Supporting Information for

Benzo[*f*]benzo[5,6]indolo[3,2-*b*]indole: a Stable Unsubstituted 4nπ-Electron Acene with an Antiaromatic 1,4-Diazapentalene Core

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***Table of Contents**:*

1. Experimental Details

General: All glass wares were thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standards techniques. Flash chromatography was carried out utilizing silica gel 200-300 mesh. HRMS were measured on a Bruke Maxis UHR TOF unless otherwise mentioned. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV600 with tetramethylsilane (TMS) as an internal standard at 298K. The infrared spectra were acquired on Nicolet 6700 FTIR Spectrometer, the UV-vis spectra were collected with a Hitachi U-4100 UV-vis spectrophotometer and the Elemental analysis was perfomed with a vario EL cube instrument. Thermogravimetric analysis (TGA) was performed using a Q500 TGA analyzer by heating the sample using the ramp of 5 ^{o}C/min from 30 to 600 ^{o}C in a nitrogen flow of 50 mL/h. Single-crystal X-ray diffraction data was collected on a Bruker Smart APEX2 diffractionmeter at 296(2) K with graphite-monochromated Mo-Kα radiation(λ = 0.71073 Å) Cyclic voltammetry was performed on an electrochemistry workstation (CHI660D, Chenhua Shanghai) using an anhydrous and argon–saturated solution of 0.1 M tetrabutylammonium perchlorate (TBAP) in tetrahydrofuran (THF) as an electrolyte and an Ag/AgCl electrode as a reference electrode. The potential of Ag/AgCl in THF was determined using ferrocene as internal standard.

Synthesis Details:

Serendipitous conversion from DHBBII (8) [1] to BBII (6). To a stirred of solution of DHBBII (**8**, 300 mg 1 mmol **)** in 20 mL of THF at room temperature was added NaH (240mg, 6 mmol) under Ar atomosphere. After 10 min at room temperature, n-octyl

bromide (0.86 ml, 5 mmol) was added to the reaction mixture and a little amount of air was let in during the addition. After being stirred at reflux for 4h, the reaction mixture was treated with 100 mL of water and a brown solid was formed. Then the crude product was collected on a filter and dried at 50^{o}C under vacuum for 5h. Acetone (400ml) was added to the mixture to dissolve the crude, and the insoluble red solid (BBII) was collected by filtration(10 mg). m.p. : > 300 ^{o}C. IR (KBr, cm^{-1}): 3398(broad), 2051, 1634, 1604, 1563, 1427, 880, 744. δ_H (600 MHz; $CDCl_3$; Me_4Si) 8.01 (1H, s), 7.76 (1H, d, J = 8.1 Hz), 7.73 (1H, d, J = 8.1 Hz), 7.62 (1H, s), 7.48 (1H, t, J=7.7Hz), 7.42 (1H, t, J=7.7Hz). δ_C (150 MHz; $CDCl_3$; Me_4Si; DEPTQ) 174.4 (s), 162.8 (s), 136.6 (s), 133.1 (s), 130.8 (d), 129.9 (d), 129.5 (d), 127.7 (d), 127.5 (d), 124.2 (s), 122.6 (d). FTMS(ESI, Bruker Apex IV FTMS) calcd. for $C_{22}H_{13}N_2[M+H]^+$, 305.10732, found 305.10827. Elemental analysis calcd. for $C_{22}H_{12}N_2$, C 86.82, H 3.97, N 9.20%, found C 86.60, H 3.96, N 9.18%.

Concentration of the yellow filtrate gave C8-DHBBII (300 mg, 60%) as a yellow solid. m.p. : 170.0-171.4 ^{o}C. IR (KBr, cm^{-1}): 3335, 2921, 2851, 1732, 1671, 1476, 1371, 1202, 849, 738. δ_H (600 MHz; $CDCl_3$; Me_4Si) 8.33 (2H, s), 8.04 (1H, d, J=8.15Hz), 8.00 (1H, d, J=8.15Hz), 7.43-7.38 (2H, m), 4.67 (2H, t, J=7.2Hz), 2.08 (2H, m), 1.50-1.23 (10H, m), 0.83 (3H, t, J=7Hz). δ_C (150 MHz; $CDCl_3$; Me_4Si) 141.8, 130.1, 128.1, 128.0, 127.6, 127.4, 124.0, 122.5, 117.1, 115.4, 105.0, 45.7, 31.8, 30.2, 29.5, 29.2, 27.3, 22.6, 14.1. HRMS(ESI) calcd. For $C_{38}H_{47}N_2[M+H]^+$, 531.3734, found 531.3703.

Conversion from DHBBII to BBII under NaH/O_2/THF conditions. To a stirred of solution of DHBBII (120 mg, 0.4 mmol) of in 20 mL of THF at room temperature was

added NaH (96mg, 2.4 mmol) under the 100% O_2 atomosphere. After being stirred at reflux for 2h, the reaction mixture was treated with 100 mL of ice-water and a red- solid was formed. It was then collected on a filter, to washed sequentially with ethyl acetate, methanol and acetone, and dried at 50^{o}C under reduced pressure for 12h to give the pure BBII (83 mg, 70%) as a red solid.

Conversion from DHBBII to BBII under NiO_2/THF conditions. To a solution DHBBII (60 mg, 0.2 mmol) in 10 ml of THF, was added freshly prepared NiO_2 [2] (400 mg, 2.4 mmol) at -20^{o}C under Ar atomosphere, then the black mixture was allowed to warm to ambient temperature and stirred for 5h. THF was then evaporated to give a black mixture which was directly subjected to silica column chromatography with $CHCl_3$:MeOH=20:1 as the eluent, pure BBII (48 mg, 80%) was obtained.

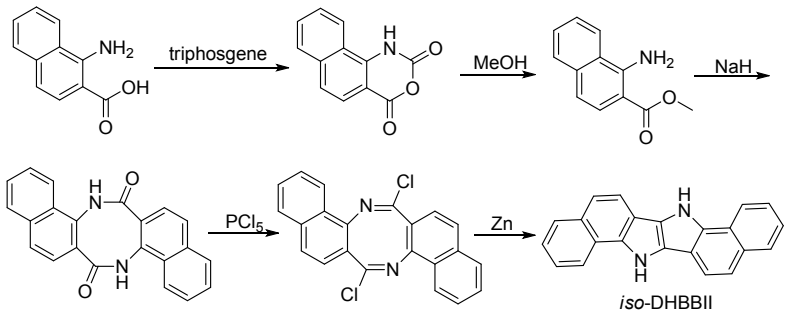
Synthesis of Indolo [3,2-b]Indole (5, II).

PbO_2 as oxidant: [3] To a solution of 5,10-dihydroindolo[3,2-*b*]indole (**10**, DHII, 40 mg, 0.2 mmol)[1] in 10 ml of ethyl acetate was added PbO_2 (400 mg, 1.7 mmol) at -30^{o}C under Ar atomosphere, then the black mixture was allowed to warm to ambient temperature and stirred for 24h, PbO_2 was filtered off and the filtrate was concentration to give the crude product (18mg, 45%) which was not pure as evidenced from NMR analysis (Page S23).

NiO_2 as oxidant: To a solution of 5,10-dihydroindolo[3,2-b]indole (**10**, DHII, 60 mg, 0.3 mmol) [1] in 6 ml of THF, was added freshly prepared NiO_2 [2] (200 mg, 1.2 mmol) at -20 ^{o}C under Ar atomosphere, then the black mixture was stirred for 1h at that temperature. NiO_2 was then filtered off and the filtrate was concentration to give the crude product, which was then washed with 10 ml ether to give the pure II (51 mg, 85%) as a bronze-

colored solid. m.p. : decomposion at 218 °C. IR (KBr, cm^{-1}): 3052, 1576, 1420, 1145, 944, 758. δ_H (600 MHz; $CDCl_3$; Me_4Si) 7.34 (1H, d, J = 7.2 Hz), 7.16 (1H, t, J=7.4 Hz), 7.12 (1H, d, J = 7.2 Hz), 6.96 (1H, t, J=7.4 Hz). δ_C (150 MHz; $CDCl_3$; Me_4Si) 175.2, 167.7, 134.4, 128.2, 125.53, 125.50, 123.6. HRMS(ESI) calcd. For $C_{14}H_9N_2[M+H]^+$, 205.0766, found 205.0758. Elemental analysis calcd. for $C_{14}H_8N_2$, C 82.33, H 3.95, N 13.72%, found C 82.23, H 3.94, N 13.71%.

Synthesis of 7,14-dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indole (11, *iso*-DHBBII):



Scheme S1 : Synthetic route to *iso*-DHBBII

a) 1*H*-naphtho[1,2-*d*][1,3]oxazine-2,4-dione: To a suspension of 1-amino-2-naphthoic acid [4] (10 g, 53.5 mmol) in 200 ml of THF, was added triphosgene (5.7 g, 19.2 mmol) , the reaction mixture was stirred for 12h, and the resulting precipitate was collected by filtration, which was then washed with 100 ml of ether to give the pure product (10.2 g, 88%) and used directly for next step.

b) Methyl 1-amino-2-naphthoate: The suspension of **1*H*-naphtho[1,2-*d*][1,3]oxazine-2,4-dione** (10.2 g, 47.9 mmol) and NaOH (0.46 g, 11.5 mmol) in 100 ml of absolute MeOH was heated to reflux for 3h, then MeOH was evaporated to give the crude product, which was then purified by silica column chromatography with PE:EA=20:1 as the eluent

to give methyl 1-amino-2-naphthoate (6 g, 60%). δ_H (600 MHz; $CDCl_3$; Me_4Si) 7.91-7.9 (2H, m), 7.77 (1H, d, J=8.2 Hz), 7.57-7.56 (1H, m), 7.49-7.48 (1H, m), 7.11 (1H, d, J=8.9 Hz), 6.83 (2H, b), 3.94 (3H, s).

c) Dinaphtho[1,2-*b*:1',2'-*f*][1,5]diazocine-7,15(8*H*,16*H*)-dione: Methyl 1-amino-2-naphthoate (5.8 g, 28.9 mmol) was added to the suspension of NaH (2.3 g, 57.8 mmol, 60%) in anhydrous THF (100 mL) at 25 ^{o}C. the resulting mixture was gradually heated to reflux, and stirred for 3 days. The mixture was cooled down to rt and then poured slowly into 300 mL of 0.1 M HCl and ice. After the ice had melted, the precipitated product was collected by filtration, washed several times with de-ionized water, and air-dried to yield the crude product, which was then recrystallized from aqueous EtOH to yield pure product (3.4 g, 70%) as a light yellow powder. m.p. : > 300 ^{o}C. IR (KBr, cm^{-1}): 3440, 3351, 3170, 3058, 1651, 1393, 824, 754. δ_H (600 MHz; DMSO-d_6; Me_4Si) 10.67 (1H, s), 8.10 (1H, d, J=8.5 Hz), 7.86 (1H, d, J = 8.1 Hz), 7.73 (1H, d, J=8.5 Hz), 7.67-7.66 (1H, m), 7.58-7.57 (1H, m), 7.33 (1H, d, J = 8.5 Hz). δ_C (150 MHz; DMSO-d_6; Me_4Si) 170.2, 134.1, 131.5, 130.7, 128.9, 128.5, 128.2, 128.0, 127.9, 124.3, 123.8. HRMS(ESI) calcd. for $C_{22}H_{14}N_2O_2Na[M+Na]^+$, 361.0948, found 361.0947.

d) 7,15-dichlorodinaphtho[1,2-*b*:1',2'-*f*][1,5]diazocine: Finely powdered Dinaphtho [1,2-*b*:1',2'-*f*][1,5]diazocine-7,15(8*H*,16*H*)-dione (3.4 g, 10 mmol) and phosphorus pentachloride (4.1 g, 20 mmol) were boiled together in chloroform (40 ml) for 4 hr. After the evaporation of the solvent, the resulting solid was wash with 150 ml of mixed-solvent (PE:DCM=1:1) and the filtrate was concentrated to give 2.6 g crude product, 0.1 g of which was further purified by silica column chromatography with PE:DCM=5:1 as the eluent to give a pure product for NMR analysis (20 mg). m.p. : 239.6-241.7 ^{o}C. IR (KBr,

cm^{-1}): 3399(broad), 3053, 2926, 2854, 1659, 1644, 1461, 1371, 1269, 1090, 1001, 806, 755. δ_H (600 MHz; $CDCl_3$; Me_4Si) 8.09 (1H, d, J = 7.7 Hz), 7.74 (1H, d, J=7.9 Hz), 7.6-7.5 (3H, m), 7.36 (1H, d, J = 8.6 Hz). δ_C (150 MHz; DMSO-d_6; Me_4Si) 156.7, 142.6, 134.3, 128.4, 127.8, 127.2, 126.3, 125.9, 124.6, 122.8, 121.5. HRMS(ESI) calcd. for $C_{22}H_{12}Cl_2N_2Na[M+Na]^+$, 397.0270, found 397.0268.

e) 7,14-dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indole (11, *iso*-DHBBII): To the solution of 7,15-dichlorodinaphtho[1,2-b:1',2'-*f*][1,5]diazocine (2.0 g, 5.34 mmol, crude) in anhydrous THF (100 ml), was added activated zinc (5.2 g, 77 mmol) in one portion, then TFA (9.2ml, 123 mmol) was added dropwise at rt. The resulting suspension was stirred for 12h at that temperature, then saturated aqueous NH_4Cl was added to quench the reaction. The mixture was extracted with EtOAc to give a suspension in organic layer, which was separated and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude product, which was then purified by recrystallization from MeOH to give the desired product as a light yellow solid (0.9 g, 30% for two steps). m.p. : > 300 ^oC. IR (KBr, cm^{-1}): 3425, 3047, 1616, 1451, 1380, 1311, 802, 750. δ_H (600 MHz; DMSO-d_6; Me_4Si) 12.10 (1H, s), 8.48 (1H, d, J = 8.3Hz); 7.99 (1H, d, J = 8.1Hz, Ar), 7.97 (1H, d, J = 8.5Hz), 7.62-7.57 (2H, m), 7.46-7.43 (1H, m). δ_C (150 MHz; DMSO-d_6; Me_4Si) 134.8, 130.1, 129.0, 126.0, 125.8, 124.0, 123.1, 121.2, 119.2, 118.5, 110.1. HRMS(ESI) calcd. for $C_{22}H_{14}N_2Na[M+Na]^+$: 329.1055, found: 329.1055.

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[1] L. Qiu, C. Yu, N. Zhao, W. Chen, Y. Guo, X. Wan, R. Yang, Y. Liu, *Chem. Commun.* **2012**, *48*, 12225.

[2] N. Nakagawa, R. Konaka, T. Nakata, *J. Org. Chem.* **1962**, 27, 1597.

[3] S. Hünig, H.-C. Steinmetzer, *Justus Liebigs Ann. Chem.* **1976**, 1090.

[4] Y.-L. Yang, F.-R. Chang, Y.-C. Wu, *Tetrahedron Lett.* **2003**, 44, 319.

2. Figures and data

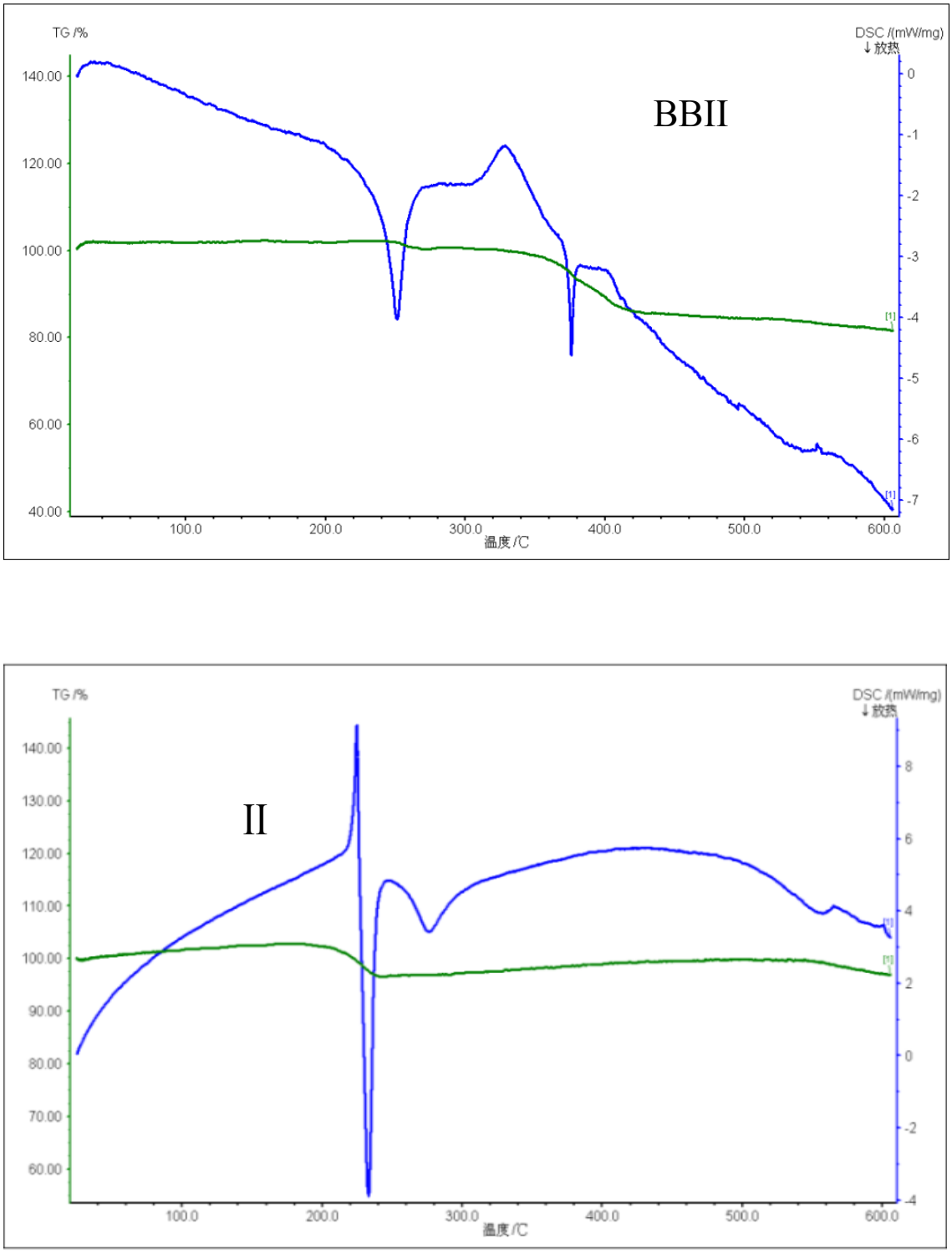

Fig. S1 Thermogravimetric analysis of BBII and II.

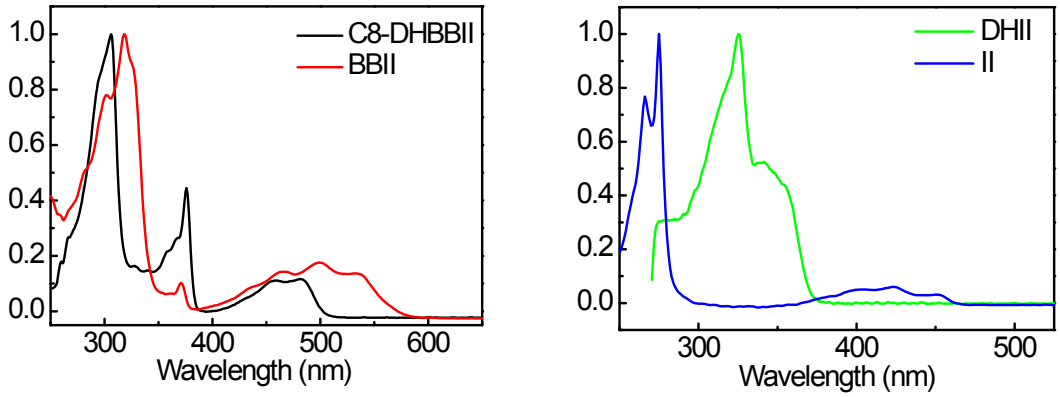

Fig. S2 Normalized UV-vis spectra of C8-DHBBII (black line), BBII (red line), DHII (green line) and II (blue line) in THF.

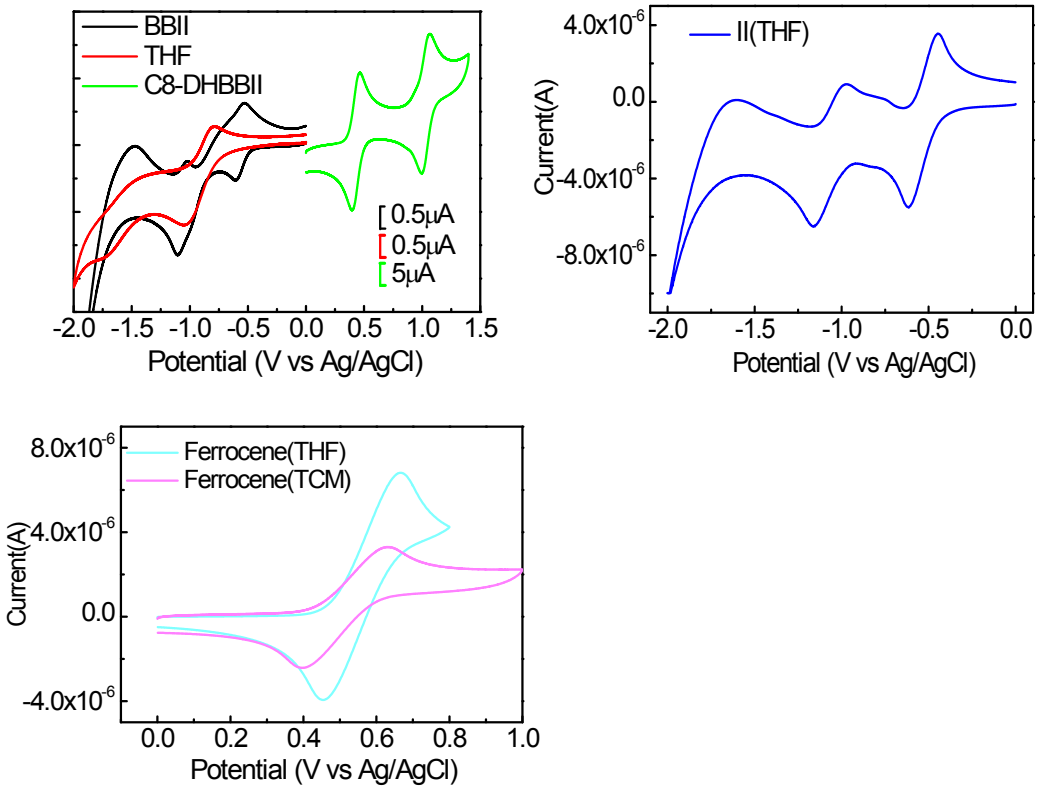

Fig. S3 Cyclic Voltammetry of C8-DHBBII (green line), BBII (black line), II (blue line) and Ferrocene (LT Cyan and LT Magenta lines) (TCM: Chloroform; electrolyte: NBu_4ClO_4, 0.1 M, scan rate: 0.1 V/s).

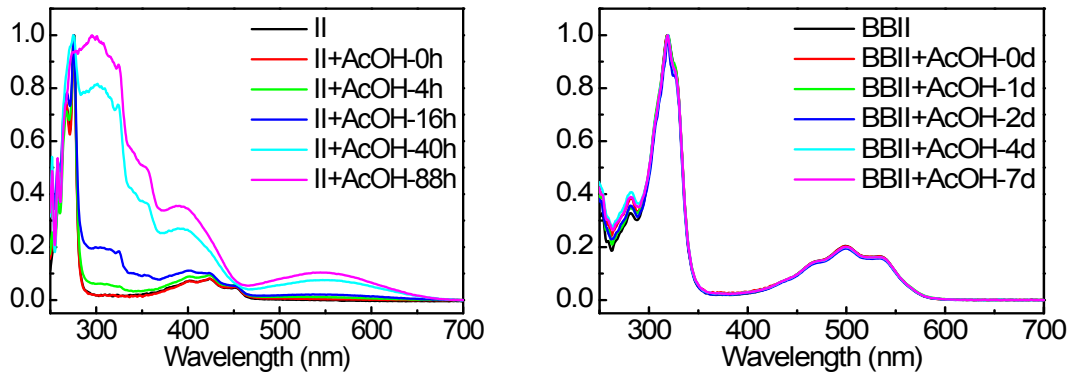

Fig. S4 The time-dependent Normalized UV-vis spectroscopy of II and BBII in THF containing of $1*10^{-5}$ M AcOH.

Theoretical calculations of the diazapentalenes and pentalenes[5]

1) ***Table S1.*** The 4 lowest excited energies (nm) of diazapentalenes and pentalenes in THF (DFT(B3LYP/6-31+G*)).

Excited state / Compounds		S_1	S_2	S_3	S_4
***iso*-BBII**	EE [a] (nm)	914.1	572.6	472.5	418.0
	OS [b]	0.00	0.08	0.00	0.00
	MC [c]	H[d]→L[e] (49.8%)	H-1→L (49.5%)	H-4→L (49.7%)	H-3→L (47.7%)
II	EE (nm)	619.3	447.5	427.4	342.1
	OS	0.00	0.00	0.27	0.08
	MC	H→L (49.9%)	H-2→L (49.8%)	H-1→L (47.2%)	H-4→L (47.1%)
BBII	EE (nm)	549.4	532.5	419.3	412.0
	OS	0.00	0.65	0.00	0.00
	MC	H-1→L (49.6%)	H→L (48.2%)	H-4→L (49.7%)	H-2→L (47.0%)
3a	EE (nm)	745.5	488.1	373.3	369.8
	OS	0.00	0.33	0.00	0.10
	MC	H→L (49.6%)	H-1→L (48.4%)	H-3→L (44.4%)	H-2→L (41.6%)
2a	EE (nm)	475.4	474.7	375.1	361.6
	OS	0.00	0.58	0.00	0.00
	MC	H-1→L (49.5%)	H→L (46.4%)	H→L+1 (37.7%)	H-2→L (34.7%)

[a] : Excited Energy; [b] : oscillator strength; [c] : Main Contribution; [d] : HOMO; [e] : LUMO.

2) Calculated UV-vis spectra (TDDFT(B3LYP/6-31+G*)).

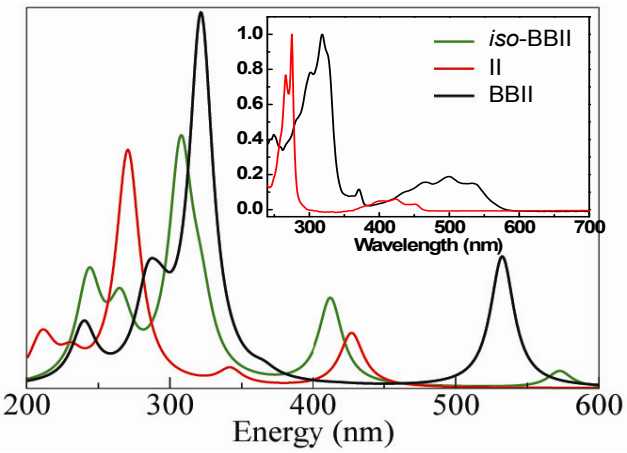

Fig. S5 Calculated UV-vis spectra of BBII, II and *iso*-BBII (bottom-left) and normalized observed UV-vis spectra of BBII and II (top-right) in THF.

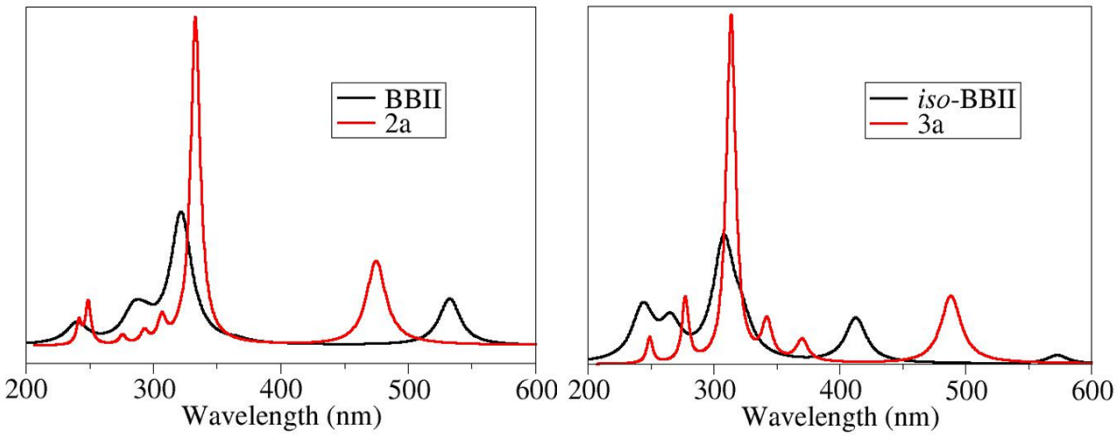

Fig. S6 Calculated UV-vis spectra of BBII and 2a (left), *iso*-BBII and 3a (right).

3) Optimized geometry configurations and Bond lengths (DFT(B3LYP/6-31+G*)).

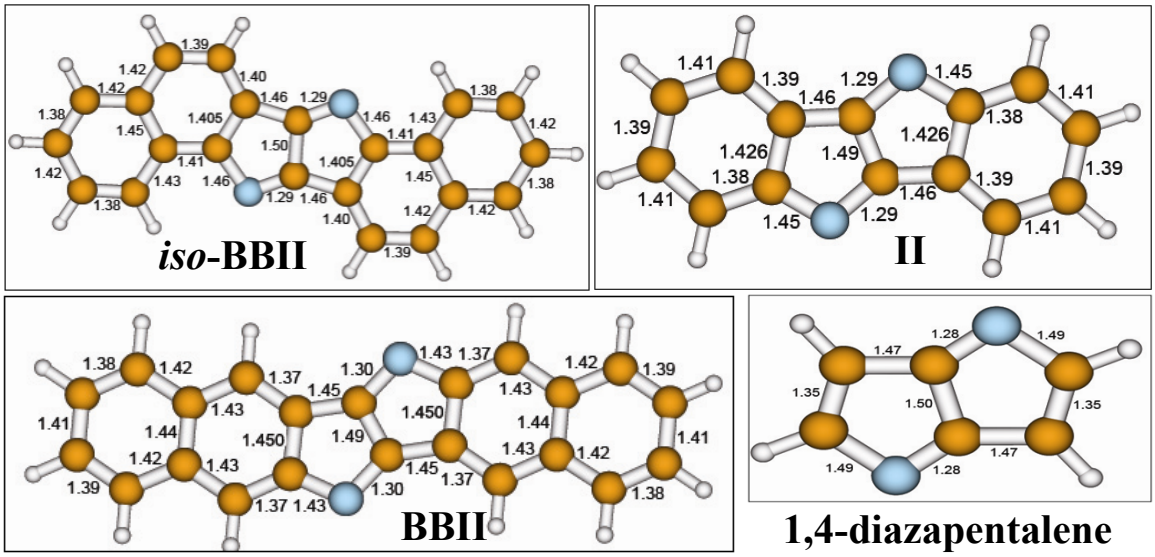

Fig. S7 The optimized geometry configurations and bond lengths.

4) NICS(1)$_{zz}$ (DFT (B3LYP/6-311++G**)).

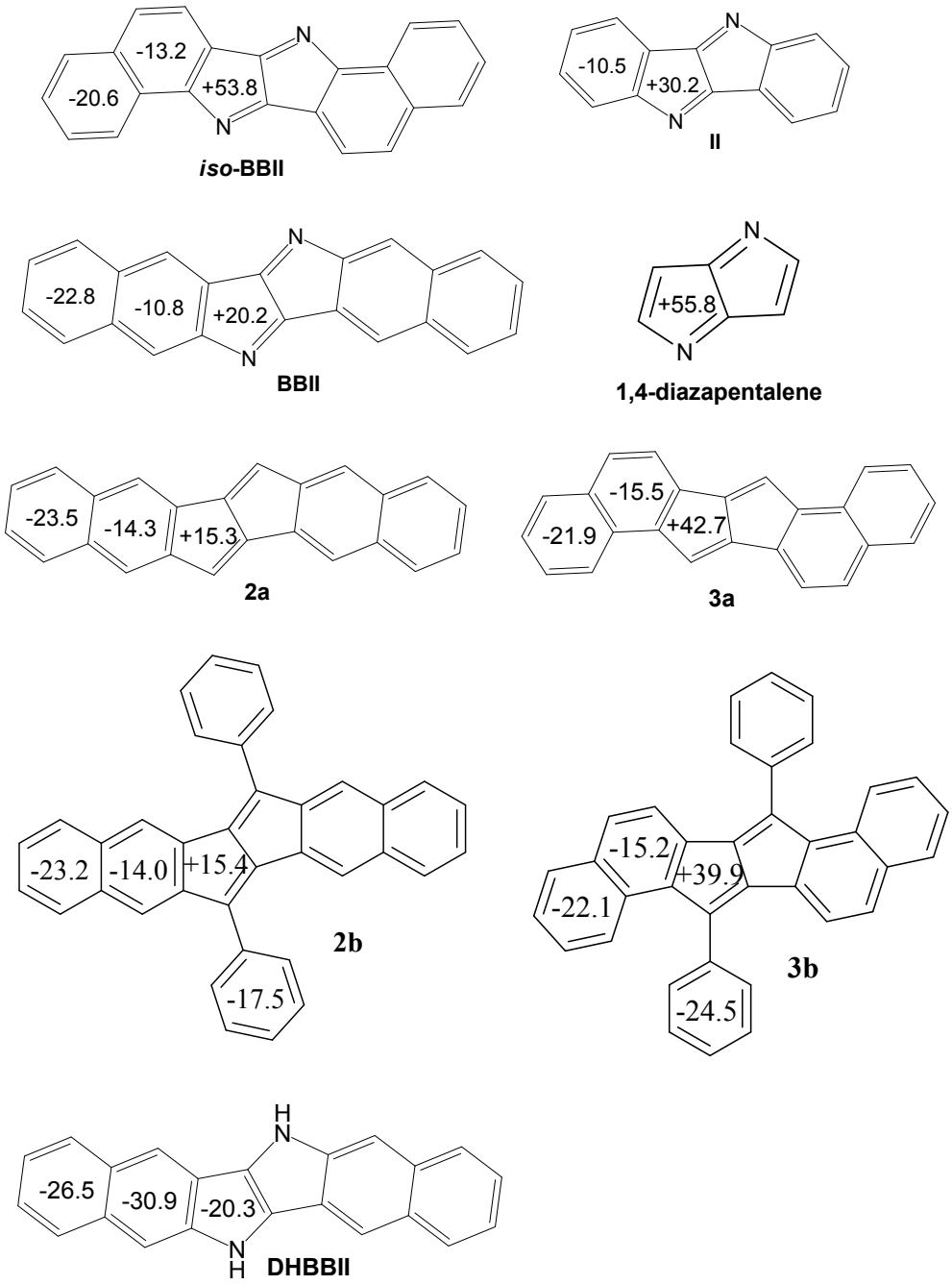

Fig. S8 NICS(1)$_{zz}$ values of the diazapentalenes.

5) Molecular orbitals (TDDFT(B3LYP/6-31+G*))**.**

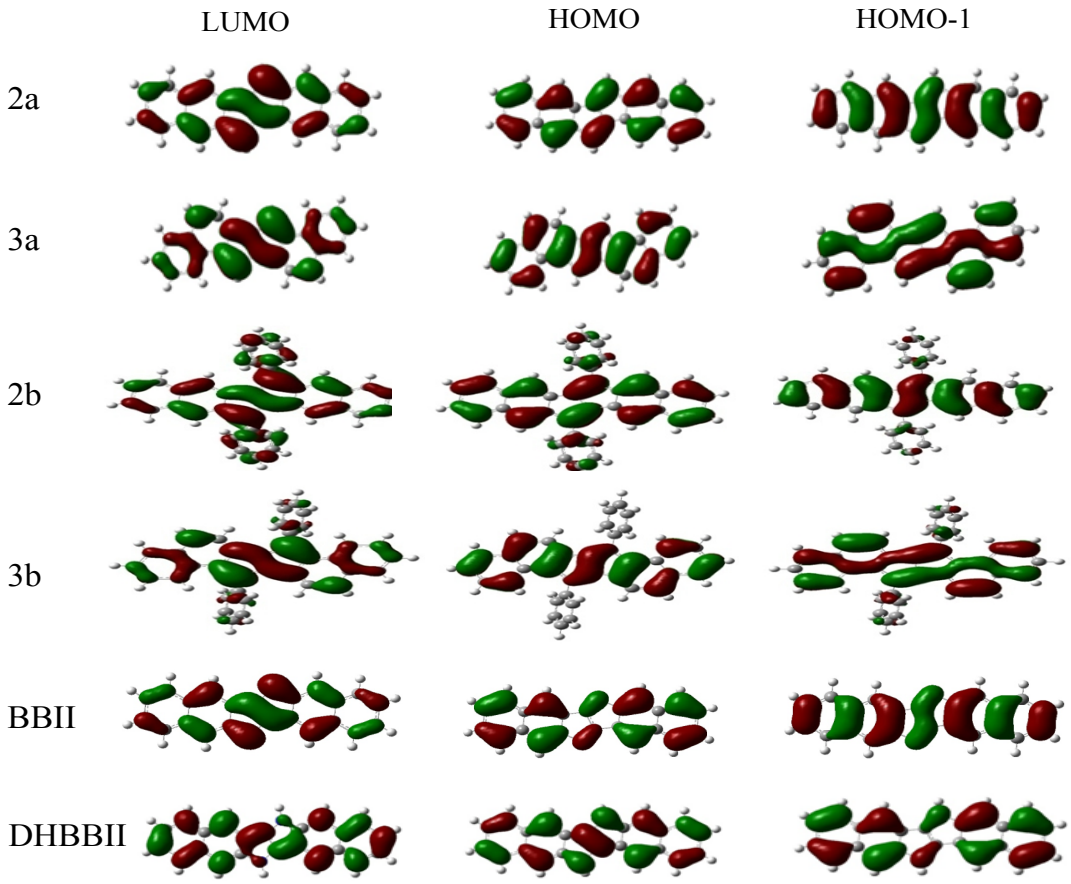

Fig. S9 Molecular orbitals of 2a, 3a, 2b, 3b, BBII and DHBBII.

6) **Table *S2*.** Energy level of Diazapentalenes and Pentalenes.

Orbitals \ Compounds	*iso*-BBII	BBII	3b	2b	3a	2a	DHBBII
LOMO	-3.66	-3.35	-2.94	-2.64	-2.94	-2.55	-1.84
HOMO	-5.76	-6.06	-5.32	-5.44	-5.34	-5.56	-4.88
HOMO-1	-6.41	-6.36	-5.87	-5.85	-5.97	-5.90	-5.84
HOMO-LUMO gap	2.10	2.71	2.38	2.80	2.40	3.01	3.04

7) Cartesian coordinates of diazapentalenes optimized at B3LYP/6-31+G* level.

***iso*-BBII**:

C	-6.289233	-0.419131	-0.000120
C	-5.665086	0.808768	-0.000006
C	-4.243951	0.908024	0.000040
C	-3.475066	-0.317284	-0.000035
C	-4.150972	-1.573025	-0.000154
C	-5.525907	-1.620025	-0.000193
C	-3.582458	2.165264	0.000162
C	-2.075021	-0.188430	0.000013
C	-2.198086	2.256108	0.000208
H	-4.183980	3.070573	0.000217
H	-7.374455	-0.476164	-0.000154
H	-6.252336	1.723896	0.000047
H	-3.559473	-2.483025	-0.000218
H	-6.037766	-2.578573	-0.000287
C	6.289236	0.419154	-0.000145
C	5.665088	-0.808745	-0.000030
C	4.243954	-0.908000	0.000021
C	3.475069	0.317307	-0.000040
C	4.150976	1.573048	-0.000177
C	5.525910	1.620048	-0.000224
C	3.582460	-2.165240	0.000132
C	2.075024	0.188454	0.000013
C	1.447759	-1.068622	0.000074
C	2.198089	-2.256084	0.000156
H	4.183982	-3.070549	0.000192
H	7.374459	0.476187	-0.000183
H	6.252338	-1.723873	0.000019
H	3.559476	2.483049	-0.000241
H	6.037769	2.578596	-0.000324
N	-1.141404	-1.305071	-0.000025
H	-1.705073	3.223868	0.000280
H	1.705075	-3.223844	0.000238
C	-1.447756	1.068646	0.000103
C	0.022534	-0.748023	0.000089
C	-0.022530	0.748047	0.000049
N	1.141408	1.305095	-0.000131

II:

C	-4.128169	-0.674112	-0.010470
C	-4.247750	0.715591	-0.010722
C	-2.858449	-1.287001	-0.010375
C	-3.107706	1.549588	-0.010852

C	-1.864550	0.946376	-0.010796
C	-1.735150	-0.473592	-0.010594
H	-2.766795	-2.369489	-0.010242
H	-3.203630	2.631341	-0.011011
C	4.128167	0.674110	-0.010461
C	4.247748	-0.715592	-0.010735
C	2.858448	1.287000	-0.010357
C	3.107704	-1.549589	-0.010877
C	1.864549	-0.946377	-0.010812
C	1.735148	0.473591	-0.010588
H	2.766794	2.369488	-0.010207
H	3.203629	-2.631342	-0.011054
C	-0.290613	-0.688086	-0.010635
C	0.290612	0.688085	-0.010623
N	-0.589429	1.633803	-0.010887
N	0.589427	-1.633804	-0.010916
H	-5.235262	1.168672	-0.010738
H	-5.020969	-1.292626	-0.010378
H	5.020968	1.292625	-0.010358
H	5.235261	-1.168673	-0.010758

BBII:

C	-6.559809	-0.935887	0.003662
C	-5.301649	-1.513290	0.003812
C	-4.132897	-0.711618	0.003758
C	-4.267956	0.720170	0.003560
C	-5.569039	1.279982	0.003412
C	-6.692889	0.470259	0.003461
C	-2.826974	-1.299047	0.003885
C	-3.097292	1.549581	0.003512
C	-1.864540	0.958690	0.003664
C	-1.724340	-0.484809	0.003809
H	-2.729203	-2.381895	0.004055
H	-7.446773	-1.563363	0.003693
H	-5.194841	-2.595497	0.003957
H	-5.674515	2.362202	0.003266
H	-7.682896	0.918261	0.003345
H	-3.200059	2.631485	0.003345
C	6.559808	0.935889	0.003666
C	5.301648	1.513292	0.003815
C	4.132896	0.711620	0.003760
C	4.267954	-0.720168	0.003560
C	5.569037	-1.279980	0.003411
C	6.692887	-0.470257	0.003462
C	2.826973	1.299049	0.003887

C	3.097290	-1.549579	0.003510
C	1.864539	-0.958688	0.003662
C	1.724339	0.484811	0.003809
H	2.729201	2.381897	0.004059
H	7.446772	1.563365	0.003697
H	5.194839	2.595499	0.003962
H	5.674513	-2.362200	0.003264
H	7.682894	-0.918260	0.003346
H	3.200057	-2.631483	0.003342
C	-0.284290	-0.686392	0.004000
C	0.284288	0.686394	0.004001
N	-0.602952	1.635341	0.003603
N	0.602951	-1.635339	0.003601

1,4-**Diazapentalene**:

C	-1.927282	0.765582	0.000000
C	-1.721159	-0.568048	0.000000
C	1.927286	-0.765577	0.000000
C	1.721162	0.568052	0.000000
C	-0.254752	-0.704459	0.000000
C	0.254755	0.704462	0.000000
N	-0.681013	1.581074	0.000000
N	0.681017	-1.581070	0.000000
H	-2.867713	1.302046	0.000000
H	-2.464914	-1.352608	0.000000
H	2.464918	1.352611	0.000000
H	2.867716	-1.302042	0.000000

8) Cartesian coordinates of diazapentalenes for NICS(1)$_{zz}$ calculation optimized at B3LYP/6-31+G* level.

***iso*-BBII**:

C	6.27030900	-0.47468200	0.00010100
C	5.66107100	0.75650200	0.00001500
C	4.24369100	0.87071700	-0.00003300
C	3.46522800	-0.34403900	0.00001200
C	4.12625200	-1.60442900	0.00009700
C	5.49675000	-1.66548500	0.00014200
C	3.59445500	2.13120600	-0.00012900
C	2.06934100	-0.20382200	-0.00003200

C	2.21506700	2.23303400	-0.00015900
H	4.20359600	3.02819900	-0.00017800
H	7.35229900	-0.54296800	0.00013800
H	6.25742600	1.66257400	-0.00001700
H	3.52315700	-2.50402400	0.00013000
H	5.99830400	-2.62653200	0.00021000
C	-6.27030600	0.47468900	0.00013300
C	-5.66107000	-0.75649500	0.00004600
C	-4.24369000	-0.87071400	-0.00001000
C	-3.46522600	0.34404300	0.00002600
C	-4.12624800	1.60443400	0.00011600
C	-5.49674600	1.66549100	0.00016800
C	-3.59445600	-2.13120300	-0.00010200
C	-2.06933800	0.20382700	-0.00002700
C	-1.45491400	-1.05557200	-0.00008000
C	-2.21506700	-2.23303100	-0.00014400
H	-4.20359700	-3.02819500	-0.00014100
H	-7.35229600	0.54297600	0.00017600
H	-6.25742600	-1.66256700	0.00001900
H	-3.52315300	2.50402900	0.00014600
H	-5.99830000	2.62653900	0.00023900
N	1.12709700	-1.31109600	-0.00002700
H	1.73010200	3.20193600	-0.00022900
H	-1.73010300	-3.20193400	-0.00021100
C	1.45491800	1.05557100	-0.00009000
C	-0.02755600	-0.74723200	-0.00011200
C	0.02755900	0.74723000	-0.00009000
N	-1.12709200	1.31109600	0.00002700
Bq	-2.81265868	-0.91581366	0.99995900
Bq	-0.94366728	0.02744551	0.99994300
Bq	0.94371820	-0.02742463	0.99998400
Bq	2.82534104	0.93563848	0.99993400
Bq	-4.86909338	0.38471158	1.00007886
Bq	4.86910207	-0.38470434	1.00005482

II:

C	-4.07276700	-0.91338700	0.00004000
C	-4.27335100	0.46262400	0.00001400
C	-2.77262800	-1.44913500	0.00003100
C	-3.18740300	1.35955100	-0.00005000
C	-1.91391100	0.83275500	0.00000500
C	-1.70199600	-0.57410800	0.00003100
H	-2.61604700	-2.52165800	0.00009500
H	-3.34202700	2.43193900	-0.00003900
C	4.07278900	0.91337500	0.00003700

C	4.27336700	-0.46263100	0.00000900
C	2.77264900	1.44912900	0.00003400
C	3.18741200	-1.35955900	-0.00004700
C	1.91392800	-0.83276800	0.00000500
C	1.70200700	0.57412100	0.00003300
H	2.61608400	2.52165600	0.00010500
H	3.34204000	-2.43194600	-0.00002900
C	-0.24773600	-0.70396500	-0.00002900
C	0.24775700	0.70397900	-0.00002700
N	-0.68257000	1.59241900	-0.00003500
N	0.68256900	-1.59241900	-0.00004000
H	-5.28367000	0.85545500	-0.00004200
H	-4.92593100	-1.58141100	0.00002000
H	4.92595300	1.58139800	0.00001500
H	5.28368400	-0.85546700	-0.00004800
Bq	-2.98327100	-0.05355000	-1.00002600
Bq	-0.84403000	0.24182900	-1.00001800
Bq	0.93592800	-0.26080100	-1.00001900
Bq	2.98329300	0.05355100	-1.00002600

BBII:

C	6.55127200	-0.89819000	0.00001800
C	5.30004400	-1.48079700	0.00002500
C	4.12818500	-0.68828300	0.00002200
C	4.25480200	0.74115200	0.00001100
C	5.55114700	1.30640700	0.00000400
C	6.67621000	0.50574900	0.00000700
C	2.82760200	-1.28160600	0.00002800
C	3.08209100	1.56220700	0.00000800
C	1.85611700	0.96641100	0.00001400
C	1.72488100	-0.47536800	0.00002500
H	2.73348700	-2.36228100	0.00003600
H	7.43996700	-1.51870300	0.00002000
H	5.20030000	-2.56113600	0.00003200
H	5.65059000	2.38664100	-0.00000400
H	7.66161300	0.95766700	0.00000200
H	3.17379000	2.64239000	0.00000000
C	-6.55127200	0.89819000	0.00000600
C	-5.30004400	1.48079700	0.00000500
C	-4.12818500	0.68828300	0.00001300
C	-4.25480200	-0.74115200	0.00002200
C	-5.55114700	-1.30640700	0.00002300
C	-6.67621000	-0.50574900	0.00001500
C	-2.82760200	1.28160600	0.00001200
C	-3.08209100	-1.56220700	0.00002900

C	-1.85611700	-0.96641100	0.00002800
C	-1.72488100	0.47536800	0.00001900
H	-2.73348700	2.36228100	0.00000400
H	-7.43996700	1.51870300	0.00000100
H	-5.20030000	2.56113600	-0.00000100
H	-5.65059000	-2.38664100	0.00003000
H	-7.66161300	-0.95766700	0.00001600
H	-3.17379000	-2.64239000	0.00003600
C	0.28617300	-0.68560600	0.00002700
C	-0.28617300	0.68560600	0.00001900
N	0.59196600	1.63458400	0.00001100
N	-0.59196600	-1.63458400	0.00003300
Bq	-0.87384933	-0.41522491	1.00002300
Bq	0.87385078	0.41523865	1.00001800
Bq	-5.39683856	0.08728454	1.00001400
Bq	5.39672372	-0.08855797	1.00001415
Bq	-2.97784297	-0.11904491	1.00001988
Bq	2.97784265	0.11905893	1.00001719

1,4-**Diazapentalene**:

C	0.75889300	-1.92992700	0.00000000
C	1.59125500	-0.86774500	0.00000000
C	-0.75889400	1.92992600	0.00000000
C	-1.59125500	0.86774500	0.00000000
C	0.68828000	0.29569500	0.00000000
C	-0.68827900	-0.29569500	0.00000000
N	-0.68827900	-1.57792300	0.00000000
N	0.68828000	1.57792300	0.00000000
H	1.01032000	-2.98301200	0.00000000
H	2.67230300	-0.87416300	0.00000000
H	-2.67230300	0.87416300	0.00000000
H	-1.01032000	2.98301200	0.00000000
Bq	0.35506691	-0.90911087	1.00000000
Bq	-0.35506691	0.90911102	1.00000000

2a

C	-6.608010	-0.948378	-0.003334
C	-5.340756	-1.503170	-0.002983
C	-4.182841	-0.683056	-0.002752
C	-4.344837	0.745891	-0.002904
C	-5.658543	1.283580	-0.003265
C	-6.767841	0.457315	-0.003459
C	-2.866420	-1.244475	-0.002359
C	-3.188701	1.587961	-0.002643

C	-1.933993	1.026422	-0.002305
C	-1.771936	-0.417460	-0.002189
H	-2.755656	-2.326735	-0.002299
H	-7.483871	-1.591841	-0.003481
H	-5.216253	-2.583895	-0.002842
H	-5.780997	2.364523	-0.003345
H	-7.766063	0.887216	-0.003714
H	-3.321764	2.667815	-0.002782
C	6.608009	0.948377	-0.003309
C	5.340755	1.503169	-0.002942
C	4.182840	0.683055	-0.002734
C	4.344836	-0.745891	-0.002926
C	5.658542	-1.283581	-0.003302
C	6.767840	-0.457315	-0.003473
C	2.866419	1.244475	-0.002326
C	3.188700	-1.587962	-0.002687
C	1.933992	-1.026423	-0.002334
C	1.771935	0.417459	-0.002179
H	2.755655	2.326734	-0.002236
H	7.483870	1.591841	-0.003438
H	5.216252	2.583895	-0.002772
H	5.780996	-2.364523	-0.003413
H	7.766062	-0.887216	-0.003740
H	3.321763	-2.667816	-0.002857
C	-0.330899	-0.658075	-0.002084
C	0.330898	0.658075	-0.002065
C	-0.603422	1.650255	-0.002192
C	0.603421	-1.650256	-0.002241
H	-0.433371	2.721887	-0.002174
H	0.433370	-2.721888	-0.002254

2b

C	-6.571486	-1.174242	-0.059439
C	-5.286540	-1.685033	-0.037253
C	-4.157956	-0.824289	-0.012862
C	-4.369846	0.596762	-0.013321
C	-5.701121	1.089823	-0.033642
C	-6.780476	0.225638	-0.056590
C	-2.824531	-1.337748	0.022683
C	-3.243453	1.476112	0.005334
C	-1.968605	0.960573	0.018232
C	-1.755347	-0.474651	0.041530
H	-2.679496	-2.414313	0.038593
H	-7.424537	-1.847447	-0.078197
H	-5.124429	-2.760730	-0.037487

H	-5.860478	2.165959	-0.031536
H	-7.793058	0.620240	-0.072522
H	-3.417697	2.548992	0.009877
C	6.571525	1.174210	-0.059514
C	5.286567	1.684997	-0.037223
C	4.158007	0.824239	-0.012780
C	4.369895	-0.596811	-0.013264
C	5.701160	-1.089862	-0.033702
C	6.780510	-0.225661	-0.056704
C	2.824579	1.337742	0.022816
C	3.243482	-1.476117	0.005443
C	1.968625	-0.960569	0.018413
C	1.755379	0.474691	0.041737
H	2.679658	2.414316	0.038718
H	7.424575	1.847414	-0.078318
H	5.124453	2.760693	-0.037439
H	5.860536	-2.165995	-0.031631
H	7.793088	-0.620273	-0.072718
H	3.417655	-2.549008	0.009998
C	-0.307552	-0.664757	0.081683
C	0.307568	0.664728	0.081759
C	-0.654656	1.644056	0.040586
C	0.654736	-1.644035	0.040483
C	-0.469679	3.106602	0.021233
C	0.375370	3.734844	0.955397
C	-1.134629	3.909079	-0.926144
C	0.554595	5.119510	0.940209
H	0.876683	3.132888	1.708461
C	-0.947182	5.292905	-0.946536
H	-1.780404	3.442981	-1.665060
C	-0.103965	5.903975	-0.012611
H	1.205846	5.585840	1.675156
H	-1.459229	5.893552	-1.693958
H	0.037342	6.981492	-0.026050
C	0.469741	-3.106594	0.021199
C	-0.375513	-3.734695	0.955274
C	1.134674	-3.909160	-0.926116
C	-0.554820	-5.119355	0.940169
H	-0.876940	-3.132635	1.708178
C	0.947168	-5.292985	-0.946403
H	1.780470	-3.443145	-1.665062
C	0.103848	-5.903925	-0.012489
H	-1.206195	-5.585622	1.675044
H	1.459216	-5.893737	-1.693736
H	-0.037507	-6.981440	-0.025845

3a

C	-6.412077	-0.396010	-0.000380
C	-5.757438	0.816299	-0.000172
C	-4.334316	0.884255	0.000001
C	-3.581705	-0.348334	-0.000052
C	-4.292295	-1.584454	-0.000255
C	-5.670018	-1.607704	-0.000417
C	-3.650188	2.129268	0.000230
C	-2.168185	-0.253960	0.000125
C	-2.264305	2.196080	0.000404
H	-4.236430	3.045221	0.000262
H	-7.498323	-0.430345	-0.000509
H	-6.322959	1.745586	-0.000135
H	-3.736087	-2.517848	-0.000284
H	-6.195998	-2.558925	-0.000577
C	6.412076	0.396026	-0.000355
C	5.757436	-0.816282	-0.000207
C	4.334314	-0.884238	-0.000042
C	3.581704	0.348351	-0.000032
C	4.292295	1.584471	-0.000191
C	5.670018	1.607721	-0.000347
C	3.650185	-2.129250	0.000112
C	2.168184	0.253978	0.000113
C	1.524126	-1.002471	0.000239
C	2.264303	-2.196061	0.000258
H	4.236427	-3.045204	0.000122
H	7.498322	0.430361	-0.000480
H	6.322957	-1.745570	-0.000217
H	3.736088	2.517866	-0.000188
H	6.195999	2.558941	-0.000467
H	-1.761877	3.159879	0.000557
H	1.761874	-3.159860	0.000388
C	-1.524128	1.002490	0.000325
C	0.083004	-0.728040	0.000409
C	-0.083005	0.728059	0.000410
C	1.141510	1.321528	0.000140
C	-1.141510	-1.321509	0.000191
H	1.354818	2.384849	-0.000030
H	-1.354818	-2.384830	0.000001

3b

C	6.004287	2.367983	-0.138911
C	4.885346	3.167660	-0.071420
C	3.575811	2.607065	-0.059161
C	3.421971	1.168986	-0.096248

C	4.606899	0.377485	-0.183730
C	5.857011	0.958601	-0.204869
C	2.431424	3.446238	-0.029503
C	2.095448	0.648191	-0.069850
C	1.151485	2.921391	-0.058409
H	2.577036	4.523532	0.000852
H	6.996643	2.810915	-0.151479
H	4.984299	4.250444	-0.035106
H	4.524210	-0.700033	-0.245015
H	6.740167	0.328820	-0.277393
C	-6.004340	-2.367917	-0.140319
C	-4.885441	-3.167633	-0.072608
C	-3.575892	-2.607081	-0.060064
C	-3.421993	-1.169008	-0.097111
C	-4.606880	-0.377464	-0.184809
C	-5.857007	-0.958538	-0.206212
C	-2.431534	-3.446278	-0.030133
C	-2.095458	-0.648246	-0.070428
C	-0.986064	-1.525894	-0.083724
C	-1.151573	-2.921468	-0.058713
H	-2.577173	-4.523570	0.000187
H	-6.996708	-2.810816	-0.153094
H	-4.984445	-4.250413	-0.036315
H	-4.524142	0.700049	-0.246041
H	-6.740134	-0.328734	-0.278896
H	0.286870	3.577870	-0.059586
H	-0.286992	-3.577990	-0.059666
C	0.986046	1.525808	-0.083453
C	0.216339	-0.692252	-0.130308
C	-0.216318	0.692142	-0.130367
C	-1.582880	0.760400	-0.065986
C	1.582892	-0.760483	-0.065555
C	2.368410	-2.011413	0.056586
C	3.076854	-2.303187	1.236392
C	2.377564	-2.952289	-0.987112
C	3.773849	-3.505858	1.367676
H	3.074023	-1.586506	2.053609
C	3.086661	-4.150459	-0.859535
H	1.835806	-2.736897	-1.904408
C	3.784952	-4.431958	0.318395
H	4.309367	-3.719178	2.289251
H	3.090215	-4.863232	-1.680251
H	4.333151	-5.364982	0.419369
C	-2.368380	2.011393	0.055783
C	-3.077017	2.303474	1.235383
C	-2.377248	2.952040	-0.988128

C	-3.774015	3.506198	1.366238
H	-3.074367	1.586997	2.052780
C	-3.086338	4.150261	-0.860978
H	-1.835264	2.736434	-1.905240
C	-3.784886	4.432042	0.316733
H	-4.309707	3.719755	2.287657
H	-3.089680	4.862854	-1.681852
H	-4.333089	5.365100	0.417376

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[5] The molecular geometries of dibenzopentalenes were fully optimized at the B3LYP/6-31+G* level of theory embedded in the Gaussian 09 software package:Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V. M. B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.

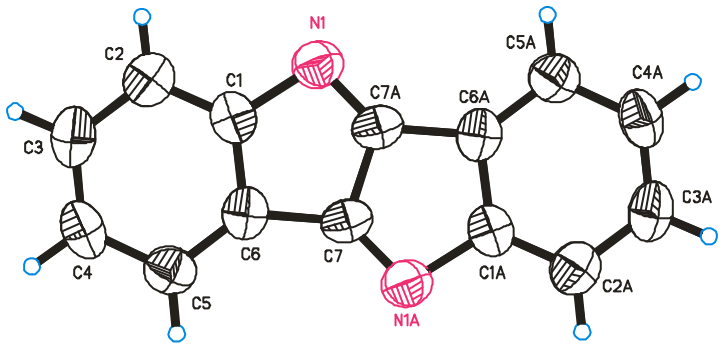


Fig. S10 ORTEP representation of of II The thermal ellipsoids are drawn at the 50% probability level. Symmetry codes for the generated atoms: –x, 1-y, -z..

Table *S3*. Bond lengths [Å] for II.

Bonds	Bond length [Å]
C(1)-C(2)	1.353(4)
C(1)-C(6)	1.412(4)
C(1)-N(1)	1.460(3)
C(2)-C(3)	1.389(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.366(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.405(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.384(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.492(4)
C(7)-N(1A)	1.270(4)
C(7)-C(7A)	1.447(5)
N(1)-C(7A)	1.270(4)

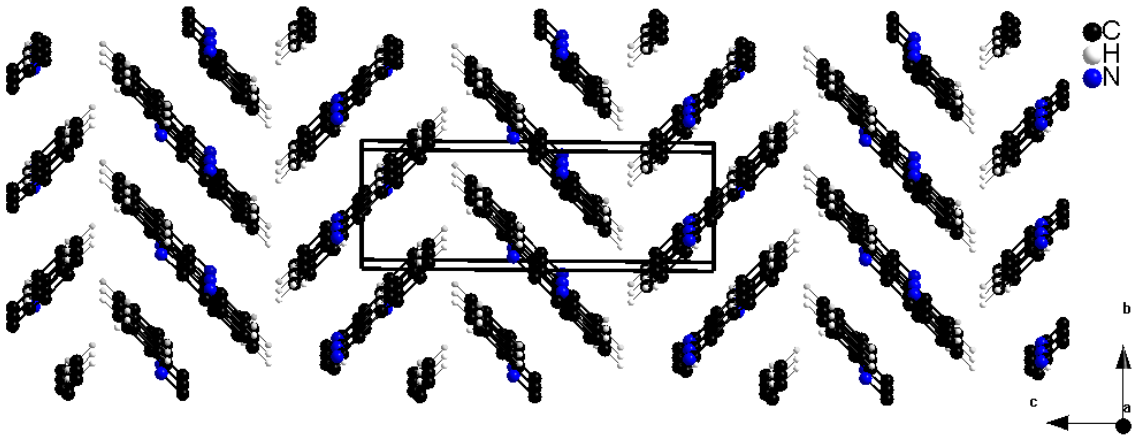
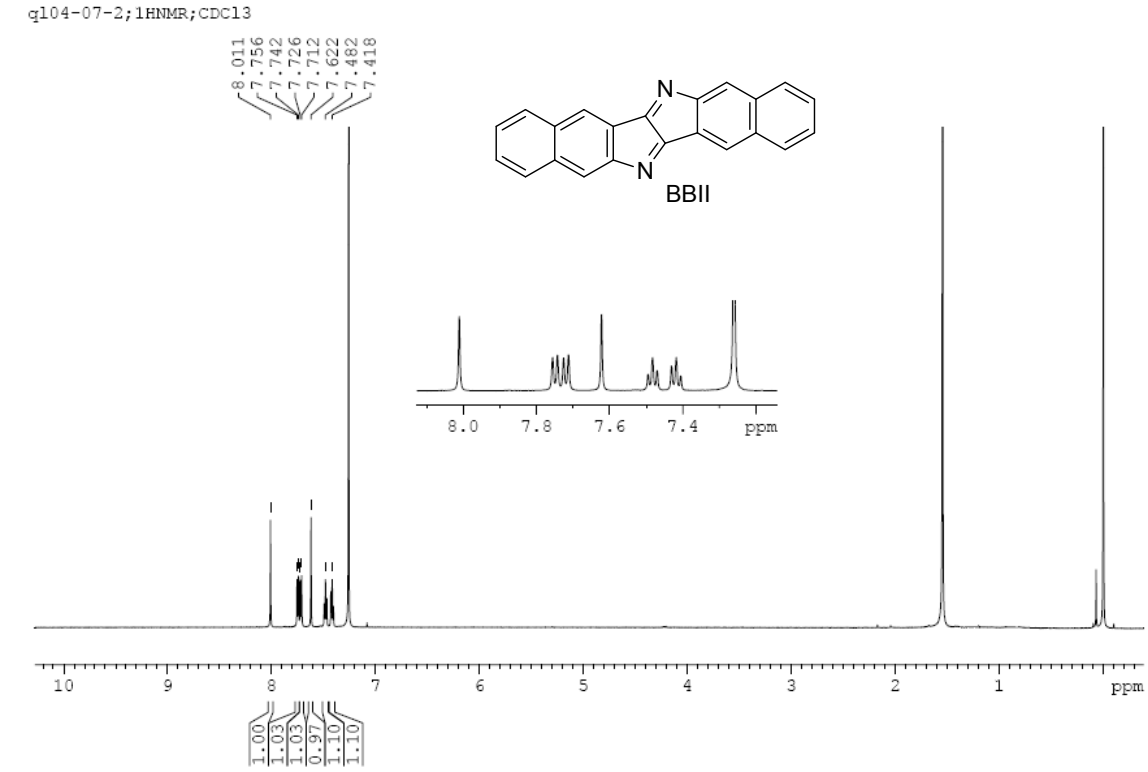
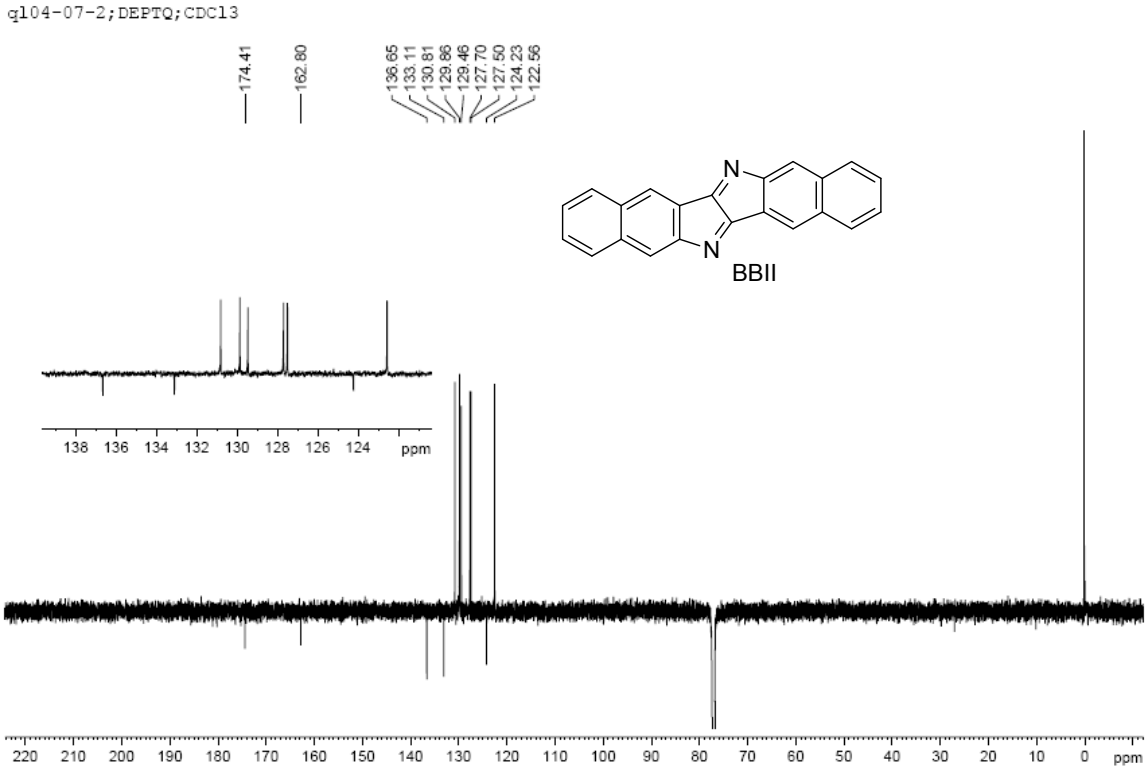


Fig. S11 Three-dimensional packing diagram of II viewing through a-axis.

3. Spectra data

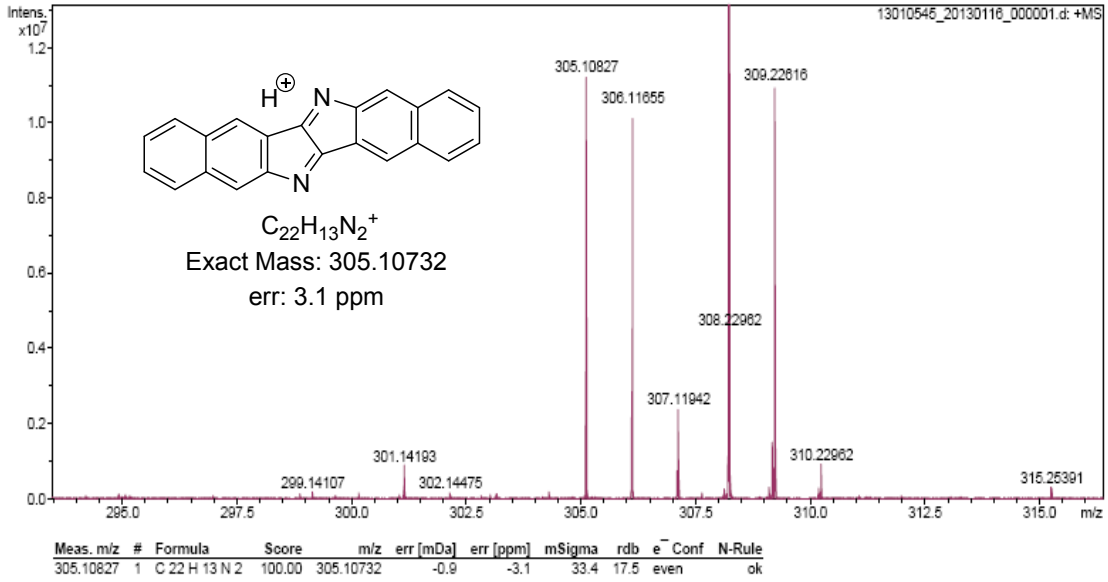




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	13010545_20130116_000001.d	Acquisition Date	1/16/2013 2:29:08 PM
Sample	q103-15-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

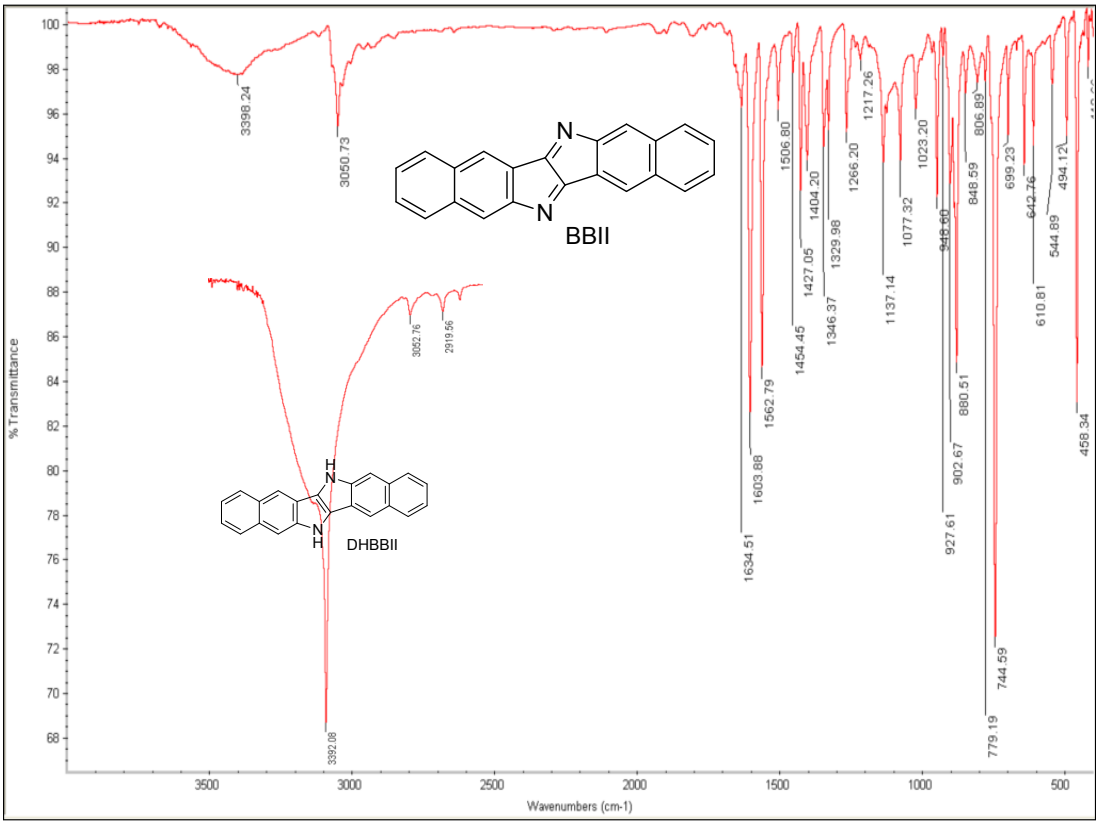


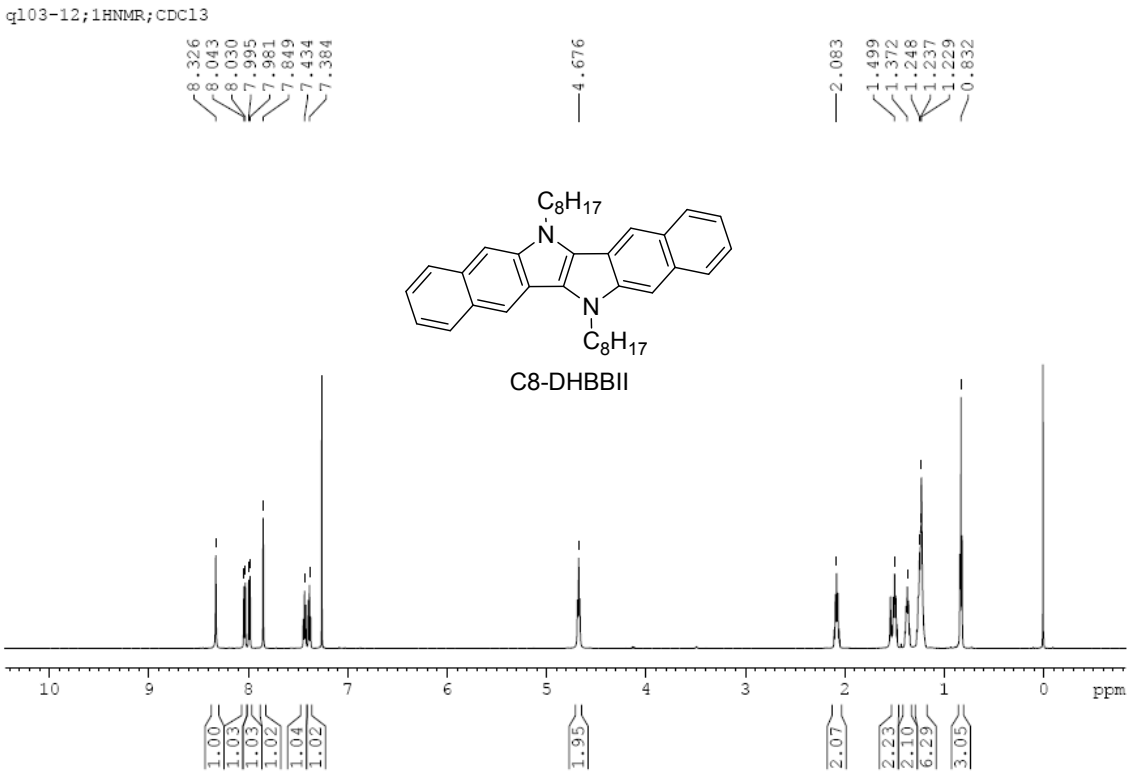
$C_{22}H_{13}N_2^+$

Exact Mass: 305.10732

err: 3.1 ppm

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
305.10827	1	C 22 H 13 N 2	100.00	305.10732	-0.9	-3.1	33.4	17.5	even	ok

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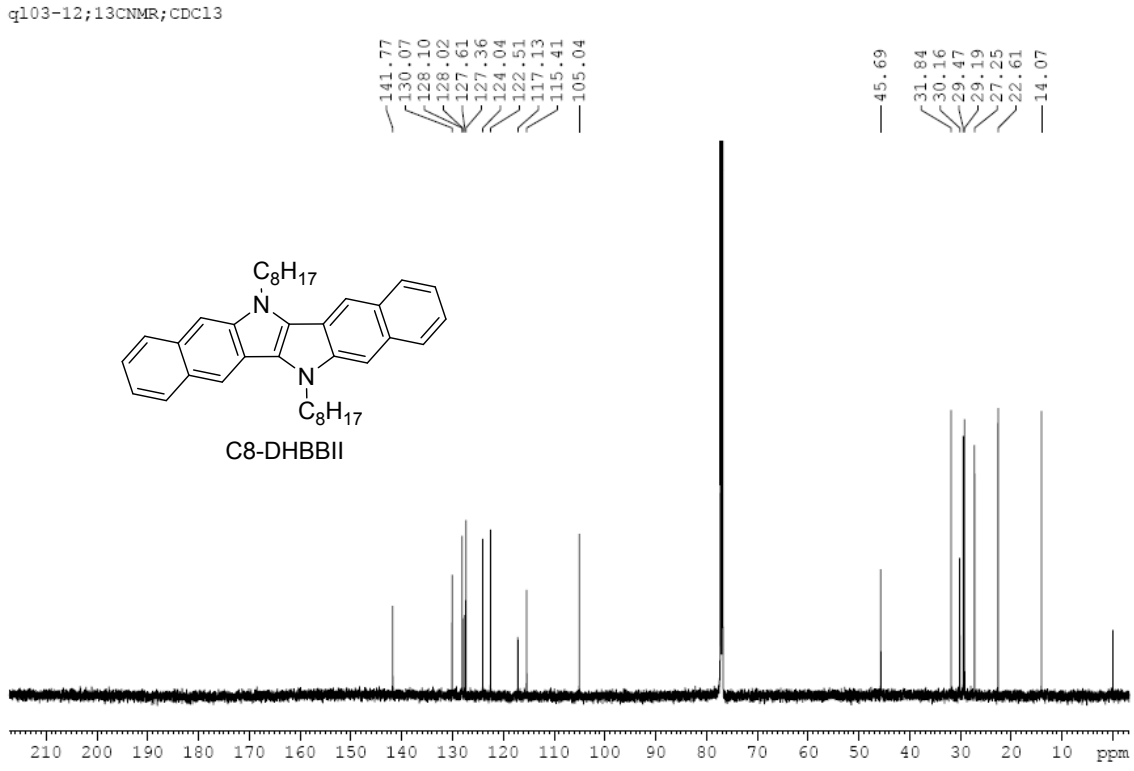
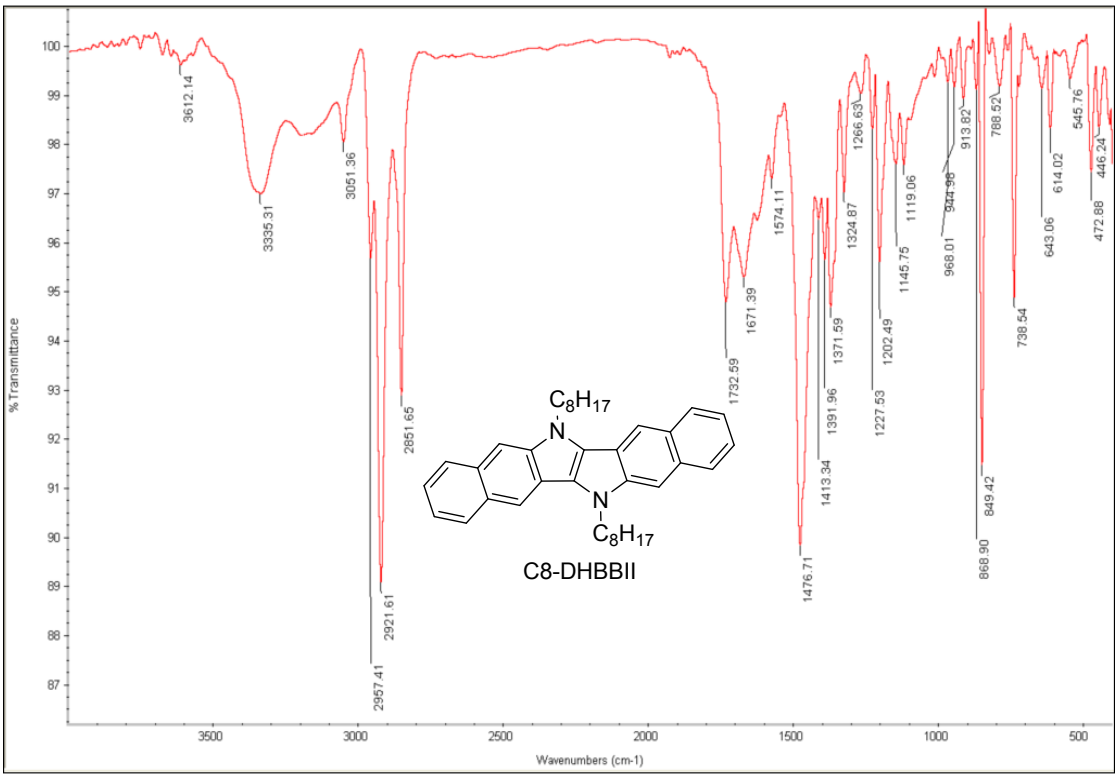
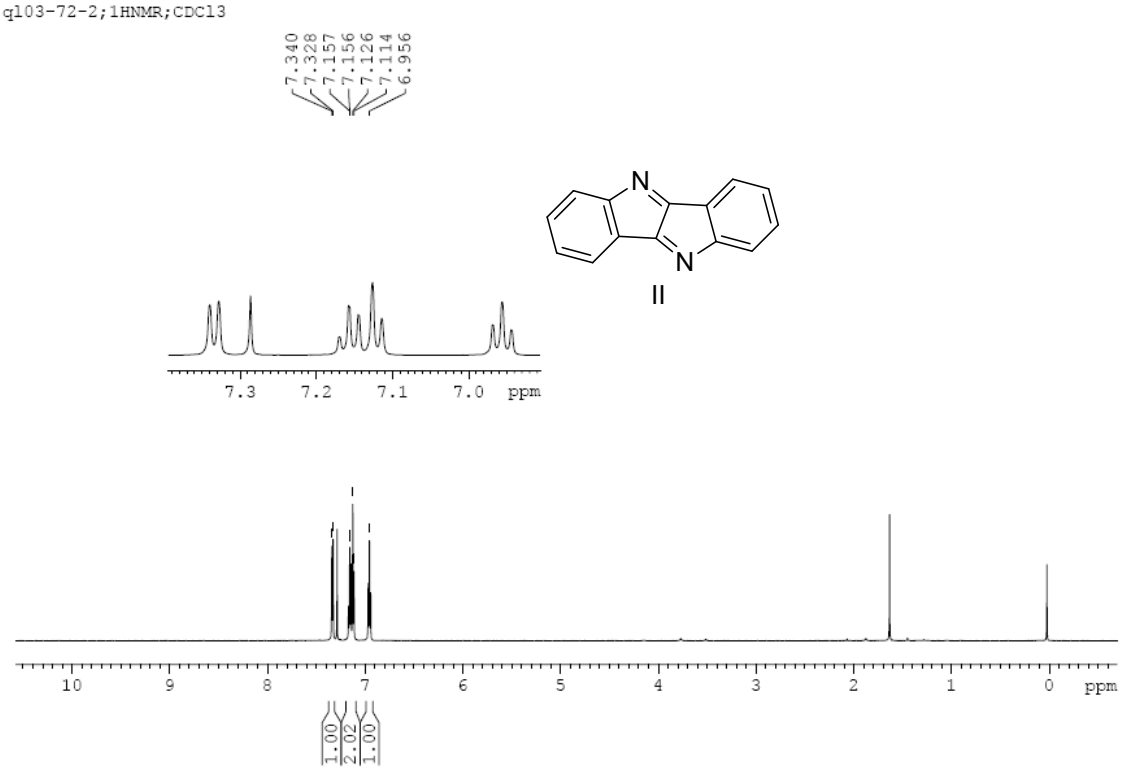
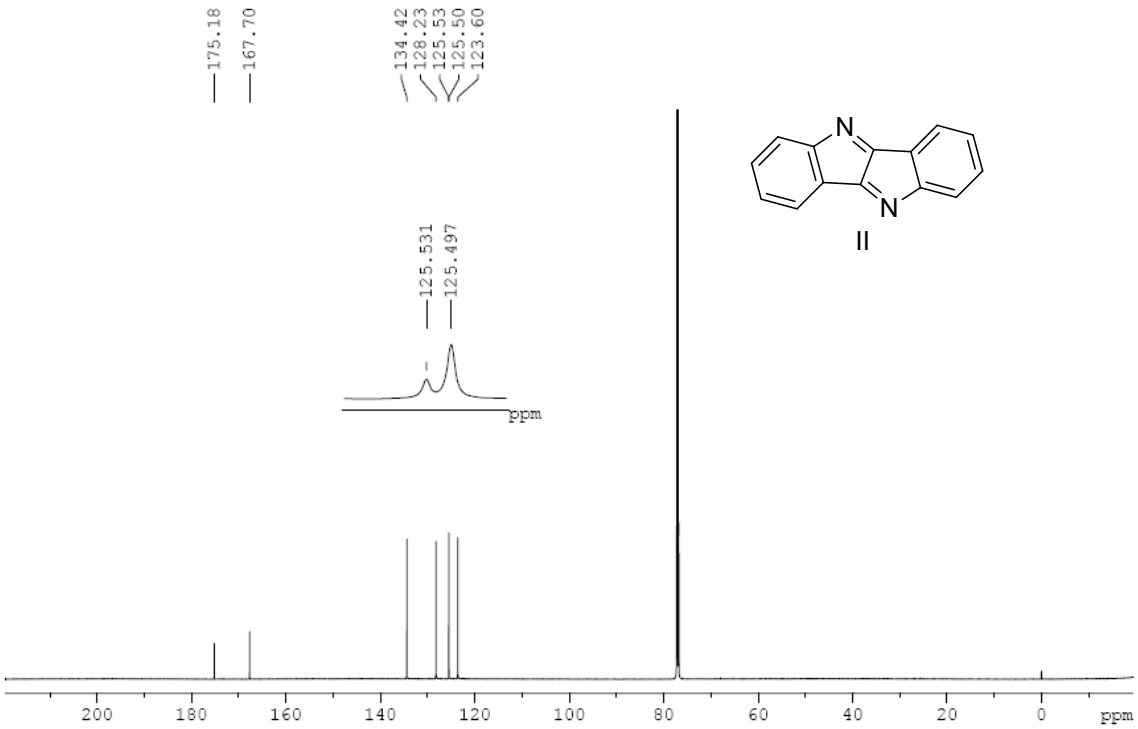
8.326
8.043
8.030
7.995
7.981
7.849
7.434
7.384
4.676
2.083
1.499
1.372
1.248
1.237
1.229
0.832
C8H17
N
N
C8H17
C8-DHBBII
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
1.03
1.02
1.04
1.02
1.95
2.07
2.23
2.10
6.29
3.05


ql03-12;13CNMR;CDCl3
141.77
130.07
128.10
128.02
127.61
127.36
124.04
122.51
117.13
115.41
105.04
45.69
31.84
30.16
29.47
29.19
27.25
22.61
14.07
C8H17
N
N
C8H17
C8-DHBBII
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


% Transmittance
Wavenumbers (cm-1)
3612.14
3335.31
3051.36
2957.41
2921.61
2851.65
1732.59
1671.39
1574.11
1476.71
1413.34
1391.96
1371.59
1324.87
1266.63
1227.53
1202.49
1145.75
1119.06
968.01
944.96
913.82
868.90
849.42
788.52
738.54
643.06
614.02
545.76
472.88
446.24
C8H17
N
N
C8H17
C8-DHBBII

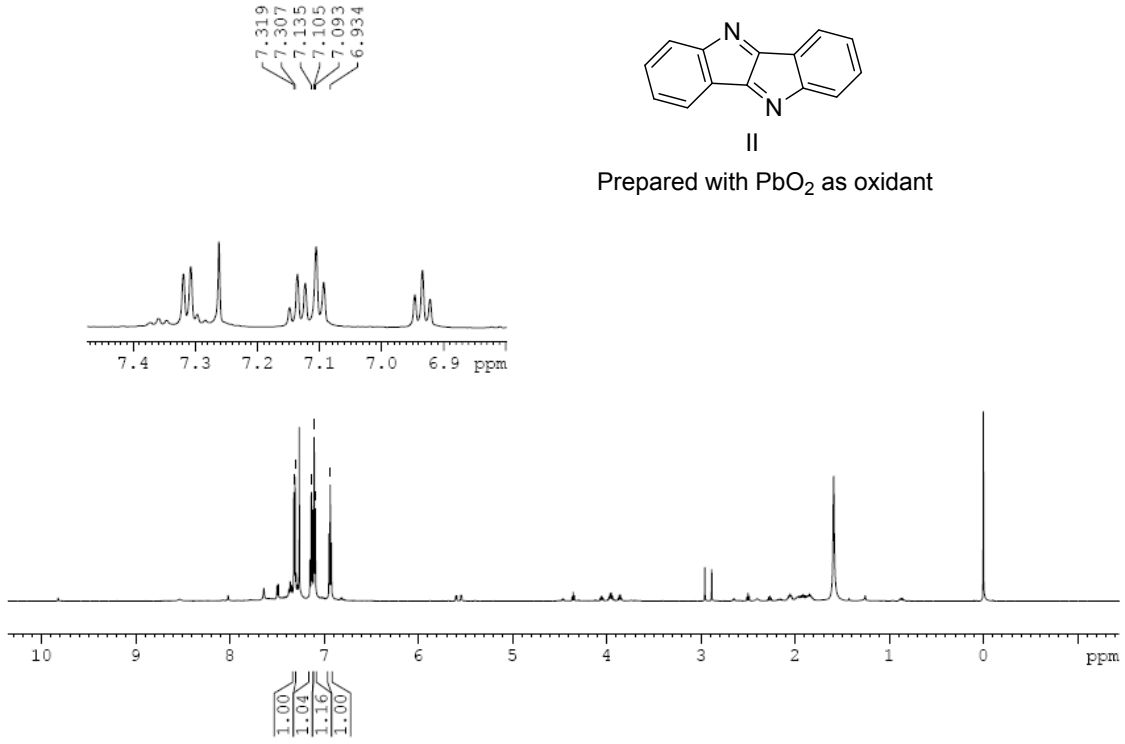

ql03-72-2;1HNMR;CDCl3
7.340
7.328
7.157
7.156
7.126
7.114
6.956
N
N
II
7.3
7.2
7.1
7.0
ppm
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.02
1.00

q103-72-2;13CNMR;CDCl3



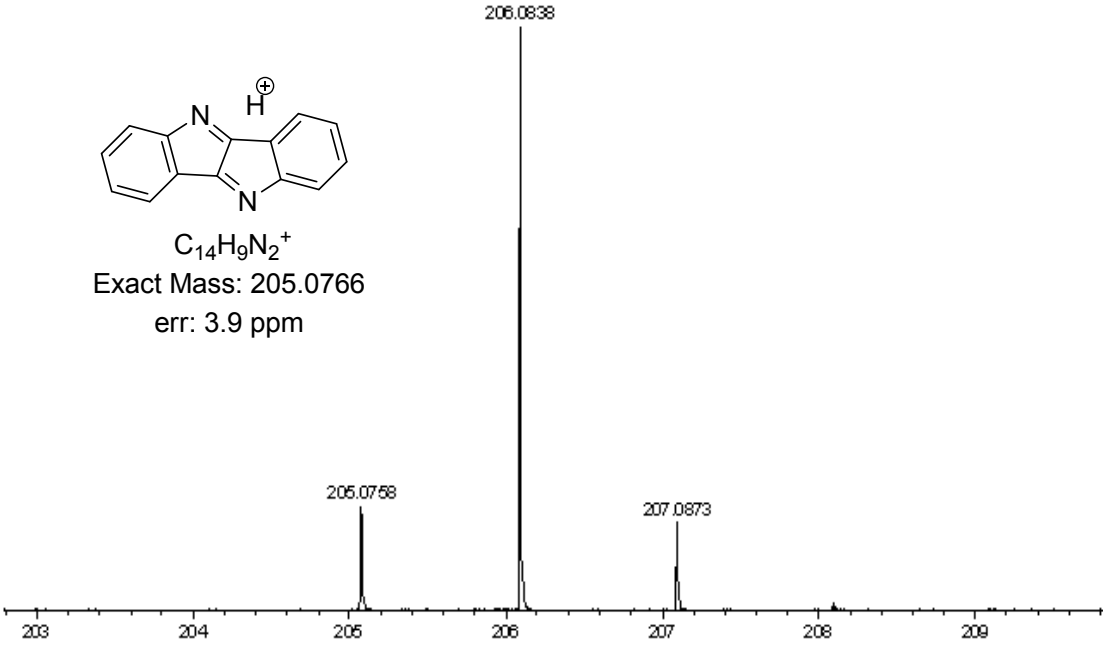
II

q103-60-3;1HNMR;CDCl3



II

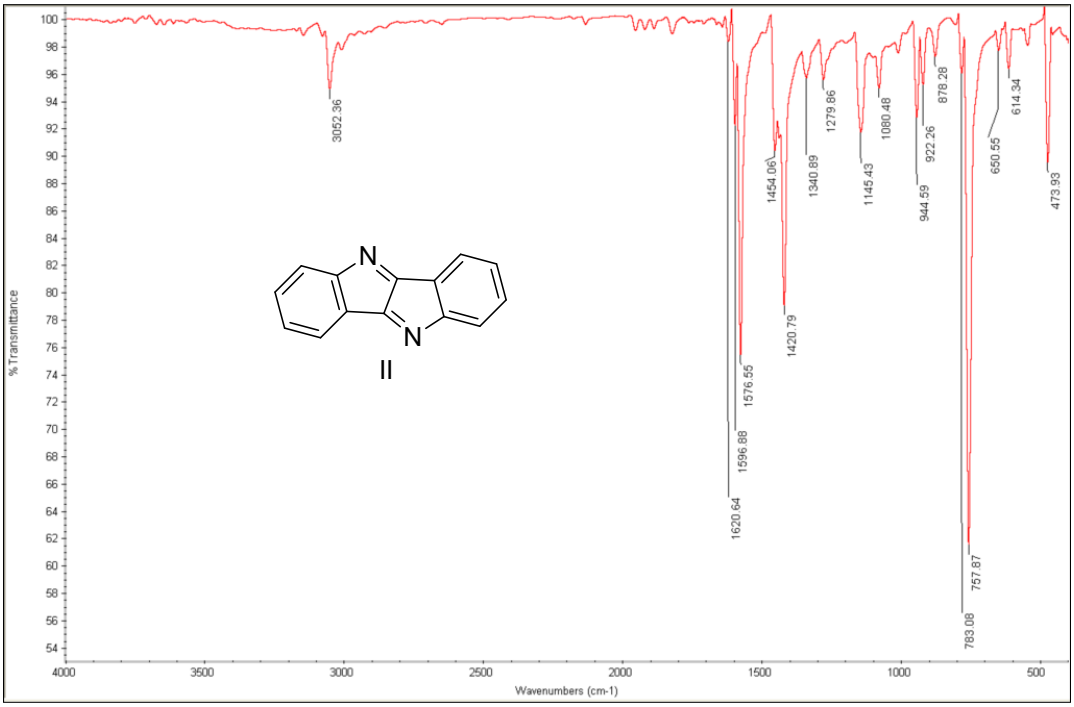
Prepared with PbO_2 as oxidant



$C_{14}H_9N_2^+$

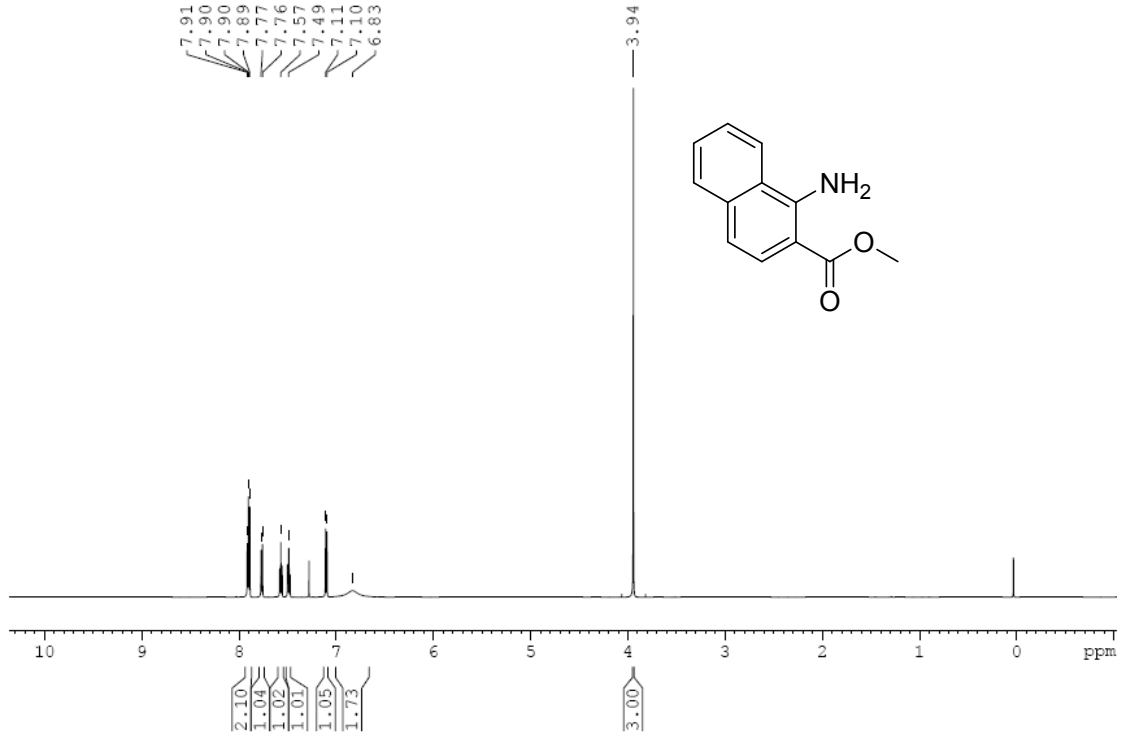
Exact Mass: 205.0766

err: 3.9 ppm

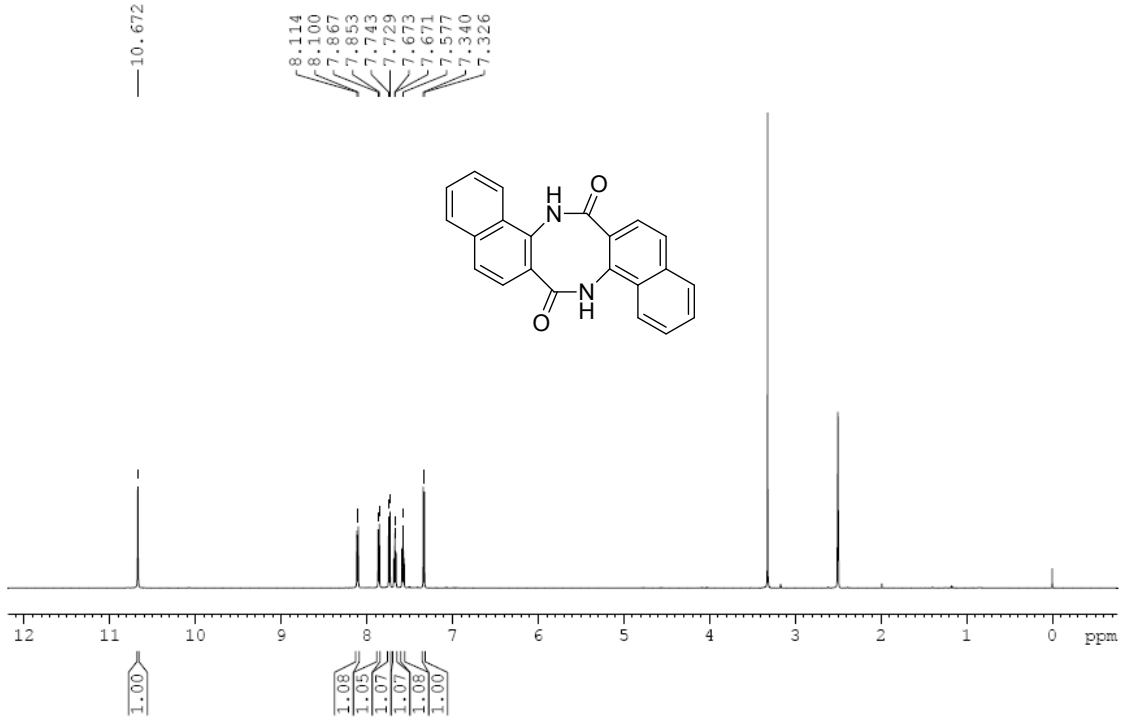


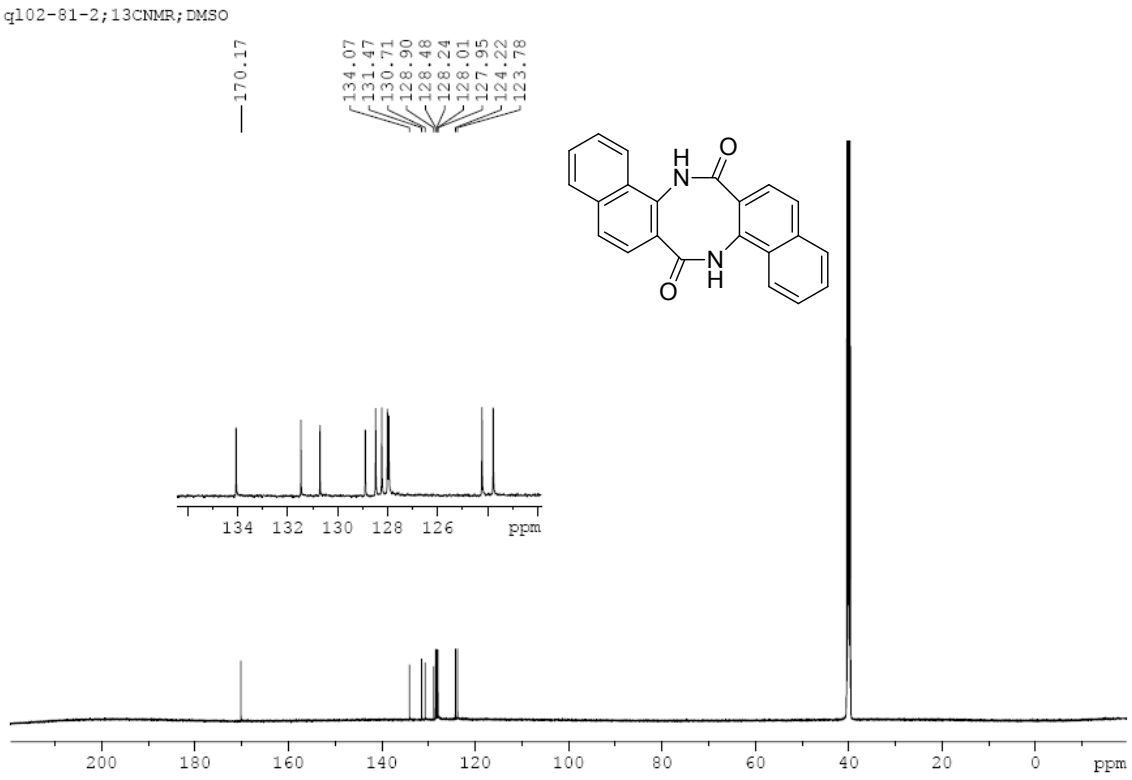
II

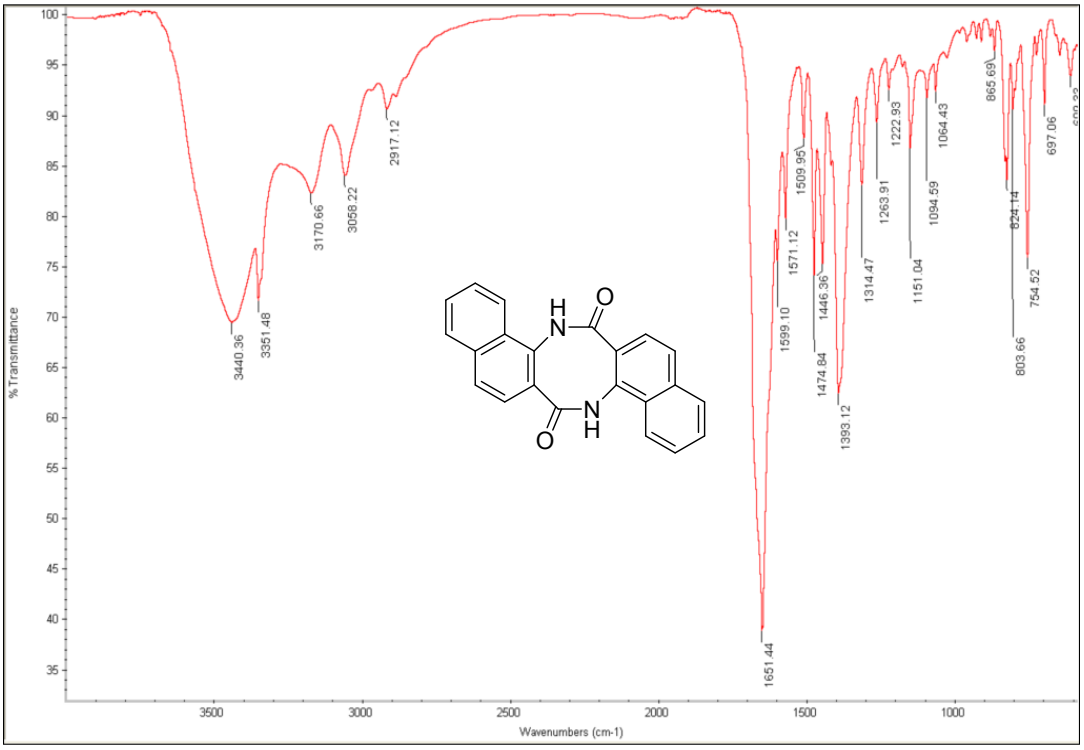
ql02-99;1HNMR;CDCl3



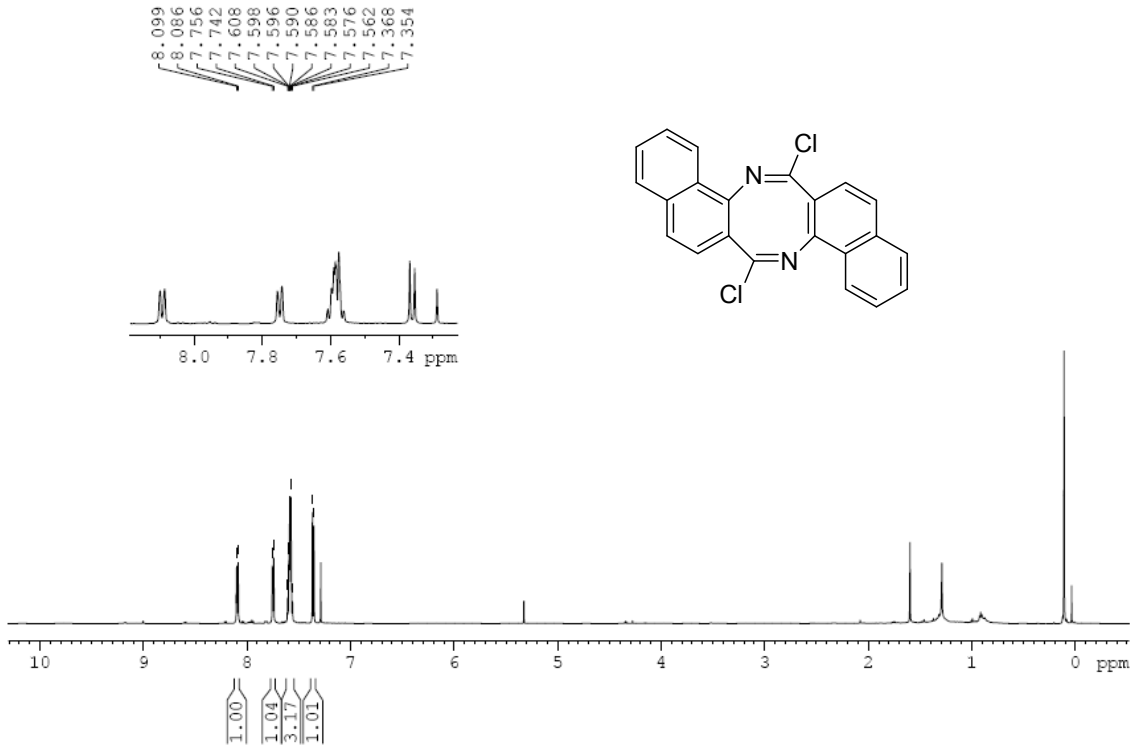
ql02-81-2;1HNMR;DMSO



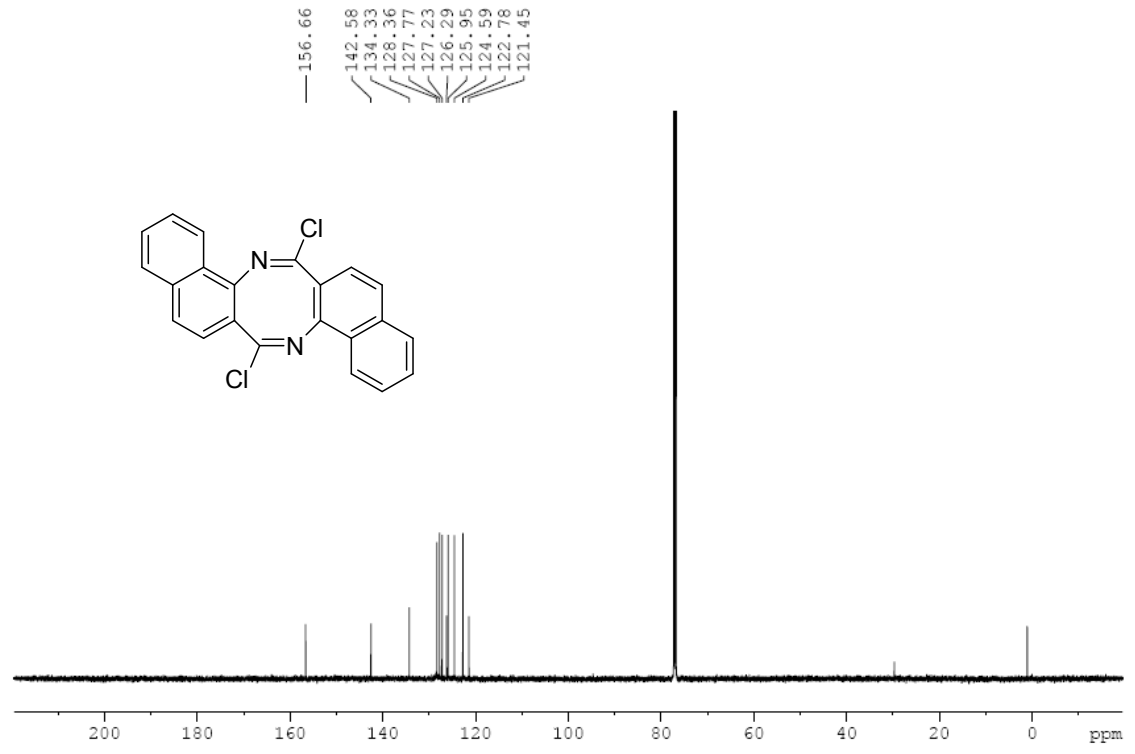

ql02-81-2;13CNMR;DMSO
170.17
134.07
131.47
130.71
128.90
128.48
128.24
128.01
127.95
124.22
123.78
134 132 130 128 126 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

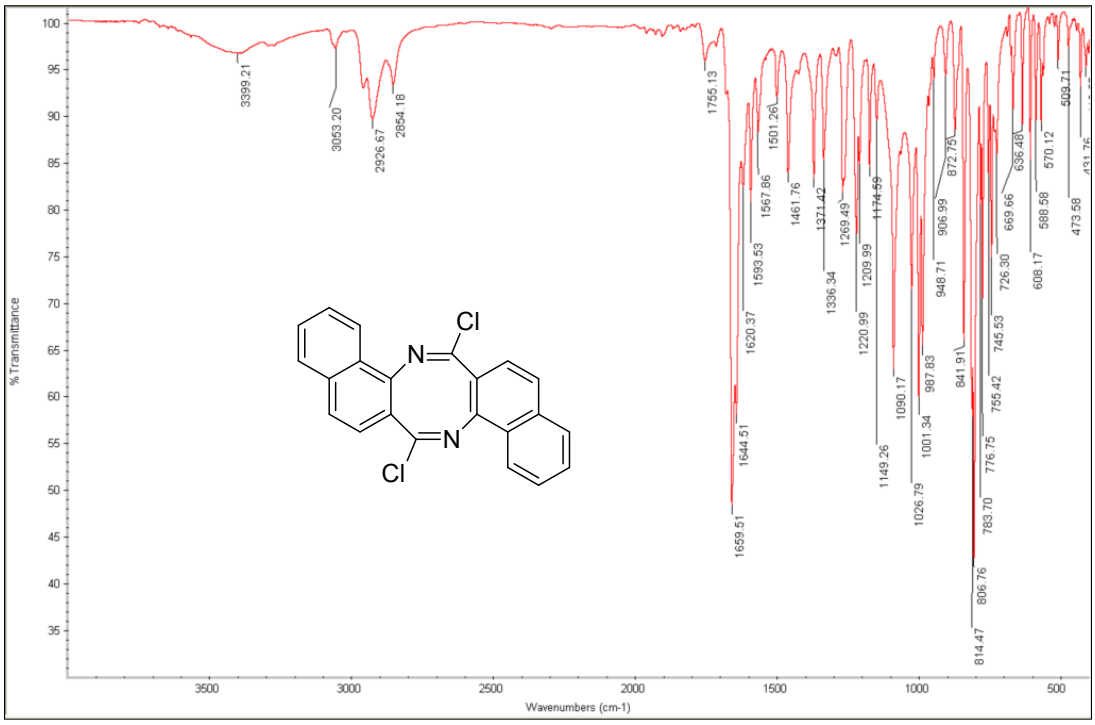

% Transmittance
3440.36
3351.48
3170.66
3058.22
2917.12
1651.44
1599.10
1571.12
1509.95
1474.84
1446.36
1393.12
1314.47
1263.91
1222.93
1151.04
1094.59
1064.43
865.69
824.14
803.66
754.52
697.06
Wavenumbers (cm-1)

ql04-06;1HNMR;CDCl3



ql04-06;13CNMR;CDCl3




%Transmittance
Wavenumbers (cm-1)
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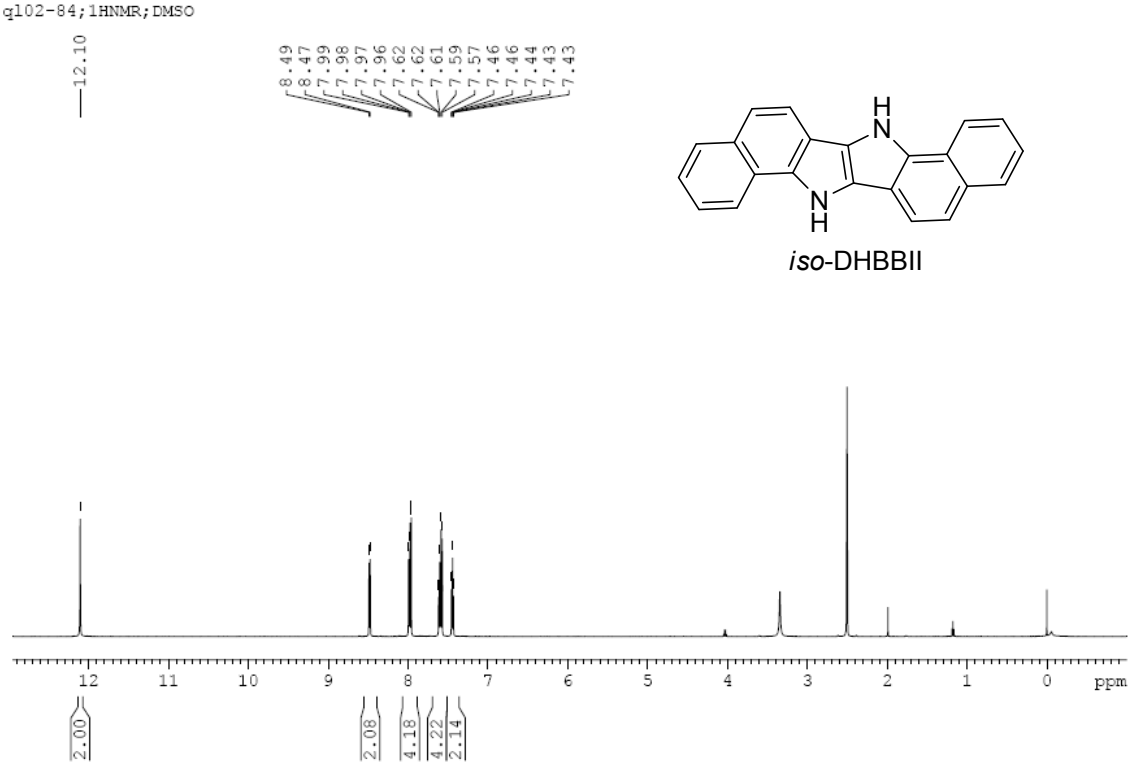
3053.20
2926.67
2854.18
1755.13
1659.51
1644.51
1620.37
1593.53
1567.86
1501.26
1461.76
1371.42
1336.34
1269.49
1220.99
1209.99
1174.59
1149.26
1090.17
1026.79
1001.34
987.83
948.71
906.99
872.75
841.91
814.47
806.76
783.70
776.75
755.42
745.53
726.30
669.66
636.48
608.17
588.58
570.12
509.71
473.58
Cl
N
N
Cl


q102-84;1HNMR;DMSO
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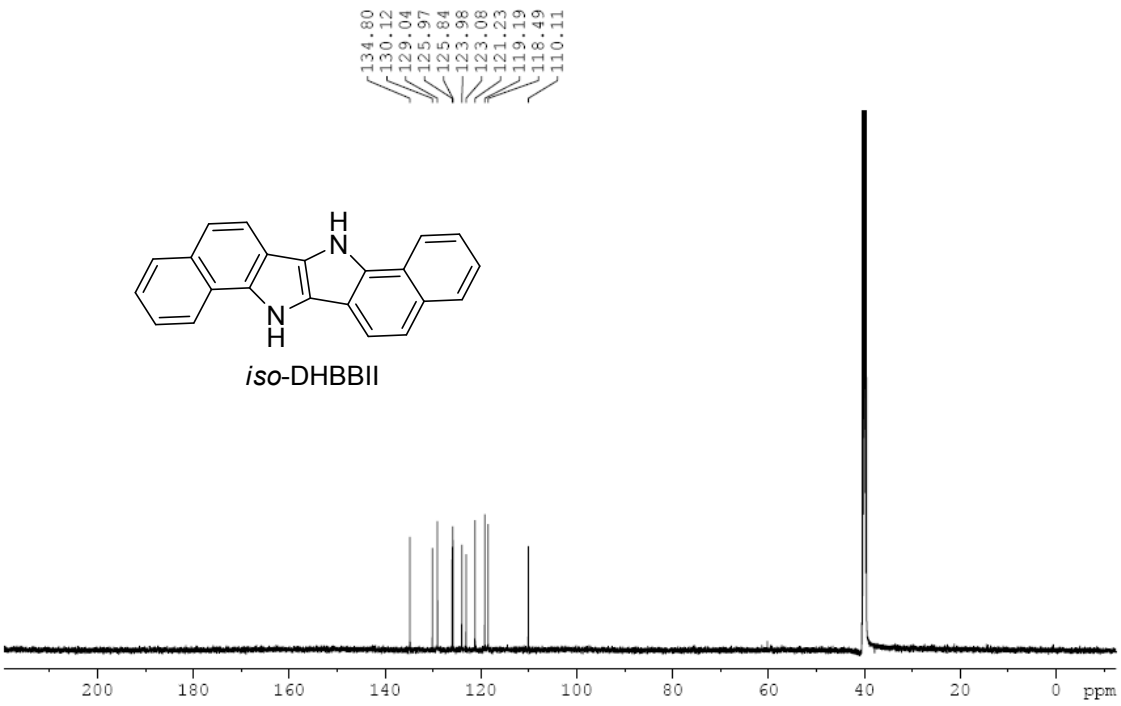
8.49
8.47
7.99
7.98
7.97
7.96
7.62
7.62
7.61
7.59
7.57
7.46
7.46
7.44
7.43
7.43
H
N
N
H
ppm
2.00
2.08
4.18
4.22
2.14

iso-DHBBII

ql02-84;13CNMR;DMSO



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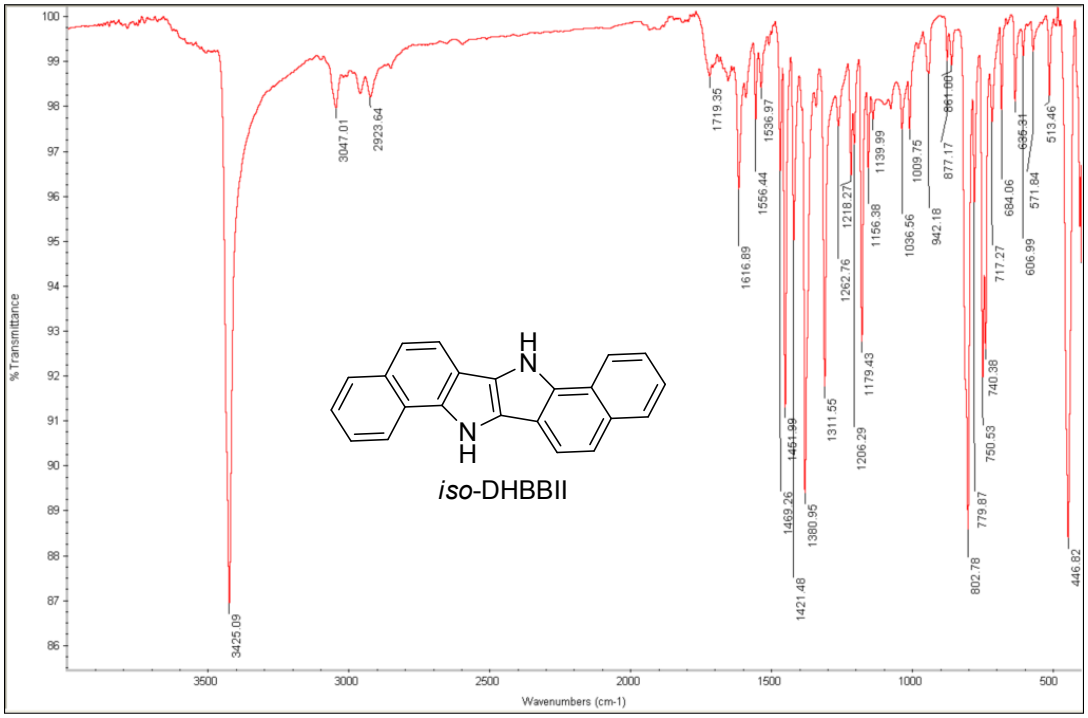

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