Supporting Information for

Clarification of a Misconception in the BINOL-Based Fluorescent Sensors: Synthesis and Study of Major-Groove BINOL-Amino Alcohols**

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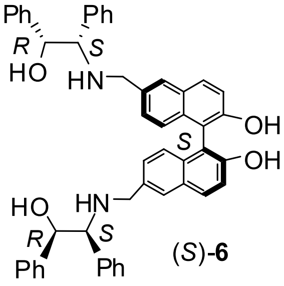
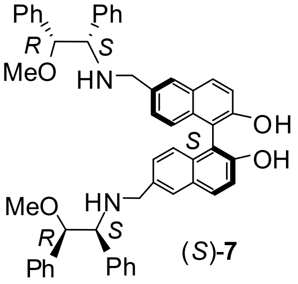
I. Preparation and Characterization of New Compounds



(*S*)-**6**

Under argon, to a 50 mL Schlenk flask were added (*S*)-6,6'-diformylBINOL[1] (224 mg, 0.65 mmol), (1*R*,2*S*)-2-amino-2-phenyl enthanol (378 mg, 1.30 mmol) and anhydrous enthanol (30 mL). The mixture was heated at reflux for overnight, and monitored by using ^{1}H NMR spectroscopy. When the reaction was complete, the solution was cooled to room temperature and dried over anhydrous Na_2SO_4. After filtration and evaporation, the resulting yellow imine product was dissolved in anhydrous methanol (25 mL), and $NaBH_4$ (99 mg, 2.60 mmol) was added to the mixture at 0 °C. The reaction temperature was maintained at 0 °C until the solution became colorless and transparent. It was then allowed to proceed at room temperature for additional 30 min. Methanol was removed, and the residue was dissolved in ethyl acetate (50 mL) and washed with water (15 mL). The aqueous layer after separation was extracted with ethyl acetate (3×30 mL). The combined ethyl acetate layer was washed with brine (15 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel eluted with ethyl acetate/petroleum ether (1/1) to afford (*S*)-**6** as a white solid in 79% yield.

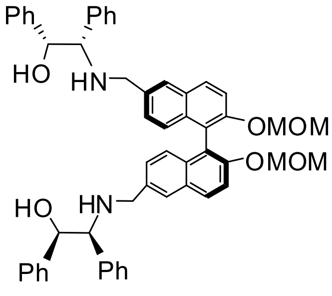
^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.62 (d, J = 13.6 Hz, 2H), 3.77 (d, J = 13.6 Hz, 2H), 3.93 (d, J = 5.6 Hz, 2H), 4.80 (d, J = 6.0 Hz, 2H), 7.03-7.33 (m, 26H), 7.59 (s, 2H), 7.84 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.9, 67.9, 76.8, 111.1, 118.0, 124.5, 126.9, 127.1, 127.7, 127.99, 128.04, 128.3, 128.4, 129.3, 131.0, 132.6, 135.3, 139.0, 140.4, 152.6. ESI-MS *m/z*: 737 ($M+H^+$). HRMS (MALDI) Calcd. for $C_{50}H_{45}N_2O_4$: 737.3374, Found: 737.3358. m.p. 123-125 ℃. $[\alpha]_D$ = +92.1 (c = 0.36, CH_2Cl_2).



(*S*)-**7**

The synthetic procedure is similar to that of (*S*)-**6**. The methylated (1*R*,2*S*)-2-amino-1,2-diphenylenthanol was synthesized according to the literature procedure.[2] The product was purified by flash column chromatography on silica gel eluted with ethyl acetate/petroleum ether (1/1) to afford (*S*)-**7** as a white solid in 55% yield.

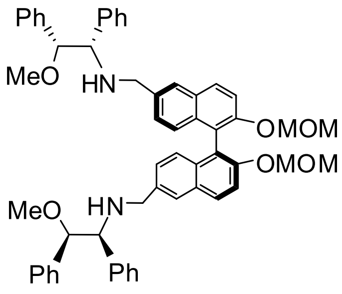
^1H NMR ($CDCl_3$, 400 MHz) δ 2.97 (s, 6H), 3.37 (d, J = 13.6 Hz, 2H), 3.54 (d, J = 13.6 Hz, 2H), 3.75 (d, J = 6.0 Hz, 2H), 4.28 (d, J = 6.0 Hz, 2H), 6.88-6.98 (m, 8H), 7.08-7.19 (m, 18H), 7.41 (s, 2H), 7.66 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.5, 57.0, 66.8, 87.2, 111.7, 117.9, 124.5, 127.0, 127.2, 127.7, 127.82, 127.85, 127.9, 128.0, 128.3, 128.7, 129.1, 130.6, 132.6, 138.6, 152.5. ESI-MS *m/z*: 765 ($M+H^+$). HRMS (MALDI) Calcd. for $C_{52}H_{48}N_2O_4Na$: 787.3506; Found: 787.3488. m.p. 119-121℃. $[\alpha]_D$ = +60 (c = 0.26, CH_2Cl_2).



(*S*)-**8**

The synthesis procedure is similar to that of (*S*)-**6**. The product was purified by flash column chromatography on silica gel eluted with ethyl acetate/petroleum ether (1/3) to afford (*S*)-**8** as a white solid in 84% yield.

^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.18 (s, 6H), 3.66 (d, J = 13.6 Hz, 2H), 3.83 (d, J = 13.6 Hz, 2H), 3.97 (d, J = 6.0 Hz, 2H), 4.86 (d, J = 6.0 Hz, 2H), 4.98 (d, J = 6.8 Hz, 2H), 5.07 (d, J = 6.8 Hz, 2H), 7.07-7.31 (m, 24H), 7.56 (s, 2H), 7.59 (d, J = 11.6 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 50.9, 55.8, 67.9, 76.8, 95.2, 117.5, 121.2, 125.7, 126.4, 126.8, 127.6, 127.7, 128.0, 128.2, 128.3, 129.1, 129.7, 133.2, 135.4, 139.1, 140.4, 152.5. ESI-MS *m/z*: 825 (M+H$^+$). HRMS (MALDI) Calcd. for $C_{54}H_{53}N_2O_6$:825.3898, Found: 825.3891. m.p. 78-80 ℃. $[\alpha]_D$ = +12.6 (c = 0.41, CH_2Cl_2).



(*S*)-**10**

The synthetic procedure is similar to that of (*S*)-**6**. The product was purified by flash column chromatography on silica gel eluted with ethyl acetate/petroleum ether (1/2) to afford (*S*)**-10** as a white solid in 75% yield.

^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.11 (s, 6H), 3.16 (s, 6H), 3.52 (d, *J* = 13.6 Hz, 2H), 3.72 (d, *J* = 13.6 Hz, 2H), 3.87 (d, *J* = 6.0 Hz, 2H), 4.36 (d, *J* = 6.0 Hz, 2H), 4.96 (d, *J* = 6.8 Hz, 2H), 5.05 (d, *J* = 6.8 Hz, 2H), 6.96-6.99 (m, 4H), 7.02-7.13 (m,4H), 7.21-7.28 (m, 16H), 7.53 (d, *J* = 6.4 Hz, 2H), 7.55 (s, 2H), 7.83 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 50.7, 55.8, 57.0, 66.9, 84.3, 87.5, 95.3, 117.4, 121.3, 125.6, 125.9, 126.4, 126.9, 127.2, 127.8, 127.9, 128.0, 128.7, 129.1, 129.7, 133.1, 135.6, 138.8, 152.4. ESI-MS *m/z*: 853 (M+H$^+$). HRMS (MALDI) Calcd. for $C_{56}H_{57}N_2O_6$: 853.4211; Found: 853.4216. m.p. 59-61℃. $[\alpha]_D$ = +7.9 (c = 0.31, CH_2Cl_2).

II. Preparation of Samples for Fluorescence Measurements.

Materials: The sensors were purified by column chromatography, and stored in refrigerator. The mandelic acid enantiomers (>99%) were obtained after recrystallization from methanol. All of the solvents were HPLC grade. The benzene stock solutions of the sensors were freshly prepared for each measurement. A 0.04 M stock solution of mandelic acid was freshly prepared using benzene containing 2% (v) DME. DME was added to improve the solubility of the acid. For the fluorescence enhancement study, a sensor solution was mixed with the mandelic acid solution at room temperature in a volumetric flask and diluted to the desired concentration. The resulting solution was allowed to stand at room temperature for 1 h and shaken well-distributed before the fluorescence measurement. The measurements were carried out with the HITACHI F-4500 fluorescence spectrometer.

III. UV and Fluorescence Spectra.

Figure S1. UV Spectra of Sensor (*S*)-**3** in Benzene at Various Concentrations. (reported in the supporting material of reference [3])

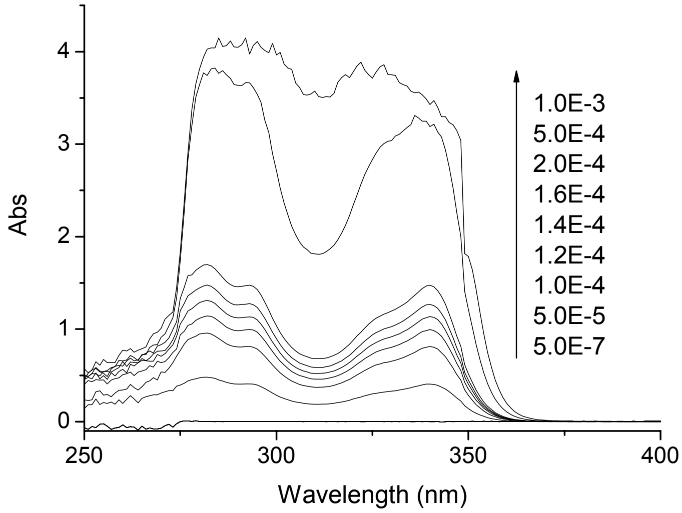


Figure S2. Fluorescence Spectra of (*S*)-**3** in Benzene at Various Concentrations (λ_{exc} = 341 nm, slit = 5.0/5.0 nm). (reported in the supporting material of reference [3])

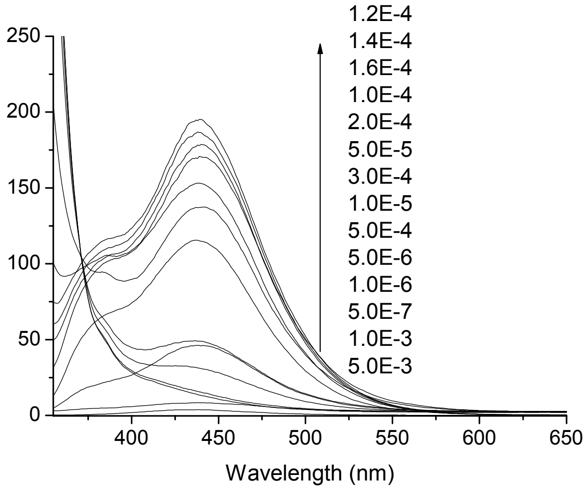


Figure S3. Fluorescence Spectra of (*S*)-**3** in benzene at 1.0×10^{-5} and 5.0×10^{-6} M (λ_{exc}=341 nm, slit: 2.5/2.5 nm). (Low scan speed and narrow slit were used in order to avoid the interference of the scattered light at the low concentrations. The solvent background signal and noise signals were subtracted).

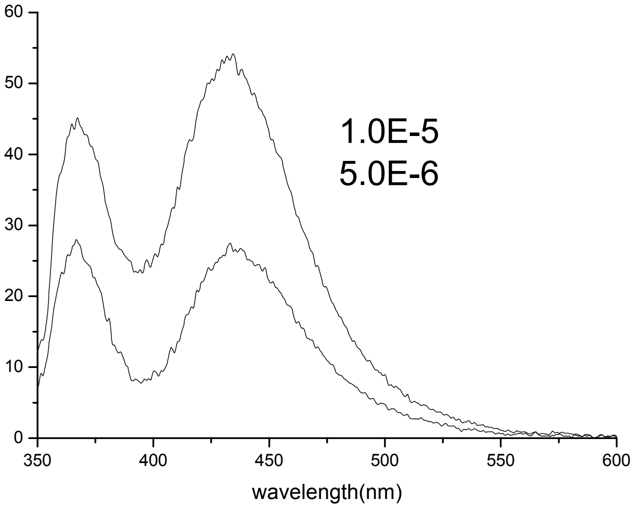


Figure S4. Fluorescence Spectra of Sensor (*S*)-**3** (5.0×10^{-4} M) in Benzene/Methanol Solutions (λ_{exc} = 341 nm, slit = 5.0/5.0 nm). (reported in the supporting material of reference [3].)

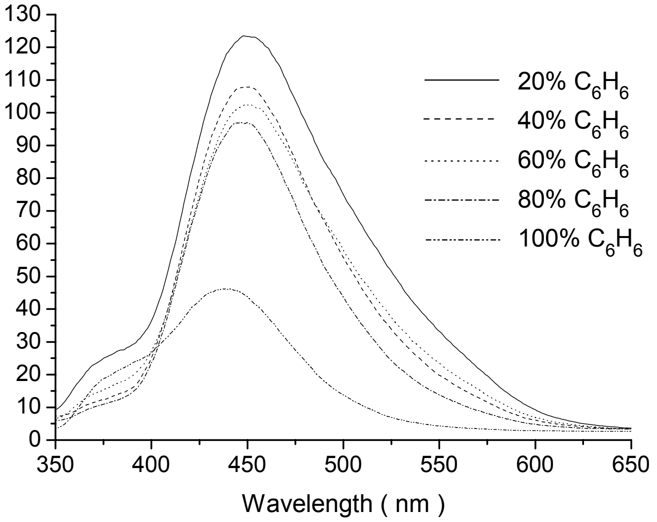


Figure S5. UV Spectra of Sensor (*S*)-**3** (5.0×10^{-4} M) in Benzene /Methanol Solutions. (reported in the supporting material of reference [3])

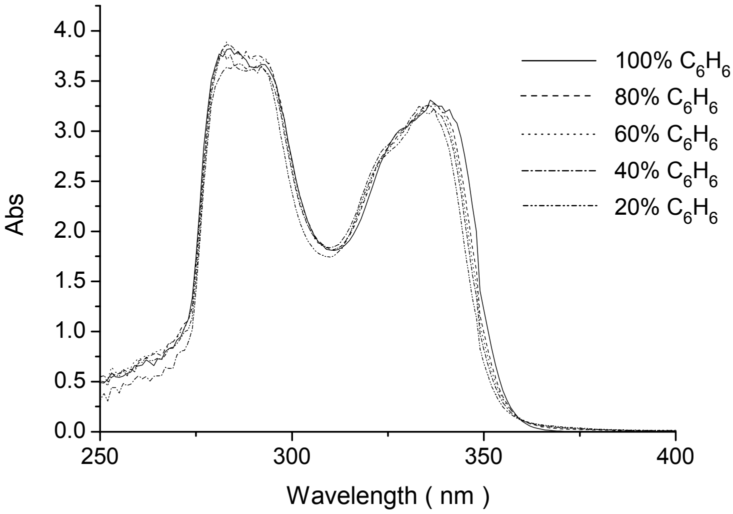


Figure S6. UV Spectra of (*S*)-**6** in Benzene at Various Concentrations.

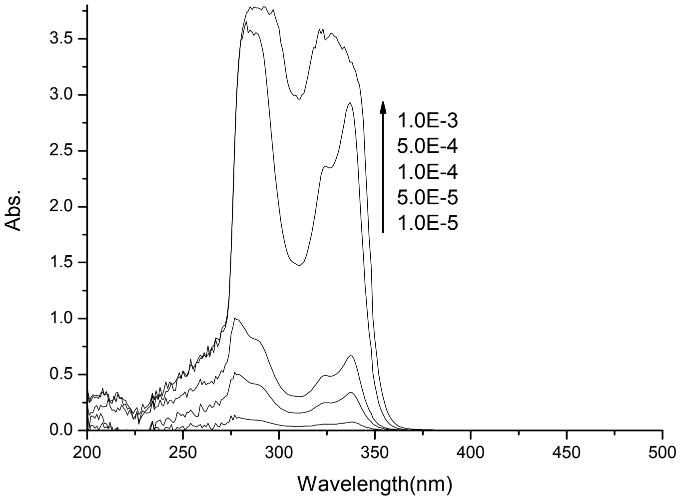


Figure S7. UV Spectra of (*S*)-**6** in CH_2Cl_2 at Various Concentrations.

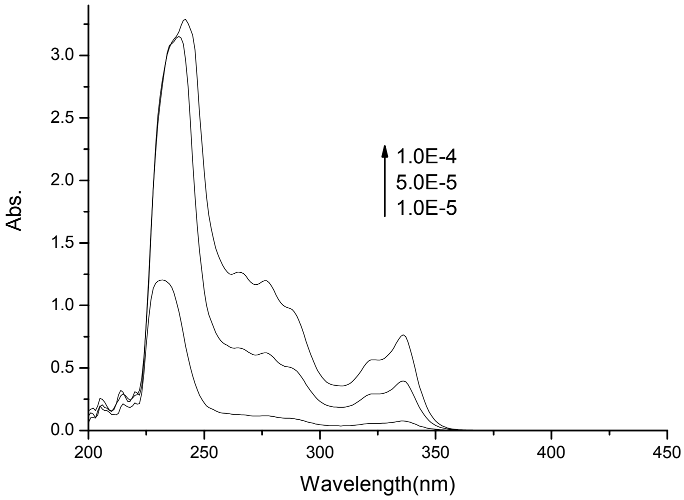


Figure S8. Fluorescence Spectra of (*S*)-**6** in Benzene at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

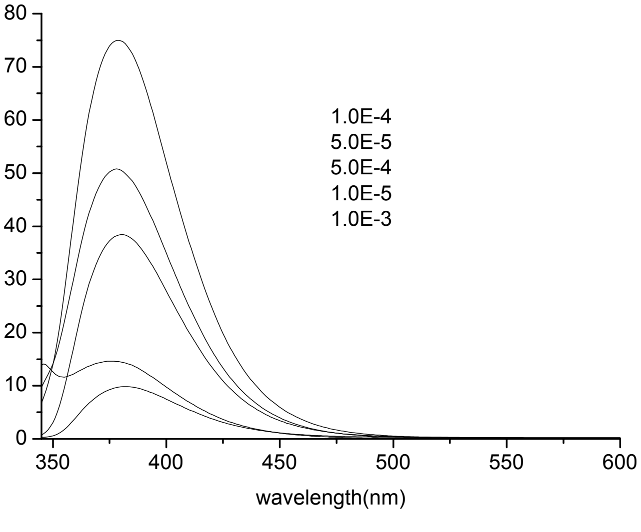


Figure S9. Fluorescence Spectra of (*S*)-**6** in CH_2Cl_2 at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

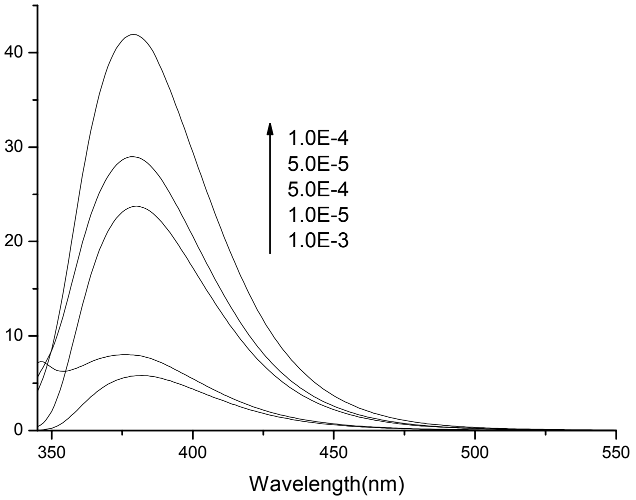


Figure S10. UV Spectra of (*S*)-**7** in Benzene at Various Concentrations.

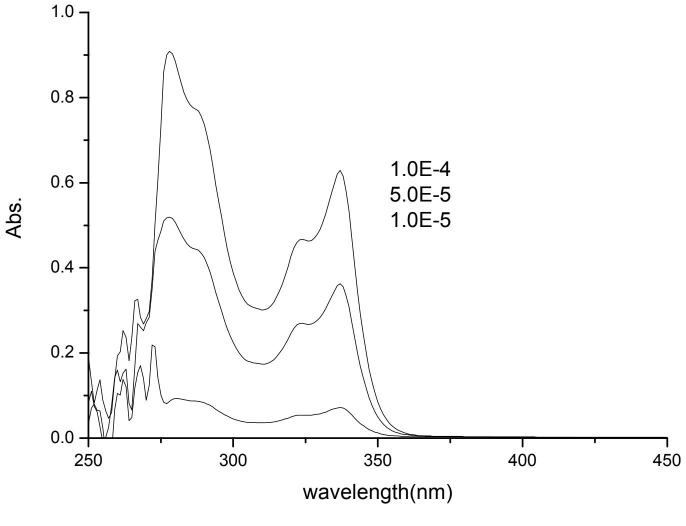


Figure S11. Fluorescence Spectra of (*S*)-**7** in Benzene at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

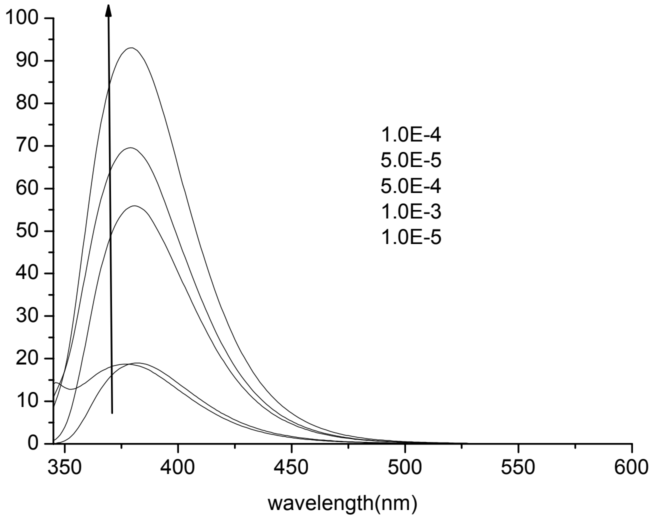


Figure S12. UV Spectra of (*S*)-**8** in Benzene at Various Concentrations.

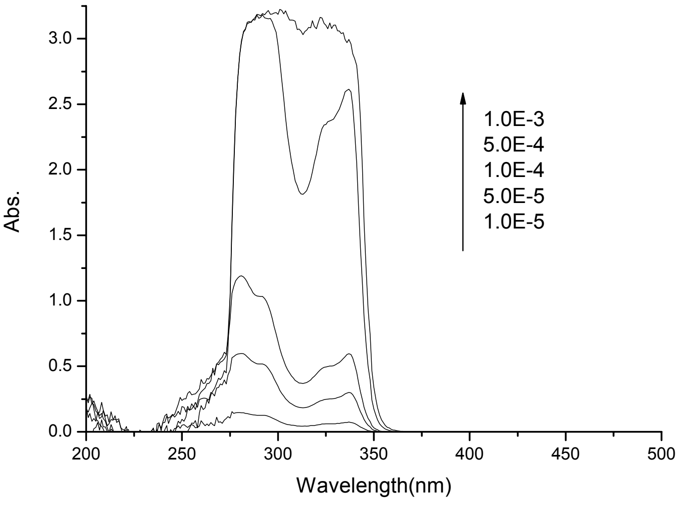


Figure S13. UV Spectra of (*S*)-**8** in CH_2Cl_2 at Various Concentrations.

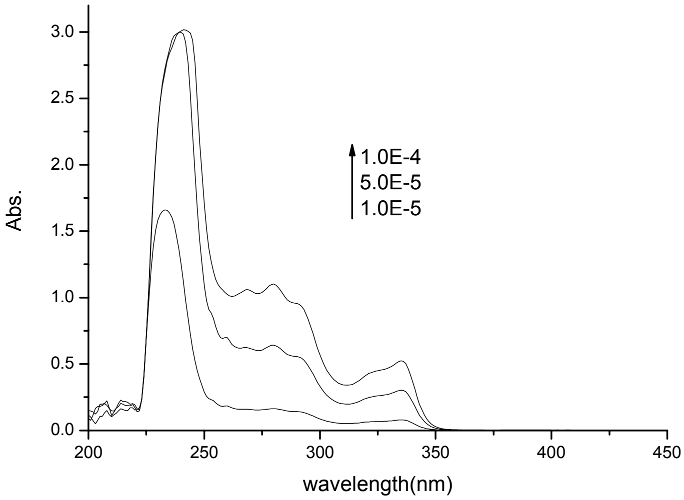


Figure S14. Fluorescence Spectra of (*S*)-**8** in Benzene at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

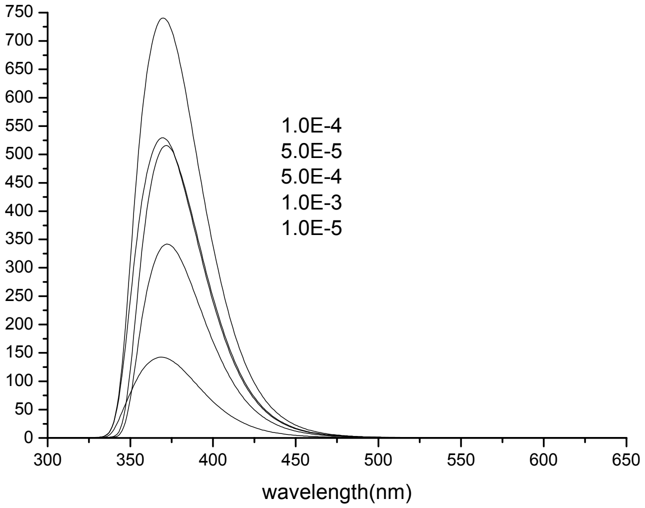


Figure S15. Fluorescence Spectra of (*S*)-**8** in CH_2Cl_2 at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

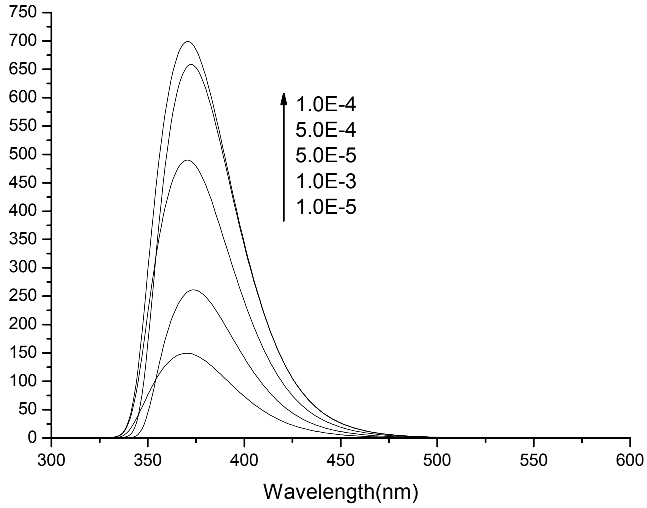


Figure S16. UV Spectra of (*S*)-**9** in Benzene at Various Concentrations.

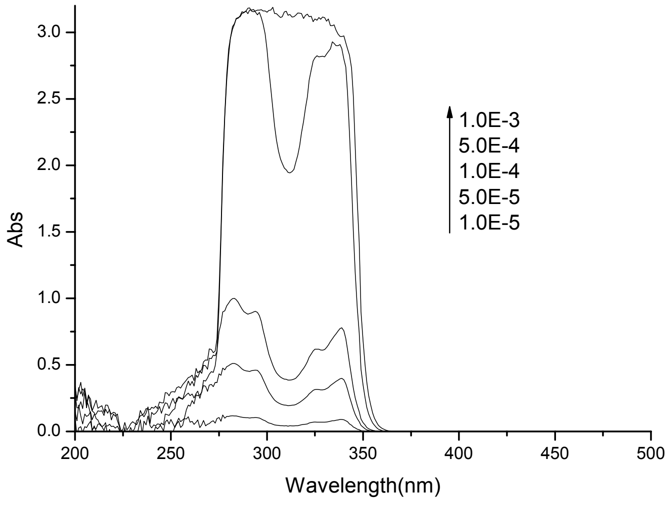


Figure S17. Fluorescence Spectra of (*S*)-**9** in Benzene at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

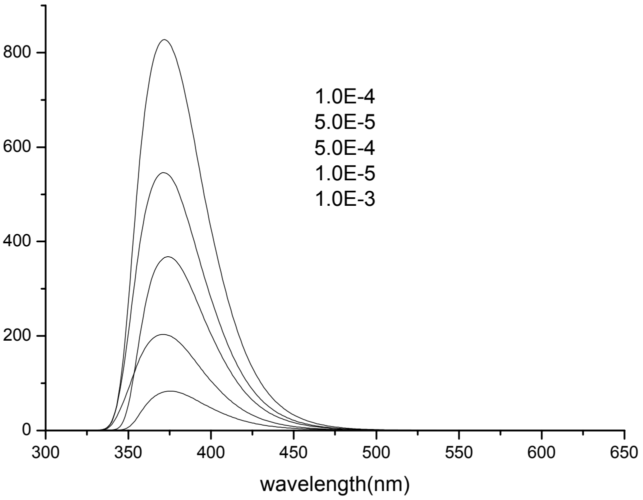


Figure S18. UV Spectra of (*S*)-**10** in Benzene at Various Concentrations.

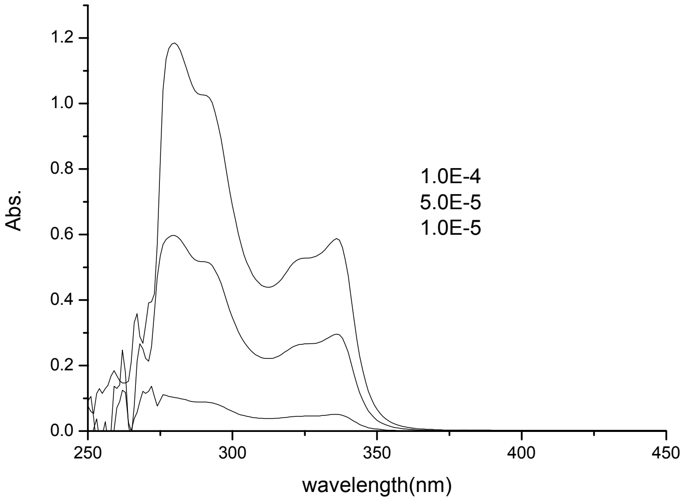


Figure S19. Fluorescence Spectra of (*S*)-**10** in Benzene at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

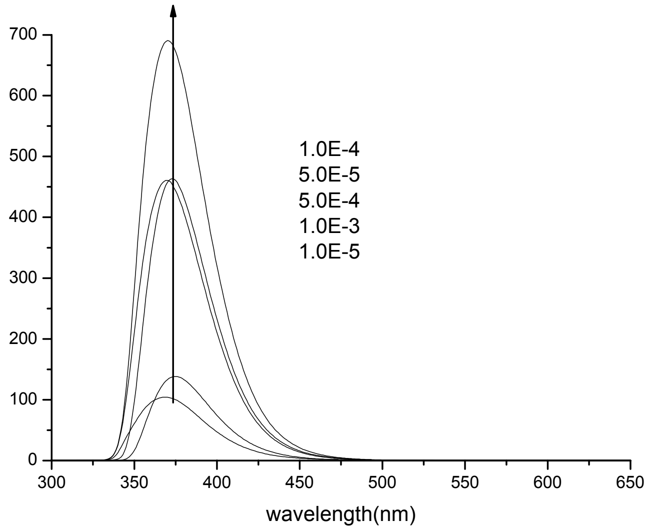


Figure S20. UV Spectra of (*S*)-BINOL in Benzene at Various Concentrations.

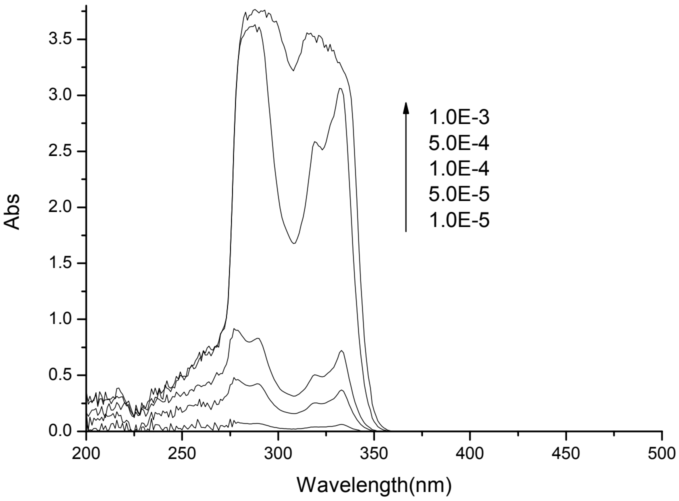


Figure S21. Fluorescence Spectra of (*S*)-BINOL in Benzene at Various Concentrations.(λ_{exc}=341 nm, slit: 5.0/5.0 nm)

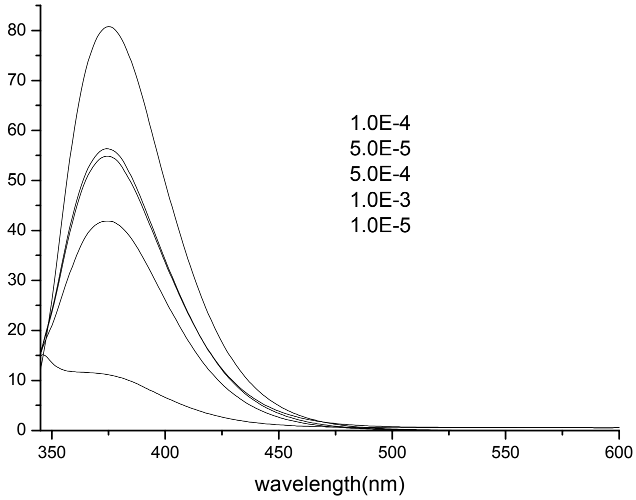


Figure S22. Enantioselective Fluorescence Enhancement Excess of (*S*)-**6** with Various Concentrations of (*R*)- and (*S*)-Mandelic Acid at λ_{em}=381 nm (4.0×10^{-3} M in Benzene Containing 0.4% DME) (λ_{exc}=341 nm, slit: 5.0/5.0 nm)

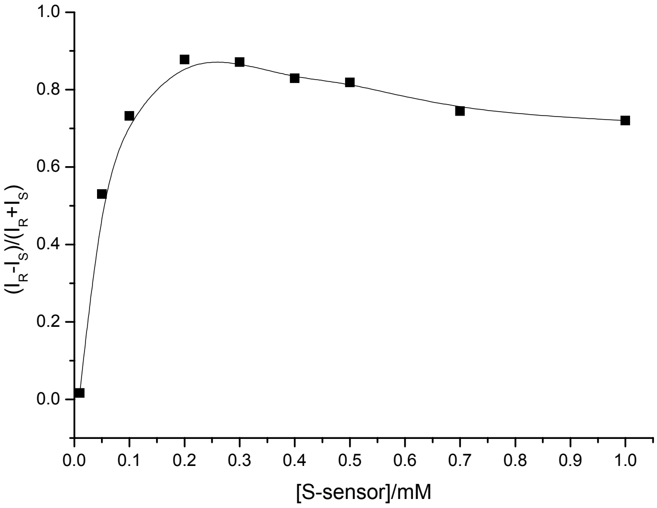
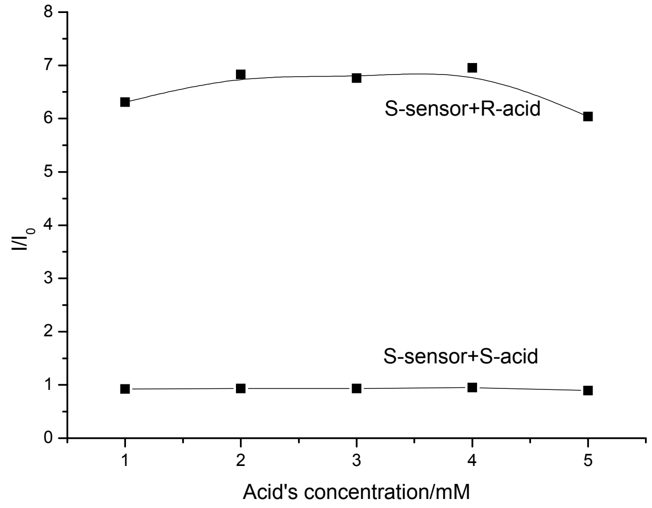


Figure S23. Fluorescence Enhancement of (*S*)-**6** (2.0×10^{-4} M) at λ_{em}=381 nm with (*R*)- and (*S*)-Mandelic Acid at Various Concentration in Benzene Containing 0.4% DME. (λ_{exc}=341 nm, slit: 5.0/5.0 nm)



IV. Images for the Interaction of (*S*)-6 and (*R*)-6 with (*R*)- and (*S*)-Mandelic Acids.

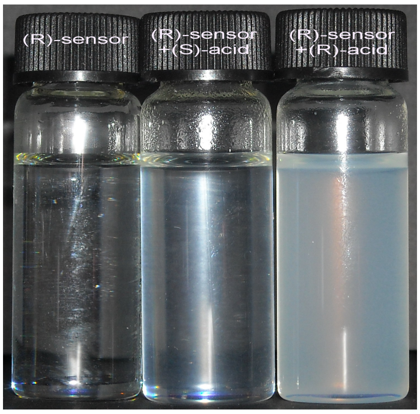
Figure S24. The Images of the Sensor (*S*)-**6** (2.0×10^{-4} M) with (*R*)- and(*S*)-Mandelic acid at 4.0×10^{-3} M in Benzene (0.4% v DME).

Figure S25. The Images of the Sensor (*S*)-**6** (2.0×10^{-4} M) with (a) (*R*)- and (b) (*S*)-Mandelic acid in Benzene (0.4% v DME).

(a)

(b)

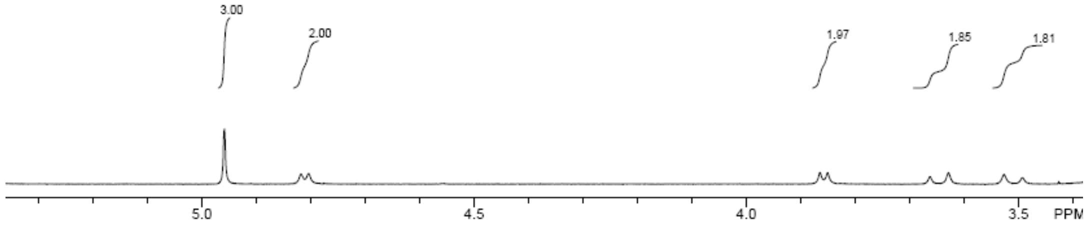
Figure S26. The Images of the Enantiomeric Sensor (*R*)-**6** (2.0×10^{-4} M) with (*R*)- and (*S*)-Mandelic acid at 4.0×10^{-3} M in Benzene (0.4% v DME).



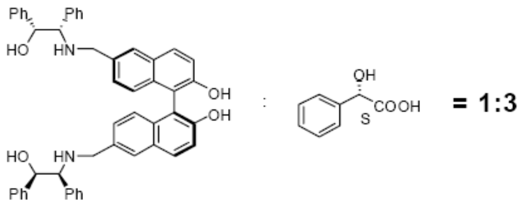
V. NMR Spectra of the Precipitates of (*S*)-6 with (*R*)- and (*S*)-Mandelic Acids

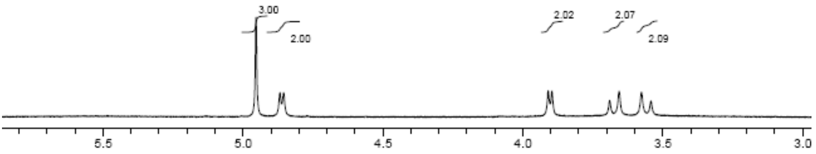
Figure S27. ^{1}H NMR (DMSO-*d*$_{6,}$ 400 MHz) Spectra of the Precipitate Generated by Sensor (*S*)-**6** (2.0□10^{-4} M) with (a) (*R*)- and (b) (*S*)-Mandelic acid in Benzene (0.4 % v DME) at 4.0□10^{-3} M.

(a) (*S*)-**6**:(*R*)-Mandelic acid = 1:3.



(a) (*S*)-**6**:(*S*)-Mandelic acid = 1:3.





(b)

VI. Measurement of the Fluorescence Quantum Yields of the Chiral Sensors.[4]

The fluorescence quantum yields of above sensors were estimated by using a quinine sulfate solution in 1N H_2SO_4 ($\phi_F = 0.546$) as the standard. The fluorescence spectra were recorded on a HITACHI F-4500 Spectrofluorometer. The excitation wavelength was 341 nm. The excitation slit was set at 2.5 nm and the emission slit at 2.5 nm. The scan speed was set at 240 nm/min. After subtracting the solvent background signal and noise signals, the integration of the area under the fluorescence signal of the sensor was calculated from 350 nm to 650 nm. The UV spectra were recorded with HITACHI U-2900 Spectrophotometer. The measured maximum absorbances of the sensors in benzene at $\square_{\mathrm{ab,max}}$ were shown in the following table. As the emission signal of the standard does not exactly match with those of the compounds, the quantum yields provided here are only estimates.

Sensor	*A*	*a*	ϕ_F
(*S*)-**3**	0.082	2565.854	0.41%
(*S*)-**6**	0.061	29793.394	6.34%
(*S*)-**7**	0.066	31796.651	6.26%
(*S*)-**8**	0.061	228899.905	48.7%
(*S*)-**9**	0.069	344227.051	64.8%
(*S*)-**10**	0.065	229974.265	46.0%
(*S*)-BINOL	0.086	15957.124	2.4%
quinine sulfate	0.059	312111.135	54.6%

Following equation is applied to calculate the quantum yield:

$$\phi_F = \phi_{F,\mathrm{ref}}\left(\frac{A_{\mathrm{ref}}}{A}\right)\left(\frac{n_D}{n_{D,\mathrm{ref}}}\right)^2\left(\frac{a}{a_{\mathrm{ref}}}\right)$$

Wherein $\phi_{F,ref}$, A_{ref}, $n_{D,ref}$ and a_{ref} are the reference quantum yield, the reference absorbance, the refraction index of the solvent of the reference, and the integration of the area under the fluorescence signal of the reference, respectively.

Figure S28. UV Spectrum of Quinine Sulfate Solution at 1.0×10^{-5} M in 1N H_2SO_4 for Fluorescence Quantum Yield Measurement.

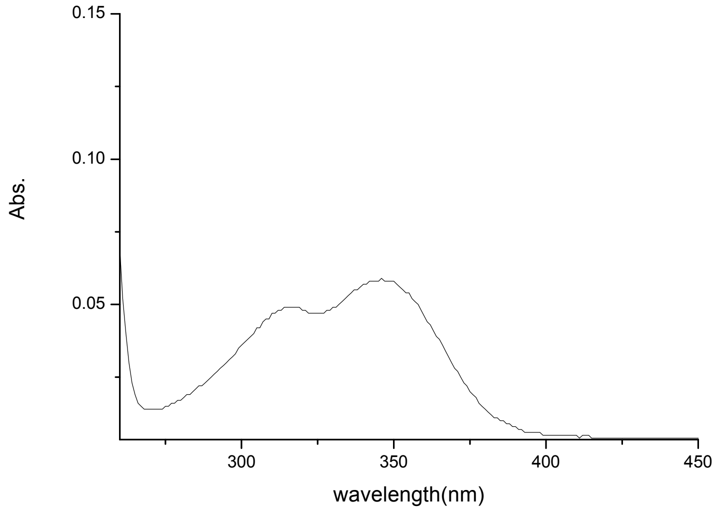


Figure S29. Fluorescence Spectrum of Quinine Sulfate Solution in 1N H_2SO_4 for Fluorescence Quantum Yield Measurement (λ_{exc}=341 nm, slit: 2.5/2.5 nm)

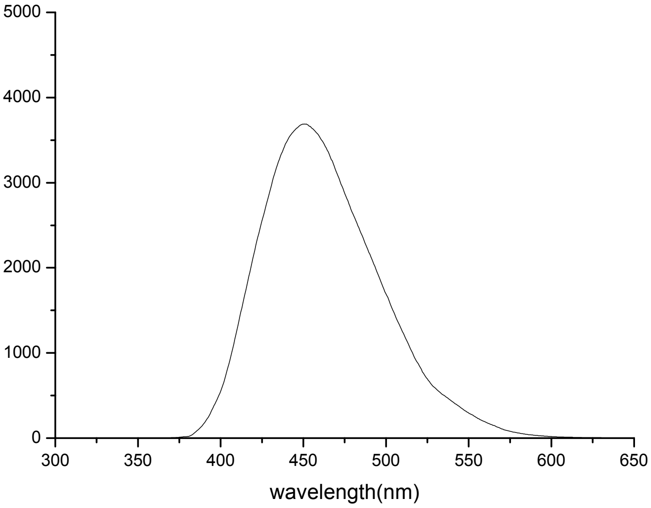


Figure S30. UV Spectrum of (*S*)-**3** at 1.0×10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement.

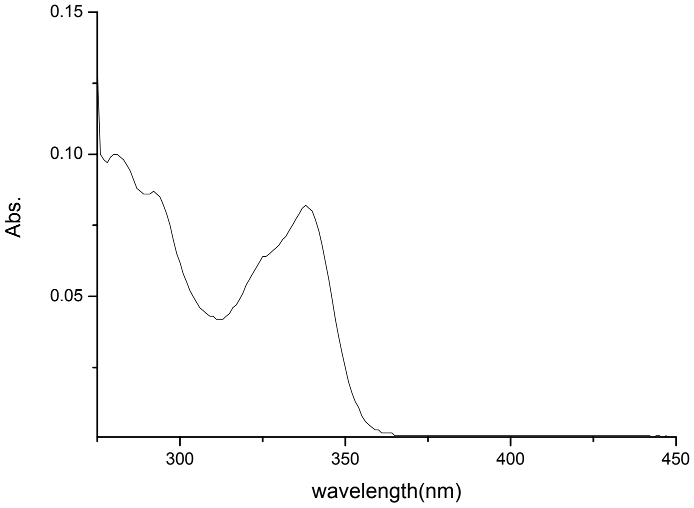


Figure S31. Fluorescence Spectrum of (*S*)-**3** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement. (□$_{exc}$=341 nm, slit: 2.5/2.5 nm)

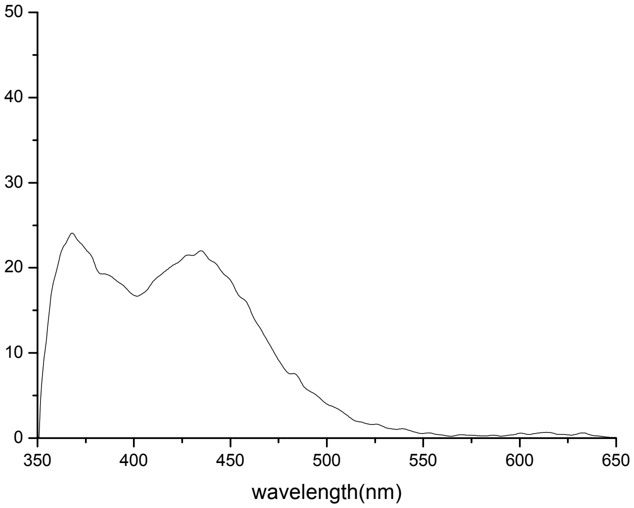


Figure S32. UV Spectrum of (*S*)-**6** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement.

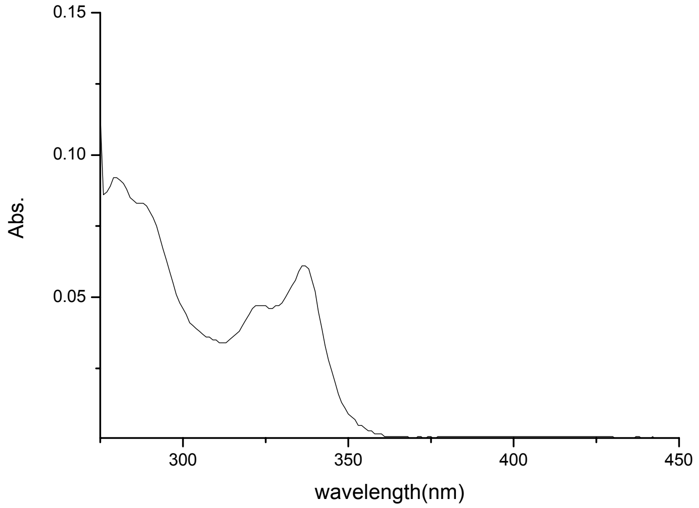


Figure S33. Fluorescence Spectrum of (*S*)-**6** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement. (□$_{exc}$=341 nm, slit: 2.5/2.5 nm)

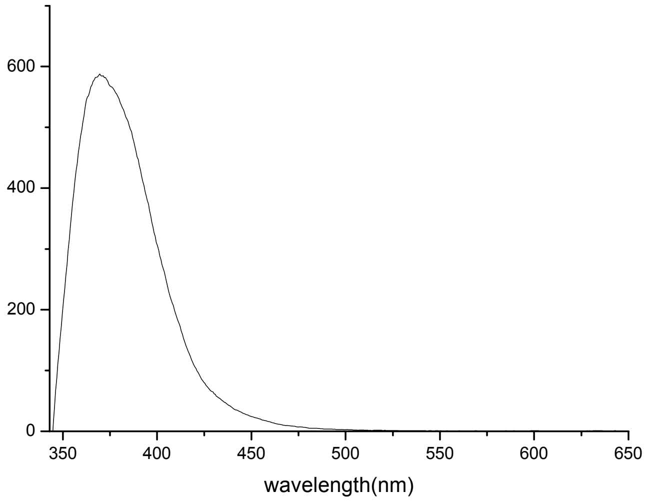


Figure S34. UV Spectrum of (*S*)-**7** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement.

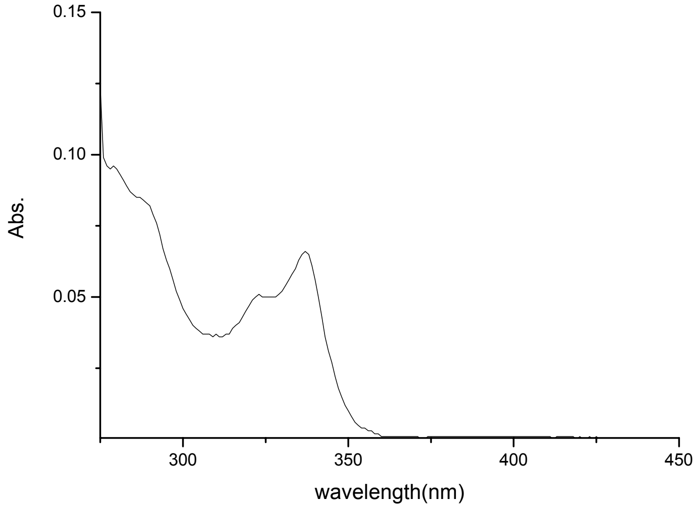


Figure S35. Fluorescence Spectrum of (*S*)-**7** at 1.0×10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement. (λ_{exc}=341 nm, slit: 2.5/2.5 nm)

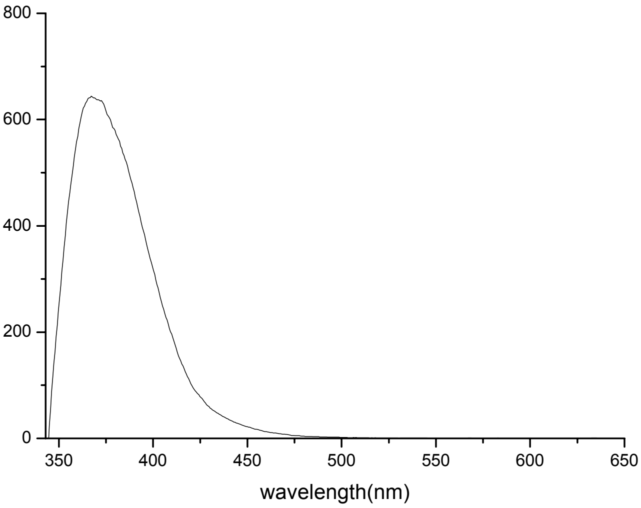


Figure S36. UV Spectrum of (*S*)-**8** at 1.0×10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement.

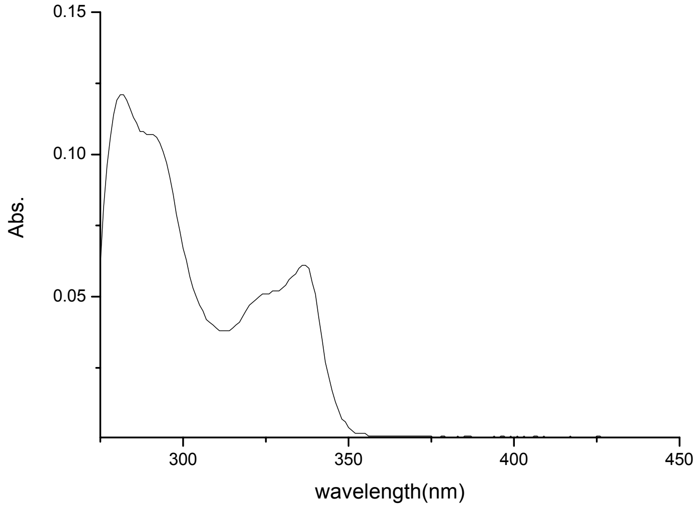


Figure S37. Fluorescence Spectrum of (*S*)-**8** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement. (□$_{exc}$=341 nm, slit: 2.5/2.5 nm)

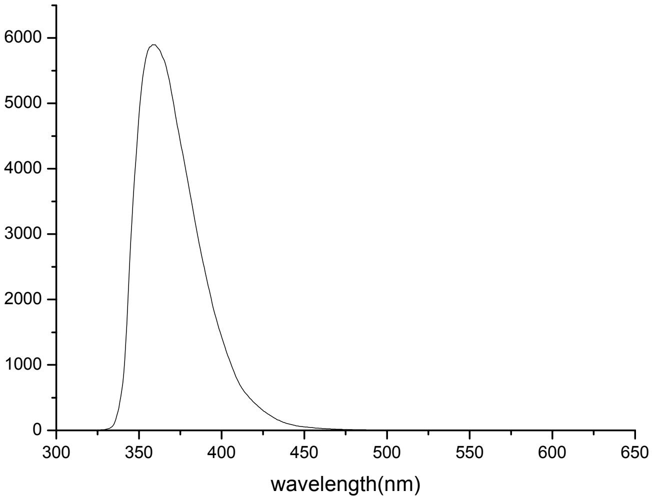


Figure S38. UV Spectrum of (*S*)-**9** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement.

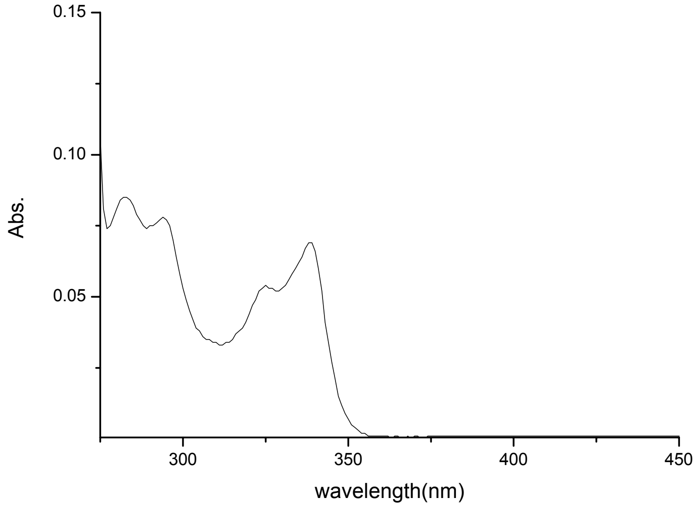


Figure S39. Fluorescence Spectrum of (*S*)-**9** at 1.0×10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement. (λ_{exc}=341 nm, slit: 2.5/2.5 nm)

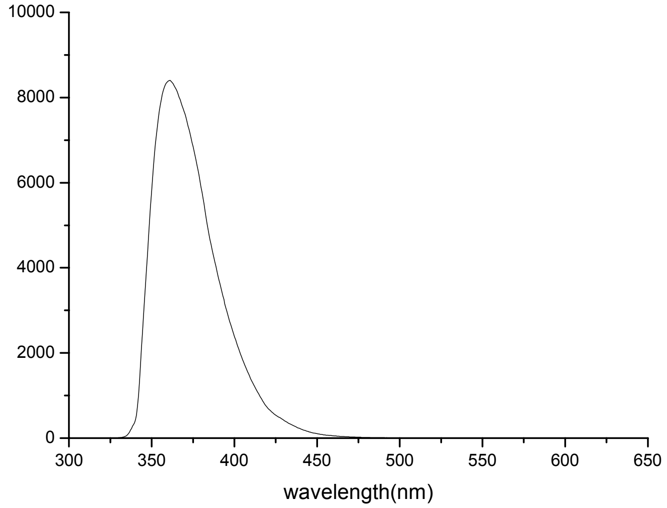


Figure S40. UV Spectrum of (*S*)-**10** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement.

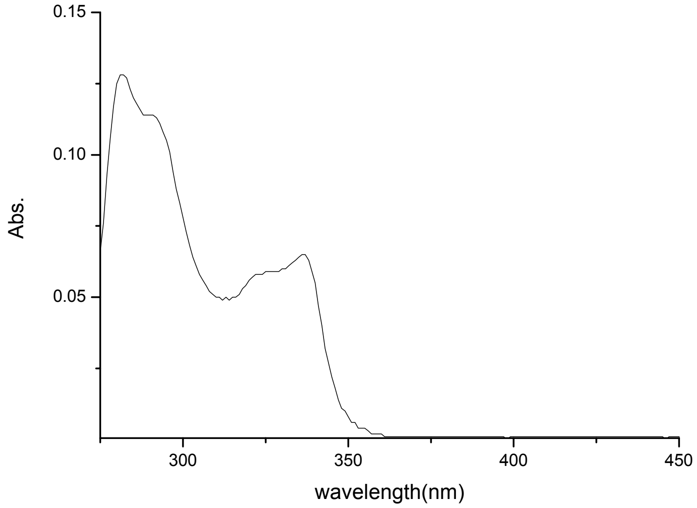


Figure S41. Fluorescence Spectrum of (*S*)-**10** at 1.0□10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement. (□$_{exc}$=341 nm, slit: 2.5/2.5 nm)

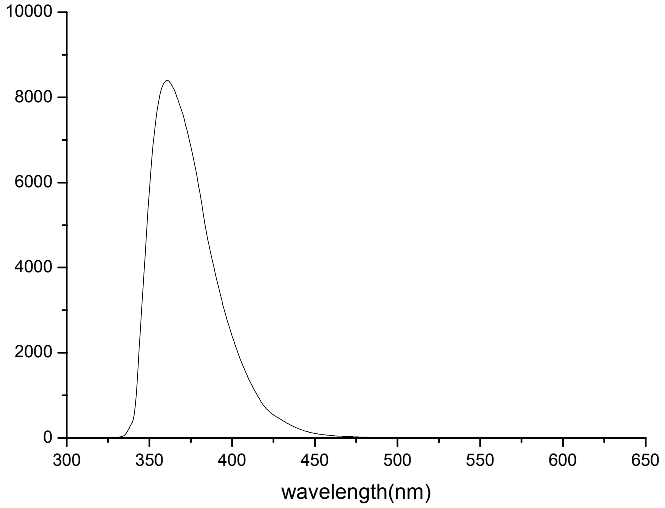


Figure S42. UV Spectrum of (*S*)-**BINOL** at 1.0×10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement.

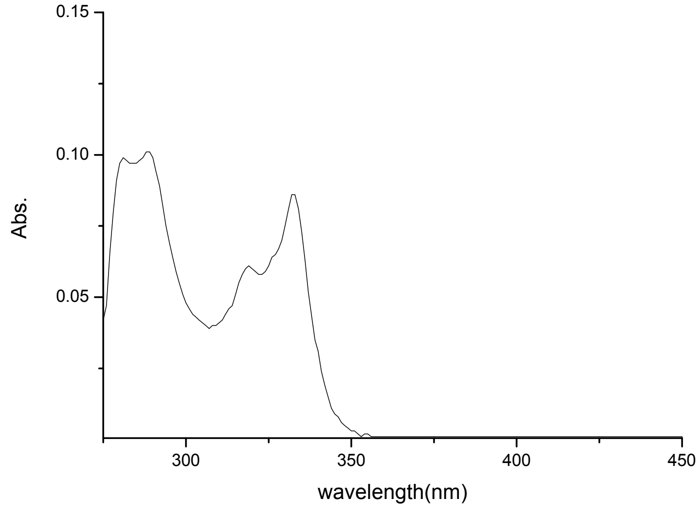
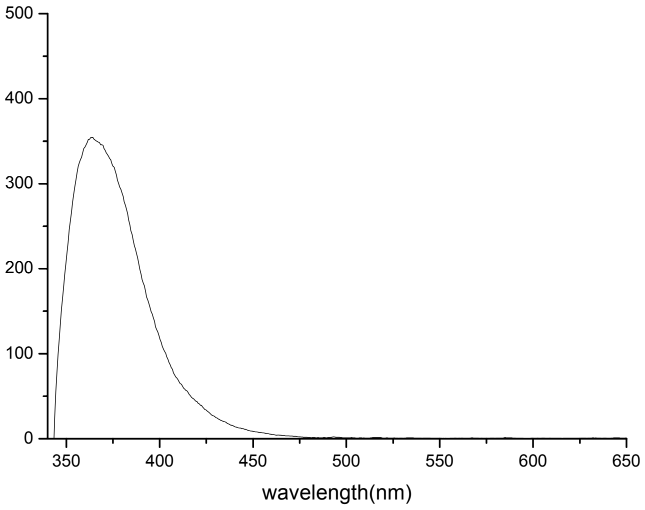
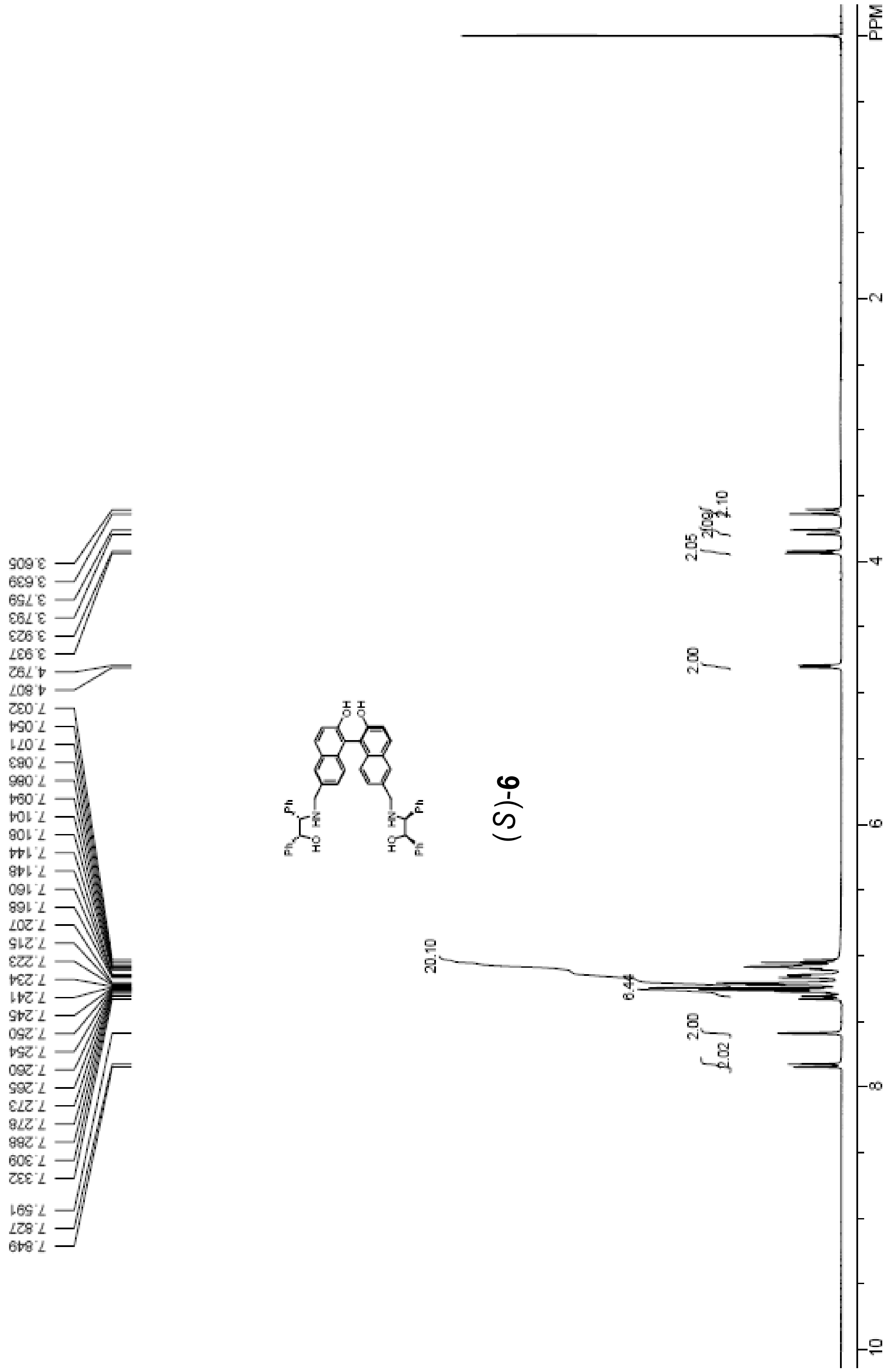


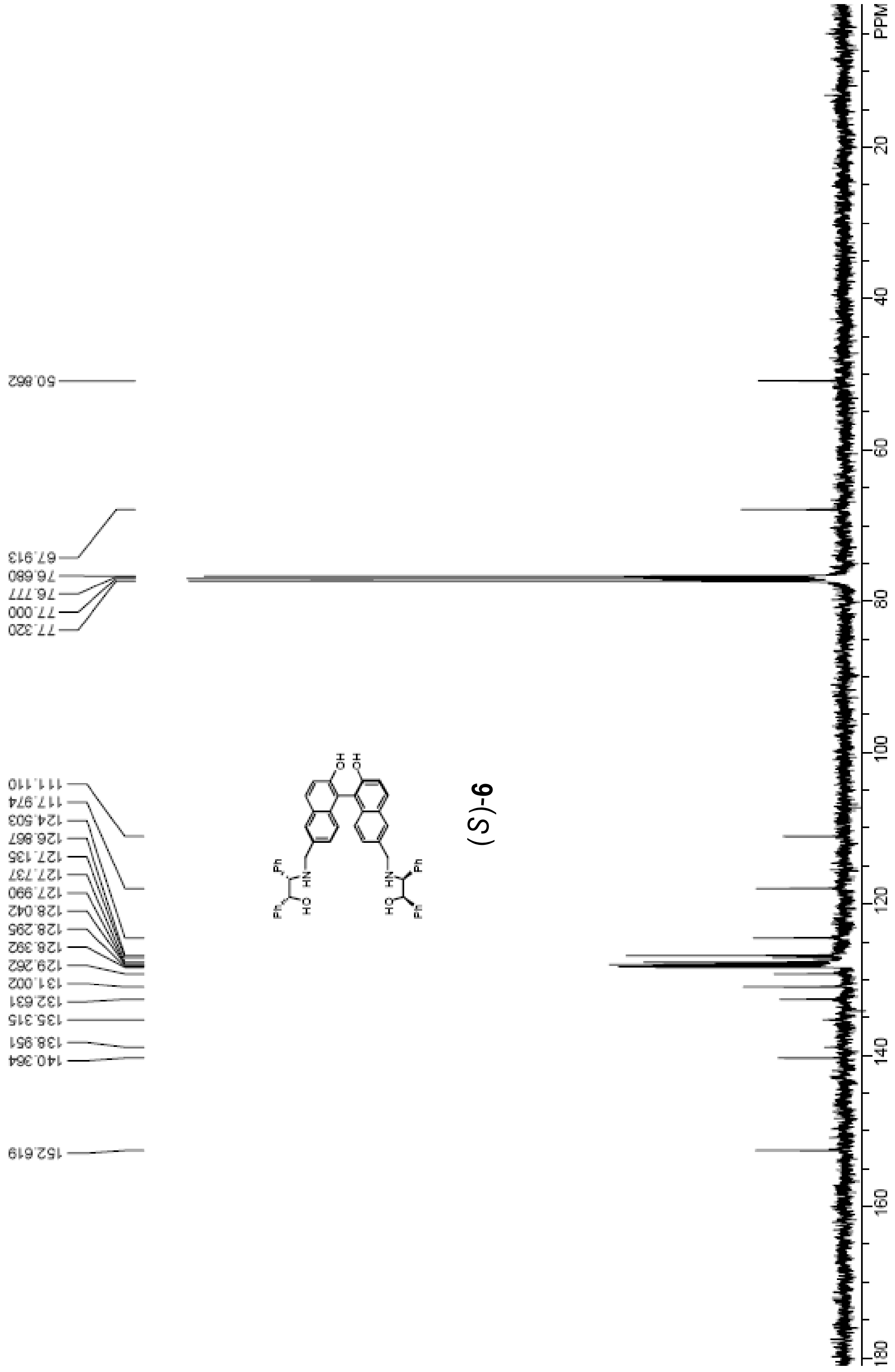
Figure S43. Fluorescence Spectrum of (*S*)-**BINOL** at 1.0×10^{-5} M in Benzene for Fluorescence Quantum Yield Measurement. (λ_{exc}=341 nm, slit: 2.5/2.5 nm)



VII. ^{1}H and ^{13}C NMR Spectra of the Compounds



(S)-6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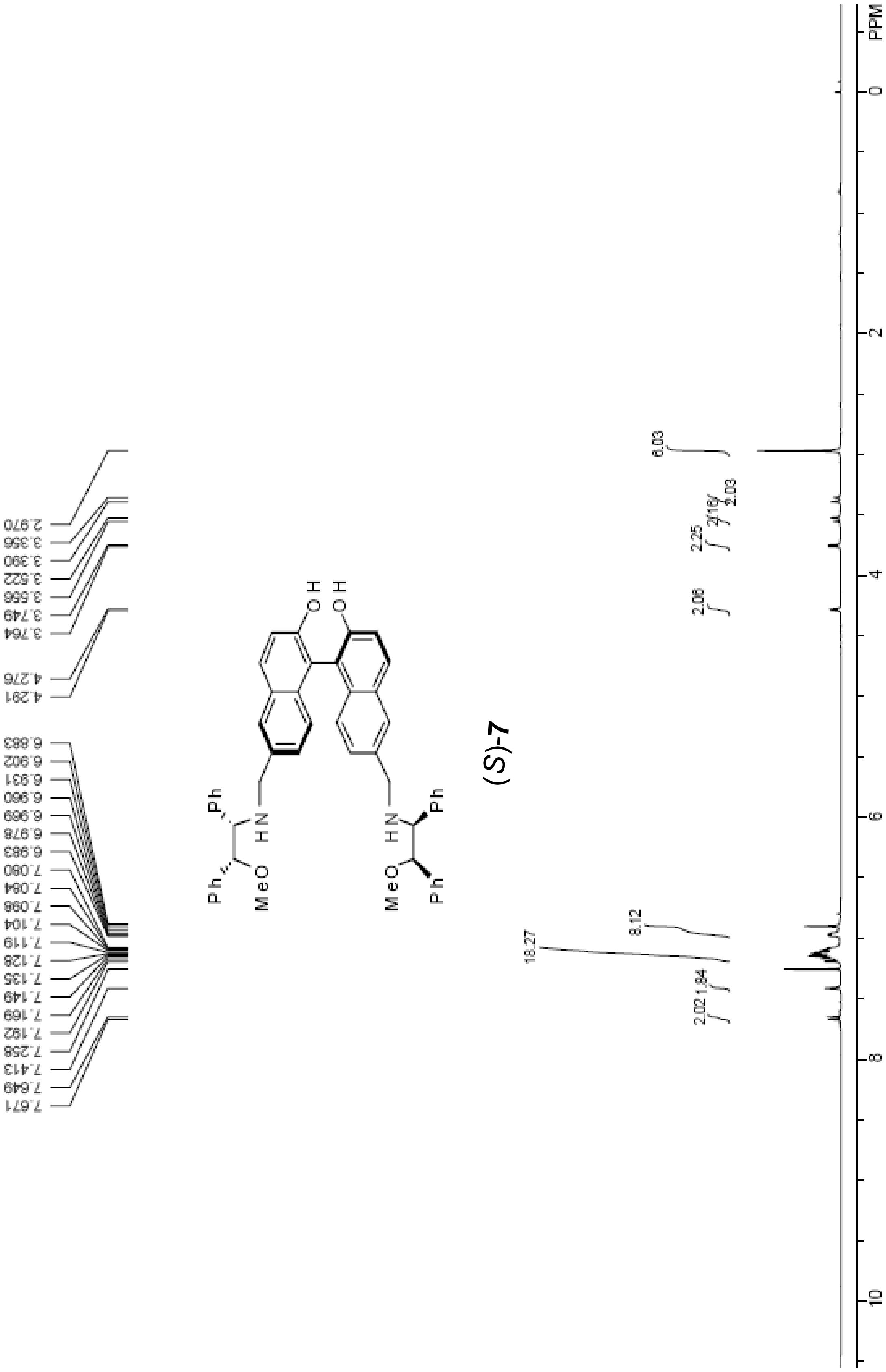
67.913
76.680
76.777
77.000
77.320
111.110
117.974
124.503
126.967
127.135
127.737
127.990
128.042
128.295
128.392
129.262
131.002
132.631
135.315
138.951
140.364
152.619
OH
OH
HN
HN
HO
HO
Ph
Ph
Ph
Ph
PPM
20
40
60
80
100
120
140
160
180

(S)-6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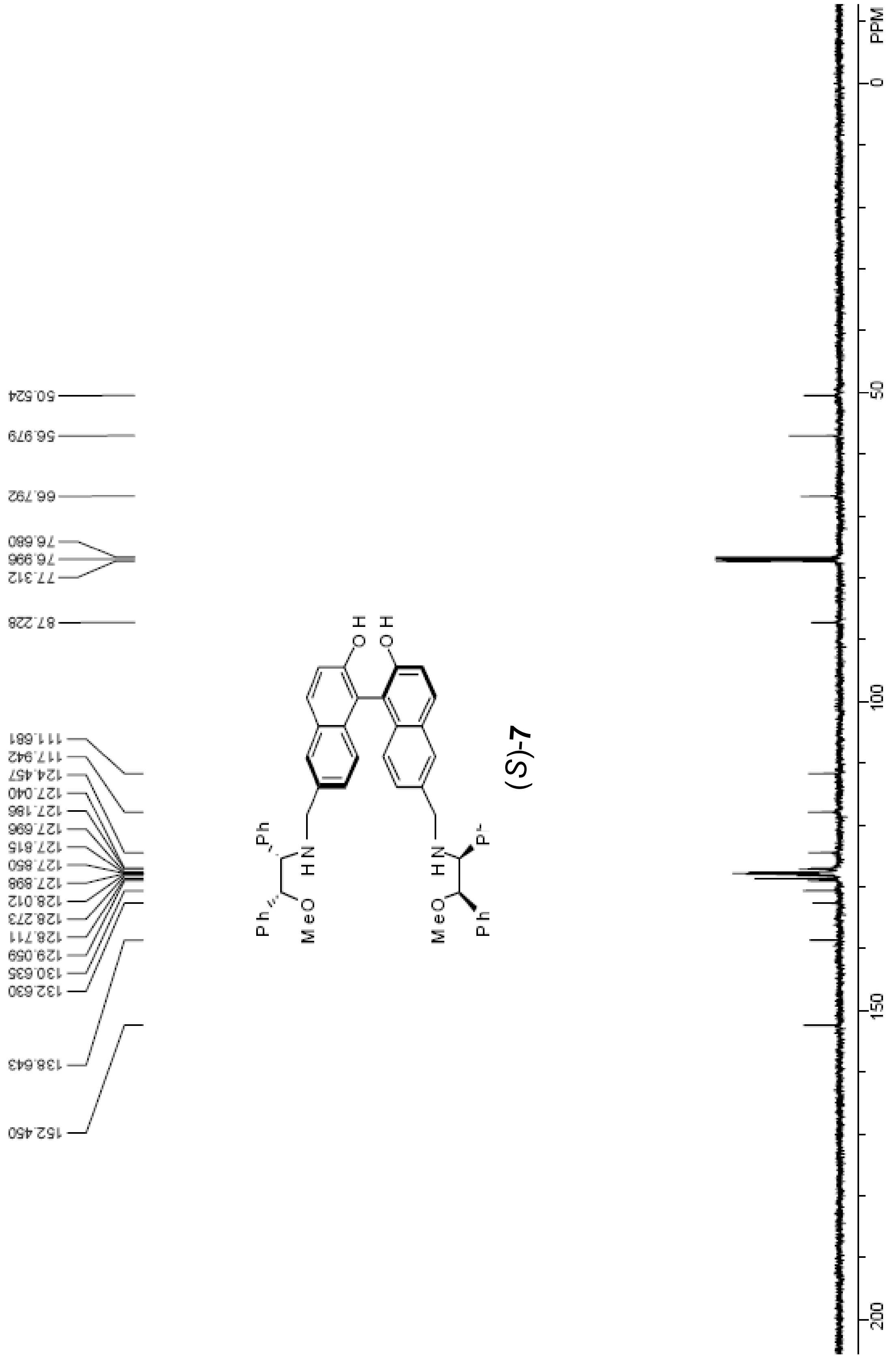
3.356
3.390
3.522
3.556
3.749
3.764
4.276
4.291
6.883
6.902
6.931
6.960
6.969
6.978
6.983
7.080
7.084
7.098
7.104
7.119
7.128
7.135
7.149
7.169
7.192
7.258
7.413
7.649
7.671
OH
OH
Ph
Ph
MeO
MeO
HN
HN
Ph
Ph
6.03
2.25
2.10
2.03
2.06
8.12
18.27
2.02
1.84
PPM
0
2
4
6
8
10

(*S*)-7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66.792
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111.681
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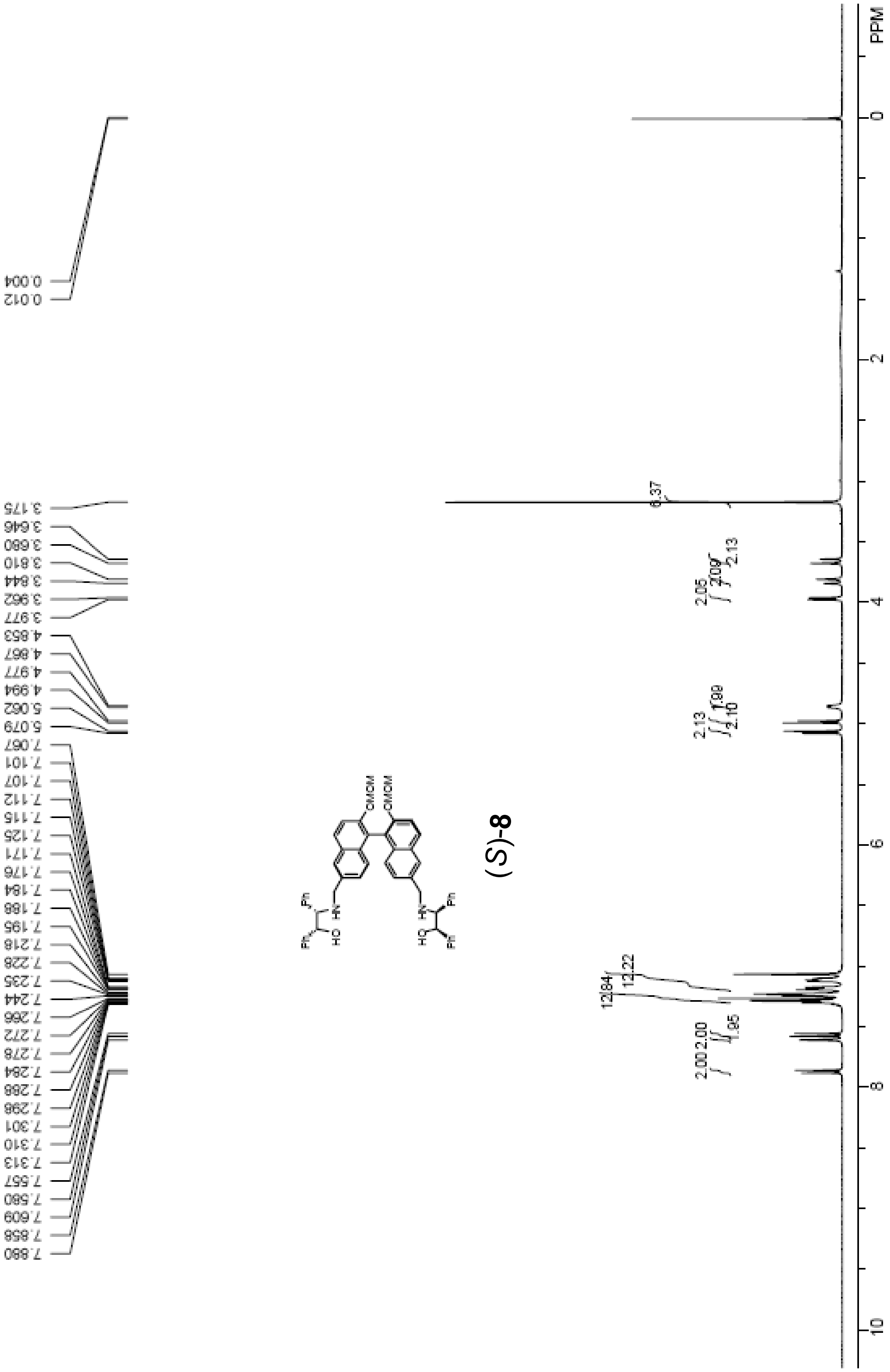
127.040
127.196
127.696
127.815
127.850
127.898
128.012
128.273
128.711
129.059
130.635
132.630
138.643
152.450
OH
OH
Ph
HN
MeO
Ph
HN
MeO
Ph
Ph
(S)-7
PPM
0
50
100
150
200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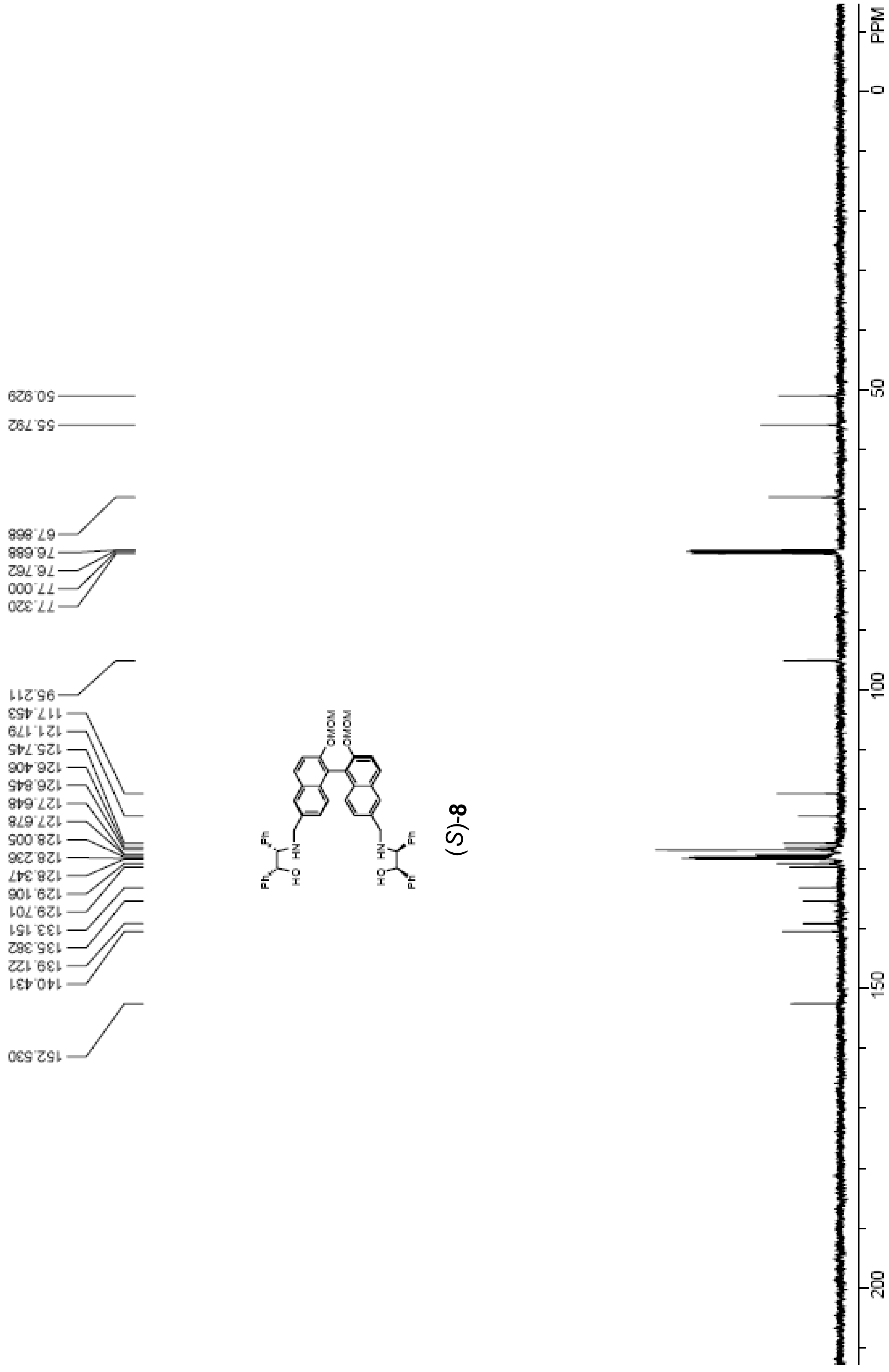
0.012
3.175
3.646
3.680
3.810
3.844
3.962
3.977
4.853
4.867
4.977
4.994
5.062
5.079
7.067
7.101
7.107
7.112
7.115
7.125
7.171
7.176
7.184
7.188
7.195
7.218
7.228
7.235
7.244
7.266
7.272
7.278
7.284
7.288
7.298
7.301
7.310
7.313
7.557
7.580
7.609
7.858
7.880
6.37
2.05
2.09
2.13
2.13
1.99
2.10
12.84
12.22
2.00
2.00
1.95
Ph
HO
HN
OMOM
PPM
0
2
4
6
8
10

(S)-8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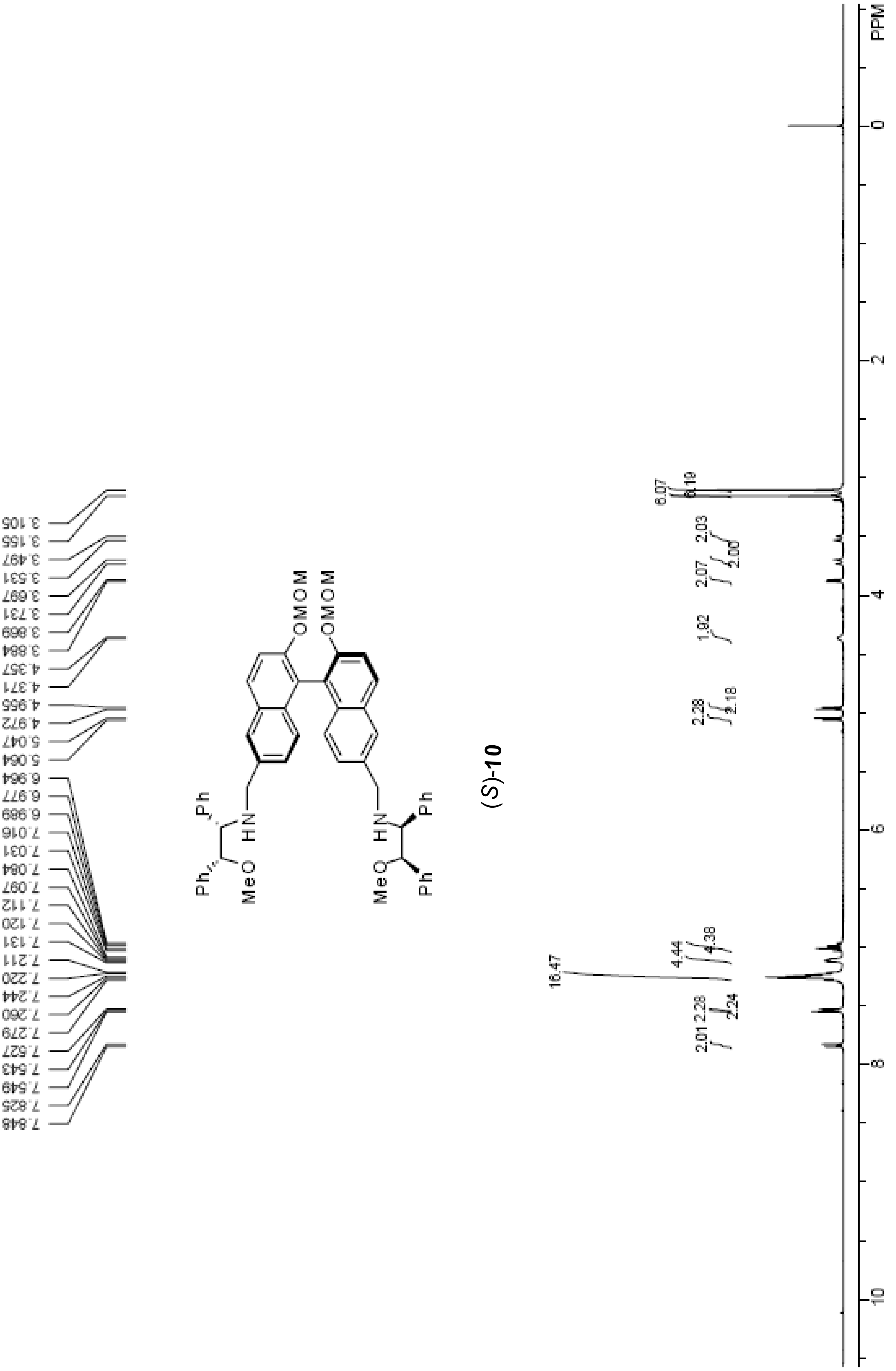
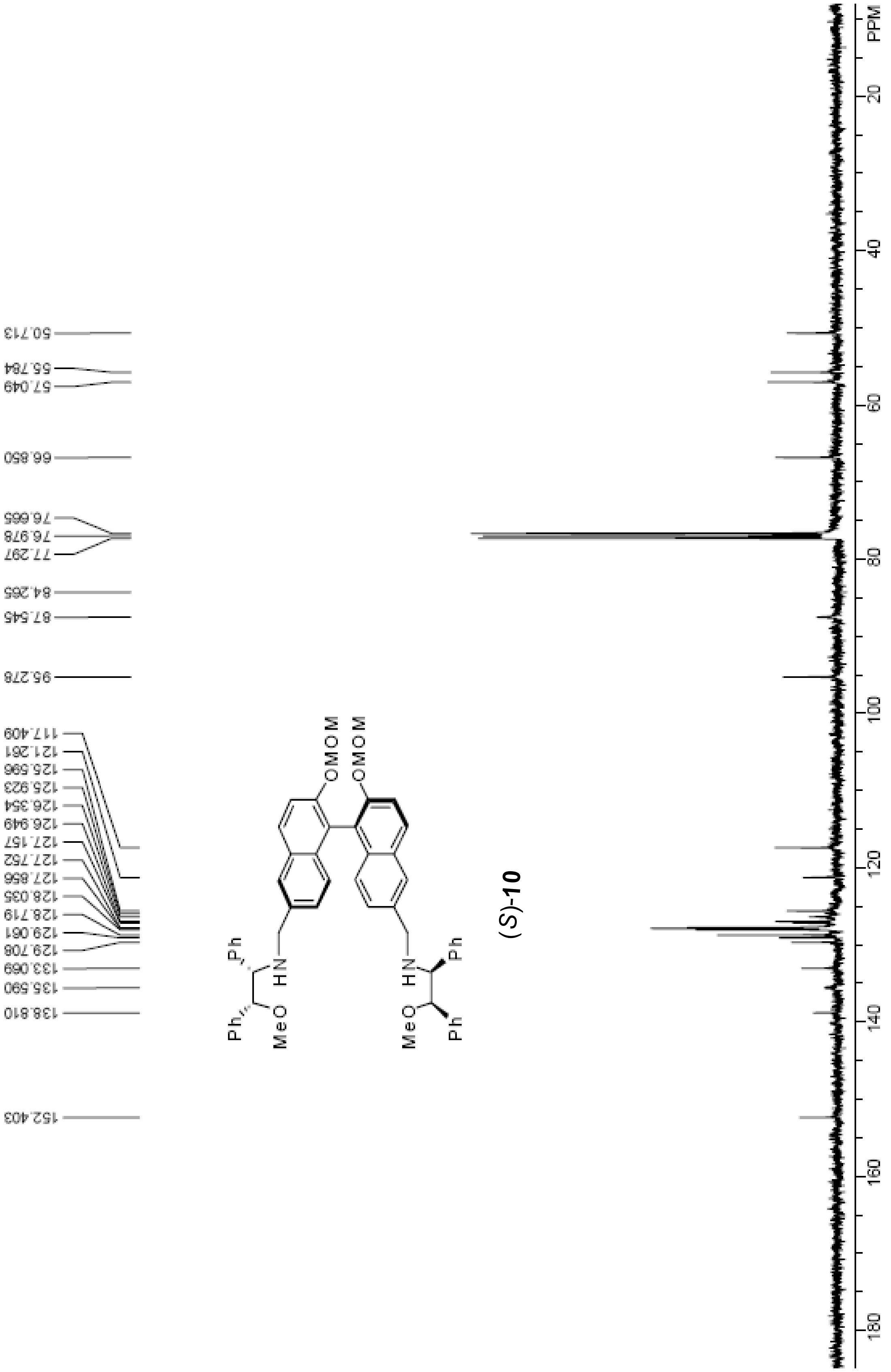
67.868
76.688
76.762
77.000
77.320
95.211
117.453
121.179
125.745
126.406
126.845
127.648
127.678
128.005
128.236
128.347
129.106
129.701
133.151
135.362
139.122
140.431
152.530
OMOM
OMOM
HN
HN
OH
HO
Ph
Ph
Ph
Ph
PPM
0
50
100
150
200

(*S*)-**8**



(*S*)-**10**

3.105
3.155
3.497
3.531
3.697
3.731
3.869
3.884
4.357
4.371
4.965
4.972
5.047
5.064
6.964
6.977
6.989
7.016
7.031
7.064
7.097
7.112
7.120
7.131
7.211
7.220
7.244
7.260
7.279
7.527
7.543
7.549
7.825
7.848
OMOM
OMOM
Ph
Ph
Ph
Ph
MeO
MeO
HN
HN
6.07
6.19
2.03
2.00
2.07
1.92
2.28
2.18
16.47
4.44
4.38
2.01
2.28
2.24
PPM
0
2
4
6
8
10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125.923
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126.949
127.157
127.752
127.856
128.035
128.719
129.061
129.708
133.069
135.590
138.810
152.403
OMOM
OMOM
Ph
HN
Ph
MeO
HN
Ph
MeO
Ph
PPM
20
40
60
80
100
120
140
160
180

(*S*)-**10**

VIII. Reference:

1. (a) Bunzen, J.; Bruhn, T.; Bringmann, G.; Lützen, A. *J. Am. Chem. Soc.* **2009**, *131*, 3621-3630. (b) Dong, C.; Zhang, J.; Zheng, W.; Zhang, L.; Yu, Z.; Choi, M. C. K.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2000**, *11*, 2449-2454.
2. Zhou, L.; Wang, Z.-Y.; Wei, S.-Y.; Sun, J. *Chem. Commun*. **2007**, 2977-2979 .
3. Liu, H. L.; Hou, X. L.; Pu, L. *Angew. Chem. Int. Ed.* **2009**, *48,* 382-385.
4. (a) Demas, J. N.; Crosby, J. *J. Phys. Chem.* **1971**, *75*, 991-1024 (see pages 1007-1011). (b) Hu, Q-S; Pugh, V.; Sabat, M.; Pu, L. *J. Org. Chem.* **1999**, *64*, 7528-7536.