Supporting Information

Direct π-extension of a conjugated carbon nanohoop using a zipper method

Kang Wei [†a], Zaitian Cheng [†b], Xinyu Zhang [a], Qiang Huang [c], Pingwu Du [*a]

[a] Key Laboratory of Precision and Intelligent Chemistry, Anhui Laboratory of Advanced Photon Science and Technology, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

[b] Anhui Province Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory, HFIPS, Chinese Academy of Sciences, Hefei 230031, China

[c] School of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, China

[†]These authors contributed equally to this work

*Corresponding author: dupingwu@ustc.edu.cn
Tel/Fax: 86-551-63606207

Table of Contents

1. Materials and General Information

All reagents including dry solvents and starting reactants for syntheses were purchased from commercial suppliers (Aldrich or Acros) and used directly. All glassware used in experiments was oven-dried and cooled under an inert atmosphere of argon. All air sensitive reactions were performed under argon atmosphere by standard Schlenk techniques. Flash column chromatography was carried out on silica gel (200～300 mesh). Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts are quoted in ppm relative to $CHCl_3$ (δ 7.26 ppm), CH_2Cl_2 (δ 5.30 ppm), $C_2H_2Cl_4$ (δ 5.98 ppm) or tetramethylsilane (δ 0.00 ppm) for ^{1}H NMR and relative to $CDCl_3$ (δ 77.0 ppm) or $C_2D_2Cl_4$ (δ 73.8 ppm) for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, m=multiplet), coupling constant (Hz), and integration. High-resolution mass spectrum (HR-MS) was acquired using MALDI-TOF- MS techniques. UV-vis spectra were recorded on a UNIC-3802 spectrophotometer in quartz cuvettes.

2. Synthetic procedures of **NECR**

Synthesis of compound 1. Compound **1** was prepared according to the published procedures. [S1]

Synthesis of compound 2. Compound **2** was prepared according to the published procedures. [S2]

Synthesis of compound 4. To a round-bottom flask (500 mL) was added compound 1 (209.01 mg, 0.186 mmol), 2 (195.52 mg, 0.186 mmol), THF (250 mL) and H_2O (40 mL), then potassium carbonate (800 mg, 5.57 mmol) and $Pd(PPh_3)_4$ (30.06 mg, 0.026 mmol) was added after argon bubbling for 25 minutes. Then, the mixture was reacted at 80 °C for 48 hours. After cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The organic layer was dried by anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford macrocycle intermediate 3 as a yellow solid for the next step without further purification. To a 50-mL round-bottom flask (vessel A) containing a magnetic stirring bar were added $SnCl_2{\cdot}2H_2O$ (274 mg, 1.21 mmol), THF (25 mL) and concentrated HCl/H_2O (0.21mL, 12 mol/L) were added, and the resultant mixture was further stirred at room temperature for 30 min. To another 200-mL round-bottom flask (vessel B) containing a magnetic stirring bar were added the above crude product 8 and dry THF (10 mL). A solution of H_2SnCl_4/THF (18 mL, 0.72 mmol, 0.04 M in THF) in vessel A was added. After stirring the mixture at room temperature for 10 h, the mixture was added aqueous saturated sodium thiosulfate, extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Purification by column

chromatography with petroleum ether/CH_2Cl_2 as the eluent (v/v, 4:1) afforded pure 4 (49.68 mg, 18%) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.23 (d, J = 8.8 Hz, 2H), 7.68 (dd, J = 8.7, 1.9 Hz, 2H), 7.56 – 7.49 (m, 26H), 7.47 (d, J = 8.4 Hz, 4H), 7.39 – 7.36 (m, 4H), 7.31 (d, J = 1.8 Hz, 2H), 7.28 (dd, J = 8.3, 2.2 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.09 (dd, J = 8.0, 1.9 Hz, 2H), 7.02 – 6.94 (m, 6H), 6.84 (dd, J = 8.3, 2.2 Hz, 2H), 6.68 (dd, J = 8.1, 2.1 Hz, 2H), 6.21 (dd, J = 8.1, 1.9 Hz, 2H), 1.08 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.29, 142.81, 141.56, 138.72, 138.57, 138.55, 138.46, 138.33, 138.28, 137.30, 137.01, 134.90, 134.28, 132.80, 132.56, 131.68, 131.59, 131.47, 131.42, 130.68, 130.41, 130.23, 130.11, 130.00, 127.46, 127.43, 127.39, 127.28, 127.23, 127.19, 127.16, 124.33, 123.77, 123.41, 122.87, 120.41, 34.19, 31.22. HR-MS (MALDI-TOF) *m/z* calcd. for: $C_{104}H_{76}Br_2$ $[M]^+$: 1485.4327, found: 1485.4568.

Synthesis of compound 6. To a round-bottom flask (100 mL) was added compound **4** (50 mg, 33.66μmol), **5** (26.32mg, 168.29μmol), THF (50 mL) and H_2O (10 mL), then potassium carbonate (55.82mg, 403.89μmol) and $Pd(PPh_3)_4$ (4 mg, 3.37μmol) was added after argon bubbling for 25 minutes. Then, the mixture was reacted at 80 °C for 48 hours. After cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2. The organic layer was dried by anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography with petroleum ether/EtOAc as the eluent (v/v, 8:1) afforded pure **6** 36.49 mg, 70%) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.72 – 7.69 (m, 2H), 7.60 – 7.53 (m, 24H), 7.51 – 7.42 (m, 14H), 7.41 –

7.35 (m, 6H), 7.32 – 7.28 (m, 4H), 7.23 (dd, *J* = 8.1, 2.0 Hz, 2H), 7.09 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.04 (dd, *J* = 8.1, 2.1 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 4H), 6.70 (dd, *J* = 8.1, 2.1 Hz, 2H), 6.31 (dd, *J* = 8.1, 1.9 Hz, 2H), 1.10 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.01, 142.88, 142.11, 139.53, 138.81, 138.64, 138.53, 138.41, 138.32, 138.30, 138.26, 137.90, 137.57, 137.39, 134.59, 133.63, 133.25, 133.21, 131.76, 131.65, 131.40, 131.06, 130.69, 130.17, 130.08, 128.91, 128.18, 127.41, 127.35, 127.26, 127.17, 127.11, 127.02, 126.80, 125.97, 124.06, 123.58, 123.27, 122.68, 34.14, 31.20. HR-MS (MALDI-TOF) *m/z* calcd. for: $C_{116}H_{84}Cl_2$ $[M]^+$: 1548.602, found: 1548.658.

Synthesis of compound NECR. A solution of **6** (20 mg, 0.013 mmol) and DDQ (35.47 mg, 0.156 mmol) in 20 mL of anhydrous CH_2Cl_2 was degassed by argon bubbling for 20 minutes. The mixture was cooled with an ice bath and then was added TfOH (0.15 mL). After stirring at 0 °C for another 30 minutes, the reaction was quenched with saturated $NaHCO_3$ solution. The organic phase was separated, washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous magnesium sulfate and evaporated. Purification by column chromatography with CS_2 as the eluent afforded pure **NECR** (7.91 mg, 40%) as an red solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 10.39 (s, 2H), 9.55 (s, 2H), 9.28 (s, 2H), 9.18 (br, J = 8.2 Hz, 6H), 9.09 (d, J = 2.2 Hz, 2H), 8.88 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.84 (dd, J = 8.7, 2.1 Hz, 2H), 7.43 – 7.26 (m, 28H), 1.94 (s, 18H). Due to the low solubility, ^{13}C NMR measurement could not be carried out. HR-MS (MALDI-TOF) *m/z* calcd. for: $C_{116}H_{84}Cl_2$ $[M]^+$: 1529.4575, found: 1529.4543.

3. OFET measurements

The bottom-gate/bottom-contact OFETs were prepared on heavily doped Si wafers with a 300 nm thermally grown SiO_2 layer as the gate dielectric. Cleaned SiO_2 was used as the substrate, and Cr/Au (thickness: 5 nm/30 nm) was deposited on its surface by thermal evaporation as source/drain electrodes. **NECR** (4 mg/mL) was drop-coated on source/drain electrodes. The device was annealed at 150 ℃ for 1 hour in a N_2 environment, which are characteristic of the channel width (W) of 2 mm and channel length (L) 200 um. Field-effect mobility (μ_{FET})was calculated from the slope of the square root of the drain current(I_D) versus the gate voltage curves in the saturation regime, using the transistor equation:

$$I_D = \frac{WC_i\mu_{FET}(V_G - V_T)^2}{2L}$$

where C_i is the area capacitance of the SiO_2 dielectric, V_G and V_T is the gate voltage and threshold voltage, respectively.

4. Computational Details:

All of density functional theory calculations were used to identify the performed by using Gaussian 16 software[S3]. Geometrical optimization were carried out at the theoretical level of B3LYP/6-31G(d,p), where DFT-D3(BJ)[S4] and Polarizable continuum model (PCM)[S5] methodologies can be used to correct dispersion force and solvent effect of dichloromethane. The following pictures are drawn with Multiwfn 3.8[S6] and VMD without special instructions.

The resultant structures were further validated by frequency analysis without imaginary frequency. The strain energy (SE) was calculated using the reported computational methods[S7]. The strain energy of **6** and **NECR** is typically evaluated following the formula:

SE(**6**) = E(**6**) + 10×E(Diphenyl) – E(**6**-Fragment) – 9×E(1,4-diphenylbenzene) **Eq(1)**

SE(**NECR**) = E(**NECR**) + 8×E(Diphenyl) – E(**NECR**-Fragment) – 7×E(1,4-diphenylbenzene) **Eq(2)**

Moreover, time-dependent density functional theory (TD-DFT) with PBE0 (25%)/6-31G(d,p)/PCM, where the ratio of Hartree-forck exchange energy was set to 25%, were used to simulate the UV spectrum and fluorescence spectrum by using ORCA software.

5. Physical characterizations and photophysical properties

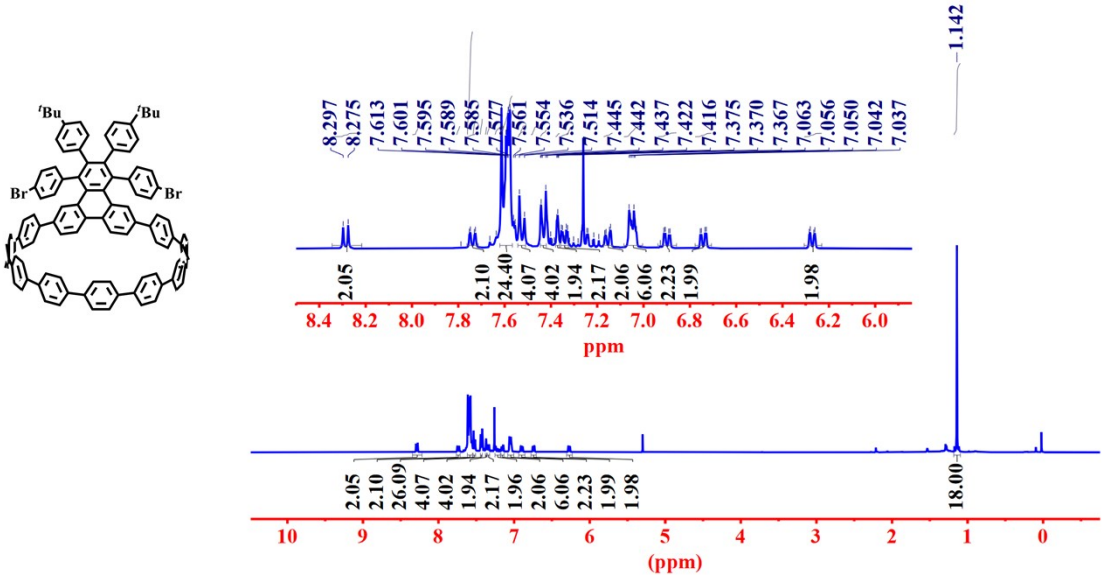

Figure S1 ^{1}H NMR spectrum of **4** in $CDCl_3$.

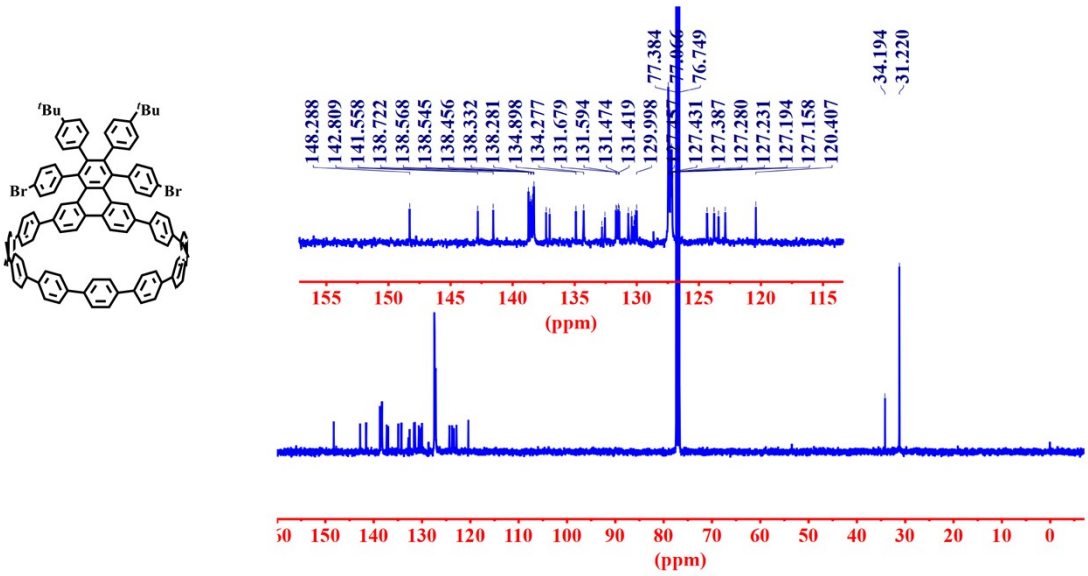

Figure S2 ^{13}C NMR spectrum of **4** in $CDCl_3$.

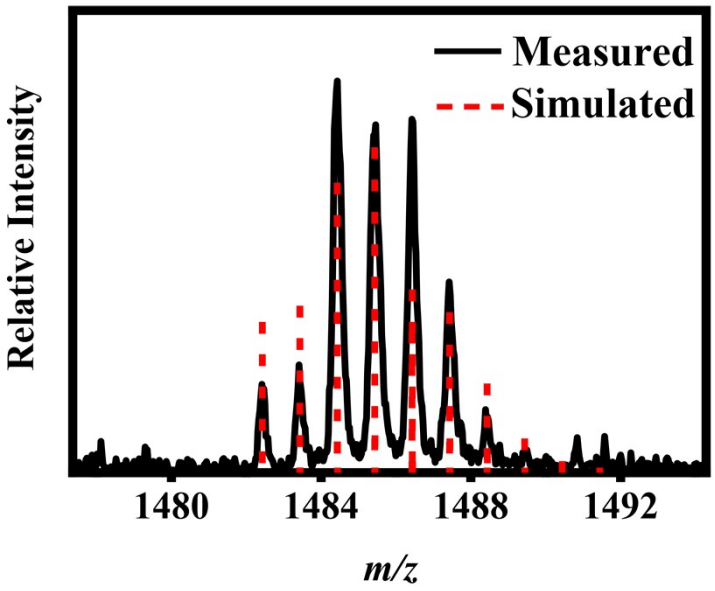

Figure S3 HR-MS (MALDI-TOF) data for **4**.

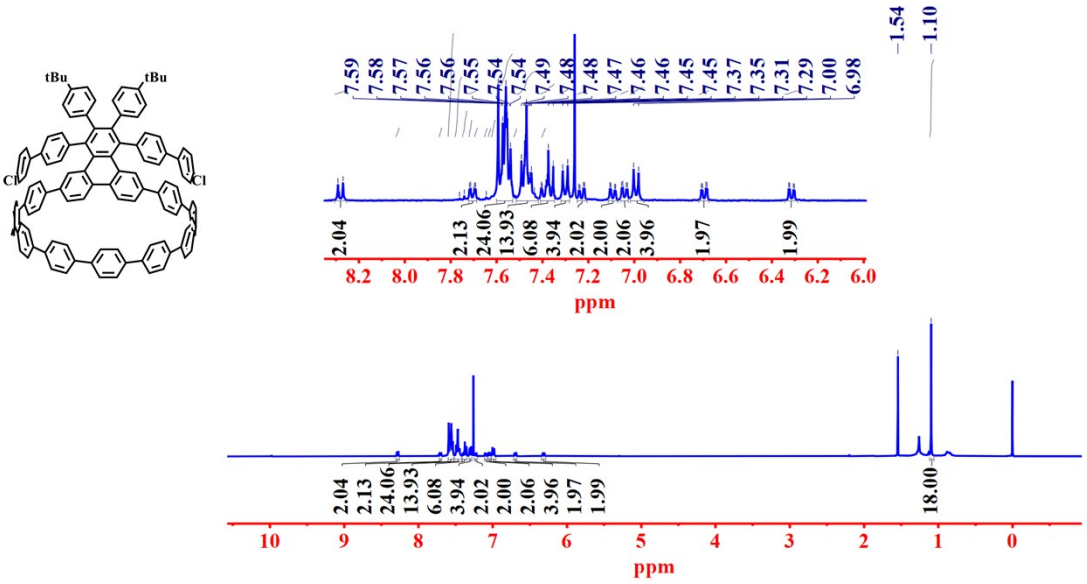

Figure S4 ^{1}H NMR spectrum of **6** in $CDCl_3$.

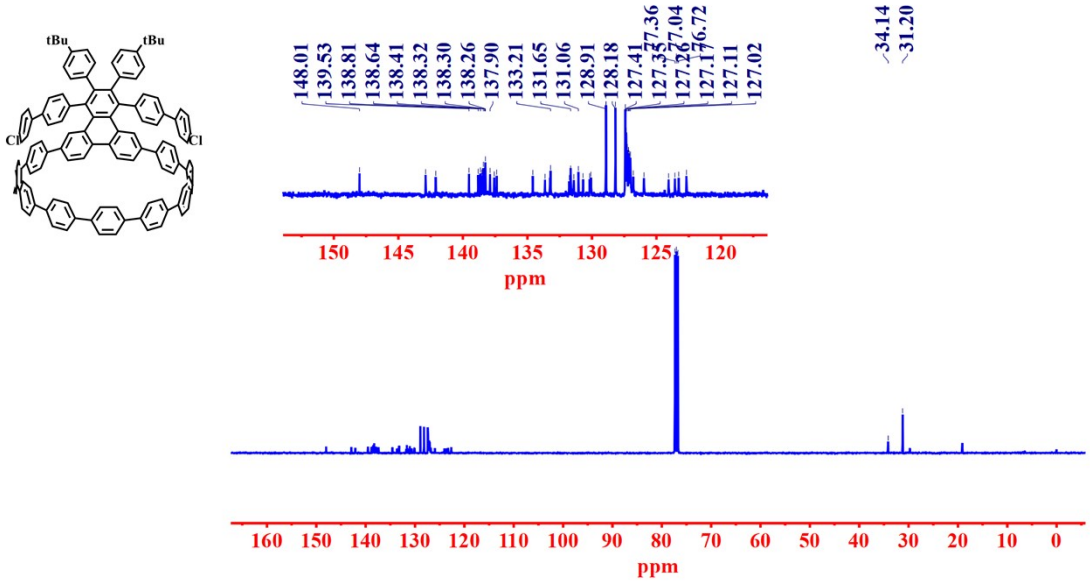

Figure S5 ^{13}C NMR spectrum of **6** in $CDCl_3$.

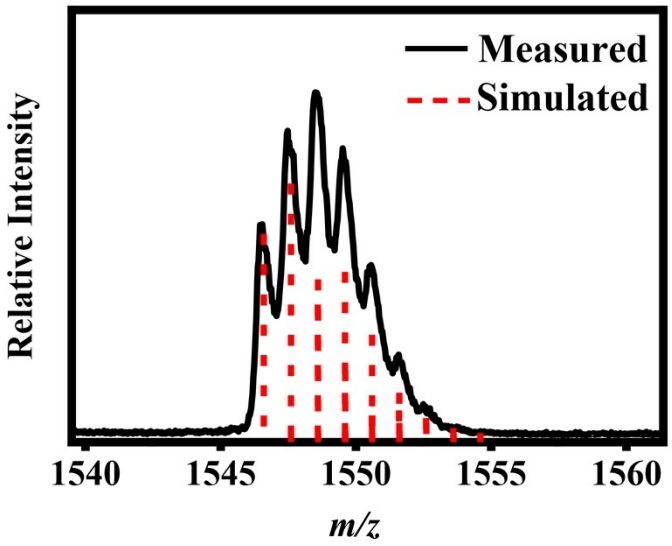

Figure S6 HR-MS (MALDI-TOF) data for **6**.

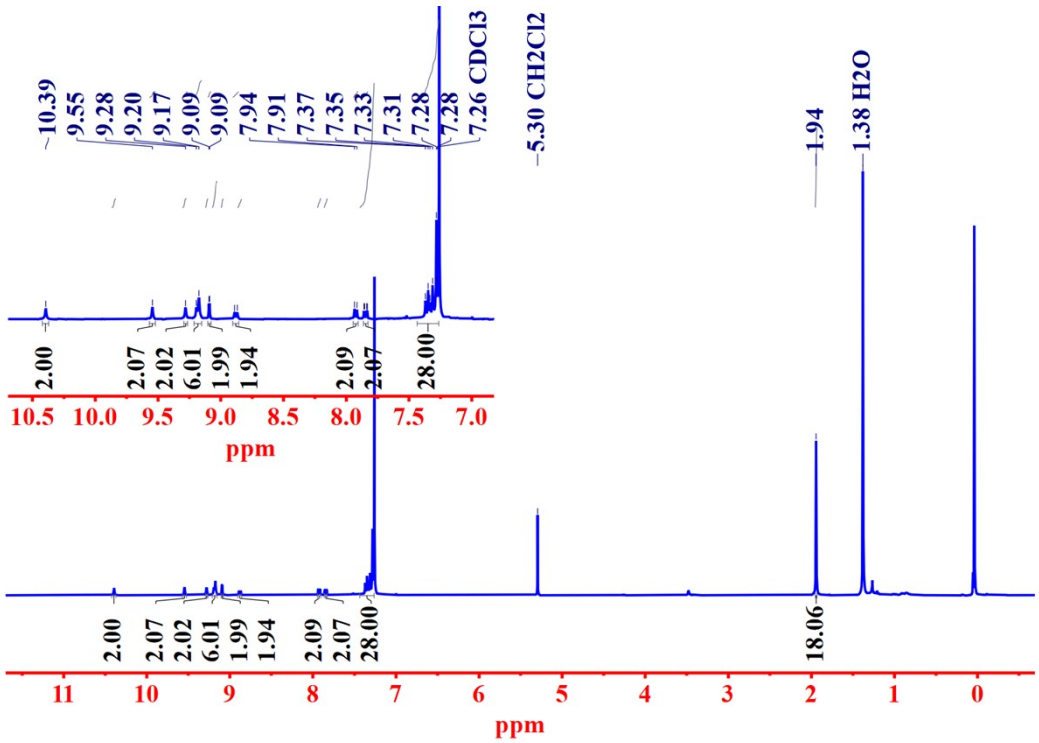

Figure S7 ^{1}H NMR spectrum of **NECR** in $CDCl_3$.

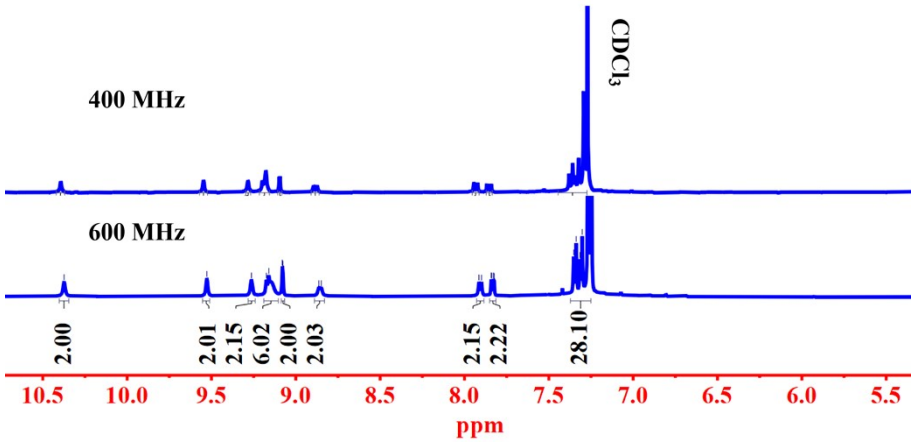

Figure S8 Comparison of ^{1}H NMR spectrum of **NECR** in $CDCl_3$ on a 400 MHz and 600 MHz spectrometer, respectively**.**

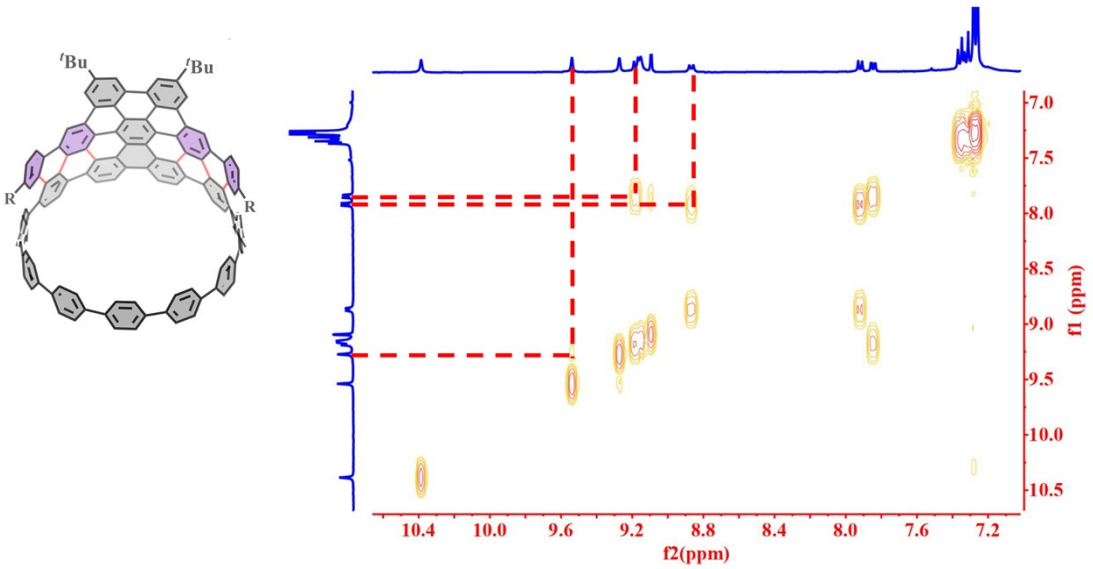

Figure S9 Expanded 2D ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $CDCl_3$) of **NECR**.

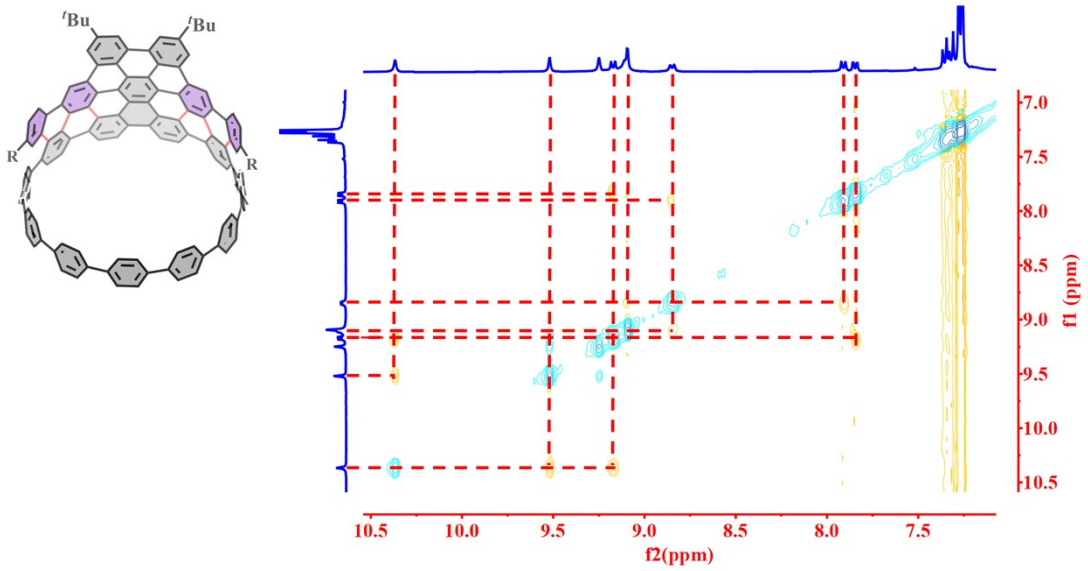

Figure S10 Expanded 2D ^{1}H-^{1}H ROESY NMR spectrum (400 MHz, $CDCl_3$) of **NECR**.

Table S1 Energy level (unit: eV) of frontier molecular orbitals for **6** and **NECR** under the theoretical level of B3LYP-D3BJ/6-31G(d,p)/PCM(dichloromethane)

E(eV)	**NECR**	**6**
E_{LUMO+3}	**-1.64**	**-1.34**
E_{LUMO+2}	**-1.71**	**-1.39**
E_{LUMO+1}	**-1.83**	**-1.54**
E_{LUMO}	**-2.26**	**-1.77**
E_{Gap}	**2.61**	**3.28**
E_{HOMO}	**-4.87**	**-5.06**
E_{HOMO-1}	**-5.28**	**-5.36**
E_{HOMO-2}	**-5.34**	**-5.46**
E_{HOMO-3}	**-5.45**	**-5.71**

Table S2 Energy (Ha.) for strain energy calculations of **6** and **NECR** under the theoretical level of B3LYP-D3BJ/6-31G(d,p)/ PCM(dichloromethane)

Label	Value
Diphenyl	-463.370414
1,4-diphenylbenzene	-694.456567
6	-5392.131578
NECR	-5381.528988
6-Fragment	-3775.768226
NECR-Fragment	-4227.347128
strain energy (kcal/mol) of 6§	26.11
strain energy (kcal/mol) of NECR§	31.87

§ The different value from previous result[5] is attributed the effect of different solvent.

Table S3 oscillator strengths (>0.2) and transitions of **6** and **NECR** from the level of PBE0/6-31G(d,p)

$\lambda_{Exp.}$	λ_{DFT}	f_{osc}	**Transitions**
6			
344	356.27	0.6752	HOMO → LUMO + 3(28.9%) HOMO -2 → LUMO (18.6%)
	363.97	1.2802	HOMO -2 → LUMO (37.7%) HOMO → LUMO +2 (29.1%)
	376.35	1.7764	HOMO → LUMO + 1(55.6%) HOMO -1 → LUMO (39.0%)
NECR			
355	429.81	0.2103	HOMO - 4 → LUMO + 2 (52.2%) HOMO - 8 → LUMO (7.4%)
382	447.47	0.2212	HOMO - 3 → LUMO + 3 (59.2%) HOMO -1 → LUMO + 4 (10.3%)
402	457.54	0.2667	HOMO - 1 → LUMO + 4 (30.1%) HOMO - 5 → LUMO (15.6%)
492	468.78	0.9488	HOMO - 2 → LUMO + 4 (38.8%) HOMO - 4 → LUMO + 1 (9.9%)
530	494.67	0.6148	HOMO -3 → LUMO + 1 (42.4%) HOMO → LUMO +5 (14.2%)

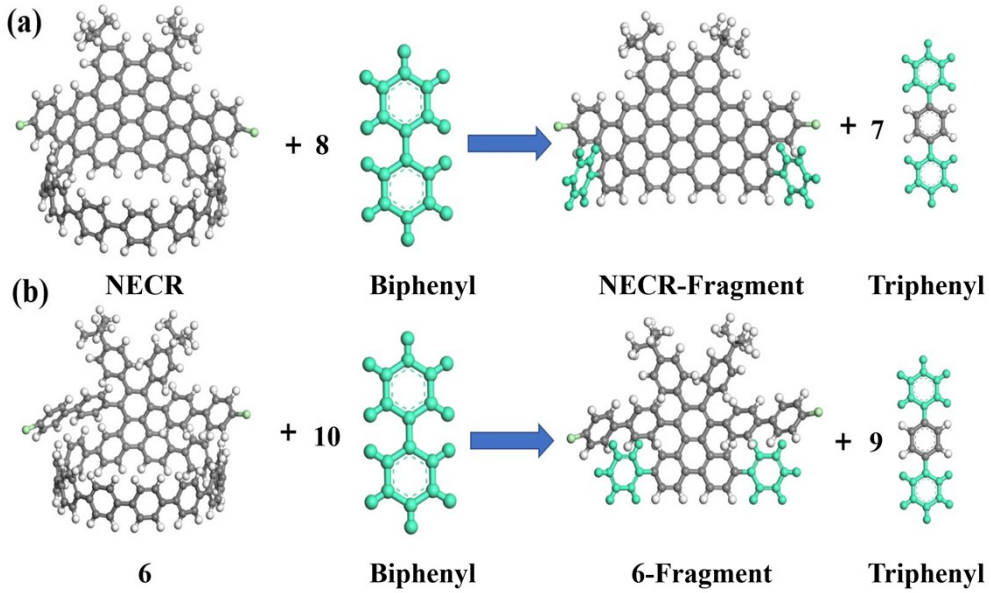

Figure S11. Homodesmotic equation for the calculation of strain energy: **NECR** (a) and **6** (b).

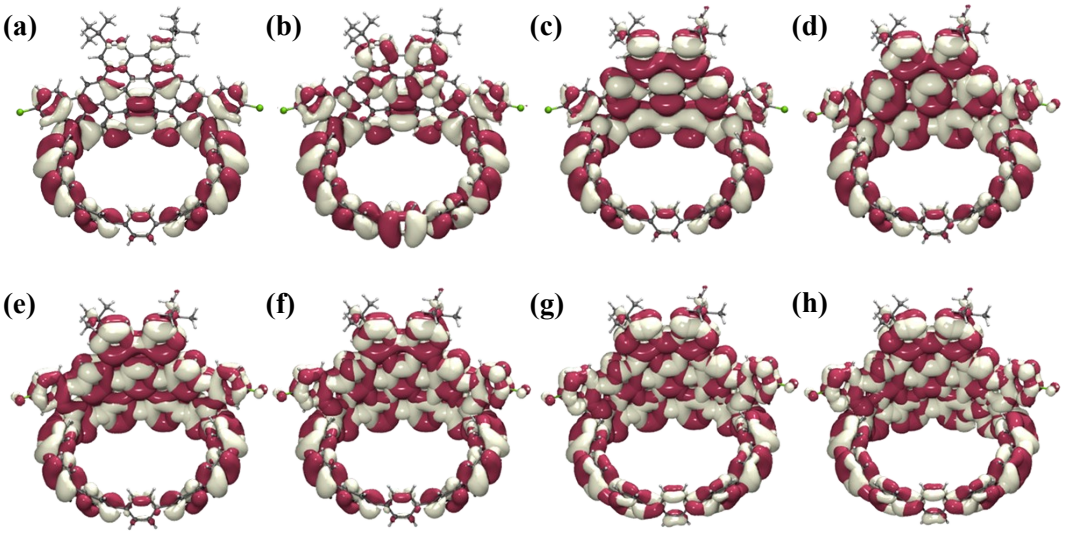

Figure S12 Frontier molecular orbitals of **NECR**: [HOMO-3(a), HOMO-2(b), HOMO-1(c), HOMO(d), LUMO(e), LUMO+1(f), LUMO+2(g) and LUMO+3(h)]

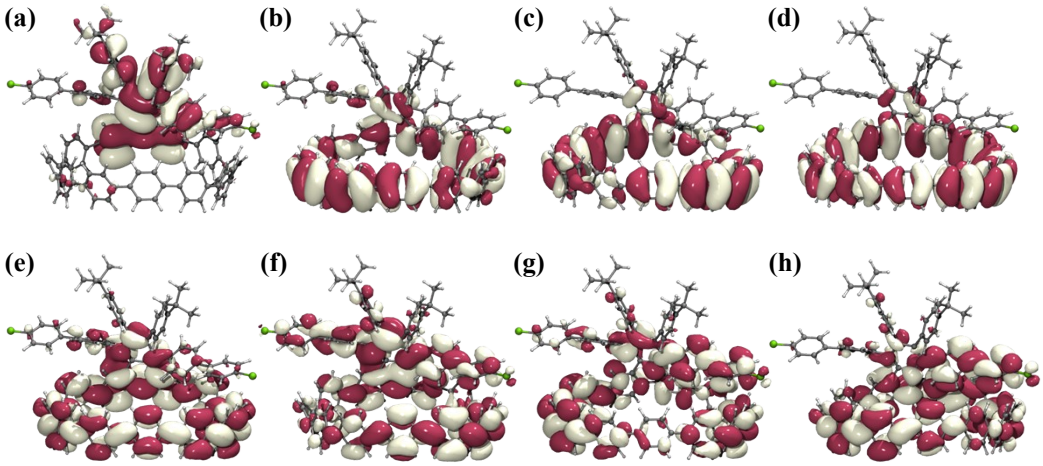

Figure S13 Frontier molecular orbitals of **6**: [HOMO-3(a), HOMO-2(b), HOMO-1(c), HOMO(d), LUMO(e), LUMO+1(f), LUMO+2(g) and LUMO+3(h)]

Table S4 relaxed structures of **6** and **NECR** under theoretical level of B3LYP-D3BJ/6-31G(d,p)

NECR							
C	1.381257	-1.56799	5.213992	C	-1.04311	-4.79107	0.121934
C	2.741564	-1.43142	5.052845	C	0.369722	-4.8892	0.120797
C	3.397061	-1.90522	3.896181	C	1.128077	-4.18779	1.091896
C	2.649446	-2.68123	2.980006	C	2.558295	-4.1252	0.977504
C	1.235457	-2.79833	3.131639	C	3.217902	-4.79937	-0.08271
C	0.579598	-2.17475	4.222531	C	4.571709	-4.53415	-0.30494
C	-0.86862	-2.07324	4.223088	C	5.305397	-3.64588	0.483449
C	-1.60612	-2.59948	3.132989	C	4.675168	-3.03531	1.600439
C	-2.98997	-2.28581	2.9825	C	3.303311	-3.29734	1.857265
C	-3.62091	-1.41258	3.898831	C	-3.10385	-3.72988	0.981337
C	-2.90481	-1.03503	5.05497	C	-3.72455	-2.80489	1.860553
C	-1.57686	-1.36046	5.215126	C	-5.04635	-2.35286	1.604157
C	0.47025	-3.47957	2.127411	C	-5.75667	-2.86902	0.487913
C	-0.94441	-3.38096	2.128155	C	-5.15519	-3.85249	-0.29996
C	-1.69548	-3.99147	1.093759	C	-3.85284	-4.30545	-0.07707
C	-7.00169	2.0118	0.308105	C	8.651093	-1.90152	0.550158
C	-7.50816	1.86603	1.612339	C	7.305101	-2.20911	0.839721
C	-8.20601	2.954892	2.15932	Cl	11.02381	-2.22221	-0.73421
C	-8.25845	4.179873	1.496408	C	3.040169	-8.32506	-3.71995
Cl	-11.2185	-0.65608	-0.72876	C	2.589444	-9.77165	-3.42246
C	-9.61767	-1.29501	-0.38687	C	2.625778	-7.94202	-5.1573
C	-9.18314	-2.44402	-1.05755	C	4.573902	-8.27034	-3.63075
C	-7.93248	-2.95144	-0.75838	C	-4.24081	-7.79561	-3.67852
C	-7.08178	-2.33587	0.182172	C	-5.03614	-6.83426	-4.58822
C	-7.53435	-1.16531	0.844263	C	-5.22334	-8.65727	-2.85608
C	-8.82395	-0.67181	0.555097	C	-3.41344	-8.73123	-4.57487
C	6.692496	-3.3045	0.17778	C	7.027476	-0.24977	2.419186
C	7.448176	-4.03376	-0.76261	C	-7.04471	3.232772	-0.34297
C	8.757701	-3.70705	-1.06198	C	-6.33812	7.91309	0.196577
C	9.34928	-2.63018	-0.3918	C	-7.60417	4.370644	0.267023
C	-1.81391	-5.48727	-0.87283	C	6.582323	-1.48514	1.885858
C	-3.22288	-5.30298	-0.9408	C	5.36449	-2.03783	2.378532
C	-3.96363	-6.06697	-1.8461	C	4.749832	-1.50579	3.546456
C	-3.36383	-6.97826	-2.71984	C	5.415977	-0.47587	4.231101
C	-1.97561	-7.1	-2.68246	C	6.494221	0.166997	3.649344
C	-1.18103	-6.37286	-1.78452	C	-4.90456	-0.82742	3.549696
C	1.035561	-5.68449	-0.8746	C	-5.41941	0.285657	4.234519
C	0.281484	-6.47499	-1.78695	C	-6.39701	1.073563	3.653063
C	0.967554	-7.29958	-2.68318	C	-6.9837	0.735857	2.423089
C	2.363738	-7.37039	-2.72638	C	-6.71664	-0.54997	1.889889
C	3.085023	-6.55441	-1.85769	C	-5.58832	-1.26808	2.382153
C	2.453444	-5.69625	-0.94667	C	-0.01237	9.636814	-3.18401
C	5.551308	8.564671	-2.71079	C	1.374999	9.539339	-3.18418
C	4.399783	9.298986	-2.97981	C	2.143977	10.14785	-2.17894
C	3.535887	9.699208	-1.94648	C	1.476544	10.99034	-1.27288
C	3.947042	9.444023	-0.62816	C	0.090359	11.08776	-1.27274

C	5.088547	8.702266	-0.36129	C	-0.6885	10.34688	-2.17862
C	5.884523	8.185094	-1.3979	C	-2.12945	10.09732	-1.94603
C	6.855983	7.108784	-1.09207	C	-3.04061	9.820852	-2.9793
C	7.39734	6.94698	0.195347	C	-4.28342	9.254744	-2.7101
C	7.944088	5.735278	0.599436	C	-4.66665	8.92646	-1.39702
C	8.003048	4.634483	-0.27282	C	-3.80643	9.328198	-0.36056
C	7.651512	4.866251	-1.61427	C	-2.57246	9.903071	-0.62763
C	7.078931	6.068285	-2.0107	C	-5.77913	7.996786	-1.09076
C	8.153876	3.262059	0.264284	C	-6.14532	6.99719	-2.00887
C	8.774751	2.980564	1.493579	C	-6.88076	5.887445	-1.61203
C	8.550241	1.774942	2.156048	C	-7.26179	5.707994	-0.27061
C	7.705807	0.795559	1.608785	C	-7.04937	6.790165	0.601088
C	7.224578	1.011846	0.304791	H	-8.76857	5.012877	1.969889
C	7.43938	2.214717	-0.34595	H	-9.82697	-2.93203	-1.77955
H	0.922352	-1.1473	6.100213	H	6.854716	1.092365	4.085999
H	3.305678	-0.91539	5.820459	H	-4.95017	0.632312	5.146779
H	-3.39062	-0.44509	5.822896	H	-6.62372	2.040458	4.089681
H	-1.06296	-1.008	6.100914	H	-0.58352	9.052989	-3.89869
H	5.043596	-4.96908	-1.17433	H	1.858758	8.881408	-3.89896
H	-5.68313	-4.21731	-1.16946	H	2.049569	11.53482	-0.52865
H	-5.04155	-5.96581	-1.85738	H	-0.40075	11.70702	-0.52841
H	-1.49693	-7.78238	-3.3684	H	-2.75676	10.01614	-4.00911
H	0.403376	-7.91321	-3.37274	H	-4.9477	9.025307	-3.53736
H	4.164472	-6.59765	-1.86698	H	-4.05254	9.082462	0.666186
H	6.177271	8.245267	-3.5381	H	-1.89194	10.09403	0.195306
H	4.146277	9.532713	-4.00953	H	-5.76449	7.034659	-3.02395
H	3.299569	9.727529	0.194771	H	-7.09214	5.111222	-2.34005
H	5.297629	8.423807	0.665319	H	-7.35346	6.710495	1.639491
H	7.319033	7.753183	0.917241	H	-6.14789	8.700753	0.918122
H	8.233552	5.613177	1.6379	H	-6.5247	3.332078	-1.28875
H	7.752332	4.068402	-2.34263	H	-6.46568	1.187024	-0.14726
H	6.707535	6.15934	-3.02588	H	-8.66347	2.860546	3.139839
H	9.39707	3.73327	1.967375	H	6.938294	2.386835	-1.29151
H	8.98986	1.616671	3.136493	H	5.000375	-0.06697	5.143597
H	6.57723	0.271212	-0.15054	H	-7.61928	-3.86395	-1.25071
H	-4.35964	-6.20898	-5.17893	H	-9.2049	0.192514	1.079613
H	-5.87314	-8.0426	-2.22706	H	7.009954	-4.89343	-1.25468
H	-4.68114	-9.34731	-2.20238	H	9.326552	-4.28092	-1.78382
H	-5.86221	-9.24656	-3.52256	H	9.149654	-1.09904	1.074287
H	-2.84535	-9.4587	-3.98659	H	1.505612	-9.88494	-3.51333
H	-2.71271	-8.17432	-5.20498	H	2.87229	-10.0655	-2.40699
H	-4.0811	-9.29038	-5.23707	H	3.059173	-10.4687	-4.12469
H	5.009082	-8.96536	-4.35496	H	2.932772	-6.9178	-5.39029
H	-5.68392	-6.1706	-4.0088	H	1.543434	-8.00689	-5.29879
H	-5.67018	-7.40085	-5.27848	H	3.098255	-8.61487	-5.88087
H	4.957526	-7.27096	-3.85957	H	4.932842	-8.55893	-2.63785

Table S5 relaxed structures of **6** under theoretical level of B3LYP-D3BJ/6-31G(d,p)

6

C	1.639016	3.724031	5.31113	C	3.225535	2.683701	-0.88193
C	0.41589	4.361278	5.424934	C	1.870578	3.079272	-0.86988
C	-0.40212	4.513099	4.289747	C	1.184144	3.24894	0.344994
C	0.127216	4.128867	3.059149	C	-0.27583	3.548292	0.228382
C	1.343537	3.447016	2.907672	C	-0.75097	4.734084	-0.34422
C	2.095806	3.183929	4.090283	C	-2.11044	4.91938	-0.57359
C	3.194745	2.227258	4.03465	C	-3.0442	3.932105	-0.22424
C	3.614771	1.755008	2.771615	C	-2.5672	2.760797	0.385838
C	4.338072	0.55357	2.711866	C	-1.20809	2.567969	0.596393
C	4.750791	-0.14275	3.844033	C	5.245846	1.802714	0.288299
C	4.500115	0.455139	5.098198	C	6.230297	2.414491	1.074202
C	3.725454	1.598057	5.184513	C	7.528949	1.918802	1.107114
C	1.852129	3.022809	1.584753	C	7.888814	0.789713	0.356228
C	3.122587	2.386965	1.540319	C	6.908837	0.197946	-0.45691
C	3.837085	2.291867	0.316605	C	5.613337	0.698963	-0.49433
C	3.988877	2.663426	-2.16243	C	-4.66189	4.462007	4.107375
C	3.619322	1.833568	-3.22399	C	-3.92177	5.085644	3.089257
C	4.351223	1.817138	-4.41013	C	-2.55001	5.26725	3.207291
C	5.475154	2.632396	-4.58524	C	-1.85281	4.815368	4.342077
C	5.835393	3.467102	-3.51569	C	-2.62175	4.375803	5.433117
C	5.112582	3.482749	-2.32911	C	-3.99746	4.211064	5.320741
C	1.167621	3.341953	-2.16185	C	5.190278	-1.54609	3.67265
C	1.501708	4.44252	-2.95274	C	4.861093	-2.52546	4.624005
C	0.806041	4.716827	-4.12992	C	4.866841	-3.8765	4.296347
C	-0.24396	3.899412	-4.56259	C	5.168806	-4.31021	2.99293
C	-0.55349	2.779604	-3.77451	C	5.684263	-3.34351	2.109903
C	0.135954	2.503215	-2.60111	C	5.713162	-1.99699	2.446849
C	-9.01096	-2.26069	-1.61961	C	-5.48855	-6.41965	-2.8722
C	-8.54098	-3.41234	-2.23712	C	-6.51715	-5.49517	-2.75671
C	-8.54905	-4.65288	-1.57503	C	-7.66718	-5.76801	-1.99495
C	-9.24663	-4.70819	-0.35545	C	-7.79343	-7.07092	-1.47788
C	-9.74764	-3.56137	0.246602	C	-6.75469	-7.99145	-1.57587
C	-9.54678	-2.28909	-0.31907	C	-5.54984	-7.65988	-2.21727
C	-9.63258	-1.05067	0.491133	C	-4.29395	-8.4189	-2.02086
C	-9.56392	-1.12158	1.894404	C	-3.28962	-8.48098	-3.00146
C	-9.22495	-0.01722	2.66162	C	-1.98841	-8.84546	-2.67316
C	-8.90255	1.215333	2.067064	C	-1.62954	-9.14574	-1.34666
C	-9.17386	1.33679	0.692384	C	-2.66866	-9.23036	-0.40435
C	-9.53677	0.234553	-0.07423	C	-3.97226	-8.88153	-0.73497
C	-8.08859	2.223155	2.786549	C	-0.22183	-9.12282	-0.8835
C	-7.29518	1.807027	3.870289	C	0.704401	-8.28029	-1.52141
C	-6.272	2.597939	4.366442	C	1.902703	-7.93257	-0.91044

C	-5.97468	3.849482	3.801842	C	2.223989	-8.40178	0.373321
C	-6.84354	4.32194	2.802354	C	1.374534	-9.36643	0.940955
C	-7.87889	3.531098	2.3112	C	0.182237	-9.72528	0.321658
C	3.247386	-7.67945	1.162738	C	9.253837	0.225284	0.431644
C	4.416903	-7.14498	0.597146	C	10.38141	1.05828	0.490441
C	5.140246	-6.15096	1.248859	C	11.66692	0.529755	0.567895
C	4.714265	-5.62709	2.483953	C	-4.48583	4.107362	-0.50348
C	3.635868	-6.27675	3.110366	C	-5.09112	5.373986	-0.46321
C	2.925404	-7.28246	2.470245	C	-6.44562	5.539689	-0.73927
Cl	13.45049	-1.5309	0.684106	C	-7.21139	4.422875	-1.06487
C	11.83163	-0.85371	0.587676	C	-6.6438	3.152127	-1.11423
C	10.73249	-1.70843	0.534498	C	-5.29004	3.005142	-0.83217
C	9.45386	-1.16383	0.457712	Cl	-8.9255	4.619499	-1.40862
C	-1.05847	4.185121	-5.8302	C	-0.94225	2.98708	-6.79689
C	-0.57224	5.444948	-6.56412	C	6.306428	2.64267	-5.87419
C	-2.53875	4.391229	-5.44032	C	5.760453	1.665618	-6.92769
C	7.759959	2.238384	-5.54538	H	6.063163	-1.27798	1.714352
C	6.29195	4.063332	-6.47881	H	-4.57086	-6.12956	-3.37344
H	2.242183	3.59727	6.202919	H	-6.36753	-4.5046	-3.17024
H	0.081028	4.713266	6.395698	H	-8.69594	-7.35544	-0.94682
H	-0.48813	4.285181	2.197019	H	-6.86157	-8.96733	-1.11155
H	4.477297	0.092245	1.747942	H	-3.5226	-8.19425	-4.0226
H	4.856201	-0.01762	6.008095	H	-1.22859	-8.84648	-3.44826
H	3.460549	1.967828	6.168227	H	-2.43521	-9.45379	0.630967
H	-0.04465	5.497826	-0.64853	H	-4.72519	-8.84474	0.045799
H	-2.44567	5.824985	-1.06863	H	0.431952	-7.79165	-2.45057
H	-3.27037	2.002228	0.712856	H	2.537299	-7.18548	-1.3762
H	-0.85547	1.65469	1.064919	H	1.628455	-9.80127	1.903054
H	5.960432	3.264527	1.692162	H	-0.46997	-10.444	0.807726
H	8.264392	2.38541	1.754753	H	4.735126	-7.47778	-0.38644
H	7.172059	-0.65448	-1.07523	H	6.016844	-5.73746	0.760815
H	4.871743	0.225327	-1.12726	H	3.264852	-5.91094	4.060599
H	2.746862	1.196826	-3.12491	H	2.027924	-7.6741	2.937815
H	4.029282	1.154255	-5.20401	H	10.87746	-2.78207	0.566017
H	6.699478	4.117679	-3.60676	H	8.595084	-1.82722	0.451417
H	5.423559	4.129635	-1.51516	H	10.25187	2.134956	0.450798
H	2.31267	5.093773	-2.64262	H	12.53329	1.180054	0.603273
H	1.092418	5.587776	-4.70688	H	-4.49986	6.242695	-0.19271
H	-1.35568	2.1134	-4.07572	H	-6.90457	6.520688	-0.6967
H	-0.14144	1.642191	-2.00226	H	-7.24816	2.290581	-1.3697
H	-8.86829	-1.31168	-2.12431	H	-4.84586	2.017981	-0.89542
H	-8.0911	-3.3273	-3.22051	H	0.47028	5.35008	-6.88367
H	-9.3158	-5.64629	0.184307	H	-0.65908	6.337683	-5.93698
H	-10.2303	-3.65519	1.213085	H	-1.18058	5.608015	-7.45895

H	-9.67662	-2.07593	2.395315	H	-2.64355	5.233776	-4.74966
H	-9.13255	-0.14182	3.734777	H	-2.95473	3.506856	-4.95009
H	-9.02063	2.286359	0.195402	H	-3.14348	4.59879	-6.3298
H	-9.67727	0.370753	-1.14172	H	-1.52375	3.172884	-7.7064
H	-7.39943	0.802357	4.261873	H	-1.31518	2.064097	-6.34456
H	-5.61679	2.185052	5.125201	H	0.100635	2.821408	-7.08474
H	-6.68083	5.30189	2.365922	H	5.77028	0.632823	-6.5656
H	-8.50056	3.923326	1.514159	H	6.382968	1.70781	-7.82663
H	-4.40359	5.319232	2.147364	H	4.736318	1.917014	-7.22069
H	-2.00446	5.672469	2.361877	H	7.794643	1.233769	-5.11265
H	-2.12615	4.049368	6.341838	H	8.218797	2.925626	-4.82941
H	-4.54944	3.79999	6.159954	H	8.371993	2.242072	-6.45386
H	4.491988	-2.22531	5.599391	H	6.71054	4.800839	-5.78854
H	4.546366	-4.59397	5.044102	H	5.269682	4.371847	-6.71896
H	5.968681	-3.62961	1.102843	H	6.884316	4.092077	-7.3998

6. References

[S1] Chen, M.; Unikela, K. S.; Ramalakshmi, R.; Li, B.; Darrigan, C.; Chrostowska, A.; Liu, S. Y. *Angew. Chem. Int. Ed.*, 2021, **60**, 1556-1560.

[S2] Gille, M.; Viertel, A.; Weidner, S.; Hecht, S. *Synlett*, 2013, **24**, 259-263.

[S3] Gaussian 16, Revision A.03, M. J. Frisch,et.al Gaussian, Inc., Wallingford CT, 2016.

[S4] Grimme S, Ehrlich S, Goerigk L. *J. Comp. Chem.*, 2011, 32, 1456-1465.

[S5] S. Miertuš, E. Scrocco, and J. Tomasi, *Chem. Phys.*, 1981, 55,117-2

[S6] Tian Lu, Feiwu Chen. *J. Comput. Chem.*, 2012, 33, 580-592.

[S7] Y. Segawa, H. Omachi, K. Itami, Org. Lett. 2010, 12, 2262-2265.