Supporting Information

Synthesis of C3-sulfone Substituted Naphthols via Rhodium(III)-Catalyzed Annulation of Sulfoxonium Ylides with Alkynylsulfones

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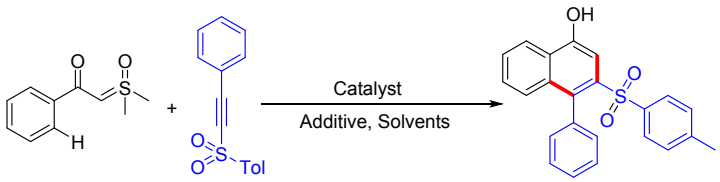
Experimental Section

General Information: All the reactions were carried out under N_2 atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 M Hz) and ^{13}C NMR (101 MHz) were recorded on a NMR spectrometer with DMSO-d_6 as solvent. Chemical shifts of ^{1}H, ^{19}F and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (DMSO-d_6: δ H = 2.50 ppm, δ C = 39.52 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200−300 mesh or alumina 200−300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectrometry (HRMS) was done on an Agilent 6210 ESI/TOF mass spectrometer. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3 \cdot xH_2O$ following a literature procedure.[1] $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ and $[Cp^*Rh(OAc)_2]$ were prepared from $[Cp^*RhCl_2]_2$ following a literature procedure.[2] Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification.

General Procedure: Preparation of the Substrates

The substrates **1a-1l**,[3] **2a-2k**,[4] **2l-2m**[5] were prepared according to the literature reports.

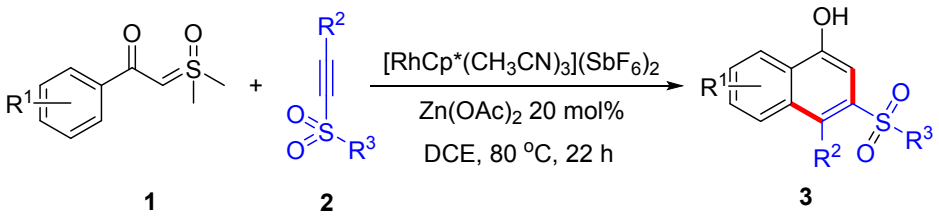
Optimization Studies：



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

Entry	proportion	Catalyst (mol%)	Additive（mol%）	T (℃)	Time（h)	Solvents (mL)	yield(%)
1	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	18	DMF(4)	0
2	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	18	MeOH(4)	11
3	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	18	MeCN(4)	0
4	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	18	Diox(4)	17
5	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	18	MB(4)	24
6	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	18	DCE(4)	69
7	2.0:1	$[Cp^*Rh(OAc)_2 \cdot H_2O]$ (8)	$Zn(OAc)_2$ (20)	80	18	DCE(4)	0
8	2.0:1	$[Cp^*RhCl_2]_2$ (4)/$AgSbF_6$(16)	$Zn(OAc)_2$ (20)	80	18	DCE(4)	65
9	2.0:1	$[Cp^*IrCl_2]_2$ (4)/$AgSbF_6$(16)	$Zn(OAc)_2$ (20)	80	18	DCE(4)	0
10	2.0:1	$Cp^*Co(CO)I_2$ (8)/$AgSbF_6$(16)	$Zn(OAc)_2$ (20)	80	18	DCE(4)	0
11	2.0:1	$[CymeneRuCl_2]_2$ (4)/$AgSbF_6$(16)	$Zn(OAc)_2$ (20)	80	18	DCE(4)	27
12	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	NaOAc(20)	80	18	DCE(4)	62
13	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	none	80	18	DCE(4)	58
14	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	22	DCE(4)	72
15	2.0:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (40)	80	22	DCE(4)	67
16	1.5:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	22	DCE(4)	78
17	1.5:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	80	26	DCE(4)	63
18	1.5:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(8)	$Zn(OAc)_2$ (20)	100	22	DCE(4)	50
19	1.5:1	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(6)	$Zn(OAc)_2$ (20)	80	22	DCE(2)	78

General Procedure for Synthesis of 3 via Rh(III)-Catalyzed C-H Activation

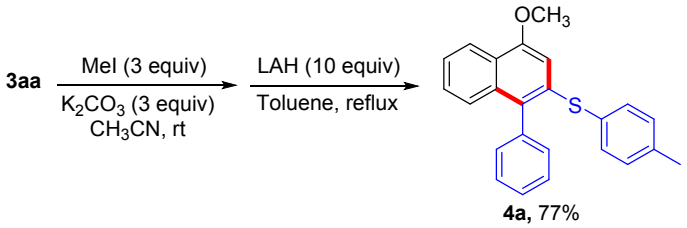


1 2 3

Condition A: A mixture of **1** (0.30 mmol, 1.5 equiv.), **2** (0.20 mmol, 1.0 equiv.), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (10.0 mg, 0.012 mmol, 6.0 mol%), and $Zn(OAc)_2$ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 80 °C for 22 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EA:PE = 1:5).

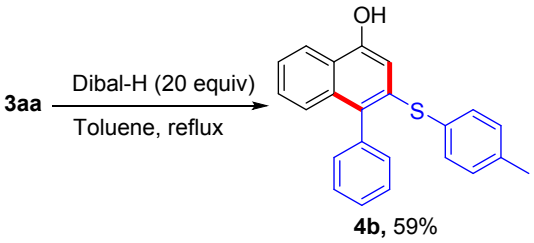
Condition B: A mixture of **1** (0.40 mmol, 1.0 equiv.), **2** (0.20 mmol, 1.0 equiv.), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (13.3 mg, 0.016 mmol, 8.0 mol%), and $Zn(OAc)_2$ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 110 °C for 22 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EA:PE = 1:5).

Derivatization of 3aa:



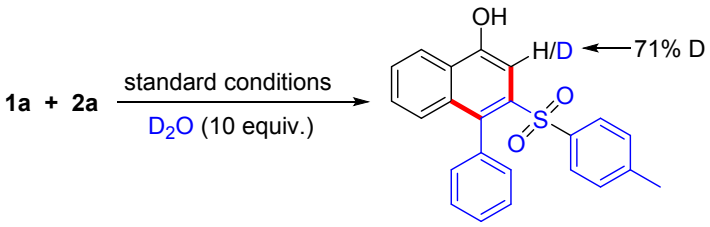
Experimental Procedures for Compound 4a[6]: Naphthol derivative **3aa** (0.1 mmol) and K_2CO_3 (0.3 mmol) were stirred in 2 mL CH_3CN for 30 min. Iodomethane (0.3 mmol) was added and stirred for 12 h. On completion of reaction (monitored by TLC), reaction mixture is filtered through celite bed. Filtrate is distilled and purified by flash column chromatography.

The product of methylating hydroxyl group was dissolved in 2 mL toluene under argon condition. Then the $LiAlH_4$ was added (1.0 mmol), and the mixture was refluxed for 22 h under N_2 atmosphere. The reaction mixture was cooled to rt and quenched by slow addition of water. The mixture was diluted with EtOAc and separated. The aqueous layer was extracted with EtOAc 3 times. The combined organic layers were dried (Na_2SO_4), and concentrated. The crude product was purified by silica gel chromatography to provide **4a** (white solid, 27.4 mg, 77 % yield).

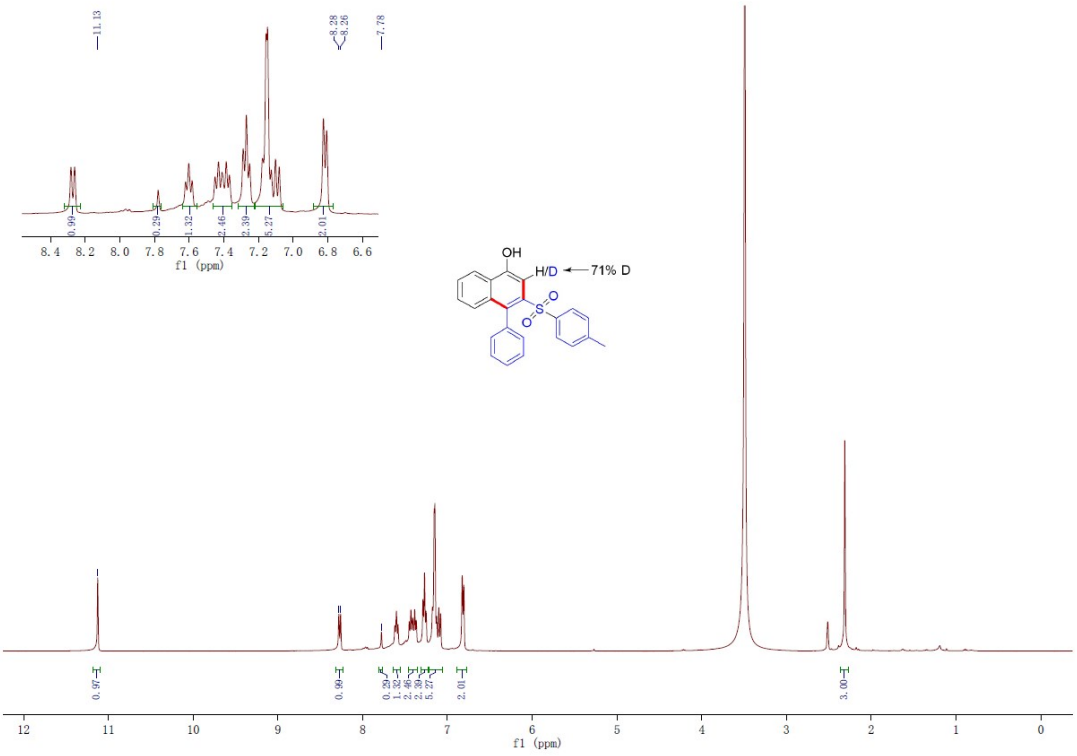


Experimental Procedures for Compound 4b: 3aa (0.1 mmol) was dissolved in anhydrous toluene (2 mL) and a 1.5 M solution of DIBAL-H (1.3 mL, 2 mmol) in toluene added dropwise. The reaction mixture was refluxed for 12 h. The reaction mixture was cooled to rt and quenched by slow addition of water. The mixture was extracted with EtOAc and the combined organic layers were dried (Na_2SO_4), and concentrated. The crude product was purified by silica gel chromatography to provide **4b** (white solid, 20.1 mg, 59 % yield).

H/D Exchange Experiment:

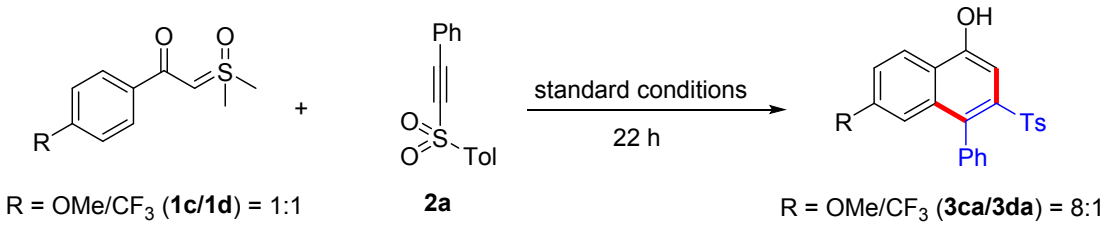


Procedure for the reaction in the presence of 2a: A mixture of *α*-benzoyl sulfur ylide **1a** (0.30 mmol, 1.5 equiv), 1-methyl-4-((phenylethynyl)sulfonyl)benzene **2a** (0.2 mmol), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (10.0 mg, 6 mol%), and $Zn(OAc)_2$ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) and D_2O (2.0 mmol, 10.0 equiv) was added and the mixture was stirred at 80 °C for 22 h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel (eluent: EA:PE = 1:5) to give the product **3aa** (48.9 mg).



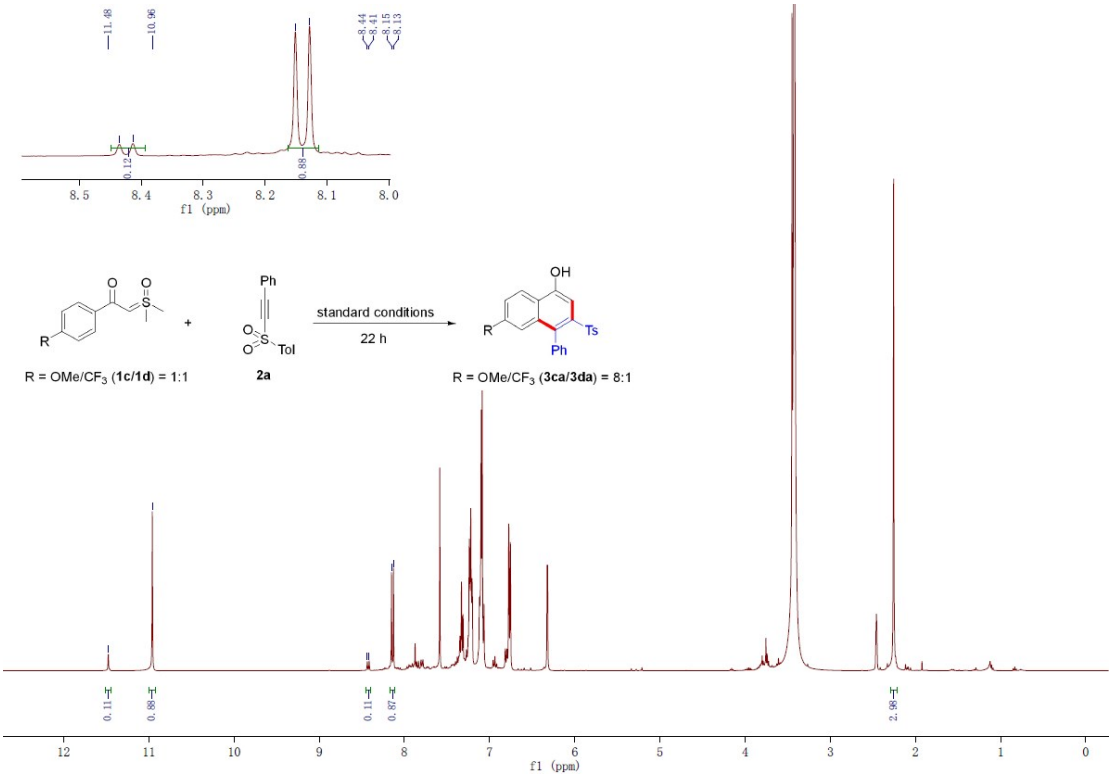
^{1}H NMR of the product **3aa** for the H/D exchange reaction in presence of **2a**

Competition Experiment:



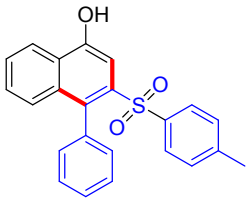
R = OMe/CF_3 (**1c/1d**) = 1:1 **2a** R = OMe/CF_3 (**3ca/3da**) = 8:1

A mixture of **1c** (0.30 mmol, 1.5 equiv) and **1d** (0.30 mmol, 1.5 equiv), 1-methyl-4-((phenylethynyl)sulfonyl)benzene **2a** (0.24 mmol, 1.2 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (10.0 mg, 6 mol%), and $Zn(OAc)_2$ (7.3 mg, 0.2 equiv.) were added to a Schlenk tube equipped with a stir bar. Dry DCE (2.0 mL) was added and the mixture was stirred at 80 °C for 22h under N_2 atmosphere. Afterwards, it was evaporated under reduced pressure and the residue was adsorbed onto small amounts of silica. The residue was purified by flash column chromatography on silica gel with EtOAc/petroleum ether to give a mixture of products **3ca** and **3da** at a ratio of 8:1.

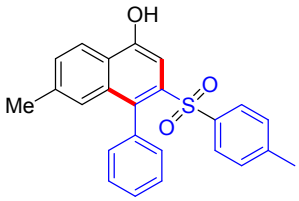


^{1}H NMR of products **3ca** and **3da** obtained from the competition experiment

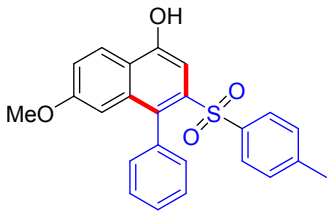
Characterization of Products



4-phenyl-3-tosylnaphthalen-1-ol ***(3aa)****:* yellow solid (58.5 mg, 78%, condition A); M.p.: 251.3-253.8 ℃; IR (cm^{-1}): *v* 3350, 1587, 1340, 1280, 1138, 1080, 684, 578; ^{1}H NMR (400 MHz, DMSO): δ 11.05 (s, 1H), 8.27 (d, J = 8.3 Hz, 1H), 7.77 (s, 1H), 7.61 (d, J = 1.0 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.19 – 7.07 (m, 5H), 2.33 (s, 3H)；^{13}C NMR (101 MHz, DMSO): δ 153.80, 143.89, 138.90, 137.44, 135.36, 134.62, 131.70, 131.10, 129.74, 128.19, 127.97, 127.95, 127.77, 127.48, 127.28, 126.79, 122.56, 105.39, 21.48. HRMS (ESI): Calcd for $C_{23}H_{18}NaO_3S$ $[M+Na]^+$ 397.08600, Found: 397.08635.

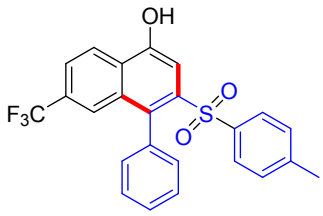


6-methyl-4-phenyl-3-tosylnaphthalen-1-ol ***(3ba)****:* pale yellow solid (50.1 mg, 65%, condition A); M.p.: 245.5-249.2 °C; IR(cm^{1}): *v* 3352, 1589, 1332, 1139, 1080, 698, 663, 580; ^{1}H NMR (400 MHz, DMSO): δ 10.96 (s, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.70 (s, 1H), 7.47 – 7.37 (m, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.15 (q, J = 8.4 Hz, 4H), 6.87 – 6.78 (m, 3H), 2.33 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 153.73, 143.83, 138.98, 137.58, 137.53, 135.45, 134.89, 131.73, 130.49, 130.04, 129.72, 127.94, 127.77, 127.44, 126.06, 125.07, 122.56, 104.79, 21.97, 21.48. HRMS (ESI): Calcd for $C_{24}H_{20}O_3NaS$ $[M+Na]^+$ 411.10208, Found 411.10226.

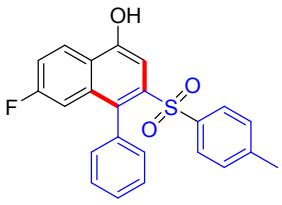


6-methoxy-4-phenyl-3-tosylnaphthalen-1-ol ***(3ca)****:* pale

yellow solid (42.0 mg, 52%, condition A); M.p.: 245.1-247.9 °C; IR (cm^{-1}): *v* 3373, 1622, 1587, 1139, 704, 667, 578;^{1}H NMR (400 MHz, DMSO): δ 10.96 (s, 1H), 8.20 (d, J = 9.2 Hz, 1H), 7.63 (s, 1H), 7.43 – 7.26 (m, 5H), 7.16 (q, J = 8.4 Hz, 4H), 6.87 – 6.78 (m, 2H), 6.38 (d, J = 2.4 Hz, 1H), 3.52 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 158.76, 153.84, 143.84, 138.94, 138.12, 136.34, 135.57, 131.67, 129.74, 129.71, 127.97, 127.85, 127.46, 124.48, 122.01, 119.39, 106.61, 103.82, 55.27, 21.47. HRMS (ESI): Calcd for $C_{24}H_{20}O_4NaS$ $[M+Na]^+$ 427.09689, Found 427.09712.

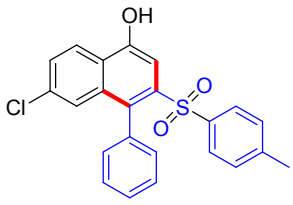


4-phenyl-3-tosyl-6-(trifluoromethyl)naphthalen-1-ol ***(3da):*** pale yellow solid (53.1 mg, 60%, condition A); M.p.: 249.1-252.1 °C; IR (cm^{-1}): *v* 3352, 1593, 1311, 1132, 1085, 902, 671, 578; ^{1}H NMR (400 MHz, DMSO): δ 11.45 (s, 1H), 8.46 (d, J = 8.8 Hz, 1H), 7.90 (s, 1H), 7.84 (dd, J = 8.9, 1.6 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.36 (s, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.19 – 7.11 (m, 4H), 6.88 – 6.82 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 153.48, 143.73, 138.79, 137.86, 133.83, 133.21, 131.18, 129.36, 128.00, 127.92, 127.66, 127.60, 127.51, 127.09, 125.18, 124.29, 124.00, 123.95, 122.59, 122.47, 107.28, 21.00. HRMS (ESI): Calcd for $C_{24}H_{17}F_3NaO_3S$ $[M+Na]^+$ 465.07427, Found 465.07412.

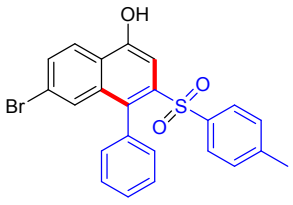


6-fluoro-4-phenyl-3-tosylnaphthalen-1-ol ***(3ea):*** reddish brown solid (31.5 mg, 40%, condition A; 46.0 mg, 59%, condition B); M.p.: 227.9-231.2 °C; IR (cm^{-1}): *v* 3373, 1622, 1587, 1462, 1332, 1139, 1026, 607, 578. ^{1}H NMR (400 MHz, DMSO): δ 11.25 (s, 1H), 8.34 (dd, J = 9.3, 6.0 Hz, 1H), 7.74 (s, 1H), 7.52 (ddd, J = 13.2, 9.5, 5.5 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.36 – 7.22 (m, 3H), 7.17 (dd, J = 19.7, 8.3 Hz, 4H), 6.84 (d, J = 7.2 Hz, 2H), 6.65 (dd, J = 11.2, 2.6 Hz, 1H), 2.34 (s, 3H). ^{13}C

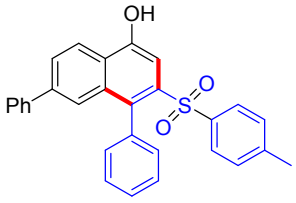
NMR (101 MHz, DMSO): δ 154.07, 144.09, 139.00, 138.56, 136.06 (d, J = 8.8 Hz), 134.91, 131.63, 130.20 (d, J = 5.5 Hz), 130.07, 129.81, 128.26, 127.98, 127.54, 126.30, 126.08 (d, J = 9.4 Hz), 123.91, 117.97 (d, J = 25.2 Hz), 110.60, 110.37, 105.19, 21.49. ^{19}F NMR (376 MHz, DMSO): δ -111.35. HRMS (ESI): Calcd for $C_{23}H_{17}O_3NaSF$ $[M+Na]^+$ 415.07684, Found 415.07690.



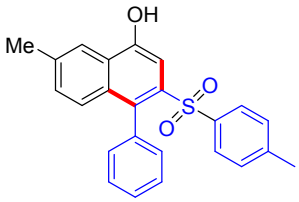
6-chloro-4-phenyl-3-tosylnaphthalen-1-ol ***(3fa)****:* pale yellow solid (40.1 mg, 49%, condition A); M.p.: 257.8-261.2 °C; IR (cm^{-1}): *v* 3344, 1587, 1334, 1141, 1087, 893, 700, 576;^{1}H NMR (400 MHz, DMSO): δ 11.36 (s, 1H), 8.27 (d, J = 9.0 Hz, 1H), 7.79 (s, 1H), 7.60 (dd, J = 9.0, 1.5 Hz, 1H), 7.41 (s, 1H), 7.29 (t, J = 7.6 Hz, 2H), 7.15 (q, J = 8.3 Hz, 4H), 6.99 (d, J = 1.2 Hz, 1H), 6.82 (d, J = 7.3 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 154.05, 144.16, 138.99, 138.44, 135.56, 134.63, 133.25, 131.71, 131.65, 130.05, 129.83, 128.35, 128.01, 127.55, 125.69, 125.16, 106.03, 21.52. HRMS (ESI): Calcd for $C_{23}H_{18}ClO_3S$ $[M+H]^+$ 409.0660, Found 409.0654.



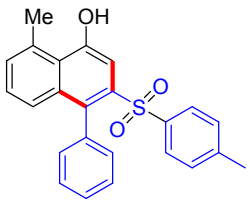
6-bromo-4-phenyl-3-tosylnaphthalen-1-ol ***(3ga)****:* pale yellow solid (47.8 mg, 53%, condition A); M.p.: 257.8-260.7 °C; IR (cm^{-1}): *v* 3342, 1583, 1334, 1141, 1083, 881, 700, 663；^{1}H NMR (400 MHz, DMSO): δ 11.35 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.43 (s, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.23 – 7.10 (m, 5H), 6.83 (d, J = 7.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 154.09, 144.19, 138.87, 138.42, 135.92, 134.60, 131.70, 130.91, 129.98, 129.86, 128.38, 128.03, 127.54, 125.33, 125.17, 122.09, 106.09, 21.54. HRMS (ESI): Calcd for $C_{23}H_{17}BrNaO_3S$ $[M+Na]^+$ 474.9974, Found 474.9979.



4,6-diphenyl-3-tosylnaphthalen-1-ol ***(3ha):*** yellow solid (57.2 mg, 64%, condition A); M.p.: 261.8-263.2°C; IR(cm^{-1}): *v* 3367, 2922, 1591, 1280, 1141, 1082, 759, 702, 669, 580; ^{1}H NMR (400 MHz, DMSO): δ 11.12 (s, 1H), 8.35 (d, J = 8.7 Hz, 1H), 7.91 (dd, J = 8.7, 1.6 Hz, 1H), 7.77 (s, 1H), 7.43 – 7.24 (m, 9H), 7.20 – 7.13 (m, 4H), 6.88 (d, J = 7.2 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, DMSO): δ 153.55, 143.68, 139.76, 139.47, 138.58, 137.75, 134.98, 134.75, 131.50, 131.01, 129.50, 129.28, 128.09, 127.85, 127.57, 127.22, 126.93, 125.65, 124.48, 123.24, 105.40, 21.21. HRMS (ESI): Calcd for $C_{29}H_{23}O_3S$ $[M+H]^+$ 451.1362, Found 451.1369.

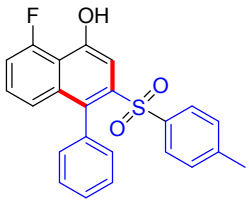


7-methyl-4-phenyl-3-tosylnaphthalen-1-ol ***(3ia)****: pale* yellow solid (45.3 mg, 58%, condition A); M.p.: 245.8-248.1 °C; IR (cm^{-1}): *v* 3779, 1587, 1342, 1139, 1080, 692, 663, 590;^{1}H NMR (400 MHz, DMSO): δ 10.97 (s, 1H), 8.04 (s, 1H), 7.73 (s, 1H), 7.37 (d, J = 7.5 Hz, 1H), 7.26 (t, J = 7.2 Hz, 3H), 7.14 (q, J = 8.3 Hz, 4H), 6.98 (d, J = 8.7 Hz, 1H), 6.80 (d, J = 7.7 Hz, 2H), 2.45 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 153.19, 143.83, 138.99, 137.82, 136.40, 135.49, 132.86, 131.67, 131.61, 131.10, 130.29, 129.72, 127.93, 127.74, 127.44, 126.95, 121.47, 121.44, 105.45, 21.81, 21.50. HRMS (ESI): Calcd for $C_{24}H_{21}O_3S$ $[M+H]^+$ 389.1206, Found 389.1207.

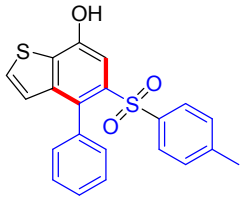


8-methyl-4-phenyl-3-tosylnaphthalen-1-ol ***(3ja)****:* pale yellow solid (15.8 mg, 20%, condition A; 15.9 mg, 20%, condition B); M.p.: 253.7-257.4 °C; IR

(cm^{-1}): *v* 3383, 1587, 1328, 1282, 1134, 769, 702, 667, 592; ^{1}H NMR (400 MHz, DMSO): δ 10.87 (s, 1H), 7.74 (s, 1H), 7.38 (t, J = 7.4 Hz, 2H), 7.32 (d, J = 7.0 Hz, 2H), 7.25 (dd, J = 16.4, 8.4 Hz, 4H), 7.18 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 8.5 Hz, 1H), 6.77 (d, J = 7.3 Hz, 2H), 2.92 (s, 3H), 2.33 (s, 3H).^{13}C NMR (101 MHz, DMSO): δ 156.38, 143.93, 138.81, 137.03, 136.42, 135.94, 135.88, 131.75, 131.11, 130.63, 129.78, 127.84, 127.46, 126.22, 106.70, 25.11, 21.52. HRMS (ESI): Calcd for $C_{24}H_{21}O_3S$ $[M+H]^+$ 389.1206 , Found 389.1201.

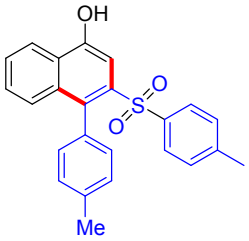


8-fluoro-4-phenyl-3-tosylnaphthalen-1-ol ***(3ka):*** pale yellow solid (18.3 mg, 23%, condition A; 22.1 mg, 28%, condition B); M.p.: 191.6-194.3 °C; IR (cm^{-1}): *v* 3593, 2922, 1593, 1396, 1298, 1149, 1083, 810, 704, 592. ^{1}H NMR (400 MHz, DMSO): δ 11.03 (s, 1H), 7.79 (s, 1H), 7.43 – 7.24 (m, 6H), 7.15 (dd, J = 25.8, 8.3 Hz, 5H), 6.88 (d, J = 8.2 Hz, 1H), 6.80 (d, J = 7.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 157.24, 153.50, 143.65, 138.12, 138.00, 136.93, 134.74, 131.19, 129.36, 127.69, 127.44, 127.05, 123.07, 113.04, 112.82, 106.80, 21.02. ^{19}F NMR (376 MHz, DMSO): δ -111.31. HRMS (ESI): Calcd for $C_{23}H_{18}FO_3S$ $[M+H]^+$ 393.0955, Found 393.0961.

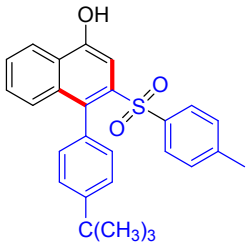


4-phenyl-5-tosylbenzo[b]thiophen-7-ol ***(3la)****:* pale yellow solid (17.3 mg, 23%, condition A; 35.1 mg, 46%, condition B); M.p.:114.3-115.8 °C; IR (cm^{-1}): *v* 3362, 1411, 1384, 1301, 1132, 1082, 704, 675, 588. ^{1}H NMR (400 MHz, DMSO): δ 7.72 (d, J = 5.5 Hz, 1H), 7.67 (s, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 7.5 Hz, 2H), 7.12 (dd, J = 18.5, 8.3 Hz, 4H), 6.87 (d, J = 7.1 Hz, 2H), 6.58 (d, J = 5.5 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 151.83, 143.33, 142.51,

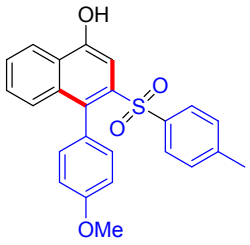
138.50, 136.59, 135.81, 131.44, 130.55, 129.60, 129.21, 127.52, 127.30, 126.97, 124.13, 106.60, 20.99. HRMS (ESI): Calcd for $C_{21}H_{16}NaO_3S_2$ $[M+Na]^+$ 403.0433, Found 403.0432.



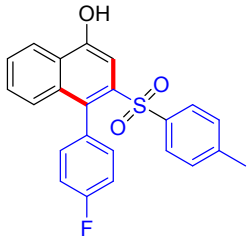
*4-(p-tolyl)-3-tosylnaphthalen-1-ol (**3ab**)*: yellow solid (28.5 mg, 37%, condition A; 47.2 mg, 61%, condition B); M.p.:257.1-258.8 ^oC; IR (cm^{-1}): *v* 3379, 1587, 1336, 1136, 1080, 686, 565. ^1H NMR (400 MHz, DMSO): δ 11.01 (s, 1H), 8.25 (d, J = 8.3 Hz, 1H), 7.73 (s, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.22 – 7.03 (m, 7H), 6.70 (d, J = 7.8 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 153.40, 143.61, 138.64, 137.35, 136.97, 134.47, 132.08, 131.25, 130.89, 129.39, 128.09, 127.86, 127.65, 127.24, 127.10, 126.51, 122.26, 105.07, 21.22, 21.13. HRMS (ESI): Calcd for $C_{24}H_{20}NaO_3S$ $[M+Na]^+$ 411.1025 , Found 411.1029.



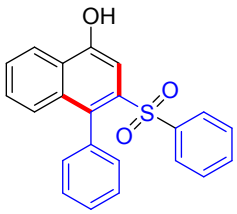
*4-(4-(tert-butyl)phenyl)-3-tosylnaphthalen-1-ol (**3ac**):* yellow solid (60.9 mg, 71%, condition A); M.p.: 190.5-195.5 ^oC; IR (cm^{-1}): *v* 3529, 2960, 1587, 1136, 1080, 810, 769, 599, 567. ^1H NMR (400 MHz, DMSO): δ 11.02 (s, 1H), 8.25 (d, J = 8.2 Hz, 1H), 7.79 (s, 1H), 7.59 (dd, J = 11.2, 4.0 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.14 – 7.00 (m, 5H), 6.70 (d, J = 8.2 Hz, 2H), 2.31 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, DMSO): δ 153.13, 149.87, 143.09, 138.14, 137.41, 134.22, 131.55, 130.99, 130.56, 129.11, 127.67, 127.43, 126.92, 126.82, 126.32, 124.02, 122.08, 104.60, 34.28, 31.20, 20.99. HRMS (ESI): Calcd for $C_{27}H_{26}O_3NaS$ $[M+Na]^+$ 453.14890, Found 453.14917.



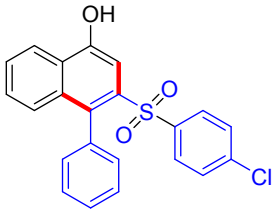
*4-(4-methoxyphenyl)-3-tosylnaphthalen-1-ol (**3ad**):* yellow solid (40.8 mg, 51%, condition A); M.p.: 243.4-247.6 °C; IR (cm^{-1}): *v* 3387, 1589, 1512,1 336, 1249, 1080, 763, 688, 567. ^{1}H NMR (400 MHz, DMSO): δ 11.06 (s, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.76 (s, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.16 (q, J = 8.3 Hz, 5H), 6.82 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 159.15, 153.63, 143.83, 138.86, 137.86, 134.99, 132.86, 130.99, 129.67, 128.13, 127.93, 127.42, 127.12, 126.81, 122.54, 113.31, 105.27, 55.67, 21.52. HRMS (ESI): Calcd for $C_{24}H_{20}O_4NaS$ $[M+Na]^+$ 427.09705, Found 427.09722.



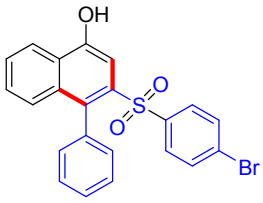
*4-(4-fluorophenyl)-3-tosylnaphthalen-1-ol (**3ae**):* pale yellow solid (57.4mg, 73%, condition A); M.p.:235.6-238.9 °C; IR (cm^{-1}): *v* 3381, 1587, 1510, 1338, 1279, 1138, 763, 688, 565; ^{1}H NMR (400 MHz, DMSO): δ 11.09 (s, 1H), 8.28 (d, J = 8.1 Hz, 1H), 7.76 (s, 1H), 7.65 – 7.60 (m, 1H), 7.50 – 7.45 (m, 1H), 7.23 – 7.16 (m, 4H), 7.13 – 7.06 (m, 3H), 6.89 – 6.80 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 154.00, 144.09, 138.85, 137.77, 133.73 (d, J = 8.3 Hz), 129.92, 129.81, 128.19 (d, J = 35.1 Hz), 127.38, 127.13, 126.80, 122.63, 114.74 (d, J = 21.5 Hz), 105.40, 21.49； ^{19}F NMR (376 MHz, DMSO): δ -114.46. HRMS (ESI): Calcd for $C_{23}H_{17}O_3NaSF$ $[M+Na]^+$ 415.07706, Found 415.07722.



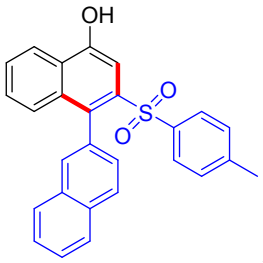
4-phenyl-3-(phenylsulfonyl)naphthalen-1-ol ***(3af)****:* pale yellow solid (43.4 mg, 60%, condition A); M.p.: 227.5 - 231.4 °C; IR (cm^{-1}): *v* 3361, 1585, 1334, 1139, 1080, 765, 688, 584. ^{1}H NMR (400 MHz, DMSO): δ 11.03 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.29 – 7.21 (m, 3H), 7.17 – 7.11 (m, 4H), 6.98 (d, J = 8.6 Hz, 1H), 6.69 (d, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO): δ 153.43, 141.22, 136.71, 134.75, 134.18, 132.99, 131.34, 131.28, 130.84, 128.90, 127.84, 127.64, 127.59, 127.40, 126.94, 126.44, 122.18, 104.90. HRMS (ESI): Calcd for $C_{22}H_{17}O_3S$ $[M+H]^+$ 361.0893, Found 361.0891.



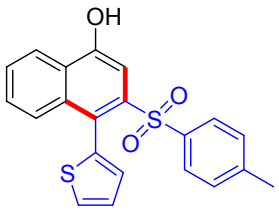
3-((4-chlorophenyl)sulfonyl)-4-phenylnaphthalen-1-ol ***(3ag)****:* pale yellow solid (14.1 mg, 18%, condition A; 16.1 mg, 20%, condition B); M.p.: 221.7-224.5 °C; IR (cm^{-1}): *v* 3379, 1587, 1309, 1141, 1085, 756, 700, 636, 430. ^{1}H NMR (400 MHz, DMSO): δ 11.07 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.67 (s, 1H), 7.56 – 7.50 (m, 2H), 7.39 – 7.27 (m, 6H), 7.17 (t, J = 7.6 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO): δ 153.91, 140.37, 138.48, 136.78, 135.04, 134.55, 131.81, 131.24, 129.49, 129.25, 128.39, 128.22, 127.90, 126.94, 122.64, 105.07. HRMS (ESI): Calcd for $C_{22}H_{16}ClO_3S$ $[M+H]^+$ 395.0503, Found 395.0503.



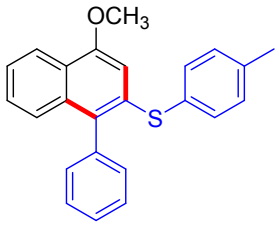
3-((4-bromophenyl)sulfonyl)-4-phenylnaphthalen-1-ol ***(3ah)****:* pale yellow solid (28.0 mg, 32%, condition A; 43.0 mg, 49%, condition B); M.p.: 252.1-256.9 °C; IR (cm^{-1}): *v* 3377, 1587, 1338, 1309, 1139, 1082, 623, 588. ^{1}H NMR (400 MHz, DMSO): δ 11.07 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.66 (s, 1H), 7.54 – 7.49 (m, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.28 (d, J = 7.4 Hz, 1H), 7.16 (t, J = 7.6 Hz, 2H), 7.01 (dd, J = 17.4, 8.5 Hz, 3H), 6.72 (d, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO): δ 153.55, 140.43, 136.38, 134.67, 134.18, 132.04, 131.36, 130.86, 128.88, 128.00, 127.83, 127.50, 127.14, 126.57, 122.25, 104.69. HRMS (ESI): Calcd for $C_{22}H_{16}BrO_3S$ $[M+H]^+$ 438.9998, Found 439.0002.



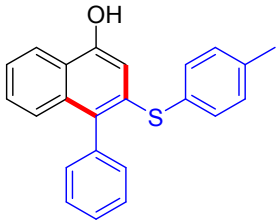
2-tosyl-[1,2'-binaphthalen]-4-ol **(*3aj*)：** pale yellow solid (38.7 mg, 46%, condition B); M.p.: 222.5-225.2 °C; IR (cm^{-1}): *v* 3418, 1635, 1590, 1336, 1139, 1080, 490. ^{1}H NMR (400 MHz, DMSO): δ 11.12 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.79 (s, 1H), 7.58 (ddd, J = 20.1, 15.8, 7.9 Hz, 5H), 7.41 (t, J = 7.7 Hz, 1H), 7.20 (s, 1H), 7.10 (d, J = 8.6 Hz, 1H), 7.04 (d, J = 7.7 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 162.94, 160.51, 153.56, 143.65, 138.35, 137.30, 134.20, 133.33, 133.25, 131.05, 131.02, 129.45, 129.37, 127.94, 127.58, 126.94, 126.69, 126.33, 122.19, 114.41, 114.20, 104.90, 21.05. HRMS (ESI): Calcd for $C_{27}H_{21}O_3S$ $[M+H]^+$ 425.1206, Found 425.1208.



4-(thiophen-2-yl)-3-tosylnaphthalen-1-ol (***3aj***)**:** pale yellow solid (20.5 mg, 27%, condition B); M.p.: 178.3-181.1 °C; IR (cm^{-1}): *v* 3377, 1589, 1334, 1284, 1138, 1086, 545, 504, 491. ^{1}H NMR (400 MHz, DMSO): δ 11.29 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.65 (dd, J = 18.2, 6.4 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.28 – 7.21 (m, 4H), 7.08 (s, 1H), 6.70 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 154.93, 144.04, 139.80, 138.44, 135.81, 134.74, 131.64, 129.87, 128.89, 128.63, 128.15, 127.45, 126.88, 126.76, 126.55, 122.54, 105.85, 21.54. HRMS (ESI): Calcd for $C_{21}H_{17}O_3S_2$ $[M+H]^+$ 381.0614, Found 381.0616.



(4-methoxy-1-phenylnaphthalen-2-yl)(p-tolyl)sulfane (***4a***)*:* white solid (27.4 mg, 77%); M.p.: 79.7-83.3 °C; IR (cm^{-1}): *v* 3437, 1587, 1461, 1239, 1108, 1083, 768, 486. ^{1}H NMR (400 MHz, DMSO): δ 8.30 (d, J = 8.4 Hz, 1H), 7.76 (s, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 7.3 Hz, 1H), 7.30 (t, J = 7.2 Hz, 2H), 7.18 (s, 4H), 7.12 (d, J = 8.5 Hz, 1H), 6.81 (d, J = 7.3 Hz, 2H), 4.18 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 155.04, 144.05, 138.75, 137.46, 134.97, 134.27, 133.14, 131.55, 129.75, 128.79, 128.58, 128.19, 127.84, 127.61, 127.46, 126.98, 122.06, 101.87, 56.63, 21.51. HRMS (ESI): Calcd for $C_{24}H_{21}OS$ $[M+H]^+$ 357.1308, Found 357.1317.



4-phenyl-3-(p-tolylthio)naphthalen-1-ol (***4b***)*:* white solid (20.1 mg, 59%); M.p.: 238.2-241.4 °C; IR (cm^{-1}): *v* 3354, 1589, 1340, 1284, 1082, 690, 581.

^{1}H NMR (400 MHz, DMSO): δ 11.08 (s, 1H), 8.26 (d, J = 8.3 Hz, 1H), 7.76 (s, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 – 7.36 (m, 2H), 7.28 (t, J = 7.3 Hz, 2H), 7.13 (dt, J = 17.5, 8.2 Hz, 5H), 6.82 (d, J = 7.3 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 153.77, 143.89, 138.81, 137.38, 135.30, 134.57, 131.68, 131.05, 129.74, 128.22, 127.97, 127.77, 127.45, 127.26, 126.73, 122.54, 105.29, 21.48. HRMS (ESI): Calcd for $C_{23}H_{19}OS$ $[M+H]^+$ 343.1151, Found 343.1162.

The crystallographic data of 3aa and 3ia:

Compounds **3aa** and **3ia** were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. The data were collected and processed using CrysAlisPro[7]. The structures were solved by direct methods using Olex2 software[8], and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018[9] using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 1999223 and 1999224 for compounds **3aa** and **3ia**, respectively.

The crystallographic data for the complex is summarized in the table below.

Compounds	**3aa**	**3ia**
Identification code	FS0827	FS02
Empirical formula	$C_{23}H_{18}O_3S$	$C_{24}H_{20}O_3S$
Formula weight	374.43	388.46
Temperature/K	100.00(10)	99.98(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	8.4310(5)	8.1695(6)
b/Å	10.6418(11)	11.1838(9)
c/Å	11.6712(14)	12.1869(10)
α/°	115.047(11)	116.288(8)

β/°	104.819(8)	102.125(7)
γ/°	94.550(7)	97.876(6)
Volume/Å^3	895.84(17)	941.83(14)
Z	2	2
ρ_{calc}g/cm^3	1.388	1.370
μ/mm^{-1}	0.202	0.195
F(000)	392.0	408.0
Crystal size/mm^3	0.12 × 0.11 × 0.1	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.066 to 50	3.914 to 49.994
Index ranges	-9 ≤ h ≤ 10, -12 ≤ k ≤ 11, -13 ≤ l ≤ 13	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -11 ≤ l ≤ 14
Reflections collected	5678	6644
Independent reflections	3149 [R_{int} = 0.0474, R_{sigma} = 0.0794]	3321 [R_{int} = 0.0289, R_{sigma} = 0.0490]
Data/restraints/parameters	3149/0/246	3321/0/256
Goodness-of-fit on F^2	1.099	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0743, wR_2 = 0.1566	R_1 = 0.0441, wR_2 = 0.1087
Final R indexes [all data]	R_1 = 0.0935, wR_2 = 0.1803	R_1 = 0.0546, wR_2 = 0.1163
Largest diff. peak/hole / e Å^{-3}	1.60/-0.56	0.38/-0.41

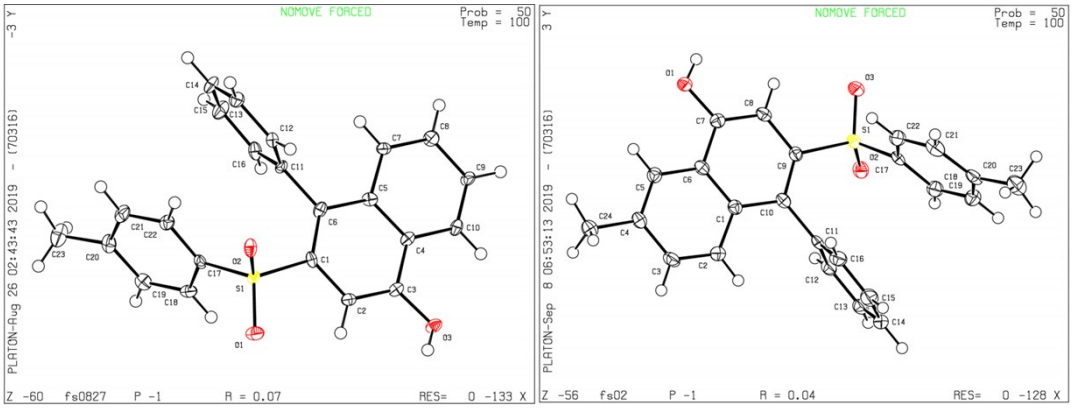
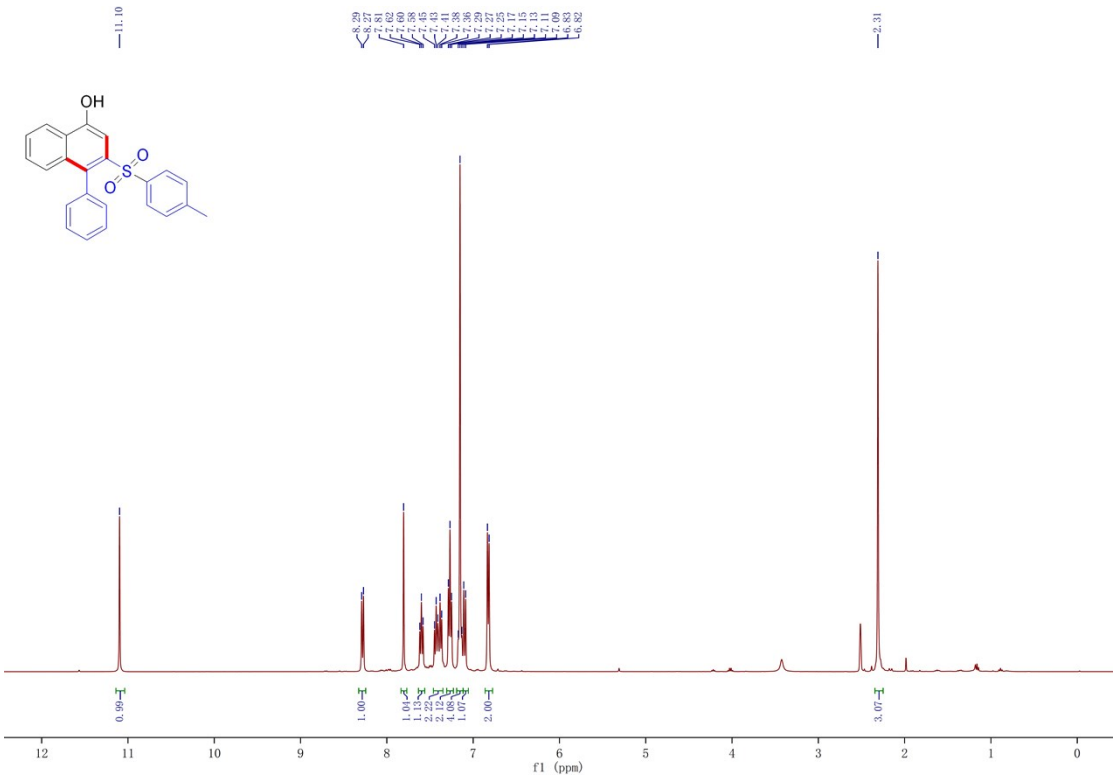
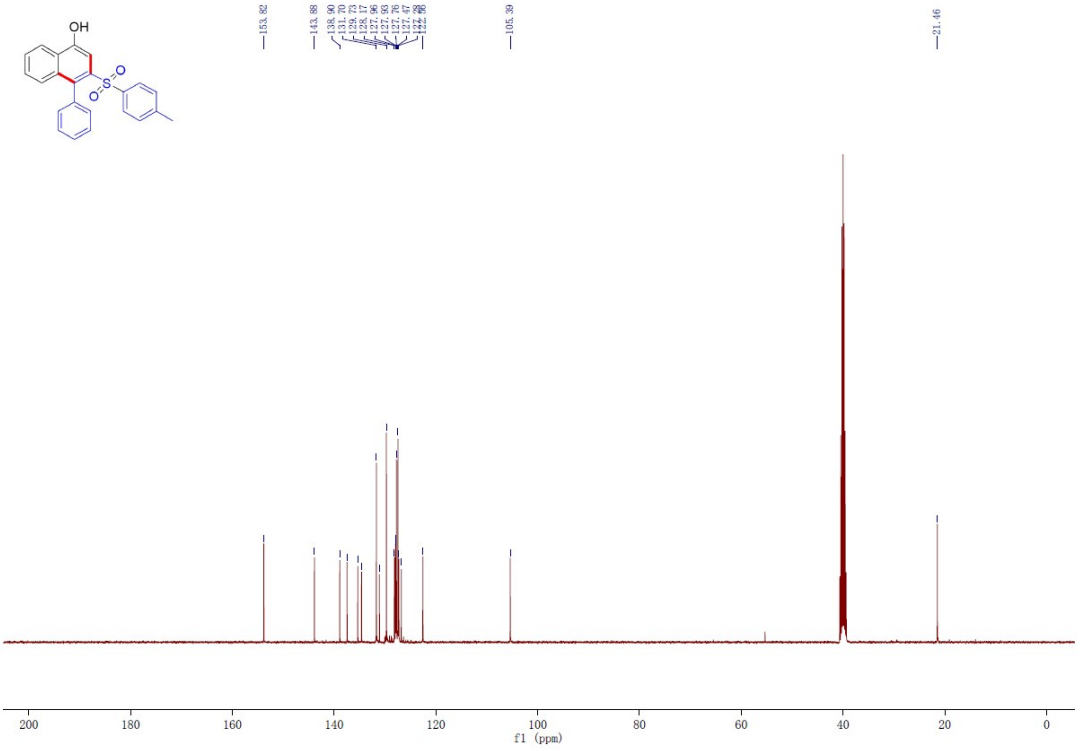


Figure S1. The molecular structure of **3aa** and **3ia.**

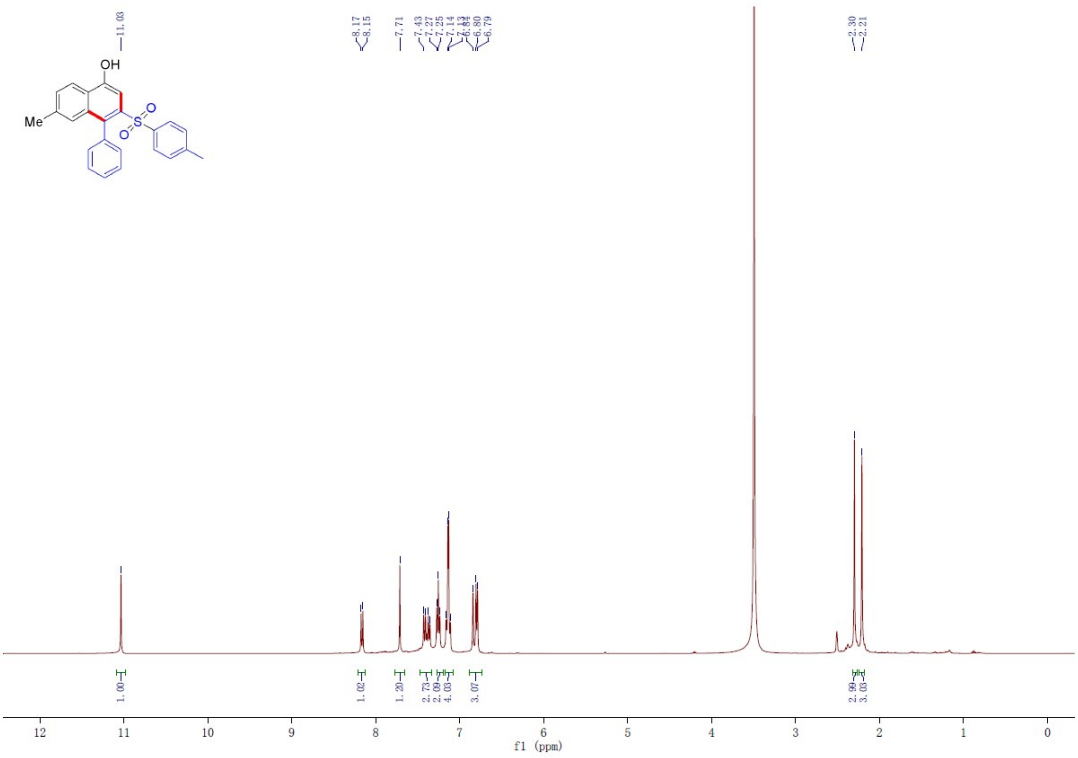
Spectral Copies of ^{1}H, ^{13}C, and ^{19}F NMR of Compounds Obtained in This Study



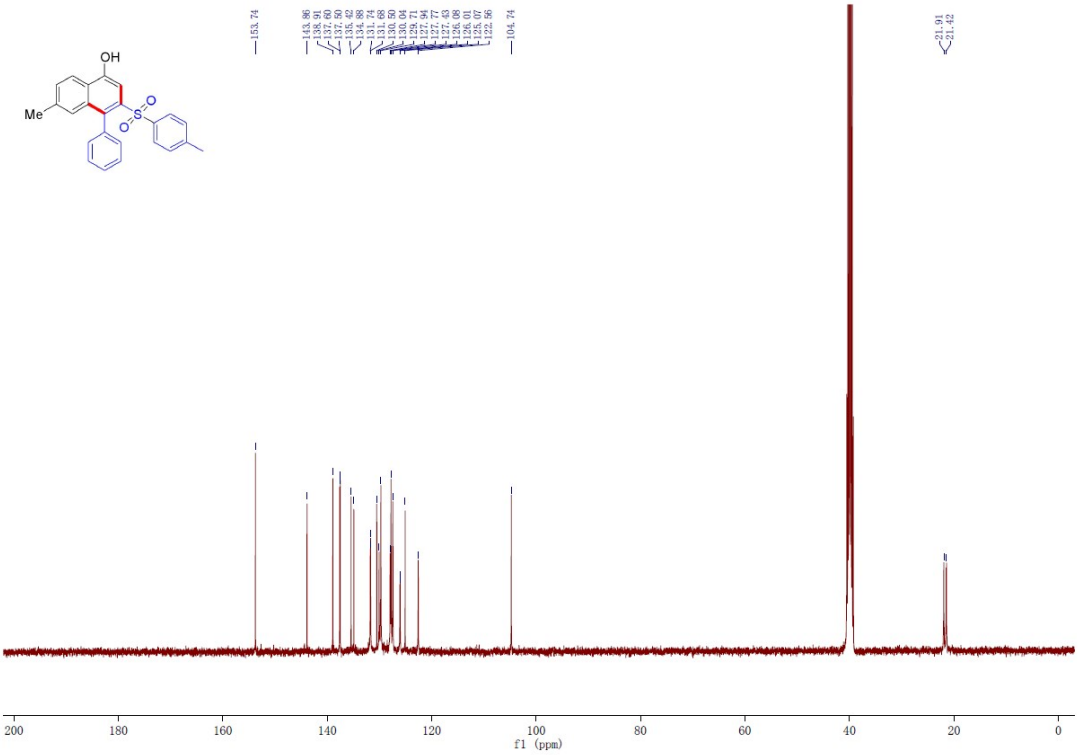
^{1}H NMR spectrum of compound **3aa**



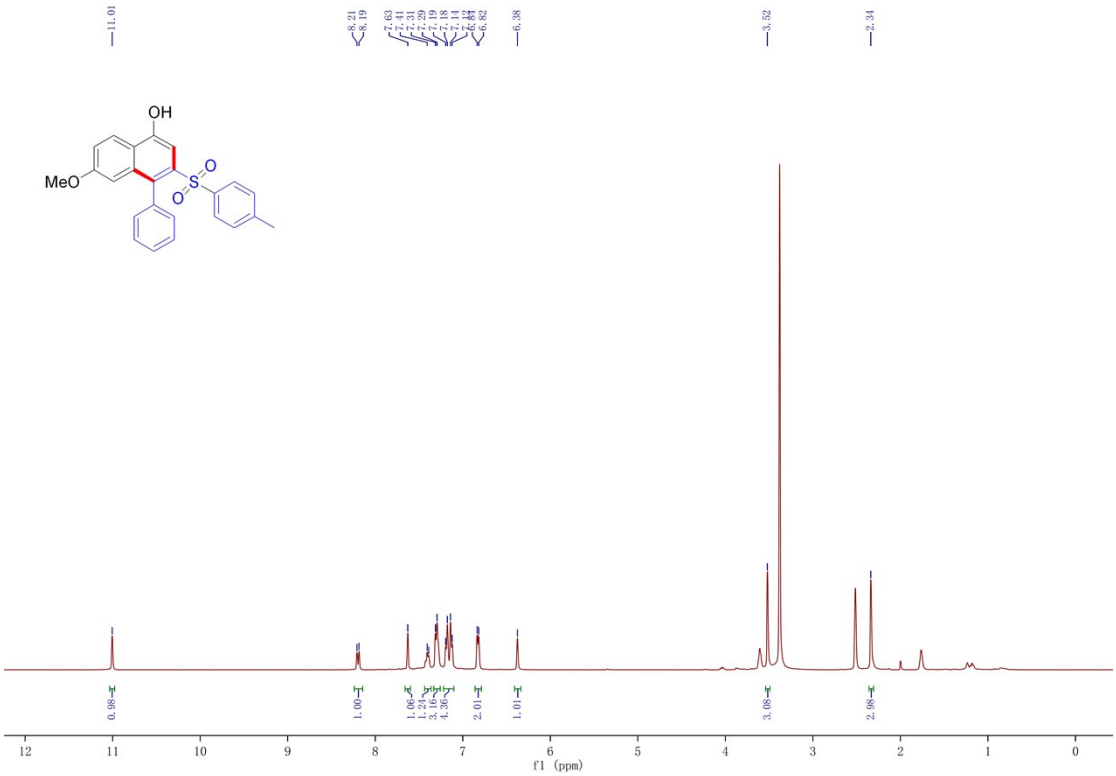
^{13}C NMR spectrum of compound **3aa**



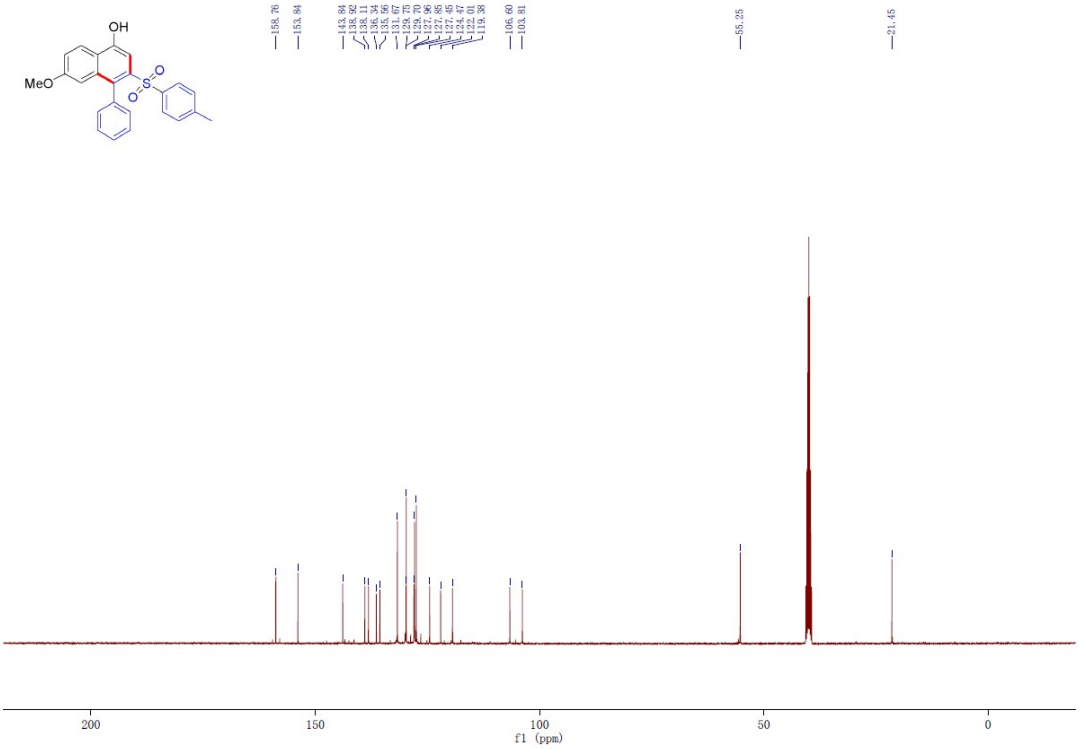
^{1}H NMR spectrum of compound **3ba**



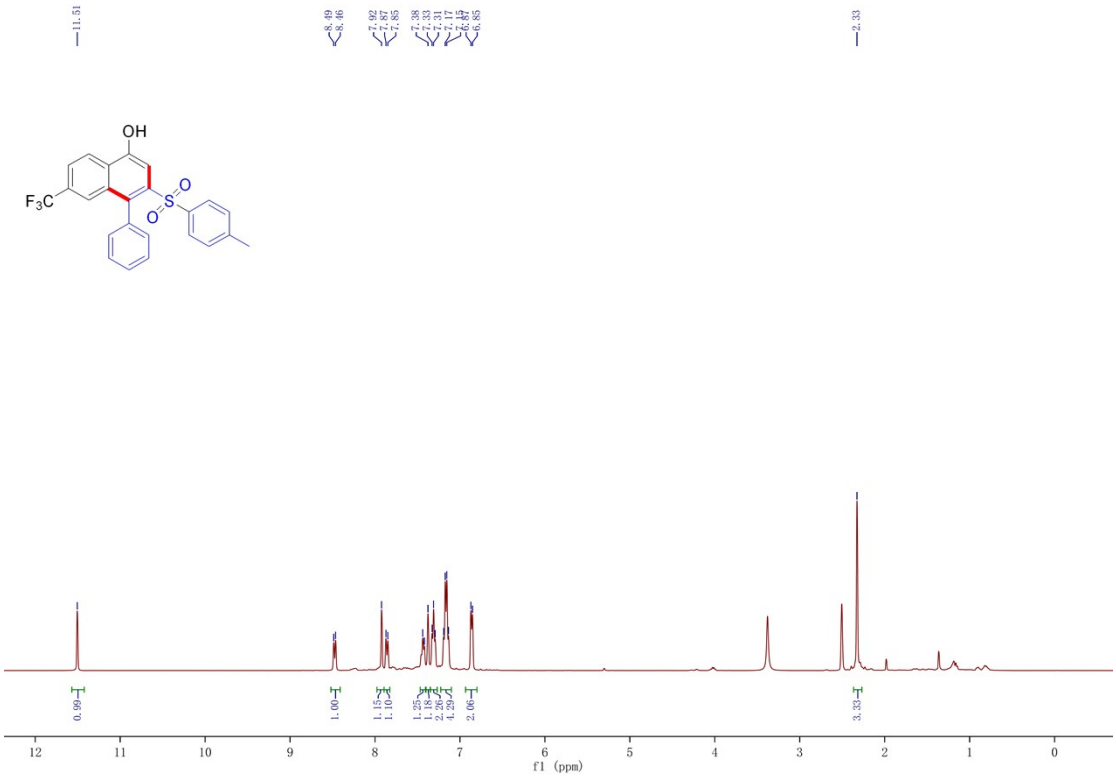
^{13}C NMR spectrum of compound **3ba**



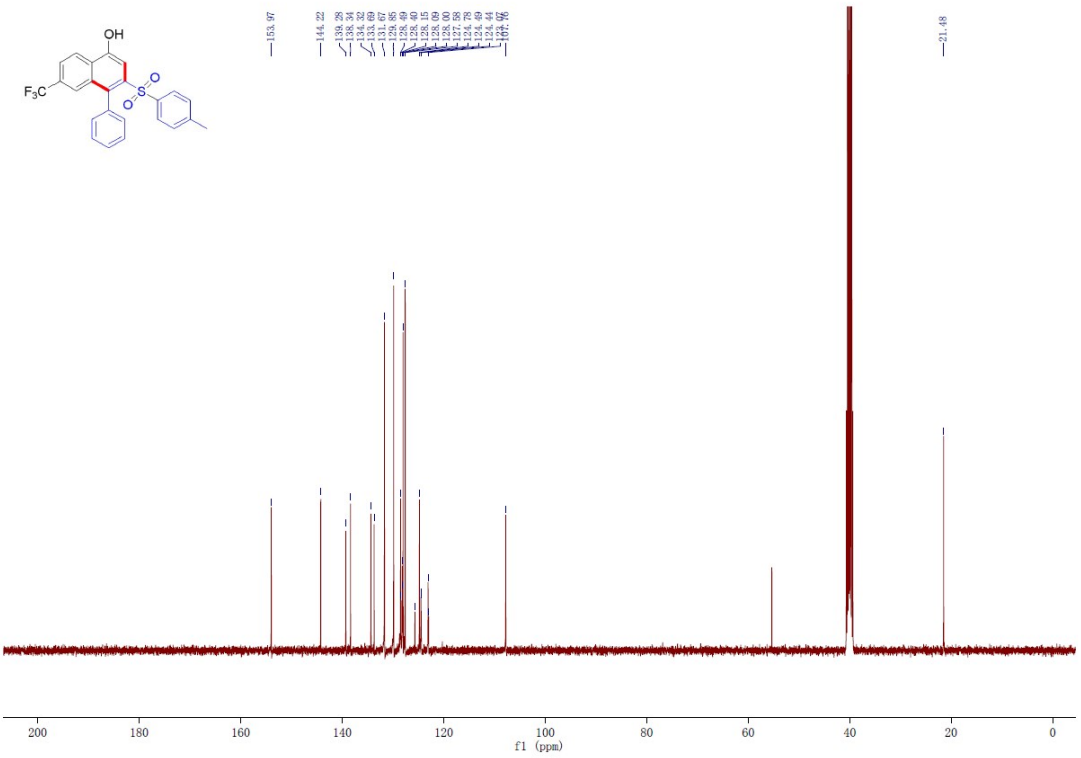
^{1}H NMR spectrum of compound **3ca**



^{13}C NMR spectrum of compound **3ca**

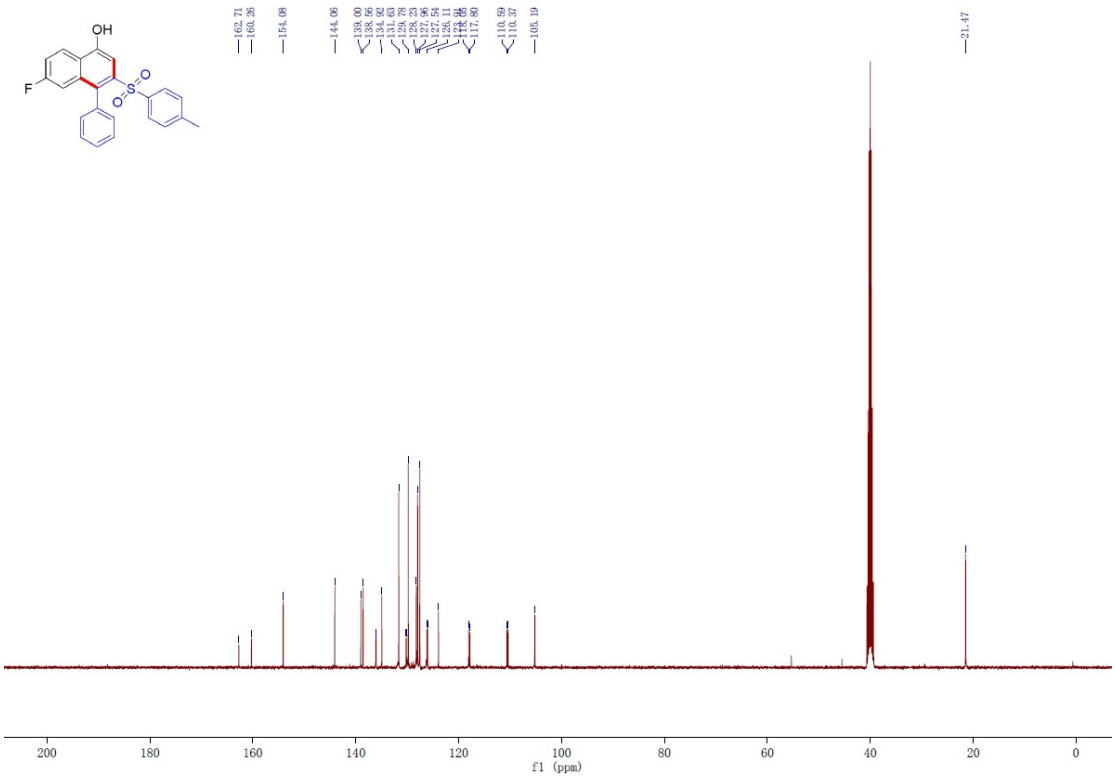


^{1}H NMR spectrum of compound **3da**

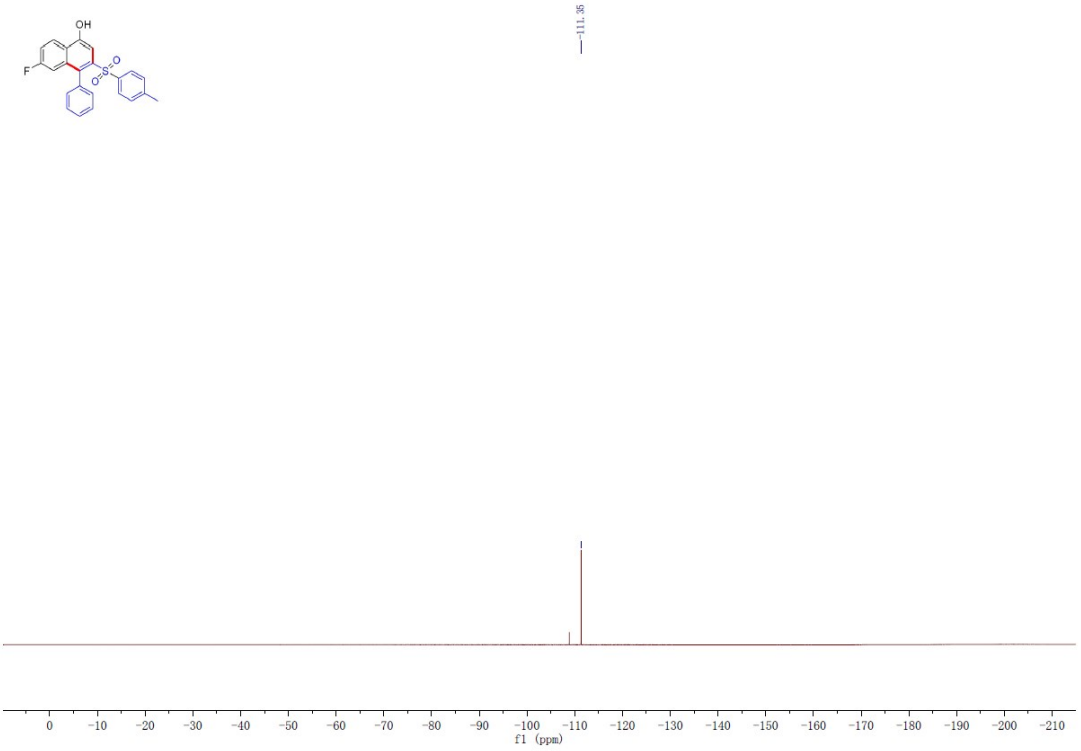


^{13}C NMR spectrum of compound **3da**

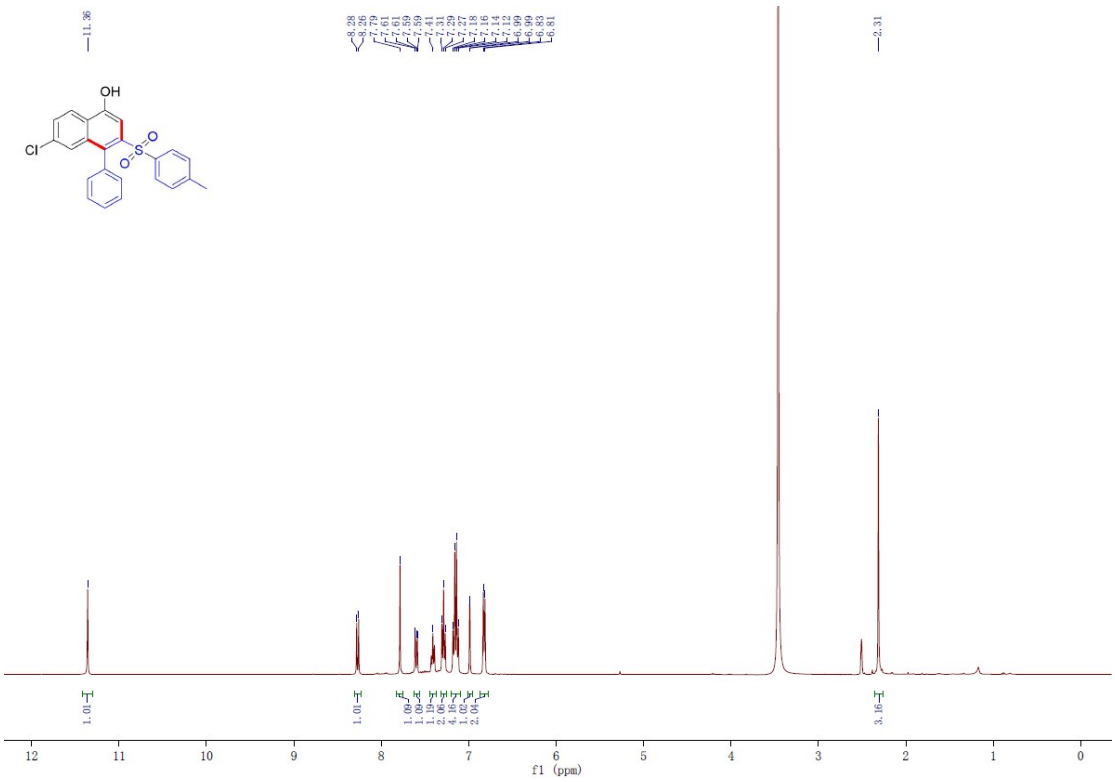
^{1}H NMR spectrum of compound **3ea**



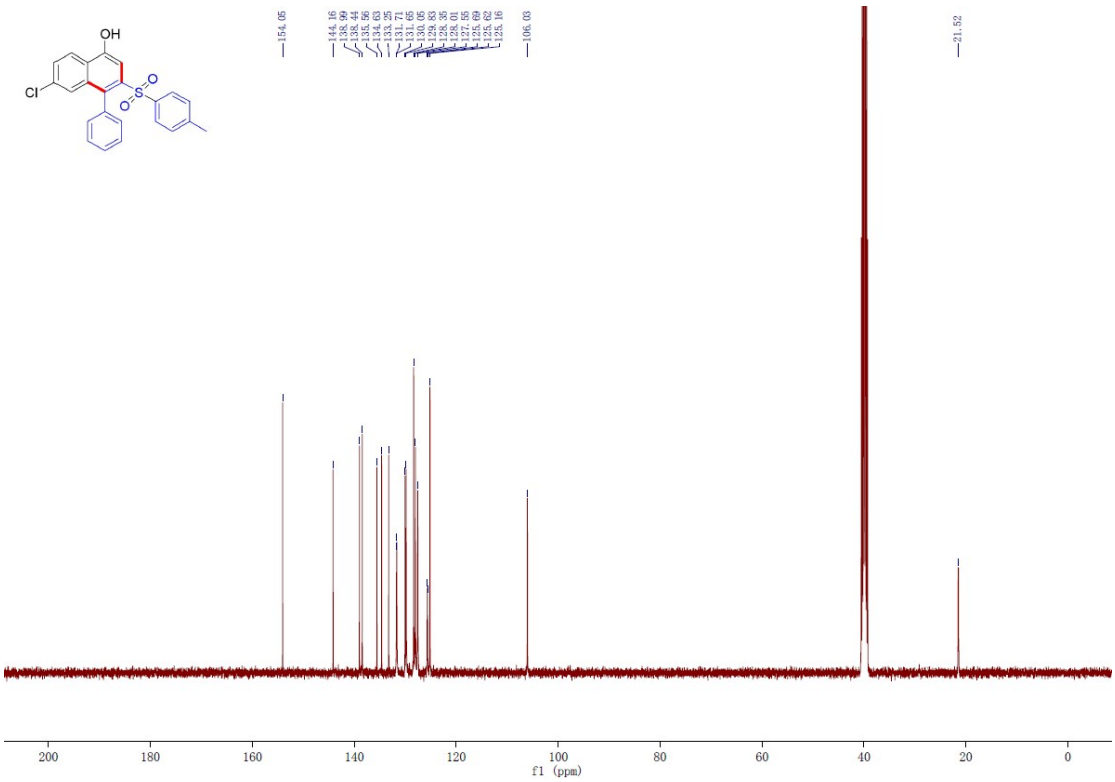
^{13}C NMR spectrum of compound **3ea**



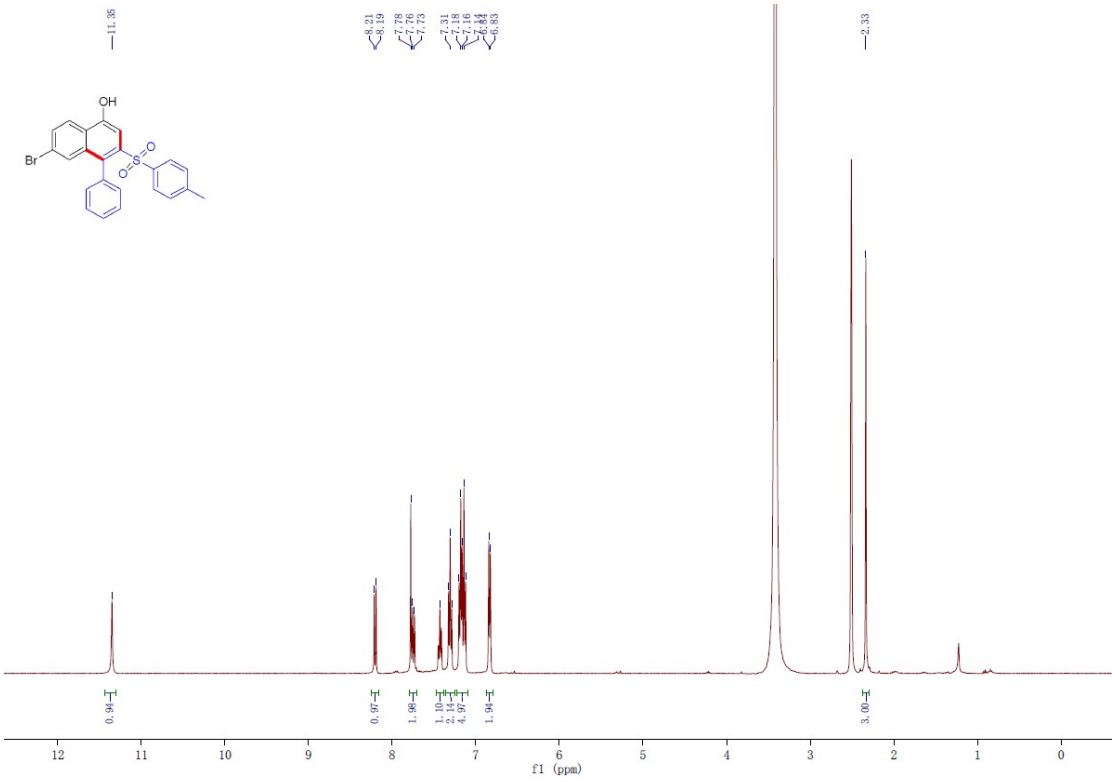
^{19}F NMR spectrum of compound **3ea**



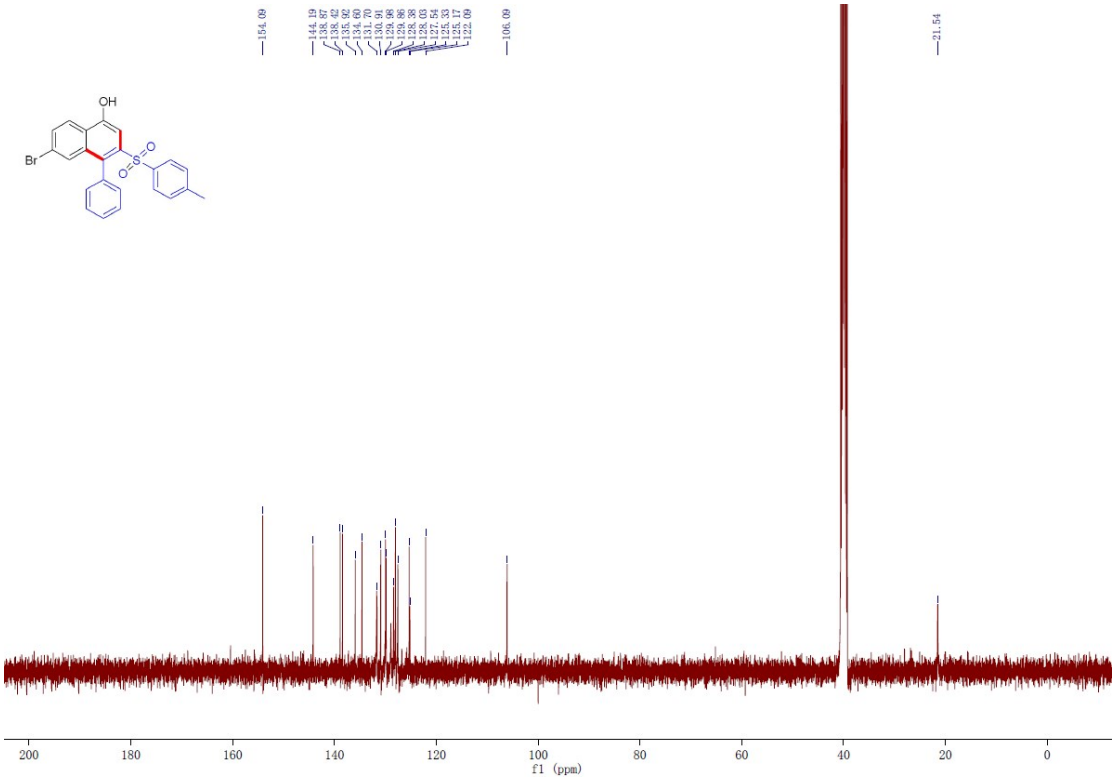
^{1}H NMR spectrum of compound **3fa**



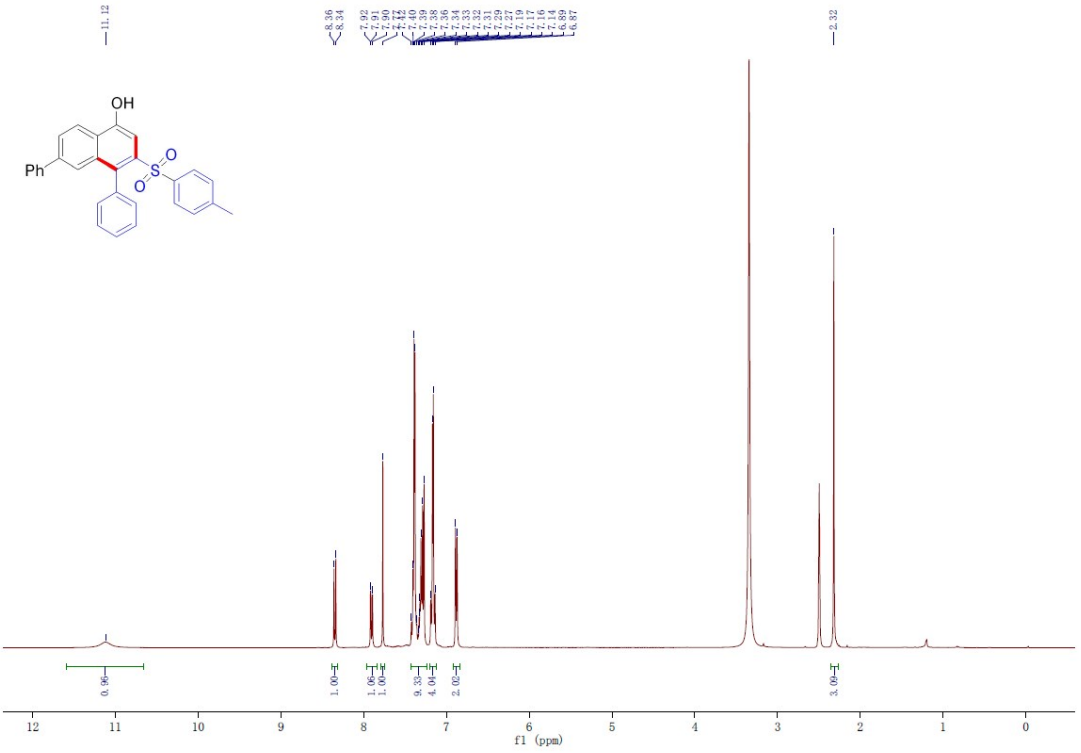
^{13}C NMR spectrum of compound **3fa**



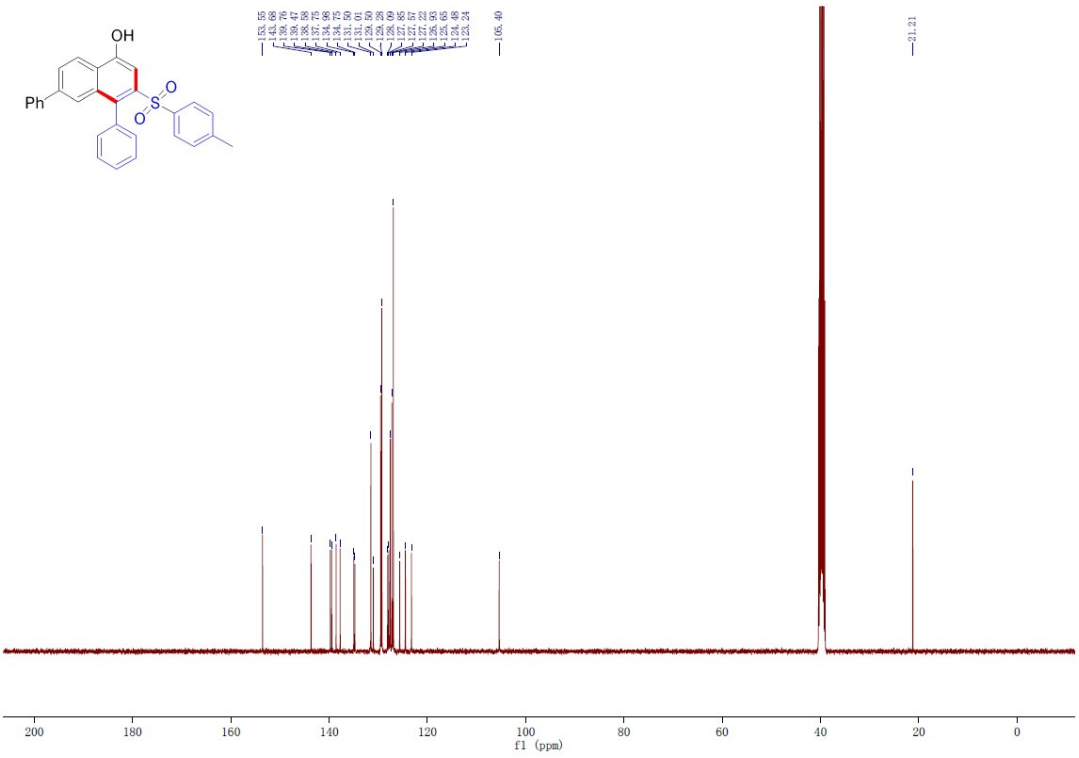
^{1}H NMR spectrum of compound **3ga**



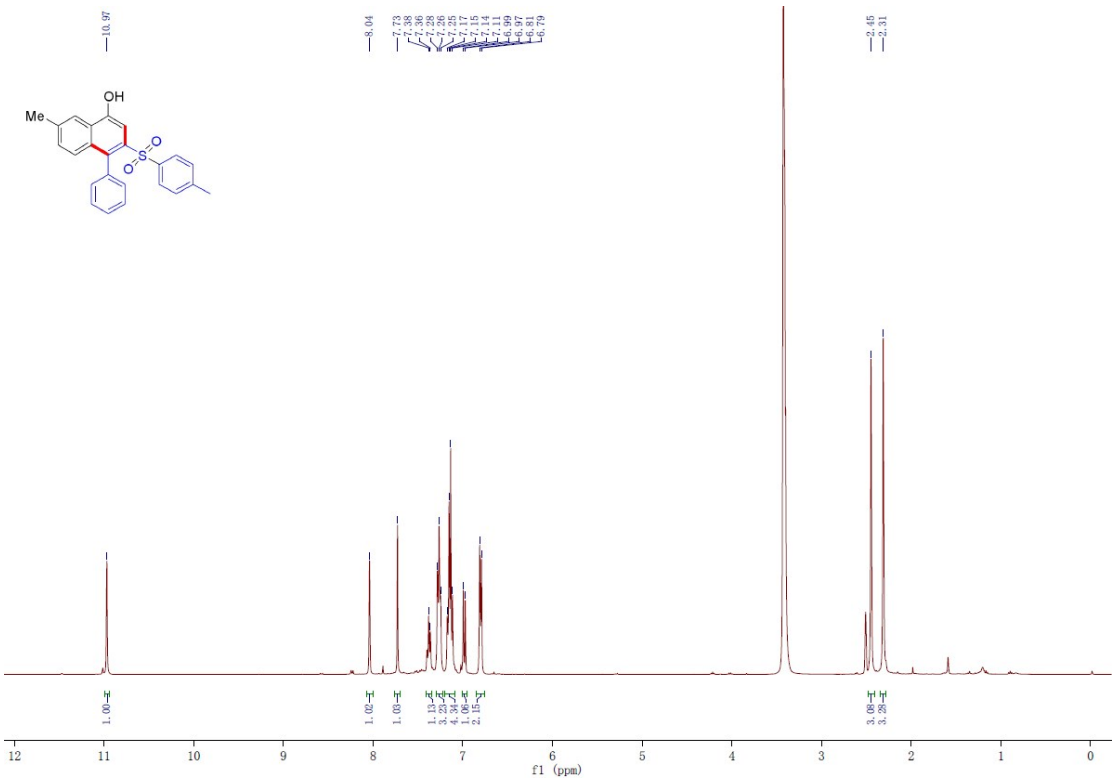
^{13}C NMR spectrum of compound **3ga**



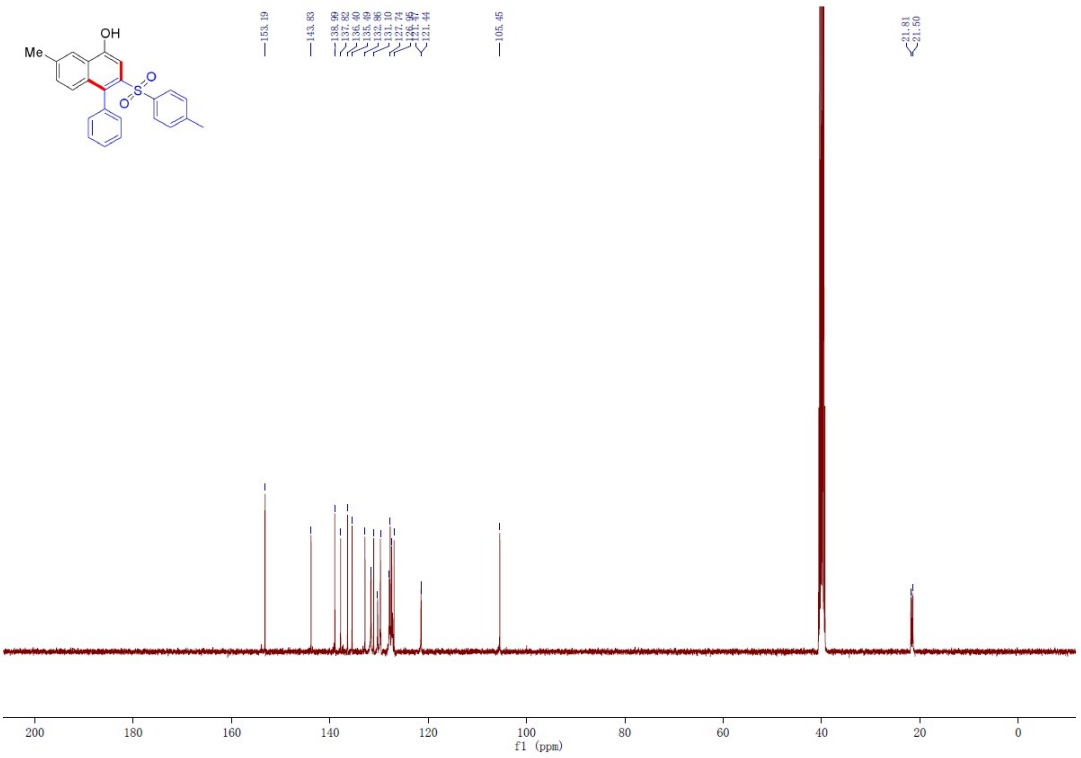
^{1}H NMR spectrum of compound **3ha**



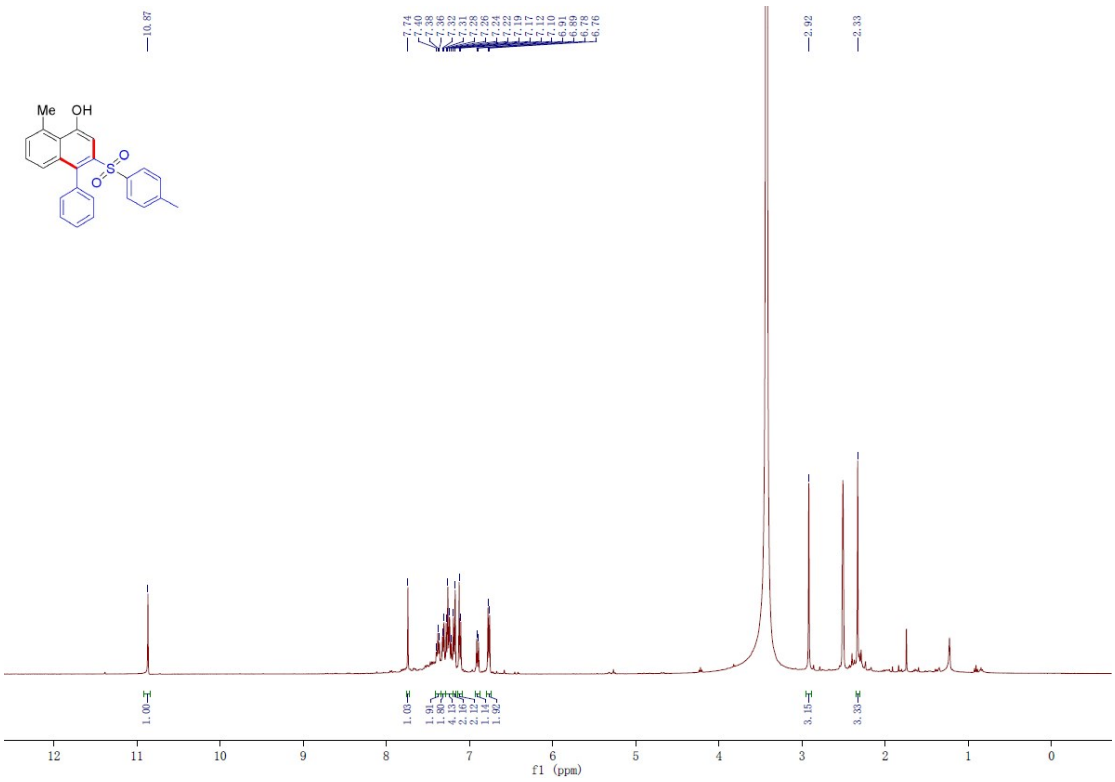
^{13}C NMR spectrum of compound **3ha**



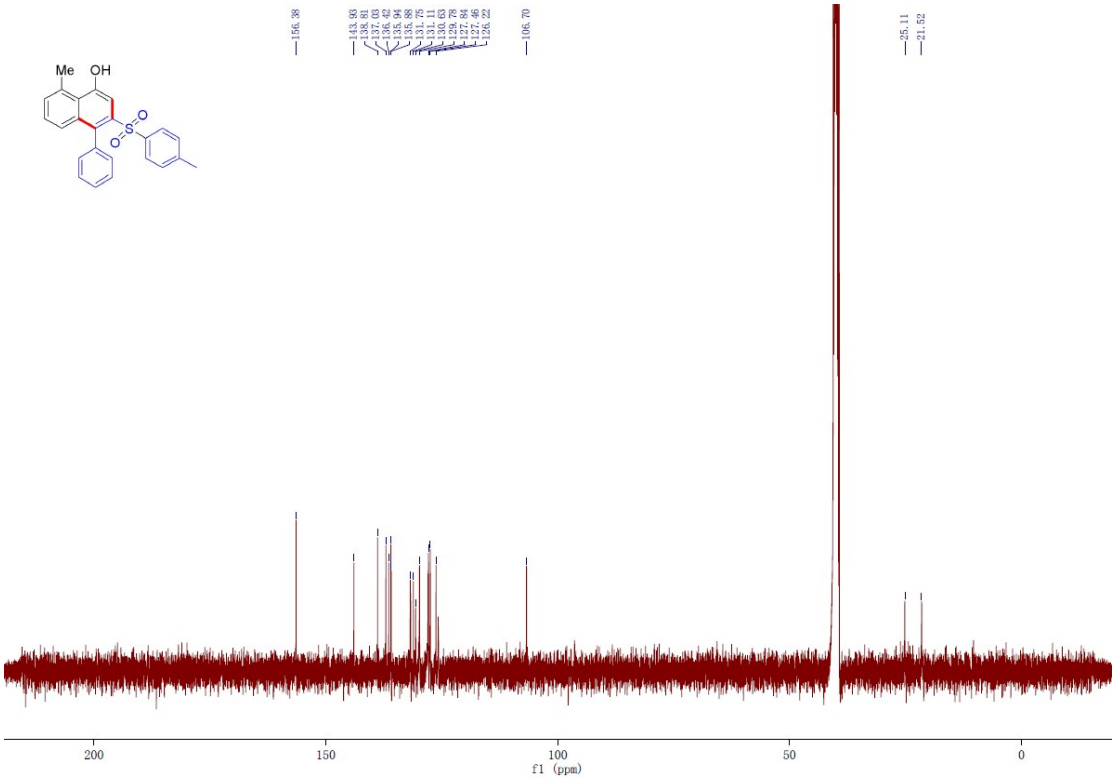
^{1}H NMR spectrum of compound **3ia**



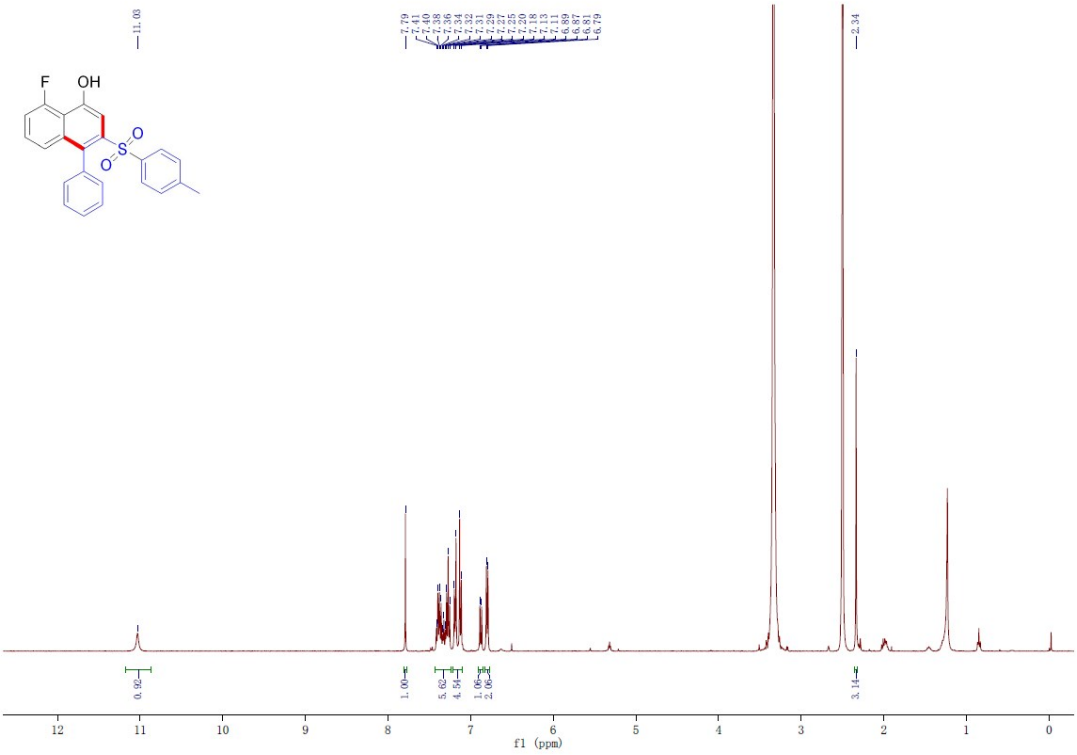
^{13}C NMR spectrum of compound **3ia**



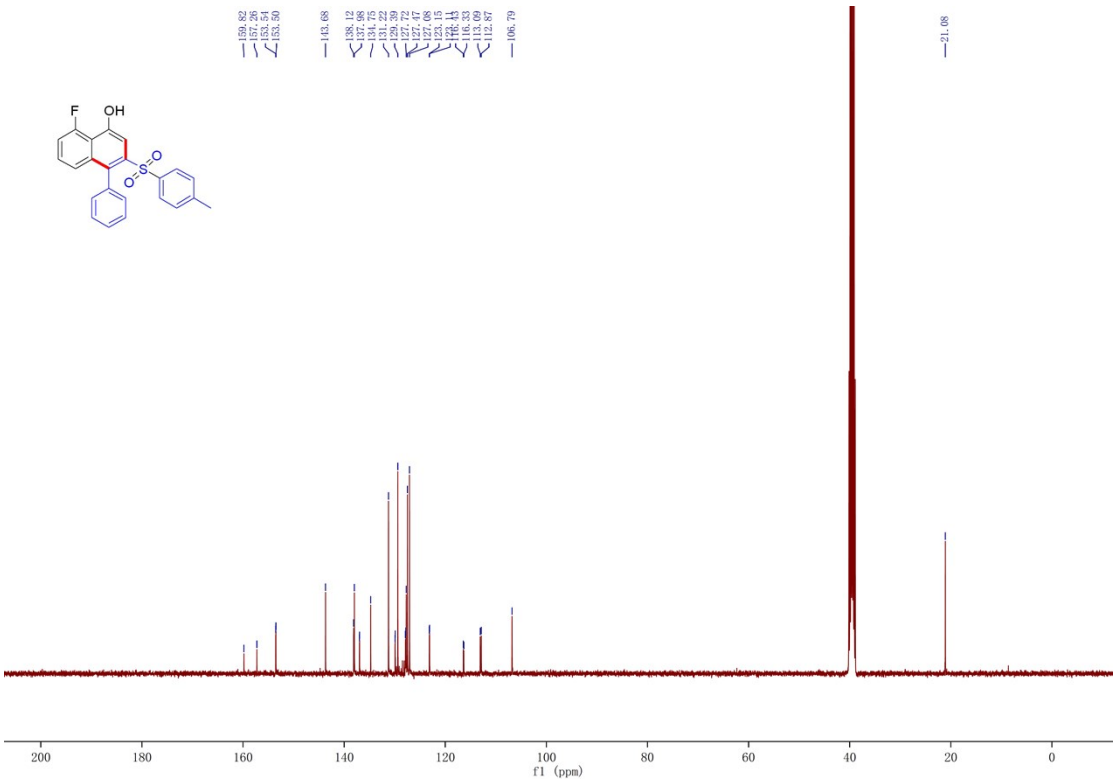
^{1}H NMR spectrum of compound **3ja**



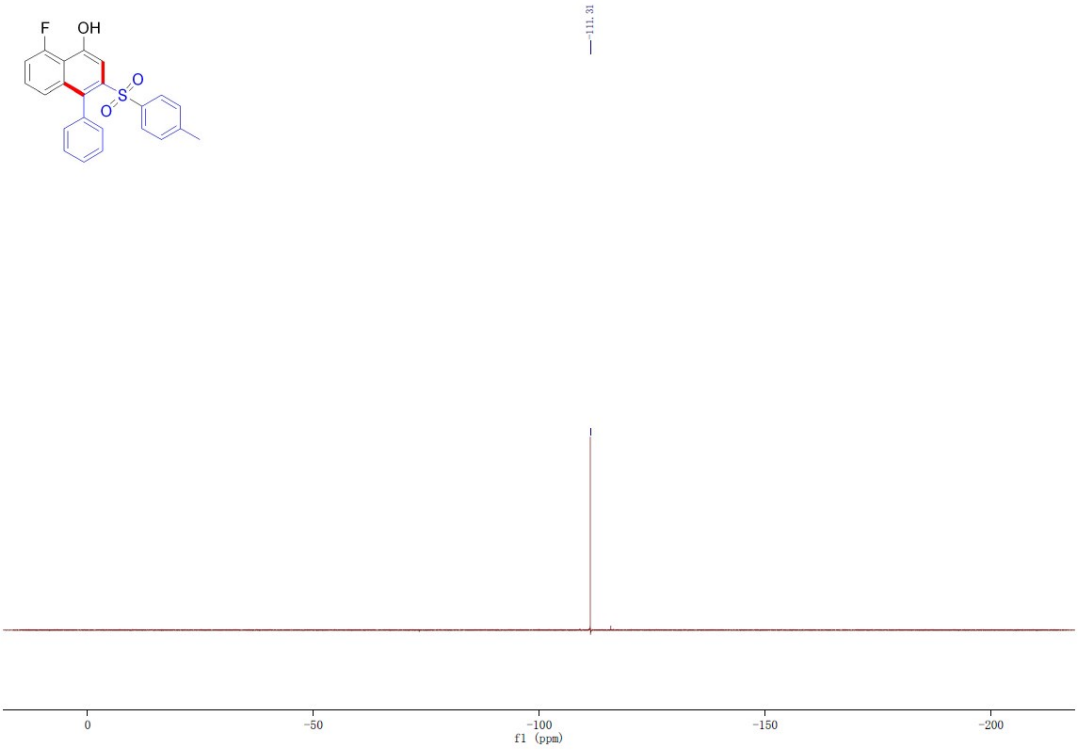
^{13}C NMR spectrum of compound **3ja**



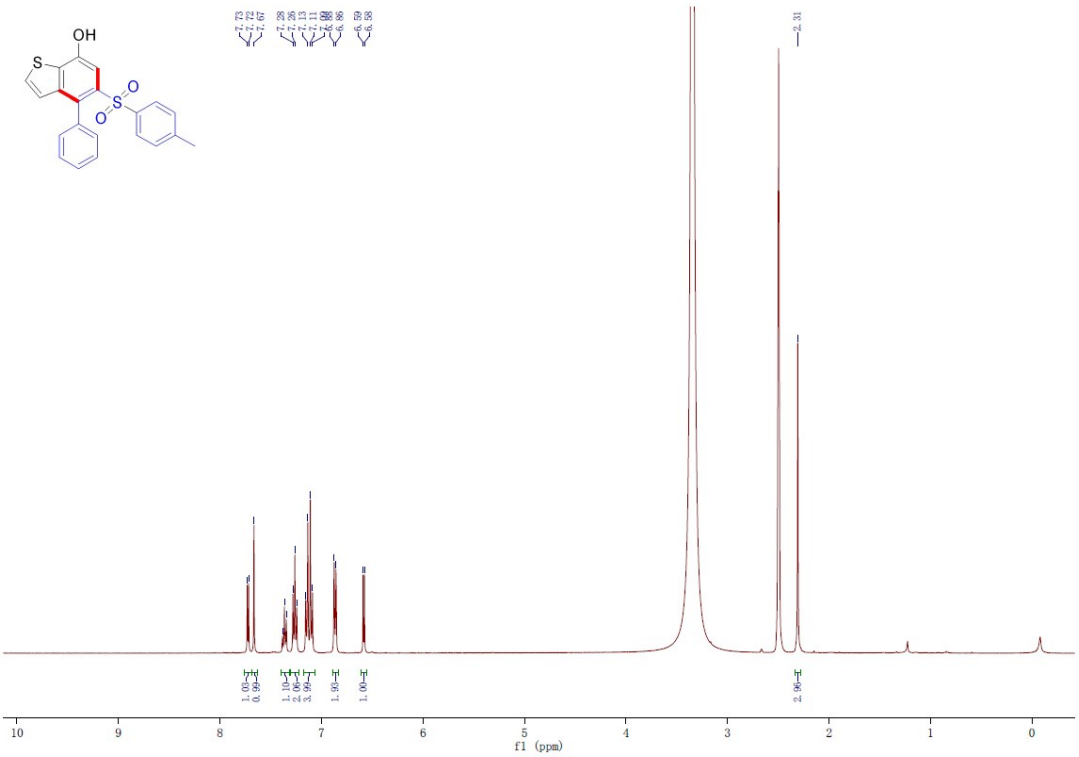
^{1}H NMR spectrum of compound **3ka**



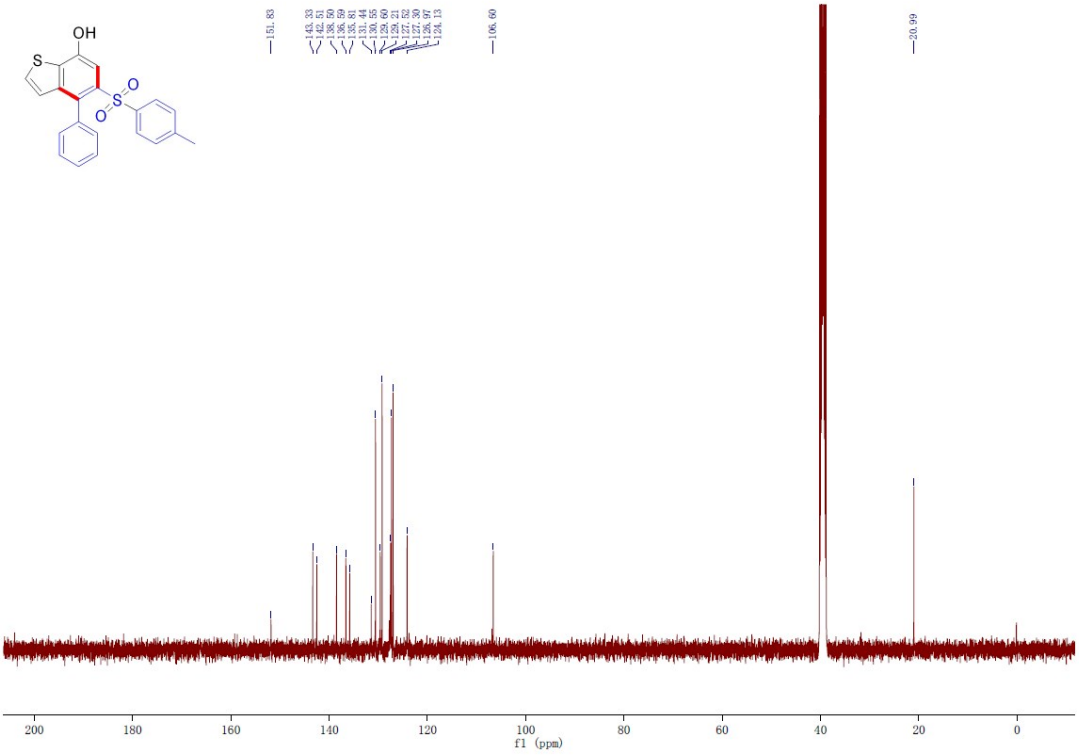
^{13}C NMR spectrum of compound **3ka**



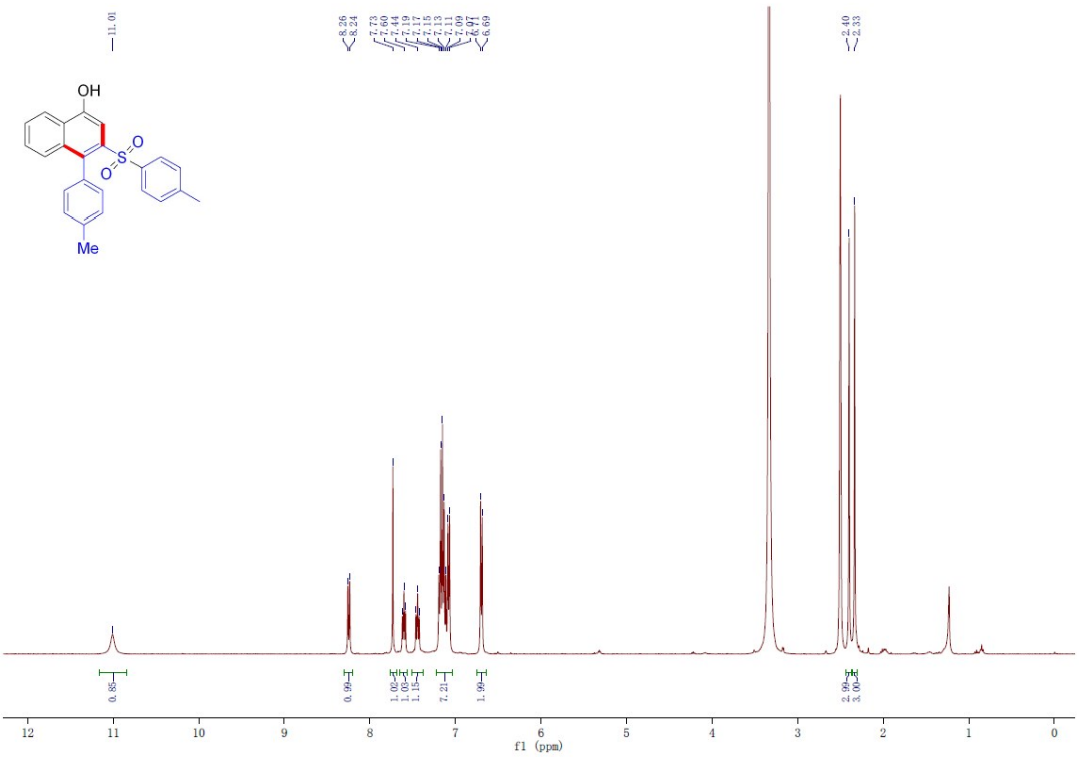
^{19}F NMR spectrum of compound **3ka**



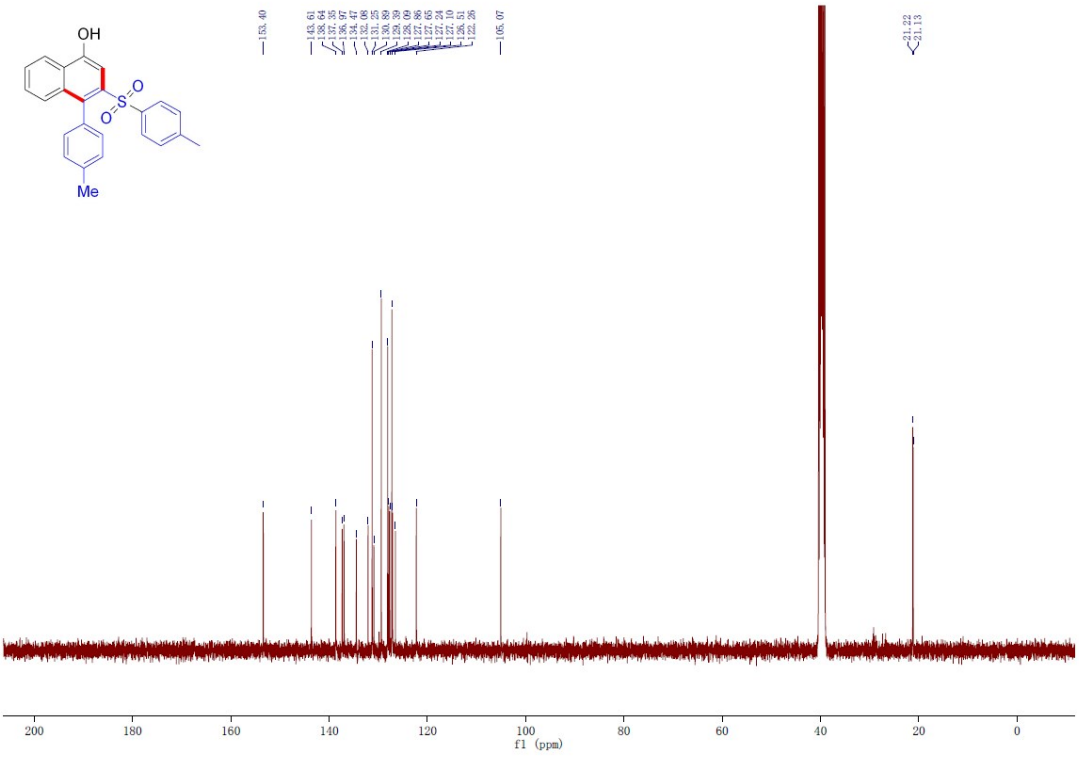
^{1}H NMR spectrum of compound **3la**



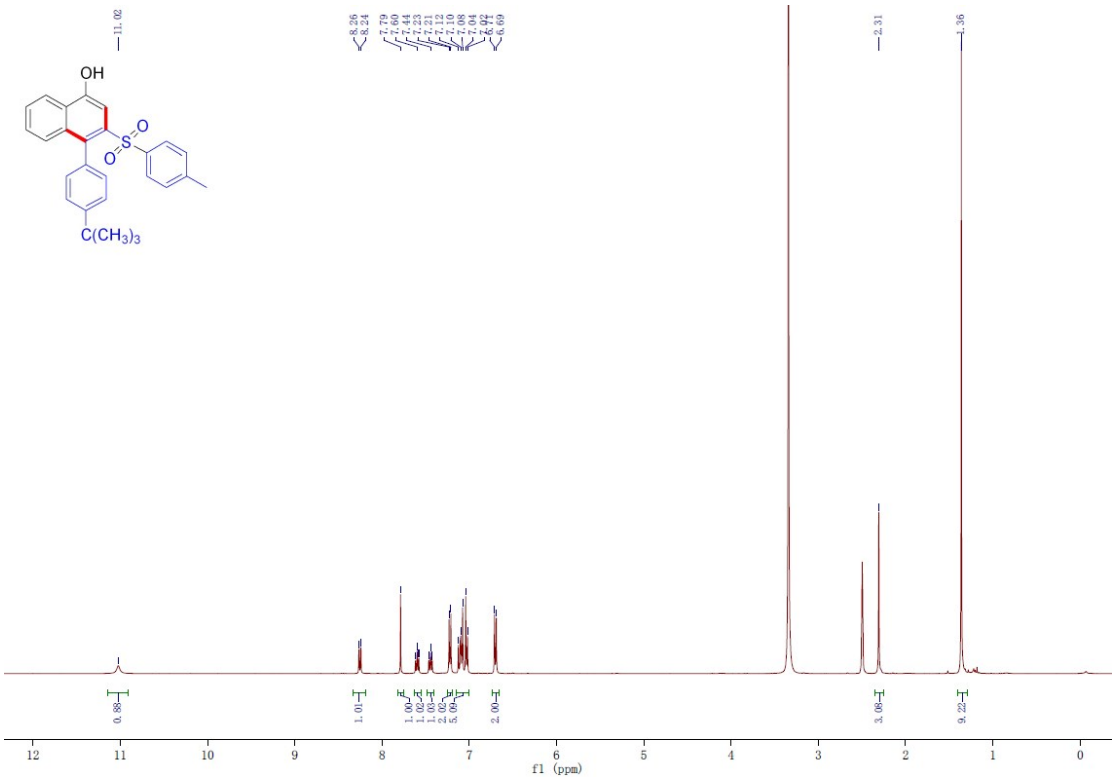
^{13}C NMR spectrum of compound **3la**



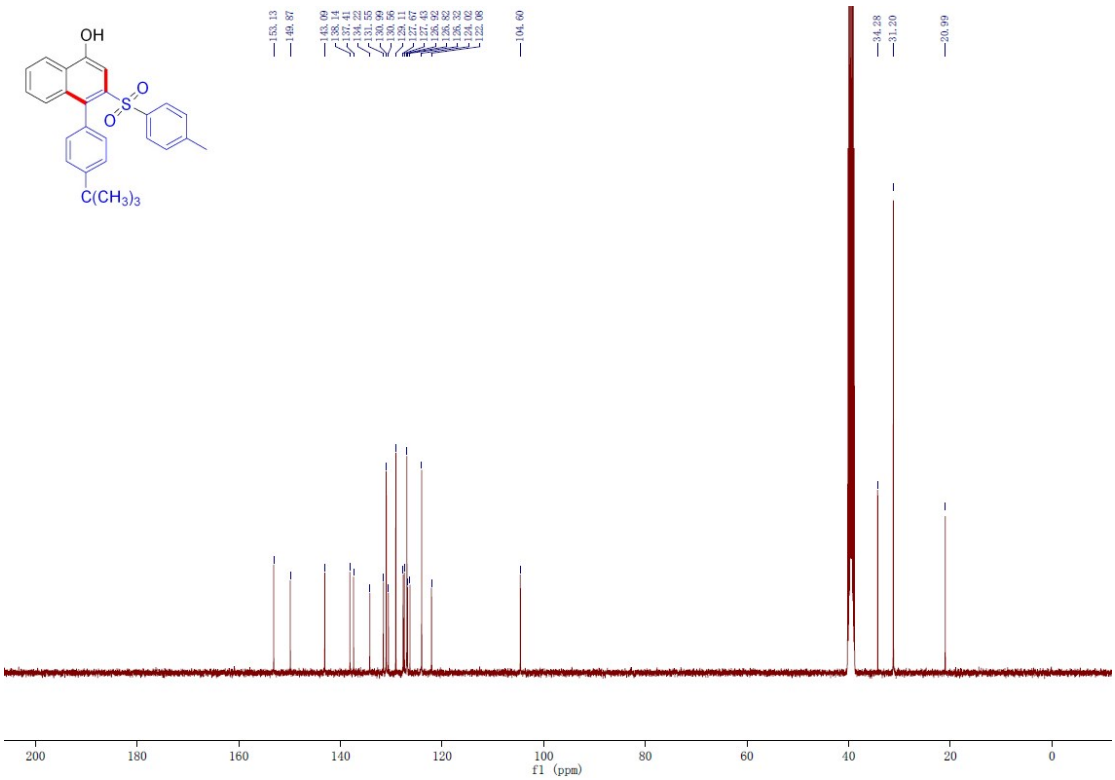
^{1}H NMR spectrum of compound **3ab**



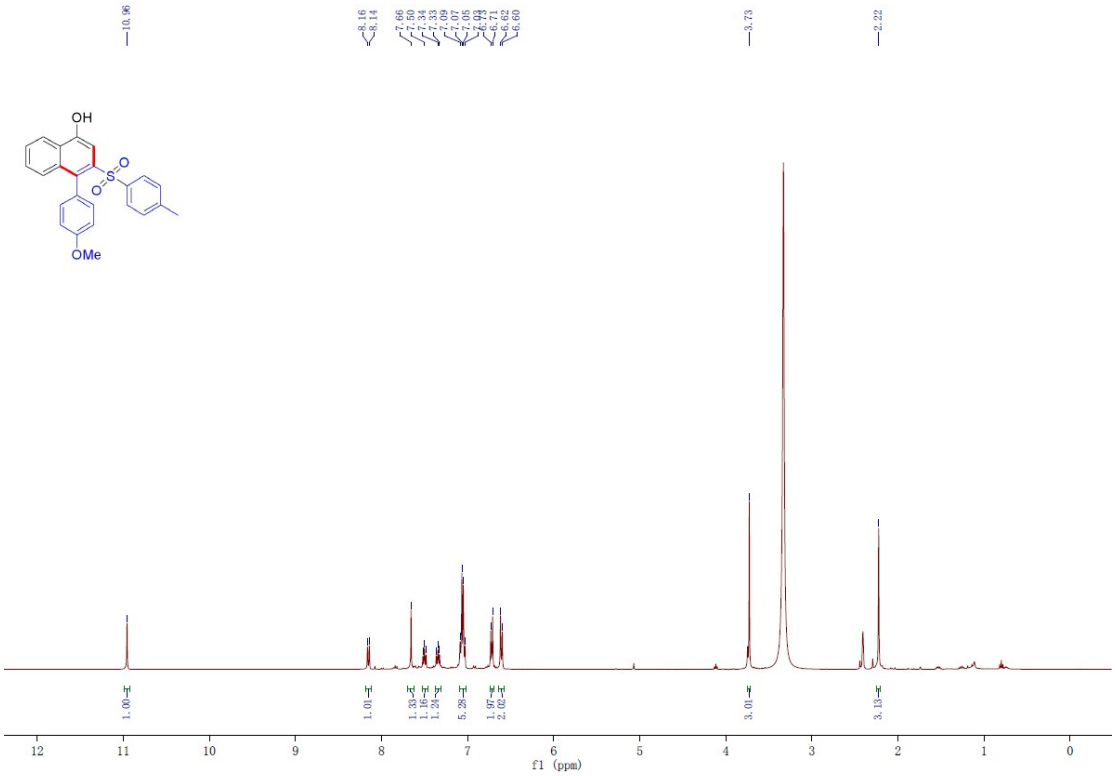
^{13}C NMR spectrum of compound **3ab**



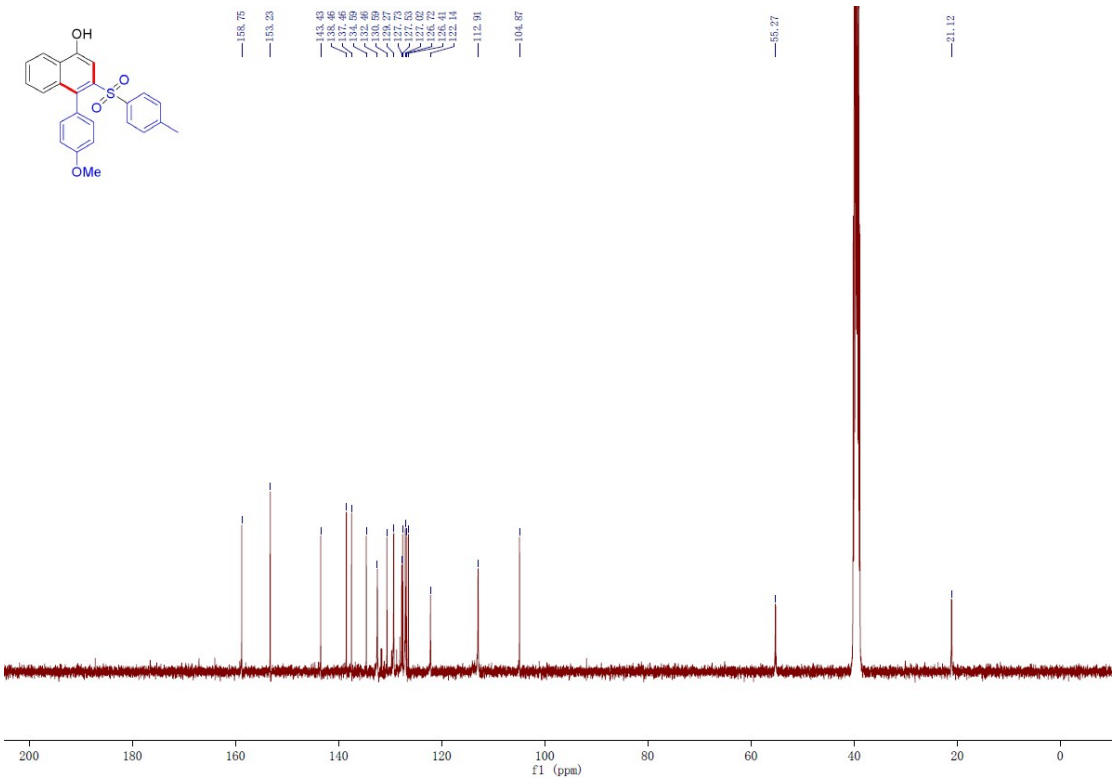
^{1}H NMR spectrum of compound **3ac**



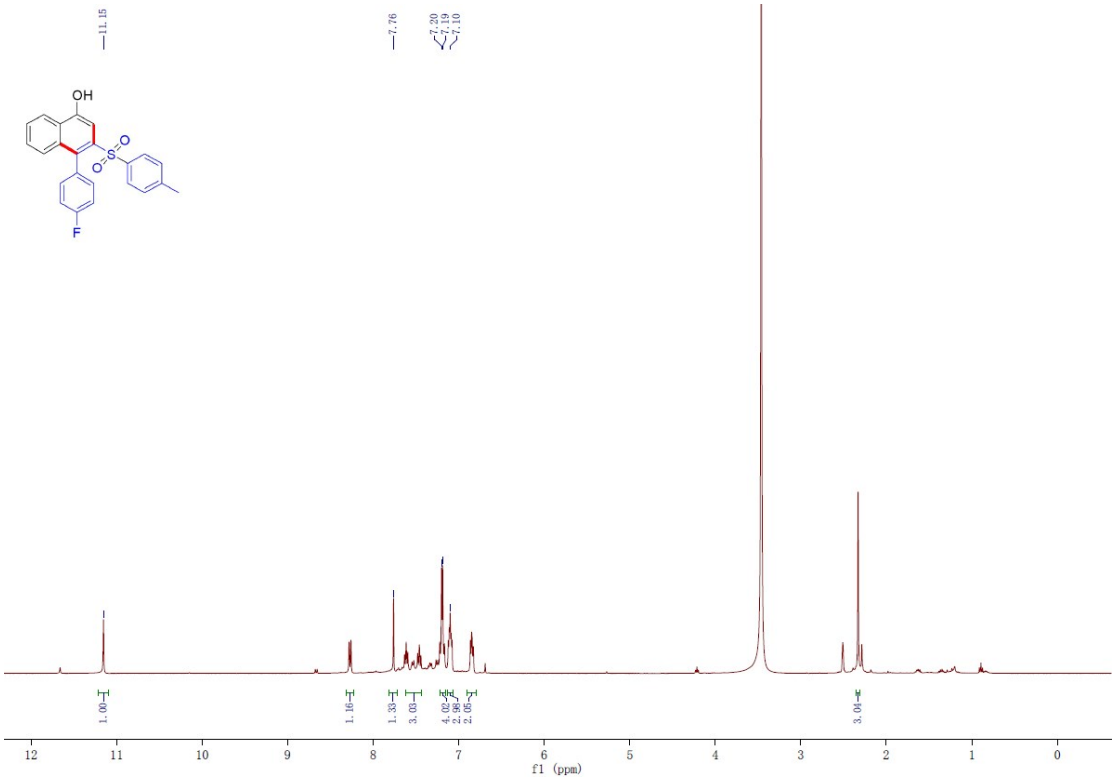
^{13}C NMR spectrum of compound **3ac**



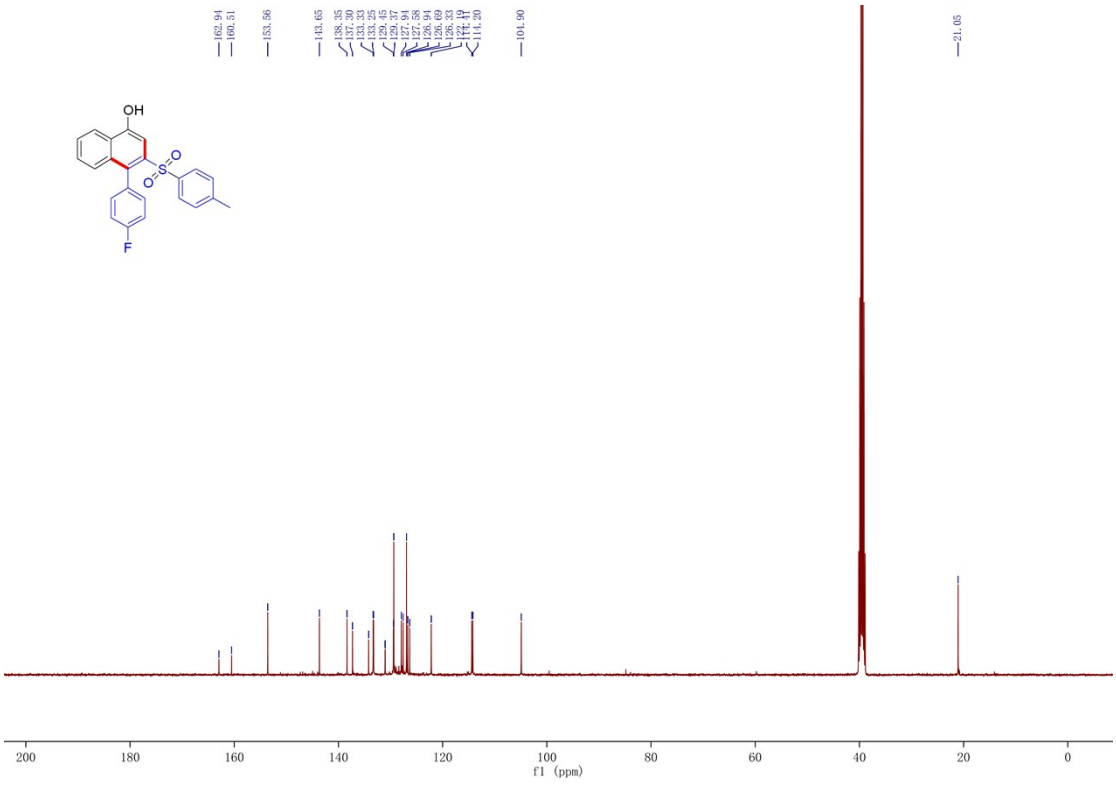
^{1}H NMR spectrum of compound **3ad**



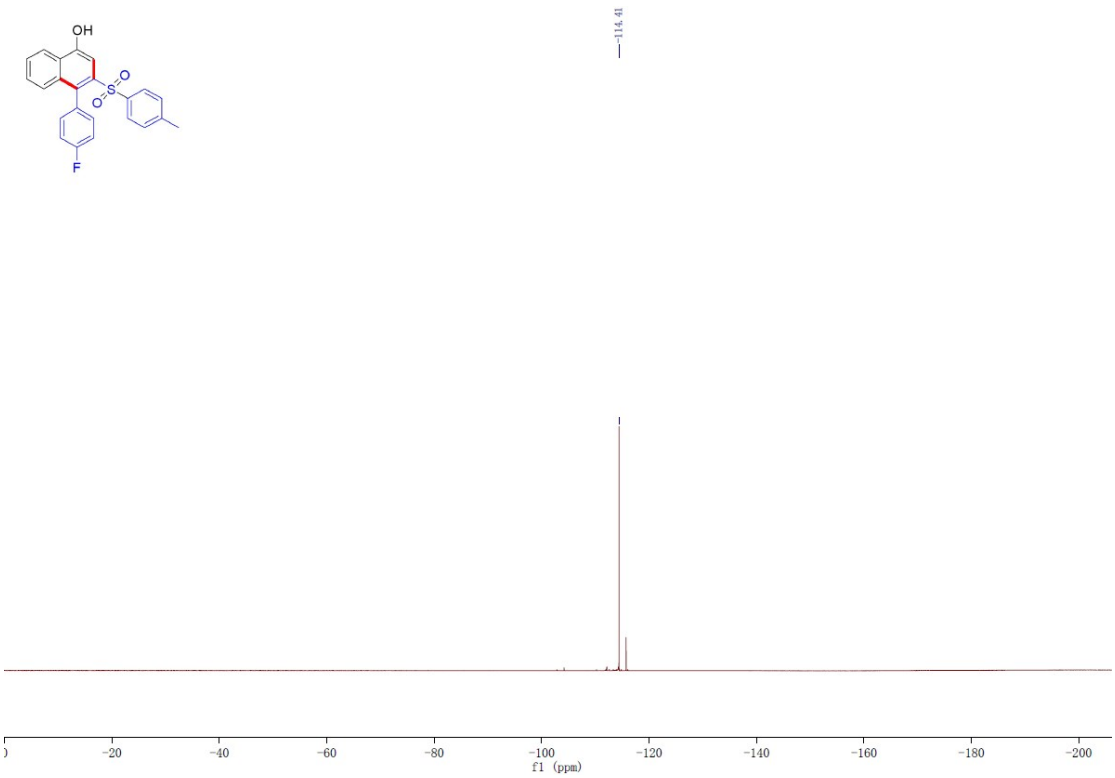
^{13}C NMR spectrum of compound **3ad**



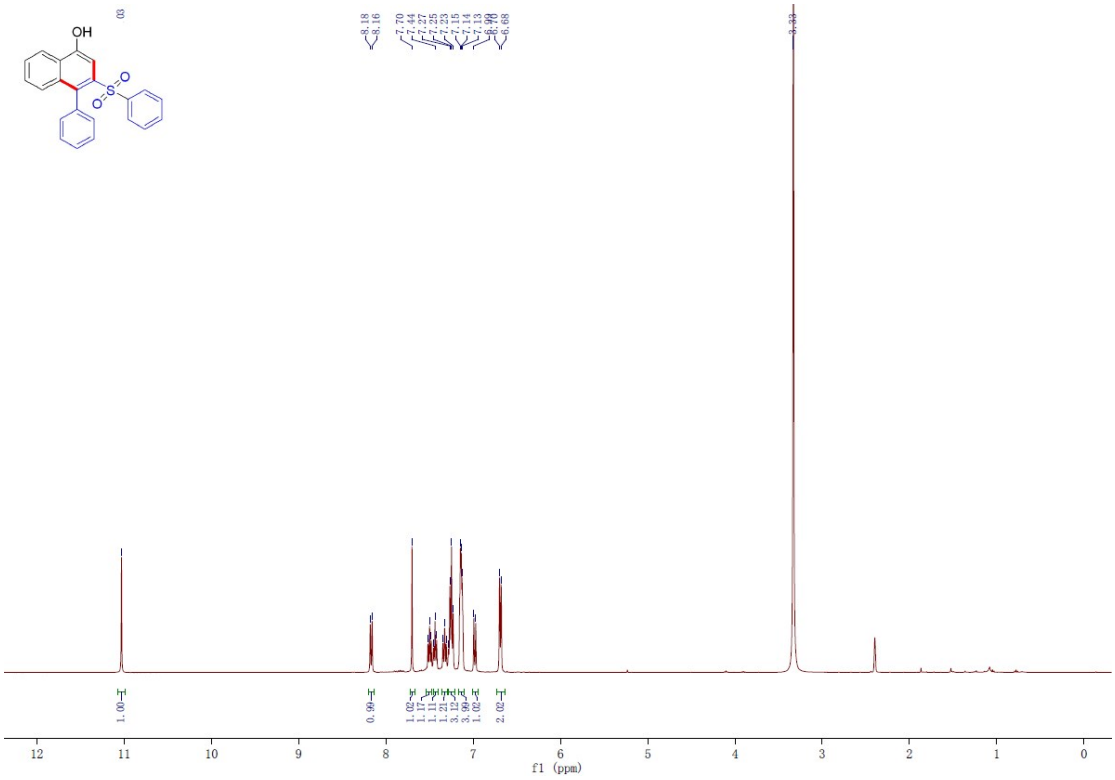
^{1}H NMR spectrum of compound **3ae**



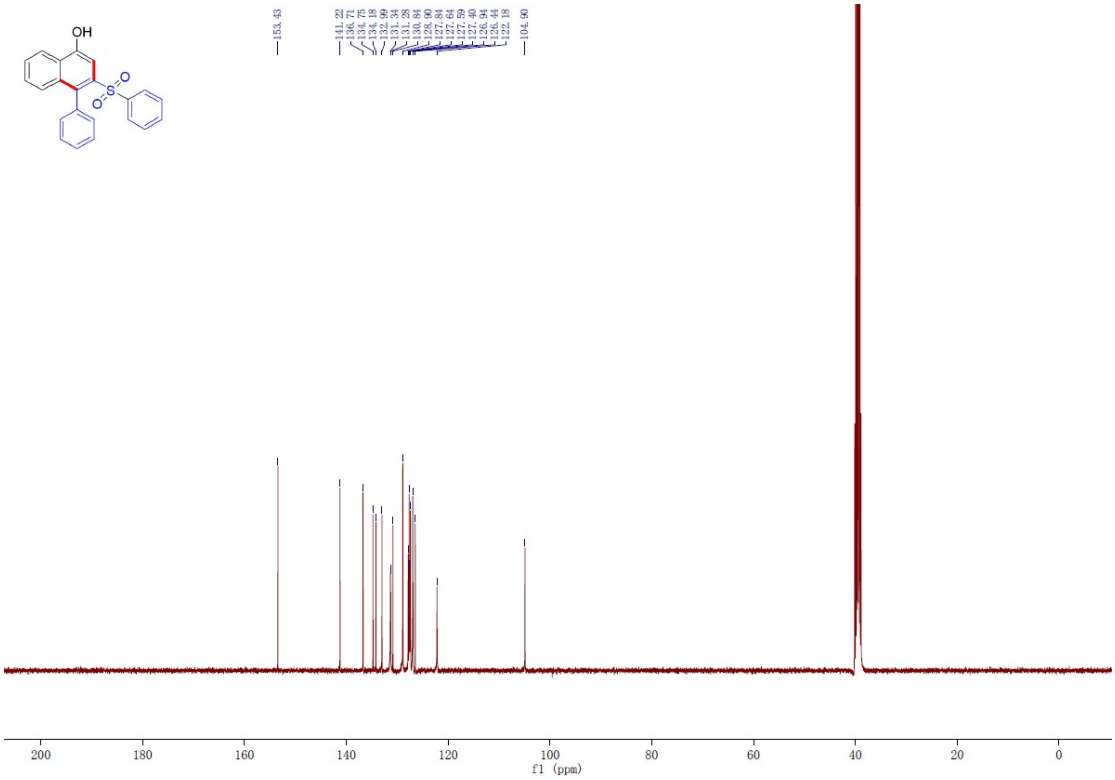
^{13}C NMR spectrum of compound **3ae**



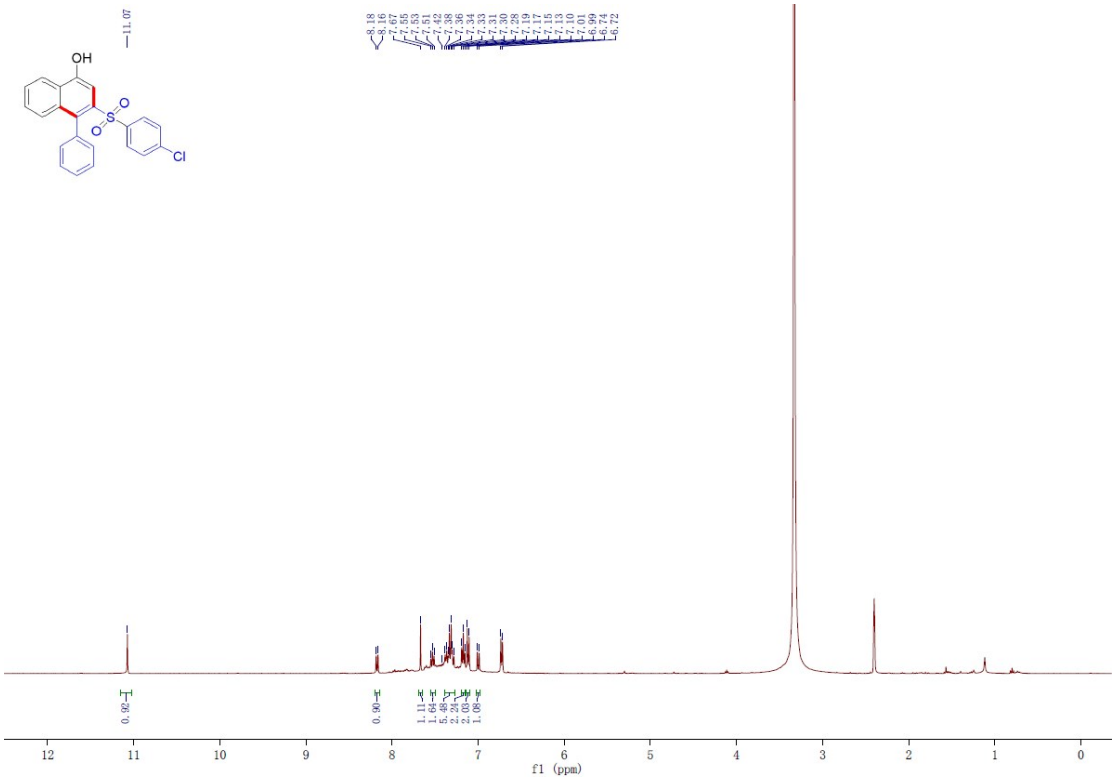
^{19}F NMR spectrum of compound **3ae**



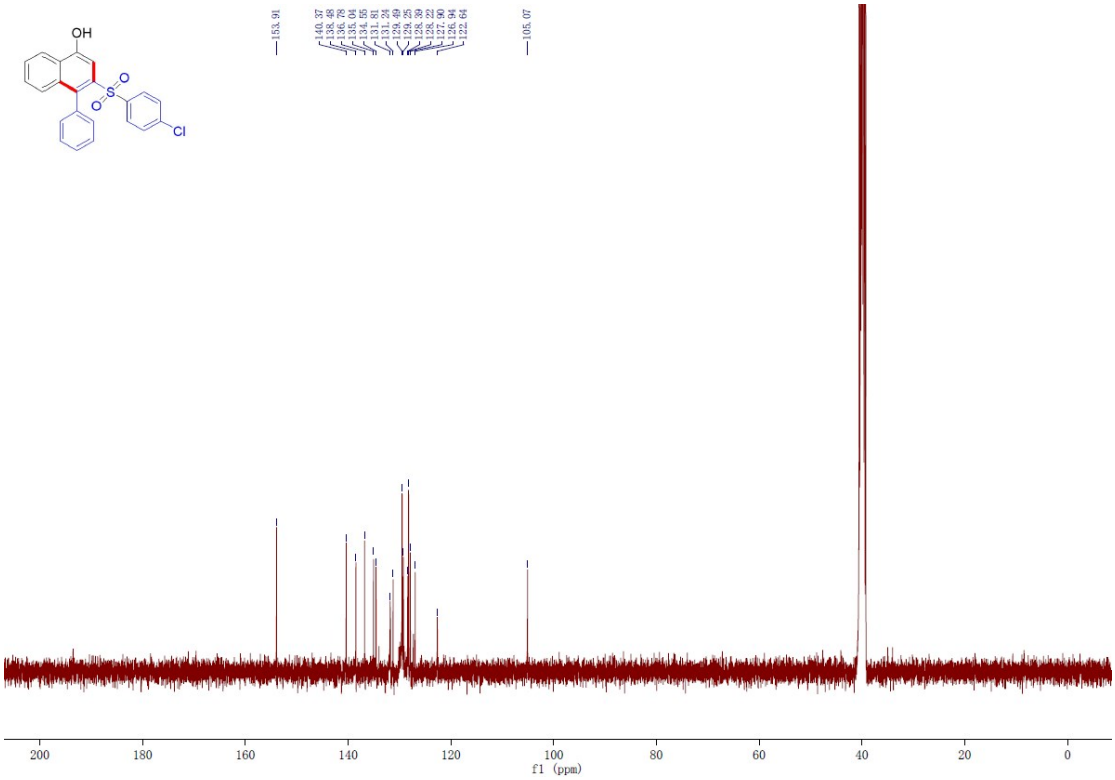
^{1}H NMR spectrum of compound **3af**



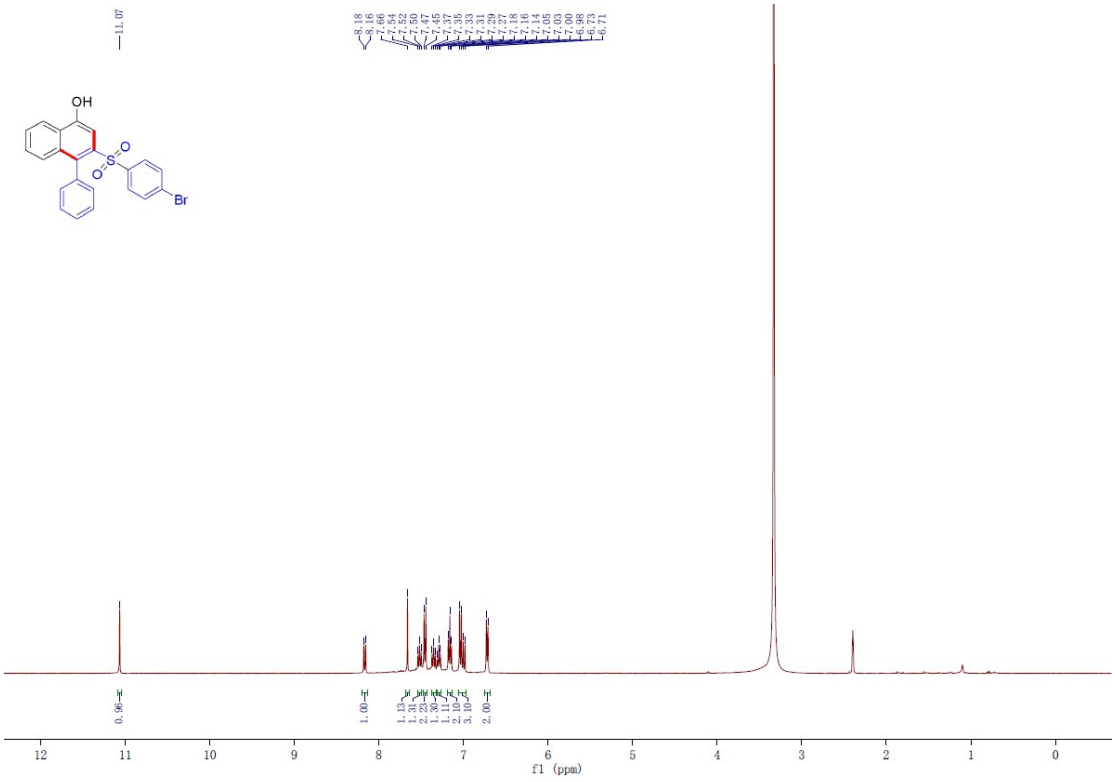
^{13}C NMR spectrum of compound **3af**



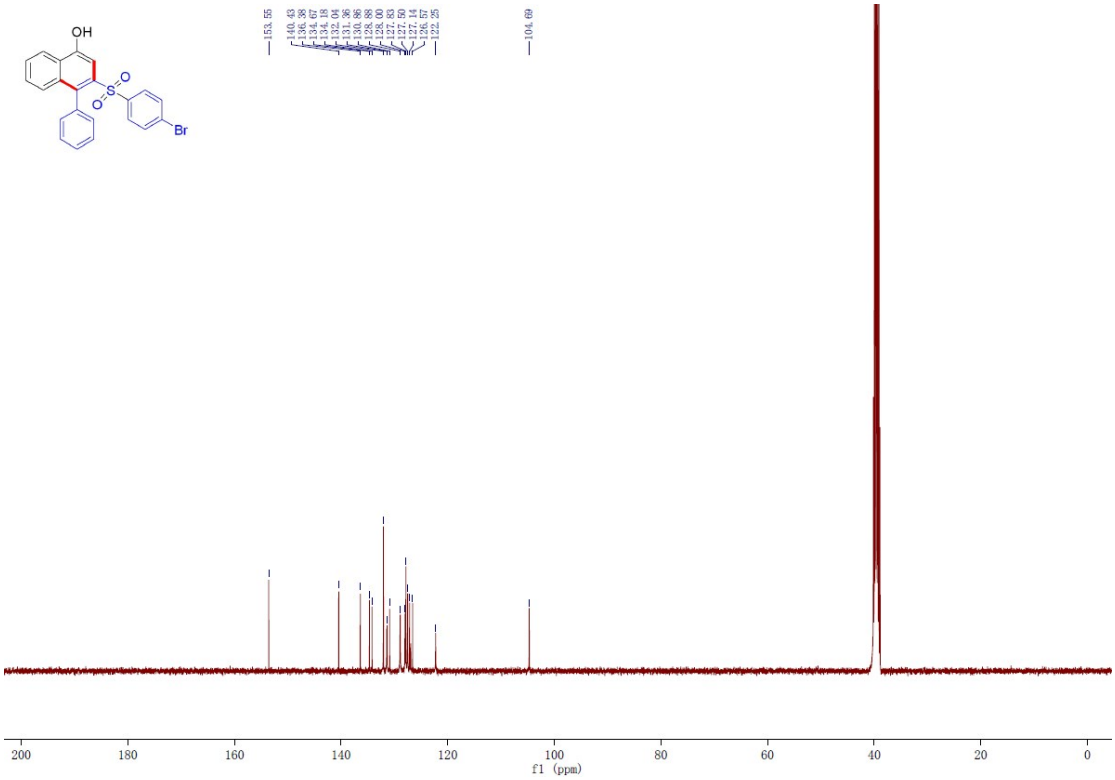
^{1}H NMR spectrum of compound **3ag**



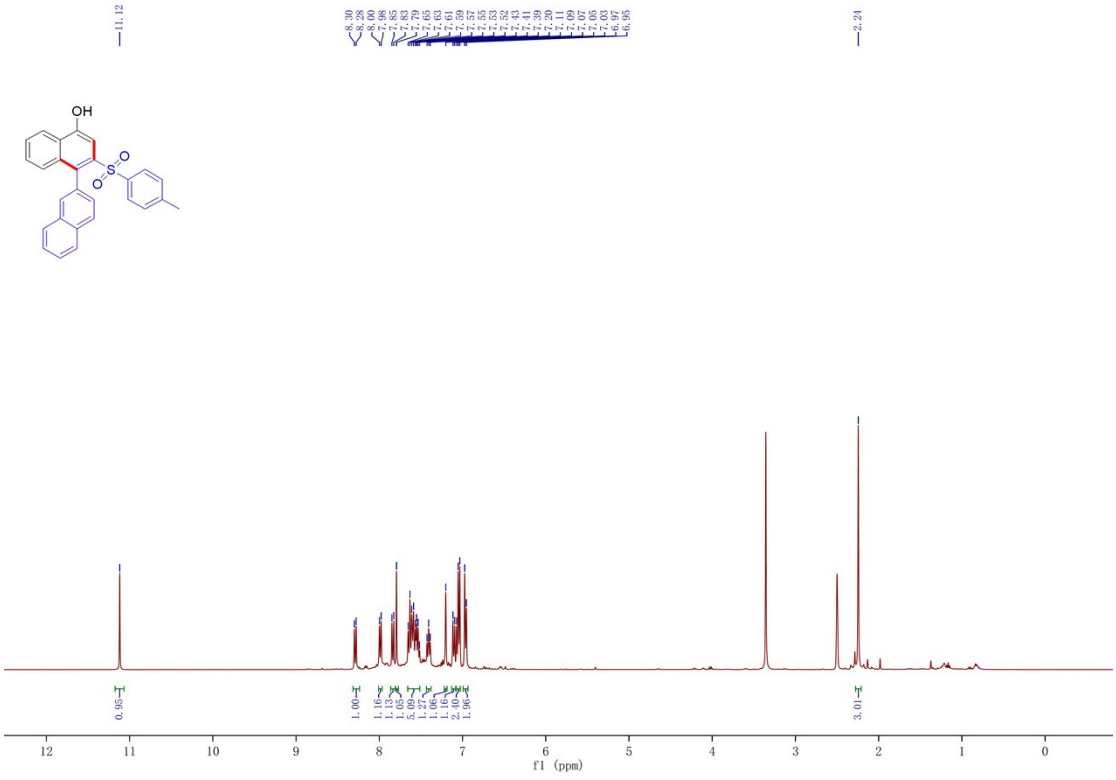
^{13}C NMR spectrum of compound **3ag**



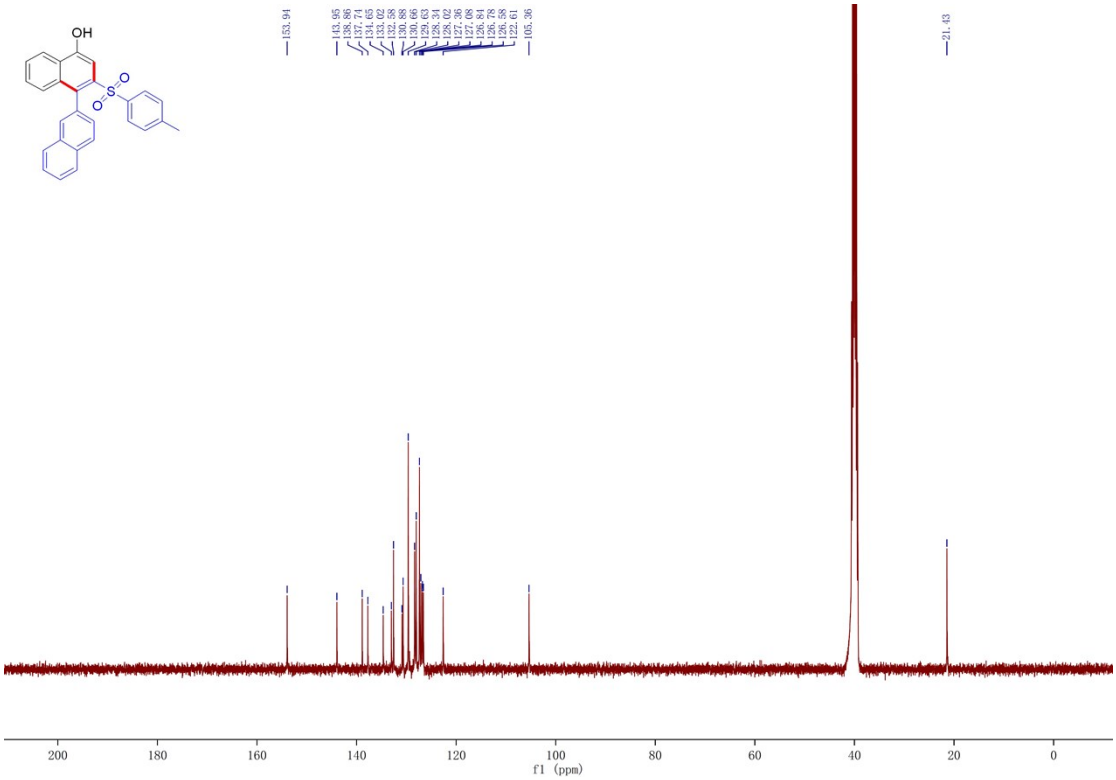
^{1}H NMR spectrum of compound **3ah**



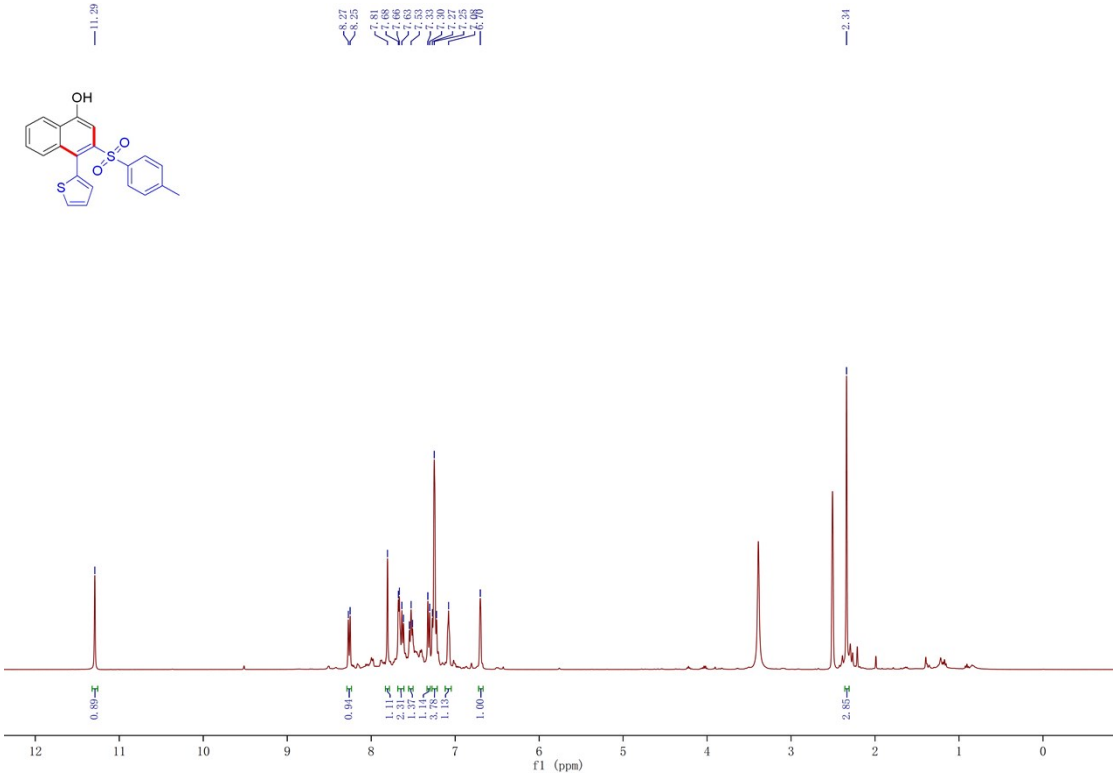
^{13}C NMR spectrum of compound **3ah**



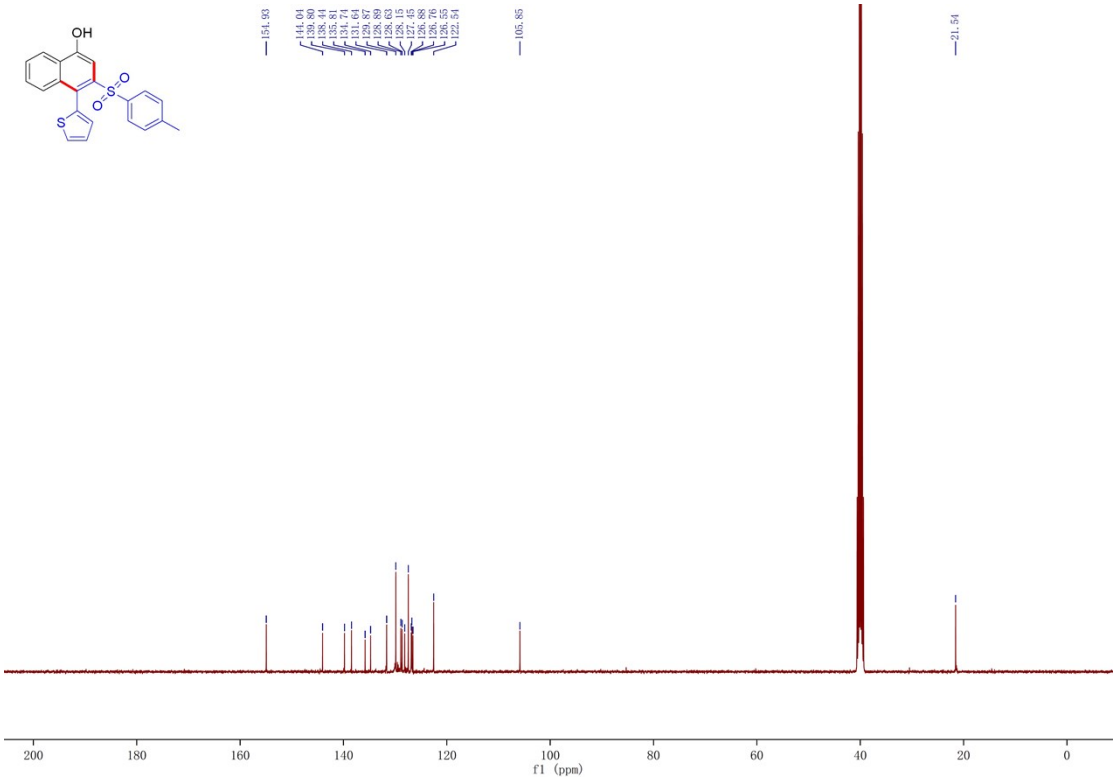
^{1}H NMR spectrum of compound **3aj**



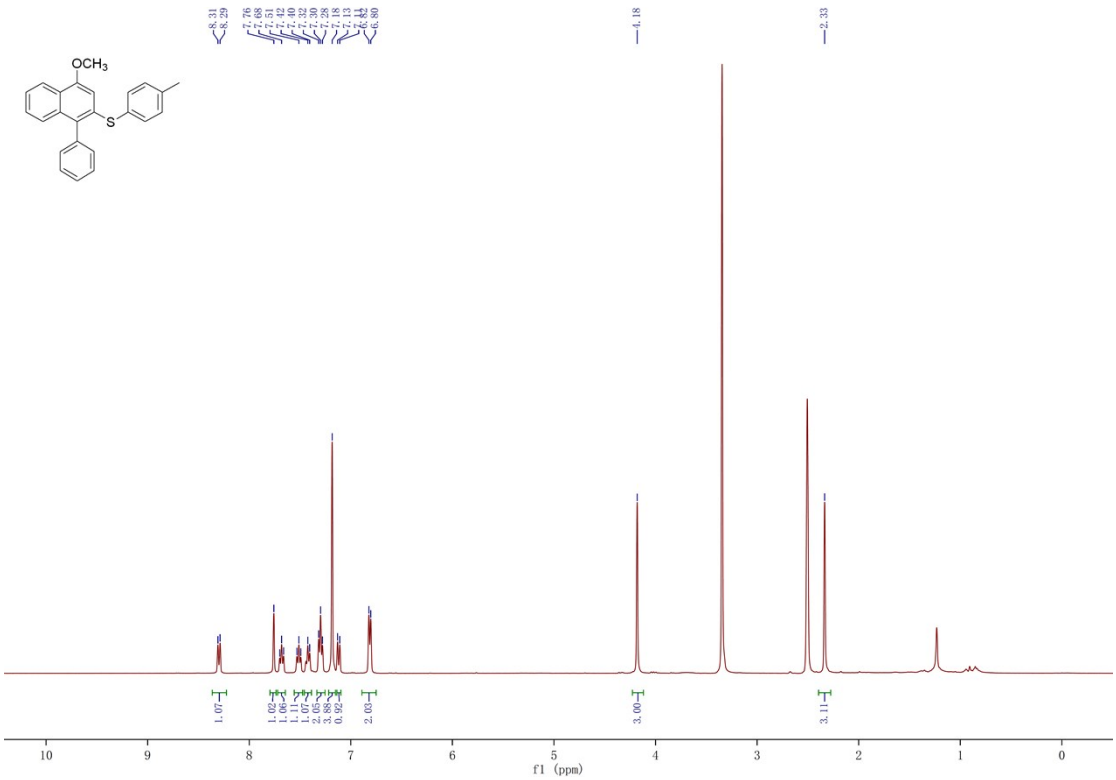
^{13}C NMR spectrum of compound **3aj**



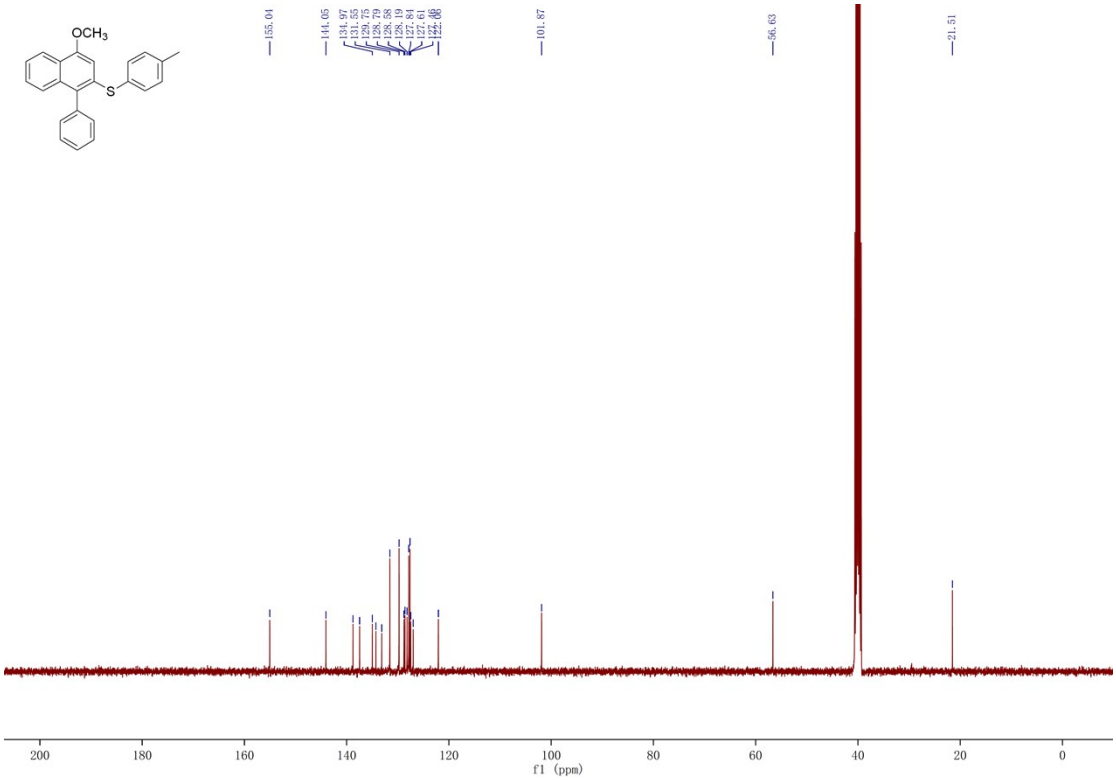
^{1}H NMR spectrum of compound **3ak**



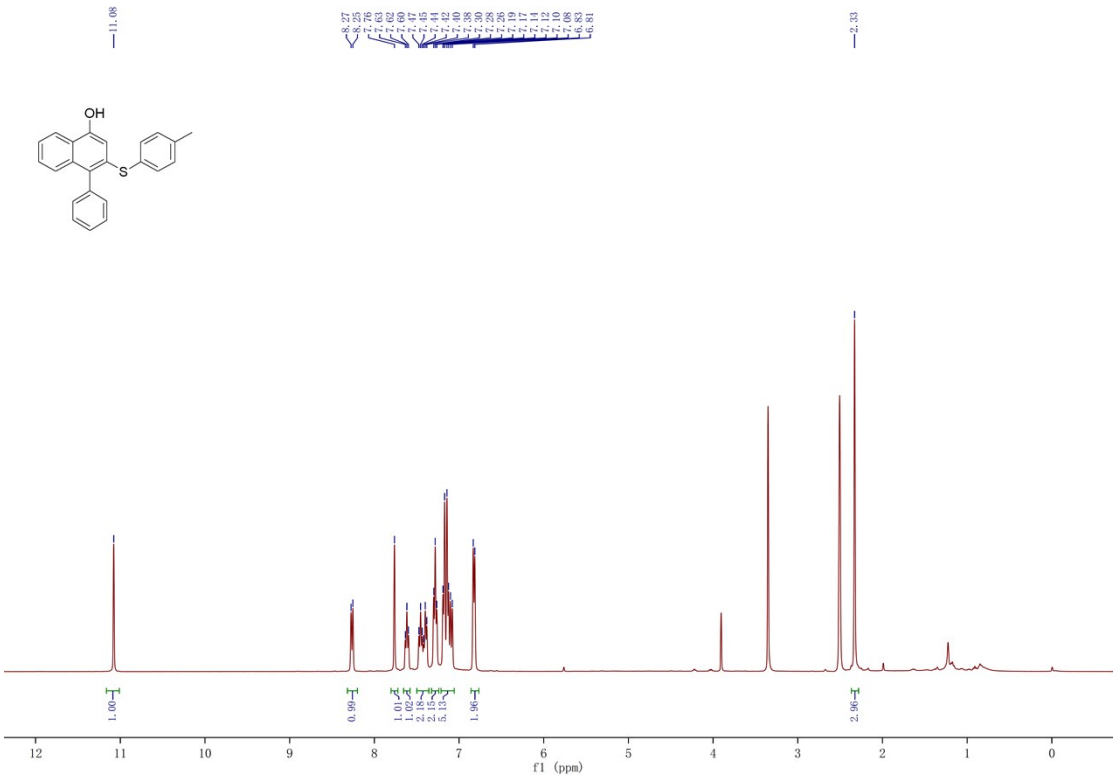
^{13}C NMR spectrum of compound **3ak**



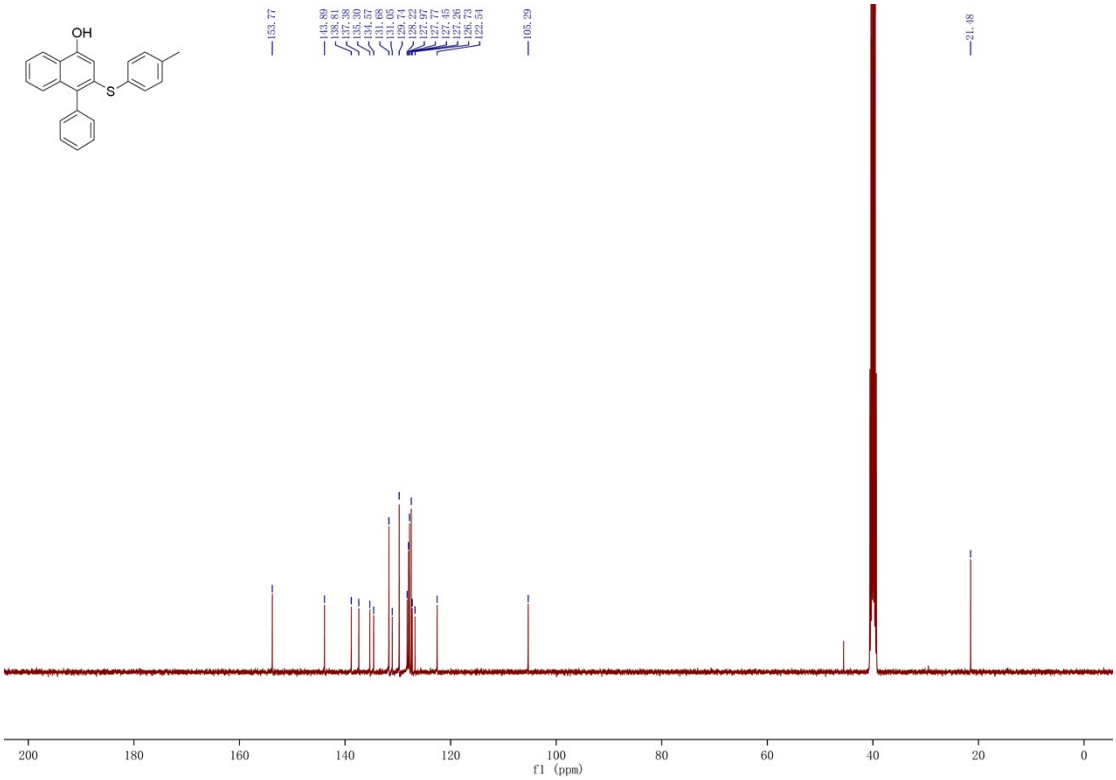
^{1}H NMR spectrum of compound **4a**



^{13}C NMR spectrum of compound **4a**



^{1}H NMR spectrum of compound **4b**



^{13}C NMR spectrum of compound **4b**

References:

[1] C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.,* 1992, **29**, 228.

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