

Supporting Information

Neutral Metallacyclic Rotors

Malaichamy Sathiyendiran,^a Jing-Yun Wu,^a Murugesan Velayudham,^a Gene-Hsiang Lee,^b
Shie-Ming Peng^b and Kuang-Lieh Lu*^a

^a*Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan and* ^b*Department of Chemistry,
National Taiwan University, Taipei 107, Taiwan.*

Contents

Experimental Section

Table S1 Crystallographic data for **1a**, **1a**·0.5C₇H₈, **1b**, and **2b**·C₃H₆O

Fig. S1 (i) The benzene rings (ABC) are closely located with the center-to-center distances (r_{AB} , r_{BC} , r_{CA}), 5.0307(1), 5.127(1), and 4.5023(2) Å, respectively. The dihedral angles among three phenyl groups (A–B, B–C, C–A) are 82.733(1), 52.860(5), and 45.490(5)°, respectively. (ii) Side-view of the metallacycle with solvent toluene molecule showing the “distorted benzene trimer”.

Fig. S2 Side-view of molecular rotor **1a** measured at 150(1) K. Half-length of the dhng (5.69 Å) is longer than the width of the rope (5.45 Å).

Fig. S3 Ball and stick representations of **1a** measured at 295(2) K showing the two possible orientations of the benzobis unit (50% occupancy). Hydrogen atoms are removed for clarity.

Fig. S4 Labeled ORTEP diagram of **1b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Fig. S5 Labeled ORTEP diagram of **2b**. Hydrogen atoms and noncoordinating solvent molecules are omitted for clarity. Thermal ellipsoids are shown at 35% probability.

Fig. S6 ¹H NMR spectra of free benzobis (bottom) and rotor **1a** (top) in DMSO-*d*₆.

Fig. S7 Variable-temperature ¹H NMR experiments (bottom-to-top: 298, 328, 348, and 378 K) run with **1a** in DMSO-*d*₆.

Fig. S8 Variable-temperature ¹H NMR experiments (bottom-to-top: 298, 223, 173, 168, and 166 K) run with **1b** in THF-*d*₈.

Table S2 Dynamic ¹H NMR data for **1a** in acetone-*d*₆.

Experimental Section

General experimental methods. All starting materials and products were found to be stable in moisture and air. Starting materials such as $\text{Re}_2(\text{CO})_{10}$, 6,11-dihydroxy-5,12-naphthacenedione ($\text{H}_2\text{-dhnq}$), and 1,4-dihydroxy-9,10-anthraquinone ($\text{H}_2\text{-dhaq}$), were purchased from commercial sources and used as received. The ligands α,α' -bis(benzimidazol-1-yl)-*p*-xylene (benzbix), and α,α' -bis(imidazol-1-yl)-*p*-xylene (bix) can be easily prepared, by a similar procedure to that reported earlier, by the replacement reactions of 1,4-bis(bromomethyl)-benzene with the imidazole.^{S1} Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Infrared spectrum was recorded on a Perkin-Elmer FT-IR Spectrometer PARAGON 1000. ^1H NMR spectra were recorded on Bruker AMX-400 and AV-400 FT-NMR spectrometers. FAB-MS data were obtained using a JEOL, JMS-700 double focusing mass spectrometer.

Synthesis of $[(\text{Re}(\text{CO})_3)_2(\text{dhaq})(\text{benzbix})]$ (2a**).** Dark-green crystals of **2a** were obtained by following the similar procedure for **1a**, using $\text{Re}_2(\text{CO})_{10}$ (218 mg, 0.33 mmol), benzbix (112 mg, 0.33 mmol) and $\text{H}_2\text{-dhaq}$ (82 mg, 0.34 mmol) in toluene (16 mL). Yield: 86% (0.344). Anal. Calcd for $\text{C}_{42}\text{H}_{24}\text{N}_4\text{O}_{10}\text{Re}_2\cdot(\text{C}_7\text{H}_8)$: C, 48.67; H, 2.67; N, 4.63. Found: C, 48.0; H, 2.71; N, 4.73. IR (CH_3COCH_3 , cm^{-1}): 2011 ($\text{C}\equiv\text{O}$), 1907 ($\text{C}\equiv\text{O}$), 1888 ($\text{C}\equiv\text{O}$). MS-FAB (m/z): 1118.1 [M^+]. ^1H NMR ($\text{DMSO-}d_6$, δ): isomer I (66%): 8.93 (s, 2H, H^2 , benzbix), 8.28 (m, 2H, H^5 , dhaq), 7.87 (d, $J = 8.16$ Hz, 2H, H^4 , benzbix), 7.79 (m, 2H, H^6 , dhaq), 7.65 (d, $J = 8.10$ Hz, 2H, H^7 , benzbix), 7.22 (m, 6H, $\text{H}^{5,6}$, benzbix; H^2 , dhaq; 5H, toluene), 6.82 (s, 4H, H^9 , benzbix), 5.43 (m, 4H, H^8 , benzbix), and 2.29 (s, 3H, CH_3 , toluene); isomer II (34%): 8.77 (s, 2H, H^2 , benzbix), 8.40 (m, 2H, H^5 , dhaq), 7.89 (d, $J = 8.16$ Hz, 2H, H^4 , benzbix), 7.79 (m, 2H, H^6 , dhaq), 7.65 (d, $J = 8.10$ Hz, 2H, H^7 , benzbix), 7.22 (m, 6H, $\text{H}^{5,6}$, benzbix; H^2 , dhaq), 6.62 (s, 4H, H^9 , benzbix), and 5.43 (m, 4H, H^8 , benzbix).

Synthesis of [(Re(CO)₃)₂(dhaq)(bix)] (2b). Dark-green crystals of **2b** were obtained by following the similar procedure for **2a**, using Re₂(CO)₁₀ (147 mg, 0.23 mmol), bix (57 mg, 0.23 mmol) and H₂-dhaq (53 mg, 0.21 mmol) in toluene (16 mL). Yield: 85% (219 mg). Anal. Calcd for C₃₄H₂₀N₄O₁₀Re₂: C, 40.16; H, 1.98; N, 5.51. Found: C, 40.34; H, 2.19; N, 5.40. MS-FAB (*m/z*): 1018.31 [M⁺]. IR (CH₃COCH₃, cm⁻¹): 2011 (C≡O), 1905 (C=O), 1888 (C=O). ¹H NMR (DMSO-*d*₆, δ): isomer I (66%): 8.35 (m, 2H, H⁵, dhaq), 8.12 (t, *J* = 1.27 Hz, 2H, H², bix), 7.79 (m, 2H, H⁶, dhaq), 7.21 (t, *J* = 1.47 Hz, 2H, H⁴, bix), 7.14 (s, 2H, H², dhaq), 6.95 (t, *J* = 1.39 Hz, 2H, H⁵, bix), 6.81 (s, 4H, H⁷, bix), and 5.11 (m, 4H, CH₂, bix); isomer II (34%): 8.35 (m, 2H, H⁵, dhaq), 8.26 (t, *J* = 1.27 Hz, 2H, H², bix), 7.90 (m, 2H, H⁶, dhaq), 7.14 (s, 2H, H², dhaq), 7.12 (t, *J* = 1.47 Hz, 2H, H⁴, bix), 6.89 (t, *J* = 1.39 Hz, 2H, H⁵, bix), 6.69 (s, 4H, H⁸, bix), and 5.09 (m, 4H, CH₂, bix).

Crystallographic Determination. Suitable single crystal of **1a** with dimensions of 0.28 × 0.15 × 0.15 mm was selected for indexing and the collection of intensity data. Measurements were performed using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer. Intensity data were collected at 295(2) K within the limits 1.58° < θ < 27.50°. Solvated crystal of **1a**·0.5C₇H₈ with dimensions of 0.30 × 0.30 × 0.22 mm suitable for single-crystal diffraction data collection was performed at 150(1) K within the limits 1.34° < θ < 27.50° by using a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). For **1b** and **2b**·C₃H₆O, suitable single crystals with dimensions of 0.35 × 0.35 × 0.20 mm, and 0.16 × 0.12 × 0.08 mm, respectively, were selected for indexing and the collection of intensity data. Measurements were performed using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer. Intensity data were collected at 150(1) K within the limits 1.71° < θ <

27.50° for **1b** and $1.34^\circ < \theta < 27.50^\circ$ for **2b**·C₃H₆O. Starting models for structure refinement were found using direct methods and the structural data were refined by full-matrix least-squares methods on F^2 using the SHELX-97 program packages.^{S2} The lower symmetric space groups of $Pna2_1$ and $P2_1/m$ have been tried to solve the structure of **1a**. However, the former structural model ($Pna2_1$) remains disordered (nearly the same as that in the space group $Pnma$). The latter model ($P2_1/m$) has double asymmetric units than the former two models in the space groups of $Pnma$ and $Pna2_1$, respectively, and contains several unrealistic bond distances and bond angles. Furthermore, even the twin refinement was tried, the problems still appear. Thus, these low symmetric space groups are not appropriately used in this structure and the space group $Pnma$ is the best solution. After carefully checking the peaks from the D-maps, the two-sided disordered benzbix ligand is apparent. The disordered benzbix molecule has been successfully modeled using the PART 1 (N1, C13, N2, C14-C19) and PART 2 (N1A, C13A, N2A, C14A-C19A) instructions. After refining as a free variable, the site-of-occupancy is almost 50%. The non-hydrogen atoms of the benzbix molecule have been constrained or restrained with appropriate instructions such as AFIX59 (N1, C13, N2, C14, C19 in PART 1, and N1A, C13A, N2A, C14A, C19A in PART 2), AFIX 66 (C14-C19 in PART 1 and C14A-C19A in PART2), DELU, and SIMU. After final refinements, the geometry of the ligand is obviously realistic. All non-hydrogen atoms were refined anisotropically. Because the crystal structure has been modeled properly, the R factors have been decreased and the final refinement converged very well. In **2b**·C₃H₆O, the acetone molecule in the asymmetric unit is disordered over two positions with site-of-occupancy of 0.35 and 0.15, respectively. All non-hydrogen atoms in the else three crystals (**1a**·0.5C₇H₈, **1b**, and **2b**·C₃H₆O) were located from the difference Fourier maps and refined anisotropically, except that the toluene molecule in **1a**·0.5C₇H₈ and the disordered

acetone molecule in **2b**·C₃H₆O, which were refined isotropically. The C–H hydrogen atoms were assigned by geometrical calculation and refined as riding model. Details of the structure determinations are given in Table S1.

References

- (S1) B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 1997, **119**, 2952.
(S2) G. M. Sheldrick, *SHELX-97* (including *SHELXS* and *SHELXL*); University of Göttingen: Göttingen, Germany, 1997.

Table S1. Crystallographic data for **1a**, **1a**·0.5C₇H₈, **1b**, and **2b**·C₃H₆O

	1a	1a ·0.5C ₇ H ₈	1b	2b ·C ₃ H ₆ O
empirical formula	C ₄₆ H ₂₆ N ₄ O ₁₀ Re ₂	C _{49.50} H ₃₀ N ₄ O ₁₀ Re ₂	C ₃₈ H ₂₂ N ₄ O ₁₀ Re ₂	C ₃₇ H ₂₆ N ₄ O ₁₁ Re ₂
<i>M_w</i>	1167.11	1213.17	1067.00	1075.02
crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	<i>Pnma</i>	<i>P2₁/n</i>	<i>Cmca</i>	<i>C2/m</i>
<i>a</i> (Å)	12.7711(2)	9.9194(3)	23.8693(6)	22.3424(8)
<i>b</i> (Å)	19.6190(3)	21.3024(8)	25.9927(7)	20.9297(7)
<i>c</i> (Å)	17.1168(3)	21.7617(8)	10.8655(3)	7.9283(3)
<i>α</i> (deg)	90	90	90	90
<i>β</i> (deg)	90	96.463(1)	90	98.913(1)
<i>γ</i> (deg)	90	90	90	90
<i>V</i> (Å ³)	4288.72(12)	4569.2(3)	6741.3(3)	3662.7(2)
<i>Z</i>	4	4	8	4
<i>T</i> (K)	295(2)	150(1)	150(1)	150(1)
<i>λ</i> (Å)	0.71073	0.71073	0.71073	0.71073
<i>D_{calc}</i> (g cm ⁻³)	1.808	1.764	2.103	1.982
<i>μ</i> (mm ⁻¹)	5.703	5.357	7.245	6.674
<i>F</i> ₀₀₀	2240	2340	4064	2096
GOF	1.159	1.197	1.111	1.189
<i>R</i> ₁ ^{<i>a</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0669	0.0313	0.0222	0.0460
w <i>R</i> ₂ ^{<i>b</i>} (<i>I</i> > 2σ(<i>I</i>))	0.1338	0.0826	0.0451	0.1081
<i>R</i> ₁ ^{<i>a</i>} (all data)	0.0896	0.0369	0.0260	0.0627
w <i>R</i> ₂ ^{<i>b</i>} (all data)	0.1431	0.0886	0.0464	0.1224
Δρ _{max} /Δρ _{min} (e Å ⁻³)	1.297/−2.474	1.427/ −0.806	1.197/ −0.599	1.749/−1.264

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\| \cdot ^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

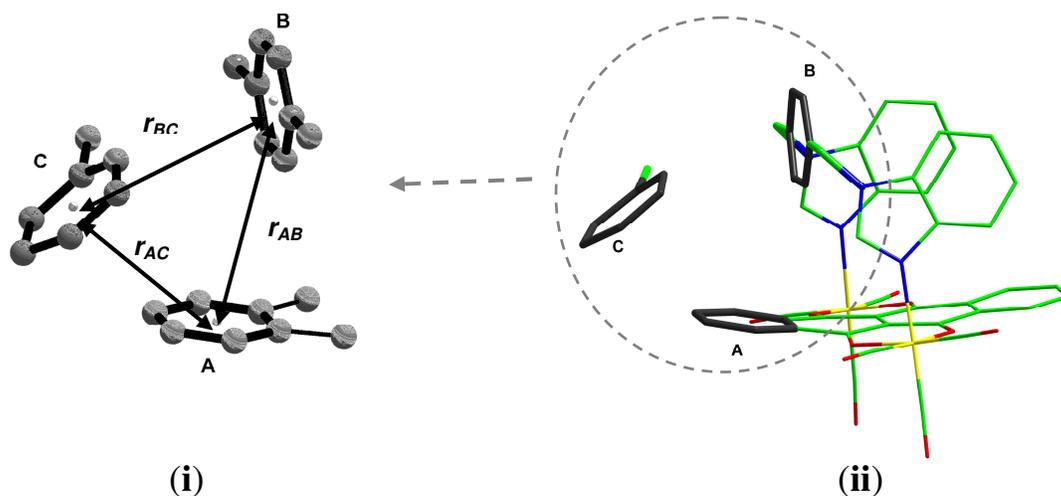


Fig. S1. (i) The benzene rings (ABC) are closely located with the center-to-center distances (r_{AB} , r_{BC} , r_{CA}), 5.0307(1), 5.127(1), and 4.5023(2) Å, respectively. The dihedral angles among three phenyl groups (A–B, B–C, C–A) are 82.733(1), 52.860(5), and 45.490(5)°, respectively. (ii) Side-view of the metallacycle with solvent toluene molecule showing the “distorted benzene trimer”.

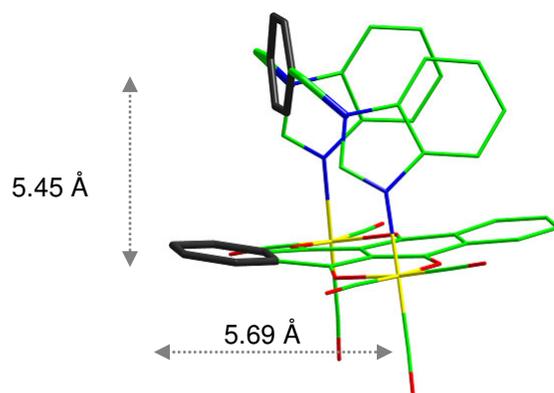


Fig. S2. Side-view of molecular rotor **1a** measured at 150(1) K. Half-length of the dhnq (5.69 Å) is longer than the width of the rope (5.45 Å).

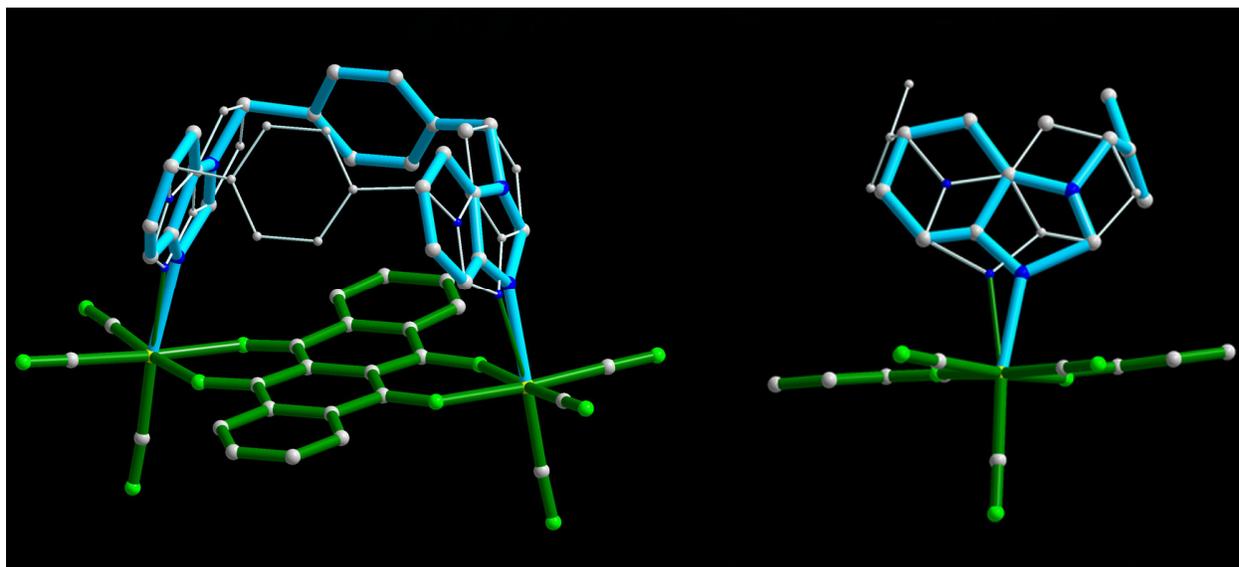


Fig. S3. Ball and stick representations of **1a** measured at 295(2) K showing the two possible orientations of the benzbix unit (50% occupancy). Hydrogen atoms are removed for clarity.

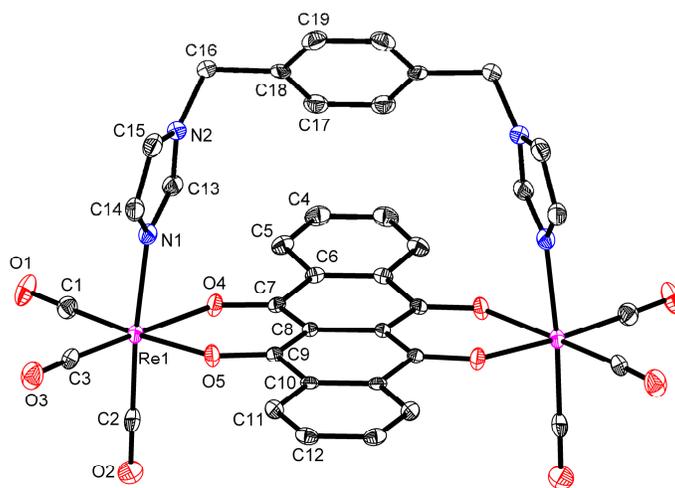


Fig. S4. Labeled ORTEP diagram of **1b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

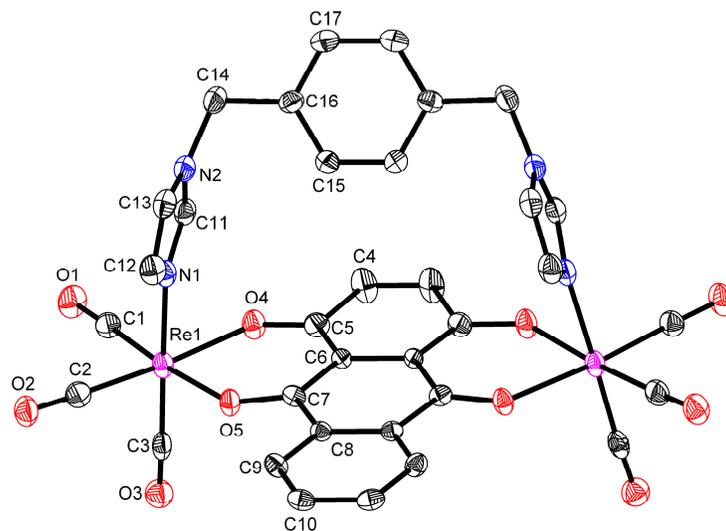


Fig. S5. Labeled ORTEP diagram of **2b**. Hydrogen atoms and noncoordinating solvent molecules are omitted for clarity. Thermal ellipsoids are shown at 35% probability.

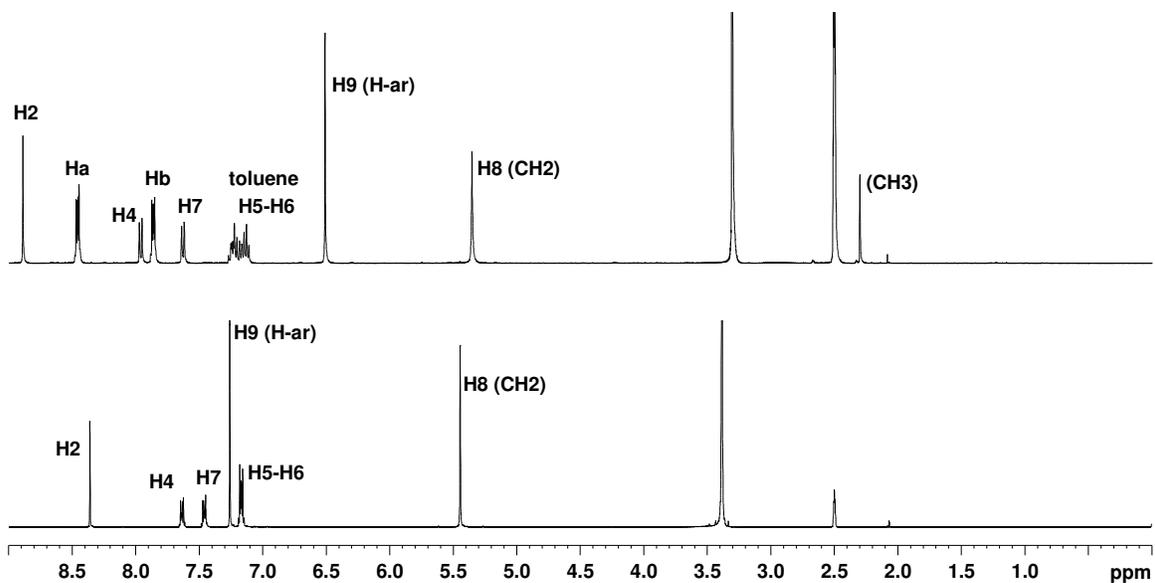


Fig. S6. ^1H NMR spectra of free benzbix (bottom) and rotor **1a** (top) in $\text{DMSO-}d_6$.

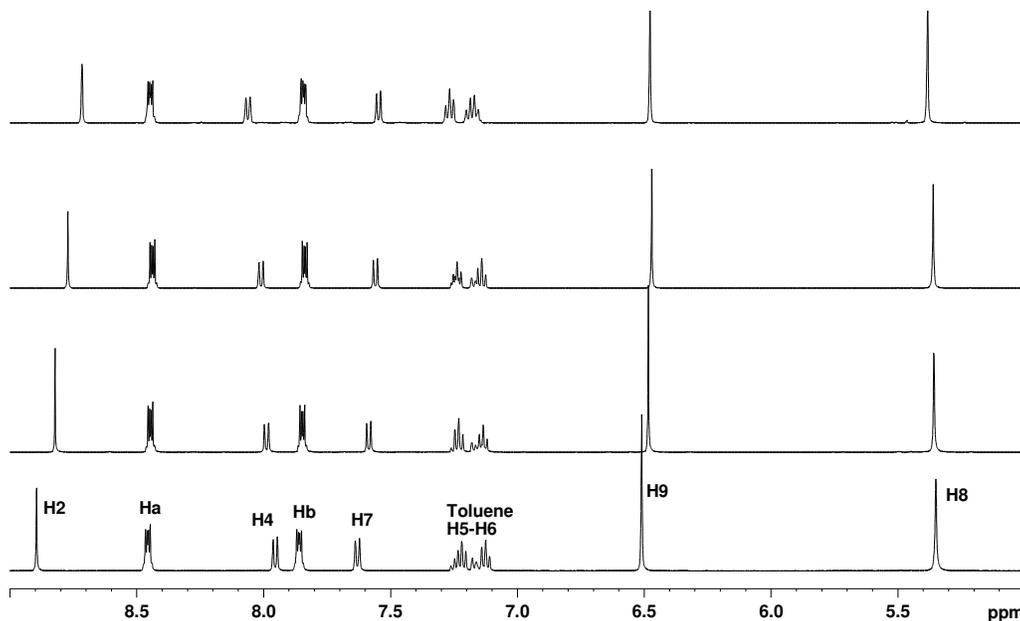


Fig. S7. Variable-temperature ^1H NMR experiments (bottom-to-top: 298, 328, 348, and 378 K) run with **1a** in $\text{DMSO-}d_6$.

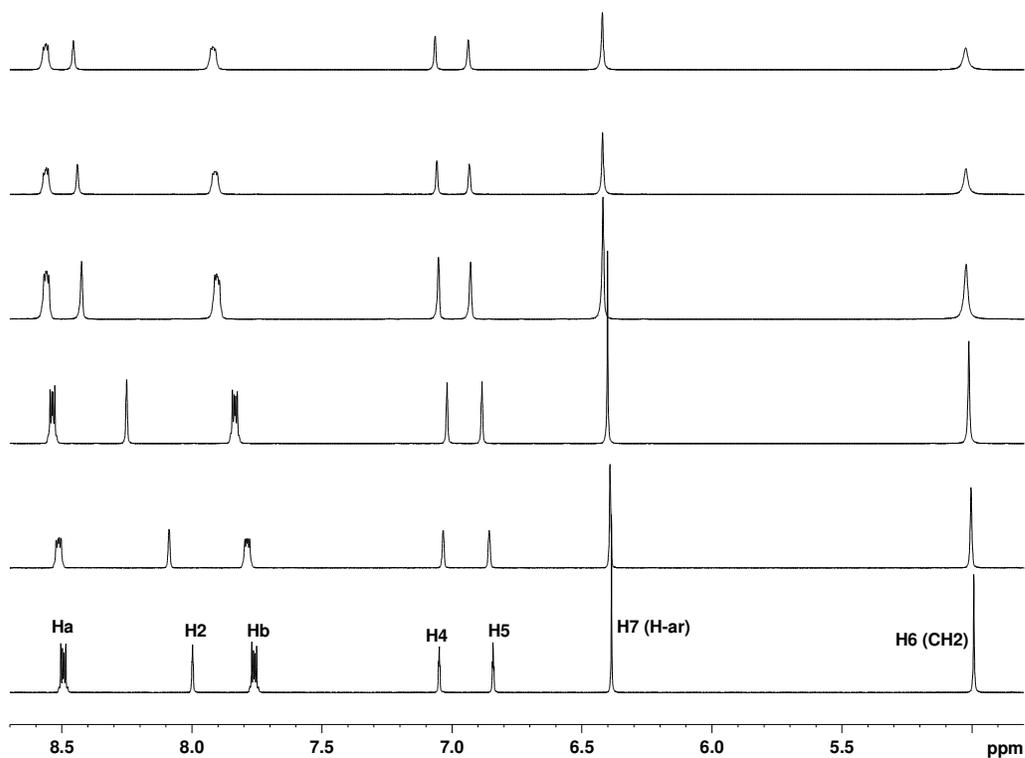


Fig. S8. Variable-temperature ^1H NMR experiments (bottom-to-top: 298, 223, 173, 168, and 166 K) run with **1b** in $\text{THF-}d_8$.

Table S2. Dynamic ^1H NMR data for **1a** in acetone- d_6 .

Proton	δ (ppm)	$\Delta\nu$ (Hz)	T_c , (K)	k (s^{-1}) ^[a]	ΔG^\ddagger (kcal mol^{-1}) ^[b]
H ⁹	6.825, 6.794	12.4	208	27.5	13.7 (14.5) ^[c]

^[a]The rate constant, k_c , for **1a** at the coalescence temperature (T_c) of 208 K was evaluated from Gutowsky–Holm equation: ($k_c = \pi\Delta\nu/2^{-1/2}$).^{S3} ^[b]Free energy of activation obtained from approximate method using the Eyring equation.^{S4} ^[c]Free energy of activation obtained from line-shape analysis using the Eyring equation.

The approximate rates at the coalescence temperatures were evaluated using Gutowsky–Holm equation: ($k_c = \pi\Delta\nu/2^{-1/2}$). The line shape for the H⁹ region was simulated, using a computer program MEXICO suite of programs, version 3.0 uncoupled TEXT (program package for line-shape calculations).^{S5} The shapes of the theoretical spectra closely approximated those obtained experimentally. In each case, the coalescence temperature (T_c) was assigned to the temperature at which a single broad peak was observed. We were gratified to observe that the free energies of activation determined by line-shape analysis were in close agreement with those obtained by the use of the approximate method.

(S3) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.* 1956, **25**, 1228.

(S4) H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*. VCH: Weinheim, 1992, 263.

(S5) A. D. Bain and G. J. Duns, *Can. J. Chem.* 1996, **74**, 819.