Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electrochemical Tandem Cyclization to Access Sulfonylated Fused Sultams *via* SO_2 Insertion with Sodium Metabisulfite

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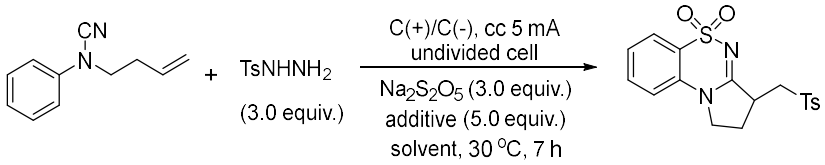
I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), and $KMnO_4$; column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a 300, 400 or 500 MHz spectrometer in $CDCl_3$ or DMSO, fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a 376 or 470 MHz spectrometer in $CDCl_3$ or DMSO, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 125 or 100 MHz spectrometer in $CDCl_3$ or DMSO unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm, DMSO = δ 2.50 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm, DMSO = δ 39.52 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Bruker MicrOTOF Q II. Melting points were measured on a melting point apparatus and were uncorrected. Electrochemical reactions were performed under air using undivided glassware. Electrochemical reactions were conducted using DJS-292potentiostat in constant potential or current mode. Cyclic voltammetry experiments were carried out in DY2113 potentiostat (Digi Ivy).

II. Initial Investigation and Optimization of Reaction Conditions

Table S1. Optimized reaction conditions: effects of additive and solvent. [a]

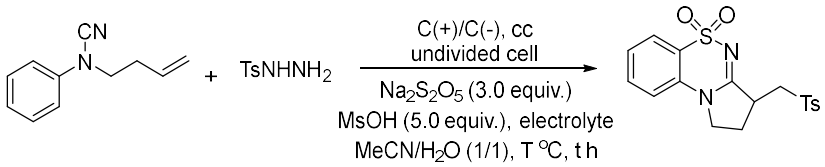


1aa **2a** **3aa**

Entry	Solvent	Additive	Conv (%) [b]	Yield (%) [b]
1	MeCN/H_2O(1/1)	-	68	17
2	MeCN/H_2O(1/1)	K_2CO_3	38	7.2
3	MeCN/H_2O(1/1)	NaOAc	31	3.7
4	MeCN/H_2O(1/1)	HOAc	38	17
5	MeCN/H_2O(1/1)	TFA	61	32
6	MeCN/H_2O(1/1)	MsOH	48	40
7	DCM/H_2O(1/1)	MsOH	48	8
8	Acetone/H_2O(1/1)	MsOH	84	trace
9	HFIP/H_2O(1/1)	MsOH	49	21
10	MeOH/H_2O(1/1)	MsOH	45	trace
11	MeCN/H_2O(3/1)	MsOH	28	24
12	MeCN/H_2O(1/3)	MsOH	79	38

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), $Na_2S_2O_5$ (3.0 equiv.), additive (5 equiv.) and solvent (c = 0.03 *M*) in an undivided cell with graphite rod anode (C-rod, Φ 6 mm), graphite plate cathode (C-plate, 1.5 × 1.5 × 0.2 cm), constant current (cc = 5.0 mA), 30℃, 7h, 4.4 F mol^{-1}. [b] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

Table S2. Optimized reaction conditions: effects of electrolyte, current and temperature [a]



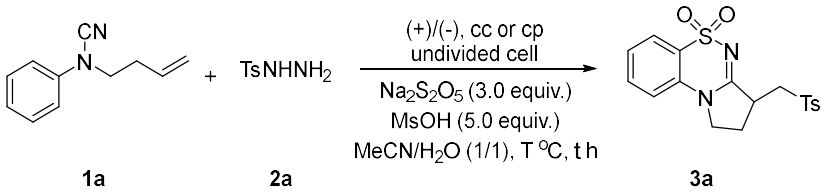
1aa **2a** **3aa**

Entry	Electrolyte	*I* (mA)	t (h)	T (℃)	Conv (%) [b]	Yield (%) [b]	Q (F mol^{-1})
1	-	5	7	30	48	40	4.4
2	Bu_4NBF_4	5	7	30	50	40	4.4
3	Bu_4NOAc	5	7	30	45	35	4.4
4	CF_3SO_3Na	5	7	30	67	39	4.4
5	-	5	14	30	77	49	8.8
6	-	10	4	30	36	21	5.0
7	-	3	13	30	62	39	4.9
8	-	5	7	60	92	52	4.4
9	-	5	7	80	88	21	4.4

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), $Na_2S_2O_5$ (3.0 equiv.), MsOH (5 equiv.), electrolyte (0.3mmol) and MeCN/H_2O (1/1) (c = 0.03 *M*) in an undivided cell with graphite rod anode (C-rod, Φ 6 mm), graphite plate cathode (C-plate, 1.5 × 1.5 × 0.2 cm),

constant current (cc = 5.0 mA), 30°C. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. Isolated yield in parenthesis.

Table S3. Optimized reaction conditions: effect of electrode and cc/cp mode [a]



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

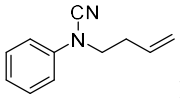
Entry	Anodic/Cathode	cc/cp mode	Conv (%) [b]	Yield (%) [b]
1	C-rod/C-rod	cc	92	52
2	C-rod/Pt	cc	83	41
3	C-rod/Ni	cc	74	27
4	RVC/C-rod	cc	45	17
5	Pt/ C-rod	cc	80	Trace
6	C-plate/C-plate	cc	63	17
7	C-rod /C-rod	cp	83	52
8	C-rod/C-plate	cp	98	74 (71)
9	C-plate/C-rod	cp	92	60
10	C-plate/C-plate	cp	98	65
11 [c]	C-rod/C-plate	cp	88	58
12 [d]	C-rod/C-plate	cp	77	68
13 [e]	C-rod/C-plate	cp	91	63
14 [f]	C-rod/C-plate	cp	100	71
15 [g]	C-rod/C-plate	cp	92	58
16 [h]	C-rod/C-plate	cp	88	53
17 [i]	C-rod/C-plate	cp	100	68

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), $Na_2S_2O_5$ (3.0 equiv.), MsOH (5 equiv.) and MeCN/H_2O (1/1) (c = 0.03 *M*) in an undivided cell with electrodes. The cc mode (cc = 5.0 mA): 60°C, 7 h; the cp mode (cp = 1.5 V, V_{cell}): 30 °C, 12 h. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. [c] $Na_2S_2O_5$ (1.0 eq). [d] $Na_2S_2O_5$ (5.0 eq). [e] MsOH (3.0 eq). [f] 60 °C. [g] $K_2S_2O_5$ (3.0 equiv.). [h] H_2SO_3 (aq.) (3 equiv.) without MsOH. [I] Under N_2. Cp = 1.5 V, 12 h, 4.6 F mol^{-1}.

cc: constant current; cp: constant potential. C-rod (graphite rod, Φ 6 mm); Pt (10 × 10 × 0.1 cm); Ni (10 × 10 × 0.1 cm); RVC: (100 PPI, 1 × 1 × 1 cm); C-plate (1.5 × 1.5 × 0.2 cm);

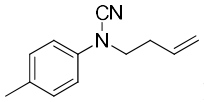
III. Preparation of Substrates

Substrates **1aa -1aq, 1ba -1ja and 1la-1na** were prepared according to the known procedure. [1, 2] The NMR spectra data of compounds **1aa -1ag, 1ai -1aq, 1ba, 1ga-1ja, and 1ma** were in accordance with the reported data of the known literatures. [1, 2] The NMR spectra data of compounds **1na** were in accordance with the reported data of the known literature. [3] Substrates **1ka** were prepared according to the known procedure. [4] The NMR spectra data of compounds **1ka** were in accordance with the reported data of the known literature. [4]



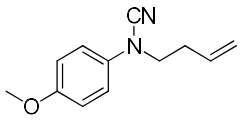
1aa

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (89% yield, 151 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.17 – 7.09 (m, 3H), 5.93 – 5.81 (m, 1H), 5.26 – 5.14 (m, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.59 (q, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 133.1, 129.7, 123.7, 118.6, 116.0, 113.5, 48.9, 31.7.



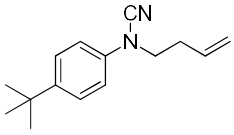
1ab

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (88% yield, 164 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 2H), 7.06 – 6.96 (m, 2H), 5.83 (m, 1H), 5.26 – 5.08 (m, 2H), 3.62 (t, *J* = 7.2 Hz, 2H), 2.60 – 2.49 (m, 2H), 2.32 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 133.4, 133.2, 130.2, 118.5, 116.2, 113.9, 49.0, 31.7, 20.6.



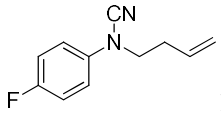
1ac

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (87% yield, 175 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.02 (m, 2H), 6.97 – 6.80 (m, 2H), 5.90 – 5.74 (m, 1H), 5.22 – 5.11 (m, 2H), 3.79 (s, 3H), 3.59 (t, *J* = 7.3 Hz, 2H), 2.53 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 133.21, 133.17, 118.5, 118.4, 114.9, 114.5, 55.6, 49.8, 31.8.



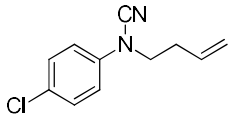
1ad

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (86% yield, 196 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 2H), 7.11 – 7.01 (m, 2H), 5.91 – 5.75 (m, 1H), 5.25 – 5.11 (m, 2H), 3.72 – 3.53 (m, 2H), 2.56 (q, J = 7.0 Hz, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 137.3, 133.2, 126.5, 118.5, 115.8, 113.8, 49.0, 34.3, 31.7, 31.3.



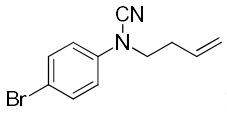
1ae

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (88% yield, 167 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.03 (m, 4H), 5.91 – 5.75 (m, 1H), 5.24 – 5.13 (m, 2H), 3.62 (t, J = 7.2 Hz, 2H), 2.56 (q, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J = 243.8 Hz), 136.1 (d, J = 2.4 Hz), 132.9, 118.7, 118.0 (d, J = 8.1 Hz), 116.5 (d, J = 23.1 Hz), 113.7, 49.2, 31.7.



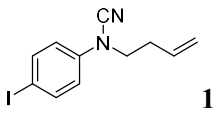
1af

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (85% yield, 176 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.08 – 7.02 (m, 2H), 5.88 – 5.76 (m, 1H), 5.22 – 5.15 (m, 2H), 3.63 (t, J = 7.2 Hz, 2H), 2.56 (q, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 132.8, 129.7, 129.0, 118.9, 117.3, 113.0, 49.0, 31.6.



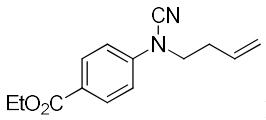
1ag

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (89% yield, 223 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 2H), 7.07 – 6.91 (m, 2H), 5.91 – 5.73 (m, 1H), 5.25 – 5.09 (m, 2H), 3.63 (t, J = 7.2 Hz, 2H), 2.56 (q, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 132.8, 132.7, 118.9, 117.7, 116.4, 112.9, 49.0, 31.6.



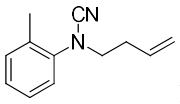
1ah

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (77% yield, 229 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.91 – 5.72 (m, 1H), 5.27 – 5.08 (m, 2H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.65 – 2.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 138.5, 132.8, 118.9, 117.9, 112.8, 86.6, 48.8, 31.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}IN_2$ 299.0040; Found 299.0036.



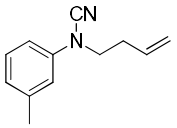
1ai

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (75% yield, 183 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 1H), 5.84 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.25 – 5.15 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.72 (t, *J* = 7.2 Hz, 2H), 2.60 (q, *J* = 7.0 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 143.7, 132.7, 131.4, 125.7, 119.0, 115.1, 112.4, 61.0, 48.7, 31.6, 14.4.



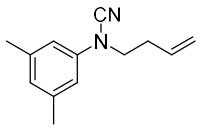
1aj

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (90% yield, 168 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 4H), 5.88 – 5.70 (m, 1H), 5.24 – 5.10 (m, 2H), 3.49 (t, *J* = 7.3 Hz, 2H), 2.56 – 2.44 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 134.0, 133.5, 131.8, 127.7, 127.2, 124.7, 118.3, 115.5, 53.1, 32.1, 17.9.



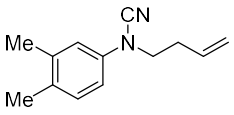
1ak

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (90% yield, 168 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.9 Hz, 1H), 6.98 – 6.86 (m, 3H), 5.90 – 5.78 (m, 1H), 5.23 – 5.13 (m, 2H), 3.64 (t, *J* = 7.0 Hz, 2H), 2.62 – 2.52 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.8, 133.1, 129.5, 124.5, 118.5, 116.8, 113.7, 113.0, 48.8, 31.7, 21.6.



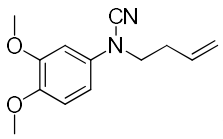
1al

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (83% yield, 166 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (s, 3H), 6.01 – 5.70 (m, 1H), 5.36 – 5.05 (m, 2H), 3.64 (t, J = 7.3 Hz, 2H), 2.76 – 2.52 (m, 2H), 2.34 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 139.6, 133.2, 125.5, 118.5, 113.9, 48.8, 31.7, 21.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2$ 201.1386; Found 201.1387.



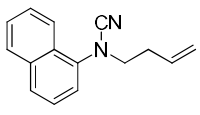
1am

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (83% yield, 166 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.8 Hz, 1H), 6.12 – 5.69 (m, 1H), 5.23 – 5.11 (m, 2H), 3.61 (t, *J* = 7.3 Hz, 2H), 2.60 – 2.48 (m, 2H), 2.26 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.6, 133.2, 132.1, 130.6, 118.4, 117.7, 114.1, 113.4, 49.0, 31.7, 20.0, 19.0.



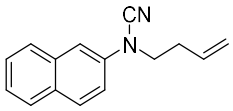
1an

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (84% yield, 195 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 2.8 Hz, 1H), 6.60 (dd, *J* = 8.7, 2.8 Hz, 1H), 5.92 – 5.74 (m, 1H), 5.27 – 5.11 (m, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 3.60 (t, *J* = 7.2 Hz, 2H), 2.65 – 2.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 145.9, 133.6, 133.2, 118.5, 114.3, 111.9, 108.2, 102.1, 56.3, 56.1, 49.7, 31.8.



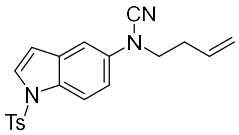
1ao

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (81% yield, 180 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.70 (m, 3H), 7.54 – 7.34 (m, 4H), 5.96 – 5.80 (m, 1H), 5.25 – 5.15 (m, 2H), 3.81 – 3.71 (m, 2H), 2.63 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 133.8, 133.1, 130.1, 130.0, 127.8, 127.24, 127.15, 125.3, 118.7, 116.5, 113.7, 112.2, 49.1, 31.7.



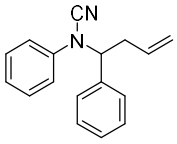
1ap

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (84% yield, 189 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.47 – 7.34 (m, 3H), 5.96 – 5.78 (m, 1H), 5.27 – 5.13 (m, 2H), 3.85 – 3.71 (m, 2H), 2.68 – 2.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.9, 133.2, 130.2, 130.1, 127.9, 127.4, 127.3, 125.4, 118.8, 116.6, 113.8, 112.3, 49.2, 31.8.



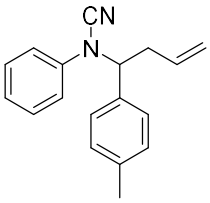
1aq

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (75% yield, 274 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 3.6 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.13 (dd, J = 9.0, 2.4 Hz, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 5.94 – 5.72 (m, 1H), 5.29 – 5.06 (m, 2H), 3.65 (t, *J* = 7.3 Hz, 2H), 2.55 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 136.2, 135.1, 133.1, 131.7, 131.5, 130.0, 128.0, 126.8, 118.6, 114.6, 114.4, 114.1, 108.9, 108.8, 49.7, 31.7, 21.6.



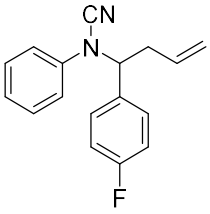
1ba

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (71% yield, 176 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 4H), 7.32 – 7.26 (m, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), δ 5.95 – 5.75 (m, 1H), 5.27 (d, *J* = 16.8, 1H), 5.17 (d, *J* = 10.2, 1H), δ 4.69 (dd, *J* = 9.3, 6.0 Hz, 1H), 3.13 – 2.97 (m, 1H), 2.85 – 2.69 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 139.3, 133.1, 129.7, 129.1, 128.5, 126.4, 124.1, 119.2, 117.3, 112.7, 62.5, 39.9.



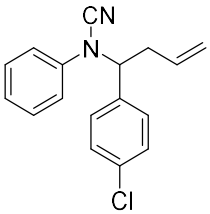
1ca

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (74% yield, 194 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.05 (t, *J* = 7.4 Hz,1H), 5.94 – 5.70 (m, 1H), 5.43 – 5.08 (m, 2H), 4.66 (dd, *J* = 9.1, 6.1 Hz,1H), 3.10 – 2.96 (m, 1H), 2.85 – 2.69 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 138.2, 136.1, 133.2, 129.7, 129.6, 126.3, 124.0, 120.0, 117.3, 112.7, 62.4, 39.8, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2$ 263.1543; Found 263.1553.



1da

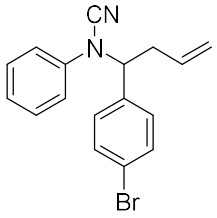
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (71% yield, 189 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.38 – 7.31 (m, 2H), 7.19 – 7.04 (m, 5H), 5.94 – 5.71 (m, 1H), 5.40 – 5.07 (m, 2H), 4.72 (dd, *J* = 9.0, 6.3 Hz, 1H), 3.17 – 2.97 (m, 1H), 2.89 – 2.68 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8 (d, *J* = 248.0 Hz), 140.3, 134.9, 132.8, 129.7, 128.2 (d, *J* = 8.4 Hz), 124.3, 119.4, 117.4, 116.1 (d, *J* = 21.6 Hz), 112.5, 62.1, 39.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.20. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}FN_2$ 267.1292; Found 267.1300.



1ea

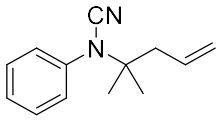
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (69% yield, 195 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (brs, 4H), 7.32 – 7.28 (m, 2H), 7.14 – 7.05 (m, 3H), 5.86 – 5.73 (m, 1H), 5.27 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.18 (dd, *J* = 10.3, 1.5 Hz, 1H), 4.70 – 4.63 (m, 1H), 3.08

– 2.95 (m, 1H), 2.81 – 2.67 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 137.7, 134.3, 132.6, 129.7, 129.3, 127.8, 124.3, 119.5, 117.4, 112.4, 62.1, 39.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}ClN_2$ 283.0997; Found 283.1002.



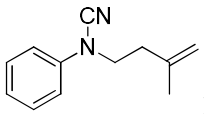
1fa

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (75% yield, 245 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.12 – 7.06 (m, 3H), 5.89 – 5.69 (m, 1H), 5.34 – 5.11 (m, 2H), 4.65 (dd, J = 9.0, 6.2 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.84 – 2.69 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 138.2, 132.6, 132.3, 129.7, 128.1, 124.3, 122.4, 119.5, 117.4, 112.4, 62.1, 39.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}BrN_2$ 327.0491; Found 327.0493.



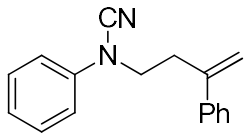
1ga

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (77% yield, 154 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.37 – 7.33 (m, 1H), 7.33 – 7.28 (m, 2H), 5.95 – 5.86 (m, 1H), 5.47 – 4.99 (m, 2H), 2.45 (dt, J = 7.3, 1.2 Hz, 2H), 1.32 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 132.7, 129.4, 128.4, 128.2, 119.5, 115.8, 61.1, 44.9, 26.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2$ 201.1386; Found 201.1388



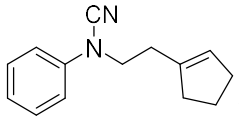
1ha

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/12) to afford the title compound (79% yield, 147 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.15 – 7.07 (m, 3H), 4.92 – 4.87 (m, 1H), 4.79 (s, 1H), 3.71 (t, J = 7.7 Hz, 2H), 2.51 (t, J = 7.5 Hz, 2H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.8, 129.7, 123.6, 116.0, 113.5, 113.3, 47.8, 35.1, 22.5.



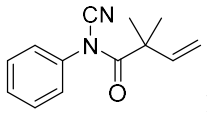
1ia

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (80% yield, 199 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 7H), 7.11-7.04 (m, 3H), 5.41 (brs, 1H), 5.20-5.19 (m, 1H), 3.70-3.68 (m, 2H), 3.02 (t, *J* = 7.4, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 139.8, 129.7, 128.7, 128.05, 126.2, 123.7, 116.1, 115.7, 113.5, 48.3, 33.4. HRMS(ESI): calcd. for $C_{17}H_{17}N_2$ ([M+H]$^+$): 249.1386, found 249.1391.



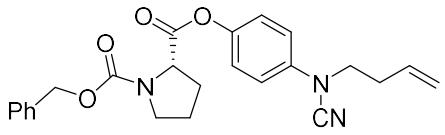
1ja

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (82% yield, 174 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.21 – 6.92 (m, 3H), 5.50 – 5.45 (m, 1H), 3.71 (t, *J* = 7.3 Hz, 2H), 2.58 (t, *J* = 7.3 Hz, 2H), 2.40 – 2.17 (m, 4H), 1.95 – 1.82 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 139.4, 129.7, 127.0, 123.6, 116.0, 113.6, 48.0, 35.2, 32.7, 29.1, 23.4.



1ka

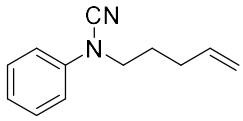
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (71% yield, 152 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 3H), 7.38 – 7.31 (m, 2H), 6.23 (dd, *J* = 17.5, 10.6 Hz, 1H), 5.50 – 5.30 (m, 2H), 1.61 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 140.4, 136.1, 129.7, 129.1, 126.2, 117.0, 110.3, 47.2, 25.8. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{15}N_2O$ 215.1179; Found 215.1172.



1la

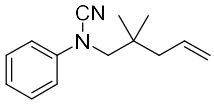
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (68% yield, 285 mg; the mixture of rotamers: 1/1) as a yellow oil. The mixture of rotamers: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 10H), 7.15 (d, *J* = 9.3 Hz, 1H), 7.12 (d, *J* = 9.3 Hz, 1H), 7.04 (d, *J* = 9.1 Hz, 2H), 6.80 (d, *J* = 9.0 Hz,

2H), 5.90 – 5.80 (m, 2H), 5.28 (d, *J* = 12.3 Hz, 1H), 5.25 – 5.15 (m, 6H), 5.10 (d, *J* = 12.3 Hz, 1H), 4.61 (dd, *J* = 8.5, 4.3 Hz, 1H), 4.56 (dd, *J* = 8.7, 4.2 Hz, 1H), 3.77 – 3.51 (m, 8H), 2.65 – 2.52 (m, 4H), 2.47 – 2.33 (m, 2H), 2.28 – 2.14 (m, 2H), 2.15 – 1.91 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 171.4, 155.0, 154.2, 146.6, 146.3, 137.6, 137.6, 136.6, 136.4, 133.0, 132.9, 129.6, 128.6, 128.5, 128.2, 128.0, 127.9, 122.7, 122.5, 118.74, 118.72, 117.02, 116.96, 115.3, 113.4, 113.3, 67.3, 67.2, 59.4, 58.9, 49.20, 49.17, 47.1, 46.6, 31.6, 31.1, 30.0, 24.5, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{26}N_3O_4$ 420.1918; Found 420.1912.



1ma

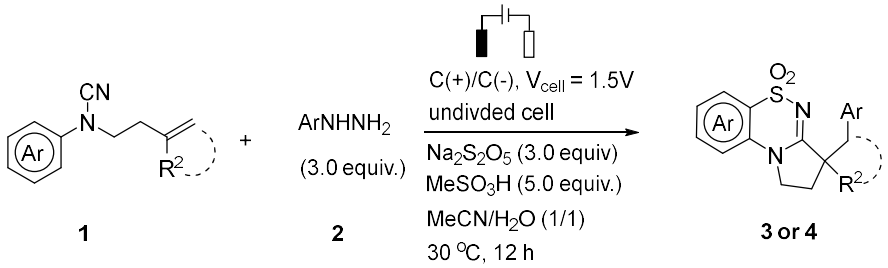
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (84% yield, 156 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 2H), 7.21 – 7.02 (m, 3H), 5.80 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.28 – 4.93 (m, 2H), 3.62 – 3.57 (m, 2H), 2.22 (q, *J* = 7.1 Hz, 2H), 1.96-1.91 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 136.7, 129.8, 123.7, 116.4, 116.0, 113.7, 48.8, 30.5, 26.6.



1na

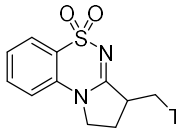
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (74% yield, 158 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.92 – 5.73 (m, 1H), 5.18 – 5.04 (m, 2H), 3.53 (s, 2H), 2.15 (d, *J* = 7.4 Hz, 1H), 1.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 133.5, 129.6, 123.7, 118.7, 116.7, 115.3, 59.4, 44.8, 37.3, 25.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}N_2$ 215.1543; Found 215.1540.

IV. General Procedure and Electrochemical Reactions



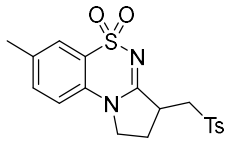
1 **2** **3 or 4**

In an undivided flask (20 mL) equipped with a stir bar, a mixture of *N*-aryl cyanamides **1** (0.3 mmol), $ArNHNH_2$ **2** (0.9 mmol), $Na_2S_2O_5$ (0.9 mmol), $MeSO_3H$ (1.5 mmol) and $MeCN/H_2O$ (v/v = 1/1, 10 mL) were added. The cell was equipped with graphite rod anode (Φ 6 mm) and graphite plate cathode (1.5×1.5×0.2 cm), then connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant voltage of 1.5 V at 30 °C for 12 h. When the reaction was finished, the mixture was extracted with EtOAc (10 mL× 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to provide the desired products **3.**



3aa

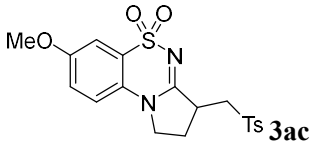
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (71% yield, 83 mg) as a white solid. mp: 240.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.23 (t, *J* = 9.6 Hz, 1H), 4.09 – 3.98 (m, 1H), 3.95-3.91 (m, 1H), 3.75-3.67 (m, 1H), 3.26 (dd, *J* = 14.0, 11.2 Hz, 1H), 3.04 – 2.88 (m, 1H), 2.50 (s, 3H), 2.46 – 2.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 145.5, 136.0, 134.4, 133.3, 130.3, 128.0, 127.0, 125.3, 122.0, 115.0, 57.5, 48.3, 39.6, 25.8, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_4S_2$ 391.0781; Found 391.0792.



3ab

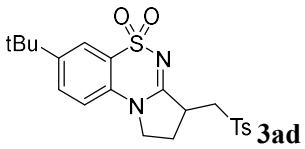
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (68% yield, 82 mg) as a white solid. mp: 248.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.76 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.25 – 4.13 (m, 1H), 4.04 – 3.95 (m, 1H), 3.93 – 3.87 (m, 1H), 3.71 – 3.62 (m, 1H), 3.32 – 3.18 (m, 1H), 2.97 – 2.85 (m, 1H), 2.48 (s, 3H), 2.44 (s, 3H), 2.37 – 2.26 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 145.5,

137.6, 136.0, 134.1, 132.1, 130.2, 128.0, 124.9, 121.8, 115.0, 57.5, 48.2, 39.6, 25.8, 21.7, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_4S_2$ 405.0937; Found 405.0949.



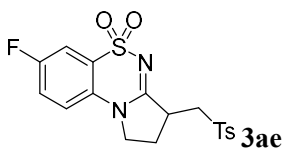
3ac

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (58% yield, 73 mg) as a white solid. mp: 228.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.80 (m, 2H), 7.52 – 7.37 (m, 3H), 7.19 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.02 (d, *J* = 9.2 Hz, 1H), 4.24 – 4.14 (m, 1H), 4.05 – 3.94 (m, 1H), 3.94 – 3.84 (m, 4H), 3.72 – 3.60 (m, 1H), 3.29 – 3.15 (m, 1H), 2.98 – 2.84 (m, 1H), 2.47 (s, 3H), 2.41 – 2.27 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 158.3, 145.5, 136.0, 130.2, 128.0, 122.8, 121.8, 116.7, 107.0, 57.5, 56.0, 48.3, 39.5, 25.7, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_5S_2$ 421.0886; Found 421.0889.



3ad

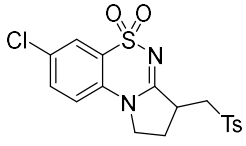
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (66% yield, 88 mg) as a white solid. mp: 210.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.63 (m, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.8 Hz,1H), 4.22 – 4.13 (m, 1H), 4.03 – 3.94 (m, 1H), 3.92 – 3.84 (m, 1H), 3.70 – 3.58 (m, 1H), 3.29 – 3.20 (m, 1H), 2.91 – 2.79 (m, 1H), 2.46 (s, 3H), 2.36 – 2.19 (m, 1H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 150.9, 145.5, 136.0, 132.0, 130.9, 130.2, 128.0, 121.5, 121.2, 115.1, 57.5, 48.3, 39.6, 35.1, 31.0, 25.7, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{27}N_2O_4S_2$ 447.1407; Found 447.1419.



3ae

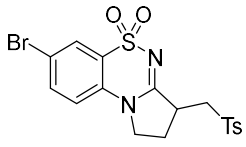
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (64% yield, 78 mg) as a white solid. mp:221.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.14 – 7.06 (m, 1H), 4.18 (td, *J* = 9.6, 2.0 Hz, 1H), 4.08 – 3.96 (m, 1H), 3.92 – 3.82 (m, 1H), 3.75 – 3.63 (m, 1H), 3.30 – 3.18 (m, 1H), 2.96 – 2.84 (m, 1H), 2.47 (s, 3H), 2.41 – 2.26 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ 162.7, 159.7 (d, *J* = 247.7 Hz), 145.4, 136.4, 131.8, 130.6, 128.4, 122.9, 121.7 (d, *J* = 23.5 Hz), 119.9 (d, *J* = 8.3 Hz), 110.9 (d, *J* = 25.5 Hz), 57.0, 49.2, 25.2, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.68. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}FN_2O_4S_2$ 409.0687; Found 409.0697.



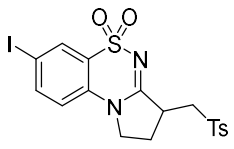
3af

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (56% yield, 71 mg) as a white solid. mp: 231.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.77 (m, 3H), 7.60 – 7.50 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.18-4.13 (m, 1H), 4.04 – 3.95 (m, 1H), 3.87 – 3.80 (m, 1H), 3.73 – 3.62 (m, 1H), 3.25 (dd, *J* = 14.0, 11.0 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.46 (s, 3H), 2.38 – 2.26 (m, 1H). ^{13}C NMR (125MHz, $CDCl_3$) δ 161.8, 145.6, 135.9, 133.4, 132.9, 132.3, 130.3, 128.0, 124.8, 122.8, 116.8, 57.4, 48.5, 39.6, 25.6, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}ClN_2O_4S_2$ 425.0391; Found 425.0403.



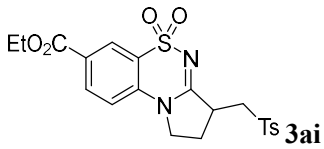
3ag

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (55% yield, 77 mg) as a white solid. mp: 243.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.69 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 1H), 4.17-4.11 (m, 1H), 4.02-3.96 (m, 1H), 3.88 – 3.77 (m, 1H), 3.73 – 3.58 (m, 1H), 3.37 – 3.18 (m, 1H), 2.93 – 2.79 (m, 1H), 2.46 (s, 3H), 2.36 – 2.23 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 145.6, 136.2, 135.9, 133.3, 130.3, 128.0, 127.7, 123.0, 119.4, 117.0, 57.4, 48.5, 39.7, 25.5, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}BrN_2O_4S_2$ 468.9886; Found 468.9879.



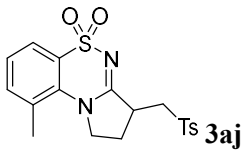
3ah

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (42% yield, 64 mg) as a white solid. mp: 254.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.9 Hz, 1H), 7.93 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 4.19-4.15 (m, 1H), 4.05 – 3.96 (m, 1H), 3.98-3.85 (m, 1H), 3.74 – 3.59 (m, 1H), 3.26 (dd, *J* = 14.0, 11.0 Hz, 1H), 2.96 – 2.85 (m, 1H), 2.49 (s, 3H), 2.42 – 2.27 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 145.6, 141.9, 135.9, 133.8, 133.6, 130.3, 128.0, 123.2, 116.8, 89.5, 57.4, 48.3, 39.7, 25.6, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}IN_2O_4S_2$ 516.9747; Found 516.9759.



3ai

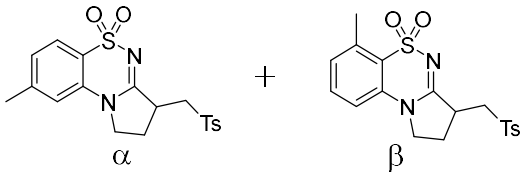
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (27% yield, 37 mg) as a white solid. mp: 217.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 1.9 Hz, 1H), 8.25 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.22 (td, *J* = 9.6, 1.8 Hz, 1H), 4.11 – 4.00 (m, 1H), 3.94 – 3.82 (m, 1H), 3.80 – 3.62 (m, 1H), 3.36 – 3.20 (m, 1H), 3.02 – 2.87 (m, 1H), 2.47 (s, 3H), 2.44 – 2.25 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 162.0, 145.6, 137.3, 135.9, 134.1, 130.2, 129.0, 128.0, 127.1, 121.6, 115.2, 61.9, 57.4, 48.6, 39.7, 25.7, 21.7, 14.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2O_6S_2$ 463.0992; Found 463.1001.



3aj

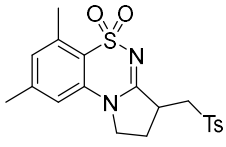
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (59% yield, 71 mg) as a white solid. mp: 237.1°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.81 (m, 3H), 7.52 – 7.41 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 1H), 4.69 – 4.59 (m, 1H), 4.57 – 4.46 (m, 1H), 3.97 (dd, *J* = 14.1, 2.6 Hz, 1H), 3.73 – 3.56 (m, 1H), 3.21 (dd, *J* = 14.1, 11.2 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.77 (s, 3H),

2.51 (s, 3H), 2.33 – 2.16 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 145.5, 137.7, 136.1, 134.3, 130.2, 127.9, 127.1, 125.4, 123.9, 123.6, 57.4, 53.2, 38.7, 27.2, 23.3, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_4S_2$ 405.0937; Found 405.0930.



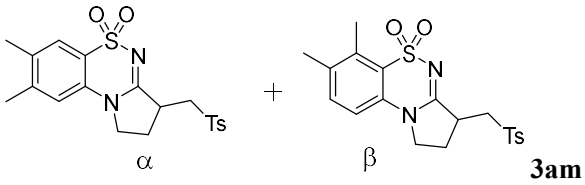
3ak

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (57% yield, 37 mg) as an inseparable white solid (α/β = 1.3/1). Major isomer (α) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.43 – 7.36 (m, 2H), 7.26 – 7.18 (m, 2H), 6.86 (s, 1H), 4.21 – 4.11 (m, 1H), 4.03 – 3.92 (m, 1H), 3.93 – 3.83 (m, 1H), 3.72 – 3.55 (m, 1H), 3.25 – 3.13 (m, 1H), 2.93 – 2.81 (m, 1H), 2.46 (brs, 6H), 2.36 – 2.20 (m, 1H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 3H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.43 – 7.36 (m, 2H),), 6.90 (d, *J* = 8.4 Hz, 1H), 4.21 – 4.11 (m, 1H), 4.03 – 3.92 (m, 1H), 3.93 – 3.83 (m, 1H), 3.72 – 3.55 (m, 1H), 3.25 – 3.13 (m, 1H), 2.93 – 2.81 (m, 1H), 2.72 (s, 3H), 2.45 (s, 3H), 2.36 – 2.20 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 159.7, 145.5, 144.4, 138.1, 135.9, 134.6, 134.8, 132.5, 130.2, 129.8, 127.98, 127.96, 125.0, 120.9, 119.3, 115.2, 113.1, 57.5, 57.4, 48.7, 48.2, 39.6, 39.5, 25.8, 25.7, 22.0, 21.7, 19.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_4S_2$ 405.0937; Found 463. 0939.



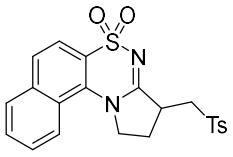
3al

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (61% yield, 76 mg) as a white solid. mp: 253.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 1H), 6.69 (s, 1H), 4.15 (t, *J* = 9.7 Hz, 1H), 3.99-3.94 (m, 1H), 3.91-3.88 (m, 1H), 3.68-3.62 (m, 1H), 3.21 (dd, *J* = 14.1, 11.3 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.68 (s, 3H), 2.47 (s, 3H), 2.40 (s, 3H), 2.35 – 2.22 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ159.6, 145.5, 143.3, 137.9, 136.0, 134.6, 130.7, 130.2, 128.0, 118.4, 113.3, 57.4, 48.6, 39.5, 25.7, 21.7, 21.7, 19.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_4S_2$ 419.1094; Found 419.1090.



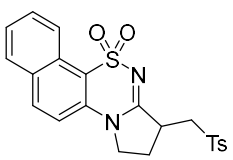
3am

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (1/1) to afford the title compound (53 % yield, 66 mg) as an inseparable mixture white solid (α/β = 4.2/1). Major isomer (α) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.3, 2.9 Hz, 2H), 7.66 (s, 1H), 7.48 – 7.32 (m, 2H), 6.83 (s, 1H), 4.26 – 4.09 (m, 1H), 4.04 – 3.92 (m, 1H), 3.91 – 3.82 (m, 1H), 3.71 – 3.53 (m, 1H), 3.22 (dd, *J* = 14.1, 11.3 Hz, 1H), 2.85 (dt, *J* = 14.1, 7.6 Hz, 1H), 2.63 (s, 1H), 2.46 (s, 3H), 2.37 – 2.24 (m,3H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.3, 2.9 Hz, 2H), 7.48 – 7.32 (m, 2H), 7.36 (s, 1H), 6.80 (s, 1H), 4.26 – 4.09 (m, 1H), 4.04 – 3.92 (m, 1H), 3.91 – 3.82 (m, 1H), 3.71 – 3.53 (m, 1H), 3.22 (dd, *J* = 14.1, 11.3 Hz, 1H), 2.85 (dt, *J* = 14.1, 7.6 Hz, 1H), 2.63 (s, 1H), 2.46 (s, 3H), 2.37 – 2.24 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 159.2, 145.5, 143.2, 136.9, 136.5, 136.01, 135.98, 134.0, 132.7, 132.3, 130.2, 129.5, 128.5, 128.0, 125.1, 121.6, 119.3, 115.8, 112.8, 57.5, 57.4, 48.5, 39.5, 39.4, 25.7, 25.6, 21.7, 20.5, 19.4, 16.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_4S_2$ 419.1094; Found 419.1098.



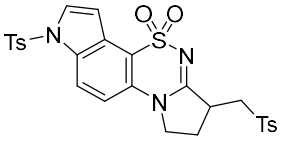
3ao

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (29% yield, 38 mg) as a white solid. mp: 257.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.6 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.97-7.94 (m, 3H), 7.74 – 7.64 (m, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 4.96 – 4.90 (m, 1H), 4.82-4.79 (m, 1H), 4.03 (dd, *J* = 14.4, 2.6 Hz, 1H), 3.84 – 3.74 (m, 1H), 3.23-3.21 (m, 1H), 3.13 – 3.02 (m, 1H), 2.51 (s, 3H), 2.34 – 2.20 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 164.2, 145.4, 136.4, 136.3, 133.4, 130.6, 129.8, 129.0, 128.40, 128.35, 127.9, 125.8, 123.2, 119.7, 118.1, 56.7, 55.6, 39.2, 27.4, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2O_6S_2$ 441.0937; Found 441.0922.



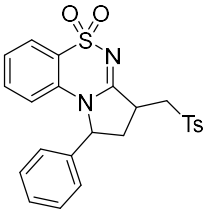
3ap

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (44% yield, 58 mg) as a white solid. mp: 255.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.89-7.86 (m, 3H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 1H), 4.34-4.16 (m, 1H), 4.18 – 4.06 (m, 1H), 3.97 (dd, *J* = 13.8, 2.6 Hz, 1H), 3.83 – 3.70 (m, 1H), 3.29 (dd, *J* = 13.7, 11.3 Hz, 1H), 3.06 – 2.91 (m, 1H), 2.51 (s, 3H), 2.46 – 2.30 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 161.4, 145.4, 136.4, 134.7, 134.3, 131.3, 130.6, 129.5, 129.5, 128.4, 127.1, 127.0, 124.3, 116.1, 115.1, 57.0, 49.6, 25.3, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2O_6S_2$ 441.0937; Found 441.0939.



3aq

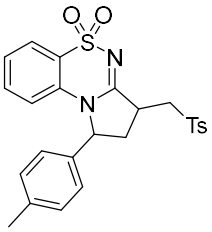
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (54% yield, 94 mg) as a white solid. mp: 225.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.74 – 7.65 (m, 3H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 3.7 Hz, 1H), 6.88 (d, *J* = 9.1 Hz, 1H), 4.19 – 4.01 (m, 1H), 4.01 – 3.90 (m, 1H), 3.85 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.72 – 3.60 (m, 1H), 3.32 – 3.18 (m, 1H), 2.84-2.76 (m, 1H), 2.42 (s, 3H), 2.31 (s, 3H), 2.29 – 2.21 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 146.0, 145.4, 136.0, 134.4, 132.8, 131.0, 129.7, 127.9, 125.8, 118.3, 112.8, 111.8, 107.7, 57.5, 48.9, 39.6, 25.6, 21.7, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{26}N_3O_6S_3$ 584.0978; Found 584.0965.



3ba

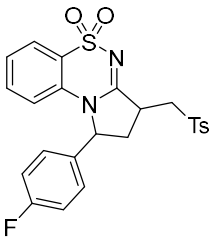
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (an inseparable mixture, 60% yield, 83 mg, dr = 1.7:1) as a white solid. The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.79-7.76 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.18 (m, 6H), 7.11 – 7.04 (m, 2H), 6.85 – 6.74 (m, 1H), 5.67 (d, *J* = 8.7 Hz, 1H), 3.92 – 3.80 (m, 1H), 3.78 – 3.63 (m, 1H), 3.41 – 3.22 (m, 1H), 2.88 – 2.72 (m, 1H), 2.69 – 2.56 (m, 1H), 2.40 (s, 3H). The minor isomer: ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.37 – 7.18 (m, 9H), 6.85 – 6.74 (m, 1H), 5.52 (t, *J* = 8.0 Hz, 1H), 3.92 – 3.80 (m, 1H), 3.78 – 3.63 (m, 1H), 3.41 – 3.22 (m, 2H), 2.40 (s, 3H), 2.11 – 1.99 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 161.7, 145.5, 139.0, 137.4, 135.9, 134.5, 133.6, 133.1, 132.7, 130.3, 130.2, 129.7, 129.6, 129.5, 128.8, 128.7, 128.2, 128.0, 127.9, 127.0, 126.7, 125.5, 125.1, 124.8, 124.44, 122.41, 122.0, 117.0, 116.8, 64.9, 63.7, 57.9, 57.0, 38.7, 37.7, 37.3, 36.1, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}N_2O_4S_2$ 467.1094; Found 467.1107.



3ca

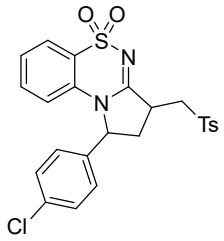
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (an inseparable mixture, 55% yield, 79 mg, dr = 2.1:1) as a white solid. The major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.28 (m, 3H), 7.15-7.11 (m, 3H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.83 – 6.78 (m, 1H),5.61 (d, *J* = 8.4 Hz, 1H), 3.96 – 3.83 (m, 1H), 3.79 – 3.66 (m, 1H), 3.33 – 3.19 (m, 2H), 2.80 – 2.71 (m, 1H), 2.43 (s, 3H), 2.31 (s, 3H), The minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ7.83 – 7.80 (m, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.28 (m, 6H), 7.15-7.11 (m, 2H), 6.83 – 6.78 (m, 1H), 5.46 (dd, *J* = 8.8, 7.1 Hz,1H), 3.96 – 3.83 (m, 1H), 3.79 – 3.66 (m, 1H), 2.70 – 2.61 (m, 2H), 2.43 (s, 3H), 2.30 (s, 3H), 2.11 – 2.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.6, 145.5, 138.8, 138.7, 136.0, 135.9, 134.6, 134.2, 133.6, 133.1, 132.7, 130.4, 130.31, 130.26, 130.2, 129.9, 128.2, 128.0, 127.9, 126.9, 126.7, 125.4, 125.0, 124.6, 122.5, 122.1, 116.9, 116.8, 64.9, 63.6, 58.0, 57.1, 38.7, 37.6, 37.5, 36.3, 21.7, 21.2, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{25}N_2O_4S_2$ 481.1250; Found 481.1263.



3da

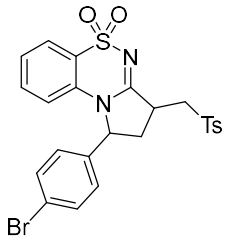
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (an inseparable mixture, 56% yield, 81 mg, dr = 2.0:1) as a white solid. The

major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.29 (m, 2H), 7.08 (dd, *J* = 8.7, 5.0 Hz, 2H), 7.05 – 6.96 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.65 (d, *J* = 8.7 Hz, 1H), 3.92 – 3.82 (m, 1H), 3.76 – 3.64 (m, 1H), 3.33 – 3.20 (m, 1H), 2.84 – 2.73 (m, 1H), 2.43 (s, 3H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.29 (m, 6H), 7.25 – 7.19 (m, 1H), 7.05 – 6.96 (m, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.54 – 5.47 (m, 1H), 3.92 – 3.82 (m, 1H), 3.76 – 3.64 (m, 1H), 3.33 – 3.20 (m, 1H), 2.68 – 2.58 (m, 2H), 2.43 (s, 3H), 2.10 – 2.00 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 162.6 (d, *J* = 248.4 Hz), 161.5, 145.6, 145.5, 135.9, 135.8, 134.8 (d, *J* = 3.3 Hz), 134.4, 133.4, 133.1, 132.7, 130.2, 130.2, 127.9, 127.9, 127.4 (d, *J* = 8.2 Hz), 127.0, 126.9 (d, *J* = 8.3 Hz), 126.8, 125.0, 124.6, 122.6, 122.1, 116.8, 116.73 (d, *J* = 22.0 Hz), 116.71 (d, *J* = 22.5 Hz), 116.7, 64.3, 63.1, 57.8, 56.6, 38.6, 37.6, 37.5, 36.1, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.16, -112.41. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}FN_2O_4S_2$ 485.1000; Found 485.1019.



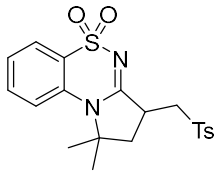
3ea

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (an inseparable mixture, 49% yield, 73 mg, dr = 3.2:1) as a white solid. The major isomer:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.39 – 7.29 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.78 – 6.68 (m, 1H), 5.62 (d, *J* = 8.7 Hz, 1H), 3.95 – 3.80 (m, 1H), 3.78 – 3.63 (m, 1H), 3.36 – 3.17 (m, 1H), 2.85 – 2.74 (m, 1H), 2.74 – 2.60 (m, 1H), 2.45 (s, 3H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.1 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.78 – 6.68 (m, 1H), 5.48 (t, *J* = 8.0 Hz, 1H), 3.95 – 3.80 (m, 1H), 3.78 – 3.63 (m, 1H), 3.36 – 3.17 (m, 2H), 2.45 (s, 3H), 2.13 – 1.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$ δ 164.0, 161.4, 145.6, 137.4, 135.9, 135.84, 135.76, 134.7, 134.3, 133.4, 133.2, 132.7, 130.3, 129.9, 128.0, 127.9, 127.1, 126.9, 126.2, 125.2, 124.8, 122.6, 122.2, 116.6, 116.5, 64.3, 63.1, 57.8, 57.0, 38.5, 37.5, 37.4, 36.1, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}ClN_2O_4S_2$ 501.0704; Found 501.0714.



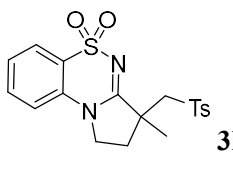
3fa

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 2/1) to afford the title compound (an inseparable mixture, 51% yield, 83 mg, dr = 1.3:1) as a white solid. The major isomer:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.55 – 7.32 (m, 6H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.81 – 6.68 (m, 1H), 5.63 (d, *J* = 8.6 Hz, 1H), 3.98 – 3.83 (m, 1H), 3.82 – 3.62 (m, 1H), 3.40 – 3.13 (m, 1H), 2.89 – 2.76 (m, 1H), 2.75 – 2.64 (m, 1H), 2.47 (s, 3H). The minor isomer:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.32 (m, 6H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.81 – 6.68 (m,1H), 5.49 (t, *J* = 8.0 Hz, 1H), 3.98 – 3.83 (m, 1H), 3.82 – 3.62 (m, 1H), 3.40 – 3.13 (m, 2H), 2.47 (s, 3H), 2.14 – 2.03 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 161.4, 145.6, 138.0, 136.3, 135.9, 135.8, 134.3, 133.4, 133.2, 132.9, 132.9, 132.8, 130.3, 127.9, 127.9, 127.2, 127.1, 126.8, 125.2, 124.8, 122.8, 122.6, 122.1, 116.6, 116.5, 64.3, 63.2, 57.8, 57.0, 38.6, 37.5, 37.3, 36.0, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}BrN_2O_4S_2$ 545.0199; Found 545.0186.



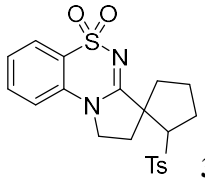
3ga

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (58% yield, 72 mg) as a white solid. mp: 241.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.64-7.60 (m, 1H), 7.47-7.43 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 3.95 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.76 – 3.65 (m, 1H), 3.19 (dd, *J* = 13.9, 11.3 Hz, 1H), 2.83 (dd, *J* = 13.1, 8.2 Hz, 1H), 2.47 (s, 3H), 2.14 (t, *J* = 12.7 Hz, 1H), 1.83 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 145.5, 136.1, 133.8, 132.7, 130.2, 127.9, 126.6, 125.9, 123.0, 116.1, 67.7, 57.6, 44.3, 36.8, 28.4, 23.9, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_4S_2$ 419.1094; Found 419.1098.



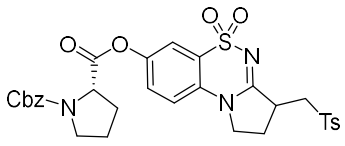
3ha

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (47% yield, 57 mg) as a white solid. mp: 194.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.46 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.12 – 4.02 (m, 1H), 3.99 – 3.89 (m, 1H), 3.46 (d, *J* = 14.4 Hz, 1H), 3.38 (d, *J* = 14.3 Hz, 1H), 2.87 – 2.74 (m, 1H), 2.28 (s, 3H), 2.25 – 2.17 (m, 1H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 145.2, 137.3, 134.4, 133.2, 130.1, 127.6, 126.8, 124.6, 121.7, 115.8, 62.2, 47.3, 46.8, 29.8, 25.1, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_4S_2$ 405.0937; Found 405.0950.



3ja

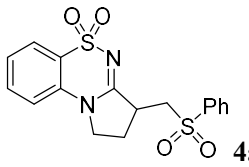
After stirring at 30 °C for 18 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (43% yield, 55 mg) as a white solid. mp: 230.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.71– 7.62 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 4.33-4.29 (m, 1H), 4.13 – 4.07 (m, 1H), 4.04-4.00 (m, 1H), 3.41 – 3.31 (m, 1H), 2.38 (s, 3H), 2.36 – 2.25 (m, 1H), 2.24 – 2.13 (m, 2H), 2.09 – 1.88 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 145.1, 136.4, 134.7, 133.0, 130.0, 128.0, 126.8, 125.1, 122.2, 115.4, 69.5, 57.0, 47.8, 41.1, 27.1, 26.4, 22.1, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}N_2O_4S_2$ 431.1094; Found 431.1104.



3la

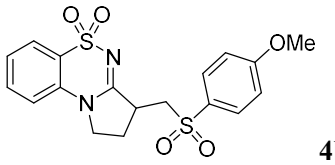
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (an inseparable mixture, 26% yield, 49 mg, dr = 1.4:1) as a white solid. The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.27 (m, 9H), 6.93 (s, 1H), 5.31 – 4.94 (m, 2H), 4.62 – 4.44 (m, 1H), 4.15 – 4.03 (m, 1H), 3.96 – 3.86 (m, 1H), 3.85 – 3.76 (m, 1H), 3.70 – 3.49 (m, 3H), 3.33 – 3.11 (m, 1H), 2.84 – 2.70 (m, 1H), 2.45 (s, 3H), 2.41 – 2.31 (m, 1H), 2.29 – 2.13 (m, 2H), 2.11 – 1.90 (m, 2H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.80 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 2.4 Hz, 1H), 7.53 (s, 1H), 7.40 – 7.27 (m, 8H), 7.00 (d, *J* = 9.1 Hz, 1H), 5.31 – 4.94 (m, 2H), 4.62 – 4.44 (m, 1H), 4.15 – 4.03 (m, 1H), 3.96 – 3.86

(m, 1H), 3.85 – 3.76 (m, 1H), 3.70 – 3.49 (m, 3H), 3.33 – 3.11 (m, 1H), 2.84 – 2.70 (m, 1H), 2.45 (s, 3H), 2.41 – 2.31 (m, 1H), 2.29 – 2.13 (m, 2H), 2.11 – 1.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 170.8, 161.6, 161.6, 155.0, 154.1, 148.44, 148.42, 148.2, 145.52, 145.48, 136.5, 136.3, 135.94, 135.91, 132.1, 132.0, 130.3, 128.7, 128.5, 128.3, 128.2, 128.1, 127.98, 127.97, 127.8, 127.22, 127.19, 127.0, 122.5, 122.3, 117.6, 116.8, 116.7, 67.4, 67.2, 59.4, 58.8, 57.4, 48.2, 47.1, 46.6, 39.59, 39.56, 31.02, 29.96, 25.5, 24.6, 23.7, 21.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{32}N_3O_8S_2$ 638.1625; Found 638.1604.



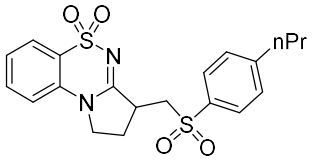
4a

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (69% yield, 77 mg) as a white solid. mp: 220.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 3H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.70 – 7.61 (m, 3H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.23 (t, *J* = 9.6 Hz, 1H), 4.08-4.01 (m, 1H), 3.97-3.92 (m, 1H), 3.79 – 3.69 (m, 1H), 3.29 (dd, *J* = 14.0, 11.2 Hz, 1H), 3.01 – 2.89 (m, 1H), 2.43 – 2.30 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 139.0, 134.4, 133.3, 129.7, 128.0, 127.0, 125.3, 122.0, 115.1, 57.4, 48.3, 39.5, 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O_4S_2$ 377.0624; Found 377.0633.



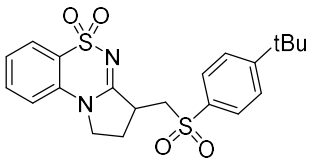
4b

After stirring at 30 °C for 18 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (58% yield, 70 mg) as a white solid. mp:208.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.03 (m, 3H), 4.20-4.12 (m, 1H), 4.03-3.98 (m, 1H), 3.91 (s, 3H), 3.86 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.71 – 3.61 (m, 1H), 3.24 (dd, *J* = 14.1, 11.1 Hz, 1H), 2.90 – 2.81 (m, 1H), 2.36 – 2.25 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 161.6, 134.4, 133.3, 130.4, 130.2, 127.0, 125.1, 121.9, 115.2, 114.8, 57.7, 55.8, 48.3, 39.7, 25.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_5S_2$ 407.0730; Found 407.0731.



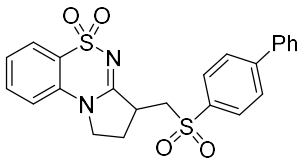
4c

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (66% yield, 82 mg) as a white solid. mp: 217.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.62 (m, 1H), 7.48 – 7.43 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.22-4.18 (m, 1H), 4.04-3.99 (m, 1H), 3.89 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.72-3.66 (m, 1H), 3.32 – 3.14 (m, 1H), 2.97 – 2.83 (m, 1H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.40 – 2.23 (m, 1H), 1.76 – 1.65 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 150.1, 136.2, 134.4, 133.3, 129.7, 128.0, 127.0, 125.2, 122.0, 115.1, 57.5, 48.3, 39.6, 38.0, 25.8, 24.2, 13.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_4S_2$ 419.1094; Found 419.1099.



4d

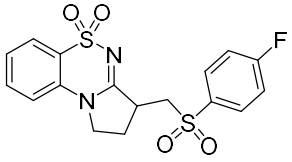
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (67% yield, 86 mg) as a white solid. mp: 236.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.68 – 7.56 (m, 3H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 4.19 (t, *J* = 9.5 Hz, 1H), 4.04-3.97 (m, 1H), 3.91 – 3.82 (m, 1H), 3.72 – 3.61 (m, 1H), 3.22 (dd, *J* = 14.0, 11.3 Hz, 1H), 2.92 (dt, *J* = 14.7, 7.9 Hz, 1H), 2.42 – 2.27 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 158.5, 135.8, 134.4, 133.3, 127.8, 127.0, 126.7, 125.2, 122.0, 115.1, 57.5, 48.3, 39.6, 35.4, 31.1, 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}N_2O_4S_2$ 433.1250; Found 433.1243.



4e

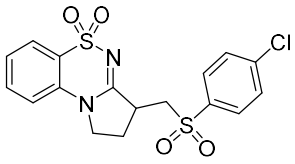
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (51% yield, 69 mg) as a white solid. mp: 225.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.67 – 7.62 (m, 3H), 7.56 – 7.41 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.21 (t, *J* = 9.7 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.95 (dd, *J* = 14.1, 2.5 Hz, 1H), 3.79

– 3.66 (m, 1H), 3.32 (dd, *J* = 14.0, 11.2 Hz, 1H), 3.01 – 2.84 (m, 1H), 2.43 – 2.26 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 147.3, 139.0, 137.3, 134.4, 133.3, 129.2, 128.8, 128.5, 128.3, 127.5, 127.0, 125.2, 121.9, 115.1, 57.5, 48.3, 39.6, 25.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}N_2O_4S_2$ 453.0937; Found 453.0933.



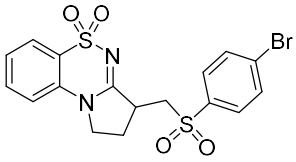
4f

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (58% yield, 68 mg) as a white solid. mp: 227.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.94 (m, 3H), 7.75 – 7.68 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 4.32 – 4.20 (m, 1H), 4.10-4.03 (m, 1H), 3.96 (dd, *J* = 14.0, 2.7 Hz, 1H), 3.85 – 3.72 (m, 1H), 3.30 (dd, *J* = 14.0, 11.0 Hz, 1H), 3.07 – 2.91 (m, 1H), 2.47 – 2.30 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 165.8 (d, *J* = 253.5 Hz), 162.6, 135.6 (d, *J* = 3.0 Hz), 134.9, 133.9, 131.7 (d, *J* = 10.0 Hz), 127.1, 124.5, 121.8, 117.4 (d, *J* = 22.7 Hz), 116.9, 57.0, 48.9, 39.9, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.99. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}FN_2O_4S_2$ 399.0530; Found 399.0542.



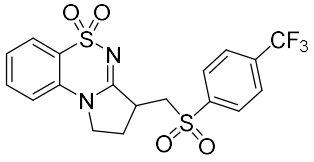
4g

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (67% yield, 82 mg) as a white solid. mp: 211.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.70 (t, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 4.25 (t, *J* = 9.6 Hz, 1H), 4.06 (td, *J* = 9.9, 7.1 Hz, 1H), 4.09-3.94 (m, 1H), 3.82 – 3.71 (m, 1H), 3.30 (dd, *J* = 14.0, 11.0 Hz, 1H), 3.03 – 2.91 (m, 1H), 2.51 – 2.24 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 141.3, 137.4, 134.3, 133.3, 130.0, 129.5, 127.1, 125.4, 122.1, 115.0, 57.5, 48.2, 39.4, 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}ClN_2O_4S_2$ 411.0235; Found 411.0240.



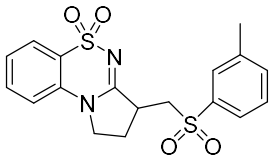
4h

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (57% yield, 77 mg) as a white solid. mp: 219.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 3H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 4.18-4.12 (m, 1H), 4.04-3.97 (m, 1H), 3.85 (dd, *J* = 14.1, 2.5 Hz, 1H), 3.74 – 3.61 (m, 1H), 3.28 (dd, *J* = 14.1, 11.0 Hz, 1H), 2.83-2.76 (m, 1H), 2.33 – 2.17 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 137.9, 134.3, 133.2, 132.0, 129.7, 129.6, 126.9, 124.9, 121.7, 115.3, 57.4, 48.3, 39.5, 25.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}BrN_2O_4S_2$ 454.9729; Found 454.9744.



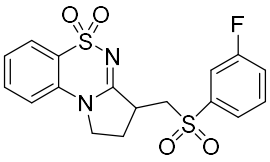
4i

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (58% yield, 77 mg) as a white solid. mp: 217.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.94 – 7.83 (m, 3H), 7.63 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 4.24 – 4.13 (m, 1H), 4.09 – 3.99 (m, 1H), 3.93 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.80 – 3.67 (m, 1H), 3.31 (dd, *J* = 14.0, 10.9 Hz, 1H), 2.96 – 2.85 (m, 1H), 2.41 – 2.25 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 142.5, 136.0 (q, *J* = 33.2 Hz), 134.3, 128.7, 127.1, 126.8 (q, *J* = 3.6 Hz), 125.2, 123.0 (q, *J* = 275.7 Hz), 121.9, 115.1, 57.4, 48.3, 39.3, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.25. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}F_3N_2O_4S_2$ 445.0498; Found 445.0510.



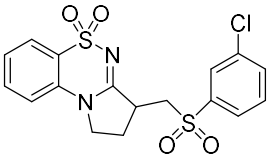
4j

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (70% yield, 81 mg) as a white solid. mp: 243.4 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.71 – 7.64 (m, 1H), 7.54 – 7.47 (m, 3H), 7.15 – 7.06 (m, 1H), 4.26-4.20 (m, 1H), 4.07-4.01 (m, 1H), 3.94 (dd, *J* = 14.0, 2.6 Hz, 1H), 3.80 – 3.62 (m, 1H), 3.26 (dd, *J* = 14.0, 11.2 Hz, 1H), 3.05 – 2.82 (m, 1H), 2.50 (s, 3H), 2.45 – 2.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 140.1, 138.8, 135.2, 134.4, 133.3, 129.5, 128.2, 127.1, 125.4, 125.0, 122.1, 114.9, 57.4, 48.3, 39.5, 25.8, 21.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_4S_2$ 391.0781; Found 391.0776.



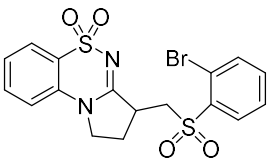
4k

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (56% yield, 66 mg) as a white solid. mp: 236.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 4.36 – 4.21 (m, 1H), 4.12 – 4.03 (m, 1H), 3.99 (dd, *J* = 13.9, 2.7 Hz, 1H), 3.81-3.74 (m, 1H), 3.31 (dd, *J* = 14.0, 11.2 Hz, 1H), 3.07 – 2.91 (m, 1H), 2.47 – 2.31 (m, 1H). ^{13}C NMR (125 MHz, DMSO) δ 162.5, 162.4 (d, *J* = 249.5 Hz), 141.3 (d, *J* = 6.7 Hz), 134.9, 133.9, 132.6 (d, *J* = 7.9 Hz), 127.1, 124.6 (d, *J* = 3.1 Hz), 124.5, 122.0 (d, *J* = 21.2 Hz), 121.8, 116.9, 115.6 (d, *J* = 24.5 Hz), 56.7, 48.9, 39.8, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.12. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}FN_2O_4S_2$ 395.0530; Found 395.0540.



4l

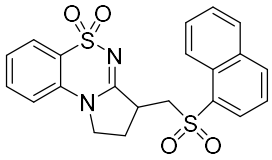
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (67% yield, 82 mg) as a white solid. mp: 211.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 5.6, 2.8 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.65 (m, 2H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 4.24 (t, *J* = 9.6 Hz, 1H), 4.10-4.03 (m, 1H), 3.98-3.93 (m, 1H), 3.85 – 3.69 (m, 1H), 3.30 (dd, *J* = 14.0, 11.1 Hz, 1H), 3.04 – 2.87 (m, 1H), 2.45 – 2.27 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 140.7, 135.9, 134.6, 134.3, 133.3, 131.1, 128.1, 127.1, 126.1, 125.3, 122.0, 115.0, 57.5, 48.3, 39.4, 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}ClN_2O_4S_2$ 411.0235; Found 411.0248.



4m

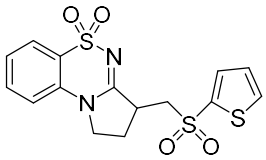
After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (62% yield, 84 mg) as a white solid. mp: 223.2 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.5, 2.0 Hz, 1H), 8.10 – 7.96 (m, 1H), 7.94 – 7.80 (m, 1H), 7.75 – 7.65 (m, 1H), 7.62 – 7.55 (m, 2H), 7.55 – 7.49 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 4.32 – 4.18 (m, 2H), 4.08-4.10 (m, 1H), 3.91 – 3.79 (m, 1H), 3.66 (dd,

J = 13.9, 11.2 Hz, 1H), 3.02 – 2.88 (m, 1H), 2.48 – 2.32 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 138.4, 135.81, 135.3, 134.4, 133.3, 131.7, 128.3, 127.1, 125.3, 122.1, 121.1, 115.0, 55.4, 48.2, 39.4, 25.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}BrN_2O_4S_2$ 454.9729; Found 454.9721.



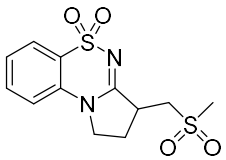
4n

After stirring at 30 °C for 18 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (55% yield, 70 mg) as a white solid. mp: 239.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.08 (dd, *J* = 13.5, 8.3 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.95 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.78 – 7.62 (m, 3H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.25 (t, *J* = 9.6 Hz, 1H), 4.11 – 3.98 (m, 2H), 3.89 – 3.68 (m, 1H), 3.37 (dd, *J* = 14.1, 11.2 Hz, 1H), 3.09 – 2.95 (m, 1H), 2.50 – 2.34 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 135.8, 135.6, 134.4, 133.3, 132.2, 130.1, 130.0, 129.7, 129.5, 128.1, 128.0, 127.1, 125.3, 122.1, 122.0, 115.0, 57.4, 48.3, 39.6, 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O_4S_2$ 427.0781; Found 427.0794.



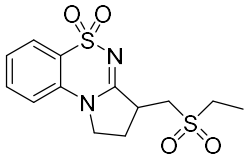
4o

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (56% yield, 64 mg) as a white solid. mp: 232.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.83-7.81 (m, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 4.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 4.24 (t, *J* = 9.5 Hz, 1H), 4.15 – 3.97 (m, 2H), 3.86 – 3.69 (m, 1H), 3.45-3.38 (m, 1H), 2.99-2.93 (m, 1H), 2.44 – 2.31 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 139.7, 134.9, 134.7, 134.3, 133.3, 128.4, 127.1, 125.4, 122.1, 115.0, 59.0, 48.2, 39.8, 25.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}N_2O_4S_3$ 383.0188; Found 383.0194.



4p

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (63% yield, 59 mg) as a white solid. mp: 209.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 4.22 (t, *J* = 9.5 Hz, 1H), 4.09-4.04 (m, 1H), 3.94 (dd, *J* = 13.8, 2.8 Hz, 1H), 3.89 – 3.78 (m, 1H), 3.26 (dd, *J* = 13.9, 10.4 Hz, 1H), 3.10 (s, 3H), 2.96 – 2.85 (m, 1H), 2.37 – 2.23 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 134.4, 133.3, 127.1, 125.2, 121.9, 115.1, 55.5, 48.3, 42.5, 39.1, 25.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O_4S_2$ 315.0468; Found 315.0472

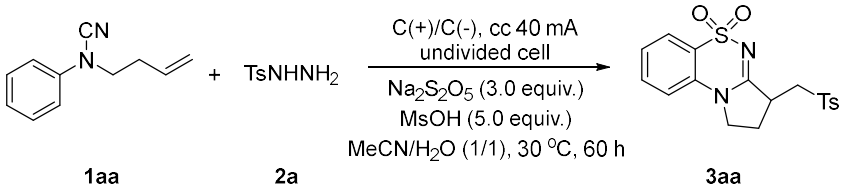


4q

After stirring at 30 °C for 12 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/1) to afford the title compound (67% yield, 66 mg) as a white solid. mp: 218.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 4.24-4.19 (m, 1H), 4.08-4.03 (m, 1H), 3.91 – 3.74 (m, 2H), 3.24 – 3.10 (m, 3H), 2.98 – 2.87 (m, 1H), 2.37 – 2.22 (m, 1H), 1.48 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 134.4, 133.3, 127.1, 125.2, 122.0, 115.1, 52.7, 49.1, 48.3, 38.8, 26.0, 6.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_4S_2$ 329.0624; Found 329.0602.

V. Scale-up Reaction and Synthetic Transformations

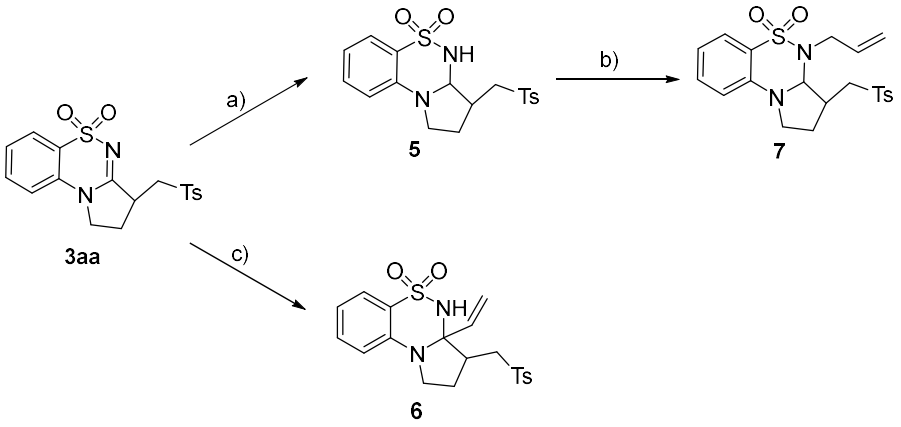
1) Scale-up Reaction for Preparation of Product 3aa



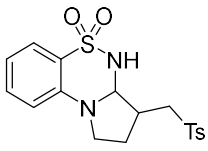
1aa **2a** **3aa**

In an undivided cell (250 mL) equipped with a stir bar, a mixture of *N*-aryl cyanamides **1** (4.6 mmol, 0.791 g), $TsNHNH_2$ **2a** (13.8 mmol, 3 equiv.), $Na_2S_2O_5$ (13.8 mmol, 3 equiv.), $MeSO_3H$ (23 mmol) and $MeCN/H_2O$ (v/v = 1/1, 112 mL) were added. The cell was equipped with graphite plate anode (15×15×0.2 cm), and graphite plate cathode (15×15×0.2 cm), then connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 40 mA at 30 °C for 60 h. When the reaction was finished, the mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to provide the desired products **3aa** (57% yield, 1.02 g).

2) Synthetic Transformations



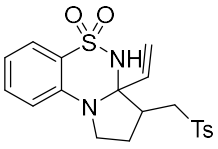
Reaction conditions: (a) DIBAL-H, toluene, reflux 10 h; (b) Allyl bromide, NaH, THF, 60 °C, 12 h; (c) Vinylmagnesium bromide, THF, rt, overnight



5

To solution of (0.2 mmol) in THF in a dried tube was added DIBAL-H (1.3 equiv.) dropwise at rt, then the reaction mixture was warmed to reflux and allowed to proceed for 10 h. The resulting mixture was cooled to rt and

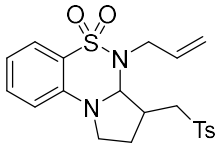
quenched by addition the solution of ammonium chloride (aq.). The aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel column (EtOAc/petroleum ether = 1/2) to afford a white solid **5** (65 mg, 83%, dr = 4.0/1, an inseparable mixture). The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.38 (m, 3H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.83 (dd, *J* = 13.2, 9.2 Hz, 1H), 4.18 (d, *J* = 13.2 Hz, 1H), 3.66 – 3.52 (m, 2H), 3.45 (q, *J* = 9.2 Hz, 1H), 3.18 (dd, *J* = 13.9, 10.8 Hz, 1H), 2.80 (dt, *J* = 13.5, 6.9 Hz, 1H), 2.70 – 2.61 (m, 1H), 2.50 (s, 3H), 2.09 – 1.94 (m, 1H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.38 (m, 3H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.22 – 5.17 (m, 1H), 4.36 (d, *J* = 13.4 Hz, 1H), 3.66 – 3.52 (m, 2H), 3.45 (q, *J* = 9.2 Hz, 1H), 3.15 – 3.07 (m, 1H), 2.50 (s, 3H), 2.40 – 2.33 (m, 1H), 2.29 – 2.19 (m, 1H),2.09 – 1.94 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ 145.14, 145.08, 142.7, 141.9, 136.9, 134.1, 133.8, 130.5, 128.23, 128.15, 124.5, 124.4, 122.7, 120.6, 117.1, 116.1, 115.6, 113.8, 74.1, 71.7, 56.7, 54.9, 47.7, 46.2, 38.6, 36.0, 28.5, 27.6, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}N_2O_4S_2$ 393.0937; Found 393.0945.



6

To solution of **3aa** (0.2 mmol) in THF in a dried tube was added vinylmagnesium bromide (1.3 equiv., 1 *M* in THF) at 0 °C, Then, the mixture was stirred at rt for overnight. Upon completion, the reaction was quenched with saturated ammonium chloride solution (aq.) and the mixture was extracted with DCM. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4. The organic layer was then concentrated under vacuum. The crude product was purified by chromatography on a silica gel column (EtOAc/petroleum ether = 1/3) to afford product **6** as a yellow solid. (59 mg, 71%, dr = 7/1, an inseparable mixture). The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.52 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.35 – 7.30 (m, 3H), 6.79 – 6.66 (m, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 5.69 (dd, *J* = 17.0, 10.3 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.88 (d, *J* = 16.9 Hz, 1H), 4.81 (s, 1H), 3.57 (t, *J* = 9.2 Hz, 1H), 3.44 – 3.31 (m, 2H), 2.90 (dd, *J* = 13.7, 11.2 Hz, 1H), 2.65 – 2.52 (m, 2H), 2.40 (s, 3H), 1.94 – 1.73 (m, 1H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.62 – 7.58 (m, 1H), 7.35-7.29 (m, 3H), 6.79 – 6.75 (m, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 5.94 (dd, *J* = 16.9, 10.1 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.69 (s, 1H), 3.57 (t, *J* = 9.2 Hz, 1H), 3.44 – 3.31 (m, 2H), 2.65 – 2.52 (m, 1H), 2.35 (s, 3H), 2.28 – 2.20 (m, 2H), 1.94 – 1.73 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ 144.4, 139.1, 135.1, 133.2, 132.8, 129.3, 128.7, 126.7, 125.4, 124.1, 120.1,

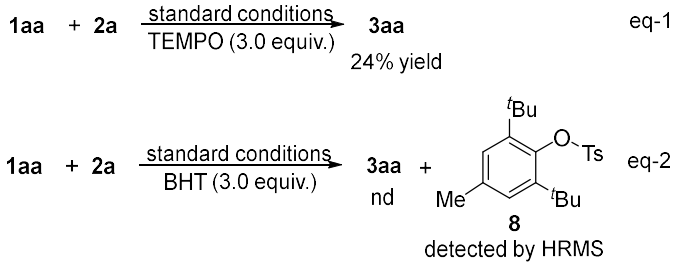
118.4, 116.1, 112.2, 79.8, 54.9, 45.3, 44.0, 30.4, 29.2, 24.6, 21.7, 20.7, 13.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}N_2O_4S_2$ 419.1094; Found 419.1098.



7

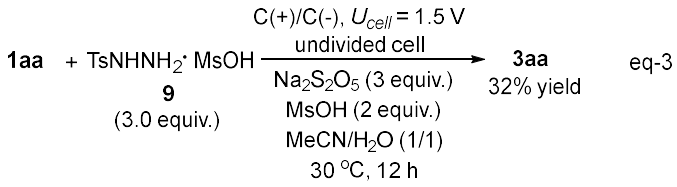
To a solution of a solution of **5** (0.10 mmol) and NaH (1.3 equiv.) in dry THF (2 mL), was added allyl bromide (1.2 equiv.). The resulting mixture was heated to 60 ºC and allowed to proceed for 12 h. The resulting mixture was cooled to rt and quenched by dropwise addition the solution of ammonium chloride (aq). The aqueous layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel column (EtOAc/petroleum ether = 1/4) to afford an inseparable mixture as white solid (29 mg, 68%, dr = 4.3/1). The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.70 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.48 – 7.40 (m, 3H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.77 – 5.63 (m, 1H), 5.35 – 5.19 (m, 2H), 5.11 (d, *J* = 10.2 Hz, 1H), 3.72 (dd, *J* = 16.8, 5.1 Hz, 1H), 3.64 (t, *J* = 9.2 Hz, 1H), 3.55 (dd, *J* = 13.8, 2.3 Hz, 1H), 3.47 – 3.30 (m, 2H), 3.15 (dd, *J* = 13.6, 11.2 Hz, 1H), 3.05 – 2.91 (m, 1H), 2.85-2.76 (m, 1H), 2.52 (s, 3H), 2.14 – 1.94 (m, 1H). The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.70 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.02 – 5.81 (m, 1H), 5.35 – 5.19 (m, 2H), 5.11 (d, *J* = 10.2 Hz, 1H), 3.72 (dd, *J* = 16.8, 5.1 Hz, 1H), 3.64 (t, *J* = 9.2 Hz, 1H), 3.55 (dd, *J* = 13.8, 2.3 Hz, 1H), 3.47 – 3.30 (m, 1H), 3.05 – 2.91 (m, 1H), 2.82 (dt, *J* = 13.4, 6.8 Hz, 1H), 2.52 (s, 3H), 2.41 – 2.35 (m, 1H), 2.14 – 1.94 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 145.2, 141.2, 136.7, 134.6, 134.5, 130.5, 128.3, 125.8, 117.9, 117.3, 116.6, 113.7, 79.7, 77.8, 58.0, 56.6, 46.0, 45.3, 35.9, 27.5, 23.5, 21.6, 19.7, 14.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}N_2O_4S_2$ 433.1250; Found 433.1259.

VI. Control Experiments



Characterization of BHT-1a-CF_3 additive compound 8 by mass spectrometry

Reaction mixture was analyzed on a LC/MS (Agilent 1290 Infinity LC System connected to the Bruker micrOTOF-QII MS instrument). The high resolution mass spectrometry was performed to confirm the elemental compositions of additive compound **8**: HRMS (ESI) m/z: $[M + Na]^+$ For $C_{22}H_{30}NaO_3S$, 397.1813, Found: 397.1806.



Preparation of compound **9**: to a solution of a solution of **2a** (1.0 mmol) in dry ether (4 mL), was added methanesulfonic acid (1.1 equiv.) at 0 °C. The mixture was stirred at rt for 2 h. Upon completion, the solution was filtered and the residue was washed with ether to afford a white solid **9** (260 mg, 92%). ^{1}H NMR (400 MHz, D_2O) δ 7.72 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 2.71 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, D_2O) δ 146.4, 131.6, 130.3, 127.9, 38.4, 20.8. HRMS (ESI) m/z: $[M-(CH_3SO_3^-)]^+$ Calcd for $C_7H_{11}N_2O_2S^+$ 187.0536; Found 187.0530.

Procedure of eq-3: in an undivided flask (20 mL) equipped with a stir bar, a mixture of *N*-aryl cyanamide **1aa** (0.3 mmol), **9** (0.9 mmol), $Na_2S_2O_5$ (0.9 mmol), $MeSO_3H$ (1.5 mmol) and MeCN/H_2O (v/v = 1/1, 10 mL) were added. The cell was equipped with graphite rod anode (Φ 6 mm) and graphite plate cathode (1.5×1.5×0.2 cm), then connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant voltage of 1.5 V at 30 °C for 12 h. When the reaction was finished, the mixture was extracted with EtOAc (10 mL× 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to provide the desired products **3aa** in 32% yield.

VII. Cyclic Voltammetry (CV) Experiments

Cyclic voltammetry experiments were carried out in DY2113 potentiostat (Digi Ivy). Working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: SCE.

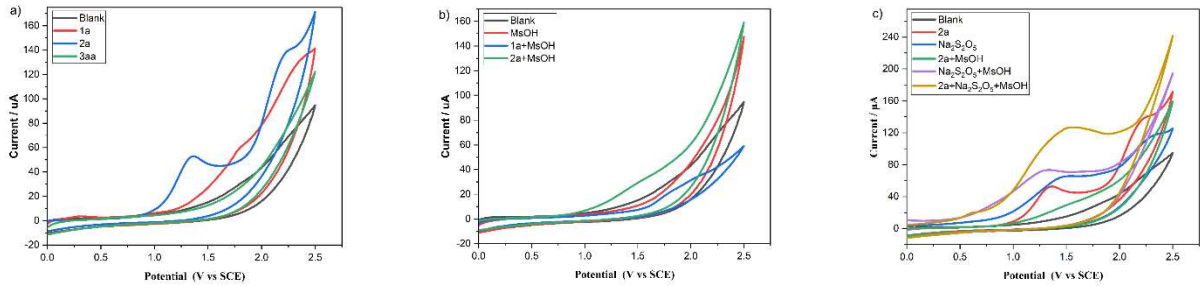
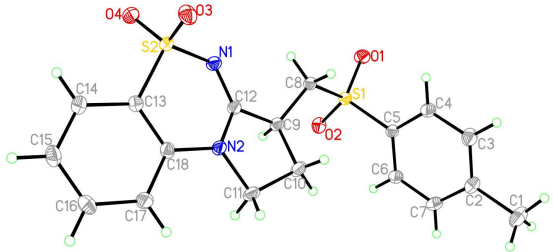


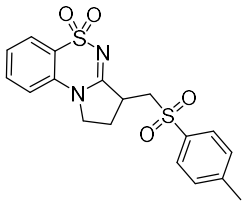
Figure S1. CV analysis. (a) blank (black line): $^{n}Bu_4NPF_6$ (0.1 M) in acetonitrile and H_2O (1/1); **1a** (red line): E_{ox} = 1.77 V; **2a** (blue line): E_{ox} = 1.36 V; **3aa** (green line). (b) blank (black line): $^{n}Bu_4NPF_6$ (0.1 M) in acetonitrile and H_2O (1/1); MsOH (red line); **1a** and MsOH (blue line): E_{ox} = 1.77 V; **2a** and MsOH (green line). (c) blank (black line): $^{n}Bu_4NPF_6$ (0.1 M) in acetonitrile and H_2O (1/1); **2a** (red line): E_{ox} = 1.36 V; $Na_2S_2O_5$ (blue line): E_{ox} = 1.46 V; **2a** and MsOH (green line); **$Na_2S_2O_5$** and MsOH (purple line): E_{ox} = 1.31 V; **2a**, $Na_2S_2O_5$ and MsOH (orange line): E_{ox} = 1.48 V. Scan rate: 50 mV/s.

VIII. References

1. Z. Li, L. Jiao, Y. Sun, Z. He, Z. Wei and W.-W. Liao, *Angew. Chem. Int. Ed.*, 2020, **59**, 7266-7270..
2. D. Chen, M. Ji and C. Zhu, *Chem. Commun.*, 2019, **55**, 7796-7799.
3. Z. Li, Y.-H. Wu, J.-M. Xi, Z.-L. Wei and W.-W. Liao, *Org. Lett.*, 2021, **23**, 9591-9596.
4. Z. Pan, S. Wang, J. T. Brethorst and C. J. Douglas, *J. Am. Chem. Soc.*, 2018, **140**, 3331-3338.

IX. Crystal Data and Structure Refinement for Compounds 3a





3aa

CCDC number: 2216999

X-ray crystal structure of compound **3aa**. Single crystal of **3aa** was obtained by slow evaporation of Petroleum ether/EtOAc solution. Crystal measurement of **3aa** was measured on R-Axis RAPID of Rigaku Corporation plus 291.2 k. Thermal ellipsoids are set at 30% probability.

Table S- crystal-1 Crystal data and structure refinement for **3aa**.

Identification code	3aa	
Empirical formula	C18 H18 N2 O4 S2	
Formula weight	390.46	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.181(2) Å	α= 90°.
	b = 8.8095(17) Å	β= 105.852(7)°.
	c = 16.111(3) Å	γ = 90°.
Volume	1799.6(6) $Å^3$	
Z	4	
Density (calculated)	1.441 Mg/m^3	
Absorption coefficient	0.323 mm^{-1}	
F(000)	816	
Crystal size	0.200 x 0.190 x 0.170 mm^3	
Theta range for data collection	2.628 to 27.593°.	
Index ranges	-17<=h<=17, -11<=k<=11, -20<=l<=20	

Reflections collected	60544
Independent reflections	4144 [R(int) = 0.0676]
Completeness to theta = 25.242°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4144 / 0 / 212
Goodness-of-fit on F^2	0.657
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1103
R indices (all data)	R1 = 0.0420, wR2 = 0.1163
Extinction coefficient	n/a
Largest diff. peak and hole	0.445 and -0.380 e.Å^{-3}

Table S- crystal-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Y. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	11002(2)	6961(3)	5662(2)	52(1)
C(2)	10321(1)	7377(2)	4769(1)	35(1)
C(3)	9441(1)	8298(2)	4679(1)	38(1)
C(4)	8811(1)	8664(1)	3862(1)	32(1)
C(5)	9060(1)	8111(1)	3134(1)	24(1)
C(6)	9940(1)	7190(2)	3223(1)	34(1)
C(7)	10570(1)	6823(2)	4041(1)	41(1)
C(8)	7011(1)	7675(2)	2011(1)	25(1)
C(9)	7005(1)	6002(2)	1784(1)	25(1)
C(10)	7560(1)	4883(2)	2489(1)	34(1)
C(11)	7028(1)	3375(2)	2162(1)	35(1)
C(12)	5903(1)	5349(2)	1493(1)	23(1)
C(13)	4166(1)	3415(1)	834(1)	24(1)

C(14)	3380(1)	2425(1)	397(1)	29(1)
C(15)	3554(1)	868(1)	450(1)	36(1)
C(16)	4515(1)	300(1)	941(1)	41(1)
C(17)	5302(1)	1290(1)	1378(1)	36(1)
C(18)	5128(1)	2847(1)	1324(1)	25(1)
N(1)	5095(1)	6129(2)	1057(1)	27(1)
N(2)	5943(1)	3864(2)	1712(1)	25(1)
O(1)	8038(1)	10194(2)	2101(1)	34(1)
O(2)	8698(1)	7964(2)	1459(1)	33(1)
O(3)	3476(1)	5682(2)	1538(1)	38(1)
O(4)	3340(1)	5859(2)	-3(1)	37(1)
S(1)	8248(1)	8583(1)	2110(1)	24(1)
S(2)	3935(1)	5368(1)	842(1)	24(1)

Table S- crystal-3 Bond lengths [Å] and angles [°] for Y.

C(1)-C(2)	1.518(2)
C(2)-C(3)	1.3900
C(2)-C(7)	1.3900
C(3)-C(4)	1.3900
C(4)-C(5)	1.3900
C(5)-C(6)	1.3900
C(5)-S(1)	1.7530
C(6)-C(7)	1.3900
C(8)-C(9)	1.518(2)
C(8)-S(1)	1.7839(16)
C(9)-C(12)	1.512(2)
C(9)-C(10)	1.530(2)
C(10)-C(11)	1.528(3)

C(11)-N(2)	1.479(2)
C(12)-N(1)	1.301(2)
C(12)-N(2)	1.352(2)
C(13)-C(14)	1.3900
C(13)-C(18)	1.3900
C(13)-S(2)	1.7477
C(14)-C(15)	1.3900
C(15)-C(16)	1.3900
C(16)-C(17)	1.3900
C(17)-C(18)	1.3900
C(18)-N(2)	1.4076(16)
N(1)-S(2)	1.6182(15)
O(1)-S(1)	1.4452(14)
O(2)-S(1)	1.4454(13)
O(3)-S(2)	1.4385(14)
O(4)-S(2)	1.4398(14)

C(3)-C(2)-C(7)	120.0
C(3)-C(2)-C(1)	119.98(13)
C(7)-C(2)-C(1)	120.01(13)
C(4)-C(3)-C(2)	120.0
C(3)-C(4)-C(5)	120.0
C(6)-C(5)-C(4)	120.0
C(6)-C(5)-S(1)	120.94(6)
C(4)-C(5)-S(1)	119.05(6)
C(5)-C(6)-C(7)	120.0
C(6)-C(7)-C(2)	120.0
C(9)-C(8)-S(1)	113.68(12)
C(12)-C(9)-C(8)	112.70(14)
C(12)-C(9)-C(10)	102.06(13)

C(8)-C(9)-C(10)	118.48(15)
C(11)-C(10)-C(9)	102.89(14)
N(2)-C(11)-C(10)	101.93(14)
N(1)-C(12)-N(2)	128.31(15)
N(1)-C(12)-C(9)	122.78(15)
N(2)-C(12)-C(9)	108.78(14)
C(14)-C(13)-C(18)	120.0
C(14)-C(13)-S(2)	120.91(6)
C(18)-C(13)-S(2)	118.93(6)
C(13)-C(14)-C(15)	120.0
C(16)-C(15)-C(14)	120.0
C(17)-C(16)-C(15)	120.0
C(16)-C(17)-C(18)	120.0
C(17)-C(18)-C(13)	120.0
C(17)-C(18)-N(2)	120.50(9)
C(13)-C(18)-N(2)	119.34(9)
C(12)-N(1)-S(2)	118.88(12)
C(12)-N(2)-C(18)	121.96(13)
C(12)-N(2)-C(11)	111.88(14)
C(18)-N(2)-C(11)	123.40(13)
O(1)-S(1)-O(2)	118.62(9)
O(1)-S(1)-C(5)	107.98(7)
O(2)-S(1)-C(5)	109.04(7)
O(1)-S(1)-C(8)	105.78(8)
O(2)-S(1)-C(8)	108.17(8)
C(5)-S(1)-C(8)	106.62(7)
O(3)-S(2)-O(4)	116.21(9)
O(3)-S(2)-N(1)	109.11(8)
O(4)-S(2)-N(1)	108.50(8)
O(3)-S(2)-C(13)	107.88(8)

O(4)-S(2)-C(13)	109.86(7)
N(1)-S(2)-C(13)	104.67(7)

Symmetry transformations used to generate equivalent atoms:

Table S- crystal-4 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Y. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	42(1)	69(2)	37(1)	10(1)	-3(1)	7(1)
C(2)	27(1)	41(1)	32(1)	3(1)	1(1)	0(1)
C(3)	31(1)	51(1)	31(1)	-4(1)	9(1)	1(1)
C(4)	24(1)	40(1)	32(1)	-3(1)	7(1)	6(1)
C(5)	20(1)	24(1)	27(1)	-1(1)	4(1)	-1(1)
C(6)	29(1)	38(1)	34(1)	-5(1)	7(1)	9(1)
C(7)	30(1)	45(1)	43(1)	-1(1)	2(1)	14(1)
C(8)	20(1)	22(1)	31(1)	-1(1)	4(1)	-1(1)
C(9)	23(1)	23(1)	28(1)	3(1)	4(1)	0(1)
C(10)	27(1)	28(1)	37(1)	7(1)	-5(1)	-1(1)
C(11)	28(1)	24(1)	44(1)	11(1)	-6(1)	1(1)
C(12)	23(1)	21(1)	24(1)	2(1)	5(1)	-1(1)
C(13)	27(1)	24(1)	22(1)	2(1)	7(1)	-2(1)
C(14)	26(1)	33(1)	28(1)	0(1)	5(1)	-5(1)
C(15)	38(1)	31(1)	38(1)	-3(1)	6(1)	-12(1)
C(16)	45(1)	23(1)	50(1)	1(1)	6(1)	-6(1)
C(17)	35(1)	23(1)	43(1)	5(1)	0(1)	-2(1)
C(18)	28(1)	22(1)	24(1)	2(1)	4(1)	-4(1)
N(1)	23(1)	23(1)	33(1)	3(1)	4(1)	0(1)

N(2)	25(1)	20(1)	26(1)	5(1)	1(1)	-1(1)
O(1)	34(1)	21(1)	45(1)	5(1)	6(1)	-2(1)
O(2)	31(1)	42(1)	30(1)	-2(1)	12(1)	-4(1)
O(3)	35(1)	42(1)	40(1)	-12(1)	18(1)	-4(1)
O(4)	37(1)	32(1)	33(1)	1(1)	-3(1)	6(1)
S(1)	22(1)	22(1)	27(1)	2(1)	6(1)	-2(1)
S(2)	20(1)	25(1)	26(1)	-2(1)	4(1)	1(1)

Table S- crystal-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Y.

	x	y	z	U(eq)
H(1A)	10727	7439	6090	78
H(1B)	11711	7301	5726	78
H(1C)	10998	5880	5734	78
H(3)	9274	8668	5166	45
H(4)	8222	9280	3802	39
H(6)	10107	6820	2736	41
H(7)	11159	6208	4101	49
H(8A)	6827	7780	2552	30
H(8B)	6473	8190	1569	30
H(9)	7325	5900	1305	30
H(10A)	8311	4843	2545	40
H(10B)	7450	5154	3042	40
H(11A)	7365	2883	1768	42
H(11B)	7034	2691	2635	42

H(14)	2737	2805	69	35
H(15)	3028	206	158	44
H(16)	4632	-742	976	49
H(17)	5945	910	1706	43