Supporting Information for "Enantioselective Molybdenum-Catalyzed Allylic Alkylation Using Chiral Bisoxazoline Ligands" by Frank Glorius and Andreas Pfaltz.

All reactions were performed under an argon atmosphere.

***N,N'*-Bis-{2-[(4*S*)-*iso*-propyloxazoline]carboxamide}-(1*S* ,2*S*)-cyclohexane (4)**

Oxazoline **7** (1.5 g, 8.1 mmol) and (1*S*,2*S*)-diaminocyclohexane (0.45 g, 4.0 mmol) were dissolved in DMSO (20 mL), sodium hydride (0.24 g, 9.9 mmol) was added and the mixture was warmed to 40 °C and stirred for one day. The solution was diluted with dichloromethane and quenched with a small amount of ice-cold water. The mixture was neutralized by the addition of saturated aqueous NH_4Cl solution and extracted with dichloromethane. The combined organic fractions were dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica-gel (hexane/EtOAc = 1:1) affording oxazoline **4** (0.34 g, 22%) as an off-white solid.

R_f = 0.30 (hexane/EtOAc = 1:2). $[\alpha]^{20}_D$ = -7.7 (*c* 0.19, $CHCl_3$). IR: 3216b, 3036w, 2958m, 2935m, 2872m, 1684s, 1638s, 1533m, 1471m, 1376m, 1367m, 1245m, 1191m, 977m, 895w, 841w, 605w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.39 (bs, 2H), 4.43 (dd, *J* = 9.5, 8.4 Hz, 2H), 4.16-4.01 (m, 4H), 3.85-3.75 (m, 2H), 2.12-2.05 (m, 2H), 2.05-1.71 (m, 4H), 1.43-1.23 (m, 4H), 0.97 (d, *J* = 6.7 Hz, 6H), 0.88 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7, 157.0, 72.8, 71.6, 53.2, 32.5, 32.2, 24.6, 18.9, 18.3. MS (EI) *m/z*: 392 (M^+, 77), 364 (11), 349 (31), 321 (5), 280 (13), 252 (26), 236 (100), 209 (33), 193 (7), 181 (20), 157 (27), 139 (10), 114 (23), 96 (55). HRMS calc'd for $C_{20}H_{32}N_4O_4$: 392.2423. Found: 392.2410.

***N,N'*-Bis-{(4*S*)-[2-phenyloxazoline]carboxamide }-(1*S*,2*S*)-cyclohexane (5a)**

General procedure: (*S*)-sodium 2-phenyloxazoline-4-carboxylate (0.54 g, 2.5 mmol) and (1*S*,2*S*)-diaminocyclohexane (0.14 g, 1.2 mmol) were dissolved in DMF (15 mL). *N*,*N*-diisopropylethylamine (1.25 mL, 7.2 mmol), 1-hydroxybenzotriazole hydrate (HOBT, 0.40 g, 2.7 mmol) and *O*-benzotriazol-1-yl-*N*,*N*,*N'*,*N'*-tetramethyluronium tetrafluoroborate (TBTU, 0.81 g, 2.5 mmol) were successively added and the resulting solution stirred at room temperature for 5 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc and dried over $NaSO_4$ and filtered. The solvent was evaporated *in vacuo* and the remaining residue purified by flash chromatography on silica-gel (hexane/EtOAc = 1:4) to yield 0.55 g (95%) of oxazoline **5a**.

R_f = 0.27 (hexane/EtOAc = 1:3). $[\alpha]^{20}_D$ = 164.7 (*c* 0.79, DMF). IR: 3261m, 3088m, 2932m, 2895w, 2855m, 1646s, 1604w, 1557m, 1496m, 1450m, 1357m, 1299m, 1249m, 1233m, 1082m, 1068m, 1027m, 972m, 779m, 691m cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.04-7.98 (m, 4H), 7.54-7.39 (m, 6H), 6.97-6.92 (bd, *J* = 7.3 Hz, 2H), 4.85 (dd, *J* = 10.2, 8,8 Hz, 2H), 4.73-4.56 (m, 4H), 3.76-3.72 (m, 2H), 2.06-1.96 (m, 2H), 1.75-1.69 (m, 2H), 1.35-1.24 (m, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.9, 165.6, 131.6, 128.2, 128.1, 126.7, 70.1, 68.6, 52.7, 31.9, 24.3. MS (EI) *m/z*: 460 (M^+, 16), 314 (100), 270 (5), 174

(5), 146 (35), 118 (16), 105 (62), 97 (5), 91 (27), 77 (16). HRMS calc'd for $C_{26}H_{28}N_4O_4$: 460.2110. Found: 460.2112.

***N,N'*-Bis-{(4*S*)-[2-propyloxazoline]carboxamide}-(1*S* ,2*S*)-cyclohexane (5b)**

R_f = 0.31 (EtOAc). $[\alpha]^{20}_D$ = 57.0 (*c* 0.89, $CHCl_3$). IR: 3266s, 3087m, 2966m, 2936m, 1669s, 1646s, 1559m, 1457m, 1384m, 1252m, 1181m, 1106w, 985m, 938w, 886w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.79 (bd, *J* = 6.7 Hz, 2H), 4.61-4.37 (m, 6H), 3.73-3.67 (m, 2H), 2.30 (t, *J* = 7.4 Hz, 4H), 2.04-1.95 (m, 2H), 1.75-1.60 (m, 6H), 1.34-1.25 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 170.8, 70.1, 68.4, 52.9, 32.3, 29.9, 24.6, 19.4, 13.7. MS (EI) *m/z*: 392 (M^+, 8), 349 (2), 280 (100), 236 (7), 210 (12), 141 (8), 112 (14), 97 (6). HRMS calc'd for $C_{20}H_{32}N_4O_4$: 392.2423. Found: 392.2415.

***N,N'*-Bis-{(4*S*)-[2-*iso*-propyloxazoline]carboxamide}-(1*S* ,2*S*)-cyclohexane (5c)**

R_f = 0.35 (EtOAc). $[\alpha]^{20}_D$ = 46.8 (*c* 1.04, $CHCl_3$). IR: 3267m, 2972m, 2936m, 2856w, 1664s, 1647s, 1559m, 1471m, 1387m, 1360w, 1332w, 1254m, 1235m, 1201m, 1150m, 1108m, 987m, 889w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.77 (bd, *J* = 6.9 Hz, 2H), 4.59-4.38 (m, 6H), 3.76-3.65 (m, 2H), 2.61 (septet, *J* = 6.8 Hz, 2H), 2.05-1.97 (m, 2H), 1.77-1.72 (m, 2H), 1.33-1.17 (m, 16H) ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.7, 172.4, 70.2, 68.4, 52.9, 32.3, 28.3, 24.6, 19.7, 19.6. MS (EI) *m/z*: 392 (M^+, 8), 349 (5), 280 (100), 236 (7), 210 (18), 141 (16), 112 (17), 97 (7), 84 (10), 71 (9). HRMS calc'd for $C_{20}H_{32}N_4O_4$: 392.2423. Found: 392.2417.

***N,N'*-Bis-{(4*S*)-[2-phenyloxazoline]carboxamide }-(1*R*,2*R*)-cyclohexane (6a)**

R_f = 0.26 (hexane/EtOAc = 1:3). $[\alpha]^{21}_D$ = -40.9 (*c* 1.03, DMF). IR: 3371m, 3281s, 3074m, 2934m, 2863m, 1669s, 1654s, 1603w, 1580m, 1548s, 1515s, 1497m, 1451m, 1357m, 1304m, 1288m, 1250m, 1230m, 1084m, 1067m, 1026m, 970m, 959m, 780m, 693s cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.01-7.95 (m, 4H), 7.58-7.40 (m, 6H), 6.82 (bd, *J* = 7.0 Hz, 2H), 4.68 (dd, *J* = 11.1, 8.3 Hz, 2H), 4.31 (dd, *J* = 11.1, 8.9 Hz, 2H), 4.05 (t, *J* = 8.6 Hz, 2H), 3.75-3.65 (m, 2H), 2.10-2.04 (m, 2H), 1.80-1.72 (m, 2H), 1.34-1.27 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 166.2, 132.1, 128.6, 128.4, 126.8, 70.3, 68.8, 52.9, 32.3, 24.7. MS (EI) *m/z*: 460 (M^+, 10), 314 (100), 174 (4), 146 (26), 118 (11), 105 (49), 97 (6), 91 (16), 77 (10). HRMS calc'd for $C_{26}H_{28}N_4O_4$: 460.2110. Found: 460.2104.

***N,N'*-Bis-{(4*S*)-[2-propyloxazoline]carboxamide}-(1*R*,2*R*)-cyclohexane (6b)**

R_f = 0.30 (EtOAc). $[\alpha]^{20}_D$ = 64.9 (*c* 0.50, $CHCl_3$). IR: 3310m, 3070w, 2963m, 2935m, 2873m, 2873m, 1661s, 1532s, 1456m, 1368m, 1267m, 1187m, 1147m, 1019w, 981m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.63 (bd, *J* = 7.3 Hz, 2H), 4.56 (dd, *J* = 11.0, 7.4 Hz, 2H), 4.41 (dd, *J* = 11.0, 8.6 Hz, 2H), 4.22 (dd, *J* = 8.6, 7.4 Hz, 2H), 3.72-3.56 (m, 2H), 2.35-2.28 (m, 4H), 2.04-1.96 (m, 2H), 1.76-1.66 (m, 6H), 1.34-1.28 (m, 4H), 0.99 (t, *J* =

7.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.0, 171.2, 70.3, 68.5, 52.7, 32.1, 30.1, 24.7, 19.3, 13.7. MS (EI) *m/z*: 392 (M^+, 3), 349 (2), 280 (100), 236 (5), 210 (5), 141 (4), 112 (17), 97 (8), 81 (6). HRMS calc'd for $C_{20}H_{32}N_4O_4$: 392.2423. Found: 392.2418.

***N,N'*-Bis-{(4*S*)-[2-*iso*-propyloxazoline]carboxamide}-(1*R*,2*R*)-cyclohexane (6c)**

R_f = 0.35 (EtOAc). $[\alpha]^{20}_D$ = 63.3 (*c* 0.96, $CHCl_3$). IR: 3358m, 2979m, 2938m, 2860w, 1669s, 1530s, 1456m, 1387m, 1363m, 1324w, 1271m, 1200m, 1149m, 1118m, 1101m, 1064w, 1015m, 970m, 940m, 728w, 611m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.59 (bd, *J* = 7.6 Hz, 2H), 4.56 (dd, *J* = 11.2, 7.6 Hz, 2H), 4.42 (dd, *J* = 11.2, 8.5 Hz, 2H), 4.18 (t, *J* = 8.4 Hz, 2H), 3.71-3.66 (m, 2H), 2.63 (septet, *J* = 7.0 Hz, 2H), 2.00-1.98 (m, 2H), 1.78-1.75 (m, 2H), 1.33-1.17 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.3, 172.0, 70.5, 68.4, 52.6, 32.4, 28.4, 24.7, 19.6. MS (EI) *m/z*: 392 (M^+, 3), 349 (2), 280 (100), 236 (5), 210 (14), 141 (13), 112 (16), 97 (8), 84 (9), 71 (8). HRMS calc'd for $C_{20}H_{32}N_4O_4$: 392.2423. Found: 392.2426.

***N,N'*-Bis-{(4*S*)-[2-*tert*-butyloxazoline]carboxamide}-(1*R*,2*R*)-cyclohexane (6d)**

R_f = 0.39 (hexane/EtOAc = 1:3). $[\alpha]^{20}_D$ = 66.4 (*c* 0.82, $CHCl_3$). IR: 3369m, 2976m, 2957m, 2937m, 2862m, 1673s, 1649m, 1529s, 1481m, 1396w, 1365w, 1307w, 1232w, 1155m, 1145m, 1017m, 970m, 736w cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.57 (bs, 2H), 4.58 (dd, *J* = 11.2, 7.8 Hz, 2H), 4.45 (dd, *J* = 11.2, 8.6 Hz, 2H), 4.17 (t, *J* = 8.2 Hz, 2H), 3.75-3.66 (m, 2H), 2.02-1.95 (m, 2H), 1.79-1.74 (m, 2H), 1.34-1.27 (m, 22H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 171.8, 70.8, 68.4, 52.4, 33.5, 32.4, 27.7, 24.7. MS (EI) *m/z*: 420 (M^+, 2), 405 (1), 363 (3), 294 (100), 250 (5), 127 (13), 97 (6), 70 (8). HRMS calc'd for $C_{22}H_{36}N_4O_4$: 420.2736. Found: 420.2729.

(*S*)-(-)-4-*iso*-Propyloxazoline-2-carboxylic acid ethyl ester (7)

Triethyloxonium tetrafluoroborate (7.5 g, 39 mmol) was dissolved in 1,2-dichloroethane (200 mL) and ethyl oxamate (4.6 g, 39 mmol) added. After stirring at room temperature for one day, (*S*)-valinol (4.5 g, 44 mmol) was added and the resulting mixture stirred at reflux for one day. The solution was cooled to room temperature and diluted with dichloromethane. The solution was poured into an ice-cold solution of aqueous ammonium chloride and the layers were separated. The organic phase was washed with saturated aqueous NH_4Cl, sat. aqueous $NaHCO_3$ solution and brine and finally dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* and the crude product purified by flash chromatography on silica-gel (hexane/EtOAc = 1:1) affording ethyl ester (S)-(-)-**7** (5.1g, 70%) as a colorless oil.

R_f = 0.32 (pentane/ether = 1:1). $[\alpha]^{26}_D$ = -89.3 (*c* 1.22, $CHCl_3$). IR: 2963m, 2908m, 2876m, 1749s, 1650s, 1469m, 1376m, 1310m, 1258m, 1151s, 1016m, 965m, 932m, 862w, 790w, 774w cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.47-4.35 (m, 3H), 4.20-4.12 (m, 2H), 1.92-1.83 (m, 1H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7, 155.6, 73.1, 71.1, 62.9, 32.3, 18.9, 18.1, 14.0. MS (EI) *m/z*: 186 (MH^+, 2), 143 (43), 112 (13), 97 (13), 83 (5), 70 (100), 56 (27),

43 (56). Anal. Calc'd for $C_9H_{15}N_1O_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.24; H, 8.25; N, 7.38.

Ref.: Meyers, A. I.; Schmidt, W.; McKennon, M. J.; *Synthesis* **1993**, 250.

(*S*)-2-Phenyloxazoline-4-carboxylic acid methyl ester (Ph-**8)**

Triethyloxonium tetrafluoroborate (7.5 g, 39.5 mmol) was dissolved in 1,2-dichloroethane (300 mL). Benzamide (4.8 g, 39.5 mmol) was added and the solution stirred at room temperature for two days resulting in precipitation of a white solid. The mixture was filtered and the residue was washed with cold ether and dissolved in 0.1 M aqueous Na_2CO_3 solution (300 mL). The resulting solution was extracted with dichloromethane and the combined organic fractions were dried over $NaSO_4$, filtered and the solvent evaporated *in vacuo*. The residue was dissolved in 1,2-dichloroethane (100 mL) and *L*-serine methyl ester hydrochloride (5.0 g, 32.3 mmol) was added. After heating under reflux for 20 h, the solution was filtered and the solvent removed by rotary evaporation. The residue was purified by flash chromatography on silica-gel (hexane/EtOAc = 6:1) affording 5.95 g (73%) of methyl ester Ph-**8**.

R_f = 0.56 (hexane/EtOAc = 1:1). IR: 3063w, 3002w, 2954m, 2908w, 2848w, 1743s, 1643s, 1603w, 1580m, 1496m, 1451m, 1437m, 1362s, 1297m, 1211s, 1179m, 1090m, 1070m, 1026m, 972m, 945m, 903w, 779m, 697s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.00-7.96 (m, 2H), 7.52-7.37 (m, 3H), 4.95 (dd, *J* = 10.6, 8.0 Hz, 1H), 4.69 (t, *J* = 8.3 Hz, 1H), 4.59 (dd, *J* = 10.6, 8.7 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 166.3, 131.9, 128.6, 128.4, 127.0, 69.6, 68.7, 52.7. MS (EI) *m/z*: 205 (M^+, 7), 146 (100), 118 (22), 105 (18), 91 (39), 77 (22), 51 (10).

(*S*)-2-Propyloxazoline-4-carboxylic acid methyl ester (^{n}Pr-**8)**

General procedure: butyramide was added to a solution of triethyloxonium tetrafluoroborate (7.6 g, 40.0 mmol) in dichloromethane (100 mL). After stirring at room temperature for one day, *N*,*N*-diisopropylethylamine (8.6 mL, 50.0 mmol) and *L*-serine methyl ester hydrochloride (6.2 g, 40.0 mmol) were added at 0 °C sequentially. The solution was stirred at room temperature for a further two days and then filtered. The residue was washed with dichloromethane and the combined organic phases washed with aqueous NH_4Cl solution and dried over Na_2SO_4 and filtered. The solvent was removed *in vacuo* and the residue purified by flash chromatography on silica-gel (pentane/ether = 1:2) affording 4.8 g (70%) of methyl ester ^{n}Pr-**8** as a colorless oil.

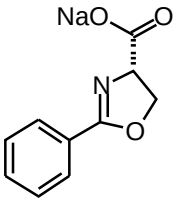
R_f = 0.46 (hexane/EtOAc = 1:1). $[\alpha]^{21}_D$ = 156.3 (*c* 1.60, $CHCl_3$). IR: 2966m, 2937m, 2877m, 1745s, 1662s, 1459m, 1438m, 1368m, 1338m, 1272m, 1204s, 1186s, 1062m, 1039m, 985m, 958m, 923m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.73 (dd, *J* = 10.5, 7.7 Hz, 1H), 4.51-4.36 (m, 2H), 3.79 (s, 3H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.68 (sextet, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.8, 170.8, 69.2, 68.1, 52.6, 29.8, 19.4, 13.7. MS (EI) *m/z*: 171 (M^+, 1), 156 (3), 143 (32), 112 (100), 84 (19), 55 (8), 42 (36). Anal. Calc'd for $C_8H_{13}N_1O_3$: C, 56.12; H, 7.65; N, 8.18. Found: C, 56.05; H, 7.61; N, 8.12.

(*S*)-2-*iso*-Propyloxazoline-4-carboxylic acid methyl ester (^{i}Pr-**8)**

R_f = 0.43 (hexane/EtOAc = 1:1). $[\alpha]^{20}_D$ = 157.1 (*c* 1.66, $CHCl_3$). IR: 2976m, 2910w, 2879w, 1744s, 1658s, 1472m, 1438m, 1388w, 1363m, 1328m, 1278m, 1204s, 1150m, 1098m, 1060m, 1037m, 982m, 954m, 921m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.75-4.69 (m, 1H), 4.50-4.36 (m, 2H), 3.79 (s, 3H), 2.64 (septet d, *J* = 7.0, 0.7 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.21 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.8, 171.9, 69.3, 68.0, 52.6, 28.2, 19.7, 19.6. MS (EI) *m/z*: 171 (M^+, 4), 156 (1), 112 (100), 84 (39), 70 (14), 55 (10), 43 (25). HRMS calc'd for $C_8H_{13}N_1O_3$: 171.0895. Found: 171.0890.

(*S*)-2-*tert*-Butyloxazoline-4-carboxylic acid methyl ester (^{t}Bu-**8)**

R_f = 0.40 (hexane/EtOAc = 1:1). $[\alpha]^{20}_D$ = 138.8 (*c* 1.25, $CHCl_3$). IR: 2975s, 2909m, 2874m, 1745s, 1650s, 1482m, 1461m, 1438w, 1396m, 1364m, 1301m, 1211s, 1180m, 1147s, 1061m, 1027m, 981m, 954m, 917m cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.71 (dd, *J* = 10.5, 7.7 Hz, 1H), 4.49-4.38 (m, 2H), 1.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.9, 172.0, 69.5, 68.2, 52.5, 33.4, 27.7. MS (EI) *m/z*: 185 (M^+, 8), 170 (6), 126 (100), 110 (5), 70 (43), 57 (61). Anal. Calc'd for $C_9H_{15}N_1O_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.12; H, 8.11; N, 7.62.

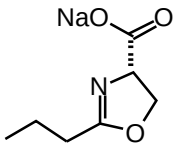


Ref.: Stammer, C. H.; Wilson, A. N.; Spencer, C. F.; Bachelor, F. W.; Holly, F. W.; Folkers, K.; *J. Am. Chem. Soc.* **1957**, *79*, 3236.

(*S*)-Sodium 2-phenyloxazoline-4-carboxylate

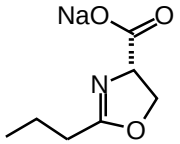
General procedure: a mixture of 2N aqueous sodium hydroxide (3.8 mL, 7.6 mmol) and methyl ester Ph-**8** (1.65 g, 8.1 mmol) was stirred for 1 h at room temperature. Water (15 mL) and acetone (150 mL) were added and the solution cooled to 0 °C. The product crystallized and was filtered and dried *in vacuo*, to afford 1.31 g (76%) of the sodium salt as a white solid.

IR: 3061w, 2983w, 2910w, 1644s, 1601s, 1497w, 1478w, 1450m, 1410s, 1358m, 1325m, 1278m, 1247w, 1095m, 1062w, 1026m, 963m, 778m, 748m, 693m cm^{-1}. ^{1}H NMR (300 MHz, D_2O): δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 4.67-4.56 (m, 2H), 4.45-4.33 (m, 1H). ^{13}C NMR (75 MHz, D_2O): δ 179.6, 166.9, 132.7, 129.1, 128.6, 126.8, 72.1, 70.1. MS (EI) *m/z*: 121 (44), 105 (100), 77 (91), 51 (32). MS (ESIpos, H_2O): 449 (2M + Na), 236 (M + Na), 214 (M + H).



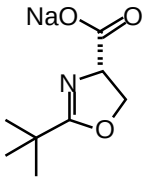
(*S*)-Sodium 2-propyloxazoline-4-carboxylate

IR: 2966m, 2935m, 2876m, 1668s, 1605s, 1411s, 1363m, 1313m, 1264m, 1189m, 1068m, 1028m, 978s, 937m, 870m, 795m, 749 cm^{-1}. ^{1}H NMR (300 MHz, d4-MeOD): δ 4.55-4.42 (m, 2H), 4.33 (t, *J* = 7.3 Hz, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.67 (sextet, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, d4-MeOD): δ 179.5, 171.7, 72.8, 71.7, 31.2, 20.6, 14.5. MS (EI): 157 (1), 87 (7), 72 (23), 59 (100), 44 (72). MS (ESIpos, MeOH): 381 (2M + Na), 202 (M + Na).



(*S*)-Sodium 2-*iso*-propyloxazoline-4-carboxylate

IR (Nujol): 3299w, 3188w, 2724w, 1661s, 1603s, 1377s, 1302m, 1269m, 1203m, 1151m, 1100m, 1071m, 1031m, 972m, 934m, 871w, 795m cm^{-1}. ^{1}H NMR (300 MHz, D_2O): δ 4.50 (bs, 2H), 4.32-4.25 (m, 1H), 2.69-2.60 (m, 1H), 1.18 (bs, 6H). ^{13}C NMR (75 MHz, D_2O): δ 179.8, 176.0, 71.8, 69.5, 28.2, 19.2. MS (EI): 157 (1), 87 (26), 72 (41), 59 (32), 44 (100), 41 (40). MS (ESIneg, Aceton): 335 (2M – Na), 156 (M – Na).



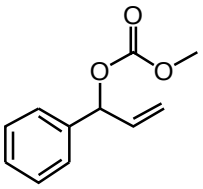
(*S*)-Sodium 2-*tert*-butyloxazoline-4-carboxylate

IR: 3206b, 2981m, 2968m, 2933m, 2909m, 2872w, 1661s, 1604s, 1482m, 1410s, 1346m, 1315m, 1247m, 1226w, 1206w, 1141s, 1063w, 1004m, 966m, 933m, 791m, 741m cm^{-1}. ^{1}H NMR (300 MHz, D_2O): δ 4.54-4.46 (m, 2H), 4.26 (t, *J* = 13.7 Hz, 1H), 1.21 (s, 9H). ^{13}C NMR (75 MHz, D_2O): δ 179.8, 178.0, 71.8, 69.7, 33.3, 27.3. MS (EI): 170 (0.2), 101 (14), 86 (9), 57 (100), 41 (70). MS (ESIneg, MEOH): 363 (2M – Na), 170 (M – Na).

Ref.: Lehmann, J.; Lloyd-Jones, G. C.; *Tetrahedron* **1995**, *51*, 8863.

(*E*)-3-Phenyl-prop-2-enyl methyl carbonate (9a)

R_f = 0.52 (hexane/EtOAc = 5:1). IR: 3060w, 3028m, 2957m, 2889w, 1751s, 1659w, 1599w, 1579w, 1497m, 1448s, 1381m, 1299s, 1262s, 1120m, 1072w, 967s, 948s, 905m, 792m, 749m, 693m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.23 (m, 5H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 12.8, 6.4 Hz, 1H), 4.78 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 136.1, 134.8, 128.6, 128.2, 126.7, 122.5, 68.4, 54.8. MS (EI) *m/z*: 192 (M^+, 49), 147 (8), 133 (30), 115 (100), 105 (38), 91 (25), 77 (22), 59 (15), 55 (5), 51 (14).



1-Phenyl-prop-2-enyl methyl carbonate

R_f = 0.69 (hexane/EtOAc = 4:1). IR: 3051w, 3033w, 2957w, 2852w, 1762s, 1644w, 1494w, 1442s, 1273s, 1200w, 1076w, 928m, 848w, 791m, 766m, 700m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.31 (m, 5H), 6.10-5.98 (m, 2H), 5.38-5.25 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.0, 138.2, 135.7, 128.6, 128.4, 127.0, 117.4, 80.1, 54.8. MS (EI) *m/z*: 192 (M^+, 6), 147 (5), 133 (5), 117 (100), 105 (11), 91 (30), 77 (15), 63 (10), 58 (7), 51 (13). Anal. Calc'd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.72; H, 6.25.

Ref.: Takeuchi, R.; Kashio, M.; *J. Am. Chem. Soc. 1998*, **120**, 8647.

(*E*)-Hex-2-enyl methyl carbonate (9b)

R_f = 0.80 (hexane/EtOAc = 4:1). IR: 3024w, 2960s, 2933m, 2875m, 1750s, 1673w, 1443s, 1381m, 1258s, 973m, 945s, 901m, 793m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.87-5.77 (m, 1H), 5.64-5.53 (m, 1H), 4.57 (dd, *J* = 6.5, 1.0 Hz, 2H), 3.78 (s, 3H), 2.04 (q, *J* = 7.0 Hz, 2H), 1.41 (sextet, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 137.3, 123.4, 68.7, 54.7, 34.3, 22.0, 13.6. MS (EI) *m/z*: 158 (M^+, 4), 99 (5), 82 (59), 77 (13), 71 (63), 67 (94), 59 (41), 55 (57), 41 (100).

Ref.: Trost, B. M.; Hachiya, I.; *J. Am. Chem. Soc.* **1998**, *120*, 1104.

(*R*)-(+)-2-(1-Phenyl-allyl) malonic acid dimethyl ester (10a)

R_f = 0.41 (hexane/EtOAc = 4:1). $[\alpha]^{23}_D$ = 34.5 (*c* 1.03, $CHCl_3$, 99% ee). IR: 3031w, 2954m, 1760s, 1740s, 1639w, 1602w, 1494w, 1435m, 1263m, 1198m, 1163m, 1027w, 992w, 925w, 765w, 702m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32-7.19 (m, 5H), 5.99 (ddd, *J* = 17.0, 10.2, 8.1 Hz, 1H), 5.15-5.06 (m, 2H), 4.14-4.08 (m,1H), 3.87 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 167.8, 139.9, 137.8, 128.7, 127.9, 127.1, 116.6, 57.4, 52.6, 52.4, 49.7. MS (EI) *m/z*: 248 (M^+, 2), 217

(2), 189 (100), 156 (19), 129 (43), 117 (100), 91 (19). Restek Rtx-1701, 30 m, 50-250 °C, 10 °/min, 60 kPa H_2, t_R = 17.1 min (**10a**), t_R = 19.7 min (*E*-**11a**). Hewlett Packard hp-5ms, 30 m, 50-250 °C, 10 °/min, 60 kPa He, t_R = 13.7 min (**10a**), t_R = 16.0 min (*E*-**11a**). (HPLC): Daicel, Chiralcel OJ, 25 cm, heptane/ethanol = 93:7, 0.5 mL/min, 20 °C, 220 nm, t_R = 30.1 min (**(S)-10 a**), t_R = 35.2 min (**(R)-10a**).

Ref.: Takeuchi, R.; Kashio, M.; *J. Am. Chem. Soc. 1998*, **120**, 8647.

(-)-2-(1-Propyl-allyl) malonic acid dimethyl ester (10b)

R_f = 0.49 (hexane/EtOAc = 6:1). $[\alpha]^{20}_D$ = -4.5 (*c* 0.62, $CHCl_3$, 98% ee). IR: 3080w, 2957m, 2874w, 1740s, 1642w, 1436m, 1256m, 1235m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.63 (ddd, *J* = 17.1, 10.2, 9.4 Hz, 1H), 5.12-5.05 (m, 2H), 3.74 (s, 3H), 3.69 (s, 3H), 3.38 (d, *J* = 8.9 Hz, 1H), 2.78 (m, 1H), 1.43-1.24 (m, 4H), 0.88 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.8, 168.6, 138.1, 117.4, 57.0, 52.4, 52.2, 44.1, 34.5, 20.2, 13.8. MS (EI) *m/z*: 215 (MH^+, 0.2), 183 (7), 171 (48), 155 (100), 139 (84), 132 (55), 126 (33), 113 (48), 100 (41), 81 (44), 55 (74). Chiraldex γ-CD-TA, 30 m, 70-110 °C, 0.5 °/min, 90 kPa H_2, t_R = 35.7 min ((+)-**10b**), t_R = 36.3 min ((-)-**10b**), t_R = 55.5 min (***Z*-11b**), t_R = 57.3 min (***E*-11b**). Restek Rtx-1701, 30 m, iso 50 °C for 3 min, 50-250 °C, 10 °/min, 60 kPa H_2, t_R = 15.4 min (**10b**), t_R = 16.5 min (*Z*-**11b**), t_R = 16.6 min (*E*-**11b**). Hewlett Packard hp-5ms, 30 m, iso 50 °C for 3 min, 50-250 °C, 10 °/min, 60 kPa He, t_R = 12.7 min (**10b**), t_R = 13.6 min (*Z*-**11b**), t_R = 13.8 min (*E*-**11b**).

Ref.: Lehmann, J.; Lloyd-Jones, G. C.; *Tetrahedron* **1995**, *51*, 8863.

***E*-2-(3-phenyl-allyl) malonic acid dimethyl ester (11a)**

R_f = 0.41 (hexane/EtOAc = 4:1). IR: 2955w, 2845w, 1730s, 1495m, 1435m, 1335m, 1260s, 1160s, 1025m, 965s, 865m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34-7.17 (m, 5H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.73 (s, 6H), 3.53 (t, *J* = 7.2 Hz, 1H), 2.80 (dt, *J* = 7.2, 0.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 136.8, 132.8, 128.3, 127.3, 126.0, 125.2, 52.5, 51.7, 32.2. MS (EI) *m/z*: 248 (M^+, 23), 188 (38), 157 (16), 129 (100), 117 (63), 91 (17). Restek Rtx-1701, 30 m, 50-250 °C, 10 °/min, 60 kPa H_2, t_R = 17.1 min (**10a**), t_R = 19.7 min (*E*-**11a**). Hewlett Packard hp-5ms, 30 m, 50-250 °C, 10 °/min, 60 kPa He, t_R = 13.7 min (**10a**), t_R = 16.0 min (*E*-**11a**).

Ref.: Takeuchi, R.; Kashio, M.; *J. Am. Chem. Soc. 1998*, **120**, 8647.

(*E*)-2-Hex-2-enyl-malonic acid dimethyl ester (11b)

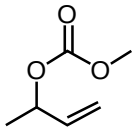
R_f = 0.41 (hexane/EtOAc = 4:1). IR: 2960s, 2930m, 2850m, 1760s, 1435s, 1340m, 1275s, 1160s, 1040m, 970m, 860w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.47 (m, 1H), 5.40-5.30 (m, 1H), 3.72 (s, 6H), 3.42 (t, *J* = 7.5, 1H), 2.58 (dt, *J* = 7.5, 1.0 Hz, 2H), 1.95 (dq, *J* = 7.4, 1.0 Hz, 2H), 1.35 (sextet, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.1, 133.7, 125.1, 52.3, 51.9, 34.2, 31.9, 22.4, 13.5. MS (EI) *m/z*: 214

(M^+, 1), 182 (3), 165 (2), 151 (39), 132 (89), 111 (100), 100 (34), 95 (48), 82 (30), 67 (41), 55 (51). Restek Rtx-1701, 30 m, iso 50 °C for 3 min, 50-250 °C, 10 °/min, 60 kPa H_2, t_R = 15.4 min (**10b**), t_R = 16.5 min (*Z*-**11b**), t_R = 16.6 min (*E*-**11b**). Hewlett Packard hp-5ms, 30 m, iso 50 °C for 3 min, 50-250 °C, 10 °/min, 60 kPa He, t_R = 12.7 min (**10b**), t_R = 13.6 min (*Z*-**11b**), t_R = 13.8 min (*E*-**11b**).

Ref.: Evans, P. A.; Nelson, J. D.; *J. Am. Chem. Soc.* **1998**, *120*, 5581.

(*E*)-But-2-enyl methyl carbonate (12)

R_f = 0.56 (hexane/EtOAc = 9:1). IR: 3028w, 2959m, 2922m, 2859w, 1750s, 1678w, 1443s, 1379m, 1268s, 969m, 944s, 914m, 794m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.88-5.80 (m, 1H), 5.64-5.58 (m, 1H), 4.56 (dt, *J* = 6.5, 1.0 Hz, 2H), 3.78 (s, 3H), 1.74-1.72 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 132.3, 124.6, 68.6, 54.7, 17.7. MS (EI) *m/z*: 130 (M^+, 5), 98 (6), 77 (13), 71 (100), 59 (33), 55 (95), 39 (49).



Ref.: Evans, P. A.; Nelson, J. D.; *J. Am. Chem. Soc.* **1998**, *120*, 5581.

3-But-1-enyl methyl carbonate

R_f = 0.65 (hexane/ether = 6:1). IR: 3089w, 2986m, 2958m, 2854w, 1749s, 1648w, 1444m, 1377m, 1336m, 1265s, 1044m, 993m, 942m, 898m, 845w, 793m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.87 (ddd, *J* = 17.0, 10.5, 6.2 Hz, 1H), 5.35-5.15 (m, 3H), 3.78 (s, 3H), 1.37 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 137.0, 116.4, 75.1, 54.5, 19.9. MS (EI) *m/z*: 130 (M^+, 1), 115 (4), 98 (4), 85 (10), 77 (24), 71 (79), 59 (48), 55 (100). Anal. Calc'd for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.61; H, 7.79.

Ref.: Evans, P. A.; Nelson, J. D.; *J. Am. Chem. Soc.* **1998**, *120*, 5581.

(*R*)-(+)-2-(1-Methyl-allyl) malonic acid dimethyl ester (13)

R_f = 0.35 (hexane/EtOAc = 4:1). $[\alpha]^{21}_D$ = 19.4 (*c* 0.76, $CHCl_3$, 93% ee). IR: 3082w, 2956m, 2852w, 1739s, 1643w, 1436m, 1268m, 1200m, 1153m, 1022m, 921m, 802w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.77 (ddd, *J* = 17.1, 10.2, 8.0 Hz, 1H), 5.13-5.00 (m, 2H), 3.74 (s, 3H), 3.71 (s, 3H), 3.32 (d, *J* = 9.0 Hz, 1H), 2.97-2.94 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 168.7, 139.7, 115.6, 57.6, 52.4, 52.3, 38.1, 18.0. MS (EI) *m/z*: 187 (MH^+, 0.5), 155 (6), 127 (100), 111 (32), 101 (28), 95 (42). Anal. Calc'd for $C_9H_{14}O_4$: C, 57.97; H, 7.63. Found: C, 58.05; H, 7.57. Chiraldex γ-CD-TA, 30 m, 50-100 °C, 1 °/min, 90 kPa H_2, t_R = 33.4 min ((*R*)-(+)-**13**), t_R = 34.7 min ((*S*)-(-

)-**13**), t_R = 41.7 min (*E*-**14**), t_R = 44.2 min (*Z*-**14**). Restek Rtx-1701, 30 m, 60-120 °C, 2 °/min, 60 kPa H_2, t_R = 23.2 min (**13**), t_R = 27.4 min (*E*-**14**), t_R = 28.1 min (*Z*-**14**).

Ref.: Evans, P. A.; Nelson, J. D.; *J. Am. Chem. Soc.* **1998**, *120*, 5581.

(*E*)-2-But-2-enyl-malonic acid dimethyl ester (14)

R_f = 0.35 (hexane/EtOAc = 4:1). IR: 2955m, 1736s, 1437m, 1268m, 1231m, 1154m, 1023m, 968m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.61-5.49 (m, 1H), 5.42-5.31 (m, 1H), 3.73 (s, 6H), 3.41 (t, *J* = 7.5 Hz, 1H), 2.57 (m, 2H), 1.64 (dd, *J* = 6.1, 1.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 128.4, 126.2, 52.4, 51.9, 31.9, 17.8. MS (EI) *m/z*: 186 (M^+, 10), 154 (8), 132 (43), 126 (55), 123 (57), 111 (100), 101 (25), 95 (31). Chiraldex γ-CD-TA, 30 m, 50-100 °C, 1 °/min, 90 kPa H_2, t_R = 33.4 min ((*R*)-(+)-**13**), t_R = 34.7 min ((*S*)-(-)-**13**), t_R = 41.7 min (*E*-**14**), t_R = 44.2 min (*Z*-**14**). Restek Rtx-1701, 30 m, 60-120 °C, 2 °/min, 60 kPa H_2, t_R = 23.2 min (**13**), t_R = 27.4 min (*E*-**14**), t_R = 28.1 min (*Z*-**14**).

Acetic acid 3-phenoxy-allyl ester (15a)

R_f = 0.26 (pentane/ether = 20:1). IR: 3066w, 3043w, 2954w, 2891w, 1739s, 1674m, 1592m, 1491s, 1383m, 1364m, 1222s, 1169m, 1137m, 1023m, 936m, 894w, 757m, 693m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34-7.29 (m, 2H), 7.11-7.06 (m, 1H), 7.01-6.98 (m, 2H), 6.78 (dt, *J* = 12.1, 0.9 Hz, 1H), 5.44 (dt, *J* = 12.1, 7.8 Hz, 1H), 4.57 (dd, *J* = 7.8, 0.9 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 156.6, 148.2, 129.7, 123.5, 117.1, 105.6, 61.5, 21.1. MS (EI) *m/z*: 192 (M^+, 30), 149 (46), 133 (40), 121 (19), 105 (48), 94 (89), 77 (87), 51 (33), 43 (87). Anal. Calc'd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.65; H, 6.38.

Ref.: Vicart, N.; Cazes, B.; Goré, J.; *Tetrahedron Lett.* **1995**, *36*, 535.

Acetic acid 3-methoxy-allyl ester (15b)

R_f = 0.78 (pentane/ether = 1:1). IR: 3072w, 3009w, 2957m, 2838w, 1739s, 1657s, 1453m, 1384m, 1365m, 1237s, 1217s, 1176m, 1022m, 946m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.63 (d, *J* = 12.6 Hz, 1H), 4.93 (dt, *J* = 12.6, 7.8 Hz, 1H), 4.50 (dd, *J* = 7.8, 0.5 Hz, 2H), 3.58 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1, 153.3, 96.9, 62.6, 56.1, 21.0. MS (EI) *m/z*: 130 (M^+, 12), 87 (77), 71 (92), 59 (19), 55 (17), 43 (100).

(-)-2-Methyl-2-(1-phenoxy-allyl) malonic acid dimethyl ester (16a)

R_f = 0.55 (hexane/EtOAc = 6:1). $[\alpha]^{19}_D$ = -17.7 (*c* 1.89, $CHCl_3$, 98% ee). IR: 3002w, 2954w, 2845w, 1739s, 1597m, 1494m, 1455m, 1435m, 1265m, 1230s, 1115m, 1096m, 988m, 888w, 755m, 692m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.26-7.21 (m, 2H), 6.96-6.89 (m, 3H), 5.95 (dq, *J* = 17.3, 5.4 Hz, 1H), 5.40-5.31 (m, 3H), 3.74 (s, 3H), 3.63 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 170.0, 158.0, 132.9, 129.3, 121.4, 119.7, 116.2, 80.1, 58.6, 52.7, 52.7, 15.0. MS (EI) *m/z*: 278 (M^+, 12), 185 (34), 159 (8), 146 (10), 133 (19), 125 (7), 71 (100). HRMS calc'd for $C_{15}H_{18}O_5$: 278.1152. Found: 278.1153. Hewlett Packard hp-5ms, 30 m, iso 60 °C for 3 min, 60-250 °C, 10 °/min, 60

kPa He, t_R = 16.9 min (**16a**), t_R = 18.8 min (**17a**), (HPLC): Daicel, Chiralcel OJ, 25 cm, heptane/ethanol = 93:7, 0.5 mL/min, 20 °C, 220 nm, t_R = 23.6 min (**(+)-16a**), t_R = 57.1 min (**(-)-16a**).

(+)-2-(1-Methoxy-allyl)-2-methyl malonic acid dimethyl ester (16b)
R_f = 0.46 (pentane/ether = 7:1). $[\alpha]^{20}_D$ = 1.5 (*c* 0.71, $CHCl_3$, 74% ee). IR: 2994w, 2954m, 1740s, 1642w, 1457m, 1436m, 1264m, 1235m, 1113m, 1096m, 998w, 941w cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.74 (ddd, 17.5, 10.0, 7.2 Hz, 1H), 5.37-5.31 (m, 2H), 4.26 (d, 7.2 Hz, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 3.29 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 170.4, 133.1, 120.0, 83.8, 58.7, 57.3, 52.6, 52.6, 15.2. MS (EI) *m/z*: 216 (M^+, 0.1), 185 (1), 157 (3), 125 (3), 71 (100), 59 (4), 41 (23). Anal. Calc'd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.45. Found: C, 55.42; H,7.54. Chiraldex γ-CD-TA, 30 m, 50-110 °C, 1 °/min, 75 kPa H_2, t_R = 42.5 min ((-)-**16b**), t_R = 34.7 min ((+)-**16b**), t_R = 55.8 min (**17b**). Hewlett Packard hp-5ms, 30 m, iso 60 °C for 3 min, 60-250 °C, 10 °/min, 60 kPa He, t_R = 10.9 min (**16b**), t_R = 12.4 min (**17b**).

***E*-2-methyl-2-(3-phenoxy-allyl) malonic acid dimethyl ester (17a)**
R_f = 0.55 (hexane/EtOAc = 6:1). ^1H NMR (300 MHz, $CDCl_3$): 7.36-7.26 (m, 2H), 7.12-6.95 (m, 3H), 6.47 (dt, *J* = 12.1, 1.1 Hz, 1H), 5.29-5.19 (m, 1H), 3.73 (s, 6H), 2.59 (dd, *J* = 8.1, 1.1 Hz, 2H), 1.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 157.0, 144.8, 129.6, 122.8, 116.5, 106.6, 54.1, 52.5, 34.0, 19.8. MS (EI) *m/z*: 278 (M^+, 23), 185 (10), 133 (100), 125 (69), 77 (42). Hewlett Packard hp-5ms, 30 m, iso 60 °C for 3 min, 60-250 °C, 10 °/min, 60 kPa He, t_R = 16.9 min (**16a**), t_R = 18.8 min (**17a**).

***E*-2-(3-methoxy-allyl)-2-methyl malonic acid dimethyl ester (17b)**
R_f = 0.46 (pentane/ether = 7:1). ^1H NMR (300 MHz, $CDCl_3$): δ 6.32 (d, *J* = 12.6 Hz, 1H), 4.58 (m, 1H), 3.72 (s, 6H), 3.50 (s, 3H), 2.48 (dd, *J* = 7.9, 1.1 Hz, 2H), 1.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.4, 150.0, 96.1, 55.8, 54.2, 52.4, 34.3, 19.6. MS (EI) *m/z*: 216 (M^+, 7), 185 (1), 169 (1), 156 (11), 125 (11), 71 (100). Chiraldex γ-CD-TA, 30 m, 50-110 °C, 1 °/min, 75 kPa H_2, t_R = 42.5 min ((-)-**16b**), t_R = 34.7 min ((+)-**16b**), t_R = 55.8 min (***E*-17b**). Hewlett Packard hp-5ms, 30 m, iso 60 °C for 3 min, 60-250 °C, 10 °/min, 60 kPa He, t_R = 10.9 min (**16b**), t_R = 12.4 min (**17b**).