Supporting Information

Indole[3,2-*b*]carbazole Modified [10]Cycloparaphenylenes: Tuning Optical Properties Through Rigid Substitution

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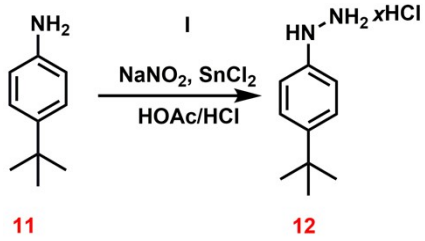
1. Materials and General Information

NMR spectra were recorded on a Bruker BioSpin (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts were reported as the delta scale in ppm relative to tetramethylsilane (δ = 0.00 ppm), $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), and integration. High resolution mass spectrometry (HR-MS) analyses were carried out using MALDI-TOF-MS techniques. All solvents for syntheses were dried by distillation under nitrogen prior to use (tetrahydrofuran and 1,4-dioxane were distilled after reflux with sodium under nitrogen). Other chemicals were obtained from commercial suppliers (Innochem or Acros). Air-sensitive reactions were all carried out under argon.

2. Synthetic details

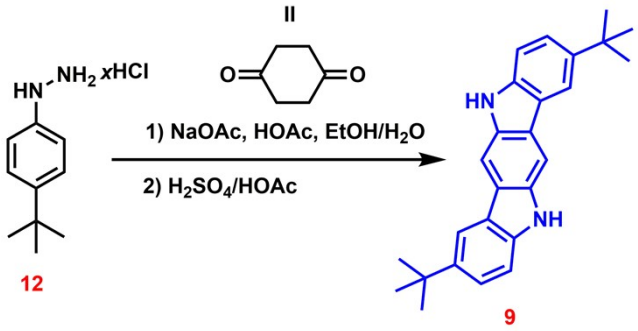
Synthesis of compound 12. Compound **11** was prepared according to the published procedure.[1, 2]



A suspension of *tert*-butylaniline **11** (10 g, 67 mmol) in acetic acid (55 mL) and concentrated HCl (160 mL) was treated with an ice cold solution of $NaNO_2$ (4.62 g, 67 mmol) in H_2O (26 mL). The temperature was maintained below -10 °C. At the same time stannous dichloride dehydrate (45.4 g, 201 mmol) was dissolved in concentrated HCl (33 mL) and the solution cooled to a temperature below -15 °C under a nitrogen atmosphere. To this mixture the diazonium mixture is slowly added over a period of 2 h and the temperature always kept below -15 °C. The reaction was completed in an ice-bath overnight. The product which was obtained after filtration was purified by dissolving the stannous salts with boiling HCl. The solid compound **12** (11.2 g, 56 mmol, 84%) was collected and dried under vacuum. An analytical sample was obtained by treating the hydrochloride with aqueous NaOH, extracting the free base into ether, and precipitating the hydrochloride from the dried ethereal phase with freshly prepared ethereal HCl solution.

^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 10.23 (br s, 3H), 7.30 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 1.24 (s, 9H);

Synthesis of compound 9.

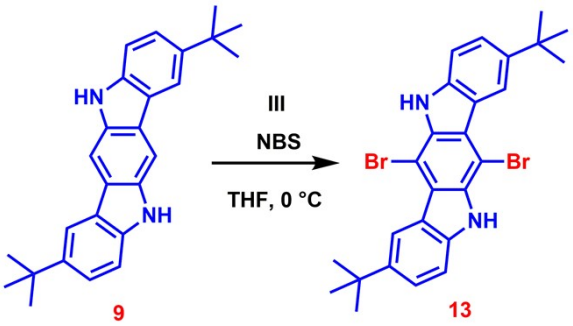


Compound **12**[3] (4.40 g, 21.92 mmol) was suspended in ethanol (32 mL) at room temperature. A solution of sodium acetate (5.39 g, 65.76 mmol) in water (16 mL) was added. The mixture was stirred at room temperature of 15 minutes. To this mixture, a solution of cyclohexane-1,4-dione (1.23 g, 10.96 mmol) in ethanol (10 mL) was added dropwise over 5 minutes. After the addition, acetic acid (8 mL) was added in one portion. The mixture was stirred for 1 hour at 50 °C and 1 hour at 0 °C. Subsequently, the reaction mixture was filtered to yield a pale yellow solid. The solid was collected and further dried under vacuum for 2 hours, before it was added portion wise over 10 minutes to a mixture of acetic acid (12 mL) and sulfuric acid (98%, 3 mL) at 10 °C. The mixture was warmed up to room temperature and stirred for another 10 minutes. The temperature was then further increased to 65 °C and maintained for 30 minutes. Subsequently, the mixture was cooled down to room temperature and poured into water (100 mL) at 0 °C. The resulting precipitate was filtered and washed extensively with methanol to give the pure product **9** as a gray solid (825 mg, 20%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.13 (d, J = 2.0 Hz, 2H), 8.04 (s,2H), 7.50 (dd, J = 8.5 Hz, 1.9 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 1.46 (s, 18H), the signals of NH

protons were not observed.

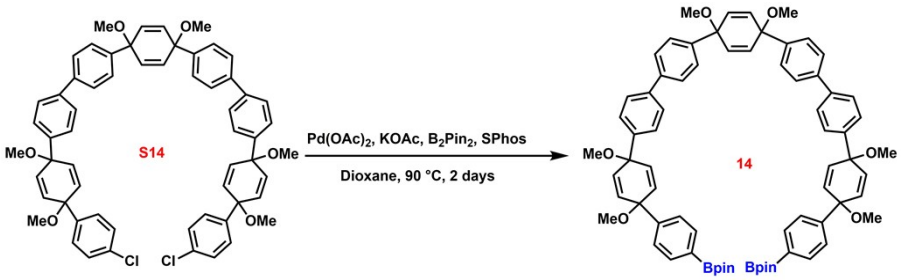
Synthesis of compound 13[3].



Compound **9** (921 mg, 2.5 mmol) was dissolved in anhydrous THF (30 mL) at 0 °C. To this mixture, a freshly prepared solution of NBS (445 mg, 2.5 mmol) in THF (15 mL) was added dropwise. The mixture was stirred at 0 °C for 10 minutes. Subsequently, another freshly prepared solution of NBS (445 mg, 2.5 mmol) in THF (15 mL) was added dropwise. The mixture was warmed up slowly and stirred at room temperature overnight. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2. The organic solution was washed by water twice and dried with $MgSO_4$. The crude product was purified through column chromatography (SiO_2, hexane/ethyl acetate 19:1 to 7:1), to give **13** as a pale yellow crystalline solid (1.10 g, 83%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.80 (d, J = 1.8 Hz, 2H), 8.24 (s, 2H), 7.60 (dd, J = 8.6, 1.9 Hz, 2H), 7.46 (dd, J = 8.6, 0.6 Hz, 2H), 1.48 (s, 18H).

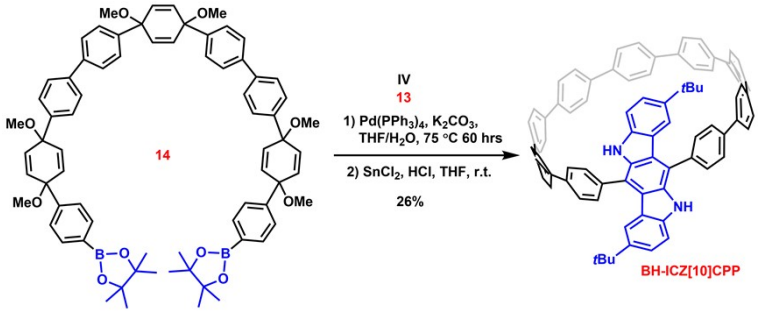
Synthesis of compound 14[4].



To a round-bottom flask (100 mL) were added dichloride **S14** (2.40 g, 2.55 mmol) which was synthesized following the literature procedure, bis(pinacolato)diboron (3.88 g, 15.3 mmol), anhydrous KOAc (2.50 g, 25.5 mmol), and dry Dioxane (20 mL). The mixture was bubbled with argon for 15 minutes then $Pd(OAc)_2$ (50 mg, 0.22 mmol) and *S*phos ligand (366 mg, 0.89 mmol,) were added quickly and the mixture was further degassed by argon bubbling for 15 minutes. The flask was sealed and heated at 90 °C for 48 hours. At the conclusion of the reaction, the reaction mixture was allowed to cool to room temperature. Water (100 mL) was added, and the reaction mixture was extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The resulting crude material was purified by silica gel chromatography using 3% acetone in CH_2Cl_2 to obtain the product **14** as a white solid (2.3 g, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, J = 8.0 Hz, 4H), 7.58 – 7.48 (m, 12H), 7.44 (dd, J =8.6, 2.0 Hz, 8H), 6.17 (s, 4H), 6.12 (m, J = 3.5 Hz, 8H), 3.51 (s, 6H), 3.45 (s, 12H), 1.31 (s, 24H).

Synthesis of compound BH-ICZ[10]CPP.



To a solution of compound **14** (209.14 mg, 0.19 mmol), compound **13** (97.80 mg, 0.19 mmol), K_2CO_3 (155 mg, 1.12 mmol), THF (200 mL) and H_2O (40 mL) was added $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) under argon atmosphere. The resulting solution was stirred at 73 °C for 60 hours and then cooled to room temperature. The solvent was removed under reduced pressure, and the remaining aqueous fraction was extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$. The solution was concentrated under reduced pressure to afford the crude product as a yellow solid for the next step without further purification.

To a mixture of $SnCl_2{\cdot}2H_2O$ (314.61 mg, 1.39 mmol) and dry THF (45 mL) was added HCl (0.23 mL, 12 mol/L) under an argon atmosphere and the resultant mixture was stirred at room temperature for 30 min. Then the above stannic acid solution was added dropwise to the above crude product with a syringe under an argon atmosphere and stirred at room temperature overnight. After reaction, the mixture was added aqueous sodium hydroxide and the solvent was removed under reduced pressure. Then the remaining aqueous fraction was extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$ and was purified by chromatography on a silica gel column with hexane/CH_2Cl_2 as the eluent (*v*/*v*, 4:1) to give compound **BH-ICZ[10]CPP** as a

yellow solid (58 mg, 20% over two steps).^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.09 (s, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.69-7.50 (m, 36H), 7.31 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 1.26 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 141.53, 140.10, 140.04, 139.18, 139.04, 138.59, 138.20, 138.03, 137.94, 136.05, 131.19, 128.16, 127.83, 127.70, 127.62, 127.43, 127.38, 127.34, 126.73, 122.97, 121.36, 119.15, 117.87, 109.83, 100.10, 34.75, 32.16. HR-MS (MALDI-TOF) *m/z* calcd. for $C_{80}H_{62}N_2$ $[M]^+$: 1050.4913, found: 1050.4988.

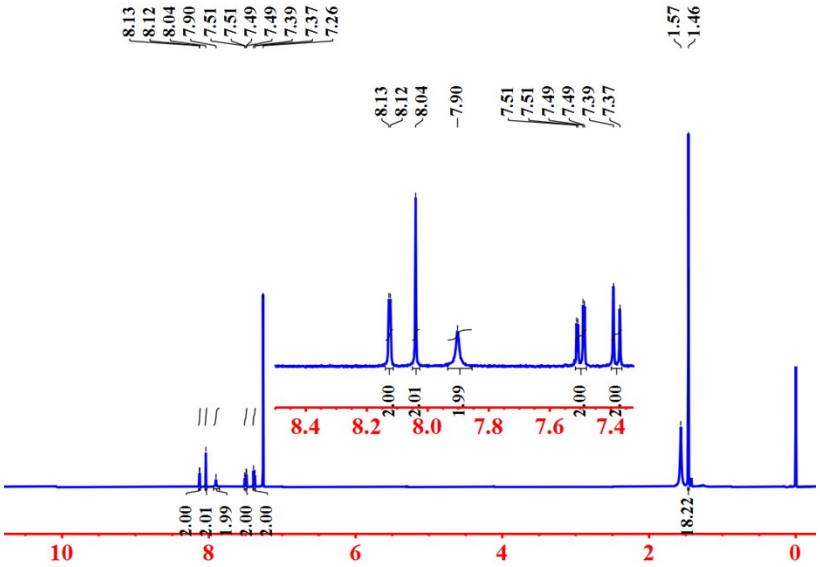


Figure S1. ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$).

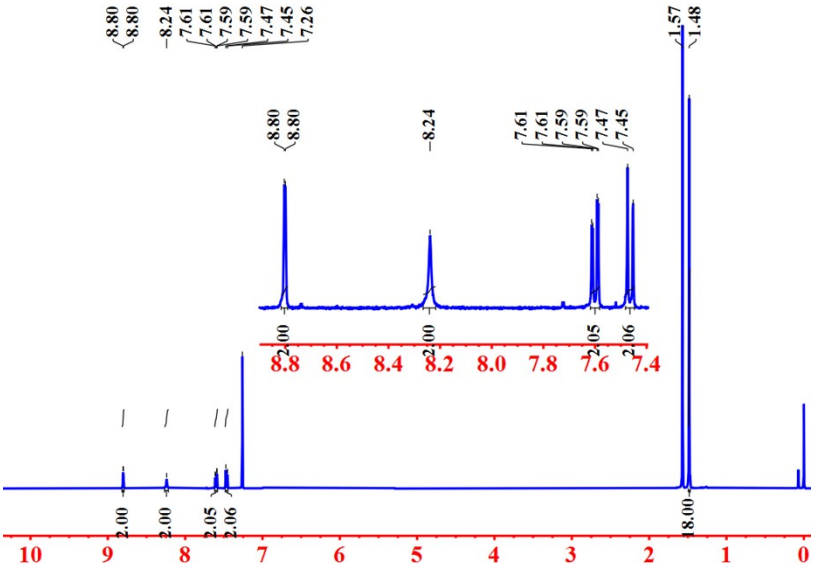


Figure S2. ^{1}H NMR spectrum of compound **13** (400 MHz, $CDCl_3$).

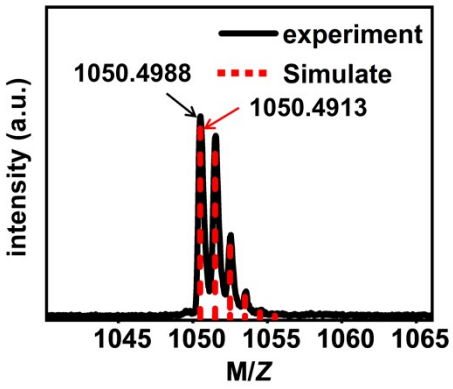


Figure S3. MALDI-TOF-MS spectrum (black solid line) and simulated data (red dash line) for compound **BH-ICZ[10]CPP**.

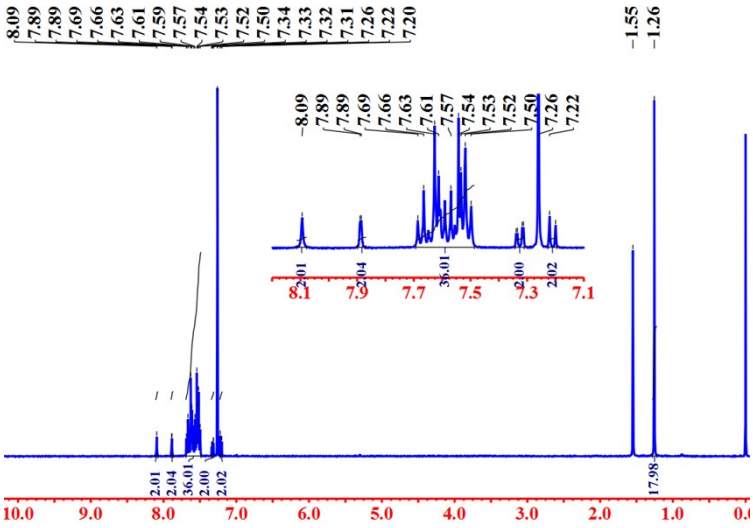


Figure S4. ^{1}H NMR spectrum of compound **BH-ICZ[10]CPP** (400 MHz, $CDCl_3$).

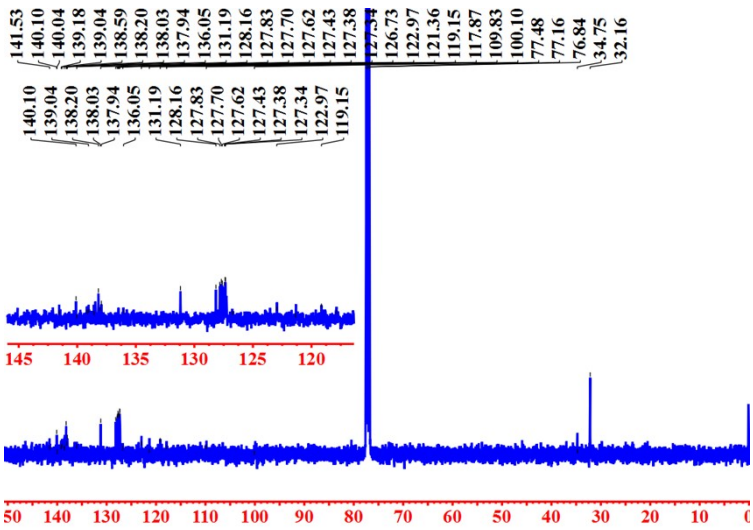


Figure S5. ^{13}C NMR spectrum of compound **BH-ICZ[10]CPP** (100 MHz, $CDCl_3$).

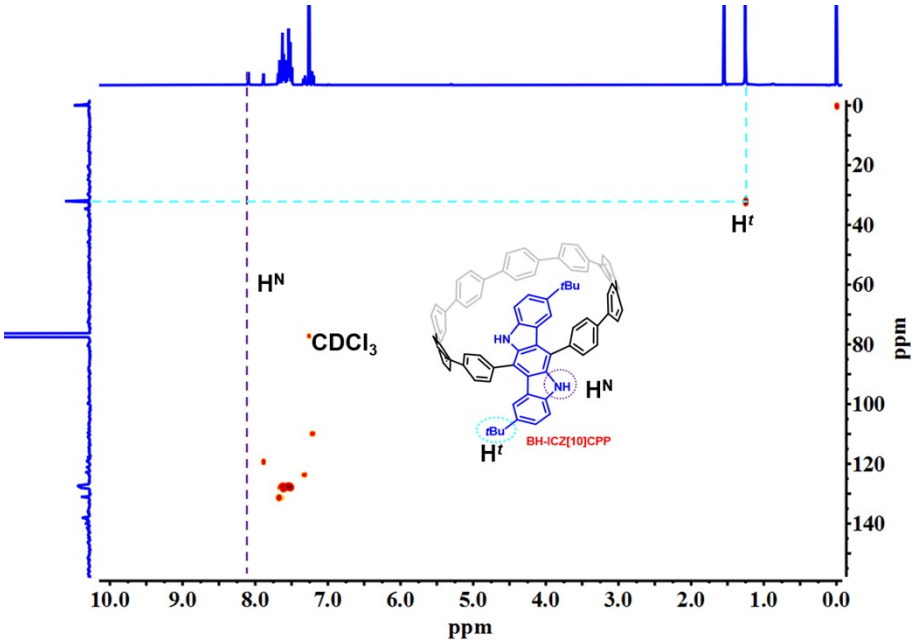


Figure S6. Expanded 2D (H, C)-HSQC NMR spectrum (400 MHz, $CDCl_3$) of **BH-ICZ[10]CPP**.

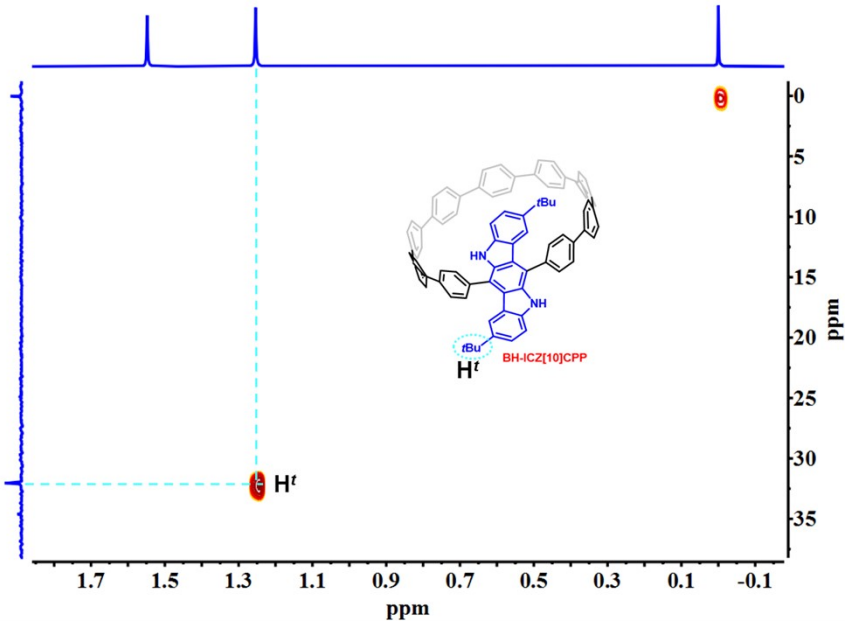


Figure S7. Expanded 2D (H, C)-HSQC NMR spectrum (400 MHz, $CDCl_3$) of **BH-ICZ[10]CPP** in the range of 0-1.35 ppm.

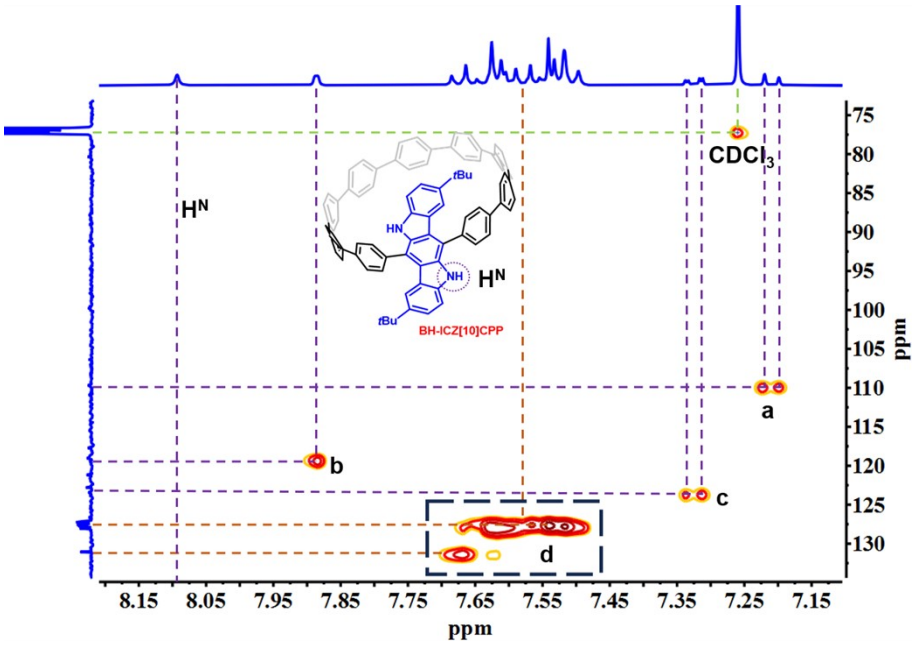


Figure S8. Expanded 2D (H, C)-HSQC NMR spectrum (400 MHz, $CDCl_3$) of **BH-ICZ[10]CPP** in the range of 7.10-8.20 ppm.

3. Photophysical studies.

The fluorescent emission experiments were performed on a F-4600 spectrofluorometer at room temperature. The fluorescence spectrum of **BH-ICZ[10]CPP** was collected under an excitation wavelength at 330 nm. UV-Vis absorption spectrum of **BH-ICZ[10]CPP** was performed on a UV-3600 spectrometer (Shimadzu, Japan) at room temperature, using a quartz cell of 1 mm layer thickness and 1 nm resolution with the samples dissolved in solvents. The fluorescent time-resolved decays were measured on a spectrometer (FLS920, Edinburgh Instruments Ltd.) with TBX picosecond photon detection module (HORIBA Scientific) using time-correlated single-photon counting technique (TCSPC). The sample was excited at 330 nm with a picosecond pulsed diode laser triggered at 3 MHz repetition rate. The detected fluorescence intensity decays were analyzed using a monoexponential model. The measurements were performed at least twice for consistency. **BH-ICZ[10]CPP** was measured in solvents with a concentration of 5.0×10^{-6} M.

Fluorescence decay lifetime.

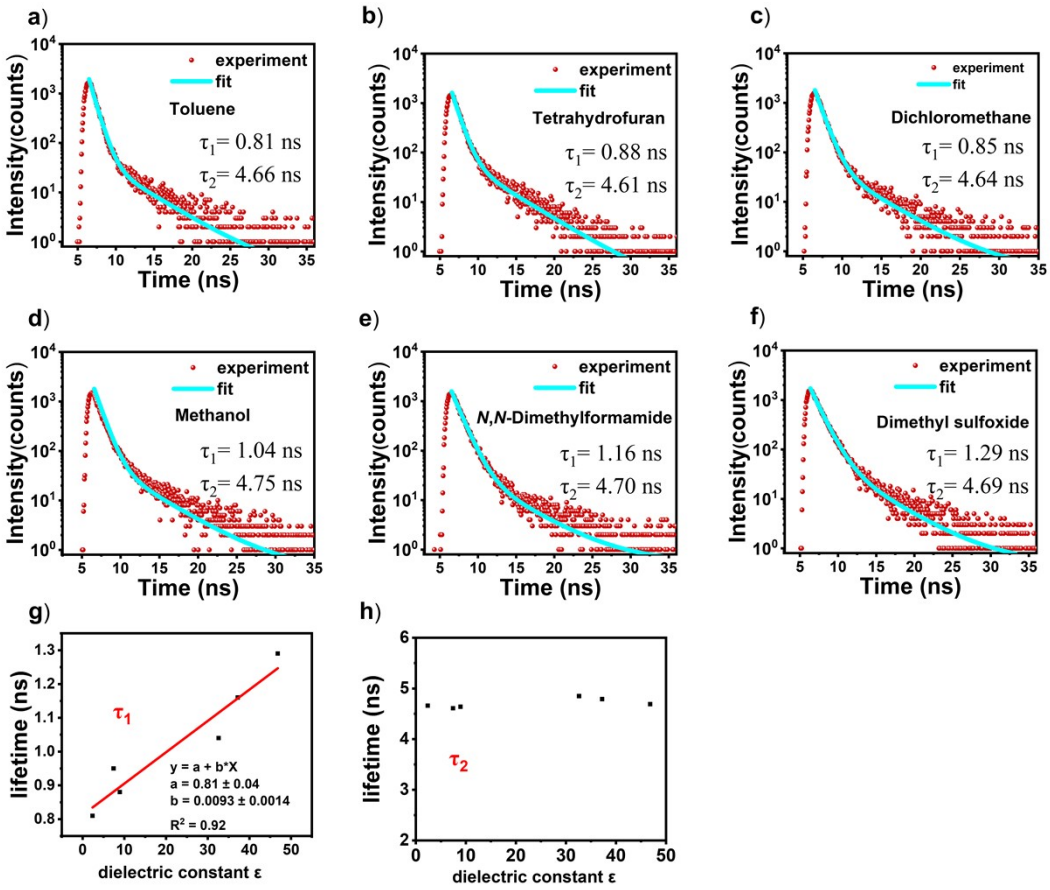


Figure S9. Fluorescence decay lifetime of BH-ICZ[10]CPP in different solvents.

Table S1. the dielectric constant ε of **BH-ICZ[10]CPP** for PLQY in different solvents.

	Toluene	THF	DCM	MeOH	DMF	DMSO
PLQY	0.75	0.61	0.92	0.50	0.58	0.54

4. Computational detail.

Density functional theory calculations were used to identify the performed by using Gaussian 16 software[5]. Geometrical optimization were carried out at the theoretical level of CAM-B3LYP/6-31G(d, p), where Polarizable continuum model (PCM)[6] methodologies were used for solvent effect. The resultant structures were further validated by frequency analysis without imaginary frequency. The strain energy was calculated using the computational methods reported by K. Itami[7, 8].

SE = *E*(**BH-ICZ[10]CPP**) + 10*E*(Biphenyl) - E(the Functional unit) - 9E(Triphenyl).

Moreover, time-dependent density functional theory (TD-DFT) with CAM-B3LYP/6-31G(d,p)//PCM and gas-phase model, were used to simulate the UV-Vis spectra.

Harmonic Oscillator Measure of Aromaticity (HOMA)[9]

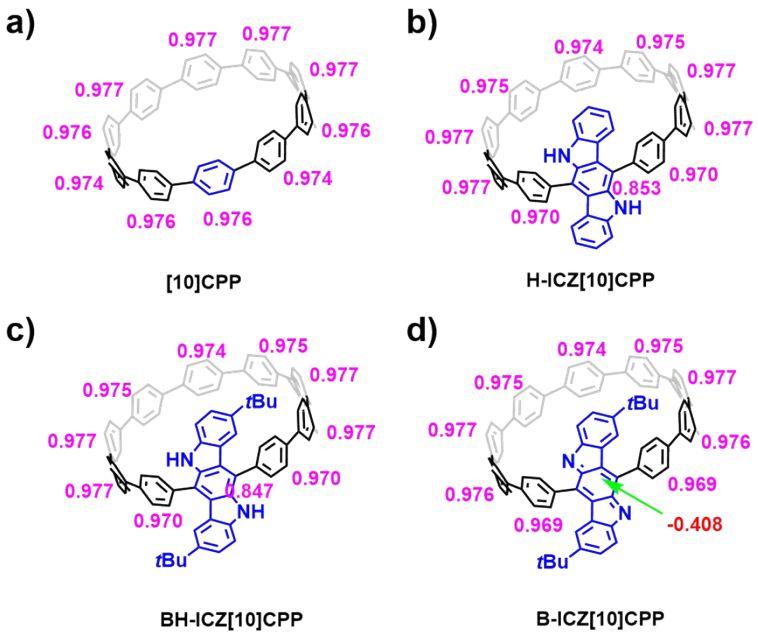


Figure S10 The HOMA of [10]CPP, H-ICZ[10]CPP, BH-ICZ[10]CPP, and B-ICZ[10]CPP.

Notice: If HOMA equals to 1, that means the ring is fully aromatic. While if HOMA equals to 0, that means the ring is completely nonaromatic.

Average macrocyclic torsion angle α.

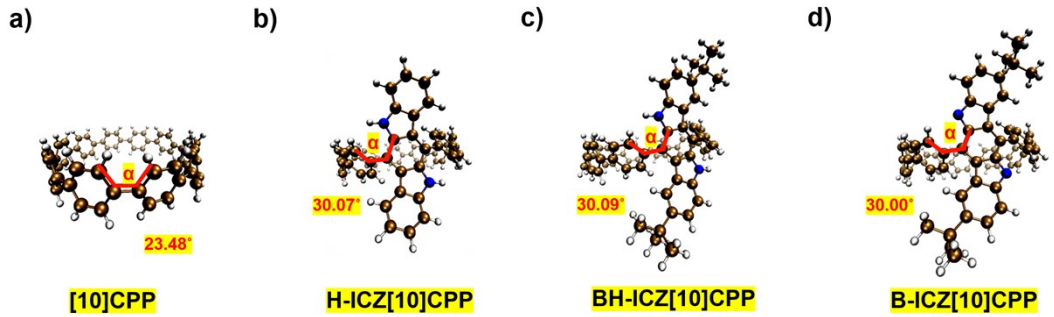


Figure S11. Optimized molecular structure of a) [10]CPP, b) H-ICZ[10]CPP and c) BH-ICZ[10]CPP, d) B-ICZ[10]CPP with the average macrocyclic torsion angle α.

Table S2 The average torsion angle α of the molecule under different calculation conditions.

Angle	**H-ICZ[10]CPP**			**BH-ICZ[10]CPP**			**B-ICZ[10]CPP**		
	A	B	C	A	B	C	A	B	C
α	30.86˚	30.07˚	28.67˚	30.89˚	30.09˚	28.61˚	31.42˚	30.00˚	29.41˚
γ	169.24˚	170.28˚	167.61˚	169.22˚	170.70˚	167.91˚	165.54˚	165.52˚	165.83˚
A, B, and C represent at the theoretical level of CAM-B3LYP/6-31+G(d, p)//gas-phase model, CAM-B3LYP/6-31G(d, p)//gas-phase model, and CAM-B3LYP/6-31G(d, p)//PCM, respectively.									

Table S3 The average torsion angle α of **BH-ICZ[10]CPP** in different solvents.

angle	**gas-phase**	**Toluene**	**THF**	**DCM**	**MeOH**	**DMF**	**DMSO**
α	30.89˚	29.42˚	28.70˚	28.61˚	28.28˚	28.26˚	28.24˚
γ	170.70˚	169.23˚	168.05˚	167.91˚	167.42˚	167.39˚	167.36˚
gas-phase refers to the Solvent-free model, and Toluene, DCM, THF, MeOH, DMF, DMSO are toluene, dichloromethane, tetrahydrofuran, *N*,*N*-dimethylformamide, and dimethyl sulfoxide, respectively, by PCM.							

Frontier molecular orbitals.

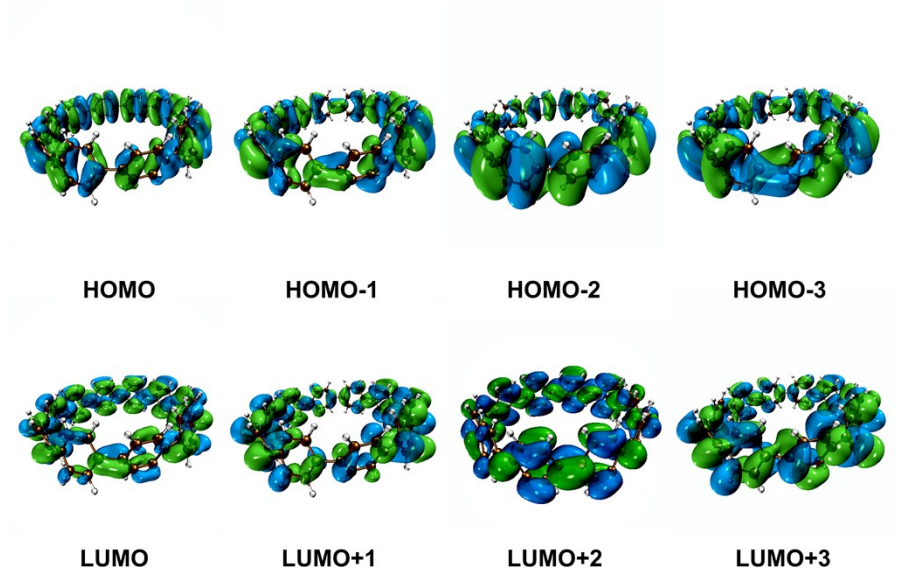


Figure S12 Frontier molecular orbitals of **[10]CPP** in gas phase: HOMO, HOMO-1, HOMO-2, HOMO-3, LUMO, LUMO+1, LUMO+2, and LUMO+3.

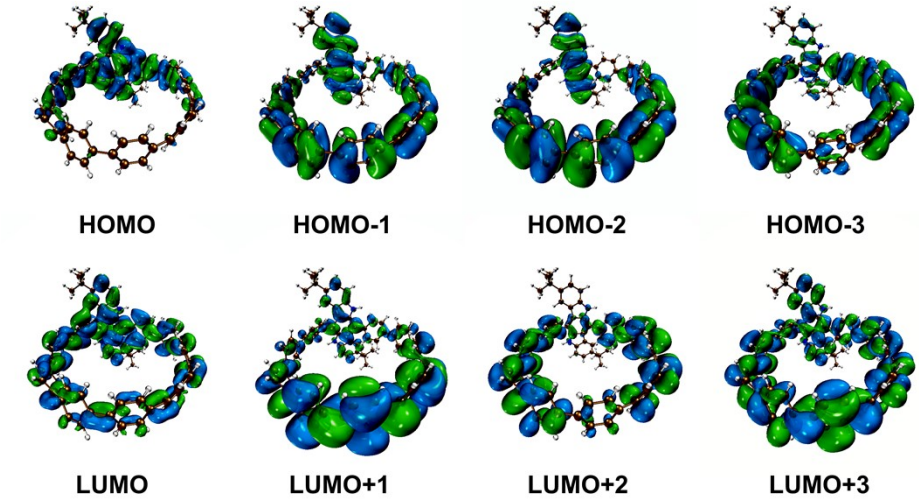


Figure S13. Frontier molecular orbitals of **BH-ICZ[10]CPP** in gas phase: HOMO, HOMO-1, HOMO-2, HOMO-3, LUMO, LUMO+1, LUMO+2, and LUMO+3.

Table S4. Molecule Orbitals Energy (eV) for **BH-ICZ[10]CPP**.

	HOMO-3	HOMO-1	HOMO	LUMO	LUMO+2	LUMO+4
Toluene	-6.780	-6.498	-5.767	-0.989	-0.199	0.866
THF	-6.826	-6.553	-5.810	-1.083	-0.252	0.678
DCM	-6.831	-6.560	-5.816	-1.095	-0.260	0.670
MeOH	-6.859	-6.589	-5.840	-1.145	-0.291	0.639
DMF	-6.861	-6.590	-5.845	-1.147	-0.293	0.637
DMSO	-6.863	-6.593	-5.847	-1.152	-0.296	0.634

Table S5. Molecule Orbitals Energy-gap(eV) for **BH-ICZ[10]CPP**.

	HOMO - LUMO+2	HOMO-3 - LUMO	HOMO - LUMO+4	HOMO-1 - LUMO+2
Toluene	5.5682	5.791	6.6333	6.2994
THF	5.558	5.7424	6.488	6.3009
DCM	5.5561	5.736	6.4861	6.2999
MeOH	5.5516	5.7145	6.4817	6.2973
DMF	5.5514	5.7133	6.4815	6.2971
DMSO	5.551	5.7116	6.4811	6.2968

Table S6. BH-ICZ[10]CPP for HOMO, LUMO, and Energy-gap（*Eg*）in different solvents.

	Tol	THF	DCM	MeOH	DMF	DMSO
HOMO	-5.77	-5.81	-5.82	-5.84	-5.84	-5.85
LUMO	-0.99	-1.08	-1.10	-1.14	-1.15	-1.15
Energy-gap（*Eg*）	4.78	4.73	4.72	4.70	4.69	4.70
	460.96	456.08	455.44	453.32	453.21	453.03
The above solvent model PCM. Except for the red is kJ/mol, and the other units are eV. The energy gap (*Eg*) refers to the energy-gap between LUMO and HOMO.						

Table S7 Oscillator strengths and transitions of the peaks from DFT calculations under the theoretical level of (CAM-B3LYP/6-31G(d,p)//PCM)

λ_{DFT}	f_{osc}	Transitions
[10]CPP		
452.10 nm	0.000	HOMO -> LUMO 85.8%
349.92 nm	2.726	HOMO-2 -> LUMO 42.2%, HOMO -> LUMO+1 39.5%
330.97 nm	1.418	HOMO-1 -> LUMO+2 31.8%, HOMO-1 -> LUMO 21.3%, HOMO -> LUMO+2 20.2%, HOMO-2 -> LUMO+1 12.1%
289.44 nm	0.004	HOMO -> LUMO+1 32.8%, HOMO-2 -> LUMO 31.6%, HOMO -> LUMO+5 9.6%
287.70 nm	0.294	HOMO-1 -> LUMO+2 30.5%, HOMO-2 -> LUMO+1 16.8%, HOMO-4 -> LUMO 16.7%, HOMO -> LUMO+4 14.0%
BH-ICZ[10]CPP		
482.71 nm	0.729	HOMO -> LUMO 90.0%
379.88 nm	0.551	HOMO-2 -> LUMO 63.0%, HOMO-1 -> LUMO 22.4%, HOMO-2 -> LUMO+1 5.1%
342.72 nm	0.660	HOMO-1 -> LUMO+1 36.1%, HOMO-1 -> LUMO 11.5%, HOMO-3 -> LUMO+2 10.4%, HOMO -> LUMO+1 9.4%, HOMO-2 -> LUMO+1 7.7%, HOMO-2 -> LUMO 7.4%
338.75 nm	2.458	HOMO -> LUMO+2 35.4%, HOMO-3 -> LUMO 31.9%, HOMO -> LUMO+4 5.7%, HOMO-1 -> LUMO+2 5.3%
313.84 nm	1.351	HOMO-4 -> LUMO 36.6%, HOMO-1 -> LUMO+1 15.7%, HOMO -> LUMO+3 11.5%, HOMO-2 -> LUMO+1 6.3%

Table S8. Energy and Strain energy for **[10]CPP**, **H-ICZ[10]CPP**, **BH-ICZ[10]CPP**, and **B-ICZ[10]CPP**

		Functional unit	**Biphenyl**	**Triphenyl**	**strain energy (kcal/mol)**
	[10]CPP	/	-463.055386	-693.987582	185.722591
Energy(a.u.)	-2309.251222				
	H-ICZ[10]CPP	-1264.159778			216.509199
Energy(a.u.)	-2879.411431				
	BH-ICZ[10]CPP	-1578.496605			217.194454
Energy(a.u.)	-3193.748519				

Charge-transfer spectra.

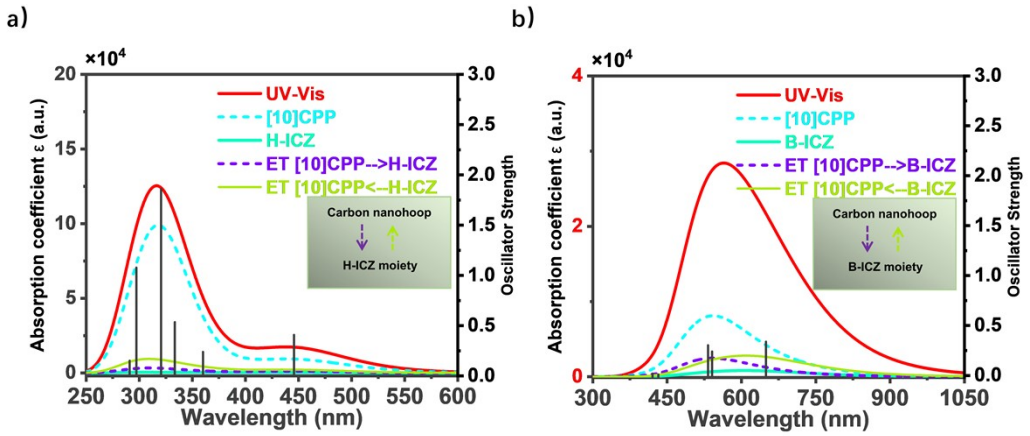


Figure S14. a) H-ICZ[10]CPP and b) B-ICZ[10]CPP of the charge-transfer spectra (CTS).

Interfragment charge transfer.

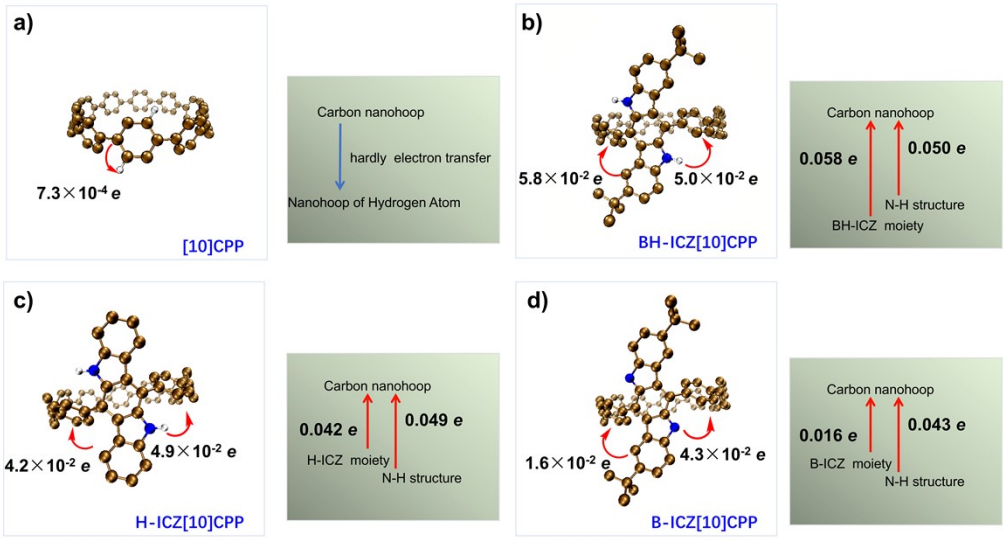


Figure S15. Interfragment charge transfer between the [10]CPP parent and the modified fragments in [10]CPP, BH-ICZ[10]CPP, H-ICZ[10]CPP, and B-ICZ[10]CPP.

[10]CPP

Atom	X	Y	Z	43C	-2.2899	-12.3853	-2.7051
1C	4.2407	9.9873	-6.2358	44C	-4.5287	-12.6993	-1.3121
2C	3.9519	8.5197	-8.3800	45C	-4.5159	-12.6877	1.2981
3C	1.6962	8.5378	-9.7633	46C	-2.2595	-12.3542	2.6722
4C	-0.1141	10.3528	-9.0913	47H	1.7936	-12.1821	2.2329
5C	0.1725	11.8207	-6.9445	48H	1.7604	-12.1976	-2.3312
6C	2.2843	11.5445	-5.3627	49H	-6.3199	-12.8636	-2.2972
7H	5.9141	9.7235	-5.0834	50H	-6.2984	-12.8536	2.2966
8H	5.4070	7.1520	-8.8400	51C	-2.2843	-11.5445	-5.3627
9H	-1.8243	10.5409	-10.2081	52C	-4.2407	-9.9873	-6.2358
10H	-1.3171	13.1322	-6.4283	53C	-0.1725	-11.8207	-6.9445
11C	2.2899	12.3853	-2.7051	54C	-3.9519	-8.5197	-8.3800
12C	4.5287	12.6993	-1.3121	55H	-5.9141	-9.7235	-5.0834
13C	0.0184	12.4163	-1.3379	56C	0.1141	-10.3528	-9.0913
14C	4.5159	12.6877	1.2981	57H	1.3171	-13.1322	-6.4283
15H	6.3199	12.8636	-2.2972	58C	-1.6962	-8.5378	-9.7633
16C	0.0008	12.4072	1.2716	59H	-5.4070	-7.1520	-8.8400
17H	-1.7604	12.1976	-2.3312	60H	1.8243	-10.5409	-10.2081
18C	2.2595	12.3542	2.6722	61C	-1.1122	-6.3776	-11.4409
19H	6.2984	12.8536	2.2966	62C	-2.9938	-4.9733	-12.6681
20H	-1.7936	12.1821	2.2329	63C	1.3283	-5.3577	-11.4169
21C	1.1122	6.3776	-11.4409	64C	-2.5343	-2.5341	-13.5031
22C	-1.3283	5.3577	-11.4169	65H	-4.8779	-5.7589	-12.8681
23C	2.9938	4.9733	-12.6681	66C	1.7869	-2.9210	-12.2506
24C	-1.7869	2.9210	-12.2506	67H	2.8433	-6.3843	-10.4947
25H	-2.8433	6.3843	-10.4947	68C	-0.1725	-1.3888	-13.1491
26C	2.5343	2.5341	-13.5031	69H	-4.0682	-1.4585	-14.3383
27H	4.8779	5.7589	-12.8681	70H	3.6468	-2.1125	-11.9560
28C	0.1725	1.3888	-13.1491	71C	-2.2315	-11.5265	5.3112
29H	-3.6468	2.1125	-11.9560	72C	-4.2954	-10.1796	6.3230
30H	4.0682	1.4585	-14.3383	73C	-0.0274	-11.6085	6.8130
31C	2.2315	11.5265	5.3112	74C	-4.0549	-8.7152	8.4574
32C	0.0274	11.6085	6.8130	75H	-6.0578	-10.0991	5.2820
33C	4.2954	10.1796	6.3230	76C	0.2220	-10.1459	8.9462
34C	-0.2220	10.1459	8.9462	77H	1.5438	-12.7945	6.2406
35H	-1.5438	12.7945	6.2406	78C	-1.7167	-8.4717	9.7365
36C	4.0549	8.7152	8.4574	79H	-5.6430	-7.5484	9.0107
37H	6.0578	10.0991	5.2820	80H	1.9826	-10.2304	9.9900
38C	1.7167	8.4717	9.7365	81C	1.2446	6.3617	11.4085
39H	-1.9826	10.2304	9.9900	82C	-1.2520	5.5182	11.9163
40H	5.6430	7.5484	9.0107	83C	3.2111	4.7519	12.2817
41C	-9.7601	-12.4072	1.2716	84C	-1.7352	3.1185	12.7596
42C	-0.0184	-12.4163	-1.3379	85H	-2.8444	6.7109	11.4336

86C	2.7343	2.3534	13.1250	**94C**	-3.2111	-4.7519	12.2817
87H	5.1542	5.3980	12.2180	**95H**	-4.3180	-1.1870	13.6952
88C	0.2399	1.3359	13.1631	**96C**	1.2520	-5.5182	11.9163
89H	-3.6879	2.5256	12.9140	**97H**	3.6879	-2.5256	12.9140
90H	4.3180	1.1870	13.6952	**98C**	-1.2446	-6.3617	11.4085
91C	-0.2399	-1.3359	13.1631	**99H**	-5.1542	-5.3980	12.2180
92C	-2.7343	-2.3534	13.1250	**100H**	2.8444	-6.7109	11.4336
93C	1.7352	-3.1185	12.7596				

BH-ICZ[10]CPP

Atom	**X**	**Y**	**Z**	**34C**	8.1926	4.2379	14.4197
1C	-10.6786	-5.1734	6.5078	**35H**	5.3140	5.0865	17.1055
2C	-9.9518	-5.0264	9.0184	**36C**	8.5840	-0.0846	13.1946
3C	-10.8130	-3.0737	10.5757	**37H**	5.9086	-2.6441	14.7271
4C	-12.7032	-1.4957	9.6094	**38C**	9.3283	2.4279	12.8631
5C	-13.4492	-1.6600	7.1032	**39H**	8.8033	6.1937	14.3119
6C	-12.3136	-3.3863	5.4447	**40H**	9.4275	-1.5447	12.0290
7H	-9.7601	-6.5516	5.3018	**41C**	10.8130	3.0737	10.5757
8H	-8.4940	-6.2927	9.7077	**42C**	12.7032	1.4957	9.6094
9H	-13.5163	-0.0410	10.8063	**43C**	9.9518	5.0264	9.0184
10H	-14.8493	-0.3395	6.3955	**44C**	13.4492	1.6600	7.1032
11C	-9.3283	-2.4279	12.8631	**45H**	13.5163	0.0410	10.8063
12C	-8.5840	0.0846	13.1946	**46C**	10.6786	5.1734	6.5078
13C	-8.1926	-4.2379	14.4197	**47H**	8.4940	6.2927	9.7077
14C	-6.5704	0.7073	14.7428	**48C**	12.3136	3.3863	5.4447
15H	-9.4275	1.5447	12.0290	**49H**	14.8493	0.3395	6.3955
16C	-6.1974	-3.6038	15.9995	**50H**	9.7601	6.5516	5.3018
17H	-8.8033	-6.1937	14.3119	**51C**	5.8796	-1.3309	-6.1759
18C	-5.2174	-1.1437	16.0617	**52C**	7.8120	-0.8875	-4.4982
19H	-5.9086	2.6441	14.7271	**53C**	9.2628	1.3391	-4.5772
20H	-5.3140	-5.0865	17.1055	**54C**	8.8301	2.9650	-6.6320
21C	-2.6286	-0.5667	16.9906	**55C**	6.9037	2.5188	-8.3451
22C	-1.7544	1.9202	17.2176	**56H**	4.6797	-2.9613	-5.8902
23C	-0.8043	-2.4730	17.1814	**57H**	8.0648	-2.1951	-2.9420
24C	0.8043	2.4730	17.1814	**58H**	10.0234	4.6157	-6.8835
25H	-3.0846	3.4780	17.2514	**59H**	6.7241	3.7666	-9.9653
26C	1.7544	-1.9202	17.2176	**60C**	10.8181	1.9858	-2.3633
27H	-1.3671	-4.4411	17.1030	**61C**	10.9696	4.4772	-1.4701
28C	2.6286	0.5667	16.9906	**62C**	11.8169	0.0928	-0.7987
29H	1.3671	4.4411	17.1030	**63C**	11.7315	4.9959	0.9817
30H	3.0846	-3.4780	17.2514	**64H**	10.2834	6.0144	-2.6417
31C	5.2174	1.1437	16.0617	**65C**	12.5527	0.6101	1.6536
32C	6.1974	3.6038	15.9995	**66H**	11.8820	-1.8439	-1.4668
33C	6.5704	-0.7073	14.7428	**67C**	12.3648	3.0508	2.6641

68H	11.6883	6.9371	1.6415	**107H**	3.5517	5.4787	-9.3130
69H	13.0949	-0.9507	2.8655	**108C**	2.4698	-4.7107	-9.8623
70C	-12.3648	-3.0508	2.6641	**109C**	0.3442	-6.3195	-9.8183
71C	-11.7315	-4.9959	0.9817	**110C**	4.8728	-5.7870	-10.1488
72C	-12.5527	-0.6101	1.6536	**111C**	0.5628	-8.9283	-10.0099
73C	-10.9696	-4.4772	-1.4701	**112C**	5.1477	-8.3923	-10.3507
74H	-11.6883	-6.9371	1.6415	**113H**	6.5060	-4.5614	-10.2062
75C	-11.8169	-0.0928	-0.7987	**114C**	2.9673	-9.9269	-10.2655
76H	-13.0949	0.9507	2.8655	**115H**	-1.0880	-10.1445	-9.9691
77C	-10.8181	-1.9858	-2.3633	**116H**	3.1637	-11.9611	-10.4154
78H	-10.2834	-6.0144	-2.6417	**117N**	-1.7859	-4.8313	-9.6001
79H	-11.8820	1.8439	-1.4668	**118H**	-3.5517	-5.4787	-9.3130
80C	-9.2628	-1.3391	-4.5772	**119C**	7.7417	-9.6511	-10.6526
81C	-7.8120	0.8875	-4.4982	**120C**	9.9009	-7.7201	-10.7021
82C	-8.8301	-2.9650	-6.6320	**121C**	8.2041	-11.4636	-8.4247
83C	-5.8796	1.3309	-6.1759	**122C**	7.8120	-11.1512	-13.1435
84H	-8.0648	2.1951	-2.9420	**123H**	9.7250	-6.4140	-12.2938
85C	-6.9037	-2.5188	-8.3451	**124H**	9.9786	-6.6082	-8.9618
86H	-10.0234	-4.6157	-6.8835	**125H**	11.7073	-8.7044	-10.8992
87C	-5.2350	-0.4398	-8.0737	**126H**	6.7703	-12.9465	-8.3268
88H	-4.6797	2.9613	-5.8902	**127H**	10.0474	-12.3828	-8.6160
89H	-6.7241	-3.7666	-9.9653	**128H**	8.1788	-10.4424	-6.6280
90C	-2.7806	-0.2076	-9.2731	**129H**	9.6527	-12.0645	-13.3817
91C	-1.1359	-2.3247	-9.5624	**130H**	6.3678	-12.6262	-13.1951
92C	-1.5348	2.1581	-9.6298	**131H**	7.4986	-9.9048	-14.7618
93C	1.5348	-2.1581	-9.6298	**132C**	-7.7417	9.6511	-10.6526
94C	1.1359	2.3247	-9.5624	**133C**	-9.9009	7.7201	-10.7021
95C	2.7806	0.2076	-9.2731	**134C**	-8.2041	11.4636	-8.4247
96C	5.2350	0.4398	-8.0737	**135C**	-7.8120	11.1512	-13.1435
97C	-2.4698	4.7107	-9.8623	**136H**	-9.7250	6.4140	-12.2938
98C	-0.3442	6.3195	-9.8183	**137H**	-9.9786	6.6082	-8.9618
99C	-4.8728	5.7870	-10.1488	**138H**	-11.7073	8.7044	-10.8992
100C	-0.5628	8.9283	-10.0099	**139H**	-6.7703	12.9465	-8.3268
101C	-5.1477	8.3923	-10.3507	**140H**	-10.0474	12.3828	-8.6160
102H	-6.5060	4.5614	-10.2062	**141H**	-8.1788	10.4424	-6.6280
103C	-2.9673	9.9269	-10.2655	**142H**	-9.6527	12.0645	-13.3817
104H	1.0880	10.1445	-9.9691	**143H**	-6.3678	12.6262	-13.1951
105H	-3.1637	11.9611	-10.4154	**144H**	-7.4986	9.9048	-14.7618
106N	1.7859	4.8313	-9.6001				

Reference

1. L. Xing, Y. An, Y. Qin, H. Xin, T. Deng, K. Meng, D. Liu and W. Xue, *New J. Chem.*, 2024, **48**, 117-130.
2. M. Zhao, B. Zhang and Q. Miao, *Angew. Chem. Int. Ed.*, 2020, **132**, 9765-9770.
3. C. Zhu, X. Ji, D. You, T. L. Chen, A. U. Mu, K. P. Barker, L. M. Klivansky, Y. Liu and L. Fang, *J. Am. Chem. Soc.*, 2018, **140**, 18173-18182.
4. E. S. Hirst and R. Jasti, *J. Org. Chem.*, 2012, **77**, 10473-10478.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
6. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
7. Y. Segawa, H. Omachi and K. Itami, *Org. Lett.*, 2010, **12**, 2262-2265.
8. H. Takaba, H. Omachi, Y. Yamamoto, J. Bouffard and K. Itami, *Angew. Chem. Int. Ed.*, 2009, **48**, 6112-6116.
9. A. Mischie, A. M. Toader, M. C. Buta and F. Cimpoesu, *Comput. Theor. Chem.*, 2023, **1230**, 114370.