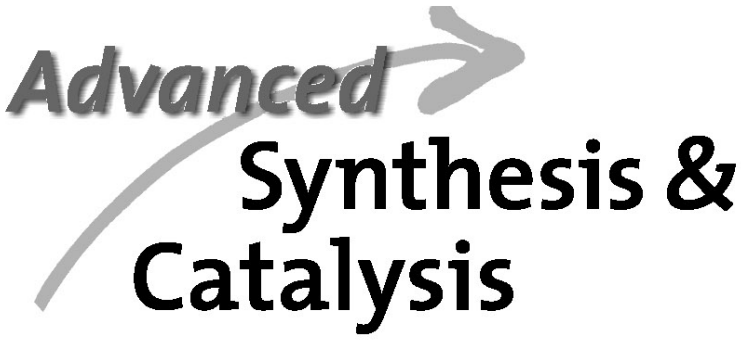


Supporting Information

**Transfer Hydrogenation of a-Branched Ketimines: Enantioselective Synthesis of Cycloalkylamines *via* Dynamic Kinetic Resolution**

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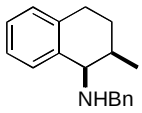
# SUPPORTING INFORMATION

**General experimental methods.** Solvents were purified and dried by standard procedures. Flash chromatography was carried out on silica-gel (0.040-0.063 mm or 0.015-0.040 mm). Melting points were recorded in a metal block and are uncorrected. $^{1}$H NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz; $^{13}$C NMR spectra were recorded at 75 MHz, 100 MHz or 125 MHz, with the solvent peak used as the internal reference. The diastereomeric excesses (de) of the products were determined by $^{1}$H NMR and the enantiomeric excess (ee) by HPLC on chiral stationary phases with $^{i}$PrOH/hexane mixtures as the eluent. Catalysts **I-III** were synthesized according to previously described procedures. [1]

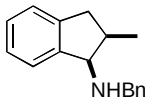
[1] (a) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521-2522. (b) K. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 285-288. (c) J. Mao, D. C. Baker, *Org. Lett*. **1999**, 841-843.

**Benzyl-[(1*R*,2*R*)-2-methyl-1,2,3,4-tetrahydro-naphthalen-1-yl]-amine (5).**




From imine **1** (crude obtained from 1.09 g, 6.8 mmol of the parent ketone) and following the method **A** with (*R,R*)-**I** as the catalyst; flash chromatography (1:30 EtOAc-hexane) gave 0.77 g (45%) of **5** (>98% de, 50% ee) as a light yellow oil: $[\alpha]^{20}_{D}$ +35.7 (*c* 0.9, $CHCl_3$) $^1$H NMR (400 MHz, $C_6D_6$) δ 0.95 (d, 3H, *J* = 6.5 Hz), 1.48 (m, 1H), 1.63 (m, 1H), 1.84 (m, 1H), 2.55 (dt, 1H, *J* = 16.8, 8.0 Hz), 2.68 (dt, 1H, *J* = 17.2, 5.6 Hz), 3.47 (d, 1H, *J* = 3.6 Hz), 3.71 (d, 1H, *J* = 14 Hz), 3.75 (d, 1H, *J* = 14 Hz), 6.98-7.22 (m, 9H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 16.5, 26.5, 28.0, 32.5, 52.6, 59.3, 125.8, 127.0, 127.2, 128.6, 128.7, 129.2, 129.5, 136.5, 140.2, 141.8; mass spectrum (EI) *m/z* (rel intensity) 251 ($M^+$, 7), 209 (40), 144 (100), 91 (59). HRMS calcd for $C_{18}H_{22}N$ 252.1752, found 252.1745; Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.31; H, 8.20; N, 5.43; HPLC (Chiralpak AD, 2-propanol/hexane 0.5:99.5, flow 0.3 mL/min, T = 30 °C): $t_R$ 16.45 min (major) and 17.37 min (minor). Using (*S*,*S*)-**II or** (*S*,*S*)-**III** as the catalysts, *cis*-**5** was obtained with >98% de in 80% and 75% yield, respectively, as near racemic mixture.

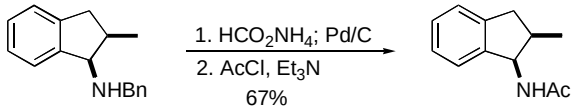
**Benzyl-[(1*R*,2*R*)-2-methyl-indan-1-yl]-amine (6).**




From imine **2** (crude obtained from 0.97 g, 4.64 mmol of the parent ketone) and following the method **A** with (*R*,*R*)-**I** as the catalyst; flash chromatography (1:40 EtOAc-toluene) gave 0.77 g (70%) of **6** (>98% de, 96% ee) as a yellow oil: $[\alpha]^{22}_{D}$ –2.7 (*c* 0.7, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 1.01 (d, 3H, *J* = 6.9 Hz), 2.64 (dd, 1H, *J* = 15.0, 4.2 Hz), 2.74 (m, 1H), 2.96 (dd, 1H, *J* = 15.0, 6.6 Hz), 3.90 (d, 1H, *J* = 13.2 Hz), 3.97 (d, 1H, *J* = 13.2 Hz), 4.17 (d, 1H, *J* = 6 Hz), 7.18-7.47 (m, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 14.1, 37.8,

38.8, 51.9, 65.0, 124.7, 125.3, 126.4, 127.2, 127.4, 128.4, 128.7, 141.1, 142.8, 145.3; mass spectrum (EI) *m/z* (rel intensity) 237 ($M^+$, 14), 236 (17), 146 (100), 91 (37). HRMS calcd for $C_{17}H_{20}N$ 238.1596, found 238.1583; HPLC (Chiralcel OB, 2-propanol/ hexane 1:99, flow 0.3 mL/ min, T = 30ºC): $t_R$ 17.58 min (minor) and 19.89 min (major). Using (*S*,*S*)-**II** as the catalyst under the same conditions, the (*S*,*S*) enantiomer *ent*-**6** was obtained in 60% yield (>98% de and 60% ee).

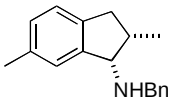
**Determination of the absolute configuration of (*R,R*)-6.**




(*R*,*R*)-**6** (*R*,*R*)-**21**

The absolute configuration of (*R*,*R*)-**6** was established after chemical correlation: To a solution of (*R*,*R*)-**6** (237 mg, 1 mmol) in MeOH (20 mL) was added $HCO_2NH_4$ (315 mg, 5 mmol) and Pd on carbon (10 wt. %, 50 mg). The mixture was stirred at room temperature overnight, then filtered through a celite pad and concentrated, and the residue was dissolved in dry $CH_2Cl_2$ (5 mL) and treated with AcCl (85 μL, 1.2 eq) and $Et_3N$ (277 μL, 2 eq). After stirring for 1 h at room temperature, the mixture was diluted with $CH_2Cl_2$ (10 mL) and washed with satd. $NaHCO_3$ (3 × 10 mL), dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography to afford know (*R*,*R*)-**21** (127 mg, 67% overall): $[\alpha]^{22}_D$ +11.8 (*c* 0.7, $CHCl_3$). Lit.: $[\alpha]^{25}_D$ +12.5 (*c* 1, $CHCl_3$). [2]

**Benzyl-[(1*S*,2*S*)-2,6-dimethylindan-1-yl]amine (7).**

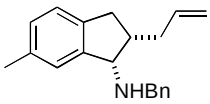



From imine **3** (crude obtained from 1.0 g, 6.25 mmol of the parent ketone) and following the method **A** with (*S*,*S*)-**I** as the catalyst; flash chromatography (1:30 EtOAc-toluene)

[2] Z. Zhang, G. Zhu, Q. Jiang, D. Xiao, X. Zhang, *J. Org. Chem*. **1999**, *64*, 1774-1775.

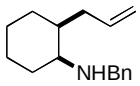
gave 1.28 g (82%) of **7** (>98% de, 96% ee) as a yellow solid: M.p. = 54-56 °C; $[\alpha]^{20}_{D}$ +7.16 (*c* 0.7, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 0.98 (d, 3H, *J* = 6.9 Hz), 2.34 (s, 3H), 2.56 (dd, 1H, *J* = 15.0, 3.6 Hz), 2.71 (m, 1H), 2.91 (dd, 1H, *J* = 15.0, 6.6 Hz), 3.88 (d, 1H, *J* = 13.5 Hz), 3.95 (d, 1H, *J* = 13.5 Hz), 4.12 (d, 1H, *J* = 6.0 Hz), 6.98-7.36 (m, 8H); $^{13}$C NMR (75 MHz,$CDCl_3$) δ 14.1, 21.7, 37.9, 38.4, 51.9, 65.0, 125.0, 125.4, 127.2, 128.2, 128.4, 128.6, 135.9, 139.7, 141.1, 145.3; mass spectrum (EI) *m/z* (rel intensity) 251 ($M^+$, 16), 250 (23), 160 (100), 91 (53). HRMS calcd for $C_{18}H_{21}N$ 251.1674, found 251.1667; HPLC analysis was performed for the corresponding benzamide: (Chiralpak AD, 2-propanol/hexane 10:90, flow 1.0 mL/min, T = 30 °C): $t_R$ 8.69 min (minor) and 12.32 min (major).

**Benzyl-[(1*S*,2*S*)-2-allyl-6-methyl-indan-1-yl]-amine (8).**




From imine **4** (crude obtained from 1.9 g, 10.2 mmol of the parent ketone) and following the method **A** with (*S*,*S*)-**I** as the catalyst; flash chromatography (1:16 EtOAc-Hexane) gave 1.9 g (67%) of **8** (>98% de, 92% ee) as a yellow oil: $[\alpha]^{20}_{D}$ +8.4 (*c* 1.2, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 2.03 (m, 1H), 2.36 (s, 3H), 2.42 (m, 1H), 2.57 (m, 1H), 2.73 (dd, 1H, *J* = 16.0, 6.5 Hz), 2.83 (dd, 1H, *J* = 15.5, 7.0 Hz), 3.88 (d, 1H, *J* = 13.5 Hz), 3.91 (d, 1H, *J* = 13.5 Hz), 4.13 (d, 1H, *J* = 6 Hz), 5.03 (d, 1H, *J* =10 Hz), 5.08 (d, 1H, *J* = 16.5 Hz), 5.88 (m, 1H), 7.01-7.43 (m, 8H); $^{13}$C NMR (125 MHz,$CDCl_3$) δ 21.4, 32.9, 35.4, 43.6, 51.8, 64.0, 115.7, 124.8, 125.0, 126.9, 128.0, 128.2, 128.4, 128.6, 135.6, 138, 139.5, 140.8, 145.4; mass spectrum (EI) *m/z* (rel intensity) 276 ($M^+$-1, 63), 234 (7), 171 (100), 143 (48). HRMS calcd for $C_{20}H_{23}N$ 277.1831, found 277.1822. HPLC analysis was performed for the corresponding benzamide: (Chiralpak AD, 2-propanol/hexane 10:90, flow 1 mL/min, T = 30 °C): $t_R$ 9.63 min (minor) and 13.94 min (major).

**Benzyl [(*S*,*S*)-2-allylcyclohex-1-yl]amine (12).**



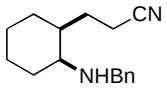

From imine **9** (crude obtained from 1.36 g, 6.00 mmol of the parent ketone) and following the method **A** with (*S*,*S*)-**II** (8.4 mg, 0.012 mmol) as the catalyst; flash chromatography (1:8 AcOEt-Hexane + 1% $Et_3N$) afforded 960 mg (70%) of (*S*,*S*)-**12** (>98% de, 63% ee) and 75 mg (5%) (*S*,*R*)-**12** as colorless oils**.**

Data for (*S*,*S*)-**12:** $[\alpha]^{20}_D$ –15.9 (*c* 1.0, $CHCl_3$) $^1$H NMR (400 MHz, $CDCl_3$) δ 1.10-1.80 (m, 10H), 1.70-2.10 (m, 1H), 2.18-2.30 (m, 1H), 2.70-2.80 (m, 1H), 3.69 (d, 1H, *J* = 12.9 Hz), 3.80 (d, 1H, *J* = 12.9 Hz), 4.90-5.10 (m, 2H), 5.70-5.90 (m, 1H), 7.20-7.40 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 22.4, 23.6, 27.3, 28.8, 34.0, 39.5, 51.4, 56.4, 115.3, 126.8, 128.2, 128.3, 138.3, 141.3; mass spectrum (CI) *m/z* (rel intensity) 258 ($M^+$ +1, 52), 162 (54), 105 (100), 77 (14). HRMS calcd for $C_{16}H_{23}N$ 229.1830, found 229.1818; Anal. calcd for $C_{16}H_{23}N{\cdot}1/3H_2O$: C 81.70, H 10.16, N 5.96; found: C 81.46, H 9.57, N 5.47; HPLC analysis was performed for the corresponding benzamide: (Chiralpak AD, 2-propanol/hexane 5:95, flow 1.0 mL/min, T = 30 °C): $t_r$ 24.9 min (minor) and 31.8 min (major).

Data for (*S*,*R*)-**12**: $[\alpha]^{20}_D$ –2.1 (*c* 1.0, $CHCl_3$) $^1$H NMR (400 MHz, $CDCl_3$) δ 0.90-1.50 (m, 6H), 1.55-1.85 (m, 3H), 1.90-2.05 (m, 1H), 2.06-2.17 (m, 1H), 2.21 (dt, 1H, *J* = 10.0, 3.6 Hz), 2.42-2.55 (m, 1H), 3.67 (d, 1H, *J* = 12.8 Hz), 3.89 (d, 1H, *J* = 12.8 Hz), 4.90-5.10 (m, 2H), 5.70-5.90 (m, 1H), 7.20-7.40 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 25.3, 25.8, 31.0, 32.4, 37.5, 42.6, 51.1, 59.9, 115.8, 126.8, 128.2, 128.4, 137.5, 141.2.

Using (*R*,*R*)-**I** (7.6 mg, 0.012 mmol) as the catalyst under the same conditions, racemic *cis*-**12** was obtained in 70% yield.

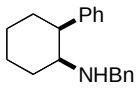
**(S,S)-3-(2-Benzylamino-cyclohexyl)-propionitrile (13).**




From imine **10** (crude obtained from 1.44 g, 6.0 mmol of the parent ketone) and following the method **A** with (*S*,*S*)-**II** (8.4 mg, 0.012 mmol) as the catalyst; flash chromatography (1:4 AcOEt-toluene + 1% $Et_3N$) afforded 870 mg (60%) of **13** (92% de; 68% ee) as a yellow oil: $^1$H NMR (500 MHz, $CDCl_3$) δ 1.30-1.47 (m, 6H), 1.47-1.60 (m, 3H), 1.65-1.81 (m, 2H), 1.83-1.93 (m, 1H), 2.17-2.27 (m, 2H), 2.70 (q, 1H, *J* = 4.2 Hz), 3.65 (d, 1H, *J* = 13.0 Hz), 3.84 (d, 1H, *J* = 13.0 Hz), 7.10-7.40 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 15.2, 22.0, 24.0, 26.1, 27.5, 28.4, 38.9, 51.5, 55.0, 127.5, 128.5, 128.7, 141.3. HPLC analysis was performed for the corresponding benzamide: (Chiralpak AD, 2-propanol/hexane 10:90, flow 1.0 mL/min, T = 30 ºC, detection at 215 nm.): $t_r$ 45.33 min (minor), 59.14 min (major), and 68.54 min (*trans*). Using (*R*,*R*)-**I** (19 mg, 0.03 mmol) as the catalyst, the reaction resulted in extensive decomposition. Using **(***S*,*S*)-**III** as the catalyst, *cis*-**13** (>98% de) was obtained in 35% yield and 8% ee.

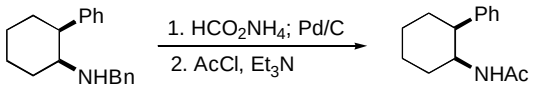
The product was further characterized as its hydrochloride: To a cooled (0 °C) solution of **13 (**242 mg, 1 mmol) in $Et_2O$ (10 mL) was added 2M HCl in ether (1 mL, 2 mmol) dropwise and the resulting white solid (165 mg, 59%, >98% de, 68% ee) was filtered off: M.p. = 142-144; $[\alpha]^{20}_D$ –21.1 (*c* 0.8, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 1.10-1.50 (m, 4H), 1.60-2.00 (m, 5H), 2.00-2.30 (m, 2H), 2.30-2.60 (m, 2H), 2.80-3.00 (m, 1H), 4.00 (br s, 2H), 7.20-7.40 (m, 3H), 7.50-7.80 (m, 2H), 9.51 (br s, 1H), 9.92 (br s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 15.3, 20.6, 22.4, 23.7, 25.0, 26.6, 34.9, 48.2, 57.1, 119.7, 129.5, 129.7, 130.1, 130.8; mass spectrum (CI) *m/z* (rel intensity) 243 ($M^+$, 29), 242 ($M^+$ -1, 24), 202 (20), 146 (63), 91 (100). HRMS calcd for $C_{16}H_{23}N_2$ 243.1861, found 243.1847; Anal. calcd for $C_{16}H_{23}ClN_2$: C 68.92, H 8.31, N 10.05; found: C 68.70, H 7.78, N 9.81;

**Benzyl-[(1S,2S)-2-phenyl-cyclohexyl]amine (14).**




From imine **11** (crude obtained from 1.58 g, 6.0 mmol of the parent ketone) and following the method **A** with (*S*,*S*)-**II** (21 mg, 0.03 mmol) as the catalyst; flash chromatography (1:12 AcOEt-Hexane + 1% $Et_3N$) gave 730 mg (55%) of **14** as a yellow oil: $^1$H NMR (300 MHz, $CDCl_3$) δ 1.10-2.10 (m, 8H), 2.22 (dq, 1H, *J* = 12.6, 3.6 Hz), 2.92 (dt, 1H, *J* = 12.6, 3.3 Hz), 3.00-3.10 (m, 1H), 3.46 (d, 1H, *J* = 13.5 Hz), 3.75 (d, 1H, *J* = 13.5 Hz), 7.0-7.45 (m, 10H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 20.1, 25.0, 26.9, 30.1, 47.5, 51.7, 57.0, 126.5, 126.8, 128.0, 128.1, 128.5, 128.7, 141.3, 144.8; mass spectrum (CI) *m/z* (rel intensity) 265 ($M^+$, 48), 266 (43), 146 (60), 91 (100). HRMS calcd for $C_{19}H_{23}N$ 265.1830, found 265.1838; $[\alpha]^{20}_D$ –33.3 (*c* 1.0, $CHCl_3$) (100% de, 50% ee); HPLC analysis was performed for the corresponding acetamide: (Chiralpak OD, 2-propanol/hexane 10:90, flow 1.0 mL/min, T = 30 °C): $t_r$ 9.06 min (minor) and 12.74 min (major).

**Determination of the absolute configuration of (*S*,*S*)-14.**

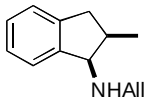



(*S*,*S*)-**14** (*S*,*S*)-**22**

The absolute configuration of (*S*,*S*)-**14** was determined by chemical correlation with know amine *(S*,*S*)**-22**: To a solution of (*S*,*S*)-**14** (263 mg, 1 mmol) in MeOH (5 mL) was added $HCO_2NH_4$ (252 mg, 4 mmol) and Pd on carbon (10 wt. %, 50 mg). The mixture was stirred at 65 °C for 2 hours, then filtered through a celite pad and concentrated, and the residue was dissolved in dry ether (2 mL) and treated with acetic anhydride (187 μL, 1.0 eq) and $Et_3N$ (277 μL, 1 eq). After stirring for 1 h at room temperature, the mixture was diluted with $CH_2Cl_2$ (10 mL) and washed with satd. $NaHCO_3$ (3 × 10 mL), dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography to afford know (*S*,*S*)-

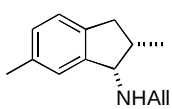
**22** (108 mg, 50% overall): $[\alpha]^{20}_D$ +14.8 (*c* 0.5, $CHCl_3$) for (*S*,*S*)-**22** of 68% ee. Lit.: $[\alpha]^{20}_D$ +30.0 (*c* 0.66, $CHCl_3$) for (*S*,*S*)-**22** of 68% ee.[3]

**Allyl-[(1*R*,2*R*)-2-methyl-indan-1-yl]-amine (18).**




From ketone **15** (0.58 g, 4 mmol) and following the method **B** with (*R*,*R*)-**I** as the catalyst; flash chromatography (1:10 EtOAc-hexane) gave 420 mg (56%) of **18** (>98% de, 90% ee) as a yellow oil: $[\alpha]^{20}_D$ –18.0 (*c* 0.8, $CHCl_3$ $^1$H NMR (300 MHz, $CDCl_3$) δ 0.94 (d, 3H, *J* = 6.9 Hz), 2.60 (dd, 1H, *J* = 15.0, 4.5 Hz), 2.67 (m, 1H), 2.94 (dd, 1H, *J* = 15.0, 6.6 Hz), 3.36 (d, 2H, *J* = 5.7 Hz), 4.12 (d, 1H, *J* = 6 Hz), 5.11 (dd, 1H, *J* = 10.2, 1.5 Hz ), 5.25 (dd, 1H, *J* = 17.1, 1.5 Hz), 5.96 (m, 1H), 7.15-7.34 (m, 4H); $^{13}$C NMR (75 MHz,$CDCl_3$) δ 13.9, 37.9, 38.7, 50.6, 65.0, 116.0, 124.7, 125.3, 126.3, 127.4, 137.4, 142.9, 145.1; Anal. calcd for $C_{13}H_{17}N$: C 83.37, H 9.15, N 7.48; found: C 82.97, H 9.27, N 7.61. HPLC analysis was performed for the corresponding acetamide: (Chiralpak AS, 2-propanol/hexane 10:90, flow 1.3 mL/min, T = 30 °C): $t_R$ 5.72 min (major) and 10.68 min (minor). In a parallel reaction carried out with a higher catalyst load of S/C = 100, **18** was obtained in 58% yield (>98% de and 74% ee) along with 20% of (*R*,*R*)-2-methylindan-1-ol as a by-product. Using (*S*,*S*)-**III** as the catalyst under the same conditions, *ent*-**18** (>98% de) was obtained in 78 % yield and with 10% ee.

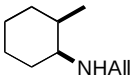
**Allyl-[(1*S*,2*S*)-2,6-dimethylindan-1-yl]-amine (19).**




[3] Hayashi, T.; Senda, T.; Ogasawara, M. *J, Am. Chem. Soc.* **2000**, *122*, 10716-10717.

From ketone **16** (1.00 g, 6.25 mmol) and following the method **B** with (*S*,*S*)-**I** as the catalyst; flash chromatography (1:12 EtOAc-toluene) gave 750 mg (60%) of **19** (>98% de, 96% ee) as a yellow oil: $[\alpha]^{20}_{D}$ +27.0 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, 3H, *J* = 7.2 Hz), 2.33 (s, 3H), 2.54 (dd, 1H, *J* = 15.2, 4.0 Hz), 2.67 (m, 1H), 2.89 (dd, 1H, *J* = 15.2, 6.8 Hz), 3.36 (d, 2H, *J* = 6 Hz), 4.09 (d, 1H, *J* = 6 Hz), 5.11 (d, 1H, *J* = 10.4 Hz), 5.25 (d, 1H, *J*=16.8 Hz), 5.97 (m, 1H), 6.97-7.15 (m, 3H); $^{13}$C NMR (75 MHz,$CDCl_3$) δ 13.9, 30.0, 38.0, 38.3, 50.6, 65.0, 116.0, 125.0, 125.4, 128.1, 135.9, 137.4, 139.7, 145.2; mass spectrum (EI) *m/z* (rel intensity) 201 ($M^+$, 3), 160 (35), 145 (100), 91 (7). HRMS calcd for $C_{14}H_{20}N$ 202.1596, found 202.1598; HPLC analysis was performed for the corresponding benzamide: (Chiralpak AD, 2-propanol/hexane 10:90, flow 1.0 mL/min, T = 30 °C): $t_R$ 8.69 min (minor) and 12.32 min (major).

***N*-Allyl-*N*-[(1*S*,2*R*)-2-methylcyclohex-1-yl]benzamide (20).**




From ketone **17** (676 mg, 6.0 mmol) and following the method **B** with (*S*,*S*)-**I** (19 mg, 0.03 mmol) as the catalyst; flash chromatography (90:9:1 $CH_2Cl_2$/MeOH/$Et_3N$) afforded 708 mg (77%) of **20** (80% de, 90% ee) as a brown oil. $^1$H NMR (300 MHz, $CDCl_3$) δ 0.86 (d, 3H, *J* = 7.0 Hz), 1.10-1.50 (m, 6H), 1.52-1.65 (m, 2H), 1.85-1.95 (m, 1H), 2.58 (dt, 1H, *J* = 4.2 Hz), 3.20 (m, 2H), 5.02-5.20 (m, 2H), 5.80-6.0 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.6, 22.2, 24.1, 28.4, 31.4, 50.0, 58.0, 115.8, 137.8. HPLC analysis was performed for the corresponding acetamide (Chiralpak AD, 2-propanol/hexane 10:90, flow 1.0 mL/min, T = 30 °): $t_r$ (minor) = 19.44 min and 22.03 min (major).

The product was further characterized as its benzamide: To a solution of **20** (1 mmol) and $Et_3N$ (1.2 mmol) in dry $CH_2Cl_2$ (1.5 mL) was added benzoyl chloride (1.2 mmol) dropwise. The reaction mixture was stirred for 2 h at room temperature, diluted with $CH_2Cl_2$ (10 mL) and washed with hot $H_2O$ (2 × 10 mL). The organic layer was dried ($MgSO_4$), concentrated

to dryness, and the resulting residue was purified by flash chromatography to yield 753 mg (75%) of *N*-allyl-*N*-[(1*S*,2*R*)-2-methylcyclohex-1-yl]benzamide $[\alpha]^{20}_{D}$ –57.0 (*c* 0.925, $CHCl_3$) $^1$H NMR (500 MHz, DMSO-$d_6$, 100 ºC) δ 1.01 (d, 3H, *J* = 7.0 Hz), 1.12-1.50 (m, 5H), 1.59-1.68 (m, 1H), 1.71-1.80 (m, 1H), 1.86 (dq, 1H, *J* = 12.5, 4.0 Hz), 2.10-2.18 (m, 1H), 3.80 (ddt, 1H, *J* = 17.0, 5.5, 1.5 Hz), 4.02 (dt, 1H, *J* = 12.5, 4.0 Hz), 4.11 (ddt, 1H, *J* = 17.0, 5.5, 1.5 Hz), 4.98-5.07 (m, 2H), 5.72-5.84 (m, 1H), 7.25-7.42 (m, 5H); $^{13}$C NMR (75 MHz, DMSO-$d_6$, 120 ºC) δ 13.7, 20.1, 25.5, 26.7, 33.3, 33.6, 47.8, 59.5, 115.8, 126.7, 128.9, 129.3, 137.1, 139.1, 172.0; mass spectrum (CI) *m/z* (rel intensity) 258 ($M^+$ +1, 52), 162 (54), 105 (100), 77 (14). HRMS calcd for $C_{17}H_{23}NO$ 258.1857, found 258.1844; Anal. calcd for $C_{17}H_{23}NO$: C 79.33, H 9.01, N 5.44; found: C 78.04, H 9.07, N 5.35.