Supporting Information

Enantioselective Conjugate Radical Addition to α' -Hydroxy Enones

Sunggi Lee, Chae Jo Lim, Sunggak Kim,* Rajesh Subramaniam, Jake Zimmerman, and Mukund P. Sibi*

Center for Molecular Design & Synthesis and Department of Chemistry, School of Molecular Science (BK-21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea, and Department of Chemistry, North Dakota State University, Fargo, ND 58105

General. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometer. The chemical shifts in CDCl_3 reported in δ (ppm) relative to CDCl_3 or Me_4Si as an internal reference. Splitting patterns are designated as follows: br; broad, s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, dt; double of triplet, td; triple of doublet, dd; double of doublet. High resolution mass spectra were obtained on a VG AUTOSPEC Ultima GC/MS system using direct insertion probe (DIP) and electron impact (EI) (70 eV) method. Flash chromatography was carried out on Merck silica 60 (230-400 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F_{254} plates. Analytical high performance liquid chromatography (HPLC) was performed on Agilent 1100 Series equipped with a variable wavelength detector using a Chiralpak AD-H, Chiralcel OD-H, or OJ-H column (0.46 cm $\times$ 25 cm) from Daicel. Optical rotation was measured on Jasco p-1020 digital polarimeter.

Materials. All reagents were purchased from Aldrich Co. All dry solvents were freshly distilled under nitrogen from the appropriate drying agent before use. $\text{Mg}(\text{NTf}_2)_2$ was prepared by the previously reported procedure¹ and chiral ligands **3a-b**, **4**, **5b**, **6** were synthesized as previously known method.² (+)-2, 2'-isopropylidene-bis[(4R)-4-phenyl-2-oxazoline] **5a** and Al-Salen **6** were purchased from Aldrich Co. and used without purifications.

¹ Earle, M. J.; Hakala, U.; McAuley, B. J.; Nieuwenhuyzen, M.; Ramani, A.; Seddon, K. R. *Chem. Commun.* **2004**, 1368.

² For **3a-b**, **5b**: Sibi, M. P.; Ji, J. *J. Org. Chem.* **1997**, 62, 3800. For **4**: Porter, N. A.; Wu, J. H.; Zhang, G.; Reed, A. D. *J. Org. Chem.* **1997**, 62, 6702. For **6**: Davies, I. W.; Gerena, L.; Lu, N.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **1996**, 61, 9629.

Experimental Details

Preparation of α' -hydroxy enones

α' -Hydroxy enones **1**, **7a**, **10a**, and **10b** were prepared as previously described, starting from the corresponding aldehydes and 3-hydroxy-3-methyl-2-butanone.³ **7b** and **7d** were prepared from ethyl vinyl ether⁴ and **7c** was synthesized by hydroxylation of 4-phenyl-3-buten-2-one.⁵

(*E*)-2-hydroxy-2-methyl-7-phenylhept-4-en-3-one (**1a**)

MW: C₁₄H₁₈O₂ = 218.30; **¹H NMR** (CDCl₃, 400 MHz) δ 1.32 (s, 6H), 2.54-2.59 (m, 2H), 2.79 (t, *J*=7.9 Hz, 2H), 3.84 (br, 1H), 6.36 (dt, *J*=15.4, 1.2, 1H), 7.10-7.20 (m, 4H), 7.25-7.29 (m, 2H); **¹³C NMR** (CDCl₃, 100 MHz) δ 26.2, 34.2, 34.3, 75.1, 122.8, 126.2, 128.3, 128.4, 140.4, 149.4, 202.2; **HRMS** (M⁺) calcd for C₁₄H₁₈O₂: 218.1307, found 218.1309.

(*E*)-4-hydroxy-4-methyl-1-phenylpent-1-en-3-one (**7a**)

MW: C₁₂H₁₄O₂ = 190.24; **¹H NMR** (CDCl₃, 400 MHz) δ 1.44 (s, 6H), 3.76 (b, 1H), 7.03 (d, *J* = 15.7 Hz, 1H), 7.36-7.39 (m, 3H), 7.55-7.58 (m, 2H), 7.82 (d, *J* = 15.7, 2H); **¹³C NMR** (CDCl₃, 100 MHz) δ 26.4, 75.5, 118.4, 128.5, 128.9, 130.9, 134.2, 145.4, 202.4; **HRMS** (M⁺) calcd for C₁₂H₁₄O₂: 190.0994, found 190.0992.

(*E*)-1-(1-hydroxycyclopentyl)-3-phenylprop-2-en-1-one (**7b**)

To a stirred solution of ethyl vinyl ether (2.87 mL, 30 mmol) in THF (50 mL) was added *t*-butyllithium (1.7 M, 17.6 mL) in pentane dropwise at -78 °C. The mixture was warmed to -10 °C and the THF solution (30 mL) of cyclohexanone was added. After being stirred overnight at room temperature, the reaction mixture was acidified with methanolic HCl. With additional stirring for 2 h, the solvent was evaporated and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with sodium bicarbonate solution and brine and the combined organic layer was dried over MgSO₄. The crude product was distilled in vacuo to give the hydroxy ketone as an oil (918 mg, 24%) and enone **7b** was prepared from the hydroxy ketone by the known method³ to afford **7b** as a yellow oil (1.39 g, 90%).

MW: C₁₄H₁₆O₂ = 216.28; **¹H NMR** (CDCl₃, 400 MHz) δ 1.74-1.83 (m, 4H), 1.97-2.10 (m, 4H), 4.08 (s, 1H), 6.95 (d, *J* = 15.7 Hz, 1H), 7.37-

³ For **1**: Palomo, C.; Oiarbide, M.; Halder, R.; Kelso, M.; Gómez-Bengoa, E.; García, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 9188. For **7a**, **10a**, and **10b**: Palomo, C.; Oiarbide, M.; García, J. M.; González, A.; Arceo, E. *J. Am. Chem. Soc.* **2003**, *125*, 13942.

⁴ He, M.; Leslie, T. M.; Sinicropi, J. A. *Chem. Mater.* **2002**, *14*, 2393.

⁵ Barbee, T. R.; Albizati, K. F. *J. Org. Chem.* **1991**, *56*, 6764.

7.39(m, 3H), 7.55-7.57 (m, 2H), 7.83 (d, J = 15.7 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 25.7, 39.2, 86.3, 118.8, 128.5, 128.9, 130.8, 134.3, 144.9, 202.1; **HRMS** (M^+) calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$: 216.1150, found 216.1151.

(E)-1-hydroxy-4-phenylbut-3-en-2-one (7c)

To a stirred solution of 4-phenyl-3-buten-2-one (1.40 g, 9.57 mmol) and triethylamine (2.0 mL, 14.4 mmol) in dry dichloromethane (20 mL) was added dropwise trimethylsilyl triflate (2.25 mL, 12.4 mmol) at -10°C under N_2 . After being stirred for 15 min, the mixture was poured into aqueous NaHCO_3 solution and extracted with dichloromethane. The organic layer was dried over MgSO_4 and concentrated under reduced pressure. The resulting residue was used without further purification.

To a slurry of *m*-CPBA (2.66 g, 11.9 mmol) in pentane (20 mL) was added a solution of the crude product in pentane (10 mL) at -15°C under N_2 atmosphere. The reaction mixture was stirred for over 2 h at room temperature and filtered through a glass filter. The filtrate was evaporated and methanol was added to the reaction mixture. With additional 2 h stirring at room temperature, the solvent was evaporated and the residue was purified by flash column chromatography (ethyl acetate/*n*-hexane = 1/20) to afford **7c** as a yellow solid (1.10 g, 71%).

MW: $\text{C}_{10}\text{H}_{10}\text{O}_2$ = 162.19; ^1H NMR (CDCl_3 , 400 MHz) δ 2.68(b, 1H), 4.52 (s, 2H), 6.74 (d, J = 16.2 Hz, 1H), 7.38-7.42 (m, 3H), 7.54-7.56 (m, 2H), 7.66 (d, J = 16.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 67.0, 121.3, 128.5, 129.1, 131.1, 133.9, 144.2, 198.0; **HRMS** (M^+) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: 162.0681, found 162.0688.

(E)-1-hydroxy-1,1,4-triphenylbut-3-en-2-one (7d)

The enone **7d** was similarly prepared from benzophenone by employing the procedure to prepare **7b**. **MW:** $\text{C}_{22}\text{H}_{18}\text{O}_2$ = 314.38; ^1H NMR (CDCl_3 , 400 MHz) δ 5.21 (s, 1H), 7.00 (d, J = 15.7 Hz, 1H), 7.33-7.40 (m, 9H), 7.43-7.46 (m, 6H), 7.84 (d, J = 15.7 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 84.6, 120.8, 128.2, 128.3, 128.5, 128.7, 128.9, 131.0, 134.1, 141.6, 144.9, 198.1; **HRMS** (M^+) calcd for $\text{C}_{22}\text{H}_{18}\text{O}_2$: 314.1307, found 314.1304.

(E)-1-(4-chlorophenyl)-4-hydroxy-4-methylpent-1-en-3-one (10a)

MW: $\text{C}_{12}\text{H}_{13}\text{ClO}_2$ = 224.68; ^1H NMR (CDCl_3 , 400 MHz) δ 1.44 (s, 6H), 3.66 (br, 1H), 6.99 (d, J = 15.7 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 15.7 Hz, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 26.4, 75.6, 118.8, 129.3,

129.7, 132.7, 136.9, 144.0, 202.3; **HRMS** (M^+) calcd for $C_{12}H_{13}ClO_2$: 224.0604, found 224.0604.

(E)-4-hydroxy-1-(4-methoxyphenyl)-4-methylpent-1-en-3-one (10b)

MW: $C_{13}H_{16}O_3$ = 220.26; **1H NMR** ($CDCl_3$, 400 MHz) δ 1.42 (s, 6H), 3.81 (s, 3H), 6.86-6.90 (m 3H), 7.52 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 15.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.5, 55.4, 75.3, 114.4, 115.9, 126.9, 130.4, 145.3, 162.0, 202.3; **HRMS** (M^+) calcd for $C_{13}H_{16}O_3$: 220.1099, found 220.1100.

Typical procedure for reductive alkylation of α' -hydroxy enone : A chiral ligand (0.033 mmol) and Lewis acid (0.030 mmol) were dissolved in CH_2Cl_2 (1 mL) in a fume-dried tube under N_2 atmosphere. After being stirred at room temperature for 2 h, a CH_2Cl_2 solution of α' -hydroxy enone (0.100 mmol) was added via cannula. With additional stirring for 1 h, the reaction mixture was cooled down to $-78^\circ C$. To the chilled solution, alkyl iodide (1.0 mmol), tributyltin hydride (0.4 mmol), triethylborane (0.3 mmol), and oxygen were added sequentially. The reaction was monitored by TLC, and after completion, the solvent was evaporated under reduced pressure and the residue was filtered through a short column of KF/silica gel (1/9 w/w) to remove organotin residue.⁶ The filtrate was concentrated and was subjected to a silica gel column chromatography using ethyl acetate and *n*-hexane as eluents to give the alkylated product. Racemic standards were prepared using $Yb(OTf)_3$ as a Lewis acid in the absence of a chiral ligand.

2-hydroxy-2,6,6-trimethyl-5-phenethylheptan-3-one (2a)

MW: $C_{18}H_{28}O_2$ = 276.41; **1H NMR** ($CDCl_3$, 400 MHz) δ 0.85 (s, 9H), 1.20-1.28 (m, 1H), 1.41 (s, 6H), 1.81-1.89 (m, 1H), 2.00-2.06 (m, 1H), 2.39 (dd, J = 18.9, 6.2 Hz, 1H), 2.44-2.56 (m, 2H), 2.71 (dd, J = 18.9, 4.5 Hz, 1H), 3.79 (br, 1H), 7.12-7.17 (m, 3H), 7.23-7.27 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 27.1 (2C), 27.4, 33.4, 34.1, 35.5, 37.7, 42.1, 76.4, 125.8, 128.2, 128.3, 142.6, 214.2; **HRMS** (M^+) calcd for $C_{18}H_{28}O_2$: 276.2089, found 276.2089; HPLC t_r (major) 9.1 min; t_r (minor) 10.9 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 95/5, 0.5 mL/min], 75% ee.

2-hydroxy-2,6-dimethyl-5-phenethylheptan-3-one (2b)

MW: $C_{17}H_{26}O_2$ = 262.39; **1H NMR** ($CDCl_3$, 400 MHz) δ 0.85 (d, J = 6.9 Hz, 6H), 1.36 (s, 6H), 1.39-1.49 (m, 1H), 1.57-1.66 (m,

⁶ Harrowven, D. C; Guy, I. L. *Chem. Commun.* **2004**, 1968.

1H), 1.73-1.80 (m, 1H), 2.02-2.09 (m, 1H), 2.41 (dd, J = 17.9, 7.1 Hz, 1H), 2.49-2.62 (m, 3H), 7.13-7.18 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 18.5, 19.3, 26.6, 26.7, 29.4, 33.3, 34.0, 37.0, 38.6, 76.3, 125.8, 128.3, 128.4, 142.4, 214.4; **HRMS** (M^+) calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: 262.1933, found 262.1939; HPLC t_r (major) 51.2 min; t_r (minor) 54.1 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 99/1, 0.2 mL/min], 68% ee.

2-hydroxy-2-methyl-5-phenethyloctan-3-one (2c)

MW: $\text{C}_{17}\text{H}_{26}\text{O}_2$ = 262.39; ^1H NMR (CDCl_3 , 400 MHz) δ 0.88 (t, J = 6, 7 Hz, 3H), 1.27-1.35 (m, 4H), 1.35 (s, 6H), 1.53-1.62 (m, 2H), 2.08-2.14 (m, 1H), 2.50 (d, J = 6.5 Hz, 2H), 2.55-2.60 (m, 2H), 3.77 (br, 1H), 7.14-7.18 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.3, 19.7, 26.5 (2C), 33.0, 33.2, 35.8, 36.0, 40.3, 76.2, 125.8, 128.2, 128.3, 142.4, 214.2; **HRMS** (M^+) calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2$: 262.1933, found 262.1934; HPLC t_r (minor) 13.5 min; t_r (major) 14.9 min [Chiralcel OJ-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 95/5, 0.5 mL/min], 72% ee.

5-ethyl-2-hydroxy-2-methyl-7-phenylheptan-3-one (2d)

MW: $\text{C}_{16}\text{H}_{24}\text{O}_2$ = 248.36; ^1H NMR (CDCl_3 , 400 MHz) δ 0.88 (t, J = 7.5 Hz, 3H), 1.33-1.41 (m, 8H), 1.53-1.62 (m, 2H), 2.03-2.06 (m, 1H), 2.50 (dd, J = 6.4, 4.6 Hz, 2H), 2.55-2.59 (m, 2H), 3.80 (br, 1H), 7.14-7.18 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 10.7, 26.1, 26.5, 33.2, 34.5, 35.3, 39.9, 76.2, 125.8, 128.2, 128.3, 142.4, 214.2; **HRMS** (M^+) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2$: 248.1776, found 248.1775; HPLC t_r (minor) 16.2 min; t_r (major) 18.1 min [Chiralcel OJ-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 95/5, 0.5 mL/min], 72% ee.

2-hydroxy-2,6,6-trimethyl-5-phenylheptan-3-one (8a)

MW: $\text{C}_{16}\text{H}_{24}\text{O}_2$ = 248.36; ^1H NMR (CDCl_3 , 400 MHz) δ 0.89 (s, 9H), 1.10 (s, 3H), 1.33 (s, 3H), 2.72-2.84 (m, 1H), 3.08-3.20 (m, 2H), 3.56 (s, 1H), 7.12-7.17 (m, 3H), 7.21-7.24 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 26.3 (2C), 28.1, 33.5, 36.9, 50.6, 76.3, 126.3, 127.7, 129.2, 142.0, 213.3; **HRMS** (M^+) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2$: 248.1776, found 248.1768; HPLC t_r (major) 6.2 min; t_r (minor) 6.7 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 98/2, 1.0 mL/min], 78% ee.

2-hydroxy-2,6-dimethyl-5-phenylheptan-3-one (8b)

MW: $\text{C}_{15}\text{H}_{22}\text{O}_2$ = 234.33; ^1H NMR (CDCl_3 , 400 MHz) δ 0.73 (d, J = 6.7 Hz, 3H), 0.95 (d, J = 6.7 Hz, 3H), 1.02 (s, 3H), 1.30 (s, 3H), 1.83-

1.90 (m, 1H), 2.79-2.86 (m, 1H), 2.93-3.02 (m, 2H), 3.59 (br, 1H), 7.10-7.17 (m, 3H), 7.21-7.25 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 20.5, 21.0, 25.9, 26.1, 32.7, 40.0, 47.6, 76.2, 126.3, 128.1, 128.2, 143.2, 213.4; **HRMS** (M^+) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$: 234.1620, found 234.1628; HPLC t_r (major) 6.1 min; t_r (minor) 7.6 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 97/3, 1.0 mL/min], 78% ee.

2-hydroxy-2-methyl-5-phenyloctan-3-one (8c)

MW: $\text{C}_{15}\text{H}_{22}\text{O}_2$ = 234.33; ^1H NMR (CDCl_3 , 400 MHz) δ 0.84 (t, J = 7.3 Hz, 3H), 1.07 (s, 3H), 1.12-1.20 (m, 2H), 1.31 (s, 3H), 1.57 (q, J = 7.7 Hz, 2H), 2.73 (dd, J = 17.1, 6.6 Hz, 1H), 2.85 (dd, J = 17.1, 7.7 Hz, 1H), 3.22-3.27 (m, 1H), 7.14-7.18 (m, 3H), 7.24-7.27 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 13.9, 20.6, 25.8, 26.2, 38.2, 40.5, 43.3, 76.1, 126.4, 127.5, 128.4, 144.3, 213.2; **HRMS** (M^+) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$: 234.1620, found 234.1625; HPLC t_r (major) 8.4 min; t_r (minor) 10.0 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 98/2, 1.0 mL/min], 86% ee.

2-hydroxy-2-methyl-5-phenylheptan-3-one (8d)

MW: $\text{C}_{14}\text{H}_{20}\text{O}_2$ = 220.31; ^1H NMR (CDCl_3 , 400 MHz) δ 0.78 (t, J = 7.3 Hz, 3H), 1.07 (s, 3H), 1.31 (s, 3H), 1.55-1.69 (m, 2H), 2.75 (dd, J = 17.1, 6.5 Hz, 1H), 2.85 (dd, J = 17.1, 7.7 Hz, 1H), 3.09-3.17 (m, 1H), 3.64 (s, 1H), 7.13-7.19 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 12.0, 25.8, 26.1, 28.9, 42.5, 42.9, 76.1, 126.4, 127.5, 128.4, 144.0, 213.2; **HRMS** (M^+) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$: 220.1463, found 220.1452; HPLC t_r (major) 8.4 min; t_r (minor) 9.7 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 97/3, 1.0 mL/min], 80% ee.

1-cyclohexyl-4-hydroxy-4-methyl-1-phenylpentan-3-one (8e)

MW: $\text{C}_{18}\text{H}_{26}\text{O}_2$ = 274.40; ^1H NMR (CDCl_3 , 400 MHz) δ 0.74-0.83 (m, 1H), 0.91-1.00 (m, 1H), 1.02 (s, 3H), 1.04-1.12 (m, 2H), 1.17-1.26 (m, 1H), 1.29 (s, 3H), 1.41-1.52 (m, 2H), 1.60-1.63 (m, 2H), 1.72-1.83 (m, 2H), 2.83-3.96 (m, 2H), 3.00-3.04 (m, 1H), 3.58 (s, 1H), 7.09-7.16 (m, 3H), 7.21-7.25 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 25.9, 26.2, 26.3, 26.4, 30.9, 31.3, 39.7, 42.4, 46.7, 76.2, 126.3, 128.1, 128.3, 143.4, 213.5; **HRMS** (M^+) calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2$: 274.1933, found 274.1928; HPLC t_r (major) 6.4 min; t_r (minor) 7.6 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 97/3, 1.0 mL/min], 67% ee.

1-(1-hydroxycyclopentyl)-4,4-dimethyl-3-phenylpentan-1-one (9a)

MW: $C_{18}H_{26}O_2 = 274.40$; **1H NMR** ($CDCl_3$, 400 MHz) δ 0.88 (s, 9H), 1.24-1.31 (m, 1H), 1.63-1.92 (m, 7H), 2.74-2.82 (m, 1H), 3.06-3.16 (m, 2H), 3.54 (s, 1H), 7.12-7.17 (m, 3H), 7.20-7.24 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 25.2 (2C), 28.1, 33.6, 37.2, 38.4, 38.8, 50.9, 87.1, 126.3, 127.7, 129.2, 142.1, 213.0; **HRMS** (M^+) calcd for $C_{18}H_{26}O_2$: 274.1933, found 274.1936; HPLC t_r (major) 16.6 min; t_r (minor) 18.3 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 99/1, 0.5 mL/min], 71% ee.

1-hydroxy-5,5-dimethyl-4-phenylhexan-2-one (9b)

MW: $C_{14}H_{20}O_2 = 220.31$; **1H NMR** ($CDCl_3$, 400 MHz) δ 0.86 (s, 9H), 2.73 (dd, $J = 15.6, 3.5$ Hz, 1H), 2.91 (dd, $J = 15.5, 11.2$ Hz, 1H), 3.02 (dd, $J = 11.2, 3.6$ Hz, 1H), 3.88 (d, $J = 18.9$ Hz, 1H), 4.13 (d, $J = 18.9$ Hz, 1H), 7.10-7.12 (m, 2H), 7.16-7.26 (m, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 27.9, 33.7, 39.8, 51.3, 68.8, 126.7, 127.9, 129.1, 141.1, 209.3; **HRMS** (M^+) calcd for $C_{14}H_{20}O_2$: 220.1463, found 220.1458; HPLC t_r (minor) 15.4 min; t_r (major) 26.0 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 97/3, 1.0 mL/min], 73% ee.

1-hydroxy-5,5-dimethyl-1,1,4-triphenylhexan-2-one (9c)

MW: $C_{26}H_{28}O_2 = 372.50$; **1H NMR** ($CDCl_3$, 400 MHz) δ 0.74 (s, 9H), 2.81 (dd, $J = 17.9, 2.7$ Hz, 1H), 2.99 (dd, $J = 11.1, 2.7$ Hz, 1H), 3.23 (dd, $J = 17.9, 11.1$ Hz, 1H), 4.42 (s, 1H), 6.97-7.03 (m, 4H), 7.16-7.34 (m, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 28.0, 33.5, 39.1, 50.7, 85.6, 126.2, 127.6, 128.0, 128.1 (2C), 128.2, 128.3, 141.3, 141.7, 209.9; **HRMS** (M^+) calcd for $C_{26}H_{28}O_2$: 372.2089, found 372.2083; HPLC t_r (minor) 9.5 min; t_r (major) 12.3 min [Chiralcel AD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 97/3, 1.0 mL/min], 2% ee.

5-(4-chlorophenyl)-2-hydroxy-2,6,6-trimethylheptan-3-one (11a)

MW: $C_{16}H_{23}ClO_2 = 282.81$; **1H NMR** ($CDCl_3$, 400 MHz) δ 0.87 (s, 9H), 1.12 (s, 3H), 1.32 (s, 3H), 2.77-2.82 (m, 1H), 3.06-3.11 (m, 2H), 3.47 (s, 1H), 7.07 (dd, $J = 6.6, 1.9$ Hz, 2H), 7.19 (dd, $J = 6.6, 1.9$ Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 26.3, 26.4, 28.0, 33.5, 36.8, 49.9, 76.3, 127.8, 130.5, 132.1, 140.6, 213.0; **HRMS** (M^+) calcd for $C_{16}H_{23}ClO_2$: 282.1387, found 282.1386; HPLC t_r (minor) 6.1 min; t_r (major) 6.6 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 98/2, 1.0 mL/min], 81% ee.

2-hydroxy-5-(4-methoxyphenyl)-2,6,6-trimethylheptan-3-one (11b)

MW: C₁₇H₂₆O₃ = 278.39; **¹H NMR** (CDCl₃, 400 MHz) δ 0.87 (s, 9H), 1.10 (s, 3H), 1.32 (s, 3H), 2.74 (dd, J = 15.6, 1.4 Hz, 1H), 3.04-3.14 (m, 2H), 3.58 (s, 1H), 3.75 (s, 3H), 6.76 (dd, J = 6.7, 2.1 Hz, 2H), 7.04 (dd, J = 6.7, 2.1 Hz, 2H); **¹³C NMR** (CDCl₃, 100 MHz) δ 26.3, 28.1, 33.6, 37.0, 49.8,

55.1, 76.3, 113.0, 130.0, 134.1, 158.0, 213.4; **HRMS** (M⁺) calcd for C₁₇H₂₆O₃: 278.1882, found 278.1887; HPLC t_r(minor) 7.1 min; t_r(major) 7.8 min [Chiralcel OD-H (0.46 cm x 25 cm) (from Daicel Chemical Ind., Ltd.) *n*-hexane/*i*-PrOH, 98/2, 1.0 mL/min], 66% ee.

4-methyl-3-phenylpentanoic acid

To a stirred solution of the α -hydroxy ketone **8b** (47.2 mg, 0.20 mmol) in methanol (0.5 mL) was added a solution of sodium periodate (428.0 mg, 2.0 mmol) in H₂O (5.0 mL). After complete addition, the reaction mixture was stirred at room temperature until all the starting material was consumed. Methanol was removed under reduced pressure and CH₂Cl₂ and 10% aqueous HCl were added. The aqueous layer was extracted with CH₂Cl₂ several times. The combined organic layer was dried over anhydrous MgSO₄, concentrated and gave the desired product (*R*)-4-methyl-3-phenylpentanoic acid (37.1 mg, 96%). Optical rotation : $[\alpha]_D^{23}$ = +28.12 (c=1.855 CHCl₃) {Lit⁷ data for *R* isomer (97% ee): $[\alpha]_D^{20}$ = +33.54 (c=2.755 CHCl₃)}.

MW: C₁₂H₁₆O₂ = 192.25; **¹H NMR** (CDCl₃, 400 MHz) δ 0.74 (d, J = 6.7 Hz, 3H), 0.91 (d, J = 6.7 Hz, 3H), 1.81-1.87 (m, 1H), 2.59 (dd, J = 15.5, 9.5 Hz, 1H), 2.77 (dd, J = 15.5, 9.5 Hz, 1H), 2.82-2.88 (m, 1H), 7.11-7.27 (m, 5H); **¹³C NMR** (CDCl₃, 100 MHz) δ 20.1, 20.5, 33.1, 38.1, 48.4, 126.4, 128.1, 128.2, 142.5, 178.9; **HRMS** (M⁺) calcd for C₁₂H₁₆O₂: 192.1150, found 192.1154.

⁷ Sibi, M. P.; Ji, J. *J. Org. Chem.* **1997**, 62, 3800.

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8b