Supporting Information

One-pot access to sulfonylated naphthalenediols/hydroquinones from naphthols/phenols with sodium sulfinates in an aqueous medium

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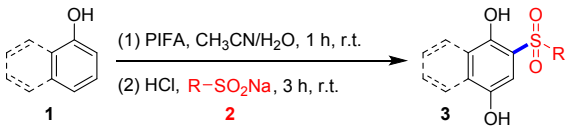
1. General Information

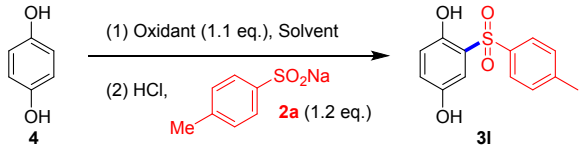
Unless otherwise mentioned, all the reagents and solvents were purchased from commercial sources and used without further purification. Reaction progress and product mixtures were routinely monitored by TLC, and compounds were visualized under ultraviolet light at 254 nm. The products were isolated by column chromatography on silica gel (200-300 mesh) by using petroleum ether and ethyl acetate as eluents. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. The spectra were recorded using DMSO-d_6 as a solvent. ^{1}H NMR chemical shifts are referenced to tetramethylsilane (TMS, 0 ppm). NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quarter, m = multiplet, br = broad), coupling (*J*) constant and integration. Melting points were measured on an XT4 microscopic apparatus uncorrected. IR spectra were recorded on Thermo Scientific Nicolet iS5 Fourier transform infrared spectrometer by dispersing samples in potassium bromide. The high-resolution mass spectra (HR-MS) was measured using the Agilent 1290 Infinity LC & 6540 UHD Q-TOF mass spectrometer.

2. General Synthetic Procedure for Products 3



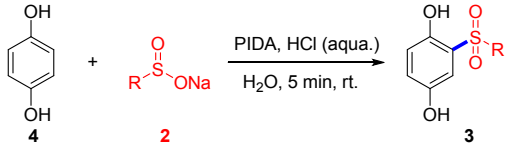
Sulfonylation of 1-naphthalenol and phenols: To a flask, the substrate **1** (0.30 mmol) was dropwise added to a solution of PIFA (283.8 mg, 0.66 mmol) in 3.0 mL of CH_3CN/H_2O (v/v=2:1), then the mixture was stirred at room temperature for 1 h under an ambient atmosphere. After that, the conc. HCl (25 μL, 0.30 mmol) and sodium sulfinates **2** (0.36 mmol) were added separately, and the reaction mixture was stirred at room temperature for 3 h. After completion of reaction monitored by TLC, the reaction mixture was diluted with 5 mL saturated brine and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate: 10/1~2/1) to afford desired products **3a-r**.

Optimazation for sulfonylation of hydroquinone **4**



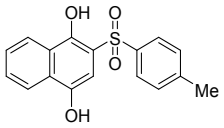
Entry[a]	Oxidant	Solvent	Time	Yield (%)[b]
1	PIDA	H_2O	3 h	88
2	*m*-CPBA	H_2O	3 h	34
3	PIFA	H_2O	3 h	63
4	H_2O_2	H_2O	3 h	N.R.
5	$K_2S_2O_8$	H_2O	3 h	N.R.
6	TBHP	H_2O	3 h	N.R.
7	PIDA	MeOH	3 h	92
8[c]	**PIDA**	**H_2O**	**5 min**	**97**
9[c]	PIFA	H_2O	5 min	38

[a] Reaction conditions: Hydroquinone **4** (0.30 mmol), oxidant (0.33 mmol, 1.1 equiv.), solvent (3.0 mL) were added to a flask and stirred at room temperature for 1 h under air; then the aqueous HCl (0.30 mmol, 1.0 equiv.), 4-methylbenzenesulfinate **2a** (0.36 mmol, 1.2 equiv.) were added, and the mixture was stirred for 3 h to generate the product. [b] Isolated yields after column chromatography; N.R. means no reaction. [c] Hydroquinone **4** (33.0 mg, 0.30 mmol) was dropwise added to oxidant (0.33 mmol) in 3.0 mL H_2O in a flask. Then conc. HCl (0.30 mmol) and **2a** (0.36 mmol) were sequentially added and the reaction mixture was stirred at room temperature for 5 min.

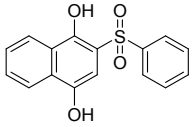


Sulfonylation of hydroquinone 4: Hydroquinone **4** (33.0 mg, 0.30 mmol) was dropwise added to a suspension of PIDA (106.3 mg, 0.33 mmol) in 3.0 mL H_2O in a flask. Then conc. HCl (25 μL, 0.30 mmol) and sodium sulfinates **2** (0.36 mmol) were sequentially added and the reaction mixture was stirred at room temperature under an ambient atmosphere for 5 min. The reaction mixture was diluted with 5 mL saturated brine and extracted with ethyl acetate (3 × 30 mL). The organic extracts were dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate: 6/1~2/1) to afford desired products **3k-p, 3s-w**.

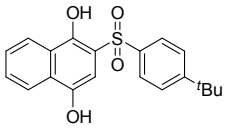
The yield of product **3a-j** is based on 1-naphthalenol **1a**. The yields of product **3k-p**, **3s-w** is based on hydroquinone **4** and **3q-r** is based on 2,5-dimethylphenol and 2,6-dimethylphenol, respectively.



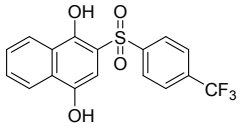
2-tosylnaphthalene-1,4-diol (3a): known compound[1], 85.9 mg, 91% yield, faint yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.20 (br, 1H), 10.02 (br, 1H), 8.18 (d, J = 7.1 Hz, 1H), 8.13 (d, J = 6.9 Hz, 1H), 7.85 (dd, J = 7.9, 5.9 Hz, 2H), 7.67 – 7.55 (m, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.26 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.7, 145.9, 144.2, 139.5, 130.0, 128.8, 128.7, 127.9, 127.2, 126.7, 123.6, 122.8, 121.3, 104.1, 21.5.



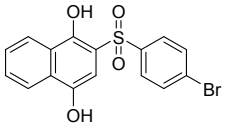
2-(phenylsulfonyl)naphthalene-1,4-diol (3b): known compound[2], 74.3 mg, 81% yield, light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.28 (br, 1H), 10.13 (br, 1H), 8.21 (dd, J = 15.3, 8.1 Hz, 2H), 8.02 – 8.00 (m, 2H), 7.69 – 7.53 (m, 5H), 7.41 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.9, 146.1, 142.4, 133.7, 129.6, 128.9, 128.8, 127.8, 127.2, 126.8, 123.7, 122.9, 121.2, 104.2.



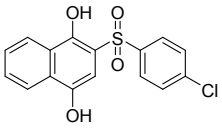
2-((4-(*tert*-butyl)phenyl)sulfonyl)naphthalene-1,4-diol (3c): known compound[1], 81.6 mg, 78% yield, brown red solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.21 (br, 1H), 10.04 (br, 1H), 8.20 (d, J = 8.2 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.28 (s, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.8, 146.8, 145.9, 139.5, 128.8, 128.7, 127.7, 127.2, 126.7, 126.5, 123.7, 122.9, 121.1, 104.2, 35.4, 31.2.



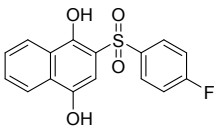
2-((4-(trifluoromethyl)phenyl)sulfonyl)naphthalene-1,4-diol (3d): known compound[3], 96.8 mg, 88% yield, light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.30 (br, 1H), 10.25 (br, 1H), 8.19 – 8.14 (m, 4H), 7.98 (d, J = 8.4 Hz, 2H), 7.65 (t, J = 7.0 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.36 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.5, 145.9, 132.9, 132.6, 128.6, 128.5, 126.8, 126.4, 126.3, 126.3, 126.1, 123.3, 122.5, 120.6, 103.6. ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.7.



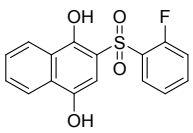
2-((4-bromophenyl)sulfonyl)naphthalene-1,4-diol (3e): unknown compound, 108.7 mg, 96% yield, brown solid, mp: 207-210 °C; IR (KBr): 3449, 3326, 1601, 1575, 1469, 1454, 1314, 1272, 1132, 1068, 628, 557 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.35 (br, 1H), 10.25 (br, 1H), 8.24 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 7.71 – 7.56 (m, 2H), 7.43 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.0, 146.2, 141.7, 132.6, 130.0, 129.0, 128.8, 127.7, 127.3, 126.9, 123.8, 123.0, 121.4, 104.1.



2-((4-chlorophenyl)sulfonyl)naphthalene-1,4-diol (3f): known compound[1], 84.5 mg, 85% yield, brown red solid; ^1H NMR (400 MHz, DMSO-d_6) δ 10.32 (br, 1H), 10.23 (br, 1H), 8.21 (d, J = 4.1 Hz, 2H), 8.02 (d, J = 3.7 Hz, 2H), 7.72 – 7.58 (m, 4H), 7.40 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.0, 146.1, 141.3, 138.7, 130.0, 129.7, 129.0, 128.8, 127.2, 126.9, 123.8, 123.0, 121.4, 104.1.

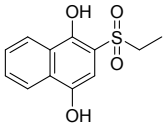


2-((4-fluorophenyl)sulfonyl)naphthalene-1,4-diol (3g): known compound[1], 83.0 mg, 88% yield, brown solid; ^1H NMR (400 MHz, DMSO-d_6) δ 10.24 (br, 1H), 10.14 (br, 1H), 8.19 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.04 (dd, J = 8.9, 5.2 Hz, 2H), 7.67 – 7.56 (m, 2H), 7.45 (t, J = 8.8 Hz, 2H), 7.31 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.1 (d, J = 252.0 Hz), 146.8, 145.9, 138.7 (d, J = 2.9 Hz), 131.1 (d, J = 9.8 Hz), 128.9, 128.8, 127.2, 126.8, 123.3 (d, J = 78.8 Hz), 121.5, 116.8, 116.6, 104.1. ^{19}F NMR (376 MHz, DMSO-d_6) δ -105.7.

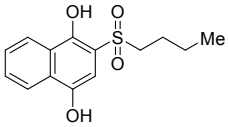


2-((2-fluorophenyl)sulfonyl)naphthalene-1,4-diol (3h): unknown compound, 89.7 mg, 94% yield, red solid, mp: 190-193 °C; IR (KBr): 3425, 3351, 1598, 1579, 1471, 1454, 1321, 1281, 1139, 1118, 1071, 698, 616 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.25 (br, 1H), 10.12 (br, 1H), 8.16 (q, J = 9.8,

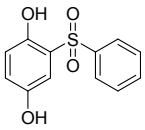
9.1 Hz, 3H), 7.77 – 7.70 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.36 – 7.31 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.4 (d, *J* = 254.1 Hz), 146.1, 145.9, 136.2 (d, *J* = 8.6 Hz), 130.4, 129.6 (d, *J* = 13.6 Hz), 128.5 (d, *J* = 14.0 Hz), 126.7, 126.2, 124.8 (d, *J* = 3.5 Hz), 123.3, 122.5, 120.8, 117.1 (d, *J* = 20.7 Hz), 103.8. ^{19}F NMR (376 MHz, DMSO-d_6) δ -110.6. HRMS (ESI) m/z: calcd for $C_{16}H_{12}O_4FS$ $[M+H]^+$: 319.0440, found: 319.0438.



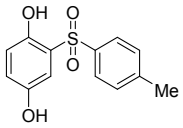
2-(ethylsulfonyl)naphthalene-1,4-diol (3i): unknown compound, 63.7 mg, 84% yield, yellow solid, mp:117-120 °C; IR (KBr): 3444, 3307, 2924, 2853, 1660, 1603, 1587, 1330, 1302, 1146, 1054, 771, 690, 610, 557 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.18 (br, 1H), 10.14 (br, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 2.1 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.11 (s, 1H), 3.48 (q, *J* = 7.3 Hz, 2H), 1.13 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.8, 145.9, 128.7, 128.6, 127.2, 126.8, 123.7, 122.9, 119.2, 104.6, 49.2, 7.6.



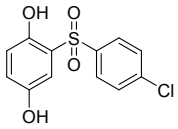
2-(butylsulfonyl)naphthalene-1,4-diol (3j): known compound[1,3], 69.4 mg, 83% yield, light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (br, 1H), 10.12 (br, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.12 (s, 1H), 3.52 – 3.43 (m, 2H), 1.54 (p, *J* = 7.5 Hz, 2H), 1.33 (h, *J* = 7.3 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.8, 145.9, 128.7, 128.6, 127.2, 126.9, 123.7, 122.9, 119.8, 104.5, 54.5, 24.9, 21.3, 13.9.



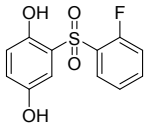
2-(phenylsulfonyl)benzene-1,4-diol (3k): known compound[4,5], 69.1 mg, 92% yield, light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (br, 1H), 9.43 (br, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.36 (s, 1H), 6.94 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.0, 148.7, 141.8, 133.6, 129.3, 128.2, 126.5, 123.4, 119.0, 114.3.



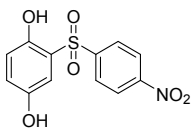
2-tosylbenzene-1,4-diol (3l): known compound[2], 78.1 mg, 97% yield, light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (br, 1H), 9.39 (br, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 3.1 Hz, 1H), 6.91 (dd, J = 8.8, 3.0 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.9, 148.6, 144.0, 139.0, 129.7, 128.3, 126.8, 123.2, 119.0, 114.2, 21.5.



2-((4-chlorophenyl)sulfonyl)benzene-1,4-diol (3m): known compound[4], 78.1 mg, 91% yield, faint yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.08 (br, 1H), 9.46 (br, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.37 (s, 1H), 6.96 (dd, J = 8.9, 2.7 Hz, 1H), 6.78 (d, J = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.7, 148.3, 140.2, 138.3, 129.9, 129.1, 125.7, 123.3, 118.7, 113.9.

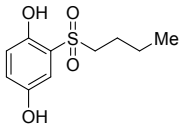


2-((2-fluorophenyl)sulfonyl)benzene-1,4-diol (3n): unknown compound, 57.6 mg, 70% yield, light yellow solid, mp: 237-241 ^{o}C; IR (KBr): 3286, 3103, 1598, 1507, 1473, 1460, 1362, 1295, 1218, 1146, 1075, 603, 518 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (br, 1H), 9.47 (br, 1H), 8.03 (td, J = 7.6, 1.8 Hz, 1H), 7.73 (tdd, J = 7.4, 5.0, 1.8 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.39 – 7.29 (m, 2H), 6.95 (dd, J = 8.8, 3.0 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.8 (d, J = 254.2 Hz), 149.8, 148.7, 136.6 (d, J = 8.6 Hz), 131.4, 129.4 (d, J = 13.5 Hz), 126.1, 125.0 (d, J = 3.6 Hz), 123.8, 118.9, 117.4 (d, J = 20.8 Hz), 114.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -110.8. HRMS (ESI) m/z: calcd for $C_{12}H_{10}O_4SF$ $[M+H]^+$: 269.0284, found: 269.0280.

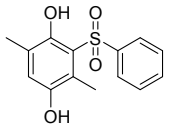


2-((4-nitrophenyl)sulfonyl)benzene-1,4-diol (3o): known compound[3], 68.4 mg, 78% yield, light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.20 (br, 1H), 9.51 (br, 1H), 8.39 (d, J = 8.8 Hz, 2H),

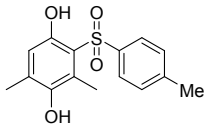
8.14 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 3.0 Hz, 1H), 6.97 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 150.1, 148.9, 147.1, 129.9, 125.1, 124.7, 124.3, 119.1, 114.2.



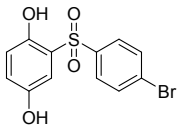
2-(butylsulfonyl)benzene-1,4-diol (3p): unknown compound, 58.7 mg, 85% yield, white solid, mp: 97-100 °C; IR (KBr): 3367, 3345, 2969, 2870, 1502, 1467, 1318, 1270, 1116, 1055, 729, 635, 564, 523 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (br, 1H), 9.33 (br, 1H), 7.10 (d, *J* = 2.9 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 3.36 (t, *J* = 1.7 Hz, 2H), 1.48 (p, *J* = 7.8, 7.4 Hz, 2H), 1.32 (h, *J* = 7.3 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.6, 148.1, 124.7, 122.4, 118.4, 114.2, 52.8, 24.3, 20.8, 13.4. HRMS (ESI) m/z: calcd for $C_{10}H_{15}O_4S$ $[M+H]^+$: 231.0691, found: 231.0684.



2,5-dimethyl-3-(phenylsulfonyl)benzene-1,4-diol (3q): known compound[3], 65.8 mg, 80% yield, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.72 (br, 1H), 9.29 (br, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.72 (t, *J* = 7.3 Hz, 1H), 7.63 (t, *J* = 7.4 Hz, 2H), 6.98 (s, 1H), 2.13 (d, *J* = 2.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.5, 148.4, 142.3, 134.1, 129.9, 126.6, 125.8, 124.4, 121.8, 120.8, 16.5, 12.7.

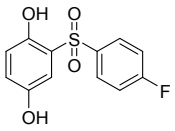


3,5-dimethyl-2-tosylbenzene-1,4-diol (3r): known compound[6], 59.2 mg, 68% yield, light orange solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (br, 1H), 8.11 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 6.59 (br, 1H), 2.36 (d, *J* = 6.3 Hz, 6H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 146.6, 144.0, 140.5, 135.2, 129.9, 127.0, 125.7, 121.0, 117.3, 21.4, 17.7, 13.6.

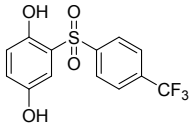


2-((4-bromophenyl)sulfonyl)benzene-1,4-diol (3s): known compound[2], 90.2 mg, 91% yield, faint

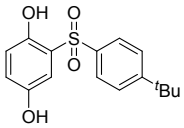
yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (br, 1H), 9.46 (br, 1H), 7.85 – 7.77 (m, 4H), 7.34 (d, J = 5.1 Hz, 1H), 6.95 (d, J = 3.0 Hz, 1H), 6.77 (d, J = 3.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.0, 148.7, 141.0, 132.4, 130.4, 127.7, 126.0, 123.7, 119.1, 114.2.



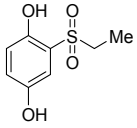
2-((4-fluorophenyl)sulfonyl)benzene-1,4-diol (3t): known compound[2], 74.9 mg, 93% yield, faint yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.07 (br, 1H), 9.45 (br, 1H), 7.99 (dd, J = 8.1, 5.2 Hz, 2H), 7.44 – 7.35 (m, 3H), 6.96 (dd, J = 8.6, 2.6 Hz, 1H), 6.78 (d, J = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.1 (d, J = 252.3 Hz), 150.0, 148.6, 138.1 (d, J = 2.9 Hz), 131.5 (d, J = 9.7 Hz), 126.4, 123.5, 119.0, 116.4 (d, J = 22.8 Hz), 114.2. ^{19}F NMR (376 MHz, DMSO-d_6) δ -105.8.



2-((4-(trifluoromethyl)phenyl)sulfonyl)benzene-1,4-diol (3u): known compound[2], 95.0 mg, 96% yield, light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.11 (br, 1H), 9.47 (br, 1H), 8.09 (d, J = 8.2 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 3.0 Hz, 1H), 6.95 (dd, J = 8.8, 3.0 Hz, 1H), 6.75 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.6, 148.4, 145.2, 132.8 (q, J = 32.2 Hz), 128.8, 126.1 (d, J = 3.7 Hz), 124.9 (d, J = 18.8 Hz), 123.6, 122.1, 118.7, 113.8. ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.7.

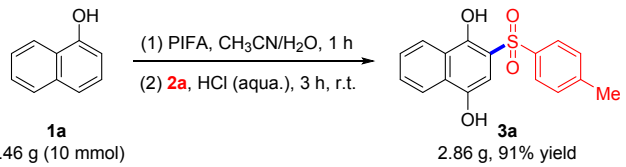


2-((4-(tert-butyl)phenyl)sulfonyl)benzene-1,4-diol (3v): known compound[2], 77.8 mg, 88% yield, faint yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.92 (br, 1H), 9.38 (br, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 3.0 Hz, 1H), 6.91 (dd, J = 8.7, 3.0 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.6, 149.9, 148.6, 139.0, 128.2, 126.8, 126.2, 123.2, 119.0, 114.3, 35.4, 31.2.



2-(ethylsulfonyl)benzene-1,4-diol (3w): known compound[2], 50.9 mg, 83% yield, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (br, 1H), 9.38 (br, 1H), 7.12 (d, J = 4.3 Hz, 1H), 6.93 (d, J = 3.0 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 3.37 (dd, J = 13.6, 6.9 Hz, 2H), 1.09 (t, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.0, 148.6, 124.4, 122.9, 118.8, 114.8, 48.0, 7.4.

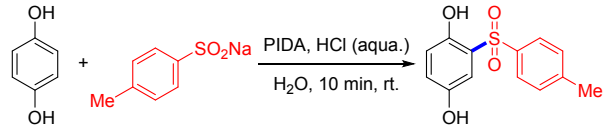
3. Scaled-up Experiments



1a
1.46 g (10 mmol)

3a
2.86 g, 91% yield

To a solution of PIFA (9.65 g, 22 mmol) in 40 mL CH_3CN/H_2O (v/v=2/1) was added dropwise a solution of 1-naphthalenol **1** (1.46 g, 10 mmol) in a 250 mL round bottom flask in 40 mL CH_3CN/H_2O (v/v=2/1), stirred at room temperature for 1 h under an ambient atmosphere. Then HCl (10 mmol) and sodium 4-methylbenzenesulfinate **2a** (2.18 g, 12 mmol) in 20 mL CH_3CN/H_2O (v/v=2/1) was added dropwise into the mixture. After stirring at room temperature for 3 h, the mixture was quenched with saturated aq. $NaHCO_3$ and concentrated to ca. 25 mL under a reduced pressure. The mixture was filtered, and the filter residue was washed with water and petroleum ether. Then the residue was redissolved in ethanol, concentrated to dryness on a rotary evaporator to afford product **3a** (2.86 g) in 91% yield.



4
1.23 g (10 mmol)

2a

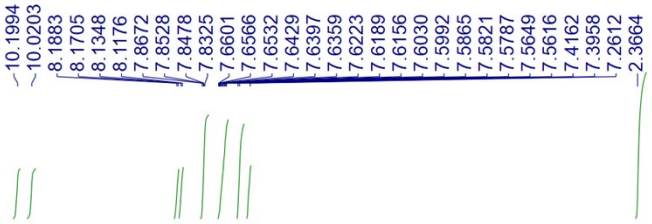
3l
2.56 g, 97% yield

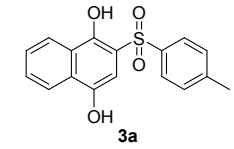
To a suspension of PIDA (3.65 g, 11 mmol) in 40 mL H_2O was added dropwise a solution of hydroquinone **4** (1.12 g, 10 mmol) in a 250 mL round bottom flask in 40 mL H_2O, stirred at room temperature. Then HCl (10 mmol) and sodium 4-methylbenzenesulfinate **2a** (2.18 g, 12 mmol) in 20 mL H_2O was added dropwise into the mixture at room temperature under an ambient atmosphere. Right after the addition of the reagents, the mixture was quenched with saturated aq. $NaHCO_3$. The mixture was filtered, and the filter residue was washed with water and hexane. Then the residue was redissolved in ethanol, concentrated to dryness on a rotary evaporator to afford product **3l** (2.56 g) in 97% yield.

4. References

1. P.-G. Li, Y.-C. Li, T. Zhu, L.-H. Zou and Z. Wu, *Eur. J. Org. Chem.*, 2017, **2017**, 6081-6084.
2. J.-W. Yuan, S.-N. Liu and L.-B. Qu, *Tetrahedron*, 2017, **73**, 6763-6772.
3. B. Li, Y. Li, L. Yu, X. Wu and W. Wei, *Tetrahedron*, 2017, **73**, 2760-2765.
4. D. Nematollahi, S. Momeni and S. Khazalpour, *Electrochim. Acta*, 2014, **147**, 310-318.
5. S. Rouhani, A. Rostami, A. Salimi and O. Pourshiani, *Biochem. Eng. J.*, 2018, **133**, 1-11.
6. J. Yadav, B. Reddy, T. Swamy and N. Ramireddy, *Synthesis*, 2004, **11**, 1849-1853.

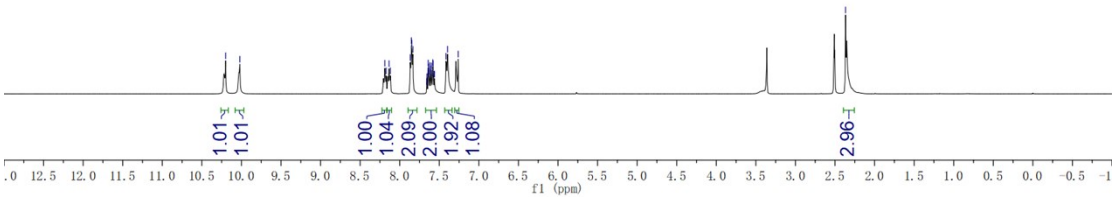
5. Copies of NMR spectra

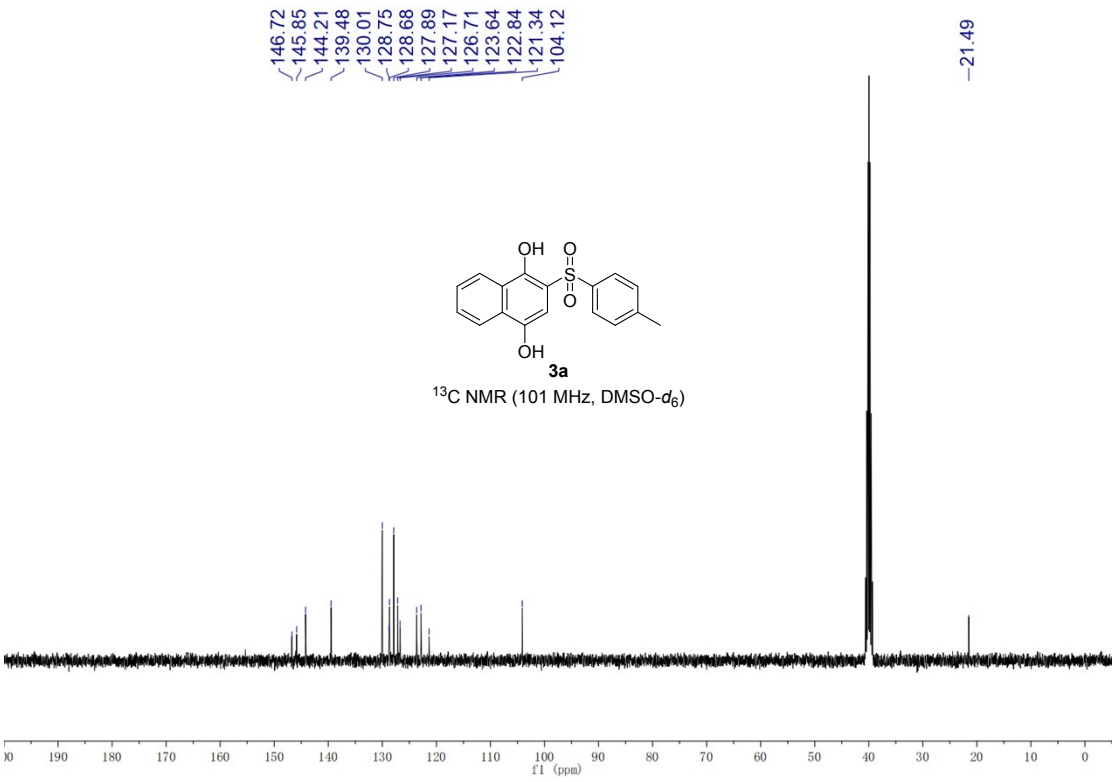




3a

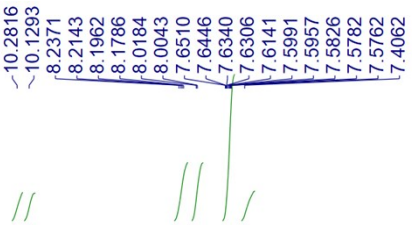
^{1}H NMR (400 MHz, DMSO-d_6)

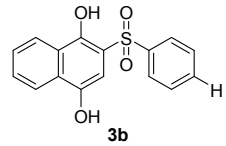




3a

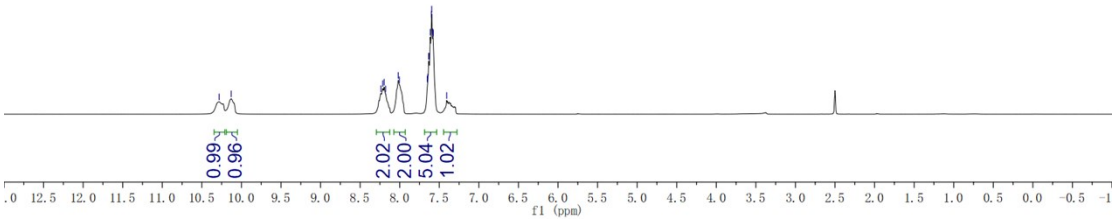
^{13}C NMR (101 MHz, DMSO-d_6)

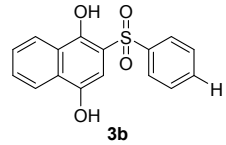




3b

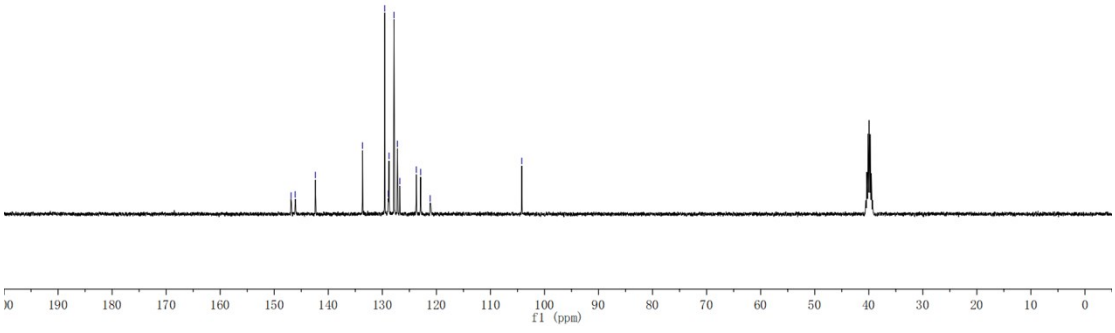
^{1}H NMR (400 MHz, DMSO-d_6)

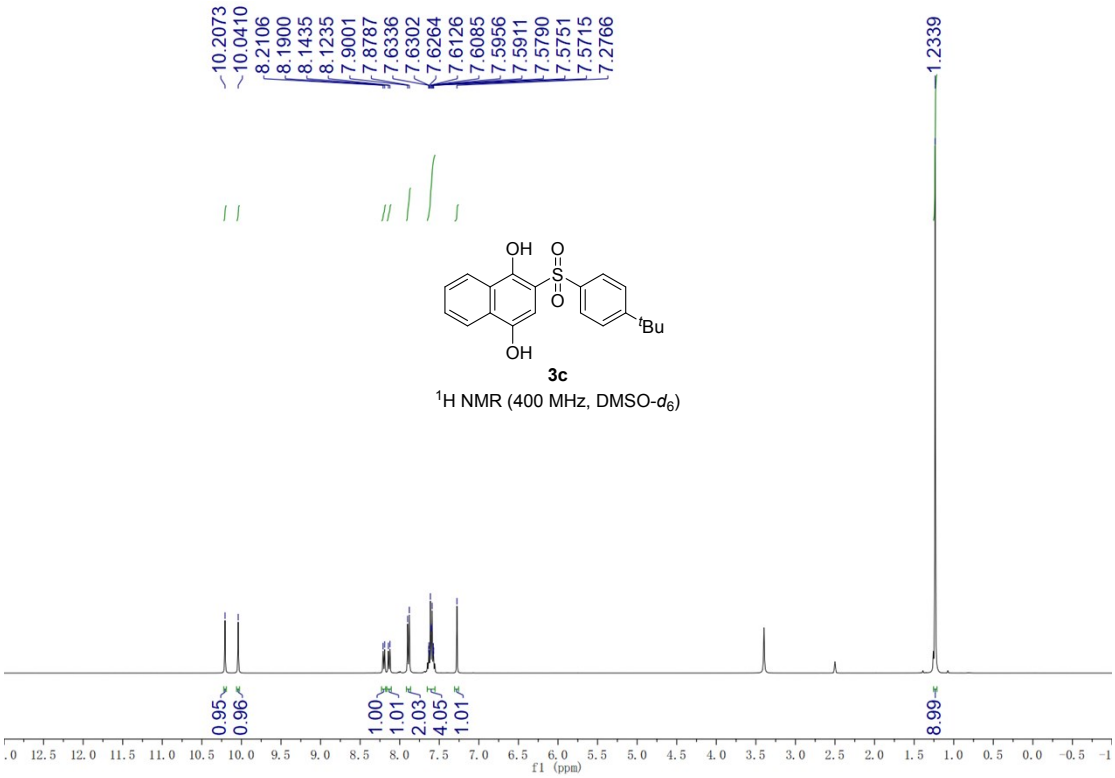




3b

^{13}C NMR (101 MHz, DMSO-d_6)





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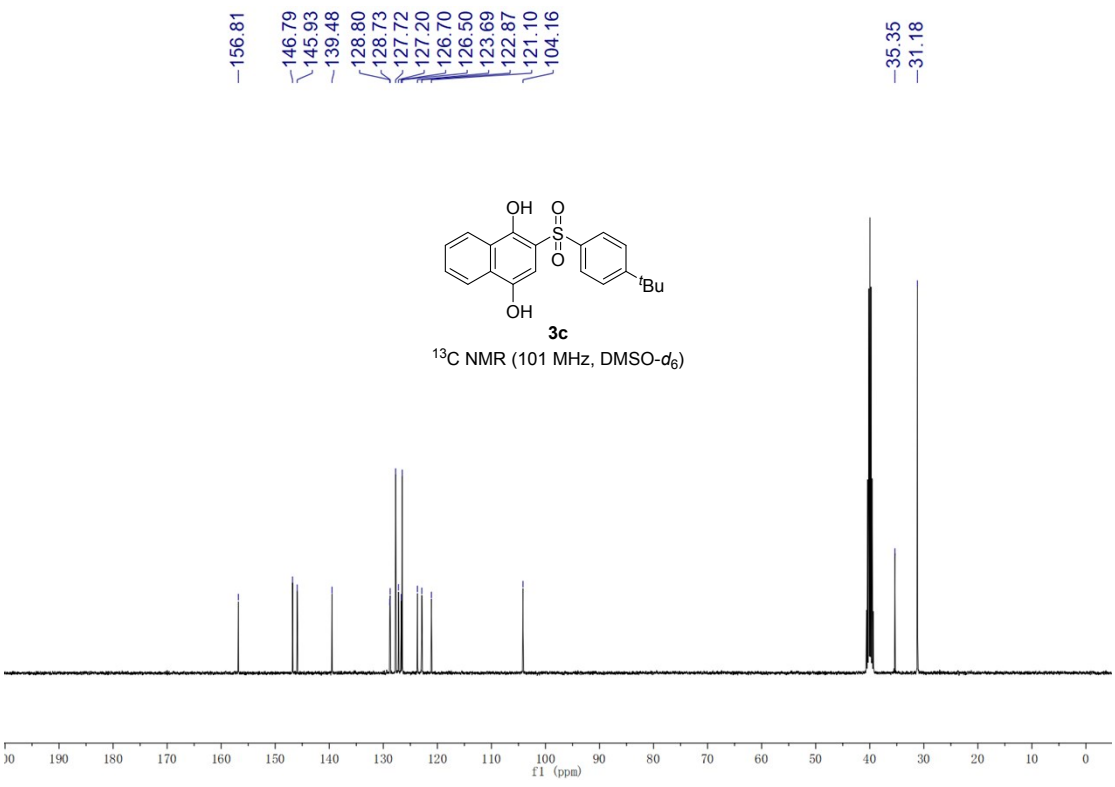
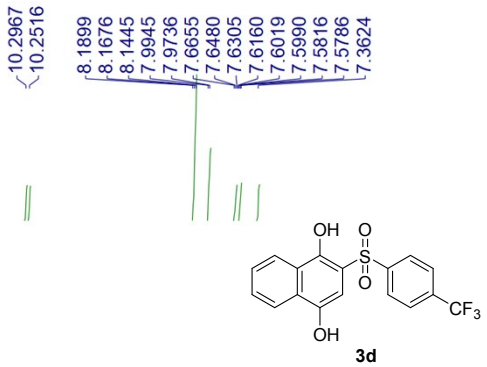
^{1}H NMR (400 MHz, DMSO-d_6)



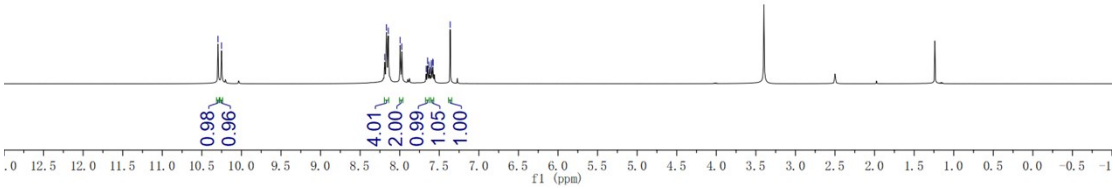
3c

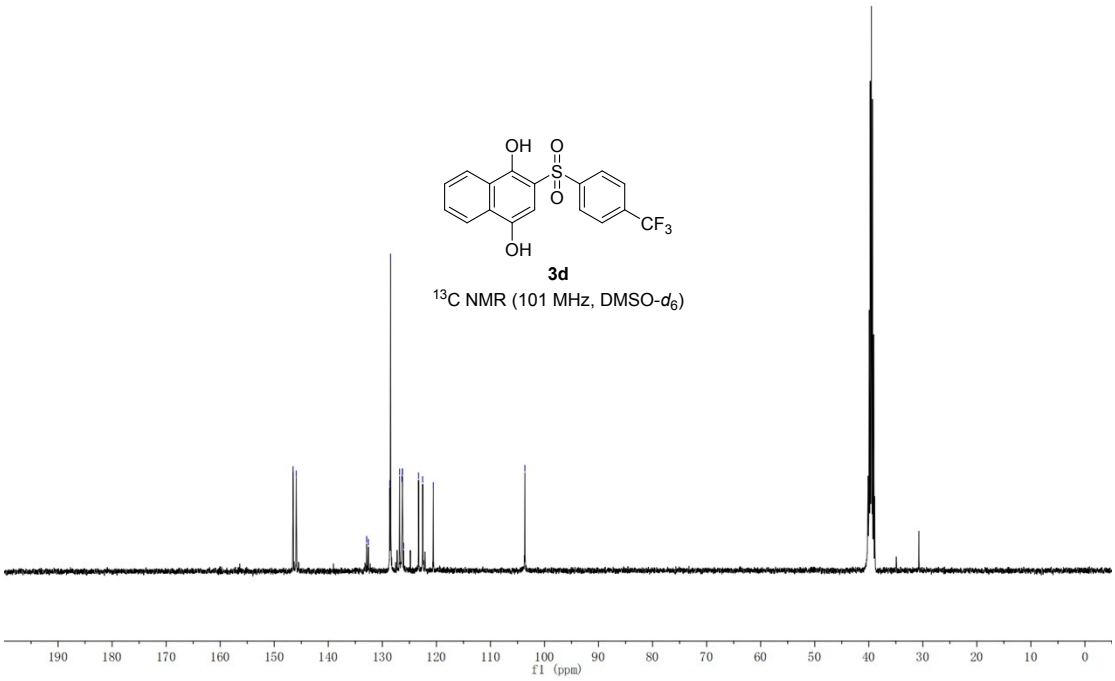
^{13}C NMR (101 MHz, DMSO-d_6)



3d

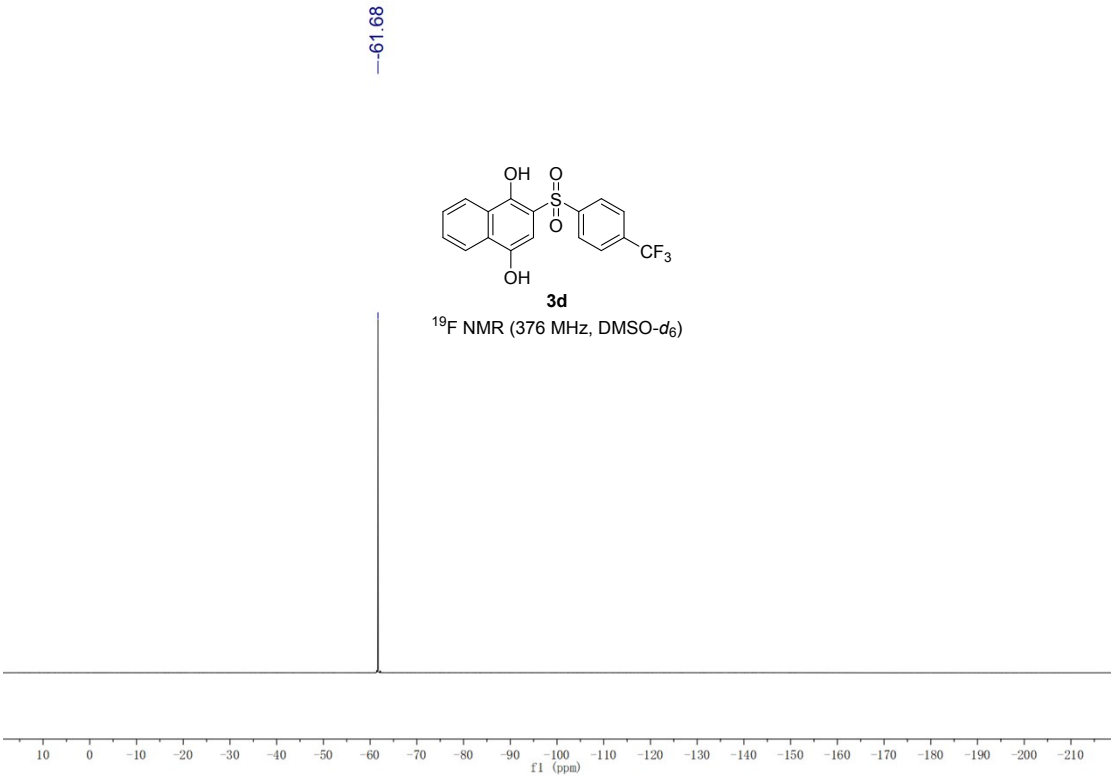
^{1}H NMR (400 MHz, DMSO-d_6)





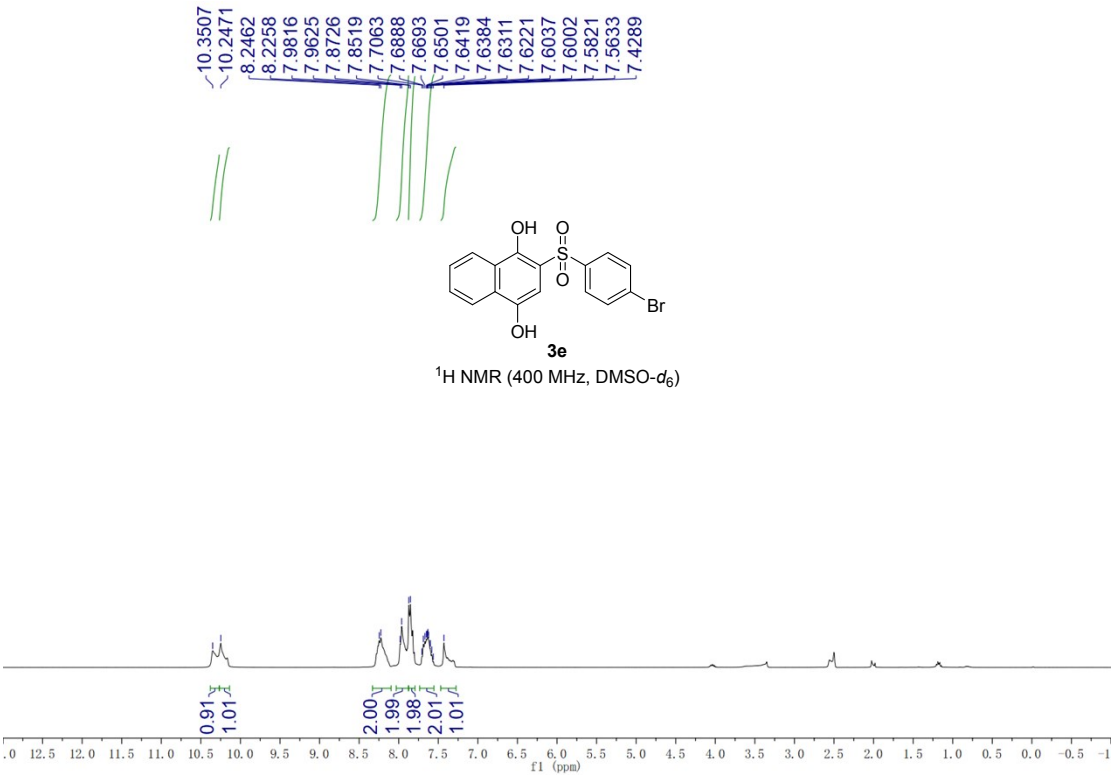
3d

^{13}C NMR (101 MHz, DMSO-d_6)



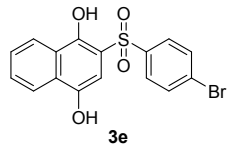
3d

^{19}F NMR (376 MHz, DMSO-d_6)



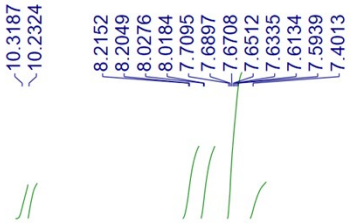
3e

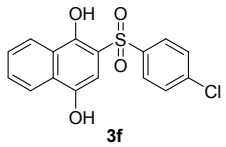
^{1}H NMR (400 MHz, DMSO-d_6)



3e

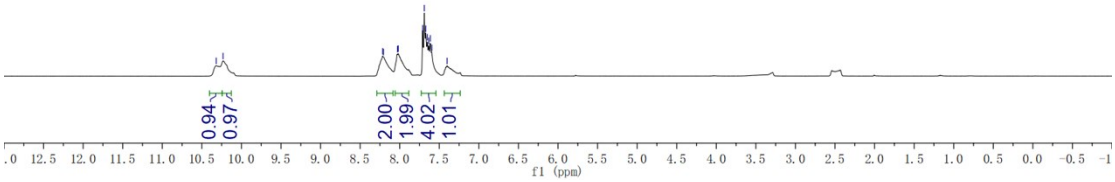
^{13}C NMR (101 MHz, DMSO-d_6)

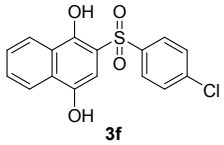




3f

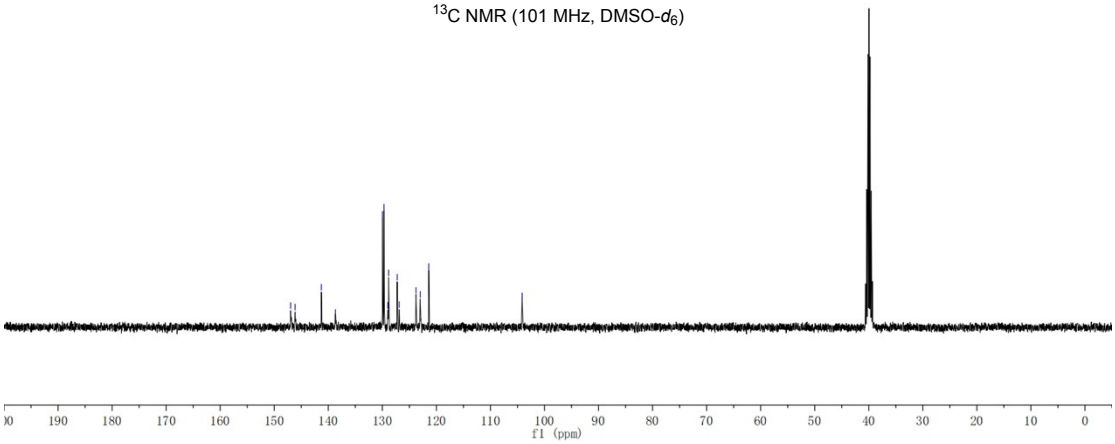
^{1}H NMR (400 MHz, DMSO-d_6)

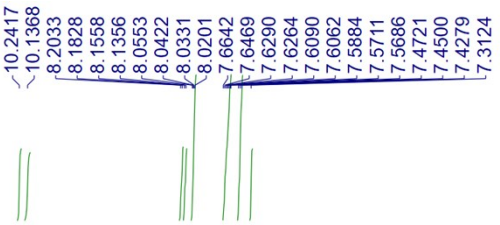


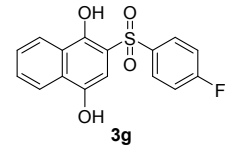


3f

^{13}C NMR (101 MHz, DMSO-d_6)

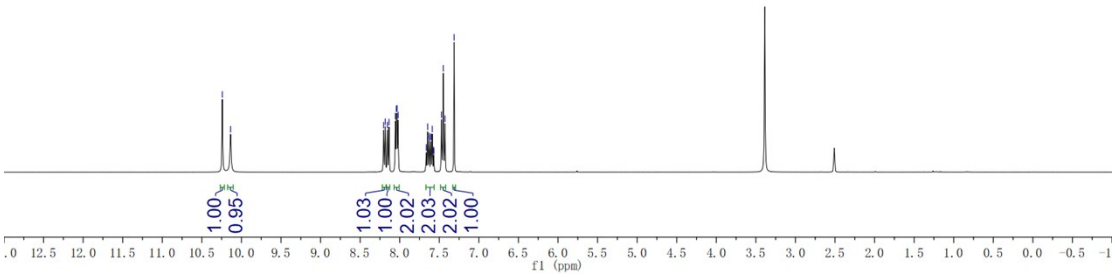


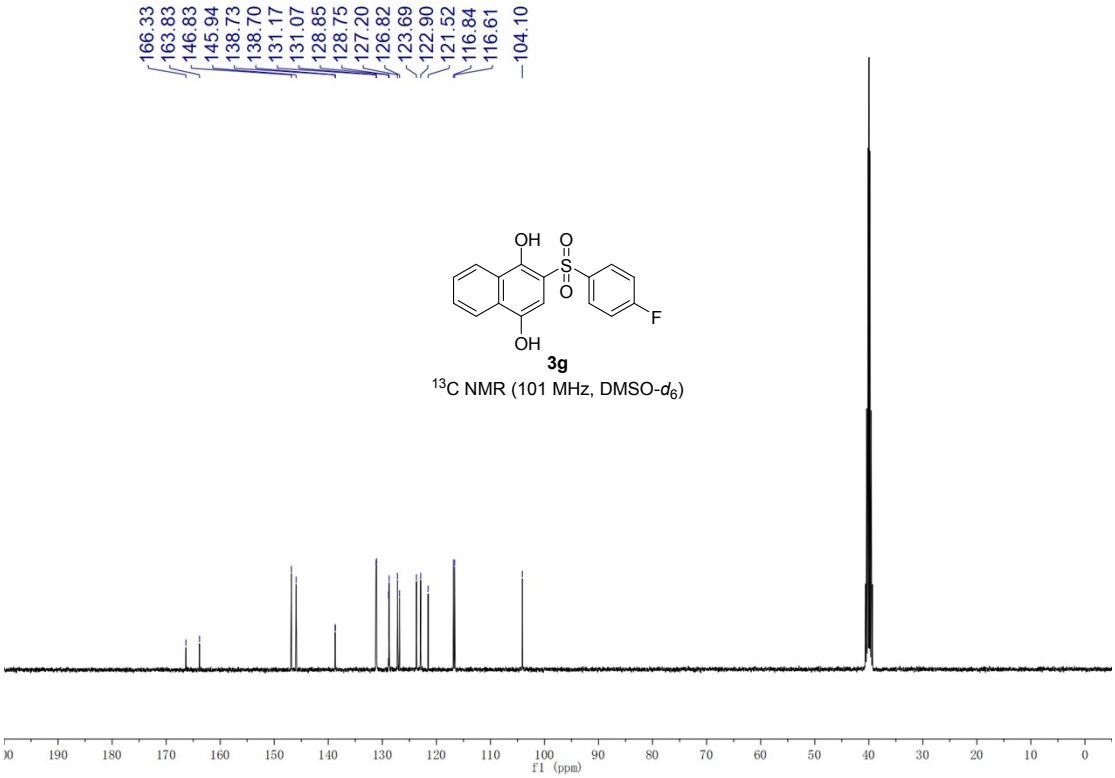




3g

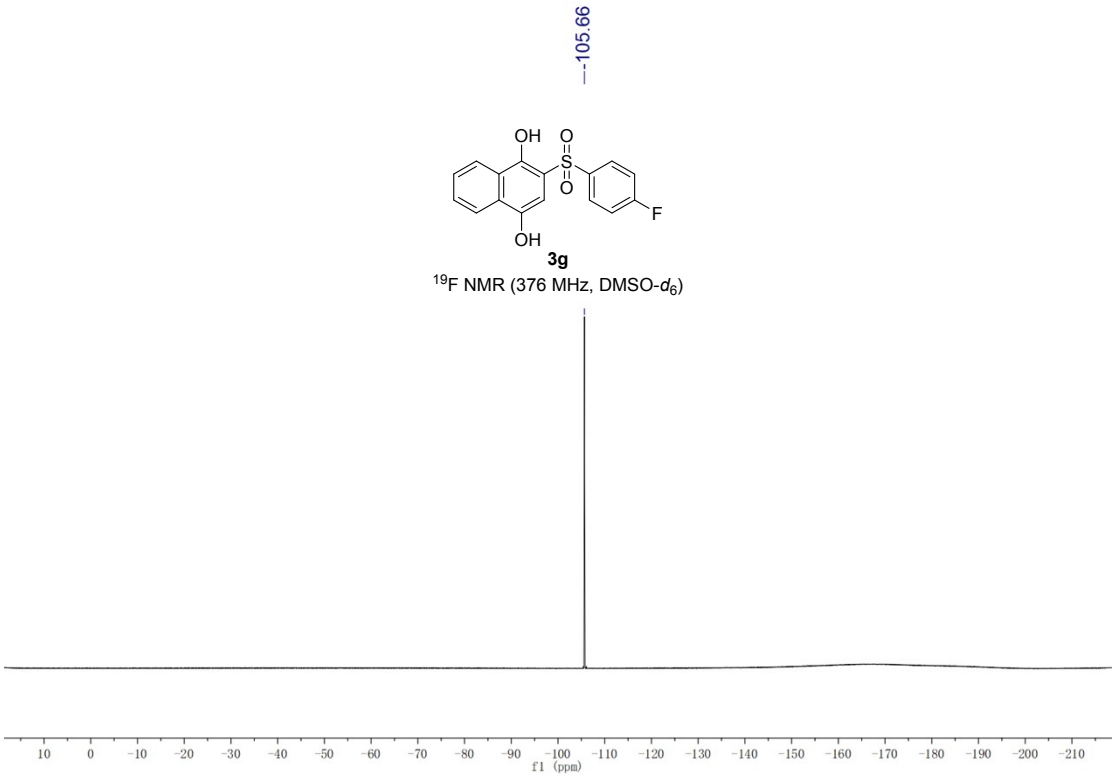
^{1}H NMR (400 MHz, DMSO-d_6)





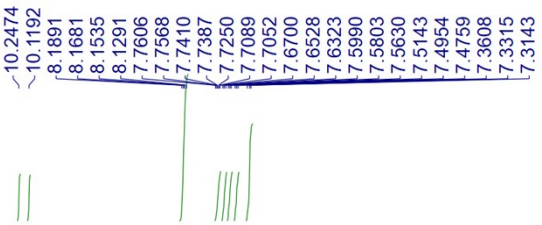
3g

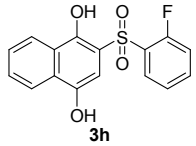
^{13}C NMR (101 MHz, DMSO-d_6)



3g

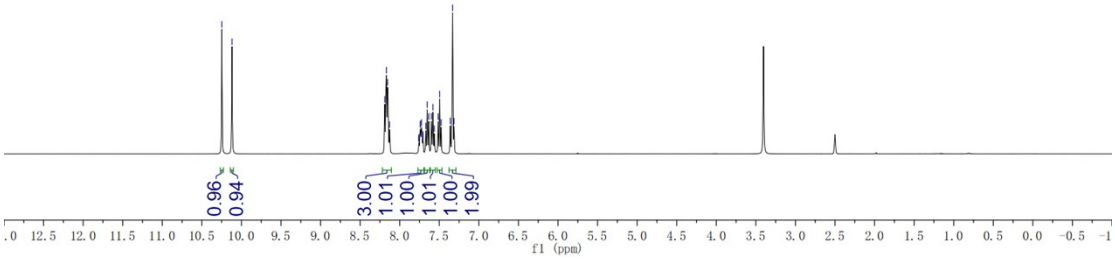
^{19}F NMR (376 MHz, DMSO-d_6)

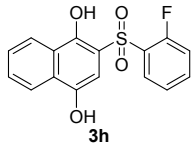




3h

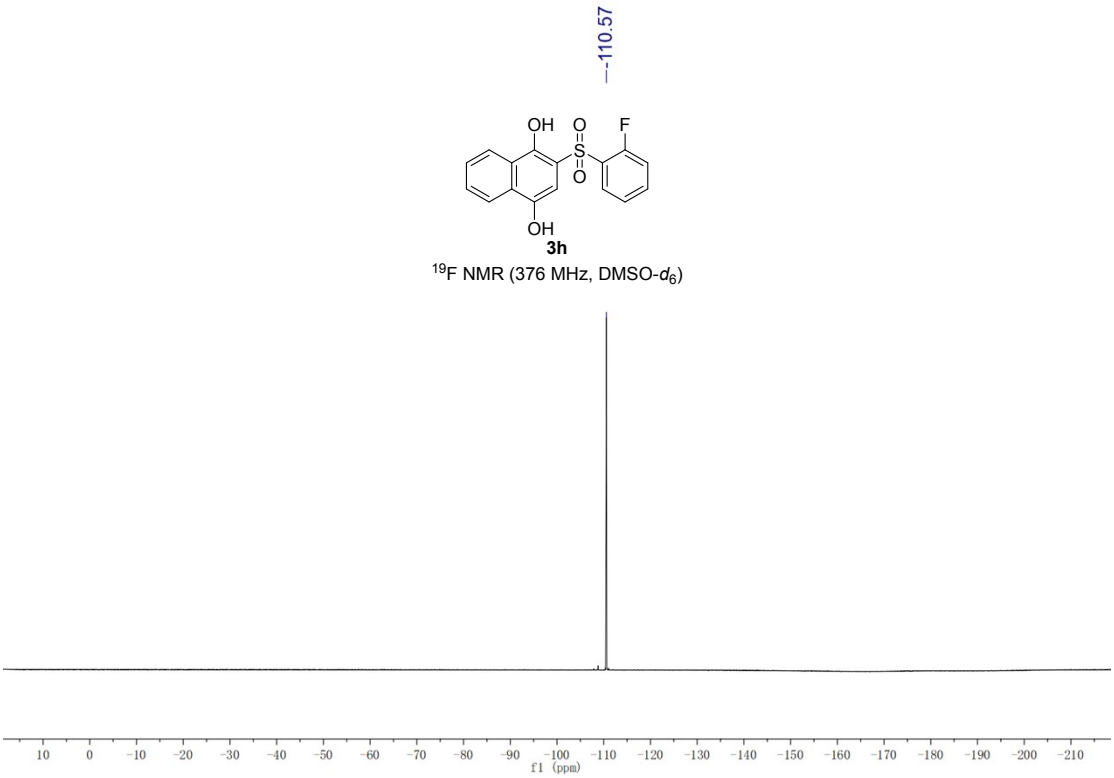
^{1}H NMR (400 MHz, DMSO-d_6)





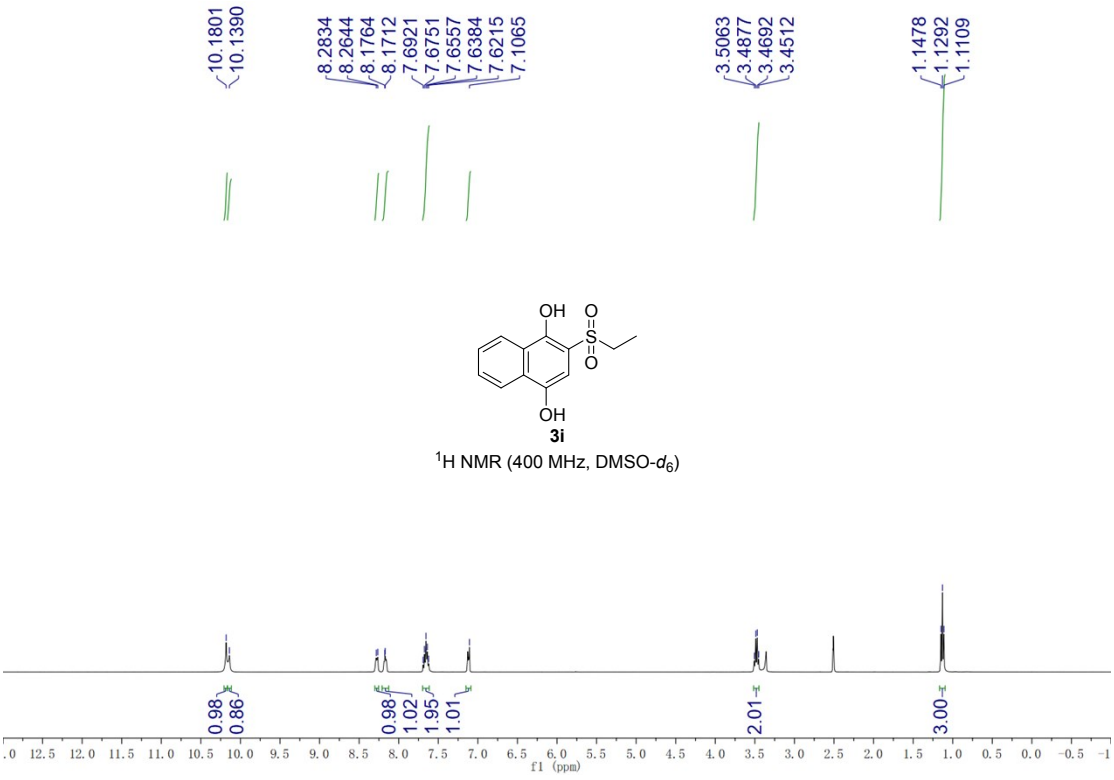
3h

^{13}C NMR (101 MHz, DMSO-d_6)



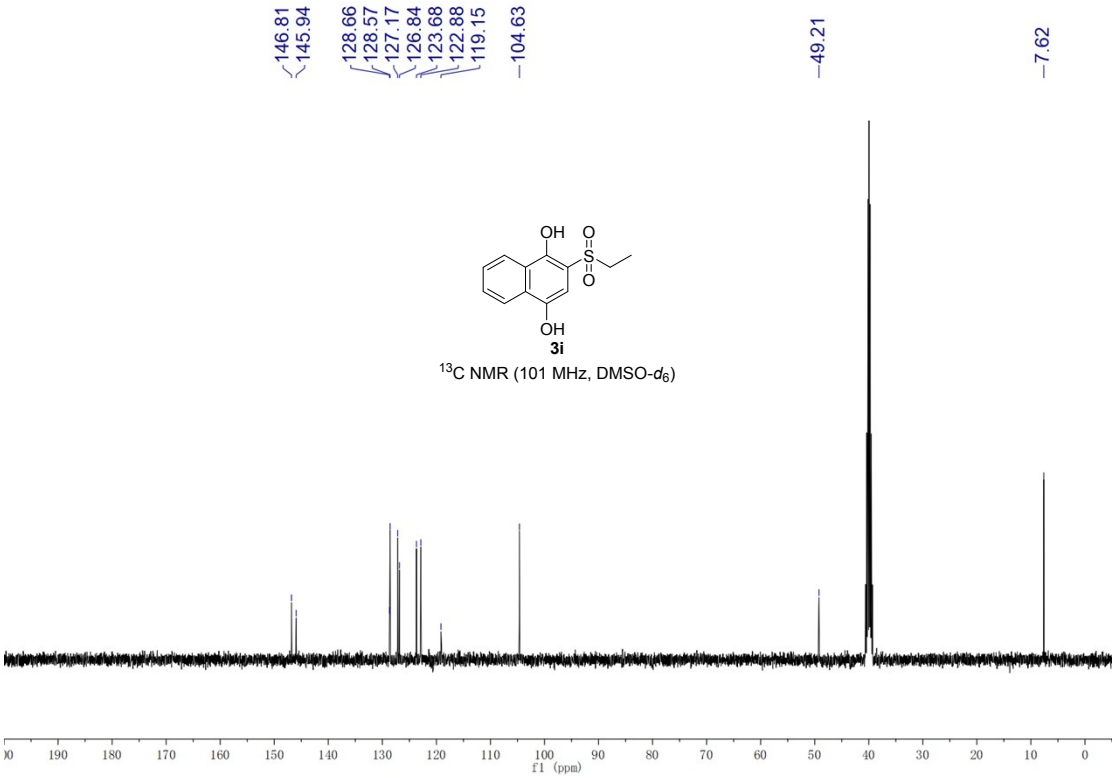
3h

^{19}F NMR (376 MHz, DMSO-d_6)



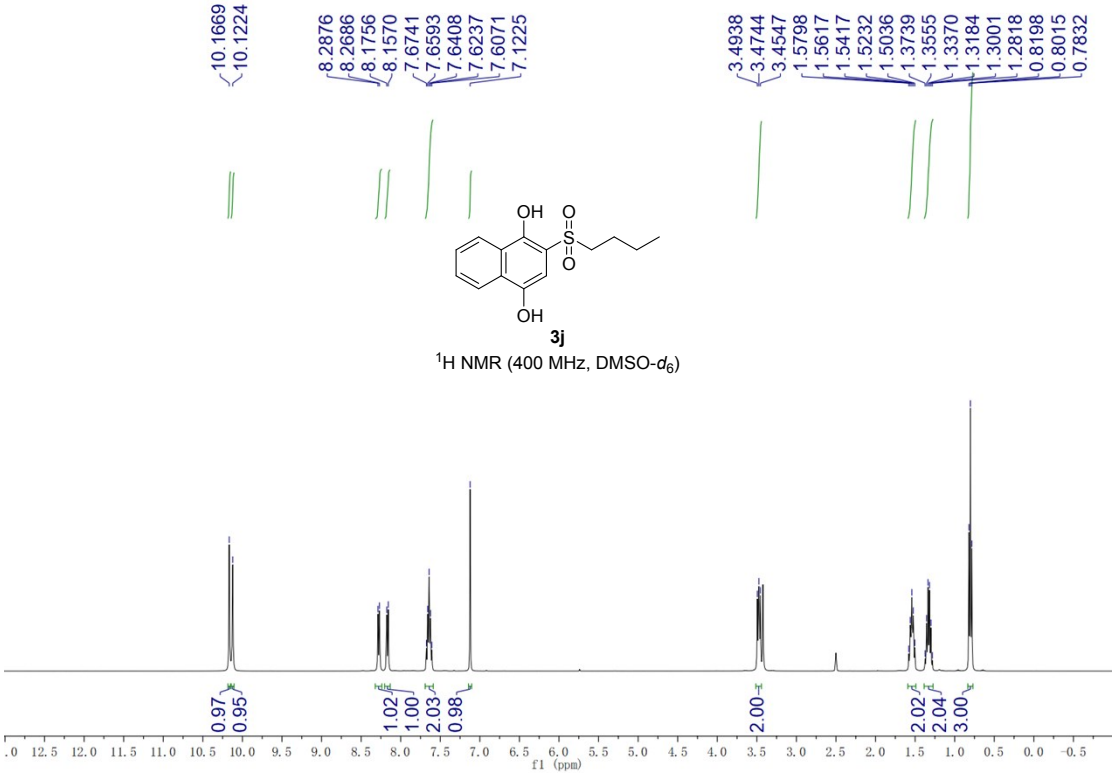
3i

^{1}H NMR (400 MHz, DMSO-d_6)



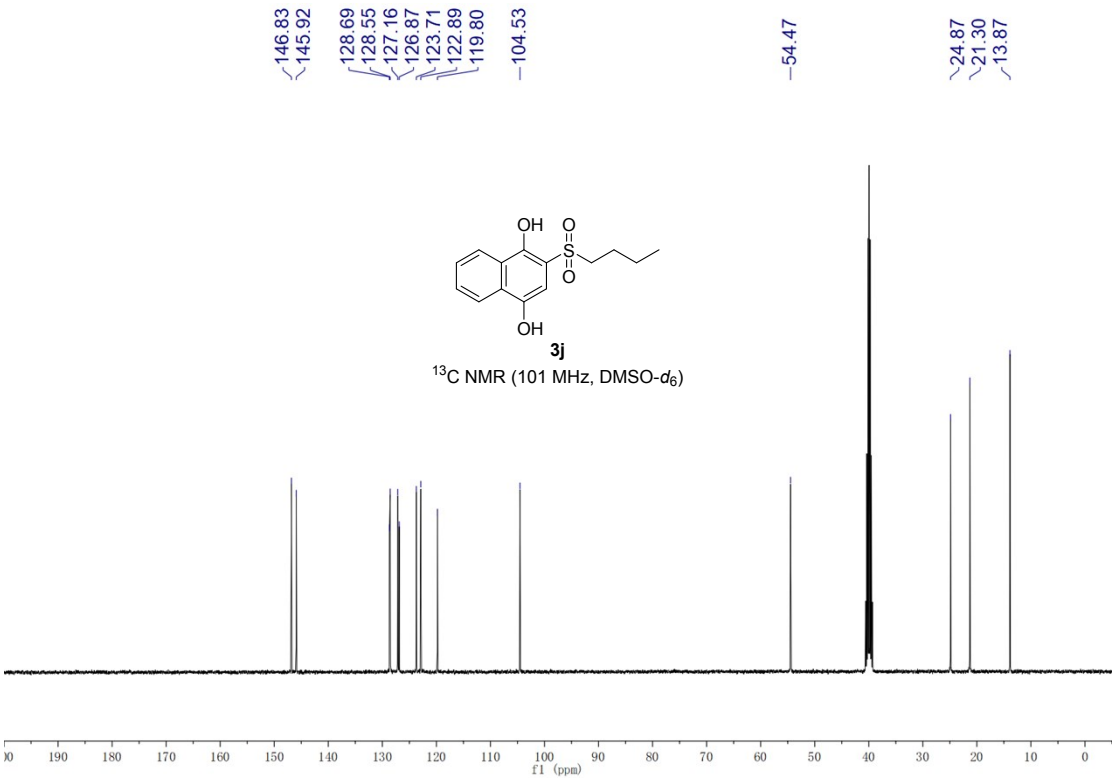
3i

^{13}C NMR (101 MHz, DMSO-d_6)



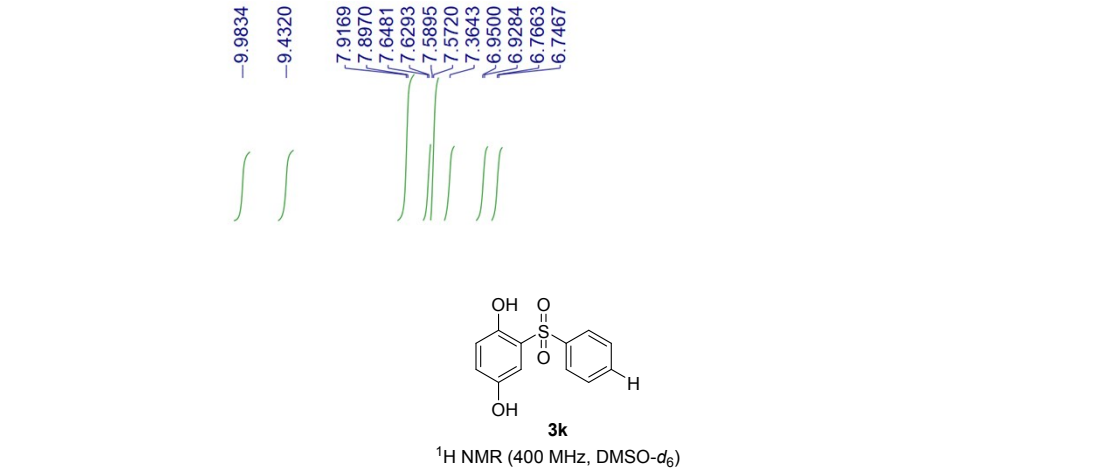
3j

^{1}H NMR (400 MHz, DMSO-d_6)



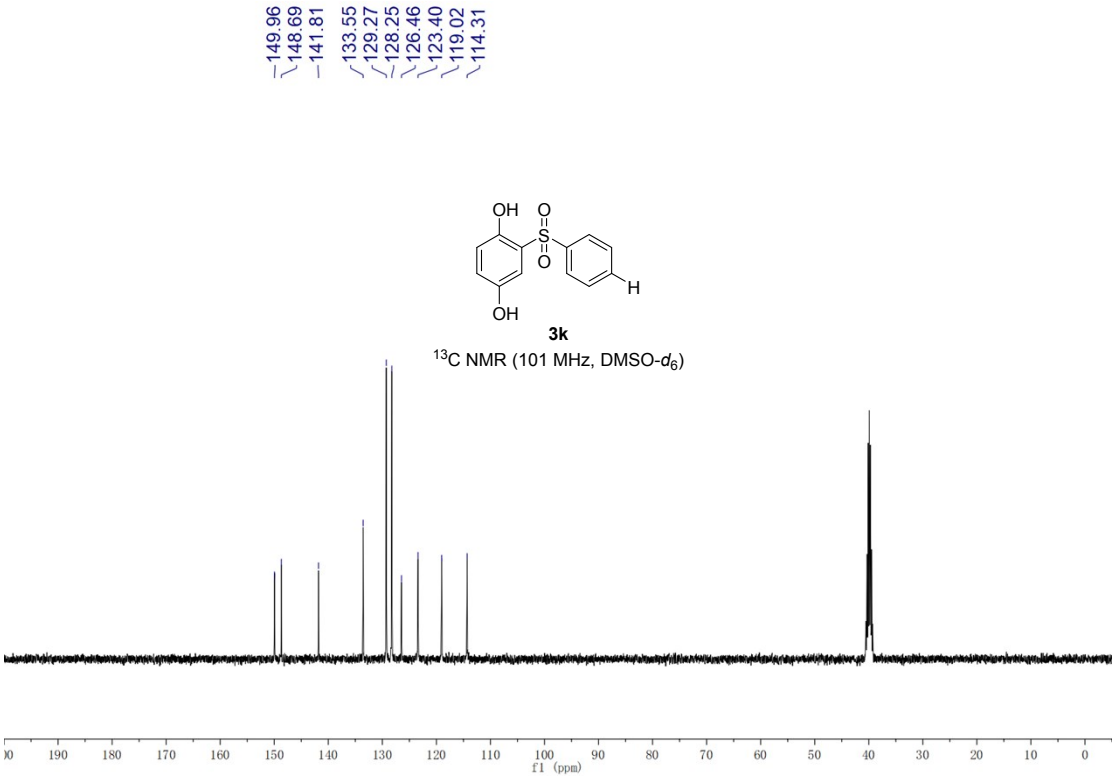
3j

^{13}C NMR (101 MHz, DMSO-d_6)



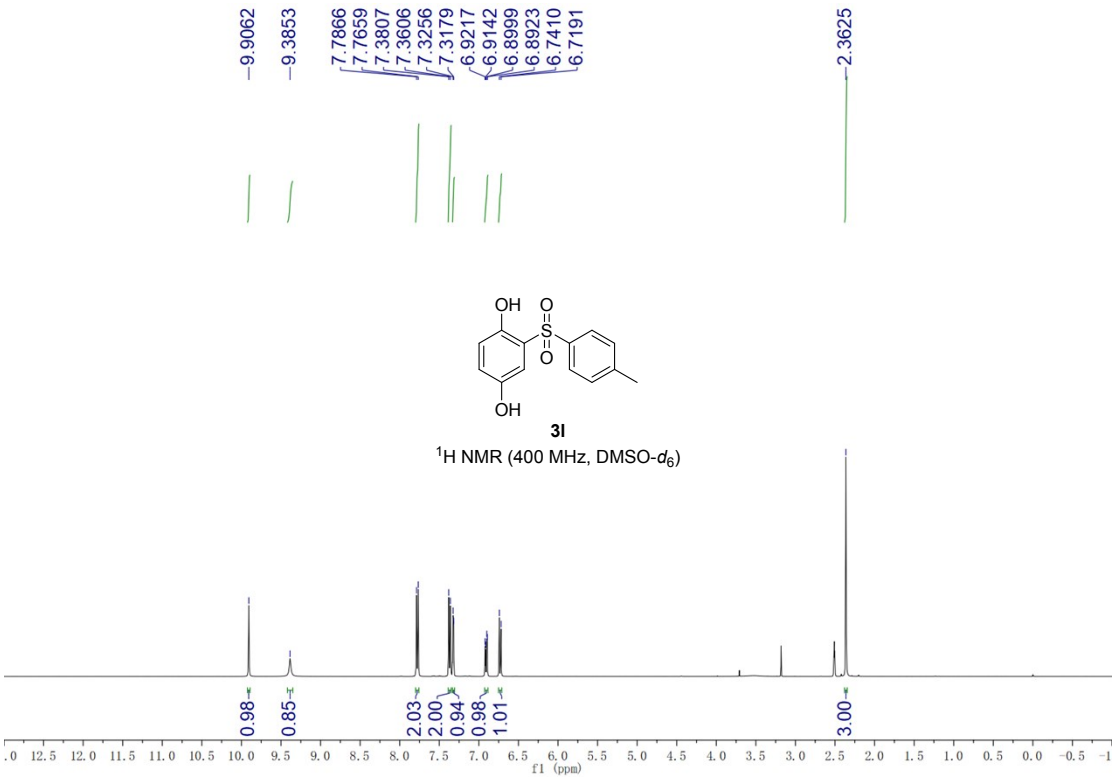
3k

^{1}H NMR (400 MHz, DMSO-d_6)



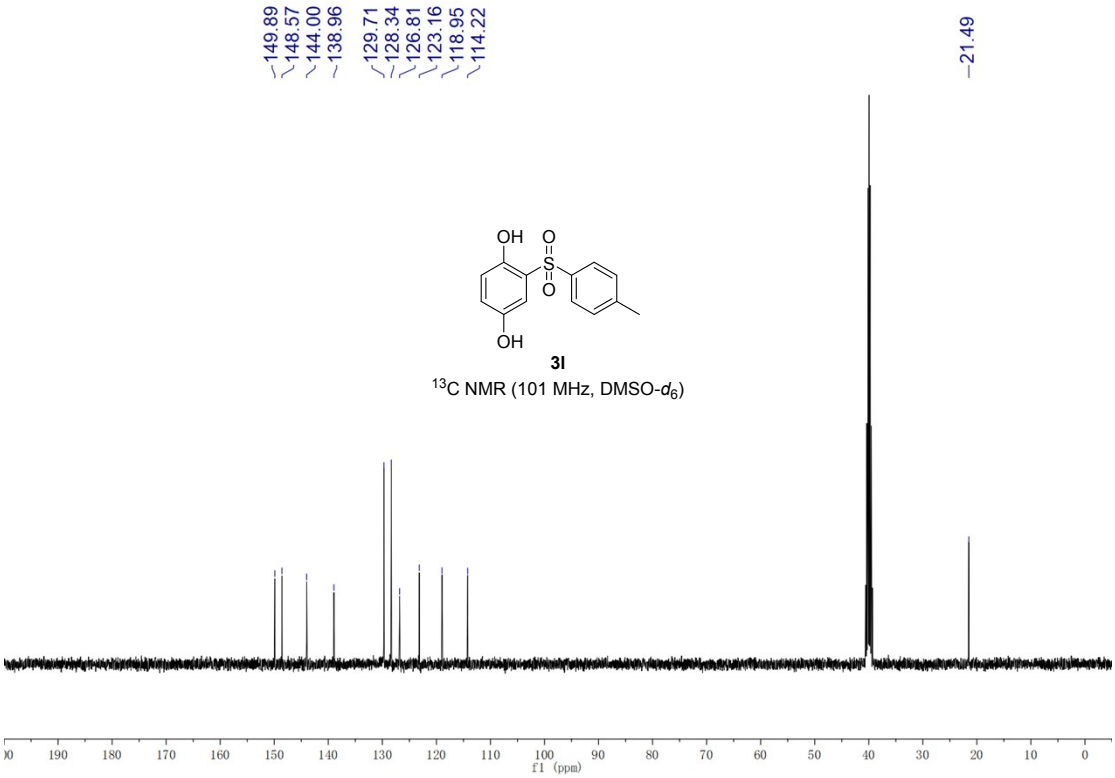
3k

^{13}C NMR (101 MHz, DMSO-d_6)



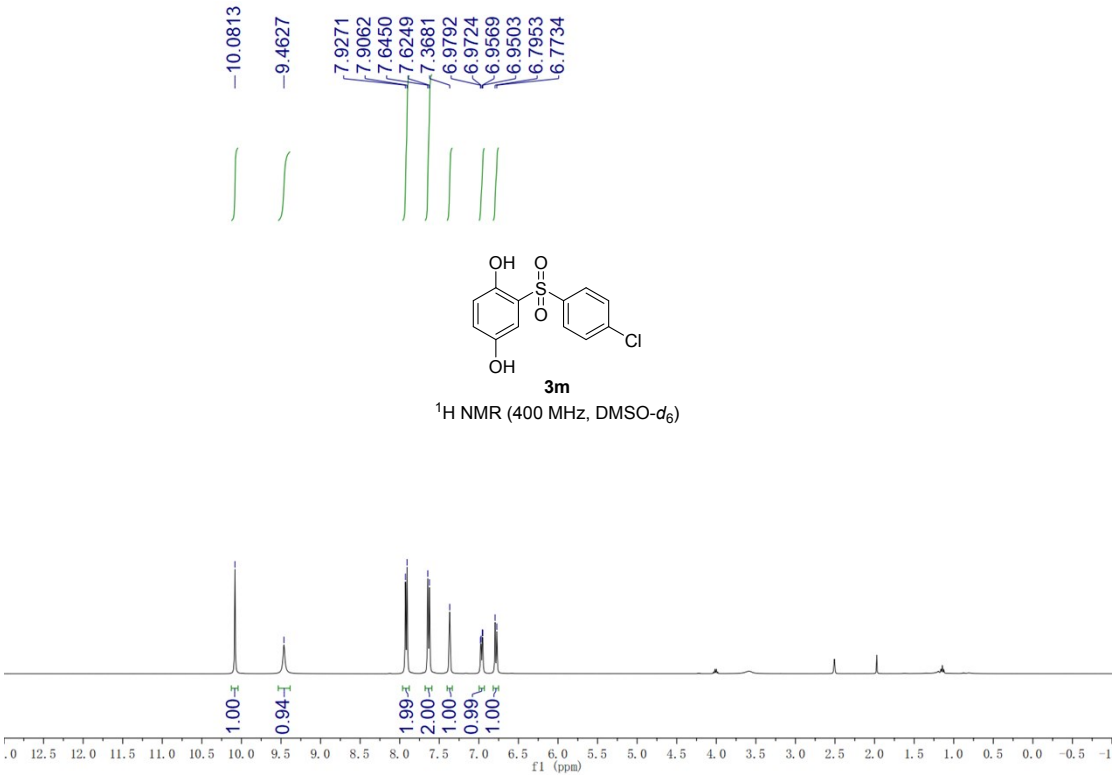
3l

^{1}H NMR (400 MHz, DMSO-d_6)



3l

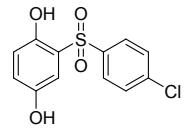
^{13}C NMR (101 MHz, DMSO-d_6)



3m

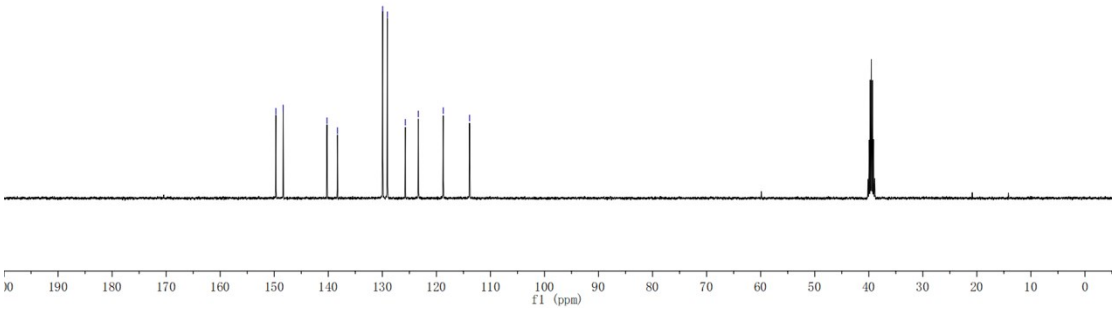
^{1}H NMR (400 MHz, DMSO-d_6)

149.69
148.34
140.24
138.31
129.94
129.07
125.74
123.34
118.73
113.87

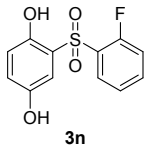


3m

^{13}C NMR (101 MHz, DMSO-d_6)

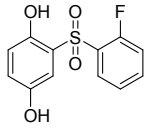


9.9846
9.4730
8.0467
8.0422
8.0276
8.0231
8.0085
8.0040
7.7597
7.7552
7.7471
7.7413
7.7360
7.7274
7.7216
7.7156
7.7077
7.7031
7.4722
7.4533
7.4340
7.3642
7.3432
7.3365
7.3171
6.9655
6.9579
6.9436
6.9361
6.7407
6.7188



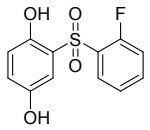
3n

^{1}H NMR (400 MHz, DMSO-d_6)



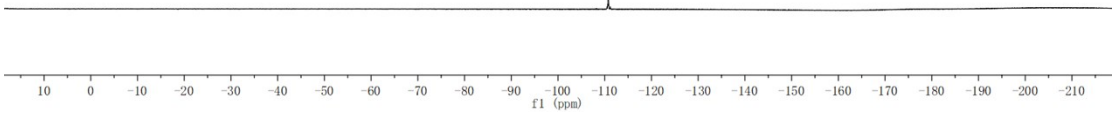
3n

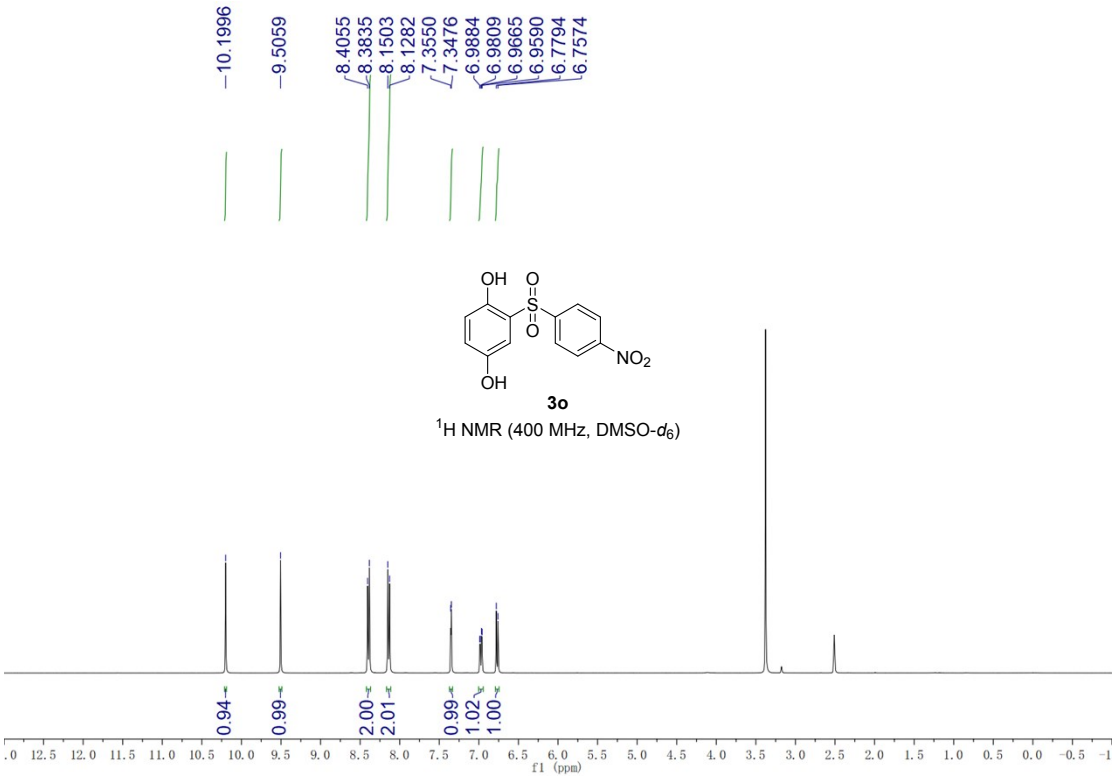
^{13}C NMR (101 MHz, DMSO-d_6)



3n

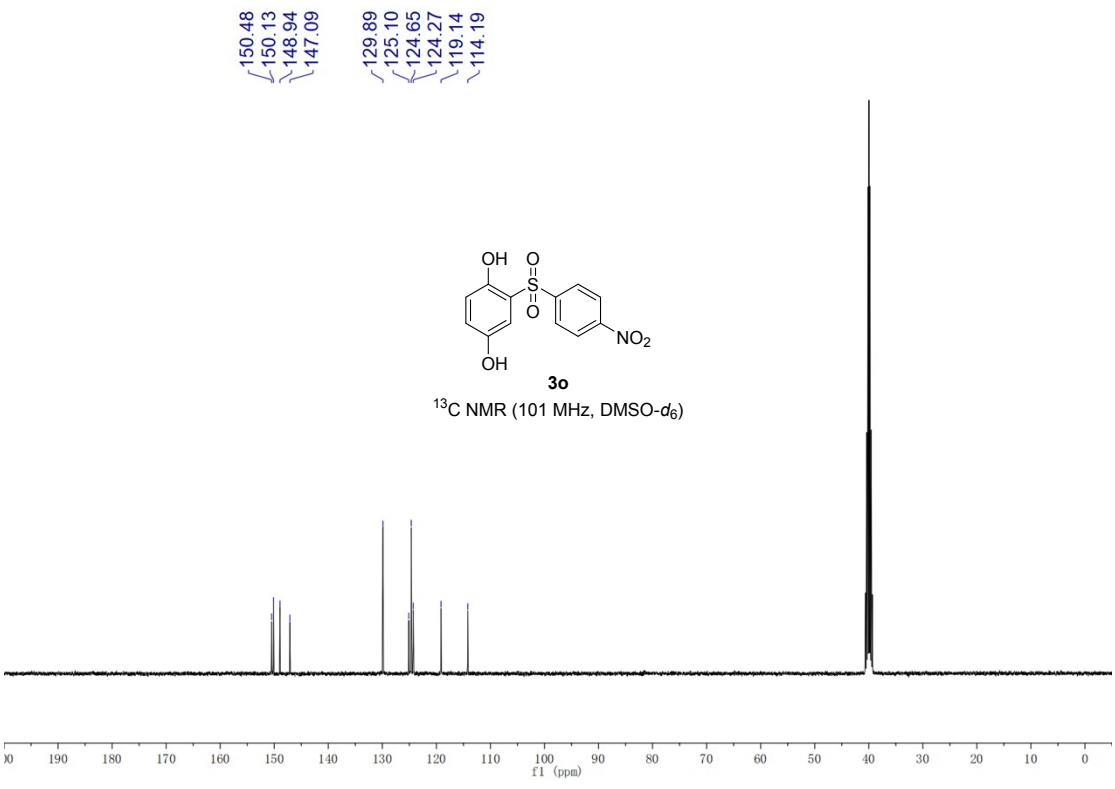
^{19}F NMR (376 MHz, DMSO-d_6)





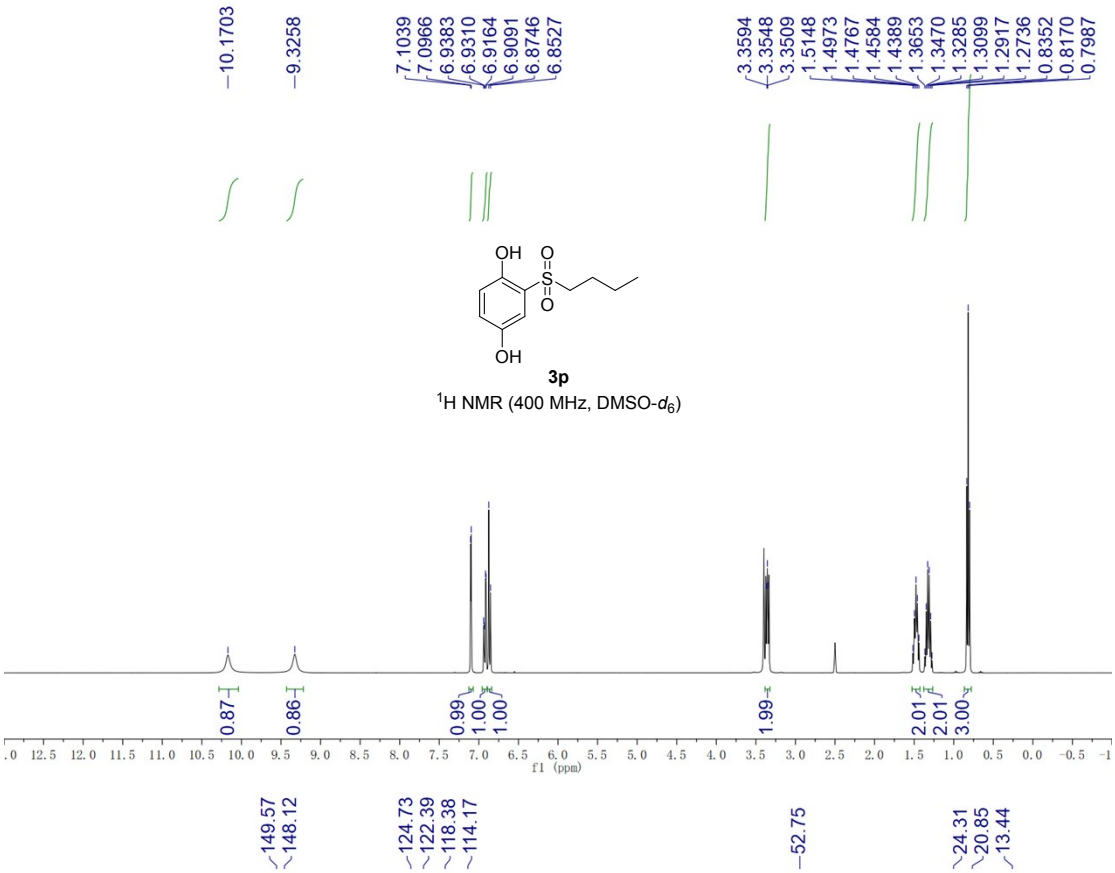
3o

^{1}H NMR (400 MHz, DMSO-d_6)



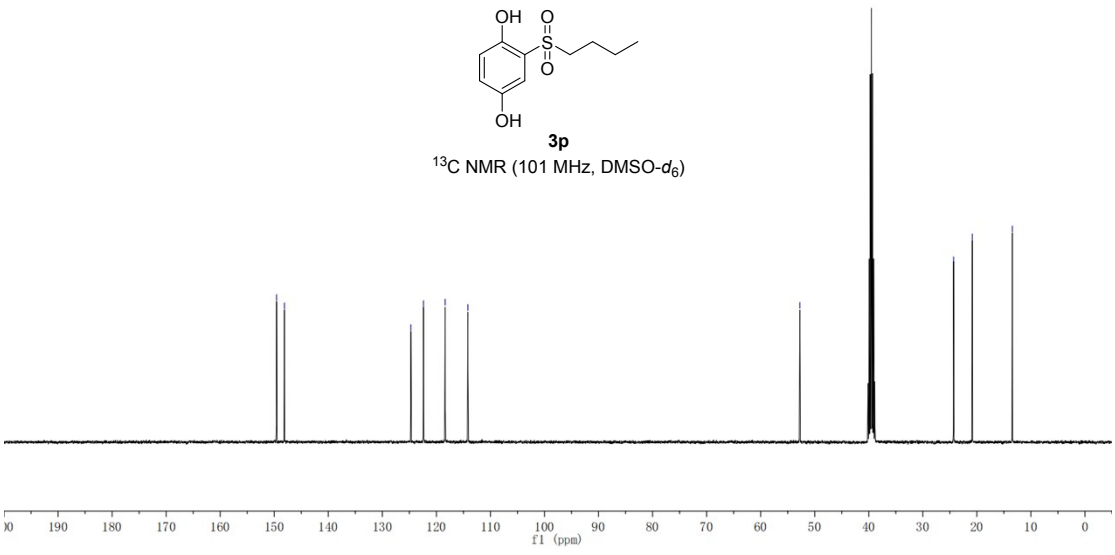
3o

^{13}C NMR (101 MHz, DMSO-d_6)



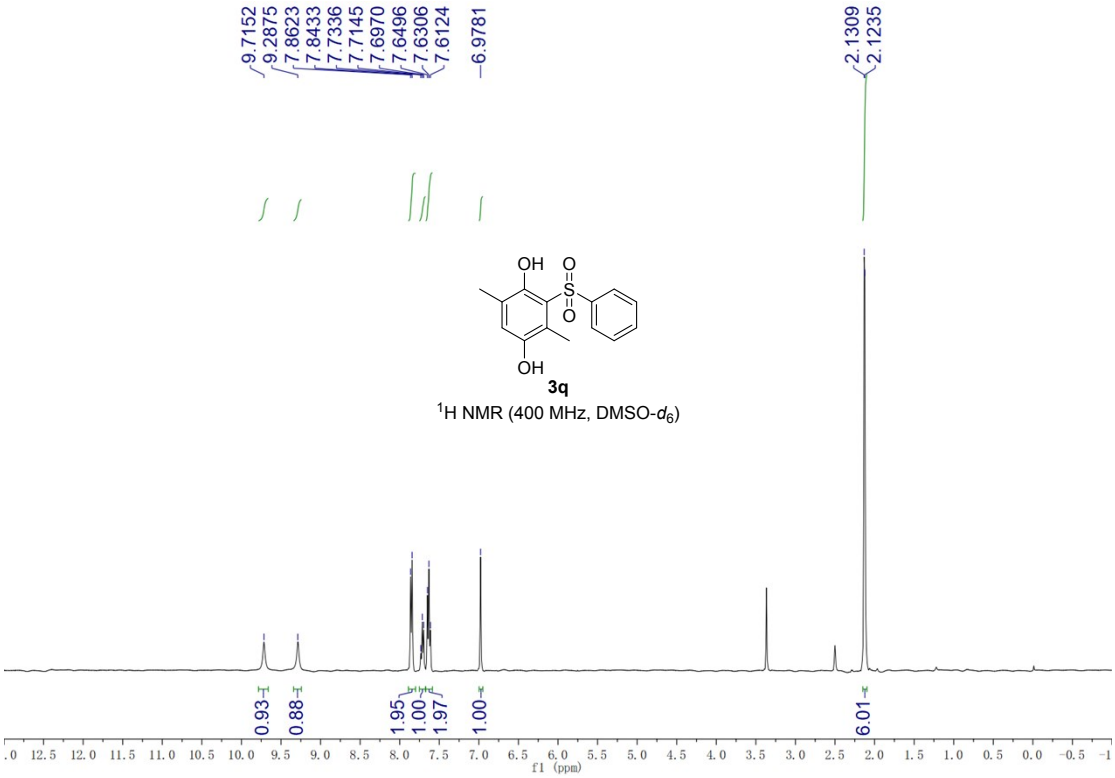
3p

^{1}H NMR (400 MHz, DMSO-d_6)



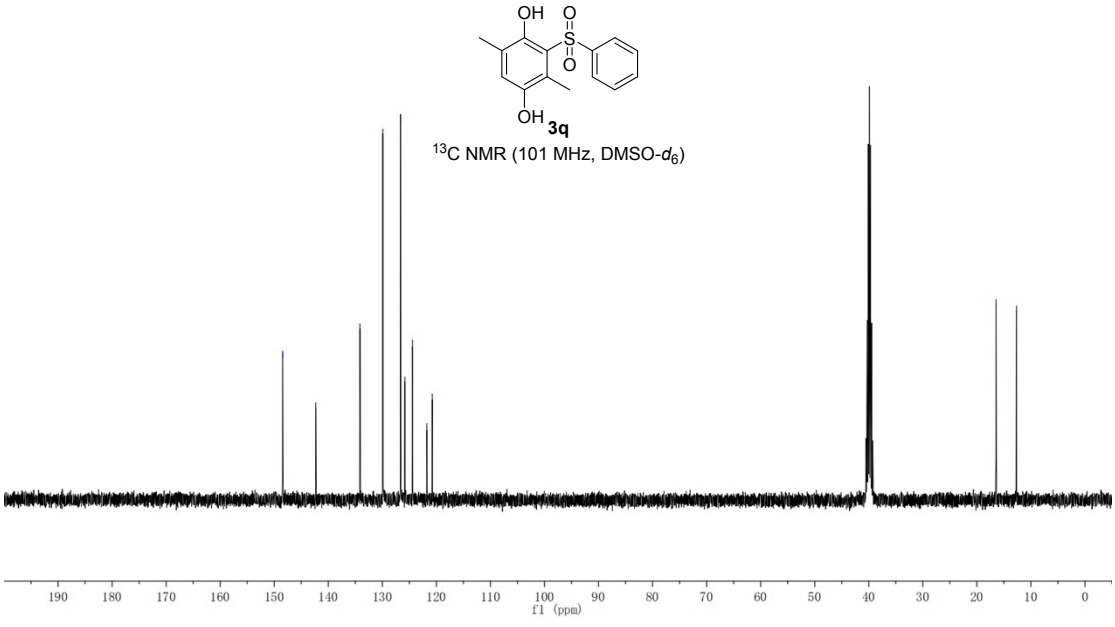
3p

^{13}C NMR (101 MHz, DMSO-d_6)



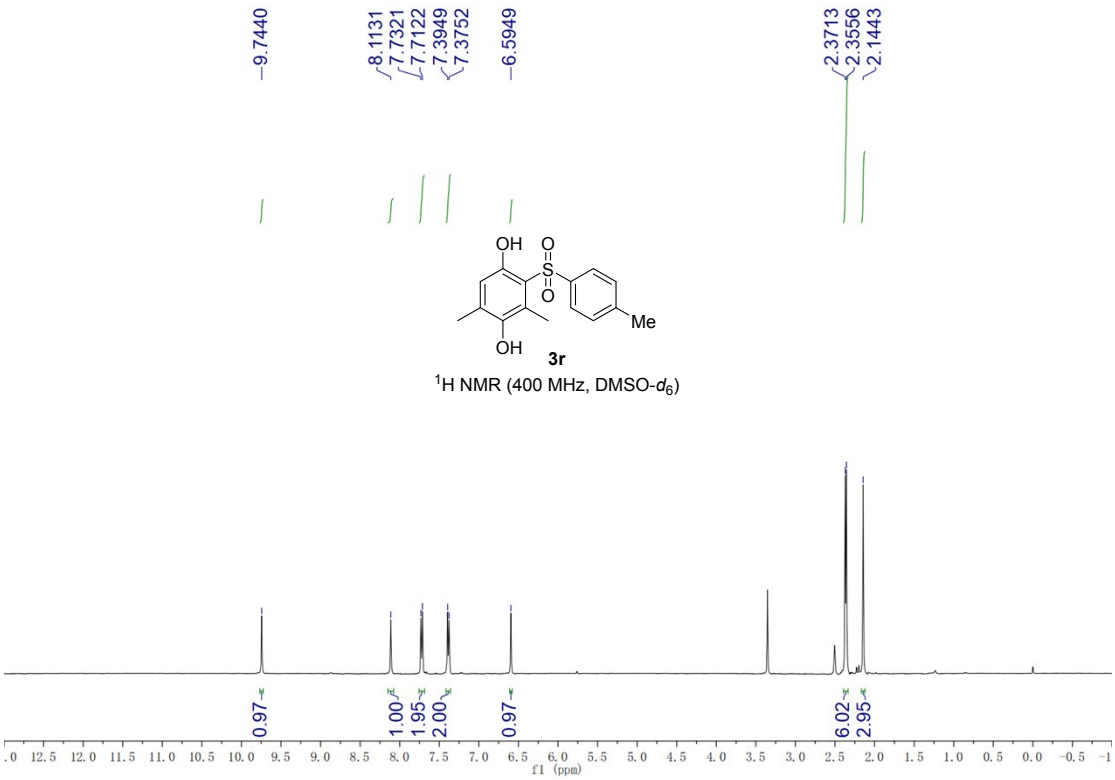
3q

^{1}H NMR (400 MHz, DMSO-d_6)



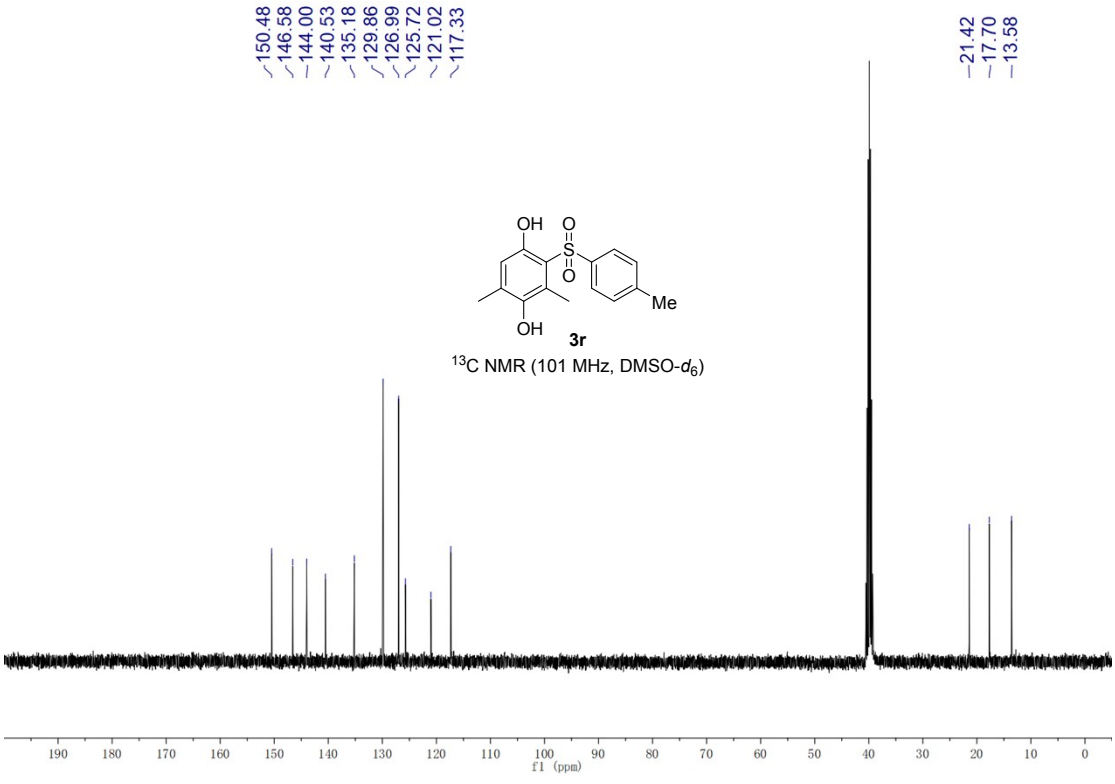
3q

^{13}C NMR (101 MHz, DMSO-d_6)



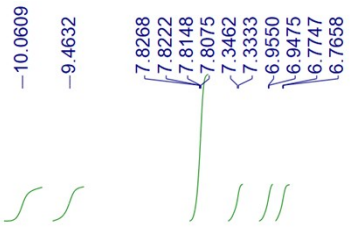
3r

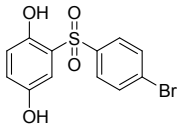
^{1}H NMR (400 MHz, DMSO-d_6)



3r

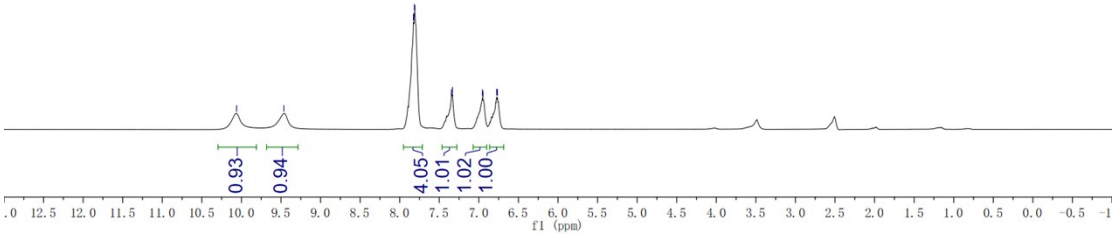
^{13}C NMR (101 MHz, DMSO-d_6)

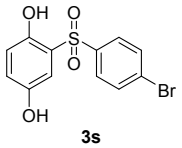




3s

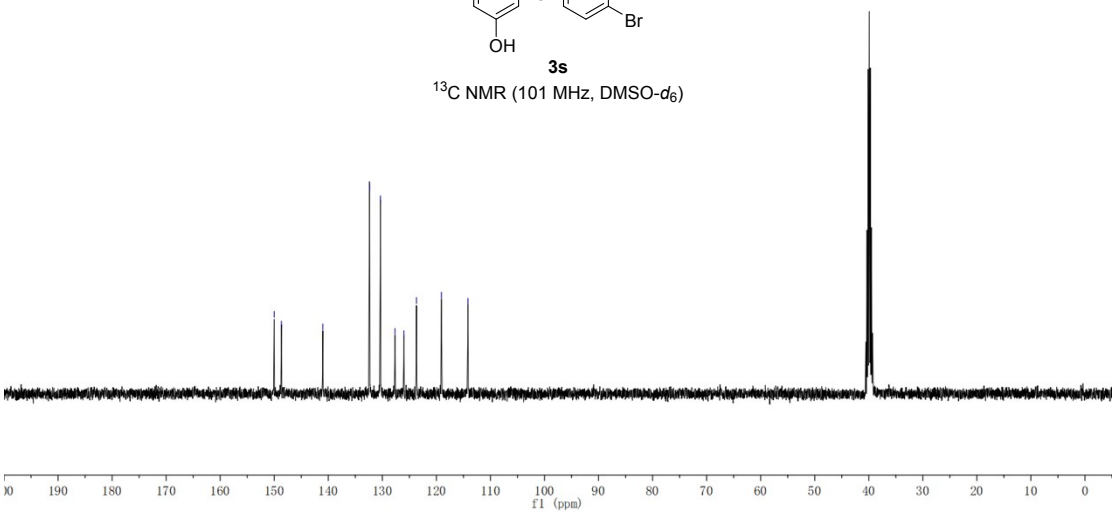
^{1}H NMR (400 MHz, DMSO-d_6)

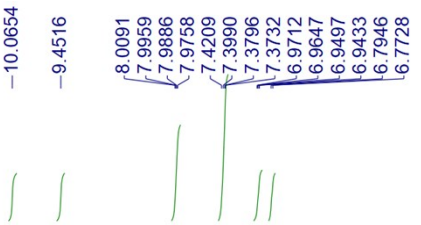


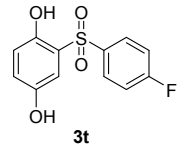


3s

^{13}C NMR (101 MHz, DMSO-d_6)

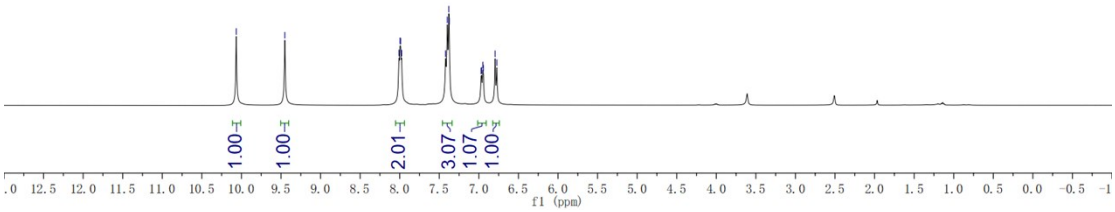


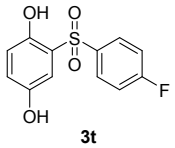




3t

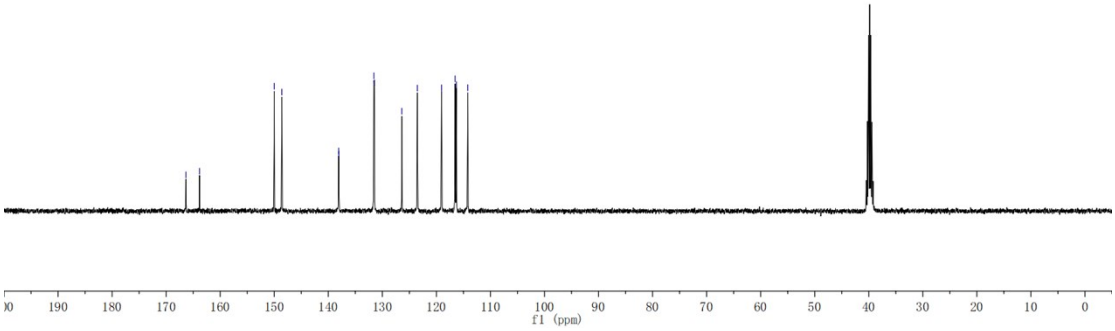
^{1}H NMR (400 MHz, DMSO-d_6)

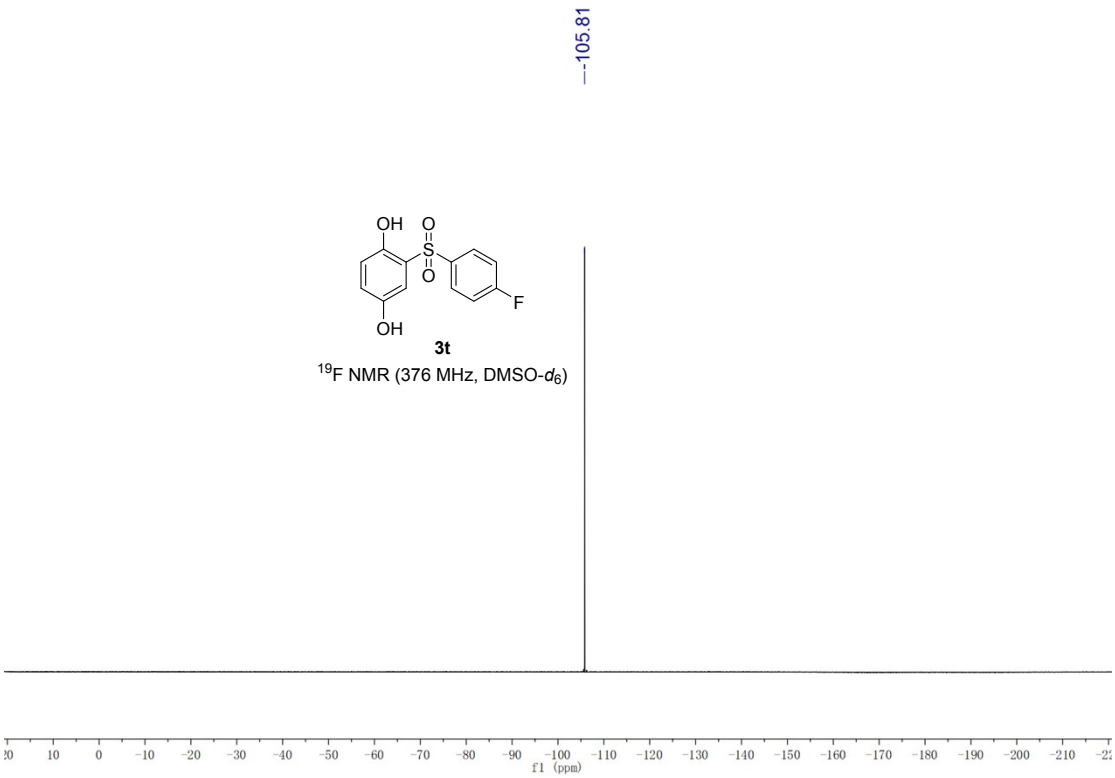




3t

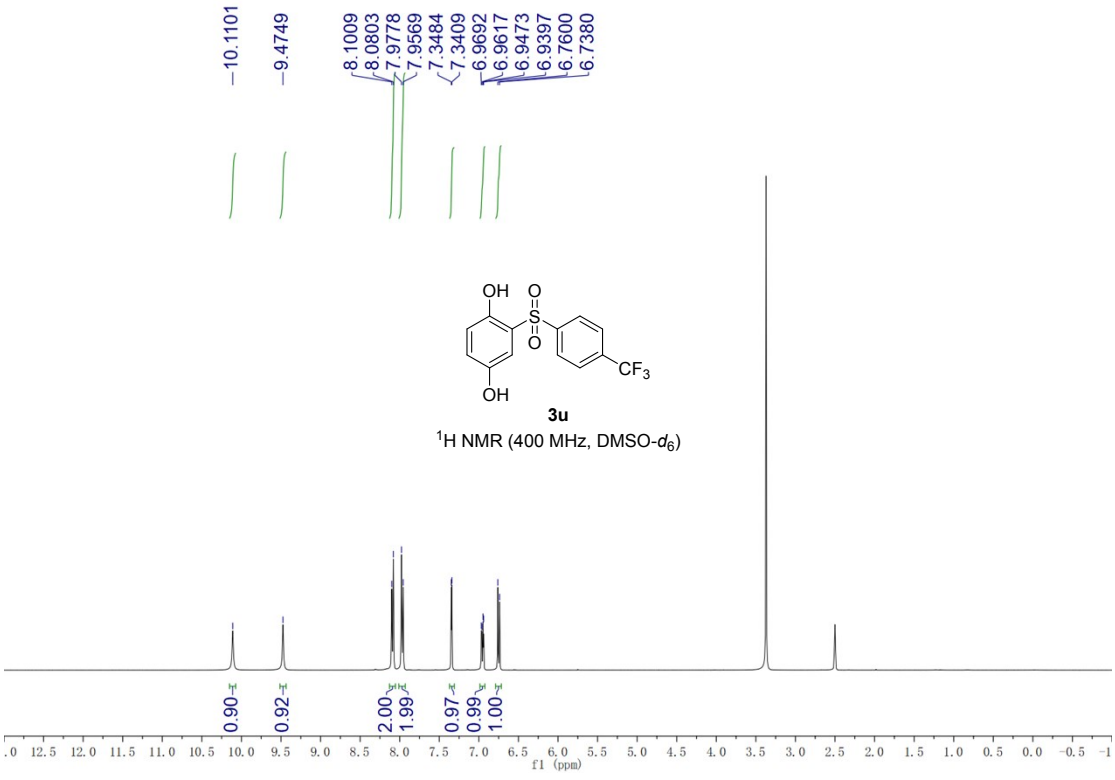
^{13}C NMR (101 MHz, DMSO-d_6)





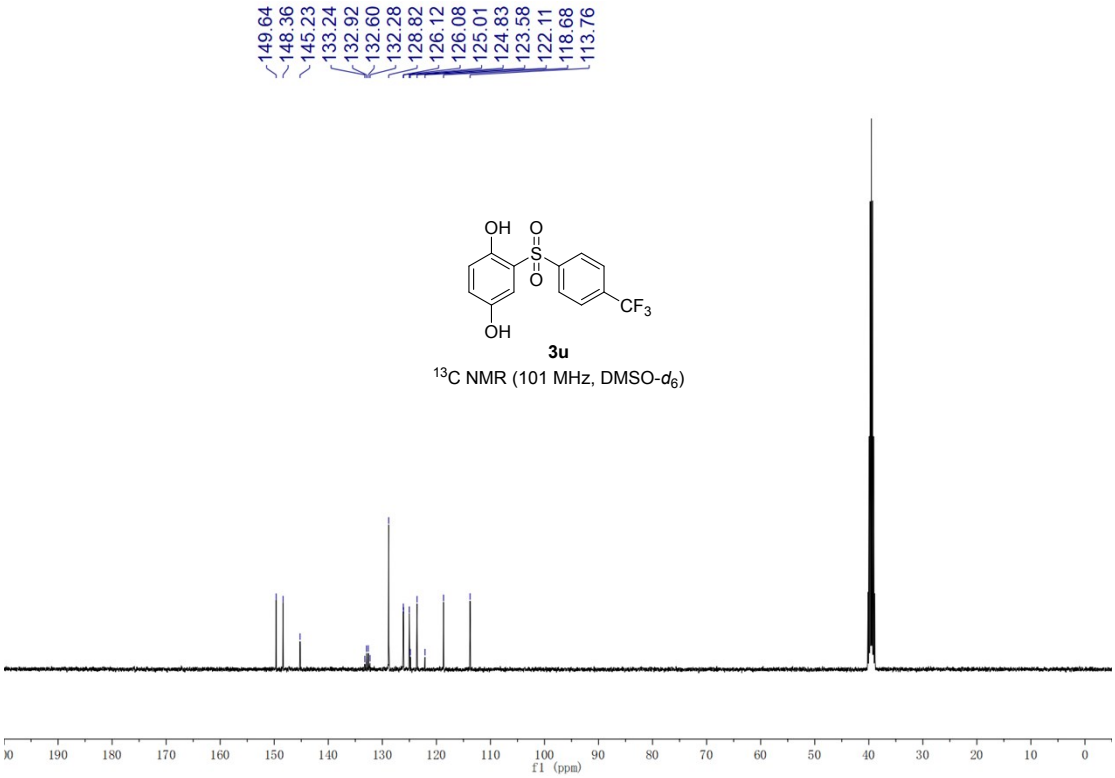
3t

^{19}F NMR (376 MHz, DMSO-d_6)



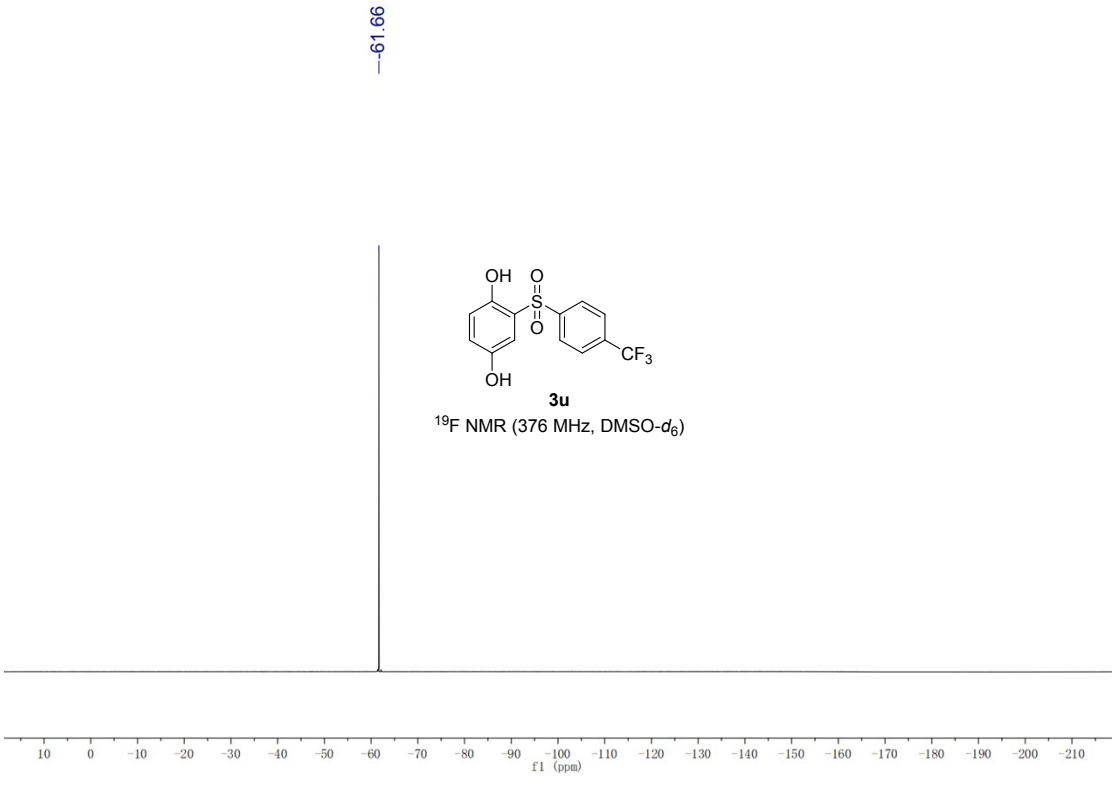
3u

^{1}H NMR (400 MHz, DMSO-d_6)



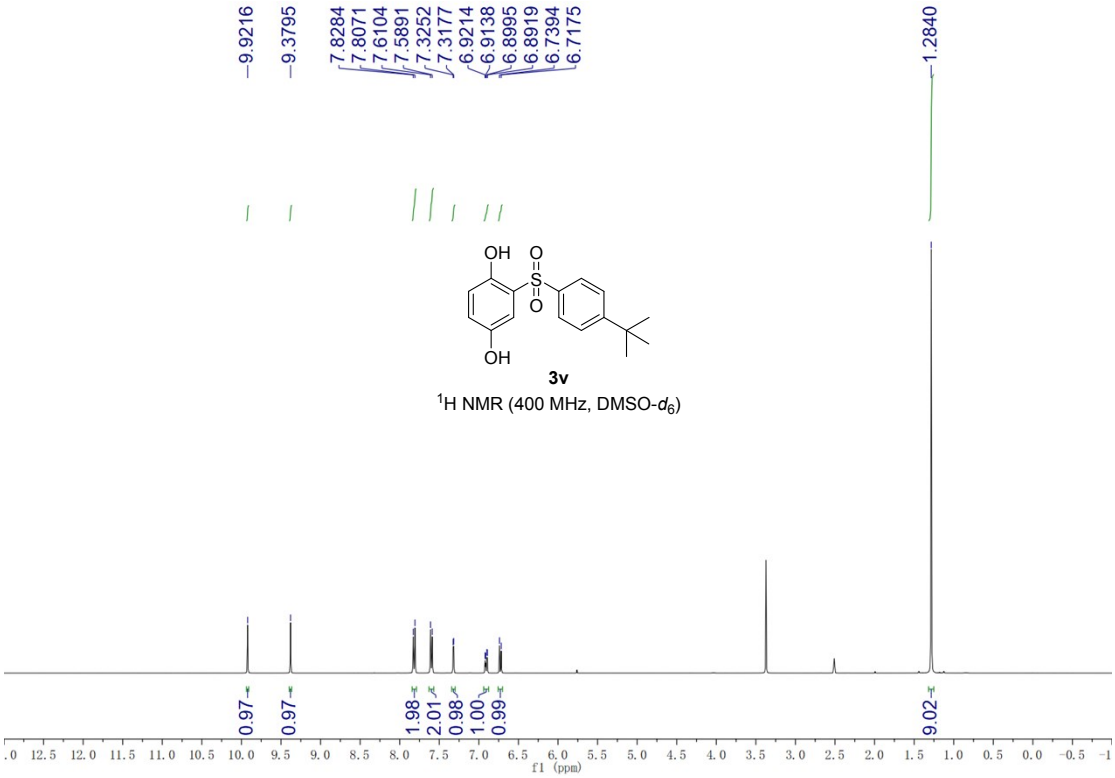
3u

^{13}C NMR (101 MHz, DMSO-d_6)



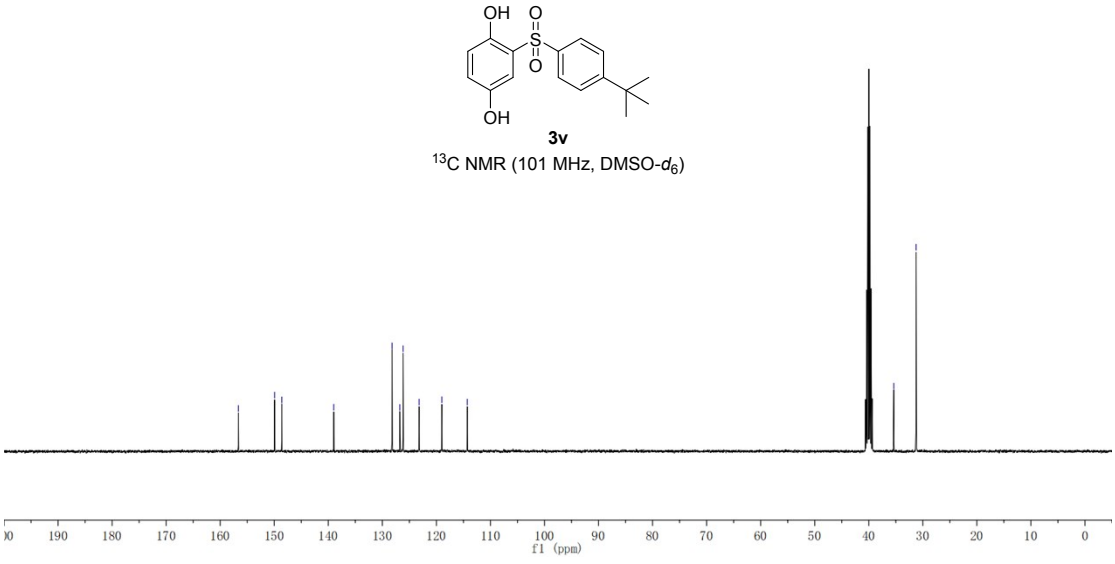
3u

^{19}F NMR (376 MHz, DMSO-d_6)



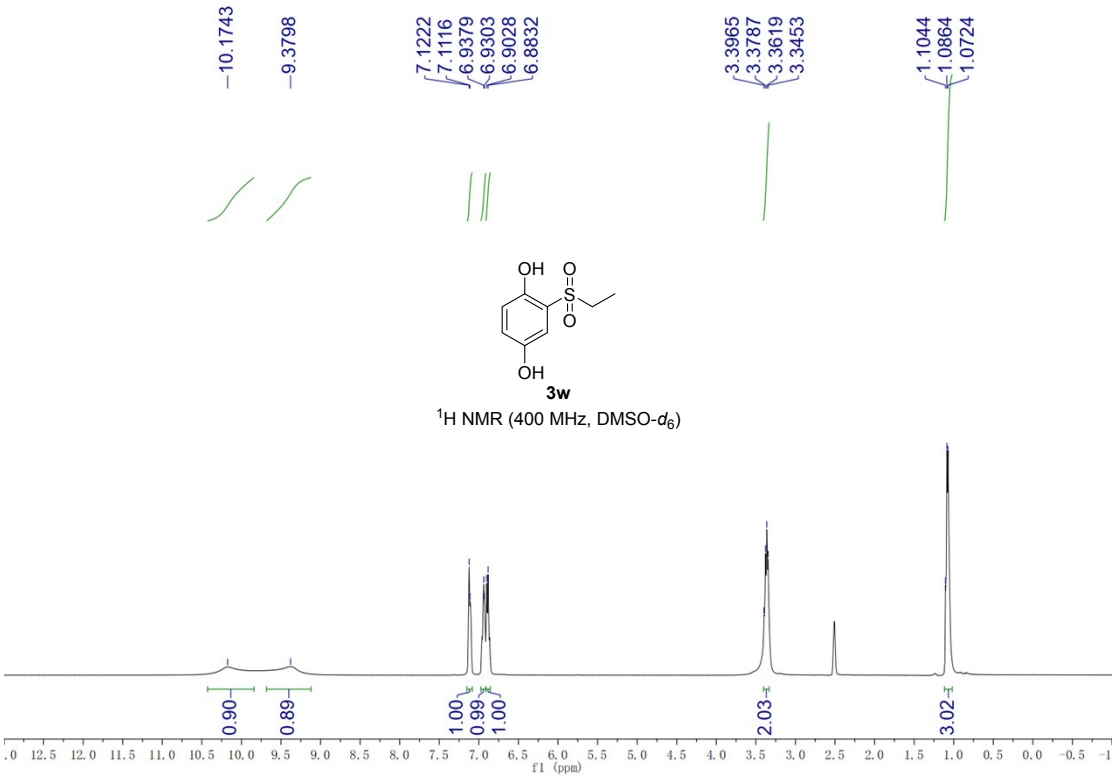
3v

^{1}H NMR (400 MHz, DMSO-d_6)



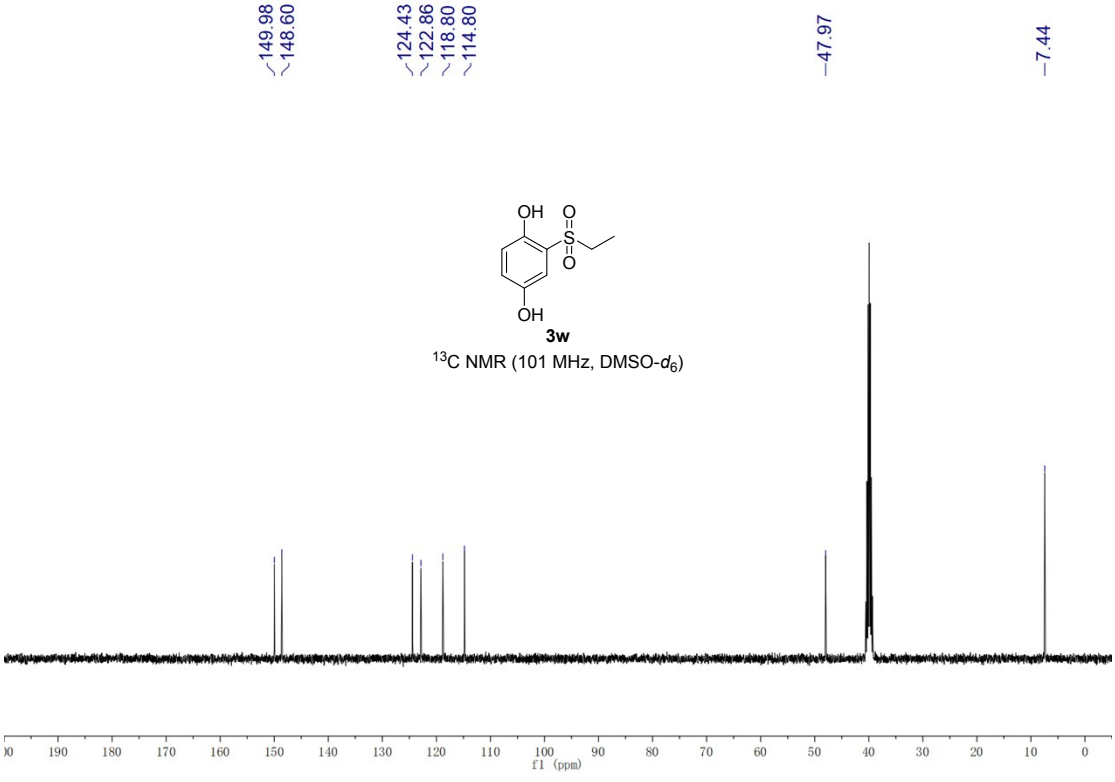
3v

^{13}C NMR (101 MHz, DMSO-d_6)



3w

^{1}H NMR (400 MHz, DMSO-d_6)



3w

^{13}C NMR (101 MHz, DMSO-d_6)