Electronic supplementary information

Chirality transcription and amplification by [2]pseudorotaxanes

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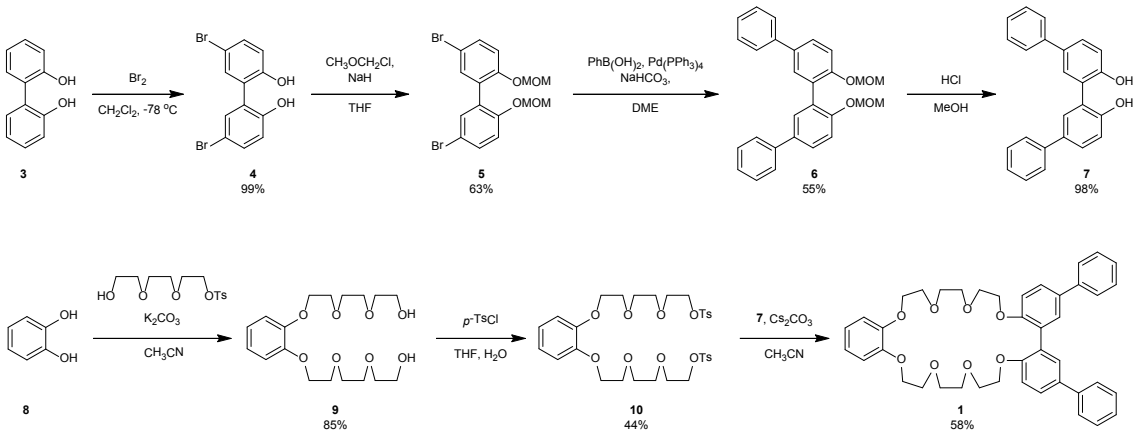
Materials and methods

IR spectra were obtained as KBr disks on a JASCO FT/IR-410 spectrophotometer. ^{1}H-NMR spectra were recorded on Jeol ECP400 (400 MHz) spectrometers. ^{13}C NMR spectra were obtained on Jeol ECP400 (100 MHz) spectrometers. All NMR spectroscopic data of $CDCl_3$ solutions are reported in ppm (δ) downfield from TMS. UV and CD spectra were recorded on JASCO V-650 and JASCO J-820 spectrometers, respectively. Silica gel 60 F254 precoated plates on glass from Merck Ltd. were used for thin layer chromatography (TLC).

Synthesis of crown ether 1



1,1':3',1":3",1"'-quaterphenyl-4',6"-diol **7**[1] and 1,2-Bis[2-[2-(2-tosyloxyethoxy)ethoxy]ethoxy] -benzene **10**[2] was synthesized according to literature procedure. A mixture of diol **7** (0.959 g, 2.8 mmol), ditosylate **10** (1.94 g, 2.8 mmol), and Cs_2CO_3 (2.14 g, 6.6 mmol) in acetonitrile (200 mL) was refluxed for 28 h. After cooling down to room temperature, the mixture was filtered and evaporated, and then $CHCl_3$ was added. After washing with brine, the organic phase was dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography on silica gel (hexane/EtOAc, v/v 1:1) to yield crown ether **1** (1.12 g, 58%) as a white solid: mp 100.0-101.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 4H), 7.52-7.50 (m, 4H), 7.41-7.38 (t, J = 7.6 Hz, 4H), 7.30-7.28 (m, 2H), 7.04 (dd, J = 8.8, 6.5 Hz, 2H), 6.93-6.88 (m, 4H), 4.20-4.09 (m, 8H), 3.87-3.56 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.7, 69.1, 69.8, 69.9, 70.97, 70.99, 112.8, 114.4, 121.5, 126.6, 126.7, 127.1, 128.7, 128.9, 130.1, 133.6, 140.7, 149.0, 156.2 ; IR (KBr) 3058, 3026, 2927, 2868, 1739, 1601, 1506, 1451, 1256, 1129, 1056, 922, 828, 765, 689 cm^{-1}; m/z (matrix: *m*-NBA) = 764 ($[M+1]^+$ 50 %), 787 ($[M+Na]^+$ 70%); Anal. Calcd for $C_{42}H_{44}O_8 \cdot 1/4H_2O$: C, 74.04; H, 6.58. Found. C, 74.02; H, 6.68.

1. S. Facchetti, D. Losi and A. Iuliano, *Tetrahedron-Asymmetr.*, 2006, **17**, 2993.

2. X. Z. Zhu and C. F. Chen, *J. Am. Chem. Soc.*, 2005, **127**, 13158.

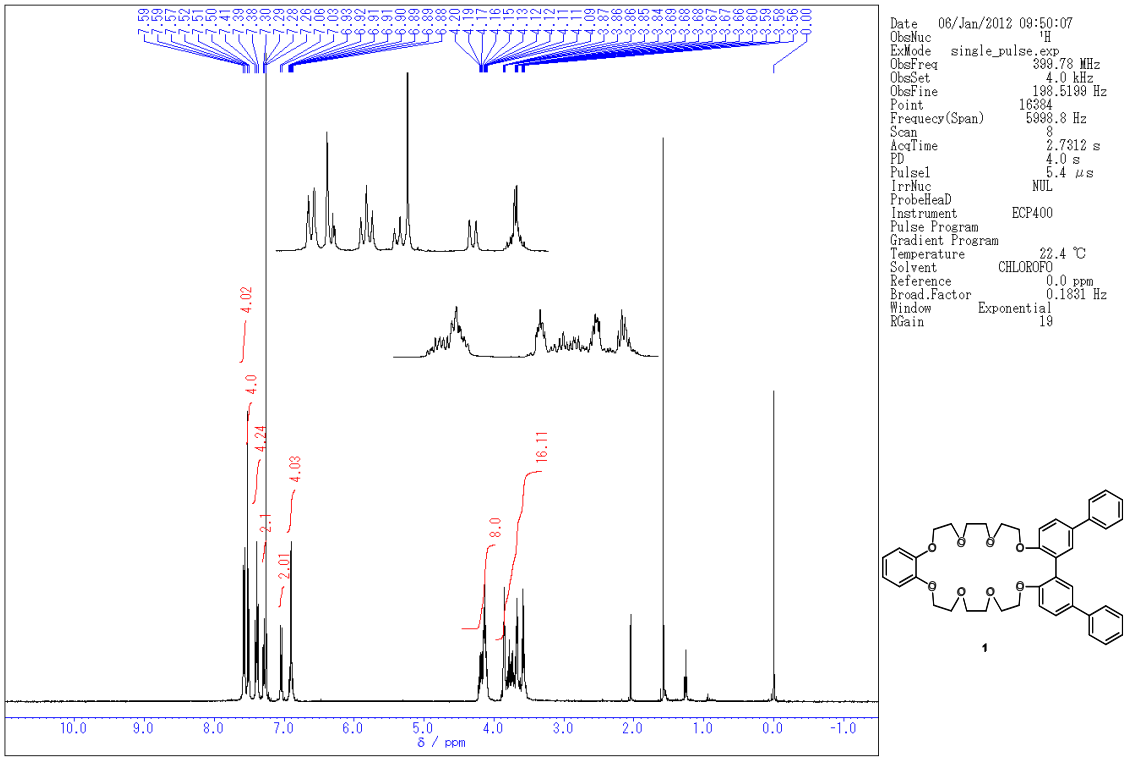


Fig. S1. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of **1**.

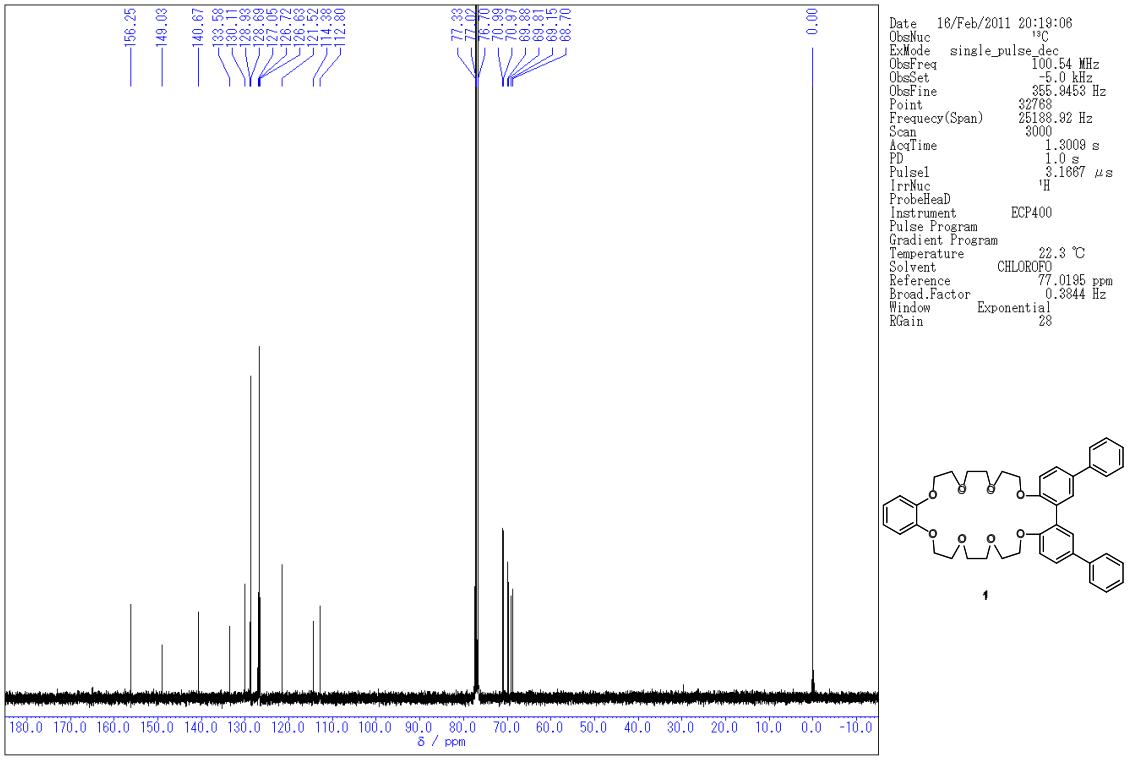
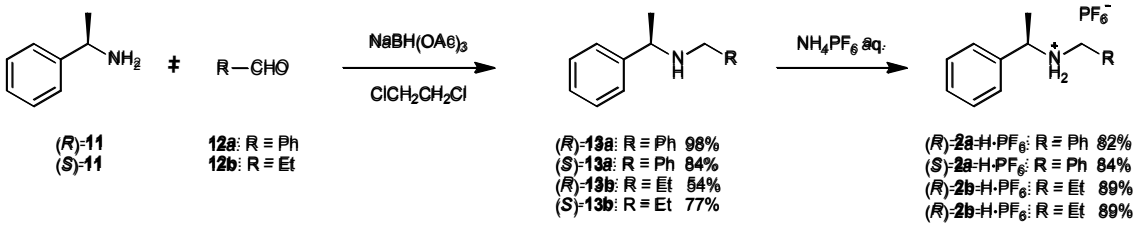


Fig. S2. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of **1**.

Synthesis of ammonium salts (*R*)-2a-H·PF_6, (*S*)-2a-H·PF_6, (*R*)-2b-H·PF_6, and (*S*)-2b-H·PF_6



Secondary amines (*R*)-**13a**, (*S*)-**13a**, (*R*)-**13b**, and (*S*)-**13b** was prepared by reductive amination of 1-phenylethanamine (*R*)-**11** or (*S*)-**11** and benzaldehyde **12**[3]. To a solution of secondary amine **13** (2.23 mmol) in CH_2Cl_2 (1 mL) was added 5 M HCl (10 mL). After stirring for 1 h, a white precipitate was formed. The solvents were evaporated and the residue was dissolved in water (3 mL). The solution was added to a saturated aqueous NH_4PF_6 and stirred for 1h. The reaction mixture was extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by recrystallization from CH_2Cl_2/hexane to give ammonium salts.

(*R*)-**2a**-H·PF_6 as colorless crystals (82%): mp 125.4-126.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.24 (m, 10H), 4.30 (q, *J* = 6.8 Hz, 1H), 3.97 (s, 2H), 1.67 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 130.3, 130.1, 130.0, 129.9, 129.4, 128.8, 127.3, 59.8, 50.7, 19.8; IR (KBr) ν_{max} 2933, 2761, 2422, 1588, 1496, 1446, 845, 768, 742, 696, 561 cm^{-1}; m/z (matrix: DTT/TG) = 212 ([M–(PF_6^-)]$^+$ 100 %); $[\alpha]_D^{25}$ +42.1 (*c* 1.47, $CHCl_3$). Anal. Calcd for $C_{15}H_{18}NF_6P$: C, 50.43; H, 5.08; N, 3.92. Found. C, 50.45; H, 4.90; N, 3.84.

(*S*)-**2a**-H·PF_6 as colorless crystals (84%): mp 125.2126.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.507.24 (m, 10H), 4.30 (q, *J* = 6.8 Hz, 1H), 3.97 (s, 2H), 1.67 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 130.3, 130.1, 130.0, 129.9, 129.4, 128.8, 127.3, 59.8, 50.7, 19.8; IR (KBr) ν_{max} 2936, 2761, 2422, 1588, 1458, 842, 768, 697, 560 cm^{-1}; m/z (matrix: DTT/TG) = 212 ([M–(PF_6^-)]$^+$ 100 %); $[\alpha]_D^{25}$ –41.9 (*c* 1.53, $CHCl_3$). Anal. Calcd for $C_{15}H_{18}NF_6P$: C, 50.43; H, 5.08; N, 3.92. Found. C, 50.31; H, 4.93; N, 3.84.

(*R*)-**2b**-H·PF_6 as colorless crystals (89%): mp 111.0-112.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.40 (m, 5H), 4.36 (m, 1H), 2.91 (m, 1H), 2.70 (m, 1H), 1.82-1.64 (m, 2H), 1.81 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 130.3, 130.0, 127.2, 60.8, 49.0, 19.6, 19.3, 10.6; IR (KBr) ν_{max} 2964, 2794, 2515, 2427, 1577, 1498, 1457, 1383, 1212, 1078, 840, 768, 703, 561 cm^{-1}; m/z (matrix: DTT/TG) = 164 ([M–(PF_6^-)]$^+$ 20 %); $[\alpha]_D^{25}$ +28.8 (*c* 1.52, $CHCl_3$). Anal. Calcd for $C_{11}H_{18}NF_6P$: C, 42.72; H, 5.87; N, 4.53. Found. C, 42.85; H, 5.77; N, 4.55.

(*S*)-**2b**-H·PF_6 as colorless crystals (89%): mp 111.0-112.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.40 (m, 5H), 4.36 (m, 1H), 2.91 (m, 1H), 2.70 (m, 1H), 1.82-1.64 (m, 2H), 1.81 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 130.3, 130.0, 127.2, 60.8, 49.0, 19.6, 19.3, 10.6; IR (KBr) ν_{max} 2964, 2794, 2515, 2427, 1577, 1498, 1457, 1383, 1212, 1078, 840, 768, 703, 561 cm^{-1}; m/z (matrix: DTT/TG) = 164 ([M–(PF_6^-)]$^+$ 80 %); $[\alpha]_D^{25}$ -29.5 (*c* 1.43, $CHCl_3$). Anal. Calcd for $C_{11}H_{18}NF_6P$: C, 42.72; H, 5.87; N, 4.53. Found. C, 42.75; H, 5.71; N, 4.24.

3. C. M. Cain, R. P. C. Cousins, G. Coumbarides and N. S. Simpkins, *Tetrahedron*, 1990, **46**, 523.

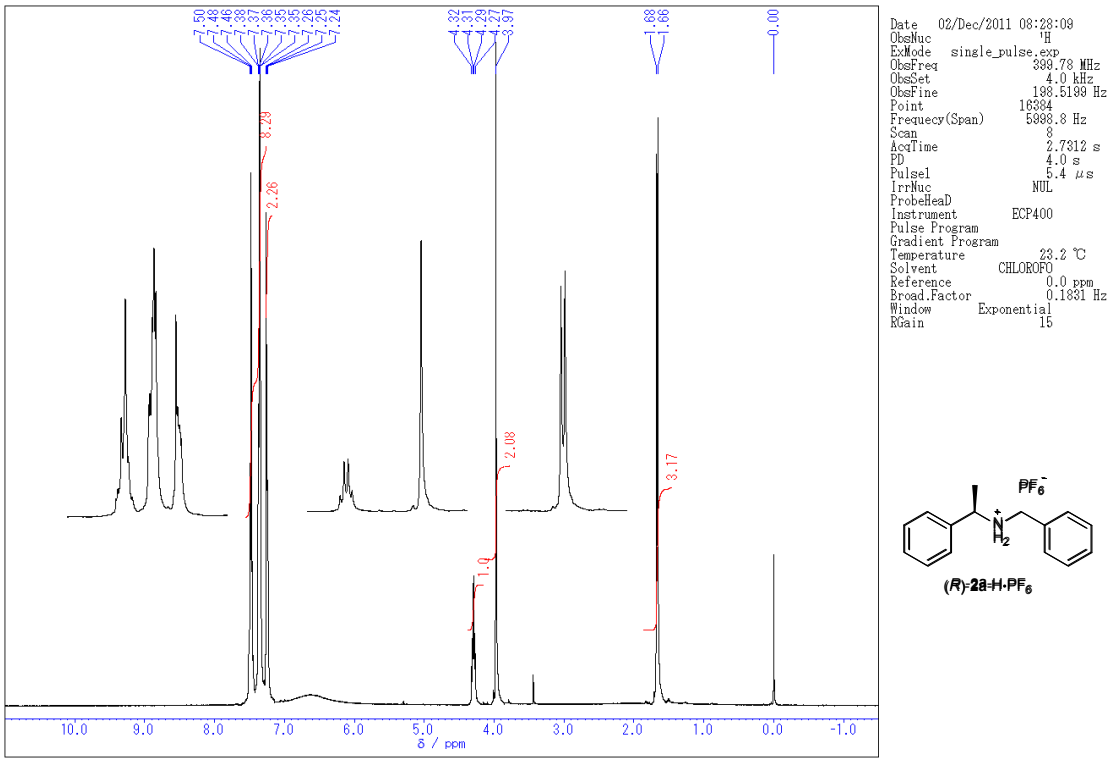


Fig. S3. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of (*R*)-**2a**-H·PF_6.

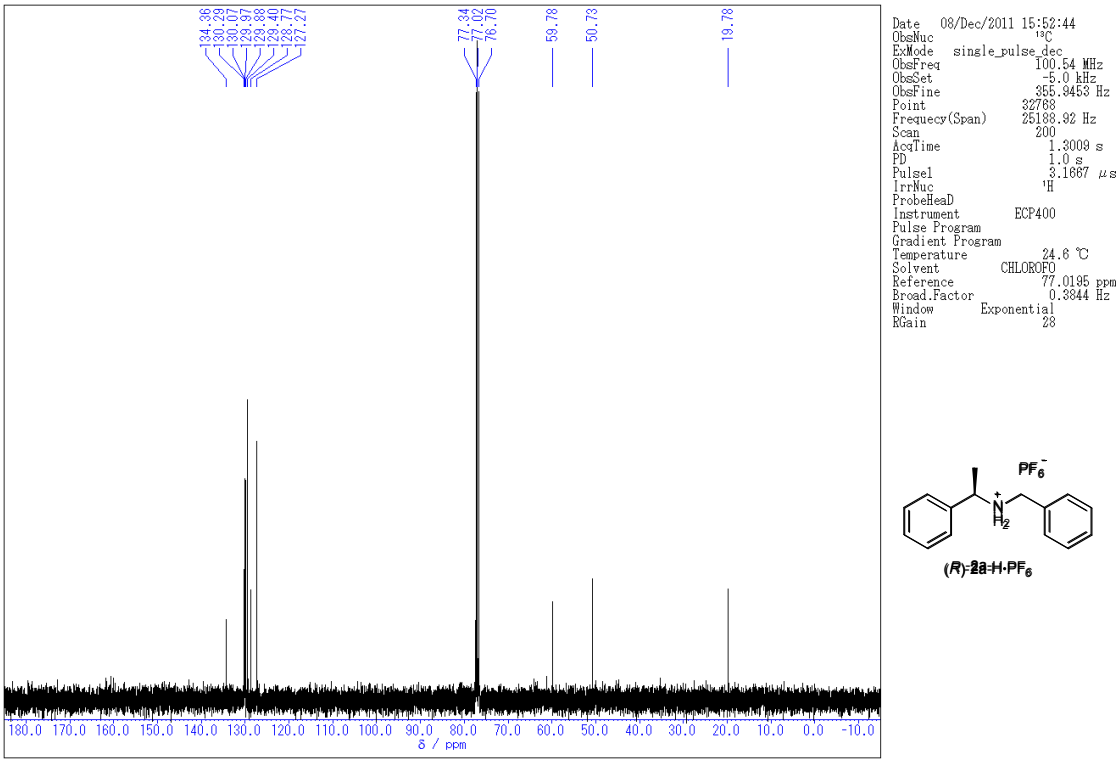


Fig. S4. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of (*R*)-**2a**-H·PF_6.

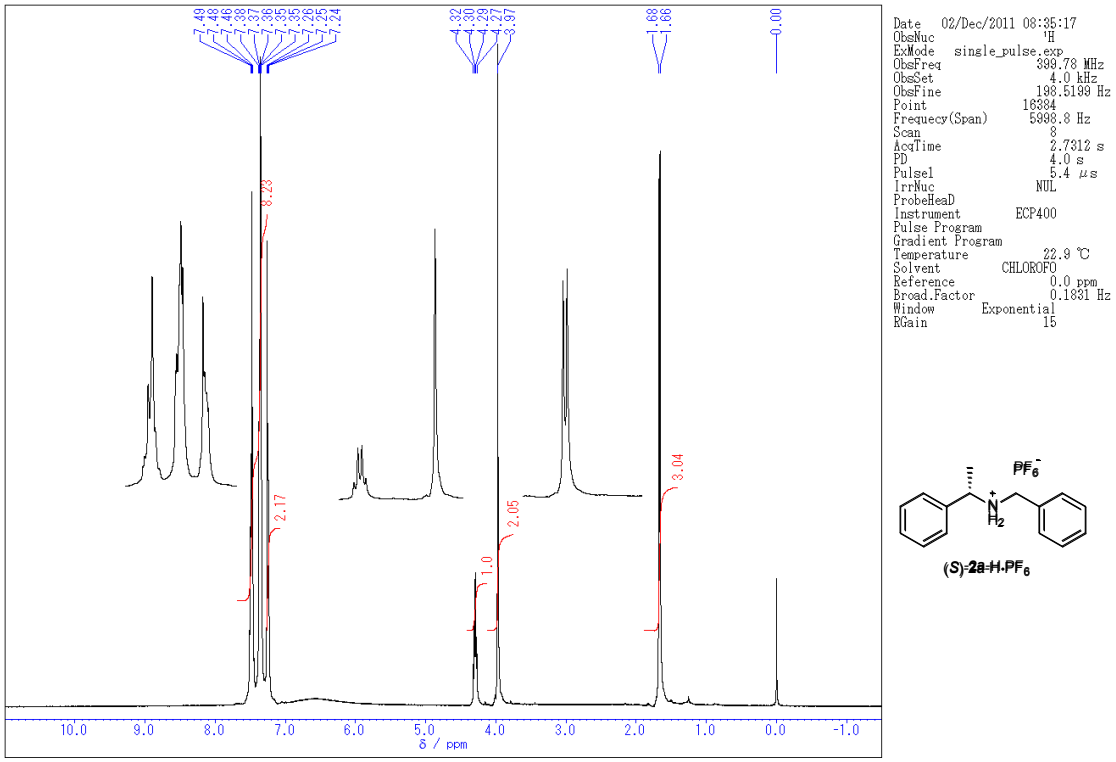


Fig. S5. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of (*S*)-**2a**-H·PF_6.

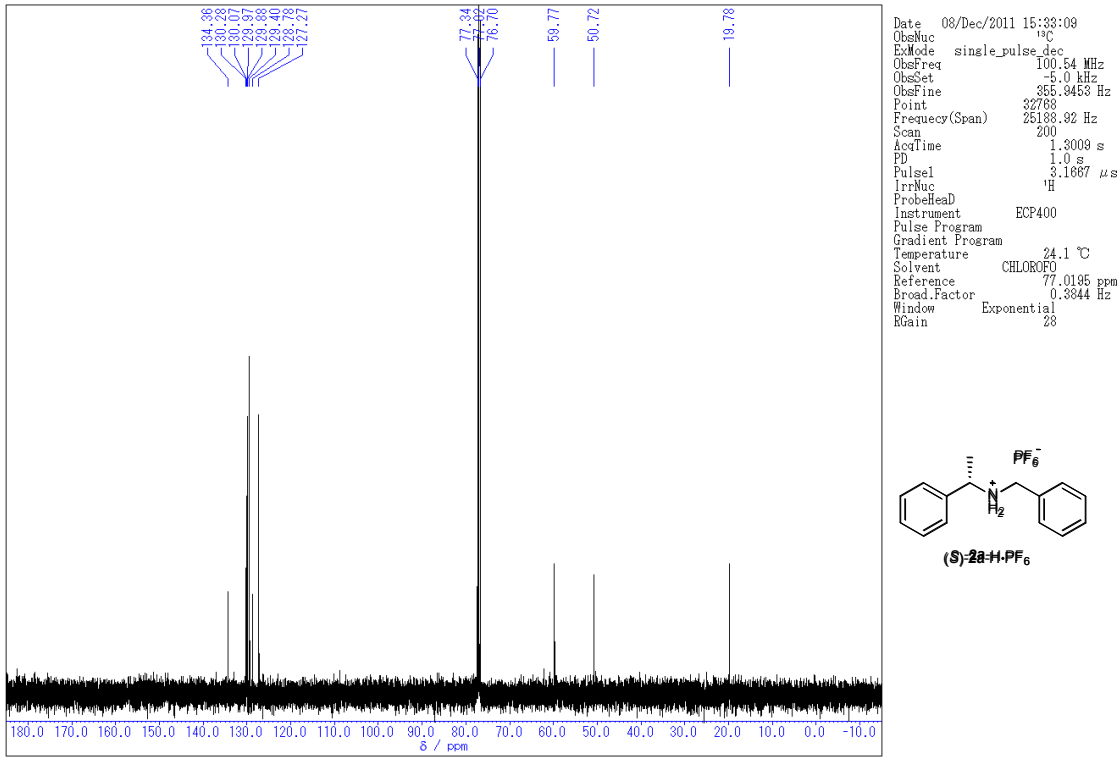


Fig. S6. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of (*S*)-**2a**-H·PF_6.

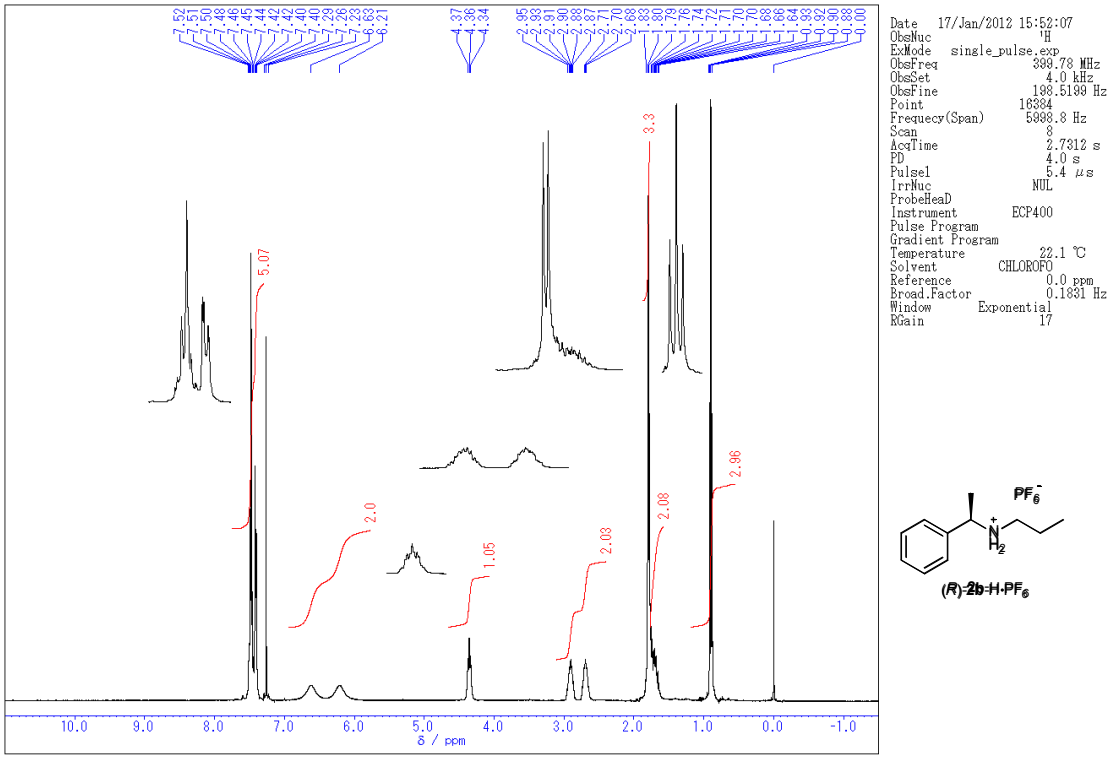


Fig. S7. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of (*R*)-**2b**-H·PF_6.

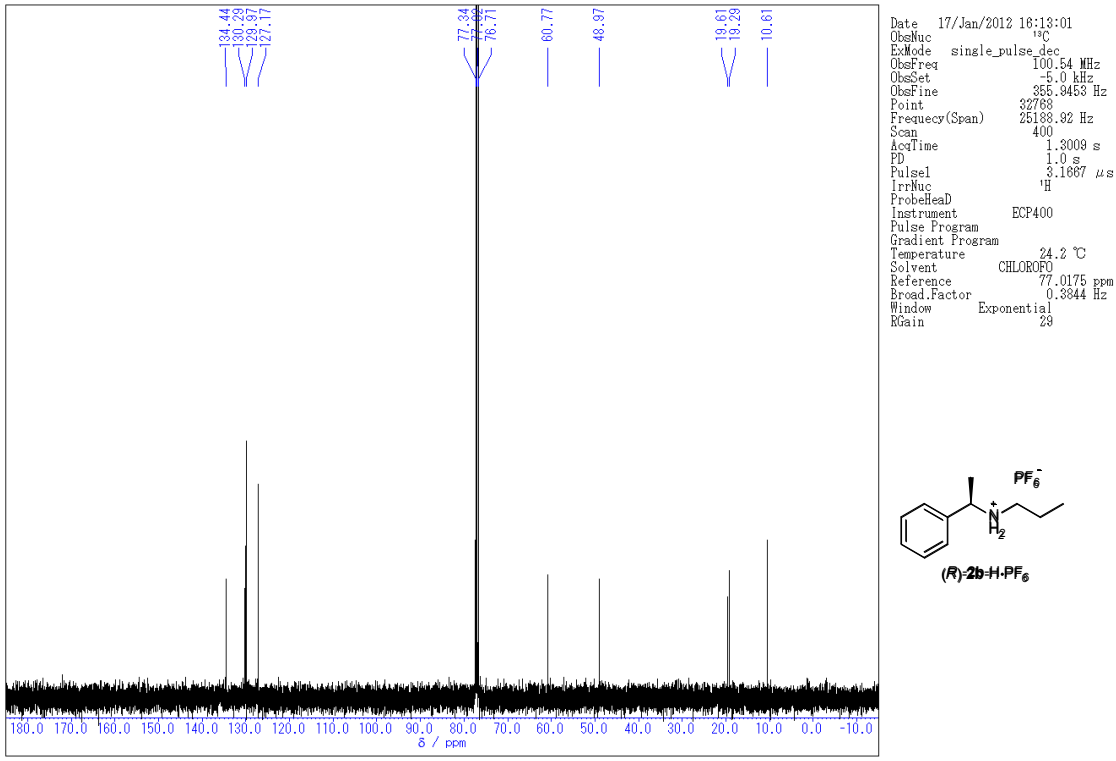


Fig. S8. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of (*R*)-**2b**-H·PF_6.

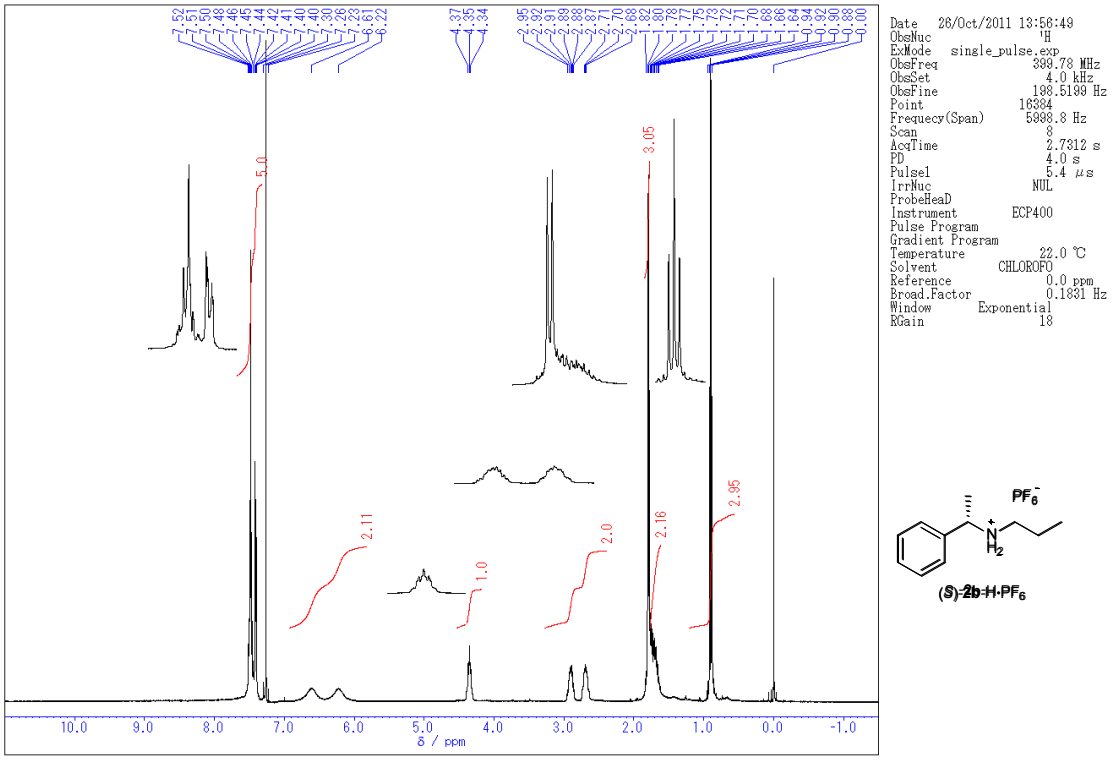


Fig. S9. ^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of (*S*)-**2b**-H·PF_6.

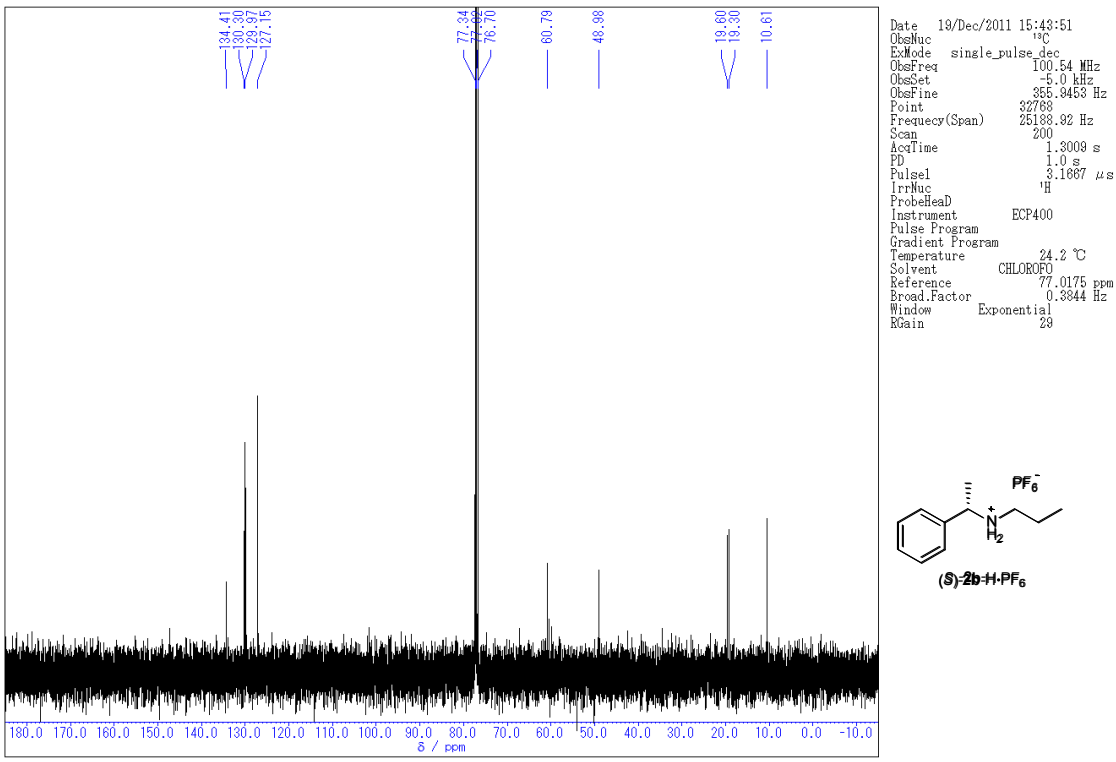


Fig. S10. ^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of (*S*)-**2b**-H·PF_6.

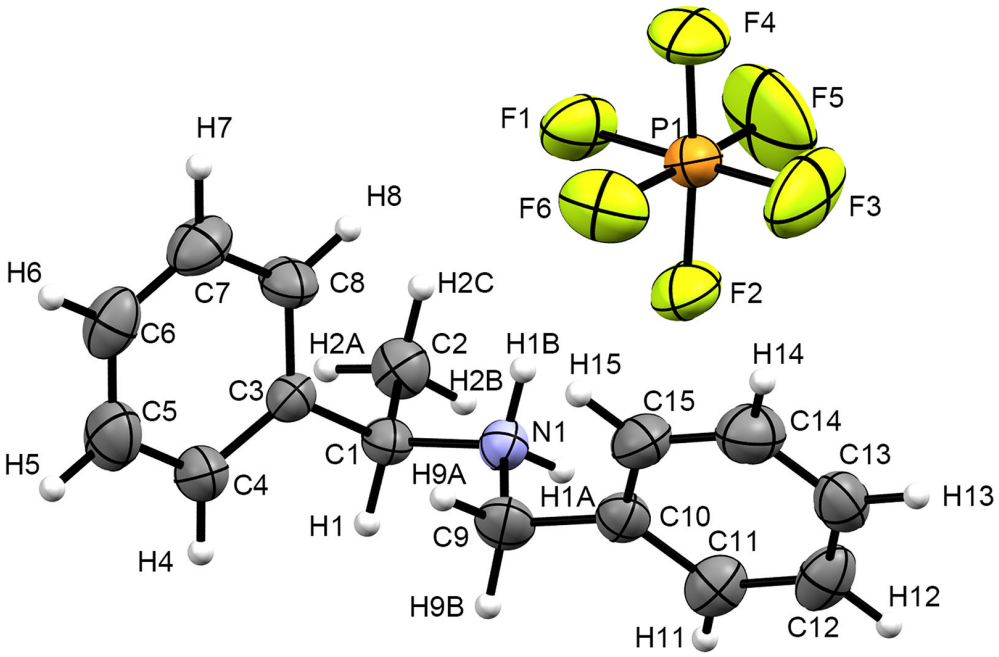


Fig. S11. ORTEP drawing of (*R*)-**2a**-H·PF_6 (50% probability level).

Table S1 Crystal data and structure refinement for (*R*)-**2a**-H·PF_6.

Empirical formula	C15 H18 F6 N P	
Formula weight	357.27	
Temperature	173 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.7662(6) Å	α= 90°.
	b = 11.1969(7) Å	β= 90°.
	c = 16.9395(12) Å	γ = 90°.
Volume	1662.68(19) $Å^3$	
Z	4	
Density (calculated)	1.427 Mg/m^3	
Absorption coefficient	0.222 mm^{-1}	
F(000)	736	
Crystal size	0.21 x 0.18 x 0.09 mm^3	
Theta range for data collection	2.18 to 24.81°.	
Index ranges	–9<=h<=10, –13<=k<=13, –16<=l<=20	
Reflections collected	8693	
Independent reflections	2864 [R(int) = 0.0425]	
Completeness to theta = 24.81°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9799 and 0.9557	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2864 / 0 / 280	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R_1 = 0.0490, wR_2 = 0.1174	
R indices (all data)	R_1 = 0.0738, wR_2 = 0.1331	
Absolute structure parameter	–0.09(19)	
Largest diff. peak and hole	0.386 and -0.225 $e.Å^{-3}$	

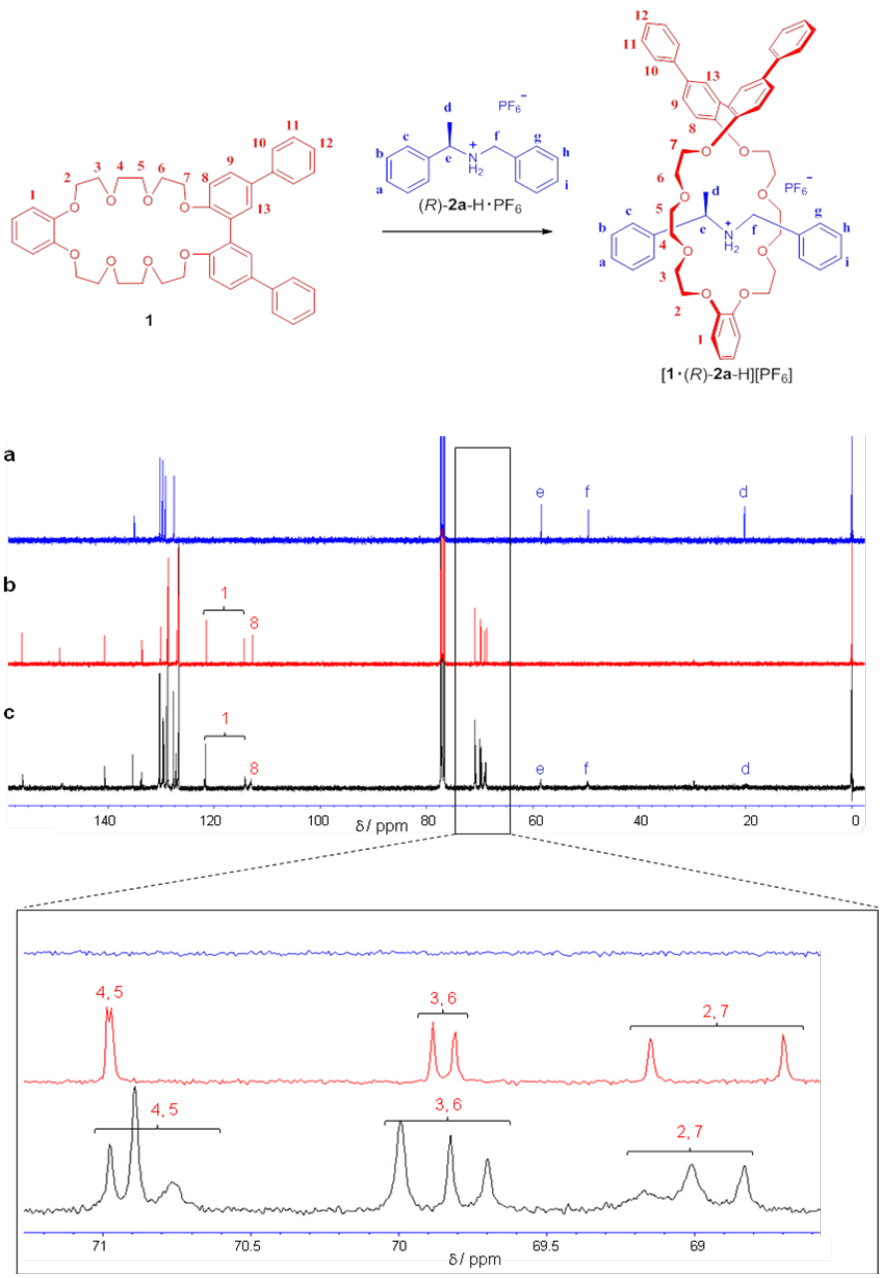


Fig. S12. ^{13}C NMR spectra (100 MHz, $CDCl_3$, 298K, [**1**] = [ammonium salts] = 14 mM) of (*R*)-**2a**-H·PF_6 (a), **1** (b), and [1·(*R*)-**2a**-H][PF_6] (c).

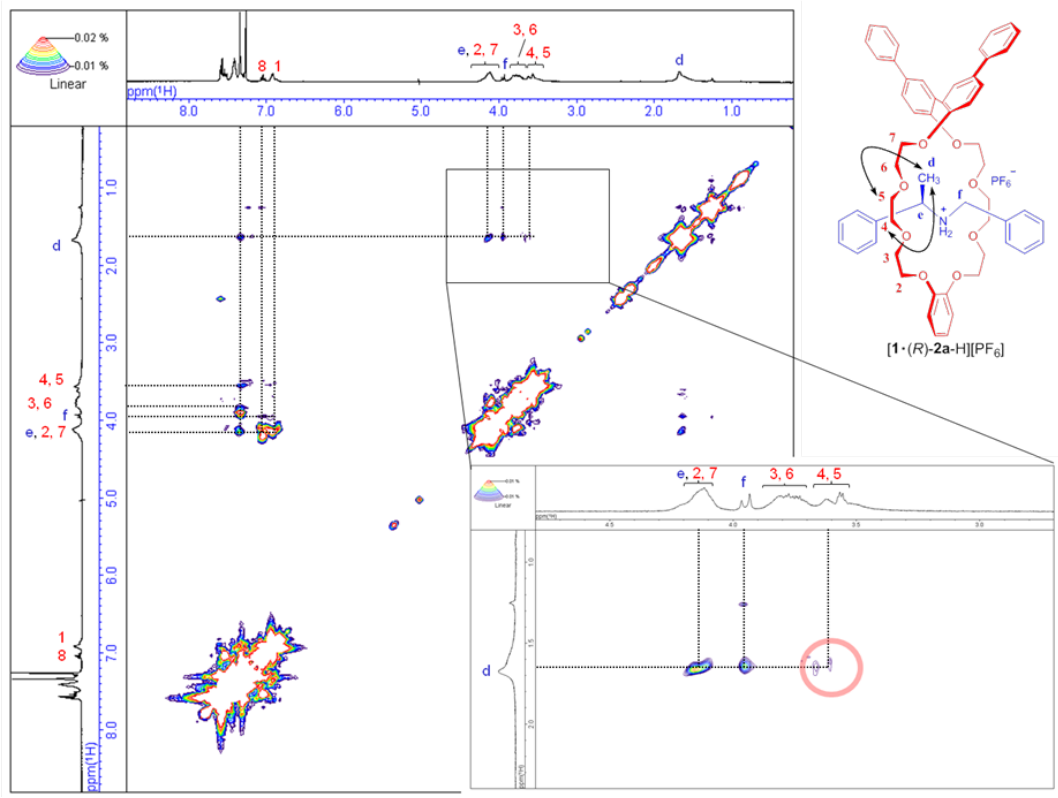


Fig. S13. NOESY spectrum (400 MHz, $CDCl_3$, 298K, 14 mM) of [**1**·(*R*)-**2a**-H][PF_6].

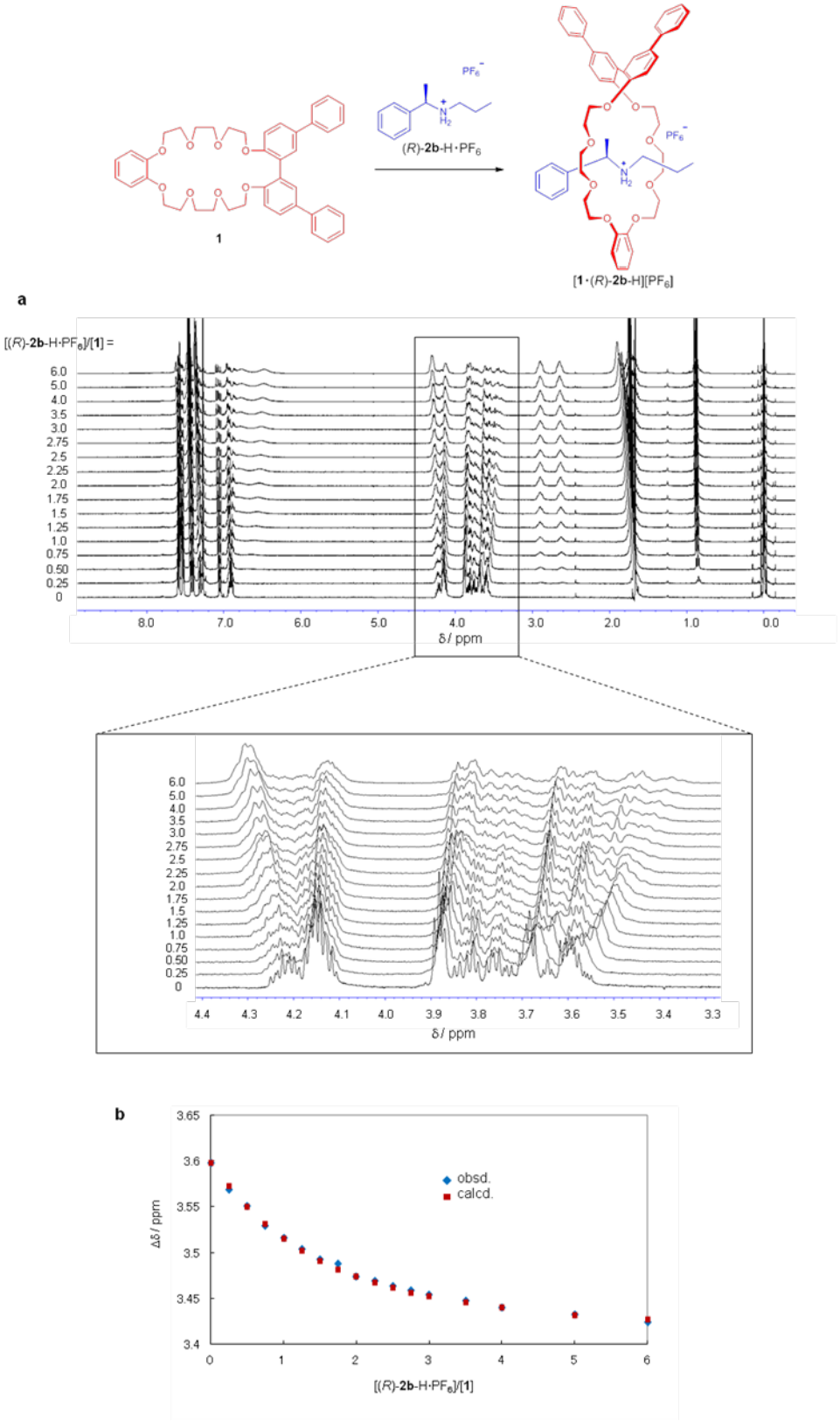


Fig. S14. ^{1}H NMR spectral changes of **1** in the absence and presence of (*R*)-**2b**-H·PF_6 (400 MHz, $CDCl_3$, 273K, [**1**] = 3.3 mM) (a), non-linear curve-fitting (b).

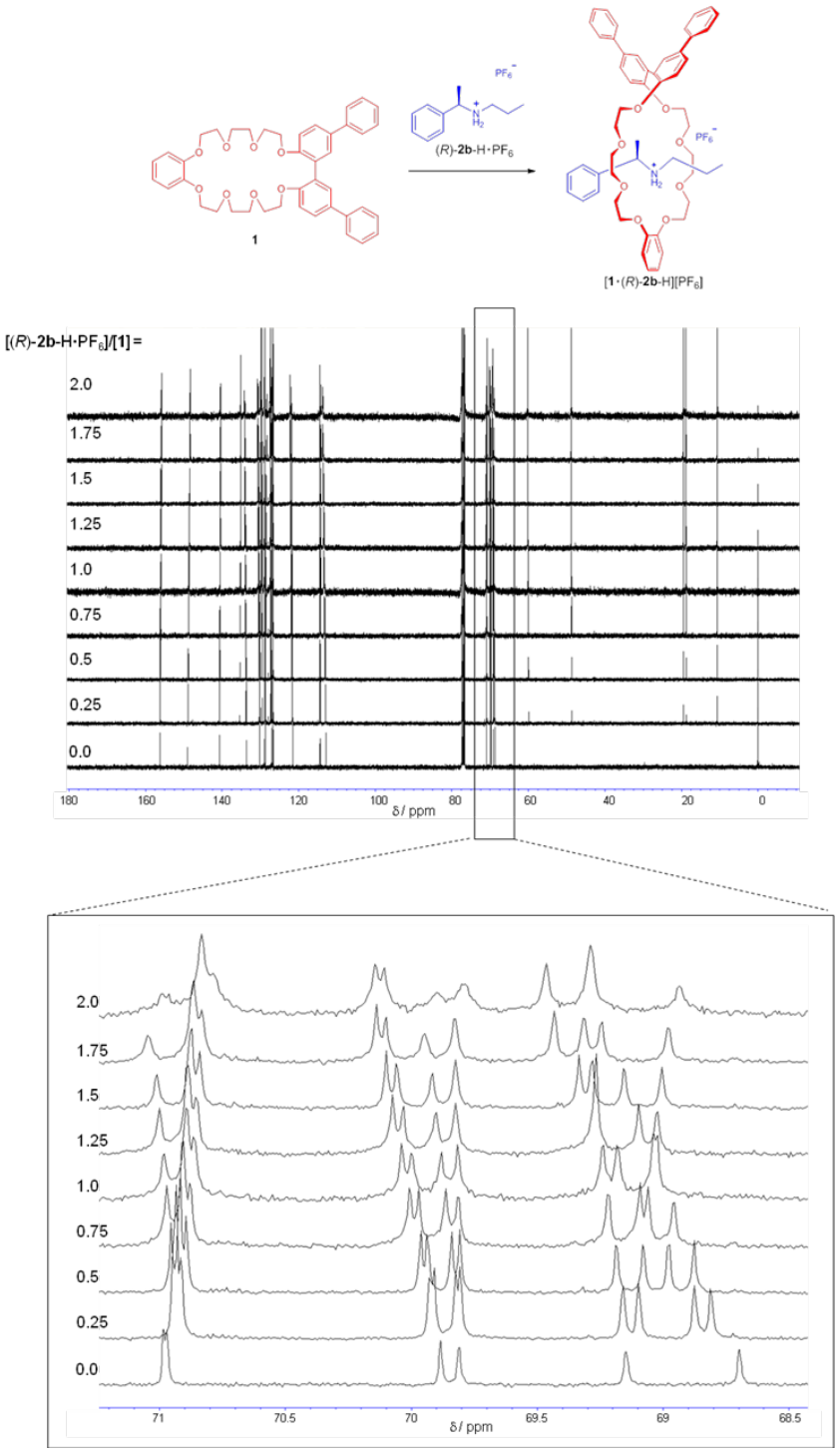


Fig. S15. ^{13}C NMR spectral changes of **1** in the absence and presence of (*R*)-**2b**-H·PF_6 (100 MHz, $CDCl_3$, 298K, [**1**] = 47 mM).

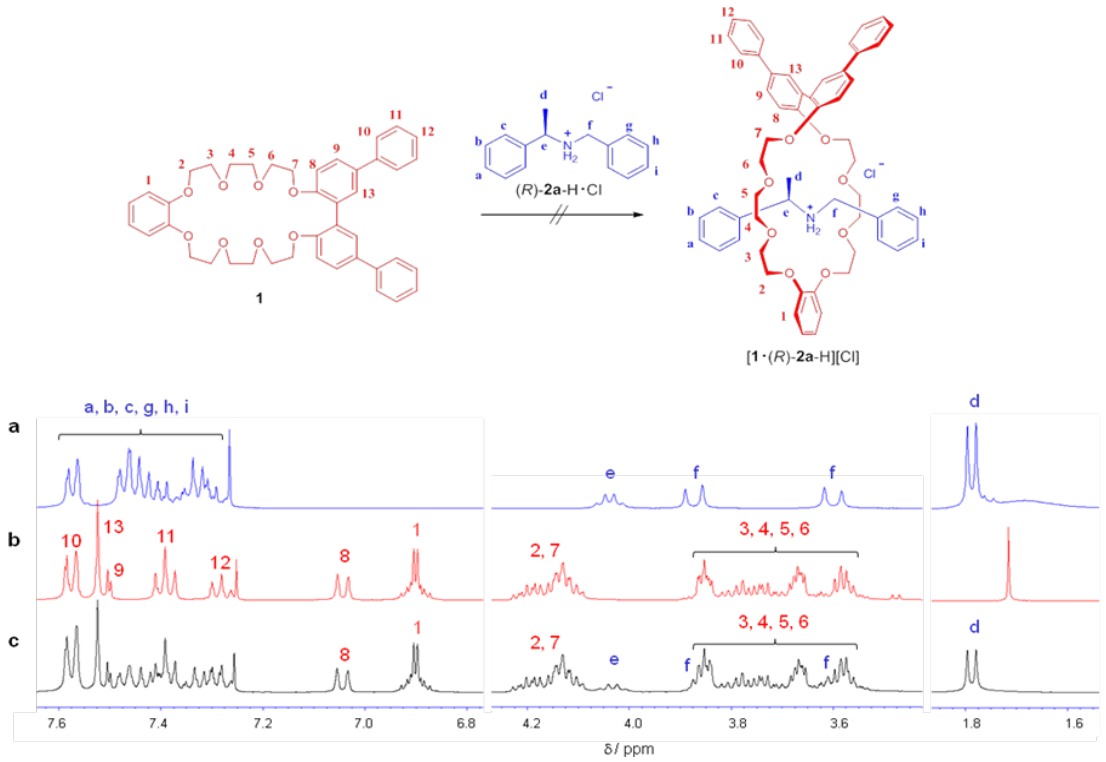


Fig. S16. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298K, [**1**] = [ammonium salts] = 32 mM) of (*R*)-**2a**-H·Cl (a), **1** (b), and [1·(*R*)-**2a**-H][Cl] (c).

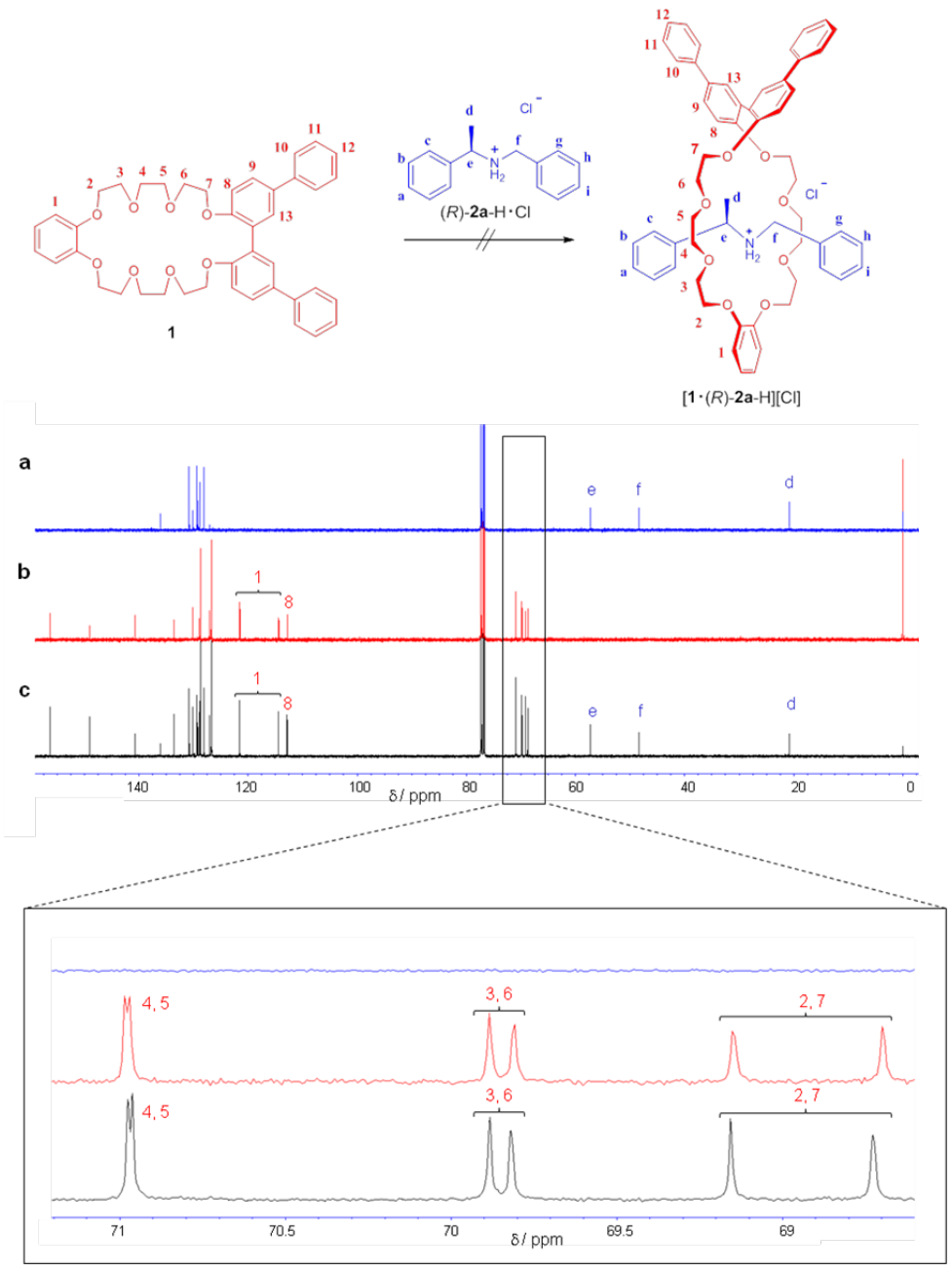


Fig. S17. ^{13}C NMR spectra (100 MHz, $CDCl_3$, 298K, [**1**] = [ammonium salts] = 32 mM) of (*R*)-**2a**-H·Cl (a), **1** (b), and [1·(*R*)-**2a**-H][Cl] (c).

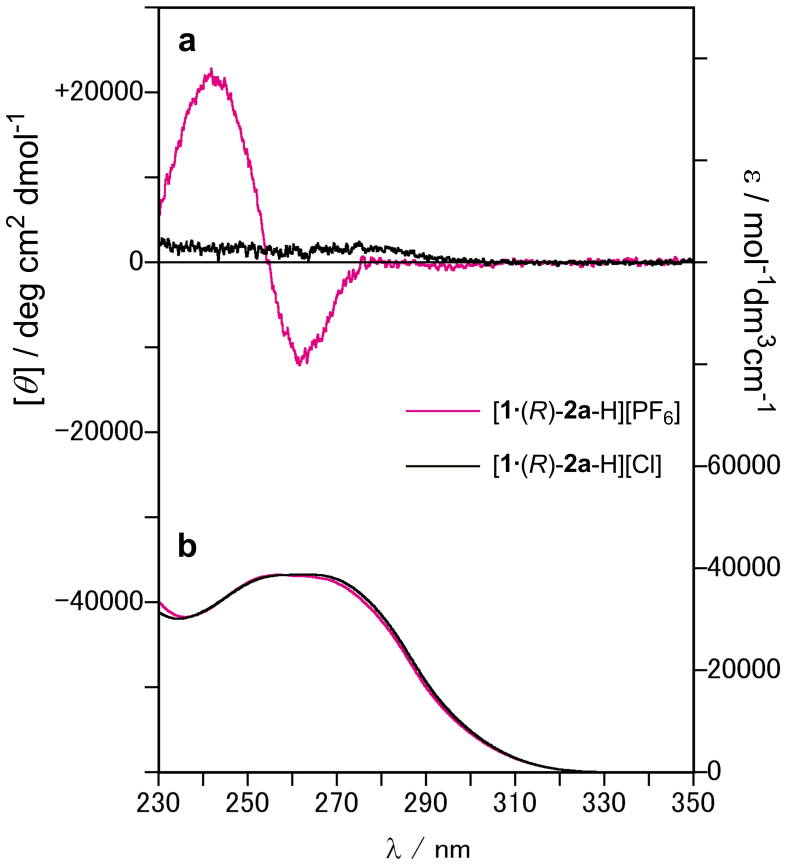


Fig. S18. CD spectra ($CHCl_3$, 273 K, [**1**] = [ammonium salts] = 3.0 mM) of [**1**·(*R*)-**2a**-H][PF_6] (pink) and [**1**·(*R*)-**2a**-H][Cl] (black) (a). UV spectra ($CHCl_3$, 293 K, [**1**] = [ammonium salts] = 0.20 mM) of [**1**·(*R*)-**2a**-H][PF_6] (pink) and [**1**·(*R*)-**2a**-H][Cl] (black) (b).

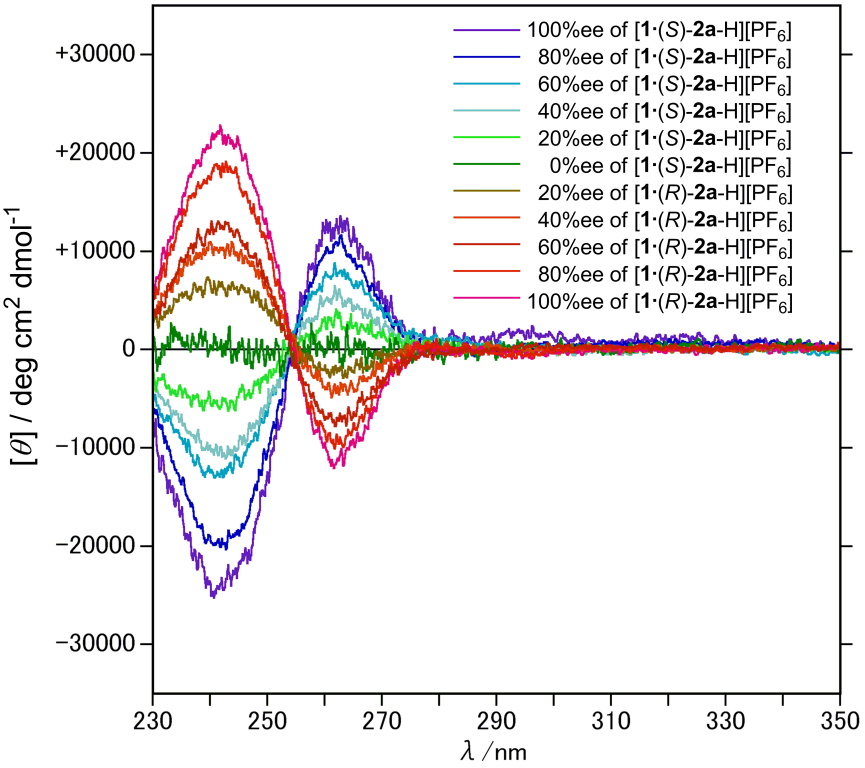


Fig. S19. CD spectra ($CHCl_3$, 273 K, [**1**] = [ammonium salts] = 3.0 mM) of [**1**·(*R*)-**2a**-H][PF_6] and [**1**·(*S*)-**2a**-H][PF_6] with varying %ee values.

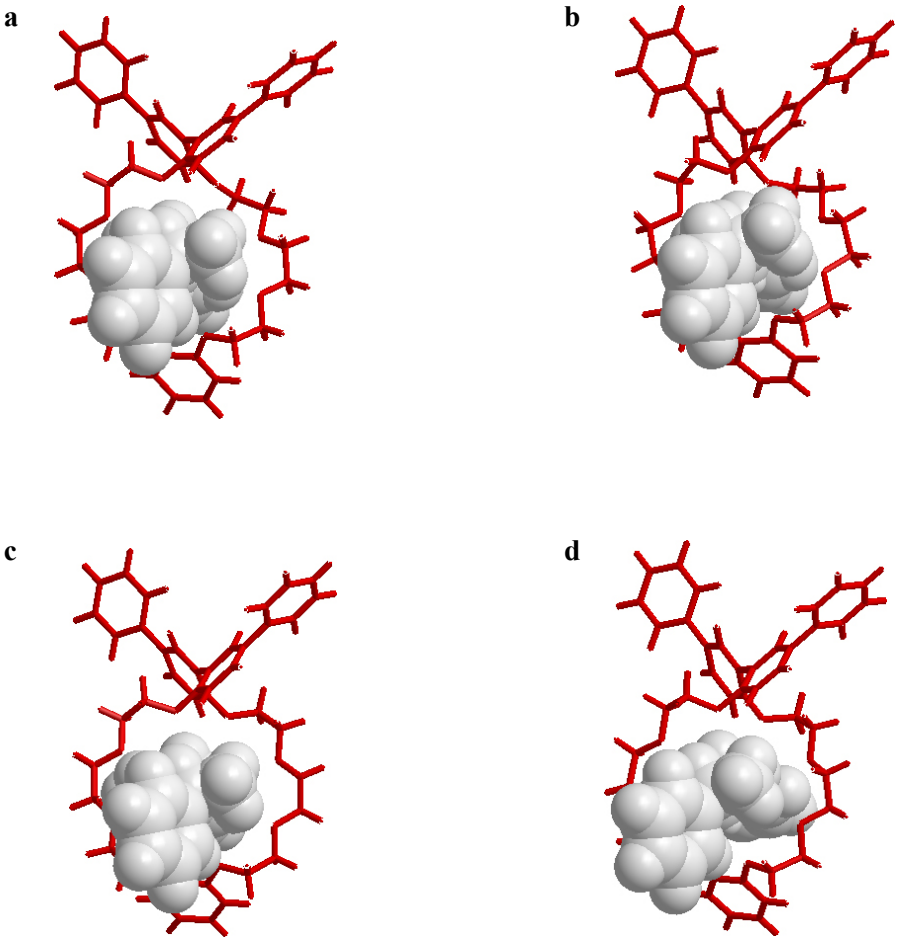


Fig. S20. Optimized structures of [**1**·(*R*)-**2a**-H]$^{+}$ complex. The B3LYP/6-31G*(a), B3LYP/3-21G*(b), HF/6-31G*(c), HF/3-21G*(d) methods were used.