Supporting Information

Enantioselective sulfonylation from sodium hydrogen sulfite, 4-substituted Hantzsch esters and 1-(arylethynyl)naphthalen-2-ols

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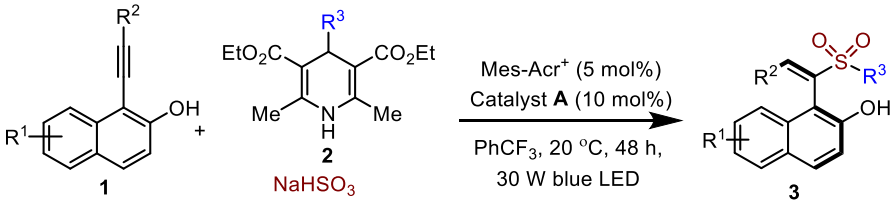
1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuterochloroform ($CDCl_3$ or CD_3CN) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. Enantioselectivities were recorded on Shimadzu HPLC using CHIRALCEL and CHIRALPAK columns. Electrospray–ionisation HRMS data were acquired on a Q–TOF mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF.

2. General procedure procedure for the preparation of (*S*,*E*)-1-(1-(alkylsulfonyl)-2-arylvinyl)naphthalen-2-ols

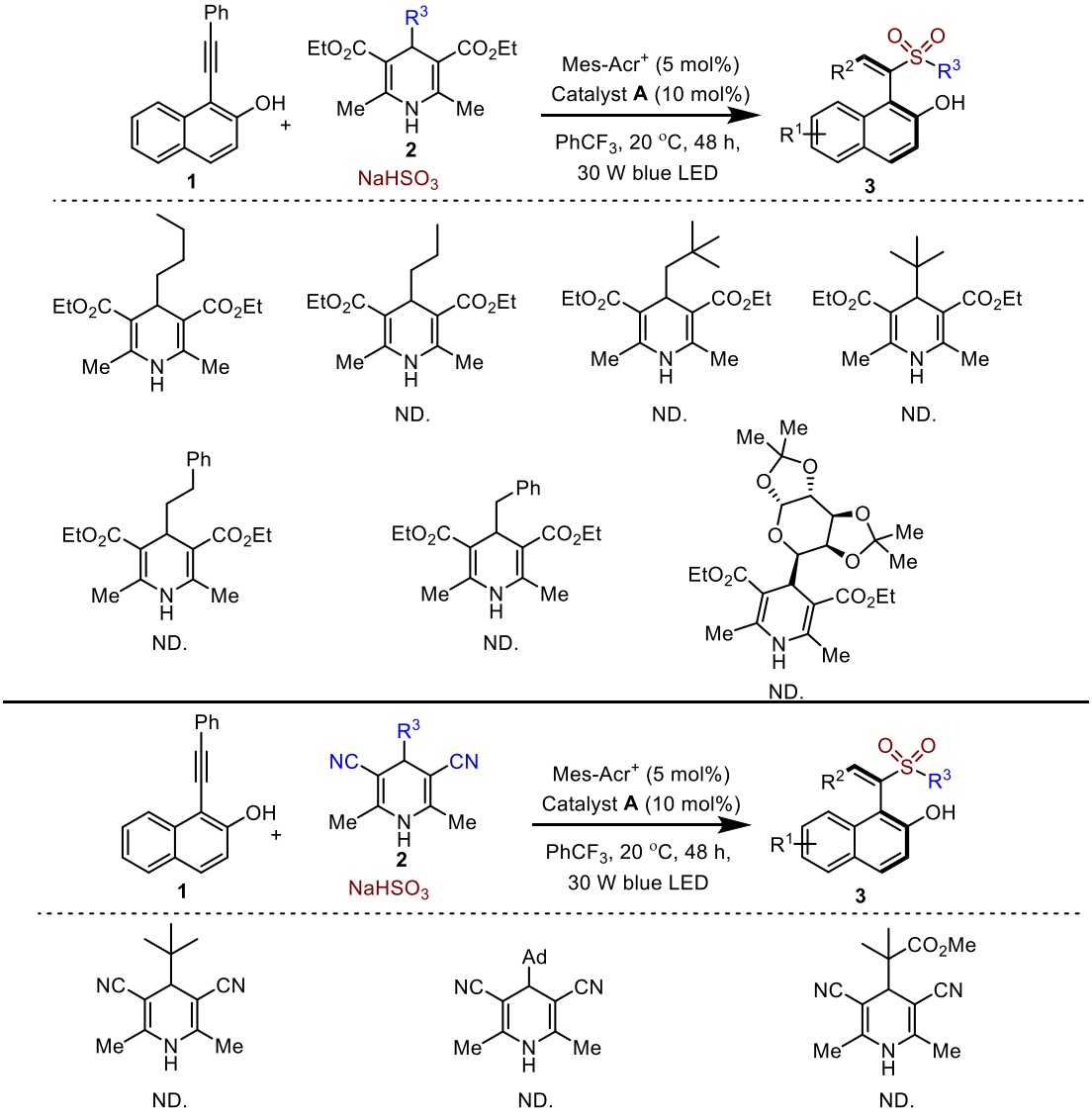


All optimization reactions were set up in a glove box under N_2 atmosphere. Substrate **1** (0.2 mmol, 1.0 equiv), 4-substituted Hantzsch esters **2** (0.4 mmol, 2 equiv), $NaHSO_3$ (0.4 mmol, 2.0 equiv), Catalyst **A** (10 mol%) were added to a solution of photocatalyst Mes–Acr^{+} (5 mol%) in dry $PhCF_3$ (2 mL) at room temperature. The

heterogenous mixture was placed in the irradiation apparatus equipped with blue LEDs. The resulting mixture was stirred at 20 °C for 48 h. Upon completion of the reaction, the resulting crude residue was concentrated in vacuum and purified by column chromatography with gradient eluents to afford the desired product **3**.

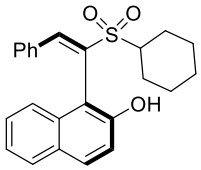
3. Substrate scopes with limitations

4-substituted Hantzsch esters **2** was employed in the reaction with 1-alkynylnaphthalen-2-ol **1** and $NaHSO_3$ under the standard reaction conditions.

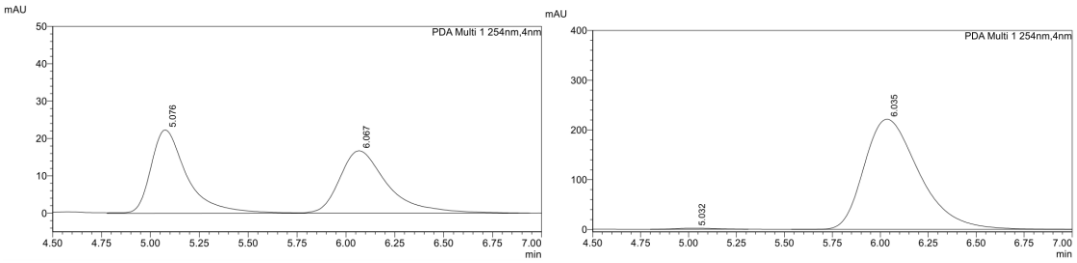


4. Characterization of all product s

(E)-1-(1-(cyclohexylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3a)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 80% yield; $[\alpha]_D^{20}$ = +147.8 (*c* = 0.12 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.11 (s, 1H), 7.99 (s, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.82–7.80 (m, 1H), 7.57–7.55 (m, 1H), 7.34–7.30 (m, 3H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 12.0 Hz, 1H), 2.22 (d, *J* = 12.4 Hz, 1H), 2.07 (d, *J* = 12.4 Hz, 1H), 1.79 (t, *J* = 12.0 Hz, 2H), 1.66–1.48 (m, 3H), 1.16 (dd, *J* = 25.6, 12.8 Hz, 1H), 1.04–0.91 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.3, 144.5, 132.4, 132.3, 132.0, 131.9, 130.7, 130.4, 129.5, 128.8, 128.6, 127.5, 124.0, 122.8, 120.4, 111.3, 58.3, 26.6, 25.1, 25.1, 24.8, 24.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 5.032 min (minor), t_R = 6.035 min (major).[1]



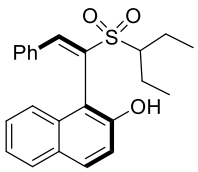
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	5.076	286913	22358	50.109
2	6.067	285662	16728	49.891

PDA Ch1 254nm

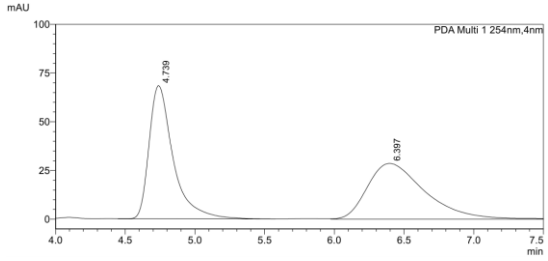
Peak#	Ret. Time	Area	Height	Aera%
1	5.032	30817	2001	0.692
2	6.035	4424090	221448	99.308

(E)-1-(1-(pentan-3-ylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3b)



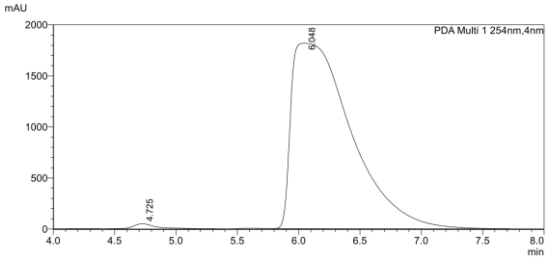
Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 61% yield; $[\alpha]_D^{20}$ = +157.1 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.14 (m, 2H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.83–7.80 (m, 1H), 7.54–7.51 (m, 1H), 7.35 (d, *J* = 9.2 Hz, 1H), 7.33–7.29 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 2.67–2.61 (m, 1H), 2.02–1.92 (m, 1H), 1.86–1.78 (m, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.5, 144.0, 132.5, 132.4, 132.3,

131.6, 130.7, 130.4, 129.5, 128.9, 128.6, 127.6, 124.0, 122.6, 120.7, 111.2, 60.5, 20.7, 18.4, 10.8, 10.6; HRMS (ESI) for $C_{23}H_{24}NaO_3S^+$ calcd. 403.1338, found: 403.1344; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 4.725 min (minor), t_R = 6.048 min (major).



PDA Ch1 254nm

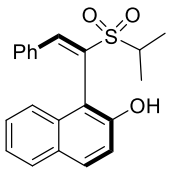
Peak#	Ret. Time	Area	Height	Aera%
1	4.739	820852	68333	49.834
2	6.397	826319	28637	50.166



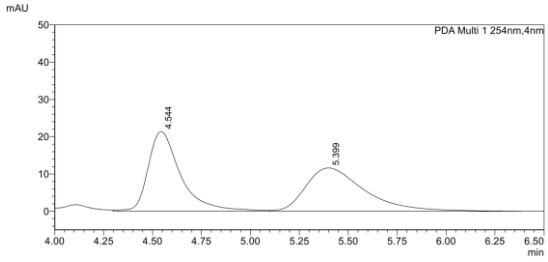
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	4.725	739184	50205	1.179
2	6.048	61933431	1816637	98.821

(E)-1-(1-(isopropylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3c)

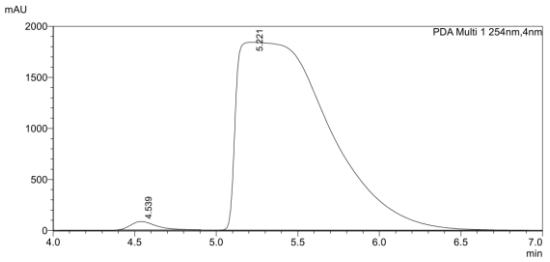


Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 70% yield; $[\alpha]_D^{20}$ = +221.5 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.15 (s, 1H), 8.07 (s, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.82–7.79 (m, 1H), 7.58–7.56 (m, 1H), 7.34–7.29 (m, 3H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 3.09–2.99 (m, 1H), 1.36 (d, *J* = 6.4 Hz, 3H), 1.29 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.4, 144.3, 132.4, 132.3, 131.9, 131.6, 130.8, 130.5, 129.5, 128.9, 128.7, 127.5, 124.0, 123.0, 120.5, 111.1, 50.4, 16.7, 14.4; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 4.539 min (minor), t_R = 5.221 min (major). [1]



PDA Ch1 254nm

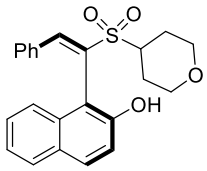
Peak#	Ret. Time	Area	Height	Aera%
1	4.544	248860	21440	50.523
2	5.399	243704	11632	49.477



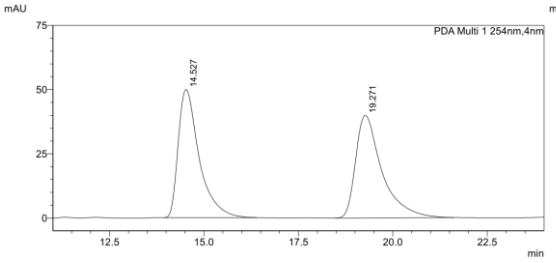
PDA Ch1 254nm

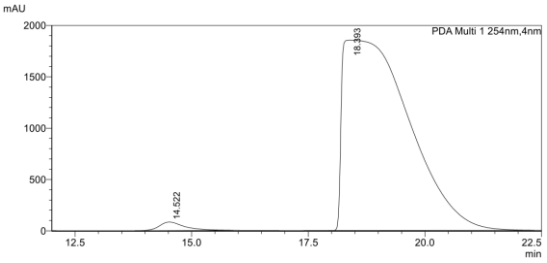
Peak#	Ret. Time	Area	Height	Aera%
1	4.539	889005	82217	1.220
2	5.221	71995935	1839510	98.780

(E)-1-(2-phenyl-1-((tetrahydro-2H-pyran-4-yl)sulfonyl)vinyl)naphthalen-2-ol (3d)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 85% yield; $[\alpha]_D^{20}$ = +140.2 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.14 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.84–7.82 (m, 1H), 7.77 (s, 1H), 7.56–7.54 (m, 1H), 7.35–7.31 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 4.02–3.95 (m, 2H), 3.15–2.99 (m, 3H), 2.04–1.82 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 153.9, 145.1, 132.5, 132.3, 132.0, 131.7, 130.9, 130.4, 129.4, 128.9, 128.7, 127.6, 124.2, 123.0, 120.0, 110.9, 66.6, 66.2, 55.9, 26.0, 24.9; HRMS (ESI) for $C_{23}H_{22}NaO_4S^+$ calcd. 417.1131, found: 417.1143; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_R = 14.522 min (minor), t_R = 18.393 min (major).





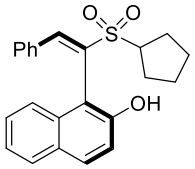
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	14.527	1924995	49920	49.912
2	19.271	1931763	39893	50.088

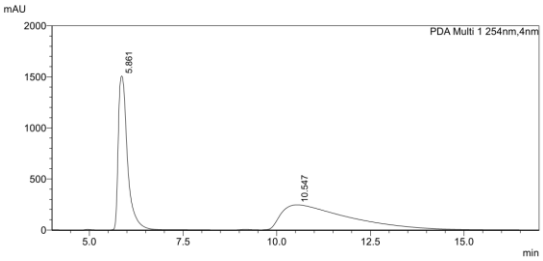
PDA Ch1 254nm

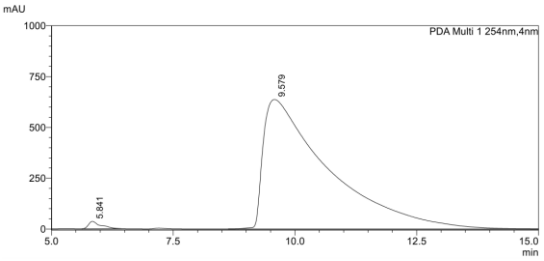
Peak#	Ret. Time	Area	Height	Aera%
1	14.522	3164209	83378	1.683
2	18.393	184856381	1853963	98.317

(E)-1-(1-(cyclopentylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3e)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 78% yield; $[\alpha]_D^{20}$ = +206.1 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.17 (s, 1H), 8.09 (s, 1H),7.91 (d, *J* = 8.8 Hz, 1H), 7.83–7.80 (m, 1H), 7.57–7.55 (m, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.33–7.28 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 3.33–3.25 (m, 1H), 2.24–2.09 (m, 2H), 1.84–1.74 (m, 3H), 1.70–1.63 (m, 1H), 1.61–1.52 (m, 1H), 1.46–1.39 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.5, 143.5, 132.5, 132.4, 132.3, 131.7, 130.8, 130.5, 129.5, 128.8, 128.6, 127.4, 124.0, 123.1, 120.7, 111.2, 58.6, 28.6, 26.3, 26.3, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 5.841 min (minor), t_R = 9.579 min (major). [1]





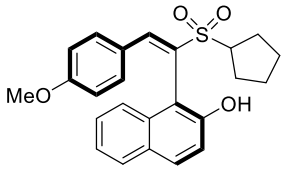
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	5.861	25907394	1506986	45.642
2	10.547	30854974	245483	54.358

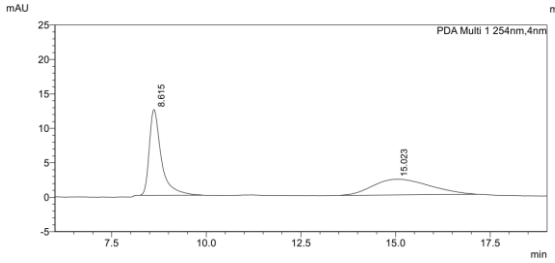
PDA Ch1 254nm

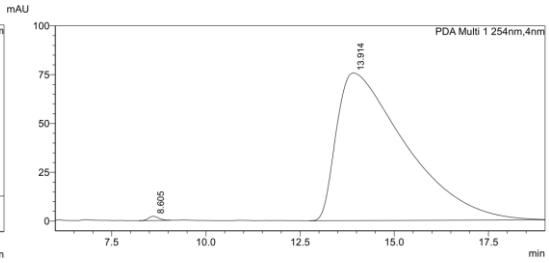
Peak#	Ret. Time	Area	Height	Aera%
1	5.841	623898	36212	1.042
2	9.579	59274555	636867	98.958

(E)-1-(1-(cyclopentylsulfonyl)-2-(4-methoxyphenyl)vinyl)naphthalen-2-ol (3f)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 52% yield; $[\alpha]_D^{20}$ = +285.2 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) 8.10 (s, 2H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.84–7.81 (m, 1H), 7.59–7.57 (m, 1H), 7.37–7.31 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 3.66 (s, 3H), 3.31–3.24 (m, 1H), 2.23–2.08 (m, 2H), 1,84–1.74 (m, 3H), 1.69–1.63 (m, 1H), 1.58–1.52 (m, 1H), 1.45–1.39 (m, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) 161.5, 154.5, 143.1, 132.6, 132.2, 131.8, 129.5, 129.1, 128.8, 127.4, 124.9, 124.0, 123.3, 120.8, 114.1, 111.4, 58.6, 55.2, 28.6, 26.4, 26.3, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 8.605 min (minor), t_R = 13.914 min (major). [1]





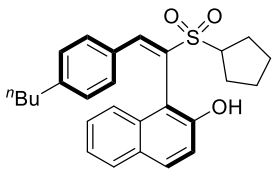
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	8.615	273014	12424	53.329
2	15.023	238929	2289	46.671

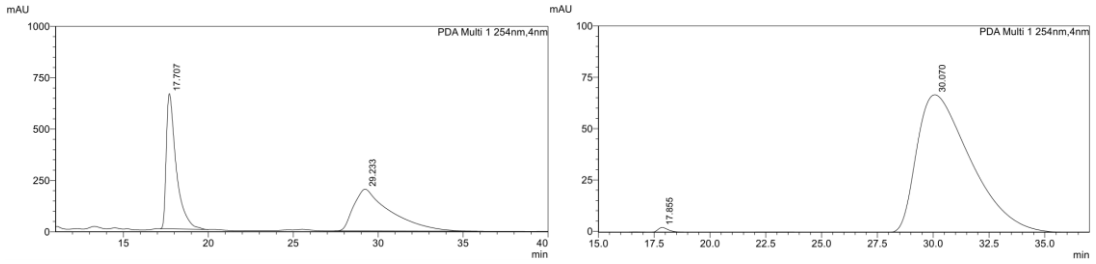
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	8.605	40761	2143	0.420
2	13.914	9667989	75620	99.580

(E)-1-(2-(4-butylphenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3g)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 71% yield; $[\alpha]_D^{20}$ = +265.6 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.14 (s, 1H), 8.05 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.83–7.79 (m, 1H), 7.60–7.58 (m, 1H), 7.36–7.30 (m, 3H), 6.89–6.84 (m, 4H), 3.32–3.25 (m, 1H), 2.43 (t, *J* = 7.6 Hz, 2H), 2.24–2.08 (m, 2H), 1.86–1.74 (m, 3H), 1.69–1.63 (m, 1H), 1.58–1.52 (m, 1H), 1.47–1.39 (m, 3H), 1.24–1.16 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.4, 146.4, 143.5, 132.2, 131.9, 131.0, 130.7, 129.7, 129.5, 128.8, 127.4, 124.0, 123.3, 120.7, 111.4, 58.6, 35.4, 33.0, 28.6, 26.4, 26.3, 26.2, 22.2, 13.9; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_R = 17.855 min (minor), t_R = 30.070 min (major). [1]



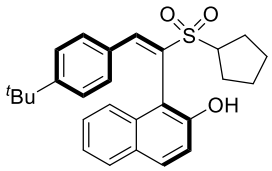
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	17.707	26794687	658097	46.719
2	29.233	30558627	203894	53.281

PDA Ch1 254nm

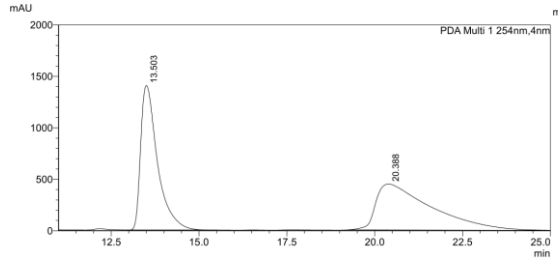
Peak#	Ret. Time	Area	Height	Aera%
1	17.855	87221	2446	0.768
2	30.070	11274239	67228	99.232

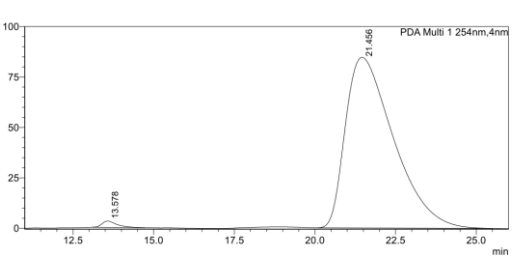
(E)-1-(2-(4-(tert-butyl)phenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3h)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 52% yield; $[\alpha]_D^{20}$ = +284.3 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.14 (s, 1H), 7.96 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.85–7.83 (m, 1H), 7.63–7.61 (m, 1H), 7.36–7.33 (m, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.32–3.24 (m, 1H), 2.24–2.08 (m, 2H), 1.86–1.74 (m, 3H), 1.71–1.64 (m, 1H), 1.58–1.52 (m, 1H), 1.45–1.41 (m, 1H), 1.16 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.5, 154.2, 143.3, 132.2, 132.0, 131.0, 130.6, 129.4, 129.4, 128.8, 127.5, 125.8, 124.0, 123.3, 120.7, 111.4, 58.6, 34.8, 30.9, 28.6, 26.4, 26.3, 26.2; HRMS (ESI) for $C_{27}H_{30}NaO_3S^+$ calcd. 457.1808, found:

457.1817; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_R = 13.578 min (minor), t_R = 21.456 min (major).





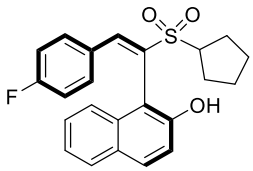
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	13.503	46642236	1404199	48.727
2	20.388	49078766	446429	51.273

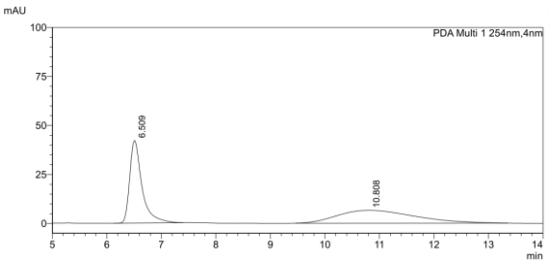
PDA Ch1 254nm

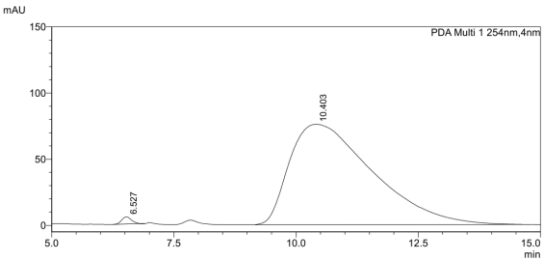
Peak#	Ret. Time	Area	Height	Aera%
1	13.578	101044	3130	1.137
2	21.456	8783167	84612	98.863

(E)-1-(1-(cyclopentylsulfonyl)-2-(4-fluorophenyl)vinyl)naphthalen-2-ol (3i)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 71% yield; $[\alpha]_D^{20}$ = +213.9 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.13 (d, *J* = 2.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.84–7.81(m, 1H), 7.54–7.51 (m, 1H), 7.37–7.31 (m, 3H), 6.96 (dd, *J* = 8.4, 5.6 Hz, 2H), 6.74 (t, *J* = 8.4 Hz, 2H), 3.32–3.25 (m, 1H), 2.21–2.09 (m, 2H), 1.85–1.75 (m, 3H), 1.70–1.67 (m, 1H), 1.59–1.53 (m, 1H), 1.47–1.41 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 163.8 (d, *J* = 251.0 Hz), 154.5, 142.1, 132.7, 132.6, 132.5, 132.1 (d, *J* = 3.0 Hz), 131.5, 129.5, 128.9, 128.6 (d, *J* = 3.0 Hz), 127.6, 124.2, 123.0, 120.8, 115.9 (d, *J* = 22.0 Hz), 110.8, 58.6, 28.6, 26.3, 26.3, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 6.527 min (minor), t_R = 10.403 min (major). [1]





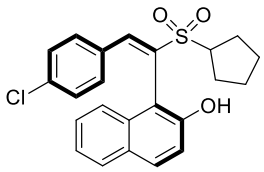
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	6.509	660777	42148	50.529
2	10.808	646950	6595	49.471

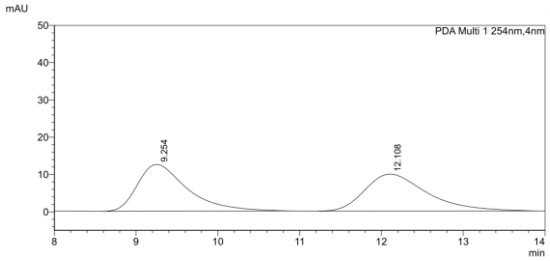
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	6.527	75817	5428	0.836
2	10.403	8994270	75949	99.164

(E)-1-(2-(4-chlorophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3j)

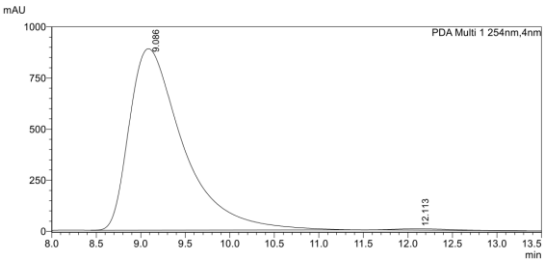


Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 61% yield; $[\alpha]_D^{20}$ = +166.0 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.11 (s, 2H), 7.91 (d, *J* = 9.2 Hz, 1H), 7.84–7.80 (m, 1H), 7.53–7.51 (m, 1H), 7.36–7.31 (m, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 3.33–3.25 (m, 1H), 2.21–2.08 (m, 2H), 1.85–1.74 (m, 3H), 1.70–1.64 (m, 1H), 1.61–1.52 (m, 1H), 1.48–1.40 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.5, 142.0, 136.8, 133.2, 132.6, 131.6, 131.5, 130.8, 129.5, 129.0, 128.9, 127.6, 124.2, 122.9, 122.3, 120.7, 110.7, 58.6, 28.6, 26.3, 26.3, 26.2; HRMS (ESI) for $C_{23}H_{21}ClNaO_3S^+$ calcd. 435.0792, found: 435.0801; **HPLC analysis**: CHIRALPAK AS-H (hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_R = 9.086 min (major), t_R = 12.113 min (minor).



PDA Ch1 254nm

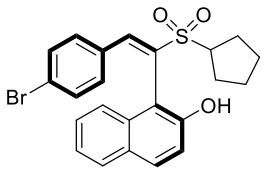
Peak#	Ret. Time	Area	Height	Aera%
1	9.254	531713	12556	50.401
2	12.108	523245	9906	49.599



PDA Ch1 254nm

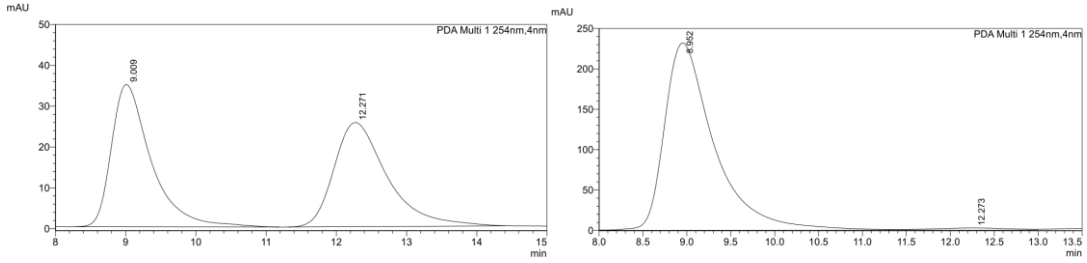
Peak#	Ret. Time	Area	Height	Aera%
1	9.086	37307311	887870	99.282
2	12.113	269896	6519	0.718

(E)-1-(2-(4-bromophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3k)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 66% yield; $[\alpha]_D^{20}$ = +248.5 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.09 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.82 (s, 1H), 7.52 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.6 Hz, 2H), 3.29 (s, 1H), 2.18–2.10 (m, 2H), 1.78 (s, 3H), 1.68 (d, *J* = 6.8 Hz, 1H), 1.57 (s, 1H), 1.43 (s, 1H), 1.26 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.4, 142.0, 133.5, 132.6, 131.9, 131.7, 131.4, 131.2, 129.5, 128.9, 127.6, 125.4, 124.2, 122.9, 120.7, 110.8, 58.7, 28.5, 26.3, 26.2; HRMS (ESI) for $C_{23}H_{21}BrNaO_3S^+$ calcd. 479.0287, found: 479.0294; **HPLC analysis**:

CHIRALPAK AS-H (hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t_R = 8.952 min (major), t_R = 12.273 min (minor).



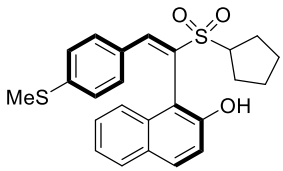
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	9.009	1374064	34836	50.518
2	12.271	1345888	25507	49.482

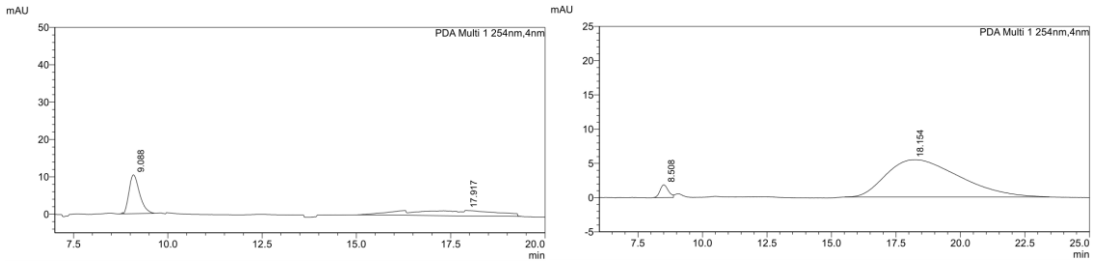
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	8.952	9132655	232049	98.033
2	12.273	183220	2795	1.967

(E)-1-(1-(cyclopentylsulfonyl)-2-(4-(methylthio)phenyl)vinyl)naphthalen-2-ol (3l)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 81% yield; $[\alpha]_D^{20}$ = +308.6 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.09 (s, 2H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.83–7.80 (m, 1H), 7.58–7.55 (m, 1H), 7.36–7.30 (m, 3H), 6.85 (s, 4H), 3.32–3.24 (m, 1H), 2.32 (s, 3H), 2.23–2.08 (m, 2H), 1.85–1.73 (m, 3H), 1.69–1.63 (m, 1H), 1.58–1.52 (m, 1H), 1.45–1.39 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.4, 143.1, 142.9, 132.3, 131.7, 131.0, 130.8, 129.5, 128.8, 128.5, 127.5, 125.3, 124.1, 123.2, 120.7, 111.2, 58.6, 28.6, 26.4, 26.3, 26.2, 14.6; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 8.508 min (minor), t_R = 18.154 min (major). [1]



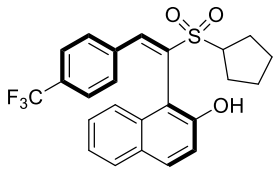
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	9.088	202912	10373	46.003
2	17.917	238174	1469	53.997

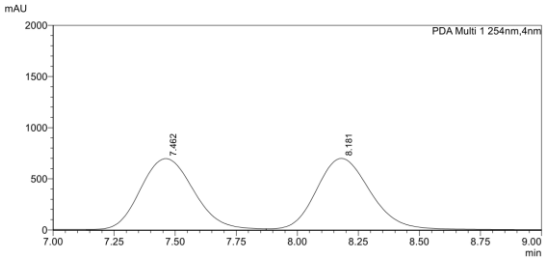
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	8.508	41906	1865	3.754
2	18.154	1074422	5452	96.246

(E)-1-(1-(cyclopentylsulfonyl)-2-(4-(trifluoromethyl)phenyl)vinyl)naphthalen-2-ol (3m)

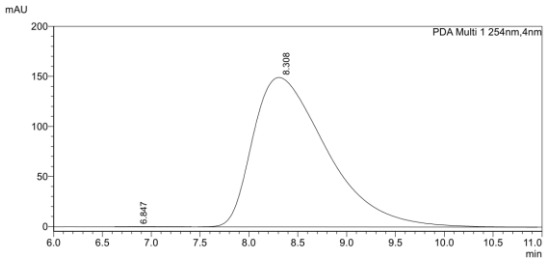


Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 53% yield; $[\alpha]_D^{20}$ = +191.0 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.19 (s, 1H), 8.07 (s, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.84–7.81 (m, 1H), 7.53–7.50 (m, 1H), 7.33 (dd, *J* = 16.8, 9.2 Hz, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.34–3.27 (m, 1H), 2.22–2.09 (m, 2H), 1.85–1.75 (m, 3H), 1.71–1.65 (m, 1H), 1.60–1.59 (m, 1H), 1.48–1.43 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.4, 141.5, 135.6, 132.7, 131.9 (q, *J* = 33.0 Hz), 131.4, 130.4, 129.4, 129.0, 127.7, 125.6 (q, *J* = 4.0 Hz), 124.3, 123.8 (q, *J* = 271.0 Hz), 122.7, 120.7, 110.5, 58.6, 29.7, 28.5, 26.3, 26.3 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 6.847 min (minor), t_R = 8.308 min (major). [1]



PDA Ch1 254nm

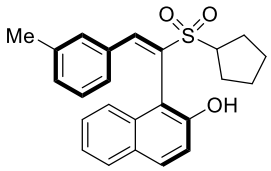
Peak#	Ret. Time	Area	Height	Aera%
1	7.462	10649937	696123	49.436
2	8.181	10892809	699342	50.564



PDA Ch1 254nm

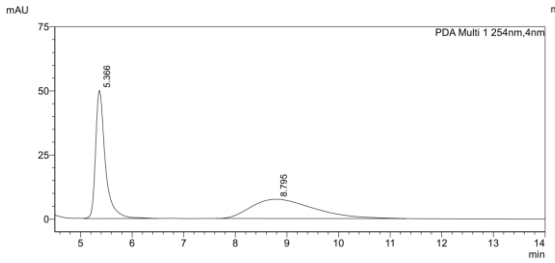
Peak#	Ret. Time	Area	Height	Aera%
1	6.847	4098	171	0.052
2	8.308	7877667	149385	99.948

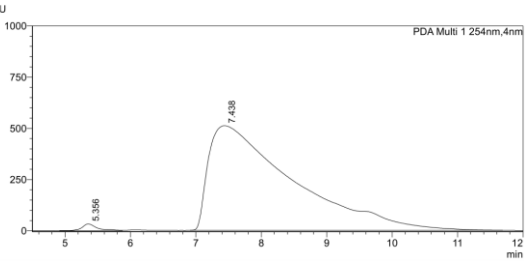
(E)-1-(1-(cyclopentylsulfonyl)-2-(m-tolyl)vinyl)naphthalen-2-ol (3n)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 54% yield; $[\alpha]_D^{20}$ = +308.6 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.13 (s, 2H), 7.91 (d, *J* = 9.2 Hz, 1H), 7.83–7.79 (m, 1H), 7.56–7.52 (m, 1H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.32–7.28 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.33–3.26 (m, 1H), 2.24–2.09 (m, 2H), 2.05 (s, 3H), 1.86–1.74 (m, 3H), 1.70–1.64 (m, 1H), 1.59–1.52 (m, 1H), 1.48–1.40 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.5, 143.7, 138.1, 132.3, 132.2, 132.1, 131.7, 131.7, 131.6, 129.5, 128.7, 128.5, 127.4, 127.2, 124.0, 123.2, 120.6, 111.3, 58.5, 28.6, 26.3, 26.3, 26.2, 21.1; HRMS (ESI) for $C_{24}H_{24}NaO_3S^+$ calcd. 415.1338, found: 417.1349; **HPLC analysis**:

CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 5.356 min (minor), t_R = 7.438 min (major).





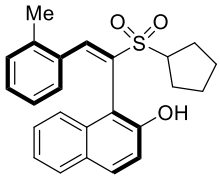
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	5.366	654162	49974	50.632
2	8.795	637837	7540	49.368

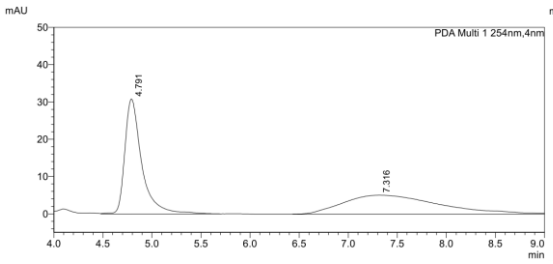
PDA Ch1 254nm

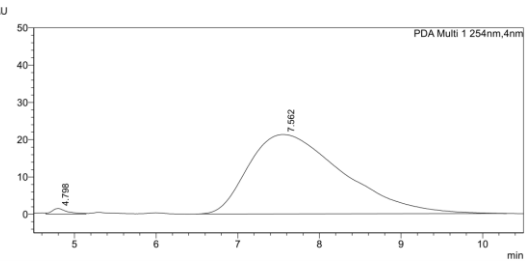
Peak#	Ret. Time	Area	Height	Aera%
1	5.356	554532	33219	1.202
2	7.438	45567689	510381	98.798

(E)-1-(1-(cyclopentylsulfonyl)-2-(o-tolyl)vinyl)naphthalen-2-ol (3o)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 77% yield; $[\alpha]_D^{20}$ = +45.8 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.42 (s, 1H), 8.21 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.28–7.22 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.99 (td, *J* = 7.2, 0.8 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 3.32–3.24 (m, 1H), 2.52 (s, 3H), 2.24–2.10 (m, 2H), 1.88–1.74 (m, 3H), 1.70–1.64 (m, 1H), 1.59–1.54 (m, 1H), 1.47–1.40 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 155.1, 142.7, 137.8, 133.4, 132.2, 131.7, 131.5, 130.2, 130.1, 129.3, 128.7, 127.9, 127.1, 125.9, 123.8, 122.9, 120.3, 111.2, 58.6, 28.6, 26.4, 26.3, 20.1; HRMS (ESI) for $C_{24}H_{24}NaO_3S^+$ calcd. 415.1338, found: 417.1349; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 4.798 min (minor), t_R = 7.562 min (major).





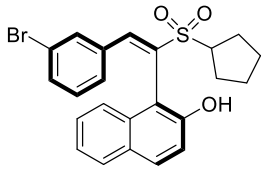
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	4.791	368961	30856	51.164
2	7.316	352172	5096	48.836

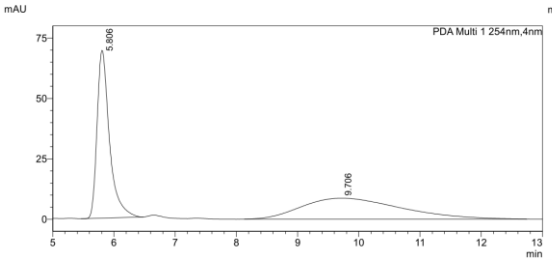
PDA Ch1 254nm

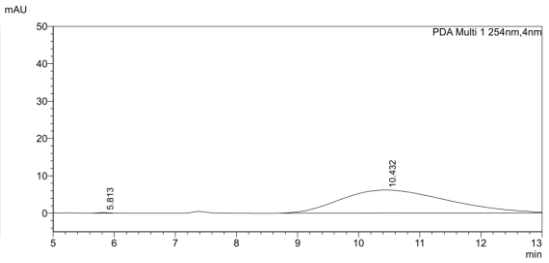
Peak#	Ret. Time	Area	Height	Aera%
1	4.798	20456	1541	1.181
2	7.562	1711791	21276	98.819

(E)-1-(2-(3-bromophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3p)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 67% yield; $[\alpha]_D^{20}$ = +16.0 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.10 (d, *J* = 20.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.83–7.81 (m, 1H), 7.52–7.50 (m, 1H), 7.36–7.31 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.16 (s, 1H), 6.89–6.81 (m, 2H), 3.34–3.27 (m, 1H), 2.21–2.09 (m, 2H), 1.86–1.75 (m, 3H), 1.71–1.68 (m, 1H), 1.59–1.56 (m, 1H), 1.47–1.42 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.5, 141.7, 134.5, 134.3, 133.5, 133.5, 132.7, 131.4, 130.1, 129.5, 128.9, 128.3, 127.6, 124.2, 122.8, 122.5, 120.6, 110.6, 58.6, 28.6, 26.3, 26.3, 26.2; HRMS (ESI) for $C_{23}H_{21}BrNaO_3S^+$ calcd. 479.0287, found: 479.0294; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 5.813 min (minor), t_R = 10.432 min (major).





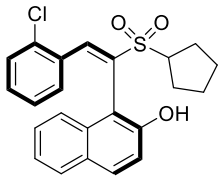
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	5.806	977592	69366	50.090
2	9.706	974086	8639	49.910

PDA Ch1 254nm

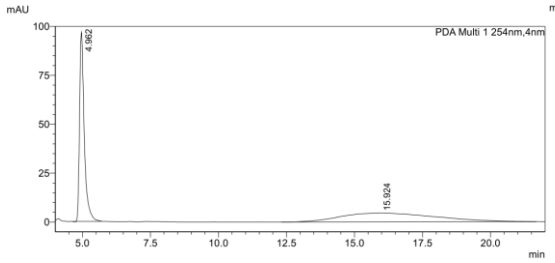
Peak#	Ret. Time	Area	Height	Aera%
1	5.813	1598	147	0.211
2	10.432	754305	6171	99.789

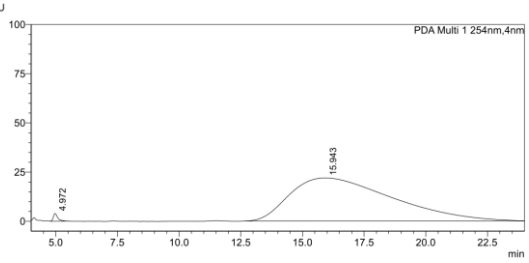
(E)-1-(2-(2-chlorophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3q)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 61% yield; $[\alpha]_D^{20}$ = -26.2 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, CD_3CN)** δ (ppm) 8.32 (s, 1H), 7.95 (s, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.41–7.36 (m, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.16–7.11 (m, 1H), 6.92 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 3.58–3.51 (m, 1H), 2.32 (s, 2H), 2.11–1.93 (m, 3H), 1.90–1.81 (m, 1H), 1.74–1.71 (m, 1H), 1.58–1.55 (m, 1H); **^{13}C NMR (100 MHz, CD_3CN)** δ (ppm) 154.3, 140.9, 138.2, 134.7, 133.6, 132.3, 132.2, 131.6, 129.9, 129.4, 129.3, 128.8, 127.7, 127.3, 124.7, 124.3, 118.7, 117.9, 111.1, 61.0, 28.3, 26.9, 26.5, 26.3; HRMS (ESI) for $C_{23}H_{21}ClNaO_3S^+$ calcd. 435.0792, found:

435.0802; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 4.972 min (minor), t_R = 15.943 min (major).





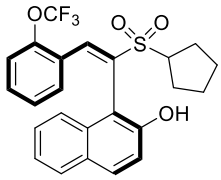
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	4.962	1166723	96747	51.374
2	15.924	1104303	4483	48.626

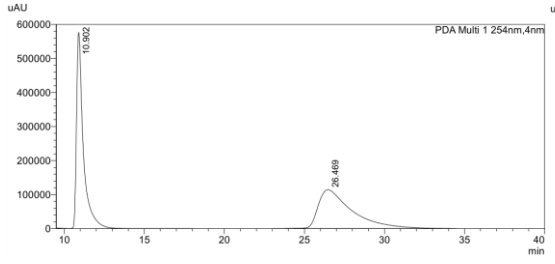
PDA Ch1 254nm

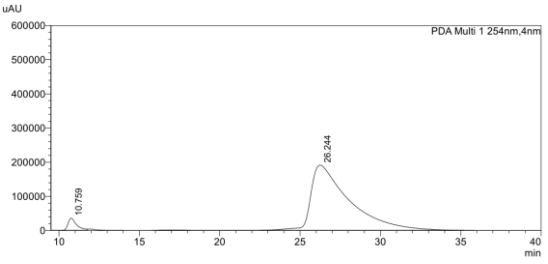
Peak#	Ret. Time	Area	Height	Aera%
1	4.972	51016	3972	0.801
2	15.943	6317613	21920	99.199

(E)-1-(1-(cyclopentylsulfonyl)-2-(2-(trifluoromethoxy)phenyl)vinyl)naphthalen-2-ol (3r)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 51% yield; $[\alpha]_D^{20}$ = +74.6 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.43 (s, 1H), 8.25 (s, 1H), 7.87 (t, *J* = 8.8 Hz, 1H), 7.76–7.74 (m, 1H), 7.50–7.48 (m, 1H), 7.34–7.26 (m, 3H), 7.17–7.14 (m, 2H), 6.75–6.70 (m, 2H), 3.33–3.26 (m, 1H), 2.24–2.11 (m, 2H), 1.89–1.77 (m, 3H), 1.73–1.66 (m, 1H), 1.62–1.55 (m, 1H), 1.48–1.42 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 155.0, 147.8, 137.4, 135.9, 132.5, 131.7, 131.4, 129.4, 129.2, 128.7, 127.4, 126.8, 126.0, 124.0, 122.7, 121.8, 120.6 (q, *J* = 257.0 Hz), 120.4, 110.8, 58.7, 28.4, 26.3, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 254 nm, t_R = 10.759 min (minor), t_R = 26.244 min (major). [1]





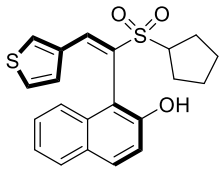
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	10.902	16994267	575629	50.497
2	26.469	16659839	113772	49.503

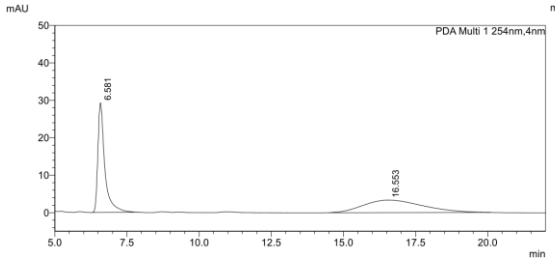
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	10.759	1304216	35312	3.987
2	26.244	31409745	190297	96.013

(E)-1-(1-(cyclopentylsulfonyl)-2-(thiophen-3-yl)vinyl)naphthalen-2-ol (3s)

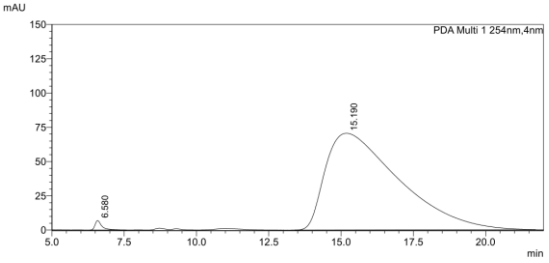


Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 66% yield; $[\alpha]_D^{20}$ = +317.4 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.18 (s, 1H), 8.05 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.84 (t, *J* = 5.2 Hz, 1H), 7.61–7.58 (m, 1H), 7.37–7.33 (m, 3H), 7.14 (d, *J* = 2.0 Hz, 1H), 6.93–6.91 (m, 1H), 6.24 (d, *J* = 5.2 Hz, 1H), 3.35–3.28 (m, 1H), 2.25–2.09 (m, 2H), 1.87–1.76 (m, 3H), 1.71–1.65 (m, 1H), 1.59–1.54 (m, 1H), 1.48–1.39 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.3, 137.2, 134.3, 132.4, 132.2, 131.9, 130.4, 129.4, 128.9, 127.6, 127.5, 126.3, 124.1, 123.2, 120.7, 111.3, 58.9, 28.6, 26.4; 26.3, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 6.580 min (minor), t_R = 15.190 min (major). [1]



PDA Ch1 254nm

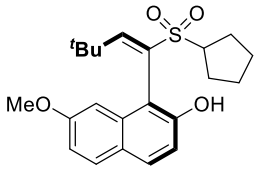
Peak#	Ret. Time	Area	Height	Aera%
1	6.581	492205	29300	50.971
2	16.553	473453	3326	49.029



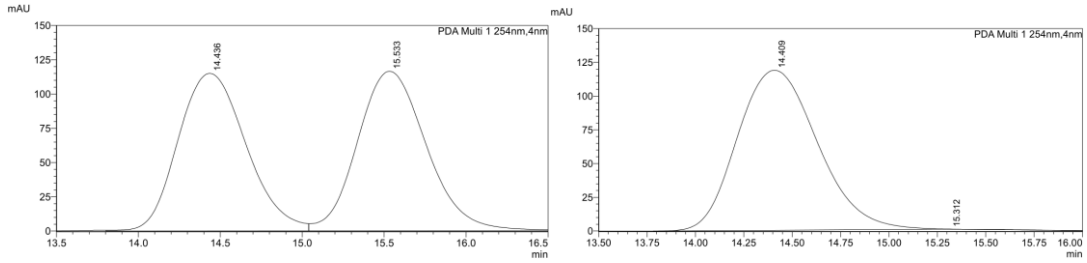
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	6.580	114655	6885	0.909
2	15.190	12495940	70597	99.091

(E)-1-(1-(cyclopentylsulfonyl)-3,3-dimethylbut-1-en-1-yl)-7-methoxynaphthalen-2-ol (3t)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 77% yield; $[\alpha]_D^{20}$ = +89.0 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.73 (dd, *J* = 19.6, 8.8 Hz, 2H), 7.56 (s, 1H), 7.37 (s, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 7.03 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 3.88 (s, 3H), 3.29–3.22 (m, 1H), 2.22–2.15 (m, 1H), 2.10–2.01 (m, 1H), 1.89–1.81 (m, 1H), 1.77–1.72 (m, 2H), 1.65–1.56 (m, 2H), 1.45–1.38 (m, 1H), 0.89 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 158.6, 155.9, 154.6, 135.5, 132.1, 131.6, 130.3, 124.2, 117.4, 115.8, 110.9, 103.4, 58.1, 55.2, 35.6, 29.0, 28.6, 26.4, 26.3, 26.2; HRMS (ESI) for $C_{22}H_{28}NaO_4S^+$ calcd. 411.1601, found: 411.1606; **HPLC analysis**: CHIRALPAK ID-H (hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 254 nm, t_R = 14.409 min (major), t_R = 15.312 min (minor).



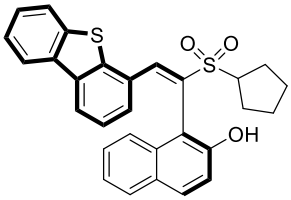
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	14.436	3323894	115007	49.285
2	15.533	3420294	116493	50.715

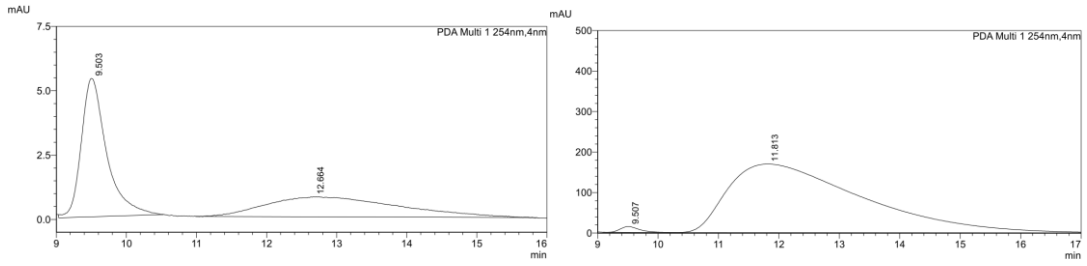
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	14.409	3420963	118619	99.997
2	15.312	111	-6	0.003

(E)-1-(1-(cyclopentylsulfonyl)-2-(dibenzo[b,d]thiophen-4-yl)vinyl)naphthalen-2-ol (3u)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 77% yield; $[\alpha]_D^{20}$ = -128.8 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.46 (s, 1H), 8.24 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.89–7.83 (m, 3H), 7.74–7.72 (m, 1H), 7.53–7.40 (m, 3H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.22–7.15 (m, 2H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 3.36–3.29 (m, 1H), 2.31–2.25 (m, 1H), 2.21–2.14 (m, 1H), 1.91–1.77 (m, 3H), 1.73–1.68 (m, 1H), 1.63–1.56 (m, 1H), 1.48–1.42 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.9, 141.5, 140.4, 138.6, 136.0, 135.4, 134.8, 132.5, 131.5, 129.4, 128.7, 127.5, 127.3, 127.3, 126.1, 124.8, 124.6, 124.0, 123.2, 122.9, 122.8, 121.8, 120.5, 111.1, 58.8, 28.6, 26.4, 26.3, 26.3; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 9.507 min (minor), t_R = 11.813 min (major). [1]



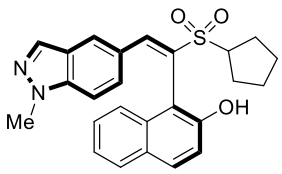
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	9.503	135246	5379	56.943
2	12.664	102267	776	43.057

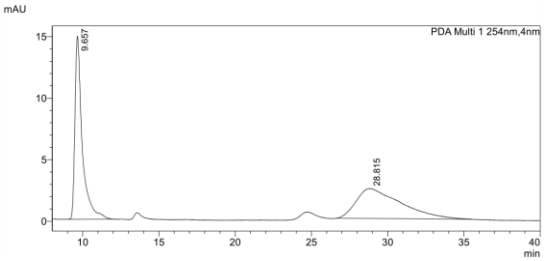
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	9.507	313662	14219	1.184
2	11.813	26179735	169241	98.816

(E)-1-(1-(cyclopentylsulfonyl)-2-(1-methyl-1H-indazol-5-yl)vinyl)naphthalen-2-ol (3v)

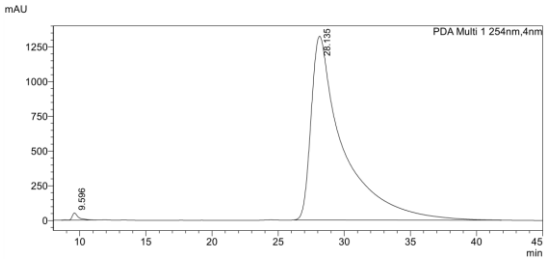


Purification by flash chromatography (petroleum ether/acetone = 2/1). White solid; 59% yield; $[\alpha]_D^{20}$ = +264.0 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.27 (s, 2H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.83–7.79 (m, 2H), 7.60–7.57 (m, 1H), 7.53 (s, 1H), 7.39 (d, *J* = 9.2 Hz, 1H), 7.31–7.25 (m, 2H), 6.94 (d, *J* = 9.2 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H), 3.35–3.27 (m, 1H), 2.26–2.10 (m, 2H), 1.85–1.75 (m, 3H), 1.71–1.65 (m, 1H), 1.61–1.54 (m, 1H), 1.46–1.40 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.7, 143.9, 140.1, 134.0, 132.3, 131.8, 130.2, 129.5, 128.8, 127.4, 127.4, 125.8, 125.2, 124.0, 123.9, 123.2, 120.7, 111.4, 109.2, 58.7, 35.5, 28.6, 26.3, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 9.596 min (minor), t_R = 28.135 min (major). [1]



PDA Ch1 254nm

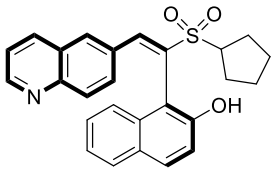
Peak#	Ret. Time	Area	Height	Aera%
1	9.657	494869	14866	49.910
2	28.815	496657	2438	50.090



PDA Ch1 254nm

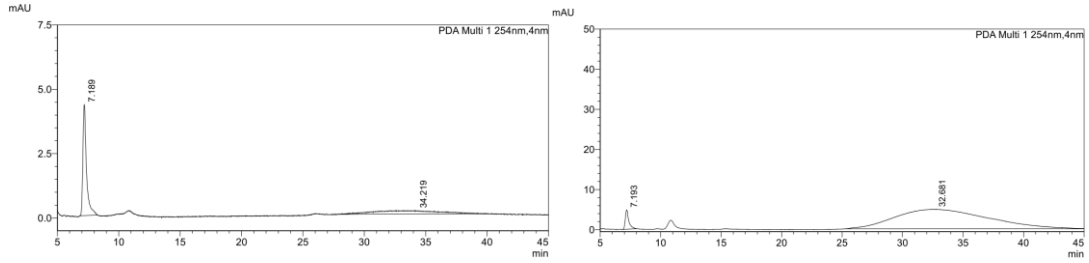
Peak#	Ret. Time	Area	Height	Aera%
1	9.596	1741460	52027	0.775
2	28.135	223010574	1323271	99.225

(E)-1-(1-(cyclopentylsulfonyl)-2-(quinolin-6-yl)vinyl)naphthalen-2-ol (3w)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 87% yield; $[\alpha]_D^{20}$ = +205.6 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 9.24 (s, 1H), 8.80 (d, *J* = 2.8 Hz, 1H), 8.28 (s, 1H), 7.90 (t, *J* = 5.6 Hz, 2H), 7.80–7.77 (m, 1H), 7.67–7.61 (m, 3H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.32–7.26 (m, 3H), 7.17 (dd, *J* = 9.2, 1.6 Hz, 1H), 3.49–3.41 (m, 1H), 2.25–2.11 (m, 2H), 1.88–1.75 (m, 4H), 1.62–1.53 (m, 1H), 1.50–1.41 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 154.5, 151.3, 147.9, 142.0, 137.2, 135.0, 132.5, 132.4, 131.8, 131.3, 129.4, 129.3, 129.1, 128.7, 127.8, 127.5, 124.0, 123.5, 121.7, 120.0, 111.0, 59.3, 27.9, 27.0, 26.3, 26.2; HRMS (ESI) for $C_{26}H_{24}NO_3S^+$

calcd. 430.1471, found: 430.1484; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 7.193 min (minor), t_R = 32.681 min (major).



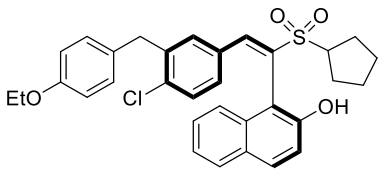
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	7.189	87629	4312	62.332
2	34.219	52956	137	37.668

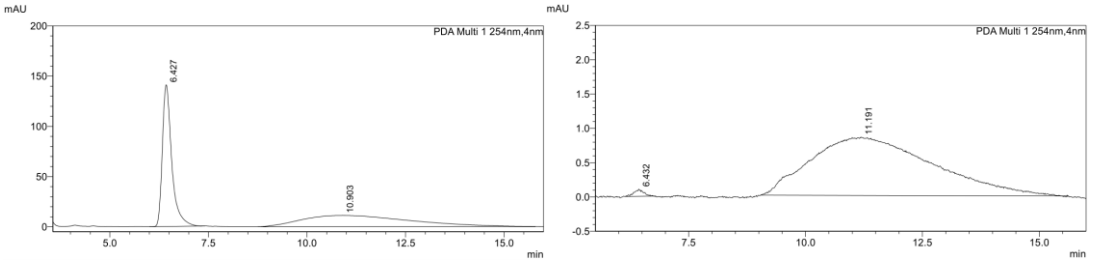
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	7.193	96151	4793	3.549
2	32.681	2613110	4846	96.451

(E)-1-(2-(4-chloro-3-(4-ethoxybenzyl)phenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3x)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 55% yield; $[\alpha]_D^{20}$ = +78.2 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.11 (s, 1H), 8.06 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.37–7.30 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.80–6.76 (m, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.71 (d, *J* = 15.2 Hz, 1H), 3.56 (d, *J* = 15.2 Hz, 1H), 3.31–3.23 (m, 1H), 2.19–2.07 (m, 2H), 1.83–1.62 (m, 5H), 1.62–1.54 (m, 1H), 1.42 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 157.4, 154.5, 142.2, 139.6, 136.8, 133.0, 132.5, 131.4, 131.0, 130.3, 129.9, 129.7, 129.4, 129.0, 127.6, 124.1, 122.9, 120.7, 114.4, 110.8, 63.4, 58.6, 38.3, 28.6, 26.3, 26.2, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 6.432 min (minor), t_R = 11.191 min (major). [1]



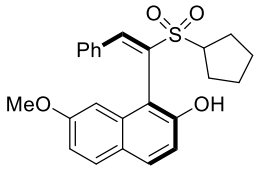
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	6.427	2342070	141047	51.850
2	10.903	2174916	11362	48.150

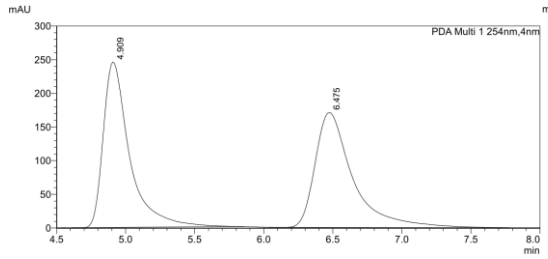
PDA Ch1 254nm

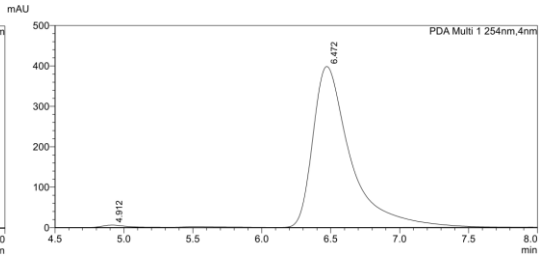
Peak#	Ret. Time	Area	Height	Aera%
1	6.432	1459	104	0.937
2	11.191	154261	848	99.063

(E)-1-(1-(cyclopentylsulfonyl)-2-phenylvinyl)-7-methoxynaphthalen-2-ol (3y)



Purification by flash chromatography (petroleum ether/acetone = 4/1). White solid; 74% yield; $[\alpha]_D^{20}$ = +362.1 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.17 (s, 1H), 8.07 (s, 1H), 7.81 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.20–7.17 (m, 2H), 7.07 (t, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.95 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 3.63 (s, 3H), 3.36–3.29 (m, 1H), 2.23–2.11 (m, 2H), 1.85–1.71 (m, 4H), 1.62–1.54 (m, 1H), 1.50–1.44 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 158.9, 155.1, 143.4, 133.1, 133.0, 132.4, 132.1, 130.8, 130.3, 130.2, 128.7, 124.7, 118.0, 116.0, 110.2, 102.6, 58.5, 55.1, 28.7, 26.3, 26.3, 26.2; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 4.912 min (minor), t_R = 6.472 min (major). [1]





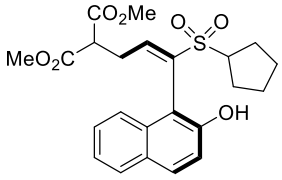
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	4.909	3261208	245808	50.182
2	6.475	3237603	170896	49.818

PDA Ch1 254nm

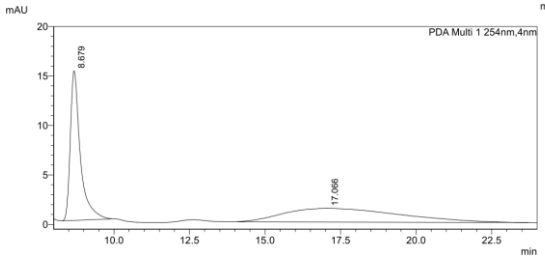
Peak#	Ret. Time	Area	Height	Aera%
1	4.912	68755	5792	0.898
2	6.472	7589091	398364	99.102

Dimethyl (E)-2-(3-(cyclopentylsulfonyl)-3-(2-hydroxynaphthalen-1-yl)allyl)malonate (3z)



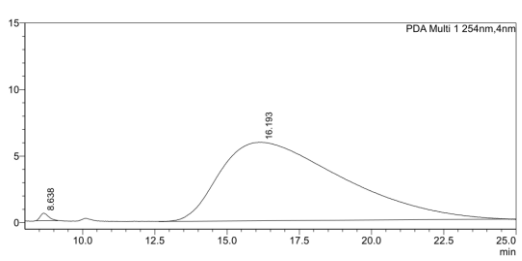
Purification by flash chromatography (petroleum ether/acetone = 2/1). White solid; 77% yield; $[\alpha]_D^{20}$ = +129.8 (*c* = 0.10 in $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.84 (t, *J* = 9.6 Hz, 3H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 6.8 Hz, 1H), 7.41–7.38 (m, 2H), 7.27–7.25 (m, 1H), 3.71 (s, 6H), 3.54 (t, *J* = 6.8 Hz, 1H), 3.27 (s, 1H), 2.58–2.53 (m, 1H), 2.41–2.35 (m, 1H), 2.14–2.06 (m, 2H), 1.83–1.74 (m, 4H), 1.57 (d, *J* = 5.6 Hz, 1H),

1.46 (d, *J* = 4.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 168.6, 168.6, 153.8, 144.8, 137.3, 132.5, 132.2, 129.2, 128.9, 127.6, 124.0, 123.1, 120.1, 109.8, 59.2, 53.0, 53.0, 49.7, 28.5, 27.9, 26.5, 26.3, 26.2; HRMS (ESI) for $C_{23}H_{26}NaO_7S^+$ calcd. 469.1291, found: 469.1301; **HPLC analysis**: CHIRALPAK AD-H (hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t_R = 8.638 min (minor), t_R = 16.193 min (major).



PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Aera%
1	8.679	349458	15136	48.659
2	17.066	368724	1393	51.341



PDA Ch1 254nm

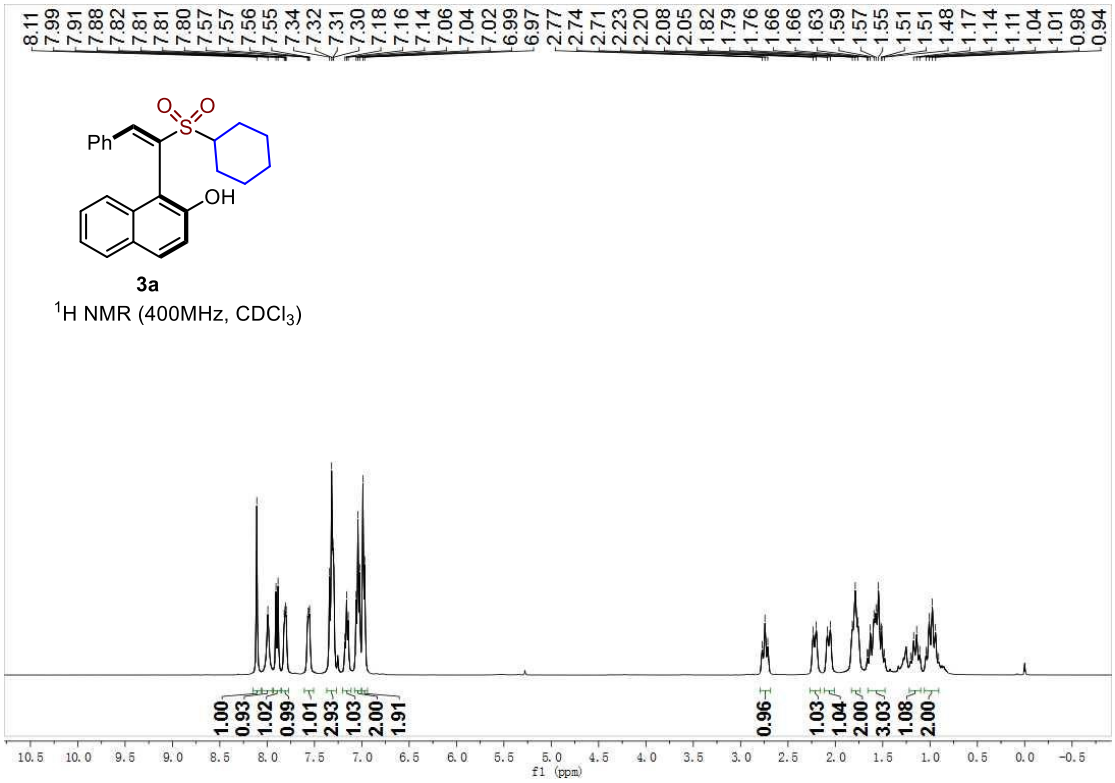
Peak#	Ret. Time	Area	Height	Aera%
1	8.638	11552	569	0.657
2	16.193	1747869	5899	99.343

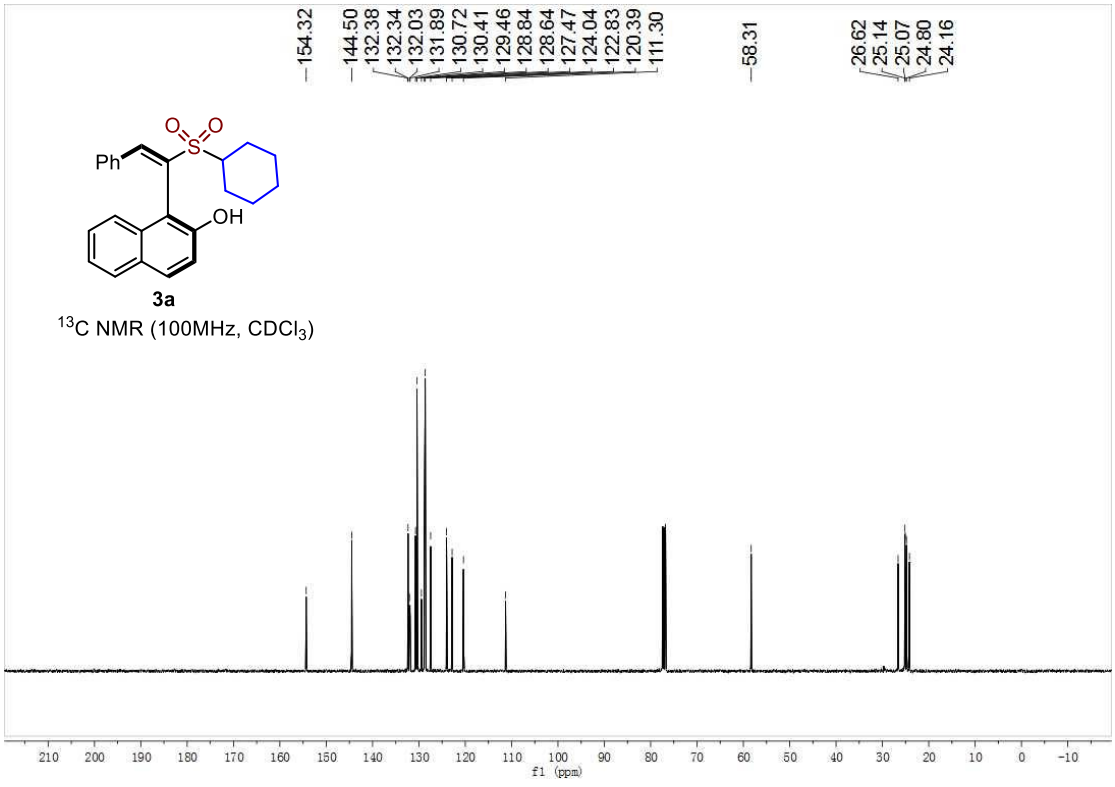
4. References

[1] C. Zhang, Z. Tang, Y. Qiu, J. Tang, S. Ye, Z. Li and J. Wu, *Chem Catal.,* 2022, **2**, 164-177.

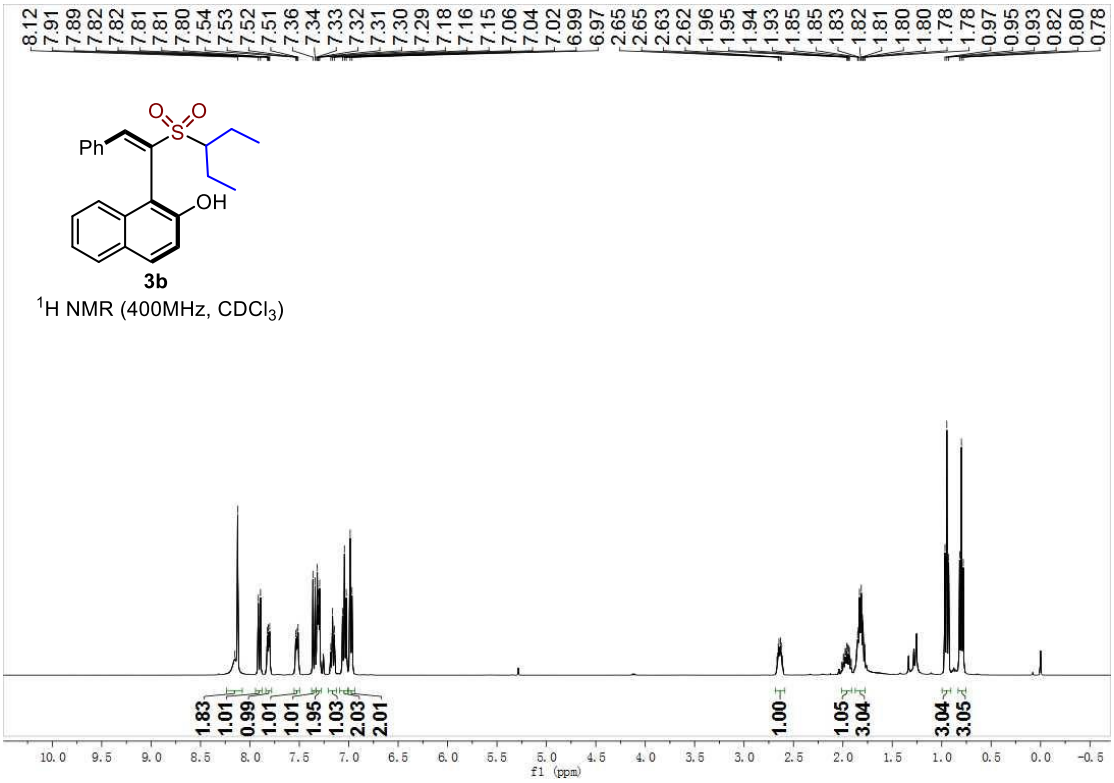
5. NMR spectra of compounds

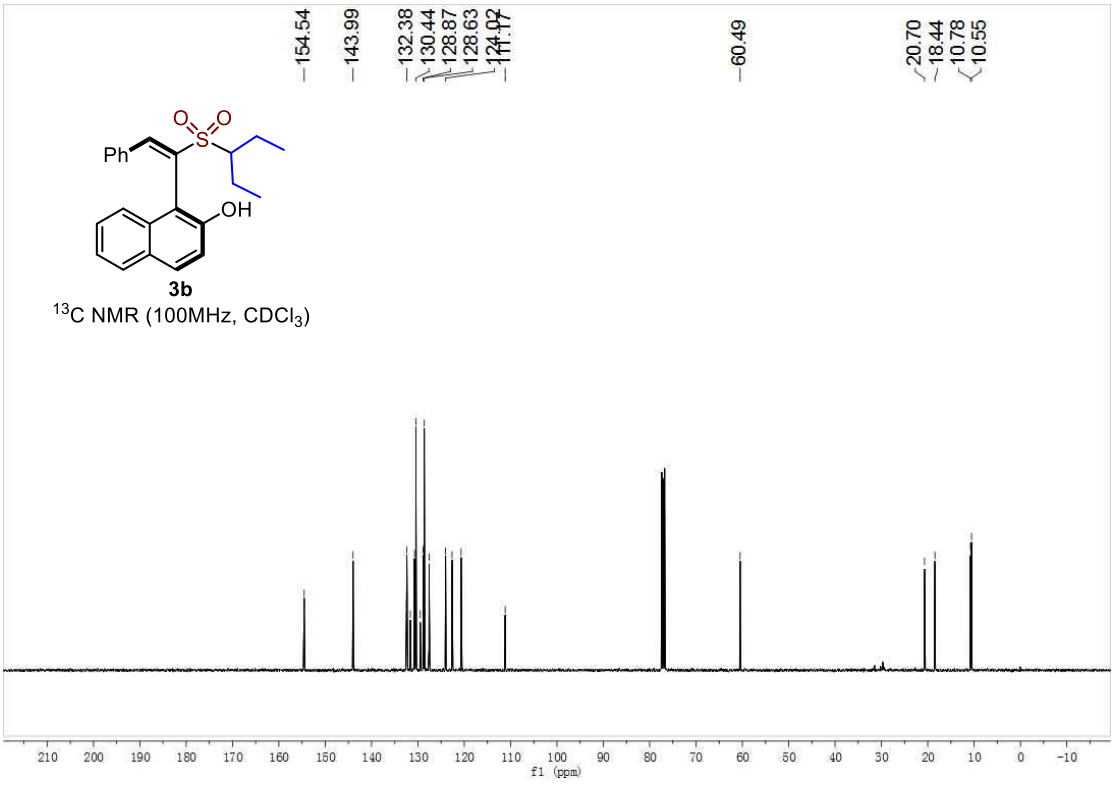
(E)-1-(1-(cyclohexylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3a)



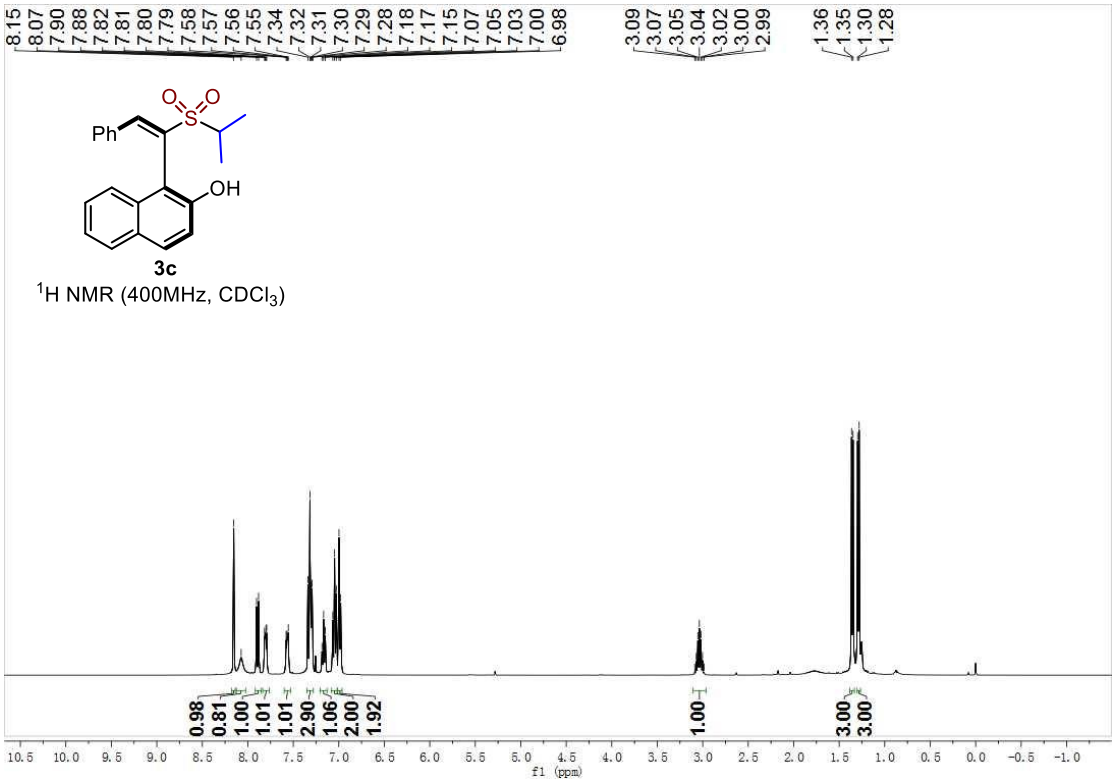


(E)-1-(1-(pentan-3-ylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3b)



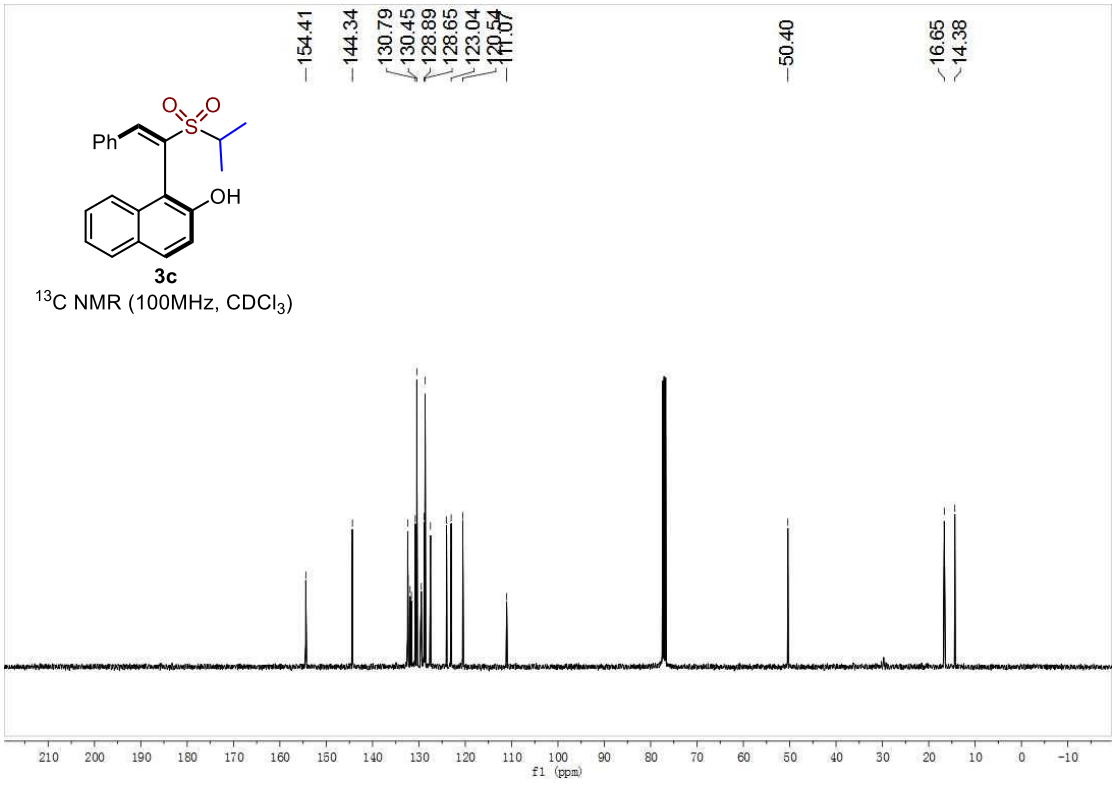


(E)-1-(1-(isopropylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3c)



3c

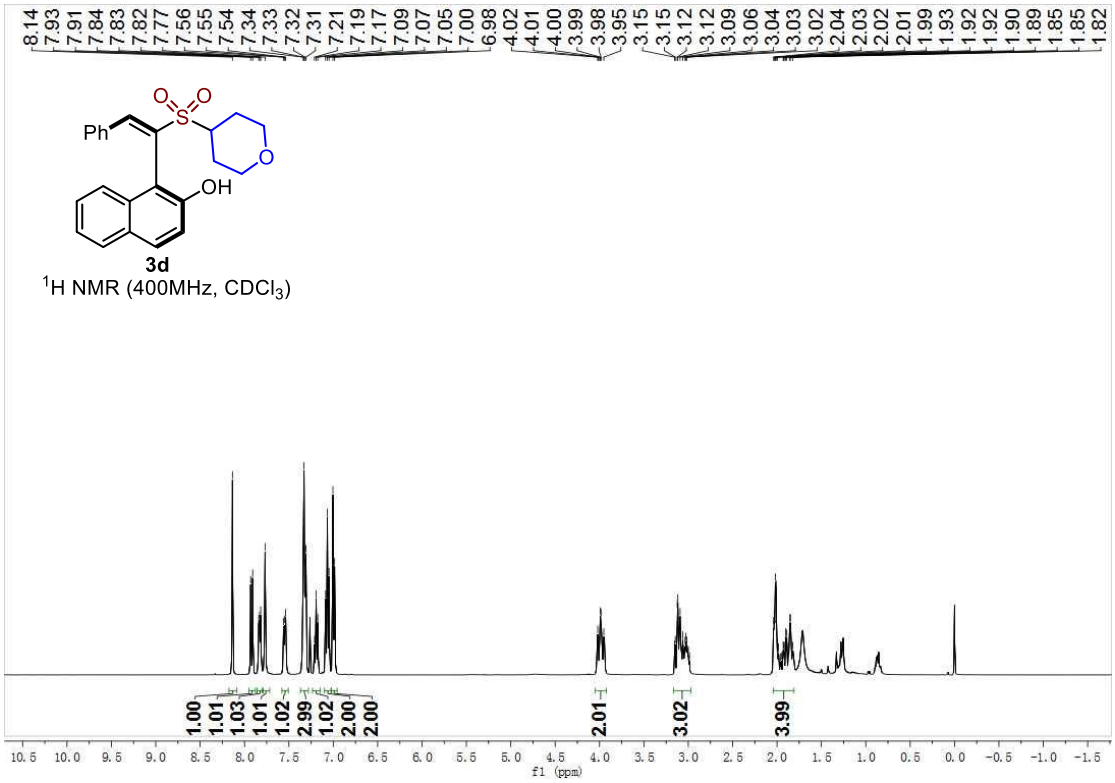
^{1}H NMR (400MHz, $CDCl_3$)

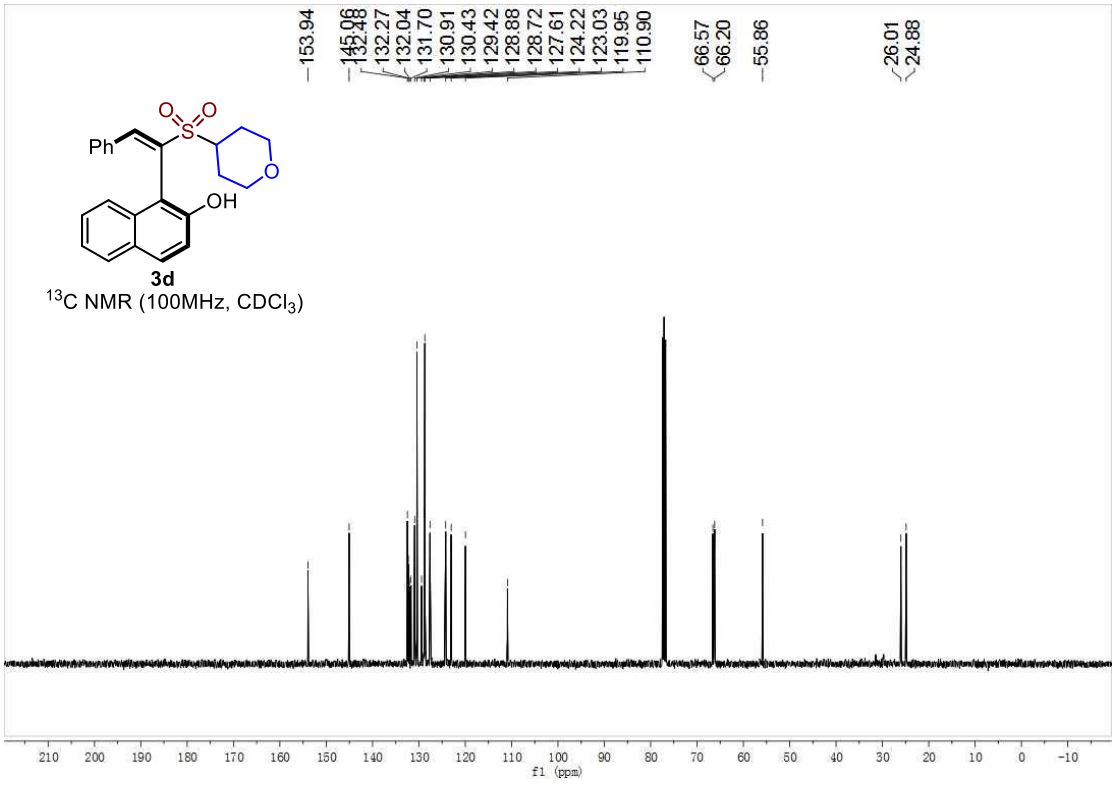


3c

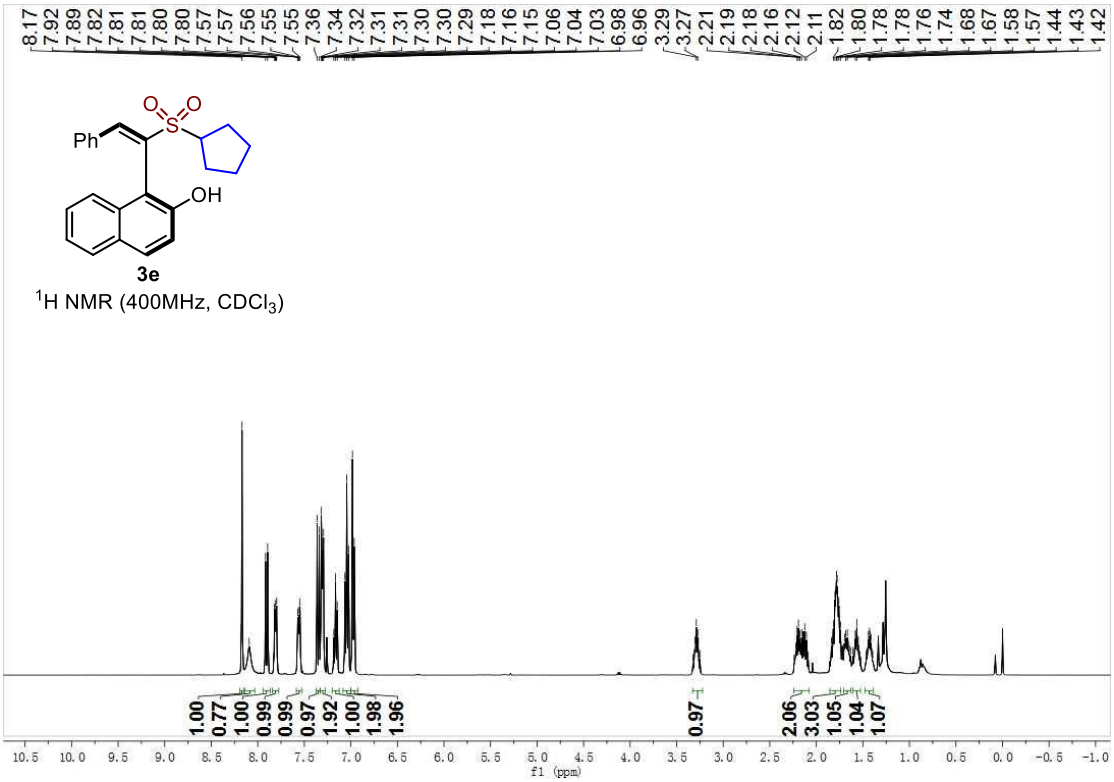
^{13}C NMR (100MHz, $CDCl_3$)

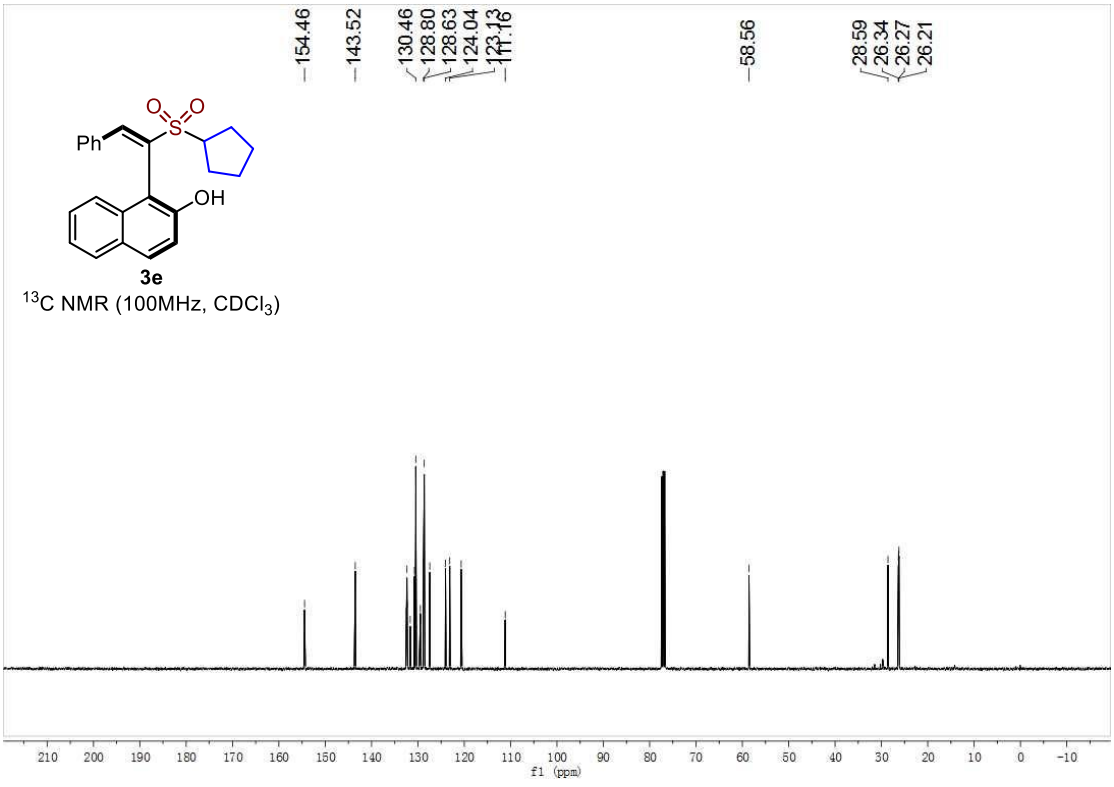
(E)-1-(2-phenyl-1-((tetrahydro-2H-pyran-4-yl)sulfonyl)vinyl)naphthalen-2-ol (3d)



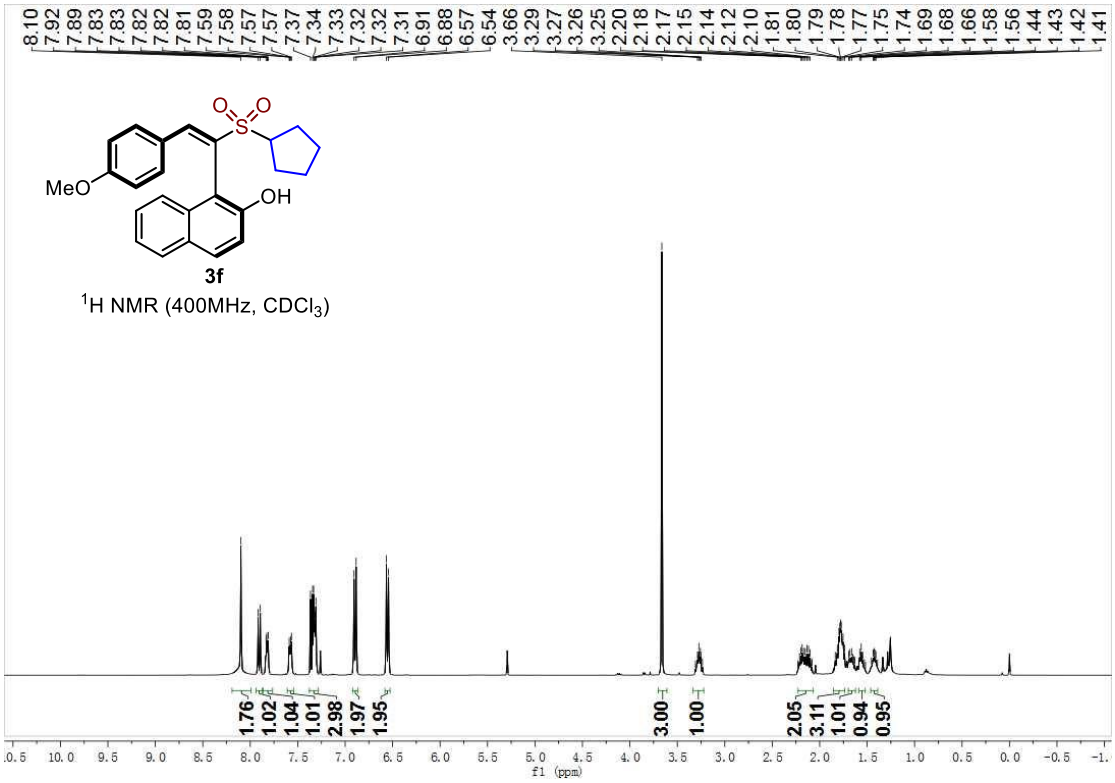


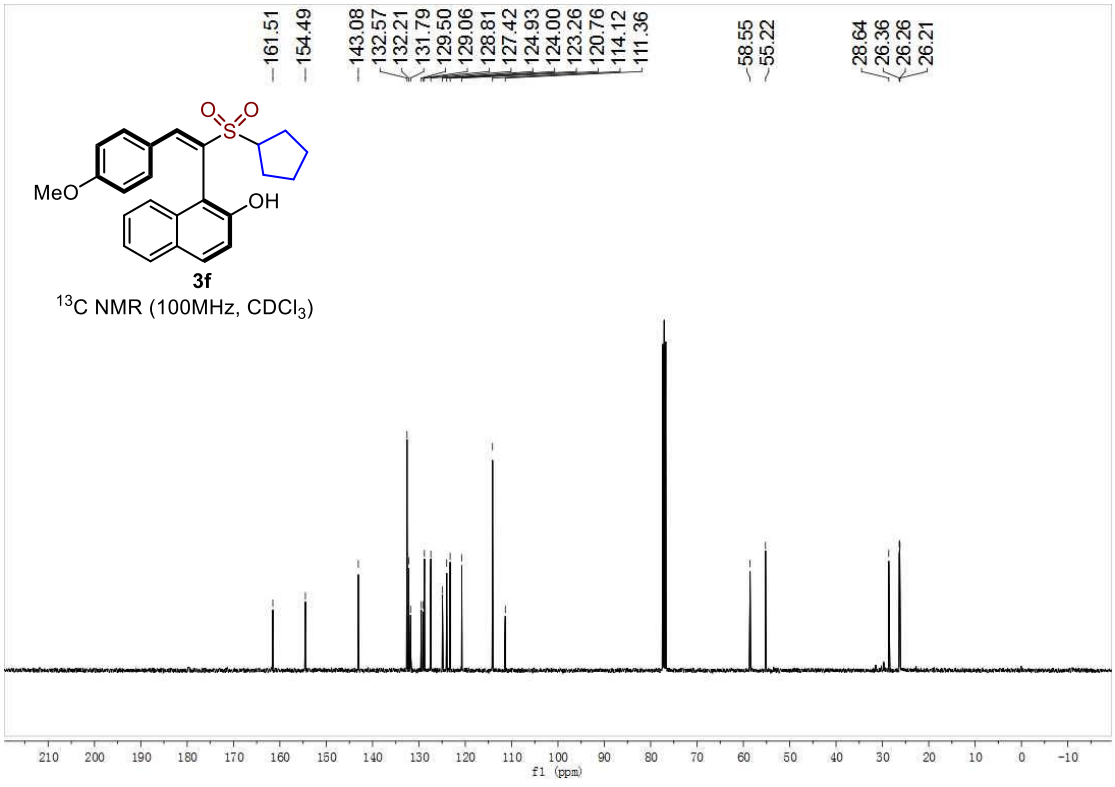
(E)-1-(1-(cyclopentylsulfonyl)-2-phenylvinyl)naphthalen-2-ol (3e)



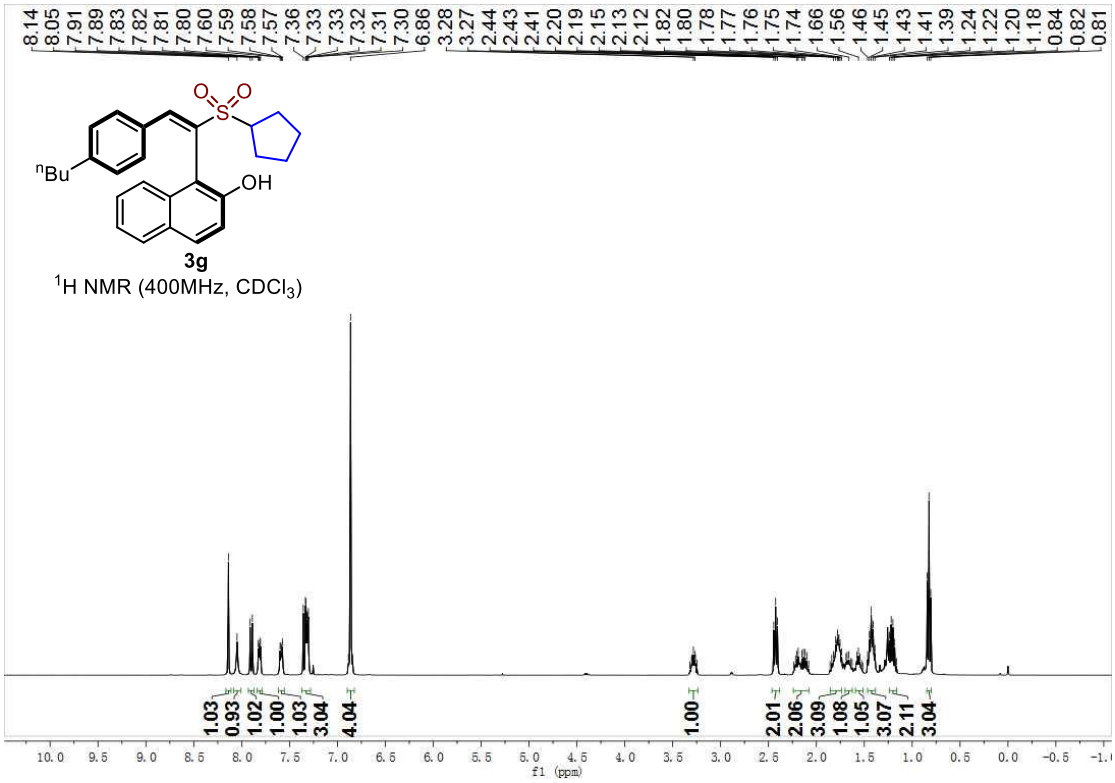


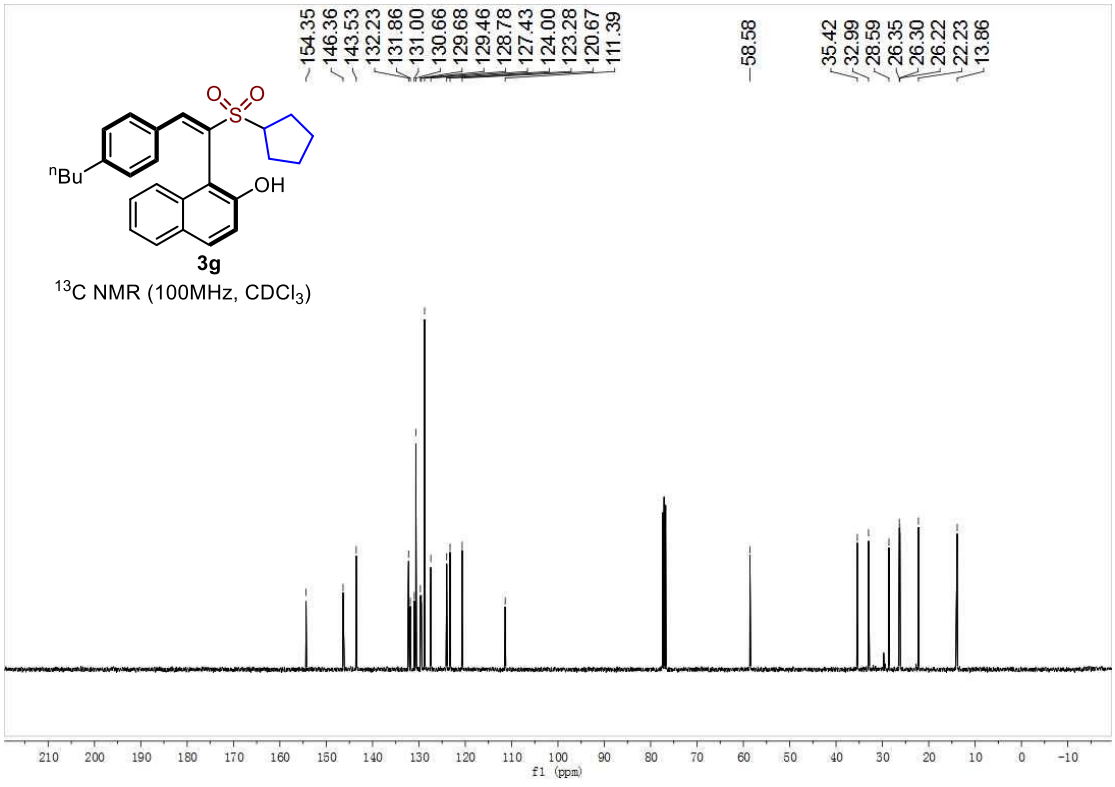
(E)-1-(1-(cyclopentylsulfonyl)-2-(4-methoxyphenyl)vinyl)naphthalen-2-ol (3f)



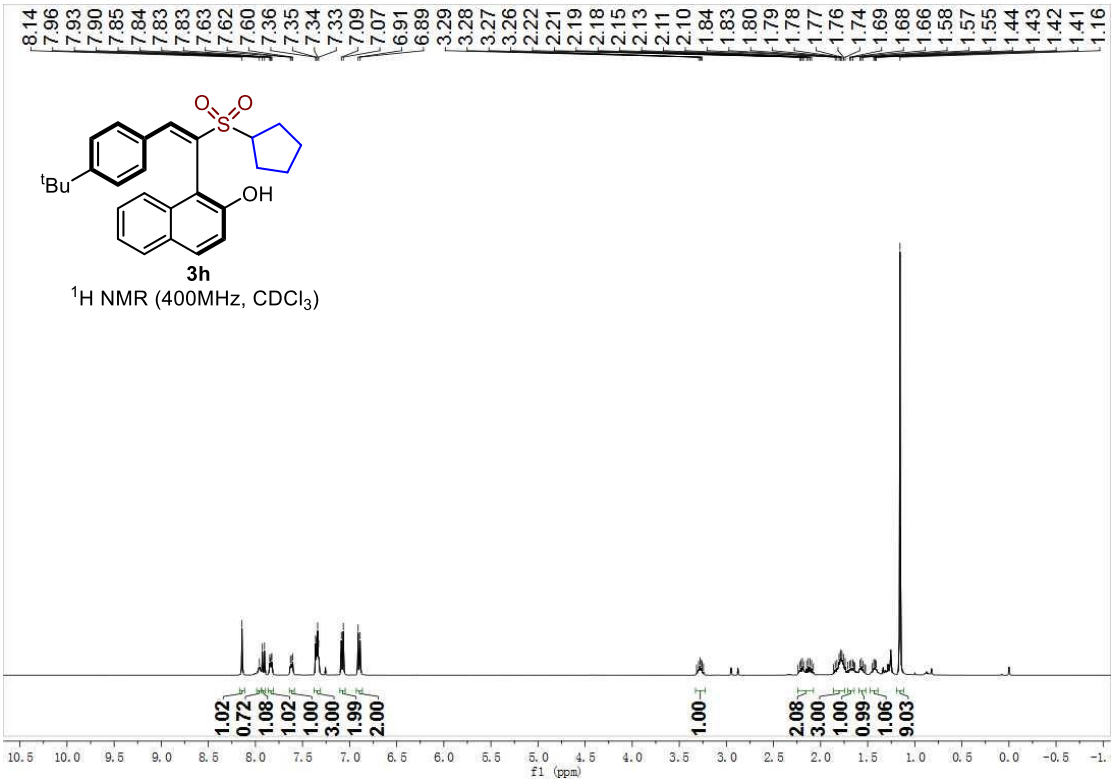


(E)-1-(2-(4-butylphenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3g)



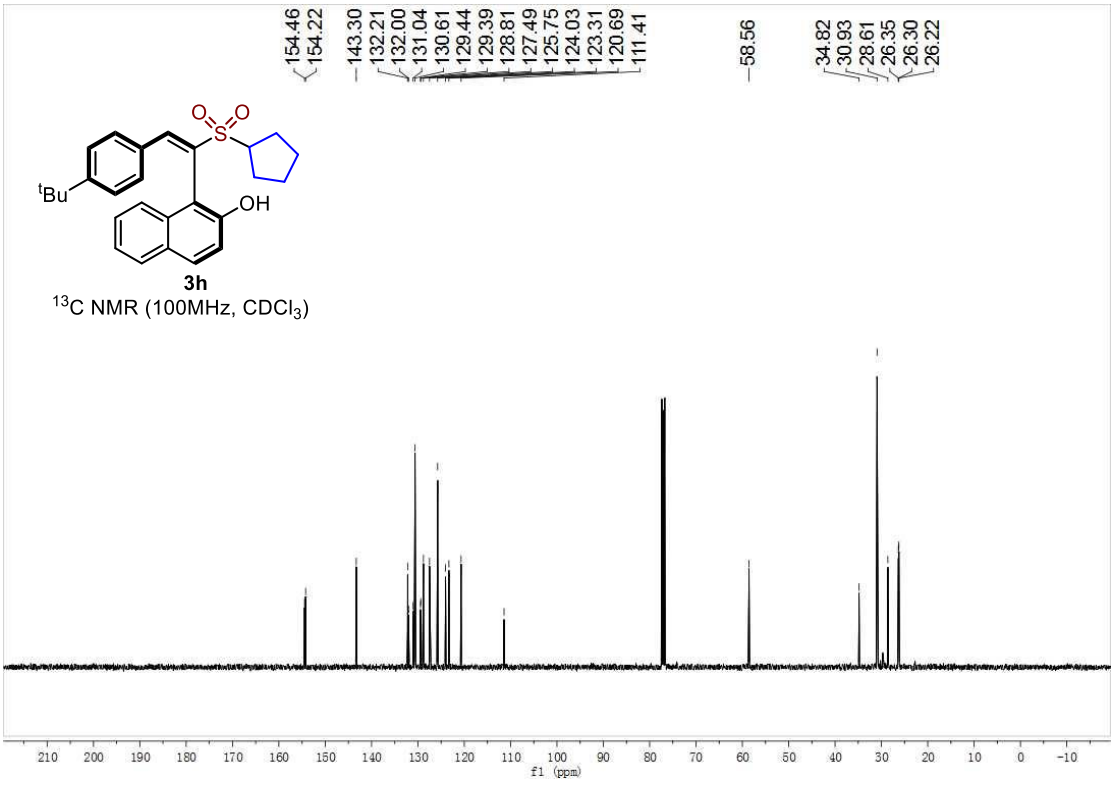


(E)-1-(2-(4-(tert-butyl)phenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3h)



3h

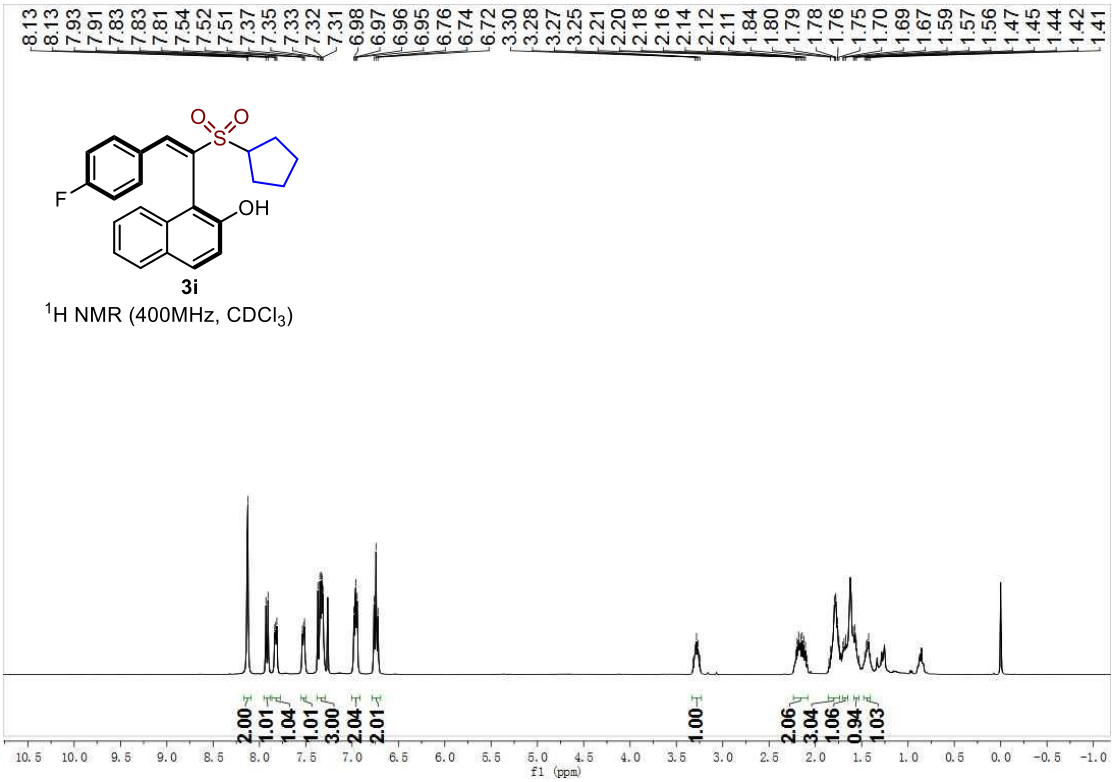
^{1}H NMR (400MHz, $CDCl_3$)

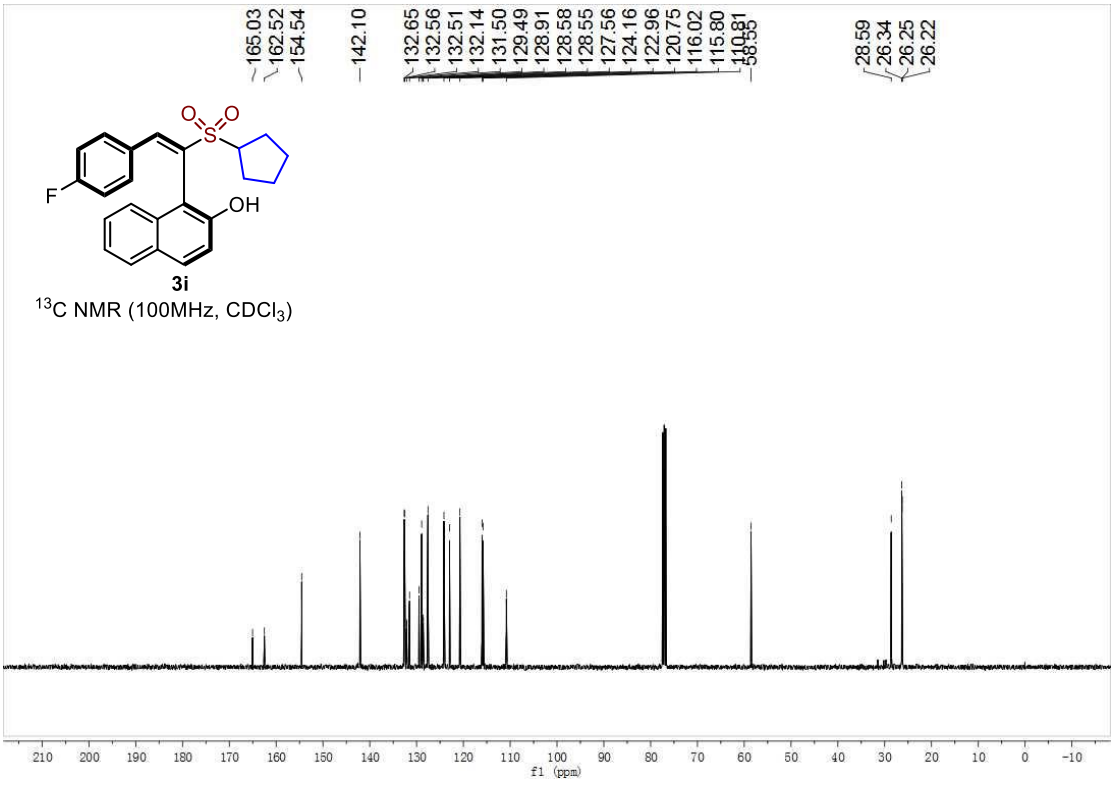


3h

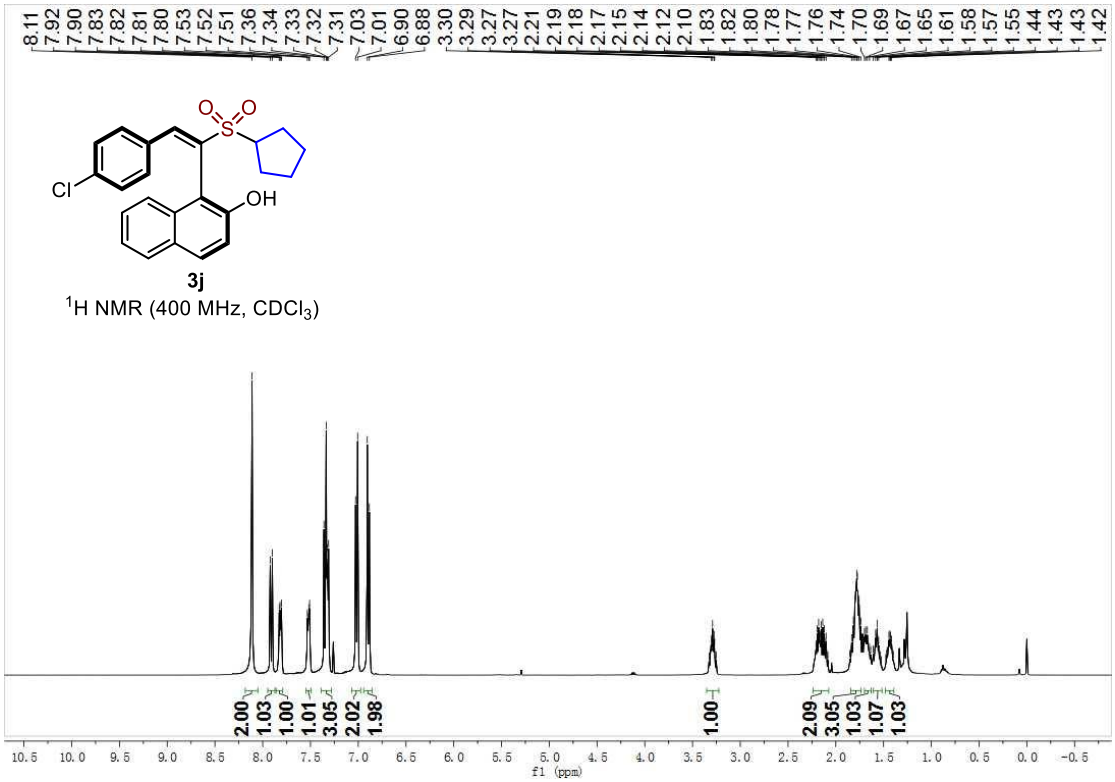
^{13}C NMR (100MHz, $CDCl_3$)

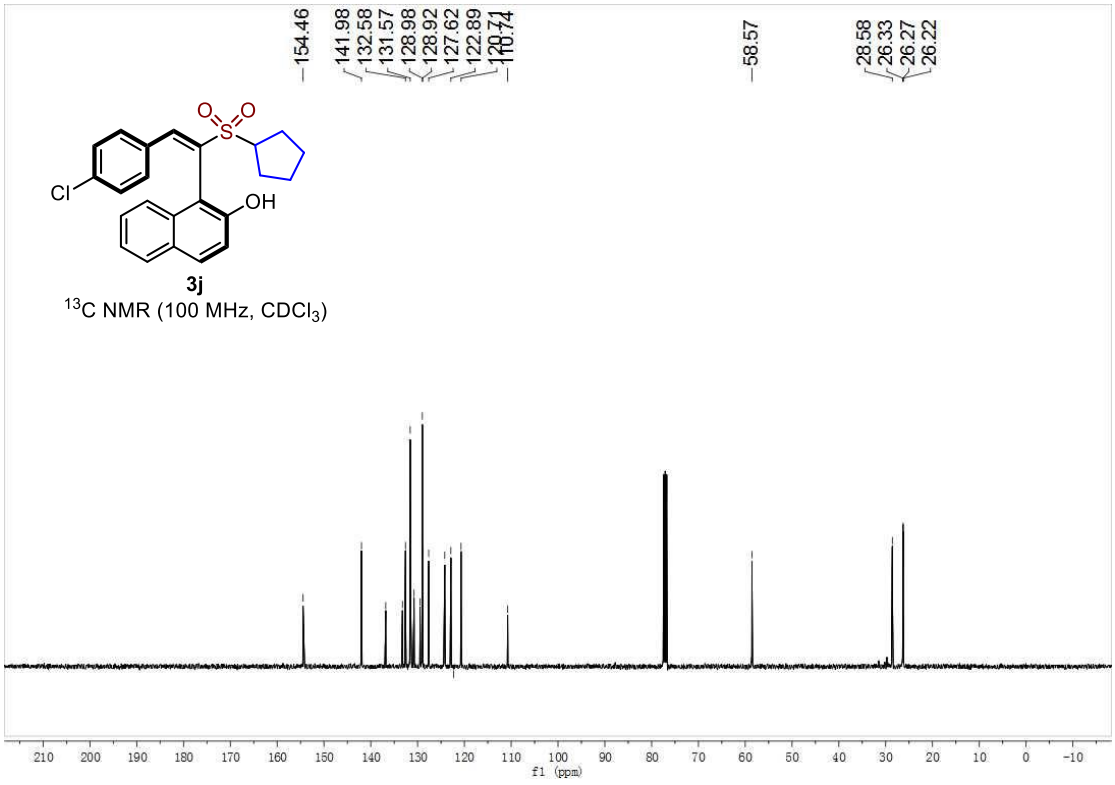
(E)-1-(1-(cyclopentylsulfonyl)-2-(4-fluorophenyl)vinyl)naphthalen-2-ol (3i)



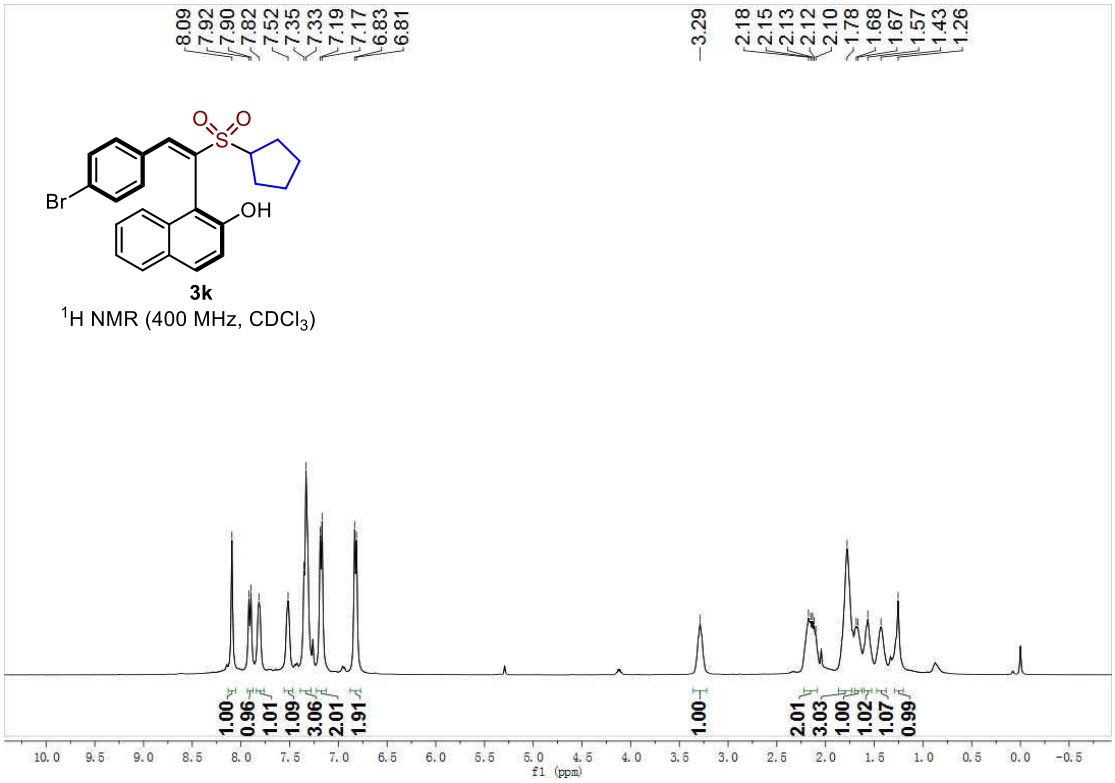


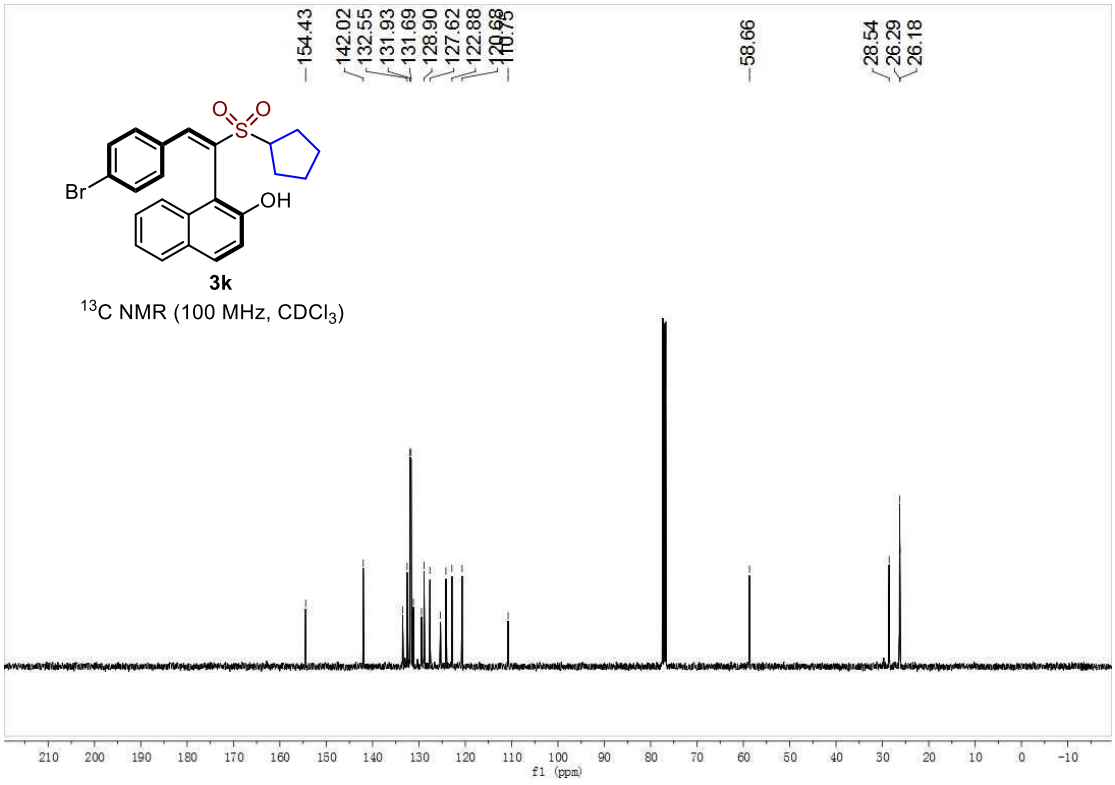
(E)-1-(2-(4-chlorophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3j)



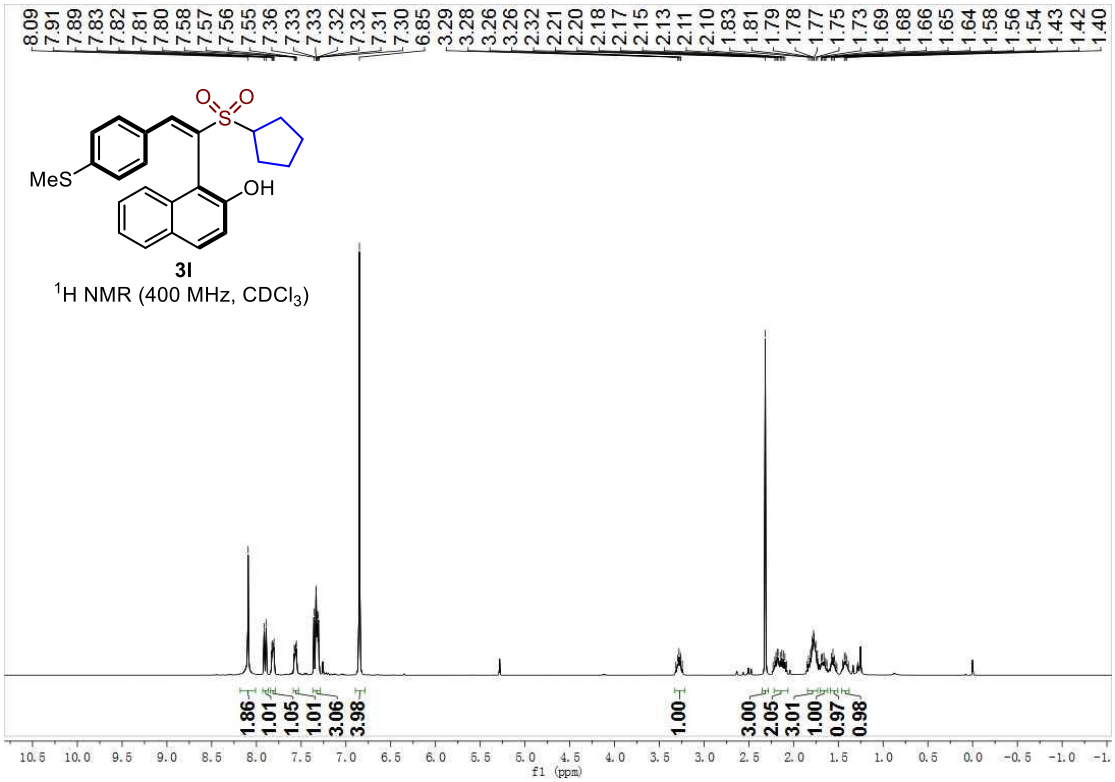


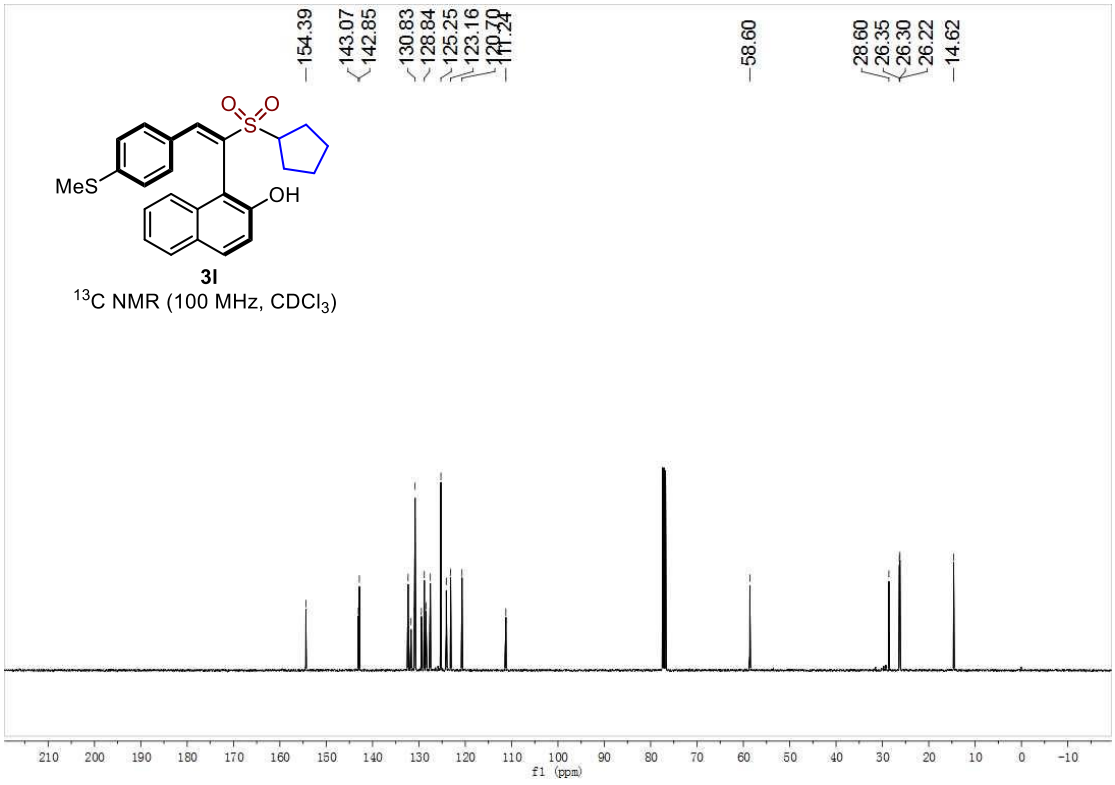
(E)-1-(2-(4-bromophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3k)



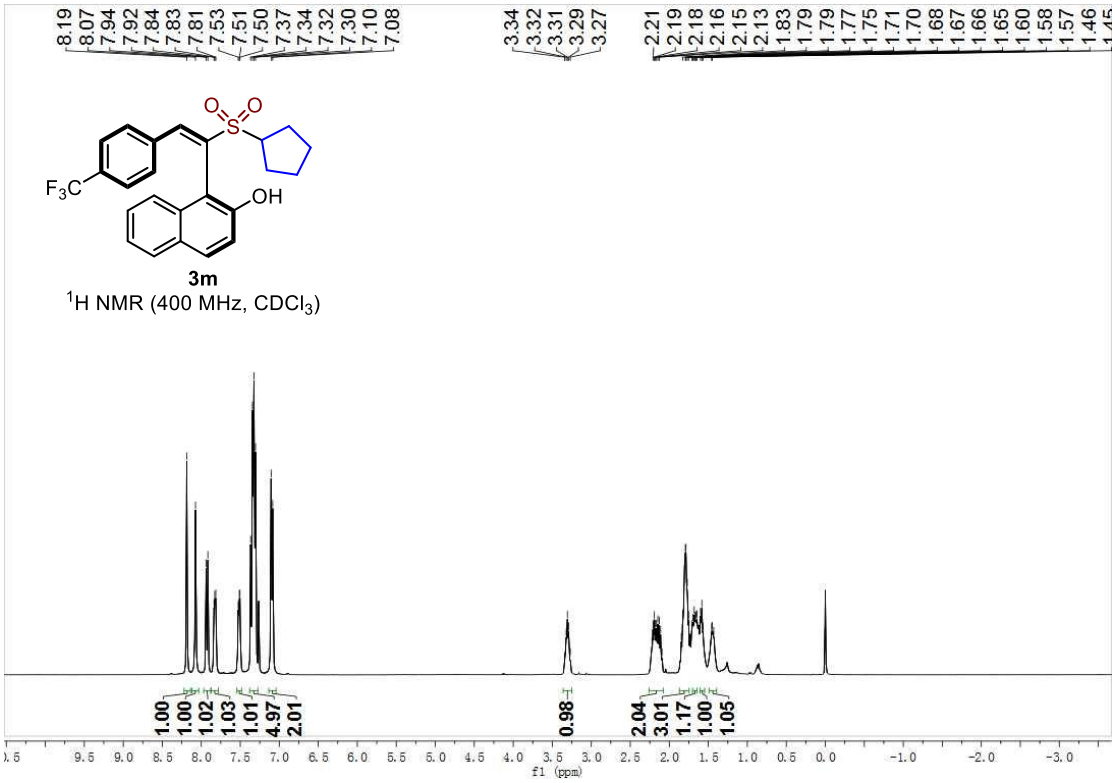


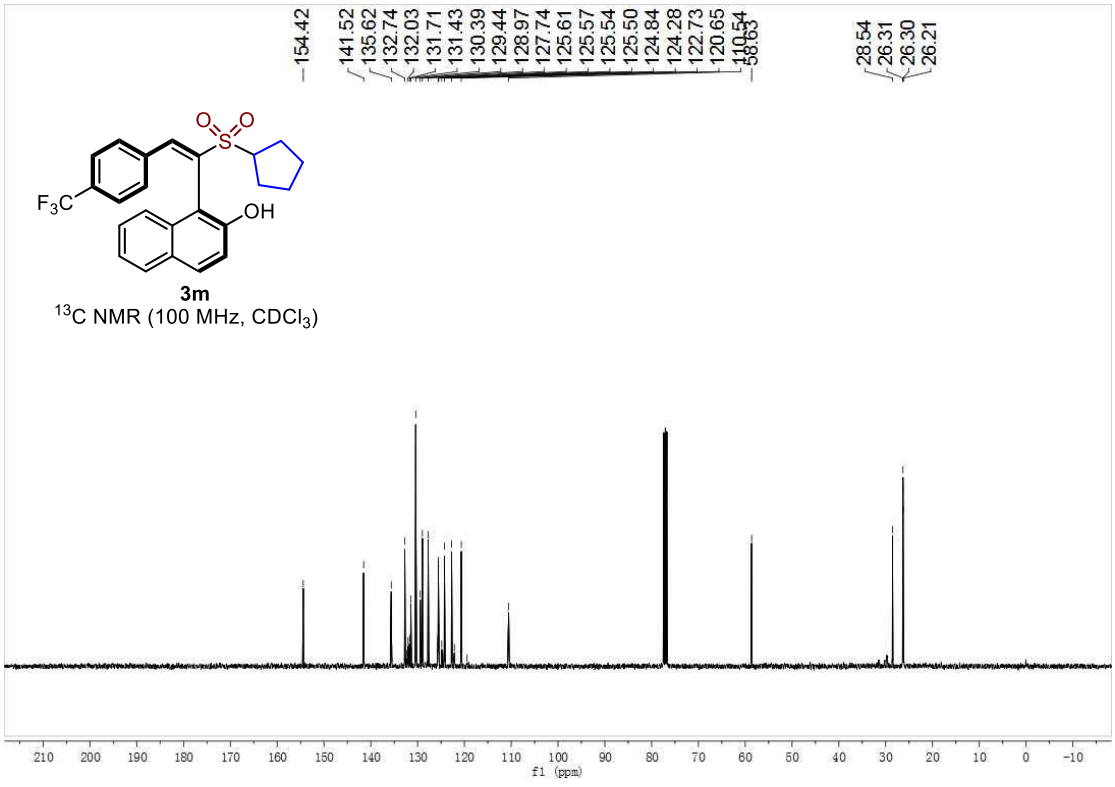
(E)-1-(1-(cyclopentylsulfonyl)-2-(4-(methylthio)phenyl)vinyl)naphthalen-2-ol (3l)



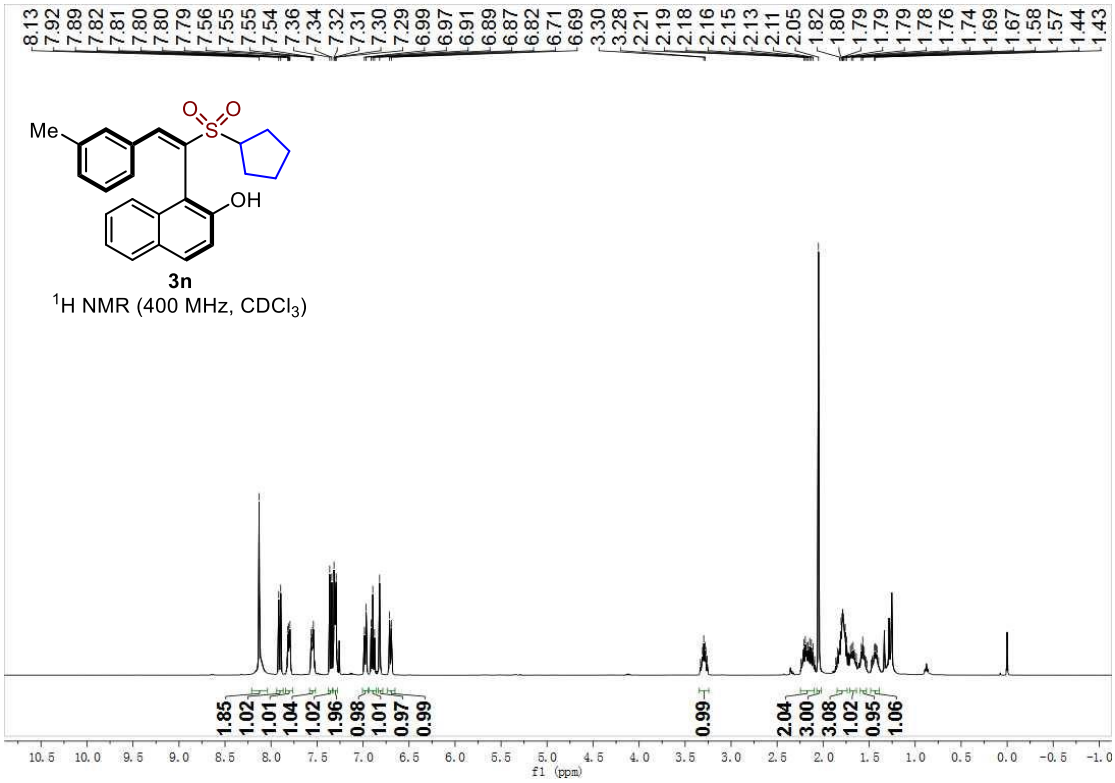


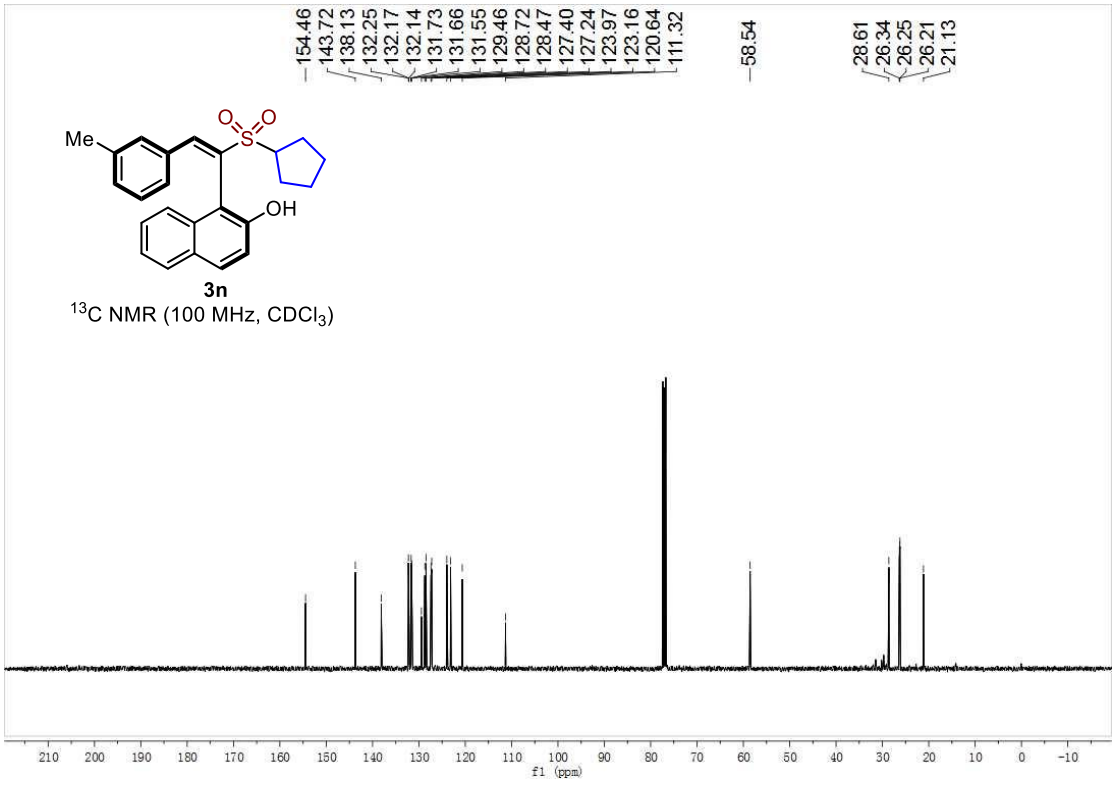
(E)-1-(1-(cyclopentylsulfonyl)-2-(4-(trifluoromethyl)phenyl)vinyl)naphthalen-2-ol (3m)



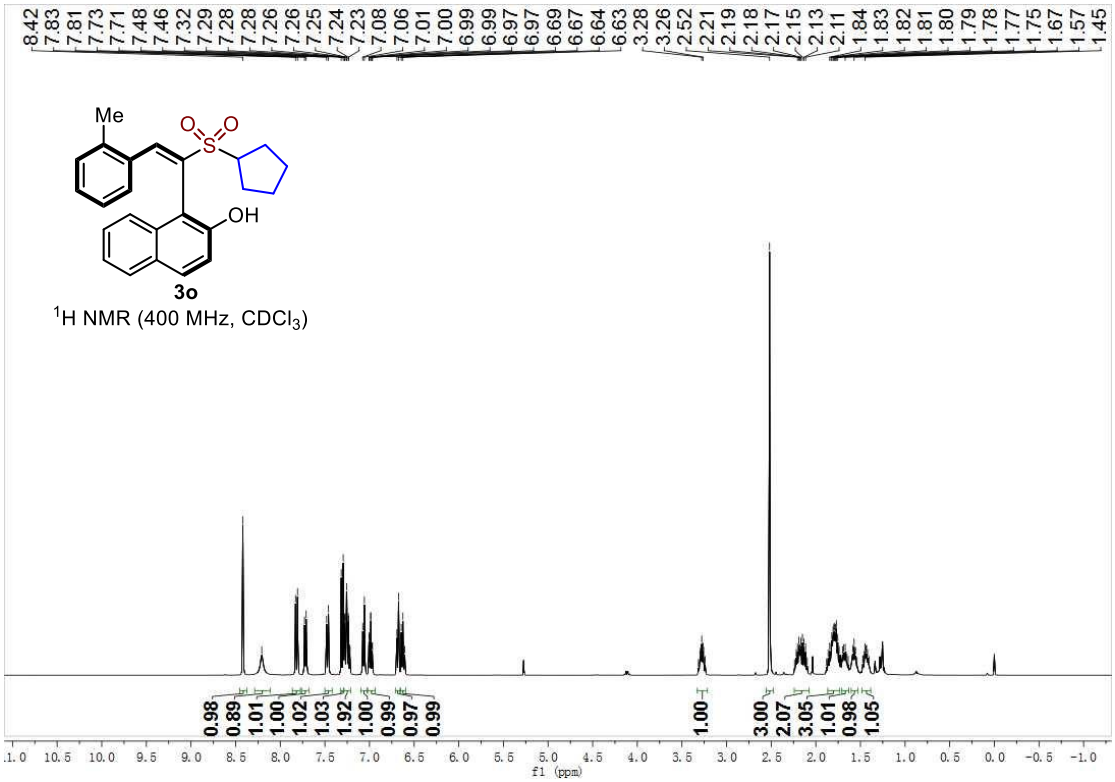


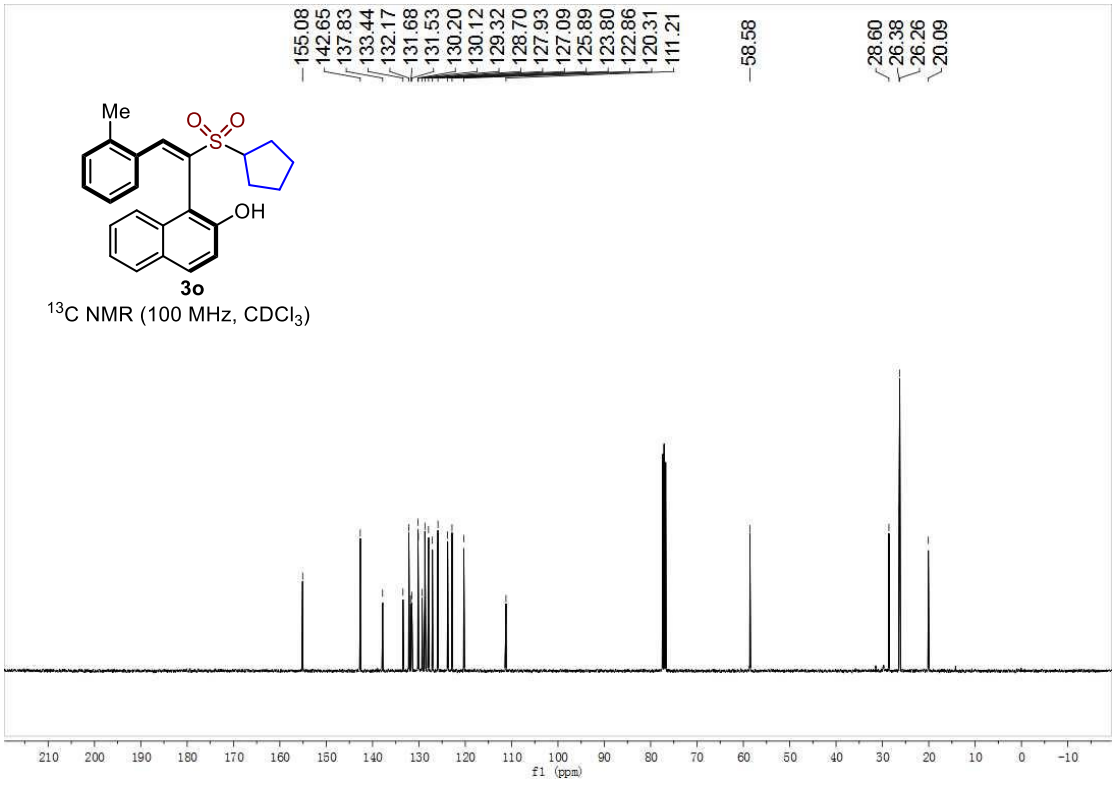
(E)-1-(1-(cyclopentylsulfonyl)-2-(m-tolyl)vinyl)naphthalen-2-ol (3n)



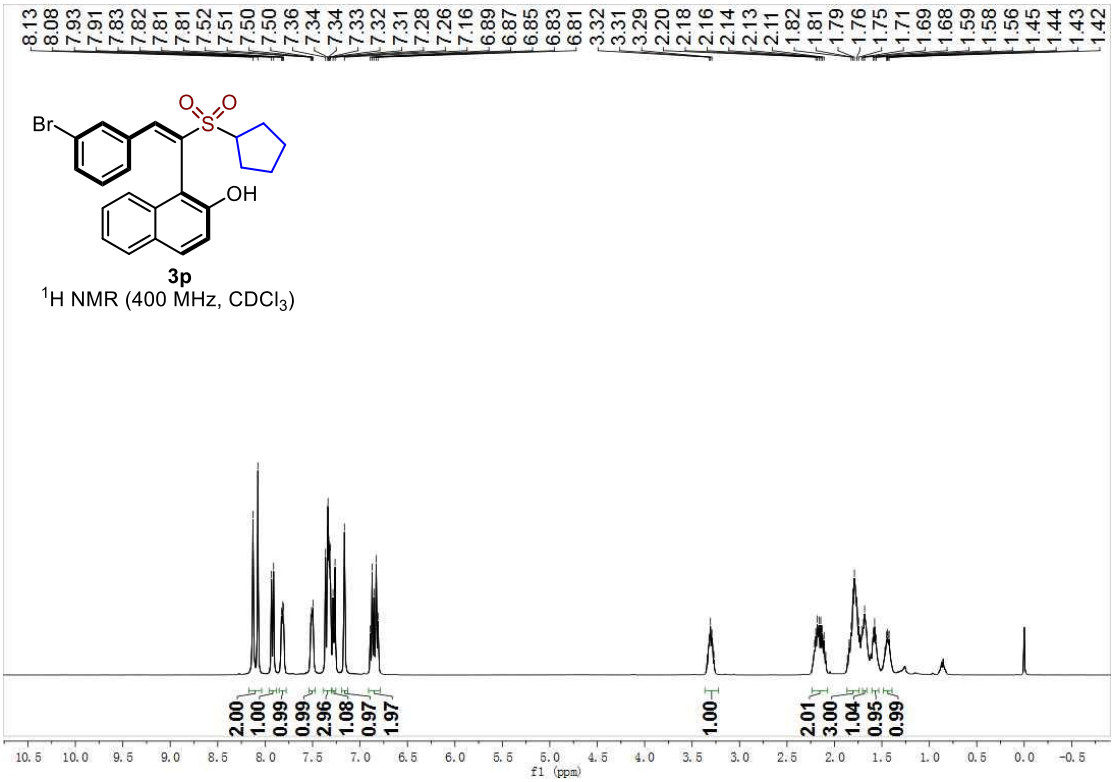


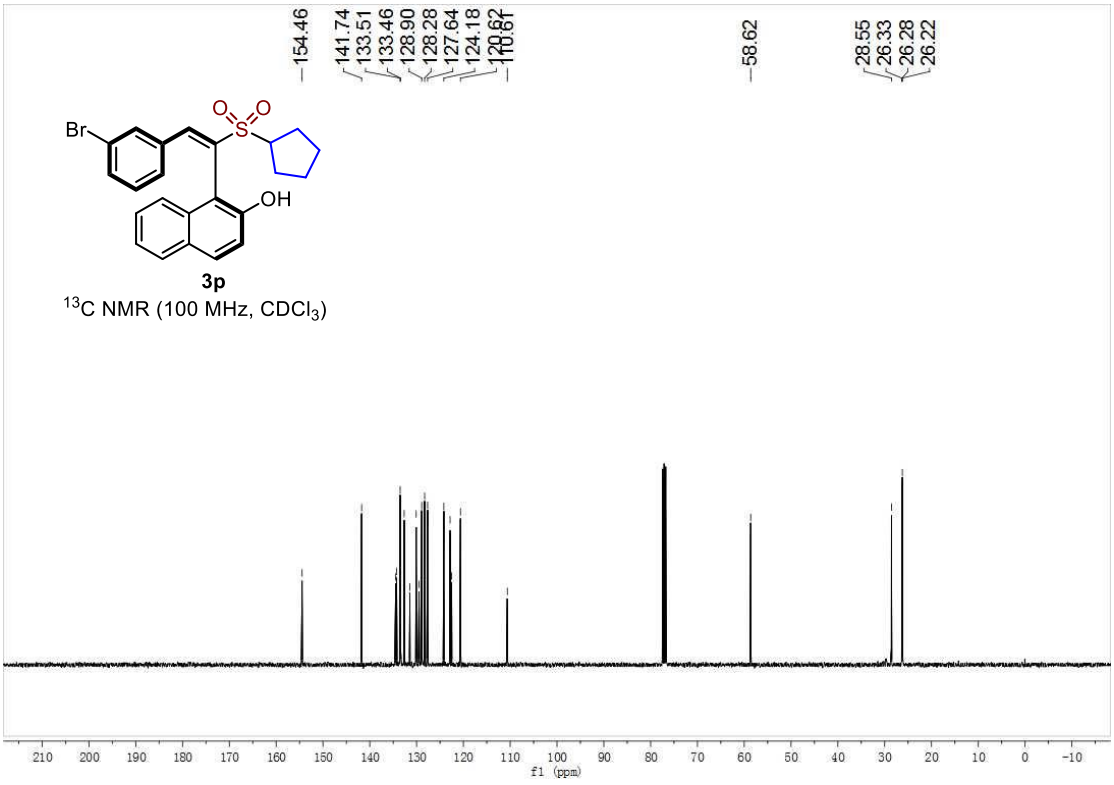
(E)-1-(1-(cyclopentylsulfonyl)-2-(o-tolyl)vinyl)naphthalen-2-ol (3o)



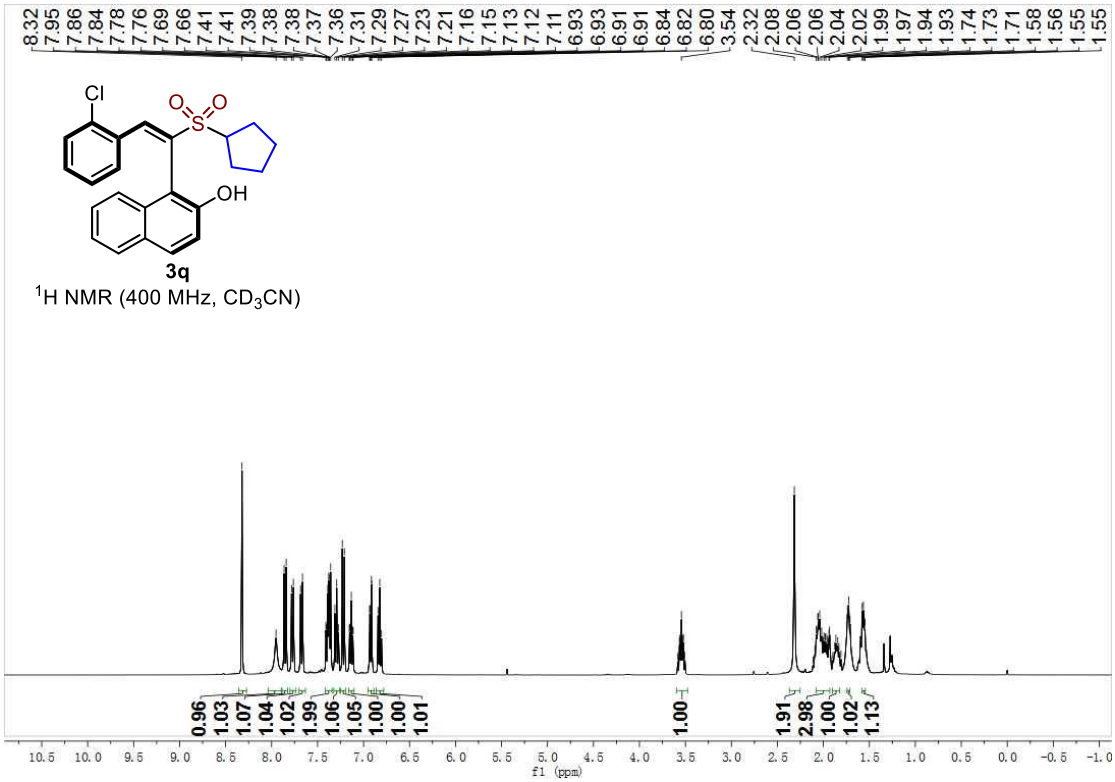


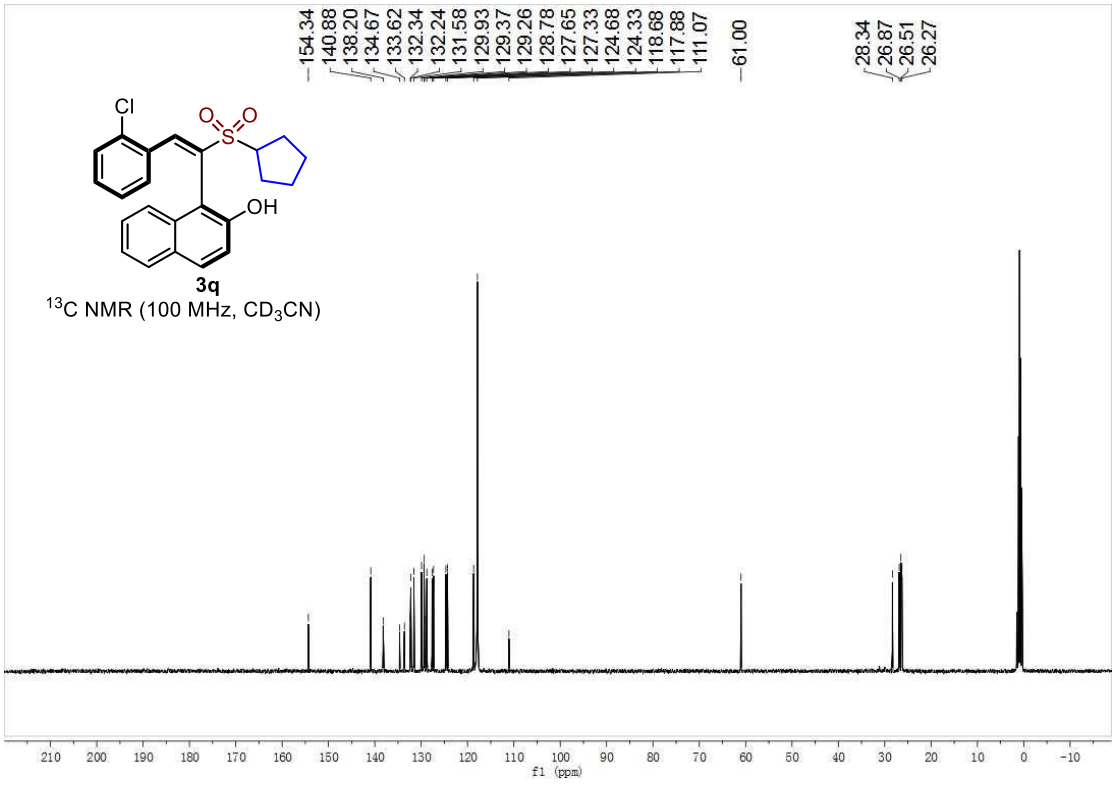
(E)-1-(2-(3-bromophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3p)



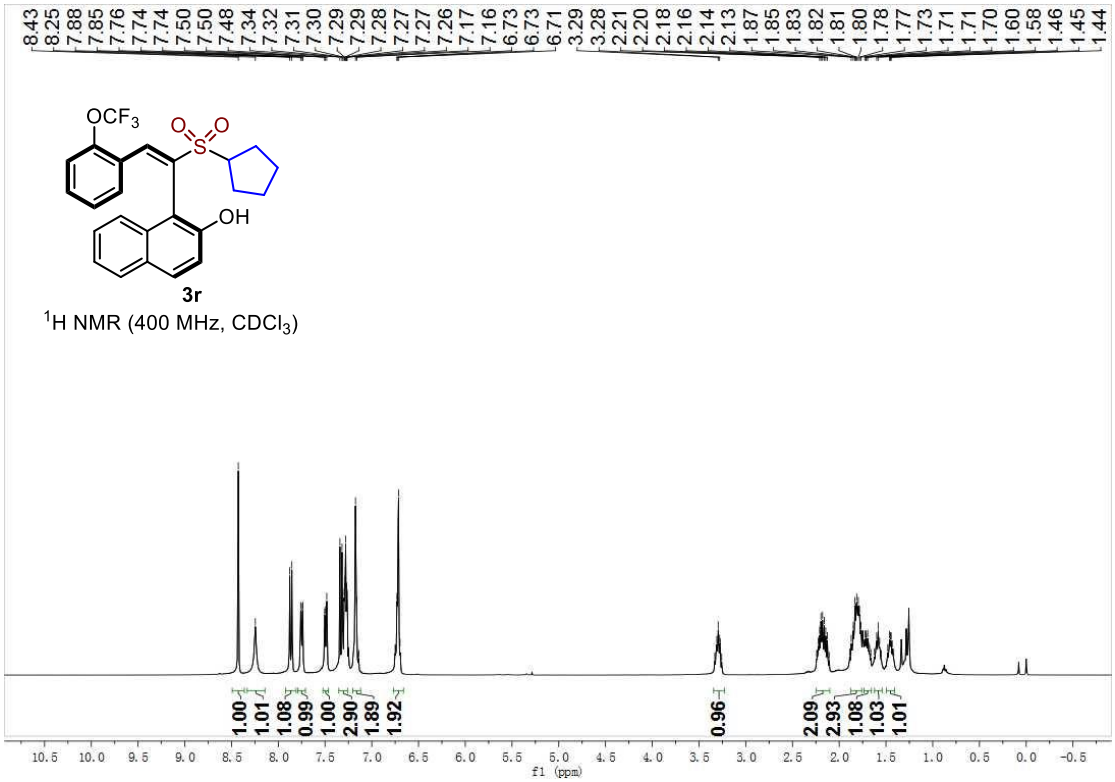


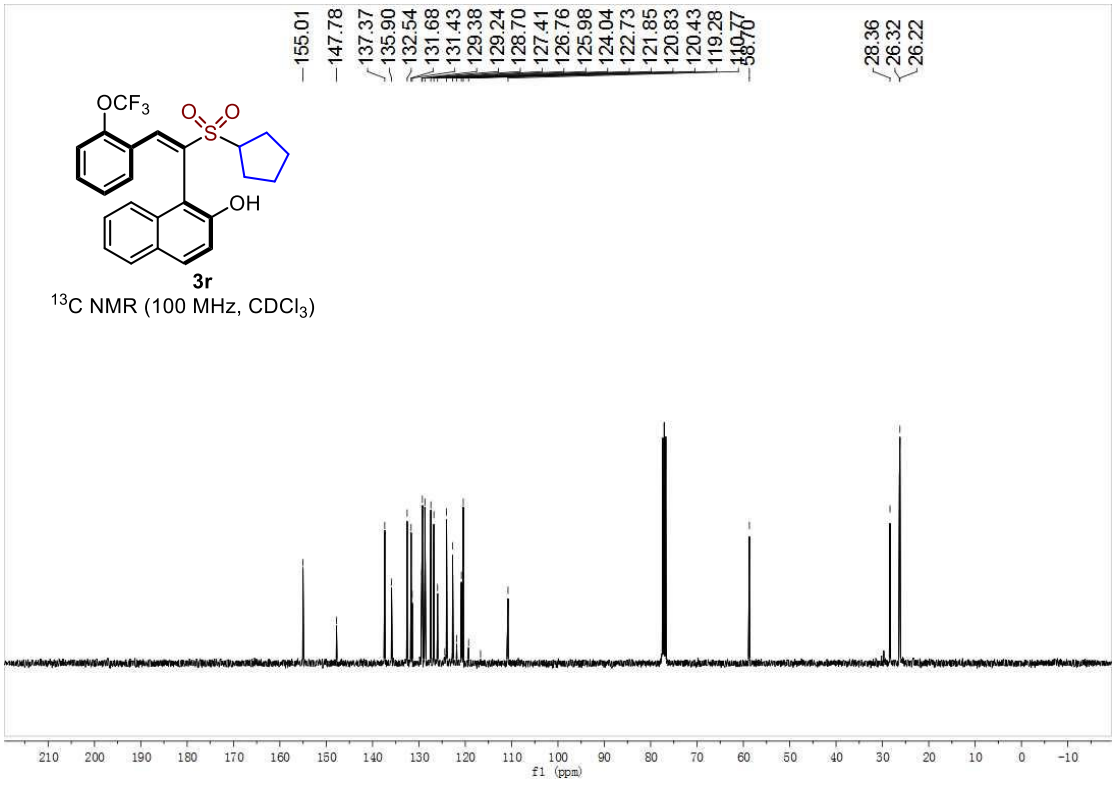
(E)-1-(2-(2-chlorophenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3q)



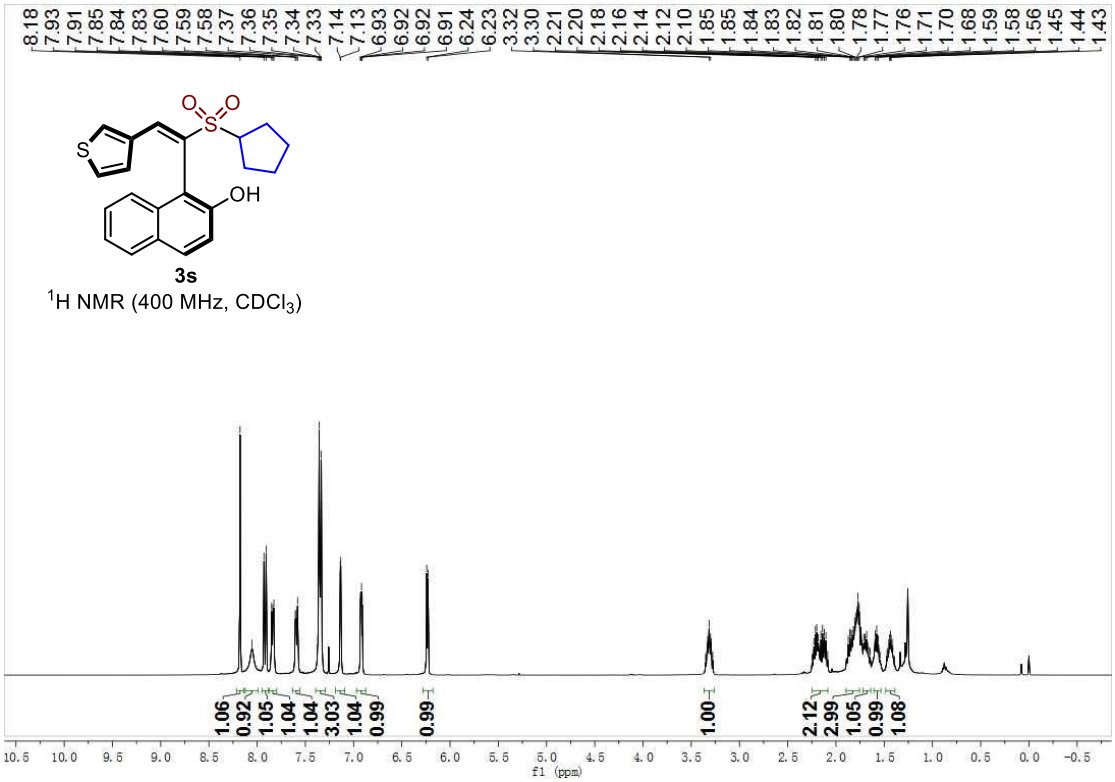


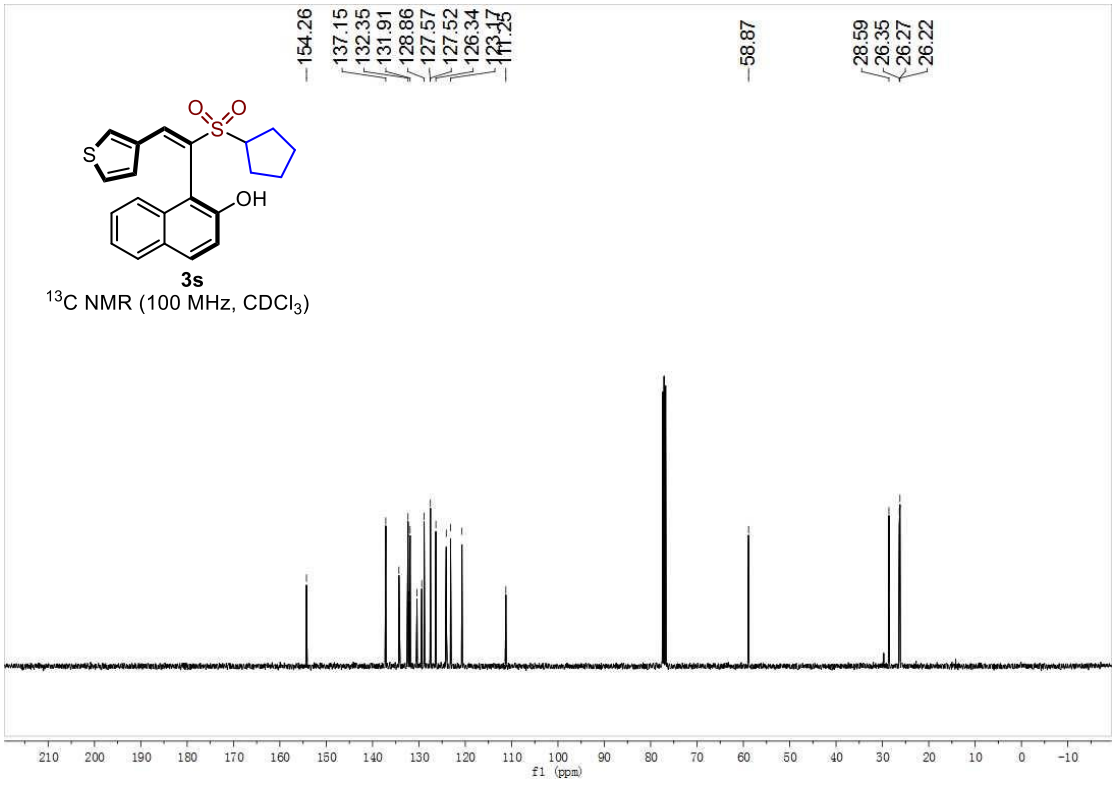
(E)-1-(1-(cyclopentylsulfonyl)-2-(2-(trifluoromethoxy)phenyl)vinyl)naphthalen-2-ol (3r)



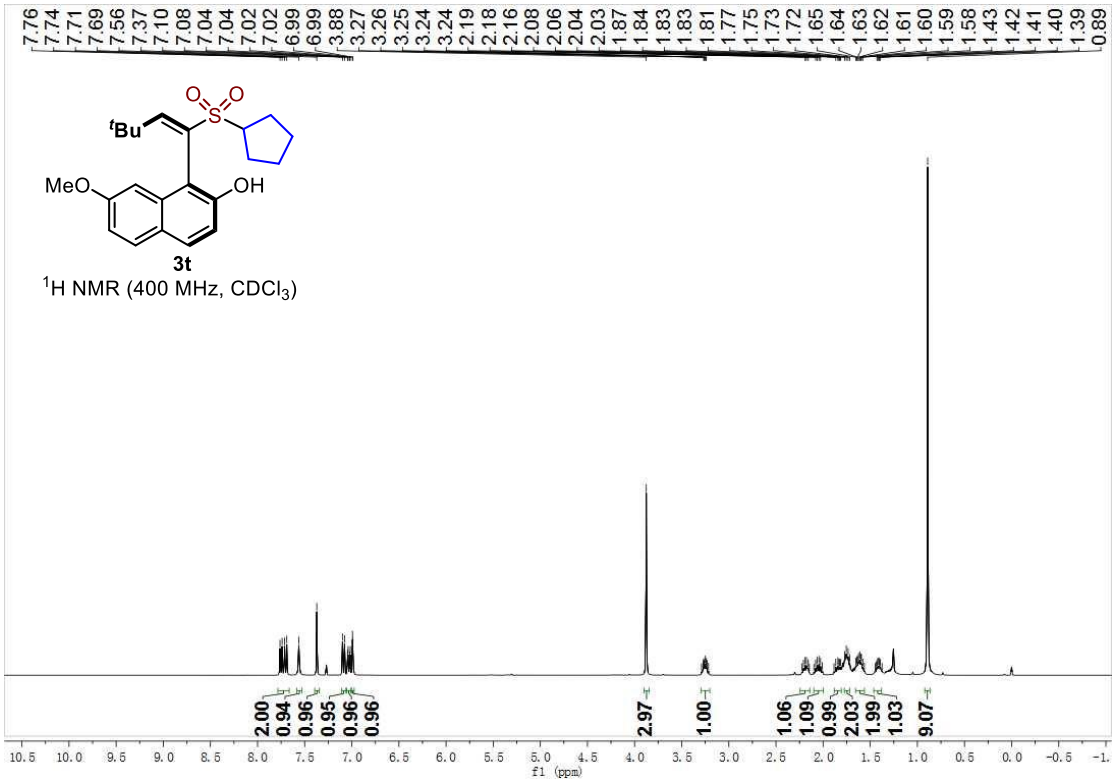


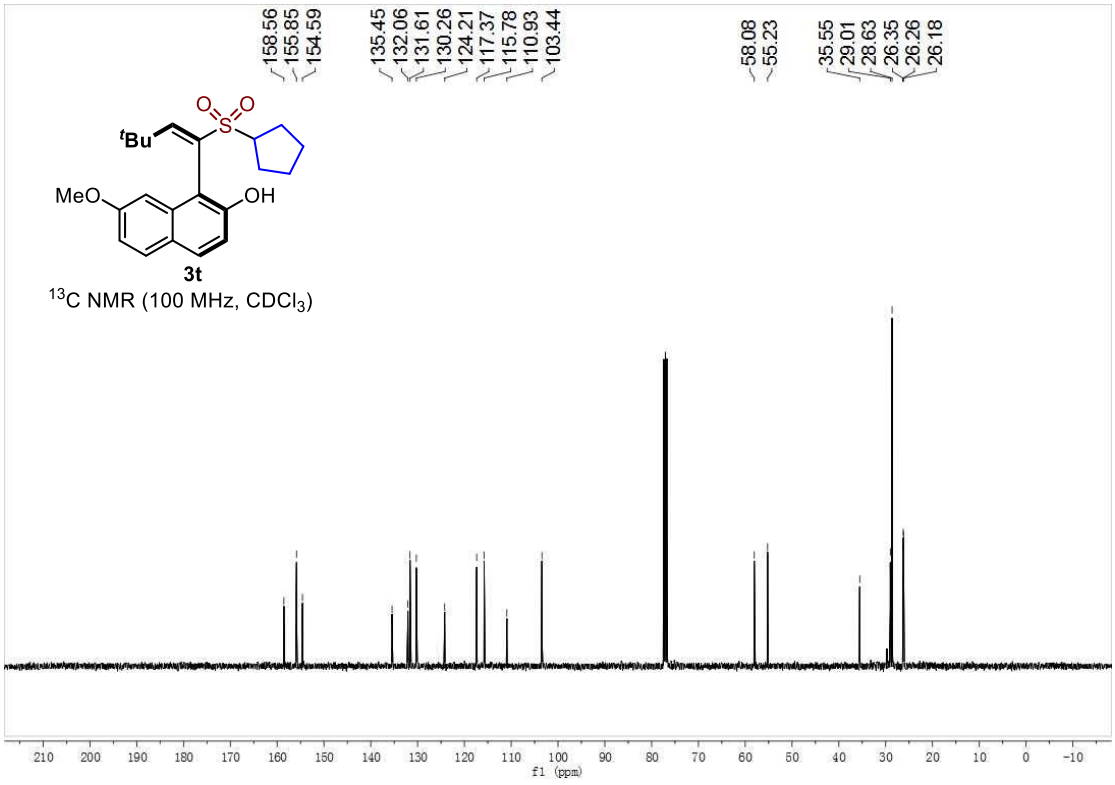
(E)-1-(1-(cyclopentylsulfonyl)-2-(thiophen-3-yl)vinyl)naphthalen-2-ol (3s)



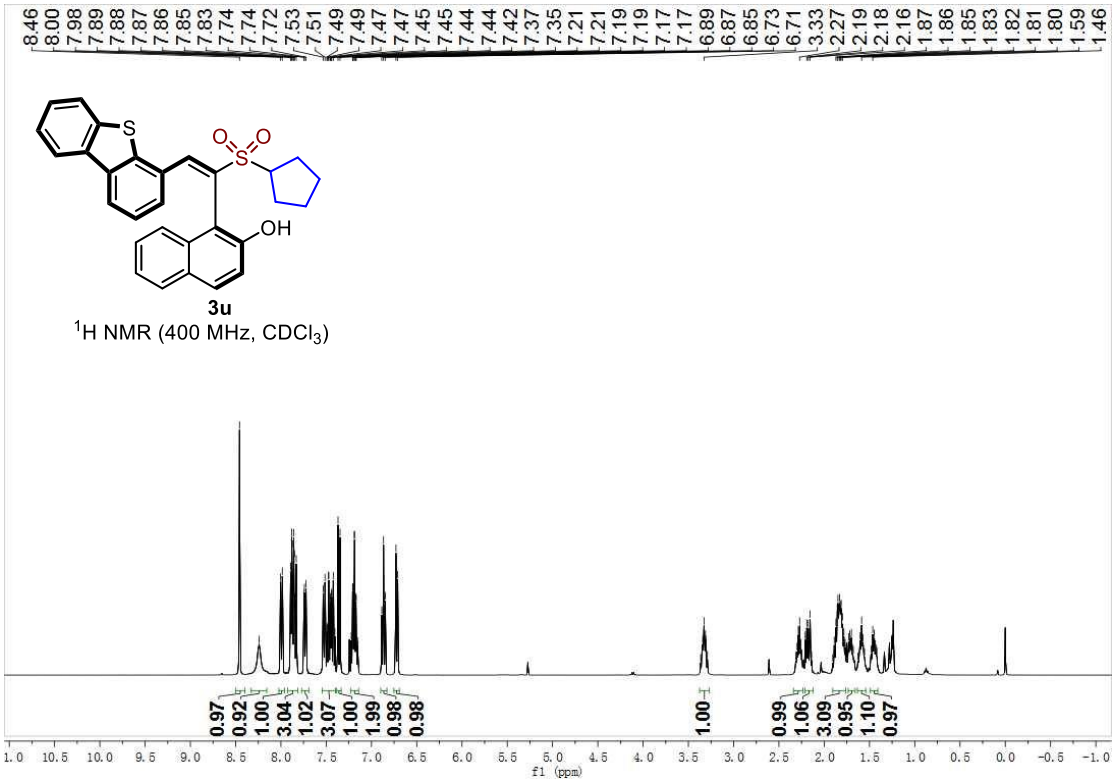


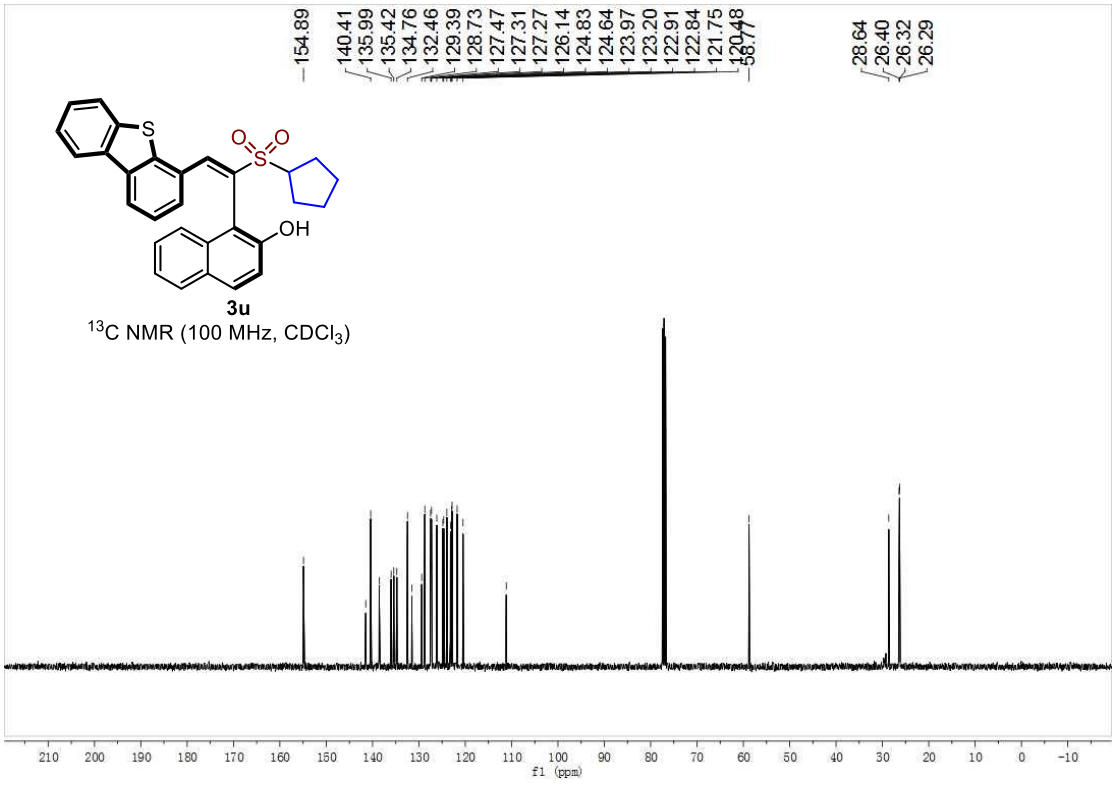
(E)-1-(1-(cyclopentylsulfonyl)-3,3-dimethylbut-1-en-1-yl)-7-methoxynaphthalen-2-ol (3t)



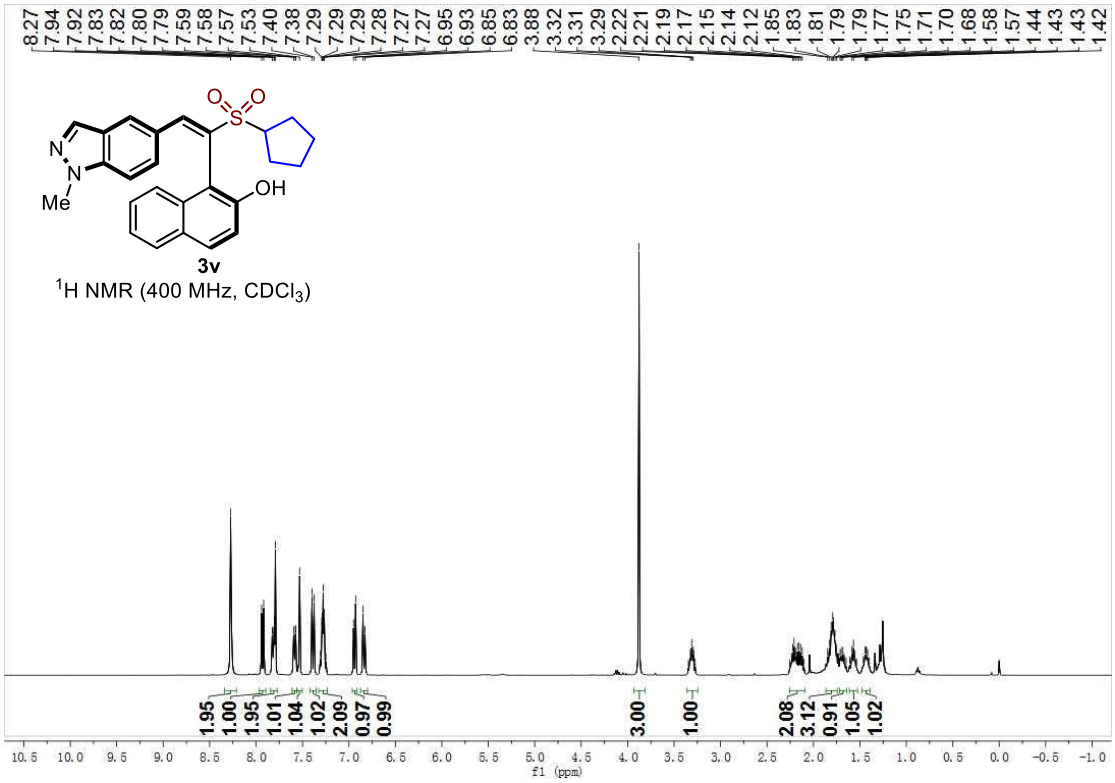


(E)-1-(1-(cyclopentylsulfonyl)-2-(dibenzo[b,d]thiophen-4-yl)vinyl)naphthalen-2-ol (3u)



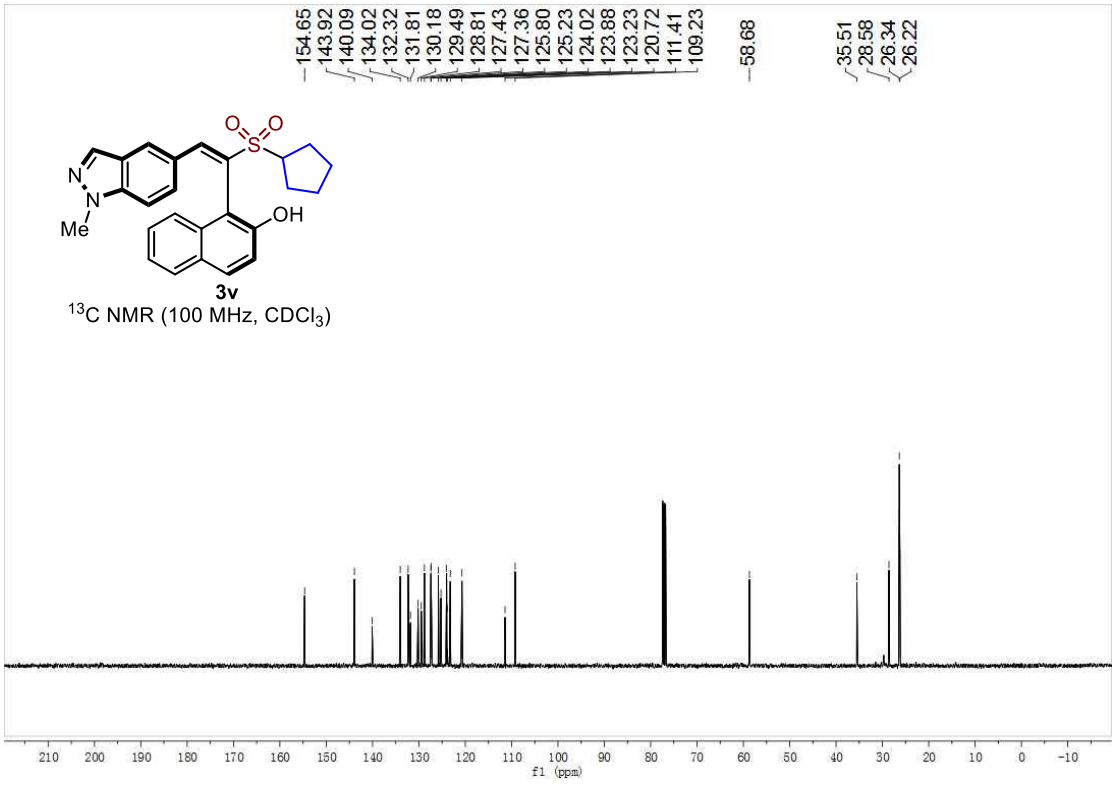


(E)-1-(1-(cyclopentylsulfonyl)-2-(1-methyl-1H-indazol-5-yl)vinyl)naphthalen-2-ol (3v)



3v

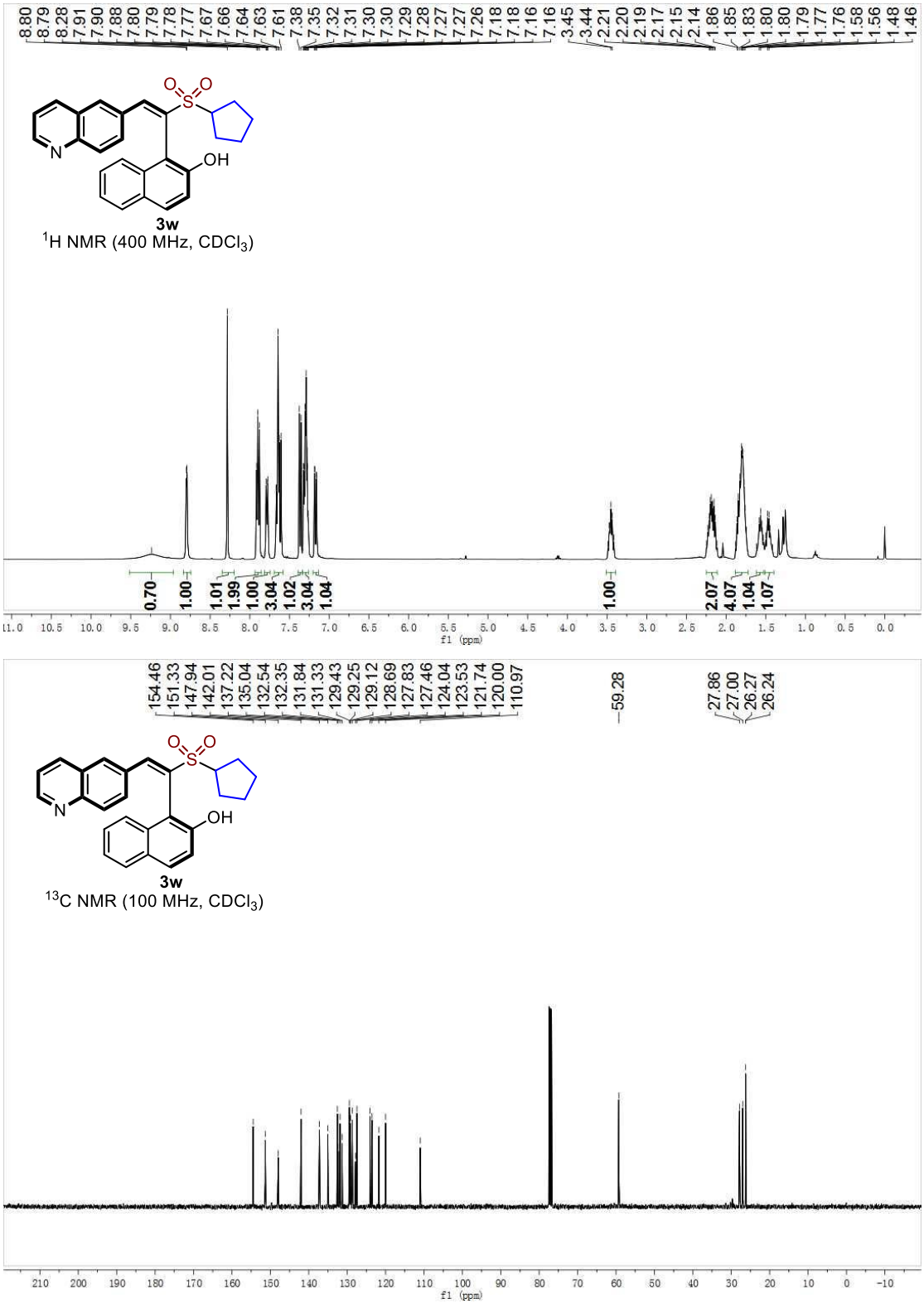
^{1}H NMR (400 MHz, $CDCl_3$)



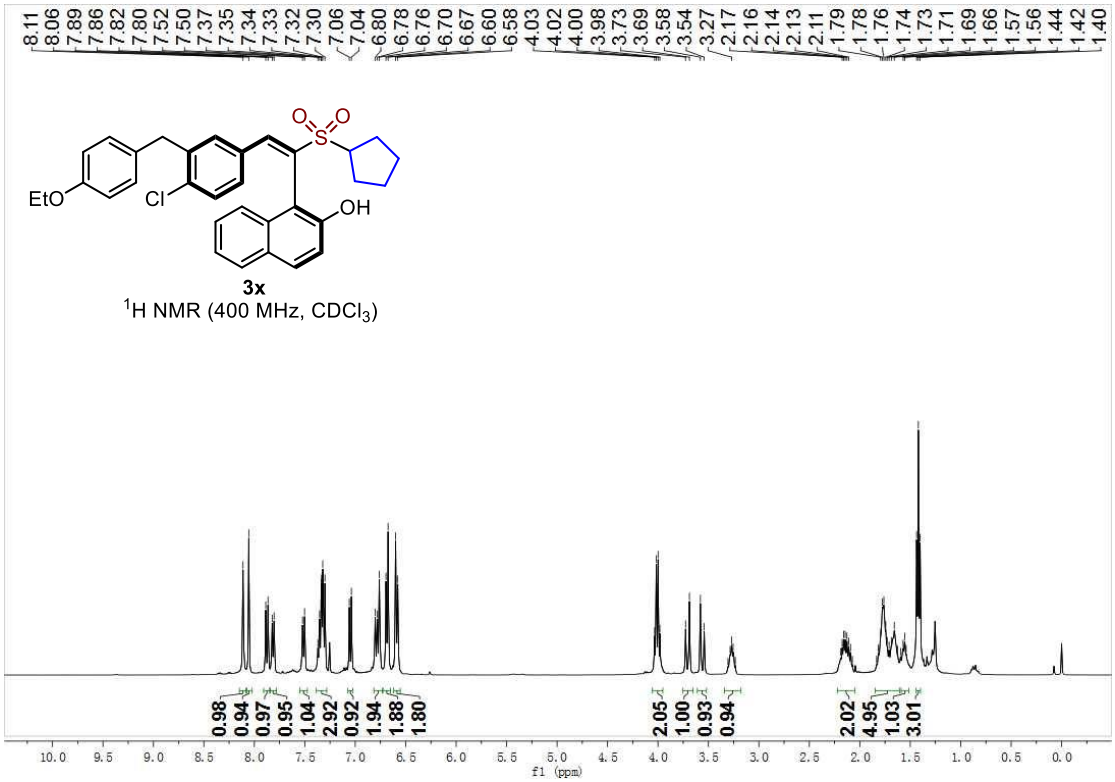
3v

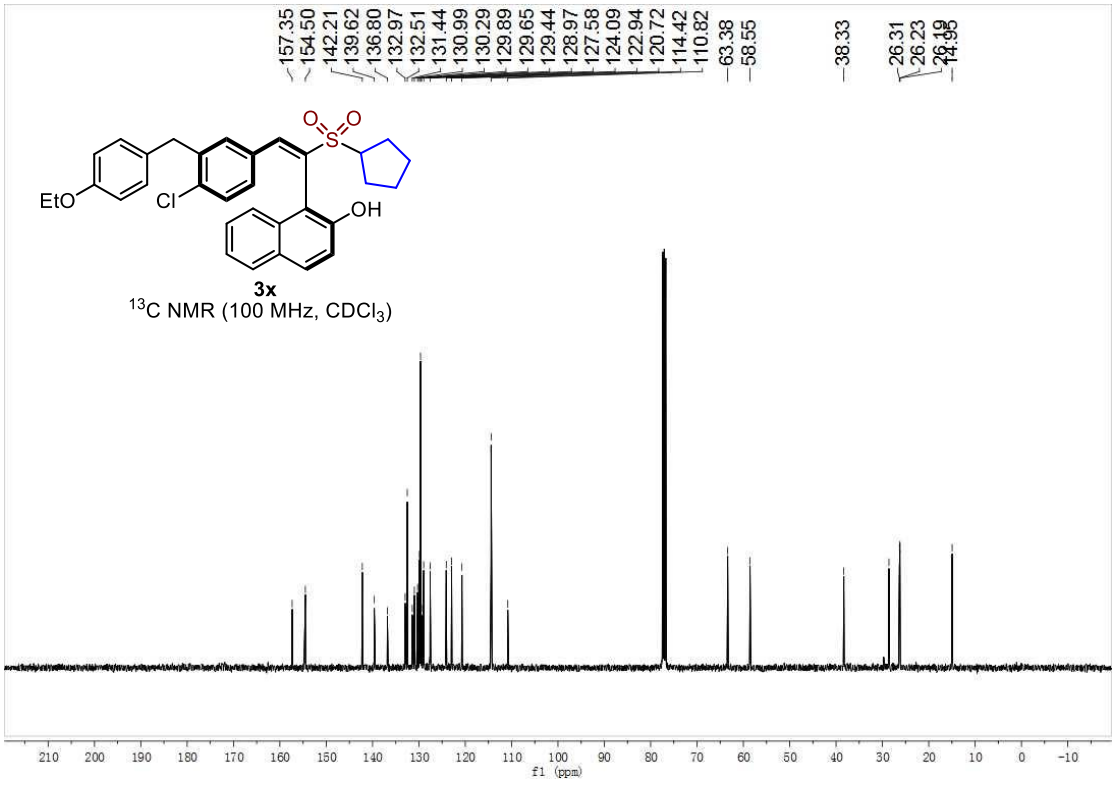
^{13}C NMR (100 MHz, $CDCl_3$)

(E)-1-(1-(cyclopentylsulfonyl)-2-(quinolin-6-yl)vinyl)naphthalen-2-ol (3w)

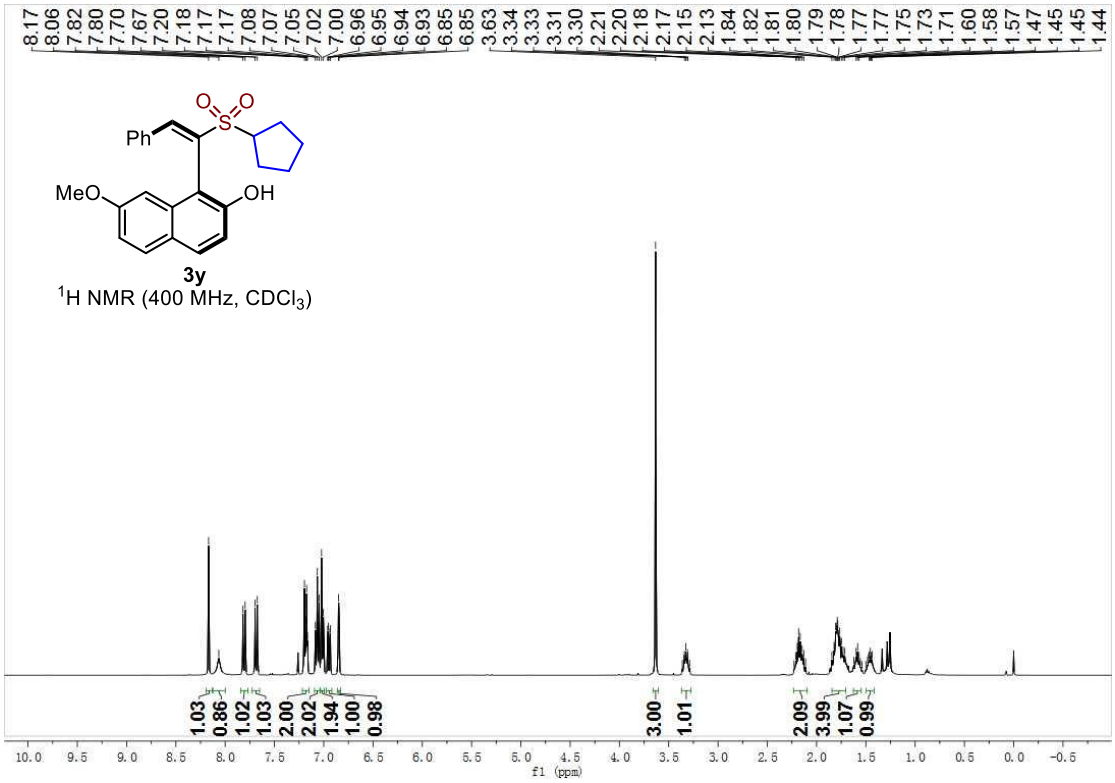


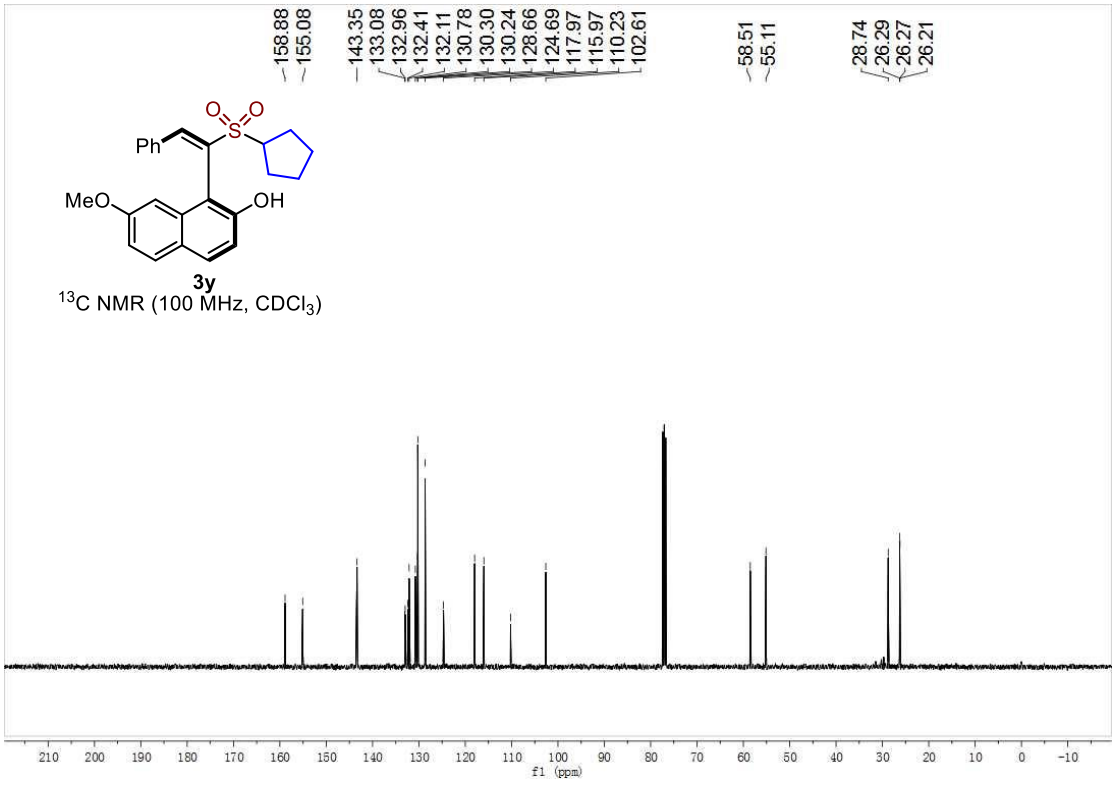
(E)-1-(2-(4-chloro-3-(4-ethoxybenzyl)phenyl)-1-(cyclopentylsulfonyl)vinyl)naphthalen-2-ol (3x)



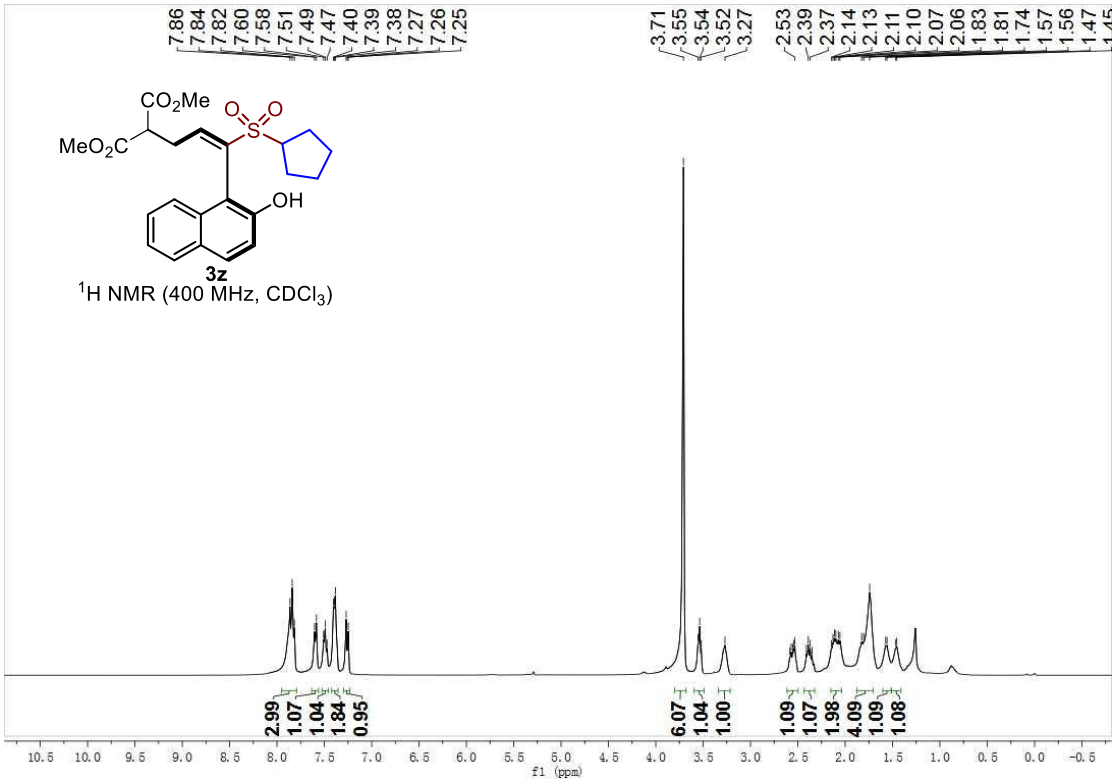


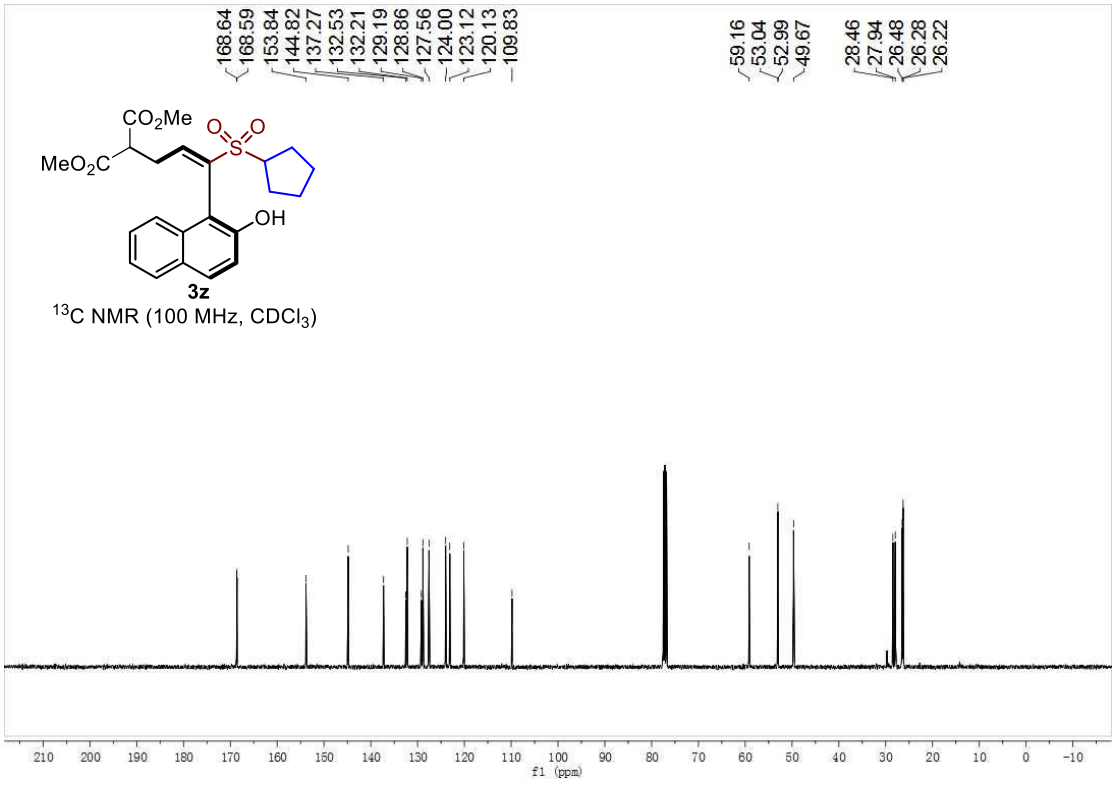
(E)-1-(1-(cyclopentylsulfonyl)-2-phenylvinyl)-7-methoxynaphthalen-2-ol (3y)





Dimethyl (E)-2-(3-(cyclopentylsulfonyl)-3-(2-hydroxynaphthalen-1-yl)allyl)malonate (3z)


7.86
7.84
7.82
7.60
7.58
7.51
7.49
7.47
7.40
7.39
7.38
7.27
7.26
7.25
3.71
3.55
3.54
3.52
3.27
2.53
2.39
2.37
2.14
2.13
2.11
2.10
2.07
2.06
1.83
1.81
1.74
1.57
1.56
1.47
CO2Me
MeO2C
O
S
O
OH
3z
1H NMR (400 MHz, CDCl3)
2.99
1.07
1.04
1.84
0.95
6.07
1.04
1.00
1.09
1.07
1.98
4.09
1.09
1.08
f1 (ppm)


168.64
168.59
153.84
144.82
137.27
132.53
132.21
129.19
128.86
127.56
124.00
123.12
120.13
109.83
59.16
53.04
52.99
49.67
28.46
27.94
26.48
26.28
26.22
CO2Me
MeO2C
O
S
O
OH
3z
13C NMR (100 MHz, CDCl3)
f1 (ppm)