Asymmetric Route to Pyridines Bearing a Highly Functionalized 2-Alkyl Substituent by Aziridine Ring Opening Reactions

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General Methods

Melting points are uncorrected. Optical rotations were measured on a digital polarimeter in a 1 dm cell and $[\alpha]_D$ -values are given in $10^{-1} \text{ deg cm}^3 \text{ g}^{-1}$. ^1H NMR spectra were recorded on 300 or 200 MHz instruments, for samples in CDCl_3 which was stored over Mg: ^1H chemical shifts are reported in ppm relative to CHCl_3 (δ_{H} 7.27) and J -values are given in. MS spectra were taken at an ionizing voltage of 70 eV on a spectrometer equipped with GLC injection. LC-electron spray ionization (ESI) mass spectra were obtained with a single-quadrupole mass spectrometer. Chromatographic separations were performed on columns of SiO_2 (230-400 mesh) or neutral aluminium oxide at medium pressure. Anhydrous THF, CH_2Cl_2 , CH_3CN were stored over molecular sieves.

(S)-2-[(R)-2-Hydroxy-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2a): Yellow oil; $[\alpha]_{\text{D}}^{20} +24.2$ (*c* 1.3, CHCl_3). IR (neat): $\nu = 3406, 2962, 2925, 1658, 1597, 1413, 1260, 1049, 794, 751$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.55$ (ddd, $J = 0.7, J = 1.3, J = 4.7$, 1 H), 7.72 (dt, $J = 1.7, J = 7.6$, 1 H), 7.38 (dt, $J = 0.9, J = 7.9$, 1 H), 7.23 (ddd, $J = 0.7, J = 4.7, J = 7.6$, 1 H), 4.86 (dd, $J = 3.6, J = 7.5$, 1 H), 3.65 (dd, $J = 4.1, J = 10.8$, 1 H), 3.38 (dd, $J = 7.7, J = 10.8$, 1 H), 3.06 (dd, $J = 3.6, J = 12.0$, 1 H), 2.97 (bs, 3 H), 2.90 (dd, $J = 7.5, J = 12.0$, 1 H), 2.43 (ddd, $J = 4.1, J = 6.7, J = 7.7$, 1 H), 1.81 (sept, $J = 6.9$, 1 H), 0.97 (d, $J = 6.8$, 3 H), 0.90 (d, $J = 6.8$, 6 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 160.3, 148.3, 136.9, 122.6, 120.6, 72.3, 64.8, 61.0, 54.0, 29.1, 19.5, 18.5$. GC-MS m/z 207 (2), 193 (26), 181(8), 175 (10), 121(44), 116 (60), 109 (100), 108 (24), 94 (25), 79 (19), 69 (11); MS (ES) m/z 225.4 ($\text{M} + \text{H}$)⁺. Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2$: C, 64.26; H, 8.99; N, 12.49. Found C, 64.06; H, 9.01; N, 12.44.

(S)-2-[(R)-2-Azido-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2b): Red oil; $[\alpha]_{\text{D}}^{20} +76.8$ (*c* 1.7, CHCl_3). IR (neat): $\nu = 3380, 2956, 2922, 2102, 1592, 1472, 1436, 1155, 1117$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.61$ (ddd, $J = 0.9, J = 1.8, J = 4.7$, 1 H), 7.74 (dt, $J = 1.8, J = 7.7$, 1 H), 7.38 (dt, $J = 0.9, J = 7.7$, 1 H), 7.26 (ddd, $J = 1.1, J = 4.7, J = 7.5$, 1 H), 4.64 (dd, $J = 5.0, J = 7.6$, 1 H), 3.59 (dd, $J = 4.1, J = 10.8$, 1 H), 3.31 (dd, $J = 7.7, J = 10.8$, 1 H), 3.30 (dd, $J = 5.0, J = 12.5$, 1 H), 3.19 (dd, $J = 7.6, J = 12.5$, 1 H), 2.39 (dd, $J = 4.1, J = 7.7$, 1 H), 2.14 (bs, 2 H), 1.77 (sept, $J = 6.9$, 1 H), 0.94 (d, $J = 6.9$, 3 H), 0.88 (d, $J = 6.9$, 3 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 157.5, 149.6, 137.0,$

123.2, 121.9, 66.7, 64.8, 61.0, 51.1, 29.2, 19.4, 18.4. MS (ES) m/z 250.2 ($M + H$)⁺, 272.1 ($M + Na$)⁺. Anal. Calcd for C₁₂H₁₉N₅O: C, 57.81; H, 7.68; N, 28.09; O, 6.42. Found C, 57.55; H, 7.70; 27.99.

(S)-2-[(R)-2-(Benzylamino)-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2c): Yellow oil; $[\alpha]_D^{20} +30.8$ (c 1.7, CHCl₃); IR (neat): ν = 3308, 3061, 3028, 2956, 2921, 2864, 1591, 1570, 1454, 1434, 1366, 1121, 1048, 749, 699. ¹H NMR (300 MHz, CDCl₃): δ = 8.63 (ddd, J = 0.8, J = 1.8, J = 4.8, 1 H), 7.63 (td, J = 1.8, J = 7.7, 1 H), 7.35 (m, 5 H), 7.28 (m, 1 H), 7.23 (ddd, J = 1.2, J = 4.8, J = 7.5, 1 H), 3.87 (dd, J = 5.9, J = 7.2, 1 H), 3.72 (d, J = 12.9, 1H), 3.61 (d, J = 12.9, 1 H), 3.59 (dd, J = 4.0, J = 10.7, 1 H), 3.35 (dd, J = 7.8, J = 10.7, 1 H), 2.91 (m, 2 H), 2.53 (bs, 3 H), 2.39 (dd, J = 4.0, J = 7.8, 1 H), 1.78 (sept, J = 6.8, 1 H), 0.86 (d, J = 6.8, 3 H), 0.88 (d, J = 6.8, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 161.7, 149.5, 140.1, 136.4, 128.3, 128.2, 126.9, 122.7, 122.3, 64.6, 63.2, 52.8, 51.6, 29.4, 19.5, 18.7. MS (ES) m/z 314.3 ($M + H$)⁺. Anal. Calcd for C₁₉H₂₇N₃O: C, 72.81; H, 8.68; N, 13.41. Found C, 72.88; H, 8.71; N, 13.37.

(S)-2-[(R)-2-(4-Methoxyphenylamino)-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2d): Red oil; $[\alpha]_D^{20} +21.1$ (c 1.3, CHCl₃). IR (neat): ν = 3333, 2957, 2928, 2872, 2828, 1592, 1512, 1465,

1435, 1239, 1039. ^{13}H NMR (300 MHz, CDCl_3): δ = 8.58 (ddd, J = 0.8, J = 1.7, J = 4.8, 1 H), 7.63 (dt, J = 1.7, J = 7.6, 1 H), 7.36 (dt, J = 0.8, J = 7.8, 1 H), 7.18 (ddd, J = 1.2, J = 4.8, J = 7.6, 1 H), 6.72 (d, J = 9.1, 2 H), 6.60 (d, J = 9.1, 2 H), 4.54 (dd, J = 4.8, J = 7.1, 1 H), 3.78 (s, 3 H), 3.62 (dd, J = 4.1, J = 10.8, 1 H), 3.38 (dd, J = 7.5, J = 10.8, 1 H), 3.13 (dd, J = 4.8, J = 11.9, 1 H), 3.05 (dd, J = 7.1, J = 11.9, 1 H), 2.73 (bs, 2 H), 2.43 (ddd, J = 4.1, J = 6.5, J = 7.5, 1 H), 1.81 (sept, J = 6.8, 1 H), 0.93 (d, J = 6.8, 3 H), 0.87 (d, J = 6.8, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 161.2, 152.4, 149.3, 141.4, 136.8, 122.4, 121.8, 115.5, 114.7, 64.8, 60.9, 60.3, 55.6, 52.4, 28.9, 19.4, 18.4; MS (ES) m/z 330.2 ($\text{M} + \text{H}$) $^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_2$: C, 69.27; H, 8.26; N, 12.76. Found C, 69.52; H, 8.30; N, 12.71.

(S)-2-((R)-2-(dibenzylamino)-2-(pyridin-2-yl)ethylamino)-3-methylbutan-1-ol (2e): Red oil; $[\alpha]_{\text{D}}^{20}$ +24.3 (c 1.4, CHCl_3). IR (neat): ν = 3357, 3061, 3028, 2959, 2925, 1589, 1453, 1434, 1261, 1072, 1027, 698. ^1H NMR (300 MHz, CDCl_3): δ = 8.60 (ddd, J = 0.8, J = 1.7, J = 4.9, 1 H), 7.71 (td, J = 1.9, J = 7.6, 1 H), 7.36 (m, 9H), 7.23 (m, 3H), 3.96 (dd, J = 6.7, J = 6.9, 1 H), 3.84 (d, J = 13.8 2H), 3.64 (dd, J = 4.1, J = 10.8, 1 H), 3.42 (d, J = 13.8 2 H), 3.37 (m, 2 H), 3.20 (dd, J = 7.4, J = 11.6, 1 H), 2.38 (dd, J = 4.1, J = 6.9, 1 H), 1.76 (sept, J = 6.8, 1 H), 0.95 (d, J = 6.8, 3 H), 0.89 (d, J = 6.8, 6 H). ^{13}C NMR (75 MHz, CDCl_3) δ = 159.4, 148.8, 139.8, 136.1, 128.7, 128.3, 127.0, 124.5, 122.2, 64.5, 62.2, 60.9, 54.3, 45.5, 29.5, 19.6, 18.9. MS (ES) m/z 404.5 ($\text{M} + \text{H}$) $^+$. Anal. Calcd for $\text{C}_{26}\text{H}_{33}\text{N}_3\text{O}$: C, 77.38; H, 8.24; N, 10.41. Found C, 77.10; H, 8.27; N, 10.37.

(S)-2-[(R)-2-(2-Naphthylthio)-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2f): Yellowish oil; $[\alpha]_{\text{D}}^{20} +51.8$ (*c* 1.7, CHCl_3). IR (neat): $\nu = 3412, 3330, 3055, 3009, 2954, 1584, 1565, 1474, 1432, 1105, 1044, 748, 692$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.56$ (ddd, $J = 0.9, J = 1.9, J = 4.8$, 1 H), 7.71 (m, 2 H), 7.69 (m, 2 H), 7.59 (dt, $J = 1.8, J = 7.7$, 1 H), 7.46 (m, 2 H), 7.39 (dd, $J = 1.8, J = 8.5$, 1 H), 7.28 (dt, $J = 0.9, J = 7.8$, 1 H), 7.16 (ddd, $J = 1.1, J = 4.9, J = 7.8$, 1 H), 4.61 (dd, $J = 6.4, J = 6.6$, 1 H), 3.60 (dd, $J = 4.1, J = 10.8$, 1 H), 3.40 (dd, $J = 6.4, J = 12.3$, 1 H), 3.33 (dd, $J = 7.4, J = 10.8$, 1 H), 3.29 (dd, $J = 6.4, J = 12.2$, 1 H), 2.65 (bs, 2 H), 2.42 (ddd, $J = 4.1, J = 6.4, J = 7.4$, 1 H), 1.78 (sept, $J = 6.8$, 1 H), 0.93 (d, $J = 6.8$, 3 H), 0.88 (d, $J = 6.8$, 3 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 159.8, 149.4, 136.6, 133.5, 132.3, 131.4, 130.9, 129.4, 128.4, 127.6, 127.4, 126.5, 126.2, 123.1, 122.4, 64.7, 60.8, 54.8, 50.5, 29.2, 19.6, 18.6$. MS (ES) m/z 367.3 ($\text{M} + \text{H}$) $^+$, 389.1 ($\text{M} + \text{Na}$) $^+$. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{OS}$: C, 72.09; H, 7.15; N, 7.64. Found C, 71.83; H, 7.16; N, 7.62.

(S)-2-[(R)-2-(Phenylthio)-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2g): Yellow oil; $[\alpha]_{\text{D}}^{20} +87.7$ (*c* 1.2, CHCl_3). IR (neat): $\nu = 3419, 3332, 3056, 3006, 2957, 2925, 2871, 1589, 1569, 1471, 1434, 1385, 1109, 1049, 1025, 747, 691$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.57$ (ddd, $J = 0.9, J = 1.8, J = 4.8$, 1 H), 7.74 (dt, $J = 1.8, J = 7.7$, 1 H), 7.33 (m, 3 H), 7.25 (m, 3 H), 7.17 (ddd, $J = 0.9, J = 4.8, J = 7.4$, 1 H), 4.47 (dd, $J = 6.7, J = 6.9$, 1 H), 3.60 (dd, $J = 4.1, J = 10.7$, 1 H), 3.35 (dd, $J =$

6.7, $J = 12.3$, 1 H), 3.31 (dd, $J = 7.6$, $J = 10.7$, 1 H), 3.26 (dd, $J = 6.9$, $J = 12.3$, 1 H), 2.48 (bs, 2 H), 2.31 (ddd, $J = 4.1$, $J = 7.1$, $J = 7.6$, 1 H), 1.77 (sept, $J = 6.9$, 1 H), 0.93 (d, $J = 6.8$, 3 H), 0.89 (d, $J = 6.8$, 6 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 159.9$, 149.3, 136.5, 134.1, 132.2, 128.8, 127.3, 123.0, 122.2, 64.5, 60.8, 55.2, 50.6, 29.2, 19.5, 18.6. MS (ES) m/z 317.1 ($\text{M} + \text{H}$) $^+$. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{OS}$: C, 67.29; H, 7.64; N, 9.23. Found C, 67.01; H, 7.65; N, 9.21.

(S)-2-[(R)-2-(Benzylthio)-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2h): Yellow oil; $[\alpha]_{\text{D}}^{20} +143.0$ (c 1.2, CHCl_3). IR (neat): $\nu = 3383$, 3061, 3028, 2956, 2925, 1590, 1494, 1471, 1453, 1434, 1049, 749, 702. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.56$ (ddd, $J = 0.8$, $J = 1.6$, $J = 4.8$, 1 H), 7.74 (dt, $J = 1.8$, $J = 7.8$, 1 H), 7.29 (m, 5 H), 7.18 (m, 2 H), 3.97 (dd, $J = 6.8$, $J = 6.8$, 1 H), 3.79 (d, $J = 13.3$, 1 H), 3.60 (d, $J = 13.3$, 1 H), 3.54 (dd, $J = 4.1$, $J = 10.7$, 1 H), 3.24 (dd, $J = 7.6$, $J = 10.7$, 1 H), 3.21 (dd, $J = 6.7$, $J = 12.1$, 1 H), 3.11 (dd, $J = 7.0$, $J = 12.1$, 1 H), 2.40 (bs, 2 H), 2.31 (dd, $J = 4.1$, $J = 7.6$, 1 H), 1.71 (sept, $J = 6.9$, 1 H), 0.89 (d, $J = 6.8$, 3 H), 0.84 (d, $J = 6.8$, 6 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 160.6$, 149.3, 137.9, 136.7, 128.9, 128.5, 127.0, 122.9, 122.2, 64.5, 60.8, 51.2, 50.6, 35.4, 29.2, 19.5, 18.6. GC-MS m/z 105 (100), 91 (93), 93 (70), 104 (40), 78 (31), 65 (30), 226 (26), 124 (26), 194 (25), 226 (18), 207 (16), 51 (16), 136 (12). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{OS}$: C, 69.05; H, 7.93; N, 8.48. Found C, 69.16; H, 7.95; N, 8.46.

(S)-2-[(R)-2-(Butylthio)-2-(2-pyridyl)ethylamino]-3-methyl-1-butanol (2i): Yellow oil; $[\alpha]_{\text{D}}^{20}$ +36.8 (*c* 1.0, CHCl_3). IR (neat): ν = 3346, 2957, 2926, 2872, 1590, 1569, 1468, 1434, 1049, 788, 748. ^1H NMR (300 MHz, CDCl_3): δ = 8.54 (ddd, J = 0.8, J = 1.8, J = 4.7, 1 H), 7.67 (dt, J = 1.8, J = 7.7, 1 H), 7.39 (dt, J = 0.8, J = 7.7, 1 H), 7.17 (ddd, J = 1.0, J = 4.7, J = 7.7, 1 H), 4.06 (dd, J = 7.1, J = 7.1, 1 H), 3.59 (dd, J = 4.2, J = 10.7, 1 H), 3.30 (dd, J = 7.5, J = 10.7, 1 H), 3.24 (dd, J = 7.1, J = 12.1, 1 H), 3.16 (dd, J = 7.1, J = 12.1, 1 H), 2.60 (bs, 2 H), 2.43 (dd, J = 6.8, J = 7.2, 2 H), 2.39 (dd, J = 4.2, J = 7.5, 1 H), 1.78 (sept, J = 6.9, 1 H), 1.47 (m, 2 H), 1.31 (m, 2 H), 0.92 (d, J = 6.9, 3 H), 0.88 (d, J = 6.9, 3 H), 0.84 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 160.9, 149.1, 136.7, 122.8, 122.1, 64.6, 60.8, 51.6, 50.6, 31.6, 30.4, 29.2, 21.9, 19.5, 18.6, 13.6. MS (ES) m/z 297.2 ($\text{M} + \text{H}$)⁺. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{OS}$: C, 64.82; H, 9.52; N, 9.45. Found C, 64.73; H, 9.52; N, 9.43.

(S)-2-[(R)-2-Hydroxy-1-(2-pyridyl)ethylamino]-3-methyl-1-butanol (3a): Yellow oil; $[\alpha]_{\text{D}}^{20}$ +38.6 (*c* 1.2, CHCl_3). IR (neat) ν = 3330, 2957, 2921, 2873, 1670, 1595, 1571, 1468, 1436, 1049, 774, 751. ^1H NMR (300 MHz, CDCl_3): δ = 8.60 (ddd, J = 0.8, J = 1.6, J = 4.9, 1 H), 7.75 (dt, J = 1.8, J = 7.7, 1 H), 7.34 (dt, J = 0.9, J = 7.7, 1 H), 7.28 (m, 1 H), 4.12 (dd, J = 4.2, J = 6.6, 1 H), 3.96 (dd, J = 4.2, J = 11.3, 1 H), 3.84 (dd, J = 6.6, J = 11.3, 1 H), 3.81 (dd, J = 3.7, J = 11.6, 1 H), 3.65 (dd, J = 6.1, J = 11.6, 1 H), 2.47 (dd, J = 3.7, J = 6.1, 1 H), 1.81 (sept, J = 6.8, 1 H), 0.95 (d, J = 6.8, 3 H), 0.90 (d, J = 6.8, 6 H). ^{13}C NMR (75 MHz, CDCl_3) δ = 159.7, 149.1, 137.1, 123.1, 122.7, 65.6,

64.1, 62.8, 61.1, 29.3, 19.3, 18.9. MS (ES) m/z 225.4 ($M + H$)⁺. Anal. Calcd for C₁₂H₂₀N₂O₂: C, 64.26; H, 8.99; N, 12.49. Found C, 64.10; H, 9.02; N, 12.45.

(S)-2-[(S)-2-Azido-1-(2-pyridyl)ethylamino]-3-methyl-1-butanol (3b): Yellow oil; $[\alpha]_D^{20} +52.8$ (*c* 1.1, CHCl₃). IR (neat): ν = 3378, 2950, 2923, 2106, 1594, 1470, 1438, 1153, 1112. ¹H NMR (300 MHz, CDCl₃): δ = 8.64 (ddd, J = 0.9, J = 1.7, J = 4.8, 1 H), 7.72 (dt, J = 1.8, J = 7.7, 1 H), 7.30 (dt, J = 0.9, J = 7.7, 1 H), 7.26 (ddd, J = 0.9, J = 4.8, J = 7.7, 1 H), 3.98 (dd, J = 6.5, J = 6.5, 1 H), 3.69 (dd, J = 3.9, J = 11.1, 1 H), 3.63 (dd, J = 6.5, J = 12.1, 1 H), 3.55 (dd, J = 6.5, J = 12.1, 1 H), 3.50 (dd, J = 5.4, J = 11.1, 1 H), 2.54 (bs, 2 H), 2.31 (dd, J = 3.9, J = 5.4, 1 H), 1.69 (sept, J = 6.8, 1 H), 0.86 (d, J = 6.8, 3 H), 0.82 (d, J = 6.8, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ = 161.7, 149.7, 136.6, 122.9, 122.7, 63.2, 31.6, 30.9, 29.5, 19.4, 18.7. MS (ES) m/z 250.2 ($M + H$)⁺. Anal. Calcd for C₁₂H₁₉N₅O: C, 57.81; H, 7.68; N, 28.09; O, 6.42. Found C, 57.58; H, 7.71; N, 28.00.

(S)-2-[(S)-2-Benzylamino-1-(2-pyridyl)ethylamino]-3-methyl-1-butanol (3c): Yellow oil. $[\alpha]_D^{20} +22.3$ (*c* 1.7, CHCl₃). IR (neat): ν = 3308, 3062, 2955, 2915, 2866, 2850, 1590, 1454, 1434, 1366, 1120, 749, 698. ¹H NMR (300 MHz, CDCl₃): δ = 8.60 (ddd, J = 0.8, J = 1.6, J = 4.8, 1 H), 7.68 (dt, J = 1.8, J = 7.6, 1 H), 7.32 (m, 5 H), 7.15 (m, 1 H), 7.18 (ddd, J = 0.8, J = 4.8, J = 7.6, 1 H), 3.91 (dd, J = 4.6, J = 8.5, 1 H), 3.69 (d, J = 12.7, 1 H), 3.64 (dd, J = 4.6, J = 11.1, 1 H), 3.63 (d, J = 12.7,

1 H), 3.42 (dd, $J = 7.7$, $J = 11.1$, 1 H), 3.03 (dd, $J = 4.4$, $J = 12.0$, 1 H), 2.90 (dd, $J = 8.6$, $J = 12.0$, 1 H), 2.67 (bs, 3 H), 2.43 (dd, $J = 4.6$, $J = 7.7$, 1 H), 1.82 (sept, $J = 6.9$, 1 H), 0.97 (d, $J = 6.9$, 3 H), 0.91 (d, $J = 6.9$, 3 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 161.9$, 149.2, 140.1, 136.4, 128.3, 128.2, 127.1, 127.1, 126.7, 122.7, 122.3, 64.7, 62.5, 61.7, 60.3, 54.5, 53.6, 30.2, 19.3, 18.7. MS (ES) m/z 314.3 ($\text{M} + \text{H}$) $^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}$: C, 72.81; H, 8.68; N, 13.41. Found C, 73.15; H, 8.71; N, 13.38.

(S)-2-[(S)-2-(4-Methoxyphenylamino)-1-(2-pyridyl)ethylamino]-3-methyl-1-butanol (3d):

Yellow oil; $[\alpha]_{\text{D}}^{20} -38.8$ (c 1.0, CHCl_3). IR (neat): $\nu = 3372$, 2956, 2922, 2104, 1598, 1464, 1116.

^1H NMR (300 MHz, CDCl_3) $\delta = 8.61$ (ddd, $J = 0.9$, $J = 1.8$, $J = 4.8$, 1 H), 7.66 (dt, $J = 1.8$, $J = 7.7$, 1 H), 7.22 (m, 2 H), 6.78 (d, $J = 9.0$, 2 H), 6.62 (d, $J = 9.0$, 2 H), 4.02 (dd, $J = 5.6$, $J = 7.3$, 1 H), 3.75 (s, 3 H), 3.61 (dd, $J = 3.9$, $J = 11.0$, 1 H), 3.43 (dd, $J = 5.4$, $J = 11.0$, 1 H), 3.40 (dd, $J = 5.6$, $J = 12.5$, 1 H), 3.29 (dd, $J = 7.3$, $J = 12.5$, 1 H), 2.69 (bs, 3 H), 2.26 (dd, $J = 3.9$, $J = 5.4$, 1H), 1.66 (sept, $J = 6.8$, 1 H), 0.84 (d, $J = 6.9$, 3 H), 0.80 (d, $J = 6.9$, 3 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 161.4$, 152.3, 149.6, 142.1, 136.5, 122.8, 122.5, 114.9, 114.7, 63.1, 61.1, 60.4, 55.7, 50.9, 29.5, 19.4, 18.9. MS (ES) $m/z = 330.2$ ($\text{M} + \text{H}$) $^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{N}_3\text{O}_2$: C, 69.27; H, 8.26; N, 12.76. Found C, 69.49; H, 8.29; N, 12.73.

(S)-2-((S)-2-(dibenzylamino)-1-(pyridin-2-yl)ethylamino)-3-methylbutan-1-ol (3e): Yellow oil. $[\alpha]_{\text{D}}^{20} -24.7$ (c 1.7, CHCl_3). IR (neat): $\nu = 3320, 3085, 3062, 3027, 2959, 1593, 1453, 1364, 1261, 1118, 1027, 780, 746, 698$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.52$ (ddd, $J = 1.0, J = 1.8, J = 5.0$, 1 H), 7.63 (dt, $J = 1.9, J = 7.7$, 1 H), 7.23 (td, $J = 1.0, J = 7.7$, 1 H), 7.18 (ddd, $J = 1.0, J = 4.9, J = 7.5$, 1 H), 3.93 (dd, $J = 7.2, J = 7.2$, 1 H), 3.73 (d, $J = 13.5$, 2 H), 3.66 (dd, $J = 4.0, J = 10.9$, 1 H), 3.58 (d, $J = 13.5$, 2 H), 3.45 (dd, $J = 4.9, J = 11.0$, 1 H), 2.73 (d, $J = 7.0$, 2 H), 2.18 (dd, $J = 4.0, J = 4.9$, 1 H), 2.09 (bs, 2H), 1.61 (sept, $J = 6.8$, 1 H), 0.80 (d, $J = 6.8$, 3 H), 0.77 (d, $J = 6.8$, 3 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 162.9, 149.1, 138.9, 136.0, 128.0, 128.9, 128.2, 127.0, 126.9, 122.0, 62.6, 60.8, 60.7, 60.1, 59.2, 29.7, 19.2, 19.0$. MS (ES) $m/z = 404.3$ ($\text{M} + \text{H}$) $^+$. Anal. Calcd for $\text{C}_{26}\text{H}_{33}\text{N}_3\text{O}$: C, 77.38; H, 8.24; N, 10.41. Found C, 77.10; H, 8.27; N, 10.37.

(S)-2-[(R)-2-(2-Naphthylthio)-1-(2-pyridyl)ethylamino]-3-methyl-1-butanol (3f): Yellowish oil; $[\alpha]_{\text{D}}^{20} +30.7$ (c 1.2, CHCl_3). IR (neat): $\nu = 3421, 3342, 3052, 2951, 1581, 1463, 1434, 1043, 1014, 742, 692$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.56$ (ddd, $J = 1.2, J = 1.7, J = 4.7$, 1 H), 7.78 (m, 2 H), 7.74 (m, 2 H), 7.62 (dt, $J = 1.8, J = 7.7$, 1 H), 7.47 (m, 2 H), 7.39 (dd, $J = 1.8, J = 8.7$, 1 H), 7.17 (m, 2 H), 3.96 (dd, $J = 6.2, J = 6.4$, 1 H), 3.61 (dd, $J = 3.8, J = 11.1$, 1 H), 3.45 (dd, $J = 5.0, J = 11.1$, 1 H), 3.43 (dd, $J = 6.4, J = 13.2$, 1 H), 3.37 (dd, $J = 6.2, J = 13.2$, 1 H), 2.81 (bs, 2 H), 2.42

(ddd, $J = 3.8$, $J = 4.8$, $J = 5.0$, 1 H), 1.62 (sept, $J = 6.9$, 1 H), 0.76 (d, $J = 6.9$, 3 H), 0.79 (d, $J = 6.9$, 3 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 160.1$, 149.7, 136.4, 133.7, 133.4, 131.7, 128.5, 127.7, 127.4, 127.1, 127.0, 126.5, 125.7, 122.9, 122.8, 63.3, 61.1, 60.4, 40.4, 29.3, 19.4, 18.7. GC-MS (EI) m/z 262 (100), 230 (55), 263 (51), 115 (46), 78 (27), 104 (15), 264 (12). MS (ES) m/z 367.3 ($\text{M} + \text{H}$)⁺, 389.0 ($\text{M} + \text{Na}$)⁺. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{OS}$: C, 72.09; H, 7.15; N, 7.64. Found C, 72.15; H, 7.17; N, 7.61.

(S)-2-[(R)-2-Phenylthio-1-(2-pyridyl)ethylamino]-3-methyl-1-butanol (3g): Yellow oil; $[\alpha]_{\text{D}}^{20} +11.4$ (c 0.9, CHCl_3). IR (neat): $\nu = 3424$, 3345, 3057, 2959, 2925, 2972, 1643, 1589, 1467, 1436, 1258, 1042, 1013, 743, 690. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.61$ (dt, $J = 1.6$, $J = 4.4$, 1 H), 7.66 (dt, $J = 1.8$, $J = 7.8$, 1 H), 7.38 (m, 1 H), 7.31 (m, 2 H), 7.21 (m, 2 H), 3.92 (dd, $J = 6.3$, $J = 7.2$, 1 H), 3.62 (dd, $J = 3.8$, $J = 11.1$, 1 H), 3.46 (dd, $J = 5.0$, $J = 11.1$, 1 H), 3.35 (dd, $J = 7.2$, $J = 13.2$, 1 H), 3.29 (dd, $J = 6.3$, $J = 13.2$, 1 H), 2.55 (bs, 2 H), 2.21 (ddd, $J = 3.8$, $J = 5.0$, $J = 6.4$, 1 H), 1.63 (sept, $J = 6.9$, 1 H), 0.82 (d, $J = 6.9$, 3 H), 0.78 (d, $J = 6.9$, 6 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 161.3$, 149.7, 136.3, 129.4, 128.9, 126.1, 122.7, 122.6, 63.0, 61.1, 60.6, 41.1, 29.4, 19.4, 18.8. GC-MS m/z 193 (100), 107 (39), 214 (35), 106 (17), 175 (12), 92 (12), 119 (11), 78 (10), 136 (9), 285 (3). Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{OS}$: C, 67.29; H, 7.64; N, 9.23. Found C, 67.58; H, 7.67; N, 9.22.

(S)-2-[(R)-2-Benzylthio-1-(2-pyridyl)ethylamino]-3-methyl-1-butanol (3h): Yellow oil; $[\alpha]_D^{20}$ -23.4 (c 1.2, CHCl_3). IR (neat): $\nu = 3382, 3060, 3030, 2951, 2922, 1590, 1491, 1472, 1044, 741, 702$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.57$ (ddd, $J = 0.9, J = 1.7, J = 4.9$, 1 H), 7.63 (dt, $J = 1.7, J = 7.6$, 1 H), 7.32 (m, 5 H), 7.26 (ddd, $J = 0.9, J = 4.9, J = 7.6$, 1 H), 7.13 d, $J = 7.6$, 1 H), 3.77 (dd, $J = 6.3, J = 6.3$, 1 H), 3.68 (s, 2 H), 3.61 (dd, $J = 3.7, J = 11.1$, 1 H), 3.46 (dd, $J = 5.1, J = 11.1$, 1 H), 2.86 (dd, $J = 6.3, J = 13.3$, 1 H), 2.77 (dd, $J = 6.3, J = 13.3$, 1 H), 2.36 (bs, 2 H), 2.39 (dd, $J = 3.7, J = 5.1$, 1 H), 1.62 (sept, $J = 7.0$, 1 H), 0.80 (d, $J = 7.0$, 3 H), 0.77 (d, $J = 7.0$, 6 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 159.7, 149.6, 138.3, 136.3, 128.9, 128.5, 127.0, 122.4, 122.5, 63.0, 61.4, 60.6, 38.8, 37.1, 29.4, 19.4, 18.8$. GC-MS m/z 91 (100), 193 (92), 107 (31), 106 (31), 228 (16), 124 (14), 65 (14), 281 (12), 136 (12), 78 (12), 175 (11), 51 (10), 299 (4), 207 (3). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{OS}$: C, 69.05; H, 7.93; N, 8.48. Found C, 69.26; H, 7.96; N, 8.45.

(R)-2-azido-2-(2-pyridyl)ethanamine: Red oil; IR (neat): $\nu = 3365, 2962, 2923, 2102, 1590, 1571, 1472, 1436, 1260, 1094, 1020, 798$. ^1H NMR (300 MHz, CDCl_3): $\delta = 8.60$ (d, $J = 4.7$, 1 H), 7.72 (dt, $J = 1.6, J = 7.9$, 1 H), 7.35 (d, $J = 7.9$, 1 H), 7.24 (ddd, $J = 1.6, J = 4.7, J = 7.9$, 1 H), 4.55 (dd, $J = 5.5, J = 13.3$, 1 H), 3.18 (dd, $J = 5.5, J = 13.3$, 1 H), 3.06 (dd, $J = 7.1, J = 13.3$, 1 H), 1.76 (bs, 2 H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 157.4, 149.6, 136.9, 123.0, 121.7, 69.0, 46.3$. MS (ES) m/z 164.3 ($\text{M} + \text{H}$) $^+$.

(R)-2-(2-Naphthylthio)-2-(2-pyridyl)ethanamine: Yellowish oil; ^1H NMR (300 MHz, CDCl_3): δ = 8.56 (ddd, J = 0.9, J = 1.8, J = 4.9, 1 H), 7.79 (m, 2 H), 7.71 (m, 2 H), 7.61 (td, J = 1.9, J = 7.8, 1 H), 7.44 (m, 4 H), 7.32 (dt, J = 0.9, J = 7.7, 1 H), 7.14 (ddd, J = 1.1, J = 4.8, J = 7.8, 1 H), 4.49 (dd, J = 6.1, J = 7.2, 1 H), 3.39 (dd, J = 7.2, J = 13.5, 1 H), 3.27 (dd, J = 6.1, J = 13.5, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 159.5, 149.4, 136.5, 134.1, 130.5, 128.8, 127.5, 127.3, 126.9, 126.6, 126.3, 126.0, 125.5, 122.9, 122.2, 57.7, 46.0. GC-MS (EI) m/z 262 (100), 230 (49), 263 (44), 115 (42), 78 (31), 51 (14), 217 (11), 160 (8).

(R)-2-(2-Phenylthio)-2-(2-pyridyl)ethanamine: Yellow oil; ^1H NMR (300 MHz, CDCl_3): δ = 8.56 (ddd, J = 1.0, J = 1.8, J = 4.8, 1 H), 7.61 (dt, J = 1.8, J = 7.7, 1 H), 7.33 (m, 2 H), 7.29 (m, 2 H), 7.19 (m, 2 H), 7.16 (m, 1 H), 4.33 (dd, J = 6.1, J = 7.2, 1 H), 3.31 (dd, J = 7.2, J = 13.4, 1 H), 3.19 (dd, J = 6.1, J = 13.4, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 170.8, 159.6, 149.4, 136.5, 134.1, 131.9, 128.8, 128.6, 124.6, 122.9, 122.2, 57.8, 46.0. GC-MS (EI) m/z 168 (100), 201 (99), 124 (20), 65 (17), 78 (16), 94 (15), 212 (9), 109 (9), 186 (4).

(*R*)-2-(Benzylthio)-2-(2-pyridyl)ethanamine: Yellow oil; ^1H NMR (300 MHz, CDCl_3): δ = 8.60 (d, J = 4.4, 1 H), 7.68 (dt, J = 1.8, J = 7.6, 1 H), 7.30 (m, 7 H), 3.90 (dd, J = 6.3, J = 7.0, 1 H), 3.72 (d, J = 13.2, 1 H), 3.64 (d, J = 13.2, 1 H), 3.25 (dd, J = 7.0, J = 13.4, 1 H), 3.16 (dd, J = 6.3, J = 13.4, 1 H), 1.94 (bs, 2 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 160.4, 149.3, 136.7, 130.3, 128.9, 128.5, 127.0, 122.9, 122.1, 54.0, 45.8, 35.3. GC-MS m/z 124 (100), 91 (28), 215 (16), 122 (14), 105 (11), 106 (10), 65 (10), 79 (9), 227 (2).

(*R*)-2-(2-Naphthylthio)-1-(2-pyridyl)ethanamine: Yellowish oil; ^1H NMR (300 MHz, CDCl_3): δ = 8.59 (m, 1 H), 7.80 (m, 2 H), 7.76 (dt, J = 1.8, J = 7.7, 1 H), 7.49 (m, 3 H), 7.33 (m, 2 H), 7.18 (ddd, J = 0.7, J = 4.8, J = 7.7, 1 H), 4.23 (dd, J = 5.4, J = 8.2, 1 H), 3.57 (dd, J = 5.4, J = 13.4, 1 H), 3.32 (dd, J = 8.2, J = 13.3, 1 H), 2.44 (bs, 2 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 162.5, 149.7, 136.9, 133.9, 129.2, 128.8, 127.9, 127.8, 127.7, 127.4, 126.8, 126.7, 126.1, 122.8, 121.9, 56.2, 42.7.

(R)-2-Benzylthio-1-(2-pyridyl)ethanamine: Yellow oil; ^1H NMR (300 MHz, CDCl_3): δ = 8.57 (m, 1 H), 7.67 (m, 1 H), 7.31 (m, 6 H), 7.21 (m, 1 H), 4.56 (dd, J = 6.8, J = 7.8, 1 H), 3.67 (s, 2 H), 3.12 (dd, J = 6.8, J = 12.9, 1 H), 2.75 (dd, J = 6.8, J = 12.9, 1 H), 2.14 (bs, 2 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 162.4, 149.4, 136.5, 135.7, 129.7, 129.4, 129.0, 126.2, 122.4, 121.6, 55.9, 42.7. GC-MS (EI) m/z 107 (100), 80 (20), 213 (4), 136 (4), 230 (2), 183 (2).

(R)-N-[2-Azido-2-(2-pyridyl)ethyl]benzamide (6b): Red oil; $[\alpha]_{\text{D}}^{20}$ +55.5 (c 1.1, CHCl_3). IR (neat): ν = 3288, 3068, 2937, 2104, 1638, 1540, 1321, 772, 707. ^1H NMR (300 MHz, CDCl_3): δ = 8.64 (dt, J = 0.7, J = 4.8, 1 H), 8.11 (d, J = 6.9, 1 H), 7.77 (m, 2 H), 7.48 (m, 1 H), 7.42 (m, 3 H), 7.31 (ddt, J = 0.8, J = 4.9, J = 7.6, 1 H), 7.16 (m, 1 H), 4.90 (t, J = 6.1, 1 H), 4.07 (ddd, J = 6.1, J = 6.9, J = 12.4, 1 H), 3.87 (ddd, J = 6.1, J = 6.9, J = 12.4, 1 H). ^{13}C NMR (75 MHz, CDCl_3): δ = 167.7, 149.4, 137.5, 134.1, 133.2, 131.6, 129.9, 128.5, 128.3, 126.9, 123.6, 122.6, 64.1, 43.3. GC-MS (280 °C) m/z 105 (100), 218 (67), 77 (61), 262 (56), 263 (29), 115 (26), 219 (24), 230 (23), 384 (13), 160 (12). MS (ES) m/z 268.2 ($\text{M} + \text{H}$) $^+$, 290.1 ($\text{M} + \text{Na}$) $^+$, 557.2 ($2\text{M} + \text{Na}$) $^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{N}_5\text{O}$: C, 62.91; H, 4.90; N, 26.20. Found C, 63.10; H, 4.92; N, 26.12.

(R)-N-[2-(2-Naphthylthio)-2-(2-pyridyl)ethyl]benzamide (6f): White crystals. (from Et₂O); m.p. = 122.0-122.5 °C; $[\alpha]_{\text{D}}^{20} +58.7$ (*c* 1.9, CHCl₃). IR (KBr): ν = 3326, 3046, 3003, 2926, 1843, 1710, 1638, 1578, 1523, 1436, 1271, 822, 745, 701. ¹H NMR (300 MHz, CDCl₃): δ = 8.56 (ddd, *J* = 0.7, *J* = 1.6, *J* = 4.9, 1 H), 7.93 (s, 1 H), 7.73 (m, 5 H), 7.58 (dt, *J* = 1.9, *J* = 7.8, 1 H), 7.45 (m, 5 H), 7.32 (m, 3 H), 7.16 (ddd, *J* = 0.7, *J* = 4.9, *J* = 7.8, 1 H), 4.85 (t, *J* = 6.6, 1 H), 4.21 (ddd, *J* = 6.1, *J* = 6.6, *J* = 13.5, 1 H), 4.15 (ddd, *J* = 6.1, *J* = 6.6, *J* = 13.5, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 167.4, 158.9, 149.0, 136.9, 133.5, 132.2, 131.2, 131.0, 129.2, 128.5, 128.3, 127.5, 127.4, 126.8, 126.4, 126.2, 123.6, 122.5, 52.3, 43.2. GC-MS (EI) (280 °C) *m/z* 384 (4), 263 (30), 230 (29), 211 (18), 160 (8), 136 (16), 115 (13), 105 (100), 77 (38). MS (ES) *m/z* = 385.1 (M + H)⁺, 791.0 (2 M + Na)⁺. Anal. Calcd for C₂₄H₂₀N₂OS: C, 74.97; H, 5.24; N, 7.29. Found C, 75.05; H, 5.26; N, 7.28.

(R)-N-[2-Phenylthio-2-(2-pyridyl)ethyl]benzamide (6g): Red oil; $[\alpha]_{\text{D}}^{20} +51.8$ (*c* 2.0, CHCl₃). IR (neat): ν = 3323, 3058, 2925, 2853, 1644, 1579, 1537, 1484, 1436, 1292, 1075, 749, 692. ¹H NMR (300 MHz, CDCl₃): δ = 8.61 (d, *J* = 4.6, 1 H), 7.74 (m, 2 H), 7.68 (td, *J* = 1.7, *J* = 7.7, 1 H), 7.49 (m, 2 H), 7.44 (m, 3 H), 7.32 (m, 2 H), 7.24 (m, 2 H), 4.72 (dd, *J* = 6.1, *J* = 6.9, 1 H), 4.16 (m, 2 H). ¹³C NMR (75 MHz, CDCl₃): δ = 167.4, 159.0, 149.1, 137.0, 134.4, 133.5, 132.5, 131.4, 129.0, 128.5, 127.7, 126.9, 123.8, 122.4, 52.5, 43.0. GC-MS (EI) *m/z* 105 (100), 77 (73), 168 (61), 213

(38), 201 (49), 334 (20), 180 (16), 225 (14), 119 (8). Anal. Calcd for C₂₀H₁₈N₂OS: C, 71.83; H, 5.42; N, 8.38. Found C, 71.58; H, 5.43; N, 8.35.

(R)-N-[2-Benzylthio-2-(2-pyridyl)ethyl]benzamide (6h): Colourless oil; $[\alpha]_{\text{D}}^{20} +26.1$ (*c* 1.0, CHCl₃). IR (neat): $\nu = 3320, 3060, 2923, 1644, 1537, 1471, 1434, 1290, 697$. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.59$ (ddd, *J* = 1.0, *J* = 1.9, *J* = 4.9, 1 H), 7.76 (m, 2 H), 7.69 (dt, *J* = 1.9, *J* = 7.8, 1 H), 7.47 (m, 5 H), 7.32 (m, 4 H), 7.25 (m, 1 H), 4.23 (dd, *J* = 6.7, *J* = 9.7, 1 H), 4.17 (ddd, *J* = 4.6, *J* = 6.7, *J* = 13.1, 1 H), 3.97 (ddd, *J* = 4.6, *J* = 9.7, *J* = 13.1, 1 H), 3.89 (d, *J* = 13.5, 1 H), 3.75 (d, *J* = 13.5, 1 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 167.4, 159.7, 148.6, 137.9, 137.3, 134.5, 131.4, 129.0, 128.6, 128.5, 127.1, 127.0, 123.8, 122.5, 48.7, 42.4, 35.7$. GC-MS (EI) *m/z* 105 (100), 124 (76), 226 (74), 77 (49), 91 (45), 257 (41). Anal. Calcd for C₂₁H₂₀N₂OS: C, 72.38; H, 5.79; N, 8.04. Found C, 72.40; H, 5.80; N, 8.02.

(R)-N-[(2-Butylthio-2-(2-pyridyl)ethyl]benzamide (6i): Yellow oil; $[\alpha]_{\text{D}}^{20} +27.4$ (*c* 1.0, CHCl₃); 3314, 3057, 2913, 1647, 1534, 1477, 1297, 694. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.58$ (ddd, *J* = 0.9, *J* = 1.7, *J* = 4.9, 1 H), 7.74 (m, 2 H), 7.71 (dt, *J* = 1.7, *J* = 7.4, 1 H), 7.47 (m, 1 H), 7.42 (m, 2 H), 7.23 (ddd, *J* = 0.9, *J* = 4.7, *J* = 7.5, 1 H), 4.29 (dd, *J* = 5.8, *J* = 7.4, 1 H), 4.11 (ddd, *J* = 6.2, *J* = 7.4, *J* = 13.6, 1 H), 4.01 (ddd, *J* = 5.8, *J* = 11.2, *J* = 13.6, 1 H), 2.57 (m, 2 H), 1.54 (m, 2 H), 1.38 (m, 2 H), 0.87 (t, *J* = 7.3, 3 H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 167.4, 160.0, 148.7, 137.4, 134.4,$

133.3, 131.4, 130.1, 128.5, 128.4, 126.9, 123.7, 122.5, 49.2, 42.8, 31.6, 30.9, 21.9, 13.6. MS (EI) m/z 314 (4), 257 (16), 181 (11), 160 (18), 124 (57), 105 (100), 93 (14), 77 (55). MS (ES) m/z = 315.2 ($M + H$)⁺, 651.3 (2 $M + Na$)⁺. Anal. Calcd for C₁₈H₂₂N₂OS: C, 68.75; H, 7.05; N, 8.91. Found C, 68.38; H, 7.08; N, 8.89.

***N*-((*S*)-2-azido-1-(pyridin-2-yl)ethyl)benzamide (7b)**: Yellow oil; $[\alpha]_D^{20} +13.4$ (c 1.2, CHCl₃); IR (neat): ν = 3282, 3071, 2932, 2108, 1631, 1547, 1315, 778. ¹H NMR (300 MHz, CDCl₃): δ = 8.63 (ddd, J = 0.8, J = 1.6, J = 4.8, 1 H), 7.88 (m, 2 H), 7.75 (dd, J = 1.9, J = 7.7, 1 H), 7.45 (m, 3 H), 7.38 (dt, J = 0.8, J = 1.6, 1 H), 7.30 (ddd, J = 1.9, J = 4.8, J = 7.4, 1 H), 5.46 (ddd, J = 4.9, J = 5.7, J = 7.3, 1 H), 3.85 (dd, J = 4.9, J = 12.2, 1 H), 3.80 (dd, J = 5.7, J = 12.2, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 167.0, 156.4, 149.3, 13.1, 134.0, 131.8, 128.6, 127.1, 127.0, 123.2, 122.6, 55.0, 53.5. MS (ES) m/z = 268.2 ($M + H$)⁺. Anal. Calcd for C₁₄H₁₃N₅O: C, 62.91; H, 4.90; N, 26.20. Found C, 63.21; H, 4.92; N, 26.18.

(*R*)-*N*-[2-Naphthylthio]-1-(2-pyridyl)ethyl]benzamide (7f): White crystals (from Et₂O); m.p. = 119.5-120 °C. $[\alpha]_D^{20} -22.7$ (c 1.3, CHCl₃). IR (Nujol): ν = 3310, 1638, 1518, 1468, 1370, 810, 729. ¹H NMR (300 MHz, CDCl₃): δ = 8.58 (ddd, J = 0.8, J = 1.6, J = 4.8, 1 H), 8.12 (d, J = 7.0, 1 H); 7.81 (m, 2 H), 7.75 (m, 3 H), 7.63 (m, 2 H), 7.47 (m, 3 H), 7.38 (m, 2 H), 7.20 (m, 2 H), 5.56 (dd, J = 5.2, J = 6.8, 1 H), 3.82 (dd, J = 5.2, J = 13.6, 1 H), 3.51 (dd, J = 7.8, J = 13.6, 1 H). ¹³C NMR (75

MHz, CDCl₃): δ = 166.8, 157.6, 149.0, 136.9, 133.7, 133.5, 131.5, 130.1, 128.5, 128.4, 127.6, 127.2, 127.1, 126.5, 125.7, 123.4, 123.6, 123.1, 53.9, 38.5. MS (ES) m/z 385.1 (M + H)⁺, 791.0 (2 M + Na)⁺. Anal. Calcd for C₂₄H₂₀N₂OS: C, 74.97; H, 5.24; N, 7.29. Found C, 75.10; H, 5.26; N, 7.27.

(R)-N-[2-Phenylthio-1-(pyridyl)ethyl]benzamide (7g): Red oil; $[\alpha]_D^{20}$ -19.2 (*c* 0.4, CHCl₃). IR (neat): ν = 3321, 3054, 2927, 2852, 1642, 1572, 1533, 1482, 1431, 1290, 1078, 747, 691. ¹H NMR (300 MHz, CDCl₃): δ = 8.58 (ddd, *J* = 0.9, *J* = 1.7, *J* = 4.9, 1 H), 7.82 (m, 2 H), 7.68 (dt, *J* = 1.8, *J* = 7.8, 1 H), 7.49 (m, 3 H), 7.42 (m, 3 H), 7.33 (dt, *J* = 0.9, *J* = 7.8, 1 H), 7.27 (m, 2 H), 7.15 (dt, *J* = 1.2, *J* = 6.5, 1 H), 5.48 (dd, *J* = 5.1, *J* = 7.2, *J* = 8.0, 1 H), 3.72 (dd, *J* = 5.1, *J* = 13.6, 1 H), 3.44 (dd, *J* = 8.0, *J* = 13.6, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 166.7, 157.5, 137.1, 134.1, 131.6, 129.2, 129.0, 128.5, 127.1, 126.1, 123.6, 123.1, 53.6, 38.7. GC-MS (EI) m/z 105 (100), 77 (69), 213 (68), 136 (47), 211 (31), 212 (26), 180 (11), 281 (5), 334 (4). Anal. Calcd for C₂₀H₁₈N₂OS: C, 71.83; H, 5.42; N, 8.38. Found C, 71.98; H, 5.41; N, 8.36..

(R)-N-[2-(Benzylthio)-1-(2-pyridyl)ethyl]benzamide (7h): Colourless oil; $[\alpha]_D^{20}$ -17.1 (*c* 0.5, CHCl₃). IR (neat): ν = 3320, 3060, 2923, 1645, 1589, 1536, 1434, 1290, 696. ¹H NMR (300 MHz,

CDCl₃): δ = 8.60 (ddd, J = 0.8, J = 1.7, J = 4.9, 1 H), 7.89 (m, 2 H), 7.48 (m, 2H), 7.39 (m, 2 H), 7.29 (m, 7 H), 5.46 (dd, J = 5.9, J = 7.5, 1 H), 3.65 (s, 2 H), 3.14 (dd, J = 5.7, J = 13.5, 1 H) 3.04 (ddd, J = 7.5, J = 13.6, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ = 168.5, 158.9, 147.8, 137.7, 137.2, 134.7, 131.7, 129.0, 128.6, 127.3, 127.2, 123.6, 122.4, 53.1, 36.7, 29.7. GC-MS (EI) m/z 105 (100), 257 (52), 77 (36), 91 (20), 136 (18), 211 (10), 258 (8). Anal. Calcd for C₂₁H₂₀N₂OS: C, 72.38; H, 5.79; N, 8.04. Found C, 72.11; H, 5.80; N, 8.03.

(R)-1-(2-Pyridyl)ethane-1,2-diamine (8): Yellow oil; $[\alpha]_D^{20}$ -45.6 (c 0.7, CHCl₃). IR (neat): ν = 3361, 2968, 2922, 2101, 1476, 1435, 1092, 1016, 794. ¹H NMR (300 MHz, CDCl₃): δ = 8.54 (ddd, J = 0.7, J = 1.7, J = 7.9, 1 H), 7.69 (dt, J = 1.7, J = 7.8, 1 H), 7.32 (d, J = 7.9, 1 H), 7.21 (ddd, J = 0.9, J = 4.7, J = 7.9, 1 H), 3.99 (dd, J = 5.2, J = 7.0, 1 H), 3.08 (dd, J = 5.2, J = 12.7, 1 H), 2.93 (dd, J = 7.0, J = 12.7, 1 H), 1.83 (bs, 4 H). ¹³C NMR (75 MHz, CDCl₃): δ = 158.7, 149.2, 137.0, 122.8, 121.7, 59.6, 54.8. MS (ES) m/z 138.2 (M + H)⁺. Anal. Calcd for C₇H₁₁N₃: C, 61.29; H, 8.08; N, 30.63. Found C, 60.99; H, 8.11; N, 30.50.