Supporting Information

Scandium Catalysed Stereoselective Thio-allylation of Allenyl-Imidates

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Table of Contents

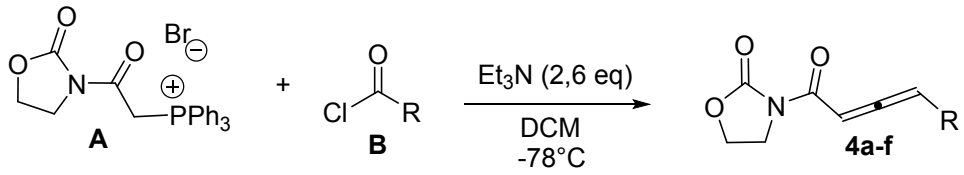
General Methods

^{1}H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ^{13}C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: 77.0 ppm). GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection or by Trace 1300 GC, ISQ Single Quadrupole MS, Thermo Fisher Scientific, Waltham, MA, USA, operating in electron impact (EI) ionization mode at 70 eV. One sample was introduced to the ion source region via a direct exposure probe (DEP). They are reported as: *m/z* (rel. intense). Elemental analyses were carried out by using a EACE 1110 CHNOS analyser.

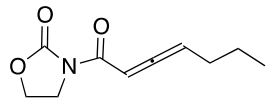
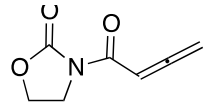
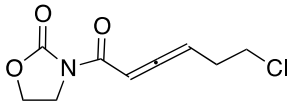
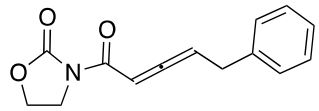
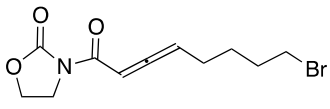
LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Elemental analyses were carried out by using an EACE 1110 CHNOS analyzer.

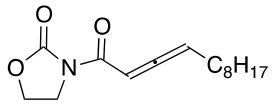
All anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Melting points were measured using open glass capillaries in a Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are calibrated by comparison with literature values (Aldrich).

General procedure for the synthesis of the allenyl-imidates (4a-f)

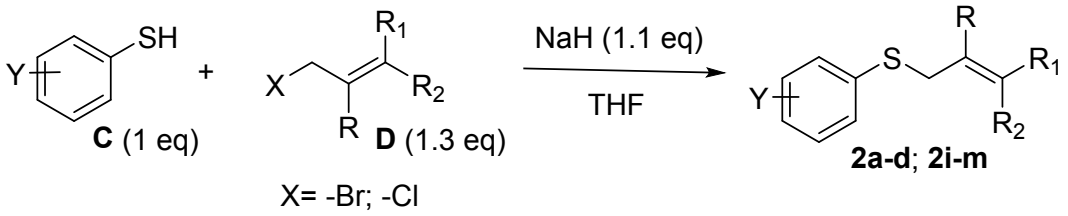


The reactions are conducted in a flame-dried three-necked round bottom flask with dropping funnel. To a solution of phosphonium bromide (**A**, 2 g, 4.25 mmol, 1 eq.)[1] in DCM (6 mL, 0.71 M) was added a solution of TEA (1.33 mL, 11.1 mmol, 2.6 eq.) in DCM (6 mL, 1.84 M) dropwise over 10 min. The mixture was then cooled at – 78 °C and a solution of the corresponding chloride (**B,** 11.06 mmol, 2.6 eq.) in DCM (12 mL, 0.92 M) was added dropwise (dropping time ca. 1 h). The reaction was stirred for 2 h at -78 °C, then concentrated under vacuum. n-Hex was added to precipitate triphenylphosphine oxide that was removed via filtration. The filtrated was evaporated and purified via flash chromatography to give the desired products **4a-f**.

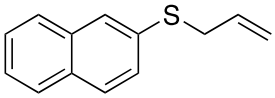
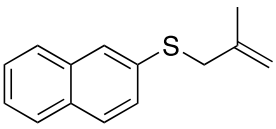
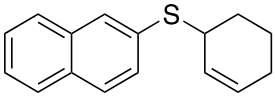
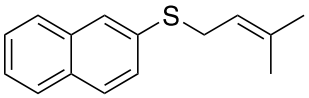
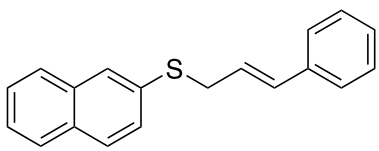
	**4a**. Yield: 65% (540 mg, *c*Hex:AcOEt: 4:1); Colorless oil **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (dt, *J* = 6.0, 2.9 Hz, 1H), 5.65 (dd, *J* = 13.2, 7.0 Hz, 1H), 4.37 (t, *J* = 8.1 Hz, 2H), 4.01 (t, *J* = 8.0 Hz, 2H), 2.08 (qd, *J* = 7.2, 2.9 Hz, 2H), 1.52 – 1.35 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.9, 164.3, 153.5, 95.5, 87.4, 62.0, 42.8, 29.3, 22.0, 13.5. ***LC-MS*** (m/z): 218.4 [M+Na$^+$]; 196.4 [M+H$^+$]. [M+H$^+$]. **Anal. Calc.** for ($C_{10}H_{13}NO_3$: 195.22): C, 61.53; H, 6.71; found: C, 61.33, H, 6.50.
	**4b**. Yield: 60% (390 mg, *c*Hex:AcOEt: 4:1); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 6.4 Hz, 1H), 5.28 (d, *J* = 6.5 Hz, 2H), 4.40 (t, *J* = 8.0 Hz, 2H), 4.05 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 217.0, 163.9, 153.4, 87.2, 79.7, 62.0, 42.8. ***LC-MS*** (m/z): 176.4 [M+Na$^+$]; 154.4 [M+H$^+$]. **Anal. Calc.** for ($C_7H_7NO_3$: 153.14): C, 54.90; H, 4.61; found: C, 54.74, H, 4.39.
	**4c**. Yield: 15% (137 mg, *c*Hex:AcOEt: 4:1); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (dt, *J* = 5.8, 2.7 Hz, 1H), 5.78 (dd, *J* = 13.3, 6.8 Hz, 1H), 4.42 (t, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 2H), 3.60 (t, *J* = 6.8 Hz, 2H), 2.62 (qd, *J* = 6.9, 2.8 Hz, 2H). ***LC-MS*** (m/z): 216 [M+H$^+$]. **Anal. Calc.** for ($C_9H_{10}ClNO_3$: 215.63): C, 50.13; H, 4.67; found: C, 50.31, H, 4.25. **Alkyne/Diene 4e** Diagnostic Signals = ^{1}H NMR (401 MHz, $CDCl_3$) δ 3.90 (d, *J* = 2.2 Hz, 2H.
	**4d**. Yield: 30% (310 mg, *c*Hex:AcOEt: 4:1); Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 7.22 (dd, *J* = 10.9, 4.2 Hz, 1H), 7.17 – 7.09 (m, 1H), 5.91 – 5.78 (m, 1H), 4.41 (t, *J* = 8.1 Hz, 2H), 4.07 (t, *J* = 8.1 Hz, 2H), 3.49 (dt, *J* = 7.6, 2.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 214.3, 164.0, 153.5, 138.5, 128.5, 128.5, 128.5, 126.6, 95.2, 87.8, 62.0, 42.8, 33.9. ***LC-MS*** (m/z): 266.4 [M+Na$^+$]; 244.4 [M+H$^+$]. **Anal. Calc.** for ($C_{14}H_{13}NO_3$: 243.26): C, 69.12; H, 5.39; found: C, 69.00, H, 5.21.
	**4e**. Yield: 35% (428 mg, *c*Hex:AcOEt: 5:1); Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12 (dt, *J* = 6.0, 2.9 Hz, 1H), 5.70 (dd, *J* = 13.2, 6.8 Hz, 1H), 4.41 (t, *J* = 8.1 Hz, 2H), 4.06 (t, *J* = 8.1 Hz, 2H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.19 (qd, *J* = 7.1, 3.0 Hz, 2H), 1.96 – 1.87 (m, 2H), 1.62 (dt, *J* = 15.5, 7.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.9, 164.2, 153.4, 95.1, 87.9, 62.0, 42.8, 33.3, 31.8, 27.0, 26.4. ***LC-MS*** (m/z): 311,0 [M+H$^+$]. **Anal. Calc.** for ($C_{11}H_{14}BrNO_3$: 288.14): C, 45.85; H, 4.90; found: C, 45.70, H, 4.69**.** **Alkyne/Diene 4e** Diagnostic Signals = **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.9, 130.6, 110.0, 62.2, 45.2, 42.6, 40.2, 32.0, 31.9, 28.0, 27.5, 26.8.

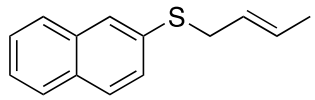
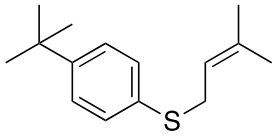
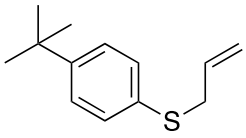
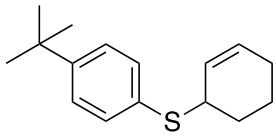
	**4f**. Yield: 44% (495 mg, *c*Hex:AcOEt: 6:1); Colorless oil **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (dt, *J* = 5.8, 2.8 Hz, 1H), 5.67 (dd, *J* = 13.3, 6.8 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 2H), 4.03 (t, *J* = 8.0 Hz, 2H), 2.11 (qd, *J* = 7.2, 2.9 Hz, 2H), 1.42 (dd, *J* = 14.6, 7.2 Hz, 2H), 1.34 – 1.15 (m, 10H), 0.84 (dd, *J* = 8.9, 4.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.9, 164.3, 153.5, 95.7, 87.4, 61.9, 42.8, 31.8, 29.2, 29.2, 28.9, 28.8, 27.3, 22.6, 14.0. ***LC-MS*** (m/z): 288.4 [M+Na$^+$]; 266.4 [M+H$^+$]. **Anal. Calc.** for ($C_{15}H_{23}BrNO_3$: 265.35): C, 67.90; H, 8.74; found: C, 67.71, H, 8.60.

General procedure for the synthesis of the thio-ethers (2a-d; 2i-m)

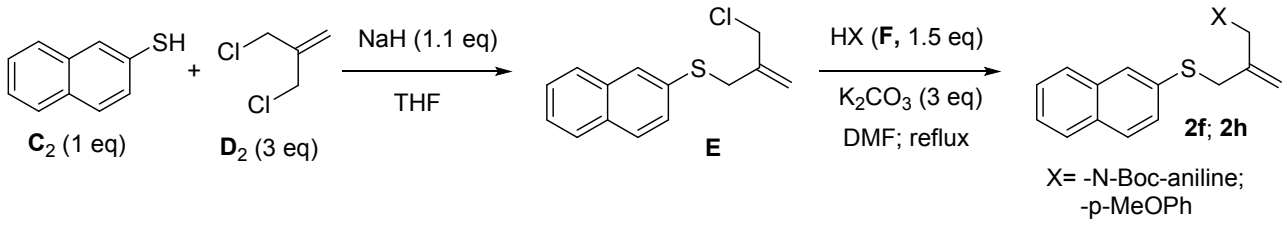


In a flame dried two-necked flask was added under nitrogen compound **C** (1,2 mmol, 1 eq.) and THF (10 mL, 0.12 M). After cooling the solution to 0 °C, NaH (1.58 mmol, 1.1 eq.) was slowly added and reaction stirred for 5 min, then compound **D** (1.87 mmol, 1.3 eq.) was added. The reaction is allowed to warm at room temperature and is stirred 10 h. After completion (monitored by TLC), water (10 mL) was added followed by extraction with Et_2O (3 x 15 mL). After draining over Na_2SO_4 the solvent was removed by rotary evaporation and the crude was purified by flash chromatography.

	**2a**. Yield: 97% (233 mg, *c*Hex); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 16.6, 7.5 Hz, 4H), 7.55 – 7.37 (m, 3H), 5.94 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.19 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.66 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.7, 133.5, 133.5, 131.9, 128.3, 127.8, 127.7, 127.7, 127.1, 126.5, 125.7, 117.8, 37.1. **GC-MS** (m/z): 200, 160, 115. **Anal. Calc.** for ($C_{13}H_{12}S$: 200.30): C, 77.95; H, 6.04; found: C, 77.69, H, 6.21.
	**2b**. Yield: 91% (234 mg, *c*Hex); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 16.6, 7.5 Hz, 4H), 7.55 – 7.37 (m, 3H), 5.94 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.19 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.66 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.7, 134.0, 133.7, 131.9, 128.2, 127.9, 127.7, 127.1, 126.4, 125.7, 114.2, 41.8, 21.3. **GC-MS** (m/z): 214, 160, 115. **Anal. Calc.** for ($C_{14}H_{14}S$: 214.33): C, 78.46; H, 6.58; found: C, 78.29, H, 6.35.
	**2c.** Yield: 96% (276 mg, *c*Hex); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 16.6, 7.5 Hz, 4H), 7.55 – 7.37 (m, 3H), 5.94 (ddt, *J* = 16.9, 10.0, 6.8 Hz, 1H), 5.19 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.66 (d, *J* = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.8, 133.5, 132.1, 130.6, 129.4, 129.0, 128.4, 127.7, 127.3, 126.9, 126.5, 125.9, 43.8, 28.9, 25.1, 19.6. **GC-MS** (m/z): 240, 160, 115. **Anal. Calc.** for ($C_{16}H_{16}S$: 240.36): C, 79.95; H, 6.71; found: C, 79.70, H, 6.43.
	**2d**. Yield: 90% (246 mg, *c*Hex); Colorless oil **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 20.5, 8.0 Hz, 4H), 7.52 – 7.34 (m, 3H), 5.38 – 5.31 (m, 1H), 3.64 (d, *J* = 7.7 Hz, 2H), 1.71 (s, 3H), 1.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.5, 134.5, 133.7, 131.7, 128.1, 127.7, 127.1, 127.0, 126.4, 125.5, 119.2, 110.0, 32.0, 25.7, 17.8. **GC-MS** (m/z): 228, 160, 115. **Anal. Calc.** for ($C_{15}H_{16}S$: 228.35): C, 78.90; H, 7.06; found: C, 78.75, H, 6.91.
	*trans*-**2i**. Yield: 89% (295 mg, *c*Hex); Yellow solid, m.p.= 94-97 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.83 – 7.71 (m, 3H), 7.47 (dt, *J* = 13.8, 7.0 Hz, 3H), 7.40 – 7.19 (m, 5H), 6.52 (d, *J* = 15.7 Hz, 1H), 6.41 – 6.23 (m, 1H), 3.83 (d, *J* = 7.1 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.7, 133.8, 133.5, 133.0, 132.0, 128.5, 128.4, 128.1, 128.0, 127.7, 127.6, 127.2, 126.5, 126.4, 125.8, 125.0, 37.0. **GC-MS** (m/z): 276, 160, 115. **Anal. Calc.** for ($C_{19}H_{16}S$: 276.40): C, 82.57; H, 5.84; found: C, 82.33, H, 5.61.

	**2j**. Yield: 93% (239 mg, *c*Hex); Colorless oil. *Z:E* ~ 75:25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 4H), 7.47 – 7.37 (m, 3H), 5.59 (dd, *J* = 11.8, 5.7 Hz, 2H), 3.63 – 3.57 (m, 2H), 1.70 – 1.62 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 133.8, 131.8, 129.2, 128.2, 127.8, 127.7, 127.5, 127.3, 127.1, 126.5, 126.0, 125.6, 36.2, 17.8. **GC-MS** (m/z): 214, 160, 115. **Anal. Calc.** for ($C_{14}H_{14}S$: 214.33): C, 78.46; H, 6.58; found: C, 78.31, H, 6.35.
	**2k**. Yield: 85% (239 mg, *c*Hex); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 5.34 – 5.27 (m, 1H), 3.51 (d, *J* = 7.7 Hz, 2H), 1.71 (s, 3H), 1.56 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.3, 136.1, 133.2, 129.9, 125.7, 119.5, 34.4, 32.6, 31.3, 25.6, 17.6. **GC-MS** (m/z): 234-151. **Anal. Calc.** for ($C_{15}H_{22}S$: 234.40): C, 76.87; H, 9.46; found: C, 76.64, H, 9.51.
	**2l**. Yield: 87% (212 mg, *c*Hex); Colorless oil **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 4H), 5.88 (ddt, *J* = 16.9, 10.0, 6.9 Hz, 1H), 5.17 – 5.02 (m, 2H), 3.58 – 3.47 (m, 2H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.4, 133.9, 132.4, 129.9, 125.8, 117.5, 37.5, 34.5, 31.3. **GC-MS** (m/z): 206, 191, 150. **Anal. Calc.** for ($C_{13}H_{18}S$: 206.35): C, 75.67; H, 8.79; found: C, 75.41, H, 8.61.
	**2m.** Yield: 86% (254 mg, *c*Hex); Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 4H), 5.78 (dt, *J* = 11.8, 10.4 Hz, 2H), 3.78 (s, 1H), 2.01 (d, *J* = 5.2 Hz, 2H), 1.90 (dd, *J* = 10.1, 6.1 Hz, 2H), 1.80 – 1.70 (m, 1H), 1.59 (dt, *J* = 7.8, 5.3 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.9, 132.3, 131.5, 130.2, 127.2, 125.9, 44.2, 34.5, 31.3, 31.3, 28.9, 25.0, 19.5. **GC-MS** (m/z): 246, 151. Anal. Calc. for ($C_{16}H_{22}S$: 246.41): C, 77.99; H, 9.00; found: C, 78.12, H, 8.75.

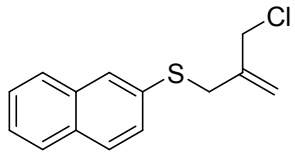
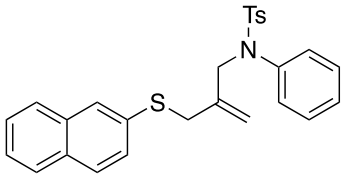
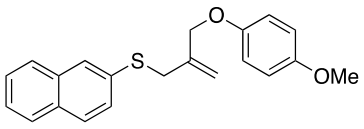
General procedure for the synthesis for the thio-ethers (2f and 2h)



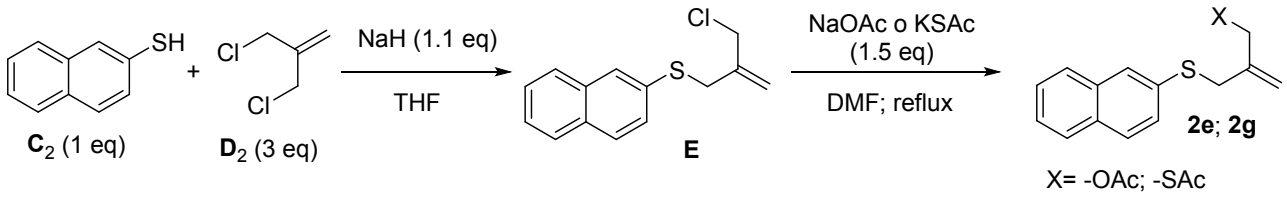
C$_2$ (1 eq) **D**$_2$ (3 eq) **E**

Compound **E** was synthetized following the same procedure as compounds **2a-i**, using 3 eq. of the corresponding allyl chloride (substrate **D**$_2$) instead of 1.3 equivalents.

In a flame dried two-necked-flask, equipped with a condenser, the derivatizing species **F** (0,6 mmol, 1.5 eq.), DMF (4 mL, 0.1 M), K_2CO_3 (1.23 mmol, 3 eq.) and the thio-allyl chloride **E** (0.41 mmol, 1 eq.) were added in a sequence. Then reaction mixture was refluxed for 12 h. When reaction completed (TLC), it was quenched with water (10 mL), extracted with Et_2O (3 x 15 mL) and the combined organic phases dried over Na_2SO_4. Solvent was removed under vacuum and the crude purified via flash chromatography to give the desired products **2f** and **2h**.

	**E.** Yield: 60% (180 mg, *c*Hex); Colorless oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.69 (m, 4H), 7.57 – 7.37 (m, 3H), 5.21 – 5.13 (m, 1H), 5.09 (d, *J* = 1.0 Hz, 1H), 4.26 (d, *J* = 0.9 Hz, 2H), 3.81 (d, *J* = 0.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.6, 133.7, 132.9, 132.0, 128.7, 128.5, 128.0, 127.7, 127.2, 126.6, 126.0, 118.1, 46.3, 37.3. **GC-MS** (m/z): 249, 160, 115. **Anal. Calc.** for ($C_{27}H_{25}O_2S_2$: 459.62): C, 70.56; H, 5.48; found: C, 70.32, H, 5.21.
	**2f**. Yield: 95% (179 mg, *c*Hex:AcOEt: 40:1); White solid, m.p. = 87-89 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 1H), 7.68 (dd, *J* = 9.3, 3.8 Hz, 3H), 7.50 – 7.38 (m, 4H), 7.34 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.11 – 6.99 (m, 2H), 4.89 (d, *J* = 1.8 Hz, 2H), 4.32 (s, 2H), 3.64 (s, 2H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 139.0, 138.8, 135.0, 133.6, 133.1, 132.0, 129. 4, 128.9, 128.8, 128.5, 128.3, 127.8, 127.6, 127.2, 126.4, 125.8, 117.8, 53.9, 37.7, 21.5. **GC-MS** (m/z): 303-130. **Anal. Calc.** for ($C_{27}H_{25}O_2S_2$: 459.62): C, 70.56; H, 5.48; found: C, 70.32, H, 5.21.
	**2h**. Yield: 80% (110 mg, *c*Hex:AcOEt: 40:1); White solid, m.p. = 96-98 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 4H), 7.49 – 7.37 (m, 3H), 6.87 – 6.81 (m, 2H), 6.81 – 6.74 (m, 2H), 5.18 (s, 1H), 5.13 (s, 1H), 4.60 (s, 2H), 3.78 (s, 2H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.0, 152.7, 140.5, 133.7, 133.3, 131.9, 128.4, 128.3, 127.9, 127.7, 127.2, 126.5, 125.8, 116.1, 115.8, 114.6, 69.9, 55.7, 37.2. **GC-MS** (m/z): 336, 177, 136, 115. **Anal. Calc.** for ($C_{21}H_{20}O_2S$: 336.45): C, 74.97; H, 5.99; found: C, 75.09, H, 5.78.

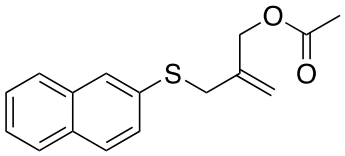
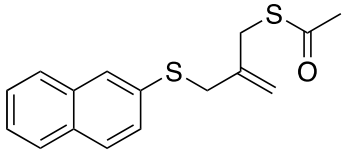
General procedure for the synthesis of the Thio-ethers (2e; 2g)



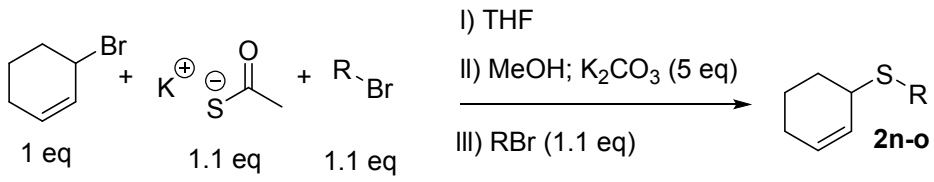
C$_2$ (1 eq) **D**$_2$ (3 eq) **E**

Compound **E** was synthetized following the same procedure as compounds **2a-i**, using 3 equivalents of the corresponding allyl chloride (substrate **D**$_2$) instead of 1.3 equivalents.

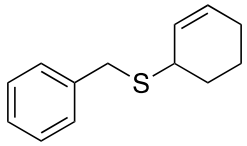
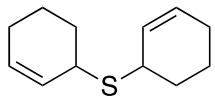
In a flame dried 2 necked-flask, furnished with a condenser, was added, under N_2, NaOAc or KSAc (0,6 mmol, 1.5 eq.), DMF (4 mL, 0.1M) and the thio-allyl chloride **E** (0.41 mmol, 1 eq). Then reaction mixture was stirred refluxing for 12 h. When reaction completed (monitored by thin layer chromatography), it was quenched with water (10 mL), extracted with Et_2O (3 x 15 mL) and the combined organic phases dried over Na_2SO_4. Solvent was removed by rotary evaporation and the crude was purified by column chromatography to give the desired product.

	**2e**. Yield: 85% (95 mg, *c*Hex:AcOEt: 60:1); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.66 (m, 4H), 7.53 – 7.35 (m, 3H), 5.09 (d, *J* = 0.7 Hz, 1H), 5.05 (d, *J* = 0.5 Hz, 1H), 4.70 (s, 2H), 3.68 (s, 2H), 2.06 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 139.2, 133.7, 133.0, 132.0, 128.8, 128.4, 128.2, 127.7, 127.2, 126.5, 125.9, 116.6, 65.3, 37.61, 20.9. **GC-MS** (m/z): 272, 211, 160, 115. **Anal. Calc.** for ($C_{16}H_{16}O_2S$: 272.36): C, 70.56; H, 5.92; found: C, 70.38, H, 5.78.
	**2g**. Yield: 82% (97 mg, *c*Hex:AcOEt: 60:1); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 16.9, 7.7 Hz, 4H), 7.44 (ddd, *J* = 15.7, 10.5, 4.9 Hz, 3H), 5.08 (s, 1H), 4.99 (s, 1H), 3.74 (s, 2H), 3.66 (s, 2H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8, 139.7, 133.7, 133.1, 132.0, 128.5, 128.3, 128.1, 127.7, 127.2, 126.5, 125.8, 117.1, 39.0, 33.0, 30.47. **GC-MS** (m/z): 288, 211, 160, 115. **Anal. Calc.** for ($C_{16}H_{16}OS_2$: 288.42): C, 66.63; H, 5.59; found: C, 66.41, H, 5.31.

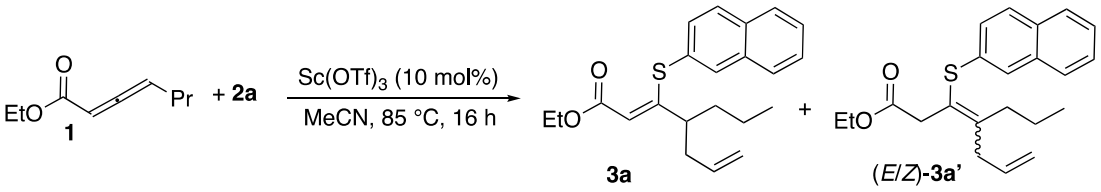
Synthesis of the thio-ethers (2n-o)



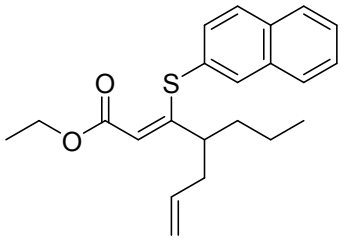
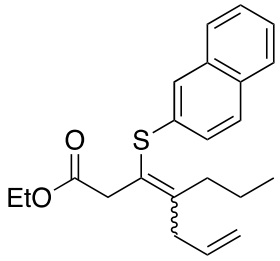
To a flame-dried two necked-flask, were added in sequence, KSAc (2.2 mmol, 1.1 eq.), THF (15 mL) and 3-bromo-cyclohexene (2 mmol, 1 eq.). The mixture was stirred at room temperature for 4 h. After disappearance of the bromide (TLC), reagent grade MeOH (15 mL) and K_2CO_3 (10 mmol, 5 eq.) were added and reaction stirred at room temperature for 3 h, then the corresponding bromide (2.2 mmol, 1.1 eq.) was added and reaction mixture stirred at room temperature for 8 h. Subsequently, the reaction was quenched with water (10 mL), extracted with Et_2O (3 x 15 mL) and the combined organic phases dried over Na_2SO_4. The volatiles were removed under vacuum and the crude purified by flash chromatography.

	**2n**. Yield: 51% (208 mg, *c*Hex); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 4H), 7.25 – 7.19 (m, 1H), 5.79 – 5.72 (m, 1H), 5.64 (ddt, *J* = 9.9, 3.8, 2.0 Hz, 1H), 3.75 (s, 2H), 3.27 (bs, 1H), 2.04 – 1.94 (m, 2H), 1.93 – 1.80 (m, 2H), 1.77 – 1.69 (m, 1H), 1.57 (dd, *J* = 6.8, 4.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 129.8, 128.8, 128.4, 127.5, 126.8, 40.0, 35.4, 29.0, 24.9, 19.8. **GC-MS** (m/z): 204. **Anal. Calc.** for ($C_{13}H_{16}S$: 204.33): C, 76.42; H, 7.89; found: C, 76.21, H, 7.59.
	**2o**. Yield: 53% (206 mg, *c*Hex); Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.84 – 5.61 (m, 4H), 3.42 (dt, *J* = 9.5, 3.3 Hz, 2H), 2.03 – 1.90 (m, 6H), 1.88 – 1.69 (m, 4H), 1.64 – 1.54 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 129.3, 129.0, 128.3, 128.2, 40.2, 40.1, 30.4, 30.1, 24.9, 24.8, 20.0, 19.7. **GC-MS** (m/z): 194, 80. **Anal. Calc.** for ($C_{12}H_{18}S$: 194.34): C, 74.17; H, 9.34; found: C, 74.01, H, 9.09.

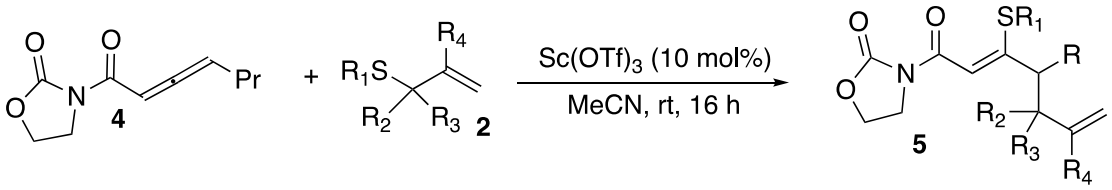
General procedure for the scandium catalyzed β-γ thio-allylation of allenoate 1



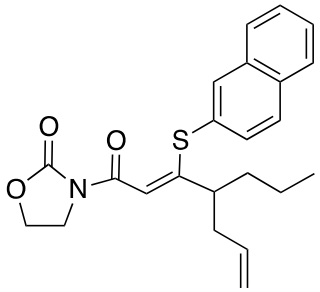
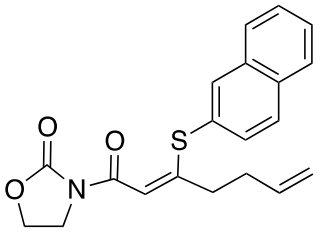
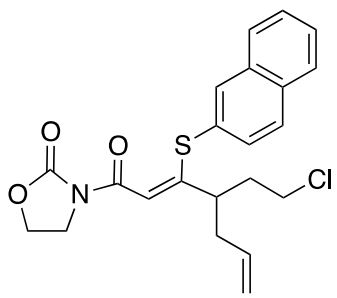
To a flame-dried Schlenk tube was added under N_2, in the following order: anhydrous MeCN (2 mL, 0.05 M), the allyl-sulfide **2a** (0.2 mmol, 2 eq.), allenoate **1** (0.1 mmol, 1 eq.) and $Sc(OTf)_3$ (0.01 mmol, 10 mol%). The reaction mixture was stirred 16 h at 85°C and after complete consumption of **1** (by TLC) the solvent was removed under vacuum and the reaction crude purified by flash-chromatography.

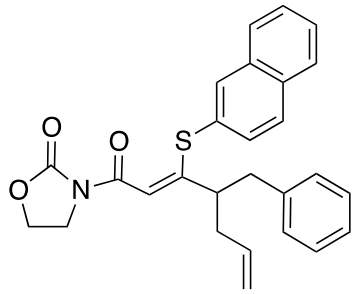
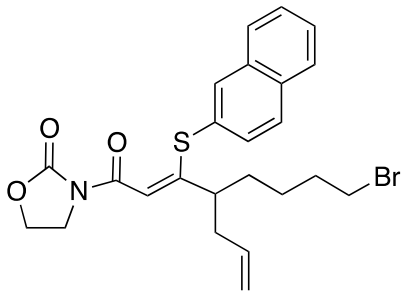
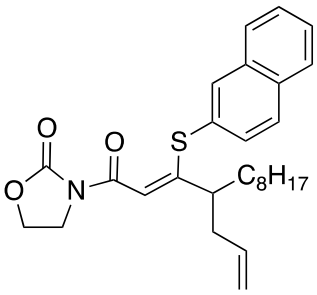
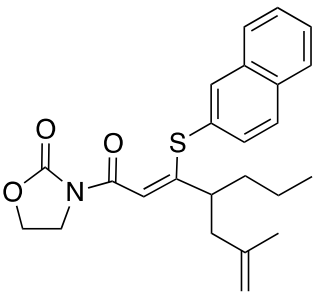
	(*Z*)-**3a**. Yield: 30% (11 mg, *c*Hex:AcOEt: 50:1); Colorless oil. *Z:E* = 98:2. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.92 – 7.73 (m, 3H), 7.58 – 7.42 (m, 3H), 5.82 (s, 1H), 5.47 (ddt, *J* = 16.9, 10.2, 7.1 Hz, 1H), 4.97 – 4.78 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.27 (dt, *J* = 13.6, 6.7 Hz, 1H), 2.18 (dt, *J* = 13.1, 6.5 Hz, 1H), 2.04 (dt, *J* = 14.1, 7.2 Hz, 1H), 1.48 – 1.25 (m, 5H), 1.23 – 1.03 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 165.2, 135.9, 135.4, 133.4, 133.2, 132.4, 128.6, 128.1, 127.8, 127.7, 127.2, 126.8, 116.8, 110.5, 60.0, 42.9, 40.0, 37.0, 20.1, 14.4, 14.1. ***GC-MS*** (m/z): 354. **Anal. Calc.** for ($C_{22}H_{26}O_2S$: 354.17): C, 74.54; H, 7.39; found: C, 74.33, H, 7.20. (Z)-**3a'** + (E)-**3a'** Diagnostic Signals: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.59 (m, 3H), 7.46 – 7.34 (m, 2H), 7.37 – 7.26 (m, 1H), 5.91 – 5.73 (m, 1H), 5.20 – 4.95 (m, 2H), 4.10 – 3.98 (m, 2H), 3.36 – 3.27 (m, 2H), 3.06 – 2.98 (m, 1H), 2.55 – 2.44 (m, 1H), 1.53 – 1.42 (m, 2H), 1.02 – 0.87 (m, 3H).
	(*Z*)-**3a'** + (*E*)-**3a'**. Yield: 25% (9 mg, *c*Hex:AcOEt: 50:1); Colorless oil. *Z:E* = 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.67 (m, 3H), 7.64 (d, *J* = 3.8 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.36 – 7.28 (m, 1H), 5.85 (tt, *J* = 16.7, 6.4 Hz, 1H), 5.21 – 5.03 (m, 2H), 4.05 (p, *J* = 7.1 Hz, 2H), 3.36 (s, 2H, (*Z*)- or (*E*)-**3a'**), 3.31 (d, *J* = 6.7 Hz, 4H, (*Z*)- or (*E*)-**3a'**), 3.04 (d, *J* = 6.2 Hz, 2H, (*Z*)- or (*E*)-**3a'**), 2.56 – 2.49 (m, 2H, (*Z*)- or (*E*)-**3a'**), 2.30 – 2.22 (m, 2H, (*Z*)- or (*E*)-**3a'**), 1.57 (ddd, *J* = 19.7, 14.8, 7.2 Hz, 2H), 1.16 (dt, *J* = 13.5, 6.8 Hz, 3H), 1.04 – 0.92 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 149.8, 135.5, 133.8, 133.4, 131.8, 128.4, 127.7, 127.1, 127.1, 127.0, 126.5, 125.6, 121.1, 116.3, 60.7, 39.0, 37.5, 35.1, 21.9, 14.3, 14.1. ***GC-MS*** (m/z): 354. **Anal. Calc.** for ($C_{22}H_{26}O_2S$: 354.17): C, 74.54; H, 7.39; found: C, 74.33, H, 7.20. Splitted Signals = **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.4, 134.9, 133.3, 127.0, 126.9, 121.3, 116.1, 60.7, 38.8, 36.7, 21.5, 14.0.

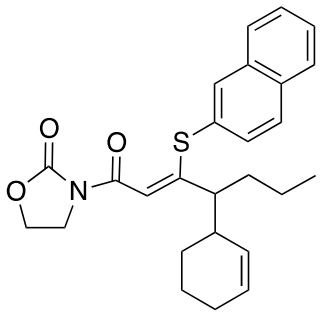
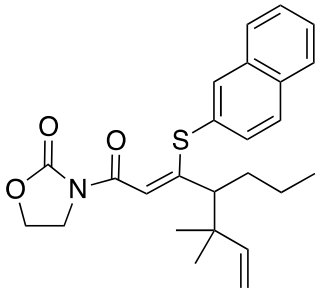
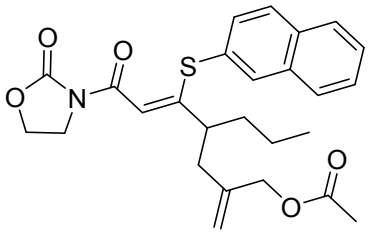
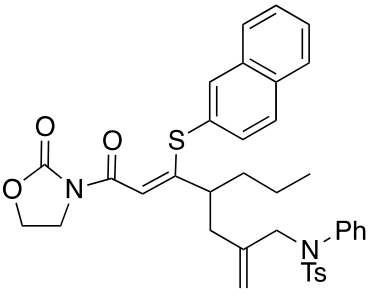
General procedure for the scandium catalyzed β-γ thio-allylation with allenyl-imidates

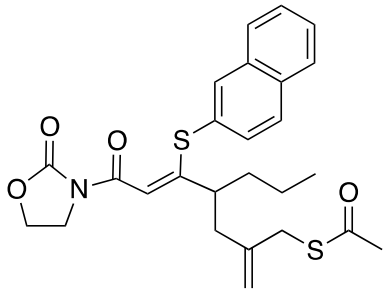
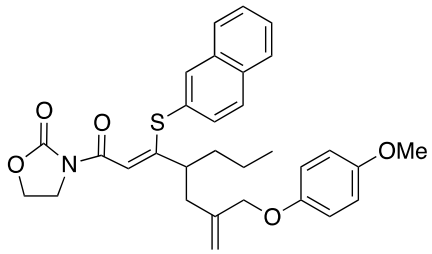
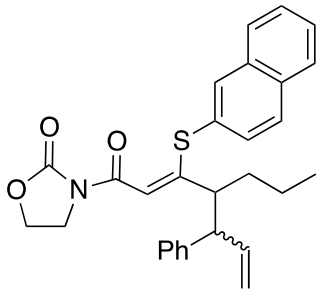
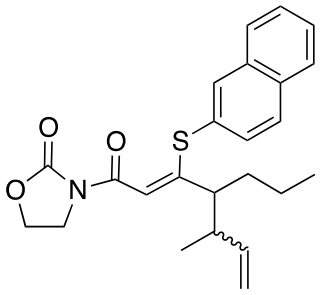


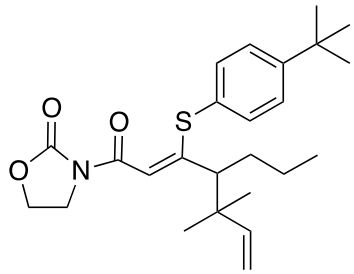
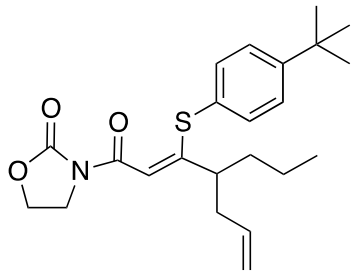
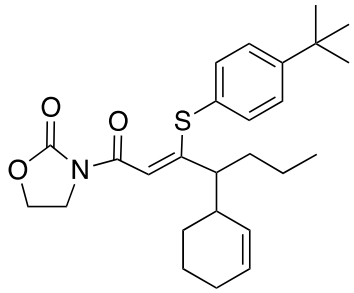
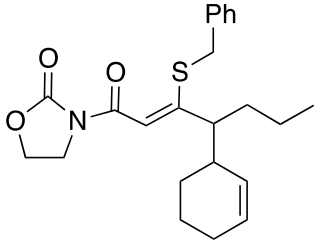
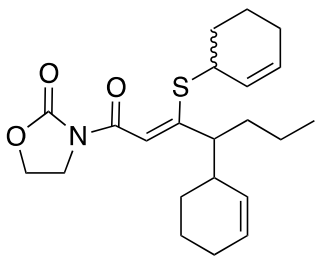
To a flame-dried Schlenk tube was added under N_2, in the following order: anhydrous MeCN (2 mL, 0.05 M), the allyl-sulfide **2** (0.2 mmol, 2 eq.), imidate **4** (0.1 mmol, 1 eq.) and $Sc(OTf)_3$ (0.01 mmol, 10 mol%). The reaction mixture was stirred 16 h at room temperature and after complete consumption of **4** (by TLC) the solvent was removed under vacuum and the reaction crude purified by flash-chromatography.

	(*Z*)-**5aa**. Yield: 91% (36 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 96:4.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.83 (dt, *J* = 9.2, 3.6 Hz, 3H), 7.60 – 7.43 (m, 3H), 7.29 (s, 1H), 5.55 – 5.42 (m, 1H), 4.98 – 4.80 (m, 2H), 4.39 (t, *J* = 8.0 Hz, 2H), 4.09 (t, *J* = 8.1 Hz, 2H), 2.35 (dt, *J* = 13.1, 6.7 Hz, 1H), 2.24 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.17 – 2.04 (m, 1H), 1.49 – 1.33 (m, 2H), 1.26 – 1.16 (m, 1H), 1.14 – 1.03 (m, 1H), 0.71 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 164.3, 153.4, 135.9, 135.4, 133.3, 133.2, 132.2, 128.7, 128.1, 127.9, 127.8, 127.3, 126.9, 116.9, 109.5, 61.8, 43.8, 42.6, 40.12 37.4, 20.1, 14.1. **LC-MS** (m/z): 418.4 [M+Na$^+$]; 396.4 [M+H$^+$]. **Anal. Calc.** for ($C_{23}H_{25}NO_3S$: 395.52): C, 69.85; H, 6.37; found: C, 69.61, H, 6.18. (*E*)-**5aa**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.48 – 6.44 (s, 1H), 5.95 – 5.79 (m, 1H), 5.20 – 5.00 (m, 2H), 4.27 – 4.14 (m, 2H), 3.92 – 3.84 (m, 2H), 2.03 – 1.94 (m, 2H), 0.98 – 0.82 (m, 2H).
	(*Z*)-**5ba**. Yield: 85% (30 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 61:39. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.1 Hz, 1H), 7.88 – 7.78 (m, 4H), 7.58 – 7.47 (m, 5H), 7.31 (s, 1H), 5.46 (ddt, *J* = 17.0, 10.5, 6.7 Hz, 1H), 4.83 – 4.69 (m, 2H), 4.40 (t, *J* = 8.0 Hz, 2H), 4.11 (t, *J* = 8.0 Hz, 2H), 2.31 (dd, *J* = 9.0, 6.2 Hz, 2H), 2.15 (dd, *J* = 14.5, 7.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 164.1, 153.4, 136.1, 135.5, 133.5, 133.4, 131.9, 128.9, 128.0, 127.9, 127.8, 127.3, 126.9, 115.8, 111.1, 61.9, 42.6, 36.8, 33.8. **LC-MS** (m/z): 376.4 [M+Na$^+$]; 354.4 [M+H$^+$]. **Anal. Calc.** for ($C_{20}H_{19}NO_3S$: 353.44): C, 67.97; H, 5.42; found: C, 67.71, H, 5.20. (*E*)-**5ba**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 6.61 (s, 1H), 5.92 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 2H), 5.18 – 4.96 (m, 3H), 4.22 (t, *J* = 8.0 Hz, 2H), 3.91 (t, *J* = 8.0 Hz, 2H), 2.99 – 2.86 (m, 2H), 2.52 – 2.41 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 162.8, 153.1, 137.3, 135.5, 133.8, 133.2, 131.4, 129.5, 127.9, 127.9, 127.4, 126.7, 126.4, 115.3, 110.0, 61.6, 42.6, 33.72, 33.4.
	(*Z*)-**5ca**. Yield: 77% (32 mg, *c*Hex:AcOEt: 8:1); Light yellow viscous oil. *Z:E* = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.84 (td, *J* = 7.5, 2.7 Hz, 3H), 7.58 – 7.48 (m, 3H), 7.24 (s, 1H), 5.45 – 5.34 (m, 1H), 4.91 (dd, *J* = 13.5, 11.9 Hz, 2H), 4.39 (t, *J* = 8.2 Hz, 2H), 4.09 (t, *J* = 8.2 Hz, 2H), 3.50 – 3.35 (m, 2H), 2.65 (dt, *J* = 9.0, 5.7 Hz, 1H), 2.29 (dt, *J* = 12.5, 6.3 Hz, 1H), 2.17 – 2.04 (m, 1H), 2.03 – 1.93 (m, 1H), 1.87 (ddd, *J* = 14.5, 7.4, 3.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 164.0, 153.5, 136.1, 134.4, 133.4, 133.3, 132.0, 128.9, 128.0, 127.8, 127.4, 127.3, 126.9, 117.8, 110.1, 61.9, 42.5, 42.0, 41.0, 39.9, 37.0. **LC-MS** (m/z): 417 [M+H$^+$]. **Anal. Calc.** for ($C_{22}H_{22}ClNO_3S$: 415.93): C, 63.53; H, 5.33; found: C, 63.35, H, 5.18. (*E*)-**5ca**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (s, 1H), 7.79 – 7.67 (m, 3H), 7.45 (s, 3H), 6.41 (s, 1H), 5.87 (m, 1H), 5.14 (dd, *J* = 39.3, 12.6 Hz, 2H),

	4.27 – 4.15 (m, 2H), 3.93 – 3.83 (m, 2H), 3.71 – 3.55 (m, 2H), 2.59 – 2.49 (m, 1H), 2.47 – 2.37 (m, 1H).
	(*Z*)-**5da**. Yield: 70% (31 mg, *c*Hex:AcOEt: 8:1); White solid, m.p. = 136-139 °C. *Z:E* = 96:4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 1H), 7.76 (dd, *J* = 20.4, 10.3 Hz, 3H), 7.59 – 7.50 (m, 2H), 7.45 (s, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.08 (m, 3H), 6.78 (d, *J* = 7.4 Hz, 2H), 5.53 (td, *J* = 17.2, 7.1 Hz, 1H), 4.94 (t, *J* = 13.7 Hz, 2H), 4.42 (t, *J* = 8.0 Hz, 2H), 4.12 (t, *J* = 8.2 Hz, 2H), 2.83 (dd, *J* = 16.0, 10.7 Hz, 1H), 2.72 – 2.58 (m, 2H), 2.29 (dt, *J* = 13.8, 6.7 Hz, 1H), 2.13 (dd, *J* = 13.6, 6.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 164.2, 153.5, 139.0, 136.1, 135.03, 133.3, 132.3, 129.2, 128.7, 128.15, 128.0, 127.6, 127.6, 127.4, 126.8, 126.2, 117.5, 109.8, 61.9, 45.7, 42.6, 41.4, 39.7. **LC-MS** (m/z): 444 [M+H$^+$]. **Anal. Calc.** for ($C_{27}H_{25}NO_3S$: 443.56): C, 73.11; H, 5.68; found: C, 73.35, H, 5.33.
	(*Z*)-**5ea**. Yield: 80% (39 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 92:8. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.84 (dt, *J* = 9.1, 3.9 Hz, 3H), 7.57 – 7.47 (m, 3H), 7.28 (s, 1H), 5.53 – 5.42 (m, 1H), 4.95 – 4.86 (m, 2H), 4.39 (t, *J* = 8.1 Hz, 2H), 4.09 (t, *J* = 8.0 Hz, 2H), 3.33 – 3.20 (m, 2H), 2.37 – 2.23 (m, 2H), 2.10 (dt, *J* = 14.1, 7.2 Hz, 1H), 1.71 – 1.60 (m, 2H), 1.52 – 1.36 (m, 2H), 1.36 – 1.27 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.2, 164.3, 153.5, 136.0, 135.1, 133.4, 133.3, 132.1, 128.9, 127.9, 127.9, 127.8, 127.4, 127.0, 117.2, 109.5, 61.9, 43.6, 42.6, 40.3, 34.2, 33.6, 32.6, 25.6. **LC-MS** (m/z): 489 [M+H$^+$]. **Anal. Calc.** for ($C_{24}H_{26}BrNO_3S$: 488.44): C, 59.02; H, 5.37; found: C, 58.82, H, 5.21. (*E*)-**5ea**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.48 (s, 1H), 5.85 (dd, *J* = 18.1, 9.1 Hz, 2H), 5.11 (dd, *J* = 42.8, 13.5 Hz, 2H), 4.21 (t, *J* = 8.2 Hz, 1H), 3.92 – 3.87 (m, 1H).
	(*Z*)-**5fa**. Yield: 92% (43 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 96:4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.90 – 7.76 (m, 3H), 7.52 (dt, *J* = 14.9, 7.2 Hz, 3H), 7.29 (s, 1H), 5.49 (ddd, *J* = 24.0, 10.2, 7.1 Hz, 1H), 4.96 – 4.85 (m, 2H), 4.39 (t, *J* = 8.0 Hz, 2H), 4.10 (t, *J* = 8.0 Hz, 2H), 2.33 (dt, *J* = 13.5, 6.8 Hz, 1H), 2.24 (dt, *J* = 13.5, 6.7 Hz, 1H), 2.10 (dt, *J* = 14.0, 7.1 Hz, 1H), 1.49 – 1.33 (m, 2H), 1.18 (dt, *J* = 62.7, 21.1 Hz, 12H), 0.85 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 164.4, 153.4, 136.0, 135.4, 133.6, 133.2, 132.2, 128.7, 128.1, 127.9, 127.8, 127.3, 126.9, 117.0, 109.3, 61.9, 43.8, 42.6, 40.2, 35.3, 31.8, 29.5, 29.4, 29.2, 27.0, 22.7, 14.10. **LC-MS** (m/z): 466 [M+H$^+$]. **Anal. Calc.** for ($C_{28}H_{35}NO_3S$: 465.65): C, 72.22; H, 7.58; found: C, 72.01, H, 7.35. (*E*)-**5fa**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.50 – 6.42 (s, 1H), 5.95 – 5.77 (m, 1H), 5.22 – 4.98 (m, 2H), 4.24 – 4.14 (m, 2H), 3.94 – 3.79 (m, 2H), 2.56 – 2.39 (m, 1H).
	(*Z*)-**5ab**. Yield: 57% (23 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 3H), 7.58 – 7.46 (m, 3H), 7.31 (s, 1H), 4.60 (s, 1H), 4.52 (s, 1H), 4.39 (t, *J* = 8.1 Hz, 2H), 4.09 (t, *J* = 8.0 Hz, 2H), 2.48 (ddd, *J* = 17.0, 8.5, 5.6 Hz, 1H), 2.27 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.03 (dd, *J* = 13.9, 8.7 Hz, 1H), 1.48 – 1.30 (m, 4H), 1.30 – 1.20 (m, 1H), 1.18 (d, *J* = 9.4 Hz, 3H), 1.13 – 1.01 (m, 1H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 164.4, 153.5, 142.5, 136.0, 133.4, 133.2, 132.2, 128.8, 128.0, 127.8, 127.7, 127.3, 126.90, 113.0, 109.3, 61.8, 44.5, 42.6, 42.1, 36.9, 21.8, 20.2, 14.1. **LC-MS** (m/z): 410 [M+H$^+$]. **Anal. Calc.** for ($C_{24}H_{27}NO_3S$: 409.54): C, 70.39; H, 6.65; found: C, 70.12, H, 6.41. (*E*)-**5ab**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 1H), 7.77 – 7.68 (m, 2H), 7.46 – 7.38 (m, 1H), 6.51 – 6.44 (s, 1H), 4.90 – 4.77 (m, 2H), 4.26 – 4.15 ((t, *J* = 8.0 Hz, 2H), 3.92 – 3.84 ((t, *J* = 7.9 Hz, 2H), 2.39 – 2.32 (m, 1H), 2.19 – 2.08 (m, 1H), 1.79 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H).

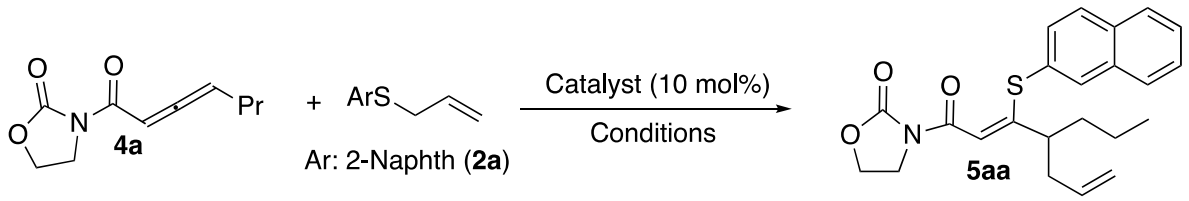
	(*Z*)-**5ac**. Yield: 81% (35 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 96:4. *Dr*: 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.91 – 7.72 (m, 3H), 7.52 (dd, *J* = 10.2, 6.2 Hz, 3H), 7.30 (s, 1H), 5.63 (d, *J* = 9.7 Hz, 1H), 5.56 (d, *J* = 10.4 Hz, 1H), 4.37 (t, *J* = 8.1 Hz, 2H), 4.06 (t, *J* = 7.8 Hz, 2H), 2.28 (d, *J* = 5.8 Hz, 2H), 1.83 (s, 2H), 1.52 – 1.30 (m, 5H), 1.30 – 1.01 (m, 3H), 0.80 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 164.2, 153.4, 136.1, 133.4, 133.2, 132.3, 128.8, 128.6, 128.3, 127.8, 127.7, 127.5, 127.3, 126.8, 109.8, 61.8, 48.4, 42.6, 40.0, 33.0, 27.6, 25.1, 21.8, 20.34, 14.32. **LC-MS** (m/z): 436 [M+H$^+$]. **Anal. Calc.** for ($C_{26}H_{29}NO_3S$: 435.58): C, 71.69; H, 6.71; found: C, 71.25, H, 6.51.
	(*Z*)-**5ad**. Yield: 76% (32 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil *Z:E* = 82:18. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.84 (dd, *J* = 14.8, 5.6 Hz, 3H), 7.53 (ddd, *J* = 6.2, 5.2, 2.5 Hz, 3H), 7.24 (s, 1H), 5.64 (dd, *J* = 17.4, 10.7 Hz, 1H), 4.86 (ddd, *J* = 18.4, 14.1, 1.1 Hz, 2H), 4.35 (t, *J* = 8.0 Hz, 2H), 4.04 (t, *J* = 8.1 Hz, 2H), 2.35 – 2.24 (m, 1H), 1.49 – 1.40 (m, 2H), 1.24 (d, *J* = 1.8 Hz, 2H), 1.07 (dd, *J* = 12.8, 6.0 Hz, 1H), 0.99 (s, 3H), 0.95 (d, *J* = 7.1 Hz, 1H), 0.91 (s, 3H), 0.81 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 153.4, 147.2, 146.1, 136.7, 136.1, 133.3, 133.2, 132.8, 131.9, 128.5, 127.9, 127.7, 127.3, 126.8, 112.2, 61.8, 52.4, 42.5, 40.8, 34.4, 26.6, 23.5, 21.5, 14.6. **LC-MS** (m/z): 424 [M+H$^+$]. **Anal. Calc.** for ($C_{25}H_{29}NO_3S$: 423.57): C, 70.89; H, 6.90; found: C, 70.59, H, 6.69. (*E*)-**5ad**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.53 (s, 1H), 6.10 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.12 – 4.99 (m, 2H), 4.19 (t, *J* = 8.2 Hz, 3H), 3.84 (t, J = 8.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 129.4, 128.6, 127.9, 127.9, 127.2, 126.5, 114.2, 111.4, 61.5, 49.1, 42.6, 31.4, 29.7, 26.1, 24.6, 21.1, 14.2.
	(*Z*)-**5ae**. Yield: 60% (28 mg, *c*Hex:AcOEt: 6:1); Colorless viscous oil *Z:E* = 67:33. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.83 (td, *J* = 8.4, 2.3 Hz, 3H), 7.61 – 7.45 (m, 3H), 7.31 (s, 1H), 4.95 (s, 1H), 4.74 (s, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 4.21 – 3.99 (m, 4H), 2.57 – 2.44 (m, 1H), 2.35 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.14 – 2.06 (m, 1H), 1.86 (s, 3H), 1.49 – 1.32 (m, 2H), 1.21 – 1.03 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 169.6, 164.3, 153.4, 140.6, 135.9, 133.4, 133.4, 132.0, 128.9, 127.8, 127.8, 127.4, 127.0, 115.4, 109.6, 94.2, 66.6, 61.9, 42.6, 42.4, 39.6, 37.5, 20.7, 20.1, 14.0. **LC-MS** (m/z): 468 [M+H$^+$]. **Anal. Calc.** for ($C_{26}H_{29}NO_5S$: 467.58): C, 66.79; H, 6.25; found: C, 66.41, H, 6.40. (*E*)-**5ae**. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.47 (s, 1H), 2.89 – 2.74 (m, 1H), 2.15 (s, 3H), 1.01 – 0.80 (t, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 61.6, 34.4, 30.5, 29.7, 22.4, 13.8.
	(*Z*)-**5af**. Yield: 60% (39 mg, *c*Hex:AcOEt: 6:1); Light yellow viscous oil *Z:E* = 75:25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.85 – 7.72 (m, 3H), 7.58 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.25 (s, 2H), 7.24 (s, 1H), 7.21 – 7.08 (m, 5H), 6.81 – 6.73 (m, 2H), 4.82 (s, 1H), 4.57 (s, 1H), 4.35 (ddd, *J* = 17.3, 9.8, 6.2 Hz, 2H), 4.07 – 3.96 (m, 2H), 3.71 (dd, *J* = 37.6, 14.9 Hz, 2H), 2.51 – 2.44 (m, 1H), 2.43 (s, 3H), 2.17 (ddd, *J* = 31.3, 14.5, 7.1 Hz, 2H), 1.39 (ddd, *J* = 10.7, 10.1, 6.5 Hz, 2H), 1.32 – 1.20 (m, 1H), 1.15 (ddd, *J* = 12.7, 11.6, 6.4 Hz, 1H), 1.09 – 0.96 (m, 1H), 0.68 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 164.2, 153.4, 143.1, 140.5, 139.0, 135.7, 135.25, 133.4, 133.1, 132.1, 129.3, 128.7, 128.6, 128.5, 128.3, 127.88, 127.74, 127.7, 127.6, 127.2, 126.8, 116.5, 110.3, 61.8, 55.0, 42.6, 42.5, 39.4, 37.7, 21.5, 20.1, 14.0. **LC-MS** (m/z): 655 [M+H$^+$]. **Anal. Calc.** for ($C_{37}H_{38}N_2O_5S_2$:

	654.84): C, 67.86; H, 5.85; found: C, 67.59, H, 5.65.
	(*Z*)-**5ag**. Yield: 56% (27 mg, *c*Hex:AcOEt: 7:1); Colorless viscous oil *Z:E* = 85:15. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 (dt, *J* = 7.7, 3.8 Hz, 3H), 7.59 – 7.47 (m, 3H), 7.29 (s, 1H), 4.93 (s, 1H), 4.64 (s, 1H), 4.38 (t, *J* = 8.1 Hz, 2H), 4.08 (t, *J* = 8.2 Hz, 2H), 3.13 (q, *J* = 14.0 Hz, 2H), 2.49 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.34 (dd, *J* = 14.5, 6.5 Hz, 1H), 2.21 (s, 3H), 2.10 (dd, *J* = 14.5, 7.8 Hz, 1H), 1.48 – 1.34 (m, 2H), 1.22 – 1.06 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.7, 169.3, 164.2, 153.4, 141.2, 135.9, 133.4, 133.2, 132.1, 128.9, 127.93, 127.9, 127.8, 127.3, 126.87, 116.1, 109.8, 61.8, 42.6, 42.4, 41.2, 37.4, 34.4, 30.3, 20.09, 14.01. **LC-MS** (m/z): 506 [M+Na$^+$]; 484 [M+H$^+$]. **Anal. Calc.** for ($C_{26}H_{29}NO_4S_2$: 483.64): C, 64.57; H, 6.04; found: C, 64.31, H, 5.88.
	(*Z*)-**5ah**.Yield: 57% (30 mg, *c*Hex:AcOEt: 7:1); Light yellow viscous oil. *Z:E* = 82:18. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.76 (dd, *J* = 17.4, 7.8 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.44 (m, 3H), 7.34 (s, 1H), 6.70 (d, *J* = 9.0 Hz, 2H), 6.50 (t, *J* = 6.4 Hz, 2H), 5.09 (s, 1H), 4.83 (s, 1H), 4.38 (t, *J* = 8.1 Hz, 2H), 4.07 (t, *J* = 8.1 Hz, 2H), 3.88 (q, *J* = 12.6 Hz, 2H), 3.75 (s, 3H), 2.57 – 2.50 (m, 1H), 2.43 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.20 (dd, *J* = 14.1, 7.9 Hz, 1H), 1.51 – 1.37 (m, 2H), 1.35 – 1.02 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 164.3, 153.7, 153.4, 152.6, 141.8, 135.9, 133.3, 133.2, 132.2, 128.8, 127.9, 127.9, 127.8, 127.3, 126.9, 115.3, 114.9, 114.5, 109.44, 70.31, 61.82, 55.71, 42.56, 42.30, 39.8, 37.5, 20.1, 14.0. **LC-MS** (m/z): 532 [M+H$^+$]. **Anal. Calc.** for ($C_{31}H_{33}NO_5S$: 531.67): C, 70.03; H, 6.26; found: C, 69.80, H, 6.01.
	(*Z*)-**5ai**. Yield: 95% (45 mg, *c*Hex:AcOEt: 8:1); White solid (m.p. = 145-148 °C) *Z:E* = 92:8. *Dr* (*Z*): 84:16. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.92 – 7.77 (m, 3H), 7.61 – 7.48 (m, 3H), 7.31 (s, 1H), 5.99 (ddd, *J* = 17.0, 10.1, 8.3 Hz, 1H), 5.03 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 17.0 Hz, 1H), 4.38 (dd, *J* = 11.6, 5.0 Hz, 2H), 4.13 – 4.02 (m, 2H), 3.30 (t, *J* = 8.8 Hz, 1H), 2.72 (td, *J* = 9.9, 3.8 Hz, 1H), 1.37 – 1.16 (m, 2H), 1.07 – 0.89 (m, 2H), 0.65 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 164.2, 153.4, 142.0, 139.3, 136.7, 133.3, 133.3, 132.7, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 127.41, 126.9, 126.4, 116.4, 110.2, 61.8, 56.6, 48.9, 42.6, 37.0, 20.2, 14.3. ***LC-MS*** (m/z): 495.4 [M+Na$^+$]; 472.4 [M+H$^+$]. (*Z*)-**5ai** diastereo-isomers. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 8.02 (s, 1H), 7.35 (d, *J* = 10.8 Hz, 2H), 7.17 – 7.10 (m, 6H), 6.85 – 6.77 (m, 4H), 5.87 – 5.73 (m, 3H), 3.54 – 3.45 (m, 2H), 2.25 – 2.08 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 142.4, 138.1, 135.8, 133.2, 132.3, 128.5, 127.9, 127.7, 127.2, 126.8, 116.9, 54.8, 49.3, 42.5, 34.7, 19.7, 14.3.
	(*Z*)-**5aj**. Yield: 76% (31 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 75:25. *Dr* (*Z*): 82:18**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.82 (dd, *J* = 8.4, 4.7 Hz, 3H), 7.56 – 7.50 (m, 3H), 7.24 (s, 1H), 5.38 (ddd, *J* = 17.0, 10.4, 6.4 Hz, 1H), 4.80 (d, *J* = 10.3 Hz, 1H), 4.73 (d, *J* = 17.2 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 4.10 (t, *J* = 8.0 Hz, 2H), 2.40 – 2.30 (m, 2H), 1.50 – 1.29 (m, 4H), 1.15 – 1.00 (m, 2H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.79 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 164.1, 153.4, 141.7, 136.2, 133.4, 133.20, 132.4, 128.7, 128.1, 127.9, 127.7, 127.3, 126.8, 114.2, 110.3, 61.8, 48.5, 42.6, 41.1, 32.5, 20.3, 14.6, 14.3. **GC-MS** (m/z): 409-354-267-163-115. (*Z*)-**5aj** diastereo-isomers. Diagnostic Signals = **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.01 (s, 1H), 7.86 (d, *J* = 2.7 Hz, 2H), 7.49 (d, *J* = 1.6 Hz, 2H),

	7.27 (s, 1H), 7.23 (s, 1H), 4.95 – 4.85 (m, 2H), 2.31 – 2.24 (m, 2H), 2.21 – 2.13 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.0, 136.4, 126.9, 48.9, 35.2, 29.7, 20.3, 18.9, 14.4, 14.1.
	(*Z*)-**5ak**. Yield: 65% (28 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil *Z:E* = 72:28. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 4H), 7.22 (s, 1H), 5.64 (dd, *J* = 17.4, 10.7 Hz, 1H), 4.91 (dd, *J* = 10.7, 1.1 Hz, 1H), 4.79 (dd, *J* = 17.4, 1.0 Hz, 1H), 4.38 (t, *J* = 8.1 Hz, 2H), 4.08 (t, *J* = 8.0 Hz, 2H), 2.28 (dd, *J* = 10.3, 4.1 Hz, 1H), 1.50 – 1.36 (m, 3H), 1.32 (s, 9H), 1.09 – 1.00 (m, 1H), 0.97 (s, 3H), 0.89 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 153.4, 153.1, 146.2, 136.7, 127.5, 125.9, 112.1, 109.7, 61.77, 51.5, 42.6, 40.6, 34.8, 34.7, 31.2, 26.6, 23.4, 21.4, 14.6. **LC-MS** (m/z): 452.4 [M+Na$^+$]; 430.4 [M+H$^+$]. **Anal. Calc.** for ($C_{25}H_{35}NO_3S$: 429.62): C, 69.89; H, 8.21; found: C, 69.56, H, 8.01.
	(*Z*)-**5al**. Yield: 90% (36 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 90:10. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 4H), 7.24 (s, 1H), 5.52 – 5.41 (m, 1H), 4.89 (t, *J* = 12.7 Hz, 2H), 4.39 (t, *J* = 8.1 Hz, 2H), 4.10 (t, *J* = 8.0 Hz, 2H), 2.37 – 2.28 (m, 1H), 2.19 (dt, *J* = 13.7, 6.7 Hz, 1H), 2.08 (dt, *J* = 14.3, 7.2 Hz, 1H), 1.40 (dd, *J* = 15.4, 8.0 Hz, 2H), 1.31 (s, 9H), 1.25 – 1.02 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 164.4, 153.5, 153.1, 136.0, 135.5, 127.0, 126.2, 116.8, 108.6, 61.8, 43.1, 42.6, 40.2, 37.2, 34.8, 31.2, 20.1, 13.9. **LC-MS** (m/z): 402 [M+H$^+$]. **Anal. Calc.** for ($C_{23}H_{31}NO_3S$: 401.57): C, 68.79; H, 7.78; found: C, 68.51, H, 7.60.
	(*Z*)-**5am**. Yield: 80% (35 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil. *Z:E* = 95:5. *Dr*(*Z*): 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (q, *J* = 8.4 Hz, 4H), 7.26 (s, 1H), 5.66 (dd, *J* = 10.3, 2.6 Hz, 1H), 5.57 (d, *J* = 11.7 Hz, 1H), 4.39 (t, *J* = 8.0 Hz, 2H), 4.09 (t, *J* = 7.9 Hz, 2H), 2.27 (dd, *J* = 10.1, 5.0 Hz, 1H), 2.19 (s, 1H), 1.85 (d, *J* = 2.1 Hz, 2H), 1.51 – 1.33 (m, 5H), 1.35 – 1.28 (m, 9H), 1.12 (ddd, *J* = 14.2, 9.6, 5.0 Hz, 3H), 0.80 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 164.2, 153.4, 153.0, 136.1, 128.6, 127.5, 127.2, 126.1, 109.0, 61.8, 47.7, 42.6, 39.9, 34.8, 32.7, 31.2, 27.5, 25.1, 21.9, 20.3, 14.3. **LC-MS** (m/z): 442 [M+H$^+$]. **Anal. Calc.** for ($C_{26}H_{35}NO_3S$: 441.63): C, 70.71; H, 7.99; found: C, 70.45, H, 7.65.
	(*Z*)-**5an**. Yield: 85% (34 mg, *c*Hex:AcOEt: 8:1); Colorless oil. *Z:E* = 95:5. *Dr* (*Z*): 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.13 (s, 1H), 5.79 (dd, *J* = 10.2, 2.1 Hz, 1H), 5.73 – 5.67 (m, 1H), 4.36 (t, *J* = 8.1 Hz, 2H), 4.07 (s, 2H), 4.02 (t, *J* = 8.1 Hz, 2H), 2.24 (bs, 1H), 1.94 (bs, 2H), 1.67 (ddd, *J* = 14.0, 9.3, 5.4 Hz, 3H), 1.55 – 1.39 (m, 2H), 1.39 – 1.10 (m, 4H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 162.6, 153.6, 135.2, 129.2, 129.1, 128.5, 128.4, 127.5, 110.3, 61.6, 46.3, 42.8, 39.4, 36.4, 33.9, 27.0, 25.4, 21.1, 20.5, 14.2. **LC-MS** (m/z): 400 [M+H$^+$]. **Anal. Calc.** for ($C_{23}H_{29}NO_3S$: 399.55): C, 69.14; H, 7.32; found: C, 68.89, H, 7.20.
	(*Z*)-**5ao**. Yield: 85% (33 mg, *c*Hex:AcOEt: 8:1); Colorless viscous oil *Z:E* = 95:5. *Dr*(*Z*): 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 5.88 (d, *J* = 9.8 Hz, 1H), 5.79 (d, *J* = 10.3 Hz, 1H), 5.71 (t, *J* = 10.6 Hz, 2H), 4.35 (t, *J* = 8.0 Hz, 2H), 4.02 (t, *J* = 8.0 Hz, 2H), 3.95 (s, 1H), 2.23 (s, 1H), 2.03 (m, 3H), 1.94 (m, 3H), 1.85 – 1.75 (m, 1H), 1.75 – 1.60 (m, 4H), 1.59 – 1.07 (m, 6H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 162.7, 153.6, 131.67, 129.3, 128.3, 125.0, 110.0, 61.2, 46.3, 42.8, 40.4, 39.4, 33.94, 27.65, 26.9, 26.8, 25.4, 24.9, 21.1, 20.5, 19.5, 14.3. **LC-MS** (m/z): 390 [M+H$^+$]. **Anal.**

	Calc. for ($C_{22}H_{31}NO_3S$: 389.55): C, 67.83; H, 8.02; found: C, 67.59, H, 7.90. Diagnostic Signals = **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.6, 129.2, 128.3, 109.9, 40.3, 39.3, 33.9, 27.6, 20.4, 19.5.

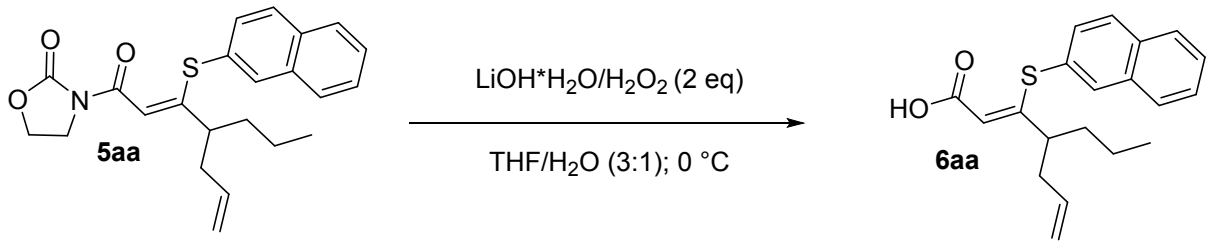
Screening of reaction conditions.[a]



Run	Catalyst	4a/2a	Solvent	T (°C)/ t (h)	*Z*:*E*[b]	Yield (%) 5aa[c]
1	$Al(OTf)_3$	1/2	CH_3CN	25/14	72:28	36
2	$Fe(OTf)_3$	1/2	CH_3CN	25/14	60:40	28
3	$Cu(OTf)_2$	1/2	CH_3CN	25/14	62:38	51
4	$Bi(OTf)_3$	1/2	CH_3CN	25/14	53:47	63
5	$Sm(OTf)_3$	1/2	CH_3CN	25/14	--	NR
6	$Zn(OTf)_2$	1/2	CH_3CN	25/14	--	NR
7	AgOTf	1/2	CH_3CN	25/14	--	NR
8	$Ni(OTf)_2$	1/2	CH_3CN	25/14	--	NR
9	$Sc(OTf)_3$	1/1.5	CH_3CN	25/1	93:7	70
10	$Sc(OTf)_3$	1/2	CH_3CN	25/14	93:7	80
11	$Sc(OTf)_3$	2/1	CH_3CN	24/48	92/8	81
12	$Sc(OTf)_3$	1/1.5	CH_3CN	0/48	93/7	76
13[d]	$Sc(OTf)_3$	1/2	CH_3CN	25/5	93/7	82
14[e]	$Sc(OTf)_3$	1/2	CH_3CN	25/14	94/6	91
15	$Sc(OTf)_3$	1/2	Et_2O	25/3	64/36	73
16	$Sc(OTf)_3$	1/2	THF	25/3	--	NR
17	$Sc(OTf)_3$	1/2	DCM	25/14	82:18	86

[a] All reactions were carried out under anhydrous conditions and dry solvents on 0.1 mmol of **4a** (0.1 M). [b] Determined by LC-MS on the reaction crude. [c] After flash chromatography. [d] 0.2 M. [e] 0.05 M. NR: no reaction.

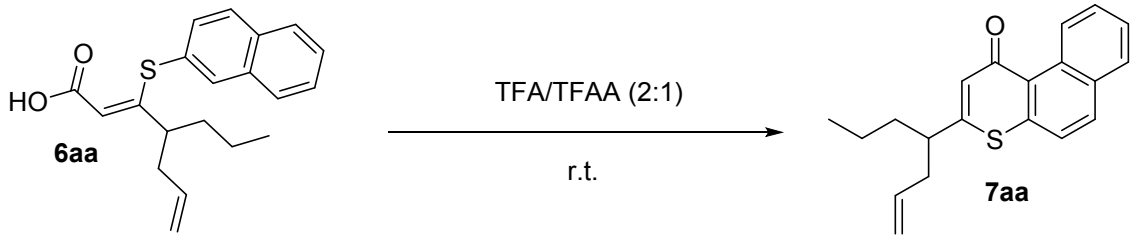
Synthetic protocol for the cleavage of the oxazolidinone unit (6aa).



To a solution of $LiOH{\cdot}H_2O/H_2O_2$ (0.56 mmol, 2 eq) in THF/H_2O (3:1, 4 mL) was added compound **5aa** (0.28 mmol, 1 eq) at 0°C. The reaction mixture was stirred 4h at 0°C for 4h. After the consumption of compound **5aa** (monitored by TLC) the reaction was quenched with HCl 2M (3 mL) extracted with DCM and the combined organic phases dried over Na_2SO_4. The volatiles were removed under vacuum and the crude purified by flash chromatography.

(*Z*)-**6aa**: Yield: 61% (56 mg, *c*Hex:AcOEt: 3:1); White solid, m.p. 153-155 °C. *Z:E* = 99:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.83 (dt, *J* = 9.4, 3.7 Hz, 3H), 7.63 – 7.43 (m, 3H), 5.86 (s, 1H), 5.56 – 5.40 (m, 1H), 4.90 (ddd, *J* = 18.6, 13.6, 1.7 Hz, 2H), 2.39 – 2.25 (m, 1H), 2.19 (dt, *J* = 13.5, 6.7 Hz, 1H), 2.06 (dt, *J* = 14.2, 7.2 Hz, 1H), 1.52 – 1.29 (m, 2H), 1.23 – 1.13 (m, 1H), 1.15 – 1.00 (m, 1H), 0.72 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 168.8, 136.1, 135.2, 133.4, 133.3, 132.3, 128.7, 127.9, 127.8, 127.7, 127.3, 126.8, 117.0, 109.5, 43.1, 40.0, 37.3, 20.1, 14.0. **LC-MS** (m/z): 349 [M+Na$^+$]; 327 [M+H$^+$]. **Anal. Calc.** for ($C_{20}H_{22}O_2S$: 326.45): C, 73.58; H, 6.79; found: C, 73.34, H, 6.55.

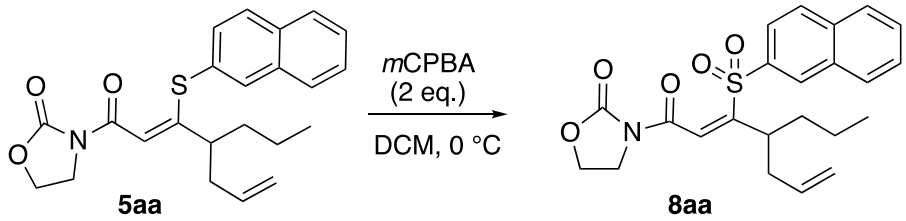
Synthetic protocol for the synthesis of the thio-flavone 7aa.



In a flame-dried Schleck tube, to a solution of TFA/TFAA (2:1, 1.5 mL) was added compound **6aa** (70 mg, 0.215 mmol). The reaction mixture was stirred at room temperature for 1h. The reaction mixture was then concentrated under reduced pressure and purified by flash chromatography.

7aa: Yield: 94% (62 mg, *c*Hex:AcOEt: 40:1); Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.14 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.71 (ddd, *J* = 8.6, 7.0, 1.4 Hz, 1H), 7.65 – 7.54 (m, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 7.00 (s, 1H), 5.72 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.12 – 4.94 (m, 2H), 2.77 – 2.57 (m, 1H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.69 (dd, *J* = 15.1, 7.8 Hz, 2H), 1.34 (tt, *J* = 14.0, 6.9 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.9, 155.1, 140.4, 135.0, 132.6, 132.5, 133.3, 128.8, 128.2, 127.4, 127.3, 127.0, 126.3, 123.7, 117.4, 47.3, 40.2, 37.1, 20.4, 13.9. **LC-MS** (m/z): 309 [M+H$^+$]. **Anal. Calc.** for ($C_{20}H_{22}OS$: 308.44): C, 77.88; H, 6.54; found: C, 77.61, H, 6.30.

Synthetic protocol for the synthesis of the sulfone 8aa.

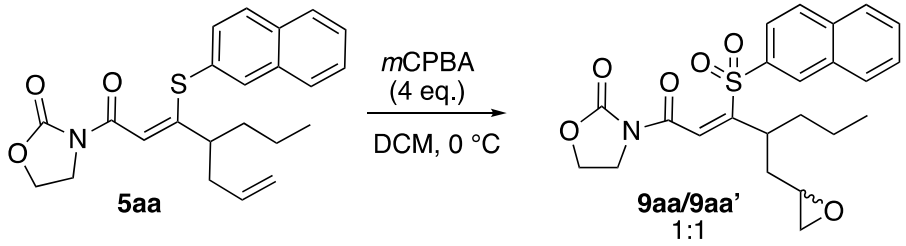


5aa **8aa**

In a flame-dried Schlenk tube, to a solution of compound **5aa** (60 mg, 0.15 mmol, 1 eq) in DCM (2 mL, 0,075 M) was added at 0°C *m*CPBA (52 mg, 0.3 mmol, 2 eq.). The reaction mixture was stirred at 0°C for 2h. Then it was extracted with DCM, washed with $NaHCO_3$ and the combined organic phases dried over Na_2SO_4. The volatiles were removed under vacuum and the crude purified by flash chromatography.

(*Z*)-**8aa:** Yield: 88% (56 mg, *c*Hex:AcOEt: 3:1); White solid, m.p = 65-67 °C. *Z:E* = 92:8. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.04 – 7.95 (m, 3H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.58 (m, 2H), 6.59 (s, 1H), 5.44 (ddd, *J* = 24.3, 10.0, 7.2 Hz, 1H), 4.78 (dd, *J* = 21.9, 13.6 Hz, 2H), 4.51 (t, *J* = 8.0 Hz, 2H), 4.15 (t, *J* = 8.1 Hz, 2H), 2.56 – 2.46 (m, 1H), 2.21 – 2.04 (m, 2H), 1.50 – 1.34 (m, 2H), 1.15 (dd, *J* = 16.6, 6.7 Hz, 1H), 1.03 – 0.91 (m, 1H), 0.64 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 153.6, 148.0, 135.4, 134.9, 134.7, 132.0, 130.9, 130.4, 129.5, 129.5, 129.4, 127.9, 127.6, 123.4, 117.4, 63.1, 42.1, 39.6, 39.4, 36.6, 19.7, 13.8. **LC-MS** (m/z): 428 [M+H$^+$]. **Anal. Calc.** for ($C_{23}H_{25}NO_5S$: 427.52): C, 64.62; H, 5.89; found: C, 64.39, H, 5.71.

Synthetic protocol for the synthesis of epoxide 9aa.



5aa **9aa/9aa'** 1:1

Stereoisomers **9aa** and **9aa'** were synthetized following the same procedure as compound **8aa** by using 4 eq. of *m*CPBA instead of 2 eq.

(*Z*)-**9aa**/**9aa'**: Yield: 75% (50 mg, *c*Hex:AcOEt: 2:1); Colorless viscous oil. *Z:E* = 98:2. *Dr* (*Z*): 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 6.5 Hz, 2H), 8.07 – 7.93 (m, 6H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.70 – 7.53 (m, 4H), 6.68 (s, 1H, **9aa** or **9aa'**), 6.63 (s, 1H, **9aa** or **9aa'**), 4.51 (t, *J* = 8.1 Hz, 4H), 4.14 (t, *J* = 7.9 Hz, 4H), 2.92 – 2.78 (m, 1H, **9aa** or **9aa'**), 2.78 – 2.58 (m, 3H, **9aa** or **9aa'**), 2.53 (t, *J* = 4.4 Hz, 1H, **9aa** or **9aa'**), 2.46 – 2.38 (m, 1H, **9aa** or **9aa'**), 2.31 (dd, *J* = 4.9, 2.6 Hz, 1H, **9aa** or **9aa'**), 2.21 (dd, *J* = 5.0, 2.6 Hz, 1H, **9aa** or **9aa'**), 1.83 – 1.72 (m, 1H), 1.65 (dt, *J* = 14.6, 7.3 Hz, 2H), 1.60 – 1.32 (m, 3H), 1.22 (dd, *J* = 16.5, 9.3 Hz, 2H), 1.16 – 0.98 (m, 2H), 0.97 – 0.78 (m, 2H), 0.57 (td, *J* = 13.5, 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 153.62, 148.4, 147.6, 135.4, 134.7, 132.0, 131.0, 130.8, 129.6, 129.5, 127.9, 127.7, 123.3, 63.1, 50.6, 47.2, 42.1, 39.3, 38.0, 37.4, 19.7, 13.7. **LC-MS** (m/z): 444.2 [M+H$^+$]. Splitted Signals = **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 135.3, 134.7, 130.9, 130.6, 129.6, 127.9, 123.2, 63.1, 49.5, 47.1, 42.0, 37.9, 36.9.

Crystallographic data collection and structure determination for *Z*-5ai and 6aa. The X-ray intensity data were measured on a Bruker Apex III CCD diffractometer. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. A full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART[2] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program,[2] and an empirical absorption correction was applied using SADABS.[3] The structures were solved by direct methods (SIR 2014)[4] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL)[5] using anisotropic thermal parameters for all non-hydrogen atoms. The aromatic and methine hydrogen atoms were placed in calculated positions, refined with isotropic thermal parameters *U(H)* = 1.2 *Ueq*(C) and allowed to ride on their carrier carbons. The naphthyl rings in both structures showed disorder over two sets of atomic sites with occupancies of 0.51 and 0.49 for ***Z*-5ai** and 0.66 and 0.34 for **6aa** which are related by a 180° rotation of the naphthyl rings about the C-S bond. In **6aa** also disorder between the allyl and propyl ends was detected. Crystal data and details of data collections for compounds ***Z*-5ai and 6aa** are reported in **Table S2**. Molecular drawings were generated using Mercury.[6] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers CCDC 1920581-1920582 (***Z*-5ai** and **6aa,** respectively). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures.

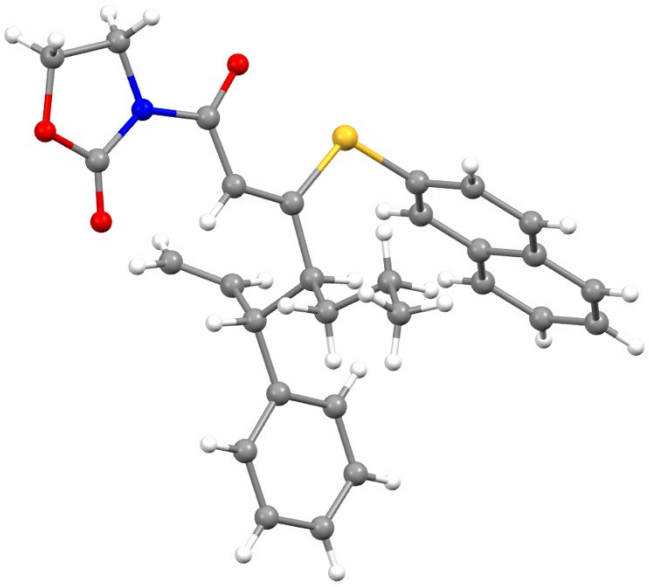


Figure S1. Crystal structure of (*Z*)-**5ai.**

Table S2. Crystal data and structure refinement for compounds ***Z*-5ai and 6aa**.

Compound	***Z*-5ai**	**6aa**
Formula	$C_{29}H_{29}NO_3S$	$C_{20}H_{22}O_2S$
Fw	471.59	326.43
T, K	296	100
λ, Å	0.71073	0.71073
Crystal symmetry	Monoclinic	Triclinic
Space group	*P2₁/n*	*P-1*
a, Å	15.601(3)	9.771(2)
b, Å	8.8913(17)	9.830(5)
c, Å	20.126(4)	11.268(3)
α	90	112.31(3)
β	108.802(18)	98.03(2)
γ	90	110.42(2)
Cell volume, Å^3	2642.8(9)	891.0(6)
Z	4	2
D_C, Mg m^{-3}	1.185	1.217
μ(Mo-K_α), mm^{-1}	0.151	0.189
F(000)	1000	348
Crystal size/ mm	0.20 x 0.20 x 0.15	0.35 x 0.30 x 0.20
θ limits, °	1.447 - 25.500	2.342 - 28.413
Reflections collected	10326	15707
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	4557 [R(int) = 0.1342]	4408 [R(int) = 0.0343]
Goodness-of-fit-on F^2	1.015	1.028
R_1 (F)[a], wR_2 (F^2) [$I > 2\sigma(I)$]	0.1178, 0.2514	0.0500, 0.1271
Largest diff. peak and hole, e.	0.315 and -0.204	0.491 and -0.436

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

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