Supporting Information

Synthesis of Imidazolidine-2-(thi)ones via C2-Selective Oxidation and Thionation of 2-Imidazolinium Halides

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General Experimental part: All reactions were carried out under inert atmospheric conditions, unless stated otherwise. Infrared (IR) spectra were obtained from neat samples or from CHCl₃ films on NaCl tablets using a Matteson Instruments 6030 Galaxy Series FT-IR spectrophotometer and wavelengths (ν) are reported in cm⁻¹. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 (400.13 and 100.61 MHz, respectively), a Bruker Avance 250 (250.13 and 62.90 MHz, respectively) with chemical shifts (δ) reported in ppm, internally referenced to residual solvent resonances of CDCl₃ (¹H δ: = 7.26 ppm; ¹³C{¹H} δ: = 77.00 ppm), and coupling constants (J) are reported in Hz. Peak assignment was also done with the aid of gs-COSY, gs-HMQC, and gs-HMBC measurements. HRMS spectra data were recorded on a Finnigan Mat 900 spectrometer (EI) or a micrOTOF-Q instrument in positive ion mode (ESI). Chromatographic purification refers to flash chromatography using the indicated solvent (mixture) and Baker 7024-02 silica gel (40 μ, 60 Å). Thin layer chromatography was performed using silica plates from Merck (Kieselgel 60 F254) on aluminium with fluorescence indicator. Compounds on TLC were visualised by UV-detection unless stated otherwise. CH₂Cl₂ was dried and freshly distilled from CaH₂ prior to use THF and Et₂O were dried and distilled from sodium benzophenone ketyl prior to use. Cyclohexane was distilled prior to use as eluent for chromatography. 2-(trimethylsilyl)ethanamine was synthesized according to literature procedure and stored in Et₂O under inert atmosphere at 4°C. 2-imidazolines 4b, 1 4e, 2 and 4f, 3 and 2-imidazolinium halides 6e-g, 2 were synthesized according to literature procedures, whereas all other commercially available reagents were used as purchased without further purification.
General Procedure I for the Synthesis of 2-Imidazolines: To a stirred solution of an amine (1, 1.0 equiv.) in freshly distilled CH₂Cl₂ (or MeOH) containing anhydrous Na₂SO₄, an aldehyde or ketone (2, 1.0 equiv.) was added and the mixture was stirred at rt for 3 h. Then, an isocyanide (3, 1.0 equiv.) and (in some cases, AgOAc (0.02 equiv.) were added and the resulting reaction mixture was stirred for an additional 18 h, followed by filtration and concentration in vacuo. The crude product was purified by flash chromatography (EtOAc:c-hexane:Et₃N = 1:4:0.01 (gradient, unless stated otherwise) to furnish the 2-imidazolines.

2-Imidazoline 4a: 100 ml of a solution of an unknown concentration of 2-(trimethylsilyl)ethanamine in ether was concentrated to approximately 10 ml. After the solution was put under inert atmosphere an excess of Na₂SO₄ and acetone (250 μl; 3.4 mmol; 1.5 eq) were successively added and at rt. The resulting mixture was stirred for 3 hours. Then, 9-isocyano-9H-fluorene (321.7 mg; 1.7 mmol; 1.5 eq) and AgOAc (18.8 mg, 0.11 mmol, 0.05 eq) were added and the resulting reaction mixture was stirred for 18 hours at rt. Then the reaction mixture was successively filtered, concentrated in vacuo and subjected to silica gel flash column chromatography (1:4 EtOAc: cyclohexane → gradient) to afford 2-imidazoline 4a as a white foam (354.3 mg; 1.160 mmol; 60%). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.64 – 7.60 (m, 2H), 7.53 – 7.48 (m, 2H), 7.35 – 7.20 (m, 2H), 3.14 – 3.06 (m, 2H), 2.902 (s, 3H), 1.09 – 1.01 (m, 2H), 1.069 (s, 6H); ¹³C NMR (63 MHz CDCl₃) δ: 157.2 (CH), 128.2 (CH), 126.2 (CH), 126.1 (CH), 119.6 (CH), 124.1 (CH), 120.1 (CH), 37.9 (CH₂), 22.7 (CH₂), 19.0 (2x CH₂), -1.8 (3x CH₃); IR (thin film): 3074, 3060, 2953, 2925, 2853, 1728, 1485, 1482, 1379, 1232, 1271, 2211, 907, 734; HRMS (EI, 70 eV) calculated for C₂₂H₂₈N₂Si 348.55662, found 348.20108.

2-Imidazoline 4c: According general procedure I, the reaction between benzylamine (214.31 mg; 218.7 μl, 2 mmol; 1 eq), 5-methylfuran-2-carbaldehyde (220.22 mg; 200.2 μl, 2 mmol, 1 eq), 9-isocyano-9H-fluorene (382.5 mg; 2 mmol; 1 eq) to afford 2-imidazoline 4c as white foam (636.6 mg; 1.630 mmol; 81%) Analysis: ¹H NMR (400 MHz CDCl₃) δ: 7.58 – 7.56 (m, 2H), 7.53 – 7.50 (m, 1H), 7.41 – 7.37 (m, 2H), 7.35 – 7.27 (m, 4H), 7.25 – 7.20 (m, 4H), 7.10 – 7.05 (m, 1H), 5.74 (d, J = 3.2, 2H), 5.67 – 5.66 (m, 1H), 4.739 (s, 1H), 4.63 (d, J = 14.8, 1H), 4.14 (d, J = 14.8, 1H), 2.08 (s, 1H); ¹³C NMR (63 MHz CDCl₃) δ: 158.1 (CH), 140.3 (c), 136.2 (C), 128.8 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 126.8 (CH), 126.1 (CH), 123.5 (CH), 119.5 (CH), 119.2 (CH), 109.8 (CH), 105.9 (CH), 66.1 (C), 50.3 (CH₃), 13.5 (CH₃); IR (thin film): 3061, 2035, 2825, 1450, 1421, 1374, 1282, 1275, 1159, 1079, 1021, 914, 790, 731, 702; HRMS (EI, 70 eV) calculated for C₂₇H₂₆N₂O (M + H⁺) 391,1810, found 391,1815.
**2-Imidazoline 4d:** According general procedure I, n-butyl Amine (213.0 mg; 202.8 μl, 2.01 mmol; 1 eq), benzaldehyde (146.8 mg; 190.6 μl, 2.01 mmol, 1 eq), methyl 2-isocyanoacetate (190.74 mg; 182.0 μl; 2.01 mmol; 1 eq) to afford 2-imidazoline 4d as white foam (206.0 mg; 0.791 mmol; 39%). (Single diastereoisomer) Analysis: \(^1\)H NMR (250 MHz CDCl\(_3\)) \(\delta\): 7.26 – 7.07 (m, 6H), 6.95 – 6.86 (m,1H), 7.41 (d, \(J = 5.5\), 1H), 4.40 – 4.37 (m, 1H), 3.64 (s, 3H), 3.07 – 2.93 (m, 1H), 2.87 – 2.80 (m, 1H), 1.38 – 1.11 (m, 2H), 1.23 – 1.11 (m, 2H), 0.72 (t, \(J = 4.6\), 3H); \(^1^3\)C NMR (63 MHz CDCl\(_3\)) \(\delta\): 172.4 (C), 157.0 (CH), 140.3 (C), 129.2 (CH), 128.7 (CH), 128.4 (CH), 128.2 (CH), 127.1 (CH), 82.0 (CH), 52.5 (CH\(_3\)), 45.0 (CH\(_2\)), 30.1 (CH\(_2\)), 19.9 (CH\(_2\)), 13.6 (CH\(_3\)); IR (thin film): 3055, 2962, 2932, 2874, 1628, 1373, 1265, 1207, 733; HRMS (ESI, 70 eV) calculated for C\(_{15}\)H\(_{21}\)N\(_2\)O\(_2\) (M + H\(^+\)) 259.1441, found 259.1435.

**2-Imidazoline 4g:** p-Toluidine (214 mg, 2 mmol, 1 equiv.) was dissolved in MeOH (20 mL) along with 5-methylfurfural (200 μL, 2 mmol, 1 equiv.). Na\(_2\)SO\(_4\) (500 mg) and AgOAc (7 mg, 0.04 mmol, 0.02 equiv.) were added and stirred for 3 h. Isocyanide 3c (350 mg, 2 mmol, 1 equiv.) was added and after 17h the mixture was filtered. The organic phase was concentrated, after which chromatography (silica, cyclohexane : EtOAc 4:1 → 1:2) afforded the product as a 3:1 mixture of diastereomers as white crystals (1.87 mmol, 94%). Mp. 145-147 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.80 (s, 1H); 7.25 (m, 2H); 7.16 (m, 1H); 7.03 (t, \(J = 8,0\) Hz, 2H); 6.91 (d, \(J = 8,0\) Hz, 2H); 6.16 (s, 1H); 5.88 (d, \(J = 4,0\) Hz, 1H); 5.49 (d, \(J = 4,0\) Hz, 1H); 3.76 (s, 3 H); 2.25 (s, 3H); 1.86 (s, 3H). \(^1^3\)C NMR (125 MHz): \(\delta\) 173.4 (C\(_q\)); 152.2 (C\(_q\)); 151.1 (CH); 142.7 (C\(_q\)); 137.7 (C\(_q\)); 136.3 (C\(_q\)); 132.5 (C\(_q\)); 129.9 (2 CH); 128.3 (CH); 127.3 (2 CH); 126.6 (2 CH); 116.8 (2 CH); 111.0 (CH); 105.6 (CH); 84.4 (C\(_q\)); 63.1 (CH); 53.3 (CH\(_3\)); 20.6 (CH\(_3\)) 13.2 (CH\(_3\)). HRMS: calcd. for C\(_{23}\)H\(_{23}\)N\(_2\)O\(_3\)\(^+\) (M + H\(^+\)) 375.1703, found 375.1703. Mp: 146-147 °C.

**General Procedure II for the Synthesis of 2-Imidazolinium halides:** Reactions were carried out at a concentration of 0.15-0.25 M of a 2-imidazoline (4) in dry CH\(_2\)Cl\(_2\), unless noted otherwise. The alkyl iodide (1.0 equiv.) was added to a stirred solution of the 2-imidazoline, and the reaction mixture was stirred at rt for 18 h. Then, the reaction mixture was concentrated in vacuo. The crude product was washed with pentane or Et\(_2\)O to afford the pure imidazolinium salt.

**General Procedure III for the Synthesis of 2-Imidazolinium halides:** Reactions were carried out at a concentration of 1 M of a 2-imidazoline (4) in acetone. The alkyl halide (1.0 equiv.) was added to a stirred solution of the 2-imidazoline and KI (1.0 equiv.). The reaction mixture was stirred at rt for 18 h and concentrated in vacuo. Then the reaction mixture was taken up in CH\(_2\)Cl\(_2\) and subsequently filtrated over Celite and concentrated in vacuo to afford the pure imidazolinium salt.
2-Imidazolinium iodide 6a: According to general procedure II, the reaction between 2-imidazoline 4a (100 mg; 0.241 mmol; 1 eq), MeI (18.9 μl; 0.241 mmol; 1 eq) to afford 2-imidazolinium iodide 6a as a pale yellow foam (130.0 mg; 0.241 mmol; 100%). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 10.110 (s, 1H), 7.72 – 7.69 (m, 2H), 7.56 – 7.45 (m, 4H), 7.40 – 7.30 (m, 2H), 3.59 – 3.52 (m, 2H), 2.90 (s, 3H), 1.23 (s, 6H), 0.15 (s, 9H); ¹³C NMR (63 MHz CDCl₃) δ: 158.1 (CH), 141.1 (C), 138.3 (C), 131.0 (CH), 128.1 (CH), 126.3 (CH), 121.1 (CH), 71.5 (CH₂), 41.1 (CH₃), 31.5 (CH₃), 29.7 (CH₃), 23.7 (CH₃), 18.3 (CH₃), -1.6 (CH₃); IR (thin film): 292, 287, 2840, 1631, 1449, 1293, 1154, 912, 859, 836, 837, 762, 750, 727; HRMS (EI, 70 eV) calculated for C₂₃H₃₁N₂Si (M - I - IMOM) 363.2251, found 363.2255.

2-Imidazolidinium iodide 6b: According to general procedure II, the reaction between 2-imidazoline 4b (338.4 mg; 1.00 mmol; 1 eq) and MeI (66.0 μl; 1.00 mmol; 1 eq) to afford imidazolinium iodide 6b as a pale yellow foam (480.1 mg; 1.00 mmol, 100%). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 9.98 (s, 1H), 7.77 – 7.62 (m, 2H), 7.60 – 7.50 (m, 2H), 7.50 – 7.38 (m, 4H), 7.37 – 7.26 (m, 4H), 4.87 (s, 2H), 2.84 (s, 3H), 1.09 (s, 6H); ¹³C NMR (63 MHz CDCl₃) δ: 159.0 (CH), 158.4 (CH), 145.8 (C), 141.0 (C), 140.7 (C), 137.7 (C), 133.9 (C), 131.0 (CH), 129.4 (CH), 129.4 (CH), 129.1 (CH), 128.9 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 128.8 (CH), 126.5 (CH), 126.1 (CH), 121.0 (CH), 119.8 (CH), 72.2 (CH₂), 69.3 (CH₃), 48.6 (C), 47.0 (C), 29.7 (C), 24.2 (2x CH₃); IR (thin film): 3072, 3033, 2932, 2902, 2342, 1633, 1577, 1540, 1448, 1363, 1285, 1210, 1153, 1101, 916, 754, 754, 724, 703; HRMS (EI, 70 eV) calculated for C₂₅H₂₅N₂ (M - I) 353.2018, found 353.1668.

2-Imidazolinium iodide 6c: According to general procedure III, the reaction between 2-imidazoline 4b (1.0725 g; 2.796 mmol; 1 eq), KI (0.5255 mg; 2.796 mmol; 1 eq) and chloro(methoxy)methane (254 mg; 142.6 μl; 2.796 mmol; 1 eq) to afford 2-imidazolinium iodide 6c as a yellow foam (1.427 g; 2.796 mmol, 100%). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 10.15 (s, 1H), 7.75 – 7.55 (m, 5H), 7.50 – 7.35 (m, 5H), 7.30 – 7.20 (m, 3H), 4.95 (s, 2H), 4.68 (s, 2H), 3.10 (s, 3H); ¹³C NMR (63 MHz CDCl₃) δ: 159.1 (CH), 140.7 (C), 138.6 (C), 133.4 (C), 130.8 (CH), 129.4 (CH), 129.3 (CH), 129.1 (CH), 128.7 (CH), 128.4 (CH), 127.7 (CH), 126.9 (CH), 126.6 (CH), 126.0 (CH), 120.8 (CH), 119.8 (CH), 81.5 (C), 78.0 (CH₂), 73.4 (C), 57.5 (CH₃), 48.9 (CH₃), 23.7 (CH₃); IR (thin film): 3468, 3433, 3005, 2951, 2824, 1620, 1451, 1354, 1265, 1192, 1103, 1049, 918, 745, 710; HRMS (EI, 70 eV) calculated for C₂₄H₂₄N₂ (M - I - IMOM) 338.1777, found 338.2598 (M⁺ - IMOM).
2-Imidazolinium iodide 6d: According to general procedure III, the reaction between 2-imidazoline 4c (600 mg; 1.53 mmol; 1 eq) and chloro(methoxy)methane (122.4 mg; 115.5 μl; 1.53 mmol; 1 eq) to afford 2-imidazolinium iodide 6d as a yellow foam. (791.7 mg; 1.41 mmol; 92%). Analysis: 1H NMR (250 MHz CDCl3) δ: 10.72 (s, 1H), 7.50 – 7.02 (m, 14H), 6.01 (m, 1H), 5.67 (m, 1H), 5.32 (d, J = 14.3), 5.30 (s, 1H), 4.55 (s, 3H), 4.50 – 4.51 (m, 1H), 4.48 (d, J = 14.3), 3.06 (s, 3H), 2.02 (s, 2H); 13C NMR (63 MHz CDCl3) δ: 160.0 (CH), 154.5 (C), 143.8 (C), 141.4 (C), 141.1 (C), 139.5 (C), 136.9 (C), 132.0 (C), 130.9 (CH), 129.5 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 128.9 (CH), 127.7 (CH), 126.5 (CH), 123.2 (CH), 20.5 (CH), 114.3 (CH), 107.1 (CH), 77.7 (CH), 67.9 (CH), 57.2 (CH), 51.5 (CH2); IR (thin film): 3032, 2924, 2855, 1624, 1451, 1366, 1261, 1192, 1111, 1018, 918, 733, 706; HRMS (EI, 70 eV) calculated for C29H27N2O2 (M - I - ) 435.2067, found 435.2076.

2-Imidazolinium iodide 6e: According to general procedure III, the reaction between 2-imidazoline 4d (200 mg; 0.77 mmol; 1 eq), KI (127.6 mg; 0.77 mmol; 1 eq) and 4-methoxybenzylbromide (154.8 mg; 111 μl; 0.77 mmol; 1 eq) to afford 2-imidazolinium iodide 6e as a yellow foam. (356.7 mg; 0.701 mmol; 91%). Analysis: 1H NMR (250 MHz CDCl3) δ: 10.18 (s, 1H), 7.39 – 7.36 (m, 2H), 2.29 – 2.26 (m, 3H), 7.19 – 7.19 (m, 3H), 6.79 – 6.73 (m, 2H), 5.30 (d, J = 14.3, 1H), 5.21 (d, J = 7.3, 1H), 4.59 (d, J = 14.3, 1H), 4.14 (d, J = 7.3, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 3.70 – 3.60 (m, 1H), 3.06 – 3.00 (m, 1H), 1.56 – 1.50 (m, 2H), 1.19 – 1.13 (m, 2H), 0.76 (t, J = 7.4, 3H); 13C NMR (63 MHz CDCl3) δ: 168.9 (C), 160.2 (C), 135.1 (C), 130.9 (CH), 130.02 (CH), 129.96 (CH), 127.1 (CH), 124.2 (C), 114.7 (CH), 113.8 (CH), 71.4 (CH), 67.7, 67.5 (2x CH), 55.3 (CH3), 46.2 (CH3), 19.6, 19.5 (2x CH3), 19.4 (CH3); IR (thin film): 3337, 2959, 2932, 2870, 1720, 1601, 1492, 1439, 1346, 1250, 1192, 1111, 1030, 945, 837, 737, 702; HRMS (EI, 70 eV) calculated for C23H29N2O3 (M - I) 381.2173, found 381.2174.

2-Imidazolinium iodide 6i: 2-Imidazoline 4g (100 mg, 0.27 mmol, 1 equiv.) was dissolved in freshly distilled acetone (1 mL) with KI (46 mg, 0.28 mmol, 1.02 equiv). Benzyl bromide (34 μL, 0.28 mmol, 1.02 equiv.) was added and the mixture stirred for 72 h at rt. It was then filtered over Celite, flushed with additional acetone. The organic phase was concentrated to dryness, washed with Et2O (2 x 4 mL) and then concentrated in vacuo, to recover the title compound as an off-white brittle salt (0.27 mmol, 100%). 1H NMR (400 MHz, DMSO): δ 9.76 (s, 1H) 7.44 – 7.16 (br. m. 14 H); 6.20 (d, J = 3.2 Hz, 1H); 5.65 (d, J = 3.2 Hz, 1H); 5.19 (d, J = 16.0 Hz, 1H); 4.75 (d, J = 16.0 Hz, 1H); 3.50 (s, 3H); 2.26 (s, 3H); 1.77 (s, 3H).
2-Imidazolinium iodide 6j: 2-Imidazoline 4g (100 mg, 0.27 mmol, 1 equiv.) was dissolved in freshly distilled CH₂Cl₂ (1 mL), after which Mel (20 μL, 0.32 mmol, 1.2 equiv.) was added. The mixture was stirred for 72 h at rt and then concentrated to dryness, washed with Et₂O (2 x 4 mL), and dried to afford the product as a yellow salt (0.25 mmol, 92%). Indicative signals: ¹H NMR (400 MHz, DMSO) δ 9.64 (s, 1H); 7.57-7.01 (br. m, 9H); 6.20 (d, J = 3.2 Hz, 1H); 5.66 (d, J = 3.2 Hz, 1H); 3.95 (s, 3H); 3.62 (s, 3H); 3.55 (s, 1H); 2.26 (s, 3H); 1.76 (s, 3H).

General procedure IV for the synthesis of Imidazolidine-2-ones: To a solution of an imidazolinium salt (6, 0.05 M) in freshly distilled CH₂Cl₂, mCPBA (3 equiv.) was added at 0°C. The reaction mixture was stirred at rt for 18 h and subsequently washed with Na₂CO₃ (2x) and concentrated in vacuo and purified by flash chromatography (EtOAc:c-hexane:NEt₃ = 1:4:0.01 → gradient, unless stated otherwise) to afford the imidazolidin-2-one.

Imidazolidine-2-one 7a: According to general procedure IV, the reaction between 2-imidazolinium iodide 6a (100 mg; 0.203 mmol; 1 eq) and mCPBA (123.6 mg; 0.609 mmol; 3 eq) to afford imidazolidine-2-one 7a as a pale yellow foam (49.1 mg; 0.130 mmol; 64 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.71 – 7.60 (m, 2H), 7.49 – 7.40 (m, 2H), 7.39 – 7.36 (m, 2H), 7.29 – 7.22 (m, 2H), 3.27 – 3.20 (m, 2H), 2.32 (s, 3H), 1.43 (s, 6H), 1.08 – 1.01 (m, 2H), 0.07 (s, 9H); ¹³C NMR (63 MHz CDCl₃) δ: 161.4 (C), 142.9 (C), 141.1 (C), 129.2 (CH), 132.9 (CH), 126.1 (CH), 120.2 (CH), 78.0 (C), 63.0 (C), 36.2 (CH₂), 26.9 (CH₃), 23.1 (CH₃), 19.1 (CH₃), -1.7 (CH₃); IR (thin film): 3059, 2951, 2855, 1689, 1447, 1396, 1346, 1246, 1150, 1037, 860, 837, 748, 733; HRMS (EI, 70 eV) calculated for C₂₃H₃₁N₂O₅Si (M + H⁺) 379.2200, found 379.2168.

Imidazolidine-2-one 7c: According to general procedure IV, the reaction between 2-imidazolinium iodide 6c (142 mg; 0.278 mmol; 1 eq) and mCPBA (169.5 mg; 0.835 mmol; 3 eq) to afford imidazolidine-2-one 7c as a pale yellow foam (78.7 mg; 0.197 mmol; 71 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.66 – 7.58 (m, 2H), 7.50 – 7.42 (m, 3H), 7.39 – 7.28 (m, 4H), 7.27 – 7.14 (m, 4H), 4.50 (s, 2H), 4.35 (s, 2H), 3.20 (s, 3H), 0.98 (s, 6H); ¹³C NMR (100 MHz CDCl₃) δ: 167.0 (C), 143.1 (C), 140.9 (C), 139.5 (C), 129.3 (CH), 128.4 (CH), 128.4 (CH), 127.2 (CH), 126.9 (CH), 128.3 (CH), 120.0 (CH), 76.5 (C), 74.5 (CH₂), 63.8 (C), 55.9 (CH₃), 44.3 (CH₃), 23.2 (2x CH₃); IR (thin film): 3063, 2924, 2855, 1689, 1447, 1396, 1354, 1296, 1273, 1072, 1030, 737, 702; HRMS (EI, 70 eV) calculated for C₂₆H₁₇N₂O₄ (M + H⁺) 399,2073, found 399,20731.
Imidazolidine-2-one 7d: According to general procedure IV, the reaction between 2-imidazolinium iodide 6d (265 mg; 0.506 mmol; 1 eq) and mCPBA (247.7 mg; 1.58 mmol; 3 eq) to afford imidazolidine-2-one 7d as a pale yellow foam (221.0 mg; 0.490 mmol; 97%). Analysis: $^1$H NMR (400 MHz CDCl$_3$) δ: 7.58 – 7.48 (m, 2H), 7.34 – 7.21 (m, 9H), 7.20 – 7.13 (m, 1H), 7.08 – 7.01 (m, 1H), 5.83 – 5.82 (m, 1H), 5.78 – 5.77 (m, 1H), 5.11 (d, $J = 13.4$, 1H), 4.57 (s, 1H), 4.37 (d, $J = 11.2$, 1H), 3.38 (d, $J = 13.4$, 1H), 3.12 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (63 MHz CDCl$_3$) δ: 161.6 (C), 152.2 (C), 146.5 (C), 146.3 (C), 141.5 (C), 140.5 (C), 139.6 (C), 136.5 (C), 129.2 (2x CH), 128.6 (2x CH), 128.4 (2x CH), 127.8 (CH), 127.5 (CH), 126.8 (CH), 125.9 (2x CH), 123.0 (2x CH), 119.8 (CH), 119.6 (CH), 73.7 (CH$_3$), 72.1 (C), 61.5 (CH), 55.6 (CH$_3$); IR (thin film): 3059, 2032, 2924, 2828, 1701, 1447, 1420, 1384, 1292, 1261, 1161, 1084, 1022, 914, 794, 737; HRMS (EI, 70 eV) calculated for C$_{29}$H$_{27}$N$_2$O$_3$ (M + H$^+$) 451.2016, found 451.2004.

Imidazolidine-2-one 7e: According to general procedure IV, the reaction between 2-imidazolinium iodide 6e (100 mg; 0.196 mmol; 1 eq) and mCPBA (123.6 mg; 0.590 mmol; 3 eq). No product could be isolated.

Imidazolidine-2-one 7j: Imidazoline salt 6j (52 mg, 0.1 mmol, 1 equiv.) was dissolved in CH$_2$Cl$_2$ at -10 °C after which m-chloroperbenzoic acid (52 mg, 0.3 mmol, 3 equiv.) was added. After 17 h stirring at rt, the mixture was concentrated. Chromatography (silica, cyclohexane : EtOAc 20:1 → 1:1) afforded the product (5 mg, 0.012 mmol, 12%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.39 (d, $J = 7.2$ Hz, 2H); 7.21 (d, $J = 7.2$ Hz, 2H); 7.08-7.03 (m, 5H); 5.95 (s, 1H); 5.84 (d, $J = 3.2$ Hz, 1H); 5.53 (d, $J = 2.4$ Hz, 2H); 3.88 (s, 3H); 2.99 (s, 3H); 2.62 (s, 3H); 1.87 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 171.8 (C$_q$); 157.5 (C$_q$); 152.3 (C$_q$); 146.2 (C$_q$); 136.2 (C$_a$); 133.1 (C$_a$); 133.0 (C$_a$); 129.2 (CH); 128.9 (CH); 128.2 (CH); 127.0 (CH); 120.3 (CH); 110.7 (CH); 105.8 (CH); 73.4 (C$_d$); 61.7 (CH); 53.0 (CH$_3$); 30.2 (CH$_3$); 21.1 (CH$_3$); 13.1 (CH$_3$). HRMS: Calculated for C$_{26}$H$_{20}$N$_2$O$_4$: 405.1809 (M+H$^+$), found: 405.1809.

**General procedure V for the Synthesis of Imidazolidine-2-thiones:** Reactions were carried out under an inert atmosphere of dry argon at a 0.04 M concentration of imidazoline salt in freshly THF. The reaction vessel was charged with imidazoline salt, KOTBu (1 eq) and S$_8$ (1 eq), flushed two times with argon. THF was added and the reaction mixture was stirred at rt for 2 h. after which water was added. The mixture was subsequently extracted with Et$_2$O (2x), EtOAc (2x), CH$_2$Cl$_2$ (2x). The combined organic layers were subsequently dried with Na$_2$SO$_4$, filtered, concentrated in vacuo and subjected to silica gel flash column chromatography EtOAc:Toluene (0:1 → gradient, visualisation on TLC with UV and iodine).
Imidazolidine-2-thione 8a: According to general procedure V, the reaction between 2-imidazolinium iodide 6a (141.3 mg; 0.288 mmol; 1 eq), KOtBu (69.8 mg; 0.288 mmol; 1 eq) and S₈ (73.3 mg; 0.288 mmol; 1 eq) to afford imidazolidine-2-thione 8a as a yellow foam (71.8 mg; 0.224 mmol; 78 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.72 – 7.41 (m, 2H), 7.41 – 7.34 (m, 4H), 7.32 – 7.22 (m, 2H), 3.70 – 3.62 (m, 2H), 2.64 (s, 3H), 1.26 – 1.12 (m, 2H), 1.11 (s, 3H); ¹³C NMR (63 MHz CDCl₃) δ: 1802, 141.9 (C), 140.9 (C), 129.5 (2x CH), 127.3 (2x CH), 126.1 (2x CH), 120.3 (2x CH), 98.0 (C), 66.87 (C), 40.1 (CH₂), 31.0 (CH₃), 22.8 (2xCH₃), 17.8 (CH₂), -1.7 (3x CH₃); IR (thin film): 3072, 3038, 2998, 2974, 2953, 2602, 2369, 2343, 1458, 14483, 1408, 1364, 1283, 1246, 1150, 1013, 858, 840, 768, 754, 735; HRMS (EI, 70 eV) calculated for C₂₃H₃₀N₂SSi 394.64820, found 394.218909.

Imidazolidine-2-thione 8b: According to general procedure V, the reaction between 2-imidazolinium iodide 6b (275.5 mg; 0.573 mmol; 1 eq), KOtBu (145.0 mg; 0.573 mmol; 1 eq) and S₈ (152.2 mg; 0.573 mmol; 1 eq) to afford imidazolidine-2-thione 8b as a pale yellow foam (154.2 mg; 0.401 mmol; 70 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.66 – 7.55 (m, 4H), 7.42 – 7.18 (m, 9 H), 5.01 (s, 2H), 2.72 (s, 3H), 1.03 (s, 6H); ¹³C NMR (63 MHz CDCl₃) δ: 141.1 (C), 138.2 (C), 133.8 (C), 131.0 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 128.9 (CH), 128.3 (CH), 128.1 (CH), 127.8 (CH), 126.7 (CH), 126.4 (CH), 126.2 (CH), 111.0 (CH), 119.7 (CH), 72.2 (CH₂), 48.4 (C), 46.9 (C), 31.5 (CH₃), 24.1 (2x CH₃); IR (thin film): 3060, 3038, 2974, 2931, 2854, 2190, 1633, 1585, 1449, 1362, 1298.22, 1210, 1153, 1101, 917, 754, 726, 704; HRMS (EI, 70 eV) calculated for C₂₅H₂₄N₂S (M⁺) 344.1660, found 344.1662.

Imidazolidine-2-thione 8c: According to general procedure V, the reaction between 2-imidazolinium iodide 6c (1.159 g; 2.79 mmol; 1 eq), KOtBu (573.2 mg; 2.79 mmol; 1 eq) and S₈ (601.7 mg; 2.79 mmol; 1 eq) to afford imidazolidine-2-thione 8c as a yellow foam (640 mg; 1.87 mmol; 67 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.64 – 7.58 (m, 4H), 7.44 – 7.16 (m, 9 H), 5.05 (s, 2H), 4.76 (s, 2H), 3.22 (s, 3H), 1.01 (s, 6H); ¹³C NMR (63 MHz CDCl₃) δ: 184.4 (C), 142.0 (C), 140.7 (C), 138.5 (C), 129.5 (CH), 128.3 (CH), 128.3 (CH), 127.4 (CH), 127.0 (CH), 126.5 (CH), 120.0 (CH), 77.3 (CH₂), 67.9 (C), 56.4 (CH₃), 48.0 (CH₂), 22.9 (CH₃); IR (thin film): 3060, 3038, 2940, 2929, 2821, 2386, 2350, 1558, 1495, 1448, 1408, 1371, 1298, 1238, 1195, 1140, 1094, 1080, 1027, 911, 831, 752, 733, 700, 618; HRMS (EI, 70 eV) calculated for C₂₆H₂₆N₂OS (M⁺) 414.56244, found 414.17617.

Imidazolidine-2-thione 8d: According to general procedure V, the reaction between 2-imidazolinium iodide 6d (100 mg; 0.177 mmol; 1 eq), KOtBu (19.9 mg; 0.177 mmol; 1 eq) and S₈ (73.3 mg; 0.288 mmol; 1 eq) to afford imidazolidine-2-thione 8d as a yellow foam (71.8 mg; 0.224 mmol; 78 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.72 – 7.41 (m, 2H), 7.41 – 7.34 (m, 4H), 7.32 – 7.22 (m, 2H), 3.70 – 3.62 (m, 2H), 2.64 (s, 3H), 1.26 – 1.12 (m, 2H), 1.11 (s, 3H); ¹³C NMR (63 MHz CDCl₃) δ: 1802, 141.9 (C), 140.9 (C), 129.5 (2x CH), 127.3 (2x CH), 126.1 (2x CH), 120.3 (2x CH), 98.0 (C), 66.87 (C), 40.1 (CH₂), 31.0 (CH₃), 22.8 (2xCH₃), 17.8 (CH₂), -1.7 (3x CH₃); IR (thin film): 3072, 3038, 2998, 2974, 2953, 2602, 2369, 2343, 1458, 14483, 1408, 1364, 1283, 1246, 1150, 1013, 858, 840, 768, 754, 735; HRMS (EI, 70 eV) calculated for C₂₃H₃₀N₂Si 394.64820, found 394.218909.
mmol; 1 eq) and S₈ (45.6 mg; 0.177 mmol; 1 eq) to afford imidazolidine-2-thione 8d as a yellow foam (49.4 mg; 0.106 mmol; 60 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.58 – 7.53 (m, 2H), 7.39 – 7.24 (m, 6H), 7.20 – 7.13 (m, 2H), 7.12 – 7.02 (m, 1H), 7.10 – 6.94 (m, 2H), 5.91 (d, J = 14.6, 1H), 5.86 (d, J = 3.0, 1H), 5.78 (d, J = 2.2, 1H), 5.00 (s, 1H), 4.79 (m, J = 11.0, 1H), 4.73 (m, J = 11.0, 1H), 4.09 (d, J = 14.5, 1H), 3.13 (s, 3H), 1.44 (s, 3H); ¹³C NMR (63 MHz CDCl₃) δ: 152.8 (C), 146.3 (C), 145.6 (C), 140.8 (C), 140.2 (C), 139.4 (C), 136.0 (C), 129.6 (C), 129.5 (C), 129.0 (2x CH), 128.5 (2x CH), 128.1 (CH), 127.8 (2x CH), 126.9 (2x CH), 126.4 (CH), 125.5 (CH), 123.1 (CH), 119.9 (CH), 119.8 (CH), 76.6 (CH₂), 65.8 (C), 64.8 (CH₂), 56.3 (CH), 49.9 (CH₂), 13.5 (CH₃); IR (thin film): 3059, 3032, 2924, 1701, 1609, 1562, 1447, 1420, 1385, 1292, 1261, 1161, 1084, 1022, 914, 795, 737, 702; HRMS (EI, 70 eV) calculated for C₂₉H₂₇N₂O₂S (M + H⁺) 467.17932, found 467.17943.

Imidazolidine-2-thione 8e: According to general procedure V, the reaction between 2-imidazolinium iodide 6e (100 mg; 0.196 mmol; 1 eq), KOtBu (22.1 mg; 0.196 mmol; 1 eq) and S₈ (50.5 mg; 0.196 mmol; 1 eq), to afford imidazolidine-2-thione 8e as a yellow foam (43.1 mg; 0.104 mmol; 53 %). Analysis: ¹H NMR (250 MHz CDCl₃) δ: 7.27 – 7.20 (m, 2H), 7.20 – 7.15 (m, 2H), 7.01 – 6.97 (m, 2H), 6.91 (s, 1H), 5.56 (d, J = 14.9, 1H), 4.79 (d, J = 4.6, 1H), 4.27 (d, J = 14.9, 1H), 4.16 – 4.03 (m, 1H), 1.48 – 1.37 (m, 2H), 1.30 – 1.15 (m, 2H), 0.81 (d, J = 7.2, 3H); ¹³C NMR (63 MHz CDCl₃) δ: 128.3 (C), 169.9 (C), 159.2 (C), 138.2 (C), 129.9 (CH), 129.4 (CH), 129.2 (CH), 129.0 (CH), 127.9 (C), 126.6 (CH), 125.5 (CH), 114.0 (CH), 65.9 (CH), 64.5 (CH), 55.2 (CH₃), 52.8 (CH₂), 49.5 (CH₂), 45.2 (CH₂), 28.9 (CH₂), 19.8 (CH₃), 13.8 (CH₃); IR (thin film): 2955, 2932, 2924, 1701, 1609, 1562, 1447, 1420, 1385, 1292, 1261, 1161, 1084, 1022, 914, 795, 737, 702; HRMS (EI, 70 eV) calculated for C₂₃H₂₉N₂O₃S (M + H⁺) 413.1893, found 413.1883.

Imidazolidine-2-thione 8f: According to general procedure V, the reaction between 2-imidazolinium iodide 6f (93 mg, 0.22 mmol), KOtBu (25 mg, 0.22 mmol) and S₈ (57 mg, 0.22 mmol to afford imidazolidine-2-thione 8f as a white foam (64 mg, 0.20 mmol, 89%). ¹H NMR (250 MHz CDCl₃) δ: 7.71 (d, J = 7.5, 2H), 7.53 – 7.35 (m, 6H), 3.96 (s, 2H), 2.58 (s, 3H), 1.74 (s, 9H); ¹³C NMR (63 MHz CDCl₃) δ: 182.5 (C), 143.4 (2×C), 139.0 (2×C), 128.7 (2×CH), 127.4 (2×CH), 122.8 (2×CH), 119.3 (2×CH), 70.9 (C), 55.8 (C), 55.5 (CH₂), 29.2 (CH₃), 27.0 (3×CH₃); IR (neat) 1471, 1446, 1418, 1399; HRMS (EI, 70 eV) calculated for C₂₉H₂₉N₂S (M⁺) 322.1504, found 322.1493.
Imidazolidine-2-thione 8g: According to general procedure V, the reaction between 2-imidazolinium iodide 6g (90 mg, 0.20 mmol), KOtBu (25 mg, 0.22 mmol) and S₈ (53 mg, 0.20 mmol) to afford imidazolidine-2-thione 8g as a white foam (66 mg, 0.15 mmol, 76%). ¹H NMR (250 MHz CDCl₃) δ: 7.55 (d, J = 7.6, 2H), 7.32 – 7.26 (m, 2H), 7.18 (d, J = 7.4, 2H), 7.09 – 7.06 (m, 2H), 6.33 (s, 2H), 4.78 (s, 2H), 3.77 (s, 2H), 2.06 (s, 3H), 1.83 (s, 6H), 1.74 (s, 9H); ¹³C NMR (63 MHz CDCl₃) δ: 184.2 (C), 143.9 (2×C), 139.5 (2×C), 137.5 (2×C), 135.9 (C), 130.4 (C), 128.9 (2×CH), 128.3 (2×CH), 127.6 (2×CH), 123.8 (2×CH), 119.7 (2×CH), 71.9 (C), 57.1 (CH₂), 57.0 (C), 43.6 (CH₂), 28.0 (3×CH₃), 19.7 (2×CH₃); IR (KBr) 1450, 1402, 1362, 1308, 1213; HRMS (EI, 70 eV) calculated for C₂₉H₃₂N₂S (M⁺) 440.2286, found 440.2265.

Imidazolidine-2-thione 8h: According to general procedure V, the reaction between 2-imidazolinium bromide 6h (553 mg, 1.0 mmol), KOtBu (118 mg, 1.05 mmol), and S₈ (256 mg, 1.0 mmol) to afford imidazolidine-2-thione 8h as a white foam (449 mg, 0.89 mmol, 89%). ¹H NMR (250 MHz CDCl₃) δ: 7.67 (d, J = 7.5, 1H), 7.59 (d, J = 7.5, 1H), 7.48 – 7.36 (m, 4H), 7.29 – 7.13 (m, 2H), 7.07 – 6.87 (m, 8H), 6.76 (d, J = 7.6, 1H), 6.00 (d, J = 15.3, 1H), 4.98 (d, J = 15.1, 1H), 4.48 (d, J = 15.3, 1H), 3.97 (d, J = 4.6, 1H), 3.86 (s, 3H), 3.70 (d, J = 15.1, 1H), 2.06 – 1.98 (m, 1H), 0.57 (d, J = 7.1, 3H), 0.47 (d, J = 7.0, 3H); ¹³C NMR (63 MHz CDCl₃) δ: 186.6 (C), 159.0 (C), 144.9 (C), 141.5 (C), 141.0 (C), 140.3 (C), 138.6 (C), 129.7 (CH), 129.4 (2×CH), 129.2 (CH), 128.3 (C), 128.0 (2×CH), 127.6 (3×CH), 127.5 (CH), 127.2 (CH), 126.6 (CH), 124.9 (CH), 120.0 (CH), 119.8 (CH), 114.0 (2×CH), 76.5 (C), 70.3 (CH), 55.3 (CH₃), 50.4 (CH₂), 48.3 (CH₂), 28.2 (CH), 19.3 (CH₃), 18.5 (CH₃); IR (KBr) 161, 1512, 1441, 1248; HRMS (EI, 70 eV) calculated for C₃₃H₃₂N₂O₅S (M⁺) 504.2235, found 504.2229; Elemental analysis: calculated for C₃₃H₃₂N₂O₅S (%): C 78.53, H 6.39, N 5.55, S 6.35, found C 77.37, H 6.88, N 5.22, S 6.47.

Imidazolidine-2-thione 8i: Imidazolinium iodide 6i (60 mg, 0.1 mmol, 1 equiv.) and S₈ (5 mg, 0.12 mmol, 1.2 equiv.) were argon flushed before being dissolved in freshly distilled and degassed THF (3 mL). In a separate flask, a solution of potassium-tert-butoxide (15 mg, 0.12 mmol, 1.2 equiv.) in fresh THF was prepared before being added to the mixture. After 2 h, H₂O (5 mL) was added and the mixture was extracted with Et₂O (2 x 10 mL), EtOAc (2 x 10 mL) and CH₂Cl₂ (2 x 10 mL). The organic phases were combined, dried over Na₂SO₄ and concentrated at reduced pressure. Chromatography (silica, cyclohexane : EtOAc, 20:1 → 1:1) afforded the title compound (50 mg, 0.1 mmol, 100%). ¹H NMR (500 MHz, CDCl₃): δ 7.32-7.20 (br. m, 10H); 7.13 (d, J = 8.0 Hz, 2H); 6.91 (d, J = 8.0 Hz, 2H); 5.80 (d, J = 3.2 Hz, 1H); 5.80 (d, J = 16.4 Hz, 1H); 5.50 (d, J = 3.2 Hz, 1H); 4.63 (d, J = 16.4 Hz, 1H); 3.26 (s, 3H); 2.30 (s, 3H); 1.87 (s, 3H); ¹³C NMR (500 MHz, CDCl₃): δ 184.4 (C₉); 169.5 (C₄); 152.8 (C₄); 144.1 (C₄); 137.7 (C₄); 137.3
Imidazolidine-2-thione 8h: Imidazolinium iodide 6j (50 mg, 0.1 mmol, 1 equiv.) and S₈ (5 mg, 0.12 mmol, 1.2 equiv.) were argon flushed before being dissolved in freshly distilled and degassed THF (3 mL). In a separate flask, a solution of potassium-tert-butoxide (15 mg, 0.12 mmol, 1.2 equiv.) in fresh THF was prepared before being added to the mixture. After 2 h, H₂O (5 mL) was added and the mixture was extracted with Et₂O (2 x 10 mL), EtOAc (2 x 10 mL) and CH₂Cl₂ (2 x 10 mL). The organic phases were combined, dried over Na₂SO₄ and concentrated at reduced pressure. Chromatography (silica, cyclohexane : EtOAc, 20:1 \(\rightarrow\) 1:1) afforded the title compound as a 3:1 mixture of diastereomers (32 mg, 0.076 mmol, 76%). Major product: \(^1\)H NMR (500 MHz, CDCl₃): δ 7.25-7.21 (m, 5H); 7.12 (d, J = 8.0 Hz, 2H); 7.02 (d, J = 8.0 Hz, 2H); 6.01 (s, 1H); 5.85 (d, J = 3.2 Hz, 1H); 5.52 (d, J = 3.2 Hz, 1H); 3.93 (s, 3H); 3.31 (s, 3H); 2.29 (s, 3H); 1.93 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl₃): δ 183.1 (C₅); 170.7 (C₅); 152.6 (C₆); 145.2 (C₇) 137.2 (C₈); 136.7 (C₉); 133.0 (C₆); 129.4 (CH); 128.4 (CH); 127.9 (CH); 127.5 (CH); 127.1 (CH); 111.9 (CH); 105.9 (CH); 77.8 (C₇); 67.2 (CH); 53.3 (CH₃); 34.3 (CH₃); 21.1 (CH₃) 13.2 (CH₃). HRMS (ESI): Calculated for C₂₄H₂₅N₂O₃S⁺ (M+H⁺) 421.1580, found: 421.1555.

References