Highly Enantioselective Michael Addition of Cyclic 1,3-Dicarbonyl Compounds to α,β -Unsaturated Ketones

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1. General Methods:

NMR spectra were recorded with tetramethylsilane as the internal standard. TLC was performed on glass-backed silica plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. ^1H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance). Chemical shifts (δ) are reported in ppm downfield from CDCl_3 ($\delta = 7.27$ ppm) for ^1H NMR and relative to the central CDCl_3 resonance ($\delta = 77.0$ ppm) for ^{13}C NMR spectroscopy. Coupling constants (J) are given in Hz. ESI-HRMS spectrometer was measured with a Finnigan LCQ^{DECA} ion trap mass spectrometer. Optical rotations were measured at 589 nm at 22 °C. Enantiomeric excess was determined by HPLC analysis on chiral Chiralpak columns. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). Primary aminocatalysts **1b-1c**¹ were prepared according to literature procedures.

2. Asymmetric Michael addition of 1,3-dicarbonyl compounds to α,β -unsaturated ketones

General procedure: **2a** 16.2 mg (0.1 mmol), **3a** 21.9 mg (0.15 mmol), **1b** 6.5 mg (0.02 mol) and TFA 2.9 μL (0.04 mol) were stirred in DCM (2 mL) at 0 °C for 96 h. Then the reaction was quenched by adding 1 mol/L HCl (0.5 mL). The mixture was extracted with EtOAc (10 mL), dried with anhydrous sodium sulfate. The solvent was removed and flash chromatography on silica gel (10% ethyl acetate/petroleum ether) gave **4aa** as a colorless solid (27 mg, 88%).

The Michael addition product was found to exist in rapid equilibrium with a pseudo-diastereomeric hemiketal form in solution. The optical resolution is changeable in related to concentration and solvent, therefore, only the optical rotation of **4aa** was measured. However, the equilibrium is very rapid and therefore no pseudo-diastereomers were observed during HPLC analysis using the mixture of hexane/ 2-propanol containing 0.1% TFA as the eluent.²

4aa, 88% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.93 (d, $J = 7.9$ Hz, 0.11H), 7.89 (d, $J = 7.8$ Hz, 0.38H), 7.79 (d, $J = 8.3$ Hz, 0.50H), 7.58-7.53 (m, 0.42H), 7.48-7.42 (m, 0.67H), 7.35-7.17 (m, 7.43H), 4.68 (d, $J = 10.1$ Hz, 0.10H), 4.25 (dd, $J = 3.6, 6.9$ Hz, 0.39H), 4.16 (dd, $J = 6.8, 11.4$ Hz, 0.52H), 3.89-3.79 (m, 0.55H), 3.39 (s, 0.34H), 3.33 (d, $J = 19.1$ Hz, 0.15H), 2.55-2.34 (m, 1.32H), 2.02-1.94 (m,

0.60H), 1.68 (s, 1.60H), 1.66 (s, 1.40H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 212.4, 161.6, 159.8, 152.8, 152.7, 143.3, 141.6, 131.9, 131.4, 129.0, 128.5, 128.1, 127.9, 127.0, 126.6, 126.3, 123.9, 123.8, 123.5, 123.0, 122.7, 116.5, 116.3, 116.1, 115.8, 103.9, 101.2, 100.6, 99.1, 45.1, 42.6, 40.1, 35.2, 34.8, 34.4, 30.0, 29.6, 27.8, 27.3; ESI-HRMS: calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_4+\text{Na}$ 331.0941, found 331.0947; $[\alpha]_{\text{D}}^{22} = -12.0$ (c 0.3, acetonitrile), $\{ \text{Lit.}^3 [\alpha]_{\text{D}}^{25} = -15.5 \pm 1$ (c 3.0, acetonitrile), 99% ee $\}$, 96% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 6.392$ min, $t_{\text{major}} = 16.251$ min.

4ab, 87% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.93 (d, $J = 7.0$ Hz, 0.1H), 7.86 (d, $J = 8.0$ Hz, 0.39H), 7.78 (d, $J = 7.9$ Hz, 0.5H), 7.56 (t, $J = 7.2$, 15.5 Hz, 0.39H), 7.49-7.43 (m, 0.60H), 7.32 (d, $J = 7.8$ Hz, 0.55H), 7.28-7.13 (m, 5.27H), 4.64 (d, $J = 8.4$ Hz, 0.08H), 4.18-4.10 (m, 0.80H), 3.83 (s, 0.56H), 3.29 (s, 0.36H), 3.22 (s, 0.05H), 2.47-2.16 (m, 1.51H), 1.96-1.87 (m, 0.52H), 1.68 (d, $J = 8.4$ Hz, 2.97H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 212.4, 161.3, 159.7, 159.0, 152.8, 141.8, 140.5, 132.5, 132.1, 131.9, 131.7, 129.4, 128.9, 128.7, 128.6, 128.4, 128.2, 124.0, 123.7, 123.0, 122.7, 116.6, 116.5, 116.2, 115.7, 103.7, 101.2, 100.2, 99.0, 45.1, 42.3, 39.9, 34.8, 34.3, 34.2, 30.0, 28.1, 27.7; ESI-HRMS: calcd. for $\text{C}_{19}\text{H}_{15}\text{ClO}_4+\text{Na}$ 365.0551, found 365.0567; 97% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 6.764$ min, $t_{\text{major}} = 19.517$ min.

4ac, 81% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.94-7.91 (m, 0.24H), 7.88 (dd, $J = 1.4$, 7.9 Hz, 0.52H), 7.77 (dd, $J = 1.5$, 7.9 Hz, 0.26H), 7.58-7.54 (m, 0.60H), 7.53-7.51 (m, 0.47H), 7.37-7.36 (m, 0.54H), 7.33-7.17 (m, 2.98H), 7.11-7.10 (m, 0.41H), 7.06 (s, 0.12H), 7.00-6.99 (m, 0.33H), 6.32-6.30 (m, 1.00H), 6.18-6.11 (m, 1.10H), 4.77-4.73 (m, 0.24H), 4.34-4.30 (m, 1.34H), 3.97 (s, 0.26H), 3.64 (dd, $J = 8.4$, 19.5 Hz, 0.25H), 3.31 (dd, $J = 3.0$, 19.5 Hz, 0.25H), 2.71 (d, $J = 1.9$ Hz, 0.23H), (d, $J = 1.9$ Hz, 0.36H), 2.36-2.22 (m, 3.07H), 1.71 (s, 2.16H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 212.0, 162.0, 159.3, 154.0, 152.9, 152.7, 142.2, 141.3, 140.9, 132.2, 132.0, 131.6, 126.0, 123.9, 123.6, 123.2, 122.8, 116.6, 116.4, 116.2, 115.5, 110.8, 110.5, 106.8, 106.4, 106.1, 99.6, 99.4, 99.1, 45.0, 38.2, 35.6, 30.3, 29.8, 29.6, 29.2, 28.1, 28.0, 27.4, 21.3; ESI-HRMS: calcd.

for $C_{20}H_{18}O_5+Na$ 361.1046, found 361.1059; 95% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 8.650$ min, $t_{\text{major}} = 23.096$ min.

4ad, 81% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.94-7.90 (m, 0.48H), 7.80-7.78 (m, 0.39H), 7.58-7.56 (m, 0.39H), 7.53-7.48 (m, 0.52H), 7.35-7.12 (m, 3.72H), 6.86-6.79 (m, 1.72H), 4.65 (d, $J = 8.6$ Hz, 0.14H), 4.24-4.20 (m, 0.37H), 4.15-4.09 (m, 0.39H), 3.70 (s, 0.36H), 3.41 (s, 0.36H), 2.53-2.27 (m, 1.62H), 2.04-1.93 (m, 0.42H), 1.68 (s, 3.00H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 212.5, 161.3, 159.5, 158.6, 158.1, 152.9, 152.8, 135.1, 133.0, 131.9, 131.7, 131.7, 131.4, 129.0, 128.0, 123.9, 123.5, 123.0, 122.7, 116.6, 116.4, 116.1, 115.9, 114.7, 114.0, 113.5, 104.3, 101.3, 100.5, 99.1, 55.2, 45.5, 42.6, 39.8, 34.5, 34.2, 33.2, 30.0, 29.6, 28.1, 27.7, 21.3, 19.7; ESI-HRMS: calcd. for $C_{17}H_{14}O_5+Na$ 321.0733, found 321.0729; 94% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AS column and hexane/2-propanol 90/10 containing 0.1% TFA as the eluent, $t_{\text{minor}} = 12.150$ min, $t_{\text{major}} = 19.946$ min.

4ae, 83% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88 (d, $J = 7.7$ Hz, 0.77H), 7.79 (s, 0.40H), 7.65-7.45 (m, 1.28H), 7.34-7.21 (m, 2.75H), 7.11 (s, 0.8H), 6.90-6.82 (m, 2.30H), 4.51 (d, $J = 4.43$ Hz, 1.00H), 3.76 (s, 0.91H), 3.35 (s, 0.31H), 2.67-2.45 (m, 1.02H), 2.41-2.04 (m, 2.15H), 1.70 (s, 2.78H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.1, 161.4, 159.3, 158.5, 152.9, 146.4, 145.5, 135.9, 132.2, 131.7, 129.0, 128.2, 127.0, 126.6, 126.0, 125.2, 124.2, 124.0, 123.6, 123.2, 122.9, 116.6, 116.3, 115.4, 103.7, 101.1, 100.3, 47.0, 42.8, 39.8, 31.5, 30.8, 29.7, 27.8, 27.7, 21.3, 19.7; ESI-HRMS: calcd. for $C_{17}H_{14}O_4S+Na$ 337.0505, found 337.0502; 93% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AS column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 12.098$ min, $t_{\text{major}} = 29.948$ min.

4af, 90% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.89-7.77 (m, 1.00H), 7.58-7.43 (m, 1.08H), 7.36-7.20 (m, 7.06H), 4.75 (s, 0.13H), 4.27-4.13 (m, 0.94H), 3.78 (s, 0.50H), 3.64 (s, 0.54H), 2.48 (s, 0.22H), 2.43-2.32 (m, 1.33H), 1.92 (s, 2.21H), 1.28-1.03 (m, 2.96H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.2, 161.4, 159.7, 159.0, 152.8, 152.8, 143.4,

141.6, 131.9, 131.4, 129.1, 128.5, 127.0, 126.4, 123.9, 123.6, 122.9, 122.6, 116.6, 116.3, 116.0, 115.6, 104.2, 102.0, 101.3, 100.8, 43.9, 40.2, 37.8, 36.0, 35.1, 33.9, 33.6, 33.3, 7.4, 7.3; ESI-HRMS: calcd. for $C_{20}H_{18}O_4+Na$ 345.1097, found 345.1101; 99% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{minor} = 6.617$ min, $t_{major} = 18.475$ min.

4ag, 82% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.94 (m, 0.18H), 7.88 (d, $J = 7.9$ Hz, 0.33H), 7.79 (d, $J = 7.8$ Hz, 0.38H), 7.59-7.45 (m, 1.00H), 7.39-7.21 (m, 6.13H), 7.15-7.09 (m, 0.17H), 7.00-6.96 (m, 0.20H), 4.72 (d, $J = 9.8$ Hz, 0.20H), 4.34-4.26 (m, 0.32H), 4.19-4.13 (m, 0.41H), 3.88-3.78 (m, 0.25H), 3.26 (d, $J = 19.7$ Hz, 0.80H), 2.66-2.31 (m, 1.50H), 2.31-2.30 (m, 0.42H), 2.26 (s, 0.30H), 1.95-1.84 (m, 1.82H), 1.64-1.54 (m, 1.96H), 1.35-1.20 (m, 0.24H), 1.02-0.88 (m, 2.84H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 215.1, 162.1, 159.7, 158.8, 152.9, 143.3, 141.5, 131.9, 131.7, 131.5, 129.2, 128.6, 128.1, 127.9, 127.1, 127.0, 126.9, 126.4, 124.0, 123.6, 123.0, 122.6, 116.6, 116.5, 116.2, 101.9, 100.5, 44.3, 43.0, 42.6, 40.7, 38.4, 35.2, 34.8, 33.9, 17.3, 16.5, 16.3, 14.1, 13.6; ESI-HRMS: calcd. for $C_{21}H_{20}O_4+Na$ 359.1254, found 359.1253; 97% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{minor} = 6.947$ min, $t_{major} = 16.165$ min.

4ah, 93% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.87 (d, $J = 7.9$ Hz, 0.50H), 7.74-7.70 (m, 0.43H), 7.49-7.37 (m, 0.96H), 7.27-7.09 (m, 2.29H), 6.97-6.93 (m, 0.15H), 3.38-3.32 (m, 0.50H), 3.28-3.20 (m, 0.50H), 3.08-2.89 (m, 0.23H), 2.80-2.77 (m, 0.51H), 2.71 (m, 0.23H), 2.35-2.21 (m, 1.26H), 2.17 (s, 1.63H), 2.15-2.10 (m, 0.5H), 2.08-1.76 (m, 0.60H), 1.77 (s, 1.00H), 1.57-1.50 (m, 1.65H), 1.49-1.29 (m, 0.81H), 1.24-1.14 (m, 1.27H), 0.96-0.89 (m, 1.44H), 0.86-0.81 (m, 1.65H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 213.9, 162.7, 162.3, 161.7, 158.1, 157.5, 152.6, 152.4, 131.5, 131.1, 128.8, 125.9, 125.7, 123.7, 123.5, 122.5, 116.5, 116.0, 106.8, 105.2, 104.9, 100.0, 98.9, 47.8, 38.1, 34.1, 33.6, 33.2, 30.0, 29.7, 29.5, 28.4, 28.2, 28.0, 21.1, 20.2, 19.3, 13.9, 13.7; ESI-HRMS: calcd. for $C_{16}H_{18}O_4+Na$ 297.1097, found 297.1086; 95% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent,

$t_{\text{minor}} = 5.117$ min, $t_{\text{major}} = 6.785$ min.

4ai, 88% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.89 (d, $J = 7.9$ Hz, 0.62H), 7.78-7.71 (m, 0.38H), 7.50-7.40 (m, 1.04H), 7.28-7.08 (m, 2.47H), 3.33-3.20 (m, 0.91H), 3.11-3.02 (m, 0.37H), 2.97 (s, 0.38H), 2.89 (s, 0.31H), 2.78-2.71 (m, 0.65H), 2.57-2.49 (m, 0.68H), 2.29-2.28 (m, 0.31H), 2.24 (s, 0.13H), 2.18 (s, 1.93H), 2.14-2.01 (m, 0.59H), 1.77 (s, 1.25H), 1.00 (s, 0.96H), 0.96 (d, $J = 6.5$ Hz, 2.00H), 0.74 (d, $J = 6.5$ Hz, 2.19H), 0.64 (d, $J = 6.8$ Hz, 0.89H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 214.2, 162.5, 161.9, 161.7, 159.5, 158.8, 152.6, 131.5, 131.1, 128.8, 125.9, 125.7, 123.7, 123.6, 123.4, 122.7, 122.6, 116.5, 116.0, 107.5, 104.9, 101.7, 99.0, 45.5, 38.4, 36.2, 33.1, 29.8, 28.5, 27.2, 26.7, 25.2, 21.4, 20.5, 16.8, 15.7; ESI-HRMS: calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_4 + \text{Na}$ 297.1097, found 297.1096; 98% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 4.933$ min, $t_{\text{major}} = 7.421$ min.

4aj, 55% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 9.72 (s, 0.77H), 7.91 (d, $J = 8.4$ Hz, 1.00H), 7.77-7.71 (m, 0.52H), 7.51-7.43 (m, 1.53H), 7.29-7.19 (m, 2.61H), 3.39-3.23 (m, 2.06H), 2.76 (s, 0.45H), 2.70 (s, 0.40H), 2.20-2.11 (m, 2.56H), 1.98-1.92 (m, 2.00H), 1.36-1.17 (m, 3.23H), 1.16-1.11 (m, 2.00H), 1.06-0.96 (m, 3.70H), 0.97-0.92 (m, 2.79H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 216.8, 161.7, 152.7, 131.5, 131.2, 123.8, 123.7, 123.6, 123.5, 122.5, 122.5, 116.6, 116.4, 116.3, 116.1, 107.2, 46.5, 35.8, 34.2, 33.9, 33.7, 33.5, 33.4, 31.5, 30.1, 29.1, 21.2, 20.3, 14.0, 13.7, 7.6, 7.4; ESI-HRMS: calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_4 + \text{Na}$ 311.1254, found 311.1260; 90% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 5.127$ min, $t_{\text{major}} = 7.052$ min.

4ak, 78% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.75 (d, $J = 7.8$ Hz, 1.00H), 7.46 (t, $J = 7.8$ Hz, 1.00H), 7.23-7.04 (m, 2.00H), 4.65 (s, 1.00H), 3.37-3.34 (m, 1.00H), 2.30-2.19 (m, 1.00H), 2.12-1.99 (m, 2.00H), 1.87-1.79 (m, 2.00H), 1.64-1.57 (m, 2.00H), 1.41-1.35 (m, 1.00H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 162.5, 161.3, 152.6, 131.6, 123.7, 122.5, 116.5, 114.9, 102.8, 102.3, 38.6, 35.8, 29.3, 28.2, 18.9; ESI-HRMS: calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_4 + \text{Na}$ 281.0784, found 281.0785; 94% ee, the

enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 6.888$ min, $t_{\text{major}} = 7.366$ min.

4ba, 87% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.67 (s, 0.43H), 7.57 (s, 0.54H), 7.36-7.15 (m, 6.89H), 7.10-7.06 (m, 0.74H), 4.72-4.69 (m, 0.01H), 4.30 (s, 0.37H), 4.23-4.08 (m, 1.01H), 3.70 (s, 0.37H), 3.33-3.26 (m, 0.01H), 2.50-2.42 (m, 2.10H), 2.37 (s, 2.42H), 2.25 (s, 0.34H), 2.00-1.84 (m, 0.67H), 1.64 (s, 2.97H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 212.3, 161.7, 159.8, 159.1, 151.0, 150.9, 143.3, 141.7, 133.6, 133.2, 132.9, 132.4, 129.0, 128.4, 128.1, 127.8, 126.9, 126.5, 126.3, 122.6, 122.3, 116.2, 116.1, 115.8, 115.5, 115.1, 103.7, 101.0, 100.5, 99.0, 45.1, 42.6, 40.1, 35.3, 34.8, 34.5, 30.0, 27.8, 27.3, 20.8, 14.1; ESI-HRMS: calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_4 + \text{Na}$ 345.1097, found 345.1091; 99% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 5.915$ min, $t_{\text{major}} = 25.934$ min.

4ca, 80% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.72 (s, 0.10H), 7.67 (s, 0.37H), 7.58 (s, 0.47H), 7.37-7.15 (m, 6.40H), 7.12-7.06 (m, 0.57H), 4.69 (d, $J = 7.4$ Hz, 0.11H), 4.27-4.23 (m, 0.40H), 4.18-4.10 (m, 0.51H), 3.85-3.78 (m, 0.56H), 3.39-3.27 (m, 0.51H), 2.76-2.30 (m, 4.23H), 2.27 (s, 0.37H), 2.04-1.93 (m, 0.53H), 1.67 (d, $J = 2.4$ Hz, 3.05H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 212.5, 162.4, 159.7, 158.9, 151.1, 143.3, 141.6, 133.6, 133.3, 133.0, 132.7, 132.5, 129.1, 128.5, 128.1, 127.9, 127.1, 127.0, 126.9, 126.6, 126.4, 122.7, 122.3, 116.3, 116.2, 115.5, 103.9, 100.4, 99.0, 45.1, 42.5, 40.1, 35.3, 34.8, 34.3, 30.1, 29.6, 28.0, 27.6, 22.6, 20.9; ESI-HRMS: calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_4 + \text{Na}$ 359.1254, found 359.1271; 98% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 6.192$ min, $t_{\text{major}} = 25.646$ min.

4da, 82% yield. ^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.98 (s, 0.48H), 7.89 (s, 0.52H), 7.62-7.60 (m, 1.00H), 7.29-7.10 (m, 5H), 7.06-6.99 (m, 1.00H), 4.15-4.10 (m, 1.00H), 2.48-2.38 (m, 1.00H), 1.96 (s, 1.00H), 1.27 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ

(ppm) 161.5, 160.8, 158.6, 151.6, 142.8, 134.7, 134.2, 130.5, 129.8, 129.5, 129.1, 128.9, 128.6, 128.2, 127.1, 126.6, 126.0, 125.6, 125.4, 118.1, 117.5, 117.1, 116.7, 116.5, 105.1, 102.2, 100.9, 42.5, 40.0, 35.3, 34.4, 29.6, 28.0, 27.6, 21.3, 19.7, 14.1; ESI-HRMS: calcd. for $C_{19}H_{15}BrO_4+Na$ 409.0046, found 409.0048; 98% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 5.842$ min, $t_{\text{major}} = 15.642$ min.

4ea, 68% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.26 (d, $J = 8.0$ Hz, 0.50H), 7.18 (d, $J = 8.0$ Hz, 0.50H), 7.54-7.10 (m, 7.53H), 7.01 (s, 0.12H), 7.00-6.97 (m, 0.25H), 4.45-4.42 (m, 0.47H), 4.32-4.26 (m, 0.55H), 2.54-2.44 (m, 0.90H), 2.38-2.12 (m, 1.48H), 2.05-1.96 (m, 0.60H), 1.66 (s, 2.97H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 183.6, 183.2, 160.3, 159.5, 144.2, 142.0, 135.7, 135.6, 130.0, 129.8, 129.6, 129.1, 128.8, 128.4, 127.8, 126.8, 126.3, 126.1, 126.0, 125.9, 125.3, 125.1, 123.6, 115.6, 112.6, 99.9, 98.4, 45.9, 42.5, 42.1, 39.7, 36.4, 36.2, 34.5, 28.0, 27.6, 24.2, 21.3, 19.7; ESI-HRMS: calcd. for $C_{19}H_{16}O_3S+Na$ 347.0712, found 347.0717; 89% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack AD column and hexane/2-propanol (80/20) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 6.299$ min, $t_{\text{major}} = 11.628$ min.

4fa, 71% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.93 (dd, $J = 1.3, 7.9$ Hz, 0.50H), 7.66-7.58 (m, 1.38H), 7.48 (t, $J = 6.9$ Hz, 1.27H), 7.32-7.28 (m, 1.53H), 7.26-7.05 (m, 6.71H), 7.00 (d, $J = 1.1$ Hz, 0.94H), 6.84 (s, 0.40H), 4.36 (d, $J = 4.0$ Hz, 0.99H), 4.06-4.00 (m, 1.27H), 3.53-3.47 (m, 4.28H), 2.34-2.22 (m, 1.05H), 2.16-2.09 (m, 0.55H), 1.85 (t, $J = 11.6, 23.3$ Hz, 0.95H), 1.55 (d, $J = 16.5$ Hz, 4.00H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 161.2, 161.0, 155.6, 155.1, 145.5, 145.1, 138.8, 130.7, 130.6, 128.0, 127.1, 127.3, 126.9, 125.4, 125.1, 122.5, 121.4, 121.3, 115.7, 115.5, 114.4, 114.3, 108.9, 107.4, 99.5, 98.1, 62.0, 43.4, 41.7, 36.4, 35.9, 28.8, 28.7, 27.6, 26.1, 25.5; ESI-HRMS: calcd. for $C_{20}H_{19}NO_3+H$ 322.1438, found 322.1440; 99% ee, the enantiomeric ratio was determined by chiral stationary phase HPLC using a Daicel Chiralpack OD column and hexane/2-propanol (90/10) containing 0.1% TFA as the eluent, $t_{\text{minor}} = 15.019$ min, $t_{\text{major}} = 17.907$ min.

References

- (1) Brunner, H.; Bügler, J.; Nuber, B. *Tetrahedron: Asymmetry* **1995**, 6, 1699.
- (2) Halland, N.; Hansen, T.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2003**, 42, 4955.
- (3) West, B. D.; Preis, S.; Schroeder, C. H.; Link, K. P. *J. Am. Chem. Soc.* **1961**, 83, 2676.

¹H NMR and ¹³C NMR

Current Data Parameters
NAME 1397-xjw-345
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060911
Time 17.30
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SF01 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 20.00 cm
F1P 11.000 ppm
F1 3301.43 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCH 0.57500 ppm/cm
HZCM 172.57475 Hz/cm

Current Data Parameters
NAME 1397-xjw-345
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060913
Time 12.27
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2274
DS 4
SWH 22875.735 Hz
FIDRES 0.348604 Hz
AQ 1.4461105 sec
RG 8192
DM 22.850 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.50 usec
PL1 -6.00 dB
SF01 75.475558 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677535 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 6.00 cm
F1P 230.050 ppm
F1 17361.36 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCH 11.52750 ppm/cm
HZCM 869.95453 Hz/cm

Current Data Parameters

NAME 1397-xjw-335
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20060824
Time 15.13
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl₃
NS 64
DS 0
SWH 9995.204 Hz
FIDRES 0.182559 Hz
AQ 2.7329011 sec
RG 512
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters

SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
CY 18.00 cm
F1P 11.000 ppm
F1 3301.43 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PQWCH 0.57500 ppm/cm
H2OH 172.57475 Hz/cm

Current Data Parameters

NAME 1397-xjw-335
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20060825
Time 12.59
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2495
DS 4
SWH 22678.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8152
DM 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00000000 sec

===== CHANNEL f1 =====

NUC1 13C
P1 5.50 usec
PL1 -0.00 dB
SFO1 75.4775998 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters

SI 32768
SF 75.4677547 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
CY 8.00 cm
F1P 230.005 ppm
F1 17357.96 Hz
F2P -0.500 ppm
F2 -33.73 Hz
PQWCH 11.52525 ppm/cm

Current Data Parameters
NAME 1397-xjw-357
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060920
Time 9.27
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 1024
CW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1308122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 10.000 ppm
F1 300.130 MHz
F2P -0.500 ppm
F2 -150.06 Hz
PPHM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm

Current Data Parameters
NAME 1397-xjw-357
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060920
Time 14.24
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 2032
DS 4
SWH 20625.736 MHz
FIDRES 0.348004 Hz
AQ 1.4451088 sec
RG 8192
CW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
S11 0.00000000 sec
S12 0.00000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 6.50 usec
PL1 0.00 dB
SFO1 75.4778588 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
P2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1310805 MHz

F2 - Processing parameters
SI 32768
SF 75.4777882 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 300.500 ppm
F1 15131.28 MHz
F2P -0.500 ppm
F2 -37.73 MHz

Current Data Parameters
NAME 1397-xjw-351
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060914
Time 9.55
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DN 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPHCH 0.52500 ppm/cm
HZCM 157.56825 Hz/cm

Current Data Parameters
NAME 1397-xjw-351
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060915
Time 9.14
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4
DS 4
SWH 20075.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DN 27.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775258 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
P2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.70 dB
SFO2 300.1312009 MHz

F2 - Processing parameters
SI 32768
SF 75.4677972 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 10.00 cm
F1P 200.500 ppm
F1 15131.25 Hz
F2P -37.73 Hz
F2 10.05000 ppm/cm
PPHCH 10.05000 ppm/cm
HZCM 756.45099 Hz/cm

Current Data Parameters
NAME 1397-xjw-349
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060914
Time 9.42
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
CW 83.400 usec
DE 5.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SF01 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WOM 6M
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PCHN 0.52500 ppm/cm
H2CN 157.56825 Hz/cm

Current Data Parameters
NAME 1397-xjw-349
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060915
Time 12.38
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2780
DS 4
SWH 20075.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451186 sec
RG 8192
CW 20.000 usec
DE 6.000 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.50 usec
PL1 0.00 dB
SF01 75.475598 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2PRG2 zgpg30
PL2 0.00 usec
PL3 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1320882 MHz

F2 - Processing parameters
SI 65536
SF 75.4677541 MHz
WOM 6M
SSB 0
LB 3.00 Hz
GB 0
PC 1.45

1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 230.526 ppm
F1 17395.32 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PCHN 11.55000 ppm/cm

Current Data Parameters
 NAME 1397-xjw-347
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060914
 Time 9.10
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182969 Hz
 AQ 2.7329011 sec
 RG 512
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 3.00 usec
 PL1 -2.00 dB
 SFO1 300.1320862 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300124 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 14.00 cm
 F1P 12.000 ppm
 F1 3601.56 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
 PRNCH 0.62500 ppm/cm
 HZCM 187.58125 Hz/cm

Current Data Parameters
 NAME 1397-xjw-347
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060915
 Time 22.45
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 976
 DS 4
 SWH 22675.736 Hz
 FIDRES 0.346004 Hz
 AQ 1.4451188 sec
 RG 8192
 DW 22.050 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.00000000 sec
 d12 0.00002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 5.50 usec
 PL1 -6.00 dB
 SFO1 75.4775588 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -2.00 dB
 PL12 17.70 dB
 PL13 17.71 dB
 SFO2 300.1312095 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677575 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 12.00 cm
 F1P 230.500 ppm
 F1 17395.32 Hz
 F2P -0.500 ppm
 F2 -37.73 Hz
 PRNCH 11.55000 ppm/cm
 HZCM 871.60250 Hz/cm

Current Data Parameters
NAME 1397-xjw-350
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060914
Time 9.46
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 30.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCH 0.62500 ppm/cm
HZCM 187.58125 Hz/cm

Current Data Parameters
NAME 1397-xjw-350
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060918
Time 12.25
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1936
DS 4
SWH 22675.736 Hz
FIDRES 0.346054 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.0300000 sec
d12 0.0000200 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775998 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677567 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 230.500 ppm
F1 17395.32 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCH 11.55000 ppm/cm
HZCM 871.65259 Hz/cm

Current Data Parameters
NAME 1397-xjw-371
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061011
Time 9.31
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 1024
OW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 20.00 cm
F1P 11.000 ppm
F1 3301.43 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCH 0.57500 ppm/cm
HZCH 172.57475 Hz/cm

Current Data Parameters
NAME 1397-xjw-371
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061011
Time 14.26
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 2147
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
OW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312085 MHz

F2 - Processing parameters
SI 32768
SF 75.4677525 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 6.00 cm
F1P 230.500 ppm
F1 17395.32 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCH 11.55000 ppm/cm
HZCH 871.65247 Hz/cm

Current Data Parameters
NAME 1397-xjw-343
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060911
Time 17.09
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DM 83.400 us
DE 6.00 us
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.00 us
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 10.000 ppb
F1 3001.30 Hz
F2P -0.500 ppb
F2 -150.06 Hz
PPMCM 0.52500 Hz
HZCM 157.56825 Hz

Current Data Parameters
NAME 1397-xjw-343
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060913
Time 8.59
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 372
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DM 22.058 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00020000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775558 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677561 MHz
WDW EX
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 6.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -0.005 ppm
F2 -0.38 Hz
PPMCM 10.00025 ppm/cm

Current Data Parameters
NAME 1397-xiw-353
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060914
Time 10.11
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SF01 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 8.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 150.06 Hz
FPMCH 0.52500 ppm/cm
HZCM 157.56825 Hz/cm

Current Data Parameters
NAME 1397-xiw-353
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060920
Time 8.55
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 15078
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.445188 sec
RG 8160
DM 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
d12 0.00002000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SF01 75.4775598 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677547 MHz
WDW EN
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 180.500 ppm
F1 13621.93 Hz
F2P -0.500 ppm
F2 -37.73 Hz
FPMCH 9.05000 ppm/cm
HZCM 682.98315 Hz/cm

Current Data Parameters
NAME 1397-xjw-202
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060914
Time 19.01
INSTRUM mvx300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl₃
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.162999 Hz
AQ 2.7529611 sec
RG 512
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
A

CHANNEL f1
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.130062 MHz

F2 - Processing Parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 10.000 ppm
F1 300.130 MHz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCH 0.52500 ppm/cm
H2CH 157.56825 Hz/cm

Current Data Parameters
NAME 1397-xjw-202
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060914
Time 18.32
INSTRUM mvx300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 2938
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DM 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

CHANNEL f1
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775998 MHz

CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677574 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 15131.29 Hz
F1 75.467 MHz
F2P -37.73 Hz
F2 10.05000 ppm/cm
H2CH 758.45099 Hz/cm

HPLC Chromatograms

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.392	54126597	49.15	2708690	63.72
2	16.251	55991549	50.85	1542242	36.28

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.483	655352	1.78	40643	3.71
2	16.361	36118226	98.22	1055865	96.29

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.764	40942915	48.46	3086867	79.99
2	19.517	43551154	51.54	772271	20.01

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.975	405539	1.26	31237	5.62
2	20.410	31823001	98.74	524200	94.38

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.650	34962261	49.48	1622691	74.70
2	23.096	35698937	50.52	549540	25.30

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	8.963	1637106	2.55	62821	6.86
2	24.772	62558655	97.45	853472	93.14

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	12.098	42262315	50.02	1147772	73.57
2	29.948	42233671	49.98	412430	26.43

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	12.200	2477060	3.30	74323	9.69
2	29.569	72619388	96.70	692680	90.31

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.617	9077294	49.62	673843	85.38
2	18.475	9214657	50.38	115398	14.62

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.654	457222	0.75	36573	4.57
2	18.391	60449491	99.25	764386	95.43

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.947	12757394	49.75	793494	79.05
2	16.165	12884670	50.25	210256	20.95

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.999	762355	1.15	41476	3.70
2	16.015	65806259	98.85	1080176	96.30

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.117	18190807	49.00	2247125	83.93
2	6.785	18930904	51.00	430217	16.07

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.099	1788489	2.22	208812	10.54
2	6.743	78783979	97.78	1771602	89.46

	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.933	17828192	49.22	2090976	82.27
2	7.421	18393469	50.78	450711	17.73

	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.930	350371	0.80	38674	3.48
2	7.395	43672798	99.20	1071246	96.52

	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.127	6408521	49.77	735039	90.16
2	7.052	6466825	50.23	80236	9.84

	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.996	5476934	4.84	487713	26.45
2	7.027	107611711	95.16	1355996	73.55

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.888	22795340	49.73	2078910	51.43
2	7.366	23043343	50.27	1963057	48.57

	Peak Name	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	Peak1	6.893	29494399	96.90	2724561	97.09
2	Peak2	7.381	944376	3.10	81693	2.91

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.915	24516547	50.33	1063334	80.02
2	25.934	24194940	49.67	265551	19.98

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.938	229627	0.75	10734	2.92
2	25.723	30577804	99.25	357137	97.08

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.192	22665744	50.34	1209981	76.53
2	25.646	22360043	49.66	371105	23.47

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.199	132454	0.83	6722	2.49
2	25.662	15879125	99.17	262906	97.51

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.842	28216308	49.37	2776182	72.92
2	15.642	28936677	50.63	1031235	27.08

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	5.777	352727	0.94	35688	2.63
2	15.561	37341639	99.06	1321519	97.37

	RT (min)	Area (V *sec)	%Area	Height (V)	% Height
1	6.299	42680945	49.86	1957456	52.08
2	11.628	42912982	50.14	1801263	47.92

	RT (min)	Area (V *sec)	%Area	Height (V)	% Height
1	6.367	911877	5.49	97005	12.76
2	11.625	15691945	94.51	663422	87.24

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	15.019	13156668	49.29	194301	51.34
2	17.907	13533632	50.71	184153	48.66

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	14.493	215437	0.69	4975	1.29
2	16.118	30866388	99.31	379706	98.71

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.392	54126597	49.15	2708690	63.72
2	16.251	55991549	50.85	1542242	36.28

(R)-warfarin

	RT (min)	Area (V *sec)	% Area	Height (V)	% Height
1	6.265	45780351	96.12	2948425	98.11
2	15.353	1849587	3.88	56822	1.89