Supporting Information for:

**Samarium Diiodide-Induced Asymmetric Synthesis of Optically Pure
Unsymmetrical Vicinal Diamines by Reductive Cross-Coupling of
Nitrones with *N-tert*-Butanesulfinyl Imines**

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1. General procedure for the cross-coupling of nitrones with *N*-*tert*-butylsulfinyl imines.

Under argon, to a 10 mL Schlenk flask charged with Sm metal powder (230 mg, 1.5 mmol) was syringed diiodomethane (0.081 mL, 1.0 mmol) in 5 mL of freshly distilled THF at room temperature. After approximately 5 mins, the color of the mixture solution turned to deep blue, indicating the formation of samarium diiodide. The mixture was stirred at room temperature for 1 hour and then cooled to -78°C . A mixture of 1.0 mmol of *tert*-butyl alcohol, 0.7 mmol of nitrone,¹ and 0.5 mmol of chiral *N*-*tert*-butylsulfinyl imine² in 6 mL of THF was then added dropwise. The reaction was monitored by TLC, and quenched with 5 mL of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$. Extraction with ethyl acetate and purification by flash column chromatography afforded the desired product.

2. Characterization of the obtained optically active unsymmetrical 1,2-diamines.

Mp $122\text{--}124^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{20} = -142.6^{\circ}$ (c 1.05, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 0.56 (d, $J = 5.4$ Hz, 3H), 1.17 (m, 12H), 2.30 (m, 1H), 2.82 (dd, $J = 10.2, 1.2$ Hz, 1H), 3.93 (d, $J = 13.8$ Hz, 1H), 4.29 (d, $J = 13.4$ Hz, 1H), 4.59 (d, $J = 10.2$ Hz, 1H), 5.68 (s, 1H), 6.64 (s, 1H), 7.24–7.34 (m, 10H); FT-IR (KBr, cm^{-1}): 3580, 3223, 3062, 3034, 2965, 1475, 1031, 1010, 702; EI-MS (m/z , %): 331 ($\text{M}^+ - \text{C}_4\text{H}_9$, 5.71), 313 ($\text{M}^+ - \text{C}_4\text{H}_9 - \text{H}_2\text{O}$, 0.59), 179 (12.75), 178 (100.00), 162 (5.92), 106 (8.67), 92 (8.39), 91 (97.72), 57 (8.14); ^{13}C NMR (75 MHz, CDCl_3): δ 20.48, 22.14, 22.44, 26.01, 55.16, 57.06, 60.87, 72.25, 127.22, 127.67, 128.17, 128.31, 128.91, 129.12, 138.23, 141.15; HRMS for $\text{C}_{22}\text{H}_{32}\text{N}_2\text{O}_2\text{S}$: calcd. 389.2257, found: 389.2295.

The X-ray diffraction data is as follows:

audit_creation_method	SHELXL-97
chemical_formula_sum	'C22 H33 N2 O2.50 S'
chemical_formula_weight	397.56
symmetry_cell_setting	Monoclinic
symmetry_space_group_name_H-M	P2(1)
cell_length_a	8.9324(8)
cell_length_b	18.4511(16)
cell_length_c	14.0752(12)
cell_angle_alpha	90.00
cell_angle_beta	92.582(2)
cell_angle_gamma	90.00
cell_volume	2317.4(3)
cell_formula_units_Z	4
cell_measurement_temperature	293(2)
cell_measurement_reflns_used	1662
cell_measurement_theta_min	5.071
cell_measurement_theta_max	47.439

Mp 166-169°C; $[\alpha]_D^{20} = -120.0^\circ$ (*c* 0.85, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 0.50 (ddd, *J* = 25.5, 13.2, 3.0 Hz, 1H), 0.86 (m, 2H), 1.14 (s, 9H), 1.26 (m, 1H), 1.39 (td, *J* = 11.7, 3.3 Hz, 2H), 1.52 (d, *J* = 11.7 Hz, 2H), 1.64 (d, *J* = 12.9 Hz, 1H), 1.92 (t, *J* = 11.7 Hz, 1H), 2.05 (m, 1H), 2.73 (d, *J* = 10.5 Hz, 1H), 3.93 (d, *J* = 13.8 Hz, 1H), 4.30 (d, *J* = 13.8 Hz, 1H), 4.60 (d, *J* = 10.2 Hz, 1H), 5.76 (s, 1H), 6.75 (br, 1H), 7.26-7.39 (m, 10H); FT-IR (KBr, cm⁻¹): 3288, 3148, 3064, 2930, 1454, 1035, 700; EI-MS (*m/z*, %): 371 (*M*⁺ - C₄H₉, 3.87), 219 (16.40), 218 (100.00), 202 (7.86), 106 (6.93), 105 (7.18), 92 (6.74), 91 (81.88), 57 (8.65); ¹³C NMR (75 MHz, CDCl₃): δ 22.45, 26.32, 27.06, 27.48, 31.33, 32.61, 37.07, 55.19, 57.15, 60.74, 72.73, 127.23, 127.65, 128.15, 128.33, 128.91, 129.07, 138.27, 141.44; HRMS for C₂₅H₃₆N₂O₂SNa (*M*⁺ + Na): calcd. 451.2390, found: 451.2417.

Mp 79-81°C; $[\alpha]_D^{20} = -96.2^\circ$ (*c* 0.85, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 0.60 (m, 1H), 0.80 (t, *J* = 7.3 Hz, 3H), 1.00-1.20 (m, 6H), 1.21 (s, 9H), 1.31 (m, 2H), 1.95 (m, 1H), 2.62 (m, 1H), 3.86 (d, *J* = 13.5 Hz, 1H), 4.16 (d, *J* = 13.4 Hz, 1H), 4.30 (d, *J* = 10.0 Hz, 1H), 5.58 (s, 1H), 6.80 (br, 1H), 7.27-7.41 (m, 10H); FT-IR (KBr, cm⁻¹): 3271, 3200, 3032, 2931, 1455, 1033, 699; EI-MS (*m/z*, %): 373 (*M*⁺ - C₄H₉, 4.18), 221 (16.28), 220 (100.00), 204 (9.95), 106 (6.79), 105 (8.04), 92 (7.54), 91 (91.14), 57 (11.03); ¹³C NMR (75 MHz, CDCl₃): δ 13.95, 22.35, 22.47, 24.53, 28.49, 29.22, 31.22, 55.26, 60.37, 60.47, 69.60,

127.16, 127.75, 128.23, 128.27, 128.75, 128.82, 138.00, 140.22; HRMS for $C_{25}H_{38}N_2O_2SNa$ ($M^+ + Na$): calcd. 453.2546, found: 453.2565.

$[\alpha]_D^{20} = -113.0^\circ$ (c 1.30, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$): δ 0.43 (d, $J = 4.5$ Hz, 3H), 0.77 (s, 3H), 0.80 (m, 1H), 1.21 (s, 9H), 1.22 (m, 1H), 1.88 (m, 1H), 2.73 (m, 1H), 3.82 (d, $J = 13.2$ Hz, 1H), 4.11 (d, $J = 13.8$ Hz, 1H), 4.26 (d, $J = 9.9$ Hz, 1H), 5.63 (s, 1H), 6.74 (s, 1H), 7.26-7.41 (m, 10H). FT-IR (KBr, cm^{-1}): 3235, 3065, 1456, 1040, 761, 701; EI-MS (m/z , %): 345 ($M^+ - C_4H_9$, 3.73), 193 (14.55), 192 (100.00), 176 (12.28), 106 (5.86), 104 (5.72), 92 (8.27), 91 (99.04), 57 (7.90); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.39, 22.51, 22.54, 26.38, 33.80, 55.33, 60.49, 61.06, 68.11, 127.20, 127.86, 128.26, 128.31, 128.80, 128.91, 138.21, 140.32; HRMS for $C_{23}H_{35}N_2O_2S$ ($M^+ + H$): calcd. 403.2414, found: 403.2399.

Mp 181-183 °C; $[\alpha]_D^{20} = -119.3^\circ$ (c 0.80, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$): δ 1.19 (s, 9H), 1.69 (m, 1H), 1.93-2.06 (m, 2H), 2.23 (m, 1H), 2.66 (m, 1H), 3.60 (d, $J = 13.8$ Hz, 1H), 4.06 (d, $J = 13.5$ Hz, 1H), 4.35 (d, $J = 9.9$ Hz, 1H), 5.46 (s, 1H), 6.58 (s, 1H), 6.87 (m, 2H), 7.14-7.39 (m, 13H); FT-IR (KBr, cm^{-1}): 3265, 3137, 3030, 1453, 1031, 699; ESI-MS ($M^+ + H$): 451.3; ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.43, 26.60, 34.02, 55.16, 60.14, 60.42, 68.17, 125.71, 127.11, 127.95, 128.19, 128.21, 128.34, 128.39, 128.81, 137.75, 140.08, 141.54; HRMS for $C_{27}H_{34}N_2O_2SNa$ ($M^+ + Na$): calcd. 473.2233, found: 473.2247.

Mp 154-157 °C; $[\alpha]_D^{20} = -135.2^\circ$ (c 1.05, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 9H), 1.08 (s, 9H), 2.95 (d, $J = 7.5$ Hz, 1H), 4.24 (AB, $\delta_A = 4.22$, $\delta_B = 4.28$, $J_{AB} = 13.8$ Hz, 2H), 4.71 (dd, $J = 7.5$, 1.8 Hz, 1H), 5.81 (s, 1H), 6.31 (s, 1H), 7.24-7.34 (m, 10H); FT-IR (KBr, cm^{-1}): 3227, 3028, 1455, 1042, 741, 701; EI-MS (m/z , %): 403 ($M^+ + H$, 0.07), 345 ($M^+ - C_4H_9$, 3.21), 193 (12.72), 192 (80.28), 135 (10.74), 106 (13.45), 92 (9.89), 91 (100.00), 57 (19.68), 41 (7.61); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.62, 29.50, 37.46, 55.02, 59.01, 65.23, 76.84, 127.00, 127.40, 128.28, 128.84, 129.19, 139.38, 142.46; HRMS for $C_{23}H_{35}N_2O_2S$ ($M^+ + H$): calcd. 403.2413, found: 403.2419.

Mp 128-130 °C; $[\alpha]_D^{20} = -131.8^\circ$ (c 1.30, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$): δ 0.58 (d, $J = 7.5$ Hz, 3H), 1.14 (s, 9H), 1.15 (d, $J = 7.5$ Hz, 3H), 2.28 (m, 1H), 2.33 (s, 3H), 2.80 (dd, $J = 9.9$, 1.2 Hz, 1H), 3.93 (d, $J = 13.8$ Hz, 1H), 4.28 (d, $J = 13.5$ Hz, 1H), 4.57 (d, $J = 9.9$ Hz, 1H), 5.65 (s, 1H), 6.58 (s, 1H), 7.10 (d, $J = 7.8$ Hz,

2H), 7.17 (d, $J = 8.1$ Hz, 2H), 7.28-7.38 (m, 5H); FT-IR (KBr, cm^{-1}): 3227, 3141, 3030, 1457, 1365, 1027; EI-MS (m/z , %): 403 ($M^+ + H$, 0.16), 345 ($M^+ - C_4H_9$, 2.84), 179 (11.09), 178 (82.61), 145 (5.65), 120 (17.58), 92 (9.39), 91 (100.00), 57 (13.35), 41 (6.54); ^{13}C NMR (75 MHz, CDCl_3): δ 20.43, 21.10, 22.03, 22.43, 25.98, 55.02, 56.63, 60.90, 72.22, 127.11, 128.22, 128.81, 128.87, 128.94, 137.21, 137.83, 138.22; HRMS for $\text{C}_{23}\text{H}_{35}\text{N}_2\text{O}_2\text{S}$ ($M^+ + H$): calcd. 403.24134, found: 403.2430.

Mp 136-138°C; $[\alpha]_D^{20} = -146.7^\circ$ (c 0.95, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 0.57 (d, $J = 7.5$ Hz, 3H), 1.15 (m, 12H), 2.29 (m, 1H), 2.77 (d, $J = 10.2$ Hz, 1H), 3.80 (s, 3H), 3.93 (d, $J = 12.9$ Hz, 1H), 4.27 (d, $J = 13.2$ Hz, 1H), 4.54 (d, $J = 10.2$ Hz, 1H), 5.65 (s, 1H), 6.59 (s, 1H), 6.83 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.26-7.38 (m, 5H); FT-IR (KBr, cm^{-1}): 3242, 3146, 3033, 1614, 1513, 1257, 1025; EI-MS (m/z , %): 419 ($M^+ + H$, 0.07), 361 ($M^+ - C_4H_9$, 2.28), 179 (12.22), 178 (86.22), 176 (10.57), 161 (11.57), 136 (46.71), 92 (10.10), 91 (100.00), 57 (12.59); ^{13}C NMR (75 MHz, CDCl_3): δ 20.43, 22.06, 22.46, 25.97, 55.03, 55.08, 56.45, 60.81, 72.35, 113.49, 127.18, 128.28, 128.89, 130.05, 133.02, 138.23, 158.94; HRMS for $\text{C}_{23}\text{H}_{35}\text{N}_2\text{O}_3\text{S}$ ($M^+ + H$): calcd. 419.2363, found: 419.2360.

Mp 46-49°C; $[\alpha]_D^{20} = -127.5^\circ$ (c 1.75, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 0.58 (d, $J = 7.5$ Hz, 3H), 1.15 (m, 12H), 2.30 (m, 1H), 2.76 (d, $J = 9.9$ Hz, 1H), 3.93 (d, $J = 12.9$ Hz, 1H), 4.27 (d, $J = 13.5$ Hz, 1H), 4.55 (d, $J = 10.2$ Hz, 1H), 5.68 (s, 1H), 6.72 (s, 1H), 7.21-7.36 (m, 9H); FT-IR (KBr, cm^{-1}): 3232, 3065, 1492, 1038; EI-MS (m/z , %): 365 ($M^+ - C_4H_7$, 0.34), 178 (20.31), 92 (9.32), 91 (100.00), 89 (4.24), 65 (8.73), 57 (12.90), 43 (7.24), 41 (6.93); ^{13}C NMR (75 MHz, CDCl_3): δ 20.54, 22.06, 22.40, 26.03, 55.18, 56.60, 60.77, 72.27, 127.28, 128.34, 128.46, 128.87, 130.31, 133.31, 138.04, 139.98; HRMS for $\text{C}_{22}\text{H}_{32}\text{N}_2\text{O}_2\text{SCl}$ ($M^+ + H$): calcd. 423.1868, found: 423.1871

$[\alpha]_D^{20} = -119.7^\circ$ (c 1.60, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 0.59 (d, $J = 7.2$ Hz, 3H), 1.13 (m, 12H), 2.28 (m, 1H), 2.75 (d, $J = 9.9$ Hz, 1H), 3.92 (d, $J = 12.9$ Hz, 1H), 4.27 (d, $J = 13.5$ Hz, 1H), 4.53 (d, $J = 10.2$ Hz, 1H), 5.66 (s, 1H), 6.64 (s, 1H), 7.16 (d, $J = 8.4$ Hz, 2H), 7.34 (m, 5H), 7.42 (d, $J = 8.4$ Hz, 2H); FT-IR (KBr, cm^{-1}): 3247, 1488, 1365, 1040; ESI-MS ($M^+ + H$): 467.1, 469.0; ^{13}C NMR (75 MHz, CDCl_3): δ 20.56, 22.29, 22.42, 26.02, 55.28, 56.57, 60.81, 72.19, 121.54, 127.33, 128.37, 128.91, 130.76, 131.43, 138.06, 140.44; HRMS for $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}_2\text{SBrNa}$ ($M^+ + \text{Na}$): calcd. 489.1182, found: 489.1181.

 $[\alpha]_D^{20} = -132.0^\circ$ (*c* 1.45, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 0.60 (d, *J* = 7.2 Hz, 3H), 1.13 (s, 9H), 1.14 (d, *J* = 6.6 Hz, 3H), 2.27 (m, 1H), 2.28 (s, 3H), 2.77 (d, *J* = 10.2 Hz, 1H), 3.93 (d, *J* = 12.9 Hz, 1H), 4.27 (d, *J* = 13.2 Hz, 1H), 4.57 (d, *J* = 10.5 Hz, 1H), 5.68 (s, 1H), 6.75 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 7.26-7.35 (m, 7H); FT-IR (KBr, cm⁻¹): 3246, 1766, 1218, 1040; ESI-MS (*M*⁺ + H): 447.1; ¹³C NMR (75 MHz, CDCl₃): δ 20.57, 21.14, 22.11, 22.43, 26.04, 55.24, 56.50, 60.86, 72.34, 121.24, 127.25, 128.32, 128.90, 129.94, 138.15, 138.70, 150.04, 169.18; HRMS for C₂₄H₃₄N₂O₄SNa (*M*⁺ + Na): calcd. 469.2131, found: 469.2132.

Mp 90-93 °C; $[\alpha]_D^{20} = -98.3^\circ$ (*c* 2.90, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.00-1.40 (m, 3H), 1.18 (s, 9H), 2.04 (m, 1H), 2.70 (m, 1H), 3.16 (t, *J* = 6.0 Hz, 2H), 3.86 (d, *J* = 13.8 Hz, 1H), 4.18 (d, *J* = 13.5 Hz, 1H), 4.30 (d, *J* = 12.6 Hz, 1H), 4.33 (s, 2H), 6.53 (s, 1H), 6.91 (s, 1H), 7.24-7.41 (m, 15H); FT-IR (KBr, cm⁻¹): 3268, 3170, 3030, 1454, 1031, 698; ESI-MS (*M*⁺ + H): 495.1; ¹³C NMR (75 MHz, CDCl₃): δ 21.22, 22.39, 28.39, 55.12, 60.24, 69.27, 69.90, 72.40, 77.21, 127.09, 127.29, 127.34, 127.75, 128.16, 128.21, 128.26, 128.64, 128.76, 137.88, 138.86, 140.12; HRMS for C₂₉H₃₉N₂O₃S (*M*⁺ + H): calcd. 495.2676, found: 495.2663.

 $[\alpha]_D^{20} = -100.1^\circ$ (*c* 1.10, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 0.99 (m, 1H), 1.19 (s, 9H), 1.36 (m, 2H), 1.98 (s, 3H), 2.00 (m, 1H), 2.68 (m, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 3.85 (d, *J* = 12.9 Hz, 1H), 4.17 (d, *J* = 13.2 Hz, 1H), 4.32 (d, *J* = 10.2 Hz, 1H), 5.52 (s, 1H), 7.00 (s, 1H), 7.30-7.39 (m, 10H); FT-IR (KBr, cm⁻¹): 3238, 2961, 1738, 1243, 1040; ESI-MS (*M*⁺ + H): 447.3; ¹³C NMR (100 MHz, CDCl₃): δ 20.88, 21.13, 22.49, 27.38, 55.36, 60.28, 60.53, 64.07, 69.09, 127.35, 128.02, 128.41, 128.46, 128.68, 128.84, 137.83, 140.13, 170.93; HRMS for C₂₄H₃₄N₂O₄SNa (*M*⁺ + Na): calcd. 469.2131, found: 469.2139.

Mp 132 °C; $[\alpha]_D^{20} = -125.4^\circ$ (*c* 0.75, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 1.10 (m, 1H), 1.19 (s, 9H), 1.27 (m, 1H), 1.43 (m, 1H), 2.05 (m, 1H), 2.77 (m, 1H), 3.70-3.90 (m, 5H), 4.18 (d, *J* = 13.2 Hz, 1H), 4.30 (d, *J* = 9.6 Hz, 1H), 4.54 (t, *J* = 4.5 Hz, 1H), 5.50 (s, 1H), 6.54 (s, 1H), 7.25-7.40 (m, 10H); FT-IR (KBr, cm⁻¹): 3250, 1454, 1141, 1030, 699; ESI-MS (*M*⁺ + H): 447.3; ¹³C NMR (75 MHz, CDCl₃): δ 18.85, 22.41, 32.08, 55.21, 60.18, 60.29, 64.58, 64.63, 69.07, 104.04, 127.17, 127.86, 128.28, 128.33, 128.68, 128.82, 137.90, 140.08; HRMS for C₂₄H₃₄N₂O₄SNa (*M*⁺ + Na): calcd. 469.2131, found: 469.2123.

3. Conversion of the cross-coupling product **3** to free diamine **4**.

Under argon, to a 5 mL of flask charged with 1 mL of acetic acid was added Cu(OAc)_2 (9 mg, 0.05 mmol) and zinc powder (162 mg, 2.5 mmol). The mixture was stirred for 15 mins, followed by the addition of a mixture of acetic acid (1 mL) and distilled water (0.35 mL) containing 194 mg of **3** (0.5 mmol). The resulting mixture was heated to 70°C and stirred for 1 hour. After cooling to room temperature, the reacting system was mixed with 0.5 g of EDTA-2Na and stirred for 10 mins. 3 N aqueous KOH solution was then added to basify the mixture to a pH value of 10. The resulting solution was extracted with ethyl acetate, and the combined organic layer was washed with saturated aqueous EDTA-2Na and brine successively. Purification by flash column chromatography afforded 185 mg of deoxygenation product as a white solid in quantitative yield. $[\alpha]_{\text{D}}^{20} = -178.6^\circ$ (*c* 0.90, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 0.84 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 7.2 Hz, 3H), 1.14 (s, 9H), 1.71 (m, 1H), 2.68 (dd, *J* = 9.0, 3.0 Hz, 1H), 2.73 (s, 1H), 3.77 (d, *J* = 12.9 Hz, 1H), 4.00 (d, *J* = 12.9 Hz, 1H), 4.20 (d, *J* = 8.7 Hz, 1H), 5.40 (s, 1H), 7.28 (m, 10H); FT-IR (KBr, cm^{-1}): 3256, 2958, 1454, 1060, 704; ESI-MS ($\text{M}^+ + \text{H}$): 373.4; ^{13}C NMR (75 MHz, CDCl_3): δ 16.31, 21.55, 22.62, 28.89, 54.78, 55.01, 59.82, 68.26, 127.12, 127.56, 128.04, 128.33, 128.42, 128.46, 140.34, 141.19; HRMS for $\text{C}_{22}\text{H}_{32}\text{N}_2\text{OSNa}$ ($\text{M}^+ + \text{Na}$): calcd. 395.2127, found: 395.2140

74 mg (0.2 mmol) of the above-obtained deoxygenation product was dissolved in 2.0 mL of methanol, to which was added 0.5 mL of 4 N HCl in 1,4-dioxane (2.0 mmol). The mixture was stirred for 30 mins at room temperature and then concentrated. The resulting solid was recrystallized using a mixture of methanol and ethyl ether to provide a white powder (60 mg), which was dissolved in methanol (5 mL) containing 16 mg of 10% $\text{Pd(OH)}_2/\text{C}$. The mixture was reacted for 24 hours under 1 atm of H_2 atmosphere and was filtrated through a pad of celite. To the filtrate was added 2.0 mL of 4 N HCl in 1,4-dioxane. The solution was then concentrated to afford a foamy solid, which was recrystallized in a mixture of methanol and ethyl ether to provide 44 mg of (*R,R*)-**4** ³ in 87% overall yield. $[\alpha]_{\text{D}}^{20} = +11.9$ (*c* 1.00, MeOH); ^1H NMR (300 MHz, D_2O): δ 0.82 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 1.79 (m, 1H), 3.83 (dd, *J* = 9.6, 3.3 Hz, 1H), 4.68 (d, *J* = 9.3 Hz, 1H), 7.48 (m, 5H).

For comparison, (*S,S*)-**4** (ent-**4**) was also prepared by the reaction of nitrone **1** with (*S*)-*N*-*tert*-butanesulfinyl imine **2** following the similar procedures

4. Determination of the enantiomeric excess.

The optical purity of diamine **4** was determined by measuring the *ee* value of their diacetate derivative.

HPLC: Daicel Chiralpak AS column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol 8:2; ¹H NMR (300 MHz, CDCl₃): δ 0.84 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 1.59 (m, 1H), 1.92 (s, 3H), 2.03 (s, 3H), 4.22 (td, *J* = 10.5, 3.3 Hz, 1H), 4.98 (dd, *J* = 10.8, 8.7 Hz, 1H), 5.99 (d, *J* = 9.9 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 7.27-7.37 (m, 5H); ESI-MS (*M*⁺ + *H*): 263.2; ¹³C NMR (75 MHz, CDCl₃): δ 15.32, 20.63, 23.22, 23.32, 27.44, 56.49, 58.61, 127.33, 127.97, 129.00, 139.61, 170.19, 171.98. HRMS for C₁₅H₂₂N₂O₂Na (*M*⁺ + Na): calcd. 285.1573, found: 285.1586.

References:

1. Nitrones were prepared from *N*-benzylhydroxyamine and the corresponding aldehydes, see: Dondoni, S.; Franco, S.; Junquera, F.; Merino, P.; Tejero, T. *Synth. Commun.* **1994**, *24*, 2537-2550.
2. Chiral *N*-*tert*-butylsulfinyl imines were prepared from Chiral *N*-*tert*-butylsulfinyl amine and the corresponding aldehydes according to Prof. Ellman's method: (a) Cogan, D. A.; Liu, G.; Kim, K.; Backes, B. J.; Ellman, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 8011-8019. (b) Liu, G.-C.; Cogan, D. A.; Owens, T. D.; Tang, T. P.;

Ellman, J. A *J. Org. Chem.* **1999**, *64*, 1278-1284. (c) Weix, D. J.; Ellman, J. A. *Org. Lett.* **2003**, *5*, 1317-1320.

3. Hydrochloro salt of chiral diamine (*S, S*)-**4** was reported with a specific optical rotation of -15.5 (*c* 0.74, MeOH), however, its optical purity was not clarified, see: Merino, P.; Lanaspa, A.; Merchan, F. L.; Tejero, T. *Tetrahedron: Asymmetry* **1997**, *8*, 2381-2401.