Supporting information

Pyrones to Pyrans: Enantioselective Radical Additions to Acyloxy Pyrones

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General: Dichloromethane and tetrahydrofuran were obtained from a Solv-Tech solvent system. Magnesium perchlorate, magnesium triflimide, scandium triflate and aluminum salen catalyst **9** were purchased from Aldrich chemicals. Cyclopropyl bisoxazoline ligand {3aS-[2(3'aR, 8'aS), 3aa, 8aa]}-2,2'-(cyclopropylidene)-bis{3a,8a-dihydro-8H-indeno[1,2d]-oxazole} was prepared according to literature procedure. Flash chromatography was performed using a Combiflash Companion (Isco) chromatography system with Analogix disposable flash chromatography columns. Reactions with air sensitive materials were carried out by standard syringe techniques.

Melting points were measured with a Fisher-Johns melting points apparatus and are uncorrected. ¹H-NMR were recorded on a Varian Unity/Inova-500 NB (500 MHz) or Varian Unity/Inova-400 NB (400 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using residual CDCl₃ (7.27 ppm) as an internal standard. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant and integration. ¹³C-NMR was recorded in a Varian Unity/Inova-500 NB (125 MHz) or Varian Unity/Inova-400 NB (100 MHz) spectrometers, using broadband proton decoupling. Chemical shifts are reported in parts per million (ppm) downfield from TMS, using the middle resonance of CDCl₃ (77.0) as an internal standard. HPLC analyses were carried out on Waters 515 HPLC pump and a 2487 dual λ absorbance detector connected to a PC with Millennium workstation. Rotation were recorded on a JASCO-DIP-370 instrument. High Resolution Mass Spectra (HRMS) (EI+) were obtained from Mass Spectrometry Laboratory, North Dakota State University.

Procedure for the synthesis of starting pyrones:

Pyromeconic acid was synthesized according to a literature procedure.¹ Pyrone **4a** was prepared by adding NaH (5.2 mmol, 60% in oil) to a solution of pyromeconic acid (5.0 mmol) in THF (20 mL). The previous mixture was stirred for 30 min. and then benzyl bromide (5.5 mmol) was added via syringe and allowed to stir 5 h. The reaction mixture was quenched with sat. NH₄Cl (1 mL) and THF was evaporated. The crude mixture was purified by column chromatography.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (2:1) as eluent to yield 0.71 g of **4a**. 70% yield; mp: 71-73 °C; IR (cm⁻¹) 3081, 3035, 2944, 2877, 1640, 1616, 1571; ¹H NMR (CDCl₃, 500 MHz) δ 5.06 (s, 2H), 6.41 (d, *J* = 6.0 Hz, 1H), 7.30-7.39 (m, 5H), 7.54 (s, 1H), 7.65 (d, *J* = 6.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 72.1, 117.0, 128.0, 128.6, 128.9, 135.9, 142.5, 148.1, 154.5, 174.4; HRMS Exact mass calcd for C₁₂H₁₀O₃Na [M + Na]⁺: 225.0522; Found: 225.0528.

Pyrone **4b** was prepared by adding acetyl chloride (10.2 mmol) to a solution of pyromeconic acid (10.0 mmol) and pyridine (10.2 mmol) in CH₂Cl₂ (40 mL) at 0°C. The solution was allowed to warm to room temp. and stirred for 2 h. The resulting mixture was diluted with CH₂Cl₂ and washed with water, 1 M HCl, brine and dried over MgSO₄. The crude product was purified by chromatography on silica gel using hexane/EtOAc (2:1) as eluent to yield 1.2 g of **4b**. 80% yield; IR (cm⁻¹) 3087, 1767, 1657, 1627; ¹H NMR (CDCl₃, 500 MHz) δ 2.32 (s, 3H), 6.48 (d, *J* = 6.0 Hz, 1H), 7.74 (d, *J* = 6.0 Hz, 1H), 7.89 (s, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 20.6, 118.1, 142.1, 148.7, 155.2, 167.9, 172.3; HRMS Exact mass calcd for C₇H₆O₄Na [M + Na]⁺: 177.0158; Found: 177.0141.

Pyrone **4c** was prepared in the same way as **4b** (using pivaloyl chloride). The crude product was purified by chromatography on silica gel using hexane/EtOAc (3:1) as eluent to yield 1.7 g of **4c**. 85% yield; mp: 105-108°C; IR (cm⁻¹) 3085, 2977, 2939, 1760, 1665, 1634; ¹H

NMR (CDCl₃, 400 MHz) δ 1.33 (s, 9H), 6.42 (d, J = 5.6 Hz, 1H), 7.71 (d, J = 5.6 Hz, 1H), 7.81 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 27.3, 39.4, 118.0, 142.4, 148.3, 155.0, 172.3, 175.8; HRMS Exact mass calcd for C₁₀H₁₂O₄Na [M + Na]⁺: 219.0628; Found: 219.0625.

Pyrones **10** and **11** were prepared by adding pivaloyl chloride (20 mmol) to a solution of kojic acid (purchased from TCI) (10.0 mmol) and pyridine (22 mmol) in CH₂Cl₂ (100 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 4 h. The resulting mixture was diluted with CH₂Cl₂ and washed with water, 1 M HCl, brine and dried over MgSO₄. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (3:1) as eluent to yield 1.0 g of **10** and 1.4 g of **11**.

10: mp: 92-94 °C; IR (cm⁻¹) 3442, 3072, 2977, 2935, 1758, 1650, 1613; ¹H NMR (CDCl₃, 400 MHz) δ 1.33 (s, 9H), 4.57 (s, 2H), 6.49 (s, 1H), 7.80 (s, 1H), ¹³C NMR (CDCl₃, 100 MHz) δ 27.3, 39.4, 61.0, 113.3, 141.5, 147.7, 168.2, 173.2, 176.0; HRMS Exact mass calcd for C₁₁H₁₄O₅Na [M + Na]⁺: 249.0733; Found: 249.0734.

11: mp: 95-97 °C; IR (cm⁻¹) 3080, 2979, 2939, 2875, 1764, 1755, 1661, 1638; ¹H NMR (CDCl₃, 400 MHz) δ 1.22 (s, 9H), 1.32 (s, 9H), 4.88 (s, 2H), 6.41 (s, 1H), 7.80 (s, 1H), ¹³C NMR (CDCl₃, 100 MHz) δ 27.26, 27.33, 39.1, 39.4, 61.1, 114.9, 141.7, 147.7, 162.9, 172.5, 175.8, 177.5; HRMS Exact mass calcd for C₁₆H₂₂O₆Na [M + Na]⁺: 333.1309; Found: 333.1310.

Representative experimental procedure for chiral Lewis acid catalyzed conjugate addition of radicals to pyrones. Under N₂, a mixture of Lewis acid (0.06 mmol) and ligand (0.06 mmol) in CH₂Cl₂ (1.0 mL) was stirred at rt for 45 min. Pyrone (0.20 mmol) (dissolved in 1 mL CH₂Cl₂) was added and the mixture was allowed to stir for 30 min and then cooled to -78 °C. For reactions using catalysts **8** and **9**, the starting pyrone and **8** or

9 were weighed together into a vial, stirred at room temp. for 30 min., cooled to $-78\text{ }^{\circ}\text{C}$ and then initiated as follows. When catalyst **9a**-NTf₂ was used (Table 4), **9** (0.1 mmol) and AgNTf₂ (0.1 mmol) were weighed into a vial and stirred in methylene chloride (1 mL) for 30-45 min. Next, the catalyst mixture was drawn up into a syringe and filtered through a nalgene syringe filter into a vial containing the starting pyrone dissolved in 1mL of methylene chloride. The reaction was then initiated by sequential addition of 2-iodo propane (or other radical precursors = RX) (1.0 mmol), *n*-Bu₃SnH (0.60 mmol), Et₃B (0.80 mmol; 1 M solution in hexanes) and oxygen (introduced via syringe). Products **5g**, **12d** and **12h** were prepared using the corresponding tertiary alkyl bromide. The addition trapping reactions (with allyl stannane) were conducted exactly the same as above except tetraallyltin was used in place of tributyltin hydride. The reaction was monitored by TLC (10-30% EtOAc in hexane) and when judged complete was quenched with silica gel, concentrated, washed with hexanes and extracted with ether. The ether extract was concentrated over silica gel and purified by silica gel chromatography (hexane-ethyl acetate) to give the products (**5b-13b**). The reaction procedure for standard racemic reactions is the same as above with the following modification. Racemic standards were prepared using Yb(OTf)₃ as a Lewis acid in the absence of a chiral ligand and methylene chloride:tetrahydrofuran (2:1) as a solvent.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 39 mg of **5b** and **6b** as an inseparable mixture of isomers (colorless oil). The enantiomeric purity for major product **5b** was determined by HPLC (254 nm, 25 °C) t_R 95.7 min (major);

t_R 102.2 min (minor) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 97/3, 1.0 mL/min] as 49% ee. Diastereomeric ratio (determined by 500 MHz 1H NMR): 99:1; IR (cm^{-1}) 2970, 2935, 2877, 1740, 1679, 1590; Major **5b**: 1H NMR ($CDCl_3$, 500 MHz) δ 0.97 (d, $J = 7.0$ Hz, 3H), 1.10 (d, $J = 7.0$ Hz, 3H), 1.96-2.11 (m, 1H), 2.12 (s, 3H), 3.96 (dd, $J = 7.5$ Hz, 2.0 Hz, 1H), 5.40 (dd, $J = 2.0$ Hz, 1.5 Hz, 1H), 5.48 (dd, $J = 6.0$ Hz, 1.5 Hz, 1H), 7.45 (d, $J = 6.0$ Hz, 1H); Minor **5b**: 1H NMR ($CDCl_3$, 500 MHz) δ 0.99 (d, $J = 7.0$ Hz, 3H), 1.02 (d, $J = 7.0$ Hz, 3H), 1.96-2.11 (m, 1H), 2.23 (s, 3H), 2.50 (dd, $J = 17.0$ Hz, 8.0 Hz, 1H), 2.67 (dd, $J = 15.0$ Hz, 2.0 Hz, 1H), 4.28 (ddd, $J = 11.5$ Hz, 5.5 Hz, 3.5 Hz, 1H), 7.40 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) (**5b**) δ 18.4, 19.1, 27.2, 28.2, 69.0, 86.6, 105.8, 163.9, 176.8, 187.3; HRMS Exact mass calcd for $C_{10}H_{14}O_4Na$ [$M + Na$] $^+$: 221.0782; Found: 221.0782.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 39 mg of **5c** as a colorless oil; 80% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 $^{\circ}C$) t_R 19.6 min (minor); t_R 23.7 min (major) [Chiralcel ODH (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99/1, 0.5 mL/min] as 70% ee. $[\alpha] = -12.8$ (c 1.0, $CHCl_3$). Diastereomeric ratio (determined by 400 MHz 1H NMR): 99:1; IR (cm^{-1}) 2970, 2935, 2877, 1740, 1679, 1590; 1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (d, $J = 6.8$ Hz, 3H), 1.07 (d, $J = 6.8$ Hz, 3H), 1.18 (s, 9H), 1.98-2.08 (m, 1H), 3.94 (dd, $J = 9.6$ Hz, 2.4 Hz, 1H), 5.33 (dd, $J = 2.4$ Hz, 1.2 Hz, 1H), 5.44 (dd, $J = 6.0$ Hz, 1.2 Hz, 1H), 7.42 (d, $J = 6.0$ Hz, 1H); The minor product **6c** could not be completely separated from **5c**; 1H NMR ($CDCl_3$, 500 MHz) (**6c**) δ 0.99 (d, $J = 2.5$ Hz, 3H), 1.01 (d, $J = 2.5$ Hz, 3H), 1.30 (s, 9H),

1.96-2.05 (m, 1H), 2.47 (dd, $J = 17.0$ Hz, 4.0 Hz, 1H), 2.67 (dd, $J = 14.5$ Hz, 2.5 Hz, 1H), 4.28 (ddd, $J = 9.5$ Hz, 5.5 Hz, 3.5 Hz, 1H), 7.35 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) (**5c**) δ 18.2, 19.2, 27.2, 28.3, 39.2, 68.8, 86.8, 105.5, 163.7, 176.8, 187.3; HRMS Exact mass calcd for $\text{C}_{13}\text{H}_{20}\text{O}_4\text{Na}$ $[\text{M} + \text{Na}]^+$: 263.1254; Found: 263.1255.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 40 mg of **5d** as a colorless oil; 74% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) for minor **6d** t_R 26.5 min (major); t_R 29.6 min (minor) as 36% ee; for **5d** t_R 26.1 min (minor); t_R 32.2 min (major) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 1.0 mL/min] as 76% ee. $[\alpha] = -4.2$ (c 0.5, CHCl_3). Diastereomeric ratio (determined by 400 MHz ^1H NMR): 99:1; IR (cm^{-1}) 2960, 2927, 2871, 1742, 1683, 1590; ^1H NMR (CDCl_3 , 400 MHz) δ 1.19 (s, 9H), 1.52-1.93 (m, 8H), 2.17-2.29 (m, 1H), 4.09 (dd, $J = 10.0$ Hz, 2.4 Hz, 1H), 5.31 (dd, $J = 2.4$ Hz, 1.2 Hz, 1H), 5.44 (dd, $J = 6.0$ Hz, 1.2 Hz, 1H), 7.40 (d, $J = 6.0$ Hz, 1H); The minor product **6d** could not be purely isolated from **5d**; ^1H NMR (CDCl_3 , 400 MHz) (**6d**) δ 1.30 (s, 9H), 1.52-1.69 (m, 6H), 1.70-1.77 (m, 1H), 1.84-1.90 (m, 1H) 2.16-2.25 (m, 1H), 2.55 (dd, $J = 17.0$ Hz, 3.5 Hz, 1H), 2.67 (dd, $J = 14.0$ Hz, 2.0 Hz, 1H), 4.28 (ddd, $J = 8.0$ Hz, 4.0 Hz, 1.5 Hz, 1H), 7.34 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) (**5d**) δ 25.2, 25.4, 26.8, 27.3, 28.8, 29.3, 30.0, 39.2, 69.9, 85.9, 105.6, 163.6, 176.8; HRMS Exact mass calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{Na}$ $[\text{M} + \text{Na}]^+$: 289.1410; Found: 289.1412.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 31 mg of **5e** as a colorless oil; 55% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 24.9 min (minor); t_R 33.0 min (major) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 93/7, 1.0 mL/min] as 70% ee. $[\alpha] = -12.5$ (c 1.0, CHCl_3). Diastereomeric ratio (determined by 400 MHz ^1H NMR): 99:1; IR (cm^{-1}) 2960, 2927, 2871, 1742, 1683, 1590; ^1H NMR (CDCl_3 ,

400 MHz) δ 1.20 (s, 9H), 1.50-1.90 (m, 10H), 2.04-2.14 (m, 1H), 4.06 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 5.33 (dd, J = 2.4 Hz, 1.2 Hz, 1H), 5.46 (dd, J = 6.0 Hz, 1.2 Hz, 1H), 7.44 (d, J = 6.0 Hz, 1H); The minor product **6e** could not be completely separated from **5e**; ^1H NMR (CDCl_3 , 400 MHz) (**6e**) δ 1.30 (s, 9H), 1.53-1.80 (m, 8H), 1.84-2.07 (m, 2H), 2.55 (dd, J = 17.0 Hz, 3.0 Hz, 1H), 2.67 (dd, J = 14.5 Hz, 2.0 Hz, 1H), 4.28 (ddd, J = 6.0 Hz, 5.5 Hz, 3.5 Hz, 1H), 7.35 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) (**5e**) δ 25.7, 25.8, 26.3, 27.3, 28.0, 29.4, 37.4, 39.3, 68.4, 85.7, 105.6, 163.9, 176.8, 187.4; HRMS Exact mass calcd for $\text{C}_{16}\text{H}_{24}\text{O}_4\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 303.1567; Found: 303.1571.

5f: $\text{C}_{14}\text{H}_{22}\text{O}_4$
Mol. Wt.: 254.32

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 38 mg of **5f** as a colorless oil; 76% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 20.8 min (minor); t_R 22.3 min (major) [Chiralcel ODH (0.46 cm x 25.0 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99/1, 0.5 mL/min] as 92% ee. $[\alpha]_D^{25} = -21.0$ (c 1.0, CHCl_3). Diastereomeric ratio (determined by 400 MHz ^1H NMR): 99:1; IR (cm^{-1}) 2964, 2937, 2875, 1737, 1683, 1598; ^1H NMR (CDCl_3 , 400 MHz) δ 1.04 (s, 9H), 1.15 (s, 9H), 3.93 (d, J = 2.4 Hz, 1H), 5.41 (dd, J = 2.4 Hz, 1.2 Hz, 1H), 5.45 (dd, J = 6.0 Hz, 1.2 Hz, 1H), 7.50 (d, J = 6.0 Hz, 1H); The minor product **6f** could not be completely separated isolated from **5f**; ^1H NMR (CDCl_3 , 400 MHz) (**6f**) δ 1.00 (s, 9H), 1.31 (s, 9H), 2.46 (dd, J = 16.5 Hz, 2.5 Hz, 1H), 2.66-2.72 (m, 1H), 3.52 (t, J = 6.5, 2H), 4.21 (dd, J = 10.5 Hz, 2.5 Hz, 1H), 7.21 (s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) (**5f**) δ 26.7, 27.1, 27.2, 34.4, 69.1, 88.5, 105.3, 164.3, 176.7, 187.2; HRMS Exact mass calcd for $\text{C}_{14}\text{H}_{22}\text{O}_4\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 277.1410; Found: 277.1407.

5g: $\text{C}_{16}\text{H}_{25}\text{ClO}_4$
Mol. Wt.: 316.82

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 28 mg of **5g** as a colorless oil; 45% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) for minor **6g**: t_R 28.8 min (minor); t_R 30.9 min (major) as 39% ee; For **5g** t_R 36.0 min (minor); t_R 39.8 min (major) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 1.0 mL/min] as 95% ee. $[\alpha]_D^{25} = -5.3$ (c 1.0, CHCl_3). Diastereomeric ratio (determined by 400 MHz ^1H NMR): 99:1;

IR (cm⁻¹) 2970, 2931, 2873, 1730, 1683, 1590; ¹H NMR (CDCl₃, 400 MHz) δ 1.02 (s, 3H), 1.04 (s, 3H), 1.16 (s, 9H), 1.41-1.65 (m, 2H), 1.71-1.79 (m, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 3.99 (d, *J* = 1.6 Hz, 1H), 5.41 (dd, *J* = 1.6 Hz, 1.6 Hz, 1H), 5.46 (dd, *J* = 6.0 Hz, 1.6 Hz, 1H), 7.50 (d, *J* = 6.0 Hz, 1H); The minor product **6g** could not be completely separated from **5g**; ¹H NMR (CDCl₃, 400 MHz) (**6g**) δ 0.97 (s, 3H), 1.00 (s, 3H), 1.31 (s, 9H), 1.38-1.55 (m, 2H), 1.71-1.81 (m, 2H), 2.46 (dd, *J* = 16.5 Hz, 2.5 Hz, 1H), 2.66-2.72 (m, 1H), 3.52 (t, *J* = 6.5, 2H), 4.21 (dd, *J* = 10.5 Hz, 2.5 Hz, 1H), 7.21 (s, 1H). ¹³C NMR (CDCl₃, 100 MHz) (**5g**) δ 23.5, 23.8, 27.1, 27.4, 36.7, 36.9, 39.1, 45.5, 69.0, 87.4, 105.5, 164.0, 176.7, 187.1; HRMS Exact mass calcd for C₁₆H₂₅ClO₄Na [M + Na]⁺: 339.1334; Found: 339.1332.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 46 mg of **12a** as a colorless oil; 85% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) *t*_R 19.6 min (minor); *t*_R 23.7 min (major) [Chiralcel ODH (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 93/7, 0.7 mL/min] as 74% ee. [α]_D = -26.0 (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 3429, 2970, 2936, 2877, 1740, 1663, 1600; ¹H NMR (CDCl₃, 400 MHz) δ 0.94 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.18 (s, 9H), 1.98-2.09 (m, 1H), 3.96 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 4.26 (s, 2H), 5.34 (dd, *J* = 2.4 Hz, 1.2 Hz, 1H), 5.65 (d, *J* = 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 18.3, 19.3, 27.2, 28.3, 39.2, 61.8, 68.6, 86.8, 100.9, 176.2, 176.9, 187.7; HRMS Exact mass calcd for C₁₄H₂₂O₅Na [M + Na]⁺: 293.1359; Found: 293.1366.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 40 mg of **12b** as a colorless oil; 67% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 49.6 min (minor); t_R 63.9 min (major) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 1.0 mL/min] as 76% ee. $[\alpha]_D^{25} = -41.8$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 3433, 2960, 2873, 1740, 1663, 1600; ¹H NMR (CDCl₃, 400 MHz) δ 1.19 (s, 9H), 1.41-1.67 (m, 6H), 1.70-1.91 (m, 2H), 2.18-2.28 (m, 1H) 4.12 (dd, J = 10.0 Hz, 2.8 Hz, 1H), 4.24 (s, 2H), 5.33 (dd, J = 2.8 Hz, 1.2 Hz, 1H), 5.65 (d, J = 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 25.2, 25.4, 27.3, 28.9, 30.1, 39.1, 39.2, 61.8, 69.8, 85.9, 101.0, 175.7, 177.0, 187.8; HRMS Exact mass calcd for C₁₆H₂₄O₅Na [M + Na]⁺: 319.1516; Found: 319.1513.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 52 mg of **12c** as a colorless oil; 91% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 18.0 min (minor); t_R 25.7 min (major) [Chiralcel ODH (0.46 cm x 25.0 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 93/7, 0.7 mL/min] as 92% ee. $[\alpha]_D^{25} = -16.9$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 3440, 2971, 2937, 2875, 1730, 1663, 1611; ¹H NMR (CDCl₃, 400 MHz) δ 1.03 (s, 9H), 1.19 (s, 9H), 3.95 (d, J = 1.6 Hz, 1H), 4.29 (s, 2H), 5.41 (d, J = 1.6 Hz, 1H), 5.66 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 26.8, 27.1, 34.5, 39.1, 61.7, 69.0, 88.5, 100.6, 176.8, 176.9, 187.9; HRMS Exact mass calcd for C₁₅H₂₄O₅Na [M + Na]⁺: 307.1516; Found: 307.1520.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 25 mg of **12d** as a colorless oil; 35% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 78.3 min (minor); t_R 98.5 min (major) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 1.0 mL/min] as 92% ee. $[\alpha]_D^{25} = -3.3$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 3435, 2966, 2927, 2873, 1737, 1663, 1613; ¹H NMR (CDCl₃, 400 MHz) δ 1.02 (s, 3H), 1.04 (s, 3H), 1.15 (s, 9H), 1.60-1.79 (m, 4H), 3.45-3.54 (m, 2H), 4.01 (d, $J = 1.6$ Hz, 1H), 4.30 (s, 2H), 5.41 (d, $J = 1.6$ Hz, 1H), 5.46 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 23.6, 23.9, 27.1, 27.4, 36.8, 36.9, 39.1, 45.6, 61.7, 68.8, 87.4, 100.8, 176.5, 176.7, 187.5; HRMS Exact mass calcd for C₁₇H₂₇ClO₅Na [M + Na]⁺: 369.1439; Found: 369.1435.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 66 mg of **12e** as a colorless oil; 92% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 33.1 min (major); t_R 37.5 min (minor) [Chiralcel ADH-semi-prep (4.6 cm x 250 cm) (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 94/6, 1.0 mL/min] as 72% ee. $[\alpha]_D^{25} = -7.7$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 2971, 2937, 2877, 1730, 1681, 1621; ¹H NMR (CDCl₃, 400 MHz) δ 0.93 (d, $J = 6.8$ Hz, 3H), 1.07 (d, $J = 6.8$ Hz, 3H), 1.18 (s, 9H), 1.22 (s, 9H), 1.97-2.09 (m, 1H), 3.96 (dd, $J = 9.6$ Hz, 2.4 Hz, 1H), 4.67 (AB q, $J = 6.4$ Hz, 2H), 5.33 (dd, $J = 2.4$ Hz, 1.2 Hz, 1H), 5.51 (d, $J = 1.2$ Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 18.2, 19.3, 27.2, 27.3, 28.2, 39.0, 39.2, 61.7, 68.4, 87.0, 101.8, 171.5, 176.8, 177.6, 187.4; HRMS Exact mass calcd for C₁₉H₃₀O₆Na [M + Na]⁺: 377.1935; Found: 377.1928.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 40 mg of **12f** as a colorless oil; 74% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 42.8 min (minor); t_R 47.2 min (major) [Chiralcel ADH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95/5, 1.0 mL/min] as 76% ee. $[\alpha]_D = -12.2$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 2962, 2916, 2873, 1740, 1683, 1621; ¹H NMR (CDCl₃, 400 MHz) δ 1.18 (s, 9H), 1.22 (s, 9H), 1.37-1.65 (m, 6H), 1.68-1.91 (m, 2H), 2.17-2.28 (m, 1H) 4.11 (dd, J = 10.0 Hz, 2.8 Hz, 1H), 4.65 (AB q, J = 15.6 Hz, 2H), 5.31 (dd, J = 2.8 Hz, 1.2 Hz, 1H), 5.49 (d, J = 1.2 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 25.2, 25.4, 27.2, 27.3, 28.8, 30.0, 39.0, 39.1, 39.2, 61.7, 69.5, 86.1, 101.8, 171.4, 176.8, 177.6, 187.4; HRMS Exact mass calcd for C₂₁H₃₂O₆Na [M + Na]⁺: 403.2091; Found: 403.2091.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 70 mg of **12g** as a colorless oil; 96% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 43.2.0 min (major); t_R 56.7 min (minor) [Chiralcel OJ-OJH (2 columns attached one after the other) (0.46 cm x 25.0 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99/1, 0.5 mL/min] as 93% ee. $[\alpha]_D = -12.1$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 2973, 2939, 2875, 1730, 1683, 1621; ¹H NMR (CDCl₃, 400 MHz) δ 1.03 (s, 9H), 1.13 (s, 9H), 1.21 (s, 9H), 3.95 (d, J = 1.2 Hz, 1H), 4.65-4.74 (m, 2H), 5.40 (d, J = 1.2 Hz, 1H), 5.49 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 26.7, 27.1, 27.3, 34.5, 39.0 (2 C), 61.8, 68.7, 88.6, 101.7, 171.9, 176.6, 177.6, 187.4; HRMS Exact mass calcd for C₂₀H₃₂O₆Na [M + Na]⁺: 391.2091; Found: 391.2098.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 66 mg of **12h** as a colorless oil; 77% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 32.0 min (major); t_R 35.2 min (minor) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 1.0 mL/min] as 90% ee. $[\alpha]_D = -9.2$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 400 MHz ¹H NMR): 99:1; IR (cm⁻¹) 2971, 2939, 2875, 1730, 1681, 1621; ¹H NMR (CDCl₃, 400 MHz) δ 1.01 (s, 3H), 1.03 (s, 3H), 1.15 (s, 9H), 1.22 (s, 9H), 1.55-1.65 (m, 2H), 1.70-1.79 (m, 2H), 3.48 (t, J = 6.4 Hz, 2H), 4.01 (d, J = 1.2 Hz, 1H), 4.70 (s, 2H), 5.41 (d, J = 1.2 Hz, 1H), 5.51 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 23.5, 23.8, 27.1, 27.3, 27.4, 36.7, 36.9, 39.0, 39.1, 45.4, 61.8, 68.6, 87.7, 101.9, 171.8, 176.6, 177.6, 187.2; HRMS Exact mass calcd for C₂₂H₃₅ClO₆Na [M + Na]⁺: 453.2014; Found: 453.2009.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 61 mg of **13a** as a colorless oil; 77% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 28.7 min (minor); t_R 35.2 min (major) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 97/3, 1.0 mL/min] as 70% ee. $[\alpha]_D = -37.6$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 500 MHz ¹H NMR): 99:1; IR (cm⁻¹) 3081, 2971, 2935, 2875, 1739, 1654, 1632; ¹H NMR (CDCl₃, 500 MHz) δ 1.05 (d, J = 7.5 Hz, 3H), 1.07 (d, J = 7.5 Hz, 3H), 1.18 (s, 9H), 1.23 (s, 9H), 2.10-2.17 (m, 1H), 2.68 (dd, J = 14.5 Hz, 7.5 Hz, 1H), 3.16 (dd, J = 14.5 Hz, 7.5 Hz, 1H), 4.45 (d, J = 3.5 Hz, 1H), 4.62 (s, 2H), 5.09-5.13 (m, 2H), 5.43 (s, 1H), 5.62-5.74 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 17.8, 21.2, 27.2, 27.3, 29.0, 37.5, 39.0, 39.3, 61.6, 80.5, 87.6, 101.4, 119.9, 131.4, 169.1, 177.1, 177.7, 188.7; HRMS Exact mass calcd for C₂₂H₃₄O₆Na [M + Na]⁺: 417.2248; Found: 417.2248.

The crude product was purified by chromatography on silica gel using hexane/EtOAc (5:1) as eluent to yield 76 mg of **13b** as a colorless oil; 90% yield. The enantiomeric purity was determined by HPLC (254 nm, 25 °C) t_R 28.1 min (minor); t_R 33.4 min (major) [Chiralcel ODH-semi-prep (4.6 cm x 250 cm)(from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 97/3, 1.0 mL/min] as 69% ee. $[\alpha]_D = -20.6$ (c 1.0, CHCl₃). Diastereomeric ratio (determined by 500 MHz ¹H NMR): 99:1; IR (cm⁻¹) 3080, 2960, 2937, 2873, 1730, 1694, 1632; ¹H NMR (CDCl₃, 500 MHz) δ 1.18 (s, 9H), 1.23 (s, 9H), 1.47-1.68 (m, 6H), 1.74-1.84 (m, 2H), 2.23-2.31 (m, 1H), 2.65 (dd, J = 14.5 Hz, 7.5 Hz, 1H), 3.12 (dd, J = 14.5 Hz, 7.5 Hz, 1H), 4.54 (d, J = 5.5 Hz, 1H), 4.60 (AB q, J = 11.5 Hz, 2H), 5.08-5.14 (m, 2H), 5.49 (s, 1H), 5.61-5.71 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 25.2, 25.4, 27.3, 27.4, 28.7, 30.5, 37.6, 39.0, 39.3, 39.7, 61.6, 80.8, 86.0, 101.9, 120.0, 131.5, 169.2, 177.1, 177.6, 189.0; HRMS Exact mass calcd for C₂₄H₃₆O₆Na [M + Na]⁺: 443.2404; Found: 443.2402.

Stereochemical Analysis:

To determine absolute stereochemistry, the radical adduct **5e** was converted to a known compound (**14**).² To the radical product **5e** (70% ee) (0.4 mmol) in 1 mL of EtOH was added SmI₂ (purchased from Aldrich as a 0.1 M solution in THF) (3 equiv, 1.2 mL) at room temp. The reaction was stirred for 15 min, quenched on silica and subjected to column chromatography. Known compound **14** was isolated in 65% yield with identical spectra as previously reported. The observed rotation of **14** was: $[\alpha]_D = -63.2$ (c 0.3, CHCl₃). The reported value is (84% ee): $[\alpha]_D = -127.2$ (c 1.0, CHCl₃).

References:

1. Liu, Z. D.; Khodr, H. H.; Liu, D. Y.; Lu, S. L.; Hider, R. C. *J. Med. Chem.* **1999**, *42*, 4814-4823.
2. Unni, A. K.; Takenaka, N.; Yamamoto, H.; Rawal, V. H. *J. Am. Chem. Soc.* **2005**, *127*, 1336-1337.

J82V-PMA-P
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 -vnmr400-
 Relax. delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 3.334 sec
 FID file 4642.f
 V1 file 4642.f
 Processing: 1024
 OBSERVED F1: 99.9355588 MHz
 DATA PROCESSING
 FT size 262144
 Total time 0 min, 56 sec

4c

J82V-KAMP
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 "vnmr400"
 Relax delay 0.300 sec
 Pulse 45.000 sec
 Acq time 3.500 sec
 Width 4662.0 Hz
 16 repetitions
 OBSERVE H1: 399.365500 MHz
 DATA PROCESSING
 FT size 262144
 Total time 0 min, 58 sec

10

JRV-KABP
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 "vnmr400"
 Relax. delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 3.314 sec
 FIDN 4662.0 Hz
 13C NMR
 OBSERVE H101 399.935550 MHz
 DATA PROCESSING
 FT size 262144
 Total time 0 min, 50 sec

11

JMR2-128VI
 Sample directory: proton-test_02Mar2000
 File: PROTON
 Pulse Sequence: s2pu1
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-500 "vnmr300"
 Relax. delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 2.808 sec
 Width 6500.9 Hz
 16 repetitions
 OBSERVE H1: 499.6716913 MHz
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 65536
 Total time 0 min, 51 sec

J82V-266-C2
 Pulse Sequence: szpu1
 Solvent: CCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 "vnmr400"
 Relax delay 0.300 sec
 Pulse 15.000000 sec
 Acq time 3.254 sec
 Width 4662.0 Hz
 16 repetitions
 OBSERVE H1: 399.935500 MHz
 DATA PROCESSING
 FT size 262144
 Total time 0 min, 58 sec

JR2VI-78-major
 Pulse Sequence: s2pu1
 Solvent: CDCl3
 Ambient Temperature
 Mercury-3000B "vnmr300"
 PULSE SEQUENCE
 Relax-delay 1.000 sec
 Pulse 66.3 degrees
 Acq. time 1.997 sec
 Width 3301.4 Hz
 16 repetitions
 OBSERVE H1, 300.137222 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 F1 size 16384
 Total time 0 min, 49 sec

J82V-264-256
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 "vnmr400"
 Relax. delay 0.300 sec
 Pulse 45.0 degree
 Acq. time 3.334 sec
 Width 4662.0 Hz
 16 repetitions
 OBSERVED F1: 399.9356500 MHz
 OBSERVED F2: 101.6251400 MHz
 FT size 262144
 Total time 0 min, 58 sec

JRZV-166
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Temp: 25.0 C / 288.1 K
 INOVA-400 -vnmr400-
 Relax. delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 3.334 sec
 Width 4662.0 Hz
 F1 100.626130 MHz
 F2 400.146300 MHz
 OBSERVATIONS
 DATA PROCESSING
 FT size 26214
 Total time 0 min, 50 sec

JR2V-253
Pulse Sequence: szpu1
400MHz

JRZV-89-93
 Pulse Sequence: szpu1
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 "vnmr400"
 Relax. delay 0.390 sec
 Pulse 45.0 degrees
 Acq. time 3.334 sec
 Width 4662.6 Hz
 16 repetitions
 OBSERVE H1: 399.9356500 MHz
 DATA PROCESSING
 1 sec/251.440 min
 Total time 9 min, 58 sec

CC(C)(C)C(C)C(O)C(=O)OCC(=O)OC(C)(C)C(C)C

JRCV-87
 Pulse Sequence: szpul
 Solvent: CDCl3
 Temp: 35.0 C / 280.1 K
 INOVA-480 vnmr480-
 Relax. delay 8.380 sec
 Pulse 45.0 degrees
 Width 14.000 sec
 Acquisition 2.000 sec
 16 repetitions
 OBSERVE H1 399.935600 MHz
 DATA PROCESSING
 FT size 26214
 Total time 0 min, 50 sec

J82V-257
 Pulse Sequence: szpu1
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 "vnmr400"
 Relax. delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 3.334 sec
 Width 4662.0 Hz
 16 Repetitions
 OBSERVE H1 399.9356580 MHz
 DATA PROCESSING
 F1 size 262144
 Total time 0 min, 50 sec

J8ZY-91
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-400 "vnmr400"
 Relax. delay 0.300 sec
 Pulse 45.0 degrees
 Acq. time 3.334 sec
 Width 4662.0 Hz
 16 repetitions
 OBSERVE M1: 399.835600 MHz
 DATA PROCESSING
 FT size 262244
 Total time 8 min, 58 sec

CC(C)(C)OC(=O)C1=CC(=C(C=C1)OC(=O)C(C)(C)C)OC(=O)C(C)(C)C

JR2VI-80

Sample directory: proton=est_02Mar2000
File: PROTON

Pulse Sequence: szpu1

Solvent: CDCl3
Temp: 25.0 C / 298.1 K
INOVA-500 "vnmr500"

Relax. delay 0.300 sec
Pulse 45.0 degrees
Acq. time 2.988 sec
Width 6500.9 Hz
18 repetitions
OBSERVED FID 99.6716913 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 0 min, 51 sec

JRZVI-97
 Sample directory: proton-test_02Mar2000
 File: PROTON
 Pulse Sequence: szput
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 INOVA-500 "vnmr500"
 Relax. delay 0.300 sec
 Pulse: 45.0 degrees
 Acq. time: 2.906 sec
 Width: 6500.9 Hz
 16 Repetitions
 OBSERVE: H1: 499.6716913 MHz
 DATA PROCESSING
 Line broadening 0.3 Hz
 FT size 65536
 Total time 0 min, 51 sec

Sample Information

SampleName JRZV-255-ODHP
Vial 1
Injection 13
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 140.0 Minutes

Sample Type Unknown
Date Acquired 5/19/2005 9:24:54 AM
Acq Method Set 10% iPrOH 1rpm
Processing Method 1
Date Processed 5/19/2005 11:28:00 AM

Auto-Scaled Chromatogram **Peak Results**

	Name	RT	Area	% Area
1		32.660	241263	1.11
2		34.029	230390	1.06
3		36.274	10484729	48.31
4		40.302	10744837	49.51

Sample Information

SampleName JRZV-256-ODHP
Vial 1
Injection 14
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 140.0 Minutes

Sample Type Unknown
Date Acquired 5/19/2005 10:17:54 AM
Acq Method Set 10% iPrOH 1rpm
Processing Method 12
Date Processed 5/19/2005 11:29:24 AM

Peak Results

Name	RT	Area	% Area
1	30.095	850515	2.69
2	32.290	1723130	5.46
3	35.991	900983	2.85
4	39.845	28096672	88.99

Sample Information

SampleName JRZIII-41-OD-H
Vial 1
Injection 1
Injection Volume 20.00 ul
Channel 2487Channel 2
Run Time 32.0 Minutes

Sample Type Unknown
Date Acquired 10/22/2003 3:44:40 PM
Acq Method Set 7% ipa 07mLmin
Processing Method c
Date Processed 10/22/2003 4:27:57 PM

Peak Results

	RT	Start Time	End Time	Height	Area	% Area	Int Type
1	18.179	16.950	21.167	969967	85678249	49.67	BV
2	22.052	21.167	28.633	823832	86803790	50.33	VB

Sample Information

SampleName JRZIII-44-OD-H
 Vial 1
 Injection 1
 Injection Volume 20.00 ul
 Channel 2487Channel 2
 Run Time 32.0 Minutes

Sample Type Unknown
 Date Acquired 10/24/2003 10:54:19 AM
 Acq Method Set 7% ipa 07mL/min
 Processing Method b
 Date Processed 10/24/2003 11:28:14 AM

Auto-Scaled Chromatogram

Peak Results

	RT	Start Time	End Time	Height	Area	% Area	Int Type
1	18.986	17.667	19.733	87784	6012620	5.76	bv
2	22.263	21.100	28.867	897963	98443526	94.24	vb

Sample Information

SampleName JRZIII-50-OD-H
Vial 1
Injection 1
Injection Volume 20.00 ul
Channel 2467Channel 2
Run Time 60.0 Minutes

Sample Type Unknown
Date Acquired 10/29/2003 10:37:43 AM
Acq Method Set 7% ipa 07mLmin
Processing Method b
Date Processed 10/29/2003 11:11:45 AM

Auto-Scaled Chromatogram

Peak Results

	RT	Start Time	End Time	Height	Area	% Area	Int Type
1	16.958	15.350	18.817	516402	41026824	49.89	Bb
2	22.919	21.350	26.000	411455	41213537	50.11	bb

Sample Information

SampleName JRZV-89-ODH
Vial 1
Injection 3
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 100.0 Minutes

Sample Type Unknown
Date Acquired 2/7/2005 4:05:51 PM
Acq Method Set 7% iPrOH 07mpm
Processing Method 11
Date Processed 2/7/2005 4:48:37 PM

Auto-Scaled Chromatogram

Peak Results

	Name	RT	Area	% Area
1		18.028	3108498	3.96
2		25.719	75348044	96.04

Sample Information

SampleName JPZV-84'-ADHP
Vial 1
Injection 2
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 150.0 Minutes

Sample Type Unknown
Date Acquired 2/3/2005 11:12:40 AM
Acq Method Set 6% iPrOH 1rpm
Processing Method 1
Date Processed 2/3/2005 3:48:57 PM

Peak Results

	Name	RT	Area	% Area
1		32.054	214845	0.20
2		33.435	230647	0.21
3		35.833	55066457	50.02
4		40.244	54580106	49.58

Sample Information

SampleName JRZV-85-ADHP
Vial 1
Injection 3
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 80.0 Minutes

Sample Type Unknown
Date Acquired 2/3/2005 3:00:05 PM
Acq Method Set 6% iPrOH 1rpm
Processing Method BnNH₂OH to Ph malonate
Date Processed 2/3/2005 3:50:18 PM

Peak Results

	Name	RT	Area	% Area
1		33.418	63356478	85.86
2		37.800	10437073	14.14

Sample Information

SampleName JRZV-249-ODHP
Vial 1
Injection 9
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 140.0 Minutes

Sample Type Unknown
Date Acquired 5/18/2005 9:46:05 AM
Acq Method Set 10% iPrOH 1rpm
Processing Method 11
Date Processed 7/5/2006 4:48:35 PM

Auto-Scaled Chromatogram

Peak Results

	Name	RT	Area	% Area
1		74.463	41579189	50.09
2		95.810	41422170	49.91

Sample Information

SampleName JFZV-265-ODHP
 Vial 1
 Injection 4
 Injection Volume 20.00 ul
 Channel 2487Channel 1
 Run Time 150.0 Minutes

Sample Type Unknown
 Date Acquired 5/26/2005 1:37:17 PM
 Acq Method Set 10% iPrOH 1rpm
 Processing Method 1
 Date Processed 5/26/2005 4:59:59 PM

Peak Results

Name	RT	Area	% Area
1	78.313	5096615	4.07
2	98.495	120061798	95.93

Sample Information

SampleName JRZV-243-ADHP
Vial 1
Injection 1
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 120.0 Minutes

Sample Type Unknown
Date Acquired 5/13/2005 2:13:56 PM
Acq Method Set 5%iPrOH 1mpmH3
Processing Method 1
Date Processed 7/6/2006 10:31:45 AM

Peak Results

	Name	RT	Area	% Area
1		42.421	28109350	50.22
2		46.917	27857578	49.78

Sample Information

SampleName JRZV-245-ADHP
Vial 1
Injection 2
Injection Volume 20.00 ul
Channel 2487Channel 1
Run Time 120.0 Minutes

Sample Type Unknown
Date Acquired 5/13/2005 3:12:33 PM
Acq Method Set 5% iPrOH 1rpmH3
Processing Method 12
Date Processed 7/6/2006 10:31:02 AM

Peak Results

	Name	RT	Area	% Area
1		42.755	16445150	12.66
2		47.188	113491393	87.34