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Supporting Information

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First Kinetic Resolution of Oxazinones - A Highly Practical and Efficient Organocatalytic Approach to Enantiomerically Pure β-Amino Acids

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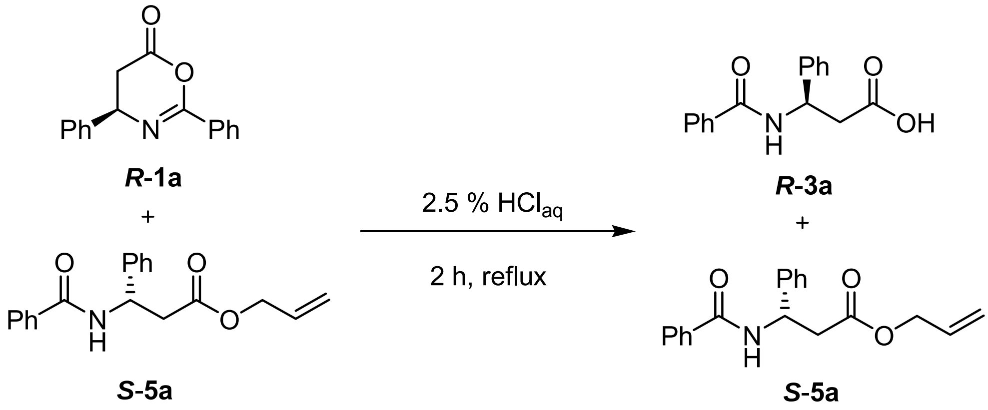
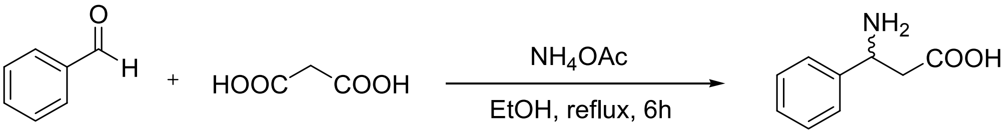
(I) Alcoholytic Kinetic Resolution of Oxazinones – work-up procedure:



To a solution of 14.0 mg of the catalyst **2a** (33.3 μmol, 0.05 eq) in 1.00 ml abs. toluene, 45.4 μl allyl alcohol (667 μmol, 1.0 eq) was added. After addition of a solution containing 168 mg of oxazinone *rac*-**1a** (667 μmol, 1.0 eq) in 3.30 ml abs. toluene, the homogeneous reaction mixture was stirred at ambient temperature. The reaction was monitored by chiral HPLC. After 2.5 h and a conversion of 59 % the enantiomeric excess of the remaining oxazinone **1a** was 98 %, the product ester **5a** was obtained in 87 % ee. After addition of 3.5 ml 2.5 % HCl$_{aq}$ the biphasic reaction mixture was heated under reflux for 2 h and allowed to cool to ambient temperature. A white solid precipitated which was filtered off and dried. All the analytical data were identical with acid **3a**. The yield of the acid **3a** is 38 % (68.7 mg, 255 μmol). Transformation to the methyl ester **6** and its analysis by chiral HPLC showed that the enantiomeric excess of the product is 97 %. The two phases of the filtrate were separated. The aqueous phase was washed with DCM, the two organic phases were combined, dried over $MgSO_4$ and the solvent was evaporated. All the analytical data of the remaining white solid were identical with allyl ester **5a**. The yield of the ester **5a** is 50 % (103 mg, 331 μmol), its enantiomeric excess is 84 %.

(II) Preparation of the racemic β-amino acids 4a-f.[1]

3-Amino-3-phenylpropanoic acid *rac*-**4a**:



A suspension of benzaldehyde (3.20 g, 30.0 mmol), malonic acid (3.10 g, 30.2 mmol) and ammonium acetate (3.10 g, 40.2 mmol) in 50.0 ml EtOH was heated for 8 h under reflux. The white precipitate was filtered off and washed with cold EtOH. After drying under reduced pressure, the crude amino acid was obtained as a colorless solid (2.40g, 14.5 mmol, 48 % yield) and was directly converted to the corresponding benzoylated compound without further purification.

3-Amino-3-(4-chlorophenyl)propanoic acid *rac*-**4b**:

The procedure described for *rac*-**4a** was followed on 40.0 mmol scale starting from *p*-chlorobenzaldehyde. The crude product was isolated as a colorless solid (5.20 g, 26.1 mmol, 65 % yield).

3-Amino-3-(4-methoxyphenyl)propanoic acid *rac*-**4c**:

The procedure described for *rac*-**4a** was followed on 60.0 mmol scale starting from *p*-methoxybenzaldehyde. The crude product was isolated as a colorless solid (5.31 g, 27.2 mmol, 45 % yield).

3-Amino-3-(3-nitrophenyl)propanoic acid *rac*-**4d**:

The procedure described for *rac*-**4a** was followed on 37.6 mmol scale starting from *m*-nitrobenzaldehyde. The crude product was isolated as a colorless solid (4.21 g, 13.4 mmol, 36 % yield).

3-Amino-3-(*tert.*-butyl)propanoic acid *rac*-**4e**:

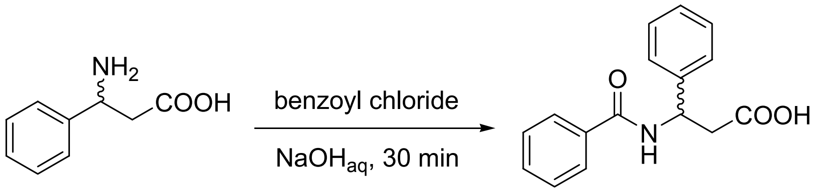
The procedure described for *rac*-**4a** was followed on 35.0 mmol scale starting from pivalaldehyde. After heating for 8 h under reflux the solvent was evaporated and the crude product was obtained as a pale yellow oil (3.96 g, 27.3 mmol, 78 % yield).

3-Amino-3-(*i*-propyl)propanoic acid *rac*-**4f**:

The procedure described for *rac*-**4a** was followed on 139 mmol scale starting from isobutyraldehyde. After heating for 8 h under reflux the solvent was evaporated and the crude product was obtained as a pale yellow oil (28.6 g).

(III) Preparation of the *N*-Benzoyl amino acids 3a-f.[2]

3-(Benzamido)-3-phenylpropanoic acid *rac*-**3a**:



To an ice-cold solution of 3-amino-3-phenylpropanoic acid *rac*-**4a** (6.55 g, 39.7 mmol) in 40.0 ml 2N $NaOH_{aq}$, benzoyl chloride (5.06 ml, 43.6 mmol) was added, followed by slow addition of 40.0 ml 2N $NaOH_{aq}$. The reaction mixture was then stirred for 30 min at ambient temperature until the solution became clear. After acidification with conc. HCl to pH <2, the precipitated solid was filtered off and recrystallized from EtOH/H_2O. The product *rac*-**3a** was isolated as a colorless solid (6.19 g, 23.0 mmol, 58 % yield). mp = 193 °C [Lit.[3] 199 °C]. ^{1}H-NMR (300 MHz, DMSO-D_6): δ = 2.78 (dd, *J* = 6.2, 15.7 Hz; 1H), 2.91 (dd, *J* = 8.9, 15.7 Hz; 1H), 5.41-5.49 (m, 1H), 7.20-7.56 (m, 8H), 7.84-7.87 (m, 2H), 8.89 (d, *J* = 8.3 Hz; 1H), 12.28 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-D_6): δ = 40.6, 50.0, 126.5, 126.9, 127.2, 128.1, 128.2, 131.1, 134.4, 142.7, 165.4, 171.8. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1711 (m), 1634 (s), 1537 (s), 1487 (m), 1294 (w), 698 (s).

3-(Benzamido)-3-(4-chlorophenyl)propanoic acid *rac*-**3b**:

The procedure as described above for *rac*-**3a** was followed on 15.0 mmol scale. The product *rac*-**3b** was isolated as a colorless solid (2.24 g, 7.37 mmol, 49 % yield). mp = 208 °C. ^{1}H-NMR (300 MHz, DMSO-D$_6$): δ = 2.79 (dd, *J* = 6.3, 15.8 Hz; 1H), 2.92 (dd, *J* = 8.8, 15.8 Hz; 1H), 5.39-5.46 (m, 1H), 7.37-7.57 (m, 7H), 7.84-7.86 (m, 2H), 8.91 (d, *J* = 8.1 Hz; 1H), 171.5 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-D$_6$): δ = 40.3, 49.5, 127.2, 128.2, 128.5, 128.8, 131.2, 131.5, 134.2, 141.7, 165.5, 171.6. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1707 (s), 1626 (s), 1536 (w), 1404 (w), 1305 (s), 1284 (s), 1233 (w), 1176 (w), 1085 (m), 1012 (m), 984 (w), 820 (s), 715 (w).

3-(Benzamido)-3-(4-methoxyphenyl)propanoic acid *rac*-**3c**:

The procedure as described above for *rac*-**3a** was followed on 15.4 mmol scale. The product was isolated as a colorless solid (2.70 g, 9.02 mmol, 59 % yield). mp = 197 °C. ^{1}H-NMR (300 MHz, DMSO-D$_6$): δ = 2.75 (dd, *J* = 6.5, 15.5 Hz; 1H), 2.88 (dd, *J* = 8.7, 15.6 Hz; 1H), 3.72 (s, 3H), 5.35-5.43 (m, 1H), 6.86-6.91 (m, 2H), 7.32-7.35 (m, 2H), 7.43-7.55 (m, 3H), 7.82-7.85 (m, 2H), 8.81 (d, *J* = 8.3 Hz; 1H), 12.23 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-D$_6$): δ = 40.7, 49.4, 55.0, 113.5, 127.2, 127.7, 128.1, 131.1, 134.4, 134.7, 158.1, 165.3, 171.8. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1704 (s), 1628 (s), 1515 (s), 1487 (w), 1279 (w), 1244 (m), 1179 (m), 1027 (w), 830 (w), 689 (w).

3-(Benzamido)-3-(3-nitrophenyll)propanoic acid *rac*-**3d**:

The procedure as described above for *rac*-**3a** was followed on 14.3 mmol scale. The product was isolated as a colorless solid (1.86 g, 5.92 mmol, 41 % yield). mp = 198 °C. ^{1}H-NMR (300 MHz, DMSO-D$_6$): δ = 2.87 (dd, *J* = 6.4, 16.0 Hz; 1H), 2.98 (dd, *J* = 8.7, 16.0 Hz; 1H), 5.48-5.56 (m, 1H), 7.45-7.57 (m, 3H), 7.62-7.67 (m, 1H), 7.83-7.90 (m, 3H), 8.10-8.14 (m, 1H), 8.29-8.31 (m, 1H), 9.05 (d, *J* = 7.9 Hz; 1H), 12.39 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-D$_6$): δ = 40.1, 49.7, 121.2, 122.0, 127.2, 128.3, 129.8, 131.4, 133.6, 134.0, 145.0, 147.8, 165.7, 171.4. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1713 (m), 1633 (m), 1529 (s), 1487 (m), 1349 (s), 1098 (w), 805 (w), 690 (m).

3-(Benzamido)-3-(*tert.*-butyl)propanoic acid *rac*-**3e**:

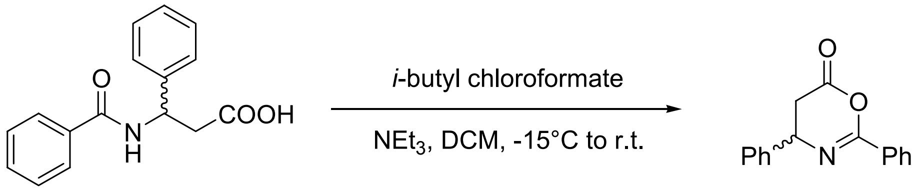
The procedure as described above for *rac*-**3a** was followed on 9.44 mmol scale. The product was isolated as a colorless solid (1.60 g, 6.42 mmol, 68 % yield). mp = 227 °C. ^{1}H-NMR (300 MHz, DMSO-D$_6$): δ = 0.90 (s, 9H), 2.41 (dd, *J* = 10.7, 15.0 Hz; 1H), 2.55 (dd, *J* = 3.3, 15.0 Hz; 1H), 4.26-4.34 (m, 1H), 7.42-7.53 (m, 3H), 7.79-7.82 (m, 2H), 8.06 (d, *J* = 9.3 Hz; 1H), 12.01 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-D$_6$): δ = 26.4, 35.0, 35.1, 54.3, 127.3, 128.0, 130.8, 135.1, 166.2, 173.2. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1700 (s), 1636 (s), 1544 (m), 1490 (w), 1354 (w), 1288 (w), 1077 (w), 695 (m).

3-(Benzamido)-3-(*i*-propyl)propanoic acid *rac*-**3f**:

The procedure as described above for *rac*-**3a** was followed on 139 mmol scale. The product was isolated as a colorless solid (4.66 g, 18.7 mmol, 14 % yield). mp = 174 °C. ^{1}H-NMR (300 MHz, DMSO-D$_6$): δ = 0.88 (d, *J* = 6.8 Hz; 6H), 1.84 (qd, *J* = 6.7, 13.4 Hz; 1H), 2.40-2.55 (m, 2H), 4.17-4.26 (m, 1H), 7.42-7.54 (m, 3H), 7.80-7.83 (m, 2H), 8.16 (d, *J* = 8.8 Hz; 1H), 12.07 (s, 1H). ^{13}C-NMR (75 MHz, DMSO-D$_6$): δ = 18.5, 18.9, 31.7, 36.4, 51.5, 127.2, 128.0, 130.9, 134.9, 165.9, 172.9. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1711 (s), 1638 (s), 1536 (s), 1489 (m), 1388 (w), 1369 (w), 1316 (w), 1284 (w), 1192 (w), 801 (w), 710 (m), 694 (m).

(IV) Preparation of the Oxazinones 1a-f.[4]

4,5-Dihydro-4-phenyl-1,3-oxazin-6-one *rac*-**1a**:



Iso-butyl chloroformate (2.89 ml, 22.3 mmol) was slowly added at -15 °C to a solution of 3-(benzamido)-3-phenylpropanoic acid *rac*-**3a** (5.00 g, 18.6 mmol) and NEt$_3$ (3.11 ml, 22.3 mmol) in 110 ml abs. DCM. The resulting mixture was stirred at this temperature for 15 min, at 0°C for 10 min and then at room temperature for another 15 min. DCM was evaporated and the residue was dried under reduced pressure.

After adding *n*-hexane the suspension was filtered. Evaporation of the filtrate afforded the crude oxazinone that was purified by column chromatography on silica gel (*n*-hexane:ethyl acetate = 8:2 as eluant). The product was obtained as a colorless crystalline solid (1.86 g, 7.40 mmol, 40 % yield). mp = 102 °C [Lit.[3] 90-97 °C]. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.67 (dd, *J* = 11.0, 16.1 Hz; 1H), 3.07 (dd, *J* = 5.2, 16.1 Hz; 1H), 5.06 (dd, *J* = 5.2, 11.0 Hz; 1H), 7.31-7.57 (m, 8H), 8.12-8.14 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 36.2, 56.6, 126.2, 127.0, 127.9, 128.5, 128.9, 130.2, 132.0, 140.5, 153.6, 165.5. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1788 (s), 1670 (s), 1601 (w), 1580 (w), 1492 (m), 1449 (m), 1274 (m), 1198 (m), 1135 (m), 1092 (m), 1064 (s), 1036 (m), 1022 (m), 1007 (s), 850 (w), 759 (w), 695 (s).

4,5-Dihydro-4-(4-chlorphenyl)-1,3-oxazin-6-one *rac*-**1b**:

The procedure as described above for *rac*-**1a** was followed on 1.65 mmol scale. The product was isolated as a colorless solid (233 mg, 816 µmol, 35 % yield). mp = 89 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.61 (dd, *J* = 11.4, 16.1 Hz; 1H), 3.05 (dd, *J* = 5.1, 16.1 Hz; 1H), 5.03 (dd, *J* = 5.1, 11.4 Hz; 1H), 7.34-7.40 (m, 4H), 7.43-7.58 (m, 3H), 8.10-8.13 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 36.1, 55.9, 127.6, 127.9, 128.5, 129.1, 130.1, 132.2, 133.7, 139.1, 153.9, 165.1. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1791 (s), 1671 (s), 1599 (w), 1578 (w), 1490 (s), 1448 (w), 1405 (w), 1342 (w), 1273 (w), 1214 (m), 1197 (m), 1132 (m), 1086 (s), 1069 (m), 1037 (m), 1008 (s), 853 (m), 823 (m), 776 (m), 695 (s).

4,5-Dihydro-4-(4-methoxyphenyl)-1,3-oxazin-6-one *rac*-**1c**:

The procedure as described above for *rac*-**1a** was followed on 4.88 mmol scale. The product was isolated as a colorless solid (514 mg, 1.83 mmol, 37 % yield). mp = 91 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.65 (dd, *J* = 10.7, 16.1 Hz; 1H), 3.03 (dd, *J* = 5.3, 16.1 Hz; 1H), 3.82 (s, 3H), 5.02 (dd, *J* = 5.3, 10.6 Hz; 1H), 6.91-6.96 (m, 2H), 7.30-7.34 (m, 2H), 7.42-7.57 (m, 3H), 8.10-8.14 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 36.4, 55.4, 56.1, 114.3, 127.4, 127.9, 128.5, 130.3, 132.0, 132.7, 153.5, 159.3, 165.7. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1787 (s), 1667 (s), 1611 (m), 1581 (w), 1511 (s), 1448 (w), 1345 (w), 1246 (s), 1215 (w), 1198 (w), 1175 (m), 1131 (m), 1087 (s), 1068 (m), 1035 (m), 852 (w), 828 (m), 778 (w), 695 (s).

4,5-Dihydro-4-(3-nitrophenyl)-1,3-oxazin-6-one *rac*-**1d**:

The procedure as described above for *rac*-**1a** was followed on 1.59 mmol scale. The product was isolated as a highly viscous, colorless oil (69 mg, 234 µmol, 15 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.63 (dd, *J* = 12.4, 16.1 Hz; 1H), 3.15 (dd, *J* = 4.9, 16.1 Hz; 1H), 5.14 (dd, *J* = 4.9; 12.4 Hz; 1H), 7.45-7.50 (m, 2H), 7.54-7.63 (m, 2H), 7.78-7.80 (m, 1H), 8.11-8.15 (m, 2H), 8.19-8.23 (m, 1H), 8.36-8.38 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 35.9, 55.8, 121.6, 122.9, 127.9, 128.6, 129.8, 129.9, 132.4, 142.9, 148.7, 154.5, 164.6. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1790 (s), 1672 (s), 1580 (w), 1527 (s), 1492 (w), 1448 (w), 1347 (m), 1277 (w), 1203 (w), 1133 (w), 1094 (w), 1069 (w), 1037 (w), 1011 (m), 850 (w), 807 (w), 779 (w), 738 (w), 695 (m).

4,5-Dihydro-4-(*tert.*-butyl)-1,3-oxazin-6-one *rac*-**1e**:

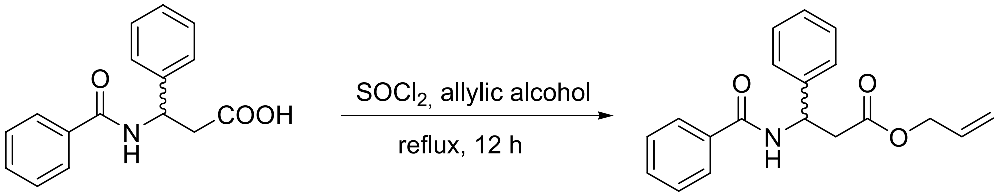
The procedure as described above for *rac*-**1a** was followed on 4.01 mmol scale. The product was isolated as a colorless solid (485 mg, 2.10 mmol, 52 % yield). mp = 62 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 9H), 2.37 (dd, *J* = 12.7, 15.9 Hz; 1H), 2.77 (dd, *J* = 4.7, 15.9 Hz; 1H), 3.48 (dd, *J* = 4.7, 12.7 Hz; 1H), 7.39-7.53 (m, 3H), 8.03-8.06 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 26.0, 29.4, 34.3, 61.7, 127.7, 128.4, 130.6, 131.6, 157.8, 167.1. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1790 (s), 1677 (s), 1449 (w), 1310 (w), 1274 (w), 1237 (w), 1237 (w), 1213 (w), 1143 (m), 1095 (m), 1049 (m), 1036 (m), 1015 (m), 853 (w), 778 (w), 696 (m).

4,5-Dihydro-4-(*i*-propyl)-1,3-oxazin-6-one *rac*-**1f**:

The procedure as described above for *rac*-**1a** was followed on 2.01 mmol scale. The product was isolated as a colorless oil (239 mg, 1.10 mmol, 55 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.06 (dd, *J* = 6.8, 8.3 Hz; 6H), 1.93 (qd, *J* = 6.7, 13.3 Hz; 1H), 2.41 (dd, *J* = 11.3, 16.0 Hz; 1H), 2.73 (dd, *J* = 5.0, 16.0 Hz; 1H), 3.61 (td, *J* = 5.5, 11.2 Hz; 1H), 7.39-7.52 (m, 3H), 8.02-8.05 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 18.3, 18.6, 31.0, 32.9, 58.4, 127.6, 128.4, 130.5, 131.6, 152.2, 167.0. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1788 (s), 1673 (s), 1579 (w), 1533 (w), 1491 (w), 1465 (w), 1449 (w), 1275 (m), 1221 (m), 1144 (m), 1060 (s), 1011 (s), 851 (w), 776 (w), 695 (s).

(V) Preparation of the racemic *N*-Benzoyl amino acid esters 5-7.

3-(Benzamido)-3-phenylpropanoic acid allyl ester *rac*-**5a**:



A suspension of 3-(benzamido)-3-phenylpropanoic acid *rac*-**4a** (750 mg, 2.78 mmol) in 10.0 ml allyl alcohol was cooled on an ice bath. $SOCl_2$ (232 µl, 3.20 mmol) was added slowly and the solution was heated for 12 h under reflux. The reaction mixture was then concentrated in vacuum to obtain a brown oil. Purification by column chromatography on silica gel (*n*-hexane:ethyl acetate = 7:3 as eluant) gave the desired ester as a colorless solid (650 mg, 2.10 mmol, 79% yield). mp = 99 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.98 (dd, *J* = 5.7, 15.8 Hz; 1H), 3.08, dd, *J* = 5.6, 15.8 Hz; 1H), 4.53-4.55 (m, 1H), 5.16-5.24 (m, 2H), 5.62-5.69 (m, 1H), 5.74-5.87 (m, 1H), 7.23-7.54 (m, 9H), 7.82-7.85 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 39.8, 49.8, 65.5, 118.6, 126.2, 127.0, 127.6, 128.6, 128.7, 131.5, 131.6, 134.2, 140.4, 166.5, 171.2. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1736 (s), 1636 (s), 1601 (w), 1578 (w), 1536 (s), 1488 (m), 1298 (m), 1166 (m), 1084 (w), 1027 (w), 987 (w), 929 (w), 761 (w), 698 (s).

3-(Benzamido)-3-phenylpropanoic acid methyl ester *rac*-**6**:

The procedure as described above for *rac*-**5a** was followed on 1.86 mmol scale using MeOH as solvent. The product was isolated as a colorless solid (509 mg, 1.80 mmol, 97 % yield). mp = 116 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.96 (dd, *J* = 5.7, 15.8 Hz; 1H), 3.06 (dd, *J* = 5.5, 15.8 Hz; 1H), 3.64 (s, 3H), 5.61-5.61 (m, 1H), 7.27-7.54 (m, 9H), 7.82-7.85 (m, 2H).^{13}C-NMR (75 MHz, $CDCl_3$): δ = 39.6, 49.8, 51.9, 126.2, 127.0, 127.6, 128.6, 128.7, 131.6, 134.2, 140.5, 166.5, 172.1. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1736 (s), 1635 (s), 1601 (w), 1577 (w), 1536 (s), 1488 (m), 1435 (m), 1298 (m), 1260 (m), 1168 (w), 1075 (m), 804 (m), 698 (s).

3-(Benzamido)-3-phenylpropanoic acid *i*-propyl ester *rac*-**7**:

The procedure as described above for *rac*-**5a** was followed on 1.90 mmol scale using *i*-PrOH as solvent. The product was isolated as a colorless solid (561 mg, 1.80 mmol, 95 % yield). mp = 109 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.3 Hz; 3H), 1.19 (d, *J* = 6.3 Hz; 3H), 2.91 (dd, *J* = 5.7, 15.4 Hz; 1H), 3.01 (dd, *J* = 5.7, 15.4 Hz; 1H), 4.93-5.02 (m, 1H), 5.62-5.69 (m, 1H), 7.24-7.55 (m, 8H), 7.62 (d, *J* = 8.1 Hz; 1H), 7.84-7.87 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 21.6, 40.2, 49.8, 68.4, 126.2, 127.0, 127.5, 128.5, 128.6, 131.5, 134.2, 140.5, 166.4, 171.1. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1728 (s), 1636 (s), 1601 (w), 1578 (w), 1533 (s), 1489 (m), 1373 (m), 1296 (m), 1266 (m), 1173 (w), 1106 (s), 968 (w), 699 (s).

3-(Benzamido)-3-(4-chlorophenyl)propanoic acid allyl ester *rac*-**5b**:

The procedure as described above for *rac*-**5a** was followed on 1.60 mmol scale. The product was isolated as a colorless solid (519 mg, 1.51 mmol, 94 % yield). mp = 112 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.95 (dd, *J* = 5.6, 15.9 Hz; 1H), 3.03 (dd, *J* = 5.5, 15.9 Hz; 1H), 4.53-4.56 (m, 2H), 5.18-5.25 (m, 2H), 5.56-5.63 (m, 1H), 5.74-5.88 (m, 1H), 7.29 (s, 4H), 7.40-7.55 (m, 3H), 7.60 (d, *J* = 8.2 Hz; 1H), 7.80-7.83 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 30.9, 39.6, 49.3, 65.6, 118.8, 127.0, 127.6, 128.6, 128.8, 131.4, 131.7, 133.9, 139.0, 166.5, 171.1. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1735 (s), 1636 (s), 1601 (w), 1577 (w), 1533 (s), 1489 (s), 1412 (w), 1344 (w), 1310 (m), 1165 (m), 1091 (m), 1014 (m), 987 (w), 931 (w), 828 (w), 693 (m).

3-(Benzamido)-3-(4-methoxyphenyl)propanoic acid allyl ester *rac*-**5c**:

The procedure as described above for *rac*-**5a** was followed on 1.67 mmol scale. The product was isolated as a colorless solid (449 mg, 1.32 mmol, 79 % yield). mp = 102 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.96 (dd, *J* = 5.9, 15.7 Hz; 1H), 2.07 (dd, *J* = 5.5, 15.7 Hz; 1H), 3.79 (s, 3H), 4.53-5.56 (m, 2H), 5.17-5.26 (m, 2H), 5.56-5.63 (m, 1H), 5.76-5.89 (m, 1H), 6.84-6.89 (m, 2H), 7.27-7.31 (m, 2H), 7.37 (d, *J* = 8.2 Hz; 1H), 7.41-7.53 (m, 3H), 7.80-7.83 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 39.8, 49.4, 55.2, 65.5, 114.1, 118.6, 127.0, 127.5, 128.5, 131.6, 132.5, 134.2, 159.0, 166.4, 171.3. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1735 (m), 1637 (s), 1611 (w), 1578 (w), 1513 (s), 1488 (m), 1303 (m), 1248 (s), 1178 (m), 1031 (w), 988 (w), 930 (w), 831 (w), 712 (w).

3-(Benzamido)-3-(3-nitrophenyl)propanoic acid allyl ester *rac*-**5d**:

The procedure as described above for *rac*-**5a** was followed on 955 µmol scale. The product was isolated as a colorless solid (279 mg, 787 µmol, 83 % yield). mp = 106°C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.97-3.11 (m, 2H), 4.54-4.56 (m, 2H), 5.18-5.26 (m, 2H), 5.67-5.87 (m, 2H), 7.41-7.55 (m, 4H), 7.70-7.73 (m, 1H), 7.82-7.86 (m, 3H), 8.10-8.13 (m, 1H), 8.21-8.23 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 39.5, 49.4, 65.8, 119.1, 121.1, 122.6, 127.1, 128.7, 129.7, 131.2, 131.9, 132.8, 133.5, 143.0, 148.4, 166.7, 170.8. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1734 (s), 1636 (s), 1601 (w), 1578 (w), 1529 (s), 1487 (m), 1349 (s), 1299 (m), 1171 (m), 1097 (w), 987 (w), 931 (w), 805 (w), 713 (m), 691 (m).

3-(Benzamido)-3-(*tert.*-butyl)propanoic acid allyl ester *rac*-**5e**:

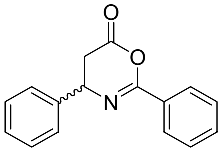
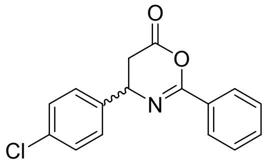
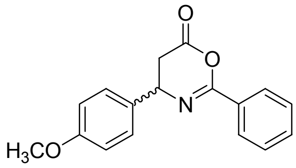
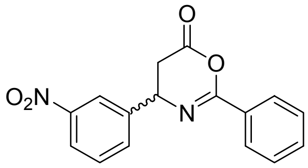
The general procedure as above was followed on 802 µmol scale. The product was isolated as a colorless solid (226 mg, 781 µmol, 97 % yield). mp = 111 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.99 (s, 9H), 2.49 (dd, J = 8.5, 14.7 Hz; 1H), 2.69 (dd, J = 4.6, 14.7 Hz; 1H), 4.42-4.50 (m, 1H), 4.52-4.55 (m, 2H), 5.16-5.31 (m, 2H), 5.79-5.93 (m, 1H), 6.62 (d, J = 9.8 Hz; 1H), 7.39-7.51 (m, 3H), 7.75-7.78 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 26.5, 35.5, 35.5, 65.6, 118.8, 126.7, 128.5, 131.3, 131.8, 134.9, 167.0, 172.0. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1736 (s), 1639 (s), 1602 (w), 1579 (w), 1536 (s), 1489 (w), 1367 (w), 1348 (w), 1298 (m), 1198 (w), 1164 (m), 1077 (w), 987 (w), 929 (w), 800 (w), 694 (m).

3-(Benzamido)-3-(*i*-propyl)propanoic acid allyl ester *rac*-**5f**:

The general procedure as above was followed on 2.13 mmol scale. The product was isolated as a colorless solid (522 mg, 1.90 mmol, 89 % yield). mp = 57 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.95 (dd, J = 2.0, 6.8 Hz; 6H), 1.91 (td, J = 6.8, 13.8 Hz; 1H), 2.57-2.70 (m, 2H), 4.19-4.28 (m, 1H), 4.47-4.60 (m, 2H), 5.16-5.30 (m, 2H), 5.79-5.92 (m, 1H), 6.96 (d, J = 9.2 Hz; 1H), 7.34-7.64 (m, 3H), 7.73-7.76 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 19.1, 19.3, 31.6, 36.2, 51.8, 65.2, 118.5, 126.8, 128.3, 131.2, 131.7, 134.6, 166.7, 171.8. FT-IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 1736 (s), 1638 (s), 1536 (s), 1488 (w), 1370 (w), 1274 (w), 1175 (m), 987 (w), 929 (w), 694 (m).

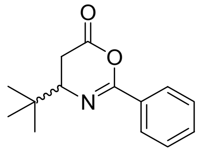
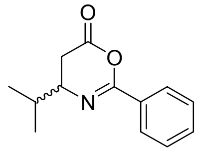
(VI) Methods to determine the enantiomeric excess of the oxazinones 1a-f:

a) HPLC methods

substrate		column	conditions	***R*-1**[a] **[min]**	***S*-1**[a] **[min]**
	*rac*-**1a**	*Daicel* Chiralpak AD	*n*-hexane/2-propanol 80:20 flow 1.0 ml/min	7.2	8.8
	*rac*-**1b**	*Daicel* Chiralcel OD-H	*n*-hexane/2-propanol 95:5 flow 1.0 ml/min	22.5	18.2
	*rac*-**1c**	*Daicel* Chiralcel OD-H	*n*-hexane/2-propanol 95:5 flow 1.2 ml/min	16.7	14.5
	*rac*-**1d**	*Daicel* Chiralcel OD-H	*n*-hexane/2-propanol 80:20 flow 1.0 ml/min	16.7	21.2

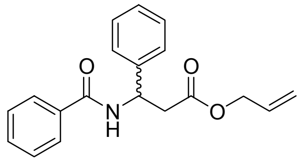
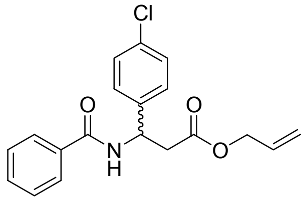
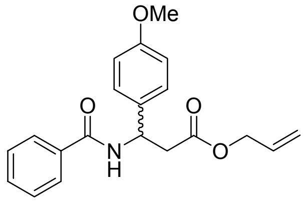
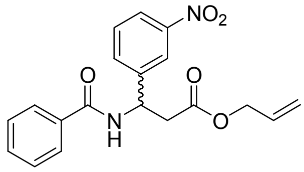
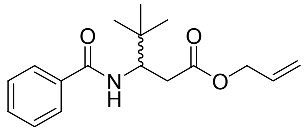
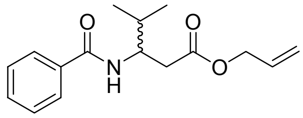
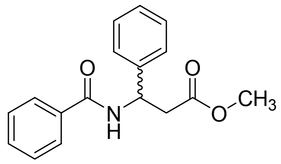
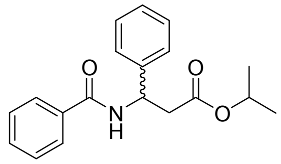
[a] The absolute configurations of the products **1b-d** are assigned in analogy to **1a**.

b) GC methods

substrate		column	conditions	***R*-1**[a] **[min]**	***S*-1**[a] **[min]**
	*rac*-**1e**	*Chrompak* CP-Chirasil-Dex	N_2, 1.00 ml/min, 150 °C	36.3	35.2
	*rac*-**1f**	*Chrompak* CP-Chirasil-Dex	N_2, 1.00 ml/min, 150 °C	53.8	52.6

[a] The absolute configurations of the products **1e** and **1f** are assigned in analogy to **1a**.

(VII) Methods to determine the enantiomeric excess of the N-Benzoylamino acid esters 5-7:

substrate		column	conditions	***R*-5-7**[a] **[min]**	***S*-5-7**[a] **[min]**
	*rac*-**5a**	*Daicel* Chiralpak AD	*n*-hexane/2-propanol 80:20 flow 1.0 ml/min	12.0	16.7
	*rac*-**5b**	*Daicel* Chiralcel OD-H	*n*-hexane/2-propanoll 95:5 flow 1.0 ml/min	32.1	55.2
	*rac*-**5c**	*Daicel* Chiralcel OD-H	*n*-hexane/2-propanol 95:5 flow 1.2 ml/min	35.7	25.5
	*rac*-**5d**	*Daicel* Chiralcel OD-H	*n*-hexane/2-propanol 80:20 flow 1.0 ml/min	12.8	10.0
	*rac*-**5e**	*Daicel* Chiralpak AD	*n*-hexane/2-propanol 95:5 flow 1.0 ml/min	12.5	15.5
	*rac*-**5f**	*Daicel* Chiralpak AD	*n*-hexane/2-propanol 95:5 flow 0.7 ml/min	19.0	21.1
	*rac*-**6**	*Daicel* Chiralpak AD	*n*-hexane/2-propanol 80:20 flow 1.0 ml/min	14.1	18.5
	*rac*-**7**	*Daicel* Chiralpak AD	*n*-hexane/2-propanol 80:20 flow 1.0 ml/min	10.3	16.3

[a] The absolute configurations of the products **5b**-**7** are assigned in analogy to **5a**.

(VIII) References

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[2] J. P. Greenstein, M. W. Winitz, *Chemistry of the Amino Acids*, Wiley, New York, **1961**.
[3] C. Giordano, *Synthesis* **1973**, 40-42.
[4] C. Drey, E. Mtetwa, *J. Chem Soc. Perkin Trans. 1* **1982**, 1587-1592.