

Supporting Information

Chiral Recognition and Enantiomer Excess Determination Based on Emission Wavelength Change of AIEgen Rotor

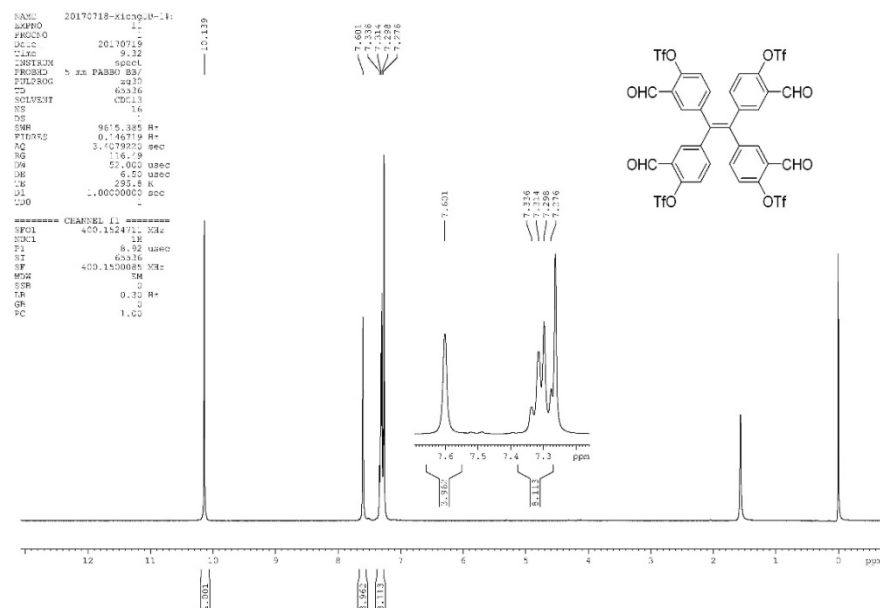
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Minghua Liu,²
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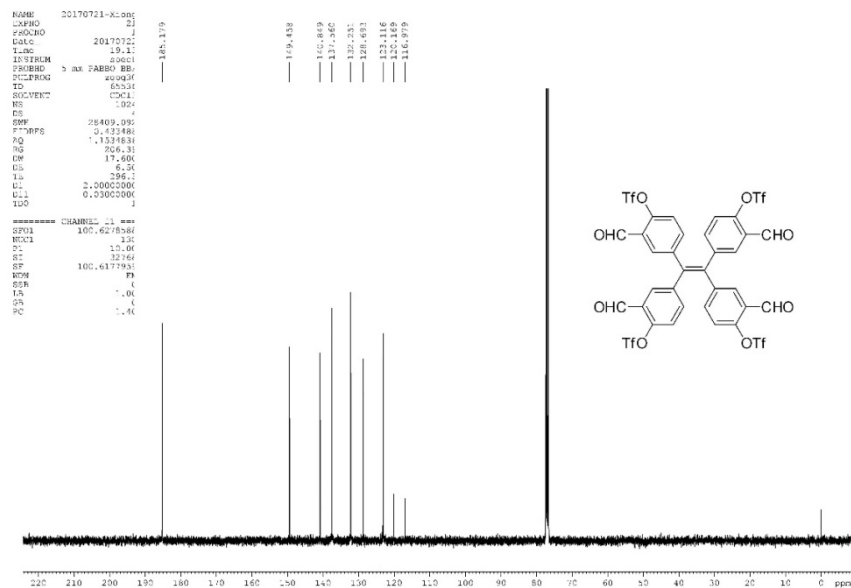
² Beijing National Laboratory for Molecular Science (BNLMS), CAS Key Laboratory of Colloid Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

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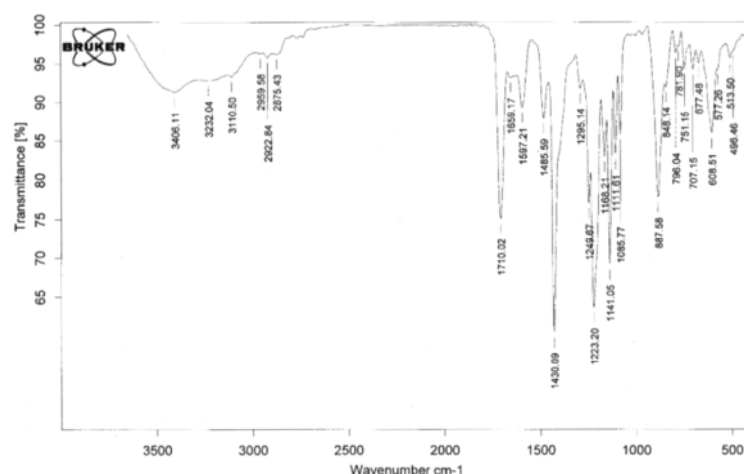
Supplementary Figures



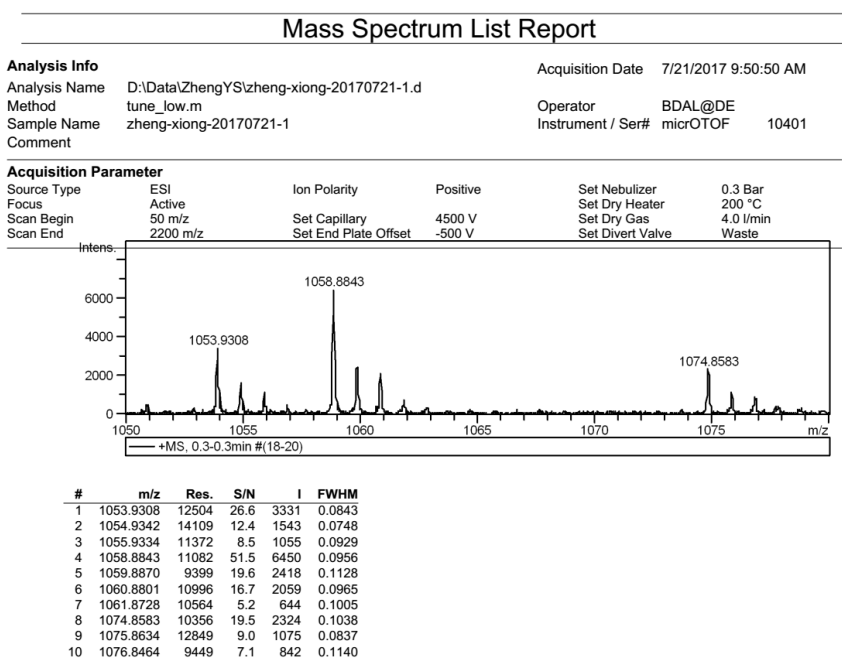
Supplementary Figure 1. ^1H NMR spectrum of compound **2** in CDCl_3 .



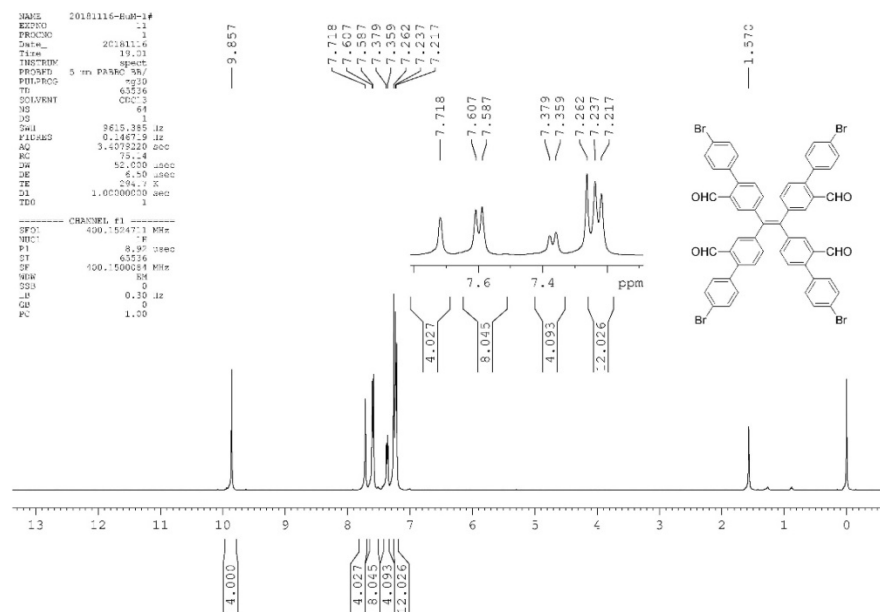
Supplementary Figure 2. ^{13}C NMR spectrum of compound **2** in CDCl_3 .



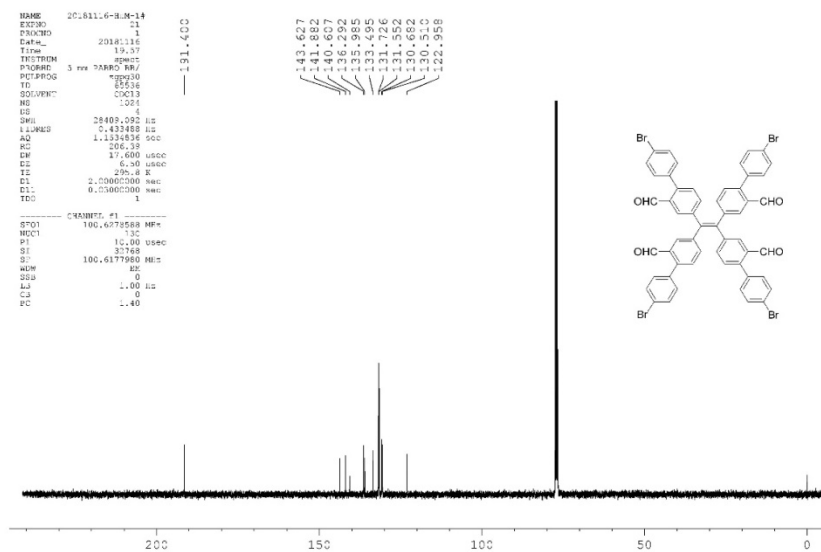
Supplementary Figure 3. IR spectrum of compound 2.



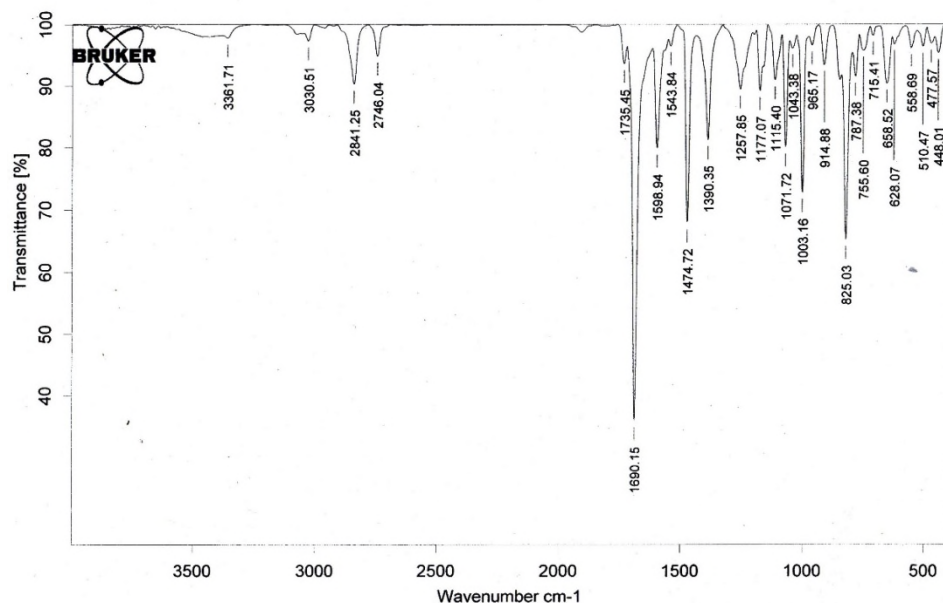
Supplementary Figure 4. HRMS spectrum of compound 2.



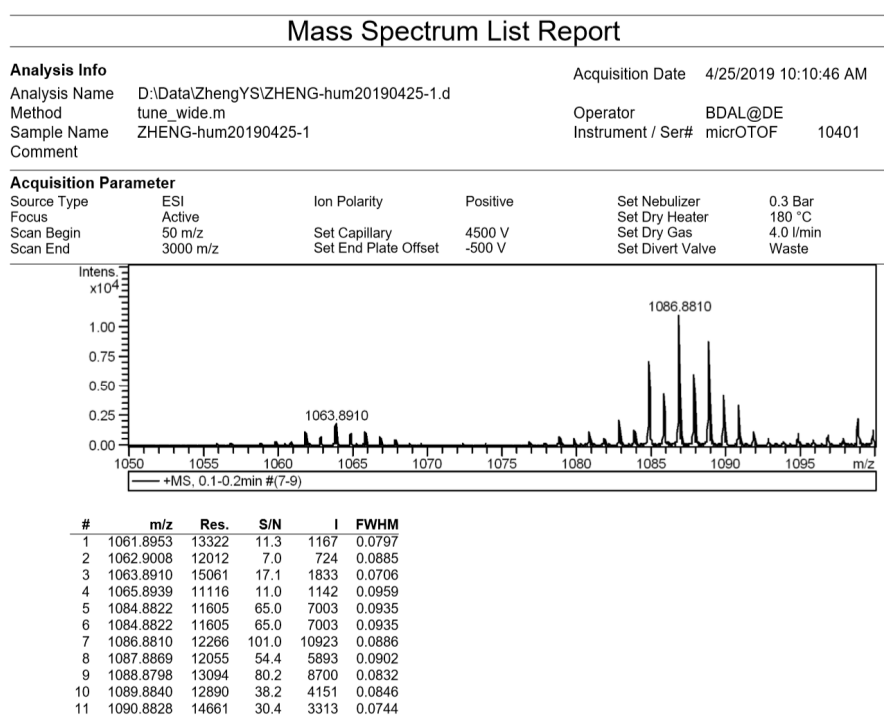
Supplementary Figure 5. ^1H NMR spectrum of compound 3 in CDCl_3 .



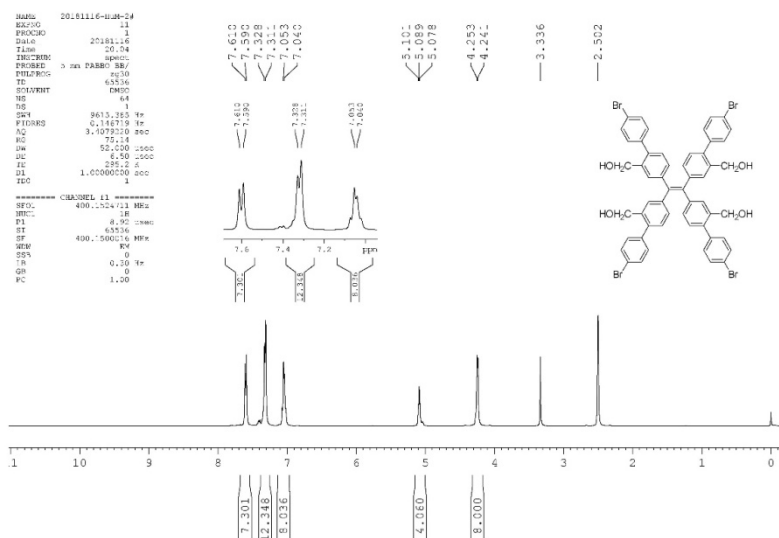
Supplementary Figure 6. ^{13}C NMR spectrum of compound 3 in CDCl_3 .



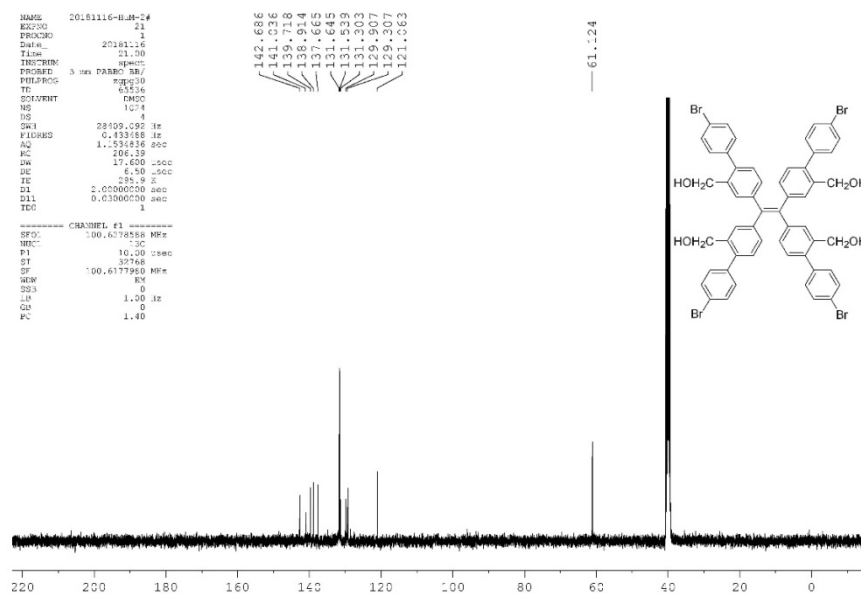
Supplementary Figure 7. IR spectrum of compound 3.



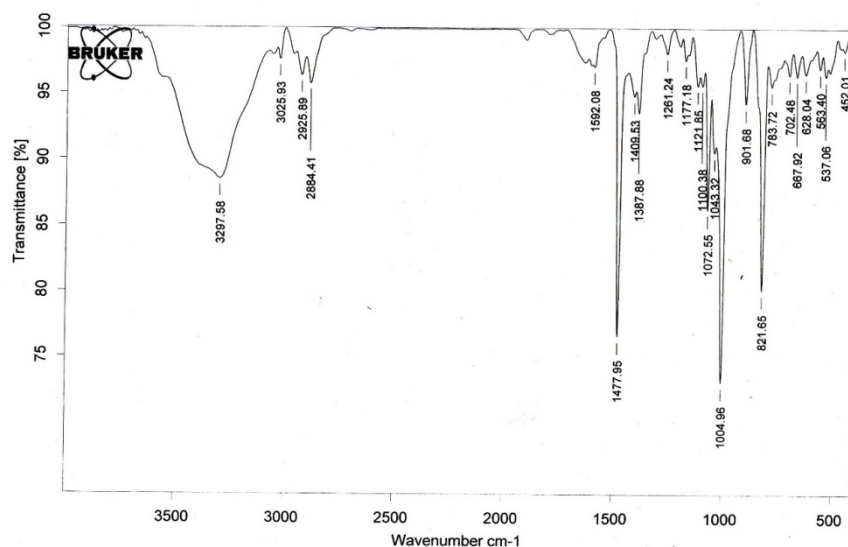
Supplementary Figure 8. HRMS spectrum of compound 3.



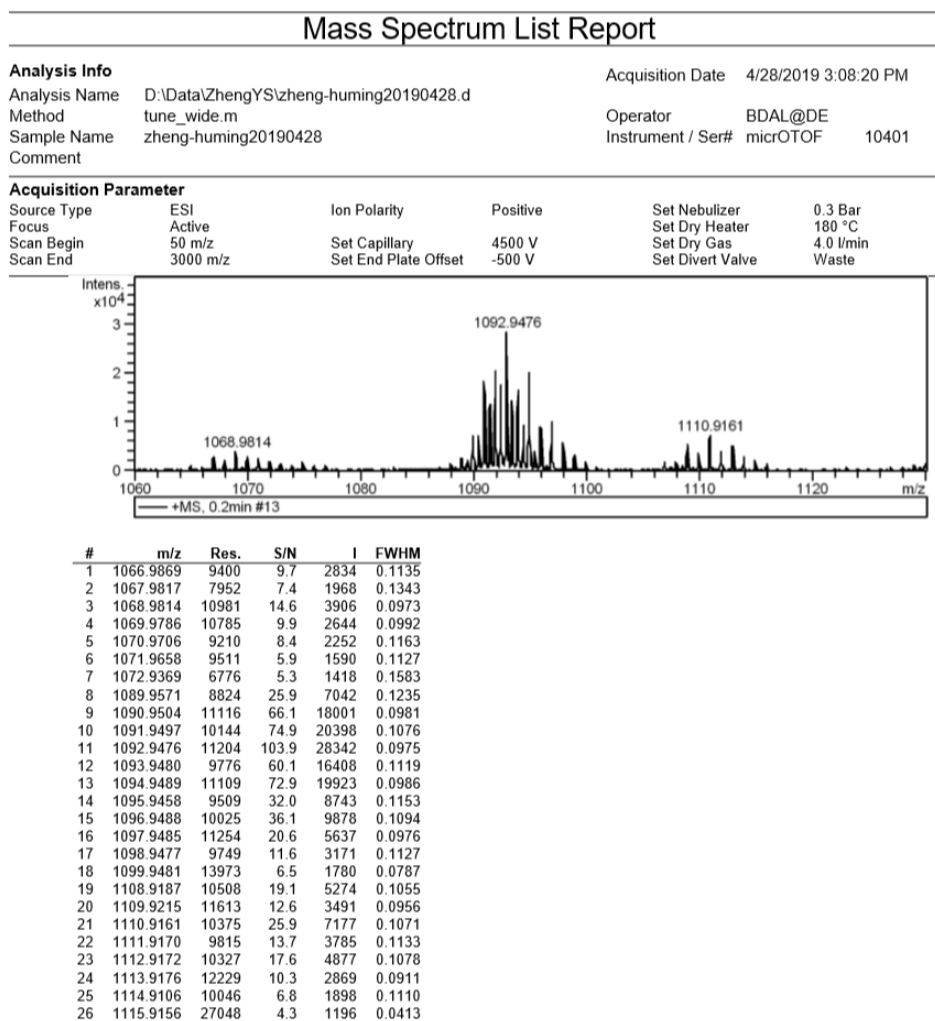
Supplementary Figure 9. ^1H NMR spectrum of compound **4** in DMSO- d_6 .



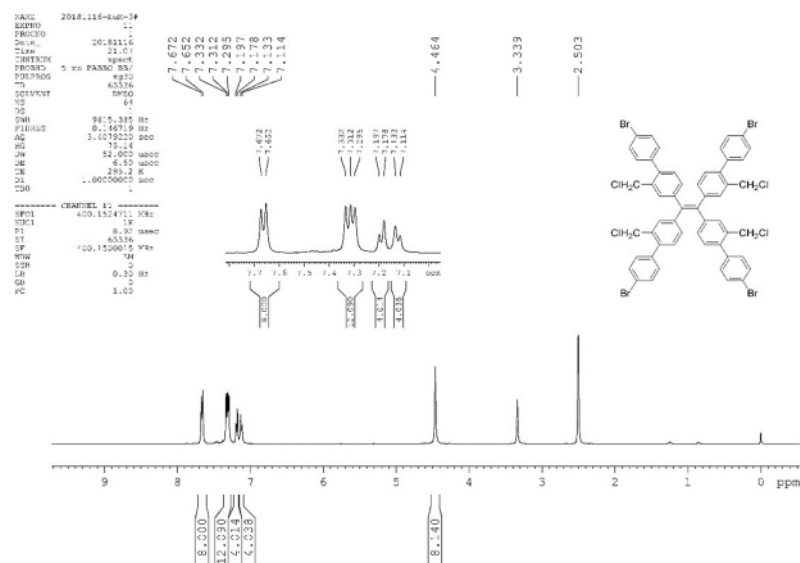
Supplementary Figure 10. ^{13}C NMR spectrum of compound **4** in DMSO- d_6 .



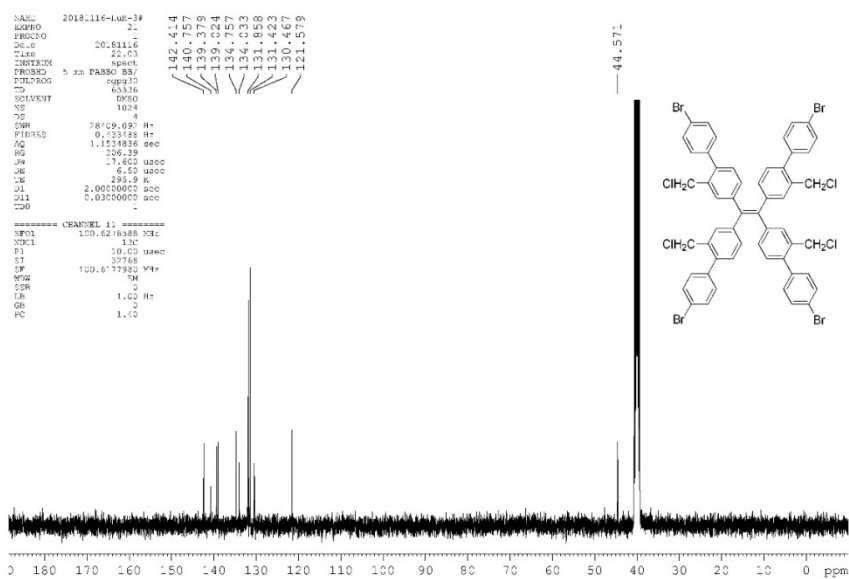
Supplementary Figure 11. IR spectrum of compound 4.



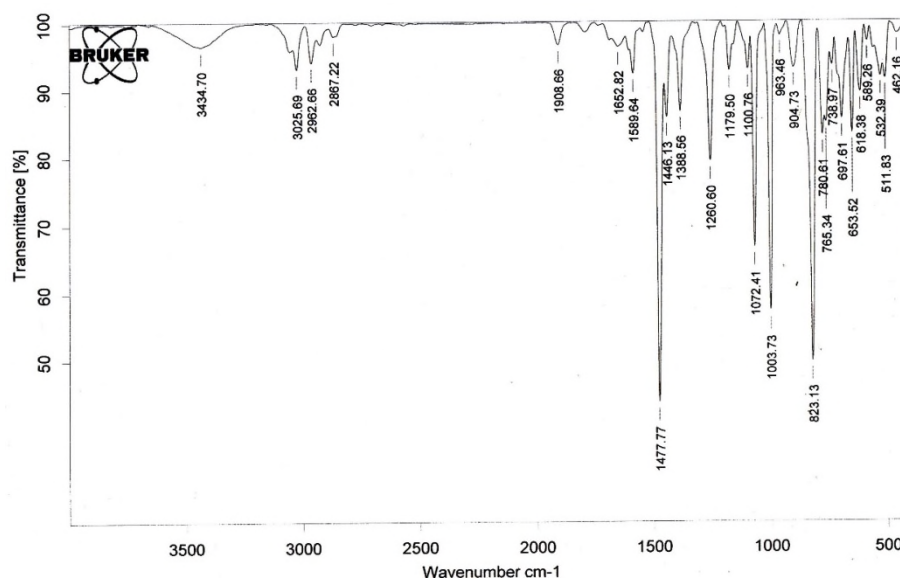
Supplementary Figure 12. HRMS spectrum of compound 4.



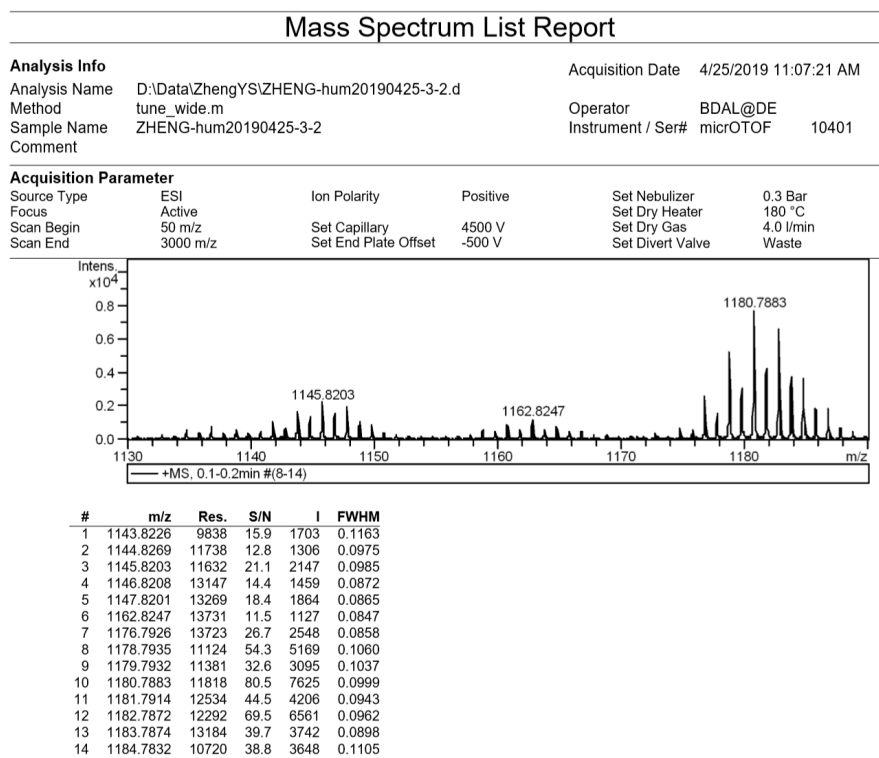
Supplementary Figure 13. ¹H NMR spectrum of compound 5 in DMSO-d₆.



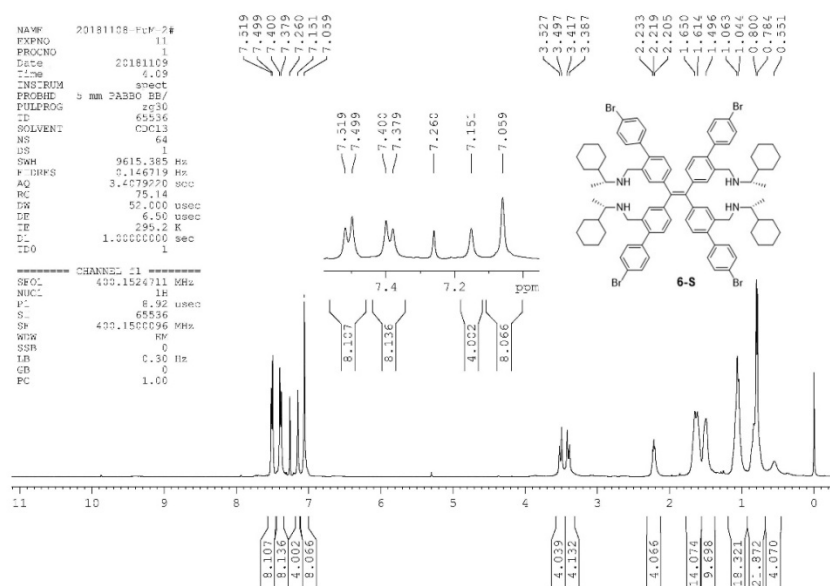
Supplementary Figure 14. ¹³C NMR spectrum of compound 5 in DMSO-d₆.



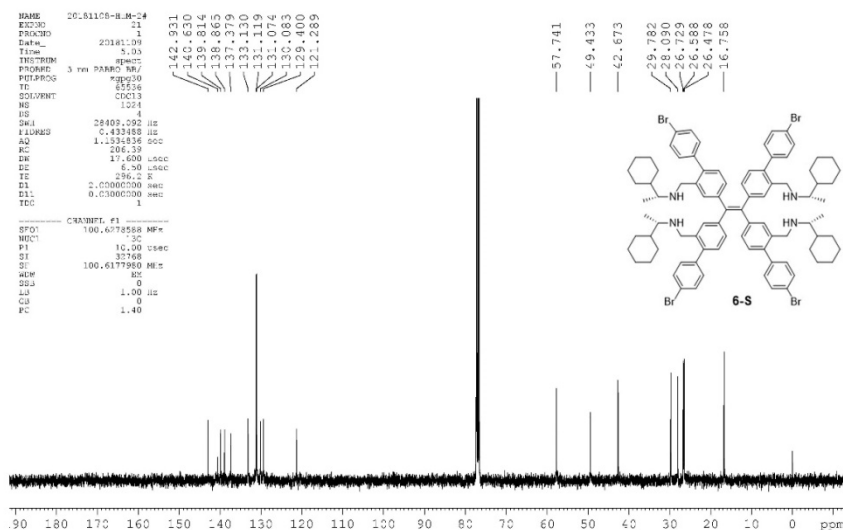
Supplementary Figure 15. IR spectrum of compound 5.



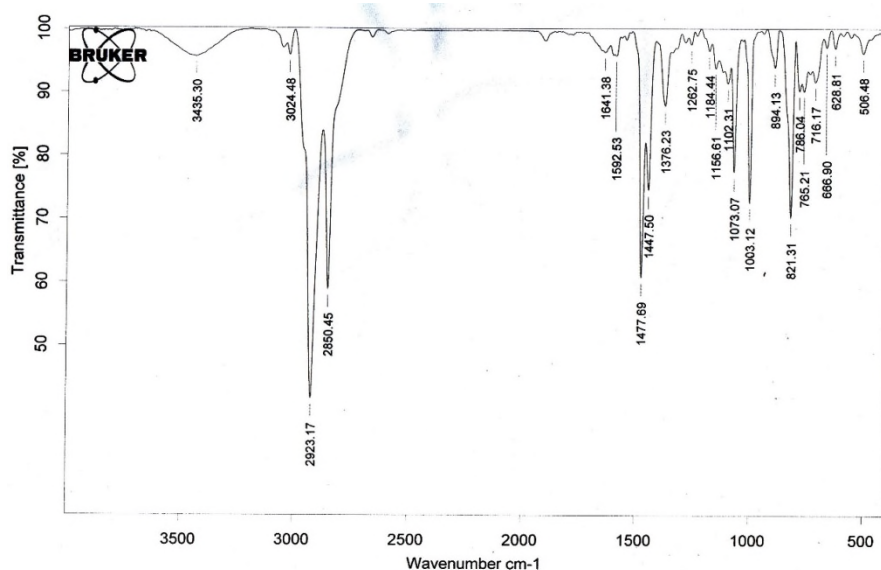
Supplementary Figure 16. HRMS spectrum of compound 5.



Supplementary Figure 17. ^1H NMR spectrum of compound (S)-6 in CDCl_3 .



Supplementary Figure 18. ^{13}C NMR spectrum of compound (S)-6 in CDCl_3 .

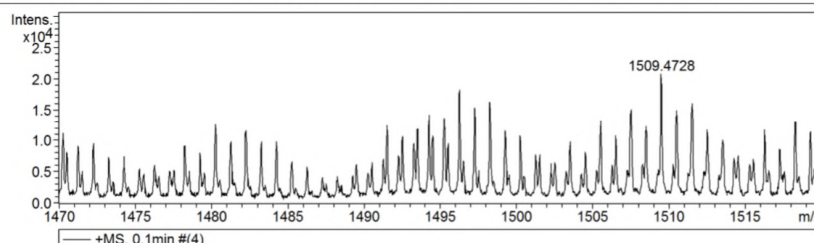


Supplementary Figure 19. IR spectrum of compound (S)-6.

Mass Spectrum List Report

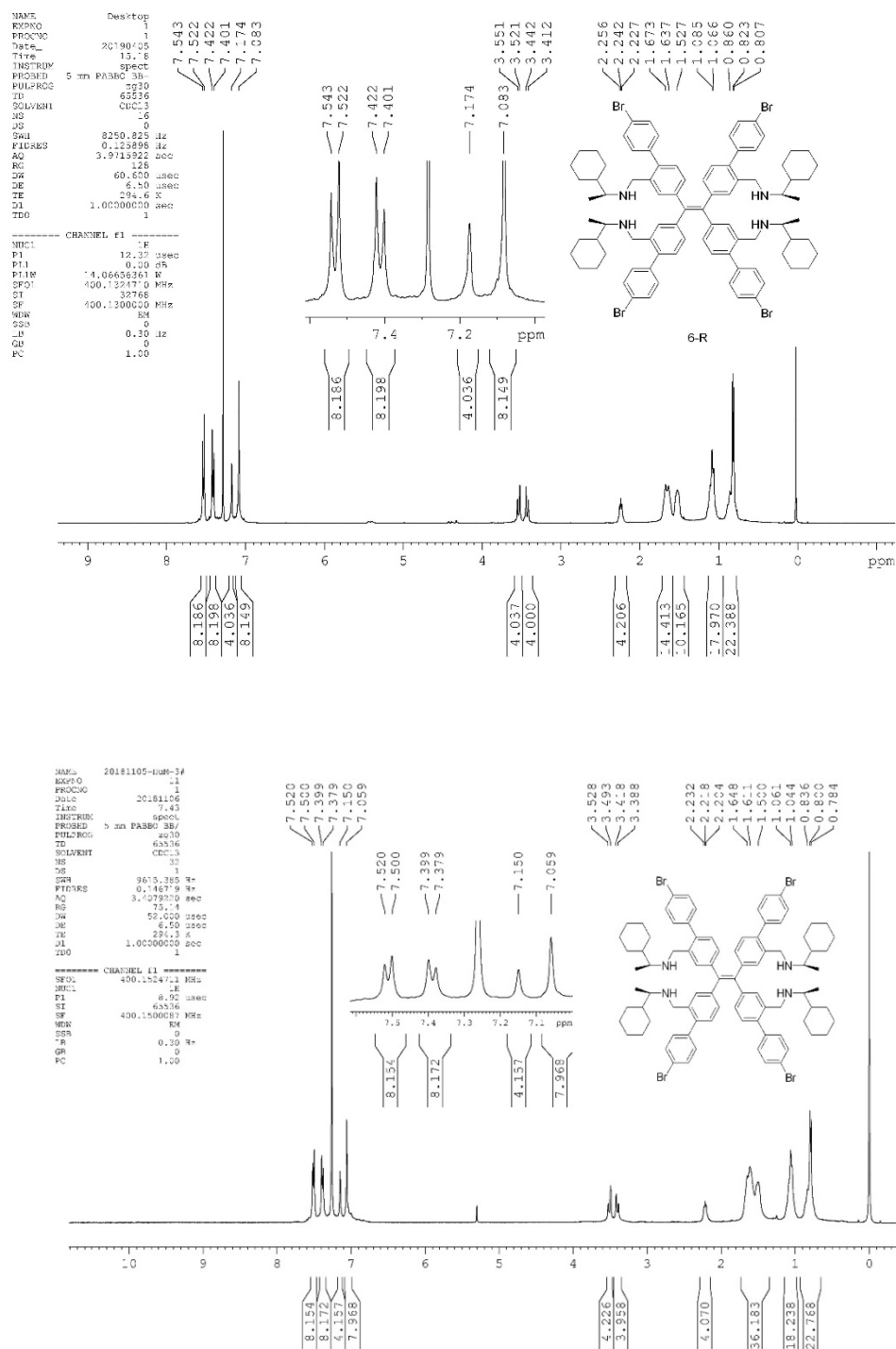
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Analysis Name	E:\p\A\-\ÖÊÆ\xzheng-huming20190404-2.d	Operator	BDAL@DE
Method	tune_wide.m	Instrument / Ser#	micrOTOF 10401
Sample Name	zheng-huming20190404-2		
Comment			

Acquisition Parameter			
Source Type	ESI	Ion Polarity	Positive
Focus	Active	Set Nebulizer	0.3 Bar
Scan Begin	50 m/z	Set Dry Heater	180 °C
Scan End	3000 m/z	Set Capillary	4500 V
		Set End Plate Offset	-500 V
		Set Dry Gas	4.0 l/min
		Set Divert Valve	Waste

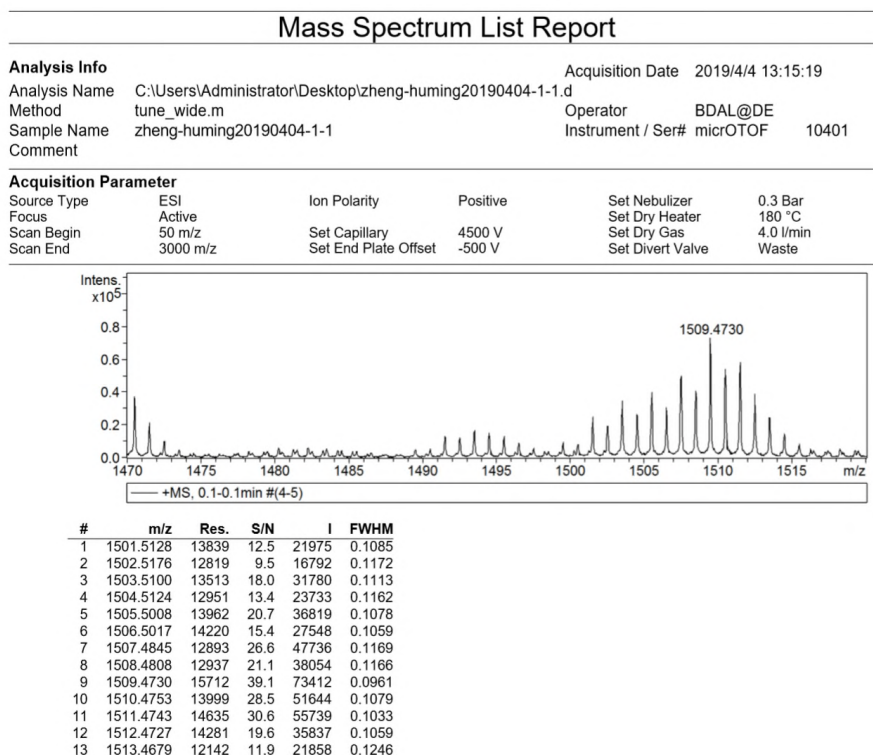


#	m/z	Res.	S/N	I	FWHM
1	1505.4953	16072	5.7	10315	0.0937
2	1506.2648	18684	1.7	3157	0.0806
3	1506.4966	14605	4.3	7798	0.1031
4	1507.4829	11331	6.6	12042	0.1330
5	1508.4731	12877	5.1	9321	0.1171
6	1509.4728	15304	9.7	20741	0.0986
7	1510.4741	12973	6.5	12026	0.1164
8	1511.4835	11153	7.1	13099	0.1355
9	1512.4847	11495	4.7	8732	0.1316
10	1513.4936	9853	3.8	7038	0.1536
11	1545.4488	14588	33.1	60553	0.1059
12	1571.4246	15167	28.4	48266	0.1036

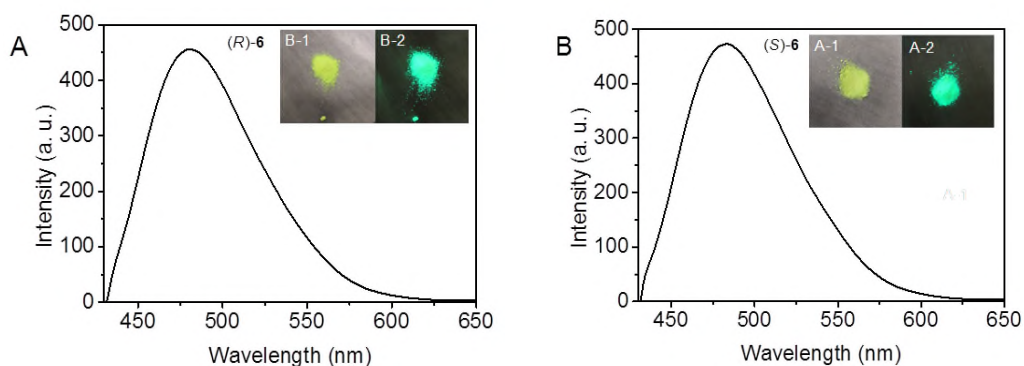
Supplementary Figure 20. HRMS spectrum of compound (S)-6.



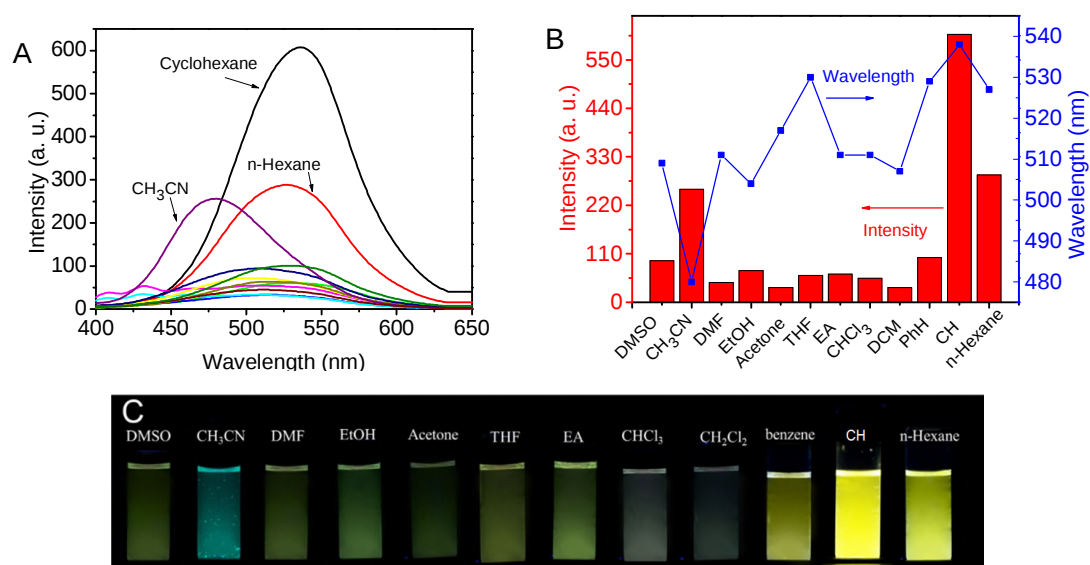
Supplementary Figure 21. ^1H NMR spectrum of compound (*R*)-6 in CDCl_3 .



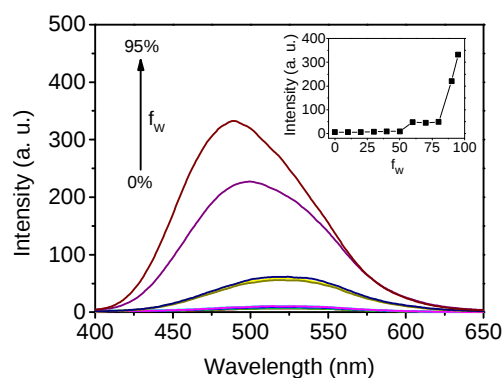
Supplementary Figure 24. HRMS spectrum of compound (*R*)-6.



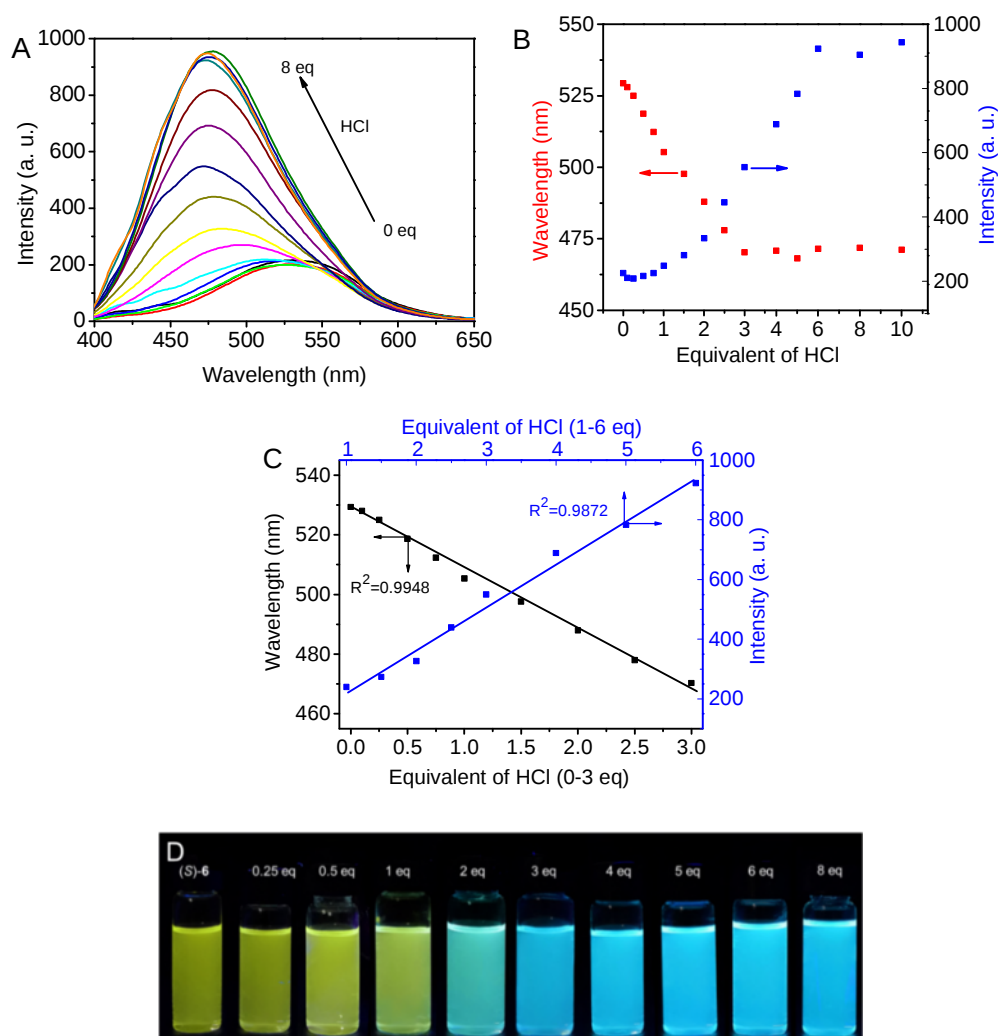
Supplementary Figure 25. Emission spectra of (*R*)-6 (A) and (*S*)-6 (B) as solid powder. Inset, photos of solid powder of (*R*)-6 (A) and (*S*)-6 under daylight (B-1 and A-1) and under a portable 365 nm lamp (B-2 and A-2). $\lambda_{\text{ex}} = 405$ nm, ex/em slit widths = 10/10 nm.



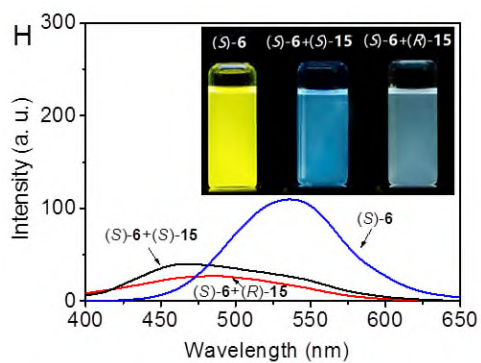
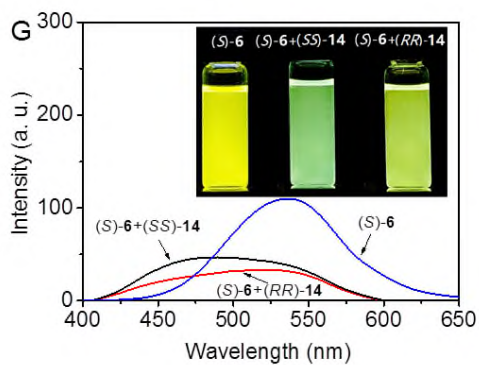
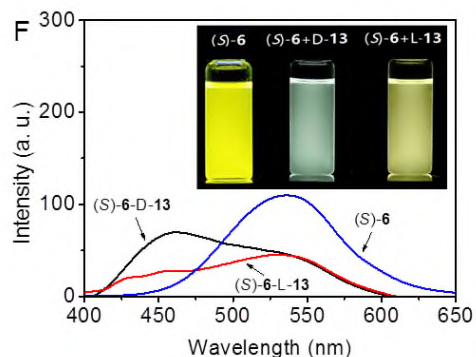
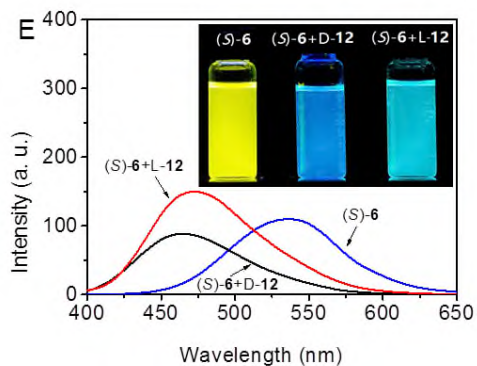
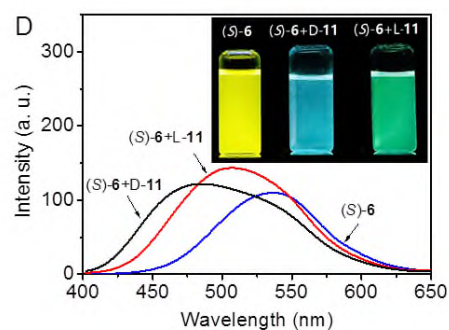
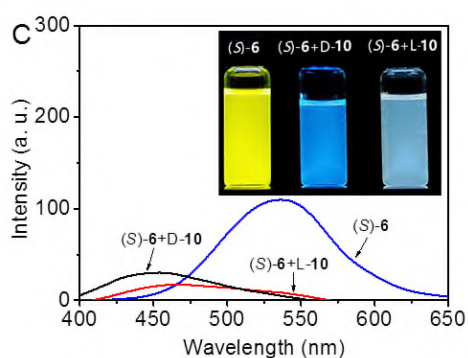
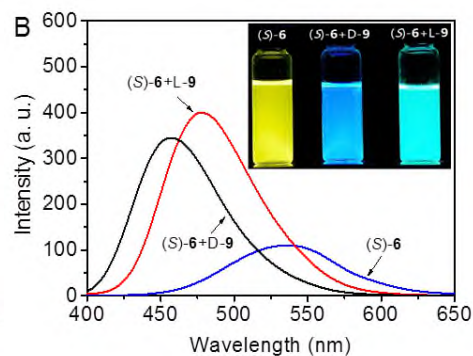
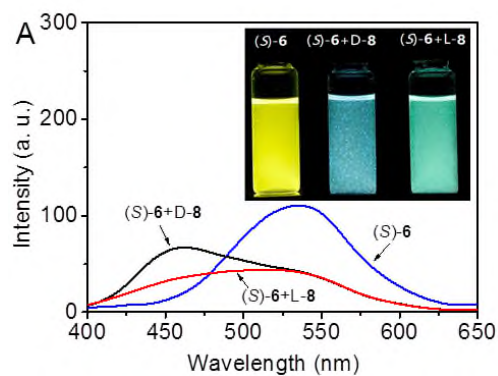
Supplementary Figure 26. (A) Emission spectra of (S)-6 in different solvents. (B) Change in intensity and emission maximum wavelength of emission spectrum of (S)-6 with different solvents. (C) Photos of (S)-6 in different solvents under a portable 365 nm lamp. [(S)-6] = 2.0×10^{-5} M, λ_{ex} = 363 nm, ex/em slit widths = 3/3 nm; EtOH: ethanol; EA: Ethyl acetate, CH: cyclohexane; the solution of (S)-6 was homogeneous and clear in all solvents except acetonitrile in which precipitates appeared.

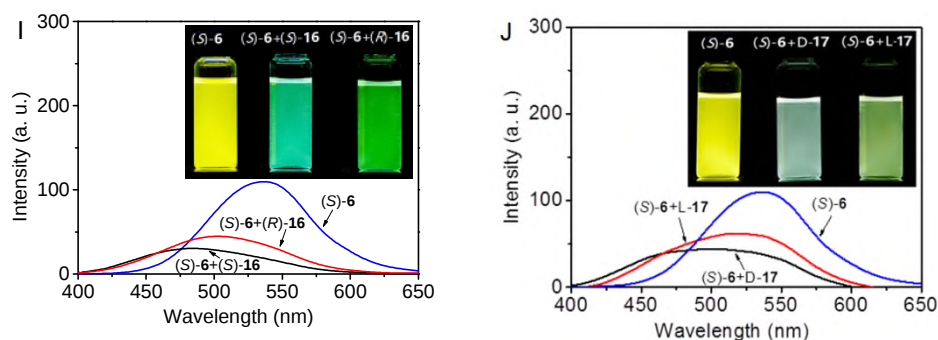


Supplementary Figure 27. Emission spectra of (S)-6 in a mixed solvent of water/THF with water fractions (f_w , volume percent, same below). Inset, curve of fluorescent intensity vs. water fraction. λ_{ex} = 363 nm, ex/em slit widths = 1.5/3 nm, [(S)-6] = 1.0×10^{-5} M).

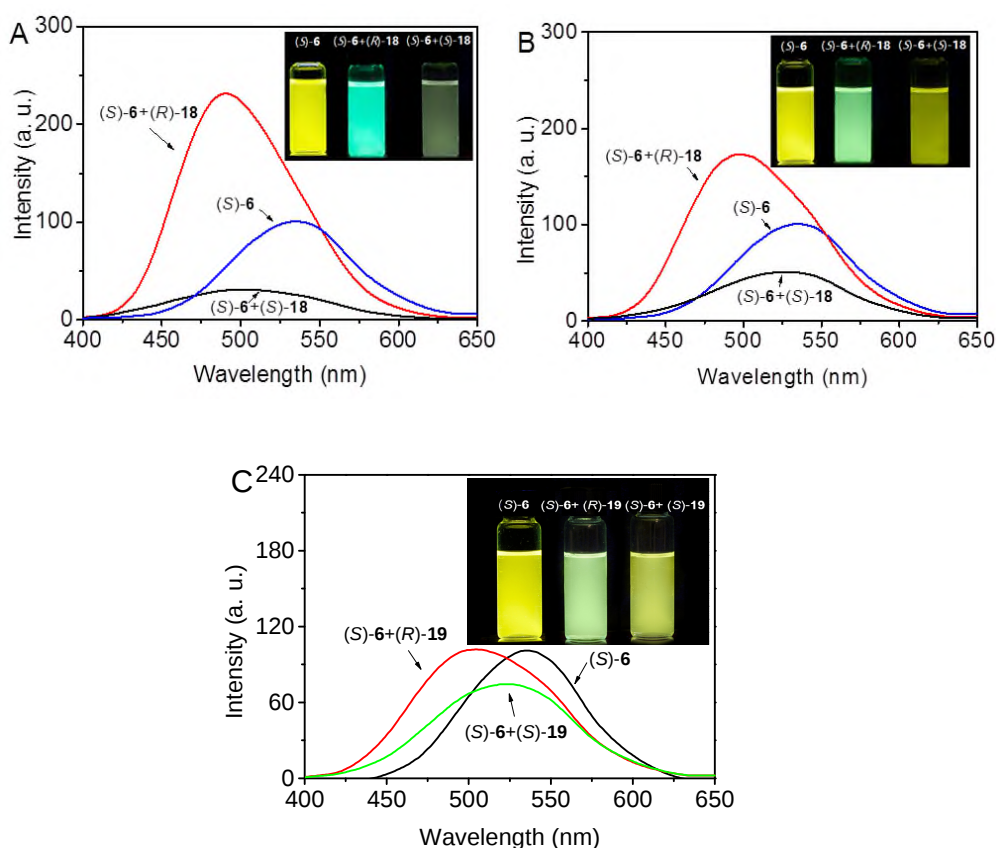


Supplementary Figure 28. (A) Change in emission spectra of (S)-6 in THF with molar equivalent of added hydrochloric acid. (B) Change of emission maximum wavelength and emission intensity with molar equivalent of added hydrochloric acid. (C) Line graph of molar equivalent of hydrochloric acid versus emission wavelength and emission intensity of (S)-6 in THF, respectively. (D) Photos of solution of (S)-6 in THF with molar equivalent of hydrochloric acid. [(S)-6] = 2.0×10^{-5} M, λ_{ex} = 363 nm, ex/em slit widths = 5/3 nm.

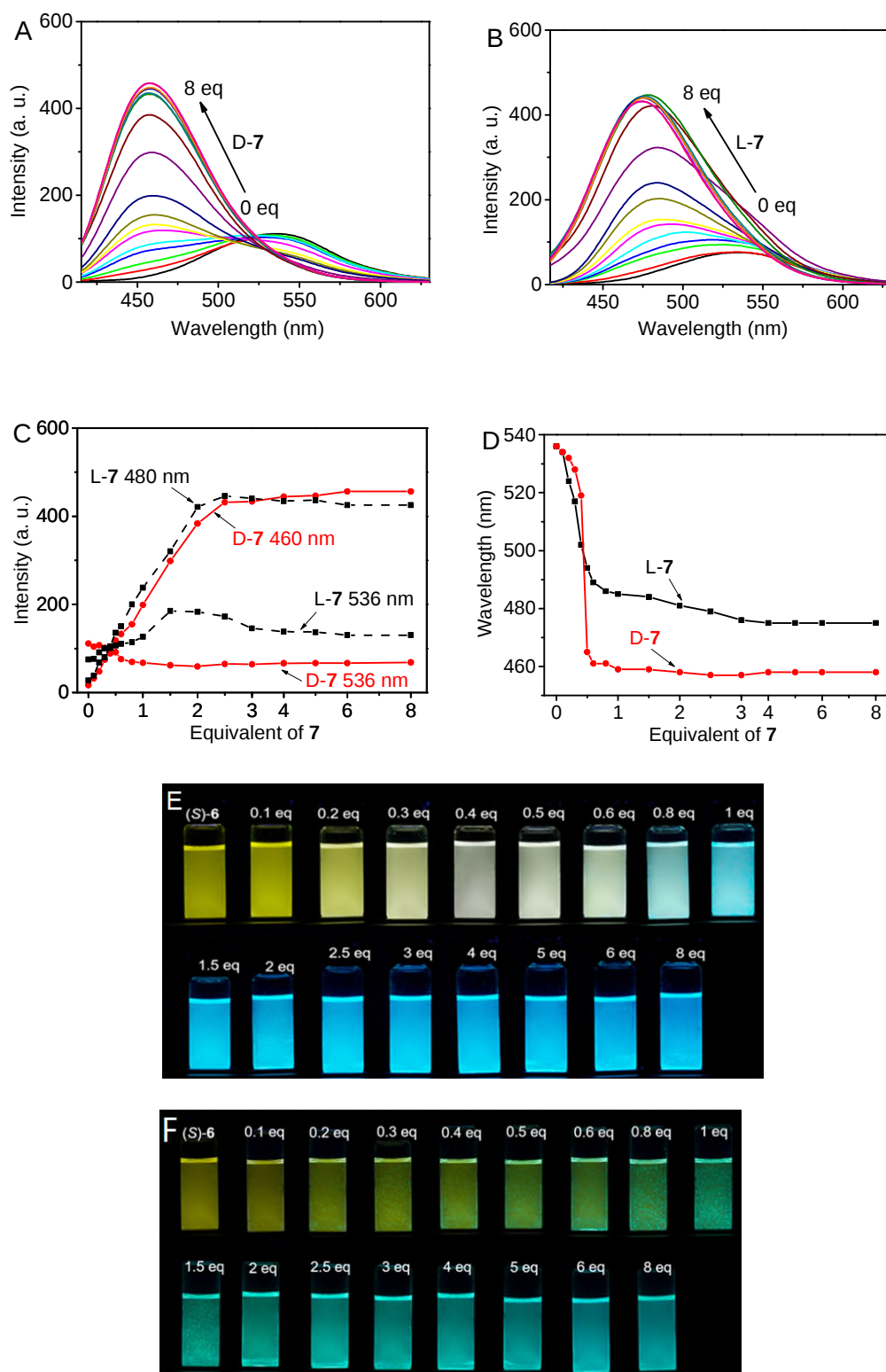




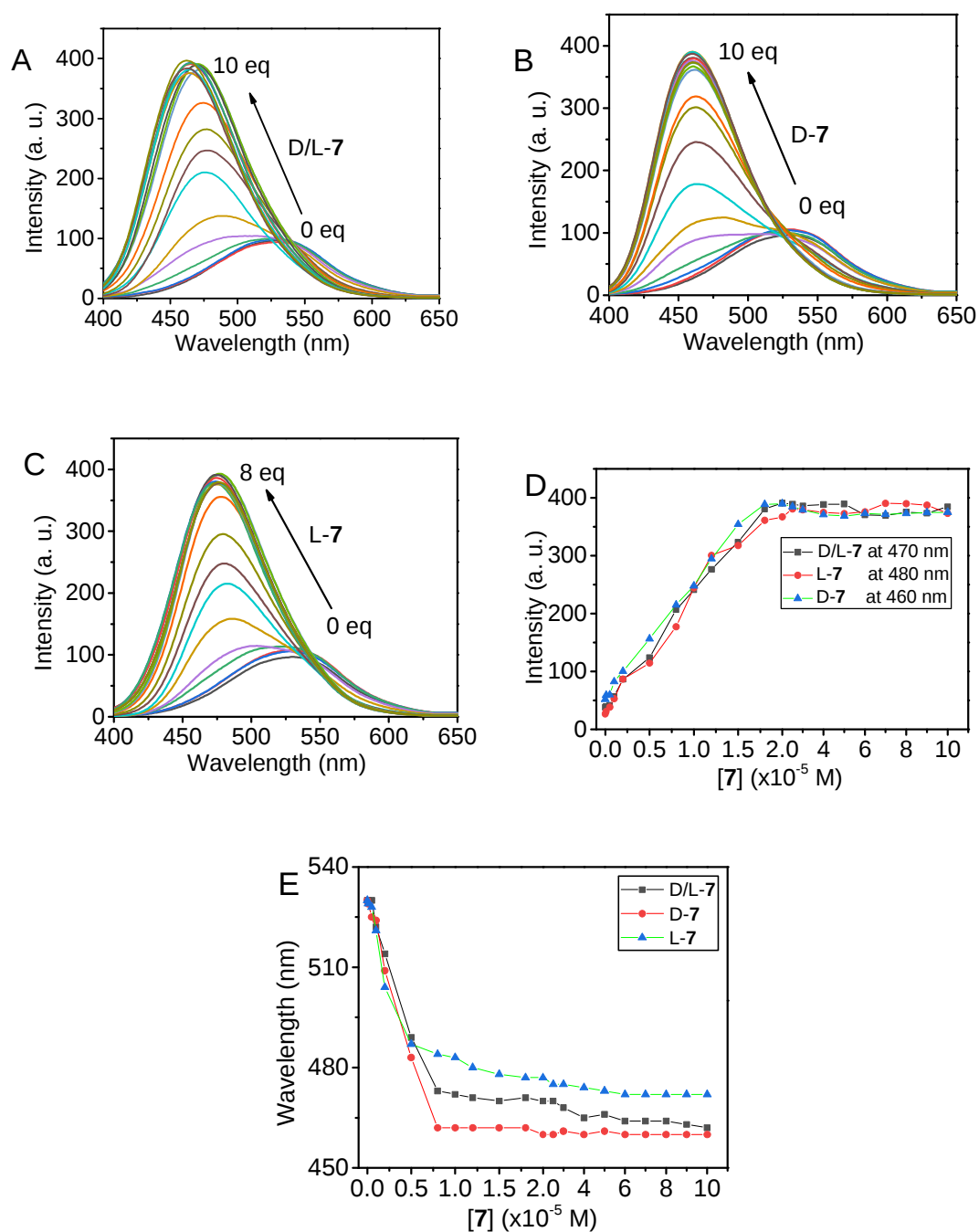
Supplementary Figure 29. Emission spectra of (S)-6 after respectively mixed with two enantiomers of a variety of chiral acids in the mixed solvent of cyclohexane/acetone 98:2. (A) Di-*p*-anisoyltartaric acid **8**/(S)-6 1:1, (B) Dibenzoyltartaric acid **9**/(S)-6 2:1. (C) Tartaric acid **10**/(S)-6 2:1. (D) Boc-glutamic acid **11**/(S)-6 2:1. (E) Boc-aspartic acid **12**/(S)-6 3:1. (F) Malic acid **13**/(S)-6 2:1. (G) 1,1-Cyclohexanedicarboxylic acid **14**/(S)-6 4:1. (H) Mandelic acid **15**/(S)-6 3:1. (I) 2-Chloromandelic acid **16**/(S)-6 4:1. (J) Pyroglutamic acid **17**/(S)-6 4:1. Insets, photos of solution of (S)-6 without and with chiral acid enantiomers under irradiation of 365 nm light. [(S)-6] = 1.0×10^{-5} M.



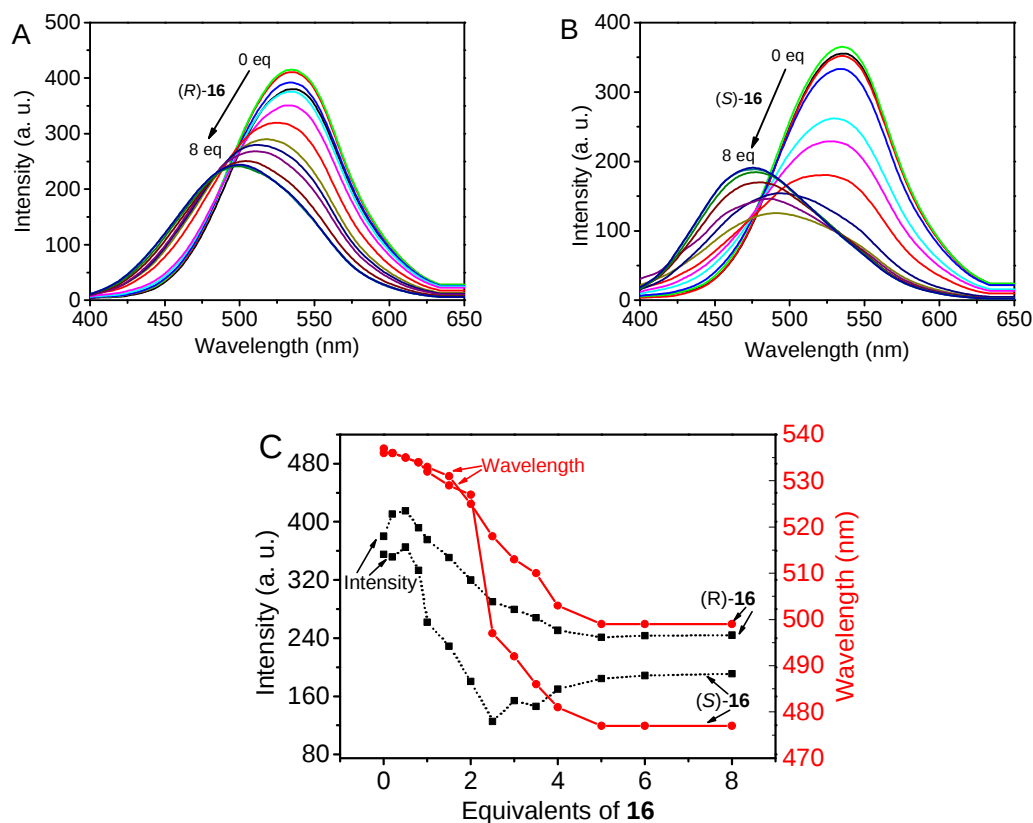
Supplementary Figure 30. Emission spectra of (S)-6 after respectively mixed with two enantiomers of 2-(2,4-dichlorophenoxy)propionic acid **18** (herbicide) with (A) **18**/(S)-6 4:1 and (B) **18**/(S)-6 2:1. (C) Emission spectra of (S)-6 after respectively mixed with two enantiomers of 2-(4-chloro-2-methylphenoxy)propionic acid **19** with **19**/(S)-6 4:1. Insets, photos of solution of (S)-6 without and with chiral acid enantiomers under irradiation of 365 nm light. [(S)-6] = 1.0×10^{-5} M in cyclohexane/acetone 98:2.



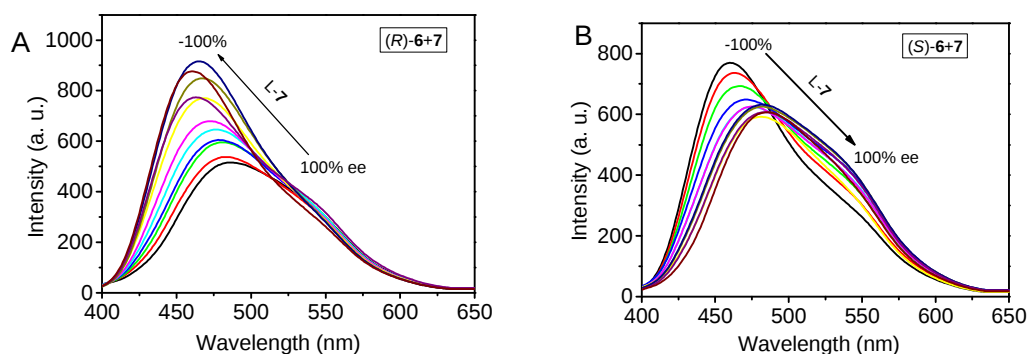
Supplementary Figure 31. Change in emission spectra of (S)-6 with molar equivalent of added D-7 (A) and L-7 (B). (C) Change of emission intensity with D-7 and L-7. (D) Change of the emission $\lambda_{\max}$ with D-7 and L-7. Photos of solution of (S)-6 in the presence of D-7 (E) and L-7 (F) under 365 nm light. [(S)-6] = 1.0×10^{-5} M in cyclohexane/acetone 98:2, λ_{ex} = 363 nm, ex/em slit widths = 1.5/3 nm.



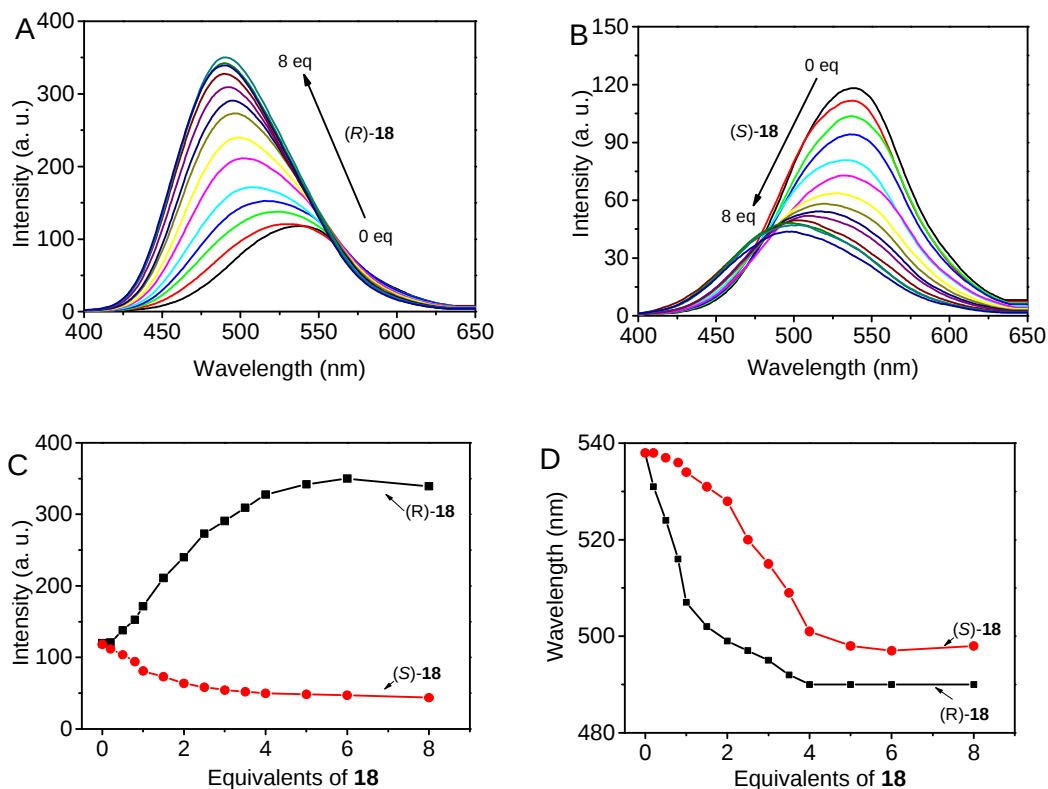
Supplementary Figure 32. Change in emission spectra of (S)-6 with concentration of added D-7 (A), L-7 (B), and racemic 7 (D/L-7) (C). (D) Change of emission intensity with concentration of D-7, L-7 and D/L-7. (E) Change of the emission $\lambda_{\max}$ with concentration of D-7, L-7 and D/L-7. [(S)-6] = 1.0×10^{-5} M in cyclohexane/acetone 98:2, λ_{ex} = 363 nm, ex/em slit widths = 1.5/3 nm.



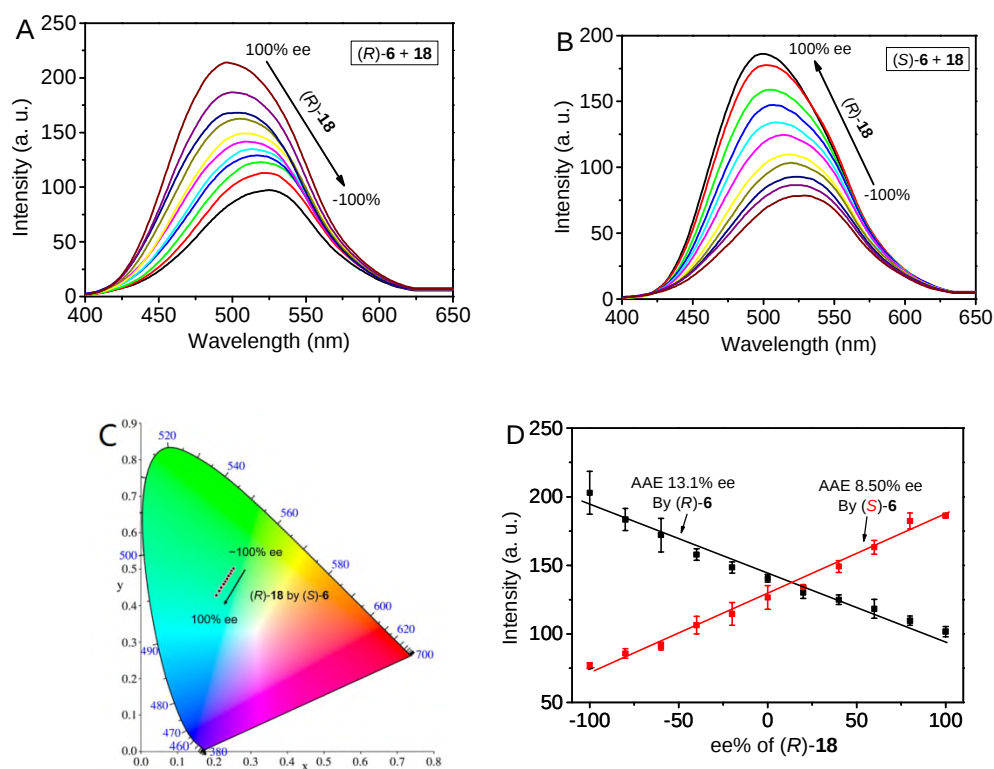
Supplementary Figure 33. Change in emission spectra of (S)-6 with molar equivalents of (R)-16 (A) or (S)-16 (B). (C) Change of emission maximum wavelength and emission intensity with molar equivalents of (R)-16 or (S)-16. [(S)-6] = 1.0×10^{-5} M in cyclohexane/acetone 98:2, λ_{ex} = 363 nm, ex/em slit widths = 3/3 nm.



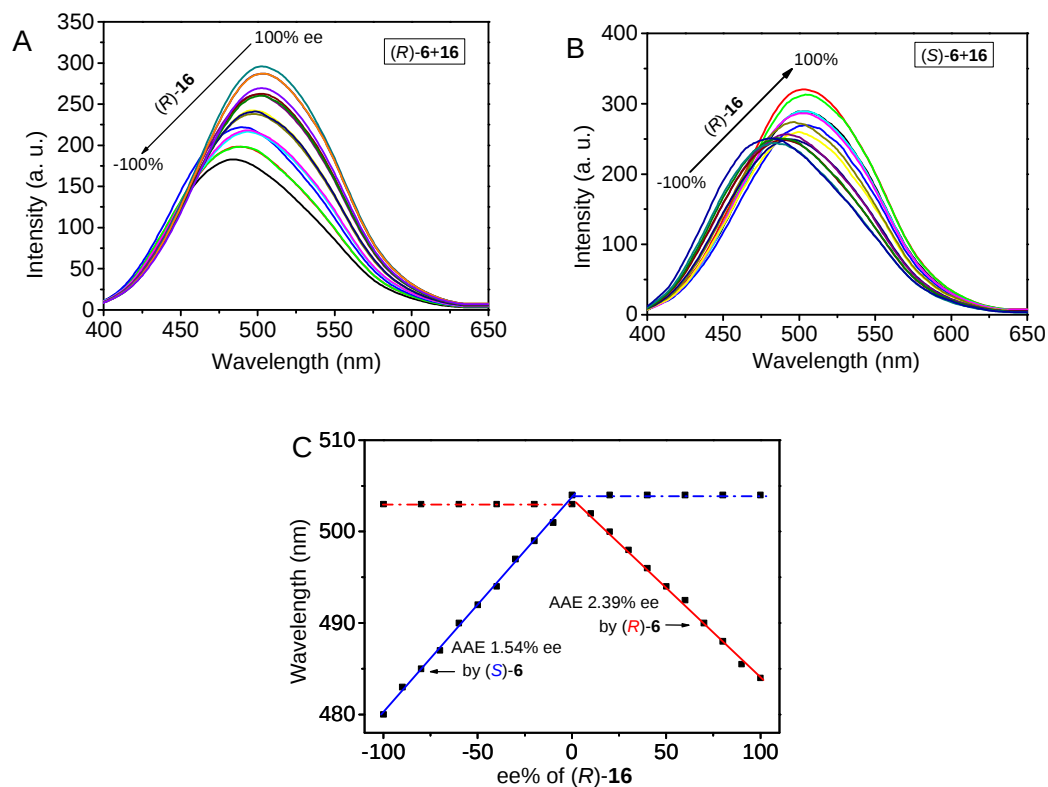
Supplementary Figure 34 (A) Emission spectrum of the solution of (R)-6 was changed with ee% of L-7. (B) Emission spectrum of the solution of (S)-6 was changed with ee% of L-7. [(R)-6] = [(S)-6] = [7] = 1.0×10^{-5} M in cyclohexane/acetone 98:2.



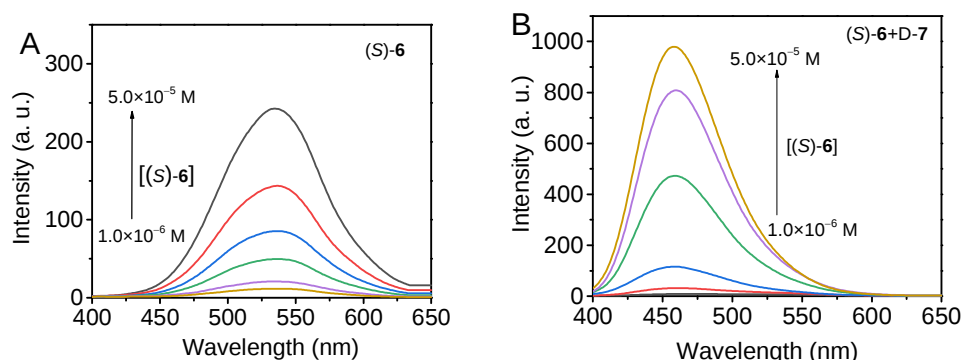
Supplementary Figure 35. Change in emission spectra of (S)-6 with molar equivalents of (R)-18 (A) or (S)-18 (B). And change of emission intensity (C) and emission maximum wavelength (D) with molar equivalents of (R)-18 or (S)-18. [(S)-6] = 1.0×10^{-5} M in cyclohexane/acetone 98:2, λ_{ex} = 363 nm, ex/em slit widths = 1.5/3 nm.

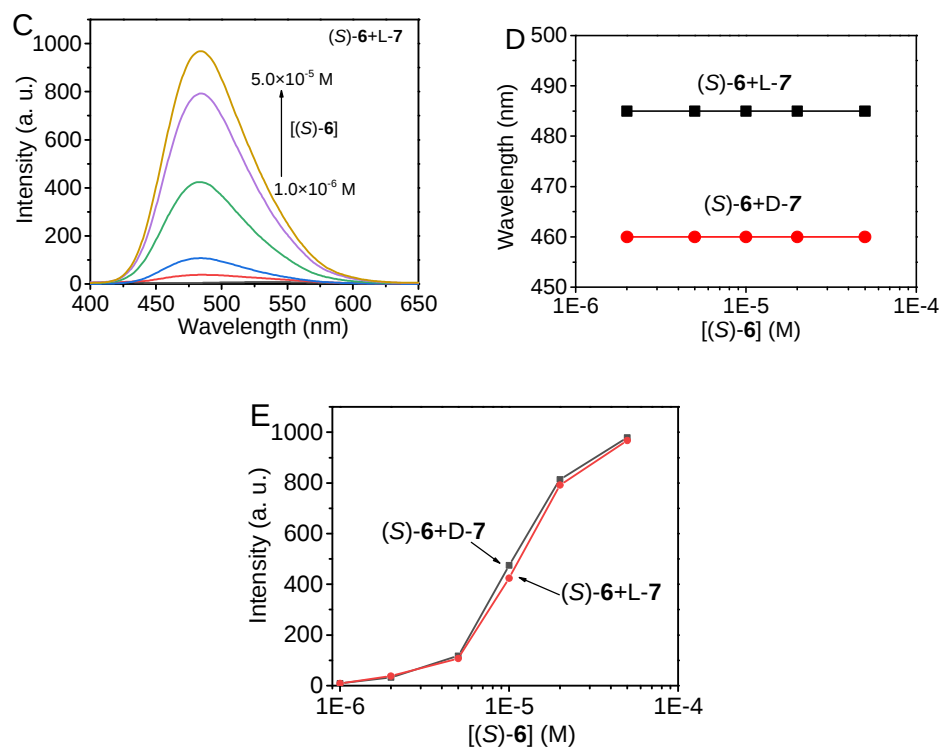


Supplementary Figure 36. (A) Emission spectrum of the solution of (*R*)-**6** was changed with ee% of (*R*)-**18**. (B) Emission spectrum of the solution of (*S*)-**6** was changed with ee% of (*R*)-**18**. (C) CIE chromaticity diagram of ee% of (*R*)-**18** measured by (*R*)-**6**. (D) Change of emission intensity of **6** with ee% of (*R*)-**18**. [(*R*)-**6**] = [(*S*)-**6**] = 1/2[**18**] = 1.0×10^{-5} M in cyclohexane/acetone 98:2; λ_{ex} = 363 nm, ex/em slit widths = 1.5/3 nm.

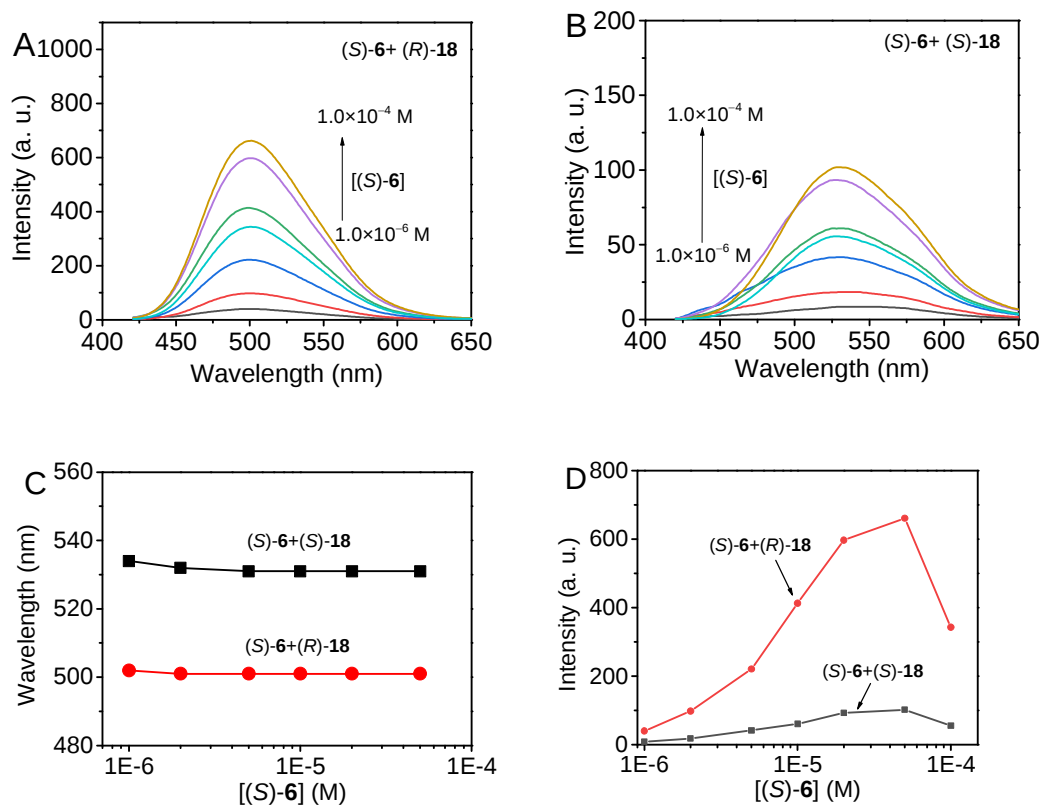


Supplementary Figure 37. (A) Emission spectrum of the solution of (*R*)-**6** was changed with ee% of (*R*)-**16**. (B) Emission spectrum of the solution of (*S*)-**6** was changed with ee% of (*R*)-**16**. (C) Change of emission maximum wavelength of **6** with ee% of (*R*)-**16**. [(*R*)-**6**] = [(*S*)-**6**] = 1/4[**16**] = 1.0×10^{-5} M in cyclohexane/acetone 98:2; λ_{ex} = 363 nm, ex/em slit widths = 3/3 nm.

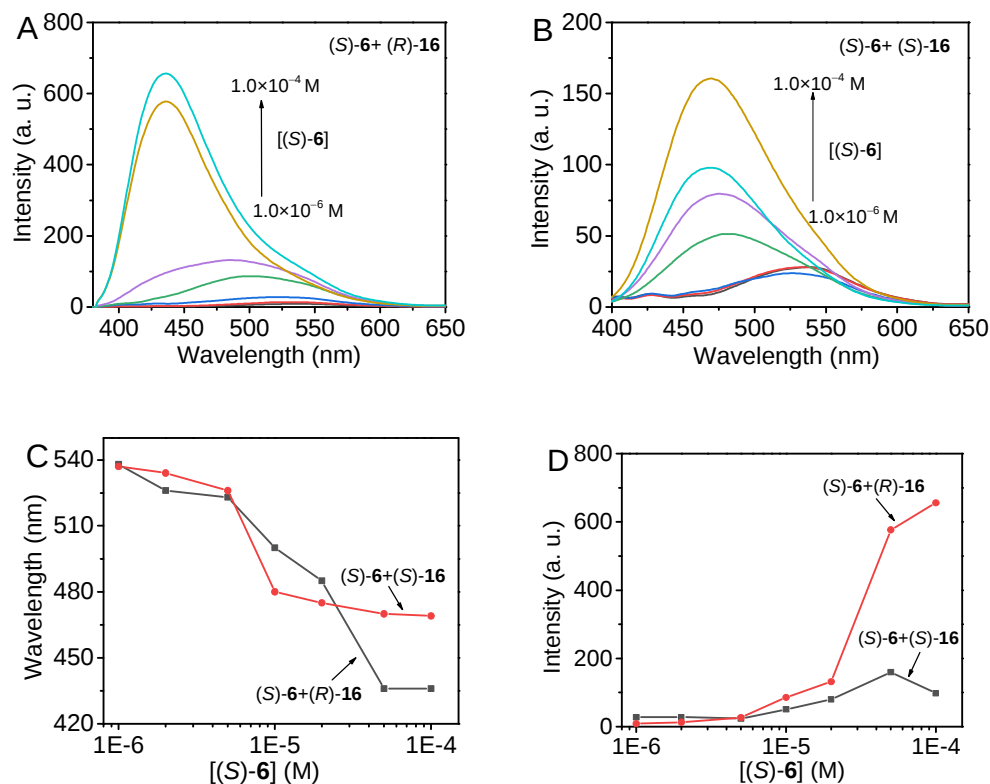




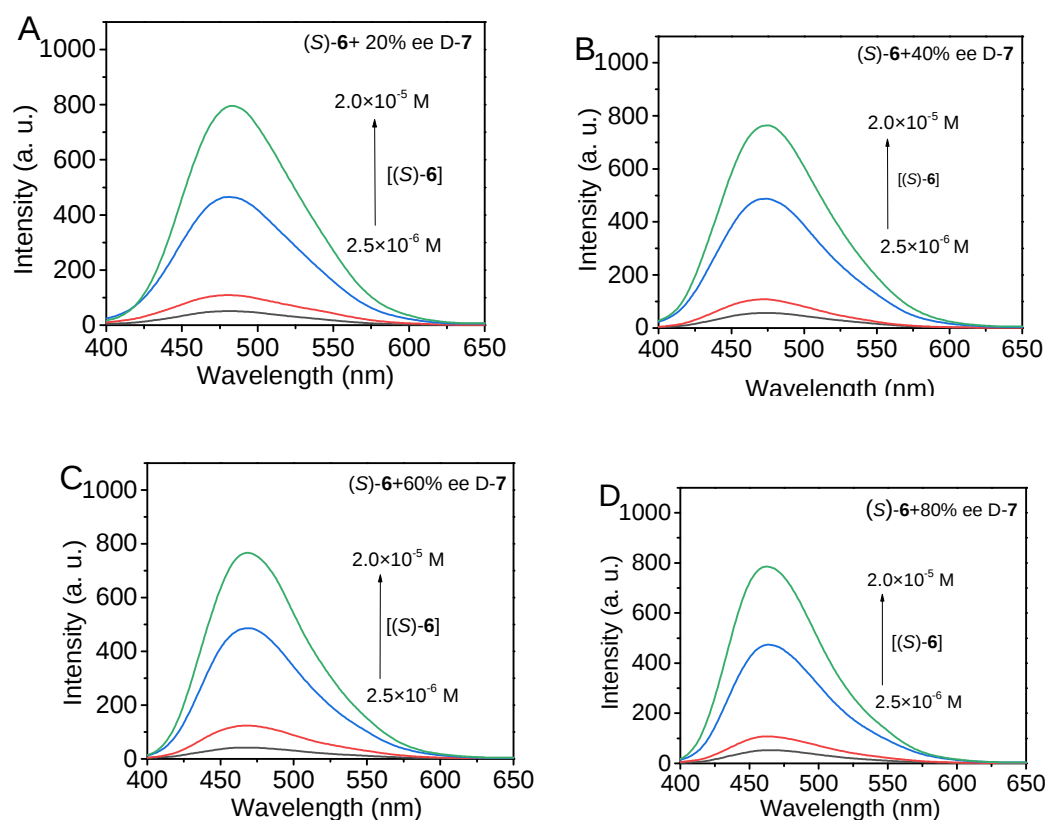
Supplementary Figure 38. Change in emission spectra of (S)-6 (A) and a mixture (1:1) of (S)-6 and D-7 (B) or a mixture (1:1) of (S)-6 and L-7 (C) with concentration in hexane/acetone 98:2. And change of emission wavelength (D) and emission intensity (E) of (S)-6 with concentration of the mixture of it and one enantiomer of 7. $\lambda_{\text{ex}} = 363$ nm, em/ex slit widths = 1.5/3 nm.



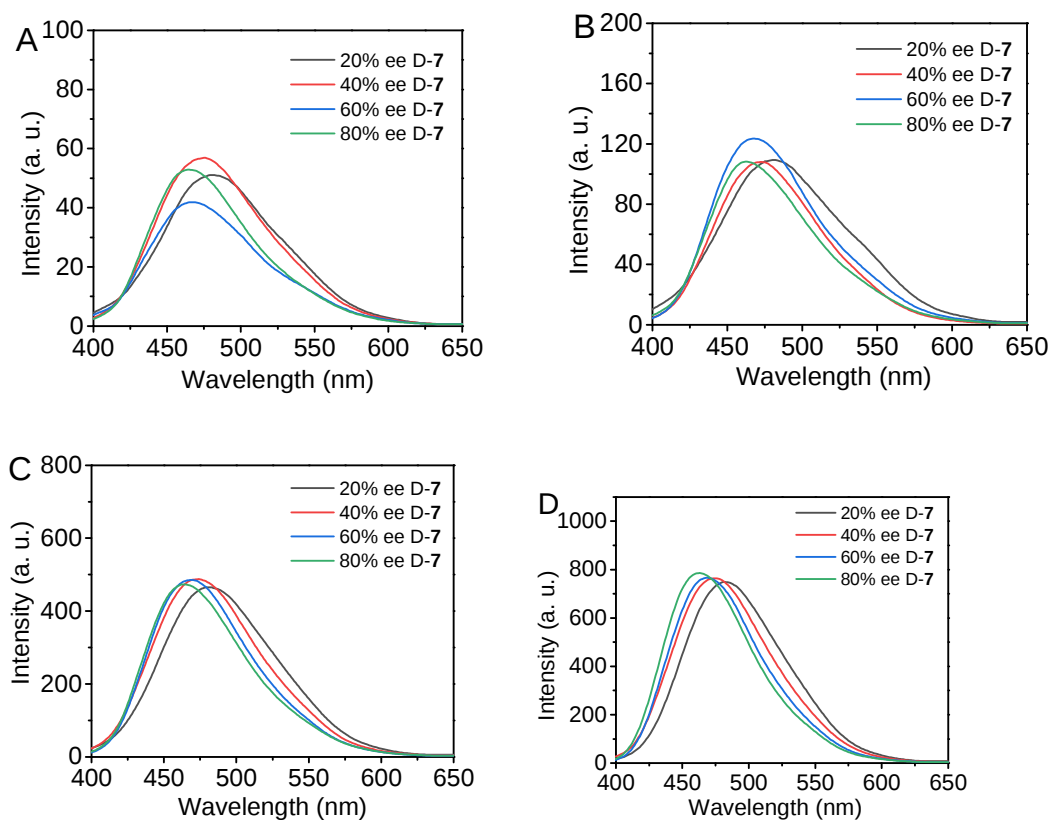
Supplementary Figure 39. Change in emission spectra of a mixture (1:2) of (S)-6 and (R)-18 (A) or a mixture (1:4) of (S)-6 and (S)-18 (B) with concentration in cyclohexane/acetone 98:2. And change of emission wavelength (C) and emission intensity (D) of (S)-6 with concentration of the mixture of it and one enantiomer of 18. $\lambda_{\text{ex}} = 363$ nm, em/ex slit widths = 1.5/3 nm.



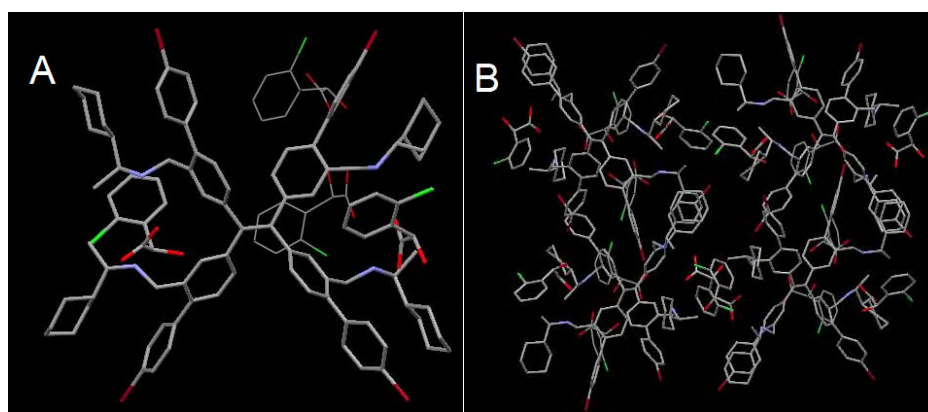
Supplementary Figure 40. Change in emission spectra of a mixture (1:4) of (S)-6 and (R)-16 (A) or a mixture (1:4) of (S)-6 and (S)-16 (B) with concentration in cyclohexane/acetone 98:2. And change of emission wavelength (C) and emission intensity (D) of (S)-6 with concentration of the mixture of it and one enantiomer of **16**. $\lambda_{\text{ex}} = 363$ nm, em/ex slit widths = 1.5/3 nm.



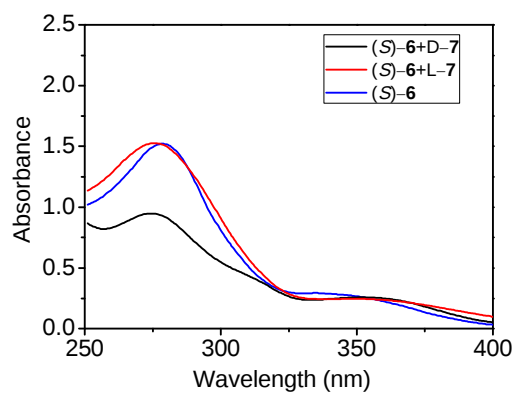
Supplementary Figure 41. Change in emission spectra of (S)-6 with concentration of it in the presence of 20% ee D-7 (A), 40% ee D-7 (B), 60% ee D-7 (C), and 80% ee D-7 (D) in cyclohexane/acetone 98:2. [(S)-6]/[7] = 1:2; [(S)-6] was changed from 2.5×10^{-6} M, 5.0×10^{-6} M, 1.0×10^{-5} M, to 2.0×10^{-5} M. $\lambda_{\text{ex}} = 363$ nm, em/ex slit widths = 1.5/3 nm.



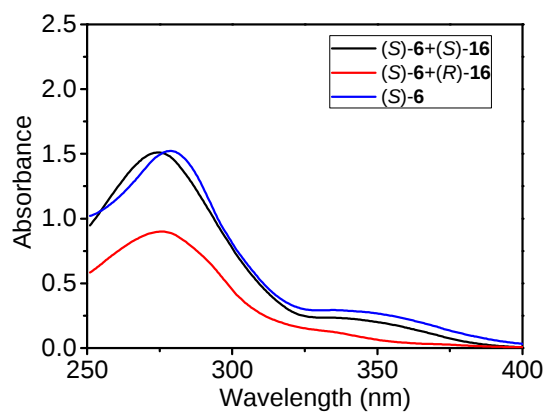
Supplementary Figure 42. Change in emission spectra of (S)-6 with enantiomeric composition of 7 when concentration of (S)-6 was at 2.5×10^{-6} M (A), 5.0×10^{-6} M (B), 1.0×10^{-5} M (C), and 2.0×10^{-5} M (D) in cyclohexane/acetone 98:2. [(S)-6]/[7] = 1:2; λ_{ex} = 363 nm, em/ex slit widths = 1.5/3 nm.



Supplementary Figure 43. Crystal structure (A) of (S)-6-(R)-16 complex grown from CHCl_3 /acetone/acetonitrile and the molecules packing (B) (hydrogen atoms were omitted for clarity).



Supplementary Figure 44. UV-vis spectra of (S)-6 and di-P-toluoyl-(D or L)-tartaric acid mixed solution in cyclohexane ($[(S)\text{-}6] = 1/2 [\text{Acid}] = 1 \times 10^{-5} \text{ M}$).



Supplementary Figure 45. UV-vis spectra of (S)-6 and (R or S)-2-Chloromandelic acid mixed solution in cyclohexane ($[(S)\text{-}6] = 1/4 [\text{16}] = 1 \times 10^{-5} \text{ M}$).

Supplementary Tables

Supplementary Table 1. The fluorescence quantum yield ($\Phi\%$)^a

Compound	Solvent	$\Phi\%$	Fluorescence Lifetime
(<i>R</i>)- 6	THF	1.55%	
(<i>S</i>)- 6	THF	1.61%	
(<i>R</i>)- 6	H ₂ O/THF 95:5	50.8%	
(<i>S</i>)- 6	H ₂ O/THF 95:5	52.6%	
(<i>R</i>)- 6	Acetone	0.72%	
(<i>S</i>)- 6	Acetone	0.79%	
(<i>R</i>)- 6	Cyclohexane/Acetone 98:2	12.8%	4.27 ns
(<i>S</i>)- 6	Cyclohexane/Acetone 98:2	12.2%	3.99 ns
(<i>S</i>)- 6 + 1eq D- 7	Cyclohexane/Acetone 98:2	24.4%	
(<i>S</i>)- 6 + 1eq L- 7	Cyclohexane/Acetone 98:2	25.6%	
(<i>S</i>)- 6 + 2eq D- 7	Cyclohexane/Acetone 98:2	29.7%	3.58 ns
(<i>S</i>)- 6 + 2eq L- 7	Cyclohexane/Acetone 98:2	31.9%	4.44 ns
(<i>S</i>)- 6 + 4eq D- 7	Cyclohexane/Acetone 98:2	44.1%	
(<i>S</i>)- 6 + 4eq L- 7	Cyclohexane/Acetone 98:2	49.8%	
(<i>S</i>)- 6 + 2eq D- 7	Acetone	23.2%	
(<i>S</i>)- 6 + 2eq L- 7	Acetone	26.7%	
(<i>S</i>)- 6 + 1eq (<i>S</i>)- 16	Cyclohexane/Acetone 98:2	12.2%	
(<i>S</i>)- 6 + 1eq (<i>R</i>)- 16	Cyclohexane/Acetone 98:2	15.3%	
(<i>S</i>)- 6 + 2eq (<i>S</i>)- 16	Cyclohexane/Acetone 98:2	11.2%	
(<i>S</i>)- 6 + 2eq (<i>R</i>)- 16	Cyclohexane/Acetone 98:2	14.1%	
(<i>S</i>)- 6 + 4eq (<i>S</i>)- 16	Cyclohexane/Acetone 98:2	8.9%	2.15 ns
(<i>S</i>)- 6 + 4eq (<i>R</i>)- 16	Cyclohexane/Acetone 98:2	9.9%	1.22 ns

^a The fluorescence quantum yield was measured using quinine sulfate ($\Phi_f = 0.546$) in 0.5 M H₂SO₄ as standard.