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Supporting Information

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# Peripheral Hexabromination, Hexaphenylation, and Hexaethynylation of *meso*-Aryl Substituted Subporphyrins

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## 1. Experimental Setup

**Time-Correlated Single Photon Counting.** Time-resolved fluorescence was detected using a time-correlated single photon counting (TCSPC) technique. A home-made cavity dumped Ti:Sapphire oscillator pumped by a CW Nd-YVO<sub>4</sub> laser (Coherent, Verdi) was used as the excitation light source; this provided ultrashort pulses (100 fs at full width half maximum) and allowed for a high repetition rate (200 ~ 400 kHz). The output pulse of the oscillator was frequency-doubled with a second harmonic crystal. The TCSPC detection system consisted of a multichannel plate photomultiplier (Hamamatsu, R3809U-51) with a cooler (Hamamatsu, C4878), a TAC (time-to-amplitude converter) (EG&G Ortec, 457), two discriminators (EG&G Ortec, 584 (signal) and Canberra, 2126 (trigger)), and two wideband amplifiers (Philip Scientific (signal) and a Mini Circuit (trigger)). A personal computer with a multichannel analyzer (Canberra, PCA3) was used for data storage and processing. The overall instrumental response function was about 60 ps (fwhm). A sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection system. The decay fittings were made by using a least-squares deconvolution fitting process (LIFETIME program with an iterative nonlinear least-squares deconvolution procedure developed at the University of Pennsylvania).

**Measurement of two-photon absorption cross-section ( $\sigma^{(2)}$ ).** The TPA experiments were

performed using the open-aperture Z-scan method with 120 fs pulses at a 5 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). The laser beam was divided into two parts. One was monitored by a Si photodiode (New Focus) as an intensity reference, and the other was used for the transmittance studies. After passing through an  $f=10$  cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction ( $z$ -axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell is 1 mm. The transmitted laser beam from the sample cell was then probed using the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point,  $I_0$ , ranged from 30 to 50 GW/cm. Assuming a Gaussian beam profile, the nonlinear absorption coefficient  $\beta$  can be obtained by curve fitting to the observed open aperture traces with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)}$$

where  $\alpha_0$  is the linear absorption coefficient,  $l$  the sample length, and  $z_0$  the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient  $\beta$ , the TPA cross-section  $\sigma^{(2)}$  (in units of 1 GM =  $10^{-50}$  cm<sup>4</sup> s/photon/molecule) of a single solute molecule sample can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N_A d \times 10^{-3}}{h\nu}$$

where  $N_A$  is the Avogadro constant,  $d$  the concentration of the TPA compound in solution,  $h$  is Planck's constant, and  $\nu$  is the frequency of the incident laser beam.

2.  $^1\text{H-NMR}$  spectra of subporphyrins 2, 3, 4, and 5.

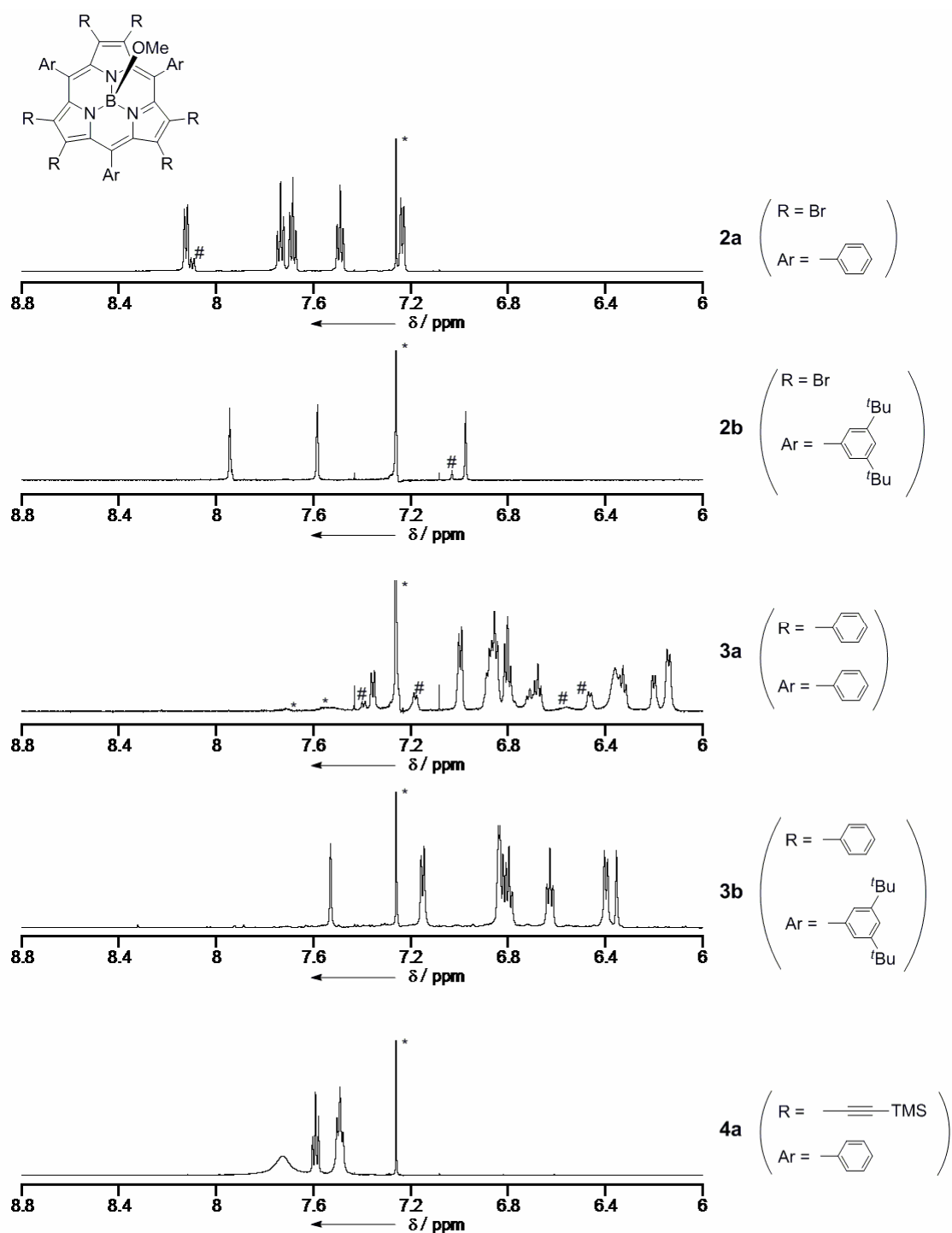


Figure S1.  $^1\text{H-NMR}$  spectra of 2a ( $-40\text{ }^\circ\text{C}$ ), 2b ( $-40\text{ }^\circ\text{C}$ ), 3a ( $-40\text{ }^\circ\text{C}$ ), 3b ( $-50\text{ }^\circ\text{C}$ ), 4a (r.t.) in  $\text{CDCl}_3$ . (\*: solvent and impurity. #: B-OH species)

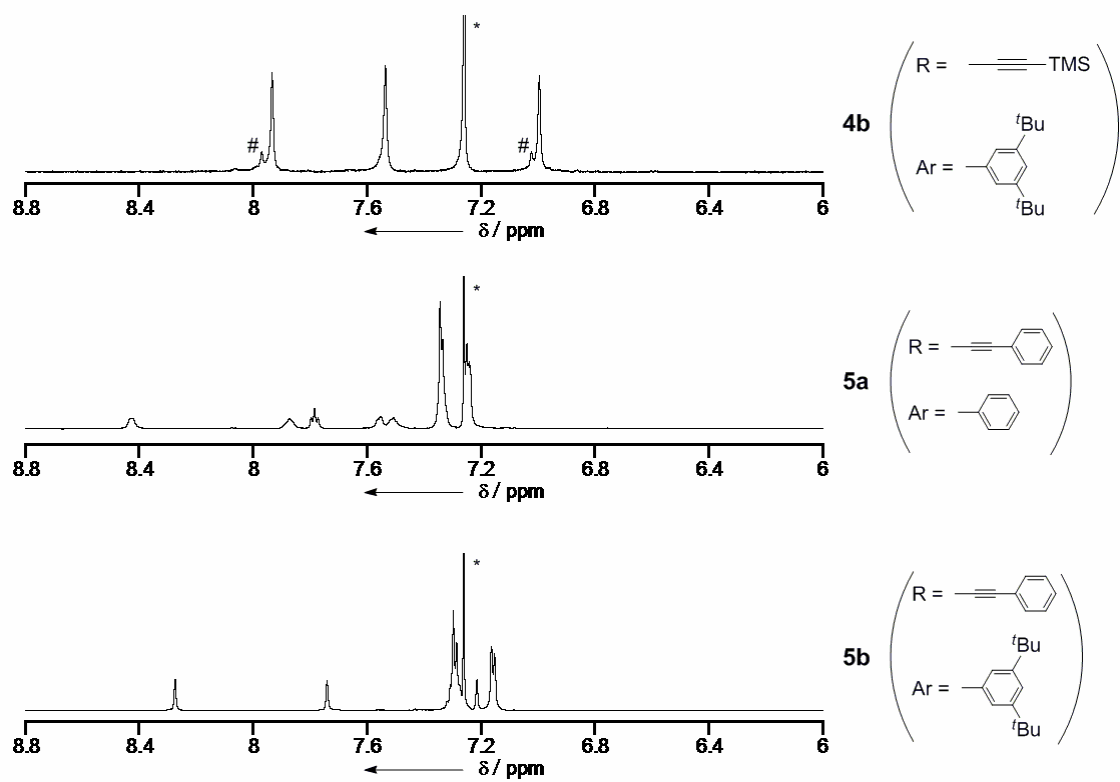


Figure S2.  $^1\text{H-NMR}$  spectra of **4b** ( $-50\text{ }^\circ\text{C}$ ), **5a** ( $-60\text{ }^\circ\text{C}$ ), **5b** ( $-60\text{ }^\circ\text{C}$ ) in  $\text{CDCl}_3$ . (\*: solvent peaks. #: B-OH species)

3. Cyclic voltammograms of 2b, 3b, 4b, and 5b.

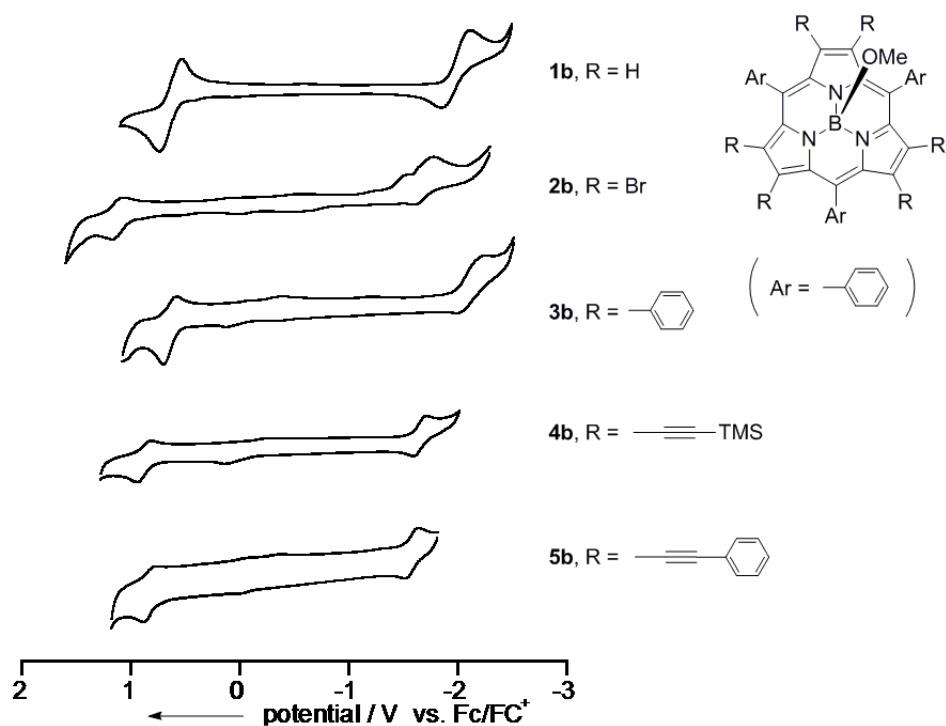


Figure S3. Cyclic voltammograms of 2b, 3b, 4b, and 5b (in V vs. ferrocene/ferrocenium cation). Measuring conditions; solvent: distilled CH<sub>2</sub>Cl<sub>2</sub>, supporting electrolyte: 0.10 M tetrabutylammonium hexafluorophosphate, working electrode: glassy carbon rod, counter electrode: platinum wire, reference electrode: Ag/0.01 M AgClO<sub>4</sub>.

#### 4. Absorption and fluorescence spectra of 2, 3, 4, and 5.

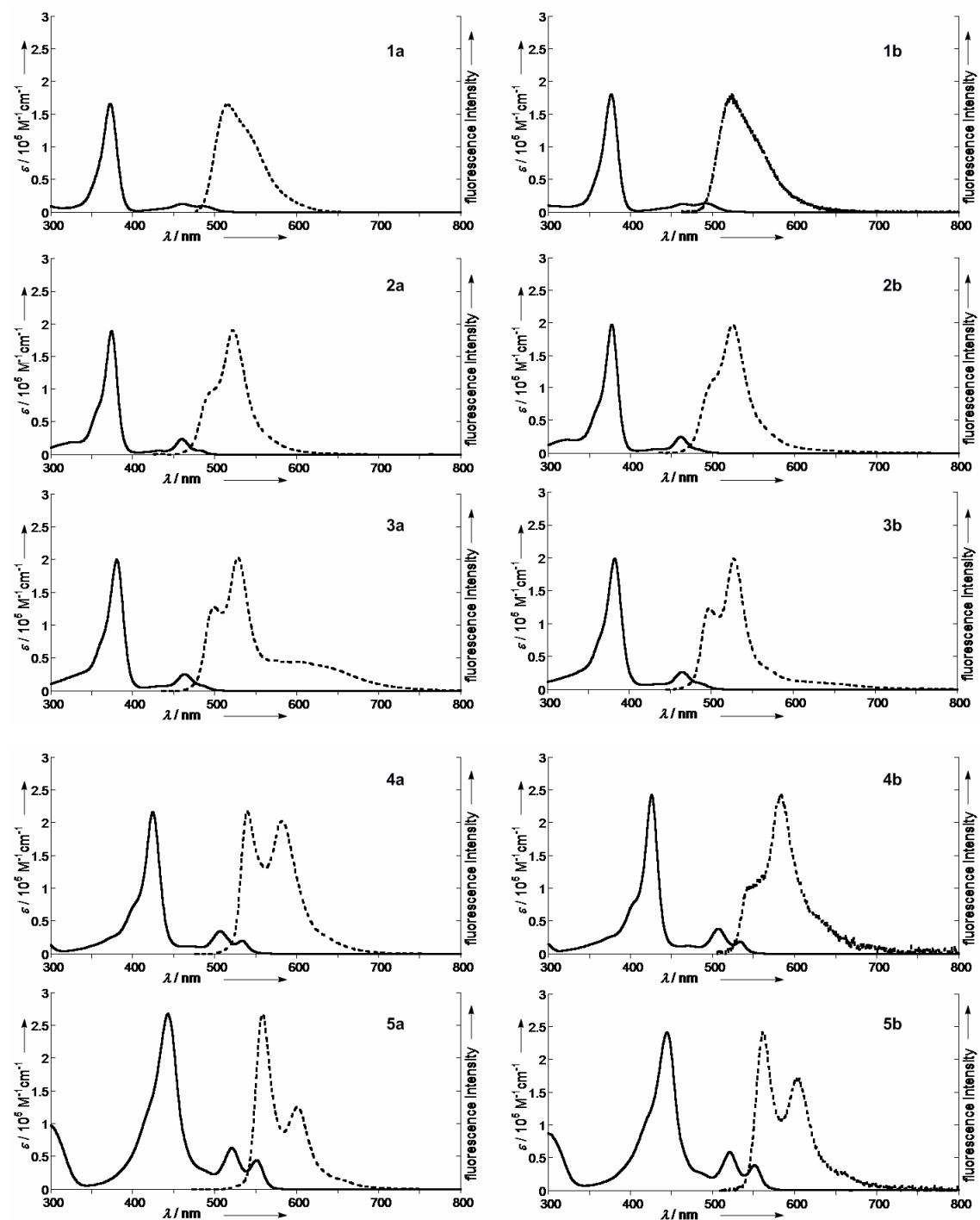


Figure S4. Absorption and fluorescence spectra of 2, 3, 4, and 5 in  $\text{CH}_2\text{Cl}_2$ . (excited at the Soret-like band)

5. Fluorescence excitation spectrum of 3a.

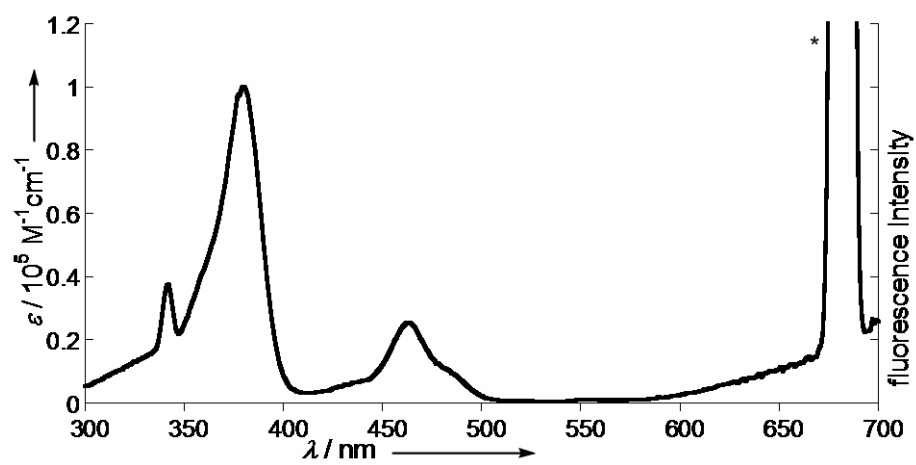


Figure S5. Fluorescence excitation spectrum of 3a in  $\text{CH}_2\text{Cl}_2$  monitored at 680 nm. (\*: monitoring wavelength)

6. Fluorescence decay profiles.

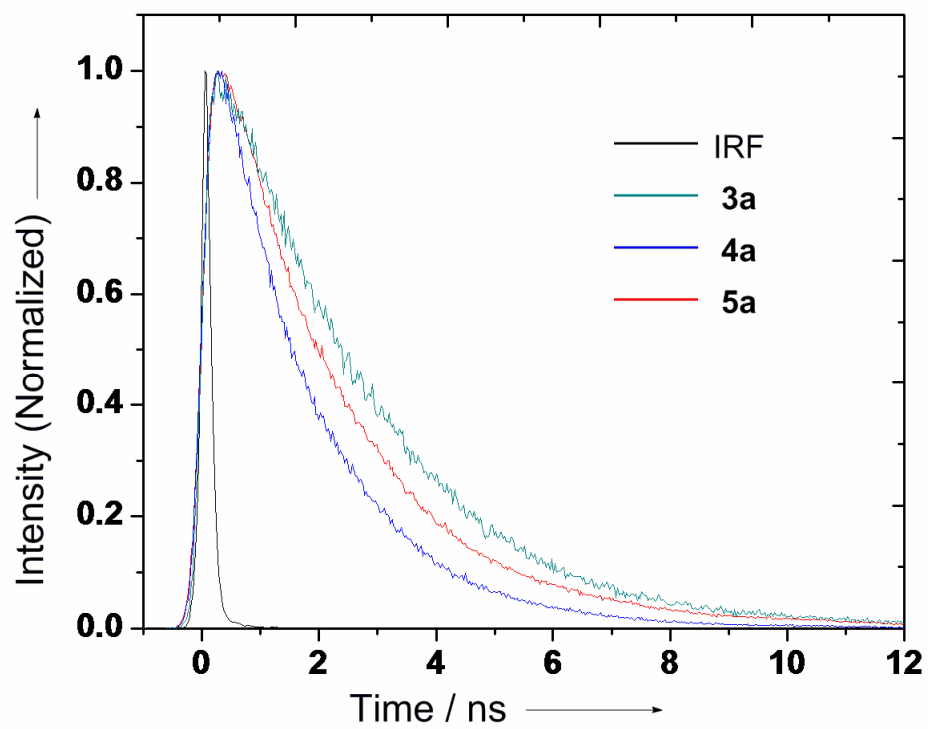


Figure S6. Fluorescence decay profiles of 3a, 4a, and 5a.

## 7. Estimation of activation energy of rotation of *meso*-aryl substituents.

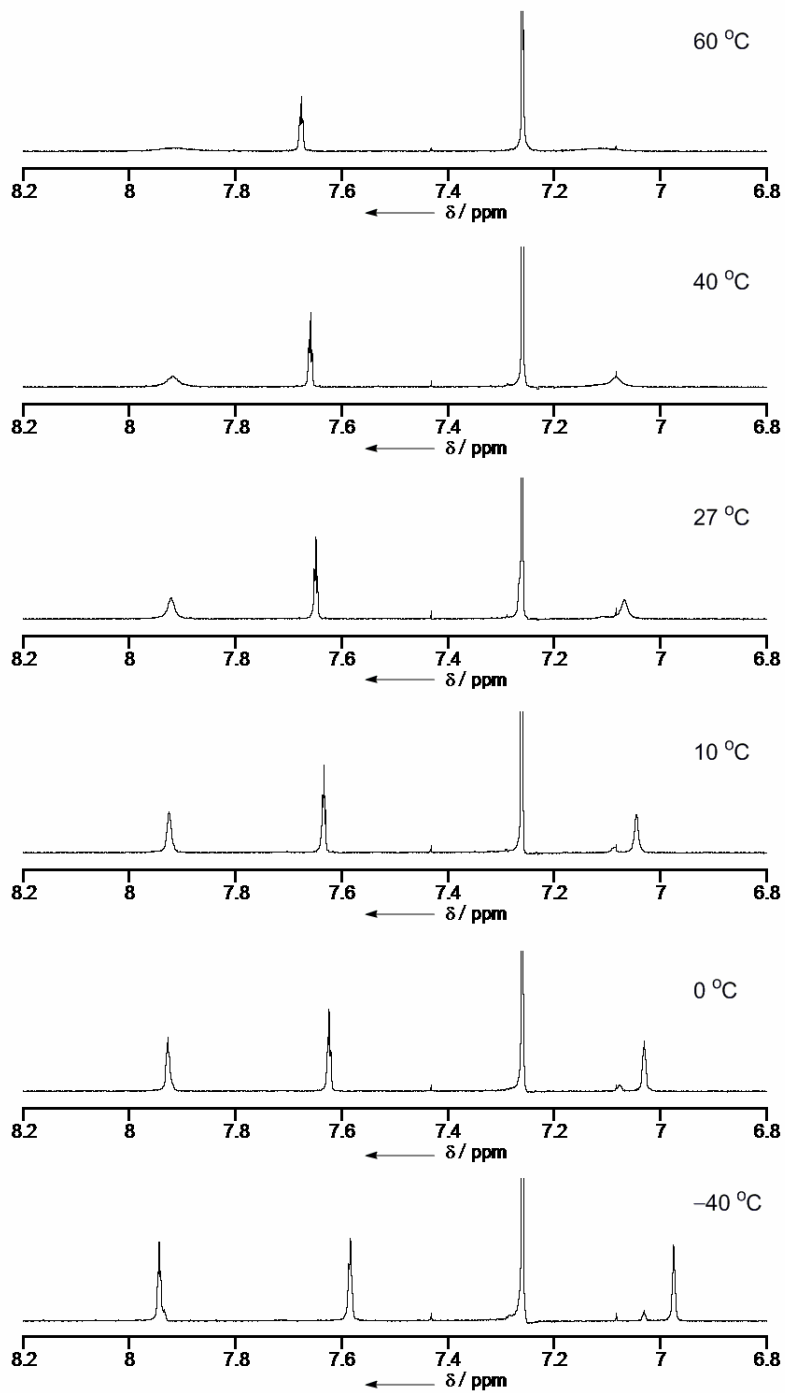


Figure S7. Variable temperature <sup>1</sup>H-NMR spectra of **2b** in CDCl<sub>3</sub>. In the <sup>1</sup>H-NMR analyses of **3b**, **4b**, and **5b**, similar peak-broadenings were observed.

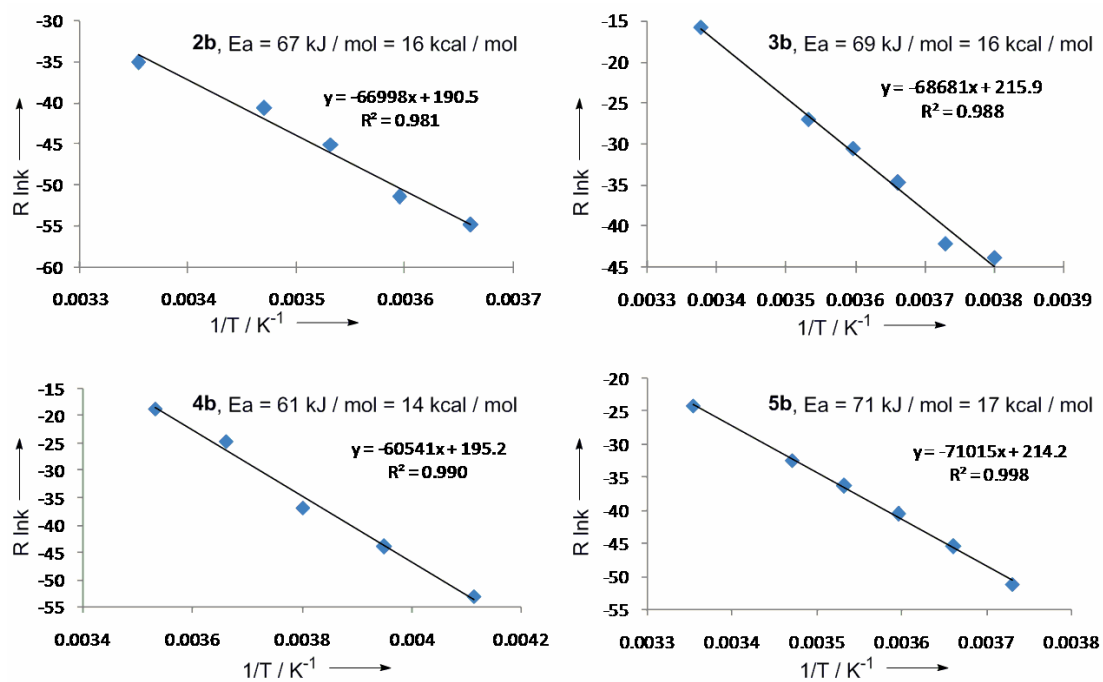


Figure S8. Arrhenius plots of rotational rates of **2b**, **3b**, **4b**, and **5b**. Activation energies were estimated from the respective slopes on the basis of Arrhenius equation ( $k = A \exp(-E_a/RT)$ , where  $k$  is the rate of exchange,  $A$  is the constant number,  $E_a$  is the activation energy,  $R$  is gas constant,  $T$  is measuring temperature.).

## 8. Reference.

### *Full Citation of Reference 19*

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