Supporting Information for

Electrosynthesis of Bridged or Fused Sulfonamides through Complex Radical Cascade Reactions: Divergence in Medium-Sized Ring Formation

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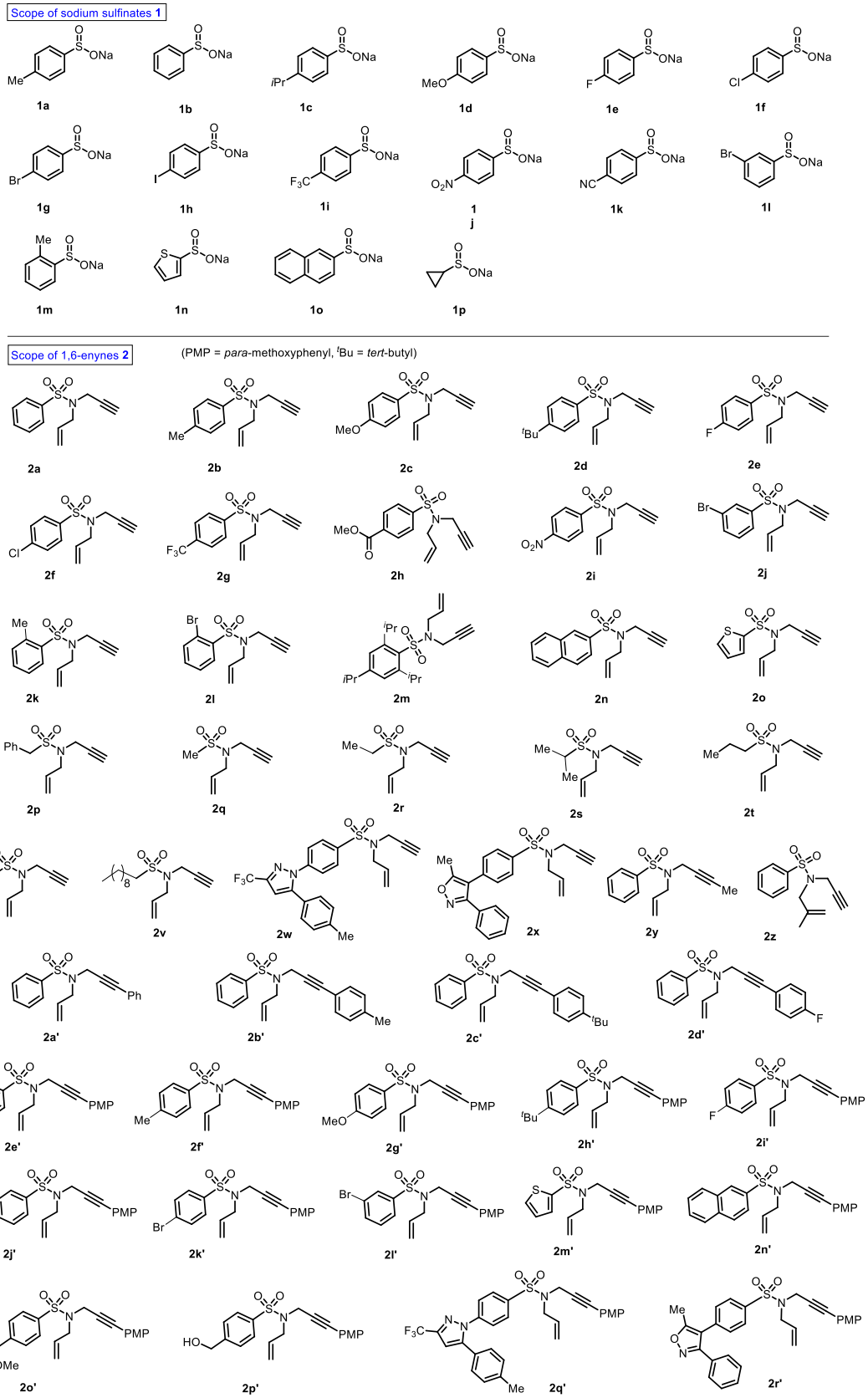
1. General Remarks

NMR spectra were recorded on BRUKER AVANCE III 400 or BRUKER AVANCE III 600. $CDCl_3$ was used as the solvent. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$: ^1H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Electrospray-ionization (ESI) mass spectra were obtained on AB Sciex LC 30A-Triple TOF 4600 apparatus. All systems are equipped with time-of-flight (TOF) analyzers. Melting points were measured with micro melting point apparatus. Platinum electrodes (10 mm × 25 mm × 0.25 mm, 99.9%; obtained from ChemPur® Karlsruhe, Germany) and graphite felt (GF) electrodes (10 mm × 25 mm × 6 mm, SIGRACELL® GFA 6 EA, obtained from SGL Carbon, Wiesbaden, Germany) were connected using stainless steel adapters. Unless otherwise noted, some materials (or alternatively chemicals) obtained from commercial suppliers were used directly without further purification. 1,6-enynes **1** were prepared according to the literatures.[1,2]

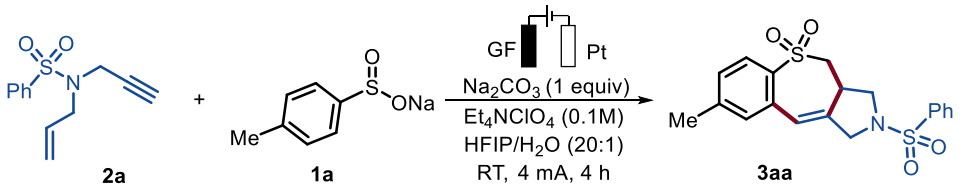
2. Scope

Table S–1. Scope of 1,6-Enynes 2 and Sodium Sulfinate 1.



3. Optimization

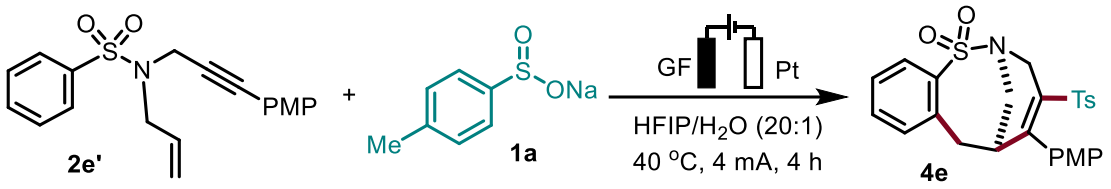
Table S–2. Optimization of the electrooxidative radical cyclization for the synthesis of the fused sulfonamide **3aa**.



Entry	Solvent	Electrolyte	T / °C	additive	Yield/%
1	MeCN	Et_4NClO_4	rt	Na_2CO_3	0
2	HFIP	Et_4NClO_4	rt	Na_2CO_3	38
3	MeCN/H_2O (3:1)	Et_4NClO_4	rt	-	13
4	MeCN/H_2O (3:1)	Et_4NClO_4	rt	Na_2CO_3	33
5	MeCN/HFIP (3:1:)	Et_4NClO_4	rt	Na_2CO_3	60
6	MeCN/HFIP/H_2O (3:1:0.2)	Et_4NClO_4	rt	Na_2CO_3	69
7	HFIP/H_2O (20:1)	Et_4NClO_4	rt	Na_2CO_3	71
8	HFIP/H_2O (10:1)	Et_4NClO_4	rt	Na_2CO_3	42
9	HFIP/H_2O (20:1)	Et_4NClO_4	rt	-	46
10	HFIP/H_2O (20:1)	Et_4NClO_4	rt	K_2CO_3	28
11	HFIP/H_2O (20:1)	Et_4NClO_4	rt	Na_2HPO_4	30
12	HFIP/H_2O (20:1)	Et_4NClO_4	40	Na_2CO_3	63
13	HFIP/H_2O (20:1)	Et_4NClO_4	60	Na_2CO_3	23
14	HFIP/H_2O (20:1)	LiOTf	rt	Na_2CO_3	23
15	HFIP/H_2O (20:1)	$LiClO_4$	rt	Na_2CO_3	24
16	HFIP/H_2O (20:1)	*n*-Bu_4NBF_4	rt	Na_2CO_3	28
17	HFIP/H_2O (20:1)	*n*-Bu_4NBF_6	rt	Na_2CO_3	21
18	HFIP/H_2O (20:1)	*n*-Bu_4NClO_4	rt	Na_2CO_3	20
19[a]	HFIP/H_2O (20:1)	Et_4NClO_4	rt	Na_2CO_3	41
20[b]	HFIP/H_2O (20:1)	Et_4NClO_4	rt	Na_2CO_3	22
21[c]	HFIP/H_2O (20:1)	Et_4NClO_4	rt	Na_2CO_3	0

Standard conditions: Undivided cell, GF anode, Pt cathode, constant current = 4 mA, **2a** (0.30 mmol), **1a** (0.60 mmol, 2.0 equiv), eletrolyte (0.1 M), solvent (4 mL), additive (1.0 equiv), under 30 °C, 4 h, 2.0 $Fmol^{-1}$. Yield of the isolated product. [a] eletrolyte (0.05 M). [b] GF(+)|Ni(−) instead of GF(+)|Pt(−). [c] Pt(+)|Pt(−) instead of GF(+)|Pt(−).

Table S–3. Optimization of electrooxidative synthesis of the product containing 9-membered ring **4e**.[a]

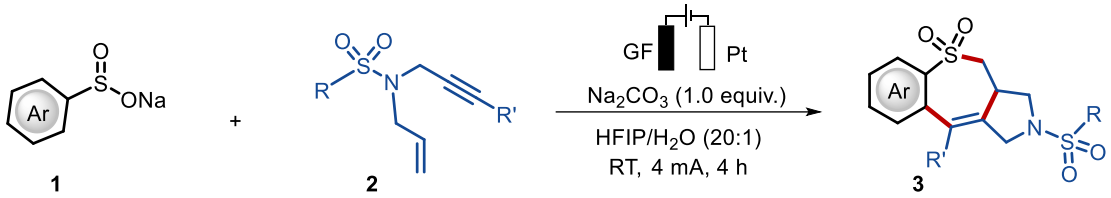


Entry	Solvent	Electrolyte	T /℃	additive	Yield/%
1	MeCN	Et_4NClO_4	rt	Na_2CO_3	trace
2	HFIP	Et_4NClO_4	rt	Na_2CO_3	20
3	MeCN/H_2O (10:1)	Et_4NClO_4	rt	Na_2CO_3	26
4	HFIP/H_2O (20:1)	Et_4NClO_4	rt	Na_2CO_3	51
5	MeCN/HFIP/H_2O (3:1:10.0 eq.)	Et_4NClO_4	rt	Na_2CO_3	24
6	HFIP/H_2O (20:1)	Et_4NClO_4	40	Na_2CO_3	43
7	HFIP/H_2O (20:1)	Et_4NClO_4	60	Na_2CO_3	34
8	HFIP/H_2O (20:1)	Et_4NClO_4	40	-	58
9	HFIP/H_2O (20:1)	Et_4NClO_4	40	K_2CO_3	28
10	HFIP/H_2O (20:1)	Et_4NClO_4	40	Na_2HPO_4	20
11	HFIP/H_2O (20:1)	*n*-Bu_4NBF_4	40	-	25
12	HFIP/H_2O (20:1)	*n*-Bu_4NBF_6	40	-	21
13	HFIP/H_2O (20:1)	*n*-Bu_4NClO_4	40	-	26
14	HFIP/H_2O (20:1)	-	40	-	20
15[b]	HFIP/H_2O (20:1)	Et_4NClO_4	40	-	14

[a] Standard conditions: Undivided cell, GF anode, Pt cathode, constant current = 4 mA, **2a** (0.30 mmol), **1a** (0.60 mmol, 2.0 equiv), eletrolyte (0.1 M), solvent (4 mL), under 40 °C, 4 h. Yield of the isolated product. [b] GF(+)|Ni(−) instead of GF(+)|Pt(−).

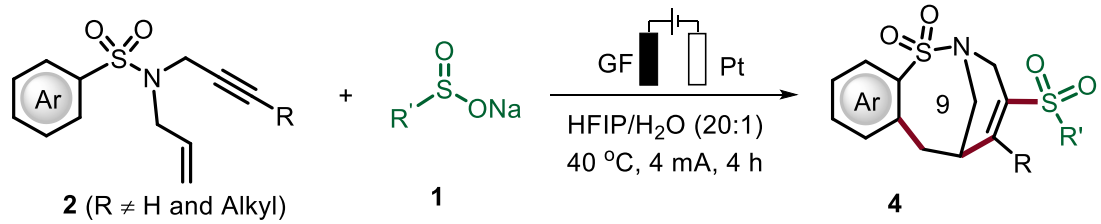
4. General Procedures

(A) General Procedure for Electrooxidative Radical Cyclization: Access to Fused Cyclic Sulfonamides.



The electrocatalysis was carried out in an undivided cell under air with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Sodium sulfonates $ArSO_2Na$ **1** (0.6 mmol, 2.0 equiv), 1,6-enynes **2** (0.3 mmol, 1.0 equiv), Na_2CO_3 (0.3 mmol, 1.0 equiv) and Et_4NClO_4 (92 mg, 0.1 M) were dissolved in a mixture of HFIP and H_2O (20:1, 4 mL). Electrocatalysis was performed at room temperature with a constant current of 4.0 mA maintained for 4 h. The GF anode was washed with ethyl acetate (3 × 3 mL) in an ultrasonic bath and transfered to the round bottom flask with the crude reaction solution. Silica was added to the flask and all volatiles were evaporated under vacuum. Purification was performed by flash column chromatography on silica gel using petroleum ether/ EtOAc as the eluent to give the corresponding products **3**.

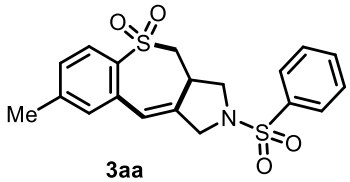
(B) General Procedure for Electrooxidative Radical Cyclization: Access to Bridged Sulfonamides.



The electrocatalysis was carried out in an undivided cell under air with a graphite felt (GF) anode (10 mm × 15 mm × 6 mm) and a platinum cathode (10 mm × 15 mm × 0.25 mm). Sodium sulfonates $ArSO_2Na$ **1** (0.6 mmol, 2.0 equiv), 1,6-enynes **2** (0.3 mmol, 1.0 equiv) and Et_4NClO_4 (92 mg, 0.1 M) were dissolved in a mixture of HFIP and H_2O (20:1, 4 mL). Electrocatalysis was performed at room temperature with a constant current of 4.0 mA maintained for 4 h. The GF anode was washed with ethyl acetate (3 × 3 mL) in an ultrasonic bath and transfered to the round bottom flask with the crude reaction solution. Silica was added to the flask and all volatiles were evaporated under

vacuum. Purification was performed by flash column chromatography on silica gel using petroleum ether/ EtOAc as the eluent to give the corresponding products **4**.

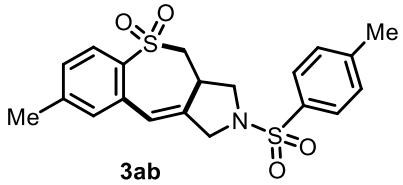
5. Characterization Data



3aa

8-Methyl-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3aa)

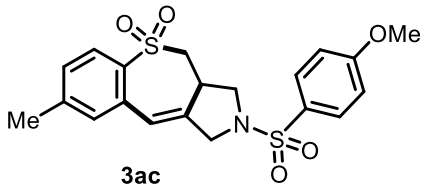
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2a** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3aa** (82.8 mg, 71%) as a white solid **M.p.**: 184–186 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 1H), 7.88–7.86 (m, 2H), 7.68–7.64 (m, 1H), 7.61– (d, J = 14.8 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.10 (s, 1H), 6.44 (d, J = 1.9 Hz, 1H), 4.23 (dt, J = 14.4, 1.6 Hz, 1H), 4.07 (dt, J = 14.5, 1.6 Hz, 1H), 3.75 (dd, J = 9.4, 7.5 Hz, 1H), 3.55 (dd, J = 13.2, 4.2 Hz, 1H), 3.45–3.31 (m, 2H), 3.10 (t, J = 9.1 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 142.0, 136.6, 135.8, 133.5, 133.5, 132.4, 129.5, 128.4, 127.8, 127.4, 123.2, 55.7, 54.1, 52.3, 38.8, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{20}NO_4S_2$ $[M+H]^+$: 390.0828, found: 390.0826.



3ab

8-Methyl-2-tosyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ab)

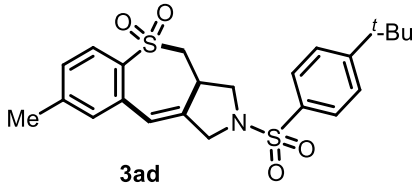
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2b** (74.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ab** (88.3 mg, 73%) as a white solid. **M.p.**: 193–195 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.10 (s, 1H), 6.44 (s, 1H), 4.21 (d, J = 14.5 Hz, 1H), 4.06 (d, J = 14.5 Hz, 1H), 3.73 (dd, J = 9.3, 7.5 Hz, 1H), 3.55 (dd, J = 12.7, 3.6 Hz, 1H), 3.43–3.32 (m, 2H), 3.08 (t, J = 9.0 Hz, 1H), 2.46 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 144.4, 142.3, 136.6, 133.5, 132.8, 132.5, 130.1, 128.4, 127.9, 127.5, 123.1, 55.9, 54.2, 52.4, 38.8, 21.7, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{22}NO_4S_2$ $[M+H]^+$: 404.0985, found: 404.0984.



3ac

2-((4-Methoxyphenyl)sulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ac)

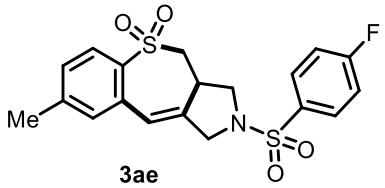
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2c** (79.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ac** (75.4 mg, 60%) as a yellow soild. **M.P.**: 201–203 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.10 (s, 1H), 7.04 (d, J = 8.9 Hz, 2H), 6.44 (d, J = 1.3 Hz, 1H), 4.20 (d, J = 14.5 Hz, 1H), 4.05 (d, J = 14.5 Hz, 1H), 3.90 (s, 3H), 3.72 (dd, J = 9.3, 7.5 Hz, 1H), 3.55 (dd, J = 12.7, 3.6 Hz, 1H), 3.44–3.36 (m, 2H), 3.07 (t, J = 9.0 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.6, 144.6, 142.4, 136.7, 133.4, 132.6, 130.0, 128.4, 127.5, 127.4, 123.1, 114.7, 56.0, 55.8, 54.2, 52.4, 38.8, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{22}NO_5S_2$ $[M+H]^+$: 420.0934, found: 420.0928.



3ad

2-((4-(Tert-butyl)phenyl)sulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ad)

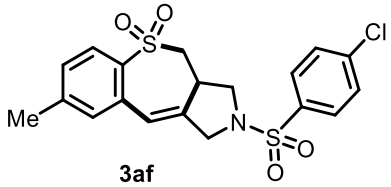
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2d** (87.3 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ad** (72.1 mg, 54%) as a white solid. **M.p.**: 232–234 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 7.10 (s, 1H), 6.45 (d, J = 1.3 Hz, 1H), 4.22 (d, J = 14.4 Hz, 1H), 4.08 (d, J = 14.5 Hz, 1H), 3.74 (dd, J = 9.3, 7.5 Hz, 1H), 3.56 (dd, J = 12.8, 3.7 Hz, 1H), 3.44–3.35 (m, 2H), 3.11 (t, J = 9.2 Hz, 1H), 2.40 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.3, 144.6, 142.4, 136.6, 133.4, 132.6, 130.3, 128.4, 127.7, 127.5, 126.5, 123.1, 56.0, 54.2, 52.3, 38.8, 35.4, 31.2, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{23}H_{28}NO_4S_2$ $[M+H]^+$: 446.1454, found: 446.1451.



3ae

2-((4-Fluorophenyl)sulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ae)

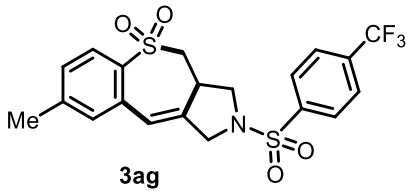
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2e** (75.9 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ae** (91.6 mg, 75%) as a white solid. **M.p.**: 201–203 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 1H), 7.89 (dd, J = 8.8, 5.0 Hz, 2H), 7.25(dd, J = 17.6, 9.2 Hz, 3H), 7.10 (s, 1H), 6.44 (d, J = 1.7 Hz, 1H), 4.22 (d, J = 14.4 Hz, 1H), 4.05 (d, J = 14.5 Hz, 1H), 3.74 (dd, J = 9.3, 7.6 Hz, 1H), 3.56 (dd, J = 13.2, 4.3 Hz, 1H), 3.47–3.41 (m, 1H), 3.38 (d, J = 13.2 Hz, 1H), 3.09 (t, J = 9.1 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6 (d, J = 256.5 Hz), 144.7, 141.8, 136.6, 133.5, 132.4, 130.5, 130.4, 128.4, 127.4, 123.3, 116.8 (d, J = 22.2 Hz), 55.5, 54.1, 52.3, 38.9, 21.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –103.99. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{19}FNO_4S_2$ $[M+H]^+$:408.0734, found: 408.0734.



3af

2-((4-Chlorophenyl)sulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3af)

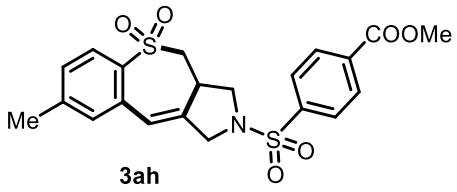
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2f** (80.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3af** (88.8 mg, 70%) as a white solid. **M.p.**: 235–237 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 7.11 (s, 1H), 6.45 (s, 1H), 4.24 (d, J = 14.4 Hz, 1H), 4.07 (d, J = 14.4 Hz, 1H), 3.74 (dd, J = 8.0, 8.0 Hz, 1H), 3.56 (dd, J = 13.3, 4.4 Hz, 1H), 3.52–3.47 (m, 1H), 3.39 (d, J = 12.8 Hz, 1H), 3.10 (t, J = 9.1 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 141.7, 140.2, 136.7, 134.6, 133.6, 132.4, 129.9, 129.2, 128.5, 127.6, 123.4, 55.6, 54.1, 52.3, 38.9, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{19}ClNO_4S_2$ $[M+H]^+$: 424.0439, found: 424.0435.



3ag

8-Methyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ag)

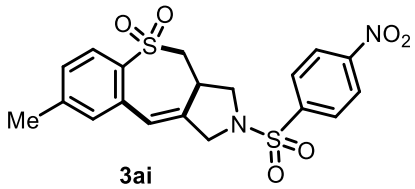
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2g** (90.9 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ag** (87.7 mg, 64%) as a white solid. **M.p.**: 252–254 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.09–8.02 (m, 4H), 7.85 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.26 (s, 1H), 6.55 (s, 1H), 4.30 (d, J = 14.9 Hz, 1H), 4.02 (d, J = 14.9 Hz, 1H), 3.84 (dd, J = 8.7, 8.7 Hz, 1H), 3.73 (dd, J = 14.6, 4.9 Hz, 1H), 3.57 (dd, J = 14.5, 12.0 Hz, 1H), 3.24–3.17 (m, 1H), 3.06 (t, J = 9.9 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (151 MHz, DMSO) δ 144.4, 142.7, 140.0, 137.4, 134.1, 133.4 (q, J = 33.2 Hz), 132.2, 129.0, 128.5, 127.2 (q, J = 3..0 Hz), 126.6, 123.9 (q, J = 273.3 Hz), 122.7, 54.6, 52.7, 52.2, 39.1, 21.2. **^{19}F NMR** (565 MHz, DMSO) δ –61.68. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{19}F_3NO_4S_2$ $[M+H]^+$: 458.0702, found: 458.0700.



3ah

Methyl-4-((8-methyl-5,5-dioxido-3a,4-dihydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrol-2(3*H*)-yl)sulfonyl)benzoate (3ah)

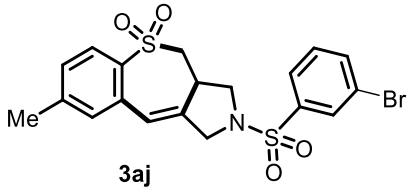
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2h** (87.9 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ah** (95.2 mg, 71%) as a white solid. **M.p.**: 95–97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.99 (s, 3H), 3.89 (d, J = 14.3 Hz, 1H), 3.79 (d, J = 16.0 Hz, 1H), 3.75 (dd, J = 10.4, 7.2 Hz, 1H), 3.24–3.20 (m, 2H), 3.11–3.00 (m, 2H), 2.49 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.7, 145.5, 145.0, 139.6, 136.1, 134.4, 130.5, 130.3, 128.1, 127.9, 109.1, 58.6, 53.0, 52.9, 51.5, 37.4, 21.8. **HR–MS** (ESI) *m/z* calc. for $C_{21}H_{22}NO_6S_2$ $[M+H]^+$: 448.0883, found: 448.0880.



3ai

8-Methyl-2-((4-nitrophenyl)sulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ai)

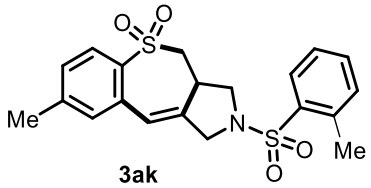
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2i** (74.0 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ai** (83.3 mg, 61%) as a white solid. **M.p.**: >250 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.44 (d, J = 8.7 Hz, 1H), 8.18 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.7 Hz, 1H), 7.99(d, J = 8.4 Hz, 1H), 7.84 (dd, J = 8.0, 2.4 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.25 (s, 1H), 6.54 (s, 1H), 4.29 (t, J = 12.8 Hz, 1H), 4.02 (t, J = 15.4 Hz, 1H), 3.84 (dd, J = 17.1, 8.1 Hz, 1H), 3.74 (dd, J = 14.6, 4.6 Hz, 1H), 3.60–3.52 (m, 1H), 3.26–3.14 (m, 1H), 3.10–3.01 (m, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 150.6, 144.4, 142.5, 137.4, 134.1, 132.2, 130.8, 129.6, 128.5, 126.6, 125.3, 122.8, 54.6, 53.2, 52.8, 39.1, 21.2. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{19}N_2O_6S_2$ $[M+H]^+$: 435.0679, found: 435.0680.



3aj

2-((3-Bromophenyl)sulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3aj)

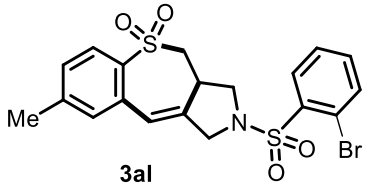
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2j** (93.6 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3aj** (100.7 mg, 72%) as a yellow solid. **M.p.**: 184–186 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02–8.00 (m, 2H), 7.80 (dd, J = 7.9, 1.3 Hz, 2H), 7.46 (dd, J = 7.9, 7.9 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.12 (s, 1H), 6.46 (d, J = 1.8 Hz, 1H), 4.25 (d, J = 14.4 Hz, 1H), 4.08 (d, J = 14.4 Hz, 1H), 3.76 (dd, J = 9.3, 7.6 Hz, 1H), 3.57 (dd, J = 13.4, 4.6 Hz, 1H), 3.51–3.46 (m, 1H), 3.37 (dd, J = 13.3, 11.9 Hz, 1H), 3.11 (t, J = 9.1 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 141.6, 137.9, 136.6, 136.5, 133.6, 132.3, 131.0, 130.6, 128.5, 127.5, 126.2, 123.6, 123.4, 55.5, 54.1, 52.3, 38.9, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{19}BrNO_4S_2$ $[M+H]^+$: 467.9937, found: 467.9930.



3ak

8-Methyl-2-(o-tolylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ak)

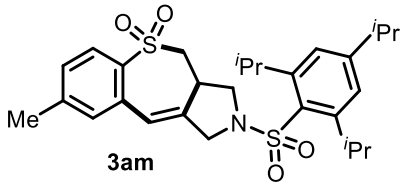
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2k** (74.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ak** (82.2 mg, 68%) as a white solid. **M.p.**: 154–156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 7.4 Hz, 1H), 7.52 (dd, J = 7.4, 7.4 Hz, 1H), 7.37 (d, J = 6.7 Hz, 2H), 7.23 (d, J = 8.1 Hz, 1H), 7.13 (s, 1H), 6.48 (d, J = 1.3 Hz, 1H), 4.26 (d, J = 14.5 Hz, 1H), 4.16 (d, J = 14.6 Hz, 1H), 3.74 (dd, J = 7.2, 7.2 Hz, 1H), 3.68 (dd, J = 15.2, 4.4 Hz, 2H), 3.41 (dd, J = 15.1, 13.5 Hz, 1H), 3.20 (t, J = 8.8 Hz, 1H), 2.68 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 142.4, 138.3, 136.6, 135.9, 133.5, 133.5, 133.0, 132.5, 130.0, 128.4, 127.4, 126.4, 123.1, 55.6, 53.5, 51.6, 39.2, 21.4, 20.7. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{22}NO_4S_2$ $[M+H]^+$: 404.0985, found: 404.0984.



3al

2-((2-Bromophenyl)sulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3al)

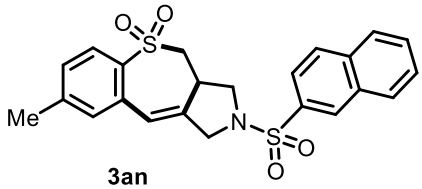
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2l** (93.6 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3al** (83.9 mg, 60%) as a yellow solid. **M.p.**: 141–143 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 7.7 Hz, 1H), 7.50–7.45 (m, 2H), 7.23 (d, J = 8.1 Hz, 1H), 7.14 (s, 1H), 6.48 (s, 1H), 4.37 (d, J = 14.4 Hz, 1H), 4.25 (d, J = 14.4 Hz, 1H), 3.92 (dd, J = 8.8, 8.8 Hz, 1H),, 3.63–3.55 (m, 2H), 3.43 (t, J = 13.3 Hz, 1H), 3.33 (t, J = 9.3 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 142.2, 137.7, 136.7, 135.9, 134.2, 133.7, 132.4, 132.3, 128.4, 127.8, 127.4, 123.1, 120.7, 55.0, 53.8, 52.0, 39.4, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{22}NO_4S_2$ $[M+H]^+$: 404.0985, found: 404.0984.



3am

8-Methyl-2-((2,4,6-triisopropylphenyl)sulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3am)

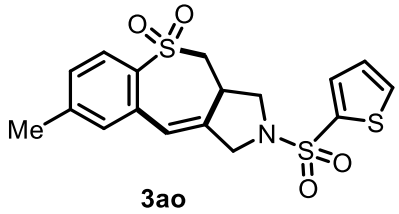
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2m** (108.3 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded **3am** (89.6 mg, 58%) as a white solid. **M.p.**: 60–62 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 1H), 7.26–7.20 (m, 3H), 7.14 (s, 1H), 6.50 (s, 1H), 4.26–4.19 (m, 3H), 4.15 (d, J = 14.5 Hz, 1H), 3.68–3.50 (m, 3H), 3.52–3.44 (m, 1H), 3.23 (t, J = 8.3 Hz, 1H), 2.94 (d, J = 6.8 Hz, 1H), 2.43 (s, 3H), 1.29 (dd, J = 6.8, 2.9 Hz, 18H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.8, 151.7, 144.6, 142.8, 136.6, 133.4, 132.9, 130.3, 128.3, 127.5, 124.1, 123.0, 56.6, 52.8, 51.0, 39.0, 34.3, 29.6, 25.1, 25.0, 23.7, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{28}H_{38}NO_4S_2$ $[M+H]^+$: 516.2237, found: 516.2237.



3an

8-Methyl-2-(naphthalen-2-ylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3an)

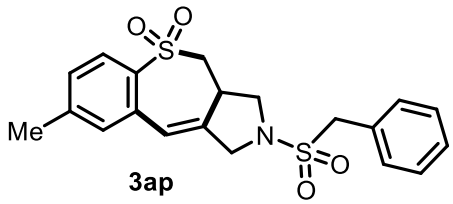
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2n** (85.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3an** (92.2 mg, 70%) as a white solid. **M.p.**: 232–234 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.54 (s, 1H), 8.24 (d, J = 7.7 Hz, 1H), 8.17 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.87 (dd, J = 8.6, 1.3 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.75–7.68 (m, 2H), 7.25 (d, J = 8.1 Hz, 1H), 7.14 (s, 1H), 6.50 (s, 1H), 4.31 (d, J = 15.1 Hz, 1H), 4.03 (d, J = 15.1 Hz, 1H), 3.89 (dd, J = 8.4, 8.4 Hz, 1H), 3.73 (dd, J = 14.6, 4.9 Hz, 1H), 3.54 (dd, J = 14.5, 12.1 Hz, 1H), 3.19–3.17 (m, 1H), 3.06 (t, J = 9.9 Hz, 1H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 144.3, 143.0, 137.4, 135.1, 134.0, 133.1, 132.3, 132.2, 130.1, 129.9, 129.6, 129.4, 128.4, 128.3, 128.2, 126.5, 123.3, 122.5, 54.6, 52.8, 52.4, 39.2, 21.2. **HR–MS** (ESI) *m/z* calc. for $C_{23}H_{22}NO_4S_2$ $[M+H]^+$: 440.0985, found: 440.0985.



3ao

8-Methyl-2-(thiophen-2-ylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ao)

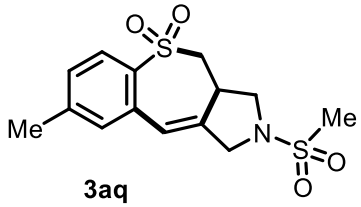
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2o** (72.3 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ao** (59.3 mg, 50%) as a white solid. **M.p.**: 235–237 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 5.0 Hz, 1H), 7.67 (d, J = 3.7 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.21 (dd, J = 4.0, 4.0 Hz, 1H), 7.13 (s, 1H), 6.48 (d, J = 1.3 Hz, 1H), 4.30 (d, J = 14.6 Hz, 1H), 4.14 (d, J = 14.6 Hz, 1H), 3.81 (dd, J = 9.5, 7.8 Hz, 1H), 3.56 (dd, J = 13.4, 4.3 Hz, 1H), 3.47–3.33 (m, 2H), 3.17 (t, J = 9.4 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 141.8, 136.7, 135.8, 133.7, 133.1, 132.8, 132.3, 128.5, 128.0, 127.5, 123.3. 55.3, 54.5, 52.5, 38.9, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{17}H_{18}NO_4S_3$ $[M+H]^+$: 396.0393, found: 396.0392.



3ap

2-(Benzylsulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ap)

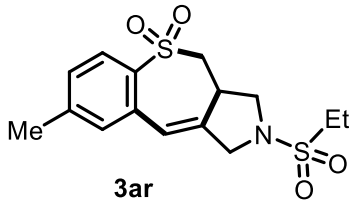
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2p** (74.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ap** (65.3 mg, 54%) as a white solid. **M.p.**: 158–160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 1H), 7.43–7.39 (m, 5H), 7.24 (d, J = 8.2 Hz, 1H), 7.14 (s, 1H), 6.39 (s, 1H), 4.34 (s, 2H), 4.17 (d, J = 14.6 Hz, 1H), 4.00 (d, J = 14.4 Hz, 1H), 3.57 (dd, J = 7.6, 7.6 Hz, 1H), 3.49–3.42 (m, 2H), 3.28 (dd, J = 15.2, 12.8 Hz,, 1H), 3.06 (t, J = 9.0 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 142.2, 136.8, 133.8, 132.2, 130.8, 129.1, 129.0, 128.9, 128.4, 127.3, 122.9, 57.6, 54.5, 54.4, 52.5, 39.3, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{22}NO_4S_2$ $[M+H]^+$: 404.0985, found: 404.0985.



3aq

8-Methyl-2-(methylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3aq)

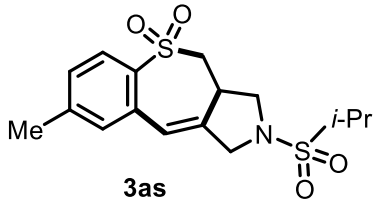
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2q** (51.9 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3aq** (46.1 mg, 47%) as a white solid. **M.p.**: 148–150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 1H), 7.26 (d, J = 8.1 Hz, 1H), 7.18 (s, 1H), 6.54 (d, J = 1.2 Hz, 1H), 4.36 (d, J = 14.6 Hz, 1H), 4.20 (d, J = 14.6 Hz, 1H), 3.84 (dd, J = 9.6, 7.6 Hz, 1H), 3.64–3.58 (m, 2H), 3.45 (dd, J = 15.2, 12.8 Hz, 1H), 3.28 (t, J = 9.2 Hz. 1H), 2.94 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (151 MHz, DMSO) δ 144.5, 143.9, 137.5, 134.3, 132.3, 128.5, 126.6, 122.3, 54.6, 52.5, 52.0, 39.5, 34.1, 21.2. **HR–MS** (ESI) *m/z* calc. for $C_{14}H_{18}NO_4S_2$ $[M+H]^+$:328.0672, found: 328.0682.



3ar

2-(Ethylsulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ar)

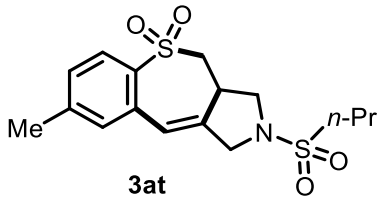
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2r** (56.1 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ar** (46.0 mg, 45%) as a white solid. **M.p.**: 122–124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.17 (s, 1H), 6.52 (s, 1H), 4.38 (d, J = 14.4 Hz, 1H), 4.23 (d, J = 14.5 Hz, 1H), 3.86 (dd, J = 9.4, 7.7 Hz, 1H), 3.67–3.57 (m, 2H), 3.43 (dd, J = 14.1, 11.9 Hz, 1H), 3.30 (t, J = 9.4 Hz, 1H), 3.09 (q, J = 7.4 Hz, 2H), 2.43 (s, 3H), 1.42 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 142.5, 136.8, 133.7, 132.3, 128.5, 127.4, 123.0, 54.9, 54.2, 52.2, 45.5, 39.6, 21.5, 8.1. **HR–MS** (ESI) *m/z* calc. for $C_{15}H_{20}NO_4S_2$ $[M+H]^+$: 342.0828, found: 342.0828.



3as

2-(Isopropylsulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3as)

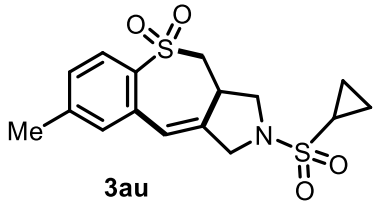
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2s** (60.3 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3as** (54.3 mg, 51%) as a white solid. **M.p.**: 168–170 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.17 (s, 1H), 6.50 (d, J = 1.1 Hz, 1H), 4.41 (d, J = 14.4 Hz, 1H), 4.25 (d, J = 14.5 Hz, 1H), 3.87 (dd, J = 9.6, 7.6 Hz, 1H), 3.64–3.56 (m, 2H), 3.42 (dd, J = 14.0, 12.0 Hz, 1H), 3.32 (t, J = 9.6 Hz, 1H), 3.28 (t, J = 6.8 Hz, 1H), 2.43 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 142.8, 136.7, 133.8, 132.3, 128.4, 127.3, 122.8, 54.6, 54.0, 52.7, 39.7, 21.4, 16.7. **HR–MS** (ESI) *m/z* calc. for $C_{16}H_{22}NO_4S_2$ $[M+H]^+$: 356.0985 found: 356.0983.



3at

8-Methyl-2-(propylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3at)

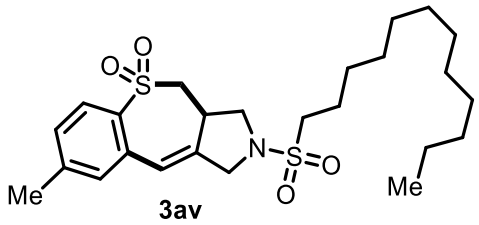
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2t** (60.3 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3at** (47.9 mg, 45%) as a yellow solid. **M.p.**: 142–144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.17 (s, 1H), 6.51 (d, J = 1.6 Hz, 1H), 4.36 (d, J = 14.5 Hz, 1H), 4.21 (d, J = 14.5 Hz, 1H), 3.84 (dd, J = 9.3, 7.7 Hz, 1H), 3.62–3.57 (m, 2H), 3.43 (dd, J = 15.3, 13.0 Hz, 1H), 3.28 (t, J = 9.4 Hz, 1H), 3.05–3.01 (m, 2H), 2.42 (s, 3H), 1.94–1.84 (m, 2H), 1.09 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 142.5, 136.7, 133.7, 132.2, 128.4, 127.3, 123.0, 54.8, 54.0, 52.4, 52.0, 39.5, 21.4, 17.1, 13.1. **HR–MS** (ESI) *m/z* calc. for $C_{16}H_{22}NO_4S_2$ $[M+H]^+$: 356.0985 found: 356.0983.



3au

2-(Cyclopropylsulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3au)

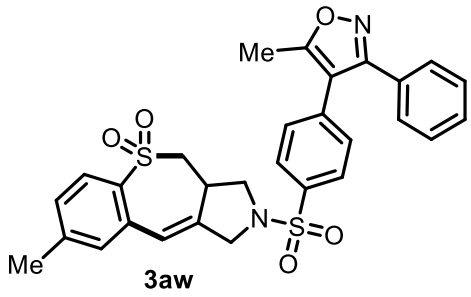
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2u** (59.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3au** (53.0 mg, 50%) as a white solid. **M.p.**: 177–179 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.17 (s, 1H), 6.53 (d, J = 1.4 Hz, 1H), 4.39 (d, J = 14.6 Hz, 1H), 4.25 (d, J = 14.6 Hz, 1H), 3.85 (dd, J = 7.6, 7.6 Hz, 1H), 3.65–3.60 (m, 2H), 3.47 (dd, J = 15.2, 13,2 Hz,, 1H), 3.31 (t, J = 9.3 Hz, 1H), 2.43 (s, 3H), 1.27–1.22 (m, 3H), 1.08–1.03 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 142.6, 136.7, 133.6, 132.5, 128.4, 127.4, 123.0, 55.4, 54.2, 52.3, 39.3, 26.9, 21.5, 4.9, 4.9. **HR–MS** (ESI) *m/z* calc. for $C_{16}H_{20}NO_4S_2$ $[M+H]^+$: 354.0838, found: 354.0830.



3av

2-(Dodecylsulfonyl)-8-methyl-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3av)

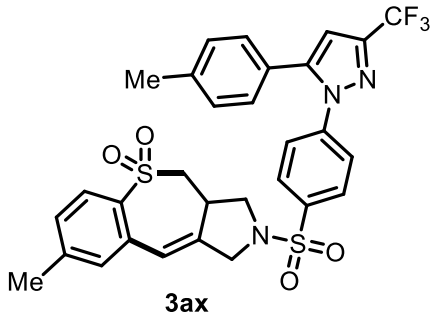
The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2v** (98.1 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3av** (71.1 mg, 49%) as a white solid. **M.p.**: 97–99 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.17 (s, 1H), 6.51 (s, 1H), 4.37 (d, J = 14.5 Hz, 1H), 4.22 (d, J = 14.5 Hz, 1H), 3.85 (dd, J = 7.6, 7.6 Hz, 1H), 3.64–3.57 (m, 2H), 3.43 (dd, J = 15.2, 12.8 Hz, 1H), 3.29 (t, J = 9.5 Hz, 1H), 3.04 (dd, J = 9.4, 6.5 Hz, 2H), 2.43 (s, 3H), 1.87–1.81 (m, 2H), 1.45–1.40 (m, 2H), 1.27 (s, 16H), 0.88 (t, J = 6.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 142.5, 136.8, 133.7, 132.3, 128.4, 127.4, 123.0, 54.8, 54.1, 52.1, 50.8, 39.5, 32.0, 29.7, 29.6, 29.4, 29.2, 28.5, 23.4, 22.8, 21.4, 14.2. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{38}NO_4S_2$ $[M+H]^+$: 482.2394, found: 482.2392.



3aw

8-Methyl-2-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3aw)

The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2w** (117.6 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3aw** (86.8 mg, 53%) as a yellow solid. **M.p.**: 207–209 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.38–7.35 (m, 7H), 7.23 (d, J = 8.1 Hz, 1H), 7.12 (s, 1H), 6.46 (d, J = 1.5 Hz, 1H), 4.26 (d, J = 14.6 Hz, 1H), 4.12 (d, J = 14.6 Hz, 1H), 3.80 (dd, J = 9.6, 7.4 Hz, 1H), 3.55 (dd, J = 12.7, 3.5 Hz, 1H), 3.40–3.30 (m, 2H), 3.17 (t, J = 9.3 Hz, 1H), 2.51 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 161.2, 144.7, 142.0, 136.6, 136.0, 135.4, 133.5, 132.3, 130.6, 129.9, 128.8, 128.6, 128.5, 128.4, 128.1, 127.4, 123.2, 114.4, 55.4, 54.2, 52.3, 38.9, 21.4, 11.9. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{27}N_2O_5S_2$ $[M+H]^+$: 547.1356, found: 547.1353.

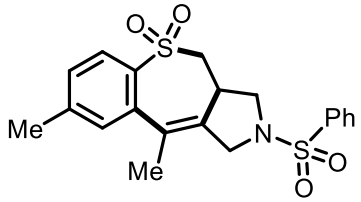


3ax

8-Methyl-2-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ax)

The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2x** (137.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ax** (110.3 mg, 60%) as a yellow solid. **M.p.**: 77–79 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 7.22–7.17 (m, 3H), 7.12 (d, J = 8.4 Hz, 3H), 6.76 (s, 1H), 6.42 (d, J = 1.7 Hz, 1H), 4.24 (d, J = 14.6 Hz, 1H), 4.03 (d, J = 14.6 Hz, 1H), 3.74 (dd, J = 9.2, 7.6 Hz, 1H), 3.54 (dd, J = 13.5, 4.6 Hz, 1H), 3.48–3.43 (m, 1H),

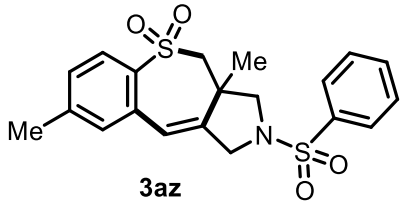
3.33 (dd, *J* = 13.4, 11.8 Hz, 1H), 3.06 (t, *J* = 9.2 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.5, 144.7, 143.2, 141.5, 140.0, 136.7, 135.2, 133.6, 132.2, 129.9, 128.8, 128.8, 128.5, 127.4, 125.8, 125.7, 123.4, 121.1 (q, *J* = 270.7 Hz), 106.5, 55.2, 54.1, 52.3, 39.0, 27.0, 21.4. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –62.45. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{27}F_3N_3O_4S_2$ $[M+H]^+$: 614,1392, found: 614.1390.



3ay

8,10-Dimethyl-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ay)

The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2y** (74.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ay** (48.4 mg, 40%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.11 (s, 1H), 4.36 (d, *J* = 14.6 Hz, 1H), 3.77(dd, *J* = 8.4, 6.0 Hz, 1H), 3.75 (d, *J* = 6.9 Hz, 1H), 3.67 (d, *J* = 14.8 Hz, 1H), 3.31 (d, *J* = 9.4 Hz, 1H), 3.03 (d, *J* = 9.4 Hz, 1H), 2.45 (s, 1H), 2.42 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 141.8, 135.0, 133.4, 130.0, 129.9, 129.4, 128.8, 128.3, 128.2, 128.0, 126.9, 68.4, 52.1, 50.7, 37.8, 21.7, 19.5. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{22}NO_4S_2$ $[M+H]^+$: 404.0985, found: 404.0982.

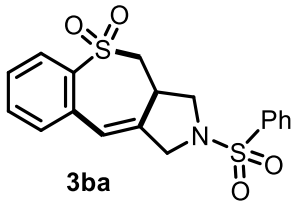


3az

3a,8-Dimethyl-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3az)

The general procedure (A) was followed using **1a** (107 mg, 0.60 mmol), **2z** (74.7 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3az** (50.8 mg, 42%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.06 (s, 1H), 6.39 (s, 1H), 4.27 (d, *J* = 14.2 Hz, 1H), 3.98 (d, *J* = 14.3 Hz, 1H), 3.62 (q, *J* = 11.5 Hz,

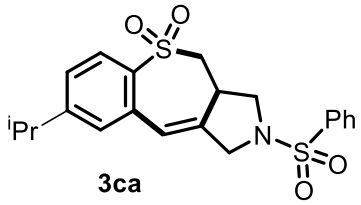
2H), 3.37 (q, *J* = 8.9 Hz, 2H), 2.41 (s, 3H), 1.22 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 146.7, 144.9, 136.2, 135.6, 134.1, 133.4, 131.4, 129.4, 128.2, 127.8, 128.7, 121.3, 67.4, 60.8, 53.9, 42.9, 26.5, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{20}H_{22}NO_4S_2$ $[M+H]^+$: 404.0985, found: 404.0986.



3ba

2-(Phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ba)

The general procedure (A) was followed using **1b** (98.4 mg, 0.60 mmol), **2a** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ba** (66.4 mg, 59%) as a white solid. **M.p.**: 139–141 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.13 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.60 (dd, *J* = 7.6, 7.6 Hz, 3H), 7.43 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 1.3 Hz, 1H), 4.24 (d, *J* = 14.9 Hz, 1H), 4.09 (d, *J* = 14.6 Hz, 1H), 3.76 (dd, *J* = 9.2, 7.5 Hz, 1H), 3.58 (dd, *J* = 12.9, 3.8 Hz, 1H), 3.44–3.35 (m, 2H), 3.11 (t, *J* = 9.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 142.3, 139.3, 135.8, 133.8, 133.5, 132.9, 132.6, 129.5, 127.8, 127.8, 127.3, 123.1, 55.6, 54.1, 52.3, 38.8. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{18}NO_4S_2$ $[M+H]^+$: 376.0672, found: 376.0673.

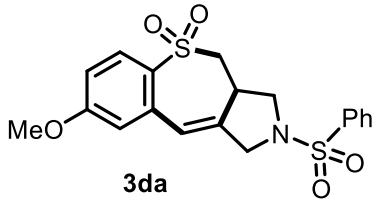


3ca

8-Isopropyl-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ca)

The general procedure (A) was followed using **1c** (123.6 mg, 0.60 mmol), **2a** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ca** (87.6 mg, 70%) as a white solid. **M.p.**: 160–162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.03 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 9.2 Hz, 1H), 7.13 (s, 1H), 6.48 (d, *J* = 1.2 Hz, 1H), 4.23 (d, *J* = 14.5 Hz, 1H), 4.08 (d, *J* =

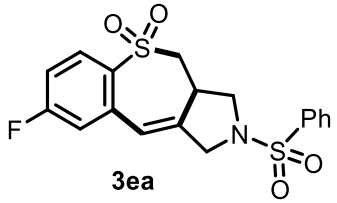
14.5 Hz, 1H), 3.74 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.56 (dd, *J* = 13.1, 4.0 Hz, 1H), 3.44–3.32 (m, 2H), 3.09 (t, *J* = 9.0 Hz, 1H), 2.98–2.91 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 155.3, 141.9, 136.8, 135.8, 133.4, 132.6, 131.1, 129.5, 127.7, 127.5, 125.9, 123.3, 55.8, 54.1, 52.3, 38.8, 34.1, 23.6, 23.6. **HR–MS** (ESI) *m/z* calc. for $C_{21}H_{24}NO_4S_2$ $[M+H]^+$: 418.1141, found: 418.1142.



3da

8-Methoxy-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3da)

The general procedure (A) was followed using **1d** (116.4 mg, 0.60 mmol), **2a** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3da** (79.0 mg, 65%) as a white solid. **M.p.**: 152–154 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.05 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 6.44 (d, *J* = 1.2 Hz, 1H), 4.20 (d, *J* = 14.7 Hz, 1H), 4.09 (d, *J* = 14.6 Hz, 1H), 3.86 (s, 3H), 3.71 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.57 (d, *J* = 8.9 Hz, 1H), 3.40–3.34 (m, 2H), 3.12 (t, *J* = 8.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 163.5, 142.6, 135.8, 135.0, 133.5, 131.3, 129.8, 129.5, 127.8, 123.1, 118.3, 112.2, 56.9, 55.8, 54.0, 52.3, 38.8. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{20}NO_5S_2$ $[M+H]^+$: 406.0778, found: 406.0777.

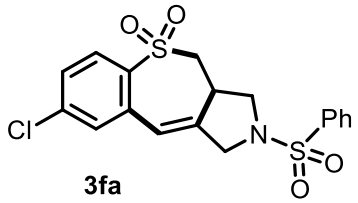


3ea

8-Fluoro-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ea)

The general procedure (A) was followed using **1e** (109.2 mg, 0.60 mmol), **2a** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ea** (67.2 mg, 57%) as a white solid. **M.p.**: 160–162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.15 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.14–7.09

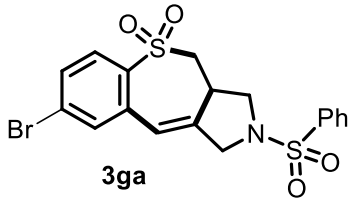
(m, 1H), 7.00 (dd, *J* = 9.3, 2.5 Hz, 1H), 6.45 (d, *J* = 1.4 Hz, 1H), 4.23 (d, *J* = 14.9 Hz, 1H), 4.11 (d, *J* = 14.9 Hz, 1H), 3.74 (dd, *J* = 9.5, 7.3 Hz, 1H), 3.61 (d, *J* = 9.0 Hz, 1H), 3.45–3.37 (m, 2H), 3.12 (t, *J* = 8.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 165.5 (d, *J* = 256.5 Hz), 144.1, 136.0 (d, *J* = 9.1 Hz), 135.8, 133.6, 130.5 (d, *J* = 9.8 Hz), 129.6, 128.2, 127.8, 122.2, 119.3 (d, *J* = 23.2 Hz), 114.8 (d, *J* = 22.2 Hz), 56.4, 54.0, 52.2, 38.9. **^{19}F NMR** (377 MHz, $CDCl_3$) *δ* –104.31. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{17}FNO_4S_2$ $[M+H]^+$: 354.0578, found: 354.0576.



3fa

8-Chloro-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3fa)

The general procedure (A) was followed using **1f** (118.8 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3fa** (62.6 mg, 51%) as a yellow solid. **M.p.**: 182–184 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 8.07 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.40 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 6.43 (d, *J* = 1.7 Hz, 1H), 4.24 (d, *J* = 14.8 Hz, 1H), 4.10 (d, *J* = 14.8 Hz, 1H), 3.75 (dd, *J* = 9.5, 7.6 Hz, 1H), 3.59 (dd, *J* = 13.5, 4.2 Hz, 1H), 3.47–3.39 (m, 2H), 3.13 (t, *J* = 9.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 144.2, 140.2, 137.8, 135.8, 134.5, 133.6, 132.4, 129.6, 129.0, 127.8, 122.1, 56.1, 54.1, 52.2, 38.9. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{17}ClNO_4S_2$ $[M+H]^+$: 410.0282, found: 410.0264.

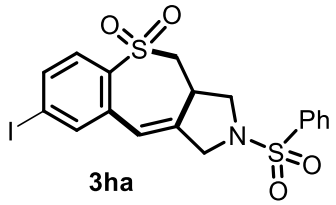


3ga

8-Bromo-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ga)

The general procedure (A) was followed using **1g** (145.2 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ga** (88.3 mg, 65%) as a yellow

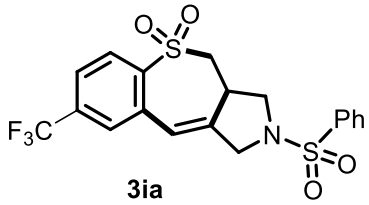
solid. **M.p.**: 212–214 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 7.1 Hz, 1H), 7.60 (dd, J = 7.5, 7.5 Hz, 2H), 7.56 (d, J = 8.5 Hz, 1H), 7.46 (s, 1H), 6.42 (s, 1H), 4.24 (d, J = 14.9 Hz, 1H), 4.10 (d, J = 14.9 Hz, 1H), 3.75 (dd, J = 9.2, 7.5 Hz, 1H), 3.59 (dd, J = 12.9, 3.7 Hz, 1H), 3.46–3.34 (m, 2H), 3.12 (t, J = 8.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.2, 138.2, 135.8, 135.3, 134.5, 133.6, 130.8, 129.56, 129.0, 128.6, 127.8, 122.0, 56.0, 54.1, 52.2, 38.9. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{17}BrNO_4S_2$ $[M+H]^+$: 453.9777, found: 453.9774.



3ha

8-Iodo-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ha)

The general procedure (A) was followed using **1h** (174.0 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ha** (61.6 mg, 41%) as a yellow solid. **M.p.**: 176–178 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H), 7.81 (dd, J = 8.4, 8.4 Hz, 2H), 7.67 (d, J = 6.9 Hz, 2H), 7.61 (dd, J = 8.4, 1.6 Hz, 2H), 7.70–7.66 (m, 2H), 7.62–7.58 (m, 2H), 6.39 (d, J = 2.0 Hz, 1H), 4.24 (dt, J = 14.8, 1.6 Hz, 1H). 4.09 (dt, J = 14.8, 1.6 Hz, 1H), 3.75 (dd, J = 9.5, 7.4 Hz, 1H), 3.58 (dd, J = 13.1, 3.9 Hz, 1H), 3.47–3.34 (m, 2H), 3.11 (t, J = =9.6 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.0, 141.3, 139.0, 138.9, 136.8, 134.1, 133.6, 129.6, 128.6, 127.8, 121.9, 101.2, 56.0, 54.1, 52.2, 38.9. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{17}INO_4S_2$ $[M+H]^+$: 501.9638, found: 501.9633.

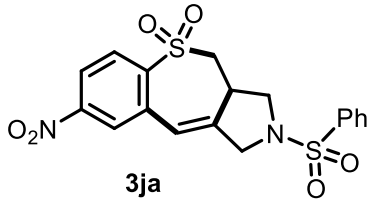


3ia

2-(Phenylsulfonyl)-8-(trifluoromethyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ia)

The general procedure (A) was followed using **1i** (139.2 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ia** (81.1 mg, 61%) as a white

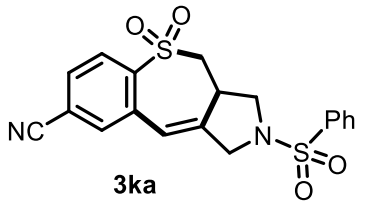
solid. **M.p.**: 198–200 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.4 Hz, 2H), 7.68 (dd, J = 7.7, 5.4 Hz, 2H), 7.61 (dd, J = 7.5, 7.5 Hz, 2H), 7.56 (s, 1H), 6.55 (d, J = 1.5 Hz, 1H), 4.27 (d, J = 15.0 Hz, 1H), 4.12 (d, J = 15.0 Hz, 1H), 3.78 (dd, J = 9.4, 7.4 Hz, 1H), 3.63 (dd, J = 12.9, 3.5 Hz, 1H), 3.49–3.38(m, 2H), 3.13 (t, J = 9.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 142.5, 135.8, 135.5, 133.7, 133.6, 129.6, 129.5, 128.3, 127.8, 124.5 (q, J = 3.0 Hz), 122.2, 55.7, 54.1, 52.2, 38.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –63.45. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{17}F_3NO_4S_2$ $[M+H]^+$: 444.0546, found: 444.0543.



3ja

8-Nitro-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ja)

The general procedure (A) was followed using **1j** (125.4 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ja** (50.4 mg, 40%) as a white solid. **M.p.**: 231–233 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.33 (d, J = 2.0 Hz, 1H), 8.26 (dd, J = 8.7, 2.0 Hz, 1H), 8.21 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.75 (dd, J = 7.3, 7.3 Hz, 1H), 7.67 (dd, J = 7.5, 7.5 Hz, 2H), 6.85 (s, 1H), 4.30 (d, J = 15.4 Hz, 1H), 3.99 (d, J = 15.4 Hz, 1H), 3.91–3.83 (m, 2H), 3.76 (dd, J = 14.8, 12.1 Hz, 1H), 3.29–3.21 (m, 1H), 3.00 (t, J = 10.0 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO) δ 150.7, 146.0, 144.8, 135.8, 134.2, 134.0, 130.1, 128.5, 128.1, 128.0, 122.5, 121.4, 54.5, 52.1, 51.5, 39.3. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{17}N_2O_6S_2$ $[M+H]^+$: 421.0523, found: 421.0515.

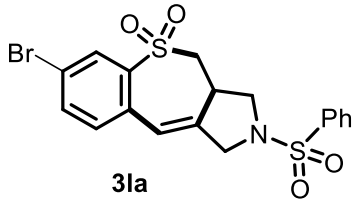


3ka

2-(Phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole-8-carbonitrile 5,5-dioxide (3ka)

The general procedure (A) was followed using **1k** (113.4 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography

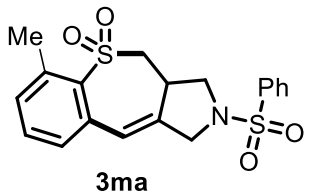
on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ka** (54.0 mg, 45%) as a white solid. **M.p.**: 215–217 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (d, J = 8.1 Hz, 1H), 7.88 (dd, J = 8.4, 1.2 Hz, 2H), 7.71 (dd, J = 8.2, 1.5 Hz, 1H), 7.68 (dd, J = 2.5, 1.6 Hz, 1H), 7.63–7.59 (m, 3H), 6.49 (d, J = 2.0 Hz, 1H), 4.27 (dt, J = 15.0, 1.2 Hz, 1H), 4.13 (dt, J = 15.1, 1.6 Hz, 1H), 3.77 (dd, J = 9.5, 7.5 Hz, 1H), 3.64 (dd, J = 13.6, 4.1 Hz, 1H), 3.49–3.40 (m, 2H), 3.14 (t, J = 9.0 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO) δ 145.9, 143.6, 137.2, 135.7, 134.0, 133.4, 131.4, 130.1, 128.0, 127.4, 121.1, 117.7, 116.6, 54.6, 52.2, 51.6, 39.3. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{17}N_2O_4S_2$ $[M+H]^+$: 401.0624, found: 401.0601.



3la

7-Bromo-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3la)

The general procedure (A) was followed using **1l** (145.2 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3la** (58.4 mg, 43%) as a white solid. **M.p.**: 62–64 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (dd, J = 7.9, 0.9 Hz, 1H), 7.88 (dd, J = 8.3, 1.1 Hz, 2H), 7.84 (dd, J = 8.0, 1.1 Hz, 1H), 7.71–7.68 (m, 1H), 7.62 (dd, J = 7.7, 7.7 Hz, 2H), 7.30 (dd, J = 7.8, 7.8 Hz, 1H), 6.73 (d, J = 2.0 Hz, 1H), 4.37 (dt, J = 15.0, 1.8 Hz, 1H), 3.95 (dd, J = 15.4, 2.4 Hz, 1H), 3.92 (dd, J = 13.8, 6.6 Hz, 1H), 3.78 (dd, J = 13.8, 11.4 Hz, 1H), 3.30 (d, J = 1.5 Hz, 1H), 3.29 (s, 1H), 3.25–3.21 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 140.5, 138. 2, 135.8, 135.1, 133.6, 129.6, 128.7, 128.0, 127.7, 125.3, 123.1, 66.5, 52.4, 52.3, 37.1. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{17}BrNO_4S_2$ $[M+H]^+$: 453.9777, found: 453.9782.

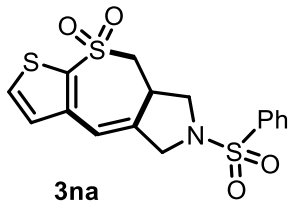


3ma

6-Methyl-2-(phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-benzo[6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3ma)

The general procedure (A) was followed using **1m** (106.8 mg, 0.60 mmol), **2b** (70.5

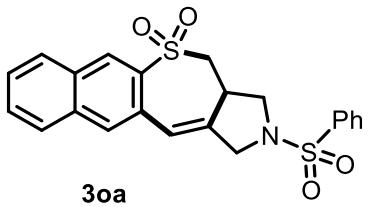
mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3ma** (70.0 mg, 60%) as a pink solid. **M.p.**: 149–151 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 7.9 Hz, 2H), 7.66 (d, J = 6.7 Hz, 1H), 7.61 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 8.1 Hz, 1H), 7.10 (s, 1H), 6.44 (s, 1H), 4.24 (d, J = 14.5 Hz, 1H), 4.08 (d, J = 14.4 Hz, 1H), 3.77 (dd, J = 9.2, 7.6 Hz, 1H), 3.55 (dd, J = 13.2, 4.2 Hz, 1H), 3.45–3.32 (m, 2H), 3.11 (t, J = 9.1 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.7, 142.1, 136.6, 133.5, 133.5, 132.5, 129.5, 128.4, 127.9, 127.8, 127.5, 123.2, 55.8, 54.2, 52.3, 38.9, 21.5. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{20}NO_4S_2$ $[M+H]^+$: 390.0828, found: 390.0836.



3na

6-(Phenylsulfonyl)-6,7,7a,8-tetrahydro-5*H*-thieno[3',2':6,7]thiepino[3,4-*c*]pyrrole 9,9-dioxide (3na)

The general procedure (A) was followed using **1n** (102.0 mg, 0.60 mmol), **2b** (70.5 mg, 0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3na** (44.6 mg, 39%) as a yellow solid. **M.p.**: 180–182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.3 Hz, 2H), 7.67 (d, J = 7.3 Hz, 1H), 7.61 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 5.0 Hz, 1H), 6.95 (d, J = 5.0 Hz, 1H), 6.50 (d, J = 2.1 Hz, 1H), 4.33 (dt, J = 15.0, 1.7 Hz, 1H), 3.99 (dt, J = 15.0, 2.0 Hz, 1H), 3.95(t, J = 9.2 Hz, 1H), 3.60–3.55 (m, 1H), 3.40 (dd, J = 14.4, 3.8 Hz, 1H), 3.30 (t, J = 12.8 Hz, 1H), 3.03 (t, J = 10.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.3, 137.9, 136.2, 135.9, 133.6, 131.6, 129.8, 129.6, 127.8, 116.8, 54.2, 52.6, 52.1, 39.2. **HR–MS** (ESI) *m/z* calc. for $C_{16}H_{16}NO_4S_3$ $[M+H]^+$: 382.0236, found: 382.0230.

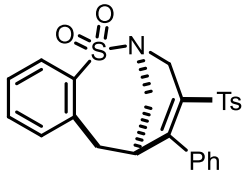


3oa

2-(Phenylsulfonyl)-2,3,3a,4-tetrahydro-1*H*-naphtho[2',3':6,7]thiepino[3,4-*c*]pyrrole 5,5-dioxide (3oa)

The general procedure (A) was followed using **1o** (128.4 mg, 0.60 mmol), **2b** (70.5 mg,

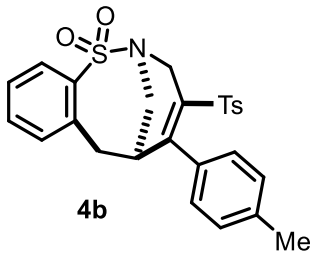
0.3 mmol) and Na_2CO_3 (31.8 mg, 0.30 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **3oa** (81.6 mg, 64%) as a yellow solid. **M.p.**: 93–95 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.93 (dd, J = 6,0, 6.0 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.68 (dd, J = 14.5, 7.3 Hz, 2H), 7.62 (d, J = 7.4 Hz, 3H), 7.21 (s, 1H), 4.48 (d, J = 14.9 Hz, 1H), 4.03 (dd, J = 13.8, 6.3 Hz, 2H), 3.86 (dd, J = 7.6, 7.6 Hz, 1H), 3.31–3.25 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 136.1, 135.5, 135.2, 133.6, 131.2, 129.5, 129.1, 128.8, 128.4, 128.0, 127.9, 127.4, 125.3, 122.9, 120.4, 68.9, 52.4, 52.3, 37.3. **HR–MS** (ESI) *m/z* calc. for $C_{22}H_{20}NO_4S_2$ $[M+H]^+$: 426.0828, found: 426.0831.



4a

5-Phenyl-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4a)

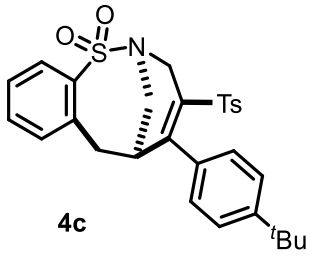
The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2a'** (93.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4a** (39.1 mg, 28%) as a yellow solid. **M.p.**: 108–110 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (dd, J = 7.7, 1.1 Hz, 1H), 7.49–7.46 (m, 1H), 7.38 (dd, J = 7.6, 7.6 Hz, 1H), 7.32 (dd, J = 7.4, 7.4 Hz, 1H), 7.23 (dd, J = 7.8, 7.8 Hz, 2H), 7.03 (s, 4H), 7.00 (d, J = 7.5 Hz, 1H), 6.68 (s, 2H), 4.47 (s, 1H), 4.44 (d, J = 5.5 Hz, 1H), 4.29 (dd, J = 19.7, 2.0 Hz, 1H), 3.61 (d, J = 14.9 Hz, 1H), 3.48 (d, J = 15.4 Hz, 1H), 2.91–2.85 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.6, 144.1, 139.7, 137.5, 136.7, 135.2, 134.8, 133.5, 132.7, 129.7, 129.4, 128.6, 127.8, 127.4, 127.3, 50.0, 45.6, 38.9, 38.6, 21.6. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{24}NO_4S_2$ $[M+H]^+$: 466.1141, found: 466.1144.



4b

5-(*p*-Tolyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4b)

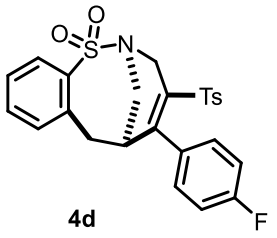
The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2b'** (97.5 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4b** (34.5 mg, 24%) as a yellow solid. **M.p.**: 193–195 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (d, J = 7.7 Hz, 1H), 7.47–7.44 (m, 1H), 7.37 (dd, J = 7.6, 7.6 Hz, 1H), 7.09 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 7.9 Hz, 4H), 6.98 (d, J = 7.5 Hz, 1H), 6.59 (s, 2H), 4.45 (d, J = 14.4 Hz, 1H), 4.42 (d, J = 16.8 Hz, 1H), 4.26 (dd, J = 19.5, 1.9 Hz, 1H), 3.61 (d, J = 14.7 Hz, 1H), 3.46 (dd, J = 14.4, 1.2 Hz, 1H), 2.91–2.85 (m, 2H), 2.39 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 149.8, 144.1, 139.8, 138.7, 137.7, 135.2, 134.5, 133.9, 133.5, 132.7, 129.7, 129.3, 128.5, 127.4, 127.4, 50.1, 45.8, 39.0, 38.7, 21.7, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{26}NO_4S_2$ $[M+H]^+$: 480.1298, found: 480.1303.



4c

5-(4-(Tert-butyl)phenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4c)

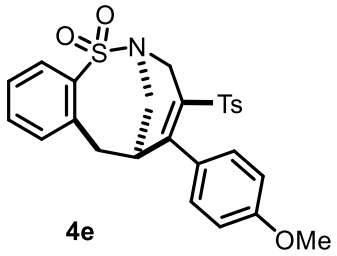
The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2c'** (110.1 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4c** (34.4 mg, 22%) as a white solid. **M.p.**: 221–223 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.7, 1.3 Hz, 1H), 7.52–7.48 (m, 1H), 7.42 (dd, J = 7.5, 7.5 Hz, 1H), 7.19 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 7.4 Hz, 1H), 6.97 (s, 4H), 6.57 (d, J = 8.2 Hz, 2H), 4.51 (d, J = 7.8 Hz, 1H), 4.47 (s, 1H), 4.32 (dd, J = 19.6, 2.2 Hz, 1H), 3.63 (d, J = 15.4 Hz, 1H), 3.49 (dd, J = 14.4, 1.7 Hz, 1H), 2.92 (dd, J = 14.9, 6.5 Hz, 1H), 2.83 (d, J = 5.8 Hz, 1H), 2.35 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8, 149.6, 143.7, 139.8, 137.7, 135.3, 135.1, 133.6, 133.5, 132.8, 129.9, 129.2, 128.0, 127.5, 127.3, 124.7, 50.1, 45.6, 39.0, 38.5, 34.7, 31.4, 21.6. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{32}NO_4S_2$ $[M+H]^+$: 522.1767, found: 522.1771.



4d

5-(4-Fluorophenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4d)

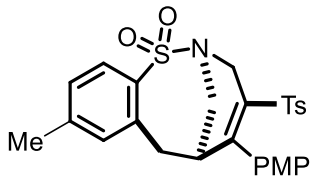
The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2d'** (98.7 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4d** (40.6 mg, 28%) as a yellow solid. **M.p.**: 180–182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.7, 1.2 Hz, 1H), 7.50–7.46 (m, 1H), 7.40 (dd, J = 7.6, 7.6 Hz, 1H), 7.08 (s, 4H), 6.98–6.91 (m, 3H), 6.68 (s, 2H), 4.48 (d, J = 7.7 Hz, 1H), 4.44 (d, J = 12.8 Hz, 1H), 4.26 (dd, J = 19.7, 2.0 Hz, 1H), 3.65 (d, J = 14.6 Hz, 1H), 3.47 (dd, J = 14.5, 1.2 Hz, 1H), 2.90–2.82 (m, 2H), 2.40 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.9 (d, J = 249.2 Hz), 148.5, 144.4, 139.9, 137.5, 135.7, 135.0, 133.3, 132.8, 132.6, 129.9, 129.5, 127.6, 127.3, 115.0 (d, J= 25.7 Hz), 50.0, 45.8, 39.0, 38.7, 21.7. **^{19}F NMR** (377 MHz, $CDCl_3$) δ –112.08. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{23}FNO_4S_2$ $[M+H]^+$: 484.1047, found: 484.1045.



4e

5-(4-Methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4e)

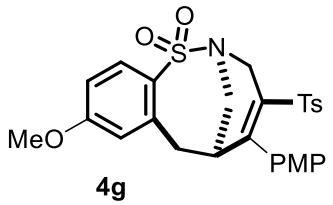
The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2e'** (102.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4e** (81.7 mg, 55%) as a white solid. **M.p.**: 128–130 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.7, 1.4 Hz, 1H), 7.48–7.44 (m, 1H), 7.39 (dd, J = 7.2, 7.2 Hz, 1H), 7.07 (dd, J = 8.5, 8.5 Hz, 4H), 6.95 (d, J = 7.3 Hz, 1H), 6.76 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 8.3 Hz, 2H), 4.48–4.42 (m, 2H), 4.25 (dd, J = 19.5, 1.7 Hz, 1H), 3.85 (s, 3H), 3.62 (q, J = 5.0 Hz, 1H), 3.45 (dt, J = 14.0, 2.0 Hz, 1H), 2.90–2.85 (m, 2H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.0, 149.6, 144.0, 139.9, 137.8, 135.2, 134.8, 133.5, 132.7, 129.8, 129.4, 128.7, 127.5, 127.4, 113.3, 55.4, 50.1, 45.9, 39.1, 38.7, 21.7. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{26}NO_5S_2$ $[M+H]^+$: 496.1247, found: 496.1266.



4f

5-(4-Methoxyphenyl)-9-methyl-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4f)

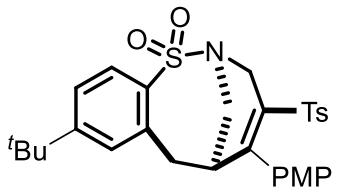
The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2f'** (107.1 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4f** (76.4 mg, 50%) as a white solid. **M.p.**: 212–214 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, J = 7.9 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 6.76 (d, J = 8.9 Hz, 2H), 6.70 (s, 1H), 6.60 (d, J = 4.8 Hz, 2H), 4.45 (s, 1H), 4.42 (d, J = 4.9 Hz, 1H), 4.23 (dd, J = 19.7, 2.2 Hz, 1H), 3.85 (s, 3H), 3.58 (d, J = 15.1 Hz, 1H), 3.43 (dd, J = 14.1, 1.7 Hz, 1H), 2.83 (d, J = 6.5 Hz, 1H), 2.77 (dd, J = 14.7, 6.5 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.0, 149.6, 144.0, 143.2, 138.0, 136.9, 135.0, 134.8, 134.4, 131.5, 129.8, 129.3, 128.7, 127.8, 127.4, 113.2, 55.4, 50.1, 45.9, 39.0, 38.6, 21.6, 21.4. **HR–MS** (ESI) *m/z* calc. for $C_{27}H_{28}NO_5S_2$ $[M+H]^+$: 510.1404, found: 510.1413.



4g

9-Methoxy-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4g)

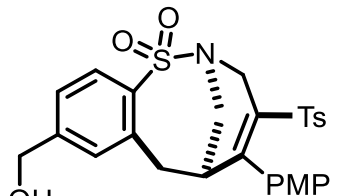
The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2g'** (111.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4g** (75.6 mg, 48%) as a yellow solid. **M.p.**: 95–97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.7 Hz, 1H), 7.12–7.06 (m, 4H), 6.83 (dd, J = 8.7, 2.4 Hz, 1H), 6.77 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.5 Hz, 2H), 6.43 (d, J = 2.4 Hz, 1H), 4.43 (d, J = 18.0 Hz, 2H), 4.22 (dd, J = 19.7, 1.9 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.59 (d, J = 14.4 Hz, 1H), 3.42 (d, J = 13.0 Hz, 1H), 2.83–2.75 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.6, 160.1, 149.5, 144.0, 138.0, 137.3, 135.0, 132.0, 131.5, 129.3, 128.8, 127.4, 119.7, 114.9, 113.3, 111.3, 55.7, 55.5, 50.1, 45.9, 39.2, 38.8, 21.7. **HR–MS** (ESI) *m/z* calc. for $C_{27}H_{28}NO_6S_2$ $[M+H]^+$: 526.1353, found: 526.1352.



4h

9-(Tert-butyl)-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4h)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2h'** (119.1 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4h** (106.3 mg, 61%) as a yellow solid. **M.p.**: 83–85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 1H), 7.31 (dd, J = 8.2, 1.7 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 1.2 Hz, 1H), 6.73 (d, J = 7.7 Hz, 2H), 6.56 (s, 2H), 4.46 (d, J = 11.5 Hz, 1H), 4.43 (s, 1H), 4.30 (dd, J = 19.6, 2.1 Hz, 1H), 3.83 (s, 3H), 3.59 (d, J = 15.1 Hz, 1H), 3.46 (dd, J = 14.3, 2.3 Hz, 1H), 2.89 (d, J = 6.5 Hz, 1H), 2.80 (dd, J = 15.1, 6.8 Hz, 1H), 2.39 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.0, 156.0, 150.1, 144.0, 138.2, 136.8, 134.6, 134.6, 131.2, 129.6, 129.4, 128.8, 127.3, 123.9, 113.2, 55.4, 50.1, 46.1, 39.5, 38.8, 35.0, 31.0, 21.7. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{34}NO_5S_2$ $[M+H]^+$: 552.1873, found: 582.1874.

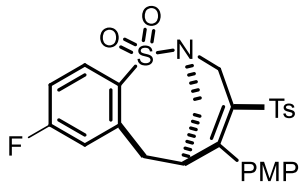


4i

9-(Hydroxymethyl)-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4i)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2p'** (111.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 1:2) yielded **4i** (74.0 mg, 47%) as a white solid. **M.p.**: 58–60 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.10–7.04 (m, 4H), 6.92 (s, 1H), 6.74 (d, J = 8.3 Hz, 2H), 6.58 (d, J = 7.9 Hz, 2H), 4.70 (s, 2H), 4.47–4.37 (m, 2H), 4.22 (d, J = 19.5 Hz, 1H), 3.83 (s, 3H), 3.59 (d, J = 13.7 Hz, 1H), 3.43 (d, J = 14.2 Hz, 1H), 2.88–2.77 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.1, 149.7, 146.1, 144.2, 138.4, 137.6, 135.4, 134.6, 131.8, 129.9, 129.3, 128.5, 127.6, 127.4, 125.2, 113.3, 64.1, 55.5, 50.1, 45.8, 39.1, 38.5, 21.7. **HR–MS** (ESI) *m/z* calc. for

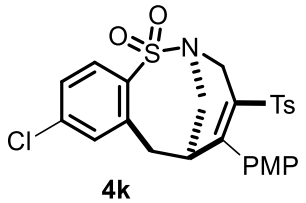
$C_{27}H_{28}NO_6S_2$ $[M+H]^+$: 526.1353, found: 526.1349.



4j

9-Fluoro-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4j)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2i'** (107.7 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4j** (61.6 mg, 40%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.6, 5.7 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 7.18 (dd, J = 6.8, 6.8 Hz, 1H), 7.09 (dd, J = 18.5, 8.3 Hz, 4H), 6.77 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.2 Hz, 2H), 4.46 (d, J = 6.8 Hz, 1H), 4.41 (s, 1H), 4.25 (dd, J = 19.6, 1.6 Hz, 1H), 3.84 (s, 3H), 3.59 (d, J = 14.5 Hz, 1H), 3.44 (d, J = 14.8 Hz, 1H), 2.85–2.77 (m, 2H), 2.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.5 (d, J = 255.2 Hz), 160.2, 149.1, 144.2, 138.60 (d, J = 8.7 Hz), 137.6, 135.9, 135.1, 132.45 (d, J = 9.6 Hz), 129.3, 128.4, 127.4, 120.6 (d, J = 22.7 Hz), 114.1 (d, J = 21.1 H)z, 113.4, 55.4, 50.0, 45.8, 39.0, 38.3, 21.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ –105.67. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}FNO_5S_2$ $[M+H]^+$: 513.1153, found: 514.1148.

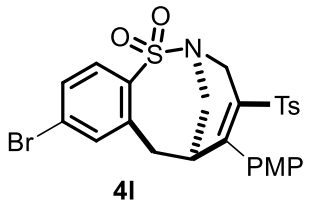


4k

9-Chloro-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4k)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2j'** (112.5 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4k** (76.2 mg, 48%) as a yellow oil. **H NMR** (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 1.9 Hz, 1H), 6.79 (d, J = 8.9 Hz, 2H), 6.61 (d, J = 5.9 Hz, 2H), 4.44 (d, J = 7.1 Hz, 1H), 4.41 (s, 1H), 4.26 (dd, J = 19.6, 2.3 Hz, 1H), 3.86 (s, 3H), 3.58 (d, J = 15.3 Hz, 1H), 3.46 (dd, J = 14.3, 1.8 Hz, 1H), 2.85 (d, J = 6.3 Hz, 1H), 2.78 (dd, J = 15.3, 7.0 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.2, 149.1,

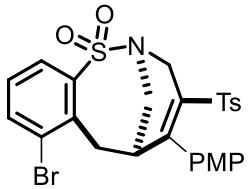
144.3, 138.7, 137.2, 135.0, 133.4, 131.1, 129.4, 128.4, 127.4, 127.4, 55.5, 50.1, 45.9, 38.9, 38.2, 21.7. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}ClNO_5S_2$ $[M+H]^+$: 530.0857, found: 530.0860.



4l

9-Bromo-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4l)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2k'** (125.7 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4l** (77.4 mg, 45%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 1H), 7.48 (dd, J = 8.3, 1.8 Hz, 1H), 7.16–7.10 (m, 4H), 7.05 (d, J = 1.8 Hz, 1H), 6.80 (d, J = 9.0 Hz, 2H), 6.61 (d, J = 7.7 Hz, 2H), 4.46–4.40 (m, 2H), 4.27 (dd, J = 19.8, 2.3 Hz, 1H), 3.86 (s, 3H), 3.58 (d, J = 15.3 Hz, 1H), 3.46 (dd, J = 14.2, 1.8 Hz, 1H), 2.86 (d, J = 6.7 Hz, 1H), 2.76 (dd, J = 15.4, 7.1 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 149.2, 144.3, 138.9, 137.7, 137.2, 136.4, 135.0, 132.8, 131.1, 130.4, 129.4, 128.3, 127.4, 127.2, 113.4, 55.5, 50.1, 45.9, 38.8, 38.1, 21.7. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}BrNO_5S_2$ $[M+H]^+$: 574.0352, found: 574.0363.

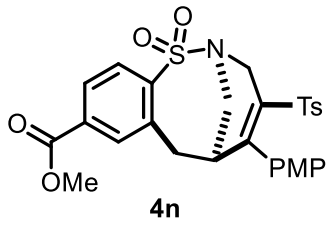


4m

8-Bromo-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4m)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2r'** (125.7 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4m** (73.9 mg, 43%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (dd, J = 7.8, 1.2 Hz, 1H), 7.74 (dd, J = 8.0, 1.3 Hz, 1H), 7.24 (dd, J = 7.9, 7.9 Hz, 1H), 7.14 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 8.9 Hz, 2H), 6.54 (d, J = 8.5 Hz, 2H), 4.55 (d, J = 19.6 Hz, 1H), 4.40 (d, J = 14.1 Hz, 1H), 4.24 (dd, J = 19.6, 2.5 Hz, 1H), 3.83 (s, 3H), 3.65 (dd, J = 16.1, 7.5 Hz, 1H), 3.46 (dd, J = 13.1, 3.3 Hz, 1H), 3.39 (d, J = 16.2 Hz, 1H), 3.01–2.97 (m, 1H), 2.37 (s, 3H). **^{13}C NMR** (151

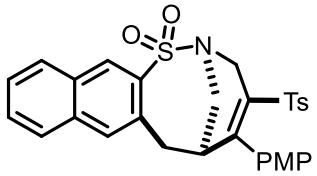
MHz, $CDCl_3$) δ 160.2, 149.4, 144.1, 142.0, 137.8, 137.6, 135.1, 135.0, 129.4, 129.3, 128.6, 128.3, 127.8, 127.5, 127.2, 113.5, 55.5, 50.6, 46.1, 38.7, 37.4, 21.7. **HR–MS** (ESI) *m/z* calc. for $C_{26}H_{25}BrNO_5S_2$ $[M+H]^+$: 574.0352, found: 574.0343.



4n

Methyl-5-(4-methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine-9-carboxylate 1,1-dioxide (4n)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2o'** (119.7 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4n** (79.6 mg, 48%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.98 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59 (s, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.55–6.53 (m, 2H), 4.45 (d, *J* = 3.5 Hz, 1H), 4.42 (d, *J* = 9.1 Hz, 1H), 4.27 (dd, *J* = 19.7, 2.2 Hz, 1H), 4.00 (s, 3H), 3.84 (s, 3H), 3.62 (d, *J* = 15.2 Hz, 1H), 3.47 (dd, *J* = 14.5, 1.8 Hz, 1H), 2.92 (dd, *J* = 15.0, 6.6 Hz, 1H), 2.86 (d, *J* = 6.2 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.5, 160.15, 149.4, 144.2, 143.7, 137.6, 135.6, 134.8, 134.4, 133.5, 129.9, 129.3, 128.7, 128.4, 128.3, 127.4, 113.2, 55.4, 52.8, 50.1, 45.8, 39.0, 38.3, 21.6. **HR–MS** (ESI) *m/z* calc. for $C_{28}H_{28}NO_7S_2$ $[M+H]^+$: 554.1302, found: 554.1311.

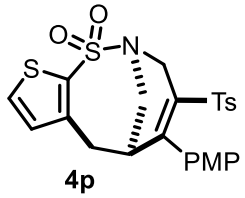


4o

5-(4-Methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanonaphtho[2,3-*h*][1,2]thiazonine 1,1-dioxide (4o)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2n'** (117.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4o** (115.5 mg, 70%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 12.9 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.58 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.36 (dd, *J* = 7.2, 7.2Hz, 1H), 7.14 (d, *J* = 11.0 Hz, 1H), 7.05–6.90 (m, 4H), 6.42 (d, *J* = 7.3 Hz, 2H), 6.06 (d, *J* = 2.5 Hz, 1H), 4.59–4.50 (m, 2H), 4.28 (dd, *J* = 19.6, 2.1 Hz, 1H), 3.95 (dd, *J* = 15.9, 7.6 Hz, 1H), 3.76

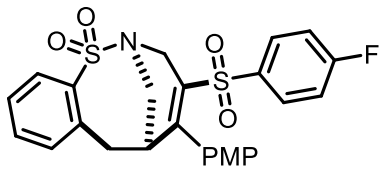
(s, 3H), 3.68 (d, *J* = 16.0 Hz, 1H), 3.50 (dd, *J* = 14.2, 2.7 Hz, 1H), 3.08 (d, *J* = 7.2 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 159.9, 149.5, 143.9, 138.3, 137.6, 135.6, 134.3, 134.1, 132.4, 129.2, 129.0, 128.3, 128.1, 128.0, 127.7, 127.2, 127.0, 125.2, 124.8, 112.9, 55.3, 50.7, 46.2, 38.3, 31.0, 21.6. **HR–MS** (ESI) *m/z* calc. for $C_{30}H_{28}NO_5S_2$ $[M+H]^+$: 546.1404, found: 546.1394.



4p

5-(4-Methoxyphenyl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanothieno[3,2-*h*][1,2]thiazonine 1,1-dioxide (4p)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2m'** (104.1 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4p** (58.6 mg, 39%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.41 (d, *J* = 4.9 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 4.9 Hz, 1H), 4.69 (d, *J* = 19.7 Hz, 1H), 4.51 (d, *J* = 14.8 Hz, 1H), 4.31 (dd, *J* = 19.6, 2.4 Hz, 1H), 3.84 (s, 3H), 3.58 (dd, *J* = 14.4 , 2.4 Hz, 1H), 3.19 (dd, *J* = 15.7, 1.8 Hz, 1H), 2.92 (dd, *J* = 15.2, 5.2 Hz, 1H), 2.72 (d, *J* = 2.3 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 156.0, 148.9, 144.2, 139.7, 137.9, 137.8, 135.2, 132.0, 129.6, 129.4, 128.5, 127.4, 113.3, 55.4, 49.7, 45.9, 37.1, 33.2, 21.7. **HR–MS** (ESI) *m/z* calc. for $C_{24}H_{24}NO_5S_3$ $[M+H]^+$: 502.0811, found: 502,0818.

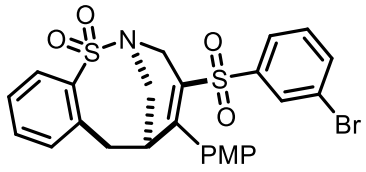


4q

4-((4-Fluorophenyl)sulfonyl)-5-(4-methoxyphenyl)-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4q)

The general procedure (B) was followed using **1e** (109.2 mg, 0.60 mmol), **2e'** (102.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4q** (77.8 mg, 52%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 8.04 (d, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.42 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.16 (dd, *J* = 8.7, 5.1 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.90 (dd, *J* = 8.5, 8.5 Hz, 2H),

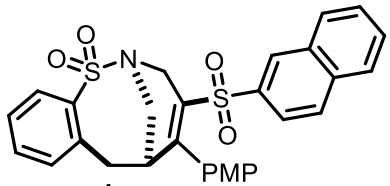
6.75 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 7.7 Hz, 2H), 4.48 (d, *J* = 14.0 Hz, 1H), 4.46 (d, *J* = 8.4 Hz, 1H), 4.31 (dd, *J* = 19.7, 1.0 Hz, 1H), 3.83 (s, 3H), 3.62 (d, *J* = 14.2 Hz, 1H), 3.47 (d, *J* = 14.3 Hz, 1H), 2.88–2.83 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 165.2 (d, *J* = 273.7 Hz), 160.1, 150.3, 139.8, 136.8 (d, *J* = 2.5 Hz), 135.1, 134.8, 133.5, 132.8, 130.05 (d, *J* = 9.6 Hz), 129.8, 128.3, 127.59, 115.7 (d, *J* = 22.7 Hz), 113.4, 55.4, 50.0, 45.7, 39.1, 38.5. **^{19}F NMR** (565 MHz, $CDCl_3$) *δ* –103.99. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{23}FNO_5S_2$ $[M+H]^+$: 500.0996, found: 500.1015.



4r

4-((3-Bromophenyl)sulfonyl)-5-(4-methoxyphenyl)-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4r)

The general procedure (B) was followed using **1l** (145.2 mg, 0.60 mmol), **2e'** (102.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4r** (80.5 mg, 48%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 8.06 (d, *J* = 7.6 Hz, 1H), 7.54–7.53 (m, 1H), 7.49–7.47 m, 1H), 7.44 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.17–7.12 (m, 3H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 7.9 Hz, 2H), 4.51 (d, *J* = 19.8 Hz, 1H), 4.47 (d, *J* = 14.3 Hz, 1H), 4.34 (dd, *J* = 19.7, 2.0 Hz, 1H), 3.85 (s, 3H), 3.63 (d, *J* = 14.6 Hz, 1H), 3.48 (d, *J* = 14.3 Hz, 1H), 2.89–2.83 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) *δ* 160.3, 150.8, 142.4, 139.7, 136.0, 135.0, 134.9, 133.4, 132.8, 130.6, 130.1, 129.8, 127.8, 127.7, 125.6, 122.5, 55.4, 50.0, 45.6, 39.1, 38.5. **HR–MS** (ESI) *m/z* calc. for $C_{25}H_{23}BrNO_5S_2$ $[M+H]^+$: 560.0196, found: 560.1292.

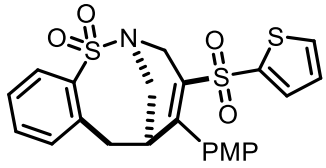


4s

5-(4-Methoxyphenyl)-4-(naphthalen-2-ylsulfonyl)-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4s)

The general procedure (B) was followed using **1o** (128.4 mg, 0.60 mmol), **2e'** (102.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4s** (66.9 mg, 42%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$)

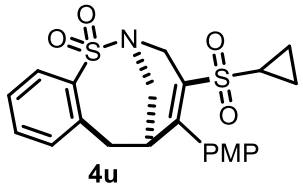
δ 8.02 (dd, J = 7.6, 0.9 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.65 (dd, J = 7.1, 7.1 Hz, 1H), 7.62 (s, 1H), 7.60–7.54 m, 2H), 7.42–7.39 (m, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.22 (dd, J = 8.6, 1.8 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.55 (s, 2H), 6.51 (d, J = 9.0 Hz, 1H), 4.58 (d, J = 19.7 Hz, 1H), 4.47 (d, J = 14.2 Hz, 1H), 4.38 (dd, J = 19.8, 2.2 Hz, 1H), 3.69 (s, 3H), 3.62 (d, J = 15.4 Hz, 1H), 3.47 (dd, J = 14.2, 1.6 Hz, 1H), 2.87–2.80 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.9, 149.9, 139.8, 137.1, 135.1, 135.1, 134.8, 133.4, 132.7, 131.8, 129.8, 129.7, 129.3, 129.2, 129.0, 128.3, 127.8, 127.5, 121.8, 113.1, 55.2, 50.1, 45.8, 39.1, 38.5. **HR–MS** (ESI) *m/z* calc. for $C_{29}H_{26}NO_5S_2$ $[M+H]^+$: 532.1247, found: 532.1253.



4t

5-(4-Methoxyphenyl)-4-(thiophen-2-ylsulfonyl)-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4t)

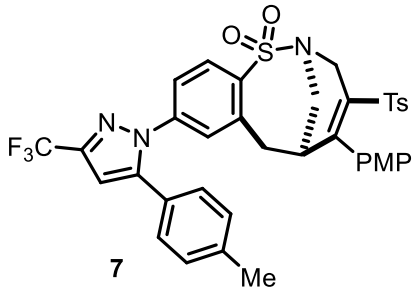
The general procedure (B) was followed using **1n** (102.0 mg, 0.60 mmol), **2e'** (102.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4t** (70.1 mg, 50%) as a yellow solid. **M.p.**: 202–204 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.97 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 4.8 Hz, 1H), 7.44 (dd, J = 7.4, 7.4 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 3.5 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H), 6.89 (dd, J = 4.2, 4.2 Hz, 1H), 6.83 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 0.6 Hz, 2H), 4.47 (d, J = 14.3 Hz, 1H), 4.43 (d, J = 19.7 Hz, 1H), 4.30 (dd, J = 19.4, 1.9 Hz, 1H), 3.85 (s, 3H), 3.63 (d, J = 15.1 Hz, 1H), 3.50 (d, J = 14.2 Hz, 1H), 2.92 (s, 1H), 2.87 (dd, J = 15.1, 6.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.1, 150.3, 141.6, 139.8, 135.1, 134.4, 134.0, 133.8, 133.5, 132.6, 129.7, 128.6, 127.5, 127.3, 113.4, 55.4, 50.1, 45.6, 39.2, 38.7. **HR–MS** (ESI) *m/z* calc. for $C_{23}H_{22}NO_5S_3$ $[M+H]^+$: 488.0655, found: 488.0673.



4u

4-(Cyclopropylsulfonyl)-5-(4-methoxyphenyl)-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (4u)

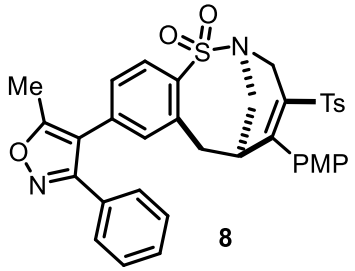
The general procedure (B) was followed using **1p** (76.8 mg, 0.60 mmol), **2e'** (102.3 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **4u** (41.4 mg, 31%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.11 (dd, J = 7.2, 0.6 Hz, 1H), 7.53–7.50 (m, 1H), 7.46 (dd J = 7.5, 7.5 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.90–6.89 (m, 4H), 4.52 (d, J = 14.3 Hz, 1H), 4.37 (d, J = 19.6 Hz, 1H), 4.21 (dd, J = 19.6, 2.3 Hz, 1H), 3.85 (s, 3H), 3.69 (d, J = 15.3 Hz, 1H), 3.53 (dd, J = 14.3, 1.7 Hz, 1H), 3.02 (d, J = 6.1 Hz, 1H), 2.94 (dd, J = 15.0, 6.6 Hz, 1H), 1.58–1.56 (m, 1H), 1.00–0.97 (m, 1H), 0.91–0.86 (m, 1H), 0.69–0.64 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.3, 148.3, 139.9, 135.3, 134.4, 133.6, 132.8, 129.8, 128.9, 127.9, 127.6, 113.7, 55.4, 50.2, 45.8, 39.2, 38.3, 32.0, 5.8, 5.4. **HR–MS** (ESI) *m/z* calc. for $C_{22}H_{24}NO_5S_2$ $[M+H]^+$: 446.1091, found: 446.1098.



7

5-(4-Methoxyphenyl)-9-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (7)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2q'** (169.5 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **7** (103.5 mg, 48%) as a white solid. **M.p.**: 150–152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 1H), 7.37 (d, J = 1.6 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.17–7.14 (m, 4H), 6.98 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.79 (s, 1H), 6.77 (dd, J = 8.4, 1.8 Hz, 1H), 6.71 (d, J = 8.8 Hz, 2H), 4.46 (d, J = 14.4 Hz, 1H), 4.36 (q, J = 19.6 Hz, 2H), 3.88 (s, 3H), 3.66 (d, J = 13.2 Hz, 1H), 3.50 (d, J = 14.3 Hz, 1H), 2.94–2.86 (m, 2H), 2.41 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 149.5, 145.2, 144.0, 141.9, 140.1, 138.8, 137.7, 137.4, 134.7, 130.0, 130.0, 129.9, 129.6, 129.3, 128.8, 128.7, 128.4, 128.3, 127.8, 127.5, 125.7, 122.8, 106.3, 55.3, 50.1, 45.8, 39.1, 38.3, 21.5, 21.4. **^{19}F NMR** (565 MHz, DMSO) δ –60.89. **HR–MS** (ESI) *m/z* calc. for $C_{37}H_{33}F_3N_3O_5S_2$ $[M+H]^+$: 720.1808, found: 720.1825.

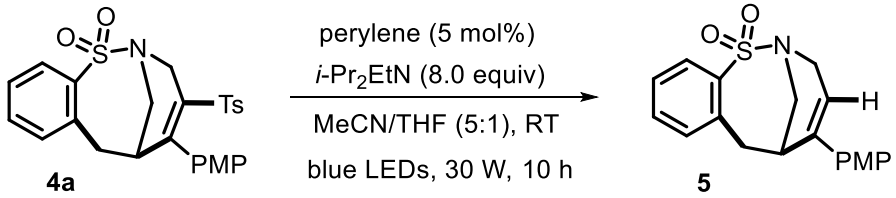


8

5-(4-Methoxyphenyl)-9-(5-methyl-3-phenylisoxazol-4-yl)-4-tosyl-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (8)

The general procedure (B) was followed using **1a** (107 mg, 0.60 mmol), **2r'** (149.4 mg, 0.3 mmol). Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) yielded **8** (56.7 mg, 29%) as a yellow solid. **M.p.**: 80–90 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 1H), 7.51 (dd, J = 7.8, 1.4 Hz, 2H), 7.48–7.43 (m, 3H), 7.27 (dd, J = 8.0, 0.9 Hz, 1H), 7.10 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.81 (s, 1H), 6.55 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 8.2 Hz, 2H), 4.55 (d, J = 19.6 Hz, 1H), 4.46 (d, J = 14.3 Hz, 1H), 4.22 (dd, J = 19.6, 2.0 Hz, 1H), 3.75 (s, 3H), 3.61 (d, J = 15.2 Hz, 1H), 3.44 (dd, J = 14.2, 1.7 Hz, 1H)., 2.84 (s, 1H), 2.79 (dd, J = 15.2, 6.7 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.5, 160.9, 160.1, 148.9, 144.1, 139.1, 137.4, 135.9, 135.7, 135.3, 134.5, 130.3, 130.0, 129.2, 129.2, 128.5, 128.3, 128.1, 127.4, 114.3, 113.1, 55.5, 49.9, 45.7, 39.3, 38.3, 21.6, 11.7. **HR–MS** (ESI) *m/z* calc. for $C_{36}H_{33}N_2O_6S_2$ $[M+H]^+$: 653.1775, found: 653.1784.

6. Derivatization of the products 4

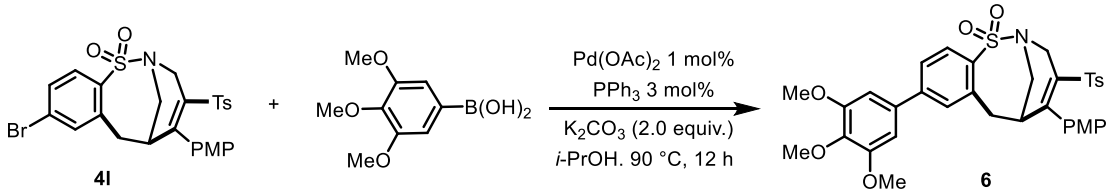


4a **5**

5-(4-Methoxyphenyl)-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (5)

Compound **4a** (0.3 mmol, 148.5 mg) was placed into a Schlenk tube, perylene (12.8 mg, 0.05 mmol) was added and the flask was evaculated and back filled with N_2. Then, *i*-Pr_2EtN (8.0 eq.) and the solvent mixture (3 mL) were added. The solution was kept stirring under irradiation of 30 W blue LEDs at room temperature for 10 h. Afterwards, the solution was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel (petroleum ether/ EtOAc

= 2:1) to obtain product **5** (35.8 mg, 35% **yield**) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 7.2 Hz, 1H), 5.42 (s, 1H), 4.56 (d, J = 14.1 Hz, 1H), 4.01–3.89 (m, 2H), 3.84 (s, 3H), 3.74 (d, J = 14.9 Hz, 1H), 3.54 (d, J = 14.1 Hz, 1H), 3.14 (d, J = 6.6 Hz, 1H), 3.00 (dd, J = 14.8, 7.1 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.5, 140.0, 138.6, 136.8, 132.8, 132.2, 132.0, 129.4, 127.2, 126.6, 119.0, 114.0, 55.4, 51.6, 46.3, 39.7, 31.9. **HR–MS** (ESI) *m/z* calc. for $C_{19}H_{20}NO_3S$ $[M+H]^+$: 342.1159, found: 342.1156.

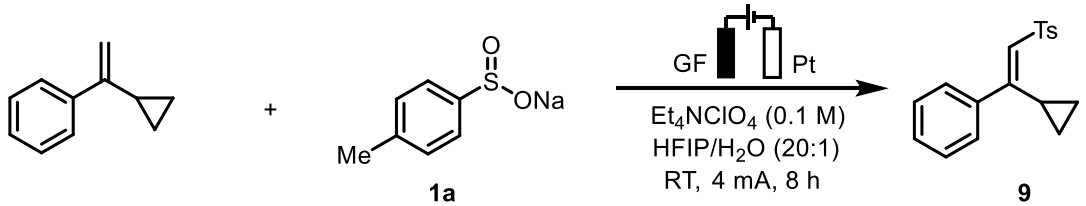


(4-Methoxyphenyl)-4-tosyl-9-(3,4,5-trimethoxyphenyl)-6,7-dihydro-3*H*-2,6-methanobenzo[*h*][1,2]thiazonine 1,1-dioxide (6)

In a 100 mL flask with a stir-bar was charged with **4l** (0.3 mmol) and (3,4,5-trimethoxyphenyl)boronic acid (0.4 mmol). *i*-PrOH (3 mL), $Pd(OAc)_2$ (0.003 mmol) and K_2CO_3 (0.6 mmol) were added and the solution was stirred at RT for 12 hours. The purification was performed by flash column chromatography on silica gel (petroleum ether/ EtOAc = 2:1) to obtain product **6** (128.9mg, 65% **yield**) as a yellow soild. **M.p.**: 207–209 ^{o}C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.09 (d, J = 8.1 Hz, 1H), 7.59 (dd, J = 8.1, 1.5 Hz, 1H), 7.09 (d, J = 5 Hz, 3H), 7.02 (d, J = 8.1 Hz, 2H), 6.75 (s, 2H), 6.72 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 7.8 Hz, 2H), 4.53 (d, J = 19.7 Hz, 1H), 4.48 (d, J = 14.2 Hz, 1H), 4.26 (dd, J = 19.7, 2.0 Hz, 1H), 3.99 (s, 6H), 3.95 (s, 3H), 3.81 (s, 3H), 3.67 (d, J = 14.7 Hz, 1H), 3.47 (d, J = 12.9 Hz, 1H), 2.96–2.91 (m, 2H), 2.29 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.1, 153.8, 149.5, 145.3, 144.1, 138.9, 138.3, 137.9, 135.6, 135.2, 134.7, 131.8, 130.4, 129.3, 128.6, 127.3, 125.6, 113.2, 104.6, 61.2, 56.5, 56.5, 55.4, 50.2, 46.0, 39.4, 38.6, 21.6. **HR–MS** (ESI) *m/z* calc. for $C_{35}H_{36}NO_8S_2$ $[M+H]^+$: 662.1877, found: 662.1888.

5. Mechanistic Studies

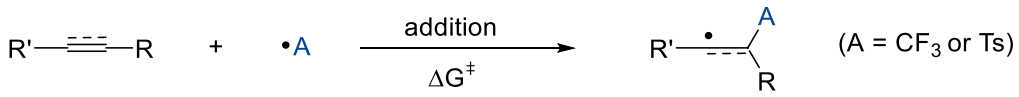
Radical Trapping Experiment

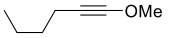
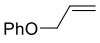
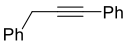
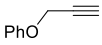
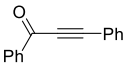


To a 25 mL Schlenk tube containing (1-cyclopropylvinyl)benzene (0.3 mmol, 1.0 equiv.), **1a** (0.3 mmol, 1.0 equiv.), Et_4NClO_4 (92 mg, 0.1 M) were added and subsequently dissolved in a mixture of HFIP/H_2O (3:1, 4 mL). Electrocatalysis was performed at room temperature with a constant current of 4.0 mA maintained for 8 h. The GF anode was washed with ethyl acetate (3 × 3 mL) in an ultrasonic bath and transfered to the round bottom flask with the crude reaction solution. Silica was added to the flask and all volatiles were evaporated under vacuum. Purification by column chromatography on silica gel (petroleum ether/ EtOAc = 3:1) delivered product **9** (53.8 mg, 60%) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.2 Hz, 2H), 7.33–7.30 (m, 1H), 7.26 (d, J = 7.7 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 7.0 Hz, 2H), 6.54 (s, 1H), 2.40 (s, 3H), 1.70–1.67 (m, 1H), 0.84–0.81 (m, 2H), 0.52–0.50 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.3, 143.6, 139.2, 133.8, 129.3, 128.4, 128.2, 127.7, 127.6, 127.0, 21.7, 20.0, 7.1. **HR–MS** (ESI) *m/z* calc. for $C_{18}H_{19}O_2S$ $[M+H]^+$: 299.1101, found: 299.1102.

6. Density Functional Theory (DFT) Computations

Table S-4 | Calculated activation barriers for radical addition to alkynes and alkenes.



Ehtry	Alkyne/Alkene	$\Delta G^‡$/(kcal/mol)[a]	$\Delta G^‡$/(kcal/mol)[b]	Ehtry	Alkyne	$\Delta G^‡$/(kcal/mol)[a]	$\Delta G^‡$/(kcal/mol)[b]
1		6.6	8.7	5		8.3	12.9
2		7.5	12.2	6		10.0	13.2
3		10.0	16.2	7		11.0	14.8
4		8.5	11.4	8		11.0	14.8

The calculated activation barriers for radical addition to various alkenes and alkynes at the M06-2X/def2svp-SMD(DMSO)//M06-2X/def2tzvp-SMD(DMSO) level of theory. [a] Additon of ·CF_3. [b] Addition of ·Ts (Ts = *p*-toluene sulfonyl).

Computational details: All density functional theory (DFT) calculations were performed using Gaussian 16.[4] Geometry optimizations and frequencies were calculated at the M06-2X/def-TZVP-SMD(DMSO) level of theory.[5,6] Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the M06-2X-D3/def2-QZVP-SMD(DMSO) level of theory with the optimized structures. Structures were generated using CYLview.[7] Grimme's quasi-RRHO correction[8] for the frequencies that are below 100 cm^{-1} and concentration correction for all species (from 1 atm to 1 mol/L) are implemented by the GoodVibes program.[9]

The calculated Cartesian coordinates and energies of structures

1

C	-2.95242	0.3394	0.00016
C	-1.95027	-0.53576	-0.00014
H	-3.98027	-0.00218	0.00007
H	-2.79416	1.41204	0.00048

H -2.18399 -1.59719 -0.00043
C -0.50944 -0.22396 -0.00008
C 0.40651 -1.27921 0.00001
C -0.01612 1.08579 -0.00011
C 1.77516 -1.03924 0.00009
H 0.03673 -2.29867 0.00001
C 1.34917 1.32614 -0.00003
H -0.70222 1.92414 -0.0002
C 2.25152 0.26522 0.00007
H 2.46796 -1.87202 0.00016
H 1.71389 2.34621 -0.00006
H 3.31741 0.45742 0.00013
M06-2X/def2QZVP-SMD(DMSO): E = -309.651970074 hartree
Corrected Gibbs Free Energy = -309.546512 hartree

2

C 4.18459 0.10512 -0.44251
C 3.15456 -0.21468 0.32683
H 5.15431 -0.36064 -0.31191
H 4.09298 0.84988 -1.22698
H 3.25605 -0.96356 1.10745
C 1.81347 0.4324 0.21633
H 1.59427 1.00504 1.12485
H 1.78036 1.11081 -0.64142
O 0.84404 -0.60482 0.06864
C -0.46486 -0.24571 0.02575
C -1.38303 -1.29584 -0.05718
C -0.91746 1.07178 0.05524
C -2.73954 -1.02772 -0.1098
H -1.0107 -2.31274 -0.07886
C -2.28719 1.32378 0.00283
H -0.2265 1.90117 0.11525
C -3.20315 0.28653 -0.07927
H -3.44167 -1.85036 -0.17353
H -2.63103 2.35092 0.02627
H -4.26481 0.49412 -0.1195
M06-2X/def2QZVP-SMD(DMSO): E = -424.185088496 hartree
Corrected Gibbs Free Energy = -424.049773 hartree

3

C -1.87335 0.6229 -0.00001
H -1.71801 1.24489 -0.88727
H -1.71779 1.24468 0.88736
O -0.97928 -0.4827 -0.00024
C 0.35386 -0.19962 -0.00011
C 1.204 -1.30703 -0.00003
C 0.88282 1.08825 -0.00009
C 2.57555 -1.12415 0.00008
H 0.76952 -2.29905 -0.00004
C 2.26686 1.25374 0.00002
H 0.24522 1.96168 -0.00017
C 3.11795 0.15987 0.00011
H 3.22692 -1.98975 0.00015
H 2.67274 2.25814 0.00004
H 4.19122 0.30079 0.0002
C -3.23833 0.10539 0.0001
C -4.36661 -0.29936 0.00017
H -5.37206 -0.65975 0.00024
M06-2X/def2QZVP-SMD(DMSO): E = -422.937891322 hartree
Corrected Gibbs Free Energy = -422.825899 hartree

4

C -1.50572 1.20422 0.00003
C -0.1187 1.20919 -0.00001
C 0.58383 0. -0.00003
C -0.1187 -1.20919 0.
C -1.50572 -1.20422 0.00004
C -2.2012 0. 0.00005
H -2.04512 2.14318 0.00004
H 0.42805 2.14376 -0.00003
H 0.42805 -2.14376 -0.00002
H -2.04512 -2.14318 0.00005
H -3.28421 0. 0.00009
C 2.01798 0. -0.00008
C 3.21996 0.00001 -0.00009
H 4.28791 -0.00004 0.00041
M06-2X/def2QZVP-SMD(DMSO): E = -308.407090476 hartree
Corrected Gibbs Free Energy = -308.324556 hartree

5

C 1.95999 -0.27618 -0.31048
C 0.83151 -0.6075 -0.06322
C -0.55856 -0.97915 0.21642
H -0.81341 -1.86996 -0.36473
H -0.64766 -1.25986 1.2697
C -1.55685 0.13886 -0.09924
H -1.46719 0.41307 -1.15443
H -1.2976 1.02693 0.48455
C -2.99214 -0.2738 0.20414
H -3.06952 -0.55542 1.25877
H -3.23993 -1.16692 -0.37763
C -3.98905 0.83567 -0.10646
H -3.94493 1.11407 -1.16217
H -5.01236 0.52782 0.11614
H -3.77235 1.72964 0.48332
O 3.18198 0.06469 -0.60236
C 3.89909 0.6728 0.49487
H 4.89216 0.89818 0.11688
H 3.39328 1.58786 0.80372
H 3.95974 -0.02708 1.32852
M06-2X/def2QZVP-SMD(DMSO): E = -349.115622141 hartree
Corrected Gibbs Free Energy = -348.973331 hartree

6

C -1.45709 -1.67302 0.07481
H -1.59019 -2.35488 -0.77066
H -1.60877 -2.2746 0.97517
C -0.08528 -1.17582 0.06303
C 1.04652 -0.76523 0.05163
C 2.38973 -0.26321 0.03732
C 2.63898 1.08303 0.32599
C 3.46045 -1.1107 -0.26683
C 3.93793 1.56934 0.30885
H 1.80996 1.73887 0.56202
C 4.75655 -0.61625 -0.28049
H 3.26833 -2.15269 -0.49049
C 4.99895 0.72269 0.00638
H 4.12229 2.61277 0.53296
H 5.58007 -1.27887 -0.51653
H 6.012 1.10533 -0.00552
C -2.52719 -0.59789 0.01392
C -2.24278 0.73476 -0.26287
C -3.85392 -0.97512 0.2263
C -3.26689 1.67595 -0.32817
H -1.2175 1.0448 -0.42784
C -4.87545 -0.03869 0.16069
H -4.08326 -2.01254 0.44546
C -4.58432 1.2938 -0.11757
H -3.02946 2.71077 -0.54394
H -5.90018 -0.34741 0.32902
H -5.3803 2.02666 -0.16756

M06-2X/def2QZVP-SMD(DMSO): E = -578.789497897 hartree

Corrected Gibbs Free Energy = -578.606781 hartree

7

C 4.12524 1.20409 0.00012
C 2.73855 1.20931 0.00012
C 2.03343 -0.00002 0.
C 2.7386 -1.20932 -0.00012
C 4.12529 -1.20404 -0.00011
C 4.82144 0.00004 0.
H 4.66454 2.14314 0.00021
H 2.19222 2.14413 0.0002
H 2.19231 -2.14417 -0.00021
H 4.66463 -2.14308 -0.0002
H 5.90441 0.00006 0.
C 0.60317 -0.00005 0.
C -0.60317 -0.00007 -0.00001
C -2.03343 -0.00003 0.
C -2.73854 1.20931 -0.00012
C -2.73861 -1.20933 0.00012
C -4.12523 1.20409 -0.00011
H -2.19221 2.14412 -0.00021
C -4.1253 -1.20404 0.00012
H -2.19233 -2.14417 0.0002
C -4.82144 0.00004 0.
H -4.66453 2.14315 -0.0002
H -4.66464 -2.14307 0.00021
H -5.90441 0.00007 0.00001

M06-2X/def2QZVP-SMD(DMSO): E = -539.480595529 hartree

Corrected Gibbs Free Energy = -539.324016 hartree

8

C 0.01229 0.92028 -0.0001
C -1.13969 0.56468 -0.00008
C -2.50187 0.1372 -0.00006
C -2.80527 -1.22915 -0.00063
C -3.53349 1.08286 0.00055
C -4.12878 -1.64003 -0.00059
H -2.00111 -1.95445 -0.0011
C -4.85349 0.66069 0.00059
H -3.29064 2.13795 0.00099
C -5.15228 -0.69791 0.00002
H -4.36304 -2.69709 -0.00104
H -5.65153 1.39244 0.00107
H -6.18521 -1.02331 0.00005
C 1.3872 1.38703 -0.00008
O 1.62876 2.57784 -0.00013
C 2.45938 0.35374 -0.00001
C 2.15983 -1.00795 0.00021
C 3.79021 0.77516 -0.00014
C 3.18656 -1.94234 0.0003
H 1.12795 -1.33795 0.00032
C 4.81178 -0.16009 -0.00005
H 4.01015 1.83526 -0.0003
C 4.5102 -1.51966 0.00016
H 2.95335 -2.99959 0.00047
H 5.84406 0.16659 -0.00016
H 5.31047 -2.24971 0.00023

M06-2X/def2QZVP-SMD(DMSO): E = -652.820211686 hartree

Corrected Gibbs Free Energy = -652.657576 hartree

CF3

C -0.00001 0.00004 0.32621
F 0.85031 0.91737 -0.0725
F 0.36939 -1.19502 -0.07252
F -1.2197 0.27762 -0.07245

M06-2X/def2QZVP-SMD(DMSO): E = -337.619368642 hartree

Corrected Gibbs Free Energy = hartree

Ts

S 2.14228 -0.0025 -0.24187
O 2.66037 1.28335 0.28921
O 2.65473 -1.28796 0.2958
C 0.35264 0.00151 -0.09773
C -0.3113 1.21798 -0.08691
C -1.69663 1.20719 -0.00805
C -2.40693 0.00756 0.02595
C -1.69965 -1.19789 -0.01166
C -0.31792 -1.21491 -0.09046
H 0.23573 2.15157 -0.11327

H -2.23354 2.14769 0.02038
H -2.24237 -2.13572 0.01414
H 0.22619 -2.15015 -0.1188
C -3.90526 -0.0032 0.10441
H -4.23718 -0.52987 1.0015
H -4.30603 1.00921 0.12814
H -4.32975 -0.5253 -0.75558

M06-2X/def2QZVP-SMD(DMSO): E = -819.590768494 hartree

Corrected Gibbs Free Energy = -337.630750 hartree

TS_1+CF3

C 1.05699 1.02421 1.37503
C 0.02813 1.39951 0.59926
H 1.88295 1.7027 1.55248
H 1.04794 0.10613 1.95221
H 0.0727 2.36799 0.10912
C -1.17328 0.60971 0.30904
C -2.19589 1.19124 -0.44815
C -1.33698 -0.71026 0.74926
C -3.35293 0.48455 -0.7477
H -2.07686 2.21017 -0.79981
C -2.49188 -1.41533 0.449
H -0.55639 -1.19182 1.32597
C -3.50512 -0.82185 -0.29981
H -4.13435 0.95359 -1.33314
H -2.60273 -2.43557 0.79594
H -4.40513 -1.37726 -0.53349
C 2.49598 -0.21487 -0.21854
F 2.77248 0.5871 -1.23027
F 3.61439 -0.62769 0.35211
F 1.79332 -1.25022 -0.64113

M06-2X/def2QZVP-SMD(DMSO): E = -647.275700911 hartree

Corrected Gibbs Free Energy = -647.166766 hartree

TS_1+Ts

C 1.8213 -1.95354 -0.90487
C 0.80327 -2.37133 -0.09842
H 2.80072 -2.40565 -0.79833
H 1.63083 -1.43617 -1.83934
H 1.04828 -3.00171 0.75098
C -0.59097 -1.97855 -0.21023
C -1.47947 -2.35223 0.80918
C -1.07937 -1.20122 -1.27283
C -2.80551 -1.94832 0.78073
H -1.11101 -2.95353 1.63297
C -2.40393 -0.80056 -1.2989
H -0.41943 -0.90415 -2.07879
C -3.27179 -1.16627 -0.27097
H -3.47576 -2.23998 1.57996
H -2.76495 -0.19343 -2.12061
H -4.30635 -0.84644 -0.29491
S 2.60381 0.1105 0.10673
O 3.52433 0.84615 -0.8025
O 3.05313 -0.18554 1.49211
C 1.06413 1.01802 0.20427
C 0.68168 1.81649 -0.8643
C -0.56971 2.41405 -0.83285
C -1.44395 2.19716 0.23414
C -1.02826 1.38606 1.292
C 0.22042 0.78292 1.28112
H 1.3533 1.97735 -1.69846
H -0.87807 3.05034 -1.65439
H -1.69562 1.21659 2.12942
H 0.53669 0.14625 2.09818
C -2.82481 2.78459 0.22285
H -2.85559 3.71192 -0.34916
H -3.52305 2.08241 -0.24272
H -3.1789 2.97974 1.2352

M06-2X/def2QZVP-SMD(DMSO): E = -1129.24929794 hartree

Corrected Gibbs Free Energy = -1129.030585 hartree

TS_2+CF3

C -2.10162 0.95283 -1.30393
C -1.45357 1.81518 -0.50954
H -3.10237 1.17584 -1.65502
H -1.58957 0.10913 -1.75113
H -1.95886 2.69655 -0.12755
C -0.05903 1.64037 -0.01619
H 0.52644 2.5429 -0.22918
H -0.07287 1.51101 1.07404
O 0.52828 0.51146 -0.63697
C 1.78993 0.16693 -0.26607
C 2.31454 -0.97178 -0.88152
C 2.55329 0.87174 0.66178
C 3.59301 -1.39985 -0.5698
H 1.70366 -1.50441 -1.60005
C 3.83873 0.42633 0.96419
H 2.16872 1.7567 1.14941
C 4.36596 -0.70309 0.35754
H 3.98998 -2.2844 -1.05313
H 4.42698 0.97908 1.68684
H 5.36573 -1.0397 0.60033
C -3.03723 -0.59026 0.25259
F -3.9402 0.05249 0.97614
F -3.60662 -1.61599 -0.3624
F -2.06519 -1.0237 1.03813

M06-2X/def2QZVP-SMD(DMSO): E = -761.807214471 hartree

Corrected Gibbs Free Energy = -761.668552 hartree

TS_2+Ts

C 2.47758 -2.0123 -0.81141
C 1.28463 -2.27044 -0.19204
H 3.35656 -2.58212 -0.5307
H 2.47768 -1.58317 -1.81034
H 1.25432 -2.85494 0.72084
C -0.01371 -1.76761 -0.72056

H 0.10922 -0.77126 -1.16108
H -0.37884 -2.4367 -1.51229
O -0.95059 -1.73088 0.34612
C -2.16581 -1.17714 0.09514
C -3.02196 -1.06433 1.19319
C -2.58201 -0.73621 -1.1597
C -4.287 -0.52531 1.03278
H -2.6764 -1.40729 2.16084
C -3.85841 -0.19465 -1.30291
H -1.93676 -0.81141 -2.02421
C -4.71579 -0.08632 -0.21893
H -4.94303 -0.44513 1.89122
H -4.17568 0.144 -2.282
H -5.7051 0.3355 -0.34217
S 3.32896 -0.05396 0.11152
O 4.28048 0.5988 -0.82496
O 3.77264 -0.33983 1.49885
C 1.83428 0.91909 0.18681
C 1.45481 1.66043 -0.92333
C 0.19529 2.24335 -0.93403
C -0.68601 2.0685 0.13481
C -0.26721 1.32451 1.2392
C 0.98582 0.73416 1.26974
H 2.12751 1.77598 -1.76414
H -0.11756 2.82231 -1.79521
H -0.94584 1.18028 2.07226
H 1.29655 0.13438 2.11613
C -2.0636 2.66383 0.10914
H -2.08335 3.60702 0.66167
H -2.38705 2.86509 -0.91207
H -2.78135 1.98893 0.5796

M06-2X/def2QZVP-SMD(DMSO): E = -1243.77764748 hartree

Corrected Gibbs Free Energy = -1243.528414 hartree

TS_3+CF3

C 0.01509 0.01808 -0.74038
H 0.1628 0.86862 -0.06469
H -0.25505 0.40655 -1.72766
O -0.99551 -0.84906 -0.24419
C -2.2402 -0.31721 -0.07972
C -3.21285 -1.19748 0.39701
C -2.56866 1.00678 -0.35552
C -4.50743 -0.75151 0.59688
H -2.93361 -2.2231 0.60428
C -3.87756 1.43881 -0.14857
H -1.83188 1.70594 -0.72596
C -4.84982 0.57191 0.32465
H -5.25568 -1.44162 0.96744
H -4.12753 2.47043 -0.36486
H -5.86333 0.91836 0.48123
C 1.25555 -0.7398 -0.83726
C 2.35705 -1.24611 -0.84024
H 3.1645 -1.92586 -1.02515
C 3.74706 0.17767 0.24851
F 4.20548 -0.40788 1.34291
F 4.75862 0.51173 -0.53698
F 3.05751 1.25686 0.5737

M06-2X/def2QZVP-SMD(DMSO): E = -760.555008809 hartree

Corrected Gibbs Free Energy = -760.440596 hartree

TS_3+Ts

C -0.03647 -2.10165 -0.47017
H -0.10843 -1.6309 -1.45681
H -0.50802 -3.09047 -0.52923
O -0.66281 -1.31109 0.52768
C -1.9798 -1.00741 0.34556
C -2.58911 -0.32242 1.3983
C -2.70832 -1.33246 -0.79431
C -3.9223 0.03649 1.30678
H -1.9998 -0.08215 2.27458
C -4.0507 -0.96127 -0.87042
H -2.25904 -1.87002 -1.61803
C -4.66358 -0.27921 0.16874
H -4.38748 0.56739 2.12859
H -4.61405 -1.21754 -1.75957
H -5.70649 0.00247 0.09922
C 1.37171 -2.23985 -0.1245
C 2.57304 -2.12135 0.13728
H 3.48946 -2.63294 0.38412
S 3.29037 -0.03838 0.15118
O 4.14874 0.13249 -1.0453
O 3.84629 0.30421 1.48189
C 1.7677 0.85692 -0.08993
C 1.18222 0.82404 -1.34945
C -0.07363 1.38388 -1.51035
C -0.74188 1.97273 -0.43298
C -0.11738 2.0035 0.8122
C 1.13252 1.42928 0.99973
H 1.69507 0.36293 -2.18539
H -0.55029 1.35838 -2.48402
H -0.62515 2.46213 1.65269
H 1.6053 1.4293 1.97371
C -2.12492 2.52246 -0.62259
H -2.50202 2.97142 0.29574
H -2.13993 3.27601 -1.41281
H -2.80753 1.72104 -0.91929

M06-2X/def2QZVP-SMD(DMSO): E = -1242.52393764 hartree

Corrected Gibbs Free Energy = -1242.298147 hartree

TS_4+CF3

C 3.03159 -1.24819 -0.22672
C 1.78935 -1.17452 0.38328
C 1.19003 0.07354 0.59742
C 1.85145 1.24045 0.19319
C 3.09355 1.15408 -0.41545
C 3.68558 -0.08711 -0.62636
H 3.4915 -2.21467 -0.39109
H 1.27451 -2.07402 0.69674

H 1.38465 2.20302 0.36047
H 3.60196 2.05815 -0.72656
H 4.65623 -0.14959 -1.10246
C -0.08958 0.15398 1.2191
C -1.22273 0.2092 1.64768
H -2.08658 0.28043 2.27541
C -2.59795 -0.01917 -0.24815
F -3.12994 -1.23044 -0.23629
F -3.55715 0.89227 -0.25241
F -1.83625 0.1252 -1.31757
M06-2X/def2QZVP-SMD(DMSO): E = -646.026822096 hartree
Corrected Gibbs Free Energy = -645.941808 hartree

TS_4+Ts
C 2.8183 -0.76805 -1.13199
C 1.49397 -1.09105 -1.3735
C 0.76516 -1.81093 -0.41194
C 1.39217 -2.21763 0.77861
C 2.71722 -1.89051 1.00373
C 3.431 -1.1612 0.055
H 3.37529 -0.20327 -1.86941
H 1.00594 -0.78132 -2.28924
H 0.82464 -2.77118 1.51617
H 3.19718 -2.19857 1.92418
H 4.46614 -0.90192 0.2399
C -0.6081 -2.06757 -0.615
C -1.83601 -2.0655 -0.69974
H -2.76214 -2.53454 -0.9777
S -2.67881 -0.08394 0.11292
O -3.17587 -0.29094 1.49638
O -3.59152 0.51772 -0.89202
C -1.18455 0.89484 0.18682
C -0.35354 0.75878 1.28997
C 0.86769 1.41556 1.28748
C 1.26737 2.18632 0.19366
C 0.40679 2.30174 -0.8996
C -0.81579 1.64625 -0.91941
H -0.65542 0.15326 2.13592
H 1.5258 1.32162 2.14383
H 0.70331 2.90244 -1.75163
H -1.47541 1.72586 -1.77447
C 2.61815 2.83993 0.17954
H 3.37175 2.12775 -0.16974
H 2.63495 3.69942 -0.49043
H 2.90925 3.16342 1.17918
M06-2X/def2QZVP-SMD(DMSO): E = -1127.99800408 hartree
Corrected Gibbs Free Energy = -1127.804329 hartree

TS_5+CF3
C 0.79043 1.3409 -0.36735
C 0.08722 0.37367 -0.1469
C 1.65849 -1.33978 0.0081
F 1.60791 -2.1136 -1.073
F 2.85368 -0.76094 0.0649
F 1.4977 -2.09954 1.08937
C -1.12612 -0.43053 0.07837
H -1.12896 -1.27424 -0.61813
H -1.08194 -0.85836 1.08406
C -2.41203 0.38165 -0.08409
H -2.44547 0.80129 -1.09367
H -2.39376 1.22477 0.6125
C -3.65529 -0.46437 0.16377
H -3.60969 -0.88259 1.17386
H -3.65678 -1.31279 -0.52722
C -4.93955 0.33796 -0.0035
H -5.01721 0.74152 -1.0159
H -5.82189 -0.27776 0.18014
H -4.96667 1.17888 0.69366
O 1.6728 2.24735 -0.61921
C 2.25084 2.86591 0.55958
H 2.97111 3.59013 0.19184
H 1.46666 3.36054 1.13135
H 2.74458 2.10404 1.16184
M06-2X/def2QZVP-SMD(DMSO): E = -686.735952166 hartree
Corrected Gibbs Free Energy = -686.590821 hartree

TS_5+Ts
C -1.34519 0.14036 -0.06604
C -0.68968 1.18712 -0.20637
S -0.03965 -1.63821 0.23117
O -0.21507 -2.61957 -0.87597
O -0.1654 -2.13455 1.6298
C 1.58132 -0.89686 0.05736
C 2.1463 -0.79685 -1.20716
C 3.34958 -0.12403 -1.34818
C 3.97977 0.46399 -0.24811
C 3.37972 0.35638 1.00618
C 2.17663 -0.31831 1.16768
H 1.65666 -1.2451 -2.06285
H 3.80624 -0.04531 -2.32827
H 3.85671 0.81023 1.86722
H 1.71307 -0.39971 2.14335
C 5.29098 1.17585 -0.41808
H 5.51134 1.8071 0.44228
H 6.10389 0.45287 -0.5232
H 5.28579 1.79481 -1.31625
C -2.71727 -0.42326 -0.02928
H -2.80722 -1.16888 -0.82506
H -2.85099 -0.95489 0.91792
C -3.79576 0.64648 -0.18784
H -3.68451 1.38736 0.60934
H -3.64195 1.17088 -1.13546
C -5.19853 0.05187 -0.1484
H -5.29544 -0.69432 -0.94262
H -5.33851 -0.47743 0.79883
C -6.27656 1.11652 -0.30768
H -7.27631 0.67958 -0.27839
H -6.21159 1.85883 0.49144

H -6.16768 1.64109 -1.25996
O 0.25585 2.03745 -0.3625
C 0.602 2.81118 0.82108
H 1.49475 3.36841 0.5555
H -0.22097 3.48418 1.05631
H 0.79837 2.13233 1.64949
M06-2X/def2QZVP-SMD(DMSO): E = -1168.70399190 hartree
Corrected Gibbs Free Energy = -1168.450742 hartree

TS_6+CF3
C 1.61939 1.20305 -0.1598
H 1.7317 1.76819 -1.08743
H 1.74195 1.90556 0.66803
C 0.263 0.6292 -0.10999
C -0.66566 -0.15749 -0.08056
C -1.84553 -0.95321 -0.04422
C -2.33683 -1.43434 1.17738
C -2.52826 -1.25612 -1.23066
C -3.48945 -2.20334 1.20589
H -1.80811 -1.19958 2.09277
C -3.68039 -2.02505 -1.19
H -2.14762 -0.8831 -2.1733
C -4.16303 -2.50063 0.02535
H -3.86426 -2.57228 2.15252
H -4.20421 -2.25504 -2.10952
H -5.06329 -3.10198 0.05222
C 2.67 0.11598 -0.07899
C 3.20232 -0.43867 -1.23951
C 3.09583 -0.35662 1.16021
C 4.14948 -1.4535 -1.1632
H 2.87402 -0.07219 -2.20597
C 4.04238 -1.37059 1.23824
H 2.68351 0.07453 2.06608
C 4.57118 -1.9216 0.07584
H 4.56014 -1.87639 -2.0721
H 4.36998 -1.72867 2.20676
H 5.31065 -2.71078 0.13618
C -0.88634 2.6482 0.04457
F -2.13062 2.42859 -0.34677
F -0.8817 3.01495 1.31822
F -0.35357 3.61202 -0.69472
M06-2X/def2QZVP-SMD(DMSO): E = -916.408479963 hartree
Corrected Gibbs Free Energy = -916.221672 hartree

TS_6+Ts
C 2.54906 -1.29317 -0.05181
H 2.51742 -1.99316 0.78576
H 2.68188 -1.88087 -0.96476
C 1.25086 -0.58157 -0.13157
C 0.58279 0.45813 -0.12407
C -0.39018 1.47861 -0.15459
C -0.71227 2.1129 -1.36865
C -1.08589 1.82811 1.01605
C -1.72115 3.05812 -1.40655
H -0.17342 1.84122 -2.26788
C -2.09865 2.77044 0.96105
H -0.83496 1.33888 1.94899
C -2.4208 3.38489 -0.24641
H -1.97025 3.54019 -2.34367
H -2.64385 3.02514 1.8617
H -3.21598 4.11926 -0.28375
C 3.69569 -0.32237 0.11669
C 4.31351 -0.16537 1.3531
C 4.13434 0.43719 -0.96683
C 5.35913 0.7395 1.50685
H 3.97621 -0.75547 2.19791
C 5.1773 1.34048 -0.81486
H 3.6548 0.316 -1.93237
C 5.79206 1.49437 0.42429
H 5.835 0.85264 2.47344
H 5.51328 1.92378 -1.66364
H 6.60649 2.19851 0.54297
S -0.18559 -2.34053 -0.43221
O 0.08328 -3.37041 0.60611
O -0.16468 -2.75222 -1.86017
C -1.76848 -1.58453 -0.08538
C -2.22941 -1.55978 1.22242
C -3.38743 -0.84967 1.50582
C -4.06459 -0.15013 0.50608
C -3.57192 -0.19481 -0.80019
C -2.42017 -0.90348 -1.10452
H -1.69451 -2.08489 2.00399
H -3.75972 -0.82071 2.52325
H -4.08765 0.34801 -1.58441
H -2.03082 -0.92162 -2.11507
C -5.29869 0.64373 0.82191
H -5.30803 1.58166 0.2643
H -6.19533 0.08505 0.54117
H -5.36071 0.86641 1.88687
M06-2X/def2QZVP-SMD(DMSO): E = -1398.37970800 hartree
Corrected Gibbs Free Energy = -1398.083795 hartree

TS_7+CF3
C 4.31105 -0.64851 -1.20256
C 2.92592 -0.63839 -1.21013
C 2.21996 -0.6198 0.00211
C 2.92512 -0.61342 1.21493
C 4.31026 -0.62366 1.2085
C 5.00579 -0.64155 0.00326
H 4.85211 -0.66156 -2.14045
H 2.37868 -0.64346 -2.14437
H 2.37726 -0.59924 2.14872
H 4.85069 -0.61725 2.14681
H 6.08873 -0.64943 0.00369
C 0.80135 -0.60155 0.00154
C -0.40886 -0.43978 0.00008
C -1.82616 -0.71364 0.00219
C -2.5155 -0.84376 -1.20646

C -2.51508 -0.8289 1.21256
C -3.87793 -1.10483 -1.19939
H -1.97839 -0.74177 -2.14141
C -3.87759 -1.08992 1.20907
H -1.97769 -0.71578 2.14607
C -4.56077 -1.22845 0.00577
H -4.40792 -1.21041 -2.13785
H -4.40732 -1.18402 2.1489
H -5.62464 -1.43099 0.00719
C -0.57411 1.82971 -0.00873
F -1.18441 2.23634 1.09548
F 0.64522 2.34169 -0.05355
F -1.26216 2.23226 -1.0679

M06-2X/def2QZVP-SMD(DMSO): E = -877.097442155 hartree

Corrected Gibbs Free Energy = -876.937191 hartree

TS_7+Ts

C 5.06737 0.82614 0.81008
C 3.68499 0.86852 0.92471
C 2.88975 0.63205 -0.19845
C 3.48263 0.33234 -1.42632
C 4.8655 0.29423 -1.53125
C 5.65848 0.54021 -0.41549
H 5.68356 1.01758 1.67975
H 3.21624 1.09005 1.87558
H 2.85726 0.13579 -2.28832
H 5.32505 0.06951 -2.48573
H 6.73761 0.50817 -0.50132
C 1.44124 0.65798 -0.07737
C 0.37898 1.29804 -0.14425
C -0.94417 1.77055 -0.13684
C -1.76011 1.609 -1.27232
C -1.47894 2.35922 1.02576
C -3.08523 2.00457 -1.22893
H -1.34462 1.15859 -2.16508
C -2.80361 2.75364 1.0503
H -0.84724 2.48187 1.89659
C -3.61173 2.57254 -0.07092
H -3.71444 1.8662 -2.09953
H -3.21422 3.19915 1.94775
H -4.6507 2.87667 -0.04278
S 0.97991 -1.45091 0.52715
O 1.26425 -1.59825 1.97728
O 1.63504 -2.38717 -0.42043
C -0.78909 -1.54026 0.28136
C -1.62826 -1.07588 1.28496
C -2.99145 -1.02068 1.03972
C -3.51657 -1.40947 -0.195
C -2.64539 -1.87584 -1.18054
C -1.27695 -1.93139 -0.9567
H -1.22297 -0.76244 2.2394
H -3.65901 -0.66096 1.81465
H -3.04207 -2.18803 -2.1396
H -0.60168 -2.27966 -1.72827
C -4.98734 -1.28275 -0.46443
H -5.292 -1.90988 -1.30183
H -5.57278 -1.55554 0.41426
H -5.23154 -0.24563 -0.71326

M06-2X/def2QZVP-SMD(DMSO): E = -1359.06753860 hartree

Corrected Gibbs Free Energy = -1358.798446 hartree

TS_8+CF3

C -0.128 0.42918 -0.2532
C 0.91138 -0.20834 -0.25461
C 2.19129 -0.81927 -0.21089
C 2.42574 -1.89986 0.65055
C 3.22391 -0.33342 -1.02537
C 3.68156 -2.48218 0.6935
H 1.62226 -2.26844 1.27589
C 4.47386 -0.92753 -0.9748
H 3.03351 0.50402 -1.68501
C 4.70407 -1.99959 -0.11786
H 3.86447 -3.31561 1.35987
H 5.27209 -0.55351 -1.60339
H 5.68381 -2.45958 -0.08143
C -1.53323 0.73135 -0.53938
O -1.84995 1.80583 -1.00402
C -2.53213 -0.33552 -0.24721
C -2.17473 -1.55198 0.33324
C -3.86788 -0.08438 -0.56964
C -3.14726 -2.50939 0.58769
H -1.14184 -1.75284 0.5878
C -4.83425 -1.04334 -0.31651
H -4.13527 0.86341 -1.01894
C -4.47443 -2.25711 0.263
H -2.86813 -3.45256 1.04011
H -5.8688 -0.84759 -0.56901
H -5.23113 -3.00635 0.46111
C 0.50311 2.5313 0.49028
F -0.3947 3.12075 1.25997
F 1.59802 2.28698 1.19105
F 0.80008 3.3037 -0.53852

M06-2X/def2QZVP-SMD(DMSO): E = -990.438481511 hartree

Corrected Gibbs Free Energy = -990.270817 hartree

TS_8+Ts

C 1.10851 -0.33221 0.55418
C 0.29784 0.59371 0.67473
C -0.80357 1.46309 0.77247
C -1.42666 1.68221 2.01438
C -1.32162 2.06062 -0.3897
C -2.55776 2.47418 2.08046
H -1.02097 1.21529 2.90295
C -2.45991 2.84317 -0.30613
H -0.83479 1.88694 -1.34132
C -3.08036 3.04919 0.92327
H -3.04174 2.64011 3.03463
H -2.86907 3.2923 -1.20257

H	-3.97237	3.66065	0.98055
C	2.53237	-0.7315	0.58997
O	2.85304	-1.78759	1.08496
C	3.52698	0.21619	0.01227
C	3.15297	1.32643	-0.74403
C	4.88016	-0.05045	0.23448
C	4.12692	2.16344	-1.27151
H	2.10765	1.53529	-0.93203
C	5.84772	0.79212	-0.28681
H	5.16054	-0.91634	0.82052
C	5.47148	1.89987	-1.04131
H	3.8348	3.02187	-1.863
H	6.89562	0.58763	-0.10674
H	6.22877	2.5573	-1.45067
S	0.01278	-2.33089	0.25134
O	-0.22206	-3.04791	1.52713
O	0.62833	-3.05488	-0.8875
C	-1.55196	-1.65072	-0.29437
C	-2.51277	-1.33176	0.65591
C	-3.6652	-0.68233	0.24279
C	-3.856	-0.3366	-1.09747
C	-2.87113	-0.6735	-2.02599
C	-1.70739	-1.31986	-1.63139
H	-2.36123	-1.58446	1.69803
H	-4.42382	-0.4248	0.97361
H	-3.00807	-0.41296	-3.06896
H	-0.93759	-1.56529	-2.35247
C	-5.09495	0.40187	-1.51276
H	-5.1795	1.3411	-0.96061
H	-5.0831	0.62656	-2.57864
H	-5.98788	-0.18683	-1.29202

M06-2X/def2QZVP-SMD(DMSO): E = -1472.40849847 hartree
Corrected Gibbs Free Energy = -1472.131933 hartree

7. References

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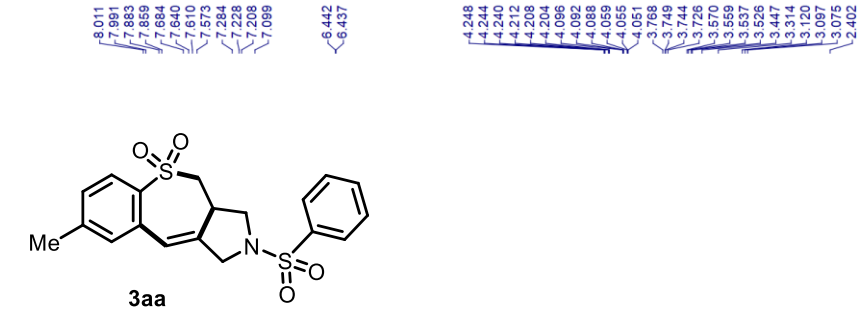
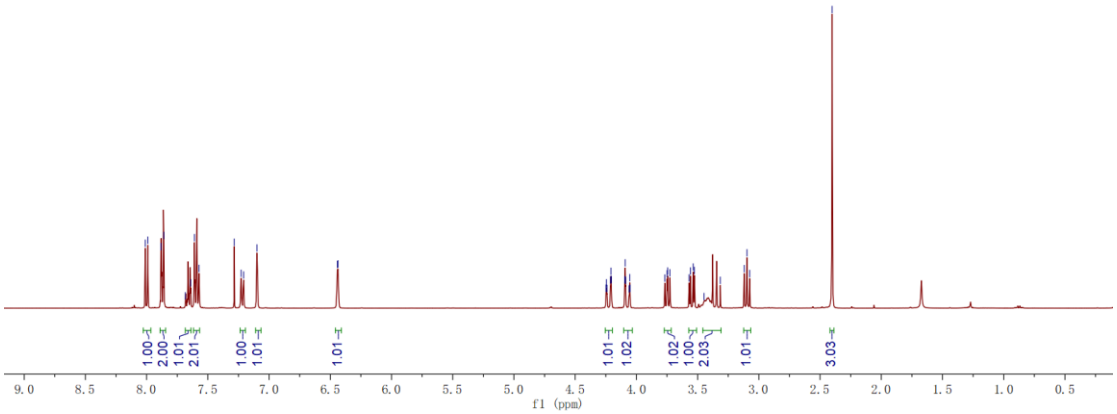
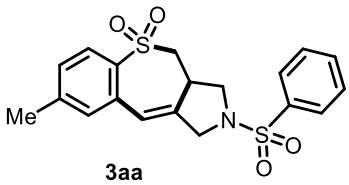
7. NMR Spectra



3aa

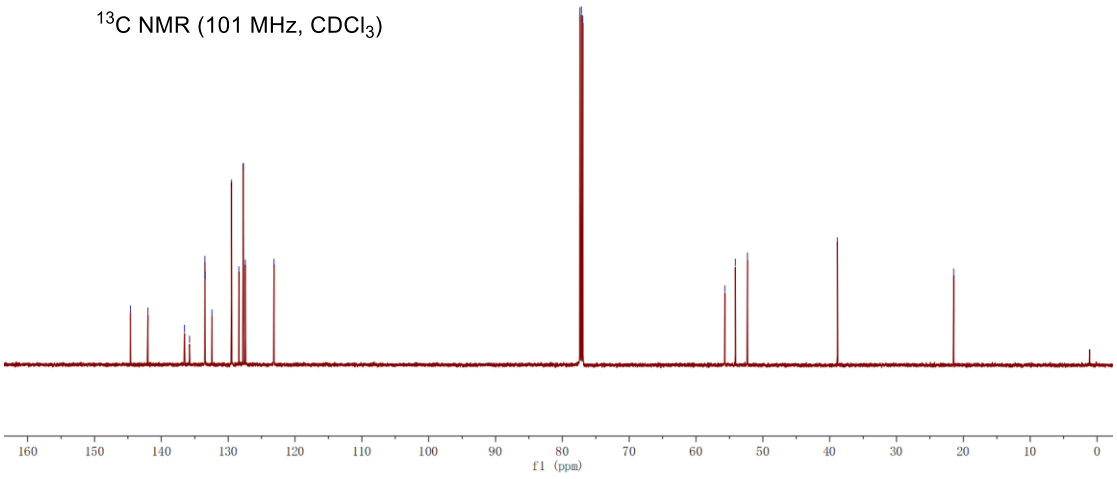
^{1}H NMR (400 MHz, $CDCl_3$)

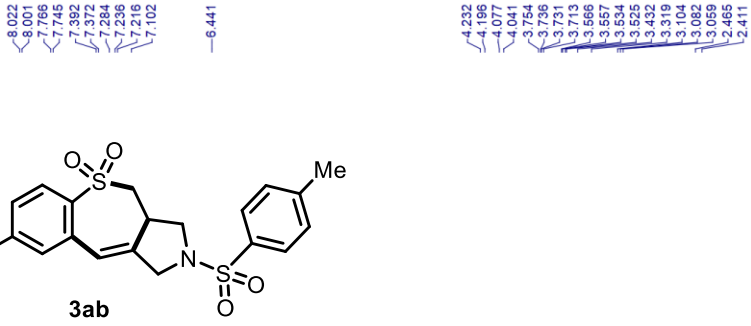




3aa

^{13}C NMR (101 MHz, $CDCl_3$)





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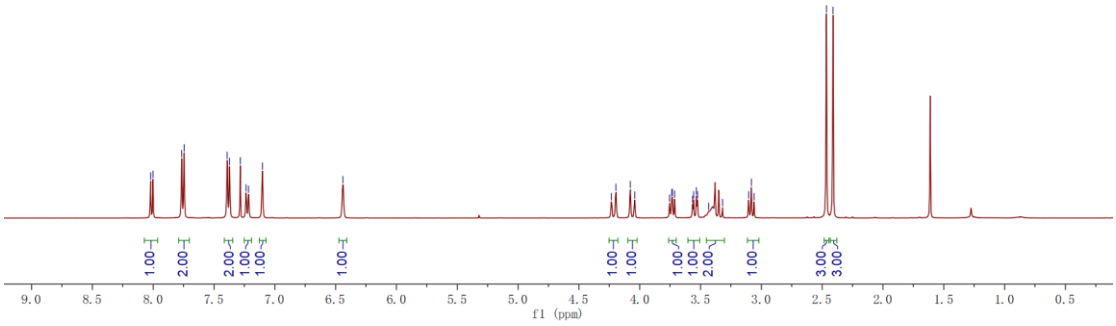
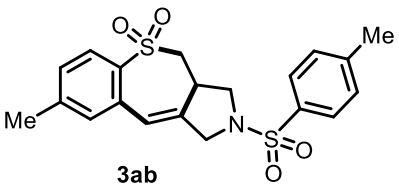
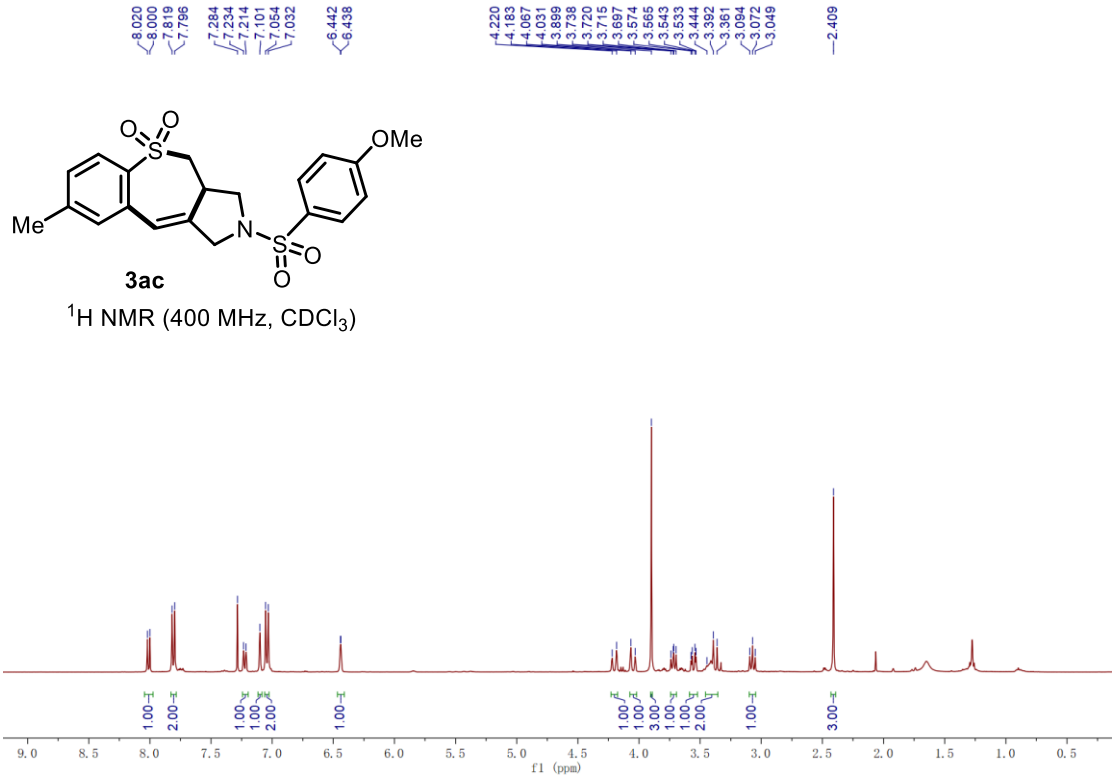




3ab

^{13}C NMR (151 MHz, $CDCl_3$)



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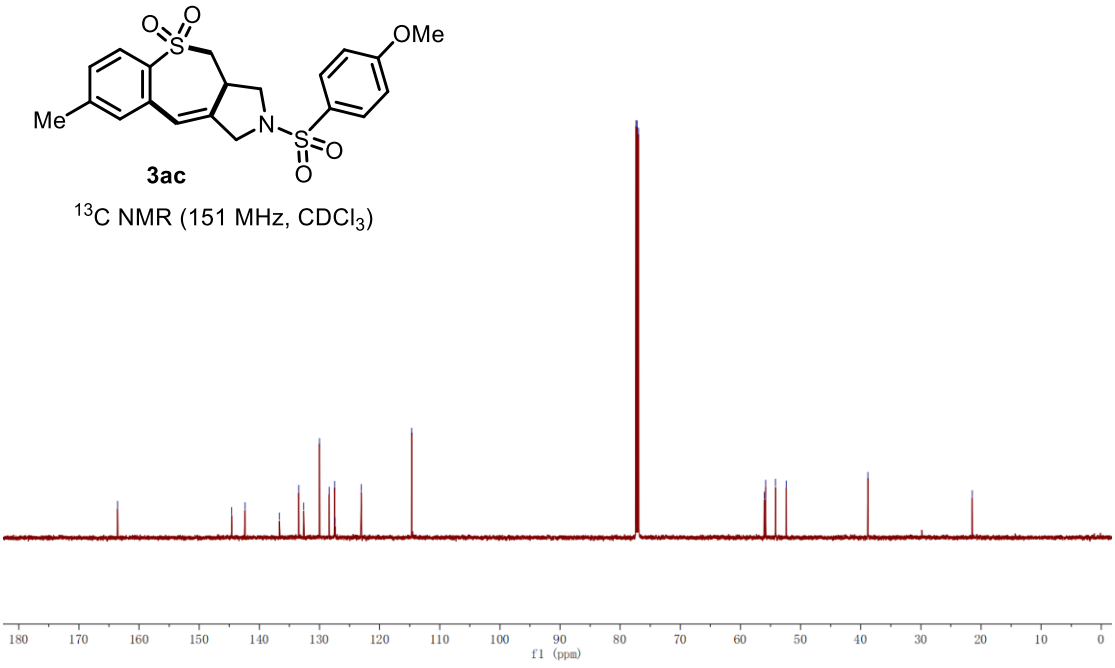

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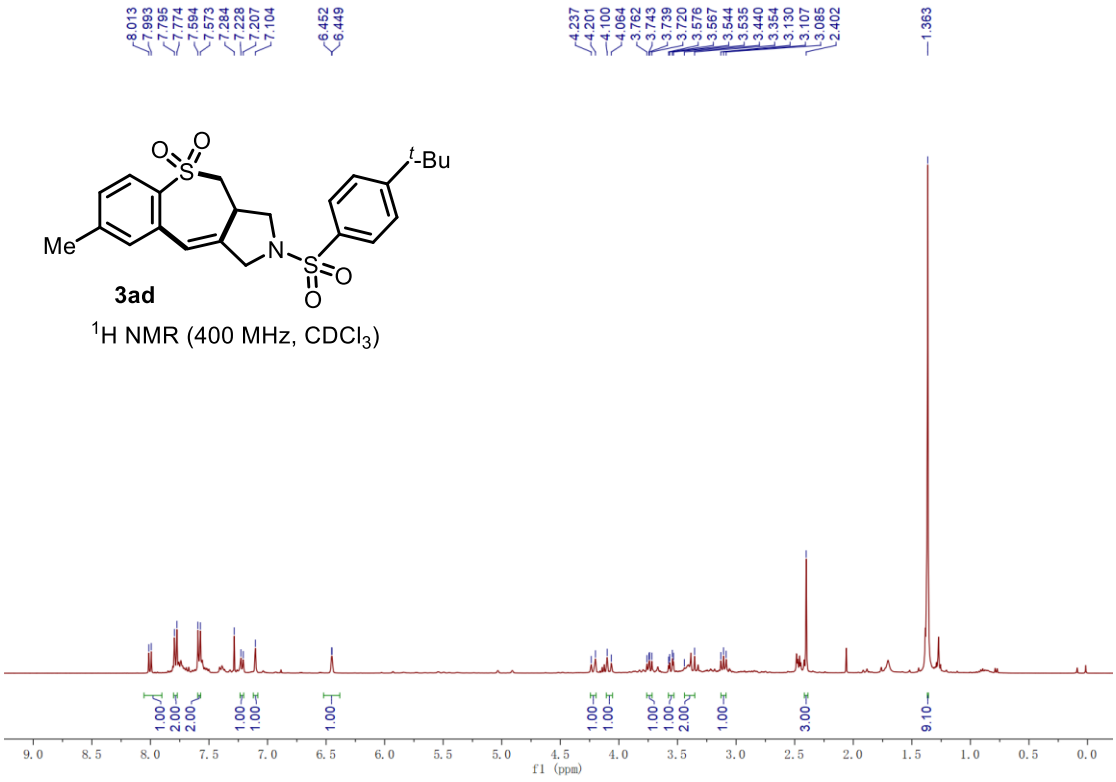

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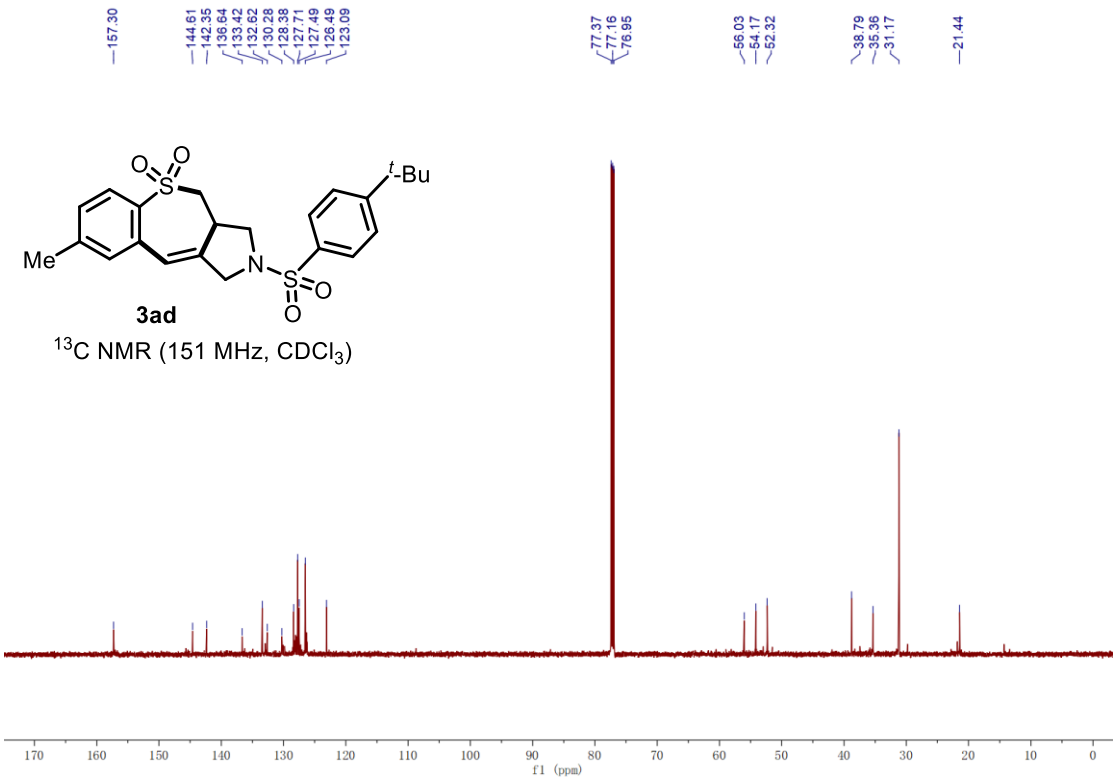

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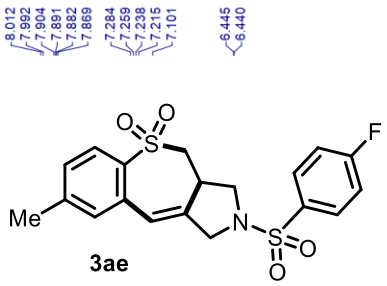

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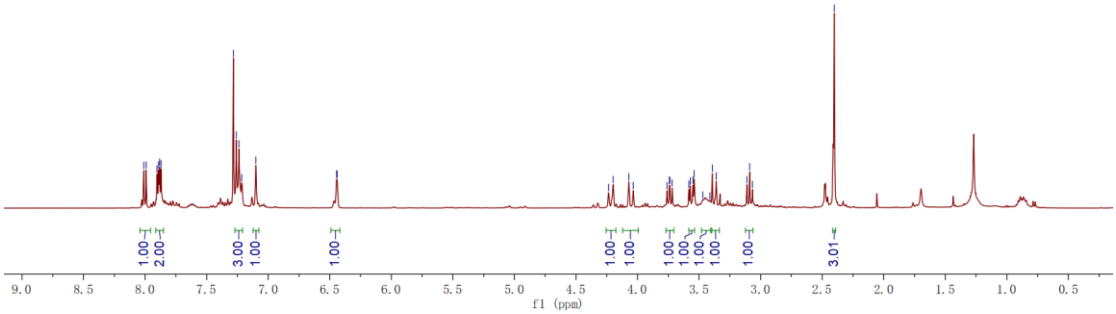
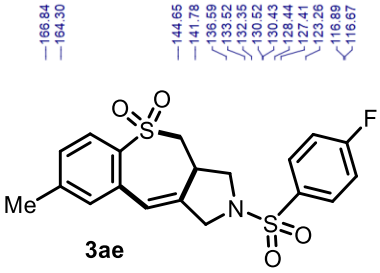
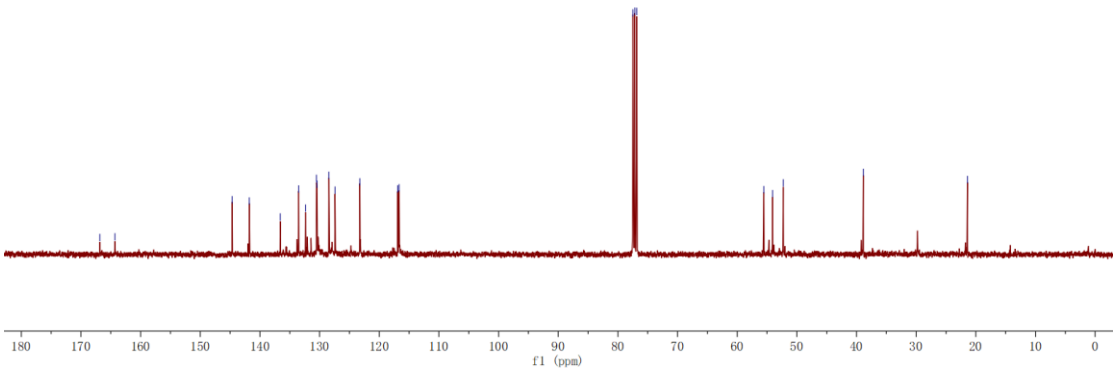
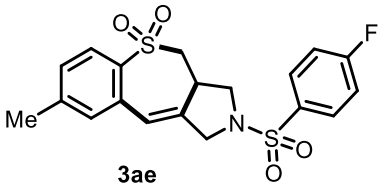




^{13}C NMR (101 MHz, $CDCl_3$)





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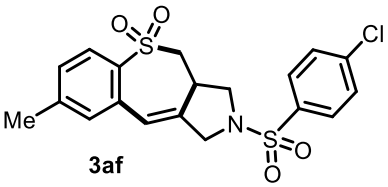
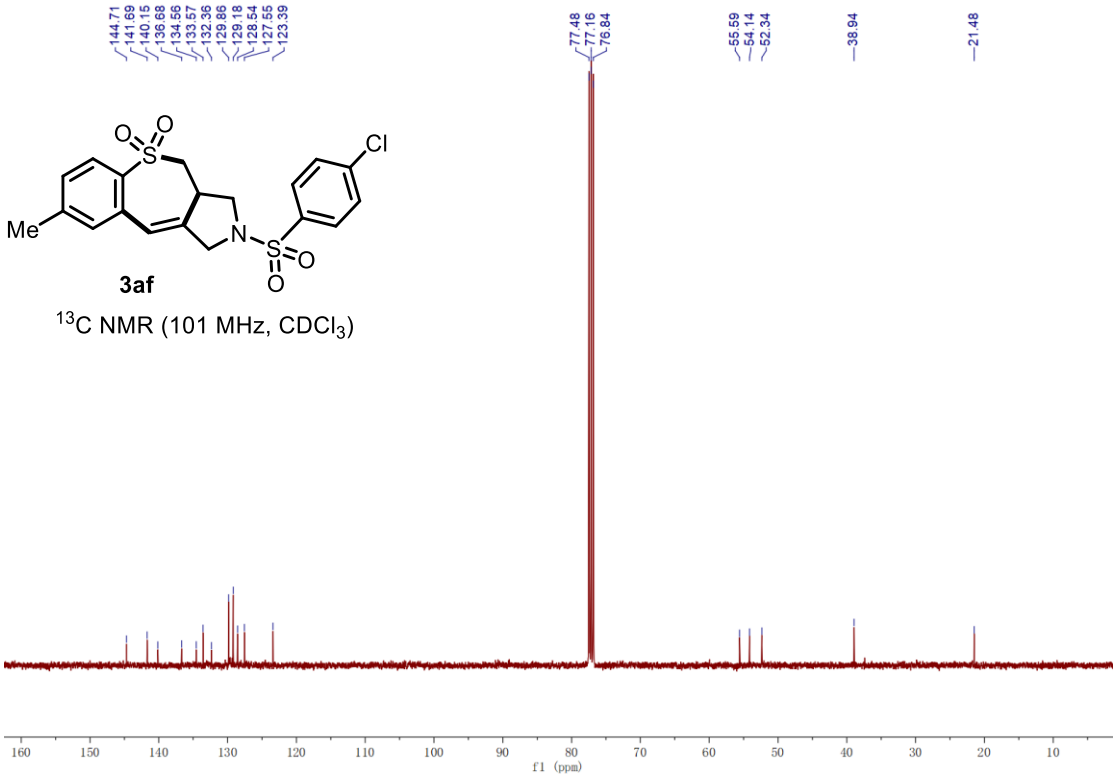
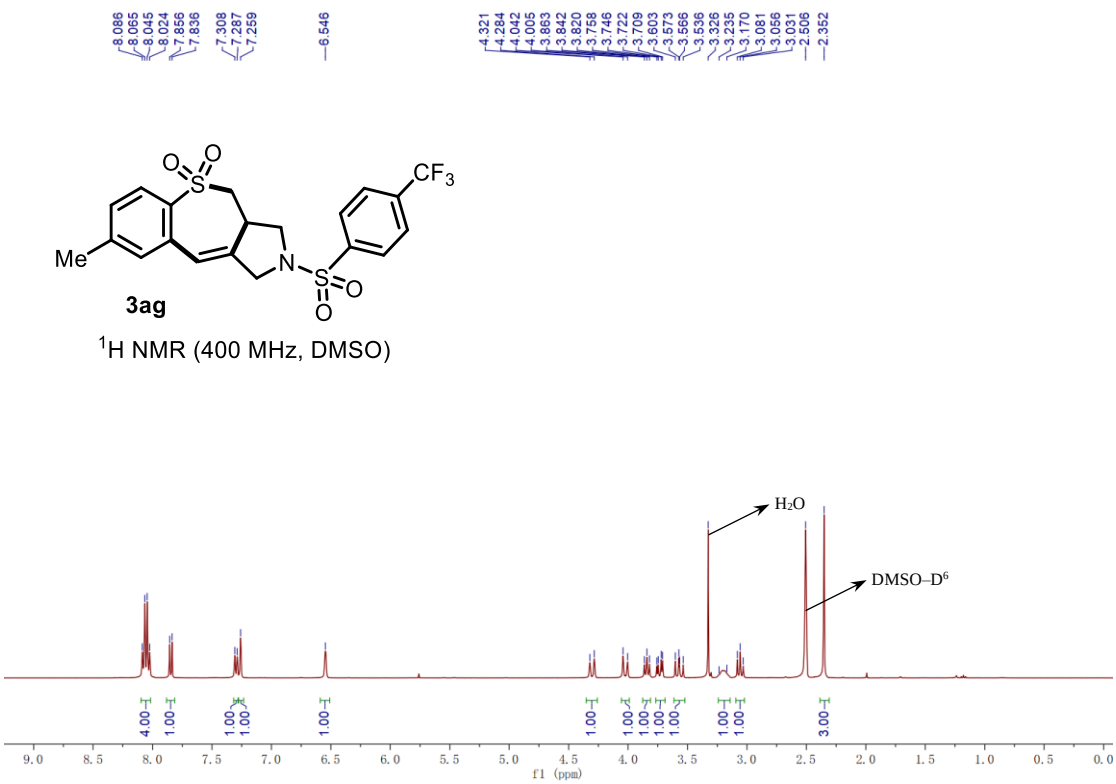


3af

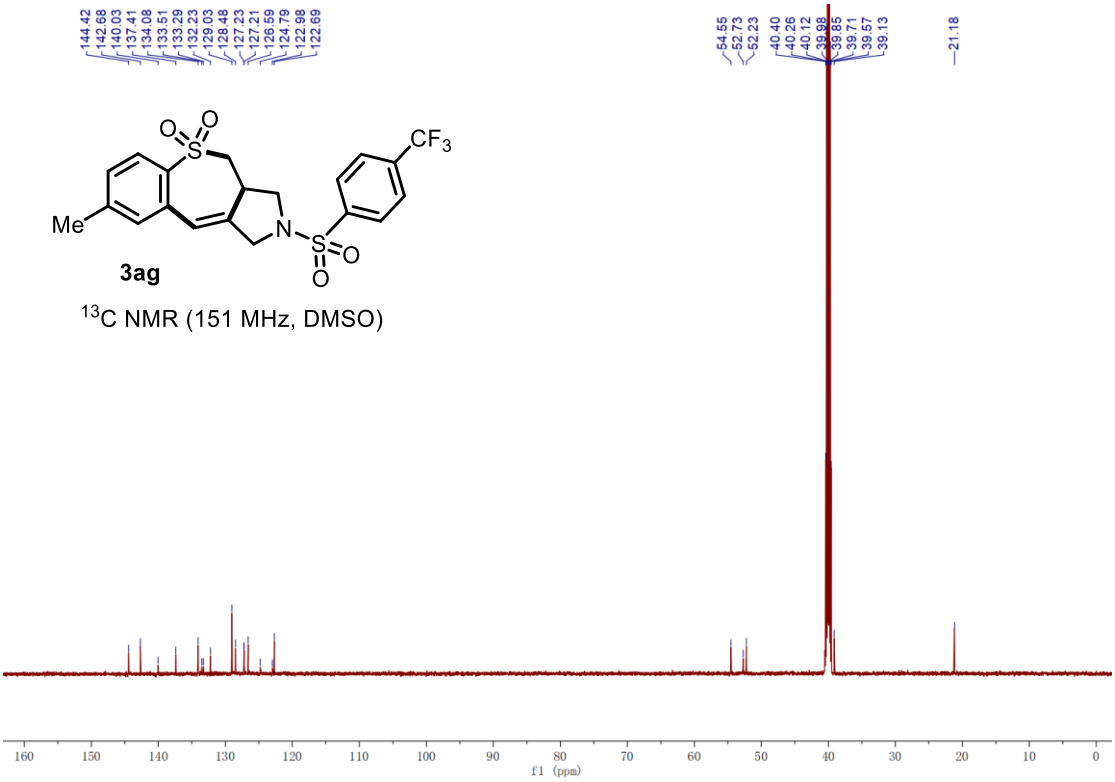
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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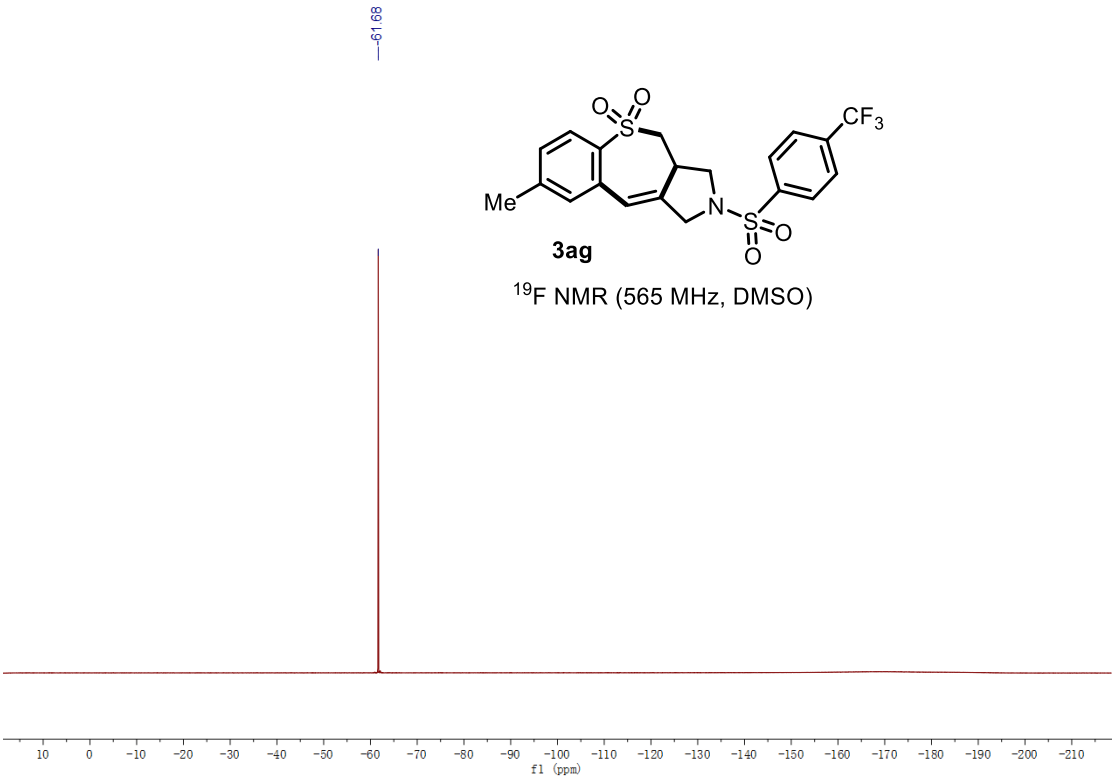

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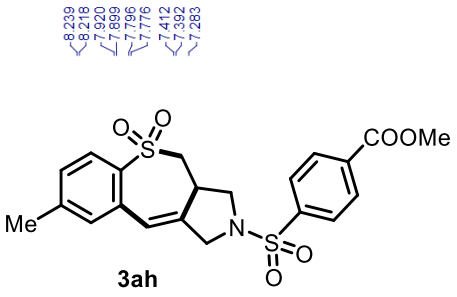
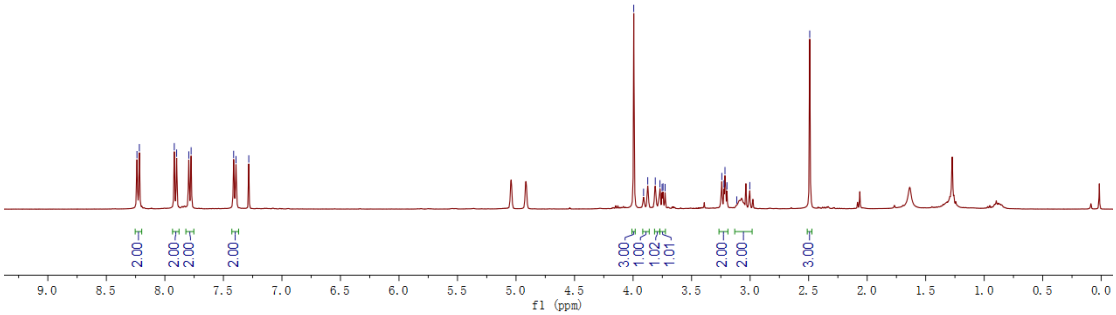
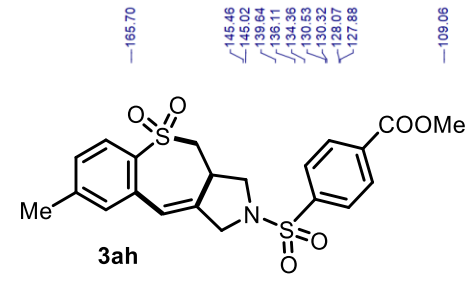


3ah

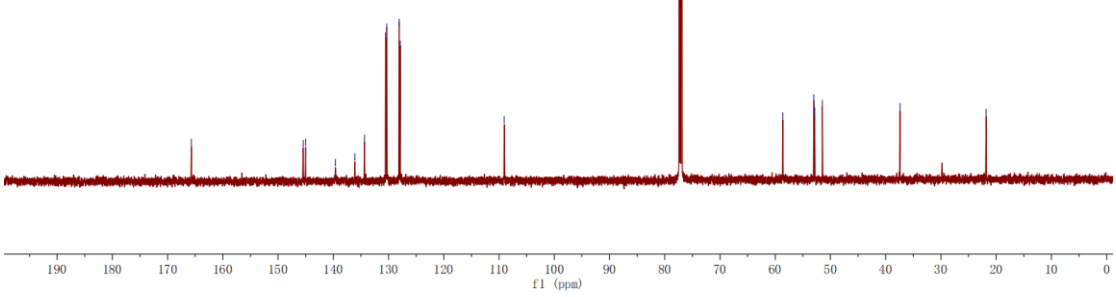
^{1}H NMR (400 MHz, CDCl3)

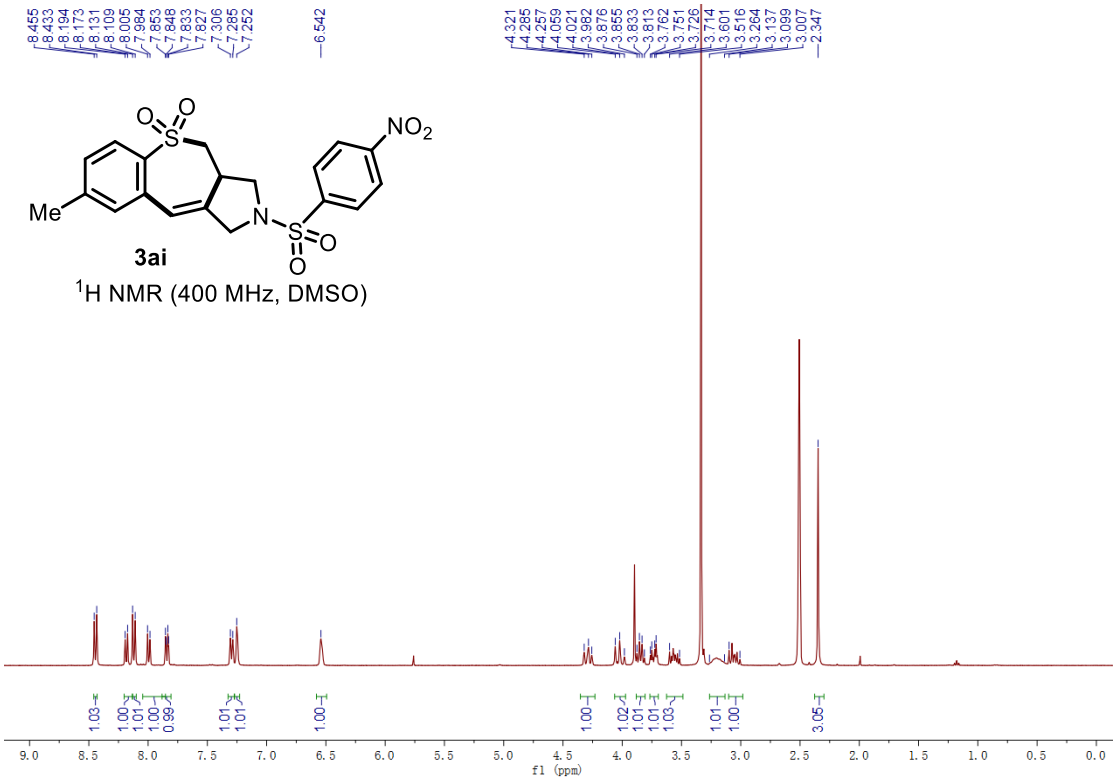




3ah

^{13}C NMR (151 MHz, $CDCl_3$)

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8.433
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8.109
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7.984
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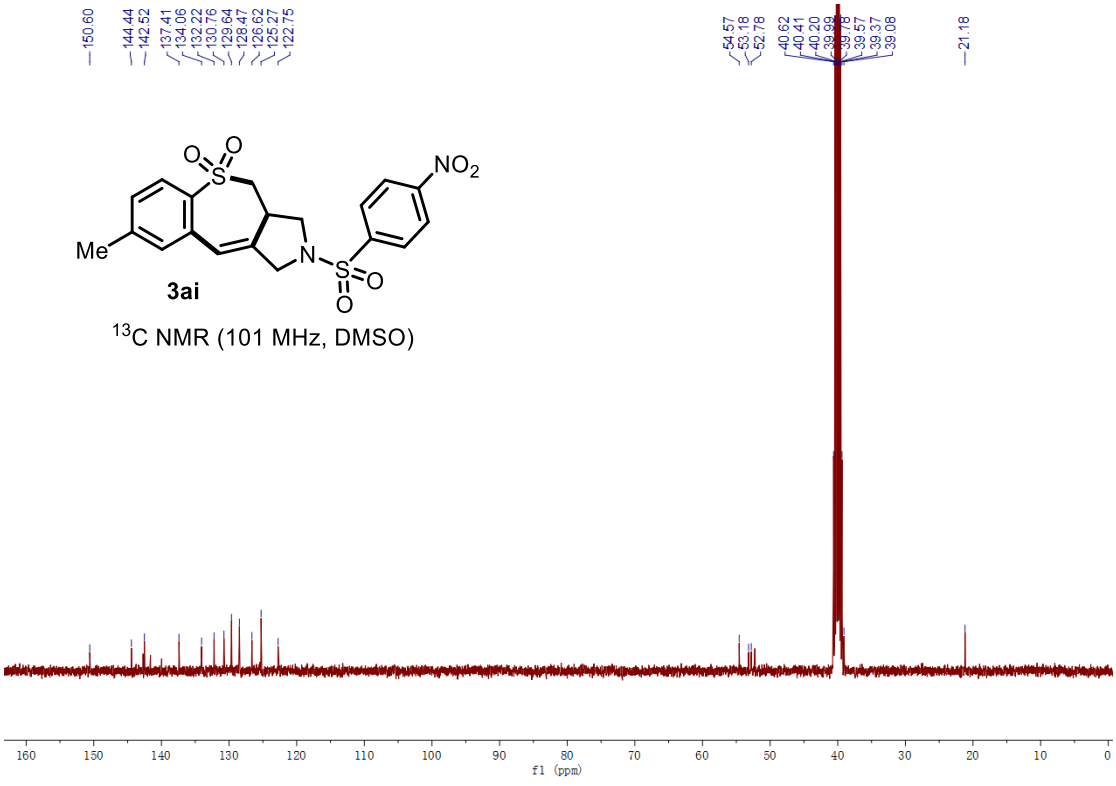
7.848
7.833
7.827
7.306
7.285
7.252
6.542
4.321
4.285
4.257
4.059
4.021
3.982
3.876
3.855
3.833
3.813
3.762
3.751
3.726
3.714
3.601
3.516
3.264
3.137
3.099
3.007
2.347
O
O
S
NO2
Me
N
S
O
O
3ai
1H NMR (400 MHz, DMSO)
1.03
1.00
1.01
1.00
0.99
1.01
1.01
1.00
1.00
1.02
1.01
1.01
1.03
1.01
1.00
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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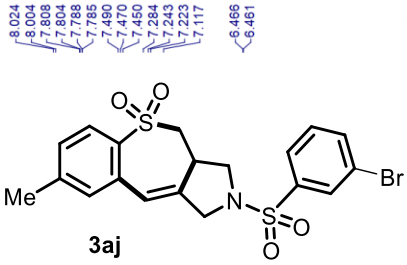
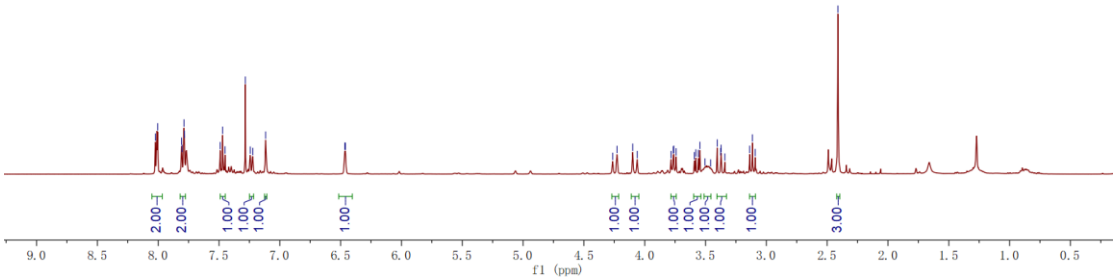
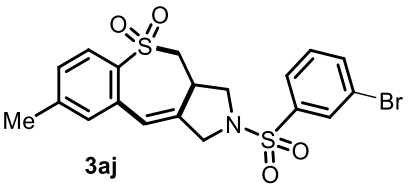
144.44
142.52
137.41
134.06
132.22
130.76
129.64
128.47
126.62
125.27
122.75
54.57
53.18
52.78
40.62
40.41
40.20
39.99
39.78
39.57
39.37
39.08
21.18
O
O
S
NO2
Me
N
S
O
O
3ai
13C NMR (101 MHz, DMSO)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3aj

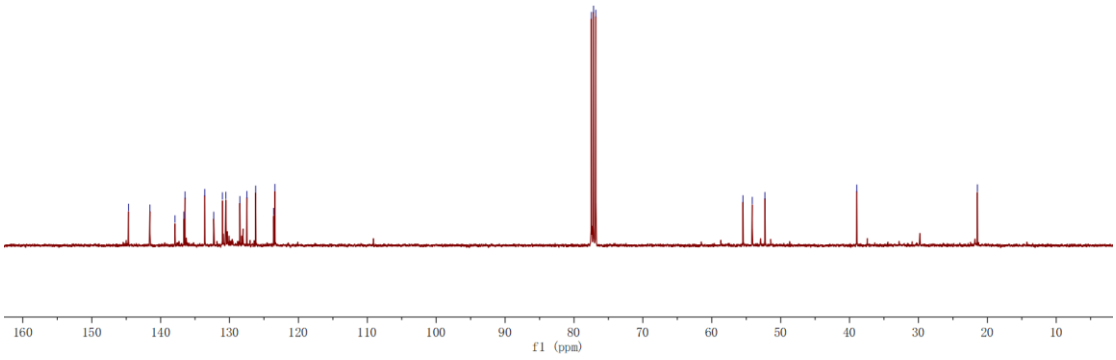
^{1}H NMR (400 MHz, $CDCl_3$)

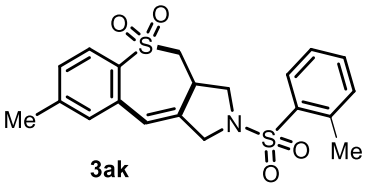




3aj

^{13}C NMR (101 MHz, $CDCl_3$)





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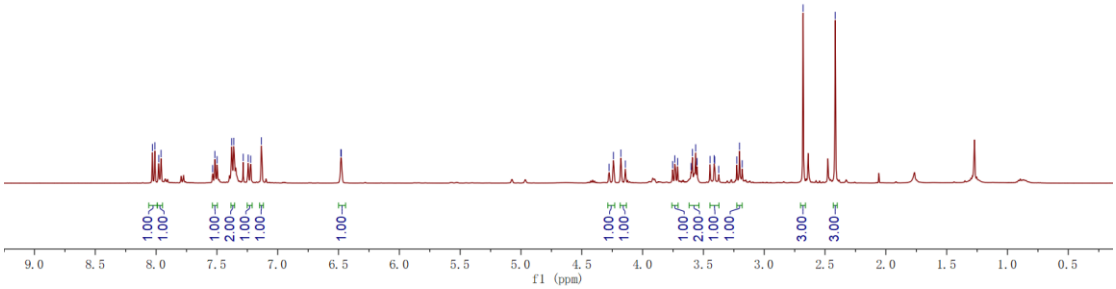
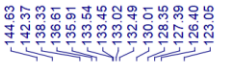
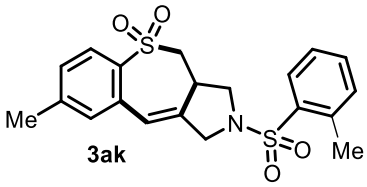
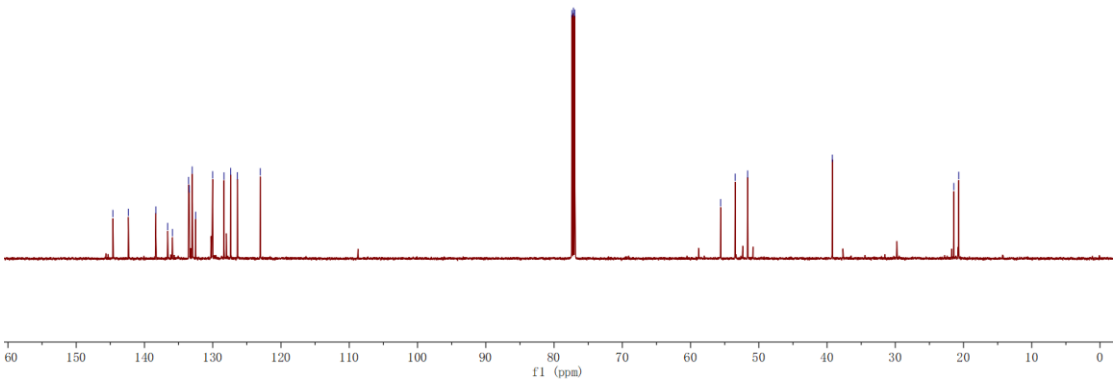


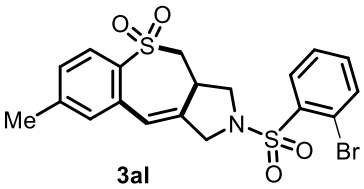




3ak

^{13}C NMR (151 MHz, $CDCl_3$)





3al

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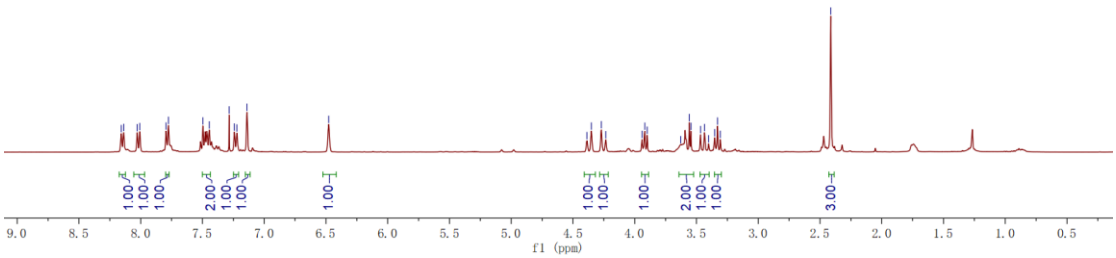
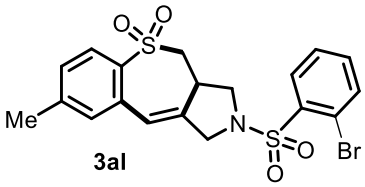
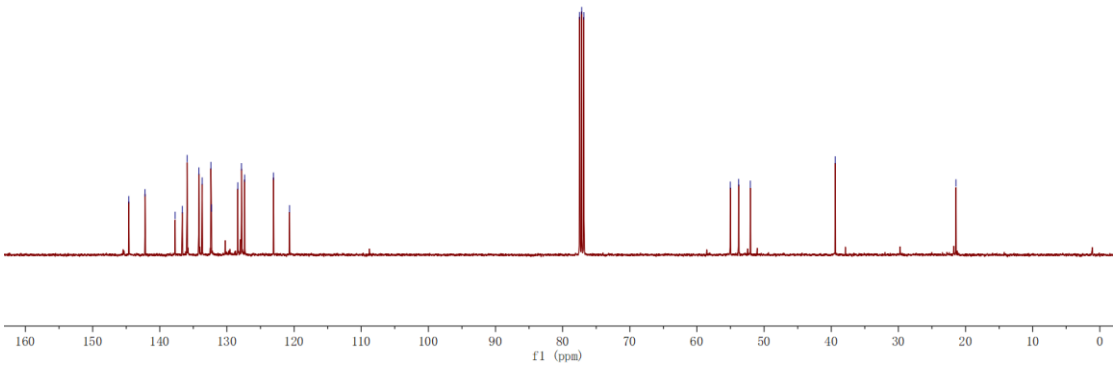
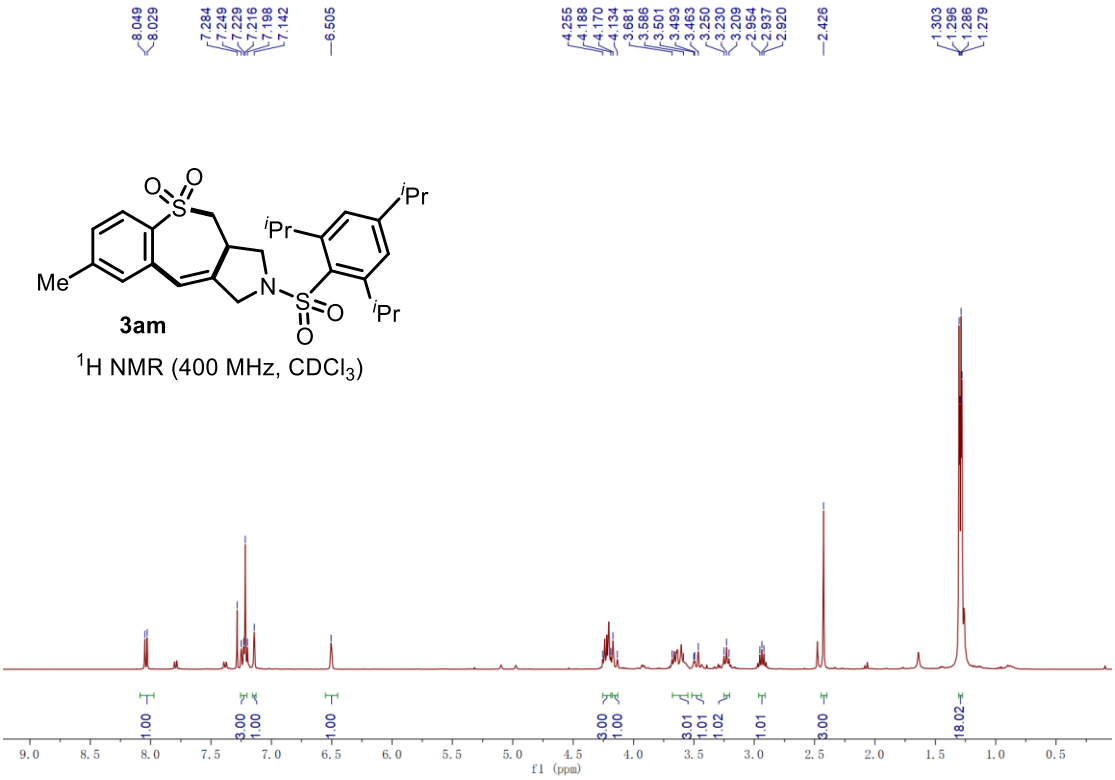


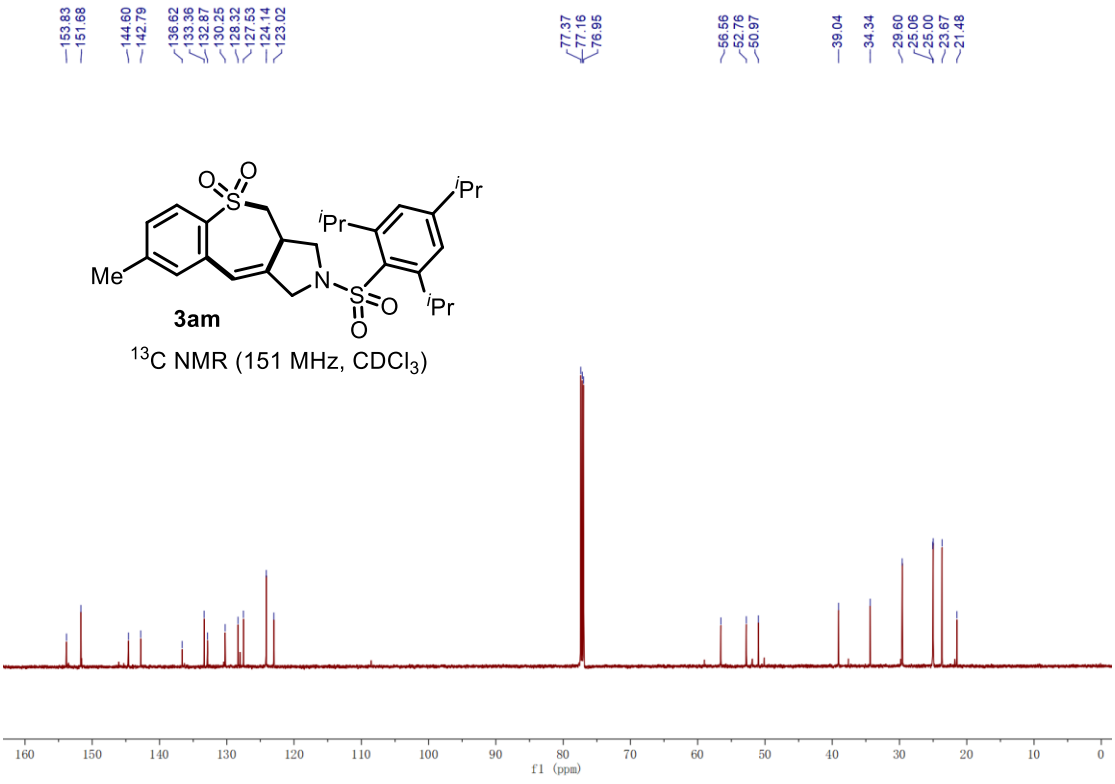


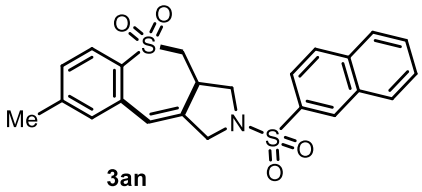
3al

^{13}C NMR (101 MHz, $CDCl_3$)



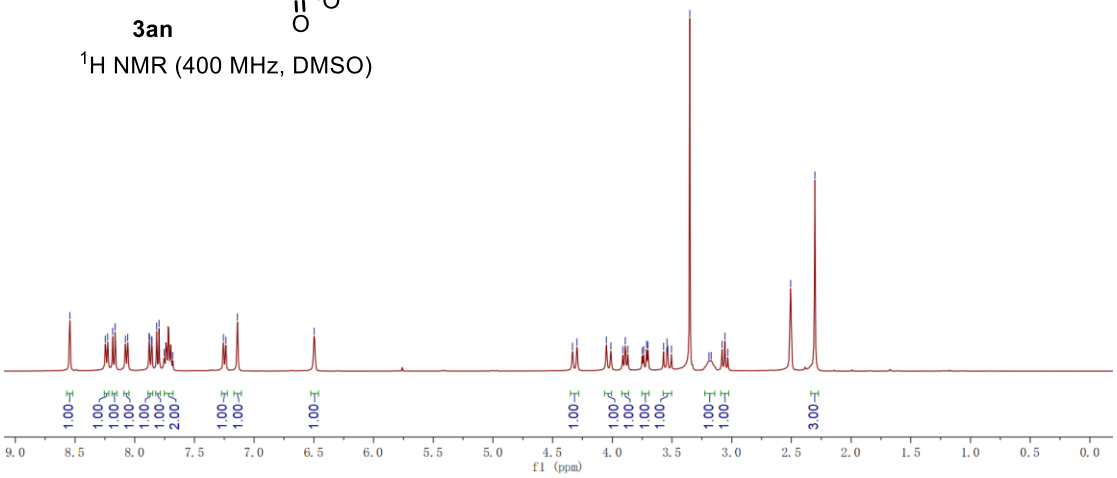

8.049
8.029
7.284
7.249
7.229
7.216
7.198
7.142
6.505
4.255
4.188
4.170
4.134
3.681
3.586
3.501
3.493
3.463
3.250
3.230
3.209
2.954
2.937
2.920
2.426
1.303
1.296
1.286
1.279
Me
N
S
O
iPr
3am
1H NMR (400 MHz, CDCl3)
1.00
3.00
1.00
1.00
3.00
1.00
3.01
1.01
1.02
1.01
3.00
18.02
f1 (ppm)

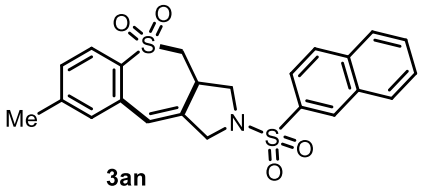

153.83
151.68
144.60
142.79
136.62
133.36
132.87
130.25
128.32
127.53
124.14
123.02
77.37
77.16
76.95
56.56
52.76
50.97
39.04
34.34
29.60
25.06
25.00
23.67
21.48
Me
N
S
O
iPr
3am
13C NMR (151 MHz, CDCl3)
f1 (ppm)



3an

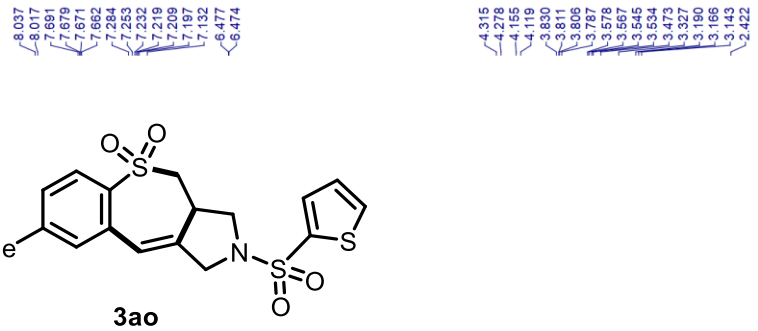
^{1}H NMR (400 MHz, DMSO)





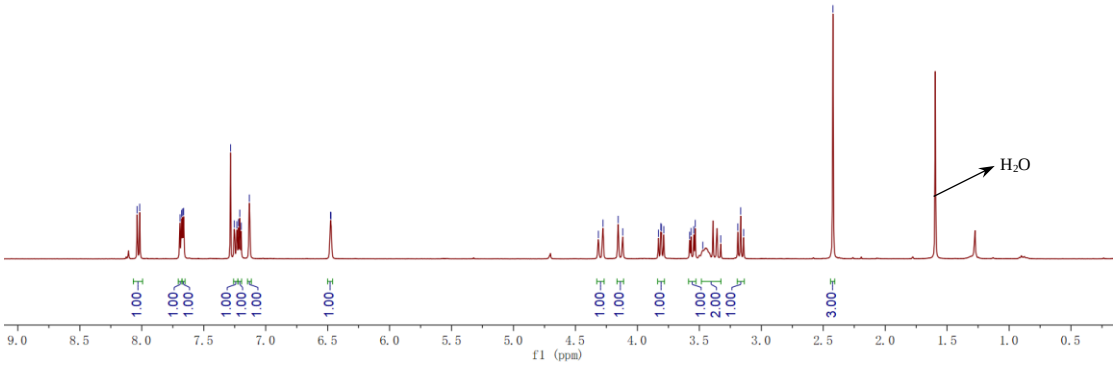
3an

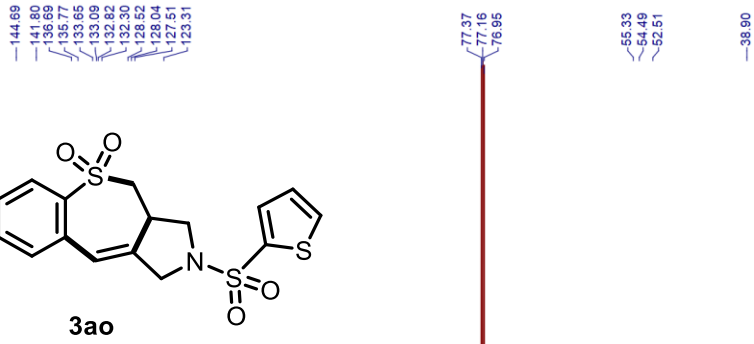
^{13}C NMR (101 MHz, DMSO)



3ao

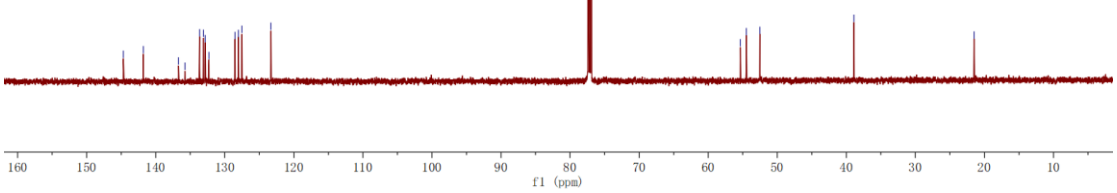
^{1}H NMR (400 MHz, $CDCl_3$)

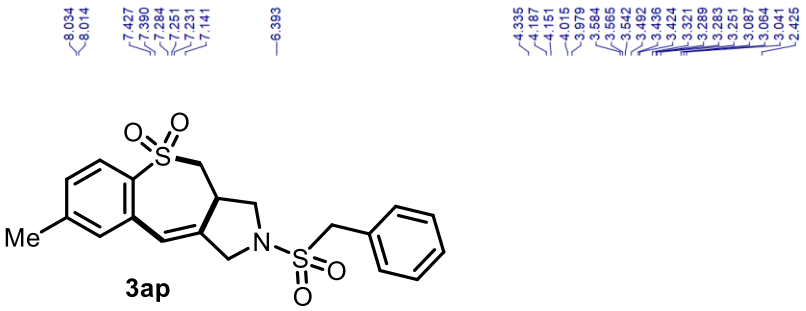




3ao

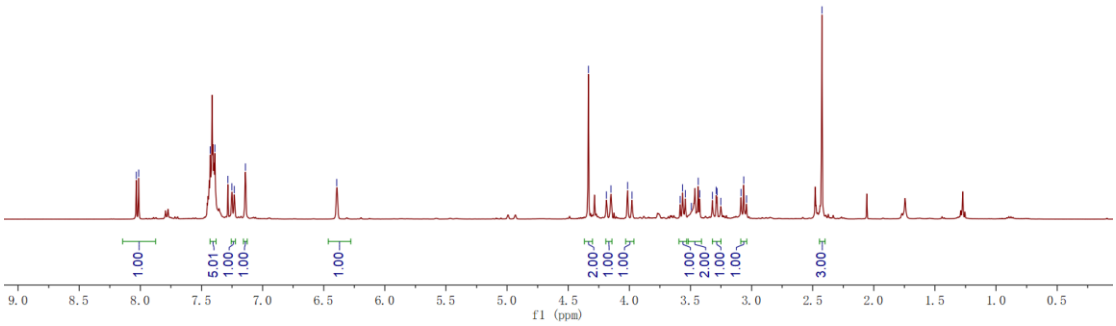
^{13}C NMR (151 MHz, $CDCl_3$)

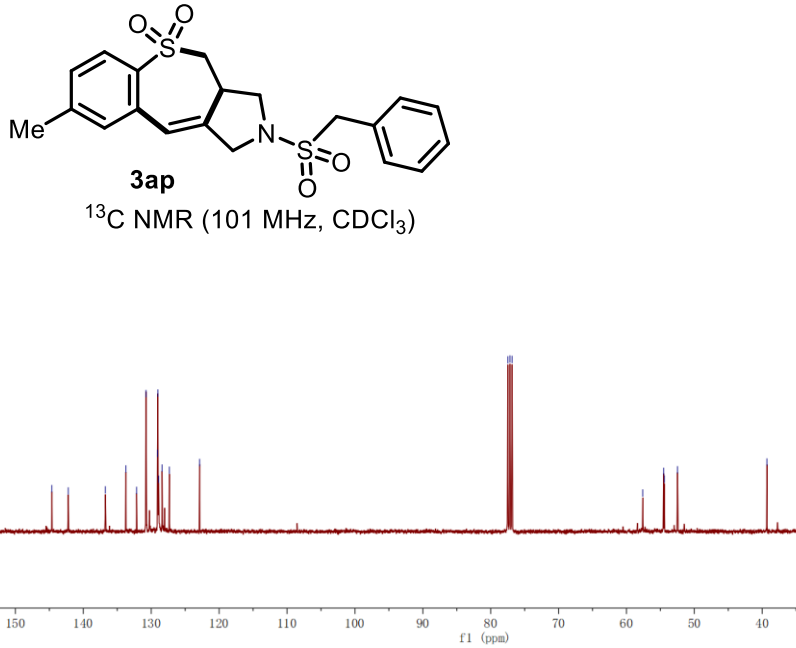




3ap

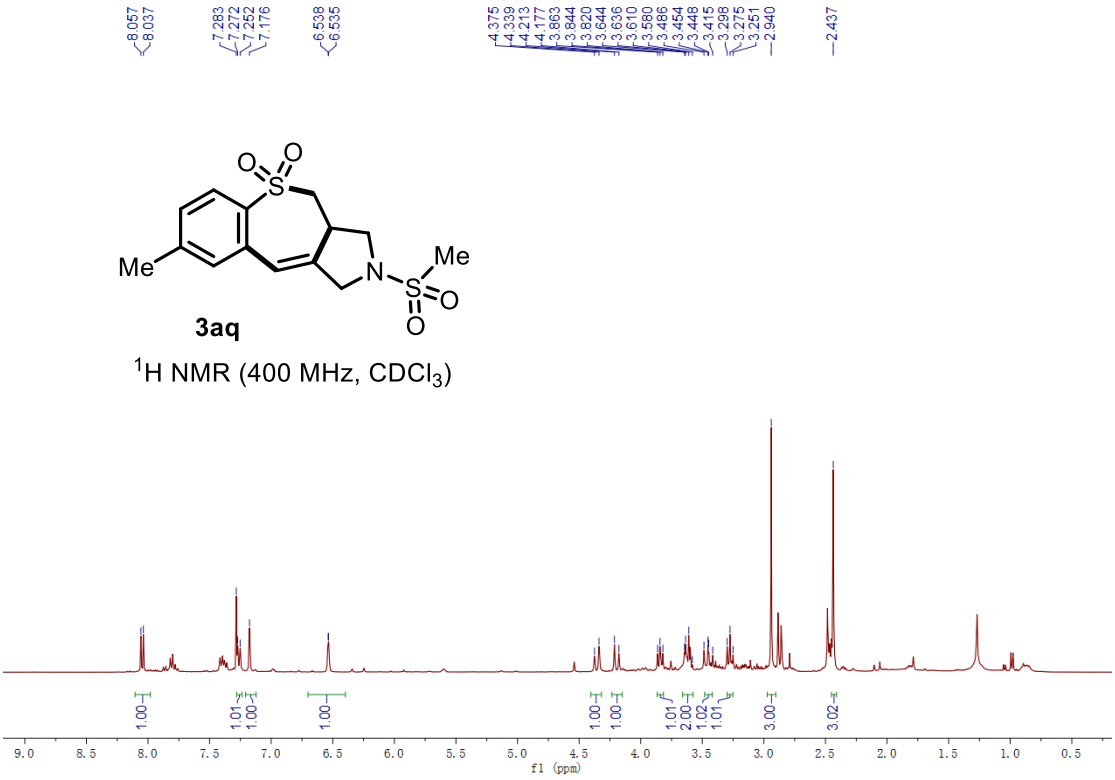
^{1}H NMR (400 MHz, $CDCl_3$)



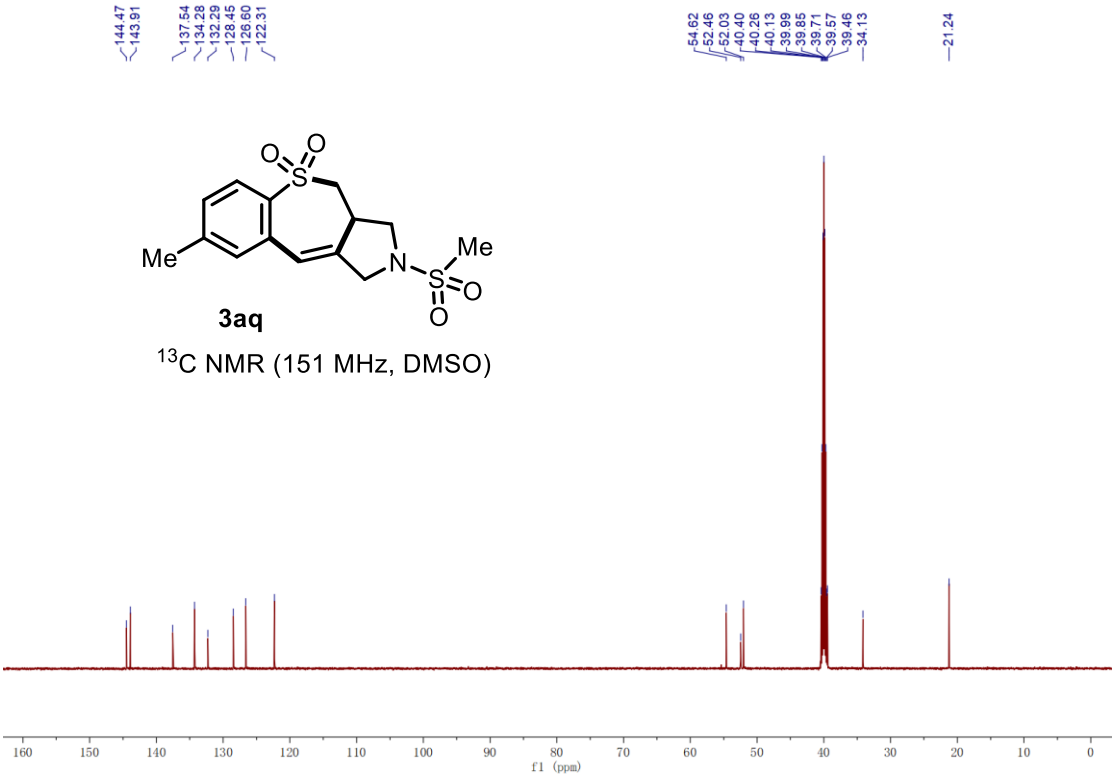


3ap

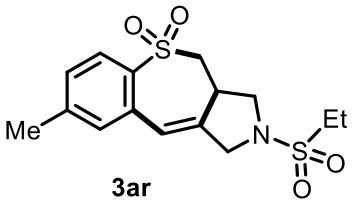
^{13}C NMR (101 MHz, $CDCl_3$)



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

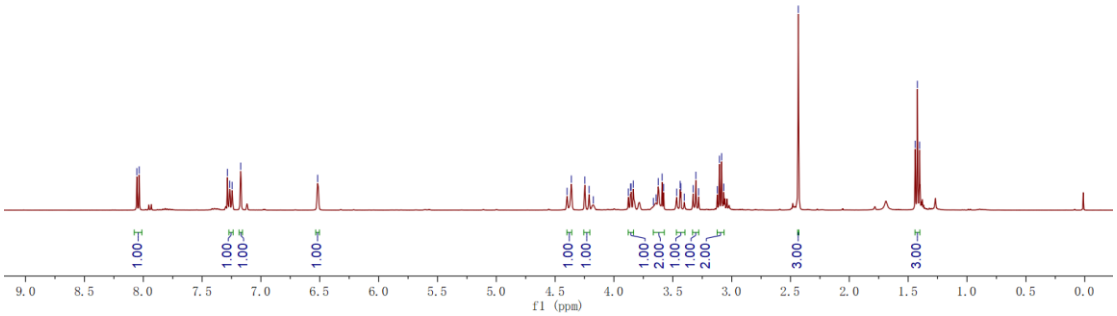


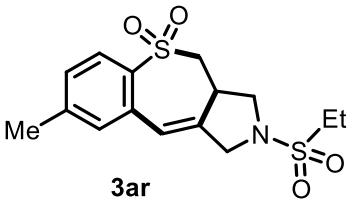
^{13}C NMR (151 MHz, DMSO)



3ar

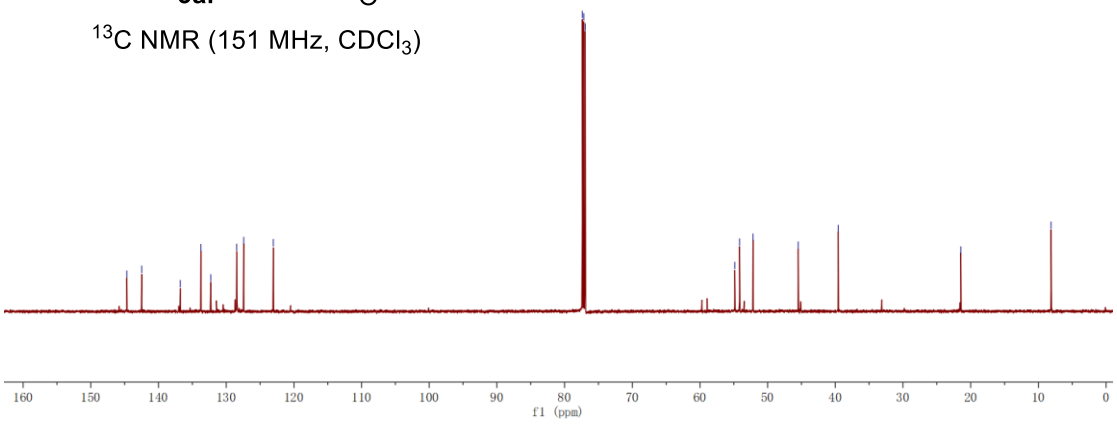
^{1}H NMR (400 MHz, $CDCl_3$)

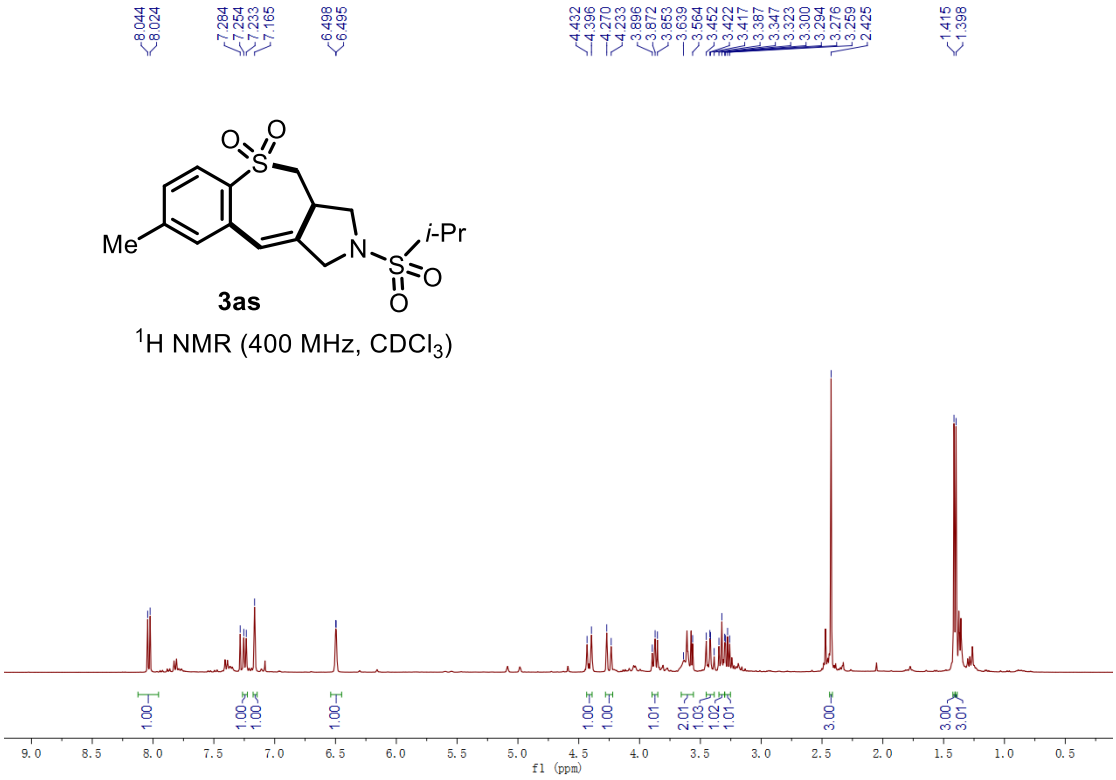




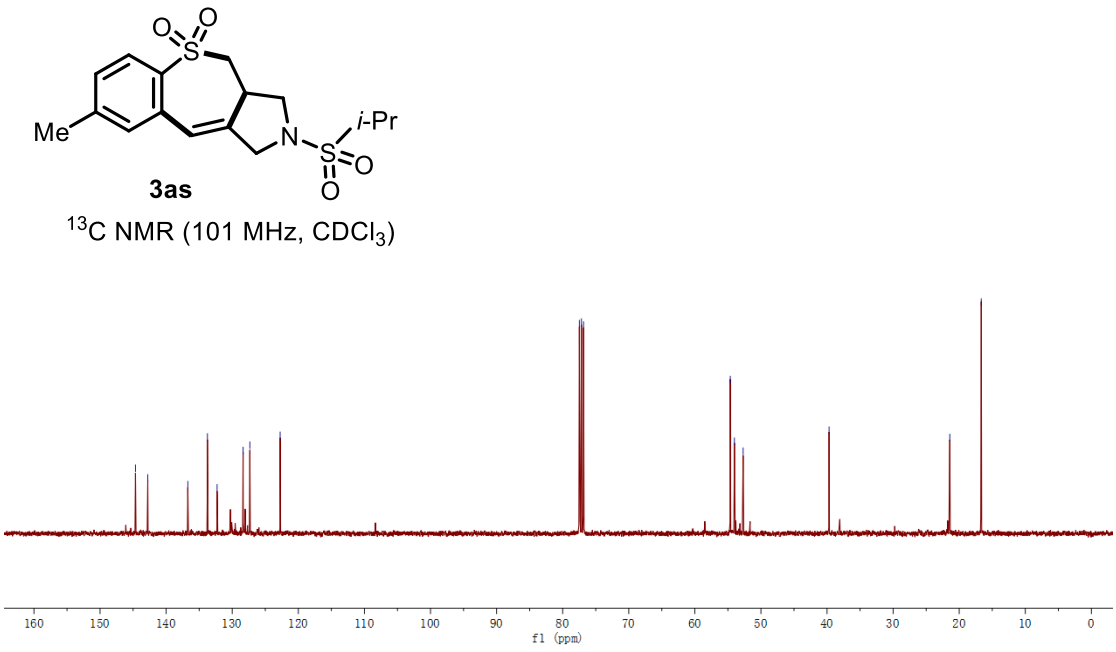
3ar

^{13}C NMR (151 MHz, $CDCl_3$)

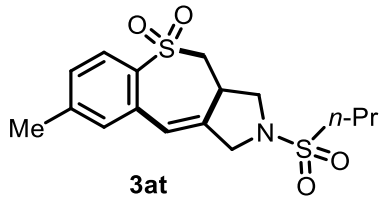




^{1}H NMR (400 MHz, $CDCl_3$)

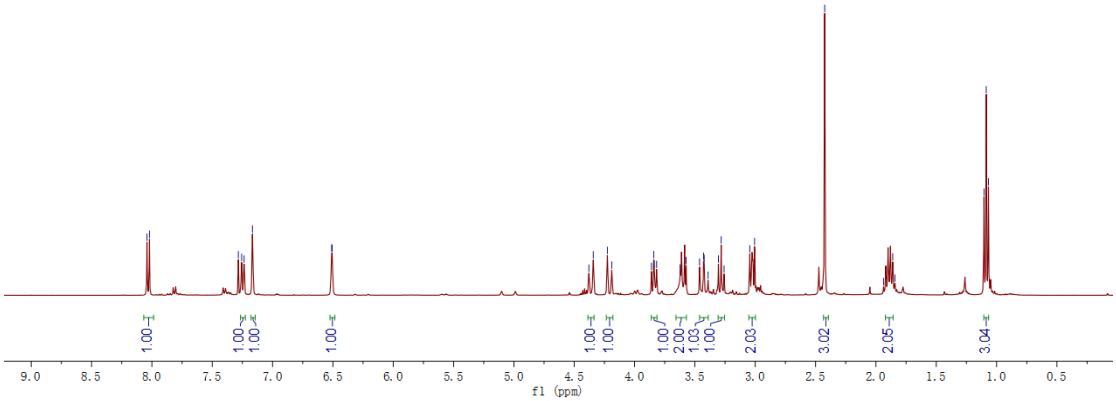


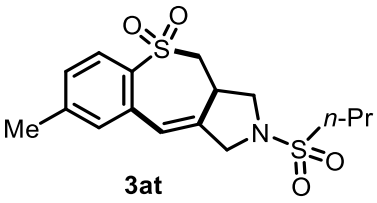
^{13}C NMR (101 MHz, $CDCl_3$)



3at

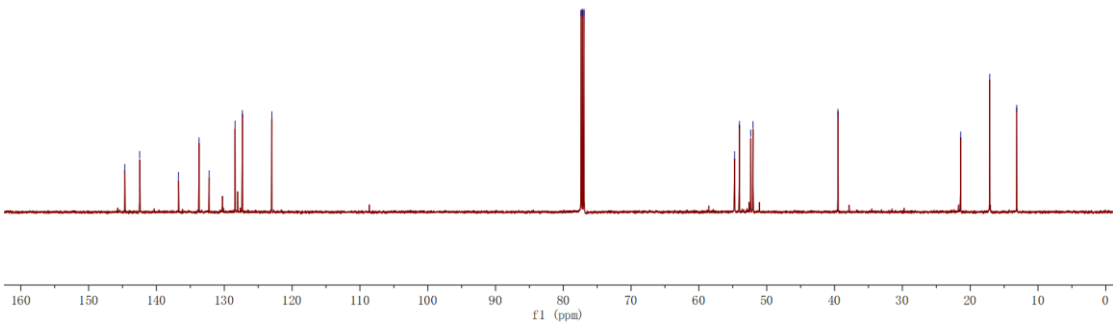
^{1}H NMR (400 MHz, $CDCl_3$)

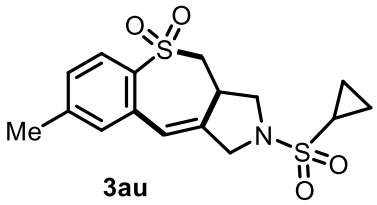




3at

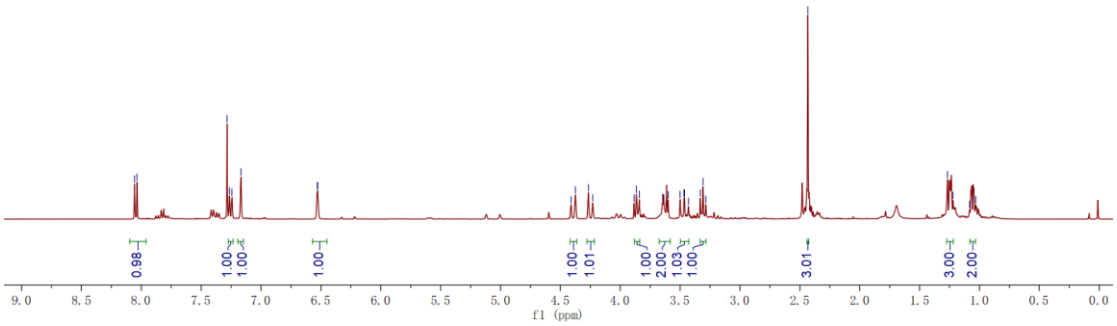
^{13}C NMR (151 MHz, $CDCl_3$)

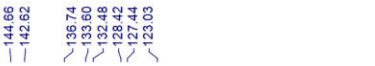


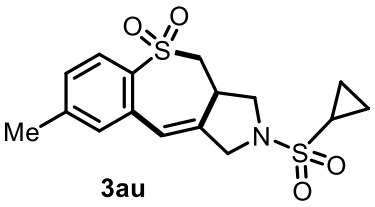


3au

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

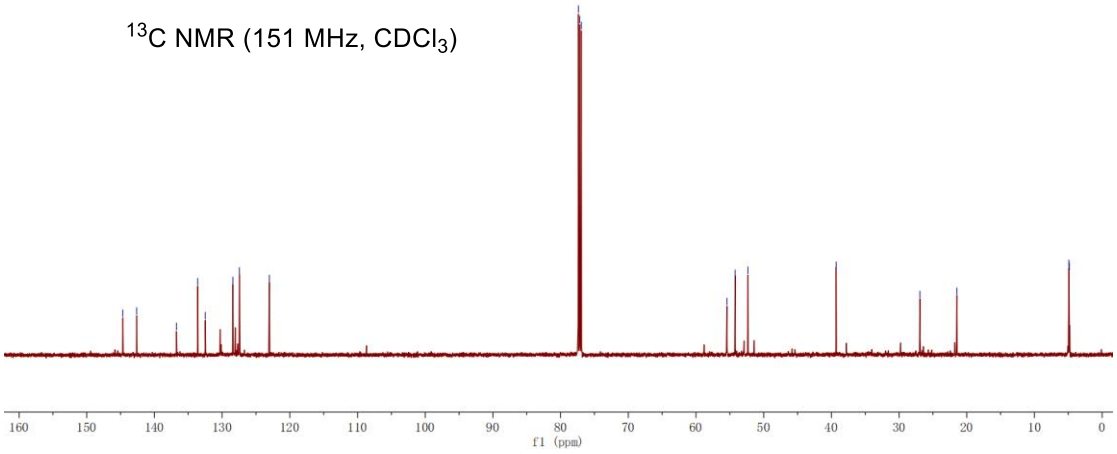


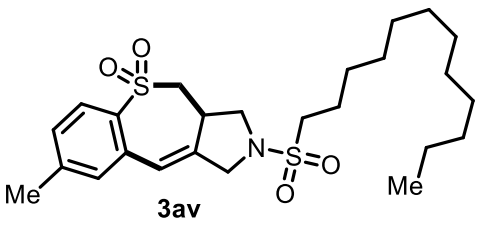




3au

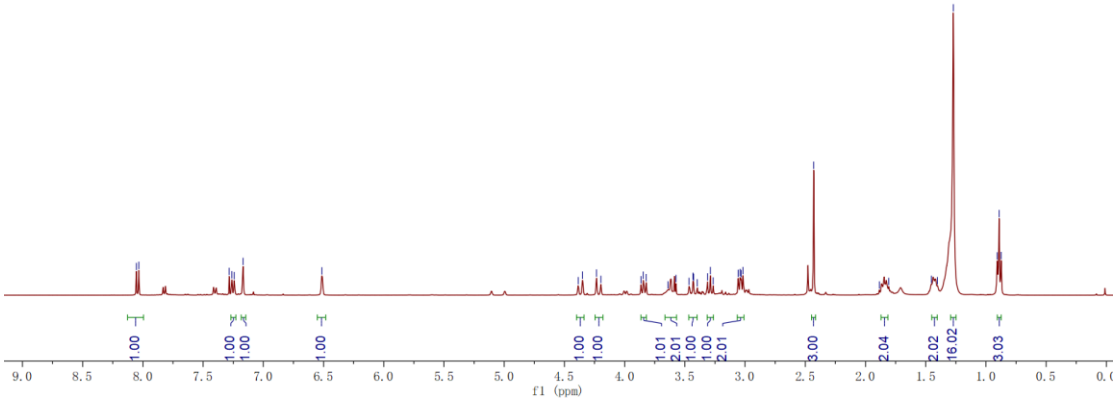
^{13}C NMR (151 MHz, $CDCl_3$)

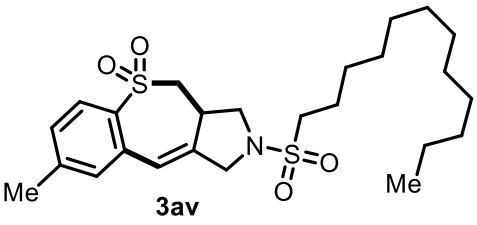




3av

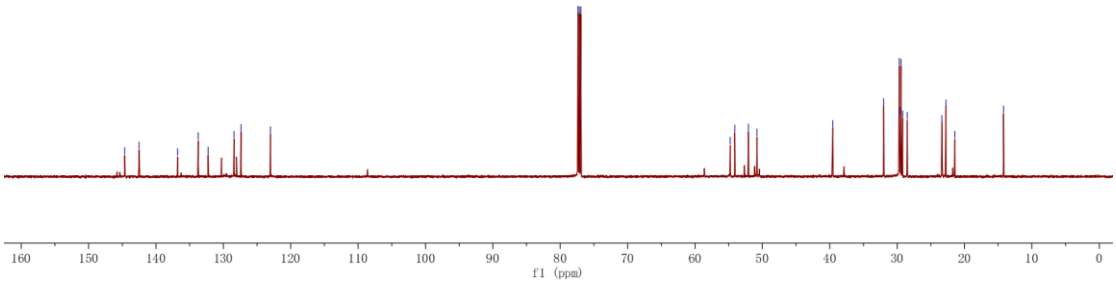
^{1}H NMR (400 MHz, $CDCl_3$)

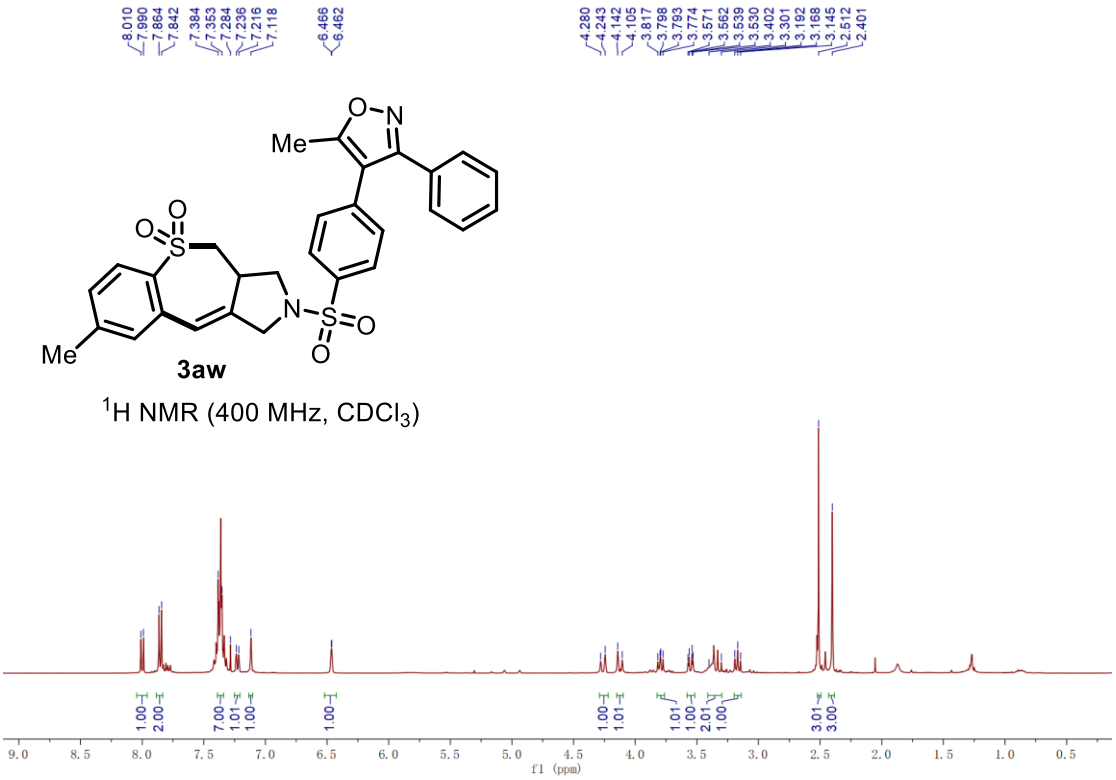




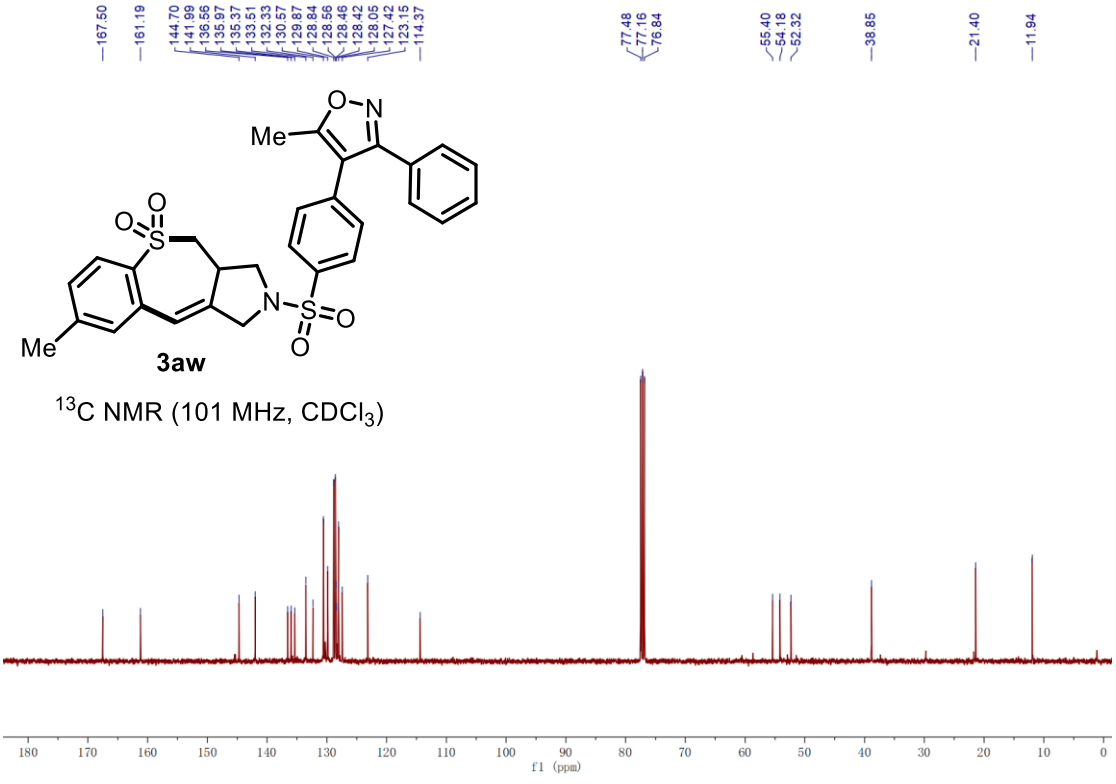
3av

^{13}C NMR (151 MHz, $CDCl_3$)

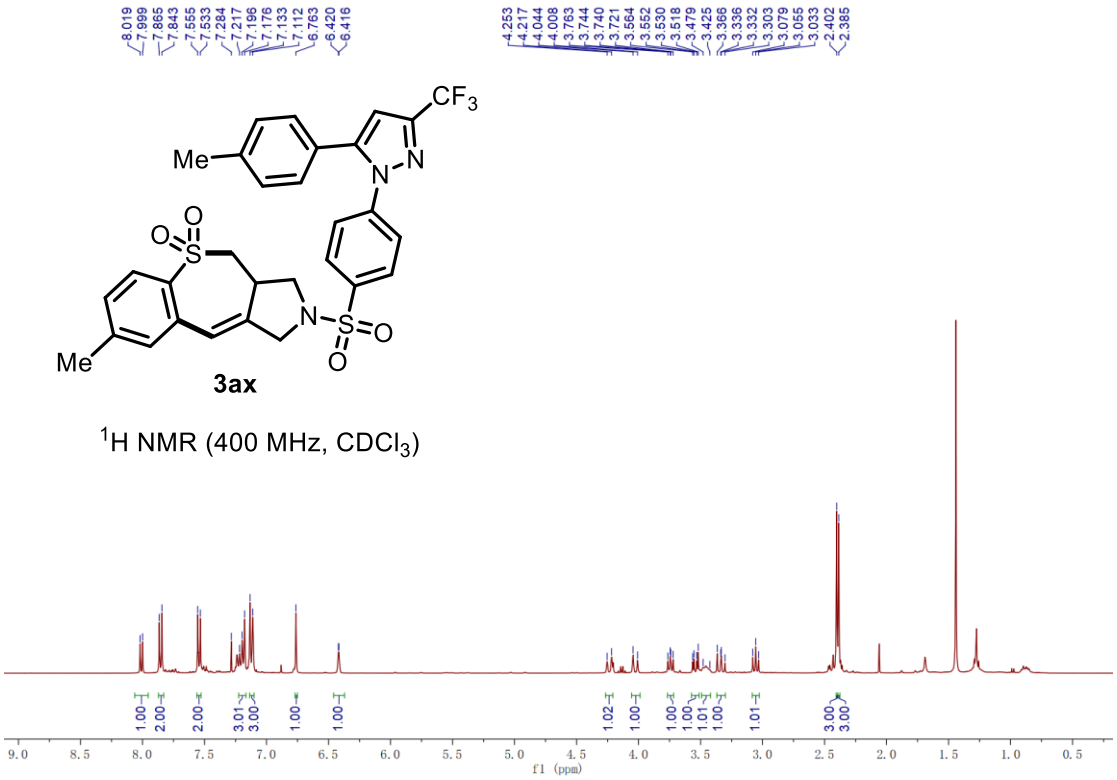


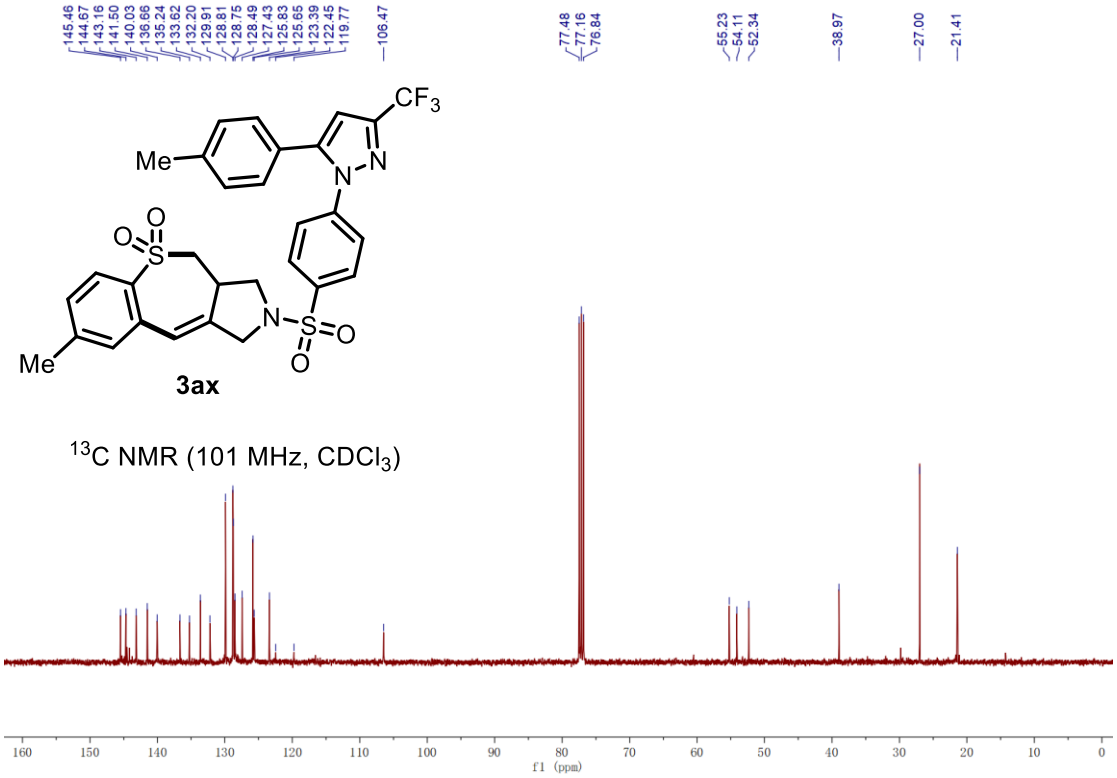


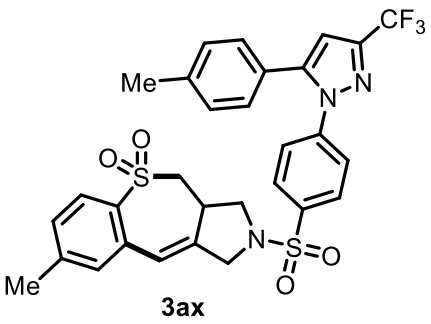
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

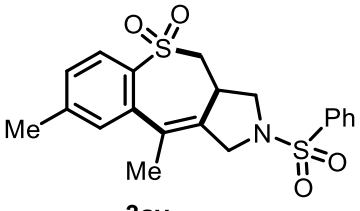

8.019
7.999
7.865
7.843
7.555
7.533
7.284
7.217
7.196
7.176
7.133
7.112
6.763
6.420
6.416
4.253
4.217
4.044
4.008
3.763
3.744
3.740
3.721
3.564
3.552
3.530
3.518
3.479
3.425
3.366
3.336
3.332
3.303
3.079
3.055
3.033
2.402
2.385
CF3
Me
N
N
O
O
S
N
S
O
O
Me
3ax
1H NMR (400 MHz, CDCl3)
1.00
2.00
2.00
3.01
3.00
1.00
1.00
1.02
1.00
1.00
1.00
1.01
1.00
1.01
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


145.46
144.67
143.16
141.50
140.03
136.66
135.24
133.62
132.20
129.91
128.81
128.75
128.49
127.43
125.83
125.65
123.39
122.45
119.77
106.47
77.48
77.16
76.84
55.23
54.11
52.34
38.97
27.00
21.41
CF3
Me
N
N
O
O
S
N
S
O
O
Me
3ax
13C NMR (101 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



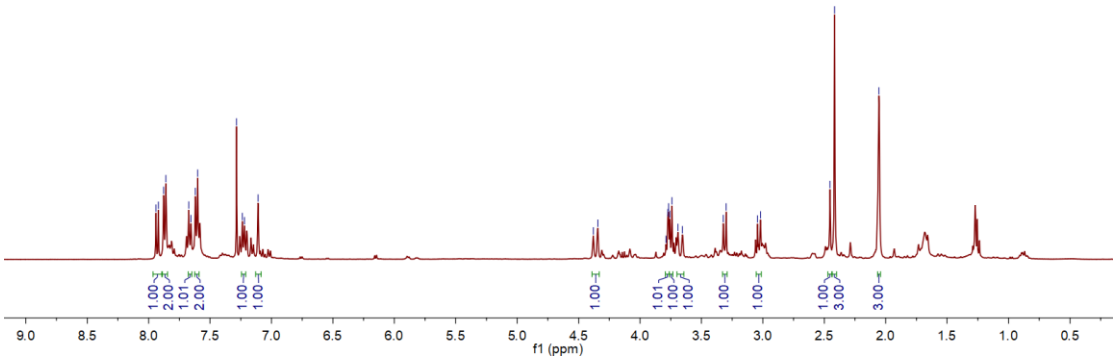
3ax

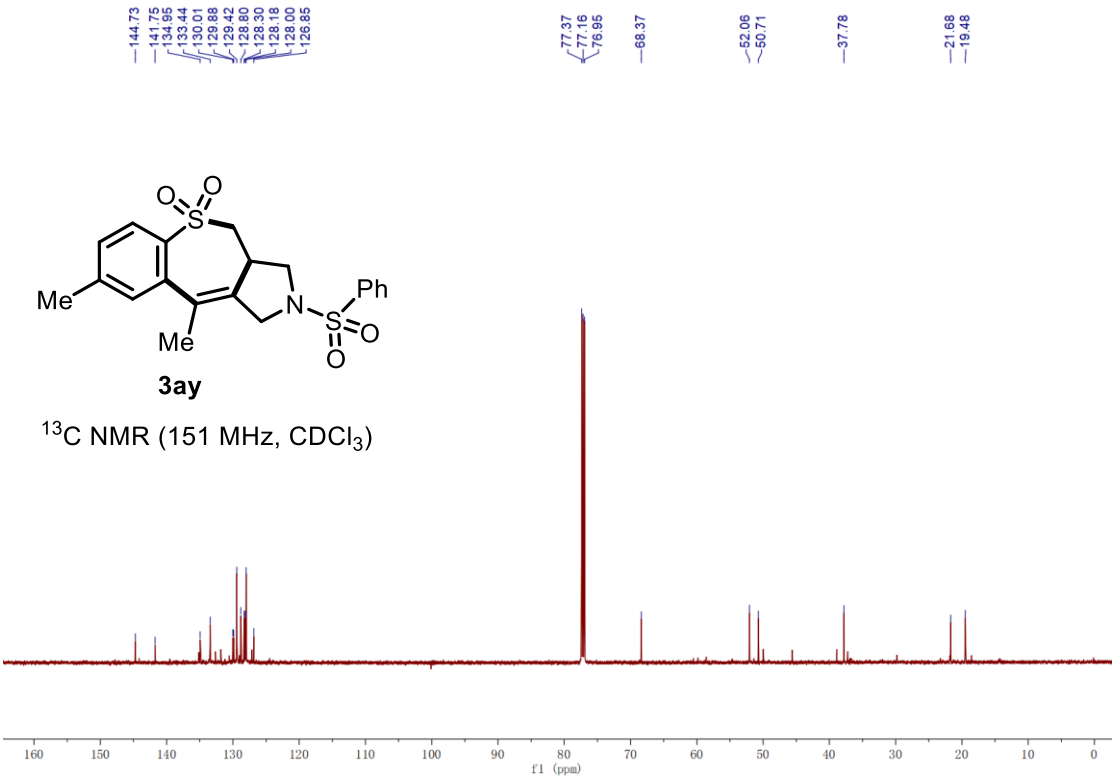
^{19}F NMR (377 MHz, $CDCl_3$)

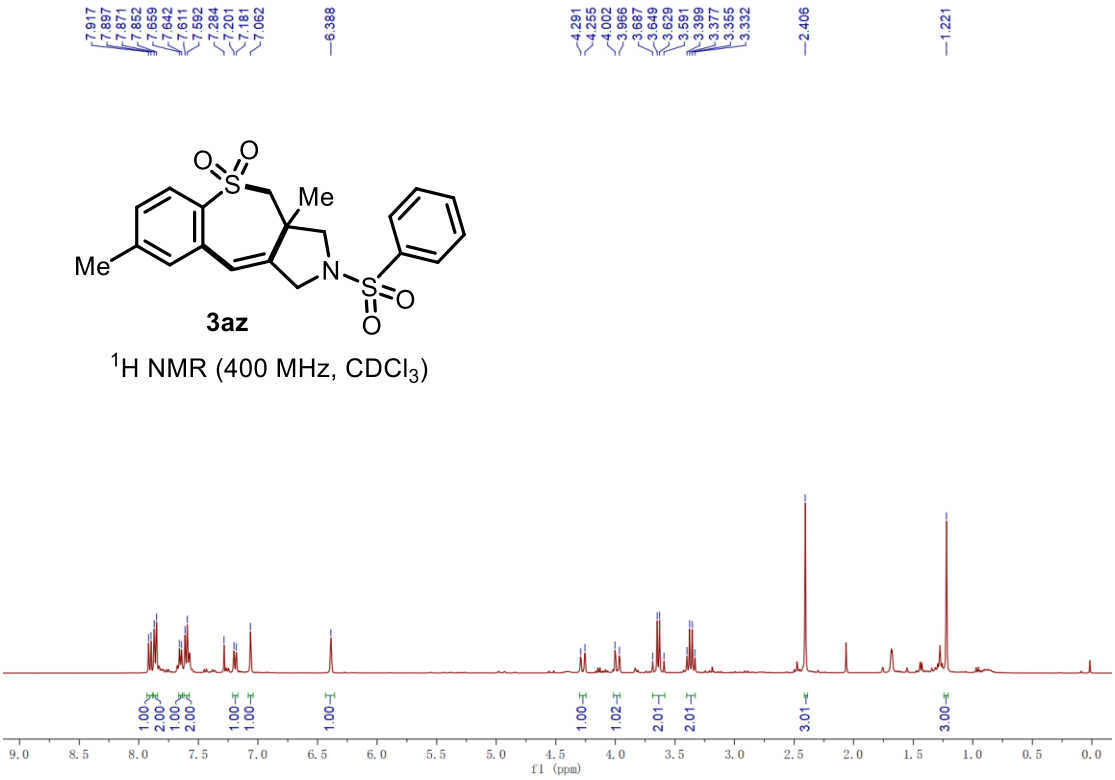


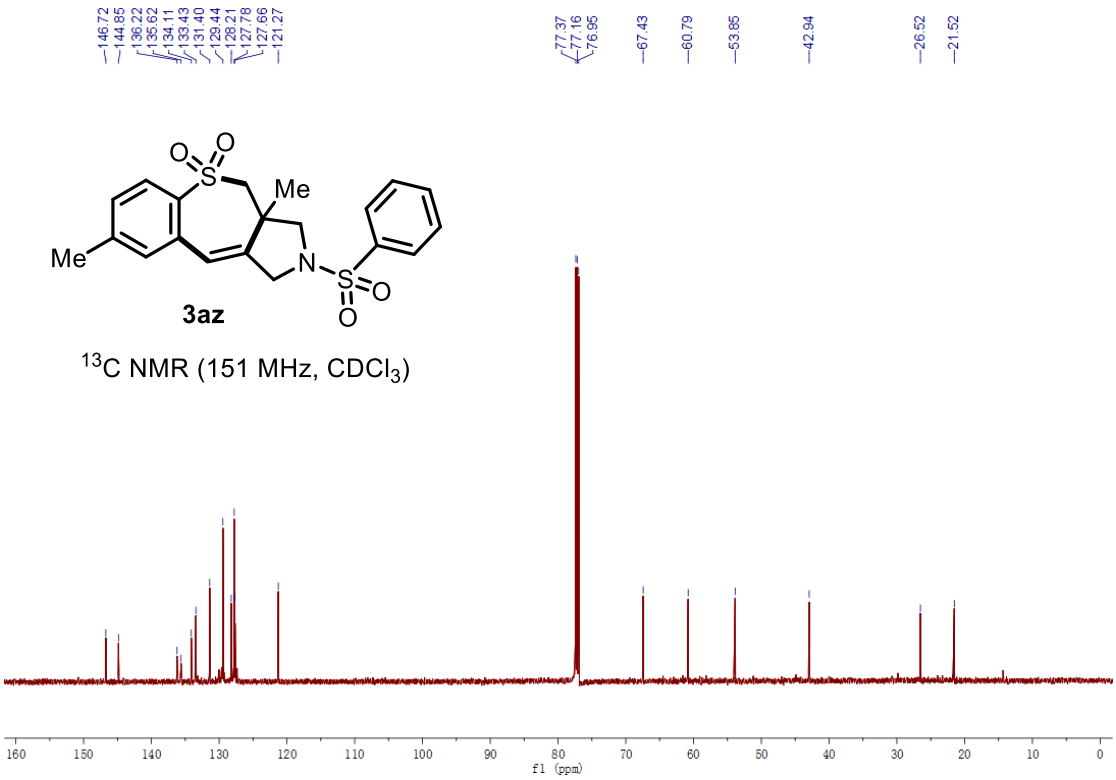
3ay

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



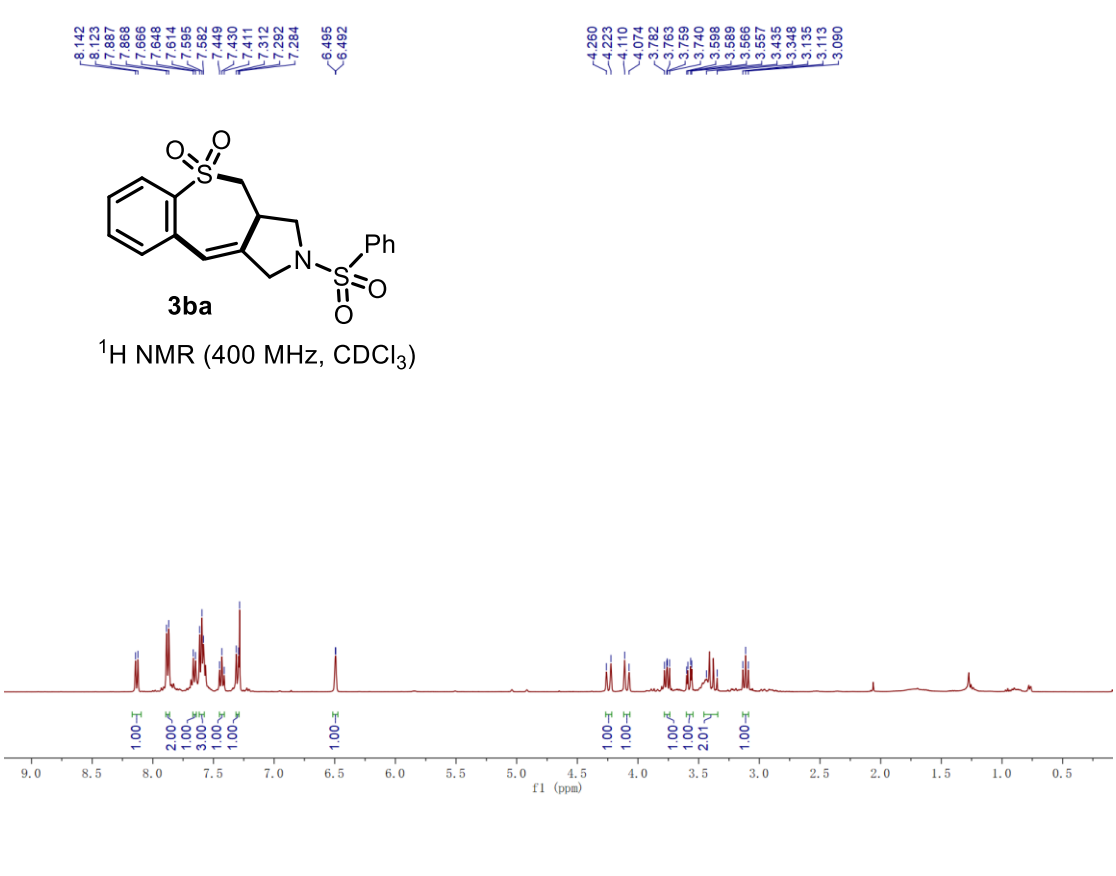

144.73
141.75
134.65
133.44
130.01
129.88
129.42
128.80
128.30
128.18
128.00
126.85
77.37
77.16
76.95
68.37
52.06
50.71
37.78
21.68
19.48
Me
Me
N
S
O
O
Ph
3ay
13C NMR (151 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.917
7.897
7.871
7.852
7.659
7.642
7.611
7.592
7.284
7.201
7.181
7.062
6.388
4.291
4.255
4.002
3.966
3.687
3.649
3.629
3.591
3.399
3.377
3.355
3.332
2.406
1.221
Me
Me
N
S
O
O
3az
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
2.00
1.00
1.00
1.00
1.00
1.02
2.01
2.01
3.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



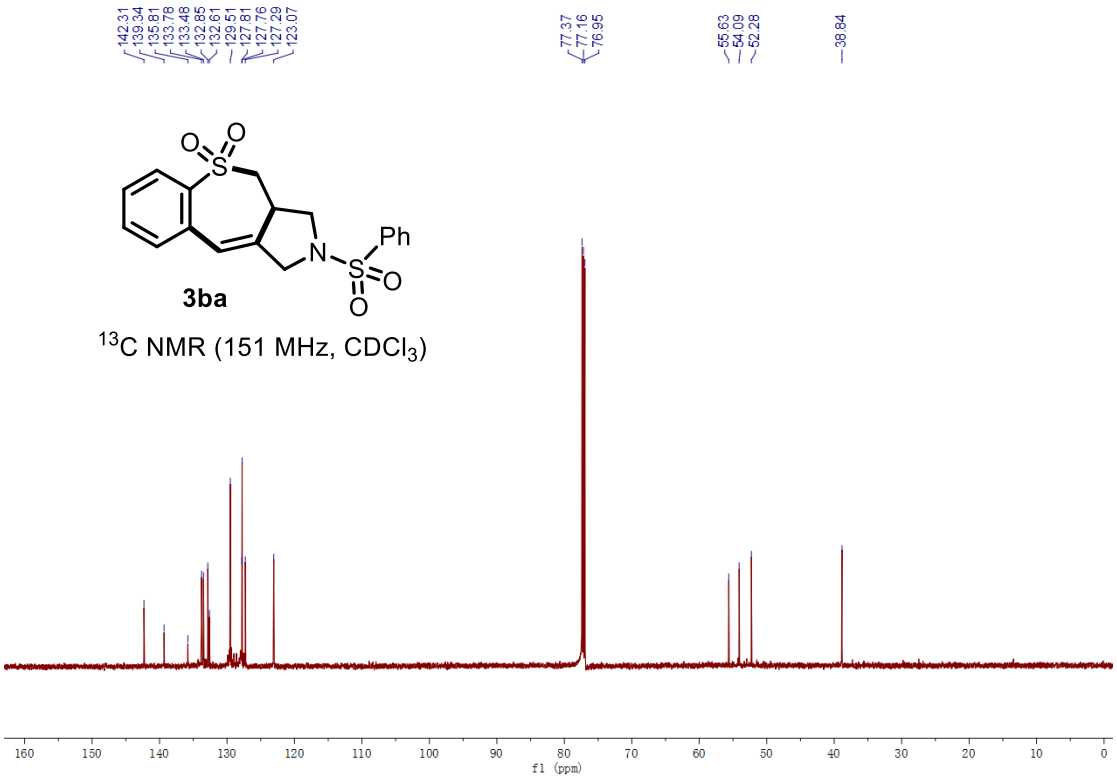
3az

^{13}C NMR (151 MHz, $CDCl_3$)



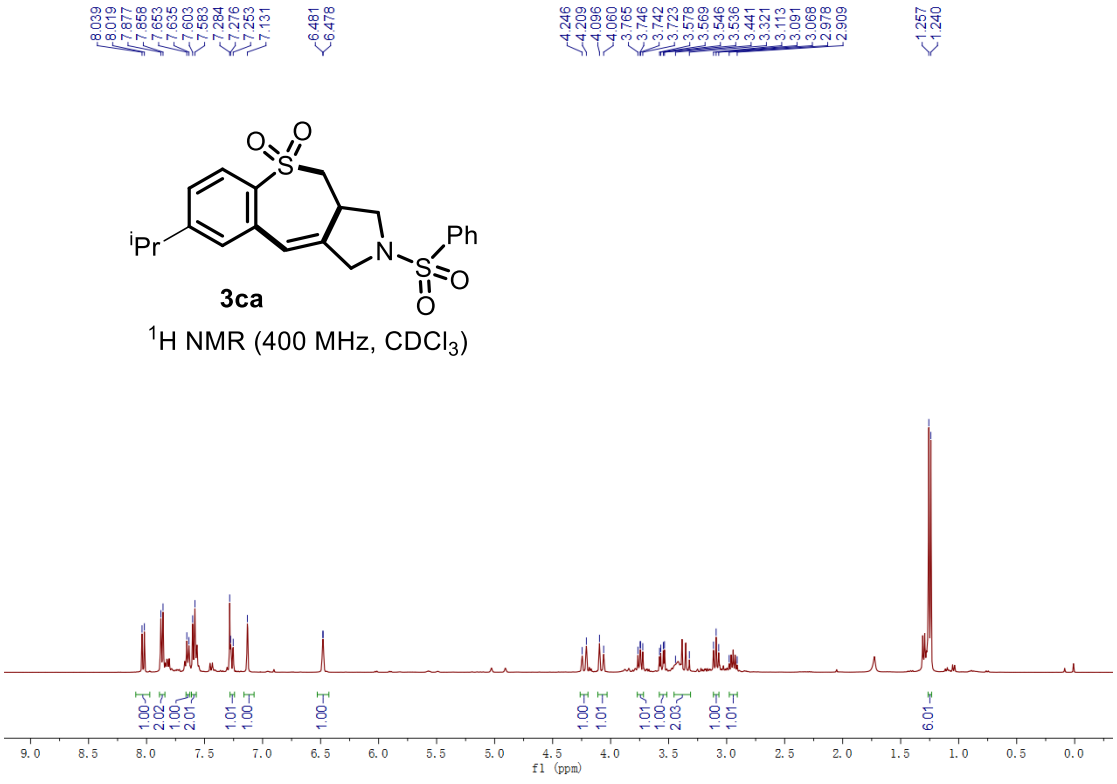
3ba

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



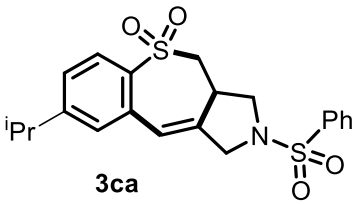
3ba

^{13}C NMR (151 MHz, $CDCl_3$)



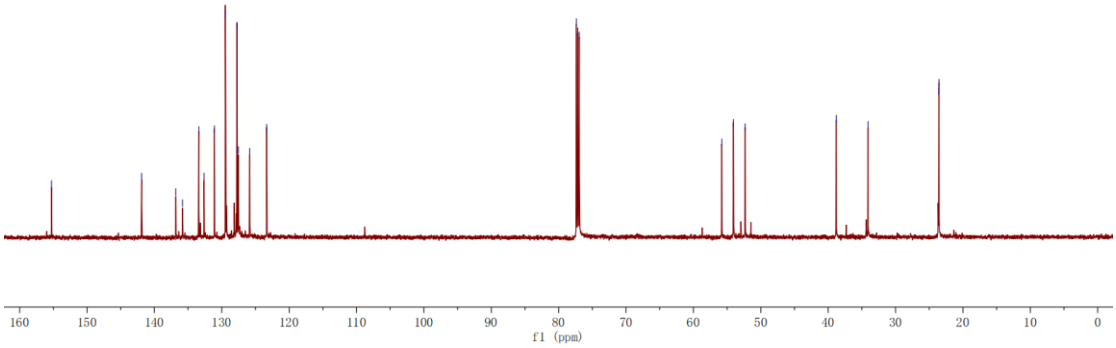
3ca

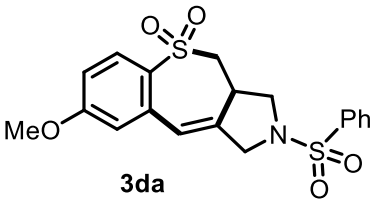
^{1}H NMR (400 MHz, $CDCl_3$)



3ca

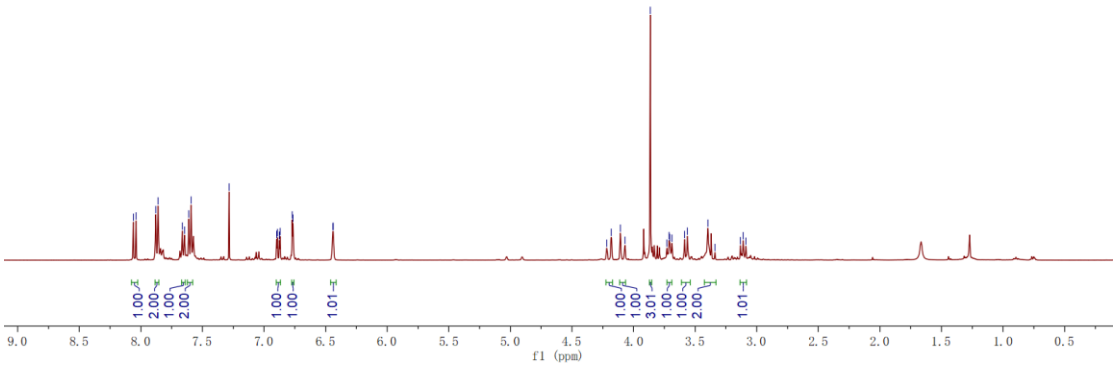
^{13}C NMR (151 MHz, $CDCl_3$)

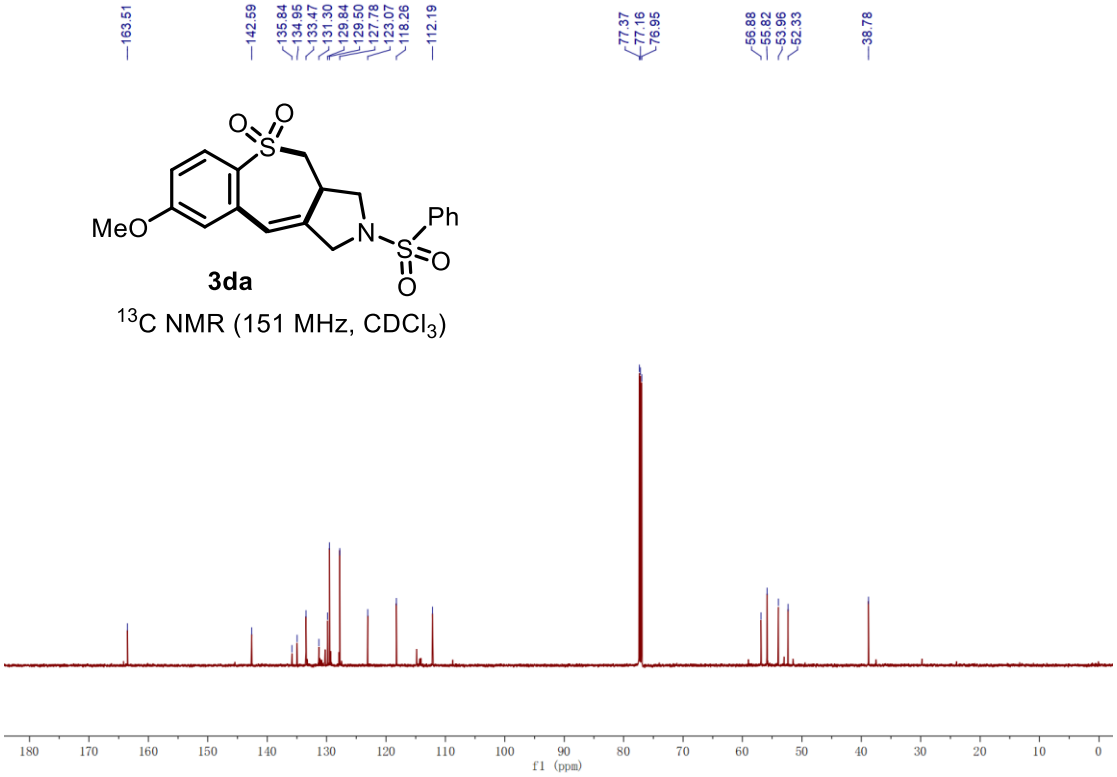




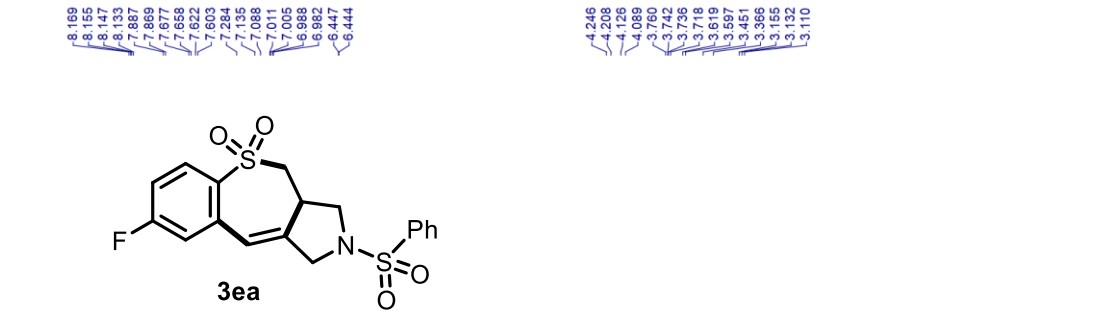
3da

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

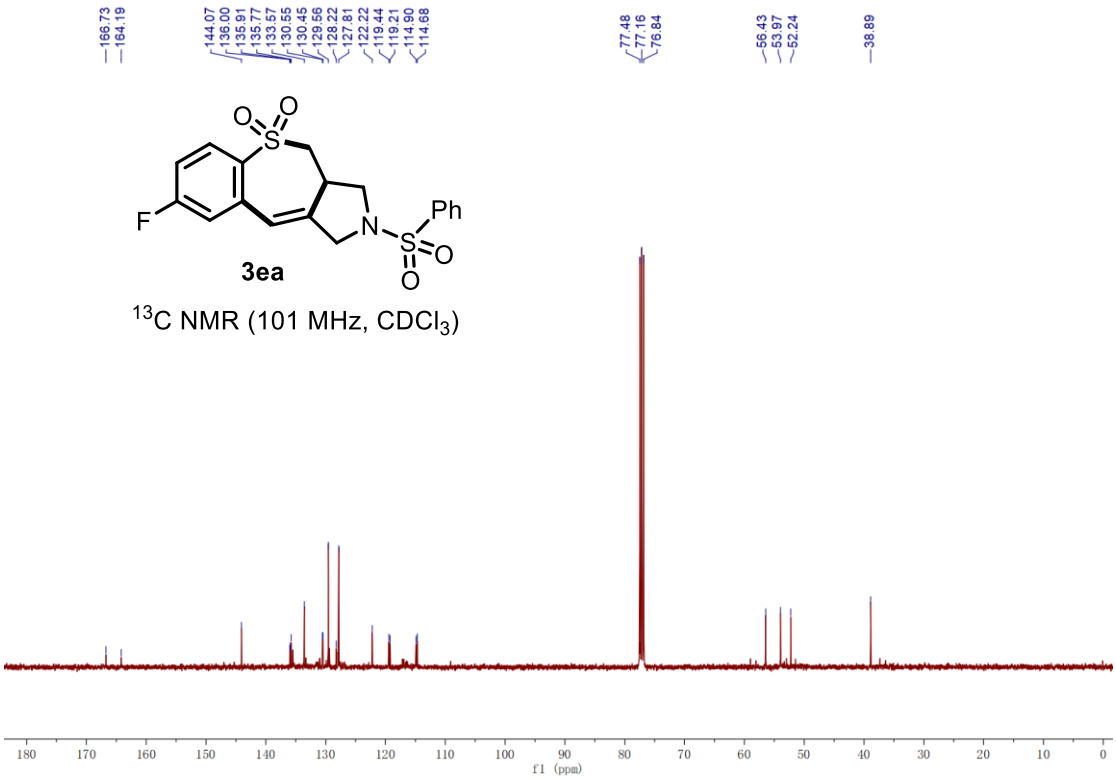




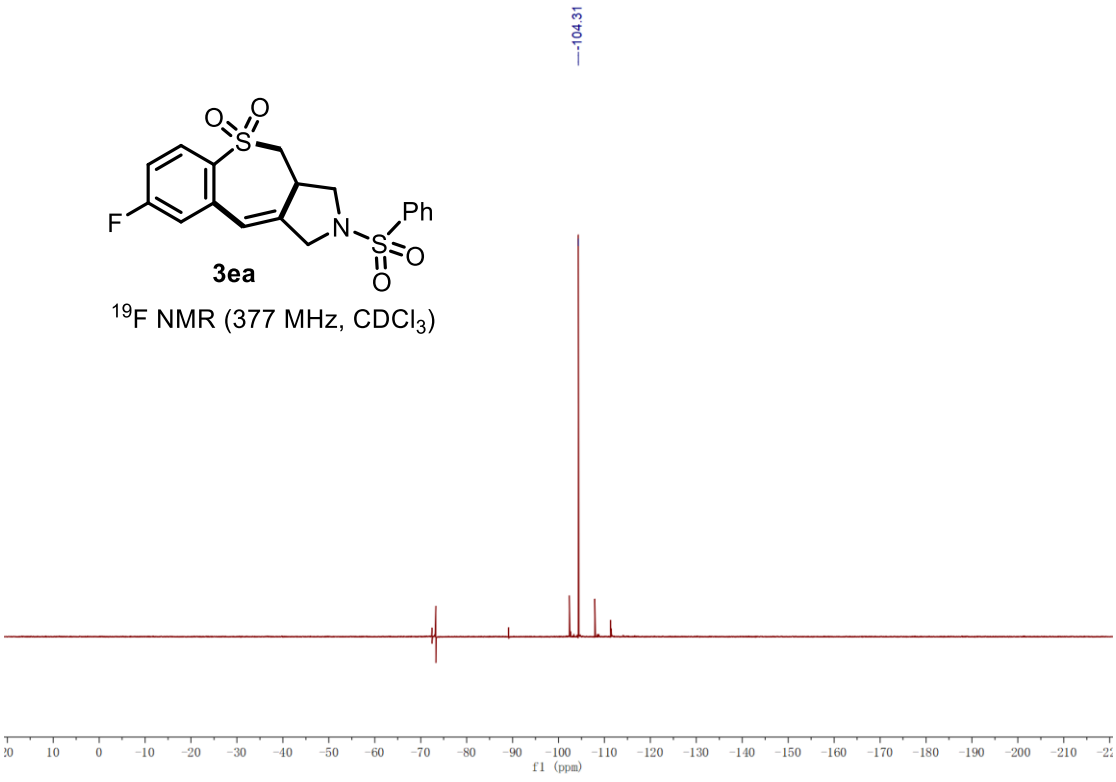
^{13}C NMR (151 MHz, $CDCl_3$)



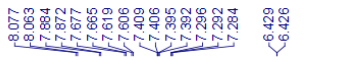
^{1}H NMR (400 MHz, $CDCl_3$)

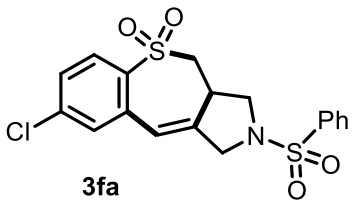


^{13}C NMR (101 MHz, $CDCl_3$)



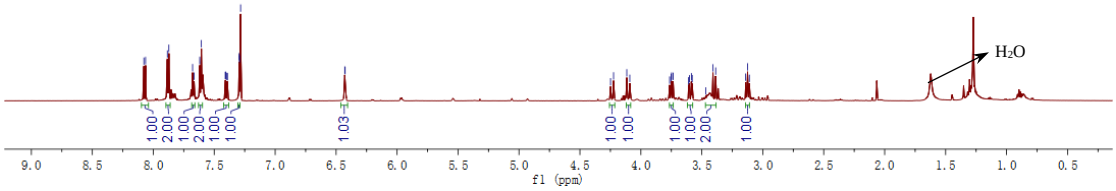
^{19}F NMR (377 MHz, $CDCl_3$)

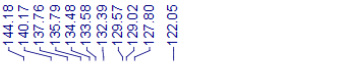


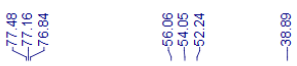


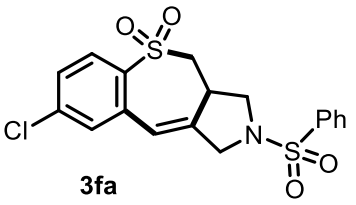
3fa

^{1}H NMR (600 MHz, $CDCl_3$)



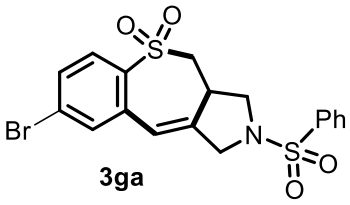






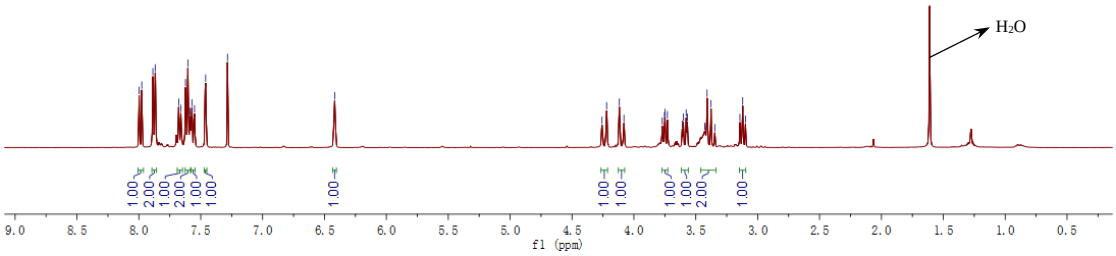
3fa

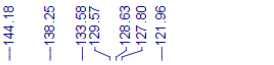
^{13}C NMR (101 MHz, $CDCl_3$)

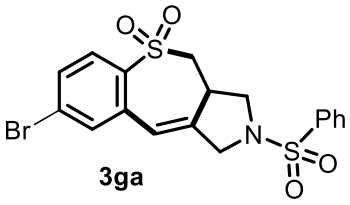


3ga

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

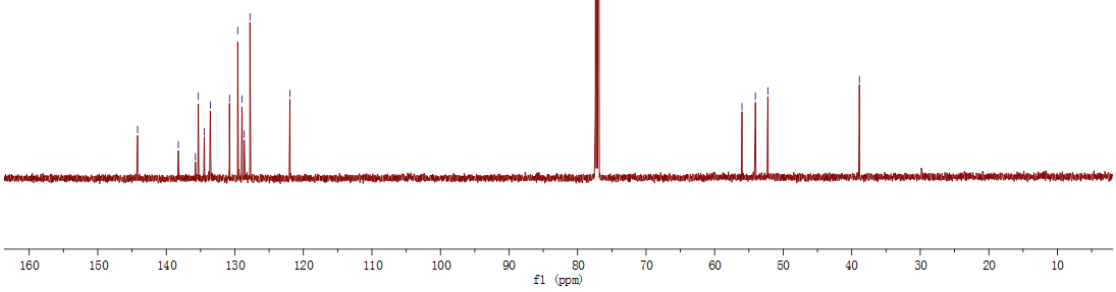


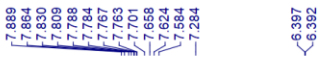


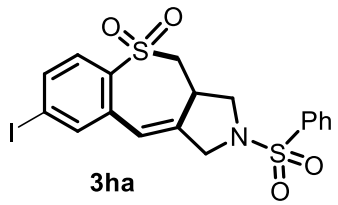


3ga

^{13}C NMR (151 MHz, $CDCl_3$)

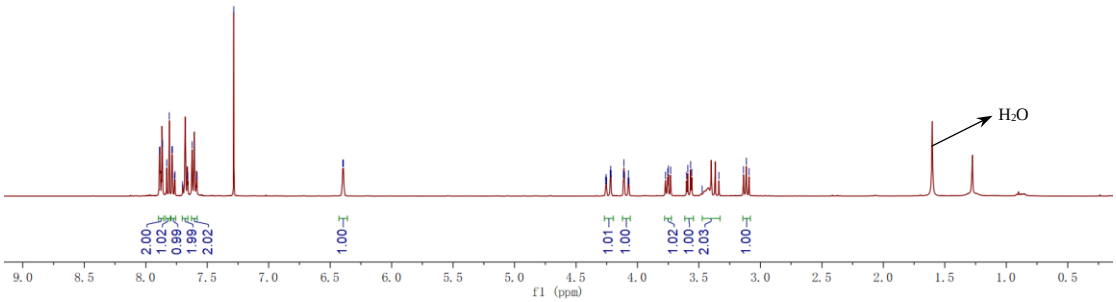


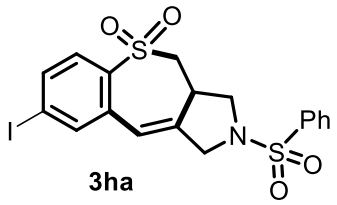




3ha

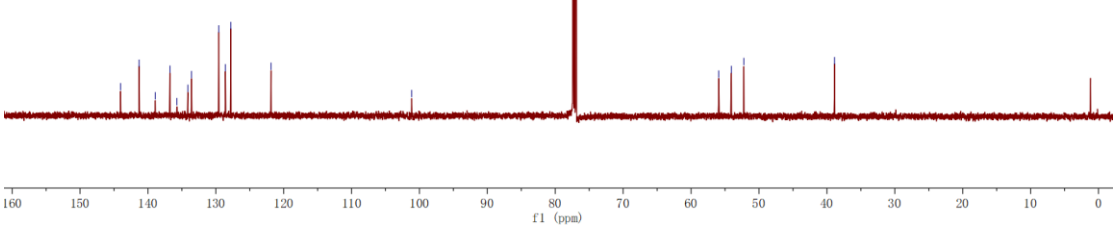
^{1}H NMR (400 MHz, $CDCl_3$)

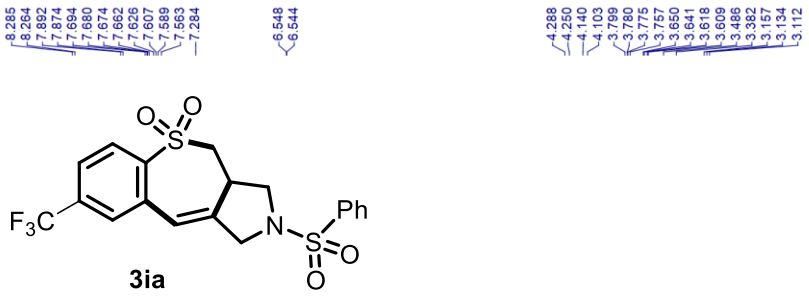




3ha

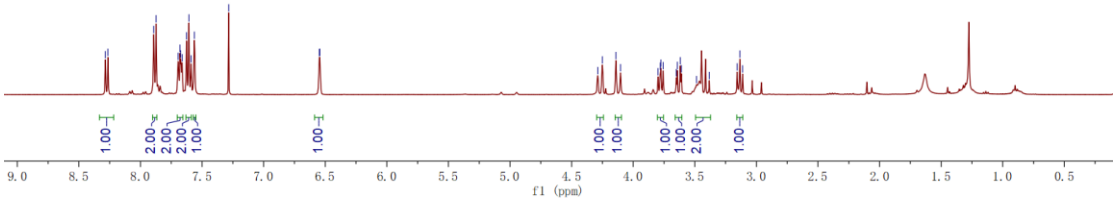
^{13}C NMR (151 MHz, $CDCl_3$)

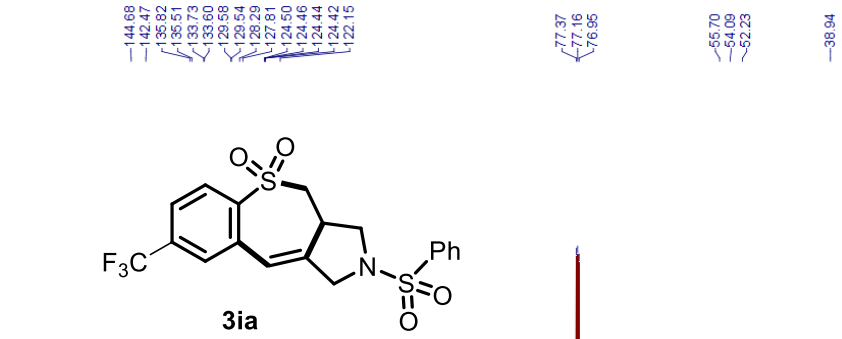




3ia

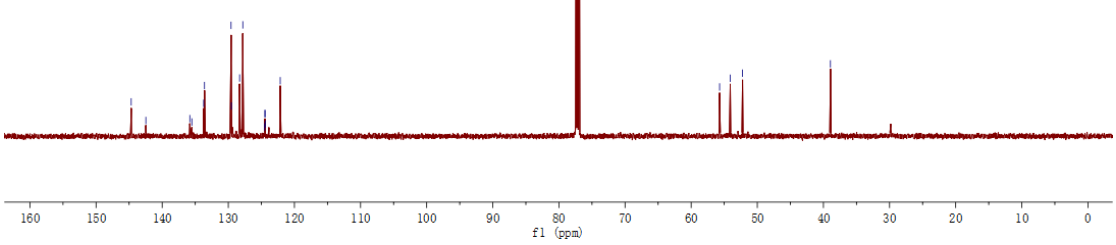
^{1}H NMR (400 MHz, $CDCl_3$)

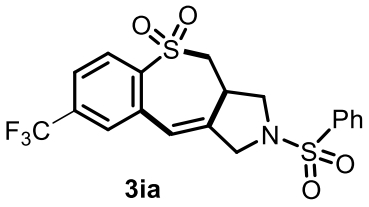




3ia

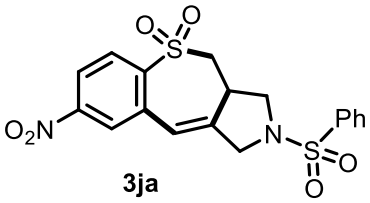
^{13}C NMR (151 MHz, $CDCl_3$)





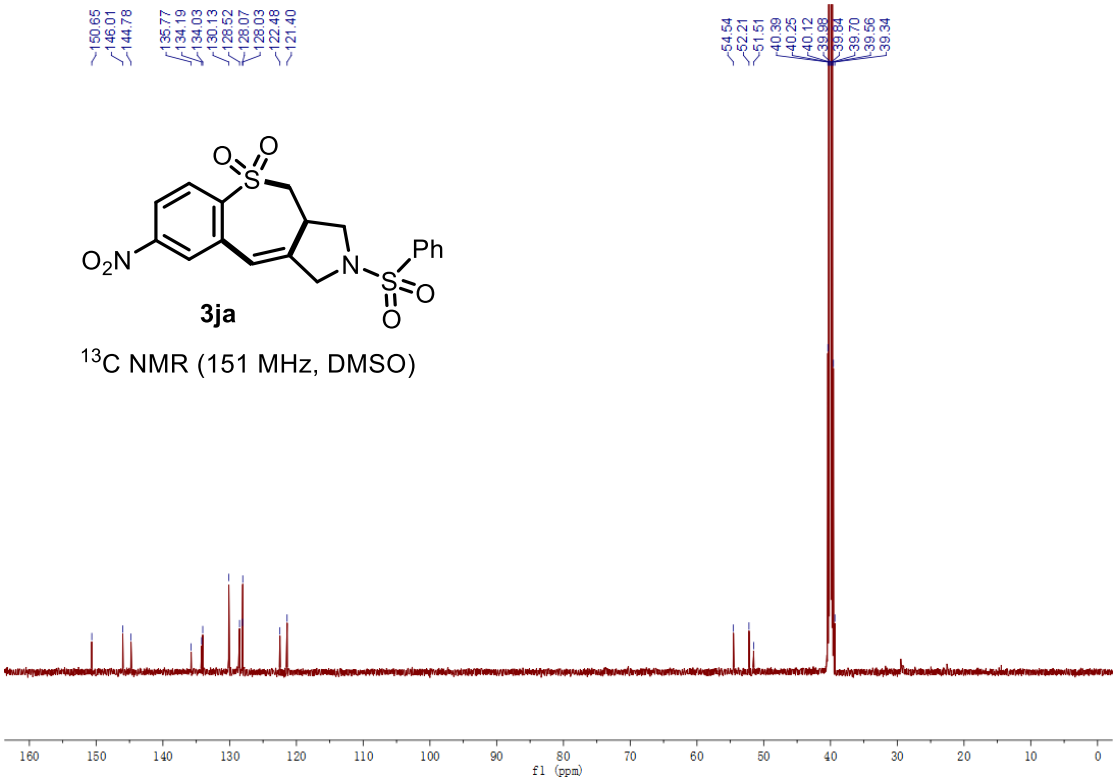
3ia

^{19}F NMR (377 MHz, $CDCl_3$)



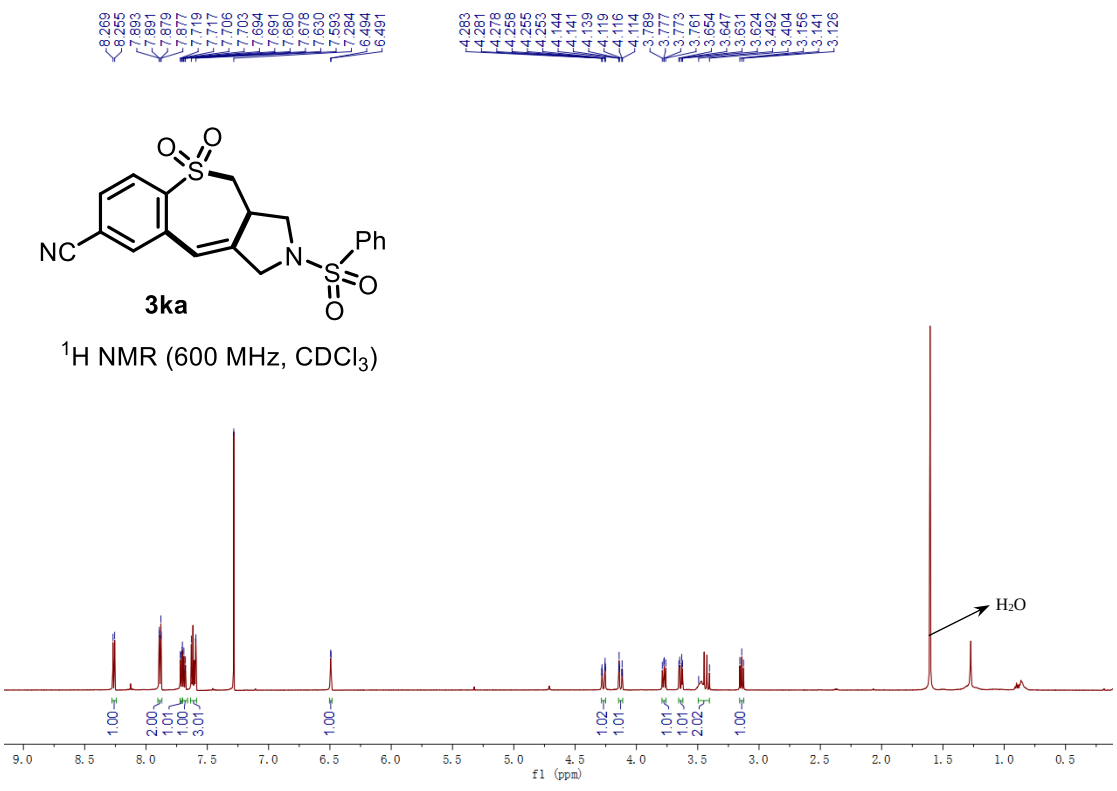
3ja

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



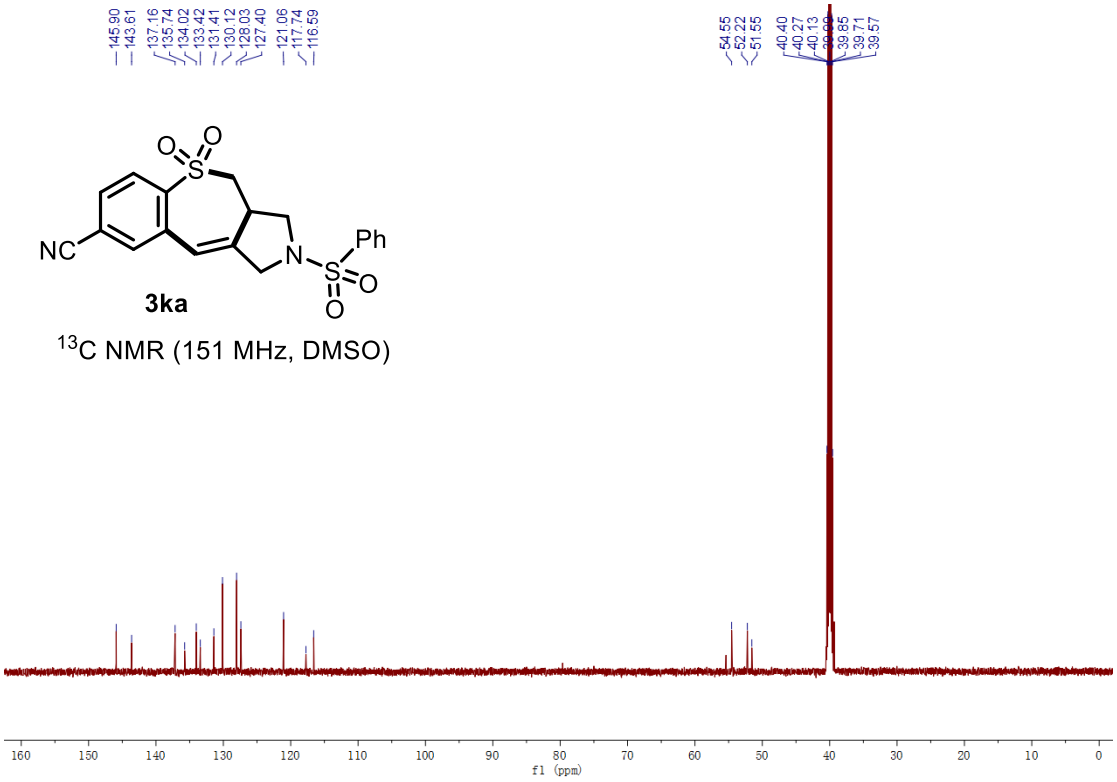
3ja

^{13}C NMR (151 MHz, DMSO)

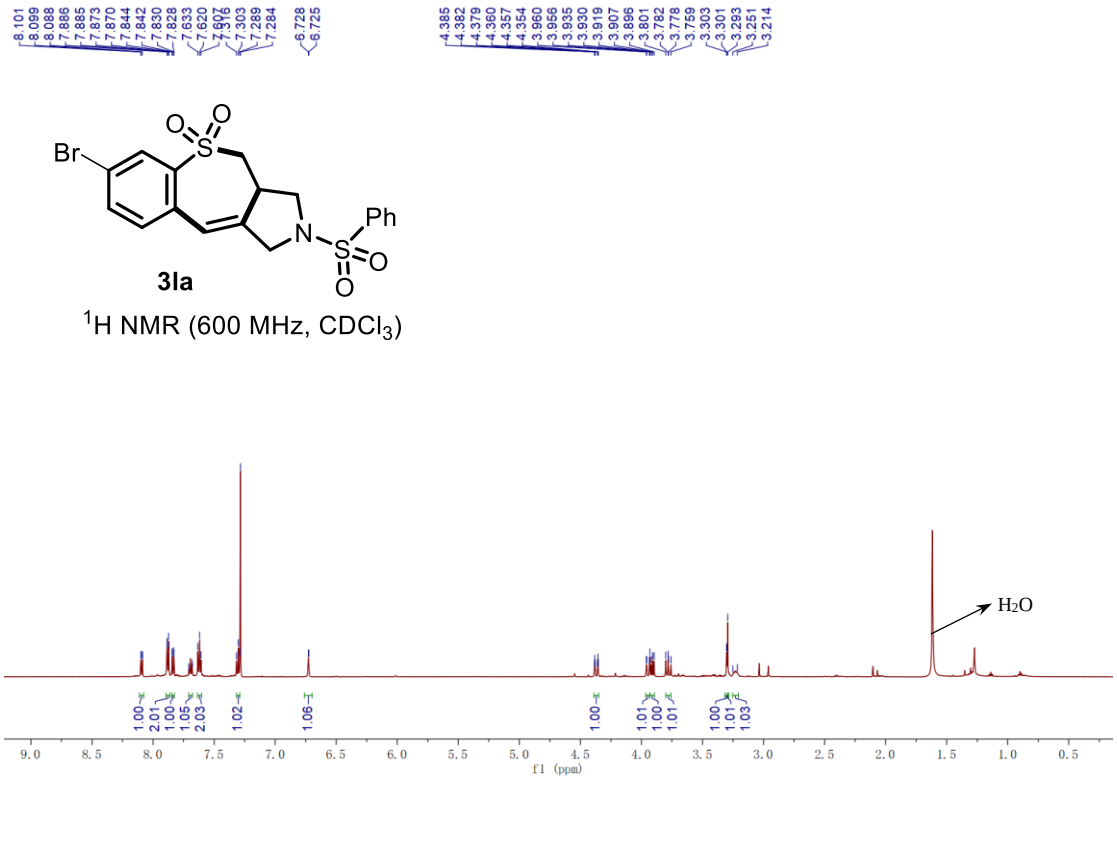


3ka

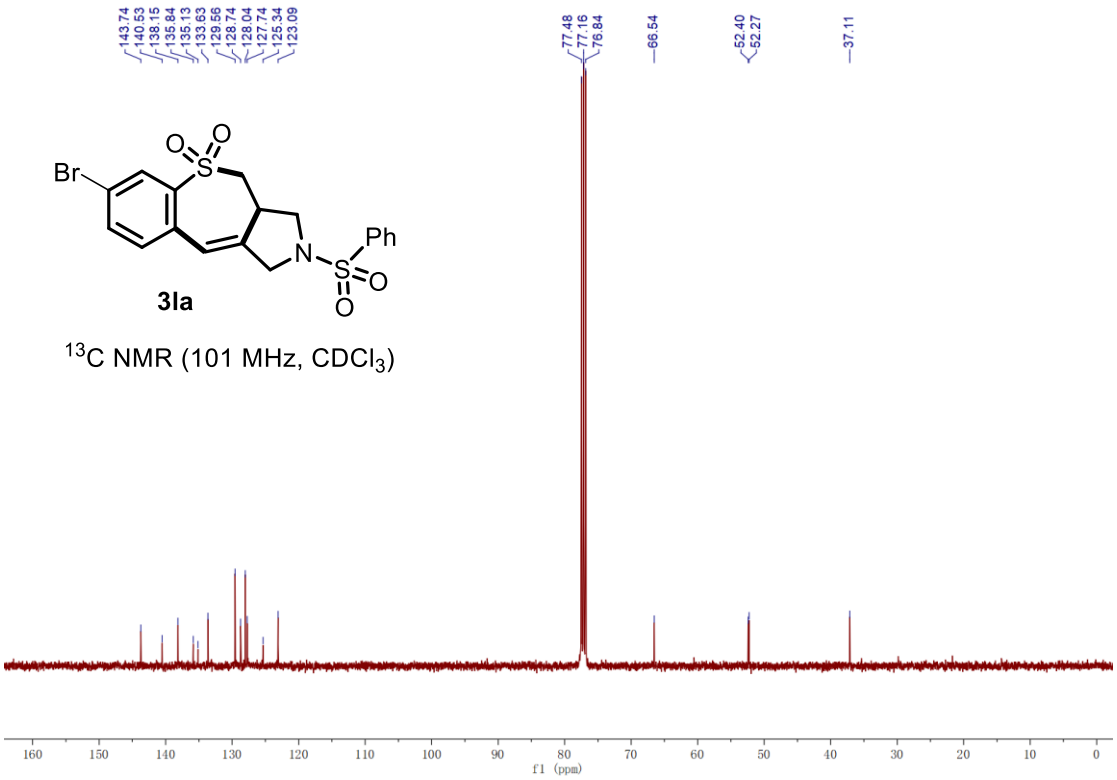
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, DMSO)

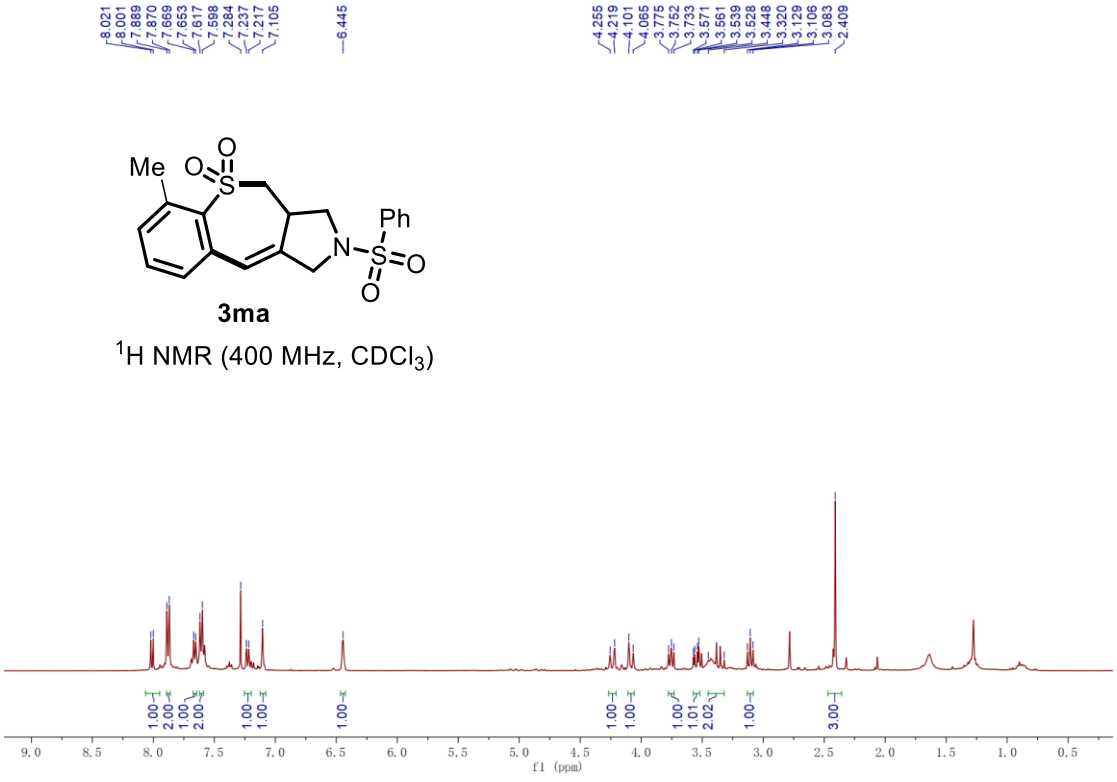


^{1}H NMR (600 MHz, $CDCl_3$)



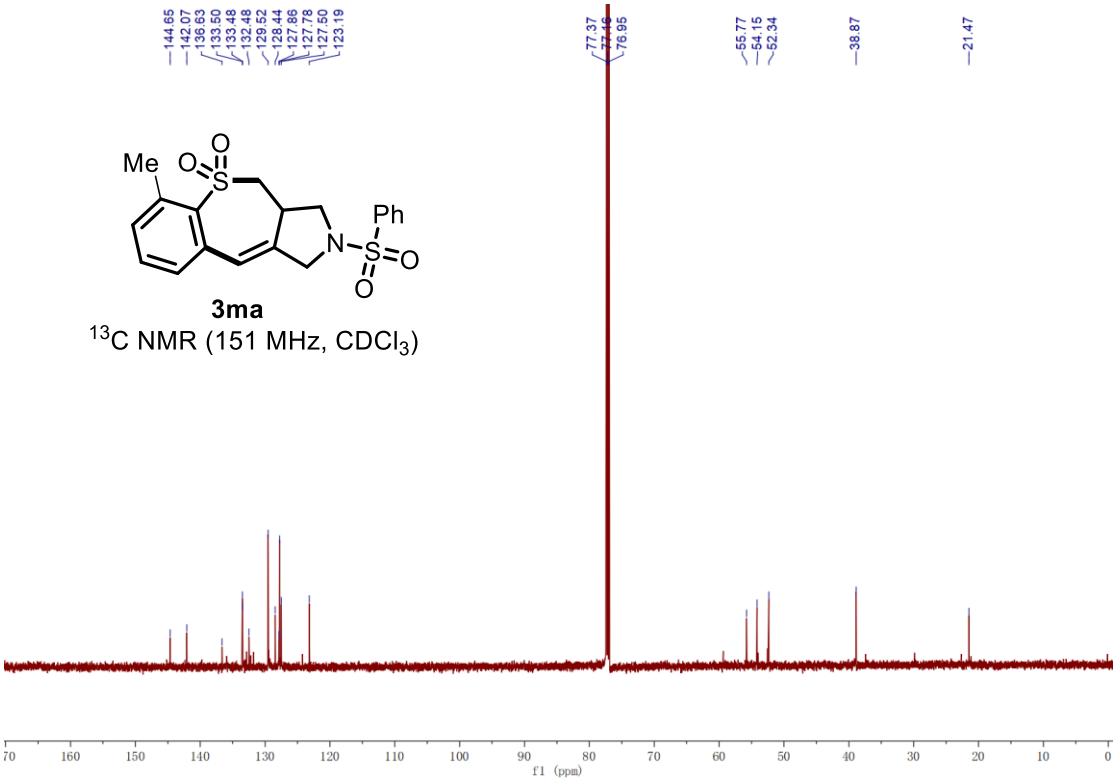
3la

^{13}C NMR (101 MHz, $CDCl_3$)



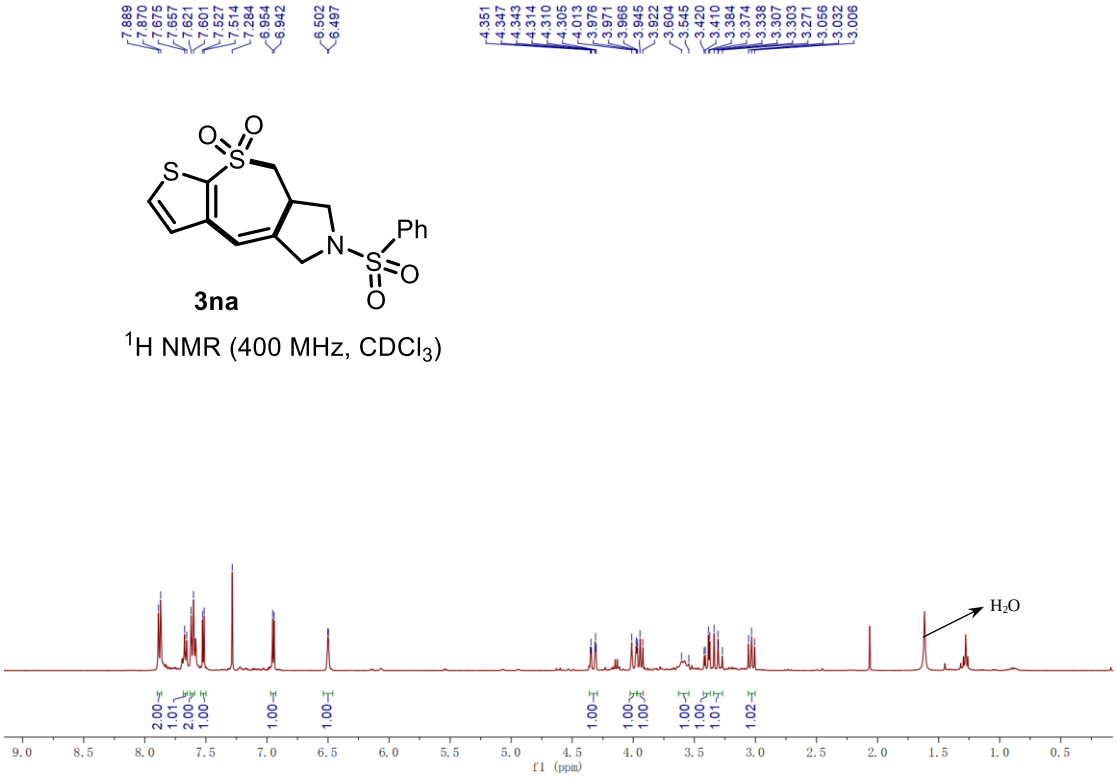
3ma

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



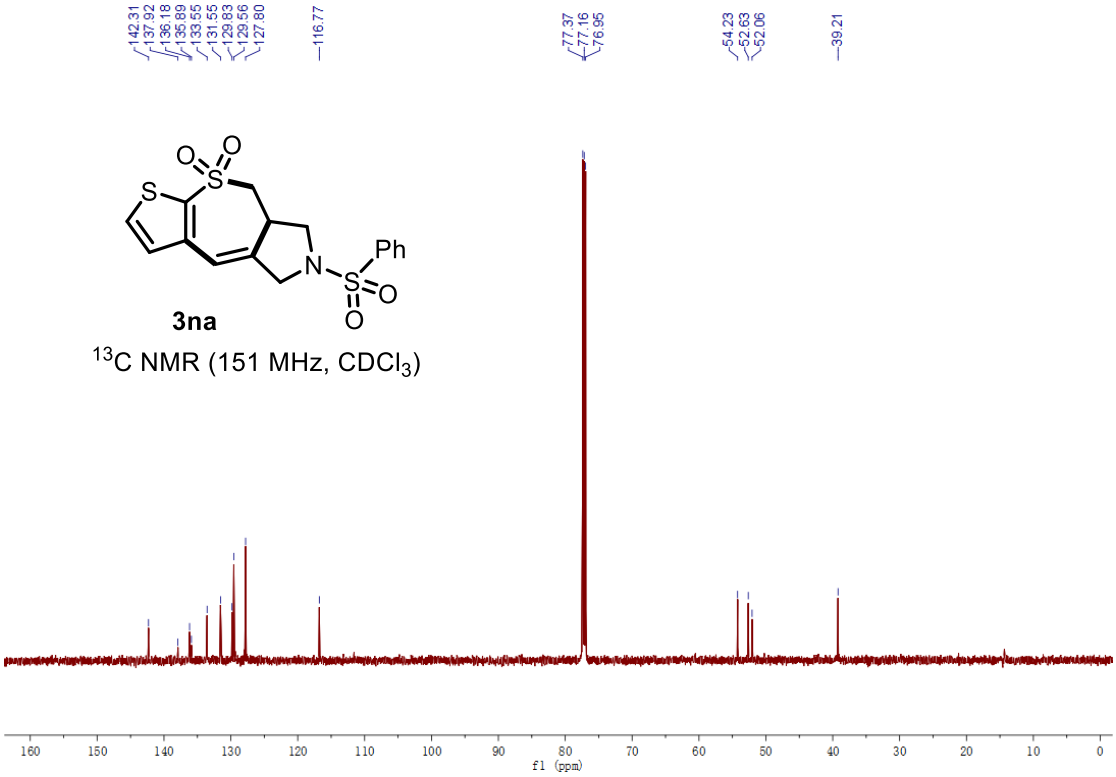
3ma

^{13}C NMR (151 MHz, $CDCl_3$)



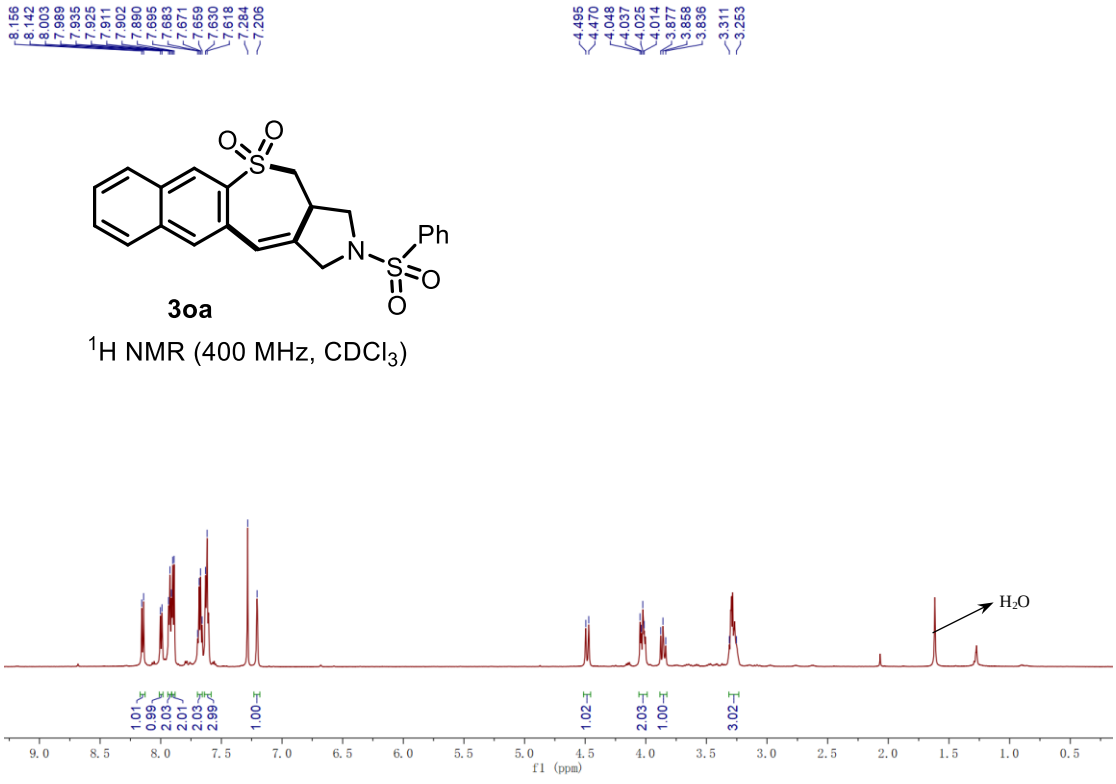
3na

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



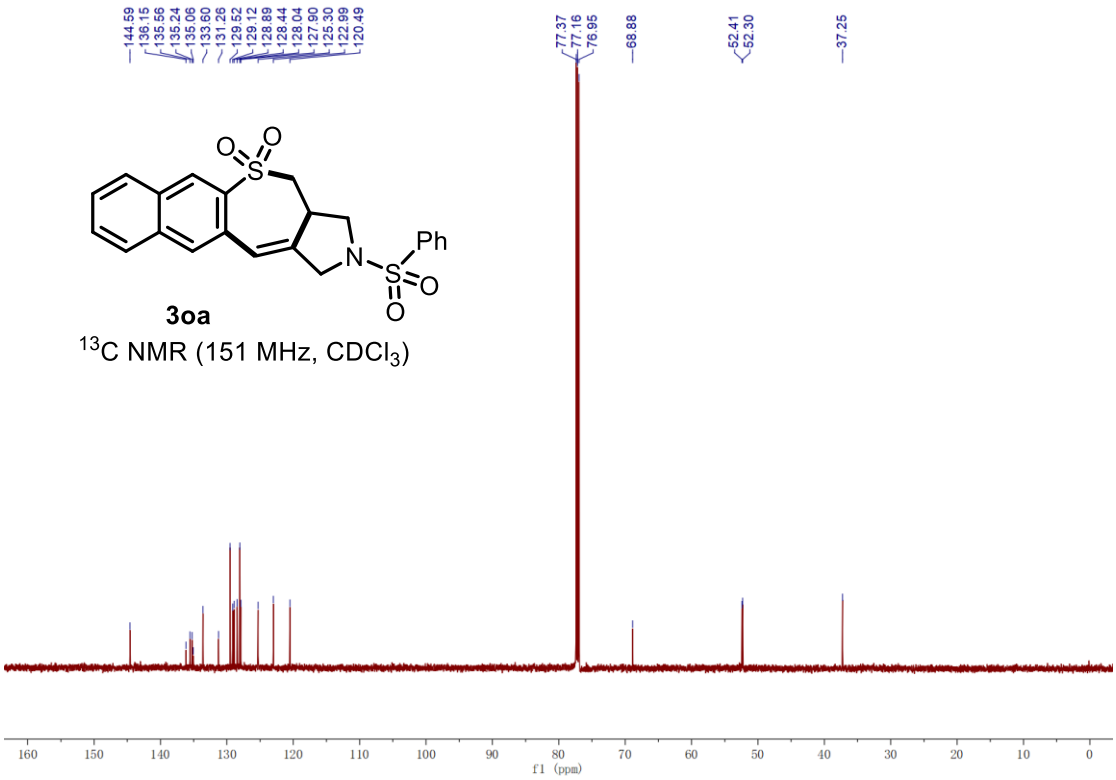
3na

^{13}C NMR (151 MHz, $CDCl_3$)



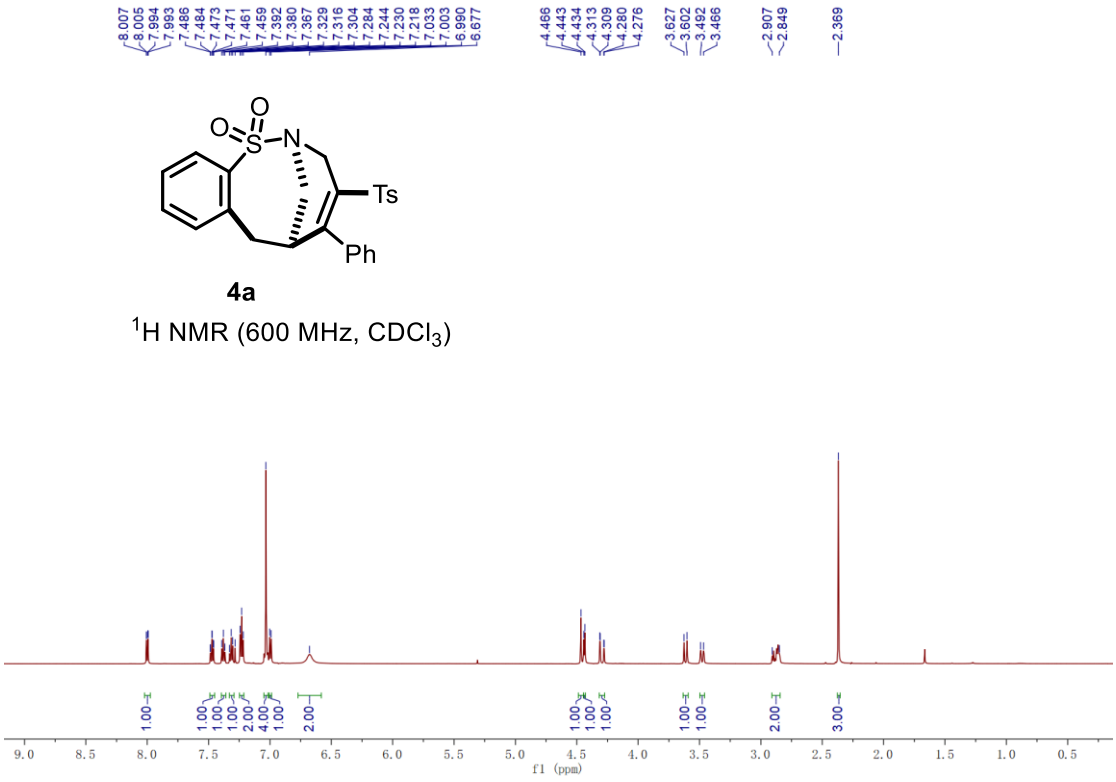
3oa

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



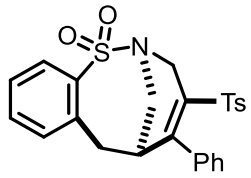
3oa

^{13}C NMR (151 MHz, $CDCl_3$)



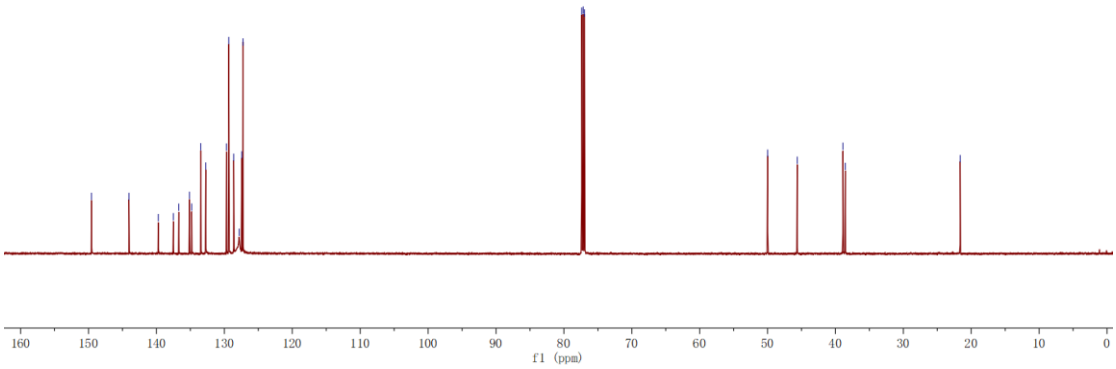
4a

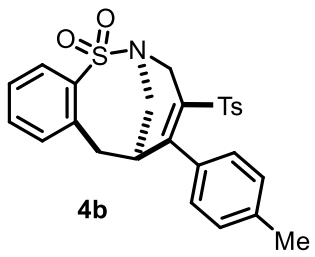
^{1}H NMR (600 MHz, $CDCl_3$)



4a

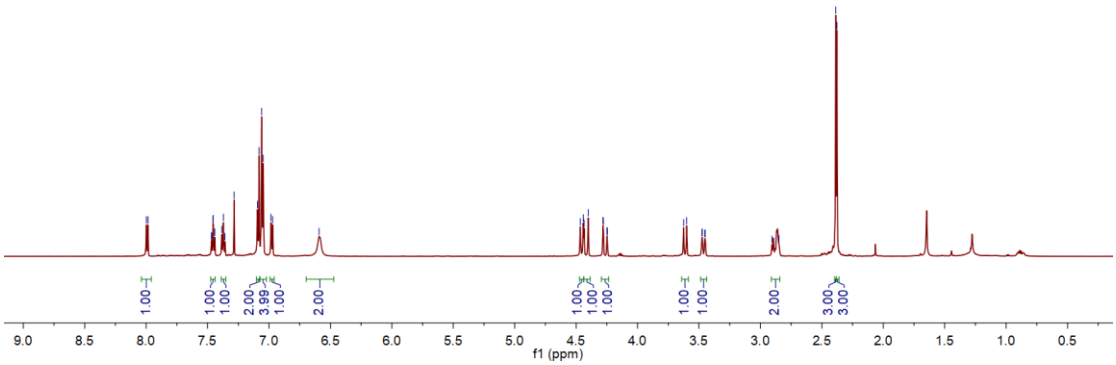
^{13}C NMR (151 MHz, $CDCl_3$)

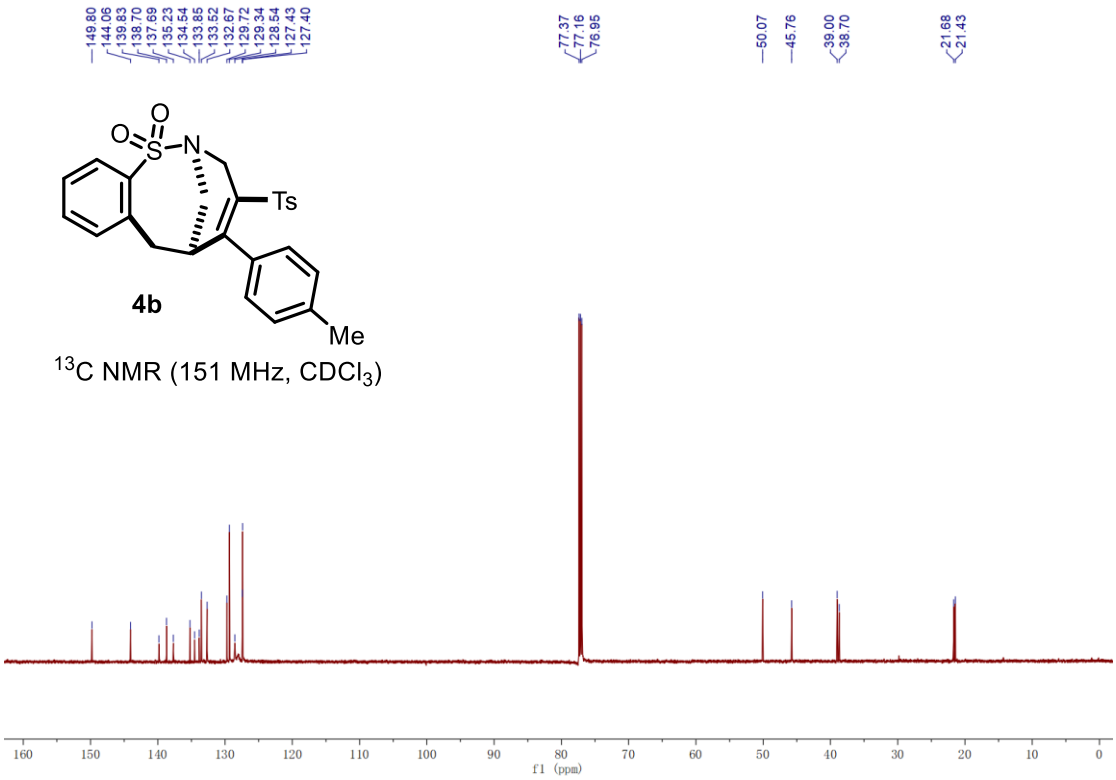


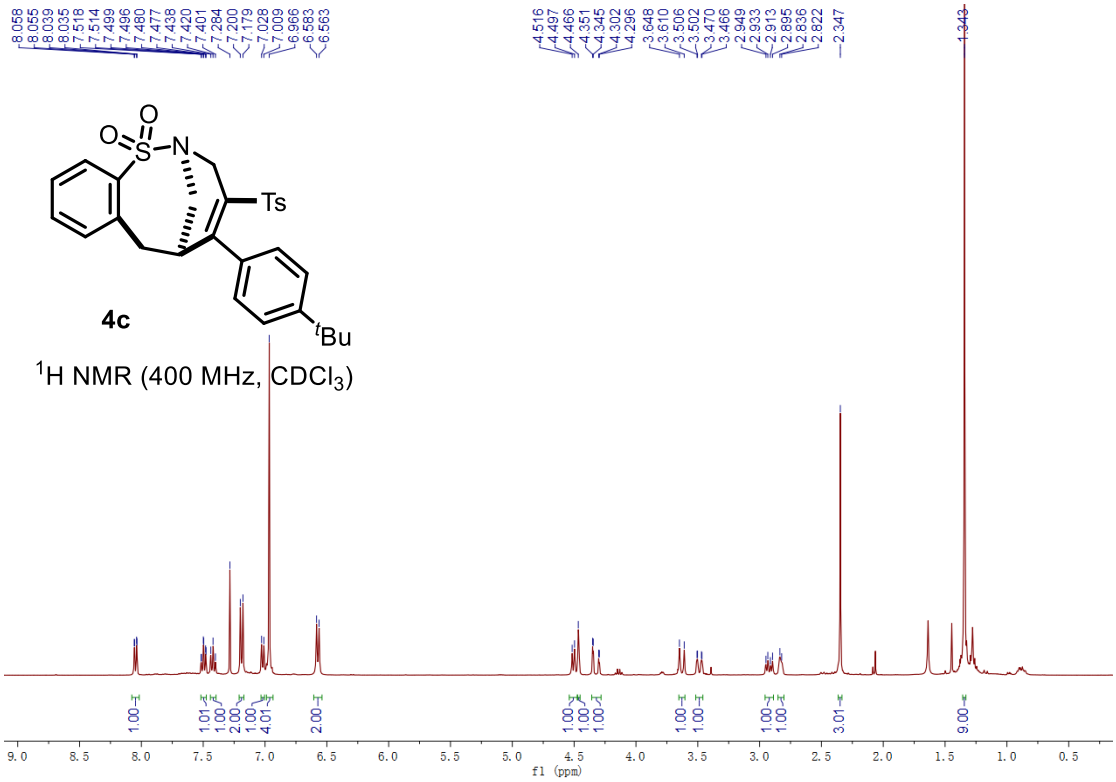


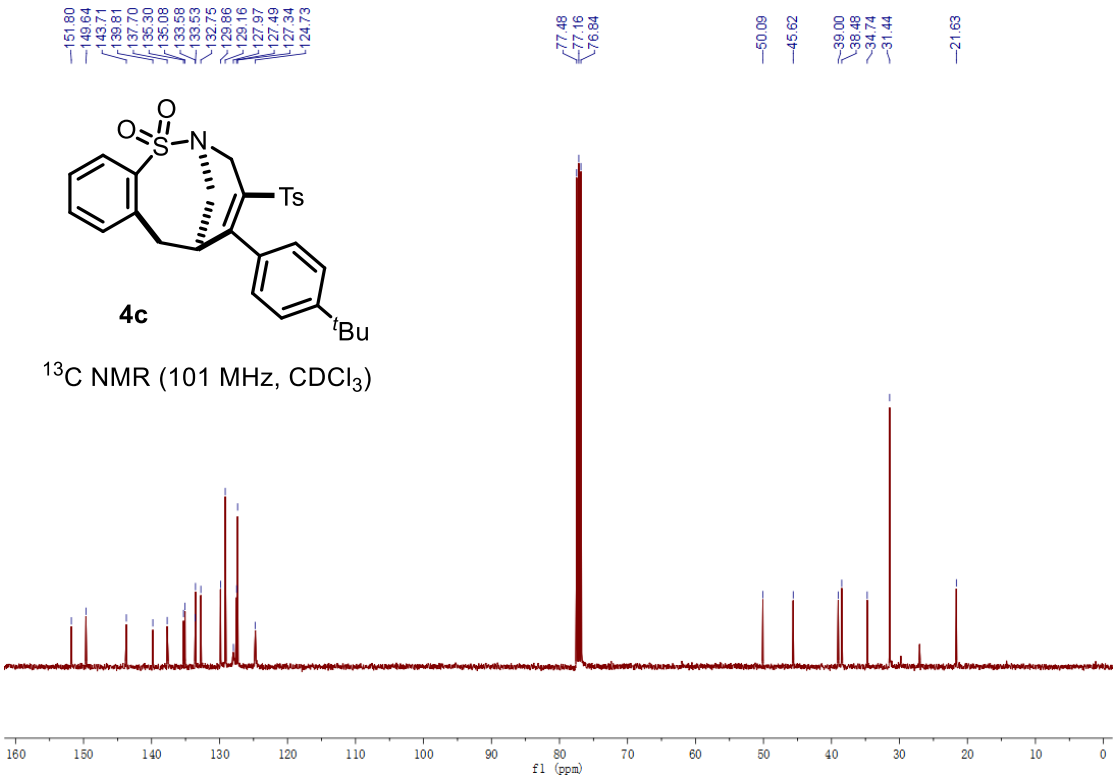
4b

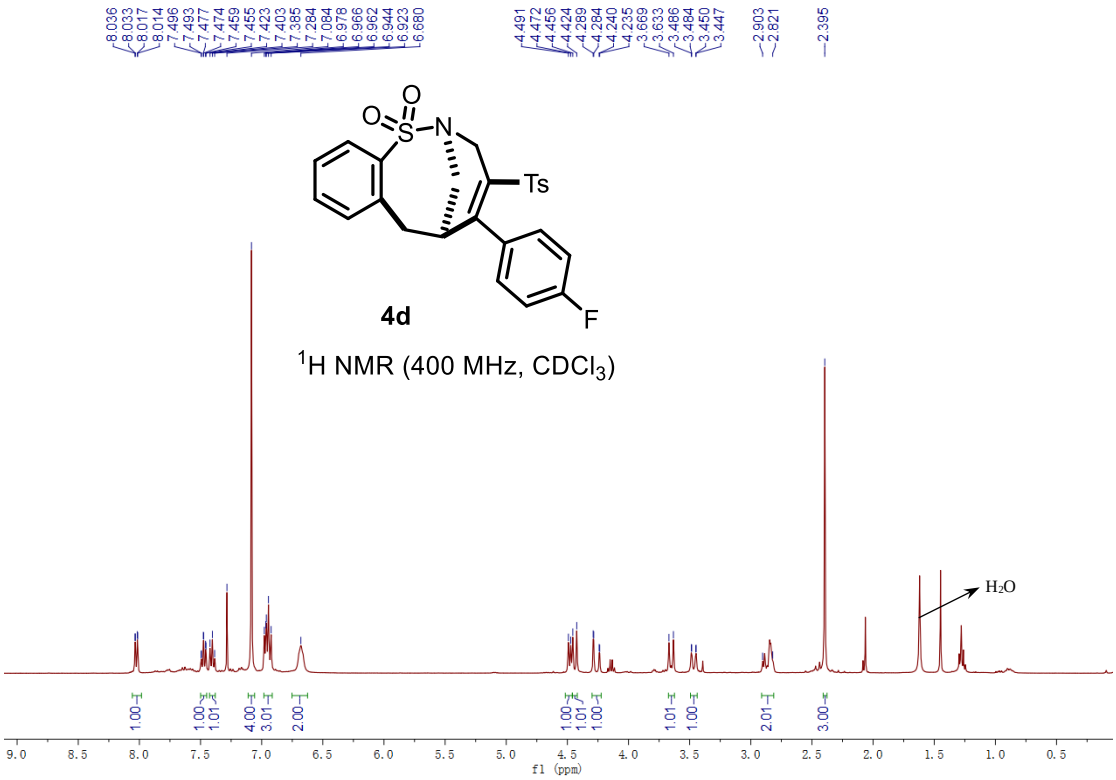
^{1}H NMR (600 MHz, $CDCl_3$)




149.80
144.06
139.83
138.70
137.69
135.23
134.54
133.85
133.52
132.67
129.72
129.34
128.54
127.43
127.40
77.37
77.16
76.95
50.07
45.76
39.00
38.70
21.68
21.43
O
O
S
N
Ts
Me
4b
13C NMR (151 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.058
8.055
8.039
8.035
7.518
7.514
7.499
7.496
7.480
7.477
7.438
7.420
7.401
7.284
7.200
7.179
7.028
7.009
6.966
6.583
6.563
4.516
4.497
4.466
4.351
4.345
4.302
4.296
3.648
3.610
3.506
3.502
3.470
3.466
2.949
2.933
2.913
2.895
2.836
2.822
2.347
1.343
O
O
S
N
Ts
tBu
4c
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.00
1.00
4.01
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.01
9.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


151.80
149.64
143.71
139.81
137.70
135.30
135.08
133.58
133.53
132.75
129.86
129.16
127.97
127.49
127.34
124.73
77.48
77.16
76.84
50.09
45.62
39.00
38.48
34.74
31.44
21.63
O
O
S
N
Ts
tBu
4c
13C NMR (101 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.033
8.017
8.014
7.496
7.493
7.477
7.474
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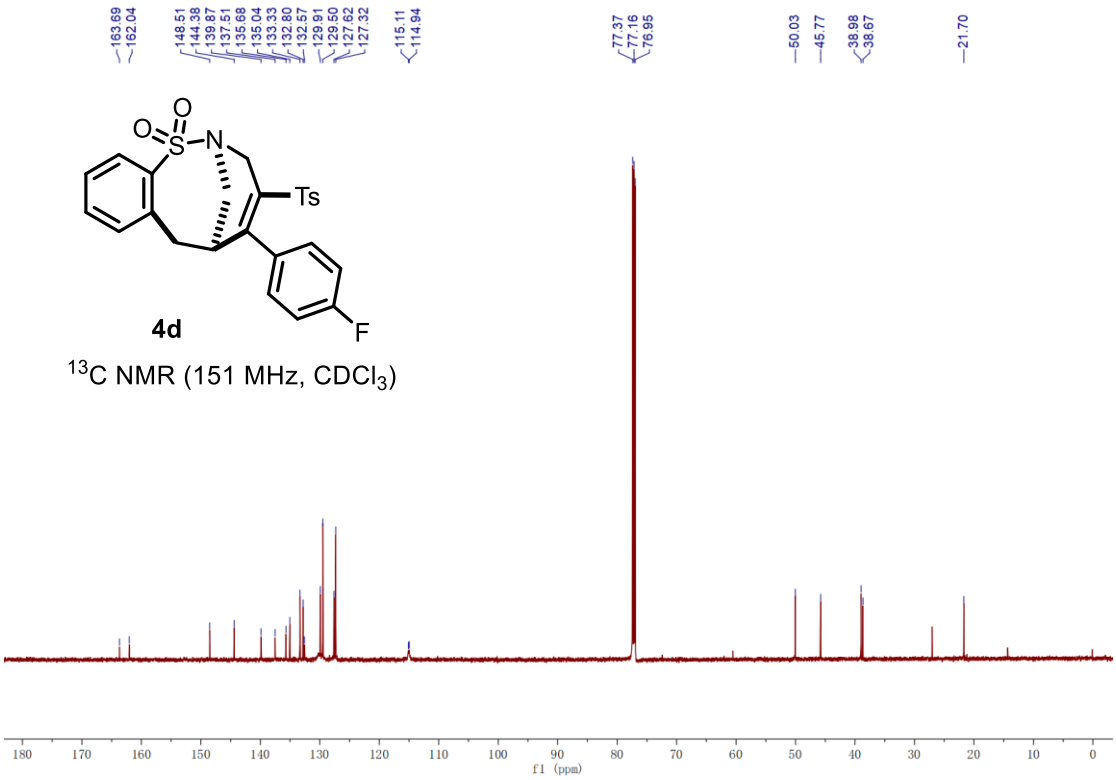
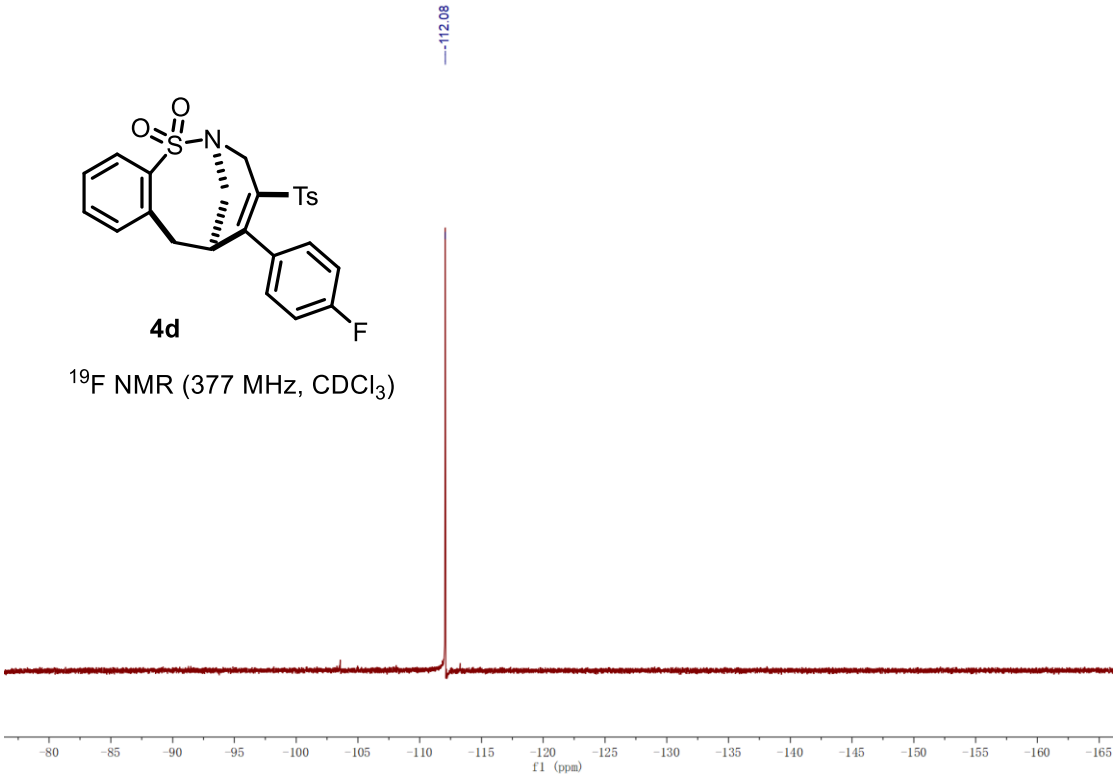
7.455
7.423
7.403
7.385
7.284
7.084
6.978
6.966
6.962
6.944
6.923
6.680
4.491
4.472
4.456
4.424
4.289
4.284
4.240
4.235
3.669
3.633
3.486
3.484
3.450
3.447
2.903
2.821
2.395
O
O
S
N
Ts
F
4d
1H NMR (400 MHz, CDCl3)
H2O
1.00
1.00
1.01
4.00
3.01
2.00
1.00
1.01
1.00
1.01
1.00
2.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



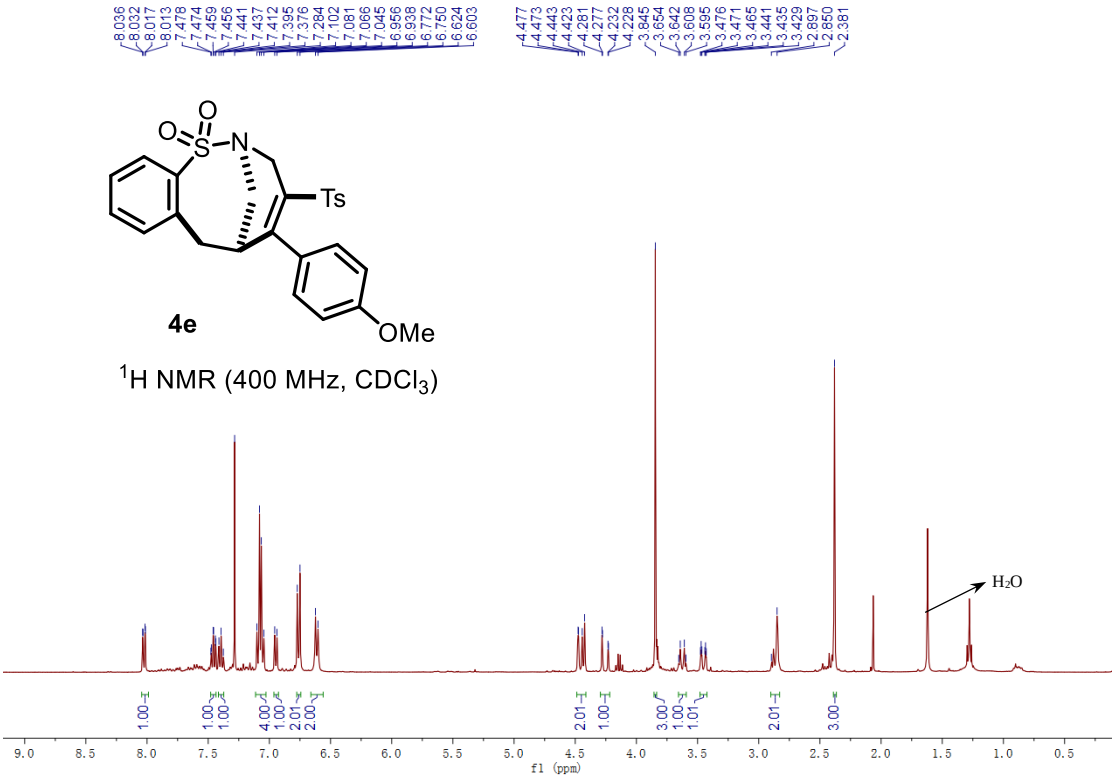
4d

^{13}C NMR (151 MHz, $CDCl_3$)



4d

^{19}F NMR (377 MHz, $CDCl_3$)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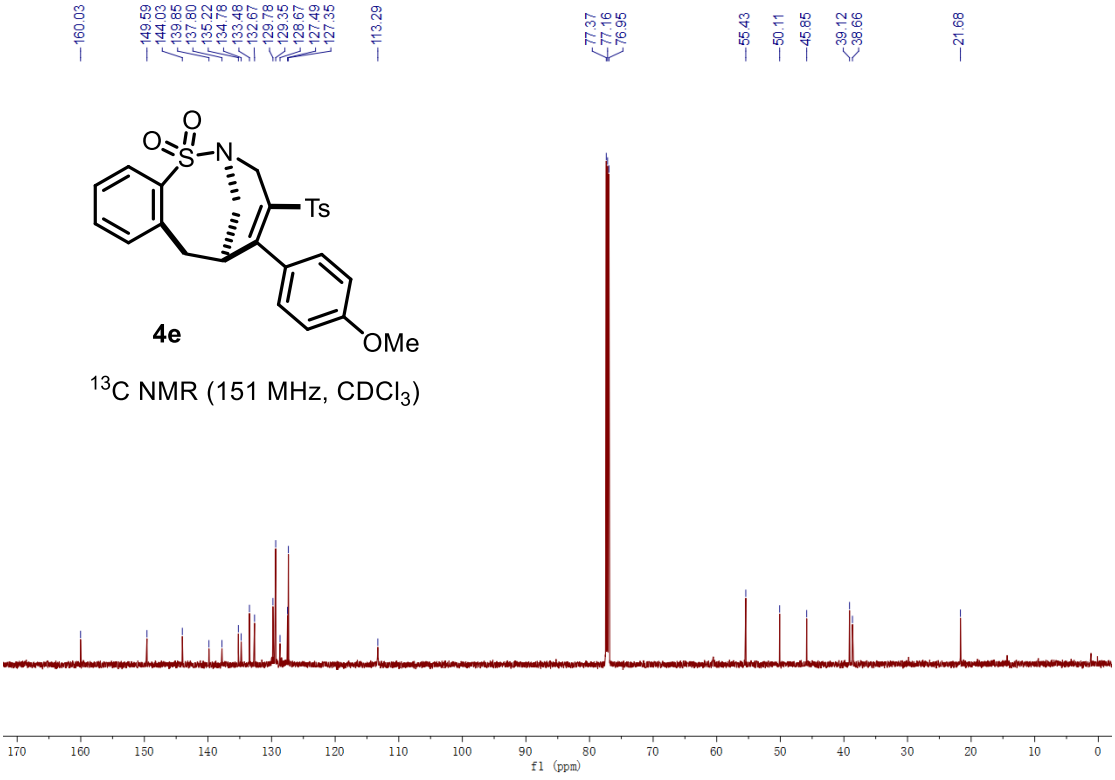
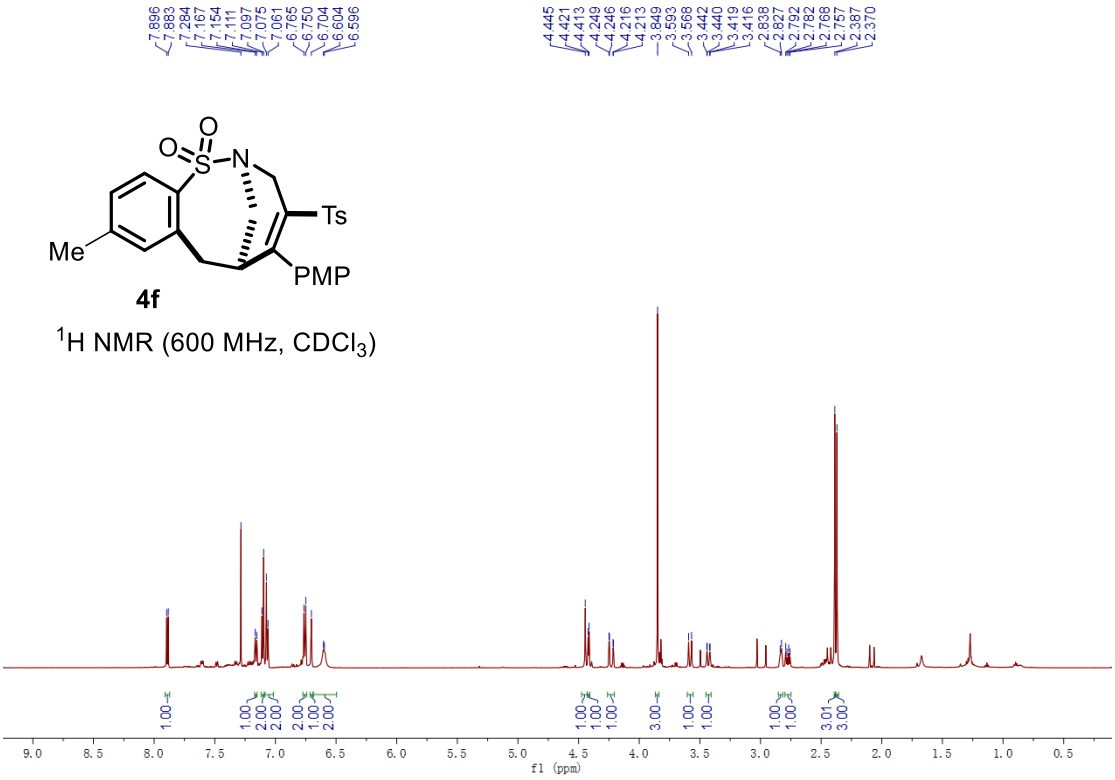
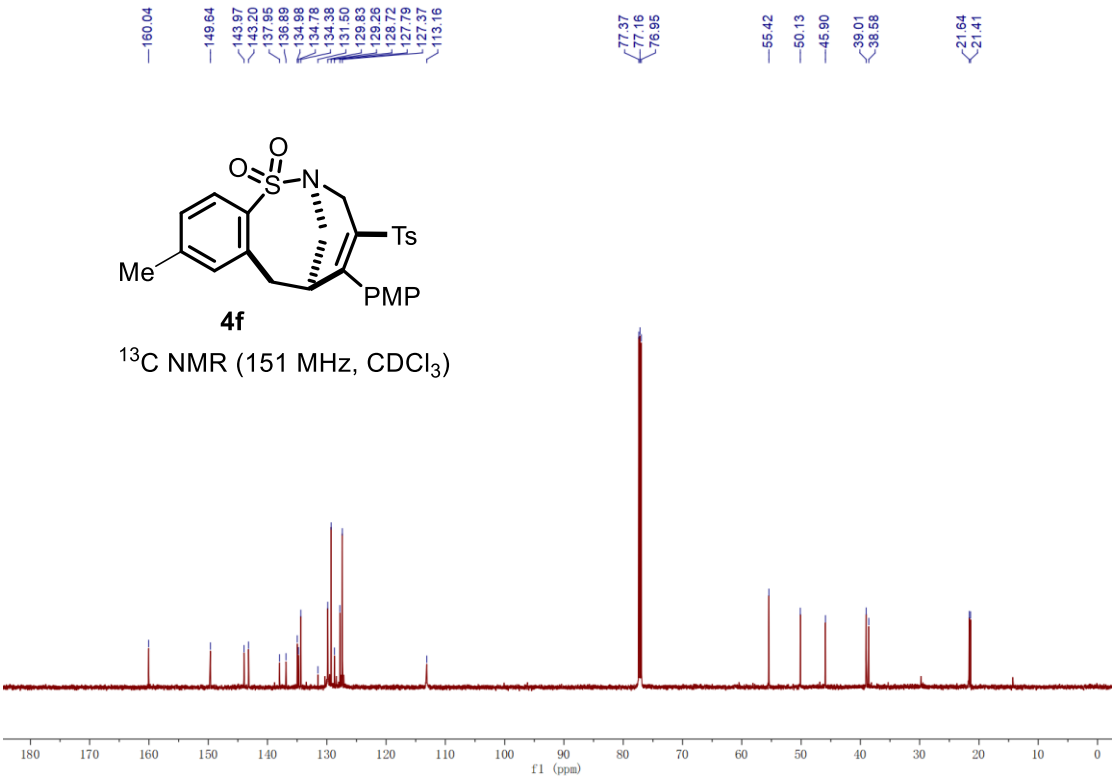
7.284
7.102
7.081
7.066
7.045
6.956
6.938
6.772
6.750
6.624
6.603
4.477
4.473
4.443
4.423
4.281
4.277
4.232
4.228
3.845
3.654
3.642
3.608
3.595
3.476
3.471
3.465
3.441
3.435
3.429
2.897
2.850
2.381
O
O
S
N
Ts
OMe
4e
1H NMR (400 MHz, CDCl3)
H2O
1.00
1.00
1.00
4.00
1.00
2.01
2.00
2.01
1.00
3.00
1.00
1.01
2.01
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


160.03
149.59
144.03
139.85
137.80
135.22
134.78
133.48
132.67
129.78
129.35
128.67
127.49
127.35
113.29
77.37
77.16
76.95
55.43
50.11
45.85
39.12
38.66
21.68
O
O
S
N
Ts
OMe
4e
13C NMR (151 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



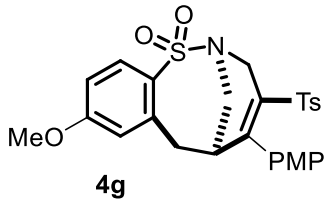
4f

^{1}H NMR (600 MHz, $CDCl_3$)



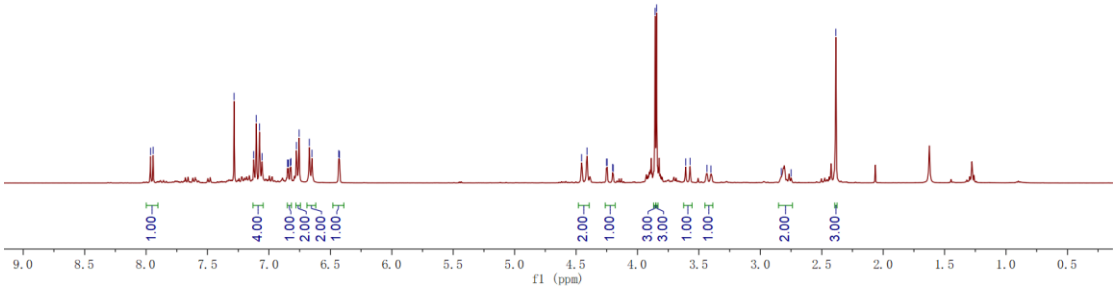
4f

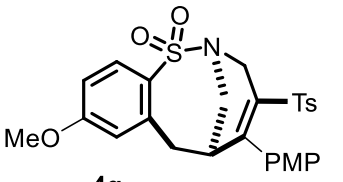
^{13}C NMR (151 MHz, $CDCl_3$)



4g

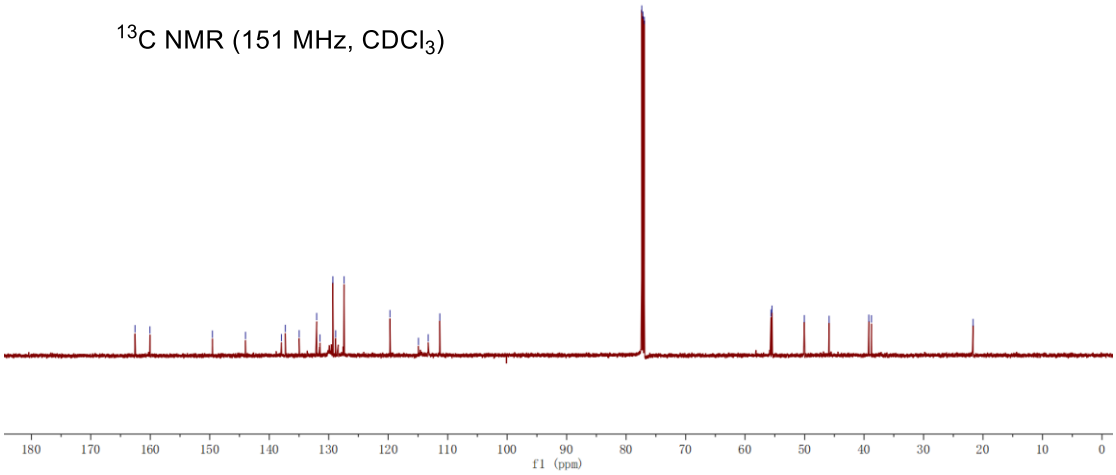
^{1}H NMR (400 MHz, $CDCl_3$)

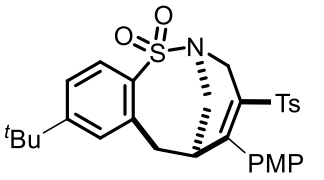




4g

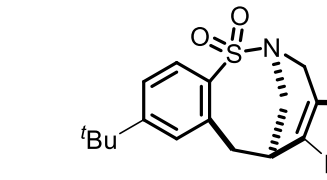
^{13}C NMR (151 MHz, $CDCl_3$)





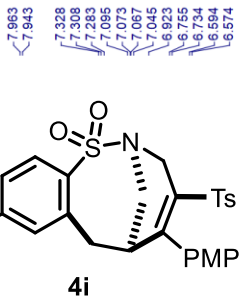
4h

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



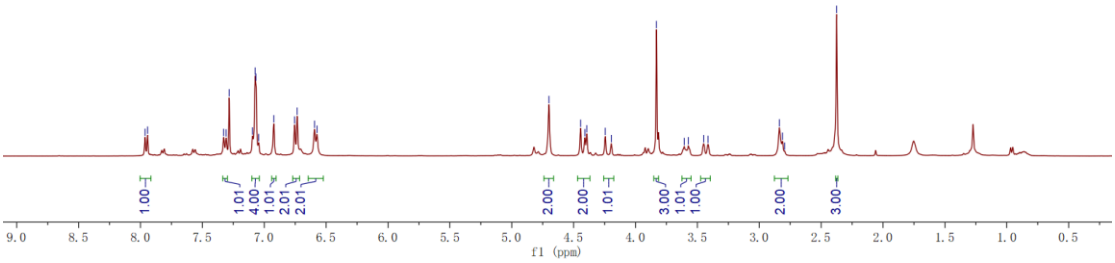
4h

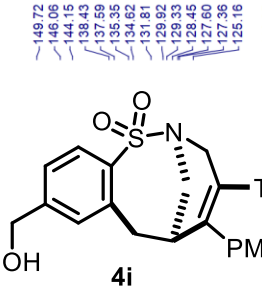
^{13}C NMR (151 MHz, $CDCl_3$)



4i

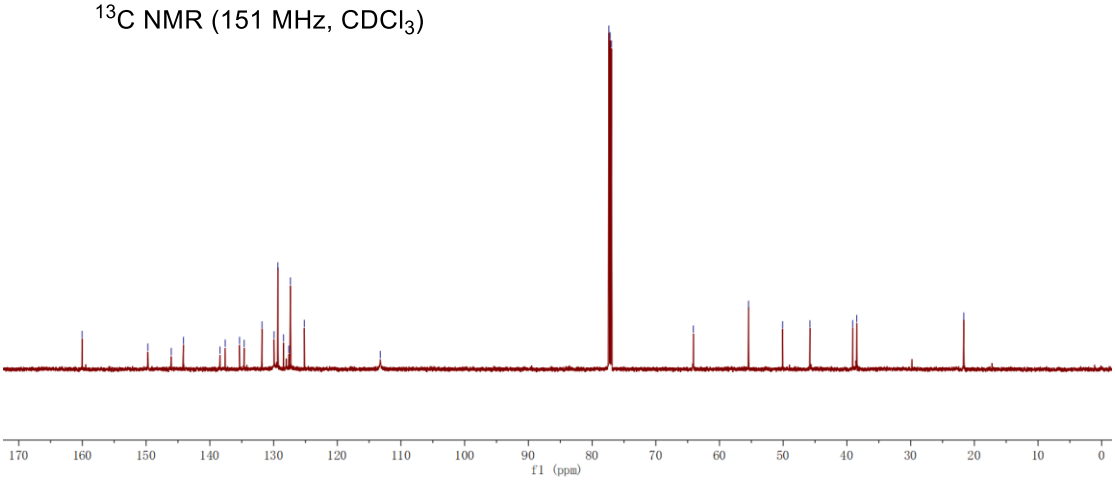
^{1}H NMR (400 MHz, $CDCl_3$)

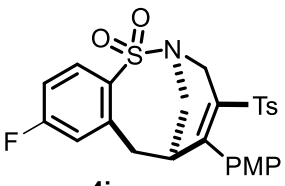




4i

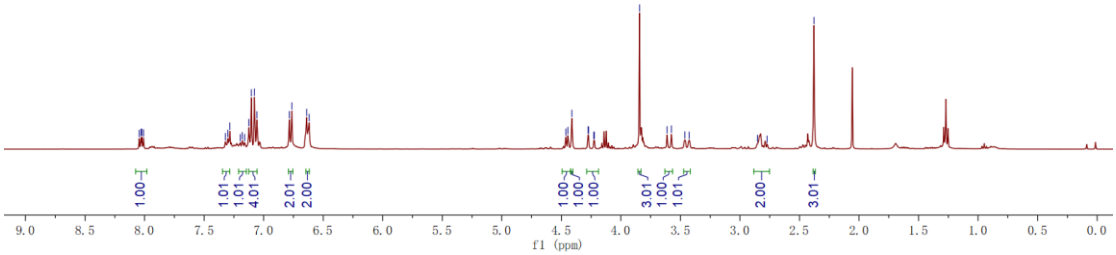
^{13}C NMR (151 MHz, $CDCl_3$)

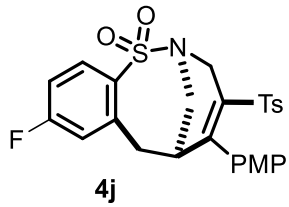




4j

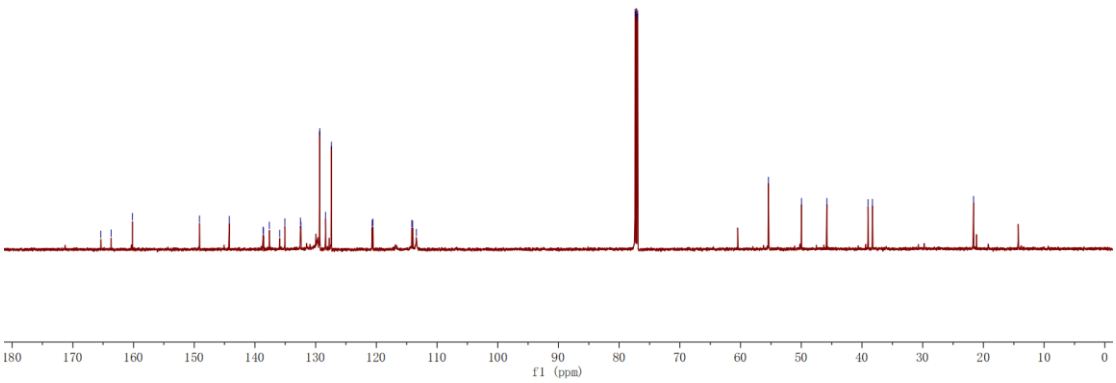
^{1}H NMR (400 MHz, $CDCl_3$)

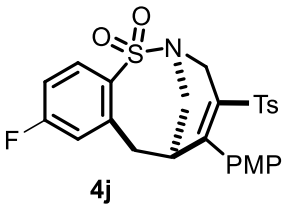




4j

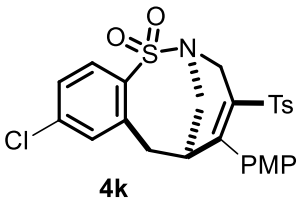
^{13}C NMR (151 MHz, $CDCl_3$)





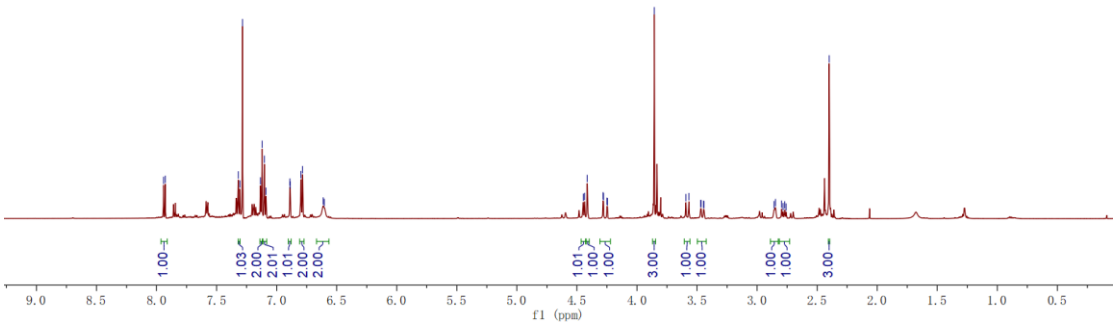
4j

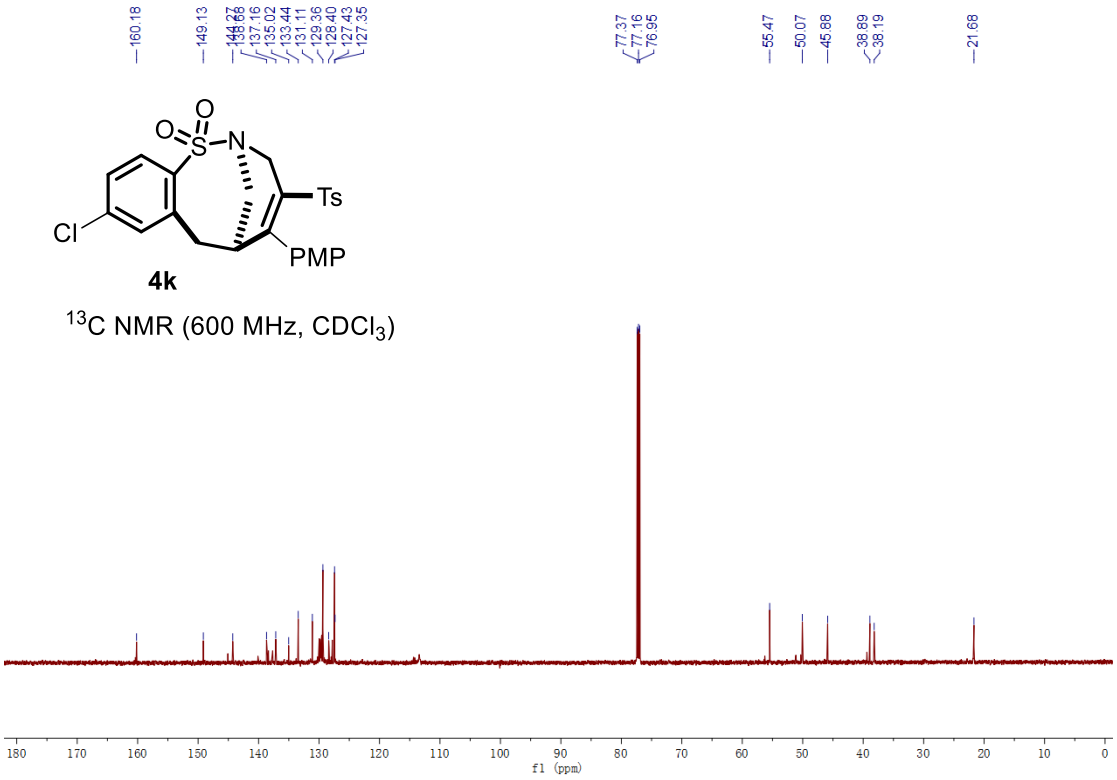
^{19}F NMR (565 MHz, $CDCl_3$)



4k

^{1}H NMR (600 MHz, $CDCl_3$)




160.18
149.13
137.16
135.02
133.44
131.11
129.36
128.40
127.43
127.35
77.37
77.16
76.95
55.47
50.07
45.88
38.89
38.19
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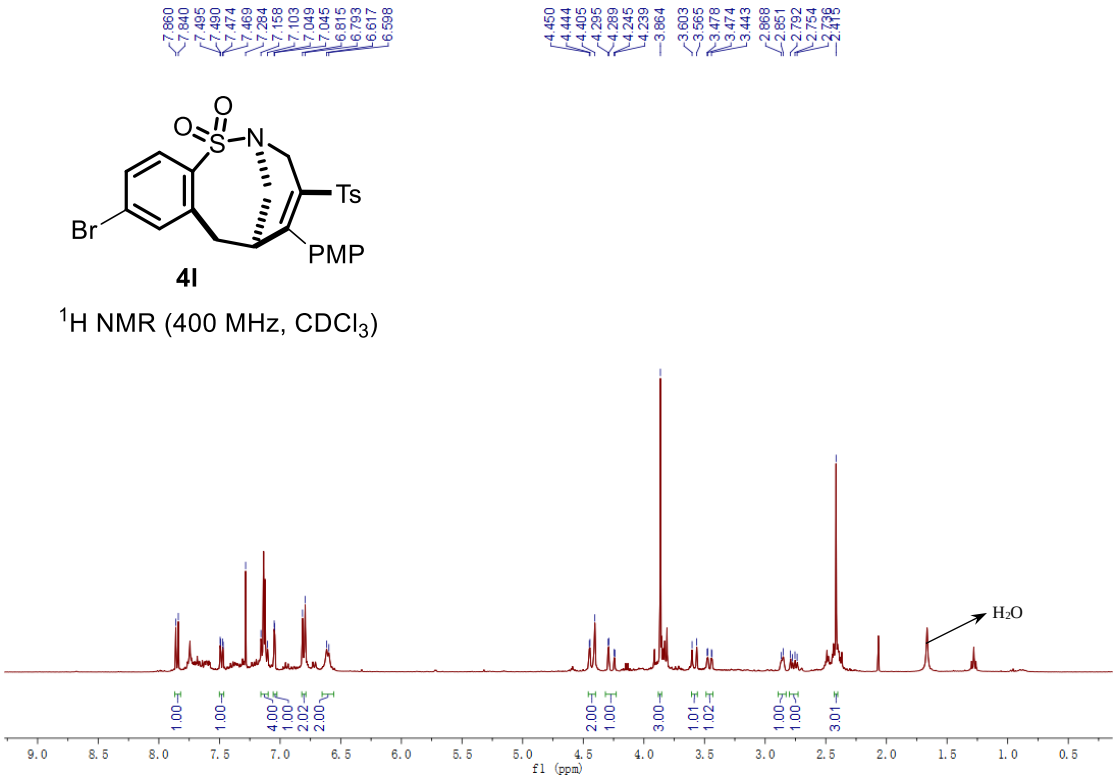
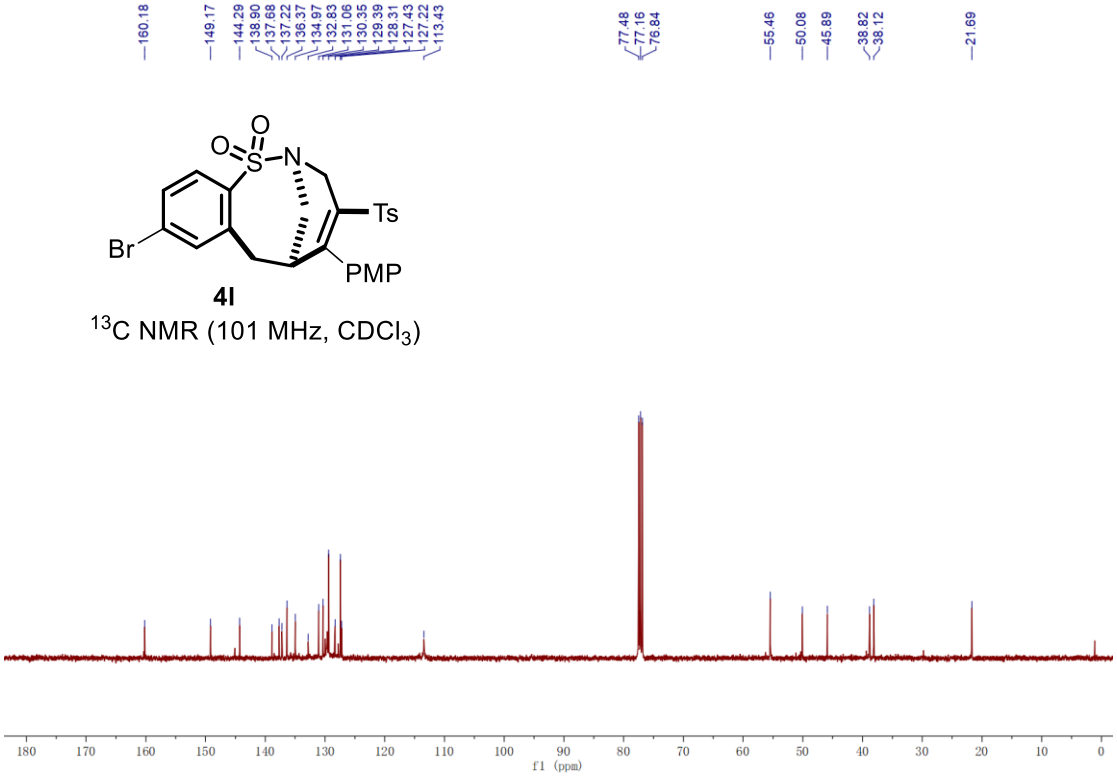
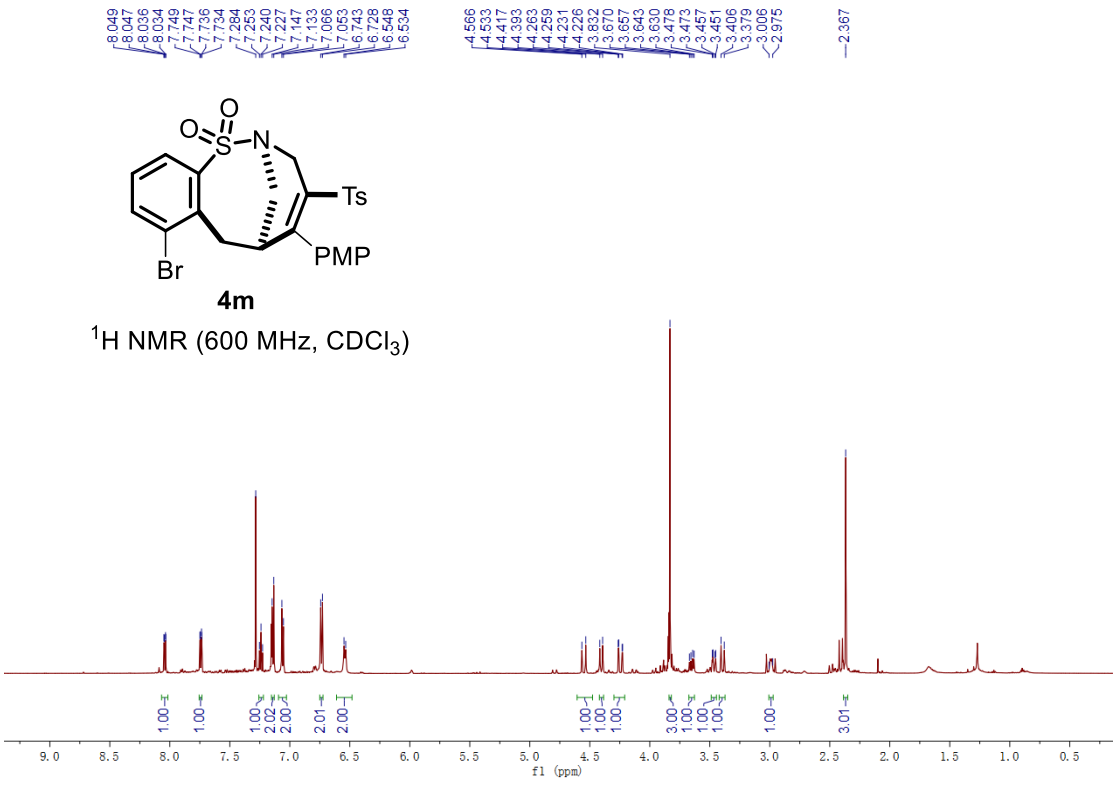
O
O
S
N
Ts
Cl
PMP
4k
13C NMR (600 MHz, CDCl3)
f1 (ppm)


7.860
7.840
7.495
7.490
7.474
7.469
7.284
7.158
7.103
7.049
7.045
6.815
6.793
6.617
6.598
4.450
4.444
4.405
4.295
4.289
4.245
4.239
3.864
3.603
3.565
3.478
3.474
3.443
2.868
2.851
2.792
2.754
2.736
2.415
O
O
S
N
Ts
Br
PMP
4l
1H NMR (400 MHz, CDCl3)
H2O
1.00
1.00
4.00
1.00
2.02
2.00
2.00
1.00
3.00
1.01
1.02
1.00
1.00
3.01
f1 (ppm)



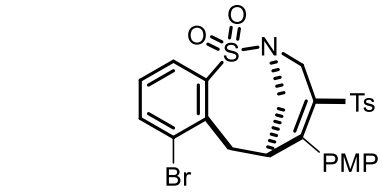
4l

^{13}C NMR (101 MHz, $CDCl_3$)



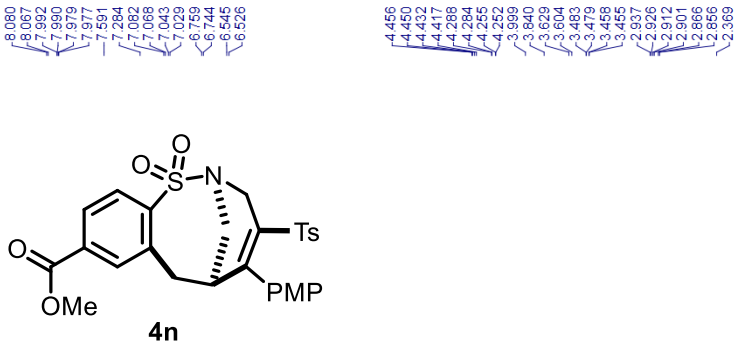
4m

^{1}H NMR (600 MHz, $CDCl_3$)



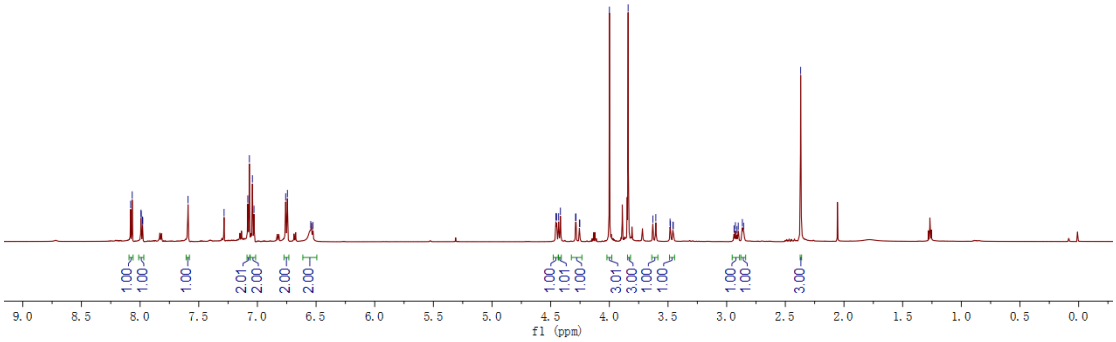
4m

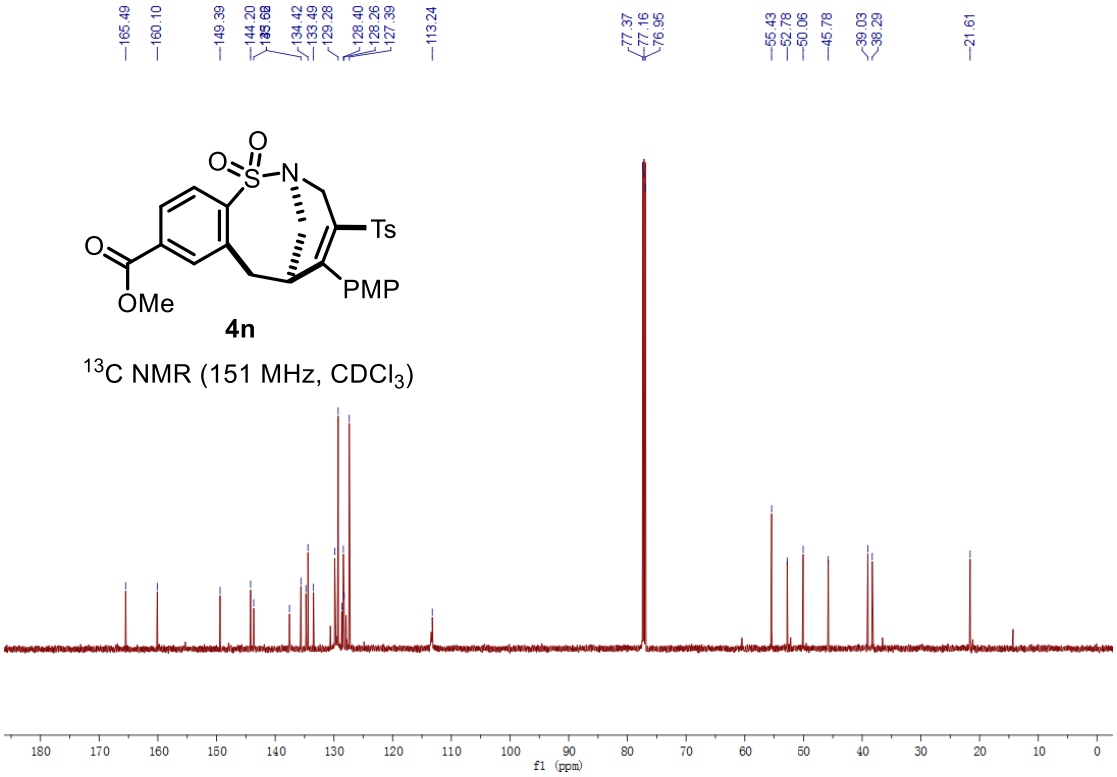
^{13}C NMR (151 MHz, $CDCl_3$)



4n

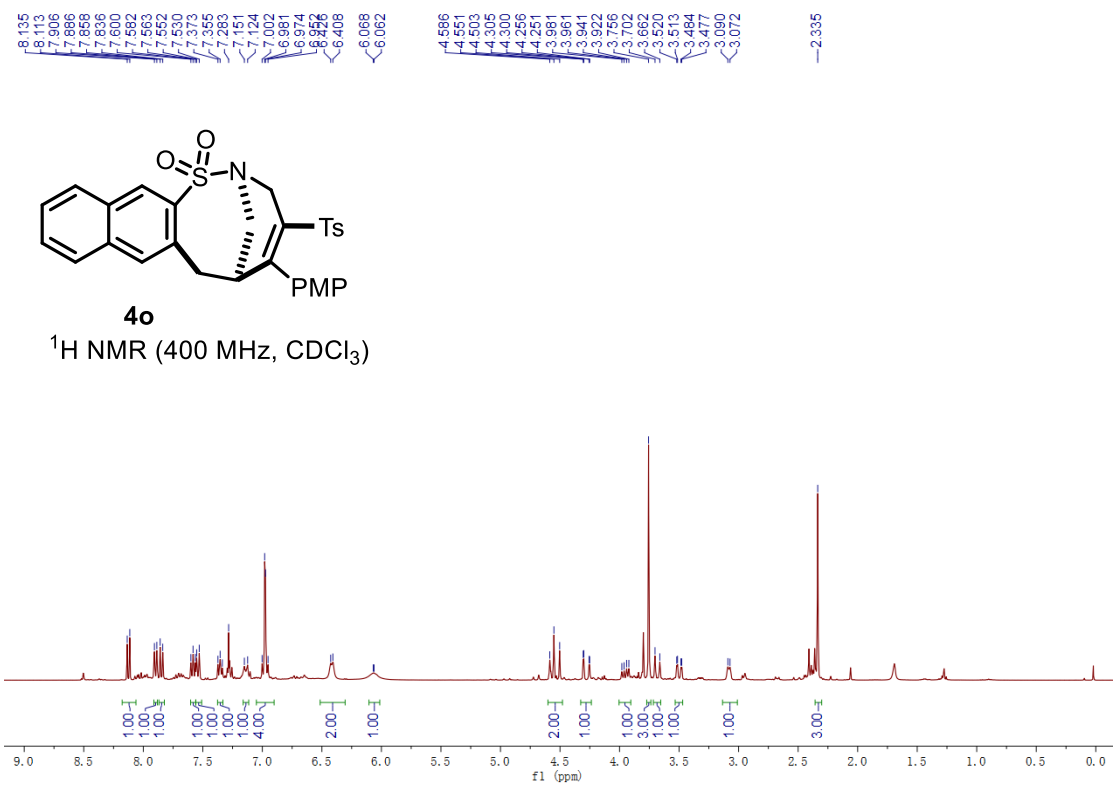
^{1}H NMR (600 MHz, $CDCl_3$)





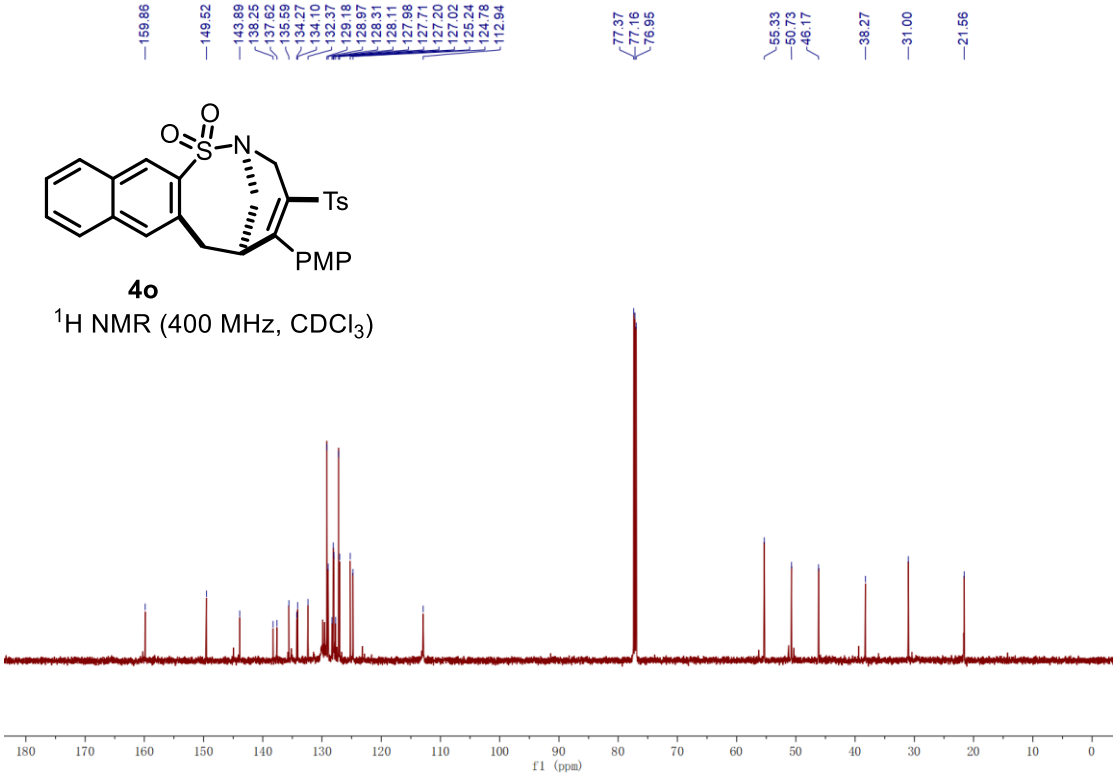
4n

^{13}C NMR (151 MHz, $CDCl_3$)



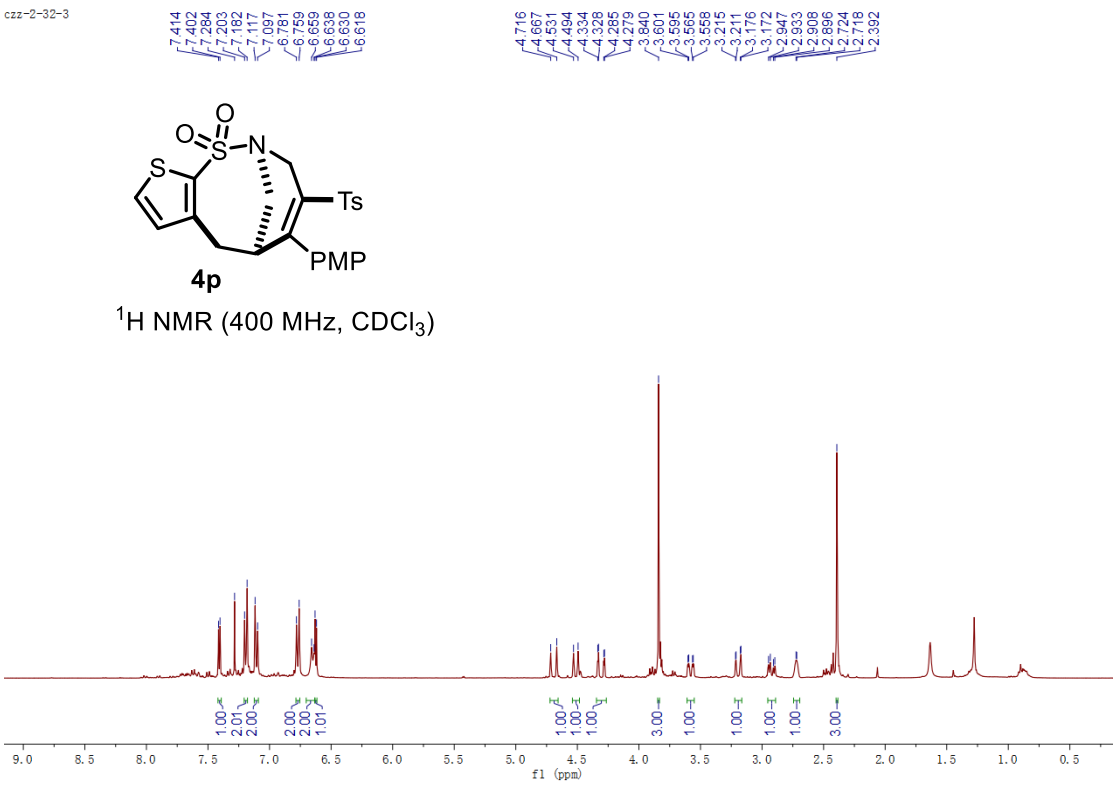
4o

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



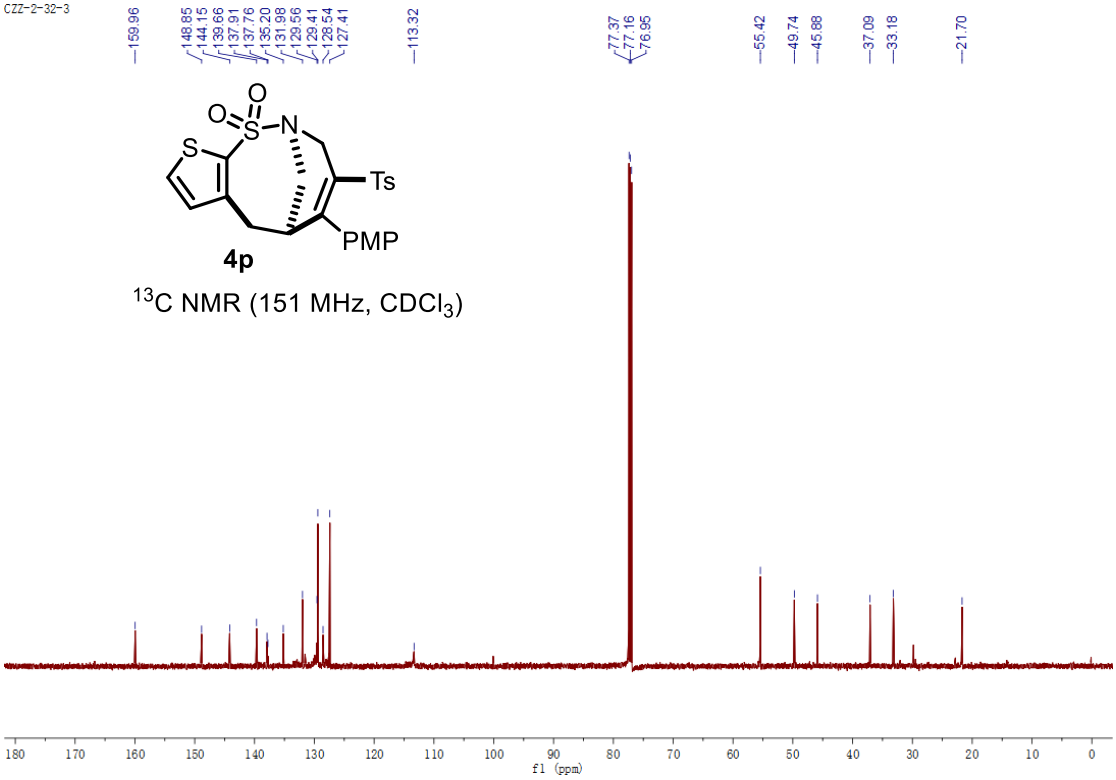
4o

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



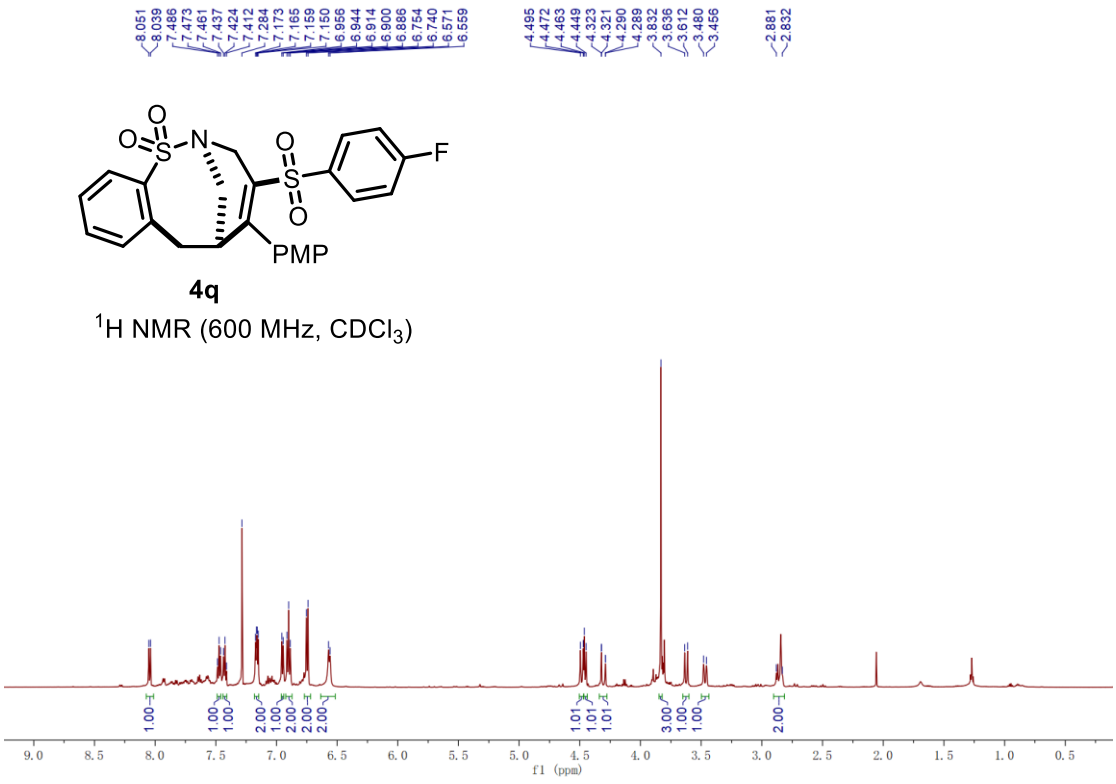
4p

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



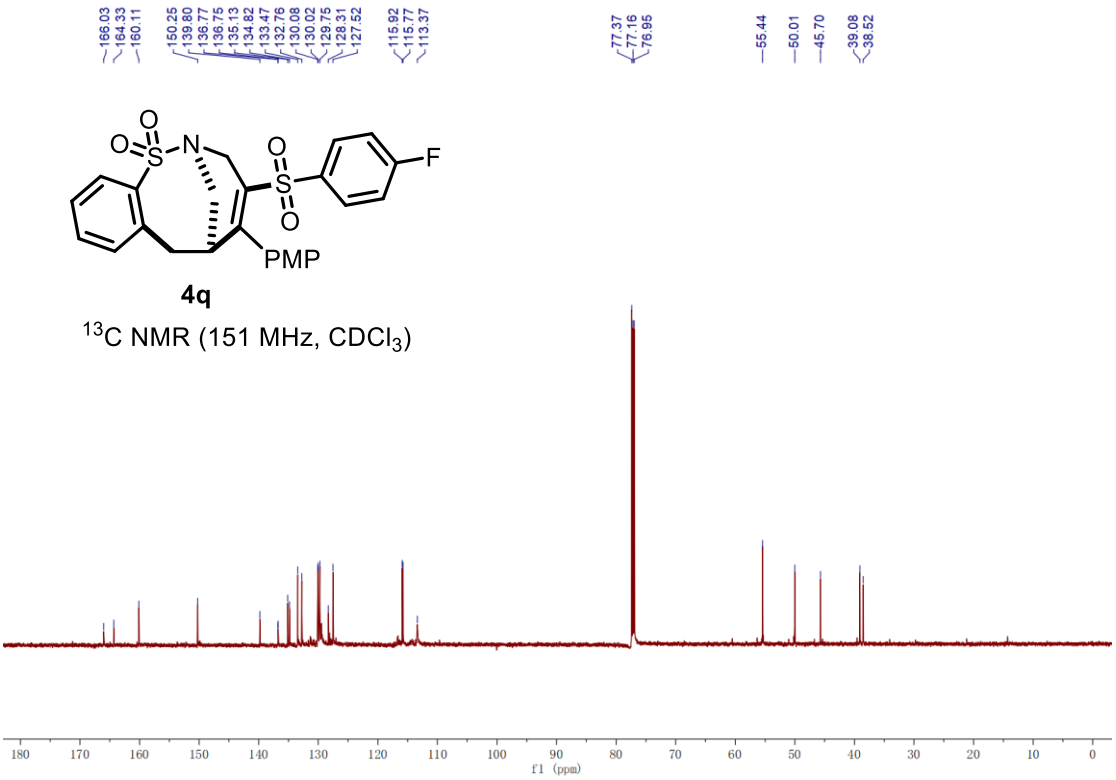
4p

^{13}C NMR (151 MHz, $CDCl_3$)



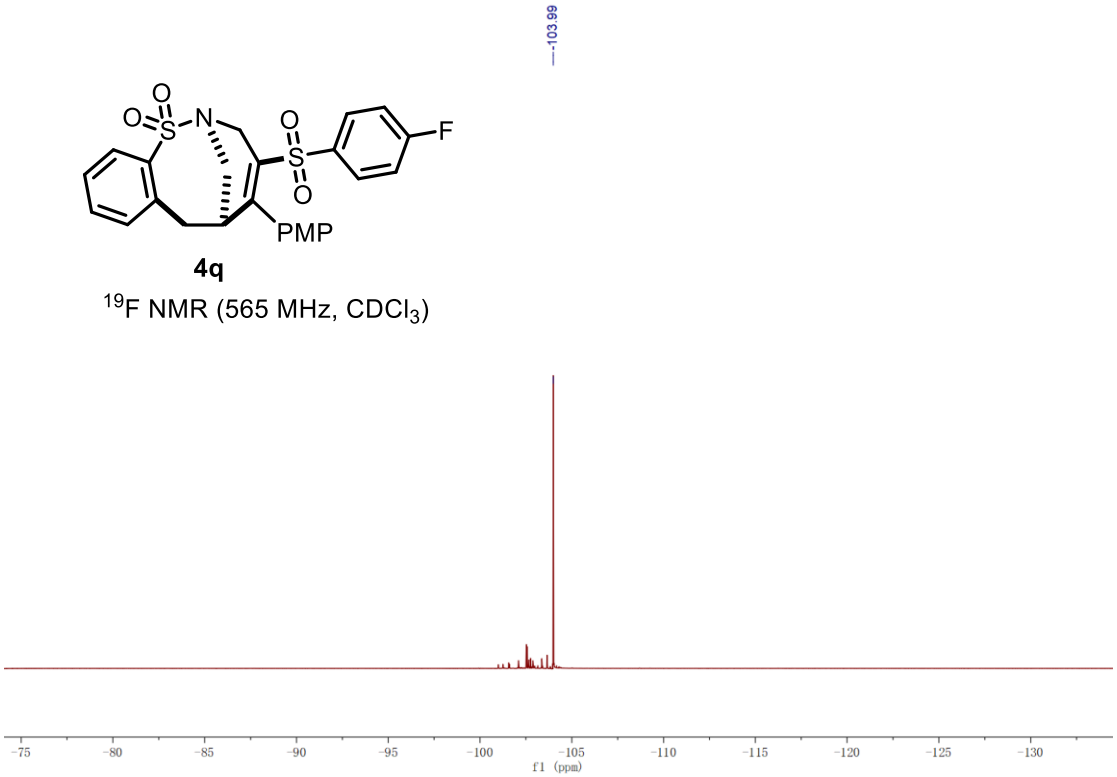
4q

^{1}H NMR (600 MHz, $CDCl_3$)



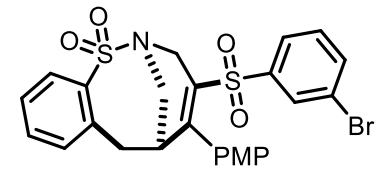
4q

^{13}C NMR (151 MHz, $CDCl_3$)



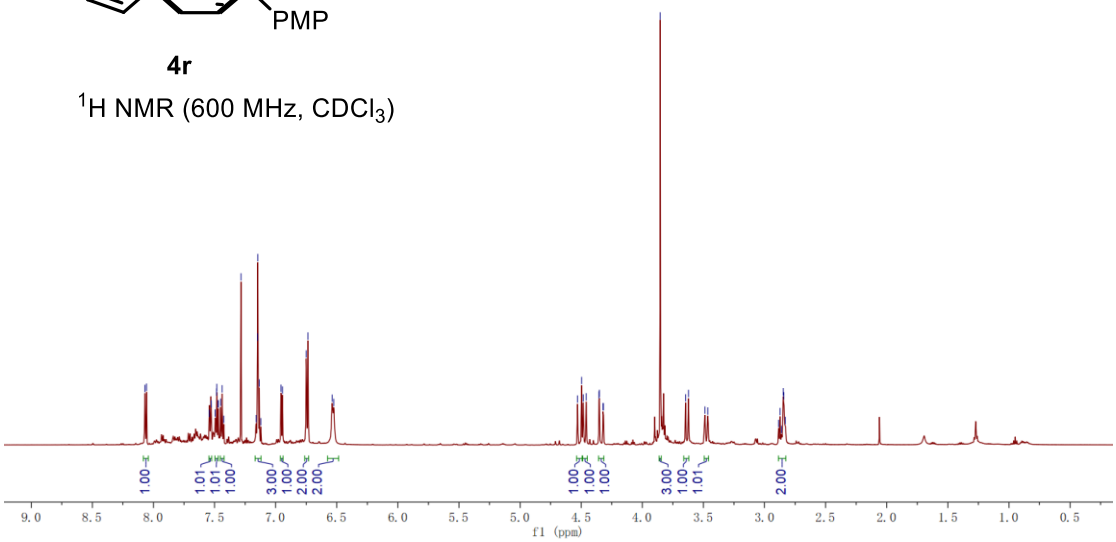
4q

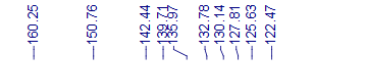
^{19}F NMR (565 MHz, $CDCl_3$)

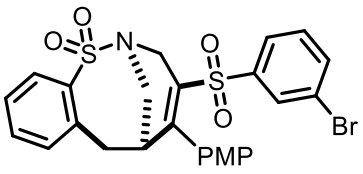


4r

^{1}H NMR (600 MHz, $CDCl_3$)

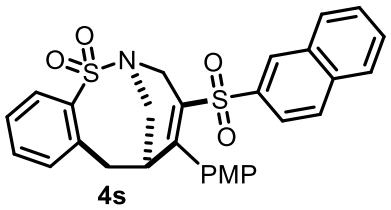






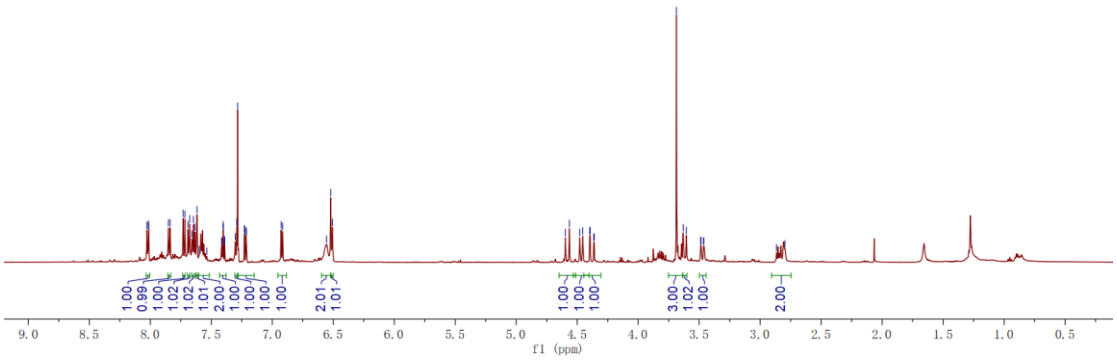
4r

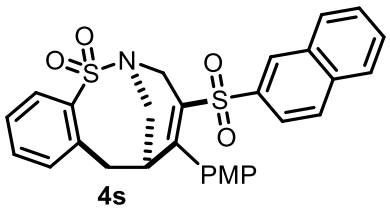
^{13}C NMR (151 MHz, $CDCl_3$)



4s

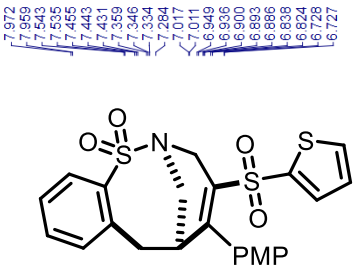
^{1}H NMR (600 MHz, $CDCl_3$)





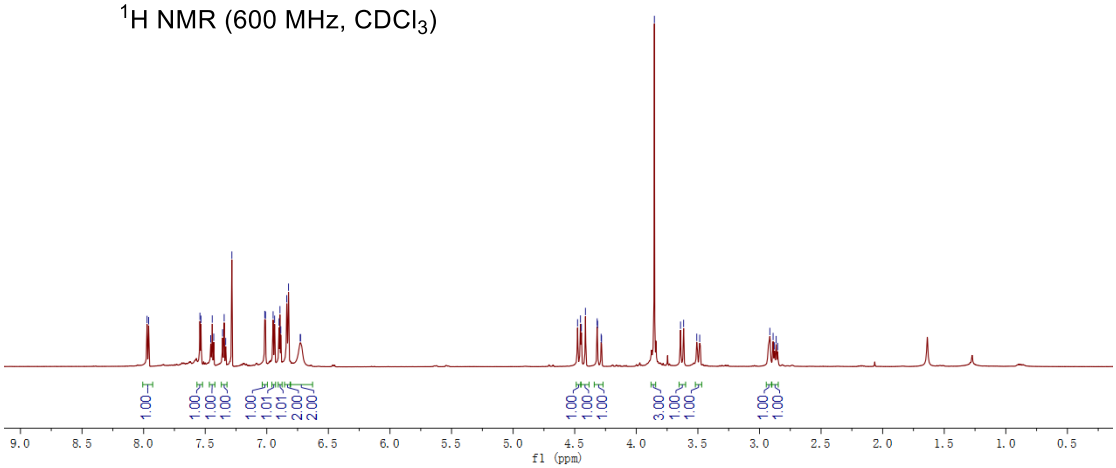
4s

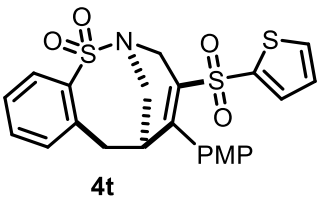
^{13}C NMR (151 MHz, $CDCl_3$)



4t

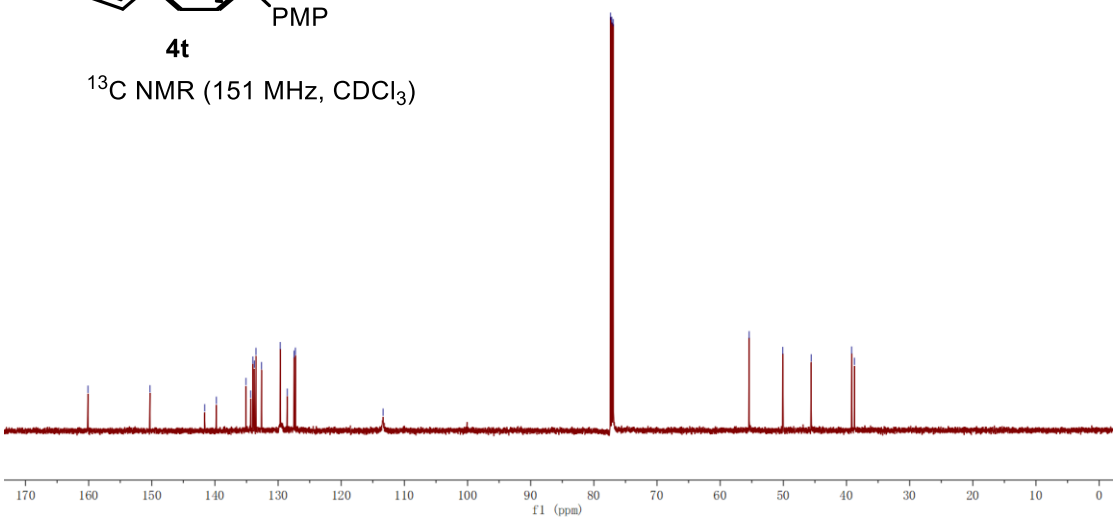
^{1}H NMR (600 MHz, $CDCl_3$)

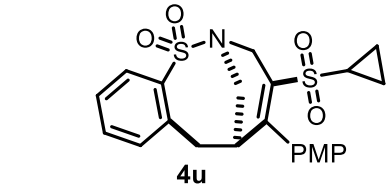




4t

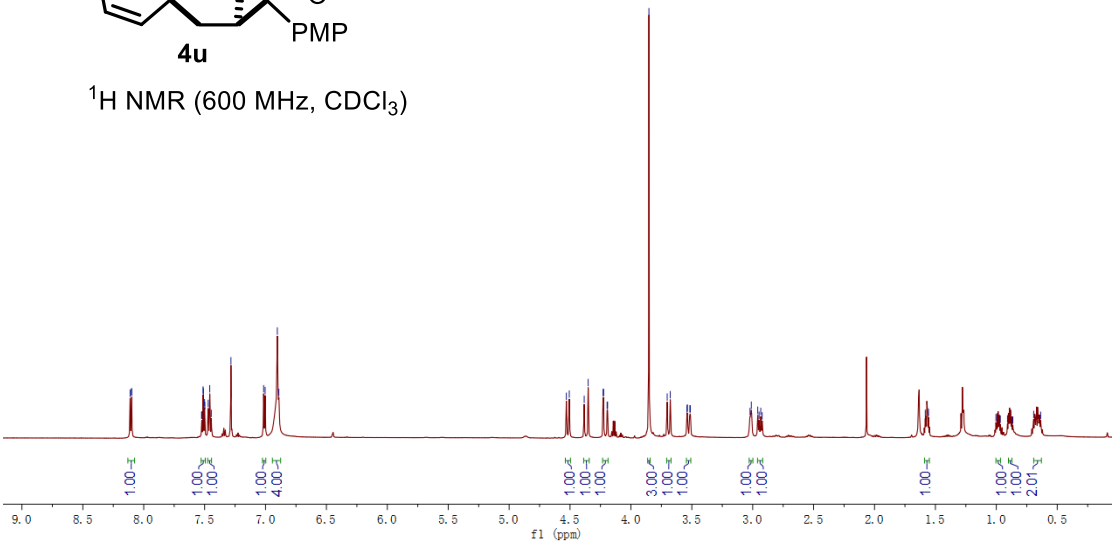
^{13}C NMR (151 MHz, $CDCl_3$)

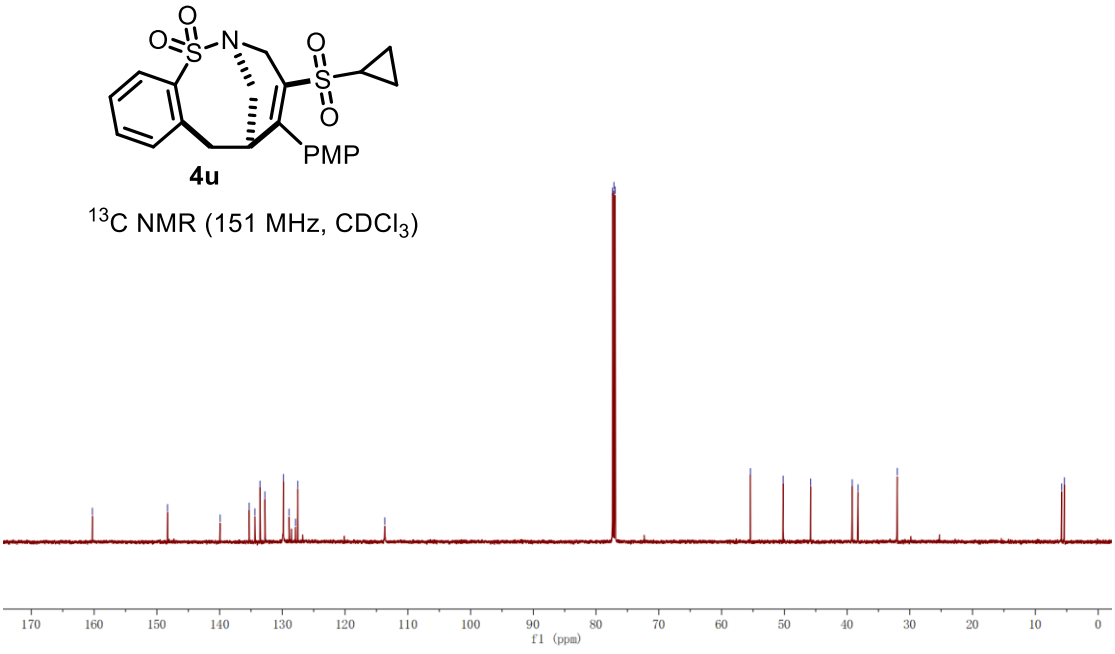




4u

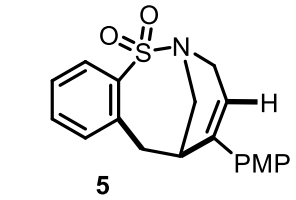
^{1}H NMR (600 MHz, $CDCl_3$)





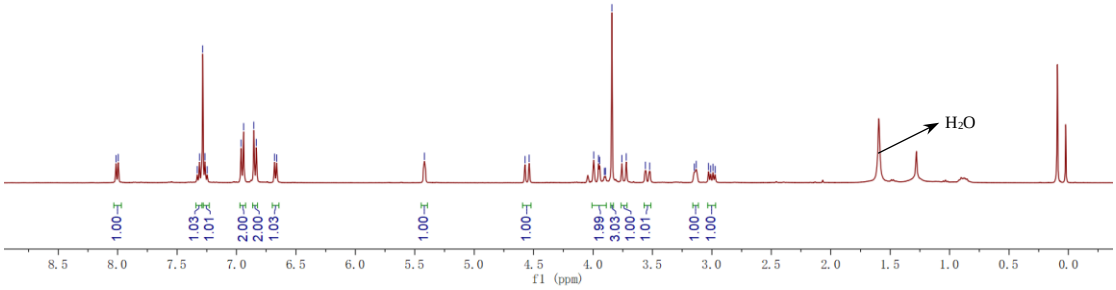
4u

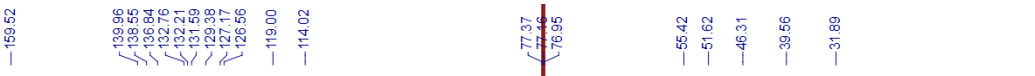
^{13}C NMR (151 MHz, $CDCl_3$)

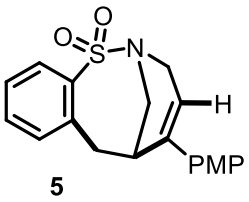


5

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

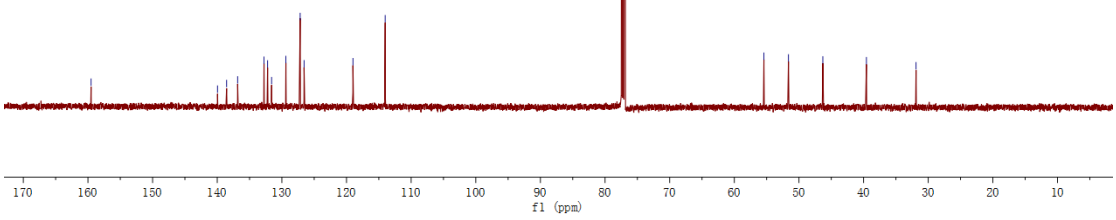


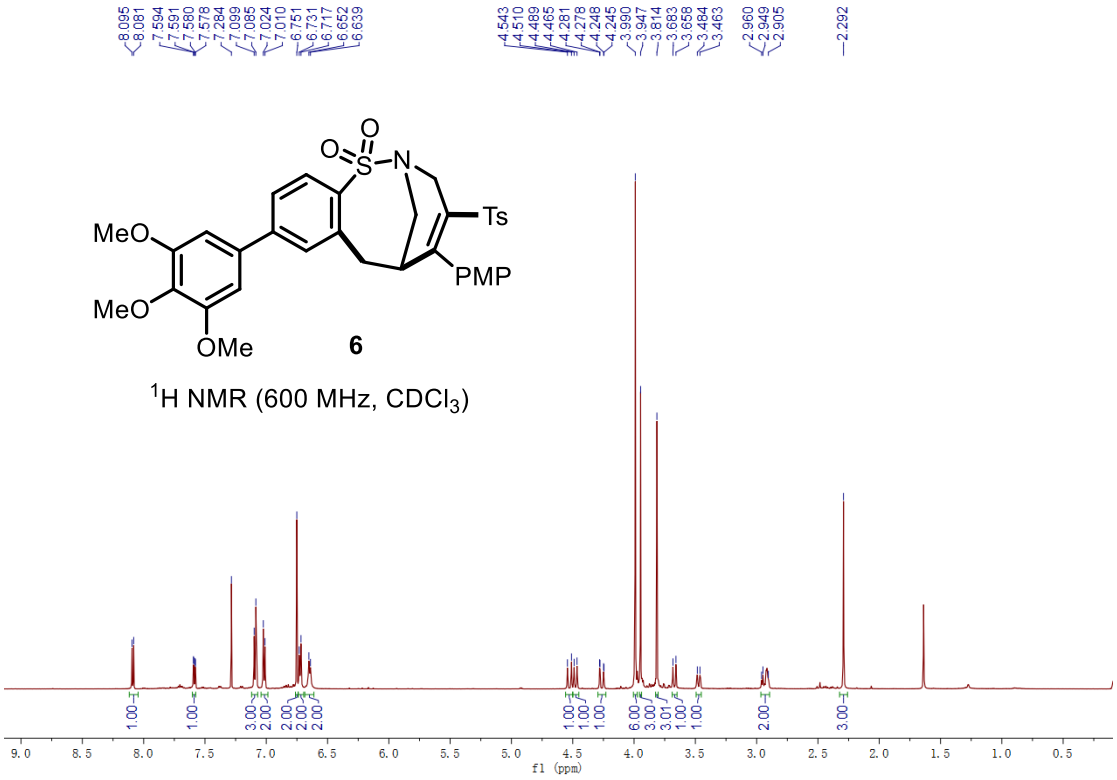




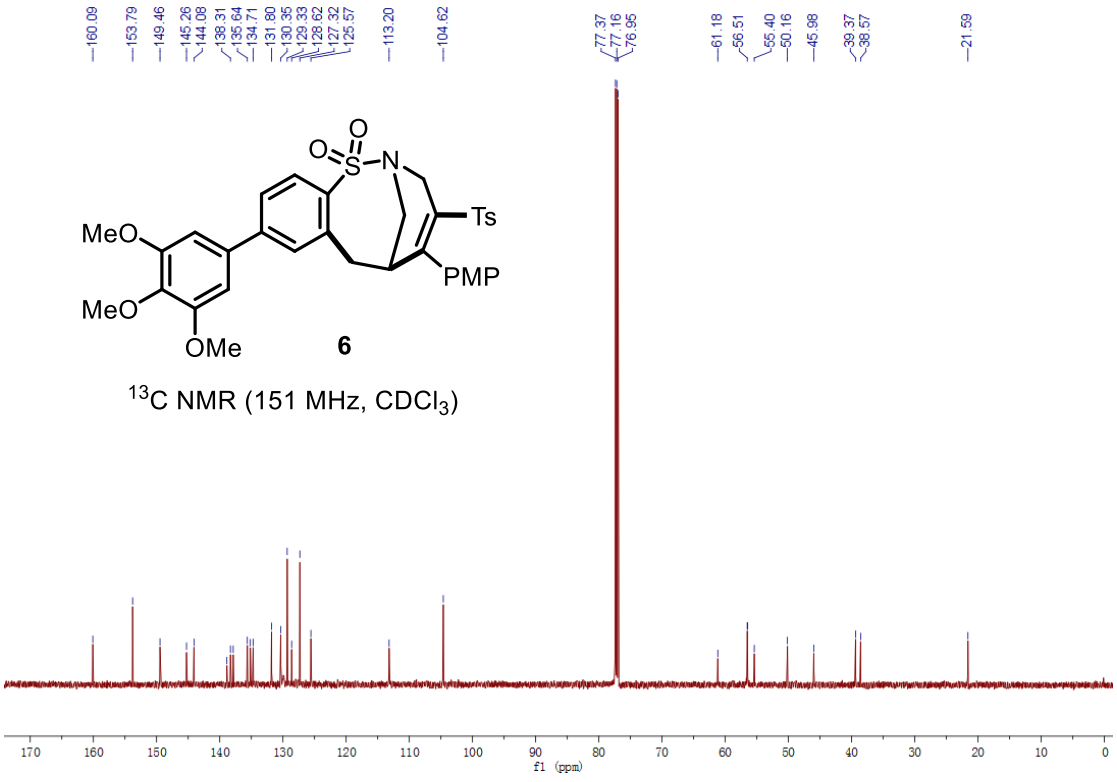
5

^{13}C NMR (151 MHz, $CDCl_3$)

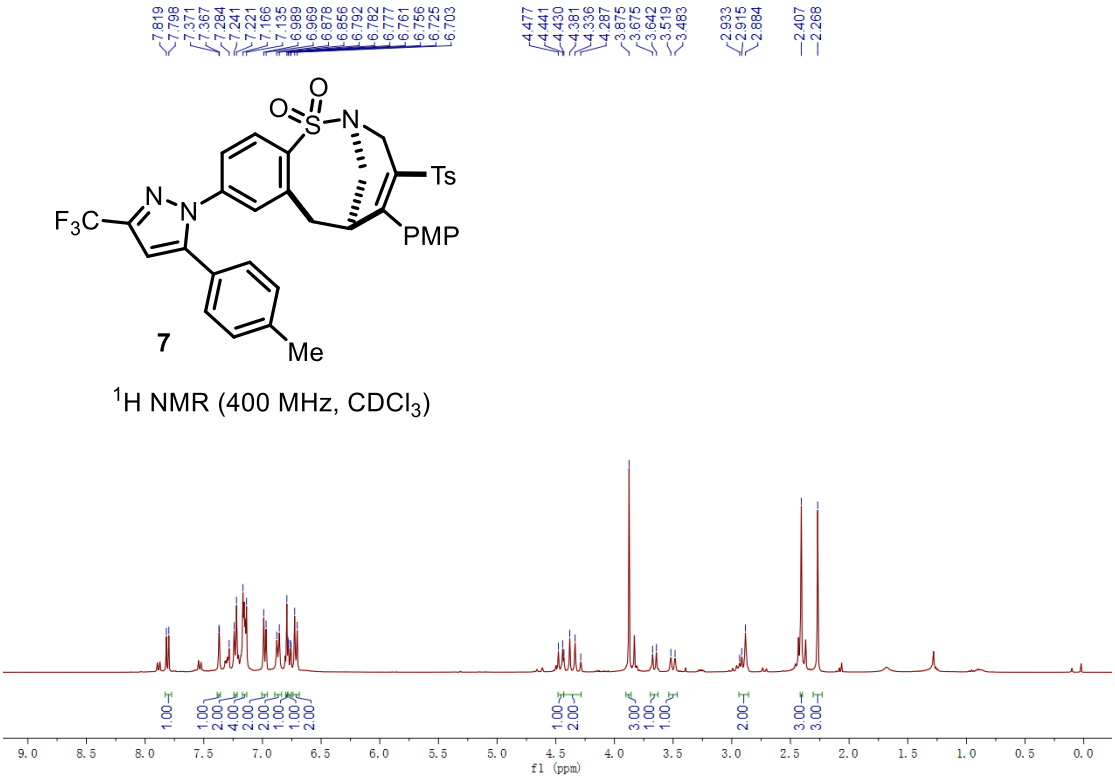




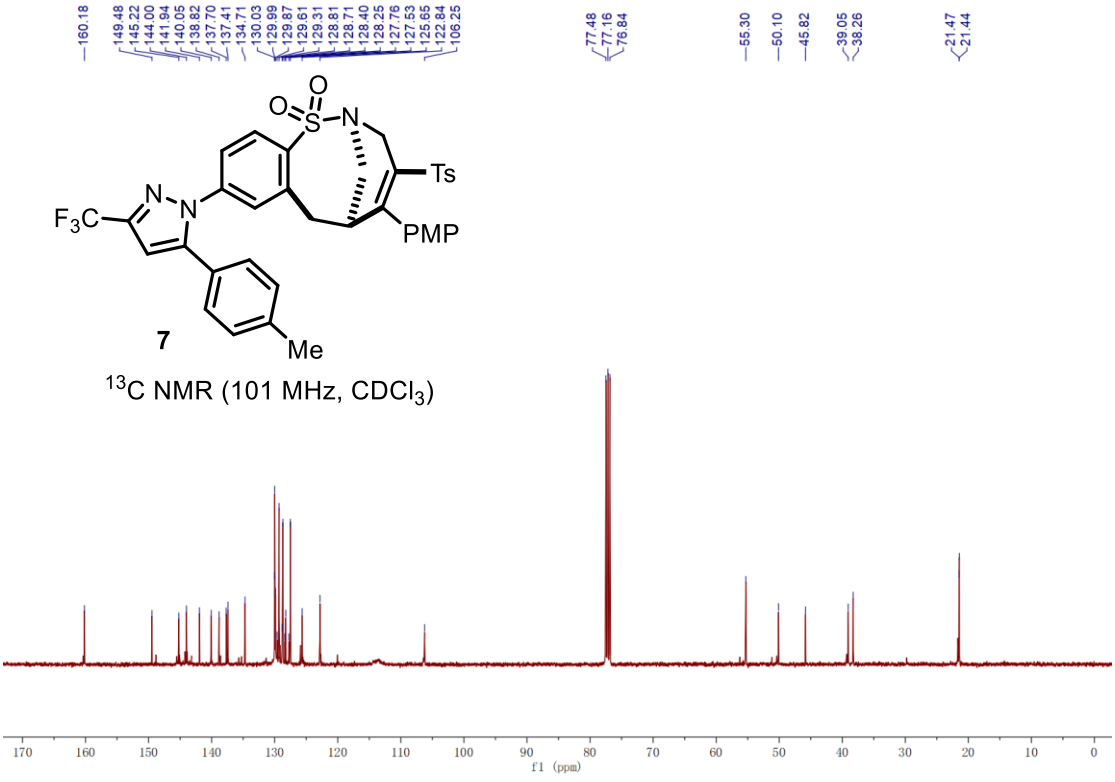
^{1}H NMR (600 MHz, $CDCl_3$)



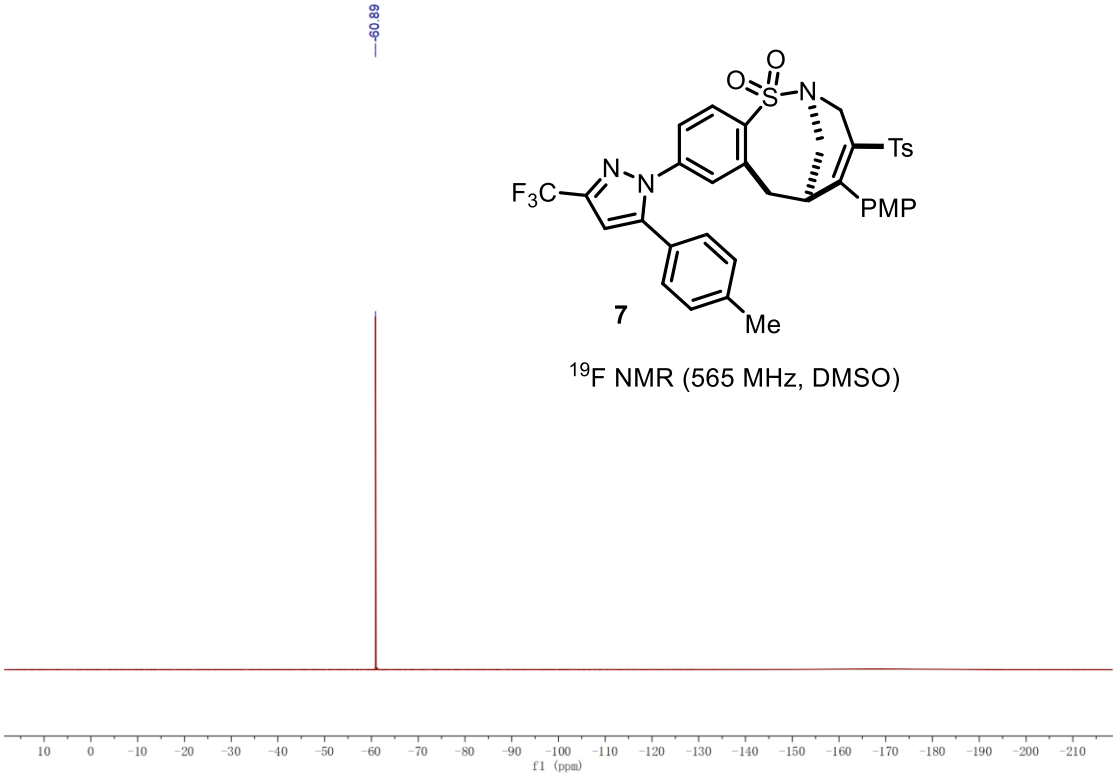
^{13}C NMR (151 MHz, $CDCl_3$)



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

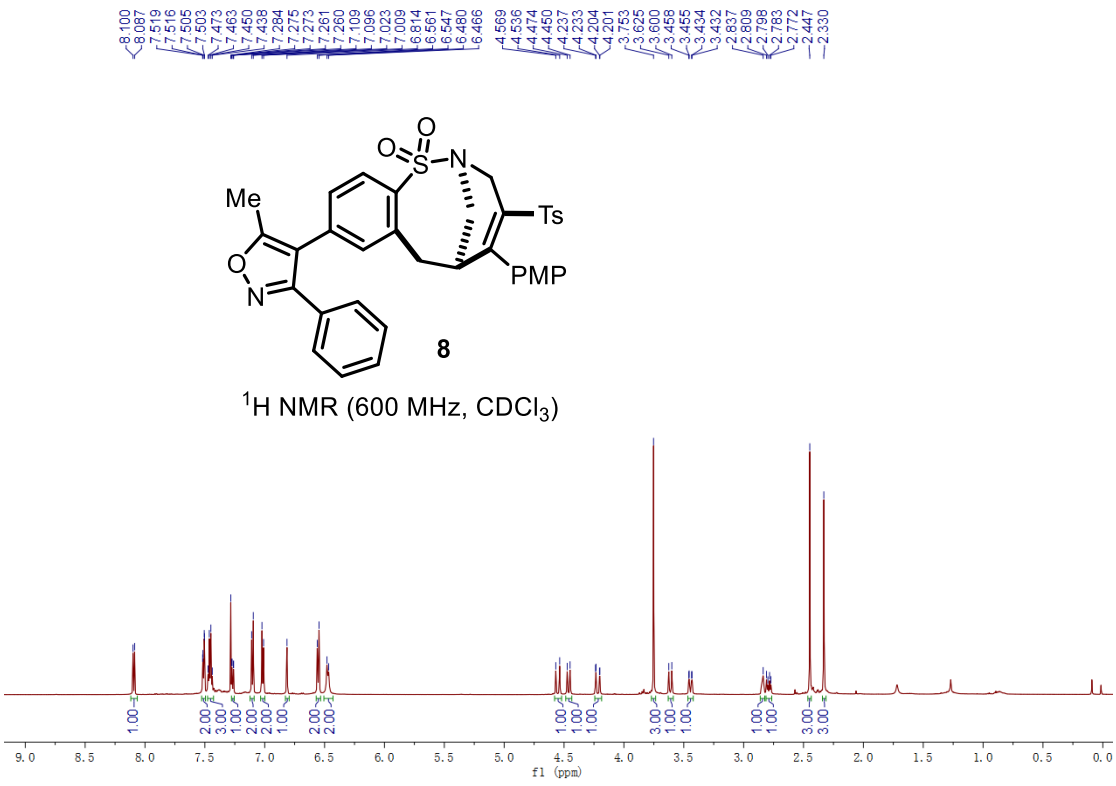


^{13}C NMR (101 MHz, $CDCl_3$)



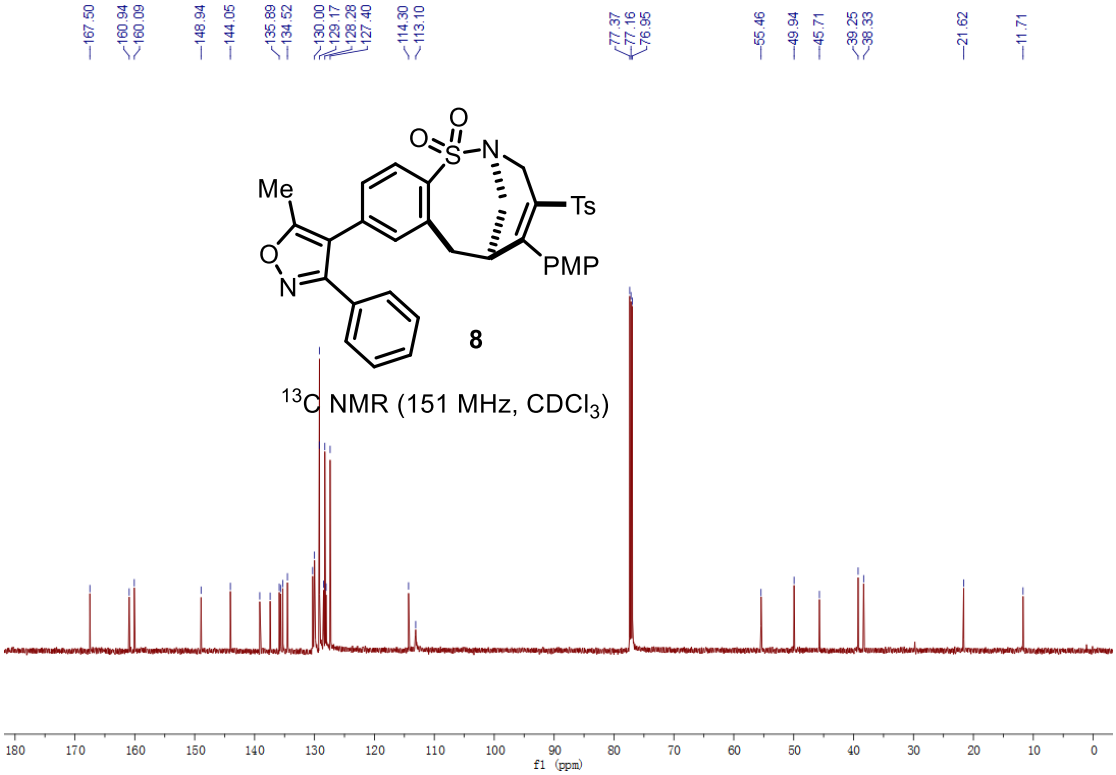
7

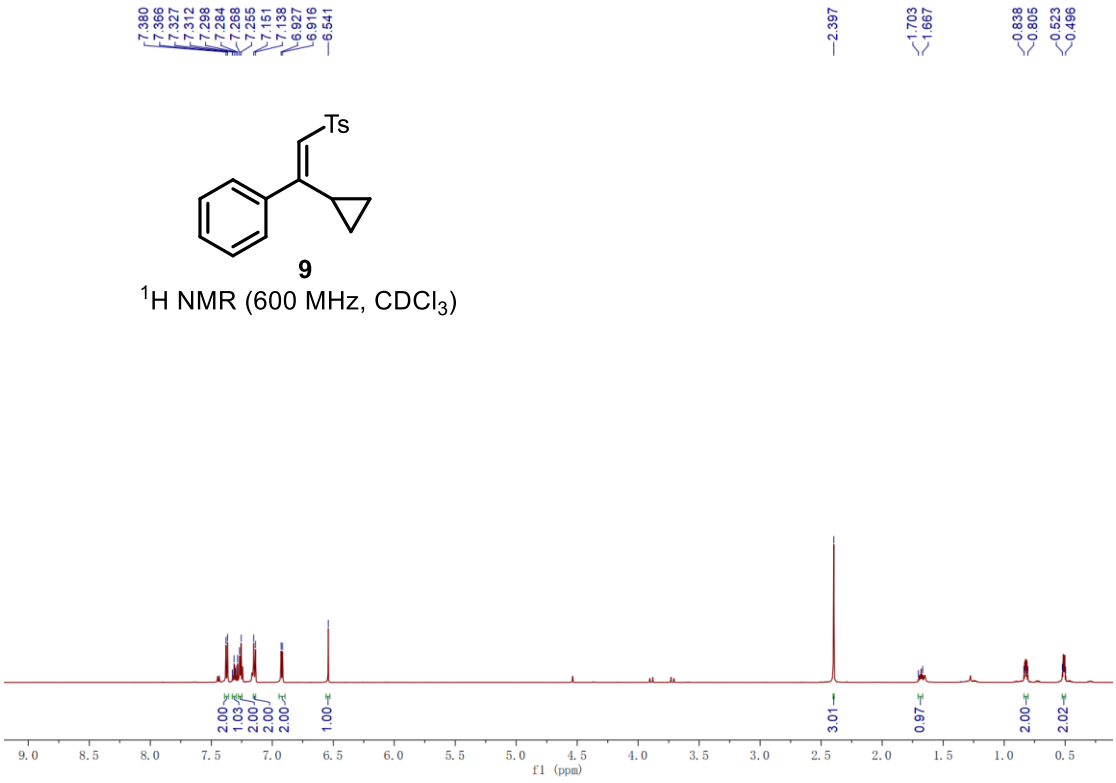
^{19}F NMR (565 MHz, DMSO)

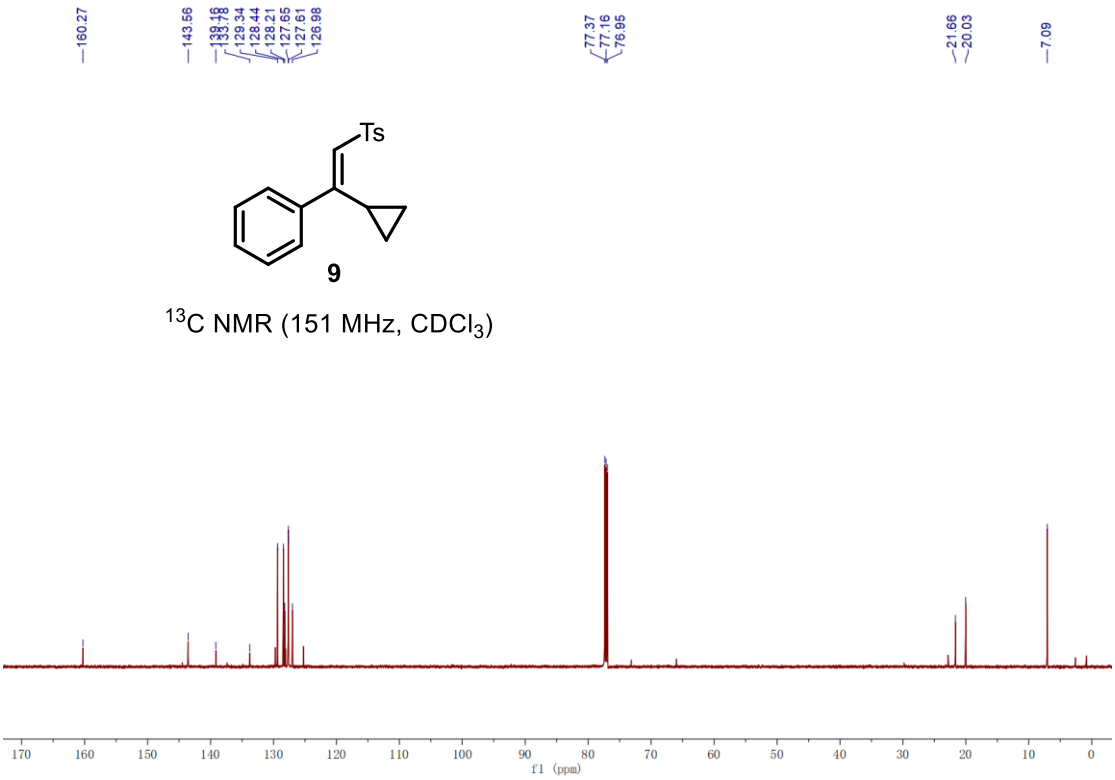


8

^{1}H NMR (600 MHz, $CDCl_3$)


167.50
160.94
160.09
148.94
144.05
135.89
134.52
130.00
129.17
128.28
127.40
114.30
113.10
77.37
77.16
76.95
55.46
49.94
45.71
39.25
38.33
21.62
11.71
Me
O
N
O
S
N
Ts
PMP
8
13C NMR (151 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.380
7.366
7.327
7.312
7.298
7.284
7.268
7.255
7.151
7.138
6.927
6.916
6.541
2.397
1.703
1.667
0.838
0.805
0.523
0.496
Ts
9
1H NMR (600 MHz, CDCl3)
2.00
1.03
2.00
2.00
1.00
3.01
0.97
2.00
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



^{13}C NMR (151 MHz, $CDCl_3$)