Solvent-sensitive Circularly Polarized Luminescent Compounds Bearing a 9,9′-Spirobi[fluorene] Skeleton

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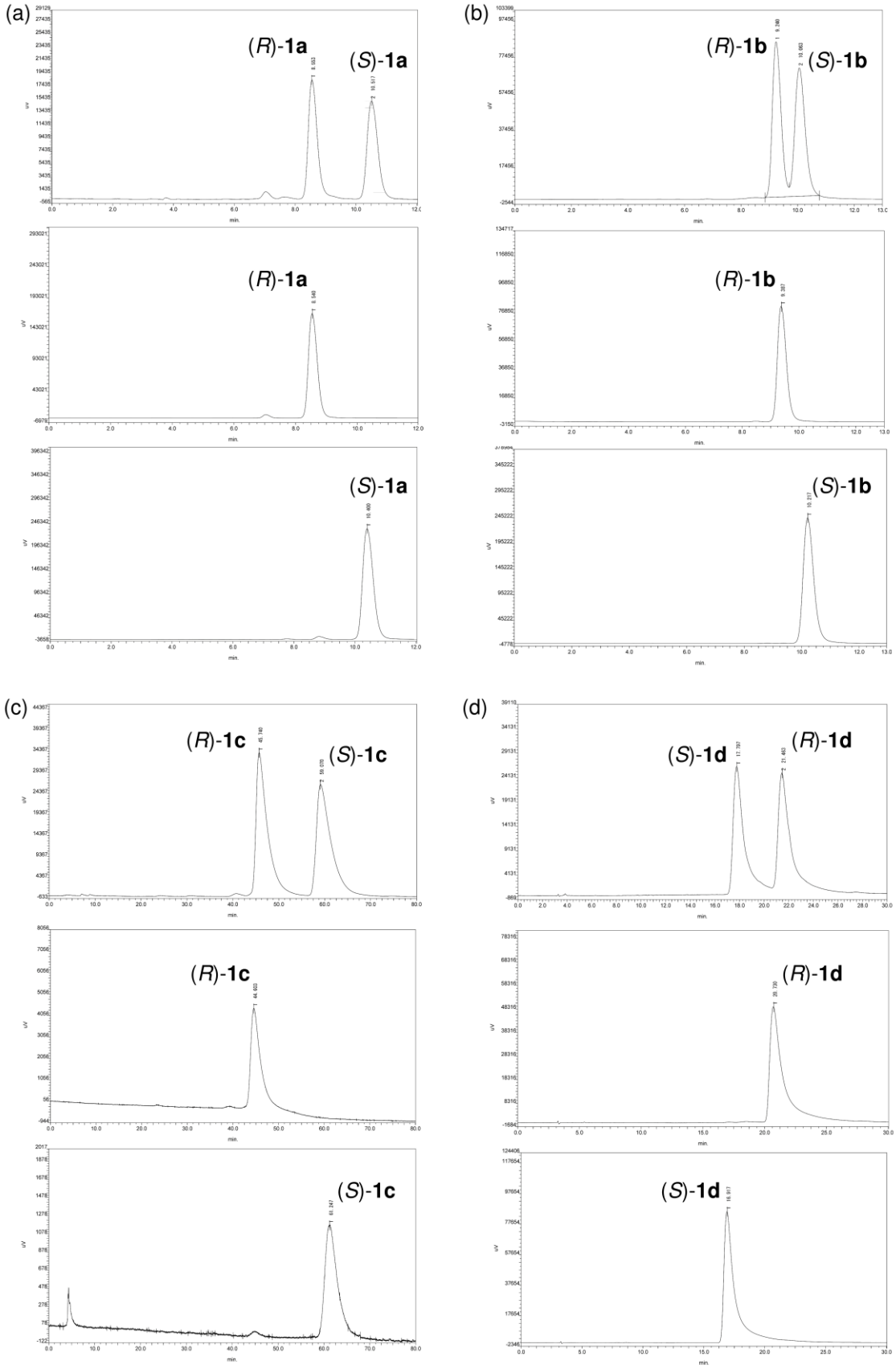

Fig. S1. Chiral HPLC chromatograms of (a) **1a**, (b) **1b**, (c) **1c**, and (d) **1d**.

Synthesis of Enantiomerically Pure 1b–1d

Racemic **2**, which was prepared according to the literatures,[1] was separated into enantiomerically pure isomers (*R*)-**2** and (*S*)-**2** by using a DAICEL CHIRALPAK® IA column (20 mm × 250 mm) ($CHCl_3$/^{i}PrOH = 95/5, v/v).[2] The first and second fractions has been assigned as (*S*)- and (*R*)-isomers, respectively.

(*R*)-3. The crude product was obtained by using (*R*)-**2** (0.52 g, 1.0 mmol), pivaloyl chloride (0.32 mL, 2.6 mmol), triethylamine (0.71 mL, 5.2 mmol), and anhydrous dichloromethane (28 mL) according to the procedure for *rac*-**3**. Purification by silica-gel column chromatography with hexane/diethyl ether (6/1, R_f = 0.25) as an eluent gave (*R*)-**3** (0.65 g, 94% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**3**.

(*S*)-3. The crude product was obtained by using (*S*)-**2** (0.70 mg, 1.4 mmol), pivaloyl chloride (0.42 mL, 3.4 mmol), triethylamine (0.95 mL, 6.9 mmol), and anhydrous dichloromethane (37 mL) according to the procedure for *rac*-**3**. Purification by silica-gel column chromatography with hexane/diethyl ether (6/1, R_f = 0.25) as an eluent gave (*S*)-**3** (0.88 g, 96% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**3**.

(*R*)-4a. The crude product was obtained by using (*R*)-**3** (0.65 g, 0.96 mmol), CuCN (0.26 g, 2.8 mmol), anhydrous *N*-methyl-2-pyrrolidone (16 mL), $FeCl_3$ (0.50 g, 3.1 mmol), and aqueous HCl (1 *M*, 17 mL) according to the procedure for *rac*-**4a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (8/1, R_f = 0.13; then 6/1) as an eluent gave (*R*)-**4a** (0.38 g, 70% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**4a**.

(*S*)-4a. The crude product was obtained by using (*S*)-**3** (0.85 g, 1.3 mmol), CuCN (0.34 g, 3.8 mmol), anhydrous *N*-methyl-2-pyrrolidone (22 mL), $FeCl_3$ (0.61 g, 3.8 mmol), and aqueous HCl (1 *M*, 23 mL) according to the procedure for *rac*-**4a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (8/1, R_f = 0.13; then 6/1) as an eluent gave (*S*)-**4a** (0.25 g, 35% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**4a**.

(*R*)-5a. The crude product was obtained by using (*R*)-**4a** (0.38 g, 0.66 mmol), a solution of sodium methoxide (28% in methanol, 5.8 mL), and dichloromethane (20 mL) according to the procedure for *rac*-**5a**. Purification by silica-gel column chromatography with chloroform/methanol (10/1, R_f = 0.50) as an eluent gave (*R*)-**5a** (0.22 g, 83% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**5a**.

(*S*)-5a. The crude product was obtained by using (*S*)-**4a** (0.23 g, 0.40 mmol), a solution of sodium methoxide (28% in methanol, 3.5 mL), and dichloromethane (12 mL) according to the procedure for *rac*-**5a**. Purification by silica-gel column chromatography with chloroform/methanol (10/1, R_f = 0.50) as an eluent gave (*S*)-**5a** (0.13 g, 79% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**5a**.

(*R*)-6a. The crude product was obtained by using (*R*)-**5a** (0.15 g, 0.37 mmol), trifluoromethanesulfonic anhydride (0.18 mL, 1.1 mmol), triethylamine (0.26 mL, 1.9 mmol), and anhydrous dichloromethane (24 mL) according to the procedure for *rac*-**6a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (3/1, R_f = 0.43) as an eluent gave (*R*)-**6a** (0.23 g, 95% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**6a**.

(*S*)-6a. The crude product was obtained by using (*S*)-**5a** (0.13 g, 0.32 mmol), trifluoromethanesulfonic anhydride (0.16 mL, 0.98 mmol), triethylamine (0.22 mL, 1.6 mmol), and anhydrous dichloromethane (21 mL) according to the procedure for *rac*-**6a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (3/1, R_f = 0.43) as an eluent gave (*S*)-**6a** (0.18 g, 85% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**6a**.

(*R*)-1a. The crude product was obtained by using (*R*)-**6a** (72 mg, 0.11 mmol), diphenylamine (57 mg, 0.34 mmol), $Pd_2(dba)_3$ (5.2 mg, 5.7 μmol), cesium carbonate (0.18 g, 0.55 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (9.2 mg, 0.022 mmol), anhydrous toluene (10 mL), and *tert*-butyl alcohol (2.0 mL) according to the procedure for *rac*-**1a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (6/1, R_f = 0.15) as an eluent and recycling preparative HPLC (chloroform as an eluent) gave (*R*)-**1a** (56 mg, 71% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**1a**.

(*S*)-1a. The crude product was obtained by using (*S*)-**6a** (46 mg, 0.070 mmol), diphenylamine (37 mg, 0.22 mmol), $Pd_2(dba)_3$ (4.3 mg, 4.7 μmol), cesium carbonate (0.12 g, 0.36 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (6.0 mg, 0.015 mmol), anhydrous toluene (6.2 mL), and *tert*-butyl alcohol (1.2 mL) according to the procedure for *rac*-**1a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (6/1, R_f = 0.15) as an eluent and recycling preparative HPLC (chloroform as an eluent) gave (*S*)-**1a** (36 mg, 74% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**1a**.

(*R*)-1b. The crude product was obtained by using (*R*)-**6a** (76 mg, 0.12 mmol), 4-(diphenylamino)phenylboronic acid (0.10 g, 0.35 mmol), $Pd(dppf)Cl_2$•$2(CH_2Cl_2)$ (9.6 mg, 0.012 mmol), potassium phosphate (98 mg, 0.46 mmol), and anhydrous THF (2.3 mL) according to the procedure for *rac*-**1a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (4/1, R_f = 0.25) as an eluent gave (*R*)-**1b** (58 mg, 59% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**1b**.

(*S*)-1b. The crude product was obtained by using (*S*)-**6a** (80 mg, 0.12 mmol), 4-(diphenylamino)phenylboronic acid (0.11 g, 0.39 mmol), $Pd(dppf)Cl_2$•$2(CH_2Cl_2)$ (11 mg, 0.013 mmol), potassium phosphate (0.11 g, 0.52 mmol), and anhydrous THF (2.6 mL) according to the procedure for *rac*-**1a**. Purification by silica-gel column chromatography with hexane/ethyl acetate (4/1, R_f = 0.25) as an eluent gave (*S*)-**1b** (56 mg, 52% yield). The ^{1}H NMR spectrum was identical to

that of *rac*-**1b**.

(*R*)-5b. The crude product of (*R*)-**4b** was obtained by using (*R*)-**3** (0.46 g, 0.68 mmol), 4-cyanophenylboronic acid (0.30 g, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (19 mg, 0.027 mmol), potassium carbonate (0.37 g, 2.7 mmol), anhydrous 1,2-dimethoxyethane (2.7 mL), and H_2O (3.0 mL). Purification by silica-gel column chromatography with hexane/ethyl acetate (1/2) as an eluent gave (*R*)-**4b** (0.22 g, 83% yield) with inseparable by-products which was used in the next step without further purification.

The crude product of (*R*)-**5b** was obtained by using the coupling product (*R*)-**4b**, a solution of sodium methoxide (28% in methanol, 3.2 mL), and dichloromethane (15 mL) according to the procedure for *rac*-**5b**. Purification by silica-gel column chromatography with hexane/ethyl acetate (3/2, R_f = 0.38) and recycling preparative HPLC (chloroform as an eluent) gave (*R*)-**5b** (0.29 g, 77% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**5b**.

(*R*)-6b. The crude product was obtained by using (*R*)-**5b** (0.24 g, 0.43 mmol), trifluoromethanesulfonic anhydride (0.21 mL, 1.3 mmol), triethylamine (0.30 mL, 2.2 mmol), and anhydrous dichloromethane (26 mL) according to the procedure for *rac*-**6b**. Purification by silica-gel column chromatography with hexane/ethyl acetate (2/1, R_f = 0.60) as an eluent gave (*R*)-**6b** (0.35 g, 99% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**6b**.

(*S*)-6b. Racemic **5b** was separated into enantiomerically pure isomers (*R*)-**5b** and (*S*)-**5b** by using a DAICEL CHIRALPAK® IA column (20 mm × 250 mm) ($CHCl_3$/^{i}PrOH = 95/5, v/v) (Fig. S2). The crude product of **(*S*)-6b** was obtained by using (*S*)-**5b** (0.15 g, 0.28 mmol), trifluoromethanesulfonic anhydride (0.14 mL, 0.84 mmol), triethylamine (0.20 mL, 1.4 mmol), and anhydrous dichloromethane (16 mL) according to the procedure for *rac*-**6b**. Purification by silica-gel column chromatography with hexane/ethyl acetate (2/1, R_f = 0.60) as an eluent gave (*R*)-**6b** (0.23 g, 94% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**6b**.

(*R*)-1c. The crude product was obtained by using (*R*)-**6b** (0.14 g, 0.18 mmol), diphenylamine (89 mg, 0.53 mmol), $Pd_2(dba)_3$ (8.0 mg, 4.2 μmol), cesium carbonate (0.29 g, 0.88 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (15 mg, 0.036 mmol), anhydrous toluene (16 mL), and *tert*-butyl alcohol (3.2 mL) according to the procedure for *rac*-**1c**. Purification by silica-gel column chromatography with hexane/ethyl acetate (5/1, R_f = 0.43) and recycling preparative HPLC (chloroform as an eluent) gave (*R*)-**1c** (88 mg, 59% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**1c**.

(*S*)-1c. The crude product was obtained by using (*S*)-**6b** (0.12 g, 0.14 mmol), diphenylamine (73 mg, 0.43 mmol), $Pd_2(dba)_3$ (6.7 mg, 7.3 μmol), cesium carbonate (0.24 g, 0.72 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (12 mg, 0.029 mmol), anhydrous toluene (13 mL),

and *tert*-butyl alcohol (2.6 mL) according to the procedure for *rac*-**1c**. Purification by silica-gel column chromatography with hexane/ethyl acetate (5/1, R_f = 0.43) and recycling preparative HPLC (chloroform as an eluent) gave (*S*)-**1c** (47 mg, 48% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**1c**.

(*R*)-1d. The crude product was obtained by using (*R*)-**6b** (0.11 g, 0.14 mmol), 4-(diphenylamino)phenylboronic acid (0.12 g, 0.41 mmol), Pd(dppf)Cl_2•2(CH_2Cl_2) (11 mg, 0.013 μμol), potassium phosphate (0.11 g, 0.54 mmol), and anhydrous THF (2.7 mL) according to the procedure for *rac*-**1d**. Purification by silica-gel column chromatography with hexane/ethyl acetate (4/1, R_f = 0.18) as an eluent gave (*R*)-**1d** (0.11 g, 80% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**1d**.

(*S*)-1d. The crude product was obtained by using (*S*)-**6b** (71 mg, 0.088 mmol), 4-(diphenylamino)phenylboronic acid (75 mg, 0.26 mmol), Pd(dppf)Cl_2•2(CH_2Cl_2) (7.1 mg, 8.7 μmol), potassium phosphate (74 mg, 0.35 mmol), and anhydrous THF (1.7 mL) according to the procedure for *rac*-**1d**. Purification by silica-gel column chromatography with hexane/ethyl acetate (4/1, R_f = 0.18) as an eluent gave (*R*)-**1d** (45 mg, 51% yield). The ^{1}H NMR spectrum was identical to that of *rac*-**1d**.

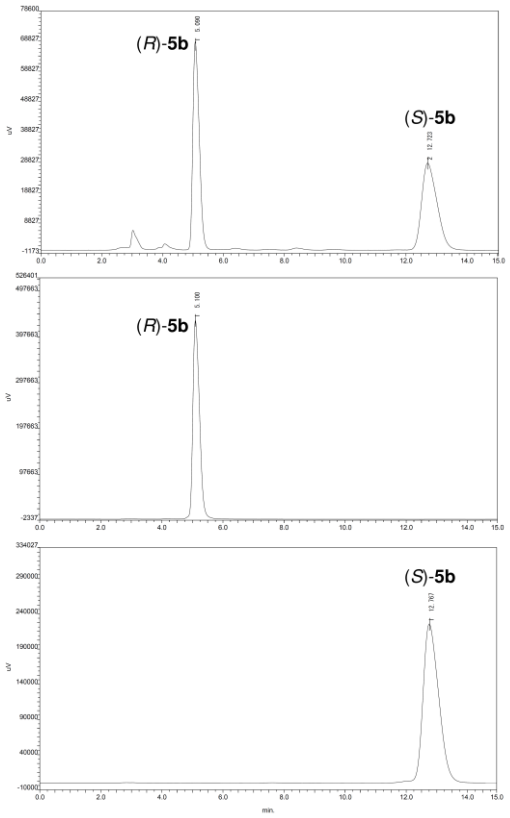

Fig. S2. Chiral HPLC chromatograms of **5b**.

Table S1. Optical Rotation of **4**–**6**

	$[\alpha]_D^{25a}$
(*R*)-**4a**	−4.5 (*c* 1.2, CH_2Cl_2)
(*R*)-**5a**	+30 (*c* 1.0, acetone)
(*R*)-**6a**	+11 (*c* 1.0, CH_2Cl_2)
(*R*)-**5b**	+332 (*c* 0.20, acetone)
(*R*)-**6b**	+182 (*c* 0.20, CH_2Cl_2)

[a]With a 50-mm cell.

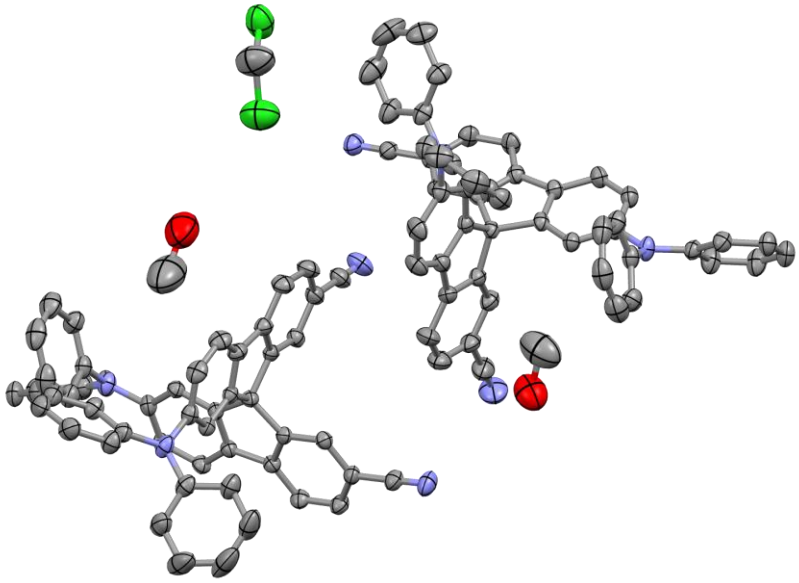

Fig. S3. ORTEP drawing of (*R*)-**1a** [50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.]

Table S2. Crystallographic Data and Structure Refinement Details for (*R*)-**1a**

Formula	$2(C_{51}H_{32}N_4)\bullet 2(CH_4O)\bullet(CH_2Cl_2)$	
Formula weight	1550.62	
Temperature	203(2) K	
Wavelength	1.54187 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.19377(18) Å	α = 90°
	b = 39.0375(7) Å	β = 116.7876(8)°
	c = 11.4370(2) Å	γ = 90°
Volume	4062.80(13) Å^3	
Z	2	
Density (calculated)	1.268 g/cm^3	
Absorption coefficient	1.179 mm^{-1}	
F(000)	1620	
Crystal size	0.55 × 0.45 × 0.12 mm^3	
Theta range for data collection	4.331 to 68.216°	
Index ranges	–12<=h<=12, –45<=k<=47, –13<=l<=13	
Reflections collected	73644	
Independent reflections	14564 [R_{int} = 0.0304]	
Completeness to theta	99.6%	
Max. and min. transmission	0.868 and 0.553	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14564 / 45 / 1072	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2sigma(I)]	R_1 = 0.0619, wR_2 = 0.1757	
R indices (all data)	R_1 = 0.0654, wR_2 = 0. 0.1809	
Absolute structure parameter	0.126(4)	
Largest diff. peak and hole	0.515 and –0.973 e/Å^3	

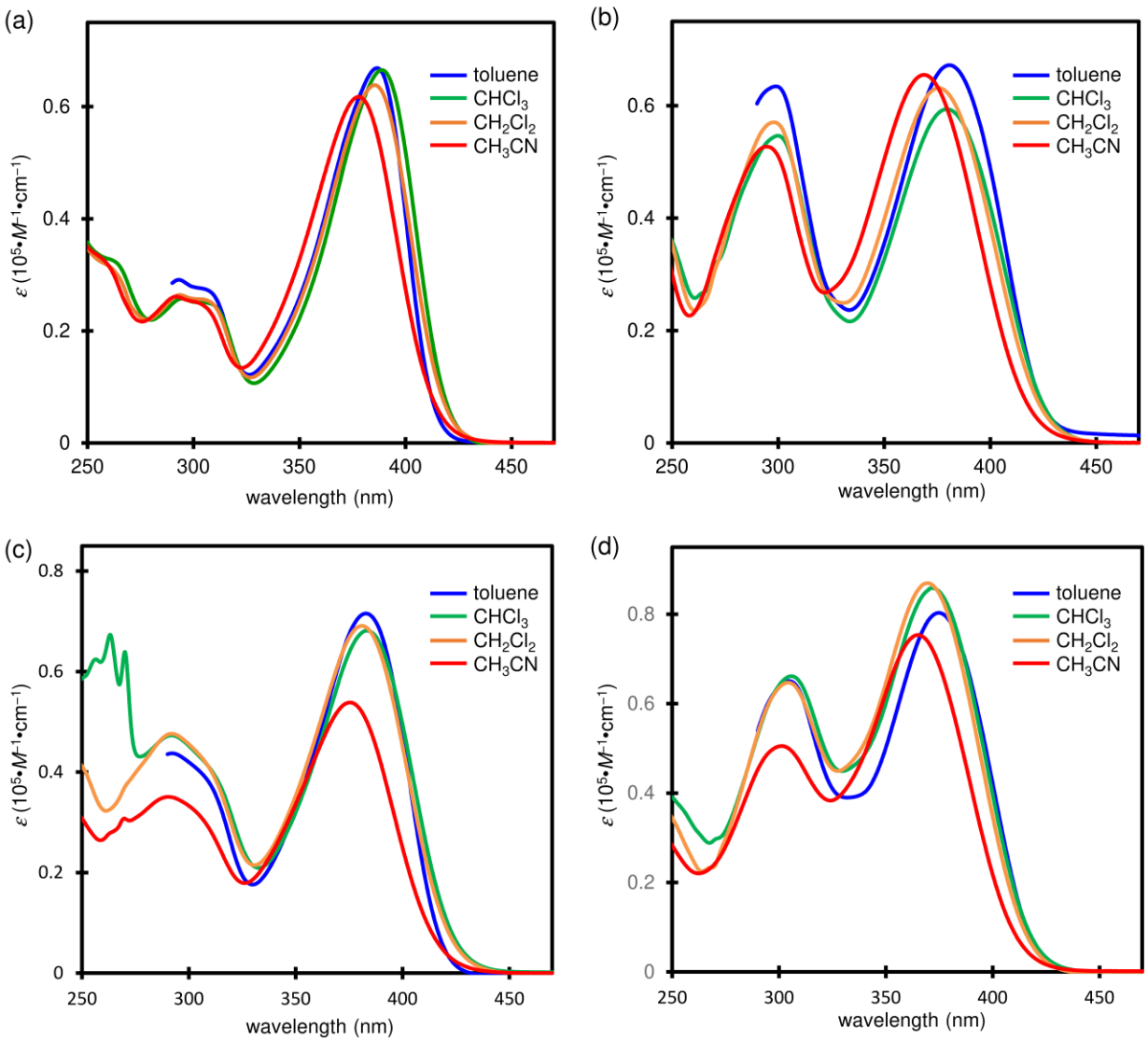

Fig. S4. UV/Vis absorption spectra of (a) *rac*-**1a**, (b) *rac*-**1b,** (c) *rac*-**1c**, and (d) *rac*-**1d** in various solvents.

Lippert–Mataga Plots

The differences between their exited- (μ_e) and ground-state (μ_g) dipole moments ($\Delta\mu = \mu_e - \mu_g$) of *rac*-**1a**–**1d** were estimated by the Lippert–Mataga plot[3] [Eq. S1, $\Delta\nu$:Stokes shift (cm^{-1}), ν_{abs} and ν_{PL}: wavenumbers of the absorption and fluorescence maxima, respectively (cm^{-1}); ε_0 (dielectric constant of vacuum); h (Planck constant); c (light velocity in vacuum); a (Onsager cavity radius); Δf (orientation polarizability). The Onsager cavity radii[4] were determined by DFT calculations at the B3LYP/6-31G(d) level of theory. The solvent orientation polarizabilities (Δf) were calculated by using Eq. S2 (ε: dielectric constant of solvent: n: refractive index of solvent).[5]

$$\Delta\nu = \nu_{abs} - \nu_{PL} = \frac{1}{4\pi\varepsilon_0}\frac{2\Delta\mu^2}{hca^3}\Delta f + \text{constant} \quad \text{(S1)}$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad \text{(S2)}$$

Table S3. Summary of Lippert–Mataga Plots

	solvent [$E_T(30)^a$]	Δf	$\Delta\nu$ (cm^{-1})	slope (cm^{-1})	a ($\times 10^{-8}$ cm)	$\Delta\mu$ (D)	μ_g (D)	μ_e (D)
1a	toluene [33.9]	0.013235	2584	10266	6.79	17.9	9.3	27.2
	$CHCl_3$ [39.1]	0.150358	3632					
	CH_2Cl_2 [40.7]	0.217103	4376					
	CH_3CN [45.6]	0.304571	5622					
1b	toluene [33.9]	0.013235	3724	15739	7.57	26.0	9.6	35.6
	$CHCl_3$ [39.1]	0.150358	4994					
	CH_2Cl_2 [40.7]	0.217103	5935					
	CH_3CN [45.6]	0.304571	8513					
1c	toluene [33.9]	0.013235	3279	15262	7.28	24.2	9.3	33.5
	$CHCl_3$ [39.1]	0.150358	4788					
	CH_2Cl_2 [40.7]	0.217103	5500					
	CH_3CN [45.6]	0.304571	7939					
1d	toluene [33.9]	0.013235	4093	19496	7.85	30.6	9.5	40.1
	$CHCl_3$ [39.1]	0.150358	5650					
	CH_2Cl_2 [40.7]	0.217103	7685					
	CH_3CN [45.6]	0.304571	9729					

[a]Solvent polarity parameter.[6]

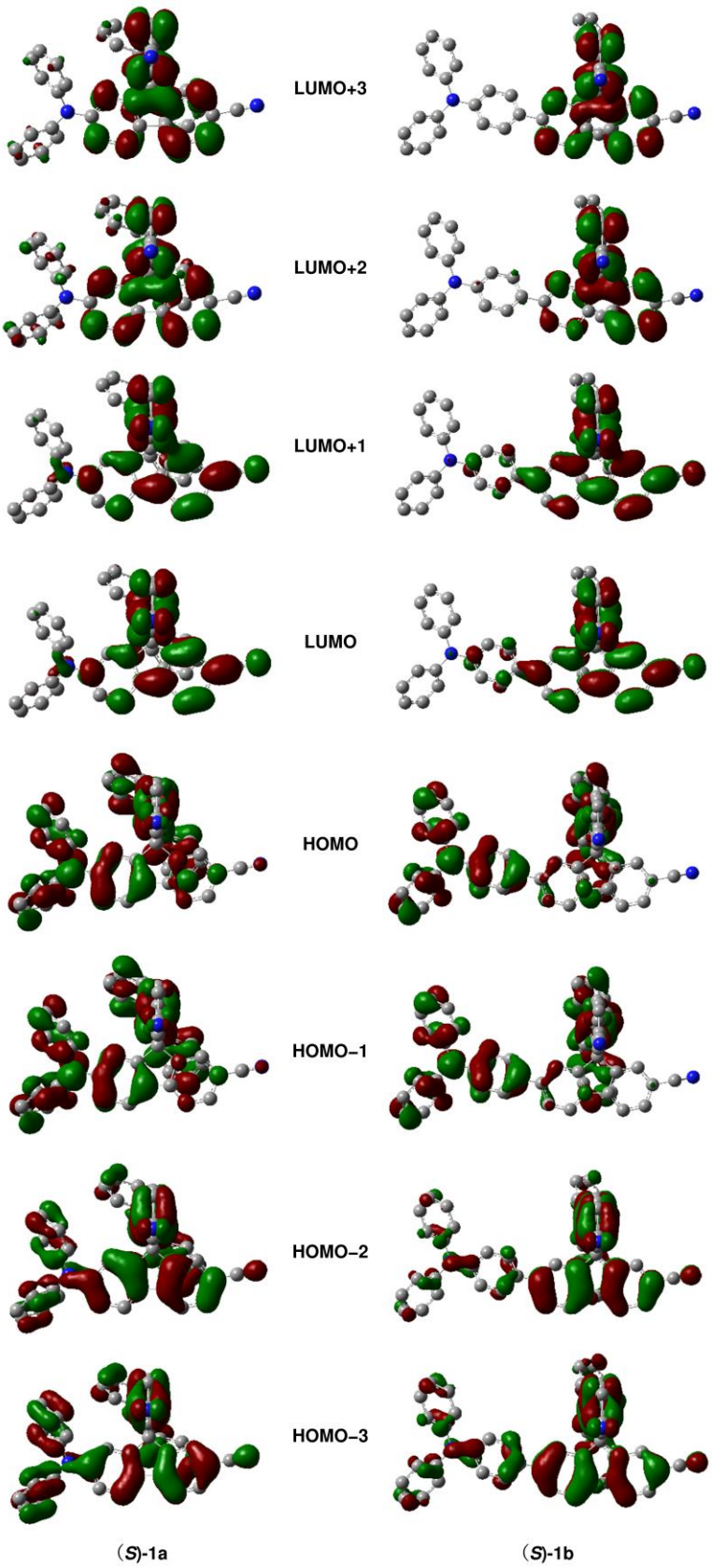

Fig. S5. Molecular orbitals of (*S*)-**1a** and (*S*)-**1b** calculated by DFT method at the B3LYP/6-31G(d) level of theory.

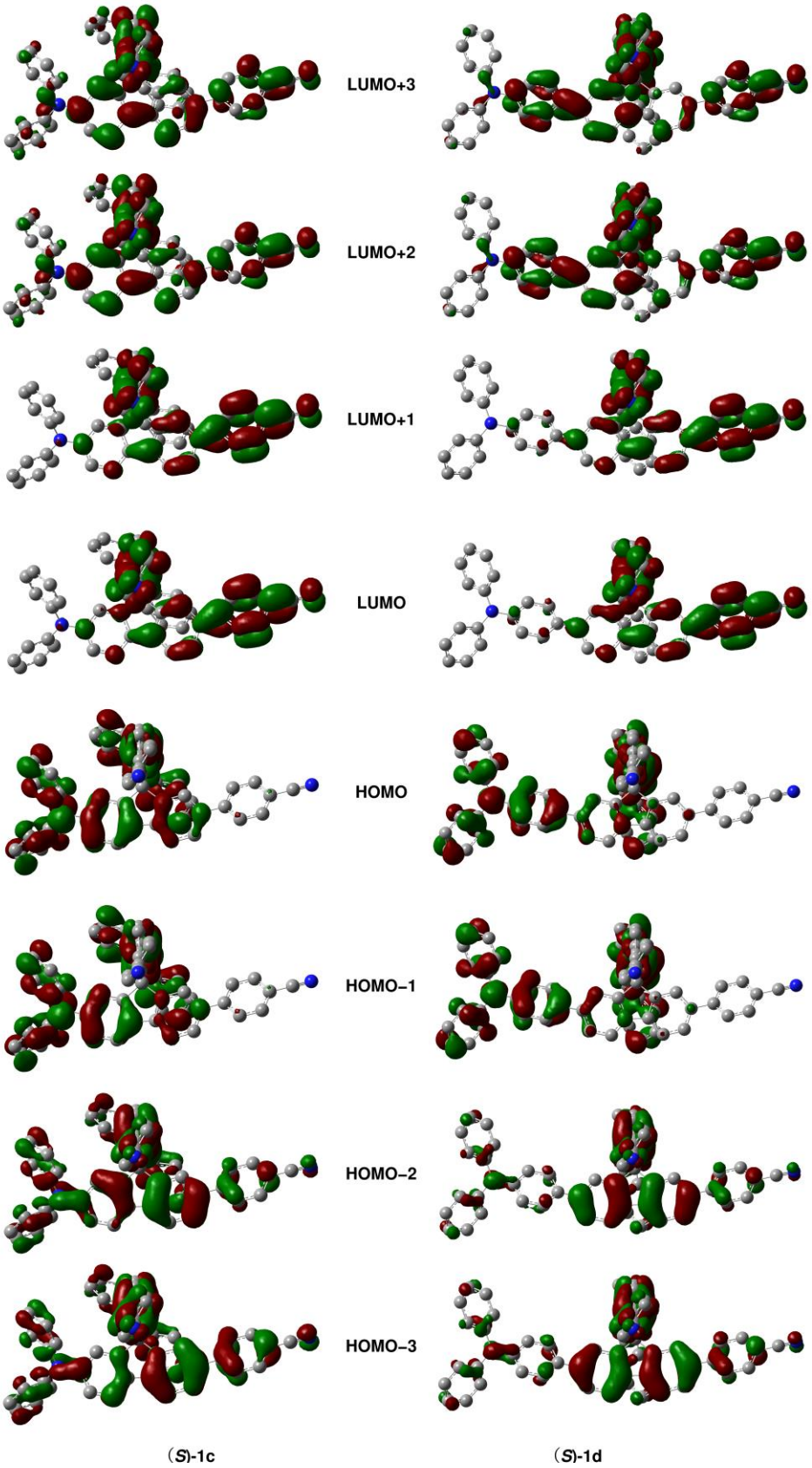

Fig. S6. Molecular orbitals of (*S*)-**1c** and (*S*)-**1d** calculated by DFT method at the B3LYP/6-31G(d) level of theory.

Table S4. Coordinates (Å) and Absolute Energy of the Optimized Structure for (*S*)-**1a**[a]

atom	x	y	z	atom	x	y	z
C	0.6387001	2.7015785	1.1106525	C	5.4136889	-0.1295637	2.1710224
C	1.5000409	4.0032955	3.4226119	H	4.7720426	0.6185807	0.2537451
C	1.6373371	3.6524132	1.0019746	H	3.8918915	-3.5140134	1.0523741
C	0.0645366	2.3889005	2.3622057	H	4.9896327	-3.3218299	3.2622829
C	0.4974228	3.0432641	3.5208370	H	5.8395068	0.8225400	2.4758460
C	2.0719388	4.3103794	2.1720113	H	5.9632125	-1.1487895	3.9940069
H	0.0623917	2.8118627	4.4883244	C	3.9448364	-2.7158685	-1.5843599
H	1.8484806	4.5218054	4.3097684	C	4.5500842	-4.9606957	-3.1620209
C	1.8813241	0.0611375	-0.3246414	C	2.9203234	-3.4318069	-2.2233472
C	1.7905315	0.6984345	-3.0709895	C	5.2746684	-3.1360818	-1.7406070
C	1.0094726	1.0274771	-0.7984484	C	5.5698943	-4.2557765	-2.5175868
C	2.7370143	-0.5983297	-1.2312668	C	3.2261088	-4.5395905	-3.0131084
C	2.6797972	-0.2623795	-2.6020526	H	1.8887479	-3.1183385	-2.0967138
C	0.9491532	1.3543242	-2.1669448	H	6.0706584	-2.5827742	-1.2522179
H	3.3467767	-0.7610200	-3.2966515	H	6.6044174	-4.5690954	-2.6290421
H	1.7700690	0.9395327	-4.1303321	H	2.4221892	-5.0839803	-3.5011921
C	-0.0000001	1.8603559	-0.0000001	H	4.7840460	-5.8284444	-3.7719571
C	-1.0094726	1.0274767	0.7984479	C	-3.9448320	-2.7158720	1.5843578
C	-2.6797964	-0.2623812	2.6020519	C	-4.5500728	-4.9607030	3.1620162
C	-0.9491532	1.3543233	2.1669444	C	-5.2746631	-3.1360873	1.7406076
C	-1.8813240	0.0611371	0.3246407	C	-2.9203165	-3.4318104	2.2233410
C	-2.7370142	-0.5983306	1.2312659	C	-3.2260984	-4.5395959	3.0131009
C	-1.7905310	0.6984330	3.0709890	C	-5.5698855	-4.2557839	2.5175860
H	-1.9083593	-0.1960419	-0.7289730	H	-6.0706551	-2.5827798	1.2522217
H	-1.7700684	0.9395306	4.1303318	H	-1.8887417	-3.1183405	2.0967054
H	-3.3467756	-0.7610224	3.2966507	H	-2.4221768	-5.0839856	3.5011813
C	-0.6387004	2.7015787	-1.1106526	H	-6.6044079	-4.5691042	2.6290435
C	-1.5000414	4.0032963	-3.4226117	H	-4.7840319	-5.8284531	3.7719513
C	-1.6373376	3.6524132	-1.0019746	C	-4.2565956	-1.4606888	-0.5056971
C	-0.0645368	2.3889012	-2.3622058	C	-5.4872639	-1.2357614	-3.0215617
C	-0.4974232	3.0432651	-3.5208370	C	-4.8124383	-0.2392438	-0.9177266
C	-2.0719399	4.3103791	-2.1720112	C	-4.3244919	-2.5686303	-1.3644884
H	-2.0852274	3.8975489	-0.0440203	C	-4.9441428	-2.4549486	-2.6085858
H	-0.0623920	2.8118640	-4.4883245	C	-5.4137028	-0.1295653	-2.1710146
H	-1.8484813	4.5218062	-4.3097682	H	-4.7720533	0.6185774	-0.2537377
H	2.0852267	3.8975494	0.0440204	H	-3.8918893	-3.5140117	-1.0523784
H	1.9083596	-0.1960418	0.7289723	H	-4.9896382	-3.3218275	-3.2622832
N	-3.6406966	-1.5816857	0.7749878	H	-5.8395254	0.8225374	-2.4758346
N	3.6406973	-1.5816841	-0.7749885	H	-5.9632284	-1.1487892	-3.9939995
C	4.2565926	-1.4606882	0.5056982	C	3.1041482	5.2979713	2.0881107
C	5.4872515	-1.2357614	3.0215673	N	3.9453653	6.1006347	2.0188381
C	4.8124290	-0.2392419	0.9177321	C	-3.1041505	5.2979698	-2.0881111
C	4.3244898	-2.5686312	1.3644875	N	-3.9453623	6.1006383	-2.0188335
C	4.9441362	-2.4549498	2.6085871				

absolute energy *E* (B3LYP): -2181.73430115 au

[a]Calculated by DFT method [B3LYP/6-31G(d)]

Table S5. Coordinates (Å) and Absolute Energy of the Optimized Structure for (*S*)-**1b**[a]

atom	x	y	z	atom	x	y	z
C	0.7659159	4.3493398	1.0292069	C	9.2226665	-4.5982437	-1.9779316
C	1.9050518	5.6364191	3.2267626	C	7.1592017	-4.8816038	-3.1930286
C	1.7416207	5.3046681	0.8047598	H	5.4054113	-4.0112749	-2.2912007
C	0.3520465	4.0279954	2.3395190	H	9.0937713	-3.4635300	-0.1496838
C	0.9231340	4.6735869	3.4409298	H	10.2931973	-4.7586614	-1.8816825
C	2.3157984	5.9539931	1.9169544	H	6.6084458	-5.2770778	-4.0423339
H	0.6111501	4.4343266	4.4530056	H	9.0616718	-5.6680633	-3.8476151
H	2.3606705	6.1489384	4.0675085	C	-7.1680738	-3.6483730	1.1027400
C	1.8414585	1.7189880	-0.5474597	C	-8.5340953	-5.1053924	3.0828690
C	1.4090257	2.3402009	-3.2619168	C	-8.5510795	-3.8676614	0.9984071
C	0.9039015	2.6732824	-0.9111387	C	-6.4763327	-4.1680455	2.2088519
C	2.5828980	1.0488089	-1.5421339	C	-7.1592015	-4.8816040	3.1930285
C	2.3456369	1.3772894	-2.8943598	C	-9.2226664	-4.5982438	1.9779316
C	0.6810295	2.9930888	-2.2636073	H	-9.0937713	-3.4635300	0.1496839
H	2.8896217	0.8485790	-3.6709740	H	-5.4054112	-4.0112751	2.2912006
H	1.2456860	2.5658351	-4.3120561	H	-6.6084457	-5.2770781	4.0423337
C	0.0000000	3.5111551	0.0000000	H	-10.2931973	-4.7586616	1.8816825
C	-0.9039015	2.6732824	0.9111388	H	-9.0616716	-5.6680636	3.8476150
C	-2.3456368	1.3772892	2.8943598	C	-6.7629110	-3.1656313	-1.2760962
C	-0.6810294	2.9930888	2.2636073	C	-7.3369977	-3.6624548	-3.9837474
C	-1.8414585	1.7189879	0.5474598	C	-6.9269798	-2.1002817	-2.1760949
C	-2.5828979	1.0488088	1.5421339	C	-6.8915493	-4.4823805	-1.7462658
C	-1.4090256	2.3402008	3.2619168	C	-7.1848615	-4.7238481	-3.0879068
H	-2.0242489	1.5030413	-0.5010734	C	-7.2021255	-2.3513639	-3.5196632
H	-1.2456859	2.5658350	4.3120561	H	-6.8394347	-1.0794607	-1.8176426
H	-2.8896216	0.8485788	3.6709741	H	-6.7606621	-5.3109821	-1.0574360
C	-0.7659160	4.3493398	-1.0292069	H	-7.2809278	-5.7490194	-3.4355258
C	-1.9050518	5.6364191	-3.2267626	H	-7.3266780	-1.5153167	-4.2027003
C	-1.7416208	5.3046681	-0.8047597	H	-7.5586915	-3.8544226	-5.0295908
C	-0.3520465	4.0279954	-2.3395189	C	3.3275597	6.9463686	1.7135848
C	-0.9231340	4.6735870	-3.4409297	N	4.1506347	7.7533866	1.5482825
C	-2.3157985	5.9539930	-1.9169543	C	-3.3275598	6.9463685	-1.7135847
H	-2.0677218	5.5574198	0.1991311	N	-4.1506348	7.7533865	-1.5482824
H	-0.6111500	4.4343267	-4.4530056	C	3.5861197	0.0227320	-1.1741698
H	-2.3606705	6.1489384	-4.0675085	C	5.5157470	-1.9405904	-0.4566779
H	2.0677218	5.5574198	-0.1991310	C	4.7598764	-0.1609239	-1.9280223
H	2.0242489	1.5030413	0.5010734	C	3.4053391	-0.8071932	-0.0524160
N	-6.4769036	-2.9150075	0.0965761	C	4.3413837	-1.7729532	0.2981747
N	6.4769036	-2.9150075	-0.0965762	C	5.7093766	-1.1137970	-1.5773433
C	6.7629109	-3.1656314	1.2760962	H	4.9571651	0.4813649	-2.7815135
C	7.3369975	-3.6624551	3.9837474	H	2.4962478	-0.7247379	0.5363267

C	6.9269798	-2.1002818	2.1760949	H	4.1596398	-2.4128585	1.1553486
C	6.8915492	-4.4823806	1.7462657	H	6.6158739	-1.2123537	-2.1653530
C	7.1848613	-4.7238483	3.0879067	C	-3.5861196	0.0227319	1.1741698
C	7.2021254	-2.3513641	3.5196633	C	-5.5157469	-1.9405904	0.4566779
H	6.8394346	-1.0794608	1.8176427	C	-4.7598764	-0.1609240	1.9280224
H	6.7606620	-5.3109822	1.0574358	C	-3.4053390	-0.8071933	0.0524160
H	7.2809276	-5.7490197	3.4355256	C	-4.3413836	-1.7729532	-0.2981748
H	7.3266778	-1.5153170	4.2027004	C	-5.7093766	-1.1137970	1.5773434
H	7.5586912	-3.8544229	5.0295907	H	-4.9571650	0.4813648	2.7815136
C	7.1680738	-3.6483729	-1.1027400	H	-2.4962478	-0.7247379	-0.5363268
C	8.5340954	-5.1053922	-3.0828691	H	-4.1596399	-2.4128585	-1.1553486
C	6.4763329	-4.1680454	-2.2088520	H	-6.6158738	-1.2123538	2.1653530
C	8.5510795	-3.8676613	-0.9984071				
absolute energy *E* (B3LYP): -2643.85167519 au							

[a]Calculated by DFT method [B3LYP/6-31G(d)]

Table S6. Coordinates (Å) and Absolute Energy of the Optimized Structure for (*S*)-**1c**[a]

atom	x	y	z	atom	x	y	z
C	1.3738513	-0.8080614	0.9990183	C	-5.6870431	-5.0061661	-3.2862165
C	2.6759793	-2.0312900	3.1229316	C	-5.9167787	-2.6062193	-3.3371287
C	2.3311295	-1.7744664	0.7358376	H	-4.4274668	-1.4917957	-2.2476878
C	1.0545981	-0.4432702	2.3224976	H	-3.9904892	-5.7694046	-2.1974024
C	1.7106866	-1.0620075	3.3899990	H	-6.0335770	-5.9956496	-3.5723768
C	3.0031294	-2.4041373	1.8038458	H	-6.4518489	-1.7138599	-3.6508703
H	1.4721561	-0.8035731	4.4180799	H	-7.2762216	-3.9687436	-4.3177961
H	3.1660987	-2.5294840	3.9540082	C	-4.0689621	3.6155378	2.1298454
C	-1.2609628	-1.8109985	-0.6126716	C	-6.3824051	3.8705281	3.7083182
C	-0.6408395	-1.2789074	-3.3111021	C	-4.5343498	4.8842896	2.5109831
C	-0.2989757	-0.8706712	-0.9452161	C	-4.7754130	2.4757082	2.5468437
C	-1.9216198	-2.5132305	-1.6404169	C	-5.9166553	2.6064790	3.3371391
C	-1.5963055	-2.2375815	-2.9845241	C	-5.6868176	5.0064160	3.2862239
C	0.0187567	-0.5909932	-2.2886019	H	-3.9902354	5.7695813	2.1974029
H	-2.0984607	-2.7875392	-3.7733230	H	-4.4273948	1.4919911	2.2476934
H	-0.4066000	-1.0876788	-4.3548681	H	-6.4517618	1.7141426	3.6508842
C	0.5375059	-0.0000109	-0.0000010	H	-6.0333080	5.9959145	3.5723854
C	-0.2989381	0.8706862	0.9452137	H	-7.2760361	3.9690621	4.3178109
C	-1.5962112	2.2376510	2.9845214	C	-2.7155365	4.3575205	0.2137206
C	0.0187794	0.5909924	2.2885998	C	-2.3588981	6.0856861	-1.9766465
C	-1.2608829	1.8110566	0.6126687	C	-1.4646965	4.9465006	-0.0327299
C	-1.9215101	2.5133164	1.6404140	C	-3.7858523	4.6438902	-0.6490455
C	-0.6407885	1.2789339	3.3110998	C	-3.6067484	5.5083433	-1.7282419
H	-1.5109541	2.0109264	-0.4243844	C	-1.2899187	5.7949999	-1.1251533
H	-0.4065600	1.0876929	4.3548660	H	-0.6344262	4.7373746	0.6344272
H	-2.0983444	2.7876294	3.7733200	H	-4.7541842	4.1877258	-0.4691718
C	1.3738880	0.8080022	-0.9990197	H	-4.4459186	5.7193111	-2.3857702

C	2.6760719	2.0311731	-3.1229319	H	-0.3149696	6.2415877	-1.3013120
C	2.3312077	1.7743660	-0.7358382	H	-2.2212549	6.7528948	-2.8225907
C	1.0546207	0.4432241	-2.3224991	C	4.0310445	-3.4400734	1.5442388
C	1.7107375	1.0619323	-3.3900001	C	5.9850964	-5.4146671	1.0536830
C	3.0032366	2.4040068	-1.8038459	C	3.9074883	-4.3282078	0.4583081
H	2.5848478	2.0273985	0.2897010	C	5.1598918	-3.5657340	2.3769484
H	1.4721968	0.8035080	-4.4180811	C	6.1250894	-4.5367412	2.1426867
H	3.1662141	2.5293454	-3.9540082	C	4.8664183	-5.3020402	0.2098477
H	2.5847604	-2.0275090	-0.2897015	H	3.0360240	-4.2715607	-0.1860556
H	-1.5110444	-2.0108556	0.4243814	H	5.2961148	-2.8782184	3.2055302
N	-2.8999897	3.4881789	1.3263898	H	6.9919289	-4.6138197	2.7908230
N	-2.9001422	-3.4880505	-1.3263925	H	4.7501349	-5.9828072	-0.6270859
C	-2.7157268	-4.3574012	-0.2137242	C	4.0311968	3.4398980	-1.5442381
C	-2.3591657	-6.0855872	1.9766394	C	5.9853356	5.4144049	-1.0536802
C	-1.4649148	-4.9464426	0.0327215	C	3.9076780	4.3280386	-0.4583083
C	-3.7860547	-4.6437224	0.6490430	C	5.1600511	3.5655077	-2.3769458
C	-3.6069894	-5.5081854	1.7282379	C	6.1252916	4.5364720	-2.1426829
C	-1.2901747	-5.7949514	1.1251436	C	4.8666508	5.3018286	-0.2098469
H	-0.6346365	-4.7373566	-0.6344381	H	3.0362099	4.2714303	0.1860537
H	-4.7543655	-4.1875124	0.4691717	H	5.2962449	2.8779852	-3.2055266
H	-4.4461682	-5.7191146	2.3857676	H	6.9921358	4.6135113	-2.7908176
H	-0.3152466	-6.2415862	1.3012990	H	4.7503962	5.9826013	0.6270860
H	-2.2215523	-6.7528034	2.8225825	C	6.9762060	6.4175403	-0.8054560
C	-4.0691223	-3.6153576	-2.1298451	N	7.7819355	7.2336957	-0.6041694
C	-6.3825836	-3.8702482	-3.7083073	C	6.9759225	-6.4178465	0.8054601
C	-4.7755274	-2.4754976	-2.5468382	N	7.7816162	-7.2340376	0.6041752
C	-4.5345667	-4.8840894	-2.5109805				

absolute energy *E* (B3LYP): -2643.85094641 au

[a]Calculated by DFT method [B3LYP/6-31G(d)]

Table S7. Coordinates (Å) and Absolute Energy of the Optimized Structure for (*S*)-**1d**[a]

atom	x	y	z	atom	x	y	z
C	0.9765921	0.8341520	2.9838219	C	2.6469889	-6.3105801	-5.5261060
C	3.0675067	2.1118389	4.2884986	C	3.6778782	-6.9168667	-6.2428487
C	0.6875315	1.7935800	3.9413429	C	2.6152615	-9.0642255	-5.9708964
C	2.3092409	0.5049072	2.6666606	H	0.7818109	-9.0733647	-4.8371171
C	3.3602710	1.1493498	3.3239953	H	2.6522877	-5.2373842	-5.3635204
C	1.7385033	2.4505197	4.6129989	H	4.4852535	-6.3040952	-6.6349642
H	4.3946485	0.9159981	3.0871248	H	2.5966657	-10.1380875	-6.1368414
H	3.8844586	2.6312743	4.7802108	H	4.4685577	-8.7628078	-7.0390332
C	-0.6688041	1.8019272	0.3540807	C	-0.8089281	-6.8513409	-4.5286808
C	-3.3469654	1.1937768	0.9782611	C	-3.4706371	-7.6090408	-5.0314134
C	-0.9688337	0.8417770	1.3082374	C	-1.7000583	-7.0704542	-3.4655670
C	-1.7097846	2.4789293	-0.3144005	C	-1.2652705	-7.0175957	-5.8462674
C	-3.0425586	2.1539581	0.0151991	C	-2.5831699	-7.4019659	-6.0905243

C	-2.3039172	0.5310091	1.6300953	C	-3.0211380	-7.4367022	-3.7196387
H	-3.8538457	2.6468505	-0.5120134	H	-1.3522608	-6.9534632	-2.4440234
H	-4.3843092	0.9622260	1.2047168	H	-0.5843660	-6.8438722	-6.6735370
C	0.0000000	0.0000000	2.1470285	H	-2.9198179	-7.5259198	-7.1163879
C	0.9688337	-0.8417770	1.3082374	H	-3.6972233	-7.6025537	-2.8850799
C	3.0425586	-2.1539581	0.0151991	H	-4.4985318	-7.9014888	-5.2256003
C	2.3039172	-0.5310091	1.6300953	C	-1.4096872	3.5073345	-1.3385592
C	0.6688041	-1.8019272	0.3540807	C	-0.8297633	5.4854034	-3.3000651
C	1.7097846	-2.4789293	-0.3144005	C	-2.2372232	4.6317757	-1.5133107
C	3.3469654	-1.1937768	0.9782611	C	-0.2837484	3.4020282	-2.1756225
H	-0.3656818	-2.0524920	0.1372143	C	0.0000000	4.3619799	-3.1405059
H	4.3843092	-0.9622260	1.2047168	C	-1.9545137	5.6048209	-2.4653912
H	3.8538457	-2.6468505	-0.5120134	H	-3.0979754	4.7714752	-0.8654892
C	-0.9765921	-0.8341520	2.9838219	H	0.3629776	2.5325596	-2.0994384
C	-3.0675067	-2.1118389	4.2884986	H	0.8635888	4.2378646	-3.7856923
C	-0.6875315	-1.7935800	3.9413429	H	-2.6002216	6.4721074	-2.5571338
C	-2.3092409	-0.5049072	2.6666606	C	1.4096872	-3.5073345	-1.3385592
C	-3.3602710	-1.1493498	3.3239953	C	0.8297633	-5.4854034	-3.3000651
C	-1.7385033	-2.4505197	4.6129989	C	2.2372232	-4.6317757	-1.5133107
H	0.3441396	-2.0212825	4.1938878	C	0.2837484	-3.4020282	-2.1756225
H	-4.3946485	-0.9159981	3.0871248	C	0.0000000	-4.3619799	-3.1405059
H	-3.8844586	-2.6312743	4.7802108	C	1.9545137	-5.6048209	-2.4653912
H	-0.3441396	2.0212825	4.1938878	H	3.0979754	-4.7714752	-0.8654892
H	0.3656818	2.0524920	0.1372143	H	-0.3629776	-2.5325596	-2.0994384
N	0.5394397	-6.4705971	-4.2752731	H	-0.8635888	-4.2378646	-3.7856923
N	-0.5394397	6.4705971	-4.2752731	H	2.6002216	-6.4721074	-2.5571338
C	0.8089281	6.8513409	-4.5286808	C	1.4506769	3.4807917	5.6397280
C	3.4706371	7.6090408	-5.0314134	C	0.9045623	5.4418416	7.5909395
C	1.7000583	7.0704542	-3.4655670	C	0.3477287	4.3459940	5.5077527
C	1.2652705	7.0175957	-5.8462674	C	2.2725571	3.6220960	6.7743111
C	2.5831699	7.4019659	-6.0905243	C	2.0105584	4.5868563	7.7388003
C	3.0211380	7.4367022	-3.7196387	C	0.0718968	5.3135379	6.4656807
H	1.3522608	6.9534632	-2.4440234	H	-0.2881183	4.2765221	4.6310381
H	0.5843660	6.8438722	-6.6735370	H	3.1144309	2.9519189	6.9155018
H	2.9198179	7.5259198	-7.1163879	H	2.6502704	4.6767488	8.6106287
H	3.6972233	7.6025537	-2.8850799	H	-0.7778041	5.9772023	6.3435730
H	4.4985318	7.9014888	-5.2256003	C	-1.4506769	-3.4807917	5.6397280
C	-1.5931755	7.0830295	-5.0110905	C	-0.9045623	-5.4418416	7.5909395
C	-3.6675656	8.2949119	-6.4739904	C	-0.3477287	-4.3459940	5.5077527
C	-2.6469889	6.3105801	-5.5261060	C	-2.2725571	-3.6220960	6.7743111
C	-1.5895633	8.4689140	-5.2375860	C	-2.0105584	-4.5868563	7.7388003
C	-2.6152615	9.0642255	-5.9708964	C	-0.0718968	-5.3135379	6.4656807
C	-3.6778782	6.9168667	-6.2428487	H	0.2881183	-4.2765221	4.6310381
H	-2.6522877	5.2373842	-5.3635204	H	-3.1144309	-2.9519189	6.9155018
H	-0.7818109	9.0733647	-4.8371171	H	-2.6502704	-4.6767488	8.6106287
H	-2.5966657	10.1380875	-6.1368414	H	0.7778041	-5.9772023	6.3435730
H	-4.4852535	6.3040952	-6.6349642	C	-0.6276482	-6.4383829	8.5810823

H	-4.4685577	8.7628078	-7.0390332	N	-0.4028907	-7.2488828	9.3862387
C	1.5931755	-7.0830295	-5.0110905	C	0.6276482	6.4383829	8.5810823
C	3.6675656	-8.2949119	-6.4739904	N	0.4028907	7.2488828	9.3862387
C	1.5895633	-8.4689140	-5.2375860				
absolute energy *E* (B3LYP): -3105.96942225 au							

[a]Calculated by DFT method [B3LYP/6-31G(d)]

Table S8. Orbital Energies of **1a**–**1d** Calculated by DFT Method at the B3LYP /6-31G(d) Level of Theory

	HOMO−3 (eV)	HOMO−2 (eV)	HOMO−1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)	LUMO+2 (eV)	LUMO+3 (eV)
1a	−6.61	−6.39	−5.17	−5.14	−1.75	−1.74	−0.87	−0.87
1b	−6.23	−6.08	−5.07	−5.07	−1.89	−1.89	−0.90	−0.88
1c	−6.24	−6.08	−5.05	−5.02	−1.81	−1.80	−0.81	−0.81
1d	−5.95	−5.81	−5.03	−5.02	−1.86	−1.85	−1.06	−1.06

Table S9. The Selected Absorption of **1a**–**1d** Calculated by TD–DFT Method at the B3LYP /6-31G(d) Level of Theory

	excited state	transition energy (eV)	wavelength (nm)	main transition configuration (CI expansion coefficient)	oscillator strength	Rotatory Strength (10^{-40} erg·esu·cm/gauss)		transition electric dipole moments (a.u.)			transition magnetic dipole moments (a.u.)		
					f	$R_{velocity}$	R_{length}	x	y	z	x	y	z
(*S*)-1a	1	2.949	420	HOMO → LUMO (0.64494)	0.0872	196.5044	198.9118	0.0001	1.0984	0.0000	0.0001	-0.7682	0.0001
	2	2.954	420	HOMO → LUMO+1 (0.63474)	0.0807	-162.2316	-163.8864	1.0486	-0.000	0.1245	0.6051	0.0001	0.4882
	3	3.006	413	HOMO-1 → LUMO (0.63317)	0.6459	-1021.0283	-1040.5517	2.8985	-0.000	0.6087	1.2128	-0.0000	1.4770
	4	3.025	410	HOMO-1 → LUMO+1 (0.64385)	0.6216	1164.8246	1189.3571	0.0000	2.8964	0.0000	0.0000	1.7420	0.0000
	5	3.663	339	HOMO → LUMO+2 (0.56872)	0.0000	-3.8806	-0.0954	0.0001	0.0014	-0.0000	0.0001	0.2816	-0.0001
	6	3.666	338	HOMO → LUMO+3 (0.50323)	0.0158	-62.2279	-48.5813	-0.4183	-0.000	0.0328	-0.4265	0.0000	0.8445
(*S*)-1b	1	2.8180	440	HOMO → LUMO+1 (0.51864)	0.7069	-1090.0199	-1116.0427	-3.1484	0.0000	-0.5724	-1.0948	-0.0000	-2.2501
	2	2.840	437	HOMO → LUMO (0.61892)	0.6034	1051.0062	1071.4180	0.0000	2.9452	-0.0000	-0.0000	-1.5433	0.0000
	3	2.857	434	HOMO-1 → LUMO (0.52186)	0.0019	-0.2066	-0.2108	0.1611	0.0000	0.0274	-0.0189	-0.0000	0.1440
	4	2.858	434	HOMO-1 → LUMO+1 (0.62078)	0.0474	70.0662	71.6523	0.0000	-0.822	0.0000	0.0000	0.3695	-0.0000
	5	3.720	333	HOMO-2 → LUOM (0.65219)	0.2160	484.4482	479.1698	-0.0000	1.5393	0.0000	-0.0000	-1.3206	-0.0000
	6	3.722	333	HOMO-2 → LUMO+1 (0.64993)	0.2187	-467.9426	-467.7610	-1.5386	-0.000	-0.1780	-1.1003	-0.0000	-1.6368
(*S*)-1c	1	2.834	438	HOMO → LUMO (0.67815)	0.1804	-314.7436	-319.2710	-0.0005	-1.611	-0.0560	0.0002	-0.8472	0.1892
	2	2.837	437	HOMO → LUMO+1 (0.67155)	0.1544	317.2137	322.4603	-1.4903	0.0006	0.0000	0.9179	0.0002	-0.0001
	3	2.881	430	HOMO-1 → LUMO (0.67066)	0.5702	1040.0633	1062.2216	-2.8421	0.0001	-0.0000	1.5855	0.0000	0.0000
	4	2.887	429	HOMO-1 → LUMO+1 (0.67694)	0.5559	-843.7610	-857.1276	-0.0002	-2.803	0.0280	0.0001	-1.2934	0.3741
	5	3.680	337	HOMO → LUMO+4 (0.51392)	0.0067	27.8392	36.9622	-0.2716	0.0006	0.0001	0.5773	0.0004	0.0011
	6	3.681	337	HOMO-1 → LUMO+4 (0.41164)	0.0588	-181.2602	-150.4616	-0.0002	-0.790	-0.1618	0.0005	-0.5768	-1.1252
(*S*)-1d	1	2.850	435	HOMO → LUMO (0.68386)	0.5244	-841.8542	-858.3830	-0.1781	-2.734	0.0000	-1.1640	-1.2557	-0.0000
	2	2.862	433	HOMO → LUMO+1 (0.67811)	0.5558	974.2142	991.9766	0.0000	0.0000	2.8156	0.0000	0.0000	-1.4946
	3	2.869	432	HOMO-1 → LUMO (0.68213)	0.1814	292.2422	298.1227	-0.0000	-0.000	-1.6068	-0.0000	-0.0000	0.7871
	4	2.874	431	HOMO-1 → LUMO+1 (0.68703)	0.2280	-328.2653	-335.1500	0.1274	1.7948	0.0000	0.7942	0.7358	-0.0000
	5	3.521	352	HOMO-2 → LUMO (0.58470)	0.6972	-1222.8205	-1229.5531	-0.1152	-2.840	0.0000	-1.5424	-1.7737	-0.0000
	6	3.528	351	HOMO-1 → LUMO+1 (0.58922)	0.7014	1343.7355	1354.6489	0.0000	0.0000	2.8488	0.0000	0.0000	-2.0173

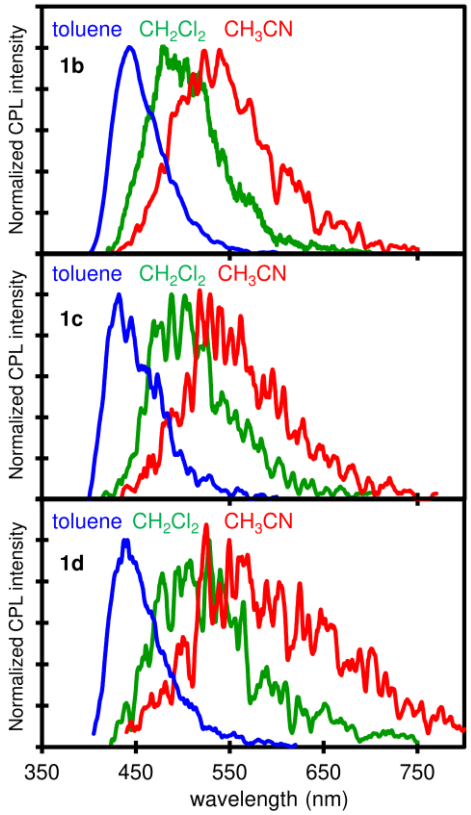

Fig. S7. Solvent dependency of CPL spectra of (*R*)-**1b–1d**.

Table S10. CPL Properties of (*R*)-**1a**–**1d** in Various Solvents.

solvent [$E_T(30)^a$]	(*R*)-**1a**	(*R*)-**1b**	(*R*)-**1c**	(*R*)-**1d**
	g_{lum} ($\times 10^{-4}$)^b	g_{lum} ($\times 10^{-4}$)^b	g_{lum} ($\times 10^{-4}$)^b	g_{lum} ($\times 10^{-4}$)^b
toluene [33.9]	+5.9 (422 nm)	+7.1 (443 nm)	+1.8 (432 nm)	+2.4 (437 nm)
CH_2Cl_2 [40.7]	+5.2 (464 nm)	+4.7 (478 nm)	+1.4 (488 nm)	+1.2 (528 nm)
CH_3CN [45.6]	+4.7 (490 nm)	+3.7 (539 nm)	+0.9 (518 nm)	+1.4 (524 nm)

^{a}Solvent polarity parameter.[6] ^{b}The value was calculated at the CPL maximum. Wavelength for the calculated value in parentheses.

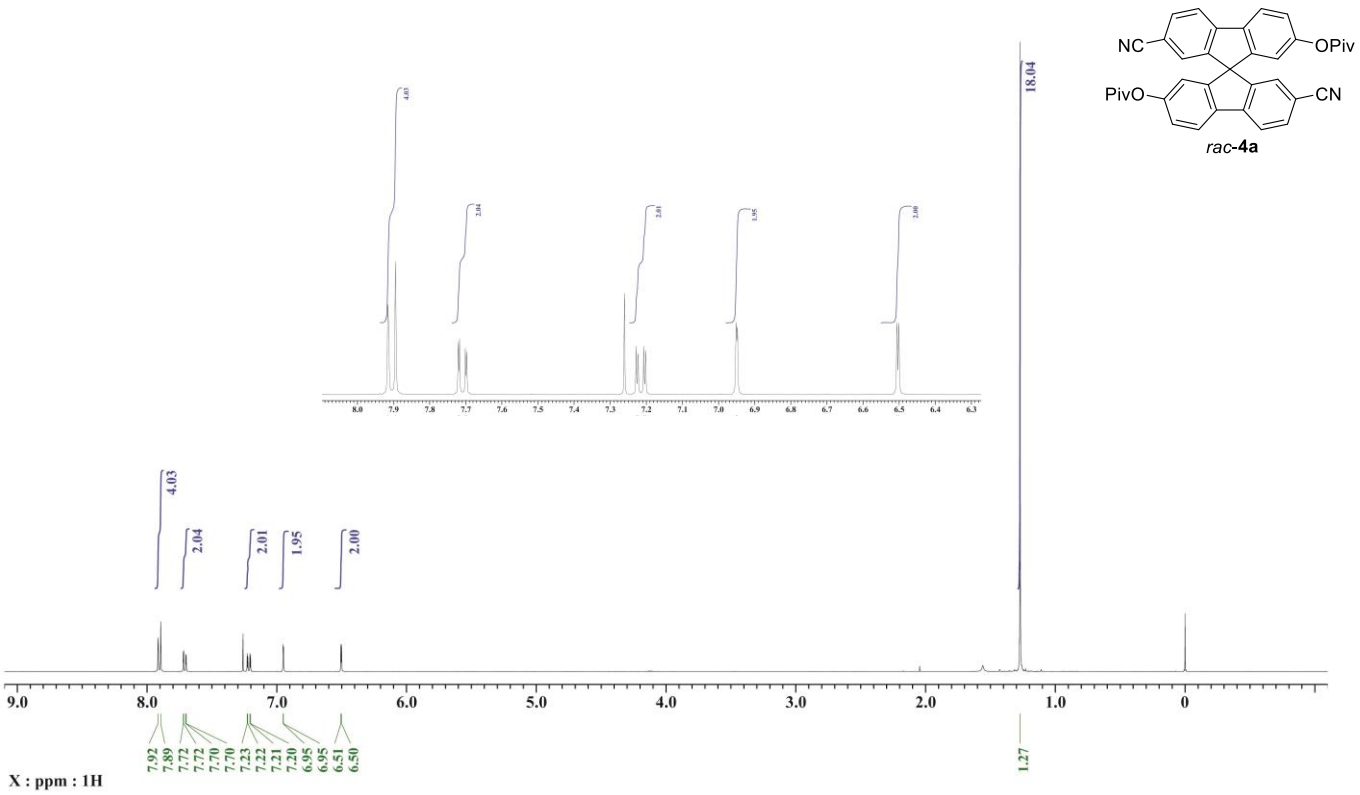

Fig. S8. ^{1}H NMR spectrum of *rac*-**4a** (400 MHz, $CDCl_3$).

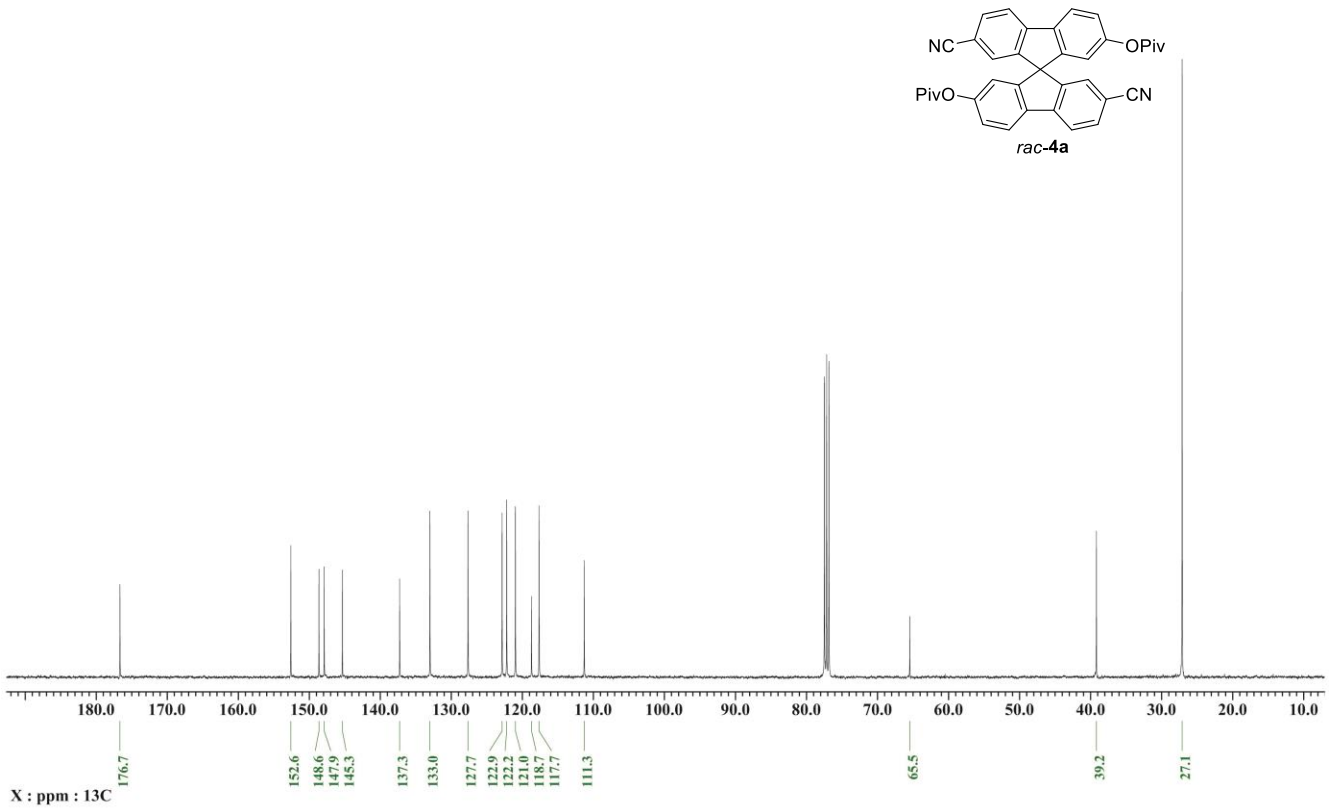

Fig. S9. ^{13}C NMR spectrum of *rac*-**4a** (101 MHz, $CDCl_3$).

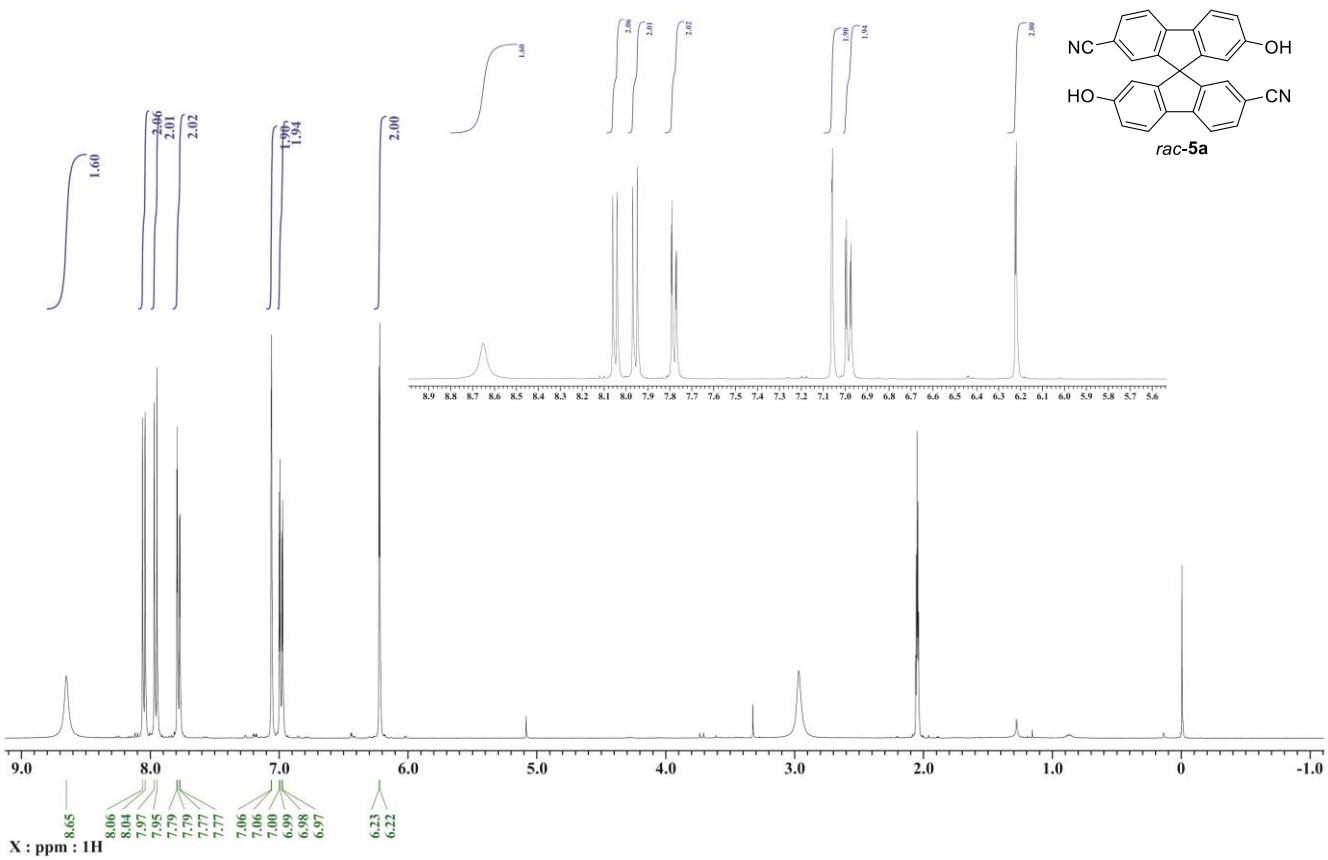

Fig. S10. ^{1}H NMR spectrum of *rac*-**5a** (400 MHz, acetone-d_6).

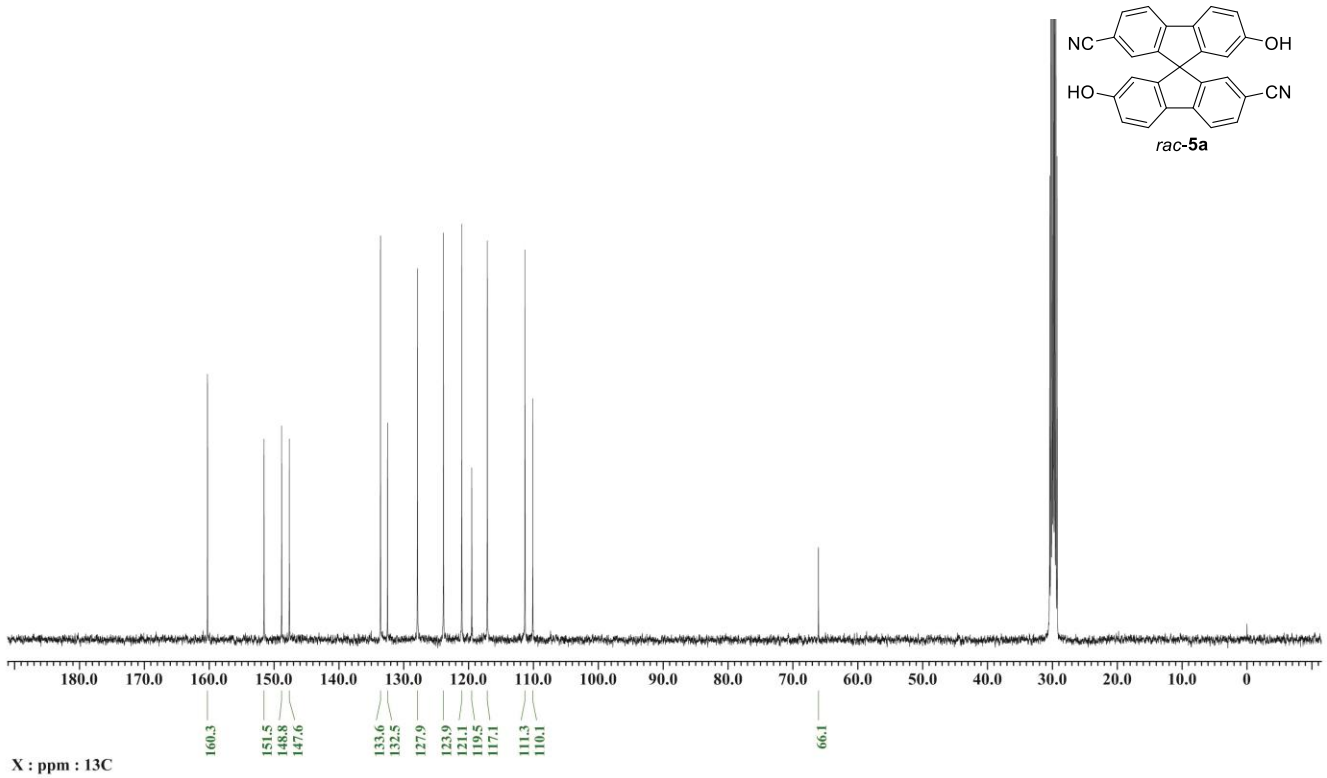

Fig. S11. ^{13}C NMR spectrum of *rac*-**5a** (101 MHz, acetone-d_6).

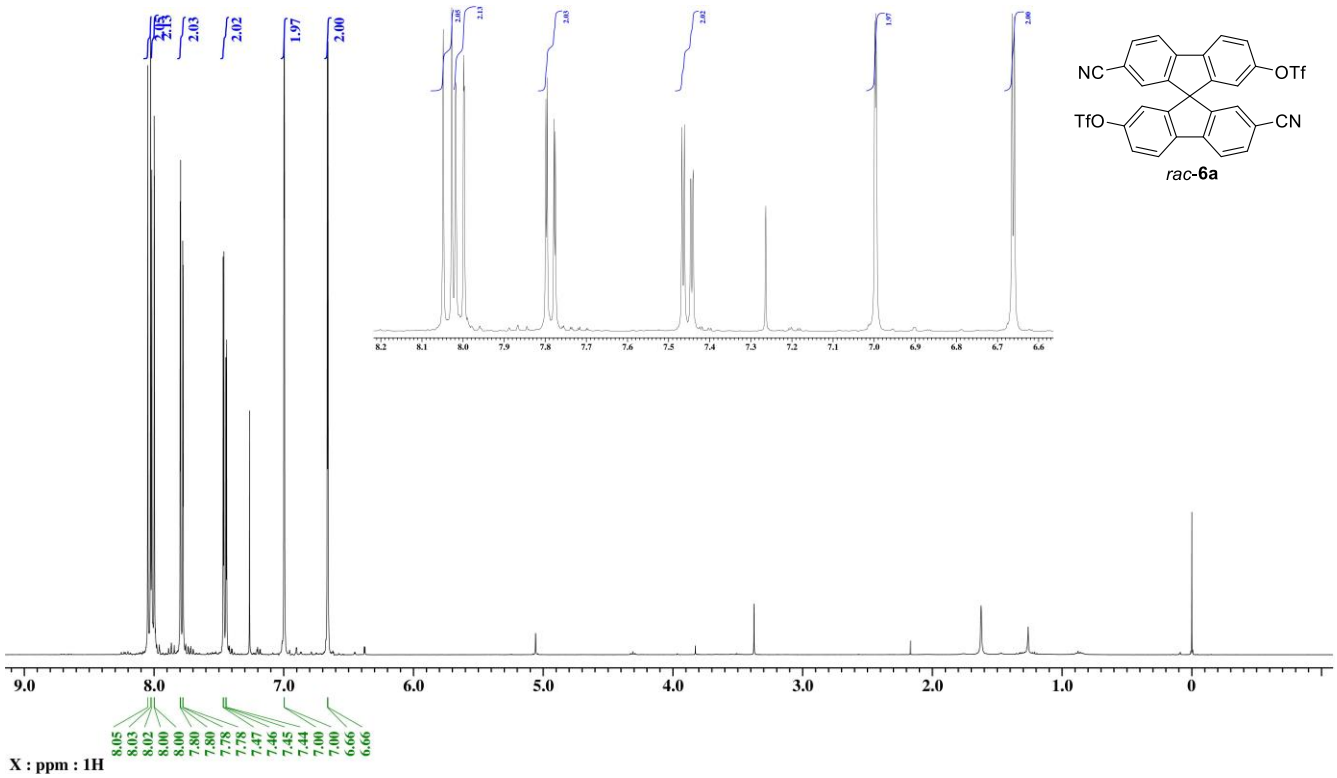

Fig. S12. ^{1}H NMR spectrum of *rac*-**6a** (400 MHz, $CDCl_3$).

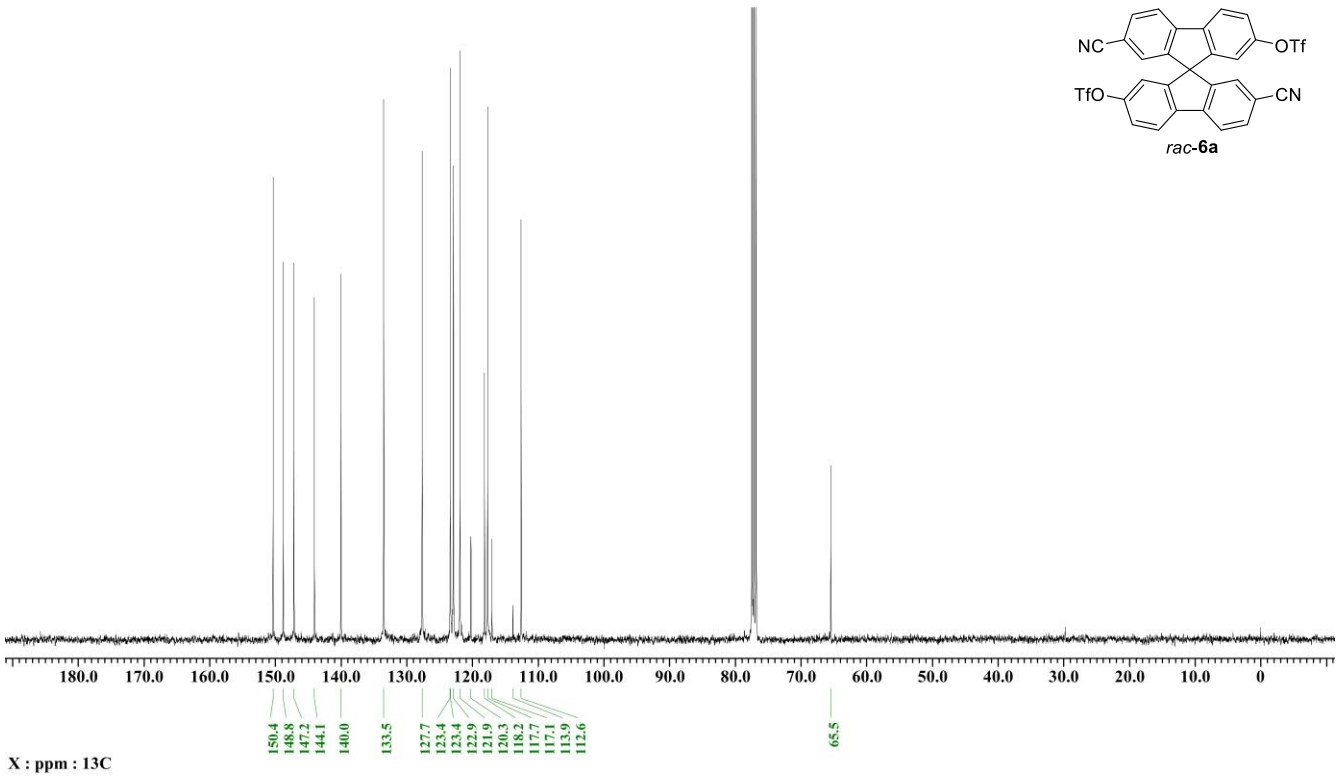

Fig. S13. ^{13}C NMR spectrum of *rac*-**6a** (101 MHz, $CDCl_3$).

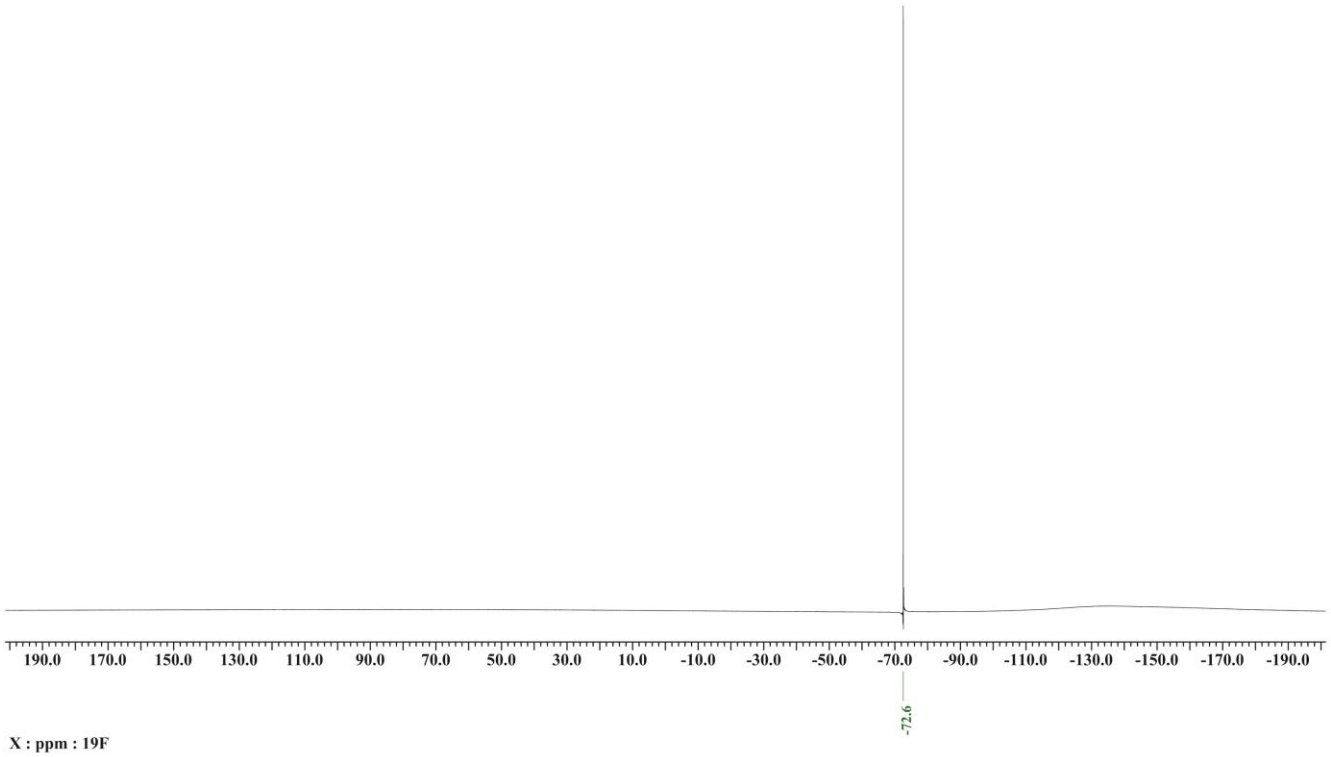

Fig. S14. ^{19}F NMR spectrum of *rac*-**6a** (376 MHz, $CDCl_3$).

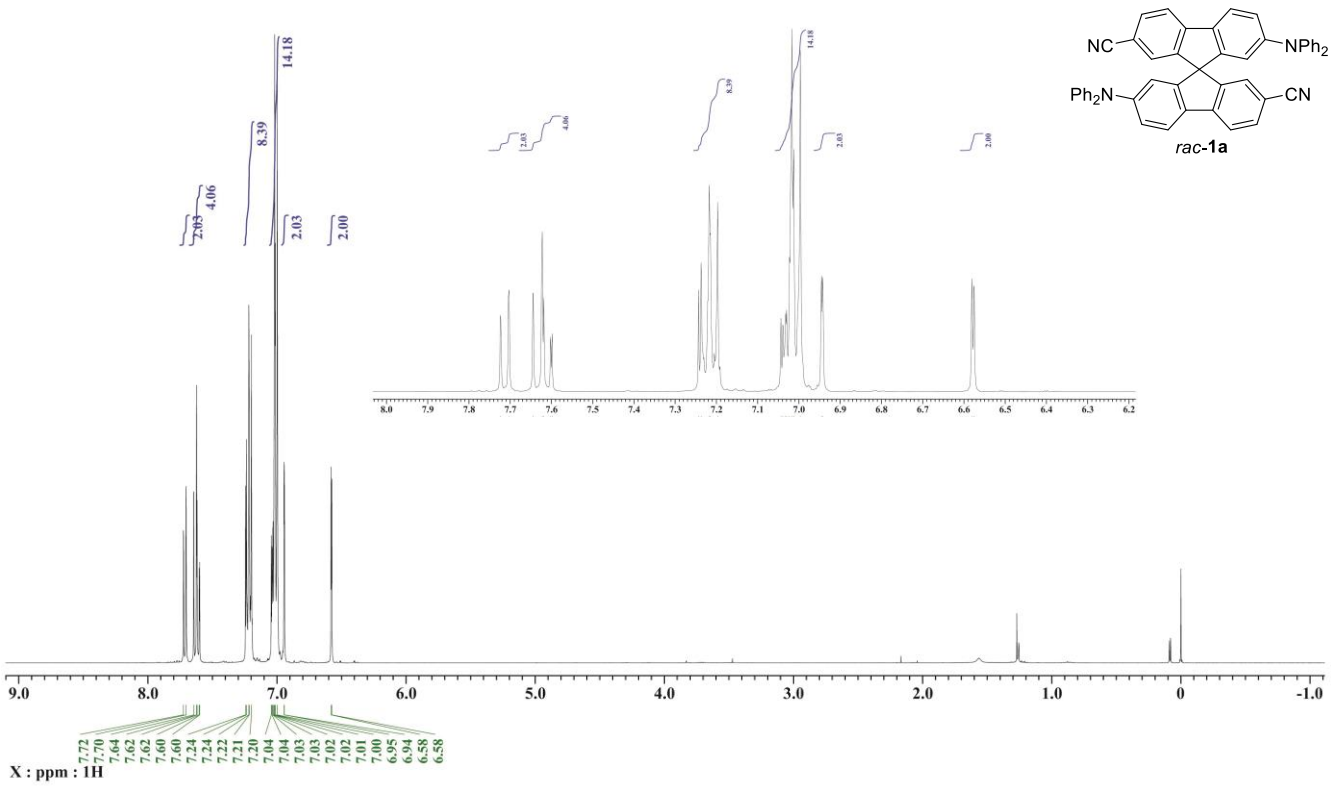

Fig. S15. ^{1}H NMR spectrum of *rac*-**1a** (400 MHz, $CDCl_3$).

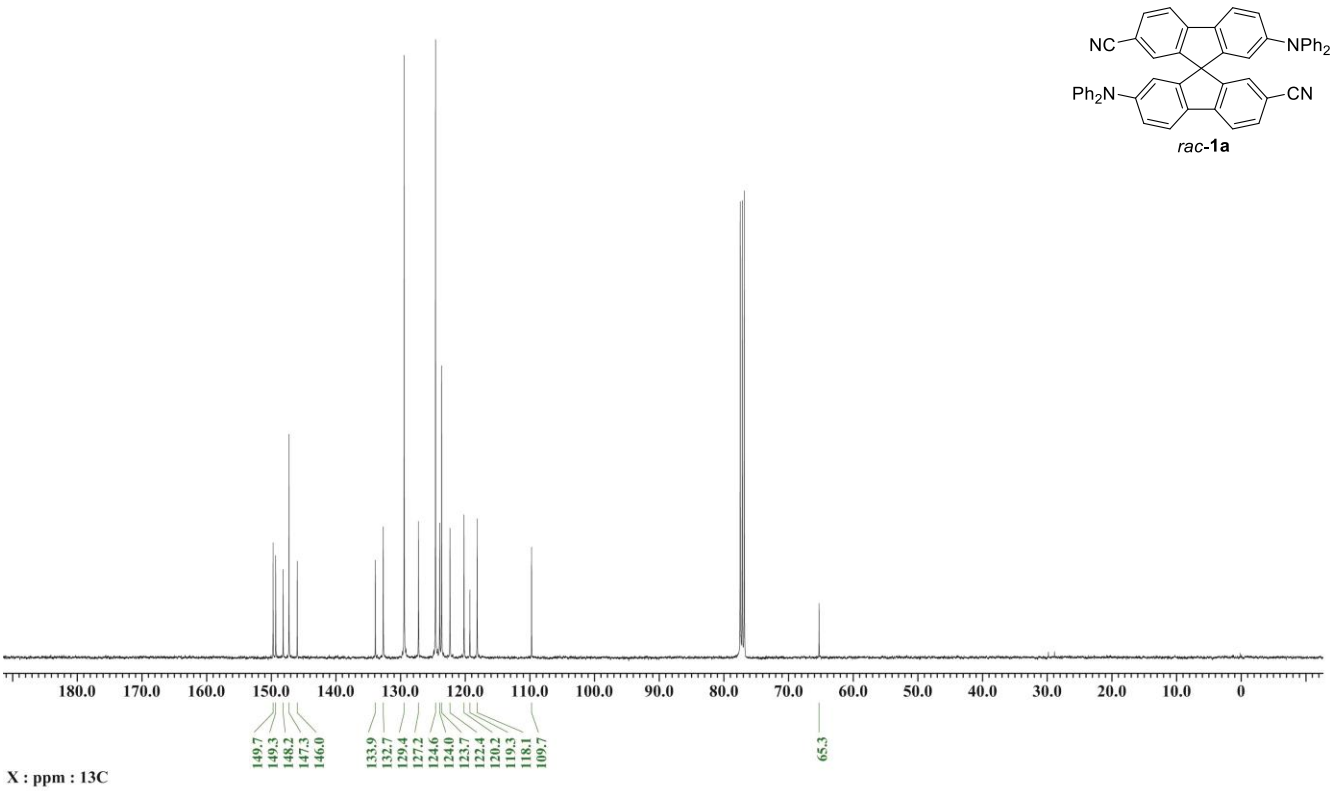

Fig. S16. ^{13}C NMR spectrum of *rac*-**1a** (101 MHz, $CDCl_3$).

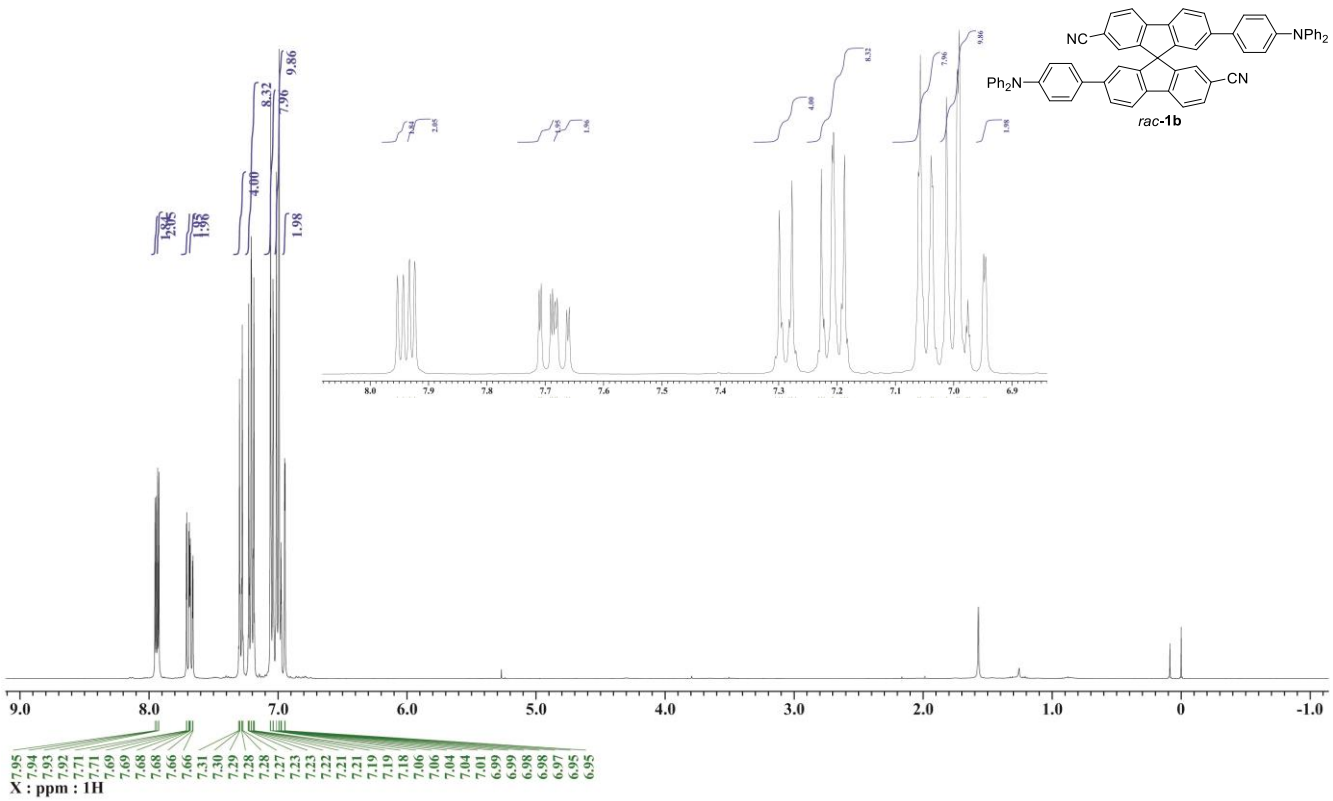

Fig. S17. ^{1}H NMR spectrum of *rac*-**1b** (400 MHz, $CDCl_3$).

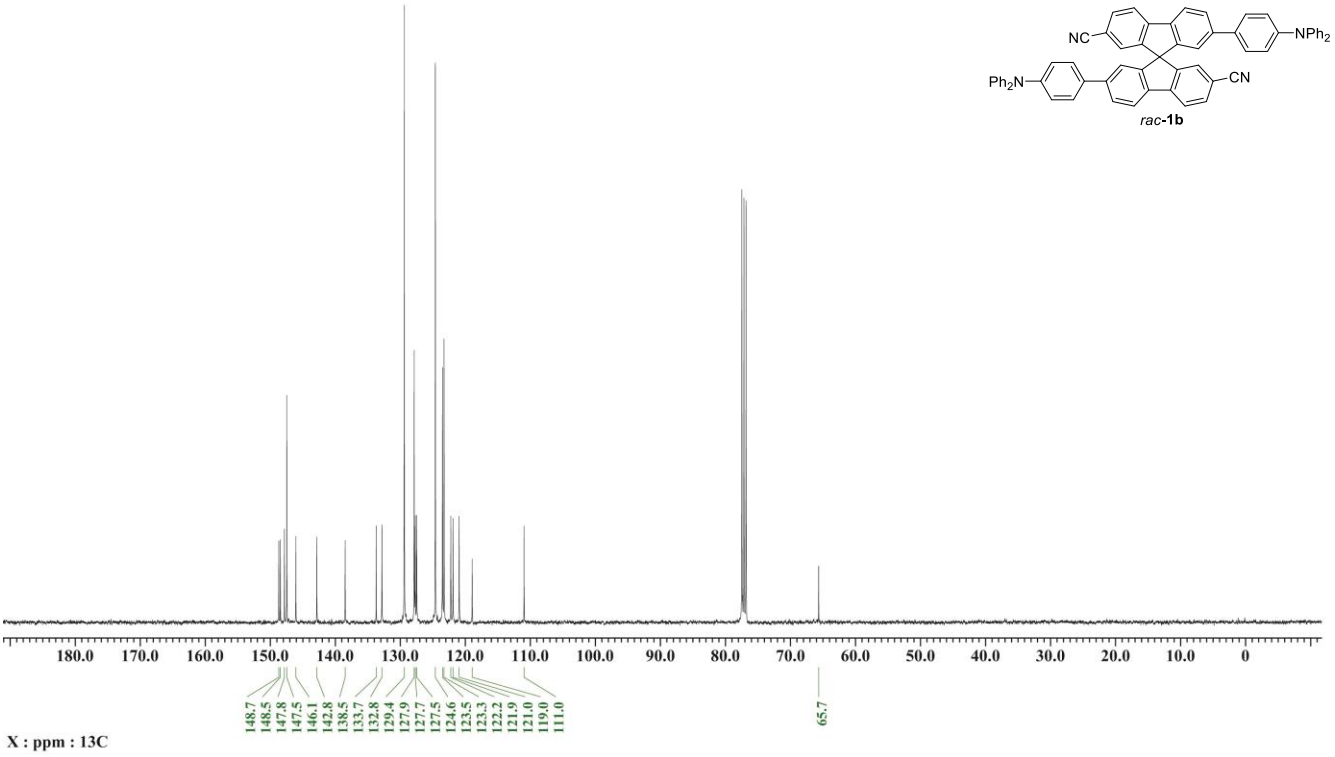

Fig. S18. ^{13}C NMR spectrum of *rac*-**1b** (101 MHz, $CDCl_3$).

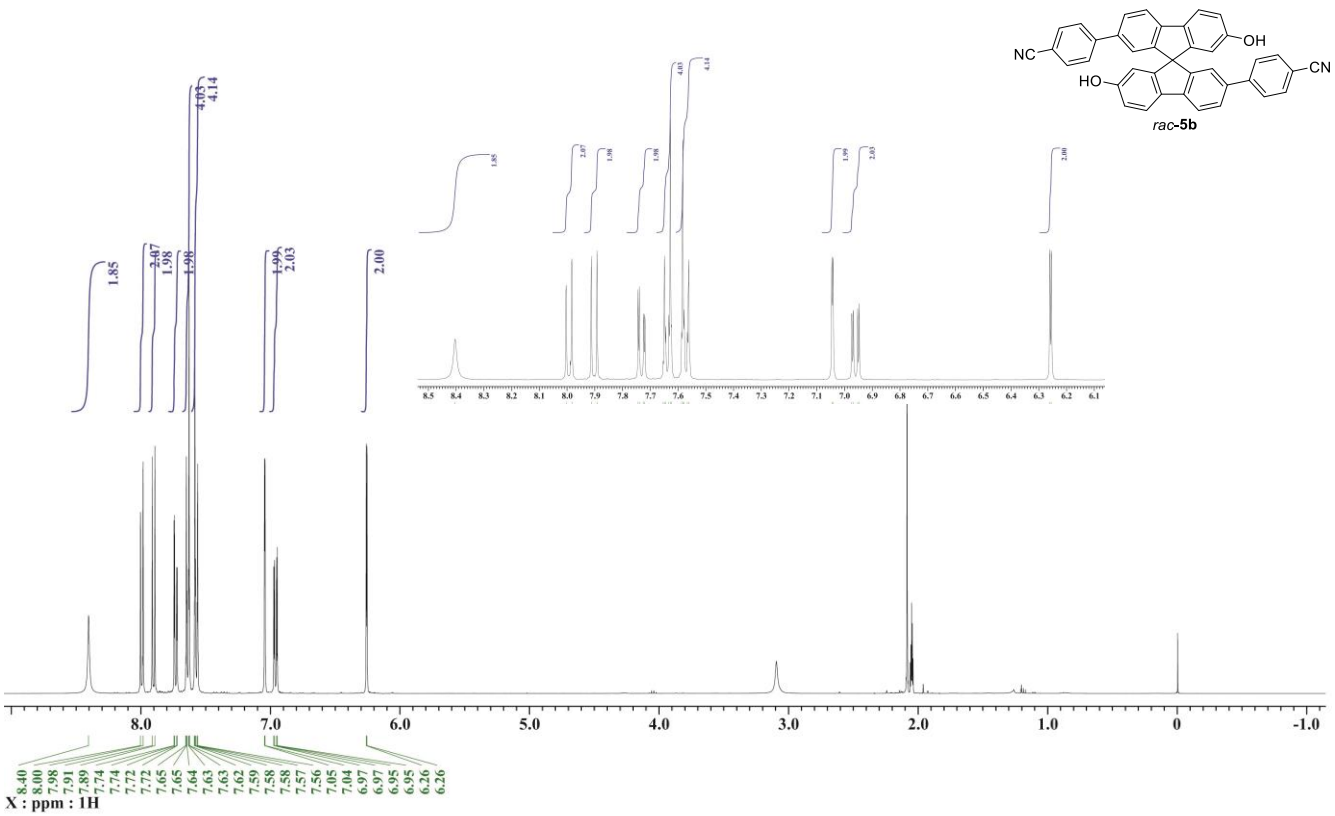

Fig. S19. ^{1}H NMR spectrum of *rac*-**5b** (400 MHz, acetone-d_6).

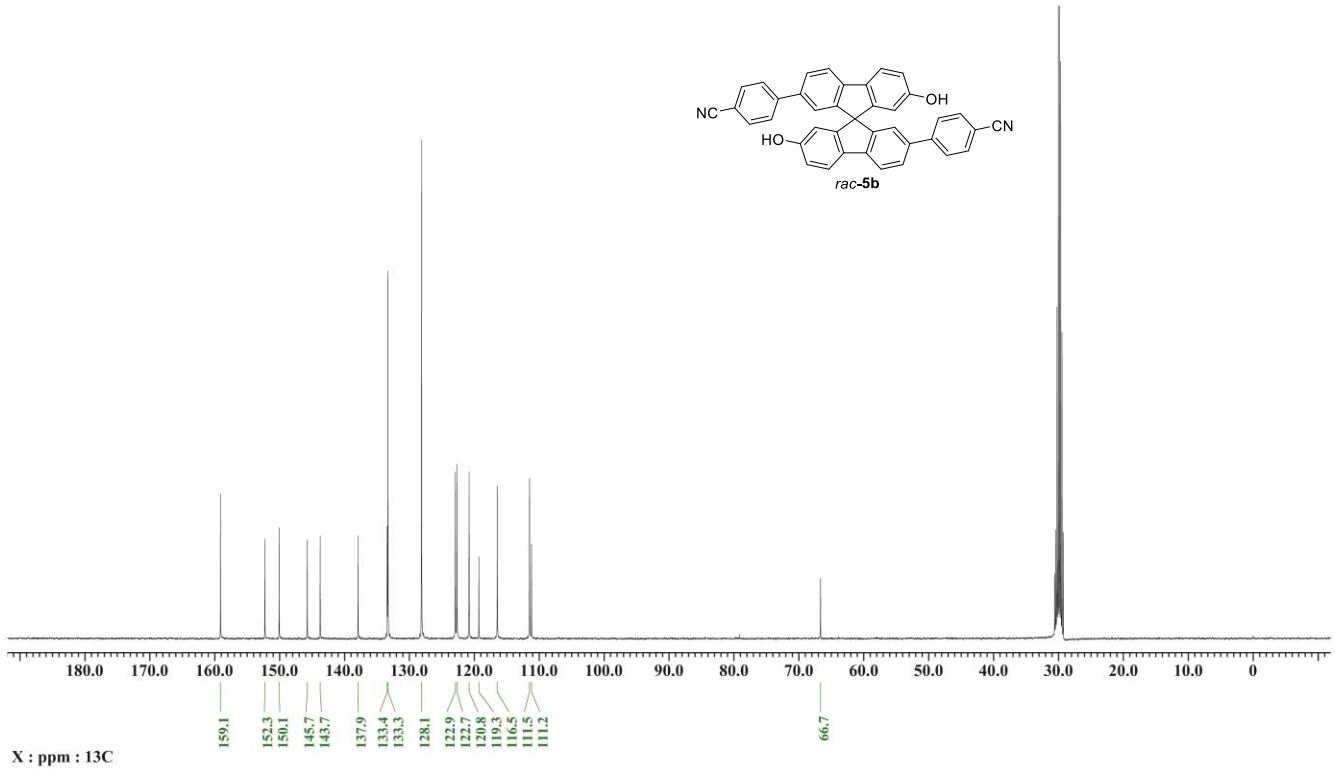

Fig. S20. ^{13}C NMR spectrum of *rac*-**5b** (101 MHz, acetone-d_6).

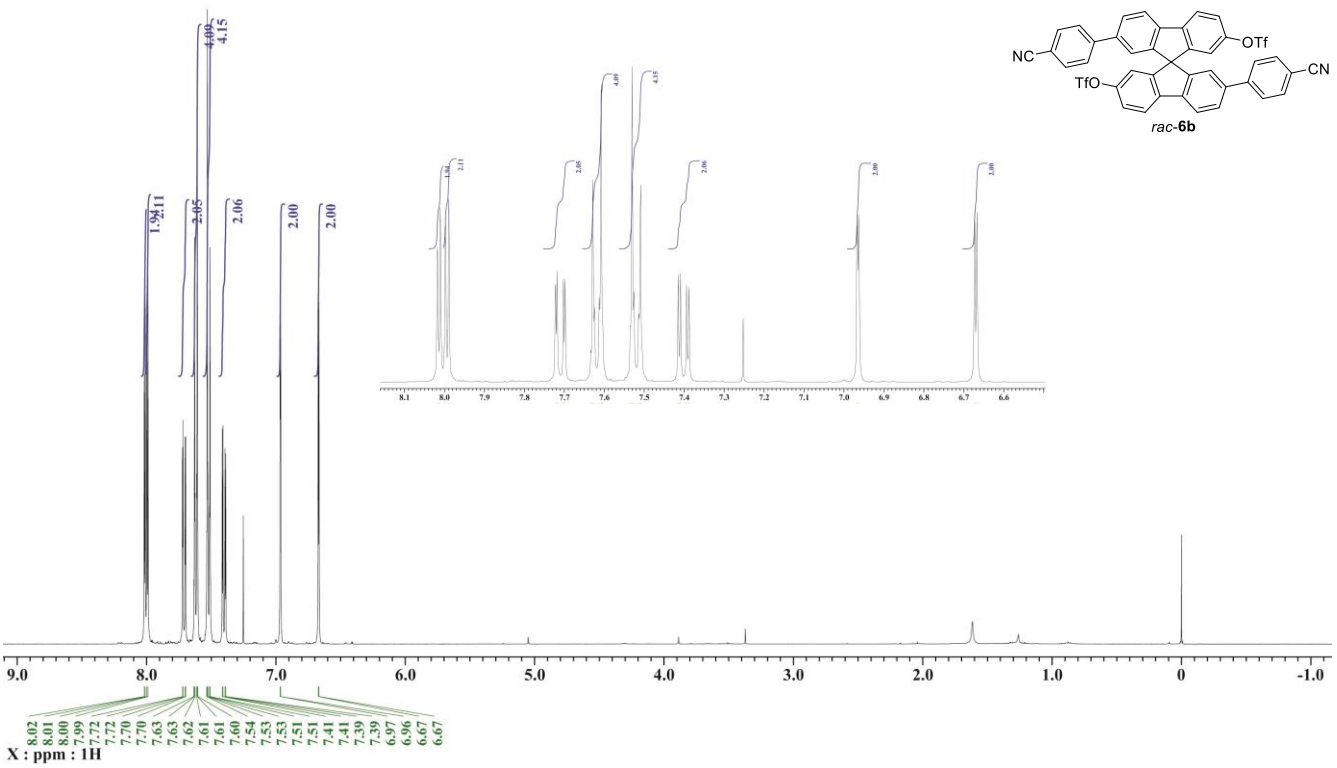

Fig. S21. ^{1}H NMR spectrum of *rac*-**6b** (400 MHz, $CDCl_3$).

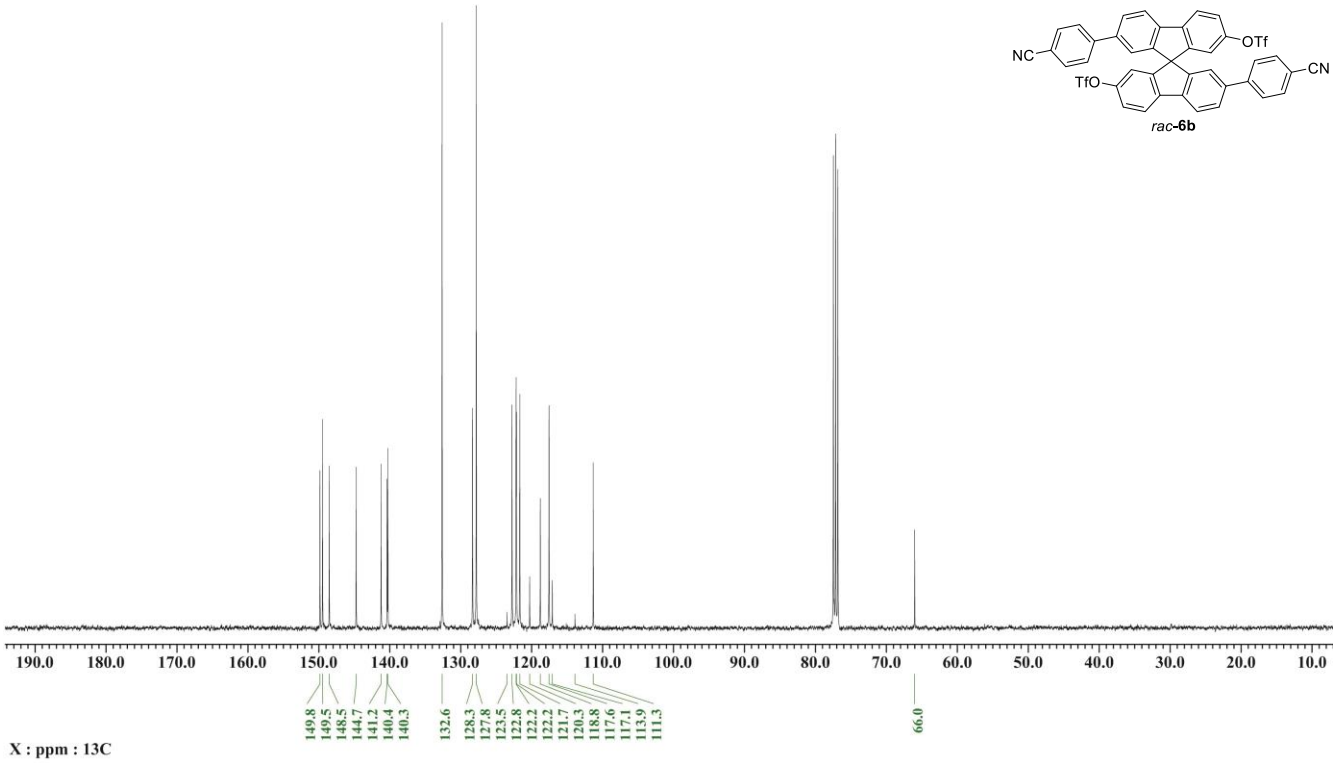

Fig. S22. ^{13}C NMR spectrum of *rac*-**6b** (101 MHz, $CDCl_3$).

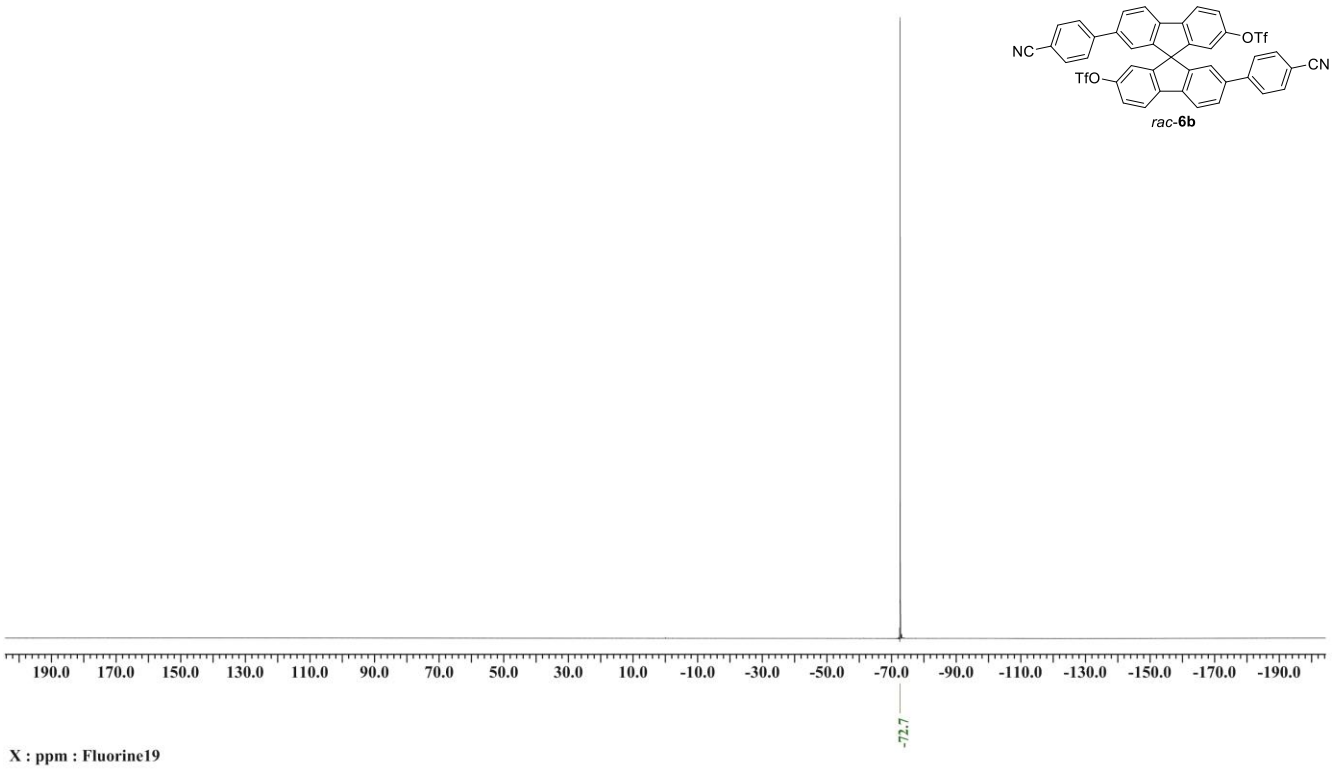

Fig. S23. ^{19}F NMR spectrum of *rac*-**6b** (376 MHz, $CDCl_3$).

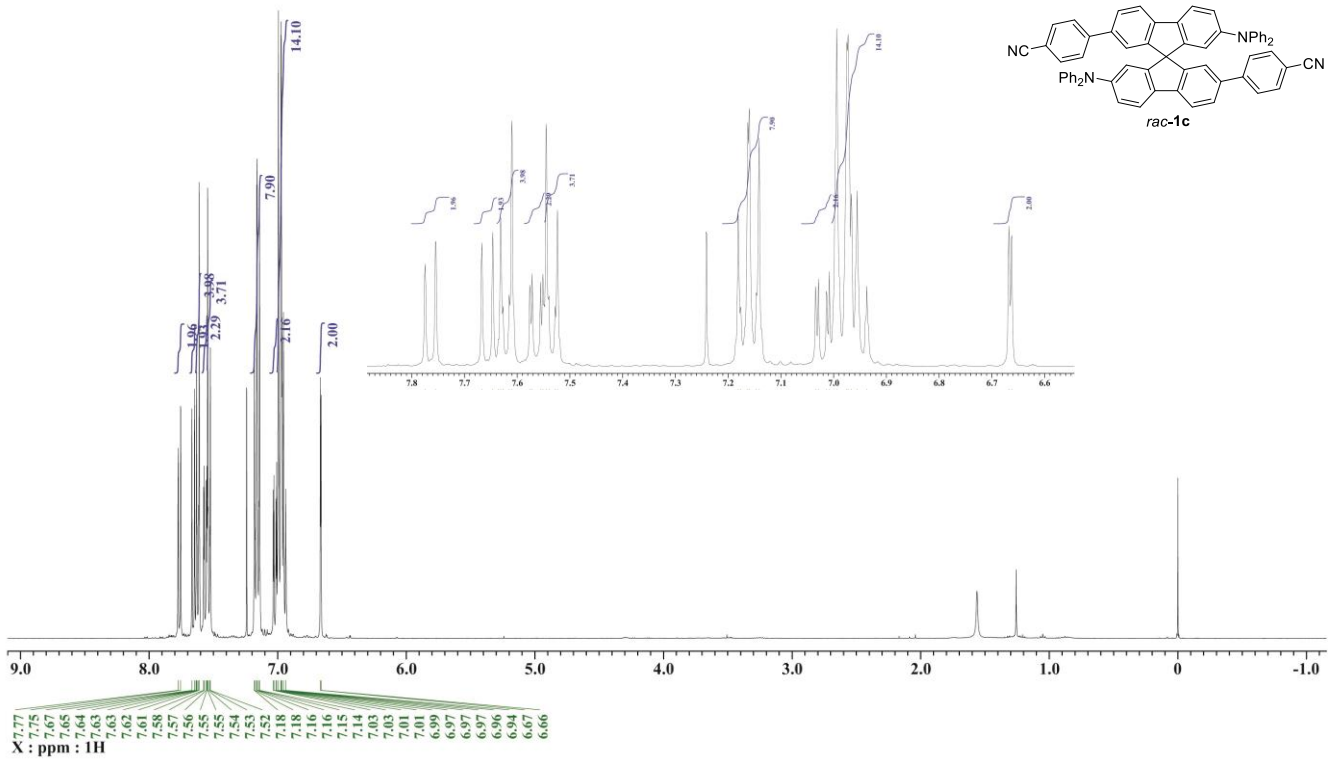

Fig. S24. ^{1}H NMR spectrum of *rac*-**1c** (400 MHz, $CDCl_3$).

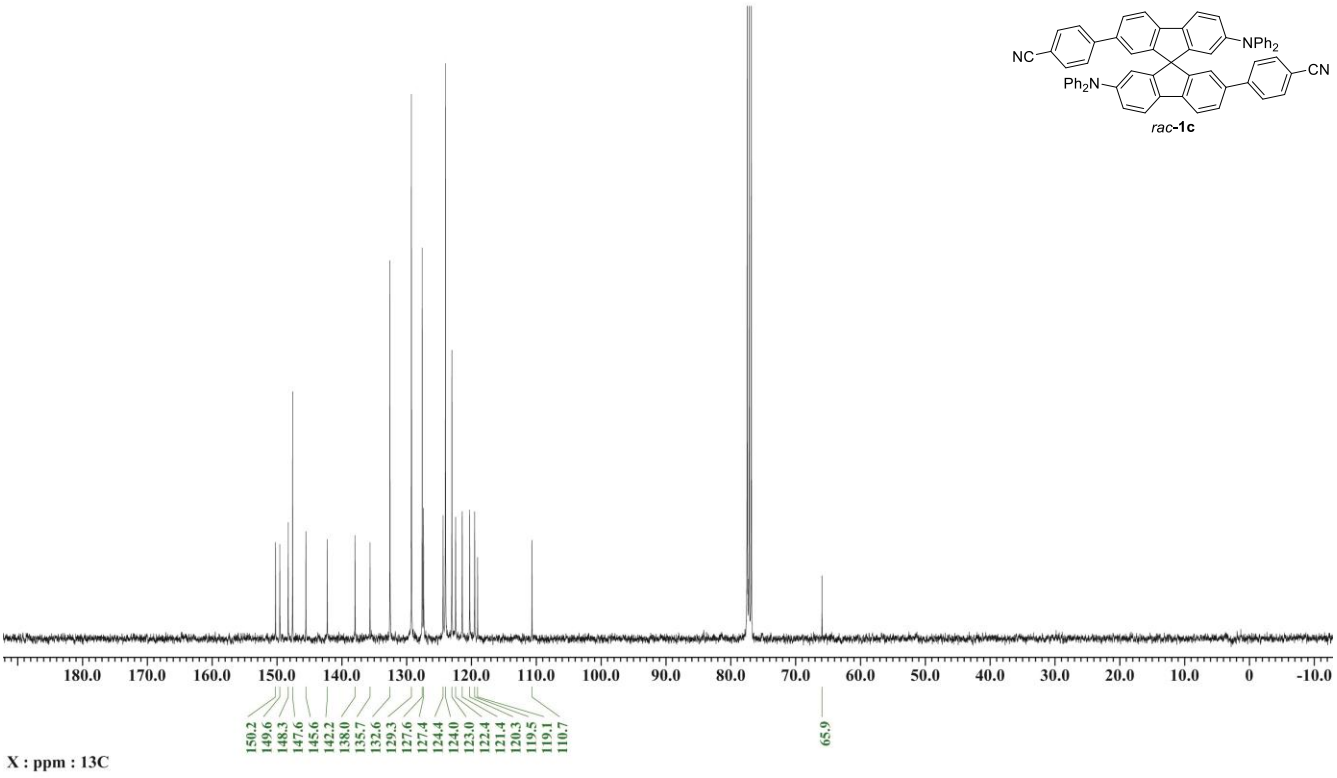

Fig. S25. ^{13}C NMR spectrum of *rac*-**1c** (101 MHz, $CDCl_3$).

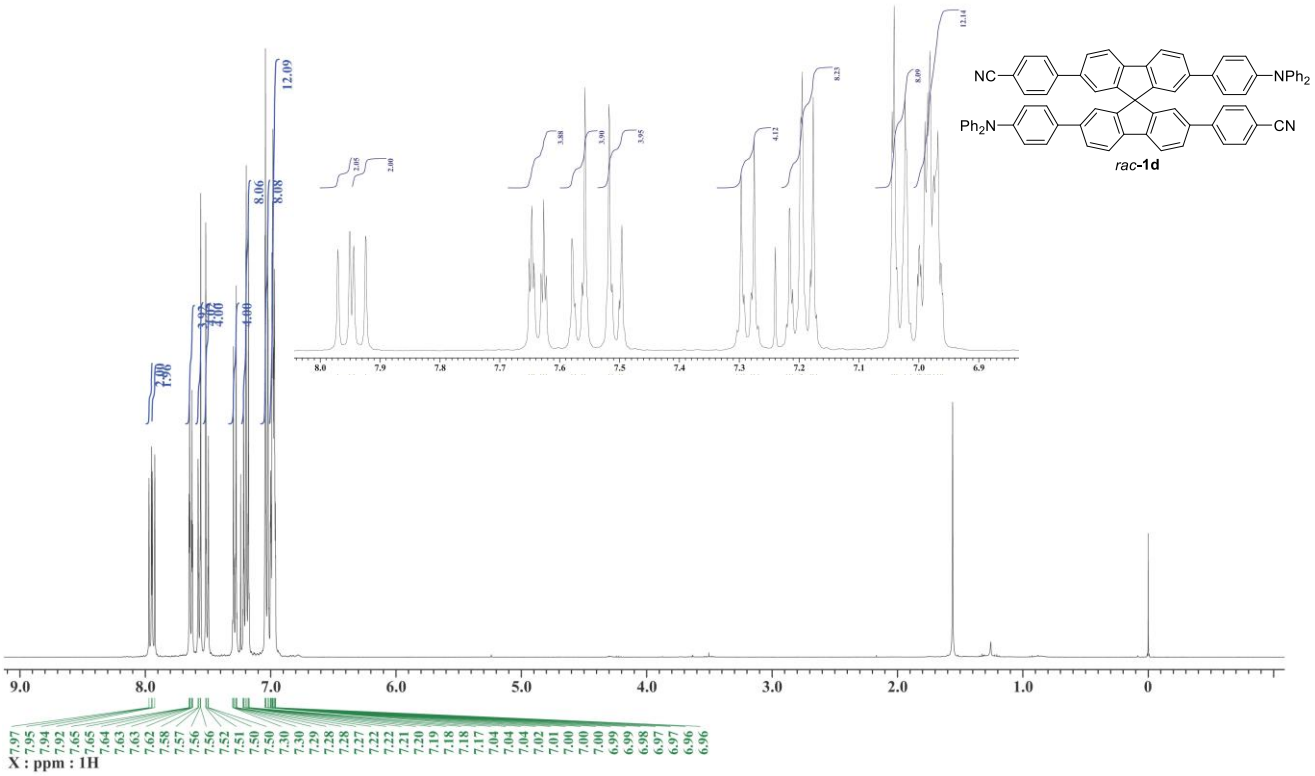

Fig. S26. ^{1}H NMR spectrum of *rac*-**1d** (400 MHz, $CDCl_3$).

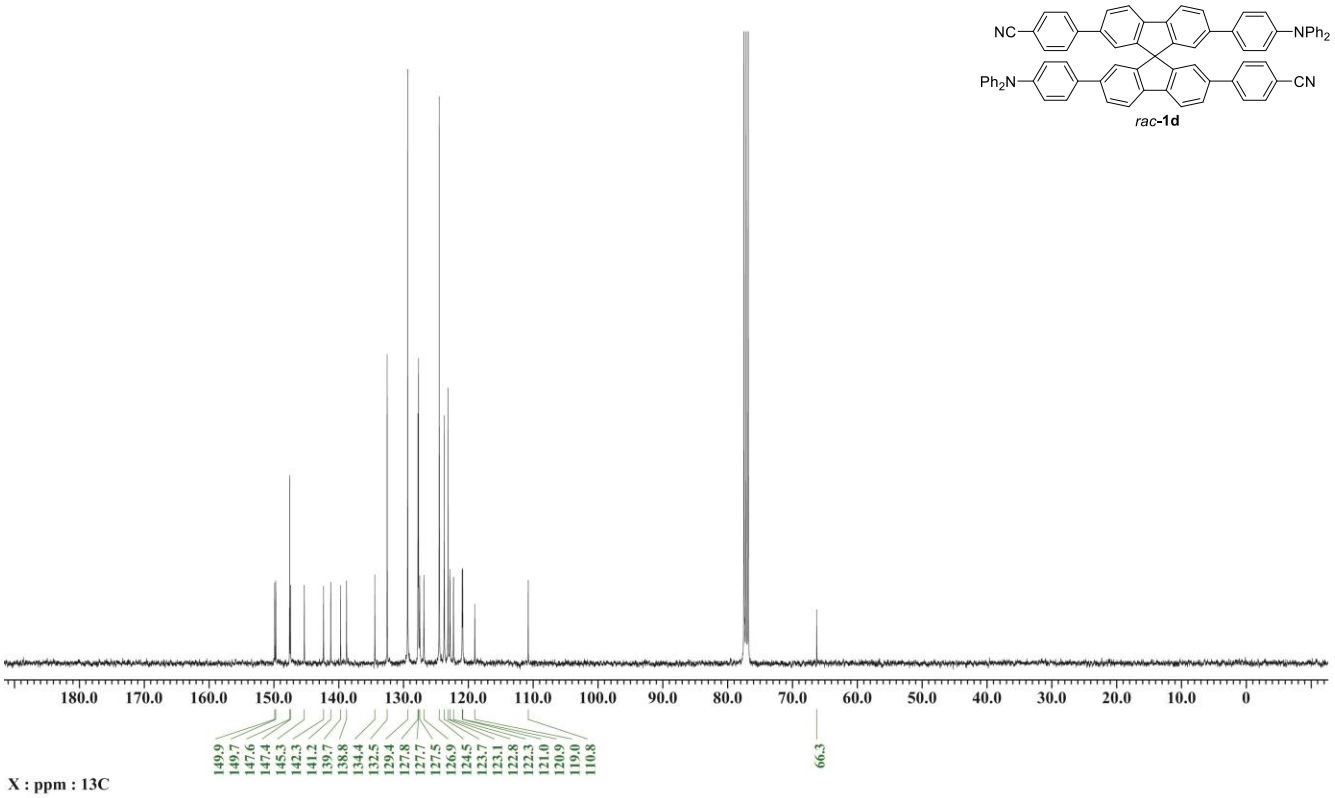

Fig. S27. ^{13}C NMR spectrum of *rac*-**1d** (101 MHz, $CDCl_3$).

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