

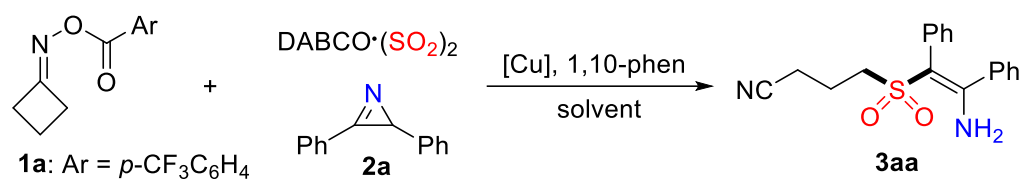
Supporting Information

1. General experimental methods (S2).
2. Table S1 (S2)
3. General experimental procedure and characterization data (S3-S17).
4. ^1H and ^{13}C NMR spectra of compounds **3**, **4**, **5**, **6** and **7** (S18-S67).

General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H and ^{13}C NMR spectra were recorded in DMSO or CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a microTOF II Instrument.

Table S1. Initial studies for the reaction of cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a**, DABCO $\cdot(\text{SO}_2)_2$, and 2,3-diphenyl-2*H*-azirine **2a** ^a

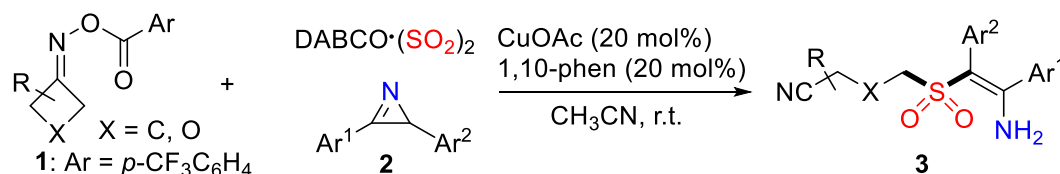


Entry	[Cu]	DABCO $\cdot(\text{SO}_2)_2$	Solvent	Yield (%) ^b
1	Cu(OAc) ₂	1.0 equiv	CH ₃ CN	47
2	Cu(OAc) ₂	1.0 equiv	toluene	n.r.
3	Cu(OAc) ₂	1.0 equiv	1,4-dioxane	37
4	Cu(OAc) ₂	1.0 equiv	CH ₂ Cl ₂	32
5	Cu ₂ O	1.0 equiv	CH ₃ CN	50
6	Cu(TFA) ₂	1.0 equiv	CH ₃ CN	45

7	CuI	1.0 equiv	CH ₃ CN	31
8	CuOAc	1.0 equiv	CH ₃ CN	52
9	CuOAc	1.5 equiv	CH ₃ CN	61
10	CuOAc	2.0 equiv	CH ₃ CN	60
11 ^c	CuOAc	1.5 equiv	CH ₃ CN	71
12 ^{c,d}	CuOAc	1.5 equiv	CH ₃ CN	69
13 ^c	-	1.5 equiv	CH ₃ CN	n.r.
14 ^{c,e}	CuOAc	1.5 equiv	CH ₃ CN	26
15 ^{c,f}	CuOAc	-	CH ₃ CN	22

^a Reaction conditions: cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (0.2 mmol), DABCO·(SO₂)₂ (0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (0.24 mmol), [Cu] (0.04 mmol), and 1,10-phen (0.04 mmol), solvent (2.0 mL), room temperature, 12 h. ^b Isolated yield based on cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a**. ^c 0.3 mmol of 2,3-diphenyl-2*H*-azirine **2a** was used. ^d 50 °C. ^e In the absence of 1,10-phen., 1,10-phen = 1,10-phenanthroline. ^f 0.6 mmol of K₂S₂O₅ was used instead of DABCO·(SO₂)₂.

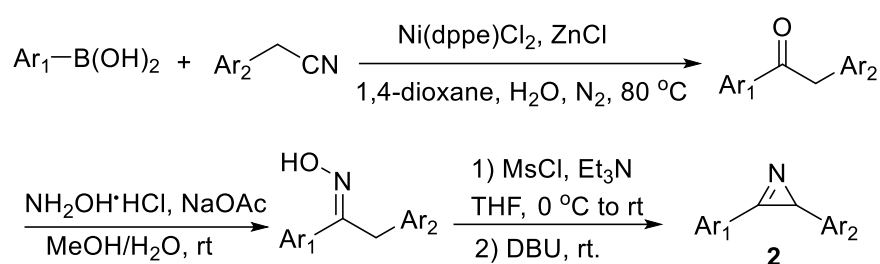
General experimental procedure (A) for the reaction of O-acyl oximes 1, DABCO·(SO₂)₂ and 2H-azirines 2.



Acetonitrile (2.0 mL) was added to a sealed tube containing *O*-acyl oxime **1** (0.2 mmol), DABCO·(SO₂)₂ (0.3 mmol), 2*H*-azirines **2** (0.3 mmol), CuOAc (0.04 mmol, 20 mol%) and 1,10-phenanthroline (0.04 mmol, 20 mol%) under N₂ atmosphere *via* a syringe. The resulting mixture was stirred at room temperature for 12 hours. After completion of reaction as monitored by TLC analysis, the mixture was diluted with ethyl acetate and washed with saturated aqueous Na₂CO₃ (10 mL), brine (10 mL), and dried over anhydrous Na₂SO₄. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (*n*-hexane/ethyl acetate = 3:1-1:1) to give the corresponding product **3**.

*General experimental procedure (B) for the synthesis of O-acyl oximes **1** and 2H-azirines **2**.*

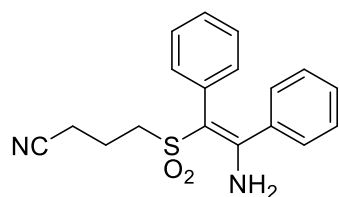
O-Acyl oximes **1a**, **1f**, **1h**, and **1k** were synthesized from the corresponding commercially available ketones according to the literature.¹ O-Acyl oximes **1b**, **1c**, **1d**, **1e** and **1g** were synthesized from the corresponding commercially available alkenes according to the literature.¹ O-Acyl oximes **1i** and **1j** were synthesized according to the literature.² All of the NMR spectra of the know compounds were consistent with the data in the literatures.¹⁻²



Step 1: A sealed round bottom flask containing Ni(dppe)Cl₂ (0.1 equiv), zinc chloride (1.5 equiv) and aryl boronic acid (2.0 equiv) was evacuated and purged with nitrogen gas three times. Then, benzyl nitrile (1.0 equiv), H₂O (1.0 equiv) and 1,4-dioxane (0.5 M) were sequentially added to the system and the resulting mixture was stirred at 80 °C for 8 h. The solution passed through a pad of Celite, and washed with DCM for several times. The filtrate was concentrated and the residue was purified on a silica gel column to give the corresponding arylketone.³

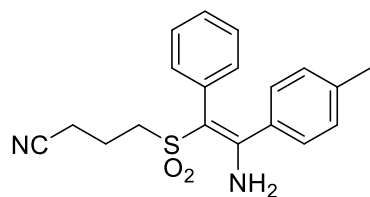
Step 2: A mixture solvent of MeOH/H₂O (v/v = 20:1) was added to a mixture of arylketone (1.0 equiv), NH₂OH·HCl (1.5 equiv) and sodium acetate (2.0 equiv) in a round bottom flask. The resulting solution was stirred at room temperature for 5 h. After completion of reaction as monitored by TLC analysis, the solvent was removed in vacuo. The resulting mixture was solved in CH₂Cl₂ and successively washed with saturated aqueous NaHCO₃ and brine, and dried over anhydrous Na₂SO₄. Then the solution was filtered, concentrated and used in the next step without further purification.

Step 3: Methanesulfonyl chloride (1.5 equiv) was added to a mixture of the crude oxime (1.0 equiv), triethylamine (1.5 equiv) and dry THF (0.5 M) in a flask at 0 °C. The solution got cloudy after the addition of methanesulfonyl chloride. The resulting mixture was stirred for 30 min, and DBU (1.5 equiv) was subsequently added over 1 min. After stirred for additional 30 min, the mixture was filtered through a pad of Celite and washed with ether. The organic solution was concentrated in vacuo and the residue was purified directly by flash column chromatography to give 2*H*-azirine **2**.



(Z)-4-((2-Amino-1,2-diphenylvinyl)sulfonyl)butanenitrile (3aa)

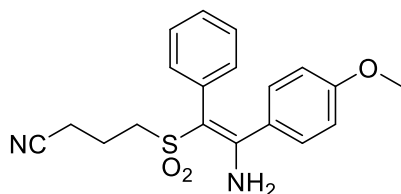
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3aa** as a white solid; ¹H NMR (400 MHz, DMSO) δ (ppm) 7.28 – 6.98 (m, 12H), 3.06 – 3.00 (m, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.06 (dd, *J* = 14.7, 7.2 Hz, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm) 158.1, 137.7, 134.8, 134.0, 129.0, 128.9, 128.1, 127.9, 127.1, 120.3, 100.4, 52.3, 19.2, 15.6. HRMS (ESI) calcd for C₁₈H₁₉N₂O₂S⁺: 327.1162 (M+H⁺), found: 327.1168.



(Z)-4-((2-Amino-1-phenyl-2-(*p*-tolyl)vinyl)sulfonyl)butanenitrile (3ab)

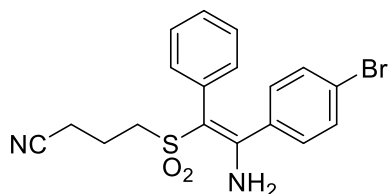
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2-phenyl-3-(*p*-tolyl)-2*H*-azirine **2b** (62.2 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title

compound **3ab** as a white solid; ^1H NMR (400 MHz, DMSO): δ (ppm) 7.21 – 7.03 (m, 9H), 6.97 (d, J = 7.8 Hz, 2H), 3.11 – 2.96 (m, 2H), 2.65 (t, J = 7.1 Hz, 2H), 2.07 (s, 3H), 2.09 – 1.94 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 158.1, 138.5, 134.9, 134.9, 134.0, 128.9, 128.7, 127.9, 127.0, 120.3, 100.3, 52.3, 21.0, 19.2, 15.6. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2\text{S}^+$: 341.1318 ($\text{M}+\text{H}^+$), found: 341.1330.



(Z)-4-((2-Amino-2-(4-methoxyphenyl)-1-phenylvinyl)sulfonyl)butanenitrile (3ac)

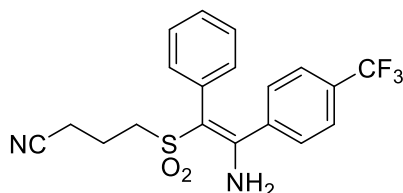
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine **2c** (67.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3ac** as a white solid; ^1H NMR (400 MHz, DMSO): δ (ppm) 7.12–7.08 (m, 9H), 6.72 (d, J = 8.2 Hz, 2H), 3.65 (s, 3H), 3.09 – 2.91 (m, 2H), 2.65 (t, J = 7.1 Hz, 2H), 2.13 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 159.8, 157.9, 135.2, 134.0, 130.6, 129.9, 128.1, 127.0, 120.4, 113.5, 100.2, 55.5, 52.4, 19.3, 15.6. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_3\text{S}^+$: 357.1267 ($\text{M}+\text{H}^+$), found: 357.1274.



(Z)-4-((2-Amino-2-(4-bromophenyl)-1-phenylvinyl)sulfonyl)butanenitrile (3ad)

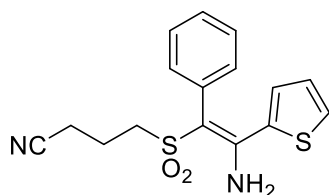
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 3-(4-bromophenyl)-2-phenyl-2*H*-azirine **2d** (81.6 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3ad** as a white solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.37 (d, J = 8.2 Hz, 2H), 7.14–7.09 (m, 9H), 3.06 – 2.98 (m, 2H), 2.65 (t, J = 7.1 Hz, 2H), 2.13 – 1.96 (m, 2H). ^{13}C NMR

(100 MHz, DMSO) δ (ppm) 156.9, 137.0, 134.5, 134.0, 131.1, 131.1, 128.1, 127.3, 122.3, 120.2, 100.8, 52.3, 19.1, 15.6. HRMS (ESI) calcd for $C_{18}H_{18}BrN_2O_2S^+$: 405.0267 ($M+H^+$), found: 405.0277.



(Z)-4-((2-Amino-1-phenyl-2-(4-(trifluoromethyl)phenyl)vinyl)sulfonyl)butanenitrile
(**3ae**)

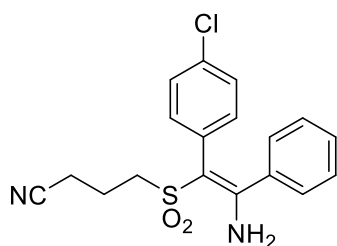
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2-phenyl-3-(4-(trifluoromethyl)phenyl)-2*H*-azirine **2e** (78.4 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 3/1) to afford the title compound **3ae** as a white solid; 1H NMR (400 MHz, DMSO) δ (ppm) 7.55 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 7.21 (s, 2H), 7.14 – 7.07 (m, 5H), 3.13 – 2.96 (m, 2H), 2.67 (t, J = 7.1 Hz, 2H), 2.15 – 1.94 (m, 2H). ^{19}F NMR (376 MHz, DMSO) δ (ppm) -61.25 (s). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 156.6, 141.9, 134.3, 134.1, 130.0, 129.3 (q, $^2J_{CF}$ = 32.0 Hz), 128.1, 127.5, 125.1 (q, $^3J_{CF}$ = 3.8 Hz), 124.2 (q, $^1J_{CF}$ = 270.5 Hz), 120.3, 101.2, 52.4, 19.2, 15.7. HRMS (ESI) calcd for $C_{19}H_{18}F_3N_2O_2S^+$: 395.1036 ($M+H^+$), found: 395.1042.



(Z)-4-((2-Amino-1-phenyl-2-(thiophen-2-yl)vinyl)sulfonyl)butanenitrile (**3af**)

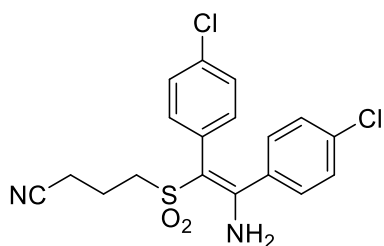
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2-phenyl-3-(thiophen-2-yl)-2*H*-azirine **2f** (59.8 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title

compound **3af** as a brown solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.52 (d, J = 5.0 Hz, 1H), 7.26 – 7.20 (m, 5H), 7.14 – 7.02 (m, 3H), 6.90 (t, J = 4.3 Hz, 1H), 3.11 – 3.03 (m, 2H), 2.67 (t, J = 7.1 Hz, 2H), 2.10 – 1.97 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 150.2, 138.3, 134.8, 134.1, 130.4, 129.8, 128.5, 128.1, 126.9, 120.3, 101.7, 52.4, 19.2, 15.7. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2\text{S}_2^+$: 333.0726 ($\text{M}+\text{H}^+$), found: 333.0737.



(*Z*)-4-((2-Amino-1-(4-chlorophenyl)-2-phenylvinyl)sulfonyl)butanenitrile (**3ag**)

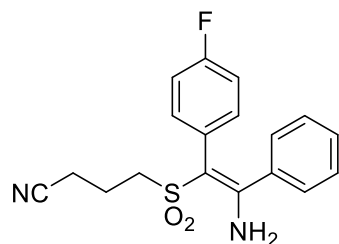
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2-(4-chlorophenyl)-3-phenyl-2*H*-azirine **2g** (68.3 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 1/1) to afford the title compound **3ag** as a white solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.26 – 7.18 (m, 7H), 7.14–7.09 (m, 4H), 3.12 – 2.98 (m, 2H), 2.66 (t, J = 7.1 Hz, 2H), 2.12 – 1.99 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 158.6, 137.5, 135.7, 134.0, 131.9, 129.3, 129.1, 128.3, 128.0, 120.4, 99.2, 52.5, 19.2, 15.7. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{ClN}_2\text{O}_2\text{S}^+$: 361.0772 ($\text{M}+\text{H}^+$), found: 361.0780.



(*Z*)-4-((2-Amino-1,2-bis(4-chlorophenyl)vinyl)sulfonyl)butanenitrile (**3ah**)

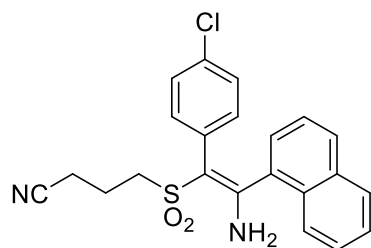
This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2,3-bis(4-chlorophenyl)-2*H*-azirine **2h** (78.6 mg, 0.3 mmol) as starting material and purified by column

chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3ah** as a white solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.19 (m, 10H), 3.08 – 3.00 (m, 2H), 2.66 (t, J = 7.0 Hz, 2H), 2.10 – 1.98 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 157.3, 136.4, 135.8, 133.9, 133.7, 132.1, 131.0, 128.4, 128.2, 120.3, 99.6, 52.5, 19.2, 15.7. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O}_2\text{S}^+$: 395.0382 ($\text{M}+\text{H}^+$), found: 395.0388.



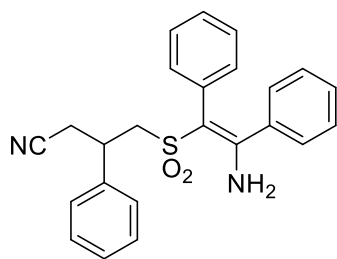
(*Z*)-4-((2-Amino-1-(4-fluorophenyl)-2-phenylvinyl)sulfonyl)butanenitrile (**3ai**)

This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2-(4-fluorophenyl)-3-phenyl-2*H*-azirine **2i** (63.4 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 3/1) to afford the title compound **3ai** as a white solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.22-7.09 (m, 9H), 6.90 (t, J = 8.5 Hz, 2H), 3.07 – 3.00 (m, 2H), 2.66 (t, J = 7.1 Hz, 2H), 2.10 – 1.98 (m, 2H). ^{19}F NMR (376 MHz, DMSO) δ (ppm) -115.33 – 155.41 (m). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 161.4 (d, $^1J_{\text{CF}}$ = 244.3 Hz), 158.5, 137.7, 136.1 (d, $^3J_{\text{CF}}$ = 8.3 Hz), 131.3, 129.2, 129.0, 128.3, 120.4, 114.9 (d, $^2J_{\text{CF}}$ = 21.2 Hz), 99.3, 52.3, 19.2, 15.7. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{FN}_2\text{O}_2\text{S}^+$: 345.1068 ($\text{M}+\text{H}^+$), found: 345.1075.



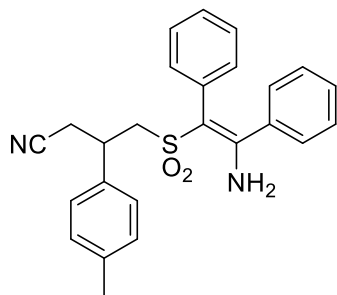
(*Z*)-4-((2-Amino-1-(4-chlorophenyl)-2-(naphthalen-1-yl)vinyl)sulfonyl)butanenitrile (**3aj**)

This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2-(4-chlorophenyl)-3-(naphthalen-1-yl)-2*H*-azirine **2j** (83.3 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3aj** as a white solid; ¹H NMR (400 MHz, DMSO) δ (ppm) 8.04 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.32 (m, 4H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.20 – 2.08 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm) 156.9, 135.0, 134.9, 133.5, 133.1, 132.1, 130.1, 129.2, 128.6, 127.7, 127.2, 127.2, 126.5, 125.3, 125.3, 120.4, 100.6, 52.5, 19.4, 15.7. HRMS (ESI) calcd for C₂₂H₂₀ClN₂O₂S⁺: 411.0929 (M+H⁺), found: 411.0939.



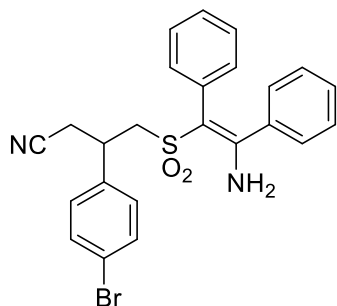
(Z)-4-((2-Amino-1,2-diphenylvinyl)sulfonyl)-3-phenylbutanenitrile (3ba)

This compound was prepared following general procedure A using 3-phenylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1b** (66.7 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3ba** as a white solid; ¹H NMR (400 MHz, DMSO) δ (ppm) 7.47 – 7.27 (m, 5H), 7.21 – 6.90 (m, 12H), 3.70 – 3.60 (m, 1H), 3.55 – 3.31 (m, 2H), 3.20 – 3.02 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm) 158.1, 141.1, 137.8, 134.7, 134.1, 129.1, 129.1, 129.0, 128.1, 128.1, 128.0, 127.9, 127.1, 119.2, 100.8, 57.7, 37.3, 24.3. HRMS (ESI) calcd for C₂₄H₂₃N₂O₂S⁺: 403.1475 (M+H⁺), found: 403.1482.



(Z)-4-((2-Amino-1,2-diphenylvinyl)sulfonyl)-3-(*p*-tolyl)butanenitrile (**3ca**)

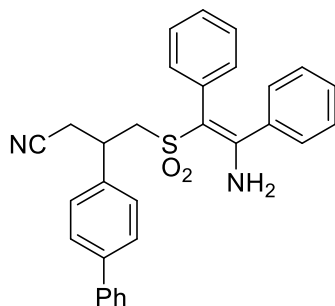
This compound was prepared following general procedure A using 3-(*p*-tolyl)cyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1c** (69.5 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3ca** as a white solid; ¹H NMR (400 MHz, DMSO) δ (ppm) 7.29 – 6.93 (m, 16H), 3.56-3.5 (m, 1H), 3.47 – 3.33 (m, 1H), 3.28 (dd, *J* = 14.4, 5.7 Hz, 1H), 3.12-2.97 (m, 2H), 2.29 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ (ppm) 158.0, 138.0, 137.7, 137.1, 134.6, 134.0, 129.6, 129.0, 128.9, 128.0, 127.8, 127.0, 119.1, 100.7, 57.6, 36.8, 24.2, 21.0. HRMS (ESI) calcd for C₂₅H₂₅N₂O₂S⁺: 417.1631 (M+H⁺), found: 417.1643.



(Z)-4-((2-Amino-1,2-diphenylvinyl)sulfonyl)-3-(4-bromophenyl)butanenitrile (**3da**)

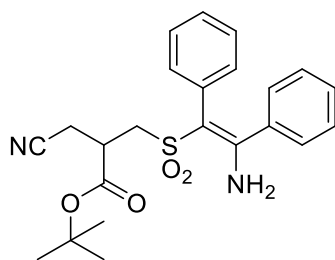
This compound was prepared following general procedure A using 3-(4-bromophenyl)cyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1d** (82.4 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3da** as a light yellow solid; ¹H NMR (400 MHz, DMSO) δ (ppm) 7.56 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.21 – 6.96 (m, 11H), 3.67 – 3.57 (m, 1H), 3.46 – 3.31 (m, 2H), 3.13 – 2.97 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ (ppm)

158.1, 140.4, 137.8, 134.6, 134.0, 131.9, 130.5, 129.1, 129.0, 128.1, 127.9, 127.1, 121.3, 119.0, 100.7, 57.4, 36.9, 24.1. HRMS (ESI) calcd for $C_{24}H_{22}BrN_2O_2S^+$: 481.0580 ($M+H^+$), found: 481.0590.



(*Z*)-3-([1,1'-Biphenyl]-4-yl)-4-((2-amino-1,2-diphenylvinyl)sulfonyl)butanenitrile (**3ea**)

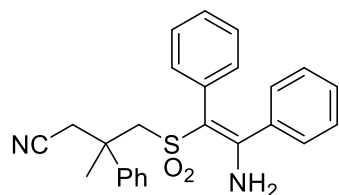
This compound was prepared following general procedure A using 3-([1,1'-biphenyl]-4-yl)cyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1e** (81.9 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3ea** as a white solid; 1H NMR (400 MHz, DMSO) δ (ppm) 7.69 (d, J = 7.9 Hz, 4H), 7.53-7.47 (m, 4H), 7.38 (t, J = 7.3 Hz, 1H), 7.20 – 6.97 (m, 12H), 3.74 – 3.64 (m, 1H), 3.51 – 3.39 (m, 2H), 3.19-3.06 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 158.1, 140.2, 140.2, 139.9, 137.8, 134.7, 134.1, 129.4, 129.1, 129.0, 128.8, 128.1, 127.9, 127.4, 127.1, 119.3, 100.9, 57.8, 37.1, 24.2. HRMS (ESI) calcd for $C_{30}H_{27}N_2O_2S^+$: 479.1788 ($M+H^+$), found: 479.1794.



tert-Butyl (*Z*)-3-((2-amino-1,2-diphenylvinyl)sulfonyl)-2-(cyanomethyl)propanoate (**3fa**)

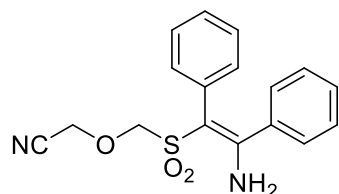
This compound was prepared following general procedure A using 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclobutane-1-carboxylate **1f** (71.5 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by

column chromatography on silica gel (*n*-hexane/ethyl acetate = 1/1) to afford the title compound **3fa** as a white solid; ¹H NMR (400 MHz, DMSO) δ (ppm) 7.25-7.15 (m, 7H), 7.14 – 7.05 (m, 5H), 3.47 - 3.42 (m, 1H), 3.23 - 3.16 (m, 2H), 3.06 – 2.88 (m, 2H), 1.43 (s, 9H). ¹³C NMR (100 MHz, DMSO) δ (ppm) 170.0, 158.6, 137.7, 134.6, 134.2, 129.2, 129.1, 128.2, 128.0, 127.3, 118.5, 100.7, 82.3, 53.7, 37.6, 27.9, 19.5. HRMS (ESI) calcd for C₂₃H₂₆N₂NaO₄S⁺: 449.1505 (M+H⁺), found: 449.1512.



(Z)-4-((2-Amino-1,2-diphenylvinyl)sulfonyl)-3-methyl-3-phenylbutanenitrile (3ga)

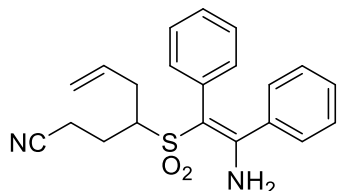
This compound was prepared following general procedure A using 3-methyl-3-phenylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1g** (69.5 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 3/1) to afford the title compound **3ga** as a light yellow solid; ¹H NMR (400 MHz, DMSO) δ (ppm) 7.50 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.19-7.11 (m, 5H), 7.07-6.96 (m, 7H), 3.59 – 3.48 (m, 2H), 3.38 – 3.21 (m, 2H), 1.73 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ (ppm) 157.1, 143.8, 137.8, 134.9, 134.1, 129.1, 129.1, 128.8, 128.2, 127.9, 127.4, 127.0, 126.5, 118.9, 103.6, 62.4, 40.4, 29.8, 25.0. HRMS (ESI) calcd for C₂₅H₂₅N₂O₂S⁺: 417.1631 (M+H⁺), found: 417.1642.



(Z)-2-(((2-Amino-1,2-diphenylvinyl)sulfonyl)methoxy)acetonitrile (3ha)

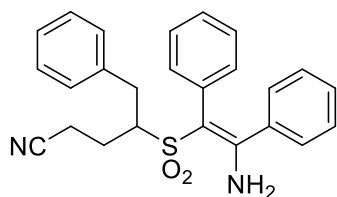
This compound was prepared following general procedure A using oxetan-3-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1h** (51.8 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 3/1) to afford the title compound **3ha** as a white

solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.27 (broad, 2H), 7.23 – 7.15 (m, 5H), 7.10 – 7.04 (m, 5H), 4.82 (s, 2H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 160.1, 137.6, 134.6, 134.3, 129.3, 129.1, 128.3, 128.0, 127.1, 117.1, 98.5, 82.9, 58.0. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{NaO}_3\text{S}^+$: 351.0774 ($\text{M}+\text{Na}^+$), found: 351.0785.



(Z)-4-((2-Amino-1,2-diphenylvinyl)sulfonyl)hept-6-enenitrile (3ia)

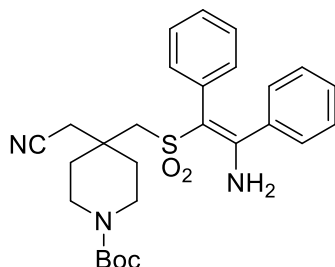
This compound was prepared following general procedure A using 2-allylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1i** (59.5 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 3/1) to afford the title compound **3ia** as a colorless oil; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.37 – 6.88 (m, 12H), 5.87–5.77 (m, 1H), 5.22–5.10 (m, 2H), 2.95–2.82 (m, 1H), 2.74 – 2.54 (m, 3H), 2.50 – 2.41 (m, 1H), 2.18 – 2.09 (m, 1H), 1.97 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 159.3, 137.9, 134.7, 134.4, 134.1, 129.1, 128.9, 128.2, 128.0, 127.2, 120.3, 118.8, 98.6, 59.6, 31.8, 23.1, 14.6. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_2\text{S}^+$: 367.1475 ($\text{M}+\text{H}^+$), found: 367.1478.



(Z)-4-((2-Amino-1,2-diphenylvinyl)sulfonyl)-5-phenylpentanenitrile (3ja)

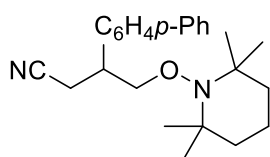
This compound was prepared following general procedure A using *O*-(4-(trifluoromethyl)benzoyl) oxime **1j** (69.5 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 3/1) to afford the title compound **3ja** as a white solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.35 – 7.06 (m, 17H), 3.42 – 3.35 (m, 1H), 3.15 – 3.07 (m, 1H), 2.87 – 2.79 (m, 1H), 2.57 – 2.37 (m, 2H), 2.12 – 2.01 (m, 1H), 1.87

– 1.69 (m, 1H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 159.4, 137.9, 137.7, 134.7, 134.0, 129.4, 129.2, 129.1, 129.1, 128.2, 128.1, 127.2, 127.2, 120.1, 98.7, 61.7, 33.9, 23.3, 14.8. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}_2\text{S}^+$: 417.1631 ($\text{M}+\text{H}^+$), found: 417.1644.



tert-Butyl (Z)-4-(((2-amino-1,2-diphenylvinyl)sulfonyl)methyl)-4-(cyanomethyl)piperidine-1-carboxylate (**3ka**)

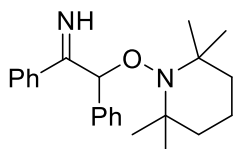
This compound was prepared following general procedure A using *tert*-butyl 2-(((4-(trifluoromethyl)benzoyl)oxy)imino)-7-azaspiro[3.5]nonane-7-carboxylate **1k** (85.3 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 2/1) to afford the title compound **3ka** as a white solid; ^1H NMR (400 MHz, DMSO) δ (ppm) 7.22 – 7.01 (m, 12H), 3.50 – 3.20 (m, 6H), 2.99 (s, 2H), 1.88 – 1.76 (m, 2H), 1.56 – 1.48 (2, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, DMSO) δ (ppm) 157.3, 154.3, 137.7, 134.9, 134.0, 129.2, 129.1, 128.2, 127.9, 127.0, 118.6, 104.0, 79.2, 57.0, 35.5, 34.0, 28.5, 25.9. HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{33}\text{N}_3\text{NaO}_4\text{S}^+$: 518.2084 ($\text{M}+\text{Na}^+$), found: 518.2097.



3-([1,1'-Biphenyl]-4-yl)-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (**4**)

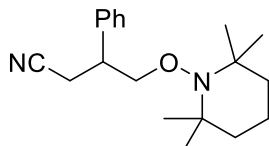
This compound was prepared following general procedure A using 3-([1,1'-biphenyl]-4-yl)cyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1e** (81.9 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) and TEMPO (62.5 mg, 0.4 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to afford the title compound **4** as a Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.62-7.59 (m, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 8.2 Hz, 3H), 4.05

(d, $J = 6.4$ Hz, 2H), 3.38-3.23 (m, 1H), 2.98 (dd, $J = 16.7, 5.7$ Hz, 1H), 2.81 (dd, $J = 16.7, 8.0$ Hz, 1H), 1.60 – 1.26 (m, 6H), 1.18-1.10 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 140.5, 140.4, 138.1, 128.7, 127.9, 127.3, 127.3, 126.9, 118.6, 78.0, 59.9, 41.6, 39.6, 39.5, 32.9, 32.9, 21.0, 20.2, 20.0, 16.9. HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{33}\text{N}_2\text{O}^+$: 377.2587 ($\text{M}+\text{H}^+$), found: 377.2588.



1,2-Diphenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-imine (**5**)⁷

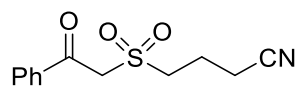
This compound was prepared following general procedure A using 2,3-diphenyl-2H-azirine **2a** (58.0 mg, 0.3 mmol) and TEMPO (62.5 mg, 0.4 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8/1) to afford the title compound **5** as a light yellow solid; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.76-7.74 (m, 2H), 7.40 – 7.12 (m, 8H), 5.79 (s, 1H), 1.59 – 1.31 (m, 9H), 1.20 (s, 3H), 1.12 (s, 3H), 0.53 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 177.8, 138.9, 137.0, 130.2, 128.1, 128.1, 127.9, 127.6, 127.2, 88.7, 60.6, 59.4, 40.3, 34.0, 33.0, 20.2, 16.9.



3-Phenyl-4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (**6**)⁸

This compound was prepared following general procedure A using 3-phenylcyclobutan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime **1b** (81.9 mg, 0.2 mmol) and TEMPO (62.5 mg, 0.4 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 8/1) to afford the title compound **6** as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.36-7.24 (m, 5H), 3.99 (d, $J = 6.4$ Hz, 2H), 3.29 – 3.14 (m, 1H), 2.92 (dd, $J = 16.7, 5.9$ Hz, 1H), 2.74 (dd, $J = 16.7, 8.0$ Hz, 1H), 1.59 – 1.18 (m, 6H), 1.11-1.07 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ

(ppm) 139.2, 128.7, 127.6, 127.5, 118.7, 78.1, 59.9, 41.9, 39.6, 39.6, 33.0, 21.0, 20.2, 20.1, 17.0.



4-((2-Oxo-2-phenylethyl)sulfonyl)butanenitrile (**7**)⁹

This compound was prepared following general procedure A using cyclobutanone *O*-(4-(trifluoromethyl)benzoyl) oxime **1a** (51.4 mg, 0.2 mmol), 2,3-diphenyl-2*H*-azirine **2a** (58.0 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane (385 mg, 2 mmol) as starting material and purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 5/1) to afford the title compound **7** as a light yellow solid; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 4.63 (s, 2H), 3.45 (t, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 7.1 Hz, 1H), 2.33-2.26 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 189.0, 135.5, 134.9, 129.3, 129.1, 118.0, 60.1, 51.8, 18.4, 16.3.

References

- 1 X.-Y. Yu, J.-R. Chen, P.-Z. Wang, M.-N. Yang, D. Liang and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2018, **57**, 738.
- 2 W. Ai, Y. Liu, Q. Wang, Z. Lu and Q. Liu, *Org. Lett.*, 2018, **20**, 409.
- 3 N. Gu, M. Liu, H. Wang, S. Sun, Z. Zhou, W. Hu, J.-T. Yu and J. Cheng, *Tetrahedron Letters* 2017, **58**, 3398.
- 4 H. Hu, Y. Liu, L. Lin, Y. Zhang, X. Liu and X. Feng, *Angew. Chem. Int. Ed.*, 2016, **55**, 10098.
- 5 Y. Wang, X. Lei and Y. Tang, *Chem. Commun.*, 2015, **51**, 4507.
- 6 B. S. KarKi, L. Devi, A. Porhriyal, R. Kant, N. Rastogi, *Chem. Asian J.* 2019, **14**, 4793.
- 7 M.-N. Zhao, Z.-H. Ren, D.-S. Yang, Z.-H. Guan, *Org. Lett.* **2018**, **20**, 1287.
- 8 Y.-R. Gu, X.-H. Duan, L. Yang, L.-N. Gu, *Org. Lett.* **2017**, **19**, 5908.
- 9 M. Zheng, G. Li, H. Lu, *Org. Lett.* **2019**, **21**, 1216.

