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Synthesis and Chiroptical Properties of Stereogenic Cyclic Dimers Based on 2,2'-Biselenophene and [2.2]Paracyclophane

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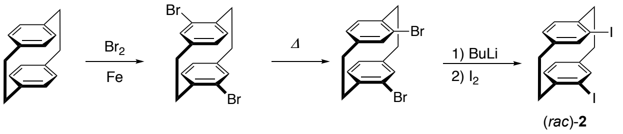
Supporting Information

S1. General

^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE-II 600 (600 MHz for ^1H NMR, 150 MHz for ^{13}C and 114 MHz for ^{77}Se NMR) or Bruker AVANCE-II 400 (400 MHz for ^1H NMR, 100 MHz for ^{13}C and 76 MHz for ^{77}Se NMR) instruments. Spectra are reported in δ, referenced to internal tetramethylsilane (Me_4Si). Mass spectra and High-resolution mass spectra were recorded on Thermo Scientific, Exactive Plus Orbitrap Mass Spectrometer for electrospray ionization (ESI). Melting points were determined with Yanaco melting point apparatus. IR spectra were recorded on JASCO FT/IR-610 spectrometer. UV-Vis spectra were recorded on JASCO V-560 spectrometer. Circular dichroism (CD) spectra were recorded on JASCO J-720 spectrometer. Optical rotation measurements were recorded on JASCO P-1030 spectrometer. Recycling Preparative HPLC was carried out using HPLCLC-9204 instrument by Japan Analytical Industry (JAI) equipped with a CHIRALPAK®IA (φ = 30 mm, l = 200 mm) and JASCO OR-2090 Plus.

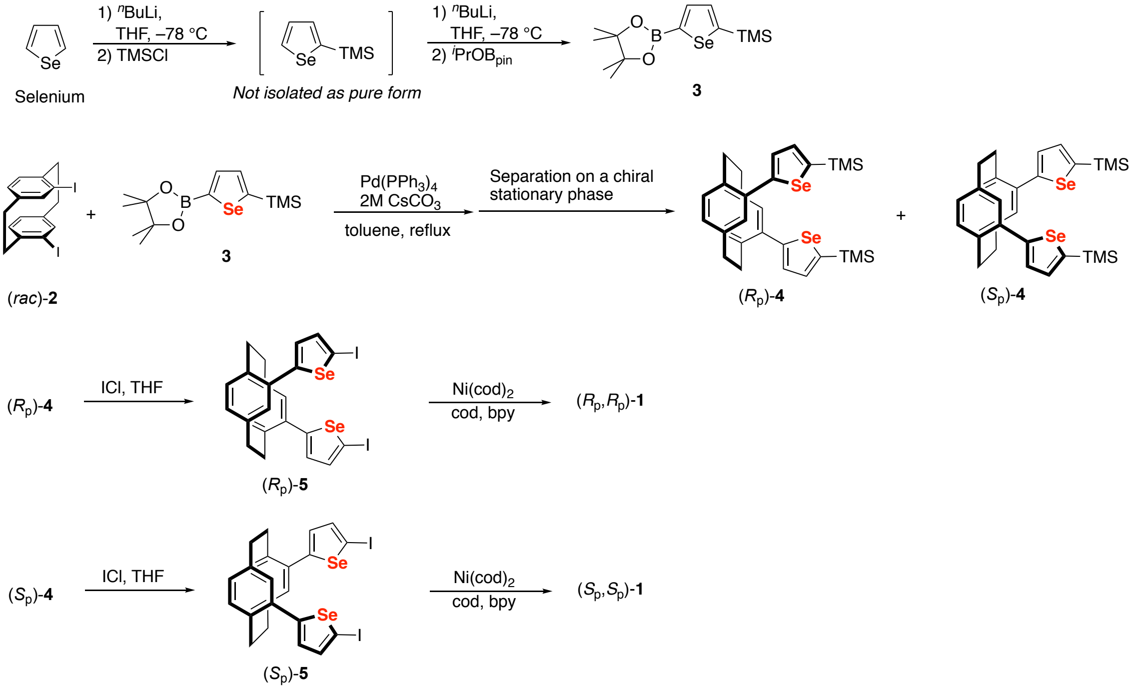
Starting racemic 4,12-diiodo[2.2]paracyclophane (**2**) was prepared according to literature procedure as shown in Scheme S1.[1] [2.2]paracyclophane was purchased from Strem Chemicals, Inc. and stored under Ar at 4 °C. Selenophene (CAS RN. 288-05-1) and 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (CAS RN. 61676-62-8) were purchased from Tokyo Chemical Industry Co. Ltd, (TCI). Other chemicals were purchased from FUJIFILM Wako Pure Chemical Corporation. Column chromatography was carried out using Kanto Chemical silica gel 60N, 60-210mm meshes. All solvents were dried by conventional procedures and distilled before use.



Scheme S1. *Synthesis of racemic **2***

S2. Preparation of 1

Compounds **1** in (R_p) and (S_p) configuration were prepared as shown in Scheme S2. Optical resolution was carried out in compound **4**, and thereafter conversions were performed separately.



Scheme S2. *Synthetic route to compounds **1** in (R_p) and (S_p) configuration*

Synthesis of (*rac*)-3

To a solution of selenophene (655 mg, 5.00 mmol) in THF (5.0 mL) ⁿBuLi (3.1 mL, 5.0 mmol) was added dropwise at –78 °C under Ar atmosphere. After 30 min stirring at the same temperature, a solution of trimethylsilyl chloride (TMSCl) (0.64 mL, 5.1 mmol) was added dropwise. The mixture was stirred for 30 min at –78 °C, and then allowed to warm up rt. Further continuous stirring was carried out at rt for 1h. Then, aqueous NH_4Cl solution was added to the mixture. The products were extracted by Et_2O. The combined organic solution was washed with saturated brine, and dried over $MgSO_4$. The solvent was carefully removed under reduced pressure due to highly volatile properties of the product. Residual oil was purified on silica gel column chromatography with the elution of hexane. The resultant colorless oil (1.02 g) contains almost pure form of 2-trimethylsiliyselenophene (> 99%). However, due to the extreme high volatility under ambient conditions, we carried out next reaction without further treatment. Data for 2-trimethylsiliylselenophene: MS (ESI-orbitrap) *m/z* = 204 (M^+); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 5.4 and 1.2 Hz, ^{1}H, together with ^{77}Se-^{1}H satellite band: *J* = 36 Hz), 7.19 (dd, *J* = 3.6 and 1.2 Hz, 1H), 7.08 (dd, *J* = 5.4 and 3.6 Hz, 2H), –0.3 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 136.3, 135.3, 130.9, 0.40; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 672.

To a solution of above mixture (1.02 g) in THF (10 mL) ^{n}BuLi (3.1 mL, 5.0 mmol) was added dropwise carefully at –78 °C under Ar atmosphere. After 1h stirring at the same temperature, a solution of 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (B_{pin}-O^{i}Pr) (1.2 mL, 5.8 mmol) was added dropwise. The mixture was stirred for 2h at –78 °C, and then allowed to warm up rt. Further continuous stirring was carried out at rt for 14h. Then, aqueous NH_4Cl solution was added to the mixture. The products were extracted by EtOAc. The combined organic solution was washed with saturated brine, and dried over $MgSO_4$. After the removal of the solvent under reduced pressure, the residue was purified recrystallization from MeOH at –20 °C to give colorless solid of **3** (742 mg, 45 % from selenophene). The molecular structure was also confirmed by X-ray crystallographic analysis. Data for **3**: Mp. 86.1-86.8 °C; HRMS (ESI-orbitrap): *m/z* calcd for $C_{13}H_{23}SeBSiO_2$ [M+H$^+$]: 331.07984, Found: 331.07980; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 3.6 Hz, 1H), 7.63 (d, *J* = 3.6 Hz, 1H), 1.34 (s, 12H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 140.5, 137.5, 84.1, 24.8, 0.34; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 742.8; IR (KBr) 2977, 2956, 1528, 1447, 1373, 1340, 1250, 1142, 1067 cm^{-1}.

Synthesis of (*rac*)-4

A mixture of 4,12-diiodo[2.2]paracyclophane **2** (140 mg, 0.30 mmol), compound **3** (400 mg, 1.22 mmol), $Pd(PPh_3)_4$ (74 mg, 0.064 mmol), and aqueous solution of Cs_2CO_3 (2M, 4.0 mL, 8.0 mmol) in toluene (10 mL) was stirred for 14h at 120 °C under Ar atmosphere. Then, the reaction mixture was filtered off through Celite pad with AcOEt. Resultant solution was washed with saturated brine and dried over $MgSO_4$. After the removal of the solvent under reduced pressure, the residue was purified on silica gel column chromatography with the elution of CH_2Cl_2-hexan solution (v/v = 1:1). Further purification was accomplished by GPC separation to give pale yellow oil of the crude product. From the analysis of NMR spectrum, the crude product contains **4** together with **4'**, whose selenophene rings are connected at 4,5-positions of [2.2]paracyclophane. In our previous report, Suzuki coupling reaction of 4,12-diiodo[2.2]paracyclophane occasionally led to rearranged compound at 4,5 positions.[s2] The farmer Fr.1-**4'** was characterized by ^{1}H, ^{13}C, and ^{77}Se NMR together with MS spectra. The reaction yields were determined by NMR ration to be 81 and 13 %, respectively. The mixture was subject to a recycling HPLC method a recycling HPLC method without further treatment. Thus, separation on a hiral stationary phase (chiralpack IA3) with the elution of $CHCl_3$-hexane (v/v = 1:8) gave Fr.1-**4'**, Fr.2-**4**, and Fr.3-**4** (Figure S1).

The obtained fraction of Fr.2-**4** exhibited large optical specific rotation of $[\alpha]_D^{25}$ = –26.5° (*c* = 5.0 x 10^{-3}) in CH_2Cl_2, while the latter Fr.3-**4** exhibited $[\alpha]_D^{25}$ = +26.0 (*c* = 3.4 x 10^{-3}) in the identical conditions. Fortunately, slow evaporation of Fr.2-(–)-**4** from CH_2Cl_2-MeOH solution gave a single crystal suitable for X-ray analysis, which suggests (S_p) configuration with sufficient flack parameter (Table S1). In summary, the fraction of 1st (–)-**4** 2nd (+)-**4** could be be determined as (S_p)- and (R_p)-

isomer, respectively.

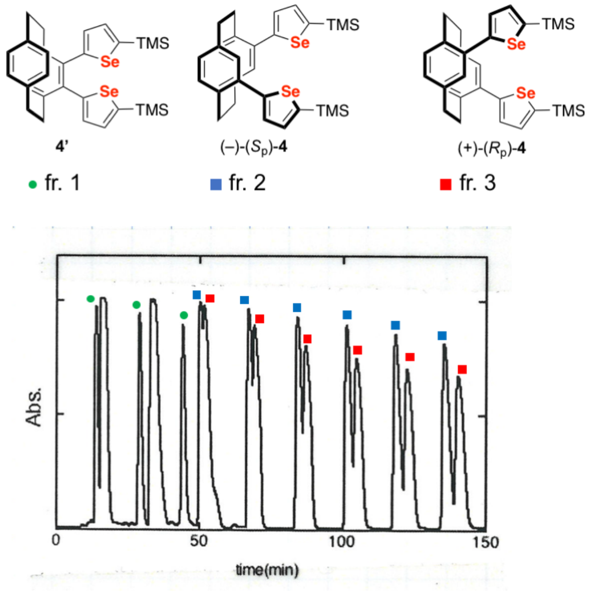


Figure S1. *HPLC chart (CHCl$_3$-hexane 8:1) of crude product.*

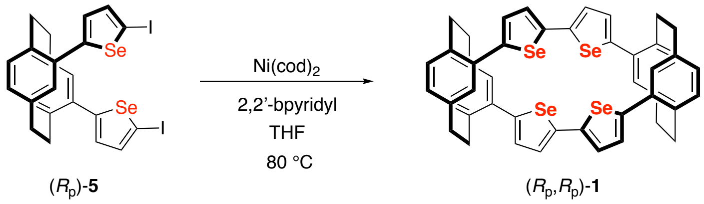
Data for (R_p)-**4**: Mp. 144-145 °C; HRMS (ESI-orbitrap): *m/z* calcd for $C_{30}H_{37}Se_2Si_2$ [M+H$^+$]: 613.07587, Found: 613.07587; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (d, J = 3.6 Hz, 2H), 7.25 (d, J = 3.6 Hz, 2H), 6.84 (d, J = 1.6 Hz, 2H), 6.65 (d, J = 7.8 Hz, 2H), 6.58 (dd, J = 7.8 and 1.6 Hz, 2H), 3.72-3.80 (m, 2H), 3.03-3.11 (m, 2H), 2.92-2.96 (m, 4H), 0.35 (s, 18H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 155.0, 148.7, 139.8, 136.7, 136.5, 136.4, 135.5, 132.2, 130.9, 129.2, 34.8, 33.9, 0.44; ^{77}Se NMR (76 MHz, CDCl$_3$) δ 678.7; $[\alpha]^{D}_{25}$ = +26.0 for (R_p)-**5** (CH_2Cl_2, c = 0.019) and −26.5 for (S_p)-**5** (CH_2Cl_2, c = 0.020); IR (KBr) 3030, 2956, 2926, 2884, 2854, 1587, 1443, 1401, 1247, 1205, 1071 cm^{-1}.

Data for **4**':colorless oil; HRMS (ESI-orbitrap): *m/z* $C_{30}H_{37}Se_2Si_2$ [M+H$^+$]: 613.07587, Found: 613.07581 ; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.29-7.31 (m, 2H), 6.95-6.98 (m, 2H), 6.84 (d, J = 1.8 Hz, 2H), 6.76 (d, J = 1.8 Hz, 2H), 6.52 (s, 2H), 3.19-3.22 (m, 2H), 3.09-3.11 (m, 2H), 3.00-3.05 (m, 2H), 2.93-2.96 (m, 2H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 153.2, 149.5, 139.8, 128.8, 125.6, 135.0, 134.1, 132.7, 131.7, 131.7, 139.4, 35.3, 33.9, 0.39; ^{77}Se NMR (114 MHz, CDCl$_3$) δ 717.7; IR (KBr) 3034, 2954, 2928, 2894, 2854, 1454, 1249, 1203 cm^{-1}.

Synthesis of (R_p)-**5**

To a solution of (R_p)-**4** (77 mg, 0.13 mmol) in THF (5 mL), ICl (0.19 M in THF, 3.0 mL, 0.57 mmol) was added dropwise at –78°C under Ar. After the reaction mixture was stirred for 4h at –78°C, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ and 10% $Na_2S_2O_4$ solution. The products were extracted with AcOEt and the combined organic phase was washed with saturated brine and dried over Na_2SO_4, subsequently. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with the elution of hexane-CH_2Cl_2 (v/v = 1:1) to give yellow solid (R_p)-5 (90 mg, 99%). The other enantiomer (S_p)-**5** was prepared in a similar manner from (S_p)-**4** (y. 99%). Data for (R_p)-**5**: Mp 122-125 °C; HRMS (ESI-orbitrap): *m/z* calcd for $C_{24}H_{19}Se_2I_2$ [M+H$^+$]: 720.79004, Found: 720.79011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 4.0 Hz, 2H), 6.80 (d, *J* = 4.0 Hz, 2H), 6.70 (d, *J* = 1.6 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.59(dd, *J* = 8.0 and 1.6 Hz, 2H), 3.64-3.71 (m, 2H), 3.07-3.14 (m, 2H), 2.83-2.94 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.0, 140.7, 140.1, 136.9, 135.9, 135.6, 132.8, 130.35, 129.2, 75.5, 34.9, 34.0; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 722.6; $[\alpha]^{D}_{25}$ = +65.7 for (R_p)-**5** (CH_2Cl_2, *c* = 0.019) and –66.5 for (S_p)-**5** (CH_2Cl_2, *c* = 0.020); IR (KBr) 2922, 2851, 1585, 1477, 1399 cm^{-1}.

Synthesis of (R_p,R_p)-**1**

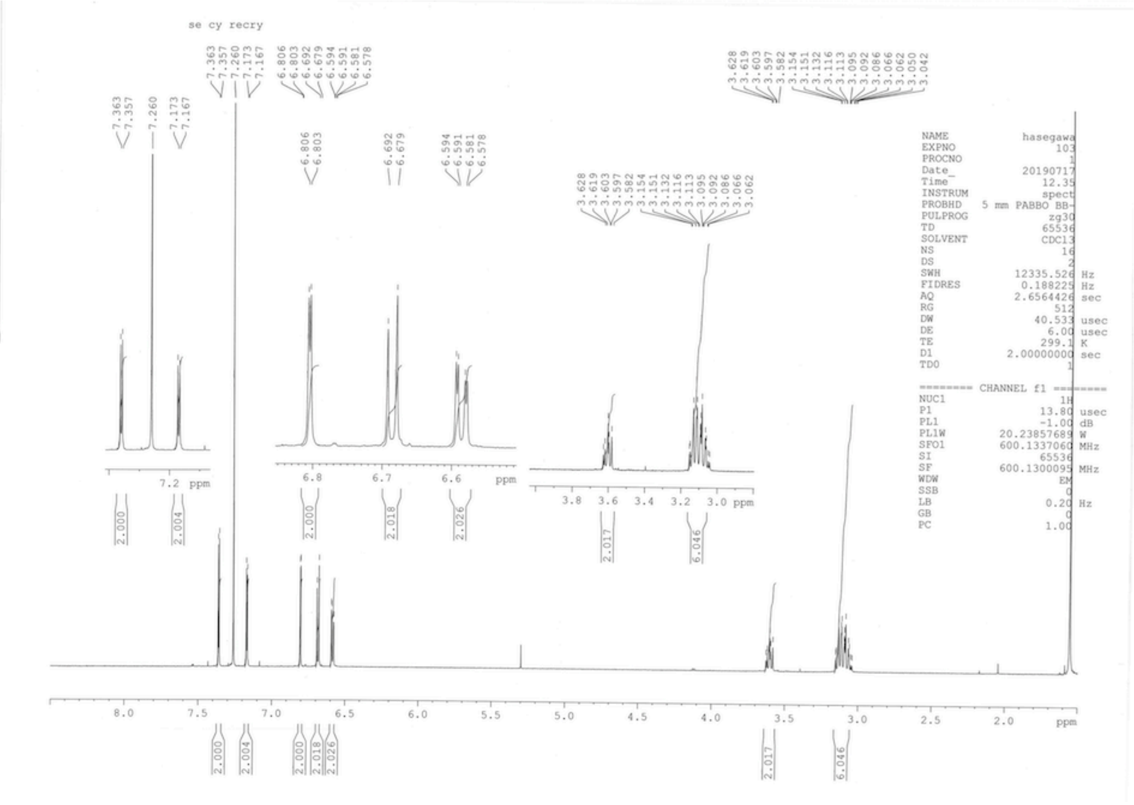


To solution of 2,2'-bipyridyl (78 mg, 0.50 mmol), Ni(cod)$_2$ (138mg, 0.50 mmol), and (R_p)-**5** (91 mg, 0.13 mmol) in THF (2.0 mL) were added under Ar atmosphere. The mixture was stirred for 5 days at 75 ºC. After the reaction was quenched by the addition of 2M HCl, then filtrated through celite pad The resultant filtrate was extracted with $CHCl_3$. The combined organic phase was washed with saturated brine and dried over Na_2SO_4. The resulting solution was evaporated, and then the residue was purified by column chromatography on silica gel with the elution of CS_2hexane-CH_2Cl_2 (v/v = 1:2:1). Further purification on GPC with the elution of $CHCl_3$ gave cyclic dimer (R_p,R_p)-**1** (12 mg, 20%) together with insoluble byproducts. The other enantiomer of (S_p,S_p)-**1** was prepared from (S_p)-**5** in a similar manner (y. 18 %). Data for (R_p,R_p)/(S_p,S_p)-**1**: Mp 314 °C (decomp.); HRMS (ESI-orbitrap): *m/z* calcd for $C_{48}H_3Se_4$ [M+H$^+$]: 930.95585, Found: 930.95593; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 3.6 Hz, 4H), 7.17 (d, *J* = 3.6 Hz, 4H), 6.80 (d, *J* = 1.8 Hz, 4H), 6.68 (d, *J* = 8.4 Hz, 4H), 6.58 (dd, *J* = 8.4 and 1.8 Hz, 4H), 3.58-3.63 (m, 4H), 3.04-3.15 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.1, 145.2, 139.5, 136.4, 136.1, 135.0, 132.9, 132.0, 128.8, 126.0, 34.5, 33.4; ^{77}Se NMR (114 Hz, $CDCl_3$) δ 631.4; $[\alpha]^{D}_{25}$ = +563 for (R_p,R_p)-**1** (CH_2Cl_2, $c = 0.8 \times 10^{-3}$) and –561 for (S_p,S_p)-**1** (CH_2Cl_2, *c*

$= 0.8 \times 10^{-3}$); IR (KBr) 2925, 2855, 1582, 1462, 1399 cm^{-1}

S3. Figure S2. ^{1}H, ^{13}C and ^{77}Se NMR Charts of (R_p,R_p)-1

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



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PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          12335.526 Hz
FIDRES        0.188225 Hz
AQ           2.6564426 sec
RG                 512
DW              40.533 usec
DE                6.00 usec
TE               299.1 K
D1          2.00000000 sec
TD0                  1

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PL1              -1.00 dB
PL1W       20.23857689 W
SFO1       600.1337060 MHz
SI               65536
SF         600.1300095 MHz
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SSB                  0
LB                0.20 Hz
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PC                1.00
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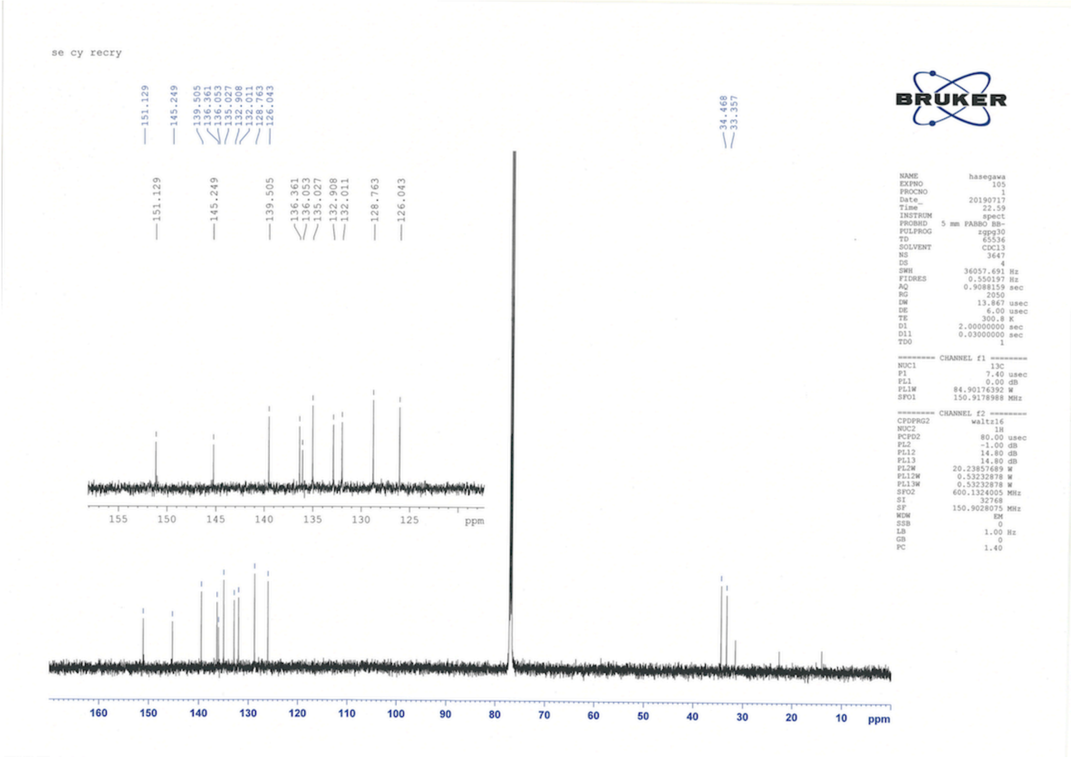
(b) ^{13}C NMR (150 MHz, $CDCl_3$)



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DS                   4
SWH          36057.691 Hz
FIDRES        0.550197 Hz
AQ           0.9088159 sec
RG                2050
DW              13.867 usec
DE                6.00 usec
TE               300.8 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                7.40 usec
PL1               0.00 dB
PL1W       84.90176392 W
SFO1       150.9178988 MHz

======== CHANNEL f2 ========
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NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             14.80 dB
PL13             14.80 dB
PL2W       20.23857689 W
PL12W       0.53232878 W
PL13W       0.53232878 W
SFO2       600.1324005 MHz
SI               32768
SF         150.9028075 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
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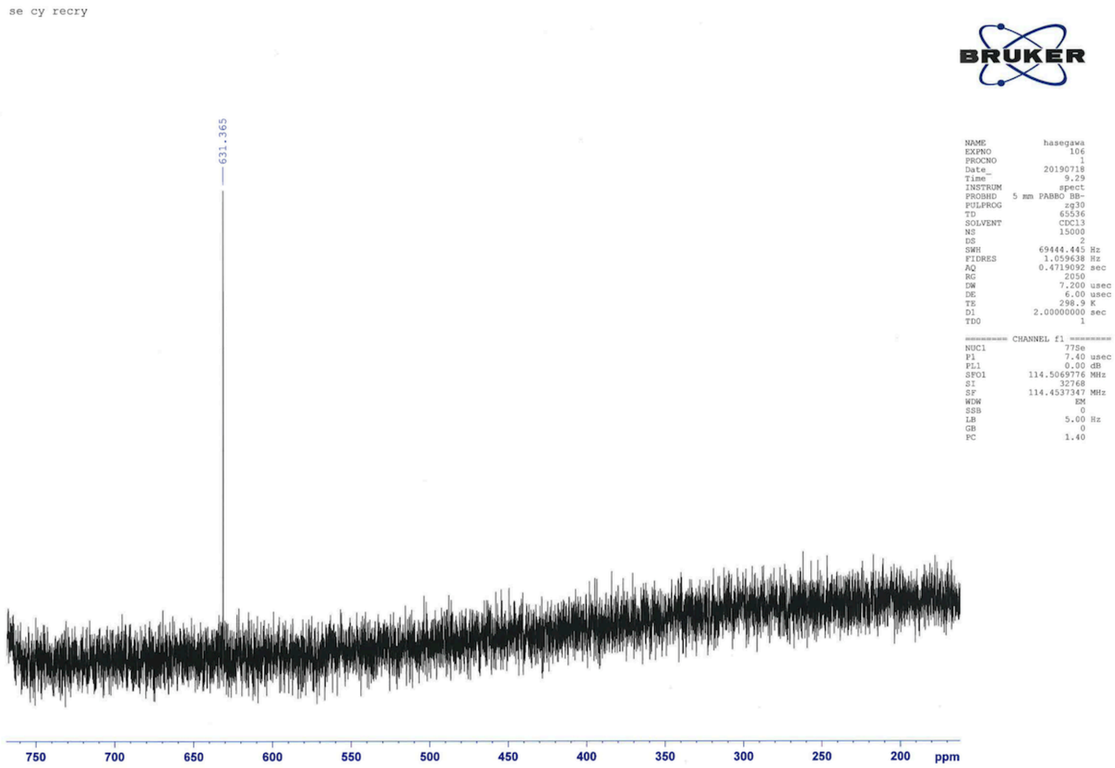
(c) ^{77}Se NMR (114 Hz, $CDCl_3$)



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FIDRES          1.059638 Hz
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RG                  2050
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DE                  6.00 usec
TE                 298.9 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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P1                  7.40 usec
PL1                 0.00 dB
SFO1         114.5069776 MHz
SI                 32768
SF           114.4537347 MHz
WDW                   EM
SSB                    0
LB                  5.00 Hz
GB                     0
PC                  1.40
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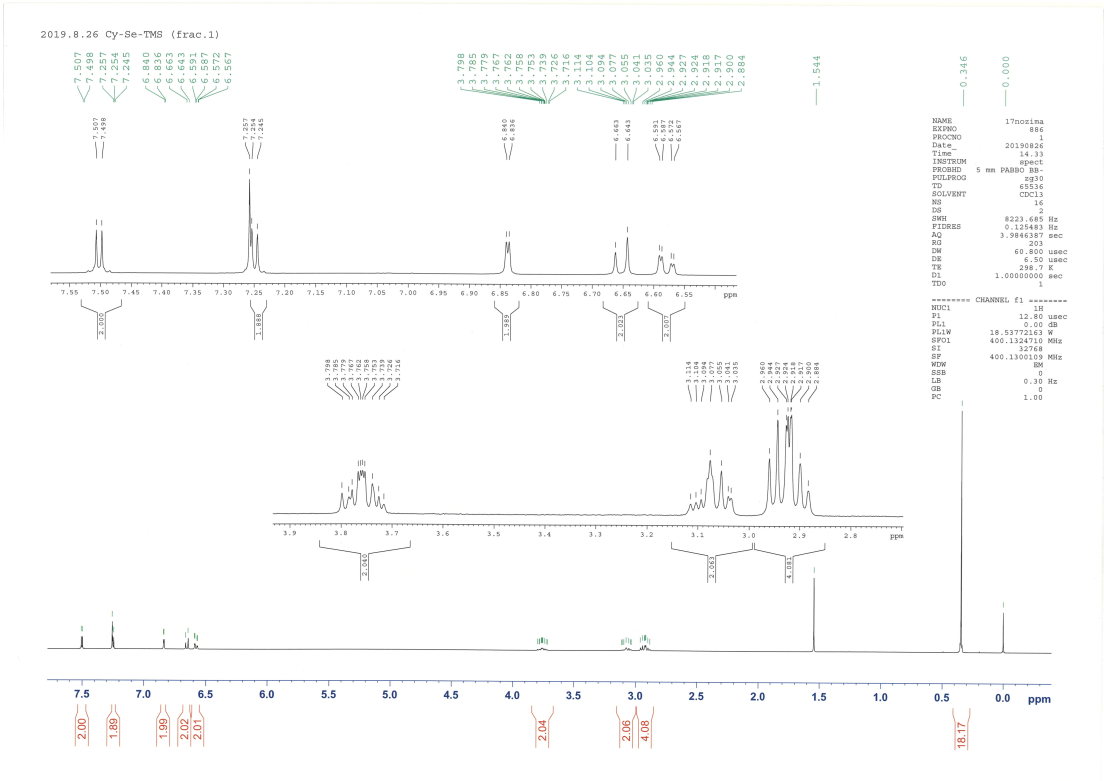
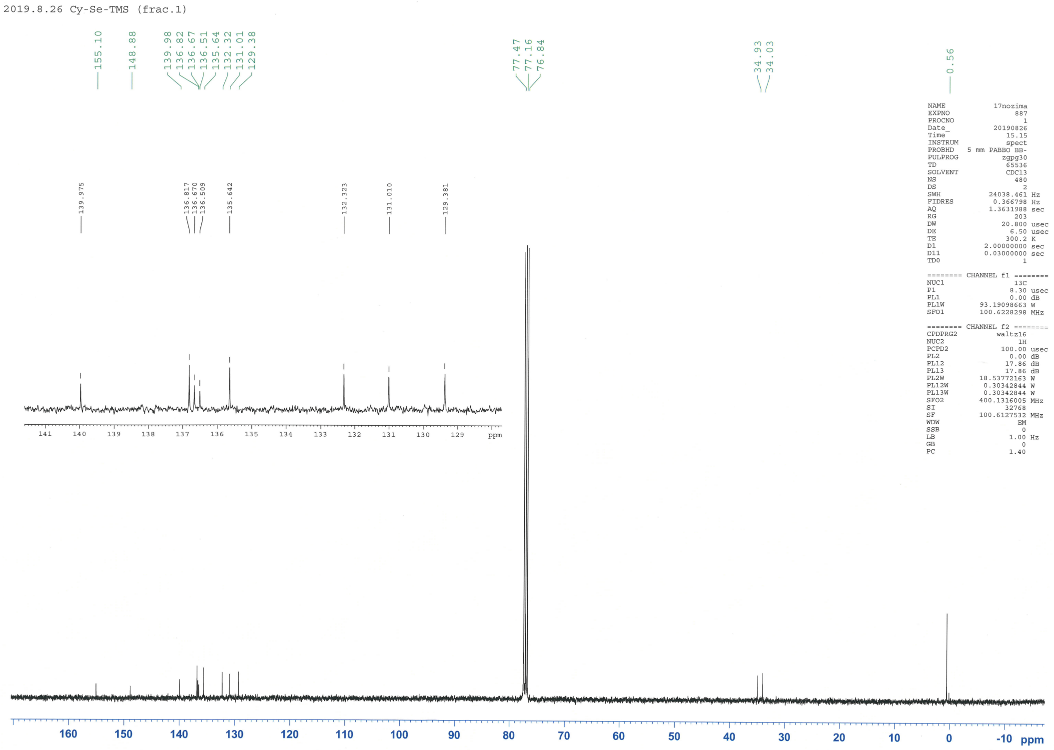
S4. Figure S3, 4 and 5. ^{1}H, ^{13}C and ^{77}Se NMR Charts of 4, 4’ and 5

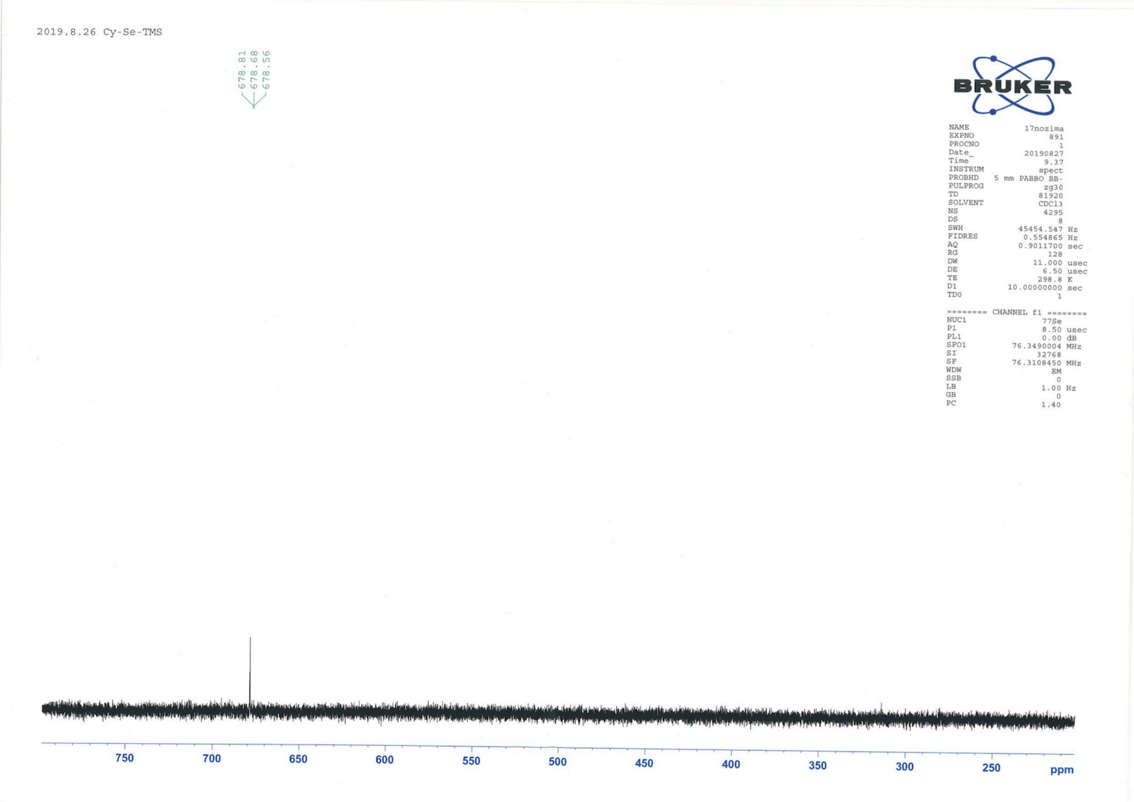
(a) ^{1}H NMR of (R_p,R_p)-**4**



(b)^{13}C NMR of (R_p,R_p)-**4**



(c)^{77}Se NMR of (R_{p},R_{p})-**4**



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FIDRES            0.554865 Hz
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RG                     128
DW                  11.000 usec
DE                    6.50 usec
TE                   298.8 K
D1             10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  77Se
P1                    8.50 usec
PL1                   0.00 dB
SFO1            76.3490004 MHz
SI                   32768
SF              76.3108450 MHz
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SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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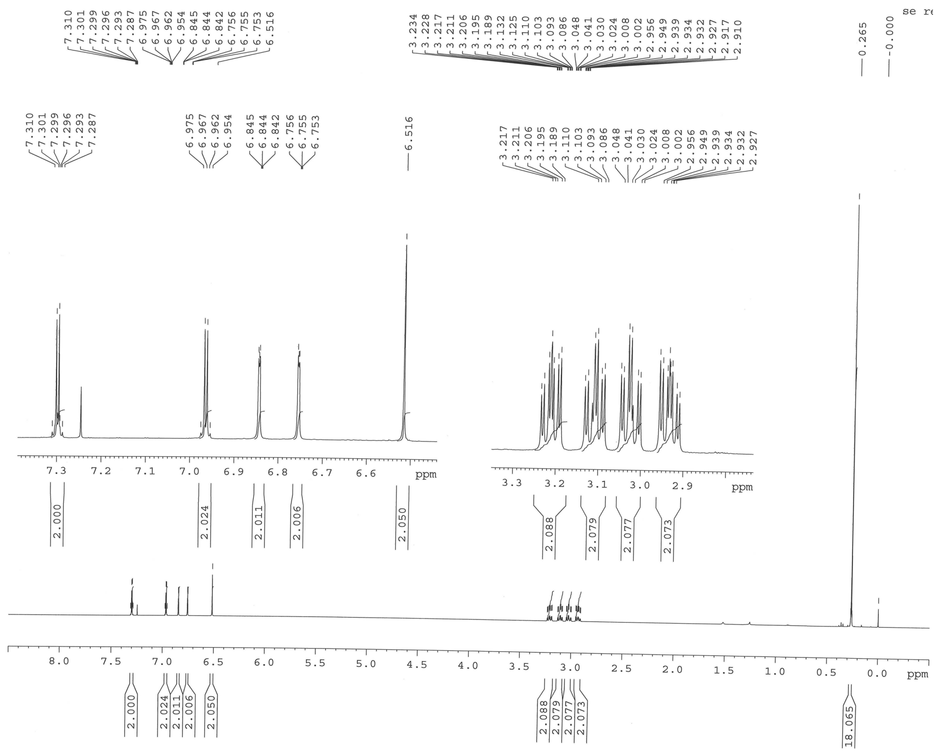
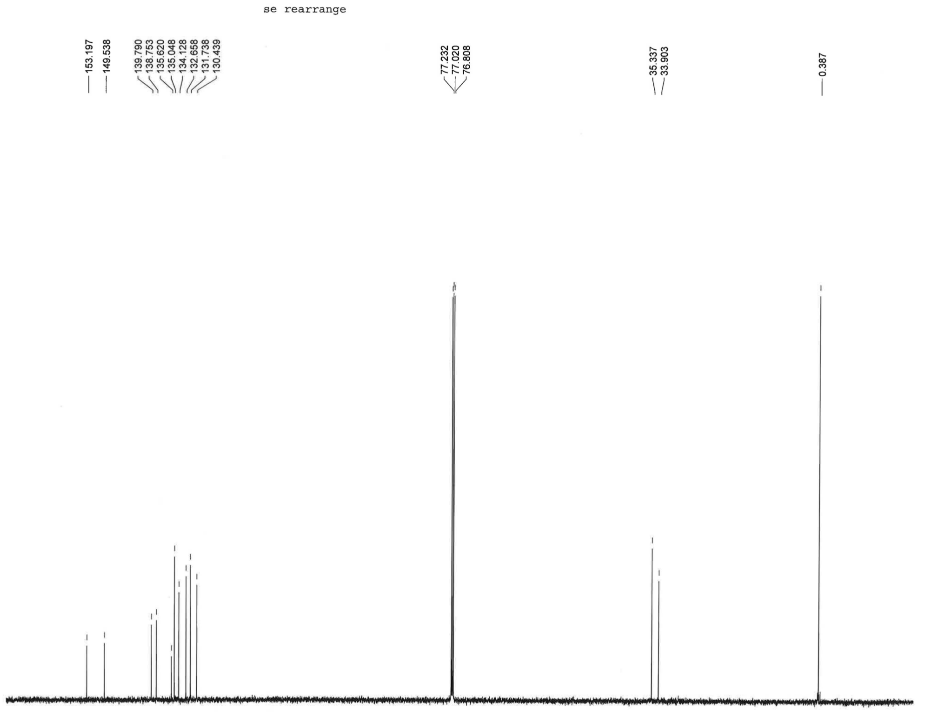
Figure S4.

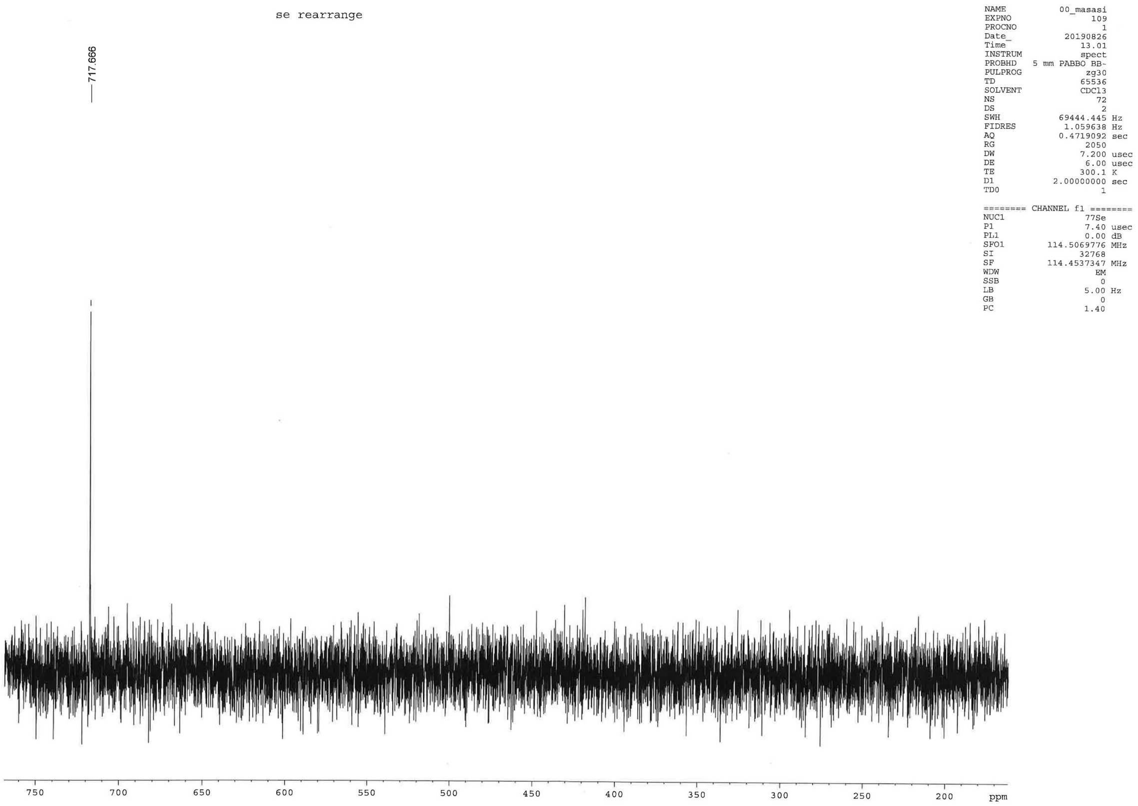
(a) ^{1}H NMR of **4’**



(b)^{13}C NMR of **4’**



(c)^{77}Se NMR of **4’**



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FIDRES           1.059638 Hz
AQ              0.4719092 sec
RG                   2050
DW                  7.200 usec
DE                   6.00 usec
TE                  300.1 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                 77Se
P1                   7.40 usec
PL1                  0.00 dB
SFO1          114.5069776 MHz
SI                  32768
SF            114.4537347 MHz
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SSB                     0
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GB                      0
PC                   1.40
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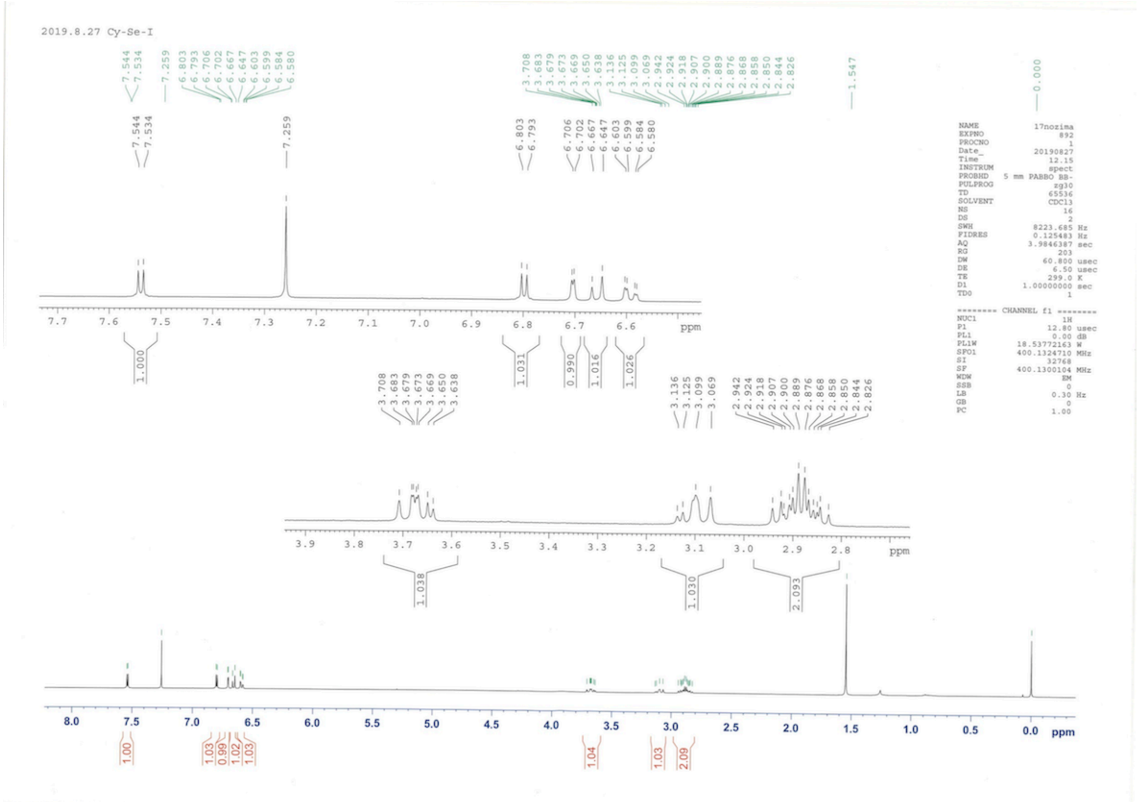
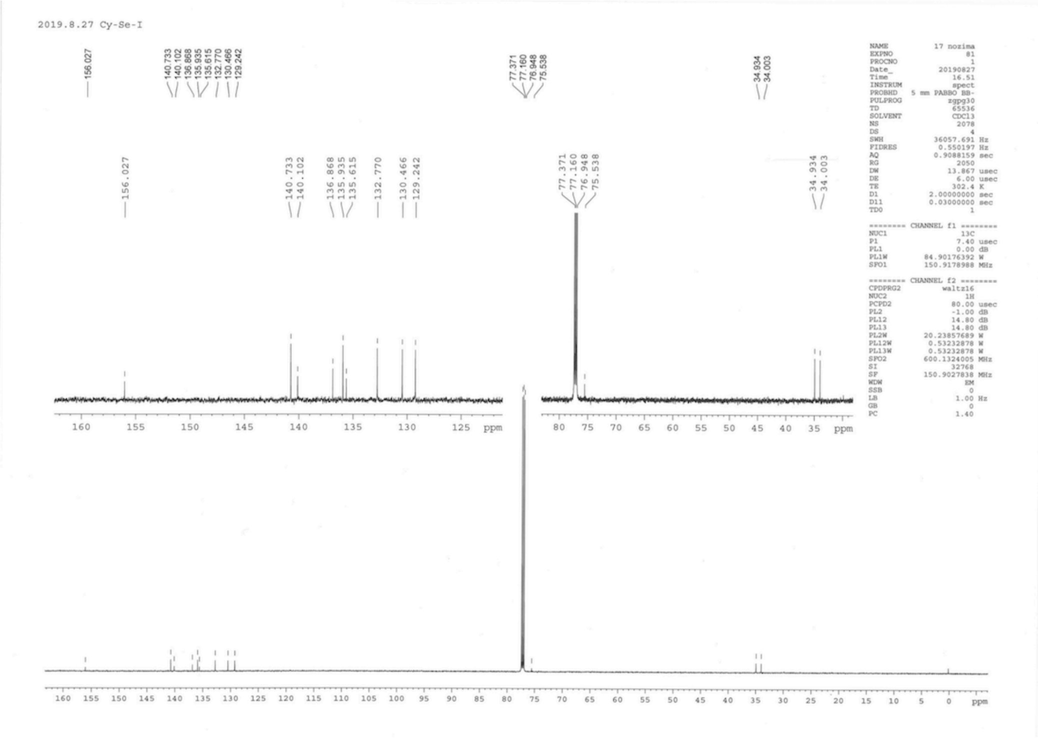
Figure S5.

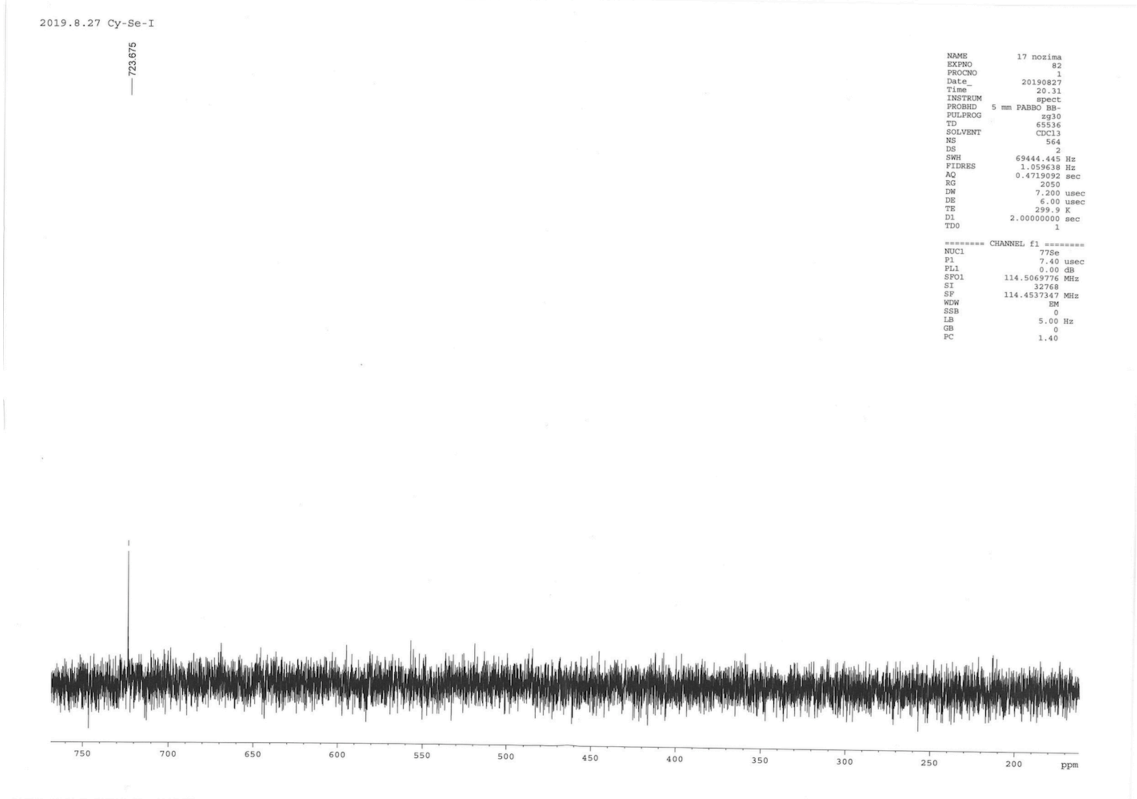
(a) ^{1}H NMR of **5**



(b) ^{13}C NMR of **5**



(c) ^{77}Se NMR of **5**



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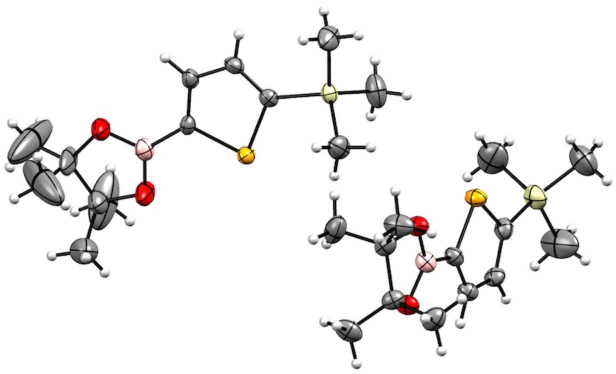
FIDRES         1.059638 Hz
AQ            0.4719092 sec
RG                 2050
DW                7.200 usec
DE                 6.00 usec
TE                299.9 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1               77Se
P1                 7.40 usec
PL1                0.00 dB
SFO1        114.5069776 MHz
SI                32768
SF          114.4537347 MHz
WDW                  EM
SSB                   0
LB                 5.00 Hz
GB                    0
PC                 1.40
```

S5. X-ray Analysis of 3, (*S*$_p$)-4 and (*R*$_p$,*R*$_p$)-1

Single crystals suitable for X-ray analysis were obtained from recrystallization from CH_2Cl_2-hexane (for **3**), CH_2Cl_2-MeOH (for (*S*$_p$)-**4**) or $CHCl_3$ (for (*R*$_p$,*R*$_p$)-**1**). The intensity data were collected on Rigaku XtaLAB Synergy-R/DW (for **3**) or a Bruker Apex-II CCD diffractometer (**1** and **4**) using monochromated Mo-Kα radiation (λ = 0.71073 Å). The detailed crystallographic data are summarized in Table S1. All structures were solved by the direct method (SHELEXT) and refined by full-matrix least-squares method by using Olex2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as the riding model.

(a)



(b)

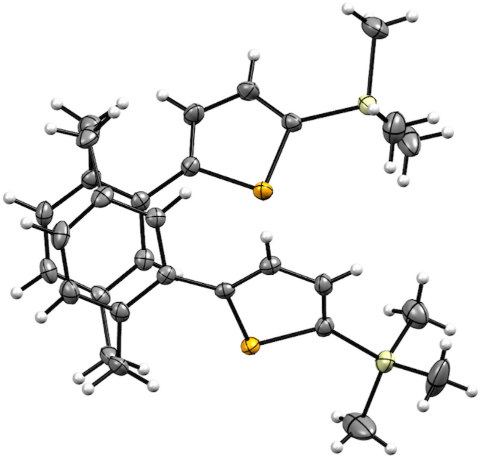


Figure S6. ORTEP Drawing of (a) **3** and (b) (*S*$_p$)-**4**

Table S1. X-ray Analyses of **3**, (S_p)-**4**, and (R_p,R_p)-**1**

Identification code	**3**	(S_p)-**4**	(R_p,R_p)-**1**
Crystal description	Colorless	Colorless	Yellow
Empirical formula	$C_{26}H_{46}B_2O_4Se_2Si_2$	$C_{30}H_{36}Se_2Si_2$	C49H37Cl3Se4
Moiety formula	$2(C_{13}H_{23}BO_2SeSi)$	$C_{30}H_{36}Se_2Si_2$	$C_{48}H_{34}Se_4$•$CHCl_3$
Formula weight	658.35	610.69	2124.1(3)
Temperature	173 K	173 K	173 K
Wavelength	Mo-*K*α 0.71073 Å	Mo-*K*α 0.71073 Å	Mo-*K*α 0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Pna2_1$ (#33)	$P2_12_12_1$ (#19)	$P2_1$ (#4)
Unite cell dimensions	a = 44.640(2) Å	a = 9.4081(4) Å	a = 9.6143(9) Å
	b = 6.5823(3) Å	b = 14.8474(6) Å	b = 16.007(2) Å
	c = 11.7225(7) Å	c = 20.8540(8) Å	c = 13.842(1) Å
	α = 90°	α = 90°	α = 90°
	β = 90°	β = 90°	β = 94.363(1)°
	γ = 90°	γ = 90°	γ = 90°
Volume	3444.5(3) Å^3	2913.0(2) Å^3	2124.1(3) Å^3
Z	4	4	2
Density (calc.)	1.270 gcm^{-1}	1.392 gcm^{-1}	1.639 gcm^{-1}
Absorption coefficient	2.243	2.637	3.678
F(000)	1360	1248	1036
Crystal size	0.2 x 0.2 x 0.1 cm^3	0.4 x 0.25 x 0.2 cm^3	0.2 x 0.2 x 0.1 mm^3
Index ranges	–56 <= h <= 63	–9 <= h <= 12	–12 <= h <= 12
	–9 <= k <= 7	–19 <= k <= 19	–14 <= k <= 21
	–14 <= l <= 11	–28 <= l <= 18	–17 <= l <= 17
Reflections collected	20867	17167	12591
Independent reflections	7337 [R_{int} = 0.0717 , R_{sigma} = 0.0821]	6914 [R_{int} = 0. 0205, R_{sigma} = 0.0464]	7631 [R_{int} = 0.0.0237, R_{sigma} = 0.0573]
Data/restraints/parameters	7337/1/339	6914/0/313	7631/43/505
Goodness-of-fit on F^2	1.032	0.941	1.035
Final *R* indices [I > 2σ(I)]	R_1 = 0.0524 wR_2 = 0.1193	R_1 = 0.0215, wR_2 = 0.0460	R_1 = 0.0335, wR_2 = 0.0810
Final *R* indices [all data]	R_1 = 0.0727 wR_2 = 0.1271	R_1 = 0.0257, wR_2 = 0.0470	R_1 = 0.0393, wR_2 = 0.0835
Flack parameters	–	0.007(3)	0.011(7)
CCDC deposition No.	1939516	1939517	1939518

S6. Geometry Optimization of (R_p,R_p)-1

Geometry optimization of (R_p,R_p)-**1** were performed by DFT calculation (Gaussian 16, Revision A.03) at B3LYP/6-31G(d,p) level of theory. The minimum energy of each conformation was confirmed by frequency calculations. We obtained three stable conformer of i, ii and iii having a local minimum energy (Table S2). The anti (R_p,R_p)-**1**-i conformation with C_1 symmetry was found as the most stable geometry. The atomic coordinate of (R_p)-**4**-i was listed below (Table S3).

Table S2. Geometry and total energy of each conformer in (R_p,R_p)-**1**

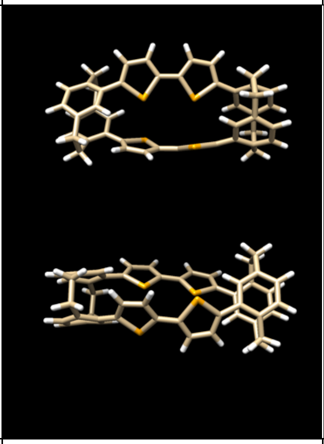
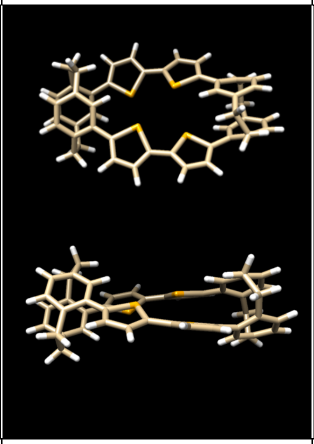
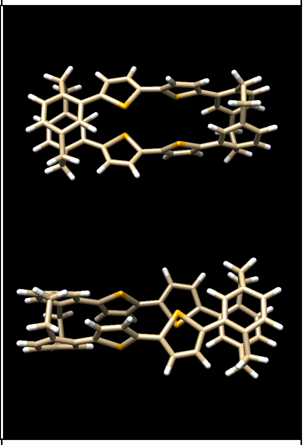
ID code	(R_p,R_p)-**1**-i	(R_p,R_p)-**1**-ii	(R_p,R_p)-**1**-iii
Geometry			
Point Group	C_1	C_2	C_2
# of img	0	0	0
Energy in HF	–11448.2931431	–11448.2880409	–11448.279405
Relative energy (kJ/mol)	0.00	+13.4	+36.0

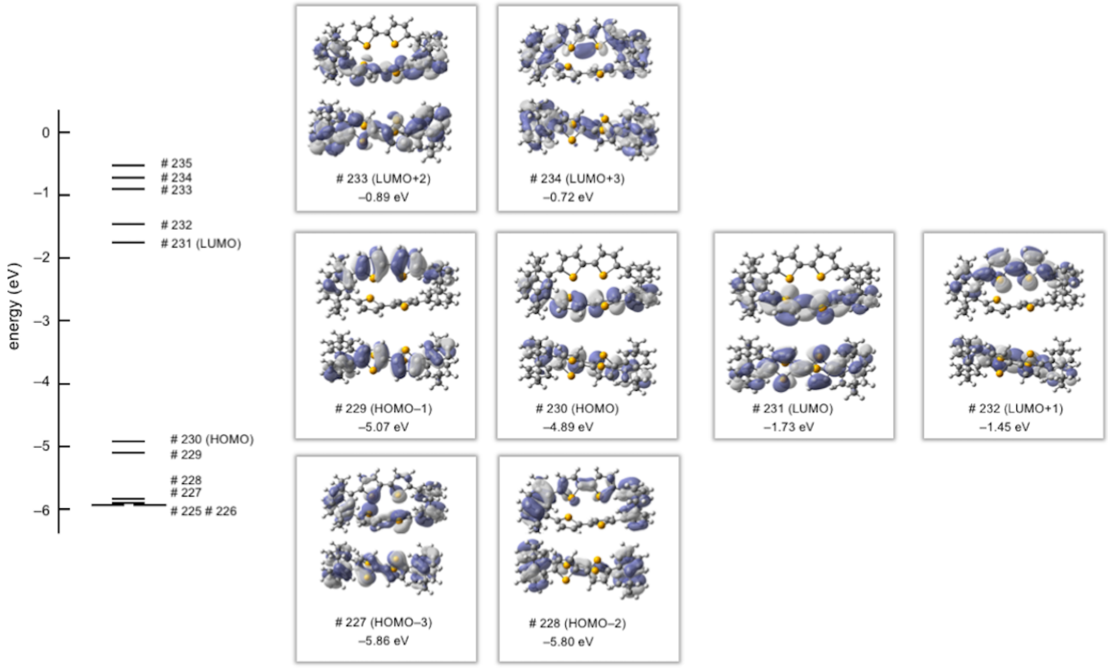
Table S3. Atomic coordinate of optimized structure of (R_p)-**4**-i

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          6           0       -4.627274   -1.515430   -0.583341
      2          6           0       -4.639795   -0.481821   -1.545237
      3          1           0       -3.693236   -0.015678   -1.804806
      4          6           0       -5.819266    0.122525   -1.979374
      5          6           0       -7.017305   -0.538981   -1.683175
      6          1           0       -7.958512   -0.168732   -2.081855
      7          6           0       -7.028004   -1.551816   -0.726831
      8          1           0       -7.983815   -1.950429   -0.394943
```

9	6	0	-5.869063	-1.940080	-0.041445
10	6	0	-4.606529	1.663540	0.785263
11	6	0	-4.729319	0.626384	1.728224
12	1	0	-3.817339	0.237244	2.171938
13	6	0	-5.952582	0.000926	1.989853
14	6	0	-7.105383	0.645849	1.524381
15	1	0	-8.086633	0.259034	1.788399
16	6	0	-5.763418	2.076663	0.074124
17	6	0	-6.027270	-2.531364	1.343553
18	1	0	-5.257773	-3.277450	1.559226
19	1	0	-6.988512	-3.051608	1.392462
20	6	0	-6.012862	-1.420916	2.511857
21	1	0	-6.914234	-1.567842	3.115812
22	1	0	-5.162238	-1.614083	3.173604
23	6	0	-5.802044	1.546839	-2.491715
24	1	0	-6.706825	1.740493	-3.076690
25	1	0	-4.951241	1.700072	-3.163353
26	6	0	-5.707873	2.657447	-1.327606
27	1	0	-4.785766	3.219189	-1.476998
28	1	0	-6.536992	3.358172	-1.470852
29	6	0	4.627251	-1.515455	0.583325
30	6	0	4.639777	-0.481858	1.545231
31	1	0	3.693221	-0.015720	1.804819
32	6	0	5.819253	0.122478	1.979376
33	6	0	7.017286	-0.539028	1.683170
34	1	0	7.958494	-0.168783	2.081852
35	6	0	7.027982	-1.551854	0.726810
36	1	0	7.983790	-1.950467	0.394911
37	6	0	5.869041	-1.940099	0.041418
38	6	0	4.606559	1.663575	-0.785248
39	6	0	4.729343	0.626428	-1.728234
40	1	0	3.817356	0.237307	-2.171943
41	6	0	5.952592	0.000956	-1.989858
42	6	0	7.105407	0.645856	-1.524363
43	1	0	8.086651	0.259032	-1.788392
44	6	0	7.003234	1.665590	-0.581056
45	1	0	7.910808	2.044828	-0.116895
46	6	0	5.763440	2.076657	-0.074095
47	6	0	5.802033	1.546786	2.491738
48	1	0	6.706804	1.740423	3.076732
49	1	0	4.951217	1.700010	3.163359

50	6	0	5.707893	2.657417	1.327647
51	1	0	4.785794	3.219172	1.477041
52	1	0	6.537023	3.358123	1.470915
53	6	0	6.027253	-2.531351	-1.343594
54	1	0	5.257762	-3.277436	-1.559293
55	1	0	6.988500	-3.051582	-1.392509
56	6	0	6.012845	-1.420876	-2.511884
57	1	0	6.914200	-1.567824	-3.115858
58	1	0	5.162201	-1.614014	-3.173612
59	6	0	-3.311563	-1.964898	-0.105152
60	6	0	-2.832260	-2.261851	1.152245
61	1	0	-3.462615	-2.266420	2.029988
62	6	0	-1.432265	-2.473395	1.261221
63	1	0	-0.951965	-2.670000	2.215020
64	6	0	-0.714159	-2.379005	0.092246
65	6	0	0.714133	-2.379011	-0.092245
66	6	0	1.432233	-2.473416	-1.261221
67	1	0	0.951944	-2.670022	-2.215024
68	6	0	2.832232	-2.261884	-1.152250
69	1	0	3.462581	-2.266463	-2.029996
70	6	0	3.311539	-1.964930	0.105143
71	34	0	-1.877957	-2.004733	-1.338091
72	34	0	1.877937	-2.004754	1.338090
73	6	0	3.273466	2.216013	-0.502824
74	6	0	2.907701	3.538154	-0.417864
75	1	0	3.635149	4.334132	-0.542027
76	6	0	1.529307	3.795648	-0.203769
77	1	0	1.138596	4.804825	-0.130532
78	6	0	0.714744	2.686743	-0.108723
79	6	0	-0.714724	2.686740	0.108736
80	6	0	-1.529291	3.795639	0.203803
81	1	0	-1.138580	4.804819	0.130581
82	6	0	-2.907681	3.538136	0.417898
83	1	0	-3.635138	4.334103	0.542083
84	6	0	-3.273443	2.215993	0.502836
85	34	0	1.749308	1.116176	-0.274198
86	34	0	-1.749280	1.116167	0.274181
87	6	0	-7.003204	1.665605	0.581089
88	1	0	-7.910781	2.044854	0.116942

S7. Figure S7. MO Diagram of (R_p,R_p)-1



233 (LUMO+2)
−0.89 eV

234 (LUMO+3)
−0.72 eV

229 (HOMO−1)
−5.07 eV

230 (HOMO)
−4.89 eV

231 (LUMO)
−1.73 eV

232 (LUMO+1)
−1.45 eV

227 (HOMO−3)
−5.86 eV

228 (HOMO−2)
−5.80 eV

S8. TD-DFT Calculation of (R_p,R_p)-**1**

The optimized C_1 (B3LYP/6-31G(d,p)) structure of (R_p,R_p)-**1** was applied for excitation energy and simulation of the ECD calculation using time-dependent density functional theory (TD-DFT) with B3LYP/6-311+G(2d,p) basis set. Selected excitation energies and their transition nature are listed as follow.

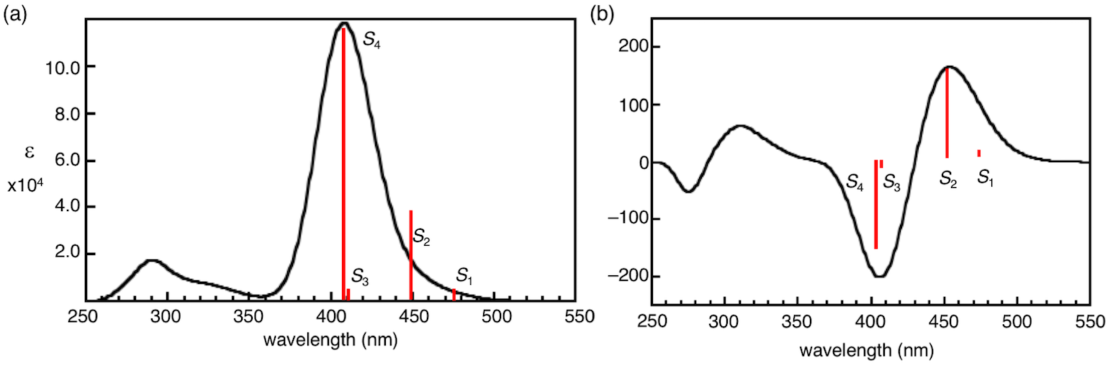


Figure S8. Simulated (a) UV-vis and (b) CD spectra of (R_p,R_p)-**1** from TD-DFT calculation (isovalue : 0.15).

Table S4. Selected electronic transition for (R_p,R_p)-**1**

State	Excitation energies / nm (Oscillator strengths, R_{vel})	Nature	
S_1	476.96 (0.002, 0.0976)	230 -> 231	0.70585
S_2	451.01 (0.0765, 476.829)	229 -> 231	0.59368
		230 -> 232	–0.37490
S_3	409.28 (0.003,–0.5115)	229 -> 232	0.70532
S_4	407.99 (1.3103,–513.8583)	229 -> 231	0.26679
		230 -> 232	0.59178

S9. References

[s1] G. Meyer-Eppler, E. Vogelsang, C. Benkhäuser, A. Schneider, G. Schnakenburg, A. Lützen, *Eur. J. Org. Chem.*, 2013, **21**, 4523.

[s2] M. Hasegawa, K. Kobayakawa, H. Matsuzawa, T. Nishinaga, T. Hirose, K. Sako, Y. Mazaki, *Chem. Eur. J.*, 2017, **23**, 326.