Supporting Information

1. General experimental methods (S2).
2. Table S1 (S2)
3. General experimental procedure and characterization data (S3-S17).
4. $^1$H 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 ¹³C NMR spectra were recorded in DMSO or CDCl₃ 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·(SO₂)₂, and 2,3-diphenyl-2H-azirine 2a.

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<th>Entry</th>
<th>[Cu]</th>
<th>DABCO·(SO₂)₂</th>
<th>Solvent</th>
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<td>Reaction conditions: cyclobutanone $O$-(4-(trifluoromethyl)benzoyl) oxime 1a (0.2 mmol), DABCO·(SO$_2$)$_2$ (0.2 mmol), 2,3-diphenyl-$2H$-azirine 2a (0.24 mmol), [Cu] (0.04 mmol), and 1,10-phen (0.04 mmol), solvent (2.0 mL), room temperature, 12 h. Isolated yield based on cyclobutanone $O$-(4-(trifluoromethyl)benzoyl) oxime 1a. 0.3 mmol of 2,3-diphenyl-$2H$-azirine 2a was used. 50 °C. In the absence of 1,10-phen, 1,10-phen = 1,10-phenanthroline. 0.6 mmol of K$_2$S$_2$O$_5$ was used instead of DABCO·(SO$_2$)$_2$.</td>
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General experimental procedure (A) for the reaction of O-acyl oximes 1, DABCO·(SO$_2$)$_2$ and 2H-azirines 2.

Acetonitrile (2.0 mL) was added to a sealed tube containing O-acyl oxime 1 (0.2 mmol), DABCO·(SO$_2$)$_2$ (0.3 mmol), 2H-azirines 2 (0.3 mmol), CuOAc (0.04 mmol, 20 mol%) and 1,10-phenanthroline (0.04 mmol, 20 mol%) under N$_2$ 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 Na$_2$CO$_3$ (10 mL), brine (10 mL), and dried over anhydrous Na$_2$SO$_4$. 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 known compounds were consistent with the data in the literatures.\(^1\)\(^-\)\(^2\)

\[\text{Ar}_1\text{B(OH)}_2 + \text{Ar}_2\text{CN} \xrightarrow{\text{Ni(dppe)Cl}_2, \text{ZnCl}} \xrightarrow{1,4\text{-dioxane, } \text{H}_2\text{O, N}_2, 80 ^\circ\text{C}} \text{Ar}_1\text{Ar}_2\]

\[\text{NH}_2\text{OH}^+\text{HCl, NaOAc} \xrightarrow{\text{MeOH/H}_2\text{O, rt}} \xrightarrow{1) \text{MsCl, Et}_3\text{N \ THF, } 0 ^\circ\text{C to rt, 2) DBU, rt.}} \text{Ar}_1^\text{N} \rightarrow 2 \text{Ar}_2\]

**Step 1:** A sealed round bottom flask containing Ni(dppe)Cl\(_2\) (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), H\(_2\)O (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/H\(_2\)O (v/v = 20:1) was added to a mixture of arylketone (1.0 equiv), NH\(_2\)OH-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 CH\(_2\)Cl\(_2\) and successively washed with saturated aqueous NaHCO\(_3\) and brine, and dried over anhydrous Na\(_2\)SO\(_4\). 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 2H-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-2H-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)-2H-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; $^1$H NMR (400 MHz, DMSO): $\delta$ (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) $\delta$ (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 C$_{19}$H$_{21}$N$_2$O$_2$S$: 341.1318 (M+H$^+$), 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-2H-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; $^1$H NMR (400 MHz, DMSO): $\delta$ (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) $\delta$ (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 C$_{19}$H$_{21}$N$_2$O$_3$S$: 357.1267 (M+H$^+$), 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-2H-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; $^1$H NMR (400 MHz, DMSO) $\delta$ (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_{2}O_{2}S^{+}: 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)-2H-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; \(^1\)H 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, \(^3\)J_{CF} = 32.0 Hz), 128.1, 127.5, 125.1 (q, \(^3\)J_{CF} = 3.8 Hz), 124.2 (q, \(^3\)J_{CF} = 270.5 Hz), 120.3, 101.2, 52.4, 19.2, 15.7. HRMS (ESI) calcd for C_{19}H_{18}F_{3}N_{2}O_{2}S^{+}: 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)-2H-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; $^1$H NMR (400 MHz, DMSO) $\delta$ (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) $\delta$ (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 C$_{16}$H$_{17}$N$_2$O$_2$S$_2^+$: 333.0726 (M+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; $^1$H NMR (400 MHz, DMSO) $\delta$ (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) $\delta$ (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 C$_{18}$H$_{18}$ClN$_2$O$_2$S$^+$: 361.0772 (M+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; $^1$H NMR (400 MHz, DMSO) $\delta$ (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) $\delta$ (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 C$_{18}$H$_{17}$ClN$_2$O$_2$S$: 395.0382$ (M+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-2H-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; $^1$H NMR (400 MHz, DMSO) $\delta$ (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) $\delta$ (ppm) -115.33 – 155.41 (m). $^{13}$C NMR (100 MHz, DMSO) $\delta$ (ppm) 161.4 (d, $^1$J$_{CF}$ = 244.3 Hz), 158.5, 137.7, 136.1 (d, $^3$J$_{CF}$ = 8.3 Hz), 131.3, 129.2, 129.0, 128.3, 120.4, 114.9 (d, $^2$J$_{CF}$ = 21.2 Hz), 99.3, 52.3, 19.2, 15.7. HRMS (ESI) calcd for C$_{18}$H$_{18}$F$_2$N$_2$O$_2$S$: 345.1068$ (M+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)-2H-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; $^1$H 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). $^{13}$C 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 C$_{22}$H$_{20}$ClN$_{2}$O$_{2}$S$: 411.0929$ (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-2H-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; $^1$H 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). $^{13}$C 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 C$_{24}$H$_{23}$N$_{2}$O$_{2}$S$: 403.1475$ (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-2H-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-2H-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)
HRMS (ESI) calcd for C_{24}H_{22}BrN_{2}O_{3}S^+: 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-2H-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; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) (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) \(\delta\) (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_{2}O_{3}S^+: 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-2H-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; $^1$H 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). $^{13}$C 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 C$_{23}$H$_{26}$N$_2$NaO$_4$S$: 449.1505 (M+H$^+$), 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-2H-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; $^1$H 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). $^{13}$C 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 C$_{25}$H$_{25}$N$_2$O$_4$S$: 417.1631 (M+H$^+$), 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-2H-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; \(^1\)H NMR (400 MHz, DMSO) \(\delta \) (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) \(\delta \) (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 C\(_{17}\)H\(_{16}\)N\(_2\)NaO\(_3\)S+: 351.0774 (M+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-
one \(O\)-(4-(trifluoromethyl)benzoyl) oxime 1i (59.5 mg, 0.2 mmol), 2,3-diphenyl-2H-
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; \(^1\)H NMR (400 MHz, DMSO) \(\delta \) (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) \(\delta \) (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 C\(_{21}\)H\(_{23}\)N\(_2\)O\(_2\)S+: 367.1475 (M+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-2H-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 white
solid; \(^1\)H NMR (400 MHz, DMSO) \(\delta \) (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, 128.2, 128.1, 127.2, 127.2, 120.1, 98.7, 61.7, 33.9, 23.3, 14.8. HRMS (ESI) calcd for C$_{25}$H$_{25}$N$_{2}$O$_{2}$S$^+$: 417.1631 (M+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-2H-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; $^1$H 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 C$_{27}$H$_{33}$N$_{3}$NaO$_{2}$S$^+$: 518.2084 (M+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-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 = 10/1) to afford the title compound 4 as a Colorless oil; $^1$H 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 C$_{25}$H$_{33}$N$_2$O$: 377.2587$ (M$^+$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; $^1$H 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 a colorless oil; $^1$H 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)

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-2H-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