S1

A Convenient Method for the Preparation of Inverted *tert*-Alkyl Carboxylates from Chiral
tert-Alcohols by a New type of Oxidation-reduction Condensation Using 2,6-Dimethyl-
1,4-benzoquinone

Teruaki Mukaiyama,* Taichi Shintou, and Kentaro Fukumoto

Center for Basic Research, The Kitasato Institute, 6-15-5 Toshima, Kita-ku, Tokyo 114-0003, Japan

Kitasato Institute for Life Sciences, Kitasato University, 5-9-1 Shirokane, Minato-ku, Tokyo 108-8641, Japan

Supporting Information

General Information. All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and are not corrected. Infrared (IR) spectra were recorded on a Nicolet AVATAR360 (ATR) or a Horiba FT300 FT-IR spectrometer (neat). ^1H NMR spectra were recorded on a JEOL JNM EX270L (270 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on EX270L (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 ; δ 77.0 ppm). High resolution mass spectra (HRMS) were reported on a JEOL LCmate. MS spectra were reported on a JEOL DX-303HF. Polarimeter was used JASCO P-1020. Analytical high performance liquid chromatography (HPLC) was performed on a Hitachi LC-Organizer (L-4000 UV Detector, L-6200 Intelligent Pump,

S2

and D-2500 Chromato-Integrator) equipped with a chiral column (ϕ 4.6×250 mm). Analytical TLC was performed on Merck preparative TLC plates (silica gel 60 GF254, 0.25 mm). Column chromatography was carried out on Merck silica gel 60 (0.063-0.200 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wakogel B-5F. Dry solvents were prepared by distillation under appropriate drying agents. Carboxylic acids were purified by recrystallization.

General procedure for the preparation of chiral tertiary alcohols. Chiral tertiary alcohols were prepared according to Walsh's procedure.^{1,2}

Bis(sulfonamide) (1).¹ Into a stirred solution of (1R,2R)-(-)-1,2-diaminocyclohexane (2.0 g, 17 mmol) and triethylamine (3.8 g, 37 mmol) in dichloromethane (200 mL) under argon atmosphere was dropped a dichloromethane (60 mL) solution of (1S)-(+)-10-camphorsulfonyl chloride (9.0 g, 36 mmol) at -78 °C. The reaction mixture was stirred for 12 h at room temperature. The solution was washed with 2 mol dm⁻³ HCl (100 mL) and water (100 mL). The organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was recrystallized from dichloromethane and hexane to afford the title compound (1) (7.5 g, 81%) as a pale yellow solid: mp 244 °C (lit.¹ mp 240 °C); [α]_D²⁴ = +26.8 (c 0.40, CHCl₃), (lit.¹ [α]_D = +21.8 (c 0.40, CHCl₃)); IR (ATR, cm⁻¹) 3309, 3243, 2931, 1748, 1728, 1432, 1319, 1149, 914, 761; ¹H NMR (270 MHz, CDCl₃) δ 5.62 (s, 2H), 3.51 (d, *J* = 15.1 Hz, 2H), 3.18 (m, 2H), 3.01 (d, *J* = 15.1 Hz, 2H), 2.42–1.86 (m, 14H), 1.73 (m, 2H), 1.50–1.23 (m,

S3

6H), 1.04 (s, 6H), 0.89 (s, 6H); ^{13}C NMR (68 MHz, CDCl_3) δ 59.0, 57.6, 50.9, 48.7, 42.9, 42.6, 33.8, 27.1, 26.3, 24.5, 19.9, 19.6; HRMS (APCI $^+$) calcd for $\text{C}_{26}\text{H}_{43}\text{N}_2\text{O}_6\text{S}_2$ $[\text{M}+\text{H}]^+$ 543.2563, found m/z 543.2574.

Bis(sulfonamide) (2).² To a stirred solution of bis(sulfonamide) (1) (5.5 g, 10 mmol) in isopropyl alcohol (110 mL) and THF (110 mL) under argon atmosphere was added NaBH_4 (2.6 g, 69 mmol) over 5 min at room temperature. The reaction mixture was stirred until the foaming subsided (about 0.5 h), then quenched carefully with sat. NH_4Cl (33 mL) at 0 °C. The organic solvents were removed from the two-phase mixture under reduced pressure. Dichloromethane (55 mL) was added to the resulting aqueous mixture, and then the organic layer was separated from the aqueous layer. The aqueous layer was extracted with dichloromethane and the combined organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulted residue was purified by column chromatography (hexane/ethyl acetate = 3/1) to afford the title compound (2) (2.9 g, 53 %) as a white solid: mp 184–185 °C (lit.² mp 181.5–182.3 °C); $[\alpha]_{\text{D}}^{25} = -33.0$ (c 3.00, CH_2Cl_2), (lit.² $[\alpha]_{\text{D}}^{20} = -34.4$ (c 3.00, CH_2Cl_2)); IR (ATR, cm^{-1}) 3512, 3245, 2936, 1453, 1319, 1147, 1073, 902; ^1H NMR (270 MHz, CDCl_3) δ 5.22 (s, 2H), 4.13–4.07 (m, 2H), 3.49 (d, $J = 13.5$ Hz, 2H), 3.12–3.05 (m, 2H), 2.91 (d, $J = 13.5$ Hz, 2H), 2.20–2.09 (m, 2H), 1.80–1.75 (m, 12H), 1.51–1.26 (m, 8H), 1.20–1.12 (m, 2H), 1.06 (s, 6H), 0.83 (s, 6H); ^{13}C NMR (68 MHz, CDCl_3) δ 60.4, 57.7, 53.8, 50.5, 48.7, 44.4, 39.0, 34.7, 30.6, 27.3, 24.8, 20.6, 19.9; HRMS (APCI $^+$) calcd for $\text{C}_{26}\text{H}_{47}\text{N}_2\text{O}_6\text{S}_2$

$[M+H]^+$ 547.2876, found m/z 547.2885.

General procedure for the preparation of chiral tertiary alcohols.² Into a stirred hexane solution of Et_2Zn (22.4 mmol) and bis(sulfonamide) **2** (153mg, 0.28 mmol) under argon atmosphere was dropped a Toluene (30 mL) solution of $\text{Ti}(\text{O}^i\text{Pr})_4$ (4.8g, 16.8 mmol) at room temperature. The reaction mixture was stirred for 1–3 day at room temperature. After completion of the reaction (detected by TLC), it was quenched with saturated aq NH_4Cl (15 mL) and mixture was extracted with CH_2Cl_2 . The organic layers were washed with H_2O (15 mL $\times$ 4 times) and dried over anhydrous sodium sulfate. After the mixture was filtered and concentrated the crude product was purified by column chromatography to afford the desired product.

(S)-2-Phenyl-2-butanol (Table 1, entries 8–11).² Colorless oil; $[\alpha]_{\text{D}}^{24} = -15.3$ (c 1.03, CHCl_3), (lit.² $[\alpha]_{\text{D}}^{20} = -16.7$ (c 0.72, Acetone)); IR (neat, cm^{-1}) 3440, 2978, 1604, 1450, 1373, 1165; ^1H NMR (270 MHz, CDCl_3) δ 7.45–7.42 (m, 2H), 7.36–7.31 (m, 2H), 7.25–7.23 (m, 1H), 1.82 (dq, $J = 7.5, 3.5$ Hz, 2H), 1.71 (br, 1H), 1.55 (s, 3H), 0.78 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 147.6, 128.0, 126.4, 124.8, 74.9, 36.7, 29.7, 8.4; HRMS (EI^+) calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ $[M]^+$ 150.1045, found m/z 150.1044.

(S)-2-(3-Methylphenyl)-2-butanol (Table 1, entry 12).² Colorless oil; $[\alpha]_{\text{D}}^{26} = -14.4$ (c 0.63, CHCl_3), (lit.² $[\alpha]_{\text{D}}^{20} = -4.08$ (c 0.6, CHCl_3)); IR (ATR, cm^{-1}) 1716, 1271, 1109; ^1H NMR (270 MHz, CDCl_3) δ 7.25–7.21 (m, 3H), 7.06–7.04 (m, 1H), 2.36 (s, 3H), 1.82 (dq, $J = 7.4, 3.8$ Hz, 2H), 1.71 (br, 1H), 1.53 (s, 3H), 0.80 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 147.6, 137.5, 127.9, 127.1, 125.5, 121.8, 74.9, 36.6, 29.7, 21.7, 8.4; HRMS (EI^+) calcd for $\text{C}_{11}\text{H}_{16}\text{O}$ $[M]^+$ 164.1201, found m/z 164.1180.

(R)-3-Phenyl-3-heptanol (Table 1, entry 13).² Colorless oil; $[\alpha]_{\text{D}}^{27} = -2.44$ (c 2.26, CHCl_3), (lit.² $[\alpha]_{\text{D}}^{20} = +2.42$ (c 2.2, CHCl_3)); IR (ATR, cm^{-1}) 1714, 1269, 1111, 760; ^1H NMR (270 MHz, CDCl_3) δ 7.39–7.29 (m, 4H), 7.24–7.18 (m, 1H), 1.91–1.70 (m, 5H),

1.28–1.01 (m, 4H), 0.83 (t, $J = 7.0$ Hz 3H), 0.75 (t, $J = 7.4$ Hz 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 145.9, 127.8, 126.1, 125.2, 77.1, 42.3, 35.4, 25.7, 23.1, 14.1, 7.9; HRMS (EI^+) calcd for $\text{C}_{13}\text{H}_{20}\text{O}$ $[\text{M}]^+$ 192.1514, found m/z 192.1551.

(S)-3-Methyl-1-phenyl-3-pentanol (Table 1, entry 14).² Colorless oil; $[\alpha]_{\text{D}}^{24} = -1.63$ (c 2.76, CHCl_3); IR (neat, cm^{-1}) 3487, 2954, 1604, 1458, 1350, 972; ^1H NMR (270 MHz, CDCl_3) δ 7.30–7.18 (m, 5H), 2.66 (dt, $J = 4.9, 3.0$ Hz, 2H), 1.75 (dt, $J = 4.9, 3.0$ Hz, 2H), 1.57 (q, $J = 7.6$ Hz, 2H), 1.51 (br, 1H), 1.21 (s, 3H), 0.93 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 142.5, 128.2 ($\times 2$), 125.6, 72.8, 43.2, 34.4, 30.3, 26.3, 8.3; HRMS (EI^+) calcd for $\text{C}_{12}\text{H}_{18}\text{O}$ $[\text{M}]^+$ 178.1358, found m/z 178.1360.

(S)-2-(4-Methoxyphenyl)-2-butanol (Table 1, entry 15).² Colorless oil; $[\alpha]_{\text{D}}^{23} = -15.3$ (c 0.99, CHCl_3), (lit.² $[\alpha]_{\text{D}}^{20} = -12.32$ (c 1.8, CHCl_3)); IR (neat, cm^{-1}) 3448, 2970, 1612, 1512, 1250, 1034, 833; ^1H NMR (270 MHz, CDCl_3) δ 7.34 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 3.79 (s, 3H), 1.80 (q, $J = 7.4$ Hz, 2H), 1.71 (br, 1H), 1.52 (s, 3H), 0.79 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 157.9, 139.8, 125.9, 113.2, 74.6, 55.2, 36.7, 29.6, 8.5; HRMS (EI^+) calcd for $\text{C}_{11}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$ 180.1150, found m/z 180.1192.

General procedure for the preparation of carboxylic acid esters with retention of stereochemistry.³ Into a stirred solution of chiral *tert*-alcohol (0.6 mmol) in Et_2O (2 mL) was dropped a hexane solution of $n\text{BuLi}$ (0.6 mmol) at 0 °C under argon atmosphere. After the solution was stirred at room temperature for 1.0 h, a Et_2O (1 mL) solution of carboxylic acid chloride (0.6 mmol) was added at 0 °C. The reaction mixture was stirred for 2.0 h at room temperature. After completion of the reaction (detected by TLC), it was quenched with saturated aq NH_4Cl and mixture was extracted with Et_2O . The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated. The crude product was purified by preparative TLC to afford the desired product.

General procedure for the preparation of inverted carboxylic acid esters. Into a

stirred solution of chiral *tert*-alcohol (1.5 mmol) in THF (5 mL) was dropped a hexane solution of n BuLi (1.5 mmol) at 0 °C under argon atmosphere. After the solution was stirred at room temperature for 1.0 h, a THF (2 mL) solution of chlorodiphenylphosphine (1.5 mmol) was added at 0 °C. The reaction mixture was stirred for 1.0 h at room temperature and the solvent was concentrated in vacuo. Immediately, carboxylic acid, DMBQ, and dichloromethane were added to the residue and the mixture was stirred for 18 h at room temperature. The same result was alternatively obtained by the following procedure: that is, after the above mentioned residue was diluted with a mixed solution of hexane (3 mL) and ethyl acetate (0.5 mL), lithium chloride was removed by filtration through celite (1.0 g) after passing it through alumina (activated, basic) (Wako Pure Chemical Industries, LTD) (7 g). The solvent was concentrated in vacuo, and crude alkoxydiphenylphosphine was obtained. To a mixture of carboxylic acid (0.60 mmol) and DMBQ (0.60 mmol) under argon atmosphere was added a dichloromethane (0.50 mL) solution of the above crude alkoxydiphenylphosphine under above condition. After the reaction that was monitored by TLC was completed, the reaction mixture was quenched by adding water and the aqueous layer was extracted with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate. After filtration and evaporation, the resulting residue was purified by preparative TLC to afford the corresponding carboxylic esters.

Adamantyl benzoate (Table 1, entry 1).⁴ White solid; mp 85–87 °C (lit.⁴ mp 66.5–67.0 °C); IR (ATR, cm^{-1}) 2907, 2848, 1704, 1270, 1048; ^1H NMR (270 MHz, CDCl_3) δ 8.01–7.97 (m, 2H), 7.55–7.49 (m, 1H), 7.44–7.37 (m, 2H), 2.26–2.22 (m, 9H), 1.72–1.65 (m, 6H); ^{13}C NMR (68 MHz, CDCl_3) δ 165.3, 132.2, 131.9, 129.3, 128.0, 81.0, 41.4, 36.3, 30.9; HRMS (APCI⁺) calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$ 257.1542, found m/z 257.1539.

S7

1-Isopropyl-4-methyl-3-cyclohexenyl benzoate (Table 1, entry 2). Colorless oil; R/S = 16/84: $[\alpha]_D^{25} = +13.2$ (*c* 1.01, CHCl₃), R/S = 86/14: $[\alpha]_D^{26} = -13.8$ (*c* 0.78, CHCl₃); IR (ATR, cm⁻¹) 1707, 1284, 1114; ¹H NMR (270 MHz, CDCl₃) δ 7.97–7.94 (m, 2H), 7.52–7.38 (m, 3H), 5.31 (s, 1H), 2.94–2.89 (m, 1H), 2.58–2.51 (m, 2H), 2.30–2.24 (m, 1H), 1.98 (m, 2H), 1.78–1.64 (m, 4H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 165.7, 133.5, 132.3, 131.9, 129.2, 128.1, 117.5, 86.8, 32.6, 30.0, 28.0, 27.6, 23.3, 17.8, 17.2; HRMS (APCI⁺) calcd for C₁₇H₂₃O₂ [M+H]⁺ 259.1698, found *m/z* 259.1703.

1-Isopropyl-4-methyl-3-cyclohexenyl-3-phenylpropionate (Table 1, entry 3). Colorless oil; R/S = 66/34: $[\alpha]_D^{24} = -5.7$ (*c* 0.57, CHCl₃), R/S = 86/14: $[\alpha]_D^{26} = -7.3$ (*c* 0.77, CHCl₃); IR (ATR, cm⁻¹) 1723, 1177, 1158; ¹H NMR (270 MHz, CDCl₃) δ 7.29–7.24 (m, 2H), 7.20–7.17 (m, 3H), 5.22 (s, 1H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.75–2.70 (m, 1H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.44–2.28 (m, 2H), 2.16–2.09 (m, 1H), 1.83 (m, 2H), 1.68–1.63 (m, 4H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 172.2, 140.6, 133.5, 128.3, 128.2, 126.0, 117.5, 86.2, 36.9, 32.4, 31.1, 29.9, 27.8, 27.4, 23.3, 17.7, 17.1; HRMS (APCI⁺) calcd for C₁₉H₂₇O₂ [M+H]⁺ 287.2011, found *m/z* 287.2008.

1,5-Dimethyl-1-vinyl-4-hexenyl benzoate (Table 1, entry 4). Colorless oil; R/S = 7/93: $[\alpha]_D^{23} = +18.6$ (*c* 1.20, CHCl₃), R/S = 95/5: $[\alpha]_D^{24} = -18.1$ (*c* 1.02, CHCl₃); IR (ATR, cm⁻¹) 1715, 1279, 1110; ¹H NMR (270 MHz, CDCl₃) δ 8.03–8.00 (m, 2H), 7.53–7.50 (m, 1H), 7.44–7.39 (m, 2H), 6.09 (dd, *J* = 10.8, 6.8 Hz 1H), 5.30–5.13 (m, 3H), 2.07–1.92 (m, 4H), 1.69 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 165.1, 141.7, 132.5, 131.8, 131.4, 129.3, 128.1, 123.7, 113.2, 83.5, 40.1, 25.7, 23.8, 22.5, 17.7; HRMS (EI⁺) calcd for C₁₇H₂₂O₂ [M]⁺ 258.1620, found *m/z* 258.1629.

1,5-Dimethyl-1-vinyl-4-hexenyl 4-methoxybenzoate (Table 1, entry 5). Colorless oil;

S8

R/S = 5/95: $[\alpha]_{\text{D}}^{23} = +19.9$ (c 0.98, CHCl_3), R/S = 95/5: $[\alpha]_{\text{D}}^{25} = -18.6$ (c 1.07, CHCl_3); IR (ATR, cm^{-1}) 1708, 1605, 1252, 1163, 1099, 769; ^1H NMR (270 MHz, CDCl_3) δ 7.97 (d, $J = 7.6$ Hz 2H), 6.90 (d, $J = 7.6$ Hz 2H), 6.08 (dd, $J = 11.1$, 6.2 Hz 1H), 5.27–5.15 (m, 3H), 3.84 (s, 3H), 2.04–1.89 (m, 4H), 1.68 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 164.8, 162.9, 141.9, 131.6, 131.3, 123.9, 123.7, 113.3, 112.9, 83.0, 55.3, 40.2, 25.7, 23.8, 22.5, 17.6; HRMS (EI^+) calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3$ $[\text{M}]^+$ 288.1725, found m/z 288.1820.

1,5-Dimethyl-1-vinyl-4-hexenyl 4-chlorobenzoate (Table 1, entry 6). Colorless oil; R/S = 20/80: $[\alpha]_{\text{D}}^{23} = +16.8$ (c 1.01, CHCl_3), R/S = 95/5: $[\alpha]_{\text{D}}^{23} = -20.0$ (c 0.96, CHCl_3); IR (ATR, cm^{-1}) 1718, 1277, 1089, 758; ^1H NMR (270 MHz, CDCl_3) δ 7.96–7.91 (m, 2H), 7.42–7.38 (m, 2H), 6.08 (dd, $J = 11.0$, 6.5 Hz 1H), 5.28–5.15 (m, 3H), 2.05–1.89 (m, 4H), 1.68 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 164.2, 141.4, 138.9, 131.9, 130.7, 129.9, 128.5, 123.6, 113.4, 83.9, 40.0, 25.7, 23.7, 22.5, 17.7; HRMS (EI^+) calcd for $\text{C}_{17}\text{H}_{21}\text{ClO}_2$ $[\text{M}]^+$ 292.1230, found m/z 292.1227.

1,5-Dimethyl-1-vinyl-4-hexenyl 3-phenylpropanoate (Table 1, entry 7). Colorless oil; R/S = 24/76: $[\alpha]_{\text{D}}^{24} = +4.7$ (c 1.12, CHCl_3), R/S = 95/5: $[\alpha]_{\text{D}}^{24} = -6.78$ (c 1.03, CHCl_3); IR (ATR, cm^{-1}) 1732, 1156, 741; ^1H NMR (270 MHz, CDCl_3) δ 7.31–7.25 (m, 2H), 7.21–7.19 (m, 3H), 5.92 (dd, $J = 10.8$, 6.8 Hz 1H), 5.13 (d, $J = 4.9$ Hz 1H), 5.08 (s, 2H), 2.93 (t, $J = 7.8$ Hz 2H), 2.59 (t, $J = 7.8$ Hz 2H), 1.94–1.75 (m, 4H), 1.67 (s, 3H), 1.57 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 171.5, 141.6, 140.5, 131.7, 128.3, 128.2, 126.0, 123.7, 113.0, 83.0, 39.9, 36.9, 31.1, 25.8, 23.6, 22.4, 17.7; HRMS (EI^+) calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$ $[\text{M}]^+$ 286.1933, found m/z 286.1930.

1-Methyl-1-phenyl-propyl benzoate (Table 1, entry 8).⁵ Colorless oil; R/S = 98/2: $[\alpha]_{\text{D}}^{23} = -40.0$ (c 1.32, CHCl_3), R/S = 2/98: $[\alpha]_{\text{D}}^{25} = +40.9$ (c 1.24, CHCl_3); IR (neat, cm^{-1}) 1720, 1450, 1273, 1111, 710; ^1H NMR (270 MHz, CDCl_3) δ 8.08–8.05 (m, 2H), 7.55–7.24 (m, 8H), 2.18 (q, $J = 7.4$ Hz, 2H), 1.96 (s, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C

NMR (68 MHz, CDCl₃) δ 164.8, 144.7, 132.6, 131.4, 129.4, 128.2, 128.1, 126.8, 124.5, 84.9, 35.6, 24.5, 8.4; HRMS (EI⁺) calcd for C₁₇H₁₈O₂ [M]⁺ 254.1307, found *m/z* 254.1284.

1-Methyl-1-phenyl-propyl 4-methoxybenzoate (Table 1, entry 9). Colorless oil; R/S = 98/2: [α]_D²³ = -56.1 (*c* 1.10, CHCl₃), R/S = 2/98: [α]_D²⁵ = +56.3 (*c* 1.15, CHCl₃); IR (neat, cm⁻¹) 2970, 1712, 1604, 1265, 1103, 764; ¹H NMR (270 MHz, CDCl₃) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.38–7.23 (m, 5H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.95 (s, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 164.5, 162.9, 144.8, 131.3, 127.9, 126.6, 124.4, 123.8, 113.3, 84.3, 55.3, 35.6, 24.5, 8.3; HRMS (EI⁺) calcd for C₁₈H₂₀O₃ [M]⁺ 284.1412, found *m/z* 284.1403.

1-Methyl-1-phenyl-propyl 4-chlorobenzoate (Table 1, entry 10). Colorless oil; R/S = 70/30: [α]_D²³ = -22.1 (*c* 1.02, CHCl₃), R/S = 2/98: [α]_D²⁶ = +37.3 (*c* 0.83, CHCl₃); IR (neat, cm⁻¹) 2931, 1720, 1281, 1103; ¹H NMR (270 MHz, CDCl₃) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.35–7.25 (m, 5H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.95 (s, 3H), 0.88 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 164.0, 144.4, 139.0, 130.8, 129.8, 128.5, 128.1, 126.9, 124.5, 85.3, 35.6, 24.4, 8.4; HRMS (EI⁺) calcd for C₁₇H₁₇ClO₂ [M]⁺ 288.0917, found *m/z* 288.0918.

1-Methyl-1-phenyl-propyl 3-phenylpropionate (Table 1, entry 11). Colorless oil; R/S = 69/31: [α]_D²⁵ = -4.0 (*c* 0.88, CHCl₃), R/S = 2/98: [α]_D²³ = +6.8 (*c* 0.65, CHCl₃); IR (neat, cm⁻¹) 1735, 1134, 702; ¹H NMR (270 MHz, CDCl₃) δ 7.29–7.19 (m, 10H), 2.94 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 1.95 (q, *J* = 7.4 Hz, 2H), 1.78 (s, 3H), 0.74 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (68 MHz, CDCl₃) δ 171.2, 144.6, 140.5, 128.3, 128.2, 128.0, 126.6, 126.1, 124.5, 84.4, 36.8, 35.2, 31.0, 24.3, 8.2; HRMS (EI⁺) calcd for C₁₉H₂₂O₂ [M]⁺ 282.1620, found *m/z* 282.1625.

1-Methyl-1-(3-methylphenyl)propyl benzoate (Table 1, entry 12). Colorless oil; R/S = 99/1: [α]_D²³ = -44.3 (*c* 1.06, CHCl₃), R/S = 1/99: [α]_D²⁴ = +46.2 (*c* 1.02, CHCl₃); IR

S10

(ATR, cm^{-1}) 3425, 2970, 1606, 1455, 1373, 1163, 781; ^1H NMR (270 MHz, CDCl_3) δ 8.08–8.05 (m, 2H), 7.58–7.53 (m, 1H), 7.47–7.42 (m, 2H), 7.24–7.17 (m, 3H), 7.07–7.04 (m, 1H), 2.34 (s, 3H), 2.16 (dq, $J = 7.4, 3.5$ Hz, 2H), 1.94 (s, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 164.8, 144.7, 137.5, 132.5, 131.5, 129.4, 128.2, 128.0, 127.6, 125.2, 121.7, 84.8, 35.7, 24.5, 21.8, 8.4; HRMS (EI^+) calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$ $[\text{M}]^+$ 268.1463, found m/z 268.1484.

1-Ethyl-1-phenyl-pentyl benzoate (Table 1, entry 13). Colorless oil; R/S = 9/91: $[\alpha]_{\text{D}}^{23} = +24.1$ (c 1.32, CHCl_3), R/S = 91/9: $[\alpha]_{\text{D}}^{25} = -23.1$ (c 0.69, CHCl_3); IR (ATR, cm^{-1}) 3488, 2956, 1446, 1378, 1147, 760; ^1H NMR (270 MHz, CDCl_3) δ 8.12–8.08 (m, 2H), 7.59–7.23 (m, 8H), 2.60–2.47 (m, 2H), 2.30–2.15 (m, 2H), 2.29–1.09 (m, 4H), 0.80 (t, $J = 7.4$ Hz, 3H), 0.75 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 164.7, 143.6, 132.6, 131.4, 129.4, 128.3, 128.0, 126.6, 125.0, 88.3, 37.6, 30.9, 25.5, 22.9, 14.1, 7.8; HRMS (EI^+) calcd for $\text{C}_{18}\text{H}_{25}\text{O}_3$ $[\text{M}]^+$ 296.1776, found m/z 296.1760.

1-Ethyl-1-methyl-3-phenyl-propyl benzoate (Table 1, entry 14). Colorless oil; R/S = 77/23: $[\alpha]_{\text{D}}^{23} = +4.9$ (c 1.12, CHCl_3), R/S = 22/78: $[\alpha]_{\text{D}}^{23} = -5.4$ (c 2.07, CHCl_3); IR (neat, cm^{-1}) 2962, 1712, 1458, 1281, 1111, 710; ^1H NMR (270 MHz, CDCl_3) δ 8.02–7.98 (m, 2H), 7.56–7.50 (m, 1H), 7.45–7.39 (m, 2H), 7.30–7.14 (m, 5H), 2.69 (t, $J = 8.6$ Hz, 2H), 2.38–1.93 (m, 4H), 1.62 (s, 3H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (68 MHz, CDCl_3) δ 165.4, 142.0, 132.4, 131.7, 129.3, 128.3 ($\times 2$), 128.1, 125.7, 85.4, 40.2, 31.2, 30.3, 23.5, 8.3; HRMS (APCI $^+$) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$ 283.1698, found m/z 283.1703.

(E)-2-(4-Methoxyphenyl)-2-butene (Table 1, entry 15).⁶ The desired ester was not detected and the corresponding olefin, that is title compound, was formed in 81% yield in case of 2-(4-methoxyphenyl)-2-butanol. Colorless oil; ^1H NMR (270 MHz, CDCl_3) δ 7.29 (d, $J = 8.9$ Hz, 2H), 6.82 (d, $J = 8.9$ Hz, 2H), 5.77 (q, $J = 7.0$ Hz, 1H), 3.78 (s, 3H), 1.99 (s, 3H), 1.76 (dd, $J = 5.9, 1.0$ Hz, 3H); HRMS (EI^+) calcd for $\text{C}_{11}\text{H}_{14}\text{O}$ $[\text{M}]^+$ 162.1045, found

S11

 m/z 162.1038.

The conditions of separating the corresponding esters were shown in Table 2.

Table 2. The conditions for analysis of chiral esters (254 nm)

Table 1 Entry	HPLC column*	Hexane / iPrOH	flow / ml/min	$t_R(R)$ /min	$t_R(S)$ /min
2	CHIRALPAK AD	500/1	0.5	12.3	13.8
3	CHIRALPAK OT	1000/1	0.5	9.3	10.7
4	CHIRALCEL OD	900/1	0.5	15.6	18.9
5	CHIRALCEL OD	900/1	0.5	32.5	44.3
6	CHIRALCEL OD	900/1	0.5	14.4	15.9
7	CHIRALCEL OD	900/1	0.5	28.1	25.7
8	CHIRALCEL OD	500/1	1.0	11.6	23.0
9	CHIRALCEL OD	500/1	1.0	27.4	58.0
10	CHIRALCEL OD	500/1	1.0	14.7	21.9
11	CHIRALPAK AD	500/1	0.5	20.1	27.5
12	CHIRALCEL OD	500/1	1.0	17.9	12.0
13	CHIRALCEL OD	500/1	0.5	19.0	15.1
14	CHIRALCEL OJ	99/1	0.5	21.5	19.3

* HPLC column of Daicel Chemical Industries, LTD.

references

- ¹Balsells, J.; Walsh, P. J. *J. Am. Chem. Soc.* **2000**, 122, 3250.
- ²Garcia, C.; Larochelle, L. K.; Walsh, P. J. *J. Am. Chem. Soc.* **2002**, 124, 10970.
- ³Crowther, G. P.; Kaiser, E. M.; Woodruff, R. A.; Hauser, C. R. *Org. Synth.*, **1988**, IV, 259.
- ⁴Shintou, T.; Kikuchi, W.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **2003**, in press.
- ⁵Kharasch, M. S.; Sosnovsky, George; Yang, N.C. *J. Am. Chem. Soc.* **1959**, 81, 5819.
- ⁶Uijtewaal, A. P.; Jonkers, F. L.; Gen A, van der. *J. Org. Chem.*, **1978**, 43, 3306.

Mon May 26 13:33:14 2003

サンブルスキャン回数: 64
バックグラウンドスキャン回数: 64
分解能: 8,000
サンブルゲイン: 8.0
ミラー速度: 0.6329
フバーチャー: 100.00

ATR
Sachiki.S

Mon May 26 13:33:11 2003
ネットワーク検出:

スペクトル: SHINTOH Sample-114
領域: 4000.00 720.00
しきい値: 92.460
感度: 50
ヒーグリスト:

位置	800.60	強度	35.466
位置	838.15	強度	97.064
位置	883.74	強度	90.655
位置	933.65	強度	91.209
位置	1006.02	強度	74.786
位置	1024.61	強度	66.945
位置	1067.80	強度	70.460
位置	1114.01	強度	49.776
位置	1175.04	強度	78.700
位置	1203.43	強度	79.997
位置	1241.87	強度	60.295
位置	1284.12	強度	34.157
位置	1312.70	強度	73.830
位置	1370.42	強度	88.160
位置	1449.18	強度	79.472
位置	1708.54	強度	46.708
位置	2929.82	強度	88.032
位置	2965.56	強度	84.689

C:\WINNR98\COMMON_DEFAULT.ALS
No34#1

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMT No34#1
DATIM Mon Apr 21 12:11:10 2003
OBNUC 1H
EXMOD NON
OBFREQ 270.05 MHz
OBSSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5402.4 Hz
SCANS 12
ACQTM 6.065 sec
PD 0.935 sec
PW1 5.2 us
IRNUC 1H
CTEMP 17.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 16

C:\WINNMR98\COMMON_DEFAULT.ALS
No. 432

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
CONAT No. 432
DATIM Wed Apr 30 14:42:31 2003
OBNUC 13C
EXMOD BCM
OBFRO 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQV 18315.0 Hz
SCANS 128
ACQTM 1.789 sec
PD 1.211 sec
PWI 4.0 us
IRNUC 1H
CTEMP 17.4 C
SLVMT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 29

File: 1241AP63

Date Run: 10-26-2002

Time Run: 22:24:49

Sample: SHINTO-7 O1/RL=0/40V MeCN R=3000

Instrument: JEOL LCmate

Run By: LCmate

Inlet: LC

Ionization mode: APCI+

Printed by: LCmate

Scan: 3-10,20-26

R.T.: 0:34.267

Base: m/z 272; 23.2%FS TIC: 1420428

UV Signal:

Selected Isotopes : H₀₋₃₀ C₀₋₃₀ N₀₋₃ O₀₋₃ P₀₋₂

Error Limit : 10 mmu

<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
287.2008	18.3%	C ₁₉ H ₂₇ O ₂	287.2011	-0.3

File: SHINTOH Sample-110

Mon May 26 13:23:33 2003

サンプルスキャン回数: 64
バックグラウンドスキャン回数: 64
分解能: 8.000
サンプルゲイン: 8.0
スキャン速度: 0.6329
パワー: 100.00

ATR
Sachiki.S

Mon May 26 13:23:28 2003

ピーク検出:
スペクトル: SHINTOH Sample-110
領域: 4000.00 720.00
しきい値: 92.998
感度: 50

位置	強度
848.68	84.974
828.85	88.353
813.80	78.376
743.74	84.969
729.90	75.313
721.09	69.457
1110.25	52.472
1069.01	74.041
1025.52	38.522
991.49	80.345
919.34	86.180
848.68	91.032
828.85	80.433
813.80	49.805
743.74	91.514
729.90	91.658

C:\WINNR98\COMMON_DEFAULT.ALS
No. 511

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
 COMNT No.511
 DATIM Sat May 17 09:50:36 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 32768
 FREQU 5405.4 Hz
 SCANS 12
 ACQTM 6.062 sec
 PD 0.935 sec
 PW1 5.2 us
 1H 18.9 c
 CDCL3 0.00 ppm
 EXREF 0.12 Hz
 BF 19
 RGAIN

C:\WINNR98\COMMON_DEFAULT.ALS
No.31 #1S

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT No.31 #1S
DATIM Tue Apr 29 13:13:00 2003
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 128
ACQTM 1.789 sec
PD 1.211 sec
PWL 4.0 us
IRNUC 1H
CTEMP 18.7 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 29

File: 0477-21E

Sample: SHINTOH Sample-110 HR

Instrument: JEOL JMS600 Ionization mode: EI+

Scan: 10-13

R.T.: 0:24.9

Base: m/z 281; 65.2%FS TIC: 4594682

#Ions: 60

Selected Isotopes : $H_{0-35}C_{0-30}O_{0-5}$

Error Limit : 20 mmu

<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
258.1629	49.3%	$C_{17}H_{22}O_2$	258.1620	-0.9
		$C_{13}H_{22}O_5$	258.1467	-16.0

File: SHINTOH Sample-112

Mon May 26 13:26:29 2003

サンプルスキャン回数: 64
 バックグラウンドスキャン回数: 64
 分解能: 8,000
 サンプルサイズ: 8.0
 スリット速度: 0.6329
 パワー: 100.00
 ATR
 Sachiki.S

Mon May 26 13:26:25 2003

ピーク検出:

スペクトル: SHINTOH Sample-112
 領域: 4000.00
 最小値: 95.234
 感度: 50

ピークリスト:

位置	強度
769.36	49.127
846.02	60.646
919.21	77.977
1029.78	57.406
1099.34	44.504
1163.14	39.709
1281.21	29.348
1315.45	48.890
1373.32	77.824
1416.70	86.281
1456.89	87.686
1509.54	84.100
1581.35	71.982
1605.22	89.244
1708.74	58.824
2930.82	51.838
2968.80	90.424
2980.82	90.763

C:\WINNMR98\COMMON_DEFAULT.ALS
No.512

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
 COMMT No.512
 DATIM Sat May 17 09:40:38 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 32768
 FREQU 5405.4 Hz
 SCANS 12
 ACQTM 6.062 sec
 PD 0.935 sec
 PW1 5.2 us
 IRNUC 1H
 CTMP 19.1 c
 CDCL3
 SLVNT
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 18

C:\WINNR98\COMMON_DEFAULT.ALS
No35_13C

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT No35_13C
DATIM Mon Apr 21 19:03:58 2003
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 128
ACQTM 1.789 sec
PD 1.211 sec
PWL 4.0 us
IRNUC 1H
CTEMP 17.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 29

File: 0477-23E

Sample: SHINTOH Sample-112 HR

Instrument: JEOL JMS600 Ionization mode: EI+

Scan: 26-41

R.T.: 1:13.3

Base: m/z 288; 71.1%FS TIC: 3866668

#Ions: 58

Selected Isotopes : $H_{0-35}C_{0-30}O_{0-5}$

Error Limit : 20 mmu

<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
288.1720	100.0%	$C_{22}H_{24}$	288.1878	16.0
		$C_{18}H_{24}O_3$	288.1725	0.5

File: SHINTOH Sample-113

Mon May 26 13:29:39 2003

サンプルスキャン回数: 64
バックグラウンドスキャン回数: 64
分解能: 8.000
サンプルサイズ: 8.0
ミラー速度: 0.6329
アパーチャー: 100.00
ATR
Sachiki.S

Mon May 26 13:29:36 2003
ピーク検出:
スペクトル: SHINTOH Sample-113
領域: 4000.00 720.00
しきい値: 93.886
感度: 50
ピークリスト:
位置: 758.71 強度: 44.747
位置: 848.59 強度: 64.003
位置: 920.10 強度: 77.607
位置: 1013.97 強度: 62.281
位置: 1088.77 強度: 43.953
位置: 1114.15 強度: 56.714
位置: 1167.66 強度: 72.575
位置: 1276.69 強度: 43.087
位置: 1373.91 強度: 85.341
位置: 1400.39 強度: 84.657
位置: 1449.91 強度: 88.686
位置: 1486.40 強度: 87.917
位置: 1593.47 強度: 79.149
位置: 1717.87 強度: 50.511
位置: 2927.11 強度: 91.807
位置: 2971.74 強度: 91.996

C:\WINNR98\COMMON_DEFAULT.ALS
No.514

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT No.514
DATIM Sat May 17 10:00:33 2003
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
SCANS 12
ACQTM 6.062 sec
PD 0.935 sec
PWL 5.2 us
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15

C:\WINNMR98\COMMON_DEFAULT.ALS
No. 492DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAINC:\WINNMR98\COMMON_DEFAULT.ALS
No. 492
Wed Apr 30 10:16:30 2003
13C
ECM67.80 MHz
135.00 KHz
5200.0 Hz
32768
18315.0 Hz
128
1.789 sec
1.211 sec
4.0 us
1H
18.5 c
CDCL3
77.00 ppm
0.12 Hz
29

File: 0477-24E

Sample: SHINTOH Sample-113 HR

Instrument: JEOL JMS600 Ionization mode: EI+

Scan: 36-41

R.T.: 1:24.3

Base: m/z 292; 84.3% FS TIC: 5131689

#Ions: 72

Selected Isotopes : $H_{0.35}C_{0.30}O_{0.5}Cl_{0.1}$

Error Limit : 20 mmu

<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
292.1227	100.0%	$C_{23}H_{16}$	292.1252	2.5
		$C_{19}H_{16}O_3$	292.1099	-13.0
		$C_{16}H_{20}O_5$	292.1310	8.3
		$C_{17}H_{21}O_2Cl$	292.1230	0.3
		$C_{13}H_{21}O_5Cl$	292.1077	-15.0

Title: SHINTOH Sample-111

Mon May 26 13:17:22 2003

サンプルスキャン回数: 64
 バックグラウンドスキャン回数: 64
 分解能: 8.000
 サンプルサイズ: 8.0
 ミラー速度: 0.6329
 Wavenumber: 100.00

ATR
 Sachiki.S

Mon May 26 13:15:10 2003

ピーク検出:
 スペクトル: SHINTOH Sample-111
 領域: 4000.00 720.00
 最小値: 95.607
 感度: 50

位置	強度
741.00	79.414
741.00	89.262
741.00	91.106
741.00	81.189
741.00	86.017
741.00	78.656
741.00	79.404
741.00	68.583
741.00	87.460
741.00	82.755
741.00	89.643
741.00	84.554
741.00	92.565
741.00	59.978
741.00	91.015
741.00	91.857

C:\WINNMR98\COMMON_DEFAULT.ALS
No. 513

D:\FILE C:\WINNMR98\COMMON_DEFAULT.ALS

COMNT No. 513
DATIM Sat May 17 09:45:10 2003
OBNUC 1H
EXMOD NON
OBFREQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5405.4 Hz
SCANS 12
ACQTM 6.062 sec
PD 0.935 sec
PWL 5.2 us
IRNUC 1H
CTEMP 19.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19

C:\WINNR98\COMMON_DEFAULT.ALS
No. 482

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMT No. 482
DATIM Tue Apr 29 10:45:09 2003
GENUC 13C
EXMOD BCM
OBFREQ 67.80 MHz
OBSET 135.00 KHz
OBSIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 128
ACQTM 1.789 sec
PD 1.211 sec
PWL 4.0 us
IRNUC 1H
CTEMP 17.6 c
SIVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 29

File: 0477-22E

Sample: SHINTOH Sample-111 HR

Instrument: JEOL JMS600 Ionization mode: EI+

Scan: 39-45

R.T.: 1:32

Base: m/z 286; 60.7% FS TIC: 4377575

#Ions: 65

Selected Isotopes : $H_{0.35}C_{0.30}O_{0.5}$

Error Limit : 20 mmu

<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
286.1930	100.0%	$C_{19}H_{26}O_2$	286.1933	0.3
		$C_{15}H_{26}O_5$	286.1780	-15.0

C:\WINNR98\COMMON_DEFAULT.ALS
No.543

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMMT No.543
DATIM Wed May 28 20:19:28 2003
OBNUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5402.4 Hz
SCANS 12
ACQTM 6.065 sec
PD 0.935 sec
PWL 5.2 us
IRNUC 1H
CTEMP 19.8 C
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14

C:\WINNR98\COMMON\DEFAULT.ALS
No.536

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT No.536
DATIM Sat May 24 12:09:35 2003
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 84
ACQTM 1.789 sec
PD 1.211 sec
PW1 4.0 us
IRNUC 1H
CTEMP 20.3 c
SIVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 29

File: 0609-25E

Sample: SHINTO Sample-126 HR

Instrument: JEOL JMS600 Ionization mode: EI+

Scan: 34-41

R.T.: 1:21.675

Base: m/z 243; 65.8%FS TIC: 2841517

#Ions: 29

Selected Isotopes : $H_{0-30} C_{0-30} N_{0-3} O_{0-3}$

Error Limit : 10 mmu

<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
254.1284	29.4%	$C_{15}H_{16}N_3O$	254.1293	0.9
		$C_{17}H_{18}O_2$	254.1307	2.3

C:\WINNR98\COMMON_DEFAULT.ALS
NO. 547

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMMT No. 547
DATIM Wed May 28 20:43:16 2003
OENUC 1H
EXMOD NON
OBFRQ 270.05 MHz
OBSET 112.00 KHz
OBFIN 5800.0 Hz
POINT 32768
FREQU 5402.4 Hz
SCANS 12
AQTM 6.065 sec
PD 0.935 sec
PWL 5.2 us
IRNUC 1H
CTEMP 18.7 C
SIVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18

C:\WINNR98\COMMON\DEFAULT.ALS
No.544

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT No.544
DATIM Wed May 28 20:51:51 2003
OBNUC 13C
EXMOD BCM
OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 128
ACQTM 1.789 sec
PD 1.211 sec
PWI 4.0 us
IRNUC 1H
CTEMP 19.6 c
SIVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 29

File: 0609-26E

Sample: SHINTO Sample-127 HR

Instrument: JEOL JMS600 Ionization mode: EI+

Scan: 100-105

R.T.: 3:44.2

Base: m/z 284; 86.1%FS TIC: 2977634

#Ions: 25

Selected Isotopes : $H_{0-30} C_{0-30} N_{0-3} O_{0-5}$

Error Limit : 10 mmu

<u>Measured Mass</u>	<u>% Base</u>	<u>Formula</u>	<u>Calculated Mass</u>	<u>Error</u>
284.1403	100.0%	$C_{21}H_{18}N$	284.1439	3.6
		$C_{20}H_{16}N_2$	284.1313	-9.0
		$C_{16}H_{18}N_3O_2$	284.1399	-0.4
		$C_{18}H_{20}O_3$	284.1412	0.9
		$C_{14}H_{22}NO_5$	284.1498	9.5
		$C_{13}H_{20}N_2O_5$	284.1372	-3.1