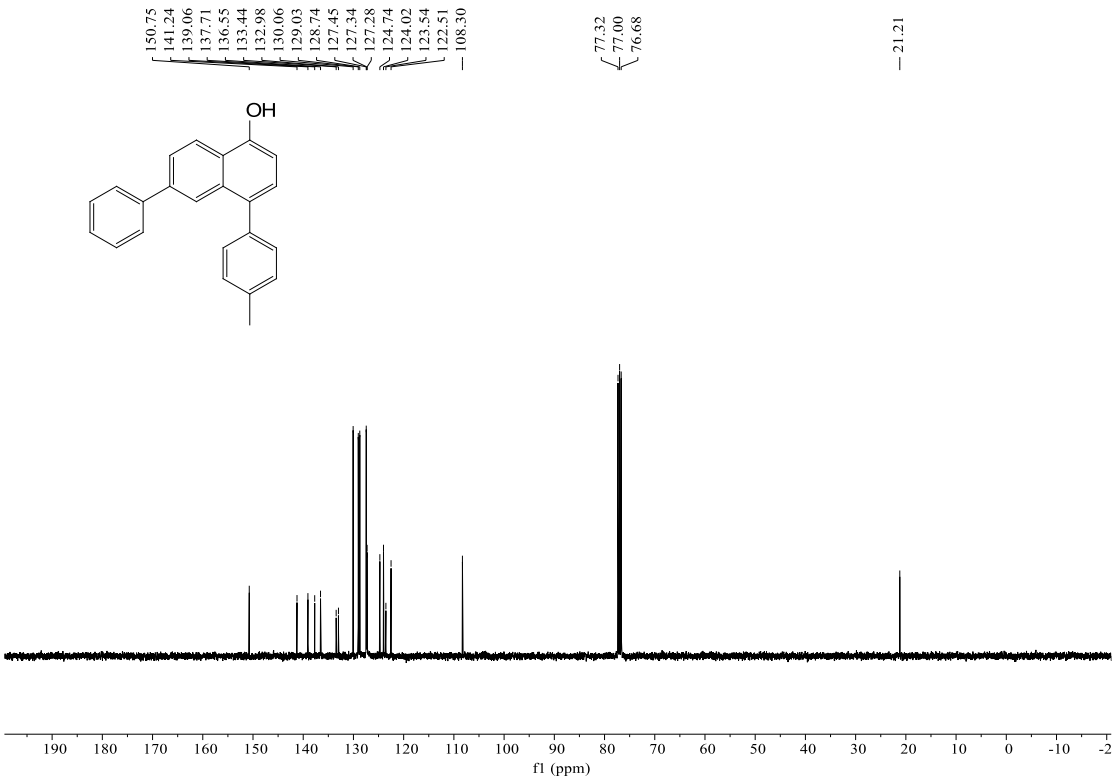
^{13}C NMR spectra of 3v (100 MHz, $CDCl_3$)



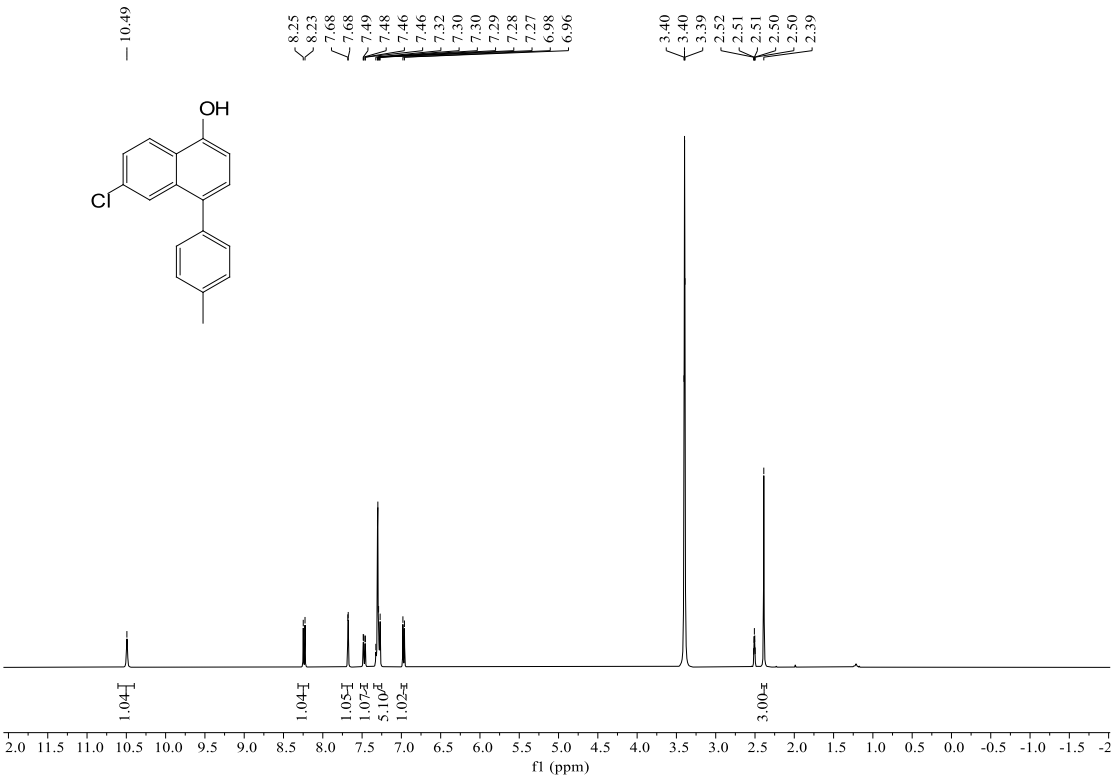
^{1}H NMR spectra of 3w (400 MHz, $CDCl_3$)



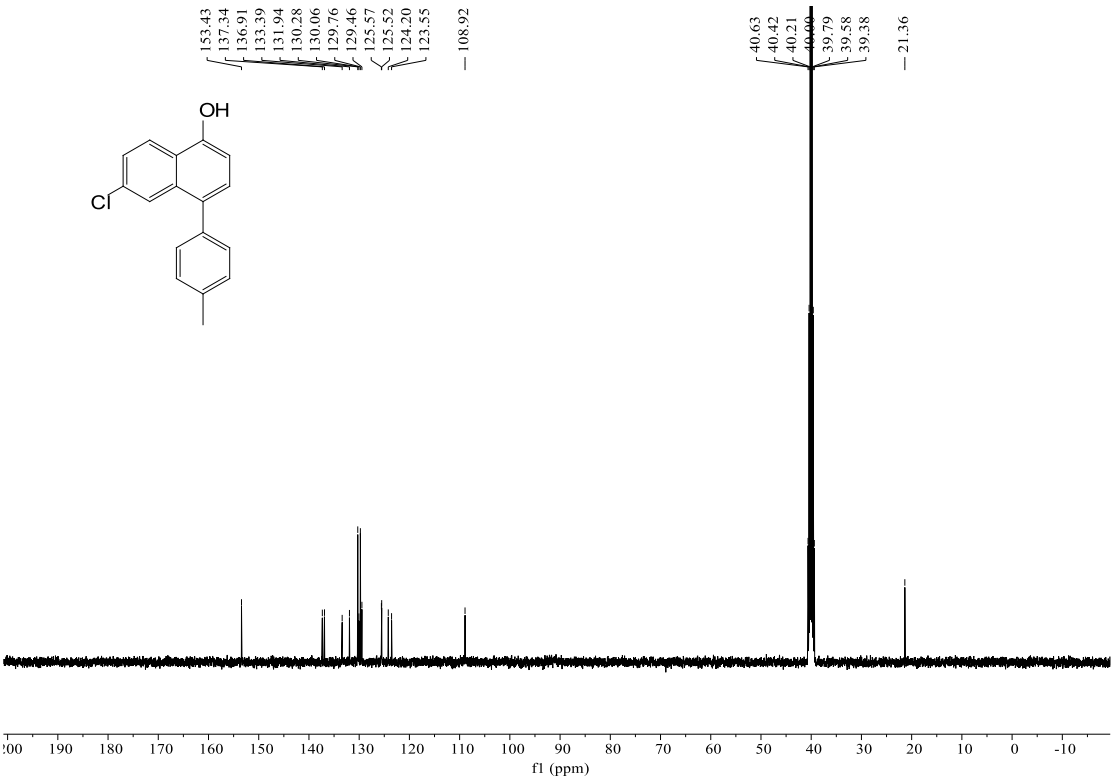
^{13}C NMR spectra of 3w (100 MHz, $CDCl_3$)



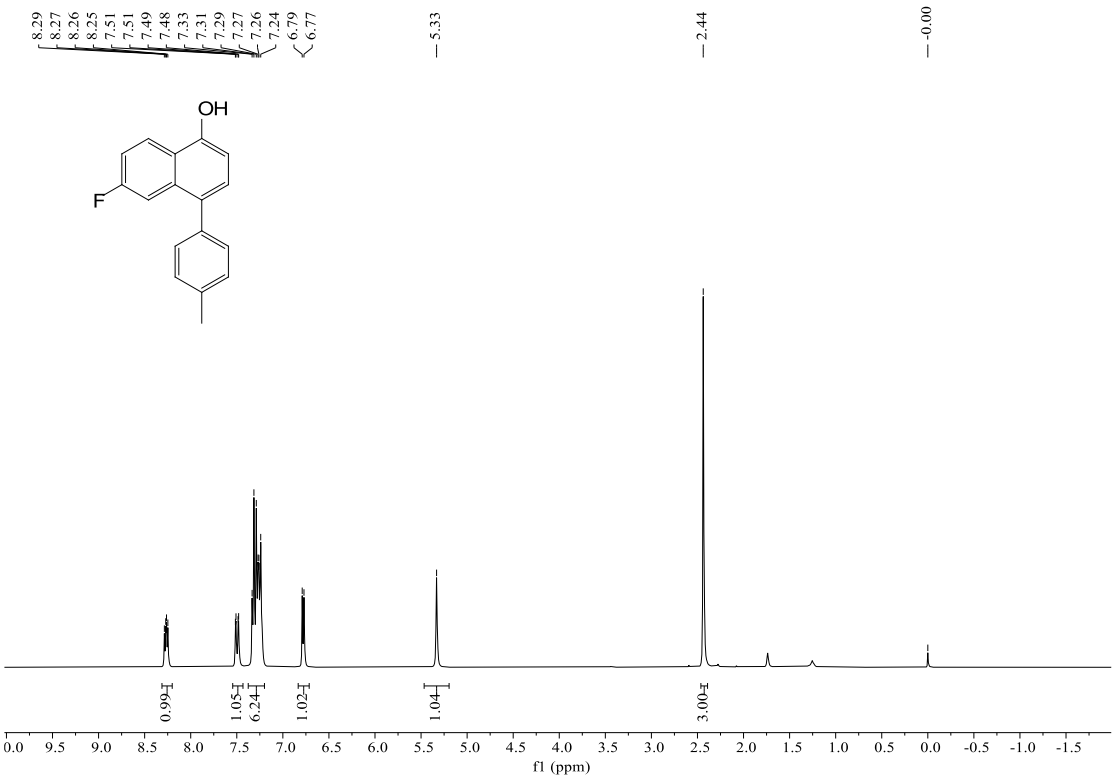
^{1}H NMR spectra of 3x (400 MHz, DMSO-d_6)



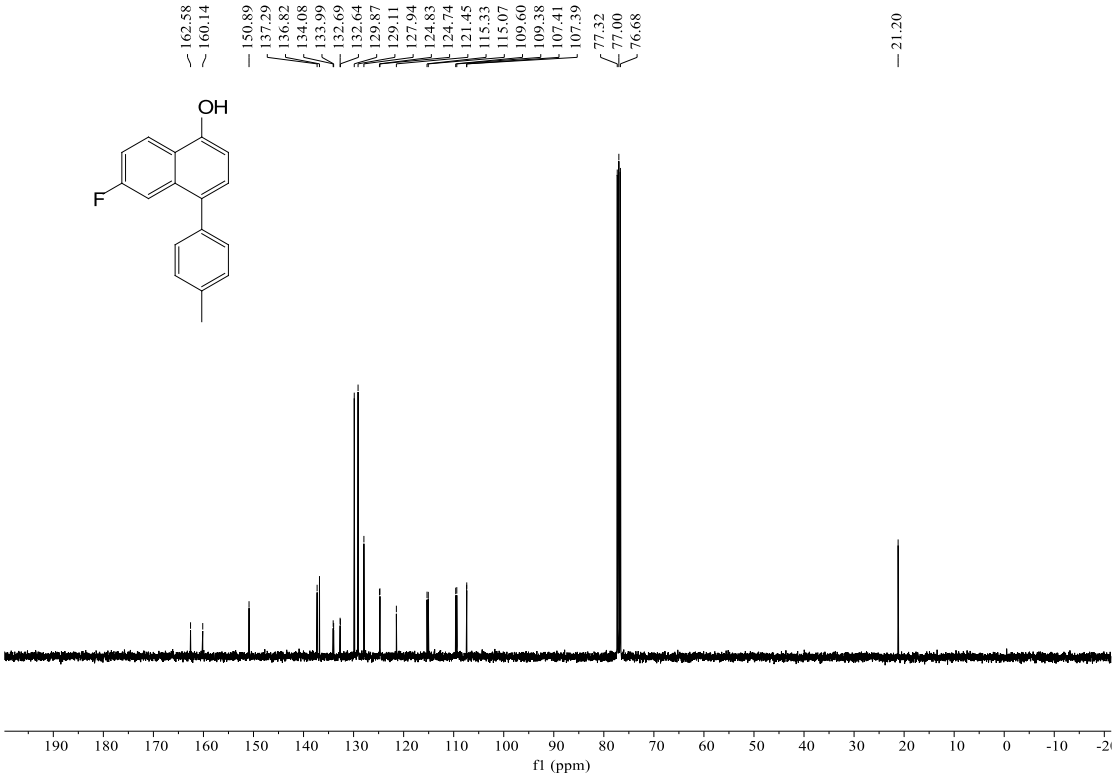
^{13}C NMR spectra of 3x (100 MHz, DMSO-d_6)



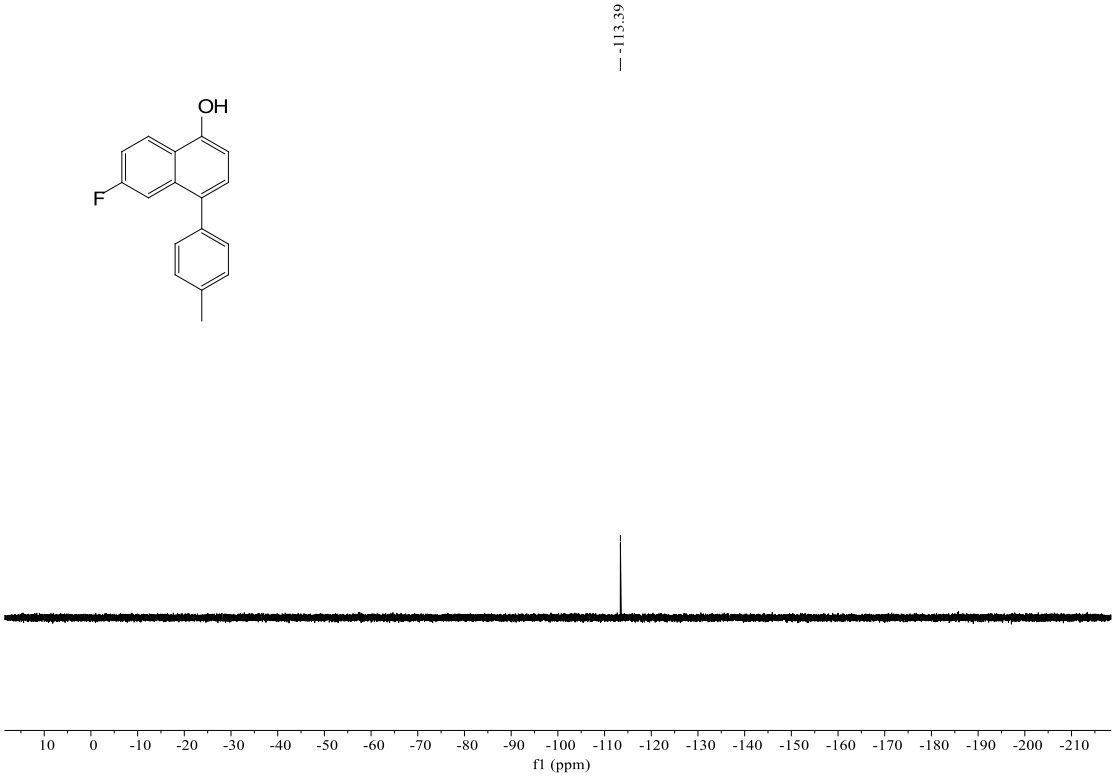
^{1}H NMR spectra of 3y (400 MHz, $CDCl_3$)



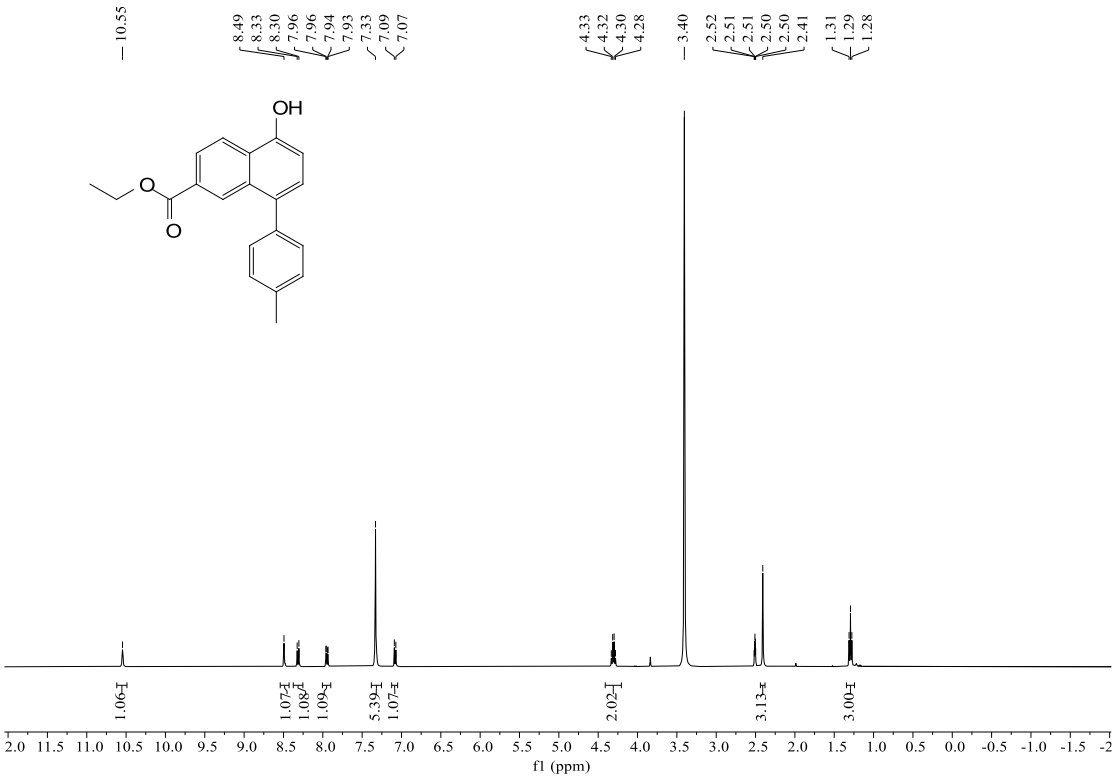
^{13}C NMR spectra of 3y (100 MHz, $CDCl_3$)



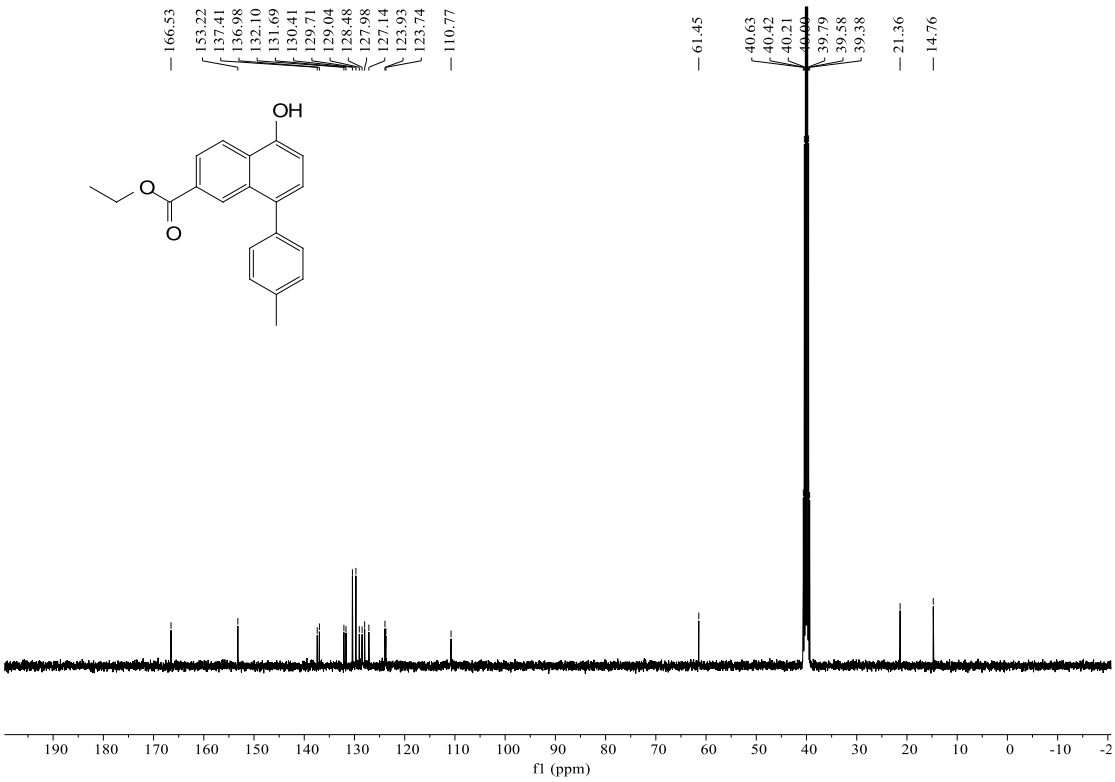
^{19}F NMR spectra of 3y (376 MHz, $CDCl_3$)



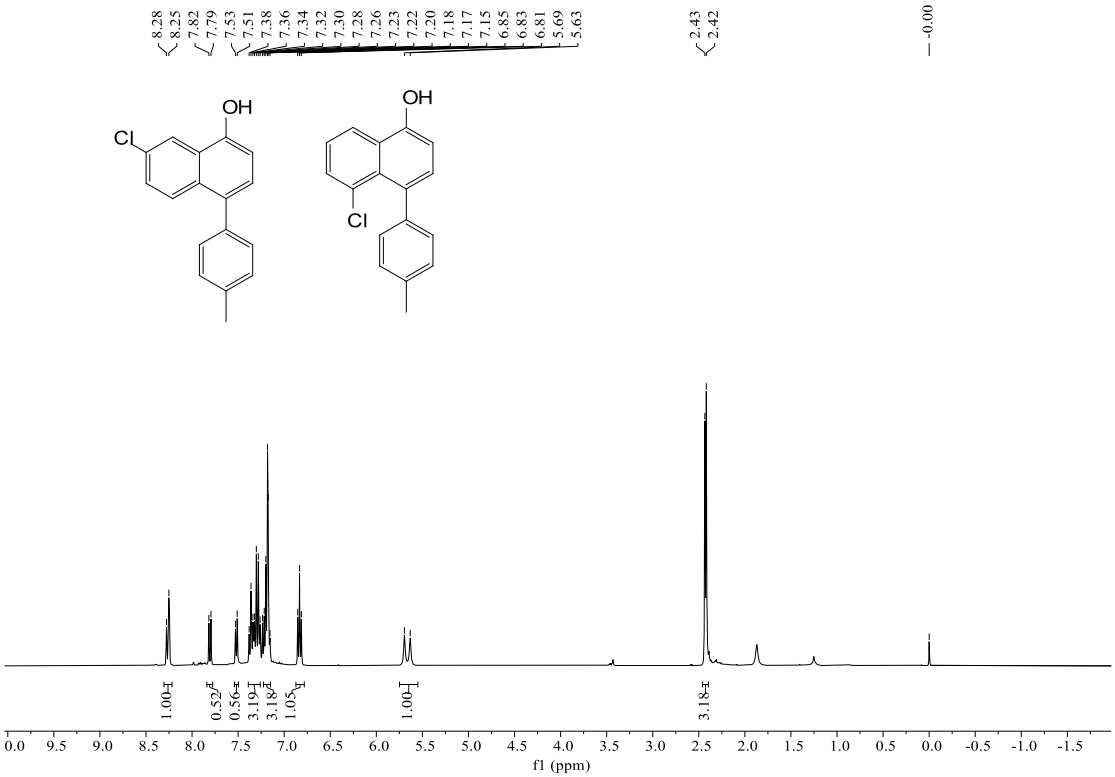
^{1}H NMR spectra of 3z (400 MHz, DMSO-d_6)



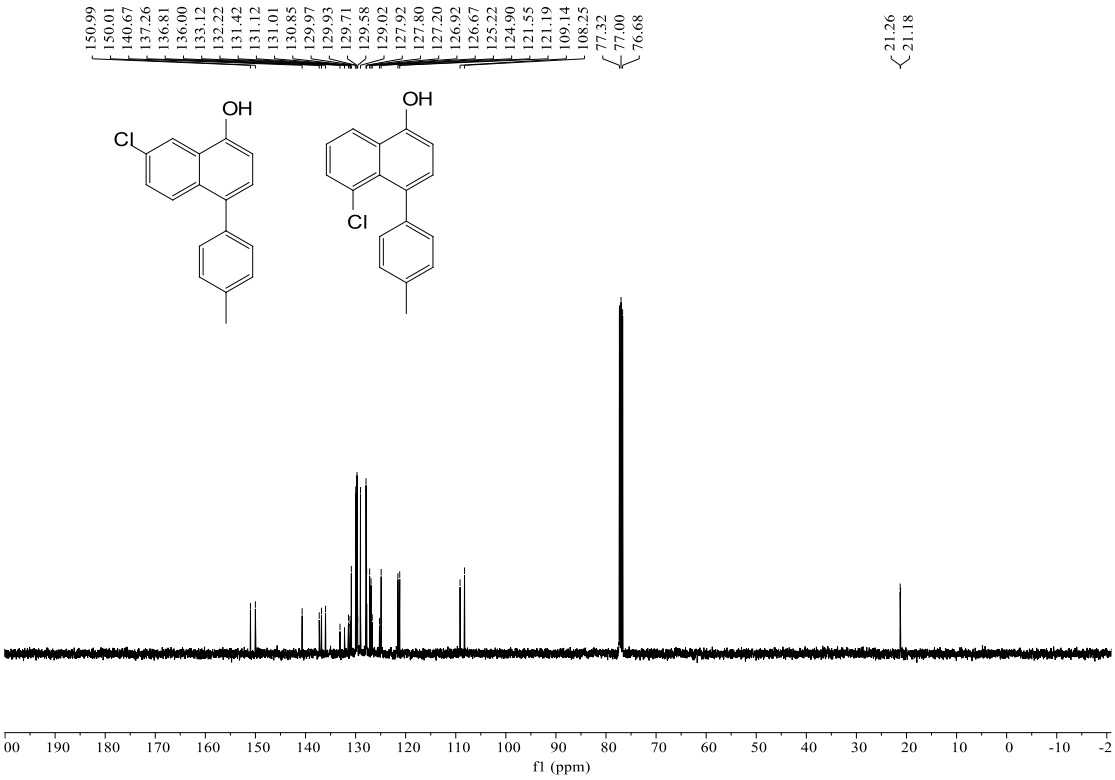
^{13}C NMR spectra of 3z (100 MHz, DMSO-d_6)



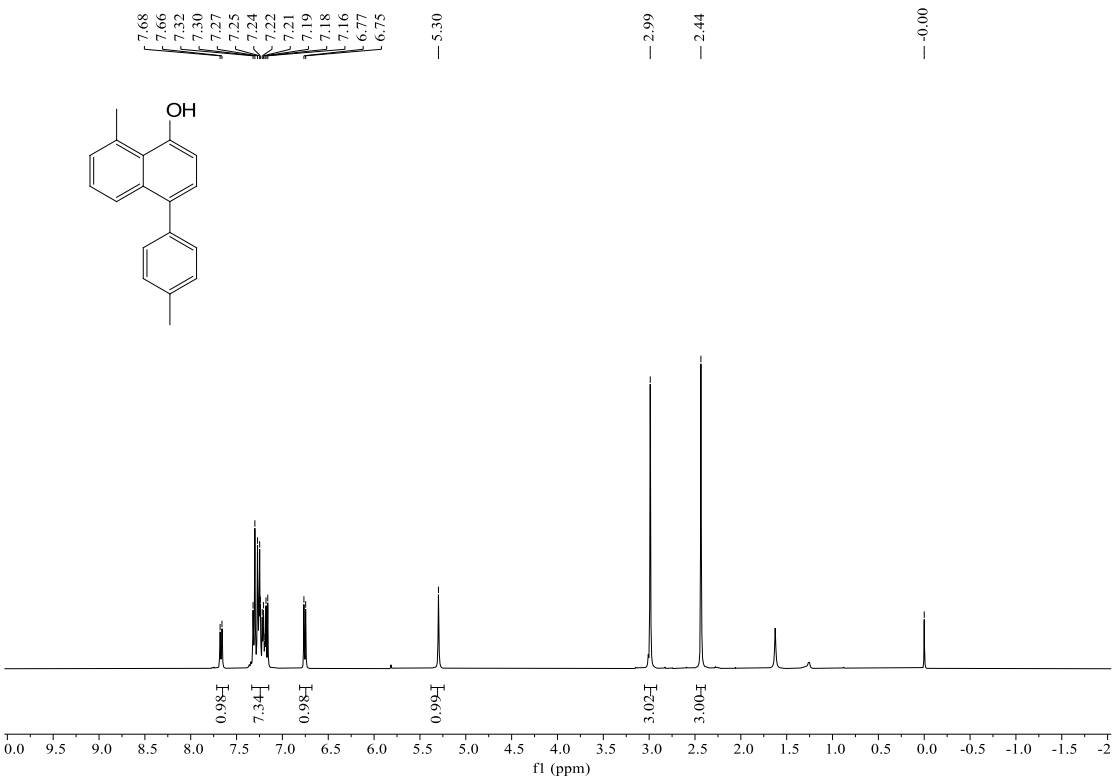
^{1}H NMR spectra of 3aa + 3aa' (400 MHz, $CDCl_3$)



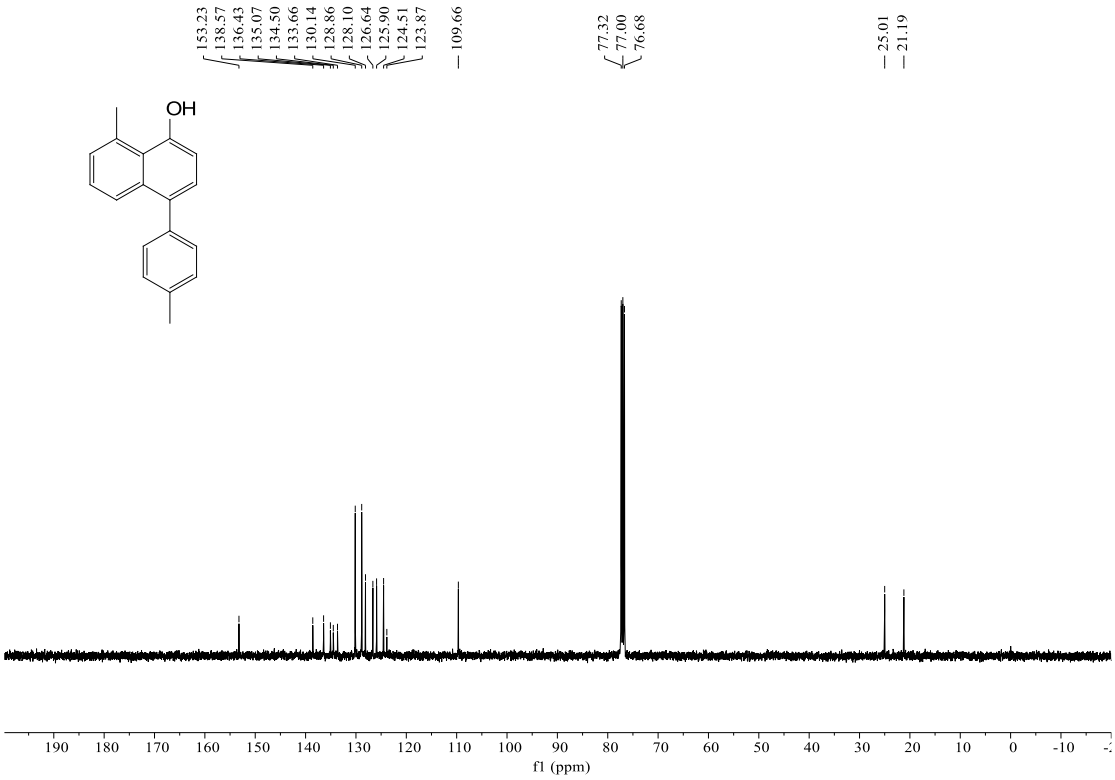
^{13}C NMR spectra of 3aa + 3aa' (100 MHz, $CDCl_3$)



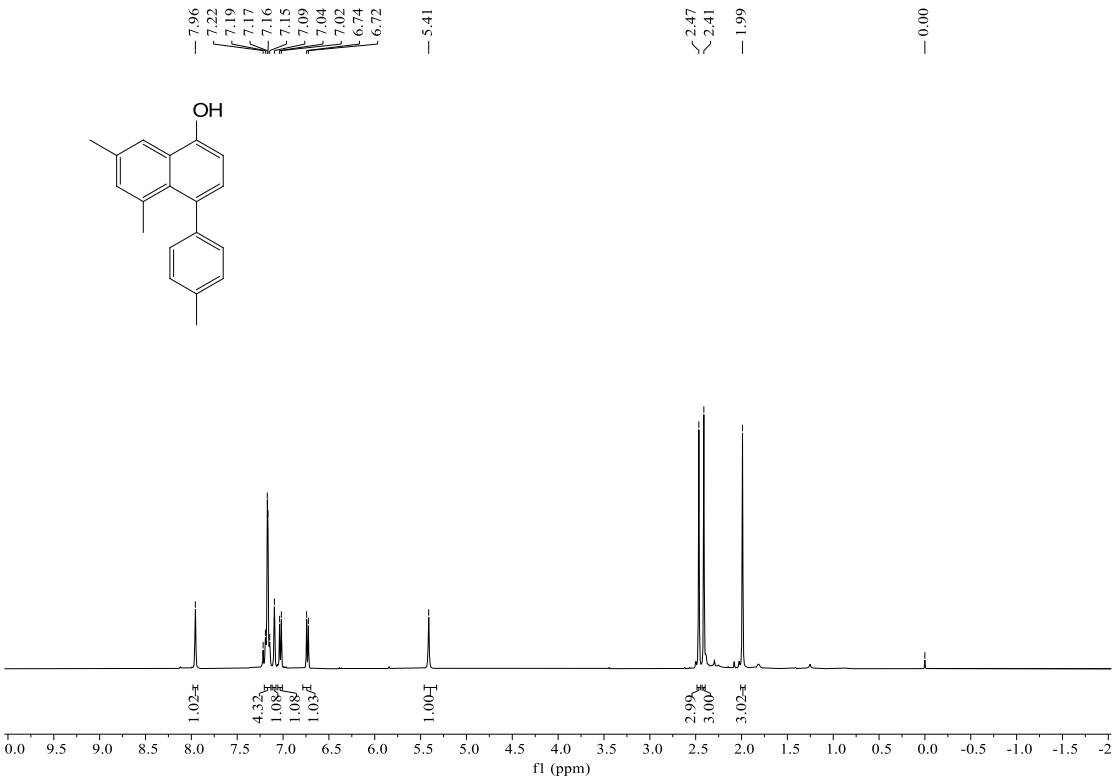
^{1}H NMR spectra of 3ab (400 MHz, $CDCl_3$)



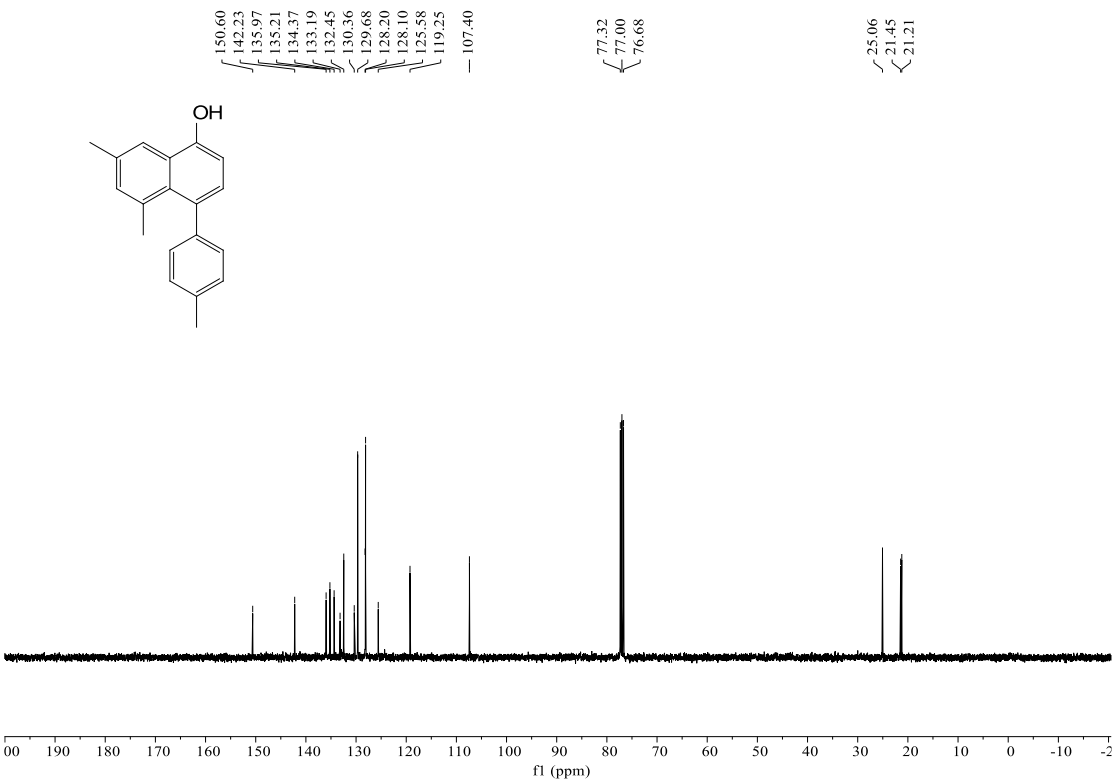
^{13}C NMR spectra of 3ab (100 MHz, $CDCl_3$)



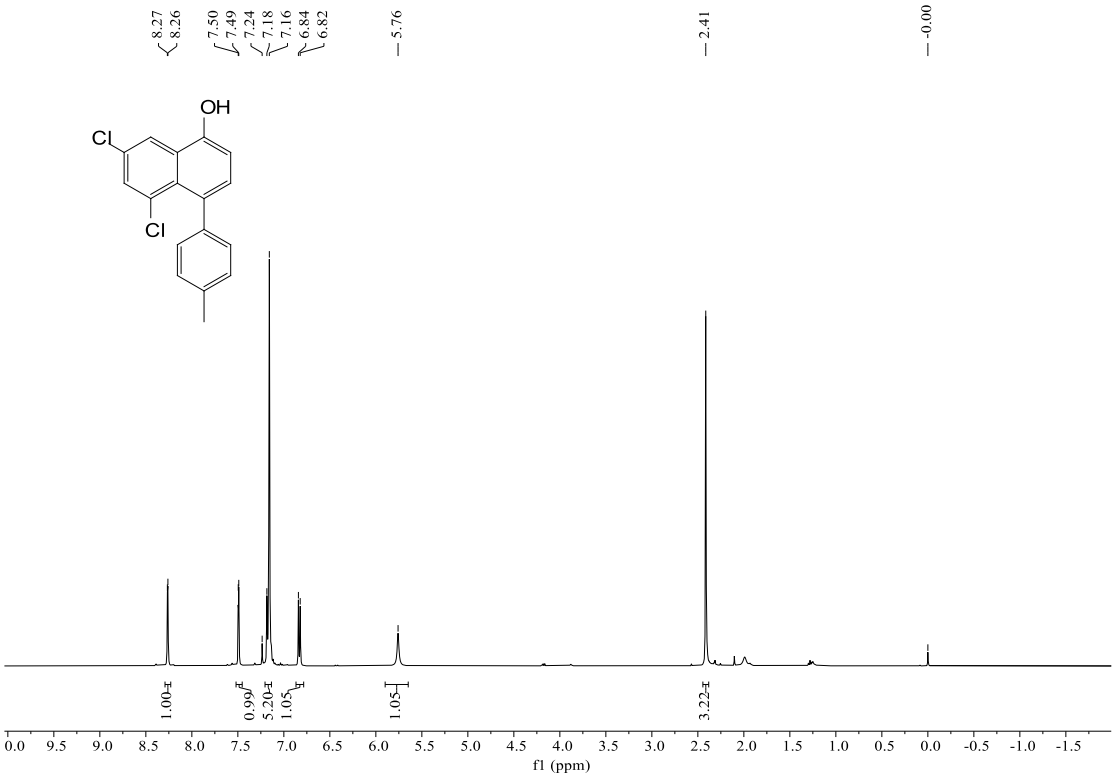
^{1}H NMR spectra of 3ac (400 MHz, $CDCl_3$)



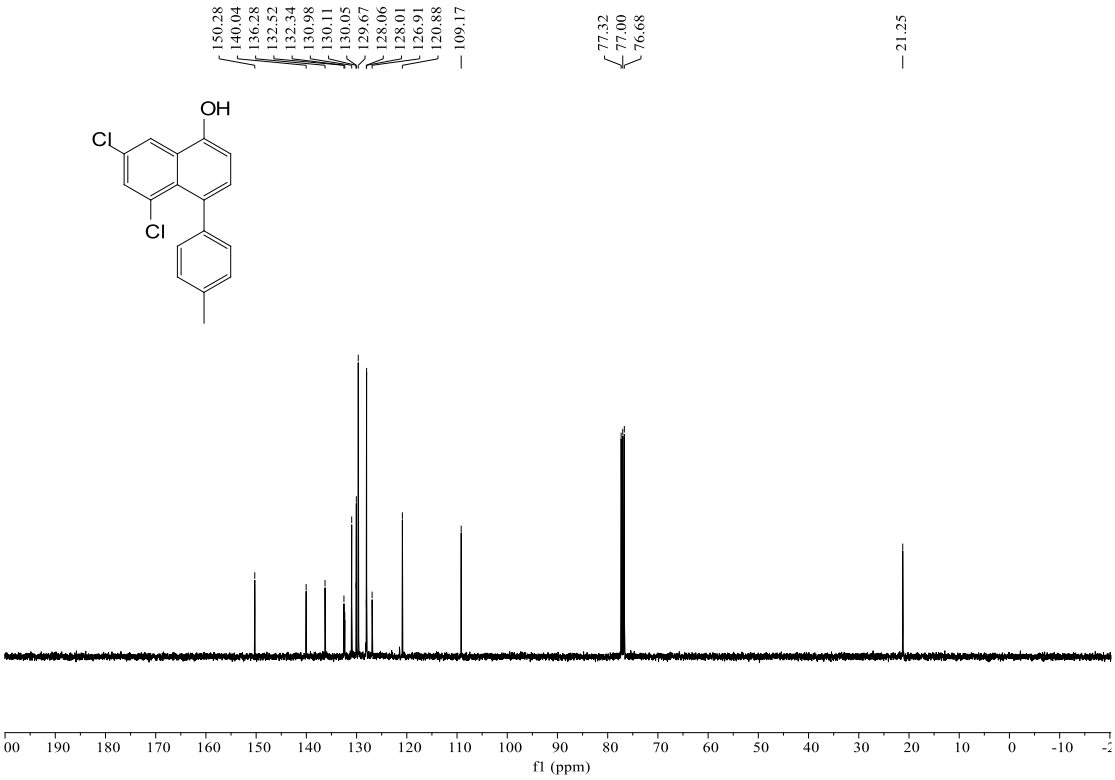
^{13}C NMR spectra of 3ac (100 MHz, $CDCl_3$)



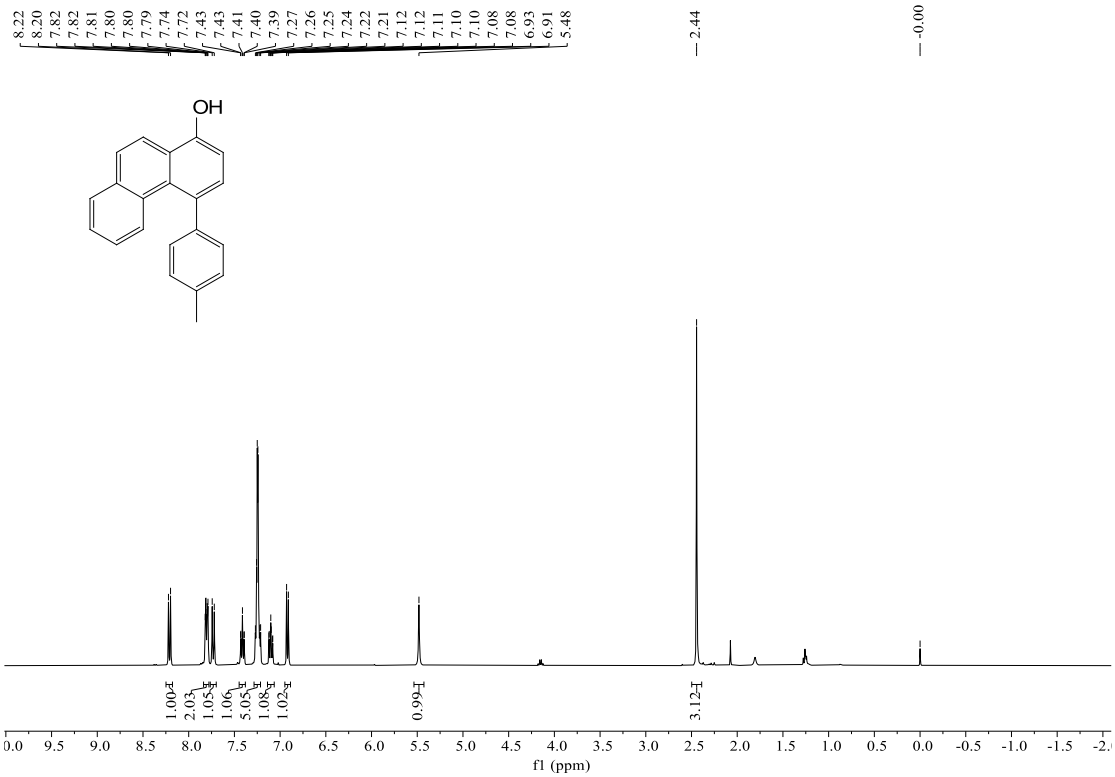
^{1}H NMR spectra of 3ad (400 MHz, $CDCl_3$)



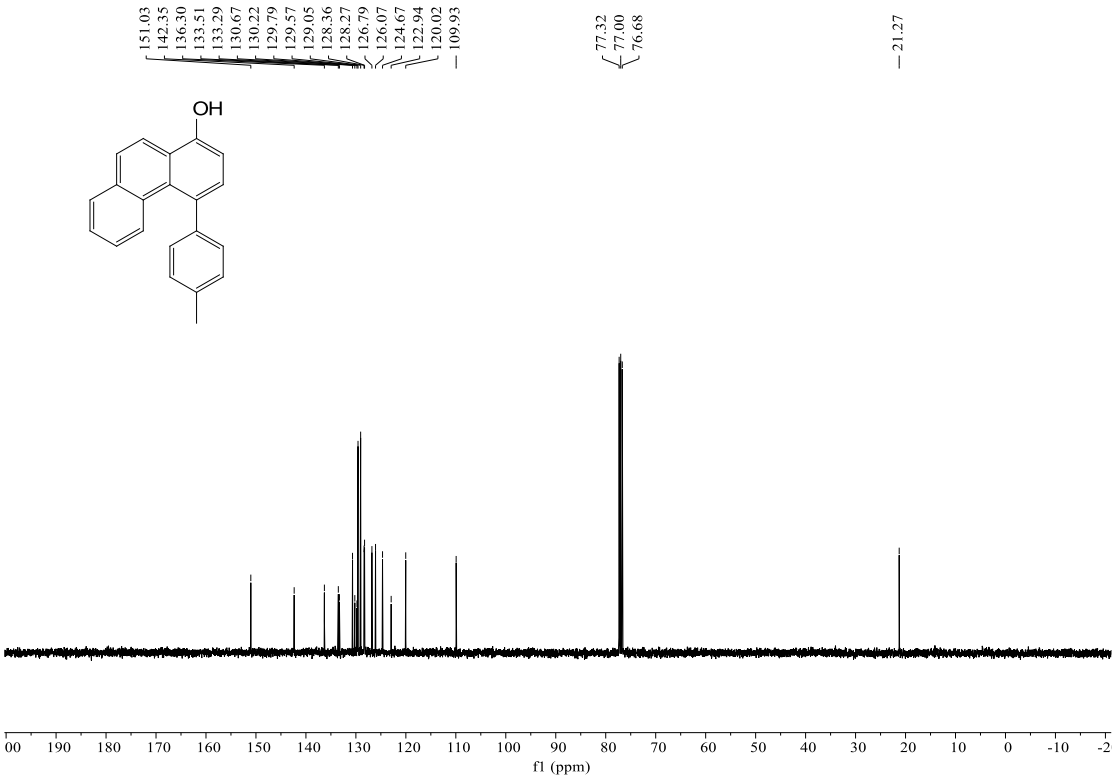
^{13}C NMR spectra of 3ad (100 MHz, $CDCl_3$)



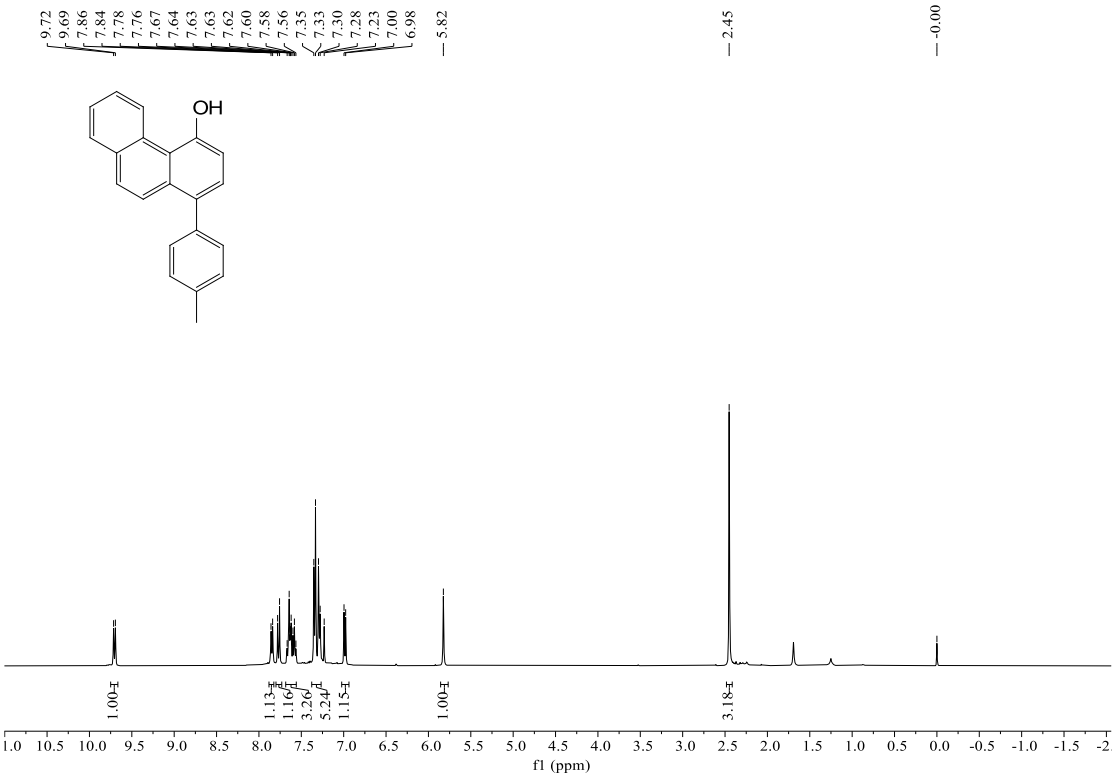
^{1}H NMR spectra of 3ae (400 MHz, $CDCl_3$)



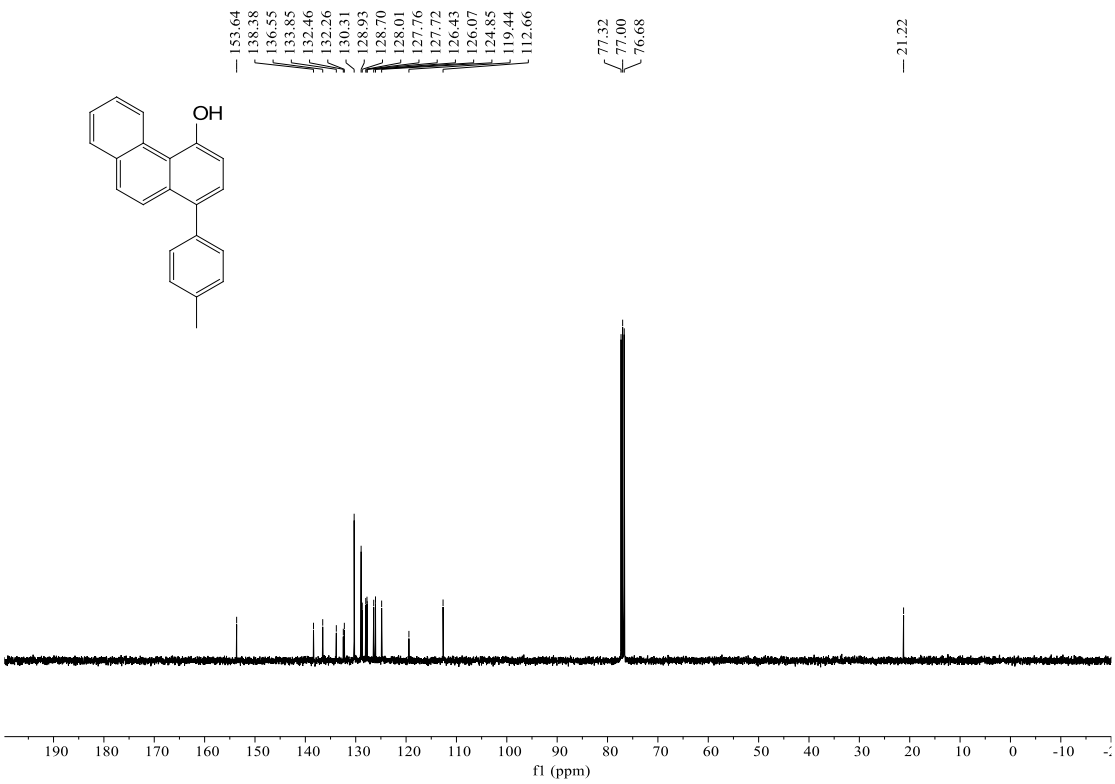
^{13}C NMR spectra of 3ae (100 MHz, $CDCl_3$)



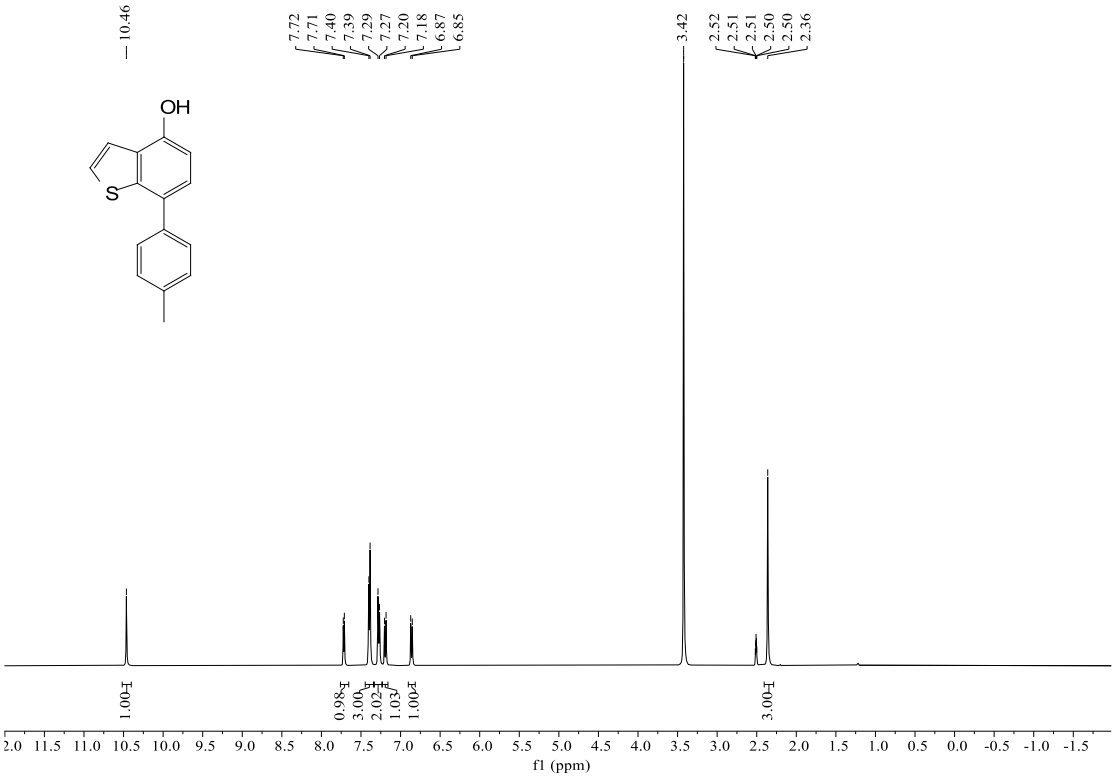
^{1}H NMR spectra of 3af (400 MHz, $CDCl_3$)



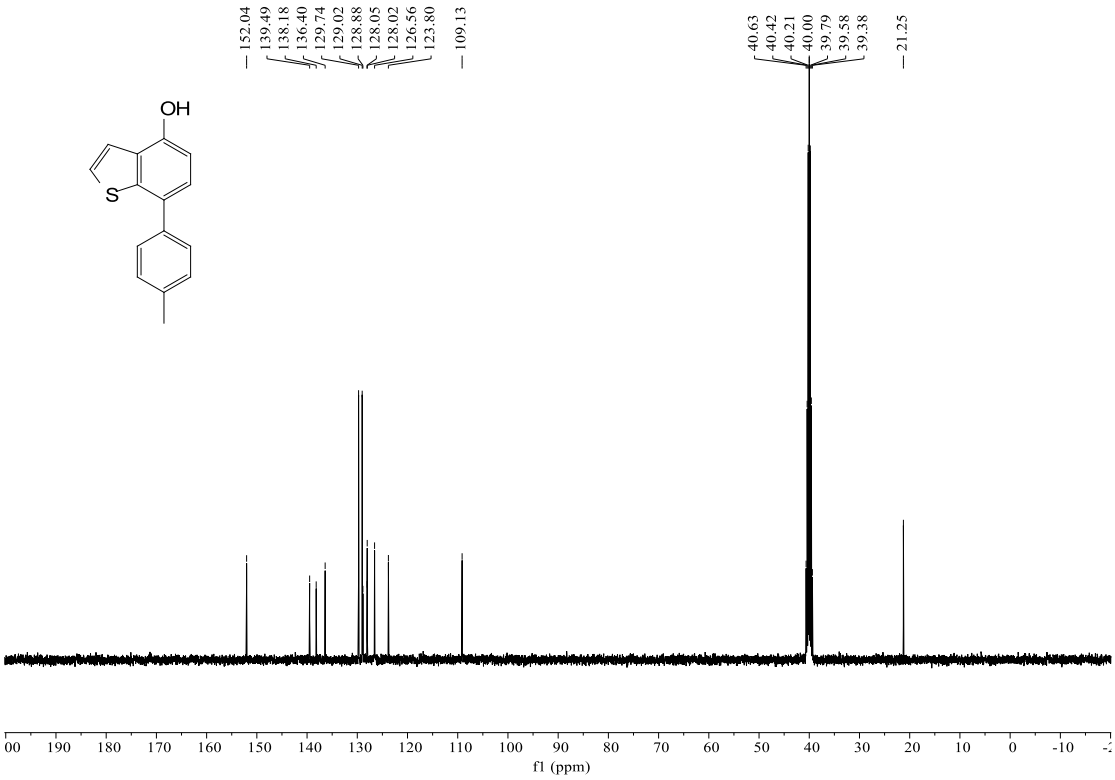
^{13}C NMR spectra of 3af (100 MHz, $CDCl_3$)



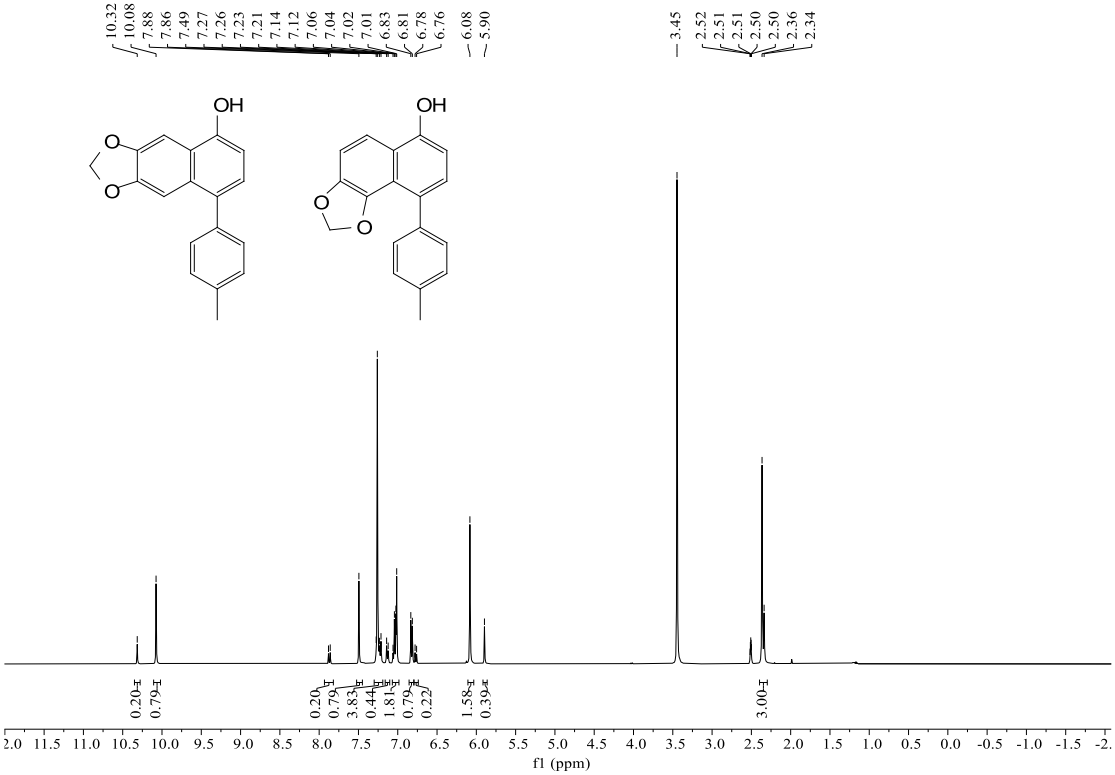
^{1}H NMR spectra of 3ag (400 MHz, DMSO-d_6)



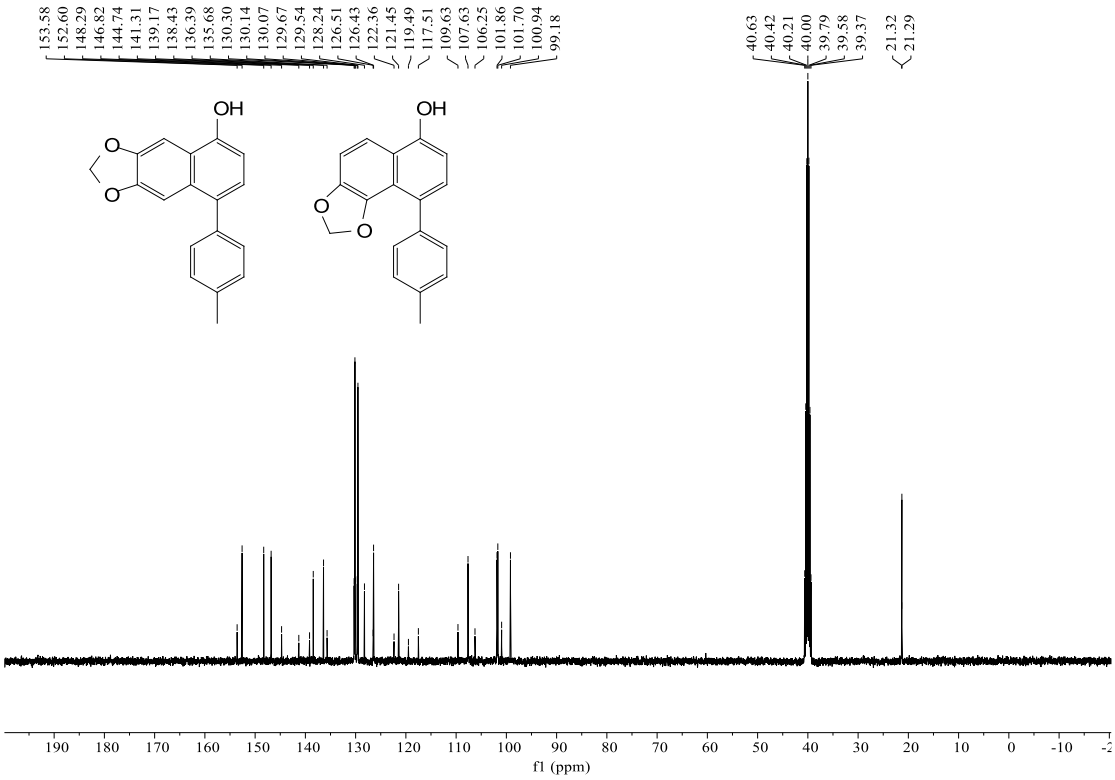
^{13}C NMR spectra of 3ag (100 MHz, DMSO-d_6)



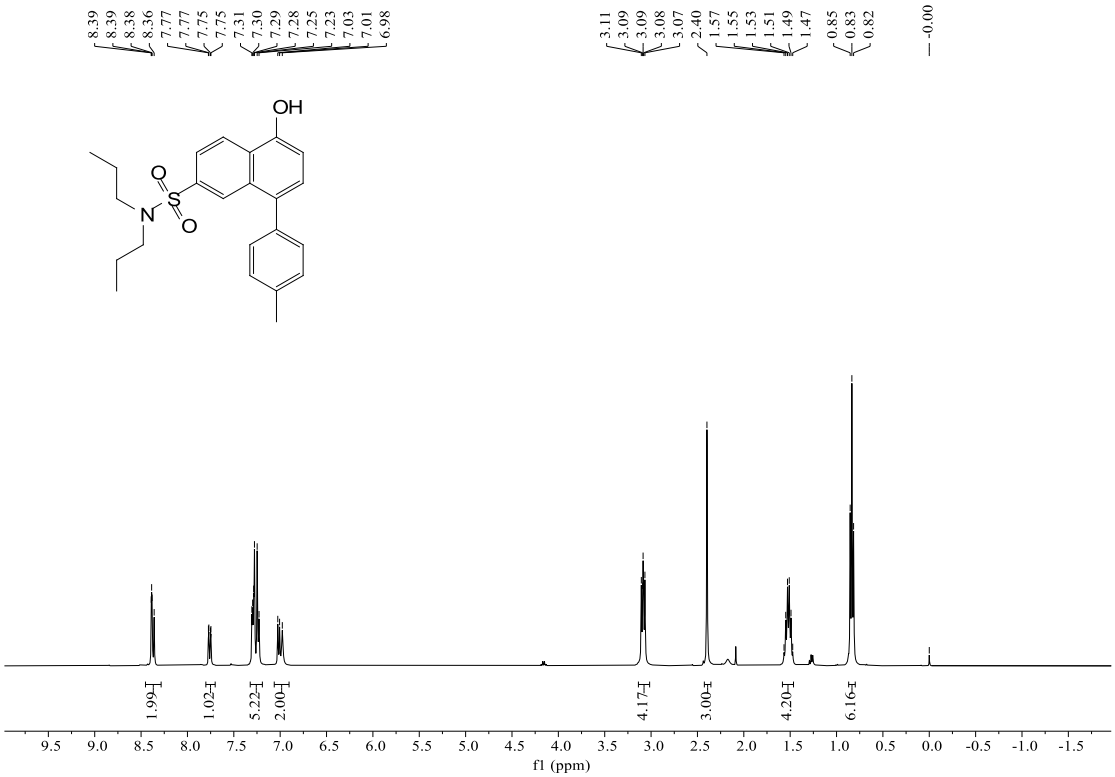
^{1}H NMR spectra of 3ah + 3ah' (400 MHz, DMSO-d_6)



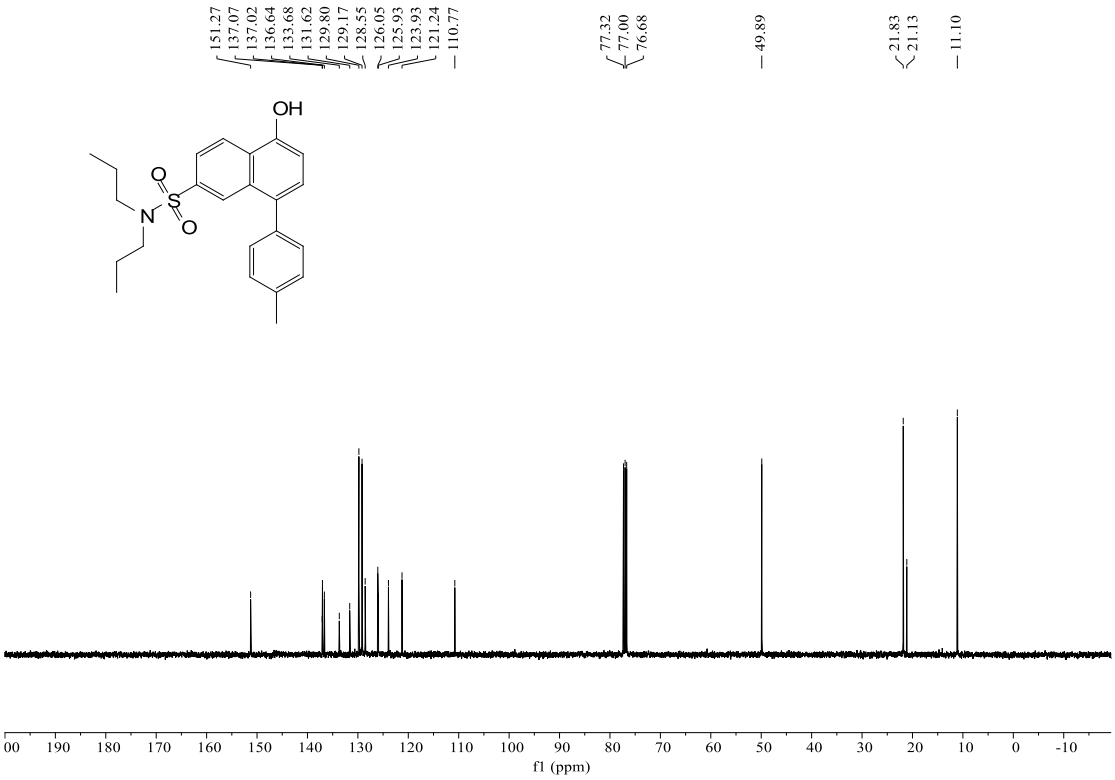
^{13}C NMR spectra of 3ah + 3ah' (100 MHz, DMSO-d_6)



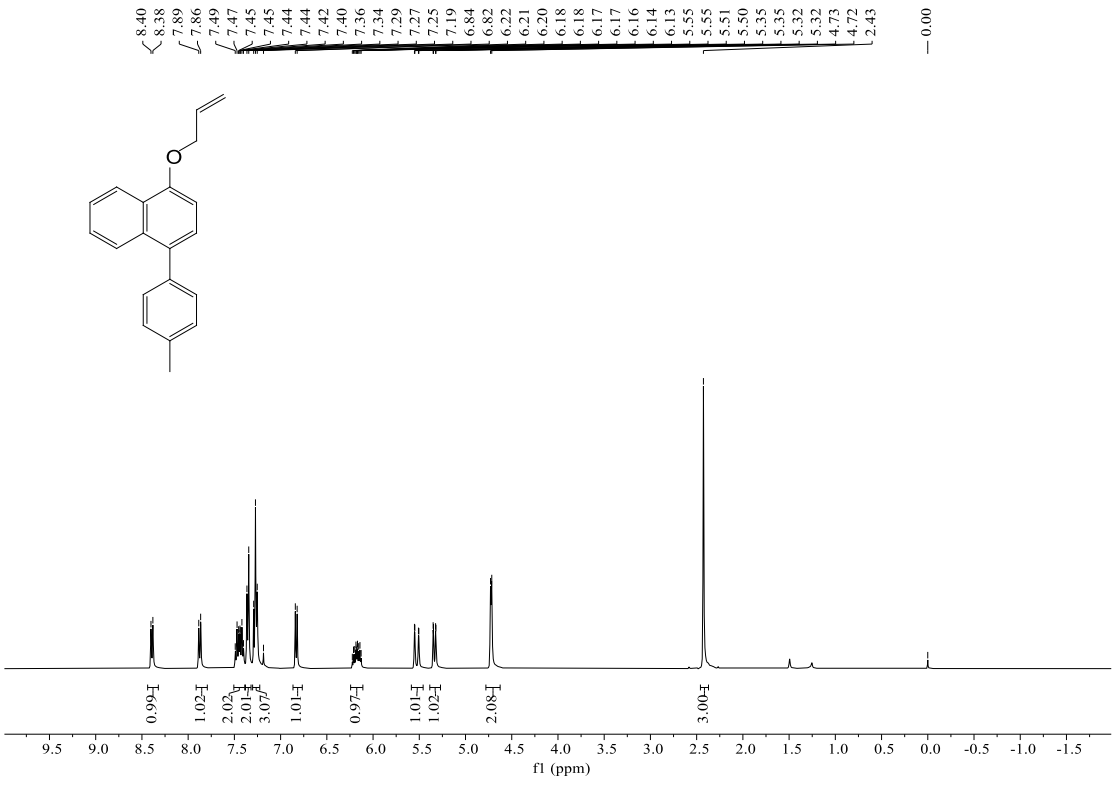
^{1}H NMR spectra of 3ai (400 MHz, $CDCl_3$)



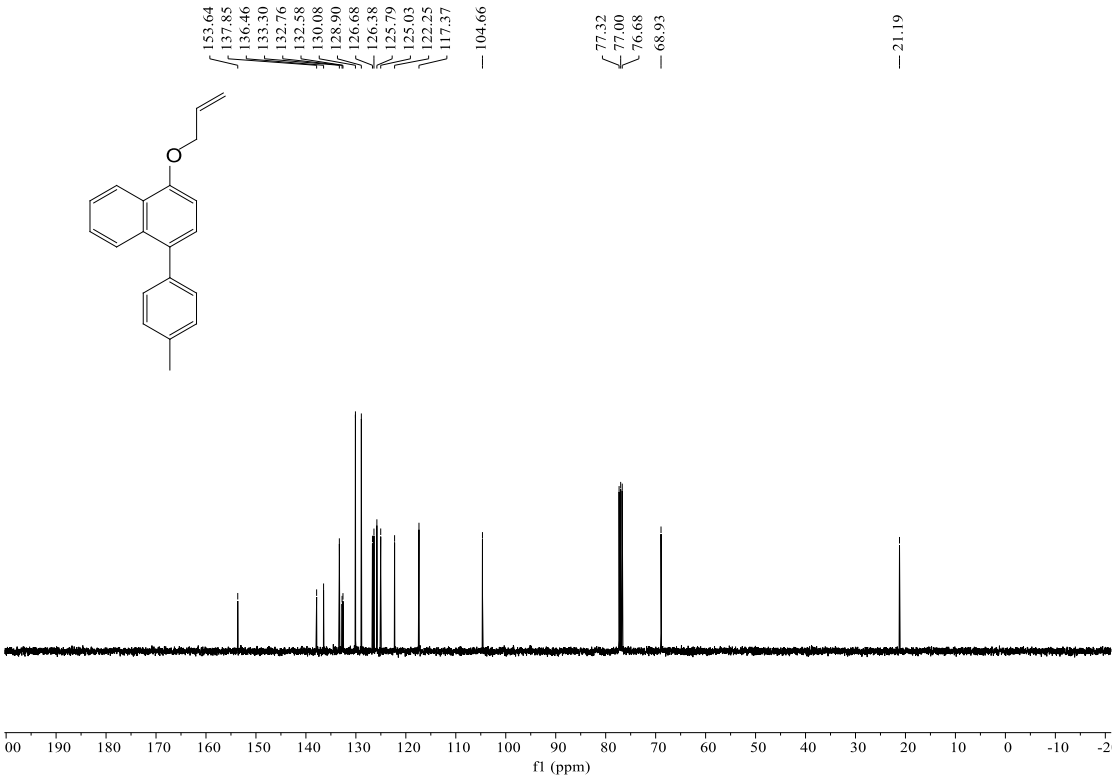
^{13}C NMR spectra of 3ai (100 MHz, $CDCl_3$)



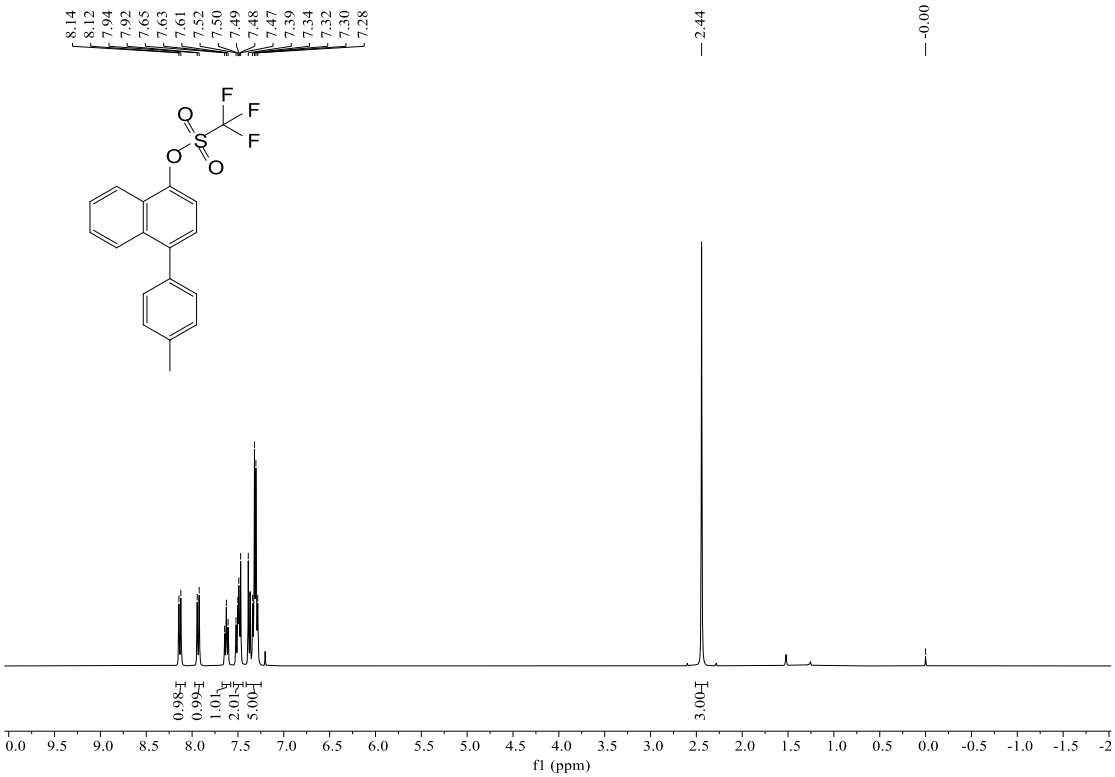
^{1}H NMR spectra of 4a (400 MHz, $CDCl_3$)



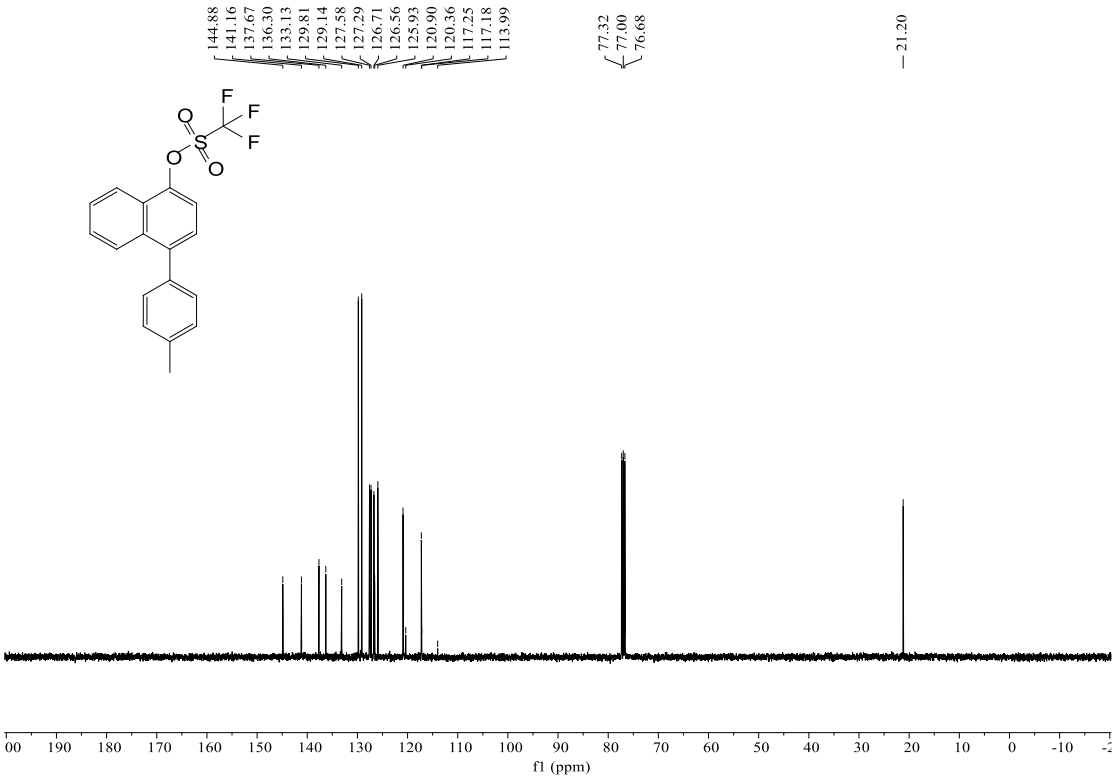
^{13}C NMR spectra of 4a (100 MHz, $CDCl_3$)



^{1}H NMR spectra of 4b (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 4b (100 MHz, $CDCl_3$)



^{19}F NMR spectra of 4b (376 MHz, $CDCl_3$)