Supporting Information

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1. General information

Melting points were obtained on a XT-4 melting-point apparatus and were uncorrected. The infrared (IR) spectra were measured on a Nicolet Avatar 360 FTIR spectrometer with 4 cm^{-1} resolution and 32 scans between wavenumber of 4000 cm^{-1} and 400 cm⁻¹. Samples were prepared as KBr disks with 1mg of samples in 100mg of KBr. Proton nuclear magnetic resonance (¹H-NMR) spectra were obtained on a Bruker Avance 400 spectrometer at 400 MHz. Carbon-13 nuclear magnetic resonance (¹³C-NMR) was obtained on Bruker Avance 400 spectrometer at 100 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer or Aglient LC/MSD TOF mass spectrometer. Optical rotations were recorded on a UV-210A spectrometer. All new compounds were characterized by IR, ¹H NMR, ¹³C NMR and HRMS. The known compounds were characterized by ¹H NMR and ¹³C NMR. Silica gel (200–300 mesh) for column chromatography and silica GF254 for TLC were produced by Qingdao Marine Chemical Company (China). THF used in the reactions were dried by distillation over metallic sodium and benzophenone. All experiments were carried out using ultrapure water. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated.

2. Experimental section

2.1 Procedures and analytical data of compounds 1a-1x and 2a-2x



Method A: (For acid sensitive substrates) To a solution of sulfinyl amines (0.5 mmol) in THF/H₂O (1:1, 10 mL) was added Na₂CO₃ (1.5 mmol, 3.0 eq.) and DMAP (0.1 mmol, 0.2 eq.). The reaction mixture was stirred for 5 min at 20 °C before addition of I₂ (1.25 mmol, 2.5 eq.) under an argon atmosphere. The resulting mixture was then stirred at 20 °C under argon for 16-24 h. After consumption of starting materials, the reaction was quenched by water (5 mL) and aqueous sodium thiosulphate (2N, 0.1 mL) at room temperature. The mixture was extracted with CH₂Cl₂ (3 × 5 mL), and the combined organic phases were dried (Na₂SO₄), and concentrated. The residue was chromatographed on basic aluminium oxide (petroleum ether 60-90 °C : ethyl acetate : Et₃N= 3 : 1 : 0.02 or ethyl acetate : Et₃N= 1 : 0.01) to afford the product.

Method B: (Other substrates less labile to acids) To a solution of sulfinyl amines (0.5 mmol) in THF/H₂O (5:1, 10 mL) was added iodine (0.1 mmol, 0.2 eq.). The reaction mixture was then stirred at 50 °C under air or under nitrogen until completely consumption of sulfinyl amines. The reaction mixture was cooled to room temperature and diluted with water (15-20 mL). After removal of THF under reduced pressure, an aqueous solution of sodium thiosulphate (0.2 N, 0.2 mL) was added. The resulting mixture was then washed with Et₂O (3×5 mL), and the aqueous phase was treated with saturated aqueous solution of NaHCO₃ (5 ml). The resulting aqueous mixture was then extracted with CH₂Cl₂ (3×5 mL) and the combined organic phases were washed with brine and dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure to afford the amines. Chromatography on basic aluminium oxide might be required for some amines.



1a: Yellow oil. $[\alpha]_{D}^{20} = -112.6$ (*c* 0.73, CHCl₃). IR v_{max} (cm⁻¹): 3278, 2973, 1708, 1639, 1207, 1157, 1063, 925, 782, 587. ¹H NMR (400 MHz, CDCl₃): δ 5.33 (2H, d, *J* = 8.4 Hz), 4.84 (1H, s), 4.53 (1H, d, *J* = 2.8 Hz), 4.08-4.04 (1H, m), 3.72-3.64 (1H, m), 3.62-3.55 (1H, m), 3.51-3.44 (2H, m), 2.74 (1H, dd, *J*_I = 4.0 Hz, *J*₂ = 15.2 Hz), 2.60 (1H, dd, *J*_I = 8.8 Hz, *J*₂ = 15.2 Hz), 2.05 (3H, s), 1.70 (3H, s), 1.63 (3H, s), 1.23-1.21 (6H, m), 1.20 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 166.67, 164.53, 146.85, 115.95, 105.57, 103.41, 102.12, 62.56, 62.53, 55.84, 55.60, 31.96, 25.53, 25.16, 22.87, 18.04, 15.31, 15.21. HRMS (EI+) *m/z* found: 417.2183, Calcd for C₁₉H₃₃NO₆S (M⁺): 417.2185.



2a: **1a** was deprotected by **Method A** to obtain **2a** in 71% yield as colorless oil. $[\alpha]_D^{20} =$ -19.7 (*c* 1.00, CHCl₃). IR v_{max} (cm⁻¹): 2976, 1720, 1642, 1392, 1271, 1206, 1057, 919,

827. ¹H NMR (400 MHz, CDCl₃): δ 5.24 (2H, d, J = 3.2 Hz), 4.88 (1H, s), 3.68-3.57 (3H, m), 3.52-3.43 (2H, m), 2.62 (1H, dd, $J_I = 4.8$ Hz, $J_2 = 14.0$ Hz), 2.42 (1H, dd, $J_I = 9.2$ Hz, $J_2 = 14.0$ Hz), 2.02 (3H, s), 1.66 (3H, s), 1.64 (3H, s), 1.59 (2H, s), 1.23-1.19 (6H, m). ¹³C NMR (100 MHz, CDCl₃): δ 164.48, 162.95, 150.26, 112.90, 104.93, 103.62, 103.44, 62.53, 62.26, 52.49, 32.55, 25.26, 17.90, 15.30. HRMS (EI+) *m/z* found: 313.1889, Calcd for C₁₆H₂₇NO₅ (M⁺): 313.1889.





1b

1b: Colorless oil. $[α]_D^{20} = -78.9$ (*c* 0.50, CHCl₃). IR v_{max} (cm⁻¹): 2954, 1595, 1486, 1455, 1236, 1156, 1070, 997, 754, 700. ¹H NMR (400 MHz, CDCl₃): δ 7.50 (1H, d, *J* = 7.6 Hz), 7.38 (2H, d, *J* = 7.6 Hz), 7.30-7.19 (4H, m), 7.08-7.01 (2H, m), 6.04 (1H, d, *J* = 4.8 Hz), 5.11 (2H, q, *J* = 5.2 Hz), 3.81 (1H, d, *J* = 4.8 Hz), 3.27 (3H, s), 1.25 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 154.55, 142.65, 130.58, 128.69, 128.65, 128.39, 127.57, 121.73, 114.20, 94.18, 56.79, 56.12, 56.05, 22.81. HRMS (EI+) *m/z* found: 347.1565, Calcd for C₁₉H₂₅NO₃S (M⁺): 347.1555.



2b

2b: **1b** was deprotected by **Method B** to obtain **2b** in 97% yield as colorless oil. $[\alpha]_D^{20}$ = -29.8 (*c* 0.5, CHCl₃); lit¹ $[\alpha]_D^{20}$ = +37.7 (*c* 0.5, CHCl₃) for R-configuration. ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.37 (3H, m), 7.29 (2H, t, *J* = 8.0 Hz), 7.22-7.18 (2H, m), 7.06 (1H, d, *J* = 8.0 Hz), 7.00 (1H, t, *J* = 7.6 Hz), 5.51 (1H, s,), 5.13 (2H, q), 3.29 (3H, s), 2.55 (2H, br s). ¹³C NMR (100 MHz, CDCl₃): δ 154.33, 144.86, 134.37, 128.27, 128.19, 127.69, 127.10, 126.73, 121.92, 114.10, 94.24, 56.04, 54.29.

Ref. 1: M. Atobe, N. Yamazaki, C. Kibayashi, J. Org. Chem. 2004, 69, 5595-5607.



1c: White powder, mp 134-135 °C. $[\alpha]_D^{20} = +143.6$ (*c* 1.20, CHCl₃), lit² $[\alpha]_D^{20} = +145.3$ (*c* 1.20, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.20 (1H, d, J = 8.4 Hz), 7.79 (2H, d, J = 7.6 Hz), 7.49 (1H, t, J = 7.6 Hz), 7.44-7.37 (3H, m), 7.31-7.26 (1H, m), 7.22 (1H, t, J = 7.6 Hz), 6.58 (1H, s), 5.21 (1H, d, J = 3.6 Hz), 3.49 (1H, s), 2.47-2.39 (1H, m), 1.25 (9H, s), 1.14 (3H, d, J = 6.8 Hz), 0.87 (3H, d, J = 6.8 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 142.69, 138.24, 137.71, 133.93, 129.58, 129.32, 126.67, 124.71, 124.07, 120.83, 115.53, 111.64, 57.99, 56.11, 33.84, 22.73, 20.07, 16.47.

Ref. 2: L. Cheng, L. Liu, Y. Sui, D. Wang, Y.-J. Chen, *Tetrahedron: Asymmetry* 2007, 18, 1833-1843.



2c: **1c** was deprotected by **Method B** and chromatographed on basic aluminium oxide (petroleum ether 60-90 °C : ethyl acetate : Et₃N= 3 : 1 : 0.02) to afford **2c** in 74% yield as colorless oil. $[\alpha]_{D}^{20}$ = 99.7 (*c* 0.5, CHCl₃). IR ν_{max} (cm⁻¹): 2961, 1594, 1451, 1368, 1178, 1089, 1035, 745, 684, 629, 580. ¹H NMR (400 MHz, CDCl₃): δ 8.19 (1H, d, *J* = 8.4 Hz), 7.71 (2H, d, *J* = 7.6 Hz), 7.49 (1H, t, *J* = 7.2 Hz), 7.43 (1H, d, *J* = 7.2 Hz), 7.37 (2H, t, *J* = 7.6 Hz), 7.30-7.20 (2H, m), 6.60 (1H, s,), 4.39 (1H, d, *J* = 5.6 Hz), 2.25-2.17 (1H, m), 1.51 (2H, br s), 0.94-0.90 (6H, m). ¹³C NMR (100 MHz, CDCl₃): δ 147.00, 138.93, 137.70, 133.80, 129.83, 129.26, 126.32, 124.47, 123.98, 120.71, 115.44, 108.86, 54.94, 33.85, 20.61, 17.07. HRMS (EI+) *m/z* found: 328.1243, Calcd for C₁₈H₂₀N₂O₂S (M⁺): 328.1245.



1d: Yellow oil. $[\alpha]_{D}^{20} = -0.7$ (*c* 0.34, CHCl₃). IR v_{max} (cm⁻¹): 2972, 1731, 1457, 1368, 1261, 1161, 1086, 754. ¹H NMR (400 MHz, CDCl₃): δ 8.14 (1H, d, *J* = 8.0 Hz), 7.60-7.57 (2H, m), 7.35-7.31 (1H, m), 7.27-7.23 (1H, m), 4.51-4.34 (2H, m),

3.45-3.42 (1H, m), 1.67 (9H, s), 1.23 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 149.68, 135.93, 129.42, 124.81, 124.57, 122.78, 119.49, 117.72, 115.48, 83.96, 55.95, 40.65, 28.30, 22.78. HRMS (EI+) *m/z* found: 350.1657, Calcd for C₁₈H₂₆N₂O₃S (M⁺): 350.1664.



2d: **1d** was deprotected by **Method B** to obtain **2d** in 89% yield as yellow oil. IR v_{max} (cm⁻¹): 2976, 1729, 1454, 1377, 1258, 1160, 1088, 753. ¹H NMR (400 MHz, CDCl₃): δ 8.14 (1H, d, J = 7.6 Hz), 7.56 (1H, d, J = 8.0 Hz), 7.50 (1H, s), 7.32 (1H, t, J = 7.2 Hz), 7.25 (1H, d, J = 7.2 Hz), 4.00 (2H, s), 1.66 (11H, s). ¹³C NMR (100 MHz, CDCl₃): δ 149.87, 135.94, 129.56, 124.58, 122.80, 122.58, 122.49, 118.93, 115.47, 83.57, 37.50, 28.31. HRMS (EI+) *m/z* found: 246.1365, Calcd for C₁₄H₁₈N₂O₂ (M⁺): 246.1368.



1e: Yellow oil. $[\alpha]_{p}^{20}$ = +34.3 (*c* 0.5, CHCl₃). IR v_{max} (cm⁻¹): 1596, 1510, 1449, 1262, 1142, 1074, 1000, 922, 752, 705, 592. ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.27 (5H, m), 7.07 (1H, s), 6.89-6.82 (2H, m), 5.19 (2H, s), 4.29-4.17 (2H, m), 4.06-3.97 (2H, m), 3.87 (3H, s), 3.51 (3H, s), 1.21 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 149.21, 146.45, 137.12, 129.57, 128.86, 128.55, 127.49, 122.96, 117.27, 111.69, 95.60, 58.68, 56.23, 56.04, 51.59, 23.43. HRMS (EI+) *m*/*z* found: 391.1818, Calcd for C₂₁H₂₉NO₄S (M⁺): 391.1817.



2e: **1e** was deprotected by **Method B** and chromatographed on basic aluminium oxide (petroleum ether 60-90 °C : ethyl acetate : Et₃N= 3 : 1 : 0.02) to afford **2e** in 84% yield as yellow oil. IR v_{max} (cm⁻¹): 2943, 1600, 1510, 1453, 1262, 1145, 1079, 1002, 925, 742. ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.30 (4H, m), 7.26-7.23 (1H, m), 7.14 (1H, d, *J* = 1.4 Hz), 6.95 (1H, dd, *J*₁ = 1.6 Hz, *J*₂ = 8.4 Hz), 6.85 (1H, d, *J* = 8.4 Hz), 5.23 (2H, s), 3.86 (3H, s), 3.79 (2H, s), 3.73 (2H, s), 3.52 (3H, s), 1.76 (1H, s). ¹³C NMR (100 MHz, CDCl₃): δ 148.89, 146.50, 140.42, 133.20, 128.47, 128.28, 127.01, 122.11, 116.65, 111.79, 95.61, 56.30, 56.06, 53.15, 52.79. HRMS (EI+) *m/z* found: 287.1523, Calcd for C₁₇H₂₁NO₃ (M⁺): 287.1521.





1f: White powder, mp 84-86 °C. $[α]_D^{20}$ = -34.6 (*c* 0.31, CHCl₃). IR *v*_{max} (cm⁻¹): 3234, 2938, 1633, 1469, 1428, 1373, 1247, 1148, 1033, 987, 930, 849, 607. ¹H NMR (400 MHz, CDCl₃): δ 5.89-5.78 (1H, m), 5.16-5.12 (2H, m), 3.91 (4H, s), 3.20 (1H, s), 2.49 (1H, dd, *J*₁ = 7.7 Hz, *J*₂ = 13.7 Hz), 2.28 (1H, dd, *J*₁ = 7.4 Hz, *J*₂ = 13.7 Hz), 2.07-2.00 (1H, m), 1.78-1.61 (5H, m), 1.58-1.53 (2H, m), 1.20 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 133.11, 120.04, 108.49, 64.39, 64.34, 56.15, 46.08, 34.83, 32.37, 30.48, 22.92. HRMS (EI+) *m*/*z* found: 301.1712, Calcd for C₁₅H₂₇NO₃S (M⁺): 301.1712.



2f: **1f** was deprotected by **Method B** to obtain **2f** in 85% yield as yellow oil. IR v_{max} (cm⁻¹): 2937, 1601, 1443, 1375, 1270, 1105, 1037, 924. ¹H NMR (400 MHz, CDCl₃): δ 5.90-5.80 (1H, m), 5.14-5.08 (2H, m), 3.91 (4H, t, J = 3.2 Hz), 2.96 (2H, br s), 2.21 (2H, d, J = 7.2 Hz), 1.81-1.75 (2H, m), 1.68-1.54 (6H, m). ¹³C NMR (100 MHz, CDCl₃): δ 133.42, 119.11, 108.64, 64.34, 51.19, 45.86, 37.32, 34.96, 30.73. HRMS (EI+) *m/z* found: 197.1408, Calcd for C₁₁H₁₉NO₂ (M⁺): 197.1416.



1g: White powder, mp 188-190 °C. $[\alpha]_D^{20} = +38.6$ (*c* 1.20, CHCl₃), lit² $[\alpha]_D^{20} = +38.0$ (*c* 1.20, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (1H, d, *J* = 8.4 Hz), 7.57-7.50 (3H, m), 7.50-7.35 (3H, m), 7.32-7.22 (7H, m), 6.92 (1H, s), 6.56 (1H, s), 3.69 (1H, brs), 1.25 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 141.81, 140.38, 138.37, 137.66, 133.73, 129.26, 129.18, 128.94, 128.45, 128.39, 126.66, 124.94, 123.96, 121.08, 115.19, 112.22, 56.83, 56.28, 22.81.

Ref. 2: L. Cheng, L. Liu, Y. Sui, D. Wang, Y.-J. Chen, *Tetrahedron: Asymmetry* 2007, 18, 1833-1843.



2g: **1g** was deprotected by **Method B** to obtain **2g** in 81% yield as yellow oil. $[\alpha]_{D}^{20}$ = -125.0 (*c* 0.53, CHCl₃). IR v_{max} (cm⁻¹): 3063, 1595, 1447, 1368, 1176, 1087, 915, 743, 695, 583. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (1H, d, *J* = 8.4 Hz), 7.59-7.56 (2H, m), 7.47 (1H, t, *J* = 7.2 Hz), 7.39 (1H, d, *J* = 7.6 Hz), 7.33-7.19 (9H, m), 6.39 (1H, s), 5.84 (1H, s), 2.04 (2H, brs). ¹³C NMR (100 MHz, CDCl₃): δ 146.51, 142.88, 138.87, 137.74, 133.76, 129.41, 129.23, 128.56, 127.56, 126.37, 124.80, 123.94, 121.01, 115.15, 110.83, 53.45. HRMS (EI+) *m/z* found: 362.1097, Calcd for C₂₁H₁₈N₂O₂S



1h: White powder, mp 62-63 °C. $[\alpha]_D^{20} = -36.3$ (*c* 0.5, CHCl₃), lit³ $[\alpha]_D^{20} = +70.0$ (*c* 1.01, CHCl₃) for (S_S, R)-configuration. ¹H NMR (400 MHz, CDCl₃): δ 8.44 (1H, s), 7.40 (2H, d, *J* = 7.2 Hz), 7.33 (2H, t, *J* = 7.2 Hz), 7.28 (1H, d, *J* = 7.2 Hz), 7.17 (1H, t, *J* = 7.2 Hz), 7.04 (1H, d, *J* = 7.6 Hz), 6.90 (1H, d, *J* = 8.0 Hz), 6.81 (1H, t, *J* = 7.6 Hz), 5.92 (1H, d, *J* = 4.0 Hz), 4.10 (1H, d, *J* = 3.6 Hz), 1.25 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 155.26, 141.31, 129.52, 129.28, 128.96, 127.90, 127.65, 126.70, 120.36, 117.78, 56.72, 56.67, 22.87.

Ref. 3: Z. Huang, H. Lai, Y. Qin, J. Org. Chem. 2007, 72, 1373-1378.



2h: **1h** was deprotected by **Method B** to obtain **2h** in 99% yield as yellow powder. [α] $_{D}^{20}$ = +144.8 (*c* 0.32, CHCl₃), lit⁴ [α]_{D}^{20} = +109.2 (*c* 0.60, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.35 (4H, m), 7.32-7.29 (1H, m), 7.16 (1H, t, *J* = 7.6 Hz), 6.90 (1H, d, *J* = 8.0 Hz), 6.79 (1H, d, *J* = 7.2 Hz), 6.73 (1H, t, *J* = 7.2 Hz), 5.31 (1H, s). ¹³C NMR (100 MHz, CDCl₃): δ 157.89, 143.03, 129.03, 128.73, 127.90, 127.04, 126.29, 119.20, 117.46, 59.93.

Ref. 4: Y.-Q. Wang C.-B. Yu, D.-W. Wang, X.-B. Wang, Y.-G. Zhou, *Org. Lett.*, **2007**, *10*, 2071-2074.



1i: White powder, mp 65-66 °C. $[\alpha]_{D}^{20} = -6.0$ (*c* 0.52, CHCl₃). IR v_{max} (cm⁻¹): 3179, 2953, 2864, 1614, 1447, 1366, 1278, 1176, 1109, 1044, 967, 755, 600, 565. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (1H, d, *J* = 8.4 Hz), 7.88 (2H, d, *J* = 8.0 Hz), 7.57-7.51 (3H, m), 7.45-7.41 (2H, m), 7.34 (1H, t, *J* = 8.0 Hz), 7.27-7.23 (1H, m), 4.47-4.31 (2H, m), 3.49-3.48 (1H, m), 1.20 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 138.23, 135.56, 133.96, 129.67, 129.39, 126.88, 125.21, 124.62, 123.48, 120.00, 113.84, 55.99, 40.53, 22.71. HRMS (EI+) *m/z* found: 390.1054, Calcd for C₁₉H₂₂N₂O₃S₂ (M⁺): 390.1072.



2i: **1i** was deprotected by **Method B** to obtain **2i** in 94% yield as yellow oil. IR v_{max} (cm⁻¹): 2921, 1601, 1445, 1365, 1279, 1175, 1121, 971, 755, 597. ¹H NMR (400 MHz, CDCl₃): δ 8.00 (1H, d, J = 8.4 Hz), 7.87 (2H, d, J = 7.6 Hz), 7.52-7.47 (3H, m), 7.42-7.38 (2H, m), 7.34-7.30 (1H, m), 7.25-7.21 (1H, m), 3.97 (2H, s), 1.56 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ 138.37, 135.63, 133.80, 129.89, 129.30, 126.80, 124.98, 123.30, 122.69, 119.57, 113.85, 37.49. HRMS (EI+) *m/z* found: 286.0768, Calcd for C₁₅H₁₄N₂O₂S (M⁺): 286.0776.



1j: White powder, mp 74-76 °C. $[\alpha]_D^{20} = +19.2$ (*c* 0.56, CHCl₃), IR ν_{max} (cm⁻¹): 3127, 2969, 1721, 1452, 1353, 1247, 1161, 1064, 901, 751. ¹H NMR (400 MHz, CDCl₃): δ 8.09 (1H, d, *J* = 7.6 Hz), 7.59 (1H, d, *J* = 8.0 Hz), 7.53 (1H, s), 7.31-7.27 (1H, m), 7.23-7.19 (1H, m), 4.29 (2H, m), 2.63 (3H, s), 1.65 (9H, s), 1.19 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 149.61, 135.64, 129.60, 124.63, 122.66, 119.35, 116.62, 115.25,

83.81, 58.54, 48.21, 33.38, 28.16, 23.51. HRMS (EI+) *m/z* found: 364.1815, Calcd for C₁₉H₂₈N₂O₃S (M⁺): 364.1821.



2j: **1j** was deprotected by **Method B** to obtain **2j** in 94% yield as yellow oil. IR v_{max} (cm⁻¹): 2974, 1730, 1608, 1452, 1377, 1257, 1160, 1081, 1016, 853, 754. ¹H NMR (400 MHz, CDCl₃): δ 8.14 (1H, d, J = 7.6 Hz), 7.59 (1H, d, J = 8.0 Hz), 7.52 (1H, s), 7.33-7.29 (1H, m), 7.25-7.21 (1H, m), 3.87 (2H, s), 2.5 (3H, s), 1.66 (10H, s). ¹³C NMR (100 MHz, CDCl₃): δ 149.85, 135.82, 130.10, 124.50, 123.57, 122.59, 119.49, 119.14, 115.38, 83.54, 46.71, 36.40, 28.31. HRMS (EI+) *m/z* found: 260.1522, Calcd for C₁₅H₂₀N₂O₂ (M⁺): 260.1525.



1k: White powder, mp 110-111 °C. $[\alpha]_D^{20} = -10.7$ (*c* 0.50, CHCl₃), IR v_{max} (cm⁻¹): 3275, 3124, 2945, 1460, 1395, 1222, 1062, 1021, 928, 697, 667, 552. ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.32 (4H, m), 7.30-7.26 (1H, m), 4.63-4.58 (1H, m), 4.01 (1H, d, *J* = 5.2 Hz), 3.73-3.68 (1H, m), 3.62-3.57 (1H, m), 2.95 (1H, s), 2.15-2.07 (1H, m), 2.05-1.97 (1H, m), 1.18 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 142.54, 128.81,

127.77, 127.14, 59.37, 56.40, 55.44, 40.23, 22.83. HRMS (EI+) *m/z* found: 255.1288, Calcd for C₁₃H₂₁NO₂S (M⁺): 255.1293.



2k

2k: **1k** was deprotected by **Method B** to obtain **2k** in 85% yield as yellow powder. $[\alpha]_{D}^{20} = +19.8$ (*c* 0.45, CHCl₃), lit⁵ $[\alpha]_{D}^{20} = +21.9$ (*c* 1.00, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.22 (5H, m), 4.13-4.10 (1H, m), 3.76 (2H, t, *J* = 5.4 Hz), 3.12 (3H, s), 1.92-1.85 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 145.72, 128.80, 127.31, 125.93, 61.68, 56.01, 39.73.

Ref. 5: P. You, J. Qiu, E. Su, D. Wei, Eur. J. Org. Chem. 2013, 557-565.



1I: A 9:1 selectivity favoring the S-epimer. Yellow oil. $[\alpha]_D^{20} = -48.3$ (*c* 0.50, CHCl₃). IR v_{max} (cm⁻¹): 3224, 2958, 1595, 1485, 1233, 1152, 1061, 1000, 917, 756. ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.22 (2H, m), 7.13 (1H, d, *J* = 8.4 Hz), 7.00 (1H, t, *J* = 7.2 Hz), 6.17-6.08 (0.9H, m) (5.99-5.91 (0.1H, m)), 5.35 (1H, t, *J* = 5.6 Hz), 5.26-5.15 (4H, m), 3.75 (1H, d, *J* = 5.6 Hz), 3.48 (3H, s), 1.20 (8.1H, s) (1.24 (0.9H, s)). ¹³C NMR (100 MHz, CDCl₃): δ 154.76, 139.23, 129.63, 128.88 (129.10), 128.53 (127.87),

122.00 (122.13), 116.15 (116.98), 114.42, 94.55, 57.06, 56.36, 55.96 (55.84), 22.70 (22.81). HRMS (EI+) m/z found: 297.1395, Calcd for C₁₅H₂₃NO₃S (M⁺): 297.1399.



21: **11** was deprotected by **Method B** to obtain **21** in 86% yield as yellow oil. IR v_{max} (cm⁻¹): 2944, 1594, 1487, 1234, 1154, 1080, 997, 921, 756. $[\alpha]_{D}^{20} = -18.4$ (*c* 0.70, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.29 (1H, dd, $J_1 = 1.2$ Hz, $J_2 = 7.6$ Hz), 7.21-7.17 (1H, m), 7.08 (1H, d, J = 8.0 Hz), 6.98 (1H, t, J = 7.4 Hz), 6.14-6.06 (1H, m), 5.26-5.19 (3H, m), 5.11 (1H, d, J = 10.4 Hz), 4.85 (1H, d, J = 5.6 Hz), 3.48 (3H, s), 2.26 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ 154.50, 141.08, 133.22, 128.24, 127.39, 122.05, 114.26, 113.69, 94.52, 56.23, 52.83. HRMS (EI+) *m/z* found: 193.1091, Calcd for C₁₁H₁₅NO₂ (M⁺): 193.1103.



1m: A 4:1 selectivity favoring the S-epimer. Yellow oil. $[\alpha]_{D}^{20} = -120.7$ (*c* 0.5, CHCl₃). IR v_{max} (cm⁻¹): 1593, 1485, 1232, 1156, 1067, 996, 919, 757, 651. ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.26 (1H, m), 7.26-7.19 (1H, m), 7.10 (1H, d, *J* = 8.4 Hz), 6.99 (1H, t, *J* = 7.6 Hz), 5.79-5.69 (1H, m), 5.23 (2H, m), 5.79-5.69 (1.6H, m) (5.06-5.00 (0.4H, m)), 4.94-4.90 (0.8H, m) (4.73 (0.2H, q)), 3.79 (0.8H, d, *J* = 4.0 Hz) (3.89 (0.2H, d, *J* = 3.17)

= 5.1 Hz)), 3.50 (3H, s), 2.70-2.63 (1H, m), 2.59-2.49 (1H, m), 1.19 (7.2H, s) (1.21 (1.8H, s)). ¹³C NMR (100 MHz, CDCl₃): δ 154.67 (154.52), 134.67, 130.71 (130.99), 128.45 (128.74), 128.05, 121.72 (121.92), 118.85 (117.65), 114.21, 94.58, 56.31 (56.15), 55.82 (55.03), 52.12, 41.99 (40.74), 22.71. HRMS (EI+) *m/z* found: 311.1555, Calcd for C₁₆H₂₅NO₃S (M⁺): 311.1555.



2m: **1m** was deprotected by **Method B** to obtain **2m** in 83% yield as yellow oil. $[\alpha]_D^{20}$ = -23.6 (*c* 0.5, CHCl₃). IR v_{max} (cm⁻¹): 3425, 2922, 1633, 1595, 1489, 1233, 1154, 1079, 998, 920, 757. ¹H NMR (400 MHz, CDCl₃): δ 7.33 (1H, dd, $J_I = 1.2$ Hz, $J_2 =$ 7.6 Hz), 7.20-7.16 (1H, m), 7.07 (1H, d, J = 7.6 Hz), 6.98 (1H, t, J = 7.6 Hz), 5.80-5.69 (1H, m), 5.21 (2H, t, J = 7.2 Hz), 5.11-5.03 (2H, m), 4.35-4.32 (1H, m), 3.45 (3H, s), 3.15 (2H, br s), 2.60-2.53 (1H, m), 2.48-2.41 (1H, m). ¹³C NMR (100 MHz, CDCl₃): δ 154.49, 135.50, 133.09, 128.13, 127.09, 121.90, 117.53, 114.05, 94.53, 56.21, 50.01, 41.52. HRMS (EI+) *m/z* found: 207.1270, Calcd for C₁₂H₁₇NO₂ (M⁺): 207.1259.





1n: White powder⁶, mp 54-56 °C. $[\alpha]_D^{20} = +35.6$ (*c* 0.51, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.25 (10H, m), 4.28 (2H, d, *J* = 15.4 Hz), 4.05 (2H, d, *J* = 15.4 Hz), 1.21 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 137.01, 128.86, 128.59, 127.54, 58.72, 51.70, 23.41.

Ref. 6: P. Sun, S. M. Weinreb, J. Org. Chem. 1997, 62, 8604-8608.



2n: **1n** was deprotected by **Method B** to obtain **2n** in 99% yield as colorless oil⁷. ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.29 (8H, m), 7.27-7.22 (2H, m), 3.81 (4H, s), 2.27 (1H, s). ¹³C NMR (100 MHz, CDCl₃): δ 139.98, 128.55, 128.38, 127.18, 53.11.

Ref. 7: (a) Y.-H. Chang, Y. Nakajima, F. Ozawa, Organometallics 2013, 32, 2210-2215. (b) P. Rattanaburi, B. Khumraksa, M. Pattarawarapan, Tetrahedron Lett. 2012, 53, 2689-2693. (c) X. Cui, X. Dai, Y. Deng, F. Shi, Chem. Eur. J. 2013, 19, 3665-3675.





10: Yellow oil. $[\alpha]_{D}^{20} = -43.8$ (*c* 0.65, CHCl₃). IR v_{max} (cm⁻¹): 2955, 1596, 1487, 1398, 1235, 1156, 1068, 1000, 758. ¹H NMR (400 MHz, CDCl₃): δ 7.30 (1H, d, *J* = 7.6 Hz), 7.27-7.24 (1H, m), 7.11 (1H, d, *J* = 8.0 Hz), 6.99 (1H, t, *J* = 7.6 Hz), 5.22 (2H, s), 4.47 (1H, dd, $J_I = 4.8$ Hz, $J_I = 13.6$ Hz), 4.19 (1H, dd, $J_I = 4.8$ Hz, $J_I = 13.6$ Hz), 3.69 (1H, t, *J* = 6.4 Hz), 3.49 (3H, s), 1.22 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 155.32, 129.69, 129.11, 127.89, 121.99, 114.27, 94.70, 56.33, 55.94, 45.43, 22.75. HRMS (EI+) *m/z* found: 271.1246, Calcd for C₁₃H₂₁NO₃S (M⁺): 271.1242.



20: **10** was deprotected by **Method B** to obtain **20** in 91% yield as yellow oil⁸. ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.18 (2H, m), 7.08 (1H, d, J = 8.0 Hz), 6.99-6.95 (1H, m), 5.23 (2H, s), 3.84 (2H, s), 3.49 (3H, s), 1.99 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ 155.18, 132.43, 128.76, 128.26, 121.94, 114.02, 94.47, 56.23, 42.62.

Ref. 8: H. Rahaman, Á. Madarász, I. Pápai, P. M. Pihko, *Angew. Chem. Int. Ed.* **2011**, 50, 6123-6127.





1p: Yellow oil. $[\alpha]_{D}^{20}$ = +20.4 (*c* 0.13, CHCl₃). IR v_{max} (cm⁻¹): 3240, 3060, 2967, 1585, 1482, 1237, 1154, 1070, 993, 911, 757, 621, 555. ¹H NMR (400 MHz, CDCl₃): δ 8.51 (1H, d, *J* = 4.4 Hz), 7.59 (2H, t, *J* = 7.6 Hz), 7.40 (1H, t, *J* = 7.6 Hz), 7.19 (1H, t, *J* = 7.2 Hz), 7.13-7.06 (2H, m), 6.98 (1H, t, *J* = 7.6 Hz), 6.09 (1H, d, *J* = 6.4 Hz), 5.22-5.16 (2H, m), 3.40 (3H, s), 1.19 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 160.70, 154.14, 149.08, 136.52, 131.06, 128.92, 122.28, 122.19, 122.11, 114.10, 94.53, 56.55, 56.24, 55.88, 22.77. HRMS (EI+) *m/z* found: 348.1505, Calcd for C₁₈H₂₄N₂O₃S (M⁺): 348.1508.



2p: **1p** was deprotected by **Method B** to obtain **2p** in 80% yield as yellow oil. $[\alpha]_D^{20}$ = +79.5 (*c* 0.12, CHCl₃). IR ν_{max} (cm⁻¹): 2906, 1589, 1483, 1234, 1154, 1079, 997, 922, 756 . ¹H NMR (400 MHz, CDCl₃): δ 8.57 (1H, d, *J* = 4.0 Hz), 7.58 (1H, t, *J* = 7.6 Hz), 7.35 (1H, d, *J* = 7.6 Hz), 7.27-7.19 (2H, m), 7.13-7.06 (2H, m), 7.00 (1H, t, *J* = 7.2 Hz), 5.55 (1H, s,), 5.16-5.13 (2H, m), 3.33 (3H, s), 2.35 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ 163.36, 154.39, 149.08, 136.36, 133.67, 128.37, 127.97, 122.11, 121.79, 114.10, 94.36, 56.11, 55.38. HRMS (EI+) *m/z* found: 244.1209, Calcd for C₁₄H₁₆N₂O₂ (M⁺): 244.1212.





1q: White powder, mp 110-112 °C. $[\alpha]_D^{20} = -100.5$ (*c* 0.35, CHCl₃); lit⁹ $[\alpha]_D^{20} = -69.6$ (*c* 0.29, EtOAc). ¹H NMR (400 MHz, CDCl₃): δ 8.61-8.52 (1H, m), 7.16-7.12 (2H, m), 6.85-6.79 (2H, m), 4.36-4.17 (2H, m), 4.13 (1H, s), 1.25 (9H, s,). ¹³C NMR (100 MHz, CDCl₃): δ 155.93, 129.87, 129.78, 124.06, 119.88, 116.77, 56.40, 46.85, 22.80.

Ref. 9: (a) Z. Zhang, P. Rooshenas, H. Hausmann, P. R. Schreiner, *Synthesis* 2009, 9, 1531-1544. (b) D. Pei, Z. Wang, S. Wei, Y. Zhang, J. Sun, *Org. Lett.* 2006, 8, 5913-5915.



2q: **1q** was deprotected by **Method B** to obtain **2q** in 78% yield as white powder¹⁰, mp 86-87 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.17 (1H, t, *J* = 7.6 Hz), 6.97 (1H, d, *J* = 7.2 Hz), 6.85 (1H, d, *J* = 8.0 Hz), 6.78 (1H, t, *J* = 7.2 Hz), 4.12 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ 158.51, 128.79, 128.05, 124.09, 119.12, 116.86, 45.51.

Ref. 10: (a) H. E. Zauqq, D. Schaef, *J*. Org. Chem. 1963, 28, 2925-2927. (b) Z.-I.
Irene, A. Venkataraman, B. Manju, R. II L. Jackson, A. O. John, B.Olivier, Chem. Res.
Toxicol. 2010, 23, 240-250. (c) S. Durot, C. Policar, F. Cisnetti, F. Lambert, J.-P.
Renault, G. Pelosi, G. Blain, H. Korri-Youssoufi, J.-P. Mahy, Eur. J. Inorg. Chem.
2005, 3513-3523.



1r: Yellow oil. $[\alpha]_{D}^{20} = +4.3$ (*c* 0.52, MeOH). IR ν_{max} (cm⁻¹): 2958, 1665, 1466, 1396, 1278, 1201, 1070, 1022, 927, 732. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (1H, m), 7.30-7.16 (12H, m), 6.73-6.69 (1H, m), 5.69 (1H, dd, $J_I = 7.2$ Hz, $J_2 = 14.4$ Hz), 4.26 (1H, dd, $J_I = 2.4$ Hz, $J_2 = 15.6$ Hz), 4.09 (1H, dd, $J_I = 6.0$ Hz, $J_2 = 15.6$ Hz), 3.97 (1H, dd, $J_I = 4.4$ Hz, $J_2 = 14.0$ Hz), 2.95-2.92 (1H, m), 2.79-2.70 (1H, m), 1.91-1.83 (4H, m), 1.16 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 171.80, 140.61, 137.28, 137.06, 133.98, 131.58, 131.52, 129.95, 129.42, 129.39, 128.61, 128.50, 127.64, 127.43, 123.87, 58.31, 51.53, 31.86, 31.77, 24.00, 23.88, 23.46, 23.43. HRMS (EI+) *m/z* found: 540.1461, Calcd for C₂₈H₃₃BrN₂O₂S (M⁺): 540.1446.



2r: **1r** was deprotected by **Method B** and chromatographed on basic aluminium oxide (petroleum ether 60-90 °C : ethyl acetate : $Et_3N=3$: 1 : 0.02) to afford **2r** in 70% yield as yellow oil. IR v_{max} (cm⁻¹): 2925, 1662, 1467, 1393, 1276, 1203, 1025, 733. ¹H

NMR (400 MHz, CDCl₃): δ 7.66 (1H, dd, $J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz), 7.30-7.12 (12H, m), 6.75 (1H, dd, $J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz), 5.65 (1H, d, J = 14.4 Hz), 3.98 (1H, d, J = 14.0 Hz), 3.71 (3H, s), 2.62-2.51 (2H, m), 2.04 (2H, t, J = 7.6 Hz), 1.87-1.78 (2H, m), 1.52 (1H, s). ¹³C NMR (100 MHz, CDCl₃): δ 172.58, 140.79, 140.53, 137.19, 133.90, 131.55, 129.80, 129.34, 128.41, 128.37, 128.14, 127.53, 126.88, 123.93, 53.78, 51.46, 48.74, 32.05, 25.45. HRMS (EI+) *m/z* found: 436.1171, Calcd for C₂₄H₂₅BrN₂O (M⁺): 436.1150.





1s: Yellow oil. $[\alpha]_{D}^{20}$ = -34.9 (*c* 0.57, CHCl₃). IR v_{max} (cm⁻¹): 3244, 3183, 2966, 1606, 1524, 1463, 1336, 1179, 1048, 794, 728, 668, 599. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (1H, d, *J* = 8.6 Hz), 7.62-7.56 (2H, m), 7.48-7.43 (1H, m), 4.58 (2H, d, *J* = 6.4 Hz), 3.92 (1H, t, *J* = 6.4 Hz), 1.18 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 148.82, 134.18, 133.70, 131.59, 129.03, 125.23, 56.26, 47.65, 22.61. HRMS (EI+) *m/z* found: 256.0888, Calcd for C₁₁H₁₆N₂O₃S (M⁺): 256.0882.



2s: **1s** was deprotected by **Method B** to obtain **2s** in 87% yield as yellow oil. IR v_{max} (cm⁻¹): 1605, 1522, 1347, 854, 787, 737, 669. ¹H NMR (400 MHz, CDCl₃): δ 7.96

(1H, d, J = 8.4 Hz), 7.61-7.56 (2H, m), 7.41-7.37 (1H, m), 4.07 (2H, s), 1.73 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ 148.52, 138.55, 133.78, 130.65, 127.97, 124.95, 44.13. HRMS (EI+) *m/z* found: 152.0586, Calcd for C₇H₈N₂O₂ (M⁺): 152.0586.



1t: Yellow powder, mp 43-45 °C. $[α]_{D}^{20}$ = -128.7 (*c* 0.25, CHCl₃). IR *v*_{max} (cm⁻¹): 3213, 2955, 1716, 1458, 1274, 1113, 1061, 708, 599. ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.95 (2H, m), 7.58-7.53 (1H, m), 7.45-7.39 (2H, m), 7.38-7.27 (5H, m), 4.63-4.58 (1H, m), 4.38-4.32 (1H, m), 4.25-4.19 (1H, m), 3.57 (1H, s), 2.54-2.48 (1H, m), 2.26-2.21 (1H, m), 1.24 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 166.55, 141.58, 133.13, 129.69, 129.09, 128.48, 128.32, 127.22, 61.75, 56.76, 56.09, 35.77, 22.74. HRMS (EI+) *m/z* found: 359.1543, Calcd for C₂₀H₂₅NO₃S (M⁺): 359.1555.



2t: **1t** was deprotected by **Method B** to obtain **2t** in 95% yield as yellow oil. $[\alpha]_{D}^{20}$ = -19.3 (*c* 0.26, CHCl₃). IR v_{max} (cm⁻¹): 3332, 2946, 1714, 1634, 1531, 1275, 1114, 707. ¹H NMR (400 MHz, CDCl₃): δ 7.91 (2H, d, *J* = 7.2 Hz), 7.53-7.44 (1H, m), 7.41-7.34 (4H, m), 7.32-7.24 (2H, m), 7.20 (1H, t, *J* = 7.2 Hz), 4.58 (2H, s), 4.33-4.22 (2H, m), 4.19-4.12 (1H, m), 2.40-2.31 (1H, m), 2.27-2.20 (1H, m). ¹³C NMR (100 MHz,

CDCl₃): § 166.59, 141.66, 133.07, 130.06, 129.66, 128.97, 128.42, 128.10, 127.01, 62.18, 53.58, 36.21. HRMS (EI+) m/z found: 255.1255, Calcd for C₁₆H₁₇NO₂ (M⁺): 255.1259.



1u: Yellow oil. $[\alpha]_{D}^{20} = -57.4$ (*c* 0.97, CHCl₃). IR v_{max} (cm⁻¹): 2997, 2883, 2806, 1600, 1489, 1445, 1363, 1079, 928, 884, 803, 750, 700. ¹H NMR (400 MHz, CDCl₃): δ 7.65 (2H, d, J = 8.4 Hz), 7.35-7.28 (5H, m), 7.23-7.19 (3H, m), 7.08 (1H, d, J = 7.6 Hz),7.01 (1H, d, J = 7.2 Hz), 6.97 (1H, s), 4.13-4.04 (4H, m), 2.43 (3H, s), 2.33 (3H, s). ¹³C NMR (100 MHz, CDCl₃): δ 141.48, 141.26, 138.16, 136.75, 136.55, 129.96, 129.74, 129.16, 128.55, 128.45, 128.40, 127.65, 126.35, 126.18, 51.38, 51.26, 21.50. HRMS (EI+) *m/z* found: 349.1506, Calcd for C₂₂H₂₃NOS (M⁺): 349.1500.



2u: 1u was deprotected by Method B to afford 2u in 93% yield as colorless oil¹¹. ¹H NMR (400 MHz, CDCl₃): δ 7.36-7.31 (3H, m), 7.28-7.24 (2H, m), 7.21 (1H, d, J = 7.6 Hz), 7.17-7.12 (2H, m), 7.07 (1H, d, J = 7.2 Hz), 3.82 (2H, s), 3.78 (2H, s), 2.35 (3H, s), 1.68 (1H, br s). ¹³C NMR (100 MHz, CDCl₃): δ 140.45, 140.34, 138.18, 129.08, 128.55, 128.44, 128.32, 127.84, 127.09, 125.34, 53.35, 53.29, 21.55.

Ref. 11: (a) X. Cui, Y. Zhang, F. Shi, Y. Deng, *Chem. Eur. J.* 2011, *17*, 2587-2591. (b)
M. Kim, B. W. Knettle, A. Dahlén, G. Hilmerssonb, R. A. Flowers II, *Tetrahedron* 2003, *59*, 10397-10402.





1v: A rotational isomer with a 1:1 rate. Yellow oil. $[α]_D^{20} = +9.4$ (*c* 0.37, CHCl₃). IR v_{max} (cm⁻¹): 2925, 1663, 1469, 1397, 1278, 1077, 935, 732. ¹H NMR (400 MHz, CDCl₃): δ 7.71-7.68 (1H, m), 7.38 (1H, dd, $J_I = 2.0$ Hz, $J_2 = 8.0$ Hz), 7.31-7.17 (9H, m), 6.77 (1H, dd, $J_I = 2.0$ Hz, $J_2 = 8.8$ Hz), 5.62 (1H, dd, $J_I = 2.0$ Hz, $J_2 = 14.4$ Hz), 4.00 (1H, d, J = 14.4 Hz), 3.17-3.07 (1H, m), 3.01-2.95 (1H, m), 2.44 (1.5H, s) (2.43 (1.5H, s)), 2.39 (1.5H, s) (2.38 (1.5H, s)), 2.00-1.90 (4H, m). ¹³C NMR (100 MHz, CDCl₃): δ 171.95, 141.12, 140.74, 137.08, 134.04, 133.99, 131.58, 129.99, 129.58, 129.42, 128.52, 127.68, 126.13, 124.00, 52.02, 51.70, 51.61, 32.41 (32.13), 31.52, 23.60, 21.47. HRMS (EI+) *m*/*z* found: 498.0974, Calcd for C₂₅H₂₇BrN₂O₂S (M⁺): 498.0977.



2v: 1v was deprotected by Method B and chromatographed on basic aluminium oxide (petroleum ether 60-90 °C : ethyl acetate : $Et_3N=3$: 1 : 0.02) to afford 2v in 77% yield as yellow oil. IR v_{max} (cm⁻¹): 2928, 2788, 1662, 1470, 1438, 1394, 1276, 1203, 1022, 765, 732. ¹H NMR (400 MHz, CDCl₃): δ 7.67 (1H, dd, $J_1 = 2.8$ Hz, $J_2 = 6.4$ Hz), 7.24-7.15 (7H, m), 6.75 (1H, dd, $J_1 = 3.2$ Hz, $J_2 = 6.4$ Hz), 5.63 (1H, d, J = 14.4 Hz), 3.98 (1H, d, J = 14.4 Hz), 2.56-2.49 (2H, m), 2.37 (3H, s), 2.03-2.00 (3H, m),1.84-1.77 (2H, m). ¹³C NMR (100 MHz, CDCl₃): δ 172.60, 140.78, 137.17, 133.97, 131.57, 129.89, 129.39, 128.46, 127.59, 123.94, 51.55, 51.44, 36.21, 32.16, 25.12. HRMS (EI+) m/z found: 360.0836, Calcd for C₁₈H₂₁BrN₂O (M⁺): 360.0837.



1w: White powder, mp 35-37 °C. $[\alpha]_D^{20} = -34.9$ (*c* 0.50, CHCl₃). IR v_{max} (cm⁻¹): 2948, 2862, 1462, 1254, 1092, 838, 775, 703. ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.30 (4H, m), 7.29-7.26 (1H, m), 4.60-4.55 (1H, m), 3.81 (1H, d, J = 4.8 Hz), 3.62-3.57 (1H, m), 3.54-3.49 (1H, m), 2.22-2.14 (1H, m), 2.07-1.92 (1H, m), 1.21 (9H, s), 0.88 (9H, s), 0.05 (6H, s). ¹³C NMR (100 MHz, CDCl₃): δ 142.35, 128.70, 127.78, 127.32,

59.86, 56.72, 55.99, 39.84, 26.03, 22.74, 18.35, -5.28, -5.30. HRMS (EI+) *m/z* found: 369.2131, Calcd for C₁₉H₃₅NO₂SSi (M⁺): 369.2158.



2w: **1w** was deprotected by **Method A** to obtain **2w** in 72% yield as colorless oil. $[\alpha]_D^{20}$ = +6.7 (*c* 0.22, CHCl₃); lit¹² $[\alpha]_D^{20}$ = +0.8 (*c* 1.0, CHCl₃) for > 99% *ee*. ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.28 (4H, m), 7.22-7.18 (1H, m), 4.07 (1H, t, *J* = 6.8 Hz), 3.67-3.62 (1H, m), 3.59-3.53 (1H, m), 1.91 (2H, br s), 1.86-1.80 (2H, m), 0.86 (9H, s), 0.00 (6H, s). ¹³C NMR (100 MHz, CDCl₃): δ 146.50, 128.58, 127.04, 126.49, 60.90, 53.61, 42.18, 26.07, 18.39, -5.24. HRMS (EI+) *m/z* found: 265.1863, Calcd for C₁₅H₂₇NOSi (M⁺): 265.1862.

Ref. 12: (a) R.-M. María, G.-U. Eduardo, G.-F. Vicente, G. Vicente, *Adv. Synth. Catal.*2010, *352*, 395-406; (b) T. Oliver, G.-F. Vicente, G. Vicente, *Tetrahedron: Asymmetry*2006, *17*, 860–866.



1x: Yellow oil. $[α]_p^{20} = +69.2$ (*c* 0.95, CHCl₃). IR v_{max} (cm⁻¹): 2973, 1617, 1445, 1371, 1064, 750, 583. ¹H NMR (400 MHz, CDCl₃): δ 8.19 (1H, d, *J* = 7.6 Hz), 7.87 (2H, d, *J* = 7.6 Hz), 7.54-7.50 (1H, m), 7.46-7.42 (3H, m), 7.31-7.27 (1H, m), 7.22 (1H, t, *J* = 7.6 Hz), 6.66 (1H, s), 5.43 (1H, d, *J* = 8.8 Hz), 5.05 (1H, s), 4.76-4.74 (1H, m), 3.81-3.77 (1H, m), 3.70-3.64 (1H, m), 3.61-3.56 (1H, m), 2.50 (1H, d, *J* = 14.4 Hz), 2.11-2.03 (1H, m), 1.29-1.21 (15H, m). ¹³C NMR (100 MHz, CDCl₃): δ 143.04, 138.16, 137.49, 134.04, 129.51, 126.68, 124.79, 124.01, 120.94, 115.20, 111.07, 102.41, 63.00, 62.16, 55.78, 49.67, 41.53, 22.89, 15.54, 15.44. HRMS (ESI+) *m/z* found: 529.1801, Calcd for C₂₅H₃₄N₂NaO₅S₂ (M + Na)⁺: 529.1807.



2x: **1x** was deprotected by **Method A** to obtain **2x** in 56% yield as yellow oil oil. $[\alpha]_{D}^{20}$ = -72.0 (*c* 1.50, CHCl₃). IR ν_{max} (cm⁻¹): 2974, 1601, 1444, 1368, 1175, 1132, 1055, 742, 584. ¹H NMR (400 MHz, CDCl₃): δ 8.18 (1H, d, *J* = 7.6 Hz), 7.74 (2H, d, *J* = 7.6 Hz), 7.50 (1H, t, *J* = 7.6 Hz), 7.43 (1H, d, *J* = 7.6 Hz), 7.38 (1H, t, *J* = 7.6 Hz), 7.31-7.26 (1H, m), 7.22 (1H, t, *J* = 7.6 Hz), 6.60 (1H, s), 4.79 (1H, t, *J* = 5.6 Hz), 4.70-4.67 (1H, m), 3.73-3.65 (2H, m), 3.62-3.48 (2H, m), 2.25-2.19 (1H, m), 2.08-2.01 (1H, m), 1.82 (2H, br s), 1.27-1.21 (6H, m). ¹³C NMR (100 MHz, CDCl₃): δ 147.18, 138.80, 137.58, 133.87, 129.73, 129.53, 126.38, 124.78, 124.03, 120.92, 115.29, 108.36, 101.73, 62.02, 61.94, 46.10, 41.15, 15.63, 15.53. HRMS (ESI+) *m/z* found: 403.1682, Calcd for C₂₁H₂₆N₂O₄S (M + Na)⁺: 403.1686.

2.2 Experiments to elaborate the proposed pathway



2.2.1 Inhibition experiments

To a solution of sulfinyl amine **1b** (174 mg, 0.5 mmol) in THF/H₂O (5:1, 10 mL) was added TEMPO (78 mg, 0.5 mmol, 1 eq. or 235 mg, 1.5 mmol, 3 eq.) and I₂ (26 mg, 0.1 mmol, 0.2 eq.). The reaction mixture was then stirred at 50 °C under air for 12 h. The mixture was diluted with water (15 mL). After removal of THF under reduced pressure, aqueous solution of sodium thiosulphate (0.2N, 0.2 mL) was added. The resulting mixture was washed with Et₂O (3×5 mL), and the residue was treated with saturated aqueous solution of NaHCO₃ (5 ml). The aqueous mixture was then extracted with CH₂Cl₂ (3×5 mL). The combined organic phases were washed with brine and dried over Na₂SO₄. After removal of the solvents, the residue was chromatographed on basic aluminium oxide (petroleum ether 60-90 °C : ethyl acetate : Et₃N= 3 : 1 : 0.02) to afford the product.

Experiments conducting with TEMPO suggested that the deprotection of *N-tert*-butanesulfinyl group might be a SET (single electron transfer) process. This iodine mediated process was significantly inhibited by addition of TEMPO.

2.2.2 Radical experiments



To a solution of sulfinyl amine **1b** (174 mg, 0.5 mmol) in dry toluene (5 mL) was added ^{*n*}Bu₃SnH (1.2 eq. 162 μ L, 0.6 mmol). The reaction mixture was then stirred at 115 °C under argon atmosphere for 24 h. After removal of the solvents, the residue was chromatographed on silica gel (200–300 mesh) to afford compound **1b** (recovery of starting material).

Experiment with *n***-Bu₃SnH** indicates that the deprotection of *N*-*tert*-butanesulfinyl group does not occur in the presence of a reductive radical initiator.

2.2.3 Deprotections of *N-tert*-butanesulfinyl amines by catalytic iodine

2.2.3.1 Deprotections in THF/H₂O



In order to identify all products of this iodine mediated process, we conducted the



following experiments and the procedure was illustrated in Scheme S1.

Scheme S1

To a stirred solution of sulfinyl amine **1b** (749 mg, 2 mmol) in THF/H₂O (5 : 1, 40 mL) was added I₂ (20%mol, 102 mg, 0.4 mmol). The reaction mixture was stirred at 50 $^{\circ}$ C under air or nitrogen until starting material **1b** was disappeared (ca. 12 h, monitored by TLC) to afford **Mixture A**.

The **mixture A** (10 μ L) was taken and dissolved in THF/H₂O (5 : 1, 1 mL) to afford the sample (**Mixture B**) for High Resolution Mass spectra on Aglient LC/MSD TOF mass spectrometer. The results were listed in **Table S1**.

Entry	Experimental data	Formula	Calculated data	Origin
1	244.1337	$(C_{15}H_{18}NO_2)^+$	244.1338	3b (Figure S1)
2	96.9589	$({\rm SO_4}^{2-} + {\rm H})^{-}$	96.9596	3b (Figure S2)
3	233.0654	$(C_8H_{18}O_2S_2 + Na)^+$	233.0646	5b (Figure S3)
4	217.0697	$(C_8H_{18}OS_2 + Na)^+$	217.0697	6b (Figure S4)

Table S1 The results of HRMS







Figure S2



Figure S3



Figure S4

Mixture A was diluted with water (30 mL). Most of the THF was removed under reduced pressure to obtain **Mixture C**. **Mixture C** was extracted with Et_2O (3 × 20 mL) to yield the organic phase **D**. The organic phase **D** was washed with brine, dried (Na₂SO₄), concentrated, and chromatographed on silica gel (petroleum ether 60-90 °C : ethyl acetate = 15 : 1) to afford a mixture of *tert*-butyl 2-methylpropane-2-sulfonothioate (**5b**) and *tert*-butyl 2-methylpropane-2-sulfonothioate (**5b**).

$$\xrightarrow{O}_{S-S} \xrightarrow{I}_{C} tert-butyl 2-methylpropane-2-sulfonothioate C8H18O2S2 Mol. Wt.: 210.36 5b$$

tert-butyl 2-methylpropane-2-sulfonothioate¹² (**5b**): ¹H NMR (400 MHz, CDCl₃): δ 1.61 (9H, s), 1.46 (9H, s). ¹³C NMR (100 MHz, CDCl₃): δ 68.25, 56.53, 31.68, 23.89. HRMS (ESI+) *m/z* found: 233.0646, Calcd for C₈H₁₈Na O₂S₂ (M + Na)⁺: 233.0646 (**Figure S3**).

$$\rightarrow$$
 $\overset{O}{\overset{}_{S-S}}$ *tert*-butyl 2-methylpropane-2-sulfinothioate $C_8H_{18}OS_2$ Mol. Wt.: 194.36 6b

tert-butyl 2-methylpropane-2-sulfinothioate¹² (**6b**): ¹H NMR (400 MHz, CDCl₃): δ 1.50 (9H, s), 1.22 (9H, s). HRMS (ESI+) *m/z* found: 217.0697, Calcd for C₈H₁₈NaOS₂ (M + Na)⁺: 217.0697 (**Figure S4**).

Ref. 12: G. Derbesy, D. N. Harpp, J. Org. Chem. 1996, 60, 1044-1052.

The aqueous phase E was concentrated to afford 3b (549 mg, 94% yiled).


(*S*)-(2-(methoxymethoxy)phenyl)(phenyl)methanaminium sulfate 3b: ¹H NMR (400 MHz, D₂O): δ 7.40-7.35 (7H, m), 7.12 (2H, d, *J* = 8.0 Hz), 5.81 (1H, s), 5.19 (2H, s), 3.13 (3H, s). ¹³C NMR (100 MHz, D₂O): δ 153.32, 136.03, 130.61, 129.04, 128.82, 128.27, 126.93, 125.12, 122.28, 114.16, 93.28, 55.80, 54.41. HRMS (ESI+) *m/z* found: 244.1337, Calcd for C₁₅H₁₈NO₂ (M – SO₄)⁺/2: 244.1338 (**Figure S1**); HRMS (ESI-) *m/z* found: 96.9589, Calcd for HSO₄ (SO₄ + H)⁻: 96.9596 (**Figure S2**).

To a solution of **3b** (549 mg) in H₂O (10 mL) was added saturated aqueous solution of NaHCO₃ (10 mL). The reaction mixture was stirred for 5 min at 20 °C. The reaction mixture was then extracted with CH₂Cl₂ (3×10 mL). The combined organic phases were washed with brine, dried (Na₂SO₄), and concentrated to give the amine **2b** (448 mg, yiled 98% from **3b**).

2.2.3.2 Deprotections in deuterated solvents (THF-d8/D₂O)



Iodine (5mg, 0.02 mmol, 0.2 eq.) and sulfinyl amine **1b** (35 mg, 0.1 mmol) were disolved in THF- $d8/D_2O$ (5:1, 2 mL) in a sealed tube equipped with a stir bar. This solution was then stirred at 50 °C for 12 h, the reaction progress might be monitored by TLC. After completely consumption of starting material, the resulting mixture (0.5 mL) was transfered to a NMR tube to conduct ¹H-NMR (**Figure S5b**) and ¹³C-NMR (**Figure S6b**) experiments on a Bruker Avance 400 spectrometer.



Figure S5. (a) ¹H-NMR spectra of sulfinyl amine **1b** (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1); (b) ¹H-NMR spectra of the resulting mixture (asterisks indicate the THF^{*d*-8} peak) in THF-*d8*/D₂O (5:1).



Figure S6. (a) ¹³C-NMR spectra of sulfinyl amine **1b** (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1); (b) ¹³C-NMR spectra of the reaction mixture (asterisks $_{S38}$

indicate the THF-d8 peak) in THF-d8/D₂O (5:1).

^{*t*}**BuOD** (4b^{*d*}): In order to determine the volatile ^{*t*}BuOD (4b^{*d*}), we carried out the following control experiment. To the deuterated reaction mixture (0.5 mL) was added ^{*t*}BuOH (3 mg). The resulting mixture was transfered to a NMR tube to obtain ¹H-NMR (Figure S7b) and ¹³C-NMR (Figure S8b) on a Bruker Avance 400 spectrometer. As indicated in Figure S7, the integrations for protons (chemical shifts at δ 1.18 ppm) and carbons (chemical shifts at δ 67.69 and 30.55 ppm) are significantly increased after addition of ^{*t*}BuOH.

Conclusion from this control experiment: ^{*t*}BuOH was produced as a by-product in this deprotection reaction.



Figure S7. (a) ¹H-NMR spectra of the deuterated reaction mixture (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1); (b) ¹H-NMR spectra of the deuterated reaction mixture after addition of ^{*t*}BuOH (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1).



Figure S8. (a) ¹³C-NMR spectra of the deuterated reaction mixture (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1); (b) ¹³C-NMR spectra of the deuterated reaction mixture after addition of ^{*t*}BuOH (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1).



Figure S9. ¹H-NMR spectra of the deuterated reaction mixture (asterisks indicate the

THF-*d8* peak) in THF-*d8*/D₂O (5:1). (a) Protons of $\mathbf{3b}^d$; (b) Protons of $\mathbf{5b}$; (c) Protons of **6b**; (d) Protons of $\mathbf{4b}^d$.

Conclusion for reactions conducted with catalytic amount of iodine: These experiments suggest that oxidation of the *tert*-butanesulfinyl groups by iodine might lead to the formation of $3b^d$, $4b^d$, 5b and 6b as shown in Figure S9.

2.2.4 Deprotections of N-tert-butanesulfinyl amines in the presence of base

2.2.4.1 Deprotections in THF/H₂O



To a solution of sulfinyl amine **1b** (749 mg 2 mmol) in THF/H₂O (1:1, 40 mL) was added Na₂CO₃ (636 mg, 6 mmol, 3.0 eq.). The reaction mixture was stirred for 5 min at 20 °C under argon. I₂ (1.27 g, 5 mmol) was then added. The reaction mixture was stirred at 20 °C for 24 h under argon. After consumption of amine **1b**, the reaction mixture was diluted with water (30 mL). The resulting mixture was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic phases were washed with NaS₂O₃ (0.2 N), dried (Na₂SO₄), concentrated, and chromatographed on basic aluminium oxide (petroleum ether 60-90 °C : ethyl acetate : Et₃N= 3 : 1 : 0.02) to afford the product **2b** (394 mg, yield 81%). The aqueous phase was concentrated under reduced pressure, and the resulting residue was chromatographed on silica gel (CH₂Cl₂ : MeOH = 3 : 1) to afford **7b** (78mg, yield 11%).



Sodium (*S*)-(2-(methoxymethoxy)phenyl)(phenyl)methylsulfamate 7b: ¹H NMR (400 MHz, D₂O): δ 7.64 (1H, d, *J* = 7.2 Hz), 7.43-7.42 (2H, m), 7.37-7.26 (4H, m), 7.15 (1H, t, *J* = 7.2 Hz), 7.05 (1H, d, *J* = 8.0 Hz), 5.86 (1H, s), 5.18 (2H, s), 3.25 (3H, s). ¹³C NMR (100 MHz, D₂O): δ 152.92, 142.12, 131.65, 128.84, 128.63, 128.52, 127.37, 127.27, 122.39, 114.52, 93.77, 56.82, 56.05. HRMS (ESI+) *m/z* found: 368.0575, Calcd for C₁₅H₁₆NNa₂O₅S (M + Na)⁺: 368.0545 (Figure S10); HRMS (ESI-) *m/z* found: 322.0758, Calcd for C₁₅H₁₆NO₅S (M - Na)⁻: 322.0755 (Figure S11).



Figure S10



Figure S11

2.2.4.2 Deprotections in deuterated solvents (THF-d8/D₂O)



To a solution of sulfinyl amine **1b** (35 mg, 0.1 mmol) in THF- $d8/D_2O$ (1:1, 2 mL) was added Na₂CO₃ (32 mg, 0.3 mmol, 3.0 eq.). The reaction mixture was stirred for 5 min at 20 °C under argon. I₂ (64 mg, 0.25 mmol) was then added. The resulting mixture was stirred at 20 °C for 24 h under an argon atmosphere. After consumption of starting material, the resulting mixture (0.5 mL) was transfered to a NMR tube to conducted ¹H-NMR (**Figure S12b**) and ¹³C-NMR (**Figure S13b**) on a Bruker Avance 400 spectrometer.



Figure S12 (a) ¹H-NMR of sulfinyl amine **1b** (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1); (b) ¹H-NMR of the resulting mixture (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1).



Figure S13 (a) 13 C-NMR of sulfinyl amine 1b (asterisks indicate the THF-d8 peak) in

THF- $d8/D_2O$ (1:1); (b) ¹³C--NMR of the resulting mixture (asterisks indicate the THF-d8 peak) in THF- $d8/D_2O$ (1:1).

^{*t*}**BuOD** (4b^{*d*}): Similar procedure, by addition of *t*-BuOH to the reaction mixture, was used to identify the formation of ^{*t*}BuOH (4b^{*d*}) in this deprotection process.

Conclusion remark for iodine mediated deprotection in the presence of base: These experiments suggest that the deprotection of *tert*-butanesulfinyl group in the presence of base might go an alternative pathway and yield **2b**, **4b**, **7b** as indicated in **Figure S14**.



Figure S14. ¹H-NMR of the deuterated reaction mixture (asterisks indicate the THF-*d8* peak) in THF-*d8*/D₂O (5:1). (a) The benzylic proton of $\mathbf{1b}^d$; (b) The benzylic proton of $\mathbf{7b}^d$; (c) The benzylic proton of $\mathbf{2b}^d$; (d) Protons of $\mathbf{4b}^d$.

2.2.5 Deprotections of *p*-toluenesulfinyl amines by catalytic iodine



To a solution of sulfinyl amine **1y** (26 mg, 0.12 mmol) in THF/H₂O (5 : 1, 3 mL) was added I₂ (6.2 mg, 0.024 mmol, 0.2 eq.). The reaction mixture was then stirred at 50 °C under air, The reaction progress was monitored by TLC. After completely consumption of sulfinyl amine **1y**, the reaction mixture was cooled to room temperature and diluted with water (10 mL). Most of the organic solvents (THF) was removed under reduced pressure. The resulting mixture was then washed with Et₂O (3 × 5 mL). The aqueous phase was concentrated to afford **3c** (28mg, yield 94%) as colorless powder.



3-Hydroxypropan-1-aminium 4-methylbenzenesulfonate (**3c**): ¹H NMR (400 MHz, D₂O): δ 7.70 (2H, d, J = 8.4 Hz), 7.37 (2H, d, J = 8.0 Hz), 3.71 (2H, t, J = 6.0 Hz), 3.10 (2H, t, J = 7.2 Hz), 2.40 (3H, s), 1.93-1.87 (2H, m). ¹³C NMR (100 MHz, D₂O): δ 142.49, 139.45, 129.45, 125.36, 58.95, 37.35, 28.97, 20.48. HRMS (ESI+) *m/z* found: 76.0758, Calcd for C₃H₁₀NO (M – OTS)⁺: 76.0762 (**Figure S15**); HRMS (ESI-) *m/z* found: 171.0126, Calcd for C₇H₇O₃S (OTS)⁻: 171.0116 (**Figure S16**).



Figure S15



Figure S16



































S63















S69

























































































S112

























































S139












S145











S150





