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Electronic Supplementary Information

for

Chiral Tetracoordinate Organoboranes Based on Double B←N Bridged Bipyridine with Circularly Polarized Luminescence

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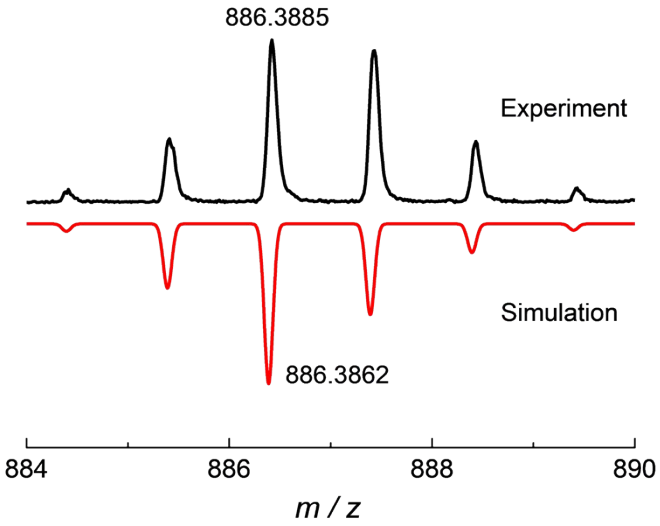

Fig. S1. High-resolution MALDI-TOF MS spectrum of **(*R*,*R*)-1**.

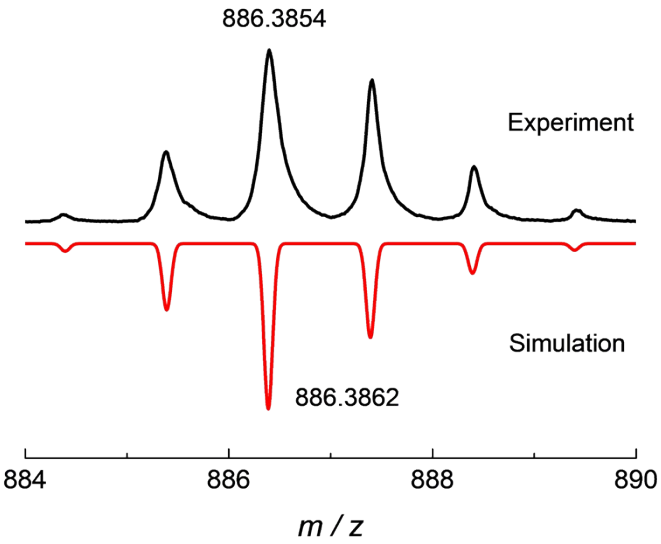

Fig. S2. High-resolution MALDI-TOF MS spectrum of **(*S*,*S*)-1**.

2. Thermal properties

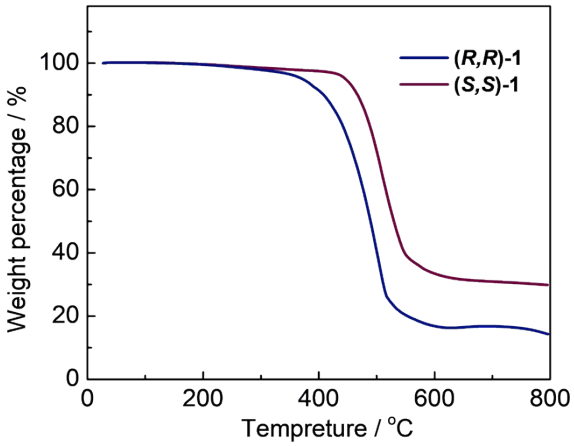

Fig. S3. Thermogravimetric analysis (TGA) curves of **(*R*,*R*)-1** and **(*S*,*S*)-1**.

3. Photophysical properties

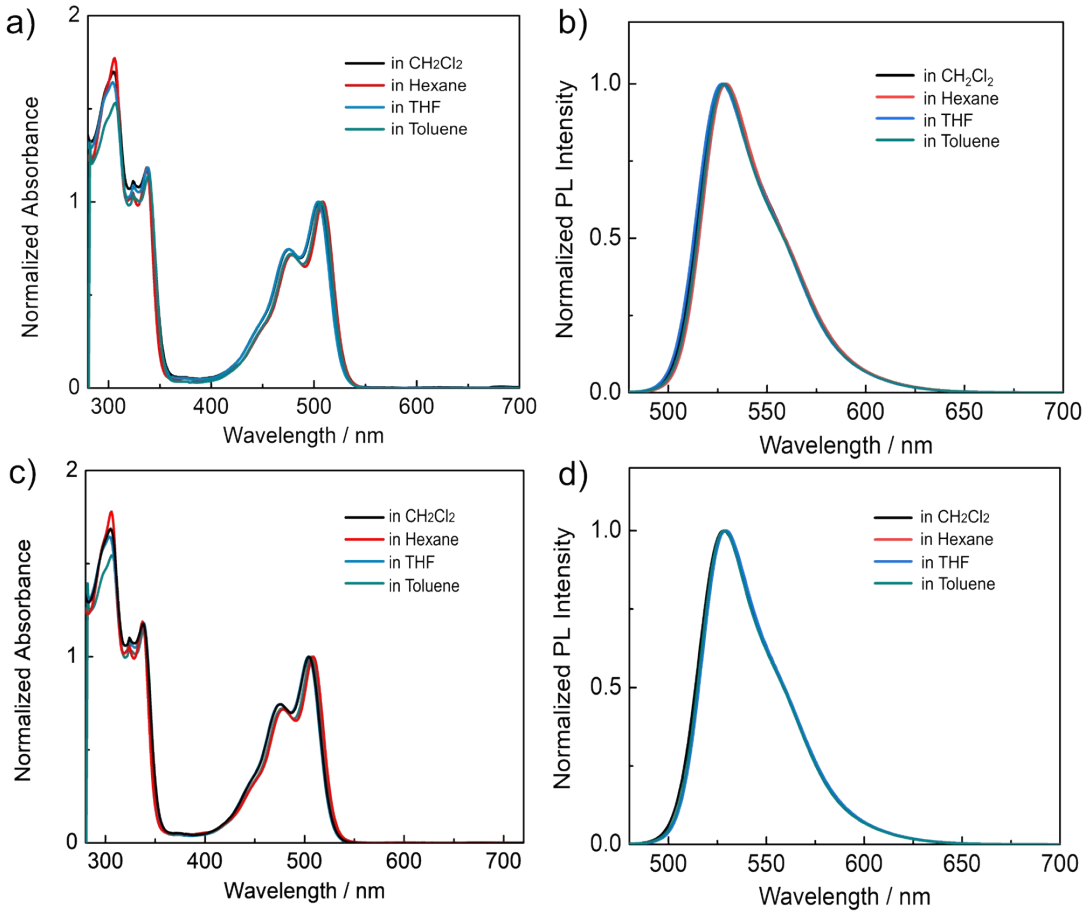

Fig. S4. UV/Vis absorption and fluorescence (λ_{ex} = 460 nm) spectra of a), b) **(*R*,*R*)-1** and c), d) **(*S*,*S*)-1** in various solvents.

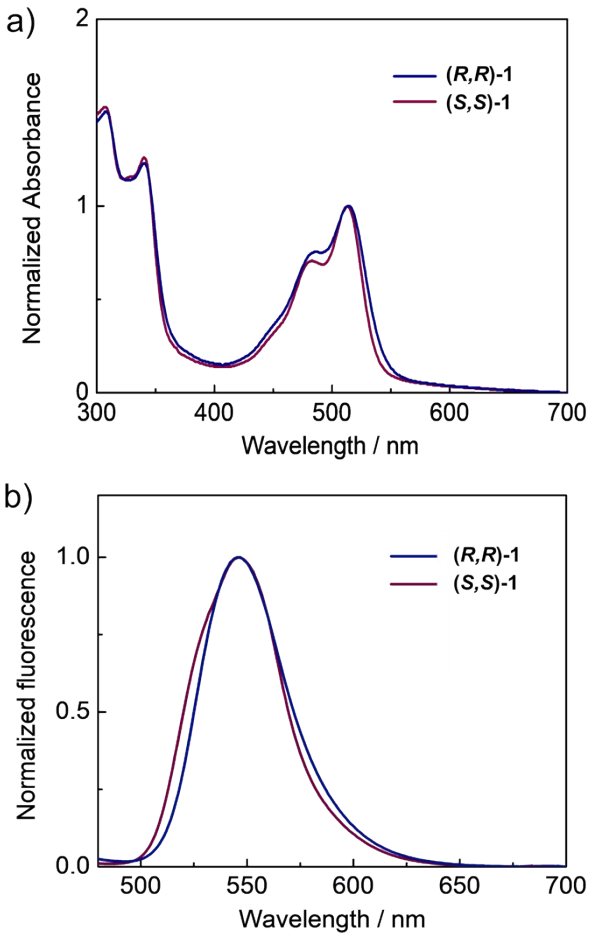

Fig. S5. a) UV/Vis absorption and b) fluorescence (λ_{ex} = 460 nm) spectra of **(*R*,*R*)-1** and **(*S*,*S*)-1** in thin films.

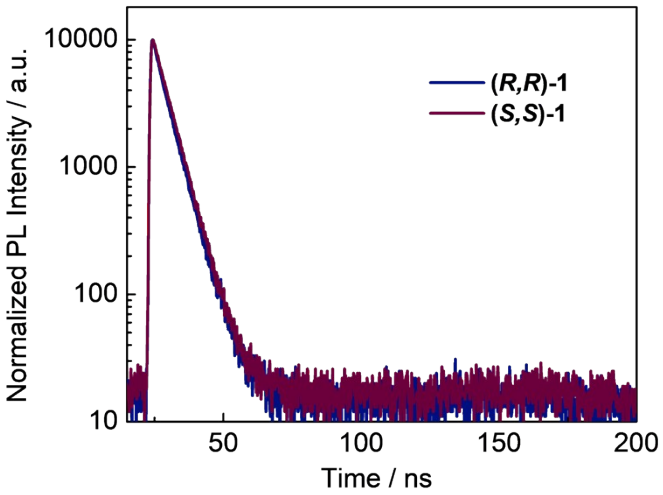

Fig. S6. Transient photoluminescence decay spectra of **(*R*,*R*)-1** and **(*S*,*S*)-1** in thin films. Both of them display the nanosecond–scaled lifetimes of 9.3 ns. There are no delayed components, indicating that **(*R*,*R*)-1** and **(*S*,*S*)-1** are typical fluorescent materials.

Table S1. Absorption and fluorescence properties, as well as the calculated energy levels of **(*R*,*R*)-1**, **(*S*,*S*)-1** and **2**.

Compd	λ_{abs}[a] (nm)	λ_F [a] (nm)	φ_F[a]	E_{LUMO}[c] (eV)	E_{HOMO}[c] (eV)
(*R*,*R*)-1	504, 474	527	0.94	–2.49	–5.38
(*S*,*S*)-1	504, 474	529	0.94	–2.56	–5.41
2	501, 471[b]	528[b]	0.98[b]	–2.75	–5.74

[a]Measured in THF solution. [b]Measured in $CHCl_3$ solution. [c]DFT calculation at the B3LYP/6-311G(d) level of theory.

The fluorescence bands and long-wavelength absorption bands of **(*R*,*R*)-1** and **(*S*,*S*)-1**, as well as their fluorescence quantum yields in solution are very comparable to that of compound **2**. These results suggest that the BNBP skeleton significantly contributes to the optical properties of **(*R*,*R*)-1** and **(*S*,*S*)-1**. On the other hand, the LUMO and HOMO energy levels of **(*R*,*R*)-1** and **(*S*,*S*)-1** are higher than that of compound **2** by 0.2−0.3 eV, indicating the electron-donating effects of the BINOL groups.

4. Chiroptical properties

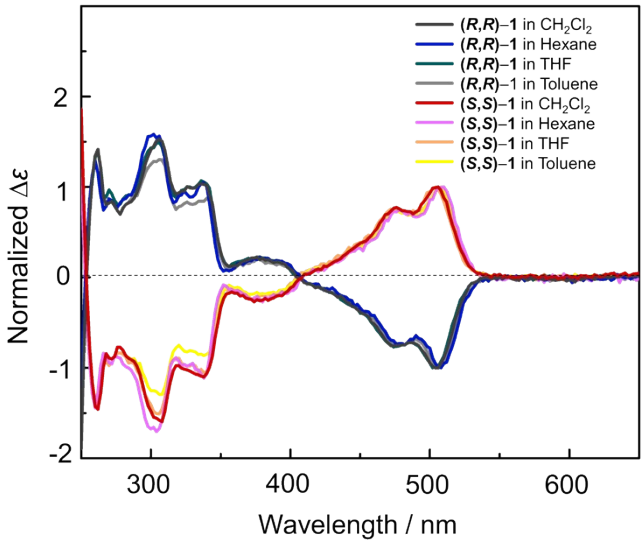

Fig. S7. Circular dichroism (CD) spectra of **(*R*,*R*)-1** and **(*S*,*S*)-1** in various solvents.

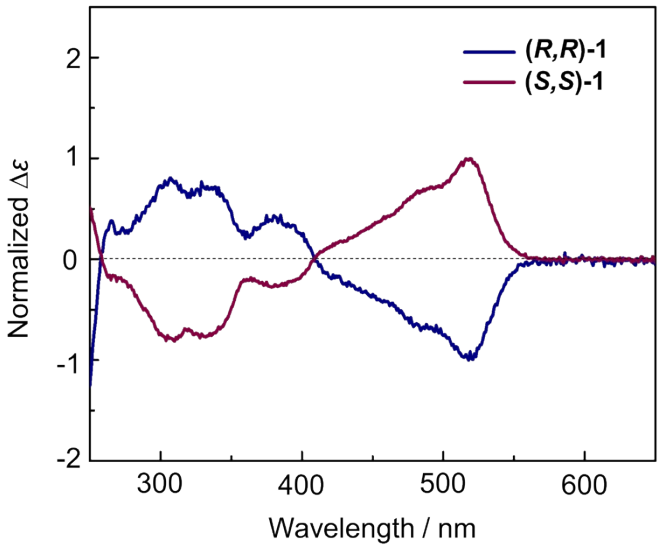

Fig. S8. Circular dichroism (CD) spectra of **(*R*,*R*)-1** and **(*S*,*S*)-1** in thin films.

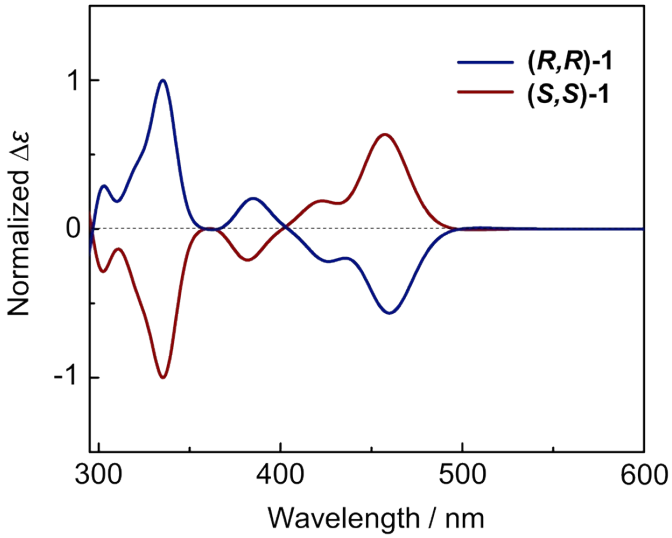

Fig. S9. Calculated circular dichroism (CD) spectra of **(*R*,*R*)-1** and **(*S*,*S*)-1**.

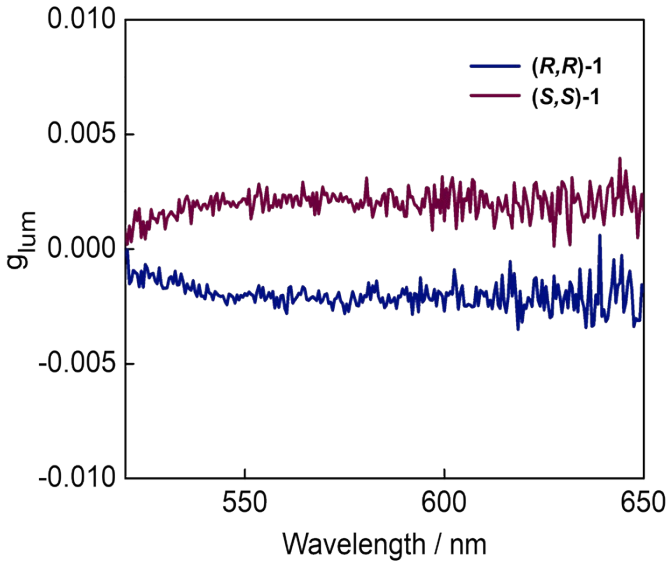

Fig. S10. The g_{lum} values of **(*R*,*R*)-1** and **(*S*,*S*)-1** in THF as a function of the emission wavelength.

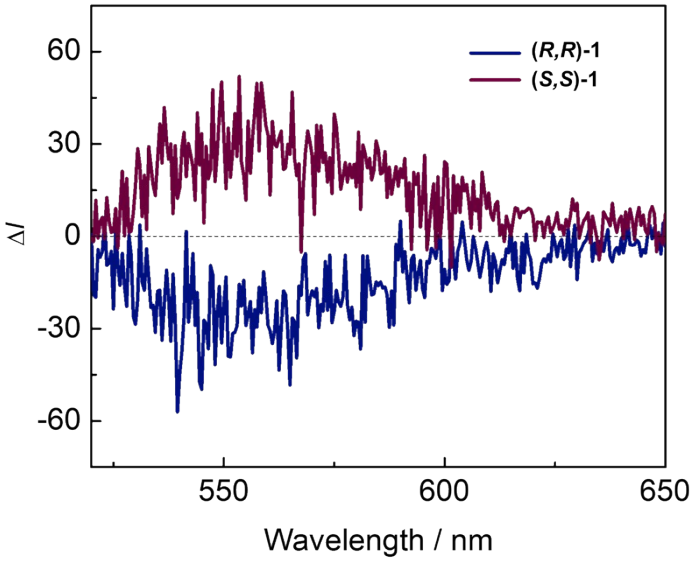

Fig. S11. Circularly polarized luminescence spectra of **(*R*,*R*)-1** and **(*S*,*S*)-1** in thin films.

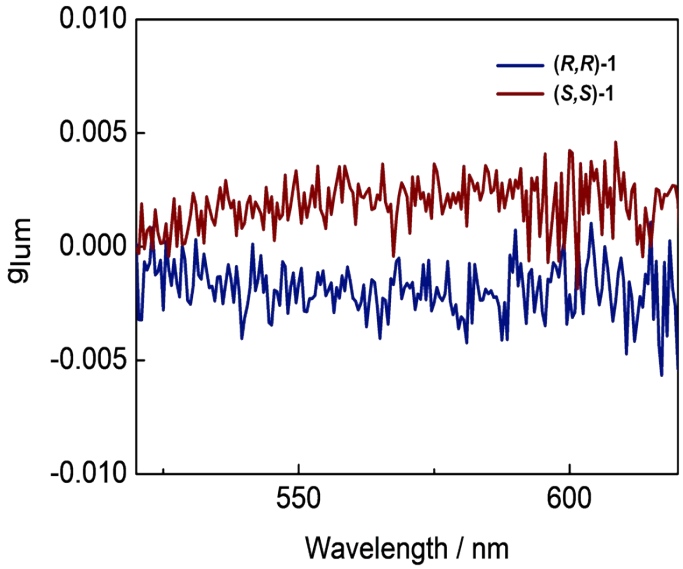

Fig. S12. The g_{lum} values of **(*R*,*R*)-1** and **(*S*,*S*)-1** in thin films as a function of the emission wavelength.

5. X-ray crystallographic analysis

Single crystal X-ray diffraction data were collected on a Rigaku RAXIS-PRID diffractometer with graphite monochromator Mo·Kα radiation. The structures were solved using the SHELXTL-97 and refined by the full-matrix least-squares on F^2 (SHELXL-97). CCDC of 2124951 and 2124961 of **(*R*,*R*)-1** and **(*S*,*S*)-1** contain the supplementary crystallographic data for this paper, respectively. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/.

X-ray crystallographic analysis of (*R*,*R*)-1. The single crystals of **(*R*,*R*)-1** and **(*S*,*S*)-1** suitable for XRD analysis were grown by slow diffusion of CH_3OH into their CH_2Cl_2 solutions.

The crystal data of **(*R*,*R*)-1** are as follows: $C_{58}H_{48}B_2N_4O_4$; FW = 886.62, Orthorhombic, space group $P2_12_12_1$, a = 10.1907(3) Å, b = 13.7025(5) Å, c = 33.1501(11), α = 90°, β = 90°, γ = 90°, V = 4629.0(3) Å^3, Z = 4, D_{calcd} = 1.272 g cm^{-3}, $R1$ = 0.0469 ($I > 2\sigma(I)$), w$R2$ = 0.1181 (all data), GOF = 1.077.

The crystal data of **(*S*,*S*)-1** are as follows: $C_{58}H_{48}B_2N_4O_4$; FW = 886.62, Orthorhombic, space group $P2_12_12_1$, a = 10.1845(4) Å, b = 13.6915(5) Å, c = 33.1377(11), α = 90°, β = 90°, γ = 90°, V = 4620.8(3) Å^3, Z = 4, D_{calcd} = 1.274 g cm^{-3}, $R1$ = 0.0271 ($I > 2\sigma(I)$), w$R2$ = 0.0675 (all data), GOF = 1.051.

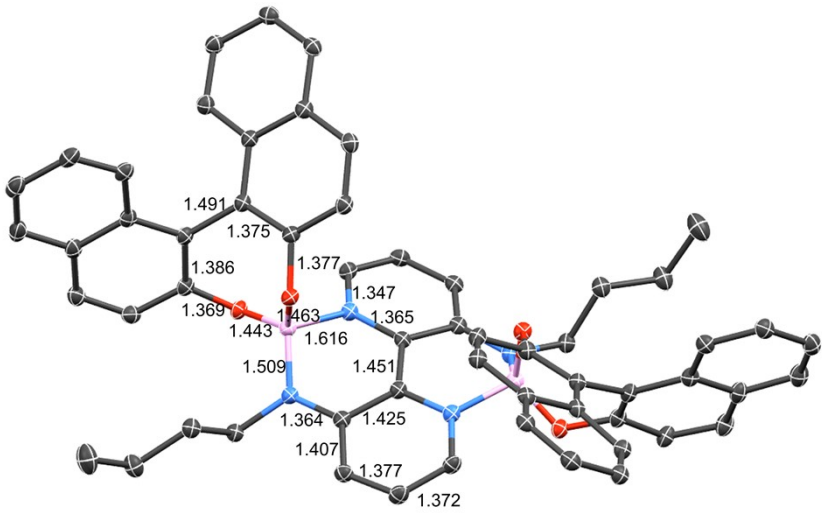

Fig. S13. Single crystal structure of **(*R*,*R*)-1** and bond-length analysis based on X-ray diffraction data. Other hydrogen atoms are not shown for clarity.

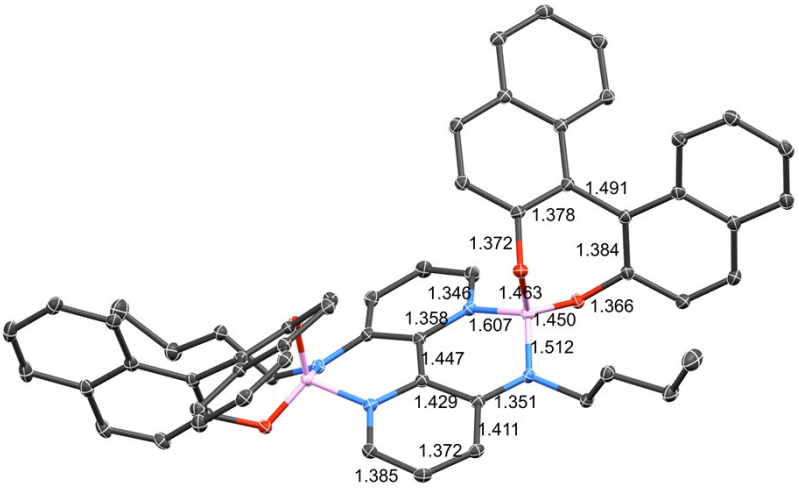

Fig. S14. Single crystal structure of **(*S*,*S*)-1** and bond-length analysis based on X-ray diffraction data. Other hydrogen atoms are not shown for clarity.

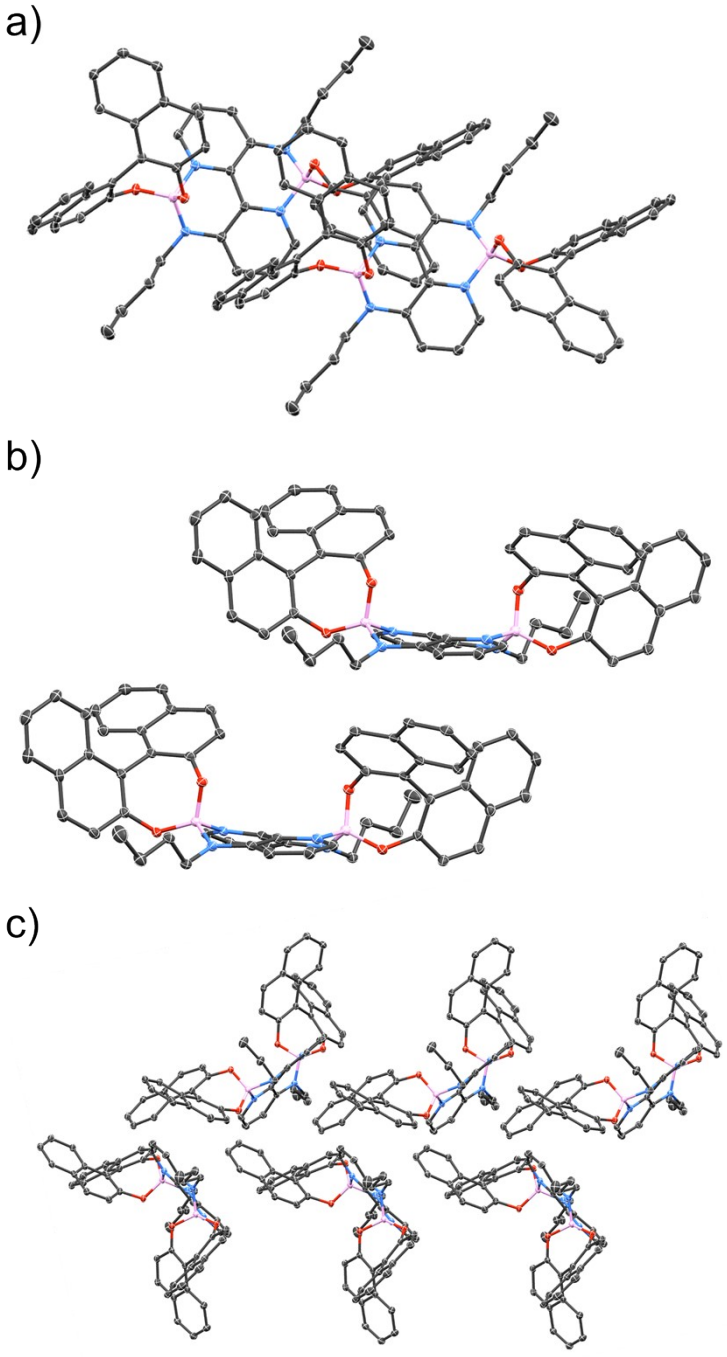

Fig. S15. a)−c) Packing structure of **(*R*,*R*)-1** in the crystalline state. Hydrogen atoms were omitted for clarity.

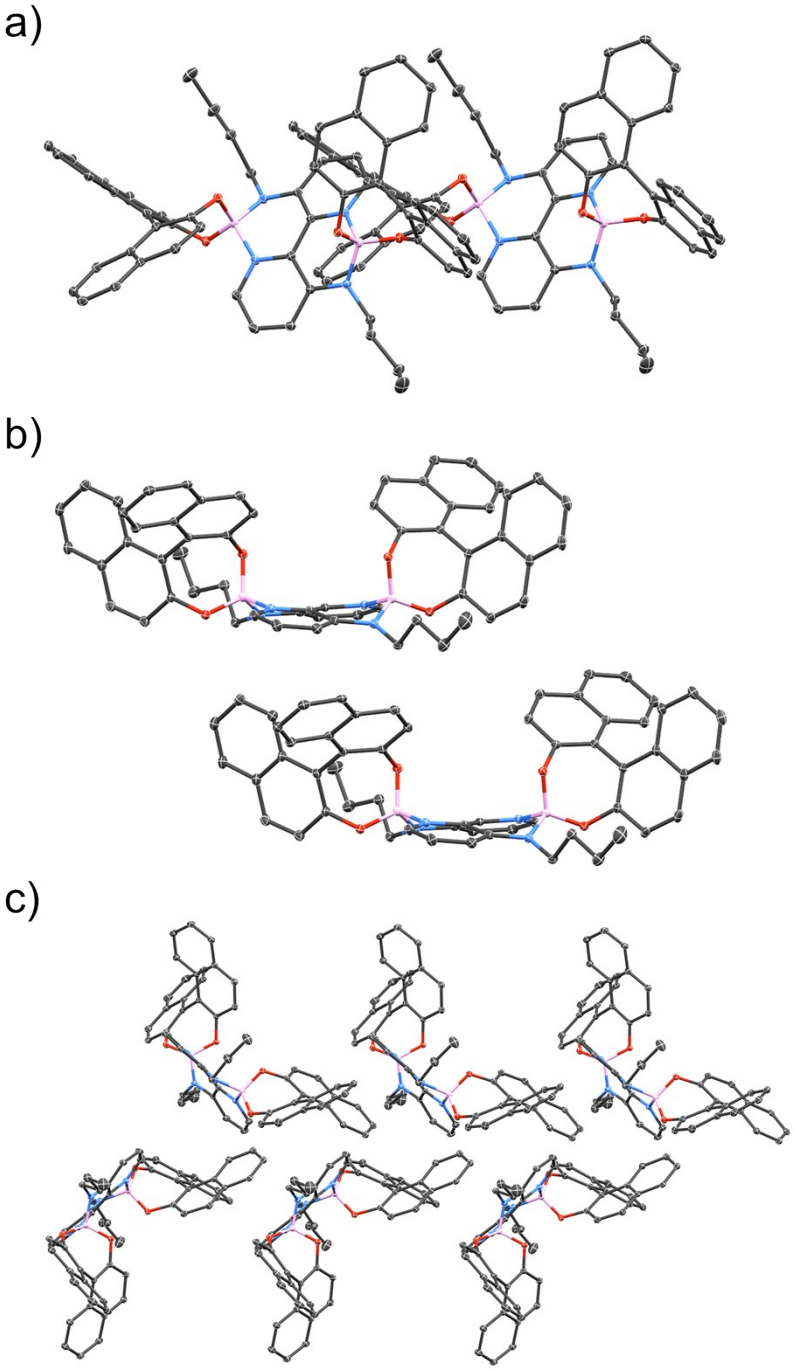

Fig. S16. a)−c) Packing structure of **(*S*,*S*)-1** in the crystalline state. Hydrogen atoms were omitted for clarity.

6. Geometry optimizations and time-dependent DFT calculations

All calculations were carried out using the Gaussian 09 program.[1] Density functional theory (DFT) calculation was performed on **(*R*,*R*)-1** and **(*S*,*S*)-1** at the B3LYP/6-311G(d) level of theory to obtain the optimized structure and molecular orbitals. Time-dependent DFT (TD-DFT) calculation was performed on **(*R*,*R*)-1** and **(*S*,*S*)-1** at the same level of theory to assign the absorption bands observed in the UV/Vis spectrum.

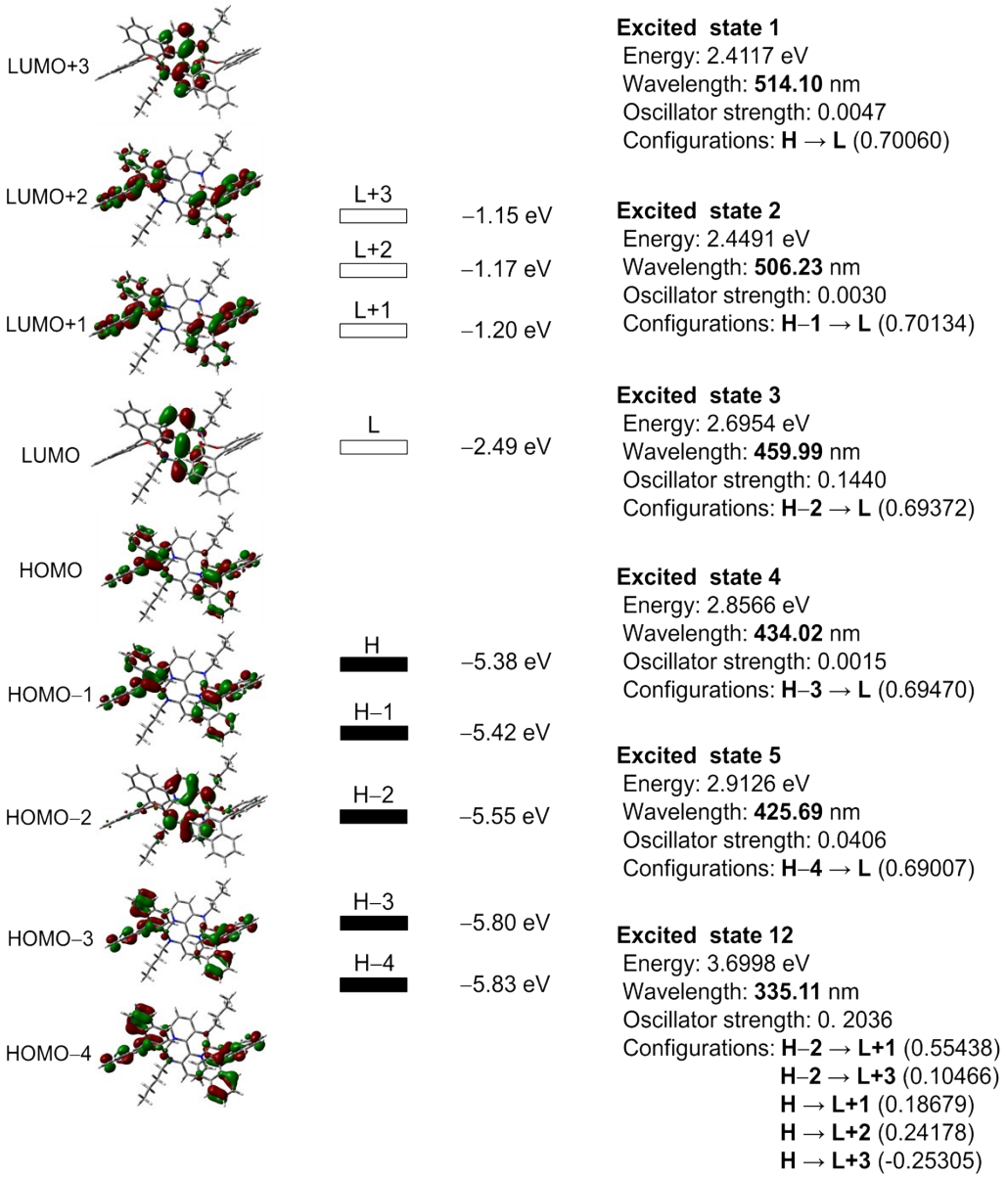

Fig. S17. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **(*R*,*R*)-1**, based on the TD-DFT (UB3LYP/6-311G(d)) calculation.

Table S1. Coordinates of the optimized structure for **(*R*,*R*)-1** at the B3LYP/6-311G(d)

level.

Atom	x	y	z
O	-3.858812	0.362169	-1.824423
O	-2.354984	-0.302454	-0.012628
O	3.858835	-0.362127	-1.824434
O	2.354977	0.302476	-0.012653
N	-1.500900	1.017673	-1.944080
N	-2.121146	-1.394621	-2.174039
N	1.500923	-1.017627	-1.944119
N	2.121150	1.394674	-2.174047
C	-1.934776	2.263646	-2.181588
H	-3.000459	2.410571	-2.108937
C	-1.038287	3.273855	-2.492934
H	-1.410076	4.271923	-2.690966
C	0.317958	3.012717	-2.503657
H	1.010138	3.816842	-2.709754
C	0.806684	1.717329	-2.214794
C	-0.178962	0.699463	-1.997940
C	0.178980	-0.699423	-1.997947
C	-0.806674	-1.717289	-2.214790
C	-0.317941	-3.012672	-2.503669
H	-1.010114	-3.816803	-2.709763
C	1.038308	-3.273805	-2.492984
H	1.410093	-4.271871	-2.691039
C	1.934801	-2.263601	-2.181658
H	3.000487	-2.410518	-2.109032
C	-4.976300	0.107818	-1.081592
C	-6.082001	-0.433809	-1.783745
H	-5.988206	-0.557513	-2.857117

C	-7.234385	-0.770342	-1.127320
H	-8.079762	-1.174656	-1.676369
C	-7.326770	-0.629620	0.280358
C	-8.472617	-1.066267	0.993807
H	-9.300940	-1.491781	0.434086
C	-8.533500	-0.973329	2.362169
H	-9.412316	-1.317718	2.897825
C	-7.435241	-0.442603	3.073694
H	-7.469260	-0.395101	4.157626
C	-6.319300	0.008903	2.409699
H	-5.484982	0.402147	2.975949
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C	-5.067879	0.409796	0.272038
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H	8.079805	1.174646	-1.676295
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C	8.472622	1.066207	0.993885
H	9.300959	1.491716	0.434183
C	8.533488	0.973239	2.362247
H	9.412306	1.317601	2.897919
C	7.435212	0.442521	3.073748
H	7.469213	0.395002	4.157680
C	6.319269	-0.008947	2.409730
H	5.484935	-0.402183	2.975962
C	6.227875	0.047938	0.991808
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C	3.979566	-1.175017	0.940916
C	4.234410	-2.376236	1.691776
C	5.509596	-3.004518	1.736919
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C	5.715327	-4.156696	2.458376
H	6.699389	-4.615019	2.466276
C	4.660524	-4.752313	3.184054
H	4.838599	-5.655959	3.758196
C	3.408727	-4.190371	3.142344
H	2.581888	-4.649441	3.677095
C	3.157120	-3.013803	2.390158
C	1.850908	-2.471689	2.288627
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C	-3.131269	-2.386759	-2.548670
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H	-4.005139	-1.833551	-2.889815
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H	-2.656145	-3.852775	-1.019309
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H	-5.757500	-6.037244	-1.095854
H	-5.468021	-4.754861	0.082172
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H	4.005100	1.833648	-2.889938
C	3.540630	3.340584	-1.415765
H	2.656183	3.852885	-1.019372
H	3.939146	2.749883	-0.585750
C	4.578480	4.371812	-1.869418
H	4.173081	4.962564	-2.701579
H	5.455741	3.849297	-2.269198
C	5.018432	5.311731	-0.744646
H	5.468339	4.754654	0.082110
H	4.171066	5.874024	-0.339725
H	5.757615	6.037176	-1.095818

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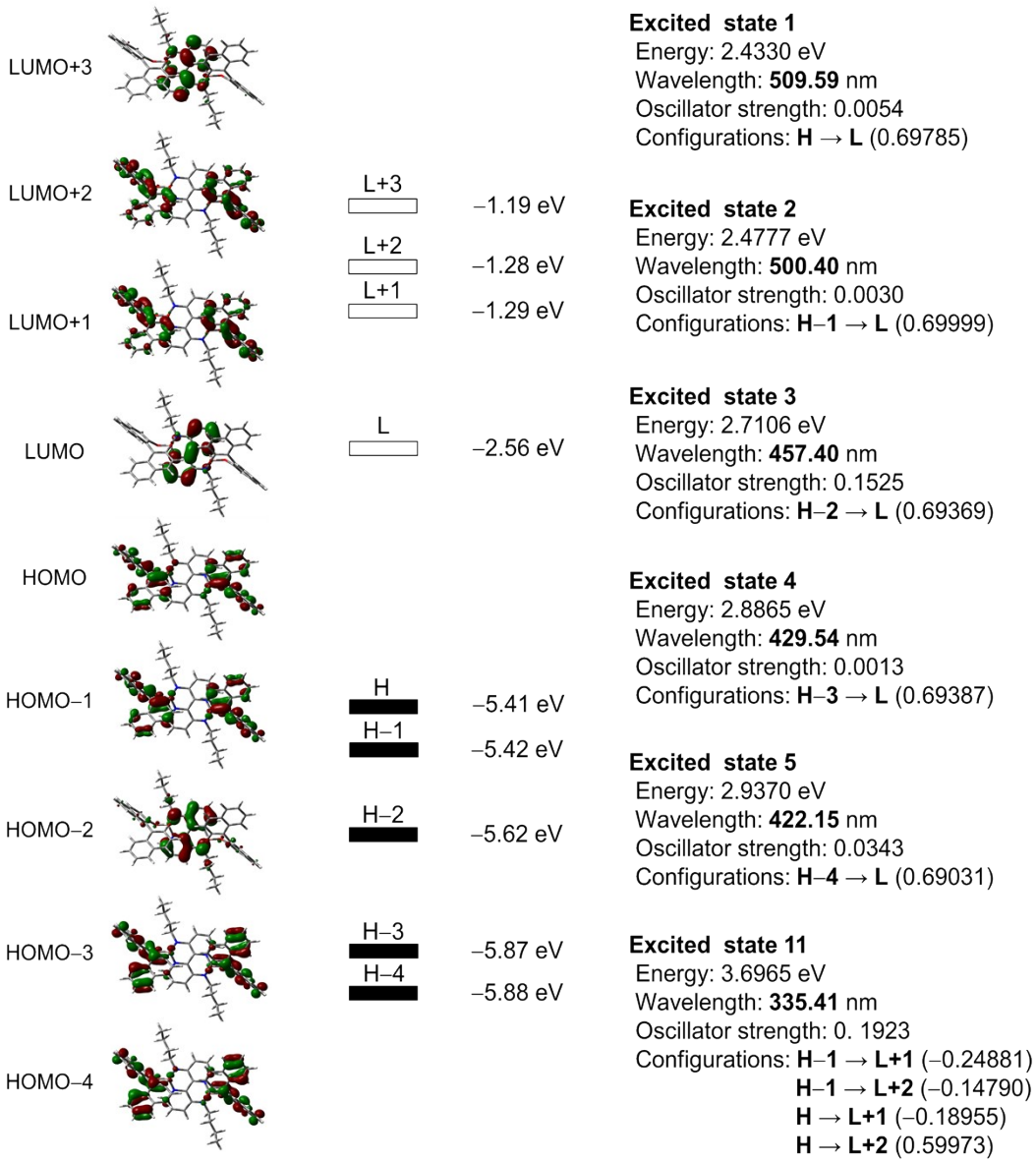

Fig. S18. The molecular orbitals, energy levels, excitation energies and oscillator strengths of **(*S*,*S*)-1**, based on the TD-DFT (UB3LYP/6-311G(d)) calculation.

Table S2. Coordinates of the optimized structure for **(*S*,*S*)-1** at the B3LYP/6-311G(d) level.

Atom	x	y	z
O	2.355123	-0.302668	-0.012402
O	3.858900	0.361510	-1.824413
O	-3.858814	-0.361922	-1.824423
O	-2.355025	0.302386	-0.012469

N	1.501112	1.017148	-1.944011
N	-1.500985	-1.017768	-1.943882
N	2.121042	-1.395259	-2.173641
N	-2.120883	1.394631	-2.173841
C	1.935153	2.263033	-2.181645
H	3.000866	2.409814	-2.109067
C	1.038788	3.273346	-2.493016
H	1.410705	4.271347	-2.691162
C	-0.317490	3.012389	-2.503632
H	-1.009575	3.816584	-2.709792
C	-0.806379	1.717093	-2.214638
C	0.179132	0.699105	-1.997779
C	-0.178999	-0.699736	-1.997683
C	0.806528	-1.717757	-2.214360
C	0.317635	-3.013092	-2.503171
H	1.009711	-3.817333	-2.709146
C	-1.038647	-3.274052	-2.492549
H	-1.410550	-4.272088	-2.690544
C	-1.935018	-2.263700	-2.181349
H	-3.000735	-2.410460	-2.108810
C	2.666063	0.750594	0.801206
C	1.606412	1.386049	1.491903
H	0.602157	0.998518	1.364178
C	1.851293	2.471943	2.288390
H	1.037211	2.950670	2.824599
C	3.157517	3.014071	2.389705
C	3.409206	4.190792	3.141627
H	2.582430	4.649960	3.676393
C	4.661006	4.752737	3.183095

H	4.839144	5.656518	3.757011
C	5.715734	4.156982	2.457415
H	6.699794	4.615317	2.465111
C	5.509924	3.004662	1.736214
H	6.331942	2.571703	1.181367
C	4.234735	2.376370	1.691339
C	3.979833	1.174989	0.940758
C	5.068086	0.409625	0.271969
C	6.228168	-0.047897	0.991740
C	6.319668	0.009249	2.409645
H	5.485345	0.402510	2.975876
C	7.435686	-0.442035	3.073658
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C	8.533947	-0.972814	2.362174
H	9.412816	-1.317032	2.897850
C	8.472976	-1.066044	0.993838
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H	8.079961	-1.175008	-1.676287
C	6.082136	-0.434348	-1.783693
H	5.988291	-0.558257	-2.857040
C	4.976436	0.107345	-1.081584
C	3.130995	-2.387636	-2.548117
H	4.004921	-1.834639	-2.889438
H	2.776875	-2.951953	-3.417588
C	3.540300	-3.341274	-1.415037
H	3.939015	-2.750514	-0.585162
H	2.655802	-3.853321	-1.018452

C	4.577892	-4.372788	-1.868610
H	5.455218	-3.850516	-2.268560
H	4.172301	-4.963594	-2.700640
C	5.017757	-5.312619	-0.743733
H	5.467685	-4.755487	0.082977
H	5.756904	-6.038155	-1.094799
H	4.170354	-5.874820	-0.338760
C	-4.976341	-0.107462	-1.081684
C	-6.081915	0.434295	-1.783940
H	-5.987989	0.558007	-2.857295
C	-7.234334	0.770912	-1.127629
H	-8.079619	1.175323	-1.676750
C	-7.326870	0.630176	0.280044
C	-8.472730	1.066943	0.993396
H	-9.300959	1.492538	0.433607
C	-8.533736	0.974022	2.361753
H	-9.412561	1.318497	2.897337
C	-7.435587	0.443199	3.073373
H	-7.469688	0.395720	4.157302
C	-6.319640	-0.008431	2.409472
H	-5.485400	-0.401730	2.975798
C	-6.228109	0.048403	0.991559
C	-5.068078	-0.409464	0.271927
C	-3.979965	-1.174866	0.940898
C	-4.235083	-2.376062	1.691704
C	-5.510368	-3.004155	1.736671
H	-6.332315	-2.571156	1.181749
C	-5.716362	-4.156316	2.458072
H	-6.700493	-4.614499	2.465832

C	-4.661737	-4.752111	3.183866
H	-4.840013	-5.655753	3.757954
C	-3.409855	-4.190353	3.142333
H	-2.583149	-4.649570	3.677155
C	-3.157979	-3.013803	2.390208
C	-1.851670	-2.471885	2.288840
H	-1.037681	-2.950635	2.825184
C	-1.606600	-1.386171	1.492170
H	-0.602273	-0.998822	1.364398
C	-2.666130	-0.750676	0.801311
C	-3.130829	2.386936	-2.548473
H	-2.776740	2.951047	-3.418087
H	-4.004818	1.833911	-2.889599
C	-3.539974	3.340843	-1.415575
H	-2.655446	3.853060	-1.019279
H	-3.938485	2.750282	-0.585472
C	-4.577701	4.372194	-1.869233
H	-4.172280	4.962785	-2.701489
H	-5.455080	3.849811	-2.268897
C	-5.017380	5.312309	-0.744537
H	-5.756508	6.037813	-1.095704
H	-5.467253	4.755403	0.082367
H	-4.169886	5.874572	-0.339839
B	2.544811	-0.117101	-1.444265
B	-2.544667	0.116544	-1.444357

7. ^{1}H NMR and ^{13}C NMR spectra

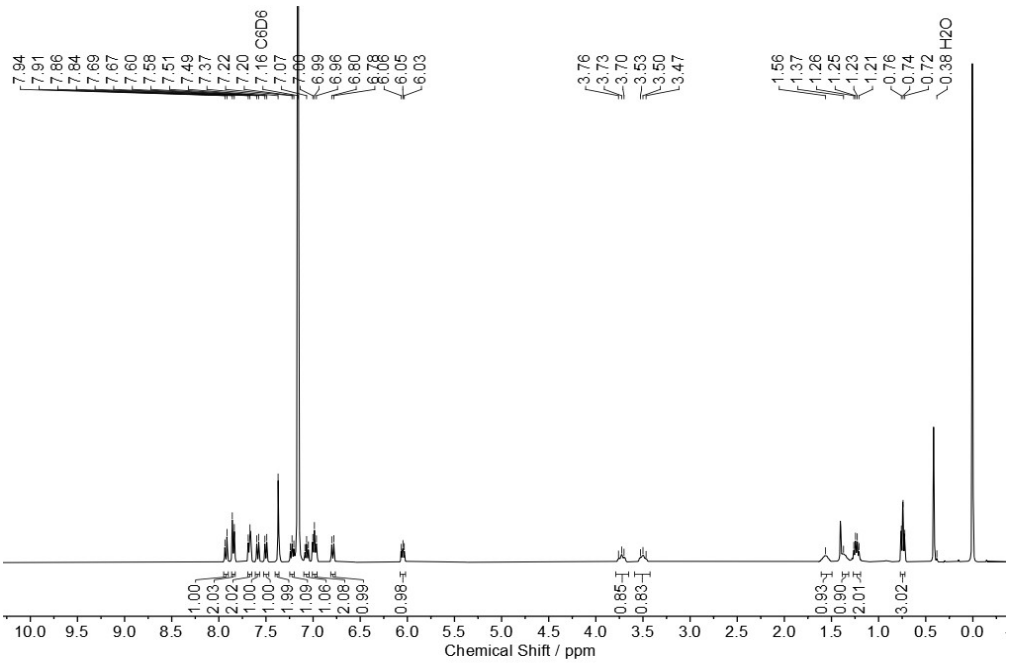

Fig. S19. ^{1}H NMR spectrum of **(*R*,*R*)-1** in C_6D_6.

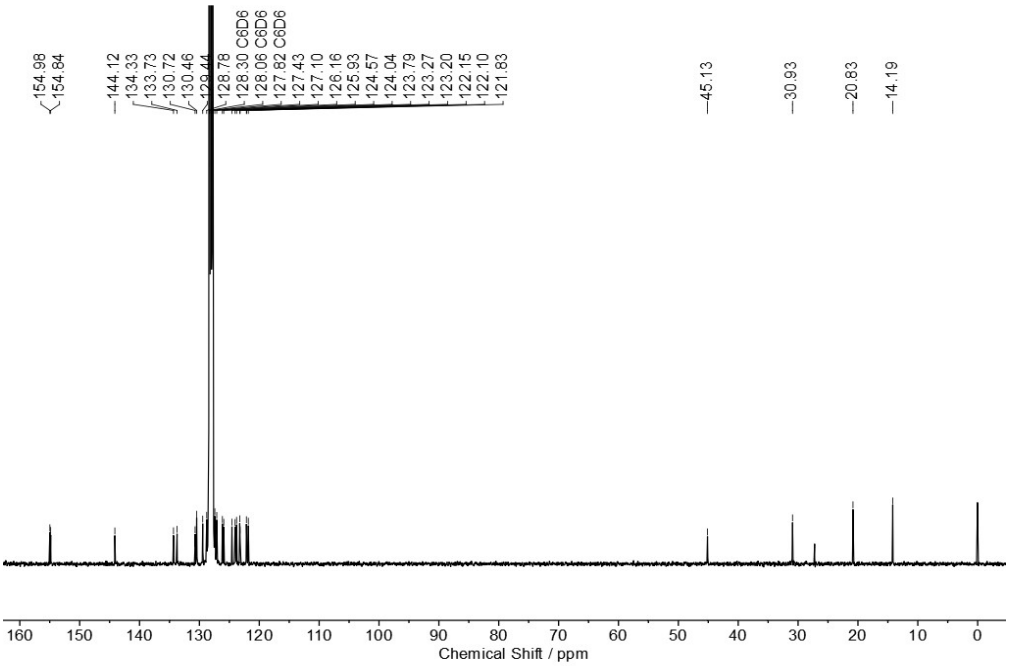

Fig. S20. ^{13}C NMR spectrum of **(*R*,*R*)-1** in C_6D_6.

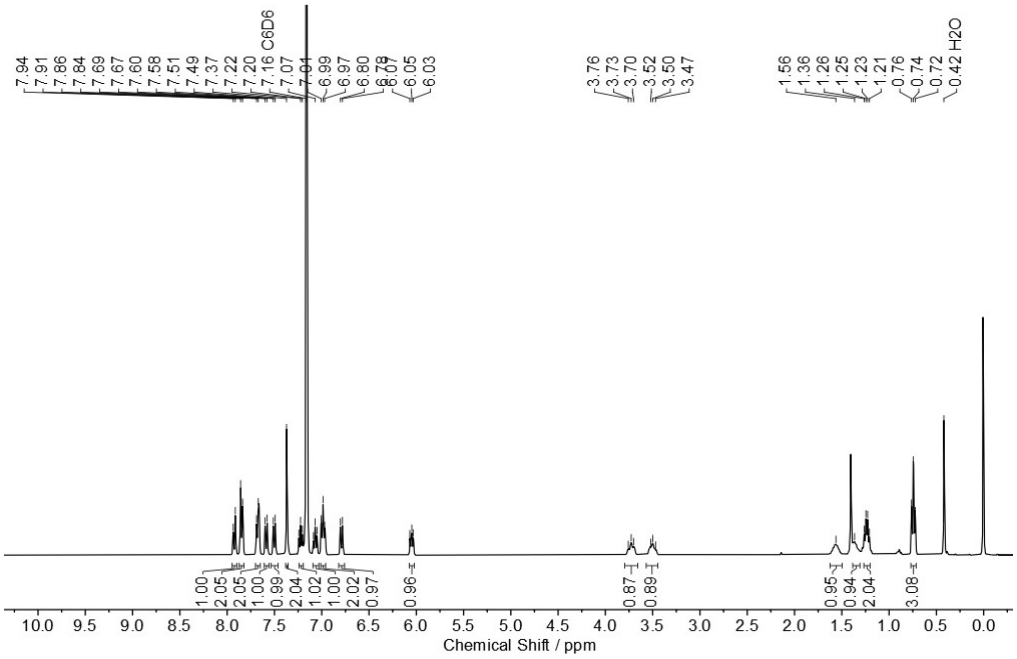

Fig. S21. ^{1}H NMR spectrum of **(*S*,*S*)-1** in C_6D_6.

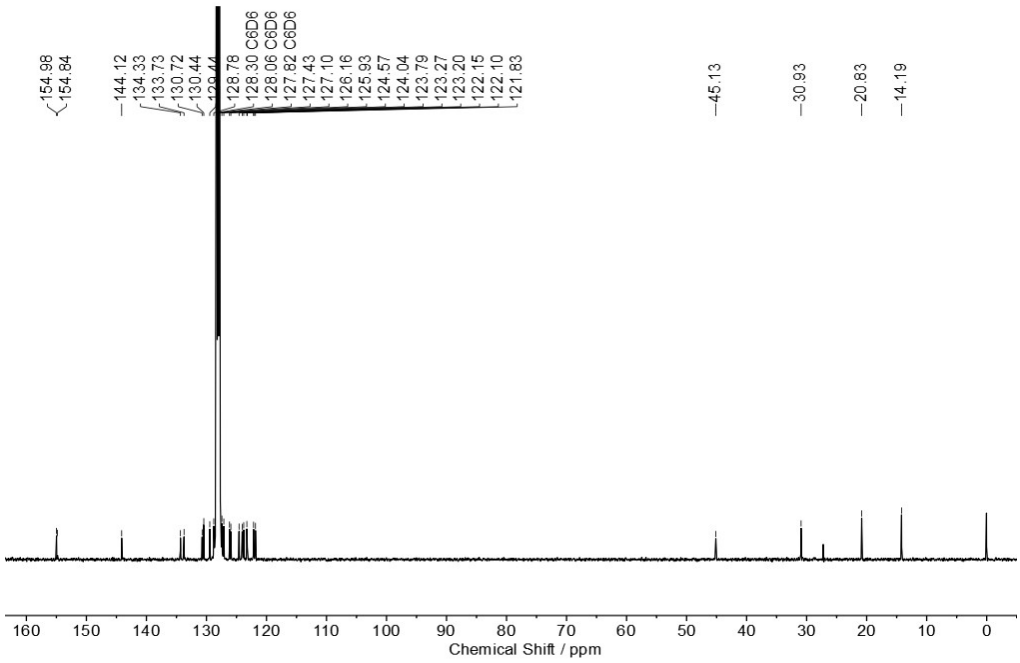

Fig. S22. ^{13}C NMR spectrum of **(*S*,*S*)-1** in C_6D_6.

8. Reference

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