Supplementary Information

Synthesis of Novel Twisted π-Conjugated Macrocycle via Double Friedel-Crafts Reaction and Its Physical Properties

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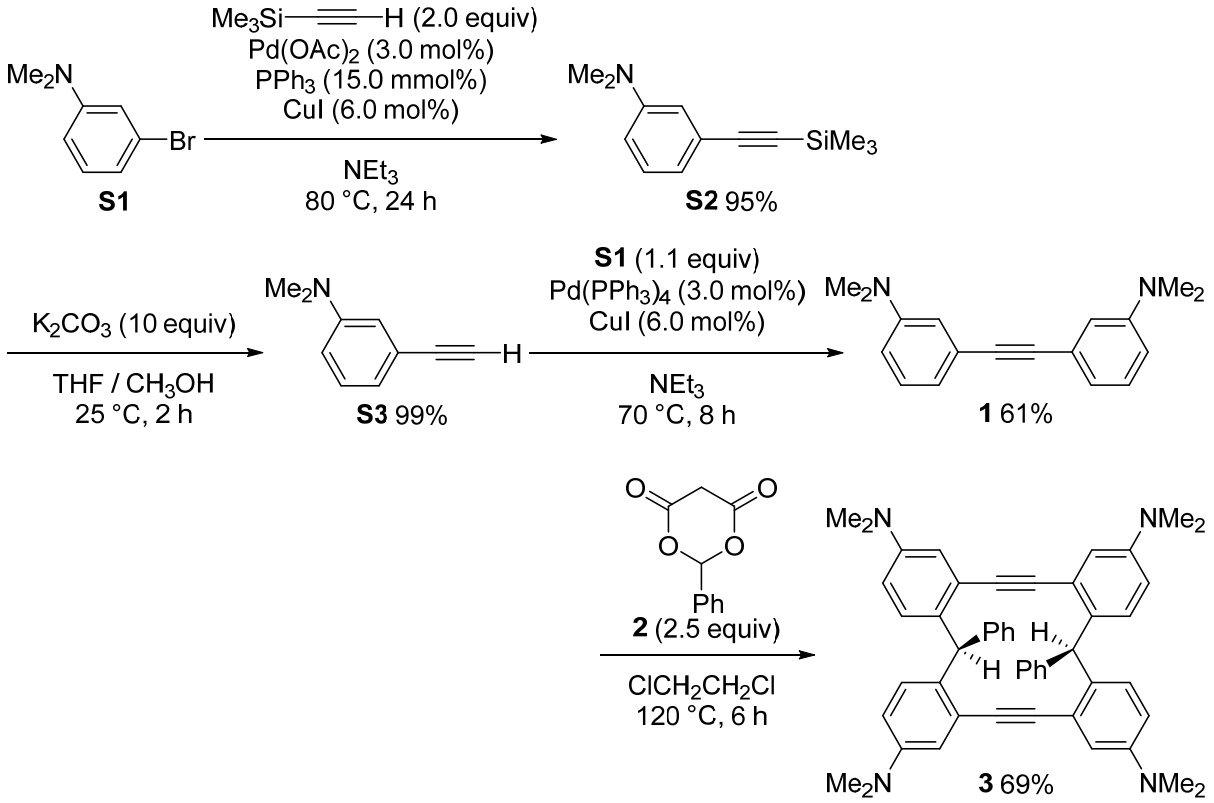
1. General

All reactions were carried out using standard Schlenk techniques under an inert atmosphere. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Column chromatography was performed on silica gel 60N (Kanto Chemical CO., Inc., spherical neutral, particle size 63-210 μm).

NMR spectra were recorded on JEOL ECZ-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) and JEOL JNM-ECA600 (600 MHz for ^{1}H NMR, 150 MHz for ^{13}C NMR). Proton and carbon chemical shifts are reported relative to the residual solvent ($CDCl_3$ (δ 7.26 for ^{1}H NMR or δ 77.16 for ^{13}C NMR), CD_2Cl_2 (δ 5.32 for ^{1}H NMR or δ 53.84 for ^{13}C NMR), acetone-d_6 (δ 2.05 for ^{1}H NMR or δ 29.84, 206.26 for ^{13}C NMR)) used as an internal reference. UV-vis absorption spectra were recorded on a V650 spectrophotometer (JASCO). Emission spectra were recorded on C9920-02 (Hamamatsu Photonics). HRMS were measured on a JEOL JMS-700 spectrometer.

2. Synthesis and Characterization of Substrates

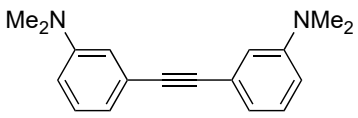


Scheme S1. Synthesis of twisted macrocycle **3**.

Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$)

$Pd(PPh_3)_4$ was prepared by the modified procedure of the reported method[1]. To a flame-dried 50 mL two-neck round bottom flask with a condenser and a magnetic stirrer were added $PdCl_2$ (0.500 g, 2.82 mmol, 1.0 equiv) and triphenylphosphine (PPh_3, 3.70 g, 14.1 mmol, 5.0 equiv) followed by the addition of degassed DMSO (33 mL). The mixture was heated at 140 °C. After the solid was completely dissolved, an orange solution was obtained. Then, the heat was turned off and the mixture was kept stirring rapidly for 1 min. Hydrazine hydrate ($N_2H_4 \cdot H_2O$, 0.56 mL) was added over 1 min via syringe. The reaction was cooled to room temperature after the addition of hydrazine hydrate, and yellow solid was precipitated. The solid was washed with ethanol (2 × 15 mL) and ether (2 × 15 mL) to give $Pd(PPh_3)_4$ (2.97 g, 2.57 mmol, 91%) as a golden yellow solid. The prepared catalyst was stored under N_2 at -15 °C and could be used without further purification.

3,3'-(Ethyne-1,2-diyl)bis(*N*,*N*-dimethylaniline) (1)

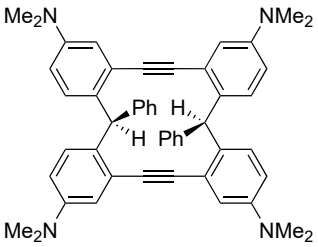


3-Bromo-*N*,*N*-dimethylaniline (**S3**, 2.00 g, 10.0 mmol, 1.0 equiv) and 3-ethynyl-*N*,*N*-dimethylaniline (**S1**, 0.870 g, 6.60 mmol, 1.1 equiv) were added in a 100 mL two-neck round bottle flask under N_2 atmosphere, followed by the addition of $Pd(PPh_3)_4$ (347 mg, 0.300 mmol, 5.0 mol%) and CuI (114 mg, 0.600 mmol, 6.0 mol%). NEt_3 (30 mL, dehydrated by MS4A and and

degassed by N_2 bubbling) was added into the flask by syringe. After stirring at 70 ℃ for 8 h, the reaction mixture was concentrated by evaporation and the residue was filtered through Celite with CH_2Cl_2 as an eluent. The mixture was purified by column chromatography on silica gel (hexane/EtOAc = 20/1 as the eluent, R_f = 0.15) to give 3,3'-(ethyne-1,2-diyl)bis(*N*,*N*-dimethylaniline) (**1**) as a yellow solid (0.96 g, 3.65 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, *J* = 8.1, 8.1 Hz, 2H), 6.94-6.88 (m, 4H), 6.75-6.68 (m, 2H), 2.97 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 129.1, 124.0, 120.2, 115.6, 112.9, 89.4, 40.7; HRMS (EI$^+$) Calcd for $C_{18}H_{20}N_2$ ([M]$^+$) 264.1626, Found 264.1626.

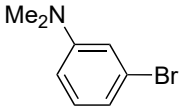
Twisted macrocycle (3)



A 20 mL reaction tube equipped with a screw cap and a magnetic stirrer bar was charged with nitrogen gas. 3,3'-(Ethyne-1,2-diyl)bis(N,N-dimethylaniline) (**1**, 423 mg, 1.60 mmol, 1.0 equiv), 2-phenyl-1,3-dioxane-4,6-dione (**2**, 769 mg, 4.00 mmol, 2.5 equiv), which was synthesized via the reported method,[2] and dehydrated 1,2-dichloroethane (8.0 mL) were added under nitrogen atmosphere. The mixture was stirred at 120 °C for 6 h. After the reaction completed, the reaction mixture was concentrated in vacuo. The mixture was purified by column chromatography on silica gel (Hexane/CH_2Cl_2/EtOAc/NEt_3 = 10:1:1:0.1 as the eluent, R_f = 0.17) to give **3** as a brown solid (387 mg, 0.549 mmol, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 7.4, 7.4 Hz, 4H), 7.14 (t, *J* = 7.5, 2H), 7.09 (s, 2H), 7.06 (d, *J* = 5.7 Hz, 4H), 6.90 (d, *J* = 8.7 Hz, 4H), 6.85 (d, *J* = 2.8 Hz, 4H), 6.63 (dd, *J* = 8.7, 2.8 Hz, 4H), 2.89 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 144.9, 133.8, 130.1, 129.4, 128.2, 125.8, 124.2, 116.2, 112.9, 91.6, 50.5, 40.7; HRMS (FAB$^+$) Calcd for $C_{50}H_{48}N_4$ ([M]$^+$) 704.3879, Found 704.3879.

3-Bromo-*N*,*N*-dimethylaniline (S1)

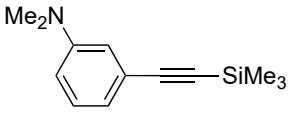


3-Bromo-*N*,*N*-dimethylaniline (**S1**) was synthesized according to the reported method[2]: A mixture of 3-bromoaniline (8.60 g, 50.0 mmol, 1.0 equiv), iodomethane (15.6 g, 110 mmol, 2.2 equiv), and K_2CO_3 (15.2 g, 110 mmol, 2.2 equiv) in dehydrated DMF (100 mL) was stirred at 75 °C for 24 h. After completion of the reaction monitored by TLC, the reaction mixture was filtered to remove the residual solid. The reaction mixture was poured into saturated $NaHCO_3$ aqueous solution and the mixture was extracted with ethyl acetate (3 x 50 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The mixture was purified by column chromatography on silica gel (hexane, R_f = 0.13) to give 3-bromo-*N*,*N*-dimethylaniline (**S1**) as a pale yellow oil (9.50 g, 47.5 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.85-6.79 (m, 2H), 6.62 (ddd, *J* = 8.4, 2.5, 1.0 Hz, 1H), 2.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 130.4, 123.5,

119.2, 115.2, 111.0, 40.5. The analytical data is in accordance with the previous report[2].

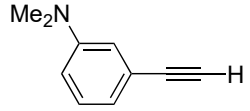
_N_,_N_-Dimethyl-3-((trimethylsilyl)ethynyl)aniline (S2)



_N_,_N_-Dimethyl-3-((trimethylsilyl)ethynyl)aniline (**S2**) was synthesized by the modified procedure of the reported method[3]: 3-Bromo-_N_,_N_-dimethylaniline (**S1**, 2.00 g, 10.0 mmol, 1.0 equiv) was added into a 200 mL two-neck round bottle flask under N_2 atmosphere, followed by the addition of $Pd(OAc)_2$ (67.4 mg, 0.300 mmol, 3.0 mol%), PPh_3 (393 mg, 0.150 mmol, 15.0 mol%) and CuI (114 mg, 0.600 mmol, 6.0 mol%). NEt_3 (100 mL, dehydrated by MS4A and degassed by N_2 bubbling) was added into the flask by syringe, followed by the slow addition of trimethylsilylacetylene (1.96 g, 20.0 mmol, 2.0 equiv). After stirring at 80 ℃ for 24 h, the reaction mixture was concentrated by evaporation and the residue was filtered through Celite with CH_2Cl_2 as the eluent. The mixture was purified by column chromatography on silica gel (using hexane to remove possible residual aniline **S1** followed by using hexane/CH_2Cl_2 = 2/1 as the eluent, R_f = 0.50) to give _N_,_N_-dimethyl-3-((trimethylsilyl)ethynyl)aniline (**S2**) as a pale yellow oil (2.07 g, 9.52 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (dd, J = 8.0, 8.0 Hz, 1H), 6.88-6.78 (m, 2H), 6.70 (dd, J = 8.4, 2.5 Hz, 1H), 2.94 (s, 6H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 129.0, 123.6, 120.5, 115.8, 113.2, 106.3, 92.8, 40.6, 0.2; HRMS (EI^+) Calcd for $C_{13}H_{19}NSi$ ($[M]^+$) 217.1287, Found 127.1287.

3-Ethynyl-_N_,_N_-dimethylaniline (S3)



3-Ethynyl-_N_,_N_-dimethylaniline (**S3**) was synthesized by the reported method[4]: _N_,_N_-Dimethyl-3-((trimethylsilyl)ethynyl)aniline (**S2**, 5.78 g, 26.6 mmol, 1.0 equiv), K_2CO_3 (36.8 g, 266 mmol, 10 equiv) were added into a 500 mL three-neck round bottom flask followed by the addition of tetrahydrofuran (90 mL) and CH_3OH (90 mL) as a solvent. The mixture was stirred at 25 ℃ for 2 h. The reaction mixture was concentrated by evaporation and poured into water and extracted with CH_2Cl_2 (3 x 30 mL). The organic layer was washed with saturated brine and dried with $MgSO_4$. $MgSO_4$ was filtered and the organic layer was concentrated in vacuo. The crude mixture was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 3/1 as the eluent, R_f = 0.20) to give 3-ethynyl-_N_,_N_-dimethylaniline (**S3**) as a pale yellow solid (3.82 g, 26.3 mmol, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.13 (m, 1H), 6.90-6.81 (m, 2H), 6.78-6.68 (m, 1H), 3.03 (s, 1H), 2.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 129.1, 122.6, 120.4, 116.0, 113.4, 84.8, 76.1, 40.6; HRMS (EI^+) Calcd for $C_{10}H_{11}N$ ($[M]^+$) 145.0891, Found 145.0890.

3. Crystal Data of Twisted Macrocycle

Experimental. Single colourless prism-shaped crystals of compound **3** were obtained by recrystallisation from toluene/hexane. A suitable crystal 0.25×0.17×0.15 mm^3 was selected and mounted on a suitable support on an XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at a steady T = 100.00(10) K during data collection. The structure was solved with the ShelXT[5] structure solution program using the Intrinsic Phasing solution method and by using **Olex2**[6] as the graphical interface. The model was refined with version 2018/3 of ShelXL 2018/3[7] using Least Squares minimisation.

Each configuration of enantiomers was named as (R_a,R_a)-**3** (Figure S1a) and (S_a,S_a)-**3** (Figure S1b) according to the definition of axial chirality.[8] The two "near" substituents NMe_2 and methine groups on the chiral axial diarylalkyne are ranked as ***a*** and ***b***, respectively. The two "far" substituents NMe_2 and methine groups are ranked as ***c*** and ***d***, respectively (priority: ***a*** > ***b*** > ***c*** > ***d***). If the direction from ***b*** to ***c*** is clockwise, the axial chirality of diarylalkyne is R_a. On the contrary, if the direction from ***b*** to ***c*** is anti-clockwise, the axial chirality of diarylalkyne is S_a.

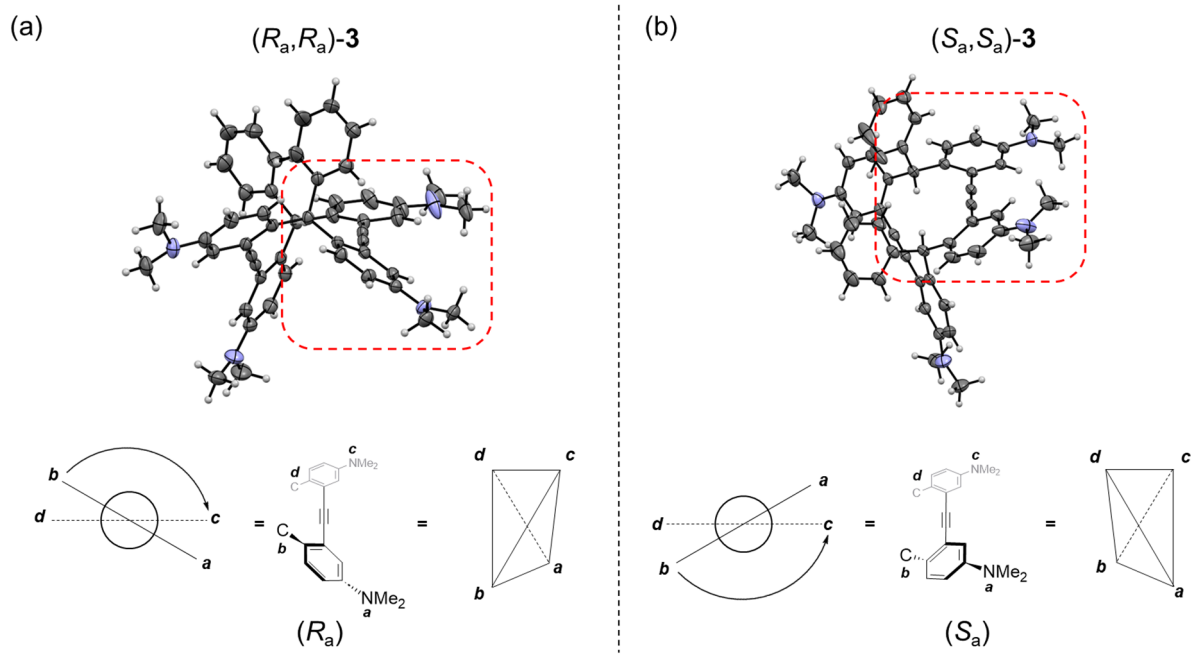


Figure S1. Assignment of the axial chirality of (a) (R_a,R_a)-**3**; (b) (S_a,S_a)-**3**.

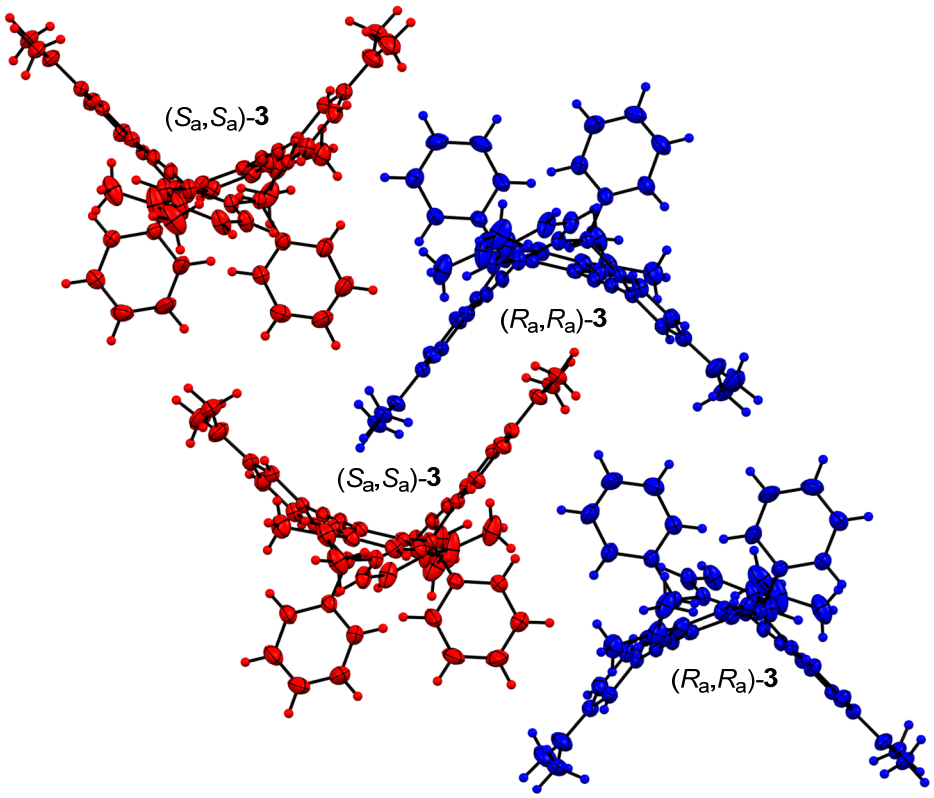


Figure S2. Single crystal X-ray structure of twisted macrocycle **3** in a unit cell.

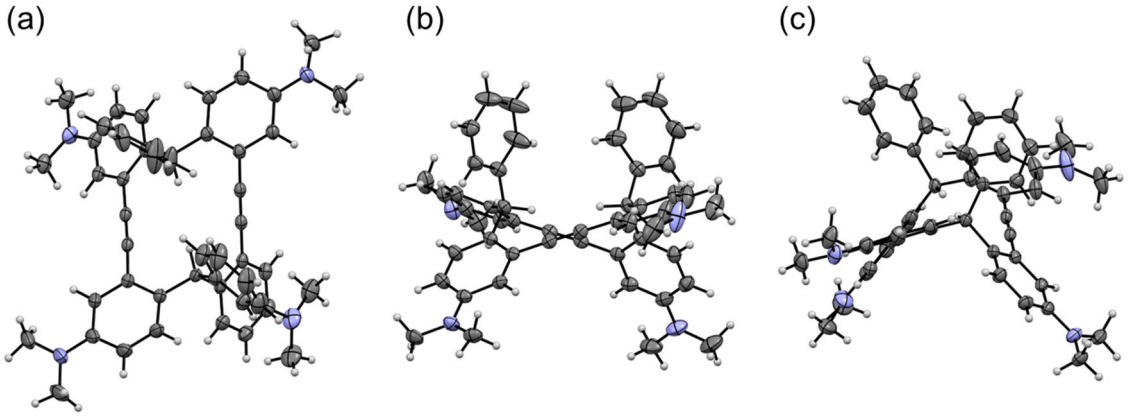


Figure S3. ORTEP drawings of (R_a,R_a)-**3**: (a) top view, (b) front view, and (c) side view. Thermal ellipsoids are drawn at 50% probability level.

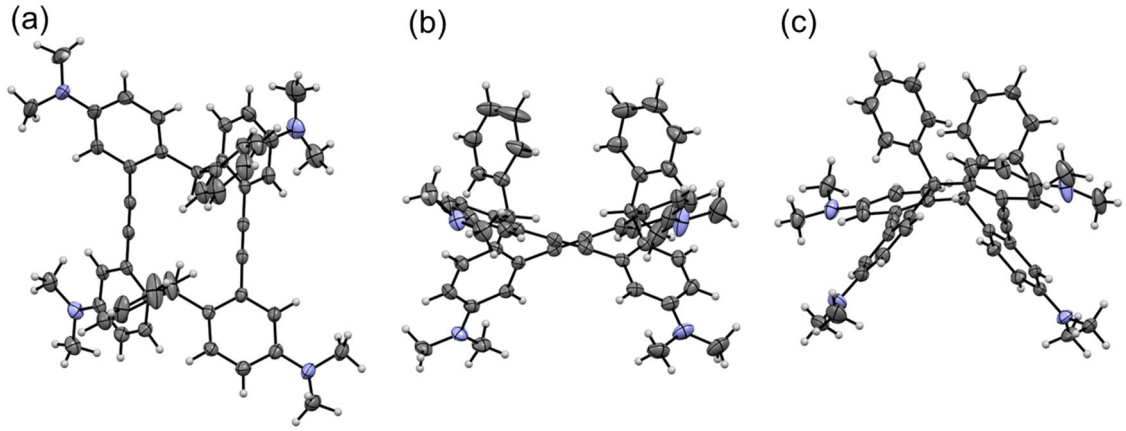


Figure S4. ORTEP drawings of (S_a,S_a)-**3**: (a) top view, (b) front view, and (c) side view. Thermal ellipsoids are drawn at 50% probability level.

Table S1. Crystal data and structure refinement for **3** (CCDC2335048)

Identification code	**molecule_3**
Empirical formula	$C_{64}H_{64}N_4$
Moiety formula	$C_{50}H_{48}N_4$, 2[C_7H_8]
Formula weight	889.19
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.6774(4)
b/Å	23.2733(8)
c/Å	17.2556(5)
α/°	90
β/°	92.162(3)
γ/°	90
Volume/Å^3	5087.6(3)
Z	4
ρ_{calc}g/cm^3	1.161
μ/mm^{-1}	0.510
F(000)	1904.0
Crystal size/mm^3	0.248 × 0.168 × 0.148
Radiation	Cu K_α (λ = 1.54184)
2θ range for data collection/°	6.38 to 151.132
Index ranges	$-9 \le h \le 15$, $-28 \le k \le 28$, $-21 \le l \le 21$
Reflections collected	36578
Independent reflections	10141 [R_{int} = 0.0322, R_{sigma} = 0.0313]
Data/restraints/parameters	10141/0/495
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0609, wR_2 = 0.1909
Final R indexes [all data]	R_1 = 0.0667, wR_2 = 0.1965
Largest diff. peak/hole / e Å^{-3}	0.33/-0.29

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
N46	3554.4(13)	4993.5(7)	4013.6(9)	38.3(4)
N49	1818.1(13)	3295.8(8)	8981.6(9)	43.4(4)
C24	5134.2(13)	3454.7(7)	7660.6(9)	28.2(3)
C23	6067.6(13)	3545.6(7)	7707.0(9)	27.6(3)
C25	4024.4(13)	3331.8(7)	7615.5(9)	27.8(3)
C22	7169.1(13)	3688.8(7)	7763.8(9)	27.5(3)
C2	3979.2(13)	3629.1(7)	5627.6(9)	26.8(3)
C9	6707.1(13)	3361.7(7)	5319.4(9)	28.8(3)
C16	7586.1(13)	2895.4(7)	6794.7(9)	27.5(3)
C8	5835.4(13)	3562.9(7)	5255.9(9)	27.6(3)
C17	7913.3(13)	3398.9(7)	7319.0(9)	27.5(3)
C5	3696.9(14)	4553.5(7)	4541.9(10)	31.3(4)
C7	4811.2(13)	3820.7(7)	5175.9(9)	26.8(3)
C30	3526.0(13)	3157.9(7)	6913.8(9)	27.4(3)
N52	8838.2(16)	4749.9(8)	8859.0(11)	52.1(5)
C1	4140.2(13)	3117.8(7)	6171.8(9)	27.6(3)
C6	4670.9(13)	4274.1(7)	4647.6(9)	28.7(3)
C15	8181.8(13)	2878.8(8)	6044.6(9)	30.8(4)
C29	2465.5(14)	3009.6(8)	6936.2(10)	31.8(4)
C10	7744.5(13)	3117.9(8)	5354.5(9)	30.7(4)
C26	3461.4(14)	3370.0(8)	8301.6(10)	32.6(4)
C31	3953.5(14)	2539.6(7)	5774.0(10)	32.2(4)
C21	7479.3(15)	4141.9(8)	8260.4(10)	33.6(4)
C37	7653.9(14)	2313.6(8)	7201.2(10)	33.4(4)
C3	3021.5(14)	3911.9(8)	5519.4(10)	32.9(4)
C27	2388.9(14)	3236.9(8)	8312.1(10)	34.6(4)
C4	2872.1(14)	4361.7(8)	4997.3(11)	34.7(4)
C28	1901.5(14)	3046.1(8)	7608.4(11)	35.5(4)
C20	8532.0(16)	4316.5(8)	8339.9(11)	37.7(4)
N43	9907.6(14)	2938.0(13)	3989.5(11)	69.4(7)
C18	8949.7(14)	3587.7(8)	7397.7(10)	34.3(4)
C19	9262.9(15)	4029.9(8)	7893.0(11)	38.3(4)
C11	8315.1(15)	3123.3(9)	4671.1(10)	39.0(4)
C36	3463.4(15)	2470.5(8)	5051.3(11)	36.6(4)
C48	2536.4(17)	5267.4(8)	3916.0(12)	41.5(4)
C47	4378.7(17)	5130.2(8)	3484.6(11)	40.5(4)
C14	9178.3(14)	2632.9(9)	6006.1(11)	38.8(4)
C12	9337.4(15)	2900.7(11)	4650.4(11)	47.5(5)
C13	9751.5(15)	2642.0(11)	5333.9(12)	46.7(5)
C42	8340.0(16)	2198.8(9)	7827.1(11)	41.0(4)
C35	3304.5(17)	1930.0(9)	4731.2(12)	44.1(5)

Atom	x	y	z	U_{eq}
C38	7007(2)	1868.6(9)	6919.6(12)	47.3(5)
C51	2390.6(18)	3445.9(11)	9704.2(11)	47.8(5)
C50	902.6(17)	2924.0(12)	9067.7(13)	51.5(6)
C34	3640(2)	1447.6(9)	5122.1(13)	57.4(6)
C41	8396(2)	1651.5(10)	8156.0(13)	52.3(5)
C54	8038(2)	5087.4(9)	9227.7(14)	55.1(6)
C45	9434.3(19)	3163.7(13)	3282.8(12)	61.3(7)
C40	7758(2)	1218.6(10)	7873.9(14)	60.6(7)
C44	10971.0(18)	2723.0(14)	3996.7(15)	65.1(7)
C39	7052(2)	1327.0(10)	7254.2(14)	61.0(7)
C53	9908(2)	4942.6(11)	8880.0(16)	63.0(7)
C32	4305(3)	2052.0(10)	6159.0(12)	62.8(7)
C33	4154(3)	1512.0(10)	5839.7(14)	84.5(11)

Table S3. Anisotropic displacement parameters ($\times 10^4$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N46	44.4(9)	31.5(8)	38.6(8)	11.1(6)	-3.5(7)	1.7(6)
N49	39.4(9)	59.2(11)	32.2(8)	6.0(7)	10.7(7)	5.6(8)
C24	36.0(9)	29.0(8)	19.8(7)	-0.7(6)	2.2(6)	4.8(6)
C23	34.7(9)	28.1(8)	20.1(7)	0.5(6)	2.4(6)	4.2(6)
C25	31.7(8)	27.2(8)	24.7(8)	2.6(6)	2.9(6)	4.0(6)
C22	33.9(8)	27.4(8)	21.2(7)	4.4(6)	-0.9(6)	1.5(6)
C2	32.8(8)	25.5(8)	21.9(7)	-0.2(6)	-1.4(6)	2.1(6)
C9	33.2(9)	33.7(8)	19.4(7)	2.5(6)	-1.2(6)	-3.0(7)
C16	27.0(8)	33.4(8)	21.8(7)	0.0(6)	-1.7(6)	4.1(6)
C8	32.9(9)	30.6(8)	19.2(7)	1.7(6)	-1.2(6)	-3.0(6)
C17	30.7(8)	30.2(8)	21.3(7)	3.7(6)	-2.0(6)	3.1(6)
C5	41.0(9)	25.6(8)	26.8(8)	0.7(6)	-5.8(7)	0.5(7)
C7	31.2(8)	26.7(8)	22.2(7)	-1.7(6)	-3.7(6)	-0.7(6)
C30	31.9(8)	25.1(7)	25.1(8)	4.3(6)	1.5(6)	5.1(6)
N52	64.0(12)	42.7(10)	49.4(10)	-11.5(8)	-2.7(9)	-15.8(8)
C1	30.4(8)	29.8(8)	22.4(7)	3.0(6)	0.1(6)	5.0(6)
C6	35.2(8)	27.2(8)	23.3(7)	0.8(6)	-2.6(6)	-4.2(6)
C15	28.6(8)	39.2(9)	24.4(8)	-3.9(7)	-0.8(6)	2.3(7)
C29	30.9(8)	34.2(9)	30.0(8)	2.6(7)	-1.5(6)	4.1(7)
C10	27.8(8)	40.3(9)	24.1(8)	-2.5(7)	-0.2(6)	-1.5(7)
C26	35.8(9)	37.0(9)	25.2(8)	0.4(7)	2.6(7)	3.4(7)
C31	40.7(9)	30.5(9)	25.8(8)	2.0(6)	5.5(7)	5.8(7)
C21	43.9(10)	30.2(8)	26.5(8)	1.1(7)	0.5(7)	-0.1(7)
C37	39.2(9)	35.4(9)	25.7(8)	-1.3(7)	1.5(7)	7.6(7)
C3	32.9(9)	34.0(9)	32.1(9)	6.0(7)	4.6(7)	6.0(7)
C27	35.9(9)	38.9(9)	29.5(9)	5.7(7)	7.0(7)	7.8(7)
C4	35.8(9)	33.6(9)	34.7(9)	4.1(7)	0.1(7)	8.4(7)
C28	31.0(9)	40.3(10)	35.4(9)	5.7(7)	2.6(7)	2.4(7)
C20	50.1(11)	31.9(9)	30.6(9)	2.2(7)	-4.9(8)	-7.2(8)
N43	33.8(9)	142(2)	33.3(9)	-20.3(11)	9.3(7)	-9.3(11)
C18	32.8(9)	40.4(10)	29.5(8)	3.8(7)	-1.8(7)	2.0(7)
C19	36.6(9)	42.2(10)	35.7(9)	4.7(8)	-5.6(7)	-8.7(8)
C11	33.3(9)	60.6(12)	23.1(8)	-2.8(8)	0.4(7)	-5.7(8)
C36	41.3(10)	32.5(9)	35.4(9)	2.3(7)	-5.7(7)	2.9(7)
C48	51.0(11)	32.5(9)	40.2(10)	10.0(8)	-6.2(8)	7.8(8)
C47	55.4(11)	32.5(9)	33.4(9)	9.6(7)	-1.9(8)	-3.3(8)
C14	30.1(9)	53.7(11)	32.3(9)	-8.4(8)	-2.6(7)	8.6(8)
C12	29.9(9)	82.3(16)	30.7(9)	-18.0(10)	4.4(7)	-8.9(9)
C13	28.0(9)	72.0(14)	40.2(10)	-18.2(10)	1.6(7)	6.5(9)
C42	45.0(10)	42.2(10)	35.1(9)	4.1(8)	-6.2(8)	7.8(8)
C35	52.3(12)	41.9(11)	37.9(10)	-5.8(8)	-1.5(8)	-1.5(9)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C38	68.6(14)	39.4(10)	33.0(10)	-2.4(8)	-9.0(9)	-3.2(10)
C51	51.8(12)	61.4(13)	31.2(10)	-0.2(9)	14.7(8)	6.5(10)
C50	38.8(10)	75.0(16)	41.4(11)	19.4(10)	11.3(8)	3.8(10)
C34	102.8(19)	30.2(10)	39.9(11)	-4.8(8)	14.4(11)	0.4(11)
C41	66.2(14)	47.8(12)	42.4(11)	9.5(9)	-6.0(10)	15.2(10)
C54	80.7(16)	34.5(10)	49.3(12)	-9.4(9)	-10.4(11)	-0.2(10)
C45	54.7(13)	99(2)	31.7(10)	-14.8(11)	16.1(9)	-22.5(13)
C40	102(2)	33.5(11)	46.6(12)	4.9(9)	-0.4(12)	12.9(12)
C44	40.9(12)	99(2)	56.4(14)	-31.1(14)	21.8(10)	-9.4(12)
C39	99(2)	36.8(11)	46.3(12)	-3.1(9)	-7.8(12)	-9.5(12)
C53	72.3(16)	55.1(14)	60.7(15)	-9.1(11)	-9.5(12)	-28.3(12)
C32	119(2)	39.5(11)	28.5(10)	-0.3(8)	-12.4(11)	25.1(13)
C33	181(4)	31.6(11)	39.9(13)	2.9(9)	-8.0(16)	30.0(16)

Table S4. Bond lengths for **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N46	C5	1.378(2)	N52	C53	1.427(3)
N46	C48	1.444(2)	C1	C31	1.525(2)
N46	C47	1.449(3)	C15	C10	1.409(2)
N49	C27	1.393(2)	C15	C14	1.391(2)
N49	C51	1.461(3)	C29	C28	1.388(3)
N49	C50	1.460(3)	C10	C11	1.407(2)
C24	C23	1.202(2)	C26	C27	1.395(3)
C24	C25	1.435(2)	C31	C36	1.381(3)
C23	C22	1.435(2)	C31	C32	1.380(3)
C25	C30	1.404(2)	C21	C20	1.397(3)
C25	C26	1.408(2)	C37	C42	1.387(3)
C22	C17	1.410(2)	C37	C38	1.397(3)
C22	C21	1.406(2)	C3	C4	1.389(2)
C2	C7	1.407(2)	C27	C28	1.413(3)
C2	C1	1.525(2)	C20	C19	1.397(3)
C2	C3	1.388(2)	N43	C12	1.376(3)
C9	C8	1.201(2)	N43	C45	1.438(3)
C9	C10	1.432(2)	N43	C44	1.438(3)
C16	C17	1.528(2)	C18	C19	1.386(3)
C16	C15	1.523(2)	C11	C12	1.397(3)
C16	C37	1.526(2)	C36	C35	1.386(3)
C8	C7	1.432(2)	C14	C13	1.392(3)
C17	C18	1.387(2)	C12	C13	1.408(3)
C5	C6	1.401(2)	C42	C41	1.395(3)
C5	C4	1.404(3)	C35	C34	1.369(3)
C7	C6	1.402(2)	C38	C39	1.387(3)
C30	C1	1.526(2)	C34	C33	1.386(4)
C30	C29	1.390(2)	C41	C40	1.370(4)
N52	C20	1.394(2)	C40	C39	1.391(4)
N52	C54	1.449(3)	C32	C33	1.383(3)

Table S5. Bond angles for **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N46	C48	119.97(16)	C14	C15	C10	116.82(16)
C5	N46	C47	120.02(16)	C28	C29	C30	122.51(16)
C48	N46	C47	119.50(15)	C15	C10	C9	121.59(15)
C27	N49	C51	118.32(16)	C11	C10	C9	117.50(15)
C27	N49	C50	117.78(18)	C11	C10	C15	120.91(16)
C50	N49	C51	115.22(16)	C27	C26	C25	121.47(16)
C23	C24	C25	178.48(18)	C36	C31	C1	124.47(15)
C24	C23	C22	176.71(17)	C32	C31	C1	117.84(16)
C30	C25	C24	120.84(14)	C32	C31	C36	117.70(18)
C30	C25	C26	121.15(16)	C20	C21	C22	121.49(17)
C26	C25	C24	117.97(15)	C42	C37	C16	123.48(17)
C17	C22	C23	121.39(15)	C42	C37	C38	118.09(18)
C21	C22	C23	117.71(15)	C38	C37	C16	118.41(16)
C21	C22	C17	120.87(16)	C2	C3	C4	122.82(16)
C7	C2	C1	120.17(14)	N49	C27	C26	121.73(17)
C3	C2	C7	116.45(15)	N49	C27	C28	121.30(17)
C3	C2	C1	123.31(15)	C26	C27	C28	116.96(16)
C8	C9	C10	177.18(17)	C3	C4	C5	121.07(16)
C15	C16	C17	112.97(14)	C29	C28	C27	121.00(17)
C15	C16	C37	110.30(13)	N52	C20	C21	121.02(19)
C37	C16	C17	113.51(13)	N52	C20	C19	121.70(18)
C9	C8	C7	178.14(18)	C21	C20	C19	117.26(16)
C22	C17	C16	121.11(14)	C12	N43	C45	120.70(19)
C18	C17	C22	116.48(15)	C12	N43	C44	119.5(2)
C18	C17	C16	122.39(15)	C44	N43	C45	119.71(19)
N46	C5	C6	121.58(16)	C19	C18	C17	122.93(17)
N46	C5	C4	121.63(16)	C18	C19	C20	120.94(17)
C6	C5	C4	116.79(15)	C12	C11	C10	121.66(17)
C2	C7	C8	120.63(14)	C31	C36	C35	121.28(17)
C6	C7	C2	121.29(15)	C15	C14	C13	122.50(18)
C6	C7	C8	118.07(15)	N43	C12	C11	121.0(2)
C25	C30	C1	120.92(15)	N43	C12	C13	122.0(2)
C29	C30	C25	116.86(15)	C11	C12	C13	117.01(17)
C29	C30	C1	122.19(15)	C14	C13	C12	120.97(18)
C20	N52	C54	119.46(19)	C37	C42	C41	120.9(2)
C20	N52	C53	119.0(2)	C34	C35	C36	120.68(19)
C53	N52	C54	119.90(19)	C39	C38	C37	121.0(2)
C2	C1	C30	114.10(13)	C35	C34	C33	118.6(2)
C2	C1	C31	113.35(13)	C40	C41	C42	120.4(2)
C31	C1	C30	110.86(14)	C41	C40	C39	119.6(2)
C5	C6	C7	121.58(16)	C38	C39	C40	120.0(2)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	C15	C16	121.08(15)	C31	C32	C33	121.2(2)
C14	C15	C16	122.09(15)	C32	C33	C34	120.5(2)

Table S6. Torsion angles for **3**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N46	C5	C6	C7	-178.97(15)	C15	C10	C11	C12	-0.9(3)
N46	C5	C4	C3	179.01(17)	C15	C14	C13	C12	-0.5(3)
N49	C27	C28	C29	177.49(17)	C29	C30	C1	C2	81.54(19)
C24	C25	C30	C1	-2.5(2)	C29	C30	C1	C31	-47.9(2)
C24	C25	C30	C29	175.65(15)	C10	C15	C14	C13	3.0(3)
C24	C25	C26	C27	-177.63(16)	C10	C11	C12	N43	-176.3(2)
C23	C22	C17	C16	-3.8(2)	C10	C11	C12	C13	3.3(3)
C23	C22	C17	C18	177.55(15)	C26	C25	C30	C1	179.94(15)
C23	C22	C21	C20	-178.84(15)	C26	C25	C30	C29	-1.9(2)
C25	C30	C1	C2	-100.44(17)	C26	C27	C28	C29	-1.7(3)
C25	C30	C1	C31	130.12(16)	C31	C36	C35	C34	-0.6(3)
C25	C30	C29	C28	2.0(2)	C31	C32	C33	C34	-0.2(5)
C25	C26	C27	N49	-177.41(17)	C21	C22	C17	C16	178.32(14)
C25	C26	C27	C28	1.8(3)	C21	C22	C17	C18	-0.4(2)
C22	C17	C18	C19	1.1(2)	C21	C20	C19	C18	-0.5(3)
C22	C21	C20	N52	-177.22(17)	C37	C16	C17	C22	-89.67(18)
C22	C21	C20	C19	1.3(3)	C37	C16	C17	C18	88.93(19)
C2	C7	C6	C5	-0.4(2)	C37	C16	C15	C10	135.56(17)
C2	C1	C31	C36	-13.9(2)	C37	C16	C15	C14	-44.9(2)
C2	C1	C31	C32	165.6(2)	C37	C42	C41	C40	-1.2(3)
C2	C3	C4	C5	0.4(3)	C37	C38	C39	C40	-0.8(4)
C9	C10	C11	C12	179.35(19)	C3	C2	C7	C8	178.86(15)
C16	C17	C18	C19	-177.54(16)	C3	C2	C7	C6	0.1(2)
C16	C15	C10	C9	-2.9(3)	C3	C2	C1	C30	-36.7(2)
C16	C15	C10	C11	177.32(17)	C3	C2	C1	C31	91.51(19)
C16	C15	C14	C13	-176.60(18)	C4	C5	C6	C7	0.7(2)
C16	C37	C42	C41	-177.45(18)	N43	C12	C13	C14	177.0(2)
C16	C37	C38	C39	178.5(2)	C11	C12	C13	C14	-2.7(3)
C8	C7	C6	C5	-179.24(15)	C36	C31	C32	C33	-1.2(4)
C17	C22	C21	C20	-0.9(2)	C36	C35	C34	C33	-0.8(4)
C17	C16	C15	C10	-96.21(19)	C48	N46	C5	C6	179.43(16)
C17	C16	C15	C14	83.4(2)	C48	N46	C5	C4	-0.3(3)
C17	C16	C37	C42	-27.0(2)	C47	N46	C5	C6	7.6(3)
C17	C16	C37	C38	154.40(17)	C47	N46	C5	C4	-172.03(17)
C17	C18	C19	C20	-0.7(3)	C14	C15	C10	C9	177.48(17)
C7	C2	C1	C30	146.32(15)	C14	C15	C10	C11	-2.3(3)
C7	C2	C1	C31	-85.51(18)	C42	C37	C38	C39	-0.3(3)
C7	C2	C3	C4	-0.1(3)	C42	C41	C40	C39	0.1(4)
C30	C25	C26	C27	0.0(3)	C35	C34	C33	C32	1.3(5)
C30	C1	C31	C36	115.90(19)	C38	C37	C42	C41	1.2(3)
C30	C1	C31	C32	-64.6(2)	C51	N49	C27	C26	-6.2(3)
C30	C29	C28	C27	-0.2(3)	C51	N49	C27	C28	174.65(18)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N52	C20	C19	C18	177.95(18)	C50	N49	C27	C26	-152.38(19)
C1	C2	C7	C8	-3.9(2)	C50	N49	C27	C28	28.5(3)
C1	C2	C7	C6	177.31(14)	C41	C40	C39	C38	0.8(4)
C1	C2	C3	C4	-177.18(16)	C54	N52	C20	C21	-10.1(3)
C1	C30	C29	C28	-179.87(16)	C54	N52	C20	C19	171.45(19)
C1	C31	C36	C35	-178.87(18)	C45	N43	C12	C11	-5.3(4)
C1	C31	C32	C33	179.3(3)	C45	N43	C12	C13	175.1(2)
C6	C5	C4	C3	-0.7(3)	C44	N43	C12	C11	177.8(2)
C15	C16	C17	C22	143.79(15)	C44	N43	C12	C13	-1.9(4)
C15	C16	C17	C18	-37.6(2)	C53	N52	C20	C21	-175.5(2)
C15	C16	C37	C42	100.97(19)	C53	N52	C20	C19	6.0(3)
C15	C16	C37	C38	-77.7(2)	C32	C31	C36	C35	1.6(3)

Table S7. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **3**.

Atom	x	y	z	U_{eq}
H16	6825.48	2956.44	6642.26	33
H1	4903.56	3123.43	6340.2	33
H6	5249.91	4394.92	4354.03	34
H29	2113.3	2878.26	6473.83	38
H26	3819.71	3489.09	8767.67	39
H21	6961.26	4333.76	8548.56	40
H3	2443.18	3792.96	5814.89	40
H4	2201.03	4542.46	4947.64	42
H28	1176.83	2941.19	7595.22	43
H18	9467.95	3405.79	7098.75	41
H19	9984.79	4139.72	7929.07	46
H11	7997.5	3282.31	4211.99	47
H36	3230.89	2799.99	4768.27	44
H48A	2012.12	4984.38	3732.23	62
H48B	2578.52	5578.53	3535.73	62
H48C	2327.49	5425.32	4413.9	62
H47A	5012.79	5254.74	3780.87	61
H47B	4138.09	5439.69	3135.73	61
H47C	4542.92	4788.78	3179.49	61
H14	9479.29	2451.95	6455.65	47
H13	10432.16	2471.08	5336.3	56
H42	8777.69	2496.94	8034.62	49
H35	2959.21	1893.73	4235.33	53
H38	6529.14	1938.03	6492.66	57
H51A	2866.59	3130.75	9858.13	72
H51B	1886.53	3511.36	10111.87	72
H51C	2802.72	3796.15	9627.21	72
H50A	346.67	3032.33	8685.34	77
H50B	639.32	2966.86	9591.32	77
H50C	1107.02	2523.33	8984.31	77
H34	3522.64	1076.63	4905.85	69
H41	8880.02	1578.63	8578.44	63
H54A	7584.68	5273.23	8829.41	83
H54B	8379.14	5381.5	9557.55	83
H54C	7610.45	4835.88	9545.54	83
H45A	8864.12	2908.2	3097.98	92
H45B	9969.29	3189.89	2888.92	92
H45C	9146.98	3546.82	3379.86	92
H40	7797.39	846.64	8099.94	73
H44A	11394.99	2918.59	4403.49	98
H44B	11275.31	2795	3492.08	98

Atom	x	y	z	U_{eq}
H44C	10967.64	2308.87	4099.35	98
H39	6601.53	1029.93	7060.18	73
H53A	10380.65	4613.26	8962.01	94
H53B	10018.49	5217.68	9305.33	94
H53C	10058.61	5129.09	8387.22	94
H32	4656.78	2088.17	6652.4	75
H33	4404.57	1182.56	6114.59	101

Table S8. Solvent masks information for **3**.

Number	x	y	z	Volume	Electron count	Content
1	-0.280	0.000	-0.780	837.0	217.9	4 toluene
2	-0.521	0.500	-0.021	837.0	217.9	4 toluene

Thermogravimetric Analysis (TGA) of Product 3 in Crystal

Thermogravimetric analysis was conducted on STA7200. Experimental details were shown below (Table S8).

Table S9. Experimental details of TGA.

Operator	TA7000
Gas	N_2 (300 mL/min)
Material of Pans	Pt
Weight of Sample	0.58 mg
Weight of Residue	0.08 mg

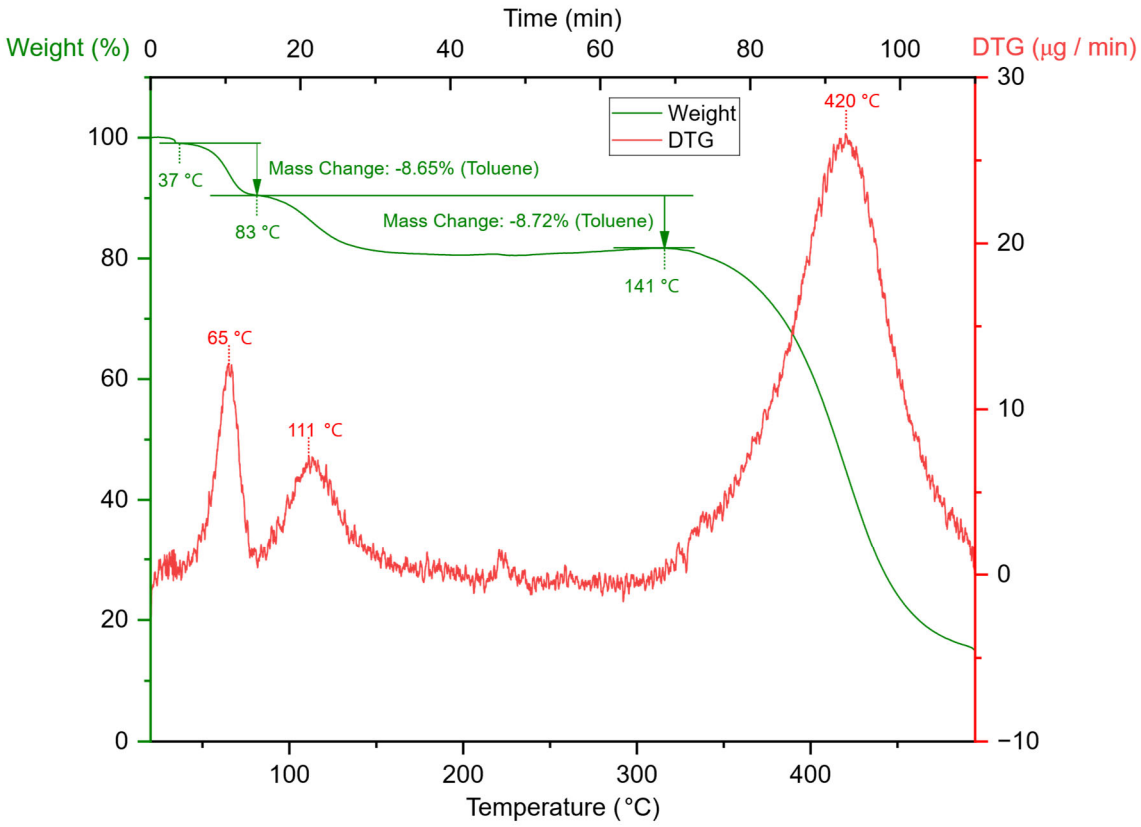


Figure S5. Thermogravimetric analysis (TGA) curves of crystal of **3**.

4. Photophysical Properties

Cuvettes with a thickness of 1.0 cm were used for the measurement of UV-Vis and fluorescence spectrums (UV-Vis absorption (Abs); Photoluminescence (PL)).

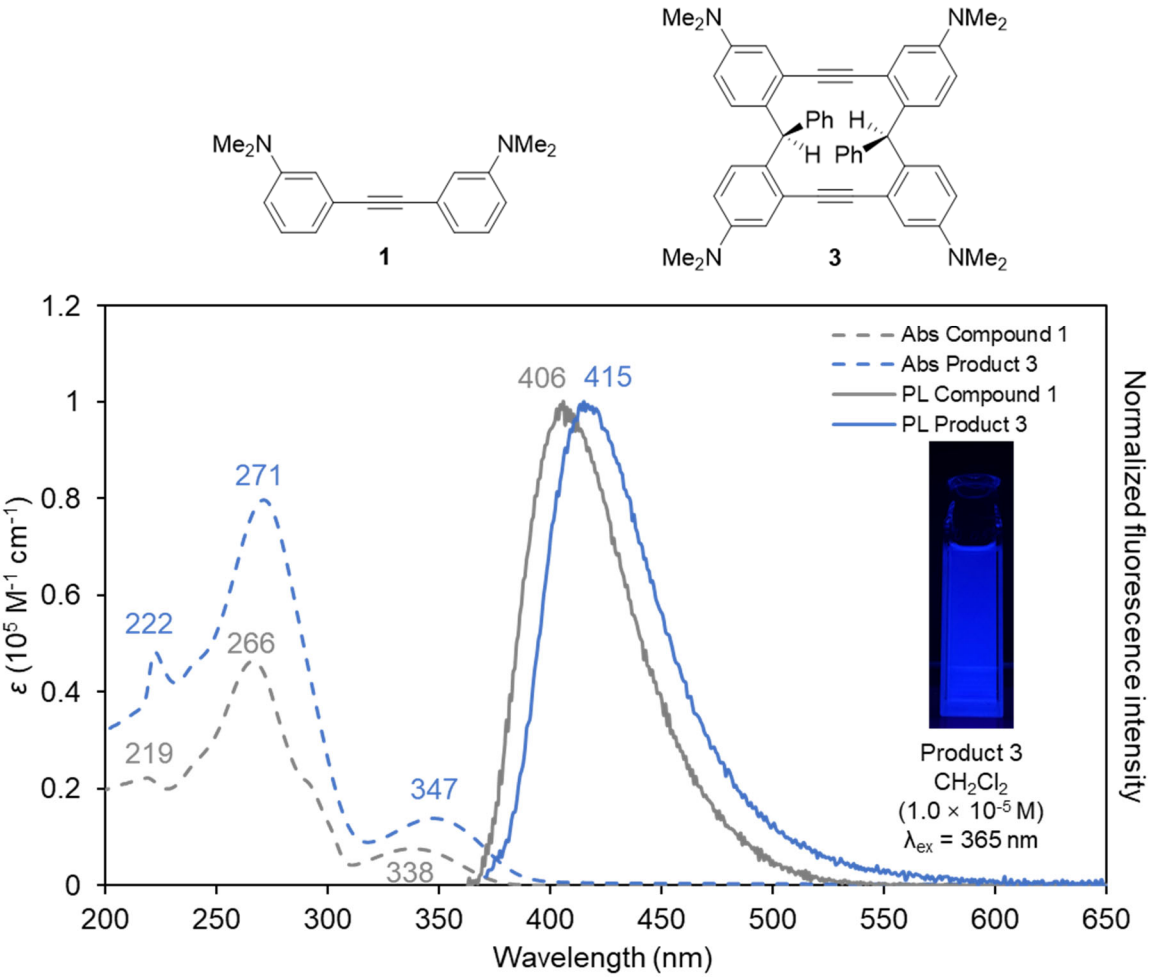


Figure S6.

Grey line: UV/Vis spectrum (dashed line) and fluorescence spectrum (solid line) of **1**;
Blue line: UV/Vis spectrum (dashed line) and fluorescence spectrum (solid line) of **3**.

Table S10. Photophysical properties of **1** and **3**.[a]

Compd.	λ_{ab} (nm)	λ_{ex} (nm)	λ_{em} (nm)	ϕ_F	FWHM (nm)
1	219, 266, 338	338	406	0.25	57
3	222, 271, 347	347	415	0.24	60

[a] Measured in CH_2Cl_2 (1.0×10^{-5} M).

5. Therotical Calculations

5.1 Geometry Optimizations

Table S11. Atomic coordinates of optimized structure of **1** by DFT**,** B3LYP/6-31G(d).

Atom	x	y	z
C	0.60815200	-1.00720200	-0.01169100
C	-0.60815200	-1.00720200	0.01169400
C	2.03448800	-1.01466900	-0.03959900
C	2.73794900	0.20221500	-0.04148100
C	2.73931500	-2.23285600	-0.05900000
C	4.14677300	0.23686300	-0.07272100
H	2.16155400	1.11784900	-0.01758500
C	4.12964800	-2.20321500	-0.07549900
H	2.19583800	-3.17148400	-0.05473800
C	4.83214600	-1.00016400	-0.07756000
H	4.68735900	-3.13637100	-0.08217000
H	5.91495100	-1.02816200	-0.08281000
C	-2.03448900	-1.01466900	0.03960100
C	-2.73794900	0.20221400	0.04148400
C	-2.73931600	-2.23285600	0.05900000
C	-4.14677300	0.23686300	0.07272300
H	-2.16155400	1.11784800	0.01758900
C	-4.12964900	-2.20321500	0.07549700
H	-2.19583800	-3.17148400	0.05473700
C	-4.83214600	-1.00016400	0.07755900
H	-4.68735900	-3.13637100	0.08216600
H	-5.91495100	-1.02816200	0.08280700
N	4.83706900	1.44604800	-0.10788000
N	-4.83706900	1.44604800	0.10788500
C	6.27315700	1.44667100	0.11121200
H	6.64406900	2.47118500	0.03906900
H	6.55962900	1.04462900	1.09702000
H	6.78788500	0.85709000	-0.65667400
C	4.11205300	2.68158300	0.13371100
H	4.80404000	3.52248900	0.05304100
H	3.32743400	2.82842700	-0.61781200

Atom	x	y	z
H	3.63956900	2.71665400	1.12914500
C	-6.27315600	1.44667100	-0.11121900
H	-6.64406900	2.47118500	-0.03907200
H	-6.55962000	1.04463600	-1.09703200
H	-6.78788900	0.85708600	0.65666000
C	-4.11205300	2.68158300	-0.13371000
H	-4.80403800	3.52248900	-0.05303500
H	-3.32743100	2.82842500	0.61781000
H	-3.63957400	2.71665400	-1.12914600

Table S12. Calculation details of diarylalkyne **1** by DFT**,** B3LYP/6-31G(d).

Calculation Type	FREQ	
Calculation Method	B3LYP	
Formula	$C_{18}H_{20}N_2$	
Basis Set	6-31G(d)	
Charge	0	
Spin	Singlet	
Solvation	None	
E(RB3LYP)	-807.39544	Hartree
RMS Gradient Norm	1.08E-07	Hartree/Bohr
Dipole Moment	3.2033	Debye
Polarizability (α)	237.85256	a.u.
Point Group	C_1	
Molecular Mass	264.16265	amu
Temperature	298.15	Kelvin
Pressure	1	atm
Frequencies scaled by	1	
Electronic Energy (EE)	-807.39544	Hartree
Zero-point Energy Correction	0.338556	Hartree
Thermal Correction to Energy	0.358449	Hartree
Thermal Correction to Enthalpy	0.359393	Hartree
Thermal Correction to Free Energy	0.287409	Hartree
EE + Zero-point Energy	-807.05688	Hartree
EE + Thermal Energy Correction	-807.03699	Hartree
EE + Thermal Enthalpy Correction	-807.03604	Hartree
EE + Thermal Free Energy Correction	-807.10803	Hartree

E (Thermal)	224.93	kcal/mol
Heat Capacity (Cv)	74.417	cal/mol-kelvin
Entropy (S)	151.503	cal/mol-kelvin
Step number	1	
Maximum force	1.00E-06	Converged
RMS force	0	Converged
Maximum displacement	0.000192	Not converged
RMS displacement	4.80E-05	Not converged
Predicted energy change	-8.22E-12	Hartree

Table S13. Atomic coordinates of optimized structure of **3** by DFT**,** B3LYP/6-31G(d).

Atom	x	y	z
C	-2.75253000	-1.47517100	-0.08575900
C	-2.97795200	-0.22591600	-0.70666900
C	-4.22037500	-0.02395200	-1.30710400
C	-5.22264300	-0.98794500	-1.28553700
C	-5.01087200	-2.23683200	-0.66186700
C	-3.75811500	-2.45376100	-0.06016500
H	-4.40841700	0.91790900	-1.81481500
H	-6.16781700	-0.76534600	-1.76467200
H	-3.53132400	-3.39215100	0.42773700
C	-1.48552100	-1.76297300	0.50103300
C	-0.37707400	-1.97227200	0.95336800
C	0.93164600	-2.19546100	1.47175700
C	1.06583600	-2.90330500	2.67578500
C	2.06930300	-1.70343500	0.78924300
C	2.32674900	-3.15800900	3.24423000
H	0.15928900	-3.24020800	3.16027100
C	3.31144800	-1.94443900	1.37334300
C	3.45293100	-2.64534500	2.56726100
H	4.20312600	-1.55923000	0.89009500
H	4.44828000	-2.78450200	2.97031200
C	-2.05269100	1.79310200	0.51217100
C	-0.90735800	2.39126100	1.08862700
C	-1.02846800	3.30117700	2.14998400
C	-3.41829200	3.04767900	2.10099100
C	-2.28207500	3.64253100	2.68823600
H	-0.11765200	3.72739600	2.54860700
H	-4.41141800	3.27983300	2.46490200
C	2.97689700	0.07606000	-0.76967700
C	4.21236800	-0.22789600	-1.34074600
C	2.75764500	1.41390300	-0.37094600
C	5.21369600	0.72437500	-1.49812900
H	4.39550500	-1.24374400	-1.67945900
C	3.76226800	2.38136300	-0.52712200
C	5.00784700	2.06255200	-1.09751800
H	6.15342900	0.42129900	-1.94255700

Atom	x	y	z
H	3.54029900	3.39015300	-0.20594700
C	1.49783100	1.79939500	0.17384000
C	1.78690400	-1.92330500	-1.73837400
C	1.40067700	-1.37715000	-2.97111700
C	2.03282700	-3.29486800	-1.66034700
C	1.25160900	-2.18461100	-4.09462400
H	1.21754700	-0.30855000	-3.04192500
C	1.88986000	-4.10756900	-2.78904400
H	2.32711500	-3.73221600	-0.71201200
C	1.49670900	-3.55835000	-4.00748800
H	0.94464100	-1.74311700	-5.03939100
H	2.08354000	-5.17417100	-2.70959900
H	1.38083200	-4.19174100	-4.88277100
N	2.45496300	-3.89003500	4.42307100
N	5.98955300	3.03348000	-1.27837700
N	-5.99377900	-3.22315400	-0.66007400
N	-2.39308900	4.51966000	3.76488600
C	-1.23167200	5.30232200	4.14598800
H	-1.48944800	5.92700800	5.00363500
H	-0.40645300	4.64910000	4.45004400
H	-0.86754100	5.95551200	3.33570000
C	-3.70027500	5.06282900	4.08506100
H	-4.14611500	5.63263400	3.25292400
H	-4.39745700	4.26324200	4.35903100
H	-3.60815800	5.72676300	4.94697100
C	-7.34725500	-2.85765800	-1.03491100
H	-7.38178700	-2.49723700	-2.06916100
H	-7.98414300	-3.74240800	-0.97504400
H	-7.77697800	-2.07536100	-0.38755500
C	-5.82324800	-4.37407000	0.20754800
H	-4.92298200	-4.93603100	-0.06482300
H	-5.74448800	-4.10134600	1.27288600
H	-6.67771800	-5.04244900	0.08432700
C	7.33872700	2.60724700	-1.60097800
H	7.36079000	2.07339700	-2.55766500
H	7.97537600	3.48832300	-1.70286800
H	7.77722700	1.94815200	-0.83349000

Atom	x	y	z
C	5.82857000	4.31681500	-0.62000700
H	4.92449700	4.82454000	-0.97408100
H	5.76305800	4.23183200	0.47729100
H	6.68083600	4.95299000	-0.86692200
C	3.72877400	-3.86513300	5.11855800
H	3.65789300	-4.48828100	6.01239400
H	4.52301700	-4.28191800	4.48954400
H	4.03364800	-2.85058200	5.42451700
C	1.26634100	-4.13555400	5.21981900
H	0.77644400	-3.20840500	5.56017500
H	0.53222000	-4.71687200	4.65139900
H	1.54210400	-4.72347300	6.09767900
C	-3.28955100	2.14621100	1.04875100
H	-4.18823300	1.70000000	0.63603300
C	-1.91039300	0.85376300	-0.67772300
H	-0.95665300	0.33829100	-0.54201700
C	0.39505700	2.08364800	0.59831500
C	-1.80160000	1.57593800	-2.01944600
C	-2.04461000	2.94140700	-2.17481100
C	-1.43290300	0.82498500	-3.14519700
C	-1.91609100	3.54783900	-3.42804700
H	-2.32554100	3.53589900	-1.31176800
C	-1.29823600	1.42709200	-4.39251500
H	-1.25202900	-0.24052700	-3.03384500
C	-1.54040300	2.79627000	-4.53925800
H	-2.10735000	4.61294500	-3.53041700
H	-1.00475900	0.82890100	-5.25143500
H	-1.43579200	3.26960700	-5.51174500
C	1.91126700	-0.98157100	-0.54202700
H	0.95852100	-0.44970300	-0.48485800

Table S14. Calculation details of **3** by DFT**,** B3LYP/6-31G(d).

Calculation Type	FREQ
Calculation Method	B3LYP
Formula	$C_{50}H_{48}N_4$
Basis Set	6-31G(d)

Charge	0	
Spin	Singlet	
Solvation	None	
E(RB3LYP)	-2153.3719	Hartree
RMS Gradient Norm	1.21E-07	Hartree/Bohr
Dipole Moment	3.8892506	Debye
Polarizability (α)	613.13214	a.u.
Point Group	C_1	
Molecular Mass	704.3879	amu
Temperature	298.15	Kelvin
Pressure	1	atm
Frequencies scaled by	1	
Electronic Energy (EE)	-2153.3719	Hartree
Zero-point Energy Correction	0.857797	Hartree
Thermal Correction to Energy	0.908123	Hartree
Thermal Correction to Enthalpy	0.909068	Hartree
Thermal Correction to Free Energy	0.768641	Hartree
EE + Zero-point Energy	-2152.5141	Hartree
EE + Thermal Energy Correction	-2152.4638	Hartree
EE + Thermal Enthalpy Correction	-2152.4629	Hartree
EE + Thermal Free Energy Correction	-2152.6033	Hartree
E (Thermal)	569.856	kcal/mol
Heat Capacity (Cv)	193.656	cal/mol-kelvin
Entropy (S)	295.553	cal/mol-kelvin
Step number	1	
Maximum force	0	Converged
RMS force	0	Converged
Maximum displacement	8.30E-05	Not converged
RMS displacement	1.30E-05	Converged
Predicted energy change	-1.43E-11	Hartree

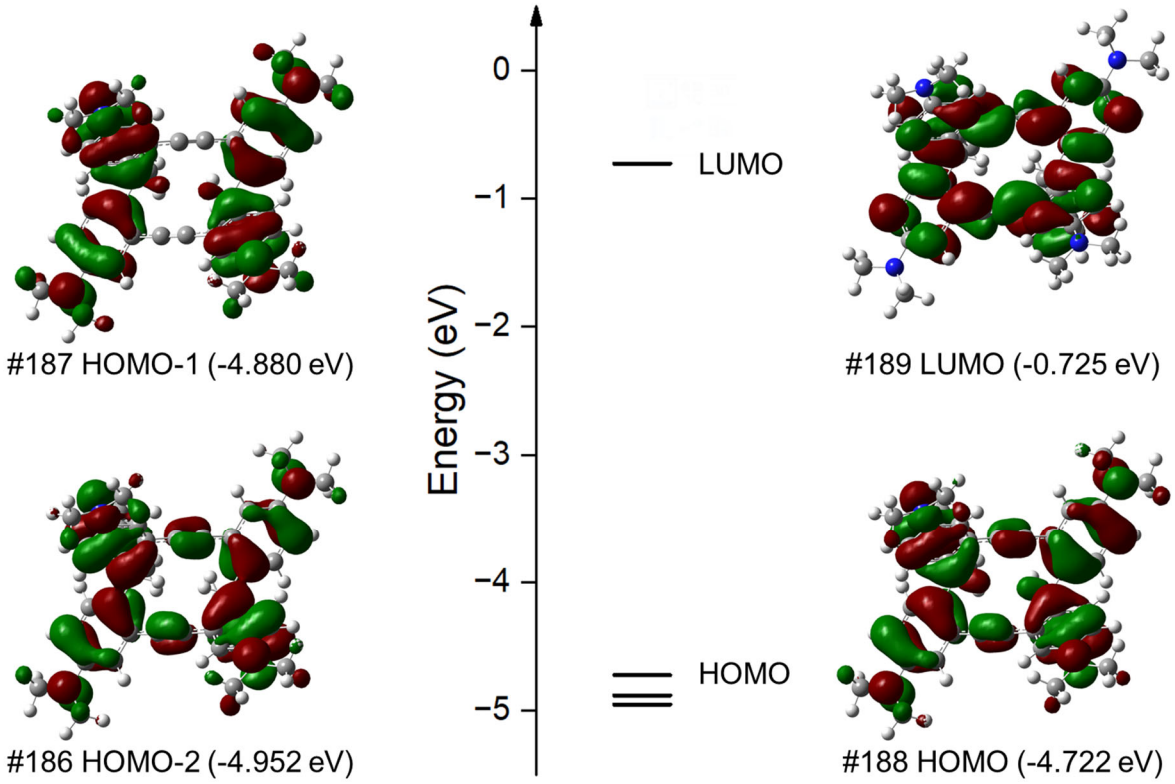


Figure S7. Molecular orbitals of (R_a,R_a)-**3** with the energy levels (Isovalue = 0.02).

5.2 Energy Barrier for the Interconversion of Two Enantiomers

Table S15. Atomic coordinates of (R_a,R_a)-**3**.

Atom	x	y	z
C	-2.86950400	-1.23888200	-0.23023500
C	-2.98440400	0.06681800	-0.75840400
C	-4.20063000	0.41588500	-1.34477600
C	-5.28031800	-0.45928200	-1.39579600
C	-5.17900600	-1.76373000	-0.86500600
C	-3.95375000	-2.12861900	-0.27837700
H	-4.30489900	1.40469500	-1.78253900
H	-6.19957500	-0.12350500	-1.85915200
H	-3.81034200	-3.11583200	0.13984000
C	-1.63582000	-1.67407300	0.33643500
C	-0.55234300	-2.00712800	0.77485600
C	0.72887700	-2.37570800	1.27874000
C	0.79358800	-3.17580600	2.42957800
C	1.90922100	-1.93331400	0.63589700
C	2.02412300	-3.57445400	2.98163100
H	-0.14189600	-3.46915700	2.88660600
C	3.12205200	-2.31807200	1.20436800
C	3.19468900	-3.11116800	2.34561600
H	4.04672000	-1.97544600	0.75205000
H	4.17157800	-3.36122100	2.74019100
C	-1.90261800	1.90807900	0.60501600
C	-0.71558700	2.36560200	1.22424300
C	-0.76805600	3.20452900	2.34785900
C	-3.17029900	3.15612200	2.27788900
C	-1.99269500	3.61022000	2.90775100
H	0.17222600	3.52341000	2.77718400
H	-4.14319800	3.44407100	2.65629100
C	2.97523900	-0.12972400	-0.78924300
C	4.18538900	-0.49478300	-1.37848700
C	2.86575800	1.18979700	-0.29545200
C	5.26419600	0.37868400	-1.46494000
H	4.28549500	-1.49548000	-1.78932800
C	3.94916500	2.07793100	-0.37948900

Atom	x	y	z
C	5.16811500	1.69718100	-0.96908400
H	6.17868500	0.03027900	-1.92839400
H	3.81005800	3.07615300	0.01330000
C	1.63839200	1.64008800	0.27317900
C	1.63004100	-1.94781100	-1.90154300
C	1.30020200	-1.28473900	-3.09261000
C	1.76082400	-3.33712500	-1.92170400
C	1.09355900	-1.99470900	-4.27148300
H	1.20688300	-0.20227900	-3.08680300
C	1.55975700	-4.05245500	-3.10607800
H	2.01049300	-3.86391000	-1.00663600
C	1.22314600	-3.38680100	-4.28269400
H	0.83173400	-1.46286900	-5.18270200
H	1.66366200	-5.13442400	-3.10305300
H	1.06200000	-3.94423500	-5.20140500
N	2.08109400	-4.39581200	4.10595700
N	6.22916100	2.59249300	-1.07748800
N	-6.24108400	-2.66131300	-0.93755500
N	-2.03790500	4.41396900	4.04476600
C	-0.81796700	5.06690900	4.48303100
H	-1.02887800	5.64747200	5.38341700
H	-0.05253000	4.32644800	4.73984500
H	-0.39459500	5.74401200	3.72270200
C	-3.29748400	5.04020800	4.40194700
H	-3.68825400	5.70387000	3.61279900
H	-4.06088500	4.28413200	4.61647700
H	-3.15648700	5.63021400	5.30979700
C	-7.55602800	-2.15680100	-1.28730100
H	-7.55172300	-1.72044100	-2.29245100
H	-8.26535400	-2.98675000	-1.29366000
H	-7.92387000	-1.39029000	-0.58525100
C	-6.17465300	-3.88263400	-0.15625600
H	-5.32260100	-4.49716200	-0.46744300
H	-6.08169800	-3.69586900	0.92633700
H	-7.08121100	-4.46585700	-0.32957200
C	7.54042000	2.07850400	-1.42739700
H	7.52533500	1.61458300	-2.42001200

Atom	x	y	z
H	8.24938200	2.90797300	-1.46433300
H	7.91608700	1.33163500	-0.70852000
C	6.17106000	3.83423000	-0.32845900
H	5.31569800	4.44046200	-0.64680800
H	6.08969000	3.67651200	0.75969800
H	7.07569400	4.41239000	-0.52698200
C	3.34666700	-4.52646800	4.80466000
H	3.21664600	-5.20284300	5.65194400
H	4.10875000	-4.96289500	4.14971800
H	3.73228400	-3.56497900	5.18244300
C	0.86955300	-4.59619600	4.88051200
H	0.45575000	-3.65738900	5.28406900
H	0.09432300	-5.07291300	4.27084000
H	1.08807000	-5.26506400	5.71549200
C	-3.10958600	2.32438900	1.16388900
H	-4.03934700	1.98558100	0.71912600
C	-1.83018600	1.04762600	-0.64909300
H	-0.92435900	0.44501000	-0.54862400
C	0.56011200	1.98529000	0.71503300
C	-1.65011700	1.85239500	-1.93500300
C	-1.77543000	3.24122400	-1.99158100
C	-1.33764400	1.15579200	-3.11155500
C	-1.58624200	3.92316900	-3.19741700
H	-2.01152400	3.79380300	-1.08819900
C	-1.14270800	1.83248300	-4.31179000
H	-1.24856200	0.07352200	-3.07737400
C	-1.26689300	3.22429300	-4.35947700
H	-1.68578200	5.00527800	-3.22274500
H	-0.89428400	1.27487100	-5.21126800
H	-1.11496500	3.75576700	-5.29498700
C	1.82299500	-1.10758300	-0.64046500
H	0.91768000	-0.50298000	-0.54728500

Table S16. Calculation details of (R_a,R_a)-**3**.

Calculation Type	SCAN
Calculation Method	RB3LYP

Formula	$C_{50}H_{48}N_4$	
Basis Set	6-31G(d)	
Charge	0	
Spin	Singlet	
Solvation	None	
E(RB3LYP)	-2153.37193	Hartree
RMS Gradient Norm	4.48E-06	Hartree/Bohr
Dipole Moment	3.889296	Debye
Point Group	C_1	
Molecular Mass	704.3879	amu

Table S17. Atomic coordinates of TS-**3**.

Atom	x	y	z
C	-1.64535100	-2.47587800	0.60877200
C	-2.63556700	-1.59202700	0.12666000
C	-3.96294600	-1.93586500	0.39007300
C	-4.32026800	-3.08088400	1.09041100
C	-3.33750400	-3.97435000	1.56829600
C	-1.99773700	-3.63776300	1.32020700
H	-4.75760700	-1.28173500	0.05351100
H	-5.37151600	-3.27280300	1.26526300
H	-1.19154500	-4.26626400	1.67358800
C	-0.25623400	-2.24662200	0.39301200
C	0.94748600	-2.12847400	0.27227900
C	2.36938900	-2.04155600	0.25980600
C	3.08169900	-3.17922500	0.67730000
C	3.04014700	-0.84216000	-0.07049900
C	4.48183500	-3.17643500	0.78533100
H	2.50658800	-4.05926300	0.93173000
C	4.42663900	-0.84062300	0.09273700
C	5.13958200	-1.96005000	0.50888000
H	4.98395800	0.06987900	-0.08750100
H	6.21342100	-1.87574200	0.61987400
C	-2.96804000	0.89333000	-0.16003300
C	-2.29564700	1.85403700	0.62533600
C	-2.99218800	2.94947100	1.16915400
C	-5.00749100	2.22378800	0.08231200
C	-4.36428000	3.14271300	0.94048900
H	-2.42179700	3.65942000	1.75250500
H	-6.04788900	2.35466300	-0.18736000
C	2.61589700	1.67945500	0.00703500
C	3.84367000	2.30297600	-0.22294100
C	1.69887400	2.36698800	0.83549400
C	4.21865800	3.48057500	0.41308200
H	4.52776900	1.87077300	-0.94612100
C	2.07444900	3.55032400	1.49527200
C	3.34441800	4.12355800	1.31577900
H	5.19194700	3.90183800	0.19429200

Atom	x	y	z
H	1.33306900	4.03025500	2.12007700
C	0.32365200	1.98738600	0.89733900
C	2.24004700	0.39909500	-2.13943600
C	1.08113300	0.84776100	-2.78500700
C	3.34329100	0.03686300	-2.91819500
C	1.02440100	0.93494800	-4.17382000
H	0.21417900	1.12236400	-2.19144800
C	3.29392400	0.13442900	-4.30994900
H	4.23738800	-0.34933300	-2.43936100
C	2.13482800	0.58232100	-4.94289500
H	0.10534200	1.25881400	-4.65160600
H	4.16054300	-0.15401400	-4.89947600
H	2.09232800	0.64525000	-6.02696800
N	5.18607400	-4.32044900	1.15467000
N	3.70654100	5.30114500	1.96518900
N	-3.68107800	-5.14141100	2.24616700
N	-5.05564300	4.20276200	1.52098000
C	-4.29588000	5.26241600	2.15841700
H	-4.98930200	5.99131800	2.58288100
H	-3.69197300	4.86288300	2.98030100
H	-3.62036100	5.78757500	1.46292500
C	-6.37116300	4.54034900	1.00861000
H	-6.36014000	4.82431800	-0.05674000
H	-7.06197600	3.69862400	1.12808800
H	-6.77203900	5.37745200	1.58372900
C	-5.03985700	-5.28505300	2.73681900
H	-5.75607300	-5.27312000	1.90793800
H	-5.13612100	-6.25005200	3.23850200
H	-5.32758300	-4.49290400	3.44760700
C	-2.63783600	-5.86862800	2.94606700
H	-1.86756700	-6.21007300	2.24583300
H	-2.14468700	-5.26791600	3.72802800
H	-3.07339500	-6.75425100	3.41316400
C	5.10314600	5.69641300	1.95719800
H	5.44756000	5.89457400	0.93587800
H	5.21432800	6.62228900	2.52492600
H	5.76747700	4.93527600	2.39848800

Atom	x	y	z
C	2.87913100	5.76914200	3.06201300
H	1.87018500	6.01562300	2.71195600
H	2.78517100	5.02914100	3.87359800
H	3.31541600	6.68126700	3.47382900
C	6.57294700	-4.18070900	1.55952400
H	6.97231900	-5.16685900	1.80519300
H	7.17757200	-3.77620700	0.74049300
H	6.70302400	-3.52431800	2.43598700
C	4.44612200	-5.44678900	1.69329200
H	3.90278000	-5.20274900	2.62142500
H	3.71878600	-5.81553600	0.96205700
H	5.14222200	-6.26121300	1.90452000
C	-4.31513300	1.13971300	-0.44124700
H	-4.83710300	0.47718100	-1.12471800
C	-2.25530800	-0.34611800	-0.67294900
H	-1.18572300	-0.18883500	-0.49382900
C	-0.88073800	1.83155800	0.81161900
C	-2.39951900	-0.54010900	-2.18692100
C	-2.52075600	0.56842100	-3.03609600
C	-2.32869300	-1.81291700	-2.76372900
C	-2.57805600	0.40855900	-4.42013300
H	-2.57468500	1.56422600	-2.60819200
C	-2.37740500	-1.97449900	-4.14857600
H	-2.23109400	-2.68390000	-2.12485400
C	-2.50514400	-0.86556000	-4.98420300
H	-2.68041200	1.28326900	-5.05757800
H	-2.31660300	-2.97284300	-4.57359200
H	-2.54753400	-0.99207000	-6.06247900
C	2.24374300	0.33959600	-0.61117400
H	1.20790500	0.15605800	-0.32027800

Table S18. Calculation details of TS-**3**.

Calculation Type	SCAN
Calculation Method	B3LYP
Formula	$C_{50}H_{48}N_4$
Basis Set	6-31G(d)

Charge	0	
Spin	Singlet	
Solvation	None	
E(RB3LYP)	-2153.359907	Hartree
RMS Gradient Norm	0.000157389	Hartree/Bohr
Dipole Moment	Debye	
Point Group	C_1	
Molecular Mass	704.3879	amu

Table S19. Atomic coordinates of (S_a,S_a)-**3**.

Atoms	x	y	z
C	-0.77868900	-2.53155600	1.11691700
C	-1.96930000	-2.00209600	0.56595300
C	-3.17170800	-2.45776900	1.10437900
C	-3.22546300	-3.40108200	2.12584300
C	-2.04487000	-3.95407800	2.66403900
C	-0.82469800	-3.48461800	2.14686600
H	-4.10443500	-2.05294800	0.72713200
H	-4.19552300	-3.69866900	2.50391700
H	0.11861900	-3.83982400	2.53935400
C	0.49865600	-2.10014100	0.65726900
C	1.59375800	-1.72779700	0.28424500
C	2.85141000	-1.28393600	-0.21744800
C	3.92487200	-2.18883400	-0.25220000
C	3.00143500	0.03066300	-0.71335300
C	5.17077500	-1.83272400	-0.79801200
H	3.75422600	-3.18234400	0.14010800
C	4.23588700	0.36677700	-1.27027000
C	5.30327300	-0.52308800	-1.30944500
H	4.36402400	1.35817300	-1.69581300
H	6.23707900	-0.19557500	-1.74903000
C	-3.04365300	-0.01438200	-0.58793400
C	-2.87469800	1.27093600	-0.02622800
C	-3.94751300	2.17563500	0.02667900
C	-5.36269000	0.57186800	-1.07545700
C	-5.21864400	1.84066500	-0.47242300
H	-3.75645500	3.15268800	0.44948500
H	-6.30545600	0.27624800	-1.51829700
C	1.97819500	1.95299600	0.59162800
C	3.20166000	2.37859300	1.10687000
C	0.81145400	2.45231900	1.21705300
C	3.29761300	3.26522100	2.17494400
H	4.11808900	1.99485200	0.67220700
C	0.89990000	3.34837000	2.29429500
C	2.14037800	3.78910500	2.78781000
H	4.28243500	3.54169800	2.53023900

Atoms	x	y	z
H	-0.02657000	3.68162500	2.74221800
C	-0.48485700	2.04534100	0.78687700
C	1.68063000	1.78895400	-1.93640500
C	1.80631300	3.17462900	-2.04908800
C	1.36550900	1.04603400	-3.08332900
C	1.61620200	3.80755100	-3.28121500
H	2.04465000	3.76373900	-1.16981500
C	1.16955400	1.67413100	-4.30952500
H	1.27074100	-0.03317400	-3.00620700
C	1.29529200	3.06259200	-4.41392500
H	1.71670100	4.88766500	-3.34998600
H	0.91962200	1.07961900	-5.18457300
H	1.14353200	3.55594400	-5.37015500
N	6.22233100	-2.74349000	-0.85459900
N	2.21992800	4.70558900	3.83433000
N	-2.08320100	-4.92555200	3.66226700
N	-6.28948300	2.72719200	-0.38079000
C	-6.01974900	4.10640100	-0.01691900
H	-6.96354100	4.65390100	0.02561700
H	-5.56134200	4.16145400	0.97643200
H	-5.35143000	4.61773300	-0.72927700
C	-7.47511600	2.46896800	-1.17766500
H	-7.27053900	2.44601800	-2.26082500
H	-7.93027400	1.51240200	-0.89847700
H	-8.21140900	3.25126600	-0.98247900
C	-3.33381200	-5.14770400	4.36497300
H	-4.11391000	-5.48338500	3.67296100
H	-3.19015900	-5.93788100	5.10474500
H	-3.70298100	-4.24759600	4.88390100
C	-0.85619700	-5.24000900	4.37159500
H	-0.09856100	-5.62737700	3.68172500
H	-0.42635500	-4.37061400	4.89595300
H	-1.06082500	-6.02090300	5.10689100
C	3.49756100	4.89006800	4.49814600
H	4.25067100	5.26191200	3.79479000
H	3.38475400	5.63987800	5.28384800
H	3.88489300	3.96370700	4.95383900

Atoms	x	y	z
C	1.02224400	4.98237500	4.60673000
H	0.23915900	5.40578600	3.96841300
H	0.61122100	4.08659000	5.10085000
H	1.25718700	5.72328500	5.37365300
C	7.55275800	-2.25245600	-1.16282100
H	8.25143400	-3.09136600	-1.15850500
H	7.58198400	-1.80567000	-2.16299600
H	7.91057300	-1.49813600	-0.44270200
C	6.11773000	-3.97492600	-0.09369200
H	5.99320100	-3.80209500	0.98801400
H	5.26873400	-4.57498000	-0.43978600
H	7.02249100	-4.56638200	-0.24719800
C	-4.29563200	-0.31808100	-1.12365900
H	-4.43524000	-1.27837100	-1.61222500
C	-1.90390400	-1.01811500	-0.59447100
H	-0.98524700	-0.44300000	-0.45353600
C	-1.59556200	1.69218300	0.44161400
C	-1.76692700	-1.69538300	-1.95818700
C	-1.47045800	-0.89058800	-3.06754700
C	-1.92070200	-3.06963500	-2.14875900
C	-1.32000700	-1.44747400	-4.33391800
H	-1.35350200	0.18038100	-2.92941700
C	-1.77659300	-3.63089700	-3.42116600
H	-2.14437200	-3.70603900	-1.29902500
C	-1.47382800	-2.82496100	-4.51657800
H	-1.08282000	-0.80599700	-5.17882200
H	-1.89805100	-4.70322300	-3.55086900
H	-1.35710100	-3.26293000	-5.50417200
C	1.86589900	1.03515800	-0.61883500
H	0.95089800	0.45452000	-0.47606400

Table S20. Calculation details of (S_a,S_a)-**3**.

Calculation Type	SCAN
Calculation Method	B3LYP
Formula	$C_{50}H_{48}N_4$
Basis Set	6-31G(d)

Charge	0	
Spin	Singlet	
Solvation	None	
E(RB3LYP)	-2153.3718	Hartree
RMS Gradient Norm	9.77E-05	Hartree/Bohr
Dipole Moment	Debye	
Point Group	C_1	
Molecular Mass	704.3879	amu

5.3 TD-DFT Calculations: Stimulated UV-Vis Spectra, Molecular Orbitals and Electronic Transitions

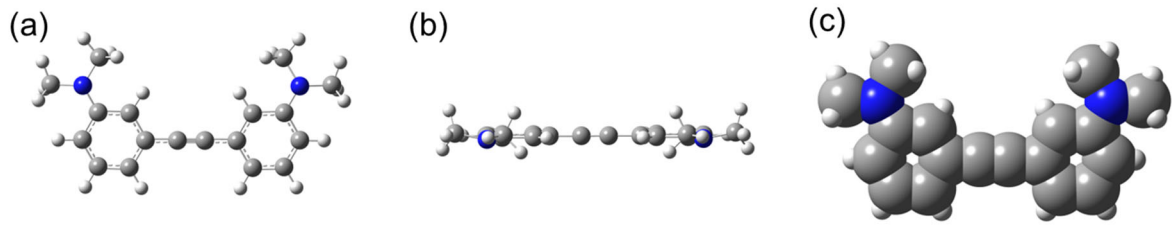


Figure S8. Optimized structure of **1**. (a) Top view, (b) Front view, and (c) Space−filling model (Top view).

Table S21. Atomic coordinate of optimized structure of **1** by TD-DFT, B3LYP/6-311++G(d,p).

Atom	x	y	z
C	4.14199900	-0.20356400	-0.04202500
C	2.73437000	-0.16975800	-0.04251200
C	2.03354100	1.04609800	0.00917800
C	2.73775800	2.26194600	0.07358900
C	4.12754000	2.23112000	0.08909000
C	4.82846800	1.02893800	0.03809400
H	2.15660100	-1.08329300	-0.08253900
H	2.19309500	3.19844400	0.11639400
H	4.68562400	3.16176800	0.14736800
H	5.91059400	1.05358500	0.06067500
C	0.60926100	1.03835700	0.00303300
C	-0.60626600	1.03447000	-0.00215300
C	-2.03056800	1.03308500	-0.00814400
C	-2.72312400	-0.18724600	-0.06556600
C	-2.74308800	2.24440000	0.05004300
C	-4.13045900	-0.23007600	-0.07703700
H	-2.13920100	-1.09706900	-0.10049900
C	-4.13272700	2.20466700	0.05372500
H	-2.20482400	3.18437700	0.09730400
C	-4.82547500	0.99800900	-0.00299800
H	-4.69723900	3.13172600	0.10707100
H	-5.90789100	1.01571700	0.01036600
N	4.83165200	-1.40924500	-0.12621900

Atom	x	y	z
N	-4.81163000	-1.44016700	-0.16683900
C	6.25565200	-1.42188400	0.15421300
H	6.49668900	-1.07069000	1.17090800
H	6.63071400	-2.44119100	0.04436400
H	6.79970300	-0.79263600	-0.55924500
C	4.09759300	-2.64869300	0.05175200
H	4.78733200	-3.48867100	-0.05065300
H	3.60628900	-2.71931300	1.03595900
H	3.32706000	-2.75847100	-0.71958400
C	-6.23783900	-1.46190500	0.10154200
H	-6.60538100	-2.48363800	-0.01114800
H	-6.48970800	-1.11199600	1.11604900
H	-6.77988300	-0.83636300	-0.61669000
C	-4.07115900	-2.67486200	0.01750600
H	-4.75459900	-3.51926100	-0.09061200
H	-3.29344100	-2.77974900	-0.74727000
H	-3.58775200	-2.74224200	1.00584200

Table S22. Calculation details of **1** by TD-DFT, B3LYP/6-311++G(d,p).

Calculation Type	SP	
Calculation Method	RB3LYP TD-FC	
Formula	$C_{18}H_{20}N_2$	
Basis Set	6-311++G(d,p)	
Charge	0	
Spin	Singlet	
Solvation	scrf=(iefpcm,solvent=dichloromethane)	
E(TD-HF/TD-DFT)	-807.5644	Hartree
RMS Gradient Norm	Hartree/Bohr	
Dipole Moment	4.539598	Debye
Point Group	C_1	
Molecular Mass	264.1627	amu

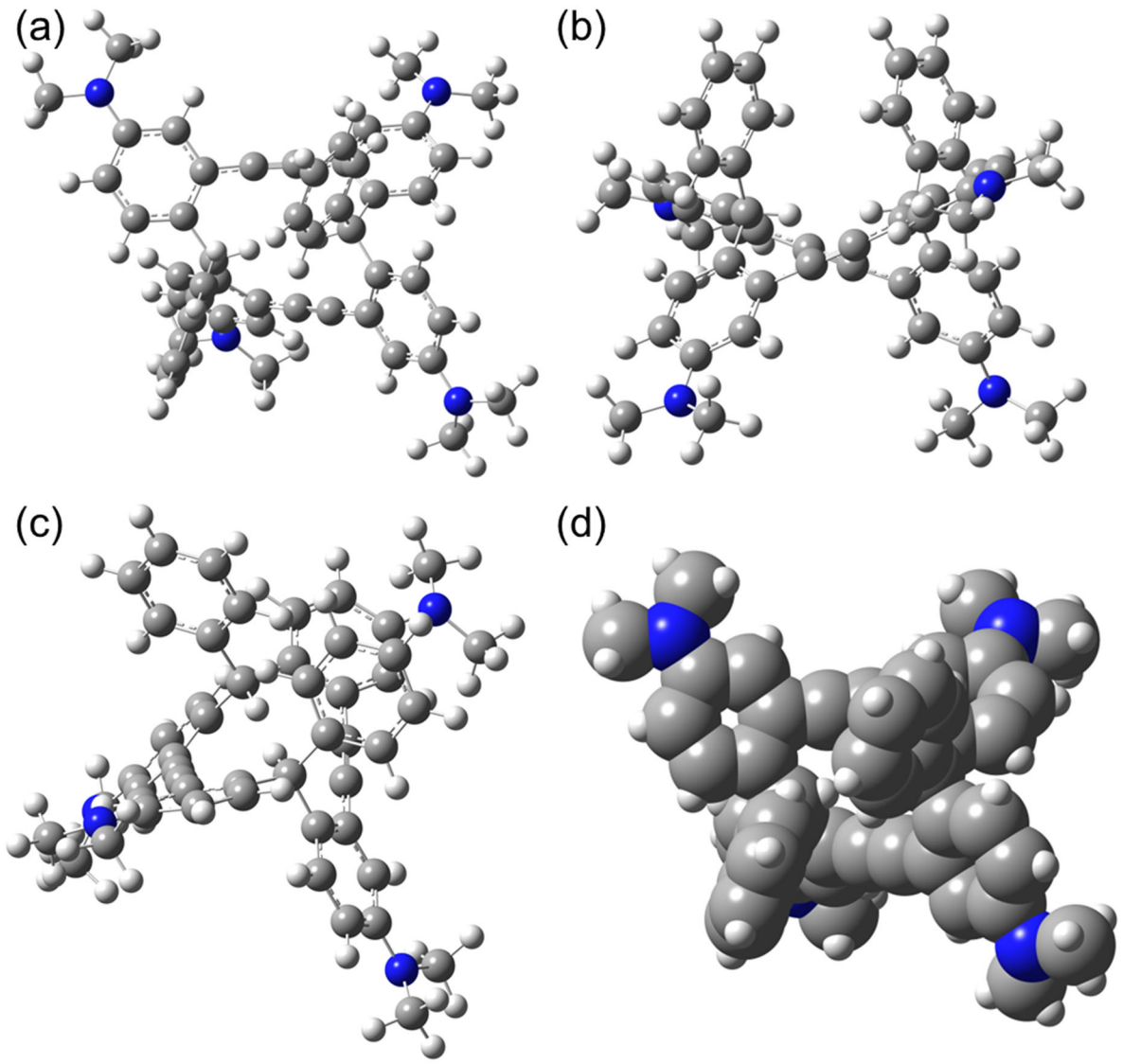


Figure S9. Optimized structure of (R_a,R_a)-**3**. (a) Top view, (b) Front view (c) Side view and (d) Space−filling model (Top view).

Table S23. Atomic coordinates and calculation details of optimized structure of (R_a,R_a)-**3** by TD-DFT, B3LYP/6-311++G(d,p).

Atom	x	y	z
C	-2.75253000	-1.47517100	-0.08575900
C	-2.97795200	-0.22591600	-0.70666900
C	-4.22037500	-0.02395200	-1.30710400
C	-5.22264300	-0.98794500	-1.28553700
C	-5.01087200	-2.23683200	-0.66186700
C	-3.75811500	-2.45376100	-0.06016500
H	-4.40841700	0.91790900	-1.81481500

Atom	x	y	z
H	-6.16781700	-0.76534600	-1.76467200
H	-3.53132400	-3.39215100	0.42773700
C	-1.48552100	-1.76297300	0.50103300
C	-0.37707400	-1.97227200	0.95336800
C	0.93164600	-2.19546100	1.47175700
C	1.06583600	-2.90330500	2.67578500
C	2.06930300	-1.70343500	0.78924300
C	2.32674900	-3.15800900	3.24423000
H	0.15928900	-3.24020800	3.16027100
C	3.31144800	-1.94443900	1.37334300
C	3.45293100	-2.64534500	2.56726100
H	4.20312600	-1.55923000	0.89009500
H	4.44828000	-2.78450200	2.97031200
C	-2.05269100	1.79310200	0.51217100
C	-0.90735800	2.39126100	1.08862700
C	-1.02846800	3.30117700	2.14998400
C	-3.41829200	3.04767900	2.10099100
C	-2.28207500	3.64253100	2.68823600
H	-0.11765200	3.72739600	2.54860700
H	-4.41141800	3.27983300	2.46490200
C	2.97689700	0.07606000	-0.76967700
C	4.21236800	-0.22789600	-1.34074600
C	2.75764500	1.41390300	-0.37094600
C	5.21369600	0.72437500	-1.49812900
H	4.39550500	-1.24374400	-1.67945900
C	3.76226800	2.38136300	-0.52712200
C	5.00784700	2.06255200	-1.09751800
H	6.15342900	0.42129900	-1.94255700
H	3.54029900	3.39015300	-0.20594700
C	1.49783100	1.79939500	0.17384000
C	1.78690400	-1.92330500	-1.73837400
C	1.40067700	-1.37715000	-2.97111700
C	2.03282700	-3.29486800	-1.66034700
C	1.25160900	-2.18461100	-4.09462400
H	1.21754700	-0.30855000	-3.04192500
C	1.88986000	-4.10756900	-2.78904400
H	2.32711500	-3.73221600	-0.71201200

Atom	x	y	z
C	1.49670900	-3.55835000	-4.00748800
H	0.94464100	-1.74311700	-5.03939100
H	2.08354000	-5.17417100	-2.70959900
H	1.38083200	-4.19174100	-4.88277100
N	2.45496300	-3.89003500	4.42307100
N	5.98955300	3.03348000	-1.27837700
N	-5.99377900	-3.22315400	-0.66007400
N	-2.39308900	4.51966000	3.76488600
C	-1.23167200	5.30232200	4.14598800
H	-1.48944800	5.92700800	5.00363500
H	-0.40645300	4.64910000	4.45004400
H	-0.86754100	5.95551200	3.33570000
C	-3.70027500	5.06282900	4.08506100
H	-4.14611500	5.63263400	3.25292400
H	-4.39745700	4.26324200	4.35903100
H	-3.60815800	5.72676300	4.94697100
C	-7.34725500	-2.85765800	-1.03491100
H	-7.38178700	-2.49723700	-2.06916100
H	-7.98414300	-3.74240800	-0.97504400
H	-7.77697800	-2.07536100	-0.38755500
C	-5.82324800	-4.37407000	0.20754800
H	-4.92298200	-4.93603100	-0.06482300
H	-5.74448800	-4.10134600	1.27288600
H	-6.67771800	-5.04244900	0.08432700
C	7.33872700	2.60724700	-1.60097800
H	7.36079000	2.07339700	-2.55766500
H	7.97537600	3.48832300	-1.70286800
H	7.77722700	1.94815200	-0.83349000
C	5.82857000	4.31681500	-0.62000700
H	4.92449700	4.82454000	-0.97408100
H	5.76305800	4.23183200	0.47729100
H	6.68083600	4.95299000	-0.86692200
C	3.72877400	-3.86513300	5.11855800
H	3.65789300	-4.48828100	6.01239400
H	4.52301700	-4.28191800	4.48954400
H	4.03364800	-2.85058200	5.42451700
C	1.26634100	-4.13555400	5.21981900

Atom	x	y	z
H	0.77644400	-3.20840500	5.56017500
H	0.53222000	-4.71687200	4.65139900
H	1.54210400	-4.72347300	6.09767900
C	-3.28955100	2.14621100	1.04875100
H	-4.18823300	1.70000000	0.63603300
C	-1.91039300	0.85376300	-0.67772300
H	-0.95665300	0.33829100	-0.54201700
C	0.39505700	2.08364800	0.59831500
C	-1.80160000	1.57593800	-2.01944600
C	-2.04461000	2.94140700	-2.17481100
C	-1.43290300	0.82498500	-3.14519700
C	-1.91609100	3.54783900	-3.42804700
H	-2.32554100	3.53589900	-1.31176800
C	-1.29823600	1.42709200	-4.39251500
H	-1.25202900	-0.24052700	-3.03384500
C	-1.54040300	2.79627000	-4.53925800
H	-2.10735000	4.61294500	-3.53041700
H	-1.00475900	0.82890100	-5.25143500
H	-1.43579200	3.26960700	-5.51174500
C	1.91126700	-0.98157100	-0.54202700
H	0.95852100	-0.44970300	-0.48485800

Table S24. Calculation details of optimized structure of (R_a,R_a)-**3** by TD-DFT, B3LYP/6-311++G(d,p).

Calculation Type	SP	
Calculation Method	RB3LYP TD-FC	
Formula	$C_{50}H_{48}N_4$	
Basis Set	6-311++G(d,p)	
Charge	0	
Spin	Singlet	
Solvation	scrf=(iefpcm,solvent=dichloromethane)	
E(TD-HF/TD-DFT)	-2153.801880	Hartree
RMS Gradient Norm		Hartree/Bohr
Dipole Moment	4.930748	Debye
Point Group	C_1	
Molecular Mass	704.387898	amu

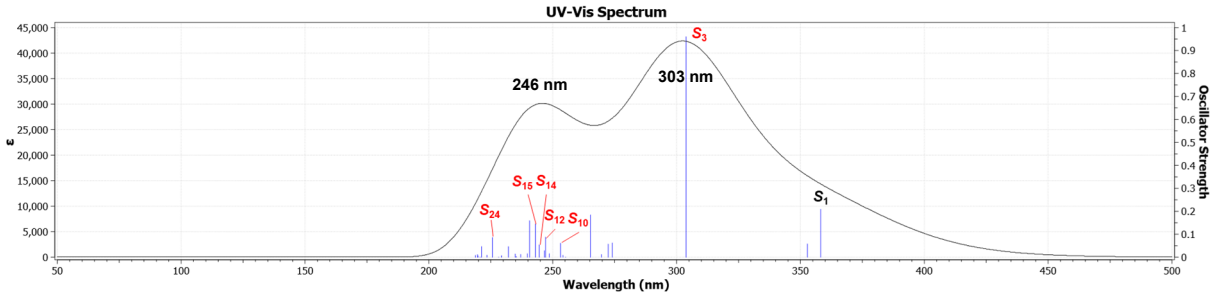


Figure S10. Simulated UV-Vis spectrum of **1** by TD-DFT calculation (red words: electronic transition with f > 0.05 from HOMO-2).

Table S25. Selected electronic transitions for **1** (listed excited states are related to HOMO-2 except excited state 1).

Excited State	Nature		Excitation energies	Wavelength	f
1	71 -> 72	0.69463	3.4615 eV	358.18 nm	0.2087
3	69 -> 72	0.68778	4.0801 eV	303.88 nm	0.9596
10	69 -> 73	-0.12361	4.8974 eV	253.16 nm	0.0606
	70 -> 75	0.56548			
	71 -> 73	-0.19057			
	71 -> 74	0.18950			
	71 -> 77	-0.19536			
	71 -> 79	0.18686			
12	69 -> 73	0.11350	5.0177 eV	247.09 nm	0.0876
	70 -> 76	-0.30374			
	70 -> 80	-0.18487			
	71 -> 74	0.11311			
	71 -> 77	0.43410			
	71 -> 78	0.32805			
	71 -> 79	0.17920			
13	69 -> 74	-0.15712	5.0272 eV	246.62 nm	0.0283
	70 -> 75	0.24594			
	70 -> 76	0.49378			
	71 -> 77	0.24827			
	71 -> 78	0.17858			
	71 -> 79	-0.21390			
14	69 -> 75	0.13439	5.0694 eV	244.58 nm	0.0540
	70 -> 77	0.57290			
	70 -> 78	0.23442			
	71 -> 80	-0.27752			

Excited State	Nature		Excitation energies	Wavelength	f
15	69 -> 74	-0.13289	5.1017 eV	243.02 nm	0.1443
	70 -> 80	-0.13705			
	71 -> 77	-0.40876			
	71 -> 78	0.50921			
17	68 -> 72	0.35881	5.1712 eV	239.76 nm	0.0154
	69 -> 73	0.54649			
	69 -> 74	0.16240			
18	68 -> 72	-0.12325	5.2300 eV	237.06 nm	0.0124
	69 -> 73	0.13850			
	69 -> 74	-0.39109			
	70 -> 76	0.15565			
	70 -> 81	-0.14789			
	71 -> 78	-0.16927			
	71 -> 79	0.45972			
19	68 -> 72	0.10606	5.2694 eV	235.29 nm	0.0035
	69 -> 73	-0.22045			
	69 -> 74	0.43344			
	69 -> 79	0.10414			
	70 -> 75	-0.10748			
	70 -> 76	0.25370			
	71 -> 74	-0.10268			
	71 -> 79	0.34939			
20	69 -> 76	0.13910	5.2792 eV	234.85 nm	0.0141
	70 -> 74	-0.12873			
	70 -> 79	0.59302			
	71 -> 75	-0.10949			
	71 -> 76	0.15320			
	71 -> 81	-0.23334			
21	66 -> 72	0.27569	5.3414 eV	232.12 nm	0.0463
	69 -> 75	0.54972			
	69 -> 76	0.17203			
	70 -> 77	-0.18847			
	70 -> 79	-0.11747			
	71 -> 76	-0.10302			
	71 -> 80	-0.10389			
22	69 -> 76	0.13207	5.4062 eV	229.34 nm	0.0067
	70 -> 77	0.10257			

Excited State	Nature		Excitation energies	Wavelength	f
	70 -> 78	0.34866			
	70 -> 82	-0.15332			
	71 -> 80	0.54712			
24	68 -> 72	0.40430	5.4951 eV	225.63 nm	0.0860
	69 -> 73	-0.21547			
	69 -> 74	-0.15457			
	69 -> 77	0.43114			
	69 -> 78	-0.11689			
	71 -> 83	0.14822			
25	66 -> 72	0.17549	5.5480 eV	223.48 nm	0.0083
	69 -> 75	-0.31017			
	69 -> 76	0.56873			
	71 -> 80	-0.10418			
26	65 -> 72	-0.14711	5.6041 eV	221.24 nm	0.0467
	69 -> 77	-0.26941			
	70 -> 85	-0.28725			
	70 -> 86	-0.15078			
	71 -> 82	-0.16961			
	71 -> 83	0.48875			
27	66 -> 72	0.14496	5.6178 eV	220.70 nm	0.0001
	69 -> 76	-0.11329			
	70 -> 79	0.12448			
	70 -> 82	-0.22751			
	70 -> 83	0.35756			
	70 -> 88	-0.11513			
	71 -> 81	0.36061			
	71 -> 85	-0.28788			
	71 -> 86	-0.15703			
28	66 -> 72	-0.15160	5.6392 eV	219.86 nm	0.0056
	69 -> 76	0.10083			
	70 -> 79	0.15667			
	70 -> 82	-0.12280			
	70 -> 83	-0.32126			
	70 -> 84	0.18399			
	71 -> 81	0.45213			
	71 -> 85	0.16015			
	71 -> 86	0.19379			

#72 LUMO, #71 HOMO, #70 HOMO-1, #69 HOMO-2

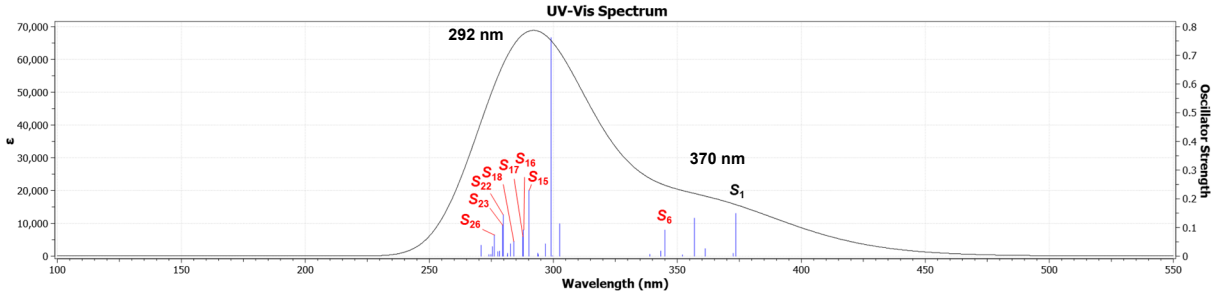


Figure S11. Simulated UV-Vis spectra of (R_a,R_a)-**3** by TD-DFT calculation (red words: electronic transition with f > 0.05 from HOMO-2).

Table S26. Selected electronic transitions for (R_a,R_a)-**3** (listed excited states are related to HOMO-2 except excited state 1).

Excited State	Nature		Excitation Energies	Wavelength	f
1	188 -> 189	0.69699	3.3185 eV	373.62 nm	0.1489
2	186 -> 189	-0.13445	3.3282 eV	372.53 nm	0.0098
	188 -> 190	0.68712			
5	186 -> 189	0.68559	3.5207 eV	352.16 nm	0.0047
	188 -> 190	0.13583			
6	185 -> 189	0.38656	3.5938 eV	344.99 nm	0.0912
	186 -> 190	0.58181			
7	185 -> 189	0.55068	3.6113 eV	343.33 nm	0.0180
	186 -> 190	-0.37654			
	187 -> 190	0.21326			
15	184 -> 190	0.20320	4.2729 eV	290.17 nm	0.2298
	186 -> 191	-0.20936			
	187 -> 191	0.53998			
	188 -> 192	-0.10142			
	188 -> 193	-0.24540			
16	186 -> 191	0.37505	4.3071 eV	287.86 nm	0.0915
	187 -> 191	0.27775			
	187 -> 192	0.24307			
	188 -> 192	-0.11357			
	188 -> 193	0.33437			
	188 -> 196	-0.10073			
	188 -> 197	0.12604			
17	186 -> 191	0.37505	4.3097 eV	287.69 nm	0.0689
	187 -> 191	0.27775			

	187 -> 192	0.24307			
	188 -> 192	-0.11357			
	188 -> 193	0.33437			
	188 -> 196	-0.10073			
	188 -> 197	0.12604			
18	183 -> 190	0.11035	4.3643 eV	284.09 nm	0.0516
	185 -> 191	0.31550			
	186 -> 192	0.30394			
	187 -> 193	0.20939			
	187 -> 196	-0.13592			
	188 -> 194	0.28048			
	188 -> 195	-0.26686			
19	185 -> 191	-0.25387	4.3856 eV	282.71 nm	0.0432
	186 -> 192	-0.13904			
	187 -> 193	-0.11654			
	187 -> 195	-0.11281			
	187 -> 199	-0.15621			
	188 -> 194	0.43153			
	188 -> 196	-0.18429			
	188 -> 197	-0.21991			
20	186 -> 191	-0.28473	4.4036 eV	281.55 nm	0.0101
	186 -> 192	0.31548			
	187 -> 196	0.15849			
	188 -> 193	0.32202			
	188 -> 195	0.35074			
	188 -> 197	-0.11323			
21	185 -> 191	-0.12333	4.4051 eV	281.46 nm	0.0034
	186 -> 191	-0.34663			
	186 -> 192	-0.27771			
	187 -> 194	0.14667			
	188 -> 193	0.36774			
	188 -> 195	-0.27467			
22	185 -> 198	-0.10670	4.4300 eV	279.87 nm	0.1445
	186 -> 191	0.10636			
	186 -> 192	-0.20116			
	187 -> 192	-0.10401			
	187 -> 194	-0.32103			
	187 -> 195	0.18707			

	188 -> 193	0.14304			
	188 -> 194	0.11368			
	188 -> 196	0.33996			
	188 -> 197	-0.16501			
	188 -> 198	-0.13547			
	188 -> 199	0.14571			
23	185 -> 191	-0.25968	4.4355 eV	279.53 nm	0.1091
	185 -> 194	0.10245			
	186 -> 191	0.11672			
	186 -> 192	0.24295			
	187 -> 193	-0.12434			
	187 -> 194	0.19129			
	187 -> 195	0.17164			
	187 -> 197	-0.16462			
	188 -> 196	0.39324			
	188 -> 199	-0.10191			
24	185 -> 191	0.18521	4.4548 eV	278.32 nm	0.0177
	185 -> 192	0.15547			
	185 -> 198	0.10738			
	186 -> 192	-0.23089			
	186 -> 194	0.13380			
	187 -> 192	-0.14336			
	187 -> 193	0.27316			
	187 -> 194	0.18095			
	187 -> 197	-0.11792			
	188 -> 195	0.29786			
	188 -> 196	0.10140			
	188 -> 198	0.20286			
	188 -> 199	-0.12639			
25	185 -> 191	-0.13858	4.4651 eV	277.67 nm	0.0160
	185 -> 192	-0.17798			
	186 -> 193	-0.10198			
	186 -> 194	-0.11217			
	187 -> 192	-0.21478			
	188 -> 194	0.20278			
	188 -> 195	0.19265			
	188 -> 197	0.46264			
	188 -> 198	-0.11515			

26	185 -> 192	0.29655	4.4884 eV	276.23 nm	0.0746
	185 -> 199	-0.12718			
	186 -> 194	0.28254			
	187 -> 194	-0.12164			
	187 -> 197	0.15639			
	187 -> 200	0.11739			
	188 -> 195	-0.10344			
	188 -> 197	0.22531			
	188 -> 198	0.15606			
	188 -> 199	0.30453			
27	185 -> 192	0.45469	4.5002 eV	275.51 nm	0.0335
	185 -> 194	-0.14122			
	186 -> 191	-0.12705			
	186 -> 195	0.17076			
	186 -> 197	0.14495			
	187 -> 198	-0.11715			
	187 -> 200	-0.11353			
	188 -> 198	-0.20384			
	188 -> 199	-0.13955			
	188 -> 200	-0.13641			
28	182 -> 190	-0.10156	4.5112 eV	274.84 nm	0.0062
	185 -> 191	-0.15366			
	185 -> 192	0.20158			
	185 -> 194	0.21601			
	186 -> 193	0.20758			
	186 -> 194	-0.11559			
	186 -> 197	0.13708			
	186 -> 198	0.10666			
	186 -> 199	-0.10529			
	187 -> 193	0.14069			
	187 -> 198	0.19151			
	187 -> 199	0.10994			
	188 -> 196	-0.14660			
	188 -> 200	0.28092			
29	185 -> 191	-0.34728	4.5242 eV	274.04 nm	0.0058
	185 -> 194	-0.12797			
	186 -> 192	0.11293			
	186 -> 193	0.15867			

	187 -> 193	0.42873			
	187 -> 194	-0.11077			
	187 -> 198	-0.12035			
	188 -> 200	-0.11267			
	188 -> 202	0.10997			
	182 -> 189	0.19891			
	185 -> 193	-0.17058			
	186 -> 194	-0.15949			
30	187 -> 194	0.30345	4.5767 eV	270.90 nm	0.0381
	187 -> 195	0.23053			
	187 -> 196	0.11295			
	187 -> 197	0.37912			

#189 LUMO, #188 HOMO, #187 HOMO-1, #186 HOMO-2

6. NMR Spectra

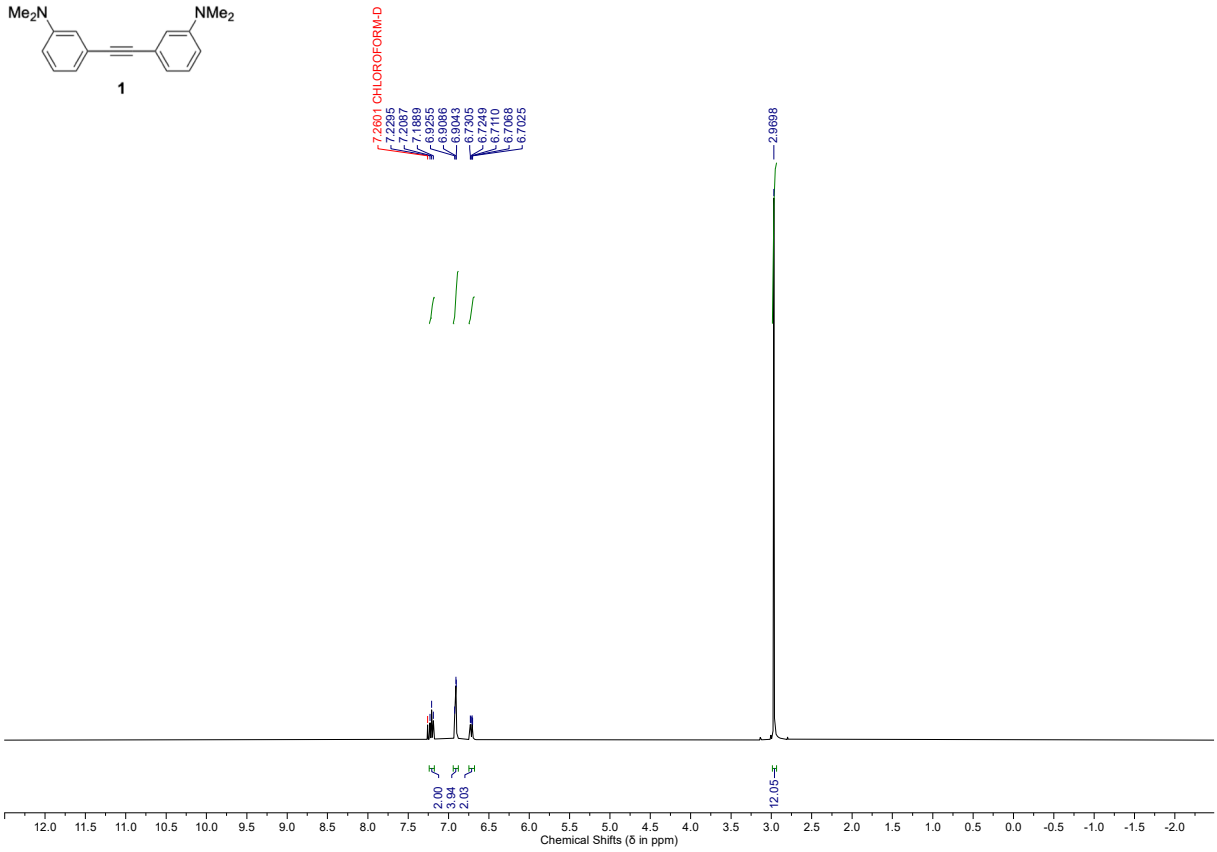


Figure S12. ^{1}H NMR ($CDCl_3$, 400 MHz): 3,3'-(Ethyne-1,2-diyl)bis(*N*,*N*-dimethylaniline) (**1**).

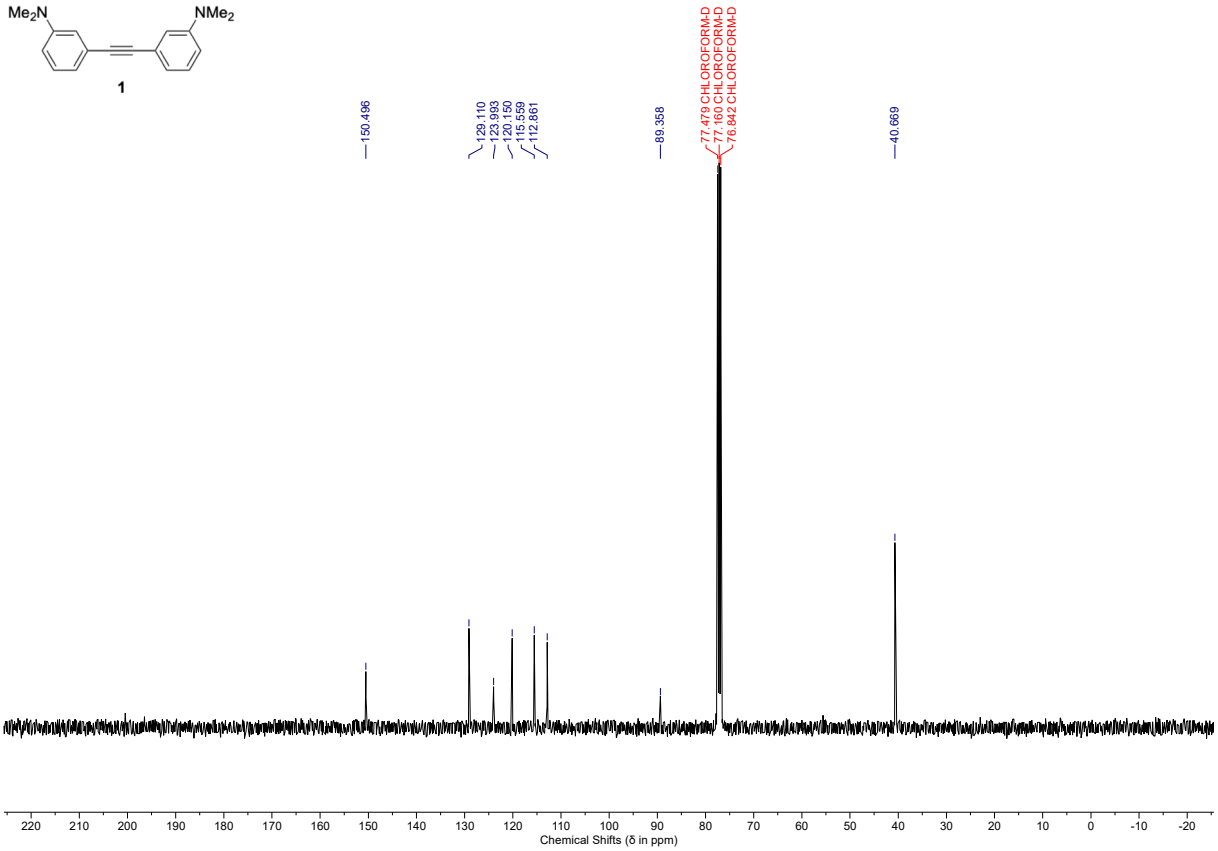


Figure S13. ^{13}C NMR ($CDCl_3$, 100 MHz): 3,3'-(Ethyne-1,2-diyl)bis(*N*,*N*-dimethylaniline) (**1**).

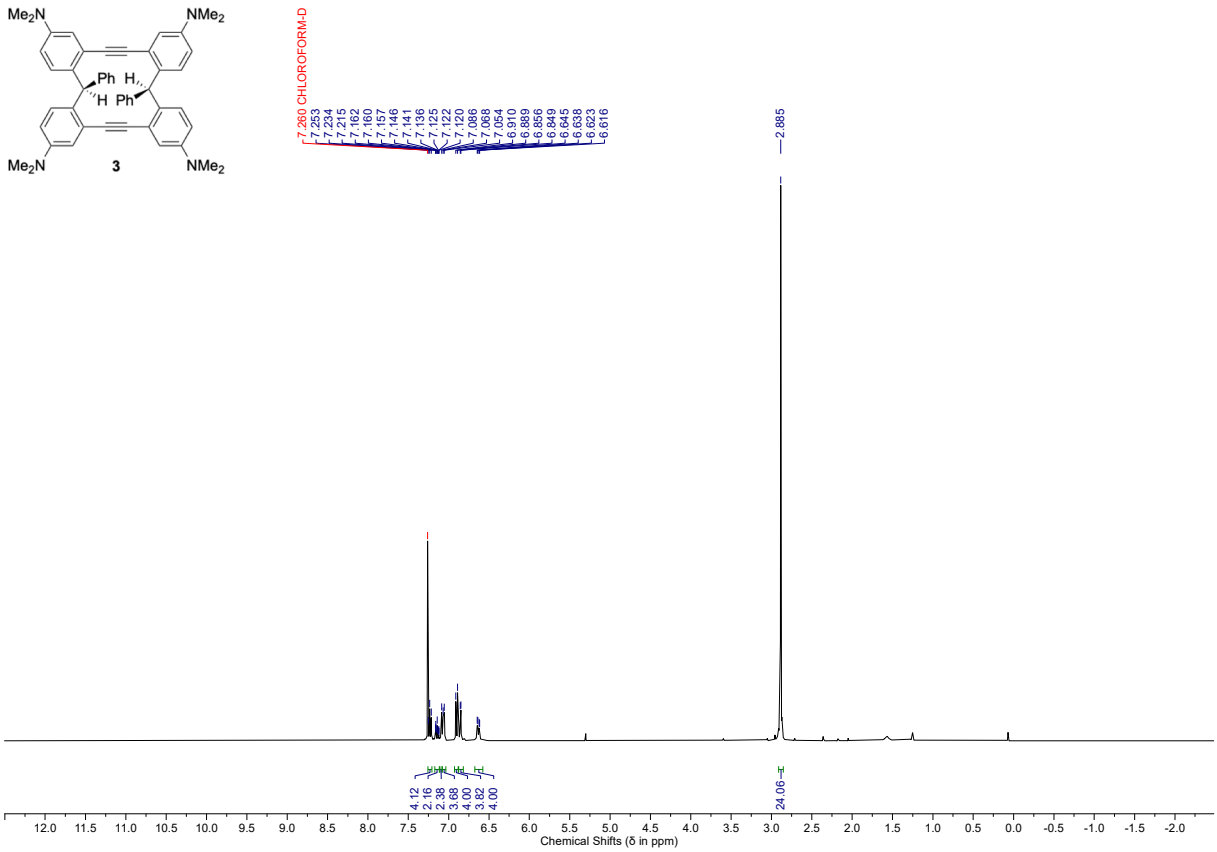


Figure S14. ^{1}H NMR ($CDCl_3$, 400 MHz): Twisted macrocycle **3**.

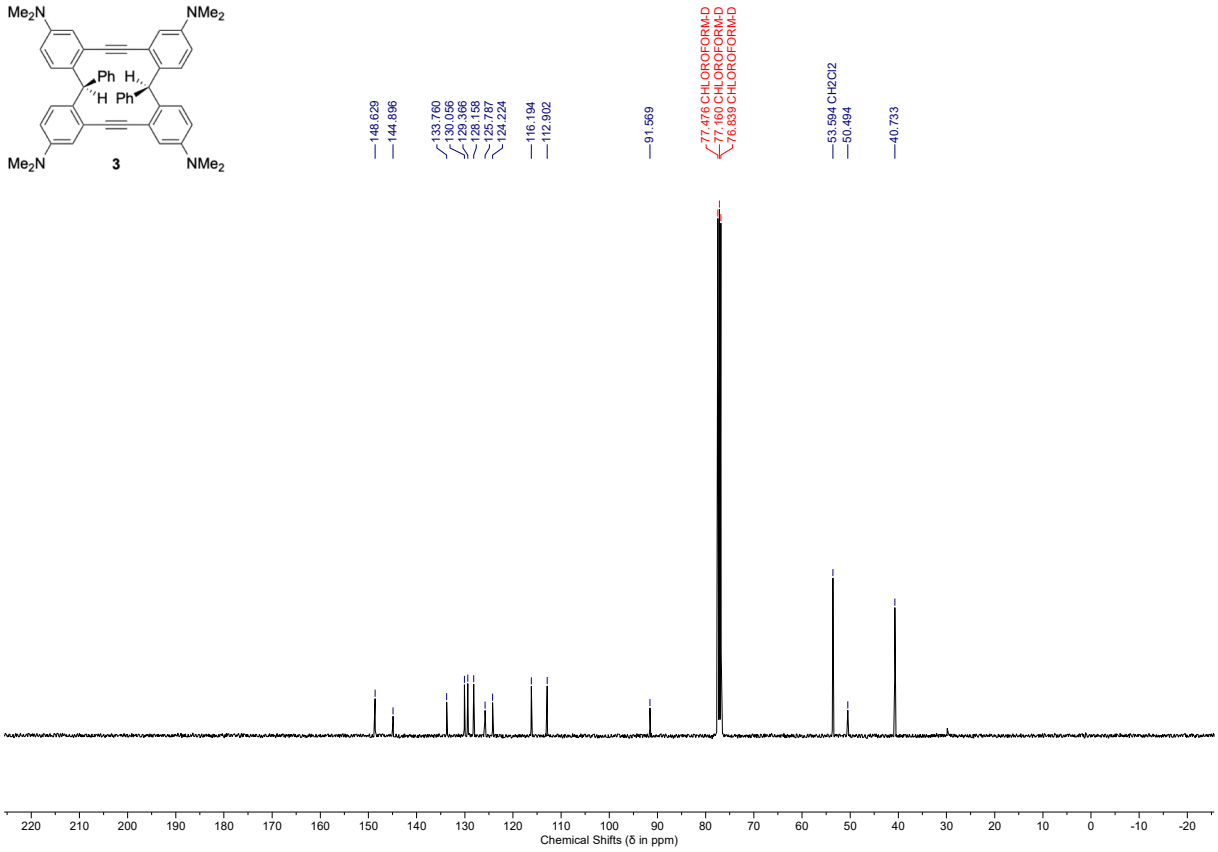


Figure S15. ^{13}C NMR ($CDCl_3$, 100 MHz): Twisted macrocycle **3**.

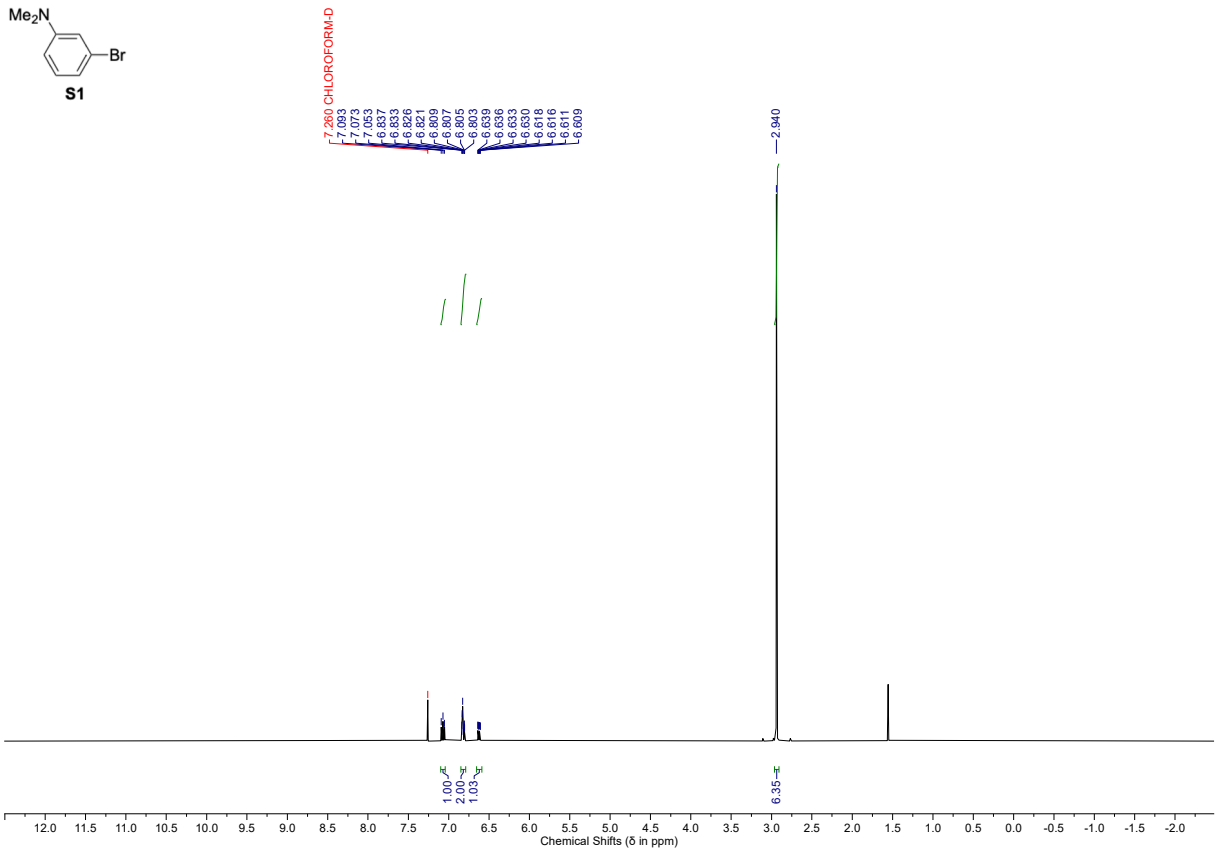


Figure S16. ^{1}H NMR ($CDCl_3$, 400 MHz): 3-Bromo-*N*,*N*-dimethylaniline (**S1**).

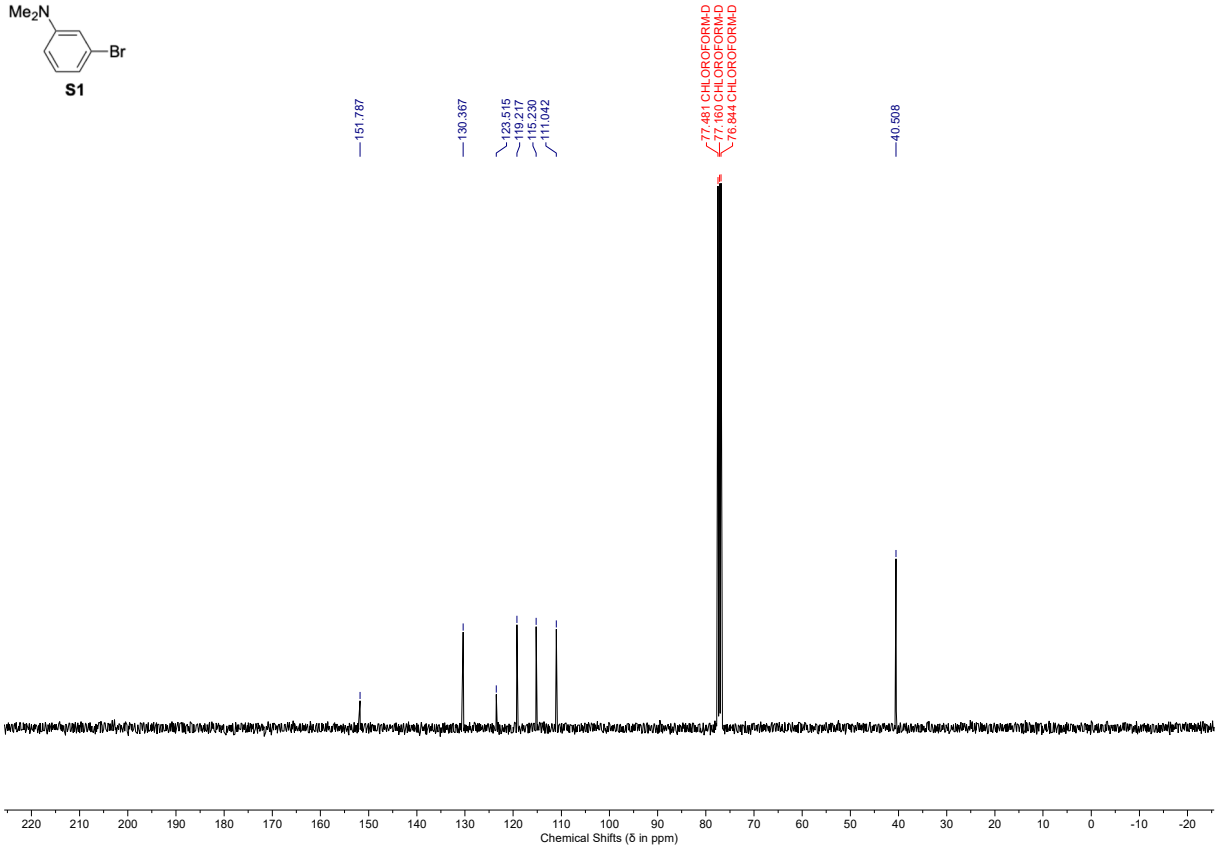


Figure S17. ^{13}C NMR ($CDCl_3$, 100 MHz): 3-Bromo-*N*,*N*-dimethylaniline (**S1**).

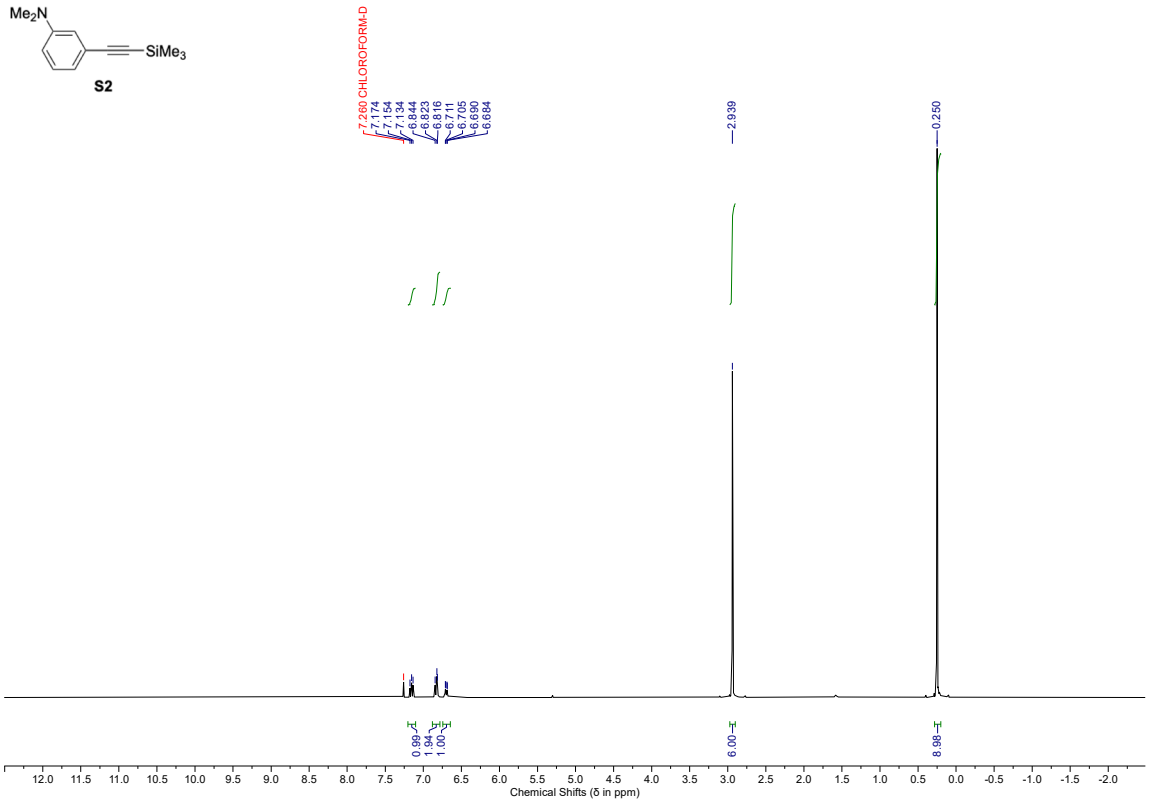


Figure S18. ^{1}H NMR ($CDCl_3$, 400 MHz): *N*,*N*-Dimethyl-3-((trimethylsilyl)ethynyl)aniline (**S2**).

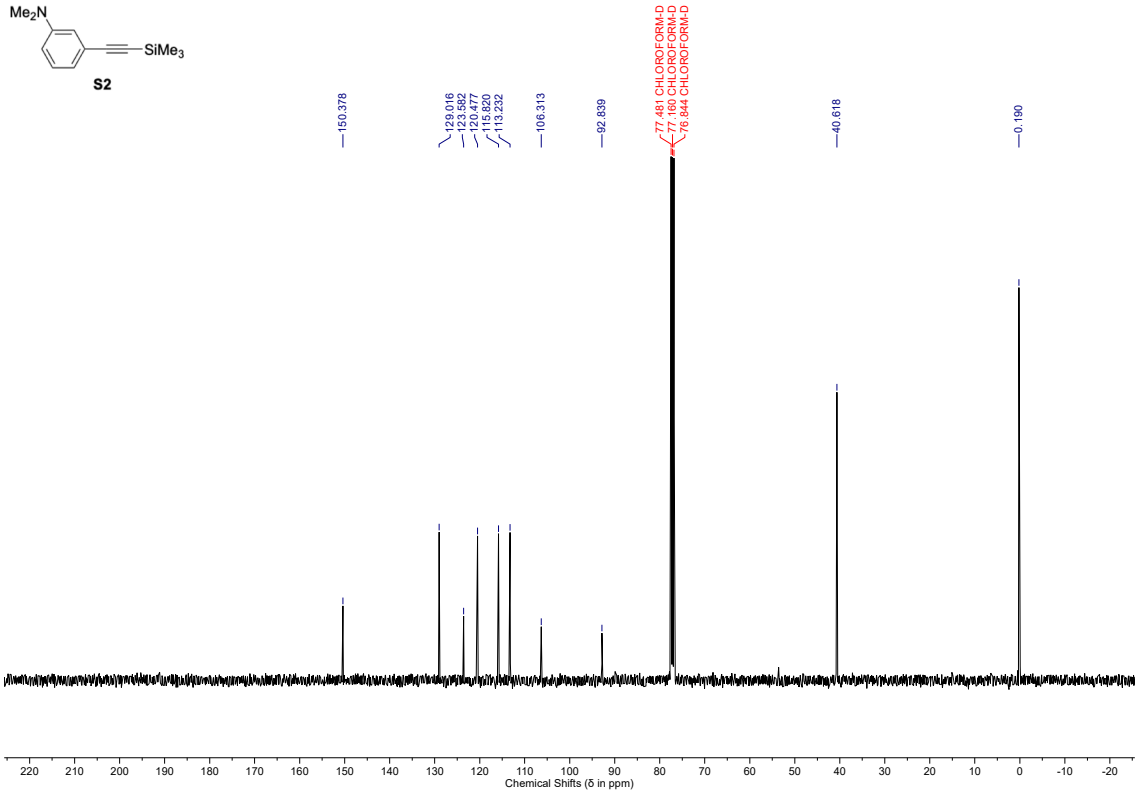


Figure S19. ^{13}C NMR ($CDCl_3$, 100 MHz): *N*,*N*-Dimethyl-3-((trimethylsilyl)ethynyl)aniline (**S2**).

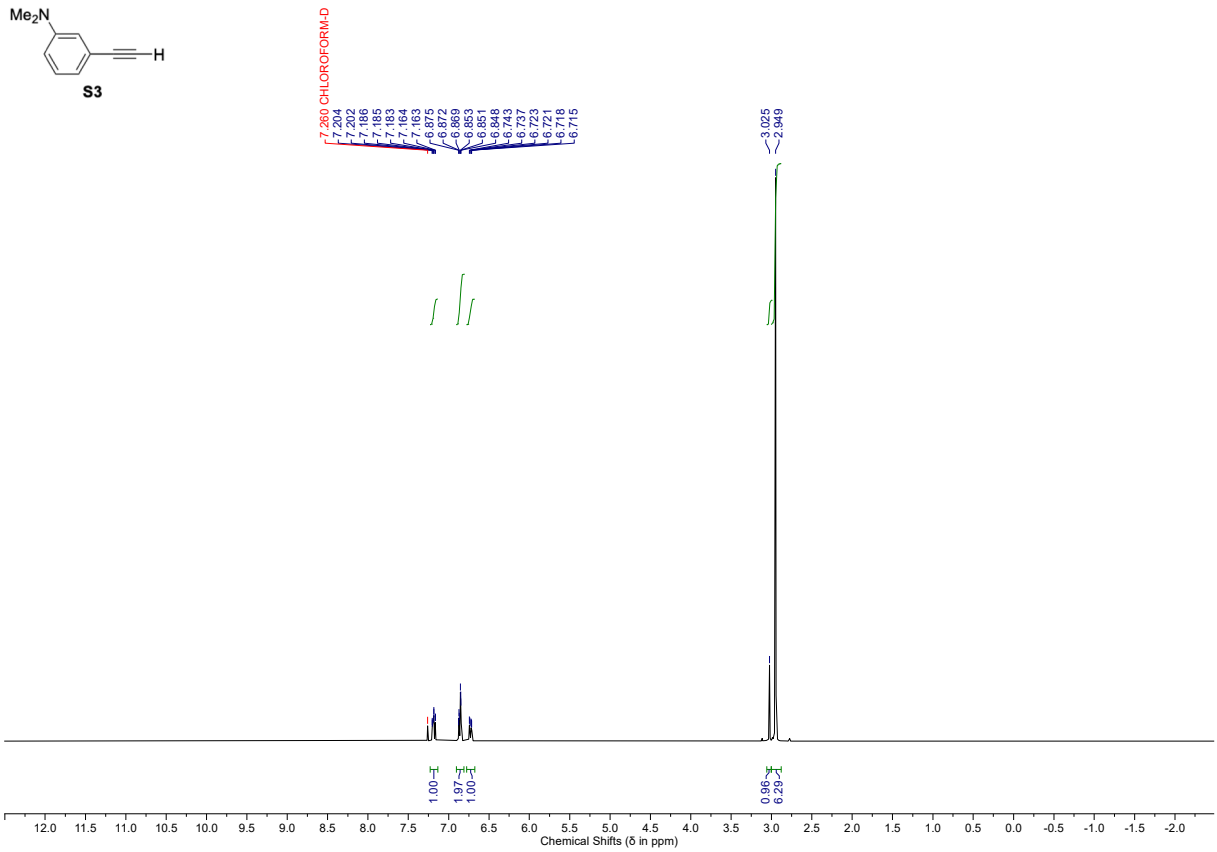


Figure S20. ^{1}H NMR ($CDCl_3$, 400 MHz): 3-Ethynyl-*N*,*N*-dimethylaniline (**S3**).

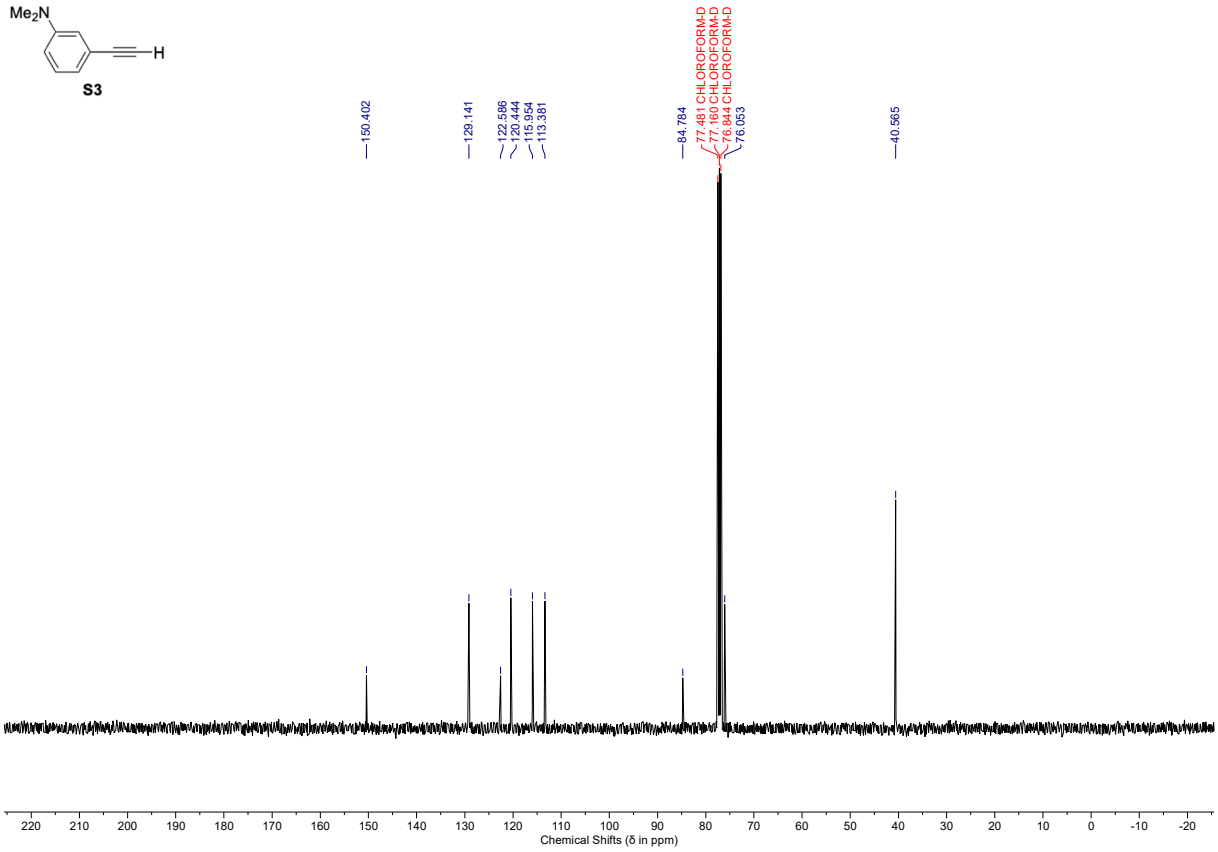


Figure S21. ^{13}C NMR ($CDCl_3$, 100 MHz): 3-Ethynyl-*N*,*N*-dimethylaniline (**S3**).

7. Circular Dichroism Spectra

All Circular Dichroism (CD) Spectra were recorded on JASCO J-1100 Circular Dichroism Spectrophotometer. The cuvette with a thickness of 0.2 cm were used for the measurement.

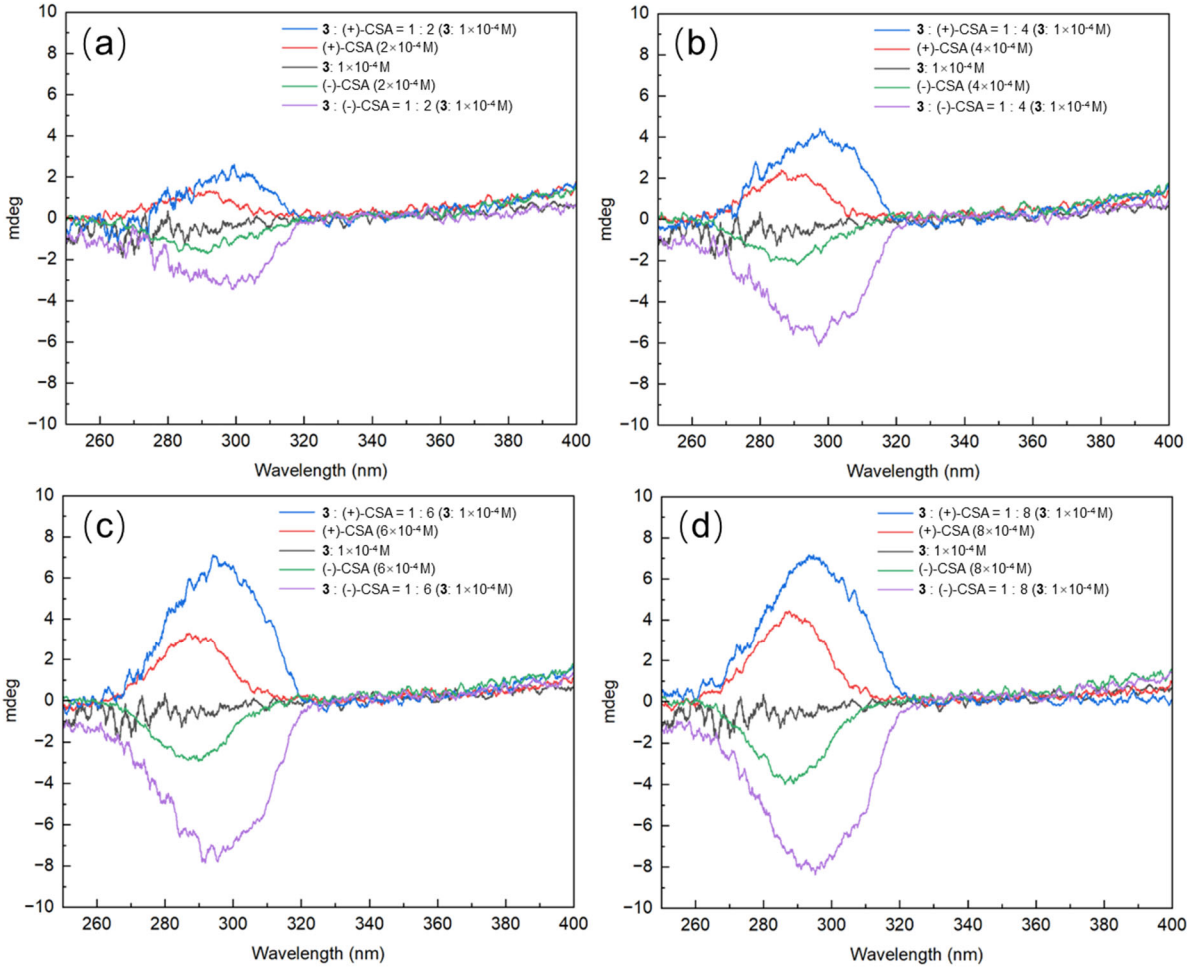


Figure S22. Experimental CD spectra about comparison between mixture and chiral additives (CSA) in dichloromethane: (a) 3:CSA = 1:2; (b) 3:CSA = 1:4; (c) 3:CSA = 1:6; (d) 3:CSA = 1:8. ((+)-CSA: (+)-10-Camphorsulfonic Acid; (-)-CSA: (-)-10-Camphorsulfonic Acid)

8. References

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