Supporting Information

Stereoselective Syntheses of 4-Hydroxy-4-substituted Glutamic Acids

Osamu Tamura,* Tomoya Shiro, Mizuho Ogasawara, Atsushi Toyao
and Hiroyuki Ishibashi*

Table of Contents

S2: Experimental procedure for 8g-8i , 6b , 6d , 6e , 8d , 7a , 7c-e , 9a-d , 9e	S27: ¹ H NMR spectrum of 23
S10: Cartesian Coordinates of TS A-D	S28: ¹³ C NMR spectrum of 24
S16: ¹ H NMR spectrum of 7a	S29: ¹ H NMR spectrum of 25
S17: ¹ H NMR spectrum of 7f	S30: ¹ H NMR spectrum of 3
S18: ¹ H NMR spectrum of 7a and 11a	S31: ¹ H NMR spectrum of 9b
S19: ¹ H NMR spectrum of 7b and 11b	S32: ¹ H NMR spectrum of 9d
S20: ¹ H NMR spectrum of 14	S33: ¹ H NMR spectrum of 9f
S21: ¹ H NMR spectrum of 15	S34: ¹ H NMR spectrum of (2 <i>S</i> ,4 <i>R</i>)- 2
S22: ¹ H NMR spectrum of (2 <i>S</i> ,4 <i>S</i>)- 2	S35: ¹ H NMR spectrum of 8g
S23: ¹ H NMR spectrum of 16	S36: ¹ H NMR spectrum of 8h
S24: ¹ H NMR spectrum of 17	S37: ¹ H NMR of 8i
S25: ¹ H NMR spectrum of 18	S38: ¹ H NMR of 6c
S26: ¹ H NMR spectrum of 21	S39: ¹ H NMR of 6d
	S40: ¹ H NMR of 6e

General Experimental Procedure: Melting points are uncorrected. IR spectra were recorded in CHCl_3 . For ^1H NMR and ^{13}C NMR spectra, δ values quoted are relative to tetramethylsilane. Compounds **10**,¹ **6f**,² **19**,¹ **8b,c,e**,³ and **8f**⁴ were prepared by previously reported methods.

2-[(4-Methoxyphenyl)methyl]acrylic Acid Ethyl Ester (8g) To a stirred solution of **10** (200 mg, 1.04 mmol) in THF (10 mL) was added a 0.5 M solution of *p*-methoxyphenylmagnesium bromide in THF (5 mL, 2.44 mmol) at $-20\text{ }^\circ\text{C}$. The mixture was allowed to warm to room temperature and further stirred for 5.5 h. Water was added to the mixture and the whole was extracted with AcOEt. The organic phase was dried (MgSO_4) and concentrated under reduced pressure. The crude product was chromatographed (hexane-AcOEt, 3:1) to give **8g** (136 mg, 54%) as a colorless oil. IR (CHCl_3) $1710, 1610\text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3) δ 1.26 (3H, t, $J = 7.3$ Hz), 3.56 (2H, s), 3.77 (3H, s), 4.18 (2H, q, $J = 7.3$ Hz), 5.43 (1H, s), 6.19 (1H, s), 6.82 (2H, d, $J = 2.0$ Hz), 6.83 (2H, d, $J = 2.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 37.2, 55.2, 60.6, 113.8, 125.5, 130.0, 130.8, 140.8, 158.1, 166.9; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3$ (MH^+) 221.1178, found 221.1176.

2-[(Naphthalene-2-yl)methyl]acrylic Acid Ethyl Ester (8h). To a 1.56 M solution of *n*-BuLi in hexane (0.64 mL, 1.0 mmol) was added a solution of 2-bromonaphthalene (207 mg, 1.0 mmol) in THF (1 mL) at $0\text{ }^\circ\text{C}$ and the mixture was stirred for 30 min at the same temperature. The mixture was added to a stirred suspension of CuI (95.2 mg, 0.5 mmol) in THF (0.5 mL) at $0\text{ }^\circ\text{C}$ and stirring was continued for 1 h at the same temperature. To the mixture was added a solution of **10** (67.6 mg, 0.35 mmol) in THF (1 mL) at $0\text{ }^\circ\text{C}$ and the mixture was stirred for 2 h. A saturated aqueous solution of NH_4Cl was added to the mixture and the whole was extracted with AcOEt. The organic phase was washed successively with water and brine, dried (MgSO_4), and concentrated under reduced pressure. The crude product was chromatographed (hexane-AcOEt, 40:1) to give **8h** (37.3 mg, 44%) as a colorless oil. IR (CHCl_3) $1710, 1630\text{ cm}^{-1}$; ^1H NMR (270 MHz, CDCl_3) δ 1.25 (3H, t, $J = 7.1$ Hz), 3.79 (2H, s), 4.18 (2H, q, $J = 7.1$ Hz), 5.49 (1H, s), 6.27 (1H, s), 7.31-7.45 (3H, m), 7.65 (1H, s), 7.75-7.82 (3H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 38.2, 60.7, 125.4,

125.9, 126.1, 127.4, 127.53, 127.57, 127.59, 127.9, 132.2, 133.6, 136.3, 140.3, 166.9; HRMS (FAB) calcd for $C_{16}H_{17}O_2$ (MH^+) 241.1229, found 241.1224.

2-[(Naphthalene-1-yl)methyl]acrylic Acid Ethyl Ester (8i). According to a procedure for the preparation of **8d**, a solution of **10** (67.6 mg, 0.35 mmol) in THF (2 mL) was treated with copper reagent prepared from a 1.56 M solution of *n*-BuLi (0.64 mL, 1.0 mmol), 1-bromonaphthalene (207 mg, 1.0 mmol), CuI (95.2 mg, 0.50 mmol) in THF (3.5 mL). After workup, crude product was chromatographed (hexane-AcOEt, 40:1) to give **8i** (17.4 mg, 21%) as a colorless oil. IR ($CHCl_3$) 1710, 1630 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 1.30 (3H, t, $J = 7.1$ Hz), 4.08 (2H, s), 4.25 (2H, q, $J = 7.1$ Hz), 5.15 (1H, s), 6.22 (1H, s), 7.32 (1H, br d, $J = 6.8$ Hz), 7.40 (1H, br t, $J = 7.6$ Hz), 7.43-7.48 (2H, m), 7.74 (1H, br t, $J = 7.8$ Hz), 7.82-7.85 (1H, m), 7.89-7.90 (1H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 34.7, 60.8, 124.2, 125.49, 125.53, 126.3, 127.3, 127.4, 128.6, 132.0, 133.9, 134.7, 140.0, 167.1; HRMS (FAB) calcd for $C_{16}H_{17}O_2$ (MH^+) 241.1228, found 241.1228.

2-[(Indol-3-yl)methyl]prop-2-en-1-ol (6b). To a stirred solution of **8c** (879 mg, 3.83 mmol) in CH_2Cl_2 (20 mL) was added a 0.95 M solution of DIBAL-H in hexane (10.0 mL, 9.58 mmol) at $-78^\circ C$ and the mixture was allowed to warm to room temperature. After being stirred for 30 min, the mixture was cooled to $-78^\circ C$. MeOH (5 mL) and water (1 mL) were added to the mixture and the mixture was allowed to warm to room temperature. Celite[®] and Et_2O were added to the mixture and the mixture was passed through a pad of Celite[®]. The filtrate was concentrated under reduced pressure. The crude product was chromatographed (hexane-AcOEt, 1:1) and recrystallized from hexane-AcOEt to give **6b** (612 mg, 85%) as colorless crystals, mp $70-71^\circ C$. IR ($CHCl_3$) 3600, 3480, 1680 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 1.56 (1H, br s), 3.55 (2H, s), 4.09 (2H, s), 5.00 (1H, s), 5.10 (1H, s), 6.98-7.35 (4H, m), 7.58 (1H, d, $J = 7.3$ Hz), 8.00 (1H, s); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.9, 66.0, 111.3, 111.5, 114.6, 119.6, 119.7, 122.4, 122.8, 128.0, 131.9, 136.9. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.93; H, 7.10; N, 7.45.

2-[(4-Methoxyphenyl)methyl]prop-2-en-1-ol (6c). According to the procedure for the preparation of **6b**, a solution of **8g** (45 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) was treated with a 0.95 M solution of DIBAL-H in hexane (0.53 mL, 0.50 mmol). After workup, the crude product was chromatographed (hexane-AcOEt, 7:1) to give **6c** (29.6 mg, 84%) as a colorless oil. IR (CHCl_3) $3610, 1650\text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3) δ 3.34 (2H, s), 3.78 (3H, s), 4.02 (2H, s), 4.87 (1H, s), 5.09 (1H, s), 6.83 (2H, d, $J = 8.8\text{ Hz}$), 7.10 (2H, d, $J = 8.8\text{ Hz}$); ^{13}C NMR (125 MHz, CDCl_3) δ 39.0, 55.2, 65.2, 111.1, 113.8, 129.8, 131.0, 148.6, 158.1; HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{15}\text{O}_2$ (MH^+) 179.1072, found 179.1069.

2-[(Naphthalen-2-yl)methyl]prop-2-en-1-ol (6d). According to the procedure for the preparation of **6b**, a solution of **8h** (17.7 mg, 0.074 mmol) in CH_2Cl_2 (2 mL) was treated with a 0.95 M solution of DIBAL-H in hexane (0.2 mL, 0.18 mmol). After workup, the crude product was chromatographed (hexane-AcOEt, 5:1) to give **6d** (12 mg, 82%) as colorless crystals, mp $59.5\text{--}61.0\text{ }^\circ\text{C}$ (hexane-AcOEt). IR (CHCl_3) $3610, 1650\text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3) δ 1.46 (1H, br s), 3.57 (2H, s), 4.07 (2H, s), 4.96 (1H, s), 5.16 (1H, s), 7.33 (1H, dd, $J = 8.5, 1.7\text{ Hz}$), 7.41–7.47 (2H, m), 7.64 (1H, s), 7.76–7.81 (3H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 40.0, 65.4, 111.8, 125.4, 126.0, 127.17, 127.23, 127.4, 127.9, 128.0, 132.2, 133.6, 136.5, 148.1; HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{15}\text{O}$ (MH^+) 199.1123, found 199.1115.

2-[(Naphthalen-1-yl)methyl]prop-2-en-1-ol (6e). According to the procedure for the preparation of **6b**, a solution of **8i** (170 mg, 0.71 mmol) in CH_2Cl_2 (5 mL) was treated with a 0.95 M solution of DIBAL-H in hexane (1.8 mL, 1.9 mmol). After workup, the crude product was chromatographed (hexane-AcOEt, 5:1) to give **6e** (159 mg, quant.) as a colorless oil. IR (CHCl_3) $3610, 1650\text{ cm}^{-1}$; ^1H NMR (500 MHz, CDCl_3) δ 3.86 (2H, s), 4.13 (2H, s), 4.76 (1H, s), 5.14 (1H, s), 7.34–7.49 (4H, m), 7.74 (1H, br d, $J = 8.3\text{ Hz}$), 7.83–7.86 (1H, m), 7.99–8.01 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 36.8, 66.0, 112.0, 124.2, 125.5, 125.6, 125.8, 127.2, 127.3, 128.6, 132.3, 133.9, 134.9, 147.7; HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{O}$ 198.1045, found 198.1043.

2-[(Indol-3-yl)methyl]acrylic Acid Benzyl Ester (8d). To a stirred solution of **8e** (36 mg, 0.18 mmol) in MeCN (2 mL) was added DBU (61 μ L, 0.99 mmol) and benzyl bromide (27 μ L, 0.22 mmol) at 0 °C and the mixture was further stirred at room temperature for 6 h. A saturated aqueous solution of NH_4Cl was added to the mixture and the whole was extracted with AcOEt. The organic phase was washed successively with water and brine, dried (MgSO_4), and concentrated under reduced pressure. The crude product was chromatographed (hexane-AcOEt, 2:1) to give **8d** (32 mg, 61%) as a colorless oil. The starting material **8e** (14 mg, 38%) was recovered. IR (CHCl_3) 3480, 1710, 1630 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.79 (2H, s), 5.19 (2H, s), 5.51 (1H, s), 6.24 (1H, s), 6.94 (1H, d, $J = 2.4$ Hz), 7.08 (1H, t, $J = 7.1$ Hz), 7.17 (1H, t, $J = 7.1$ Hz), 7.29-7.32 (6H, m), 7.52 (1H, d, $J = 7.1$ Hz), 7.97 (1H, br s); ^{13}C NMR (125 MHz, CDCl_3) δ 27.6, 66.4, 111.1, 112.8, 119.0, 119.3, 121.9, 122.8, 125.8, 127.3, 128.1, 128.5, 136.0, 136.3, 139.5, 167.1. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_2$: C, 78.23; H, 5.88; N, 4.81. Found: C, 78.23; H, 5.98; N, 4.62

(2S,5S,8aS)-2-(Hydroxymethyl)-2-methyl-5-phenyl-1,5,6,8a-tetrahydro-3,7-dioxaindolizin-8-one (7a) (Table 1, Entry 1). According to the general procedure, **5** (100 mg, 0.52 mmol) was treated with **6a** (57 mg, 0.78 mmol) and $\text{MgBr}_2 \cdot \text{OEt}_2$ (202 mg, 0.78 mmol) in CH_2Cl_2 (8 mL) at room temperature for 10 h. After workup, the crude product was chromatographed (hexane-AcOEt, 5:1) to give **7a** (121 mg, 88%) as a syrup. $[\alpha]_D^{20} +61.1$ (c 0.70, CHCl_3); IR (CHCl_3) 1752 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 1.31 (3H, s), 2.56 (1H, br), 2.62 (1H, dd, $J = 13.2, 6.8$ Hz), 2.75 (1H, dd, $J = 13.2, 8.8$ Hz), 3.51-3.53 (2H, m), 4.26-4.41 (4H, m), 7.34-7.42 (5H, m); HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4$ 263.1159, found 263.1158.

(2S,5S,8aS)-2-(Hydroxymethyl)-2-[(4-methoxyphenyl)methyl]-5-phenyl-1,5,6,8a-tetrahydro-3,7-dioxaindolizin-8-one (7c) (Table 1, Entry 3). According to the general procedure, nitrone **5** (21 mg, 0.11 mmol) was treated with **6c** (29 mg, 0.17 mmol) and $\text{MgBr}_2 \cdot \text{OEt}_2$ (42 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) at room temperature for 20 h. After workup, the crude product was chromatographed (CHCl_3 -AcOEt, 10:1) to give **7c** (39 mg, 98%) as a syrup. $[\alpha]_D^{25} +83.3$ (c 0.100, CHCl_3); IR (CHCl_3) 3630, 1750 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.30 (1H, t, $J = 6.4$ Hz), 2.54 (1H, dd, $J = 13.2, 8.3$ Hz), 2.70 (1H, dd, $J = 13.2, 7.3$ Hz), 2.82 (1H, d, $J = 13.4$ Hz), 2.87 (1H, d, $J = 13.4$ Hz), 3.49 (1H, dd, $J = 11.7, 6.4$ Hz), 3.56 (1H, dd, $J = 11.7, 6.4$ Hz), 3.78 (3H, s), 4.12 (1H,

dd, $J = 9.8, 3.9$ Hz), 4.24 (1H, dd, $J = 12.2, 9.8$ Hz), 4.37 (2H, m), 6.78 (2H, d, $J = 8.8$ Hz), 7.01 (2H, d, $J = 8.8$ Hz), 7.39 (5H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 37.9, 40.2, 55.2, 61.8, 63.5, 67.0, 69.1, 85.3, 113.7, 127.5, 127.7, 128.9, 131.3, 135.6, 158.5, 169.6. Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_5$: C, 68.28; H, 6.28; N, 3.79. Found: C, 68.20; H, 6.39; N, 3.59.

(2*S*,5*S*,8*aS*)-2-(Hydroxymethyl)-2-[(naphthalen-2-yl)methyl]-5-phenyl-1,5,6,8*a*-tetrahydro-3,7-dioxaindolizin-8-one (7d) (Table 1, Entry 4). According to the general procedure, nitrone **5** (7.6 mg, 0.039 mmol) was treated with **6d** (10 mg, 0.047 mmol) and $\text{MgBr}_2 \cdot \text{OEt}_2$ (15 mg, 0.059 mmol) in CH_2Cl_2 (0.5 mL) at room temperature for 3.5 days. After workup, the crude product was chromatographed (CHCl_3 -AcOEt, 50:1) to give **7d** (15 mg, 98%) as colorless crystals, mp 189–190 °C (THF-hexane). $[\alpha]_D^{25} +46.4$ (c 0.0960, THF); IR (CHCl_3) 1750 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 2.25 (1H, t, $J = 6.3$ Hz), 2.61 (1H, dd, $J = 13.0, 8.3$ Hz), 2.80 (1H, dd, $J = 13.0, 7.9$ Hz), 3.05 (1H, d, $J = 13.7$ Hz), 3.15 (1H, d, $J = 13.7$ Hz), 3.51 (1H, dd, $J = 11.6, 6.3$ Hz), 3.60 (1H, dd, $J = 11.6, 6.3$ Hz), 4.13 (1H, dd, $J = 9.6, 3.3$ Hz), 4.23 (1H, dd, $J = 11.6, 9.6$ Hz), 4.35 (1H, dd, $J = 11.6, 3.3$ Hz), 4.42 (1H, br t, $J = 8.1$ Hz), 7.22 (1H, dd, $J = 8.2, 1.7$ Hz), 7.41–7.52 (8H, m), 7.67–7.73 (2H, m), 7.79–7.82 (1H, m); ^{13}C NMR (67.5 MHz, CDCl_3) δ 38.8, 42.0, 62.5, 64.2, 67.3, 69.8, 85.9, 126.2, 126.5, 127.8, 128.0, 128.1, 128.3, 129.0, 129.1, 129.3, 129.4, 129.5, 132.8, 133.8, 136.0, 170.0; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_4$ (MH^+) 390.1705, found 390.1694. Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4 \cdot 1/2\text{H}_2\text{O}$: C, 75.52; H, 5.83; N, 3.52. Found: C, 75.50; H, 5.94; N, 3.46.

(2*S*,5*S*,8*aS*)-2-(Hydroxymethyl)-2-[(naphthalen-1-yl)methyl]-5-phenyl-1,5,6,8*a*-tetrahydro-3,7-dioxaindolizin-8-one (7e) (Table 1, Entry 5). According to the general procedure, nitrone **5** (9.0 mg, 0.047 mmol) was treated with **6e** (15 mg, 0.071 mmol) and $\text{MgBr}_2 \cdot \text{OEt}_2$ (18 mg, 0.071 mmol) in CH_2Cl_2 (0.5 mL) at room temperature for 4 days. After workup, the crude product was chromatographed (benzene-AcOEt, 2:1) to give **7e** (17 mg, 94%) and a small amount (0.7 mg, 3.8%) of its isomer. **7e**: $[\alpha]_D^{25} +41.6$ (c 0.096, THF); IR (CHCl_3) 1750 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.41 (1H, br s), 2.61 (1H, dd, $J = 12.9, 8.5$ Hz), 2.71 (1H, dd, $J = 12.9, 7.6$ Hz), 3.37 (1H, d, $J = 14.7$ Hz), 3.46 (1H, d, $J = 14.7$ Hz), 3.63 (1H, dd, $J = 11.5, 6.1$ Hz), 3.68 (1H, dd, $J = 11.5, 6.1$ Hz), 3.86 (1H, dd, $J = 7.6, 5.1$ Hz), 4.11–4.15 (2H, m), 4.32 (1H, br t, $J = 8.1$ Hz), 7.25–7.45 (9H, m), 7.78 (1H, br d, $J = 8.3$ Hz), 7.84 (1H, br d, $J = 7.3$ Hz), 7.97

(1H, br d, $J = 8.3$ Hz); ^{13}C NMR (67.5 MHz, CDCl_3) δ 36.3, 37.9, 61.6, 63.0, 68.0, 68.8, 85.7, 124.4, 125.2, 125.6, 126.0, 127.4, 127.8, 128.4, 128.7, 128.8, 129.4, 132.0, 133.0, 133.8, 135.5, 169.3. Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4 \cdot 1/4\text{H}_2\text{O}$: C, 73.25; H, 5.83; N, 3.52. Found: C, 73.09; H, 6.19; N, 3.35. **Isomer of 7e**: ^1H NMR (500 MHz, CDCl_3) δ 2.58 (1H, br s), 2.67 (1H, dd, $J = 13.2, 9.8$ Hz), 2.82 (1H, dd, $J = 13.2, 2.0$ Hz), 3.11 (1H, d, $J = 14.7$ Hz), 3.74 (1H, d, $J = 14.7$ Hz), 3.84 (2H, m), 3.94 (1H, m), 3.99 (1H, br t, $J = 11.2$ Hz), 4.06 (1H, br d, $J = 9.3$ Hz), 4.22 (1H, dd, $J = 11.2, 4.9$ Hz), 7.24-7.51 (9H, m), 7.85 (2H, m), 8.09 (1H, br d, $J = 8.3$ Hz).

(2S,5S,8aS)-2-(Hydroxymethyl)-2-isobutyl-5-phenyl-1,5,6,8a-tetrahydro-3,7-dioxaindolizine-8-one (7f) (Table 1, Entry 6). According to the general procedure, nitrone **5** (20 mg, 0.10 mmol) was treated with **6f** (36 mg, 0.30 mmol) and $\text{MgBr}_2 \cdot \text{OEt}_2$ (40 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) at room temperature for 18 h. After workup, the crude product was chromatographed (hexane-AcOEt, 2:1) to give **7f** (30.6 mg, 95%) and a small amount (1.6 mg, 4.7%) of isomer of **7f**. **7f**: $[\alpha]_D^{26} +90.3$ (c 0.532, CHCl_3); IR (CHCl_3) 1750 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.85 (3H, d, $J = 6.6$ Hz), 0.91 (3H, d, $J = 6.6$ Hz), 1.52 (1H, dd, $J = 14.2, 7.1$ Hz), 1.61 (1H, dd, $J = 14.2, 5.9$ Hz), 1.64-1.72 (1H, m), 2.56 (1H, br t, $J = 5.4$ Hz), 2.67 (1H, dd, $J = 13.2, 6.8$ Hz), 2.71 (1H, dd, $J = 13.2, 8.8$ Hz), 3.60 (2H, d, $J = 5.4$ Hz), 4.25 (1H, dd, $J = 9.8, 3.4$ Hz), 4.30 (1H, dd, $J = 11.7, 9.8$ Hz), 4.33 (1H, dd, $J = 8.8, 6.8$ Hz), 4.44 (1H, dd, $J = 11.7, 3.4$ Hz), 7.33-7.43 (5H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 23.8, 24.1, 24.4, 39.2, 44.8, 61.7, 63.9, 67.8, 68.9, 85.5, 127.3, 128.6, 128.9, 129.1, 135.8, 170.0; HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_4$ (M^+) 305.1627, found 305.1625. **Isomer of 7f**: ^1H NMR (500 MHz, CDCl_3) δ 0.94 (3H, d, $J = 6.8$ Hz), 0.95 (3H, d, $J = 6.8$ Hz), 1.54 (1H, dd, $J = 14.2, 7.1$ Hz), 1.59 (1H, dd, $J = 14.2, 5.9$ Hz), 1.69-1.75 (1H, m), 2.54 (1H, br d, $J = 13.2$ Hz), 2.69 (1H, br s), 2.83 (1H, dd, $J = 13.2, 9.5$ Hz), 3.62 (1H, d, $J = 11.7$ Hz), 3.68 (1H, d, $J = 11.7$ Hz), 4.28 (1H, br s), 4.51 (1H, d, $J = 12.2$ Hz), 4.53 (1H, d, $J = 12.2$ Hz), 5.17 (1H, br s), 7.33-7.43 (5H, m).

(2R,5S,8aS)-2-Methyl-8-oxo-5-phenyl-1,5,6,8a-tetrahydro-3,7-dioxaindolizine-2-carboxylic Acid Methyl Ester (9a) (Table 2, Entry 1).

A solution of nitrone **5** (30 mg, 0.16 mmol) and **8a** (23.3 mg, 0.23 mmol) in CH_2Cl_2 (2.5 mL) was stirred at room temperature for 2 days. After concentration, the crude product was chromatographed (hexane-AcOEt, 3:1) to give **9a** (45.3 mg, 98%) as colorless crystals, mp 113-114 °C (hexane:AcOEt). $[\alpha]_D^{25} +66.7$ (c 0.400, CHCl_3); IR (CHCl_3) 1750 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.51 (3H, s), 2.68 (1H, dd, $J = 13.2, 7.8$ Hz), 3.28 (1H, dd, $J = 13.2, 9.8$ Hz), 3.69

(3H, s), 4.22 (1H, br t, $J = 11.2$ Hz), 4.29 (1H, dd, $J = 11.7, 3.9$ Hz), 4.41 (1H, dd, $J = 10.3, 3.9$ Hz), 4.48 (1H, br t, $J = 8.8$ Hz), 7.33–7.43 (5H, m); ^{13}C NMR (67.5 MHz, CDCl_3) δ 24.0, 43.0, 52.7, 62.0, 62.9, 70.1, 82.9, 127.7, 127.8, 128.6, 128.8, 129.0, 135.2, 168.2, 173.4. Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.70; H, 5.89; N, 4.63.

(2R,5S,8aS)-2-[(Indol-3-yl)methyl]-8-oxo-5-phenyl-1,5,6,8a-tetrahydro-3,7-dioxaindolizine-2-carboxylic Acid Methyl Ester (9b) (Table 2, Entry 2). A solution of nitron 5 (12 mg, 0.062 mmol) and 8b (20 mg, 0.093 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 2 days. After concentration, the crude product was chromatographed (hexane-AcOEt, 1:1) to give 9b (25 mg, 99%) as a syrup. $[\alpha]_D^{25} +36.3$ (c 0.400, CHCl_3); IR (CHCl_3) 3480, 1750 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 2.89 (1H, dd, $J = 13.2, 8.6$ Hz), 3.25 (1H, dd, $J = 13.2, 9.6$ Hz), 3.31 (2H, s), 3.67 (3H, s), 4.02 (1H, br t, $J = 8.9$ Hz), 4.16 (1H, dd, $J = 11.2, 9.9$ Hz), 4.24–4.34 (2H, m), 7.08 (1H, br d, $J = 2.3$ Hz), 7.11–7.23 (2H, m), 7.34–7.45 (6H, m), 7.65 (1H, br d, $J = 7.9$ Hz), 8.13 (1H, br s); ^{13}C NMR (125 MHz, CDCl_3) δ 32.2, 40.1, 52.7, 62.1, 63.3, 70.2, 86.2, 108.9, 111.1, 119.2, 119.6, 119.8, 122.2, 123.9, 127.7, 127.9, 128.7, 128.8, 135.2, 135.9, 168.4, 173.5; HRMS (FAB) calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_5$ (MH^+) 407.1607, found 407.1610.

(2R,5S,8aS)-2-[(Indol-3-yl)methyl]-8-oxo-5-phenyl-1,5,6,8a-tetrahydro-3,7-dioxaindolizine-2-carboxylic Acid Ethyl Ester (9c) (Table 2, Entry 3). A solution of nitron 5 (140 mg, 0.730 mmol) and 8c (250 mg, 1.09 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 2 days. After concentration, the crude product was chromatographed (hexane-AcOEt, 5:1) to give 9c (257 mg, 84%) as a syrup. $[\alpha]_D^{29} +40.5$ (c 0.400, CHCl_3); IR (CHCl_3) 1750 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.11 (3H, t, $J = 7.3$ Hz), 2.85 (1H, dd, $J = 13.2, 8.3$ Hz), 3.23 (1H, dd, $J = 13.2, 9.3$ Hz), 3.26 (1H, d, $J = 14.7$ Hz), 3.30 (1H, d, $J = 14.7$ Hz), 3.99 (1H, t, $J = 8.8$ Hz), 4.06 (2H, m), 4.14 (1H, dd, $J = 11.7, 10.3$ Hz), 4.26 (1H, dd, $J = 11.7, 3.4$ Hz), 4.30 (1H, dd, $J = 10.3, 3.4$ Hz), 7.07 (1H, d, $J = 2.0$ Hz), 7.10–7.13 (1H, m), 7.17–7.20 (1H, m), 7.33–7.45 (6H, m), 7.64, (1H, d, $J = 11.8$ Hz), 8.09 (1H, s); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 31.5, 40.1, 61.9, 62.1, 63.2, 70.1, 86.1, 108.8, 111.1, 119.1, 119.6, 122.0, 124.0, 127.3, 127.7, 127.9, 128.6, 128.7, 135.3, 135.8, 168.5, 173.1; HRMS calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5$ (M^+) 420.1685, found 420.1689. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5$: C,

68.56; H, 5.75; N, 6.66. Found: C, 68.29; H, 5.92; N, 6.22.

(2*R*,5*S*,8*aS*)-2-[(Indol-3-yl)methyl]-8-oxo-5-phenyl-1,5,6,8*a*-tetrahydro-3,7-dioxaindolizine-2-carboxylic Acid Benzyl Ester (9d) (Table 2, Entry 4). A solution of nitrone **5** (18.8 mg, 0.097 mmol) and **8d** (34 mg, 0.12 mmol) in CH₂Cl₂ (3 mL) was stirred at room temperature for 3.5 days. After concentration, the crude product was chromatographed (hexane-AcOEt, 2:1) to give an inseparable mixture of **9d** and its isomer (45.8 mg, 98%) as a syrup. The ratio of **9d** and its isomer was determined as 95:5 by integrations of signals due to C1-H in the ¹H NMR spectrum δ 2.75 (dd, *J* = 13.5, 6.9 Hz, minor), 2.86 (dd, *J* = 13.2, 8.8 Hz, major). **9d**: IR (CHCl₃) 3480, 1750 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.86 (1H, dd, *J* = 13.2, 8.8 Hz), 3.22-3.30 (3H, m), 4.01 (1H, t, *J* = 8.8 Hz), 4.10 (1H, br t, *J* = 11.2 Hz), 4.19 (1H, dd, *J* = 11.7, 3.4 Hz), 4.26 (1H, dd, *J* = 10.7, 3.4 Hz), 4.98 (1H, d, *J* = 12.2 Hz), 5.09 (1H, d, *J* = 12.2 Hz), 6.90 (1H, d, *J* = 2.0 Hz), 7.08 (1H, t, *J* = 7.8 Hz), 7.13-7.17 (3H, m), 7.23-7.35 (9H, m), 7.58 (1H, d, *J* = 7.8 Hz), 8.08 (1H, br s); ¹³C NMR (125 MHz, CDCl₃) δ 32.2, 40.2, 62.1, 63.1, 65.8, 67.6, 70.1, 86.2, 108.7, 111.1, 119.2, 119.6, 122.1, 124.0, 127.6, 128.4, 128.5, 128.7, 134.9, 135.2, 168.5, 172.8; HRMS (FAB) calcd for C₂₉H₂₇N₂O₅(MH⁺) 483.1920, found 483.1914.

(2*R*,5*S*,8*aS*)-2-[(Ethoxycarbonyl)ethyl]-8-oxo-5-phenyl-1,5,6,8*a*-tetrahydro-3,7-dioxaindolizine-2-carboxylic Acid Ethyl Ester (9f) (Table 2, Entry 6). A solution of nitrone **5** (19 mg, 0.097 mmol) and **8f** (29 mg, 0.15 mmol) in CH₂Cl₂ (1.5 mL) was stirred at room temperature for 2 days. After concentration, the crude product was chromatographed (hexane-AcOEt, 3:1) to give an inseparable mixture of **9f** and its isomer (33 mg, 87%) as a syrup. The ratio of **9f** and its isomer was determined as 96:4 by integrations of signals due to C1-H in the ¹H NMR spectrum δ 2.67 (dd, *J* = 13.0, 6.4 Hz, minor), 2.73 (dd, *J* = 13.2, 8.3 Hz, major). **9f**: IR (CHCl₃) 1750, 1730 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.20 (3H, t, *J* = 7.3 Hz), 1.22 (3H, t, *J* = 7.3 Hz), 2.12-2.43 (4H, m), 2.73 (1H, dd, *J* = 13.2, 8.3 Hz), 3.22 (1H, dd, *J* = 13.2, 8.3 Hz), 4.12 (1H, dq, *J* = 18.6, 7.3 Hz), 4.18 (1H, dq, *J* = 18.6, 7.3 Hz), 4.23 (1H, dd, *J* = 12.7, 10.7 Hz), 4.35-4.41 (3H, m), 7.32-7.44 (5H, m); ¹³C NMR (125 MHz, CDCl₃) δ 13.9, 14.1, 29.1, 32.1, 41.4, 60.5, 62.0, 62.2, 62.3, 69.8, 84.4, 127.8, 128.5, 128.7, 128.88, 128.93, 135.3, 168.4, 172.1, 172.4; HRMS (FAB) calcd for C₂₆H₂₅NO₇(MH⁺) 392.1709, found 392.1734.

References

- (1) Villieras, J.; Rambaud, M. *Synthesis* **1982**, 924
- (2) Jose, B.; Jose-L, F-S.; Jose-M, C.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, 77.
- (3) Holzapfel, xC. W.; Bischofberger, K.; Olivier, J. *Synth. Commun.* **1994**, 24, 3197.
- (4) Amri, H.; Rambaud, M.; Villieras, J. *Tetrahedon Lett.* **1989**, 30, 7381.

Cartesian Coordinates of TS A-D

TS D

MacSPARTAN PRO Semi-Empirical Program: (PowerPC)
Job run on machine : çâ€ G4-1(G4/466)

Release 1.0.2

PRE-TS4, PM3.1

Run type: Transition state optimization
(Analytical Gradient)
(Analytical Frequency in TSOPT)
(Analytical Gradient in FREQ)
(Numerical Frequency)

Model: RHF/PM3

Number of shells: 59

38 S shells

21 P shells

Number of basis functions: 101

Number of electrons: 112

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Point Group = C1 Order = 1 Nsymop = 1

This system has 108 degrees of freedom

Heat of Formation: -74.238 kcal/mol

Calculating Hessian

Memory Used: 15.302 Mb

Reason for exit: Successful completion

Semi-Empirical Program CPU Time : 000:07:27.8

Semi-Empirical Program Wall Time: 000:08:19.3

MacSPARTAN PRO Properties Program: (PowerPC)

Release 1.0.2

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Electrons: 112

		Cartesian Coordinates (Angstroms)		
Atom		X	Y	Z

1 C	C7	1.9614980	0.3429709	-1.4481092
2 C	C6	0.6694259	0.8482420	-0.8654821
3 N	N1	-0.1487249	-0.3158242	-0.3343254
4 C	C1	-1.2848133	-0.7046000	-1.0295659
5 C	C2	-1.5336509	-0.1430098	-2.3787561
6 O	O1	-2.2602838	-0.5695884	-3.2477755

7 O O2	-0.9084597	1.0012660	-2.8025754
8 C C3	-0.1466877	1.7107568	-1.8433479
9 H H5	0.5081191	2.3400066	-2.4699227
10 H H4	-0.8397931	2.3716263	-1.2847653
11 H H3	-1.6610544	-1.7330185	-0.8612283
12 O O3	-0.1168572	-0.5746185	0.8974697
13 H H7	0.9209538	1.5118169	0.0073925
14 C C8	2.0055276	-0.3751200	-2.6439927
15 C C9	3.2233589	-0.8210500	-3.1455228
16 C C10	4.4033574	-0.5548834	-2.4594349
17 C C11	4.3643144	0.1606442	-1.2674204
18 C C12	3.1494095	0.6083718	-0.7618577
19 H H1	3.1279205	1.1669174	0.1819997
20 H H2	5.2912300	0.3708951	-0.7232351
21 H H6	5.3608643	-0.9083048	-2.8564280
22 H H8	3.2499264	-1.3837585	-4.0849615
23 H H9	1.0856453	-0.5870741	-3.2020438
24 H H10	-3.4012715	-0.6692694	0.1509231
25 C C16	-2.6445918	0.1013018	0.3148135
26 C C17	-1.9321882	0.1457036	1.5190312
27 C C4	-1.4962459	1.4739865	2.0511788
28 H H11	-1.2412114	2.1697506	1.2382459
29 H H12	-0.6181631	1.3948147	2.7054328
30 H H13	-2.3023842	1.9350316	2.6382110
31 C C5	-2.1272249	-0.9794124	2.4808758
32 O O4	-2.5837962	-2.0827612	2.2368405
33 O O5	-1.7535371	-0.7001179	3.7684192
34 C C13	-1.8565311	-1.7224812	4.7351941
35 H H14	-1.4812826	-1.2301291	5.6359389
36 H H15	-1.2334261	-2.5873268	4.4842373
37 H H17	-2.8933663	-2.0443141	4.8796334
38 H H16	-2.8560023	1.0325598	-0.2150868

TS E

MacSPARTAN PRO Semi-Empirical Program: (PowerPC)

Release 1.0.2

Job run on machine : G4-1(G4/466)

PRE-TS3,PM3.1

Run type: Transition state optimization

(Analytical Gradient)

(Analytical Frequency in TSOPT)

(Analytical Gradient in FREQ)

(Numerical Frequency)

Model: RHF/PM3

Number of shells: 59

38 S shells

21 P shells

Number of basis functions: 101

Number of electrons: 112

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Heat of Formation: -73.960 kcal/mol

Calculating Hessian

Memory Used: 15.302 Mb

Reason for exit: Successful completion

Semi-Empirical Program CPU Time : 000:07:27.6

Semi-Empirical Program Wall Time: 000:08:18.9

MacSPARTAN PRO Properties Program: (PowerPC)

Release 1.0.2

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Electrons: 112

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z

1 C C7	2.0213660	0.3603508	-1.3470107
2 C C6	0.5766414	0.7062931	-1.1072359
3 N N1	-0.0025650	-0.2109601	-0.0443114
4 C C1	-0.9030543	-1.1929597	-0.4291705
5 C C2	-1.0976681	-1.4720215	-1.8713969
6 O O1	-1.5787853	-2.4561918	-2.3868414
7 O O2	-0.7156130	-0.5712963	-2.8311534
8 C C3	-0.2798484	0.6997708	-2.3847619
9 H H5	0.2860563	1.0805547	-3.2520424
10 H H4	-1.1791507	1.3331022	-2.2459893
11 H H3	-1.0401016	-2.0569118	0.2495198
12 O O3	-0.0794550	0.1992310	1.1442296
13 H H7	0.5375495	1.7569264	-0.7067074
14 C C8	3.0022964	1.2190138	-0.8433700
15 C C9	4.3485119	0.9373807	-1.0441169
16 C C10	4.7261981	-0.2013831	-1.7478095
17 C C11	3.7531636	-1.0582772	-2.2507269
18 C C12	2.4050400	-0.7812200	-2.0521553
19 H H1	1.6514936	-1.4641321	-2.4623913
20 H H2	4.0464656	-1.9557128	-2.8061889
21 H H6	5.7871224	-0.4227500	-1.9051525
22 H H8	5.1117218	1.6139897	-0.6448594
23 H H9	2.7143960	2.1168493	-0.2824742
24 H H10	-3.1159831	-1.1554905	0.5797834
25 C C16	-2.5903065	-0.2341004	0.3238981
26 C C17	-2.0751398	0.6013303	1.3200798
27 C C4	-2.0467921	2.0785186	1.0762337
28 H H11	-1.7923133	2.3126808	0.0321328
29 H H12	-1.3199107	2.5893499	1.7217872
30 H H13	-3.0326451	2.5185673	1.2821852
31 C C5	-2.1252087	0.1908003	2.7557300
32 O O6	-2.1451781	0.9200418	3.7303176
33 O O7	-2.1651246	-1.1647590	2.9575451
34 C C14	-2.1816881	-1.6469474	4.2831787
35 H H14	-2.1969756	-2.7299886	4.1370773
36 H H15	-3.0768264	-1.3216580	4.8240190
37 H H17	-1.2861716	-1.3483184	4.8383515
38 H H16	-2.9415109	0.2103269	-0.6102029

TS F

MacSPARTAN PRO Semi-Empirical Program: (PowerPC)

Release 1.0.2

Job run on machine : çãê" G4-1(G4/466)

PRE-TS1-2,PM3.1

Run type: Transition state optimization

(Analytical Gradient)
 (Analytical Frequency in TSOPT)
 (Analytical Gradient in FREQ)
 (Numerical Frequency)

Model: RHF/PM3

Number of shells: 59

38 S shells

21 P shells

Number of basis functions: 101

Number of electrons: 112

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Heat of Formation: -76.133 kcal/mol

Calculating Hessian

Memory Used: 15.302 Mb

Reason for exit: Successful completion

Semi-Empirical Program CPU Time : 000:10:37.1

Semi-Empirical Program Wall Time: 000:12:46.4

MacSPARTAN PRO Properties Program: (PowerPC)

Release 1.0.2

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Electrons: 112

		Cartesian Coordinates (Angstroms)		
Atom		X	Y	Z

1 C	C7	-0.1675490	-2.1885401	-0.6308896
2 C	C6	-0.0606120	-0.6878958	-0.6815073
3 N	N1	-0.4716836	-0.1011989	0.6551463
4 C	C1	-1.6850153	0.5688304	0.7509897
5 C	C2	-2.6394015	0.4982644	-0.3826138
6 O	O1	-3.8250762	0.7465239	-0.3733294
7 O	O2	-2.2401663	0.1030729	-1.6298776
8 C	C3	-0.8467578	-0.0524700	-1.8407058
9 H	H5	-0.8092145	-0.6834765	-2.7449610
10 H	H4	-0.4306434	0.9444421	-2.0890549
11 H	H3	-2.1458131	0.6445514	1.7549686
12 O	O3	0.4056200	0.2006621	1.5069366
13 H	H7	1.0193308	-0.4228081	-0.8543872
14 C	C8	-1.3981364	-2.8467660	-0.6302851
15 C	C9	-1.4468010	-4.2356915	-0.5861768
16 C	C10	-0.2709950	-4.9768319	-0.5421835
17 C	C11	0.9577418	-4.3253670	-0.5437047
18 C	C12	1.0115708	-2.9370837	-0.5879711
19 H	H1	1.9851004	-2.4312465	-0.5860589
20 H	H2	1.8860323	-4.9053890	-0.5090762
21 H	H6	-0.3125287	-6.0705449	-0.5070096
22 H	H8	-2.4164661	-4.7450447	-0.5874875
23 H	H9	-2.3348189	-2.2784880	-0.6745218
24 H	H10	-1.7034560	2.8887408	1.4427374
25 C	C16	-0.8838629	2.4605596	0.8615070
26 C	C17	0.3560031	2.2506761	1.4807220
27 C	C4	1.5862065	2.3898862	0.6515553
28 O	O4	1.7017515	2.1379670	-0.5391519

29 O O5	2.6771660	2.8669921	1.3200269
30 C C13	3.8913116	3.0152677	0.6154028
31 H H11	4.5641086	3.3934251	1.3898109
32 H H12	3.8029430	3.7392378	-0.2017125
33 H H13	4.2560636	2.0598108	0.2243921
34 C C5	0.4615123	2.4547828	2.9566655
35 H H14	1.3007118	1.8960728	3.3917429
36 H H15	-0.4542022	2.1247518	3.4666155
37 H H17	0.6116883	3.5171544	3.1939429
38 H H16	-0.9283424	2.7217660	-0.1983520

TS G

MacSPARTAN PRO Semi-Empirical Program: (PowerPC)
 Job run on machine : çãé G4-1(G4/466)

Release 1.0.2

PRE-TS1,PM3.1

Run type: Transition state optimization
 (Analytical Gradient)
 (Analytical Frequency in TSOPT)
 (Analytical Gradient in FREQ)
 (Numerical Frequency)

Model: RHF/PM3

Number of shells: 59

38 S shells

21 P shells

Number of basis functions: 101

Number of electrons: 112

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Heat of Formation: -74.579 kcal/mol

Calculating Hessian

Memory Used: 15.302 Mb

Reason for exit: Successful completion

Semi-Empirical Program CPU Time : 000:07:16.7

Semi-Empirical Program Wall Time: 000:08:06.9

MacSPARTAN PRO Properties Program: (PowerPC)

Release 1.0.2

Use of molecular symmetry disabled

Molecular charge: 0

Spin multiplicity: 1

Electrons: 112

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z

1 C C7	-0.1062003	-2.1118303	-0.6281515
2 C C6	-0.0569944	-0.6084498	-0.6879330
3 N N1	-0.4769115	-0.0330681	0.6508413
4 C C1	-1.7070847	0.6001010	0.7555193
5 C C2	-2.6660158	0.5101384	-0.3711124
6 O O1	-3.8557427	0.7362462	-0.3586098
7 O O2	-2.2673598	0.1196704	-1.6211963
8 C C3	-0.8745083	-0.0094034	-1.8449596
9 H H5	-0.8332435	-0.6523176	-2.7408149
10 H H4	-0.4849992	0.9927885	-2.1135463

11 H H3	-2.1612408	0.6663370	1.7632580
12 O O3	0.3997623	0.2912216	1.4965861
13 H H7	1.0113115	-0.3061384	-0.8694310
14 C C8	-1.3089502	-2.8179203	-0.6771836
15 C C9	-1.3051753	-4.2072821	-0.6207149
16 C C10	-0.1046167	-4.9009224	-0.5145232
17 C C11	1.0965713	-4.2014271	-0.4655517
18 C C12	1.0981377	-2.8126315	-0.5220949
19 H H1	2.0502723	-2.2694308	-0.4775371
20 H H2	2.0442384	-4.7438718	-0.3805292
21 H H6	-0.1049468	-5.9950880	-0.4694427
22 H H8	-2.2532348	-4.7545401	-0.6606399
23 H H9	-2.2642906	-2.2876117	-0.7691079
24 H H10	-1.7847106	2.9149870	1.4621976
25 C C16	-0.9484152	2.5218266	0.8795254
26 C C17	0.2873925	2.3315310	1.5088839
27 C C4	1.5663067	2.5548984	0.7749319
28 O O4	2.6335024	2.9190451	1.2292509
29 O O5	1.4934015	2.3268278	-0.5807527
30 C C13	2.6481343	2.5343020	-1.3641237
31 H H11	3.4650417	1.8667466	-1.0697628
32 H H12	2.9879041	3.5745738	-1.3242986
33 H H13	2.2943105	2.2858758	-2.3682968
34 C C5	0.3599054	2.5045170	2.9928548
35 H H14	1.2418837	2.0097175	3.4213329
36 H H15	-0.5291701	2.0850814	3.4837627
37 H H17	0.4176733	3.5697683	3.2569798
38 H H16	-1.0019279	2.7957323	-0.1756098

08-DEC-97 13:49:17

DFILE Q1H

ORNUC 1H

EXMOD NON

OFFR

ORSET 270.05 MHz

ORFIN 112.00 KHz

POINT 5800.0 Hz

FREQ 32768

SCANS 5405.4 Hz

ACQTM 16

PD 3.031 sec

PW1 3.969 sec

IRNUC 1H 5.3 us

CTEMP 23.9 C

SLVNT CDCL3

EXREF 0.00 ppm

BF 0.16 Hz

RGAIN 17

OPERATOR :

JEOL

23-SEP-03 00:59:20
 DFILE Q1H
 COMNT TS348F21-26
 EXMOD SGNON
 OBNUC 1H
 OBFIN 9817.0 HZ
 POINT 32768
 FREQ 15015.0 HZ
 SCANS 16
 ACQTM 1.091 sec
 PD 3.909 sec
 PW1 7.0 us
 IRFIN 10157.0 HZ
 IRATN 15
 IRRPW 60 us
 TEMP. 22.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.46 HZ
 RGAIN 1.4
 XE 5001.5990 HZ
 XS -550.9961 HZ

19-MAY-03 21:27:07
 DFIL DU1:
 COMNT TS273
 EXMOD SGNDN
 OBNUC 1H
 OFEIN 10300.0 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 32
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 US
 IREFIN 10157
 IRATN 5
 IRRPW 50 US
 TEMP. 22.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 13
 XE 5001.6000 HZ
 XS -119.4521 HZ

02-MAY-03 14:47:45
 DFIL: DU4:
 COMNT 218
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10989.5 Hz
 POINT 32768
 FREQU 8000.0 Hz
 SCANS 20
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 7.2 us
 IRFIN 10157.0 Hz
 IRATN 0
 IRAPW 50 us
 TEMP. 27.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.10 Hz
 RGAIN 15
 XE 5001.599
 XS 610.739

JEOL

12-SEP-02 22: 26: 17
 DFILE 01H
 COMNT SHOYAKU
 EXMOD SGNON
 OBNUC 1H
 OBFIN 9923.3 HZ
 POINT 32768
 FREQ 15015.0 HZ
 SCANS 16
 ACQTM 1.091 sec
 PD 3.909 sec
 PM1 7.8 US
 IRFIN 10157.0 HZ
 IRATN 15
 IRPFW 60 US
 TEMP. 22.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.46 HZ
 RGAIN 15
 XE 5001.5990 HZ
 XS -445.6045 HZ

10-SEP-02 16:56:45
 FILE D01:
 COMNT TS010200F21-51
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 32
 ACQTM 2.048 sec
 PD 1.000 sec
 PM1 4.0 us
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT CD3OD
 EXREF 4.87 PPM
 BF 0.20 HZ
 RGAIN 18
 XE 5001.5990 HZ
 YC

20-SEP-02 21:03:14
 DFILE DU1:
 COMNT TS010204N02
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 128
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT D2O
 EXREF 4.79 ppm
 BF 0.20 HZ
 RGAIN 23
 XE 5001.5990 HZ
 XS -1.7949 HZ

06-OCT-02 22:31:36
 DFILE Q1H
 COMNT TS010212
 EXMOD SGNON
 OBNUC 1H
 OBFIN 9771.6 HZ
 POINT 32768
 FREQU 45015.0 HZ
 SCANS 16
 ACQTM 1.091 sec
 PD 3.909 sec
 PW1 7.8 us
 IRFIN 10157.0 HZ
 IRATN 15
 IRRPW 60 us
 TEMP. 22.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.46 HZ
 RGAIN 14
 XE 5001.5990 HZ
 XS -594.9854 HZ

JEOL

31-JAN-03 19:55:31
 DFILE DU1:
 COMNT TS235F65-87
 EXMOD SGNON
 OBNUC 1H
 OFEIN 10300.0 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 16
 ACQTM 2.046 sec
 PD 1.000 sec
 PW1 4.0 US
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 US
 TEMP. 22.0 C
 SLVNT CD3OD
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 20
 XE 5001.5990 HZ
 XS -66.9946 HZ

06-FEB-03 11:42:10
 DF1E DU1:
 COMNT 235
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 Hz
 POINT 32768
 FREQU 8000.0 Hz
 SCANS 16
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRFIN 10157.0 Hz
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT D2O
 EXREF 4.79 ppm
 BF 0.20 Hz
 RGAIN 22
 XE 5001.5990 Hz
 XS -1.7949 Hz

20-MAY-03 11:13:23
 DF: TS278
 COM: TS278
 EXMOD: SGNON
 OBNUC: 1H
 OBFIN: 10300.0 HZ
 POINT: 32768
 FREQ: 8000.0 HZ
 SCANS: 32
 ACQTM: 2.048 sec
 PD: 1.000 sec
 PM1: 4.0 US
 IRFIN: 10157.0 HZ
 IRATN: 500
 IRRPM: 50 US
 TEMP: 22.0 C
 SLVNT: CDCL3
 EXREF: 0.00 ppm
 BF: 0.20 HZ
 RGAIN: 11
 XE: 5001.5990 HZ
 XS: -92.8738 HZ

28-AUG-03 14:09:52
 DFILE DU1:
 COMNT TS290, 291
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 32
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRRIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 18
 XE 5001.5990 HZ
 XS -66.0181 HZ

528

19-MAY-03	20: 58: 50	
DFILE	Q13C	
CONNNT	TS276F17-30	
EXMOD	SGBCM	
DBNUC	13C	
DBFIN	10404.0	Hz
POINT	32768	
FREQU	37878.8	Hz
SCANS	558	
ACQTM	0.433	sec
PD	1.567	sec
PM1	6.0	us
IRFIN	10167.0	Hz
IRATN	33	
IRAPW	50	us
TEMP.	22.0	c
BLVNT	CDCL3	
EXREF	0.00	ppm
BF	1.50	Hz
RGAIN	30	
XE	28297.2000	Hz
XS	-3423.5390	Hz

09-JUN-03 16:20:48
 FILE DU1:
 COMNT TS292F20-39
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQU 8000.0 HZ
 SCANS 32
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 15
 XE 5001.5990 HZ
 XS -62.1118 HZ

21-JUN-03 17:51:57
 DF FILE DU1:
 COMNT TS300HCL
 EXMOD SGNON
 OBNUC 1H
 OFIN 10300.0 HZ
 POINT 3276A
 FREQ 80C
 SCANS
 ACQTM 2.
 PD 1.
 PM1 4.0 us
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT D2O
 EXREF 3.70 ppm
 BF 0.20 HZ
 RGAIN 18
 XE 5001.5990 HZ
 XS -62.5945 HZ

14-JAN-04 17:32:09
 DF:FILE DVI:
 COMNT TS393
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQU 8000.0 HZ
 SCANS 128
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 17
 XE 5001.5990 HZ
 XS -75.7837 HZ

11-OCT-03 19:34:58
 DFILE DU4:
 COMNT TS360F10-18
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10989.5 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 64
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 7.2 us
 IRRIN 10157.0 HZ
 IRRATN 0
 IRRPW 50 us
 TEMP. 27.0 C
 SLVNT CDCL3
 EXREF 0.00 DPM
 BF 0.10 HZ
 RGAIN 14
 XE 5001.5990 HZ
 XS 606.8335 HZ

21-APR-03 23:14:56
 DFILE DU4:
 COMNT TS264F15-21
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10989.5 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 16
 ACQTM 2.048 sec
 PD 1.000 sec
 PM1 7.2 us
 IREFIN 10157.0 HZ
 IRATN 0
 IRRPW 50 us
 TEMP. 27.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.10 HZ
 RGAIN 14
 XE 5001.5990 HZ
 XS 623.9233 HZ

09-DEC-03 21:23:57
DFILE DU1:
COMET TS397
EXMOD SGNON
OBNUC 1H
OBFIN 10300.0 HZ
POINT 32768
FREQU 8000.0 HZ
SCANS 128
ACQTM 2.048 sec
PD 1.000 sec
PW1 4.0 us
IRFIN 10157.0 HZ
IRATN 500
IRRPW 50 us
TEMP. 22.0 C
SLVNT D2O
EXREF 3.70 ppm
BF 0.20 HZ
RGAIN 24
XE 5001.5990 HZ
XS -43.0632 HZ

12-NOV-03 00:14:54
 DFILE D01:
 COMNT TS379
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQV 8000.0 HZ
 SCANS 32
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IREFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 14
 XE 5001.5990 HZ
 XS -72.8540 HZ

14-NOV-03 12:53:13
 DFILE D01:
 COMNT TS251
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 16
 ACQTM 2.048 sec
 PD 1.000 sec
 PM1 4.0 us
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 18
 XE 5004.5990 HZ
 XS -78.7134 HZ

17-NOV-03 19:18:24
 DFIL DU1:
 COMET TS382
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQU 8000.0 HZ
 SCANS 32
 ACQTM 2.0
 PD 1.06
 PW1 4.0 us
 IRFIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 15
 XE 5001.5990 HZ
 XS -87.5027 HZ

14-NOV-03 12:16:17
 DF FILE DU1:
 COMNT TS380
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 16
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRRIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SILVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 14
 XE 5001.5990 HZ
 XS -74.3188 HZ

13-DEC-03 14:45:23
 DF FILE DU1:
 COMNT TS400
 EXMOD SGNON
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQ 8000.0 HZ
 SCANS 32
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRFIN 10457.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT CDCL3
 EXREF 0.00 PPM
 BF 0.20 HZ
 RGAIN 24
 XE 5001.5990 HZ
 XS -76.2720 HZ

19-NOV-03 13:10:04
 FILE DU1:
 COMNT TS383
 EXMOD SGNDN
 OBNUC 1H
 OBFIN 10300.0 HZ
 POINT 32768
 FREQU 8000.0 HZ
 SCANS 32
 ACQTM 2.048 sec
 PD 1.000 sec
 PW1 4.0 us
 IRRIN 10157.0 HZ
 IRATN 500
 IRRPW 50 us
 TEMP. 22.0 C
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.20 HZ
 RGAIN 13
 XE 5001.5990 HZ
 XS -99.7097 HZ