Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electrochemical cyclization of *N*-cyanamide alkenes with CF_3SO_2Na to access C, *N*- (bis)trifluoromethylated cyclic amidines and related compounds

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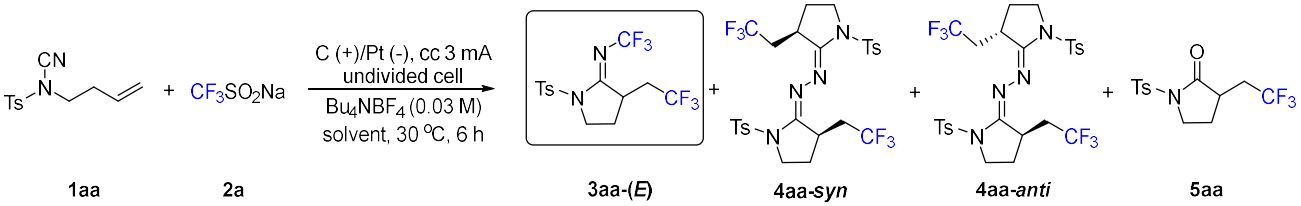
I. General Information

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

II. Reaction Conditions Screening

Table S1. Optimized reaction conditions: effect of solvent [a]

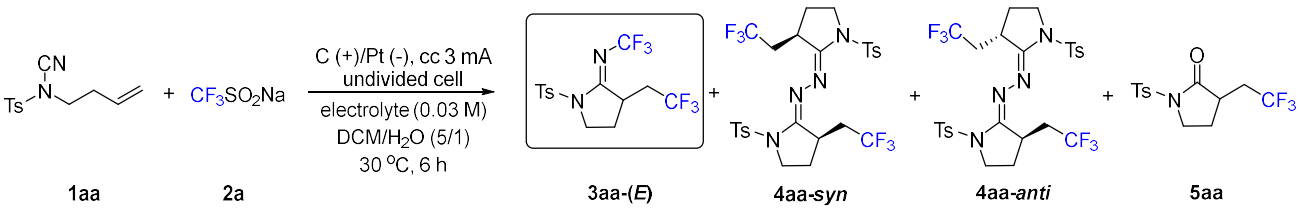


1aa 2a 3aa-(*E*) 4aa-*syn* 4aa-*anti* 5aa

Entry	Solvent	Yield (%) [b]			
		3aa	**4aa-*syn***	**4aa-*anti***	**5aa**
1	*DCM/H_2O (5/1)*	*30*	*17*	*16*	*17*
2	$CHCl_3$/H_2O (5/1)	28	10	10	13
3	THF/H_2O (5/1)	nd	nd	nd	0
4	dioxane/H_2O (5/1)	8	6	5	< 1
5	CH_3CN/H_2O (5/1)	28	12	14	< 1
6	Acetone/H_2O (5/1)	30	5	5	< 1
7	DMF/H_2O (5/1)	12	5	4	6
8	HFIP/H_2O (5/1)	27	0	0	0
9	CH_3OH/H_2O (5/1)	11	4	4	< 1
10	DCM/HFIP/H_2O (5/1/1)	30	14	13	7
11	DCM	24	5	3	0

[a] Reaction conditions: **1aa** (0.3 mmol), **2a** (0.9 mmol), Bu_4NBF_4 (0.3 mmol) and solvent (c = 0.03 *M*) in an undivided cell with graphite rod (Φ 6 mm) and Pt plate cathode (10 × 10 × 0.1 mm), constant current = 3.0 mA, 30 °C, 6 h. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethylbenzene as the internal standard.

Table S2. Optimized reaction conditions: effect of electrolyte [a]

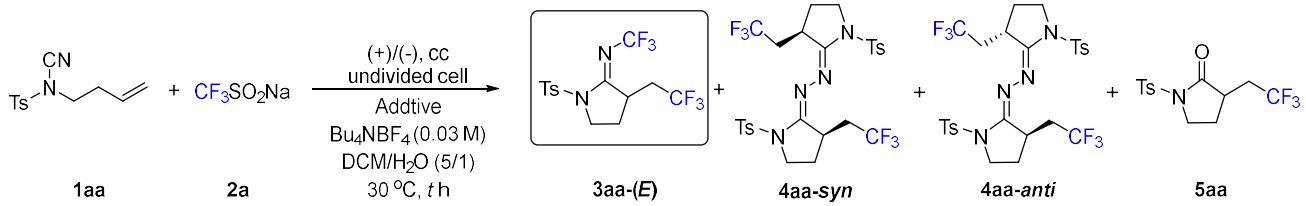


1aa 2a 3aa-(*E*) 4aa-*syn* 4aa-*anti* 5aa

Entry	Electrolyte	Yield (%) [b]			
		3aa	**4aa-*syn***	**4aa-*anti***	**5aa**
1	*Bu_4NBF_4*	*30*	*18*	*16*	*17*
2	$LiClO_4$	0	0	0	0
3	Bu_4NClO_4	24	17	19	13
4	Bu_4NPF_6	25	15	15	24
5	TBAB	16	8	9	18
6	Bu_4NOAc	16	3	3	8
7	Et_4NOTs	6	0	0	0

[a] Reaction conditions: **1aa** (0.3 mmol), **2a** (0.9 mmol), Bu_4NBF_4 (0.3 mmol) and DCM/H_2O (5/1) (c = 0.03 *M*) in an undivided cell with graphite rod (Φ 6 mm) and Pt plate cathode (10 × 10 × 0.1 mm), constant current = 3.0 mA, 30 °C, 6 h. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethylbenzene as the internal standard.

Table S3. Optimized reaction conditions: effects of current, electrode and additive [a]

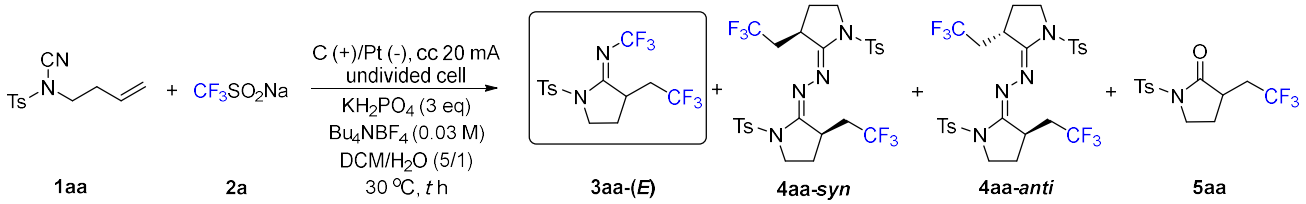


1aa 2a 3aa-(*E*) 4aa-*syn* 4aa-*anti* 5aa

Entry	+/-	I (mA)	*t* (h)	Additive	Yield (%) [b]			
					3aa	**4aa-*syn***	**4aa-*anti***	**5aa**
1	C/C	3	6	-	30	18	16	17
2	C/C	5	6	-	37	17	17	25
3	C/C	10	3	-	45	3	3	36
4	C/Pt	10	3	-	49	3	3	40
5	C/Fe	10	3	-	41	4	4	28
6	C-plate/Pt	10	3	-	43	3	4	37
7	RVC/Pt	10	3	-	30	15	15	18
8	C/Pt	10	3	TFA (3 eq)	48	3	3	39
9	C/Pt	10	3	AcOH (3 eq)	49	2	2	37
10	C/Pt	10	3	AcONa (3 eq)	48	2	2	34
11	C/Pt	10	3	KH_2PO_4 (3 eq)	54	2	3	31
12	C/Pt	10	3	K_3PO_4 (3 eq)	42	2	3	30
13	C/Pt	10	3	KH_2PO_4 (1 eq)	51	6	6	32
14	C/Pt	10	3	KH_2PO_4 (5 eq)	52	9	9	23
15 [c]	C/Pt	10	3	KH_2PO_4 (3 eq)	56 (52)	14	16	9
16 [c]	*C/Pt*	*20*	*3*	*KH_2PO_4 (3 eq)*	*65 (61)*	*0*	*0*	*24 (21)*
17 [c]	C/Pt	28	3	KH_2PO_4 (3 eq)	52	0	0	19

[a] Reaction conditions: **1aa** (0.3 mmol), **2a** (0.9 mmol), Bu_4NBF_4 (0.3 mmol), additive and DCM/H_2O (5/1) (c = 0.03 *M*) in an undivided cell with graphite rod (Φ 6 mm), C-plate (10 × 10 × 1 mm), Ni (10 × 10 × 1 mm), Fe (10 × 10 × 1 mm), RVC (100 PPI, 1 cm × 1 cm × 1 cm) and Pt plate cathode (10 × 10 × 0.1 mm) constant current, 30 °C. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. Isolated yields were given in parentheses. [c] **2a** (1.2 mmol).

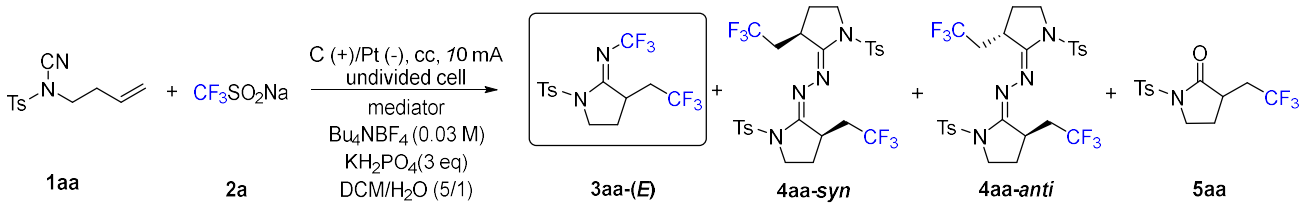
Table S4. Optimized reaction conditions: effects of other parameters [a]



Entry	*t* (h)	Additive	Yield (%) [b]			
			3aa	**4aa-*syn***	**4aa-*anti***	**5aa**
1	3	KH_2PO_4 (3 eq)	64	0	0	24
2	1	KH_2PO_4 (3 eq)	63	11	10	0
3	1.5	KH_2PO_4 (3 eq)	63	6	6	13
4	*2*	*KH_2PO_4 (3 eq)*	*64 (61)*	*0*	*0*	*22 (20)*
5 [c]	2	KH_2PO_4 (3 eq)	56 (52)	0	0	19 (15)
6 [d]	2	KH_2PO_4 (3 eq)	56	0	0	23
7 [e]	4	KH_2PO_4 (3 eq)	56 (54)	0	0	23 (20)
9 [f]	2	-	-	-	-	-
10 [g]	2	KH_2PO_4 (3 eq)	-	-	-	-
11 [h]	2	KH_2PO_4 (3 eq)	60	trace	trace	20

[a] Reaction conditions: **1aa** (0.3 mmol), **2a** (1.2 mmol), Bu_4NBF_4 (0.3 mmol), additive and DCM/H_2O (5/1) (c = 0.03 *M*) in an undivided cell with graphite rod (Φ 6 mm) and Pt plate cathode (10 × 10 × 0.1 mm), constant current = 20 mA, 30 °C. [b] Determined by ^1H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. Isolated yields were given in parentheses. [c] $(CF_3SO_2)_2Zn$ (0.6 mmol). [d] Under N_2. [e] Constant potential = 10 V (I = 17.6-14.3 mA). [f] The constant current mode cannot be supported due to the out of range of voltage when the reaction was performed with constant current = 20 mA without KH_2PO_4. [g] Without electricity. [h] IKA ElectraSyn 2.0. I = 20 mA: 1 h, 2.49 F·mol^{-1}; 1.5 h, 3.74 F·mol^{-1}; 2 h, 4.97 F·mol^{-1}; 3 h, 7.5 F mol^{-1}.

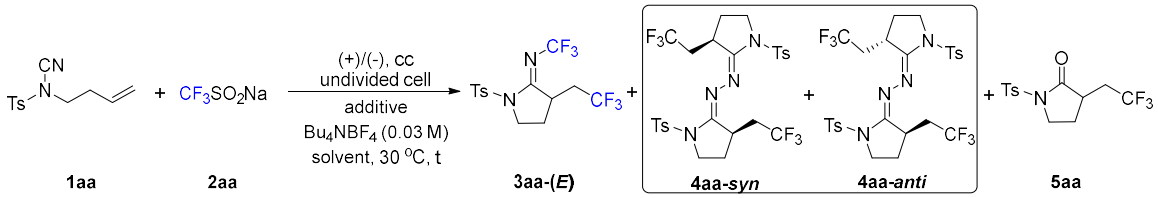
Table S5. Optimized reaction conditions: effect of mediator [a]



Entry	Mediator (mol %)	Yield (%) [b]			
		3aa	**4aa-*syn***	**4aa-*anti***	**5aa**
1	$Mn(OAc)_2$•$4H_2O$ (10)	52	15	15	11
2	$MnBr_2$•$4H_2O$ (20)	53	12	14	15
3	KBr (100)	36	13	14	15

[a] Reaction conditions: **1aa** (0.3 mmol), **2a** (1.2 mmol), Bu_4NBF_4 (0.3 mmol), KH_2PO_4 (3 equiv) and DCM/H_2O (5/1) (c = 0.03 *M*) in an undivided cell with graphite rod (Φ 6 mm) and Pt plate cathode (10 × 10 × 0.1 mm), constant current, 30 °C. [b] Determined by ^1H NMR analysis using 1,3,5-trimethylbenzene as the internal standard.

Table S6. Optimized reaction conditions for Dimer 4aa [a]

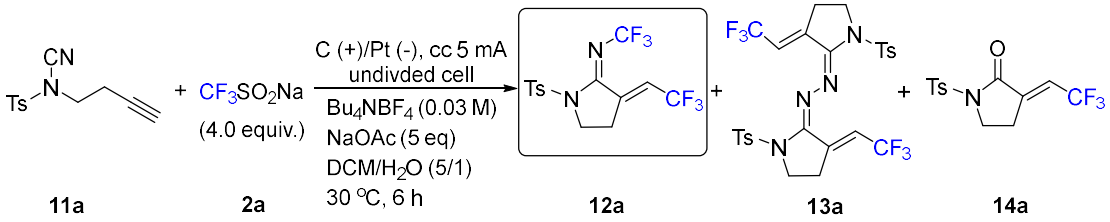


1aa 2aa 3aa-(*E*) 4aa-*syn* 4aa-*anti* 5aa

Entry	+/-	I (mA)	t (h)	Additive	Yield (%) [b]			
					3aa	**4aa-*syn***	**4aa-*anti***	**5aa**
1	C/C	3	6	-	30	17	18	16
2	C/C	2	8	-	28	17	18	16
3	C/C	1	16	-	23	18	19	21
4[c]	C/C	1	16	-	23	15	16	17
5	C/Pt	1	16	-	20	17	17	24
6	RVC/Pt	1	16	-	16	18	19	20
7	C-plate/Pt	1	16	-	12	15	15	12
8	C/C	1	16	KH_2PO_4 (3 equiv)	22	13	12	16
9	C/C	1	16	NaOAc (3 equiv)	25 (23)	21(20)	21(21)	3
10	C/C	1	16	NaOAc (1.5 equiv)	35	19	17	14
11	*C/C*	*1*	*16*	*NaOAc (5 equiv)*	*26 (24)*	*24 (22)*	*22 (21)*	*2*
12 [d]	C/C	1	16	NaOAc (5 equiv)	28	19	17	0
13 [e]	C/C	1	16	NaOAc (3 equiv)	16	21	22	0
14 [f]	*C/C*	*1*	*16*	*NaOAc (3 equiv)*	*25 (23)*	*24 (26)*	*25 (27)*	*0*

[a] Reaction conditions: **1aa** (0.3 mmol), **2a** (0.9 mmol, 3 equiv), Bu_4NBF_4 (0.3 mmol), KH_2PO_4 (3 equiv) and DCM/H_2O (5/1) (c = 0.03 M) in an undivided cell, constant current, 30 °C. [b] Determined by ^1H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. Isolated yields were given in parentheses. [c] **2a** (0.75 mmol, 2.5 equiv). [d] c = 0.015 *M*. [e] Under nitrogen atmosphere. [f] IKA ElectraSyn 2.0. I = 1 mA, 16 h, 1.99 F mol^{-1}.

Table S7. Optimized reaction conditions for 12a [a]

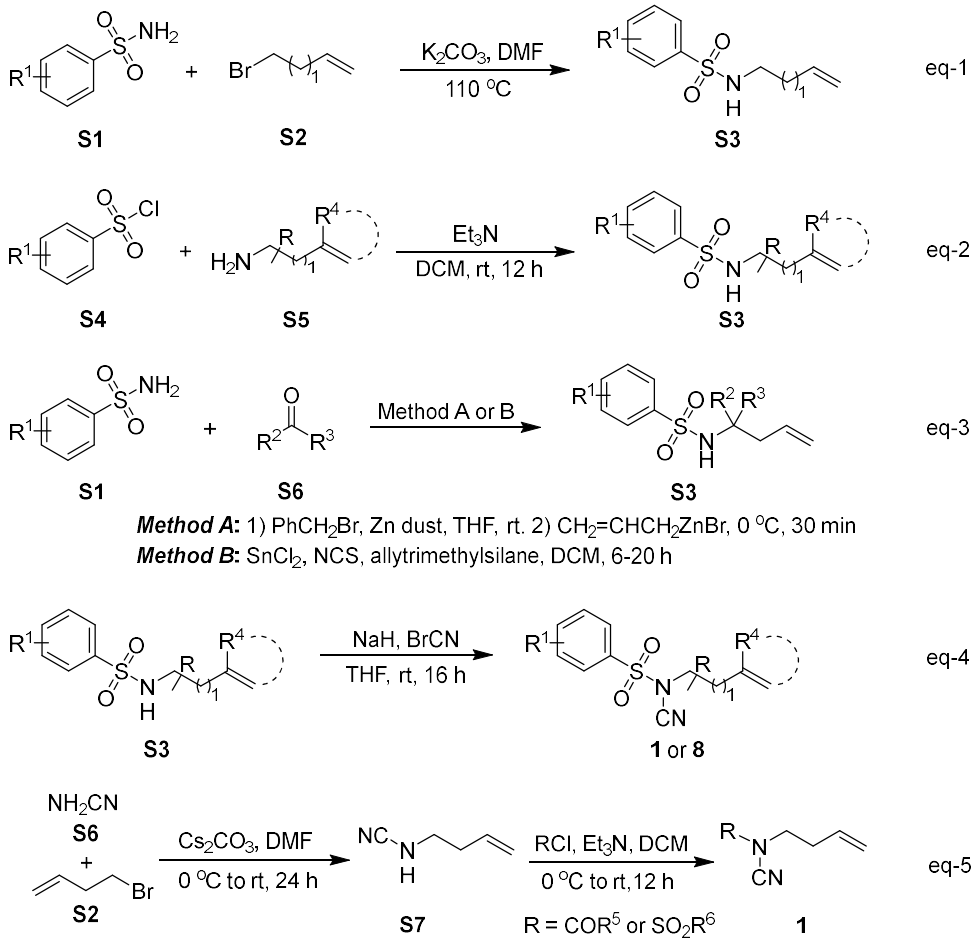


Entry	Deviation from standard conditions	Yield (%) [b]		
		12a	**13a**	**14a**
1	*none*	*41 (38)*	*< 1*	*4*
2	KH_2PO_4 (3 eq) instead of NaOAc (5 eq)	30	3	2
3	NaOAc (3 eq) instead of NaOAc (5 eq)	36	2	4
4	Bu_4NClO_4 instead of Bu_4NBF_4	39	2	5
5	Bu_4NPF_6 instead of Bu_4NBF_4	31	2	10
6	MeCN/H_2O (5/1) instead of DCM/H_2O (5/1)	12	0	0
7	Acetone/H_2O (5/1) instead of DCM/H_2O (5/1)	0	0	0
8	DCM/H_2O (2/1) instead of DCM/H_2O (5/1)	37	3	5
9	DCM/H_2O (10/1) instead of DCM/H_2O (5/1)	27	6	4
10	C(+)/Ni(-) instead of C(+)/Pt(+)	31	6	1
11	C(+)/C(-) instead of C(+)/Pt(+)	< 1	0	< 1
12	C-plate(+)/Pt(-) instead of C(+)/Pt(+)	24	9	1
13	RVC(+)/Pt(-) instead of C(+)/Pt(+)	21	4	1
14	2 mA, 8 h instead of 5 mA, 6 h	19	4	1
15	10 mA, 3 h instead of 5 mA, 6 h	37	4	3
16	cp = 5 V, 8 h instead of cc = 5 mA, 6 h	35	< 1	3
17	under nitrogen atmosphere	37	5	4
18	IKA ElectraSyn 2.0	39	< 1	< 1
19	No electricity	nd	nd	nd

[a] Reaction conditions: **11a** (0.3 mmol), **2a** (1.2 mmol), Bu_4NBF_4 (0.3 mmol), NaOAc (5 equiv) and DCM/H_2O (5/1) (c = 0.03 *M*) in an undivided cell with graphite rod (Φ 6 mm) and Pt plate cathode (10 × 10 × 0.1 mm), constant current = 5 mA, 30 °C, 6 h. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. Isolated yields were given in parentheses. **12a** (*E*-(C=N), *E*-(C=C))/ **12a** (*E*-(C=N), *Z*-(C=C)) > 19/1; **13a** as an exclusive (*E*)-form. I = 5 mA, 6 h, 3.73 F mol^{-1}.

III. Preparation of Substrates

1) Preparation of Substrates 1 and 8



Eq-1: [1]To a round-bottomed flask equipped with a stirring bar was charged with aryl sulfonamide **S1** (1.2 equiv.), K_2CO_3 (2 equiv.) and dry DMF (0.3 M). Bromide **S2** (1 equiv.) was slowly added and heated to 110 °C. The reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and added water and extracted with ethyl acetate. The combined organic layers were washed by brine and then dried over anhydrous Na_2SO_4, filtered, concentrated and eventually purified silica gel column chromatography with petroleum ether/ethyl acetate to give the desired compounds **S3**.

Eq-2: [2] To a solution of primary amine **S5** (1.0 equiv.) in DCM (0.5 M for amine) and triethylamine (1.5 equiv.) was added sulfonyl chloride **S4** (1.2 equiv.) in DCM (0.5 M for sulfonyl chloride) at 0 °C. The reaction mixture was warmed and stirred at room temperature. Upon completion, washed with HCl (0.5 M, aq.), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash silica column chromatography to afford Ts-substituted amine **S3**.

Eq-3: ***Method A***: [3] A Schlenk tube was charged with zinc dust (3 equiv.), evacuated, and backfilled with argon. Benzyl bromide (2 equiv.) and THF (0.5 M) were added. After the mixture was stirred at room temperature for 15 min, amide **S1** (1 equiv.) and aldehyde **S6** (1.5 equiv.) were successively added. The reaction mixture was stirred at room temperature until the amide disappeared as monitored by TLC. The mixture was quenched with brine and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel or recrystallization to provide the desired product benzene sulfonyl

imine. Then to a solution of benzene sulfonyl imine in THF (0.2 M) at 0 ºC, allyl zinc reagent was added slowly to the mixture. The reaction mixture was stirred at 0 ºC. Upon completion, quenched with saturated NH_4Cl and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel or recrystallization to provide the desired product **S3**.

***Method B*:** [4] To a solution of $SnCl_2$ (1.1 equiv.), $TsNH_2$ (1equiv.) and aldehyde or ketone (1 equiv.) in DCM (0.3 M) in an ice-bath, then NCS (1.1 equiv.) in DCM (0.2 M) was added, followed by allyl trimethylsilane (1.5 equiv.) The reaction mixture was stirred at room temperature. Upon completion, quenched with saturated NH_4Cl and extracted with DCM. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel or recrystallization to provide the desired product **S3**.

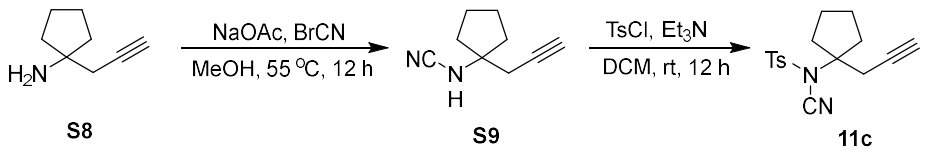
Eq-4: [5] A 50 mL flask with a stir-bar was charged with NaH (60% wt, 2 equiv.), which was then evacuated and backfilled with N_2 for three times. THF (0.3 M) was added and the solution was cooled to 0 ºC. Then a THF solution of sulfonamide **S3** (1 equiv.) was added slowly to the solution and the reaction was kept at room temperature for 30 min. Then cyanogen bromide (2 equiv.) was added into the reaction solution. After the addition, the reaction mixture was stirred at room temperature overnight. Upon completion, saturated ammonium chloride was added and the mixture was extracted with EtOAc, 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 to give the desired compounds **1** or **8**.

Eq-5: [6] To a flame-dried Schlenk tube equipped with a magnetic stir bar, a solution of NH_2CN (**S6**, 3 equiv.) in DMF (0.25 M) was added, Cs_2CO_3 (1 equiv) was added slowly in nitrogen atmosphere. Then **S2** (1 equiv.) was added dropwise *via* syringe to the solution at 0 °C. The tube was stirred at room temperature for 24 h. After completion, H_2O was added to the solution. Then the aqueous phase was extracted with EtOAc, 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 chromatography to give the desired compounds **S7**. To a solution of cyanamide **S7** (1 equiv.) and Et_3N (2 equiv.) in DCM (0.2 M) at 0 °C was slowly added acyl chloride (1.2 equiv.). [7] The resulting mixture was allowed to warm up to room temperature and stir for 12 h. Upon completion, the reaction mixture was quenched with H_2O and the aqueous phase was extracted with DCM. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography to give the desired substrates.

Substrates**1aa-1ar**, **1aw** and **8i** were prepared according to the procedures of eq-1 and eq-4. Substrates **8a-8d**, **8k-8n**, were prepared according to the procedures of eq-2 and eq-4. Substrates **8e-8h**, **8j** were prepared according to the procedures of eq-3 and eq-4. Substrates **1as-1av**, **1ba**, **1ca**, **1fa**, **1ga** were prepared according to the procedures of eq-5.

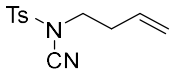
2) Preparation of Substrates 11

Substrates **11a** was prepared according to the known procedures[8] and similar procedure eq-4. Substrate **11b** was prepared according to the similar procedures of eq-3 and eq-4, and substrate **11d** was prepared according to the similar procedures of eq-2 and eq-4. Substrate **11c** was prepared according to the following procedures.



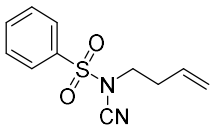
S8 **S9** **11c**

A solution of BrCN (1.2 equiv.) in MeOH (0.3 M) was slowly added to a mixture of aniline **S-8** [9] (1 equiv.) and NaOAc (3 equiv.) in MeOH (0.3 M) at 0 °C. The reaction mixture was stirred for 1 h, then was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was neutralized with saturated aqueous $NaHCO_3$ and concentrated to a small volume. The residue was taken up to water and extracted with DCM. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The product **S9** was purified by flash column chromatography. To a solution of primary amine **S9** (1.0 equiv.) in DCM (0.5 M for amine) and triethylamine (1.5 equiv.) was added tosyl chloride (1.2 equiv.) in DCM (0.5 M for TsCl) at 0 °C. The reaction mixture was warmed and stirred at room temperature. Upon completion, washed with HCl (1 M, aq.), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by flash silica column chromatography to afford **11c**.



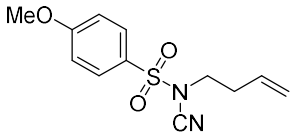
1aa

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/6) to afford the title compound (91% yield, 228 mg) as white solid, mp: 40 - 41 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.63 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.15 – 5.06 (m, 2H), 3.44 (t, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 2.40 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.56, 133.83, 132.09, 130.54, 127.96, 119.26, 108.57, 49.55, 32.17, 21.86. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}N_2NaO_2S$ 273.0668; Found 273.0669.



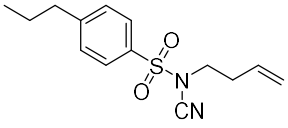
1ab

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (91% yield, 215 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.9 Hz, 2H), 5.62 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.14 – 5.06 (m, 2H), 3.47 (t, *J* = 7.2 Hz, 2H), 2.40 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.81, 135.12, 131.97, 129.95, 127.85, 119.30, 108.35, 49.62, 32.11. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{13}N_2O_2S$ 237.0692; Found 237.0684.



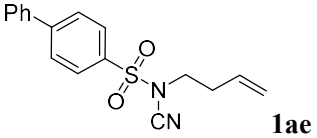
1ac

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (94% yield, 250 mg) as white solid, mp: 48 - 49 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 5.63 (ddt, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.15 – 5.07 (m, 2H), 3.91 (s, 3H), 3.43 (t, *J* = 7.2 Hz, 2H), 2.39 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.88, 132.16, 130.30, 127.89, 119.16, 115.10, 108.71, 56.01, 49.39, 32.12. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}N_2NaO_3S$ 289.0617; Found 289.0607.



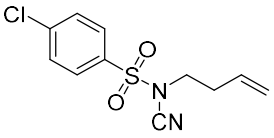
1ad

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (91% yield, 253 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 5.62 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.14 – 5.04 (m, 2H), 3.45 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.40 (q, *J*= 7.0 Hz, 2H), 1.74 – 1.63 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.08, 133.91, 132.06, 129.90, 127.89, 119.12, 108.50, 49.47, 37.97, 32.07, 24.10, 13.68. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}N_2O_2S$ 279.1162; Found 279.1158.



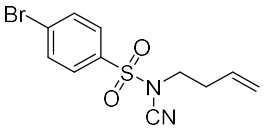
1ae

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (60% yield, 187 mg) as white solid, mp: 62 - 63 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 6.9 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.50 – 7.42 (m, 1H), 5.66 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.22 – 4.99 (m, 2H), 3.51 (t, *J* = 7.2 Hz, 2H), 2.44 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.06, 138.56, 135.05, 132.01, 129.30, 129.17, 128.41, 127.47, 119.33, 108.46, 49.62, 32.17. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}N_2O_2S$ 313.1005; Found 313.0998.



1af

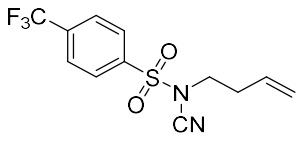
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (91% yield, 246 mg) as white solid, mp: 77 - 78 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 5.63 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.21 – 5.04 (m, 2H), 3.48 (t, *J* = 7.1 Hz, 2H), 2.42 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.79, 134.94, 131.66, 130.06, 129.07, 119.23, 107.86, 49.52, 31.89. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{11}ClN_2NaO_2S$ 293.0122; Found 293.0113.



1ag

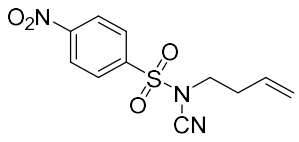
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (92% yield, 290 mg) as white solid, mp: 95 - 96 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 4H), 5.63 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.19 – 5.05 (m, 2H), 3.47 (t, *J* = 7.1 Hz, 2H), 2.42 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ

135.73, 133.31, 131.87, 130.67, 129.29, 119.52, 108.09, 49.78, 32.15. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{11}BrN_2NaO_2S$ 336.9617; Found 336.9610.



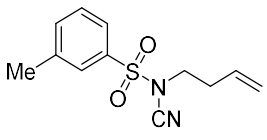
1ah

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (92% yield, 280 mg) as white solid, mp: 36 - 37 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 5.62 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.18 – 5.00 (m, 2H), 3.51 (t, *J* = 7.1 Hz, 2H), 2.43 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.28, 136.66 (q, *J* = 33.2 Hz), 131.75, 128.53, 127.15, 122.92 (q, *J* = 273.5 Hz), 119.65, 50.03, 32.21. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}F_3N_2O_2S$ 305.0566; Found 305.0555.



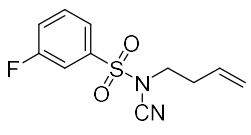
1ai

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (87% yield, 245 mg) as yellow solid, mp: 80 - 81 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.6 Hz, 2H), 8.16 (d, *J* = 8.7 Hz, 2H), 5.63 (ddt, *J* = 16.7, 9.8, 6.7 Hz, 1H), 5.21 – 5.01 (m, 2H), 3.54 (t, *J* = 7.1 Hz, 2H), 2.45 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.46, 142.14, 131.63, 129.34, 125.15, 119.85, 107.54, 50.22, 32.20. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}N_3O_4S$ 282.0543; Found 282.0547.



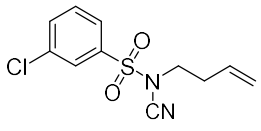
1aj

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/7) to afford the title compound (93% yield, 233 mg) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.58 – 7.46 (m, 2H), 5.63 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.15 – 5.05 (m, 2H), 3.45 (t, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 2.40 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.41, 136.57, 135.85, 131.98, 129.67, 127.97, 124.97, 119.16, 108.37, 49.51, 32.09, 21.37. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O_2S$ 251.0849; Found 251.0841.



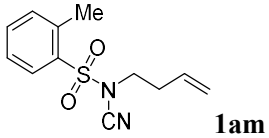
1ak

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (88% yield, 224 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 1H), 7.68 – 7.61 (m, 2H), 7.49 – 7.43 (m, 1H), 5.63 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.15 – 5.08 (m, 2H), 3.50 (t, *J* = 7.1 Hz, 2H), 2.43 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.61, 161.59, 138.51 (d, *J* = 6.6 Hz), 131.84, 123.75, 122.47 (d, *J* = 21.1 Hz), 119.47, 115.24 (d, *J* = 25.0 Hz), 107.94, 49.86, 32.12. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}FN_2O_2S$ 255.0598; Found 255.0586.



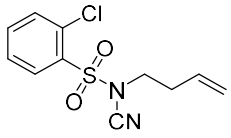
1al

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (89% yield, 241 mg) as white solid, mp: 83 - 84 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 5.62 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.18 – 5.05 (m, 2H), 3.50 (t, *J* = 7.1 Hz, 2H), 2.43 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.40, 136.27, 135.26, 131.85, 131.28, 127.81, 126.03, 119.59, 107.94, 49.91, 32.19. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{11}ClN_2NaO_2S$ 293.0122; Found 293.0120.



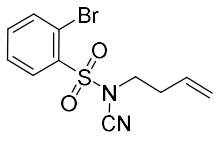
1am

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (90% yield, 225 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.42 – 7.38 (m, 2H), 5.54 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.13 – 5.03 (m, 2H), 3.43 (t, *J* = 7.1 Hz, 2H), 2.72 (s, 3H), 2.40 (q, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.93, 135.10, 135.01, 133.59, 132.04, 131.03, 126.90, 119.37, 108.30, 49.26, 32.17, 21.09. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O_2S$ 251.0849; Found 251.0843.



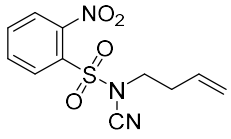
1an

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (90% yield, 243 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.58 (m, 2H), 7.53 – 7.45 (m, 1H), 5.63 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.21 – 5.05 (m, 2H), 3.56 (t, *J* = 7.2 Hz, 2H), 2.46 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.98, 134.33, 133.11, 132.89, 132.70, 131.90, 127.65, 119.48, 107.68, 50.12, 32.34. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{11}ClN_2NaO_2S$ 293.0122; Found 293.0121.



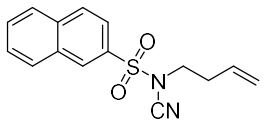
1ao

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (90% yield, 284 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 1H), 7.88 – 7.75 (m, 1H), 7.60 – 7.42 (m, 2H), 5.64 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.23 – 4.95 (m, 2H), 3.56 (t, *J* = 7.2 Hz, 2H), 2.47 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.31, 135.87, 133.36, 131.90, 128.20, 121.05, 119.48, 107.74, 50.13, 32.30. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{11}BrN_2NaO_2S$ 336.9617; Found 336.9609.



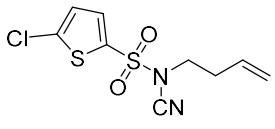
1ap

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (85% yield, 239 mg) as yellow solid, mp: 59 - 60 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 – 8.20 (m, 1H), 7.95 – 7.80 (m, 3H), 5.73 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.27 – 5.13 (m, 2H), 3.74 (t, *J* = 7.1 Hz, 2H), 2.53 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.97, 136.27, 132.88, 132.45, 131.91, 129.94, 125.25, 119.68, 107.38, 50.77, 32.58. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{12}N_3O_4S$ 282.0543; Found 282.0533.



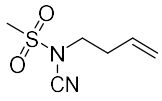
1aq

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (87% yield, 249 mg) as white solid, mp: 47 - 48 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.05 (t, *J* = 9.1 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.78 – 7.66 (m, 2H), 5.62 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.15 – 5.01 (m, 2H), 3.51 (t, *J* = 7.2 Hz, 2H), 2.42 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.76, 133.47, 131.99, 130.46, 130.21, 130.11, 129.67, 128.38, 128.18, 121.91, 119.29, 108.47, 49.63, 32.16. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}N_2O_2S$ 287.0849; Found 287.0849.



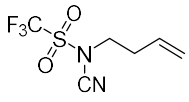
1ar

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (89% yield, 246 mg) as white solid, mp: 43 - 44 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 4.1 Hz, 1H), 7.06 (d, *J* = 4.1 Hz, 1H), 5.67 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.21 – 5.10 (m, 2H), 3.52 (t, *J* = 7.1 Hz, 2H), 2.46 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.35, 134.92, 133.57, 131.79, 127.86, 119.54, 107.62, 50.04, 32.10. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_9ClN_2NaO_2S_2$ 298.9686; Found 298.9673.



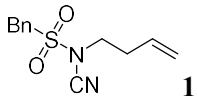
1as

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (30% yield, 52 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.33 – 5.18 (m, 2H), 3.63 (t, *J* = 7.0 Hz, 2H), 3.22 (s, 3H), 2.54 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.25, 119.59, 107.96, 49.72, 40.84, 32.40. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_6H_{11}N_2O_2S$ 175.0536; Found 175.0540.



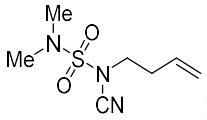
1at

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (67% yield, 153 mg) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.42 – 5.16 (m, 2H), 3.76 (t, *J* = 7.0 Hz, 2H), 2.59 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.91, 120.74, 119.25 (q, *J* = 322.9 Hz), 104.92, 52.50, 32.36. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_6H_8F_3N_2O_2S$ 229.0253; Found 229.0238.



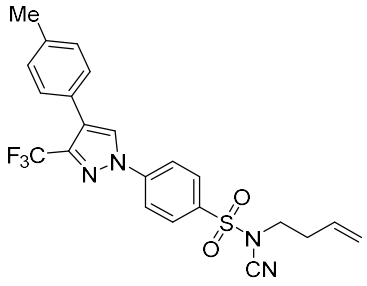
1au

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (25% yield, 63 mg) as white solid, mp: 61 - 62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 5H), 5.68 – 5.54 (m, 1H), 5.17 – 5.10 (m, 2H), 4.56 (s, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.30 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.05, 130.95, 130.04, 129.44, 126.37, 119.39, 108.14, 59.82, 50.87, 32.68. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}N_2O_2S$ 251.0849; Found 251.0854.



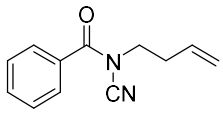
1av

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (25% yield, 51 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.27 – 5.16 (m, 2H), 3.54 (t, *J* = 7.2 Hz, 2H), 3.03 (s, 6H), 2.52 (q, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.48, 119.34, 109.53, 50.63, 38.88, 32.56. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_7H_{14}N_3O_2S$ 204.0801; Found 204.0798.



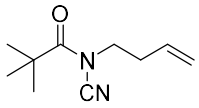
1aw

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (91% yield, 419 mg) as white solid, mp: 105 - 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.76 (s, 1H), 5.61 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.16 – 5.05 (m, 2H), 3.48 (t, *J* = 7.1 Hz, 2H), 2.42 (q, *J* = 7.0 Hz, 2H), 2.4 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.60, 144.99 (q, *J* = 38.5 Hz), 144.48, 140.28, 135.81, 131.87, 130.02, 128.96, 128.84, 125.84, 125.63, 121.03 (q, *J* = 269.4 Hz), 119.57, 108.01, 107.00, 49.81, 32.12, 21.43. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}F_3N_4O_2S$ 461.1254; Found 461.1264.



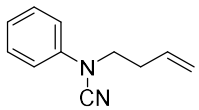
1ba

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (87% yield, 176 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.72 (m, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 5.82 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.31 – 5.14 (m, 2H), 3.84 (t, *J* = 7.0 Hz, 2H), 2.57 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.55, 133.20, 133.07, 131.23, 128.71, 128.64, 118.99, 111.14, 46.89, 32.07.



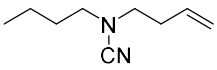
1ca

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (95% yield, 171 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.20 – 5.10 (m, 2H), 3.67 (t, *J* = 6.9 Hz, 2H), 2.43 (q, *J* = 6.9 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.89, 133.29, 118.71, 111.57, 47.62, 41.17, 32.06, 27.17. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{17}N_2O_2$ 181.1335; Found 181.1330.



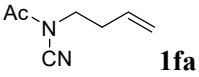
1da

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (88% yield, 151 mg) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 2H), 7.16 – 7.04 (m, 3H), 5.84 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.28 – 5.11 (m, 2H), 3.66 (t, *J* = 7.3 Hz, 2H), 2.58 (q, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.95, 133.16, 129.80, 123.76, 118.70, 116.12, 113.62, 48.95, 31.78.



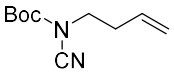
1ea

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (44% yield, 67 mg) as a colorless oil. ^{1}H NMR (300 MHz, CDCl3) δ 5.85 – 5.69 (m, 1H), 5.22 – 5.05 (m, 2H), 3.05 (t, J = 7.2 Hz, 2H), 2.98 (t, J = 6.0 Hz, 2H), 2.47 – 2.32 (m, 2H), 1.67 – 1.54 (m, 2H), 1.46 – 1.29 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.81, 117.83, 117.62, 51.32, 50.95, 32.08, 29.68, 19.67, 13.62.



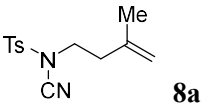
1fa

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (78% yield, 108 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.18 – 5.09 (m, 2H), 3.61 (t, *J* = 7.0 Hz, 2H), 2.40 (q, *J* = 7.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.26, 132.84, 118.70, 110.79, 45.23, 31.91, 22.14. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_7H_{11}N_2O$ 139.0866; Found 139.0867.



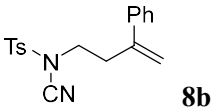
1ga

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (91% yield, 179 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.25 – 5.01 (m, 2H), 3.53 (t, *J* = 7.0 Hz, 2H), 2.43 (q, *J* = 7.0 Hz, 2H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.99, 132.95, 118.75, 109.64, 85.55, 46.96, 32.27, 27.88. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{17}N_2O_2$ 197.1285; Found 197.1272.



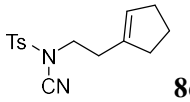
8a

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (91% yield, 241 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 4.83 (s, 1H), 4.72 (s, 1H), 3.50 (t, *J* = 7.4 Hz, 2H), 2.49 (s, 3H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.57, 139.70, 133.78, 130.54, 127.93, 114.17, 108.49, 48.40, 35.79, 22.07, 21.85. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_2S$ 265.1005; Found 265.1015.



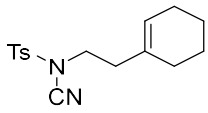
8b

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (65% yield, 212 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.26 (m, 5H), 5.38 (s, 1H), 5.13 (s, 1H), 3.46 (t, *J* = 7.5 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.51, 142.73, 139.10, 133.77, 130.53, 128.71, 128.14, 127.90, 126.07, 116.20, 108.58, 49.04, 34.10, 21.88. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}N_2O_2S$ 327.1162; Found 327.1166.



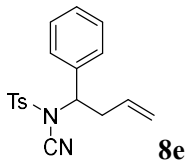
8c

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/6) to afford the title compound (71% yield, 206 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.39 (brs, 1H), 3.48 (t, *J* = 7.3 Hz, 2H), 2.48 (s, 3H), 2.43 – 2.39 (m, 2H), 2.30 – 2.22 (m, 2H), 2.20 – 2.11 (m, 2H), 1.88 – 1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.47, 138.23, 133.84, 130.51, 127.89, 127.83, 108.50, 48.52, 34.71, 32.61, 29.55, 23.27, 21.87. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}N_2O_2S$ 291.1162; Found 291.1168.



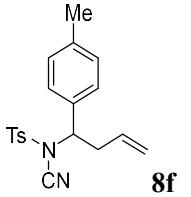
8d

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (93% yield, 283 mg) as white solid, mp: 71 - 72 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 5.43 (brs, 1H), 3.44 (t, *J* = 7.3 Hz, 2H), 2.47 (s, 3H), 2.24 (t, *J* = 7.2 Hz, 2H), 2.00 – 1.91 (m, 2H), 1.88 – 1.81 (m, 2H), 1.61 – 1.55 (m, 2H), 1.53 – 1.47 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.40, 134.04, 131.87, 130.50, 127.90, 125.75, 108.64, 48.75, 36.27, 27.93, 25.29, 22.71, 22.08, 21.85. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}N_2O_2S$ 305.1318; Found 305.1323.



8e

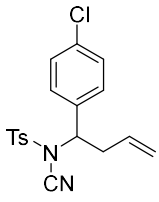
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (90% yield, 294 mg) as white solid, mp: 89 - 90 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.18 (m, 7H), 5.59 – 5.51 (m, 1H), 5.18 (d, *J* = 17.0 Hz, 1H), 5.04 (d, *J* = 10.2 Hz, 1H), 4.85 (dd, *J* = 9.2, 6.5 Hz, 1H), 2.83 – 2.73(m, 1H), 2.70 – 2.62 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.01, 137.12, 134.37, 131.95, 130.00, 128.97, 128.00, 126.92, 119.84, 107.79, 63.74, 38.54, 21.80. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_2S$ 349.0981; Found 349.0975.



8f

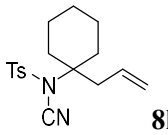
Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (83% yield, 283 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.59 – 5.48 (m, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 5.02 (d, *J* = 10.1 Hz, 1H),

4.82 (dd, *J* = 9.0, 6.8 Hz, 1H), 2.82 – 2.70 (m, 1H), 2.69 – 2.60 (m, 1H), 2.41 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.95, 138.92, 134.43, 133.97, 132.05, 129.94, 129.53, 127.95, 126.84, 119.62, 107.76, 63.60, 38.35, 21.73, 21.16. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}N_2NaO_2S$ 363.1138; Found 363.1136.



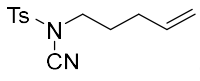
8g

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (80% yield, 289 mg) as white solid, mp: 80 - 81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 5.57 – 5.47 (m, 1H), 5.17 (d, *J* = 16.0 Hz, 1H), 5.04 (d, *J* = 10.2 Hz, 1H), 4.82 (dd, *J* = 9.0, 6.7 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.67 – 2.58 (m, 1H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.33, 135.56, 134.95, 134.21, 131.48, 130.07, 129.09, 128.28, 127.89, 120.09, 107.56, 62.85, 38.32, 21.75. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}ClN_2O_2S$ 361.0772; Found 361.0771.



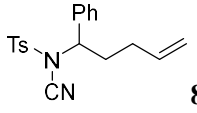
8h

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (20% yield, 64 mg) as white solid, mp: 69 - 70 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.81 – 5.73 (m, 1H), 5.24 – 5.14 (m, 2H), 2.64 (d, *J* = 7.3 Hz, 2H), 2.49 (s, 3H), 2.15 – 1.98 (m, 2H), 1.81 – 1.67 (m, 2H), 1.53 – 1.45 (m, 2H), 1.43 – 1.30 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.00, 136.47, 131.25, 130.21, 128.06, 120.54, 109.29, 71.69, 42.87, 34.81, 24.96, 22.10, 21.87. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{23}N_2O_2S$ 319.1475; Found 319.1471.



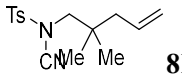
8i

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (90% yield, 238 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 5.77 – 5.62 (m, 1H), 5.07 – 4.97 (m, 2H), 3.37 (t, *J* = 7.3 Hz, 2H), 2.48 (s, 3H), 2.08 (q, *J* = 7.0 Hz, 2H), 1.83 – 1.69 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.54, 136.11, 133.72, 130.57, 127.91, 116.54, 108.69, 49.67, 29.98, 27.00, 21.88. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}N_2O_2S$ 265.1005; Found 265.0992.



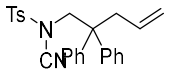
8j

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (73% yield, 249 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.22 – 7.18 (m, 2H), 7.18 – 7.16 (m, 2H), 7.16 – 7.14 (m, 2H), 5.78 – 5.68 (m, 1H), 5.06 – 4.98 (m, 2H), 4.84 – 4.75 (m, 1H), 2.38 (s, 3H), 2.14 – 2.07 (m, 1H), 2.07 – 1.97 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.96, 137.23, 136.02, 134.29, 129.96, 128.91, 127.86, 126.89, 116.65, 107.88, 63.40, 33.50, 30.02, 21.72. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_2S$ 341.1318; Found 341.1315.



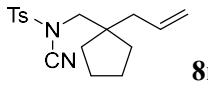
8k

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (83% yield, 243 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 5.76 (ddt, *J* = 17.4, 10.1, 7.5 Hz, 1H), 5.14 – 5.01 (m, 2H), 3.19 (s, 2H), 2.48 (s, 3H), 2.07 (d, *J* = 7.4 Hz, 2H), 1.01 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.51, 133.81, 133.34, 130.54, 128.08, 118.96, 110.70, 60.50, 44.30, 35.88, 24.87, 21.90. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}N_2O_2S$ 293.1318; Found 293.1311.



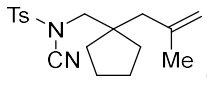
8l

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (73% yield, 304 mg) as white solid, mp: 108 - 109 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.26 – 7.22 (m, 2H), 7.14 – 7.08 (m, 4H), 5.38 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.14 – 4.95 (m, 2H), 4.13 (s, 2H), 3.07 (d, *J* = 7.0 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.46, 143.99, 133.24, 132.79, 130.45, 128.43, 128.29, 128.20, 127.20, 119.91, 109.03, 56.65, 50.30, 40.82, 21.91. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{25}N_2O_2S$ 417.1631; Found 417.1639.



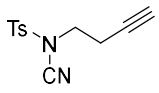
8m

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (95% yield, 303 mg) as white solid, mp: 58 - 59 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 5.74 (ddt, *J* = 14.8, 10.6, 7.4 Hz, 1H), 5.13 – 5.03 (m, 2H), 3.25 (s, 2H), 2.47 (s, 3H), 2.20 (d, *J* = 7.4 Hz, 2H), 1.66 – 1.59 (m, 4H), 1.55 – 1.47 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.49, 133.83, 133.61, 130.51, 128.01, 118.93, 110.49, 57.15, 46.80, 41.03, 35.05, 24.50, 21.85. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{23}N_2O_2S$ 319.1475; Found 319.1484.



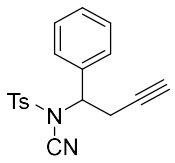
8n

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (93% yield, 309 mg) as white solid, mp: 59 - 60 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 4.86 (s, 1H), 4.71 (s, 1H), 3.32 (s, 2H), 2.48 (s, 3H), 2.21 (s, 2H), 1.75 (s, 3H), 1.67 – 1.57 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.48, 142.20, 133.64, 130.51, 128.05, 115.43, 110.59, 57.10, 46.76, 44.87, 35.60, 25.07, 24.42, 21.88. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{25}N_2O_2S$ 333.1631; Found 333.1632.



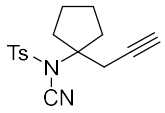
11a

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (80% yield, 199 mg) as white solid, mp: 80 - 81 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 3.56 (t, *J* = 7.2 Hz, 2H), 2.56 (td, *J* = 7.2 Hz, 2.6 Hz, 2H), 2.49 (s, 3H), 2.00 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.79, 133.74, 130.64, 128.05, 108.36, 78.12, 71.86, 48.82, 21.91, 18.79. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}N_2O_2S$ 249.0692; Found 249.0678.



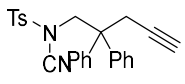
11b

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (71% yield, 230 mg) as white solid, mp: 75 - 76 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.15 (m, 7H), 5.03 (dd, *J* = 8.5, 7.0 Hz, 1H), 2.94 – 2.79 (m, 2H), 2.42 (s, 3H), 1.89 (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.27, 135.92, 134.21, 130.13, 129.41, 129.08, 128.15, 126.90, 107.29, 77.99, 72.15, 62.56, 24.56, 21.82. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_2S$ 325.1005; Found 325.1000.



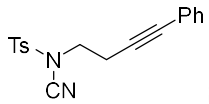
11c

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/6) to afford the title compound (an inseparable mixture, 80% yield, 181 mg, dr = 2.6:1) as colorless oil. The major isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 2.81 (d, *J* = 2.5 Hz, 2H), 2.46 (s, 3H), 2.30 – 2.20 (m, 2H), 2.02 – 1.95 (m, 2H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.69 – 1.63 (m, 2H), 1.61 – 1.53 (m, 2H). The minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.54 (d, *J* = 2.5 Hz, 2H), 2.43 (s, 2H), 2.04 (t, *J* = 2.7 Hz, 1H), 1.94 – 1.88 (m, 2H), 1.86 – 1.78 (m, 4H), 1.78 – 1.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.18, 144.31, 135.72, 130.22, 129.74, 128.10, 126.88, 108.75, 78.99, 78.76, 75.93, 72.05, 71.94, 71.40, 39.54, 37.13, 30.35, 28.37, 23.47, 22.63, 21.86, 21.69. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}N_2O_2S$ 303.1162; Found 303.1163.



11d

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (89% yield, 369 mg) as white solid, mp: 173 - 174 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.27 (m, 6H), 7.18 – 7.07 (m, 4H), 4.26 (s, 2H), 3.17 (d, *J* = 2.4 Hz, 2H), 2.49 (s, 3H), 1.95 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.63, 142.86, 133.40, 130.56, 128.53, 128.23, 127.64, 108.67, 80.08, 72.92, 57.24, 50.16, 28.43, 21.94. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}N_2O_2S$ 415.1475; Found 415.1486.

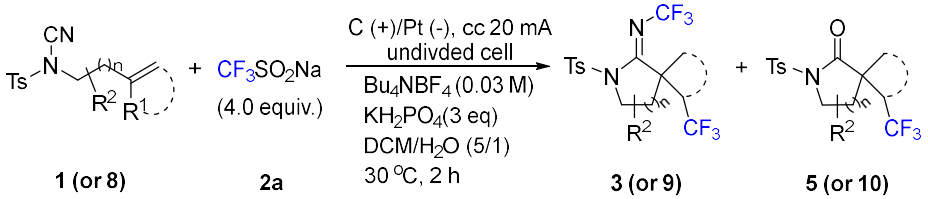


S10

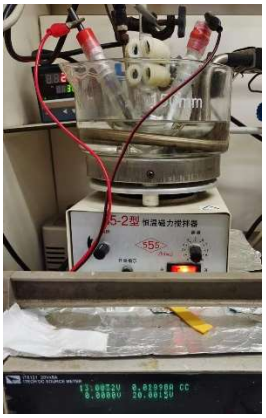
S10 was prepared according to the literature[8]. Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (81% yield, 263 mg) as yellow solid, mp: 95 - 96 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.32 (m, 4H), 7.30 – 7.26 (m, 3H), 3.65 (t, *J* = 7.0 Hz, 2H), 2.78 (t, *J* = 7.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.65, 133.81, 131.76, 130.58, 128.35, 122.80, 108.49, 83.66, 83.51, 49.14, 21.84, 19.76. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_2S$ 325.1005; Found 325.1013.

IV. General Procedure and Experimental Details

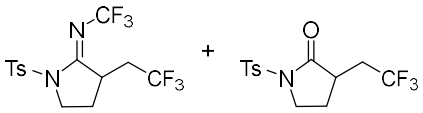
1. General procedure for preparation of products 3 (or 9) and 5 (or 10)



1 (or 8) 2a 3 (or 9) 5 (or 10)



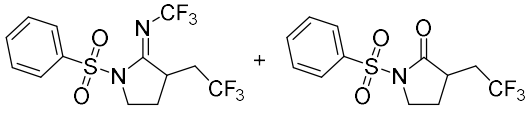
In an undivided three necked-flask (25 mL) equipped with a stir bar, a mixture of alkene **1** (or **8)** (0.3 mmol), CF_3SO_2Na **2a** (1.2 mmol), Bu_4NBF_4 (0.3 mmol), KH_2PO_4 (0.9 mmol) and DCM/H_2O (v/v = 5/1, 10 mL) were added. The cell was equipped with graphite rod (Φ 6 mm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 30 °C for 2 h. Upon completion, H_2O (5 mL) was added, the mixture was extracted with DCM (8 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products **3** (or **9)** and **5 (**or **10)**.



3aa (major) 5aa

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3aa** (61% yield, 71 mg) as white solid, mp: 120 - 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.15 – 4.05 (m, 1H), 3.97 – 3.90 (m, 1H), 3.42 – 3.28 (m, 1H), 2.45 (s, 3H), 2.40 – 2.27 (m, 1H), 2.24 – 2.09 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.80 (q, *J* = 6.9 Hz), 145.92, 133.93, 129.54, 129.17, 125.65 (q, *J* = 277.5 Hz), 123.28 (q, *J* = 257.0 Hz), 46.66, 37.33, 33.84 (q, *J* = 29.4 Hz), 25.33, 21.83. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.74, -64.40 (t, *J* = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}F_6N_2O_2S$ 389.0753; Found 389.0756.

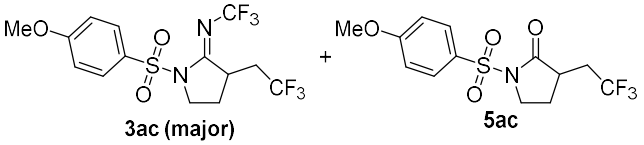
Compound **5aa** (20% yield, 19 mg) as white solid, mp: 119 - 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 4.12 – 3.96 (m, 1H), 3.77 – 3.59 (m, 1H), 2.83 – 2.63 (m, 2H), 2.43 – 2.39 (m, 1H), 2.41(s, 3H), 2.17 – 1.96 (m, 1H), 1.92 – 1.81 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.44, 145.68, 134.80, 129.90, 128.15, 126.41 (q, *J* = 276.7 Hz), 45.42, 38.35, 34.56 (q, *J* = 29.6 Hz), 25.91, 21.79. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.01 (t, *J* = 10.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}F_3NO_3S$ 322.0719; Found 322.0717.



3ab (major) 5ab

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3ab** (48% yield, 54 mg) as white solid, mp: 86 - 88 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.8 Hz, 2H), 4.18 – 4.06 (m, 1H), 4.02 – 3.87 (m, 1H), 3.45 – 3.28 (m, 1H), 2.43 – 2.29 (m, 1H), 2.26 – 2.09 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.81 (q, J = 7.1 Hz), 136.98, 134.65, 129.13, 128.92, 125.64 (q, J = 277.3 Hz), 123.22 (q, J = 257.1 Hz), 46.69, 37.33, 33.88 (q, J = 29.2 Hz), 25.35. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.93, -64.38 (t, J = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}F_6N_2O_2S$ 375.0596; Found 375.0605.

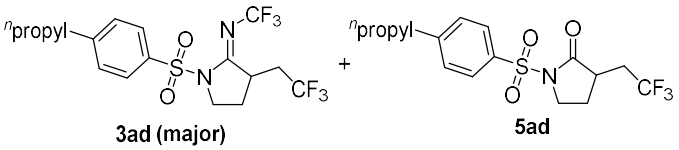
Compound **5ab** (18% yield, 17 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.3 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 4.16 – 3.95 (m, 1H), 3.76 – 3.61 (m, 1H), 2.83 – 2.64 (m, 2H), 2.52 – 2.37 (m, 1H), 2.13 – 1.97 (m, 1H), 1.95 – 1.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.48, 137.84, 134.51, 129.35, 128.18, 126.41 (q, J = 276.2 Hz), 45.49, 38.40, 34.62 (q, J = 29.6 Hz), 25.98. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.00 (t, J = 10.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{13}F_3NO_3S$ 308.0563; Found 308.0572.



3ac (major) 5ac

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3ac** (47% yield, 57 mg) as white solid, mp: 115 - 117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 4.13 – 4.05 (m, 1H), 3.97 – 3.90 (m, 1H), 3.88 (s, 3H), 3.40 – 3.32 (m, 1H), 2.42 – 2.28 (m, 1H), 2.27 – 2.07 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.75 (q, J = 6.4 Hz), 164.54, 131.57, 128.21, 125.67 (q, J = 277.8 Hz), 123.32 (q, J = 256.7 Hz), 114.05, 55.86, 46.63, 37.35, 33.89 (q, J = 29.2 Hz), 25.31. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.63, -64.38 (t, J = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}F_6N_2O_3S$ 405.0702; Found 405.0710.

Compound **5ac** (27% yield, 27 mg) as white solid, mp: 120 - 122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 4.11 – 3.98 (m, 1H), 3.87 (s, 3H), 3.75 – 3.57 (m, 1H), 2.82 – 2.65 (m, 2H), 2.52 – 2.36 (m, 1H), 2.11 – 1.95 (m, 1H), 1.94 – 1.78 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.46, 164.39, 130.55, 129.19, 126.44 (q, J = 276.6 Hz), 114.46, 55.87, 45.42, 38.39, 34.65 (q, J = 29.5 Hz), 25.96. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.01 (t, J = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}F_3NO_4S$ 338.0668; Found 338.0670.

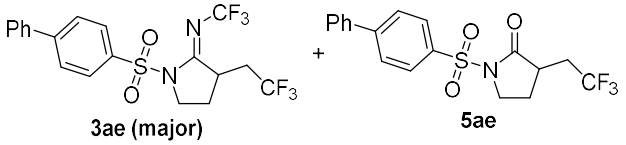


3ad (major) 5ad

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3ad** (54% yield, 67 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.18 – 4.06 (m, 1H), 4.00 – 3.88 (m, 1H), 3.43 – 3.29 (m, 1H), 2.73 – 2.61 (m, 2H), 2.40 – 2.27 (m, 1H), 2.25 – 2.07 (m, 3H), 1.75 – 1.59 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.79 (q, J = 6.9 Hz), 150.49, 134.13, 129.18, 128.95, 125.66 (q, J = 277.5 Hz), 123.28 (q, J =

256.9 Hz), 46.65, 38.08, 37.34, 33.86 (q, J = 29.5 Hz), 25.32, 24.17, 13.71. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.79, -64.40 (t, J = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}F_6N_2O_2S$ 417.1066; Found 417.1071.

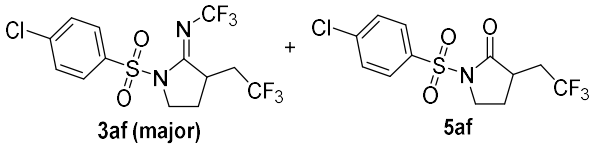
Compound **5ad** (16% yield, 17 mg) as white solid, mp: 78 - 79 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 4.08 – 3.99 (m, 1H), 3.75 – 3.64 (m, 1H), 2.83 – 2.70 (m, 2H), 2.69 – 2.64 (m, 2H), 2.51 – 2.37 (m, 1H), 2.11 – 1.96 (m, 1H), 1.94 – 1.82 (m, 1H), 1.72 – 1.61 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.46, 150.30, 135.03, 129.36, 128.22, 126.44 (q, J = 276.4 Hz), 45.46, 38.42, 38.13, 34.66 (q, J = 29.5 Hz), 25.98, 24.23, 13.89. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.00 (t, J = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}F_3NO_3S$ 350.1032; Found 350.1037.



3ae (major) 5ae

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/1) to afford the title compound **3ae** (70% yield, 94 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 4.20 – 4.07 (m, 1H), 4.04 – 3.94 (m, 1H), 3.46 – 3.19 (m, 1H), 2.48 – 2.33 (m, 1H), 2.31 – 2.11 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.83 (q, J = 6.9 Hz), 147.58, 139.05, 135.43, 129.76, 129.26, 128.99, 127.56, 127.47, 125.67 (q, J = 277.6 Hz), 123.29 (q, J = 257.1 Hz), 46.71, 37.37, 33.98 (q, J = 29.6 Hz), 25.41. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.76, -64.33 (t, J = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{17}F_6N_2O_2S$ 451.0909; Found 451.0914.

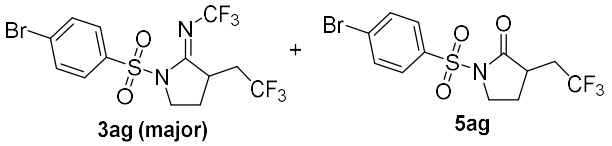
Compound **5ae** (15% yield, 16 mg) as white solid, mp: 154 - 156 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 4.13 – 4.04 (m, 1H), 3.78 – 3.69 (m, 1H), 2.85 – 2.69 (m, 2H), 2.55 – 2.41 (m, 1H), 2.14 – 1.99 (m, 1H), 1.97 – 1.86 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.52, 147.49, 139.12, 136.30, 129.27, 128.95, 128.76, 127.93, 127.54, 126.44 (q, J = 276.3 Hz), 45.52, 38.44, 34.67 (q, J = 29.6 Hz), 26.03. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.98 (t, J = 10.6 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}F_3NO_3S$ 384.0876; Found 384.0872.



3af (major) 5af

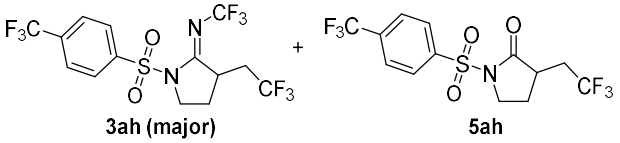
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/1) to afford the title compound **3af** (51% yield, 63 mg) as white solid, mp: 139 - 142 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 4.12 – 4.05 (m, 1H), 4.00 – 3.91 (m, 1H), 3.41 – 3.32 (m, 1H), 2.44 – 2.32 (m, 1H), 2.30 – 2.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.84 (q, J = 6.8 Hz), 141.48, 135.38, 130.70, 129.26, 125.62 (q, J = 277.7 Hz), 123.14 (q, J =257.3 Hz), 46.72, 37.31, 34.00 (q, J = 29.4 Hz), 25.39. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.01, -64.34 (t, J = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}ClF_6N_2O_2S$ 409.0207; Found 409.0216.

Compound **5af** (16% yield, 16 mg) as white solid, mp: 128 - 129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 4.08 – 3.94 (m, 1H), 3.75 – 3.65 (m, 1H), 2.83 – 2.66 (m, 2H), 2.51 – 2.41 (m, 1H), 2.14 – 1.99 (m, 1H), 1.96 – 1.79 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.52, 141.35, 136.18, 129.72, 129.68, 126.35 (q, *J* = 276.4 Hz), 45.51, 38.37, 34.59 (q, *J* = 29.7 Hz), 26.00. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.99 (t, *J* = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}ClF_3NO_3S$ 342.0173; Found 342.0179.



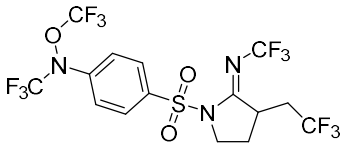
After stirring at 30 ℃ for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/1) to afford the title compound **3ag** (58% yield, 79 mg) as white solid, mp: 143 - 145 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 4.13 – 4.05 (m, 1H), 4.01 – 3.90 (m, 1H), 3.40 – 3.31 (m, 1H), 2.47 – 2.32 (m, 1H), 2.31 – 2.13 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.83 (q, *J* = 6.8 Hz), 135.93, 132.27, 130.72, 130.14, 125.62 (q, *J* = 277.6 Hz), 123.13 (q, *J* = 257.2 Hz), 46.72, 37.31, 34.01 (q, *J* = 29.5 Hz), 25.40. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.01, -64.33 (t, *J* = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}BrF_6N_2O_2S$ 452.9702; Found 452.9707.

Compound **5ag** (20% yield, 23 mg) as white solid, mp: 141 - 142 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 4.06 – 3.97 (m, 1H), 3.78 – 3.63 (m, 1H), 2.84 – 2.65 (m, 2H), 2.50 – 2.41 (m, 1H), 2.13 – 1.98 (m, 1H), 1.97 – 1.83 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.52, 136.71, 132.67, 129.97, 129.73, 126.35 (q, *J* = 277.0 Hz), 45.50, 38.35, 34.57 (q, *J* = 29.7 Hz), 25.98. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.98 (t, *J* = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}BrF_3NO_3S$ 385.9668; Found 385.9664.



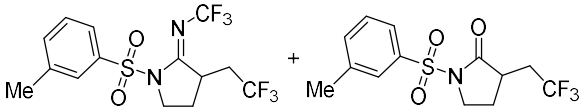
After stirring at 30 ℃ for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/2) to afford the title compound **3ah** (62% yield, 82 mg) as white solid, mp: 76 - 77 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 4.19 – 4.08 (m, 1H), 4.03 – 3.94 (m, 1H), 3.43 – 3.34 (m, 1H), 2.46 – 2.33 (m, 1H), 2.32 – 2.16 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.95 (q, *J* = 6.9 Hz), 140.47, 136.13 (q, *J* = 33.0 Hz), 129.86, 124.07, 125.60 (q, *J* = 277.9 Hz), 123.16 (q, *J* = 273.3 Hz), 123.05 (q, *J* = 257.4 Hz), 46.79, 37.31, 34.04 (q, *J* = 29.6 Hz), 25.44. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.30, -63.38, -64.41 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}F_9N_2O_2S$ 443.0470; Found 443.0479.

Compound **5ah** (20% yield, 23 mg) as white solid, mp: 115 - 117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 4.11 – 4.02 (m, 1H), 3.80 – 3.69 (m, 1H), 2.93 – 2.60 (m, 2H), 2.53 – 2.43 (m, 1H), 2.14 – 2.00 (m, 1H), 1.98 – 1.85 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.58, 141.21, 136.05 (q, *J* = 32.8 Hz), 128.88, 126.50, 126.32 (q, *J* = 276.6 Hz), 123.14 (q, *J* = 273.3 Hz), 45.58, 38.36, 34.55 (q, *J* = 29.8 Hz), 26.01. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.33, -65.00 (t, *J* = 10.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}F_6NO_3S$ 376.0437; Found 376.0444.



3ai

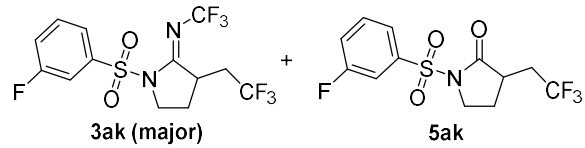
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/1) to afford the title compound (13% yield, 21 mg) as white solid, mp: 65 - 66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 4.20 – 4.07 (m, 1H), 4.04 – 3.93 (m, 1H), 3.47 – 3.36 (m, 1H), 2.47 – 2.33 (m, 1H), 2.32 – 2.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.79 (q, J = 6.3 Hz), 144.83, 138.05, 130.64, 125.59 (q, J = 277.2 Hz), 124.69, 123.04 (q, J = 256.8 Hz), 122.41 (q, J = 264.9 Hz), 121.32 (q, J = 267.8 Hz), 46.76, 37.29, 34.10 (q, J = 29.6 Hz), 25.40. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.35, -64.37 (t, J = 10.1 Hz), -65.45, -70.42. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}F_{12}N_3O_3S$ 542.0402; Found 542.0414.



3aj (major) **5aj**

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3aj** (55% yield, 64 mg) as white solid, mp: 59 - 60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 4.14 – 4.06 (m, 1H), 4.00 – 3.91 (m, 1H), 3.39 – 3.32 (m, 1H), 2.44 (s, 3H), 2.40 – 2.29 (m, 1H), 2.27 – 2.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.73 (q, J = 6.3 Hz), 139.25, 136.72, 135.43, 129.78, 128.80, 126.02, 125.66 (q, J = 277.4 Hz), 123.27 (q, J = 257.1 Hz), 46.66, 37.34, 33.91 (q, J = 29.4 Hz), 25.34, 21.33. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.87, -64.38 (t, J = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}F_6N_2O_2S$ 389.0753; Found 389.0746.

Compound **5aj** (17% yield, 16 mg) as white solid, mp: 76 - 77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.50 – 7.38 (m, 2H), 4.08 – 4.00 (m, 1H), 3.75 – 3.64 (m, 1H), 2.84 – 2.68 (m, 2H), 2.49 – 2.40 (m, 1H), 2.45 (s, 3H), 2.12 – 1.96 (m, 1H), 1.95 – 1.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.29, 139.56, 137.55, 135.20, 129.06, 128.25, 126.29 (q, J = 277.8 Hz), 125.16, 77.28, 45.36, 38.29, 34.52 (q, J = 29.9 Hz), 25.85, 21.38. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.00 (t, J = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}F_3NO_3S$ 322.0719; Found 322.0729.

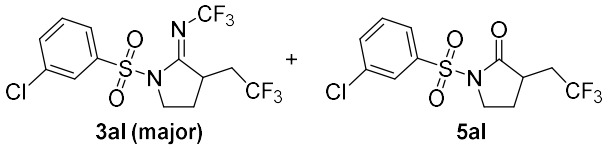


3ak (major) **5ak**

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3ak** (57% yield, 67 mg) as white solid, mp: 76 - 77 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.9 Hz, 1H), 7.75 (dt, J = 8.0, 2.0 Hz, 1H), 7.55 (td, J = 8.1, 5.3 Hz, 1H), 7.39 (td, J = 8.2, 2.4 Hz, 1H), 4.14 – 4.07 (m, 1H), 4.00 – 3.91 (m, 1H), 3.43 – 3.35 (m, 1H), 2.45 – 2.33 (m, 1H), 2.30 – 2.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.84 (q, J = 6.8 Hz), 162.12 (d, J = 252.0 Hz), 138.82 (d, J = 7.2 Hz), 130.72 (d, J

= 7.7 Hz), 125.61 (q, *J* = 277.5 Hz), 124.99, 123.12 (q, *J* = 257.3 Hz), 121.94 (d, *J* = 21.4 Hz), 116.56 (d, *J* = 25.0 Hz), 46.77, 37.31, 33.99 (q, *J* = 29.5 Hz), 25.40. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.18, -64.37 (t, *J* = 10.2 Hz), -109.50 (td, *J* = 8.0, 5.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}F_7N_2O_2S$ 393.0502; Found 393.0511.

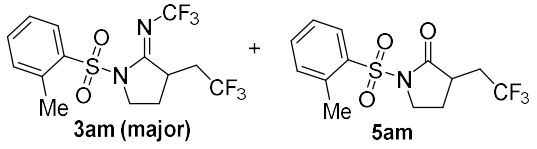
Compound **5ak** (7% yield, 7 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.75 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.62 – 7.51 (m, 1H), 7.38 (td, *J* = 8.3, 2.4 Hz, 1H), 4.10 – 3.99 (m, 1H), 3.78 – 3.64 (m, 1H), 2.84 – 2.68 (m, 2H), 2.52 – 2.42 (m, 1H), 2.14 – 1.98 (m, 1H), 1.97 – 1.84 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.49, 163.39, 161.39, 131.18 (d, *J* = 7.4 Hz), 126.36 (q, *J* = 275.6 Hz), 124.04, 121.85 (d, *J* = 21.2 Hz), 115.61 (d, *J* = 24.9 Hz), 45.56, 38.37, 34.59 (q, *J* = 29.8 Hz), 25.99. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.98 (t, *J* = 10.8 Hz), -108.72 (td, *J* = 8.0, 5.6 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}F_4NO_3S$ 326.0469; Found 326.0471.



3al (major) **5al**

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3al** (45% yield, 55 mg) as white solid, mp: 64 - 65 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 4.17 – 4.08 (m, 1H), 4.04 – 3.94 (m, 1H), 3.45 – 3.35 (m, 1H), 2.49 – 2.34 (m, 1H), 2.33 – 2.13 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.81 (q, *J* = 6.3 Hz), 138.52, 135.17, 134.75, 130.16, 129.18, 127.45, 125.61 (q, *J* = 277.5 Hz), 123.10 (q, *J* = 257.7 Hz), 46.75, 37.29, 34.03 (q, *J* = 29.8 Hz), 25.41. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.18, -64.31 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}ClF_6N_2O_2S$ 409.0207; Found 409.0214.

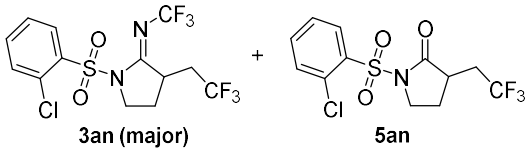
Compound **5al** (15% yield, 15 mg) as white solid, mp: 109 - 111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 4.11 – 3.97 (m, 1H), 3.82 – 3.64 (m, 1H), 2.86 – 2.64 (m, 2H), 2.53 – 2.40 (m, 1H), 2.14 – 1.99 (m, 1H), 1.97 – 1.84 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.49, 139.40, 135.57, 134.66, 130.62, 128.11, 126.48, 126.36 (q, *J* = 276.7 Hz), 45.57, 38.37, 34.59 (q, *J* = 29.8 Hz), 26.00. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.98 (t, *J* = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}ClF_3NO_3S$ 342.0173; Found 342.0166.



3am (major) **5am**

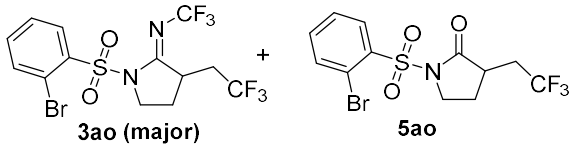
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3am** (40% yield, 47 mg) as white solid, mp: 134 - 136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.26 – 4.19 (m, 1H), 4.04 – 3.97 (m, 1H), 3.46 – 3.35 (m, 1H), 2.60 (s, 3H), 2.48 – 2.35 (m, 1H), 2.33 – 2.18 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.69 (q, *J* = 6.7 Hz), 138.30, 135.88, 134.36, 132.58, 132.42, 126.29, 125.66 (q, *J* = 277.6 Hz), 123.06 (q, *J* = 256.9 Hz), 46.33, 37.39, 33.92 (q, *J* = 29.0 Hz), 25.62, 20.53. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.17, -64.36 (t, *J* = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}F_6N_2O_2S$ 389.0753; Found 389.0749.

Compound **5am** (13% yield, 13 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.1 Hz, 1H), 7.53 (t, *J* = 8.1 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 4.17 – 4.01 (m, 1H), 3.93 – 3.76 (m, 1H), 2.91 – 2.65 (m, 2H), 2.62 (s, 3H), 2.57 – 2.43 (m, 1H), 2.09 – 1.99 (m, 1H), 1.99 – 1.87 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.40, 138.09, 136.31, 134.38, 132.74, 131.52, 126.64, 126.41 (q, *J* = 276.5 Hz), 45.37, 38.41, 34.56 (q, *J* = 29.5 Hz), 26.29, 20.58. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.94 (t, *J* = 10.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}F_3NO_3S$ 322.0719; Found 322.0729.



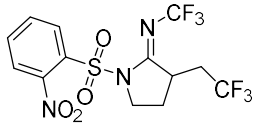
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3an** (45% yield, 55 mg) as white solid, mp: 158 - 159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.53 – 7.45 (m, 2H), 4.42 – 4.25 (m, 1H), 4.16 – 3.99 (m, 1H), 3.48 – 3.23 (m, 1H), 2.47 – 2.20 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.78 (q, *J* = 6.6 Hz), 135.23, 135.03, 131.54, 127.18, 125.64 (q, *J* = 277.5 Hz), 123.93 (q, *J* = 257.2 Hz), 46.53, 37.37, 33.97 (q, *J* = 29.7 Hz), 25.72. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.49, -64.46 (t, *J* = 9.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}ClF_6N_2O_2S$ 409.0207; Found 409.0216.

Compound **5an** (16% yield, 16 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.47 (m, 2H), 4.28 – 4.17 (m, 1H), 4.04 – 3.93 (m, 1H), 2.91 – 2.80 (m, 1H), 2.76 – 2.60 (m, 1H), 2.58 – 2.48 (m, 1H), 2.11 – 1.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.52, 135.71, 135.26, 133.73, 132.07, 131.85, 127.52, 126.40 (q, *J* = 283.1 Hz), 45.74, 38.21, 34.50 (q, *J* = 29.8 Hz), 26.49. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.95 (t, *J* = 10.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}ClF_3NO_3S$ 342.0173; Found 342.0180.



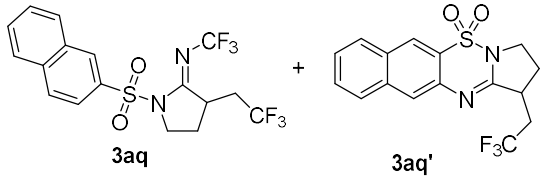
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/1) to afford the title compound **3ao** (60% yield, 81 mg) as white solid, mp: 163 - 164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 4.44 – 4.29 (m, 1H), 4.17 – 4.09 (m, 1H), 3.47 – 3.35 (m, 1H), 2.46 – 2.29 (m, 3H), 2.28 – 2.21 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.72 (q, *J* = 6.9 Hz), 136.99, 135.56, 135.17, 135.04, 127.70, 122.89 (q, *J* = 257.1 Hz), 125.65 (q, *J* = 277.4 Hz), 119.62, 46.71, 37.34, 34.06 (q, *J* = 29.2 Hz), 25.72. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.47, -64.42 (t, *J* =10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}BrF_6N_2O_2S$ 452.9702; Found 452.9712.

Compound **5ao** (16% yield, 18 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.6 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.55 (t, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 4.34 – 4.22 (m, 1H), 4.07 – 3.97 (m, 1H), 2.93 – 2.81 (m, 1H), 2.78 – 2.62 (m, 1H), 2.60 – 2.50 (m, 1H), 2.11 – 1.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.49, 137.43, 135.36, 135.20, 134.22, 128.07, 126.39 (q, *J* = 276.7 Hz), 120.14, 45.88, 38.19, 34.53 (q, *J* = 30.0 Hz), 26.46. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.95 (t, *J* = 10.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}BrF_3NO_3S$ 385.9668; Found 385.9662.



3ap

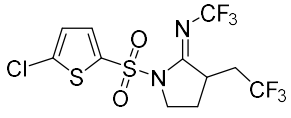
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/3) to afford the title compound (14% yield, 18 mg) as white solid, mp: 146 - 147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.6 Hz, 1H), 7.86 – 7.74 (m, 3H), 4.29 – 4.16 (m, 1H), 4.10 – 3.98 (m, 1H), 3.50 – 3.39 (m, 1H), 2.51 – 2.34 (m, 3H), 2.32 – 2.22 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.17 (q, *J* = 6.8 Hz), 148.32, 136.43, 135.53, 131.79, 130.79, 125.66 (q, *J* = 276.7 Hz), 124.47, 122.96 (q, *J* = 256.9 Hz), 46.59, 37.39, 33.81 (q, *J* = 29.7 Hz), 25.80. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.33, -64.47 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}F_6N_3O_4S$ 420.0447; Found 420.0451.



3aq **3aq'**

After stirring at 30 °C, 10 mA for 3.5 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound **3aq** (5% yield, 6 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.08 – 7.89 (m, 4H), 7.74 – 7.61 (m, 2H), 4.23 – 4.12 (m, 1H), 4.07 – 3.94 (m, 1H), 3.44 – 3.26 (m, 1H), 2.42 – 2.28 (m, 1H), 2.26 – 2.08 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.74 (q, *J* = 6.8 Hz), 135.80, 133.63, 132.04, 131.85, 129.87, 129.84, 129.19, 128.08, 127.95, 125.63 (q, *J* = 277.2 Hz), 123.23 (q, *J* = 256.9 Hz), 123.09, 46.79, 37.37, 33.98 (q, *J* = 29.5 Hz), 25.43. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.88, -64.35 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}F_6N_2O_2S$ 425.0753; Found 425.0763.

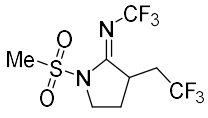
Compound **3aq'** (32% yield, 34 mg) as white solid, mp: 162 - 163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 – 8.77 (m, 1H), 7.95 – 7.80 (m, 3H), 7.75 – 7.56 (m, 2H), 4.37 – 4.22 (m, 1H), 4.17 – 4.03 (m, 1H), 3.55 – 3.22 (m, 2H), 2.79 – 2.59 (m, 1H), 2.41 – 2.20 (m, 1H), 2.08 – 1.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.84, 141.01, 135.71, 129.59, 129.46, 128.00, 127.75, 127.38, 125.44, 126.65 (q, *J* = 276.4 Hz), 119.60, 116.98, 43.46, 39.08 (q, *J* = 2.8 Hz), 35.89 (q, *J* = 29.4 Hz), 26.73. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.57 (t, *J* = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}F_3N_2O_2S$ 355.0723; Found 355.0730.



3ar

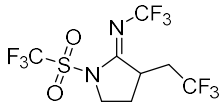
After stirring at 30 °C, 10 mA for 3.5 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/8) to afford the title compound (46% yield, 57 mg) as yellow solid, mp: 84 - 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 4.2 Hz, 1H), 6.99 (d, *J* = 4.1 Hz, 1H), 4.09 – 4.01 (m, 1H), 3.97 – 3.88 (m, 1H), 3.49 – 3.39 (m, 1H), 2.52 – 2.36 (m, 1H), 2.33 – 2.16 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.92 (q, *J* = 6.6 Hz), 140.80, 135.90, 134.02, 126.92, 125.62 (q, *J* = 277.8 Hz), 124.22 (q, *J* = 257.4 Hz), 46.72, 37.39, 34.13 (q,

J = 29.1 Hz), 25.35. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.96, -64.31 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}ClF_6N_2O_2S_2$ 414.9771; Found 414.9779.



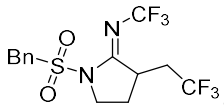
3as

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (44% yield, 41 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 – 3.95 (m, 1H), 3.91 – 3.81 (m, 1H), 3.58 – 3.46 (m, 1H), 3.35 (s, 3H), 2.60 – 2.45 (m, 1H), 2.43 – 2.17 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.53 (q, *J* = 6.7 Hz), 125.70 (q, *J* = 277.6 Hz), 123.31 (q, *J* = 256.9 Hz), 45.96, 40.79, 37.67, 34.12 (q, *J* = 29.6 Hz), 25.37. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.94, -64.28. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_{11}F_6N_2O_2S$ 313.0440; Found 313.0449.



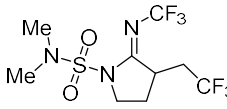
3at

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/2) to afford the title compound (49% yield, 54 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.15 – 4.05 (m, 1H), 4.02 – 3.93 (m, 1H), 3.61 – 3.53 (m, 1H), 2.60 – 2.46 (m, 1H), 2.42 – 2.26 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.49 (q, *J* = 7.5 Hz), 125.40 (q, *J* = 277.5Hz), 122.79 (q, *J* = 258.9 Hz), 119.55 (q, *J* = 324.2 Hz), 48.00, 37.20, 33.76 (q, *J* = 29.6 Hz), 25.50. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.90, -64.23 (t, *J* = 10.0 Hz), -72.94. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_8F_9N_2O_2S$ 367.0157; Found 367.0164.



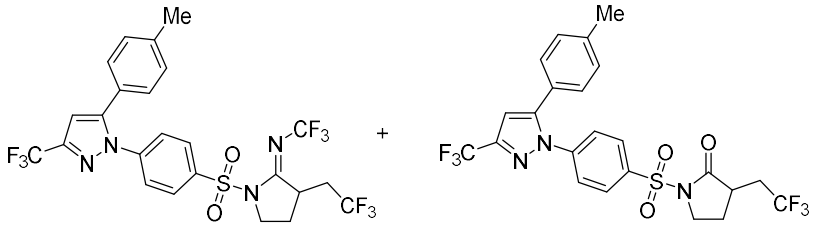
3au

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/10) to afford the title compound (27% yield, 32 mg) as white solid, mp: 103 - 104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 5H), 4.83 (d, *J* = 14.3 Hz, 1H), 4.75 (d, *J* = 14.3 Hz, 1H), 3.47 – 3.37 (m, 2H), 3.37 – 3.28 (m, 1H), 2.44 – 2.30 (m, 1H), 2.06 – 1.74 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.64 (q, *J* = 6.9 Hz), 130.48, 129.82, 129.16, 127.72, 125.53 (q, *J* = 277.6 Hz), 123.45 (q, *J* = 257.3 Hz), 58.03, 47.45, 37.54, 33.69 (q, *J* = 30.6 Hz), 25.44. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.68, -64.56 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}F_6N_2NaO_2S$ 411.0572; Found 411.0584.



3av

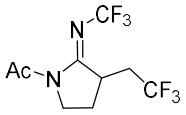
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/5) to afford the title compound (27% yield, 28 mg) as white solid, mp: 84 - 85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 – 3.93 (m, 1H), 3.90 – 3.82 (m, 1H), 3.51 – 3.44 (m, 1H), 2.95 (s, 6H), 2.57 – 2.44 (m, 1H), 2.39 – 2.24 (m, 2H), 2.22 – 2.13 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.85 (q, J = 6.6 Hz), 125.75 (q, J = 277.0 Hz), 123.72 (q, J = 256.6 Hz), 48.37, 38.57, 37.15, 34.21 (q, J = 29.2 Hz), 25.70. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.36, -64.31 (t, J = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_{14}F_6N_3O_2S$ 342.0705; Found 342.0711.



3aw (major) **5aw**

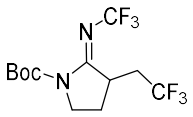
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/1) to afford the title compound **3aw** (58% yield, 104 mg) as white solid, mp: 118 - 121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 6.75 (s, 1H), 4.23 – 4.07 (m, 1H), 4.03 – 3.89 (m, 1H), 3.47 – 3.32 (m, 1H), 2.39 (s, 3H), 2.43 – 2.32 (m, 1H), 2.30 – 2.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.81 (q, J = 6.8 Hz), 145.59, 144.44 (q, J = 38.2 Hz), 144.05, 140.15, 136.09, 130.31, 129.92, 128.85, 125.71, 125.62 (q, J = 277.6 Hz), 125.09, 123.09 (q, J = 257.5 Hz), 121.14 (q, J = 269.9 Hz), 106.66, 46.75, 37.29, 34.04 (q, J = 29.8 Hz), 25.41, 21.39. ^{19}F NMR (470 MHz, $CDCl_3$) δ -52.03, -62.53, -64.26 (t, J = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}F_9N_4O_2S$ 599.1158; Found 599.1165.

Compound **5aw** (11% yield, 18 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.75 (s, 1H), 4.04 – 3.95 (m, 1H), 3.74 – 3.63 (m, 1H), 2.81 – 2.67 (m, 2H), 2.56 – 2.42 (m, 1H), 2.39 (s, 3H), 2.12 – 1.97 (m, 1H), 1.94 – 1.81 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.41, 145.52, 144.53 (q, J = 38.5 Hz), 144.06, 140.15, 137.01, 129.98, 129.33, 128.86, 126.36 (q, J = 276.5 Hz), 125.73, 125.51, 121.12 (q, J = 268.9 Hz), 106.70, 45.51, 38.34, 34.57 (q, J = 29.7 Hz), 25.95, 21.48. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.56, -64.94 (t, J = 10.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}F_6N_3O_3S$ 532.1124; Found 532.1123.



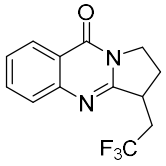
3fa

After stirring at 30 °C, 5 mA for 6 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (37% yield, 31 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 – 4.02 (m, 1H), 3.77 – 3.63 (m, 1H), 3.61 – 3.53 (m, 1H), 2.57 (s, 3H), 2.53 – 2.41 (m, 1H), 2.36 – 2.21 (m, 1H), 2.20 – 2.11 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.60, 168.11 (q, J = 6.1 Hz), 125.88 (q, J = 253.4 Hz), 125.78 (q, J = 278.1 Hz), 77.41, 44.74, 38.33, 34.41 (q, J = 29.1 Hz), 26.98, 24.06. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.69, -64.41 (t, J = 10.1 Hz). HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_9H_{10}F_6N_2NaO$ 299.0590; Found 299.0598.



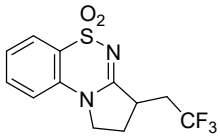
3ga

After stirring at 30 ℃, 5 mA for 6 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (47% yield, 47 mg) as white solid, mp: 124 - 125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 – 3.88 (m, 1H), 3.81 – 3.68 (m, 1H), 3.53 – 3.44 (m, 1H), 2.62 – 2.43 (m, 1H), 2.33 – 2.20 (m, 1H), 2.19 – 2.04 (m, 2H), 1.53 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.07 (q, J = 5.0 Hz), 149.34, 125.88 (q, J = 278.0 Hz), 124.44 (q, J = 257.2 Hz), 84.08, 45.98, 37.67, 34.17 (q, J =29.0 Hz), 28.08, 24.53. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.08, -64.40 (t, J = 10.2 Hz). HRMS (ESI) m/z: $[M – Boc + H]^+$ Calcd for $C_7H_9F_6N_2$ 235.0664; Found 235.0656.



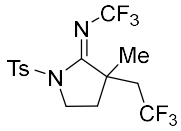
6

After stirring at 30 °C for 2 hours (Scheme 5b), the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/2) to afford the title compound (54% yield, 43 mg) as white solid, mp: 124 - 127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.20 (m, 1H), 7.77 – 7.69 (m, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.49 – 7.41 (m, 1H), 4.45 – 4.31 (m, 1H), 4.04 – 3.83 (m, 1H), 3.59 – 3.43 (m, 1H), 3.34 – 3.14 (m, 1H), 2.73 – 2.57 (m, 1H), 2.38 – 2.17 (m, 1H), 2.12 – 1.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.83, 158.65, 148.99, 134.39, 127.18, 126.78, 126.70 (q, J = 276.7 Hz), 126.56, 120.95, 44.81, 38.45 (q, J = 2.8 Hz), 36.07 (q, J = 29.1 Hz), 27.59. ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.68 (t, J = 10.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}F_3N_2O$ 269.0896; Found 269.0906. NMR spectra data were in accordance with the reported data[11].



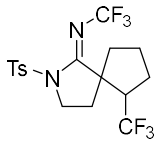
7

After stirring at 30 ℃ for 2 hours (Scheme 5b), the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/1) to afford the title compound (41% yield, 38 mg) as white solid, mp: 192 - 195 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.81 (m, 1H), 7.74 – 7.58 (m, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 8.3 Hz, 1H), 4.24 – 4.13 (m, 1H), 4.07 – 3.91 (m, 1H), 3.57 – 3.34 (m, 1H), 3.19 – 2.96 (m, 1H), 2.81 – 2.58 (m, 1H), 2.40 – 2.20 (m, 1H), 2.18 – 2.01 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.93, 134.53, 133.29, 127.01, 126.40 (q, J = 276.4 Hz), 125.22, 122.02, 115.16, 48.11, 39.45, 35.67 (q, J = 29.6 Hz), 26.11. NMR spectra data were in accordance with the reported data. [10]



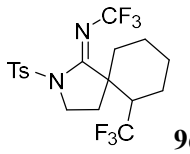
9a

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (60% yield, 72 mg) as white solid, mp: 103 - 104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.05 – 3.98 (m, 1H), 3.97 – 3.89 (m, 1H), 2.59 – 2.47 (m, 1H), 2.45 (s, 3H), 2.41 – 2.28 (m, 2H), 2.09 – 1.98 (m, 1H), 1.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.79 (q, *J* = 6.8 Hz), 145.70, 133.77, 129.48, 129.34, 125.84 (q, *J* = 278.4 Hz), 122.80 (q, *J* = 255.3 Hz), 45.38, 45.25, 39.02 (q, *J* = 28.1 Hz), 33.94, 22.21, 21.88. ^{19}F NMR (470 MHz, $CDCl_3$) δ -46.02, -59.93 (t, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}F_6N_2O_2S$ 403.0909; Found 403.0919.



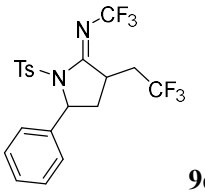
9c

After stirring at 30 °C, 10 mA for 3.5 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/10) to afford the title compound (39% yield, 50 mg) as white solid, mp: 110 - 112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.06 – 3.98 (m, 1H), 3.90 – 3.82 (m, 1H), 3.25 – 3.08 (m, 1H), 2.44 (s, 3H), 2.40 – 2.31 (m, 1H), 2.10 – 1.95 (m, 2H), 1.94 – 1.86 (m, 1H), 1.84 – 1.72 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.34 (q, *J* = 6.6 Hz), 145.47, 133.98, 129.48, 129.21, 126.68 (q, *J* = 279.1 Hz), 122.90 (q, *J* = 255.3 Hz), 55.05, 47.78 (q, *J* = 26.1 Hz), 45.43, 36.32, 30.19, 24.82, 21.87, 21.52. ^{19}F NMR (470 MHz, $CDCl_3$) δ -45.31, -64.54 (d, *J* = 9.0 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{19}F_6N_2O_2S$ 429.1066; Found 429.1076.



9d

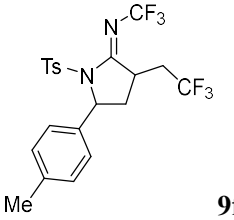
After stirring at 30 °C, 10 mA for 3.5 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/10) to afford the title compound (37% yield, 49 mg) as white solid, mp: 112 - 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.01 – 3.87 (m, 2H), 2.91 – 2.75 (m, 1H), 2.43 (s, 3H), 4.01 – 3.87 (m, 1H), 2.11 – 2.03 (m, 1H), 1.93 – 1.85 (m, 1H), 1.85 – 1.77 (m, 2H), 1.73 – 1.65 (m, 1H), 1.63 – 1.54 (m, 1H), 1.44 – 1.25 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.46 (q, *J* = 6.7 Hz), 145.23, 133.70, 129.43, 128.97, 126.62 (q, *J* = 281.1 Hz), 122.72 (q, *J* = 254.7 Hz), 49.66, 45.02, 43.97 (q, *J* = 25.9 Hz), 32.92, 26.48, 23.79, 22.55, 21.72, 21.16. ^{19}F NMR (470 MHz, $CDCl_3$) δ -44.47, -66.64 (d, *J* = 8.8 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}F_6N_2O_2S$ 443.1222; Found 443.1230.



9e

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the major isomer (48% yield, 66 mg) as white solid, mp: 88 - 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.20 – 7.07 (m, 4H), 5.45 (t, *J* = 7.4 Hz, 1H), 3.56 – 3.43 (m, 1H), 2.71 – 2.52 (m, 2H), 2.40 (s, 3H), 2.37 – 2.26 (m, 1H), 2.25 – 2.15 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.48 (q, *J* = 7.0 Hz), 145.44, 139.80, 134.39, 129.62, 129.00, 128.71, 126.97, 125.78 (q, *J* = 278.2 Hz), 123.38 (q, *J* = 257.4 Hz), 63.17, 36.86, 36.08, 35.31 (q, *J* = 29.4 Hz), 21.77. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.42, -64.17 (t, *J* = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}F_6N_2O_2S$ 465.1066; Found 465.1070.

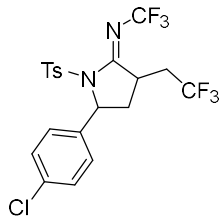
The minor isomer (14% yield, 20 mg) as white solid, mp: 170 - 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 2H), 5.70 (d, *J* = 9.1 Hz, 1H), 3.37 (t, *J* = 10.1 Hz, 1H), 2.79 – 2.67 (m, 1H), 2.40 (s, 3H), 2.44 – 2.34 (m, 1H), 2.22 (d, *J* = 13.5 Hz, 1H), 2.07 – 1.83 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.29 (q, *J* = 7.5 Hz), 145.97, 141.31, 134.24, 130.06, 129.32, 128.36, 125.28, 125.58 (q, *J* = 277.8 Hz), 123.21 (q, *J* = 256.9 Hz), 63.41, 36.52, 36.21 (q, *J* = 29.7 Hz), 35.51, 21.90. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.72, -65.45 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}F_6N_2O_2S$ 465.1066; Found 465.1073.



9f

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the major isomer (40% yield, 57 mg) as white solid, mp: 117 - 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.10 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.40 (t, *J* = 7.4 Hz, 1H), 3.58 – 3.40 (m, 1H), 2.67 – 2.52 (m, 2H), 2.40 (s, 3H), 2.37 (s, 3H), 2.34 – 2.23 (m, 1H), 2.22 – 2.12 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.52 (q, *J* = 6.9 Hz), 145.38, 138.58, 136.83, 134.47, 129.62, 128.91, 126.88, 125.78 (q, *J* = 277.4 Hz), 123.40 (q, *J* = 257.7 Hz), 63.05, 36.84, 36.14, 35.22 (q, *J* = 29.4 Hz), 21.75, 21.25. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.34, -64.22 (t, *J* = 10.2 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}F_6N_2O_2S$ 479.1222; Found 479.1223.

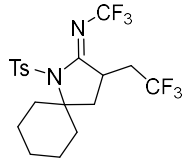
The minor isomer (10% yield, 14 mg) as white solid, mp: 175 - 177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.67 (d, *J* = 9.1 Hz, 1H), 3.35 (t, *J* = 10.0 Hz, 1H), 2.77 – 2.65 (m, 1H), 2.46 (s, 3H), 2.44 – 2.40 (m, 1H), 2.37 (s, 3H), 2.20 (d, *J* = 13.5 Hz, 1H), 2.05 – 1.91 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.35 (q, *J* = 6.8 Hz), 145.90, 138.32, 138.12, 134.29, 130.05, 129.96, 129.29, 125.62 (q, *J* = 277.7 Hz), 125.15, 123.23 (q, *J* = 256.9 Hz), 63.33, 36.52, 36.24 (q, *J* = 28.9 Hz), 35.57, 21.89, 21.22. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.68, -65.45 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}F_6N_2O_2S$ 479.1222; Found 479.1232.



9g

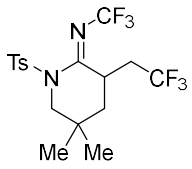
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the major isomer (41% yield, 61 mg) as white solid, mp: 118 - 120 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.41 (t, *J* = 7.5 Hz, 1H), 3.58 – 3.40 (m, 1H), 2.63 – 2.51 (m, 2H), 2.42 (s, 3H), 2.36 – 2.22 (m, 1H), 2.17 – 2.03 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.41 (q, *J* = 6.6 Hz), 145.75, 138.46, 134.58, 134.33, 129.49, 129.17, 129.12, 128.30, 125.70 (q, *J* = 277.4 Hz), 123.30 (q, *J* = 257.7 Hz), 62.48, 36.74, 35.95, 35.04 (q, *J* = 29.8 Hz), 21.79. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.62, -64.17 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}ClF_6N_2O_2S$ 499.0676; Found 499.0684.

The minor isomer (12% yield, 18 mg) as white solid, mp: 203 - 206 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 5.65 (d, *J* = 9.2 Hz, 1H), 3.37 (t, *J* = 10.1 Hz, 1H), 2.82 – 2.65 (m, 1H), 2.47 (s, 3H), 2.47 – 2.32 (m, 1H), 2.19 (d, *J* = 13.6 Hz, 1H), 2.00 – 1.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.05 (q, *J* = 6.4 Hz), 146.19, 140.01, 134.30, 134.04, 130.02, 129.56, 129.42, 126.71, 125.49 (q, *J* = 277.8 Hz), 123.13 (q, *J* = 256.9 Hz), 77.41, 62.82, 36.44, 36.22 (q, *J* = 30.4 Hz), 35.37, 21.92. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.85, -65.31 (t, *J* = 10.0 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}ClF_6N_2O_2S$ 499.0676; Found 499.0675.



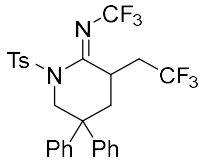
9h

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/10) to afford the title compound (49% yield, 67 mg) as white solid, mp: 155 - 156 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.26 (t, *J* = 10.4 Hz, 1H), 2.92 – 2.82 (m, 1H), 2.63 – 2.48 (m, 1H), 2.43 (s, 3H), 2.41 – 2.36 (m, 1H), 2.26 – 2.13 (m, 1H), 2.06 (dd, *J* = 13.8, 9.4 Hz, 1H), 1.90 (d, *J* = 13.9 Hz, 1H), 1.84 (d, *J* = 11.8 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.52 – 1.41 (m, 1H), 1.40 – 1.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.25 (q, *J* = 6.4 Hz), 145.09, 135.73, 129.85, 129.00, 125.83 (q, *J* = 277.5 Hz), 123.08 (q, *J* = 256.5 Hz), 72.82, 38.36, 36.58 (q, *J* = 29.1 Hz), 36.33, 35.81, 34.59, 24.50, 24.20, 23.50, 21.78. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.00, -64.18 (t, *J* = 10.0 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}F_6N_2O_2S$ 457.1379; Found 457.1391.



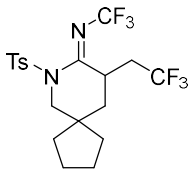
9k

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/10) to afford the title compound (25% yield, 32 mg) as white solid, mp: 121 - 122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.97 (dd, *J* = 13.5, 1.7 Hz, 1H), 3.46 (d, *J* = 13.5 Hz, 1H), 3.38 – 3.28 (m, 1H), 2.44 (s, 3H), 2.39 – 2.26 (m, 2H), 1.83 – 1.65 (m, 2H), 1.12 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.38 (q, *J* = 7.0 Hz), 145.29, 134.94, 129.82, 129.16, 125.85 (q, *J* = 278.0 Hz), 122.98 (q, *J* = 257.0 Hz), 56.44, 38.82, 37.98 (q, *J* = 28.8 Hz), 32.72, 32.00, 28.42, 26.46, 21.82. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.01, -63.83 (t, *J* = 9.9 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}F_6N_2O_2S$ 431.1222; Found 431.1232.



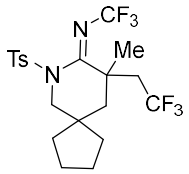
9l

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/10) to afford the title compound (33% yield, 55 mg) as white solid, mp: 153 - 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 3H), 7.15 – 7.09 (m, 3H), 7.07 (t, *J* = 7.3 Hz, 2H), 6.90 (d, *J* = 7.4 Hz, 2H), 4.62 (dd, *J* = 12.8, 2.7 Hz, 1H), 4.30 (d, *J* = 12.8 Hz, 1H), 3.55 – 3.26 (m, 1H), 3.07 – 2.94 (m, 1H), 2.45 (s, 3H), 2.43 – 2.30 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.97 (q, *J* = 6.6 Hz), 157.78, 145.16, 144.97, 140.96, 134.26, 129.81, 129.18, 129.02, 128.93, 127.46, 127.19, 126.30, 125.90 (q, *J* = 278.3 Hz), 122.69 (q, *J* = 257.4 Hz), 55.43, 46.37, 39.02 (q, *J* = 28.9 Hz), 38.15, 34.15, 21.80. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.90, -63.63 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}F_6N_2O_2S$ 555.1535; Found 555.1538.



9m

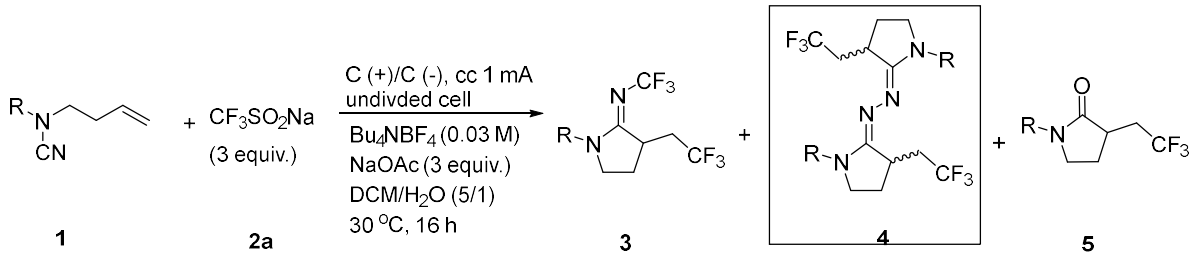
After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the title compound (32% yield, 44 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.87 (dd, *J* = 13.0, 2.1 Hz, 1H), 3.57 (d, *J* = 13.0 Hz, 1H), 3.41 – 3.33 (m, 1H), 2.44 (s, 3H), 2.41 – 2.33 (m, 2H), 2.02 – 1.89 (m, 1H), 1.83 – 1.76 (m, 1H), 1.73 – 1.59 (m, 5H), 1.55 – 1.47 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.28 (q, *J* = 6.9 Hz), 145.25, 134.87, 129.73, 129.20, 125.89 (q, *J* = 278.0 Hz), 122.93 (q, *J* = 257.5 Hz), 55.41, 43.14, 38.81, 38.24 (q, *J* = 28.9 Hz), 38.09, 36.67, 33.53, 24.53, 24.45, 21.83. ^{19}F NMR (470 MHz, $CDCl_3$) δ -51.36, -63.88 (t, *J* = 10.1 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}F_6N_2O_2S$ 457.1379; Found 457.1389.



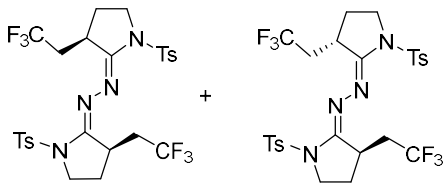
9n

After stirring at 30 °C for 2 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/10) to afford the title compound (10% yield, 14 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 3.63 (d, J = 11.5 Hz, 1H), 3.48 (d, J = 11.7 Hz, 1H), 2.55 – 2.48 (m, 2H), 2.45 (s, 3H), 2.11 (d, J = 14.2 Hz, 1H), 1.72 (s, 1H), 1.70 – 1.62 (m, 4H), 1.59 – 1.51 (m, 2H), 1.47 – 1.40 (m, 2H), 1.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.31, 144.90, 135.55, 129.50, 128.93, 126.23 (q, J = 278.9 Hz), 121.83 (q, J = 256.8 Hz), 56.23, 48.65, 43.02, 42.82, 42.71 (q, J = 27.2 Hz), 37.73, 36.94, 25.81, 24.43, 24.05, 21.80. ^{19}F NMR (470 MHz, $CDCl_3$) δ -58.30 (t, J = 10.9 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{25}F_6N_2O_2S$ 471.1535; Found 471.1542.

2. General procedure for preparation of products 4



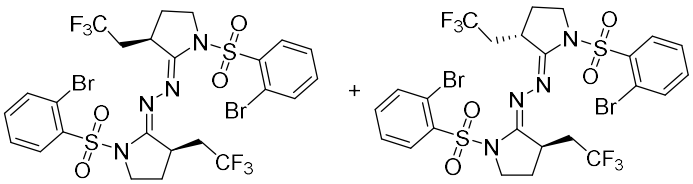
In the IKA ElectraSyn 2.0 undivided cell (25 mL) equipped with a stir bar, a mixture of **1** (0.3 mmol), CF_3SO_2Na **2a** (0.9 mmol), Bu_4NBF_4 (0.3 mmol), NaOAc (0.9 mmol) and DCM/H_2O (v/v = 5/1, 10 mL) were added. The cell was equipped with two graphite plate electrodes (0.8 cm × 1.5 cm × 0.2 cm). The reaction mixture was stirred and electrolyzed at a constant current of 1 mA at 30 °C for 16 h. Upon completion, 5 mL H_2O was added, the mixture was extracted with DCM (8 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products **4**.



4aa-*syn* **4aa-*anti***

After stirring at 30 ℃, 1 mA for 16 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound **4aa-*syn*** (21% yield, 20 mg) as white solid, mp: 238 - 240 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 4H), 7.27 (d, *J* = 8.4 Hz, 4H), 4.10 – 3.80 (m, 4H), 3.52 – 3.42 (m, 2H), 3.05 – 2.74 (m, 2H), 2.41 (s, 6H), 2.24 – 2.00 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.44, 144.66, 136.04, 129.62, 127.54, 126.50 (q, *J* = 277.6 Hz), 48.21, 35.16, 33.47 (q, *J* = 28.0 Hz), 24.62, 21.71. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55 (t, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}F_6N_4O_4S_2$ 639.1529; Found 639.1539.

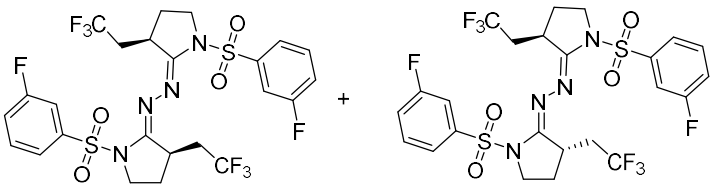
Compound **4aa-*anti*** (21% yield, 20 mg) as white solid, mp: 249 - 251 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 4H), 4.14 – 4.05 (m, 2H), 3.87 – 3.76 (m, 2H), 3.51 – 3.42 (m, 2H), 2.96 – 2.78 (m, 2H), 2.43 (s, 6H), 2.26 – 2.07 (m, 4H), 2.05 – 1.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.43, 144.81, 135.76, 129.60, 127.64, 126.47 (q, *J* = 278.4 Hz), 48.16, 35.36, 32.94 (q, *J* = 28.6 Hz), 24.42, 21.78. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.44 (t, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}F_6N_4O_4S_2$ 639.1529; Found 639.1540.



4ao-*syn* 4ao-*anti*

After stirring at 30 ℃, 1 mA for 16 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/5) to afford the title compound **4ao-*syn*** (20% yield, 22 mg) as white solid, mp: 254 - 257 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.74 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.54 – 7.42 (m, 4H), 4.25 – 4.10 (m, 4H), 3.25 – 3.04 (m, 2H), 2.88 – 2.75 (m, 2H), 2.24 – 1.97 (m, 6H). ^{13}C NMR (125 MHz, DMSO) δ 159.84, 137.57, 135.49, 135.15, 132.12, 126.60 (q, *J* = 278.6 Hz), 119.16, 47.87, 34.50, 32.42 (q, *J* = 27.2 Hz), 24.00. ^{19}F NMR (470 MHz, DMSO) δ -61.29 (t, *J* = 11.4 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}Br_2F_6N_4O_4S_2$ 766.9426; Found 766.9417.

Compound **4ao-*anti*** (20% yield, 22 mg) as white solid, mp: 265 - 268 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.69 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.51 – 7.35 (m, 4H), 4.37 – 4.18 (m, 2H), 4.09 – 3.91 (m, 2H), 3.29 – 3.12 (m, 2H), 2.80 – 2.58 (m, 2H), 2.23 – 1.90 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.71, 138.62, 135.43, 134.51, 133.21, 127.60, 126.37 (q, *J* = 278.4 Hz), 120.14, 48.12, 35.11, 32.83 (q, *J* = 28.5 Hz), 24.09. ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.85 (t, *J* = 10.9 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}Br_2F_6N_4O_4S_2$ 766.9426; Found 766.9419.

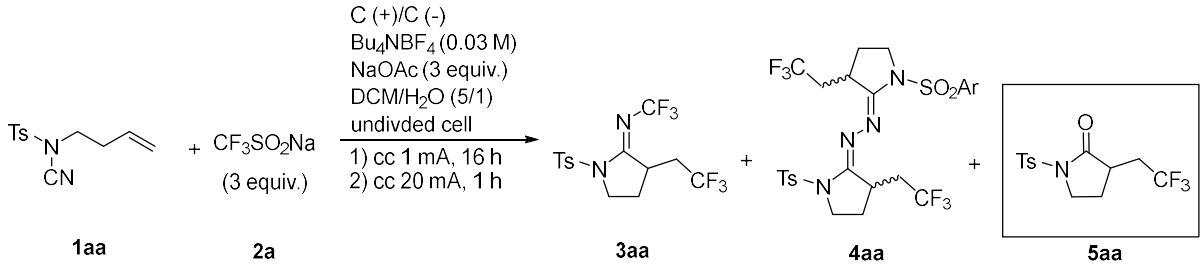


4ak-*syn* 4ak-*anti*

After stirring at 30 ℃, 1 mA for 16 hours, the residue was purified by column chromatography (silica gel, EtOAc /Petroleum ether: 1/3) to afford the title compound **4ak-*syn*** (23% yield, 23 mg) as yellow solid, mp: 225 - 247 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.52 – 7.44 (m, 2H), 7.36 – 7.27 (m, 2H), 4.14 – 3.97 (m, 2H), 3.93 – 3.80 (m, 2H), 3.54 – 3.36 (m, 2H), 3.14 – 2.87 (m, 2H), 2.36 – 2.06 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.28 (d, *J* = 251.7 Hz), 160.56, 140.77 (d, *J* = 7.0 Hz), 130.86 (d, *J* = 7.7 Hz), 126.42 (q, *J* = 277.8 Hz), 123.29 (d, *J* = 3.3 Hz), 120.95 (d, *J* = 21.2 Hz), 115.10 (d, *J* = 24.8 Hz), 48.36, 35.32 (q, *J* = 2.8 Hz), 33.84 (q, *J* = 28.4 Hz), 24.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.83 (t, *J* = 10.8 Hz), -109.47 – -109.57 (m). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}F_8N_4O_4S_2$ 647.1027; Found 647.1018.

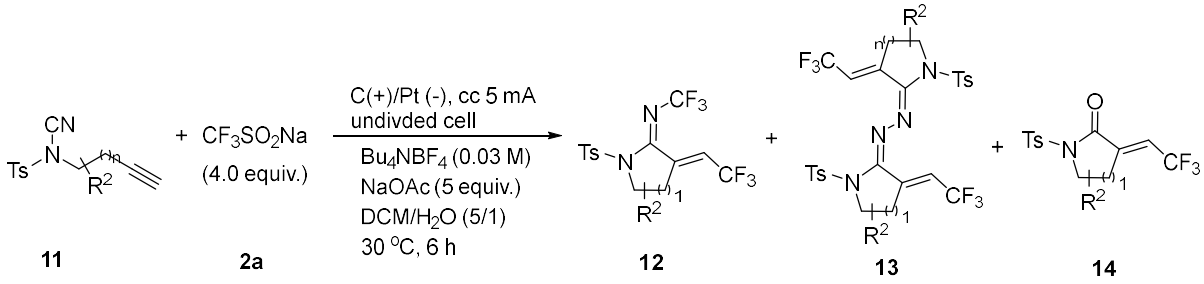
Compound **4ak-*anti*** (24% yield, 23 mg) as white solid, mp: 253 - 255 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.54 – 7.45 (m, 2H), 7.37 – 7.29 (m, 2H), 4.20 – 4.07 (m, 2H), 3.88 – 3.74 (m, 2H), 3.56 – 3.41 (m, 2H), 2.93 – 2.75 (m, 2H), 2.34 – 1.96 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.24 (d, *J* = 251.7 Hz), 160.63, 140.38 (d, *J* = 6.9 Hz), 130.90 (d, *J* = 7.7 Hz), 126.37 (q, *J* = 277.7 Hz), 123.20 (d, *J* = 3.4 Hz), 121.08 (d, *J* = 21.2 Hz), 115.20 (d, *J* = 24.9 Hz), 48.34, 35.44 (q, *J* = 3.0 Hz), 33.14 (q, *J* = 28.4 Hz), 24.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.65 (t, *J* = 10.9 Hz), -109.38 – -109.52 (m). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}F_8N_4O_4S_2$ 647.1027; Found 647.1019.

3. One pot method for preparation of products 5aa



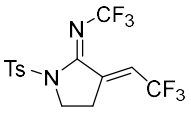
In an undivided three necked-flask (25 mL) equipped with a stir bar, a mixture of **1aa** (0.3 mmol, 75 mg), CF_3SO_2Na **2a** (0.9 mmol), Bu_4NBF_4 (0.3 mmol), NaOAc (0.9 mmol) and DCM/H_2O (v/v = 5/1, 10 mL) were added. The cell was equipped with two graphite rod (Φ 6 mm) electrodes and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 1 mA at 30 °C for 16 h. Then, the reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 30 °C for 1 h. Upon completion, 5 mL H_2O was added, the mixture was extracted with DCM (8 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 ºC)) to provide the desired products **5aa** (42,4 mg, 44% yield), **3aa** (23.2 mg, 20% yield).

4. General procedure for preparation of products 12



11 **2a** **12** **13** **14**

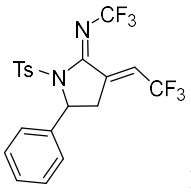
In an undivided three necked-flask (25 mL) equipped with a stir bar, a mixture of alkyne **11** (0.3 mmol), CF_3SO_2Na **2a** (1.2 mmol), Bu_4NBF_4 (0.3 mmol), NaOAc (1.5 mmol) and DCM/H_2O (v/v = 5/1, 10 mL) were added. The cell was equipped with graphite rod (Φ 6 mm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at 30 °C for 6 h. Upon completion, 5 mL H_2O was added, the mixture was extracted with DCM (8 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products **12**.



12a

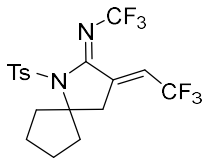
After stirring at 30 °C for 6 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/10) to afford the major isomer **12a** (*E*-(C=N), *E*-(C=C)) (38% yield, 44 mg) as white solid, mp: 131 - 133 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.63 – 6.56 (m, 1H), 4.05 (t, *J* = 6.9 Hz, 2H), 3.07 – 2.99 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.37 (q, *J* = 7.4 Hz), 146.15, 139.27 (q, *J* = 5.0 Hz), 133.64, 129.69, 129.53, 125.03 (qq, *J* = 36.5, 8.1 Hz), 122.34 (q, *J* = 256.5 Hz), 122.28 (q, *J* = 272.0 Hz), 45.88, 25.87, 21.86. ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.13, -60.63 (dt, *J* = 7.7, 2.5 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}F_6N_2O_2S$ 387.0596; Found 387.0606.

Purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the minor isomer **12a** (*E*-(C=N), *Z*-(C=C)) (1% yield, 1 mg) as white solid, mp: 138 - 141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.85 (q, *J* = 8.2 Hz, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 2.75 (t, *J* = 6.3 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.14 (q, *J* = 8.0 Hz), 145.91, 138.54 (q, *J* = 5.0 Hz), 134.24, 129.65, 129.12, 121.83 (q, *J* = 255.9 Hz), 121.02 (q, *J* = 37.8 Hz), 120.24 (q, *J* = 270.7 Hz), 46.43, 33.41, 21.84. ^{19}F NMR (470 MHz, $CDCl_3$) δ -54.62 (q, *J* = 10.0 Hz), -62.56 (t, *J* = 9.4 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}F_6N_2O_2S$ 387.0596; Found 387.0600.



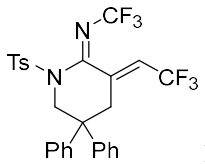
12b

After stirring at 30 °C for 6 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (26% yield, 36 mg) as yellow solid, mp: 123 - 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.20 – 7.08 (m, 4H), 6.81 – 6.65 (m, 1H), 5.60 (d, J = 8.9 Hz, 1H), 3.55 – 3.32 (m, 1H), 3.05 (d, J = 18.5 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.40 (q, J = 7.3 Hz), 145.78, 139.61, 138.95 (q, J = 4.3 Hz), 133.71, 130.02, 129.28, 126.42, 125.58 (qq, J = 31.5, 5.0 Hz), 122.49 (q, J = 256.8 Hz), 122.19 (q, J = 272.7 Hz), 61.42, 36.12, 21.81. ^{19}F NMR (470 MHz, $CDCl_3$) δ -48.95, -60.57 (dt, J = 7.3, 2.7 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{17}F_6N_2O_2S$ 463.0909; Found 463.0918.



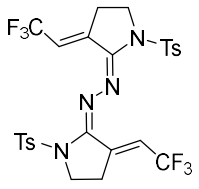
12c

After stirring at 30 °C, 10 mA for 3 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (30% yield, 40 mg) as white solid, mp: 78 - 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.60 – 6.46 (m, 1H), 2.90 – 2.85 (m, 2H), 2.82 – 2.72 (m, 2H), 2.45 (s, 3H), 2.09 – 1.98 (m, 2H), 1.80 – 1.65 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.73 (q, J = 7.5 Hz), 145.48, 138.28 (q, J = 5.0 Hz), 135.26, 129.95, 129.19, 123.89 (qq, J = 30.9, 3.8 Hz), 122.36 (q, J = 257.2 Hz), 122.30 (q, J = 271.2 Hz), 74.92, 44.07, 38.12, 24.48, 21.82. ^{19}F NMR (470 MHz, $CDCl_3$) δ -49.12, -59.78 (dt, J = 7.5, 2.6 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}F_6N_2O_2S$ 441.1066; Found 441.1073.



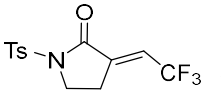
12d

After stirring at 30 °C for 6 hours, the residue was purified by column chromatography (silica gel, DCM/Petroleum ether: 1/1) to afford the title compound (6% yield, 10 mg) as white solid, mp: 130 - 133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.29 – 7.15 (m, 6H), 7.13 – 6.98 (m, 6H), 6.32 – 6.12 (m, 1H), 4.60 (s, 2H), 3.48 – 3.39 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.67 (q, J = 7.8 Hz), 144.87, 144.47, 139.78 (q, J = 3.8 Hz), 134.45, 129.64, 129.02, 127.42, 126.95, 125.02 (q, J = 35.4 Hz), 122.54 (q, J = 256.6 Hz), 121.91 (q, J = 273.0 Hz), 54.34, 47.61, 37.59, 21.78. ^{19}F NMR (470 MHz, $CDCl_3$) δ -48.09, -59.01 (dt, J = 7.8, 2.4 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{23}F_6N_2O_2S$ 553.1379; Found 553.1373.



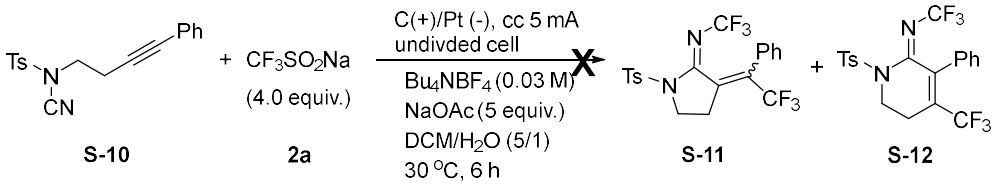
13a

After stirring at 30 °C for 6 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/5) to afford the title compound (2% yield, 4 mg) as yellow solid, mp: 208 - 211 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 4H), 7.23 (d, *J* = 8.1 Hz, 4H), 3.96 (t, *J* = 7.3 Hz, 4H), 3.00 – 2.93 (m, 4H), 2.42 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.17, 144.87, 137.00 (q, *J* = 5.0 Hz), 135.15, 129.67, 127.82, 126.73 (q, *J* = 34.4 Hz), 123.36 (q, *J* = 272.4 Hz), 47.02, 25.64, 21.78. ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.35 (dt, *J* = 8.5, 2.4 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}F_6N_4O_4S_2$ 635.1216; Found 635.1220.



14a

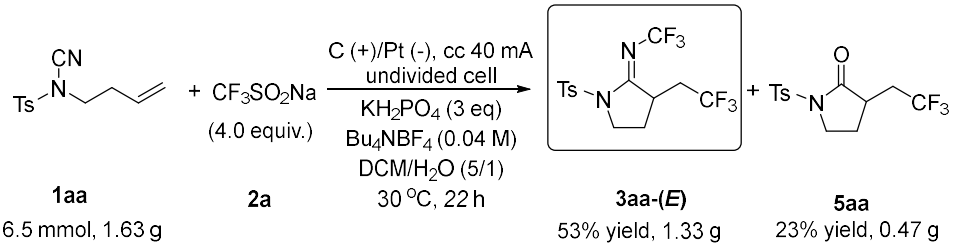
After stirring at 30 °C for 6 hours, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether: 1/9) to afford the title compound (8% yield, 8 mg) as white solid, mp: 156 - 158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.56 – 6.45 (m, 1H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.06 – 2.98 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.12, 146.07, 140.31 (q, *J* = 5.0 Hz), 134.41, 129.99, 128.49, 122.75 (q, *J* = 271.3 Hz), 121.62 (q, *J* = 36.1 Hz), 43.99, 22.50, 21.83. ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.38 (dt, *J* = 7.3, 3.3 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}F_3NO_3S$ 320.0563; Found 320.0571.



Scheme S1. Unsuccessful cyanamide bearing internal alkyne moiety

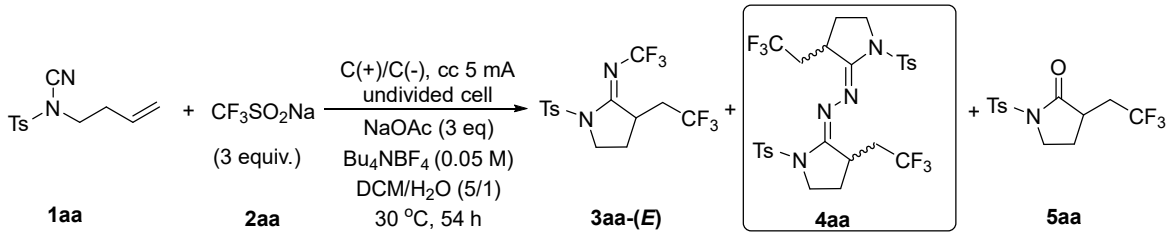
V. Scale-up Experiment and Synthetic Transformations

1. Gram-Scale Experiment



1aa 6.5 mmol, 1.63 g | **2a** | **3aa-(*E*)** 53% yield, 1.33 g | **5aa** 23% yield, 0.47 g

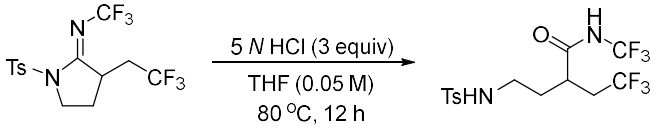
In an undivided cell (250 mL) equipped with a stir bar, a mixture of **1aa** (6.5 mmol, 1.63 g), CF_3SO_2Na **2a** (26 mmol, 4.1 g), Bu_4NBF_4 (6.5 mmol, 2.14 g), KH_2PO_4 (19.5 mmol, 2.65 g) and DCM/H_2O (v/v = 5/1, 162 mL) were added. The cell was equipped with graphite plate (2 cm × 2 cm × 0.1 cm) as the anode and platinum plate (2 cm × 2 cm × 0.02 cm) as the cathode and connected to a DC regulated power supply (the distance between the electrodes is about 10 mm). The reaction mixture was stirred and electrolyzed at a constant current of 40 mA at 30 °C for 22 h. When the reaction was finished, the mixture was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60 - 90 °C)) to provide the desired product **3aa** (53% yield, 1.33 g).



1aa 5 mmol, 1.25 g | **2aa** | **3aa-(*E*)** 13% yield, 0.24 g | **4aa** 45% yield, 0.718 g *anti/syn* = 1/1 | **5aa** trace

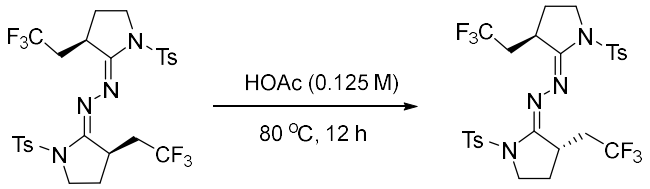
In an undivided cell (100 mL) equipped with a stir bar, a mixture of **1aa** (5 mmol, 1.25 g), CF_3SO_2Na **2a** (15 mmol, 2.46 g), Bu_4NBF_4 (5 mmol, 1.65 g), NaOAc (15 mmol, 1.23 g) and DCM/H_2O (v/v = 5/1, 100 mL) were added. The cell was equipped with two graphite rod (Φ 6 mm) electrodes (the immersion length is 2 cm), and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at 30 °C for 54 h. When the reaction was finished, the mixture was extracted with DCM. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60 - 90 °C)) to provide the desired product **4aa** (45% yield, 0.718 g, *anti/syn* = 1/1).

2. Transformations of the Product 3aa and 4aa



3aa-(*E*) → **15**, 62% yield

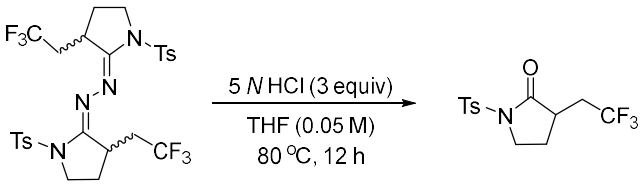
To solution of **3aa** (0.2 mmol, 77.7 mg) in THF (0.05 *M,* 4 mL) in a dried tube was added HCl (5 *N*, 0.12 mL) at room temperature, then the reaction mixture was warmed to 80 °C and allowed to proceed for 12 h. Upon completion, the mixture was cooled to room temperature and the solution was concentrated *in vacuo* to get the crude product. The crude product was washed with DCM (1 mL × 2) to afford the title compound **15** (62% yield, 50 mg) as white solid, mp: 149 - 151 °C. ^{1}H NMR (500 MHz, DMSO) δ 11.16 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 5.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.78 – 2.65 (m, 3H), 2.60 – 2.52 (m, 1H), 2.48 – 2.39 (m, 1H), 2.38 (s, 3H), 1.74 – 1.56 (m, 2H). ^{13}C NMR (125 MHz, DMSO) δ 172.25, 142.74, 137.23, 129.65, 126.55, 126.51 (q, *J* = 277.1 Hz), 118.99 (q, *J* = 259.5 Hz), 39.85, 37.00, 34.09 (q, *J* = 27.8 Hz), 31.63, 20.92. ^{19}F NMR (470 MHz, DMSO) δ -56.26, -63.59 (t, *J* = 11.2 Hz). HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}F_6N_2NaO_3S$ 429.0678; Found 429.0674.



4aa-*syn* → **4aa-*anti***

82% yield of **4aa-*anti***
84% conv. of **4aa-*syn***

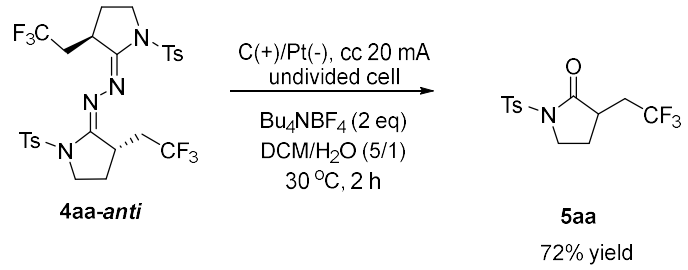
To a flame-dried sealed tube equipped with a magnetic stir bar were added **4aa-*syn*** (0.05 mmol, 1 equiv, 31.9 mg), HOAc (0.125 M, 0.1 mL). The tube was stirred at 80 °C for 12 h. Then the mixture was cooled to room temperature and the solvent was then removed *in vacuo*. Purification of the crude mixture by flash column chromatography (silica gel, EtOAc/Petroleum ether = 1: 3) afforded **4aa-*anti*** in 82% yield as a white solid.



4aa → **5aa**

74% yield from **4aa-*syn***
76% yield from **4aa-*anti***

To solution of **4aa-*syn* or 4aa-*anti*** (0.1 mmol, 63.86 mg) in THF (0.05 *M,* 2 mL) in a dried tube was added HCl (5 *N*, 0.06 mL) at room temperature, then the reaction mixture was warmed to 80 °C and allowed to proceed for 12 h. Upon completion, the mixture was cooled to room temperature and the solution was concentrated *in vacuo*. Purification of the crude mixture by flash column chromatography (silica gel, EtOAc/Petroleum ether = 1: 5) afforded **5aa** in 74% - 76% yield as a white solid.

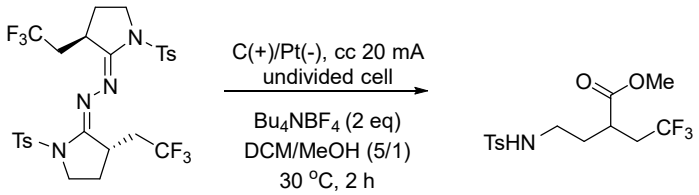


4aa-*anti*

5aa

72% yield

In an undivided three necked-flask (25 mL) equipped with a stir bar, a mixture of **4aa-*anti*** (0.1 mmol, 63.8 mg), Bu_4NBF_4 (0.2 mmol, 2 equiv, 66 mg) and DCM/H_2O (v/v = 5/1, 6.6 mL) were added. The cell was equipped with graphite rod (Φ 6 mm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 30 °C for 2 h. Upon completion, the solution was concentrated *in vacuo*. Purification of the crude mixture by flash column chromatography (silica gel, EtOAc/Petroleum ether = 1: 5) afforded **5aa** (72% yield, 46 mg) as a white solid.



4aa-*anti*

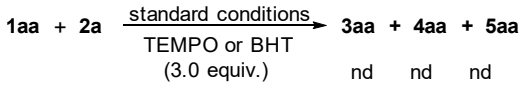
18

67% yield

In a flame-dried undivided three necked-flask (25 mL) equipped with a stir bar, a mixture of **4aa-*anti*** (0.1 mmol, 63.8 mg), Bu_4NBF_4 (0.2 mmol, 2 equiv, 66 mg) and DCM/MeOH (v/v = 5/1, 6.6 mL) were added. The cell was equipped with graphite rod (Φ 6 mm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 30 °C for 2 h. Upon completion, the solution was concentrated *in vacuo*. Purification of the crude mixture by flash column chromatography (silica gel, EtOAc/Petroleum ether = 1: 3) afforded **18** (67% yield, 47 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.07 (t, J = 6.3 Hz, 1H), 3.68 (s, 3H), 3.04 – 2.94 (m, 1H), 2.94 – 2.84 (m, 1H), 2.82 – 2.73 (m, 1H), 2.64 – 2.48 (m, 1H), 2.42 (s, 3H), 2.23 – 2.08 (m, 1H), 1.90 – 1.71 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.95, 143.78, 136.79, 129.92, 127.16, 126.06 (q, J = 277.2 Hz), 52.48, 40.75, 36.94, 35.79 (q, J = 29.0 Hz), 32.00, 21.60. ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.04 (t, J = 10.6 Hz). HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}F_3NO_4S$ 354.0981; Found 354.0987.

VI. Control Experiments

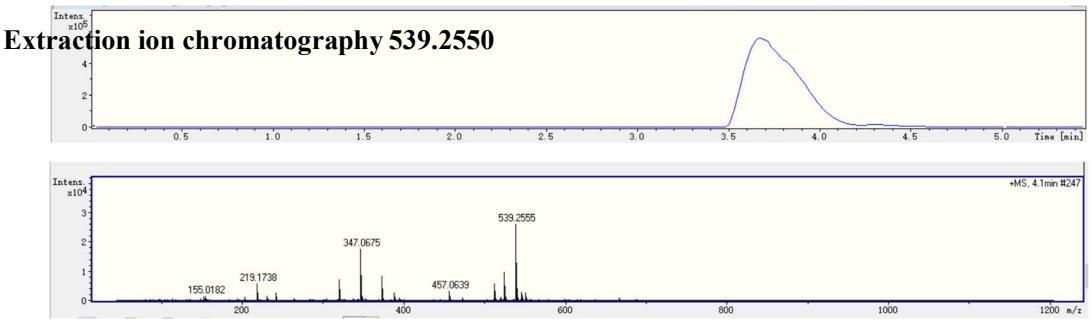
1. Radical scavenger trapping



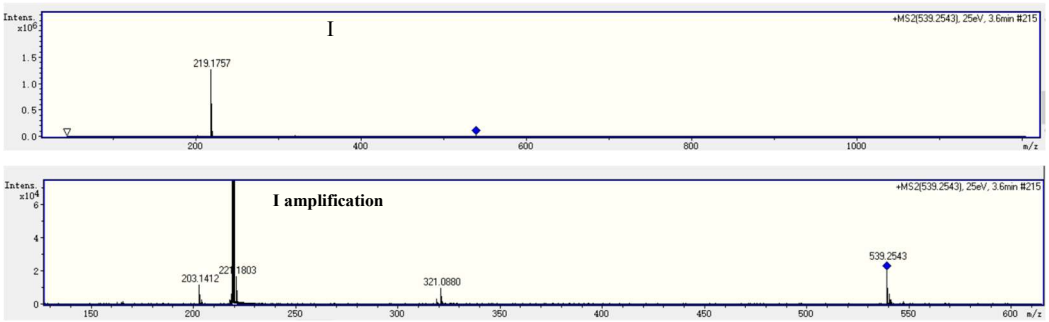
Characterization of BHT-1a-CF_3 additive product S-3 by mass spectrometry

Reaction mixture was analyzed on a LC/MS (Agilent 1290 Infinity LC System connected to the Bruker micrOTOF-QII MS instrument). The high resolution mass spectrometry was performed to confirm the elemental compositions of BHT-**1aa**-CF_3 additive product **S-13**. **S-13**: HRMS (ESI) calculated for HRMS(ESI): calcd. for $C_{28}H_{38}F_3N_2O_3S$ ($[M+H]^+$): 539.2550, found 539.2560. (Figure S1, a). The major product ions were observed in the fragmentation of protonated BHT additive product by CID mass spectra with argon as collision gas after isolation of the target precursor ion (Figure S1, b). The possible chemical structure of BHT additive product **S-13** and the major product ions observed in the fragmentation of its $[M+H]^+$ ionwere given in Figure S1, c.

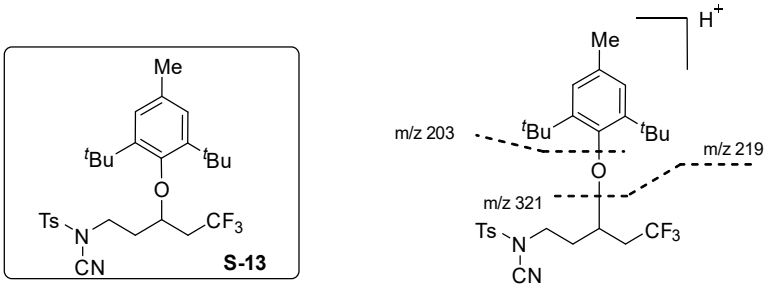
a)



b)



c)

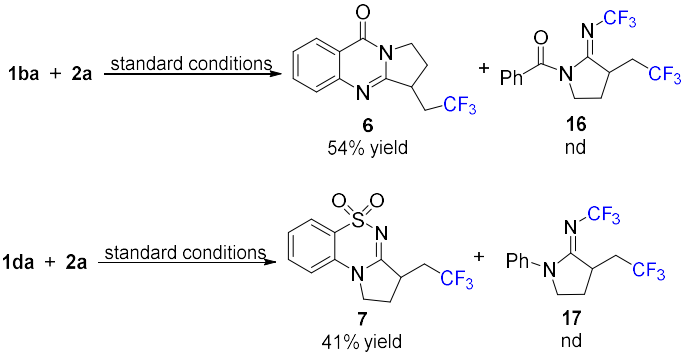


S-13: HRMS(ESI): calcd. for $C_{28}H_{38}F_3N_2O_3S$ ($[M+H]^+$): 539.2550, found 539.2543.

Figure S1. a) High resolution mass spectra of BHT additive product **S-13** from reaction mixture by LC/MS. b) MS^2 mass spectra of

protonated BHT additive product **S-13**. c) The possible chemical structure of BHT additive product **S-13** and the major product ions observed in the fragmentation of its $[M+H]^+$ ion.

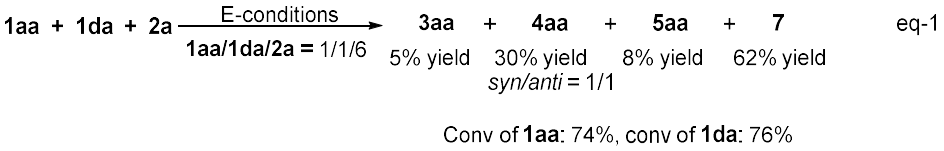
2. Effects of N-substituted group



In an undivided three necked-flask (25 mL) equipped with a stir bar, a mixture of **1ba** (or **1da)** (0.3 mmol), CF_3SO_2Na **2a** (1.2 mmol), Bu_4NBF_4 (0.3 mmol), KH_2PO_4 (0.9 mmol) and DCM/H_2O (v/v = 5/1, 10 mL) were added. The cell was equipped with graphite rod (Φ 6 mm) as the anode and platinum plate (1 cm × 1 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 30 °C for 2 h. Upon completion, H_2O (5 mL) was added, the mixture was extracted with DCM (8 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether (60-90 °C)) to provide the desired products **6** (or **7)**.

3. Radical cross-coupling

3-1.



In an undivided three necked-flask (25 mL) equipped with a stir bar (eq-1), a mixture of **1aa** (0.15 mmol), **1da** (0.15 mmol), CF_3SO_2Na **2a** (0.9 mmol), Bu_4NBF_4 (0.3 mmol), NaOAc (0.9 mmol) and DCM/H_2O (v/v = 5/1, 10 mL) were added. The cell was equipped with two graphite plate electrodes (0.8 cm × 1.5 cm × 0.2 cm). The reaction mixture was stirred and electrolyzed at a constant current of 1 mA at 30 °C for 16 h. Upon completion, 5 mL H_2O was added, the mixture was extracted with DCM (8 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The yields were determined by ^{19}F NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

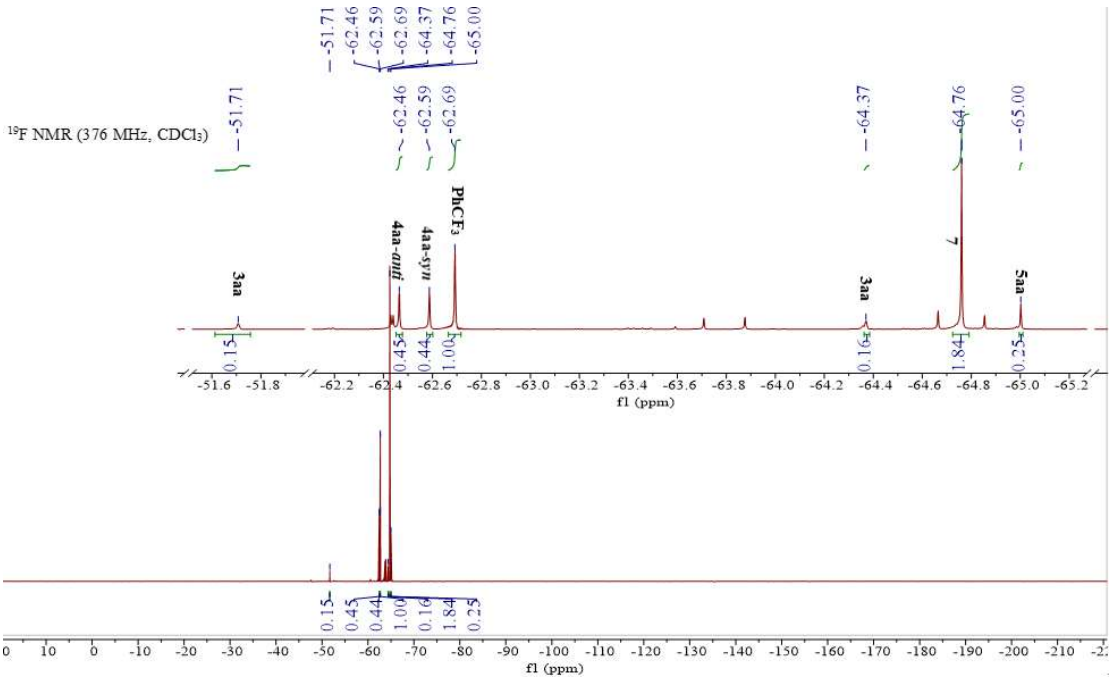
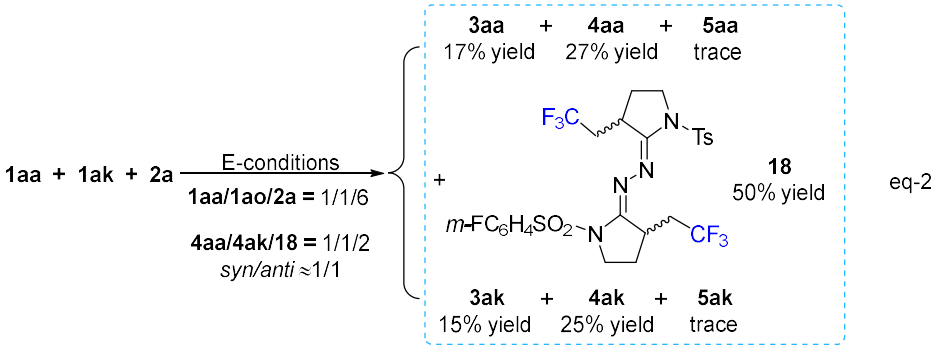


Figure S2. ^{19}F NMR analyses of the mixture (eq-1).

3-2.



E-conditions: C (+)/C (-), cc 1 mA, undivded cell, Bu_4NBF_4, NaOAc, DCM/H_2O (5/1), 30 °C, 16 h

The procedure of eq-2 was similar to that of eq-1.

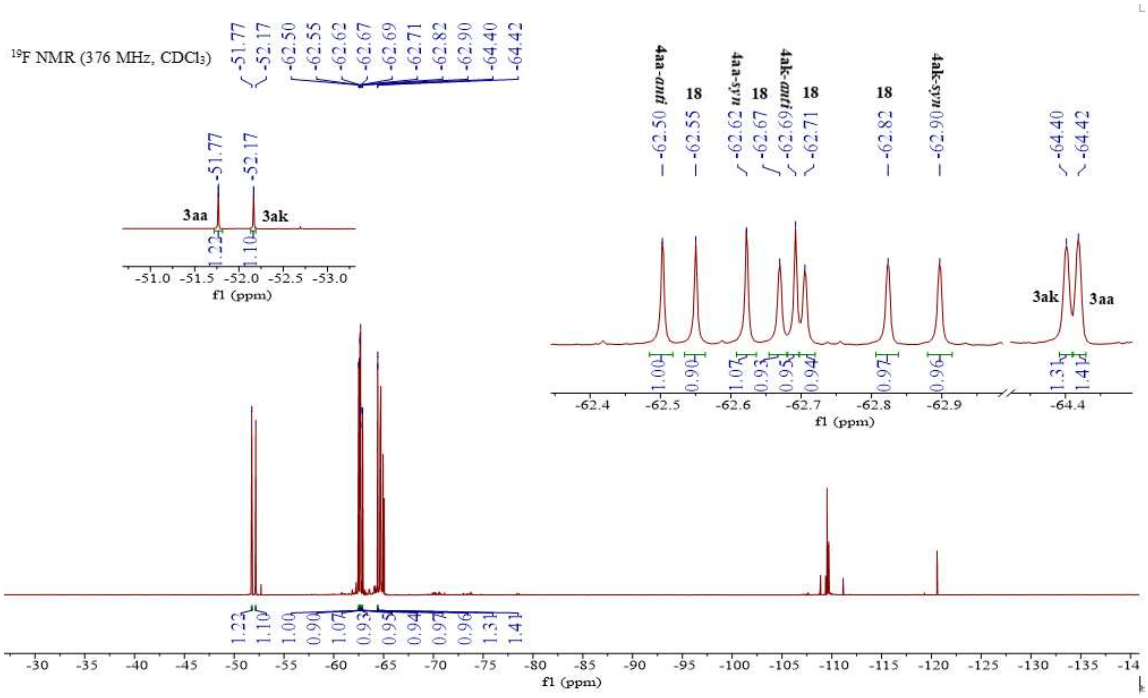
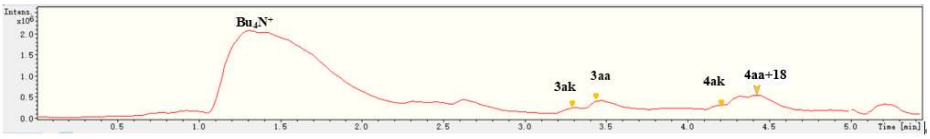
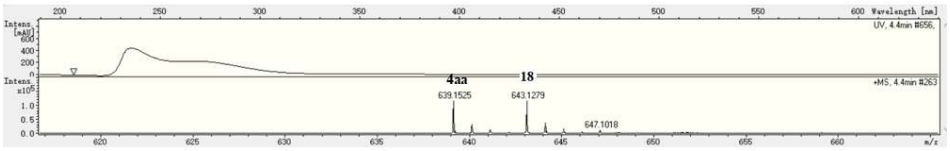


Figure S3. ^{19}F NMR analyses of the mixture (eq-2).

a)



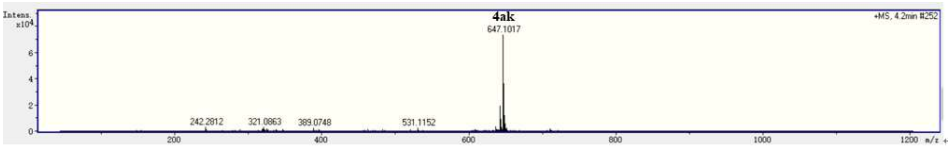
b)



4aa: HRMS(ESI): calcd. for $C_{26}H_{29}F_6N_4O_4S_2$ ([M+H]$^+$): 639.1529, found 639.1525.

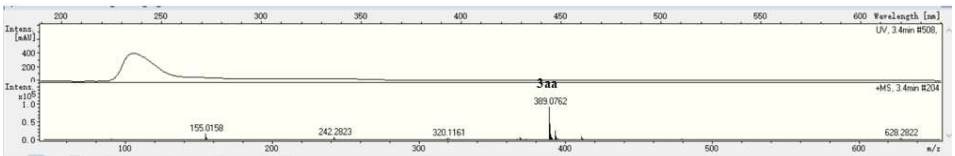
18: HRMS(ESI): calcd. for $C_{25}H_{26}F_7N_4O_4S_2$ ([M+H]$^+$): 643.1278, found 643.1279.

c)



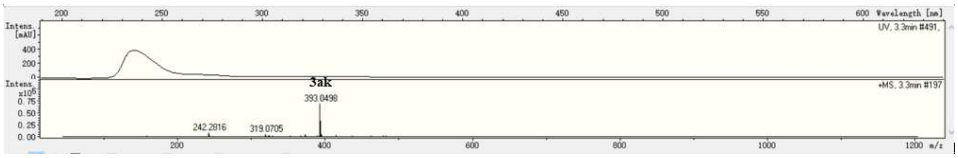
4ak: HRMS(ESI): calcd. for $C_{24}H_{23}F_8N_4O_4S_2$ ([M+H]$^+$): 647.1027, found 647.1017.

d)



3aa: HRMS(ESI): calcd. for $C_{14}H_{15}F_6N_2O_2S$ ([M+H]$^+$): 389.0753, found 389.0762.

e)



3ak: HRMS(ESI): calcd. for $C_{13}H_{12}F_7N_2O_2S$ ([M+H]$^+$): 393.0497, found 393.0498.

f)

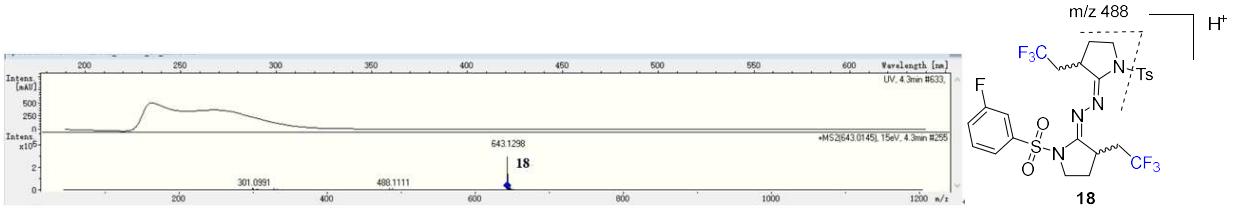
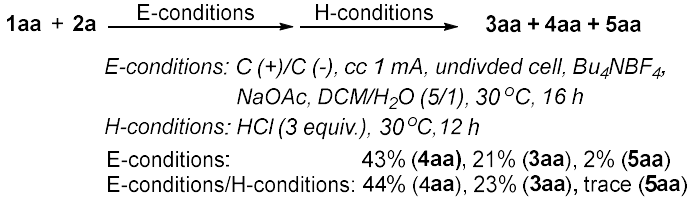


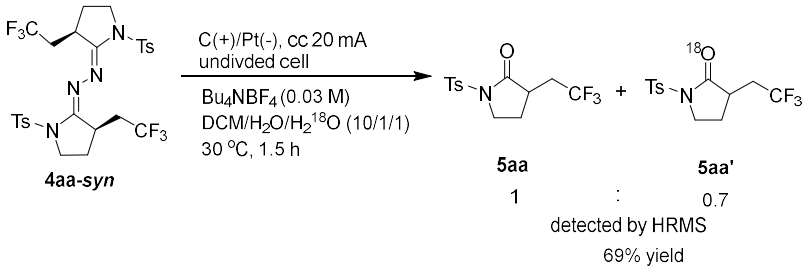
Figure S4. High-resolution mass analyses of the mixture (eq-2). a-e) The high-resolution mass analyses of **3aa**, **4aa**, **3ak**, **4ak** and **18** from reaction mixture by LC/MS. f) MS^2 mass spectra of protonated **18**.

4. Electrochemical/ hydrolytic reaction



The formation of **5aa** was not observed when the resulting mixture of electrochemical process was subjected further to the hydrolytic reaction conditions at 30 °C.

5. The ^{18}O deuterium label experiment

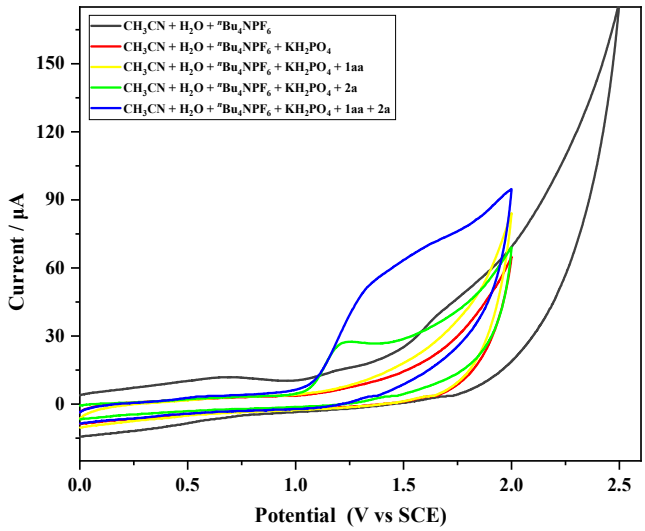


This result indicated that the oxygen atom of amide was derived from the solvent of water.

VII. Cyclic Voltammetry (CV) Experiments

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

a)



b)

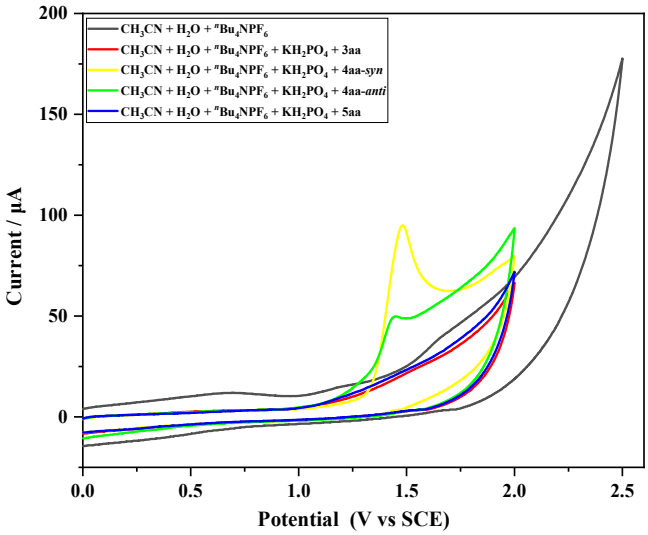


Figure S5. Cyclic voltammograms. **Black line**: $^{n}Bu_4NPF_6$ (0.1 M) and in 5 mL acetonitrile and 1 mL H_2O (background). a) **red line:** KH_2PO_4 (0.006 M), $^{n}Bu_4NPF_6$ (0.1 M) and in 5 mL acetonitrile and 1 mL H_2O; **yellow line: 1aa** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and KH_2PO_4 (0.006 M) in 5 mL acetonitrile and 1 mL H_2O; **green line**: **2a** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and KH_2PO_4 (0.006 M) in 5 mL acetonitrile and 1 mL H_2O, the oxidation peak of **2a**: 1.21 V; **blue line**: **1aa** (0.002 M), **2a** (0.008 M), $^{n}Bu_4NPF_6$ (0.1 M) and KH_2PO_4 (0.006 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.33 V.

b) red line: 3aa (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and KH_2PO_4 (0.006 M) in 5 mL acetonitrile and 1 mL H_2O; **yellow line**: **4aa-*syn*** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and KH_2PO_4 (0.006 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.50 V**; green line**: **4aa-*anti*** (0.002

M), $^{n}Bu_4NPF_6$ (0.1 M) and KH_2PO_4 (0.006 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.44 V; **blue line: 5aa** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and KH_2PO_4 (0.006 M) in 5 mL acetonitrile and 1 mL H_2O. Scan rate: 50 mV/s.

In Figure S5, the voltammogram disclosed that no oxidative peaks were observed for compounds **1aa**, **3aa** and **5aa** in the potential window of interest. The anodic oxidation of the **2a**, followed by an irreversible reaction, occurred at a potential of ca. 1.21 V (*vs*. SCE) (the oxidation peak of **2a**: 1.4 V vs Ag/AgCl in acetonitrile [12]), which may account for the oxidative generation of CF_3 radical. Besides, azine **4aa** also showed distinct oxidation peaks at 1.50 V (*syn*) and 1.44 V (*anti*) (*vs.* SCE) which were high than that of **2a**.

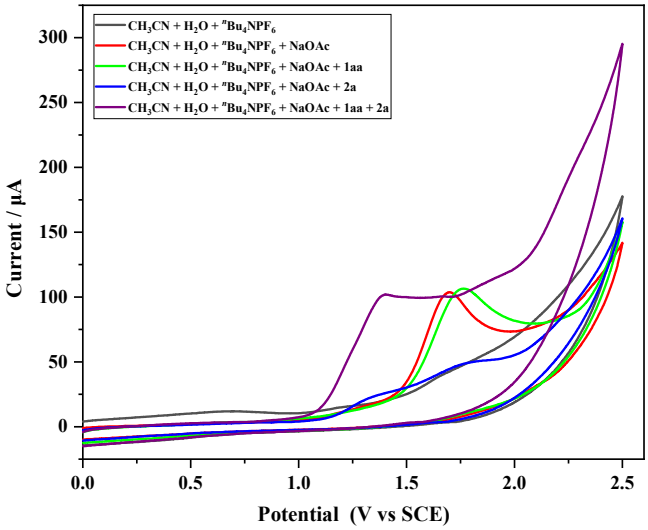


Figure S6. Cyclic voltammograms. **Black line**: $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O (background); **red line: NaOAc** (0.006 M), $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O, the oxidation peak of NaOAc: 1.69 V; **green line**: **1aa** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and NaOAc (0.006 M) in 5 mL acetonitrile and 1 mL H_2O, the oxidation peak of NaOAc: 1.75 V; **blue line: 2a** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and NaOAc (0.006 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.31, 1.76 V (NaOAc); **blue line**: **1aa** (0.002 M), **2a** (0.006 M), $^{n}Bu_4NPF_6$ (0.1 M) and NaOAc (0.006 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.39 V; Scan rate: 50 mV/s.

In the presence of NaOAc (0.006 M) (Figure S6), the anodic oxidation of the **2a** occurred at a potential of ca. 1.31 V (*vs* SCE). The oxidation peak of NaOAc was assigned to 1.69 V (TBAOAc: 1.78 V vs Ag/AgCl in acetonitrile [13]).

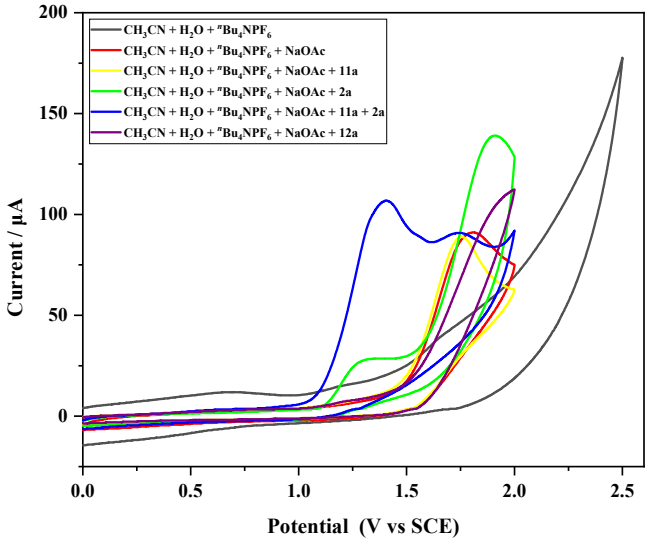


Figure S7. Cyclic voltammograms. **Black line**: $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O (background); **red line:** NaOAc (0.01 M), $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O, the oxidation peak of NaOAc: 1.80 V; **yellow line**: **11a** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and NaOAc (0.01 M) in 5 mL acetonitrile and 1 mL H_2O; **green line**: **2a** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and NaOAc (0.01 M) in 5 mL acetonitrile and 1 mL H_2O, the oxidation peak of 2a: 1.28 V; **blue line: 11a** (0.002 M), **2a** (0.008 M), $^{n}Bu_4NPF_6$ (0.1 M) and NaOAc (0.01 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.40; **purple line: 12a** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) and NaOAc (0.01 M) in 5 mL acetonitrile and 1 mL H_2O; Scan rate: 50 mV/s.

When **11a** was employed (Figure S7), the anodic oxidation of the **2a** occurred at a potential of 1.28 V (*vs* SCE) in the presence of NaOAc (0.01 M), while product **12a** didn't display any oxidative peak in the potential window of interest.

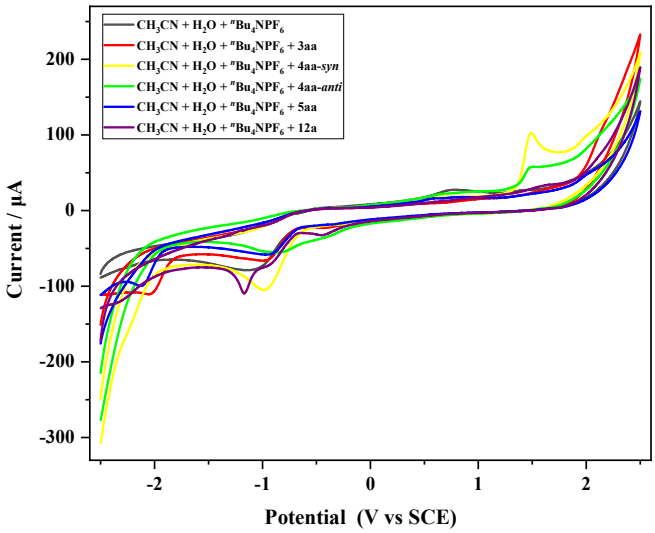
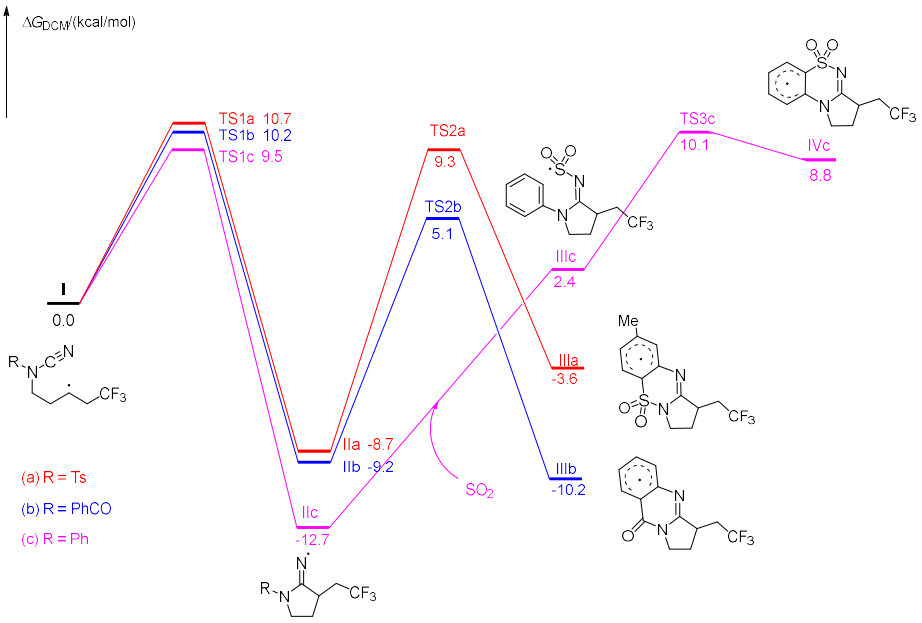


Figure S8. Cyclic voltammograms. **Black line**: $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O (background); **red line: 3aa** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O, reduction peak: -2.05 V; **yellow line: 4aa-*syn*** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.49 V; **green line**: **4aa-*anti*** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O, oxidation peak: 1.48 V; **blue line: 5aa** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O, reduction peak: -2.12 V; **purple line: 12a** (0.002 M), $^{n}Bu_4NPF_6$ (0.1 M) in 5 mL acetonitrile and 1 mL H_2O, reduction peak: -1.16, -2.42 V. Scan rate: 50 mV/s.

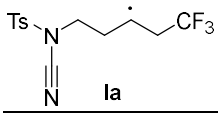
Further cyclic voltammetric (CV) experiments indicated that no reductive peaks of **4aa** can be observed, while compounds **3aa** and **5aa** demonstrated high reductive peaks at -2.05 V (vs SCE) and -2.12 V (vs SCE) respectively. In addition, the reductive peak of compound **12a** was observed at a potential of -1.16 V and -2.42 V (vs SCE) (Figure S8).

VIII. DFT Calculations

All Density functional theory (DFT) calculations were carried out in the Gaussian 16 program suite [14] at the B3LYP level of theory with 6-311G(d,p) basis set.



Scheme S2. DFT calculations.



Zero-point correction=	0.255926 (Hartree/Particle)
Thermal correction to Energy=	0.277662
Thermal correction to Enthalpy=	0.278606
Thermal correction to Gibbs Free Energy=	0.199371

Sum of electronic and zero-point Energies= -1461.430948

Sum of electronic and thermal Energies= -1461.409212

Sum of electronic and thermal Enthalpies= -1461.408268

Sum of electronic and thermal Free Energies= -1461.487503

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
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4	6	0.000001451	0.000001467	0.000002356
5	6	0.000000996	0.000002275	0.000004399
6	6	0.000007246	0.000006184	-0.000003138
7	7	0.000003190	0.000004443	-0.000008386
8	6	0.000004414	0.000001878	-0.000001193
9	6	-0.000002024	-0.000002500	-0.000006944
10	6	0.000000800	-0.000003903	-0.000004298
11	6	0.000000325	0.000001626	0.000000811
12	6	-0.000003347	-0.000001724	0.000000802
13	6	-0.000000382	-0.000005272	0.000002361
14	6	-0.000000013	-0.000000563	0.000000973
15	16	0.000003165	0.000002125	-0.000013598
16	8	-0.000006849	-0.000011201	-0.000006997
17	8	0.000002525	0.000000153	0.000007470
18	6	0.000001030	-0.000000847	0.000006724
19	9	0.000000106	-0.000000102	0.000009868
20	9	0.000000983	0.000005883	0.000007383
21	9	-0.000003454	0.000001101	0.000011377
22	1	0.000002579	0.000006374	-0.000000003
23	1	-0.000000354	-0.000000395	0.000000740
24	1	-0.000000904	-0.000001396	-0.000001213
25	1	0.000000067	0.000002086	-0.000003936
26	1	0.000001583	0.000004280	0.000004197
27	1	-0.000001785	-0.000001867	0.000003560
28	1	-0.000000056	0.000003429	0.000003735
29	1	0.000001037	-0.000001025	-0.000008344
30	1	0.000000950	0.000000598	-0.000005821
31	1	-0.000001597	-0.000002560	0.000004444
32	1	-0.000002117	-0.000003953	0.000001782
33	1	0.000000721	0.000001758	-0.000000202
34	1	-0.000001332	-0.000002689	0.000000533
35	1	-0.000000694	0.000000208	0.000003968

TS1a

Zero-point correction=	0.256848 (Hartree/Particle)
Thermal correction to Energy=	0.277244
Thermal correction to Enthalpy=	0.278188
Thermal correction to Gibbs Free Energy=	0.203282
Sum of electronic and zero-point Energies=	-1461.416979
Sum of electronic and thermal Energies=	-1461.396583
Sum of electronic and thermal Enthalpies=	-1461.395639
Sum of electronic and thermal Free Energies=	-1461.470545

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
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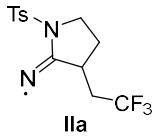
4	6	-0.000000942	-0.000000990	-0.000001084
5	6	-0.000001387	0.000001204	0.000000588
6	6	0.000000302	-0.000000999	-0.000003261
7	7	0.000002401	0.000002182	0.000000442
8	6	0.000000187	0.000000163	0.000002447
9	6	-0.000001265	-0.000000732	0.000002346
10	6	-0.000000981	-0.000000411	0.000002063
11	6	0.000000247	0.000000421	0.000001742
12	6	0.000001258	0.000001589	0.000001695
13	6	0.000001151	0.000001358	0.000002181
14	6	0.000000354	0.000000616	0.000001040
15	16	0.000000021	0.000000381	0.000003409
16	8	-0.000001355	-0.000001024	0.000003555
17	8	0.000000733	0.000001320	0.000003908
18	6	-0.000000428	-0.000000474	-0.000004824
19	9	0.000000203	-0.000000286	-0.000006098
20	9	-0.000000913	-0.000001466	-0.000004516
21	9	0.000001412	0.000000002	-0.000005408
22	1	0.000000949	0.000000460	-0.000001963
23	1	-0.000001061	-0.000000983	-0.000000218
24	1	-0.000001872	-0.000002242	-0.000001879
25	1	-0.000001480	-0.000001303	-0.000000155
26	1	-0.000001991	-0.000001736	0.000001211
27	1	0.000001379	0.000000538	-0.000003884
28	1	-0.000000206	-0.000001207	-0.000004132
29	1	-0.000001711	-0.000001381	0.000002458
30	1	-0.000001658	-0.000001364	0.000001749

31	1	0.000002146	0.000002106	0.000001578
32	1	0.000001869	0.000002232	0.000002433
33	1	-0.000000402	-0.000000344	0.000000859
34	1	0.000000547	0.000000862	0.000002252
35	1	0.000001089	0.000001164	0.000000264



IIa

Zero-point correction= 0.260405 (Hartree/Particle)
Thermal correction to Energy= 0.280343
Thermal correction to Enthalpy= 0.281288
Thermal correction to Gibbs Free Energy= 0.208020
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Sum of electronic and thermal Energies= -1461.429013
Sum of electronic and thermal Enthalpies= -1461.428068
Sum of electronic and thermal Free Energies= -1461.501336

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
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3	6	-0.000000047	-0.000001016	-0.000001448
4	6	-0.000001038	0.000000134	-0.000003554
5	6	-0.000001060	0.000000640	-0.000002060
6	6	0.000000395	-0.000000851	-0.000001279
7	7	0.000000348	-0.000002717	-0.000000833
8	6	-0.000000062	0.000000272	0.000000360
9	6	-0.000000564	0.000001663	0.000000915
10	6	-0.000000176	0.000001378	0.000002029
11	6	0.000000497	0.000000737	0.000003058
12	6	0.000000977	-0.000000316	0.000002522
13	6	0.000000525	-0.000000836	0.000001079
14	6	0.000000773	0.000001085	0.000005111
15	16	-0.000000402	0.000000026	-0.000001287
16	8	-0.000001331	0.000001267	-0.000002280
17	8	0.000000200	-0.000000723	-0.000002913
18	6	0.000000363	-0.000000628	-0.000000717
19	9	0.000000886	-0.000001098	0.000000484
20	9	-0.000000211	-0.000000393	-0.000001797

21	9	0.000001216	-0.000002539	-0.000001201
22	1	0.000000207	-0.000001761	-0.000002779
23	1	-0.000000893	0.000000008	-0.000003989
24	1	-0.000000967	0.000000508	-0.000002747
25	1	-0.000000888	0.000001776	-0.000001006
26	1	-0.000001290	0.000001452	-0.000002931
27	1	0.000001037	-0.000001751	-0.000000176
28	1	-0.000000936	-0.000000491	0.000000088
29	1	-0.000000920	0.000002334	0.000000297
30	1	-0.000000585	0.000002872	0.000002967
31	1	0.000001356	-0.000001410	0.000002960
32	1	0.000000890	-0.000001537	0.000000236
33	1	0.000000429	0.000001673	0.000004977
34	1	0.000000769	0.000000998	0.000004984
35	1	0.000001133	0.000000076	0.000005168

TS2a

Zero-point correction= 0.259811 (Hartree/Particle)
Thermal correction to Energy= 0.278760
Thermal correction to Enthalpy= 0.279705
Thermal correction to Gibbs Free Energy= 0.210271
Sum of electronic and zero-point Energies= -1461.423221
Sum of electronic and thermal Energies= -1461.404271
Sum of electronic and thermal Enthalpies= -1461.403327
Sum of electronic and thermal Free Energies= -1461.472760

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
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4	6	0.000002186	-0.000002981	-0.000000196
5	6	0.000003226	-0.000002610	-0.000000654
6	6	-0.000000580	-0.000002979	-0.000000166
7	7	-0.000000481	0.000000442	0.000000330
8	6	0.000000915	0.000002418	-0.000000455
9	6	0.000000370	0.000002591	-0.000000580
10	6	-0.000001165	0.000003371	0.000000049
11	6	-0.000002395	0.000003699	-0.000000075
12	6	-0.000001826	0.000003638	0.000000087
13	6	-0.000000686	0.000002800	-0.000000546

14	6	-0.000004122	0.000004313	0.000000363
15	16	0.000003031	0.000001152	-0.000001333
16	8	0.000003867	0.000001173	-0.000001310
17	8	0.000003522	0.000002489	-0.000001485
18	6	-0.000000983	-0.000005330	0.000001158
19	9	-0.000002091	-0.000005873	0.000001676
20	9	0.000000374	-0.000006103	0.000001092
21	9	-0.000002189	-0.000005309	0.000001378
22	1	-0.000000277	-0.000002366	0.000000506
23	1	0.000002798	-0.000002850	-0.000000359
24	1	0.000002679	-0.000004520	0.000000064
25	1	0.000003357	-0.000002499	-0.000000597
26	1	0.000004478	-0.000001740	-0.000001056
27	1	-0.000001604	-0.000002732	0.000000960
28	1	0.000000502	-0.000003394	0.000000884
29	1	0.000001248	0.000002185	-0.000000785
30	1	-0.000001608	0.000003308	-0.000000136
31	1	-0.000002802	0.000003864	0.000000163
32	1	0.000000250	0.000003295	-0.000000591
33	1	-0.000004801	0.000003494	0.000000811
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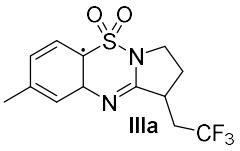
35	1	-0.000004840	0.000004885	0.000000586



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Thermal correction to Enthalpy= 0.281257
Thermal correction to Gibbs Free Energy= 0.211106
Sum of electronic and zero-point Energies= -1461.443044
Sum of electronic and thermal Energies= -1461.423981
Sum of electronic and thermal Enthalpies= -1461.423037
Sum of electronic and thermal Free Energies= -1461.493188

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
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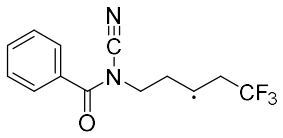
4	6	-0.000000116	0.000000415	-0.000000791

5	6	0.000000144	0.000000161	-0.000001414
6	6	-0.000000446	0.000000404	0.000000296
7	7	-0.000000255	0.000000324	0.000000102
8	6	0.000000065	-0.000000870	-0.000000411
9	6	-0.000000192	-0.000000935	-0.000000488
10	6	0.000000281	-0.000000632	0.000000434
11	6	0.000000647	-0.000000084	0.000001083
12	6	-0.000000116	0.000000550	0.000000533
13	6	-0.000000188	0.000000383	0.000000003
14	6	0.000000170	-0.000000375	0.000001456
15	16	0.000000453	0.000000524	-0.000001525
16	8	-0.000000199	-0.000000961	-0.000001583
17	8	-0.000000379	0.000000446	-0.000001808
18	6	0.000000682	-0.000000481	0.000001427
19	9	0.000000329	-0.000000509	0.000001511
20	9	-0.000000223	0.000000758	-0.000000576
21	9	-0.000000545	0.000001863	0.000000476
22	1	-0.000000573	0.000001166	0.000000194
23	1	-0.000000308	0.000001007	-0.000001285
24	1	-0.000000432	0.000000312	-0.000000784
25	1	-0.000000189	-0.000000568	-0.000001362
26	1	-0.000000840	-0.000000502	-0.000001740
27	1	0.000000070	-0.000000298	0.000001463
28	1	0.000000669	-0.000000059	0.000000017
29	1	-0.000000025	-0.000001223	-0.000000991
30	1	0.000000332	-0.000001477	0.000000501
31	1	0.000000002	0.000000393	0.000001310
32	1	-0.000000188	0.000000844	-0.000000370
33	1	0.000000524	-0.000000936	0.000001944
34	1	0.000000425	-0.000000599	0.000001683
35	1	0.000000326	0.000000211	0.000001954



Ib

Zero-point correction= 0.229066 (Hartree/Particle)

Thermal correction to Energy= 0.247298

Thermal correction to Enthalpy= 0.248243

Thermal correction to Gibbs Free Energy= 0.177516

Sum of electronic and zero-point Energies= -986.868256

Sum of electronic and thermal Energies= -986.850023

Sum of electronic and thermal Enthalpies= -986.849079

Sum of electronic and thermal Free Energies= -986.919805

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000019860	-0.000012614	-0.000016154
2	7	-0.000016955	0.000013160	0.000011067
3	6	0.000004647	-0.000008694	0.000002756
4	6	0.000001581	-0.000005631	-0.000006145
5	7	0.000003381	-0.000000746	-0.000003598
6	6	-0.000016665	0.000005065	0.000003933
7	8	-0.000016223	0.000002958	0.000005882
8	6	0.000001049	0.000004566	0.000002685
9	6	-0.000007041	0.000004985	0.000001211
10	6	0.000010346	-0.000001240	0.000000948
11	6	0.000007765	0.000000720	0.000000288
12	6	0.000010596	-0.000010579	-0.000003176
13	6	0.000005748	0.000007056	-0.000004388
14	6	0.000004085	-0.000001658	0.000004860
15	6	0.000009686	0.000007875	0.000004818
16	9	-0.000002292	-0.000007036	-0.000006800
17	6	-0.000003674	-0.000002165	0.000007869
18	9	0.000000207	0.000001462	0.000000113
19	9	-0.000004693	0.000004601	-0.000001587
20	1	-0.000003076	0.000006249	-0.000000328
21	1	-0.000001386	0.000002668	0.000003116
22	1	0.000000389	-0.000000987	0.000001500
23	1	0.000001249	0.000000044	0.000001559
24	1	-0.000000946	0.000000994	-0.000000857
25	1	-0.000000690	-0.000001546	0.000000342
26	1	0.000001158	0.000001716	0.000000229
27	1	-0.000000820	-0.000001726	-0.000001489
28	1	-0.000002340	-0.000000769	-0.000000497
29	1	0.000001239	-0.000000107	0.000000826
30	1	-0.000002171	-0.000003843	-0.000002349
31	1	-0.000004012	-0.000004776	-0.000006632

TS1b

Zero-point correction= 0.229593 (Hartree/Particle)

Thermal correction to Energy= 0.246525

Thermal correction to Enthalpy= 0.247470

Thermal correction to Gibbs Free Energy= 0.181062

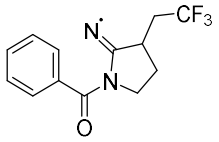
Sum of electronic and zero-point Energies= -986.855017

Sum of electronic and thermal Energies= -986.838084

Sum of electronic and thermal Enthalpies= -986.837140

Sum of electronic and thermal Free Energies= -986.903548

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000001011	0.000000377	-0.000003948
2	7	0.000000792	-0.000000056	-0.000000814
3	6	-0.000001211	-0.000000636	-0.000001195
4	6	0.000000615	0.000001144	0.000000228
5	6	-0.000000222	0.000001084	-0.000003269
6	8	-0.000000377	0.000000788	-0.000005363
7	6	-0.000001081	-0.000000658	-0.000002386
8	6	-0.000000156	0.000000375	-0.000002716
9	6	0.000000412	0.000001032	-0.000003393
10	6	0.000000924	0.000002084	-0.000005323
11	6	0.000000911	0.000001342	-0.000004511
12	6	-0.000000599	-0.000001136	0.000001679
13	6	0.000001231	0.000000163	0.000002990
14	6	-0.000000321	-0.000001128	0.000005483
15	7	0.000001414	0.000000638	0.000001788
16	9	0.000001944	-0.000000113	0.000006720
17	6	0.000000253	-0.000001056	0.000006386
18	9	0.000000112	-0.000002183	0.000008557
19	9	-0.000001269	-0.000001684	0.000005472
20	1	-0.000001813	-0.000001183	-0.000002262
21	1	0.000000304	0.000000378	-0.000001518
22	1	-0.000001312	-0.000001449	-0.000000103
23	1	-0.000001248	-0.000000671	-0.000001163
24	1	0.000000541	0.000001282	-0.000004148
25	1	0.000001743	0.000002851	-0.000006615
26	1	0.000001642	0.000002516	-0.000006118
27	1	-0.000001331	-0.000001334	0.000001413
28	1	-0.000002537	-0.000002145	0.000001595
29	1	0.000001288	0.000000785	0.000002269
30	1	-0.000000964	-0.000001495	0.000005076
31	1	0.000001325	0.000000087	0.000005191



IIc

Zero-point correction=	0.233304 (Hartree/Particle)
Thermal correction to Energy=	0.249783
Thermal correction to Enthalpy=	0.250728
Thermal correction to Gibbs Free Energy=	0.186032
Sum of electronic and zero-point Energies=	-986.887362
Sum of electronic and thermal Energies=	-986.870882
Sum of electronic and thermal Enthalpies=	-986.869938
Sum of electronic and thermal Free Energies=	-986.934634

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000019602	-0.000001496	0.000019662
2	7	-0.000009466	0.000042981	0.000013651
3	6	-0.000000353	-0.000007302	-0.000000723
4	6	0.000011130	-0.000039791	-0.000030150
5	6	-0.000013553	0.000004889	-0.000023176
6	8	-0.000001822	-0.000002330	-0.000007589
7	6	-0.000001418	0.000001032	0.000013233
8	6	0.000004473	-0.000004641	0.000003196
9	6	-0.000002054	0.000010414	-0.000003977
10	6	-0.000005993	-0.000001525	0.000007953
11	6	0.000007340	-0.000003566	0.000009493
12	6	0.000001558	0.000000753	-0.000010180
13	6	-0.000000704	0.000004404	0.000013324
14	6	-0.000005768	-0.000010097	-0.000005564
15	7	-0.000004242	0.000004405	0.000006478
16	9	-0.000005440	-0.000004646	-0.000000245
17	6	0.000026448	0.000013113	0.000013128
18	9	-0.000002342	-0.000002448	-0.000000871
19	9	-0.000018590	-0.000014794	-0.000020179
20	1	0.000002800	0.000001980	-0.000002338
21	1	0.000001665	0.000000125	-0.000004084
22	1	0.000003101	-0.000000611	-0.000001605
23	1	0.000000281	0.000005468	0.000009371
24	1	-0.000000887	0.000000414	0.000006872
25	1	-0.000000447	-0.000001144	0.000000919
26	1	-0.000001761	-0.000000211	-0.000000945

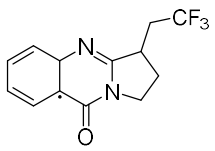
27	1	0.000001296	-0.000000339	-0.000001832
28	1	-0.000000807	0.000002731	-0.000003669
29	1	-0.000001977	0.000000201	-0.000002335
30	1	-0.000000317	0.000001212	0.000000567
31	1	-0.000001754	0.000000820	0.000001616

TS2b

Zero-point correction= 0.229593 (Hartree/Particle)
Thermal correction to Energy= 0.246525
Thermal correction to Enthalpy= 0.247470
Thermal correction to Gibbs Free Energy= 0.181062
Sum of electronic and zero-point Energies= -986.855017
Sum of electronic and thermal Energies= -986.838084
Sum of electronic and thermal Enthalpies= -986.837140
Sum of electronic and thermal Free Energies= -986.903548

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000001011	0.000000377	-0.000003948
2	7	0.000000792	-0.000000056	-0.000000814
3	6	-0.000001211	-0.000000636	-0.000001195
4	6	0.000000615	0.000001144	0.000000228
5	6	-0.000000222	0.000001084	-0.000003269
6	8	-0.000000377	0.000000788	-0.000005363
7	6	-0.000001081	-0.000000658	-0.000002386
8	6	-0.000000156	0.000000375	-0.000002716
9	6	0.000000412	0.000001032	-0.000003393
10	6	0.000000924	0.000002084	-0.000005323
11	6	0.000000911	0.000001342	-0.000004511
12	6	-0.000000599	-0.000001136	0.000001679
13	6	0.000001231	0.000000163	0.000002990
14	6	-0.000000321	-0.000001128	0.000005483
15	7	0.000001414	0.000000638	0.000001788
16	9	0.000001944	-0.000000113	0.000006720
17	6	0.000000253	-0.000001056	0.000006386
18	9	0.000000112	-0.000002183	0.000008557
19	9	-0.000001269	-0.000001684	0.000005472
20	1	-0.000001813	-0.000001183	-0.000002262
21	1	0.000000304	0.000000378	-0.000001518
22	1	-0.000001312	-0.000001449	-0.000000103
23	1	-0.000001248	-0.000000671	-0.000001163
24	1	0.000000541	0.000001282	-0.000004148

25	1	0.000001743	0.000002851	-0.000006615
26	1	0.000001642	0.000002516	-0.000006118
27	1	-0.000001331	-0.000001334	0.000001413
28	1	-0.000002537	-0.000002145	0.000001595
29	1	0.000001288	0.000000785	0.000002269
30	1	-0.000000964	-0.000001495	0.000005076
31	1	0.000001325	0.000000087	0.000005191

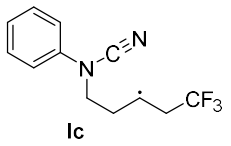


IIIb

Zero-point correction= 0.234204 (Hartree/Particle)
Thermal correction to Energy= 0.249655
Thermal correction to Enthalpy= 0.250599
Thermal correction to Gibbs Free Energy= 0.189507
Sum of electronic and zero-point Energies= -986.891404
Sum of electronic and thermal Energies= -986.875954
Sum of electronic and thermal Enthalpies= -986.875010
Sum of electronic and thermal Free Energies= -986.936101

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000002780	0.000011511	0.000008331
2	7	-0.000005322	-0.000008028	0.000003821
3	6	0.000006526	-0.000001569	0.000002125
4	6	-0.000001171	0.000004596	0.000003906
5	6	0.000000041	-0.000009116	-0.000003747
6	8	0.000005618	-0.000004445	0.000006374
7	6	0.000003423	0.000007458	0.000000333
8	6	0.000002816	-0.000004664	-0.000004494
9	6	-0.000002103	-0.000006357	0.000000306
10	6	0.000005935	0.000003040	-0.000005810
11	6	-0.000008716	0.000005362	0.000010261
12	6	0.000001910	-0.000004092	-0.000001270
13	6	-0.000000102	-0.000000058	0.000004613
14	6	-0.000001077	-0.000001636	-0.000006668
15	7	0.000001141	-0.000007866	-0.000006637
16	9	-0.000003700	-0.000005404	-0.000001128
17	6	0.000001973	0.000017105	-0.000007157

18	9	-0.000004475	0.000008663	-0.000003523
19	9	-0.000006421	0.000002605	-0.000000617
20	1	0.000000844	0.000000179	0.000004685
21	1	0.000003002	-0.000001987	0.000004526
22	1	0.000000133	-0.000004011	-0.000004302
23	1	-0.000002060	-0.000000175	-0.000005912
24	1	-0.000001994	0.000002109	-0.000007024
25	1	0.000000748	0.000001401	0.000003429
26	1	0.000001162	-0.000000290	0.000002034
27	1	0.000001439	-0.000001343	0.000002534
28	1	0.000002184	-0.000004106	0.000001571
29	1	0.000000107	-0.000003238	-0.000003617
30	1	-0.000000924	0.000001251	0.000002390
31	1	-0.000003717	0.000003104	0.000000667



Ic

Zero-point correction= 0.219777 (Hartree/Particle)
Thermal correction to Energy= 0.236120
Thermal correction to Enthalpy= 0.237064
Thermal correction to Gibbs Free Energy= 0.170604
Sum of electronic and zero-point Energies= -873.322783
Sum of electronic and thermal Energies= -873.306441
Sum of electronic and thermal Enthalpies= -873.305497
Sum of electronic and thermal Free Energies= -873.371957

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000000564	-0.000000539	0.000003742
2	6	-0.000001895	0.000000555	0.000004367
3	6	-0.000001233	0.000000431	0.000004587
4	6	0.000000223	-0.000000742	0.000002288
5	6	0.000000861	-0.000001124	0.000002014
6	6	0.000000107	-0.000000777	0.000002639
7	7	0.000001543	0.000001872	0.000001890
8	6	0.000002444	-0.000001464	0.000000631
9	6	0.000000807	-0.000000195	-0.000001138
10	6	-0.000000808	-0.000001043	-0.000001776
11	6	-0.000000459	-0.000002657	0.000003005

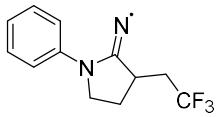
12	6	-0.000001043	0.000000530	-0.000004612
13	7	0.000000022	0.000000294	0.000003893
14	9	-0.000001006	0.000003467	-0.000007451
15	6	-0.000002638	0.000000832	-0.000004466
16	9	-0.000000606	0.000001270	-0.000007322
17	9	0.000001184	0.000000593	-0.000006294
18	1	-0.000001276	0.000000236	0.000004515
19	1	-0.000002954	0.000001190	0.000005466
20	1	-0.000002709	0.000000543	0.000003640
21	1	0.000001690	-0.000001976	0.000000650
22	1	0.000001636	-0.000001212	0.000002392
23	1	0.000002763	-0.000000107	-0.000000905
24	1	0.000002711	-0.000002127	0.000000390
25	1	0.000001562	-0.000000672	-0.000000718
26	1	0.000001833	-0.000001260	-0.000002134
27	1	-0.000001234	0.000001211	-0.000001944
28	1	0.000000151	0.000000316	-0.000004124
29	1	-0.000001113	0.000002554	-0.000003224

TS1c

Zero-point correction= 0.220317 (Hartree/Particle)
Thermal correction to Energy= 0.235427
Thermal correction to Enthalpy= 0.236372
Thermal correction to Gibbs Free Energy= 0.174869
Sum of electronic and zero-point Energies= -873.311339
Sum of electronic and thermal Energies= -873.296229
Sum of electronic and thermal Enthalpies= -873.295285
Sum of electronic and thermal Free Energies= -873.356787

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000000273	0.000003987	-0.000001283
2	6	-0.000000092	0.000002544	-0.000006791
3	6	-0.000000137	0.000000792	-0.000006929
4	6	0.000000058	0.000000115	-0.000001084
5	6	0.000000156	0.000001746	0.000004700
6	6	0.000000355	0.000003383	0.000004306
7	7	-0.000000298	-0.000001802	-0.000000821
8	6	-0.000000353	-0.000002254	0.000005798
9	6	-0.000000025	-0.000006881	0.000003650
10	6	-0.000000250	-0.000003863	-0.000002237
11	6	0.000000555	-0.000001182	-0.000005888

12	6	-0.000000058	0.000001284	-0.000000468
13	7	-0.000000542	-0.000001177	-0.000011531
14	9	-0.000000271	-0.000001845	-0.000002847
15	6	0.000000205	0.000001798	0.000001035
16	9	0.000000820	0.000008162	0.000001733
17	9	-0.000000390	-0.000000923	0.000007021
18	1	0.000000366	0.000005323	-0.000001498
19	1	-0.000000084	0.000002753	-0.000010998
20	1	-0.000000367	-0.000000390	-0.000010872
21	1	-0.000000466	0.000001322	0.000008302
22	1	0.000000569	0.000004609	0.000008515
23	1	0.000000511	0.000002105	0.000006791
24	1	0.000000506	-0.000005114	0.000008370
25	1	-0.000000645	-0.000011125	0.000002954
26	1	-0.000000216	-0.000006237	0.000008029
27	1	-0.000000713	-0.000006989	-0.000004893
28	1	0.000000245	0.000005064	0.000002482
29	1	0.000000285	0.000004794	-0.000005548



IIc

Zero-point correction= 0.223910 (Hartree/Particle)
Thermal correction to Energy= 0.238530
Thermal correction to Enthalpy= 0.239474
Thermal correction to Gibbs Free Energy= 0.179555
Sum of electronic and zero-point Energies= -873.347808
Sum of electronic and thermal Energies= -873.333188
Sum of electronic and thermal Enthalpies= -873.332244
Sum of electronic and thermal Free Energies= -873.392163

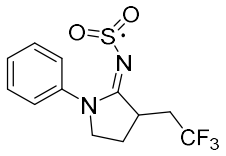
Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000004337	-0.000016378	-0.000000751
2	6	-0.000016136	0.000013982	-0.000005925
3	6	-0.000002233	-0.000001655	0.000006113
4	6	-0.000015676	0.000011559	-0.000006724
5	6	0.000004926	-0.000008672	0.000000267
6	6	0.000009257	0.000007373	-0.000004217
7	7	0.000002027	-0.000032406	-0.000001310
8	6	0.000007432	0.000030806	-0.000006929

9	6	-0.000002460	0.000001613	0.000010710
10	6	-0.000011819	-0.000029065	-0.000019947
11	6	-0.000012406	0.000038922	-0.000006823
12	6	0.000013068	-0.000001705	0.000017277
13	7	0.000025087	-0.000017519	0.000011392
14	9	-0.000021080	0.000009301	-0.000014669
15	6	0.000042312	0.000024380	0.000052683
16	9	-0.000002501	-0.000006551	-0.000002044
17	9	-0.000019546	-0.000037956	-0.000011584
18	1	0.000001092	0.000003274	-0.000004124
19	1	-0.000000166	0.000000420	0.000002103
20	1	-0.000004318	0.000003649	0.000001143
21	1	0.000008630	0.000005958	-0.000005993
22	1	0.000002299	-0.000000793	-0.000007780
23	1	0.000000586	-0.000004759	-0.000004010
24	1	-0.000007950	-0.000001686	-0.000005666
25	1	0.000002949	0.000012405	-0.000002246
26	1	0.000005595	-0.000001417	-0.000002189
27	1	-0.000003073	0.000003008	0.000010934
28	1	-0.000004581	-0.000005327	-0.000003510
29	1	-0.000005651	-0.000000760	0.000003820

SO_2

Zero-point correction= 0.006645 (Hartree/Particle)
Thermal correction to Energy= 0.009740
Thermal correction to Enthalpy= 0.010684
Thermal correction to Gibbs Free Energy= -0.017598
Sum of electronic and zero-point Energies= -548.598199
Sum of electronic and thermal Energies= -548.595104
Sum of electronic and thermal Enthalpies= -548.594160
Sum of electronic and thermal Free Energies= -548.622442

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	16	0.000000000	0.000000000	0.000333150
2	8	0.000000000	0.000311124	-0.000166575
3	8	0.000000000	-0.000311124	-0.000166575



IIIc

Zero-point correction= 0.234499 (Hartree/Particle)
Thermal correction to Energy= 0.252493
Thermal correction to Enthalpy= 0.253438
Thermal correction to Gibbs Free Energy= 0.185717
Sum of electronic and zero-point Energies= -1421.941732
Sum of electronic and thermal Energies= -1421.923737
Sum of electronic and thermal Enthalpies= -1421.922793
Sum of electronic and thermal Free Energies= -1421.990514

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000003850	0.000008352	0.000003718
2	6	0.000004121	0.000007211	0.000004845
3	6	-0.000001328	0.000004303	0.000007906
4	6	0.000005178	0.000004166	0.000001038
5	6	-0.000004014	0.000008202	-0.000000524
6	6	-0.000009855	0.000009608	0.000004321
7	7	-0.000006891	-0.000003573	-0.000004155
8	6	-0.000007452	-0.000002839	-0.000007884
9	6	-0.000008469	-0.000002358	0.000003116
10	6	-0.000000437	-0.000020248	-0.000002406
11	6	0.000003973	0.000023976	-0.000005344
12	6	0.000008430	0.000007127	-0.000012174
13	7	0.000002725	-0.000010839	-0.000006354
14	16	0.000013689	0.000003627	0.000013616
15	8	0.000005275	0.000009493	0.000007186
16	8	0.000005032	0.000008806	0.000001910
17	9	0.000010584	-0.000007187	0.000000947
18	6	0.000005525	-0.000032484	0.000004536
19	9	0.000001276	-0.000015415	-0.000008962
20	9	-0.000004766	0.000002115	-0.000009010
21	1	-0.000002465	0.000011969	0.000006377
22	1	0.000003114	0.000006172	0.000005013
23	1	0.000002963	0.000000183	0.000000844
24	1	-0.000006304	0.000007266	0.000003110
25	1	-0.000007280	0.000012796	0.000004885
26	1	-0.000004416	-0.000001926	-0.000001769
27	1	-0.000007838	0.000000541	0.000000318

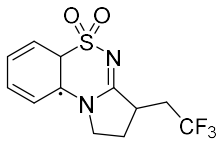
28	1	-0.000005865	-0.000000824	-0.000001862
29	1	-0.000002052	-0.000008350	-0.000002168
30	1	0.000003725	-0.000004924	-0.000002335
31	1	0.000006071	-0.000011391	-0.000004981
32	1	0.000001599	-0.000013556	-0.000003758

TS3c

Zero-point correction= 0.234079 (Hartree/Particle)
Thermal correction to Energy= 0.250892
Thermal correction to Enthalpy= 0.251837
Thermal correction to Gibbs Free Energy= 0.187999
Sum of electronic and zero-point Energies= -1421.932150
Sum of electronic and thermal Energies= -1421.915337
Sum of electronic and thermal Enthalpies= -1421.914392
Sum of electronic and thermal Free Energies= -1421.978230

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000002490	0.000005367	0.000002667
2	6	0.000002256	0.000005049	0.000002034
3	6	0.000001566	0.000001905	-0.000000250
4	6	0.000000782	0.000001411	0.000002232
5	6	-0.000000849	0.000002941	0.000002668
6	6	0.000000881	0.000005097	0.000003522
7	7	-0.000000796	-0.000000327	-0.000001000
8	6	-0.000000393	-0.000000843	-0.000003151
9	6	0.000000134	-0.000003975	-0.000002632
10	6	0.000000762	-0.000005816	0.000000131
11	6	-0.000002126	0.000000386	-0.000003051
12	6	-0.000001799	-0.000005352	-0.000004291
13	7	-0.000003329	-0.000000505	0.000001635
14	16	-0.000003343	0.000000412	0.000006026
15	8	-0.000002861	0.000001819	0.000004242
16	8	-0.000002891	0.000001222	0.000004012
17	9	0.000001460	0.000000225	-0.000001885
18	6	-0.000002450	0.000000334	-0.000000104
19	9	0.000000668	-0.000002905	-0.000002473
20	9	0.000001214	-0.000001718	-0.000005302
21	1	0.000002470	0.000006474	0.000003799
22	1	0.000002674	0.000004442	0.000001348
23	1	0.000002676	0.000002727	-0.000000936
24	1	0.000003678	0.000001522	0.000002914

25	1	0.000001016	0.000005361	0.000004501
26	1	0.000002108	-0.000000719	-0.000003493
27	1	0.000000783	-0.000002586	-0.000002369
28	1	-0.000000942	-0.000004415	-0.000003071
29	1	0.000000746	-0.000004754	-0.000004008
30	1	-0.000002370	-0.000004633	-0.000000620
31	1	-0.000002413	-0.000002749	0.000000503
32	1	-0.000001803	-0.000005397	-0.000003599



IVc

Zero-point correction= 0.234765 (Hartree/Particle)
Thermal correction to Energy= 0.251914
Thermal correction to Enthalpy= 0.252858
Thermal correction to Gibbs Free Energy= 0.188068
Sum of electronic and zero-point Energies= -1421.933757
Sum of electronic and thermal Energies= -1421.916608
Sum of electronic and thermal Enthalpies= -1421.915664
Sum of electronic and thermal Free Energies= -1421.980453

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000003398	0.000009010	-0.000002931
2	6	0.000000186	0.000003642	-0.000001323
3	6	-0.000002280	-0.000003117	0.000006520
4	6	-0.000004342	0.000003606	0.000000795
5	6	0.000002513	-0.000006745	-0.000001715
6	6	0.000006373	0.000003572	-0.000002054
7	7	-0.000020060	0.000008711	0.000010174
8	6	-0.000000069	0.000002234	0.000020593
9	6	-0.000003812	-0.000006754	-0.000003402
10	6	0.000005003	-0.000012501	-0.000000936
11	6	0.000009325	-0.000005214	-0.000003819
12	6	0.000003697	-0.000004640	0.000011413
13	7	-0.000013306	-0.000004713	-0.000000394
14	16	0.000003286	0.000019349	-0.000014900
15	8	-0.000000441	0.000000757	-0.000015575
16	8	-0.000007795	-0.000001881	-0.000001549
17	9	-0.000010659	0.000018171	-0.000009159

18	6	0.000036047	-0.000017067	-0.000017723
19	9	0.000007961	-0.000001132	0.000001069
20	9	-0.000010617	0.000005141	0.000008825
21	1	0.000003814	0.000008703	-0.000004949
22	1	0.000003487	0.000004627	0.000000758
23	1	-0.000002572	-0.000003813	-0.000001832
24	1	0.000001295	0.000002552	-0.000004851
25	1	0.000001440	0.000008480	-0.000008211
26	1	0.000001996	-0.000004453	0.000008304
27	1	-0.000001715	0.000003399	0.000005358
28	1	-0.000002668	-0.000007465	0.000005716
29	1	0.000000578	-0.000005484	0.000006058
30	1	-0.000005099	-0.000007349	0.000000331
31	1	-0.000000625	-0.000000893	0.000004055
32	1	-0.000004337	-0.000008735	0.000005352

IX. References

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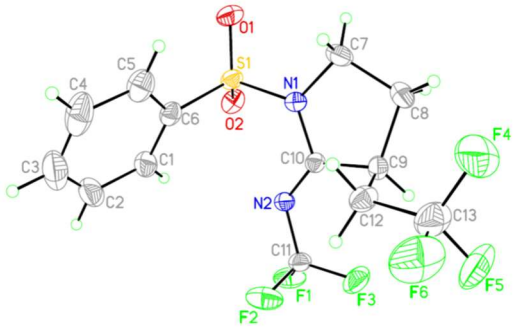
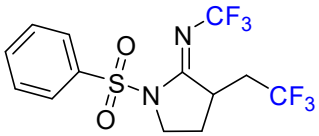
X. Crystal Data and Structure Refinements

1. Compound 3ab-(*E*):





3ab-(*E*)

CCDC number: 2189917

Table 1. Crystal data and structure refinement for **3ab**.

Identification code	3ab	
Empirical formula	C13 H12 F6 N2 O2 S	
Formula weight	374.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.9474(9) Å	α= 90°.
	b = 33.043(3) Å	β= 104.806(2)°.
	c = 8.2924(9) Å	γ = 90°.
Volume	3165.0(5) $Å^3$	
Z	8	
Density (calculated)	1.571 Mg/m^3	
Absorption coefficient	0.279 mm^{-1}	
F(000)	1520	
Crystal size	0.200 x 0.180 x 0.170 mm^3	
Theta range for data collection	2.555 to 25.150°.	
Index ranges	-14<=h<=14, -39<=k<=39, -9<=l<=9	
Reflections collected	159031	
Independent reflections	5657 [R(int) = 0.0881]	
Completeness to theta = 25.150°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5657 / 0 / 409	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0863, wR2 = 0.2041	

R indices (all data)	R1 = 0.0958, wR2 = 0.2130
Extinction coefficient	n/a
Largest diff. peak and hole	0.917 and -0.697 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)	8280(1)	334(1)	6867(1)	78(1)
C(2)	8424(1)	-42(1)	6191(2)	110(1)
C(3)	9502(1)	-228(1)	6602(2)	129(1)
C(4)	10437(1)	-40(1)	7688(2)	118(1)
C(5)	10293(1)	336(1)	8364(2)	84(1)
C(6)	9215(1)	523(1)	7954(1)	59(1)
C(7)	10560(2)	1574(1)	8580(2)	71(1)
C(8)	10486(2)	1910(1)	7322(3)	74(1)
C(9)	9850(2)	1722(1)	5632(2)	56(1)
C(10)	9042(1)	1420(1)	6163(2)	47(1)
C(11)	7669(2)	1296(1)	3654(2)	58(1)
C(12)	10622(2)	1491(1)	4746(2)	64(1)
C(13)	11371(2)	1740(1)	3985(3)	102(1)
C(14)	3641(1)	725(1)	10691(1)	69(1)
C(15)	4045(1)	576(1)	12303(1)	92(1)
C(16)	5138(1)	402(1)	12800(2)	92(1)
C(17)	5829(1)	377(1)	11685(2)	89(1)
C(18)	5425(1)	526(1)	10073(2)	68(1)
C(19)	4331(1)	700(1)	9576(1)	50(1)
C(20)	5142(2)	1327(1)	6088(2)	58(1)
C(21)	5295(2)	1780(1)	6047(2)	59(1)
C(22)	5287(1)	1923(1)	7807(2)	45(1)
C(23)	4448(1)	1623(1)	8268(2)	43(1)
C(24)	3811(2)	1971(1)	10298(2)	68(1)
C(25)	6457(1)	1892(1)	9106(2)	54(1)
C(26)	7313(2)	2200(1)	8913(3)	72(1)
F(1)	6534(1)	1288(1)	3288(1)	91(1)
F(2)	7972(1)	992(1)	2802(2)	104(1)
F(3)	7968(1)	1622(1)	2954(2)	122(1)
F(4)	12162(1)	1943(1)	5103(2)	164(1)

F(5)	10802(2)	1993(1)	2875(2)	147(1)
F(6)	11986(1)	1513(1)	3171(2)	149(1)
F(7)	2907(1)	1995(1)	10805(2)	152(1)
F(8)	4645(2)	1999(1)	11534(2)	254(1)
F(9)	3826(2)	2314(1)	9644(2)	231(1)
F(10)	7673(1)	2146(1)	7529(2)	120(1)
F(11)	8274(1)	2192(1)	10129(2)	110(1)
F(12)	6911(1)	2573(1)	8836(2)	121(1)
N(1)	9501(1)	1336(1)	7826(2)	55(1)
N(2)	8136(1)	1237(1)	5352(2)	51(1)
N(3)	4448(1)	1282(1)	7319(2)	50(1)
N(4)	3825(1)	1635(1)	9317(2)	51(1)
O(1)	9808(1)	994(1)	10506(2)	85(1)
O(2)	7822(1)	1032(1)	8726(2)	72(1)
O(3)	4152(1)	578(1)	6450(2)	79(1)
O(4)	2571(1)	924(1)	7268(2)	76(1)
S(1)	9022(1)	976(1)	8902(1)	57(1)
S(2)	3774(1)	850(1)	7528(1)	54(1)

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

C(1)-C(2)	1.3900
C(1)-C(6)	1.3900
C(1)-H(1)	0.9300
C(2)-C(3)	1.3900
C(2)-H(2)	0.9300
C(3)-C(4)	1.3900
C(3)-H(3)	0.9300
C(4)-C(5)	1.3900
C(4)-H(4)	0.9300
C(5)-C(6)	1.3900
C(5)-H(5)	0.9300
C(6)-S(1)	1.7358(13)
C(7)-N(1)	1.485(2)
C(7)-C(8)	1.510(3)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700

C(8)-C(9)	1.543(3)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(12)	1.524(3)
C(9)-C(10)	1.531(2)
C(9)-H(9)	0.9800
C(10)-N(2)	1.2709(19)
C(10)-N(1)	1.3748(19)
C(11)-F(1)	1.312(2)
C(11)-F(3)	1.317(2)
C(11)-F(2)	1.329(2)
C(11)-N(2)	1.390(2)
C(12)-C(13)	1.472(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-F(5)	1.300(3)
C(13)-F(4)	1.325(3)
C(13)-F(6)	1.347(3)
C(14)-C(15)	1.3900
C(14)-C(19)	1.3900
C(14)-H(14)	0.9300
C(15)-C(16)	1.3900
C(15)-H(15)	0.9300
C(16)-C(17)	1.3900
C(16)-H(16)	0.9300
C(17)-C(18)	1.3900
C(17)-H(17)	0.9300
C(18)-C(19)	1.3900
C(18)-H(18)	0.9300
C(19)-S(2)	1.7308(10)
C(20)-N(3)	1.478(2)
C(20)-C(21)	1.512(3)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(22)	1.536(2)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-C(23)	1.528(2)

C(22)-C(25)	1.535(2)
C(22)-H(22)	0.9800
C(23)-N(4)	1.281(2)
C(23)-N(3)	1.3733(19)
C(24)-F(8)	1.237(2)
C(24)-F(7)	1.257(3)
C(24)-F(9)	1.258(3)
C(24)-N(4)	1.379(2)
C(25)-C(26)	1.480(3)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-F(12)	1.317(3)
C(26)-F(11)	1.321(2)
C(26)-F(10)	1.337(3)
N(1)-S(1)	1.6736(16)
N(3)-S(2)	1.6691(14)
O(1)-S(1)	1.4189(13)
O(2)-S(1)	1.4160(14)
O(3)-S(2)	1.4206(15)
O(4)-S(2)	1.4196(15)

C(2)-C(1)-C(6)	120.0
C(2)-C(1)-H(1)	120.0
C(6)-C(1)-H(1)	120.0
C(1)-C(2)-C(3)	120.0
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	120.0
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(5)-C(4)-C(3)	120.0
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(6)-C(5)-C(4)	120.0
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(1)	120.0
C(5)-C(6)-S(1)	119.63(6)

C(1)-C(6)-S(1)	120.25(6)
N(1)-C(7)-C(8)	101.83(14)
N(1)-C(7)-H(7A)	111.4
C(8)-C(7)-H(7A)	111.4
N(1)-C(7)-H(7B)	111.4
C(8)-C(7)-H(7B)	111.4
H(7A)-C(7)-H(7B)	109.3
C(7)-C(8)-C(9)	105.09(15)
C(7)-C(8)-H(8A)	110.7
C(9)-C(8)-H(8A)	110.7
C(7)-C(8)-H(8B)	110.7
C(9)-C(8)-H(8B)	110.7
H(8A)-C(8)-H(8B)	108.8
C(12)-C(9)-C(10)	108.27(14)
C(12)-C(9)-C(8)	114.93(15)
C(10)-C(9)-C(8)	101.66(15)
C(12)-C(9)-H(9)	110.5
C(10)-C(9)-H(9)	110.5
C(8)-C(9)-H(9)	110.5
N(2)-C(10)-N(1)	120.23(15)
N(2)-C(10)-C(9)	132.22(14)
N(1)-C(10)-C(9)	107.45(13)
F(1)-C(11)-F(3)	107.19(15)
F(1)-C(11)-F(2)	105.52(15)
F(3)-C(11)-F(2)	104.04(16)
F(1)-C(11)-N(2)	110.78(16)
F(3)-C(11)-N(2)	118.50(15)
F(2)-C(11)-N(2)	109.89(15)
C(13)-C(12)-C(9)	115.76(19)
C(13)-C(12)-H(12A)	108.3
C(9)-C(12)-H(12A)	108.3
C(13)-C(12)-H(12B)	108.3
C(9)-C(12)-H(12B)	108.3
H(12A)-C(12)-H(12B)	107.4
F(5)-C(13)-F(4)	108.7(2)
F(5)-C(13)-F(6)	104.9(2)
F(4)-C(13)-F(6)	104.4(2)
F(5)-C(13)-C(12)	113.5(2)

F(4)-C(13)-C(12)	112.7(2)
F(6)-C(13)-C(12)	111.9(2)
C(15)-C(14)-C(19)	120.0
C(15)-C(14)-H(14)	120.0
C(19)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.0
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.0
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	120.0
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(19)-C(18)-C(17)	120.0
C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(18)-C(19)-C(14)	120.0
C(18)-C(19)-S(2)	120.39(6)
C(14)-C(19)-S(2)	119.42(6)
N(3)-C(20)-C(21)	101.92(14)
N(3)-C(20)-H(20A)	111.4
C(21)-C(20)-H(20A)	111.4
N(3)-C(20)-H(20B)	111.4
C(21)-C(20)-H(20B)	111.4
H(20A)-C(20)-H(20B)	109.2
C(20)-C(21)-C(22)	104.66(13)
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(25)	108.60(12)
C(23)-C(22)-C(21)	101.66(12)
C(25)-C(22)-C(21)	114.86(14)
C(23)-C(22)-H(22)	110.5
C(25)-C(22)-H(22)	110.4
C(21)-C(22)-H(22)	110.5

N(4)-C(23)-N(3)	119.97(14)
N(4)-C(23)-C(22)	133.01(14)
N(3)-C(23)-C(22)	107.01(13)
F(8)-C(24)-F(7)	107.29(19)
F(8)-C(24)-F(9)	101.10(19)
F(7)-C(24)-F(9)	101.30(19)
F(8)-C(24)-N(4)	114.84(18)
F(7)-C(24)-N(4)	112.89(16)
F(9)-C(24)-N(4)	117.82(17)
C(26)-C(25)-C(22)	114.07(14)
C(26)-C(25)-H(25A)	108.7
C(22)-C(25)-H(25A)	108.7
C(26)-C(25)-H(25B)	108.7
C(22)-C(25)-H(25B)	108.7
H(25A)-C(25)-H(25B)	107.6
F(12)-C(26)-F(11)	106.95(18)
F(12)-C(26)-F(10)	106.03(19)
F(11)-C(26)-F(10)	104.13(17)
F(12)-C(26)-C(25)	113.30(18)
F(11)-C(26)-C(25)	113.17(18)
F(10)-C(26)-C(25)	112.55(17)
C(10)-N(1)-C(7)	113.26(14)
C(10)-N(1)-S(1)	125.02(11)
C(7)-N(1)-S(1)	121.49(11)
C(10)-N(2)-C(11)	122.50(15)
C(23)-N(3)-C(20)	113.39(13)
C(23)-N(3)-S(2)	124.79(12)
C(20)-N(3)-S(2)	121.80(11)
C(23)-N(4)-C(24)	121.49(15)
O(2)-S(1)-O(1)	120.08(9)
O(2)-S(1)-N(1)	109.17(8)
O(1)-S(1)-N(1)	103.71(8)
O(2)-S(1)-C(6)	108.24(7)
O(1)-S(1)-C(6)	109.09(8)
N(1)-S(1)-C(6)	105.62(7)
O(4)-S(2)-O(3)	118.98(9)
O(4)-S(2)-N(3)	109.56(8)
O(3)-S(2)-N(3)	103.70(8)

O(4)-S(2)-C(19)	108.59(8)
O(3)-S(2)-C(19)	109.37(6)
N(3)-S(2)-C(19)	105.84(6)

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)	95(1)	64(1)	78(1)	2(1)	25(1)	-13(1)
C(2)	177(2)	69(1)	90(1)	-12(1)	45(1)	-36(1)
C(3)	225(3)	63(1)	129(2)	1(1)	100(1)	2(2)
C(4)	153(2)	85(1)	145(2)	27(1)	90(1)	49(1)
C(5)	82(1)	79(1)	98(1)	13(1)	35(1)	18(1)
C(6)	69(1)	58(1)	56(1)	11(1)	27(1)	2(1)
C(7)	69(1)	78(1)	56(1)	-14(1)	2(1)	-15(1)
C(8)	77(1)	68(1)	73(1)	-10(1)	13(1)	-23(1)
C(9)	59(1)	45(1)	59(1)	5(1)	7(1)	-7(1)
C(10)	51(1)	44(1)	44(1)	1(1)	11(1)	4(1)
C(11)	58(1)	68(1)	43(1)	2(1)	4(1)	-6(1)
C(12)	56(1)	80(1)	56(1)	10(1)	15(1)	-4(1)
C(13)	86(1)	140(2)	82(1)	15(1)	27(1)	-29(1)
C(14)	86(1)	69(1)	54(1)	4(1)	22(1)	-14(1)
C(15)	144(2)	88(1)	47(1)	-1(1)	31(1)	-38(1)
C(16)	147(2)	63(1)	53(1)	8(1)	-1(1)	-24(1)
C(17)	105(2)	54(1)	83(1)	4(1)	-21(1)	-4(1)
C(18)	82(1)	50(1)	67(1)	1(1)	7(1)	-4(1)
C(19)	69(1)	36(1)	41(1)	1(1)	8(1)	-10(1)
C(20)	78(1)	60(1)	40(1)	-5(1)	24(1)	-2(1)
C(21)	76(1)	66(1)	38(1)	4(1)	20(1)	-12(1)
C(22)	53(1)	42(1)	40(1)	6(1)	15(1)	0(1)
C(23)	58(1)	38(1)	34(1)	3(1)	13(1)	1(1)
C(24)	79(1)	66(1)	70(1)	-32(1)	38(1)	-24(1)
C(25)	57(1)	58(1)	48(1)	4(1)	15(1)	3(1)
C(26)	67(1)	74(1)	76(1)	-6(1)	20(1)	-9(1)
F(1)	56(1)	151(1)	61(1)	-7(1)	3(1)	3(1)

F(2)	105(1)	145(1)	63(1)	-28(1)	23(1)	17(1)
F(3)	134(1)	125(1)	75(1)	48(1)	-29(1)	-49(1)
F(4)	132(1)	242(2)	126(1)	-13(1)	44(1)	-114(1)
F(5)	170(1)	152(1)	128(1)	73(1)	56(1)	-15(1)
F(6)	112(1)	231(2)	128(1)	7(1)	76(1)	-7(1)
F(7)	135(1)	154(1)	205(1)	-114(1)	116(1)	-54(1)
F(8)	174(2)	312(1)	206(1)	-214(1)	-77(1)	116(1)
F(9)	445(2)	66(1)	289(1)	-51(1)	288(1)	-28(1)
F(10)	108(1)	169(1)	99(1)	-13(1)	56(1)	-52(1)
F(11)	68(1)	147(1)	103(1)	-2(1)	0(1)	-24(1)
F(12)	102(1)	61(1)	186(2)	-3(1)	14(1)	-18(1)
N(1)	59(1)	57(1)	44(1)	1(1)	6(1)	-4(1)
N(2)	55(1)	54(1)	42(1)	0(1)	10(1)	-7(1)
N(3)	78(1)	38(1)	39(1)	2(1)	24(1)	-3(1)
N(4)	64(1)	49(1)	48(1)	-9(1)	27(1)	-9(1)
O(1)	112(1)	89(1)	45(1)	8(1)	4(1)	5(1)
O(2)	72(1)	80(1)	73(1)	13(1)	37(1)	15(1)
O(3)	147(1)	45(1)	46(1)	-11(1)	26(1)	-6(1)
O(4)	68(1)	73(1)	73(1)	11(1)	-8(1)	-13(1)
S(1)	69(1)	61(1)	43(1)	5(1)	16(1)	6(1)
S(2)	80(1)	39(1)	37(1)	-1(1)	8(1)	-8(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(1)	7559	459	6592	94
H(2)	7799	-168	5464	132
H(3)	9599	-480	6150	155
H(4)	11158	-165	7963	142
H(5)	10918	462	9091	101
H(7A)	11254	1413	8689	85
H(7B)	10544	1680	9665	85
H(8A)	11253	2001	7296	89
H(8B)	10056	2138	7590	89

H(9)	9401	1929	4895	67
H(12A)	11109	1309	5542	77
H(12B)	10132	1326	3879	77
H(14)	2909	841	10359	82
H(15)	3583	593	13050	110
H(16)	5408	303	13879	111
H(17)	6560	261	12017	107
H(18)	5887	509	9326	82
H(20A)	4730	1223	5004	70
H(20B)	5881	1189	6453	70
H(21A)	4666	1903	5215	71
H(21B)	6022	1848	5796	71
H(22)	4982	2199	7771	54
H(25A)	6329	1917	10210	65
H(25B)	6780	1625	9029	65

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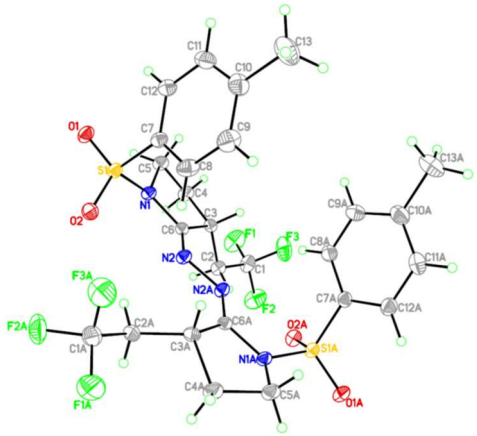
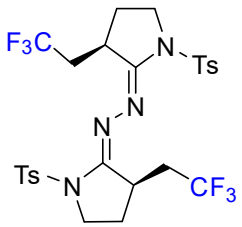
2. Compound 4aa-*syn*:





4aa-*syn*

CCDC number: 2189919

Table 1. Crystal data and structure refinement for **4aa-*syn***.

Identification code	**4aa-*syn***
Empirical formula	C26 H28 F6 N4 O4 S2
Formula weight	638.64
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	C2/c	
Unit cell dimensions	a = 19.8426(6) Å	α= 90°.
	b = 14.7342(4) Å	β= 112.8380(10)°.
	c = 21.7333(9) Å	γ = 90°.
Volume	5855.9(3) $Å^3$	
Z	8	
Density (calculated)	1.449 Mg/m^3	
Absorption coefficient	0.259 mm^{-1}	
F(000)	2640	
Crystal size	0.200 x 0.180 x 0.170 mm^3	
Theta range for data collection	2.765 to 23.737°.	
Index ranges	-22<=h<=22, -16<=k<=16, -24<=l<=24	
Reflections collected	99617	
Independent reflections	4444 [R(int) = 0.0283]	
Completeness to theta = 23.737°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9572 and 0.9500	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4444 / 0 / 381	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0994	
R indices (all data)	R1 = 0.0438, wR2 = 0.1054	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.236 and -0.339 $e.Å^{-3}$	

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)	6872(1)	1398(1)	8755(1)	40(1)
F(1)	3820(1)	257(2)	9214(1)	101(1)
F(2)	3089(1)	-149(2)	8247(1)	100(1)
F(3)	3353(1)	1242(1)	8454(1)	104(1)
O(1)	7437(1)	1343(1)	9405(1)	52(1)
O(2)	6933(1)	884(1)	8223(1)	50(1)
N(1)	6120(1)	1072(1)	8858(1)	38(1)
N(2)	5366(1)	1040(1)	7730(1)	39(1)

C(1)	3642(1)	416(2)	8573(1)	61(1)
C(2)	4249(1)	316(2)	8344(1)	45(1)
C(3)	4857(1)	1017(1)	8647(1)	36(1)
C(4)	5315(1)	877(2)	9392(1)	51(1)
C(5)	6060(1)	1262(2)	9506(1)	47(1)
C(6)	5426(1)	1027(1)	8338(1)	33(1)
C(7)	6723(1)	2546(2)	8522(1)	41(1)
C(8)	6332(1)	2781(2)	7863(1)	59(1)
C(9)	6209(2)	3688(2)	7702(1)	72(1)
C(10)	6474(2)	4363(2)	8175(2)	63(1)
C(11)	6876(2)	4108(2)	8822(1)	62(1)
C(12)	7000(1)	3208(2)	9004(1)	51(1)
C(13)	6338(2)	5356(2)	7982(2)	95(1)
S(2)	9287(1)	2616(1)	8861(1)	52(1)
F(4)	7507(1)	3754(2)	5666(1)	119(1)
F(5)	8347(1)	4205(1)	5361(1)	104(1)
F(6)	8204(1)	2797(1)	5484(1)	112(1)
O(3)	8740(1)	2766(1)	9123(1)	69(1)
O(4)	9940(1)	3140(1)	9101(1)	64(1)
N(3)	8867(1)	2809(1)	8052(1)	50(1)
N(4)	9885(1)	2695(1)	7771(1)	47(1)
C(14)	8194(2)	3609(2)	5750(1)	70(1)
C(15)	8723(1)	3654(2)	6456(1)	51(1)
C(16)	8594(1)	2916(2)	6894(1)	47(1)
C(17)	7905(1)	3076(2)	7037(1)	70(1)
C(18)	8066(1)	2675(2)	7716(1)	66(1)
C(19)	9197(1)	2812(1)	7581(1)	42(1)
C(20)	9505(2)	1456(2)	8946(1)	56(1)
C(21)	10199(2)	1176(2)	9057(2)	80(1)
C(22)	10370(2)	268(3)	9152(2)	102(1)
C(23)	9863(3)	-368(2)	9128(2)	93(1)
C(24)	9164(2)	-83(2)	9016(2)	92(1)
C(25)	8977(2)	835(2)	8927(2)	76(1)
C(26)	10054(3)	-1373(2)	9225(2)	141(2)

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

S(1)-O(1)	1.4253(15)
S(1)-O(2)	1.4256(15)
S(1)-N(1)	1.6640(17)
S(1)-C(7)	1.758(2)
F(1)-C(1)	1.320(3)
F(2)-C(1)	1.340(3)
F(3)-C(1)	1.327(3)
N(1)-C(6)	1.402(2)
N(1)-C(5)	1.487(2)
N(2)-C(6)	1.280(2)
N(2)-N(2)#1	1.406(3)
C(1)-C(2)	1.478(3)
C(2)-C(3)	1.529(3)
C(2)-H(2A)	0.9003
C(2)-H(2B)	0.9296
C(3)-C(6)	1.521(3)
C(3)-C(4)	1.533(3)
C(3)-H(3)	1.0000
C(4)-C(5)	1.510(3)
C(4)-H(4A)	0.9578
C(4)-H(4B)	0.9884
C(5)-H(5A)	0.9681
C(5)-H(5B)	0.9554
C(7)-C(12)	1.380(3)
C(7)-C(8)	1.381(3)
C(8)-C(9)	1.380(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.379(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.374(4)
C(10)-C(13)	1.516(4)
C(11)-C(12)	1.379(4)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
S(2)-O(4)	1.4214(19)

S(2)-O(3)	1.4231(17)
S(2)-N(3)	1.653(2)
S(2)-C(20)	1.755(3)
F(4)-C(14)	1.321(4)
F(5)-C(14)	1.334(3)
F(6)-C(14)	1.333(3)
N(3)-C(19)	1.411(3)
N(3)-C(18)	1.483(3)
N(4)-C(19)	1.277(3)
N(4)-N(4)#2	1.416(3)
C(14)-C(15)	1.486(4)
C(15)-C(16)	1.531(3)
C(15)-H(15A)	0.9328
C(15)-H(15B)	0.9327
C(16)-C(19)	1.514(3)
C(16)-C(17)	1.534(3)
C(16)-H(16)	1.0000
C(17)-C(18)	1.504(4)
C(17)-H(17A)	1.0164
C(17)-H(17B)	0.9153
C(18)-H(18A)	0.9651
C(18)-H(18B)	1.0513
C(20)-C(21)	1.366(4)
C(20)-C(25)	1.380(4)
C(21)-C(22)	1.376(5)
C(21)-H(21)	0.9500
C(22)-C(23)	1.361(6)
C(22)-H(22)	0.9500
C(23)-C(24)	1.377(5)
C(23)-C(26)	1.523(5)
C(24)-C(25)	1.396(4)
C(24)-H(24)	0.9500
C(25)-H(25)	0.9500
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800

O(1)-S(1)-O(2)	119.49(10)

O(1)-S(1)-N(1)	104.61(9)
O(2)-S(1)-N(1)	108.51(9)
O(1)-S(1)-C(7)	108.70(10)
O(2)-S(1)-C(7)	109.58(10)
N(1)-S(1)-C(7)	104.93(9)
C(6)-N(1)-C(5)	110.94(16)
C(6)-N(1)-S(1)	123.83(13)
C(5)-N(1)-S(1)	118.62(13)
C(6)-N(2)-N(2)#1	113.06(19)
F(1)-C(1)-F(3)	106.6(3)
F(1)-C(1)-F(2)	106.0(2)
F(3)-C(1)-F(2)	105.3(2)
F(1)-C(1)-C(2)	114.7(2)
F(3)-C(1)-C(2)	111.9(2)
F(2)-C(1)-C(2)	111.6(2)
C(1)-C(2)-C(3)	113.5(2)
C(1)-C(2)-H(2A)	106.1
C(3)-C(2)-H(2A)	111.6
C(1)-C(2)-H(2B)	105.7
C(3)-C(2)-H(2B)	108.9
H(2A)-C(2)-H(2B)	111.0
C(6)-C(3)-C(2)	114.45(16)
C(6)-C(3)-C(4)	103.33(16)
C(2)-C(3)-C(4)	114.14(17)
C(6)-C(3)-H(3)	108.2
C(2)-C(3)-H(3)	108.2
C(4)-C(3)-H(3)	108.2
C(5)-C(4)-C(3)	105.29(17)
C(5)-C(4)-H(4A)	113.1
C(3)-C(4)-H(4A)	113.3
C(5)-C(4)-H(4B)	108.2
C(3)-C(4)-H(4B)	107.1
H(4A)-C(4)-H(4B)	109.5
N(1)-C(5)-C(4)	101.97(16)
N(1)-C(5)-H(5A)	109.0
C(4)-C(5)-H(5A)	111.8
N(1)-C(5)-H(5B)	108.0
C(4)-C(5)-H(5B)	113.4

H(5A)-C(5)-H(5B)	112.0
N(2)-C(6)-N(1)	120.03(17)
N(2)-C(6)-C(3)	131.85(17)
N(1)-C(6)-C(3)	108.04(15)
C(12)-C(7)-C(8)	120.6(2)
C(12)-C(7)-S(1)	119.18(17)
C(8)-C(7)-S(1)	120.25(17)
C(9)-C(8)-C(7)	118.6(2)
C(9)-C(8)-H(8)	120.7
C(7)-C(8)-H(8)	120.7
C(10)-C(9)-C(8)	122.0(3)
C(10)-C(9)-H(9)	119.0
C(8)-C(9)-H(9)	119.0
C(11)-C(10)-C(9)	117.9(2)
C(11)-C(10)-C(13)	121.1(3)
C(9)-C(10)-C(13)	120.9(3)
C(10)-C(11)-C(12)	121.7(2)
C(10)-C(11)-H(11)	119.2
C(12)-C(11)-H(11)	119.2
C(11)-C(12)-C(7)	119.2(2)
C(11)-C(12)-H(12)	120.4
C(7)-C(12)-H(12)	120.4
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(4)-S(2)-O(3)	119.78(12)
O(4)-S(2)-N(3)	107.92(10)
O(3)-S(2)-N(3)	104.58(11)
O(4)-S(2)-C(20)	109.69(12)
O(3)-S(2)-C(20)	107.69(12)
N(3)-S(2)-C(20)	106.34(11)
C(19)-N(3)-C(18)	110.71(19)
C(19)-N(3)-S(2)	126.05(16)
C(18)-N(3)-S(2)	120.10(16)
C(19)-N(4)-N(4)#2	112.4(2)

F(4)-C(14)-F(6)	105.9(3)
F(4)-C(14)-F(5)	106.4(3)
F(6)-C(14)-F(5)	105.6(3)
F(4)-C(14)-C(15)	114.4(3)
F(6)-C(14)-C(15)	111.3(2)
F(5)-C(14)-C(15)	112.5(2)
C(14)-C(15)-C(16)	112.9(2)
C(14)-C(15)-H(15A)	105.0
C(16)-C(15)-H(15A)	112.3
C(14)-C(15)-H(15B)	107.1
C(16)-C(15)-H(15B)	110.4
H(15A)-C(15)-H(15B)	108.8
C(19)-C(16)-C(15)	115.23(18)
C(19)-C(16)-C(17)	103.93(19)
C(15)-C(16)-C(17)	113.2(2)
C(19)-C(16)-H(16)	108.1
C(15)-C(16)-H(16)	108.1
C(17)-C(16)-H(16)	108.1
C(18)-C(17)-C(16)	105.7(2)
C(18)-C(17)-H(17A)	108.0
C(16)-C(17)-H(17A)	109.8
C(18)-C(17)-H(17B)	112.6
C(16)-C(17)-H(17B)	108.7
H(17A)-C(17)-H(17B)	111.8
N(3)-C(18)-C(17)	102.1(2)
N(3)-C(18)-H(18A)	109.3
C(17)-C(18)-H(18A)	111.6
N(3)-C(18)-H(18B)	109.8
C(17)-C(18)-H(18B)	112.7
H(18A)-C(18)-H(18B)	111.0
N(4)-C(19)-N(3)	120.3(2)
N(4)-C(19)-C(16)	131.87(19)
N(3)-C(19)-C(16)	107.73(18)
C(21)-C(20)-C(25)	120.4(3)
C(21)-C(20)-S(2)	120.2(2)
C(25)-C(20)-S(2)	119.3(2)
C(20)-C(21)-C(22)	119.6(3)
C(20)-C(21)-H(21)	120.2

C(22)-C(21)-H(21)	120.2
C(23)-C(22)-C(21)	121.9(4)
C(23)-C(22)-H(22)	119.1
C(21)-C(22)-H(22)	119.1
C(22)-C(23)-C(24)	118.4(3)
C(22)-C(23)-C(26)	121.6(4)
C(24)-C(23)-C(26)	120.0(4)
C(23)-C(24)-C(25)	121.0(3)
C(23)-C(24)-H(24)	119.5
C(25)-C(24)-H(24)	119.5
C(20)-C(25)-C(24)	118.7(3)
C(20)-C(25)-H(25)	120.6
C(24)-C(25)-H(25)	120.6
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 -x+2,y,-z+3/2

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)	36(1)	48(1)	35(1)	-2(1)	12(1)	0(1)
F(1)	88(1)	173(2)	62(1)	24(1)	49(1)	-4(1)
F(2)	66(1)	132(2)	110(1)	0(1)	43(1)	-38(1)
F(3)	76(1)	99(1)	158(2)	22(1)	69(1)	29(1)
O(1)	40(1)	65(1)	41(1)	1(1)	5(1)	3(1)
O(2)	46(1)	59(1)	48(1)	-8(1)	22(1)	2(1)
N(1)	39(1)	47(1)	25(1)	0(1)	11(1)	-2(1)
N(2)	36(1)	53(1)	28(1)	-2(1)	13(1)	-1(1)
C(1)	51(1)	76(2)	63(2)	14(1)	28(1)	0(1)
C(2)	47(1)	52(1)	40(1)	6(1)	20(1)	-4(1)

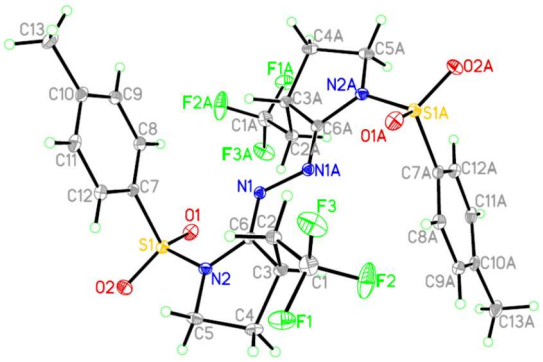
C(3)	43(1)	39(1)	30(1)	3(1)	18(1)	4(1)
C(4)	53(1)	72(2)	30(1)	2(1)	19(1)	-2(1)
C(5)	52(1)	60(1)	27(1)	-1(1)	16(1)	-1(1)
C(6)	38(1)	33(1)	29(1)	1(1)	14(1)	0(1)
C(7)	38(1)	46(1)	42(1)	-1(1)	17(1)	-7(1)
C(8)	70(2)	57(2)	43(1)	3(1)	14(1)	-15(1)
C(9)	80(2)	68(2)	58(2)	20(1)	16(1)	-7(2)
C(10)	65(2)	52(2)	79(2)	10(1)	35(2)	-3(1)
C(11)	66(2)	52(2)	73(2)	-12(1)	32(1)	-11(1)
C(12)	52(1)	54(1)	46(1)	-4(1)	17(1)	-5(1)
C(13)	121(3)	56(2)	120(3)	20(2)	59(2)	7(2)
S(2)	67(1)	52(1)	52(1)	-3(1)	37(1)	4(1)
F(4)	65(1)	180(2)	87(1)	26(1)	4(1)	14(1)
F(5)	132(2)	108(2)	60(1)	23(1)	22(1)	-13(1)
F(6)	144(2)	94(1)	67(1)	-27(1)	7(1)	-15(1)
O(3)	87(1)	71(1)	73(1)	0(1)	58(1)	14(1)
O(4)	74(1)	68(1)	55(1)	-7(1)	30(1)	-9(1)
N(3)	48(1)	58(1)	55(1)	2(1)	31(1)	2(1)
N(4)	48(1)	58(1)	44(1)	0(1)	26(1)	0(1)
C(14)	77(2)	68(2)	57(2)	0(1)	17(1)	-6(2)
C(15)	55(1)	43(1)	52(1)	0(1)	18(1)	-4(1)
C(16)	48(1)	41(1)	52(1)	-6(1)	19(1)	-8(1)
C(17)	47(1)	91(2)	69(2)	5(2)	21(1)	-4(1)
C(18)	52(2)	80(2)	77(2)	2(2)	36(1)	-4(1)
C(19)	47(1)	39(1)	46(1)	-3(1)	25(1)	-4(1)
C(20)	74(2)	55(1)	51(1)	1(1)	37(1)	8(1)
C(21)	92(2)	78(2)	95(2)	20(2)	63(2)	24(2)
C(22)	131(3)	87(3)	119(3)	32(2)	83(3)	48(2)
C(23)	156(4)	66(2)	68(2)	13(2)	56(2)	35(2)
C(24)	134(3)	58(2)	86(2)	2(2)	44(2)	-10(2)
C(25)	83(2)	65(2)	85(2)	4(2)	39(2)	0(2)
C(26)	263(6)	68(2)	101(3)	23(2)	82(4)	57(3)

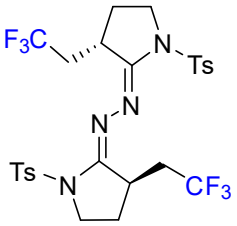
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Y.

	x	y	z	U(eq)

H(2A)	4047	355	7896	54
H(2B)	4440	-260	8480	54
H(3)	4627	1632	8587	44
H(4A)	5101	1143	9676	61
H(4B)	5367	216	9471	61
H(5A)	6079	1912	9578	56
H(5B)	6451	954	9848	56
H(8)	6151	2327	7529	71
H(9)	5934	3853	7251	86
H(11)	7074	4563	9153	75
H(12)	7272	3045	9456	61
H(13A)	6501	5487	7619	143
H(13B)	6611	5735	8369	143
H(13C)	5815	5487	7833	143
H(15A)	9183	3607	6435	61
H(15B)	8679	4228	6616	61
H(16)	8538	2323	6656	57
H(17A)	7821	3753	7063	83
H(17B)	7517	2801	6709	83
H(18A)	7824	3006	7955	80
H(18B)	7942	1979	7697	80
H(21)	10560	1605	9069	96
H(22)	10856	80	9238	122
H(24)	8804	-518	9000	111
H(25)	8495	1028	8854	91
H(26A)	9653	-1706	9279	212
H(26B)	10503	-1454	9624	212
H(26C)	10129	-1606	8834	212

3. Compound 4aa-*anti*:





4aa-*anti*

CCDC number: 2189918

Table 1. Crystal data and structure refinement for **4aa-*anti***.

Identification code	**4aa-*anti***	
Empirical formula	C26 H28 F6 N4 O4 S2	
Formula weight	638.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.6979(5) Å	α= 90°.
	b = 13.7295(6) Å	β= 117.729(3)°.
	c = 11.9468(5) Å	γ = 90°.
Volume	1408.01(12) $Å^3$	
Z	2	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	0.270 mm^{-1}	
F(000)	660	
Crystal size	0.210 x 0.200 x 0.180 mm^3	
Theta range for data collection	2.700 to 27.500°.	
Index ranges	-12<=h<=12, -17<=k<=17, -15<=l<=15	
Reflections collected	51146	
Independent reflections	3225 [R(int) = 0.0300]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3225 / 0 / 191	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0753	
R indices (all data)	R1 = 0.0346, wR2 = 0.0784	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.357 and -0.384 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)	-1868(1)	-2352(1)	-1411(1)	18(1)
F(1)	2498(1)	-1686(1)	4532(1)	34(1)
F(2)	3576(1)	-468(1)	4139(1)	56(1)
F(3)	1750(1)	-247(1)	4669(1)	44(1)
O(1)	-1676(1)	-1904(1)	-2413(1)	25(1)
O(2)	-2053(1)	-3387(1)	-1415(1)	28(1)
N(1)	-387(1)	-431(1)	-317(1)	16(1)
N(2)	-310(1)	-2118(1)	-56(1)	17(1)
C(1)	2206(2)	-802(1)	3979(1)	27(1)
C(2)	990(2)	-824(1)	2618(1)	20(1)
C(3)	1554(1)	-1244(1)	1712(1)	18(1)
C(4)	1936(2)	-2338(1)	1857(1)	23(1)
C(5)	407(2)	-2846(1)	976(1)	21(1)
C(6)	229(1)	-1178(1)	372(1)	15(1)
C(7)	-3424(1)	-1776(1)	-1308(1)	17(1)
C(8)	-4258(2)	-1048(1)	-2162(1)	20(1)
C(9)	-5503(2)	-610(1)	-2078(1)	23(1)
C(10)	-5900(2)	-886(1)	-1143(1)	23(1)
C(11)	-5021(2)	-1604(1)	-281(1)	23(1)
C(12)	-3793(2)	-2062(1)	-359(1)	20(1)
C(13)	-7295(2)	-441(1)	-1097(2)	32(1)

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

S(1)-O(2)	1.4309(10)
S(1)-O(1)	1.4326(10)
S(1)-N(2)	1.6525(11)
S(1)-C(7)	1.7586(12)
F(1)-C(1)	1.3479(17)
F(2)-C(1)	1.3320(18)
F(3)-C(1)	1.3395(18)

N(1)-C(6)	1.2759(16)
N(1)-N(1)#1	1.418(2)
N(2)-C(6)	1.3981(16)
N(2)-C(5)	1.4853(16)
C(1)-C(2)	1.5005(18)
C(2)-C(3)	1.5351(17)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(6)	1.5187(16)
C(3)-C(4)	1.5375(18)
C(3)-H(3)	1.0000
C(4)-C(5)	1.530(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(7)-C(8)	1.3874(18)
C(7)-C(12)	1.3943(18)
C(8)-C(9)	1.3940(19)
C(8)-H(8)	0.9500
C(9)-C(10)	1.392(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.394(2)
C(10)-C(13)	1.5093(18)
C(11)-C(12)	1.3886(19)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800

O(2)-S(1)-O(1)	119.22(6)
O(2)-S(1)-N(2)	104.60(6)
O(1)-S(1)-N(2)	108.65(6)
O(2)-S(1)-C(7)	109.67(6)
O(1)-S(1)-C(7)	108.35(6)
N(2)-S(1)-C(7)	105.50(6)
C(6)-N(1)-N(1)#1	110.69(12)

C(6)-N(2)-C(5)	111.52(10)
C(6)-N(2)-S(1)	123.62(9)
C(5)-N(2)-S(1)	122.97(9)
F(2)-C(1)-F(3)	108.02(13)
F(2)-C(1)-F(1)	105.74(13)
F(3)-C(1)-F(1)	105.39(11)
F(2)-C(1)-C(2)	112.99(11)
F(3)-C(1)-C(2)	111.09(12)
F(1)-C(1)-C(2)	113.13(12)
C(1)-C(2)-C(3)	114.42(11)
C(1)-C(2)-H(2A)	108.7
C(3)-C(2)-H(2A)	108.7
C(1)-C(2)-H(2B)	108.7
C(3)-C(2)-H(2B)	108.7
H(2A)-C(2)-H(2B)	107.6
C(6)-C(3)-C(2)	108.42(10)
C(6)-C(3)-C(4)	102.64(10)
C(2)-C(3)-C(4)	115.72(11)
C(6)-C(3)-H(3)	109.9
C(2)-C(3)-H(3)	109.9
C(4)-C(3)-H(3)	109.9
C(5)-C(4)-C(3)	105.21(10)
C(5)-C(4)-H(4A)	110.7
C(3)-C(4)-H(4A)	110.7
C(5)-C(4)-H(4B)	110.7
C(3)-C(4)-H(4B)	110.7
H(4A)-C(4)-H(4B)	108.8
N(2)-C(5)-C(4)	101.13(10)
N(2)-C(5)-H(5A)	111.5
C(4)-C(5)-H(5A)	111.5
N(2)-C(5)-H(5B)	111.5
C(4)-C(5)-H(5B)	111.5
H(5A)-C(5)-H(5B)	109.4
N(1)-C(6)-N(2)	121.53(11)
N(1)-C(6)-C(3)	129.84(11)
N(2)-C(6)-C(3)	108.62(10)
C(8)-C(7)-C(12)	121.22(12)
C(8)-C(7)-S(1)	119.87(10)

C(12)-C(7)-S(1)	118.92(10)
C(7)-C(8)-C(9)	119.11(12)
C(7)-C(8)-H(8)	120.4
C(9)-C(8)-H(8)	120.4
C(10)-C(9)-C(8)	120.77(13)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	118.94(12)
C(9)-C(10)-C(13)	120.42(14)
C(11)-C(10)-C(13)	120.60(13)
C(12)-C(11)-C(10)	121.27(12)
C(12)-C(11)-H(11)	119.4
C(10)-C(11)-H(11)	119.4
C(11)-C(12)-C(7)	118.66(12)
C(11)-C(12)-H(12)	120.7
C(7)-C(12)-H(12)	120.7
C(10)-C(13)-H(13A)	109.5
C(10)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(10)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

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)	19(1)	19(1)	18(1)	-4(1)	10(1)	0(1)
F(1)	45(1)	38(1)	21(1)	13(1)	15(1)	14(1)
F(2)	38(1)	93(1)	24(1)	3(1)	4(1)	-33(1)
F(3)	71(1)	36(1)	23(1)	-4(1)	21(1)	4(1)
O(1)	25(1)	36(1)	18(1)	-3(1)	14(1)	1(1)
O(2)	31(1)	19(1)	35(1)	-9(1)	16(1)	-1(1)
N(1)	15(1)	16(1)	16(1)	1(1)	8(1)	-1(1)

N(2)	17(1)	16(1)	17(1)	2(1)	8(1)	2(1)
C(1)	32(1)	30(1)	18(1)	3(1)	11(1)	-3(1)
C(2)	21(1)	20(1)	17(1)	2(1)	8(1)	2(1)
C(3)	16(1)	20(1)	16(1)	4(1)	6(1)	4(1)
C(4)	24(1)	22(1)	20(1)	4(1)	8(1)	9(1)
C(5)	27(1)	18(1)	22(1)	6(1)	14(1)	6(1)
C(6)	13(1)	18(1)	15(1)	1(1)	8(1)	1(1)
C(7)	14(1)	18(1)	18(1)	-4(1)	8(1)	-3(1)
C(8)	19(1)	21(1)	19(1)	-1(1)	8(1)	-3(1)
C(9)	17(1)	20(1)	26(1)	-2(1)	5(1)	-1(1)
C(10)	14(1)	23(1)	28(1)	-12(1)	8(1)	-6(1)
C(11)	19(1)	30(1)	22(1)	-7(1)	12(1)	-7(1)
C(12)	18(1)	23(1)	19(1)	-1(1)	9(1)	-3(1)
C(13)	18(1)	35(1)	44(1)	-17(1)	14(1)	-3(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(2A)	612	-152	2348	23
H(2B)	96	-1216	2547	23
H(3)	2471	-865	1781	21
H(4A)	2753	-2488	1606	28
H(4B)	2304	-2548	2743	28
H(5A)	594	-3474	661	25
H(5B)	-247	-2960	1400	25
H(8)	-3984	-852	-2795	24
H(9)	-6088	-117	-2666	28
H(11)	-5268	-1783	374	27
H(12)	-3216	-2561	222	24
H(13A)	-7622	144	-1628	49
H(13B)	-7019	-265	-223	49
H(13C)	-8152	-913	-1410	49