Electronic Supplementary Material (ESI) for Photochemical and Photobiological Science

Supporting Information

To accompany

Asymmetric Photocycloaddition of Naphthamide with Diene Using the Provisional Molecular Chirality in a Chiral Crystal

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General experimental

General. NMR spectra were recorded on $CDCl_3$ solutions on a BRUKER 300 operating 300 MHz for ^{1}H- and ^{13}C-NMR spectroscopy, respectively. Chemical shifts were reported in parts per million (ppm) relative to TMS as internal standards. IR spectra were recorded on a JASCO FT/IR-230 spectrometer as KBr disks. Eikosya 500 W high pressure mercury lamp and SAN-EI ELECTRIC 350 W super high pressure mercury lamp were used as the irradiation sources.

Preparation of *N*-(2-methoxy-1-naphthoyl)piperidine 1 and *N*-(2-ethoxy-1-naphthoyl)pyrrolidine 4

N-(2-methoxy-1-naphthoyl)piperidine **1** and *N*-(2-ethoxy-1-naphthoyl)pyrrolidine **4** used for photoreaction were prepared according to the literature.[4] 2,5-Dimethylhexa-2,4-diene **2** were commercially available, and were purified by distillation before use. The crystals of **1** used for the asymmetric synthesis were prepared by stirred crystallization at high temperature, by which the completely melted sample of **1** at 120°C (mp: 110-112°C) was cooled and solidified by lowering the temperature to 100°C with stirring. A high level of reproducibility of both chiral crystallization and asymmetric photoreaction was achieved by this method. Of course, the desired crystals of **1** could be selectively prepared in large quantities by the addition of a corresponding seed crystal during the crystallization process.

Typical procedure for the photoreaction of 1 with diene 2

Crystals of **1** were added to a cooled and deoxygenated (by bubbling argon) toluene solution containing diene **2** (0.1 mol/L), and the solution was irradiated with a Pyrex filtered light using a 350-W super-high pressure mercury lamp for 0.25 - 1.0 h at the same temperature. After removing the solvent in vacuo, the crude photolysate was subjected to chromatography on silica gel. The 2+2 cycloadduct **3** was isolated. The chemical yield of **3** was determined on the basis of the consumed naphthamide **1**.

Spectral data of *endo*-3

Viscous oil: IR (cm^{-1}, neat) 1641; ^{1}H-NMR: ($CDCl_3$) δ 0.44 (s, 3H), 1.25-1.40 (m, 6H), 1.57 (s, 3H), 1.73 (s, 3H), 1.77 (s, 3H), 2.70-2.85 (m, 2H), 3.22 (s, 3H), 3.53 (d, J = 10.6 Hz, 1H), 3.83-3.86 (m, 1H), 5.24 (d, J = 10.6 Hz, 1H), 6.15 (d, J = 10.2 Hz, 1H), 6.61 (d, J = 10.2 Hz, 1H), 6.90-6.93 (m, 1H), 7.07-7.10 (m, 1H), 7.13-7.17 (m, 2H); ^{13}C-NMR: ($CDCl_3$) δ 18.3, 23.8, 24.4, 24.6, 25.5, 26.2, 28.2, 30.0, 43.4, 44.2, 47.6, 49.7, 54.4, 58.2, 76.8, 119.1,

124.8, 126.4, 126.5, 127.4, 128.0, 129.0, 131.1, 134.4, 135.8, 171.9; HRMS (ESI-MS) *m/z* calcd for $C_{25}H_{33}NO_2Na$ 402.2404, found 402.2389.

Spectral data of *endo*-5

Mp: 158-159°C; IR (cm^{-1}, neat) 1628; ^{1}H-NMR: ($CDCl_3$) δ 0.46 (s, 3H), 1.06 (t, J = 7.0 Hz, 3H), 1.40-1.60 (m, 2H), 1.58 (s, 3H), 1.70-1.80 (m, 2H), 1.70 (s, 3H), 1.74 (s, 3H), 3.17-3.22 (m, 2H), 3.43 (q, J = 7.0 Hz, 2H), 3.40-3.46 (m, 2H), 3.65 (d, J = 10.6 Hz, 1H), 5.27 (d, J = 10.6 Hz, 1H), 6.19 (d, J = 10.1 Hz, 1H), 6.59 (d, J = 10.1 Hz, 1H), 6.90-6.93 (m, 1H), 7.06-7.10 (m, 1H), 7.13-7.18 (m, 2H); ^{13}C-NMR: ($CDCl_3$) δ 16.1, 18.4, 23.5, 23.8, 25.0, 26.2, 26.5, 26.8, 43.4, 46.9, 47.0, 53.9, 57.0, 59.2, 60.8, 75.7, 118.9, 126.4, 126.4, 126.7, 127.3, 128.2, 128.9, 131.8, 134.6, 135.2, 172.8; HRMS (ESI-MS) *m/z* calcd for $C_{25}H_{33}NO_2Na$ 402.2404, found 402.2390.

X-Ray crystallographic analyses of *endo*-5

Crystal data of *endo*-**5**: (recrystallized from a mixture of $CHCl_3$ and hexane); $C_{25}H_{33}NO_2$, Mr = 379.52, Orthorhombic space group $P2_1/c$, a = 7.525(9) Å, b = 24.63(3) Å, c = 11.729(15) Å, β = 98.548(18)°, V = 2150(5) $Å^3$, Z = 4, ρ = 1.173 Mg/m^3, in the final least-squares refinement cycles on F^2, the model converged at R_1 = 0.0515, $wR2$ = 0.1057, and GOF = 0.905 for 3963 reflections CCDC 810675.

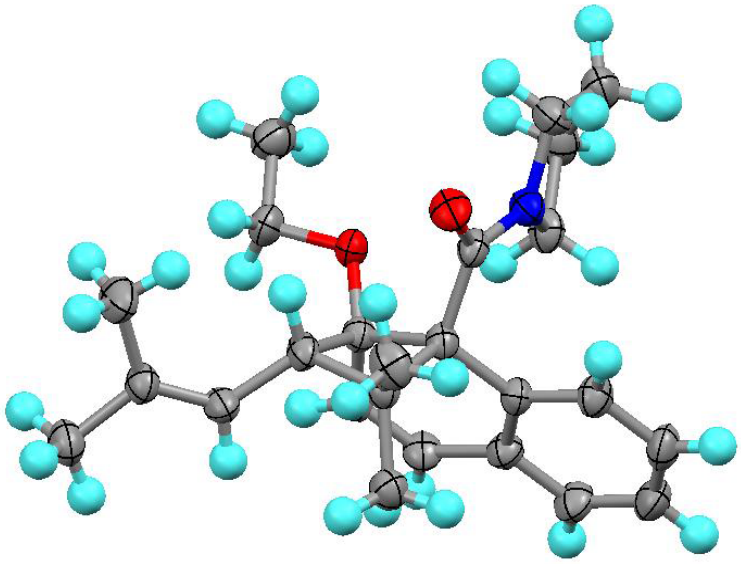

Fig. S1. Ortep view of *endo*-**5** showing the atoms and thermal ellipsoids at 40% probability.

Figure S2. ^{1}H NMR spectrum of *endo*-3

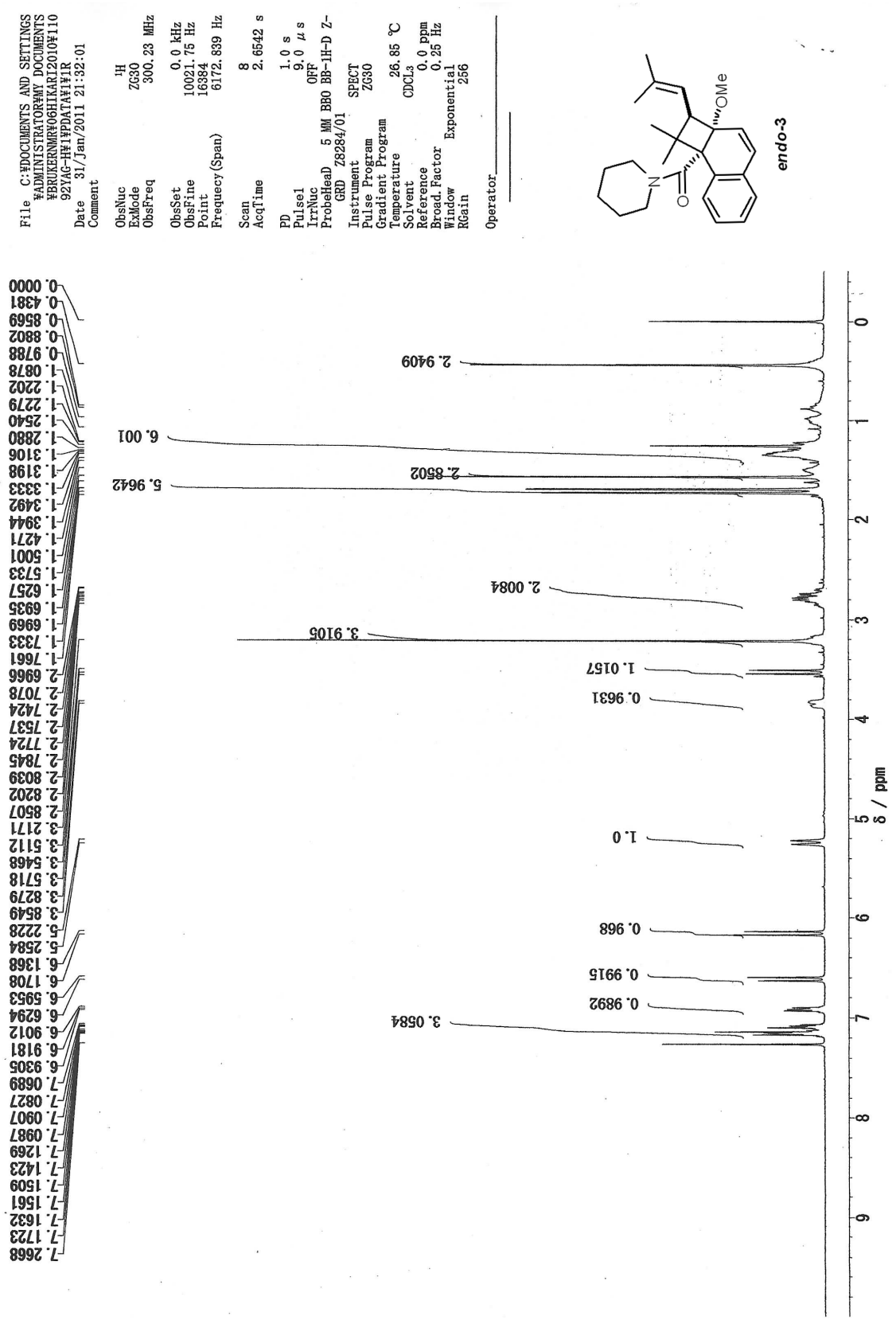

Figure S3. ^{13}C NMR spectrum of *endo*-3

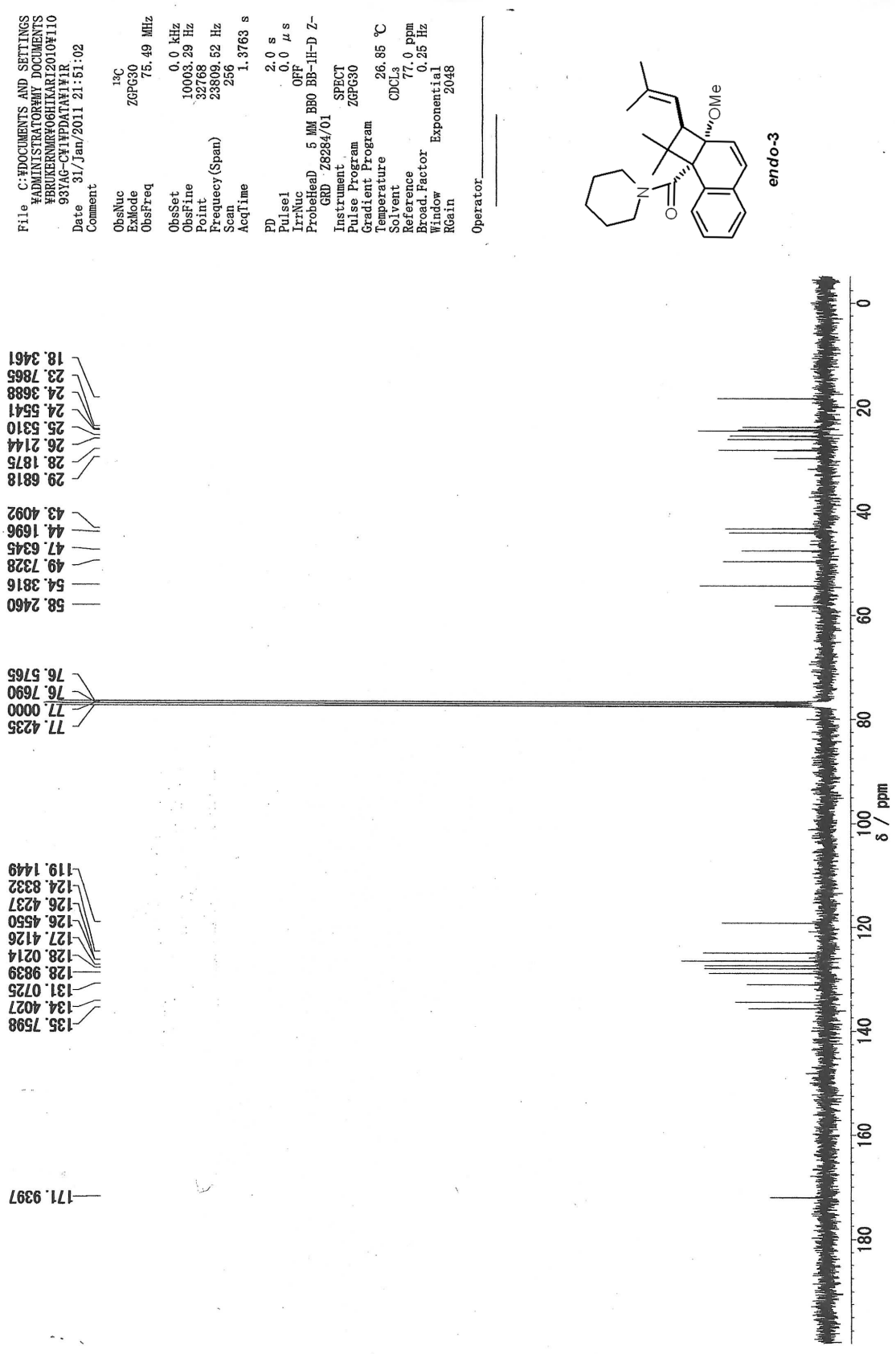

Figure S4. ^{1}H NMR spectrum of *endo*-5

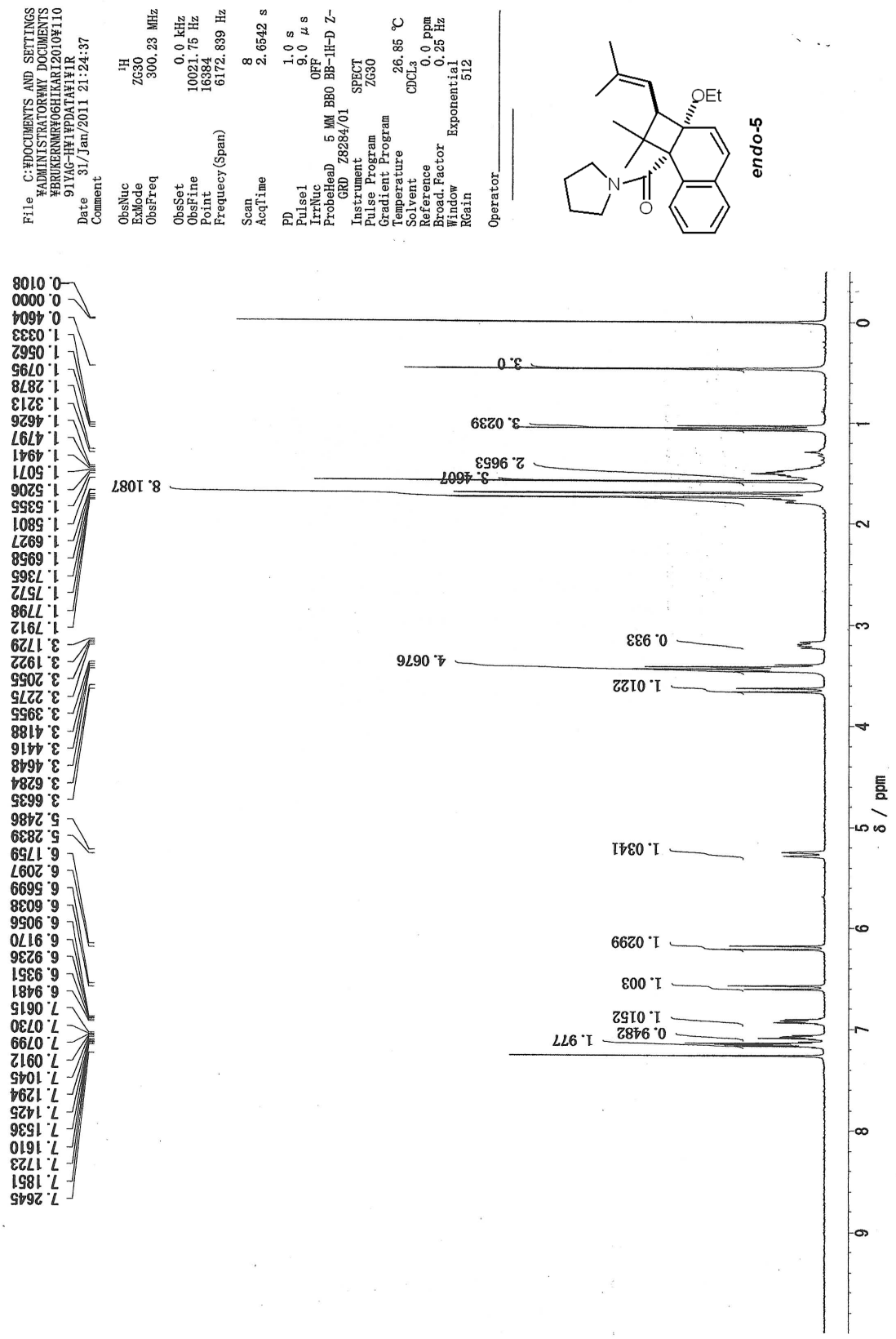

Figure S5. ^{13}C NMR spectrum of *endo*-5