Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Practical and general method for optical resolution of *gem*-dihalo- and monohalo- cyclopropanecarboxylic acids utilizing chiral 1,1'-binaphthol monomethyl ethers: Application to the synthesis of three chiral pesticides

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Electronic supplementary information

(1*R*,3*R*)- and (1*S*,3*S*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2,2-dichloro-1,3-dimethylcyclopropanecarboxylate [(1*R*,3*R*)-3b and (1*S*,3*S*)-3b]. (Table 1, entry 2)

Following the procedure for the preparation of (1*R*)-**3a** and (1*S*)-**3a**, the reaction of (±)-acid **1b** (110 mg, 0.60 mmol) and (*R*)-**2** (150 mg, 0.50 mmol) using TsCl (114 mg, 0.60 mmol) and *N*-methylimidazole (123 mg, 1.50 mmol) gave the desired products (1*R*,3*R*)-**3b** (90 mg, 39%) and (1*S*,3*S*)-**3b** (88 mg, 38%).

(1*R*,3*R*)-**3b**: Colorless crystals; mp 144-146 ˚C; R_f = 0.33 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{24}$ +88.8 (*c* 1.09, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (3H, s), 1.07 (3H, d, *J* = 6.5 Hz), 1.29 (1H, q, *J* = 6.5 Hz), 3.73 (3H, s), 7.14 (1H, d, *J* = 8.3 Hz), 7.19-7.48 (7H, m), 7.82 (1H, d, *J* = 7.9 Hz), 7.88-8.00 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.5, 20.2, 35.7, 36.6, 56.7, 67.2, 113.7, 117.5, 121.5, 123.7, 125.3, 125.4, 125.6, 126.1, 126.5, 126.7, 127.7, 128.1, 129.0, 129.2, 130.0, 131.9, 133.7, 133.8. IR (KBr) 1757, 1306, 1265, 1252, 1236, 1211, 1140, 1127, 1084, 808 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{22}Cl_2O_3$ ($M+Na^+$) 487.0844, found 487.0840.

(1*S*,3*S*)-**3b**: Colorless crystals; mp 98-99 ˚C; R_f = 0.40 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{24}$ -51.6 (*c* 1.52, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80 (3H, s), 1.09 (3H, d, *J* = 6.5 Hz), 1.26 (1H, q, *J* = 6.5 Hz), 3.77 (3H, s), 7.11 (1H, d, *J* = 8.6 Hz), 7.16-7.24 (1H, m), 7.25-7.33 (2H, m), 7.35-7.49 (3H, m), 7.82 (1H, d, *J* = 7.9 Hz),

7.92 (1H, d, J = 8.3 Hz), 7.96 (2H, d, J = 8.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.4, 20.0, 35.7, 36.5, 56.6, 67.3, 113.5, 117.4, 121.6, 123.7, 125.2, 125.3, 125.6, 126.1, 126.5, 126.6, 127.6, 128.1, 128.9, 129.0, 130.0, 131.8, 133.6, 133.7, 146.4, 154.9, 166.4. IR (KBr) 1751, 1263, 1252, 1235, 1213, 1136, 1125, 1084, 808 cm^{-1}.

(1*R*,3*S*)- and (1*S*,3*R*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2,2-dichloro-1,3-dimethylcyclopropanecarboxylate [(1*R*,3*S*)-3c and (1*S*,3*R*)-3c]. (Table 1, entry 3)

Following the procedure for the preparation of (1*R*)-**3a** and (1*S*)-**3a**, the reaction of (±)-acid **1c** (110 mg, 0.60 mmol) and (*R*)-**2** (150 mg, 0.50 mmol) using TsCl (114 mg, 0.60 mmol) and *N*-methylimidazole (123 mg, 1.50 mmol) gave the desired products (1*R*,3*S*)-**3c** (90 mg, 39%) and (1*S*,3*R*)-**3c** (90 mg, 39%).

(1*R*,3*S*)-**3c**: Colorless crystals; mp 67-69 ˚C; R_f = 0.40 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{24}$ +92.5 (*c* 3.35, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.63 (3H, s), 0.95 (3H, d, J = 6.5 Hz), 2.07 (1H, q, J = 6.5 Hz), 3.73 (3H, s), 7.12-7.19 (1H, m), 7.20-7.36 (4H, m), 7.37-7.49 (3H, m), 7.83 (1H, d, J = 7.91 Hz), 7.88-8.01 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.68, 11.1, 30.5, 37.0, 56.7, 66.8, 113.7, 117.5, 121.5, 123.7, 125.2, 125.3, 125.6, 126.2, 126.5, 126.7, 127.7, 128.2, 128.9, 129.2, 130.0, 131.9 133.6, 133.8 146.6, 155.0, 167.9. IR (KBr) 1753, 1508, 1462, 1265, 1213, 1157, 1123, 1086, 808, 748 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{22}Cl_2O_3$ ($M+Na^+$) 487.0844, found 487.0849.

(1*S*,3*R*)-**3c**: Colorless crystals; mp 69-70 ˚C; R_f = 0.49 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{24}$ -33.2 (*c* 3.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.62 (3H, s), 0.88 (3H, d, J = 6.5 Hz), 2.03 (1H, q, J = 6.5 Hz), 3.78 (3H, s), 7.12 (1H, d, J = 7.9 Hz), 7.17-7.33 (4H, m), 7.37-7.49 (3H, m), 7.83 (1H, d, J = 7.9 Hz), 7.88-8.02 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.6, 11.0, 30.6, 36.9, 56.7, 66.9, 113.5, 117.4, 121.7, 123.7, 125.0, 125.3, 125.6, 126.1, 126.5, 126.7, 127.7, 128.2, 128.9, 129.1, 130.0, 131.9, 133.6, 133.7, 146.7, 154.9, 168.1. IR (KBr) 1753, 1508, 1262, 1213, 1159, 1084, 808, 748 cm^{-1}.

(1*R*,3*S*)- and (1*S*,3*R*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2,2-dichloro-1-methyl-3-phenylcyclopropanecarboxylate [(1*R*,3*S*)-3d and (1*S*,3*R*)-3d]. (Table 1, entry 4)

Following the procedure for the preparation of (1*R*)-**3a** and (1*S*)-**3a**, the reaction of (±)-acid **1d** (147 mg, 0.60 mmol) and (*R*)-**2** (150 mg, 0.50 mmol) using TsCl (114 mg, 0.60 mmol) and *N*-methylimidazole (123 mg, 1.50 mmol) gave the desired products (1*R*,3*S*)-**3d** (98 mg, 37%) and (1*S*,3*R*)-**3d** (95 mg, 36%).

(1*R*,3*S*)-**3d**: Colorless crystals; mp 160-162 ˚C; R_f = 0.28 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{25}$ +52.9 (*c* 1.33, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.64 (3H, s), 3.31 (1H, s), 3.76 (3H, s), 6.87-6.97 (2H, m), 7.14-7.38 (8H, m), 7.40-7.55 (3H, m), 7.81-7.89 (1H, m), 7.92-8.06 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$):

δ 13.9, 39.1, 39.4, 56.7, 65.6, 113.6, 117.5, 121.5, 123.8, 125.3, 125.7, 126.2, 126.6, 126.8, 127.4, 127.8, 128.2, 128.3, 129.0,129.3, 129.8, 130.1, 131.5, 132.0, 133.6, 133.8, 146.6, 155.1, 167.5. IR (KBr) 1757, 1265, 1252, 1213, 1192, 1138, 1127, 1084, 808, 750 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{24}Cl_2O_3$ ($M+Na^+$) 549.1000, found 549.9995.

(1*S*,3*R*)-**3d**: Colorless crystals; mp 70-71 ˚C; R_f = 0.33 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{25}$ +62.4 (*c* 1.24, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.55 (3H, s), 3.27 (1H, s), 3.78 (3H, s), 6.66-6.85 (2H, m), 7.09-7.66 (11H, m), 7.78-8.14 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 39.0, 39.5, 56.7, 65.7, 113.6, 117.5, 121.7, 123.8, 125.2, 125.3, 125.7, 126.1, 126.6, 126.8, 127.4, 127.8, 128.2, 129.0, 129.2, 129.8, 130.1, 131.3, 131.9, 133.7, 146.6, 155.0, 167.7. IR (KBr) 1753, 1508, 1456, 1252, 1213, 1192, 1140, 1084, 808, 748 cm^{-1}.

(1*R*,3*S*)- and (1*S*,3*R*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2,2-dichloro-1-ethyl-3-methylcyclopropanecarboxylate [(1*R*,3*S*)-3e and (1*S*,3*R*)-3e]. (Table 1, entry 5)

Following the procedure for the preparation of (1*R*)-**3a** and (1*S*)-**3a**, the reaction of (±)-acid **1e** (118 mg, 0.60 mmol) and (*R*)-**2** (150 mg, 0.50 mmol) using TsCl (114 mg, 0.60 mmol) and *N*-methylimidazole (123 mg, 1.50 mmol) gave the desired products (1*R*,3*S*)-**3e** (88 mg, 37%) and (1*S*,3*R*)-**3e** (90 mg, 38%).

(1*R*,3*S*)-**3e**: Colorless crystals; mp 158-159 ˚C; R_f = 0.54 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{25}$ -62.5 (*c* 2.50, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ -0.04 (3H, t, *J* = 7.2 Hz), 0.98 (3H, d, *J* = 6.5 Hz), 1.05-1.19 (1H, m), 1.71-1.87 (1H, m), 2.07 (1H, q, *J* = 6.5 Hz), 3.81 (3H, s), 7.14 (1H, d, *J* = 8.3 Hz), 7.18-7.34 (4H, m), 7.39-7.51 (3H, m), 7.82 (1H, d, *J* = 8.3 Hz), 7.90-8.03 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.6, 9.5, 20.7, 30.2, 42.6, 56.8, 66.6, 113.6, 117.5, 121.7, 123.7, 125.1, 125.4, 125.6, 126.1, 126.5, 126.7, 127.6, 128.1, 129.1, 129.1, 130.1, 131.8, 133.6, 133.9, 146.8, 155.0, 167.9. IR (KBr) 2971, 2938, 2880, 2672, 2594,1705, 1462, 1420, 1306, 1252, 1194, 936, 868, 828 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{24}Cl_2O_3$ ($M+Na^+$) 549.1000, found 549.9994.

(1*S*,3*R*)-**3e**: Colorless crystals; mp 157-158 ˚C; R_f = 0.59 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{25}$ +98.6 (*c* 2.10, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.12 (3H, t, *J* = 7.6 Hz), 1.00 (3H, d, *J* = 6.5 Hz), 1.02-1.14 (1H, m), 1.47-1.69 (1H, m), 2.09 (1H, q, *J* = 6.5 Hz), 3.74 (3H, s), 7.16-7.49 (8H, m), 7.82 (1H, d, *J* = 7.6 Hz), 7.89-8.01 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.6, 9.8, 20.5, 30.2, 42.6, 56.8, 66.5, 113.9, 117.6, 121.5, 123.7, 125.3, 125.6, 126.1, 126.5, 126.6, 127.7, 128.1, 129.2, 129.3, 130.1, 131.9, 133.6, 133.8, 146.7, 155.2, 167.7. IR (KBr) 2971, 2938, 2880, 2668, 2594,1705, 1462, 1420, 1306, 1252, 933, 868, 828 cm^{-1}.

(1*R*)- and (1*S*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]1-(4-ethoxyphenyl)-2,2-dichlorocyclopropanecarboxylate

[(1*R*)-3f and (1*S*)-3f]. (Table 1, entry 6)

Following the procedure for the preparation of (1*R*)-**3a** and (1*S*)-**3a**, the reaction of (±)-acid **1f** (330 mg, 1.20 mmol) and (*R*)-**2** (300 mg, 1.00 mmol) using TsCl (229 mg, 1.20 mmol) and *N*-methylimidazole (246 mg, 3.00 mmol) gave the desired products (1*R*)-**3f** (218 mg, 39%) and (1*S*)-**3f** (221 mg, 40%).

(1*R*)-**3f**: Colorless crystals; mp 78-79 ˚C; R_f = 0.27 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{23}$ -61.0 (*c* 1.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (3H, t, *J* = 6.9 Hz), 1.84 (1H, d, *Jgem* = 7.6 Hz), 2.38 (1H, d, *Jgem* = 7.6 Hz), 3.58 (3H, s), 3.91-4.08 (2H, m), 6.41 (2H, d, *J* = 8.6 Hz), 6.88 (2H, d, *J* = 8.6 Hz), 7.01 (1H, d, *J* = 8.6 Hz), 7.06-7.34 (5H, m), 7.38-7.46 (2H, m), 7.79 (2H, d, *J* = 9.3 Hz), 7.93 (2H, t, *J* = 9.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.9, 30.3, 44.2, 56.2, 61.6, 63.2, 113.2, 113.7, 116.8, 121.3, 123.4, 124.9, 125.1, 125.5, 126.1, 126.4, 127.7, 128.1, 128.9, 128.9, 129.8, 131.2, 131.8, 133.7, 146.6, 154.7, 158.6, 165.9. IR (KBr) 3449, 3059, 2936, 1753, 1593, 1508, 1458, 1252, 1213, 1142, 1084, 1057, 808, 747 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{26}Cl_2O_4$ (M+Na$^+$) 578.4197, found 578.4201.

(1*S*)-**3f**: Colorless crystals; mp 79-80 ˚C; R_f = 0.33 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{24}$ +51.3 (*c* 1.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (3H, t, *J* = 6.9 Hz), 1.75 (1H, d, *Jgem* = 7.6 Hz), 2.33 (1H, d, *Jgem* = 7.6 Hz), 3.62 (3H, s), 3.96-4.07 (2H, m), 6.48-6.55 (2H, m), 6.73-6.81 (2H, m), 7.01 (1H, d, *J* = 8.3 Hz), 7.13-7.32 (5H, m), 7.39-7.47 (2H, m), 7.77 (1H, d, *J* = 8.3 Hz), 7.81-7.97 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.0, 30.7, 43.9, 56.4, 61.7, 63.3, 113.4, 113.7, 117.1, 121.4, 123.4, 125.1, 125.2, 125.6, 126.1, 126.4, 126.4, 127.7, 128.1, 128.8, 128.9, 129.9, 131.3, 131.8, 133.6, 133.6, 146.7, 154.7, 158.5, 165.9. IR (KBr) 3449, 2978, 2934, 2361, 1750, 1611, 1593, 1512, 1476, 1460, 1250, 1213, 1171, 1086, 1042, 806, 767, 748 cm^{-1}.

(1*R*)- and (1*S*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2,2-dibromo-1-methylcyclopropanecarboxylate [(1*R*)-3g and (1*S*)-3g]. (Table 1, entry 7)

Following the procedure for the preparation of (1*R*)-**3a** and (1*S*)-**3a**, the reaction of (±)-acid **1g** (155 mg, 0.60 mmol) and (*R*)-**2** (150 mg, 0.50 mmol) using TsCl (114 mg, 0.60 mmol) and *N*-methylimidazole (123 mg, 1.50 mmol) gave the desired products (1*R*)-**3g** (101 mg, 37%) and (1*S*)-**3g** (100 mg, 37%).

(1*R*)-**3g**: Colorless crystals; mp 109-110 ˚C; R_f = 0.18 (hexane : AcOEt = 10 : 1); $[\alpha]_D^{23}$ +81.3 (*c* 3.21, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (3H, s), 1.35 (1H, d, *Jgem* = 7.9 Hz), 2.17 (1H, d, *Jgem* = 7.9 Hz), 3.75 (3H, s), 7.13-7.37 (5H, m), 7.39-7.51 (3H, m), 7.81-8.03 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.7, 29.3, 32.4, 34.7, 56.7, 113.7, 117.4, 121.5, 123.7, 125.3, 125.6, 126.2, 126.5, 126.7, 127.8, 128.2, 129.0, 129.2, 130.1, 131.9, 133.6, 133.8, 146.6, 155.1, 167.4. IR (KBr) 1751, 1507, 1271, 1250, 1213, 1130, 1084, 818, 752 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{20}Br_2O_3$ (M+Na$^+$) 560.9677, found 560.9672.

(1*S*)-**3g**: Colorless crystals; mp 79-80 ˚C; R_f = 0.27 (hexane : AcOEt = 10 : 1); $[\alpha]_D^{23}$ -51.4 (*c* 3.42, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (3H, s), 1.29 (1H, d, *Jgem* = 7.9 Hz), 2.11 (1H, d, *Jgem* = 7.9 Hz), 3.81

(3H, s), 7.09-7.15 (1H, m), 7.18-7.35 (4H, m), 7.41-7.53 (3H, m), 7.80-8.03 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 29.4, 32.3, 34.7, 56.7, 113.4, 117.4, 121.6, 123.7, 125.0, 125.2, 125.6, 126.1, 126.5, 126.7, 127.7, 128.2, 128.9, 129.1, 130.0, 131.9, 133.6, 133.7, 146.6, 154.9, 167.6. IR (KBr) 1753, 1508, 1263, 1213, 1142, 1086, 1057, 806, 748 cm^{-1}.

(1*S*)-2,2-Dichloro-1-methylcyclopropanecarboxylic acid [(1*S*)-1a].[3] (Table 2, entry 2)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*S*)-**3a** (3.48 g, 7.71 mmol) gave the desired product (1*S*)-**1a** (1.35 g, 96%) with recovery of (*R*)-**2** (2.23 g, 96%).

Yellow oil: $[\alpha]_D^{23}$ -51.0 (*c* 1.33, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (1H, d, *Jgem* = 7.6 Hz), 1.16 (3H, s), 2.30 (1H, d, *Jgem* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.02, 31.18, 35.12, 62.61, 175.52. IR (neat) 3001, 1709, 1416, 1316, 945 cm^{-1}.

(1*R*,3*R*)-2,2-Dichloro-1,3-dimethylcyclopropanecarboxylic acid [(1*R*,3*R*)-1b].[5b,c] (Table 2, entry 3)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*S*,3*S*)-**3b** (279 mg, 0.60 mmol) gave the desired product (1*R*,3*R*)-**1b** (88 mg, 80%) with recovery of (*R*)-**2** (171 mg, 95%).

Yellow crystals: mp 90-92 ˚C; $[\alpha]_D^{23}$ +25.5 (*c* 1.03, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 (3H, d, *J* = 6.5 Hz), 1.61 (1H, q, *J* = 6.5 Hz), 1.62 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.74, 21.13, 36.60, 67.67, 174.94. IR (KBr) 2999, 2941, 1707, 1460, 1412, 1310, 1256, 1184 cm^{-1}.

(1*S*,3*S*)-2,2-Dichloro-1,3-dimethylcyclopropanecarboxylic acid [(1*S*,3*S*)-1b].[5b,c] (Table 2, entry 4)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*S*,3*S*)-**3b** (651 mg, 1.40 mmol) gave the desired product (1*S*,3*S*)-**1b** (202 mg, 79%) with recovery of (*R*)-**2** (391 mg, 93%).

Yellow crystals: mp 90-91 ˚C; $[\alpha]_D^{23}$ -27.5 (*c* 0.79, $CHCl_3$).

(1*R*,3*S*)-2,2-Dichloro-1,3-dimethylcyclopropanecarboxylic acid [(1*R*,3*S*)-1c].[5b,c] (Table 2, entry 5)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*R*,3*S*)-**3c** (161 mg, 0.35 mmol) gave the desired product (1*R*,3*S*)-**1c** (56 mg, 89%) with recovery of (*R*)-**2** (101 mg, 96%).

Yellow crystals: mp 61-62 ˚C; $[\alpha]_D^{25}$ +43.9 (*c* 2.80, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, d, *J* = 6.5 Hz), 1.41 (3H, s), 2.41 (1H, q, *J* = 6.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.00, 11.89, 31.24, 36.75, 67.38, 175.82. IR (KBr) 3192, 1726, 1682, 1399, 1221, 1184, 970, 909 cm^{-1}.

(1*S*,3*R*)-2,2-Dichloro-1,3-dimethylcyclopropanecarboxylic acid [(1*S*,3*R*)-1c].[5b,c] (Table 2, entry 6)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*S*,3*R*)-**3c** (218 mg, 0.47 mmol) gave the desired product (1*S*,3*R*)-**1c** (76 mg, 88%) with recovery of (*R*)-**2** (130 mg, 92%).

Yellow crystals: mp 64-65 ˚C; $[\alpha]_D^{25}$ -42.8 (*c* 2.55, $CHCl_3$).

(1*R*,3*S*)-2,2-Dichloro-1-methyl-3-phenylcyclopropanecarboxylic acid [(1*R*,3*S*)-1d].[6b] (Table 2, entry 7)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*R*,3*S*)-**3c** (762 mg, 1.44 mmol) gave the desired product (1*R*,3*S*)-**1c** (325 mg, 92%) with recovery of (*R*)-**2** (402 mg, 93%).

Colorless crystals: mp 122-123 ˚C; $[\alpha]_D^{25}$ -22.1 (*c* 2.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (3H, s), 3.66 (1H, s), 7.23-7.42 (5H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.51, 39.01, 39.89, 65.91, 127.73, 128.51, 130.00, 131.36, 175.55. IR (KBr) 3000, 2300, 1710, 1310 cm^{-1}.

(1*S*,3*R*)-2,2-Dichloro-1-methyl-3-phenylcyclopropanecarboxylic acid [(1*S*,3*R*)-1d].[6b] (Table 2, entry 8)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*S*,3*R*)-**3d** (832 mg, 1.58 mmol) gave the desired product (1*S*,3*R*)-**1d** (336 mg, 87%) with recovery of (*R*)-**2** (432 mg, 91%).

Colorless crystals : mp 113-114 ˚C; $[\alpha]_D^{25}$ +23.0 (*c* 3.60, $CHCl_3$).

(1*R*,3*S*)-2,2-Dichloro-1-ethyl-3-methylcyclopropanecarboxylic acid [(1*R*,3*S*)-1e]. (Table 2, entry 9)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*R*,3*S*)-**3e** (94 mg, 0.22 mmol) gave the desired product (1*R*,3*S*)-**1e** (40 mg, 95%) with recovery of (*R*)-**2** (60 mg, 94%).

Pale yellow crystals; mp 92-93 ˚C; $[\alpha]_D^{25}$ +10.8 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (3H, t, *J* = 7.6 Hz), 1.23 (3H, d, *J* = 6.9 Hz), 1.42-1.57 (1H, m), 2.19-2.32 (1H, m), 2.36 (1H, q, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.8, 11.1, 20.7, 30.6, 42.6, 66.6, 174.7. IR (KBr) 3491, 3061, 2975, 2934, 2878, 2838, 1759, 1622, 1591, 1508, 1460, 1265, 1155, 1090, 808, 748 cm^{-1}. Anal. Calcd for $C_7H_{10}Cl_2O_2$; C, 44.66; H, 5.11, found: C, 44.6; H, 5.1.

(1*S*,3*R*)-2,2-Dichloro-1-ethyl-3-methylcyclopropanecarboxylic acid [(1*S*,3*R*)-1e]. (Table 2, entry 10)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*S*,3*R*)-**3e** (42 mg, 0.09 mmol) gave the desired product (1*S*,3*R*)-**1e** (16 mg, 94%) with recovery of (*R*)-**2** (24 mg, 91%).

Colorless crystals; mp 100-101 ˚C; $[\alpha]_D^{27}$ -10.9 (*c* 0.80, $CHCl_3$).

(*R*)-1-(4-ethoxyphenyl)-2,2-dichlorocyclopropanecarboxylic acid [(1*R*)-1f].[11] (Table 2, entry 11)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*R*)-**3f** (184 mg, 0.33 mmol) gave the desired product (1*R*)-**1f** (89 mg, 98%) with recovery of (*R*)-**2** (95 mg, 96%).

Colorless crystals; mp 169-170 ˚C; $[\alpha]_D^{23}$ -92.3 (*c* 3.60, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (3H, t, *J* = 6.9 Hz), 2.05 (1H, d, *Jgem* = 7.6 Hz), 2.60 (1H, d, *Jgem* = 7.6 Hz), 4.03 (2H, q, *J* = 6.9 Hz), 6.79-6.91 (2H, m), 7.29-7.40 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.8, 30.7, 44.0, 61.8, 63.5, 114.2, 125.5, 131.9,

159.2, 173.4. IR (KBr) 3221, 2990, 2922, 1732, 1694, 1609, 1514, 1393, 1254, 1202, 1115, 1044, 920, 814 cm^{-1}.

(*S*)-1-(4-ethoxyphenyl)-2,2-dichlorocyclopropanecarboxylic acid [(1*S*)-1f].[11] (Table 2, entry 12)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*S*)-**3f** (190 mg, 0.34 mmol) gave the desired product (1*S*)-**1f** (88 mg, 94%) with recovery of (*R*)-**2** (96 mg, 94%).

Pale yellow crystals; mp 169-170 ˚C; $[\alpha]_D^{24}$ +93.8 (*c* 2.65, $CHCl_3$).

(*R*)-2,2-Dibromo-1-methylcyclopropanecarboxylic acid [(1*R*)-1g].[2] (Table 2, entry 13)

Following the procedure for the preparation of (1*R*)-**1a**, the reaction of (1*R*)-**1g** (209 mg, 0.39 mmol) gave the desired product (1*R*)-**1g** (89 mg, 89%) with recovery of (*R*)-**2** (111 mg, 95%).

Colorless crystals : mp 56-58 ˚C; $[\alpha]_D^{25}$ +54.9 (*c* 4.45, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (1H, d, *Jgem* = 7.9 Hz), 1.64 (3H, s), 2.43 (1H, d, *Jgem* = 7.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.52, 29.25, 32.94, 34.78, 175.55. IR (KBr) 3088, 3005, 2936, 1703, 1456, 1402, 1260, 1196, 1026, 689 cm^{-1}.

(*S*)-2,2-Dibromo-1-methylcyclopropanecarboxylic acid [(1*S*)-1g].[2] (Table 2, entry 14)

Following the procedure for the preparation of (1*R*)-**1a** the reaction of (1*S*)-**1g** (221 mg, 0.41 mmol) gave the desired product (1*S*)-**1g** (98 mg, 93%) with recovery of (*R*)-**2** (116 mg, 94%).

Colorless crystals : mp 56-57 ˚C; $[\alpha]_D^{25}$ -54.2 (*c* 4.90, $CHCl_3$).

(1*S*,2*R*)- and (1*S*,2*S*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2-chloro-1-methylcyclopropanecarboxylate [(1*S*,2*R*)-4a and (1*S*,2*S*)-4a]. (Table 3, entry 2)

Following the procedure for the preparation of (1*R*,2*R*)-**4a** and (1*R*,2*S*)-**4a**, the reaction of (1*S*)-**3b** (400 mg, 0.89 mmol) gave the desired product (1*S*,2*R*)-**4a** (169 mg, 46%) and (1*S*,2*S*)-**4a** (88 mg, 24%).

(1*S*,2*R*)-**4a**: Pale yellow crystals; mp 50-52 ˚C; R_f = 0.60 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{24}$ -20.8 (*c* 3.90, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.56 (1H, t, *J* = 5.5 Hz), 1.04 (3H, s), 1.06 (1H, dd, *J* = 5.5, 7.9 Hz), 2.99 (1H, dd, *J* = 5.5, 7.9 Hz), 3.76 (3H, s), 7.07 (1H, d, *J* = 8.3 Hz), 7.19-7.38 (4H, m), 7.40-7.51 (3H, m), 7.88 (1H, d, *J* = 8.3 Hz), 7.91-8.05 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 24.1, 24.4, 39.4, 56.5, 113.3, 117.3, 121.6, 123.7, 124.9, 125.1, 125.5, 126.1, 126.4, 126.6, 127.9, 128.1, 128.9, 129.0, 130.1, 131.7, 133.5, 133.5, 146.8, 154.9, 168.5. IR (KBr) 3439, 3061, 3005, 2965, 2940, 1746, 1622, 1593, 1508, 1319, 1140,

1084, 810, 748 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}ClO_3$ ($M+Na^+$) 439.1077, found 439.1072.

(1*S*,2*S*)-**4a**: Pale yellow crystals; mp 180-182 ˚C; R_f = 0.46 (hexane : AcOEt = 5 : 1); $[\alpha]_D^{24}$ +3.1 (*c* 1.75, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.72 (3H, s), 0.84 (1H, t, *J* = 6.9 Hz), 1.38 (1H, dd, *J* = 5.2, 6.9 Hz), 2.87 (1H, dd, *J* = 5.2, 6.9 Hz), 3.77 (3H, s), 7.14 (1H, d, *J* = 8.3 Hz), 7.19-7.35 (4H, m), 7.38-7.51 (3H, m), 7.84 (1H, d, *J* = 8.3 Hz), 7.90-8.01 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.6, 22.0, 27.2, 38.5, 56.7, 113.5, 117.7, 122.0, 123.6, 124.9, 125.3, 125.4, 126.1, 126.4, 126.6, 127.6, 128.1, 128.9, 129.9, 131.7, 133.6, 133.7, 146.5, 154.8, 170.9. IR (KBr) 3449, 3063, 2971, 2938, 2841, 1753, 1622, 1593, 1508, 1318, 1136, 1128, 1084, 810 cm^{-1}.

(1*R*,2*R*,3*S*)- and (1*R*,2*S*,3*S*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2-chloro-1-methyl-3-phenylcyclopropanecarboxylate [(1*R*,2*R*,3*S*)-4b and (1*R*,2*S*,3*S*)-4b]. (Table 3, entry 3)

Following the procedure for the preparation of (1*R,*2*S*)-**4a** and (1*R*,2*R*)-**4a**, the reaction of (1*R*,3*S*)-**3b** (150 mg, 0.28 mmol) gave the desired products (1*R*,2*R,*3*S*)-**4b** (56 mg, 40%) and (1*R*,2*S*,3*S*)-**4b** (53 mg, 38%).

(1*R*,2*R,*3*S*)-**4b**: Pale yellow crystals; mp 69-71 ˚C; $[\alpha]_D^{23}$ +35.2 (*c* 1.75, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.48 (3H, s), 2.99 (1H, d, *J* = 5.5 Hz), 3.26 (1H, d, *J* = 5.5 Hz), 3.77 (3H, s), 6.74-6.84 (2H, m), 7.14-7.35 (8H, m), 7.40-7.50 (2H, m), 7.54 (1H, d, *J* = 8.6 Hz), 7.83 (1H, d, *J* = 8.6 Hz), 7.92-8.03 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 33.2, 37.2, 42.2, 56.7, 113.7, 117.8, 121.9, 123.7, 125.0, 125.4, 125.5, 126.1, 126.4, 126.7, 127.2, 127.7, 128.1, 128.3,128.6, 129.0, 130.0, 131.8, 133.6, 133.8, 134.0, 146.7, 155.0, 168.3. IR (KBr) 3449, 3059, 2936, 2839, 1748, 1622, 1593, 1508, 1215, 1123, 1086, 808, 748 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{25}ClO_3$ ($M+Na^+$) 515.1390, found 515.1392.

(1*R*,2*S*,3*S*)-**4b**: Colorless crystals; mp 173-175 ˚C; $[\alpha]_D^{23}$ -37.4 (*c* 1.50, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.82 (3H, s), 2.34 (1H, d, *J* = 8.3 Hz), 3.34 (1H, d, *J* = 8.3 Hz), 3.75 (3H, s), 6.76-6.88 (2H, m), 7.09-7.54 (11H, m), 7.86 (1H, d, *J* = 8.3 Hz), 7.91-8.07 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 28.1, 32.2, 43.0, 56.6, 113.3, 117.3, 121.6, 123.8, 125.2, 125.6, 126.1, 126.5, 126.7, 126.9, 128.0, 128.1, 128.9, 129.1,130.3, 130.6, 131.8, 132.0, 133.5, 133.6, 146.6, 154.9, 171.5. IR (KBr) 3451, 3057, 2934, 2839, 1732, 1620, 1593, 1508, 1211, 1123, 1082, 810, 748 cm^{-1}.

(1*S*,2*R*,3*R*)- and (1*S*,2*S*,3*R*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2-chloro-1-methyl-3-phenylcyclopropanecarboxylate [(1*S*,2*R*,3*R*)-4b and (1*S*,2*S*,3*R*)-4b]. (Table 3, entry 4)

Following the procedure for the preparation of (1*R*,2*R*,3*S*)-**4b** and (1*R*,2*S*,3*S*)-**4b**, the reaction of (1*S*,3*R*)-**3b** (100 mg, 0.19 mmol) gave the desired product (1*S*,2*R*,3*R*)-**4b** (37 mg, 40%) and (1*S*,2*S*,3*R*)-**4b** (34 mg, 37%).

(1*S*,2*R*,3*R*)-**4b**: Colorless crystals; mp 58-60 ˚C; $[\alpha]_D^{23}$ +142.4 (*c* 1.65, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76 (3H, s), 2.25(1H, d, *J* = 8.3 Hz), 3.53 (1H, d, *J* = 8.3 Hz), 3.79 (3H, s), 6.75-6.84 (2H, m), 7.11 (1H, d, *J* = 8.3 Hz), 7.17-7.37 (7H, m), 7.42-7.54 (3H, m), 7.81 (1H, d, *J* = 8.3 Hz), 7.92-8.05 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.0, 28.1, 32.5, 43.2, 56.7, 113.5, 117.6, 121.7, 123.8, 125.1, 125.6, 126.1, 126.5, 126.7, 126.9, 127.9, 128.2, 129.0, 129.0,130.2, 130.5, 131.8, 132.1, 133.5, 133.6, 146.6, 154.9, 171.7. IR (KBr) 3449, 3054, 2969, 2934, 2839, 1742, 1622, 1593, 1508, 1213, 1121, 1084, 810, 748 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{25}ClO_3$ ($M+Na^+$) 515.1390, found 515.1395.

(1*S*,2*S*,3*R*)-**4b**: Colorless crystals; mp 70-72 ˚C; $[\alpha]_D^{23}$ +67.4 (*c* 1.70, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.45 (3H, s), 2.95 (1H, d, *J* = 5.9 Hz), 3.27 (1H, d, *J* = 5.9 Hz), 3.76 (3H, s), 6.59-6.68 (2H, m), 7.16-7.50 (10H, m), 7.53 (1H, d, *J* = 8.3 Hz), 7.86 (1H, d, *J* = 8.3 Hz), 7.91-8.04 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 33.0, 37.5, 42.3, 56.7, 113.6, 117.8, 122.0, 123.7, 125.1, 125.4, 125.5, 126.1, 126.4, 126.7, 127.1, 127.7, 128.2, 128.6, 129.0, 129.9, 131.8, 133.7, 133.8, 146.8, 155.0, 168.3. IR (KBr) 3449, 3059, 2936, 2839, 1746, 1622, 1593, 1508, 1215, 1123, 1084, 808, 748 cm^{-1}.

(1*R*,2*R*)- and (1*R*,2*S*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2-bromo-1-methylcyclopropanecarboxylate [(1*R*,2*R*)-4c and (1*R*,2*S*)-4c]. (Table 3, entry 5)

Following the procedure for the preparation of (1*R*,2R)-**4a** and (1*R*,2*S*)-**4a**, the reaction of (1*R*)-**3c** (50 mg, 0.09 mmol) gave the desired product (1*R*,2*R*)-**4c** (18 mg, 42%) and (1*R*,2*S*)-**4c** (15 mg, 35%).

(1*R*,2*R*)-**4c**: Colorless crystals; mp 60-62 ˚C; $[\alpha]_D^{23}$ +30.9 (*c* 1.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.71 (3H, s), 0.99 (1H, dd, *J* = 6.5, 7.6 Hz), 1.50 (1H, dd, *J* = 5.5, 6.5 Hz), 2.74 (1H, dd, *J* = 5.5, 7.6 Hz), 3.75 (3H, s), 7.16 (1H, d, *J* = 8.3 Hz), 7.20-7.34 (4H, m), 7.39-7.53 (3H, m), 7.83 (1H, d, *J* = 8.3 Hz), 7.91-8.01 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.8, 22.1, 25.3, 26.6, 56.7, 113.7, 117.7, 121.9, 123.6, 125.0, 125.4, 126.2, 126.4, 126.6, 127.7, 128.1, 129.0, 129.9, 131.8, 133.6, 133.8, 146.8, 155.0, 168.7. IR (KBr) 3449, 3059,

2934, 2839, 1752, 1622, 1593, 1508, 1319, 1138, 1124, 1084, 808, 748 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}BrO_3$ ($M+Na^+$) 483.0572, found 483.0574.

(1*R*,2*S*)-**4c**: Colorless crystals; mp 50-52 ˚C; $[\alpha]_D^{22}$ +64.0 (*c* 2.15, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.66 (1H, t, *J* = 5.5 Hz), 1.13 (3H, s), 1.31 (1H, dd, *J* = 5.5, 7.9 Hz), 2.62 (1H, dd, *J* = 5.5, 7.9 Hz), 3.76 (3H, s), 7.04 (1H, d, *J* = 8.3 Hz), 7.18-7.38 (4H, m), 7.39-7.50 (3H, m), 7.85-8.06 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.6, 23.7, 24.4, 28.1, 56.5, 113.3, 117.2, 121.6, 123.7, 124.9, 125.1, 125.5, 126.2, 126.5, 126.6, 127.9, 128.1, 128.9, 129.0, 130.2, 131.7, 133.5, 133.6, 146.5, 154.8, 170.9. IR (KBr) 3632, 3449, 3059, 2936, 2839, 1746, 1624, 1593, 1508, 1312, 1138, 1127, 1086, 810, 747 cm^{-1}.

(1*S*,2*R*)- and (1*S*,2*S*)-[(*R*)-2'-Methoxy-1,1'-binaphth-2-yl]2-bromo-1-methylcyclopropanecarboxylate [(1*S*,2*R*)-4c and (1*S*,2*S*)-4c]. (Table 3, entry 6)

Following the procedure for the preparation of (1*R*,2*R*)-**4c** and (1*R*,2*S*)-**4c**, the reaction of (1*S*)-**3c** (163 mg, 0.31 mmol) gave the desired product (1*S*,2*R*)-**4c** (55 mg, 40%) and (1*S*,2*S*)-**4c** (46 mg, 33%).

(1*S*,2*R*)-**4c**: Colorless oil; $[\alpha]_D^{24}$ -36.5 (*c* 2.30, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.63 (1H, t, *J* = 5.5 Hz), 1.06 (3H, s), 1.17 (1H, dd, *J* = 5.5, 8.3 Hz), 2.90 (1H, dd, *J* = 5.5, 8.3 Hz), 3.76 (3H, s), 7.06 (1H, d, *J* = 8.3 Hz), 7.19-7.37 (4H, m), 7.40-7.49 (3H, m), 7.87 (1H, d, *J* = 8.3 Hz), 7.91-8.04 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.4, 23.6, 24.6, 28.2, 56.5, 113.3, 117.3, 121.6, 123.7, 124.9, 125.1, 125.5, 126.1, 126.5, 126.7, 127.9, 128.1, 128.8, 129.0, 130.2, 131.7, 133.5, 133.5, 146.5, 154.8, 170.9. IR (KBr) 3632, 3449, 3059, 2936, 2839, 1746, 1624, 1593, 1508, 1312, 1138, 1127, 1086, 810, 747 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}BrO_3$ ($M+Na^+$) 483.0572, found 483.0574.

(1*S*,2*S*)-**4c**: Colorless crystals; mp 177-178 ˚C; $[\alpha]_D^{23}$ -8.8 (*c* 0.95, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.74 (3H, s), 0.90 (1H, t, *J* = 7.2 Hz), 1.40 (1H, dd, *J* = 5.5, 7.2 Hz), 2.76 (1H, dd, *J* = 5.5, 7.2 Hz), 3.78 (3H, s), 7.15 (1H, d, *J* = 7.9 Hz), 7.19-7.35 (4H, m), 7.39-7.54 (3H, m), 7.84 (1H, d, *J* = 7.9 Hz), 7.91-8.01 (3H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.8, 22.1, 25.4, 26.6, 56.7, 113.5, 117.7, 122.0, 123.6, 124.9, 125.4, 125.5, 126.1, 126.4, 126.6, 127.6, 128.1, 128.9, 129.9, 131.8, 133.6, 133.7, 146.8, 154.9, 168.8. IR (KBr) 3483, 3084, 3061, 3003, 2971, 2841, 1752, 1622, 1593, 1508, 1319, 1136, 1082, 810, 760 cm^{-1}.

(1*R*,2*S*)-2-Chloro-1-methylcyclopropanecarboxylic acid [(1*R*,2*S*)-5a]. (Table 4, entry 2)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*R*,2*S*)-**4a** (156 mg, 0.38 mmol) gave the desired product (1*R*,2*S*)-**5a** (48 mg, 95%).

Pale yellow oil; $[\alpha]_D^{23}$ +81.9 (*c* 0.90, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 1.02 (1H, t, *J* = 5.2 Hz), 1.45 (3H, s), 1.79 (1H, dd, *J* = 5.2, 8.3 Hz), 3.63 (1H, dd, *J* = 5.2, 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 24.4, 25.3, 40.3, 180.3. IR (KBr) 2982, 2936, 2577, 1693, 1460, 1422, 1325, 1267, 1192, 966, 949, 839

cm^{-1}. Anal. Calcd for $C_5H_7ClO_2$; C, 44.63; H, 5.24, found: C, 44.3; H, 4.9.

(1*S*,2*R*)-2-Chloro-1-methylcyclopropanecarboxylic acid [(1*S*,2*R*)-5a]. (Table 4, entry 3)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*S*,2*R*)-**4a** (78 mg, 0.19 mmol) gave the desired product (1*S*,2*R*)-**5a** (23 mg, 92%).

Pale yellow oil; $[\alpha]_D^{23}$ -83.5 (*c* 1.00, $CHCl_3$).

(1*S*,2*S*)-2-Chloro-1-methylcyclopropanecarboxylic acid [(1*S*,2*S*)-5a]. (Table 4, entry 4)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**,, the reaction of (1*S*,2*S*)-**4a** (40 mg, 0.10 mmol) gave the desired product (1*S*,2*S*)-**5a** (12 mg, 92%).

Colorless oil; $[\alpha]_D^{23}$ +29.1 (*c* 0.55, $CHCl_3$).

(1*R*,2*R*,3*S*)-2-Chloro-1-methyl-3-phenylcyclopropanecarboxylic acid [(1*R*,2*R*,3*S*)-5b]. (Table 4, entry 5)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*R*,2*R*,3*S*)-**4b** (105 mg, 0.21 mmol) gave the desired product (1*R*,2*R*,3*S*)-**5b** (42 mg, 93%).

Colorless oil (> 99% ee); $[\alpha]_D^{23}$ -33.3 (*c* 0.70, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (3H, s), 3.46 (1H, d, *J* = 5.9 Hz), 3.54 (1H, d, *J* = 5.9 Hz), 7.16-7.38 (5H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 33.1, 38.1, 43.0, 127.5, 128.6, 128.8, 133.9, 176.7. IR (KBr) 3032, 2976, 2926, 2720, 2596, 1698, 1462, 1420, 1310, 1263, 1240, 1177, 928, 698 cm^{-1}. Anal. Calcd for $C_{11}H_{11}ClO_2$; C, 62.72; H, 5.26, found: C, 62.5; H, 5.1.

(1*R*,2*S*,3*S*)-2-Chloro-1-methyl-3-phenylcyclopropanecarboxylic acid [(1*R*,2*S*,3*S*)-5b]. (Table 4, entry 6)[6b]

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*R*,2*S*,3*S*)-**4b** (30 mg, 0.06 mmol) gave the desired product (1*R*,2*S*,3*S*)-**5b** (12 mg, 92%).

Colorless crystals (> 99% ee); mp 88-89 ˚C; $[\alpha]_D^{23}$ -87.3 (*c* 0.60, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (3H, s), 3.06 (1H, d, *J* = 8.3 Hz), 4.04 (1H, d, *J* = 8.3 Hz). 7.23-7.39 (5H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1, 28.3, 33.3, 43.9, 127.3, 128.3, 130.7, 132.1, 180.3. IR (KBr) 3063, 3029, 2926, 2855, 2658, 2556, 1692, 1458, 1426, 1335, 1304, 1267, 1162, 947, 909, 706 cm^{-1}.

(1*S*,2*R*,3*R*)-2-Chloro-1-methyl-3-phenylcyclopropanecarboxylic acid [(1*S*,2*R*,3*R*)-5b].[6b] (Table 4, entry 7)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*S*,2*R*,3*R*)-**4b** (33 mg, 0.07 mmol) gave the desired product (1*S*,2*R*,3*R*)-**5b** (13 mg, 93%).

Colorless crystals; mp 89-90 ˚C; $[\alpha]_D^{23}$ +84.6 (*c* 0.65, $CHCl_3$).

(1*S*,2*S*,3*R*)-2-Chloro-1-methyl-3-phenylcyclopropanecarboxylic acid [(1*S*,2*S*,3*R*)-5b].[6b] (Table 4, entry 8)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*S*,2*S*,3*R*)-**4b** (30 mg, 0.06 mmol) gave the desired product (1*S*,2*S*,3*R*)-**5b** (12 mg, 92%).

Colorless oil: $[\alpha]_D^{23}$ +29.6 (*c* 0.60, $CHCl_3$).

(1*R*,2*R*)-2-Bromo-1-methylcyclopropanecarboxylic acid [(1*R*,2*R*)-5c]. (Table 4, entry 9).

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*R*,2*R*)-**4c** (90 mg, 0.21 mmol) gave the desired product (1*R*,2*R*)-**5c** (33 mg, 92%).

Colorless oil (> 99% ee); $[\alpha]_D^{23}$ -19.9 (*c* 0.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (1H, dd, *J* = 5.9, 7.6 Hz), 1.41 (3H, s), 1.41 (1H, t, *J* = 5.9 Hz), 3.02 (1H, dd, *J* = 5.9, 7.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 23.2, 26.2, 26.3, 177.3. IR (KBr) 2976, 2930, 2724, 2618, 1699, 1468, 1421, 1325, 1223, 1206, 928, 905 cm^{-1}. Anal. Calcd for $C_5H_7BrO_2$; C, 33.55; H, 3.94, found C, 33.3; H, 3.9.

(1*R*,2*S*)-2-Bromo-1-methylcyclopropanecarboxylic acid [(1*R*,2*S*)-5c]. (Table 4, entry 10)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*R*,2*S*)-**4c** (126 mg, 0.27 mmol) gave the desired product (1*R*,2*S*)-**5c** (45 mg, 94%).

(1*R*,2*S*)-**5c**: Colorless oil; $[\alpha]_D^{24}$ +85.0 (*c* 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (1H, t, *J* = 5.5 Hz), 1.48 (3H, s), 1.90 (1H, dd, *J* = 5.5, 8.3 Hz), 3.56 (1H, dd, *J* = 5.5, 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.4, 23.7, 25.7, 28.9, 180.0. IR (KBr) 2980, 2922, 2604, 1692, 1414, 1319, 1250, 1186, 957, 885 cm^{-1}. Anal. Calcd for $C_5H_7BrO_2$; C, 33.55; H, 3.94, found C, 33.2; H, 3.7.

(1*S*,2*R*)-2-Bromo-1-methylcyclopropanecarboxylic acid [(1*S*,2*R*)-5c] . (Table 4, entry 11)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*S*,2*R*)-**4c** (46 mg, 0.10 mmol) gave the desired product (1*S*,2*R*)-**5c** (17 mg, 94%).

Colorless oil (> 99% ee); $[\alpha]_D^{23}$ -82.4 (*c* 0.85, $CHCl_3$).

(1*S*,2*S*)-2-Bromo-1-methylcyclopropanecarboxylic acid [(1*S*,2*S*)-5c]. (Table 4, entry 12)

Following the procedure for the preparation of (1*R*,2*R*)-**5a**, the reaction of (1*S*,2*S*)-**4c** (60 mg, 0.13 mmol) gave the desired product (1*S*,2*S*)-**5c** (22 mg, 96%).

Colorless oil (> 99% ee); $[\alpha]_D^{23}$ +19.5 (*c* 1.10, $CHCl_3$).