Supporting Information
for

Chiroptical properties of 1,3-diphenylallene-anchored tetrathiafulvalene and its polymer synthesis

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Email: Masashi Hasegawa - masasi.h@kitastato-u.ac.jp; Yasuhiro Mazaki - mazaki@kitasato-u.ac.jp
*Corresponding author

Experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR charts, recyclable chiral HPLC chart and DFT calculation summary

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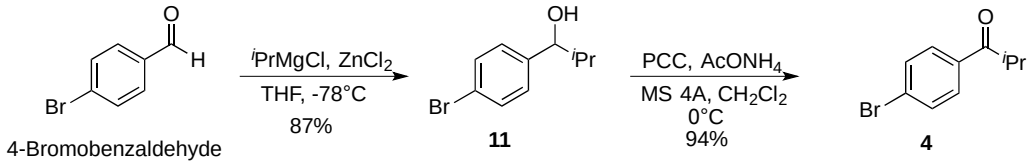
S1. Synthesis of 4



Scheme S1. Synthesis of **4**.

Although 1-(4-bromophenyl)-2-methylpropanone (**4**) is know compound, we modified its synthesis in order to obtain in a large quantity. Scheme 1 is depicted the synthesis of **4** via alcohol **11**.[s1]

1. Synthesis of **11**

To a suspension of $ZnCl_2$ (9.4 g, 69 mmol), which was dried for 4h at 200 °C in vacuo, in THF (100 mL), ^{i}PrMgCl (206 mmol) in THF (100 mL) was added dropwise under Ar atmosphere at rt. The resultant colorless suspension was stirred for 1h, and then cooled at 0°C. 4-Bromobenzaldehyde (12.7 g, 69 mmol) in THF (69 mL) was added and stirred for 14h at 0°C. Several portions of HCl (2M) were added into the reaction mixture at 0°C, and then the products were extracted by Et_2O three times. The organic layer was washed with saturated brine and dried over Na_2SO_4. The volatiles were removed under reduced pressure, and the resultant crude products were purified on silica gel column chromatography with CH_2Cl_2 as the eluent to give pale yellow oil of **11** (13.6 g, 87%). Data for **10**: MS (GC) *m/z* = 228 (100%, M^+: $C_{10}H_{13}Br^{79}O$), 230 (100%, M^+: $C_{10}H_{13}Br^{81}O$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (2H, d, *J* = 8.4 Hz), 7.14 (2H, d, *J* = 8.4 Hz), 4.28 (1H, dd, *J* = 6.6 and 1.2 Hz), 2.24 (1H, d, *J* = 1.2 Hz), 1.83-1.91 (1H, m), 0.94 (3H, d, J = 6.6 Hz), 0.77 (3H, d, J = 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 13.14, 128.4, 121.3, 79.2, 35.2, 19.0, 18.1.

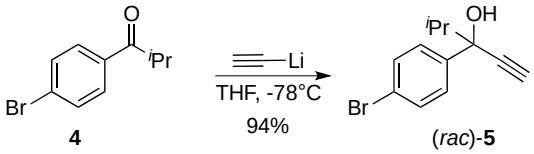
2. Synthesis of **4**

To a suspension of **11** (13.6 g, 60 mmol), $AcONH_4$ (13.8 g, 178 mmol), and molecular sieves 4Å (30 g) in CH_2Cl_2 (500 mL), PCC (19.2 g, 89 mmol) was added portionwise at 0°C. The mixture was allowed to warming up to rt, and stirred for 14h. The mixture was filtrated through a pad of celite with CH_2Cl_2. The volatiles were removed under reduced pressure, and the products were purified on silica gel column chromatography with

CH_2Cl_2 as the eluent to give pale yellow oil of **4** (12.7 g, 94%). Data for **4**: MS (GC) *m/z* = 226 (100%, M^+: $C_{10}H_{11}Br^{79}O$), 228 (100%, M^+: $C_{10}H_{11}Br^{81}O$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (2H, d, *J* = 8.6 Hz), 7.59 (2H, d, *J* = 8.6 Hz), 3.49 (1H, sept, *J* = 6.8 Hz), 1.2 (6H, d, *J* = 6.8 Hz). ^{13}C NMR (100MHz, $CDCl_3$) δ 203.3, 135.0, 142.7, 132.0, 129.9, 127.9, 35.5, 19.1.

S2. Synthesis of 7 from 4

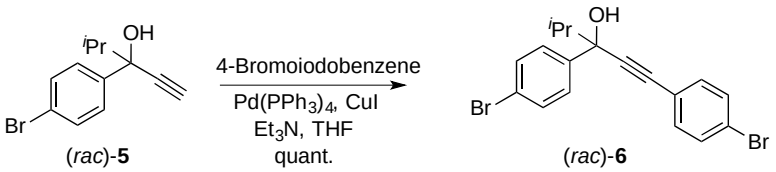
1. Synthesis of (*rac*)-**5**



Scheme S2. Synthesis of **5**.

In 1L three-necked flask containing THF (120 mL) under Ar atmosphere, acetylene gas, purified through cold trap and sulfuric acid in the upper course, was filled from a needle as the gas-inlet at -78°C. $^nC_4H_9Li$ (in hexane, 27.4 mL, 45 mmol) was carefully added dropwise to the solution. The mixture was stirred for 30min, and the inlet gas was stopped. Then, compound **4** (6.8 g, 30 mmol) in THF (50 mL) was added dropwise at -78°C. The mixture was slowly allowed to warming to rt, and stirred for 16h at rt. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution, and the mixture was extracted by Et_2O three times. The organic phase was washed with saturated brine and dried over $MgSO_4$. After removal of the volatiles, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to give pale yellow powder of **5** (7.1 g, 94%). Data for **5**: Mp. 39.8-40.0 °C. MS (GC) *m/z* = 252 (100%, M^+: $C_{12}H_{13}Br^{79}O$) and 254 (100%, M^+: $C_{12}H_{13}Br^{81}O$). ^1H NMR (600 MHz, $CDCl_3$) δ 7.46-7.49 (4H, m), 2.69 (1H, s), 2.37 (1H, s), 2.06 (1H, sept, 6.6 Hz), 1.05 (3H, d, *J* = 6.6 Hz), 0.83 (3H, d, *J* = 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.5, 131.0, 128.0, 121.8, 84.6, 76.6, 75.2, 40.2, 17.7, 17.2. IR (KBr) 3366, 3291, 2993, 2971, 2925, 2873, 2113, 1914, 1651, 1586, 1489, 1469, 1397, 1386, 1346, 1306 cm^{-1}. Anal. Calcd for $C_{12}H_{13}BrO$: C, 56.94 %; H, 5.18 % Found: C, 57.21%; H, 5.17 %.

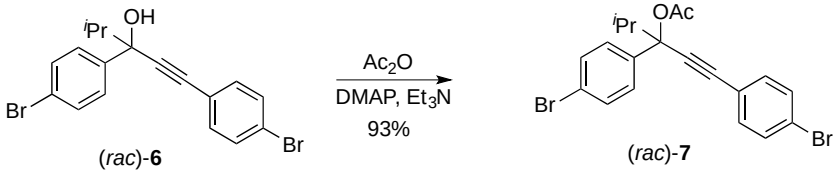
2. Synthesis of (*rac*)-**6**



Scheme S3. Synthesis of **6**.

A mixture of **5** (12.7g, 50 mmol), 4-bromoiodobenzene (17.0 g, 60 mmol), CuI (0.95 g, 5.0 mmol), Et_3N (5 mL), and $Pd(PPh_3)_4$ (1.0 g, 0.88 mmol) in THF (220 mL) was stirred for 16h under Ar atmosphere. Then, the resultant mixture was filtrated through a pad of celite with CH_2Cl_2. After removal the volatiles, the residue was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent to give yellow oil of **6** (20.3 g, 100 %). Data for **6**: MS (APCI) *m/z* = 406 (19%, M^+), 389 (100%, M^+-OH). ^1H NMR ($CDCl_3$, 600 MHz) δ 7.48-7.50 (2H, m), 7.43-7.47 (4H, m), 7.30-7.32 (2H, m), 2.60 (1H, s), 2.11 (1H, sept, *J* = 6.6 Hz), 1.07 (3H, d, *J* = 6.6 Hz), 0.87 (3H, d, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 142.8, 133.2, 131.7, 131.1, 128.0, 123.0, 121.8, 121.4, 91.2, 86.0, 77.1, 40.5, 18.0, 17.5. IR (KBr) 3434, 2965, 2224, 1901, 1782, 1731, 1645 cm^{-1}. HRMS (APCI-orbitrap) calcd. for $C_{18}H_{16}Br_2O$ (M^+) 405.9568, found 405.9544.

3. Synthesis of (*rac*)-**7**



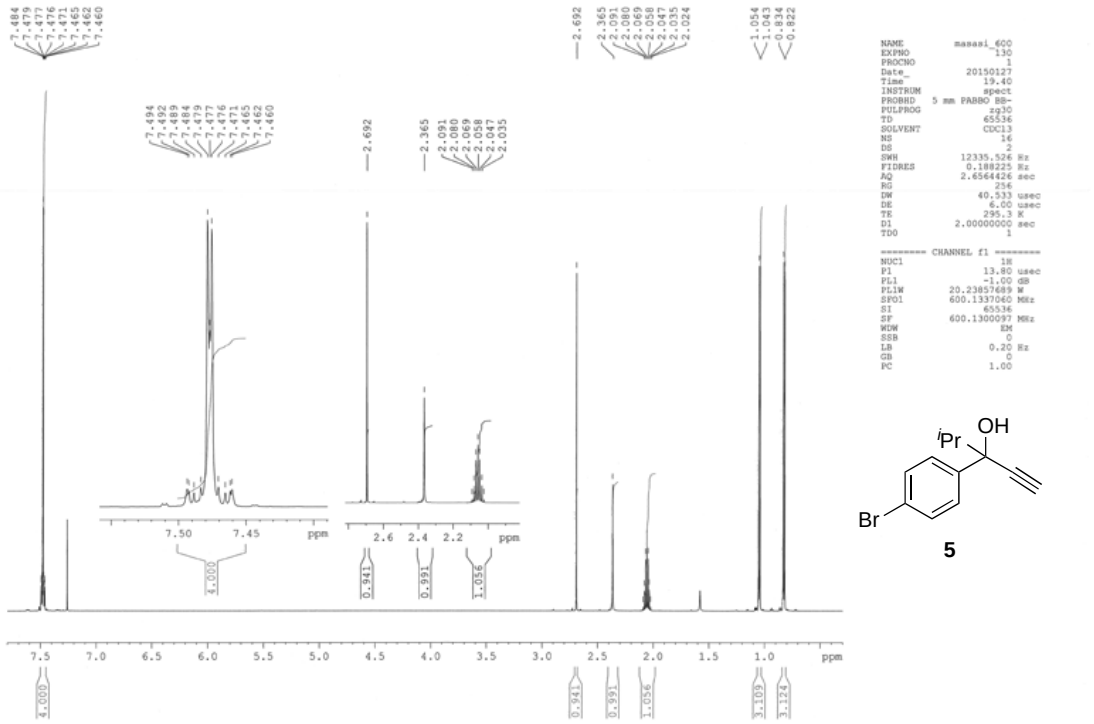
Scheme S4. Synthesis of **7**.

To a solution of **6** (5.0 g, 12 mmol), DMAP (0.23 g, 1.9 mmol) in CH_2Cl_2 (30 mL), Et_3N (30 mL, excess) and Ac_2O (5.8 mL, 62 mmol) were added under Ar atmosphere at rt. The mixture was stirred for 16h, and then saturated aqueous NH_4Cl was added. The product was extracted by Et_2O, and the combined organic phase was washed with saturated brine and dried over $MgSO_4$. The volatiles were removed in vacuo to give colorless solid of **7** (5.2 g, 93 %). Compound **7** is unstable to silica gel, and therefore further purification was not carried out. Data for **7**: Mp. = 84.0-86.5 °C. MS (APCI) *m/z* = 399 (50%, M^+-OAc: $C_{18}H_{15}Br^{79}{}_2$), 391 (100%, M^+-OAc: $C_{18}H_{15}Br^{79}Br^{81}$), 393 (50%,

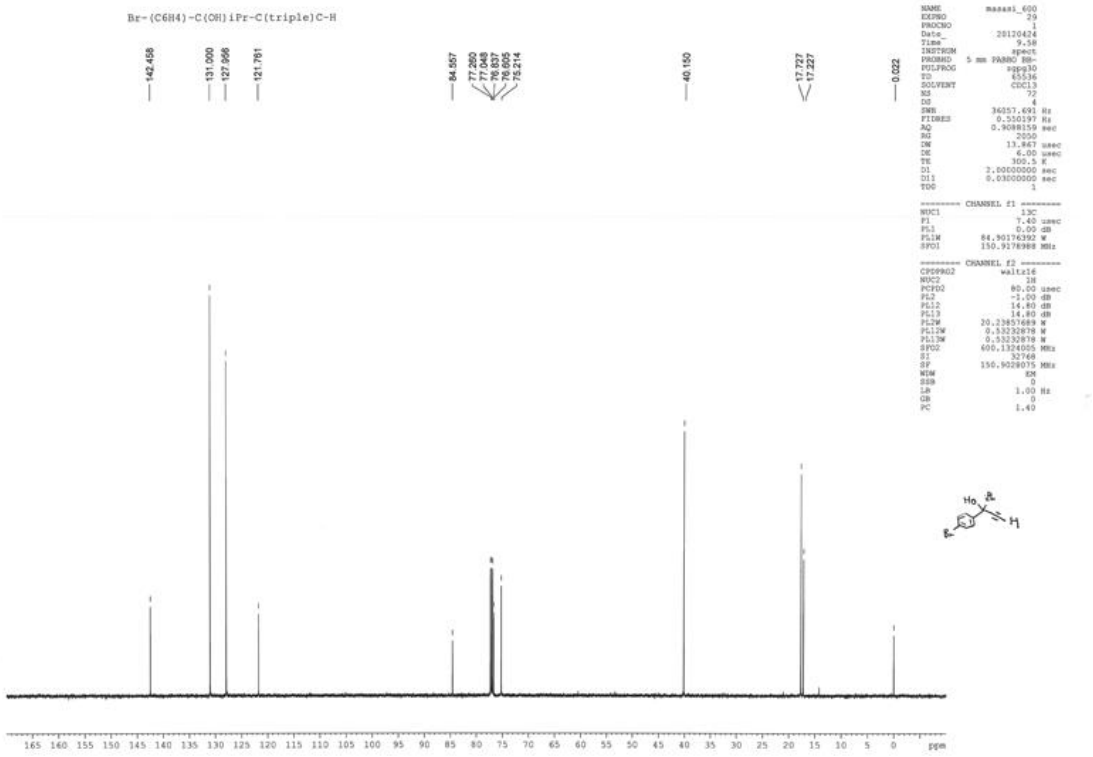
M^+-OAc: $C_{18}H_{15}Br^{81}{}_2$), 408 (0.2%, M^+: $C_{20}H_{18}Br^{79}{}_2O_2$), 410 (0.4%, M^+: $C_{20}H_{18}Br^{79}Br^{81}O_2$), 412 (0.2%, M^+: $C_{20}H_{18}Br^{81}{}_2O_2$). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.34-7.39 (4H, m), 7.30-7.34 (4H, m), 2.18 (1H, sept, *J* = 6.6 Hz), 1.98 (3H, s), 1.14 (3H, d, *J* = 6.6 Hz), 0.68 (3H, d, *J* = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 169.4, 140.1, 133.5, 131.6, 131.3, 127.6, 123.1, 121.8, 121.3, 88.0, 86.3, 82.6, 40.3, 21.7, 18.1, 17.2. IR (KBr) 3066, 2969, 2932, 2874, 2229, 1902, 1748, 1489 cm^{-1}. Anal. Calcd for $C_{20}H_{18}Br_2O_2$: C, 53.36 %; H,4.03 % Found: C, 53.32 %; H, 4.03 %.

S3. Figure S1. ^{1}H and ^{13}C NMR Chart of 5

(a) ^{1}H NMR (600 MHz, $CDCl_3$)

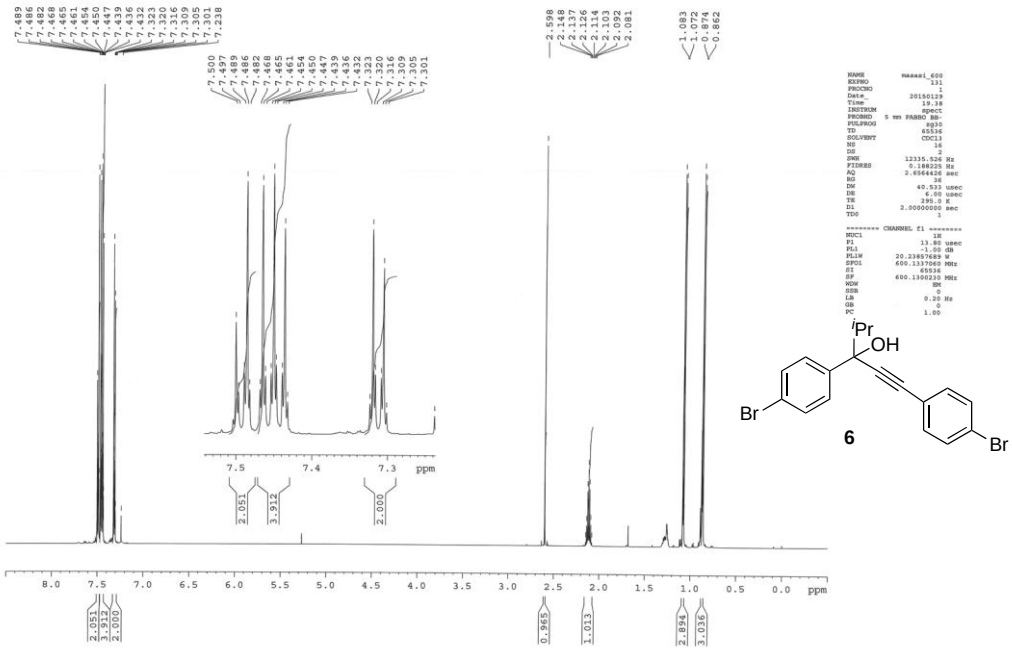


(b) ^{13}C NMR (150 MHz, $CDCl_3$)

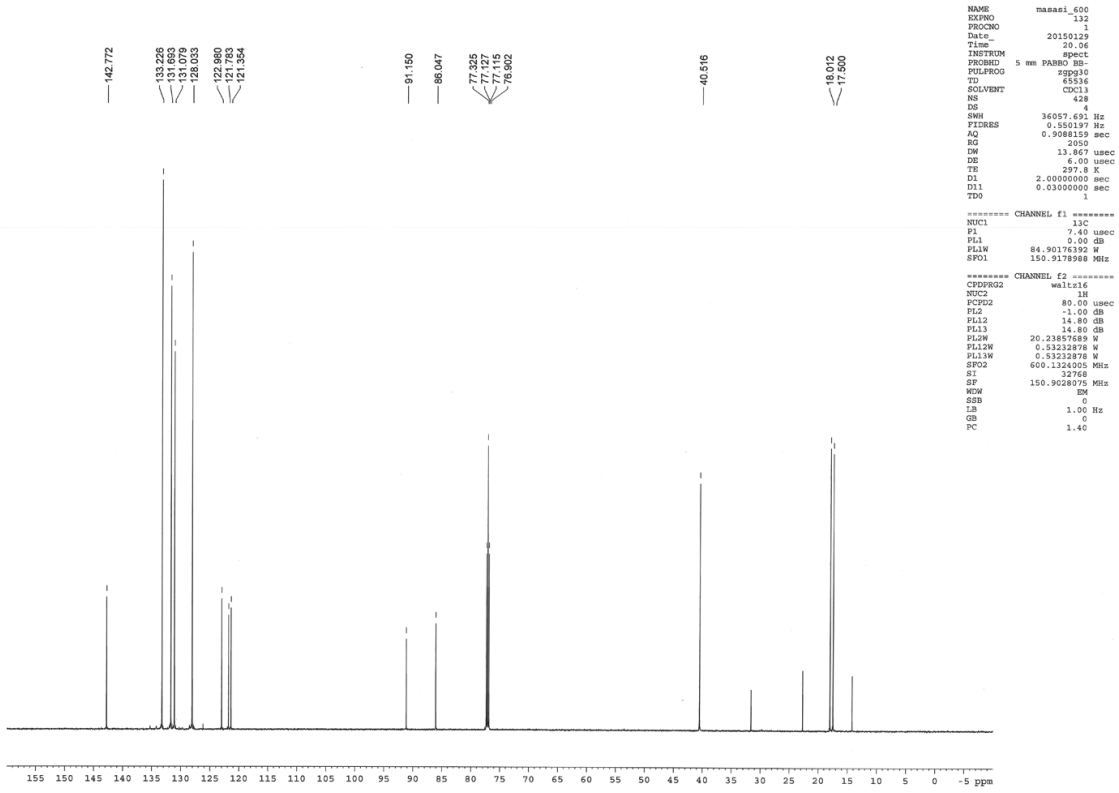


S4. Figure S2. ^{1}H and ^{13}C NMR Chart of 6

(a) ^{1}H NMR (600 MHz, $CDCl_3$)

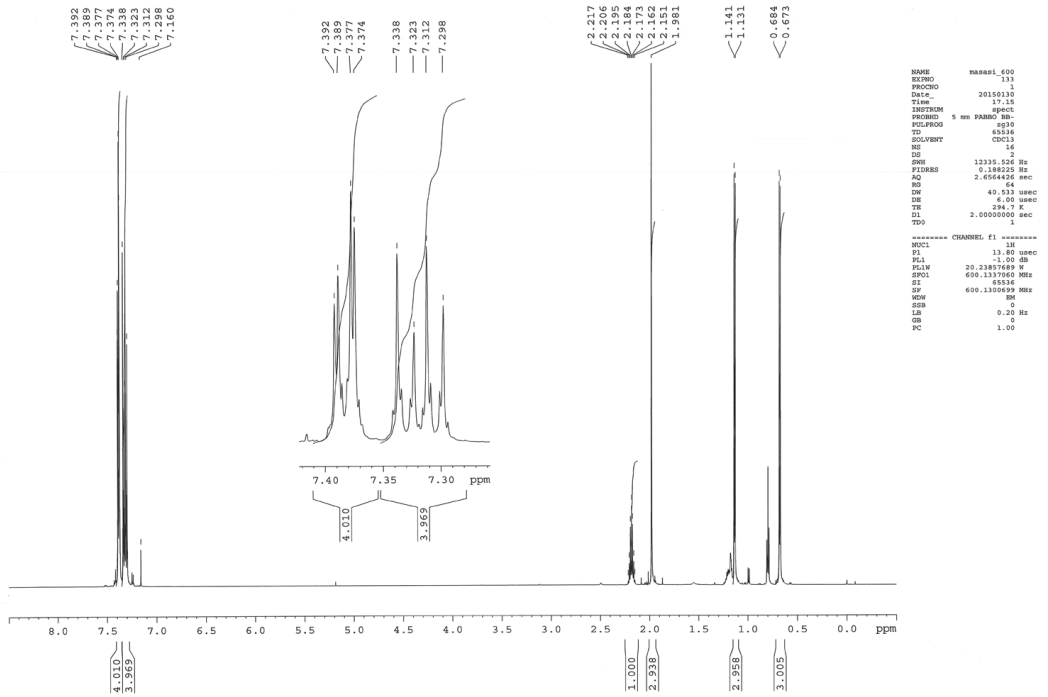


(b) ^{13}C NMR (150 MHz, $CDCl_3$)

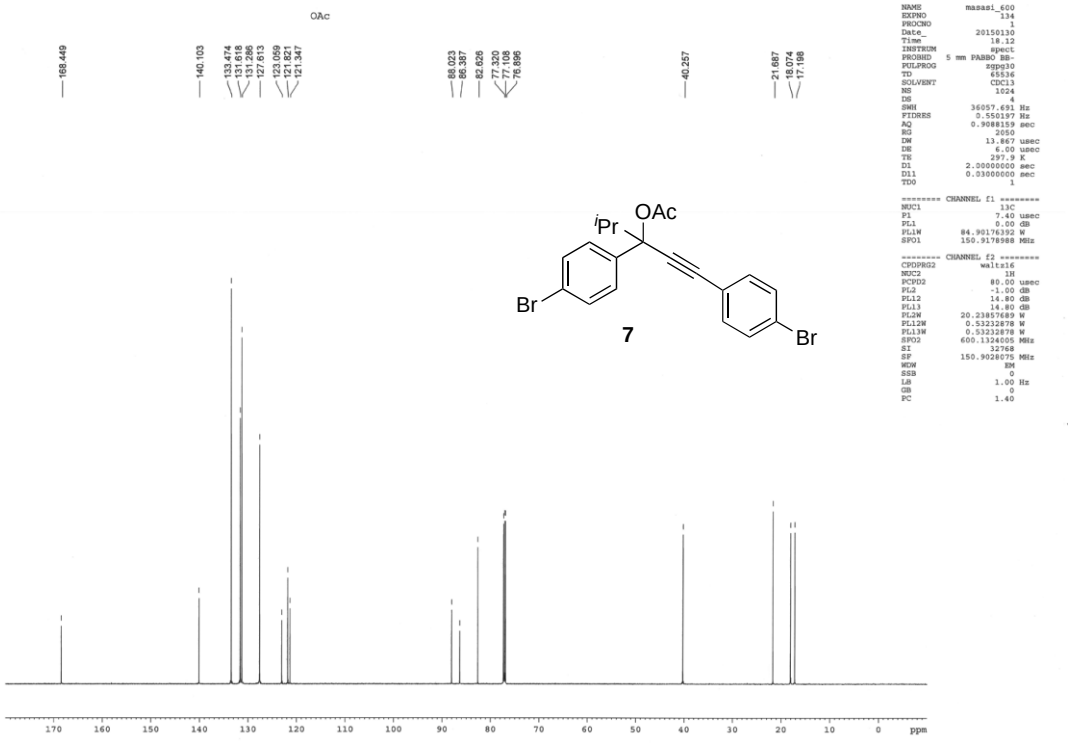


S5. Figure S3. ^{1}H and ^{13}C NMR Chart of 7

(a) ^{1}H NMR (600 MHz, $CDCl_3$)

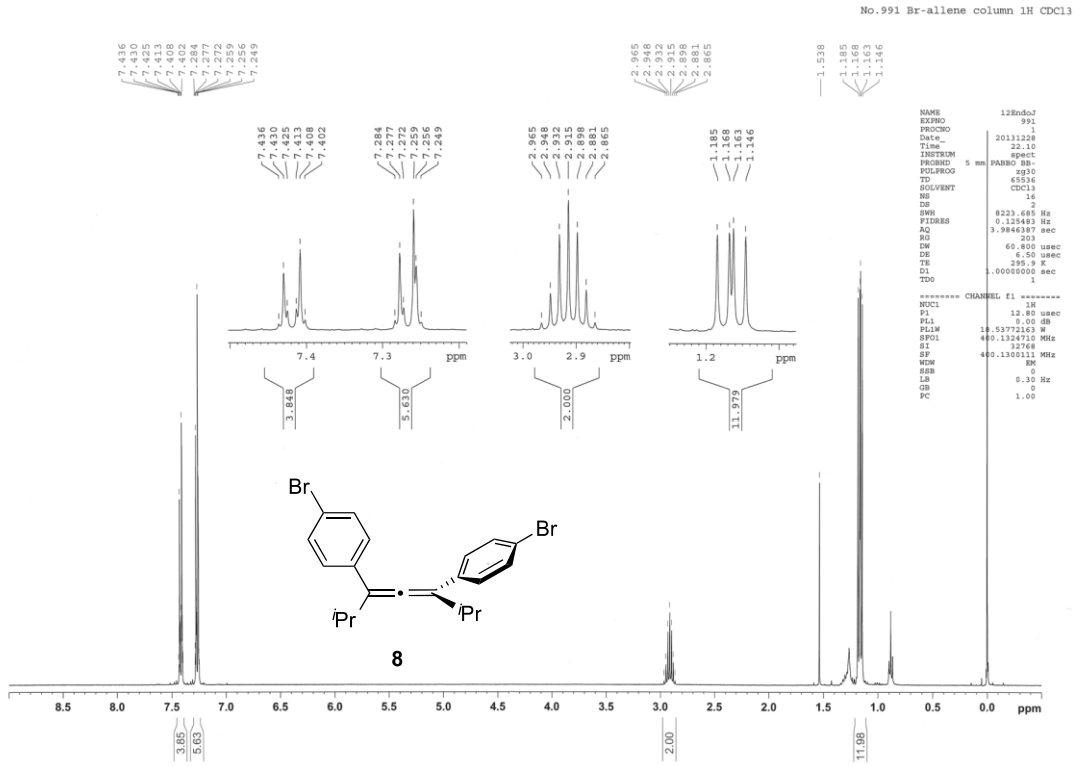


(b) ^{13}C NMR (150 MHz, $CDCl_3$)

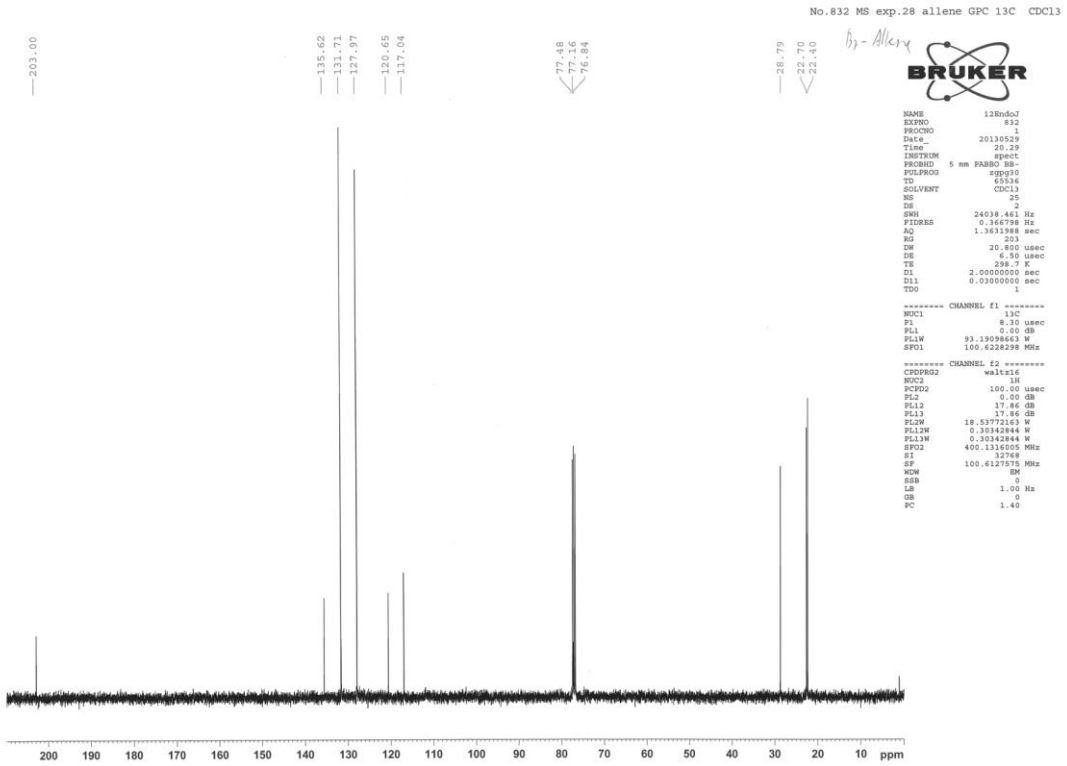


S6. Figure S4. ^{1}H and ^{13}C NMR Chart of 8

(a) ^{1}H NMR (400 MHz, $CDCl_3$)

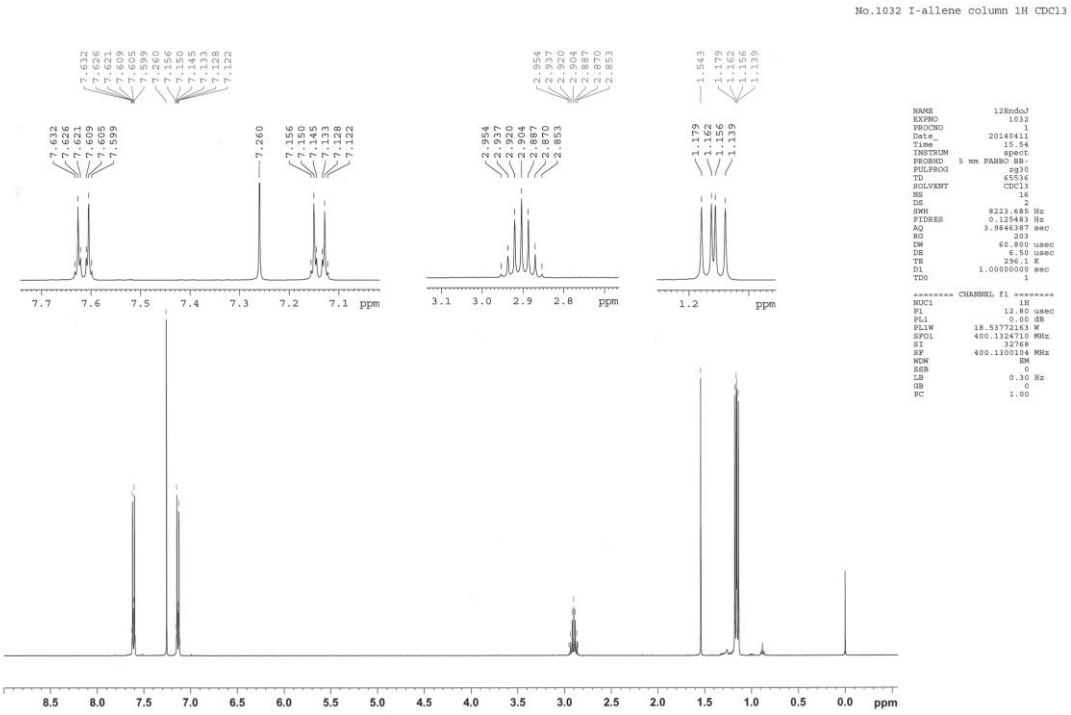


(b) ^{13}C NMR ($CDCl_3$, 100 MHz)

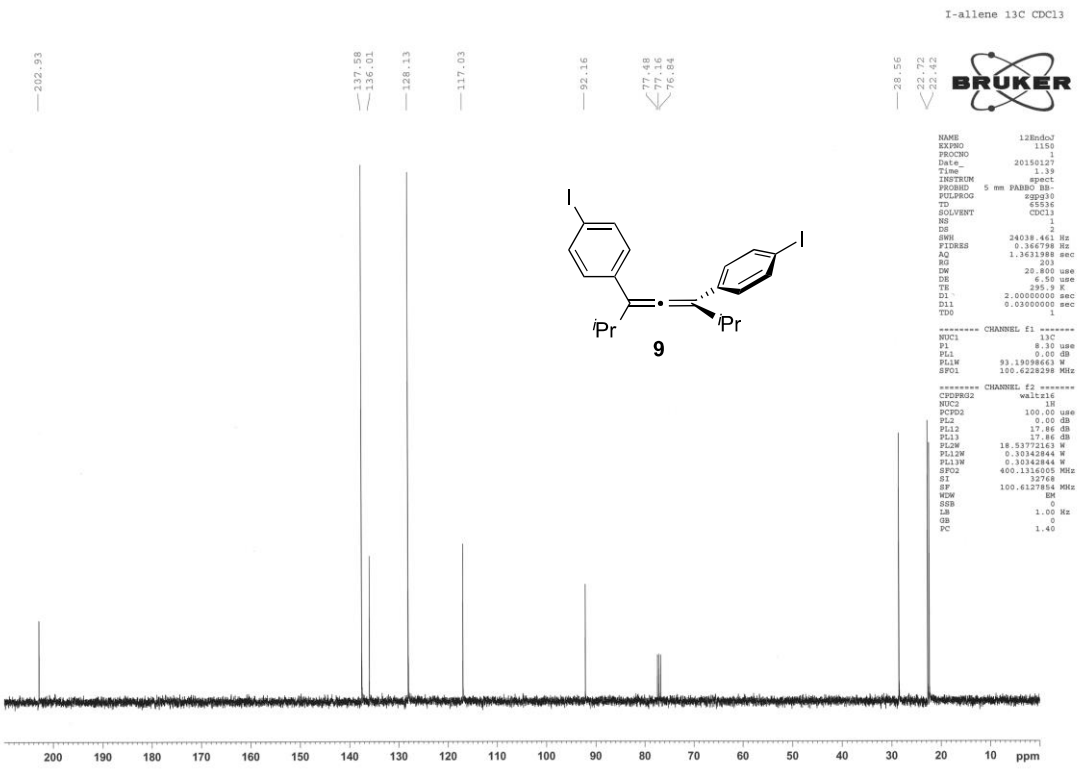


S7. Figure S5. ^{1}H and ^{13}C NMR Chart of 9

(a) ^{1}H NMR (400 MHz, $CDCl_3$)

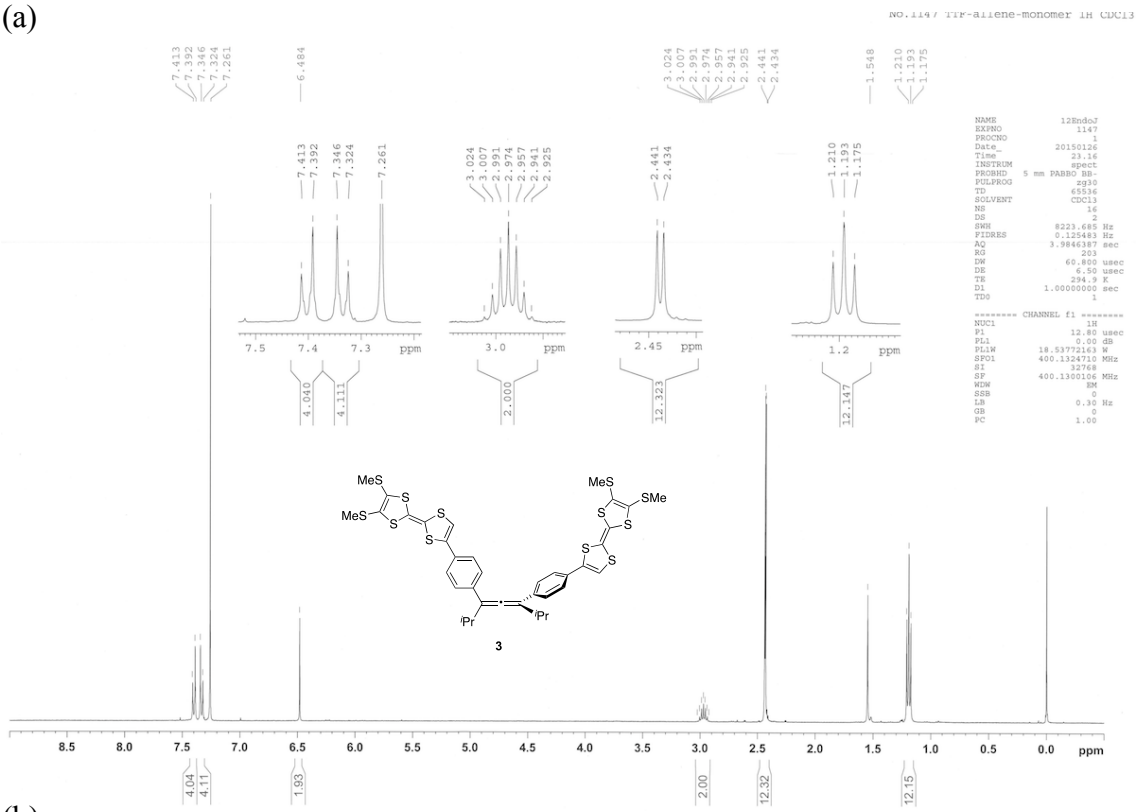


(b) ^{13}C NMR (100 MHz, $CDCl_3$)

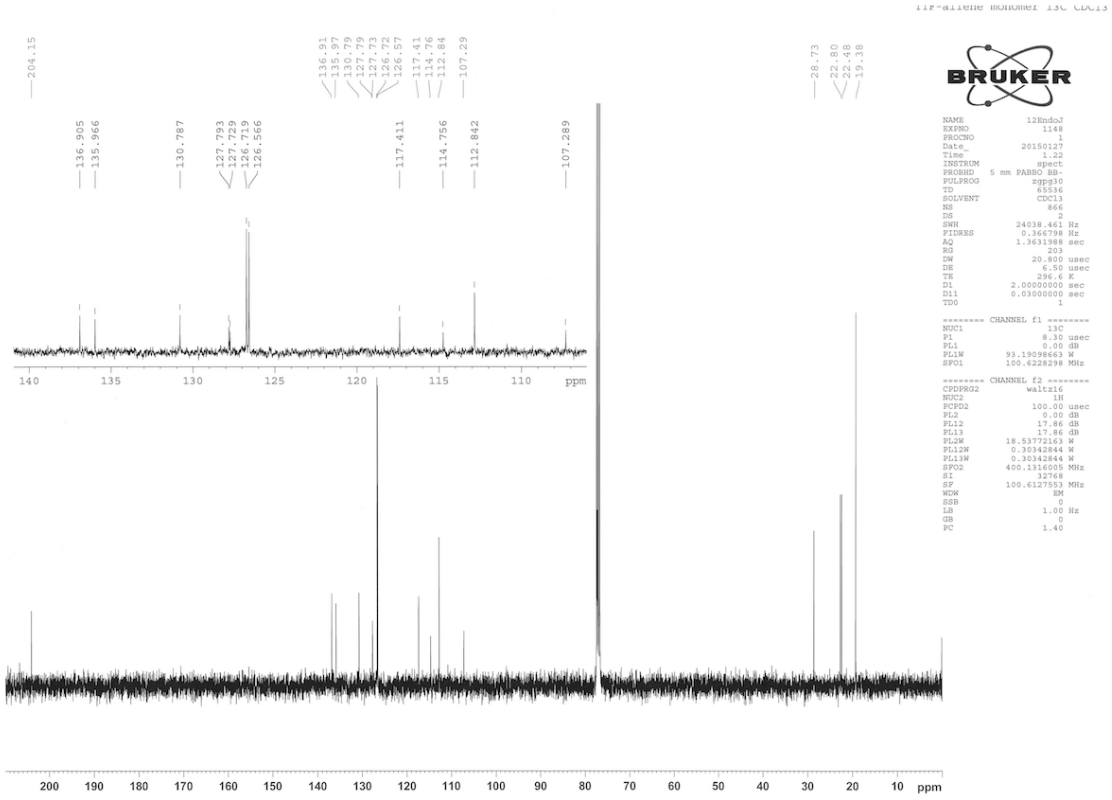


S8. Figure S6. ^{1}H and ^{13}C NMR Chart of 3

(a)

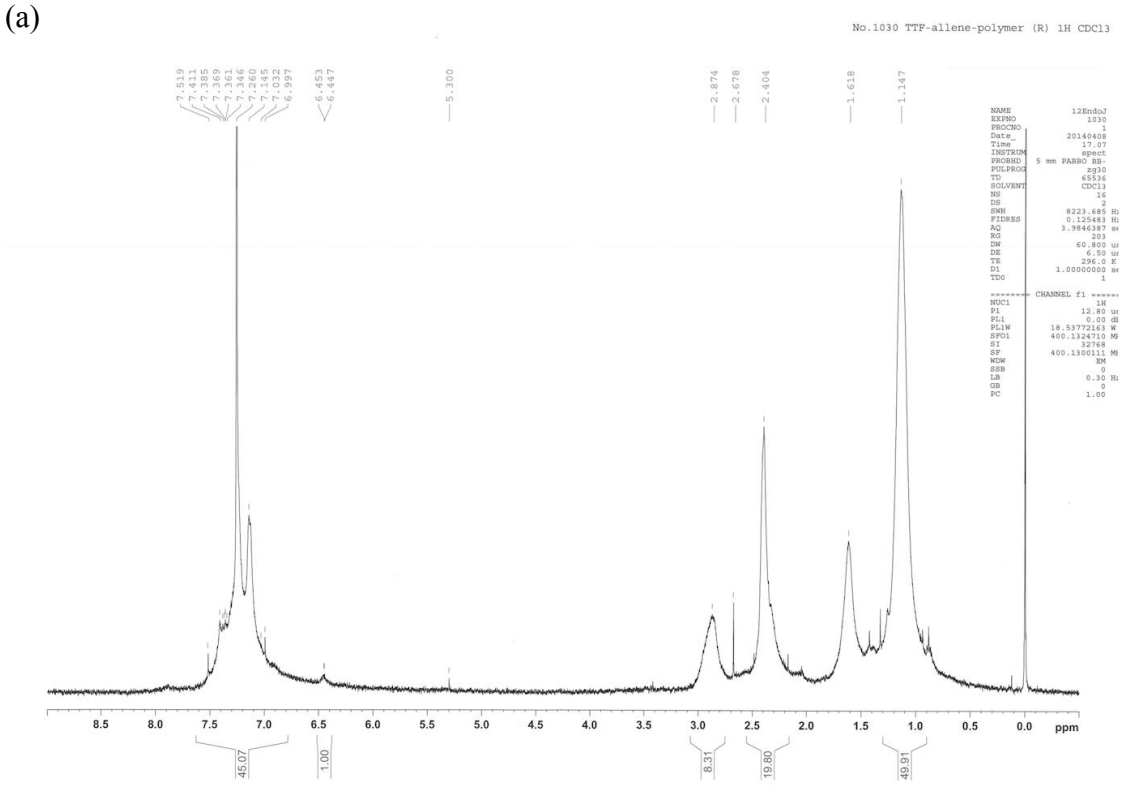


(b)

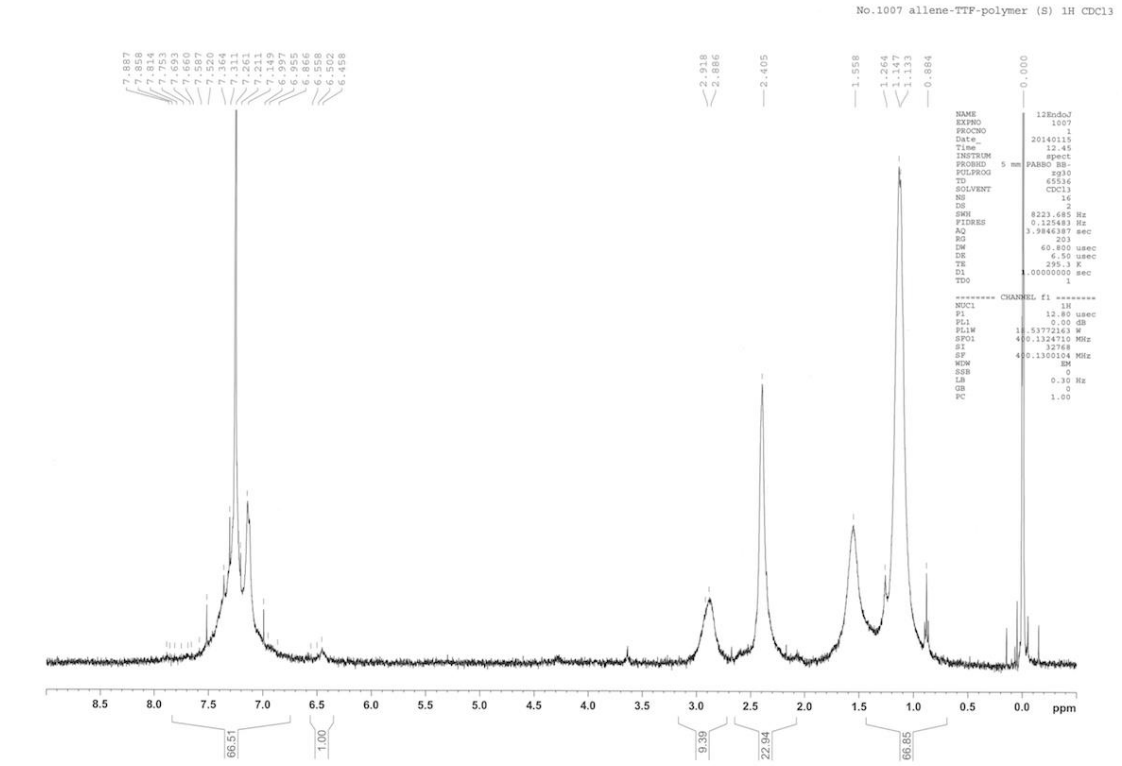


S9. Figure S7. ^{1}H NMR Spectrum of (a) (*R*)-PTDPA and (b) (*S*)- PTDPA

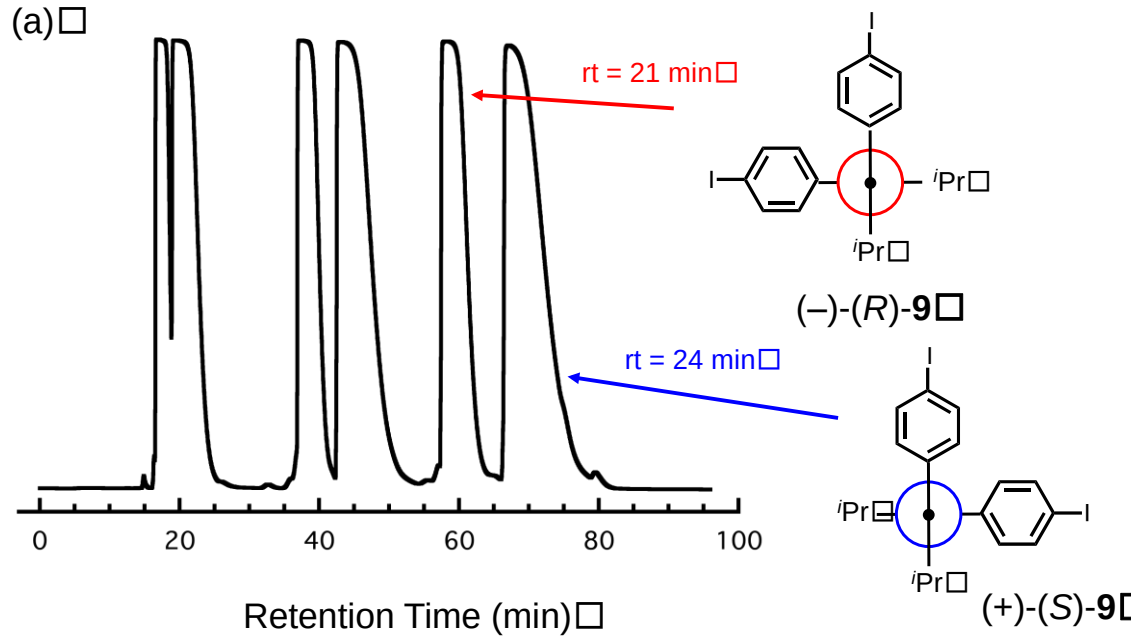
(a)

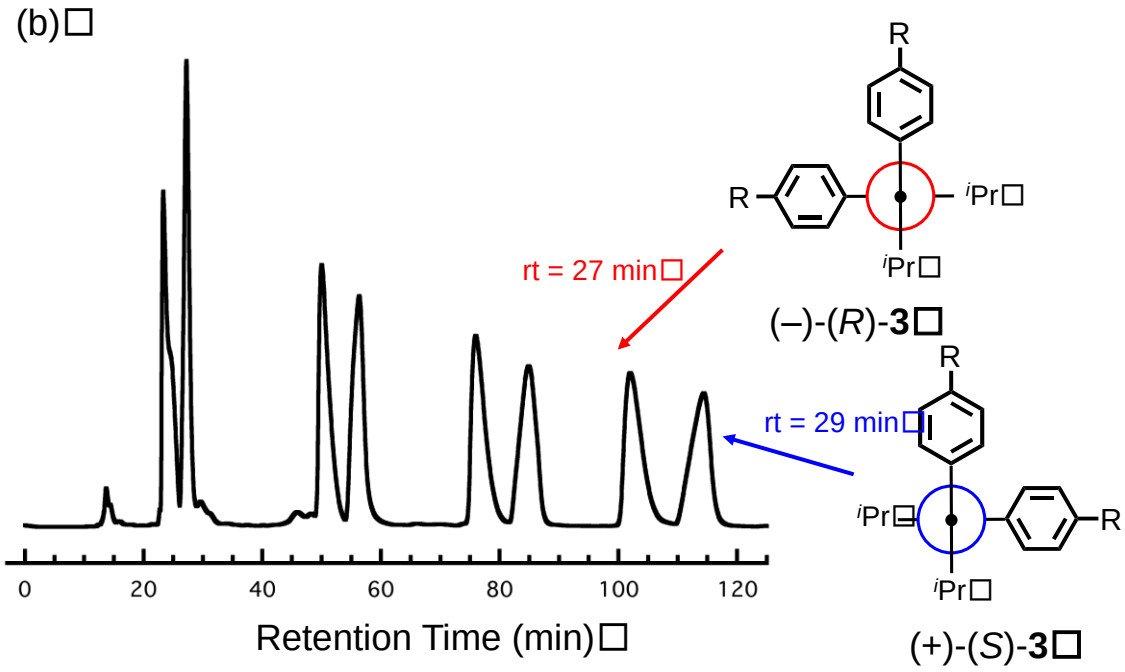


(b)



S10. Figure S8. Chiral HPLC Chart of (a) 9 and (b) 3





S11. DFT Calculations of 9 and 3

(a) DFT calculation of (*R*)-**9**

The geometry optimization was performed by DFT calculation with B3LYP/6-31G(d,p) (for C and H) and LANL2DZ (for I) basis sets. The optimized structure was confirmed by further frequency calculations. The geometry having the lowest energy was treated further TD-B3LYP calculation.

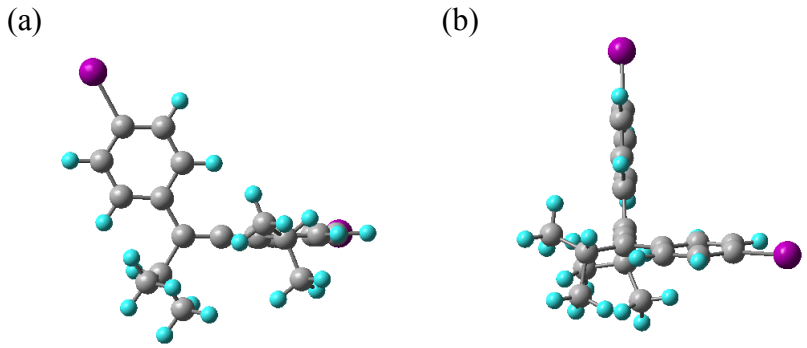


Figure S10. Optimized structure of (*R*)-**9**. (a) Top View (b) side view.

Table S1. Molecular coordinate of optimized structure of (*R*)-**9**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	1.966285
2	6	0	-0.333544	1.276477	1.952512
3	6	0	0.354735	2.227021	1.024030
4	6	0	0.000000	3.583765	0.946682
5	1	0	-0.788602	3.984553	1.572699
6	6	0	0.642901	4.459738	0.068207
7	1	0	0.345146	5.501810	0.034122
8	6	0	1.658903	3.982320	-0.752676
9	6	0	2.034758	2.638913	-0.704588
10	1	0	2.824023	2.261092	-1.344626
11	6	0	1.385737	1.780362	0.175917
12	1	0	1.679067	0.735693	0.204972
13	6	0	0.333544	-1.276477	1.952512
14	6	0	-0.354735	-2.227021	1.024030
15	6	0	0.000000	-3.583765	0.946682
16	1	0	0.788602	-3.984553	1.572699
17	6	0	-0.642901	-4.459738	0.068207
18	1	0	-0.345146	-5.501810	0.034122

19	6	0	-1.658903	-3.982320	-0.752676
20	6	0	-2.034758	-2.638913	-0.704588
21	1	0	-2.824023	-2.261092	-1.344626
22	6	0	-1.385737	-1.780362	0.175917
23	1	0	-1.679067	-0.735693	0.204972
24	53	0	2.658362	5.314920	-2.101764
25	53	0	-2.658362	-5.314920	-2.101764
26	6	0	1.411537	-1.804497	2.911444
27	1	0	2.018859	-2.524190	2.347265
28	6	0	-1.411537	1.804497	2.911444
29	1	0	-2.018859	2.524190	2.347265
30	6	0	-0.769938	2.546742	4.102411
31	1	0	-1.540740	3.008340	4.729062
32	1	0	-0.205252	1.844108	4.724806
33	1	0	-0.080850	3.331501	3.778277
34	6	0	-2.362280	0.709493	3.411875
35	1	0	-1.828311	-0.041483	4.002622
36	1	0	-3.138145	1.147108	4.048375
37	1	0	-2.853531	0.192708	2.582202
38	6	0	2.362280	-0.709493	3.411875
39	1	0	1.828311	0.041483	4.002622
40	1	0	3.138145	-1.147108	4.048375
41	1	0	2.853531	-0.192708	2.582202
42	6	0	0.769938	-2.546742	4.102411
43	1	0	1.540740	-3.008340	4.729062
44	1	0	0.205252	-1.844108	4.724806
45	1	0	0.080850	-3.331501	3.778277

Name: (*R*)-**9** (file: iodo)

Method: B3LYP/6-31G(d,p) (for C and H) and LAN2DZ (for I)

Key word: opt freq scf=(direct, tight)

Symmetry: C_2

# of imaginary frequency: 0

Energy: -836.2298235 Hartrees

(b) DFT calculation of (*R*)-**3**

The geometry optimizations were performed by DFT calculation with B3LYP/6-31G(d,p) basis set. We started with two conformations of (*R*)-**3**-A and (*R*)-**3**-B, which have different orientations of TTF moieties. These conformers were obtained from Z-matrix formatted initial structures. The minimum energy of each conformation

was confirmed by frequency calculations. The geometry having the lowest energy (*R*)-**3**-A was treated further TD-B3LYP calculation.

(a) (b)

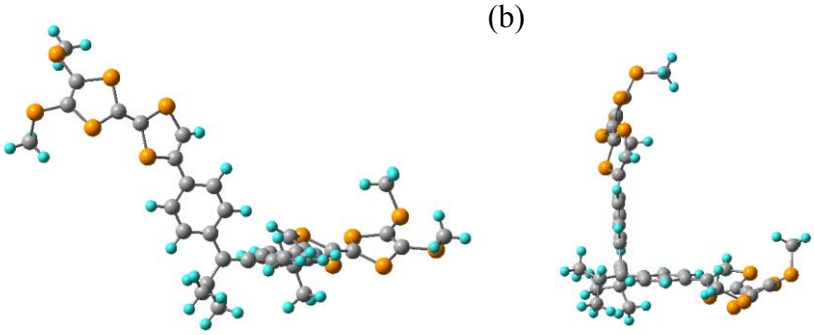


Figure S11. Optimized structure of (*R*)-**3**-A. (a) Top View (b) side view.

Table S2. Molecular coordinate of optimized structure of (*R*)-**3**-A.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000067	3.902933	-0.000003
2	6	0	1.146859	3.897909	-0.652891
3	6	0	2.247715	2.974710	-0.241488
4	6	0	3.461811	2.896373	-0.942808
5	1	0	3.634078	3.516766	-1.814072
6	6	0	4.472817	2.020656	-0.552132
7	1	0	5.387195	1.975676	-1.135755
8	6	0	4.316534	1.180831	0.560026
9	6	0	3.104965	1.264427	1.274368
10	1	0	2.964988	0.657848	2.163731
11	6	0	2.099874	2.131248	0.878367
12	1	0	1.177315	2.171396	1.448355
13	6	0	-1.146728	3.898019	0.652877
14	6	0	-2.247670	2.974920	0.241465
15	6	0	-3.461560	2.896291	0.943107
16	1	0	-3.633591	3.516386	1.814630
17	6	0	-4.472635	2.020653	0.552433
18	1	0	-5.386842	1.975426	1.136304
19	6	0	-4.316624	1.181207	-0.560050
20	6	0	-3.105270	1.265107	-1.274718
21	1	0	-2.965529	0.658838	-2.164329
22	6	0	-2.100112	2.131855	-0.878726

23	1	0	-1.177728	2.172250	-1.448978
24	6	0	-1.369751	4.863805	1.828460
25	1	0	-1.900443	4.302139	2.608184
26	6	0	1.369985	4.863718	-1.828441
27	1	0	1.900860	4.302093	-2.608071
28	6	0	2.257779	6.049970	-1.401669
29	1	0	2.498408	6.680482	-2.264428
30	1	0	1.733003	6.670237	-0.667082
31	1	0	3.196880	5.721156	-0.948831
32	6	0	0.061848	5.367685	-2.450604
33	1	0	-0.520103	5.953928	-1.732682
34	1	0	0.277360	6.009213	-3.311019
35	1	0	-0.567087	4.540391	-2.792170
36	6	0	-0.061567	5.367901	2.450413
37	1	0	0.520165	5.954295	1.732435
38	1	0	-0.277007	6.009326	3.310925
39	1	0	0.567548	4.540665	2.791785
40	6	0	-2.257754	6.049943	1.401813
41	1	0	-2.498286	6.680469	2.264589
42	1	0	-1.733193	6.670232	0.667091
43	1	0	-3.196910	5.720991	0.949184
44	6	0	-5.371133	0.243476	-0.973237
45	6	0	-5.187935	-0.933865	-1.600938
46	6	0	-7.751807	-0.874889	-1.168912
47	1	0	-4.216832	-1.345598	-1.846507
48	6	0	5.370983	0.243025	0.973192
49	6	0	5.187704	-0.934502	1.600520
50	6	0	7.751650	-0.875327	1.168984
51	1	0	4.216567	-1.346342	1.845776
52	16	0	-7.075322	0.694997	-0.672937
53	16	0	-6.587410	-1.896499	-2.052034
54	16	0	6.587126	-1.897213	2.051619
55	16	0	7.075220	0.694697	0.673375
56	6	0	9.028071	-1.242856	0.928382
57	6	0	11.253882	-1.594938	-0.406922
58	6	0	11.036098	-2.772858	0.228722
59	6	0	-9.028187	-1.242507	-0.928225
60	6	0	-11.253840	-1.595046	0.407221
61	6	0	-11.036120	-2.772758	-0.228831
62	16	0	9.737569	-2.785574	1.460383
63	16	0	10.211995	-0.222743	0.077932
64	16	0	-9.737726	-2.785066	-1.460630
65	16	0	-10.212019	-0.222685	-0.077302
66	16	0	-12.576225	-1.259052	1.529008
67	16	0	-12.030595	-4.224150	-0.074117

68	16	0	12.030570	-4.224215	0.073644
69	16	0	12.576444	-1.258575	-1.528394
70	6	0	-10.789614	-5.473982	0.448588
71	1	0	-10.376573	-5.221878	1.426465
72	1	0	-11.334086	-6.418462	0.516424
73	1	0	-9.989450	-5.570794	-0.286172
74	6	0	-11.662610	-0.731019	3.033069
75	1	0	-12.428171	-0.448211	3.759026
76	1	0	-11.069409	-1.554867	3.432829
77	1	0	-11.024401	0.129272	2.827663
78	6	0	10.789692	-5.473748	-0.450034
79	1	0	10.377050	-5.221223	-1.427971
80	1	0	11.334107	-6.418250	-0.518030
81	1	0	9.989238	-5.570773	0.284381
82	6	0	11.663111	-0.729542	-3.032276
83	1	0	12.428831	-0.446649	-3.758032
84	1	0	11.069678	-1.553009	-3.432475
85	1	0	11.025169	0.130865	-2.826529

Name: (*R*)-**3**-A

Method: B3LYP/6-31G(d,p)

Key word: opt freq scf=(direct, tight)

Symmetry: C_2

# of imaginary frequency: 0

Energy: -6209.80702127 Hartrees

(a) (b)

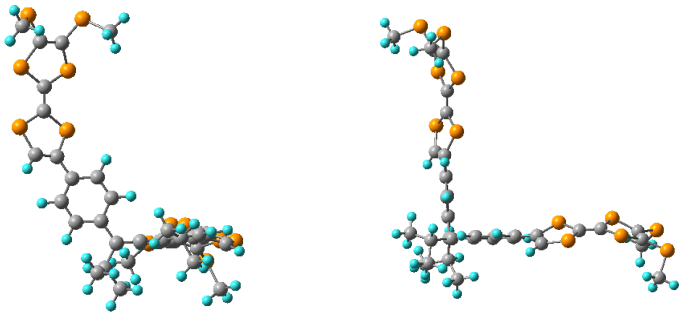


Figure S12. Optimized structure of (*R*)-**3**-B. (a) Top View (b) side view.

Table S3. Molecular coordinate of optimized structure of (*R*)-**3**-B.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	4.654233
2	6	0	1.154784	-0.638245	4.645318

3	6	0	1.374170	-1.793648	3.722494
4	6	0	2.619858	-2.437200	3.612465
5	1	0	3.464809	-2.101754	4.201937
6	6	0	2.814065	-3.499040	2.734735
7	1	0	3.800598	-3.944350	2.651722
8	6	0	1.766766	-3.981932	1.934602
9	6	0	0.520987	-3.334445	2.032192
10	1	0	-0.314502	-3.684098	1.433408
11	6	0	0.333911	-2.270972	2.903253
12	1	0	-0.639009	-1.793214	2.955380
13	6	0	-1.154784	0.638245	4.645318
14	6	0	-1.374170	1.793648	3.722494
15	6	0	-2.619858	2.437200	3.612465
16	1	0	-3.464809	2.101754	4.201937
17	6	0	-2.814065	3.499040	2.734735
18	1	0	-3.800598	3.944350	2.651722
19	6	0	-1.766766	3.981932	1.934602
20	6	0	-0.520987	3.334445	2.032192
21	1	0	0.314502	3.684098	1.433408
22	6	0	-0.333911	2.270972	2.903253
23	1	0	0.639009	1.793214	2.955380
24	6	0	-2.278259	0.217179	5.606917
25	1	0	-3.214675	0.238712	5.034057
26	6	0	2.278259	-0.217179	5.606917
27	1	0	3.214675	-0.238712	5.034057
28	6	0	2.406570	-1.217909	6.772750
29	1	0	3.271125	-0.970337	7.398166
30	1	0	1.512583	-1.181269	7.404660
31	1	0	2.523933	-2.246877	6.422833
32	6	0	2.112719	1.210979	6.140767
33	1	0	1.200290	1.310201	6.737078
34	1	0	2.961377	1.472740	6.780777
35	1	0	2.060580	1.941772	5.328588
36	6	0	-2.112719	-1.210979	6.140767
37	1	0	-1.200290	-1.310201	6.737078
38	1	0	-2.961377	-1.472740	6.780777
39	1	0	-2.060580	-1.941772	5.328588
40	6	0	-2.406570	1.217909	6.772750
41	1	0	-3.271125	0.970337	7.398166
42	1	0	-1.512583	1.181269	7.404660
43	1	0	-2.523933	2.246877	6.422833
44	6	0	-1.973477	5.124038	1.031270
45	6	0	-2.825621	6.148020	1.227629
46	6	0	-1.583863	6.808703	-0.960420
47	1	0	-3.440761	6.263476	2.111462

48	6	0	1.973477	-5.124038	1.031270
49	6	0	2.825621	-6.148020	1.227629
50	6	0	1.583863	-6.808703	-0.960420
51	1	0	3.440761	-6.263476	2.111462
52	16	0	-1.059373	5.169743	-0.504795
53	16	0	-2.962685	7.401245	0.002997
54	16	0	2.962685	-7.401245	0.002997
55	16	0	1.059373	-5.169743	-0.504795
56	6	0	1.015953	-7.520070	-1.957172
57	6	0	-0.873475	-8.571703	-3.435574
58	6	0	0.000000	-9.584246	-3.210432
59	6	0	-1.015953	7.520070	-1.957172
60	6	0	0.873475	8.571703	-3.435574
61	6	0	0.000000	9.584246	-3.210432
62	16	0	1.562721	-9.136652	-2.461749
63	16	0	-0.338050	-6.933815	-2.951552
64	16	0	-1.562721	9.136652	-2.461749
65	16	0	0.338050	6.933815	-2.951552
66	16	0	2.399392	8.704883	-4.314987
67	16	0	0.199725	11.253818	-3.750992
68	16	0	-0.199725	-11.253818	-3.750992
69	16	0	-2.399392	-8.704883	-4.314987
70	6	0	0.052394	12.179170	-2.170784
71	1	0	0.868340	11.920274	-1.494299
72	1	0	0.125218	13.235059	-2.440891
73	1	0	-0.909334	11.995254	-1.690452
74	6	0	3.603324	8.106826	-3.062473
75	1	0	4.574476	8.108361	-3.562405
76	1	0	3.634633	8.781253	-2.205384
77	1	0	3.366379	7.093061	-2.737299
78	6	0	-0.052394	-12.179170	-2.170784
79	1	0	-0.868340	-11.920274	-1.494299
80	1	0	-0.125218	-13.235059	-2.440891
81	1	0	0.909334	-11.995254	-1.690452
82	6	0	-3.603324	-8.106826	-3.062473
83	1	0	-4.574476	-8.108361	-3.562405
84	1	0	-3.634633	-8.781253	-2.205384

85	1	0	-3.366379	-7.093061	-2.737299

Name: (*R*)-**3**-B

Method: B3LYP/6-31G(d,p)

Key word: opt freq scf=(direct, tight)

Symmetry: C_2

# of imaginary frequency: 0

Energy: -6209.80655334 Hartrees

S12. TD-DFT Calculations and MO diagram of 9 and 3

(a) Compound **9**

Table S4. Selected electronic transition for (*R*)-**9**

excited state	energy	oscillator strengths	Rotational Strength in cgs (10^{-40}esu^{2}cm^2)	Nature	
S_1	278 nm 4.459 eV	1.0388	-394.472	80 ->82 81 ->83	0.47828 0.49995
S_2	264 nm 4.704 eV	0.0877	174.519	80 ->83 81 ->82	0.38091 0.37065
S_3	253 nm 4.907 eV	0.1599	133.333	80->83 80->85	-0.30825 -0.30371

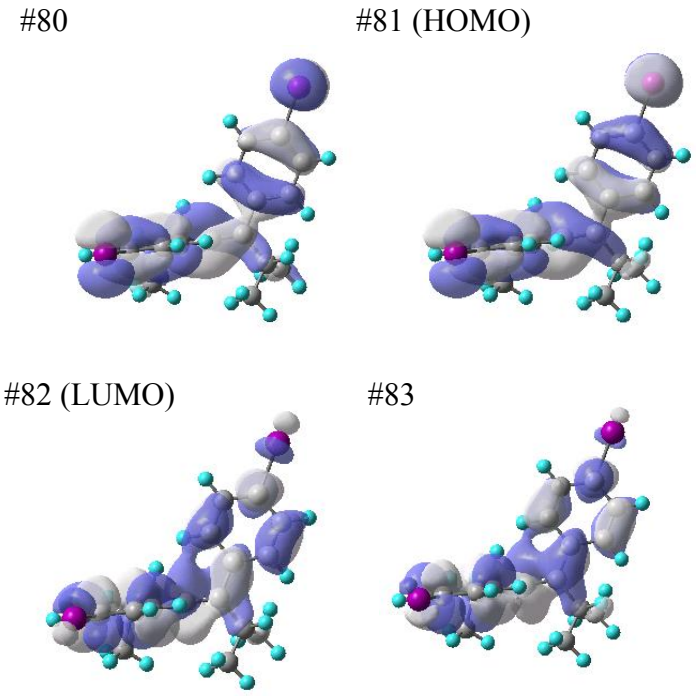


Figure S13. MO diagram of (*R*)-**9**.

(b) Compound (*R*)-**3**-A

Table S5. Selected electronic transition for (*R*)-**3**

excited state	energy	oscillator strengths	Rotational Strength in cgs (10^{-40}esu^{2}cm^2)	Nature	
S_1	452 nm 2.745 eV	0.0878	-36.3764	224 ->226 225 ->227	0.40915 0.3678
S_2	426 nm 2.909 eV	0.1832	-75.8371	224 ->229 225 ->228	0.39293 0.39384
S_3	372 nm 3.331 eV	0.0415	109.017	224 ->231 225 ->230	0.48046 0.48110
S_4	330 nm 3.753 eV	0.4030	138.119	224 ->233 225 ->232	0.39970 0.44770
S_5	329 nm 3.769 eV	0.0428	-123.679	224 ->232 225 ->233	0.47300 0.41671
S_6	317 nm 3.915 eV	0.6504	238.909	222 ->227	0.52053

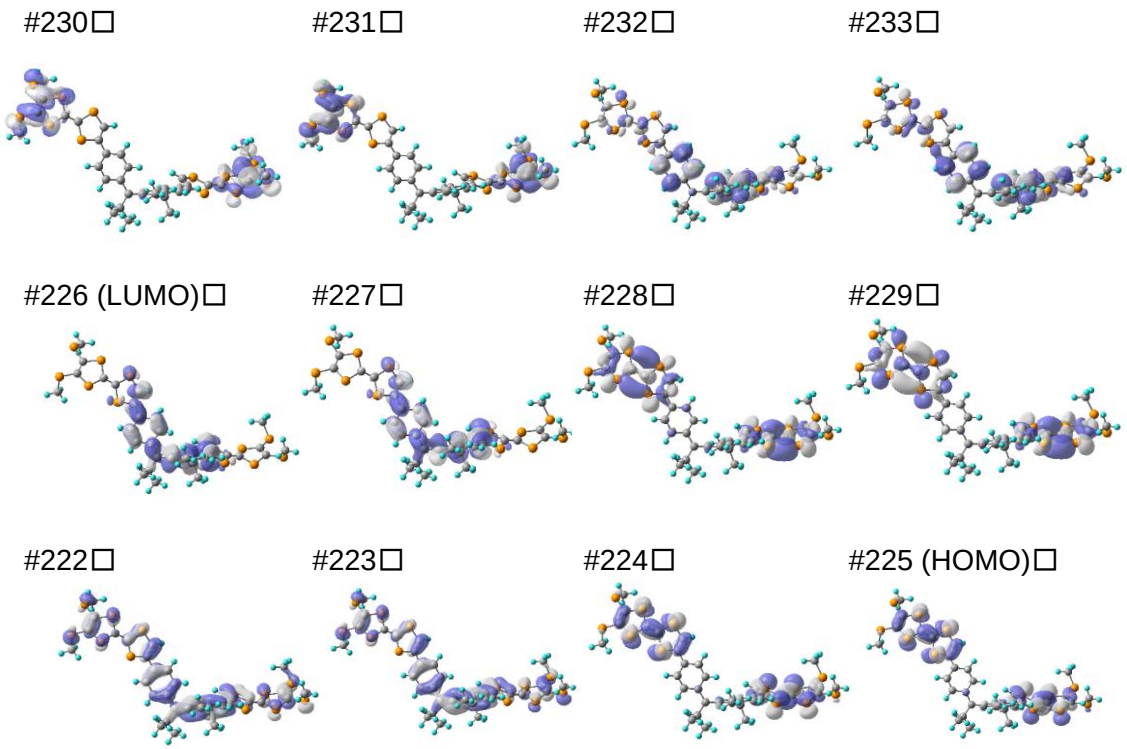


Figure S14. MO diagram of (*R*)-**3**.

S13. ECD Spectra of Cationic Species of (*R*)-3 and (*R*)-PTDTA

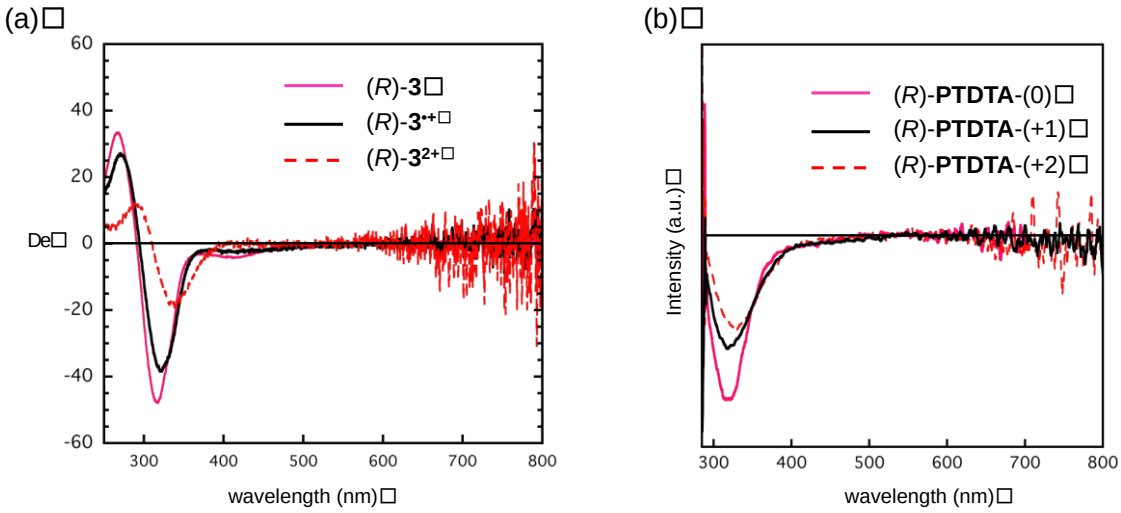


Figure S15. ECD Spectra of (a) (*R*)-**3** and its cation radicals, and (b) (*R*)-**PTDTA** and its cationic states.

S14. Examination of the Photoracemization

Racemization behavior was examined under daylight in CH_2Cl_2 solution. The photoracemization was evaluated from the decrease of the ellipticity at 340 nm (for (*R*)-**1**, 320 nm (for (*R*)-**3**), and 250 nm (for (*R*)-**PTDTA**). Data of (*R*)-**1** was obtained from ref. 10. Consequently, the ellipticity of (*R*)-**3** and (*R*)-**PTDTA** almost did not change under ambient light.

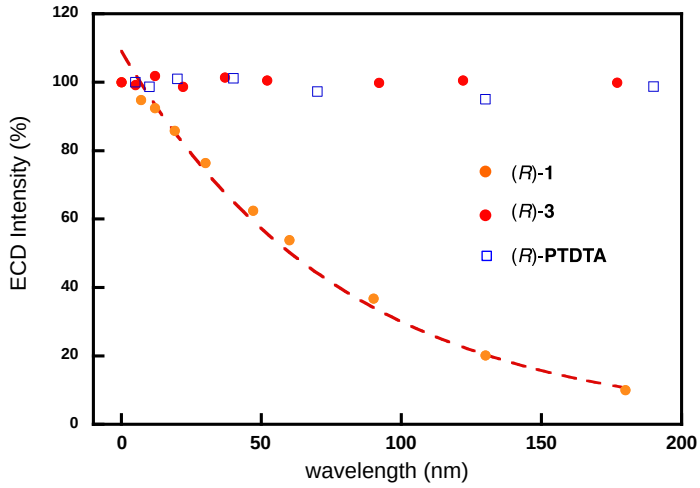


Figure S16. Relative ellipticity of (*R*)-**1**, (*R*)-**3**, and (*R*)- **PTDTA** in ECD spectra (in CH_2Cl_2, 25°C).

S15. References

S1. M. Hatano, S. Suzuki, K. Ishihara, *Synlett*, **2009**, 321.