

Supplementary Information

Photodimerization of Chromone

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Experimental

General. NMR spectra were recorded on CDCl₃ solutions on a BRUKER 300 operating 300 MHz, respectively, for ¹H- and ¹³C-NMR spectroscopy. Chemical shifts are 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. UV-VIS spectra were recorded on a JASCO V-650, and fluorescence spectra were recorded on a JASCO FP-6200DS spectrometer. Eikosya 500 W high pressure mercury lamp was used as the irradiation source. An uranyl glass filter was used for isolation of 365 nm line. Chromone **1** used for photochemical reaction was purified by recrystallization of the commercially available material from CHCl₃-hexane twice.

General procedure for the photoreaction of chromone 1

A benzene solution containing chromone at various concentrations was irradiated with a 500-W high pressure mercury lamp under argon atmosphere. After removing the solvent in *vacuo*, the crude photolysate was subjected to chromatography on silica gel. Two photodimers, **2** and **3**, were obtained as sole products.

Spectral data of *cis-cis-anti* head-to-tail photodimer **2**.

Mp. 223.5-224.5°C; IR (cm⁻¹, KBr) 1604, 1670; ¹H-NMR: (CDCl₃) δ 3.89 (dd, *J* = 4.8 and 6.9 Hz, 2H), 5.42 (dd, *J* = 4.8 and 6.9 Hz, 2H), 7.02 (dd, *J* = 1.0 and 8.3 Hz, 2H), 7.09 (ddd, *J* = 1.0, 7.3 and 7.8 Hz, 2H), 7.55 (ddd, *J* = 1.7, 7.3 and 8.3 Hz, 2H), 7.92 (dd, *J* = 1.7 and 7.8 Hz, 2H); ¹³C-NMR

(CDCl₃) δ 51.4, 74.9, 118.8, 119.2, 122.3, 127.2, 137.1, 159.5, 188.6; EI-MS m/z 292 (M⁺).

Spectral data of *cis-trans* head-to-tail photodimer **3**.

Mp. 173.5-174.2°C; IR (cm⁻¹, KBr) 1606, 1685, 1716; ¹H-NMR: (CDCl₃) δ 3.54 (dd, J = 4.8 and 13.2 Hz, 1H), 3.62 (dd, J = 5.4 and 9.0 Hz, 1H), 5.20 (dd, J = 9.0 and 13.2 Hz, 1H), 5.52 (dd, J = 4.8 and 5.4 Hz, 2H), 7.0 -7.26 (m, 4H), 7.47-7.54 (m, 4H), 7.92-7.97 (m, 4H); ¹³C-NMR (CDCl₃) δ 49.2, 52.5, 73.9, 77.2, 118.3, 118.7, 119.4, 122.2, 122.4, 123.4, 127.3, 128.1, 135.6, 136.9, 160.3, 160.8, 187.2, 187.9; EI-MS m/z 292 (M⁺).

Crystal data for the, *cis-cis-anti* head-to-tail dimer **2**, (recrystallized from a mixture of CHCl₃ and hexane): Monoclinic, space group *C2/c*, a = 14.8002(10) Å, b = 8.2800(6) Å, c = 22.2830(19) Å, β = 103.7710(10)°, V = 2652.2(3) Å³, Z = 8, ρ = 1.464 Mg m⁻³; 7287 reflections measured, 3007 unique, R_{int} = 0.024, in the final least-square refinement cycles on F^2 , the model converged to R_1 = 0.0420, wR_2 = 0.1053. CCDC 714210 contains crystallographic data.

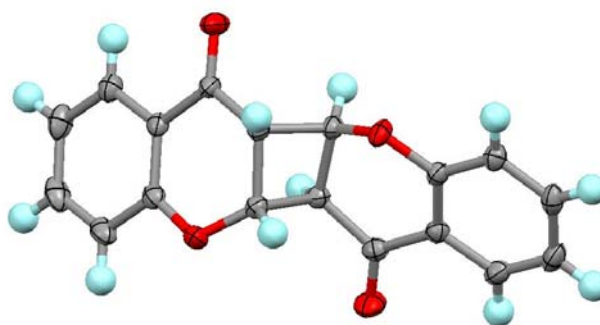


Figure S1. Ortep drawing of **2**. The ellipsoids were drawn in 50% probability.

Crystal data for the, *cis-trans* head-to-tail dimer **3**, (recrystallized from a mixture of CHCl₃ and hexane): Monoclinic, space group *P21/c*, a = 10.5496(13) Å, b = 10.5496(13) Å, c = 14.7098(18) Å, β = 98.247(2)°, V = 1318.2(3) Å³, Z = 4, ρ = 1.473 Mg m⁻³; 7195 reflections measured, 3043 unique,

$R_{\text{int}} = 0.018$, in the final least-square refinement cycles on F^2 , the model converged to $R_1 = 0.0477$, $wR_2 = 0.1260$. CCDC 714211 contains crystallographic data.

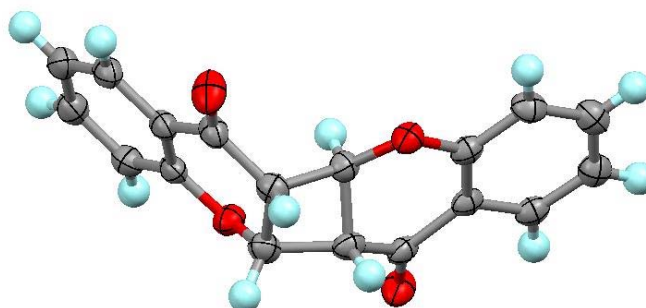


Figure S2. Ortep drawing of **3**. The ellipsoids were drawn in 50% probability.

Spectral changes for the photoreaction of chromone **1**

A 0.1 M benzene solution of chromone was irradiated with a 500-W high pressure mercury lamp under argon atmosphere up to 20 % conversion. Residual mixture containing two dimers and unreacted **1** was diluted to 1000 times with benzene.

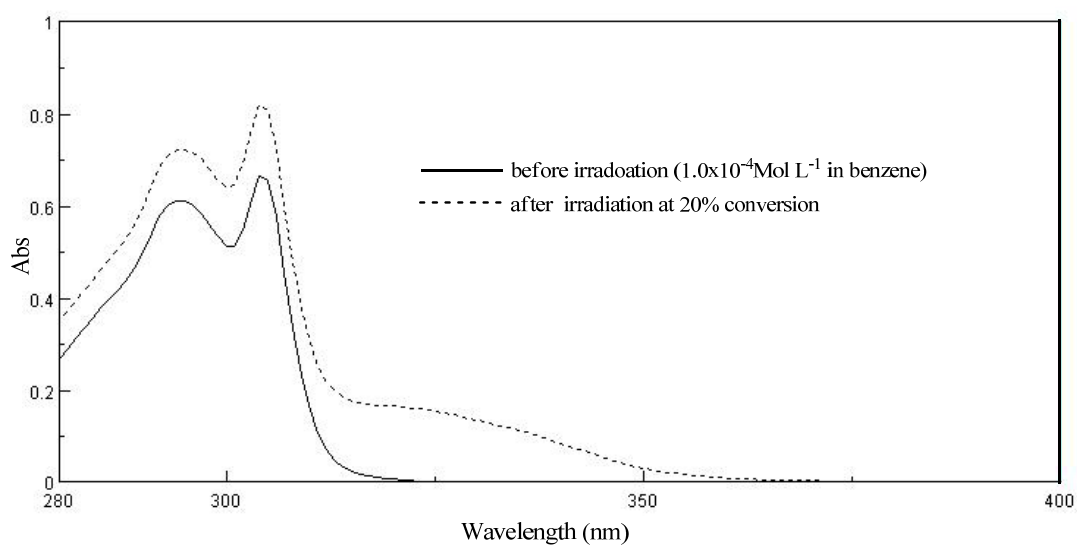


Figure S3. UV spectra before and after irradiation of chromone **1**. A benzene solution of **1** ($1.0 \times 10^{-1} \text{ mol L}^{-1}$) was irradiated until 20% conversion.

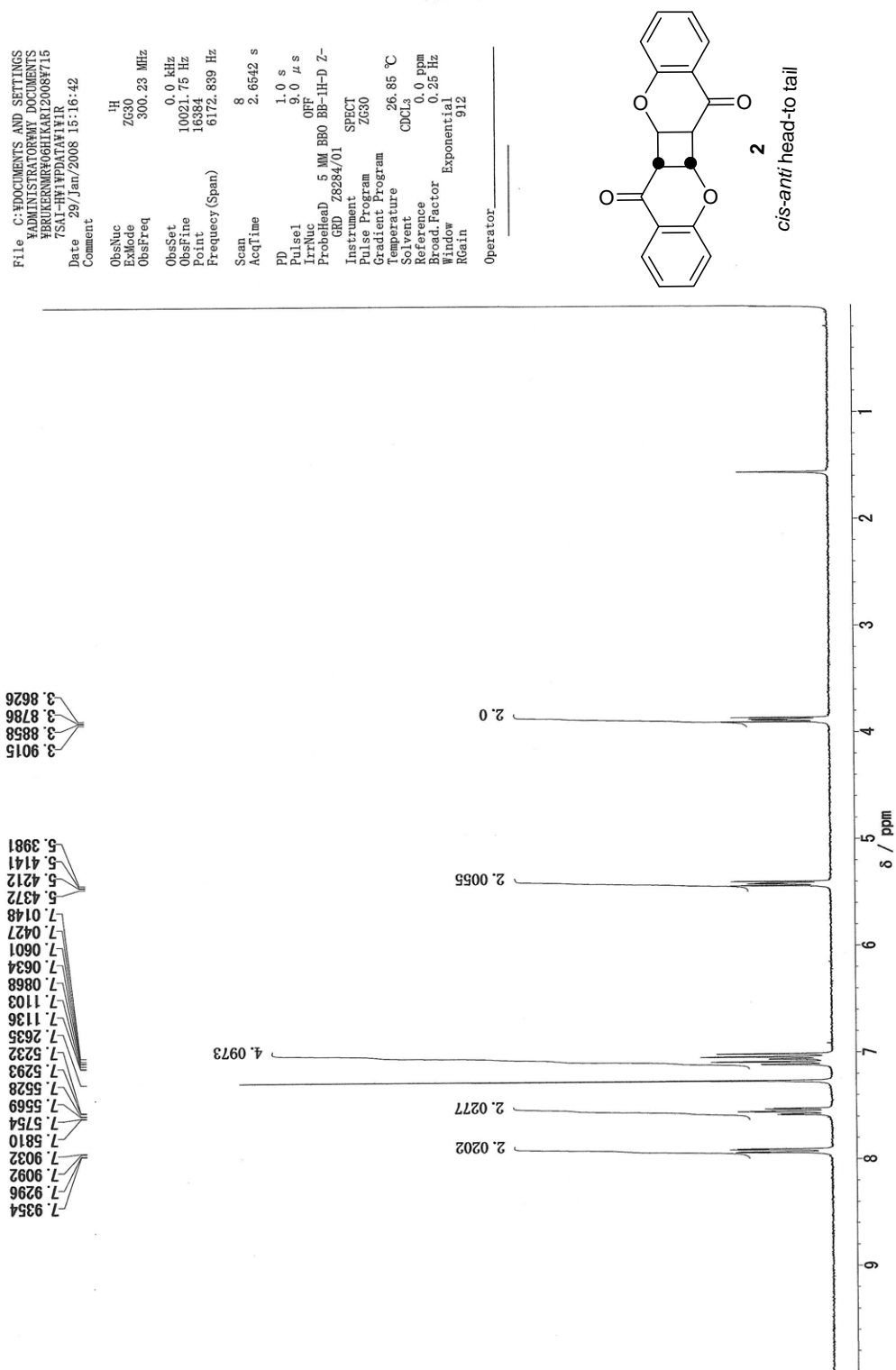


Figure S4. ¹H NMR spectrum of *cis-cis-anti* H-T dimer 2

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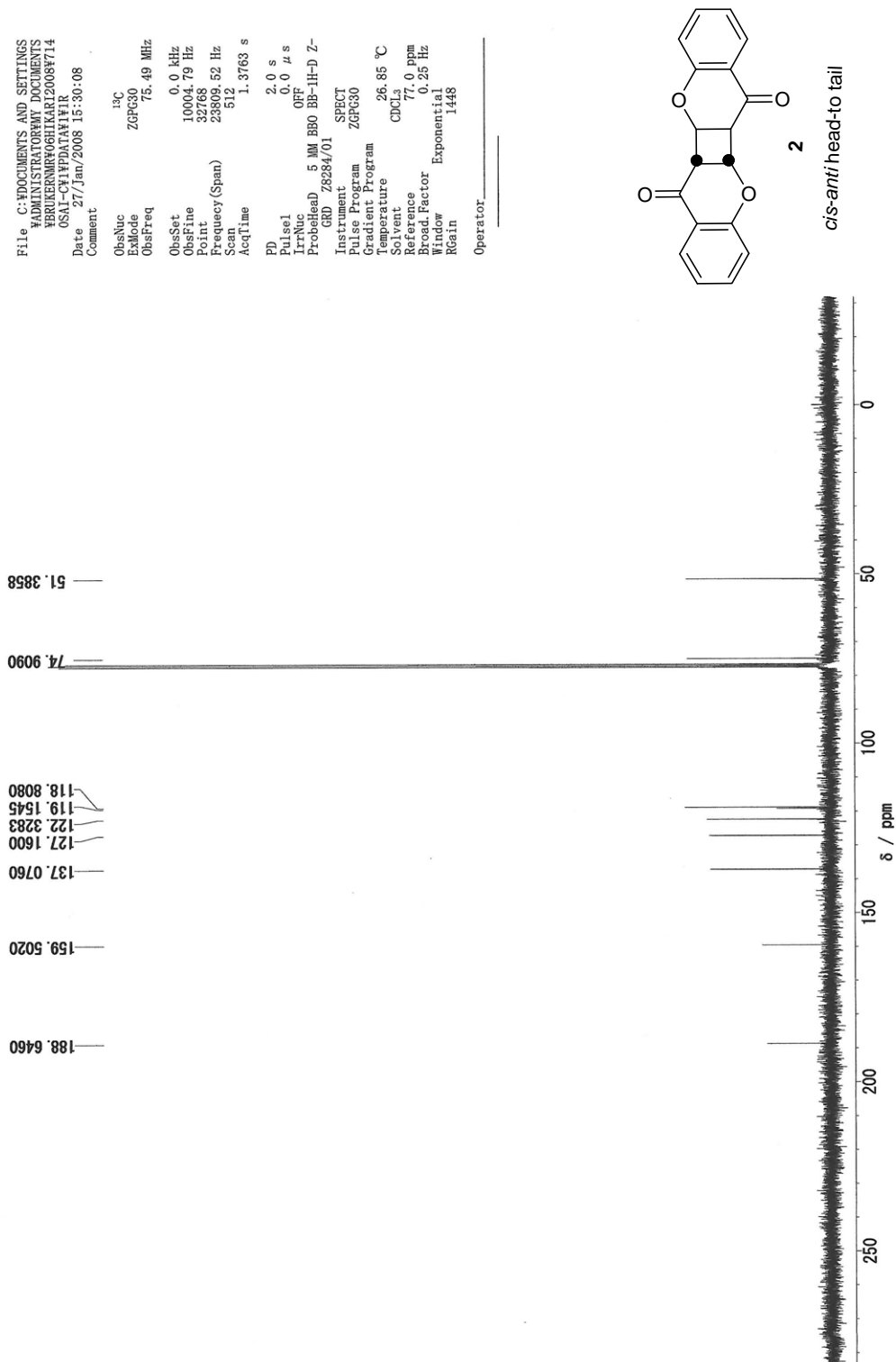


Figure S5. ¹³C NMR spectrum of *cis-cis anti* H-T dimer 2

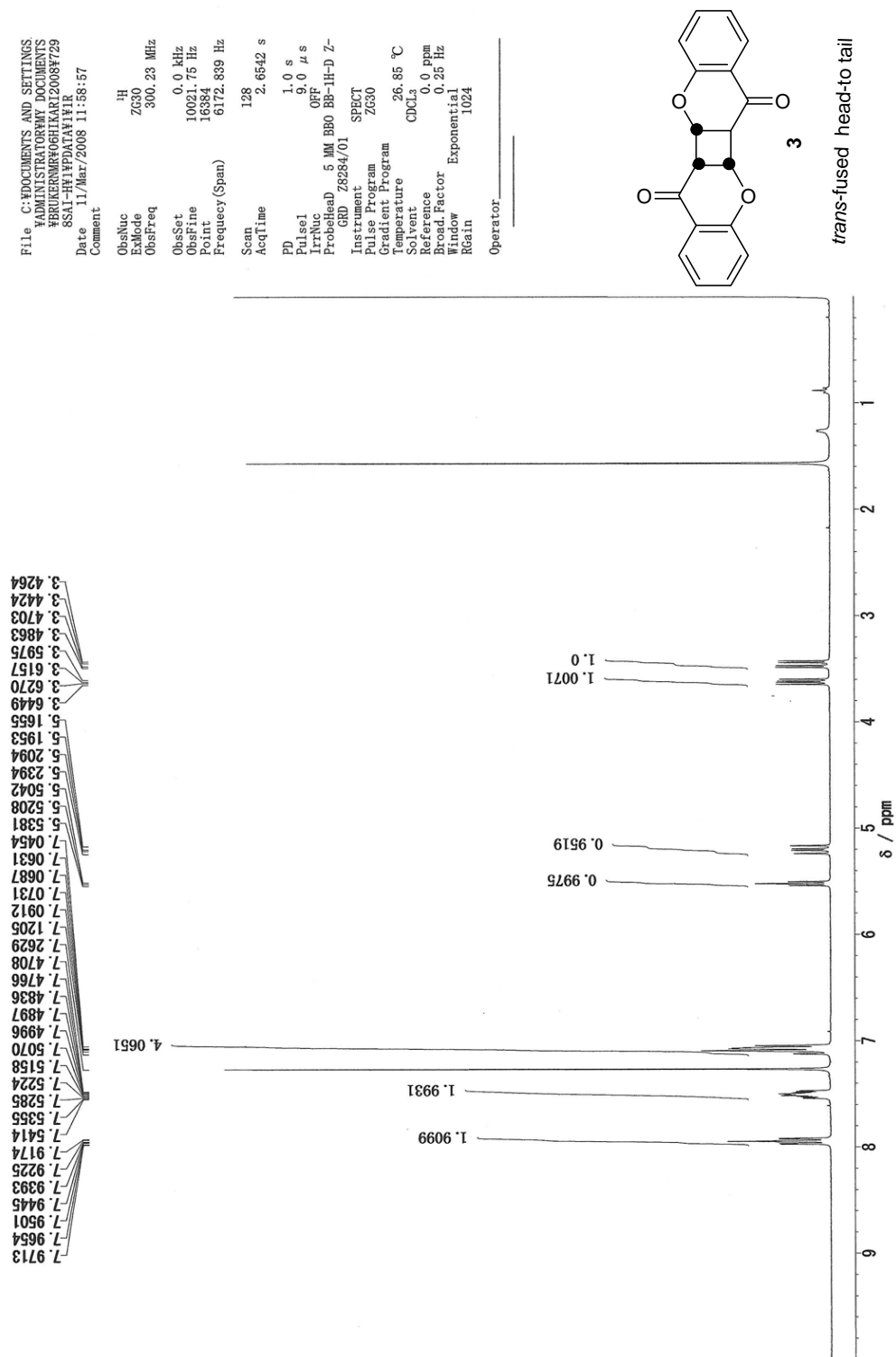


Figure S6. ¹H NMR spectrum of *trans-anti* H-T dimer **3**

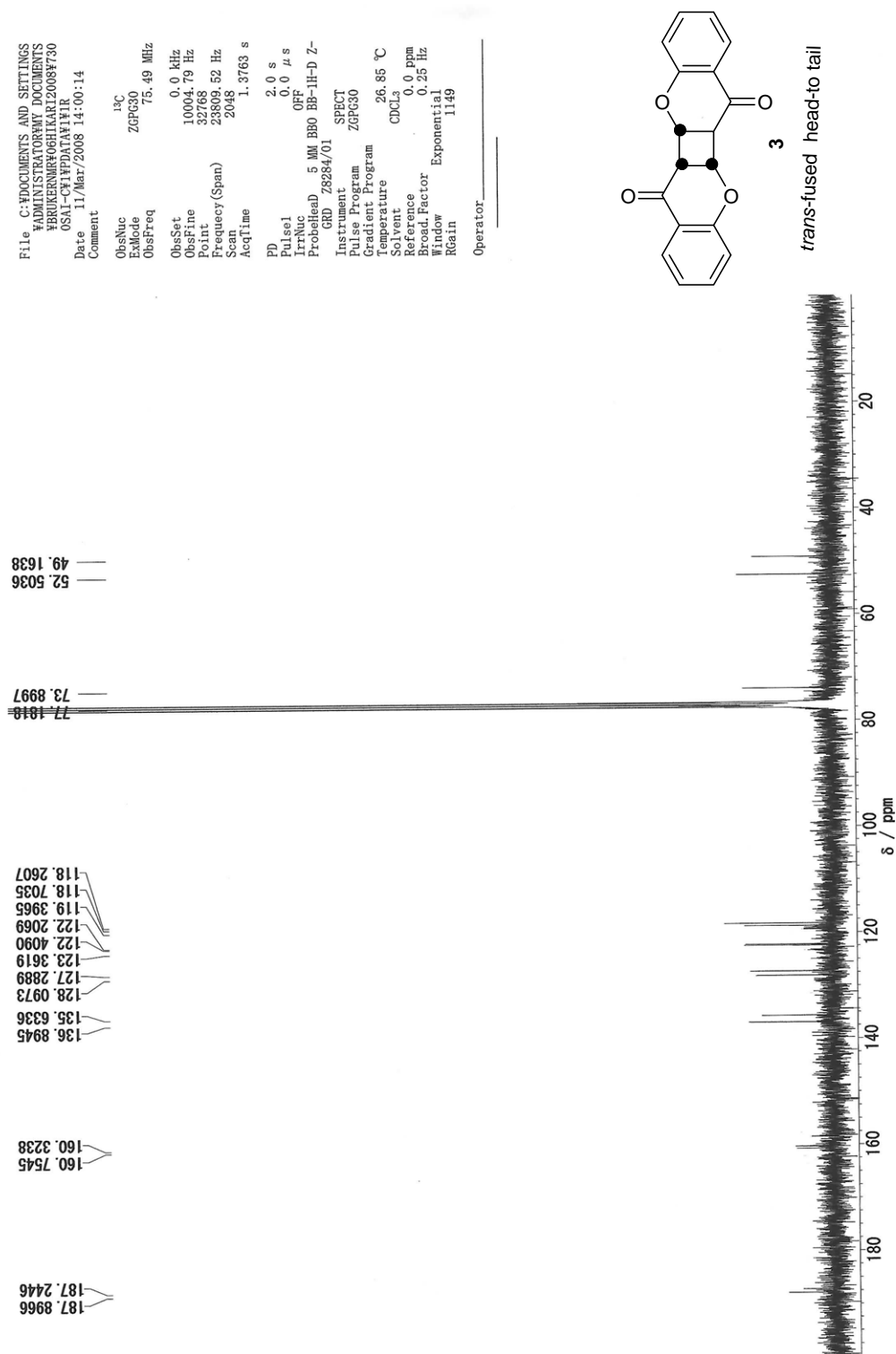


Figure S7. ¹³C NMR spectrum of *trans anti* H-T dimer **3**