

Electronic Supporting Information

for

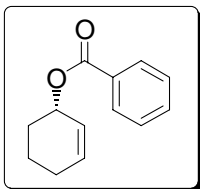
Studies on Enantioselective Allylic Oxidation of Olefins using Peresters Catalyzed by Cu(I)-Complexes of Chiral Pybox Ligands

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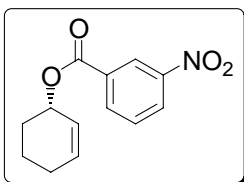
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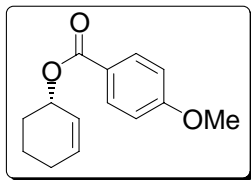
Analytical Data for Allylic Oxidation Products:



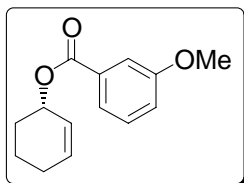
(S)-2-Cyclohexenyl-1-benzoate (Table 1, entry 1).^{1a,1b} It was obtained in a maximum of 91% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3; flow rate 0.5 mL/min; t_R = 11.52 min (*R*), 12.63 min (*S*); $[\alpha]_D^{25}$ -167.2 (c 4.4, CHCl₃) [lit.^{1a} (86% ee); $[\alpha]_D^{25}$ - 157.0 (c 2.8, CHCl₃)].



(S)-2-Cyclohexenyl-*m*-nitrobenzoate (Table 1, entry 4). It was obtained in a maximum of 88% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; t_R = 17.78 min (*R*), 19.71 min (*S*); $[\alpha]_D^{25}$ - 159.1 (c 1.5, CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3088, 3034, 2937, 1719, 1534, 1349, 1258, 1135, 914, 718; δ_H (400 MHz; CDCl₃; Me₄Si) 1.70 - 2.23 (6H, m, cyclic 3 × CH₂), 5.54-5.57 (1H, m, OCHCH₂), 5.82-5.86 (1H, m, CHCHCH₂), 6.03-6.08 (1H, m, CHCHCH), 7.65 (1H, t, J = 7.8 Hz, Ar), 8.40 (2H, t, J = 8.7 Hz, Ar), 8.86 (1H, s, Ar); δ_C (100 MHz; CDCl₃; Me₄Si) 18.7, 24.8, 28.2, 69.7, 124.4, 124.9, 127.1, 129.4, 132.4, 133.5, 135.2, 148.1, 163.9. Anal. Calcd for C₁₃H₁₃NO₄: C, 63.15; H, 5.30; N, 5.67. Found: C, 62.90; H, 5.44.



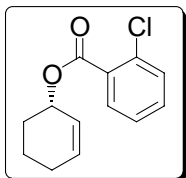
(S)-2-Cyclohexenyl-*p*-methoxybenzoate (Table 1, entry 5). It was obtained in a maximum of 93% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; $t_R = 20.22$ min (*R*), 21.38 min (*S*); $[\alpha]_D^{25} -175.7$ (c 2.0 CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3157, 3031, 2937, 1707, 1256, 1106, 1028, 772; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.67-2.15 (6H, m, cyclic $3 \times \text{CH}_2$), 3.85 (3H, s, OCH_3), 5.48 (1H, bs, OCHCH_2), 5.81-5.84 (1H, m, CHCHCH_2), 5.98-6.00 (1H, m, CHCHCH), 6.90 (2H, d, $J = 9.0$ Hz, Ar), 8.0 (2H, d, $J = 9.0$ Hz, Ar); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 18.9, 24.9, 28.4, 55.3, 68.2, 113.4, 123.1, 125.9, 131.5, 132.5, 163.1, 165.9. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3$: C, 72.39; H, 6.94. Found: C, 72.14; H, 6.83.



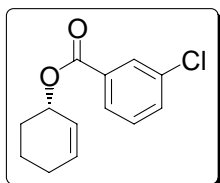
(S)-2-Cyclohexenyl-*m*-methoxybenzoate (Table 1, entry 7). It was obtained in a maximum of 91% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3]; flow rate 0.5 mL/min; $t_R = 21.72$ min (*R*), 23.59 min (*S*); $[\alpha]_D^{25} -176.6$ (c 1.2 CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3072, 3030, 2937, 1713, 1276, 1103, 1044, 923, 756; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.70-2.16 (6H, m, cyclic $3 \times \text{CH}_2$), 3.85 (3H, s, OCH_3), 5.50 (1H, bs, OCHCH_2), 5.81-5.84 (1H, m, CHCHCH_2), 5.99-6.02 (1H, m, CHCHCH), 7.08 (1H, d, $J = 7.8$, Ar), 7.33 (1H, t, $J = 8.1$, Ar), 7.57 (1H, s, Ar), 7.65 (1H, d, $J = 7.4$ Hz, Ar); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 18.9, 24.9, 28.3, 55.4, 68.7, 114.1, 119.1,

121.9, 125.6, 129.2, 132.1, 132.8, 159.5, 166.0. Anal. Calcd for C₁₄H₁₆O₃: C, 72.39; H, 6.94.

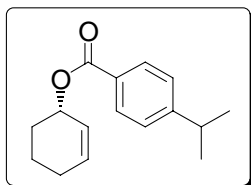
Found: C, 72.08; H, 7.01.



(S)-2-Cyclohexenyl-*o*-chlorobenzoate (Table 1, entry 9).^{2a} It was obtained in a maximum of 88% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3]; flow rate 0.5 mL/min; t_R = 13.62 min (*R*), 14.97 min (*S*); $[\alpha]_D^{25}$ -164.6 (*c* 1.2 CHCl₃).

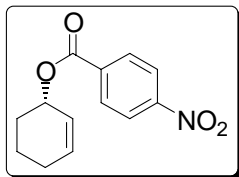


(S)-2-Cyclohexenyl-*m*-chlorobenzoate (Table 1, entry 10).^{2a} It was obtained in a maximum of 89% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3]; flow rate 0.5 mL/min; t_R = 9.79 min (*R*), 10.78 min (*S*); $[\alpha]_D^{25}$ -176.7 (*c* 1.4 CHCl₃).

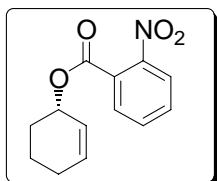


(S)-2-Cyclohexenyl-*p*-isopropylbenzoate (Table 1, entry 11). It was obtained in a maximum of 91% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3]; flow rate 0.5 mL/min; t_R = 13.35 min (*R*), 15.60 min (*S*); $[\alpha]_D^{25}$ -176.2 (*c* 5.0 CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3069, 3032, 2959, 1713, 1271, 1108, 774; δ_H (400 MHz; CDCl₃; Me₄Si) 1.26 (6H, d, J = 6.8, 2 × CH₃CH) 1.66-2.16 (6H, m, cyclic 3

$\times \text{CH}_2$), 2.95 (1H, septet, $J = 7.1$ Hz, CH_3CHCH_3), 5.48-5.52 (1H, m, OCHCH_2), 5.80-5.84 (1H, m, CHCHCH_2), 5.97-6.02 (1H, m, CHCHCH), 7.28 (2H, d, $J = 8.4$ Hz, Ar), 7.98 (2H, d, $J = 8$, Ar); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 18.9, 23.6, 24.9, 28.4, 34.1, 68.2, 125.8, 126.3, 128.3, 129.7, 132.6, 154.0, 166.1. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2$: C, 78.65; H, 8.25. Found: C, 78.33; H, 8.38.

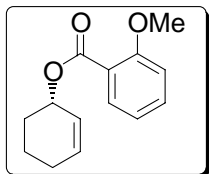


(S)-2-Cyclohexenyl-*p*-nitrobenzoate (Table 1, entry 15).^{2b} mp 73-75 °C (lit^{2b} mp 75-76 °C). It was obtained in a maximum of 87% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; $t_{\text{R}} = 19.56$ min (*R*), 20.98 min (*S*); $[\alpha]_{\text{D}}^{25} -156.4$ (c 0.5, CHCl_3) [lit^{2b} (78% ee)]; $[\alpha]_{\text{D}}^{25} = -134.7$ (c 0.38 CHCl_3).

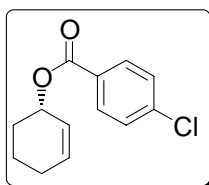


(S)-2-Cyclohexenyl-*o*-nitrobenzoate (Table 1, entry 16). It was obtained in a maximum of 83% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; $t_{\text{R}} = 25.56$ min (*R*), 28.88 min (*S*); $[\alpha]_{\text{D}}^{25} - 107.8$ (c 0.9, CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3070, 3034, 2938, 1726, 1535, 1353, 1285, 1128, 908, 735; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.67-1.75 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.89–2.20 (4H, m, $2 \times \text{CH}_2\text{CH}_2\text{CH}$), 5.53 (1H, bs, OCHCH_2), 5.80-5.83 (1H, m CHCHCH_2), 6.00-6.05 (1H, m, CHCHCH), 7.59-7.68 (2H, m, Ar), 7.75 (1H, d, $J = 6.4$ Hz, Ar), 7.90 (1H, d, $J = 8$ Hz, Ar); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 18.5, 24.7, 27.7, 70.4, 123.7, 124.3, 128.0, 129.8, 131.5, 132.8,

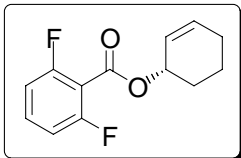
133.7, 148.1, 165.0. Anal. Calcd for C₁₃H₁₃NO₄: C, 63.15; H, 5.30; N, 5.67. Found: C, 62.73; H, 5.42.



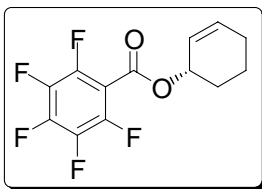
(S)-2-Cyclohexenyl-*o*-methoxybenzoate (Table 1, entry 19). It was obtained in a maximum of 98% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; $t_R = 30.27$ min (*S*), 31.62 min (*R*); $[\alpha]_D^{25} -179.3$ (c 1.5 CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3073, 3031, 2939, 1722, 1251, 1077, 758; δ_H (400 MHz; CDCl₃; Me₄Si) 1.67-2.15 (6H, m, cyclic 3 × CH₂), 3.89 (3H, s, OCH₃), 5.50 (1H, bs, OCHCH₂), 5.82-5.87 (1H, m, CHCHCH₂), 5.97-6.01 (1H, m, CHCHCH), 6.94-6.98 (2H, m, Ar), 7.44 (1H, dt, $J = 6.0$ and 1.7 Hz, Ar), 7.78 (1H, dd, $J = 7.8$ and 1.7 Hz, Ar); δ_C (100 MHz; CDCl₃; Me₄Si) 18.8, 24.8, 28.3, 55.9, 68.2, 111.9, 119.9, 120.6, 125.7, 131.4, 132.6, 133.1, 159.0, 165.7. Anal. Calcd for C₁₄H₁₆O₃: C, 72.39; H, 6.94. Found: C, 72.73; H, 7.01.



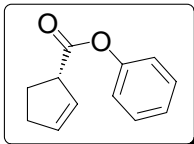
(S)-2-Cyclohexenyl-*p*-chlorobenzoate (Table 1, entry 21).^{2a} It was obtained in a maximum of 89% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3]; flow rate 0.5 mL/min; $t_R = 12.20$ min (*R*), 14.40 min (*S*); $[\alpha]_D^{25} -186.5$ (c 1.1, CHCl₃).



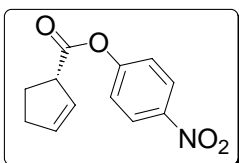
(S)-2-Cyclohexenyl-(2,6-difluorobenzoate) (Table 1, entry 25). It was obtained in a maximum of 79% ee. $[\alpha]_{\text{D}}^{25} -129.3$ (*c* 6.8 CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3105, 3069, 3034, 2941, 1728, 1468, 1290, 1116, 1012, 908, 797; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.54-2.15 (6H, m cyclic $3 \times \text{CH}_2$), 5.56 (1H, bs, OCHCH_2), 5.82-5.86 (1H, m, CHCHCH_2), 6.02-6.04 (1H, m, CHCHCH), 6.93 (2H, t, $J = 8.0$ Hz, Ar), 7.35-7.42 (1H, m, Ar); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 18.5, 24.8, 28.1, 69.9, 111.7, 112.0, 124.8, 128.7, 132.4, 133.6, 159.2, 161.8. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{F}_2\text{O}_2$: C, 65.54; H, 5.08. Found: C, 65.39; H, 5.25.



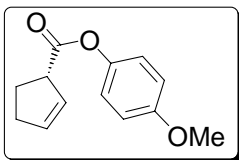
(S)-2-Cyclohexenyl pentafluorobenzoate (Table 1, entry 26). It was obtained in a maximum of 52% ee. $[\alpha]_{\text{D}}^{25} -96.8$ (*c* 4.9 CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3037, 2944, 1737, 1519, 1499, 1341, 1233, 1002, 904; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.65-2.17 (6H, m cyclic $3 \times \text{CH}_2$), 5.55 (1H, bs, OCHCH_2), 5.81-5.85 (1H, m, CHCHCH_2), 6.04-6.08 (1H, m, CHCHCH); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 18.4, 24.8, 28.1, 71.1, 124.2, 134.3; δ_{F} (376 MHz; CDCl_3 ; Me_4Si) -141.16 to -141.22 (m, 2F), -151.87 (t, $J = 20.7$, 1F), -163.06 to -163.21 (m, 2F). Anal. Calcd for $\text{C}_{13}\text{H}_9\text{F}_5\text{O}_2$: C, 53.44; H, 3.10. Found: C, 53.65; H, 2.97.



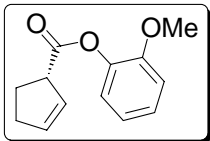
(S)-2-Cyclopentenyl benzoate (Table 2, entry 1).^{1b,3} It was obtained in a maximum of 70% ee. The optical purity was determined by HPLC on chiralcel OD column [hexane/2-propanol 99.9:0.1; flow rate 0.5 mL/min; $t_R = 26.82$ min (*S*), 32.35 min (*R*). $[\alpha]_D^{25} -136.2$ (*c* 0.9, CHCl₃) [lit.³ (93% ee); $[\alpha]_D^{17} -179.0$ (*c* 0.37, CHCl₃)].



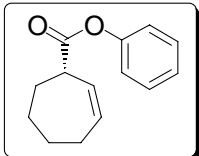
(S)-2-Cyclopentenyl-*p*-nitrobenzoate (Table 2, entry 2).^{2b} mp 78-80 °C (lit^{2b} mp 81-83 °C). It was obtained in a maximum of 62% ee. The optical purity was determined by HPLC on chiralpak AS-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; $t_R = 31.84$ min (*R*), 34.17 min (*S*); $[\alpha]_D^{25} -119.6$ (*c* 2.2 CHCl₃) [lit.^{2b} (82% ee); $[\alpha]_D^{25} -169.7$ (*c* 0.38 CHCl₃)].



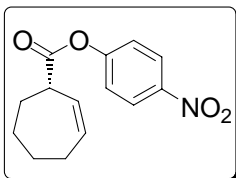
(S)-2-Cyclopentenyl-*p*-methoxybenzoate (Table 2, entry 3).³ It was obtained in a maximum of 77% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; $t_R = 20.74$ min (*R*), 22.51 min (*S*); $[\alpha]_D^{25} -158.8$ (*c* 2.4 CHCl₃) [lit.³ (68% ee); $[\alpha]_D^{19} -71$ (*c* 0.75 CHCl₃)].



(S)-2-Cyclopentenyl-*o*-methoxybenzoate (Table 2, entry 4). It was obtained in a maximum of 80% ee. The optical purity was determined by HPLC on chiralpak OD column [hexane/2-propanol 98.0:2.0]; flow rate 0.5 mL/min; $t_R = 21.62$ min (*S*), 29.70 min (*R*); $[\alpha]_D^{25} -140.8$ (c 3.9 CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3076, 2945, 1725, 1248, 1017, 757; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.95-2.78 (4H, m, $\text{CHCH}_2\text{CH}_2\text{CH}$), 3.89 (3H, s, OCH_3), 5.95-5.98 (2H, m), 6.13-6.15 (1H, m, CHCHCH), 6.94-6.98 (2H, m, Ar), 7.43-7.47 (1H, m, Ar), 7.75-7.80 (1H, m, Ar); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 29.7, 31.0, 55.8, 80.7, 111.9, 119.9, 120.4, 129.3, 131.3, 133.1, 137.4, 159.0, 165.9. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$: C, 71.54; H, 6.47. Found: C, 71.29; H, 6.63.

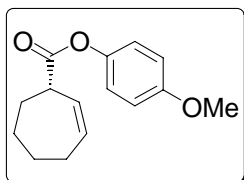


(S)-2-Cycloheptenyl benzoate (Table 2, entry 5).^{1a,1b} It was obtained in a maximum of 86% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3; flow rate 0.5 mL/min; $t_R = 15.70$ min (*R*), 16.37 min (*S*); $[\alpha]_D^{25} -57.8$ (c 0.6, CHCl_3) [lit.^{1a} (82% ee) $[\alpha]_D^{25} -38.2$ (c 1, CHCl_3)].

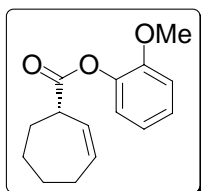


(S)-2-Cycloheptenyl-*p*-nitrobenzoate (Table 2, entry 6).^{2b} It was obtained in a maximum of 90% ee. The optical purity was determined by HPLC on chiralpak AD-H column

[hexane/2-propanol 98.0:2.0]; flow rate 0.5 mL/min; t_R = 23.31 min (*R*), 26.19 min (*S*); $[\alpha]_D^{25}$ -47.7 (*c* 2.2, CHCl₃) [lit.^{2b} (99% ee); $[\alpha]_D^{25}$ -63.1 (*c* 0.65 CHCl₃)].

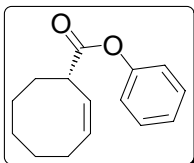


(*S*)-2-Cycloheptenyl-*p*-methoxybenzoate (Table 2, entry 7). It was obtained in a maximum of 94% ee. The optical purity was determined by HPLC on chiralpak AS-H column [hexane/2-propanol 99.7:0.3]; flow rate 0.5 mL/min; t_R = 22.93 min (*R*), 24.65 min (*S*); $[\alpha]_D^{25}$ -52.1 (*c* 3.2 CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3071, 3028, 2922, 1703, 1273, 1109, 1024, 766; δ_H (400 MHz; CDCl₃; Me₄Si) 1.29-2.56 (8H, m, cyclic 4 × CH₂), 3.86 (3H, s, OCH₃), 5.61-5.64 (1H, m, OCHCH₂), 5.70-5.90 (2H, m, CHCHCHCH₂), 6.91 (2H, d, J = 8.8 Hz, Ar), 8.01 (2H d, J = 8.8 Hz, Ar); δ_C (100 MHz; CDCl₃; Me₄Si) 26.4, 26.6, 28.5, 32.8, 55.4, 74.4, 113.4, 123.0, 131.5, 131.8, 133.6, 163.2, 165.6. Anal. Calcd for C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C, 72.90; H, 7.45.

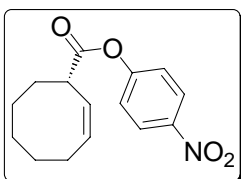


(*S*)-2-Cycloheptenyl-*o*-methoxybenzoate (Table 2, entry 8). It was obtained in a maximum of 91% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; t_R = 19.20 min (*R*), 22.46 min (*S*); $[\alpha]_D^{25}$ -42.0 (*c* 2.6 CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3074, 3027, 2930, 1722, 1252, 1079, 757; δ_H (400 MHz; CDCl₃; Me₄Si) 1.42-2.29 (8H, m, cyclic 4 × CH₂), 3.90 (3H, s, OCH₃), 5.63-5.66 (1H, m, OCHCH₂), 5.79-6.00 (2H, m, CHCHCHCH₂), 6.93-6.99 (2H, m, Ar), 7.44-7.48 (1H, m, Ar), 7.79 (1H, dd, J = 7.8 and 1.7 Hz, Ar); δ_C (100 MHz; CDCl₃; Me₄Si) 26.4, 26.6, 28.4,

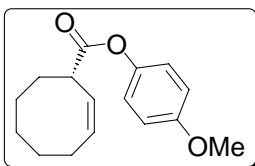
32.7, 55.8, 74.3, 111.9, 119.9, 120.5, 131.3, 131.7, 133.2, 133.5, 159.0, 165.4. Anal. Calcd for C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C, 73.30; H, 7.28.



(S)-2-cyclooctenyl benzoate (Table 2, entry 9).^{1a,1b} It was obtained in a maximum of 94% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3; flow rate 0.5 mL/min; t_R = 21.79 min (*S*), 12.63 min (*R*); $[\alpha]_D^{25} +86.5$ (c 1.2, CHCl₃) [lit.^{1a} (82% ee) $[\alpha]_D^{25} + 72.6^\circ$ (c 1.25, CHCl₃)].

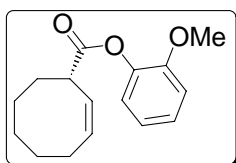


(S)-2-Cyclooctenyl-p-nitrobenzoate (Table 2, entry 10).^{2a} mp 80-83 °C (lit.^{2a} mp 85 °C); It was obtained in a maximum of 91% ee. The optical purity was determined by HPLC on chiralcel OD-H column [hexane/2-propanol 99.0:1.0]; flow rate 0.5 mL/min; t_R = 18.77 min (*R*), 22.32 min (*S*); $[\alpha]_D^{25} + 80.1$ (c 1.6, CHCl₃).

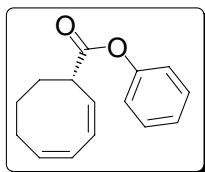


(S)-2-Cyclooctenyl-p-methoxybenzoate (Table 2, entry 11). It was obtained in a maximum of 96% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 95.0:5.0; flow rate 0.5 mL/min; t_R = 17.14 min (*S*), 19.47 min (*R*); $[\alpha]_D^{25} +88.6$ (c 1.6 CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3071, 3013, 2929, 1710, 1257, 1107, 1027, 772; δ_H (400 MHz; CDCl₃; Me₄Si) 1.41-1.74 (7H, m), 2.04-2.19 (2H, m), 2.29-2.36 (1H, m),

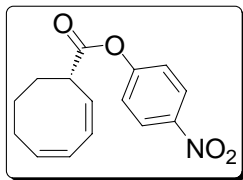
3.86 (3H, s, OCH₃), 5.59-5.63 (1H, m, OCHCH₂), 5.68-5.74 (1H, m, CHCHCH₂), 5.84-5.97 (1H, m, CHCHCH), 6.91 (2H, d, *J* = 8.8 Hz, Ar), 8.00 (2H, d, *J* = 8.8 Hz, Ar); δ_{C} (100 MHz; CDCl₃; Me₄Si) 23.4, 25.8, 26.3, 28.8, 35.1, 55.3, 72.6, 113.4, 123.1, 129.6, 130.8, 131.5, 163.2, 165.7. Anal. Calcd for C₁₆H₂₀O₃: C, 73.82; H, 7.74. Found: C, 73.60; H, 7.65.



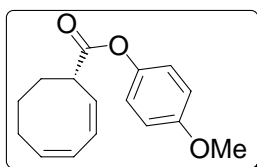
(S)-2-Cyclooctenyl-*o*-methoxybenzoate (Table 2, entry 12). It was obtained in a maximum of 92% ee. The optical purity was determined by HPLC on chiralpak AS-H column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; *t_R* = 11.06 min (*R*), 12.13 min (*S*); $[\alpha]_{\text{D}}^{25} + 82.1$ (*c* 1.4 CHCl₃); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3073, 3020, 2929, 1723, 1252, 1077, 756; δ_{H} (400 MHz; CDCl₃; Me₄Si) 1.20-1.73 (6H, m, cyclic 3 × CH₂), 2.05-2.35 (4H, m, cyclic 2 × CH₂) 3.89 (3H, s, OCH₃), 5.59-5.63 (1H, m, OCHCH₂), 5.67-5.74 (1H, m, CHCHCH₂), 5.88-5.92 (1H, m, CHCHCH), 6.95-6.99 (2H, m, Ar), 7.45 (1H, dt, *J* = 7.6 Hz, Ar), 7.79 (1H, dd, *J* = 7.4 Hz, Ar); δ_{C} (100 MHz; CDCl₃; Me₄Si) 23.4, 25.8, 26.3, 28.8, 35.0, 55.0, 72.6, 112.0, 120.0, 120.7, 129.7, 130.7, 131.3, 133.2, 159.1, 165.5. Anal. Calcd for C₁₆H₂₀O₃: C, 73.82; H, 7.74. Found: C, 73.59; H, 7.84.



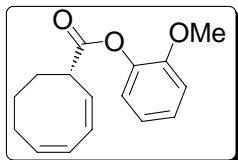
(S)-2,4-Cyclooctadienyl benzoate (Table 2, entry 13).^{1b} It was obtained in a maximum of 80% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 99.7:0.3; flow rate 0.5 mL/min; *t_R* = 17.71 min (*S*), 19.01 min (*R*): $[\alpha]_{\text{D}}^{25} - 132.0$ (*c* 0.6, CHCl₃).



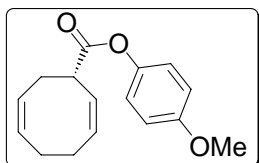
(S)-2,4-Cyclooctadienyl-*p*-nitrobenzoate (Table 2, entry 14).^{4,5} mp 100-103 °C (lit⁵ mp 112-113 °C). It was obtained in a maximum of 66% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/ 2-propanol 98.0:2.0]; flow rate 0.5 mL/min; $t_R = 39.83$ min (*S*), 42.27 min (*R*); $[\alpha]_D^{25} -76.3$ (*c* 2, CHCl₃).



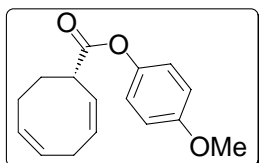
(S)-2,4-Cyclooctadienyl-*p*-methoxybenzoate (Table 2, entry 15).⁴ It was obtained in a maximum of 96% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; $t_R = 19.30$ min (*S*), 20.73min (*R*); $[\alpha]_D^{25} -118.0$ (*c* 2.6 CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3070, 3009, 2932, 1709, 1256, 1106, 1028, 772; δ_H (400 MHz; CDCl₃; Me₄Si) 1.48-1.70 (2H, m, CH₂CH₂CH₂), 1.87-1.95 (2H, m, CH₂CH₂CH), 2.02-2.10 (1H, m), 2.33-2.49 (1H, m), 3.86 (3H, s, OCH₃), 5.60-5.66 (2H, m), 5.75-5.81 (1H, m), 5.92-6.00 (2H, m), 6.91 (2H, d, $J = 8.8$ Hz, Ar), 8.01 (2H, d, $J = 8.8$ Hz, Ar); δ_C (100 MHz; CDCl₃; Me₄Si) 21.6, 28.3, 30.0, 55.4, 74.0, 113.5, 123.0, 125.8, 125.9, 131.1, 131.5, 133.0, 163.2, 165.5. Anal. Calcd for C₁₆H₁₈O₃: C, 74.39; H, 7.02. Found: C, 74.45; H, 7.08.



(S)-2,4-Cyclooctadienyl-*o*-methoxybenzoate (Table 2, entry 16).⁴ It was obtained in a maximum of 86% ee. The optical purity was determined by HPLC on chiralpak AS-H column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; t_R = 11.60 min (*R*), 12.61 min (*S*); $[\alpha]_D^{25}$ -64.2 (*c* 2.1 CHCl₃); $\nu_{\max}/\text{cm}^{-1}$ (film) 3075, 3009, 2934, 1722, 1252, 1078, 757; δ_H (400 MHz; CDCl₃; Me₄Si) 1.48-1.54 (1H, m), 1.58-1.70 (1H, m), 1.83-2.08 (3H, m), 2.32-2.40 (1H, m), 3.89 (3H, s, OCH₃), 5.60-5.67 (2H, m), 5.73-5.80 (1H, m), 5.91-5.99 (2H, m), 6.95-6.99 (2H, m, Ar), 7.43-7.48 (1H, m, Ar), 7.79 (1H, dd, J = 7.8 and 1.7 Hz, Ar); δ_C (100 MHz; CDCl₃; Me₄Si) 21.6, 28.2, 29.9, 55.8, 74.1, 111.9, 119.9, 120.5, 125.7, 125.9, 130.9, 131.3, 132.9, 133.2, 159.1, 165.2. Anal. Calcd for C₁₆H₁₈O₃: C, 74.39; H, 7.02. Found: C, 74.05; H, 7.14.

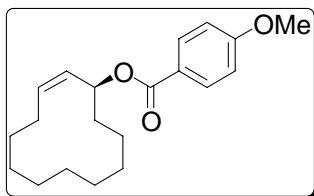


(S)-2,6-Cyclooctadienyl-*p*-methoxybenzoate (2a) (Table 3, entry 1).⁴ It was obtained in a maximum of 93% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; t_R = 18.67 min (*R*), 19.48 min (*S*).

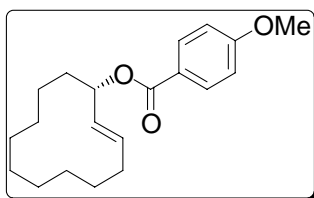


(S)-2,5-Cyclooctadienyl-*p*-methoxybenzoate (2b) (Table 3, entry 1).⁴ It was obtained in a maximum of 94% ee. The optical purity was determined by HPLC on chiralpak AD-H

column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; $t_R = 21.21$ min (*S*), 22.86 min (*R*).

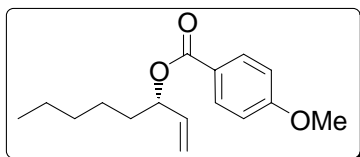


(*S, Z*)-2-Cycloaddodecenyl-*p*-methoxybenzoate (3a) (Table 4, entry 1).⁴ It was obtained in a maximum of 17% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; $t_R = 10.73$ min (*R*), 12.06 min (*S*); $[\alpha]_D^{25} -5.6$ (c 1.3 CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3075, 3003, 2929, 1711, 1251, 1075, 756; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.20-1.70 (12H, m), 1.78-1.84 (2H, m), 1.98-2.02 (1H, m), 2.15-2.21 (3H, m), 3.85 (3H, s, OCH_3), 5.44 (1H, td, $J = 10.6$ and 1.7 Hz, OCHCH_2), 5.55 (1H, td, $J = 11.2$ and 4.6 Hz, CHCHCH_2), 5.96 (1H, dt, $J = 13.6$, 6.8 Hz, CHCHCH), 6.90 (2H, d, $J = 9.0$ Hz, Ar), 7.99 (2H, d, $J = 9.0$ Hz, Ar). Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_3$: C, 75.91; H, 8.92. Found: C, 75.65; H, 9.02.



(*S, E*)-2-Cycloaddodecenyl-*p*-methoxybenzoate (3b) (Table 4, entry 2).⁴ It was obtained in a maximum of 57% ee. The optical purity was determined by HPLC on chiralpak AD-H column [hexane/2-propanol 95.0:5.0]; flow rate 0.5 mL/min; $t_R = 15.95$ min (*R*, major), 22.98 min (*S*, minor); $[\alpha]_D^{25} + 23.1$ (c 3.6 CHCl_3); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3074, 3002, 2931, 1721, 1251, 1076, 757; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 1.25-1.53 (12H, m), 1.57-1.61 (2H, m), 1.66-1.73 (1H, m), 1.84-1.92 (1H, m), 1.99-2.08 (1H, m), 2.22-2.28 (1H, m), 3.85 (3H, s, OCH_3), 5.41 (1H, td, $J = 8.8$ and 3.6 Hz, OCHCH_2), 5.51 (1H, dd, $J = 15.0$ and 8.3 Hz,

CHCHCH₂), 5.73-5.80 (1H, m, CHCHCH), 6.90 (2H, d, $J = 8.8$ Hz, Ar), 7.99 (2H, d, $J = 8.8$ Hz, Ar). Anal. Calcd for C₂₀H₂₈O₃: C, 75.91; H, 8.92. Found: C, 76.03; H, 9.01.



(S)-1-Octenyl-3-(*p*-methoxybenzoate) (4a) (Table 5, entry 1).⁴ It was obtained in a maximum of 31% ee. The optical purity was determined by HPLC on chiralcel OD column [hexane/2-propanol 99.9:0.1]; flow rate 0.5 mL/min; $t_R = 72.35$ min (*S*, major), 86.09 min (*R*, minor).

References and Notes

- (a) G. Sekar, A. DattaGupta and V. K. Singh, *J. Org. Chem.*, 1998, **63**, 2961-2967; (b) S. K. Ginotra and V. K. Singh, *Tetrahedron*, 2006, **62**, 3573-3581.
- (a) M. B. Andrus and X. Chen, *Tetrahedron*, 1997, **53**, 16229-16240; (b) M. B. Andrus and Z. Zhou, *J. Am. Chem. Soc.*, 2002, **124**, 8806-8807.
- K. Kawasaki and T. Katsuki, *Tetrahedron*, 1997, **53**, 6337-6350.
- The absolute stereochemistry is temporarily assigned based on other cyclic olefins.
- The compound (Table 2, entry 14) is known in the racemic form. For reference, see: T. Itoh, K. Jitsukawa, K. Kaneda and S. Teranishi, *J. Am. Chem. Soc.*, 1979, **101**, 159-169.