

Supporting Information

Asymmetric [2+2] Olefin Cross Photoaddition in a Self-assembled Host with Remote Chiral Auxiliaries

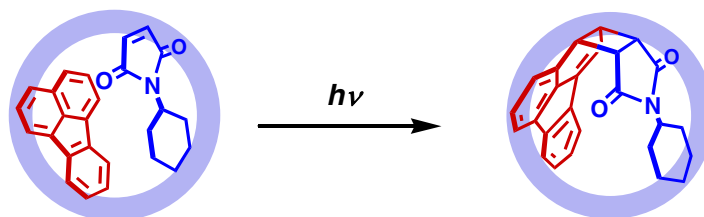
Yuki Nishioka, Takumi Yamaguchi, Masaki Kawano and Makoto Fujita*

Contents:

- Materials and Instrumentations
- [2+2] photodimerization of fluoranthene (**2a**) and *N*-cyclohexylmaleimide (**3**) within cage **1a**: ¹H, ¹³C, COSY, NOESY, and HSQC NMR spectra.
- [2+2] photodimerization of 3-methylfluoranthene (**2b**) and *N*-cyclohexylmaleimide (**3**) within cage **1a**: ¹H, ¹³C, COSY, NOESY, and HSQC NMR spectra.
- Synthesis of *cis*-((1*R*, 2*R*)-*N*, *N'*-diethyl-1,2-diaminocyclohexane)dinitratopalladium(II) (**5**).
- Self-assembly of cage **1b**.
- HPLC analyses of **4a** and **4b**.
- X-ray crystallographic analysis of **4a**.
- VCD spectrum and DFT vibration analysis of **4a**.
- Optimized structure of **1b** and dihedral angles of pyridine rings on triazine ligands.
- Optimized structures of **2a**.

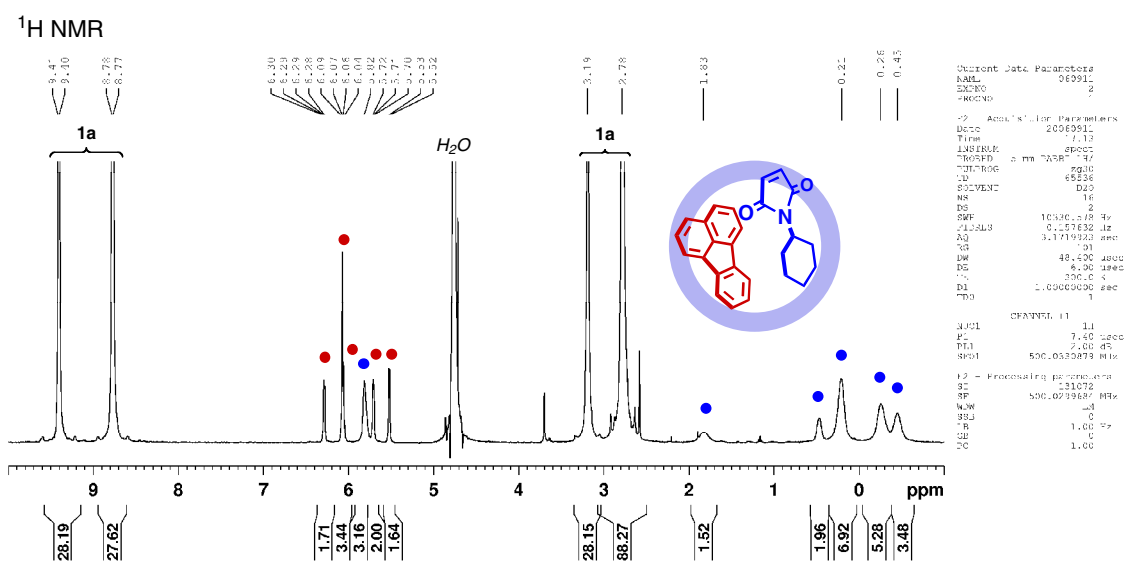
Materials and Instrumentations: ¹H, ¹³C NMR, and other 2D NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer. TMS (CDCl₃ solution) in a capillary served as external standard ($\delta = 0$ ppm). CD spectra were recorded on a Jasco J-820 spectropolarimeter. IR measurements were carried out as KBr pellets using a DIGILAB Scimitar FTS-2000 instrument. MALDI-TOF MS data was obtained by Applied Biosystem Voyager DE-STR instruments. Melting points were determined with a Yanaco MF-500 V micro melting point apparatus. Photo irradiation was carried out with a SEN LIGHTS CORP. HB400X-15 400-W high-pressure mercury lamp or a SAN-EI ELECTRIC CO. UVF-352S 350-W ultra high-pressure mercury lamp. Force-field calculations and DFT calculation were carried out with the use of Cerius² version 3.5 software package (Molecular Simulation Inc., San Diego, CA, 1997) and Spartan '06 software package (Wavefunction Inc., Irvine, CA, 92612), respectively. HPLC analyses were Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co. Deuterated H₂O was acquired from Cambridge Isotope Laboratories, Inc. and used as supplied for the complexation reactions and NMR measurements.

[2+2] Photodimerization of fluoranthene (**2a**) and *N*-cyclohexylmaleimide (**3**) within **1a**.

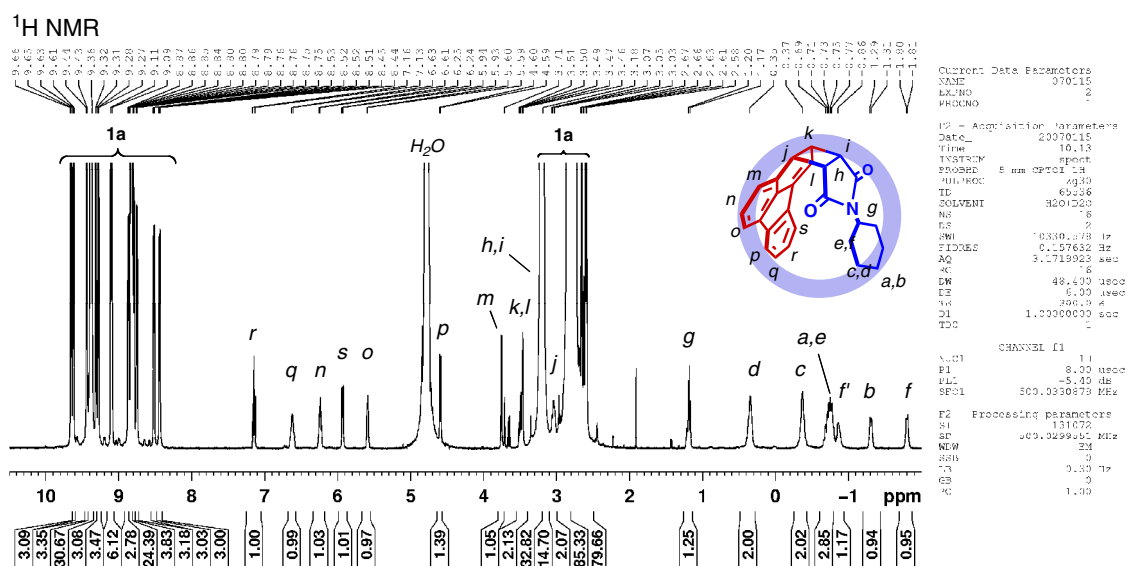


Typical procedure: fluoranthene (**2a**, 3.03 mg; 15.0 μ mol) and *N*-cyclohexylmaleimide (**3**, 2.69 mg; 15.0 μ mol) were suspended in a D₂O solution (1.0 mL) of cage **1a** (5.0 μ mol) and the solution was stirred at room temperature for 30 min to give **1a**•(**2a**•**3**) complex in 60% yield. The solution was irradiated (ultra high pressure mercury lamp with HOYA U-360 filter) for 5 min at room temperature. ¹H NMR analysis of the solution revealed the formation of **1a**•**4a** complex in 55% yield based on **1a** (91% yield based on **1a**•(**2a**•**3**)). After filtration, extraction with CHCl₃, and purification by column chromatography (CHCl₃), *N*-cyclohexyl-1,2,2a,10a-tetrahydrocyclobut[*b*]fluorantane-1,2-dicarboximide (**4a**) was isolated as a white solid. A control experiment in the absence of cage **1a** did not give the product at all.

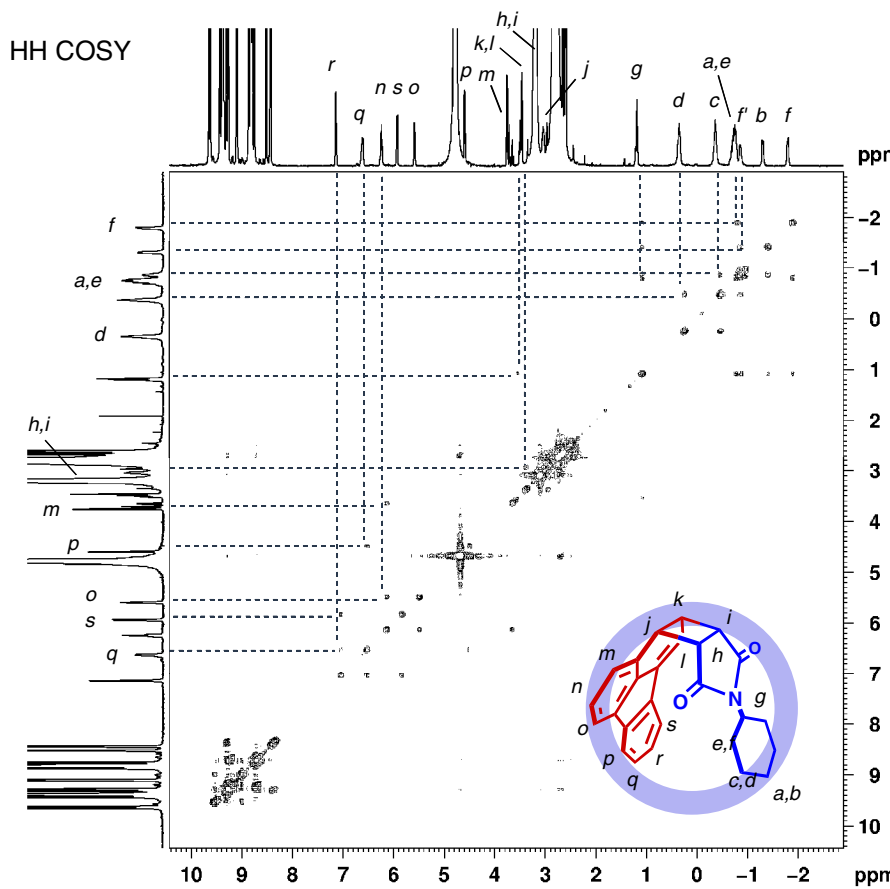
Physical data of **1a**•(**2a**•**3**): ¹H-NMR (500 MHz, D₂O, 27 °C): δ = -0.45 (br, 2H, -CH₂-, **3**), -0.26 (br, 2H, -CH₂-, **3**), 0.21 (br, 4H, -CH₂-, **3**), 0.47 (br, 2H, -CH₂-, **3**), 1.83 (br, 1H, -CH-, **3**), 2.78 (s, 72H, -CH₃, **1a**), 3.19 (s, 24H, -CH₂-, **1a**), 5.53 (d, *J* = 5.5 Hz, 2H, CH, **2a**), 5.71 (dd, *J* = 5.5 Hz, 2H, CH, **2a**), 5.82 (s, 2H, CH, **3**), 6.06 (dd, *J* = 5.5 Hz, 2H, CH, **2a**), 6.08 (d, *J* = 6.0 Hz, 2H, CH, **2a**), 6.30 (d, *J* = 5.5 Hz, 2H, CH, **2a**), 8.78 (d, *J* = 5.5 Hz, 24H, PyH _{β} , **1a**), 9.41 (s, *J* = 5.5 Hz, 24H, PyH _{α} , **1a**).



Physical data of **1a•4a**: ¹H-NMR (500 MHz, D₂O, 27 °C): δ = -1.80 (br, 1H, H_f, **4a**), -1.30 (d, J = 10.0 Hz, 1H, H_b, **4a**), -0.86 (br, 1H, H_f, **4a**), -0.76 (m, 3H, H_a and H_e, **4a**), -0.37 (br, 2H, H_c, **4a**), 0.35 (br, 2H, H_d, **4a**), 1.19 (m, 1H, H_g, **4a**), 2.77 (m, 72H, -CH₃, **1a**), 2.84 (m, 72H, -CH₃, free **1a**), 3.05 (t, J = 10.0 Hz, 1H, H_j, **4a**), 3.19 (m, 24H, -CH₂-, **1a**), 3.22 (m, 26H, -CH₂- H_h and H_p, free **1a** and **4a**), 3.36 (m, 2H, H_i and H_k, **4a**), 3.71 (d, J = 5.0 Hz, 1H, H_m, **4a**), 4.60 (d, J = 7.5 Hz, 1H, H_p, **4a**), 5.60 (d, J = 7.5 Hz, 1H, H_o, **4a**), 5.94 (d, J = 7.5 Hz, 1H, H_s, **4a**), 6.26 (dd, J = 7.5 Hz, 1H, H_n, **4a**), 6.63 (dd, J = 7.5 Hz, 1H, H_q, **4a**), 7.26 (dd, J = 7.5 Hz, 1H, H_r, **4a**), 8.44 (d, J = 5.0 Hz, 4H, PyH, **1a**), 8.52 (d, J = 4.5 Hz, 4H, PyH, **1a**), 8.76 (d, J = 5.5 Hz, 4H, PyH, **1a**), 8.80 (d, J = 5.5 Hz, 4H, PyH, **1a**), 8.83 (d, J = 6.0 Hz, 18H, PyH_β, free **1a**), 8.87 (d, J = 5.5 Hz, 4H, PyH, **1a**), 9.11 (d, J = 6.0 Hz, 6H, PyH_β, free **1a**), 9.28 (d, J = 6.0 Hz, 4H, PyH, **1a**), 9.31 (d, J = 5.5 Hz, 4H, PyH, **1a**), 9.39 (d, J = 6.0 Hz, 24H, PyH_α, free **1a**), 9.44 (d, J = 6.0 Hz, 4H, PyH, **1a**), 9.62 (d, J = 5.5 Hz, 4H, PyH, **1a**), 9.66 (d, J = 6.0 Hz, 4H, PyH, **1a**)



HH COSY



```

Current Data Parameters
NAME      07011b
EXPNO     3
PROCNO    1

F2 - Acquisition Parameters
Date_     20070115
Time      10.15
INSTRUM   spect
PROBHD    5 mm QNP1H
PULPROG   zgpg30
TD         65536
SOLVENT   H2O+D2O
NS         4
DS         8
SWH        6665.667 Hz
FIDRES     3.755208 Hz
AQ         0.1536500 sec
RG         203
BW         78.333 usec
DE         6.00 usec
TE         300.3 K
d0         0.30000000 sec
d1         1.46272600 sec
d12        0.30000000 sec
d16        0.30020000 sec
d18        0.30015000 sec

----- CHANNEL f1 -----
NUC1       1H
AQ         8.00 usec
SI         8.00 usec
P1         -3.40 dB
SFO1       500.0319938 MHz

----- GRADIENT CHANNEL -----
G1NAME1    8 NR. 100
G1NAME2    8 NR. 100
G2P1       10.00 usec
G2P2       10.00 usec
P12        100.00 usec

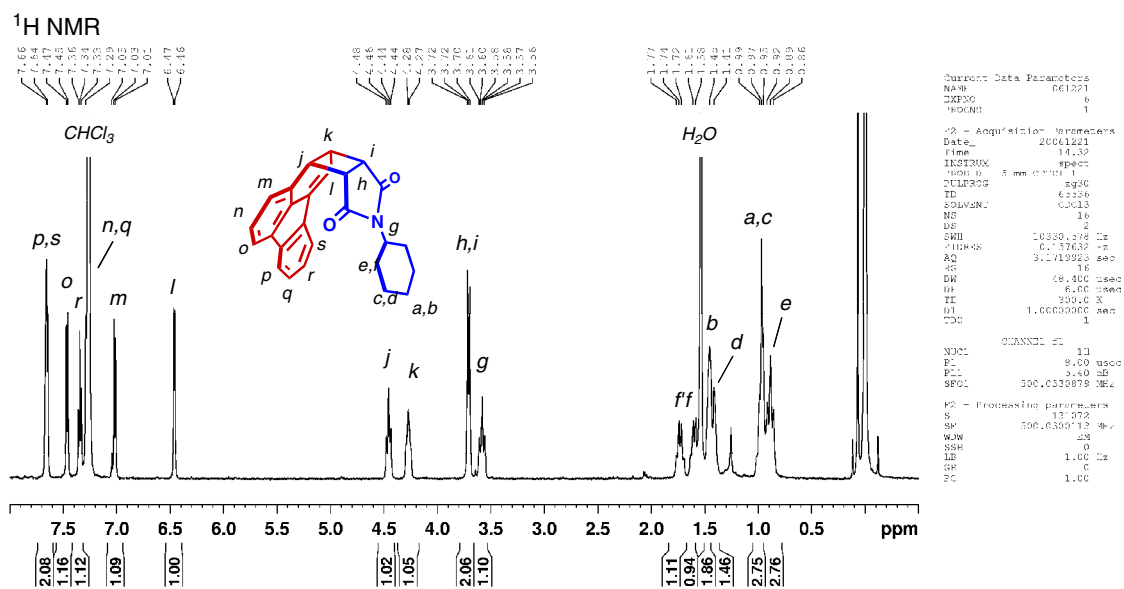
F1 - Acquisition parameters
AQ         128
TD         65536
SFO1       500.0319 MHz
FIDRES     3.755332 Hz
SW         13.332 ppm
P1         0.00 usec
PC         1.00

F2 - Processing parameters
SI         1024
SF         500.030098 MHz
WDW        SINE
SFB         0
GB         0.00 Hz
CB         0
PC         1.00

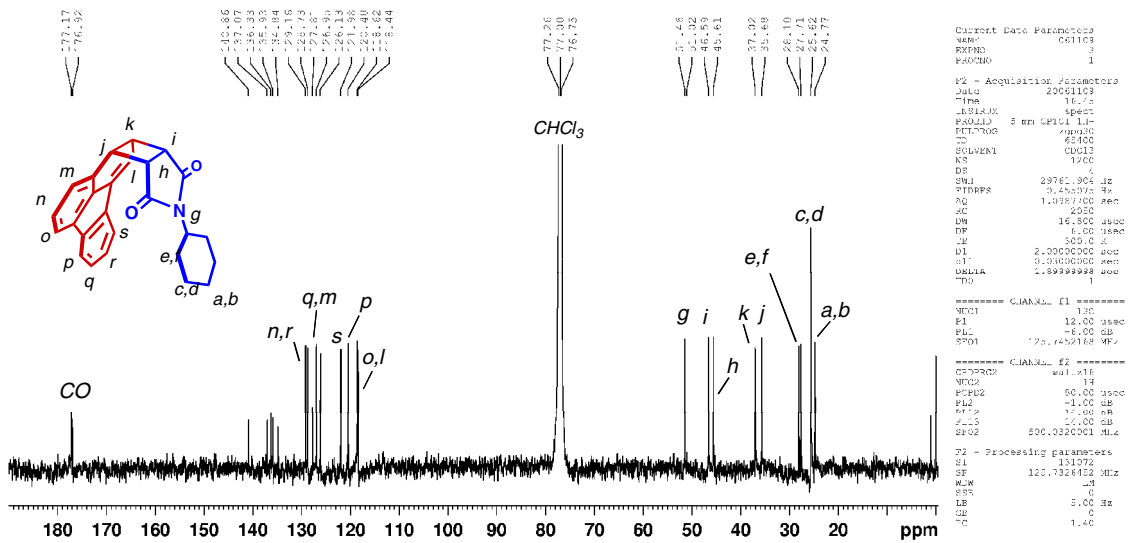
F1 - Processing parameters
SI         1024
SF         500.030098 MHz
WDW        SINE
SFB         0
GB         0.00 Hz
CB         0

```

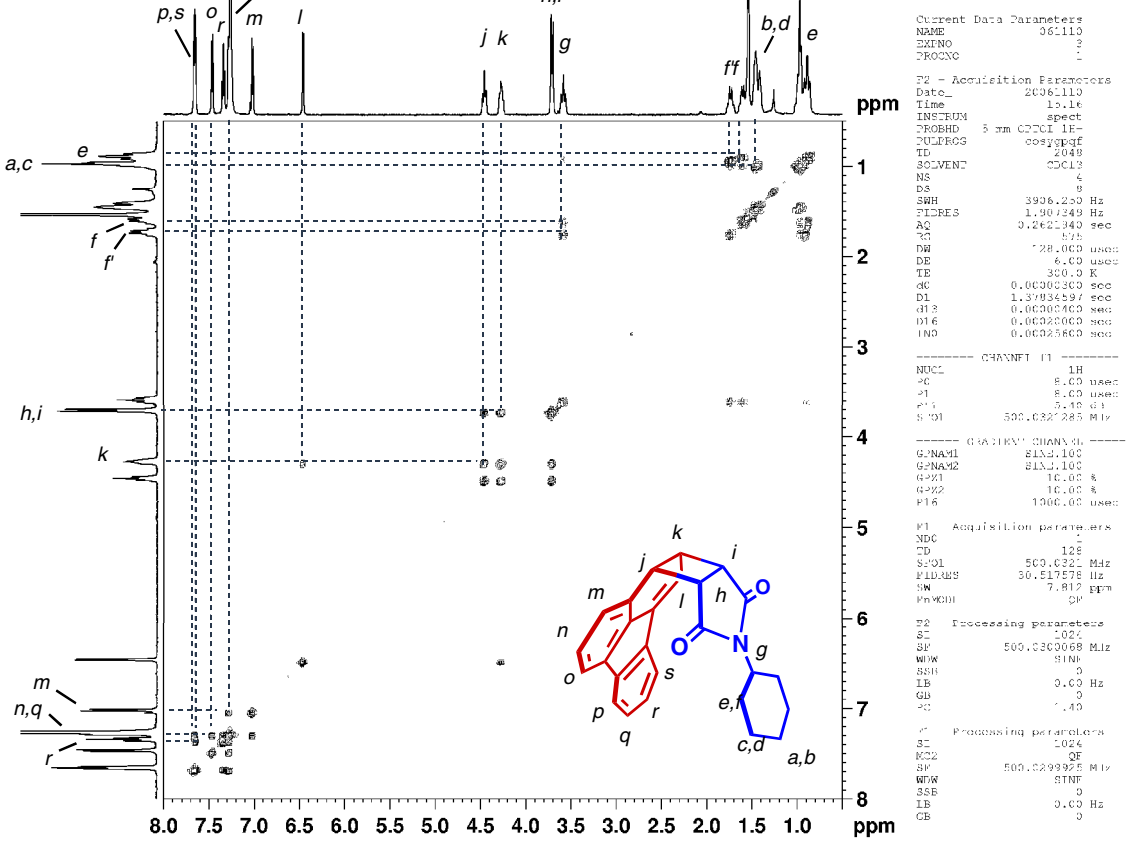
Physical data of **4a**: $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 27 °C): δ = 0.89 (t, J = 10.0 Hz, 2H, H_e), 0.96 (m, 3H, H_a and H_c), 1.41 (br, 1H, H_b), 1.45 (br, 2H, H_d), 1.60 (q, J = 12.0 Hz, 1H, H_f), 1.74 (q, J = 12.0 Hz, 1H, H_f), 3.58 (m, 1H, H_g), 3.71 (dd, 2H, J = 10.5 Hz, H_n and H_i), 4.27 (m, 1H, H_k), 4.45 (dd, 1H, J = 10.5 Hz, H_j), 6.46 (d, J = 5.0 Hz, 1H, H_l), 7.01 (d, J = 7.5 Hz, 1H, H_m), 7.26 (m, 2H, H_n and H_q), 7.34 (dd, J = 7.5 Hz, 1H, H_r), 7.46 (d, J = 7.5 Hz, 1H, H_o), 7.65 (m, 2H, H_p and H_s); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 27 °C): δ = 24.8 ($C_{a,b}$), 25.6 ($C_{c,d}$), 27.7 (C_e), 28.1 (C_f), 35.9 (C_j), 37.0 (C_k), 45.6 (C_h), 46.6 (C_l), 51.5 (C_g), 118.4 (C_i), 118.6 (C_o), 120.5 (C_p), 122.0 (C_s), 126.1 (C_m), 127.0 (C_q), 127.8 (C_q), 128.7 (C_r), 129.2 (C_n), 134.8 (C_q), 136.0 (C_q), 136.3 (C_q), 137.1 (C_q), 140.9 (C_q), 176.9 (CO), 177.2 (CO); MALDI-TOF MS: m/z = 407.26; IR (KBr, cm^{-1}): 2929, 2859, 2362, 2342, 1767, 1691, 1447, 1397, 1367, 1344, 1261, 1202, 1183, 1134, 1029, 807, 772, 753, 626; m.p.: 171–174 °C; E.A. Calcd. for $\text{C}_{26}\text{H}_{23}\text{NO}_2 \cdot 1.1\text{H}_2\text{O}$: C, 77.82; H, 6.33; N, 3.49. Found: C, 77.79; H, 6.35; N, 3.29.

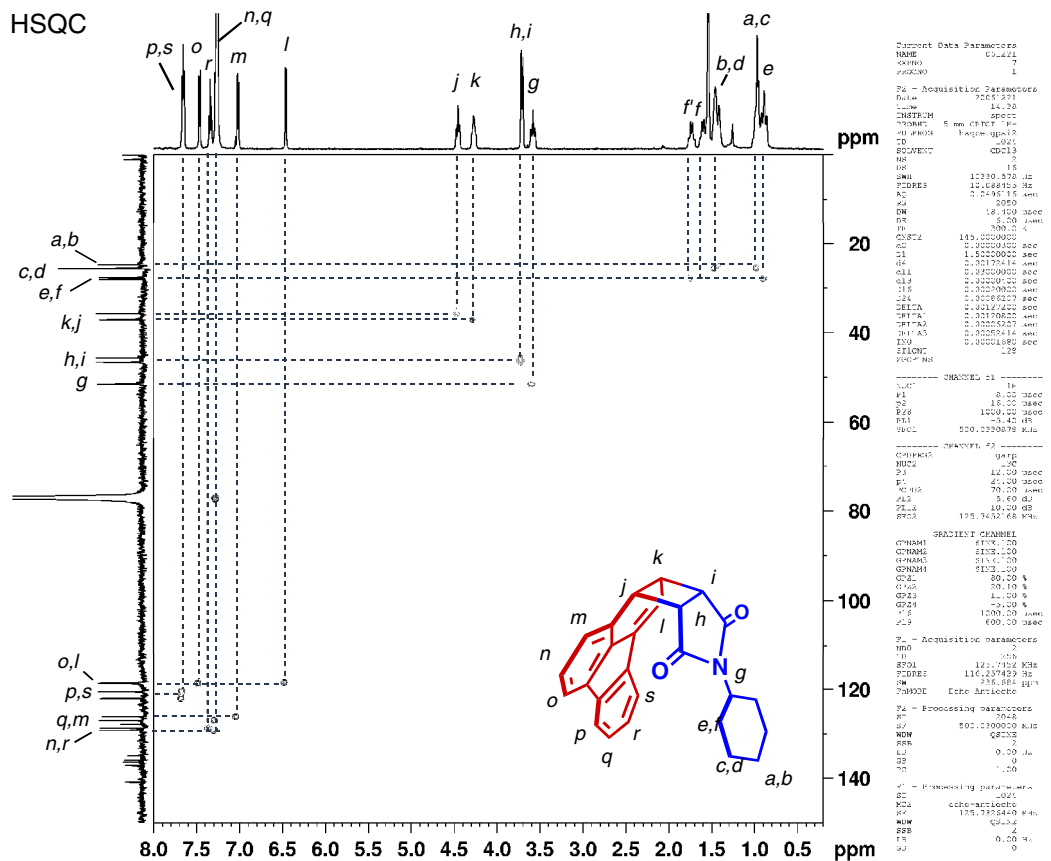
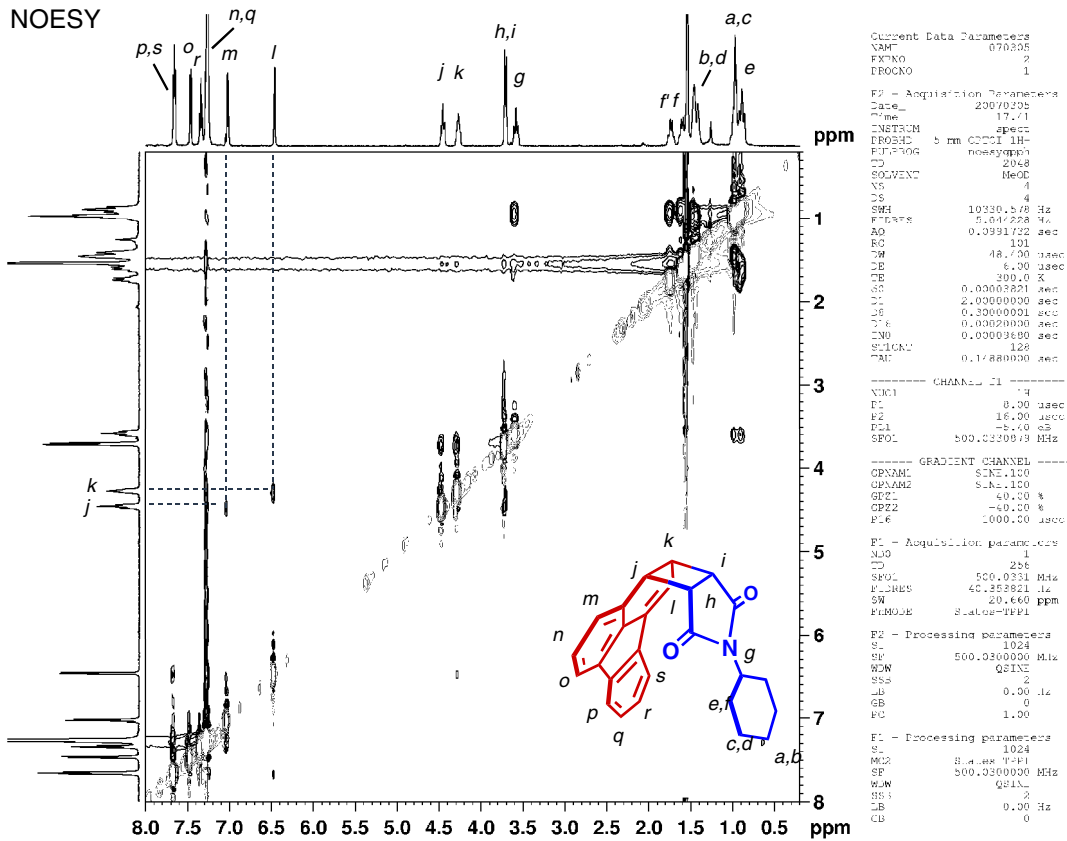


¹³C NMR

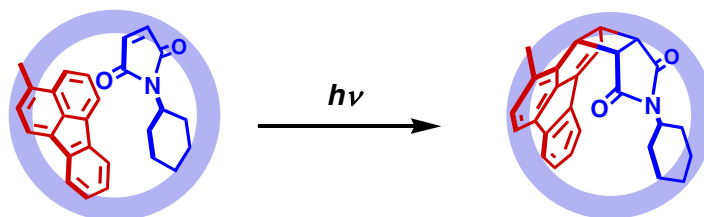


HH COSY



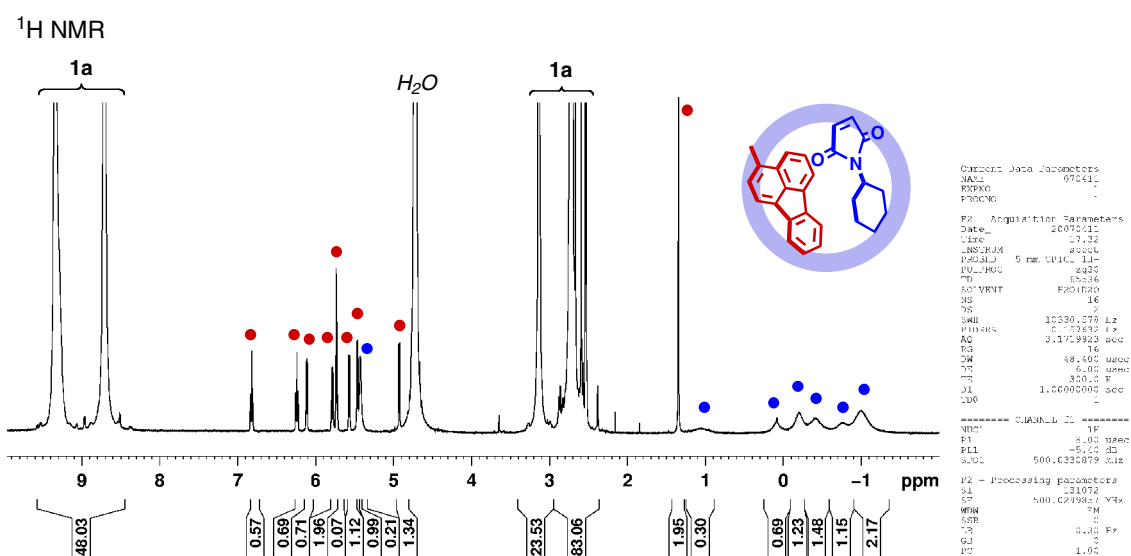


[2+2] Photodimerization of 3-methylfluoranthene (**2b**) and *N*-cyclohexylmaleimide (**3**) within **1a**.

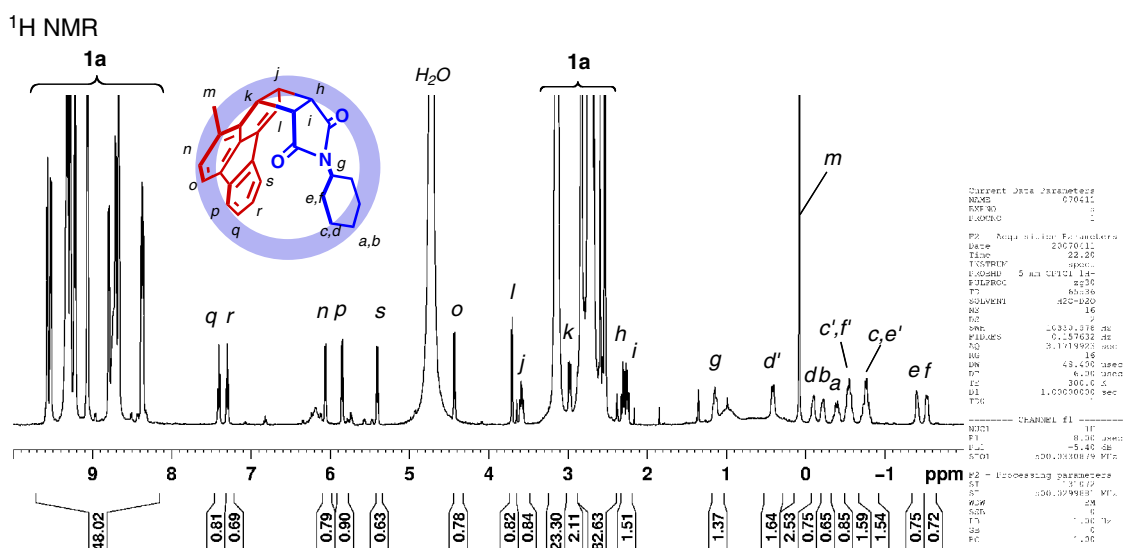


Typical procedure: 3-methylfluoranthene (**2b**, 3.03 mg; 15.0 μmol) and *N*-cyclohexylmaleimide (**3**, 2.69 mg; 15.0 μmol) were suspended in a D_2O solution (1.0 mL) of cage **1a** (5.0 μmol) and the solution was stirred at room temperature for 30 min to give **1a**•(**2b**•**3**) complex in 75% yield. The solution was irradiated (ultra high pressure mercury lamp with HOYA U-360 filter) for 15 min at room temperature. ^1H NMR analysis of the solution revealed the formation of **1a**•**4b** complex in 75% yield based on **1a** (>99% yield based on **1a**•(**2b**•**3**)). After filtration, extraction with CHCl_3 , and purification by column chromatography (CHCl_3), *syn* [2+2] photoadduct **4b** was isolated as a white solid.

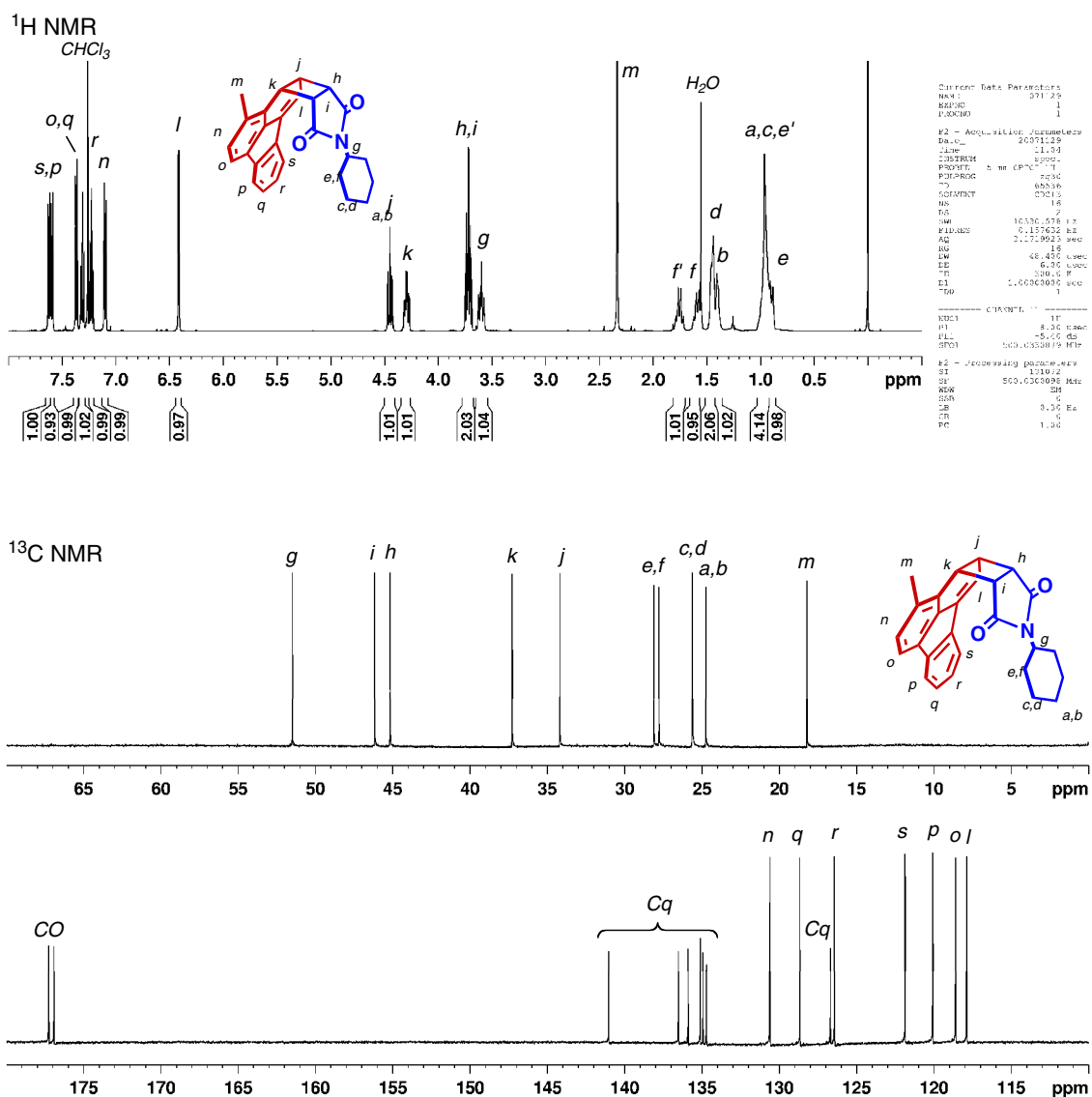
Physical data of **1a**•(**2b**•**3**): ^1H -NMR (500 MHz, D_2O , 27 $^\circ\text{C}$): δ = -1.00 (br, 3H, $-\text{CH}_2-$, **3**), -0.77 (br, 1H, $-\text{CH}_2-$, **3**), -0.41 (br, 2H, $-\text{CH}_2-$, **3**), -0.20 (br, 3H, $-\text{CH}_2-$, **3**), -0.09 (br, 1H, $-\text{CH}_2-$, **3**), 1.06 (br, 1H, $-\text{CH}-$, **3**), 1.35 (s, 3H, $-\text{CH}_3$, **2b**), 2.72 (s, 72H, $-\text{CH}_3$, **1a**), 3.14 (s, 24H, $-\text{CH}_2-$, **1a**), 4.93 (d, J = 7.0 Hz, 2H, $-\text{CH}-$, **2b**), 4.93 (d, J = 7.0 Hz, 1H, $-\text{CH}-$, **2b**), 5.43 (br, 2H, $-\text{CH}-$, **3**), 5.47 (d, J = 6.5 Hz, 1H, $-\text{CH}-$, **2b**), 5.57 (d, J = 6.5 Hz, 1H, $-\text{CH}-$, **2b**), 5.73 (m, 2H, $-\text{CH}-$, **2b**), 5.79 (t, J = 6.5 Hz, 1H, $-\text{CH}-$, **2b**), 6.11 (d, J = 7.5 Hz, 1H, $-\text{CH}-$, **2b**), 6.24 (t, J = 7.5 Hz, 1H, $-\text{CH}-$, **2b**), 6.82 (t, J = 7.5 Hz, 1H, $-\text{CH}-$, **2b**), 8.71 (br, 24H, PyH_β , **1a**), 9.35 (s, 24H, PyH_α , **1a**).



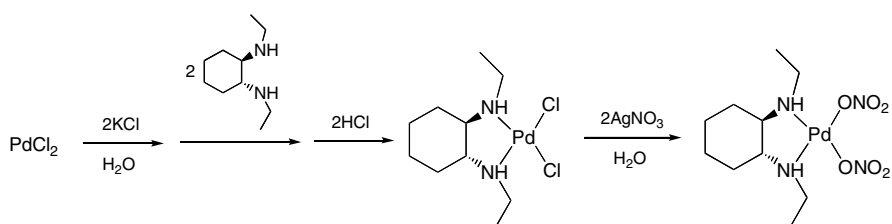
Physical data of **1a•4b**: $^1\text{H-NMR}$ (500 MHz, D_2O , 27 °C): $\delta = -1.53$ (d, $J = 8.5$ Hz, 1H, H_f , **4b**), -1.40 (br, 1H, H_e , **4b**), -0.76 (m, 2H, H_c and $H_{c'}$, **4b**), -0.54 (m, 2H, $H_{c'}$ and H_f , **4b**), -0.39 (q, $J = 15.0$ Hz, 1H, H_d , **4b**), -0.23 (br, 1H, H_b , **4b**), -0.10 (br, 1H, H_d , **4b**), 0.08 (s, 3H, H_m , **4b**), 0.41 (d, $J = 11.5$ Hz, 1H, H_d , **4b**), 1.15 (m, 1H, H_g , **4b**), 2.23 (q, $J = 10.0$ Hz, 1H, H_i , **4b**), 2.29 (q, $J = 10.0$ Hz, 1H, H_h , **4b**), 2.70 (s, 72H, $-\text{CH}_3$, **1a**), 3.14 (d, $J = 5.0$ Hz, 24H, $-\text{CH}_2-$, **1a**), 2.98 (m, 1H, H_k , **4b**), 3.60 (m, 1H, H_j , **4b**), 3.71 (d, $J = 4.5$ Hz, 1H, H_l , **4b**), 4.43 (d, $J = 7.5$ Hz, 1H, H_o , **4b**), 5.40 (d, $J = 7.5$ Hz, 1H, H_s , **4b**), 5.85 (d, $J = 8.0$ Hz, 1H, H_p , **4b**), 6.06 (d, $J = 7.5$ Hz, 1H, H_n , **4b**), 7.30 (dd, $J = 7.5$ Hz, 1H, H_r , **4b**), 7.41 (dd, $J = 7.5$ Hz, 1H, H_q , **4b**), 8.37 (m, 8H, PyH, **1a**), 8.67 (d, $J = 6.0$ Hz, 24H, PyH $_{\beta}$, free **1a**), 8.71 (d, $J = 6.0$ Hz, 4H, PyH, **1a**), 8.79 (d, $J = 6.0$ Hz, 4H, PyH, **1a**), 9.07 (m, 8H, PyH, **1a**), 9.23 (m, 8H, PyH, **1a**), 9.28 (d, $J = 6.0$ Hz, 24H, PyH $_{\beta}$, free **1a**), 9.31 (m, 8H, PyH, **1a**), 9.52 (d, $J = 6.0$ Hz, 4H, PyH, **1a**) 9.57 (d, $J = 6.0$ Hz, 4H, PyH, **1a**).



Physical data of **4b**: $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 27 $^\circ\text{C}$): δ = 0.90 (d, J = 12.5 Hz, 1H, H_e), 0.96 (br, 4H, H_a , H_c and H_e), 1.41 (br, 1H, H_b), 1.45 (br, 2H, H_d), 1.58 (q, J = 12.5 Hz, 1H, H_f), 1.75 (q, J = 12.5 Hz, 1H, H_f), 2.33 (s, 3H, H_m), 3.60 (m, 1H, H_g), 3.72 (dd, 2H, J = 9.0 Hz, H_h and H_i), 4.29 (m, 1H, H_k), 4.45 (dd, 1H, J = 10.0 Hz, H_j), 6.41 (d, J = 5.0 Hz, 1H, H_l), 7.10 (d, J = 7.5 Hz, 1H, H_n), 7.22 (dd, J = 7.5 Hz, 1H, H_r), 7.31 (dd, J = 7.5 Hz, 1H, H_q), 7.36 (d, J = 7.5 Hz, 1H, H_o), 7.59 (d, J = 7.5 Hz, 1H, H_p), 7.62 (d, J = 7.5 Hz, 1H, H_s); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 27 $^\circ\text{C}$): δ = 18.2 (C_m), 24.8 ($C_{a,b}$), 25.6 ($C_{c,d}$), 27.8 (C_e), 28.1 (C_f), 34.2 (C_j), 37.3 (C_k), 45.2 (C_h), 46.2 (C_i), 51.5 (C_g), 117.9 (C_l), 118.6 (C_o), 120.1 (C_p), 121.9 (C_s), 126.4 (C_r), 126.7 (C_q), 128.6 (C_q), 128.7 (C_r), 130.6 (C_n), 134.7 (C_q), 134.9 (C_q), 135.1 (C_q), 135.9 (C_q), 136.5 (C_q), 141.0 (C_q), 176.9 (CO), 177.2 (CO); MALDI-TOF MS : m/z = 395.53; IR (KBr, cm^{-1}): 2933, 2860, 1767, 1690, 1449, 1397, 1367, 1342, 1260, 1186, 1133, 819, 791; m.p.: 275–278 $^\circ\text{C}$; E.A. Calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_2 \cdot 0.4\text{H}_2\text{O}$: C, 80.53; H, 6.46; N, 3.48. Found: C, 80.62; H, 6.45; N, 3.30.



Synthesis of *cis*-((1*R*, 2*R*)-*N*, *N'*-diethyl-1,2-diaminocyclohexane)dinitratopalladium(II) (**5**).

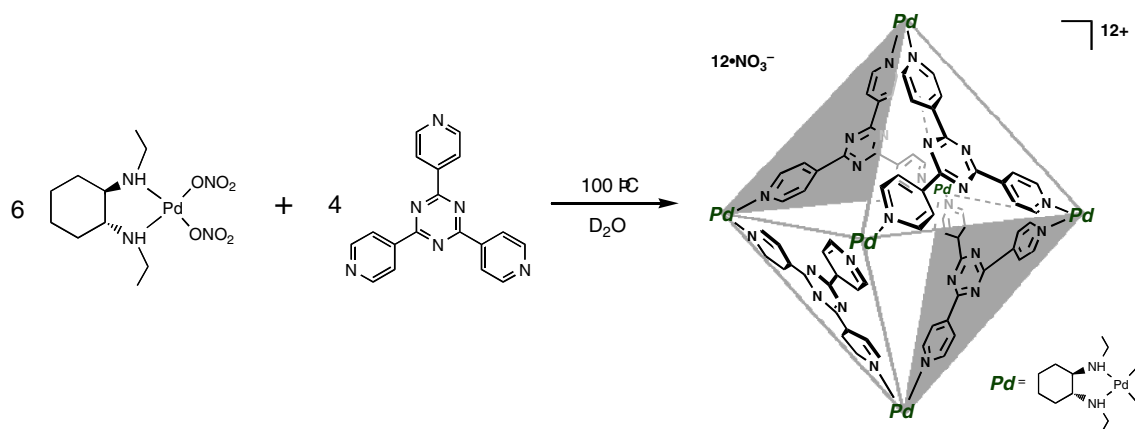


Typical procedure: after the aqueous solution (ca. 10 ml) of PdCl₂ (380 mg; 2.1 mmol) and KCl (320 mg; 4.3 mmol) was heated at 100 °C for 30 min, (1*R*, 2*R*)-*N*, *N'*-diethyl-1,2-diaminocyclohexane (740 mg; 4.4 mmol) was added and stirred at 80 °C for 4 h. After the solution was cooled to room temperature, 5*N* HCl (0.86 ml, 4.3 mmol) was added dropwise and stirred at room temperature for 3 h. The resulting yellow precipitate was collected by filtration and washed with water, ethanol and diethylether to give *cis*-dichloro((1*R*, 2*R*)-*N*, *N'*-diethyl-1,2-diamino cyclohexane)palladium(II) (468 mg, 1.4 mmol) in 63% yield. To a suspended aqueous solution (ca. 30ml) of *cis*-dichloro((1*R*, 2*R*)-*N*, *N'*-diethyl-1,2-diamino cyclohexane)palladium(II) (350 mg, 1.0 mmol), AgNO₃ (342 mg, 2.0 mmol) and a few drops of HNO₃ were added and stirred at 100 °C for 3 h under a dark atmosphere. The resulting yellow solution was treated with activated carbon and then filtrated with sellite. The concentration of the solution under low pressure and purification by recrystallization were done to afford the target compound **5** as a yellow solid (165 mg, 0.41 mmol) in 41% yield.

Physical data of 5: ¹H-NMR (500 MHz, D₂O, 27 °C): δ 1.08 (m, 4H, -CH₂-) 1.48 (t, *J* = 7.5 Hz, 6H, -CH₃) 1.62 (br, 2H, -CH₂-) 2.24 (br, 2H, -CH₂-) 2.26 (q, *J* = 7.0 Hz, 2H, -NHCH₂ CH₃) 2.46 (q, *J* = 7.0 Hz, 2H, -NHCH₂ CH₃) 2.56 (br, 2H, -CH₂-); E.A. Calcd. for C₁₀H₂₂N₄O₆Pd : C, 29.97; H, 5.53; N, 13.98. Found: C, 29.85; H, 5.34; N, 13.71.

Reference: Bennani, Y. L.; Hanessian, S. *Tetrahedron*, **1996**, 52, 13837-13866.

Self-assembly of cage **1b**.



Typical procedure: An aqueous solution (ca. 1 ml) of **5** (2.40 mg; 6.0 μmol) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (1.25 mg; 4.0 μmol) was stirred at 100 °C for 30 min. The resulting complex was identified as a cage **1b**.

Physical data: ¹H-NMR (500 MHz, D₂O, 27 °C): δ 1.0-2.8 (m, 120H), 8.3-9.4 (m, 48H)

HPLC analyses of **4a** and **4b**.

Asymmetric photocycloadditions of **4** and **3** within cage **1b-1d** were carried out by irradiation for 30 min with high pressure Hg lamp. For control experiments, the cage with the inverse chiral auxiliaries ((1*S*, 2*S*)-*N*, *N'*-1,2-diaminocyclohexane derivatives) on each Pd center was also prepared. After irradiation, the products were extracted with chloroform and the solution (ca. 10 μ l) was injected to HPLC system connected with a chiral column (DAICEL CHIRALPAK® IA). The developing solvent was chloroform and hexane mixture (1:4). The retention times of enantiomers were ca. 17 and 22 min (**4a**) and ca.12 and 18 min (**4b**), respectively.

(1) HPLC analyses of **4a** produced inside cage **1b**.

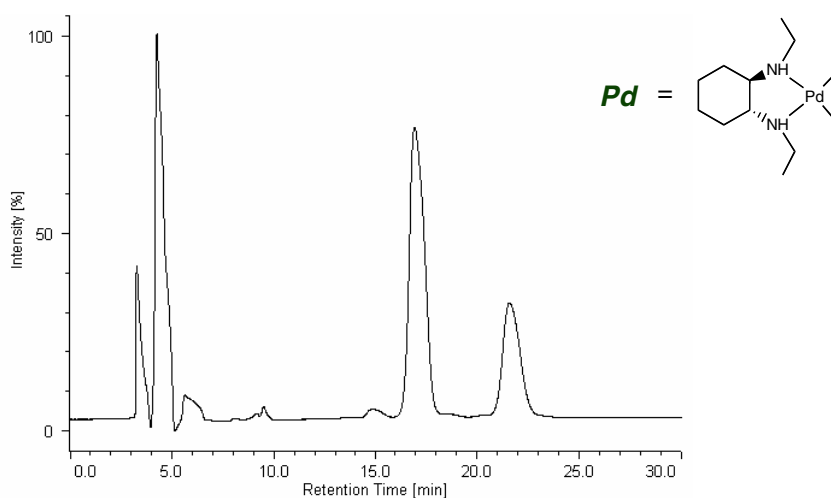


Figure S1-1. The HPLC analysis of **4a** produced inside cage **1b** with the chiral auxiliary ((1*R*, 2*R*)-*N*, *N'*-diethyl-1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 7:3 ratio.

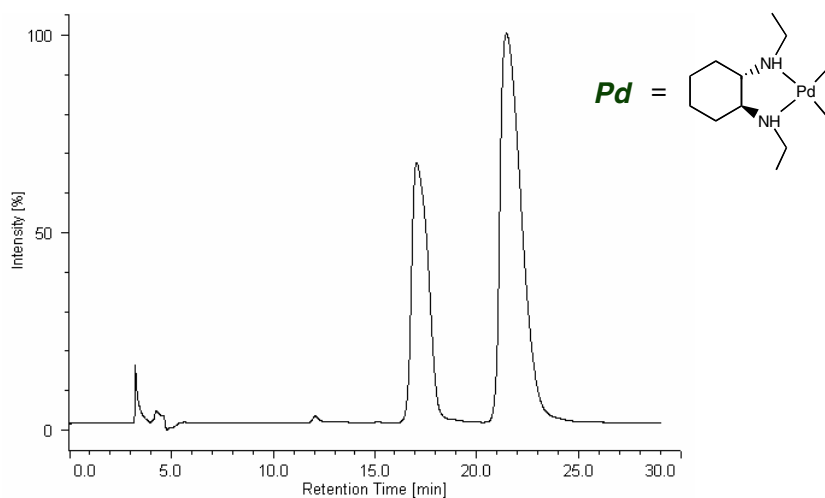


Figure S1-2. The HPLC analysis of **4a** produced inside cage **1b** with the chiral auxiliary ((1*S*, 2*S*)-*N*, *N'*-diethyl-1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 3:7 ratio.

(2) HPLC analyses of **4a** produced inside cage **1c**.

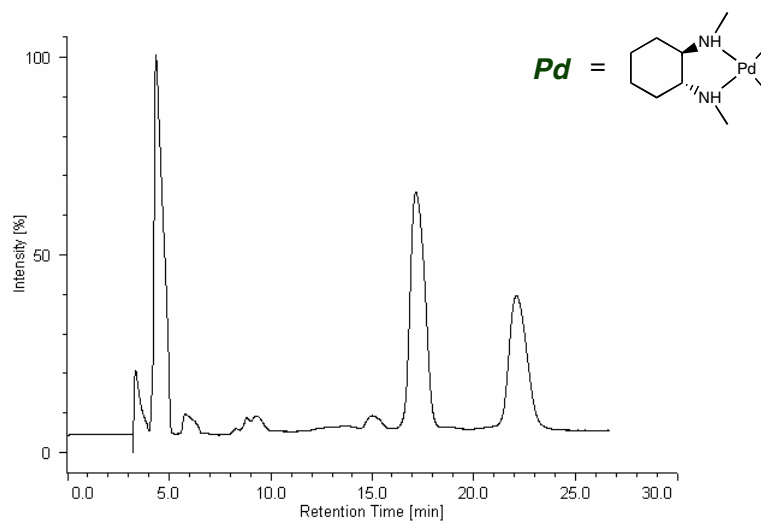


Figure S2-1. The HPLC analysis of **4a** produced inside cage **1c** with the chiral auxiliary ((1*R*, 2*R*)-*N*, *N'*-dimethyl-1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 3:2 ratio.

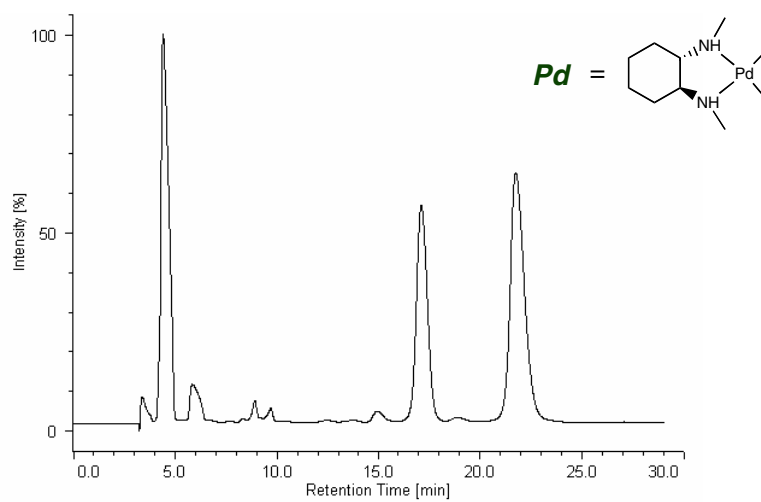


Figure S2-2. The HPLC analysis of **4a** produced inside cage **1c** with the chiral auxiliary ((1*S*, 2*S*)-*N*, *N'*-dimethyl-1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 2:3 ratio.

(3) HPLC analyses of **4a** produced inside cage **1d**.

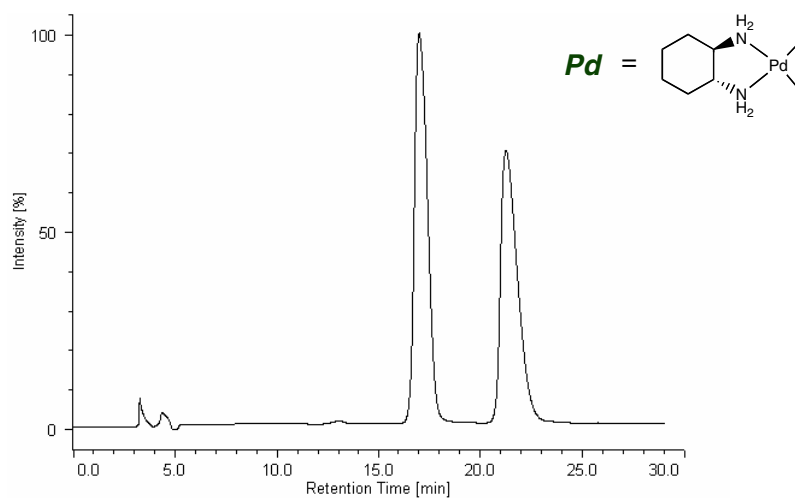


Figure S3-1. The HPLC analysis of **4a** produced inside cage **1d** with the chiral auxiliary ((1*R*, 2*R*)-1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 52:48 ratio.

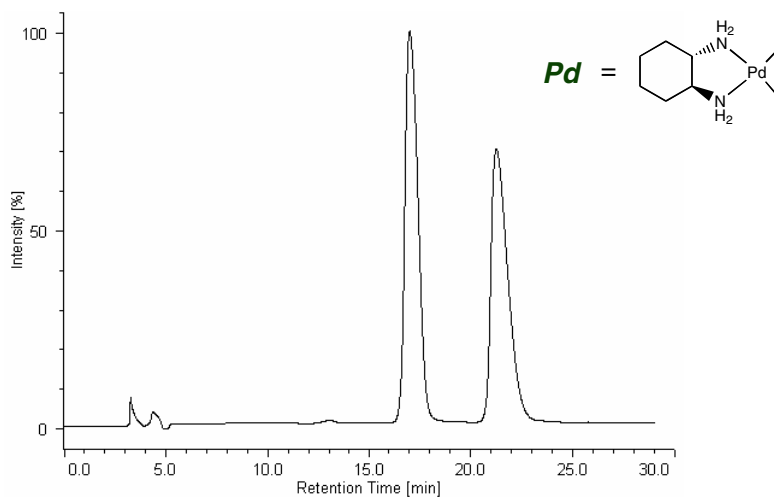


Figure S3-2. The HPLC analysis of **4a** produced inside cage **1d** with the chiral auxiliary ((1*S*, 2*S*)-1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 48:52 ratio.

(4) HPLC analyses of **4b** produced inside cage **1b**.

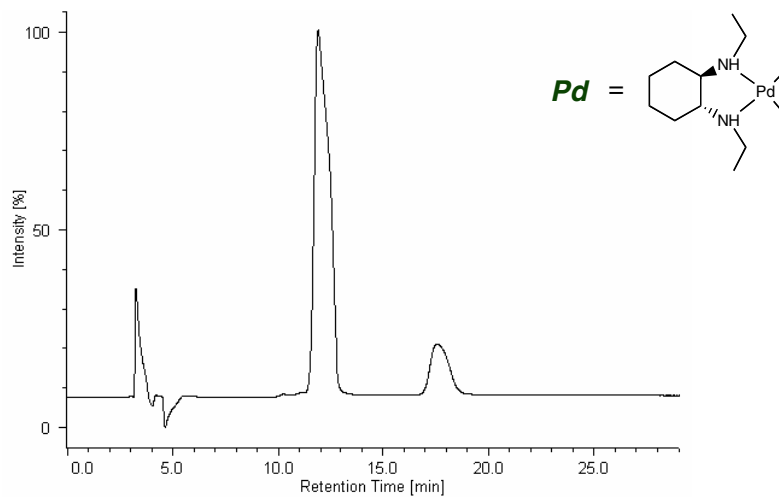


Figure S4-1. The HPLC analysis of **4b** produced inside cage **1b** with the chiral auxiliary ((1*R*, 2*R*)-*N*, *N'*- diethyl - 1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 3:1 ratio.

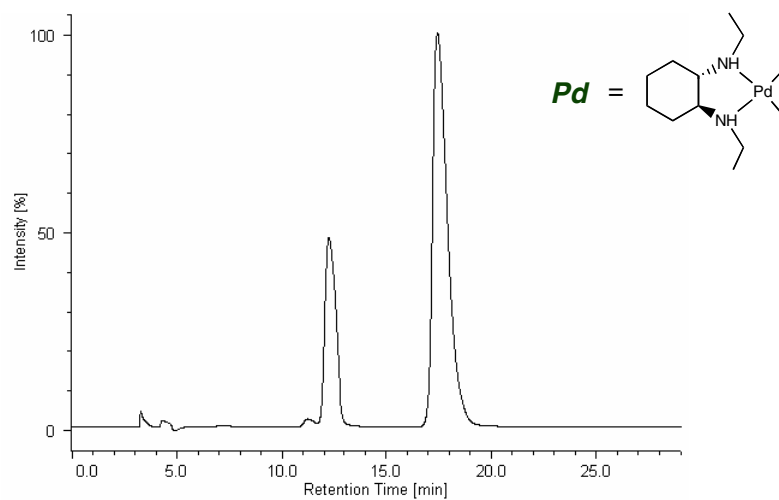


Figure S4-2. The HPLC analysis of **4b** produced inside cage **1b** with the chiral auxiliary ((1*S*, 2*S*)-*N*, *N'*- diethyl - 1,2-diaminocyclohexane) on each Pd center. The enantiomers were formed in 1:3 ratio.

X-ray crystallographic analysis and VCD measurement of **4a**.

The major enantiomer was obtained in an optically pure form by resolving racemic **4a** with preparative chiral HPLC and recrystallized from chloroform. X-ray diffraction study using Cu K_{α} radiation could successfully determine the absolute configuration which showed the Flack parameter of 0.02(13). The result shows that the major enantiomer has 1*S*,2*R*, 2*aR*,10*aR* configuration. And we also examined the absolute configuration by VCD measurement, which also indicated the same absolute configuration as the X-ray structure for the major enantiomer on the basis of the DFT calculation with BLYP/6-31G* level of theory.

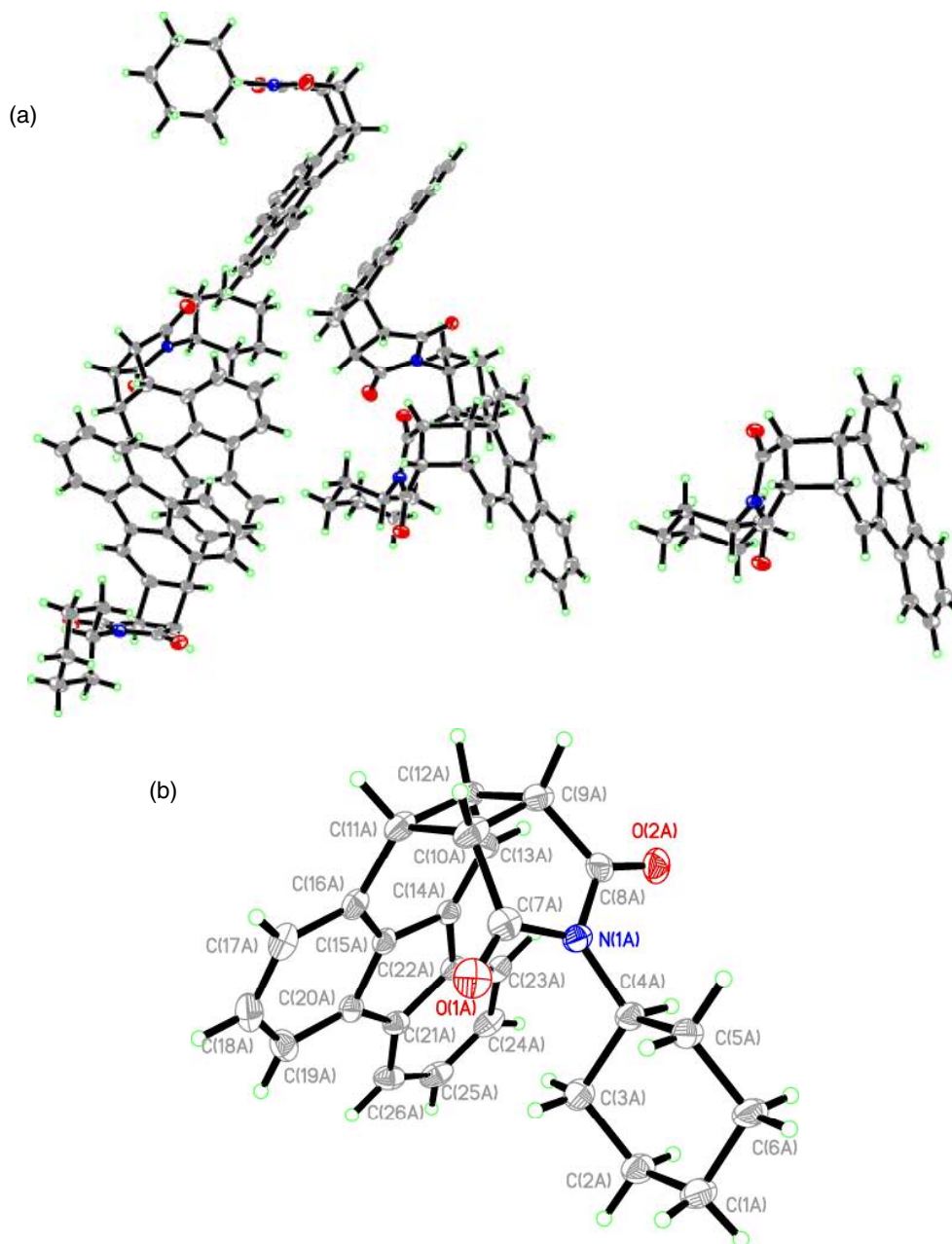


Figure S5. ORTEP view of (1*S*, 2*R*, 2*aR*, 10*aR*)-**4a** (30% probability level).

Table S1. Crystal data and structure refinement for **4a**.

Identification code	nishioka	
Empirical formula	C ₂₆ H ₂₃ NO ₂	
Formula weight	381.45	
Temperature	150(2) K	
Wavelength	1.54186 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁	
Unit cell dimensions	<i>a</i> = 19.2325(4) Å	$\alpha = 90^\circ$.
	<i>b</i> = 9.97896(18) Å	$\beta = 106.0721(7)^\circ$.
	<i>c</i> = 31.6956(6) Å	$\gamma = 90^\circ$.
Volume	5845.27(18) Å ³	
Z	12	
Density (calculated)	1.300 Mg/m ³	
Absorption coefficient	0.643 mm ⁻¹	
F(000)	2424	
Crystal size	0.57 x 0.18 x 0.05 mm ³	
Theta range for data collection	3.12 to 68.29°.	
Index ranges	-23 ≤ <i>h</i> ≤ 23, -11 ≤ <i>k</i> ≤ 10, -38 ≤ <i>l</i> ≤ 38	
Reflections collected	97698	
Independent reflections	20642 [R(int) = 0.0291]	
Completeness to theta = 68.29°	99.1 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9685 and 0.7106	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20642 / 1 / 1567	
Goodness-of-fit on F ²	1.064	
Final R indices [I > 2σ(I)]	<i>R</i> ₁ = 0.0384, <i>wR</i> ₂ = 0.0828	
R indices (all data)	<i>R</i> ₁ = 0.0569, <i>wR</i> ₂ = 0.0998	
Absolute structure parameter	0.02(13)	
Extinction coefficient	none	
Largest diff. peak and hole	0.228 and -0.201 e.Å ⁻³	

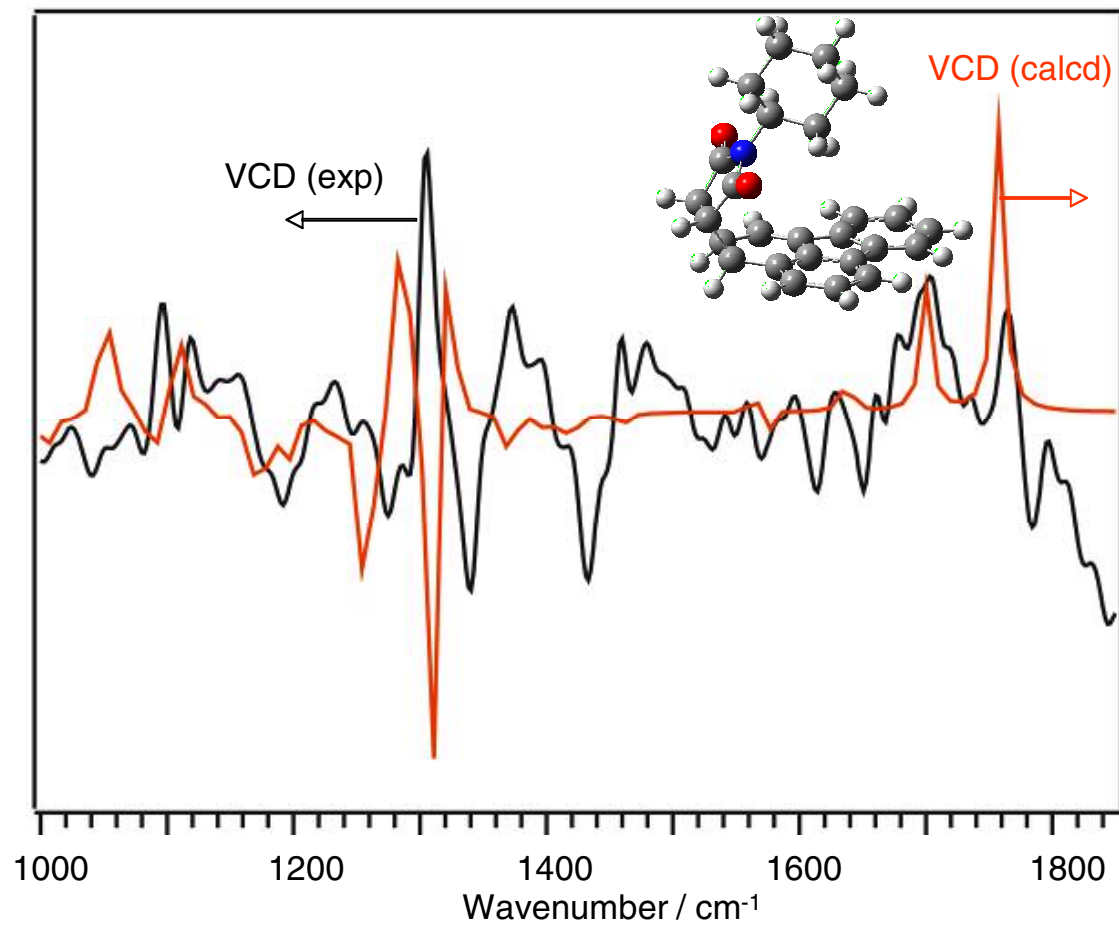


Figure S6. The VCD spectrum of the major enantiomer of **4a** (CDCl₃, 0.011 M, BaF₂, 491 μm path length) with the predicted spectrum (B3LYP/6-31G*, scale factor = 0.95). The VCD spectrum was recorded with 4 h data collection time at 4 cm⁻¹ resolution. The baseline was obtained from the spectrum of CDCl₃.

The optimized structure of cage **1b**.

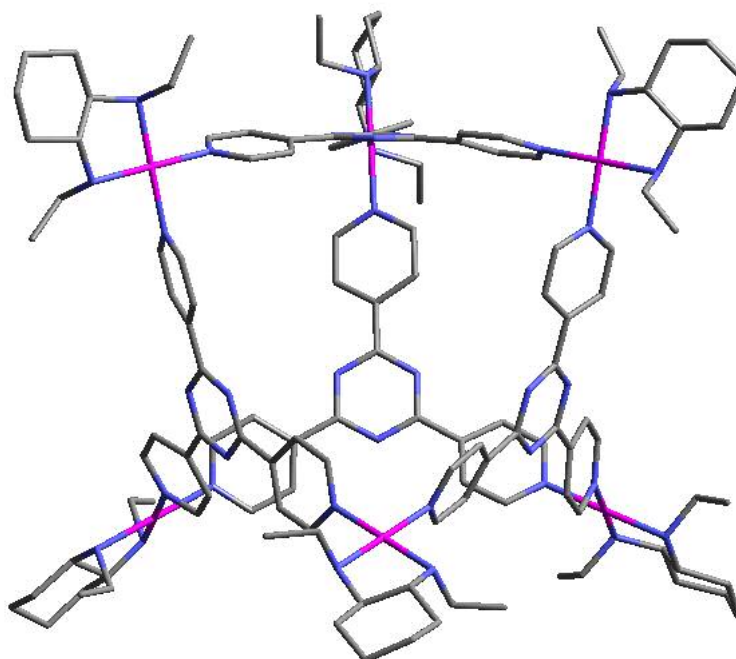



Figure S7. Optimized structure of **1b**. Note that three pyridine rings on the ligand are tilted toward the triazine ring in the same direction (clockwise). When the chiral auxiliaries were switched to (1*S*, 2*S*) isomers, the tilted direction of all pyridine rings was reversed (counterclockwise).

Table S2. Dihedral angles between the pyridine rings and the triazine ring on the ligand of **1a-1d**.

	1b	1c	1d	1a
	17P	13P	~0P	0P
<i>ee</i> (%)	40	20	5	0

The optimized structure of **2a**.

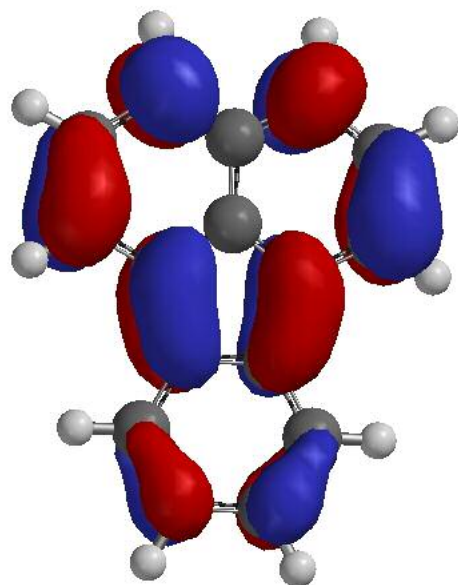


Figure S7. The LUMO of **2a**. The structure was optimized by the DFT calculation at the B3LYP level of theory with 6-31G* basis set.