Electronic Supplementary Information

New Six- and Seven- Membered Ring Pyrrole-Pyridine Hydrogen Bond Systems Undergoing Excited-State Intramolecular Proton Transfer

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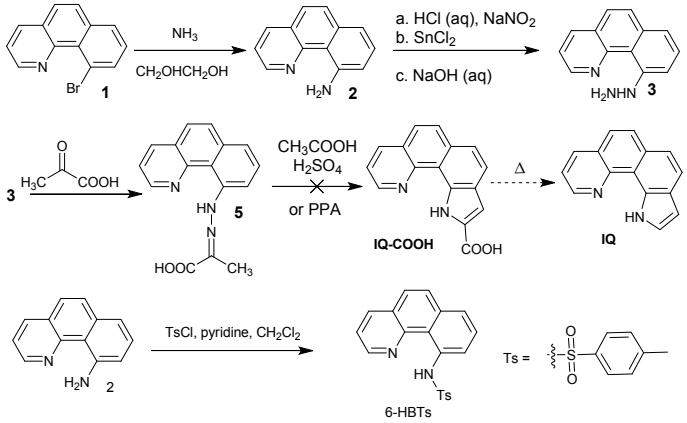
Materials, Characterization and Syntheses. All solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated glassic sheets (0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV light at 254 nm and 365 nm. Flash column chromatography was carried out using silica gel from Merck (230-400 mesh). The FT-IR spectra were recorded in the 4000–1000 cm^{-1} region by a Nicolet Magna II 550 FTIR spectrophotometer using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Unity 400 or Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, respectively. Low and high resolution mass spectra were recorded by Gas Chromatograph-Mass Spectrometer (Finnigan MAT TSQ-46C GC/MS/MS/ DS). The X-ray diffraction intensity data were collected at 293 K, 140 K or 133 K on a Rigaku RAXIS RAPID IP imaging plate system with MoKα radiation (λ = 0.71073 Å).



Scheme S1.Synthetic routes of **IQ** and **6-HBTs**.

Synthesis of 10-bromobenzo[h]quinoline (1). This compound was prepared by a literature procedure.[S1] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.09 (dd, J = 2.0, 2.4 Hz, 1H), 8.16 (dd, J = 2.0, 6.0 Hz, 1H), 8.09 (dd, J = 1.2, 6.4 Hz, 1H), 7.87 (dd, J = 1.2, 6.4 Hz, 1H), 7.77 (d, J = 8.4Hz, 1H), 7.70 (d, J = 8.8Hz, 1H), 7.57-7.54 (m, 1H), 7.45 (t, J = 7.6Hz, 1H).

Synthesis of benzo[h]quinolin-10-amine (2). Ammonia was passed into 70 mL of stirred reagent grade ethylene glycol at 0 °C until 5.27 g (310 mmol) of the gas was dissolved. To this solution, 10-bromobenzo[*h*]quinoline (**1**) (2.00 g, 7.75 mmol) and CuI (74 mg, 0.39 mmol) was added, and the solution was sealed in a Schlenk pressure

tube and heated to 100 °C for 15 h. Then the bomb was allowed to cool and the pressure was released. The resulting black solution was poured into water, and extracted with CH_2Cl_2. The combined organic layer was dried with anhydrous Na_2SO_4 and filtered. Then the solvent was evaporated under reduced pressure, and the residue was purified through a neutral alumina column (CH_2Cl_2: hexane, 1:1) to give a yellow solid product with 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 8.92 (dd, J = 1.6, 2.4 Hz, 1H), 8.34 (dd, J = 1.6, 6.4 Hz, 1H), 8.09 (br, 2H,-NH_2), 7.75-7.68 (m, 2H), 7.58 (dd, J = 4.8, 3.2 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 7.6Hz, 1H), 6.94 (dd, J = 1.2, 6.4 Hz, 1H). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ = 149.06, 148.87, 146.53, 135.61, 135.54, 129.09, 128.85, 126.24, 125.12, 119.98, 114.54, 113.88, 112.25.

Synthesis of 10-hydrazinylbenzo[h]quinoline (3). This compound was prepared by modification of a literature procedure.[S2] Benzo[*h*]quinolin-10-amine (**2**) (0.50 g, 2.57 mmol) dissolved in ethanol (20 mL) was added to Conc HCl (35 mL), and then another 60 mL of H_2O was added. At 0 °C, sodium nitrite (0.18 g, 2.57 mmol) in 10 mL of H_2O was added dropwise. After stirring for 10 h at 0 °C, the resulting brown solution was treated with $SnCl_2{\cdot}2H_2O$ (1.74 g, 2.57 mmol) dissolved in 5 mL conc. HCl. After stirring at 0 °C for 3 h, the resulting orangish-red solution was concentrated, basified with 10% aqueous NaOH at 0 °C under nitrogen atmosphere and extracted with degassed CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated to give thick yellow oil, which was used in the next step immediately without further purification because of oxygen-sensitive of hydrazine compounds.

Synthesis of 10-(2-cyclohexylidenehydrazinyl)benzo[h]quinoline (4). A mixture of 10-hydrazinylbenzo[*h*]quinoline (**3**) and cyclohexanone (0.26 g, 2.65 mmol) in absolute ethanol (15mL) was heated for 1-3 h. After cooling the yellow solution, first to room temperature, and then in the freezer, the resulting yellow crystals were collected by suction filtration, washed with cold ethanol (5-10 mL) and dried under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 13.85 (br, 1H), 8.88 (dd, J = 2.0, 2.8 Hz, 1H), 8.15 (dd, J = 2.0, 6.0 Hz, 1H), 7.93 (dd, J = 1.2, 6.8 Hz, 1H), 7.74 (d, J = 9.2 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.26

(dd, J = 0.8, 6.8 Hz, 1H), 2.71 (t, J = 6.4 Hz, 2H), 2.53 (t, J = 6.0 Hz, 2H), 1.84-1.75 (m, 4H), 1.72-1.67 (m, 2H).^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ = 148.90, 146.42, 145.82, 135.61, 129.63, 129.41, 127.06, 124.74, 119.54, 116.70, 113.95, 109.06, 35.26, 27.59, 27.16, 25.96, 25.91. MS (EI, 70 eV): m/z (relativeintensity) 289 (M^+, 100), HRMS calcd. for $C_{19}H_{19}N_3$ 289.1579, found 289.1576.

Synthesis of 10,11,12,13-tetrahydro-9H-quinolino[8,7-a]carbazole (6-HB). A solution of 10-(2-cyclohexylidenehydrazinyl)benzo[*h*]quinoline (**4**) (0.15 g 0.52 mmol) in 8 mL of polyphosphoric acid (PPA) was heated to 120 °C during which the temperature rose spontaneously to 150 °C. The mixture was held at 150 °C for 1 h, after which 200 mL of 40% sodium hydroxide solution was added, and the mixture was allowed to stand overnight. The resulting light-green precipitate was removed by filtration, washed with water, and dried. The crude was purified by column chromatography with aluminum oxide (elution with ether) to give 82 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 11.55 (S, 1H), 9.04 (dd, J = 1.2, 3.2 Hz, 1H), 8.22 (dd, J = 1.6, 6.4 Hz, 1H), 7.94 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.62-7.57 (m, 2H), 7.51-7.48 (m, 1H), 2.99 (t, J = 5.6 Hz, 2H), 2.88 (t, J = 6.4 Hz, 2H), 2.04-1.93 (m, 4H).^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ = 147.75, 135.54, 134.57, 131.67, 129.57, 129.03, 126.59, 125.77, 121.78, 120.22, 119.83, 118.80, 116.73, 110.72, 23.64, 23.49, 23.40, 21.13. MS (EI, 70 eV): m/z (relativeintensity) 272 (M^+, 100), HRMS calcd. for $C_{19}H_{16}N_2$ 272.1313, found 272.1309.

Synthesis of 13-methyl-10,11,12,13-tetrahydro-9H-quinolino[8,7-a]carbazole (6-NCH$_3$). NaH (60%, 0.15 g, 3.75 mmol) was added to a solution of 10,11,12,13-tetrahydro-9H-quinolino[8,7-a]carbazole (**6-HB**) (50 mg, 0.18 mmol) dissolved in dry THF (6 mL) at 0 °C under N_2. After 1.5 h, methyl iodide (0.5 mL) was added to the mixture and the solution was stirred at room temperature for 2 h. Then, the mixture was quenched with ice and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude product was purified by silica gel column chromatography with CH_2Cl_2/hexcene mixture as eluent to afford **6-NCH$_3$**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.00 (dd, J = 1.6, 2.4 Hz, 1H), 8.19 (dd, J = 1.6, 6.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 1.6, 6.8 Hz, 1H), 7.60-7.58 (m, 2H), 7.46-7.43 (m, 1H), 3.95 (s, 3H), 2.88-2.83 (m, 4H), 2.02-1.99 (m, 2H), 1.94-1.88 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.38, 145.09, 139.94, 135.17, 133.76, 131.02, 129.35, 128.53, 127.00, 122.02, 120.0, 119.53, 119.45, 111.29, 36.90, 30.87, 23.52, 23.29, 23.23, 21.15. MS (EI, 70 eV): m/z (relativeintensity) 272 (M^+, 100), HRMS calcd. for $C_{20}H_{18}N_2$ 286.1470, found 272.1366.

Synthesis of 2-(2-(1h-pyrrol-2-yl)cyclopent-1-en-1-yl)pyridine (7-HB). A solution of 1,2-dibromocyclopent-1-ene (0.30 g, 1.33 mmol)**,** 2-(tributylstannyl)pyridine[S3] (0.49 g, 1.33 mmol) and $Pd(PPh_3)_4$ (62 mg, 0.05 mmol) in toluene (100 mL) was stirred at 100 °C for 12 h under nitrogen to afford crude product (**7-PyBr).** Sequentially, a stirred mixture of crude **7-PyBr**, 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole[S4] (0.26 g, 1.33 mmol), $Pd(PPh_3)_4$ (62 mg, 0.05 mmol) and Na_2CO_3 (1.33 mL, 2M, 2.66 mmol) in toluene/ ethanol (50:5 mL) under nitrogen was heated at 100 °C for 12 h, and then the solvent was evaporated under vacuum. The residue was extracted sequentially with water (10 mL), CH_2Cl_2 (3 × 10 mL), dried ($MgSO_4$) and evaporated under vacuum. The crude product was purified by flash chromatography eluting with 1:4 EtOAc/hexane to afford **7-HB** (132 mg, 32 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 13.96 (br, 1H), 8.63 (d, J = 4.4 Hz, 1H), 7.75-7.71(m, 1H), 7.37 (d, J = 8 Hz, 1H), 7.18-7.15 (m, 1H), 6.94 (s, 1H), 6.41 (d, J = 1.6 Hz, 1H), 6.27 (s, 1H), 3.08 (t, J = 8 Hz, 2H), 2.99 (t, J = 7.2 Hz, 2H), 2.04-1.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 154.94, 146.42,137.55,129.65, 126.97,122.98, 120.66, 119.08, 110.96, 109.14, 38.37, 37.80, 21.96. MS (EI, 70eV): m/z (relative intensity) 210 (M^+, 100), HRMS calcd. for $C_{14}H_{14}N_2$ 210.1157, found 210.1154.

Synthesis of 2-(2-(1-methyl-1H-pyrrol-2-yl)cyclopent-1-en-1-yl)pyridine (7-NCH_3). A solution of 1,2-dibromocyclopent-1-ene (0.30 g, 1.33 mmol)**,** 2-(tributylstannyl)pyridine[S3] (0.49 g, 1.33 mmol) and $Pd(PPh_3)_4$ (62 mg, 0.05 mmol) in toluene (100 mL) was stirred at 100 °C for 12 h under nitrogen to prepare crude product (**7-PyBr).** Then, a solution of 1-methyl-2-(tributylstannyl)-1H-pyrrole[S5] (0.49 g, 1.33 mmol) in toluene was added to the mixture, and the mixture was stirred at 100 °C for another 12 h. The solvent was evaporated under vacuum, and the residue was purified by flash chromatography eluting with 1:5 EtOAc/hexane to afford **7-NCH_3** (83 mg, 28 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 8.54 (dd, J = 4,

0.8 Hz, 1H), 7.41-7.38 (m, 1H), 7.03-7.01 (m, 1H), 6.72 (d, J = 8 Hz, 1H), 6.56-6.55 (m, 1H), 6.16-6.14 (m, 1H), 6.08 (dd, J = 3.6, 2 Hz, 1H), 3.09-3.04 (m, 5H), 3.01-2.80 (m, 2H), 2.07-1.71 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 156.73, 149.02, 139.53, 135.57, 133.75, 130.48, 122.43, 122.35, 121.08, 107.98, 107.88, 40.78, 36.28, 34.07, 22.09. MS (EI, 70eV): m/z (relative intensity) 224 (M^+, 100), HRMS calcd. for $C_{15}H_{16}N_2$ 224.1313, found 224.1317.

Synthesis of 2-(2-(benzo[h]quinolin-10-yl)hydrazono)propanoic acid (5). A solution of sodium acetate (0.50 g, 5.68 mmol) in degassed water (10 mL) and pyruvic acid (0.27 g, 3.08 mmol) was added all at once to a solution of 10-Hydrazinylbenzo[*h*]quinoline (**3**) (0.50 g, 2.58 mmol) in degassed isopropyl alcohol (10 mL), after which the mixture was refluxed for 1 h. It was then cooled, and the resulting precipitate was removed by filtration. Recrystallization from methanol gave **5** as a brown solid. Yield: 233 mg, 35%. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 14.50 (S, 1H), 9.02 (d, J = 3.2 Hz, 1H), 8.49 (dd, J = 1.6, 6.4 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H), 7.92-7.82 (m, 2H), 7.72-7.68 (m, 2H), 7.56 (d, J = 7.6 Hz, 1H), 2.29 (S, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 166.16, 147.23, 146.99, 143.69, 136.81, 135.08, 129.12, 128.90, 127.08, 125.64, 121.06, 120.00, 114.40, 110.55, 12.08.

Synthesis of N-(benzo[h]quinolin-10-yl)-4-methylbenzenesulfonamide (6-HBTs). Pyridine (0.23 mL, 2.8 mmol) and TsCl (100 mg, 0.53 mmol) were sequentialy added to a solution of benzo[*h*]quinolin-10-amine (**2**) (90 mg, 0.46 mmol) in dry CH_2Cl_2 (10 mL) at under N_2, and the mixture was stirred at room temperature over night. The solution was removed under reduced pressure, and the residue was washed with ethanol to give the pure compound. Yield: 133 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 15.22 (br, 1H), 8.97 (dd, J = 1.6, 2.8 Hz, 1H), 8.23 (dd, J = 1.6, 6.4 Hz, 1H), 7.90 (dd, J = 2.0, 5.1 Hz, 1H), 7.77 (d, J = 8.3, 2H), 7.73 (d, J = 8.8 Hz, 1H), 7.62-7.50 (m, 4H), 7.07 (d, J = 8.1 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 152.30, 151.02, 146.46, 137.62, 134.50, 130.54, 129.27, 128.16, 119.67, 116.31, 22.50. MS (EI, 70 eV): m/z (relative intensity) 224 (M^+, 100), HRMS calcd. for $C_{20}H_{16}N_2O_2S$ 348.0932, found 348.0927.

N-H deuterated 6-HB and 7-HB (6-DB and 7-DB). **6-DB** or **7-DB** was prepared by dissolving **6-DB** or **7-DB** in CH_3OD. CH_3OD was then gradually evaporated in the

vacuum line. This process was repeated several times. The formation of **6-DB** or **7-DB** was checked by proton NMR where ~92% of the N-H proton disappeared after deuteration.

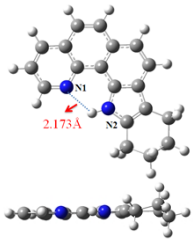
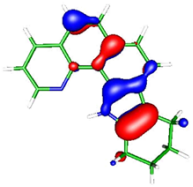
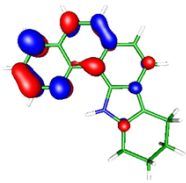
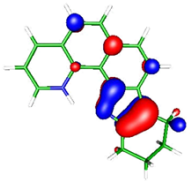
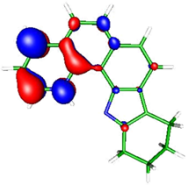
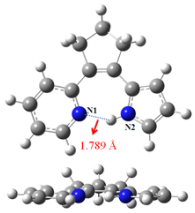
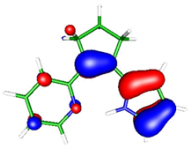
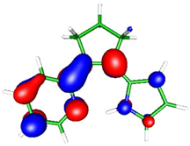
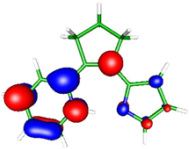
Spectroscopic and Dynamic Measurements

Steady-state absorption and emission spectra were recorded by a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. Detailed time-resolved spectroscopic measurements were reported previously elsewhere.[S6] In brief, nanosecond time-resolved studies were performed by an Edinburgh FL 900 time-correlated single photon-counting (TCSPC) system with a pulsed hydrogen- /or nitrogen-filled lamp as the excitation light source. Data were fitted with sum of exponential functions using the nonlinear least-squares procedure in combination with the convolution method.

The femtosecond fluorescence up-conversion (FOG100, CDP) was utilized to study ultrafast dynamics of the titled compounds. The excitation light source was generated from the same femtosecond oscillator. The cross correlation (instrument response function) obtained from the Raman scattering signal showed a full width at half-maximum (FWHM) of ~180 fs and therefore a temporal resolution of ~ 130 fs after deconvolution could be obtained. The polarization of the excitation laser pulses was set parallel, vertical, or at the magic angle (54.7°) by a λ/2 waveplate with respect to the detection polarization direction for ultrafast anisotropic measurement or anisotropy-free fluorescence decay.

Computational Methodology. The geometries of the singlet ground states were optimized by the density functional theory (DFT) method and the excited-state structures and related optical properties of all molecules were calculated with time-dependent density functional theory (TDDFT) methodology with a CAM-B3LYP hybrid function in combination with a polarizable continuum model (PCM) in cyclohexane. The 6-31+G(d,p) basis set was employed for all atoms.

Table S1. Calculated optimized structures and frontier orbitals for **6-HB** and **7-HB** of normal and tautomer form involved in the first singlet excitation[a]

Normal form			Tautomer form	
Optimized structure	HOMO	LUMO	HOMO	LUMO
				
				

[a] CAM-B3LYP/6-31+G(d,p)

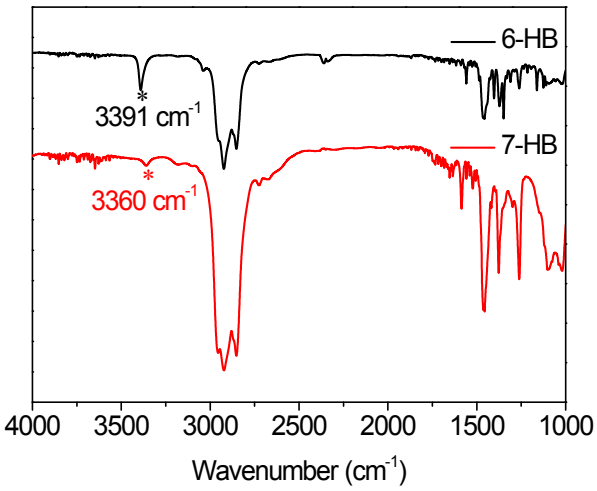


Fig. S1 FT-IR spectrum of **6-HB** and **7-HB**. The starred "*" signals are attributed to the NH stretching vibrations.

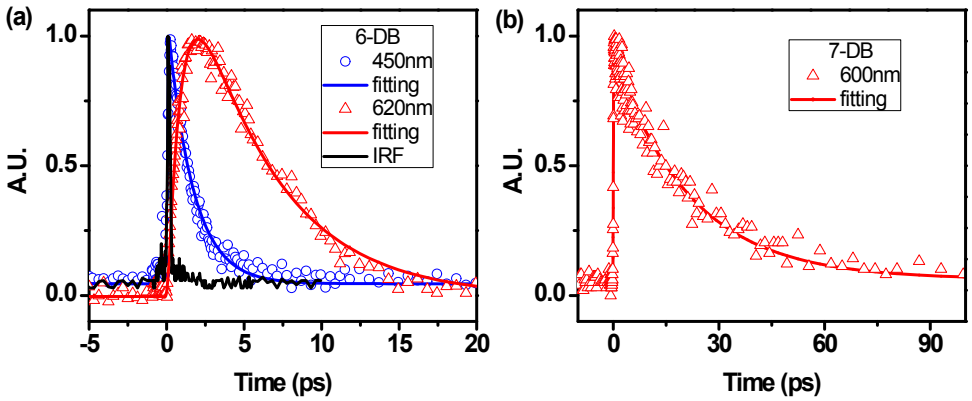


Fig. S2 The femtosecond time-resolved fluorescence spectra of (a) **6-DB**, and (b) **7-DB** in cyclohexane at 295 K.

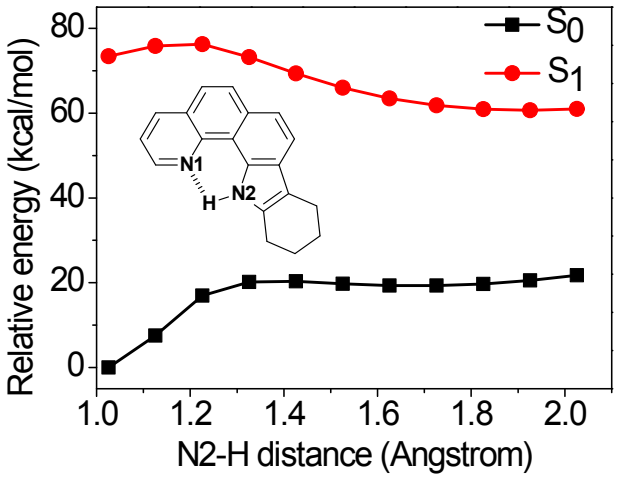


Fig. S3 Calculated potential energy diagram for the S_0 and S_1 states of **6-HB** with fixed N2-H distance.

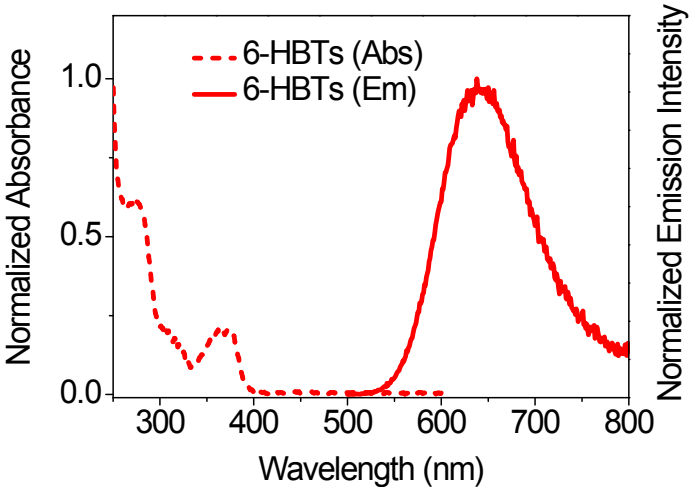


Fig. S4 The absorption and emission spectra of **6-HBTs** in cyclohexane at 293 K.

Table S2. Crystal data and structure refinement for compounds **6-HB** and **6-HBTs**

	6-HB	**6-HBTs**
CCDC NO.	1013476	1013475
Empirical formula	C19 H16N2	C20H16N2O2S
Formula weight	272.34	348.41
Temperature	150(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
Unit cell dimensions	a = 7.2642(8) Å α= 90° c = 15.7830(16) Å β= 98.804(3)° b = 11.9445(12) Å γ = 90°	a = 7.2225(5) Å α= 90° b = 8.1395(6) Å β= 91.373(2)° c = 27.359(2) Å γ = 90°
Volume	1353.3(2) $Å^3$	1607.9(2) $Å^3$
Z	4	4
Density (calculated)	1.337 mg/m^3	1.439 mg/m^3
Absorption coefficient	0.079 mm^{-1}	0.218 mm^{-1}
F(000)	576	728
Crystal size	0.25 x 0.14 x 0.07 mm^3	0.55 x 0.22 x 0.12 mm^3
Theta range for data collection	2.15 to 27.50°	2.61 to 27.50°
Index ranges	-9 ≤ h ≤ 9, -15 ≤ k ≤ 14, -20 ≤ l ≤ 18	-8 ≤ h ≤ 9, -10 ≤ k ≤ 10, -35 ≤ l ≤ 35
Reflections collected	8950	11985
Independent reflections	3119 [R(int) = 0.0675]	3696 [R(int) = 0.0287]
Completeness to theta = 27.50°	99.9%	100.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9945 and 0.9805	0.9743 and 0.8895
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3119 / 0 / 194	3696 / 0 / 231
Goodness-of-fit on F^2	1.095	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0692, wR2 = 0.1311	R1 = 0.0445, wR2 = 0.1089
R indices (all data)	R1 = 0.1157, wR2 = 0.1487	R1 = 0.0541, wR2 = 0.1141
Largest diff. peak and hole	0.264 and -0.227 $e.Å^{-3}$	0.316 and -0.317 $e.Å^{-3}$

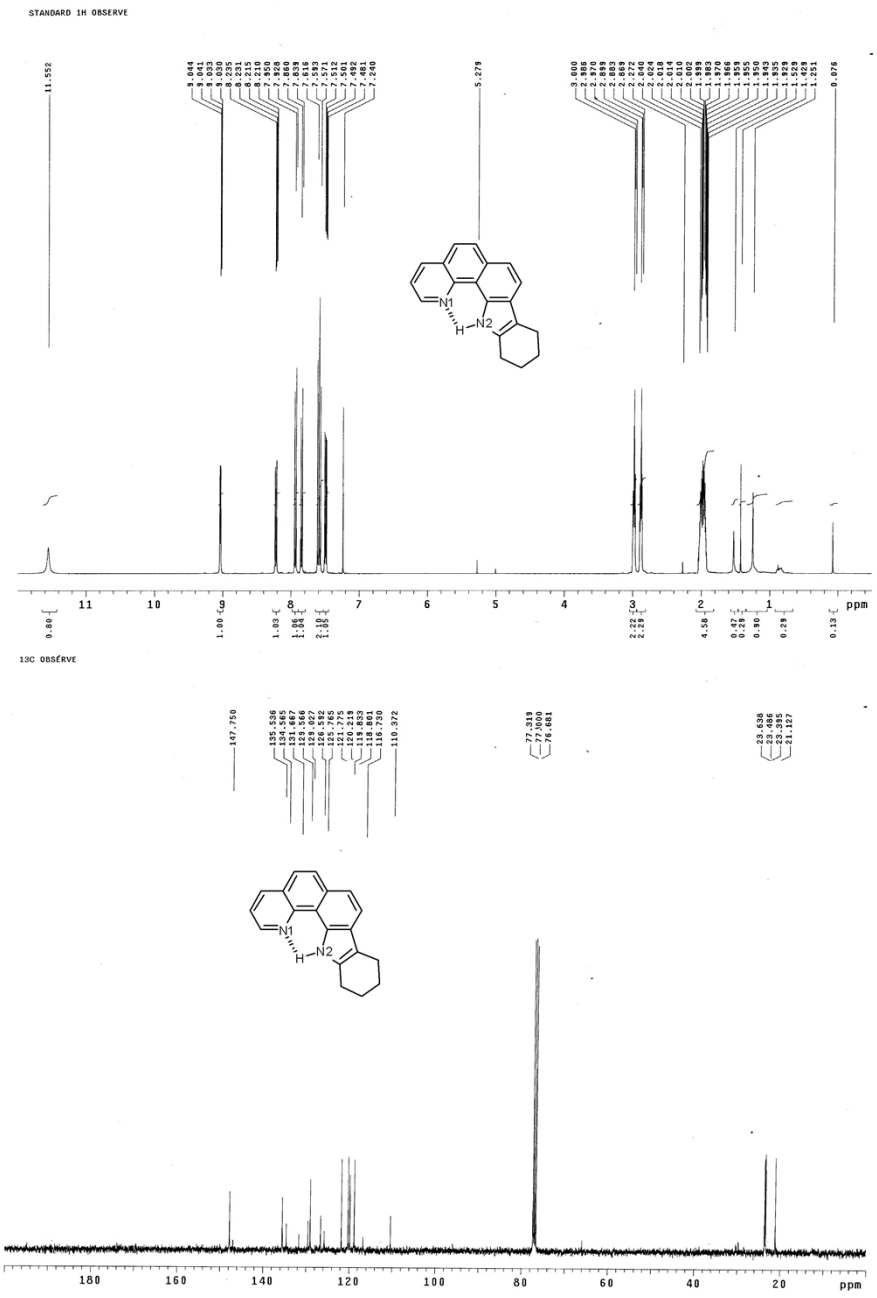


Fig. S5 ^{1}H NMR and ^{13}C NMR spectra of **6-HB**.

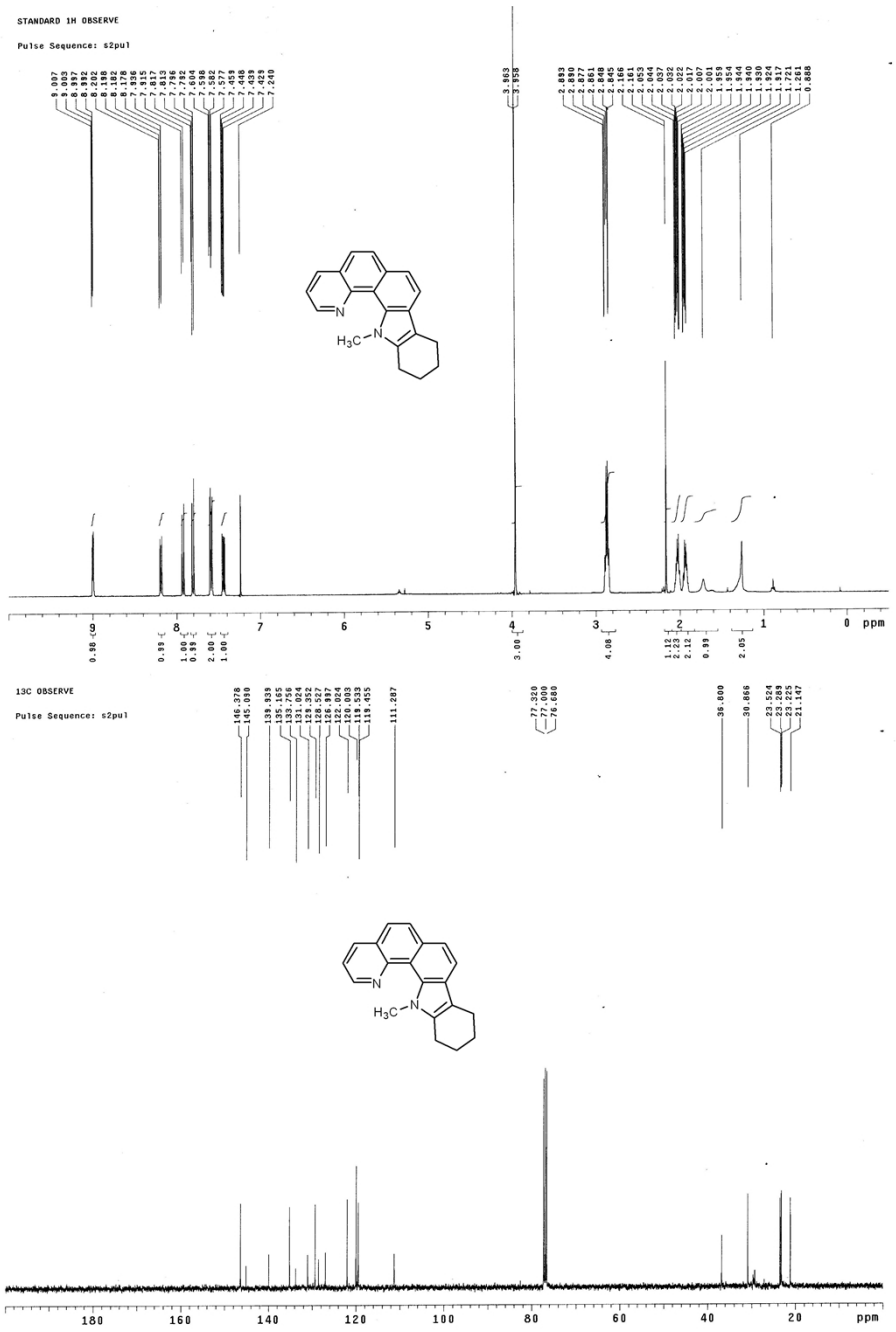


Fig. S6 ^{1}H NMR and ^{13}C NMR spectra of **6-NCH$_3$**.

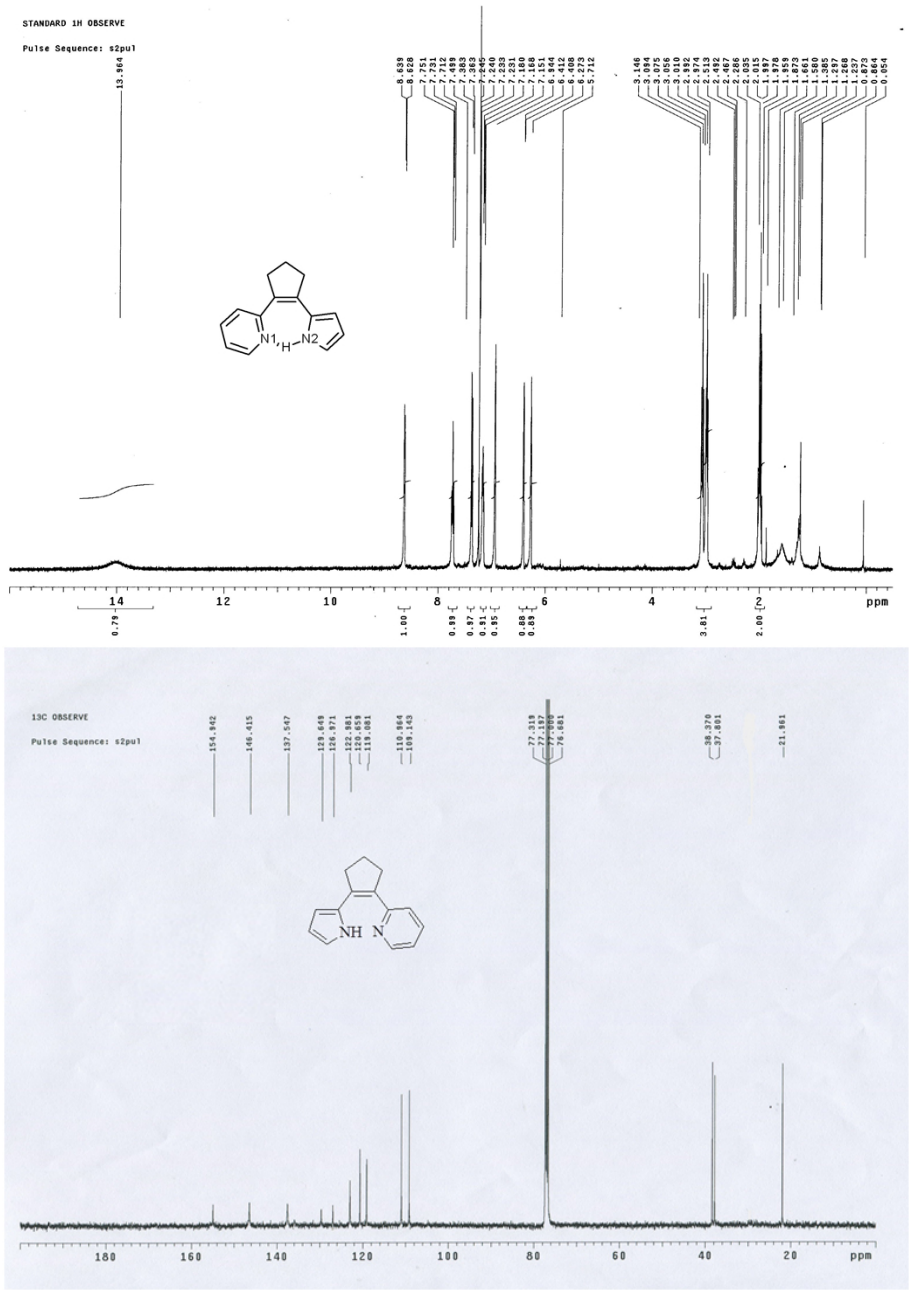


Fig. S7 ^{1}H NMR and ^{13}C NMR spectra of **7-HB**.

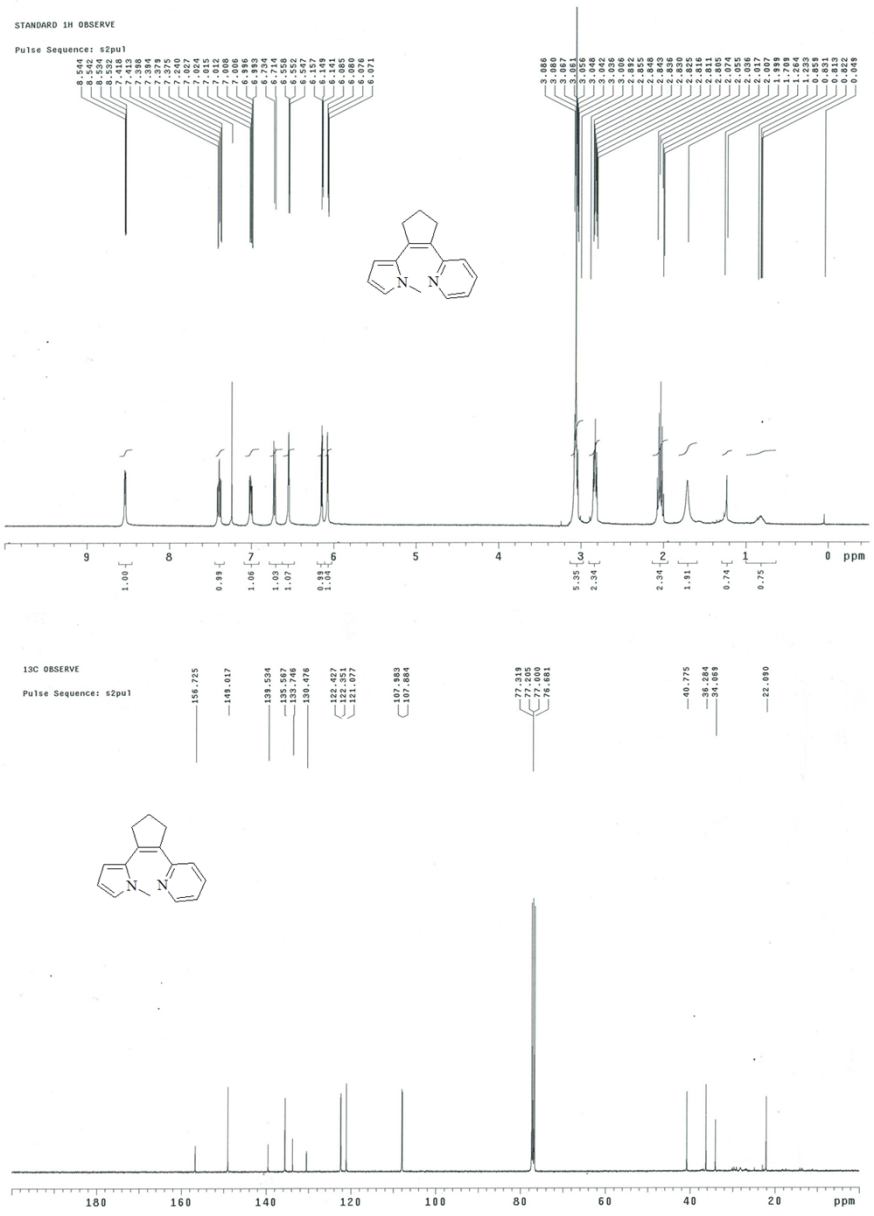


Fig. S8 ^{1}H NMR and ^{13}C NMR spectra of **7-NCH$_3$**.

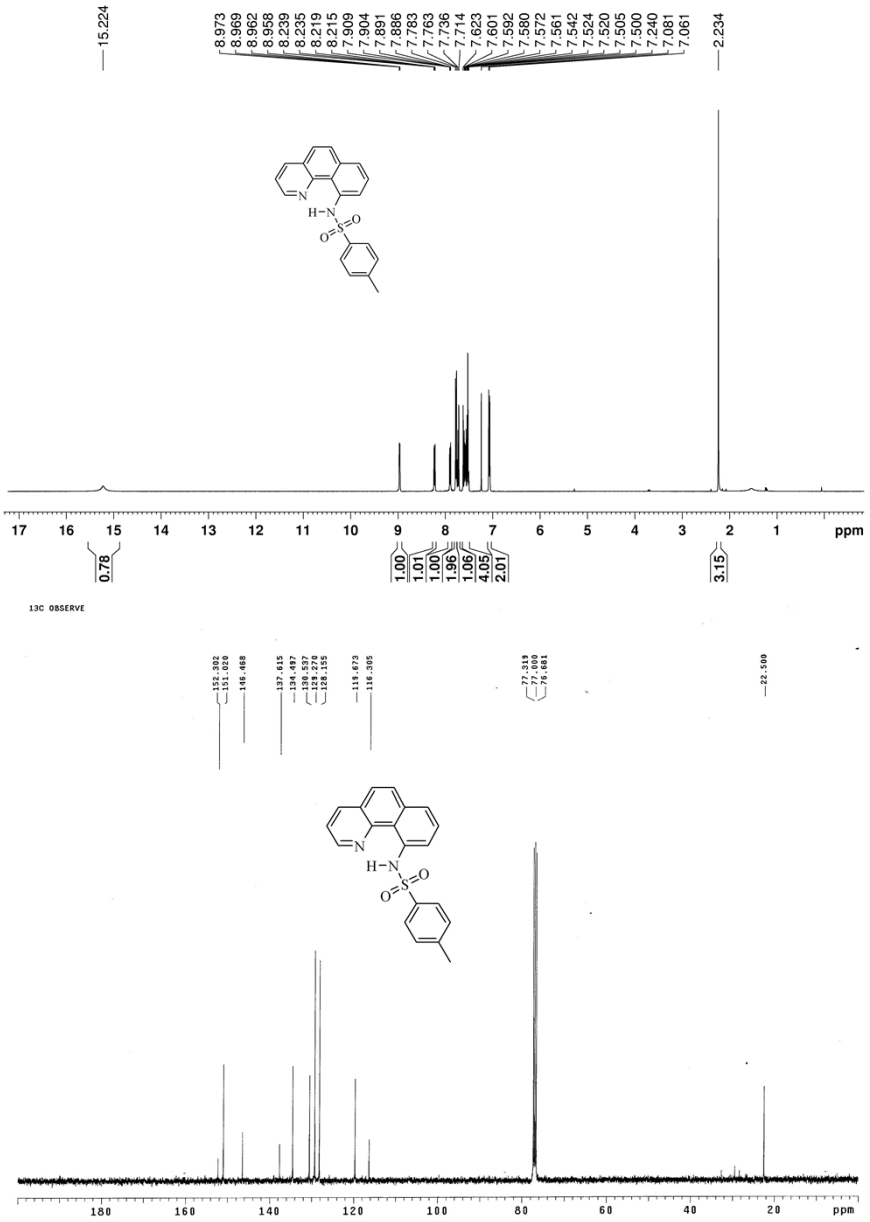


Fig. S9 ^{1}H NMR and ^{13}C NMR spectra of **6-HBTs**.

References:

S1 M. Weimar, R. Correa da Costa, F.-H. Lee, M. J. Fuchter, *Org. Lett.,* **2013**, *15*,1706–1709.

S2 V. Hegde, P. Madhukar, J. D. Madura, R. P. Thummel, *J. Am. Chem. Soc.* **1990**, *112*, 4549-4550.

S3 M. Iwao, T. Takeuchi, N. Fujikawa, T. Fukuda, F. Ishibashi, *Tetrahedron Letters*, **2003**, 44, 4443-4446.

S4 T. Hoang, M. Humbert-Droz, T. Dutronc,L, Guenee, C. Besnard, C. Piguet, *Inorg.*

Chem., **2013**, 52, 5570-5580.

S5 J. Takagi, K. Sato, J. Hartwig, T. Ishiyama, N. Miyaura,*Tetrahedron Letters*, **2002**, 43, 5649-5651.

S6 P.-T. Chou, S.-C. Pu, Y.-M. Cheng, W.-S. Yu, Y.-C. Yu, F.-T. Hung, W.-P. Hu, *J. Phys. Chem. A* **2005,** *109*, 3777-3787.