Supporting Information

Photocatalyzed Sulfoximination/Amidation of (Het)Arylethenes Tethered N-Tosyl Amide: A Versatile Entry to Sulfoximidoyl β - And γ -Lactams

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General Procedures and New Compounds Characterization

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1.General Information

All commercially available compounds were purchased from Energy Chemical, Tansoole or Bide Pharmatech Ltd, and used without further purification, unless otherwise noted. The reactions were monitored by thin layer chromatography (TLC) with aluminium sheets silica gel GF254 from Energy Chemical. Flash column chromatography was performed on silica gel (particle size 300-400 mesh). NMR spectra were recorded on Bruker 400 (400 MHz for ¹H; 376 MHz for ¹⁹F; 101 MHz for ¹³C) spectrometer. The chemical shifts (δ) are given in parts per million relative to CDCl₃ (7.26 ppm for ¹H), TMS (0 ppm for ¹H) and CDCl₃ (77.0 ppm for ¹³C), DMSO d_6 (2.50 ppm for ¹H), DMSO- d_6 (40.0 ppm for ¹³C). ¹H, ¹³C and ¹⁹F multiplicities are reported as following: singlet (s), doublet (d), doublet of doublets (dd), quartet (q), multiplet (m). High resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-IT-TOF. DCM (99.9%, Super Dry) was purchased from Admas-beta and was used without further purification, but degassing is required before use. The irradiation source was purchased from Taobao (30 W blue LED, 2.3.2 Optimized procedure for details). Low-temperature Stirring Reaction Bath (DHJF-8005) equipment purchased from Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd.

2. Experimental Section

2.1 Optimization of the reaction conditions Optimized procedure

2.1.1 Optimization of the Reaction Conditions

Sulfoximidoyl thianthrene salts **1a** (0.15 mmol), **2a** (0.1 mmol), photocatalysis (1 mol%) and base (0.2 mmol) in a Penicillin vial was evacuated and backfilled with argon via Schlenk line three times. Subsequently, DCM (anhydrous, 1.0 mL) were added and irradiated by 30 W blue LED strip light for various time. After completion of the reaction. Yields were determined by ¹H NMR with CH_2Br_2 as an internal standard. The

results were listed in Table S1-S4

Table S1. Base optimization ^a

NHTs 0	+ N_{S}^{\bullet} $He BF_4^{-}$ Ph $He BF_4^{-}$ Ph S_{S}^{\bullet} $He BF_4^{-}$ Ph S_{S}^{\bullet} $He BF_4^{-}$ Ph S_{S}^{\bullet} $He BF_4^{-}$	Me Ne Ne Ne Ne Ne Ne Ne N
Entrv	Base	Vield (%) ^b
1	KOAc	trace
2	K2CO3	trace
3	K ₃ PO ₄	20
4	NaOH	22
5	t-BuOK	25
6	Et ₃ N	27
7	DBU	26
8	DIPEA	17
9	DABCO	25
10	TMEDA	7
11	Ph ₃ N	7
12	N-Methylpiperidine	27
13	N-Methyl-2-pyrrolidone	trace
14	Pyridine	32
15	2,4,6-Trimethylpyridine	42
16	Piperidine	trace
17	2,6-Dichloropyridine	trace
18	2-Phenylpyridine	15
19	2,6-Dimethoxypyridine	trace
20	2,6-Lutidine	36
21	DMAP	25
22	N, N-Dimethylaniline	0
23	Pyrazine	0
24	Pyrimidine	0

[a] Reaction condition: 0.1 mmol 2a, 0.2 mmol base, 0.15 mmol 1a, 30W blue LED, 12 hours.

[b]Yield were determined by ${}^{1}H$ NMR with $CH_{2}Br_{2}$ as an internal standard.

Table S2. photocatalysis optimization ^a

NHTs 0	+ S N BF ₄ - Ph BF ₄ - Ph BF ₄ - Ph S S S S S S S S S S S S S	$ \begin{array}{c} Me \\ S \\ N, \\ N, \\ N, \\ N \\ N \\ Ts \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ $
Entry	Photocatalyst	Yield (%) ^b
1	Ru(bpy) ₂ Cl ₂	20
2	$Ir(ppy)_3$	42
3	Ir(dF(Me)ppy) ₂ (dtbbpy)[PF ₆]	55
4	[Ir(dtbbpy)(ppy)2][PF6]	23
5	Ir(ppy) ₂ (dtbbpy)[PF ₆]	30
6	Ir(dF-mppy) ₂ (dtppy)[PF ₆]	32
7	Ir(dF(CF ₃)ppy) ₂ (dtbby)[PF ₆]	52
8	Ir(dF-ppy) ₂ (dtbbpy)[PF ₆]	50
9	9H-Thioxanthen-9-one,	trace
	4a,9a-dihydro-	
10	Solvent Red	11
11	Fluorescein Sodium	trace
12	Eosin Y-Na ₂	trace
13	none	0

[a] Reaction condition: 0.1 mmol **2a**, 0.2 mmol 2,4,6-Trimethylpyridine, 0.15 mmol **1a**, 30 W blue LED, 12 hours. [b]Yields were determined by ¹H NMR with CH₂Br₂ as an internal standard.

Table S3. Solvents optimization ^a

Ph NHPG +	$S \\ O \\ S \\ S \\ S \\ S \\ S \\ O \\ BF_4 Ph$	Ir(dF(Me)ppy) ₂ (dt 2,4,6-Trimethy 30W Blue LED, s	bbpy)(PF ₆) (1 mol%), Ipyridine (2 equiv.) solvent (0.1M), rt, 12h	Ph O N N Ph N Ph Ts
1	2			3
Entry		Solvents	Yield	(%) ^b
1		DCM	5	5
2		DCE	1	8
3		DMSO		5
4		CH ₃ CN	1	7
5		EtOAc	()

[a] Reaction condition: 0.1mmol **2a**, 0.2 mmol 2,4,6-Trimethylpyridine, 0.15 mmol **1a**, 30 W blue LED, 12 hours. [b]Yields were determined by ¹H NMR with CH₂Br₂ as an internal standard.

Table S4. Temperature optimization ^a

Ph	$NHPG + N_{S} Me \\ BF_{4} Ph^{-} Ph^{-} $	Ir(dF(Me)ppy) ₂ (dtbbpy)(PF ₆) (1 mol ⁻ 2,4,6-Trimethylpyridine (2 equiv. 30W Blue LED, CH ₂ Cl ₂ (0.1M), T,	$ \begin{array}{c} Ph \\ N'' \\ N'' \\ 12h \\ Ph \\ N'' \\ Ph \\ N'' \\ N''$
Entry	Temperature (°C)	Protecting group (PG)	Yield (%) ^b
1	rt	Ts	55
2	-20	Ts	72
3	-20	Н	trace
4	-20	Bn	trace
5	-20	OBn	trace

[a] Reaction condition: 0.1 mmol **2a**, 0.2 mmol 2,4,6-Trimethylpyridine, 0.15 mmol **1a**, 30 W blue LED, 12 hours. [b]Yields were determined by ¹H NMR with CH₂Br₂ as an internal standard.

2.1.2 Optimized procedure

Reagent 2 (1 equiv), Ir(dF(Me) ppy)₂(dtbbpy)[PF₆] (1 mol%) and 1 (1.5 equiv) in a Penicillin vial was evacuated and backfilled with argon via Schlenk line three times. Subsequently, DCM (anhydrous, 1 M) and 2,4,6-Trimethylpyridine (2 equiv), were added, cooled to -20 °C and irradiated by 30 W blue LED strip light for 12 hours. The reaction mixture was concentrated in vacuo and purified by column chromatography to afford the desired product.



Figure S1. Reaction Equipment

2.2 Synthesis of sulfoximidoyl thianthrene salts^[1-2]

2.2.1 Synthesis of NH-sulfoximines



The sulfide (10 mmol), (diacetoxyiodo) benzene (21 mmol, 2.1 equiv.) and ammonium bicarbonate (3.0 equiv) were added to a flask containing a stirrer bar. MeOH (25 mL, 0.4 M) was added and the reaction was stirred at room temperture for 3 hours. Removal of the solvent under reduced pressure and subsequent flash column chromatography of the obtained residue on silica gel with pure petroleum ether/ethyl acetate (1:1) or ethyl acetate as eluent afforded the desired products (light yellow oil) (yield 90-100%).

2.2.2 Synthesis of N-chlorosulfoximine.



The acetonitrile solution (0.4 M) of sulfoximine (10 mmol, 1.0 equiv.) was stirred in an ice bath, *N*-chlorosuccinimide (1.1 equiv.) was added after 30 minutes. After 24 hours, removal of the solvent under reduced pressure and subsequent flash column chromatography of the obtained residue on silica gel with pure petroleum ether/ethyl acetate (2:1) as eluent afforded the desired products (yield 70-80%).

2.2.3 Synthesis of sulfoximidoyl disulfides salts^[3]



To a stirred chloroform solution (0.4 M) of *N*-chlorosulfoximine (8 mmol, 1.0 equiv.), thianthrene (1.1 equiv.) was added at room temperature and the solution was stirred overnight. To the solution, NaBF₄ (2.0 equiv.), was added and the solution was continued to stir for 24 hours. The chloroform solution was diluted with dichloromethane and washed with water, dried over MgSO₄, and evaporated under vacuum. Crystals obtained were recrystallized from ethanol-hexane (yield 70-80%). The spectral data were fully consistent with those previously reported.

2.3 Synthesis of (E)-4-aryl-N-tosylbut-3-enamide (1a-1o, 6)^[4]

2.3.1 Synthesis of (E)-4-arylbut-3-enoic acid



A flame-dried, 100-mL, Schlenk flask equipped with stir bar, argoninlet, septum, glass stopper, magnetic stir bar, and digital thermocouple was charged with (2-carboxyethyl)triphenylphosphonium bromide (4.568 g, 11 mmol, 1.1 equiv). The flask was evacuated and back-filled with argon. THF (20 mL) was added by syringe through a septum and the solution was cooled to -20 °C. To the white suspension was added sodium bis(trimethylsilyl)amide (NaHMDS) (4.401g, 24.0 mL, 24.00 mmol, 2.4 equiv) dropwise via syringe over 5 min. The resulting orange solution was stirred for 30 min and became homogenous gradually. A solution of aldehyde (10.00 mmol) in 2-5 mL THF was added by syringe at -20 °C. The resulting mixture was allowed to warm to room temperature (23 °C) slowly while stirring overnight. The heterogeneous reaction mixture was quenched with water (50 mL) and washed with ether (2 x 50 mL), then the aqueous layer was acidified to pH 1 by dropwise addition of HCl (2 M) and then was extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried over MgSO4, filtered and concentrated by rotary evaporation. Most carboxylic acids were taken forward as crude products into the next step. The acids determined to be too

impure were subjected to silica gel flash chromatography.

2.3.2 Synthesis of (E)-4-aryl-N-tosylbut-3-enamide



A flame-dried, 100-mL, Schlenk flask equipped with a magnetic stir bar and argon inlet was added carboxylic acid (1 equiv, 5-10 mmol) and then was dissolved in THF (0.2 M). To the stirred solution was added 4-methylbenzenesulfonyl isocyanate (1 equiv.) and the solution was stirred at room temperature (25 °C) for 10 minutes. Triethylamine (1 equiv) was added dropwise to the reaction mixture by syringe and the mixture was stirred for 3 hours at room temperature (25 °C). The reaction solution was diluted with ether and washed with 1 M HCl (1 x 15 mL). The aqueous layer was extracted with ethyl acetate (3 x 20 mL), and the combined organic layers were washed with brine, dried over magnesium sulfate, filtered then concentrated by rotary evaporation. The crude product was purified by silica gel flash chromatography (60-90%).



1a, 1b, 1c, 1d, 1g,1m, The spectral data were fully consistent with those previously reported ^[4]. 6 The spectral data were fully consistent with those previously reported.^[6]

(E)-4-(3-methoxyphenyl)-N-tosylbut-3-enamide(1e)



¹H NMR (400 MHz, CDCl₃) δ 9.05 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.18 (t, J = 7.9 Hz, 1H), 6.87 (d, J = 7.7 Hz, 1H), 6.82 (s, 1H), 6.78 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 6.15 (dt, J = 15.8, 7.1 Hz, 1H), 3.77 (s, 3H), 3.19 (dd, J = 7.1, 1.4 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.7, 159.7, 145.2, 137.6, 135.4, 135.3, 129.6, 129.5, 128.4, 120.0, 119.1, 113.7, 111.6, 55.2, 40.4, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₈H₁₉NO₄SNa⁺:368.0927; Found: 368.0927.

(E)-4-(4-(tert-butyl)phenyl)-N-tosylbut-3-enamide (1f)

¹H NMR (400 MHz, CDCl₃) δ 9.01 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.33 – 7.29 (m, 4H), 7.24 (d, J = 8.4 Hz, 2H), 6.44 (d, J = 15.9 Hz, 1H), 6.12 (dt, J = 15.8, 7.2 Hz, 1H), 3.20 (dd, J = 7.2, 1.4 Hz, 2H), 2.42 (s, 3H), 1.31 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 151.1, 145.2, 135.4, 135.3, 133.4, 129.6, 128.4, 126.1, 125.4, 118.8, 40.6, 34.5, 31.2, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₁H₂₅NO₃SNa⁺:394.1448; Found: 394.1448.

(E)-4-(4-cyanophenyl)-N-tosylbut-3-enamide (1h)



¹H NMR (400 MHz, CDCl₃) δ 9.03 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.34 (dd, J = 14.0, 8.2 Hz, 4H), 6.45 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 15.9, 6.9 Hz, 1H), 3.23 (dd, J = 7.0, 1.3 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 145.5, 140.6, 135.2, 133.6, 132.4, 129.7, 128.4, 126.8, 124.0, 118.8, 111.1, 40.1, 21.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₈H₁₆N₂O₃S Na⁺:363.0774; Found: 363.0774.

(E)-4-(4-fluorophenyl)-N-tosylbut-3-enamide (1i)



CI

F¹ WMR (400 MHz, CDCl₃) δ 9.41 (s, 1H), 7.97 (d, J = 8.0Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.23 (dd, J = 8.5, 5.4 Hz, 2H), 6.94 (t, J = 8.5 Hz, 2H), 6.40 (d, J = 15.9 Hz, 1H), 6.09 (dt, J = 15.8, 7.1 Hz, 1H), 3.39 – 3.01 (m, 2H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.2, 162.3 (d, J = 247.3 Hz), 145.2, 135.2, 134.0, 132.4 (d, J = 3.3 Hz), 129.6, 128.3, 127.8 (d, J = 8.0 Hz), 119.4 (d, J =2.4 Hz), 115.3 (d, J = 21.6 Hz), 40.2, 21.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -113.89. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₇H₁₆FNO₃S Na⁺:356.0728; Found: 356.0728.

(E)-4-(3-chlorophenyl)-N-tosylbut-3-enamide (1j)

NHTs

Ô ¹H NMR (400 MHz, CDCl₃) δ 9.28 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.21 (s, 1H), 7.17 (d, J = 5.4 Hz, 2H), 7.15 (d, J = 1.7 Hz, 1H), 7.13 (tt, J = 4.4, 2.1 Hz, 1H), 6.35 (d, J = 15.8 Hz, 1H), 6.16 (dt, J = 15.8 Hz, 1H), 15.9, 7.0 Hz, 1H), 3.21 (dd, J = 7.0, 1.4 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 145.3, 138.0, 135.2, 134.4, 133.8, 129.7, 129.6, 128.3, 127.7, 126.3, 124.5, 121.4, 40.2, 21.6. HRMS **(IT-TOF)**: $[M+Na]^+$ Calcd for C₁₇H₁₆ClNO₃SNa⁺:372.0432, 374.0403; Found: 372.0434, 374.0404.

(E)-4-(2-bromophenyl)-N-tosylbut-3-enamide (1k)

/NHTs

Ô ¹**H NMR (400 MHz, CDCl₃)** δ 9.20 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.22 (ddd, J = 7.6, 6.3, 1.4 Hz, 1H), 7.15 – 6.99 (m, 1H), 6.95 – 6.60 (m, 1H), 6.16 (dt, J = 15.8, 7.1 Hz, 1H), 3.29 (dd, J = 7.1, 1.5 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.8, 147.1, 145.3, 136.2, 135.4, 133.9, 132.9, 129.7, 129.2, 128.4, 127.5, 127.2. 123.1. 40.3. 21.7. **HRMS** (**IT-TOF**): $[M+Na]^+$ Calcd for C₁₇H₁₆BrNO₃SNa⁺:415.9927, 417.9906; Found: 415.9925, 417.9904.

(E)-4-([1,1'-biphenyl]-4-yl)-N-tosylbut-3-enamide (11)



^{Ph} ⁽¹⁾ ¹H NMR (400 MHz, CDCl₃) δ 8.50 (s, 1H), 7.96 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.36 – 7.29 (m, 3H), 6.51 (d, J = 15.8 Hz, 1H), 6.19 (dt, J = 15.8, 7.2 Hz, 1H), 3.22 (dd, J = 7.2, 1.3 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 145.3, 140.9, 140.5, 135.5, 135.4, 135.0, 129.7, 128.8, 128.5, 127.4, 127.3, 126.9, 126.9, 119.5, 40.7, 21.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₃H₂₁NO₃SNa⁺:414.1135; Found: 414.1134.

(E)-4-(naphthalen-1-yl)-N-tosylbut-3-enamide (1n)



¹H NMR (400 MHz, CDCl₃) δ 9.17 (s, 1H), 7.97 (dd, J = 8.8, 6.6 Hz, 3H), 7.86 – 7.79 (m, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 7.1 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.38 (t, J = 7.7 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 15.4Hz, 1H), 6.19 (dt, J = 15.6, 7.1 Hz, 1H), 3.33 (dd, J = 7.1, 1.5 Hz, 2H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 145.2, 135.3, 133.8, 133.5, 132.6, 130.9, 129.6, 128.4, 128.3, 128.2, 126.1, 125.8, 125.5, 123.9, 123.5, 122.8, 40.7, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₁H₁₉NO₃S Na⁺:388.0977; Found: 388.0977.

(E)-4-(thiophen-2-yl)-N-tosylbut-3-enamide(10)

NHTs **I**H NMR (400 MHz, CDCl₃) δ 8.89 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 4.9 Hz, 1H), 6.92 (dd, J = 5.1, 3.5 Hz, 1H), 6.89 (d, J = 3.6 Hz, 1H), 6.57 (d, J = 15.7 Hz, 1H), 5.96 (dt, J = 15.6, 7.2 Hz, 1H), 3.16 (dd, J = 7.1, 1.5 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.5, 145.3, 141.0, 135.3, 129.7, 128.7, 128.4, 127.3, 126.1, 124.7, 119.0, 40.2, 21.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₅H₁₅NO₃S₂Na⁺:344.0386; Found: 344.0385.

2.4 Synthesis of 3-aryl-N-tosylbut-3-enamide (4a-4i)

2.4.1 Synthesis of 3-aryl-3-butenoic acids ^[5]



According to literatures, with a slight modification, the Grignard reagent was prepared from Mg turning (0.40g, 16.5 mmol) and aryl bromide (15.0 mmol) in 20 mL THF. Diketene (1.05g, 12.5 mmol) and Pd (PPh₃)₄ (0.375 mmol, 3 mol%) in dry THF 20 mL under nitrogen were added dropwise to a suspension of arylzinc chloride, prepared by adding anhydrous ZnCl₂ (2.3 g, 16.8 mmol) in THF 15 mL to aryl magnesium bromide with ice-water cooling and the resulting mixture was stirred for additional 3 h at 0 °C. The reaction mixture was poured into a cold 2 equiv. HCl aq and extracted with ether. The separated organic layer was extracted with 3 equiv. NaOH aq. The alkaline extracts was acidified with 6 equiv HCl aq, and then extracted with ether (40 mL × 3). The ether extracts were combined, washed with brine and dried over anhydrous Na₂SO₄. After removal of the solvent, most of the acids can be purified by recrystallization in hexane to give the corresponding 3-aryl-3-butenoic acids (60-85% isolated yields), which were used directly.

2.4.2 Synthesis of 3-aryl-N-tosylbut-3-enamide



A flame-dried, 100-mL, Schlenk flask equipped with a magnetic stir bar and argon inlet was added 3-aryl-3-butenoic Acids (1 equiv, 5-10 mmol) and then was dissolved in THF (0.2 M). To the stirred solution was added 4-methylbenzenesulfonyl isocyanate (1 equiv.) and the solution was stirred at room temperature (25 °C) for 10 minutes. Triethylamine (1 equiv.) was added dropwise to the reaction mixture by syringe and the mixture was stirred for 3 hours at room temperature (25°C). The reaction solution was diluted with ether and washed with 1 M HCl (1 x 15 mL). The aqueous layer was extracted with ethyl acetate (3 x 20 mL), and the combined organic layers were washed with brine, dried over magnesium sulfate, filtered then concentrated by rotary evaporation. The crude product was purified by silica gel flash chromatography (60-90%).



3-phenyl-*N*-tosylbut-3-enamide (4a)

¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.42 – 7.30 (m, 5H), 7.24 (d, J = 8.2 Hz, 2H), 5.70 (s, 1H), 5.29 (s, 1H), 3.48 (s, 2H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 144.9, 140.1, 137.8, 135.0, 129.4, 128.8, 128.5, 128.2, 125.5, 118.3, 44.2, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₇H₁₇NO₃SNa⁺:338.0822; Found: 338.0821.

3-(p-tolyl)-N-tosylbut-3-enamide (4b)



Me ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H), 7.71 (d, J = 8.4Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 5.63 (s, 1H), 5.20 (s, 1H), 3.43 (s, 2H), 2.42 (s, 3H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.1, 144.8, 139.9, 138.4, 129.7, 129.4, 129.4, 128.3, 126.4, 125.4, 117.4, 44.2, 21.6, 21.1. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₈H₁₉NO₃SNa⁺:352.0978; Found: 352.0978.

3-(m-tolyl)-N-tosylbut-3-enamide (4c)



¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 1H), 7.71 (d, J = 8.4Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.15 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.8 Hz, 2H), 7.04 (s, 1H), 5.63 (s, 1H), 5.23 (s, 1H), 3.44 (d, J = 1.1 Hz, 2H), 2.41 (s, 3H), 2.25 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 144.8, 140.1, 138.3, 137.9, 135.0, 129.4, 129.2, 128.6, 128.2, 126.2, 122.7, 118.1, 44.1, 21.6, 21.3. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₈H₁₉NO₃SNa⁺:352.0978; Found: 352.0977.

3-(o-tolyl)-*N*-tosylbut-3-enamide (4d)



Me ¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.19 – 7.10 (m, 2H), 7.04 (td, J = 7.2, 1.8 Hz, 1H), 6.94 (d, J = 1.4 Hz, 1H), 5.36 (d, J = 1.2 Hz, 1H), 5.11 (d, J = 1.2 Hz, 1H), 3.29 (d, J = 1.2Hz, 2H), 2.44 (s, 3H), 2.19 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.6, 145.0, 141.2, 140.0, 135.2, 134.8, 130.6, 129.5, 128.3, 128.0, 127.7, 125.8, 120.2, 45.9, 21.6, 19.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₈H₁₉NO₃SNa⁺:352.0978; Found: 352.0978.

N-tosyl-3-(4-(trifluoromethyl)phenyl)but-3-enamide (4e)



F₃C⁷ ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.66 (s, 1H), 5.33 (s, 1H), 3.48 (d, J = 1.1 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.00, 145.2, 141.7, 138.9, 134.9, 130.0 (q, J = 32.5 Hz), 129.5, 128.1, 125.9, 125.5 (q, J = 3.9 Hz), 123.9 (q, J = 272.1 Hz), 120.1, 43.6, 21.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₈H₁₆F₃NO₃SNa⁺:406.0696; Found: 406.0695.

3-(4-fluorophenyl)-N-tosylbut-3-enamide(4f)



F¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 7.71 (d, J = 8.4Hz, 2H), 7.22 (dd, J = 8.6, 5.5 Hz, 4H), 6.90 (t, J = 8.7 Hz, 2H), 5.58 (s, 1H), 5.23 (s, 1H), 3.43 (d, J = 1.1 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 162.7 (d, J = 248.4 Hz), 145.1, 139.1, 134.9, 129.4, 128.2, 127.3 (d, J = 8.2 Hz), 118.1, 115.7, 115.5, 44.3, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -113.2. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₇H₁₆FNO₃SNa⁺:356.0728; Found: 356.0729.

3-(3-fluorophenyl)-N-tosylbut-3-enamide(4g)



¹H NMR (400 MHz, CDCl₃) δ 8.66 (s, 1H), 7.75 (d, J = 8.3Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.19 (dd, J = 8.0, 6.0 Hz, 1H), 7.08 – 7.00 (m, 1H), 6.99 – 6.79 (m, 2H), 5.63 (s, 1H), 5.27 (s, 1H), 3.43 (s, 2H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 162.8 (d, J = 246.3 Hz), 145.2, 140.4 (d, J = 7.4 Hz), 139.0 (d, J = 2.4 Hz), 134.9, 130.2 (d, J = 8.4 Hz), 129.5, 128.1, 121.3 (d, J = 2.8 Hz), 119.2, 115.1 (d, J = 21.2 Hz), 112.6 (d, J = 22.4 Hz), 43.7, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.4. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₇H₁₆FNO₃SNa⁺:356.0728; Found: 356.0727.

3-(naphthalen-2-yl)-N-tosylbut-3-enamide(4h)



¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.95 – 7.80 (m, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.64 – 7.54 (m, 1H), 7.53 (d, J = 5.3 Hz, 6H), 6.89 (t, J = 5.7 Hz, 2H), 6.01 – 5.76 (m, 1H), 5.55 – 5.32 (m, 1H), 3.60 (d, J = 4.3 Hz, 2H), 2.24 (s, 3H).¹³C NMR (101 MHz, CDCl₃) δ 168.0, 144.7, 140.0, 134.8, 134.6, 133.1, 129.2, 128.5, 128.5, 128.0, 127.5, 126.6, 126.4, 124.7, 123.3, 118.8, 44.4, 21.5. **HRMS (IT-TOF)**: [M+Na]⁺ Calcd for C₂₁H₁₉NO₃SNa⁺:388.0978; Found: 388.0978.

3-(naphthalen-1-yl)-N-tosylbut-3-enamide(4i)



¹H NMR (400 MHz, CDCl₃) δ 8.50 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.40 (m, 2H), 7.30 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 7.0, 1.2 Hz, 1H), 5.57 (d, *J* = 1.4 Hz, 1H), 5.33 (d, *J* = 1.2 Hz, 1H), 3.46 (s, 2H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.5, 144.9, 139.9, 138.1, 135.0, 133.7, 130.5, 129.4, 128.5, 128.2, 128.2, 126.4, 125.9, 125.2, 125.2, 124.8, 121.6, 46.3, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₁H₁₉NO₃SNa⁺:388.0978; Found: 388.0979.

3 New Compounds Characterization

trans-4-((methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)amino)-5-phenyl-1tosylpyrrolidin-2-one (3aa-1)



General procedure A: Unsaturated N-tosyl amide 1a (0.6 Sulfoximidoyl salts (0.4)mmol), thianthrene 2a mmol) and Ir(dF(Me)ppy)₂(dtbbpy)[PF₆] (1 mol%) in a Penicillin vial was evacuated and backfilled with argon via Schlenk line three times. Subsequently, DCM (anhydrous, 4.0 mL) and 2,4,6-Trimethylpyridine (0.8 mmol) were added, cooled to -20 °C and irradiated by 30 W blue LED strip light for 12 hours. Then the reaction mixture was concentrated in vacuo and purified by column chromatography to afford the desired product as colorless oil 75 mg (40%). (PE/EA=1:1, $R_f = 0.6$). ¹H NMR (400 MHz, **CDCl**₃) δ 7.74 (dd, J = 7.8, 4.3 Hz, 4H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.25 - 7.12 (m, 4H), 7.05 - 6.91 (m, 2H), 5.17 (d, J = 2.5 Hz, 1H), 3.52 (dt, J = 6.0, 2.8 Hz, 1H), 3.05 (s, 3H), 2.76 (dd, J = 17.2, 6.3 Hz, 1H), 2.48 (dd, J = 17.2, 3.1 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 144.6, 139.1, 138.5, 135.7, 133.2, 129.5, 129.1, 128.6, 128.5, 128.3, 127.9, 126.1, 72.4, 56.7, 45.2, 41.0, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₄H₂₄N₂O₄S₂Na⁺:491.1070; Found: 491.1069.

trans-4-((methyl(oxo)(phenyl)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3aa-2)



Ts Isolated colorless oil 60 mg (32%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.1 Hz, 2H), 7.84 – 7.76 (m, 2H), 7.60 (t, J = 7.3 Hz, 1H), 7.54 (d, J = 7.7 Hz, 2H), 7.28 (m, 5H),7.19 (d, J = 6.4 Hz, 2H), 5.49 (s, 1H), 3.44 (d, J = 5.9 Hz, 1H), 3.01 (s, 3H), 2.69 (dd, J = 16.9, 6.0 Hz, 1H), 2.43 (s, 3H), 2.19 (d, J = 17.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 144.6, 139.3, 138.6, 135.8, 133.3, 129.7, 129.1, 128.7, 128.4, 127.8, 125.8, 73.7, 57.0, 45.4, 39.8, 21.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₄H₂₄N₂O₄S₂Na⁺:491.1070; Found: 491.1069.

trans-4-(((4-methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ab-1)



Following General Procedure A, isolated colorless oil 86 mg

(43%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.20 (d, J = 8.1 Hz, 2H), 7.00 (dd, J =7.5, 2.0 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 5.17 (d, J = 2.6 Hz, 1H), 3.87 (s, 3H), 3.51 (dt, J = 6.2, 3.1 Hz, 1H), 3.02 (s, 3H), 2.75 (dd, J = 17.2, 6.3 Hz, 1H), 2.47 (dd, J = 17.2, 3.4 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 163.4, 144.6, 138.6, 135.8, 130.5, 130.1, 129.1, 128.6, 128.5, 127.9, 126.1, 114.7, 72.47, 56.7, 55.7, 45.6, 41.1, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₅S₂Na⁺:521.1176; Found: 521.1175.

trans-4-(((4-methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ab-2)



Ts Isolated colorless oil 62 mg (31%). (PE/EA=1:1, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.22 – 7.16 (m, 2H), 6.98 (d, J = 8.9 Hz, 2H), 5.48 (s, 1H), 3.85 (s, 3H), 3.43 (d, J = 6.0 Hz, 1H), 2.99 (s, 3H), 2.69 (dd, J = 16.9, 6.0 Hz, 1H), 2.43 (s, 3H), 2.18 (d, J = 16.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 163.5, 144.6, 138.8, 135.8, 130.5, 130.3, 129.1, 128.7, 127.8, 125.7, 114.9, 73.7, 57.0, 55.7, 45.7, 39.8, 21.7. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₅H₂₇N₂O₅S₂⁺:499.1356; Found: 499.1355.

trans-4-((methyl(oxo)(p-tolyl)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ac-1)



Ts Following General Procedure A, isolated colorless oil 81 mg (42%). (PE/EA=1:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.26 – 7.16 (m, 5H), 6.97 (dd, J = 7.7, 1.9 Hz, 2H), 5.18 (d, J = 2.4 Hz, 1H), 3.51 (dt, J = 6.0, 2.8 Hz, 1H), 3.03 (s, 3H), 2.75 (dd, J = 17.2, 6.3 Hz, 1H), 2.47 (dd, J = 17.2, 3.2 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 144.6, 144.1, 138.5, 135.9, 135.7, 130.1, 129.0, 128.6, 128.5, 128.4, 127.9, 126.0, 72.5, 56.7, 45.3, 41.0, 21.6, 21.5. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1228.

trans-4-((methyl(oxo)(p-tolyl)- λ^6 -sulfaneylidene)amino)-5-phenyl-1tosylpyrrolidin-2-one (3ac-2)



Ts Isolated colorless oil 64 mg (33%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.26 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 5.49 (s, 1H), 3.42 (d, J = 6.0Hz, 1H), 2.99 (s, 3H), 2.68 (dd, J = 16.9, 6.0 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H), 2.18 (d, J = 16.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 144.6, 144.3, 138.7, 136.1, 135.8, 130.3, 129.1, 128.7, 128.4, 127.8, 125.7, 73.7, 57.0, 45.4, 39.8, 21.6, 21.4. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1226.

trans-4-((methyl(oxo)(m-tolyl)-λ⁶-sulfaneylidene)amino)-5-phenyl-1tosylpyrrolidin-2-one (3ad-1)



Following General Procedure A, isolated colorless oil 79 mg (41%). (PE/EA=1:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.2 Hz, 2H), 7.59 (s, 1H), 7.57 – 7.51 (m, 1H), 7.39 (d, J = 7.1 Hz, 2H), 7.21 (dd, J = 9.5, 7.5 Hz, 5H), 7.04 – 6.87 (m, 2H), 5.18 (d, J = 2.4 Hz, 1H), 3.52 (dt, J = 5.9, 2.8 Hz, 1H), 3.05 (s, 3H), 2.76 (dd, J = 17.2, 6.3 Hz, 1H), 2.48 (dd, J = 17.2, 3.0 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 144.7, 140.0, 139.0, 138.6, 135.80, 134.1, 129.5, 129.1, 128.8, 128.7, 128.6, 128.0, 126.1, 125.5, 72.4, 56.7, 45.3, 41.1, 21.6, 21.4. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1228.

trans-4-((methyl(oxo)(m-tolyl)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ad-2)



Ts Isolated colorless oil 73 mg (38%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.1 Hz, 2H), 7.61 (s, 1H), 7.59 – 7.54 (m, 1H), 7.39 (d, J = 6.2 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.22 – 7.18 (m, 2H), 5.49 (s, 1H), 3.45 (d, J =5.9 Hz, 1H), 3.00 (s, 3H), 2.69 (dd, J = 16.9, 6.0 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H), 2.19 (d, J = 17.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 144.6, 140.0, 139.2, 138.7, 135.8, 134.1, 129.5, 129.1, 128.8, 127.8, 125.8, 125.4, 73.7, 57.0, 45.4, 39.8, 21.7, 21.4. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1227.

trans-4-((methyl(oxo)(o-tolyl)-λ⁶-sulfaneylidene)amino)-5-phenyl-1tosylpyrrolidin-2-one (3ae-1)



Following General Procedure A, isolated colorless oil 42 mg (22%). (PE/EA=1:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.58 – 7.44 (m, 1H), 7.35 (d, J = 7.2 Hz, 2H), 7.18 (dd, J = 8.5, 1.9 Hz, 5H), 6.91 – 6.76 (m, 2H), 5.14 (d, J = 1.9 Hz, 1H), 3.55 (d, J = 6.1 Hz, 1H), 3.12 (s, 3H), 2.79 (dd, J = 17.3, 6.2 Hz, 1H), 2.68 (s, 3H), 2.51 (dd, J = 17.3, 2.5 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0 144.7, 138.4, 137.7, 135.7, 133.3, 133.2, 130.5, 129.1, 128.7, 128.6, 128.0, 126.9, 126.1, 72.0, 56.6, 44.2, 41.0, 21.6, 20.2. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1228.

trans-4-((methyl(oxo)(o-tolyl)-λ⁶-sulfaneylidene)amino)-5-phenyl-1tosylpyrrolidin-2-one (3ae-2)



Ts Isolated colorless oil 37 mg (19%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.33 – 7.23 (m, 6H), 7.20 – 7.13 (m, 2H), 5.54 (s, 1H), 3.41 (d, J = 5.6 Hz, 1H), 3.09 (s, 3H), 2.69 (dd, J = 16.9, 6.0 Hz, 1H), 2.57 (s, 3H), 2.43 (s, 3H), 2.19 (d, J = 16.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 144.6, 138.7, 137.6, 137.2, 135.8, 133.3, 133.1, 130.9, 129.1, 128.8, 128.7, 127.8, 127.0, 125.7, 73.6, 57.4, 44.3, 39.5, 21.7, 20.0. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1226.

trans-4-(((4-fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1tosylpyrrolidin-2-one (3af-1)



Ts Following General Procedure A, isolated colorless oil 66 mg (34%). (PE/EA=1:1, $R_f = 0.7$). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (dt, J = 8.9, 2.6 Hz, 2H), 7.31 – 7.22 (m, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.13 (t, J = 8.5 Hz, 1H), 7.03 – 6.95 (m, 1H), 5.15 (d, J = 2.9 Hz, 1H), 3.50 (dt, J = 6.5, 3.4 Hz, 1H), 3.05 (s, 3H), 2.76 (dd, J = 17.2, 6.5 Hz, 1H), 2.49 (dd, J = 17.8, 3.0 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 165.5 (d, J = 256.0 Hz), 144.7, 138.5, 135.7, 134.9 (d, J = 3.1 Hz), 131.1 (d, J = 9.5 Hz), 129.1, 128.7, 128.5, 128.0, 126.2, 116.7 (d, J = 22.5 Hz), 72.3, 56.8, 45.4, 41.0, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -104.4. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₄H₂₃FN₂O₄S₂Na⁺:509.0976; Found: 509.09765.

trans-4-(((4-fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1tosylpyrrolidin-2-one (3af-2)



Ts Isolated colorless oil 47 mg (24%). (PE/EA=1:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 7.81 (dd, J = 8.8, 5.1 Hz, 2H), 7.32 – 7.22 (m, 5H), 7.23 – 7.11 (m, 4H), 5.47 (s, 1H), 3.43 (d, J = 6.0 Hz, 1H), 3.01 (s, 3H), 2.70 (dd, J = 17.0, 6.0 Hz, 1H), 2.42 (s, 3H), 2.18 (d, J = 16.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 165.6 (d, J = 256.1 Hz), 144.7, 138.5, 135.7, 135.2, 131.1 (d, J = 9.5 Hz), 129.1, 128.8, 128.7, 127.9, 125.7, 116.9 (d, J = 22.6 Hz), 73.6, 56.9, 45.6, 39.7, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -104.3. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₄H₂₃FN₂O₄S₂Na⁺:509.0976; Found: 509.0976.

trans-4-(((3-chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ag-1)



Fs Following General Procedure A, isolated colorless oil 76 mg (38%). (PE/EA=1:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.45 (t, J = 7.9 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.22 (d, J = 8.1 Hz, 2H), 7.09 – 6.93 (m, 2H), 5.20 (d, J = 2.4 Hz, 1H), 3.52 (dt, J = 5.9, 2.8 Hz, 1H), 3.09 (s, 3H), 2.80 (dd, J = 17.3, 6.3 Hz, 1H), 2.51 (dd, J = 17.3, 3.1 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 144.7, 141.1, 138.3, 135.8, 135.7, 133.4, 130.8, 129.1, 128.7, 128.5, 128.5, 128.1, 126.4, 126.0, 72.4, 56.7, 45.1, 40.9, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₄H₂₃ClN₂O₄S₂Na⁺:525.0680, 527.0651; Found: 525.0680, 527.0649.

trans-4-(((3-chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ag-2)



Ts Isolated colorless oil 58 mg (29%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 2H), 7.82 (t, J = 2.0 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.61 – 7.55 (m, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.36 – 7.26 (m, 5H), 7.21 (dd, J =7.7, 1.8 Hz, 2H), 5.49 (s, 1H), 3.46 (d, J = 6.0 Hz, 1H), 3.05 (s, 3H), 2.74 (dd, J = 16.9, 6.0 Hz, 1H), 2.45 (s, 3H), 2.22 (d, J = 16.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.7, 144.7, 141.4, 138.4, 135.9, 135.7, 133.5, 130.9, 129.1, 128.8, 128.7, 128.5, 127.9, 126.3, 125.8, 73.5, 56.9, 45.3, 39.7, 21.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₄H₂₃ClN₂O₄S₂Na⁺:525.0680, 527.0651; Found: 525.0680, 527.0652.

trans-4-(((2-bromophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ah)



Ts Following General Procedure A, isolated colorless oil 145 mg (66%). dr = 1.27:1. (PE/EA=1:1, R_f = 0.6) ¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, J = 7.9, 1.8 Hz, 0.45H), 8.14 (dd, J = 7.3, 2.3 Hz, 0.55H), 7.89 (d, J = 8.3 Hz, 1H), 7.82 (dd, J = 7.2, 1.9 Hz, 0.55H), 7.78 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 7.8 Hz, 0.45H), 7.55 – 7.45 (m, 1.39H), 7.45 – 7.39 (m, 0.7H), 7.30 – 7.12 (m, 6H), 6.94 (dd, J = 6.4, 2.8 Hz, 1H), 5.48 (s, 0.45H), 5.36 (s, 0.55H), 3.42 – 3.28 (m, 2.74H), 3.24 (s, 1.28H), 2.71 (ddd, J = 39.6, 17.1, 6.0 Hz, 1H), 2.53 – 2.25 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 173.0, 172.9, 144.6, 138.7, 138.4, 138.3, 137.7, 135.8, 134.5, 133.4, 133.4, 129.1, 129.1, 128.8, 128.7, 128.7, 128.7, 128.5, 128.4, 127.9, 127.8, 125.9, 125.7, 120.7, 120.6, 73.4, 72.0, 57.6, 56.9, 43.0, 42.9, 40.6, 39.2, 29.7, 21.7, 21.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₄H₂₃BrN₂O4S₂Na⁺:569.0175, 571.0155; Found: 569.0174, 571.0154.

trans-4-((methyl(oxo)(pyridin-2-yl)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ai-1)



Fs Following General Procedure A, isolated colorless oil 60 mg (32%). (PE/EA=1:1, $R_f = 0.3$). ¹H NMR (400 MHz, CDCl₃) δ 8.95 – 8.69 (m, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.92 (td, *J* = 7.7, 1.7 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.55 (ddd, *J* = 7.7, 4.7, 1.2 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.98 – 6.73 (m, 2H), 5.14 (s, 1H), 3.61 (d, *J* = 6.1 Hz, 1H), 3.19 (s, 3H), 2.79 (dd, *J* = 17.1, 6.1 Hz, 1H), 2.49 – 2.29 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 157.8, 150.6, 144.6, 138.5, 138.2, 135.8, 129.1, 128.7, 127.8, 127.0, 125.7, 123.4, 77.3, 72.5, 56.3, 41.5, 40.7, 21.7. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₃H₂₄N₃O₄S₂⁺:470.1203; Found: 470.1203.

trans-4-((methyl(oxo)(pyridin-2-yl)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ai-2)



Ts Isolated colorless oil 56 mg (30%). (PE/EA=1:1, $R_f = 0.2$). ¹H NMR (400 MHz, CDCl₃) δ 8.69 (ddd, J = 4.7, 1.8, 0.9 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.90 (td, J = 7.7, 1.7 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.47 (ddd, J = 7.6, 4.7, 1.2 Hz, 1H), 7.34 – 7.24 (m, 5H), 7.21 (dd, J = 7.6, 1.8 Hz, 2H), 5.47 (s, 1H), 3.47 (d, J = 6.1 Hz, 1H), 3.17 (s, 3H), 2.60 (dd, J = 17.1, 6.2 Hz, 1H), 2.42 (s, 3H), 2.18 (dd, J = 16.9, 1.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 157.4 150.6, 144.6, 138.8, 138.1, 135.8, 129.1, 128.8, 128.7, 127.9, 126.9, 125.9, 123.3, 73.4, 56.8, 41.6, 39.8, 21.7. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₃H₂₄N₃O₄S₂⁺:470.1203; Found: 470.1202.

trans-4-((ethyl(4-methoxyphenyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3aj-1)



Following General Procedure A, isolated colorless oil 92 mg (45%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.23 (d, J = 8.1 Hz, 2H), 7.06 (dd, J = 6.6, 2.7 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 5.22 (d, J = 2.6 Hz, 1H), 3.89 (s, 3H), 3.58 (dt, J = 6.2, 3.0 Hz, 1H), 3.11 (qd, J = 7.2, 3.7 Hz, 2H), 2.78 (dd, J = 17.2, 6.3 Hz, 1H), 2.49 (dd, J = 17.2, 3.3 Hz, 1H), 2.42 (s, 3H), 1.19 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 163.4, 144.7, 138.8, 135.8, 131.3, 129.1, 128.7, 128.5, 128.2, 127.9, 126.2, 114.7, 72.7, 56.7, 55.7, 51.4, 41.3, 21.7, 7.4. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₆H₂₉N₂O₅S₂⁺:513.1513; Found: 513.1512.

trans-4-((ethyl(4-methoxyphenyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3aj-2)



Ts Isolated colorless oil 82 mg (40%). (PE/EA=1:1, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.21 (d, J = 7.8 Hz, 3H), 6.97 (d, J = 8.8 Hz, 2H), 5.47 (s, 1H), 3.84 (s, 3H), 3.48 (d, J = 5.8 Hz, 1H), 3.04 (dq, J = 9.5, 7.1 Hz, 2H), 2.71 (dd, J = 16.9, 6.0 Hz, 1H), 2.42 (s, 3H), 2.18 (d, J = 16.9 Hz, 1H), 1.19 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 163.5, 144.6, 138.8, 135.8, 131.2, 129.1, 128.7, 128.6, 127.7, 125.7, 114.8, 74.0, 56.9, 55.6, 51.4, 39.8, 21.6, 7.0. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₆H₂₉N₂O₅S₂⁺:513.1513; Found: 513.1513.

trans-4-(((4-chlorophenyl)(ethyl)(oxo)-
tosylpyrrolidin-2-one (3ak-1) λ^6 -sulfaneylidene)amino)-5-phenyl-1-



Following General Procedure A, isolated colorless oil 81 mg (39%). (PE/EA=1:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.29 (t, J = 3.8 Hz, 3H), 7.22 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.1 Hz, 2H), 5.18 (d, J = 2.8 Hz, 1H), 3.56 (dt, J = 6.5, 3.3 Hz, 1H), 3.14 (p, J = 7.2 Hz, 2H), 2.79 (dd, J = 17.2, 6.3 Hz, 1H), 2.52 (dd, J = 17.1, 3.8 Hz, 1H), 2.42 (s, 3H), 1.21 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 144.7, 139.9, 138.5, 135.8, 135.7, 130.5, 129.7, 129.1, 128.7, 128.5, 128.1, 126.2, 72.4, 56.7, 51.1, 41.2, 21.6, 7.2. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₅ClN₂O₄S₂Na⁺:539.0837, 541.0807; Found: 539.0839, 541.0809.

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trans-4-(((4-chlorophenyl)(ethyl)(oxo)-
tosylpyrrolidin-2-one (3ak-2)
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 λ^6 -sulfaneylidene)amino)-5-phenyl-1-



Ts Isolated colorless oil 58 mg (28%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.32 – 7.24 (m, 5H), 7.24 – 7.18 (m, 2H), 5.48 (s, 1H), 3.48 (d, J = 6.0 Hz, 1H), 3.19 – 2.98 (m, 2H), 2.74 (dd, J = 16.9, 6.0 Hz, 1H), 2.45 (s, 3H), 2.20 (d, J = 17.0 Hz, 1H), 1.23 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 144.6, 140.1, 138.6, 136.4, 135.8, 130.5, 129.9, 129.1, 128.8, 128.7, 127.9, 125.7, 73.8, 56.8, 51.3, 39.8, 21.6, 6.9. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₅H₂₆ClN₂O₄S₂⁺:517.1018, 519.0988; Found: 517.1017, 519.0988.

trans-4-((benzyl(4-methoxyphenyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3al-1)



Following General Procedure A, isolated colorless oil 62 mg (27%). (PE/EA=1:1, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.2 Hz, 2H), 7.42 – 7.14 (m, 10H), 7.05 (dd, J = 6.7, 2.7 Hz, 2H), 6.98 (d, J = 7.1 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 5.22 (d, J = 2.6 Hz, 1H), 4.40 – 4.17 (m, 2H), 3.84 (s, 3H), 3.58 (dt, J = 6.2, 3.1 Hz, 1H), 2.75 (dd, J = 17.1, 6.2 Hz, 1H), 2.55 – 2.41 (m, 1H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 163.4, 144.7, 138.8, 135.8, 131.7, 131.2, 129.1, 128.8, 128.7, 128.6, 128.4, 128.3, 127.9, 127.6, 126.1, 114.2, 72.8, 63.5, 57.0, 55.7, 41.2, 21.7. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₁H₃₁N₂O₅S₂⁺:575.1669; Found: 575.1668.

trans-4-((benzyl(4-methoxyphenyl)(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3al-2)



Ts Isolated colorless oil 48 mg (21%). (PE/EA=1:1, $R_f = 0.4$) ¹**H NMR (400 MHz, CDCl₃)** δ 7.91 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 7.9 Hz, 3H), 7.26 – 7.20 (m, 5H), 7.17 (dd, J = 7.7, 1.8 Hz, 2H), 6.97 (d, J = 7.2 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 5.52 (s, 1H), 4.47 – 4.19 (m, 1H), 3.82 (s, 3H), 3.53 (d, J = 5.7 Hz, 1H), 2.73 (dd, J = 16.9, 6.0 Hz, 1H), 2.42 (s, 3H), 2.32 (d, J = 16.9 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 163.7, 144.7, 138.5, 135.7, 131.7, 131.2, 129.2, 129.0, 128.7, 128.4, 127.9, 125.7, 114.5, 73.5, 63.3, 56.9, 55.7, 39.5, 21.7. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₁H₃₁N₂O₅S₂⁺:575.1669; Found: 575.1670.

trans-4-((dimethyl(oxo)- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2one (3am)



Ts Following General Procedure A, isolated colorless oil 72 mg (44%). (EA, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 2H), 7.40 – 7.27 (m, 3H), 7.23 (d, J = 7.8 Hz, 4H), 5.25 (d, J = 1.9 Hz, 1H), 3.77 (d, J = 6.3 Hz, 1H), 2.94 (s, 3H), 2.85-2.80 (m,4H), 2.41 (s, 3H), 2.30 (dd, J = 17.1, 2.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 144.7, 138.7, 135.7, 129.1, 128.9, 128.6, 128.1, 126.1, 73.3, 56.4, 42.9, 42.3, 40.6, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₁₉H₂₂N₂O₄S₂Na⁺:429.0914; Found: 429.0913.

trans-4-((1-oxidotetrahydro- $1\lambda^6$ -thiophen-1-ylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3an)



Ts Following General Procedure A, Isolated colorless oil 106 mg (61%). (PE/EA=1:1, $R_f = 0.3$). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.25 – 7.19 (m, 4H), 5.27 (d, J = 2.1 Hz, 1H), 4.42 – 3.47 (m, 1H), 3.46 – 2.89 (m, 4H), 2.87 – 2.74 (m, 1H), 2.40 (s, 3H), 2.32 (dd, J = 17.1, 2.6 Hz, 1H), 2.25 – 1.96 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 144.7, 138.7, 135.6, 129.1, 128.8, 128.5, 128.1, 126., 73.1, 57.7, 53.0, 52.6, 40.6, 23.5, 23.3, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₁H₂₅N₂O₄S₂⁺:433.1251; Found: 433.1251.

trans-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-5-phenyl-1-tosylpyrrolidin-2-one (3ao)



Ts Following General Procedure A, isolated colorless oil 176 mg (83%). (PE/EA=2:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.82 (m, 4H),

7.80 (d, J = 7.2 Hz, 2H), 7.53 (q, J = 7.3 Hz, 2H), 7.45 (q, J = 7.5 Hz, 4H), 7.35 – 7.22 (m, 4H), 7.16 (t, J = 7.3 Hz, 3H), 5.45 (d, J = 1.7 Hz, 1H), 3.66 (d, J = 5.8 Hz, 1H), 2.79 (dd, J = 16.9, 5.9 Hz, 1H), 2.39 (dd, J = 16.9, 2.0 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 144.5, 140.3, 140.2, 138.6, 135.7, 132.8, 132.7, 129.3, 129.2, 129.1, 128.8, 128.5, 128.3, 128.3 127.9, 125.9, 73.4, 56.9, 40.5, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₉H₂₇N₂O₄S₂⁺:531.1407; Found: 531.1408.

trans-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-5-(p-tolyl)-1-tosylpyrrolidin-2one (3bo)



Me⁻ Following General Procedure A, isolated colorless solid 163 mg (75%). (PE/EA=2:1, R_f = 0.7). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (t, J = 8.1 Hz, 4H), 7.80 (dd, J = 8.4, 1.3 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.49 – 7.40 (m, 4H), 7.15 (d, J = 7.8 Hz, 2H), 7.08 (q, J = 8.2 Hz, 4H), 5.42 (s, 1H), 3.63 (d, J = 5.7 Hz, 1H), 2.79 (dd, J = 16.9, 5.9 Hz, 1H), 2.39-2.35 (m, 4H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 144.5, 140.4, 140.3, 137.7, 135.8, 135.7, 132.8, 132.7, 129.4, 129.3, 129.2, 129.1, 128.5, 128.4, 128.3, 125.7, 73.3, 57.0, 40.5, 21.6, 21.1. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₃₀H₂₈N₂O₄S₂Na⁺:567.1383; Found: 567.1383.

trans-4-((oxodiphenyl-λ⁶-sulfaneylidene)amino)-5-(o-tolyl)-1-tosylpyrrolidin-2-one (3co)



 Me
 Following General Procedure A, isolated colorless oil 128 mg (59%).

 (PE/EA=2:1, R_f = 0.6). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.3 Hz, 2H), 7.82

 (d, J = 7.2 Hz, 4H), 7.57 - 7.48 (m, 2H), 7.43 (q, J = 7.8 Hz, 4H), 7.19 - 7.04 (m, 6H),

 5.65 (d, J = 1.4 Hz, 1H), 3.94 - 3.20 (m, 1H), 2.78 (dd, J = 16.6, 5.4 Hz, 1H), 2.40 (s,

3H), 2.37-2.33 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 173.5, 144.4, 140.5, 140.5, 136.3, 135.7, 135.4, 132.8, 132.7, 130.9, 129.3, 129.1, 129.0, 128.6, 128.3, 128.2, 127.8, 126.2, 124.9, 70.6, 55.3, 40.6, 21.6, 19.5. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₀H₂₉N₂O₄S₂⁺:545.1564; Found: : 545.1564.

trans-5-(4-methoxyphenyl)-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosylpyrrolidin-2-one (3do)



MeO Following General Procedure A, isolated colorless oil 135 mg (60%). (PE/EA=2:1, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.5 Hz, 4H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.53 (q, *J* = 7.2 Hz, 2H), 7.46 (dd, *J* = 7.8, 6.0 Hz, 4H), 7.15 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.39 (s, 1H), 3.79(s, 3H), 3.62 (d, J = 5.5 Hz, 1H), 2.79 (dd, J = 16.9, 5.9 Hz, 1H), 2.39 (dd, J = 16.9, 2.2 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 159.3, 144.5, 140.4, 140.3, 135.8, 132.8, 132.7, 130.7, 129.3, 129.2, 129.1, 128.5, 128.3, 128.3, 127.1, 114.2, 21.6. HRMS (IT-TOF): $[M+H]^+$ 73.0. 56.9. 55.3. 40.5, Calcd for C₃₀H₂₉N₂O₄S₂⁺:561.1513; Found: 561.1512.

trans-5-(3-methoxyphenyl)-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosylpyrrolidin-2-one (3eo)



Following General Procedure A, isolated colorless oil 121 mg

(54%). (PE/EA=2:1, R_f = 0.4). ¹**H NMR (400 MHz, CDCl**₃) δ 7.87 (dd, *J* = 8.3, 1.8 Hz, 4H), 7.81 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.46 (td, *J* = 7.6, 5.6 Hz, 4H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.18 – 7.12 (m, 2H), 6.82 – 6.74 (m, 2H), 6.65 (s, 1H), 5.45 – 5.41 (m, 1H), 3.70 (s, 3H), 3.66 (dt, *J* = 5.9, 1.9 Hz, 1H), 2.79 (dd, *J* = 16.9, 5.9 Hz,

1H), 2.39 (dd, J = 16.9, 2.1 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 159.9, 144.6, 140.1, 140.1, 140.1, 135.6, 132.9, 132.8, 129.9, 129.3, 129.2, 129.1, 128.5, 128.3, 128.3, 118.1, 113.8, 111.0, 73.2, 56.8, 55.1, 40.5, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₀H₂₉N₂O₄S₂⁺:561.1513; Found: 561.1513.

trans-5-(4-(tert-butyl)phenyl)-4-((oxodiphenyl-λ⁶-sulfaneylidene)amino)-1tosylpyrrolidin-2-one (3fo)



tΒι Following General Procedure A, isolated colorless oil 190 mg (81%). (PE/EA=2:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.83 (m, 5H), 7.81 (d, J = 1.5 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.49 – 7.41 (m, 4H), 7.28 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 5.44 (d, J = 1.4 Hz, 1H), 4.06 - $3.39 \text{ (m, 1H)}, 2.81 \text{ (dd, } J = 16.9, 5.8 \text{ Hz}, 1\text{H}), 2.37 \text{ (dd, } J = 17.2, 2.0 \text{ Hz}, 1\text{H}), 2.34 \text{ (s, } J = 17.2, 2.0 \text{ Hz}, 1\text{Hz}), 2.34 \text{ (s, } J = 17.2, 2.0 \text{ Hz}, 1\text{Hz}), 2.34 \text{ (s, } J = 17.2, 2.0 \text{ Hz}, 1\text{Hz}), 2.34 \text{ (s, } J = 17.2, 2.0 \text{ Hz}), 2.34 \text{ (s, } J = 17.2, 2.0 \text{ Hz}), 3.34 \text{ (s,$ 3H), 1.29 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 150.9, 144.4, 140.5, 140.4, 135.9, 135.4, 132.8, 132.7, 129.3, 129.2, 129.1, 128.5, 128.4, 128.3, 125.7, 125.6, 73.3, 31.3. 21.6. HRMS (**IT-TOF**): $[M+H]^+$ 56.8. 40.6. 34.5. Calcd for $C_{33}H_{35}N_2O_4S_2^+$:587.2033; Found: 587.2033.

trans-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosyl-5-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (3go)



F₃C **Following General Procedure A**, isolated colorless oil 177 mg (74%). (PE/EA=2:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 7.1 Hz, 2H), 7.78 (d, J = 7.1 Hz, 2H), 7.59 – 7.50 (m, 4H), 7.45 (ddd, J = 13.1, 8.3, 6.8 Hz, 4H), 7.33 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 5.48 (s, 1H), 3.63 (dt, J = 6.0, 2.2 Hz, 1H), 2.75 (dd, J = 16.9, 6.0 Hz, 1H), 2.42 (dd, J = 16.9, 2.3

Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 144.9, 142.8, 140.1, 139.9, 135.4, 133.0, 132.9, 130.2 (q, *J* = 32.6 Hz), 129.40, 129.2, 129.2, 128.4, 128.3, 128.1, 126.3, 125.8 (q, *J* = 3.9 Hz), 123.9 (q, *J* = 272.1 Hz), 72.8, 56.8, 40.3, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₃₀H₂₅F₃N₂O₄S₂Na⁺:621.1101; Found: 621.1101.

trans-5-oxo-3-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosylpyrrolidin-2-yl)benzonitrile (3ho)



NC Following General Procedure A, isolated colorless oil 113 mg (51%). (PE/EA=2:1, $R_f = 0.3$). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.3 Hz, 2H), 7.84 – 7.75 (m, 4H), 7.60 (d, J = 8.1 Hz, 2H), 7.54 (dd, J = 10.0, 7.3 Hz, 2H), 7.46 (q, J = 7.4 Hz, 4H), 7.34 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.47 (d, J = 1.8 Hz, 1H), 3.60 (dd, J = 5.2, 2.7 Hz, 1H), 2.72 (dd, J = 17.0, 6.0 Hz, 1H), 2.40 (dd, J = 16.9, 2.3 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 145.0, 144.2, 140.0, 139.9, 135.3, 133.0, 132.9, 132.6, 129.5, 129.3, 129.2, 128.5, 128.3, 128.0, 126.7, 118.4, 111.9, 72.9, 56.7, 40.3, 21.7. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₀H₂₆N₃O₄S₂⁺:556.1360; Found: 556.1359.

trans-5-(4-fluorophenyl)-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosylpyrrolidin-2-one (3io)



F Following General Procedure A, isolated colorless oil 151 mg (69%). (PE/EA=2:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (dd, J = 7.8, 2.8 Hz, 4H), 7.79 (d, J = 7.4 Hz, 2H), 7.54 (q, J = 7.2 Hz, 2H), 7.46 (q, J = 7.7 Hz, 4H), 7.15 (t, J = 7.9 Hz, 4H), 6.98 (t, J = 8.6 Hz, 2H), 5.41 (d, J = 1.9 Hz, 1H), 3.61 (d, J = 7.4 Hz, 2H), 7.15 (d, J = 7.9 Hz, 4H), 6.98 (f, J = 8.6 Hz, 2H), 5.41 (d, J = 1.9 Hz, 1H), 3.61 (d, J = 7.4 Hz, 2H), 7.15 (d, J = 7.9 Hz, 4H), 6.98 (f, J = 8.6 Hz, 2H), 5.41 (d, J = 1.9 Hz, 1H), 3.61 (d, J = 7.4 Hz, 2H), 7.15 (d, J = 7.9 Hz, 4H), 6.98 (f, J = 8.6 Hz, 2H), 5.41 (d, J = 1.9 Hz, 1H), 3.61 (d

6.0 Hz, 1H), 2.76 (dd, J = 17.0, 6.0 Hz, 1H), 2.40 (dd, J = 17.0, 2.3 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.9, 144.7, 140.2 (d, J = 2.6 Hz), 135.7, 134.6 (d, J = 3.3 Hz), 132.9, 132.8, 129.4, 129.2, 128.5, 128.3, 128.2, 127.7, 127.6, 115.8, 115.6, 72.7, 56.9, 40.4, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.3. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₉H₂₅FN₂O₄S₂Na⁺:571.1132; Found: 571.1133.

trans-5-(3-chlorophenyl)-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosylpyrrolidin-2-one (3jo)



Following General Procedure A, isolated colorless oil 124 mg (55%). (PE/EA=2:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.82 (m, 4H), 7.79 (d, J = 7.4 Hz, 2H), 7.54 (q, J = 7.3 Hz, 2H), 7.46 (q, J = 7.6 Hz, 4H), 7.25 – 7.22 (m, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.14 – 7.04 (m, 1H), 6.99 (s, 1H), 5.38 (d, J = 1.9 Hz, 1H), 3.61 (d, J = 6.0 Hz, 1H), 2.77 (dd, J = 17.0, 6.1 Hz, 1H), 2.42 (dd, J = 17.0, 2.4 Hz, 1H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 144.8, 140.7, 140.1, 140.0, 135.5, 134.7, 132.9, 132.8, 130.1, 129.3, 129.2, 129.2, 128.4, 128.3, 128.2, 128.1, 126.0, 124.2, 72.6, 56.7, 40.4, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₉H₂₆ClN₂O₄S₂⁺:565.1018, 567.0988; Found: : 565.1020, 567.0986.

trans-5-(2-bromophenyl)-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosylpyrrolidin-2-one (3ko)



Br Following General Procedure A, isolated colorless oil 117 mg (48%). (PE/EA=2:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.4 Hz, 2H), 7.91 – 7.83 (m, 2H), 7.80 (dd, J = 8.4, 1.3 Hz, 2H), 7.57 – 7.46 (m, 3H), 7.50 – 7.44 (m, 2H), 7.41 (dt, J = 7.7, 6.5 Hz, 2H), 7.31 (ddd, J = 15.7, 7.5, 1.6 Hz, 2H), 7.15 (td,

J = 7.5, 1.6 Hz, 3H), 5.74 (d, J = 1.6 Hz, 1H), 3.79 (dt, J = 5.2, 1.8 Hz, 1H), 2.69 (dd, J = 16.6, 5.2 Hz, 1H), 2.41 (dd, J = 16.6, 1.9 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.4, 144.6, 140.7, 140.4, 137.4, 135.5, 133.4, 132.7, 132.6, 129.5, 129.2, 129.1, 129.0, 128.6, 128.6, 128.2, 127.8, 122.5, 72.4, 55.5, 40.7, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₉H₂₆BrN₂O₄S₂⁺:609.0512, 611.0492; Found: : 609.0511, 611.0490.

trans-5-([1,1'-biphenyl]-4-yl)-4-((oxodiphenyl-λ⁶-sulfaneylidene)amino)-1tosylpyrrolidin-2-one (3lo)



Ph Following General Procedure A, isolated colorless oil 170 mg (70%). (PE/EA=2:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (t, J = 7.2 Hz, 4H), 7.81 (d, J = 7.3 Hz, 2H), 7.58 – 7.50 (m, 6H), 7.48 (d, J = 7.8 Hz, 2H), 7.46 – 7.41 (m, 4H), 7.35 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 5.49 (s, 1H), 3.70 (d, J = 5.9 Hz, 1H), 2.83 (dd, J = 16.9, 5.9 Hz, 1H), 2.42 (dd, J = 16.9, 2.2 Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 144.6, 141.0, 140.5, 140.3, 140.3, 137.7, 135.8, 132.8, 132.7, 129.3, 129.2, 129.2, 128.8, 128.6, 128.4, 128.3, 127.5, 127.4, 127.1, 126.3, 73.2, 56.9, 40.6, 21.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₃₅H₃₀N₂O₄S₂Na⁺:629.1540; Found: 629.1541.

trans-5-(naphthalen-2-yl)-4-((oxodiphenyl-λ⁶-sulfaneylidene)amino)-1tosylpyrrolidin-2-one (3mo)



Following General Procedure A, isolated colorless oil 173 mg (76%). (PE/EA=2:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.85 (m, 4H), 7.80 (d, J = 7.5 Hz, 3H), 7.75 (d, J = 8.5 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.57 (s, 1H),

7.52 (t, J = 7.3 Hz, 2H), 7.47 (d, J = 7.3 Hz, 4H), 7.39 (t, J = 7.7 Hz, 2H), 7.21 (dd, J = 8.4, 1.8 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 5.60 (s, 1H), 3.74 (d, J = 6.0 Hz, 1H), 2.84 (dd, J = 17.0, 6.0 Hz, 1H), 2.45 (dd, J = 16.9, 2.2 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 144.6, 140.2, 140.2, 135.9, 135.8, 133.1, 132.9, 132.8, 132.7, 129.3, 129.1, 128.7, 128.5, 128.3, 128.3, 128.0, 127.6, 126.4, 126.2, 124.6, 123.9, 73.4, 56.7, 40.6, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₃H₂₉N₂O₄S₂⁺:581.1564; Found:581.1565.

trans-5-(naphthalen-1-yl)-4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-1-tosylpyrrolidin-2-one (3no)



Following General Procedure A, isolated colorless oil 148 mg

(64%). (PE/EA=2:1, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 7.8 Hz, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 7.3 Hz, 3H), 7.77 (d, J =8.2 Hz, 1H), 7.59 – 7.36 (m, 10H), 7.13 (d, J = 7.9 Hz, 2H), 6.23 (s, 1H), 3.83 (d, J =4.8 Hz, 1H), 2.71 (dd, J = 16.4, 5.0 Hz, 1H), 2.32-2.27 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 173.8, 144.4, 140.6, 140.5, 135.7, 133.9, 133.8, 132.8, 132.7, 130.2, 129.3, 129.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.2, 126.5, 125.9, 125.4, 123.6, 71.4, 55.7, 40.8, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₃H₂₉N₂O₄S₂⁺:581.1564; Found:581.1565.

trans-4-((oxodiphenyl-λ⁶-sulfaneylidene)amino)-5-(thiophen-2-yl)-1tosylpyrrolidin-2-one (300)



Following General Procedure A, isolated colorless oil 97 mg (45%). (PE/EA=2:1, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (dd, J = 10.0, 7.7 Hz, 4H), 7.81 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 6.6 Hz, 2H), 7.47 (t, J = 7.6 Hz, 4H), 7.18 (dd, J =
5.0, 1.2 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 3.5 Hz, 1H), 6.92 (dd, J = 5.0, 3.6 Hz, 1H), 5.64 (s, 1H), 3.96 – 3.54 (m, 1H), 2.93 (dd, J = 17.0, 5.8 Hz, 1H), 2.44 (dd, J = 17.0, 1.6 Hz, 1H), 2.33 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.4, 144.5, 141.8, 140.2, 140.2, 135.7, 132.8, 132.8, 129.3, 129.2, 129.1, 128.4, 128.3, 128.3, 126.9, 125.7, 125.1, 69.2, 56.8, 40.9, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₇H₂₄N₂O₄S₂Na⁺:559.0791; Found: : 559.0792.

4-(((methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)amino)methyl)-4-phenyl-1tosylazetidin-2-one (5aa)



Ph' Ts Following General Procedure A, isolated colorless oil 152 mg (81%). dr = 1.02:1. (PE/EA=2:1, R_f = 0.4). ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.91 (m, 2H), 7.81 (t, *J* = 8.5 Hz, 2H), 7.70 – 7.50 (m, 3H), 7.39 (dd, *J* = 6.8, 2.9 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.24 (dd, *J* = 5.4, 3.3 Hz, 3H), 4.11 (d, *J* = 12.8 Hz, 0.5H), 3.88 – 3.76 (m, 1.5H), 3.69 (dd, *J* = 34.5, 13.2 Hz, 1H), 3.05 (s, 1.57H), 3.05 – 2.92 (m, 2.60H), 2.42 (s, 1.60H), 2.40 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 164.7, 144.5, 144.4, 139.78, 139.1, 138.8, 138.8, 137.0, 136.7, 133.1, 133.0, 129.5, 129.4, 129.3, 129.2, 128.7, 128.5, 128.4, 1282, 128.1, 128.0, 127.7, 127.7, 126.2, 126.0, 71.1, 70.9, 48.3, 48.2, 47.5, 47.0, 45.5, 43.2, 21.6, 21.5. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₄H₂₅N₂O₄S₂⁺:469.1251; Found: 469.1251.

4-((((4-methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5ab)



Ph' Ts Following General Procedure A, isolated colorless oil 183 mg (92%). dr = 1.11:1. (PE/EA=2:1, $R_f = 0.3$). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, J = 9.0, 7.6 Hz, 2H), 7.80 (dd, J = 10.1, 8.3 Hz, 2H), 7.39 (dd, J = 6.7, 3.1 Hz, 1H), 7.31

- 7.27 (m, 3H), 7.25 - 7.22 (m, 3H), 7.03 (dd, J = 8.9, 3.8 Hz, 2H), 4.08 (d, J = 12.8 Hz, 0.51H), 3.88 (s, 1.36H), 3.87 (s, 1.68H), 3.84 - 3.76 (m, 1.47H), 3.68 (dd, J = 42.7, 12.9 Hz, 1H), 3.04 (s, 1.68H), 3.02 - 2.90 (m, 2.42H), 2.42 (s, 1.42H), 2.40 (s, 1.58H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 164.8, 163.4, 163.3, 144.5, 144.4, 139.0, 138.9, 137.1, 136.9, 131.3, 130.9, 130.4, 130.2, 129.4, 129.2, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 126.2, 126.0, 114.7, 114.5, 71.2, 71.1, 55.6, 55.6, 48.4, 48.3, 47.6, 47.1, 45.9, 43.4, 21.6, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₅H₂₇N₂O₅S₂⁺:499.1356; Found: 499.1356.

4-(((methyl(oxo)(p-tolyl)-λ⁶-sulfaneylidene)amino)methyl)-4-phenyl-1tosylazetidin-2-one (5ac)



Ph² Ts Following General Procedure A, isolated colorless oil 174 mg (90%). dr = 1.15:1. (PE/EA=2:1, R_f = 0.4). ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.72 (m, 4H), 7.45 – 7.33 (m, 3H), 7.32 – 7.27 (m, 3H), 7.24 (dd, *J* = 5.4, 3.4 Hz, 3H), 4.08 (d, *J* = 12.8 Hz, 0.5H), 3.89 – 3.75 (m, 1.5H), 3.68 (dd, *J* = 36.3, 12.9 Hz, 1H), 3.10 – 2.87 (m, 4H), 2.45 (s, 1.66H), 2.44 (s, 1.43H), 2.42 (s, 1.66H), 2.40 (s, 1.34H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 164.7, 144.5, 144.4, 144.0, 143.9, 139.0, 138.9, 137.1, 136.9, 136.9, 136.1, 130.2, 130.0, 129.4, 129.2, 128.8, 128.5, 128.5, 128.2, 128.1, 127.8, 127.8, 126.3, 126.1, 71.2, 71.0, 48.4, 48.3, 47.6, 47.1, 45.7, 43.4, 21.6, 21.6, 21.5. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1228.

 $\label{eq:approx} \begin{array}{l} \mbox{4-(((methyl(oxo)(m-tolyl)-\lambda^6-sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5ad) \end{array}$



Ph' Ts Following General Procedure A, isolated colorless oil 141 mg (73%). dr = 1.14:1. (PE/EA=2:1, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.63

(m, 4H), 7.50 - 7.40 (m, 2H), 7.39 (dd, J = 6.9, 2.9 Hz, 1H), 7.32 - 7.26 (m, 3H), 7.27 - 7.20 (m, 3H), 4.09 (d, J = 12.8 Hz, 0.49H), 3.91 - 3.74 (m, 1.51H), 3.77 - 3.58 (m, 1H), 3.16 - 2.81 (m, 4H), 2.46 (s, 1.44H), 2.45 (s, 1.62H), 2.41 (s, 1.40H), 2.40 (s, 1.60H). ¹³**C NMR (101 MHz, CDCl₃)** δ 164.8, 164.7, 144.5, 144.4, 139.9, 139.8, 139.6, 138.9, 138.9, 137.1, 136.9, 133.9, 133.8, 129.4, 129.4, 129.2, 129.2, 129.2, 128.5, 128.5, 128.5, 128.2, 128.1, 127.8, 127.8, 126.3, 126.1, 125.8, 125.1, 71.2, 70.9, 48.4, 48.3, 47.6, 47.1, 45.6, 43.3, 21.6, 21.4, 21.3. **HRMS (IT-TOF)**: [M+H]⁺ Calcd for $C_{25}H_{27}N_2O_4S_2^+$:483.1407; Found: 483.1406.

4-(((methyl(oxo)(o-tolyl)-λ⁶-sulfaneylidene)amino)methyl)-4-phenyl-1tosylazetidin-2-one (5ae)



Ph² Ts Following General Procedure A, isolated colorless oil 73 mg (38%). dr = 1.36:1. (PE/EA=2:1, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.56 – 7.44 (m, 1H), 7.42 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.28 – 7.24 (m, 3H), 7.21 (d, J = 8.4 Hz, 2H), 4.05 (d, J= 12.9 Hz, 0.51H), 3.89 – 3.73 (m, 1.49H), 3.72 – 3.60 (m, 1H), 3.12 – 2.93 (m, 4H), 2.73 (s, 1.29H), 2.71 (s, 1.69H), 2.40 (s, 1.73H), 2.39 (s, 1.28H). ¹³C NMR (101 MHz, CDCl₃) δ 164.7, 164.6, 144.5, 144.4, 139.0, 138.6, 138.2, 138.0, 138.0, 137.6, 137.0, 136.7, 133.1, 133.1, 133.0, 133.0, 130.6, 130.1, 129.3, 129.1, 128.5, 128.2, 128.1, 128.0, 127.8, 126.8, 126.4, 126.1, 48.4, 48.3, 47.5, 47.0, 44.3, 43.0, 21.6, 20.4, 20.3. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₅H₂₇N₂O₄S₂⁺:483.1407; Found: 483.1408.

4-((((4-fluorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5af)



Ts Following General Procedure A, isolated colorless oil 138 mg (71%).

dr = 1.29:1. (PE/EA=2:1, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dt, J = 9.2, 4.8 Hz, 2H), 7.78 (dd, J = 8.4, 3.2 Hz, 2H), 7.49 – 7.33 (m, 1H), 7.30 (dd, J = 5.2, 2.0 Hz, 3H), 7.23 (dq, J = 5.1, 3.2, 2.7 Hz, 5H), 4.15 (d, J = 12.8 Hz, 0.52H), 3.88 – 3.77 (m, 1.52H), 3.76 – 3.61 (m, 1H), 3.10 (s, 1.62H), 3.09 (s, 1.32H), 3.01 (dd, J = 15.3, 10.0 Hz, 1H), 2.43 (s, 1.68H), 2.41 (s, 1.32H). ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 166.8, 164.8, 164.7, 164.3, 164.3, 144.7, 144.5, 138.8, 137.1, 136.9, 136.0 (d, J = 3.0 Hz), 134.9 (d, J = 2.9 Hz), 131.7 (d, J = 9.5 Hz), 130.9 (d, J = 9.4 Hz), 129.5, 129.3, 128.6 128.5, 128.3, 128.2, 127.6, 126.2, 126.0, 116.9, 116.6, 116.6, 116.4, 71.1, 71.0, 48.3, 48.3, 47.7, 47.1, 45.8, 43.1, 21.6, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -105.1, -105.1. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₄H₂₄FN₂O₄S₂⁺:487.1157; Found: 487.1156.

4-((((3-chlorophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5ag)



Ph² Ts **Following General Procedure A**, isolated colorless oil 115 mg (57%). dr = 1.08:1. (PE/EA=2:1, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (dt, *J* = 6.8, 1.9 Hz, 1H), 7.90 (dt, *J* = 17.3, 7.7, 1.5 Hz, 1H), 7.82 (dd, *J* = 8.2, 5.7 Hz, 2H), 7.61 (ddt, *J* = 6.0, 4.7, 1.6 Hz, 1H), 7.54 (td, *J* = 7.9, 3.2 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.35 – 7.31 (m, 2H), 7.28 (td, *J* = 5.6, 1.9 Hz, 4H), 4.13 (d, *J* = 12.8 Hz, 0.48H), 3.87 – 3.76 (m, 1.52H), 3.76 – 3.65 (m, 1H), 3.17 – 2.86 (m, 4H), 2.44 (s, 1.56H), 2.43 (s, 1.44H). ¹³C NMR (101 MHz, CDCl₃) δ 164.7, 164.5, 144.6, 144.5, 141.8, 141.1, 138.7, 138.7, 137.1, 136.8, 135.7, 135.5, 133.3, 133.2, 130.8, 130.7, 129.5, 129.3, 128.9, 128.5, 128.5, 128.29, 128.2, 128.1, 127.7, 126.9, 126.3, 126.2, 126.0, 71.0, 70.8, 48.4, 48.3, 47.6, 47.1, 45.5, 43.3, 21.6, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₄H₂₄ClN₂O₄S₂⁺:503.0861, 505.0832; Found: 503.0863, 505.0833.

4-((((2-bromophenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5ah)



Ph['] Ts Following General Procedure A, isolated colorless oil 114 mg (52%). dr = 1.14:1. (PE/EA=2:1, R_f = 0.4). ¹H NMR (400 MHz, CDCl₃) δ 8.45 – 8.13 (m, 1H), 7.85 (dd, *J* = 13.6, 8.4 Hz, 2H), 7.80 (td, *J* = 8.0, 1.2 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.48 (td, *J* = 7.7, 1.7 Hz, 1H), 7.44 (dd, *J* = 6.7, 2.8 Hz, 1H), 7.40 (dd, *J* = 6.7, 3.0 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.23 (d, *J* = 8.1 Hz, 1H), 3.96 (d, *J* = 12.9 Hz, 0.50H), 3.90 – 3.74 (m, 1.50H), 3.52 – 3.32 (m, 1H), 3.18 (s, 1.63H), 3.15 (s, 1.38H), 3.05 (dd, *J* = 15.4, 9.5 Hz, 1H), 2.44 (s, 1.45H), 2.42 (s, 1.55H). ¹³C NMR (101 MHz, CDCl₃) δ 164.6, 164.5, 144.4, 144.4, 137.0, 138.9, 138.6, 138.4, 136.7, 136.6, 135.8, 135.6, 134.2, 134.2, 133.2, 132.8, 129.3, 129.1, 128.5, 128.3, 128.3, 128.2, 128.1, 128.1, 126.3, 126.3, 120.8, 120.3, 70.6, 70.5, 48.5, 48.4, 47.4, 47.3, 42.9, 42.4, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₄H₂₄BrN₂O₄S₂⁺:547.0356, 549.0335; Found: 547.0354, 549.0336.

4-(((methyl(oxo)(pyridin-2-yl)-λ⁶-sulfaneylidene)amino)methyl)-4-phenyl-1tosylazetidin-2-one (5ai)



Ph² Ts Following General Procedure A, isolated colorless oil 109 mg (58%). dr = 1.54:1. (EA, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 8.78 (d, J = 4.6 Hz, 0.40H), 8.72 (d, J = 4.6 Hz, 0.60H), 8.15 (d, J = 7.9 Hz, 0.60H), 8.07 (d, J = 7.8 Hz, 0.40H), 8.00 – 7.92 (m, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.61 – 7.46 (m, 1H), 7.45 – 7.34 (m, 2H), 7.33 – 7.12 (m, 5H), 4.10 (d, J = 13.0 Hz, 0.68H), 3.89 – 3.73 (m, 1.32H), 3.73 – 3.52 (m, 1H), 3.12 (s, 3H), 2.98 (dd, J = 15.4, 12.0 Hz, 1H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 164.4, 157.6, 157.4, 150.4, 150.0, 144.5, 144.4, 139.0, 138.2, 138.0, 136.7, 136.4, 129.3, 129.1, 128.5, 128.5, 128.5, 128.2, 128.1, 126.8, 126.7, 126.2, 126.1, 123.5, 123.0, 71.0, 70.9, 48.4, 48.3, 47.2, 47.1, 41.3, 40.3, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₃H₂₄N₃O₄S₂⁺:470.1203; Found: 470.1202. 4-(((ethyl(4-methoxyphenyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5aj)



Phí Ts Following General Procedure A, isolated colorless oil 84 mg (82%). dr = 3.73:1. (PE/EA= $2:1, R_f = 0.4$)¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.83 (m, 0.79H), 7.78 (dd, J = 18.0, 8.6 Hz, 3.19H), 7.52 – 7.37 (m, 1.66H), 7.33 – 7.20 (m, 5.34H), 7.01 (d, J = 8.9 Hz, 2H), 4.05 – 3.81 (m, 4H), 3.79 – 3.66 (m, 2H), 3.25 – 2.85 (m, 3H), 2.42 (s, 3H), 1.23 (t, J = 7.4 Hz, 0.64H), 1.13 (t, J = 7.4 Hz, 2.41H). ¹³C NMR (101 MHz, CDCl₃) δ 164.9, 164.7, 163.4, 163.3, 144.5, 139.1, 139.0, 137.2, 136.9, 131.6, 131.0, 129.4, 129.7, 129.0, 128.7, 128.4, 128.1, 128.1, 127.8, 127.8, 126.4, 126.0, 71.5, 71.1, 55.6, 55.6, 52.0, 50.2, 48.5, 48.3, 47.3, 46.8, 21.6, 8.0, 7.2. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₆H₂₉N₂O₅S₂⁺:513.1513; Found: 513.1513.



Ph Ts Following General Procedure A, isolated colorless oil 128 mg (62%). dr = 1.54:1. (PE/EA=2:1, R_f = 0.4). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.7 Hz, 1H), 7.80 (dd, *J* = 8.4, 3.1 Hz, 3H), 7.53 (dd, *J* = 10.5, 8.5 Hz, 2H), 7.39 (dd, *J* = 6.8, 2.9 Hz, 1H), 7.30 (d, *J* = 2.6 Hz, 2H), 7.28 – 7.17 (m, 4H), 4.06 (d, *J* = 12.7 Hz, 0.50H), 3.90 – 3.75 (m, 1.51H), 3.74 – 3.58 (m, 1H), 3.25 – 3.07 (m, 2H), 3.01 (dd, *J* = 18.6, 15.2 Hz, 1H), 2.42 (s, 1.42H), 2.41 (s, 1.62H), 1.27 (t, *J* = 7.4 Hz, 1.63H), 1.16 (t, *J* = 7.4 Hz, 1.34H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 164.6, 144.6, 144.6, 139.8, 139.8, 138.8, 137.1, 136.8, 136.1, 136.1, 131.1, 130.4, 129.8, 129.6, 129.4, 129.4, 128.5, 128.2, 128.2, 127.7, 127.6, 126.3, 125.9, 71.3, 70.9, 51.8, 49.9, 48.4, 48.3, 47.3, 46.8, 21.6, 8.0, 7.1. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₅H₂₆ClN₂O4S₂⁺:517.1018, 519.0988; Found: 517.1018, 519.0989.

4-(((benzyl(4-methoxyphenyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5al)



Ph² Ts **Following General Procedure A**, isolated colorless oil 117 mg (51%). dr = 1.20:1. (PE/EA=2:1, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.37 (d, J = 8.9 Hz, 1H), 7.32 – 7.26 (m, 4H), 7.25 – 7.09 (m, 6H), 6.95 (d, J = 8.9 Hz, 1H), 6.90 – 6.80 (m, 2H), 4.36 (d, J = 13.4 Hz, 1.75H), 4.30 – 4.20 (m, 0.70H), 4.16 – 4.04 (m, 1H), 3.85 (d, J = 2.6 Hz, 3.34H), 3.76 – 3.35 (m, 2H), 2.93 (dd, J = 22.4, 15.2 Hz, 1H), 2.43 (s, 1.38H), 2.39 (s, 1.63H). ¹³C NMR (101 MHz, CDCl₃) δ 164.9, 164.6, 163.4, 163.3 144.5, 144.5, 139.2, 139.0, 137.2, 136.8, 131.8, 131.5, 131.4, 131.1, 129.4, 129.4, 129.3, 129.0, 128.6, 128.5, 128.4, 128.4, 128.2, 128.2, 128.1, 128.1, 128.1, 127.9, 127.7, 126.2, 126.0, 114.4, 114.1, 71.5, 71.4, 63.8, 62.7, 55.6, 48.3, 48.26, 47.1, 46.8, 21.7, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₃₁H₃₁N₂O₅S₂⁺:575.1669; Found: 575.1669.

4-(((dimethyl(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one (5am)

Ph Ts Following General Procedure A, isolated colorless oil 84 mg (56%). (EA, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.1 Hz, 2H), 7.52 – 6.67 (m, 7H), 4.10 (d, J = 12.7 Hz, 1H), 3.90 – 3.73 (m, 2H), 3.12 (s, 3H), 3.05 (s, 3H), 2.98 (d, J = 15.2 Hz, 1H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 144.6, 139.0, 137.1, 129.5, 128.6, 128.3, 127.5, 126.0, 71.4, 48.1, 47.7, 43.7, 39.9, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₁₉H₂₃N₂O₄S₂⁺:407.1094; Found: 407.1095. 4-(((1-oxidotetrahydro-1λ⁶-thiophen-1-ylidene)amino)methyl)-4-phenyl-1tosylazetidin-2-one (5j)



Ph² Ts Following General Procedure A, isolated colorless oil 111 mg (64%). (EA, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.4 Hz, 2H), 7.34 – 7.26 (m, 5H), 7.24 (d, J = 8.2 Hz, 2H), 4.05 (d, J = 12.8 Hz, 1H), 3.90 – 3.74 (m, 2H), 3.50 (dt, J = 13.0, 6.9 Hz, 1H), 3.23 (dt, J = 12.8, 7.5 Hz, 1H), 3.15 – 3.01 (m, 1H), 2.97 (d, J = 15.2 Hz, 1H), 2.89 (dt, J = 12.6, 7.5 Hz, 1H), 2.42 (s, 3H), 2.35 – 2.22 (m, 3H), 2.22 – 2.10 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 144.5, 138.8, 137.1, 129.4, 128.6, 128.2, 127.4, 126.0, 71.1, 54.4, 49.5, 48.8, 48.1, 24.3, 23.1, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₁H₂₅N₂O₄S₂⁺:433.1251; Found: 433.1250.

$\label{eq:constraint} \begin{array}{l} \mbox{4-(((oxodiphenyl-λ^6-sulfaneylidene)amino)methyl)-4-phenyl-1-tosylazetidin-2-one} \\ \mbox{(5ao)} \end{array}$



Ph² Ts Following General Procedure A, isolated colorless oil 176 mg (83%). (PE/EA=2:1, $R_f = 0.6$). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, J = 8.2, 1.6 Hz, 2H), 7.94 (dd, J = 8.1, 1.6 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.49 (ddd, J = 10.0, 7.0, 5.0 Hz, 6H), 7.40 – 7.31 (m, 2H), 7.30 – 7.23 (m, 3H), 7.20 (d, J = 8.2 Hz, 2H), 4.00 (d, J = 12.9 Hz, 1H), 3.88 – 3.63 (m, 2H), 3.03 (d, J = 15.2 Hz, 1H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.7, 144.5, 140.8, 140.1, 139.1, 136.8, 132.5, 132.5, 129.3, 129.2, 129.1, 128.8, 128.5, 128.2, 128.1, 127.8, 126.0, 71.4, 48.5, 46.8, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₉H₂₇N₂O₄S₂⁺:531.1407; Found: 531.1408.

 $\label{eq:constraint} \begin{array}{l} \mbox{4-((((4-methoxyphenyl)(methyl)(oxo)-$\lambda^6-sulfaneylidene)amino)methyl)-4-(p-tolyl)-1-tosylazetidin-2-one (5bb) \end{array}$



Me **Following General Procedure A**, isolated colorless oil 176 mg (86%). dr = 1.56:1. (PE/EA=2:1, R_f = 0.4). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, *J* = 8.9, 3.6 Hz, 2H), 7.80 (t, *J* = 8.7 Hz, 2H), 7.26 (td, *J* = 4.7, 4.3, 2.0 Hz, 3H), 7.23 – 7.14 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 9.1, 2.7 Hz, 3H), 4.08 (d, *J* = 12.7 Hz, 0.50H), 3.88 (s, 1.63H), 3.87 (s, 1.37H), 3.85 – 3.74 (m, 1.50H), 3.67 (dd, *J* = 43.3, 12.7 Hz, 1H), 3.12 – 2.80 (m, 4H), 2.42 (s, 1.90H), 2.40 (s, 1.21H), 2.34 (s, 1.80H), 2.29 (s, 1.20H). ¹³C NMR (101 MHz, CDCl₃) δ 165.1, 165.0, 163.3, 163.3, 144.5, 144.4, 138.1, 137.9, 137.1, 136.9, 135.9, 135.8, 131.3, 131.0, 130.3, 130.2, 129.4, 129.2, 129.2, 129.1, 127.8, 127.7, 126.4, 126.1, 125.9, 114.7, 114.5, 71.1, 70.9, 55.6, 48.3, 48.2, 47.6, 47.1, 46.0, 43.3, 21.6, 21.6, 21.0, 21.0. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₆H₂₉N₂O₅S₂⁺:513,1513; Found: 513,1514.

4-((((4-methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-(m-tolyl)-1-tosylazetidin-2-one (5cb)



Following General Procedure A, isolated colorless oil 148 mg (72%). dr = 1.40:1. (PE/EA=2:1, R_f = 0.4). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.79 (dd, *J* = 9.8, 8.3 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.18 (d, *J* = 1.3 Hz, 1H), 7.14 – 7.07 (m, 2H), 7.03 (dd, *J* = 8.9, 2.1 Hz, 3H), 4.10 (d, *J* = 12.7 Hz, 0.48H), 3.88 (s, 1.51H), 3.86 (s, 1.50H), 3.84 – 3.76 (m, 1.51H), 3.76 – 3.61 (m, 1H), 3.06 (s, 1.55H), 3.04 (s, 1.42H), 2.97 (dd, *J* = 15.3, 13.8 Hz, 1H), 2.42 (s, 1.54H), 2.40 (s, 1.42H), 2.23 (s, 1.60H), 2.18 (s, 1.40H). ¹³C NMR (101 MHz, CDCl₃) δ 165.0, 164.9, 163.4, 163.3, 144.5, 144.4, 138.8, 138.7, 138.1, 137.2 137.0, 131.5, 131.0, 130.4,

130.2, 129.4, 129.2, 128.9, 128.8, 128.4, 128.3, 127.7, 127.6, 126.9, 126.7, 123.2, 123.1, 114.7, 114.5, 71.0, 70.9, 55.6, 55.6, 48.5, 48.5, 47.5, 47.0, 46.0, 43.2, 21.6, 21.6, 21.3, 21.3. **HRMS (IT-TOF)**: [M+H]⁺ Calcd for C₂₆H₂₉N₂O₅S₂⁺:513.1513; Found: 513.1512.

4-((((4-methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-(o-tolyl)-1-tosylazetidin-2-one (5db)



Following General Procedure A, isolated colorless oil 84 mg (41%). dr = 1.50:1. (PE/EA=2:1, $R_f = 0.4$) ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.71 (dd, J = 7.3, 2.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.21 – 7.07 (m, 3H), 7.01 (dd, J = 8.9, 3.9 Hz, 1H), 4.12 – 3.78 (m, 4.58H), 3.72 (d, J = 13.9 Hz, 0.45H), 3.49 (dd, J = 45.0, 13.8 Hz, 1H), 3.09 – 2.79 (m, 4H), 2.45 (s, 1.80H), 2.42 (s, 1.20H), 2.15 (s, 1.17H), 2.13 (s, 1.80H). ¹³C NMR (101 MHz, CDCl₃) δ 165.3, 165.3, 163.3, 163.2, 144.6, 144.5, 138.0, 138.0, 137.1, 136.9, 133.6, 131.7, 131.6, 131.2, 130.7, 130.1, 129.4, 129.1, 128.4, 128.3, 128.1, 127.9, 127.5, 127.5, 125.9, 125.9, 114.7, 114.4, 76.7, 76.6, 76.5, 55.6, 46.6, 46.4, 46.4, 46.4, 45.6, 43.2, 21.6, 21.6, 20.4, 20.3. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₆H₂₉N₂O₅S₂⁺:513.1513; Found: 513.1514.

$\label{eq:linear} \begin{array}{l} \mbox{4-((((4-methoxyphenyl)(methyl)(oxo)- λ^6-sulfaneylidene)amino)methyl)-1-tosyl-4-((trifluoromethyl)phenyl)azetidin-2-one (5eb) \end{array}$



Following General Procedure A, isolated colorless oil 84 mg (77%). dr = 1.30:1. (PE/EA=2:1, R_f = 0.6). ¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.72

(m, 4H), 7.53 (s, 2H), 7.51 – 7.37 (m, 2H), 7.31 – 7.18 (m, 2H), 7.03 (dd, J = 8.8, 5.8 Hz, 2H), 3.98 (d, J = 12.8 Hz, 0.50H), 3.91 – 3.77 (m, 14.55H), 3.75 – 3.58 (m, 1H), 3.18 – 2.86 (m, 4H), 2.42 (s, 1.70H), 2.40 (s, 1.30H). ¹³C NMR (101 MHz, CDCl₃) δ 164.2, 164.2, 163.5, 163.4, 144.9, 144.8, 142.9, 142.8, 136.7, 136.5, 130.8, 130.4 (q, J = 29.4 Hz), 130.3 (q, J = 31.4 Hz), 130.2, 130.1, 129.6, 129.5, 129.3, 127.7, 127.6, 126.8, 126.6, 126.4, 125.4 (dd, J = 5.1, 3.3 Hz), 123.8 (q, J = 273.0 Hz), 123.7 (q, J = 273.2 Hz), 114.8, 114.6, 70.4, 70.1, 55.7, 48.7, 48.5, 47.6, 46.9, 45.8, 43.8, 21.6, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.7, -62.8. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₆H₂₅F₃N₂O₅S₂Na⁺:589.1050; Found: 589.1050.

4-(4-fluorophenyl)-4-((((4-methoxyphenyl)(methyl)(oxo)- λ^6 sulfaneylidene)amino)methyl)-1-tosylazetidin-2-one (5fb)



F⁻ Following General Procedure A, isolated colorless oil 157 mg (76%). dr = 1.01:1. (PE/EA=2:1, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, *J* = 12.9, 8.9 Hz, 2H), 7.81 (t, *J* = 8.4 Hz, 2H), 7.40 (dd, *J* = 8.9, 5.1 Hz, 1H), 7.33 – 7.21 (m, 3H), 7.05 (dd, *J* = 8.9, 5.5 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 1H), 6.94 (t, *J* = 8.6 Hz, 1H), 4.03 (d, *J* = 12.7 Hz, 0.51H), 3.91 (s, 1.50H), 3.90 (s, 1.50H), 3.87 – 3.76 (m, 1.49H), 3.74 – 3.58 (m, 1H), 3.11 – 2.80 (m, 4H), 2.45 (s, 1.50H), 2.43 (s, 1.50H). ¹³C NMR (101 MHz, CDCl₃) δ 164.6 (d, *J* = 8.6 Hz), 163.5 (d, *J* = 7.9 Hz), 163.4 (d, *J* = 9.1 Hz), 161.1 (d, *J* = 7.6 Hz), 144.7, 144.6, 136.9, 136.7, 131.0, 130.8, 130.2, 130.2, 129.6, 129.5, 129.3, 128.2 (d, *J* = 8.2 Hz), 128.0 (d, *J* = 8.2 Hz), 127.7, 127.6, 126.4, 125.4, 115.5, 115.4, 115.2, 115.2, 114.8, 114.6, 70.4, 70.2, 55.6, 55.6, 48.5, 48.4, 47.7, 47.1, 45.9, 43.6, 21.6, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) δ -113.6, -113.7. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₅FN₂O₅S₂Na⁺:539.1082; Found: 539.1081.

4-(3-fluorophenyl)-4-((((4-methoxyphenyl)(methyl)(oxo)- λ^6 sulfaneylidene)amino)methyl)-1-tosylazetidin-2-one (5gb)



Following General Procedure A, isolated colorless oil 118 mg (57%). dr = 1.00:1. (PE/EA=2:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (dd, J = 10.3, 8.9 Hz, 2H), 7.82 (dd, J = 11.4, 8.4 Hz, 2H), 7.34 – 7.22 (m, 3H), 7.22 – 7.15 (m, 1H), 7.10 – 7.06 (m, 1H), 7.03 (dd, *J* = 8.9, 4.2 Hz, 2H), 7.00 – 6.93 (m, 1H), 4.01 (d, J = 12.8 Hz, 0.50H), 3.88 (s, 1.46H), 3.87 (s, 1.57H), 3.86 – 3.74 (m, 1.55H), 3.74 -3.58 (m, 1H), 3.10 - 2.83 (m, 4H), 2.42 (s, 1.50H), 2.40 (s, 1.49H). ¹³C NMR (101) **MHz, CDCl₃**) δ 164.4 (d, J = 9.1 Hz), 163.8 (d, J = 4.3 Hz), 163.4 (d, J = 8.8 Hz), 161.4 (d, J = 4.2 Hz), 144.8, 144.7, 136.8, 136.6, 131.0, 130.8, 130.2, 130.1, 130.0 (d, J = 3.6 Hz), 129.6, 129.5, 129.4, 129.3, 128.2 (d, J = 8.8 Hz), 127.7, 127.6, 126.3, 121.9 (d, J = 2.9 Hz), 121.7 (d, J = 2.9 Hz), 115.2 (d, J = 9.6 Hz), 115.0 (d, J = 9.6 Hz), 114.7,114.6, 113.7 (d, J = 23.1 Hz), 113.5 (d, J = 23.2 Hz), 70.5 (d, J = 2.1 Hz), 70.3 (d, J = 2 2.1 Hz), 55.6, 55.6, 48.5, 48.4, 47.5, 46.9, 45.8, 43.5, 21.6, 21.6. ¹⁹F NMR (376 MHz, CDCl₃) -112.0, -112.0. HRMS (**IT-TOF**): δ $[M+H]^+$ Calcd for C₂₅H₂₆FN₂O₅S₂⁺:517.1262; Found: 517.1263.

4-((((4-methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)amino)methyl)-4-(naphthalen-2-yl)-1-tosylazetidin-2-one (5hb)



Following General Procedure A, isolated colorless oil 177 mg (81%). dr = 1.19:1. (PE/EA=2:1, R_f = 0.3).¹H NMR (400 MHz, CDCl₃) δ 7.94 (dd, J = 8.9, 6.6 Hz, 2H), 7.85 – 7.72 (m, 3H), 7.75 – 7.60 (m, 3H), 7.52 – 7.48 (m, 1H), 7.48 – 7.44 (m, 1H), 7.36 (ddd, J = 40.5, 8.6, 2.0 Hz, 1H), 7.17 (t, J = 8.2 Hz, 2H), 7.04 (dd, J = 8.9, 6.7 Hz, 2H), 4.20 (d, J = 12.7 Hz, 0.45H), 4.02 – 3.86 (m, 4.56H), 3.86 – 3.77

(m, 1H), 3.31 - 2.92 (m, 4H), 2.39 (s, 1.63H), 2.37 (s, 1.38H). ¹³C NMR (101 MHz, CDCl₃) δ 164.9, 164.8, 163.4, 163.4, 144.6, 144.5, 137.1, 136.9, 136.0, 136.0, 132.9, 132.9, 132.8, 132.8, 131.0, 130.3, 129.4, 129.3, 128.4, 128.3, 128.3, 128.2, 127.7, 127.6, 127.5, 127.4 126.6, 126.5, 126.5, 126.4, 125.7, 125.5, 123.7, 123.5, 114.8, 114.6, 70.9, 70.9, 55.7, 55.6, 48.6, 48.6, 47.6, 46.9, 46.1, 43.4, 21.6. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₉H₂₉N₂O₅S₂⁺:549.1513; Found: 549.1512.

4-((((4-methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)amino)methyl)-4-(naphthalen-1-yl)-1-tosylazetidin-2-one (5ib)



Following General Procedure A, isolated colorless solid 110 mg (50%). (PE/EA=2:1, R_f = 0.4) ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.4 Hz, 2H), 7.92 (dd, J = 8.1, 3.4 Hz, 2H), 7.89 – 7.83 (m, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.52 – 7.36 (m, 5H), 7.39 – 7.33 (m, 1H), 7.04 (d, J = 8.9 Hz, 2H), 4.20 (dd, J = 14.5, 10.3 Hz, 2H), 3.91 (d, J = 12.6 Hz, 4H), 3.12 (d, J = 14.9 Hz, 1H), 3.00 (s, 3H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.4, 163.3, 144.7, 136.8, 135.5, 134.1, 131.2, 130.1, 129.4, 129.1, 129.1, 128.5, 126.1, 125.7, 125.5, 125.1, 123.8, 114.5, 76.6, 55.7, 47.2, 47.1, 43.2, 21.7. HRMS (IT-TOF): [M+H]⁺ Calcd for C₂₉H₂₉N₂O₅S₂⁺:549.1513; Found: 549.1514.

(5R,6S)-5-((methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)amino)-6-phenyl-1tosylpiperidin-2-one (7-1)



Following General Procedure A, isolated colorless oil 37 mg (19%). (PE/EA=1:1, $R_f = 0.5$). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 7.0 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H), 7.68 (dd, J = 12.8, 7.2 Hz, 3H), 7.25 – 7.21 (m, 3H), 7.16 (d,

J = 8.1 Hz, 2H), 6.98 – 6.87 (m, 2H), 5.64 – 5.21 (m, 1H), 3.54 (d, J = 3.3 Hz, 1H), 3.13 (s, 3H), 2.97 (ddd, J = 18.8, 11.2, 8.0 Hz, 1H), 2.54 – 2.23 (m, 5H), 1.73 (dt, J =11.2, 4.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 171.0, 144.2, 139.6, 139.4, 136.5, 133.3, 129.7, 129.2, 128.7, 128.6, 128.5, 127.6, 126.3, 67.9, 54.2, 45.6, 29.4, 23.9, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1227.

trans-5-((methyl(oxo)(phenyl)-λ⁶-sulfaneylidene)amino)-6-phenyl-1tosylpiperidin-2-one (7-2)



Isolated colorless oil 33 mg (17%). (PE/EA=1:1, $R_f = 0.4$). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, J = 8.1 Hz, 2H), 7.96 – 7.85 (m, 2H), 7.68 – 7.60 (m, 1H), 7.57 (t, J = 7.5 Hz, 2H), 7.32 – 7.24 (m, 4H), 7.21 (t, J = 9.1 Hz, 3H), 5.75 (t, J = 2.1 Hz, 1H), 3.57 (d, J = 3.2 Hz, 1H), 3.03 (s, 3H), 2.81 (ddd, J = 19.0, 11.4, 8.0 Hz, 1H), 2.51 – 2.35 (m, 5H), 1.35 (ddd, J = 11.9, 7.5, 3.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 144.2, 140.3, 140.1, 136.6, 133.2, 129.6, 128.7, 128.6, 128.2, 127.5, 126.1, 69.3, 54.2, 45.5, 29.2, 22.7, 21.6. HRMS (IT-TOF): [M+Na]⁺ Calcd for C₂₅H₂₆N₂O₄S₂Na⁺:505.1227; Found: 505.1228.

(4R,5S)-5-(4-fluorophenyl)-4-((methyl(oxo)(phenyl)-λ⁶-

sulfaneylidene)amino)pyrrolidin-2-one (8a)



F General procedure B: Under argon atmosphere, to a solution of lactams **3** (0.1 mmol) in dry THF (1 mL) at 0 °C was added a solution of SmI₂ (0.1 M in THF, 2 mL, 0.2 mmol). The reaction mixture was stirred at 0 °C for 6 h. Then the reaction mixture was quenched with saturated sodium thiosulfate (2 mL), extracted with ethyl acetate (3 \times 10 mL), the organic layer was dried over MgSO₄, filtered and

evaporated to afford a crude product. Then the crude product was concentrated in vacuo and purified by column chromatography to afford the desired product as colorless oil 28 mg (85 %). (DCM/Acetone=1:3, $R_f = 0.5$). ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.22 (m, 7H), 6.87 (dd, J = 12.5, 4.9 Hz, 2H), 5.73 (s, 1H), 4.51 (d, J = 7.2 Hz, 1H), 3.42 (q, J = 8.1 Hz, 1H), 3.04 (s, 3H), 2.74 – 2.50 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 175.6, 165.3 (d, J = 255.6 Hz), 140.0, 131.3(d, J = 10.1 Hz), 128.8, 128.4, 126.9, 116.4, 116.3, 66.4, 60.8, 45.4, 41.1. ¹⁹F NMR (471 MHz, CDCl₃) δ -105.0. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₁₇H₁₈FN₂O₂S⁺: 333.1073; Found: 333.1057.

(4R,5S)-4-(((4-methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)amino)-5-



phenylpyrrolidin-2-one (8b)

Following General Procedure B, Isolated colorless oil 32 mg (92%) (DCM/Acetone=1:3, $R_f = 0.3$) ¹H NMR (500 MHz, CDCl₃) δ 7.35 (dd, J = 5.1, 2.2 Hz, 3H), 7.29 – 7.26 (m, 2H), 7.26 – 7.20 (m, 2H), 6.66 (d, J = 8.9 Hz, 2H), 5.72 (s, 1H), 4.52 (d, J = 7.1 Hz, 1H), 3.81 (s, 3H), 3.45 (dt, J = 9.0, 7.4 Hz, 1H), 3.02 (s, 3H), 2.70 – 2.49 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 175.9, 163.1, 140.2, 130.7, 128.7, 128.2, 126.9, 114.4, 66.5, 60.7, 55.6, 45.6, 41.2, 29.3. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₁₈H₂₁N₂O₃S⁺: 345.1273; Found: 345.1254.

(4R,5S)-4-(((4-chlorophenyl)(ethyl)(oxo)-λ⁶-sulfaneylidene)amino)-5-

phenylpyrrolidi-2-one(8c)



Following General Procedure B, Isolated colorless oil 30 mg (82%) (DCM/Acetone=1:3, R_f = 0.3) ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.33 (m, 3H), 7.28 (dd, *J* = 6.7, 4.9 Hz, 2H), 7.15 (s, 4H), 5.84 (s, 1H), 4.51 (d, *J* = 7.3 Hz, 1H),

3.45 (dt, J = 9.6, 7.5 Hz, 1H), 3.22 – 3.03 (m, 2H), 2.59 (ddd, J = 26.1, 16.7, 8.5 Hz, 2H), 1.17 (t, J = 7.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 175.8, 140.0, 139.6, 130.7, 129.3, 128.8, 128.3, 126.9, 60.7, 50.1, 41.3, 7.4. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₁₈H₂₀ClN₂O₂S⁺: 363.0934; Found: 363.0919.

$(4R, 5S) - 5 - (3 - chlorophenyl) - 4 - ((oxodiphenyl - \lambda^6 - sulfaneylidene) amino) pyrrolidin-like (amino) pyrrolidin-like$





Following General Procedure B, Isolated colorless oil 37 mg (89%) (PE/EA=1:3, $R_f = 0.3$) ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 7.7 Hz, 2H), 7.58 – 7.42 (m, 6H), 7.34 – 7.21 (m, 6H), 6.10 (s, 1H), 4.69 (d, J = 6.3 Hz, 1H), 3.59 (q, J = 7.5 Hz, 1H), 2.71 – 2.53 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 176.0, 142.4, 140.2, 139.4, 134.7, 132.8, 132.6, 130.0, 129.3, 129.1, 128.5, 128.3, 128.2, 126.8, 124.9, 66.5, 60.3, 40.6, 29.3. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₂₂H₁₉ClN₂O₂S⁺: 411.0934; Found: 411.0919.

4-((2S,3R)-5-oxo-3-((oxodiphenyl-λ⁶-sulfaneylidene)amino)pyrrolidin-2-

yl)benzonitrile(8e)



Following General Procedure B, Isolated colorless oil 36 mg (89%) (PE/EA=1:3, $R_f = 0.3$) ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 8.0 Hz, 4H), 7.54 – 7.50 (m, 1H), 7.47 (dd, J = 8.2, 1.6 Hz, 5H), 7.33 (t, J = 7.3 Hz, 2H), 6.25 (s, 1H), 4.77 (d, J = 5.9 Hz, 1H), 3.58 (q, J = 6.8 Hz, 1H), 2.74 – 2.44 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 176.1, 145.7, 140.1, 132.9, 132.8, 132.5, 129.3, 129.2, 128.3, 128.2, 127.3, 118.5, 112.1, 66.7, 60.1, 40.4. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₂₃H₂₀N₃O₂S⁺: 402.1276; Found: 402.1258.

4-((((4-methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4phenylazetidin-2-one(9a)



General procedure C: Under argon atmosphere, to a solution of **5** (0.1 mmol) in dry THF (2 mL) at 0 °C was added a solution of SmI2 (0.1 M in THF, 4 mL, 0.4 mmol). After 5 minutes, the reaction mixture was warm to room temperature and stirred for 6 h. Then the reaction mixture was quenched with saturated sodium thiosulfate (2 mL), extracted with ethyl acetate (3 ×10 mL), the organic layer was dried over MgSO₄, filtered and evaporated to afford a crude product. Then the crude product was concentrated in vacuo and purified by column chromatography to afford the desired product as colorless oil 28 mg (80%). dr = 1.26:1 (PE/EA=1:3, R_f = 0.3). ¹H NMR (500

MHz, CDCl₃) δ 7.71 (d, J = 8.8 Hz , 0.83H), 7.60 (m , 1.16H), 7.41 – 7.32 (m, 2H),

 $7.31-7.26\ (m,\, 3H),\, 7.14\ (s,\, 0.58H),\, 6.99\text{-}6.95\ (m,\, 2H),\, 6.86\ (s,\, 0.46H)\ ,\ \ 3.86\ (m,\, 3H),$

3.41-3.15(m, 3H), 3.02 (s, 3H), 2.98-2.91 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 168.0, 167.4, 163.4, 163.4, 142.4, 130.8, 130.7, 130.5, 130.4, 128.2, 128.2, 127.1, 127.0, 126.0, 125.8, 114.8, 114.7, 59.7, 59.6, 55.6, 53.5, 53.5, 51.8, 48.1, 48.0, 45.6, 45.1, 29.3. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₁₈H₂₁N₂O₃S⁺: 345.1273; Found: 345.1256.

4-(4-fluorophenyl)-4-((((4-methoxyphenyl)(methyl)(oxo)- λ^{6} sulfaneylidene)amino)methyl)azetidin-2-one(9b)



FFollowing General Procedure C, Isolated colorless oil 30 mg(82%) dr = 1.17:1(PE/EA=1:3, $R_f = 0.3$) ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J =

9.2 Hz, 0.87H), 7.61 (d, J = 9.2 Hz, 1.02H), 7.27-7.25 (m, 2H), 7.13 (s, 0.54H), 7.05-6.96 (m, 4H), 6.88 (s, 0.46H), 3.85 (m, 3H), 3.41-3.29 (m, 1.44H), 3.25-3.19 (m, 0.87H), 3.11-3.08 (m, 0.68H), 3.01 (s, 3H), 2.93 -2.87 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 167.9, 167.2, 163.5, 163.4, 162.0 (d, J = 243.8 Hz), 162.0 (d, J = 243.8 Hz), 138.2, 130.7, 130.4, 127.7 (d, J = 8.0 Hz), 127.6 (d, J = 8.0 Hz), 115.1, 115.1, 115.0, 114.9, 114.8,114.8, 59.3, 59.1, 55.7, 53.7, 51.8, 48.3, 48.3, 45.7, 45.1, 29.3. ¹⁹F NMR (471 MHz, CDCl₃) δ -115.4, -115.7. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₁₈H₂₀FN₂O₃S⁺: 363.1179; Found: 363.1164.

4-((((4-methoxyphenyl)(methyl)(oxo)-λ⁶-sulfaneylidene)amino)methyl)-4-(naphthalen-2-yl)azetidin-2-one(9c)



Following General Procedure C, Isolated colorless oil 31 mg (78%). dr = 1.17:1 (PE/EA=1:3, R_f = 0.3) ¹H NMR (500 MHz, CDCl₃) δ 7.83-7.69 (m, 5.19H), 7.54-7.39 (m, 4.21H), 7.18(s, 0.46H), 6.93 (d, *J* = 8.6 Hz, 0.98H), 6.85-6.82 (m, 1.21H), 3.83 (m, 3H), 3.56-3.17(m, 3.22H), 3.06-2.98 (m, 0.47H), 3.02 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.0, 167.2, 163.4, 139.7, 133.1, 133.0, 132.4, 130.8, 130.7, 130.5, 128.1, 128.0, 127.9, 127.6, 126.4, 126.3, 126.1, 126.0, 124.8, 124.6, 124.0, 123.9, 114.7, 59.9, 59.7, 55.6, 53.6, 51.7, 48.3, 48.2, 45.6, 45.1, 29.7. HRMS (Quadrupole-Orbitrap): [M+H]⁺ Calcd for C₂₂H₂₃N₂O₃S⁺: 395.1429; Found: 395.1412.

4-(((oxodiphenyl-λ⁶-sulfaneylidene)amino)methyl)-4-phenylazetid in-2-one(9d)



Following General Procedure C, Isolated colorless oil 29 mg (76%) (PE/EA=1:2, $R_f = 0.4$) ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, J = 7.8 Hz, 2H), 7.48 (ddd, J = 32.8, 20.1, 7.7 Hz, 6H), 7.34 – 7.23 (m, 7H), 5.97 (s, 1H), 4.81 (d, J = 5.6 Hz, 1H), 3.65 (dd, J = 15.4, 8.2 Hz, 1H), 2.89 (dd, J = 17.0, 9.0 Hz, 1H), 2.50 (dd, J = 17.0, 8.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 175.3, 140.8, 140.3, 132.9, 132.7, 129.3, 129.2, 128.7, 128.6, 127.9, 127.6, 127.1, 72.9, 51.6, 37.4, 29.3. HRMS (Quadrupole-Orbitrap): [M+Na]⁺ Calcd for C₂₂H₂₀N₂O₂SNa⁺: 399.1143; Found: 399.1124.

4 Mechanistic investigations

4.1 Cyclic voltammograms of thiophene sulfoxide imine

Cyclic voltammograms were recorded using an CS150H potentiostat and a Pt working electrode, a silver wire reference electrode and a Pt sheet auxiliary electrode, referenced to $Fc^{0/+}$ couple. The voltammograms were recorded at room temperature in 0.1 M tetrabutylammonium hexafluorophosphate in DCM (5 mL) containing sulfoximidoyl thianthrenium tetrafluoroborate salts **2a** (0.01 mmol) or 2,4,6 - Trimethylpyridine (0.02 mmol). The scan rate was 100 mV s⁻¹.



Figure S2. Cyclic voltammetry studies with 2a (black) referenced to Fc^{0/+}couple (red)



Figure S3. Cyclic voltammetry studies with 2,4,6-Trimethylpyridine (black) referenced to Fc^{0/+}couple (red)

4.2 Stern-Volmer Luminescence Quenching Studies

Visible light luminescence intensities were recorded using a PerkinElmer LS 55 spectrofluorometer. All luminescence measurements were recorded using a quartz cuvette (Shufu fluorescence quartz cuvette, $12.5 \times 12.5 \times 4.5 \text{ mm}$, 3.5 mL). All solutions of Ir(dF-mppy)₂(dtbbpy)[PF₆] (10 mM), reagents sulfoximidoyl thianthrenium tetrafluoroborate salts **2a** (45.7 mg, 0.1 mmol), 2,4,6-Trimethylpyridine (24.2 mg, 0.200 mmol) were prepared in DCM (mL) . In a typical procedure, Ir(dF-mppy)₂(dtbbpy)[PF₆] (50 uL, 10 mM) and Quencher (**2a**, 2,4,6-Trimethylpyridine) were added fluorescence quartz cuvette and diluted to a final volume of 3.5 mL. All solutions were excited at 400 nm and the emission was measured from 450 to 700 nm. Quenching was analyzed by plotting I₀/I according to the Stern-Volmer relationship:

 $I_0/I = kq\tau_0[Q] + 1$

where I_0 represents the integral of the luminescence over the range of 450 to 700 nm in the absence of a quencher, I is the integral of luminescence over the range of 450 to 700 nm in the presence of a quencher, kq represents the quenching rate constant, [Q] is the concentration of a given quencher, and τ_0 is the excited state lifetime of the emissive photocatalyst in the absence of quencher.



Figure S4. Emission spectra for Ir(dF-mppy)₂(dtbbpy)[PF₆] luminescence quenching by **2a** as additive (left) and Stern-Volmer plot (right)



Figure S5. Emission spectra for Ir(dF-mppy)₂(dtbbpy)[PF₆] luminescence quenching by 2,4,6-Trimethylpyridine (left) and Stern-Volmer plot (right).



Figure S6. Stern-Volmer quenching experiments.

4.3 TEMPO trap

Reagent **1a** (0.1 mmol), **2a** (0.15 mmol), $Ir(dF-mppy)_2(dtbbpy)[PF_6]$ (1% mmol), TEMPO (0.2 mmol) in a Penicillin vial was evacuated and backfilled with argon via

Schlenk line three times. Subsequently, DCM (anhydrous, 1.0 mL) and 2,4,6-Trimethylpyridine (0.2 mmol) were added, cooled to -20 °C and irradiated by 30 W blue LED strip light for 12 hours. After the reaction is complete, dichloromethane is removed, and acetonitrile as solvent were added to detect TEMPO capture products **10** by mass spectrometry.



Figure S7. HRMS analysis of TEMPO trap reaction.

5. X-Ray crystallographic analysis

X-Ray Chrystallographic Data 3bo, 5ib

Experimental 1

4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-5-(p-tolyl)-1-tosylpyrrolidin-2-one

 $(3bo)^{[7]}$ was crystallized from a dichloromethane/petroleum ether mixture (1/1, v/v). The crystallographic data are summarized in the following table.



Figure S8. X-ray structure of 4-((oxodiphenyl- λ^6 -sulfaneylidene)amino)-5-(p-tolyl)-1-tosylpyrrolidin-2-one (**3bo**).

Experimental 2

3-((((4-methoxyphenyl)(methyl)(oxo)- λ^6 -sulfaneylidene)amino)methyl)-4-(naphthalen-1-yl)-1-tosylazetidin-2-one (5ib)^[8] was crystallized from a dichloromethane/petroleum ether mixture (1/1, v/v). The crystallographic data are summarized in the following table.



Figure S9. X-ray structure of $3-((((4-methoxyphenyl)(methyl)(oxo)- <math>\lambda^6$ -sulfaneylidene)amino)methyl)-4-(naphthalen-1-yl)-1-tosylazetidin-2-one (**5ib**).

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[7] Crystal data for **3bo** : C₃₀H₂₈N₂O₄S₂, MW = 544.66, monoclinic, space group P21/c, final R indices [I > 2σ (I)]: R1 = 0.0487, wR2 = 0.1266; R indices (all data): R1 = 0.0954, wR2 = 0.1549; a = 10.8535(5), b = 19.1389(10), c = 13.1871(8) Å, α = 90.00, β = 102.0857(17), γ = 90, *V*= 2678.6(2) Å³, T= 150 K, Z=4, reflections collected/unique : 52763 / 5499 [R(int) = 0.1058] number of observations [> 2s(I)]: 5499, parameters : 345. CCDC 2261877 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

[8] Crystal data for **5ib**: C₂₉H₂₈N₂O₅S₂, MW = 548.65, monoclinic, space group P21/c, final R indices [I > 2σ (I)]: R1 = 0.0491, wR2 = 0.1251; R indices (all data): R1 = 0.0608, wR2 = 0.1352; a = 12.4216(3), b = 12.3863(3), c = 18.4643(6) Å, α = 90.00, β = 103.3797(10), γ = 90, *V*= 2763.77(13) Å³, T= 150 K, Z=4, reflections collected/unique : 62147 / 5643 [R(int) = 0.0628]; number of observations [> 2s(I)]: 5643, parameters : 346. CCDC 2261890 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

7. NMR Spectroscopes of New Compounds



¹H NMR (400 MHz, CDCl₃) of 1f



¹³C NMR (101 MHz, CDCl₃) of **1f**



¹H NMR (400 MHz, CDCl₃) of **1h**



¹³C NMR (101 MHz, CDCl₃) of **1h**







¹H NMR (400 MHz, CDCl₃) of 1i



¹³C NMR (101 MHz, CDCl₃) of **1i**



¹H NMR (400 MHz, CDCl₃) of 1j





¹³C NMR (101 MHz, CDCl₃) of **1k**



¹H NMR (400 MHz, CDCl₃) of 11





¹H NMR (400 MHz, CDCl₃) of 1n





¹H NMR (400 MHz, CDCl₃) of 10



¹³C NMR (101 MHz, CDCl₃) of **10**



¹H NMR (400 MHz, CDCl₃) of 4a


¹³C NMR (101 MHz, CDCl₃) of 4a



 1 H NMR (400 MHz, CDCl₃) of **4b**





¹H NMR (400 MHz, CDCl₃) of **4c**





 1 H NMR (400 MHz, CDCl₃) of **4d**



^{13}C NMR (101 MHz, CDCl₃) of 4d



¹⁹F NMR (376 MHz, CDCl₃) of 4e







¹H NMR (400 MHz, CDCl₃) of 4f



^{13}C NMR (101 MHz, CDCl₃) of 4f



 ^{19}F NMR (376 MHz, CDCl_3) of 4g





¹³C NMR (101 MHz, CDCl₃) of 4g



1 H NMR (400 MHz, CDCl₃) of **4h**



¹³C NMR (101 MHz, CDCl₃) of **4h**





 $^{13}\mathrm{C}$ NMR (101 MHz, CDCl₃) of 4i





¹H NMR (400 MHz, CDCl₃) of 3aa-1



¹H NMR (400 MHz, CDCl₃) of 3aa-2

¹³C NMR (101 MHz, CDCl₃) of 3aa-2





¹H NMR (400 MHz, CDCl₃) of **3ab-1**

¹³C NMR (101 MHz, CDCl₃) of **3ab-1**





¹³C NMR (101 MHz, CDCl₃) of **3ab-2**





¹H NMR (400 MHz, CDCl₃) of 3ac-1







¹H NMR (400 MHz, CDCl₃) of 3ac-2

¹³C NMR (101 MHz, CDCl₃) of **3b-2**







¹³C NMR (101 MHz, CDCl₃) of 3ad-2





¹³C NMR (101 MHz, CDCl₃) of **3ae-1**





¹³C NMR (101 MHz, CDCl₃) of 3ae-2





¹H NMR (400 MHz, CDCl₃) of 3af-1



¹³C NMR (101 MHz, CDCl₃) of **3af-1**









¹H NMR (400 MHz, CDCl₃) of 3af-2

¹³C NMR (101 MHz, CDCl₃) of **3af-2**





¹³C NMR (101 MHz, CDCl₃) of **3ag-1**





¹H NMR (400 MHz, CDCl₃) of 3ag-2



¹³C NMR (101 MHz, CDCl₃) of **3ah**



¹H NMR (400 MHz, CDCl₃) of **3ah**





¹³C NMR (101 MHz, CDCl₃) of **3ai-2**











¹H NMR (400 MHz, CDCl₃) of 3ak-2

¹³C NMR (101 MHz, CDCl₃) of 3ak-2





¹H NMR (400 MHz, CDCl₃) of 3al-1



¹³C NMR (101 MHz, CDCl₃) of 3al-2







¹³C NMR (101 MHz, CDCl₃) of **3an**




¹H NMR (400 MHz, CDCl₃) of **3ao**

¹³C NMR (101 MHz, CDCl₃) of **3ao**





¹³C NMR (101 MHz, CDCl₃) of **3bo**





¹H NMR (400 MHz, CDCl₃) of **3co**

¹³C NMR (101 MHz, CDCl₃) of **3co**





¹³C NMR (101 MHz, CDCl₃) of **3do**





¹³C NMR (101 MHz, CDCl₃) of **3eo**



S111



¹³C NMR (101 MHz, CDCl₃) of **3fo**



S112







¹H NMR (400 MHz, CDCl₃) of **3ho**





 $^{19}\mathrm{F}$ NMR (376 MHz, CDCl₃) of **3io**





¹³C NMR (101 MHz, CDCl₃) of **3io**



S116



¹H NMR (400 MHz, CDCl₃) of **3jo**

S117



¹³C NMR (101 MHz, CDCl₃) of **3ko**



¹H NMR (400 MHz, CDCl₃) of 3ko



¹³C NMR (101 MHz, CDCl₃) of **3lo**



S119





¹³C NMR (101 MHz, CDCl₃) of **3no**





1 H NMR (400 MHz, CDCl₃) of **300**

¹³C NMR (101 MHz, CDCl₃) of **300**





¹³C NMR (101 MHz, CDCl₃) of 5aa







ó



¹³C NMR (101 MHz, CDCl₃) of 5ac





¹³C NMR (101 MHz, CDCl₃) of 5ad





¹³C NMR (101 MHz, CDCl₃) of 5ae







¹H NMR (400 MHz, CDCl₃) of 5af







0.0



¹H NMR (400 MHz, CDCl₃) of 5ah



¹³C NMR (101 MHz, CDCl₃) of 5ag







¹H NMR (400 MHz, CDCl₃) of 5ak



¹³C NMR (101 MHz, CDCl₃) of 5aj



¹³C NMR (101 MHz, CDCl₃) of **5ak**

¹H NMR (400 MHz, CDCl₃) of 5al





¹³C NMR (101 MHz, CDCl₃) of 5al



¹H NMR (400 MHz, CDCl₃) of 5an



¹³C NMR (101 MHz, CDCl₃) of **5**j



¹H NMR (400 MHz, CDCl₃) of 5ao





1 H NMR (400 MHz, CDCl₃) of **5bb**







$^{13}\mathrm{C}$ NMR (101 MHz, CDCl₃) of **5cb**



¹⁹F NMR (376 MHz, CDCl₃) of **5eb**





¹³C NMR (101 MHz, CDCl₃) of **5eb**




$^{19}\mathrm{F}$ NMR (376 MHz, CDCl₃) of **5fb**



¹³C NMR (101 MHz, CDCl₃) of **5fb**



¹⁹F NMR (376 MHz, CDCl₃) of **5gb**



S144



¹H NMR (400 MHz, CDCl₃) of **5gb**







1 H NMR (400 MHz, CDCl₃) of **5hb**

¹³C NMR (101 MHz, CDCl₃) of **5hb**











¹H NMR (400 MHz, CDCl₃) of 7-1





¹³C NMR (101 MHz, CDCl₃) of 7-2



¹⁹F NMR (471 MHz, CDCl₃) of 8a



¹³C NMR (126 MHz, CDCl₃) of 8a





¹³C NMR (126 MHz, CDCl₃) of 8c



¹³C NMR (126 MHz, CDCl₃) of 8d



¹³C NMR (126 MHz, CDCl₃) of 8e



¹³C NMR (126 MHz, CDCl₃) of **9a**



¹H NMR (500 MHz, CDCl₃) of **9b**





¹H NMR (500 MHz, CDCl₃) of **9c**



¹³C NMR (126 MHz, CDCl₃) of **9c**





