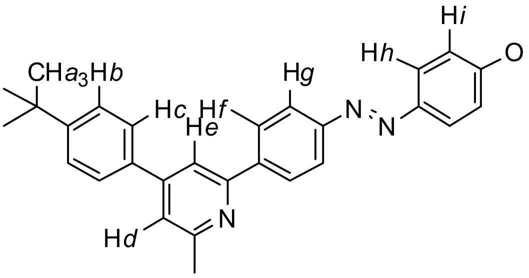
Supporting Information

Switching of Molecular Insertion in a Cyclic Molecule via Photo- and Thermal Isomerization

*Satoshi Umeki, Shoko Kume, and Hiroshi Nishihara**

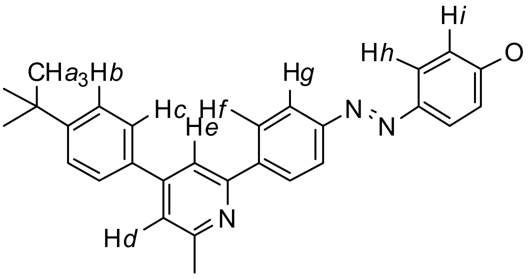
Department of Chemistry, School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Japan 113-0033

Table S1. ^{1}H NMR Data for *o*AB-2OH and *o*AB-O13 in $CDCl_3$



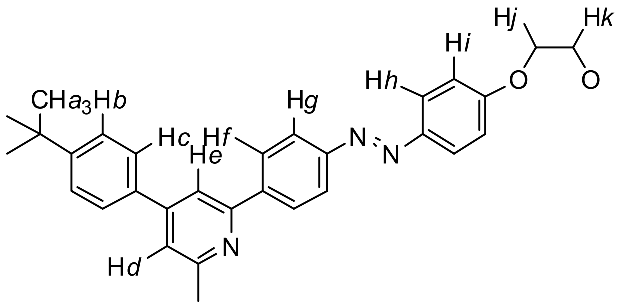
	δ(*o*AB-2OH) / ppm	δ(*o*AB-O13) / ppm	Δδ / ppm
H*a*	1.42	1.42	0.00
H*b*	7.60	7.60	0.00
H*c*	7.82	7.78	0.04
H*d*	8.90	8.21	**0.69**
H*e*	8.06	8.12	–0.06
H*f*	8.37	8.47	–0.10
H*g*	8.04	8.07	–0.03
H*h*	7.92	7.96	–0.04
H*i*	6.97	7.09	–**0.12**

Table S2. [1]H NMR Data for *o*AB-2OH and *o*AB-bpy in CD_2Cl_2



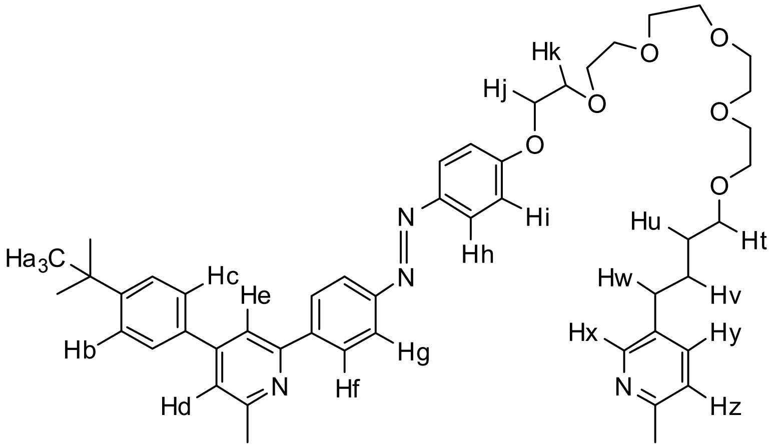
	δ(*o*AB-2OH) / ppm	δ(*o*AB-bpy) / ppm	$\Delta\delta$ / ppm
H*a*	1.42	1.42	0.00
H*b*	7.63	7.61	0.02
H*c*	7.88	7.82	0.06
H*d*	8.95	8.76	**0.19**
H*e*	8.16	8.10	0.06
H*f*	8.45	8.41	0.04
H*g*	8.06	8.04	0.02
H*h*	7.94	7.99	-0.05
H*i*	7.00	7.13	**-0.13**

Table S3. ^{1}H NMR Data for *o*AB-O13 in CD_2Cl_2



	δ(*trans*$_2$-*o*AB-O13) / ppm	δ(*cis*$_2$-*o*AB-O13) / ppm	$\Delta\delta$ / ppm
H*a*	1.41	1.40	0.01
H*b*	7.65	7.60	0.05
H*c*	7.95	7.84	0.11
H*d*	8.54	8.87	**–0.33**
H*e*	8.25	8.06	0.19
H*f*	8.42	8.23	0.19
H*g*	8.11	7.04	**1.07**
H*h*	7.99	6.99	**1.00**
H*i*	7.10	6.82	0.28
H*j*	4.29	4.07	0.22
H*k*	3.90	3.77	0.13

Table S4. [1]H NMR Data for *o*AB-bpy in CD_2Cl_2



	δ(*trans*$_2$-*o*AB-bpy) / ppm	δ(*cis*$_2$-*o*AB-bpy) / ppm	$\Delta\delta$ / ppm
H*a*	1.42	1.39	0.03
H*b*	7.61	7.57	0.04
H*c*	7.82	7.79	0.03
H*d*	8.76	8.82	**–0.06**
H*e*	8.10	8.01	0.09
H*f*	8.41	8.22	0.19
H*g*	8.04	7.01	**1.03**
H*h*	7.99	6.97	**1.02**
H*i*	7.13	6.80	0.33
H*j*	4.30	4.04	0.26
H*k*	3.97	3.74	0.23
H*t*	3.26	3.39	–0.13
H*u*	2.39	2.60	–0.21
H*v*	1.46	1.65	–0.19
H*w*	1.46	1.65	–0.19
H*x*	8.15	8.41	–0.26
H*y*	7.26	7.53	–0.27
H*z*	7.94	8.25	–0.31

Kinetic analysis of the two-step thermal isomerization behavior of cis$_2$-*o*AB-O13

$$cis_2\text{-}o\text{AB-O13} \xrightarrow{k_1} cis\text{-}trans\text{-}o\text{AB-O13} \xrightarrow{k_2} trans_2\text{-}o\text{AB-O13}$$

The ratio of each isomer is defined as follows;

$$\begin{cases} [\text{A}] = [cis_2\text{-}o\text{AB-O13}] \\ [\text{B}] = [cis\text{-}trans\text{-}o\text{AB-O13}] \\ [\text{C}] = [trans_2\text{-}o\text{AB-O13}] \end{cases}$$

$$t = 0;\ [\text{A}] = [\text{A}]_0,\ [\text{B}] = [\text{B}]_0,\ [\text{C}] = [\text{C}]_0$$

The changes of the ratio are described as follows;

$$\frac{d[\text{A}]}{dt} = -k_1[\text{A}],\ \frac{d[\text{B}]}{dt} = k_1[\text{A}]-k_2[\text{B}],\ \frac{d[\text{C}]}{dt} = k_2[\text{B}]$$

The ratio of each isomer is determined as follows;

$$\begin{cases} [\text{A}] = e^{-k_1 t} \\ [\text{B}] = k_1[\text{A}]_0(e^{-k_1 t}-e^{-k_2 t})/(k_2-k_1)+[\text{B}]_0 e^{-k_2 t} \\ [\text{C}] = [\text{A}]_0+[\text{B}]_0+[\text{C}]_0-[\text{A}]-[\text{B}] \end{cases}$$

k_1 and k_2 were calculated by the method of least squares (see Figure S1). The result is as follows;

$$k_1 = 8.0 \times 10^{-5}\ \text{s}^{-1}$$
$$k_2 = 1.3 \times 10^{-5}\ \text{s}^{-1}$$

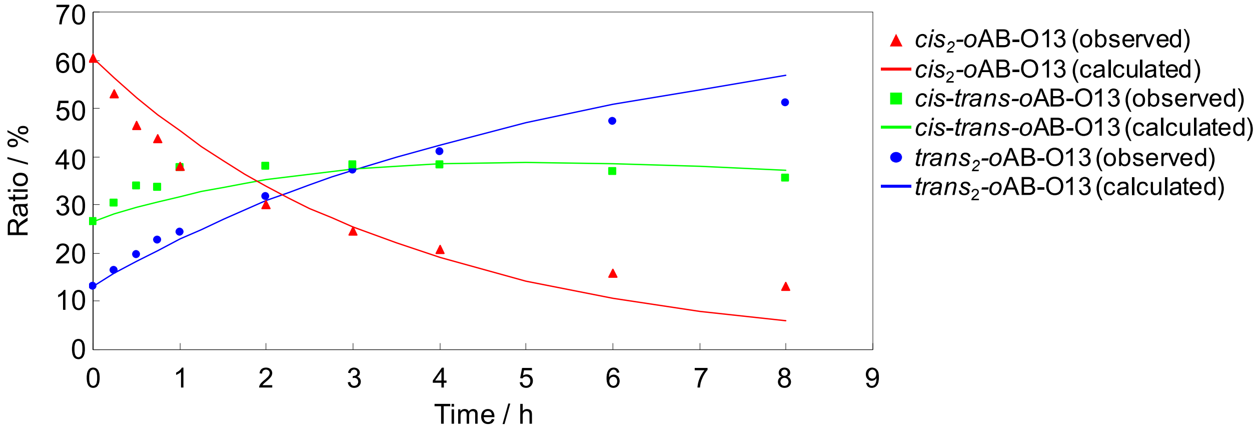


Figure S1. Ratios of *o*AB-O13 isomers obtained by the ^{1}H NMR spectral analysis (CD_2Cl_2, 1.5×10^{-3} M, 298 K in the dark).

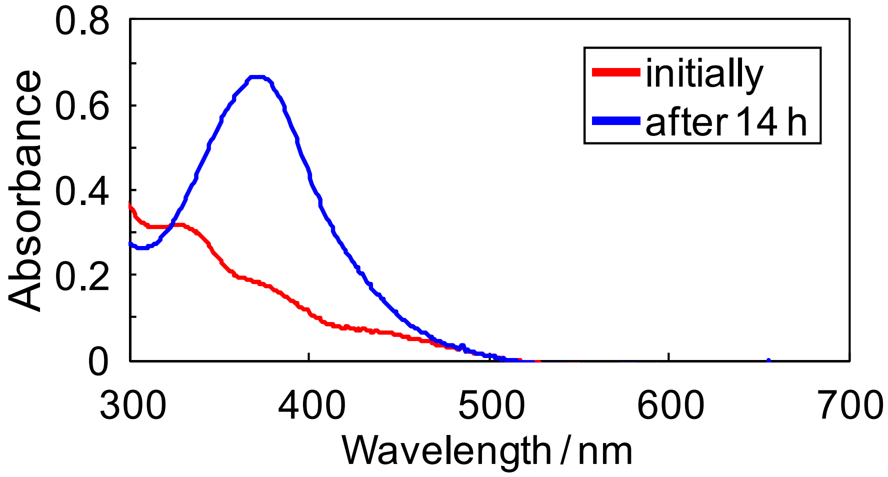


Figure S2. Absorption spectral changes of *o*AB-O13 (1.0×10^{-5} M) in CH_2Cl_2 upon the thermal *cis*-to-*trans* isomerization (298 K in the dark).

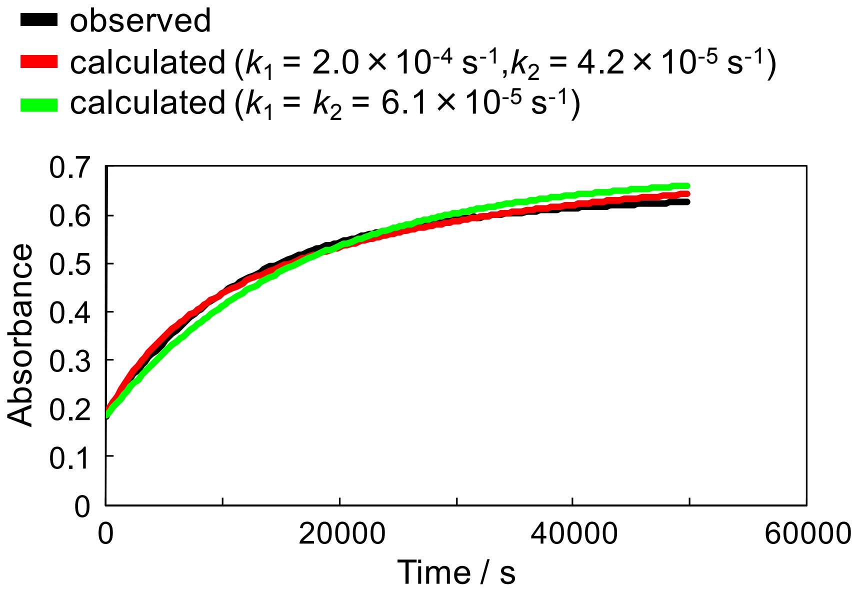


Figure S3. Plots of the absorbance at 370 nm against the time passage for *o*AB-O13 (1.0×10^{-5} M) in CH_2Cl_2 upon the thermal *cis*-to-*trans* isomerization (298 K in the dark).

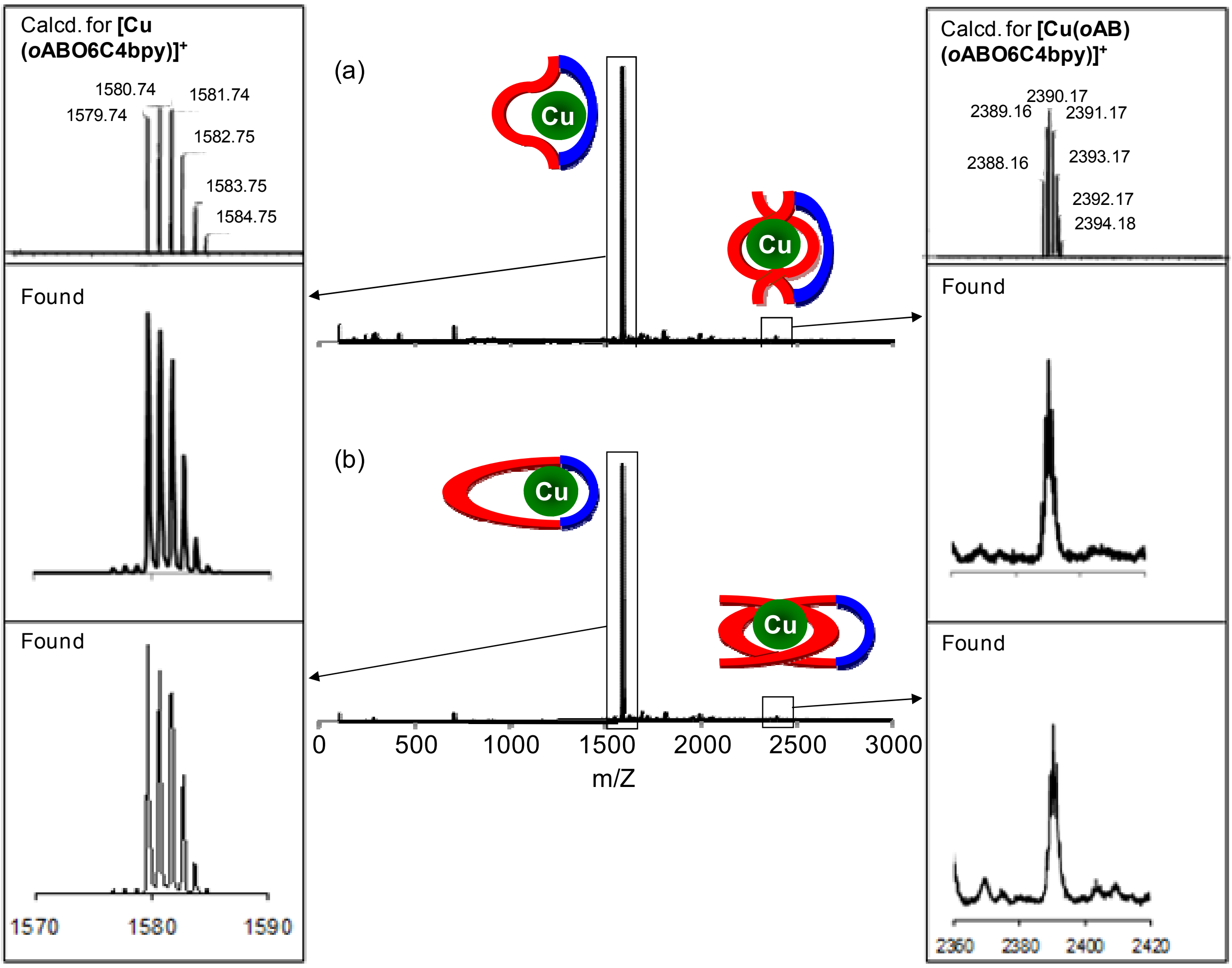


Figure S4. ESI-MS spectrum of a solution containing *o*AB-bpy, *o*AB, and $[Cu(CH_3CN)_4]BF_4$ (a) in the *cis* form and (b) in the *trans* form.