Supporting Information

Selective Synthesis of Functionalized *α*, *β*-Multi-substituted α-Amino Cyclopentanones *via α*-Iminol Rearrangement Enabled by Pd-Catalyzed Addition of Arylboronic Acids to Nitriles

Qian-Qian Ma, [a] *Cheng-Jing Li,*[a] *Wei-Wei Liao* [a, b*]

[a] Department of Organic Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, P R China.

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P R China

E-mail: wliao@jlu.edu.cn

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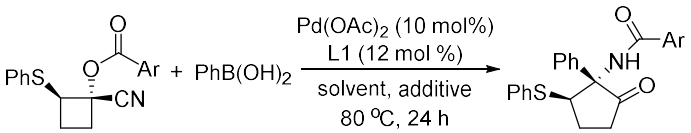
I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), $KMnO_4$, *p*-anisaldehyde stain, and phosphomolybdic acid (PMA) stain; column chromatography purifications were carried out using silica gel. For reactions that require heating, oil bath was used. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a 300, 400 or 500 MHz spectrometer in $CDCl_3$ or DMSO, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 125 or 100 MHz spectrometer in $CDCl_3$ or DMSO unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm, DMSO = δ 2.50 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm, DMSO = δ 39.52 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Bruker MicrOTOF Q II.

II. Reaction Conditions Screening

Table S1. Optimization of Solvents and Additives [a]

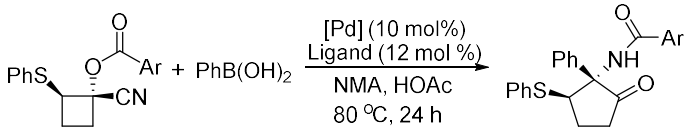


1a-*anti* **2a** **3aa**-*anti*

Entry	Solvent	Additive (equiv.)	Conv. (%) [b]	Yield (%) [c]
1	THF	-	45	28
2	Dioxane	-	22	18
3	DCE	-	47	33
4	Toluene	-	24	20
5	NMP	-	68	39
6	NMA	-	79	66
7	DMA	-	62	65
8	DMF	-	69	63
9	NMA	HOAc (0.4)	79	69
10	NMA	TFA (0.4)	76	61
11	NMA	HOAc (0.2)	85	67
12	NMA	HOAc (1.0)	83	68
13	NMA	NaOAc (2.0)	94	10
14	NMA	CsF (2.0)	85	13

[a] Reaction conditions: **1a**-*anti* (0.2 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (10 mol %), bpy (12 mol %), additive and HOAc (0.4 equiv.) in solvent (c = 0.2 *M*) at 80 °C. [b] Calculation based on recovered starting material **1a**. [c] Isolated yields. L1: 2,2′-bipyridine.

Table S2. Optimization of catalysts and ligands [a]



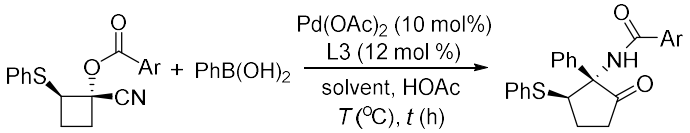
1a-*anti* **2a** **3aa**-*anti*

Entry	Cat.	ligand	Conv. (%) [b]	Yield (%) [c]
1	$Pd(OAc)_2$	L1	79	69
2	$Pd(TFA)_2$	L1	76	61
3	$Pd(acac)_2$	L1	87	65
4	$PdCl_2$	L1	50	41
5	$Pd(OAc)_2$	L2	85	68
6	$Pd(OAc)_2$	L3	86	73
8	$Pd(OAc)_2$	L4	91	71
9	$Pd(OAc)_2$	L5	15	10
10	$Pd(OAc)_2$	L6	80	68

[a] Reaction conditions: **1a**-*anti* (0.2 mmol), **2a** (0.4 mmol), catalyst (10 mol %), ligand (12 mol %) and HOAc (0.4 equiv.) in NMA (c = 0.2 *M*) at 80 °C. [b] Calculation based on recovered starting material **1a**. [c] Isolated yields.

L1: 2,2′-bipyridine. L2: 4,4′-di-methyl-2,2′-bipyridine. L3: 4,4′-di-tert-butyl-2,2′-bipyridine. L4: 5,5′-di-methyl-2,2′-bipyridine. L5: 6,6′-di-methyl-2,2′-bipyridine. L6: 1,10-phenanthroline.

Table S3. Optimization of other parameters [a]



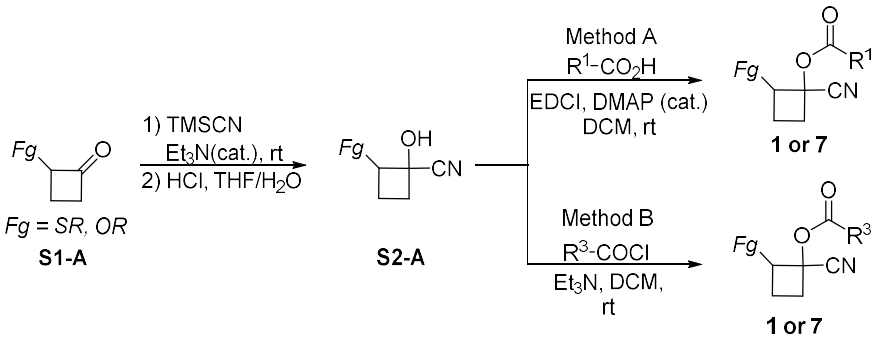
1a-*anti* **2a** **3aa**-*anti*

Entry	Solvent	T (°C)	*t* (h)	Conv. (%) [b]	Yield (%) [c]
1	NMA	80	24	86	73
2	NMA	60	24	92	77
3	NMA	40	24	57	51
4	NMA	100	24	89	73
5	NMA	60	12	91	74
6	NMA	60	36	92	81
7 [d]	NMA	60	24	96	83
8 [d, e]	NMA	60	24	88	75
9 [d, f]	NMA	60	24	50	39
10 [d]	DMA	60	24	94	87
11 [d]	DMF	60	24	96	83
12 [d]	DMA	80	24	99	89
13 [d]	DMF	80	24	100	92
14 [d]	NMA	80	24	100	85
15 [d, g]	DMF	80	24	95	89
16 [d, h]	DMF	80	24	nr	nd
17 [d, i]	DMF	80	24	nr	nd

[a] Reaction conditions: **1a**-*anti* (0.2 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (10 mol %), L3 (12 mol %) and HOAc (0.4 equiv.) in NMA (c = 0.2 *M*). [b] Calculation based on recovered starting material **1a**. [c] Isolated yields. [d] c = 0.4 *M*. [e] **2a** (0.3 mmol). [f] $Pd(OAc)_2$ (5 mol %), L3 (6 mol %). [g] 4Å MS was added. [h] Without $Pd(OAc)_2$. [i] Without L3.

III. Preparation of Substrates

1) Preparation of substrates 1 or 7:



To a mixture of **S1-A** [1-3] (1.0 equiv.) and Et_3N (10 mol %), TMSCN (1.1 equiv.) was slowly added at rt. [4] Upon completion, the reaction was concentrated *in vacuum*. The residue was treated with THF-HCl (4*N,* aq.) (1/1), and the mixture was stirred at rt. Upon completion, the aqueous phase extracted with EtOAc. The combined organic phases were washed with brine before being dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc/Petroleum ether (60−90 °C)) to give the desired compounds **S2-A** as separable *anti*- and *syn*-mixtures which can be easily separated by flash column chromatography.

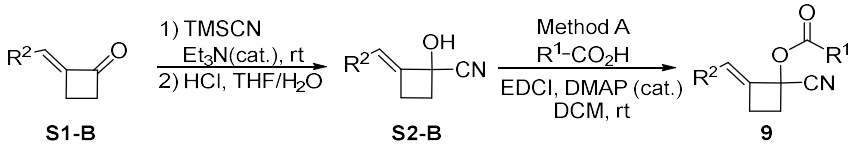
Method A for 1a-1j, 1l, 1n-1u and 7: [5]

A mixture of cyanohydrin **S2-A** (1 mmol, *anti*- or *syn*-isomer), acid (1.2 equiv.), DMAP (10 mol %) and EDCI (1.2 equiv.) in DCM (0.2 *M*) was stirred at room temperature. Upon completion, water was added and the mixture was extracted with DCM, and the combined organic layers were washed by brine and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc/Petroleum ether (60−90 °C)) to give the desired compounds **1 or 7**.

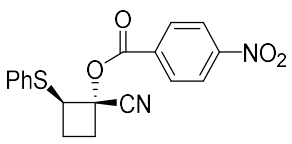
Method B for 1k and 1m: [6]

To a solution of acyl chloride (1.2 equiv.) and Et_3N (1.2 equiv.) in DCM (0.2 *M*) at 0 °C was slowly added a solution of **S2-A** (1.0 mmol, *anti*- or *syn*-isomer) in DCM. The resulting mixture was allowed to warm to room temperature. Upon completion, the resulting mixture was washed with 1*N* HCl, and extracted with DCM. The combined organic layers were washed by brine and dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc/Petroleum ether (60−90 °C)) to give compounds **1**.

2) Preparation of substrates 9:

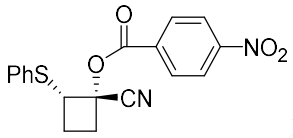


The substrates **9** were prepared from compounds **S2-B**, which were synthesized from compounds **S1-B**, [7] according to the similar procedures for compounds **1** or **7**.



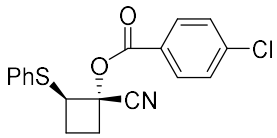
1a-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (77% yield, 273 mg) as a yellow solid. mp: 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.9 Hz, 2H), 7.64-7.54 (m, 2H), 7.41 – 7.32 (m, 3H), 4.23 – 4.16 (m, 1H), 3.15 – 3.05 (m, 1H), 2.57 – 2.34 (m, 2H), 2.22 – 2.02 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 151.2, 133.6, 133.5, 132.8, 131.1, 129.4, 128.2, 123.8, 115.8, 50.7, 50.7, 33.2, 22.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}N_2O_4SNa$ 377.0566; Found 377.0561.



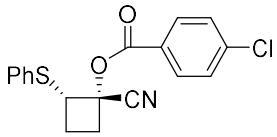
1a-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (75% yield, 266 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.9 Hz, 2H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 4.63 – 4.54 (m, 1H), 3.03 – 2.90 (m, 1H), 2.82 – 2.66 (m, 1H), 2.26 – 2.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 151.1, 134.2, 133.8, 131.2, 129.9, 129.4, 127.3, 123.8, 117.7, 70.6, 50.9, 32.8, 23.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}N_2O_4SNa$ 377.0566; Found 377.0569.



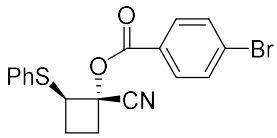
1b-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (76% yield, 261 mg) as a white solid. mp: 105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 6.5 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.41 – 7.31 (m, 3H), 4.25 – 4.13 (m, 1H), 3.17 – 3.04 (m, 1H), 2.62 – 2.34 (m, 2H), 2.24 – 2.01 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 140.8, 133.7, 132.4, 131.3, 129.3, 129.1, 128.0, 126.7, 116.1, 76.9, 50.5, 33.2, 22.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}ClNO_2SNa$ 366.0326; Found 366.0325.



1b-*syn*

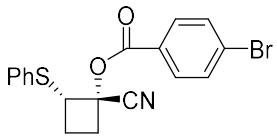
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/25) to afford the title compound (69% yield, 237 mg) as a white solid. mp: 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.22 (m, 1H), 4.58 – 4.50 (m, 1H), 2.98 – 2.85 (m, 1H), 2.79 – 2.61 (m, 2H), 2.25 – 2.11 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 140.8, 134.4, 131.5, 130.2, 129.4, 129.2, 127.4, 127.0, 118.1, 70.1, 51.2, 32.9, 23.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}ClNO_2SNa$ 366.0326; Found 366.0323.



1c-*anti*

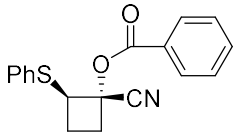
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (83% yield, 322 mg) as a white solid. mp: 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.60 – 7.53 (m,

4H), 7.38 – 7.28 (m, 3H), 4.23 – 4.10 (m, 1H), 3.07 – 3.02 (m, 1H), 2.52 – 2.33 (m, 2H), 2.17 – 2.00 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 133.8, 132.8, 132.2, 131.4, 129.5, 129.3, 128.0, 127.2, 116.1, 50.6, 33.2, 29.8, 22.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}BrNO_2SNa$ 409.9821; Found 409.9818.



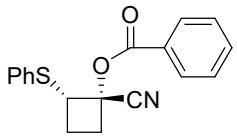
1c-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (75% yield, 291 mg) as a white solid. mp: 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.26-7.24 (m, 3H), 4.56 – 4.48 (m, 1H), 3.01 – 2.90 (m, 1H), 2.83 – 2.64 (m, 2H), 2.28 – 2.14 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 133.7, 133.3, 132.5, 131.7, 131.3, 123.9, 121.6, 117.6, 70.6, 51.2, 32.7, 23.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}BrNO_2SNa$ 409.9821; Found 409.9807.



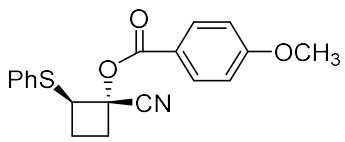
1d-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (80% yield, 248 mg) as a white solid. mp: 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 2H), 7.64 – 7.54 (m, 3H), 7.43 (t, J = 7.9 Hz, 2H), 7.39 – 7.27 (m, 3H), 4.23 – 4.14 (m, 1H), 3.12 – 3.02 (m, 1H), 2.51 – 2.34 (m, 2H), 2.17 – 2.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 134.2, 134.0, 132.2, 130.0, 129.3, 128.8, 128.3, 127.9, 116.3, 76.8, 50.5, 33.2, 22.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_2SNa$ 332.0716; Found 332.0708.



1d-*syn*

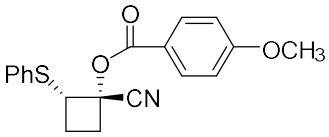
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (72% yield, 223 mg) as a white solid. mp: 81 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 6.8 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.44 (d, J = 7.7 Hz, 2H), 7.41 (d, J = 7.3 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 7.7 Hz, 1H), 4.57 – 4.50 (m, 1H), 2.97 – 2.87 (m, 1H), 2.79 – 2.59 (m, 2H), 2.25 – 2.14 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 134.4, 134.1, 130.4, 130.2, 129.4, 128.8, 128.6, 127.4, 118.3, 70.0, 51.4, 32.9, 24.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_2SNa$ 332.0716; Found 332.0710.



1e-*anti*

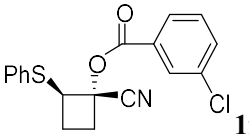
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (78% yield, 265 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.9 Hz, 2H), 7.56 (d, J = 6.8 Hz, 2H), 7.34 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 4.18 – 4.14 (m, 1H), 3.86 (s, 3H), 3.07 – 3.03 (m, 1H), 2.48 – 2.35 (m, 2H), 2.12 – 2.04 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 163.8, 134.0, 132.1, 132.0,

129.2, 127.7, 120.5, 116.4, 114.0, 76.6, 55.6, 50.3, 33.2, 22.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_3S$ 340.1002; Found 340.1005.



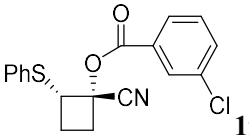
1e-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (79% yield, 268 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.9 Hz, 2H), 7.41 (d, J = 7.0 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.28 – 7.20 (m, 1H), 6.90 (d, J = 8.9 Hz, 2H), 4.54 – 4.49 (m, 1H), 3.86 (s, 3H), 2.96 – 2.84 (m, 1H), 2.77 – 2.57 (m, 2H), 2.25 – 2.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 164.0, 134.5, 132.4, 130.3, 129.3, 127.3, 120.9, 118.4, 114.0, 69.7, 55.7, 51.3, 32.9, 24.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_3S$ 340.1002; Found 340.0997.



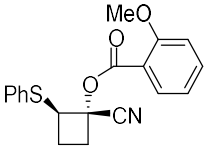
1f-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (88% yield, 302 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.60 – 7.55 (m, 3H), 7.39 – 7.31 (m, 4H), 4.20 – 4.15 (m, 1H), 3.13 – 2.99 (m, 1H), 2.52 – 2.33 (m, 2H), 2.16 – 2.02 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 134.8, 134.1, 133.6, 132.3, 130.1, 130.0, 129.9, 129.3, 128.1, 128.1, 116.0, 77.1, 50.5, 33.2, 22.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}ClNO_2SNa$ 366.0326; Found 366.0322.



1f-*syn*

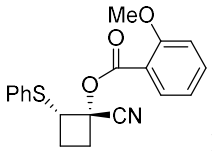
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (75% yield, 257 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.88 (m, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.43 – 7.37 (m, 3H), 7.36 – 7.34 (m, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.29 – 7.26 (m, 1H), 4.60 – 4.49 (m, 1H), 2.99 – 2.86 (m, 1H), 2.79 – 2.59 (m, 2H), 2.26 – 2.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 134.9, 134.3, 134.2, 130.3, 130.1, 130.0, 129.4, 128.3, 127.4, 118.0, 70.2, 51.1, 32.9, 23.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}ClNO_2SNa$ 366.0326; Found 366.0323.



1g-*anti*

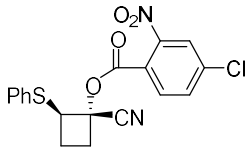
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (84% yield, 285 mg) as a white solid. mp: 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 7.8, 1.8 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.34 – 7.27 (m, 3H), 6.99 (d, J = 7.5 Hz, 1H), 6.97 – 6.93 (m, 1H), 4.25 – 4.11 (m, 1H), 3.87 (s, 3H), 3.11 – 3.05 (m, 1H), 2.52 – 2.34 (m, 2H), 2.14 – 2.05 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 170.4, 139.7, 133.9, 131.7, 129.2, 128.8, 128.8, 128.4, 127.7, 126.7, 116.1, 49.9, 35.6, 32.9, 30.7, 22.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for

$C_{19}H_{17}NO_3SNa$ 362.0821; Found 362.0823.



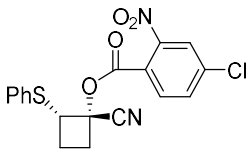
1g-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (76% yield, 258 mg) as a white solid. mp: 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.42 (dd, *J* = 7.0, 1.6 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.20 (m, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.97 – 6.91 (m, 1H), 4.52 – 4.43 (m, 1H), 3.89 (s, 3H), 2.96 – 2.83 (m, 1H), 2.77 – 2.57 (m, 2H), 2.27 – 2.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 160.6, 135.2, 134.6, 132.7, 130.5, 129.3, 127.3, 120.3, 118.4, 117.4, 112.3, 70.0, 56.0, 51.4, 33.0, 24.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}NO_3SNa$ 362.0821; Found 362.0822.



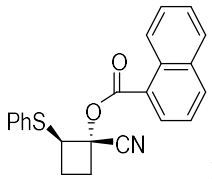
1h-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (71% yield, 276 mg) as a yellow solid. mp: 83 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.8 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.31 – 7.19 (m, 3H), 4.43 (t, *J* = 8.2 Hz, 1H), 2.93 – 2.72 (m, 2H), 2.71 – 2.52 (m, 1H), 2.34 – 2.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 148.7, 139.2, 133.5, 133.4, 131.8, 131.6, 129.3, 127.8, 124.6, 123.9, 115.5, 77.6, 49.8, 32.0, 22.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}ClN_2O_4SNa$ 411.0177; Found 411.0174.



1h-*syn*

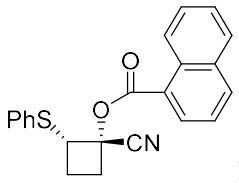
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (79% yield, 307 mg) as a yellow solid. mp: 84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.4 Hz, 1H), 7.66 (s, 1H), 7.66 – 7.63 (m, 1H), 7.36 – 7.34 (m, 2H), 7.31 – 7.21 (m, 3H), 4.52 – 4.36 (m, 1H)), 2.93 – 2.76 (m, 2H), 2.68 – 2.54 (m, 1H), 2.30 – 2.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 148.8, 139.2, 134.0, 133.3, 131.8, 130.8, 129.3, 127.6, 124.7, 123.9, 117.2, 71.8, 51.4, 31.9, 24.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}ClN_2O_4SNa$ 411.0177; Found 411.0180.



1i-*anti*

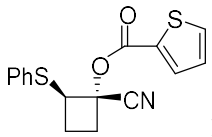
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (75% yield, 269 mg) as a white solid. mp: 119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.50 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.24 (m, 3H), 4.26 – 4.17 (m, 1H) , 3.16 – 3.10 (m, 1H), 2.52 – 2.41 (m, 2H), 2.16 – 2.06 (m, 1H). ^{13}C NMR (125 MHz,

$CDCl_3$) δ 164.6, 135.0, 134.0, 133.9, 132.1, 131.6, 131.4, 129.3, 128.8, 128.6, 127.8, 126.7, 125.5, 124.4, 124.3, 116.4, 76.8, 50.5, 33.3, 22.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{17}NO_2SNa$ 382.0872; Found 382.0862.



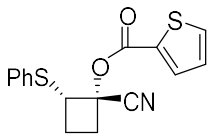
1i-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (70% yield, 252 mg) as a white solid. mp: 120 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, J = 8.6 Hz, 1H), 8.20 (d, J = 7.3 Hz, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.58 – 7.51 (m, 1H), 7.50 – 7.39 (m, 3H), 7.27 – 7.21 (m, 2H), 7.33 – 7.27 (m, 1H), 4.66 – 4.48 (m, 1H), 3.03 – 2.88 (m, 1H), 2.88 – 2.73 (m, 1H), 2.77 – 2.62 (m, 1H), 2.33 – 2.14 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 135.0, 134.4, 133.9, 131.8, 130.5, 129.3, 128.8, 128.5, 127.4, 126.7, 125.8, 124.6, 124.4, 118.5, 70.1, 51.5, 33.0, 24.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{17}NO_2SNa$ 382.0872; Found 382.0873.



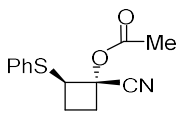
1j-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (77% yield, 243 mg) as a yellow solid. mp: 100 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 3.8 Hz, 1H), 7.66 (d, J = 5.0 Hz, 1H), 7.44 – 7.31 (m, 5H), 7.19 – 7.14 (m, 1H), 4.15 – 4.00 (m, 1H), 3.11 – 2.95 (m, 1H), 2.69 – 2.47 (m, 1H), 2.45 – 2.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 136.9, 135.1, 134.1, 131.8, 128.8, 128.3, 128.2, 127.5, 116.8, 75.2, 50.1, 33.1, 19.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{13}NO_2S_2Na$ 338.0280; Found 338.0267.



1j-*syn*

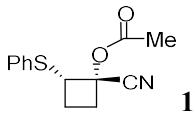
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/30) to afford the title compound (73% yield, 230 mg) as a yellow solid. mp: 107 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, J = 3.8, 1.3 Hz, 1H), 7.64 (dd, J = 4.9, 1.3 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.12 (dd, J = 5.0, 3.8 Hz, 1H), 4.19 – 4.15 (m, 1H), 3.08 – 3.01 (m, 1H), 2.51 – 2.37 (m, 2H), 2.14 – 2.01 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 135.2, 134.3, 134.1, 131.6, 131.3, 129.3, 128.3, 127.7, 116.1, 77.0, 50.3, 33.1, 22.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{13}NO_2S_2Na$ 338.0280; Found 338.0271.



1k-*anti*

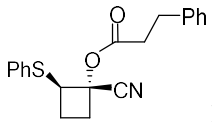
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (62% yield, 153 mg) as a light yellow liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.1 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.29 – 7.24 (m, 1H), 4.02 (t, J = 9.9 Hz, 1H), 3.01 – 2.88 (m, 1H), 2.49 – 2.37 (m, 1H), 2.34 – 2.21 (m, 1H),

2.08 (s, 3H), 2.08 – 1.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 133.9, 131.6, 129.2, 127.6, 116.2, 76.1, 49.8, 32.9, 22.5, 20.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{13}NO_2SNa$ 270.0559; Found 270.0554.



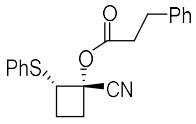
1k-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/25) to afford the title compound (58% yield, 144 mg) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.1 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.28 – 7.25 (m, 1H), 4.39 – 4.36 (m, 1H), 2.82 – 2.72 (m, 1H), 2.66 – 2.55 (m, 2H), 2.19 (s, 3H), 2.17 – 2.08 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7, 134.0, 131.2, 129.3, 127.7, 118.2, 69.9, 51.6, 32.6, 24.3, 20.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}NO_2S$ 248.0740; Found 248.0738.



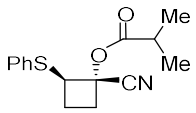
1l-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (83% yield, 313 mg) as a white solid. mp: 84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 –7.43 (m, 2H), 7.35 – 7.23 (m, 5H), 7.26 – 7.17 (m, 1H), 7.16 (d, J = 8.4 Hz, 2H), 3.98 – 3.88 (m, 1H), 2.95 – 2.87 (m, 3H), 2.66 – 2.60 (m, 2H), 2.42 – 2.29 (m, 1H), 2.17 – 2.09 (m, 1H), 2.05 – 1.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 139.7, 133.9, 131.6, 129.2, 128.8, 128.4, 127.7, 126.7, 116.2, 76.2, 49.9, 35.5, 32.9, 30.7, 22.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{19}NO_2SNa$ 360.1029; Found 360.1026.



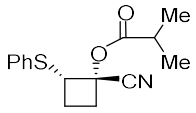
1l-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (78% yield, 294 mg) as a white solid. mp: 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.24 (m, 5H), 7.24 – 7.17 (m, 3H), 4.37 – 4.31 (m, 1H), 2.95 (t, J = 7.8 Hz, 2H), 2.76 – 2.67 (m, 3H), 2.58 – 2.41 (m, 2H), 2.11 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 139.8, 134.1, 130.9, 129.2, 128.7, 128.4, 127.5, 126.6, 118.1, 69.9, 51.4, 35.5, 32.5, 30.6, 24.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{19}NO_2SNa$ 360.1029; Found 360.1025.



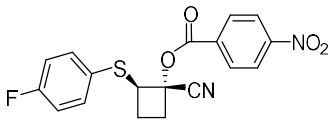
1m-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (61% yield, 168 mg) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 4.40 – 4.36 (m, 1H), 2.84 – 2.74 (m, 1H), 2.68 – 2.51 (m, 3H), 2.15 – 2.04 (m, 1H), 1.20 (d, J = 1.5 Hz, 3H), 1.19 (d, J = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 134.3, 130.6, 129.2, 127.4, 118.3, 69.5, 51.4, 34.0, 32.7, 24.2, 18.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{17}NO_2SNa$ 298.0872; Found 298.0875.



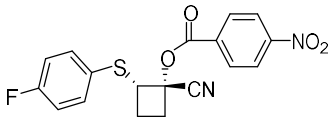
1m-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (56% yield, 154 mg) as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.24 (m, 1H), 4.03 (t, *J* = 9.9 Hz, 1H), 2.98 – 2.93 (m, 1H), 2.57 – 2.50 (m, 1H), 2.44 – 2.37 (m, 1H), 2.27 – 2.18 (m, 1H), 2.07 – 1.98 (m, 1H), 1.15 (d, *J* = 3.6 Hz, 3H), 1.13 (d, *J* = 3.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 134.0, 131.5, 129.1, 127.6, 116.2, 76.2, 49.9, 33.7, 33.0, 22.1, 18.6, 18.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{17}NO_2SNa$ 298.0872; Found 298.0871.



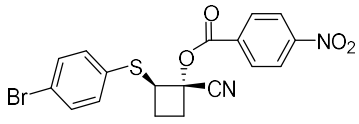
1n-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (76% yield, 283 mg) as a white solid. mp: 128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.9 Hz, 2H), 7.98 (d, *J* = 8.9 Hz, 2H), 7.66 – 7.57 (m, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 4.15 – 4.06 (m, 1H), 3.13 – 3.03 (m, 1H), 2.53 – 2.35 (m, 2H), 2.17 – 2.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 249.4 Hz), 162.2, 151.2, 135.9 (d, *J* = 8.3 Hz), 133.5, 131.1, 123.9, 128.2 (d, *J* = 3.1 Hz), 116.5 (d, *J* = 21.9 Hz), 115.8, 77.3, 51.3, 33.0, 22.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}FN_2O_4SNa$ 395.0472; Found 395.0475.



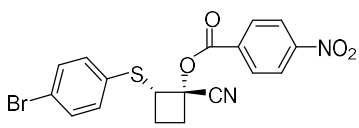
1n-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (78% yield, 290 mg) as a white solid. mp: 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.9 Hz, 2H), 8.20 (d, *J* = 8.9 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.06 – 6.99 (m, 2H), 4.50 – 4.42 (m, 1H), 2.97 – 2.87 (m, 1H), 2.80 – 2.61 (m, 2H), 2.28 – 2.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 248.5 Hz), 162.5, 151.2, 133.8, 133.4 (d, *J* = 8.2 Hz), 131.3, 128.8 (d, *J* = 3.5 Hz), 123.9, 117.5, 116.6 (d, *J* = 22.1 Hz), 70.7, 52.3, 32.5, 24.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}FN_2O_4SNa$ 395.0472; Found 395.0476.



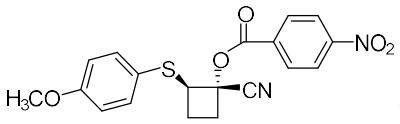
1n-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (86% yield, 373 mg) as a white solid. mp: 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.43 (m, 4H), 4.23 – 4.15 (m, 1H), 3.16 – 3.05 (m, 1H), 2.57 – 2.39 (m, 2H), 2.21 – 2.03 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 151.1, 134.1, 133.4, 132.5, 132.4, 131.0, 123.8, 122.4, 115.6, 77.1, 50.4, 33.0, 22.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}BrN_2O_4SNa$ 454.9672; Found 454.9676.



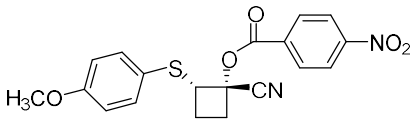
1n-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (74% yield, 321 mg) as a white solid. mp: 139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 4.58 – 4.49 (m, 1H), 3.02 – 2.84 (m, 1H), 2.83 – 2.65 (m, 2H), 2.32 – 2.14 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 133.7, 133.3, 132.5, 131.7, 131.3, 123.9, 121.6, 117.6, 70.6, 51.2, 32.7, 23.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}BrN_2O_4SNa$ 454.9672; Found 454.9667.



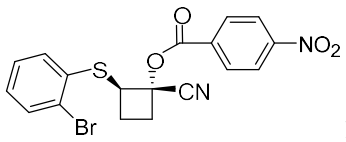
1p-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (87% yield, 334 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.47 – 4.38 (m, 1H), 3.80 (s, 3H), 2.94 – 2.86 (m, 1H), 2.75 – 2.56 (m, 2H), 2.33 – 2.12 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 160.0, 151.2, 134.1, 134.0, 131.4, 123.9, 123.7, 117.7, 115.0, 70.8, 55.5, 52.8, 32.5, 24.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2O_5SNa$ 407.0672; Found 407.0665.



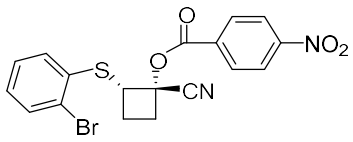
1p-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (70% yield, 261 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.9 Hz, 2H), 7.97 (d, *J* = 8.9 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), δ 4.11 – 4.03 (m, 1H), 3.85 (s, 3H), 3.12 – 3.04 (m, 1H), 2.49 – 2.35 (m, 2H), 2.14 – 2.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 160.4, 151.2, 136.1, 133.7, 131.2, 123.8, 123.4, 116.0, 114.9, 77.5, 55.6, 51.8, 33.1, 22.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2O_5SNa$ 407.0672; Found 407.0669.



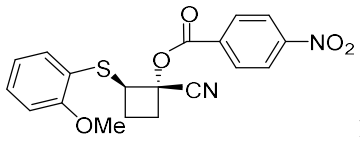
1q-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (65% yield, 282 mg) as a yellow solid. mp: 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.64 (m, 2H), 7.34 – 7.27 (m, 1H), 7.25 – 7.16 (m, 1H), 4.33 (t, *J* = 9.7 Hz, 1H), 3.18 – 3.07 (m, 1H), 2.61 – 2.41 (m, 2H), 2.24 – 2.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 151.2, 134.7, 134.0, 133.7, 133.6, 131.2, 129.5, 128.1, 127.0, 123.9, 115.7, 49.1, 33.3, 29.9, 22.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}BrN_2O_4SNa$ 454.9672; Found 454.9668.



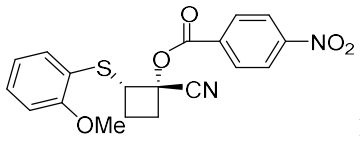
1q-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (80% yield, 347 mg) as a yellow solid. mp: 188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 6.7 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.17 – 7.08 (m, 1H), 4.70 – 4.62 (m, 1H), 3.09 – 2.95 (m, 1H), 2.90 – 2.71 (m, 2H), 2.33 – 2.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 151.2, 136.0, 133.7, 133.4, 131.3, 129.3, 128.4, 128.0, 123.9, 123.3, 117.7, 70.1, 49.7, 33.1, 23.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}BrN_2O_4SNa$ 454.9672; Found 454.9679.



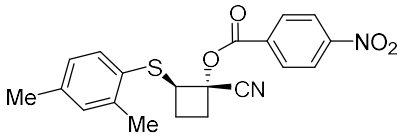
1r-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (74% yield, 284 mg) as a yellow solid. mp: 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.00 – 6.93 (m, 2H), 4.35 – 4.24 (m, 1H), 3.91 (s, 3H), 3.15 – 3.03 (m, 1H), 2.54 – 2.36 (m, 2H), 2.16 – 2.04 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 158.8, 151.1, 134.6, 133.7, 131.1, 130.0, 123.8, 121.3, 121.1, 115.8, 111.1, 77.4, 56.0, 48.5, 33.3, 22.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2O_5SNa$ 407.0672 ; Found 407.0666.



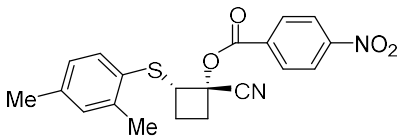
1r-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (80% yield, 307 mg) as a yellow solid. mp: 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$ δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H), 7.35 – 7.25 (m, 2H), 6.93 – 6.88 (m, 2H), 4.72 – 4.60 (m, 1H), 3.90 (s, 3H), 3.01 – 2.90 (m, 1H), 2.87 – 2.75 (m, 1H), 2.75 – 2.62 (m, 1H), 2.25 – 2.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)) δ 162.5, 157.9, 151.1, 133.9, 131.4, 131.3, 129.0, 123.8, 122.0, 121.3, 117.9, 111.0, 70.7, 55.9, 49.5, 33.0, 23.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2O_5SNa$ 407.0672; Found 407.0669.



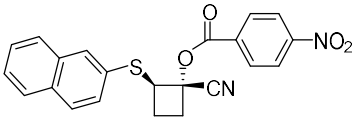
1s-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (85% yield, 327 mg) as a yellow solid. mp: 156 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.10 (s, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 4.13 – 4.07 (m, 1H), 3.13 – 3.02 (m, 1H), 2.48 (s, 3H), 2.47 – 2.36 (m, 2H), 2.34 (s, 3H), 2.18 – 2.07 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 151.2, 140.0, 138.4, 133.7, 133.4, 131.6, 131.2, 129.4, 127.4, 123.8, 115.9, 77.4, 50.4, 33.2, 22.4, 21.2, 20.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}N_2O_4SNa$ 405.0879; Found 405.0873.



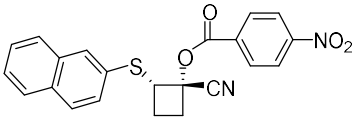
1s-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (60% yield, 231 mg) as a yellow solid. mp: 174 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.03 (s, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), δ 4.50 – 4.44 (m, 1H), 2.98 – 2.88 (m, 1H), 2.84 – 2.74 (m, 1H), 2.72 – 2.63 (m, 1H), 2.36 (s, 3H), 2.30 (s, 3H), 2.25 – 2.15 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.1, 138.4, 137.6, 133.9, 131.5, 131.3, 130.9, 129.6, 127.7, 123.8, 117.7, 70.6, 50.8, 32.8, 23.9, 21.0, 20.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}N_2O_4SNa$ 405.0879; Found 405.0880.



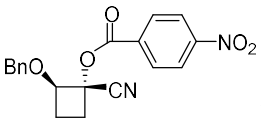
1t-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (75% yield, 287 mg) as a yellow solid. mp: 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.09 (m, 2H), 8.09 (s, 1H), 7.89 – 7.76 (m, 5H), 7.63 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.60 – 7.49 (m, 2H), 4.34 – 4.24 (m, 1H), 3.16 – 3.06 (m, 1H), 2.58 – 2.38 (m, 2H), 2.27 – 2.10 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 151.1, 133.8, 133.5, 132.8, 131.9, 131.1, 130.7, 129.9, 129.0, 127.9, 127.6, 127.1, 127.0, 123.8, 115.8, 77.6, 50.8, 33.3, 22.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}N_2O_4S$ 405.0904; Found 405.0899.



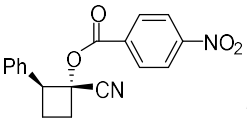
1t-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (72% yield, 275 mg) as a yellow solid. mp: 106 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.99 – 7.94 (m, 2H), 7.84 – 7.77 (m, 3H), 7.71 – 7.66 (m, 1H), 7.51 – 7.43 (m, 3H), 4.74 – 4.67 (m, 1H), 3.02 – 2.92 (m, 1H), 2.87 – 2.69 (m, 2H), 2.28 – 2.17 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.1, 133.7, 132.3, 131.4, 131.2, 129.1, 128.9, 127.9, 127.4, 127.3, 127.1, 126.6, 123.7, 117.8, 70.7, 51.0, 33.0, 23.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{16}N_2O_4SNa$ 427.0723; Found 427.0722.



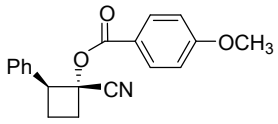
1u-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (67% yield, 236 mg) as a white solid. mp: 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 7.37 – 7.27 (m, 5H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.57 – 4.48 (m, 1H), 2.60 – 2.50 (m, 2H), 2.50 – 2.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 151.1, 136.8, 134.1, 131.2, 128.7, 128.3, 128.0, 123.9, 117.5, 77.1, 72.8, 71.9, 27.6, 27.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2O_5Na$ 375.0951; Found 35.0955.



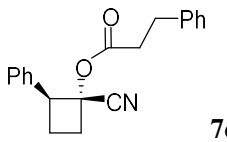
7a-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (40% yield, 128 mg) as a white solid. mp: 188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 8.9 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.33 (m, 3H), 4.12 – 4.08 (m, 1H), 3.11 – 3.03 (m, 1H), 2.63 – 2.50 (m, 1H), 2.48 – 2.42 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 151.2, 136.6, 133.9, 131.2, 128.9, 128.4, 127.5, 123.9, 116.4, 75.8, 50.2, 33.0, 19.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}N_2O_4Na$ 345.0846; Found 345.0853.



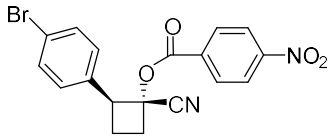
7b-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (54% yield, 166 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.9 Hz, 2H), 7.45 – 7.36 (m, 4H), 7.33 (t, *J* = 7.1 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.08 – 4.04 (m, 1H), 3.87 (s, 3H), 3.06 – 2.98 (m, 1H), 2.54 – 2.43 (m, 1H), 2.43 – 2.33 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 164.1, 137.1, 132.2, 128.7, 128.0, 127.5, 120.8, 117.1, 114.0, 74.8, 55.7, 50.0, 33.1, 19.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}NO_3Na$ 330.1101; Found 330.1102.



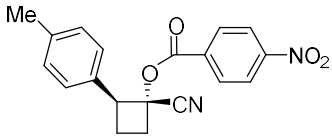
7c-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (70% yield, 214 mg) as a solid. mp: 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.4 Hz, 2H), 7.32-7.27 (m, 3H), 7.25 – 7.19 (m, 5H), 3.84 – 3.74 (m, 1H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.93 – 2.75 (m, 1H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.39 – 2.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 139.8, 136.9, 128.7, 128.6, 128.4, 128.0, 127.4, 126.6, 116.8, 74.5, 49.8, 35.4, 32.8, 30.7, 18.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{19}NO_2Na$ 328.1308; Found 328.1300.



7d-*anti*

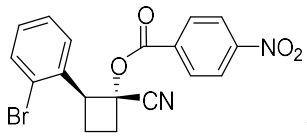
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (81% yield, 324 mg) as a white solid. mp: 186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.9 Hz, 2H), 8.23 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.07 – 4.02 (m, 1H), 3.10 – 3.00 (m, 1H), 2.63 – 2.43 (m, 1H), 2.46 – 2.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 151.2, 135.6, 133.8, 132.0, 131.2, 129.2, 123.9, 122.4, 116.3, 75.4, 49.7, 32.8, 19.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{13}BrN_2O_4Na$ 422.9951; Found 422.9947.



7e-*anti*

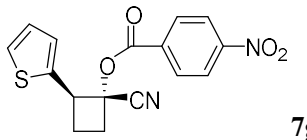
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (89% yield, 299 mg) as a yellow solid. mp: 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* =

8.8 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 4.08 – 4.05 (m, 1H), 3.12 – 3.02 (m, 1H), 2.61 – 2.52 (m, 1H), 2.48 – 2.39 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 151.2, 138.1, 134.0, 133.5, 131.2, 129.6, 127.4, 123.9, 116.5, 75.9, 50.0, 32.9, 21.3, 19.1. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}N_2O_4Na$ 359.1002; Found 359.1001.



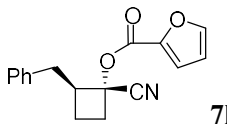
7f-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (75% yield, 301 mg) as a white solid. mp: 188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.9 Hz, 2H), 8.27 (d, *J* = 8.9 Hz, 2H), 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.58 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.29 – 7.19 (m, 1H), 4.64 – 4.59 (m, 1H), 3.07 – 3.00 (m, 1H), 2.62 – 2.45 (m, 2H), 2.45 – 2.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.2, 135.3, 133.9, 133.3, 131.4, 130.1, 129.6, 128.0, 125.0, 123.9, 116.2, 76.0, 48.9, 32.6, 19.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}BrN_2O_4$ 401.0131 ; Found 401.0125.



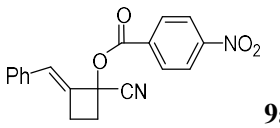
7g-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (92% yield, 301 mg) as a yellow solid. mp: 164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.9 Hz, 2H), 8.24 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.09 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.25 – 4.19 (m, 1H), 3.07 – 3.03 (m, 1H), 2.59 – 2.49 (m, 2H), 2.49 – 2.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 151.2, 139.1, 133.8, 131.3, 127.5, 126.3, 125.7, 123.9, 116.1, 76.2, 45.8, 32.7, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{13}N_2O_4S$ 329.0591 ; Found 329.0586.



7h-*anti*

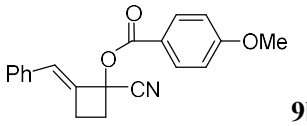
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (79% yield, 222 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.7 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 7.16 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.54 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.41 – 3.29 (m, 1H), 3.04 – 2.85 (m, 3H), 2.45 – 2.33 (m, 1H), 2.14 – 2.01 (m, 1H), 1.88 – 1.75 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 147.5, 143.3, 138.3, 128.9, 128.7, 126.6, 119.8, 117.1, 112.3, 73.3, 46.9, 38.2, 32.4, 20.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}NO_3Na$ 304.0944; Found 304.1948.



9a

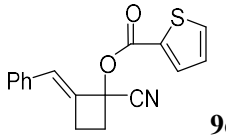
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (88% yield, 294 mg) as a yellow solid. mp: 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.9 Hz, 2H), 8.26 (d, *J* = 8.6

Hz, 2H), 7.44 – 7.30 (m, 5H), 7.01 (s, 1H), 3.35 – 3.20 (m, 1H), 3.23 – 3.09 (m, 2H), 2.86 – 2.73 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 151.2, 134.9, 134.1, 133.9, 131.3, 130.5, 129.0, 128.9, 128.7, 123.9, 116.7, 73.1, 33.4, 27.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{14}N_2O_4Na$ 357.0846; Found 357.0851.



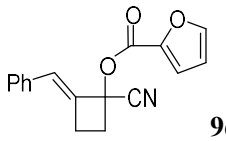
9b

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (65% yield, 145 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.28 (m, 5H), 6.98 – 6.95 (m, 2H), 6.94 (s, 1H), 3.87 (s, 3H), 3.28 – 3.06 (m, 3H), 2.81 – 2.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.2, 135.2, 134.9, 132.3, 129.5, 128.8, 128.6, 128.5, 120.9, 117.5, 114.0, 71.9, 55.6, 33.6, 27.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}NO_3Na$ 342.1101; Found 342.1096.



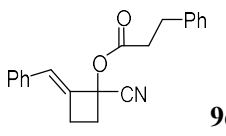
9c

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/15) to afford the title compound (81% yield, 239 mg) as a yellow solid. mp: 101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.65 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.41 – 7.28 (m, 5H), 7.15 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.97 (t, *J* = 2.6 Hz, 1H), 3.32 – 3.21 (m, 1H), 3.21 – 3.03 (m, 2H), 2.85 – 2.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 135.1, 135.0, 134.5, 134.1, 131.9, 130.0, 128.9, 128.6, 128.6, 128.2, 117.1, 72.4, 33.5, 27.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{13}NO_2SNa$ 318.0559; Found 318.0554.



9d

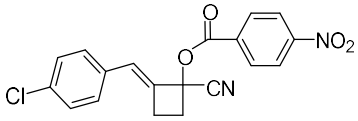
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (76% yield, 212 mg) as a yellow solid. mp: 94 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.7 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.34 – 7.28 (m, 4H), 6.98 (d, *J* = 2.9 Hz, 1H), 6.56 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.29 – 3.19 (m, 1H), 3.18 – 3.04 (m, 2H), 2.81 – 2.69 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 147.5, 143.2, 135.0, 134.2, 130.2, 128.8, 128.6, 120.0, 116.9, 112.4, 72.3, 33.4, 27.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{13}NO_3Na$ 302.0788; Found 302.0792.



9e

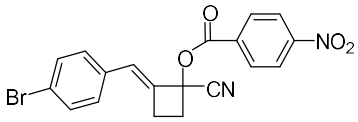
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (96% yield, 305 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.25 (m, 5H), 7.25 – 7.17 (m, 3H), 6.80 (t, *J* = 2.7 Hz, 1H), 3.18 – 3.05 (m, 2H), 3.04 – 2.89 (m, 3H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.57 – 2.44 (m,

1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 139.9, 135.1, 134.6, 129.6, 128.8, 128.7, 128.6, 128.5, 128.4, 126.6, 117.1, 71.8, 35.7, 33.4, 30.8, 27.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}NO_2Na$ 340.1308; Found 340.1304.



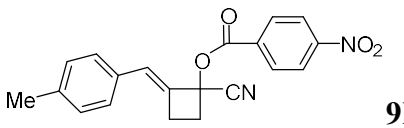
9f

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (82% yield, 302 mg) as a yellow solid. mp: 146 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.97 (s, 1H), 3.32 – 3.21 (m, 1H), 3.21 – 3.11 (m, 2H), 2.85 – 2.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 151.2, 134.7, 134.6, 133.9, 133.3, 131.3, 129.8, 129.3, 129.1, 123.9, 116.5, 72.9, 33.3, 27.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{13}ClN_2O_4Na$ 391.0456; Found 391.0464.



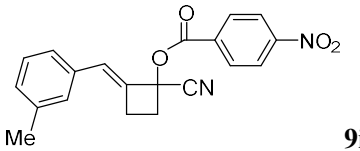
9g

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (78% yield, 322 mg) as a white solid. mp: 145 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.8 Hz, 2H), 8.26 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.96 (s, 1H), 3.31 – 3.20 (m, 1H), 3.19 – 3.08 (m, 2H), 2.85 – 2.75 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 151.2, 134.8, 133.9, 133.7, 132.2, 131.3, 130.1, 129.5, 123.9, 123.0, 116.5, 72.9, 33.3, 27.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{13}BrN_2O_4Na$ 434.9951; Found 434.9946.



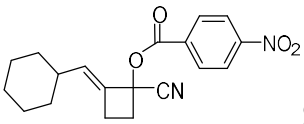
9h

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (75% yield, 261 mg) as a white solid. mp: 116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.9 Hz, 2H), 8.26 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.97 (s, 1H), 3.32 – 3.22 (m, 1H), 3.19 – 3.08 (m, 2H), 2.83 – 2.73 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 151.2, 139.0, 134.1, 132.7, 132.1, 131.3, 130.5, 129.7, 128.6, 123.9, 116.8, 73.1, 33.4, 27.7, 21.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{16}N_2O_4Na$ 371.1003; Found 371.1002.



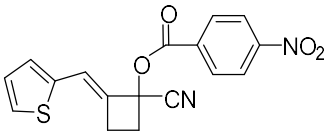
9i

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (71% yield, 247 mg) as a yellow solid. mp: 121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.9 Hz, 2H), 8.24 (d, J = 8.9 Hz, 2H), 7.27 (t, J = 7.7 Hz, 1H), 7.17 – 7.10 (m, 3H), 6.96 (s, 1H), 3.34 – 3.22 (m, 1H), 3.22 – 3.08 (m, 2H), 2.85 – 2.74 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 151.0, 138.4, 134.7, 133.9, 133.6, 131.1, 130.4, 129.5, 129.4, 128.7, 125.5, 123.7, 116.6, 72.9, 33.3, 27.7, 21.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{16}N_2O_4Na$ 371.1003; Found 371.1005.



9j

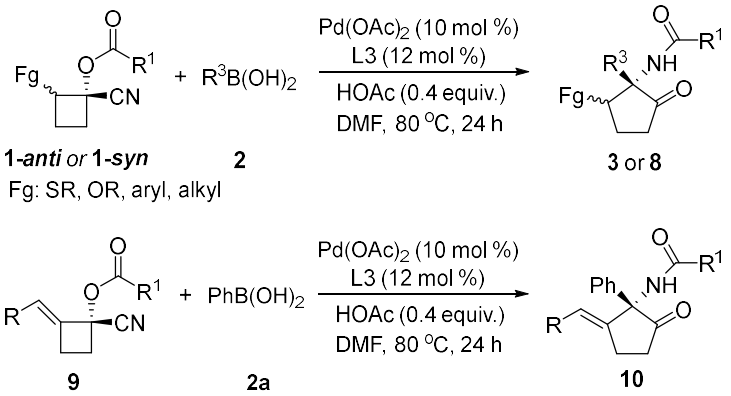
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/20) to afford the title compound (81% yield, 276 mg) as a yellow solid. mp: 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.28 (m, 2H), 8.27 – 8.17 (m, 2H), 6.01 – 5.95 (m, 1H), 3.02 – 2.94 (m, 1H), 2.93 – 2.78 (m, 2H), 2.67 – 2.55 (m, 1H), 2.16 – 2.04 (m, 1H), 1.80 – 1.57 (m, 5H), 1.37 – 1.09 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 151.1, 137.6, 134.2, 131.2, 123.8, 117.1, 72.4, 37.8, 32.5, 32.4, 32.2, 26.0, 25.8, 24.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}N_2O_4Na$ 341.1494; Found 341.1487.



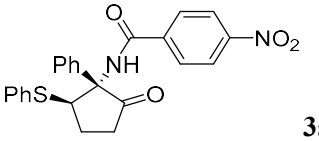
9k

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (82% yield, 279 mg) as a white solid. mp: 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.9 Hz, 2H), 8.25 (d, J = 8.9 Hz, 2H), 7.41 (d, J = 5.1 Hz, 1H), 7.27 (d, J = 2.3 Hz, 1H), 7.14 (d, J = 3.6 Hz, 1H), 7.08 (dd, J = 5.1, 3.6 Hz, 1H), 3.25 – 3.02 (m, 3H), 2.86 – 2.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 151.2, 138.4, 134.0, 131.8, 131.3, 129.3, 128.1, 127.6, 124.5, 123.9, 116.6, 72.5, 32.7, 27.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{12}N_2O_4SNa$ 363.0410; Found 363.0404.

IV. General Procedure and Experimental Detail

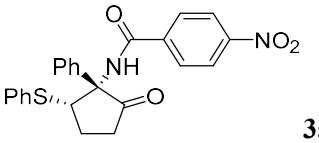


Substrate **1** or **9** (0.2 mmol), **2** (2.0 equiv.), $Pd(OAc)_2$ (10 mol %), 5,5'-dimethyl-2'-bipyridine (L3, 12 mol %) and DMF (0.4 *M*) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 80 °C for the desired time. Upon completion, the mixture was cooled to room temperature, the reaction mixture was treated with saturated $NaHCO_3$ and then extracted with DCM for three times. The combined organic layers were washed by brine and dried over Na_2SO_4, then concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, EtOAc/Petroleum ether (60−90 °C)) to give the desired compounds **3** or **8** or **10**.



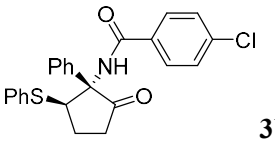
3aa-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (92% yield, 79 mg) as a yellow solid. mp: 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.44 – 7.36 (m, 4H), 7.25 – 7.12 (m, 3H), 6.60 (brs,1H), 5.09 – 5.02 (m, 1H), 3.00 – 2.85 (m, 1H), 2.72 – 2.63 (m, 1H), 2.61 –2.50 (m, 1H), 2.07 –1.91 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.4, 164.4, 149.8, 139.6, 134.9, 133.2, 133.0, 129.4, 129.1, 129.0, 128.5, 128.1, 127.5, 123.8, 70.3, 51.8, 31.0, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}N_2O_4S$ 433.1217; Found 433.1214.



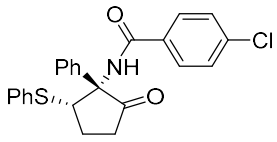
3aa-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (87% yield, 75 mg) as a yellow solid. mp: 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.49-7.47 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.21 (m, 4H), 5.41 (d, *J* = 4.3 Hz, 1H), 2.64 – 2.52 (m, 1H), 2.37 – 2.20 (m, 2H), 2.17 – 2.02 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.1, 165.4, 150.0, 139.2, 135.2, 135.0, 131.5, 129.4, 129.3, 129.0, 128.4, 127.5, 127.4, 123.9, 71.5, 51.4, 37.1, 26.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}N_2O_4S$ 433.1217; Found 433.1213.



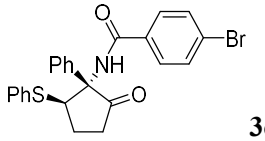
3ba-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (83% yield, 70 mg) as a yellow solid. mp: 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.41 – 7.30 (m, 4H), 7.26 – 7.25 (m, 1H), 7.24 – 7.14 (m, 3H), 6.51 (brs, 1H), 5.08 – 4.99 (m, 1H), 2.99 – 2.84 (m, 1H), 2.69 – 2.61 (m, 1H), 2.61 – 2.51 (m, 1H), 2.06 – 1.88 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.4, 165.9, 138.4, 135.5, 134.4, 131.9, 131.3, 129.2, 129.2, 128.9, 128.8, 128.5, 127.4, 127.1, 71.8, 49.4, 35.4, 24.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}ClNO_2S$ 422.0976; Found 422.0970.



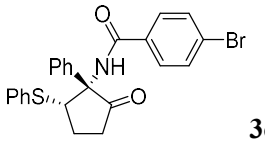
3ba-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (70% yield, 59 mg) as a yellow solid. mp: 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.55 – 7.47 (m, 2H), 7.44 – 7.37 (m, 4H), 7.37 – 7.31 (m, 4H), 7.28 (brs, 1H), 5.41 (d, *J* = 4.6 Hz, 1H), 2.76 – 2.54 (m, 1H), 2.41 – 2.19 (m, 2H), 2.14 – 2.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 166.3, 138.5, 135.6, 135.1, 132.0, 131.4, 129.3, 129.2, 129.0, 128.9, 128.6, 127.4, 127.2, 71.1, 51.6, 37.1, 26.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{21}ClNO_2S$ 422.0976; Found. 422.0978.



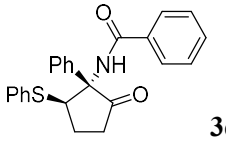
3ca-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (70% yield, 65 mg) as a white solid. mp: 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 4H), 7.46 – 7.38 (m, 5H), 7.38 – 7.32 (m, 2H), 7.21 – 7.11 (m, 3H), 6.63 (brs, 1H), 5.06 – 4.99 (m, 1H), 2.98 – 2.83 (m, 1H), 2.68 – 2.54 (m, 1H), 2.57 – 2.47 (m, 1H), 2.06 – 1.90 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.4, 166.4, 135.4, 135.4, 132.4, 131.9, 131.3, 129.2, 129.1, 128.8, 128.7, 127.4, 127.1, 126.8, 71.0, 51.5, 37.0, 26.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{20}BrNO_2SNa$ 466.0471; Found 466.0467.



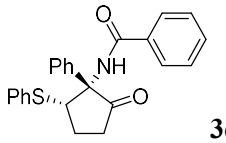
3ca-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (76% yield, 71 mg) as a white solid. mp: 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 6.3 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 3H), 7.31 (d, *J* = 6.4 Hz, 2H), 5.41 (d, *J* = 4.5 Hz, 1H), 2.68 – 2.55 (m, 1H), 2.46 – 2.20 (m, 2H), 2.18 – 2.03 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 165.4, 135.3, 133.3, 133.2, 132.8, 131.8, 129.3, 129.0, 128.9, 128.8, 127.9, 127.5, 126.5, 70.0, 52.0, 31.2, 23.7. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{20}BrNO_2SNa$ 466.0471; Found 466.0465.



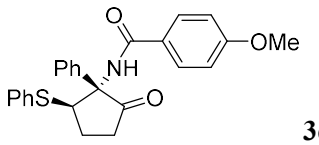
3da-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (81% yield, 62 mg) as a white solid. mp: 113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.56 – 7.45 (m, 6H), 7.45 – 7.38 (m, 4H), 7.24 – 7.12 (m, 3H), 6.78 (brs, 1H), 5.15 – 5.06 (m, 1H), 3.05 – 2.90 (m, 1H), 2.72 – 2.63 (m, 1H)., 2.61 – 2.51 (m, 1H), 2.12 – 1.95 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 166.2, 135.5, 133.9, 133.4, 133.1, 131.7, 129.2, 128.9, 128.6, 128.5, 127.7, 127.4, 127.2, 69.8, 52.1, 31.3, 23.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $[M + H]^+$ Calcd for $C_{24}H_{22}NO_2S$ 388.1366; Found 388.1369.



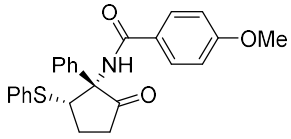
3da-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (83% yield, 64 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H), 7.61 – 7.54 (m, 2H), 7.51 – 7.44 (m, 3H), 7.42 – 7.35 (m, 2H), 7.39 – 7.36 (m, 1H), 7.38 – 7.30 (m, 2H), 7.32 – 7.29 (m, 2H), 7.30 – 7.24 (m, 2H), 5.38 (d, *J* = 4.5 Hz, 1H), 2.65 – 2.51 (m, 1H), 2.35 – 2.18 (m, 2H), 2.13 – 1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 166.2, 135.4, 133.9, 133.4, 133.1, 131.7, 129.2, 128.9, 128.6, 128.5, 127.7, 127.4, 127.2, 69.8, 52.1, 31.2, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}NO_2S$ 388.1366; Found 388.1365.



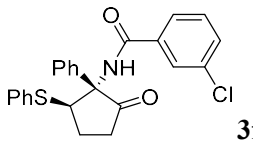
3ea-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (68% yield, 57 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.9 Hz, 2H), 7.49 – 7.38 (m, 5H), 7.36 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.22 – 7.09 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.58 (brs, 1H), δ 5.09 – 5.00 (m, 1H), 3.85 (s, 3H), 3.05 – 2.84 (m, 1H), 2.69 –2.48 (m, 2H), 2.08 – 1.89 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.9, 165.9, 162.5, 135.7, 133.6, 133.2, 129.2, 129.1, 128.9, 128.6, 127.8, 127.5, 126.3, 113.8, 69.9, 55.6, 52.3, 31.4, 23.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{23}NO_3SNa$ 440.1291; Found 440.1285.



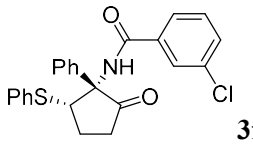
3ea-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (55% yield, 46 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.47 (d, *J* = 6.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.27 – 7.19 (m, 3H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.37 (d, *J* = 3.3 Hz, 1H), 3.79 (s, 3H), 2.67 – 2.48 (m, 1H·), 2.41 – 2.16 (m, 2H), 2.16 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 165.8, 162.4, 135.6, 133.5, 133.0, 129.2, 129.0, 128.8, 128.6, 127.7, 127.4, 126.2, 113.7, 69.7, 55.4, 52.2, 31.4, 23.8. (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_3S$ 418.1471; Found 418.1469.



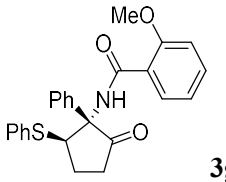
3fa-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (86% yield, 73 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.52 – 7.47 (m, 2H), 7.46 – 7.39 (m, 5H), 7.41 – 7.34 (m, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.12 (m, 3H), 6.58 (s, 1H), 5.11 – 4.99 (m, 1H), 3.03 – 2.84 (m, 1H), 2.70 – 2.59 (m, 1H), 2.59 – 2.49 (m, 1H), 2.07 – 1.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 166.1, 135.4, 135.4, 135.0, 134.8, 132.1, 131.4, 130.0, 129.3, 129.2, 128.9, 127.4, 127.3, 125.2, 71.1, 51.5, 37.0, 26.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}ClNO_2S$ 422.0976; Found 422.0982.



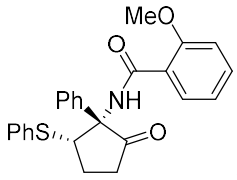
3fa-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (67% yield, 57 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 6.9 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.28 (m, 4H), 7.28 – 7.24 (m, 2H), 5.37 (d, *J* = 4.7 Hz, 1H), 2.64 – 2.51 (m, 1H), 2.36 – 2.26 (m, 1H), 2.27 – 2.18 (m, 1H), 2.12 – 2.01 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 165.0, 135.8, 135.2, 134.8, 133.2, 131.9, 129.9, 129.3, 129.0, 128.8, 127.9, 127.7, 127.5, 125.2, 70.1, 52.0, 31.2, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}ClNO_2S$ 422.0976; Found 422.0979.



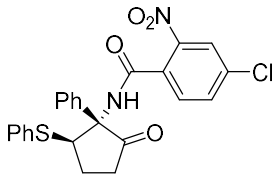
3ga-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (68% yield, 57 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (brs, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.41 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.20 – 7.05 (m, 4H), 6.95 (d, *J* = 8.3 Hz, 1H), 5.08 – 5.00 (m, 1H), 3.90 (s, 3H), 3.10 – 2.94 (m, 1H), 2.73 – 2.60 (m, 1H), 2.60 – 2.49 (m, 1H), 2.08 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.5, 164.6, 157.9, 136.5, 135.2, 133.6, 132.3, 131.3, 129.0, 128.8, 128.7, 127.2, 126.8, 121.5, 120.5, 111.4, 70.6, 56.2, 52.0, 37.3, 27.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_3S$ 418.1471; Found 418.1473.



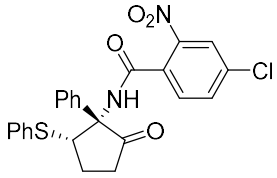
3ga-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (51% yield, 43 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.36 – 7.29 (m, 2H), 7.29 – 7.23 (m, 3H), 7.25 – 7.18 (m, 1H), 7.04 – 6.92 (m, 2H), 5.32 – 5.24 (m, 1H), 4.06 (s, 3H), 2.64 – 2.51 (m, 1H), 2.35 – 2.21 (m, 2H), 2.18 – 2.03 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 164.4, 158.0, 136.3, 133.9, 133.2, 133.0, 132.3, 129.1, 128.8, 128.3, 127.6, 127.4, 121.2, 121.0, 111.6, 70.3, 56.3, 52.6, 31.9, 24.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{23}NO_3SNa$ 440.1285; Found 440.1283.



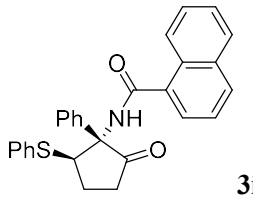
3ha-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (79% yield, 74 mg) as a yellow solid. mp: 191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.62 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.47 – 7.42 (m, 3H), 7.42 – 7.37 (m, 3H), 7.37 – 7.29 (m, 3H), 6.55 (brs, 1H), 5.01 – 4.92 (m, 1H).2.91 – 2.76 (m, 1H), 2.70 – 2.62 (m, 1H), 2.56 – 2.44 (m, 1H), 2.10 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 165.3, 147.3, 137.2, 135.2, 134.4, 133.8, 132.9, 130.3, 130.0, 129.4, 129.3, 129.0, 127.7, 127.2, 125.1, 71.1, 52.4, 37.1, 27.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}ClN_2O_4S$ 467.0827; Found 467.0829.



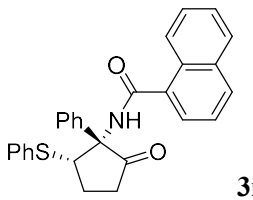
3ha-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (66% yield, 62 mg) as a yellow solid. mp: 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.60 – 7.56 (m, 3H), 7.56 – 7.52 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.31 (m, 4H), 7.07 (brs, 1H), 5.37 (d, *J* = 4.2 Hz, 1H), 2.63 – 2.45 (m, 1H), 2.45 – 2.25 (m, 1H), 2.25 – 2.17 (m, 1H), 2.12 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 164.2, 146.5, 136.5, 133.8, 133.4, 132.9, 130.7, 130.3, 129.4, 129.0, 128.9, 128.2, 127.5, 124.7, 70.2, 52.2, 30.8, 23.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}ClN_2O_4S$ 467.0827; Found 467.0836.



3ia-*anti*

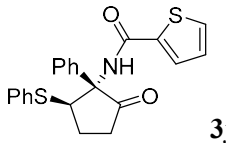
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (72% yield, 69 mg) as a yellow solid. mp: 152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.52 (m, 4H), 7.49 – 7.38 (m, 7H), 7.37 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 6.62 (brs, 1H), 5.33 – 5.21 (m, 1H), 3.14 – 2.98 (m, 1H), 2.84 – 2.71 (m, 1H), 2.71 – 2.59 (m, 1H), 2.18 – 1.96 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 169.6, 135.5, 133.7, 133.2, 131.6, 131.1, 130.3, 129.4, 129.1, 128.8, 128.4, 127.5, 127.5, 127.3, 126.6, 125.4, 125.3, 124.7, 71.5, 52.2, 37.2, 27.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{24}NO_2S$ 438.1522; Found 438.1523.



3ia-*syn*

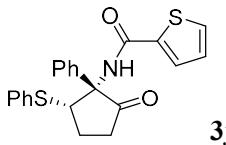
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (62% yield, 60 mg) as a yellow solid. mp: 159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.22 (m, 1H), 7.92 (d, *J* = 8.3 Hz,

1H), 7.89 – 7.82 (m, 1H), 7.72 – 7.64 (m, 3H), 7.64 – 7.58 (m, 2H), 7.55 – 7.47 (m, 2H), 7.47 – 7.43 (m, 3H), 7.41 – 7.33 (m, 4H), 7.18 (brs, 1H), 5.50 (d, J = 3.9 Hz, 1H), 2.72 – 2.57 (m, 1H), 2.42 – 2.24 (m, 2H), 2.24 – 2.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.5, 168.6, 135.7, 133.8, 133.7, 133.6, 133.4, 130.9, 130.4, 129.4, 129.0, 128.8, 128.2, 128.0, 127.5, 127.2, 126.5, 125.7, 125.3, 124.7, 70.1, 52.6, 31.5, 24.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{24}NO_2S$ 438.1522; Found 438.1526.



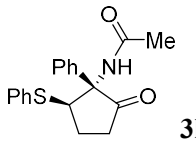
3ja-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (78% yield, 61 mg) as a yellow solid. mp:125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 7H), 7.39 (d, J = 7.5 Hz, 2H), 7.25 – 7.13 (m, 3H), 7.07 (d, J = 4.4 Hz, 1H), 6.56 (brs, 1H), 5.09 – 5.00 (m, 1H), 2.99 – 2.85 (m, 1H), 2.73 – 2.60 (m, 1H), 2.60 – 2.51 (m, 1H), 2.07 – 1.94 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.5, 161.8, 137.7, 135.6, 135.0, 131.4, 130.9, 129.2, 129.0, 128.9, 127.8, 127.4, 127.1, 70.9, 51.9, 37.0, 27.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_2S_2$ 394.0930; Found 394.0928.



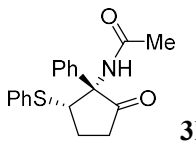
3ja-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (74% yield, 57 mg) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 3.8 Hz, 1H), 7.51 (d, J = 7.1 Hz, 2H), 7.46 (d, J = 4.9 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.35 – 7.30 (m, 3H), 7.28 (t, J = 3.5 Hz, 1H), 7.15 (brs, 1H), 7.09 – 7.02 (m, 1H). 5.38 (d, J = 4.7 Hz, 1H), 2.62 – 2.55 (m, 1H), 2.34 – 2.29 (m, 1H), 2.28 – 2.18 (m, 1H), 2.14 – 2.05 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.4, 160.8, 138.5, 135.3, 133.4, 133.2, 130.5, 129.2, 128.9, 128.7, 128.6, 127.8, 127.7, 127.5, 70.0, 52.2, 31.2, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_2S_2$ 394.0930; Found 394.0925.



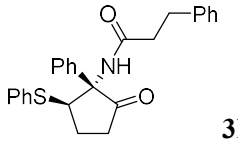
3ka-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (74% yield, 48 mg) as a white solid. mp: 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 5H), 7.34 – 7.31 (m, 2H), 7.31 – 7.28 (m, 1H), 7.27 – 7.18 (m, 2H), 6.12 (brs, 1H), 4.97 – 4.84 (m, 1H), 2.90 – 2.74 (m, 1H), 2.65 – 2.51 (m, 1H), 2.50 – 2.40 (m, 1H), 1.93 (s, 3H), 1.92 – 1.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 170.2, 135.4, 135.2, 131.2, 129.2, 129.1, 128.7, 127.4, 127.1, 70.7, 51.5, 37.1, 26.9, 23.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}NO_2S$ 326.1209; Found 326.1205.



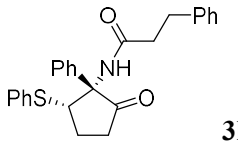
3ka-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (57% yield, 37 mg) as a white solid. mp: 135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 4H), 7.37 – 7.27 (m, 6H), 6.58 (brs, 1H), 5.24 (d, J = 4.3 Hz, 1H), 2.58 – 2.41 (m, 1H), 2.29 – 2.18 (m, 1H), 2.18 – 2.07 (m, 1H), 2.04 – 1.96 (m, 1H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 169.3, 135.6, 133.4, 133.1, 129.2, 128.8, 128.5, 127.8, 127.3, 69.7, 52.1, 31.3, 23.7, 23.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}NO_2S$ 326.1209; Found 326.1204.



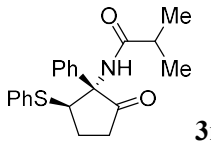
3la-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (91% yield, 76 mg) as a white solid. mp: 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 5H), 7.29 – 7.27 (m, 3H), 7.25 – 7.15 (m, 7H), 5.92 (brs, 1H), 4.95 – 4.86 (m, 1H), 2.97 – 2.77 (m, 3H), 2.64 – 2.53 (m, 1H), 2.53 – 2.42 (m, 3H), 2.00 – 1.84 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 172.1, 140.5, 135.5, 135.3, 131.3, 129.2, 129.1, 128.8, 128.8, 128.5, 127.3, 127.2, 126.5, 70.6, 51.7, 37.9, 37.1, 31.3, 27.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2S$ 416.1679; Found 416.1681.



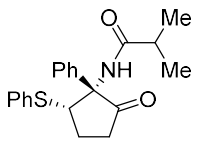
3la-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (82% yield, 68 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.44 – 7.43 (m, 2H), 7.33 – 7.27 (m, 6H), 7.20 – 7.17 (m, 2H), 7.15 – 7.12 (m, 1H), 7.08 (d, J = 6.9 Hz, 2H), 6.53 (brs, 1H), 5.23 (d, J = 4.7 Hz, 1H), 2.90–2.81 (m, 2H), 2.58 – 2.34 (m, 3H), 2.25 – 2.16 (m, 1H), 2.17 – 2.08 (m, 1H), 2.08 – 1.95 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 171.4, 140.8, 135.6, 133.6, 133.1, 129.3, 128.8, 128.5, 128.4, 127.8, 127.4, 126.2, 69.7, 52.1, 37.9, 31.4, 31.2, 23.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2S$ 416.1679; Found 416.1678.



3ma-*anti*

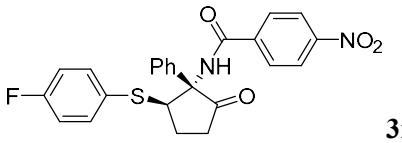
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (64% yield, 43 mg) as a yellow solid. mp: 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 5H), 7.37 (d, J = 7.2 Hz, 2H), 7.32 – 7.23 (m, 3H), 6.15 (brs, 1H), 4.94 – 4.89 (m, 1H), 2.94 – 2.84 (m, 1H), 2.66 – 2.46 (m, 2H), 2.42 – 2.35 (m, 1H), 2.05 – 1.89 (m, 1H), 1.15 – 1.12 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 177.0, 135.7, 135.4, 131.4, 129.2, 129.0, 128.7, 127.4, 127.1, 70.3, 52.1, 37.0, 35.2, 27.1, 19.5, 19.3. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{23}NO_2SNa$ 376.1342; Found 376.1346.



3ma-*syn*

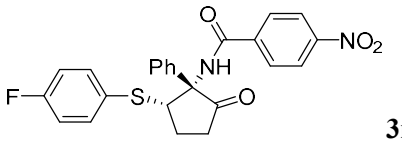
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (38% yield,

27 mg) as a yellow solid. mp:122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 5H), 7.36 – 7.30 (m, 2H), 7.30 – 7.18 (m, 3H), 6.06 (brs, 1H), 4.92 – 4.78 (m, 1H), 2.96 – 2.78 (m, 1H), 2.68 – 2.55 (m, 1H), 2.55 – 2.43 (m, 1H), 2.42 – 2.30 (m, 1H), 2.04 – 1.87 (m, 1H), 1.12 – 1.03 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.0, 177.0, 135.8, 135.5, 131.4, 129.2, 129.0, 128.8, 127.4, 127.2, 70.4, 52.2, 37.1, 35.3, 27.1, 19.5, 19.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{24}NO_2S$ 354.1522; Found 354.1516.



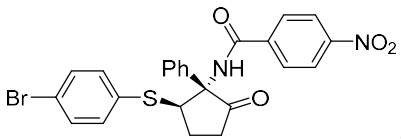
3na-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (88% yield, 79 mg) as a yellow solid. mp: 173 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.42 – 7.38 (m, 2H), 7.34 (dd, J = 8.5, 5.2 Hz, 2H), 6.90 (t, J = 8.5 Hz, 2H), 6.77 (brs, 1H), 4.94 – 4.86 (m, 1H), 2.89 – 2.80 (m, 1H), 2.71 – 2.58 (m, 1H), 2.55 – 2.45 (m, 1H), 2.05 – 1.92 (m, 1H). δ 212.0, 165.4, 162.4 (d, J = 248.5 Hz), 149.9, 139.0, 135.0, 134.4 (d, J = 8.1 Hz), 129.8, 129.4, 129.0, 128.3, 127.3, 124.0, 116.4 (d, J = 22.1 Hz), 71.3, 52.4, 37.0, 26.8. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}FN_2O_4SNa$ 473.0942; Found 473.0946.



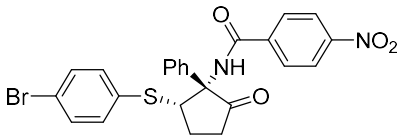
3na-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (62% yield, 56 mg) as a yellow solid. mp: 139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 7.0 Hz, 2H), 7.49 (dd, J = 8.7, 5.3 Hz, 2H), 7.42 – 7.29 (m, 4H), 7.01 (t, J = 8.6 Hz, 2H), 5.30 (d, J = 4.6 Hz, 1H), 2.64 – 2.51 (m, 1H), 2.41 – 2.29 (m, 1H), 2. 27 – 2.18 (m, 1H), 2.10 – 1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 164.4, 162.9 (d, J = 248.8 Hz), 149.8, 139.5, 135.9 (d, J = 8.2 Hz), 134.8, 129.1, 129.1, 128.4, 128.0 (d, J = 3.4 Hz), 127.4, 123.9, 116.6 (d, J = 21.9 Hz), 70.3, 52.5, 30.9, 23.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}FN_2O_4S$ 451.1122; Found 451.1117.



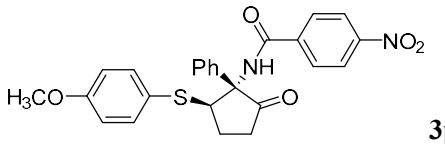
3oa-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (87% yield, 89 mg) as a yellow solid. mp: 172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.47 – 7.36 (m, 5H), 7.29 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.72 (brs, 1H), 5.04 – 4.97 (m, 1H), 2.94 – 2.82 (m, 1H), 2.69 – 2.60 (m, 1H), 2.57 – 2.47 (m, 1H), 2.03 – 1.90 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 165.4, 149.9, 138.9, 134.9, 134.1, 133.0, 132.3, 129.4, 129.0, 128.3, 127.4, 124.0, 121.4, 71.4, 51.4, 37.0, 26.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrN_2O_4S$ 511.0322; Found 511.0320.



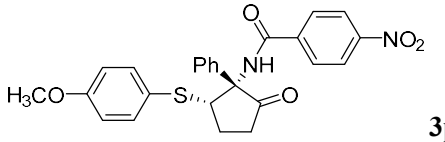
3oa-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (80% yield, 82 mg) as a yellow solid. mp: 175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.38 – 7.30 (m, 5H), 5.36 (d, *J* = 4.6 Hz, 1H), 2.63 – 2.48 (m, 1H), 2.40 – 2.19 (m, 2H), 2.14 – 2.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 164.3, 149.9, 139.4, 134.7, 134.7, 132.5, 132.3, 129.2, 129.1, 128.4, 127.4, 123.9, 122.4, 70.3, 51.9, 31.0, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrN_2O_4S$ 511.0322; Found 511.0318.



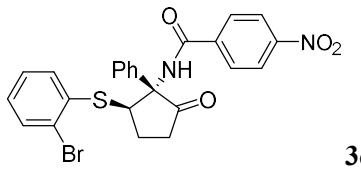
3pa-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (46% yield, 43 mg) as a yellow solid. mp: 173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.9 Hz, 2H), 7.49 – 7.42 (m, 5H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.65 (brs, 1H), δ 4.91 – 4.79 (m, 1H), 3.70 (s, 3H), 2.93 – 2.78 (m, 1H), 2.72 – 2.58 (m, 1H), 2.56 – 2.44 (m, 1H), 2.07 – 1.91 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 165.2, 159.6, 150.0, 139.2, 135.1, 134.7, 129.3, 129.0, 128.4, 127.5, 125.0, 123.9, 114.9, 71.3, 55.4, 52.9, 36.9, 26.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_5S$ 463.1322; Found 463.1324.



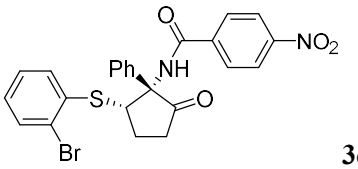
3pa-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (50% yield, 46 mg) as a yellow solid. mp: 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.20 (m, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 7.0 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.40 – 7.28 (m, 4H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.23 (d, *J* = 4.6 Hz, 1H), 3.79 (s, 3H), 2.65 – 2.49 (m, 1H), 2.41 – 2.26 (m, 1H), 2.25 – 2.11 (m, 1H), 2.08 – 1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 164.4, 160.2, 149.8, 139.7, 136.1, 135.0, 129.1, 129.0, 128.5, 127.5, 123.8, 123.1, 115.0, 70.4, 55.5, 52.4, 31.0, 23.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_5S$ 463.1322; Found 463.1329.



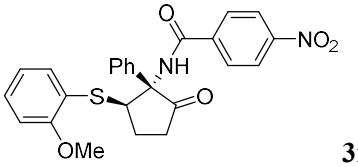
3qa-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/) to afford the title compound (69% yield, 71 mg) as a yellow solid. mp: 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.54 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.51 – 7.42 (m, 6H), 7.19 – 7.10 (m, 1H), 7.09 – 7.00 (m, 1H), 6.77 (brs, 1H), 5.04 – 4.90 (m, 1H), 3.01 – 2.82 (m, 1H), 2.76 – 2.63 (m, 1H), 2.63 – 2.51 (m, 1H), 2.17 – 1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 165.4, 150.0, 139.1, 135.8, 134.9, 133.7, 133.3, 129.5, 129.2, 128.9, 128.4, 128.1, 127.4, 127.2, 124.0, 71.0, 51.1, 37.0, 26.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrN_2O_4S$ 511.0322; Found 511.0318.



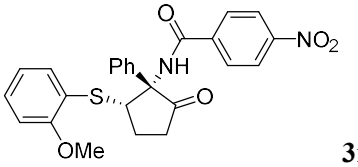
3qa-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/) to afford the title compound (95% yield, 97 mg) as a yellow solid. mp: 140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.62 – 7.57 (m, 3H), 7.53 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.42 (brs, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.29 – 7.27 (m, 1H), 7.13 – 7.07 (m, 1H), 5.52 (d, *J* = 4.6 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.43 – 2.25 (m, 2H), 2.09 – 1.96 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.1, 164.3, 149.8, 139.4, 134.7, 134.5, 134.4, 133.6, 129.3, 129.1, 129.0, 128.5, 128.3, 128.1, 127.5, 123.8, 70.2, 51.5, 31.3, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrN_2O_4S$ 511.0322; Found 511.0321.



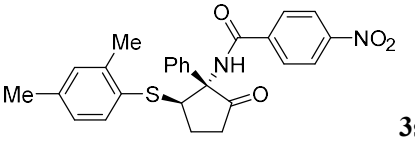
3ra-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (63% yield, 58 mg) as a yellow solid. mp: 135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.50 – 7.40 (m, 5H), 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.22 – 7.17 (m, 1H), 6.86 – 6.79 (m, 1H), 6.76 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.73 (brs, 1H), 5.10 – 4.97 (m, 1H), 3.67 (s, 3H), 2.93 – 2.79 (m, 1H), 2.73 – 2.58 (m, 1H), 2.58 – 2.47 (m, 1H), 2.11 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 164.8, 158.7, 149.8, 139.1, 135.0, 134.0, 129.4, 129.2, 128.9, 128.3, 127.3, 123.8, 122.0, 121.0, 111.2, 71.0, 55.8, 49.5, 36.9, 26.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{22}N_2O_5SNa$ 485.1142; Found 485.1140.



3ra-*syn*

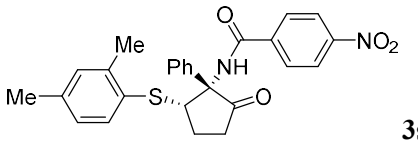
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (48% yield, 44 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.28 – 7.17 (m, 1H), 6.90 – 6.79 (m, 2H), 5.43 (d, *J* = 2.8 Hz, 1H), 3.86 (s, 3H), 2.64 – 2.50 (m, 1H), 2.40 – 2.19 (m, 2H), 2.07 – 1.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 164.2, 159.7, 149.7, 139.5, 135.3, 134.9, 129.9, 128.8, 128.7, 128.4, 127.4, 123.7, 121.2, 120.5, 111.2, 70.1, 55.9, 49.7, 31.6, 23.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_5S$ 463.1322; Found 463.1323.



3sa-anti

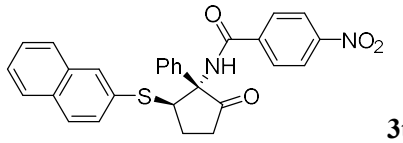
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (82% yield,

76 mg) as a yellow solid. mp: 162 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.53 – 7.38 (m, 5H), 7.27 (d, *J* = 7.9 Hz, 1H), 6.97 (brs, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 4.85 – 4.73 (m, 1H), 2.94 – 2.77 (m, 1H), 2.71 – 2.59 (m, 1H), 2.57 – 2.48 (m, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 2.13 – 2.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 165.2, 149.9, 140.2, 139.2, 138.1, 135.1, 133.7, 131.7, 130.1, 129.3, 129.0, 128.4, 127.5, 127.4, 123.9, 71.2, 51.5, 36.9, 26.9, 21.0, 20.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_4S$ 461.1530; Found 461.1528.



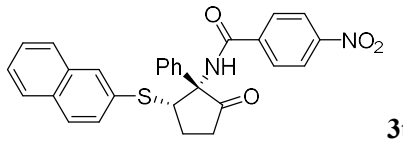
3sa-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (80% yield, 74 mg) as a yellow solid. mp: 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.27 (m, 5H), 7.03 (brs, 1H), 6.96 (dd, *J* = 7.9, 2.0 Hz, 1H), 5.29 (d, *J* = 4.6 Hz, 1H), 2.65 – 2.51 (m, 1H), 2.43 (s, 3H), 2.38 – 2.30 (m, 1H), 2.28 (s, 3H), 2.27 – 2.09 (m, 1H), 2.00 – 1.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 164.4, 149.8, 141.8, 139.7, 138.7, 135.0, 134.9, 131.7, 129.1, 129.0, 128.5, 128.1, 127.6, 127.5, 123.8, 70.5, 50.8, 31.0, 23.2, 21.2, 20.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{24}N_2O_4SNa$ 483.1373; Found 483.1380.



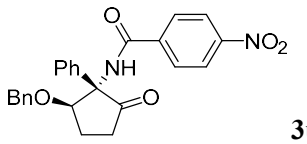
3ta-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (65% yield, 63 mg) as a yellow solid. mp: 164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.84 (s, 1H), 7.71 – 7.64 (m, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.52 – 7.44 (m, 3H), 7.44 – 7.37 (m, 5H), 6.59 (brs, 1H), 5.25 – 5.11 (m, 1H), 2.98 – 2.86 (m, 1H), 2.72 – 2.64 (m, 1H), 2.63 – 2.54 (m, 1H), 2.08 – 1.96 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.9, 165.2, 149.8, 138.8, 135.1, 133.7, 132.3, 132.2, 130.1, 129.4, 129.0, 128.9, 128.2, 127.7, 127.6, 127.3, 126.9, 126.5, 123.7, 71.6, 51.0, 37.0, 26.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}N_2O_4S$ 483.1373; Found 483.1380.



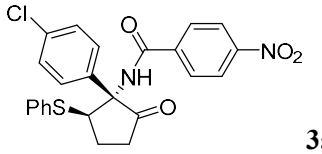
3ta-*syn*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (49% yield, 47 mg) as a white solid. mp: 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.91 (brs, 1H), 7.85 – 7.75 (m, 4H), 7.73 – 7.66 (m, 1H), 7.63 – 7.56 (m, 2H), 7.58 – 7.55 (m, 1H), 7.52 – 7.42 (m, 2H), 7.42 – 7.36 (m, 3H), 7.37 – 7.26 (m, 1H), 5.50 (d, *J* = 4.1 Hz, 1H), 2.68 – 2.53 (m, 1H), 2.42 – 2.32 (m, 1H), 2.32 – 2.22 (m, 1H), 2.19 – 2.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 164.3, 149.8, 139.3, 134.9, 133.7, 132.7, 132.3, 130.3, 130.1, 129.2, 129.1, 129.0, 128.3, 127.8, 127.5, 127.5, 126.8, 126.7, 123.7, 70.5, 51.4, 31.1, 23.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}N_2O_4S$ 483.1373; Found 483.1365.



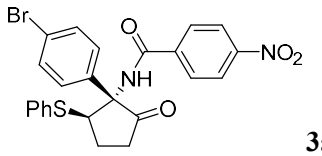
3ua-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (26% yield, 22 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.46 – 7.38 (m, 3H), 7.25 – 7.11 (m, 5H), 6.51 (brs, 1H), 5.27 – 5.17 (m, 1H), 4.75 (d, *J* = 12.2 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 2.83 – 2.69 (m, 1H), 2.69 – 2.55 (m, 1H), 2.53 – 2.41 (m, 1H), 1.97 – 1.81 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.8, 164.9, 150.0, 139.1, 138.4, 134.6, 129.1, 129.0, 128.6, 128.5, 128.4, 127.9, 127.7, 123.9, 80.0, 72.6, 71.0, 35.9, 24.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_5$ 431.1601; Found 431.1596.



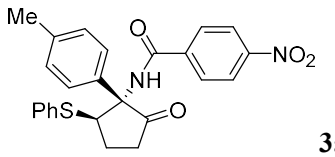
3ab-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (56% yield, 52 mg) as a yellow solid. mp: 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.45 – 7.37 (m, 4H), 7.27 – 7.19 (m, 3H), 6.55 (brs, 1H), 5.17 – 4.98 (m, 1H), 3.04 – 2.87 (m, 1H), 2.74 – 2.64 (m, 1H), 2.64 – 2.51 (m, 1H), 2.11 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5, 165.4, 150.0, 138.9, 135.5, 134.7, 133.4, 131.5, 129.4, 129.2, 129.0, 128.4, 127.5, 123.2, 71.0, 51.3, 36.9, 26.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}ClN_2O_4SNa$ 489.0646; Found 489.0643.



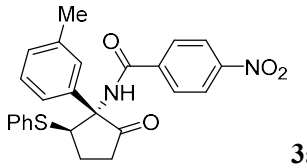
3ac-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (45% yield, 46 mg) as a yellow solid. mp: 184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.28 (m, 2H), 7.23 – 7.13 (m, 3H), 6.53 (brs, 1H), 5.09 – 4.99 (m, 1H), 3.02 – 2.84 (m, 1H), 2.74 – 2.50 (m, 2H), 2.12 – 1.87 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3, 165.5, 150.0, 138.9, 134.7, 134.0, 132.1, 131.5, 129.4, 129.3, 128.4, 127.5, 123.9, 123.7, 71.1, 51.3, 36.9, 26.7. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{20}BrN_2O_4S$ 511.0322; Found 511.0318.



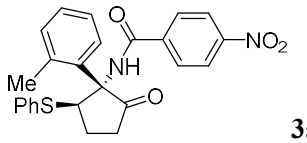
3ad-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (87% yield, 78 mg) as a white solid. mp: 156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.25 (m, 4H), 7.23 – 7.09 (m, 3H), 6.60 (brs, 1H), 5.08 – 4.98 (m, 1H), 2.99 – 2.81 (m, 1H), 2.71 – 2.62 (m, 1H), 2.60 – 2.50 (m, 1H), 2.40 (s, 3H), 2.11 – 1.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.1, 165.4, 150.0, 139.5, 139.3, 135.1, 132.2, 131.5, 129.7, 129.3, 128.4, 127.3, 127.2, 124.0, 71.3, 51.5, 37.0, 26.8, 21.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_4S$ 447.1373; Found 447.1370.



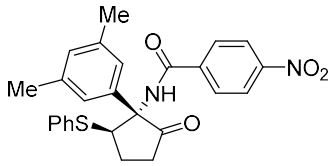
3ae-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (69% yield, 62 mg) as a yellow solid. mp: 152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 6.6 Hz, 2H), 7.34 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.20 (t, J = 8.2 Hz, 3H), 7.18 – 7.12 (m, 2H), 6.66 (brs, 1H), 5.07 – 5.00 (m, 1H), 2.95 – 2.83 (m, 1H), 2.71 – 2.62 (m, 1H), 2.59 – 2.49 (m, 1H), 2.42 (s, 3H), 2.05 – 1.92 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.2, 165.4, 149.9, 139.2, 138.8, 135.1, 135.0, 131.5, 130.2, 129.3, 128.8, 128.4, 127.9, 127.3, 124.5, 123.9, 71.4, 51.4, 37.1, 26.7, 21.9. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{22}N_2O_4SNa$ 469.1192; Found 469.1187.



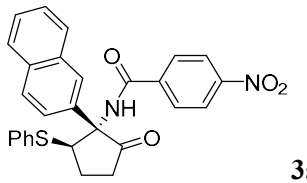
3af-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (26% yield, 23 mg) as a yellow solid. mp: 123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.9 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.26 – 7.16 (m, 4H), 7.16 – 7.09 (m, 1H), 6.95 (s, 1H), 5.07 – 4.96 (m, 1H), 3.01 – 2.81 (m, 1H), 2.78 (s, 3H), 2.77 – 2.60 (m, 2H), 2.28 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 165.1, 150.0, 139.4, 137.4, 135.5, 133.9, 133.6, 130.9, 129.3, 129.2, 128.7, 128.3, 127.1, 126.2, 124.1, 72.3, 52.7, 37.5, 27.9, 23.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{22}N_2O_4Na$ 469.1192; Found 469.1196.



3ag-*anti*

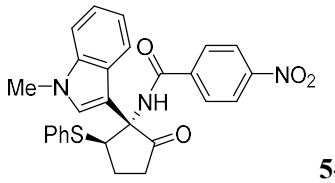
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (72% yield, 66 mg) as a yellow solid. mp: 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.46 – 7.35 (m, 2H), 7.25 – 7.12 (m, 3H), 7.07 (s, 1H), 6.96 (s, 2H), 6.63 (s, 1H), 5.08 – 4.97 (m, 1H), 2.97 – 2.80 (m, 1H), 2.74 – 2.62 (m, 1H), 2.58 – 2.47 (m, 1H), 2.38 (s, 6H), 2.08 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 165.4, 149.9, 139.3, 138.7, 135.1, 135.1, 131.5, 131.1, 129.3, 128.4, 127.3, 125.0, 124.0, 71.4, 51.3, 37.1, 26.7, 21.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}N_2O_4S$ 461.1530; Found 461.1528.



3ah-*anti*

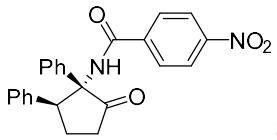
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (59% yield, 57 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.90 – 7.83

(m, 2H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.63 – 7.51 (m, 3H), 7.45 – 7.36 (m, 2H), 7.24 – 7.12 (m, 3H), 6.82 (brs, 1H), 5.15 – 5.08 (m, 1H), 3.02 – 2.89 (m, 1H), 2.83 – 2.67 (m, 1H), 2.67 – 2.50 (m, 1H), 2.15 – 1.95 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.9, 165.5, 149.9, 139.1, 135.1, 133.2, 132.7, 132.2, 131.4, 129.3, 128.8, 128.5, 128.4, 127.8, 127.4, 127.4, 127.3, 127.1, 124.6, 123.8, 71.6, 51.6, 37.1, 26.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{22}N_2O_4S$ 483.1373; Found 483.1369.



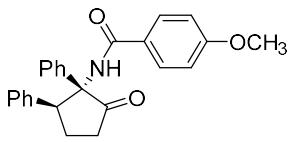
5-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (25% yield, 24 mg) as a red solid. mp:126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.50 (s, 1H), 7.44 – 7.36 (m, 3H), 7.35 – 7.28 (m, 1H), 7.23 – 7.10 (m, 4H), 6.87 (s, 1H), 5.17 – 5.05 (m, 1H), 3.86 (s, 3H), 2.92 – 2.72 (m, 1H), 2.66 – 2.53 (m, 2H), 2.43 – 2.29 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.1, 164.6, 149.9, 139.3, 137.4, 135.2, 131.7, 129.5, 129.3, 128.3, 127.4, 126.0, 123.9, 122.9, 121.4, 120.7, 110.1, 106.1, 68.9, 51.9, 35.7, 33.4, 27.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}N_3O_4SNa$ 508.1301; Found 508.1309.



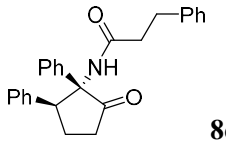
8a-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (85% yield, 68 mg) as a white solid. mp: 201 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.22 (m, 2H), 7.95 (t, *J* = 8.1 Hz, 2H), 7.34 – 7.19 (m, 2H), 7.19 – 7.12 (m, 4H), 6.78 (d, *J* = 7.4 Hz, 2H), 6.72 – 6.55 (m, 3H), 4.81 – 4.70 (m, 1H), 3.08 – 2.90 (m, 1H), 2.83 – 2.69 (m, 1H), 2.35 – 2.24 (m, 1H), 2.24 – 2.10 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.2, 165.4, 150.0, 139.6, 138.3, 135.8, 128.8, 128.7, 128.5, 128.4, 128.1, 127.4, 127.2, 124.1, 73.1, 48.3, 37.4, 22.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}N_2O_4$ 401.1496; Found 401.1489.



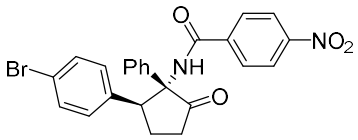
8b-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (57% yield, 44 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.17 – 7.11 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 6.9 Hz, 2H), 6.63 (d, *J* = 7.4 Hz, 2H), 6.49 (brs, 1H), 4.83 – 4.76 (m, 1H), 3.85 (s, 3H), 3.12 – 3.01 (m, 1H), 2.82 – 2.69 (m, 1H), 2.32 – 2.23 (m, 1H), 2.21 – 2.08 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.2, 166.7, 162.7, 138.7, 136.4, 129.1, 128.9, 128.4, 128.3, 128.0, 127.2, 127.1, 126.2, 114.0, 72.5, 55.6, 48.3, 37.5, 22.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_3$ 386.1751; Found 386.1755.



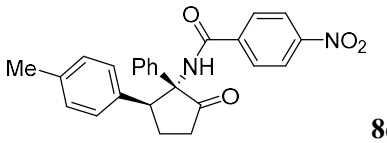
8c-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (73% yield, 71 mg) as a white solid. mp: 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 5H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.14 – 7.09 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 6.9 Hz, 2H), 6.48 – 6.40 (m, 2H), 6.00 (brs, 1H), 4.62 – 4.52 (m, 1H), 3.18 – 3.04 (m, 1H), 3.04 – 2.97 (m, 1H), 2.97 – 2.88 (m, 1H), 2.73 – 2.66 (m, 1H), 2.66 – 2.59 (m, 2H), 2.23 – 2.14 (m, 1H), 2.14 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.1, 172.0, 140.6, 138.4, 135.9, 128.8, 128.7, 128.6, 128.2, 128.1, 127.8, 127.1, 127.0, 126.4, 72.4, 48.4, 37.9, 37.4, 31.2, 22.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}NO_2$ 384.1958; Found 384.1961.



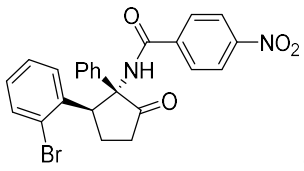
8d-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (86% yield, 82 mg) as a white solid. mp: 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.71 – 6.58 (m, 5H), 4.76 – 4.69 (m, 1H), 3.07 – 2.90 (m, 1H), 2.84 – 2.71 (m, 1H), 2.33 – 2.20 (m, 1H), 2.20 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.8, 165.5, 150.0, 139.3, 137.3, 135.5, 131.2, 130.5, 128.9, 128.7, 128.4, 127.1, 124.1, 121.4, 73.0, 47.8, 37.3, 22.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrN_2O_4$ 479.0601; Found 479.0607.



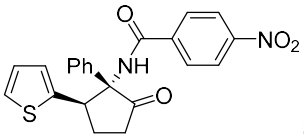
8e-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (89% yield, 74 mg) as a white solid. mp: 160 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.75 – 6.59 (m, 4H), 6.53 (brs, 1H), 4.77 – 4.69 (m, 1H), 3.15 – 2.91 (m, 1H), 2.81 – 2.72 (m, 1H), 2.31 (s, 3H), 2.29 – 2.21 (m, 1H), 2.18 – 2.07 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.4, 165.3, 149.9, 139.6, 137.0, 135.7, 135.1, 128.8, 128.7, 128.6, 128.4, 127.3, 124.0, 73.1, 47.9, 37.4, 22.8, 21.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_4$ 415.1652; Found 415.1653.



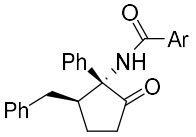
8f-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (67% yield, 64 mg) as a white solid. mp: 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 6.7 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.24 – 7.14 (m, 2H), 7.05 – 6.99 (m, 1H), 6.90 – 6.80 (m, 1H), 6.74 – 6.65 (m, 3H), 6.08 (d, *J* = 8.0 Hz, 1H), 5.34 – 5.25 (m, 1H), 3.22 – 3.07 (m, 1H), 2.83 – 2.70 (m, 1H), 2.35 – 2.24 (m, 1H), 2.21 – 2.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.4, 165.8, 149.8, 139.6, 138.1, 136.1, 133.0, 130.5, 128.8, 128.7, 128.6, 127.2, 126.6, 125.9, 123.9, 72.8, 47.4, 37.6, 24.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}BrN_2O_4$ 479.0601; Found 479.0602.



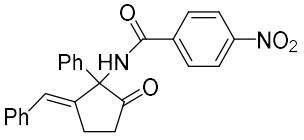
8g-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (78% yield, 63 mg) as a white solid. mp: 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 6.3 Hz, 1H), 6.89 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.65 (brs, 1H), 6.52 (d, *J* = 3.3 Hz, 1H), 4.99 – 4.93 (m, 1H), 3.08 – 2.93 (m, 1H), 2.81 – 2.68 (m, 1H), 2.54 – 2.39 (m, 1H), 2.22 – 1.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.1, 165.5, 150.0, 141.6, 139.6, 135.6, 128.9, 128.7, 128.4, 126.9, 126.8, 125.4, 124.4, 124.1, 72.8, 37.3, 24.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O_4S$ 407.1060; Found 407.1058.



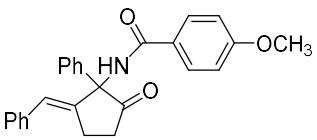
8h-*anti*

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (24% yield, 17 mg), **8h**-*anti*/**8h**-*syn* =5/1. **8h**-*anti*: a yellow solid. mp: 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.39 – 7.33 (m, 3H), 7.33 – 7.28 (m, 3H), 7.26 – 7.20 (m, 2H), 7.04 (d, *J* = 3.5 Hz, 1H), 6.46 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.97 – 3.78 (m, 1H), 3.04 – 2.92 (m, 1H), 2.44 – 2.21 (m, 2H), 2.14 – 2.02 (m, 1H), 1.92 – 1.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.9, 157.3, 147.8, 144.2, 139.8, 136.8, 129.3, 129.0, 128.6, 128.5, 127.4, 126.5, 114.7, 112.3, 70.2, 43.3, 34.9, 31.5, 20.6. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}NO_3Na$ 382.1414; Found 382.1412. **8h**-*syn:* a yellow solid. mp: 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 4H), 7.25 – 7.17 (m, 4H), 7.17 – 7.12 (m, 2H), 7.06 (d, *J* = 6.5 Hz, 2H), 6.92 (brs, 1H), 6.52 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.71 – 3.61 (m, 1H), 3.14 – 2.96 (m, 1H), 2.90 – 2.68 (m, 1H), 2.68 – 2.52 (m, 1H), 2.09 – 1.88 (m, 2H), 1.58 – 1.40 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 216.91, 158.07, 147.65, 144.28, 139.70, 136.88, 129.30, 129.02, 128.60, 128.41, 126.74, 126.20, 115.14, 112.50, 71.09, 45.67, 37.59, 37.40, 24.17. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}NO_3Na$ 382.1414; Found 382.1406.



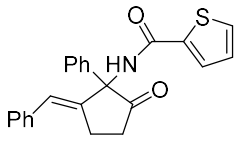
10a

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (90% yield, 74 mg) as a light yellow solid. mp: 155 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.72 – 7.62 (m, 2H), 7.46 – 7.35 (m, 7H), 7.32 – 7.27 (m, 1H), 6.98 (brs, 1H), 6.65 (brs, 1H), 3.42 – 3.30 (m, 1H), 3.03 – 2.90 (m, 1H), 2.83 – 2.73 (m, 1H), 2.59 – 2.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 163.94 150.0, 141.1, 138.9, 136.5, 136.4, 129.6, 129.5, 129.1, 128.6, 128.5, 127.9, 127.5, 126.3, 124.0, 70.8, 35.1, 25.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}N_2O_4$ 413.1496; Found 413.1491.



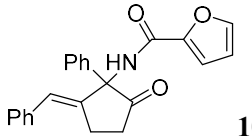
10b

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (40% yield, 32 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.69 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.48 – 7.32 (m, 7H), 7.29 – 7.22 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.79 (brs, 1H), 6.65 (brs, 1H), 3.85 (s, 3H), 3.46 – 3.30 (m, 1H), 2.99 – 2.89 (m, 1H), 2.88 – 2.78 (m, 1H), 2.59 – 2.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.2, 165.4, 162.7, 142.2, 137.2, 136.8, 129.4, 129.2, 129.1, 128.5, 128.0, 127.2, 125.9, 125.5, 114.0, 70.3, 55.6, 35.2, 25.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{24}NO_3$ 398.1751; Found 398.1753.



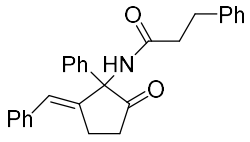
10c

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (75% yield, 56 mg) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.6 Hz, 2H), 7.54 (d, *J* = 3.7 Hz, 1H), 7.47 (d, *J* = 4.9 Hz, 1H), 7.44 – 7.32 (m, 7H), 7.29 – 7.20 (m, 1H), 7.07 – 7.03 (m, 1H), 6.80 (brs, 1H), 6.67 (brs, 1H), 3.42 – 3.25 (m, 1H), 3.05 – 2.86 (m, 1H), 2.85 – 2.66 (m, 1H), 2.59 – 2.40 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.9, 157.0, 147.1, 144.4, 141.4, 136.6, 134.1, 129.4, 129.2, 129.1, 128.5, 127.9, 127.3, 126.4, 115.5, 112.5, 70.0, 35.0, 25.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}NO_2S$ 374.1209; Found 374.1213.



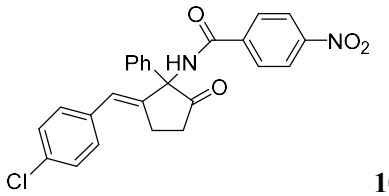
10d

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (80% yield, 57 mg) as a yellow solid. mp: 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.43 – 7.39 (m, 5H), 7.39 – 7.34 (m, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 7.09 (brs, 1H), 6.66 (brs, 1H), 6.51 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.44 – 3.29 (m, 1H), 3.06 – 2.85 (m, 1H), 2.85 – 2.65 (m, 1H), 2.65 – 2.39 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.9, 157.0, 147.1, 144.4, 141.4, 136.6, 134.0, 129.3, 129.2, 129.0, 128.4, 127.8, 127.2, 126.3, 115.5, 112.5, 70.0, 35.0, 25.4. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{19}NO_3Na$ 380.1257; Found 380.1260.



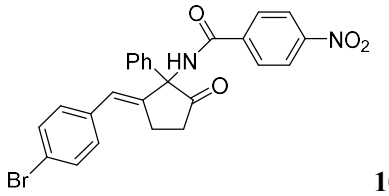
10e

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (77% yield, 61 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.42 – 7.32 (m, 7H), 7.31 – 7.23 (m, 2H), 7.26 – 7.16 (m, 4H), 6.44 (brs, 1H), 6.15 (brs, 1H), 3.38 – 3.24 (m, 1H), 3.07 – 2.92 (m, 2H), 2.91 – 2.79 (m, 1H), 2.79 – 2.65 (m, 1H), 2.65 – 2.52 (m, 2H), 2.52 – 2.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.1, 170.7, 141.9, 140.7, 136.9, 136.8, 129.3, 129.1, 129.0, 128.8, 128.6 128.5, 127.8, 127.2, 126.4, 125.9, 70.1, 37.4, 35.1, 31.5, 25.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{26}NO_2$ 396.1958; Found 396.1963.



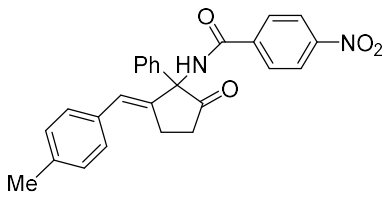
10f

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (70% yield, 63 mg) as a yellow solid. mp: 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.65 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.49 – 7.39 (m, 3H), 7.38 – 7.29 (m, 4H), 6.92 (s, 1H), 6.61 (s, 1H), 3.38 – 3.27 (m, 1H), 3.07 – 2.89 (m, 1H), 2.89 – 2.73 (m, 1H), 2.63 – 2.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 164.0, 150.1, 141.8, 138.7, 136.1, 135.0, 133.3, 130.3, 129.7, 129.6, 128.8, 128.6, 127.8, 125.1, 124.1, 70.8, 35.0, 25.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}ClN_2O_4$ 447.1106; Found 447.1103.



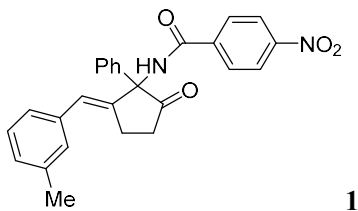
10g

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (71% yield, 70 mg) as a yellow solid. mp: 211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.70 – 7.58 (m, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.32 – 7.22 (m, 2H), 7.00 (s, 1H), 6.59 (s, 1H), 3.39 – 3.24 (m, 1H), 2.99 – 2.84 (m, 1H), 2.84 – 2.67 (m, 1H), 2.63 – 2.47 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 164.0, 150.0, 142.0, 138.7, 136.1, 135.3, 131.7, 130.6, 129.6, 129.5, 128.6, 127.8, 125.1, 124.0, 121.4, 70.8, 35.0, 25.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}BrN_2O_4$ 491.0601; Found Found 491.0600.



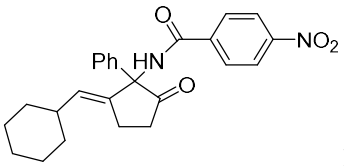
10h

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (82% yield, 70 mg) as a yellow solid. mp: 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.7 Hz, 2H), 7.65 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.10 (brs, 1H), 6.61 (brs, 1H), 3.39 – 3.28 (m, 1H), 2.98 – 2.87 (m, 1H), 2.79 – 2.70 (m, 1H), 2.55 – 2.44 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 163.9, 150.0, 140.0, 138.9, 137.4, 136.5, 133.7, 129.6, 129.4, 129.3, 129.0, 128.5, 127.9, 126.2, 124.1, 70.8, 35.1, 25.5, 21.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O_4$ 427.1652; Found 427.1654.



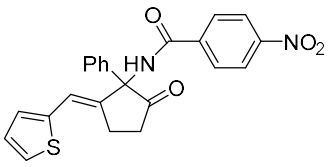
10i

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (94% yield, 80 mg) as a yellow solid. mp: 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.6 Hz, 2H), 7.95 (dd, *J* = 8.8, 1.8 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 12.2 Hz, 3H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.62 (brs, 1H), 3.42 – 3.28 (m, 1H), 3.07 – 2.83 (m, 1H), 2.81 – 2.65 (m, 1H), 2.57 – 2.44 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 164.0, 149.8, 140.9, 138.8, 138.7, 136.4, 136.3, 129.8, 129.4, 129.3, 128.5, 128.4, 128.2, 127.9, 126.3, 126.1, 123.9, 70.7, 35.0, 25.4, 21.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}N_2O_4$ 427.1652; Found 427.1649.



10j

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (71% yield, 59 mg) as a yellow solid. mp: 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.64 – 7.58 (m, 2H), 7.44 – 7.34 (m, 3H), 6.78 (brs, 1H), 5.49 (d, *J* = 9.2 Hz, 1H), 3.13 – 3.00 (m, 1H), 2.79 – 2.66 (m, 1H), 2.63 – 2.50 (m, 1H), 2.50 – 2.35 (m, 1H), 1.87 – 1.73 (m, 2H), 1.73 – 1.64 (m, 3H), 1.46 – 1.12 (m, 5H), 1.12 – 0.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 163.8, 149.8, 139.3, 136.4, 132.9, 129.4, 129.2, 128.4, 127.9, 124.0, 69.6, 37.4, 34.9, 33.1, 33.0, 26.1, 26.1, 25.8, 23.0. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}N_2O_4$ 419.1965; Found 419.1970.

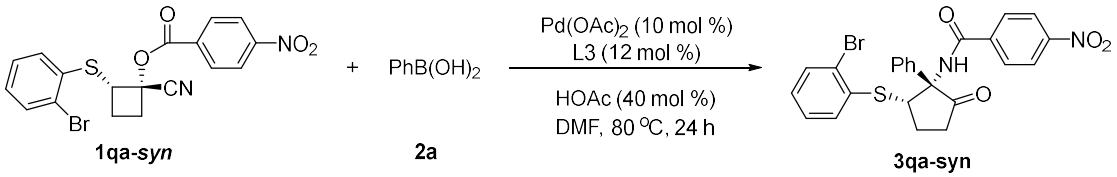


10k

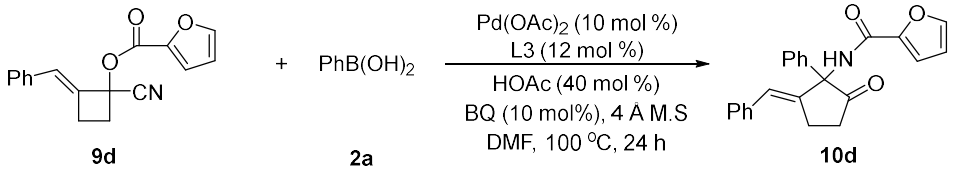
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (60% yield, 50 mg) as a yellow solid. mp: 152°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.61 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.37 (d, *J* = 5.0 Hz, 1H), 7.10 – 7.03 (m, 2H), 7.00 (brs, 1H), 6.85 (brs, 1H), 3.47 – 3.38 (m, 1H), 3.00 – 2.90 (m, 1H), 2.89 – 2.79 (m, 1H), 2.65 – 2.53 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.3, 164.0, 150.0, 140.1, 139.4, 138.7, 136.6, 129.6, 129.5, 128.6, 127.9, 127.7, 127.3, 126.3, 124.0, 119.9, 70.7, 34.7, 25.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{19}N_2O_4S$ 419.1060; Found 419.1056.

V. Scale-up Experimental Procedures and Synthetic Transformations

1) Scale-up Experimental Procedures

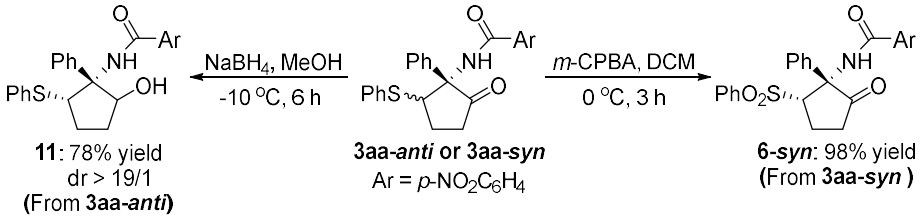


Compound **1q-*syn*** (1 mmol), **2a** (2.0 equiv.), $Pd(OAc)_2$ (10 mol %), 5,5'-dimethyl-2'-bipyridine (L3, 12 mol %) , BQ (10 mol %), 4Å M.S (400 mg) and DMF (0.4 M) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 80 °C for 24 h. Upon completion, the mixture was cooled to room temperature, the reaction mixture was treated with saturated $NaHCO_3$ and then extracted with DCM for three times. The combined organic layers were washed by brine and dried over Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C): 1/5) to give the desired compounds **3qa-*syn*** (419 mg, 82%).



Compound **9d** (1 mmol), **2a** (2.0 equiv.), $Pd(OAc)_2$ (10 mol %), 5,5'-dimethyl-2'-bipyridine (L3, 12 mol %) , BQ (10 mol %), 4Å M.S (400 mg) and DMF (0.4 M) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 80 °C for 24 h. Upon completion, the mixture was cooled to room temperature, the reaction mixture was treated with saturated $NaHCO_3$ and then extracted with DCM for three times. The combined organic layers were washed by brine and dried over Na_2SO_4, then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C): 1/3) to give the desired compounds **10d** (272 mg, 76%).

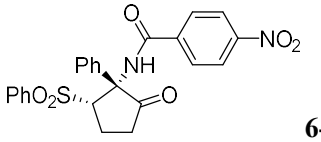
2) Synthetic Transformations



To a dried tube was added **3aa-*anti*** (0.1 mmol) and MeOH (0.5 *M*), then $NaBH_4$ (4 equiv.) was added at -10 °C.[8] The reaction mixture was stirred for 12 h in -10 °C. Upon completion, the mixture was concentrated under reduced pressure, and water was added. The aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound **11** (78% yield, 34 mg) as a yellow solid. mp: 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 8.22 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.47 – 7.33 (m, 8H), 7.13 (s, 1H), 5.19 (d, J = 1.3 Hz, 1H), 4.73 – 4.63 (m, 1H), 3.92 – 3.77 (m, 1H), 2.59 – 2.48 (m, 1H), 2.37 – 2.30 (m, 1H), 2.15 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 150.0, 138.9, 135.2, 135.0, 132.4,

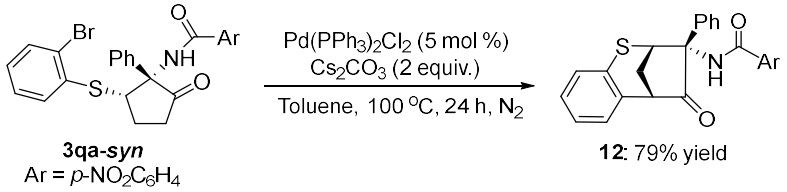
130.0, 128.6, 128.3, 128.2, 128.1, 128.0, 124.0, 79.8, 73.5, 58.1, 30.3, 29.3. HRMS (ESI) m/z: HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{24}H_{23}N_2O_4$ 435.1373; Found 435.1371.

To the solution of **3aa-*syn*** (0.1 mmol) in DCM (0.1 M) was added a solution of *m*-CPBA (2.3 equiv.) in DCM (0.1 *M*) dropwise at 0 °C and stirred for 3 h.[9] Then, the solution was diluted with a saturated solution of Na_2SO_3 (aq.) and extracted with DCM. The organic phase was washed with a saturated solution of $NaHCO_3$ (aq.) and brine, then dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel column (EtOAc/petroleum ether = 1/1) to afford the title compound **6-*syn*** (98% yield, 46 mg) as a white solid.



6-*syn*

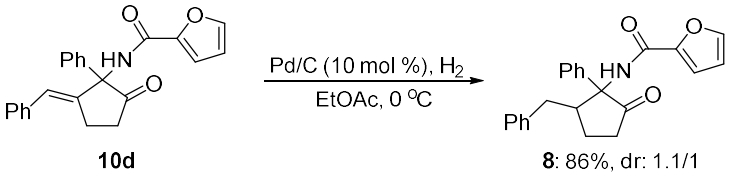
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (99% yield, 46 mg) as a white solid. mp: 249 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.60 – 7.48 (m, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.33 (d, *J* = 7.0 Hz, 1H), 5.09 – 4.99 (m, 1H), 2.87 – 2.66 (m, 2H), 2.50 – 2.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 164.8, 149.9, 138.9, 138.6, 134.5, 134.0, 129.4, 129.2, 129.1, 128.6, 128.5, 126.9, 123.7, 67.6, 64.3, 31.8, 20.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{24}H_{21}N_2O_6S$ 465.1115; Found 465.1119.



3qa-*syn*
Ar = *p*-$NO_2C_6H_4$

12: 79% yield

Compound **3qa-*syn*** (0.1 mmol), $Pd(PPh_3)_2Cl_2$ (5 mol %), Cs_2CO_3 (2 equiv.) and toluene (0.05 M) were placed in a sealed tube under nitrogen atmosphere.[10] The mixture was stirred at 100 °C for 24 h. Upon completion, the mixture was diluted with EtOAc and extracted with water. The organic layer was washed with brine, dried with Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel column (EtOAc/petroleum ether = 1/5) to afford the title compound **12** (79% yield, 34 mg) as red solid. mp: 176 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 6.7 Hz, 2H), 7.19 – 7.11 (m, 1H), 7.06 (d, *J* = 7.4 Hz, 2H), 5.27 – 5.23 (m, 1H), 3.70 (dd, *J* = 6.0, 2.4 Hz, 1H), 2.78 – 2.63 (m, 1H), 2.31 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 164.9, 149.8, 139.7, 136.4, 134.4, 132.0, 129.4, 129.2, 129.0, 128.6, 128.5, 127.3, 126.0, 124.8, 123.9, 75.6, 48.9, 46.1, 28.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{24}H_{19}N_2O_4S$ 431.1060; Found 431.1049.



10d

8: 86%, dr: 1.1/1

Pd/C (10 mol%) was placed in a sealed bottle, then the solution of substrate **7da** (0.1 mmol) in methanol (0.2 M) was added. The mixture was stirred at room temperature under H_2 atmosphere for 24 h. Upon completion, the mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica

gel, EtOAc/Petroleum ether (60-90 °C): 1/5) to give product **8h** (31 mg, 86%, *anti/syn* = 1.1/1). The NMR data were identical to **8h**.

V. References

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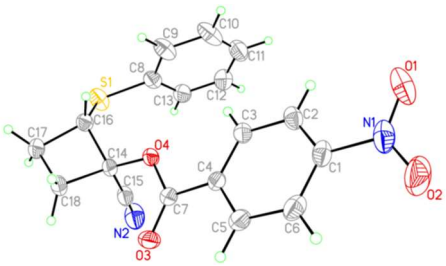
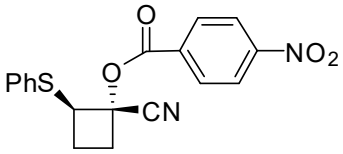
VI. Crystal Data and Structure Refinements

1. Compound 1a-*anti*:





1a-*anti*

CCDC number: 2207694

Table 1. Crystal data and structure refinement for **1a-*anti***.

Identification code	**1a-*anti***	
Empirical formula	C18 H14 N2 O4 S	
Formula weight	354.37	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.2811(6) Å	α= 90°.
	b = 17.0181(11) Å	β= 112.312(2)°.
	c = 12.0473(6) Å	γ = 90°.
Volume	1760.37(18) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	0.208 mm^{-1}	
F(000)	736	
Crystal size	0.200 x 0.180 x 0.170 mm^3	
Theta range for data collection	2.666 to 27.488°.	
Index ranges	-12<=h<=12, -22<=k<=22, -13<=l<=15	
Reflections collected	48870	
Independent reflections	4021 [R(int) = 0.0517]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9654 and 0.9595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4021 / 0 / 203	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1460	

R indices (all data)	R1 = 0.0985, wR2 = 0.1855
Extinction coefficient	0.016(2)
Largest diff. peak and hole	0.506 and -0.417 e.Å^{-3}

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

	x	y	z	U(eq)
C(1)	301(2)	4870(1)	-1614(1)	67(1)
C(2)	156(2)	4223(1)	-959(1)	65(1)
C(3)	1366(2)	4023(1)	107(1)	58(1)
C(4)	2720(2)	4471(1)	520(1)	55(1)
C(5)	2864(2)	5118(1)	-135(2)	68(1)
C(6)	1655(2)	5317(1)	-1202(2)	74(1)
C(7)	4054(3)	4274(2)	1620(2)	57(1)
C(8)	2544(2)	1906(1)	2963(2)	73(1)
C(9)	1140(3)	2313(1)	2551(2)	95(1)
C(10)	11(2)	2139(2)	1431(2)	115(2)
C(11)	287(3)	1560(2)	723(2)	113(2)
C(12)	1691(3)	1153(2)	1135(2)	115(1)
C(13)	2820(2)	1327(1)	2255(2)	90(1)
C(14)	4888(3)	3494(2)	3386(2)	53(1)
C(15)	6023(3)	2999(2)	3142(3)	72(1)
C(16)	4218(3)	3138(2)	4254(2)	62(1)
C(17)	5497(4)	3562(2)	5289(2)	71(1)
C(18)	5672(3)	4124(2)	4353(2)	63(1)
N(1)	-966(4)	5083(2)	-2707(2)	87(1)
N(2)	6936(4)	2618(3)	2993(3)	119(1)
O(1)	-2188(3)	4732(2)	-2977(2)	113(1)
O(2)	-758(4)	5626(2)	-3286(3)	134(1)
O(3)	5328(2)	4555(2)	1919(2)	84(1)
O(4)	3680(2)	3725(1)	2276(1)	56(1)
S(1)	4036(1)	2104(1)	4378(1)	91(1)

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

C(1)-C(2)	1.3900
C(1)-C(6)	1.3900
C(1)-N(1)	1.440(3)
C(2)-C(3)	1.3900
C(3)-C(4)	1.3900
C(4)-C(5)	1.3900
C(4)-C(7)	1.468(3)
C(5)-C(6)	1.3900
C(7)-O(3)	1.197(3)
C(7)-O(4)	1.351(3)
C(8)-C(9)	1.3900
C(8)-C(13)	1.3900
C(8)-S(1)	1.7733(19)
C(9)-C(10)	1.3900
C(10)-C(11)	1.3900
C(11)-C(12)	1.3900
C(12)-C(13)	1.3900
C(14)-O(4)	1.435(3)
C(14)-C(15)	1.463(4)
C(14)-C(16)	1.531(4)
C(14)-C(18)	1.547(3)
C(15)-N(2)	1.135(4)
C(16)-C(17)	1.536(4)
C(16)-S(1)	1.780(3)
C(17)-C(18)	1.534(4)
N(1)-O(1)	1.212(4)
N(1)-O(2)	1.216(4)

C(2)-C(1)-C(6)	120.0
C(2)-C(1)-N(1)	119.8(2)
C(6)-C(1)-N(1)	120.2(2)
C(3)-C(2)-C(1)	120.0
C(2)-C(3)-C(4)	120.0
C(5)-C(4)-C(3)	120.0
C(5)-C(4)-C(7)	117.59(14)
C(3)-C(4)-C(7)	122.39(15)
C(4)-C(5)-C(6)	120.0
C(5)-C(6)-C(1)	120.0

O(3)-C(7)-O(4)	122.9(2)
O(3)-C(7)-C(4)	125.3(2)
O(4)-C(7)-C(4)	111.73(19)
C(9)-C(8)-C(13)	120.0
C(9)-C(8)-S(1)	122.21(15)
C(13)-C(8)-S(1)	117.79(15)
C(10)-C(9)-C(8)	120.0
C(9)-C(10)-C(11)	120.0
C(12)-C(11)-C(10)	120.0
C(11)-C(12)-C(13)	120.0
C(12)-C(13)-C(8)	120.0
O(4)-C(14)-C(15)	109.8(2)
O(4)-C(14)-C(16)	111.63(19)
C(15)-C(14)-C(16)	114.8(2)
O(4)-C(14)-C(18)	119.3(2)
C(15)-C(14)-C(18)	112.4(2)
C(16)-C(14)-C(18)	87.51(19)
N(2)-C(15)-C(14)	177.7(3)
C(14)-C(16)-C(17)	88.8(2)
C(14)-C(16)-S(1)	121.7(2)
C(17)-C(16)-S(1)	117.7(2)
C(18)-C(17)-C(16)	87.81(19)
C(17)-C(18)-C(14)	88.3(2)
O(1)-N(1)-O(2)	123.8(3)
O(1)-N(1)-C(1)	118.5(3)
O(2)-N(1)-C(1)	117.6(3)
C(7)-O(4)-C(14)	116.80(18)
C(8)-S(1)-C(16)	99.86(12)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	69(2)	84(2)	46(1)	-1(1)	19(1)	23(2)
C(2)	60(2)	74(2)	55(1)	-13(1)	14(1)	9(1)

C(3)	58(1)	62(2)	52(1)	-2(1)	18(1)	3(1)
C(4)	53(1)	68(2)	45(1)	1(1)	21(1)	2(1)
C(5)	62(2)	86(2)	59(2)	12(1)	26(1)	0(1)
C(6)	78(2)	89(2)	61(2)	21(2)	34(2)	18(2)
C(7)	54(1)	70(2)	48(1)	3(1)	19(1)	-4(1)
C(8)	73(2)	67(2)	73(2)	17(2)	19(2)	-14(1)
C(9)	73(2)	78(2)	113(3)	1(2)	10(2)	-12(2)
C(10)	69(2)	100(3)	139(4)	16(3)	-1(2)	-18(2)
C(11)	90(3)	144(4)	86(3)	8(3)	12(2)	-34(3)
C(12)	113(3)	140(4)	91(3)	-20(3)	39(2)	-19(3)
C(13)	83(2)	107(3)	77(2)	10(2)	26(2)	-5(2)
C(14)	51(1)	58(1)	44(1)	-2(1)	11(1)	-1(1)
C(15)	61(2)	88(2)	59(2)	-14(2)	12(1)	6(2)
C(16)	60(2)	67(2)	53(1)	7(1)	15(1)	-4(1)
C(17)	75(2)	84(2)	49(1)	-1(1)	16(1)	-3(2)
C(18)	67(2)	65(2)	51(1)	-7(1)	14(1)	-7(1)
N(1)	89(2)	106(2)	54(1)	1(2)	14(1)	36(2)
N(2)	90(2)	154(3)	105(2)	-39(2)	26(2)	35(2)
O(1)	92(2)	119(2)	85(2)	-17(2)	-16(1)	17(2)
O(2)	122(2)	178(3)	87(2)	59(2)	23(2)	46(2)
O(3)	56(1)	120(2)	69(1)	22(1)	15(1)	-21(1)
O(4)	52(1)	66(1)	44(1)	5(1)	11(1)	-6(1)
S(1)	96(1)	71(1)	79(1)	24(1)	2(1)	-14(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Y.

	x	y	z	U(eq)
H(2)	-769	3917	-1241	78
H(3)	1268	3581	555	70
H(5)	3790	5424	147	82
H(6)	1753	5760	-1649	89
H(9)	952	2709	3035	114
H(10)	-948	2417	1149	138
H(11)	-485	1442	-43	136

H(12)	1879	757	651	138
H(13)	3779	1049	2536	108
H(16)	3192	3391	4118	74
H(17A)	5122	3817	5867	86
H(17B)	6430	3236	5707	86
H(18A)	6767	4237	4470	76
H(18B)	5063	4615	4248	76

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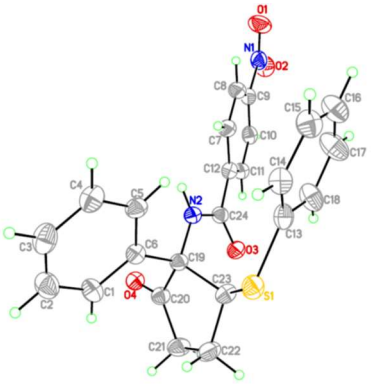
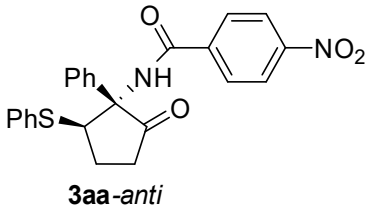
2. Compound 3aa-*anti*:





3aa-*anti*

CCDC number: 2207692

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

Identification code	3**aa-*anti***	
Empirical formula	C24 H20 N2 O4 S	
Formula weight	432.49	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P-42$_1$c	
Unit cell dimensions	a = 23.1883(6) Å	α= 90°.
	b = 23.1883(6) Å	β= 90°.
	c = 7.9822(3) Å	γ = 90°.
Volume	4292.0(3) Å^3	
Z	8	
Density (calculated)	1.339 Mg/m^3	
Absorption coefficient	0.184 mm^{-1}	
F(000)	1808	

Crystal size	0.200 x 0.180 x 0.170 mm^3
Theta range for data collection	2.699 to 25.574°.
Index ranges	-28<=h<=28, -28<=k<=28, -9<=l<=9
Reflections collected	60524
Independent reflections	4029 [R(int) = 0.0647]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9693 and 0.9640
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4029 / 0 / 282
Goodness-of-fit on F^2	1.098
Final R indices [I>2sigma(I)]	R1 = 0.0891, wR2 = 0.2481
R indices (all data)	R1 = 0.1224, wR2 = 0.4116
Absolute structure parameter	-0.3(5)
Extinction coefficient	0.018(9)
Largest diff. peak and hole	0.692 and -0.381 e.$Å^{-3}$

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

	x	y	z	U(eq)
S(1)	6987(1)	5005(1)	6459(4)	89(1)
O(1)	5837(5)	8022(6)	-936(15)	145(4)
O(2)	5627(5)	8678(5)	829(17)	138(4)
O(3)	6699(3)	6921(3)	7123(9)	88(2)
O(4)	8027(3)	6935(3)	7714(9)	83(2)
N(1)	5839(4)	8211(6)	485(16)	107(3)
N(2)	7281(3)	6488(3)	5221(10)	71(2)
C(1)	8564(5)	5686(4)	6499(17)	92(3)
C(2)	8997(6)	5359(6)	5783(19)	109(4)
C(3)	8933(6)	5136(5)	4220(20)	110(4)
C(4)	8444(5)	5245(4)	3357(17)	94(3)
C(5)	8004(5)	5574(4)	4036(11)	81(2)
C(6)	8054(4)	5793(4)	5652(12)	72(2)
C(7)	6642(5)	7052(5)	2620(14)	84(3)
C(8)	6392(5)	7374(5)	1383(15)	89(3)
C(9)	6121(5)	7880(5)	1807(16)	87(3)

C(10)	6097(5)	8070(5)	3439(17)	89(3)
C(11)	6347(5)	7742(4)	4685(15)	81(2)
C(12)	6620(4)	7234(5)	4293(13)	76(2)
C(13)	6580(4)	5120(4)	4592(17)	85(3)
C(14)	6695(5)	4754(5)	3276(16)	86(3)
C(15)	6369(5)	4777(5)	1830(20)	101(4)
C(16)	5949(6)	5180(6)	1670(20)	115(4)
C(17)	5838(7)	5546(7)	2970(30)	135(6)
C(18)	6139(5)	5517(6)	4450(20)	111(4)
C(19)	7555(4)	6119(4)	6452(10)	67(2)
C(20)	7773(4)	6485(4)	7937(12)	77(2)
C(21)	7658(7)	6196(5)	9558(14)	100(3)
C(22)	7399(7)	5610(6)	9078(16)	105(4)
C(23)	7128(5)	5709(4)	7352(13)	82(2)
C(24)	6873(4)	6877(4)	5667(11)	71(2)

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

S(1)-C(13)	1.784(13)
S(1)-C(23)	1.811(11)
O(1)-N(1)	1.216(17)
O(2)-N(1)	1.221(17)
O(3)-C(24)	1.235(11)
O(4)-C(20)	1.211(12)
N(1)-C(9)	1.459(17)
N(2)-C(24)	1.354(12)
N(2)-C(19)	1.450(12)
N(2)-H(2N)	0.8600
C(1)-C(2)	1.382(17)
C(1)-C(6)	1.385(15)
C(1)-H(1)	0.9300
C(2)-C(3)	1.36(2)
C(2)-H(2)	0.9300
C(3)-C(4)	1.35(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.386(15)
C(4)-H(4)	0.9300

C(5)-C(6)	1.391(13)
C(5)-H(5)	0.9300
C(6)-C(19)	1.522(13)
C(7)-C(8)	1.368(16)
C(7)-C(12)	1.401(15)
C(7)-H(7)	0.9300
C(8)-C(9)	1.374(17)
C(8)-H(8)	0.9300
C(9)-C(10)	1.376(19)
C(10)-C(11)	1.380(16)
C(10)-H(10)	0.9300
C(11)-C(12)	1.373(14)
C(11)-H(11)	0.9300
C(12)-C(24)	1.494(14)
C(13)-C(14)	1.377(16)
C(13)-C(18)	1.381(16)
C(14)-C(15)	1.383(19)
C(14)-H(14)	0.9300
C(15)-C(16)	1.356(19)
C(15)-H(15)	0.9300
C(16)-C(17)	1.36(2)
C(16)-H(16)	0.9300
C(17)-C(18)	1.37(2)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-C(20)	1.543(13)
C(19)-C(23)	1.550(13)
C(20)-C(21)	1.481(15)
C(21)-C(22)	1.534(17)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.532(18)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23)	0.9800

C(13)-S(1)-C(23)	106.8(5)
O(1)-N(1)-O(2)	121.8(12)

O(1)-N(1)-C(9)	119.2(13)
O(2)-N(1)-C(9)	118.9(14)
C(24)-N(2)-C(19)	121.4(8)
C(24)-N(2)-H(2N)	119.3
C(19)-N(2)-H(2N)	119.3
C(2)-C(1)-C(6)	121.1(12)
C(2)-C(1)-H(1)	119.4
C(6)-C(1)-H(1)	119.4
C(3)-C(2)-C(1)	120.7(14)
C(3)-C(2)-H(2)	119.7
C(1)-C(2)-H(2)	119.7
C(4)-C(3)-C(2)	119.1(12)
C(4)-C(3)-H(3)	120.4
C(2)-C(3)-H(3)	120.4
C(3)-C(4)-C(5)	121.6(12)
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-H(4)	119.2
C(4)-C(5)-C(6)	120.2(12)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(1)-C(6)-C(5)	117.3(10)
C(1)-C(6)-C(19)	122.2(9)
C(5)-C(6)-C(19)	120.5(9)
C(8)-C(7)-C(12)	120.5(10)
C(8)-C(7)-H(7)	119.7
C(12)-C(7)-H(7)	119.7
C(7)-C(8)-C(9)	118.9(11)
C(7)-C(8)-H(8)	120.6
C(9)-C(8)-H(8)	120.6
C(8)-C(9)-C(10)	121.6(11)
C(8)-C(9)-N(1)	118.4(12)
C(10)-C(9)-N(1)	120.0(12)
C(9)-C(10)-C(11)	119.3(11)
C(9)-C(10)-H(10)	120.3
C(11)-C(10)-H(10)	120.3
C(12)-C(11)-C(10)	120.1(11)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9

C(11)-C(12)-C(7)	119.5(10)
C(11)-C(12)-C(24)	119.3(9)
C(7)-C(12)-C(24)	121.2(9)
C(14)-C(13)-C(18)	119.5(12)
C(14)-C(13)-S(1)	116.3(8)
C(18)-C(13)-S(1)	124.0(10)
C(13)-C(14)-C(15)	120.6(10)
C(13)-C(14)-H(14)	119.7
C(15)-C(14)-H(14)	119.7
C(16)-C(15)-C(14)	119.6(12)
C(16)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2
C(15)-C(16)-C(17)	119.8(14)
C(15)-C(16)-H(16)	120.1
C(17)-C(16)-H(16)	120.1
C(16)-C(17)-C(18)	121.9(13)
C(16)-C(17)-H(17)	119.1
C(18)-C(17)-H(17)	119.1
C(17)-C(18)-C(13)	118.5(14)
C(17)-C(18)-H(18)	120.7
C(13)-C(18)-H(18)	120.7
N(2)-C(19)-C(6)	110.0(7)
N(2)-C(19)-C(20)	109.9(7)
C(6)-C(19)-C(20)	110.2(7)
N(2)-C(19)-C(23)	113.4(7)
C(6)-C(19)-C(23)	112.0(7)
C(20)-C(19)-C(23)	101.0(7)
O(4)-C(20)-C(21)	127.3(9)
O(4)-C(20)-C(19)	121.3(8)
C(21)-C(20)-C(19)	111.3(8)
C(20)-C(21)-C(22)	104.6(9)
C(20)-C(21)-H(21A)	110.8
C(22)-C(21)-H(21A)	110.8
C(20)-C(21)-H(21B)	110.8
C(22)-C(21)-H(21B)	110.8
H(21A)-C(21)-H(21B)	108.9
C(23)-C(22)-C(21)	104.7(10)
C(23)-C(22)-H(22A)	110.8

C(21)-C(22)-H(22A)	110.8
C(23)-C(22)-H(22B)	110.8
C(21)-C(22)-H(22B)	110.8
H(22A)-C(22)-H(22B)	108.9
C(22)-C(23)-C(19)	104.2(9)
C(22)-C(23)-S(1)	107.1(8)
C(19)-C(23)-S(1)	119.2(7)
C(22)-C(23)-H(23)	108.6
C(19)-C(23)-H(23)	108.6
S(1)-C(23)-H(23)	108.6
O(3)-C(24)-N(2)	122.1(9)
O(3)-C(24)-C(12)	121.2(9)
N(2)-C(24)-C(12)	116.7(8)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	88(2)	70(1)	108(2)	11(1)	-4(1)	-12(1)
O(1)	140(9)	193(12)	102(7)	18(8)	-35(6)	33(9)
O(2)	134(8)	114(7)	166(10)	39(7)	-20(7)	25(6)
O(3)	86(4)	104(5)	75(4)	-5(4)	13(3)	5(4)
O(4)	90(4)	79(4)	79(4)	-10(3)	0(3)	-7(3)
N(1)	80(6)	124(9)	117(8)	29(7)	-7(6)	1(6)
N(2)	71(4)	78(4)	63(4)	2(3)	2(3)	1(3)
C(1)	84(6)	87(6)	107(7)	-4(6)	-13(6)	8(5)
C(2)	100(8)	107(8)	119(9)	-7(7)	-5(7)	26(7)
C(3)	101(8)	87(7)	142(11)	-6(7)	29(8)	12(6)
C(4)	103(7)	77(5)	101(7)	-22(5)	22(6)	-1(5)
C(5)	92(6)	85(6)	65(5)	-7(4)	6(4)	-7(5)
C(6)	76(5)	66(4)	75(5)	-4(4)	2(4)	-4(4)
C(7)	80(6)	96(7)	77(6)	0(5)	2(5)	8(5)
C(8)	80(6)	111(8)	77(6)	8(6)	-6(5)	11(5)
C(9)	72(5)	99(7)	90(7)	7(5)	-1(5)	-9(5)
C(10)	80(6)	75(5)	111(8)	4(6)	-5(5)	-3(5)

C(11)	86(6)	76(5)	81(6)	-1(5)	0(5)	-2(5)
C(12)	72(5)	81(5)	76(5)	2(4)	3(4)	-2(4)
C(13)	73(5)	71(5)	111(7)	-6(5)	5(5)	-11(4)
C(14)	82(6)	75(5)	102(7)	-7(5)	4(5)	2(5)
C(15)	104(8)	87(6)	113(9)	-15(6)	-3(7)	-1(6)
C(16)	111(9)	110(8)	125(9)	-27(8)	-28(8)	9(8)
C(17)	125(11)	123(10)	157(14)	-27(10)	-53(11)	42(9)
C(18)	85(7)	108(8)	141(11)	-35(8)	-15(8)	23(6)
C(19)	74(5)	68(4)	60(4)	-2(4)	1(4)	-4(4)
C(20)	87(6)	75(5)	69(5)	-4(4)	-2(4)	-5(5)
C(21)	128(9)	107(8)	65(5)	-4(5)	-3(6)	-10(7)
C(22)	126(9)	108(8)	82(6)	22(6)	8(6)	-22(7)
C(23)	95(6)	75(5)	75(5)	6(4)	11(5)	-7(4)
C(24)	69(4)	74(5)	70(5)	-4(4)	-1(4)	0(4)

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

	x	y	z	U(eq)
H(2N)	7380	6460	4186	85
H(1)	8616	5837	7568	111
H(2)	9335	5292	6377	130
H(3)	9223	4911	3745	131
H(4)	8401	5095	2283	113
H(5)	7674	5649	3410	97
H(7)	6828	6709	2349	101
H(8)	6405	7253	273	107
H(10)	5915	8415	3700	106
H(11)	6331	7865	5793	97
H(14)	6994	4488	3363	103
H(15)	6438	4518	959	122
H(16)	5737	5207	689	138
H(17)	5551	5823	2847	162
H(18)	6047	5760	5339	133
H(21A)	7387	6419	10224	120

H(21B)	8011	6147	10191	120
H(22A)	7697	5317	9022	126
H(22B)	7110	5492	9885	126
H(23)	6760	5910	7501	98

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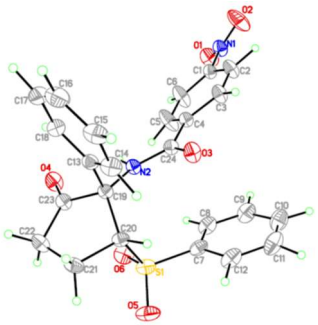
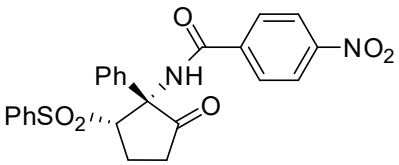
3. Compound 6-*syn*:





6-*syn*

CCDC number: 2207693

Table 1. Crystal data and structure refinement for **6-syn**.

Identification code	**6-syn**	
Empirical formula	C24 H20 N2 O6 S	
Formula weight	464.48	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 28.9553(14) Å	α= 90°.
	b = 9.2913(4) Å	β= 129.8880(10)°.
	c = 21.3693(18) Å	γ = 90°.
Volume	4411.2(5) Å^3	
Z	8	
Density (calculated)	1.399 Mg/m^3	
Absorption coefficient	0.191 mm^{-1}	
F(000)	1936	
Crystal size	0.200 x 0.180 x 0.170 mm^3	
Theta range for data collection	2.817 to 27.506°.	
Index ranges	-37<=h<=37, -12<=k<=12, -27<=l<=27	
Reflections collected	47966	
Independent reflections	5050 [R(int) = 0.0561]	

Completeness to theta = 25.242°	99.8 %
Max. and min. transmission	0.9682 and 0.9627
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5050 / 0 / 299
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1359
R indices (all data)	R1 = 0.0946, wR2 = 0.1723
Extinction coefficient	0.0023(4)
Largest diff. peak and hole	0.383 and -0.301 e.Å^{-3}

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

	x	y	z	U(eq)
C(1)	-911(1)	944(3)	7546(2)	56(1)
C(2)	-392(1)	212(3)	7904(2)	72(1)
C(3)	148(1)	929(3)	8448(2)	65(1)
C(4)	162(1)	2355(3)	8615(1)	50(1)
C(5)	-375(1)	3034(3)	8276(3)	100(1)
C(6)	-919(1)	2326(3)	7738(2)	99(1)
C(7)	1244(1)	3665(4)	11031(2)	63(1)
C(8)	656(1)	3222(4)	10604(2)	75(1)
C(9)	540(2)	1787(5)	10641(2)	90(1)
C(10)	1011(2)	821(5)	11089(2)	96(1)
C(11)	1594(2)	1282(5)	11521(2)	94(1)
C(12)	1719(1)	2706(4)	11499(2)	78(1)
C(13)	1558(1)	5295(3)	9206(1)	51(1)
C(14)	2092(1)	4531(3)	9607(2)	63(1)
C(15)	2352(1)	4334(4)	9249(2)	76(1)
C(16)	2093(2)	4903(4)	8505(3)	86(1)
C(17)	1567(2)	5661(4)	8095(2)	87(1)
C(18)	1295(2)	5849(3)	8444(2)	69(1)
C(19)	1244(1)	5512(3)	9574(1)	46(1)
C(20)	1711(1)	5581(3)	10509(1)	51(1)
C(21)	1992(1)	7095(3)	10669(2)	65(1)
C(22)	1488(1)	8064(3)	9996(2)	72(1)
C(23)	996(1)	7056(3)	9366(2)	59(1)

C(24)	760(1)	3097(3)	9169(1)	50(1)
N(1)	-1495(1)	225(3)	6956(2)	73(1)
N(2)	735(1)	4544(2)	9203(1)	49(1)
O(1)	-1937(1)	761(3)	6803(2)	101(1)
O(2)	-1508(1)	-851(3)	6637(2)	135(1)
O(3)	1234(1)	2439(2)	9560(1)	68(1)
O(4)	481(1)	7350(2)	8798(1)	80(1)
O(5)	1866(1)	5928(3)	11839(1)	93(1)
O(6)	838(1)	6287(3)	10538(1)	80(1)
S(1)	1395(1)	5494(1)	11011(1)	66(1)

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

C(1)-C(6)	1.352(4)
C(1)-C(2)	1.355(4)
C(1)-N(1)	1.470(3)
C(2)-C(3)	1.381(4)
C(3)-C(4)	1.366(4)
C(4)-C(5)	1.376(4)
C(4)-C(24)	1.499(3)
C(5)-C(6)	1.383(4)
C(7)-C(8)	1.382(4)
C(7)-C(12)	1.385(4)
C(7)-S(1)	1.761(3)
C(8)-C(9)	1.389(5)
C(9)-C(10)	1.380(5)
C(10)-C(11)	1.376(5)
C(11)-C(12)	1.380(5)
C(13)-C(18)	1.381(4)
C(13)-C(14)	1.387(4)
C(13)-C(19)	1.551(3)
C(14)-C(15)	1.388(4)
C(15)-C(16)	1.357(5)
C(16)-C(17)	1.368(5)
C(17)-C(18)	1.401(5)
C(19)-N(2)	1.453(3)
C(19)-C(20)	1.536(3)

C(19)-C(23)	1.537(4)
C(20)-C(21)	1.550(4)
C(20)-S(1)	1.804(2)
C(21)-C(22)	1.522(4)
C(22)-C(23)	1.503(4)
C(23)-O(4)	1.204(3)
C(24)-O(3)	1.219(3)
C(24)-N(2)	1.351(3)
N(1)-O(2)	1.197(4)
N(1)-O(1)	1.207(3)
O(5)-S(1)	1.435(2)
O(6)-S(1)	1.440(2)

C(6)-C(1)-C(2)	122.3(2)
C(6)-C(1)-N(1)	117.3(2)
C(2)-C(1)-N(1)	120.4(2)
C(1)-C(2)-C(3)	118.7(3)
C(4)-C(3)-C(2)	121.0(2)
C(3)-C(4)-C(5)	118.3(2)
C(3)-C(4)-C(24)	118.5(2)
C(5)-C(4)-C(24)	123.2(2)
C(4)-C(5)-C(6)	121.2(3)
C(1)-C(6)-C(5)	118.2(3)
C(8)-C(7)-C(12)	121.2(3)
C(8)-C(7)-S(1)	119.4(2)
C(12)-C(7)-S(1)	119.4(2)
C(7)-C(8)-C(9)	119.3(3)
C(10)-C(9)-C(8)	119.8(3)
C(11)-C(10)-C(9)	120.3(4)
C(10)-C(11)-C(12)	120.8(4)
C(11)-C(12)-C(7)	118.7(3)
C(18)-C(13)-C(14)	118.2(3)
C(18)-C(13)-C(19)	119.4(2)
C(14)-C(13)-C(19)	122.4(2)
C(13)-C(14)-C(15)	120.7(3)
C(16)-C(15)-C(14)	120.5(3)
C(15)-C(16)-C(17)	120.2(3)
C(16)-C(17)-C(18)	119.9(3)

C(13)-C(18)-C(17)	120.5(3)
N(2)-C(19)-C(20)	118.3(2)
N(2)-C(19)-C(23)	107.29(18)
C(20)-C(19)-C(23)	101.25(19)
N(2)-C(19)-C(13)	111.23(18)
C(20)-C(19)-C(13)	110.62(18)
C(23)-C(19)-C(13)	107.0(2)
C(19)-C(20)-C(21)	102.9(2)
C(19)-C(20)-S(1)	114.40(15)
C(21)-C(20)-S(1)	107.80(18)
C(22)-C(21)-C(20)	106.2(2)
C(23)-C(22)-C(21)	105.2(2)
O(4)-C(23)-C(22)	127.7(3)
O(4)-C(23)-C(19)	123.4(2)
C(22)-C(23)-C(19)	108.9(2)
O(3)-C(24)-N(2)	122.5(2)
O(3)-C(24)-C(4)	122.3(2)
N(2)-C(24)-C(4)	115.2(2)
O(2)-N(1)-O(1)	123.4(3)
O(2)-N(1)-C(1)	117.9(3)
O(1)-N(1)-C(1)	118.7(3)
C(24)-N(2)-C(19)	125.13(19)
O(5)-S(1)-O(6)	118.25(15)
O(5)-S(1)-C(7)	107.23(15)
O(6)-S(1)-C(7)	109.16(14)
O(5)-S(1)-C(20)	105.99(12)
O(6)-S(1)-C(20)	109.03(12)
C(7)-S(1)-C(20)	106.57(12)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	42(1)	51(1)	55(1)	-2(1)	22(1)	-7(1)
C(2)	53(2)	50(2)	94(2)	-12(1)	38(2)	-3(1)

C(3)	43(1)	51(1)	83(2)	-1(1)	33(1)	5(1)
C(4)	36(1)	50(1)	52(1)	-1(1)	23(1)	-1(1)
C(5)	40(2)	56(2)	144(3)	-29(2)	32(2)	-3(1)
C(6)	37(1)	58(2)	137(3)	-15(2)	25(2)	1(1)
C(7)	50(1)	94(2)	49(1)	8(1)	34(1)	2(1)
C(8)	51(2)	104(2)	70(2)	13(2)	38(2)	1(2)
C(9)	70(2)	112(3)	91(2)	17(2)	53(2)	-6(2)
C(10)	97(3)	107(3)	102(3)	27(2)	72(2)	1(2)
C(11)	84(2)	119(3)	93(2)	41(2)	63(2)	25(2)
C(12)	54(2)	115(3)	66(2)	19(2)	39(2)	10(2)
C(13)	49(1)	52(1)	51(1)	-10(1)	32(1)	-12(1)
C(14)	47(1)	76(2)	68(2)	-10(1)	38(1)	-5(1)
C(15)	64(2)	89(2)	87(2)	-29(2)	54(2)	-21(2)
C(16)	97(3)	94(2)	106(3)	-39(2)	82(2)	-38(2)
C(17)	125(3)	82(2)	78(2)	-15(2)	76(2)	-26(2)
C(18)	81(2)	66(2)	61(2)	-2(1)	46(2)	-4(2)
C(19)	33(1)	51(1)	44(1)	-2(1)	20(1)	-2(1)
C(20)	35(1)	68(2)	44(1)	-4(1)	22(1)	-6(1)
C(21)	51(2)	74(2)	62(2)	-20(1)	33(1)	-17(1)
C(22)	64(2)	57(2)	83(2)	-17(2)	42(2)	-11(1)
C(23)	48(1)	55(2)	63(2)	0(1)	31(1)	2(1)
C(24)	37(1)	54(1)	50(1)	1(1)	24(1)	-1(1)
N(1)	53(1)	61(2)	73(2)	-7(1)	25(1)	-13(1)
N(2)	32(1)	49(1)	50(1)	-1(1)	20(1)	-2(1)
O(1)	44(1)	101(2)	110(2)	-19(2)	27(1)	-13(1)
O(2)	82(2)	94(2)	157(3)	-66(2)	43(2)	-27(2)
O(3)	39(1)	62(1)	80(1)	7(1)	28(1)	6(1)
O(4)	56(1)	63(1)	86(1)	7(1)	29(1)	14(1)
O(5)	82(2)	141(2)	56(1)	-28(1)	44(1)	-27(2)
O(6)	64(1)	94(2)	97(2)	-5(1)	58(1)	9(1)
S(1)	50(1)	94(1)	56(1)	-9(1)	35(1)	-4(1)

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

	x	y	z	U(eq)

H(2)	-395	-864	7752	87
H(3)	542	422	8696	78
H(5)	-379	3971	8496	120
H(6)	-1333	2829	7525	119
H(8)	309	3921	10279	90
H(9)	43	1438	10245	109
H(10)	910	-260	11132	115
H(11)	1949	609	11928	112
H(12)	2158	3098	11875	93
H(14)	2304	4189	10194	75
H(15)	2811	3823	9586	91
H(16)	2323	4781	8277	103
H(17)	1336	6041	7498	104
H(18)	942	6333	8193	83
H(20)	2035	4737	10818	61
H(21A)	2186	7468	11243	78
H(21B)	2297	6948	10617	78
H(22A)	1619	8676	9715	86
H(22B)	1291	8694	10197	86
H(2N)	341	5040	8845	58