Supporting Information

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Synthetic Modifiers for Platinum in the Enantioselective Hydrogenation of Ketopantolactone: a Test for the Mechanistic Models of Ketone Hydrogenation

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Synthesis of new modifiers

Melting points were determined using a Büchi B-540 melting point apparatus and are not corrected. Optical rotation was measured on a Perkin-Elmer polarimeter 241. NMR-Spectra were recorded on a Bruker Avance 500 spectrometer with TMS as internal reference. Spectra were measured at 300 K. Signal assignment was sometimes assisted through correlation spectroscopy (COSY). IR spectra were recorded on a Bruker vector 33 FT-IR spectrometer (KBr, thin film). UV spectra were measured on a Varian Cary 400 UV-Vis spectrometer in MeOH.

Method A. (*R*)-1-(1-naphthyl)ethylamine **1** (0.64 ml, 4 mmol) and typically 5 mmol of the corresponding ketone (4 mmol in case of an aldehyde) were dissolved in titanium(IV)isopropoxide (1.5 ml) and the viscous solution was stirred at r.t. in a flask equipped with a $CaCl_2$-tube. After 4 h $NaBH_3CN$ (170 mg, 2.7 mmol) and EtOH (4 ml) were added. The reaction was stirred over-night. Then again $NaBH_3CN$ (170 mg, 2.7 mmol) and a few drops of HOAc were added. The following day the reaction was quenched with water (2 ml), the resulting precipitate filtered over celite and washed with EtOH. The filtrate was concentrated in vacuum, dissolved in ethyl acetate and filtered over celite again. The filtrate was concentrated and the crude mixture was purified by flash chromatography (ethyl acetate : hexane = 1:15 plus addition of triethylamine), where – in the case of diastereoisomers – the two could be separated.

7: (+)-(*1R*)-*N*-dodecyl-1-(1-naphthyl)ethylamine: yield: 238 mg waxy gel (17.5 %), which solidifies in the fridge; $[\alpha]_D^{20}$ = +74.3 (c = 1, $CHCl_3$); IR (cm^{-1}) 2925, 2854, 1510, 1466, 1375, 1328, 1135; UV (MeOH, nm) 204, 224, 281 (broad); HRMS found $[M]^+$ = 339.2943 (calculated 339.2926); MS (EI) m/z (%): 322.3 (3), 209.2 (6), 197.1 (22), 156.1 (15), 155.1 (100); ^{1}H-NMR (δ, $CDCl_3$) 8.34 (d, 1H (H8"), $J_{7",8"}$ = 8.2Hz), 7.87 (dd, 1H, H(6"), J = 7.9Hz, J = 1.7 Hz), 7.77 (d, 1H, H(4"), $J_{3",4"}$ = 8.2Hz), 7.66 (d, 1H, H(2"), $J_{2",3"}$ = 7.1Hz), 7.54-7.47 (m, 2H, H(5"), H(7")), 7.45 (dd, 1H, H(3"), $J_{2",3"} \sim J_{3",4"} \sim$

7.3Hz), 4.93 (q, 1H, H(1), $J_{1,2}$ = 6.5Hz), 3.26 (br.t, 1H, NH, $J_{NH,1'}$ ~ 6.9Hz), 1.75 (q, 1H, H(1'), $J_{1',2'}$ ~ $J_{NH,1'}$ ~ 7.2Hz), 1.74 (q, 1H, H(1'), $J_{1',2'}$ ~ $J_{NH,1'}$ ~ 7.3Hz), 1.54 (d, 3H, H(2), $J_{1,2}$ = 6.6Hz), 1.49-1.44 (br.m, 2H, H(2')), 1.31-1.24 (m, 18H, H(3')-H(11')), 0.88 (t, 3H, H(12'), $J_{11',12'}$ = 7.0Hz); ^{13}C-NMR (δ, $CDCl_3$) 138.78 (C(1")*), 134.14 (C(4a")*), 131.35 (C(8a")*), 128.94 (CH), 127.90 (CH), 126.00 (CH), 125.64 (CH), 125.60 (CH), 123.15 (CH), 120.96 (CH), 48.42 (C(1)), 33.97 (C(1')), 31.91 (CH_2), 29.59 (3x CH_2**), 29.48 (CH_2), 29.33 (2x CH_2**), 29.03 (CH_2), 25.57 (CH_2), 24.24 (CH_2), 22.69 (C(2)), 14.12 (C(12')); * interchangeable; ** signals overlap

9: (+)-(*1R*)-*N*-(2-furanylmethyl)-1-(1-naphthyl)ethylamine: yield: 839 mg pale yellow oil (83.5 %); $[\alpha]_D^{20}$ = +43.2 (c = 1, $CHCl_3$); IR (cm^{-1}) 3333, 3051, 2967, 2926, 1596, 1508, 1456, 1394, 1370, 1327, 1259, 1171, 1147, 1114, 1074, 1057, 1011; UV (MeOH, nm) 223, 282 (broad); HRMS: found $[M]^+$ = 251.1298 (calcd. 251.1310); MS (EI) m/z (%): 251.1 (5) $[M]^+$, 236.1 (11) $[M–CH_3]^+$, 204.1 (7), 178.9 (4), 168.0 (5), 153.1 (100), 141.0 (11), 127.1 (39) [naphthyl]$^+$, 115.0 (10), 96.0 (23), 81.0 (65); ^{1}H-NMR (δ, $CDCl_3$) 8.11 (dd, 1H, aromat., J = 7.3Hz, J = 1.9Hz), 7.86 (dd, 1H, aromat., J = 7.1Hz, J = 2.4Hz), 7.75 (d, 1H, aromat., J = 8.2Hz), 7.72 (d, 1H, aromat., J = 7.0Hz), 7.50-7.45 (m, 3H, aromat.), 7.36 (dd, 1H, H(5'), $J_{4',5'}$ = 1.7Hz, $J_{3',5'}$ = 0.6Hz), 6.29 (dd, 1H, H(4'), $J_{3',4'}$ = 3.1Hz, $J_{4',5'}$ = 1.8Hz), 6.08 (dd, 1H, H(3'), $J_{3',4'}$ = 3.1Hz, $J_{3',5'}$ = 0.5Hz), 4.66 (q, 1H, H(1), $J_{1,2}$ = 6.6Hz), 3.77 (d, 1H, CH_2, J_{gem} = 14.5Hz, A of an AB-system), 3.68 (d, 1H, CH_2, J_{gem} = 14.5Hz, B of an AB-system), 1.81 (br. s, 1H, NH), 1.49 (d, 3H, H(2), $J_{1,2}$ = 6.6Hz); ^{13}C-NMR: (δ, $CDCl_3$) 154.12 (C(2')), 141.78 (C(5')), 140.63 (C(1")*), 134.03 (C(4a")*), 131.37 (C(8a")*), 128.95 (CH, naphthyl), 127.30 (CH, naphthyl), 125.76 (CH, naphthyl), 125.32 (CH, naphthyl), 122.96 (CH, naphthyl), 122.93 (CH, naphthyl), 110.11 (C(3')**), 106.90 (C(4')**), 52.32 (C(1)), 44.13 (CH_2), 23.45 (C(2)), two aromatic ^{13}C signals appear at the same shift; *,** interchangeable.

10: (+)-(*1'R,2R*)-*N*-[1'-(1-naphthyl)ethyl]-2-amino-1-methoxypropane: yield: 757 mg as pale oil (78 %, sum of diastereoisomers); the (*2R*) and the (*2S*) diastereoisomers form in the ratio of 65 : 35; the

(*2R*) diastereoisomer comes first off the column; $[\alpha]_D^{20}$ = +39.0 (c = 1, $CHCl_3$); IR (cm^{-1}) 3058, 2969, 2925, 2872, 2827, 1596, 1510, 1451, 1369, 1323, 1229, 1161, 1108, 1020, 1000; UV (MeOH, nm) 223, 282 (broad); HRMS found $[M–CH_3]^+$ = 228.1383 (calcd. 228.1388); MS (EI) m/z (%): 243.2 (0.21) $[M]^+$, 228.2 (1) $[M–CH_3]^+$, 198.2 (10), 155.1 (100), 128.0 (20) [naphthyl]$^+$, 115.0 (4), 90.2 (4), 76.0 (6); ^{1}H-NMR (δ, $CDCl_3$) 8.22 (d, 1H, aromat., J = 8.6Hz), 7.85 (dd, 1H, aromat., J = 8.1Hz, J = 1.5Hz), 7.72 (d, 1H, aromat., J = 8.2Hz), 7.69 (d, 1H, aromat., J = 7.1Hz), 7.52-7.44 (m, 3H, aromat.), 4.77 (q, 1H, H(1'), $J_{1',2'}$ = 6.6Hz), 3.35 (dd, 1H, H(1), J_{gem} = 9.3Hz, $J_{1,2}$ = 4.5Hz, A of an ABX-system), 3.34 (s, 3H, OCH_3), 3.25 (dd, 1H, H(1), J_{gem} = 9.3Hz, $J_{1,2}$ = 5.8Hz, B of an ABX-system), 2.94-2.87 (m, 1H, H(2), $J_{1,2}$ = 4.5Hz, X of an ABX-system), 1.71 (br.s, 1H, NH), 1.47 (d, 3H, H(2'), $J_{1',2'}$ = 6.6Hz), 0.99 (d, 3H, H(3), $J_{2,3}$ = 6.5Hz); ^{13}C-NMR (δ, $CDCl_3$) 142.17 (C(1")*), 133.99 (C(4a")*), 131.20 (C(8a")*), 128.93 (CH), 127.01 (CH), 125.67 (CH), 125.65 (CH), 125.22 (CH), 123.00 (CH), 76.84 (OCH_3), 59.00 (C(1)), 50.95 (C(1')), 50.66 (C(2)), 24.01 (C(2')), 18.62 (C(3)), two aromatic ^{13}C signals appear at the same shift; * interchangeable.

18 and **19:** yield: 319 mg as colorless oil (28.1 %, sum of diastereoisomers), the (*2R*) and the (*2S*) diastereoisomers (**18** and **19**, resp.) form in the ratio of 70 : 30 as identified by NOE-measurements;[56] the (*2R*)-diastereoisomer **18** comes first off the column;

18: (–)-(*1'R,2R*)-*N*-[1'-(1-naphthyl)ethyl]-2-amino-3,3-dimethyl-γ-butyrolactone: $[\alpha]_D^{20}$ = –36.6 (c = 1, $CHCl_3$); IR (cm^{-1}) 3335, 3058, 2965, 2929, 1770, 1597, 1511, 1463, 1395, 1365, 1287, 1258, 1202, 1168, 1142, 1010; UV (MeOH, nm) 223, 272 (broad), 282 (broad); elemental analysis calcd. (%) for the TFA salt of **18** $C_{20}H_{22}F_3NO_4$ (397.39): C 60.45, H 5.58, N 3.52, O 16.10, F 14.34; found: C 60.58, H 5.61, N 3.52, O 16.07, F 14.22; HRMS found $[M–CH_3]^+$ = 268.1334 (calculated 268.1338); MS (EI) m/z (%): 283.2 (1) $[M]^+$, 268.2 (11) $[M–CH_3]^+$, 170.1 (20), 153.1 (100) 128.0 (15) [naphthyl]$^+$, 76.0 (26); ^{1}H-NMR (δ, $CDCl_3$) 8.14 (d, 1H, aromat., J = 8.4Hz), 7.87 (dd, 1H, aromat., J = 8.1Hz, J = 1.2Hz), 7.76 (d, 1H, aromat., J = 8.0Hz), 7.64 (d, 1H, aromat., J = 6.8Hz), 7.53-7.44 (m, 3H, aromat.),

4.88 (q, 1H, H(1'), $J_{1',2'}$ = 6.6Hz), 3.87 (d, 1H, H(4), J_{gem} = 8.8Hz, A of an AB-system), 3.68 (d, 1H, H(4), J_{gem} = 8.8Hz, B of an AB-system), 3.21 (br.s, 1H, H(2)), 1.50 (d, 3H, H(2'), $J_{1',2'}$ = 6.7Hz), 1.09 (s, 3H, methyl), 1.02 (s, 3H, methyl); ^{13}C-NMR (δ, $CDCl_3$) 178.16 (C(1)), 140.21 (C(1")*), 134.18 (C(4a")*), 131.66 (C(8a")*), 129.18 (CH), 127.71 (CH), 126.24 (CH), 125.92 (CH), 125.66 (CH), 122.84 (CH), 122.58 (CH), 76.59 (C(4)), 63.53 (C(2)), 52.02 (C(1')), 41.15 (C(3)), 24.08 (methyl**), 24.03 (methyl**), 20.24 (C(2')**); *,** interchangeable

19: (+)-(*1'R,2S*)-*N*-[1'-(1-naphthyl)ethyl]-2-amino-3,3-dimethyl-γ-butyrolactone: $[\alpha]_D^{20}$ = +127.8 (c = 1, $CHCl_3$); IR (cm^{-1}) 3046, 2962, 2927, 2892, 1764, 1595, 1511, 1465, 1394, 1363, 1287, 1260, 1202, 1127, 1011; UV (MeOH, nm) 223, 281 (broad); ^{1}H-NMR (δ, $CDCl_3$) 8.33 (d, 1H, aromat., J = 8.3Hz), 7.89 (dd, 1H, aromat., J = 7.5Hz, J = 1.7Hz), 7.84 (d, 1H, aromat., J = 7.1Hz), 7.78 (d, 1H, aromat., J = 8.1Hz), 7.55-7.48 (m, 3H, aromat.), 5.30 (q, 1H, H(1'), $J_{1',2'}$ = 6.5Hz), 3.87 (d, 1H, H(4), J_{gem} = 8.8Hz, A of an AB-system), 3.69 (d, 1H, H(4), J_{gem} = 8.9Hz, B of an AB-system), 3.00 (s, 1H, H(2)), 1.60 (d, 3H, H(2'), $J_{1',2'}$ = 6.6Hz), 1.09 (s, 3H, methyl), 0.91 (s, 3H, methyl); ^{13}C-NMR (δ, $CDCl_3$) 179.08 (C(1)), 140.39 (C(1")*), 134.16 (C(4a")*), 131.79 (C(8a")*), 129.02 (CH), 127.78 (CH), 126.02 (CH), 125.65 (CH), 125.64 (CH), 124.34 (CH), 123.46 (CH), 76.80 (C(4)), 64.30 (C(2)), 52.74 (C(1')), 40.48 (C(3)), 24.57 (methyl**), 23.00 (methyl**), 19.91 (C(2')**); *,** interchangeable

20a and **20b:** yield: 480 mg as clear colourless oil (34.4%), sum of diastereoisomers in the ratio 27 : 73; the diastereoisomers could not be further identified.

20a: (+)-isopropyl *N*-[1'-(1-naphthyl)ethyl]-2-amino-2-phenyl-acetate: major diastereoisomer, $[\alpha]_D^{20}$ = +61.1 (c = 1, $CHCl_3$); IR (cm^{-1}) 3059, 2979, 2925, 1730, 1597, 1510, 1454, 1373, 1289, 1201, 1174, 1144, 1106; UV (MeOH, nm) 224, 282 (broad); elemental analysis calcd (%) for $C_{23}H_{25}NO_2$ (347.45): C 79.51, H 7.25, N 4.03, O 9.21; found C 79.54, H 7.21, N 4.16, O 9.15; MS (EI) m/z (%): 348.2 (2) $[M+H]^+$, 261.1 (23), 260.1 (100) $[M–C_4H_7O_2]^+$, 156.1 (43), 155.1 (60), 153.1 (26), 128.1 (13), 127.1 (14) $[naphthyl]^+$, 106.1 (31), 104.1 (12), 77.0 (9); ^{1}H-NMR (δ, $CDCl_3$) 7.99 (d, 1H, aromat.,

J = 8.3Hz), 7.89 (d, 1H, aromat., J = 8.1Hz), 7.79 (d, 1H, aromat., J = 8.2Hz), 7.74 (d, 1H, aromat., J = 7.1Hz), 7.52 (dd, 1H, aromat., J ~ J ~ 7.6Hz), 7.48 (ddd, 1H, aromat., J ~ J ~ 7.5Hz, J = 1.1Hz), 7.44 (ddd, 1H, aromat., J = 8.5Hz, J = 6.7Hz, J = 1.5Hz), 7.33-7.24 (m, 5H, phenyl), 5.02 (septet, 1H, OCH, iPr, J = 6.3Hz), 4.49 (q, 1H, H(1'), $J_{1',2'}$ = 6.6Hz), 4.31 (s, 1H, H(2)), 2.61 (br.s, 1H, NH), 1.50 (d, 3H, H(2'), $J_{1',2'}$ = 6.6Hz), 1.21 (d, 3H, CH_3, iPr, J = 6.3Hz), 1.06 (d, 3H, CH_3, iPr, J = 6.3Hz); ^{13}C-NMR (δ, $CDCl_3$) 172.61 (C(1)), 140.69 (C(1")*), 138.86 (C(4a")*), 134.14 (C(8a")*), 131.47 (C(2)C*), 128.98 (CH), 128.65 (2x CH), 127.96 (CH), 127.81 (2x CH), 127.50 (CH), 125.92 (CH), 125.81 (CH), 125.46 (CH), 68.75 (CHO), 63.01 (C(2)), 50.37 (C(1')), 24.01 (C(2')**), 21.85 (methyl**), 21.53 (methyl**); *,** interchangeable

20b: (–)-isopropyl *N*-[1'-(1-naphthyl)ethyl]-2-amino-2-phenyl-acetate: minor diastereoisomer, $[\alpha]_D^{20}$ = – 20.3 (c = 1, $CHCl_3$); IR (cm^{-1}) 3066, 2980, 2931, 1726, 1597, 1510, 1495, 1453, 1374, 1290, 1205, 1178, 1145, 1105; UV (MeOH, nm) 281 (br); ^{1}H-NMR (δ, $CDCl_3$) 8.13 (m, 1H, aromat.), 7.87 (m, 1H, aromat.), 7.78-7.76 (m, 2H, aromat.), 7.50-7.42 (m, 3H, aromat.), 7.34-7.21 (m, 5H, phenyl), 5.06 (septett, 1H, OCH, iPr, J = 6.3Hz), 4.68 (q, 1H, H(1'), $J_{1',2'}$ = 6.5Hz), 4.22 (s, 1H, H(2)), 2.07 (br.s, 1H, NH), 1.53 (d, 3H, H(2'), $J_{1',2'}$ = 6.5Hz), 1.17 (d, 3H, CH_3, iPr, J = 6.3Hz), 1.09 (d, 3H, CH_3, iPr, J = 6.3Hz); ^{13}C-NMR (δ, $CDCl_3$) 173.52 (C(1)), 140.30 (C(1")*), 138.72 (C(4a")*), 134.03 (C(8a")*), 131.46 (C(2)C*), 128.93 (CH), 128.61 (2x CH), 127.76 (CH), 127.43 (CH), 127.09 (2x CH), 125.79 (CH), 125.71 (CH), 123.64 (CH), 68.61 (CHO), 63.14 (C(2)), 52.26 (C(1')), 24.00 (C(2')**), 21.83 (methyl**), 21.49 (methyl**); *,** interchangeable

25: (+)-(*1R*)-*N*-(2',2',6',6'-tetramethylpiperidin-4-yl)-1-(1-naphthyl)ethylamine: synthesis as in method A but without HOAc, workup after 5 days: quenching with aqueous NaOH solution, filtration over celite and extraction of the filtrate with ethyl acetate; purification by flash chromatography (hexane : acetone = 70:30 plus addition of 1 % triethylamine); yield: 0.935g white cristals (75.40 %); m.p. = 53.8 °C; $[\alpha]_D^{20}$ = +13.7 (c = 1, $CHCl_3$); UV (MeOH, nm) 225, 282 (br); HRMS: found $[M]^+$ =

310.2397 (calculated 310.2409); MS (EI) m/z (%): 310.24 (2) $[M]^+$, 295.21 (8) $[M\text{-}CH_3]^+$, 155.13 (100), 140.18 (16), 112.12 (7), 98.10 (67), 58.07 (31); ^{1}H-NMR (δ, $CDCl_3$) 8.21 (d, 1H, aromat., J = 8.4Hz), 7.87 (d, 1H, aromat., J = 7.9Hz), 7.74 (d, 1H, aromat., J = 8.1Hz), 7.66 (d, 1H, aromat., J = 7.1Hz), 7.53-7.46 (m, 3H, aromat.), 4.87 (q, 1H, H(1), $J_{1,2}$ = 6.5Hz), 2.90 (tt, 1H, H(1'), $J_{1',2'}$ = 11.7Hz, $J_{1',2'}$ = 3.5Hz), 1.97 (br.d, 1H, H(2'), $J_{1',2'}$ = 11.2Hz), 1.81 (br.d, 1H, H(2'), $J_{1',2'}$ = 11.1Hz), 1.49 (d, 3H, H(2), $J_{1,2}$ = 6.5Hz), 1.12 (s, 3H, C(3')CH_3), 1.11 (s, 3H, C(3')CH_3), 1.05 (s, 3H, C(3')CH_3), 0.98 (s, 3H, C(3')CH_3), 0.96-0.89 (m, 2H, H(2')); ^{13}C-NMR (δ, $CDCl_3$) 141.77 (C(1")*), 133.97 (C(4a")*), 131.22 (C(8a")*), 129.00 (CH), 127.15 (CH), 125.73 (CH), 125.67 (CH), 125.28 (CH), 122.87 (2x CH), 51.50 (C(3')), 49.60 (C(1)**), 47.11 (C(1')**), 46.69 (C(2')), 46.58 (C(2')), 34.83 (CH_3), 34.79 (CH_3), 28.40 (CH_3), 28.31 (CH_3), 24.03 (C(2)); *,** interchangeable

Method B. (*R*)-1-(1-naphthyl)ethylamine **1** (0.64 ml, 4 mmol) and typically 4 mmol of the corresponding ketone were dissolved in dry toluene (16 ml) and the solution was refluxed under nitrogen for 5 h in a flask equipped with a Dean-Stark apparatus. After cooling to r.t. and removal of water the solvent was evaporated. The crude imine was dissolved in dry toluene (20 ml) and HOAc (1 ml), and pre-reduced catalyst (40 mg of a 5 wt% Pt/Al_2O_3 catalyst, Engelhard 4759) was added. The imine was reduced under hydrogen (50 bar) within 0.5 h. The catalyst was then filtered off and the solvent evaporated. The crude product was purified by flash chromatography (ethyl acetate : hexane = 1:10 plus addition of triethylamine).

4: (+)-(*1R*)-*N*-cyclohexyl-1-(1-naphthyl)ethylamine: yield: 1.22 g pale yellow oil (96.3 %); $[\alpha]_D^{20}$ = +33.5 (c = 1, $CHCl_3$); IR (cm^{-1}) 3060, 3015, 2927, 2854, 1598, 1510, 1449, 1393, 1370, 1257, 1214, 1170, 1124; UV (MeOH, nm) 223, 272, 282; HRMS: found $[M]^+$ = 253.1833 (calcd. 253.1830); MS (EI) m/z (%): 253.2 (18) $[M]^+$, 238.2 (77) $[M–CH_3]^+$, 210.1 (6), 155.1 (100) [M–cyclohexylamine]$^+$, 129.1 (9) [naphthyl]$^+$, 98.0 (6); ^{1}H-NMR (δ, $CDCl_3$) 8.19 (d, 1H, aromat., J = 8.4Hz), 7.86 (dd, 1H,

aromat., J = 7.7Hz, J = 1.3Hz), 7.73 (d, 1H, aromat., J = 8.2Hz), 7.63 (d, 1H, aromat., J = 7.1Hz), 7.52-7.45 (m, 3H, aromat.), 4.83 (q, 1H, H(1), $J_{1,2}$ = 6.6Hz), 2.42-2.38 (m, 1H, H(1')), 1.98-1.96 (m, 1H), 1.84-1.82 (m, 1H), 1.70-1.65 (m, 2H), 1.55-1.53 (m, 1H), 1.45 (d, 3H, H(2), $J_{1,2}$ = 6.6Hz), 1.35-1.20 (br.m, 1H, NH), 1.20-1.05 (m, 5H); ^{13}C-NMR (δ, $CDCl_3$) 142.06 (C(1")*), 134.01 (C(4a")*), 131.32 (C(8a")*), 128.98 (CH), 126.94 (CH), 125.72 (CH), 125.71 (CH), 125.24 (CH), 122.92 (CH), 122.69 (CH), 53.93 (C(1')), 49.68 (C(1)), 34.60 (CH_2), 33.78 (CH_2), 26.21 (CH_2), 25.32 (CH_2), 25.04 (CH_2), 24.49 (C(2)); * interchangeable

5: (+)-(*1R*)-*N*-cyclooctyl-1-(1-naphthyl)ethylamine: yield: 160 mg pale yellow viscous oil (42.3 % based on recovered educt **1**; $[\alpha]_D^{20}$ = +9.4 (c = 1, $CHCl_3$); IR (cm^{-1}) 3460-3124, 3053, 2919, 2851, 1644, 1595, 1510, 1470, 1446, 1393, 1367, 1125; UV (MeOH, nm) 223, 273, 282 (broad); HRMS: found $[M]^+$ = 281.2140 (calculated 281.2143); MS (EI) m/z (%): 281.1 (10) $[M]^+$, 266.2 (16), 180.0 (6), 155.1 (100), 128.1 (19) [naphthyl]$^+$; ^{1}H-NMR (δ, $CDCl_3$) 8.20 (d, 1H, aromat., J = 8.4Hz), 7.86 (dd, 1H, aromat., J = 7.9Hz, J = 1.5Hz), 7.73 (d, 1H, aromat., J = 8.2Hz), 7.63 (d, 1H, aromat., J = 7.1Hz), 7.52-7.45 (m, 3H, aromat.), 4.75 (q, 1H, H(1), $J_{1,2}$ = 6.6Hz), 2.62 (septett, 1H, H(1'), J ~ 4Hz), 1.81-1.71 (m, 2H), 1.69-1.63 (m, 2H), 1.57-1.30 (m, 13H, from where can be attributed: 1.45 (d, 3H, H(2), $J_{1,2}$ = 6.6Hz)); ^{13}C-NMR (δ, $CDCl_3$) 142.08 (C(1")*), 134.01 (C(4a")*), 131.41 (C(8a")*), 128.97 (CH), 126.94 (CH), 125.72 (CH), 125.67 (CH), 125.23 (CH), 122.97 (CH), 122.75 (CH), 54.68 (C(1')), 50.18 (C(1)), 33.74 (CH_2), 31.50 (CH_2), 27.76 (CH_2), 27.26 (CH_2), 25.65 (CH_2), 24.44 (C(2)), 24.14 (CH_2), 23.74 (CH_2); * interchangeable

22: (+)-(*1'R*)-*N*-[1'-(1-naphthyl)ethyl]butan-3-onamide: formed as main product when we tried to synthesize **16** according to this procedure; yield: 193 mg white crystals (18.9 %) after recrystallization from ethyl acetate/hexane; m.p. = 114.5 °C; $[\alpha]_D^{20}$ = +44.6 (c = 1, $CHCl_3$); IR (cm^{-1}) 3292 (broad), 3065, 2975, 1717, 1642, 1542, 1359, 1160; UV (MeOH, nm) 224, 270, 281 (broad, weak); elemental analysis calcd. (%) for $C_{16}H_{17}NO_2$ (255.31): C 75.27, H 6.71, N 5.49, O 12.53; found C 75.33, H 6.54,

N 5.36, O 12.50; MS (EI) m/z (%): 255.2 (1) $[M]^+$, 240.1 (2) $[M–CH_3]^+$, 197.1 (26), 173.5 (11), 168.1 (51), 153.1 (84), 138.9 (15), 127.1 (100) [naphthyl]$^+$, 98.9 (15), 78.0 (26), 63.0 (13); ^{1}H-NMR (δ, $CDCl_3$) 8.09 (d, 1H, aromat., J = 8.3Hz), 7.87-7.85 (m, 1H, aromat.), 7.79 (d, 1H, aromat., J = 8.1Hz), 7.55-7.44 (m, 4H, aromat.), 7.24 (br.s, 1H, NH), 5.95 (dquartett, 1H, H(1'), J ~ J = 7.2Hz), 3.44 (d, 1H, H(2), J_{gem} = 17.2Hz, A of an AB-system), 3.38 (d, 1H, H(2), J_{gem} = 17.2Hz, B of an AB-system), 2.24 (s, 3H, H(4)), 1.66 (d, 3H, H(2'), $J_{1',2'}$ = 6.8Hz); ^{13}C-NMR (δ, $CDCl_3$) 204.49 (C(3)), 164.41 (C(1)), 138.34 (C(1")*), 133.96 (C(4a")*), 130.94 (C(8a")*), 128.85 (CH), 128.28 (CH), 126.48 (CH), 125.82 (CH), 125.31 (CH), 123.28 (CH), 122.53 (CH), 49.70 (C(2)), 44.86 (C(1')), 30.93 (C(4)), 21.16 (C(2')); * interchangeable

Method C. As method B but reduction of the imine was carried out in EtOH p.a. with Pd/C catalyst (84 mg of 10 wt% Pd) under hydrogen at 15 bar for 3.5 h. The crude product was purified by flash chromatography (EtOH : hexane = 1:6).

11: (–)-(*1R*)-*N*-(2-hydroxybenzyl)-1-(1-naphthyl)ethylamine: yield: 850 mg yellow viscous oil (72.6 %); $[\alpha]_D^{20}$ = –48.0 (c = 1, $CHCl_3$); IR (cm^{-1}) 3349-3273, 3046, 2970, 2853, 2627, 1614, 1590, 1511, 1491, 1473, 1397, 1256, 1173, 1102, 1032; UV (MeOH, nm) 223, 273, 282; HRMS: found $[M]^+$ = 277.1458 (calcd. 277.1467); MS (EI) m/z (%): 277.1 (19) $[M]^+$, 262.1 (19) $[M–CH_3]^+$, 170.1 (6), 156.1 (74), 155.1 (100), 129.1 (23) [naphthyl]$^+$, 107.0 (11), 78.0 (10); ^{1}H-NMR (δ, $CDCl_3$) 8.05-8.02 (m, 1H, aromat.), 7.90-7.87 (m, 1H, aromat.), 7.80-7.78 (m, 1H, aromat.), 7.55-7.46 (m, 4H, aromat.), 7.18-7.13 (m, 1H, aromat.), 6.87-6.81 (m, 2H, aromat.), 6.74-6.70 (m, 1H, aromat.), 4.74 (q, 1H, H(1), $J_{1,2}$ = 6.7Hz), 3.96 (1H, H(1'), J_{gem} = 13.8Hz, A of an AB-system), 3.82 (1H, H(1'), J_{gem} = 13.8Hz, B of an AB-system), 1.60 (d, 3H, H(2), $J_{1,2}$ = 6.7Hz); ^{13}C-NMR (δ, $CDCl_3$) 158.14 (C-OH), 139.44 (C(1")*), 134.04 (C(4a")*), 131.24 (C(8a")*), 129.14 (CH), 128.79 (CH), 128.44 (CH), 127.92 (CH), 126.27

(CH), 125.74 (CH), 125.64 (CH), 122.81 (CH), 122.53 (CH), 122.38 (CH), 119.12 (CH), 116.46 (CH), 52.42 (C(1)), 50.64 (C(1')), 23.01 (C(2)); * interchangeable

Method D. Reduction of the ester group with $LiAlH_4$ in dry diethyl ether according to standard procedures, purification by flash chromatography (ethyl acetate : hexane = 1:5 with addition of triethylamine).

12: (–)-(*1'R,2R*)-*N*-[1'-(1-naphthyl)ethyl]-2-amino-1-propanol was obtained from amino ester **14;** yield: 273 mg muddy white gel (41.4 %) that solidified in the fridge; m.p. ~ r.t.; $[\alpha]_D^{20}$ = –12.4 (c = 1, $CHCl_3$); IR (cm^{-1}) 3300 (broad), 3053, 2963, 2871, 1596, 1510, 1455, 1039; UV (MeOH, nm) 223, 273 (weak), 282; HRMS: found $[M–CH_3]^+$ = 214.1233 (calcd. 214.1232); MS (EI) m/z (%): 229.2 (0.4) $[M]^+$, 198.2 (5), 153.1 (100), 141.1 (3), 128.0 (16) $[naphthyl]^+$, 76.0 (12); ^{1}H-NMR (δ, $CDCl_3$) 8.16 (br.d, 1H, aromat., J = 8.4Hz), 7.87 (dd, 1H, aromat., J = 8.0Hz, J = 1.5Hz), 7.75 (d, 1H, aromat., J = 8.1Hz), 7.59 (d, 1H, aromat., J = 7.1Hz), 7.52-7.46 (m, 3H, aromat.), 4.76 (q, 1H, H(1'), $J_{1',2'}$ = 6.6Hz), 3.62 (dd, 1H, H(1), J_{gem} = 10.5Hz, $J_{1,2}$ = 4.1Hz, A of an ABXY-system), 3.21 (dd, 1H, H(1), J_{gem} = 10.5Hz, $J_{1,2}$ = 5.9Hz, B of an ABXY-system), 2.86 (ddq, 1H, H(2), $J_{1,2} \sim J_{2,3} \sim$ 6.3 Hz, $J_{1,2}$ = 4.1Hz, X of an ABXY-system), 2.00 (br.s, 2H, NH, OH), 1.49 (d, 3H, H(2'), $J_{1',2'}$ = 6.6Hz), 1.06 (d, 3H, H(3), $J_{2,3}$ = 6.5Hz, Y of an ABXY-system); ^{13}C-NMR (δ, $CDCl_3$) 141.87 (C(1")*), 133.98 (C(4a")*), 131.05 (C(8a")*), 129.07 (CH), 127.38 (CH), 126.01 (CH), 125.65 (CH), 125.49 (CH), 122.74 (CH), 122.47 (CH), 65.25 (C(1)), 51.71 (C(2)), 50.24 (C(1')), 23.70 (C(2')), 18.20 (C(3)); * interchangeable; ^{15}N-NMR (δ, nitromethane as reference, $CDCl_3$) –321.7 ppm (N)

13: (–)-(*1'R,3S*)-*N*-[1'-(1-naphthyl)ethyl]-3-amino-1-butanol: was obtained from amino ester **17;** yield: 451 mg white crystals (85.1 %); mp = 94.0 °C, $[\alpha]_D^{20}$ = –45.1 (c = 1, $CHCl_3$); IR (cm^{-1}) 3289 (broad), 3051, 2957, 2924, 2857, 1596, 1511, 1456, 1375, 1258, 1076; UV (MeOH, nm) 198, 202, 223, 281 (broad, weak); elemental analysis: calcd. (%) for $C_{16}H_{21}NO$ (243.35): C 78.97, H 8.70, N 5.76, O

6.57; found C 78.93, H 8.57, N 5.71, O 6.77; MS (EI) m/z (%): 243.2 (0.14) $[M]^+$, 228.1 (2) $[M–CH_3]^+$, 168.0 (15), 155.1 (100), 141.0 (3), 129.1 (5); ^{1}H-NMR (δ, $CDCl_3$) 8.13 (d, 1H, aromat., J = 8.5Hz), 7.87 (dd, 1H, aromat., J = 8.0Hz, J = 1.4Hz), 7.76 (dd, 1H, aromat., J = 7.6Hz, J = 0.8Hz), 7.55-7.45 (m, 4H, aromat.), 4.83 (q, 1H, H(1'), $J_{1',2'}$ = 6.6Hz), 3.94 (ddd, 1H, H(1), J_{gem} = 10.9Hz, $J_{1,2}$ = 6.8Hz, $J_{1,2}$ = 3.4Hz, A of an ABXY-system), 3.85 (ddd, 1H, H(1), J_{gem} = 10.9Hz, $J_{1,2}$ = 6.5Hz, $J_{1,2}$ = 3.5Hz, B of an ABXY-system), 3.07 (ddq, 1H, H(3), $J_{2,3} \sim J_{3,4} \sim$ 6.5Hz, $J_{2,3}$ = 3.5Hz), 1.86-1.80 (m, 1H, H(2)), 1.51 (d, 3H, H(2'), $J_{1',2'}$ = 6.6Hz), 1.49-1.43 (m, 1H, H(2)), 1.17 (d, 3H, H(4), $J_{3,4}$ = 6.4Hz); ^{13}C-NMR (δ, $CDCl_3$) 141.38 (C(1")*), 133.95 (C(4a")*), 130.92 (C(8a")*), 129.12 (CH), 127.51 (CH), 126.13 (CH), 125.71 (CH), 125.55 (CH), 122.49 (CH), 122.38 (CH), 62.21 (C(1)), 51.55 (C(3)), 49.86 (C(1')), 36.72 (C(2)), 23.01 (C(2')), 20.70 (C(4)); * interchangeable

Method E. **6: (+)-*N*-(2'-adamantanyl)-1-(1-naphthyl)ethylamine: 1** (0.48 ml, 2.6 mmol) and adamantanone (480 mg, 3.2 mmol, Aldrich) were dissolved in dry toluene (5 ml) and 3 drops of HOAc. The flask was closed with a $CaCl_2$ tube and stirred over night. Then the $CaCl_2$ tube was changed to a Dean-Stark apparatus and dry toluene (10 ml) and a catalytic amount of PPTS were added. The solution was refluxed under nitrogen for 5 h and cooled to r.t over night. In another flask $LiAlH_4$ (120 mg, 3.2 mmol) was suspended in dry diethyl ether (25 ml), cooled to 0 °C under nitrogen and the solution of imine in toluene was added slowly via septum under intensive stirring. After 15 min the cooling bath was removed and the reaction continued for 3 h at r.t. The mixture was again cooled to 0 °C and during vigorous stirring water (1.5 ml), an aqueous NaOH solution (1.5 ml, 15%), and water (4.5 ml) were added in this order. The white precipitate was filtered over celite and the filtrate was concentrated in vacuum. The crude residue was dissolved in an aqueous $NaHCO_3$ solution and extracted with ethyl acetate four times. After drying over $MgSO_4$, the crude product was purified by flash chromatography (ethyl acetate : hexane = 1:20 with addition of triethylamine) and yielded 237 mg product as a pale

yellow, sticky substance (30.0 %); $[\alpha]_D^{20}$ = +3.0 (c = 1, $CHCl_3$); IR (cm^{-1}) 3229 (broad), 2900, 2850, 1449, 1375, 1361, 1304, 1101, 1088, 1057, 1022; UV (MeOH, nm) 223, 281 (br); HRMS: found $[M]^+$ = 305.2141 (calcd. 305.2143); MS (EI) m/z (%): 305.2 (11) $[M]^+$, 290.2 (100) $[M–CH_3]^+$, 219.0 (16), 155.1 (34), 153.1 (10), 150.1 (19), 135.1 (46) [adamantanyl]$^+$, 131.0 (16), 119.0 (12), 93.1 (9), 69.0 (53); ^{1}H-NMR (δ, d-DMSO) 8.24 (d, 1H, aromat., J = 8.1Hz), 7.89 (dd, 1H, aromat., J = 7.6Hz, J = 1.9Hz), 7.74 (d, 1H, aromat., J = 8.2Hz), 7.69 (d, 1H, aromat., J = 7.2Hz), 7.50-7.44 (m, 3H, aromat.), 4.65 (q, 1H, H(1), $J_{1,2}$ = 6.6Hz), 2.55 (br.s, 1H, H(1')), 2.16-2.07 (m, 2H), 1.87-1.39 (m, 12H), 1.36 (d, 3H, H(2), $J_{1,2}$ = 6.6Hz); ^{13}C-NMR (δ, d-DMSO) 143.05 (C(1")*), 134.11 (C(4a")*), 131.52 (C(8a")*), 129.28 (CH), 127.10 (CH), 126.32 (CH), 126.25 (CH), 125.83 (CH), 123.58 (CH), 123.47 (CH), 59.46 (C(1)), 39.11 (C(1')), 38.15 (CH_2), 37.83 (CH_2), 37.47 (CH_2), 33.32 (C(2')), 31.72 (CH_2), 31.43 (CH_2), 31.28 (C(2')), 27.79 (C(4')), 27.76 (C(4')), 25.25 (C(2)); * interchangeable

Synthesis of modifiers **14**-**17**,[31] **21**,[57] and **20a** and **20b**[43] has been published elsewhere. Modifiers **16** and **17** were obtained in a ratio of 26 : 74 and were separated by flash chromatography (ethyl acetate : hexane = 1:10 with addition of triethylamine). The diastereoisomers were identified, compound **17** eluted first off the column. The absolute configuration of the diastereoisomers **16** and **17** was assigned by comparison between the experimental spectra of the fractions obtained after column chromatography and the VCD spectra calculated using density functional theory (DFT). The experimental VCD spectra were measured on a Bruker PMA 37 accessory coupled to a VECTOR/33 Fourier transform infrared spectrometer. Spectra were recorded in $CHCl_3$ using a transmission cell equipped with KBr windows and a 1 mm Teflon spacer. The theoretical spectra were determined as follows: first the conformational space of **16** and **17** was studied, in order to identify the most stable conformers, and among them only those were selected whose energy differed from the lowest value by less than 0.5 kcal/mol. The level of theory used for the optimizations, that comprised all degrees of

freedom, was B3LYP and B3PW91 hybrid functionals and 6-31G(d,p) basis set. Rotational strengths were then calculated at the same level of theory and a synthetic spectrum was generated using gaussian functions centered at the excitation energies and scaled with the calculated rotational strengths. All calculations were performed with the Gaussian 98 program package.[58] The reliability of this method of assigning of the absolute configuration was verified comparing experimental and calculated spectra of pentahelicene.[59]

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