

Supporting Information

Photoswitching of Dextro-/Levo- Rotation with Axially Chiral Binaphthyls linked to an Azobenzene

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1. UV-vis and CD spectra of (R)-4-9 and (S)-4.

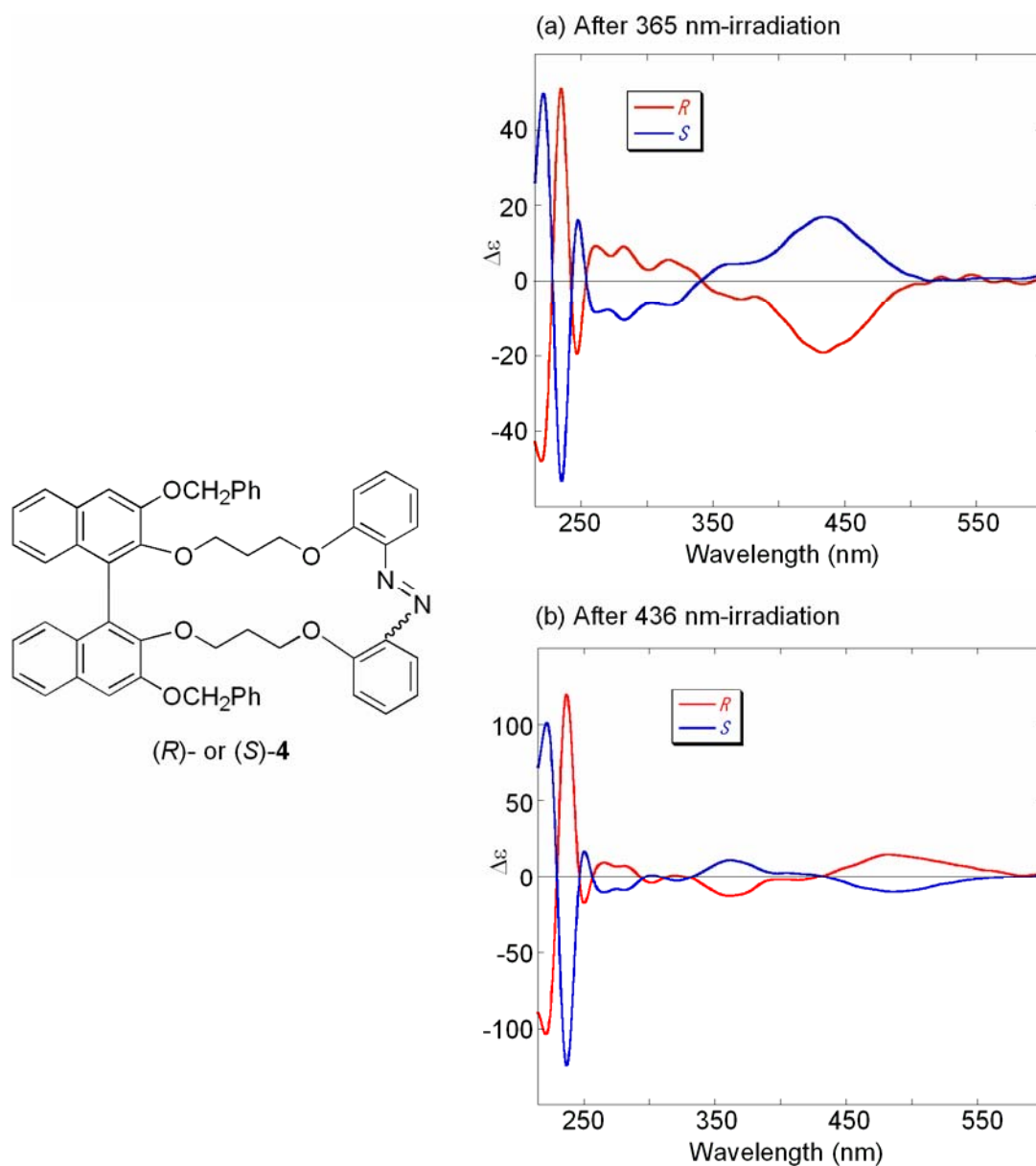


Figure S-1. CD spectra of (R)-4 (red line) and (S)-4 (blue line) after (a) 365 nm-irradiation and (b) 436 nm-irradiation. Conditions: 1,4-Dioxane, 1.0×10^{-5} M, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm², 100 s), 436 nm (10 mW/cm², 100 s).

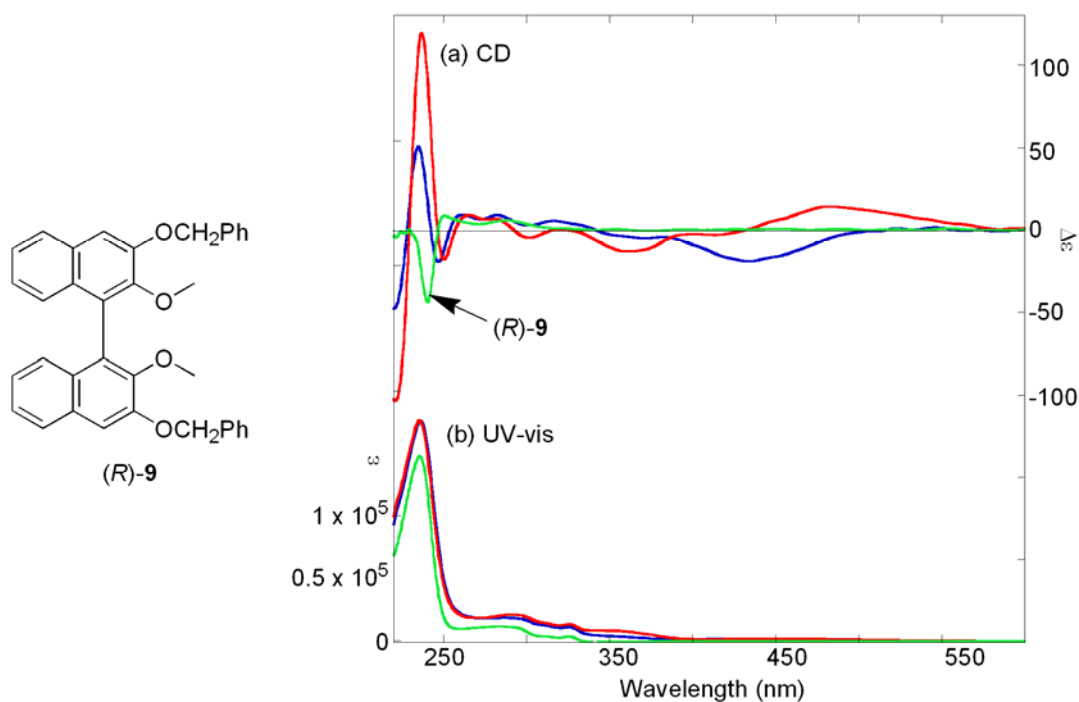


Figure S-2. CD and UV-vis spectra of (R)-4 and (R)-9^{s1}. ((R)-4 after 365 nm-irradiation (blue line), (R)-4 after 436 nm-irradiation (red line), (R)-9 (green line)). Conditions: 1,4-Dioxane, 1.0×10^{-5} M, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm², 100 s), 436 nm (10 mW/cm², 100 s).

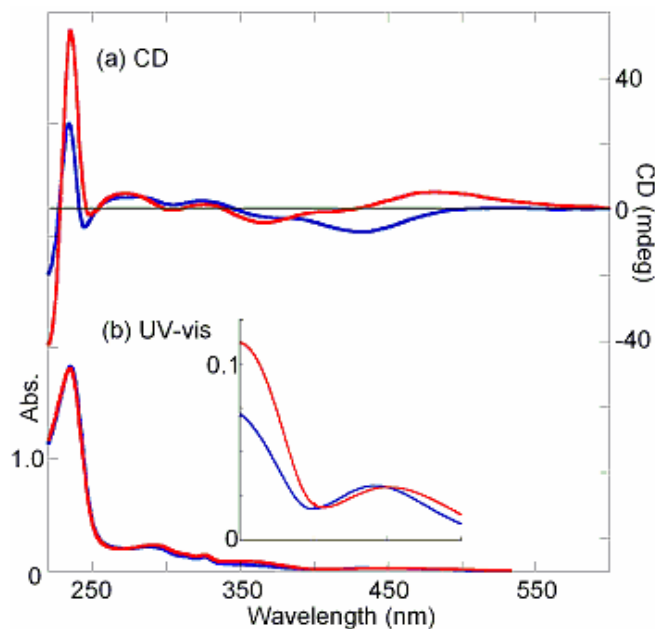


Figure S-3. (a) CD spectra of (R)-4, (b) Absorption spectra of (R)-4; after 365 nm-irradiation (blue line), after 436 nm-irradiation (red line). Conditions: Methanol, saturated concentration, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm², 100 s), 436 nm (10 mW/cm², 100 s).

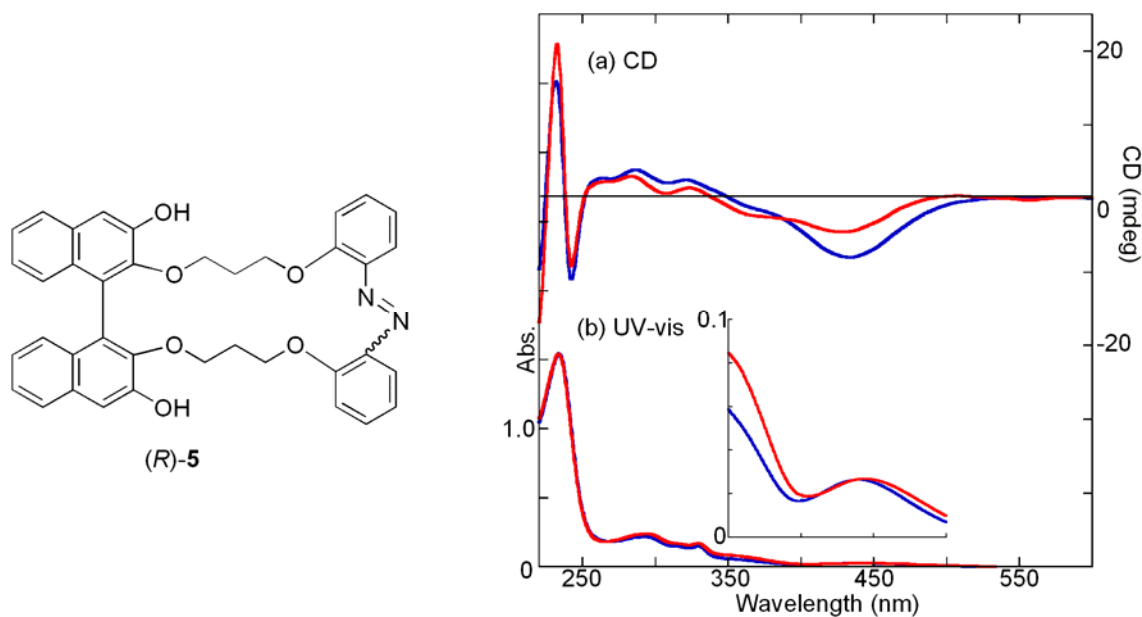


Figure S-4. (a) CD spectra of (R)-5, (b) Absorption spectra of (R)-5; after 365 nm-irradiation (blue line), after 436 nm-irradiation (red line). Conditions: Methanol, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm², 100 s), 436 nm (10 mW/cm², 100 s).

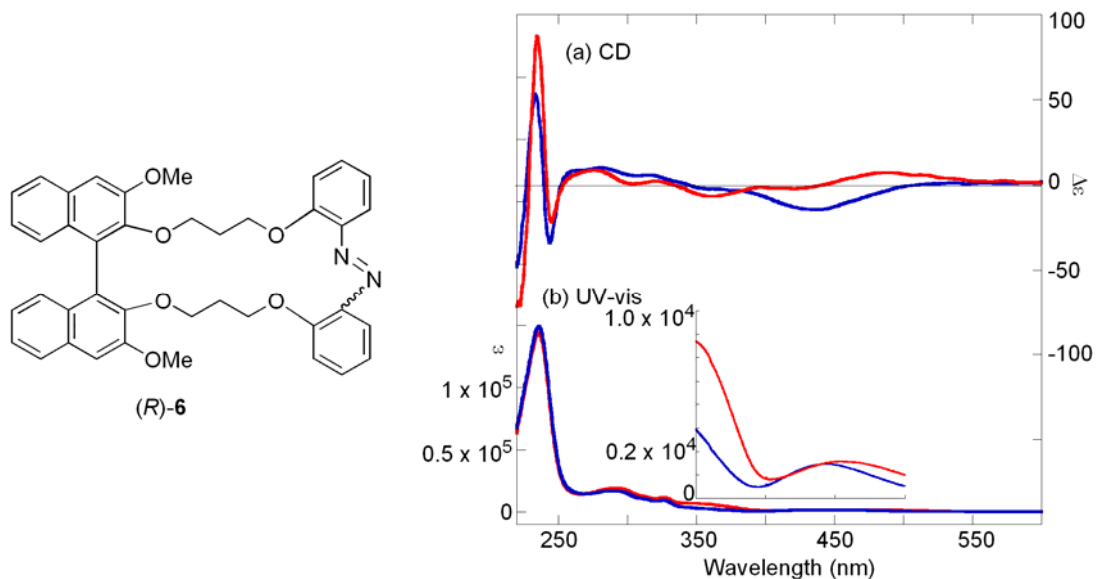


Figure S-5. (a) CD spectra of (R)-6, (b) Absorption spectra of (R)-6; after 365 nm-irradiation (blue line), after 436 nm-irradiation (red line). Conditions: 1,4-Dioxane, 1.0 x 10⁻⁵ M, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm², 100 s), 436 nm (10 mW/cm², 100 s).

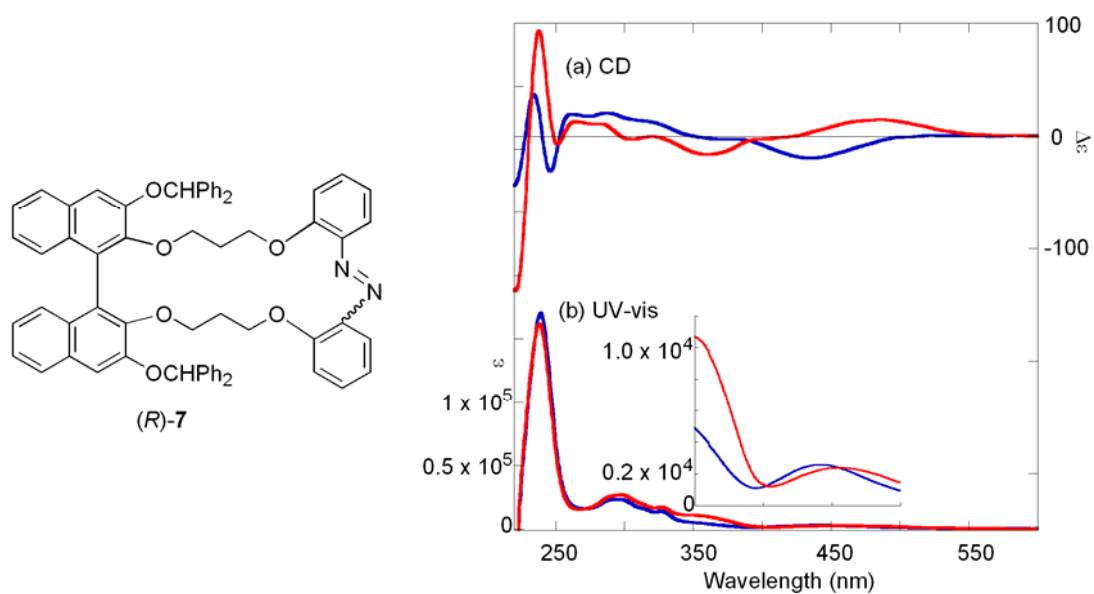


Figure S-6. (a) CD spectra of (R)-7, (b) Absorption spectra of (R)-7; after 365 nm-irradiation (blue line), after 436 nm-irradiation (red line). Conditions: 1,4-Dioxane, 1.0×10^{-5} M, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm^2 , 100 s), 436 nm (10 mW/cm^2 , 100 s).

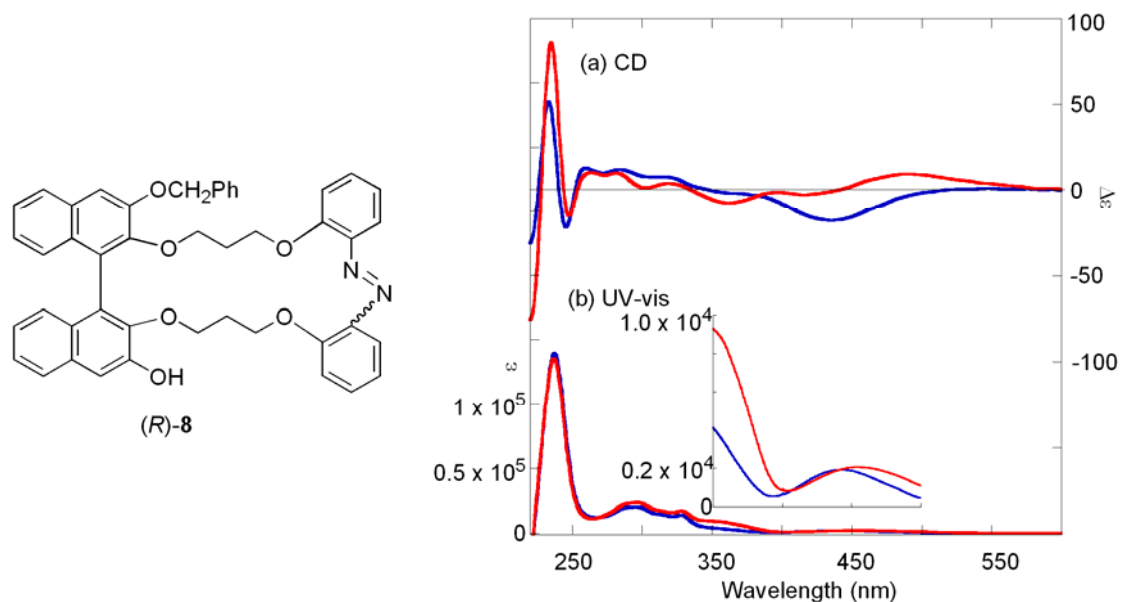


Figure S-7. (a) CD spectra of (R)-8, (b) Absorption spectra of (R)-8; after 365 nm-irradiation (blue line), after 436 nm-irradiation (red line). Conditions: 1,4-Dioxane, 1.0×10^{-5} M, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm^2 , 100 s), 436 nm (10 mW/cm^2 , 100 s).

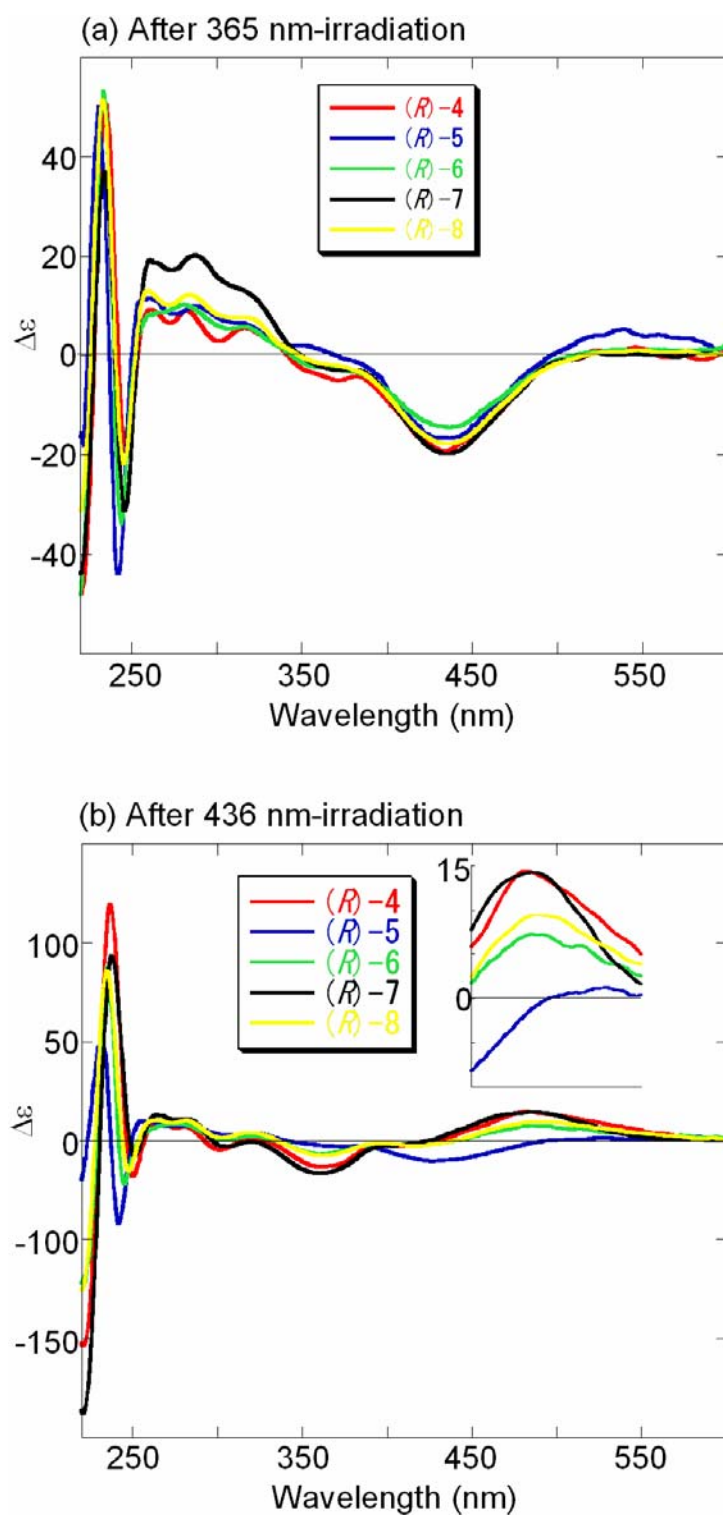


Figure S-8. CD spectra of (R)-4-8 after (a) 365 nm-irradiation and (b) 436 nm-irradiation. Conditions: 1,4-Dioxane, 1.0×10^{-5} M, 20 °C, light-path length = 10 mm, irradiation wavelength: 365 nm (10 mW/cm², 100 s), 436 nm (10 mW/cm², 100 s).

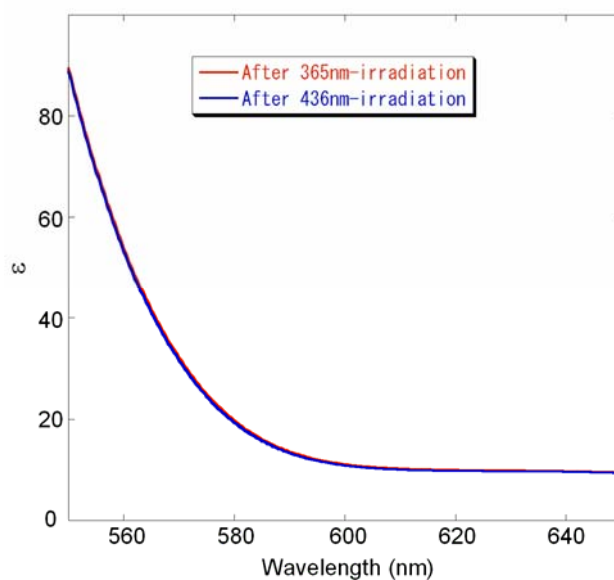


Figure S-9. Absorption spectra of concentrated (*R*)-**4** after photo-irradiation. Conditions: CHCl₃, **0.0126 M (0.01 g/dl)**, light path length = 10 mm, 20 °C, Irradiation wavelength: 365 nm (10 mW/cm², 500 s), 436 nm (10 mW/cm², 500 s).

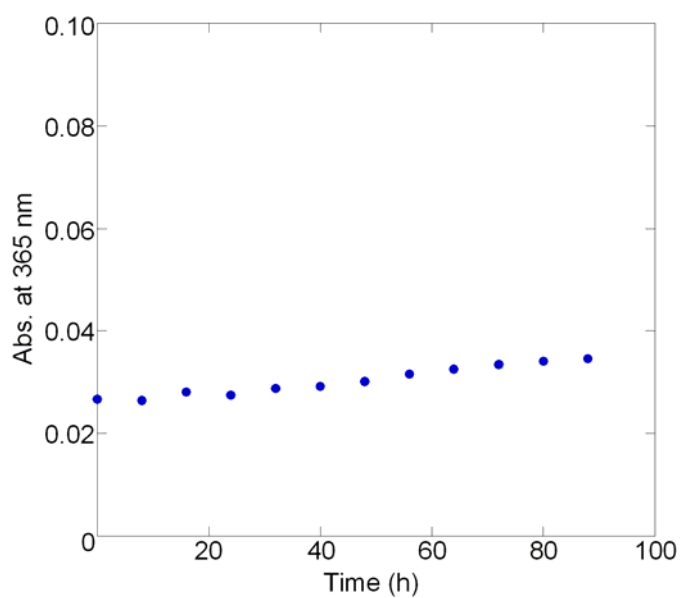


Figure S-10. Time-dependent change in absorbance of (*R*)-**4** after 365 nm-irradiation. Conditions: 1,4-Dioxane, light path length = 10 mm, 20 °C in the dark, Monitoring wavelength: 365 nm, Irradiation wavelength: 365 nm (10 mW/cm², 100 s).

2. Thermodynamic parameters of *cis-trans* isomerization process of (R)-4 and (R)-7.

For the thermal *cis-trans* isomerization,

$$\ln \frac{[cis]_t}{[cis]_0} = -kt \quad (1)$$

Where $[cis]_t$ and $[cis]_0$ are the concentrations of the *cis*-azobenzene at time t and time zero, respectively, and k is the rate constant for the thermal *cis-trans* isomerization. The first-order rate constant was determined by fitting the experimental data to the equation,

$$\ln \frac{A_\infty - A_t}{A_\infty - A_0} = -kt \quad (2)$$

where A_t , A_0 and A_∞ are the absorbance at 365 nm at time t , time zero and infinite time, respectively. The first order plots according to equation 2 for the *cis-trans* thermal isomerization of (R)-4 and (R)-7 at various temperatures are shown in Figure S-11.

Furthermore thermodynamic parameters such as enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) were determined according to the Eyring equation^{S2}:

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (3)$$

where R , k_B , and h are gas constant, Boltzmann constant, and Planck's constant, respectively. Substituting into equation 3,

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad (4).$$

Figure S-12 shows Eyring plots for *cis* to *trans* thermal isomerization of (R)-4 and (R)-7. The values of ΔH^\ddagger and ΔS^\ddagger were obtained from intersect and aslope, respectively, of the linear plot of $\ln(hk/k_B T)$ versus $1/T$ extrapolated to $T \rightarrow \infty$.

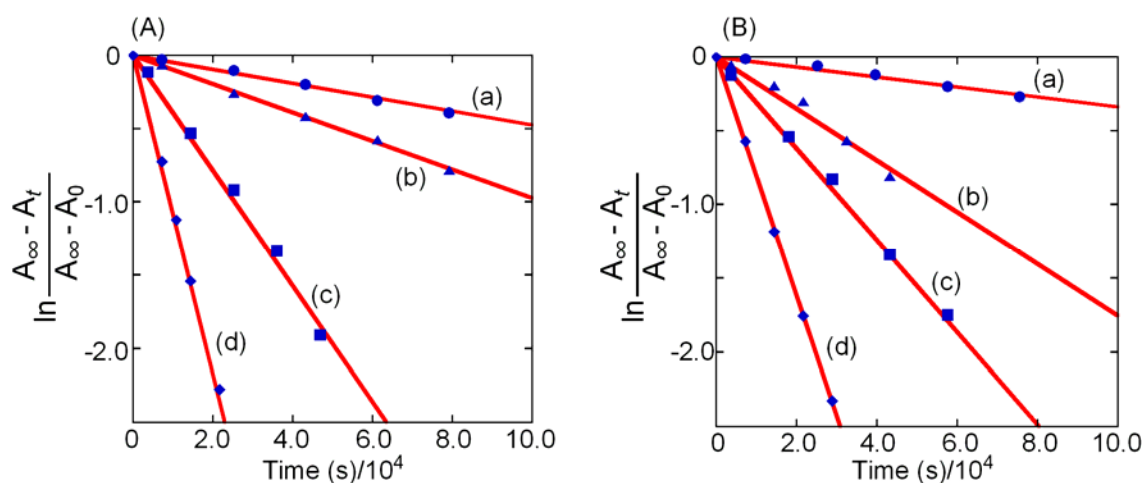


Figure S-11. First-order plots for *cis* to *trans* thermal isomerization of (R)-4 (A) and (R)-7 (B). (a) 35 °C, (b) 45 °C, (c) 55 °C, (d) 65 °C. Conditions: 1,4-Dioxane, 1.0 x 10⁻⁵ M.

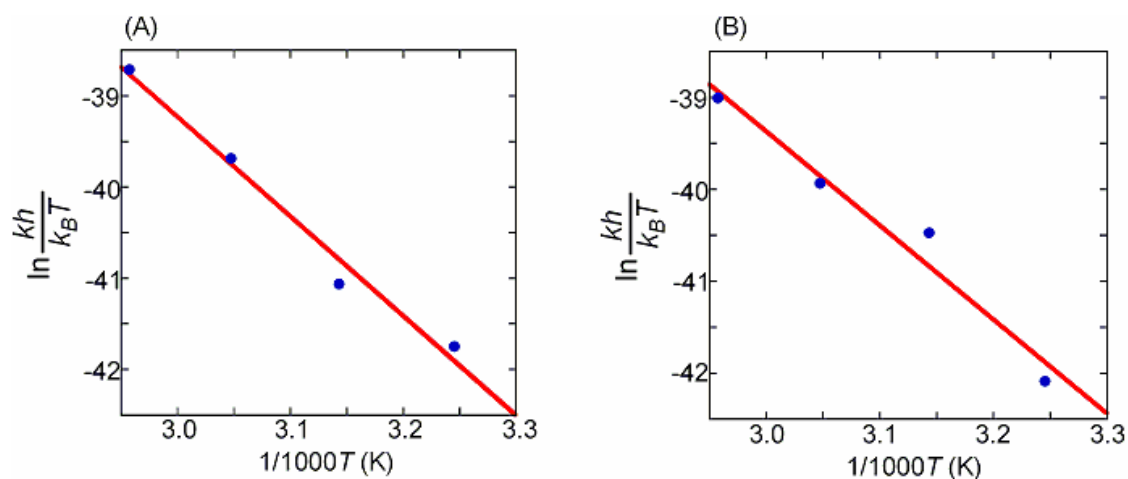


Figure S-12. Eyring plots for *cis* to *trans* thermal isomerization of (R)-4 and (R)-7. Conditions: 1,4-Dioxane, 1.0 x 10⁻⁵ M.

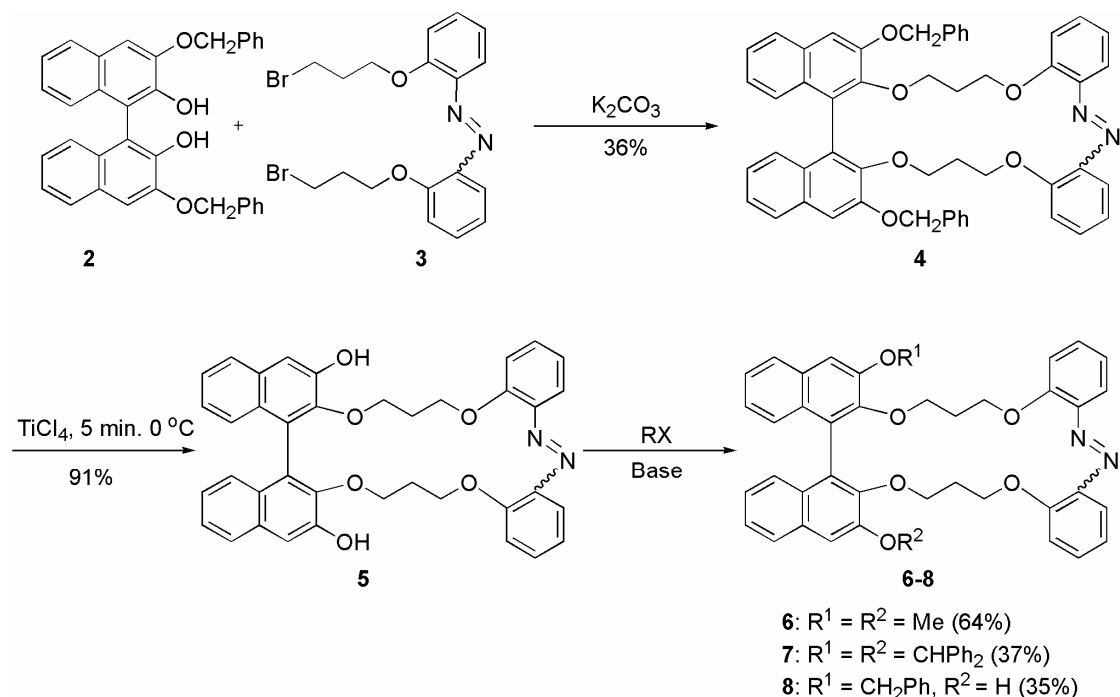
Table S-1. Rate coefficients k (s⁻¹) of *cis* to *trans* isomerization and the values of ΔH^\ddagger and ΔS^\ddagger of (R)-4 and (R)-7.

	k at 35 °C	k at 45 °C	k at 55 °C	k at 65 °C	ΔH^\ddagger	ΔS^\ddagger
(R)-4	4.7×10^{-6}	9.8×10^{-6}	4.0×10^{-5}	1.1×10^{-4}	22 kcal/mol	-13 cal/mol·K
(R)-7	3.4×10^{-6}	1.8×10^{-5}	3.1×10^{-5}	8.1×10^{-5}	20 kcal/mol	-17 cal/mol·K

Conditions: 1,4-Dioxane, 1.0 x 10⁻⁵ M.

3. Synthesis

Synthetic route of binaphthyl with azobenzene **4-8** is shown below. Binaphthyl **2**^{S3} and dibromide **3**^{S4} was prepared by following the reported procedure.



3,3'-Dibenzyloxybinaphthyl with azobenzene (*S*)-**4**

A suspension of (*S*)-**2** (100 mg, 0.201 mmol), NaH (10.6 mg, 0.442 mmol, 2.2 eq.) and **3** (91 mg, 0.201 mmol, 1.0 eq.) in DMF (15 ml) was stirred for 12 hours at room temperature. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2 ; *n*-hexane/chloroform = 1/2) and GPC to afford (*S*)-**4** (57 mg, 0.0719 mmol, 36%). Red amorphous; IR (KBr) 2959, 1439, 1281, 1250, 1017, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.2-2.1 (m, 4H), 3.2-4.3 (m, 8H), 4.88, 5.19 (ABq, $\nu_{AB} = 61.7 \text{ Hz}$, $J_{AB} = 11.2 \text{ Hz}$; s, 4H), 6.4-7.5 (m, 26H), 7.73, 7.78 (two d, $J = 8.4 \text{ Hz}$, 8.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 29.5, 29.7, 64.8, 65.1, 68.9, 70.1, 70.5, 70.6, 108.4, 108.4, 113.1, 113.9, 119.4, 120.2, 124.0, 124.2, 125.0, 125.6, 125.7, 125.2, 126.3, 127.8, 127.9, 128.2, 128.5, 128.8, 128.8, 130.5, 130.6, 130.8, 136.4, 136.5, 142.6, 143.7, 145.9, 146.4, 151.1, 151.3, 152.8 (Some peaks overlapped); HRMS (ESI^+) Calcd for $\text{C}_{52}\text{H}_{44}\text{N}_2\text{O}_6\text{Na}$ ($\text{M}+\text{Na}^+$): 815.3097. Found: 815.3076; LR MS (FAB^+) 792.4 (M^+).

3,3'-Dimethoxybinaphthyl with azobenzene (R)-6

A suspension of (R)-5 (30 mg, 0.0490 mmol), K₂CO₃ (34 mg, 0.245 mmol, 5 eq.) and MeI (30 µl, 0.490 mmol, 10 eq.) in DMF (1.5 ml) was stirred for 12 hours at room temperature. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO₂; *n*-hexane/chloroform/ethyl acetate = 4/3/1, then 2/3/1) and GPC to afford (R)-6 (20 mg, 0.0312 mmol, 64%). Red amorphous; IR (KBr) 2959, 1281, 1250, 1022, 748 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.2-2.1 (m, 4H), 3.2-4.2 (m, 8H), 3.65, 3.83 (two s, 6H), 6.52, 6.61 (two d, *J* = 8.1 Hz, 8.1 Hz, 2H), 6.6-7.5 (m, 14H), 7.66, 7.71 (two d, *J* = 8.1 Hz, 8.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 29.7, 29.9, 55.1, 55.3, 64.9, 65.5, 69.1, 70.4, 107.0, 107.2, 113.1, 114.6, 119.4, 120.5, 120.5, 121.1, 123.9, 124.1, 125.1, 125.2, 125.6, 125.9, 126.2, 126.3, 126.5, 126.7, 128.1, 128.6, 130.5, 130.8, 130.9, 131.1, 142.7, 144.2, 145.9, 146.2, 151.8, 152.1, 152.3, 152.9; HRMS (ESI⁺) Calcd for C₄₀H₃₆N₂O₆Na (M+Na)⁺: 663.2471. Found: 663.2464; LR MS (FAB⁺) 640.3 (M)⁺.

3,3'-Bis(diphenylmethoxy)binaphthyl with azobenzene (R)-7

A suspension of (R)-5 (64 mg, 0.104 mmol), K₂CO₃ (72 mg, 0.522 mmol, 5 eq.) and α-bromodiphenylmethane (257 mg, 1.04 mmol, 10 eq.) in DMF (4.0 ml) was stirred for 14 hours at 50 °C. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by GPC to afford (R)-7 (36 mg, 0.0381 mmol, 37%). Red amorphous; IR (KBr) 2960, 1283, 1248, 748 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.2-2.0 (m, 4H), 3.2-4.4 (m, 8H), 6.07, 6.43 (two s, 2H), 6.4-7.5 (m, 36H), 7.56, 7.61 (two d, *J* = 8.4 Hz, 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 29.2, 29.7, 64.5, 65.5, 69.1, 70.8, 82.3, 82.9, 111.4, 111.7, 112.9, 114.3, 119.4, 120.3, 120.6, 122.2, 124.1, 124.3, 124.8, 125.6, 125.8, 126.1, 126.6, 126.7, 126.8, 127.0, 127.4, 127.6, 127.8, 127.9, 128.2, 128.6, 128.7, 128.7, 128.9, 130.5, 130.6, 140.8, 140.9, 140.9, 141.1, 142.9, 143.8, 146.4, 147.1, 150.1, 150.4, 152.9; HRMS (FAB⁺) Calcd for C₆₄H₅₃N₂O₆ (M+H)⁺: 945.3907. Found: 945.3893; LR MS (FAB⁺) 944.4 (M)⁺.

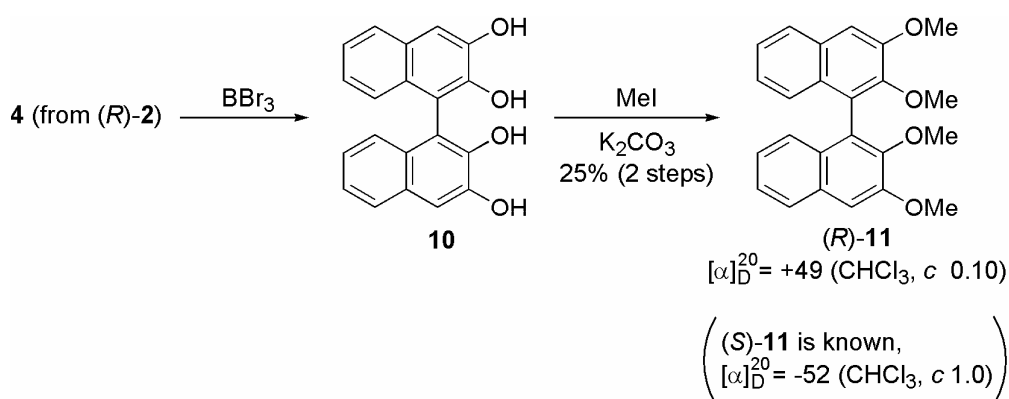
3-Benzyloxy-3'-hydroxy-binaphthyl with azobenzene (R)-8

A suspension of (R)-5 (40 mg, 0.0653 mmol), K₂CO₃ (10.8 mg, 0.0783 mmol, 1.2 eq.) and benzyl bromide (8.2 µl, 0.0686 mmol, 1.05 eq.) in DMF (4.0 ml) was stirred for 24 hours at 60 °C. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was

purified by GPC to afford (*R*)-**8** (16 mg, 0.0228 mmol, 35%), (*R*)-**4** (15 mg, 0.0189 mmol, 29%), unreacted (*R*)-**5** (10 mg, 0.0163 mmol, 25%). Red amorphous; IR (KBr) 3447, 3065, 1283, 1250, 748 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.2-2.1 (m, 4H), 3.0-4.6 (m, 8H), 5.19, 5.30 (AB q, $\nu_{\text{AB}} = 17.2$ Hz, $J_{\text{AB}} = 11.2$ Hz; s, 2H), 6.5-7.8 (m, 23H); ^{13}C NMR (150 MHz, CDCl_3) δ 28.9, 29.2, 29.9, 30.1, 65.3, 66.0, 67.1, 68.7, 68.7, 69.1, 69.6, 70.4, 70.7, 71.8, 108.9, 109.3, 110.5, 111.7, 113.6, 114.0, 114.4, 116.6, 118.8, 119.1, 119.3, 120.6, 121.2, 121.5, 121.7, 122.2, 123.4, 123.7, 124.0, 124.4, 124.7, 124.8, 125.1, 125.2, 125.4, 125.8, 125.8, 125.9, 126.1, 126.2, 126.4, 126.5, 126.6, 126.6, 126.9, 127.5, 127.6, 128.0, 128.1, 128.2, 128.4, 128.5, 128.7, 128.8, 129.0, 129.0, 129.6, 130.4, 130.8, 131.0, 131.1, 131.2, 131.5, 131.6, 136.6, 136.7, 142.4, 144.4, 144.5, 144.6, 144.9, 146.3, 146.4, 146.6, 148.3, 151.5, 151.6, 152.8, 153.6 (Some peaks overlapped); HRMS (FAB^+) Calcd for $\text{C}_{45}\text{H}_{38}\text{N}_2\text{O}_6$ (M) $^+$: 702.2730. Found: 702.2729; LR MS (FAB^+) 702.3 (M) $^+$.

4. Determination of configuration of (R)-4.

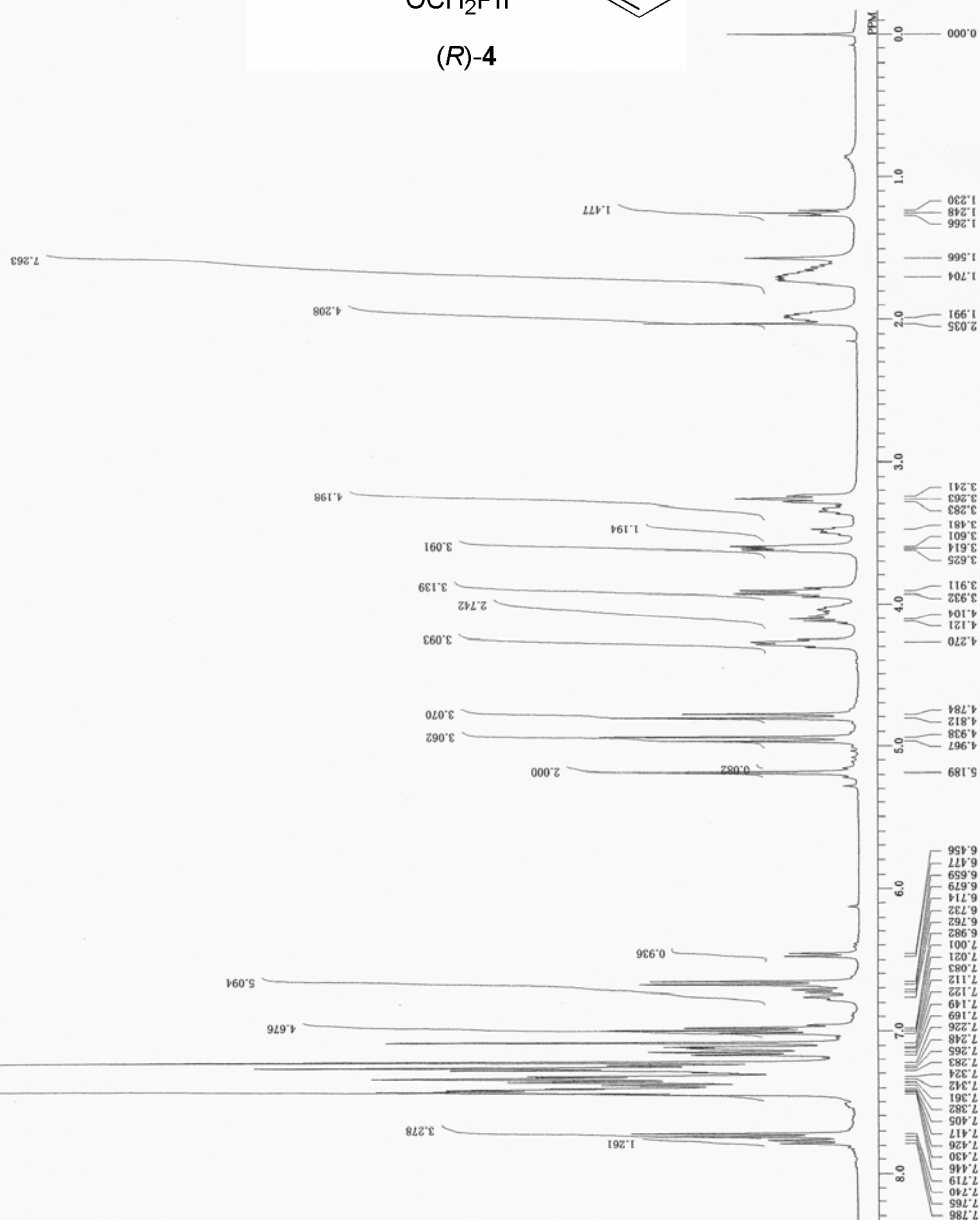
As a precautionary measure, **4** was derivatized to known compound **11**^{SS} to certify that inversion did not occur during the synthesis of **4** from (R)-**2**. Below is a scheme that outlined the derivatization of **4** synthesized from (R)-**2** to **11**. The specific optical rotation of derivatized **11** was +49°, whereas that of known compound (S)-**11** was -52°. Thus, the absolute configuration of **4** synthesized from (R)-**2** was (R) without inversion or racemization.



Tetramethoxybinaphthyl (R)-11.

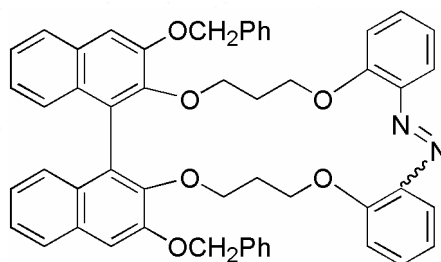
A suspension of (R)-**4** (100 mg, 0.126 mmol) in CH₂Cl₂ (4.5 ml) containing BBr₃ (1.51 mmol, 12 eq.) was stirred for 24 hours at 0 °C. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to afford crude (R)-**10**. Next, a suspension of crude (R)-**10** (ca. 40 mg), K₂CO₃ (139 mg, 1.01 mmol, 8.0 eq.) and MeI (93 μl, 1.51 mmol, 12 eq.) in DMF (2.0 ml) was stirred for 24 hours at room temperature. The reaction mixture was poured into the mixed solvent of ethyl acetate and water. The organic layer was separated and washed successively with 0.1 N hydrochloric acid solution, water (twice) and brine. After dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by preparative TLC (SiO₂; *n*-hexane/chloroform/ethyl acetate = 9/3/1) and GPC and preparative TLC (SiO₂; *n*-hexane/chloroform/ethyl acetate = 8/3/1) to afford (R)-**11** (12 mg, 0.0321 mmol, 25% over 2 steps). Colorless powder; $[\alpha]_{\text{D}}^{20} = +49$ (*c* 0.6, CHCl₃); IR (KBr) 2940, 1464, 1420, 1254, 1117 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.61 (s, 6H), 4.06 (s, 6H), 7.0-7.2 (m, 4H), 7.3-7.5 (m, 4H), 7.78 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 55.6, 60.7, 107.2, 124.0, 125.2, 125.7, 125.9, 126.5, 128.9, 131.2, 147.3, 152.3; HR MS (ESI⁺) Calcd for C₂₄H₂₂O₄Na (M+Na)⁺: 397.1416. Found: 397.1411; LR MS (FAB⁺) 374.2 (M)⁺.

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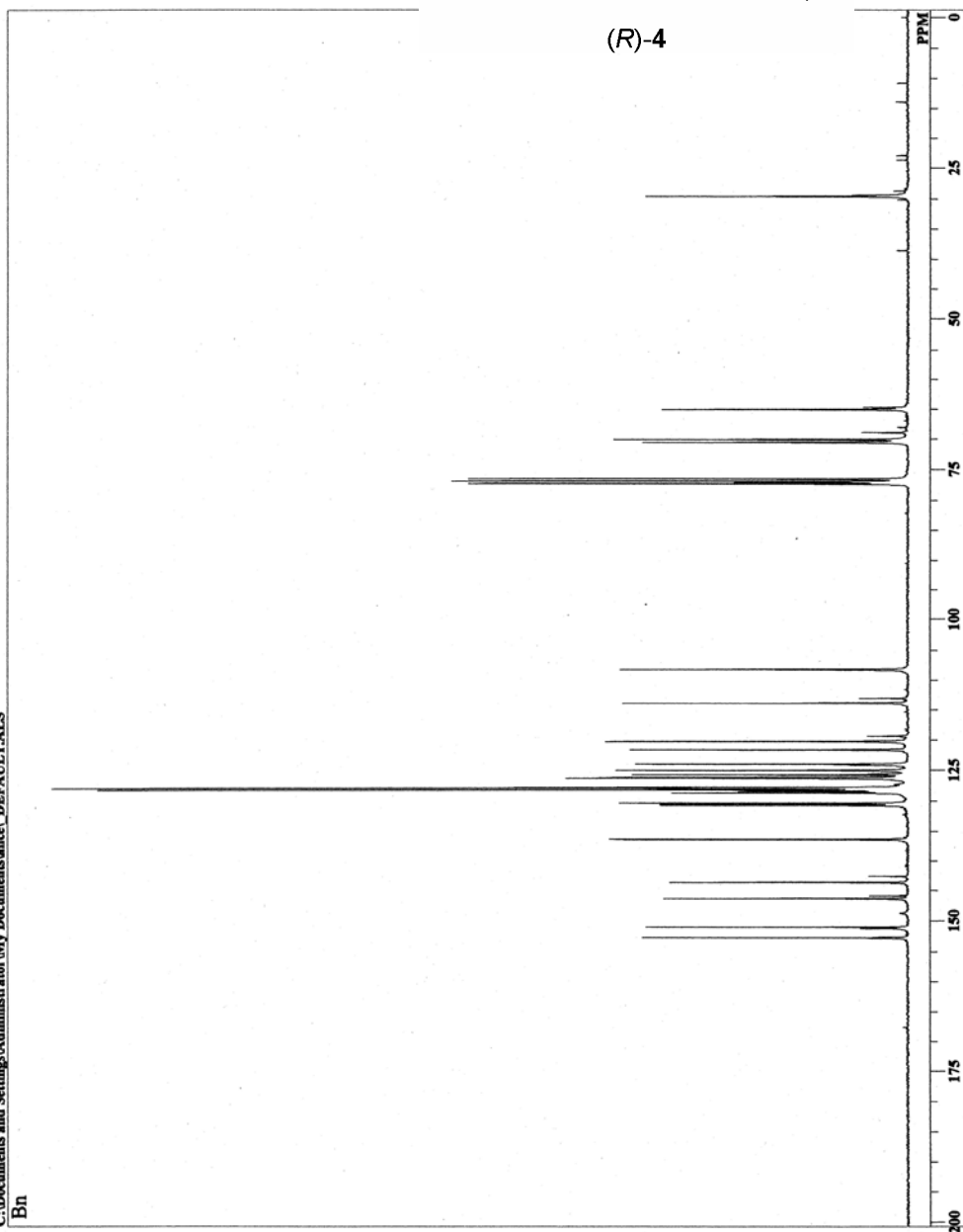


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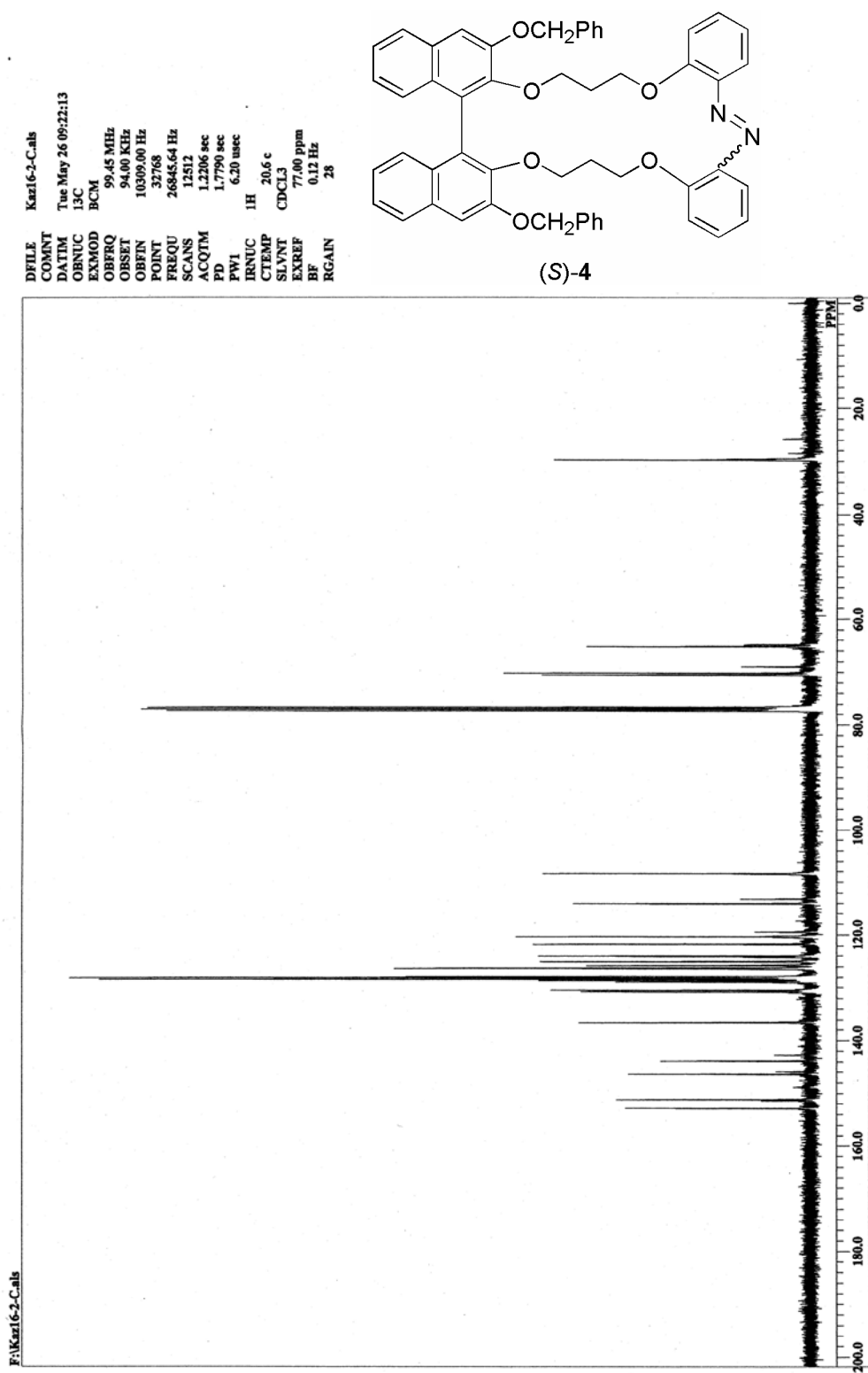


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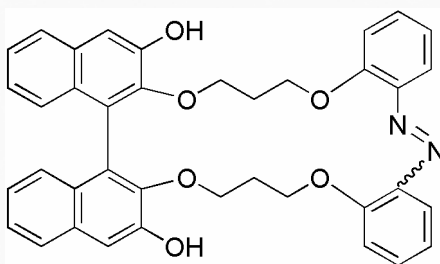


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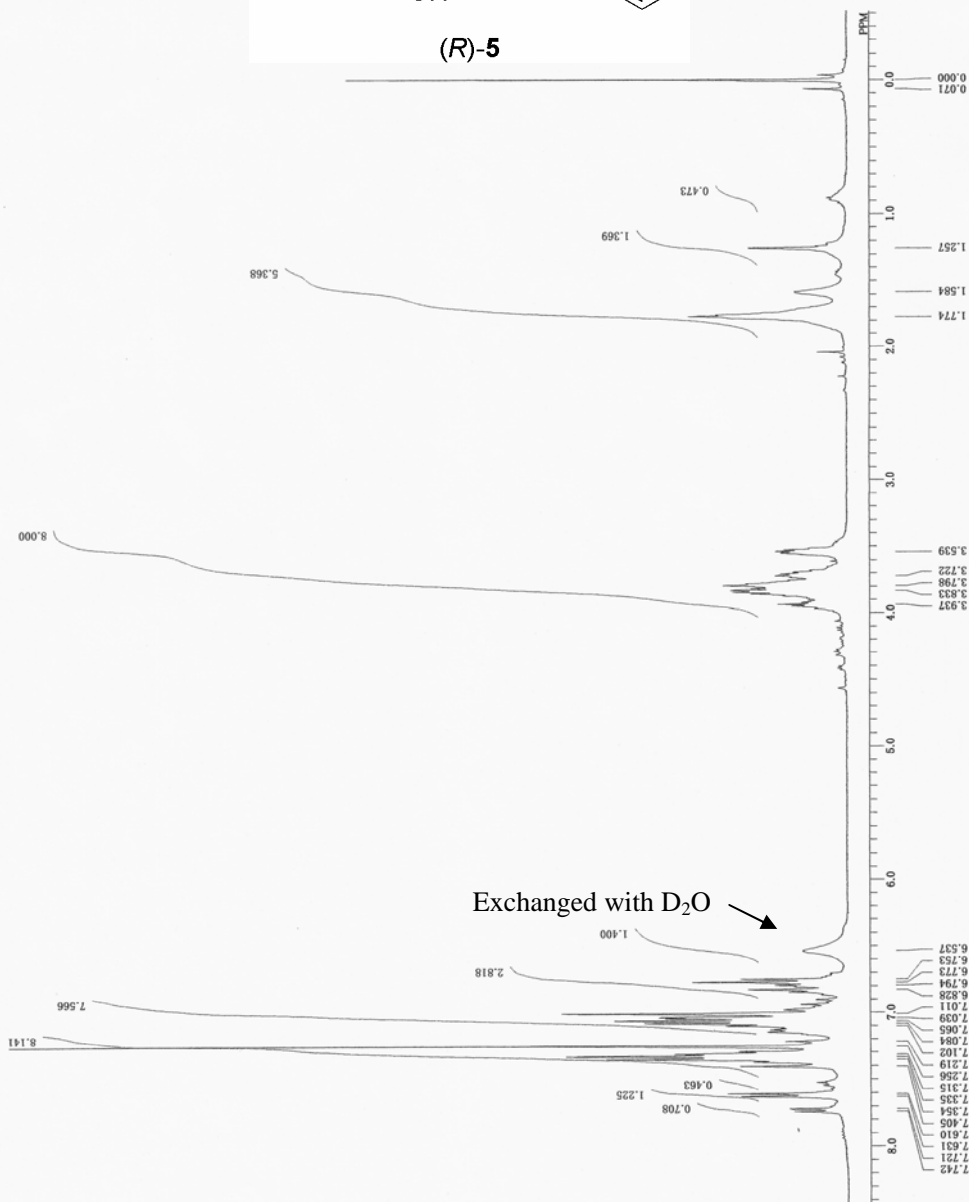




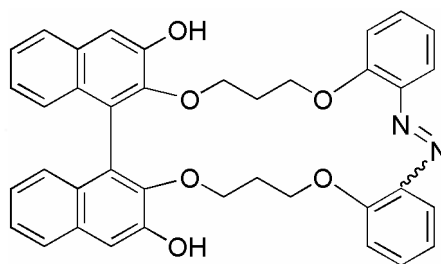
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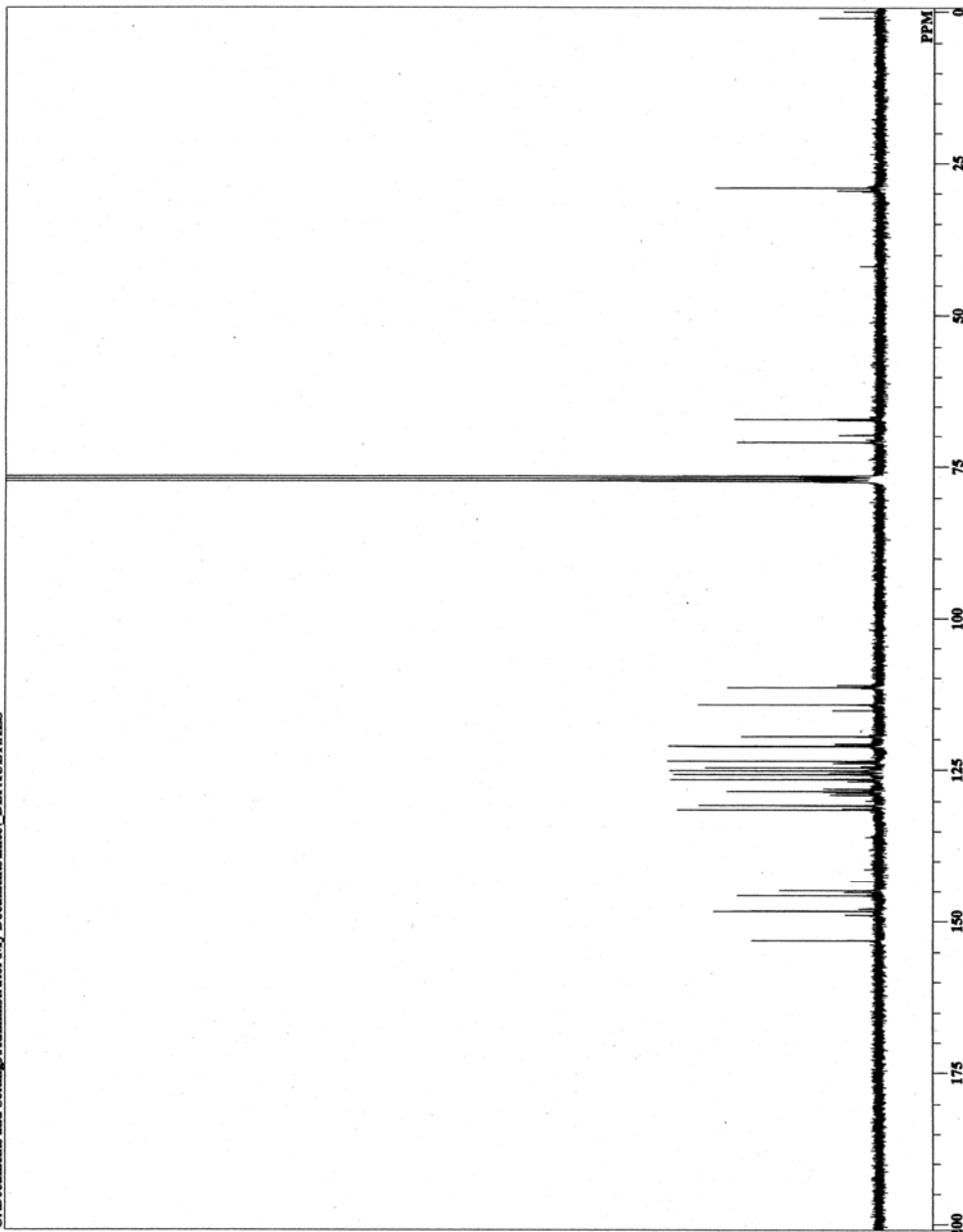
(R)-5



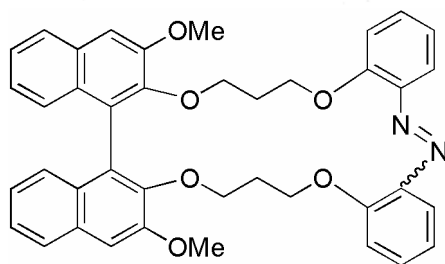
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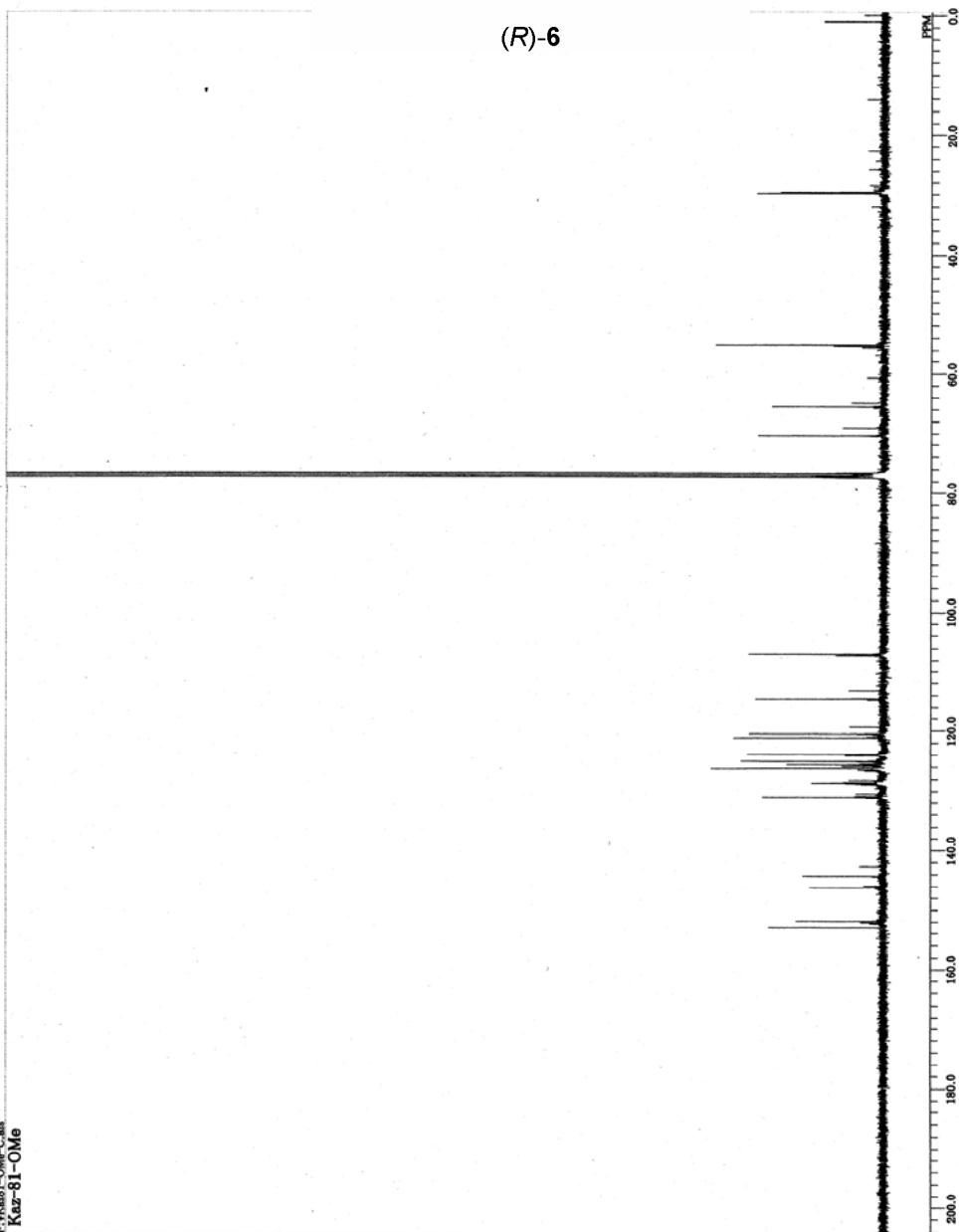
(R)-5



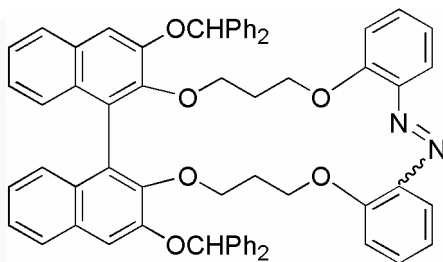
DEFILE	99.45 MHz
COMANT	94.00 MHz
DATIM	109.50 Hz
ORBIT	109.50 Hz
ORNUC	28845.64 Hz
EXMOD	13444
OBRRQ	1.2206 sec
ORSET	1.7790 sec
ORNSN	6.20 usec
POINT	1H 19.9 c
FREQU	CDCL3
SCANS	77.00 ppm
ACQTM	0.12 Hz
PD	28
IRNUC	
IRPMT	
SVANT	
EXREF	
BF	
RGAIN	



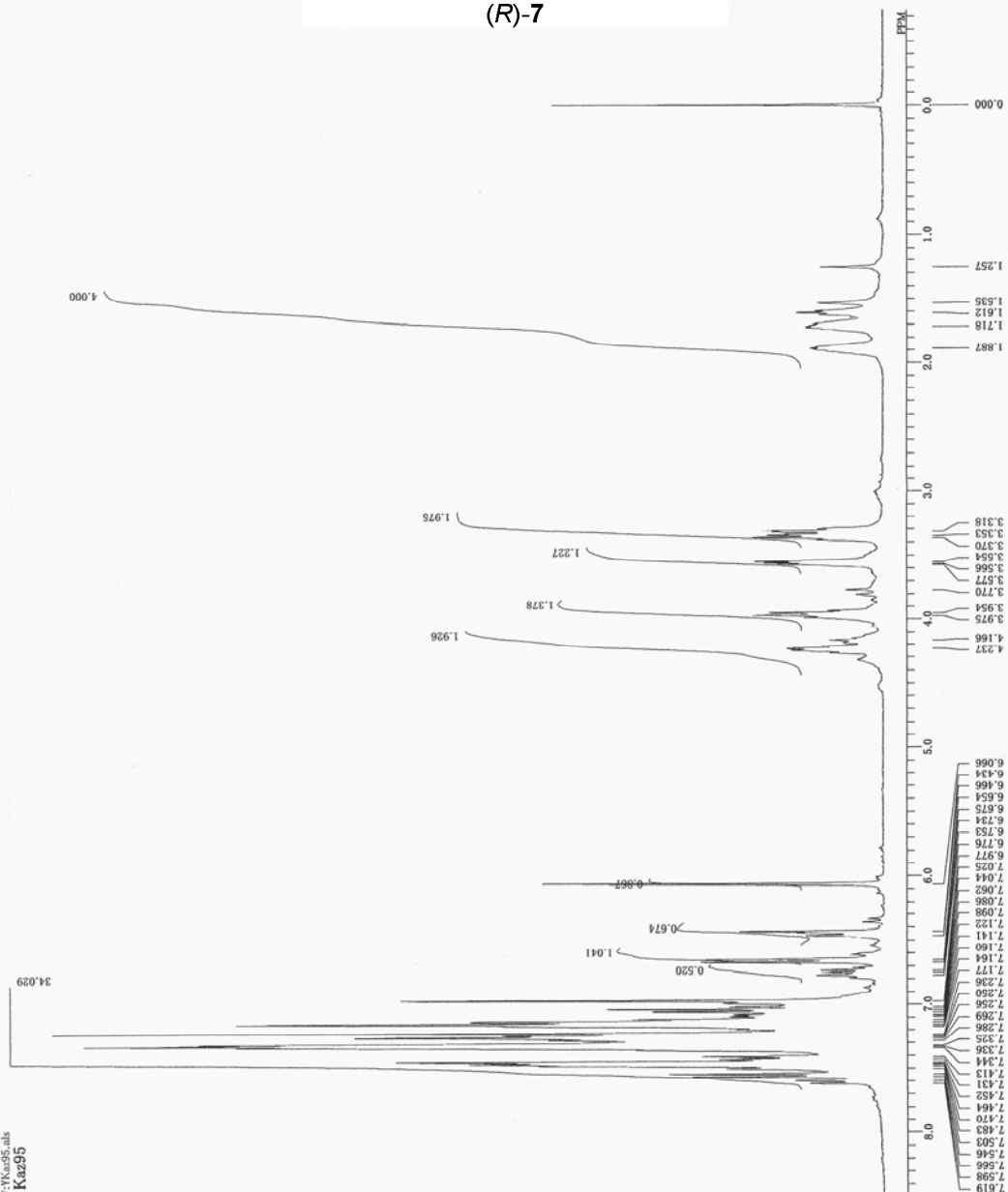
(R)-6



D:\Kaz95\Kaz95_als
 F:\Kaz95\Kaz95_als
 Date: Dec 25 11:24:12 2008
 DATUM 1H
 EXMOD 1H
 OBSFREQ 500.13575 MHz
 OBSFREQ 127.000 MHz
 OBSFREQ 10277.00 Hz
 POINT 16384
 PULPROG zgpg30
 SCANS 32
 ACQTM 2.0705 sec
 PD 4.9250 sec
 DELTA 6.30 usec
 INJ 1H 22.7 °C
 CTMP CDCL3
 SLVNT CDCL3
 REF 0.00 ppm
 BR 0.12 Hz
 RGAIN 13

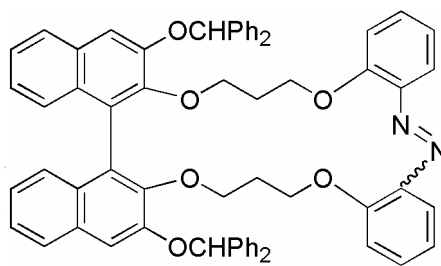


(R)-7

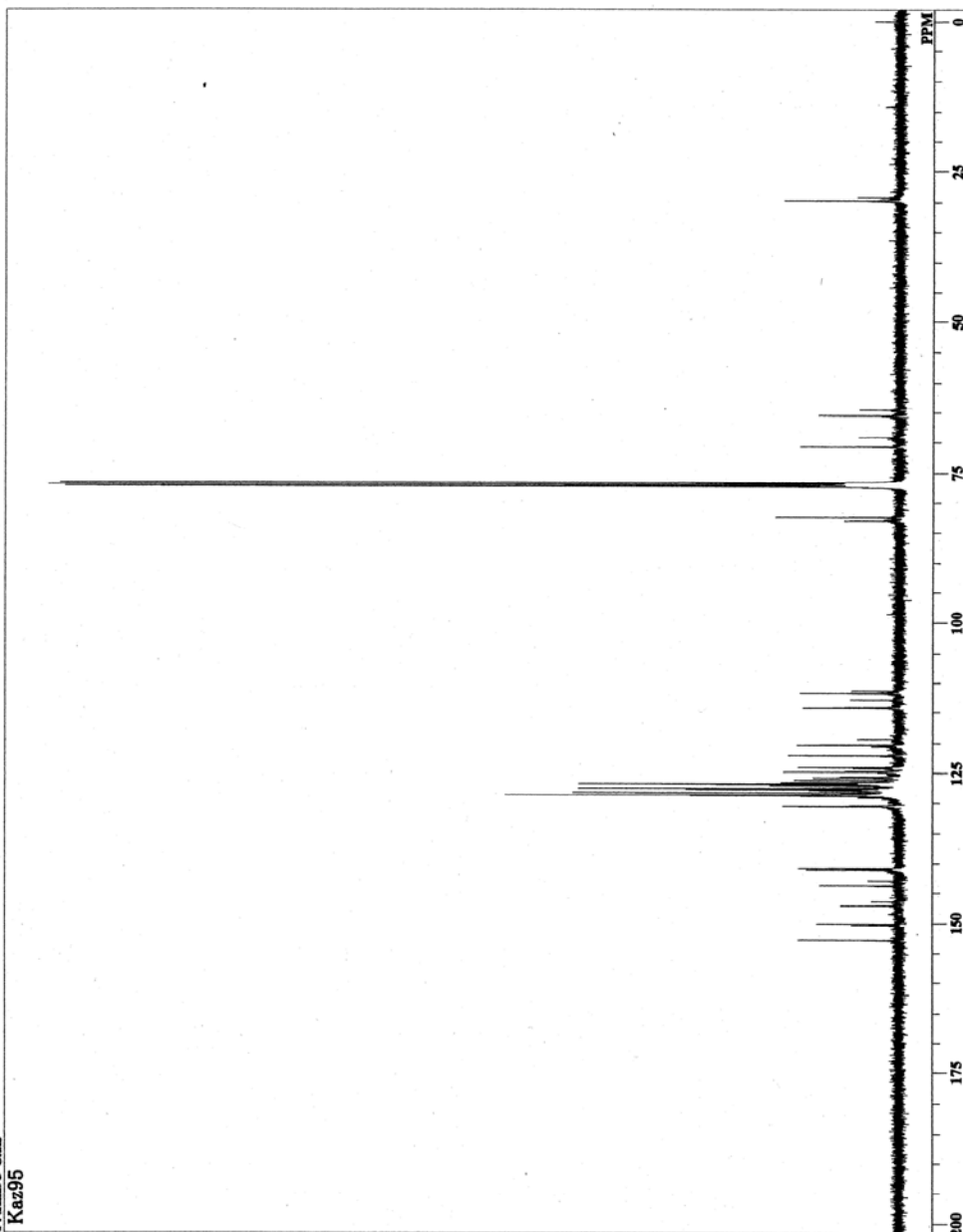


F:\Kaz95-Cals
Kaz95

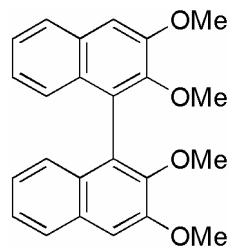
DFILE Kaz95-Cals
COMNT Kaz95
DATIM Sat May 23 10:00:59
ORNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 13442
AQTM 1.2206 sec
PD 1.7790 sec
FW1 6.20 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 28



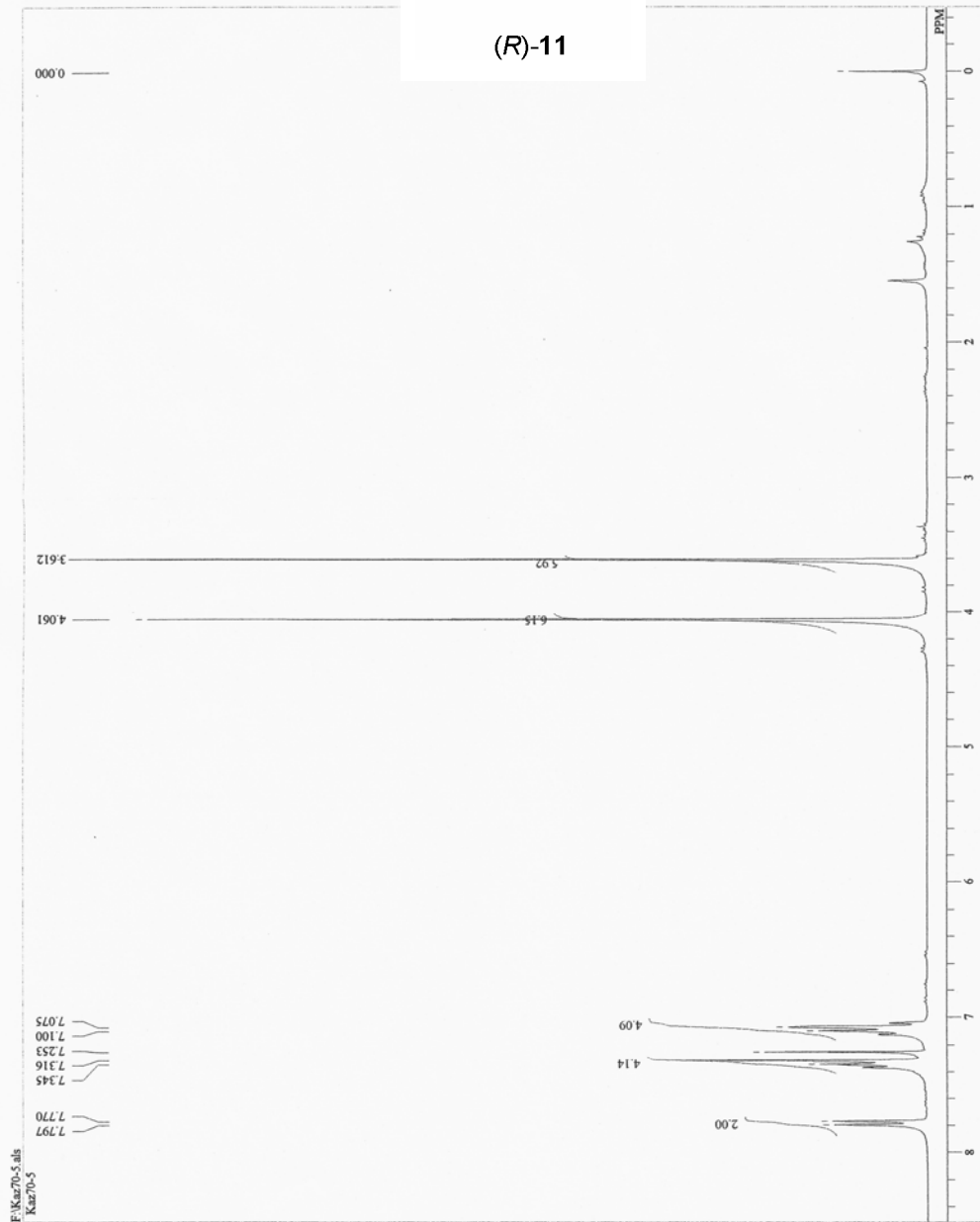
(R)-7



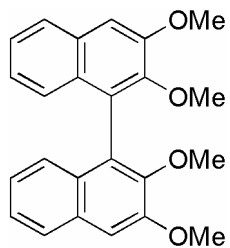
DFILE Kar70-5.als
 CONNT Kar70-5
 DATIM Mon Nov 10 13:56:22 2008
 EXMOD 1H
 OBNUC NON
 OBSFQ 300.40 MHz
 OBSST 130.00 KHz
 OBFIN 1150.00 Hz
 POINT 16384
 FREQU 6006.01 Hz
 SCANS 16
 ACQTM 2.7279 sec
 PD 4.2720 sec
 PW1 5.50 usec
 IRNUC 1H
 CTMP 23.2 c
 SVPRT CDCL3
 EXREF 0.00 ppm
 BF 0.24 Hz
 RGAIN 15



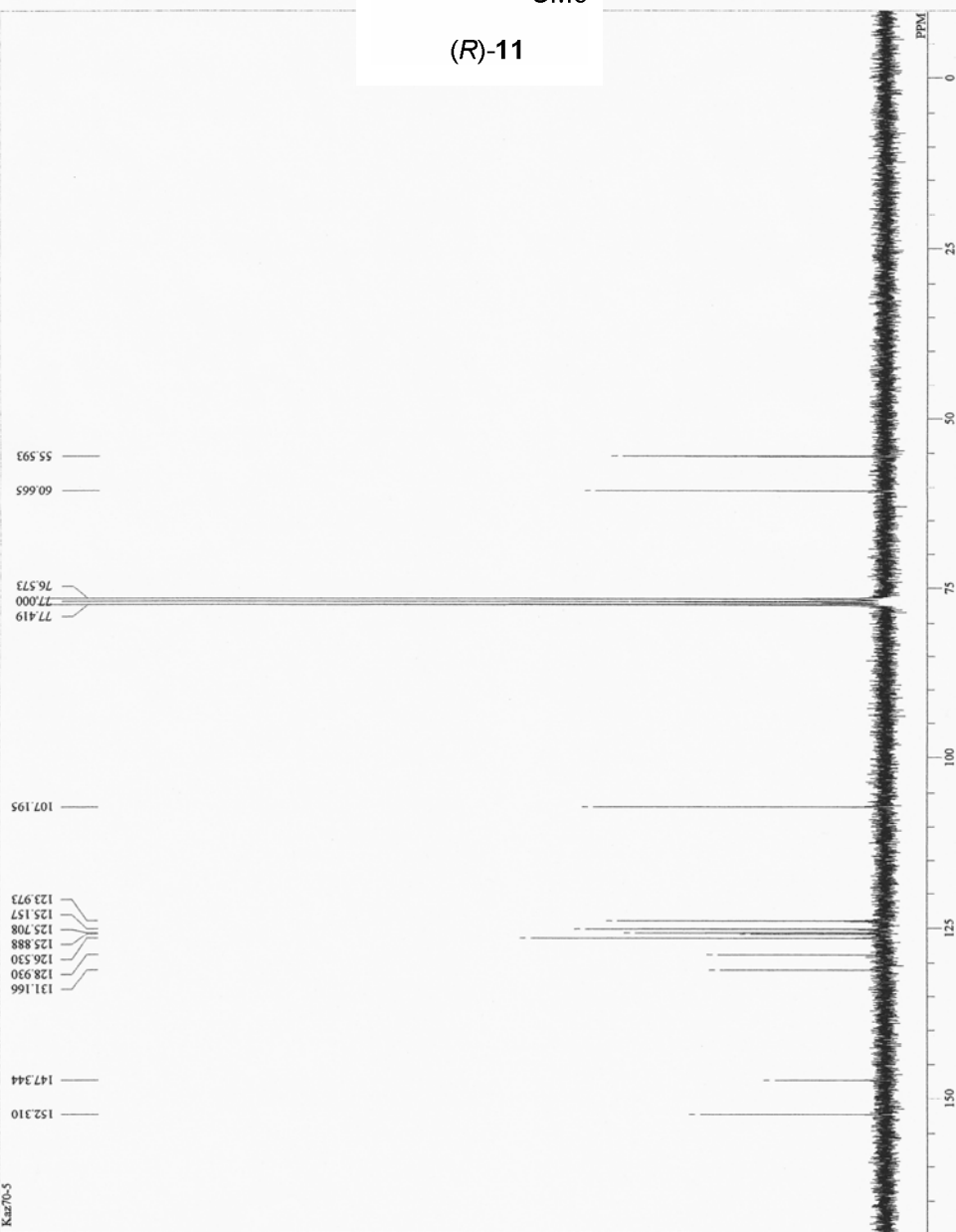
(R)-11



F:\Kar70-5.Calls
 Kar70-5
 DFILE Kar70-5.Calls
 CONNT Kar70-5
 DATIM Mon Nov 10 14:47:21 2008
 OBNUC 13C
 EXMOD BCM
 OBFRQ 75.45 MHz
 OBSET 124.00 KHz
 OBFEN 1840.00 Hz
 POINT 32768
 FREQU 20356.23 Hz
 SCANS 1000
 ACQTM 1.6097 sec
 PD 1.3900 sec
 PW1 4.20 usec
 IRNUC 1H
 CHIRP 22.3 c
 SNUC CDCL₃
 SNUF 77.00 ppm
 EXREF 0.24 Hz
 BF 24
 RGAIN 24



(R)-11



References

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- (S2) Eyring, H. *Chem. Rev.* **1935**, 17, 65.
- (S3) Tsubaki, K.; Morikawa, H.; Tanaka, H.; Fuji, K. *Tetrahedron: Asymmetry* **2003**, 14, 1393-1396.
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