Chiral Hydantoin; A New Dienophile for Diels-Alder Reaction

Wongsiri SANKHAVASI,† Shigeo KOHMOTO, Makoto YAMAMOTO, Takehiko NISHIO,††
Ikuo IIDA, and Kazutoshi YAMADA*
Department of Materials Science, Faculty of Engineering, Chiba University, Chiba 260
† Graduate School of Science and Technology, Chiba University, Chiba 260
†† Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
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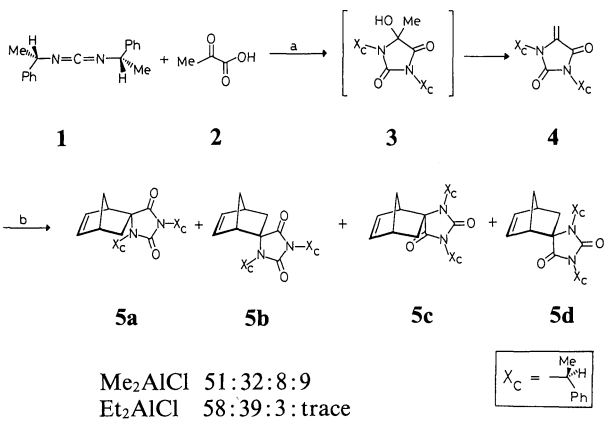
Synopsis. A chiral hydantoin derivative, 5-methylene-1,3-bis[(*S*)-1-phenylethyl]-2,4-imidazolidinedione, was synthesized and the scope of this compound in Diels–Alder reaction was investigated.

Hydantoin ring systems are structural units frequently encoutered in naturally occurring substances. They are well-known as anticonvulsants,[1] antimicrobial reagents,[2] and also effect neurotransmission.[3] One more important utility of hydration skeleton is that it has been used as an α-amino acid intermediate,[4] but yet its application as chiral synthon in asymmetric reaction remains almost unexplored.[5]

Herein, we report the first Diels–Alder cyclization of chiral 5-methylene hydantion bearing *S*-(1)-phenylethyl groups at N1 and N3 as a chiral source. This new synthetic method proved to be an efficient route to various new enantiomerically pure hydantions, and therefore, to optically pure cyclic α-amino acids.

Chiral 5-methylene hydantion (**4**) was easily prepared in a reasonable yield (45%) by treatment of pyruvic acid (**2**) with bis[(*S*)-1-phenylethyl]carbodiimide[6] (**1**) at room temperature in dry CH_3CN for 2 d (Scheme 1).

Thermal cyclization of **4** with cyclopentadiene upto 110 °C yielded no product. However, the reaction with cyclopentadiene catalyzed by Lewis acid (Me_2AlCl, 1.2 equiv) proceeded smoothly at 0 °C to produce four cyclized products in 93% isolated yield (Scheme 1). These four diastereomers were separated by high-performance liquid chromatography (HPLC) to give ≧99% ee of each stereoisomer (determined by 500 MHz ^1H NMR spectral data). The absolute configuration of major adduct (**5a**) was confirmed by X-ray crystallographic analysis[7] (Fig. 1) and the absolute configuration of minor adducts (**5b**, **5c**, and **5d**) were ascertained from NOESY spectra (Fig. 2). The *endo* and *exo* product ratio was improved upto >30:1 in the reaction with Et_2AlCl as Lewis acid (1.2 equiv, 0 °C, 3 h, 84% yield, Scheme 1).



Scheme 1. a) CH_3CN, rt, 2 days. b) Lewis acid, −70 °C, 1 h then cyclopentadiene, 0 °C, 3 h, CH_2Cl_2.

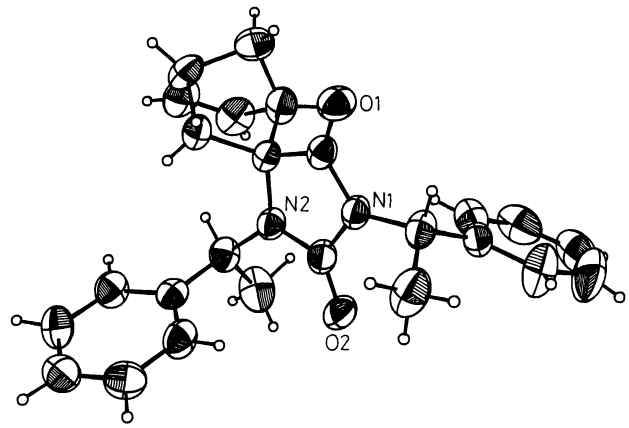


Fig. 1. ORTEP drawing of **5a**.

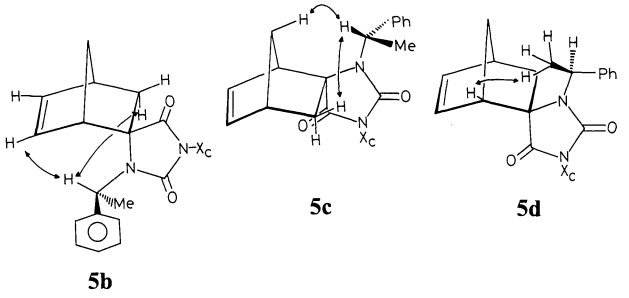


Fig. 2. NOESY spectral data of **5b**, **5c**, and **5d**.

While the reaction with *trans*-1,3-pentadiene and cyclohexadiene did not exhibit any selectivity, the cyclization with isoprene gave four isomers in the ratio of 14:2:1:trace in 71% yield and in the case of 2,3-dimethyl-1,3-butadiene two cyclized adducts were obtained in the ratio of 5:1 in 79% yield.[8] These results showed that the substitution at 2- and 3-positions of the diene increased the selectivity of the reactions.

The trial to convert Diels–Alder product to an α-amino acid derivative was done with **5a**.[9] Initially, **5a** was hydrogenated in a quantitative yield with H_2–Pd/C in EtOH to give **6a**, which was subsequently hydrolyzed with a large excess of saturated NaOH methanol–water (2:1) solution at 170 °C for 8 h in a sealed tube to give N-protected α-amino acid. Without purification, exposure of this acid to diazomethane afforded N-protected

α-amino acid methyl ester **7a** in 82% overall yield. Similar treatment of **5b** gave a comparable yield of **7b**.

Experimental

Preparation of 5-Methylene-2,4-imidazolidinedione (4). To a solution of pyruvic acid **2** (0.440 g, 4.50 mmol) in 5 ml dry acetonitrile at 0 °C was added 0.07 ml (0.1 equiv) of triethylamine and stirring was continued for 10 min under nitrogen before the solution of bis[(*S*)-1-phenylethyl]carbodiimide (1.249 g, 4.50 mmol) in 5 ml dry acetonitrile was added dropwise for 10 min. An ice-water bath was then removed and the mixture was allowed to react at ambient temperature for 2 d. After the reaction was completed the solid residue was filtered off and the filtrate was evaporated to give brown oil. Flash chromatography (ethyl acetate–hexane) gave yellow oil **4** (0.448 g, 45%); $[\alpha]_D^{23}=-62.6°$ (*c* 1.07, $CHCl_3$); IR ($CHCl_3$) 3049, 2995, 2950, 1770, 1720, 1649, 1408, 1378, 1195, 1175, and 710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ=1.74 (d, *J*=7.3 Hz, 3H), 1.90 (d, *J*=7.3 Hz, 3H), 4.42 (d, *J*=1.9 Hz, 1H), 5.21 (d, *J*=1.9 Hz, 1H), 5.42 (q, *J*=7.3 Hz, 1H), 5.59 (q, *J*=7.3 Hz, 1H), 7.2—7.6 (m, 10H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=16.1 (CH_3), 17.3 (CH_3), 50.0 (CH), 50.6 (CH), 96.1 (CH_2), 126.4 (CH), 127.2 (CH), 127.5 (CH), 127.7 (CH), 128.4 (CH), 128.5 (CH), 133.4 (C), 138.5 (C), 139.9 (C), 153.8 (C=O), 162.1 (C=O). HRMS Found: *m/z* 320.1535. Cald for $C_{20}H_{20}N_2O_2$: M, 320.1526.

General Procedure for the Diels-Alder Reaction of 4. To a solution of **4** in dry dichloromethane (about 0.2 M, 1M= 1 mol dm^{-3}) under nitrogen at −70 °C was added Me_2AlCl (1.01 M in hexane, 1.1—1.2 equiv). Stirring was continued for 1 h and freshly distilled diene (1.5 equiv) was added dropwise. The mixture was then allowed to react at 0 °C. After quenching with 1 M HCl aqueous solution, an organic layer was separated and the aqueous layer was extracted with dichloromethane for two times. The combined organic phase was dried ($MgSO_4$) and evaporated to give crude product which was purified by flash column chromatography.

5a. White solid; mp 129.0—131.0 °C; $[\alpha]_D^{23}=+69.4°$ (*c* 1.26, $CHCl_3$); IR ($CHCl_3$) 2980, 1760, 1701, 1422, 1375, 1359, and 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=1.33—1.40 (m, visible with *J*=8.8, 12.6 Hz, 2H), 1.81 (d, *J*=7.1 Hz, 3H), 1.86 (d, *J*=7.3 Hz, 3H), 2.14 (dd, *J*=3.7, 12.6 Hz, 1H), 2.54 (d, *J*=8.8 Hz, 1H), 2.93 (br m, 1H, COSY spectra show couplings with proton at δ=2.14 and 6.31), 2.98 (br m, 1H, COSY spectra show coupling with proton at δ=6.31), 4.50 (q, *J*=7.1 Hz, 1H), 5.38 (q, *J*=7.3 Hz, 1H), 6.31 (dd, *J*=2.9, 5.5 Hz, 1H), 6.52 (dd, *J*=3.2, 5.5 Hz, 1H), 7.0—7.4 (m, 10H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ=16.8 (CH_3), 19.6 (CH_3), 33.8 (CH_2), 42.2 (CH), 47.6 (CH_2), 49.9 (CH), 52.5 (CH), 54.9 (CH), 69.2 (C), 125.7 (CH), 126.8 (CH), 127.3 (CH), 127.5 (CH), 128.4 (CH), 128.5 (CH), 132.9 (CH), 140.3 (C), 141.7 (CH), 141.9 (C), 155.5 (C=O), 176.8 (C=O). MS *m/z* (rel intensity, %) 386 (M^+, 43), 320 (26), 216 (29), 105 (100), 77 (57), 66 (45), 51 (11), 39 (13), 27 (14). Found: C, 77.81; H, 6.80; N, 7.25%. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25%.

5b. White solid; mp 145.0—147.0 °C; $[\alpha]_D^{21}=-68.8°$ (*c* 1.26, $CHCl_3$); IR ($CHCl_3$) 3001, 2990, 1760, 1701, 1422, 1360, and 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=1.30 (m, visible with *J*=3.4, 8.8 Hz, 1H), 1.51 (dd, *J*=3.4, 12.6 Hz, 1H), 1.66 (d, *J*=7.4 Hz, 3H), 1.88 (d, *J*=7.4 Hz, 3H), 2.29 (dd, *J*=3.6, 12.6 Hz, 1H), 2.54 (d, *J*=8.8 Hz, 1H), 2.82 (br m, 1H, COSY spectra show coupling with proton at δ=5.57), 2.97 (br m, 1H, COSY spectra show couplings with proton at δ=2.29 and 6.37), 4.40 (q, *J*=7.4 Hz, 1H), 5.42 (q, *J*=7.4, 1H), 5.57 (dd, *J*=2.9, 5.6 Hz, 1H), 6.37 (dd, *J*=3.2, 5.6 Hz, 1H), 7.2—7.5 (m, 10H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ=17.4 (CH_3), 20.1 (CH_3), 34.7 (CH_2), 41.9 (CH), 47.8 (CH_2), 50.2 (CH), 53.1 (CH), 54.0 (CH), 68.9 (C), 125.9 (CH), 126.5 (CH), 127.1 (CH), 127.4 (CH), 128.4 (CH), 133.4 (CH), 140.4 (CH), 140.6 (C), 141.9 (C), 155.3 (C=O), 176.8 (C=O). HRMS Found: *m/z* 386.1997. Calcd for $C_{25}H_{26}N_2O_2$: M, 386.1996. Found: C, 77.69; H, 6.80; N, 7.25%. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25%.

5c. Colorless oil; IR (neat) 2976, 1760, 1708, 1498, 1450, 1416, 1376, 1336, 1312, 1182, 1168, 1030, 754, 718, 698, and 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=1.63 (ddd, *J*=1.1, 1.1, 11.7 Hz, 1H, COSY spectra show couplings with proton at δ=1.72 and 1.96), 1.72 (dd, *J*=2.6, 11.7 Hz, 1H, COSY spectra show couplings with proton at δ=1.63 and 1.96), 1.77 (d, *J*=7.3 Hz, 3H), 1.90 (d, *J*=7.1 Hz, 3H), 1.96 (m, 2H), 2.87 (br m, 1H), 3.07 (br m, 1H), 4.74 (q, *J*=7.1 Hz, 1H), 5.28 (q, *J*=7.3 Hz, 1H), 6.15 (dd, *J*=3.1, 5.7 Hz, 1H, COSY spectra show coupling with proton at δ=2.87), 6.4 (dd, *J*=3.1, 5.7 Hz, 1H, COSY spectra show cocupling with proton at δ=3.07), 7.2—7.4 (m, 10 H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=16.7 (CH_3), 18.8 (CH_3), 34.6 (CH_2), 43.1 (CH), 48.2 (CH_2), 49.8 (CH), 51.9 (CH), 54.4 (CH), 70.5 (C), 125.8 (CH), 126.9 (CH), 127.3 (CH), 127.4 (CH), 128.2 (CH), 128.4 (CH), 134.0 (CH), 140.0 (CH), 140.3 (C), 141.3 (C), 154.7 (C=O), 174.9 (C=O). HRMS Found: *m/z* 386.1986. Calcd for $C_{25}H_{26}N_2O_2$: M, 386.1996.

5d. White solid; mp 140.0—141.5 °C; IR (KBr) 3004, 2980, 1756, 1702, 1444, 1422, 1378, 1330, 1172, 752, and 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=1.34 (ddd, visible with *J*=1.2, 9.5 Hz, 1H), 1.76 (m, visible with *J*=9.5, 12.9 Hz, 2H), 1.83 (d, *J*=7.1 Hz, 3H), 1.84 (d, *J*=7.3 Hz, 3H), 2.00 (dd, *J*=3.6, 12.9 Hz, 1H, COSY spectra show coupling with proton at δ=3.05), 2.62 (br m, 1H), 3.05 (br m, 1H), 4.67 (q, *J*=7.1 Hz, 1H), 5.36 (q, *J*=7.3 Hz, 1H), 5.99 (dd, *J*=3.3, 5.5 Hz, 1H, COSY spectra show coupling with proton at δ=2.62), 6.34 (dd, *J*=2.9, 5.5 Hz, 1H, COSY spectra show coupling with proton at δ=3.05), 7.2—7.5 (m, 10H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=17.5 (CH_3), 21.3 (CH_3), 35.3 (CH_2), 42.9 (CH), 48.2 (CH_2), 50.2 (CH), 53.4 (CH), 53.9 (CH), 70.5 (C), 126.2 (CH), 126.9 (CH), 127.1 (CH), 127.4 (CH), 128.3 (CH), 128.5 (CH), 134.1 (CH), 139.7 (CH), 140.6 (C), 142.4 (C), 155.3 (C=O), 175.1 (C=O). HRMS Found: *m/z* 386.1997. Calcd for $C_{25}H_{26}N_2O_2$: M, 386.1996. Found: C, 77.77; H, 6.83; N, 7.24%. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25%.

Major Adduct of the Reaction with Isoprene. Colorless oil; $[\alpha]_D^{20}=-30.9°$ (*c* 1.06, $CHCl_3$); IR (neat) 3024, 2972, 2932, 1762, 1712, 1498, 1450, 1420, 1368, 1328, 1310, 1266, 1220, 1174, 1068, 1030, 758, and 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=1.69 (s, 3H), 1.7—1.8 (m, 3H), 1.80 (d, *J*=7.1 Hz, 3H), 1.84 (d, *J*=7.3 Hz, 3H), 2.2—2.3 (m, 1H), 2.38 (br m, 2H), 4.50 (q, *J*=7.1 Hz, 1H), 5.35 (q, *J*=7.3 Hz, 1H), 5.42 (br m, 1H), 7.2—7.5 (m, 10H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=17.2 (CH_3), 21.0 (CH_3), 23.2 (CH_3), 26.6 (CH_2), 29.3 (CH_2), 31.0 (CH_2), 49.8 (CH), 52.6 (CH), 61.9 (C), 116.4 (CH), 126.3 (CH), 126.9 (CH), 127.0 (CH), 127.4 (CH), 128.3 (CH), 128.4 (CH), 134.4 (C), 140.5 (C), 142.7 (C), 154.7 (C=O), 175.3 (C=O). HRMS Found: *m/z* 388.2160. Calcd for $C_{25}H_{28}N_2O_2$: M, 388.2152.

Major Adduct of the Reaction with 2,3-Dimethyl-1,3-butadiene. Colorless oil; $[\alpha]_D^{21}$ δ=−26.2° (*c* 1.22, $CHCl_3$); IR (neat) 3020, 2980, 2928, 1760, 1704, 1498, 1450, 1422, 1374, 1314, 1268, 1240, 1220, 1176, 1056, 1028, 756, and 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=1.64 (s, 3H), 1.69 (s, 3H), 1.70—1.72 (m, 2H), 1.80—1.84 (m, 1H), 1.80 (d, *J*=7.2 Hz, 3H), 1.84 (d, *J*=7.2 Hz, 3H), 2.24 (br dm, visible with *J*=17.6 Hz, 2H), 2.36 (br d, *J*=17.6 Hz, 1H), 4.48 (q, *J*=7.2 Hz, 1H), 5.34 (q, *J*=7.2 Hz, 1H), 7.2—7.4 (m, 10 H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=17.2 (CH_3), 18.7 (CH_3), 18.8 (CH_3), 21.0 (CH_3), 28.0 (CH_2), 29.6 (CH_2), 36.6 (CH_2), 49.8 (CH), 52.6 (CH), 63.0 (C), 121.3 (C), 126.0 (C), 126.2 (CH), 126.9 (CH), 127.0 (CH), 127.3 (CH), 128.3 (CH), 128.4 (CH), 140.5 (C), 142.8 (C), 154.7 (C=O), 175.3 (C=O). HRMS Found: *m/z* 402.2296. Calcd for $C_{26}H_{30}N_2O_2$: M, 402.2309.

General Procedure for the Hydrogenation of Diels-Alder

Adducts. The Diels–Alder adduct was dissolved in EtOH (about 0.1 M) and 5% Pd–carbon was added as catalyst. The reaction mixture was subjected to hydrogen atmosphere for 3 h at room temperature under atmospheric pressure. After filtration of Pd–carbon, the solvent was allowed to evaporate under reduced pressure to give a quantitative yield of the adduct. Purification by flash chromatography (hexane:ethyl acetate) gave pure **6a** and **6b**.

6a. White solid; mp 122.5—124.0 °C; $[\alpha]_D^{21}$ =+94.2° (*c* 1.46, $CHCl_3$); IR (neat) 2968, 2944, 1758, 1706, 1498, 1444, 1422, 1376, 1318, 1218, 1170, 1064, 758, 698, and 666 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=1.1—2.1 (m, 8H), 1.84 (d, *J*=7.4 Hz, 3H), 2.05 (d, *J*=7.2 Hz, 3H), 2.2-2.6 (m, 2H), 4.37 (q, *J*=7.2 Hz, 1H), 5.35 (q, *J*=7.4 Hz, 1H), 7.0-7.5 (m, 10H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=16.5 (CH_3), 21.8 (CH_3), 24.2 (CH_2), 28.3 (CH_2), 34.7 (CH_2), 35.9 (CH), 37.0 (CH_2), 49.7 (CH), 54.5 (CH), 70.6 (C), 125.7 (CH), 126.8 (CH), 127.2 (CH), 127.4 (CH), 128.2 (CH), 128.5 (CH), 140.2 (C), 142.3 (C), 156.4 (C=O), 176.7 (C=O). HRMS Found: *m/z* 388.2143. Calcd for $C_{25}H_{28}N_2O_2$: M, 388.2152. Found: C, 77.53; H, 7.30; N, 7.25%. Calcd for $C_{25}H_{28}N_2O_2$: C, 77.29; H, 7.27; N, 7.21%.

6b. White solid; mp 137.0—139.0 °C; $[\alpha]_D^{21}$ =+21.6° (*c* 1.02, $CHCl_3$); IR (neat) 3020, 2944, 1758, 1738, 1706, 1498, 1422, 1370, 1340, 1318, 1174, 1064, 756, 698, and 666 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=1.0—1.7 (m, 6H), 1.72 (d, *J*=7.0 Hz, 3H), 1.84 (d, *J*=7.2 Hz, 3H), 2.0—2.7 (m, 4H), 4.42 (q, *J*=7.0 Hz, 1H), 5.36 (q, *J*=7.2 Hz, 1H), 7.1—7.6 (m, 10Hz); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=17.4 (CH_3), 20.2 (CH_3), 23.9 (CH_2), 28.3 (CH_2), 48.6 (CH), 50.0 (CH), 54.0 (CH), 70.7 (C), 125.9 (CH), 126.6 (CH), 127.0 (CH), 127.4 (CH), 128.3 (CH), 140.5 (C), 142.0 (C), 155.7 (C=O), 176.9 (C=O). HRMS Found: *m/z* 388.2147. Calcd for $C_{25}H_{28}N_2O_2$: M, 388.2152. Found: C, 77.18; H, 7.27; N, 7.18%. Calcd for $C_{25}H_{28}N_2O_2$: C, 77.29; H, 7.27; N, 7.21%.

General Procedure for the Preparation of N-Protected Amino Acid Methyl Ester. Compound **6a** or **6b** was dissolved in methanol (about 0.1 M) and saturated NaOH methanol: H_2O (2:1) solution was added to the mixture. After heating at 170 °C in a sealed tube for 8 h, ethyl acetate was added to the mixture and methanol was evaporated under reduced pressure. The residue was again dissolved in ethyl acetate and diazomethane in ether was added. The reaction mixture was stirred for 1 to 2 h and organic layer was separated. Extraction by ethyl acetate for two times and evaporation of the combined organic layers gave crude oil, which on purification by flash chromatography (hexane:ethyl acetate) gave N-protected amino acid methyl ester in 82% yield.

Methyl (1*S*,2*R*,4*R*)-2-[(*S*)-1-Phenylethylamino]bicyclo[2.2.1]heptane-2-carboxylate (7a). Colorless oil; $[\alpha]_D^{21}$ = −50.48° (*c* 1.28, $CHCl_3$); IR (neat) 2948, 2868, 1728, 1456, 1274, 1260, 1238, 1210, 1178, 1156, 1126, 1108, 1082, 760, and 702 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=1.0—1.5 (m, 6H), 1.28 (d, *J*=6.9 Hz, 3H), 1.7—1.9 (m, 1H), 1.85 (s, 1H), 2.1—2.5 (m, 3H), 3.5 (s, 3H), 3.59 (q, *J*=6.9 Hz, 1H), 7.25 (s, 5H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ=21.7 (CH_2), 25.2 (CH_3), 29.4 (CH_2), 36.3 (CH), 37.8 (CH_2), 41.5 (CH_2), 43.9 (CH), 51.3 (CH_3), 55.4 (CH), 69.4 (C), 126.6 (CH), 126.8 (CH), 128.0 (CH), 146.0 (C), 177.3 (C=O). HRMS Found *m/z* 273.1731. Calcd for $C_{17}H_{23}NO_2$: M, 273.1737.

Methyl (1*R*,2*S*,4*S*)-2-[(*S*)-1-Phenylethylamino]bicyclo-[2.2.1]heptane-2-carboxylate (7b). Colorless oil; $[\alpha]_D^{22}$ = +67.0° (*c* 0.66, $CHCl_3$); IR ($CHCl_3$) 3352, 2952, 1730, 1450, 1206, 1078, 760, and 702 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ=0.85 (dm, 1H), 1.1—1.5 (m, 5H), 1.29 (d, *J*=7.0 Hz, 3H), 1.81 (s, 1H), 1.9—2.2 (m, 3H), 2.3 (br s, 1H), 3.30 (s, 3H), 3.59 (q, *J*=7.0 Hz, 1H), 7.22 (s, 5H); ^{13}C NMR (125.6 MHz, $CDCl_3$) δ=22.2 (CH_2), 26.0 (CH_3), 29.0 (CH_2), 36.4 (CH), 37.9 (CH_2), 41.4 (CH_2), 43.7 (CH), 51.4 (CH_3), 55.4 (CH), 69.1 (C), 126.5 (CH), 126.7 (CH), 128.1 (CH), 146.6 (C), 177.3 (C=O). HRMS Found: *m/z* 273.1729. Calcd for $C_{17}H_{23}NO_2$: M, 273.1737.

X-Ray Crystallographic Analysis of 3a. A colorless rod crystal of $C_{25}H_{26}N_2O_2$ having approximate dimension of 0.43×0.53×0.15 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation on Enraf–Nonius CAD4 computor-controlled kappa axis diffractometer equipped with a graphite, incident beam monochromator. The orthorhombic cell paprameters and calculated volume are: a=9.751(1), b=10.048(1), c=21.379(2) Å, V=2094.6 $Å^3$. For Z=4 and FW=386.50 the calculated density is 1.23 g cm^{-3}. A total of 1702 unique reflections with $F(0)>3\sigma(F_o)$ were obtained by using ω–2θ scan technique with a 2θ scan speed of 4 min^{-1} to 2θ=50°. The structure was solved by the MOLEN system on the basis of the direct method and refined to a final R value of 0.039. Further crystallographic details are deposited as Document No. 8981 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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