

Electronic Supplementary Information

Enantioselective Synthesis of Cyclopropylcarboxamides using s-BuLi/Sparteine-Mediated Metallation

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Compound physical characteristics, specific rotation data, HPLC parameters for ee determination, and spectroscopic data for non-racemic compounds described in the Table, prepared according to the general protocol given in the Footnote ‡.

(1*S*, 2*S*)-2-iodo-1-methyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3a**

Colourless solid (m.p. 74–76 °C), $[\alpha]_{\text{D}}^{18}$ 117 (*c*, 0.97, CHCl₃); ee = 88% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, η_{hexane} : EtOH, 98 : 2, 1 mL/min, retention time : 5.5 min (major), 6.2 min (minor). ν_{max} (CDCl₃)/cm⁻¹ 2968, 2934, 2875, 1628, 1461, 1370, 1345, 1041. δ_{H} (400 MHz, CDCl₃) 1.18 (1H, dd, *J* 8.0, 6.2, *CHH*), 1.22 (3H, d, *J* 6.6), 1.37 (3H, s, *CH*₃), 1.39 (6H, d, *J* 6.6), 1.40 (3H, d, *J* 6.6), 1.41 (1H, ap.t, *J* 6.2, *CHH*), 2.55 (1H, dd, *J* 8.0, 6.2, *CHI*), 3.27 (1H, sept, *J* 6.6, *NCH*), 4.15 (1H, sept, *J* 6.6, *NCH*). δ_{C} (100 MHz, CDCl₃) -6.0 (*CHI*), 20.1 (*CH*₃), 20.5 (*CH*₃), 21.3 (*CH*₃), 21.7 (*CH*₃), 22.0 (*CH*₃), 24.3 (*CH*₂), 28.3 (*C*), 46.1 (*CH*), 48.7 (*CH*), 169.7 (*C=O*). HRMS (ESI+) C₁₁H₂₁INO requires 310.0673; found 310.0671 [*M*+*H*]. CHN: C₁₁H₂₀INO requires C, 42.73; H, 6.52; N, 4.53%; found C, 42.68; H, 6.54; N, 4.42%.

(1*R*, 2*S*)-1,2-dimethyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3b**

Colourless oil, $[\alpha]_{\text{D}}^{18}$ 62 (*c*, 0.95, CHCl₃); ee = 90% as determined by chiral HPLC, chiral support CHIRALPAK OJ-H, η_{hexane} : EtOH, 98 : 2, 1 mL/min, retention time : 4.2 min (minor), 5.0 min (major). ν_{max} (CDCl₃)/cm⁻¹ 2957, 2934, 2872, 2253, 1626, 1460, 1370, 1348, 1040. δ_{H} (400 MHz, CDCl₃) 0.52 (1H, dd, *J* 8.3, 4.9, *CHH*), 0.74 (1H, ap. t, *J* 4.9, *CHH*), 0.90 (1H, m, *CHCH*₃), 1.01 (3H, d, *J* 6.1, *CH*₃), 1.19 (6H, d, *J* 6.6), 1.22 (3H, s, *CH*₃), 1.36 (6H, t, *J* 6.4), 3.30 (1H, sept, *J* 6.6, *NCH*), 4.41 (1H, sept, *J* 6.4, *NCH*). δ_{C} (100 MHz, CDCl₃) 15.8 (*CH*₃), 19.7 (*CH*₂), 20.1 (*CH*₃), 20.7 (*CH*₃), 20.8 (*CH*), 21.0 (*CH*₃), 21.7 (*CH*₃), 22.9 (*CH*₃), 27.4 (*C*), 45.5 (*CH*), 48.1 (*CH*), 171.8 (*C=O*). HRMS (ESI+) C₁₂H₂₄NO requires 198.1852; found 198.1848 [*M*+*H*].

(1*S*, 2*S*)-1-methyl-2-(phenylthio)-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3c**

Colourless solid (m.p. 98 °C), $[\alpha]_{\text{D}}^{18}$ 307 (*c*, 1.00, CHCl₃); ee = 90% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, η_{hexane} : EtOH, 98 : 2, 1 mL/min, retention time : 9 min (minor), 13 min (major). ν_{max} (CDCl₃)/cm⁻¹ 2968, 2934, 2874, 2255, 1627, 1585, 1461, 1380, 1370, 1348, 1090, 1039. δ_{H} (400 MHz, CDCl₃) 1.23 (3H, d, *J* 6.8), 1.31 (5H, m), 1.43

(6H, d, J 6.8), CH_3), 1.47 (3H, d, J 6.8), 2.39 (1H, dd, J 7.0, 5.3, CHSPh), 3.36 (1H, sept, J 6.8, NCH), 4.38 (1H, sept, J 6.8, NCH), 7.14 (1H, t, J 7.3, Ar, CH), 7.27 (2H, t, J 7.3, Ar, CH), 7.35 (2H, dd, J 7.3, 1.0, Ar, CH). δ_{C} (100 MHz, CDCl_3) 20.3 (CH_3), 20.5 (CH_3), 20.6 (CH_3), 21.1 (CH_3), 22.8 (CH_3), 24.3 (CH_2), 26.9 (CH), 30.7 (C), 46.0 (CH), 48.8 (CH), 125.2 (Ar, CH), 127.3 (Ar, CH), 128.7 (Ar, CH), 138.2 (Ar, C), 169.4 (C=O). HRMS (ESI+) $\text{C}_{17}\text{H}_{26}\text{NOS}$ requires 292.1729; found 292.1728 [$\text{M}+\text{H}$], $\text{C}_{17}\text{H}_{25}\text{NOSNa}$ requires 314.1555; found 314.1559 [$\text{M}+\text{Na}$]. CHN: $\text{C}_{17}\text{H}_{25}\text{NOS}$ requires C, 70.06; H, 8.65; N, 4.81%; found C, 69.81; H, 8.67; N, 4.80%.

(1*S*, 2*S*)-2-benzoyl-1-methyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3d**

Colourless solid (m.p. 59-61 °C), $[\alpha]_{\text{D}}^{18}$ -29 (c , 0.79, CHCl_3); ee = 90% as determined by chiral HPLC, chiral support CHIRALPAK OJ-H, "hexane : EtOH, 98 : 2, 1 mL/min, retention time : 9.2 min (minor), 13.7 min (major). ν_{max} (CDCl_3)/ cm^{-1} 2968, 2934, 2872, 1673, 1628, 1450, 1380, 1370, 1350, 1043, 994. δ_{H} (400 MHz, CDCl_3) 1.01 (3H, d, J 6.6), 1.20 (1H, dd, J 7.7, 4.1, CHH), 1.24 (3H, d, J 6.6), 1.35 (3H, d, J 6.8), 1.39 (3H, d, J 6.8), 1.51 (3H, s, CH_3), 2.11 (1H, dd, J 5.5, 4.1, CHH), 2.74 (1H, dd, J 7.7, 5.5, CHCOPh), 3.26 (1H, sept, J 6.8, NCH), 4.36 (1H, sept, J 6.6, NCH), 7.46 (2H, t, J 7.3, Ar, CH), 7.54 (1H, t, J 7.3, Ar, CH), 8.00 (2H, d, J 7.3, Ar, CH). δ_{C} (100 MHz, CDCl_3) 20.2 (CH_3), 20.4 (CH_3), 20.7 (CH_3), 20.9 (CH_3), 22.9 (CH_3), 23.0 (CH_2), 32.1 (CH), 36.6 (C), 45.9 (CH), 48.6 (CH), 128.1 (Ar, CH), 128.4 (Ar, CH), 132.3 (Ar, CH), 138.5 (Ar, C), 168.9 (C=O), 197.2 (C=O). HRMS (ESI+) $\text{C}_{18}\text{H}_{26}\text{NO}_2$ requires 288.1958; found 288.1942 [$\text{M}+\text{H}$].

(1*R*, 2*S*)-1-methyl-2-prenyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3e**

Colourless oil, $[\alpha]_{\text{D}}^{18}$ 106 (c , 1.4, CHCl_3); ee = 90% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, "hexane : EtOH, 98 : 2, 1 mL/min, retention time : 4.2 min (minor), 4.5 min (major). ν_{max} (CDCl_3)/ cm^{-1} 2968, 2932, 2253, 1622, 1454, 1378, 1370, 1347, 1039, 900. δ_{H} (400 MHz, CDCl_3) 0.55 (1H, dd, J 8.3, 4.9, CHH), 0.78 (1H, t, J 4.9, CHH), 0.88 (1H, m, CH), 1.21 (6H, t, J 6.8), 1.23 (3H, s, CH_3), 1.37 (7H, m), 1.56 (3H, s, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 1.67 (3H, s, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$), 2.46 (1H, m, $\text{CHHCH}=\text{C}(\text{CH}_3)_2$), 3.28 (1H,

sept, J 6.8, NCH), 4.44 (1H, sept, J 6.5, NCH), 5.17 (1H, tt, J 6.5, 1.3, $CH_2CH=C(CH_3)_2$). δ_C (100 MHz, $CDCl_3$) 17.7 (CH), 18.6 (CH_2), 20.1 (CH_3), 20.7 (CH_3), 21.0 (CH_3), 21.6 (CH_3), 22.9 (CH_3), 25.6 (CH_3), 26.7 (CH_3), 27.2 (C), 29.2 (CH_2), 45.6 (CH), 48.2 (CH), 123.3 ($CH=C(CH_3)_2$), 131.7 ($CH=C(CH_3)_2$), 171.7 (C=O). HRMS (ESI+) $C_{16}H_{30}NO$ requires 252.2331; found 252.2350 $[M+H]$, $C_{16}H_{29}NONa$ requires 274.2147; found 274.2167 $[M+Na]$.

(1*R*, 2*S*)-2-(1-hydroxybenzyl)-1-methyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3f**

Major diastereoisomer

Colourless solid (m.p. 91-93 °C), $[\alpha]_D^{18}$ 49 (c , 1.03, $CHCl_3$); ee = 82% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, η hexane : EtOH, 98 : 2, 1 mL/min, retention time : 13.9 min (minor), 24.3 min (major). ν_{max} ($CDCl_3$)/ cm^{-1} 3334, 2969, 2934, 2872, 1613, 1596, 1454, 1382, 1370, 1352, 1052, 1040, 908. δ_H (400 MHz, $CDCl_3$) 0.88 (2H, m, 2 $\times CHH$), 1.23 (3H, d, J 6.7), 1.28 (4H, m), 1.34 (3H, s, CH_3), 1.42 (3H, d, J 6.8), 1.47 (3H, d, J 6.8), 3.37 (1H, sept, J 6.8, NCH), 3.98 (1H, d, J 10.0, $CHOH$), 4.61 (1H, sept, J 6.7, NCH), 6.01 (1H, br s, $CHOH$), 7.26 (1H, tt, J 7.3, 2.2, Ar, CH), 7.34 (2H, t, J 7.3, Ar, CH), 7.48 (2H, d, J 7.3, Ar, CH). δ_C (100 MHz, $CDCl_3$) 17.9 (CH_2), 20.2 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 20.8 (CH_3), 23.2 (CH_3), 27.1 (C), 34.0 (CH), 46.1 (CH), 49.0 (CH), 76.3 ($CHOH$), 125.8 (Ar, CH), 127.0 (Ar, CH), 128.1 (Ar, CH), 143.2 (Ar, C), 173.0 (C=O). HRMS (ESI+) $C_{18}H_{27}NO_2Na$ requires 312.1934; found 312.1950 $[M+Na]$.

Minor diastereoisomer

Colourless solid (m.p. 62-64 °C), $[\alpha]_D^{18}$ 161 (c , 1.07, $CHCl_3$); ee = 78% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, η hexane : EtOH, 98 : 2, 1 mL/min, retention time : 10.4 min (major), 14.1 min (minor). ν_{max} ($CDCl_3$)/ cm^{-1} 3467, 3156, 2971, 2933, 2902, 2254, 1817, 1794, 1596, 1462, 1381, 1371, 1353, 1096, 987, 946, 889. δ_H (400 MHz, $CDCl_3$) 0.69 (1H, q, J 7.4, CHH), 1.12 (3H, d, J 6.6), 1.23 (5H, m), 1.33 (3H, s, CH_3), 1.38 (3H, d, J 6.8), 1.42 (3H, d, J 6.8), 3.30 (1H, sept, J 6.8, NCH), 3.63 (1H, d, J 3.9, $CHOH$), 4.56 (1H, sept, J 6.6, NCH), 5.36 (1H, s, $CHOH$), 7.23 (1H, tt, J 7.2, 1.4, Ar, CH), 7.32 (2H, t, J 7.2, Ar, CH), 7.39 (d, J 7.2, 2H, Ar, CH). δ_C (100 MHz,

CDCl₃) 14.4 (CH₂), 20.0 (CH₃), 20.2 (CH₃), 20.4 (CH₃), 20.6 (CH₃), 23.5 (CH₃), 25.5 (C), 32.2 (CH), 45.9 (CH), 49.2 (CH), 69.5 (CHOH), 126.4 (Ar, CH), 126.9 (Ar, CH), 128.0 (Ar, CH), 143.8 (Ar, C), 174.0 (C=O). HRMS (ESI+) C₁₈H₂₈NO₂ requires 312.1934; found 312.1936 [M+H]

(1*R*, 2*S*)-2-(1-hydroxycyclohexyl)-1-methyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3g**
Colourless oil, $[\alpha]_{\text{D}}^{18}$ 77 (*c*, 1.05, CHCl₃); ee = 88% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, n_{hexane} : EtOH, 98 : 2, 0.5 mL/min, retention time : 9.9 min (major), 11.1 min (minor).

ν_{max} (CDCl₃)/cm⁻¹ 3408, 2931, 2862, 1610, 1592, 1460, 1381, 1370, 1354, 1124, 1049, 988, 966. δ_{H} (400 MHz, CDCl₃) 0.61 (1H, dd, *J* 8.9, 4.4, *CHH*), 0.87 (1H, dd, *J* 8.9, 6.8, *CH*), 0.96 (1H, dd, *J* 6.8, 4.4, *CHH*), 1.15 (5H, m), 1.21 (3H, d, *J* 6.8), 1.25 (3H, s, *CH*₃), 1.32 (3H, d, *J* 6.8), 1.37 (4H, m), 1.38-1.75 (6H, m, 3 × *CH*₂), 2.02 (1H, d, *J* 13.0, *CHH*), 3.27 (1H, sept, *J* 6.8, *NCH*), 3.78 (1H, s, *OH*), 4.61 (1H, sept, *J* 6.8, *NCH*). δ_{C} (100 MHz, CDCl₃) 14.9 (CH₂), 20.1 (CH₃), 20.1 (CH₃), 20.2 (CH₃), 20.6 (CH₃), 21.6 (CH₂), 21.9 (CH₂), 24.2 (CH₃), 25.5 (C), 26.0 (CH₂), 35.8 (CH₂), 36.4 (CH), 39.4 (CH₂), 45.8 (CH), 49.1 (CH), 68.8 (COH), 174.5 (C=O). HRMS (ESI+) C₁₇H₃₁NO₂Na requires 304.2252; found 304.2273 [M+Na]

(1*R*, 2*S*)-2-(1-hydroxy-1-methylethyl)-1-methyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3h**

Colourless oil, $[\alpha]_{\text{D}}^{18}$ 49 (*c*, 1.10, CHCl₃); ee = 90% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, n_{hexane} : EtOH, 99.5 : 0.5, 1 mL/min, retention time : 11.4 min (minor), 12.5 min (major).

ν_{max} (CDCl₃)/cm⁻¹ 3344, 2970, 2934, 2872, 1594, 1461, 1382, 1370, 1359, 1283, 1123, 1045, 1036. δ_{H} (400 MHz, CDCl₃) 0.68 (1H, dd, *J* 8.9, 4.8, *CHH*), 0.90 (1H, dd, *J* 6.5, 4.8, *CHH*), 1.00 (3H, s, *CH*₃), 1.03 (1H, m, *CH*), 1.18 (3H, d, *J* 6.8), 1.24 (3H, d, *J* 6.8), 1.28 (3H, s, *CH*₃), 1.36 (3H, d, *J* 6.8), 1.40 (3H, d, *J* 6.8), 1.43 (3H, s, *CH*₃), 3.31 (1H, sept, *J* 6.8, *NCH*), 4.63

(1H, sept, *J* 6.8, NCH), 4.76 (1H, s, OH). δ_{C} (100 MHz, CDCl₃) 16.4 (CH₂), 20.1 (CH₃), 20.2 (CH₃), 20.4 (CH₃), 20.8 (CH₃), 24.4 (CH₃), 25.9 (C), 26.9 (CH₃), 31.6 (CH₃), 36.4 (CH), 46.0 (CH), 49.3 (CH), 68.9 (COH), 174.0 (C=O). HRMS (ESI+) C₁₄H₂₇NO₂Na requires 264.1939; found 264.1960 [M+Na]

(1*R*, 2*S*)-2-iodo-1-phenyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3i**

Colourless solid (m.p. 105-107 °C), $[\alpha]_{\text{D}}^{18}$ 249 (*c*, 1.10, CHCl₃); ee = 85% as determined by chiral HPLC, chiral support CHIRALPAK OJ-H, *n*hexane : EtOH, 99 : 1, 0.5 mL/min, retention time : 12.5 min (major), 14.0 min (minor).

ν_{max} (CDCl₃)/cm⁻¹ 2968, 2934, 2875, 1631, 1448, 1371, 1339, 1133, 1040. δ_{H} (400 MHz, CDCl₃) 0.18 (3H, d, *J* 6.6), 1.19 (4H, m), 1.32 (3H, d, *J* 6.8), 1.37 (3H, d, *J* 6.8), 1.94 (1H, ap.t, *J* 5.7, CHH), 3.16 (1H, sept, *J* 6.8, NCH), 3.45 (1H, dd, *J* 8.3, 5.7, CHI), 4.01 (1H, sept, *J* 6.6, NCH), 7.10 (1H, t, *J* 7.1, Ar, CH), 7.14 (2H, t, *J* 4.2, Ar, CH), 7.18 (2H, m, Ar, CH). δ_{C} (100 MHz, CDCl₃) -10.4 (CHI), 18.6 (CH₃), 19.2 (CH₃), 20.3 (CH₃), 21.3 (CH₃), 25.6 (CH₂), 37.3 (C), 45.7 (CH), 48.8 (CH), 126.2 (Ar, CH), 126.5 (Ar, CH), 128.4 (Ar, CH), 138.8 (Ar, C), 167.8 (C=O). HRMS (ESI+) C₁₆H₂₃INO requires 372.0824; found 372.0815 [M+H], C₁₆H₂₂INONa requires 394.0644; found 394.0631 [M+Na]

(1*R*, 2*S*)-2-methyl-1-phenyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3j**

Colourless solid (m.p. 77-79 °C), $[\alpha]_{\text{D}}^{18}$ 156 (*c*, 1.25, CHCl₃); ee = 88% as determined by chiral HPLC, chiral support CHIRALPAK OJ-H, *n*hexane : EtOH, 99 : 1, 1 mL/min, retention time : 4.7 min (major), 6.0 min (minor).

ν_{max} (CDCl₃)/cm⁻¹ 2966, 2933, 2873, 1624, 1454, 1371, 1342, 1134, 1039. δ_{H} (400 MHz, CDCl₃) 0.40 (3H, d, *J* 6.7), 0.80 (1H, dd, *J* 8.9, 4.4, CHH), 1.11 (3H, d, *J* 6.7), 1.23 (3H, d, *J* 6.2, CH₃), 1.41 (1H, m, CHH), 1.45 (6H, t, *J* 6.7), 1.95 (1H, m, CHCH₃), 3.25 (1H, sept, *J* 6.7, NCH), 4.28 (1H, sept, *J* 6.7, NCH), 7.19 (1H, m, Ar, CH), 7.28 (4H, m, Ar, 2 × CH). δ_{C} (100 MHz, CDCl₃) 14.9 (CH₃), 17.8 (CH), 19.0 (CH₃), 19.5 (CH₃), 20.9 (CH₃), 21.6 (CH₃), 22.6

(CH₂), 37.0 (C), 45.7 (CH), 48.7 (CH), 126.0 (Ar, CH), 126.4 (Ar, CH), 128.4 (Ar, CH), 142.0 (Ar, C), 169.9 (C=O). HRMS (ESI+) C₁₇H₂₆NO requires 260.2014, found 260.2034 [M+H]; C₁₇H₂₅NONa requires 282.1834, found 282.1846 [M+Na].

(1*S*, 2*S*)-1-phenyl-2-(phenylthio)-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3k**

Colourless solid (m.p. 110-112 °C), [α]_D¹⁸ 152 (*c*, 1.22, CHCl₃); ee = 90% as determined by chiral HPLC, chiral support CHIRALPAK OJ-H, "hexane : EtOH, 98 : 2, 1 mL/min, retention time : 8.6 min (minor), 15.0 min (major).

ν_{max} (CDCl₃)/cm⁻¹ 2968, 1632, 1451, 1371, 1342, 1133, 1037. δ_{H} (400 MHz, CDCl₃) 0.53 (3H, d, *J* 6.6), 0.86 (1H, d, *J* 6.7, *CHH*), 1.17 (3H, d, *J* 6.6), 1.49 (3H, d, *J* 6.8), 1.55 (3H, d, *J* 6.8), 1.93 (1H, ap. t, *J* 5.4, *CHH*), 3.32 (2H, m), 4.30 (1H, sept, *J* 6.6, *NCH*), 7.14 (1H, m, Ar, *CH*), 7.22 (1H, t, *J* 7.4, Ar, *CH*), 7.27 (1H, m, Ar, *CH*), 7.35 (3H, m, Ar, *CH*), 7.39 (2H, s, Ar, *CH*), 7.47 (2H, dd, *J* 8.3, 1.1, Ar, *CH*). δ_{C} (100 MHz, CDCl₃) 19.4 (CH₃), 19.7 (CH₃), 20.6 (CH₃), 21.1 (CH₃), 25.2 (CH₂), 25.6 (CH), 39.4 (C), 46.1 (CH), 49.2 (CH), 125.6 (Ar, CH), 126.5 (Ar, CH), 126.9 (Ar, CH), 127.9 (Ar, CH), 128.5 (Ar, CH), 128.8 (Ar, CH), 139.9 (Ar, 2 × C), 167.5 (C=O). HRMS (ESI+) C₂₂H₂₈NOS requires 354.1886; found 354.1889 [M+H]; C₂₂H₂₇NOSNa requires 376.1706, found 376.376.1721 [M+Na]

(1*S*, 2*S*)-2-benzoyl-1-phenyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3l**

Colourless solid (m.p. 72-74 °C), [α]_D¹⁸ 81 (*c*, 1.19, CHCl₃).

ν_{max} (CDCl₃)/cm⁻¹ 2967, 2933, 1694, 1632, 1451, 1372, 1096, 898. δ_{H} (400 MHz, CDCl₃) 0.70 (3H, d, *J* 6.7), 0.94 (3H, d, *J* 6.7), 1.36 (3H, d, *J* 6.8), 1.38 (3H, d, *J* 6.8), 1.76 (1H, dd, *J* 8.0, 4.7, *CHH*), 2.47 (1H, dd, *J* 6.1, 4.7, *CHH*), 3.12 (1H, dd, *J* 8.0, 6.1, *CHCOPh*), 3.21 (1H, sept, *J* 6.8, *NCH*), 4.31 (1H, sept, *J* 6.7, *NCH*), 7.30 (1H, t, *J* 7.3, Ar, *CH*), 7.38 (2H, t, *J* 7.3, Ar, *CH*), 7.46 (4H, m, Ar, 2 × *CH*), 7.53 (1H, t, *J* 7.3, Ar, *CH*), 8.01 (2H, d, *J* 7.3, Ar, *CH*). δ_{C} (100 MHz, CDCl₃) 19.9 (CH₃), 20.0 (CH₃), 20.1 (CH₃), 20.2 (CH₃), 20.3 (CH₂), 44.3 (CH), 45.0 (C), 45.9 (CH), 48.9 (CH), 126.1 (Ar, CH), 127.2 (Ar, CH), 128.2 (Ar, CH), 128.4 (Ar, CH),

128.8 (Ar, CH), 130.1 (Ar, CH), 132.5 (Ar, CH), 138.5 (Ar, C), 139.3 (Ar, C), 166.9 (C=O), 196.2 (C=O). HRMS (ESI+) $C_{23}H_{28}NO_2$ requires 350.2115; found 350.2126 [M+H]; $C_{23}H_{27}NO_2Na$ requires 372.1939, found 372.1962 [M+Na].

(1*R*, 2*S*)-1-phenyl-2-prenyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3m**

Colourless solid (m.p. 67-68 °C), $[\alpha]_D^{18}$ 190 (*c*, 1.00, CHCl₃)

ν_{max} (CDCl₃)/cm⁻¹ 2967, 2932, 1625, 1452, 1371, 1342, 1134, 1038; δ_H (400 MHz, CDCl₃) 0.41 (3H, d, *J* 6.8), 0.82 (1H, dd, *J* 8.4, 4.4, *CHH*), 1.09 (3H, d, *J* 6.8), 1.43 (7H, dd, *J* 6.8, 6.8, *CHHCH=C(CH₃)₂*), 1.64 (3H, s, *CH₂CH=C(CH₃)₂*), 1.69 (1H, m, *CHH*), 1.73 (3H, s, *CH₂CH=C(CH₃)₂*), 1.86 (1H, m, *CH*), 2.53 (1H, m, *CHHCH=C(CH₃)₂*), 3.23 (1H, sept, *J* 6.8, *NCH*), 4.28 (1H, sept, *J* 6.8, *NCH*), 5.29 (1H, d, *J* 6.8 1.2 *CH₂CH=C(CH₃)₂*), 7.17 (1H, m, Ar, *CH*), 7.25 (4H, m, Ar, 2 × *CH*); δ_C (100 MHz, CDCl₃) 17.8 (CH₃), 19.0 (CH₃), 19.5 (CH₃), 20.8 (CH₃), 21.3 (CH₃), 21.4 (CH₃), 24.2 (CH), 25.6 (CH₃), 28.3 (CH₂), 36.7 (C), 45.7 (CH), 48.7 (CH), 122.9 (*CH=C(CH₃)₂*), 126.0 (Ar, CH), 126.3 (Ar, CH), 128.4 (Ar, CH), 132.2 (*CH=C(CH₃)₂*), 141.8 (Ar, C), 168.7 (C=O). HRMS (ESI+) $C_{21}H_{32}NO$ requires 314.2478; found 314.2475 [M+H], $C_{21}H_{31}NONa$ requires 336.2298; found 336.2307 [M+Na]

(1*R*, 2*S*)-2-(1-hydroxycyclohexyl)-1-phenyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3n**

Colourless oil, $[\alpha]_D^{18}$ 17 (*c*, 1.05, CHCl₃); ee = 79% as determined by chiral HPLC, chiral support CHIRALPAK AD-H, η hexane : EtOH, 99 : 1, 0.5 mL/min, retention time : 10.7 min (major), 11.9 min (minor). Spectroscopic data were identical to those for the racemic material.

ν_{max} (CDCl₃)/cm⁻¹ 3395, 2969, 2934, 2859, 1596, 1457, 1372, 1347, 1038, 987; δ_H (400 MHz, CDCl₃) 0.61 (3H, d, *J* 6.5), 1.13 (1H, t, *J* 8.0, *CHH*), 1.16 (3H, d, *J* 7.0), 1.23 (1H, m, *CHH*), 1.35 (1H, m, *CHH*), 1.40 (1H, m, *CHH*), 1.47 (6H, m), 1.52 (2H, m, *CH₂*), 1.69 (5H, m, 2 × *CH₂*, *CHH*), 1.73 (2H, m, *CH₂*), 2.22 (1H, d, *J* 16.5, *CHOH*), 3.32 (2H, sept, *J* 7.0, *NCH*), 3.91 (1H, s, *OH*), 4.48 (1H, sept, *J* 6.5, *NCH*), 7.17-7.25 (3H, m, Ar, *CH*), 7.28-7.32 (2H, m, Ar, *CH*); δ_C (100 MHz, CDCl₃) 12.7 (CH₂), 19.3 (CH₃), 19.5 (CH₃), 20.0 (CH₃), 20.4 (CH₃), 21.9

(2 × CH₂), 26.1 (CH₂), 34.4 (C), 37.0 (CH₂), 39.0 (CH₂), 42.5 (CH), 46.1 (CH), 49.5 (CH), 68.7 (CHOH), 125.4 (Ar, CH), 126.2 (Ar, CH), 128.6 (Ar, CH), 141.4 (Ar, C), 172.8 (C=O); HRMS (ESI+) C₂₂H₃₃NO₂Na requires 366.2406; found 366.2420 [M+Na];

(1*S*, 2*S*)-1-benzyl-2-iodo-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3o**

Colourless solid (m.p. 76-78 °C)

ν_{max} (CDCl₃)/cm⁻¹ 2968, 2934, 1627, 1454, 1380, 1370, 1355, 1317, 1038. δ_{H} (400 MHz, CDCl₃) 1.23 (6H, br s), 1.34 (3H, d, *J* 6.8), 1.44 (4H, m), 1.51 (1H, br s, *CHH*), 2.49 (1H, d, *J* 14.4, *CHHPh*), 2.59 (1H, dd, *J* 7.7, 5.7, *CHI*), 3.31 (1H, m, *NCH*), 3.50 (1H, d, *J* 14.4, *CHHPh*), 4.23 (1H, br s, *NCH*), 7.18 (2H, d, *J* 7.2, Ar, *CH*), 7.22 (1H, t, *J* 7.2, Ar, *CH*), 7.28 (2H, t, *J* 7.2, Ar, *CH*). δ_{C} (100 MHz, CDCl₃) -8.3 (*CHI*), 17.4 (CH₂), 19.8 (CH₃), 20.1 (CH₃), 20.7 (CH₃), 21.2 (CH₃), 32.4 (C), 40.7 (CH₂), 46.5 (CH), 48.9 (CH), 126.9 (Ar, CH), 128.5 (Ar, CH), 139.4 (Ar, CH), 137.1 (Ar, C), 168.8 (C=O). HRMS (ESI+) C₁₇H₂₅INO requires 386.0975; found 386.0986 [M+H], C₁₇H₂₄INONa requires 408.0795; found 408.0805 [M+Na]

(1*S*, 2*S*)-1-benzyl-2-(phenylthio)-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3p**

Colourless solid (m.p. 68-70 °C)

ν_{max} (CDCl₃)/cm⁻¹ 2967, 2930, 1621, 1454, 1370, 1319, 1090, 1037. δ_{H} (400 MHz, CDCl₃) 0.91 (3H, br s, N(CH(CH₃)₂)), 1.16 (3H, br s, N(CH(CH₃)₂)), 1.27 (1H, br s, *CHH*), 1.35 (3H, d, *J* 6.8, N(CH(CH₃)₂)), 1.43 (3H, d, *J* 6.8, N(CH(CH₃)₂)), 1.48 (1H, br s, *CHH*), 2.38 (1H, dd, *J* 6.9, 5.5, *CHSPh*), 2.66 (1H, d, *J* 14.1, *CHHPh*), 3.28 (1H, m, N(CH(CH₃)₂)), 3.43 (1H, d, *J* 14.1, *CHHPh*), 4.28 (1H, br s, N(CH(CH₃)₂)), 7.13 (1H, t, *J* 7.4, Ar, *CH*), 7.23-7.29 (6H, m, Ar, *CH*), 7.32 (3H, t, *J* 7.4, Ar, *CH*). δ_{C} (100 MHz, CDCl₃) 20.0 (CH₃), 20.5 (CH₃), 21.0 (2 × CH₃), 22.1 (CH₂), 24.9 (CH), 35.0 (C), 41.8 (CH₂), 46.2 (CH), 48.8 (CH), 125.1 (Ar, CH), 126.8 (Ar, CH), 127.3 (Ar, CH), 128.4 (Ar, CH), 128.6 (Ar, CH), 129.6 (Ar, CH), 137.2 (Ar,

C), 168.3 (C=O). HRMS (ESI+) $C_{23}H_{30}NOS$ requires 368.2043, found 368.2063 [M+H]; $C_{23}H_{29}NOSNa$ requires 390.1868, found 390.1892 [M+Na].

(1*S*, 2*S*)-2-iodo-1-trifluoromethyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3q**

(from 0.84 mmol), m = 0.16 g, 52% yield, white solid (m.p. 77-79 °C)

$\nu_{\max}$ (CDCl₃)/cm⁻¹ 2970, 2936, 2879, 1650, 1452, 1372, 1345, 1321, 1134, 1061, 1034. δ_H (400 MHz, CDCl₃) 1.20 (3H, d, *J* 6.0, N(CH(CH₃)₂)), 1.31 (1H, br s, CHH), 1.40 (6H, d, *J* 6.8, N(CH(CH₃)₂)), 1.47 (3H, d, *J* 6.0, N(CH(CH₃)₂)), 2.13 (1H, br s, CHH), 3.02 (1H, br s, CHI), 3.42 (1H, br s, N(CH(CH₃)₂)), 4.27 (1H, br s, N(CH(CH₃)₂)). δ_C (100 MHz, CDCl₃) -14.2 (CHI), 20.3 (4 × CH₃), 20.5 (CH₂), 22.2 (C), 47.1 (CH), 49.5 (CH), 124.6 (CF₃), 161.2 (C=O). HRMS (ESI+) $C_{11}H_{18}F_3NO$ requires 364.0379; found 364.0375 [M+H], $C_{11}H_{17}F_3NONa$ requires 386.0199; found 386.0195 [M+Na].

(1*S*, 2*S*)-2-(phenylthio)-1-trifluoromethyl-*N,N*-bis(isopropyl)cyclopropanecarboxamide **3r**

Colourless solid (m.p. 94-96 °C)

$\nu_{\max}$ (CDCl₃)/cm⁻¹ 2970, 2937, 2256, 1645, 1586, 1454, 1372, 1348, 1136, 1077, 1035. δ_H (400 MHz, CDCl₃) 1.19 (3H, d, *J* 6.4, N(CH(CH₃)₂)), 1.27 (3H, d, *J* 6.4, N(CH(CH₃)₂)), 1.41 (4H, d, *J* 6.0, N(CH(CH₃)₂), CHH), 1.49 (3H, d, *J* 6.0, N(CH(CH₃)₂)), 1.99 (1H, br s, CHH), 2.91 (1H, br s, CHSPh), 3.42 (1H, sept, *J* 6.4, N(CH(CH₃)₂)), 4.37 (1H, br s, N(CH(CH₃)₂)), 7.21 (1H, t, *J* 6.8, Ar, CH), 7.31 (2H, t, *J* 6.8, Ar, CH), 7.39 (2H, d, *J* 6.8, Ar, CH). δ_C (100 MHz, CDCl₃) 19.8 (2 × CH₃), 20.4 (2 × CH₃), 20.6 (CH), 20.9 (CH₂), 23.9 (C), 46.9 (CH), 49.7 (CH), 123.1 (CF₃), 125.8 (Ar, C), 127.5 (Ar, CH), 129.0 (Ar, CH), 160.8 (C=O). HRMS (ESI+) $C_{17}H_{23}F_3NOS$ requires 346.1447, found 346.1442 [M+H]; $C_{17}H_{22}F_3NOSNa$ requires 368.1266, found 368.1272 [M+Na]