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ELECTRONIC SUPPLEMENTARY INFORMATION

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B E L O N G I N G T O T H E P A P E R

Diastereoselective Ritter reactions of chiral secondary benzylic alcohols

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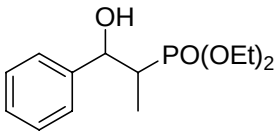
1 Synthetic procedures and spectroscopical data

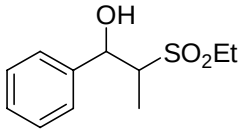
Preparation of diethyl 1-hydroxy-1-phenylpropan-2-ylphosphonate (6):



In a dry 100 mL Schlenk tube under argon, 20 mL dry tetrahydrofuran and 2.11 mL (15.0 mmol) diisopropylamine were cooled to 0 °C and 5.60 mL (14.0 mmol, 2.50 M) *n*-butyl lithium in hexane were added. The mixture was stirred at 0 °C for 15 minutes and subsequently cooled to –78 °C. Diethyl ethylphosphonate (2.00 g, 12.0 mmol) was added in one portion and the reaction was stirred for 1.5 hours. Benzaldehyde (1.40 g, 13.2 mmol) was added dropwise and stirring at –78 °C was continued for one hour. The reaction was warmed to room temperature over four hours and stopped by the addition of 20 mL saturated NH_4Cl-solution. The reaction was extracted with ethyl acetate (20 mL) and dichloromethane (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. After purification by flash chromatography (pentane/ethyl acetate = 1/9 → 0/1) 2.32 g (71%, d.r. = 55/45) of **6** were obtained as a colourless solid. R_f = 0.37 (ethyl acetate); major diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.02 (dd, $^3J_{HP}$ = 18.4 Hz, $^3J_{HH}$ = 7.4 Hz, 3 H), 1.36 (td, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 2.1 Hz, 6 H), 2.16-2.26 (m, 1 H), 4.04-4.25 (m, 4 H), 5.29 (dd, $^3J_{HH}$ = 9.9 Hz, $^3J_{HP}$ = 2.1 Hz, 1 H), 7.21-7.36 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 6.4 (dq, $^2J_{CP}$ = 3.2 Hz), 16.6 (dq, $^3J_{CP}$ = 5.6 Hz), 38.7 (dd,

$^1J_{CP}$ = 136.1 Hz), 62.1 (dt, $^2J_{CP}$ = 7.0 Hz), 62.4 (dt, $^2J_{CP}$ = 6.9 Hz), 70.9 (d), 127.0 (d), 127.3 (d), 128.2 (d), 141.5 (d, $^3J_{CP}$ = 12.8 Hz); minor diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.86 (dd, $^3J_{HP}$ = 17.4 Hz, $^3J_{HH}$ = 7.3 Hz, 3 H), 1.30 (td, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 5.3 Hz, 6 H), 2.11-2.18 (m, 1 H), 4.04-4.25 (m, 4 H), 4.69 (dd, $^3J_{HH}$ = 11.0 Hz, $^3J_{HP}$ = 9.4 Hz, 1 H), 7.21-7.36 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 11.9 (dq, $^2J_{CP}$ = 5.8 Hz), 16.5 (dq, $^3J_{CP}$ = 5.0 Hz), 39.3 (dd, $^1J_{CP}$ = 135.4 Hz), 62.2 (dt, $^2J_{CP}$ = 6.5 Hz), 62.3 (dt, $^2J_{CP}$ = 7.1 Hz), 74.9 (d, $^3J_{CP}$ = 3.5 Hz), 125.9 (d), 128.0 (d), 128.4 (d), 141.7 (d, $^3J_{CP}$ = 13.3 Hz); MS (EI, 70 eV), *m/z* (%): 272 (1) [M^+], 227 (3), 166 (100), 139 (41), 122 (18), 111 (32), 82 (13), 45 (6); HRMS (EI) ($C_{13}H_{21}O_4P$): calc.: 272.1177; found: 272.1172.

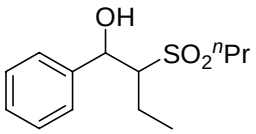
Preparation of 2-(ethylsulfonyl)-1-phenylpropan-1-ol (7)



In a dry 100 mL Schlenk tube under argon 30 mL dry tetrahydrofuran and 2.70 g (22.0 mmol) diethyl sulfone were cooled to −78 °C and 8.30 mL (20.0 mmol, 2.40 M) *n*-butyl lithium in hexane were added. The mixture was stirred at −78 °C for one hour. Benzaldehyde (2.12 g, 20.0 mmol) was added dropwise and stirring at −78 °C was continued for one hour. The reaction was warmed to room temperature over two hours and stopped by the addition of 30 mL saturated NH_4Cl-solution. The reaction was extracted with ethyl acetate (30 mL) and dichloromethane (2 × 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. After purification by flash chromatography (pentane/ethyl acetate = 1/1) 2.66 g (58%, d.r. = 66/34) of **7** were obtained as a colourless solid.

R_f = 0.13 (ethyl acetate/pentane = 1/1); m.p. = 89 °C; major diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.30 (d, ^3J = 7.3 Hz, 3 H), 1.42 (t, ^3J = 7.5 Hz, 3 H), 3.00-3.38 (m, 3 H), 5.61 (d, ^3J = 1.4 Hz, 1 H), 7.27-7.43 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 5.9 (q), 6.3 (q), 45.4 (t), 63.7 (d), 69.9 (d), 125.8 (d), 128.7 (d), 129.0 (d), 140.3 (s); minor diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.04 (d, ^3J = 7.3 Hz, 3 H), 1.43 (t, ^3J = 7.5 Hz, 3 H), 3.00-3.38 (m, 3 H), 4.94 (d, ^3J = 1.4 Hz, 1 H), 7.27-7.43 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 6.5 (q), 10.9 (q), 48.7 (t), 62.4 (d), 74.7 (d), 127.1 (d), 128.1 (d), 128.9 (d), 140.6 (s); MS (EI, 70 eV), *m/z* (%): 228 (9) [M^+], 134 (58), 117 (34), 107 (100), 94 (34), 79 (52), 66 (32); CHN ($C_{11}H_{16}O_3S$): calc.: C 57.87, H 7.06, S 14.04; found: C 57.93, H 7.05, S 14.09.

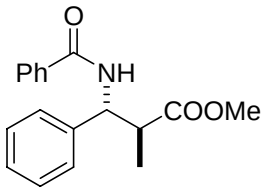
Preparation of 1-phenyl-2-(propylsulfonyl)butan-1-ol (15)



In a dry 100 mL Schlenk tube under argon 20 mL dry tetrahydrofuran and 2.06 mL (15.6 mmol) diisopropylamine were cooled to 0 °C and 5.60 mL (14.0 mmol, 2.50 M) *n*-butyllithium in hexane were added. The mixture was stirred at 0 °C for 15 minutes and subsequently cooled to −78 °C. Dipropyl sulfone (2.00 g, 13.3 mmol) was added in one portion and the reaction was stirred for two hours. Benzaldehyde (1.55 g, 14.6 mmol) was added dropwise and stirring at −78 °C was continued for one hour. The reaction was warmed to room temperature over four hours and stopped by the addition of 20 mL saturated NH_4Cl-solution. The reaction was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. After purification by flash chromatography (pentane/ethyl acetate = 5/1 → 2/1) 3.09 g (91%, d.r. = 70/30) of **15** were obtained as a colourless solid. R_f = 0.38 (ethyl acetate); major diastereoisomer: ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.81 (t, ^3J = 7.5 Hz, 3 H), 1.08 (t, ^3J = 7.4 Hz, 3 H), 1.83-1.98 (m, 4 H), 2.89-3.04 (m, 3 H), 5.57-5.58 (m, 1 H), 7.28-7.43 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 13.3 (q), 13.4 (q), 15.5 (t), 15.9 (t), 54.6 (t), 70.4 (d), 71.1 (d), 125.7 (d), 128.7 (d), 129.0 (d), 140.4 (s); minor diastereoisomer ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.82 (t, ^3J = 7.5 Hz, 3 H), 1.09 (t, ^3J = 7.4 Hz, 3 H), 1.83-1.98 (m, 4 H), 2.89-3.04 (m, 3 H), 5.58-5.59 (m, 1 H), 7.28-7.43 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 13.7 (q), 13.8 (q), 15.4 (t), 15.7 (t), 53.4 (t), 68.7 (d), 70.4 (d), 125.8 (d), 127.0 (d), 128.0 (d), 140.5 (s); MS (EI, 70 eV), *m/z* (%): 256 (4) [M^+], 214 (2), 148 (58), 107 (43), 91 (22), 57 (19), 43 (100); HRMS (EI) ($C_{13}H_{20}O_3S$): calc.: 256.1133; found: 256.1128.

Preparation of methyl 3-(benzamido)-2-methyl-3-phenylpropanoate (*anti*-3a) – Representative Procedure for the Ritter reactions catalysed by trifluoromethanesulfonic acid: In a typical experiment methyl 3-hydroxy-2-methyl-3-phenylpropanoate[1] (**1**) (48 mg, 250 μmol) and benzonitrile (103 mg, 1.0 mmol) were dissolved in dichloromethane (1 mL) and stirred at 0 °C. TfOH (28 μL, 312 μmol) was added dropwise and the solution was stirred for 1.5 h. The reaction was stopped by the addition of 5 mL saturated $NaHCO_3$-solution and diluted with 5 mL dichloromethane. The layers were separated, the aqueous layer was extracted with dichloromethane (2 × 10 mL), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent was

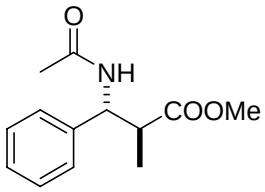
removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (64 mg, 86%) in a diastereomeric ratio of 94/6 (*anti*/*syn*).



R_f = 0.07 (pentane/ethyl acetate = 10/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.36 (d, ^3J = 7.1 Hz, 3 H), 3.11 (qd, ^3J = 7.1 Hz, ^3J = 4.7 Hz, 1 H), 3.60 (s, 3 H), 5.38 (dd, ^3J = 9.0 Hz, ^3J = 4.7 Hz, 1 H), 7.28-7.36 (m, 5 H), 7.41-7.55 (m, 3 H), 7.87-7.90 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 16.2 (q), 44.8 (d), 52.1 (d), 55.6 (q), 126.3 (d), 127.2 (d), 127.6 (d), 128.7 (d), 128.8 (d), 131.8 (d), 134.4 (s), 140.7 (s), 167.0 (s), 176.4 (s); MS (EI, 70 eV), *m/z* (%): 297 (4) [M^+], 211 (28), 192 (28), 166 (43), 105 (100), 77 (42); HRMS (EI) ($C_{18}H_{19}NO_3$): calc.: 297.1365, found: 297.1362.

The analytical data for *anti*-**3a** are in line with the data described in the literature.[2]

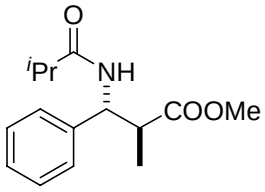
Methyl 3-acetamido-2-methyl-3-phenylpropanoate (*anti*-3b)



Methyl 3-hydroxy-2-methyl-3-phenylpropanoate[1] (**1**) (48 mg, 250 μmol), acetonitrile (41 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 1.5 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (52 mg, 88%) in a diastereomeric ratio of 93/7 (*anti*/*syn*). R_f = 0.18 (pentane/ethyl acetate = 1/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 7.1 Hz, 3 H), 2.02 (s, 3 H), 2.96 (qd, ^3J = 7.1 Hz, ^3J = 5.6 Hz, 1 H), 3.56 (s, 3 H), 5.16 (dd, ^3J = 9.2 Hz, ^3J = 5.6 Hz, 1 H), 7.00 (d, ^3J = 9.2 Hz, 1 H, NH), 7.20-7.23 (m, 3 H), 7.27-7.31 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 15.7 (q), 23.4 (q), 44.7 (d), 51.9 (d), 55.1 (q), 126.4 (d), 127.5 (d), 128.6 (d), 140.5 (s), 169.8 (s), 175.8 (s).

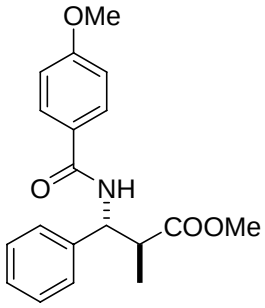
The analytical data for **3b** are in line with the data described in the literature.[3]

Methyl 3-(isobutyramido)-2-methyl-3-phenylpropanoate (*anti*-3c)



Methyl 3-hydroxy-2-methyl-3-phenylpropanoate[1] (**1**) (48 mg, 250 μmol), isobutyronitrile (69 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 3 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (55 mg, 84%) in a diastereomeric ratio of 98/2 (*anti*/*syn*). R_f = 0.22 (pentane/ethyl acetate = 1/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.18 (d, ^3J = 6.9 Hz, 3 H), 1.21 (d, ^3J = 6.9 Hz, 3 H), 1.27 (d, ^3J = 7.1 Hz, 3 H), 2.47 (hept., ^3J = 6.9 Hz, 1 H), 2.99 (qd, ^3J = 7.1 Hz, ^3J = 5.1 Hz, 1 H), 3.57 (s, 3 H), 5.17 (dd, ^3J = 9.1 Hz, ^3J = 5.1 Hz, 1 H), 6.96 (d, ^3J = 9.1 Hz, 1 H, NH), 7.21-7.33 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 15.9 (q), 19.6 (q), 19.9 (q), 36.0 (d), 44.8 (d), 51.9 (d), 54.7 (q), 126.3 (d), 127.5 (d), 128.7 (d), 140.9 (s), 176.1 (s), 176.6 (s); MS (EI, 70 eV), *m/z* (%): 263 (12) [M^+], 232 (5), 192 (82), 176 (24), 121 (19), 106 (100), 43 (28); HRMS (EI) ($C_{15}H_{21}NO_3$): calc.: 263.1521, found: 263.1522.

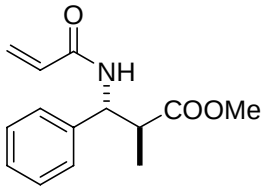
Methyl 3-(4-methoxybenzamido)-2-methyl-3-phenylpropanoate (*anti*-3d)



Methyl 3-hydroxy-2-methyl-3-phenylpropanoate[1] (**1**) (48 mg, 250 μmol), 4-methoxybenzonitrile (133 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 1.5 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (71 mg, 87%) in a diastereomeric ratio of 92/8 (*anti*/*syn*). R_f = 0.17 (pentane/ethyl acetate = 5/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.31 (d, ^3J = 7.1 Hz, 3 H), 3.06 (qd, ^3J = 7.1 Hz, ^3J = 4.7 Hz, 1 H), 3.56 (s, 3 H), 3.82 (s, 3 H), 5.33 (dd, ^3J = 8.9 Hz, ^3J = 4.7 Hz, 1 H), 6.91 (d, ^3J = 8.8 Hz, 2 H), 7.15-7.34 (m, 5 H), 7.81 (d, ^3J = 8.8 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 16.2 (q), 44.8 (d), 52.1 (d), 55.3 (q), 55.6 (q), 126.3 (d), 127.2 (d), 127.6 (d), 128.7 (d), 128.8 (d), 131.8 (d), 134.4 (s), 140.7 (s), 167.0 (s), 176.4 (s); MS (EI, 70 eV), *m/z* (%): 327 (14)

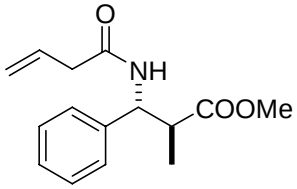
[M^+], 240 (27), 192 (70), 135 (100), 77 (18); HRMS (EI) ($C_{19}H_{21}NO_4$): calc.: 327.1471, found: 327.1471.

Methyl 3-(acrylamido)-2-methyl-3-phenylpropanoate (*anti*-3e)



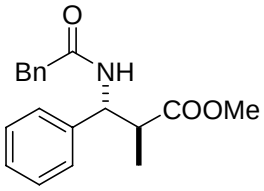
Methyl 3-hydroxy-2-methyl-3-phenylpropanoate[1] (**1**) (48 mg, 250 μmol), acrylonitrile (53 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 3.5 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (58 mg, 94%) in a diastereomeric ratio of 92/8 (*anti*/*syn*). R_f = 0.06 (pentane/ethyl acetate = 3/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.28 (d, ^3J = 7.1 Hz, 3 H), 3.03 (qd, ^3J = 7.1 Hz, ^3J = 5.1 Hz, 1 H), 3.57 (s, 3 H), 5.26 (dd, ^3J = 9.1 Hz, ^3J = 5.1 Hz, 1 H), 5.67 (dd, ^3J = 9.9 Hz, ^3J = 1.8 Hz, 1 H), 6.20 (dd, ^2J = 17.0 Hz, ^3J = 9.9 Hz, 1 H), 6.30 (dd, ^2J = 17.0 Hz, ^3J = 1.8 Hz, 1 H), 7.13 (d, ^3J = 9.1 Hz, 1 H, NH), 7.21-7.32 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 15.9 (q), 44.6 (d), 52.0 (d), 55.2 (q), 126.4 (d), 126.9 (t), 127.6 (d), 128.7 (d), 131.0 (d), 140.4 (s), 165.3 (s), 176.0 (s); MS (EI, 70 eV), *m/z* (%): 247 (10) [M^+], 192 (46), 160 (47), 106 (100), 77 (9), 55 (61); HRMS (EI) ($C_{14}H_{17}NO_3$): calc.: 247.1208, found: 247.1209.

Methyl 3-(but-3-enamido)-2-methyl-3-phenylpropanoate (*anti*-3f)



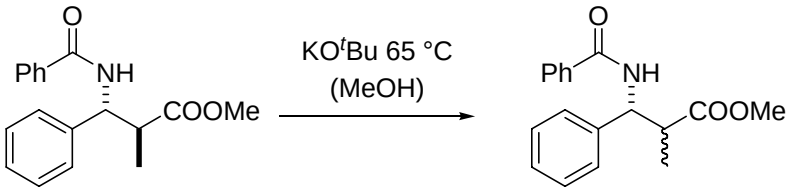
Methyl 3-hydroxy-2-methyl-3-phenylpropanoate[1] (**1**) (48 mg, 250 μmol), but-3-enenitrile (67 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 4.5 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (57 mg, 87%) in a diastereomeric ratio of 91/9 (*anti*/*syn*). R_f = 0.77 (pentane/ethyl acetate); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.25 (d, ^3J = 7.1 Hz, 3 H), 2.98 (qd, ^3J = 7.1 Hz, ^3J = 5.2 Hz, 1 H), 3.07 (dd, ^3J = 7.1 Hz, ^4J = 1.1 Hz, 1 H), 3.56 (s, 3 H), 5.17 (dd, ^3J = 9.2 Hz, ^3J = 5.2 Hz, 1 H), 5.24-5.31 (m, 2 H), 5.93-6.05 (m, 2 H), 7.10 (d, ^3J = 9.2 Hz, 1 H, NH), 7.19-7.33 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 15.9 (q), 41.9 (t), 44.8 (d), 51.9 (d), 55.1 (q), 120.1 (t), 126.3 (d), 127.6 (d), 128.7 (d), 131.3 (d), 140.5 (s), 170.3 (s), 175.9 (s); MS (EI, 70 eV), *m/z* (%): 261 (4) [M^+], 230 (2), 192 (21), 121 (20), 106 (36), 91 (100), 59 (33); HRMS (EI) ($C_{15}H_{19}NO_3$): calc.: 261.1365, found: 261.1360.

Methyl 3-(2-phenylacetamido)-2-methyl-3-phenylpropanoate (*anti*-3g)



Methyl 3-hydroxy-2-methyl-3-phenylpropanoate[1] (**1**) (48 mg, 250 μmol), 2-phenylacetonitrile (117 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 4 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (75 mg, 96%) in a diastereomeric ratio of 94/6 (*anti*/*syn*). R_f = 0.58 (pentane/ethyl acetate = 1/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.15 (d, ^3J = 7.1 Hz, 3 H), 2.89 (qd, ^3J = 7.1 Hz, ^3J = 5.4 Hz, 1 H), 3.44 (s, 3 H), 3.62 (d, ^4J = 3.8 Hz, 2 H), 5.13 (dd, ^3J = 9.1 Hz, ^3J = 5.4 Hz, 1 H), 6.86 (d, ^3J = 9.1 Hz, 1 H, NH), 7.05-7.10 (m, 2 H), 7.16-7.41 (m, 8 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 16.0 (q), 44.4 (t), 45.2 (d), 52.1 (d), 55.4 (q), 126.5 (d), 127.8 (d), 127.8 (d), 128.9 (d), 129.4 (d), 129.8 (d), 135.3 (d), 140.7 (s), 171.0 (s), 175.6 (s); MS (EI, 70 eV), *m/z* (%): 311 (4) [M^+], 225 (29), 192 (13), 106 (30), 91 (100); HRMS (EI) ($C_{19}H_{21}NO_3$): calc.: 311.1521, found: 311.1516.

Epimerisation of *anti*-3a:



Methyl 3-(benzamido)-2-methyl-3-phenylpropanoate (*anti*-**3a**) (69 mg, 232 mmol) and 56 mg K^{t}OBu (112 mmol) were dissolved in 2 mL methanol and heated to 65 °C. After stirring for 2.5 h the reaction was stopped by the addition of 5 mL water. The aqueous phase was extracted with ethyl acetate (20 mL) and dichloromethane (2 × 20 mL). The combined organic extracts were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (59 mg, 86%) in a diastereomeric ratio of 51/49 (*anti*/*syn*).

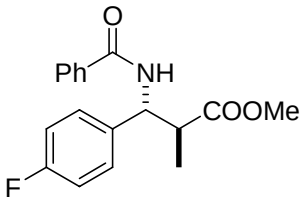
Spectroscopic data of *syn*-**3a**: ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.21 (d, ^3J = 7.1 Hz, 3 H), 3.06-3.14 (m, 1 H), 3.64 (s, 3 H), 5.44 (dd, ^3J = 8.7 Hz, ^3J = 6.0 Hz, 1 H), 7.22-7.35 (m, 5 H), 7.40-7.54

(m, 3 H), 7.80-7.82 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 13.7 (q), 44.7 (d), 52.0 (d), 55.7 (q), 127.1 (d), 127.1 (d), 127.8 (d), 128.7 (d), 128.7 (d), 131.7 (d), 134.5 (s), 139.3 (s), 166.6 (s), 174.6 (s).

Proof of the kinetic product formation for substrate 3a:

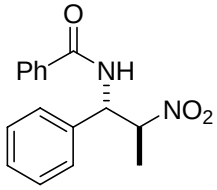
Methyl 3-(benzamido)-2-methyl-3-phenylpropanoate (*anti*-**3a**/*syn*-**3a** = 51/49) (48 mg, 250 μmol), benzonitrile (77 mg, 0.75 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 1.5 h. After aqueous work-up the ^{1}H NMR spectra of the crude product showed an unchanged diastereomeric ratio of 51/49 (*anti*/*syn*) for **3a**. The result rules out a thermodynamic product formation.

Methyl 3-(benzamido)-3-(4-fluorophenyl)-2-methylpropanoate



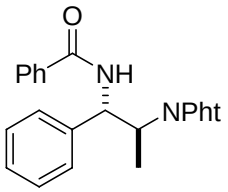
Methyl 3-(4-fluorophenyl)-3-hydroxy-2-methylpropanoate[4] (48 mg, 250 μmol), benzonitrile (103 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 1 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 3/1) to give a colourless solid (63 mg, 80%) in a diastereomeric ratio of 93/7 (*anti*/*syn*). R_f = 0.07 (pentane/ethyl acetate = 10/1); m.p. = 131 °C; ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.35 (d, ^3J = 7.1 Hz, 3 H), 3.06 (qd, ^3J = 7.1 Hz, ^3J = 4.7 Hz, 1 H), 3.60 (s, 3 H), 5.34 (dd, ^3J = 8.8 Hz, ^3J = 4.7 Hz, 1 H), 6.96-7.02 (m, 2 H), 7.24-7.32 (m, 2 H), 7.38-7.54 (m, 3 H), 7.85-7.89 (m, 2 H), 7.94 (d, ^3J = 8.8 Hz, 1 H, NH); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 16.2 (q), 44.8 (d), 52.1 (d), 55.0 (q), 115.6 (dd, $^2J_{CF}$ = 21.5 Hz), 127.1 (d), 127.9 (dd, $^3J_{CF}$ = 8.2 Hz), 128.8 (d), 131.8 (d), 134.2 (s), 136.6 (d, $^4J_{CF}$ = 3.2 Hz), 162.1 (d, $^1J_{CF}$ = 248.8 Hz), 167.0 (s), 176.3 (s); MS (EI, 70 eV), *m/z* (%): 315 (5) [M^+], 229 (44), 210 (30), 105 (100), 77 (34), 51 (7); HRMS (EI) ($C_{18}H_{18}FNO_3$): calc.: 315.1271, found: 315.1268.

***N*-(2-Nitro-1-phenylpropyl)benzamide (*anti*-9)**



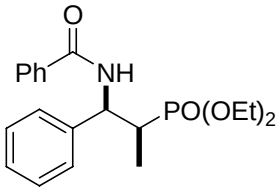
2-Nitro-1-phenylpropan-1-ol[5] (**4**) (45 mg, 250 μmol), benzonitrile (103 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 4.5 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 5/1) to give a colourless solid (60 mg, 85%) in a diastereomeric ratio of 90/10 (*anti*/*syn*). R_f = 0.22 (pentane/ethyl acetate = 5/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.65 (d, ^3J = 6.8 Hz, 3 H), 5.14 (virt. q, $^3J \tilde{=}$ 6.5 Hz, 1 H), 5.68 (dd, ^3J = 9.2 Hz, ^3J = 6.0 Hz, 1 H), 7.28-7.59 (m, 8 H), 7.82-7.84 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 17.5 (q), 55.7 (d), 86.8 (d), 126.5 (d), 127.2 (d), 128.7 (d), 128.9 (d), 129.3 (d), 132.2 (d), 133.7 (s), 137.1 (s), 167.2 (s); MS (EI, 70 eV), *m/z* (%): 238 (14), 224 (39), 147 (36), 105 (100), 77 (68), 51 (14); HRMS (EI) ($C_{16}H_{16}NO$): calc.: 238.1232, found: 238.1228.

_N_-(2-(1,3-Dioxoisoindolin-2-yl)-1-phenylpropyl)benzamide (*anti*-10)



2-(1-Hydroxy-1-phenylpropan-2-yl)isoindoline-1,3-dione[6] (**5**) (70 mg, 250 μmol), benzonitrile (103 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 3 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 3/1 → 0/1) to give a colourless solid (75 mg, 78%) in a diastereomeric ratio of 75/25 (*anti*/*syn*). R_f = 0.27 (pentane/ethyl acetate = 3/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.57 (d, ^3J = 7.1 Hz, 3 H), 5.01 (qd, ^3J = 7.1 Hz, ^3J = 6.1 Hz, 1 H), 5.75 (dd, ^3J = 8.8 Hz, ^3J = 6.1 Hz, 1 H), 7.13-7.29 (m, 5 H), 7.45-7.56 (m, 3 H), 7.65-7.67 (m, 2 H), 7.75-7.77 (m, 2 H), 7.98-8.01 (m, 2 H), 8.56 (d, ^3J = 8.8 Hz, 1 H, NH); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 15.9 (q), 51.2 (d), 56.8 (d), 123.6 (d), 126.0 (d), 127.2 (d), 127.3 (d), 128.7 (d), 128.8 (d), 131.7 (d), 134.2 (s), 134.3 (s), 134.4 (d), 139.3 (s), 166.9 (s), 168.4 (s); MS (EI, 70 eV), *m/z* (%): 384 (8) [M^+], 309 (5), 210 (78), 105 (100), 77 (26), 44 (8); HRMS (EI) ($C_{24}H_{20}N_2O_3$): calc.: 384.1474, found: 384.1469.

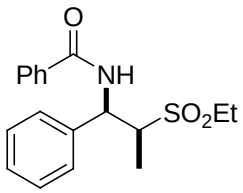
Diethyl 1-(benzamido)-1-phenylpropan-2-ylphosphonate (*syn*-11)



Diethyl 1-hydroxy-1-phenylpropan-2-ylphosphonate (**6**) (68 mg, 250 μmol), benzonitrile (103 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 5 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 2/1) to give a colourless

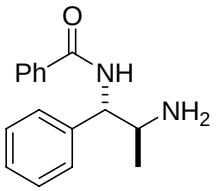
solid (84 mg, 90%) in a diastereomeric ratio of 8/92 (*anti*/*syn*). R_f = 0.22 (pentane/ethyl acetate = 1/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.09 (t, ^3J = 7.1 Hz, 3 H), 1.16 (dd, $^3J_{HP}$ = 17.2 Hz, $^3J_{HH}$ = 7.4 Hz, 3 H), 1.29 (t, ^3J = 7.1 Hz, 3 H), 2.44 (dqd, $^3J_{HP}$ = 19.9 Hz, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 4.5 Hz, 1 H), 3.81-4.00 (m, 2 H), 4.03-4.14 (m, 2 H), 5.42 (ddd, $^3J_{HP}$ = 27.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.5 Hz, 1 H), 7.20-7.50 (m, 8 H), 7.91-7.94 (m, 2 H), 8.45 (d, ^3J = 7.8 Hz, 1 H, NH); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 11.5 (dq, $^2J_{CP}$ = 4.6 Hz), 16.1 (dq, $^3J_{CP}$ = 6.3 Hz), 16.5 (dq, $^3J_{CP}$ = 5.7 Hz), 36.8 (dd, $^1J_{CP}$ = 138.3 Hz), 54.9 (dd, $^2J_{CP}$ = 4.3 Hz), 61.7 (dt, $^2J_{CP}$ = 7.3 Hz), 62.2 (dt, $^2J_{CP}$ = 6.6 Hz), 127.2 (d), 127.4 (d), 127.5 (d), 128.2 (d), 128.6 (d), 131.5 (d), 134.3 (s), 139.0 (d, $^3J_{CP}$ = 7.5 Hz), 166.1 (s); MS (EI, 70 eV), *m/z* (%): 375 (1) [M^+], 271 (1), 166 (100), 139 (36), 111 (27), 91 (6).

_N_-(2-(Ethylsulfonyl)-1-phenylpropyl)benzamide (*syn*-12)



2-(Ethylsulfonyl)-1-phenylpropan-1-ol (**7**) (57 mg, 250 μmol), benzonitrile (103 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 3.5 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 3/1 → 1/1) to give a colourless solid (76 mg, 92%) in a diastereomeric ratio of 4/96 (*anti*/*syn*). R_f = 0.05 (pentane/ethyl acetate = 3/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 1.36 (t, ^3J = 7.4 Hz, 3 H), 1.45 (d, ^3J = 7.2 Hz, 3 H), 2.64-2.96 (m, 2 H), 5.58 (qd, ^3J = 7.2 Hz, ^3J = 3.9 Hz, 1 H), 5.70 (dd, ^3J = 7.7 Hz, ^3J = 3.9 Hz, 1 H), 7.32-7.55 (m, 8 H), 7.81 (d, ^3J = 7.7 Hz, 1 H, NH), 7.86-7.87 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 5.8 (q), 10.4 (q), 45.6 (t), 53.6 (d), 61.0 (d), 127.2 (d), 127.2 (d), 128.3 (d), 128.8 (d), 128.9 (d), 131.9 (d), 134.0 (s), 137.3 (s), 166.8 (s); MS (EI, 70 eV), *m/z* (%): 309 (4), 238 (41), 210 (9), 105 (100), 77 (35); HRMS (EI) ($C_{16}H_{16}NO$): calc.: 238.1232, found: 238.1232.

Preparation of _N_-(2-amino-1-phenylpropyl)benzamide (*anti*-14) from _N_-(2-nitro-1-phenyl-propyl)benzamide (*anti*-9):



N-(2-Nitro-1-phenylpropyl)benzamide (*anti*-**9**) (284 mg, 1.0 mmol) and 431 mg zinc (6.6 mmol) were suspended in 4 mL ethanol at ambient temperature. A mixture of water and concentrated sulphuric acid (1.6 mL/0.4 mL) was added dropwise. After stirring for 19 h the reaction mixture was concentrated under reduced pressure to remove most of the ethanol and the resulting aqueous phase was washed with diethyl ether (10 mL) to remove non-basic impurities. The aqueous layer was made strongly basic with 50% NaOH and extracted with dichloromethane (2 × 20 mL) and ethyl acetate (20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to yield 246 mg (97%) of a colourless solid in a diastereomeric ratio of 90/10 (*anti*/*syn*).

Preparation of *N*-(2-amino-1-phenylpropyl)benzamide (*anti*-14) from *N*-(2-(1,3-dioxoiso-indolin-2-yl)-1-phenylpropyl)benzamide (*anti*-10):

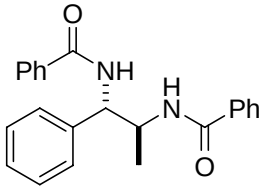
N-(2-(1,3-Dioxoisoindolin-2-yl)-1-phenylpropyl)benzamide (*anti*-**10**) (84 mg, 220 μmol) and 33 mg hydrazine monohydrate (660 μmol) were dissolved in 2 mL ethanol and were refluxed for 2.5 h. The reaction mixture was concentrated under reduced pressure to remove most of the ethanol. The oily residue was diluted with dichloromethane (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined extracts were washed with saturated $NaHCO_3$-solution, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. After purification by flash chromatography (dichloromethane/methanol/Et_3N = 100/0/1 → 100/10/1) 43 mg (76%, d.r. = 75/25) of *anti*-**14** were obtained as a colourless solid.

R_f = 0.10 (ethyl acetate); *anti*-diastereoisomer: ^{1}H-NMR (500 MHz, DMSO): δ = 0.85 (d, ^3J = 6.5 Hz, 3 H), 3.22-3.27 (m, 1 H), 5.02 (*virt* t, ^3J = 8.1 Hz, 1 H), 5.62 (s, 2 H, NH_2), 7.22-7.55 (m, 8 H), 7.84-7.88 (m, 2 H), 8.68 (d, ^3J = 8.1 Hz, 1 H, NH); ^{13}C-NMR (90.6 MHz, DMSO): δ = 15.5 (q), 55.9 (d), 59.4 (d), 126.6 (d), 127.3 (d), 127.5 (d), 127.9 (d), 128.1 (d), 131.1 (d), 134.7 (s), 141.9 (s), 166.0 (s);

syn-diastereoisomer: ^{1}H-NMR (500 MHz, DMSO): δ = 0.90 (d, ^3J = 6.5 Hz, 3 H), 3.17-3.22 (m, 1 H), 4.74 (*virt* t, ^3J = 8.0 Hz, 1 H), 5.62 (s, 2 H, NH_2), 7.22-7.55 (m, 8 H), 7.89-7.91 (m, 2 H), 8.62 (d, ^3J = 8.0 Hz, 1 H, NH);

MS (EI, 70 eV), *m/z* (%): 252 (1), 211 (100), 210 (31), 193 (16), 132 (15), 118 (35), 105 (94), 77 (42), 44 (32); HRMS (EI) ($C_{14}H_{13}NO$): calc.: 211.0997, found: 211.0995.

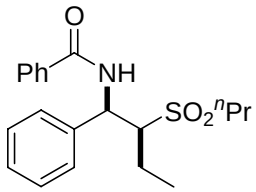
Preparation of *anti*-*N,N'*-dibenzoyl 1-methyl-2-phenylethylendiamine



N-(2-amino-1-phenylpropyl)benzamide (*anti*-**14**) (50 g, 197 μmol), benzoyl chloride (200 mg, 1.42 mmol), were stirred in 2 mL pyridine for 15 h. The reaction was stopped by the addition of 10 mL saturated NH_4Cl-solution. The reaction was extracted with dichloromethane (2 × 20 mL) and ethyl acetate (20 mL). The combined organic extracts were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1 → 0/1) to give a colourless solid.

The analytical data were in line with the data described in literature and therefore prove the *anti*-configuration of *anti*-**14**.[7]

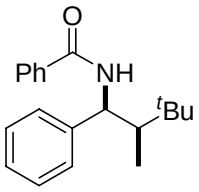
***N*-(1-phenyl-2-(propylsulfonyl)butyl)benzamide (*anti*-16)**



1-Phenyl-2-(propylsulfonyl)butan-1-ol (**15**) (64 mg, 250 μmol), benzonitrile (103 mg, 1.0 mmol) and TfOH (28 μL, 312 μmol) were stirred in 1 mL dichloromethane for 1 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 3/1) to give a colourless solid (78 mg, 87%) in a diastereomeric ratio of 12/88 (*anti*/*syn*). R_f = 0.20 (pentane/ethyl acetate = 3/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.4 Hz, 3 H), 1.23 (t, ^3J = 7.4 Hz, 3 H), 1.72-1.83 (m, 3 H), 1.99-2.11 (m, 1 H), 2.57-2.65 (m, 1 H), 3.30-3.35 (m, 1 H), 3.45-3.54 (m, 1 H), 5.80 (dd, ^3J = 8.7 Hz, ^3J = 3.5 Hz, 1 H), 7.29-7.54 (m, 8 H), 7.86-7.89 (m, 2 H), 8.26 (d, ^3J = 8.7 Hz, 1 H, NH); ^{13}C-NMR (90.6 MHz, $CDCl_3$) δ = 12.5 (q), 13.2 (q), 14.6 (t), 20.1 (t), 51.8 (d), 53.0 (t), 70.0 (d), 127.2 (d), 127.8 (d), 128.5 (d), 128.8 (d), 128.8 (d), 132.0 (d), 133.9 (s), 136.5 (s), 166.2 (s); MS (EI, 70 eV), *m/z* (%): 252 (82), 210 (36), 105 (100), 84 (27), 77 (41), 57 (69); HRMS (EI) ($C_{14}H_{13}NO$): calc.: 252.1388, found: 252.1386.

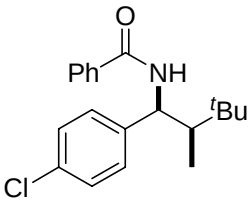
Preparation of *N*-(2,3,3-trimethyl-1-phenylbutyl)benzamide (*syn*-13) – Representative Procedure for the Ritter reactions catalysed by dinitrobenzenesulfonic acid (DNBSA):

In a typical experiment 2,3,3-trimethyl-1-phenylbutan-1-ol[8] (**8**) (48 mg, 250 μmol) was dissolved in benzonitrile (2 mL) and DNBSA (15 mg, 51 μmol) was added at 65 °C. After 2 h the reaction was stopped by the addition of 5 mL saturated $NaHCO_3$-solution and diluted with dichloromethane. The layers were separated, the aqueous layer was extracted with dichloromethane (2 × 20 mL), the combined organic extracts were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1) to give a colourless solid (51 mg, 69%) in a diastereomeric ratio of 13/87 (*anti*/*syn*).



R_f = 0.31 (pentane/ethyl acetate = 10/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.94 (d, ^3J = 7.2 Hz, 3 H), 1.07 (s, 9 H), 1.82 (qd, ^3J = 7.2 Hz, ^3J = 1.5 Hz, 1 H), 5.69 (dd, ^3J = 9.1 Hz, ^3J = 1.5 Hz, 1 H), 6.58 (d, ^3J = 9.1 Hz, 1 H, NH), 7.19-7.34 (m, 5 H), 7.44-7.52 (m, 3 H), 7.80-7.82 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 8.3 (q), 28.3 (q), 33.7 (s), 48.8 (d), 52.7 (d), 126.0 (d), 126.7 (d), 126.9 (d), 128.5 (d), 128.8 (d), 131.6 (d), 135.0 (s), 143.7 (s), 166.4 (s); MS (EI, 70 eV), *m/z* (%): 295 (1) [M^+], 238 (4), 210 (56), 166 (78), 139 (29), 105 (100), 77 (26); HRMS (EI) ($C_{20}H_{25}NO$): calc.: 295.1936, found: 295.1931.

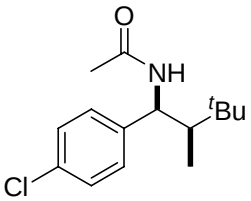
***N*-(1-(4-chlorophenyl)-2,3,3-trimethylbutyl)benzamide (*syn*-18a)**



1-(4-Chlorophenyl)-2,3,3-trimethylbutan-1-ol[9] (**17**) (57 mg, 250 μmol) was dissolved in benzonitrile (2 mL) and DNBSA (15 mg, 51 μmol) was added at 65 °C and stirred for 2 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1) to give a colourless solid (69 mg, 84%) in a diastereomeric ratio of 8/92 (*anti*/*syn*). R_f = 0.28 (pentane/ethyl acetate = 10/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.91 (d, ^3J = 7.2 Hz, 3 H), 1.05 (s, 9 H), 1.75 (qd, ^3J = 7.2 Hz, ^3J = 1.6 Hz, 1 H), 5.60 (d, ^3J = 8.6 Hz, 1 H), 6.53 (d, ^3J = 8.6 Hz, 1 H, NH), 7.18 (d, ^3J = 8.5 Hz, 2 H), 7.27 (d, ^3J = 8.5 Hz, 2 H), 7.43-7.54 (m, 3 H), 7.76-7.80 (m, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 8.2 (q), 28.3 (q), 33.7 (s), 48.8 (d), 52.5 (d), 126.9 (d), 127.4 (d), 128.6 (d),

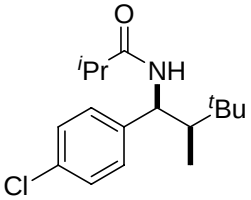
128.9 (d), 131.8 (d), 132.4 (s), 134.7 (s), 142.4 (s), 166.4 (s); MS (EI, 70 eV), *m/z* (%): 329 (2) [M^+], 272 (5), 244 (28), 105 (100), 77 (21); HRMS (EI) ($C_{20}H_{24}ClNO$): calc.: 329.1546, found: 329.1541.

_N_-(1-(4-chlorophenyl)-2,3,3-trimethylbutyl)acetamide (*syn*-18b)



1-(4-Chlorophenyl)-2,3,3-trimethylbutan-1-ol[9] (**17**) (57 mg, 250 μmol) was dissolved in acetonitrile (2 mL) and DNBSA (15 mg, 51 μmol) was added at 65 °C and stirred for 2 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1) to give a colourless solid (52 mg, 78%) in a diastereomeric ratio of 9/91 (*anti*/*syn*). R_f = 0.16 (pentane/ethyl acetate = 10/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.78 (d, ^3J = 7.2 Hz, 3 H), 0.98 (s, 9 H), 1.61 (qd, ^3J = 7.2 Hz, ^3J = 1.9 Hz, 1 H), 2.03 (s, 3 H), 5.40 (d, ^3J = 8.8 Hz, 1 H), 5.97 (d, ^3J = 8.8 Hz, 1 H, NH), 7.11 (d, ^3J = 8.5 Hz, 2 H), 7.25 (d, ^3J = 8.5 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 8.2 (q), 23.6 (q), 28.2 (q), 33.7 (s), 48.4 (d), 52.1 (d), 127.4 (d), 128.5 (d), 132.3 (s), 142.6 (s), 169.2 (s); MS (EI, 70 eV), *m/z* (%): 267 (5) [M^+], 210 (7), 182 (81), 140 (100), 43 (34); HRMS (EI) ($C_{15}H_{22}ClNO$): calc.: 267.1390, found: 267.1387.

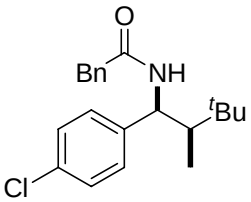
_N_-(1-(4-chlorophenyl)-2,3,3-trimethylbutyl)isobutyramide (*syn*-18c)



1-(4-Chlorophenyl)-2,3,3-trimethylbutan-1-ol[9] (**17**) (28 mg, 125 μmol) was dissolved in *iso*-butyronitrile (1 mL) and DNBSA (7 mg, 25 μmol) was added at 65 °C and stirred for 26 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1) to give a colourless solid (35 mg, 95%) in a diastereomeric ratio of 12/88 (*anti*/*syn*). R_f = 0.19 (pentane/ethyl acetate = 10/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.81 (d, ^3J = 7.2 Hz, 3 H), 0.99 (s, 9 H), 1.18 (d, ^3J = 6.9 Hz, 3 H), 1.19 (d, ^3J = 6.9 Hz, 3 H), 1.64 (qd, ^3J = 7.2 Hz, ^3J = 1.8 Hz, 1 H), 2.43 (hept., ^3J = 6.9 Hz, 1 H), 5.39 (d, ^3J = 8.5 Hz, 1 H), 5.82 (d, ^3J = 8.5 Hz, 1 H, NH), 7.10 (d, ^3J = 8.3 Hz, 2 H), 7.27 (d, ^3J = 8.3 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 8.2 (q), 19.6 (q), 19.7 (q), 28.2 (q), 33.7 (s), 36.1 (d), 48.6 (d), 51.6 (d), 127.3 (d), 128.6 (d), 132.3 (s), 142.8 (s), 175.6 (s); MS (EI, 70

eV), *m/z* (%): 295 (4) [M^+], 238 (6), 210 (52), 168 (19), 140 (100), 71 (23), 57 (14), 43 (50); HRMS (EI) ($C_{17}H_{26}ClNO$): calc.: 295.1703, found: 295.1701.

_N_-(1-(4-chlorophenyl)-2,3,3-trimethylbutyl)-2-phenylacetamide (*syn*-18d)



1-(4-Chlorophenyl)-2,3,3-trimethylbutan-1-ol[9] (**17**) (28 mg, 125 μmol) was dissolved in phenylacetonitrile (1 mL) and DNBSA (7 mg, 25 μmol) was added at 65 °C and stirred for 23 h. The crude product was purified by flash chromatography (pentane/ethyl acetate = 10/1) to give a colourless solid (37 mg, 86%) in a diastereomeric ratio of 12/88 (*anti*/*syn*). R_f = 0.22 (pentane/ethyl acetate = 10/1); ^{1}H-NMR (360 MHz, $CDCl_3$): δ = 0.45 (d, ^3J = 7.2 Hz, 3 H), 0.89 (s, 9 H), 1.50 (qd, ^3J = 7.2 Hz, ^3J = 1.7 Hz, 1 H), 3.63 (d, ^4J = 3.6 Hz, 2 H), 5.30 (d, ^3J = 8.6 Hz, 1 H), 5.72 (d, ^3J = 8.6 Hz, 1 H, NH), 6.92-6.95 (m, 2 H), 7.23 (d, ^3J = 8.5 Hz, 2 H), 7.30-7.45 (m, 5 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 7.4 (q), 28.1 (q), 33.5 (s), 44.3 (t), 48.8 (d), 51.9 (d), 127.2 (d), 127.9 (d), 128.5 (d), 129.4 (d), 129.6 (d), 132.3 (s), 134.9 (s), 142.4 (s), 169.7 (s); MS (EI, 70 eV), *m/z* (%): 343 (4) [M^+], 286 (7), 258 (67), 176 (33), 140 (100), 91 (53), 58 (61); HRMS (EI) ($C_{21}H_{26}ClNO$): calc.: 343.1703, found: 343.1698.

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