Electronic Supplementary Information

Conformationally flexible heterohelicenes as stimuli-controlled soft molecular springs

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1. Materials, Methods and Instrumentation

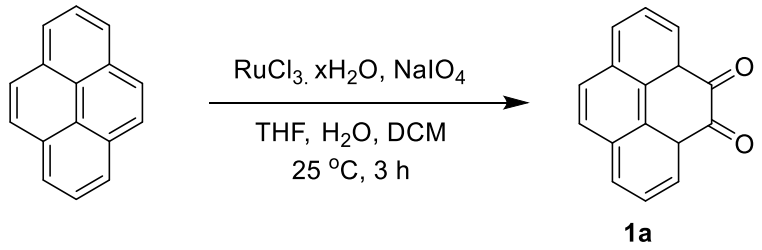
Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents, $RhCl_3.xH_2O$ and other chemicals were purchased from Aldrich. $[Cp^*RhCl_2]_2$ was synthesized according to the reported procedure.[S1]

^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded on Bruker AVANCE III 400, 500 and 700 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard ($CHCl_3$: δ = 7.26 ppm for ^1H spectra, 77.2 ppm for $^{13}C\{^1H\}$ spectra; CH_3CN: δ = 1.94 ppm for ^1H spectra, 1.3 ppm for $^{13}C\{^1H\}$ spectra; DMSO: 2.50 ppm for ^1H spectra, 39.5 ppm for $^{13}C\{^1H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for ^1H–^1H couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet). ESI mass spectroscopy was performed on a Bruker microTOF QII spectrometer instrument. For sample preparation, acetonitrile was used as a solvent for cationic heterohelicenes molecules. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II/Bruker D8 VENTURE PHOTON 100 diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at low temperatures. Data reduction was performed by Bruker Apex II software Suite and the crystal structure was solved by Intrinsic Phasing using the ShelXT program[S2] All structures were refined by the full-matrix least-squares (L.S) method using ShelXL present in the Olex2 software (version 1.3.0). The crystal images were created using Mercury 2020.3.0 program."

Steady-state absorption spectra were recorded on Cary 100 UV-vis spectrophotometer. All steady-state fluorescence measurements were performed on HORIBA Jobin Yvon Fluorolog spectrofluorometer (Fluorolog-3-21). Time-resolved fluorescence spectroscopy was carried out using time-correlated single-photon counting (TCSPC) spectrometer (Delta Flex-01-DD/HORIBA).

2. Synthesis of Sub-Expanded Heterohelicene Precursors

Pyrene-4,5-dione (1a)[S3]

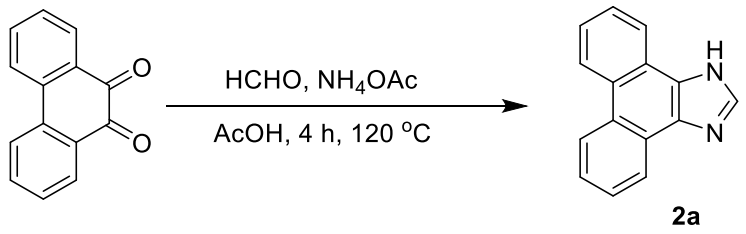


Scheme S1. Synthesis of Pyrene-4,5-dione (**1a)**

Pyrene (10.0 mmol) was dissolved in a mixture of CH_2Cl_2 (40 mL) and THF (40 mL). To it, $NaIO_4$ (44.5 mmol), H_2O (50 mL) and $RuCl_3 \cdot 3H_2O$ (1.0 mmol) were added and stirred at room temperature for 3 h. Next, the dark brown reaction mixture was poured into H_2O (400 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). Finally, all organic layers were mixed and washed with H_2O (3 x 200 mL) to give a dark orange solution. The solvent was removed under reduced pressure, and the crude mixture was subjected to column chromatography (silica gel, in $CHCl_3$) to isolate the desired product as a dark orange solid. Yield = 40 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 7.5 Hz, 2H), 8.18 (d, J = 7.9 Hz, 2H), 7.85 (s, 2H), 7.76 (t, J = 7.7 Hz, 2H).

1H-phenanthro[9,10-*d*]imidazole (2a)[S4]



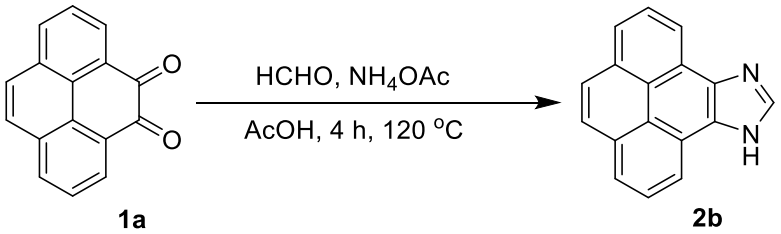
Scheme S2. Synthesis of 1H-phenanthro[9,10-*d*]imidazole (**2a**)

A mixture of 9,10-phenanthrenequinone (9.6 mmol), formaldehyde (1.6 mL, 37 wt %), glacial acetic acid (38 mL), and ammonium acetate (198 mmol) were taken in a 100 mL round bottom flask and refluxed for 5 h. After cooling the reaction mixture to room temperature, water (60 mL) was added to the reaction mixture and neutralized with aqueous ammonia (28-30% wt) to pH 7-8, and immediately white precipitate came. The precipitate was filtered washed with

water, acetone and ethyl ether to yield the desired product as an off-white powder. Yield = 97%.

^{1}H NMR (500 MHz, DMSO-d_6) δ 13.41 (s, 1H), 8.84 (dd, J = 18.6, 8.1 Hz, 2H), 8.52 (d, J = 7.8 Hz, 1H), 8.35 (d, J = 7.8 Hz, 1H), 8.31 (s, 1H), 7.71 (q, J = 7.2 Hz, 2H), 7.62 (q, J = 8.1 Hz, 2H).

9H-pyreno[4,5-*d*]imidazole(2b)[S5]

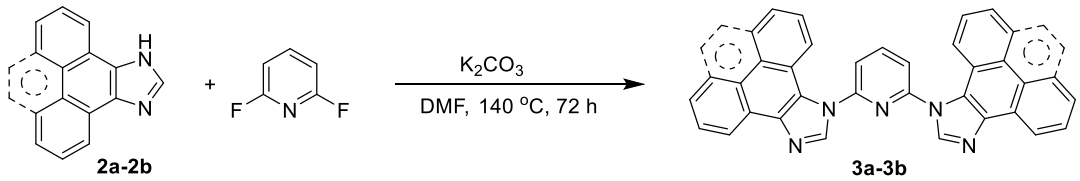


Scheme S3. Synthesis of 9H-pyreno[4,5-*d*]imidazole (**2b**)

A mixture of pyrene-4,5-dione (2.15 mmol) and ammonium acetate (43 mmol) was taken in 15 mL glacial acetic acid, and formaldehyde (0.2 mL of a 37% aqueous solution, 2.7 mmol) solution was added to it. Then, the reaction mixture was refluxed for 12 h. After cooling, water (30 mL) was added to the reaction mixture and neutralized with aqueous ammonia (28-30%) solution slowly and immediately, an off-white precipitate came. The precipitate was filtered, washed with water, methanol and ethyl ether and dried to get the desired product as an off-white powder. Yield = 93%.

^{1}H NMR (500 MHz, DMSO-d_6) δ 13.67 (s, 1H), 8.77 (s, 1H), 8.63 (s, 1H), 8.44 (s, 1H), 8.23 (d, J = 7.5 Hz, 2H), 8.19 (s, 2H), 8.12 (t, J = 7.6 Hz, 2H).

Synthesis of heterohelicene precursor n-Pybim1 and n-Pybim1



Scheme S4. Synthesis of **n-Pybim1 and n-Pybim1**

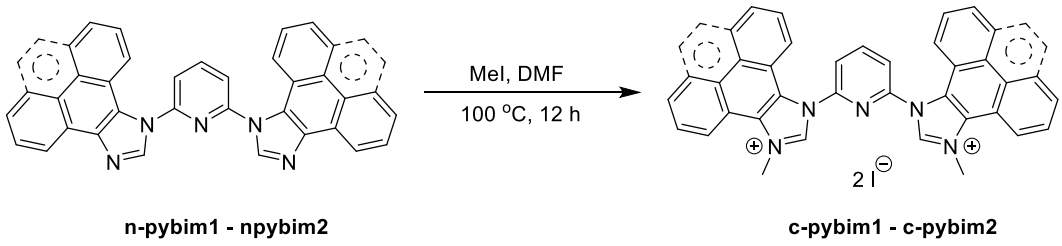
A mixture of 2,6-difluoropyridine (1.0 mmol), substituted imidazole (**2a** or **2b**) (3.0 mmol) and K_2CO_3 (6.0 mmol) was taken in a sealed tube. To it, 4 mL dry DMF was added and heated at 140 °C with stirring for 72 h. After that, the reaction mixture was cooled to room temperature,

and water (40 ml) was added. The reaction mixture was extracted with CH_2Cl_2 (40 mL x 2) by solvent extraction procedure. The combined CH_2Cl_2 layer was collected and concentrated under reduced pressure. The resulting crude product was subjected to column chromatography (silica gel, 1-5% MeOH in $CHCl_3$) to get the pure product as a white powder.

2,6-bis(1H-phenanthro[9,10-*d*]imidazol-1-yl)pyridine(n-Pybim1): 286 mg, 56% yield. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.92 (d, J = 8.4 Hz, 2H), 8.87 (d, J = 8.3 Hz, 2H), 8.66 (s, 3H), 8.61 (dd, J = 8.0, 1.5 Hz, 2H), 8.27 (d, J = 7.9 Hz, 2H), 7.76 (t, J = 7.5 Hz, 2H), 7.68 (m, 4H), 7.60 (ddd, J = 8.3, 7.0, 1.3 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 149.6, 143.7, 143.0, 137.7, 128.5, 127.9, 127.5, 126.7, 126.6, 126.0, 125.7, 125.1, 124.5, 123.7, 122.1, 122.1, 121.9, 121.8. **HRMS** (ESI, positive ion): $[M+H]^+$ = 512.1900 (calculated = 512.1870 for $[C_{35}H_{22}N_5]^+$).

2,6-bis(9H-pyreno[4,5-d]imidazol-9-yl)pyridine(n-Pybim2): 298 mg, 53% yield. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.87 (d, J = 1.2 Hz, 1H), 8.86 (d, J = 1.2 Hz, 1H), 8.84 (s, 2H), 8.74 (d, J = 7.8 Hz, 1H), 8.40 (d, J = 7.8 Hz, 2H), 8.31 (d, J = 1.3 Hz, 1H), 8.30 (d, J = 1.2 Hz, 1H), 8.25 – 8.16 (m, 8H), 8.02 (d, J = 7.9 Hz, 2H), 7.76 (t, J = 7.8 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO) δ 149.6, 143.7, 143.3, 138.2, 131.7, 131.3, 127.8, 127.7, 126.7, 125.8, 125.7, 125.7, 124.8, 124.8, 122.4, 122.4, 122.0, 121.2, 119.3, 119.1. **HRMS** (ESI, positive ion): $[M+H]^+$ = 560.1861 (calculated = 560.1870 for $[C_{39}H_{22}N_5]^+$).

Synthesis of cationic nanographene precursor c-Pybim1 and c-Pybim2



Scheme S5. Synthesis of **Pybim1-Pybim2**

To a solution of **n-Pybim1**/**n-Pybim2** (0.5 mmol) in 2 mL DMF, MeI (5 mmol) was added. Then, the solution was stirred at 100 °C under N_2 atmosphere for 12 h. After cooling the reaction mixture to room temperature, dry THF (10 mL) was added to it, and the resulting solid precipitate was filtered and washed with THF (10 mL x 2) and diethyl ether (20 mL). The solid product was dried under a vacuum to give an off-white powder.

1,1'-(pyridine-2,6-diyl)bis(3-methyl-1H-phenanthro[9,10-d]imidazol-3-ium) Salt (c-Pybim1): 348 mg, 87% yield**. ^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.34 (s, 2H), 9.14 – 9.10 (m, 2H), 9.09 (d, J = 8.6 Hz, 2H), 9.03 (t, J = 7.9 Hz, 1H), 8.81 – 8.77 (m, 2H), 8.70 (d, J = 8.0 Hz, 2H), 7.95 (td, J = 7.2, 6.6, 3.6 Hz, 4H), 7.84 (ddd, J = 8.5, 6.2, 2.1 Hz, 2H), 7.63 – 7.56 (m, 4H), 4.67 (s, 6H). **^{13}C NMR** (176 MHz, DMSO-d_6) δ 147.2, 146.1, 142.6, 129.7, 129.5, 128.8, 128.6, 128.4, 126.4, 126.1, 125.6, 125.1, 124.8, 122.8, 122.0, 120.6, 119.4, 54.4. HRMS (ESI, positive ion): M^{2+} = 270.6146 (calculated = 270.6128 for $[C_{37}H_{27}N_5]^{2+}$).

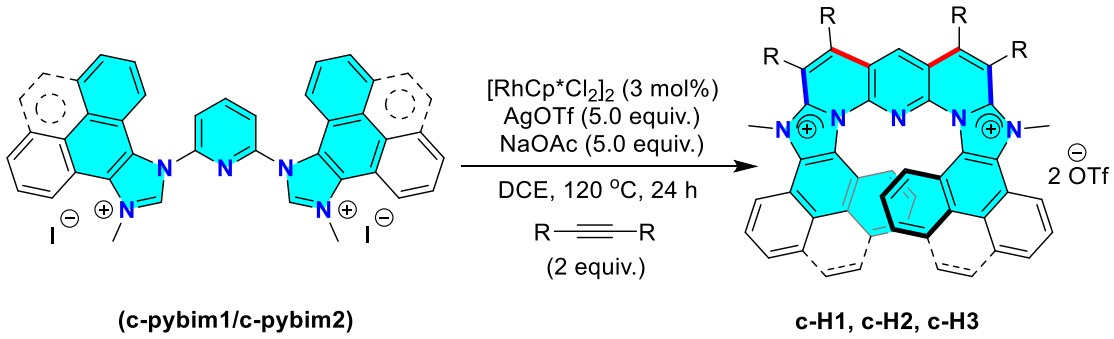
9,9'-(pyridine-2,6-diyl)bis(11-methyl-9H-pyreno[4,5-d]imidazol-11-ium) Salt (c-Pybim2): 357 mg, 84% yield. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.47 (s, 2H), 9.18 – 9.03 (m, 3H), 8.81 (d, J = 7.9 Hz, 2H), 8.58 (d, J = 7.8 Hz, 2H), 8.48 (d, J = 7.7 Hz, 2H), 8.38 – 8.30 (m, 6H), 8.01 (t, J = 7.8 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 4.80 (s, 6H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 147.2, 146.2, 142.9, 142.8, 131.7, 131.5, 128.4, 128.2, 127.9, 127.7, 127.4, 127.1, 127.0, 126.4, 126.2, 123.0, 122.8, 120.8, 119.8, 119.7, 118.7, 54.4. HRMS (ESI, positive ion): M^{2+} = 294.6099 (calculated = 294.6128 for $[C_{41}H_{27}N_5]]^{2+}$).

3. Procedure for the Synthesis of Ph-thiophene Alkyne

The alkyne was prepared by following the described procedure. A 50 mL Schlenk round bottom flask containing a magnetic stir bar was purged with N_2 gas and $[PdCl_2(PPh_3)_2]$ (3 mol %), CuI (10 mol %), PPh_3 (10 mol%) and aryl bromide (5 mmol) were added to it. Then, dry toluene (25 mL) and DBU (30 mmol) and H_2O (50 mol%) were added by syringe under a nitrogen flow. Finally, trimethylsilylacetylene (2.5 mmol) was added to the reaction mixture by syringe. The reaction setup was covered with aluminium foil and stirred at 80 °C for 24 h. After that, the organic layer was extracted with EtOAc (50 mL) and distilled water (30 mL x 2). The organic layer was washed with saturated aqueous NaCl (30 mL), dried over Na_2SO_4, filtered, and removed the solvent in vacuo. The crude product was purified by silica gel column chromatography using a 1-5% ethylacetate/hexane mixture as eluent. Yield = 35%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, J = 8.01, 1.37 Hz, 4H), 7.39 (t, J = 7.59 Hz, 4H), 7.31 – 7.28 (m,2H), 7.27 (s, 2H), 2.62 (s, 6H), 1.56 (s, 6H). The ^{1}H NMR data matches exactly with the reported ^{1}H NMR of the alkyne.[S6]

4. Synthesis and Characterization of Cationic Sub-Expanded Heterohelicenes

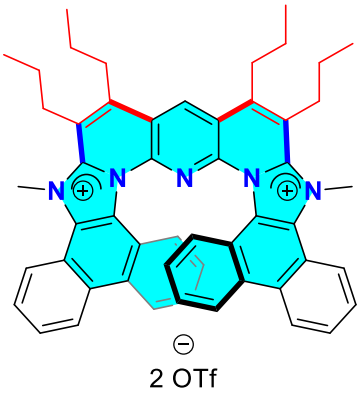


Scheme S6. Synthesis of cationic sub-expanded heterohelicenes

To an oven-dried sealed tube, cationic azole **c-Pybim1**or **c-Pybim2** (0.05 mmol, 1.0 equiv.), NaOAc (0.25 mmol, 5.0 equiv.), $[RhCp^*Cl_2]_2$ (0.0015 mmol, 3 mol%), AgOTf (0.25 mmol, 5.0 equiv.) and alkyne (0.11 mmol, 2.1 equiv.) were loaded. Dry and degassed DCE (2.0 mL) was added to this mixture, and the reaction mixture was stirred at 120 ºC for 24 h under dark. After cooling the reaction mixture to room temperature, the whole reaction solution was passed through a short celite pad and washed with dichloromethane (20 mL x 2). The combined filtrate was concentrated under reduced pressure. Finally, the annulated product was separated and purified by silica gel column chromatography, using 1-10% MeOH/$CHCl_3$ as eluent.

Experimental Characterization Data for the Cationic Sub-Expanded Heterohelicenes (c-H1, c-H2, c-H3)

Cationic heterohelicene c-H1 (racemic)



Yield = 42 mg, 80%. **^{1}H NMR** (500 MHz, CD_3CN) δ 9.87 (s, 1H), 9.43 (d, J = 8.2 Hz, 2H), 9.20 (d, J = 8.0 Hz, 2H), 8.84 (d, J = 8.2 Hz, 2H), 8.60 (d, J = 7.5 Hz, 2H), 8.55 (d, J = 7.5 Hz, 2H), 8.21 (d, J = 8.2 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 6.45 (t, J = 7.5 Hz, 2H), 5.18 (s, 6H), 4.08 (t, J = 8.4 Hz, 4H), 4.00 – 3.93 (m, 2H), 3.84 (m, 2H), 2.58 – 2.54 (m, 4H), 2.50 – 2.43 (m, 4H), 1.92 (td, J = 7.2, 3.4 Hz, 12H). **^{13}C NMR** (126 MHz, CD_3CN) δ 148.7, 147.7, 140.5,

136.4, 132.9, 130.5, 130.1, 129.1, 128.5, 126.2, 126.1, 125.9, 125.7, 124.8, 124.6, 124.3, 123.4, 122.3, 120.9, 120.8, 120.4, 118.6, 40.6, 31.2, 31.0, 25.5, 25.1, 14.7, 14.3. **HRMS** (ESI, positive ion): M^{2+} = 378.7049 (calculated = 378.7067 for $[C_{53}H_{51}N_5]^{2+}$).

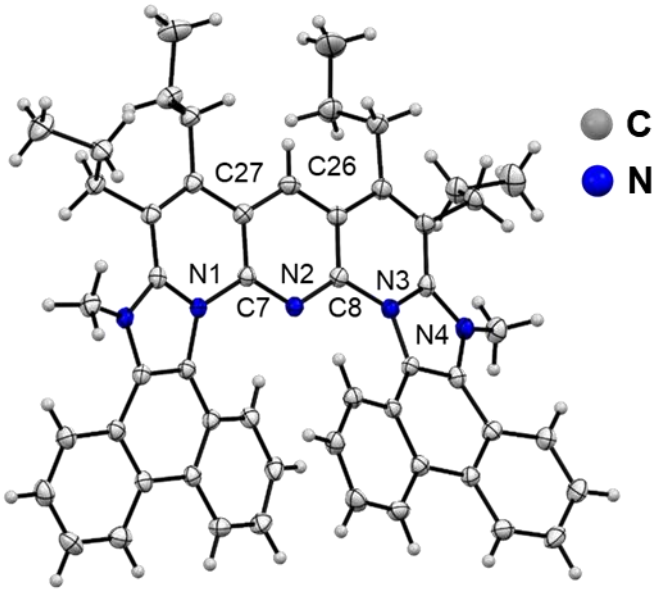
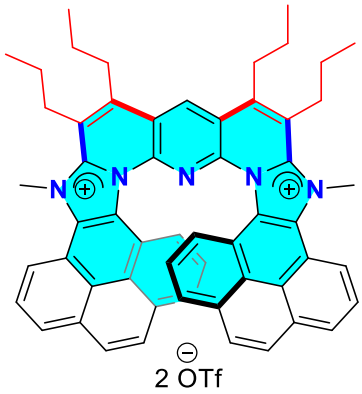


Figure S1. Molecular structure of (***M***)-helicene in racemic **c-H1** (50% probability level). Counter anions (2 OTf^-) and dichloroethane solvent molecule are omitted for clarity. CCDC Number 2158816.

Cationic heterohelicene c-H2 (racemic)



Yield = 34 mg, 62 % **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.69 (s, 1H), 9.24 (d, J = 8.0 Hz, 2H), 8.68 (d, J = 7.7 Hz, 2H), 8.42 (t, J = 8.4 Hz, 4H), 8.34 (d, J = 8.8 Hz, 2H), 7.92 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 7.5 Hz, 2H), 6.17 (t, J = 7.8 Hz, 2H), 5.04 (s, 6H), 3.73 (t, J = 8.2 Hz, 4H), 3.52 (q, J = 8.8 Hz, 4H), 2.06 (dt, J = 15.9, 6.8 Hz, 4H), 1.93 (dq, J = 21.5, 7.2 Hz, 4H), 1.33 (dt, J = 13.4, 7.2 Hz, 12H). **^{13}C NMR** (176 MHz, DMSO-d_6) δ 147.4, 147.2, 139.4, 135.8,

132.0, 131.6, 130.0, 128.1, 127.0, 126.9, 125.4, 124.6, 123.9, 123.8, 123.2, 122.7, 121.9, 121.6, 119.8, 119.6, 118.9, 54.9, 29.8, 29.7, 24.6, 23.9. **HRMS** (ESI, positive ion): M^{2+} = 402.7059 (calculated = 402.7067 for $[C_{57}H_{51}N_5]^{2+}$).

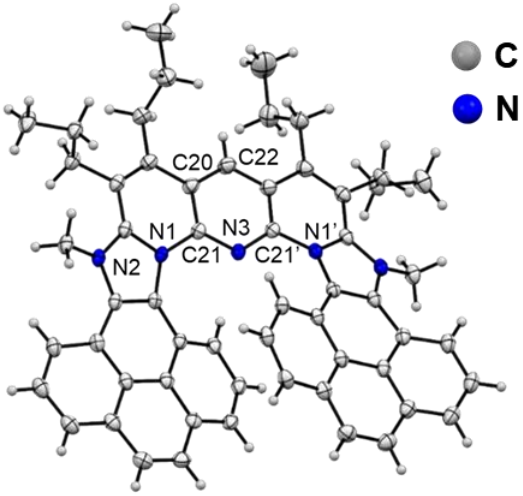
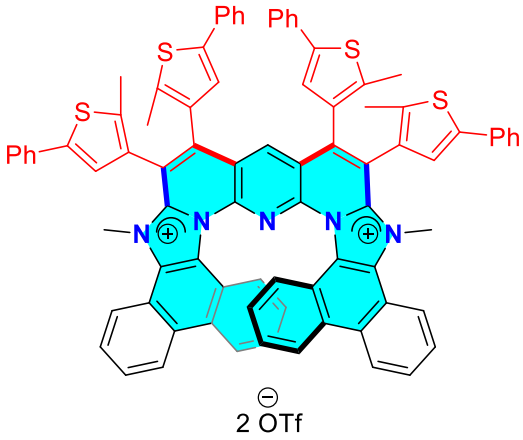


Figure S2. Molecular structure of (***M***)-helicene in racemic **c-H2** (50% probability level). Counter anions (2 OTf^-) are omitted for clarity. CCDC number 2158813.

Cationic heterohelicene c-H3 (racemic)

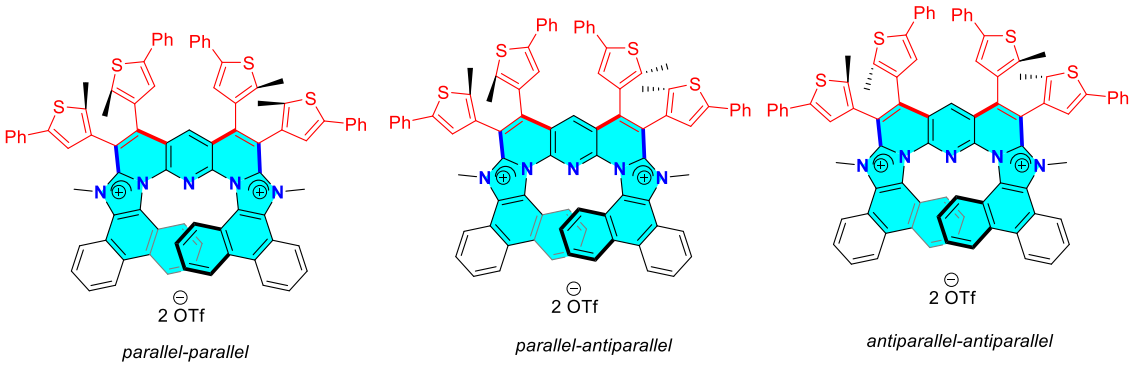
The compound was obtained as a mixture of three isomers, where the orientation of the thiophene group is different.



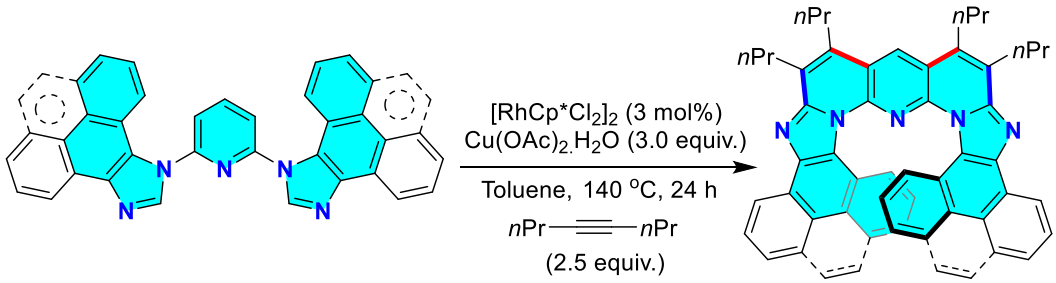
Yield = 42 mg, 53 %. **^{1}H NMR** (500 MHz, CD_3CN) δ 9.12 – 8.93 (m, 2H), 8.80 (m, 2H), 8.65 – 8.50 (m, 2H), 8.49 – 8.36 (m, 2H), 8.11 – 7.99 (m, 4H), 8.00 – 7.92 (m, 4H), 7.80 – 7.56 (m, 6H), 7.54 – 7.07 (m, 17H), 6.61 – 6.30 (m, 2H), 4.47 – 4.21 (m, 6H), 2.63 – 2.51 (m, 2H), 2.48 – 2.37 (m, 3H), 2.35 – 2.18 (m, 7H).).**^{13}C NMR** (126 MHz, CD_3CN) δ 145.0, 144.8, 144.8, 144.7, 144.6, 144.5, 143.6, 143.5, 143.5, 143.4, 143.4, 143.3, 143.1, 143.0, 142.9, 142.3, 141.9, 141.8, 141.6, 141.5, 141.5, 141.3, 141.2, 141.0, 140.9, 140.9, 140.8, 140.8, 140.7, 139.9, 139.8,

139.7, 139.7, 139.6, 139.6, 134.4, 134.3, 134.3, 134.2, 134.1, 133.0, 132.7, 132.6, 130.8, 130.7, 130.7, 130.5, 130.4, 130.3, 130.2, 130.2, 130.2, 130.1, 130.1, 130.0, 130.0, 129.9, 129.9, 129.7, 129.2, 129.2, 129.1, 129.0, 128.9, 127.1, 127.0, 126.9, 126.6, 126.6, 126.5, 126.5, 126.5, 126.4, 126.3, 126.3, 126.3, 126.2, 126.0, 125.7, 125.6, 125.3, 125.2, 124.9, 124.9, 124.8, 124.5, 124.4, 124.4, 123.2, 122.7, 122.4, 121.6, 121.4, 121.2, 121.0, 121.0, 120.9, 120.7, 39.7, 39.7, 39.7, 39.6, 39.6, 39.5, 39.5, 39.3, 39.2, 39.2, 39.1, 15.1, 15.0, 15.0, 14.8, 14.8, 14.7, 14.6, 14.6, 14.6, 14.5, 14.5, 14.4, 14.3, 14.3, 14.2, 14.2. **HRMS** (ESI, positive ion): M^{2+} = 638.6850 (calculated = 638.6821 for $[C_{85}H_{59}N_5S_4]^{2+}$).

Possible three region-isomers of **c-H3**



5. Synthesis and Characterization of Neutral Sub-Expanded Heterohelicenes



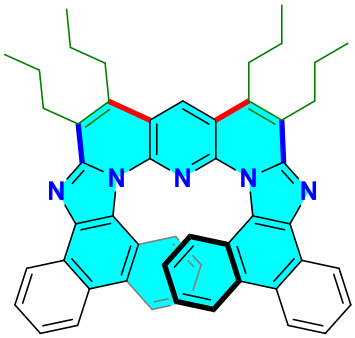
Scheme S7. Synthesis of neutral sub-expanded heterohelicenes

A mixture of neutral azole **n-Pybim1** or **n-Pybim2** (0.05 mmol, 1.0 equiv.), $[RhCp^*Cl_2]_2$ (3 mol %) and $Cu(OAc)_2.H_2O$ (0.15 mmol, 3.0 equiv.) were taken in a sealed tube, and 1.5 ml toluene was added to it. Next, the alkyne (0.12 mmol, 2.5 equiv.) was added to the reaction mixture and kept it stirring at 140 ^oC for a time of 24 h. After that, the mixture was cooled to room temperature. CH_2Cl_2 (15 mL) was added to this mixture and the organic layer was washed with ethylenediamine in water (300 μL ethylenediamine in 10 mL water) to remove Cu-salts. After collecting the organic layer, the aqueous layer was again extracted with CH_2Cl_2 (10 ml),

and the combined organic layers were evaporated to dryness. The crude mixture was subjected to column chromatography (silica gel) by using 1-5% MeOH in $CHCl_3$ solvent system to obtain the pure product.

Experimental Characterization Data for the Neutral Sub-Expanded Heterohelicenes (n-H1, n-H2, c-H3)

Neutral heterohelicene n-H1 (racemic)



Yield = 24 mg, 66% **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.05 (dd, J = 7.8, 1.5 Hz, 2H), 8.89 (dd, J = 8.4, 1.2 Hz, 2H), 8.87 (s, 1H), 8.74 (d, J = 8.1 Hz, 2H), 8.50 (d, J = 8.2 Hz, 2H), 7.80 (t, J = 7.0 Hz, 2H), 7.77 – 7.72 (m, 2H), 6.98 – 6.92 (m, 2H), 6.15 (t, J = 7.3 Hz, 2H), 3.42 (m, 4H), 3.23 (m, 4H), 2.11 – 1.97 (m, 4H), 1.90 (m, 4H), 1.27 (dt, J = 13.2, 7.3 Hz, 12H). **^{13}C NMR** (126 MHz, CDCl3) δ 149.7, 141.3, 140.6, 133.6, 130.9, 130.2, 129.9, 128.2, 127.1, 127.1, 126.9, 126.6, 125.6, 124.8, 124.2, 123.9, 123.1, 122.3, 117.4, 30.9, 30.5, 24.1, 23.6, 14.9, 14.9. **HRMS** (ESI, positive ion): $[M+H]^+$ = 728.3760 (calculated = 728.3748 for $[C_{51}H_{46}N_5]^+$).

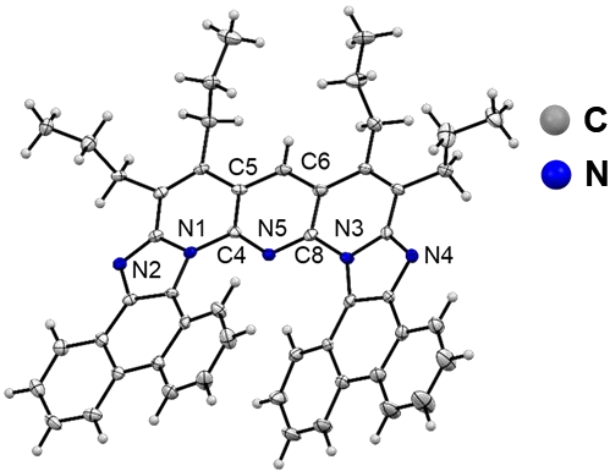
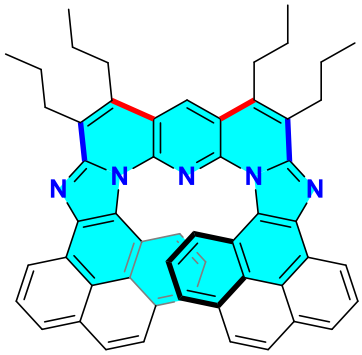


Figure S3. Molecular structure of (***P***)-helicene in racemic **n-H1** (50% probability level). (CCDC 2165994).

Neutral heterohelicene n-H2 (racemic)



Yield = 17 mg, 43% ^{1}H NMR (500 MHz, Chloroform-d) δ 9.29 (dd, J = 7.5, 1.2 Hz, 2H), 9.11 (dd, J = 8.0, 1.0 Hz, 2H), 8.89 (s, 1H), 8.29 (dd, J = 7.7, 1.2 Hz, 2H), 8.20 (t, J = 7.5 Hz, 2H), 8.10 (d, J = 8.7 Hz, 2H), 7.93 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 7.2 Hz, 2H), 6.00 (t, J = 7.8 Hz, 2H), 3.49 (ddd, J = 9.5, 6.7, 4.1 Hz, 4H), 3.24 (t, J = 8.3 Hz, 4H), 2.08 (m, 4H), 1.93 (m, 4H), 1.30 (td, J = 7.3, 2.1 Hz, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.0, 141.9, 140.7, 133.8, 131.8, 131.0, 130.8, 130.0, 128.2, 126.6, 126.1, 125.4, 125.2, 125.2, 124.4, 124.2, 123.5, 123.0, 122.7, 120.6, 117.6, 30.9, 30.6, 29.9, 24.1, 23.7, 15.0, 1.2, 0.2. **HRMS** (ESI, positive ion): $[M+H]^+$ = 776.3711 (calculated = 776.3753 for $[C_{55}H_{46}N_5]^+$).

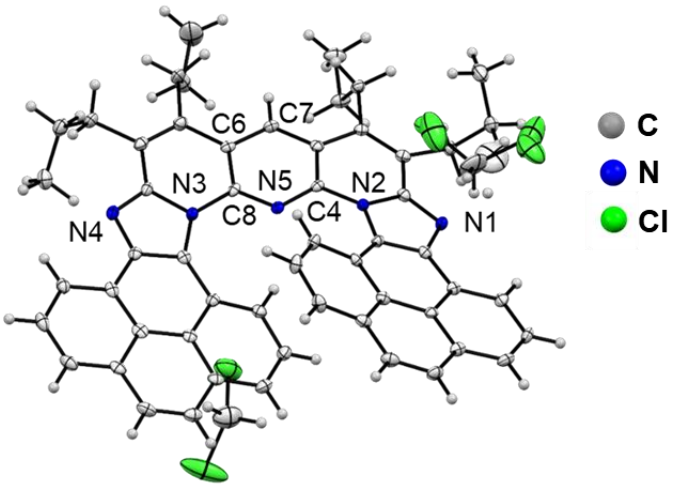
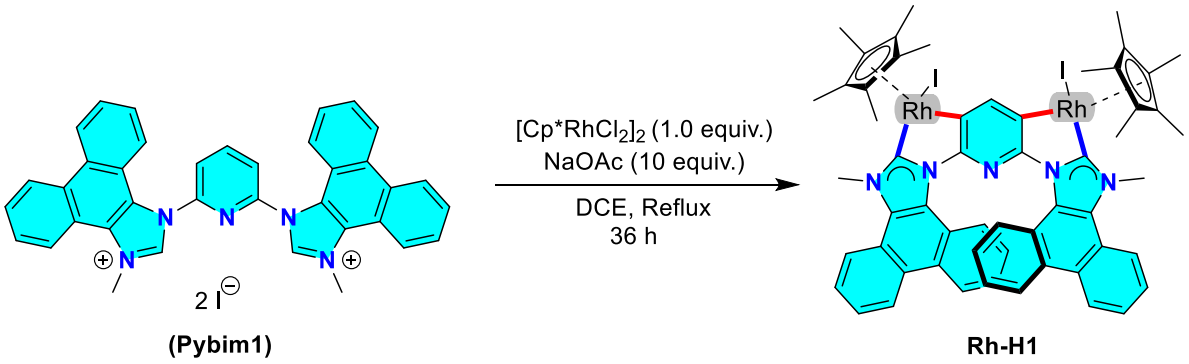


Figure S4. Molecular structure of (*M*)-helicene in racemic **n-H2** (50% probability level) (CCDC 2165995).

6. Synthesis of the Intermediate Rh-H1 (racemic)



Scheme S8. Synthesis of **Rh-H1**

A mixture of **c-Pybim1** (0.05 mmol, 1.0 equiv.), NaOAc (0.5 mmol, 10 equiv.) and $[Cp^*RhCl_2]_2$ (0.05 mmol, 1.0 equiv.) was taken in a Schlenk tube under inert conditions. To this mixture, degassed DCE (4 mL) was added by a syringe and refluxed at 120 °C for 36 h. After that, the reaction mixture was cooled to room temperature, the solution was passed through celite pad and washed it with DCM (3×10 mL). The combined filtrate was taken and concentrated under reduced pressure. Finally, the compound was purified by recrystallization using DCM/ether. Yield= 48 %.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (d, J = 8.3 Hz, 2H), 8.87 (d, J = 7.7 Hz, 2H), 8.65 (dd, J = 7.9, 1.3 Hz, 2H), 8.58 (d, J = 8.3 Hz, 2H), 8.44 (s, 1H), 7.73 (dddd, J = 16.7, 8.2, 7.0, 1.4 Hz, 4H), 7.15 (t, J = 7.6 Hz, 2H), 6.20 (t, J = 7.6 Hz, 2H), 4.73 (s, 6H), 1.92 (s, 30H).**^{13}C NMR** (176 MHz, $CDCl_3$) δ 193.38 (d, J = 54.4 Hz), 160.4, 153.2, 147.6, 147.4, 129.6, 129.4, 128.8, 128.1, 127.3, 126.4, 125.8, 125.4, 124.4, 122.2, 121.9, 121.8, 121.3, 98.9 (d, J = 3.8 Hz), 41.8, 10.7. **HRMS** (ESI, positive ion): $[M]^+$ = 1140.1434 (calculated = 1140.1450 for $[C_{57}H_{53}IN_5Rh_2]^+$).

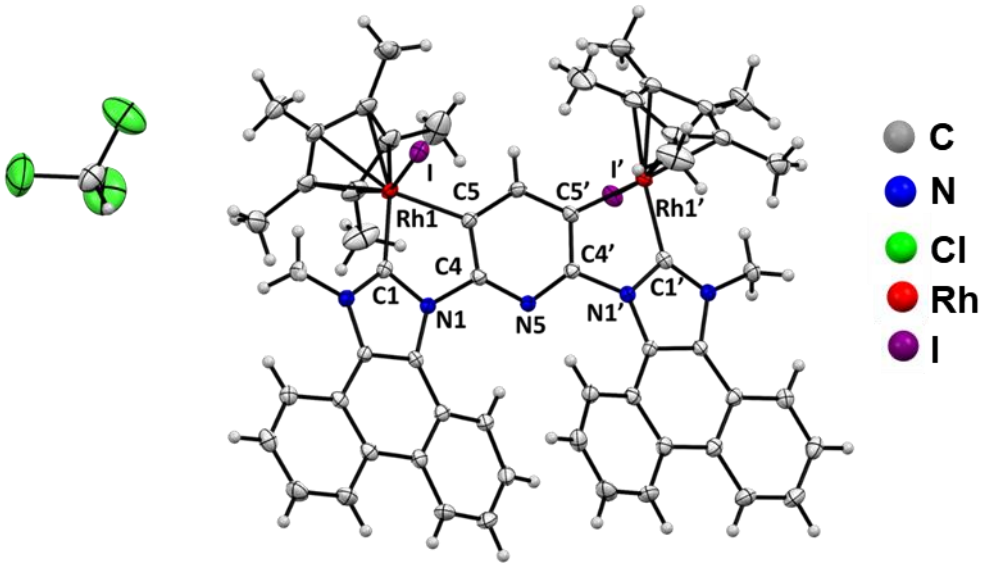
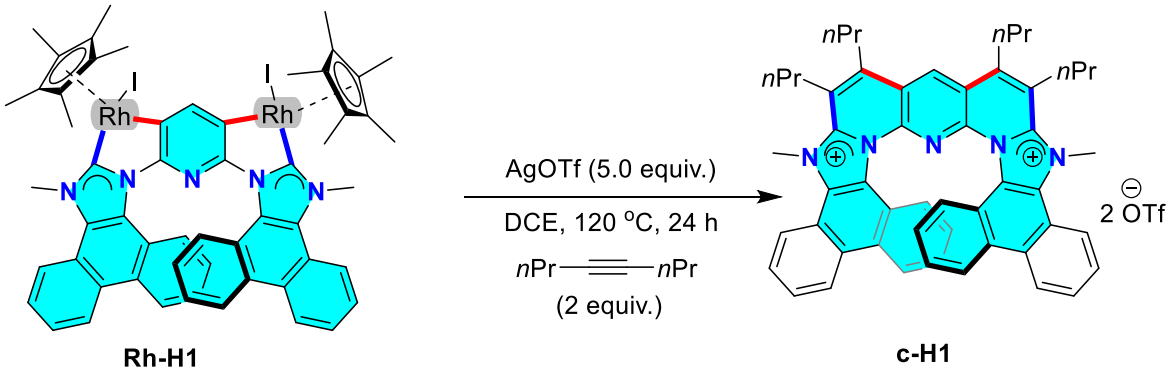


Figure S5. Molecular structure of (***M***)-helicene in racemic **Rh-H1** (50% probability level). Selected bond lengths (Å) and bond angles (°): Rh_1-C_1 = 1.988, Rh_1-C_5 = 2.021, N_1-C_1 = 1.369, C_1-N_2 = 1.369, C_1-Rh_1-C_5 = 77.28, C_1-Rh_1-I_1 = 91.90, N_1-C_1-Rh_1 =118.42. CCDC number 2158814.

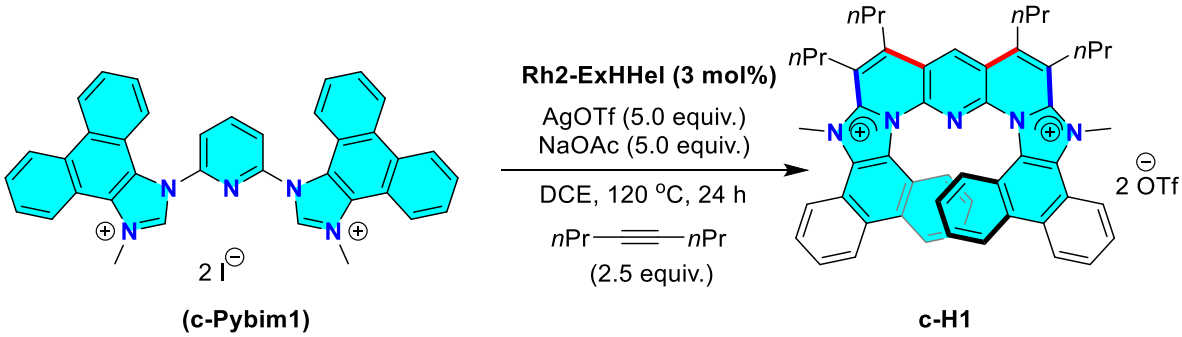
Stoichiometric reaction of the Rh-H1 with alkyne



Scheme S9. Stoichiometric reaction of **Rh-H1** with alkyne.

A mixture of **Rh-H1** (32 mg, 0.025 mmol), AgOTf (32 mg, 0.125 mmol) and 4-octyne (0.07 mmol) in dry and degassed DCE (2.0 mL) were stirred in a sealed tube at a temperature of 120 °C under dark. After 24 h. Next, the whole reaction mixture was filtered through a short celite pad using dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure and final product **(c-H1)** was separated by silica gel column chromatography, using 1-10% MeOH/$CHCl_3$ as eluent. Isolated yield = 68%.

Catalytic reaction of the Rh-H1



Scheme S10. Catalytic reaction of **Rh-H1** with **c-Pybim1** and alkyne.

A mixture of **c-Pybim1** (40 mg, 0.05 mmol), **Rh-H1** (3 mol%), AgOTf (64 mg, 0.25 mmol), NaOAc (21 mg, 0.25 mmol) and 4-octyne (0.12 mmol) in dry and degassed DCE (2.0 mL) were stirred in a sealed tube at a temperature of 120 °C under dark. After 24 h. Next, the whole reaction mixture was filtered through a short celite pad using dichloromethane (3×5 mL). The combined filtrate was concentrated under reduced pressure and final product **(c-H1)** was separated by silica gel column chromatography, using 1-10% MeOH/$CHCl_3$ as eluent. Isolated yield = 72%.

7. Single Crystal X-Ray Analysis

Table S1a. Crystal data and structure refinement for **Rh-H1**

CCDC	2158814
Empirical formula	$C_{59}H_{55}Cl_6I_2N_5Rh_2$
Formula weight	1506.40
Temperature/K	296.15
Crystal system	monoclinic
Space group	C2/c
a/Å	15.6999(9)
b/Å	18.4945(10)
c/Å	20.4988(11)
α/°	90
β/°	91.779(3)
γ/°	90
Volume/Å^3	5949.2(6)
Z	4
ρ_{calc}g/cm^3	1.682
μ/mm^{-1}	1.904
F(000)	2968.0
Crystal size/mm^3	0.145 × 0.133 × 0.066
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.404 to 57.4
Index ranges	-21 ≤ h ≤ 21, -24 ≤ k ≤ 24, -26 ≤ l ≤ 26
Reflections collected	25663
Independent reflections	7506 [R_{int} = 0.0401, R_{sigma} = 0.0442]
Data/restraints/parameters	7506/0/341
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0766
Final R indexes [all data]	R_1 = 0.0429, wR_2 = 0.0810

Table S1b. Crystal data and structure refinement for **c-H1**

CCDC	2158816
Empirical formula	$C_{57}H_{55}Cl_2F_6N_5O_6S_2$
Formula weight	1155.08
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.1750(4)
b/Å	18.4493(5)
c/Å	18.0160(5)
α/°	90
β/°	102.4970(10)
γ/°	90
Volume/Å^3	5248.9(2)
Z	4
ρ_{calc}g/cm^3	1.462
μ/mm^{-1}	0.283
F(000)	2400.0
Crystal size/mm^3	0.18 × 0.1 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.578 to 56.408
Index ranges	$-21 \leq h \leq 21$, $-21 \leq k \leq 24$, $-21 \leq l \leq 23$
Reflections collected	51285
Independent reflections	12731 [R_{int} = 0.0385, R_{sigma} = 0.0531]
Data/restraints/parameters	12731/53/746
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1785
Final R indexes [all data]	R_1 = 0.1006, wR_2 = 0.1994

Table S1c. Crystal data and structure refinement for **c-H2**

CCDC	2158813
Empirical formula	$C_{59}H_{51}F_6N_5O_6S_2$
Formula weight	1104.16
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.116(7)
b/Å	17.029(5)
c/Å	16.379(8)
α/°	90
β/°	124.270(10)
γ/°	90
Volume/Å^3	5098(3)
Z	4
ρ_{calc}g/cm^3	1.439
μ/mm^{-1}	0.186
F(000)	2296.0
Crystal size/mm^3	0.21 × 0.13 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.458 to 57.196
Index ranges	-29 ≤ h ≤ 29, -22 ≤ k ≤ 22, -20 ≤ l ≤ 22
Reflections collected	58133
Independent reflections	6474 [R_{int} = 0.0702, R_{sigma} = 0.0376]
Data/restraints/parameters	6474/125/428
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0594, wR_2 = 0.1554
Final R indexes [all data]	R_1 = 0.0786, wR_2 = 0.1713

Table S1d. Crystal data and structure refinement for **n-H1**

CCDC	2165994
Empirical formula	$C_{51}H_{45}N_5$
Formula weight	727.92
Temperature/K	140.01
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.4766(9)
b/Å	15.6816(16)
c/Å	28.099(2)
α/°	90
β/°	95.655(3)
γ/°	90
Volume/Å^3	3717.0(6)
Z	4
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.077
F(000)	1544.0
Crystal size/mm^3	0.25 × 0.05 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.904 to 52.74
Index ranges	$-10 \leq h \leq 10$, $-19 \leq k \leq 19$, $-35 \leq l \leq 35$
Reflections collected	45331
Independent reflections	7602 [R_{int} = 0.1350, R_{sigma} = 0.1134]
Data/restraints/parameters	7602/0/509
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0735, wR_2 = 0.1281
Final R indexes [all data]	R_1 = 0.1547, wR_2 = 0.1526

Table S1e. Crystal data and structure refinement for **n-H2**

CCDC	2165995
Empirical formula	$C_{57}H_{49}Cl_4N_5$
Formula weight	945.81
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.0926(14)
b/Å	16.4670(12)
c/Å	17.5046(13)
α/°	90
β/°	113.674(2)
γ/°	90
Volume/Å^3	4512.3(6)
Z	4
ρ_{calc}g/cm^3	1.392
μ/mm^{-1}	0.310
F(000)	1976.0
Crystal size/mm^3	0.19 × 0.07 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.306 to 54.366
Index ranges	$-21 \leq h \leq 21$, $-21 \leq k \leq 21$, $-22 \leq l \leq 22$
Reflections collected	98282
Independent reflections	10026 [R_{int} = 0.1167, R_{sigma} = 0.0759]
Data/restraints/parameters	10026/17/627
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0789, wR_2 = 0.1489
Final R indexes [all data]	R_1 = 0.1370, wR_2 = 0.1730

Structural analysis of expanded helicenes

d_{AI} = The vertical distance between the centroid of the ring A and ring I.

$\theta_{A\text{-}I}$ = The intersecting angle between two terminal ring A and I

$<\phi_{AE}>$ = Mean torsion angle from ring A to ring E

$<\phi_{IE}>$ = Mean torsion angle from ring I to ring E

$d_{A\text{-}E}$ = Distance from the centroid of ring A to plane E

$d_{I\text{-}E}$ = Distance from the centroid of ring I to plane of ring E

$\theta_{A\text{-}E}$ / $\theta_{K\text{-}E}$ = The intersecting angle between two terminal ring and the central plane along ring F

(A)

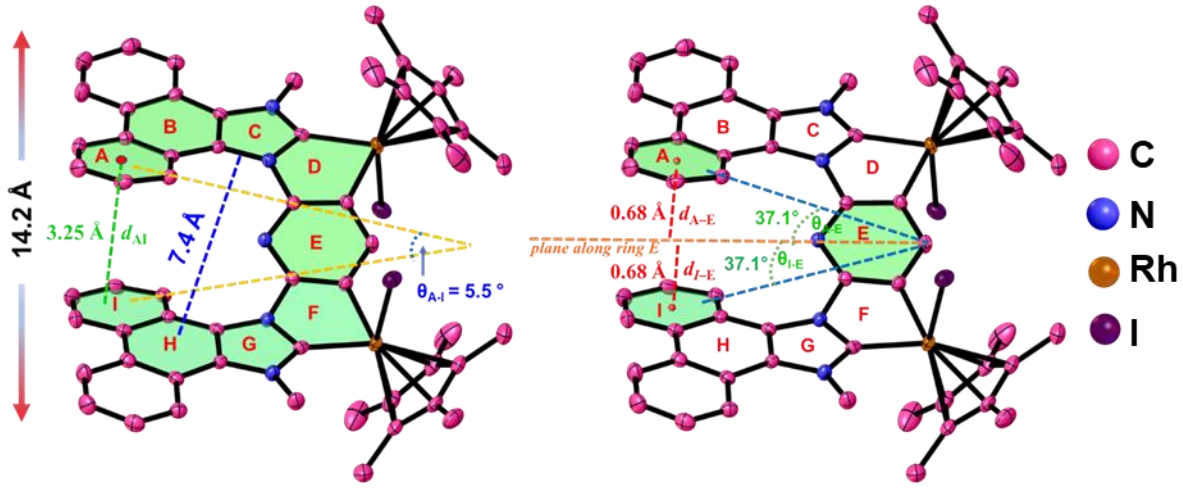


Figure S6a. Crystal structure of **Rh-H1** (top view, H-atoms and free solvents are omitted for clarity).

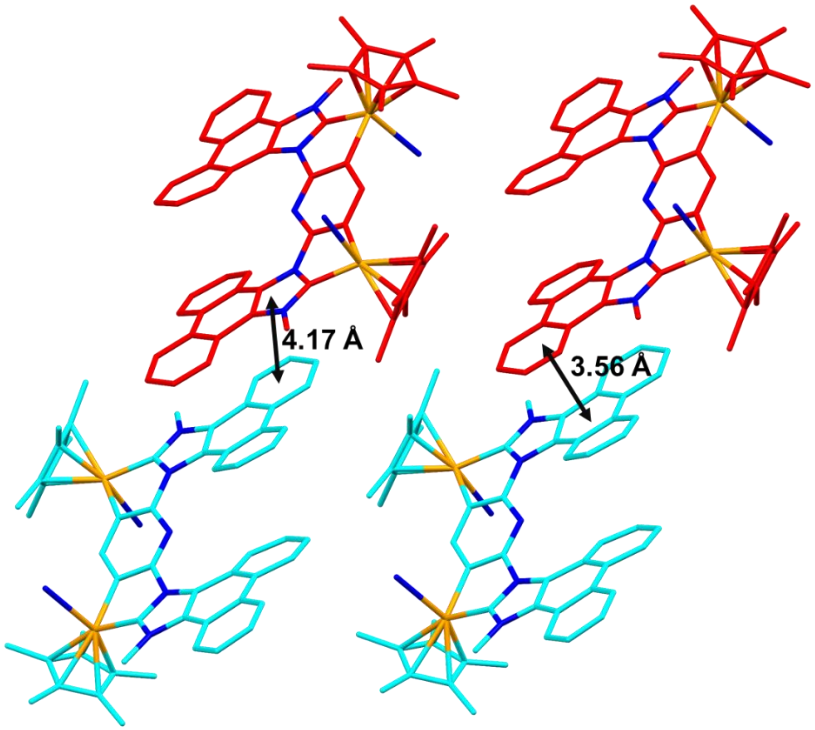


Figure S6b. Crystal packing structure of **Rh-H1** (H-atoms and free solvent molecule are omitted for clarity, the distances shown are centroid to centroid distance).

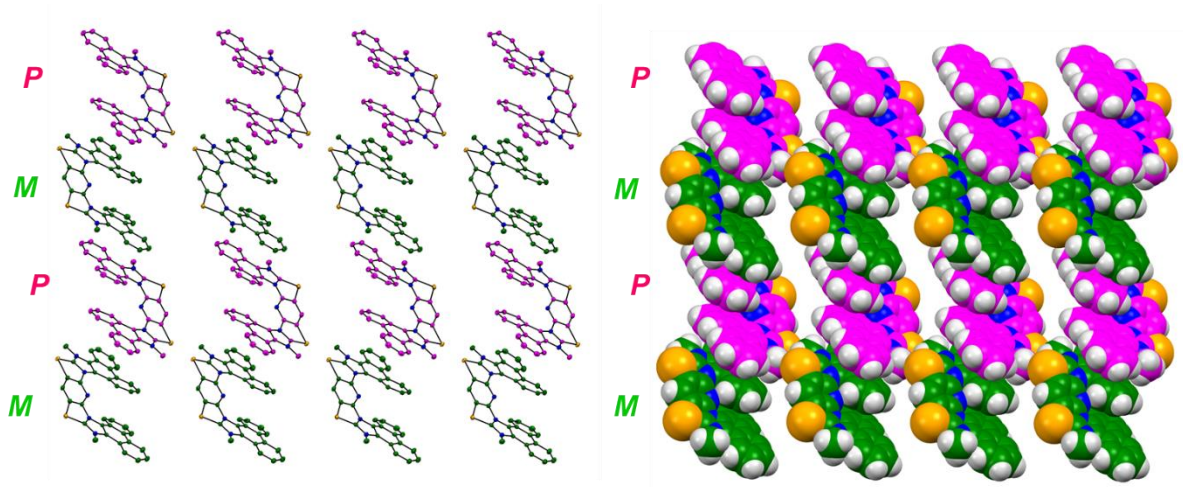


Figure S6c. Crystal packing structure of racemic **Rh-H1** (H-atoms, Cp* group and free solvent molecule are omitted for clarity).

(B)

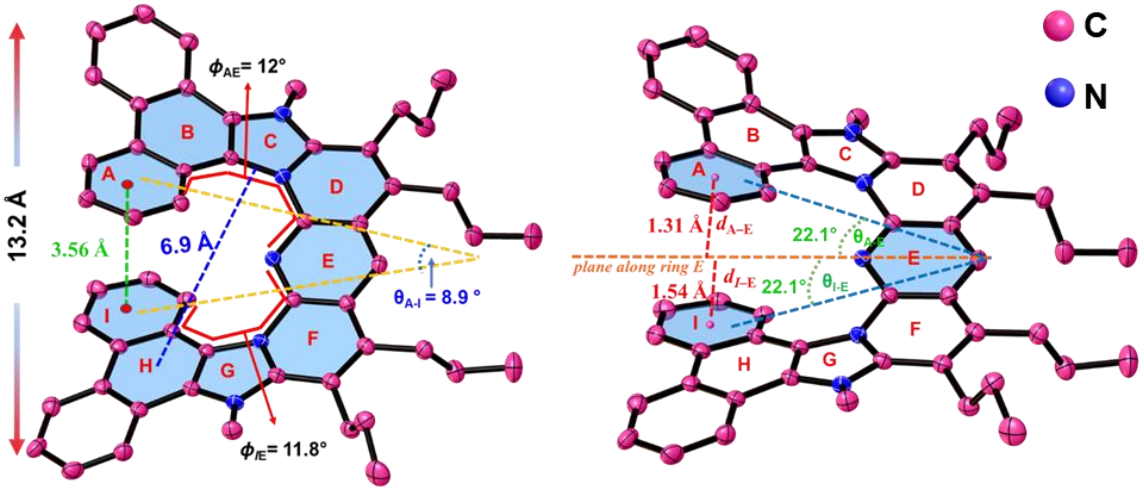


Figure S7a. Crystal structure of **c-H1** (top view, free solvent molecules, hydrogens and counter anions are omitted for clarity).

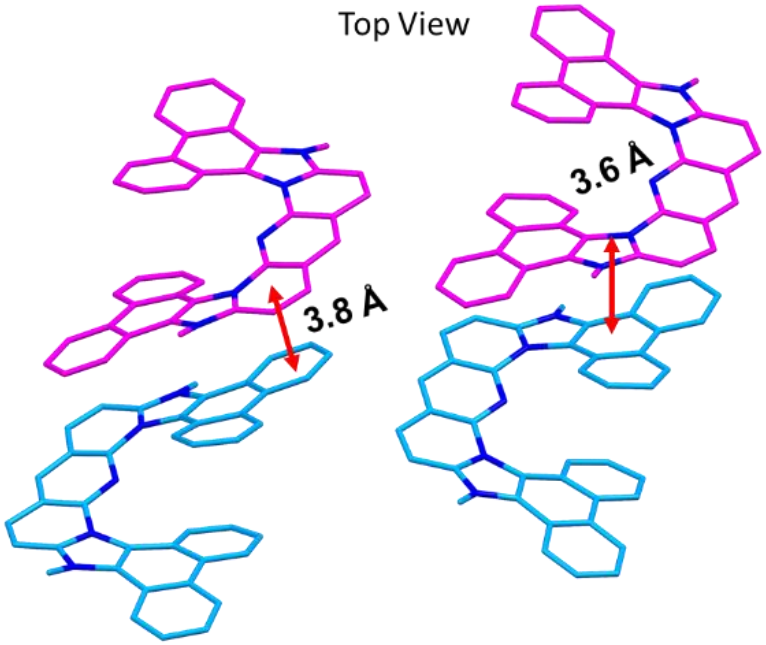


Figure S7b. Crystal packing structure of **c-H1** (H atoms, *n*-propyl side chains, free solvent molecules and anions are omitted for clarity, distances shown are centroid to centroid distance).

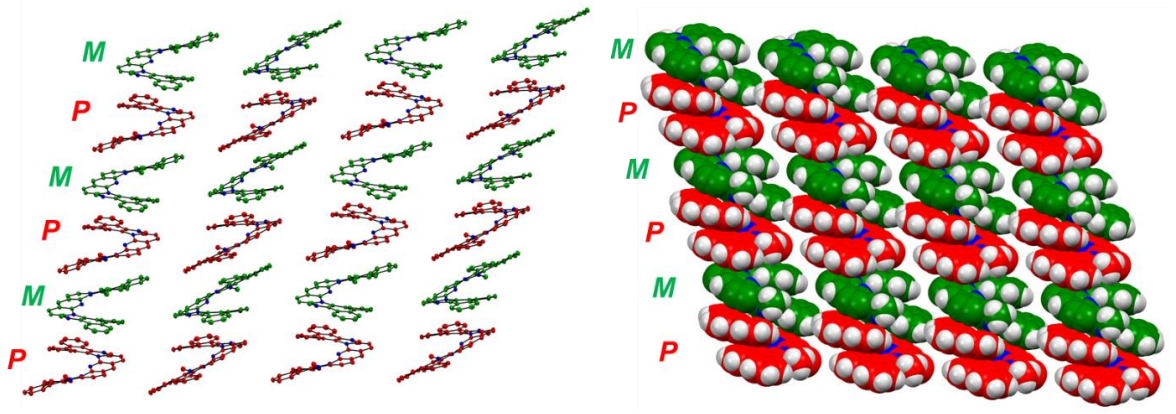


Figure S7c. Crystal packing structure of racemic **c-H1** (H-atoms, *n*-propyl chains, counter anions and free solvent molecule are omitted for clarity).

(C)

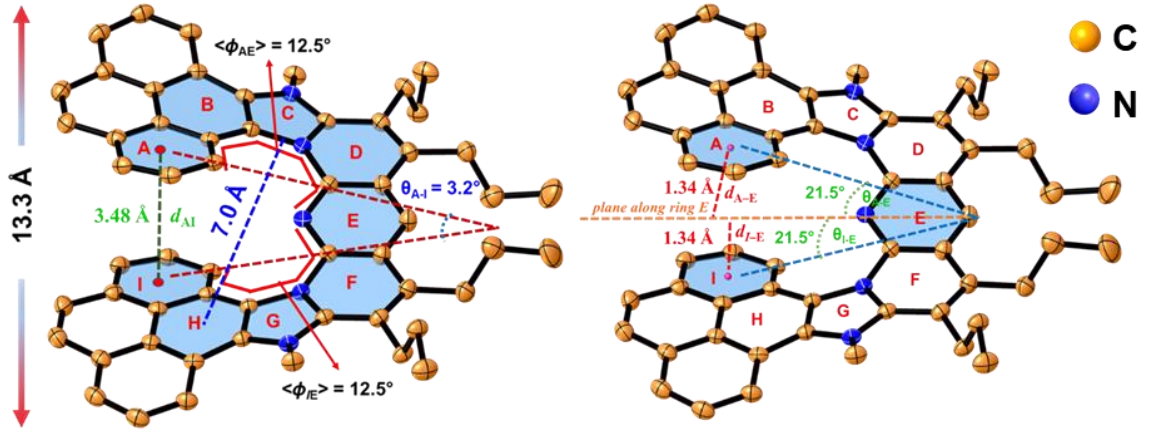


Figure S8a. Crystal structure of **c-H2** (top view, H-atoms and counter anions are omitted for clarity).

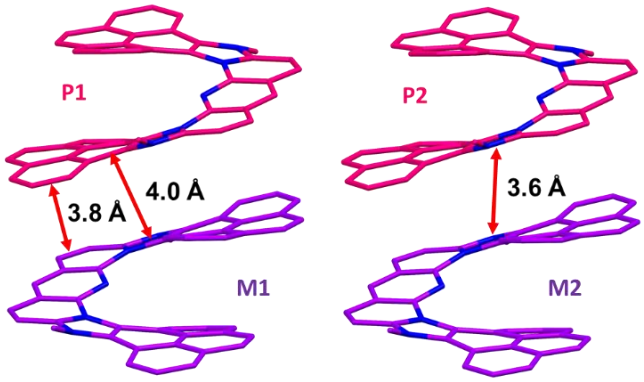


Figure S8b. Crystal packing structure of **c-H2** (H atoms, *n*-propyl side chains, free solvent molecules and anions are omitted for clarity, distances shown are centroid to centroid distance).

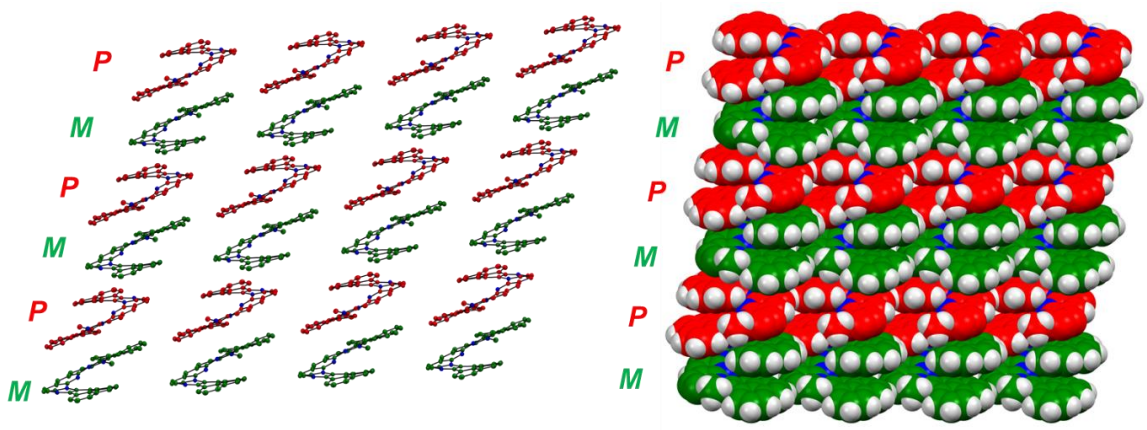


Figure S8c. Crystal packing structure of racemic **c-H2** (H-atoms, *n*-propyl chains, counter anions and free solvent molecule are omitted for clarity).

(D)

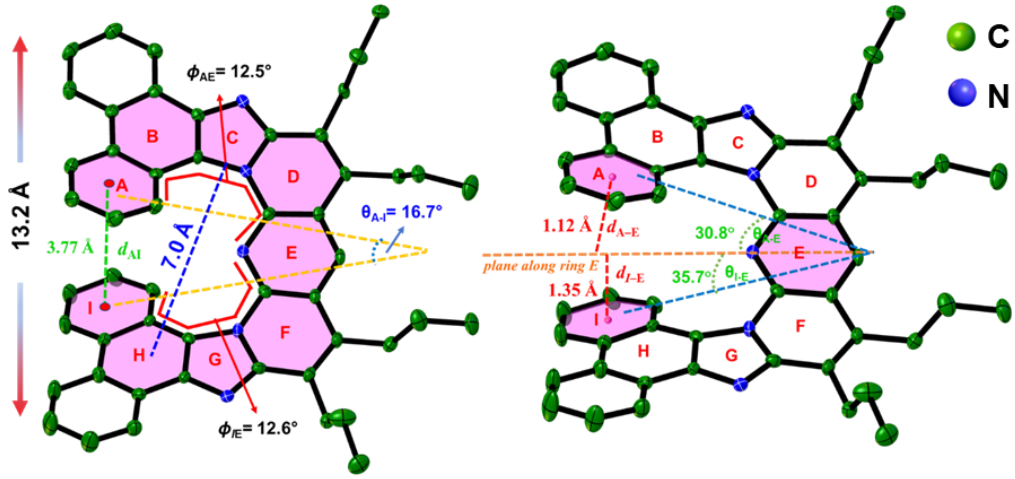


Figure S9a. Crystal structure of **n-H1** (top view, H-atoms are omitted for clarity).

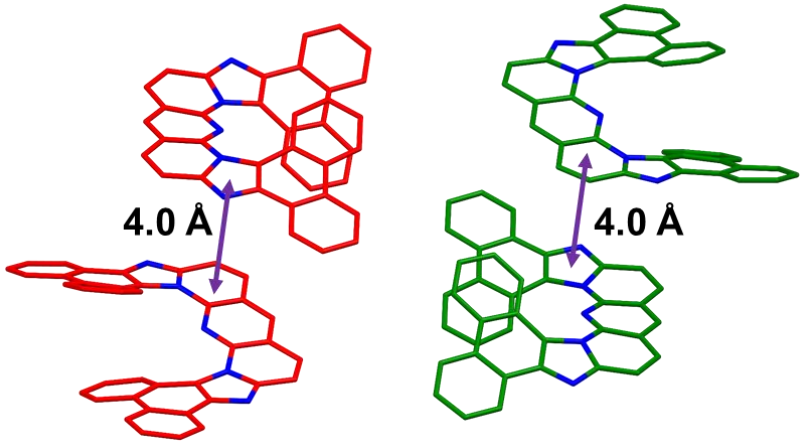


Figure S9b. Crystal packing structure of **n-H1** (H atoms, *n*-propyl side chains are omitted for clarity, distances shown are centroid to centroid distance).

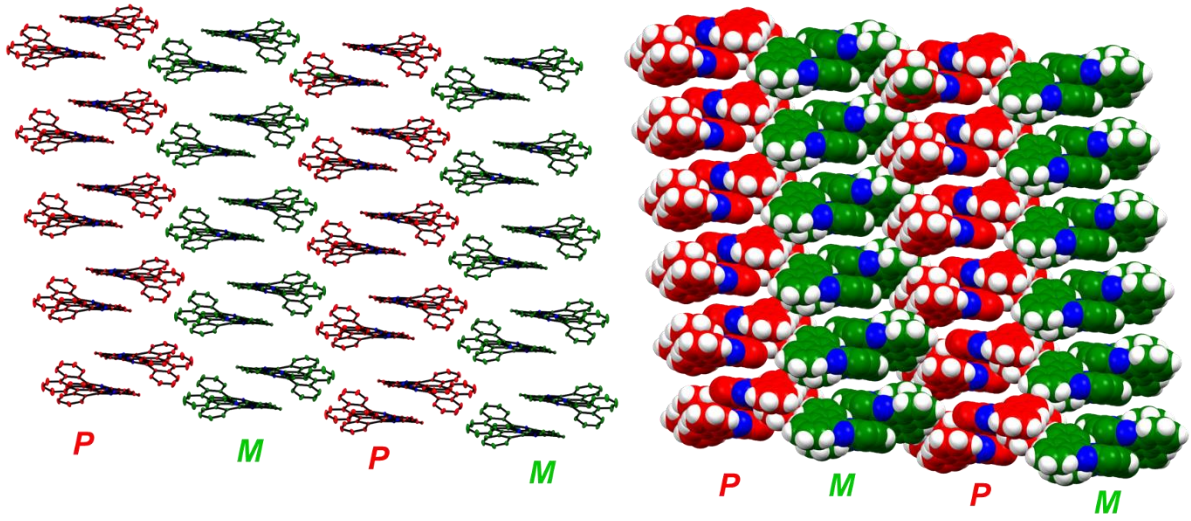


Figure S9c. Crystal packing structure of racemic **n-H1** (H-atoms and *n*-propyl chains are omitted for clarity).

(E)

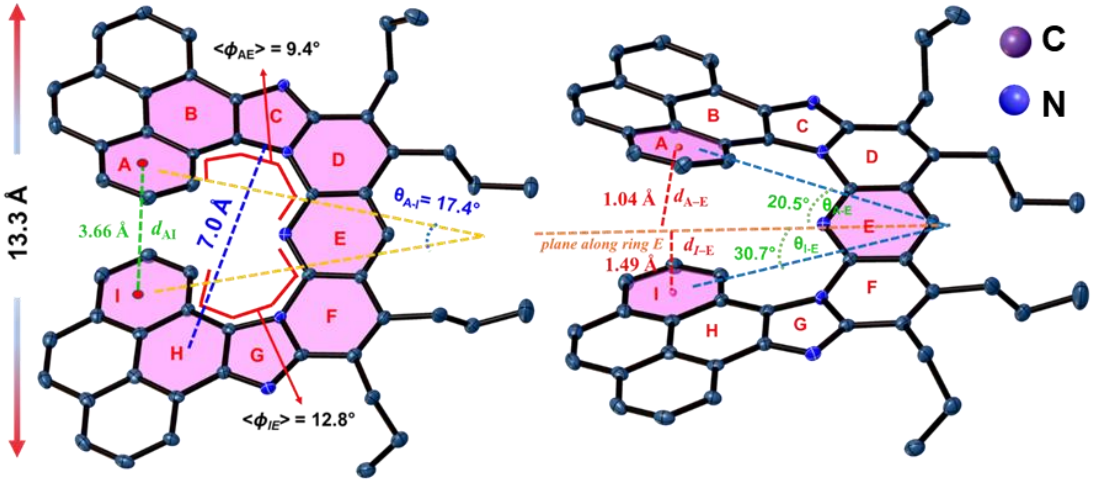


Figure S10a. Crystal structure of **n-H2** (top view, H-atoms are omitted for clarity).

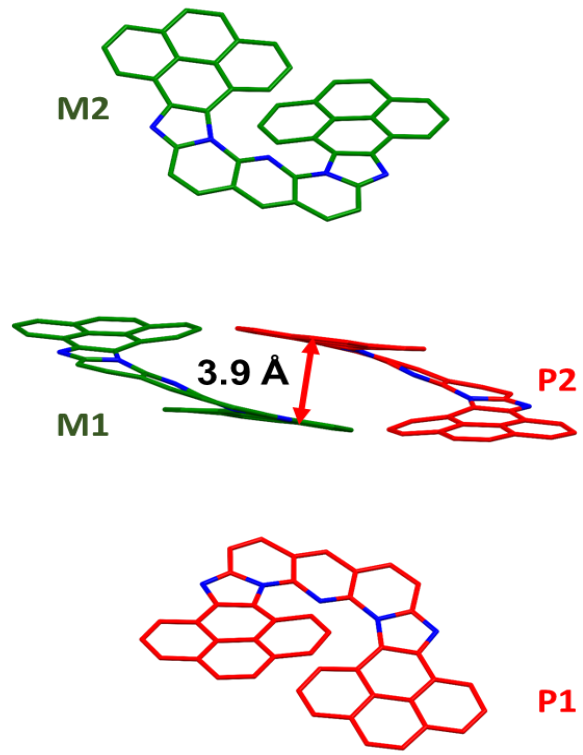


Figure S10b. Crystal packing structure of **n-H2** (H atoms, *n*-propyl side chains and solvent molecules are omitted for clarity, distances shown are centroid to centroid distance).

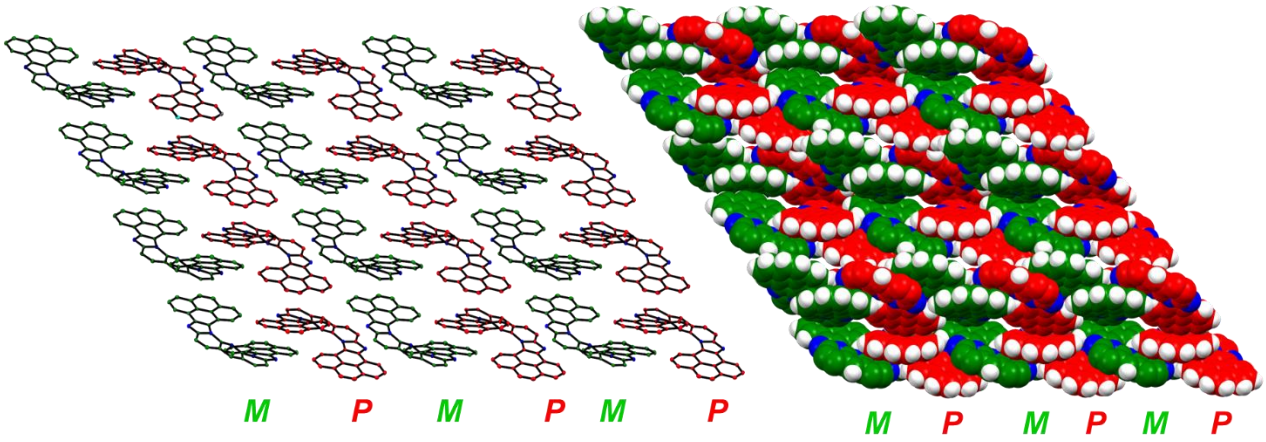


Figure S10c. Crystal packing structure of racemic **n-H2** (H-atoms and *n*-propyl chains are omitted for clarity).

(F) Geometrical shrinkage of cationic helicenes (c-H1, c-H2)

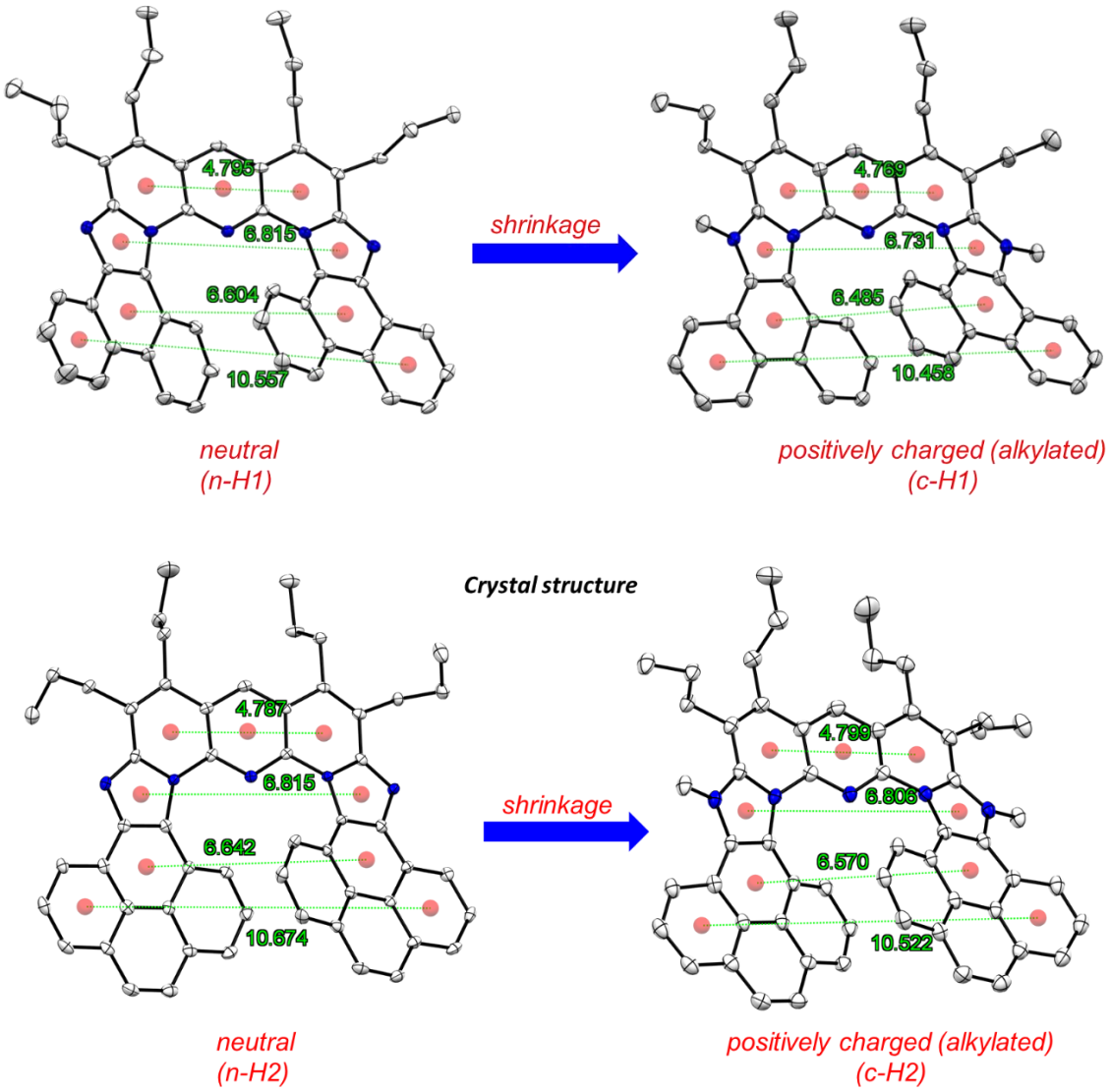


Figure S11. Geometrical shrinkage of cationic helicenes (**c-H1, c-H2**) upon quaternization (alkylation) of **n-H1** and **n-H2** respectively.

Table S2: Summary of crystallographic parameters and molecular interactions

	Rh-H1	**c-H1**	**c-H2**	**n-H1**	**n-H2**
CCDC	2158814	2158816	2158813	2165994	2165995
Space group	C 2/c	P 2_1/c	C 2/c	P21/n	P21/n
d_{AI} **(Å)**	3.84	3.56	3.48	3.77	3.66
$\theta_{A\text{-}I}$ **(°)**	5.5	8.9	3.2	16.7	17.4
$\langle\phi_{AE}\rangle$, $\langle\phi_{IE}\rangle$ **(°)**	14.7	12, 11.8	12.5, 12.5	12.5, 12.6	9.4, 12.8
$\theta_{A\text{-}E}$ / $\theta_{I\text{-}E}$ **(°)**	37.1, 37.1	22.1, 22.1	21.5, 21.5	30.8, 35.7	20.5, 30.6

8. Racemization Barrier Calculation

Gaussian 09 software was used to carry out all the theoretical studies.[S7,S8] Transition state (TS) for the racemization process in the ground state (S_0) calculated at the B3LYP/6-31g(d,p) level of theory in dichloromethane using CPCM model at 298.15 K and 1 atm. The rate constant (k) was estimated using Eyring equation as follows: $k=(k_BT/h)\cdot\exp(-\Delta H^{\ddagger}/RT)\cdot\exp(\Delta S^{\ddagger}/R)$, where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the activation enthalpy and entropy for the racemization process, respectively, T is temperature, and k_B, h, and R are the Boltzman constant, Planck constant, and molar gas constant, respectively.

Table S3: Thermodynamic parameter for the helical inversion process

Expanded helicene	ΔH‡ (kJ·mol^{-1})	ΔS‡ (kJ·mol^{-1})	ΔG‡/kJ·mol^{-1} (kcal·mol^{-1})	k [s^{-1}]	$\tau_{1/2}$ (s)
c-H1	62.9	−29.0	71.6 (17.1)	1.80	0.39
c-H2	74.1	−7.5	76.3 (18.2)	0.26	2.62
n-H1	67.5	−26.2	75.3 (17.9)	0.40	1.74
n-H2	66.7	−7.8	68.9 (16.5)	5.1	0.13

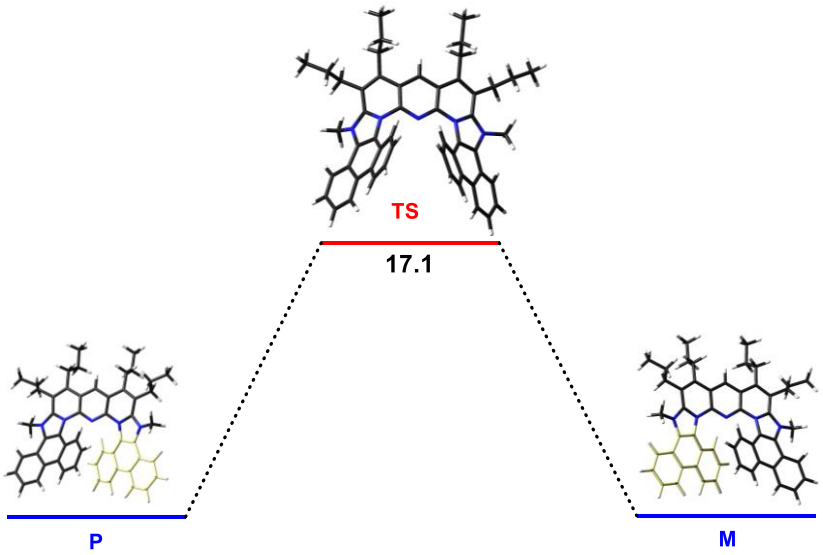


Figure S12a. Racemization process between (***P***)-**c-H1** and (***M***)-**c-H1** and the relative Gibbs free energy (kcal mol^{-1}) calculated at the B3LYP/6-31g(d,p) level of theory.

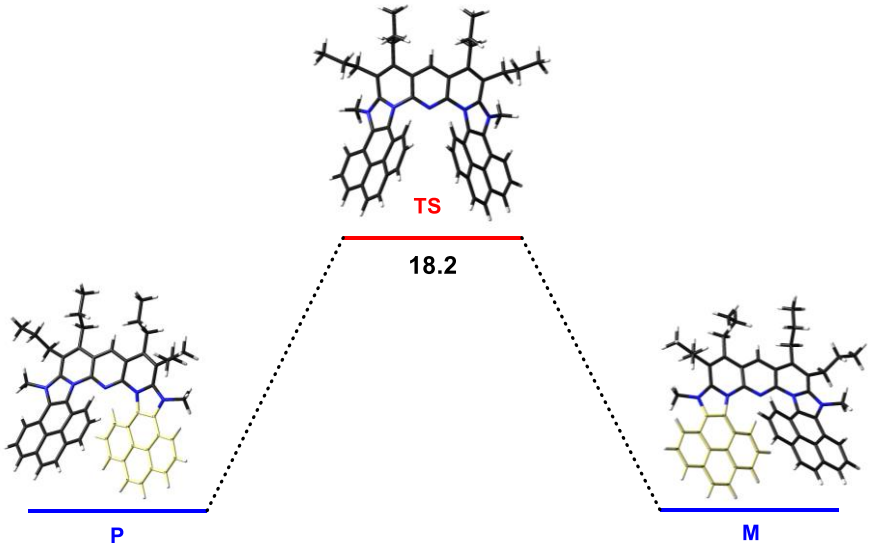


Figure S12b. Racemization process between (***P***)-**c-H2** and (***M***)-**c-H2** and the relative Gibbs free energy (kcal mol^{-1}) calculated at the B3LYP/6-31g(d,p) level of theory.

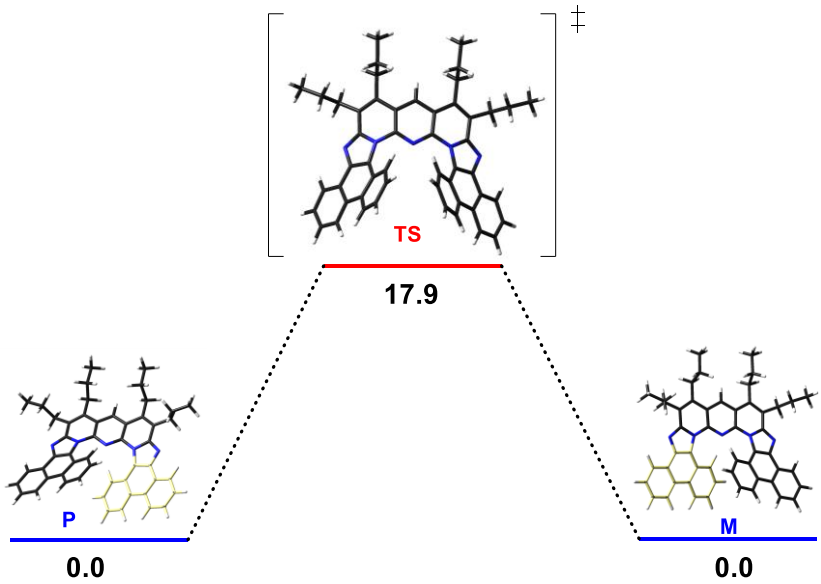


Figure S12c. Racemization process between (***P***)-**n-H1** and (***M***)-**n-H1** and the relative Gibbs free energy (kcal mol^{-1}) calculated at the B3LYP/6-31g(d,p) level of theory.

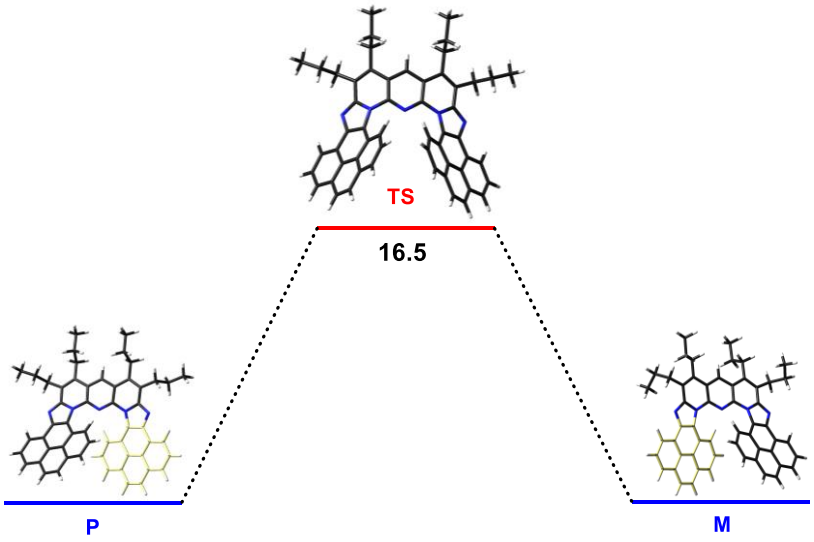


Figure S12d. Racemization process between (***P***)-**n-H2** and (***M***)-**n-H2** and the relative Gibbs free energy (kcal mol^{-1}) calculated at the B3LYP/6-31g(d,p) level of theory.

9. Molecular Spring Constant Calculation

Gaussian 09 software was used to carry out all the theoretical studies.[S7,S8] DFT calculations were performed with B3LYP exchange-correlation functional by using 6-311g(2d,p) basis set for H, C, and N atoms.[S8] Initially, geometry optimizations were carried out at B3LYP/6-311g(2d,p) level of theory in the gas phase for **c-H1** and **n-H1**.The distance between the two carbon atoms at the end of the molecule was r = 5.14, 4.83 for **c-H1** and **n-H1** respectively. A relaxed potential energy surface was scanned with 10 steps in 0.2 Å increments. Where molecular geometry was optimized in each step with a fixed distance between the two carbon atoms (r). The change of potential energy upon elongation of the distance between two carbon atoms is plotted and fitted based on the following equation

$$y = Ax^2 \text{.....(1)}$$

where the coefficient A has the unit of $kJ \cdot mol^{-1} \cdot Å^{-2}$. By comparing the equation 1 with $\Delta E = (1/2) \cdot k \cdot (\Delta r^2)$, where E = relative energy, k = force constant, and r = the elongation of the distance between the two carbon atoms at the edge of the molecule, the force constant k ($N \cdot m^{-1}$) was calculated from A ($kJ \cdot mol^{-1} \cdot Å^{-2}$) as follows: $k = (2 \times 10^{23} \cdot N_A^{-1}) \cdot A$, where N_A is the Avogadro constant. From this result, the force constant of the molecular spring was determined.

(A) Spring constant at B3LYP/6-311g(2d,p) level of theory for **c-H1**

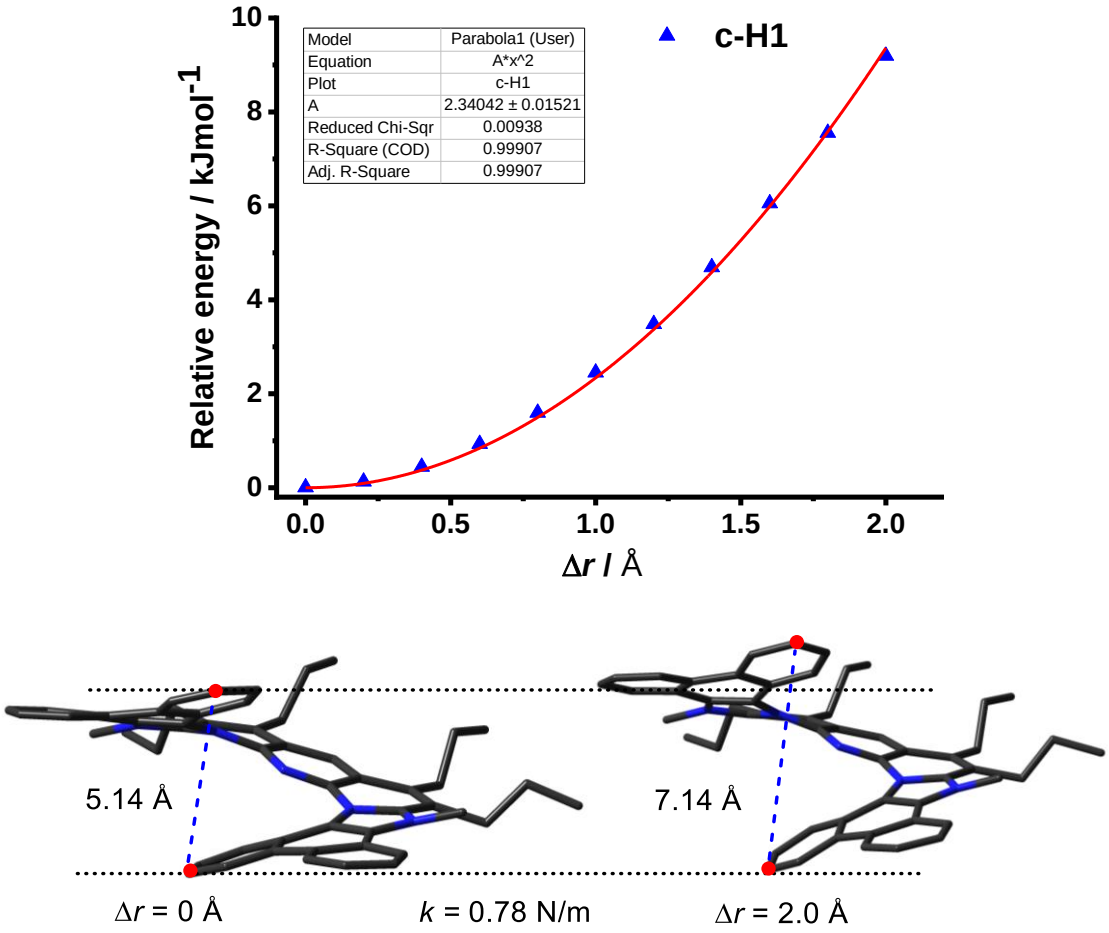
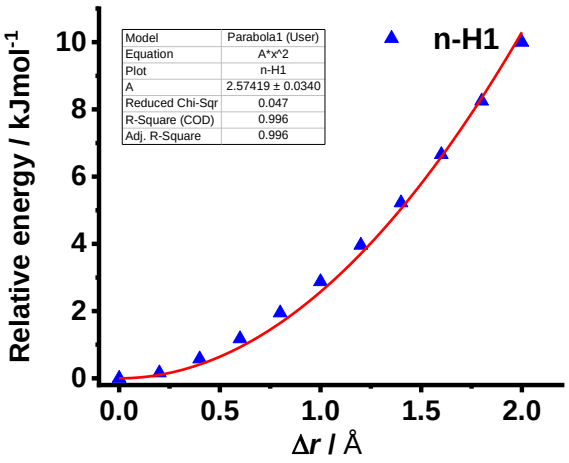


Figure S13a Spring constant at B3LYP/6-311g(2d,p) level of theory for **c-H1.**

(B) Spring constant at B3LYP/6-311g(2d,p) level of theory for **n-H1**



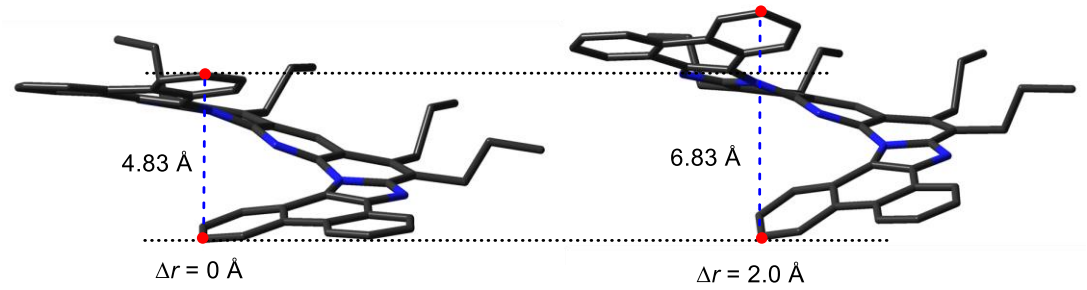


Figure S13b Spring constant at B3LYP/6-311g(2d,p) level of theory for **n-H1.**

10. Spectroscopic Measurements

Steady-state absorption spectroscopy: Steady-state absorption spectra were recorded on Cary 100 UV-Vis spectrophotometer. Conventional quartz cells of 1 cm path length were used for all the measurements.

Steady-state fluorescence spectroscopy: All steady-state fluorescence measurements were done on HORIBA Jobin Yvon Fluorolog spectrofluorimeter (Fluorolog-3-21). The fluorescence and UV-Vis spectra were recorded by using a 1 cm path length quartz cuvette. Both excitation and emission slit were kept at 1 nm while recording the fluorescence spectra. All the experiments were carried out at ambient temperature (298K). All the measurements for **c-H3** were carried out in the dark. Fluorescence quantum yields of expanded heterohelicenes (**c-H1, n-H1, n-H2)** by comparison with Coumarin 30 dye in CH_3CN (Φ_f = 0.67). Fluorescence quantum yields of **c-H2** and **c-H3** were estimated using Fluorescein dye in EtOH (Φ_f = 0.79) as a reference dye.

$$\Phi_{f,i} = \Phi_{f,s} * \frac{F_i}{F_s} * \frac{f_s}{f_i} * \frac{n_i^2}{n_s^2} \quad \text{.....(2)}$$

Where Φ_f = fluorescence quantum yield, subscript ***i*** denotes sample, and the subscript *s* refers to the standard dye, F = fluorescence integral, n = refractive index of the solvent, f is the absorption factor at the excitation wavelength given by the following equation $f = 1 - 10^{-Abs}$, where Abs is the absorbance at the excitation wavelength. The excitation wavelengths were 430 nm, 455 nm, 460 nm, 430 nm, 431 nm for **c-H1**, **c-H2, c-H3, n-H1, n-H2** respectively.

Time-resolved fluorescence spectroscopy: All the measurements were carried out using time-correlated single-photon counting (TCSPC) spectrometer (Delta Flex-01-DD/HORIBA). Delta diode laser 468 nm was used as the excitation source. The instrument response function (IRF) was measured before and after fluorescence lifetime measurement using a dilute suspension of

Ludox (colloidal silica, purchased from Sigma-Aldrich). The emission polarizer was positioned at the magic angle (54.7º) polarization with respect to the excitation polarizer. Decay curves were analyzed by nonlinear least-squares iteration using Horiba EzTime decay analysis software. The quality of the fitted data was judged from the reduced chi-squared (χ^2) value (<1.2). All the measurements were carried out at ambient temperature (298K).

Photophysical Properties in Solutions

To explored the electronic properties, UV−vis absorption and emission properties were studied for both cationic and neutral sub-expanded helicenes in the various solvents. The compounds **c-H1, c-H2, c-H3** exhibited well-resolved π-π* absorption band around 433- 483 nm region along with additional higher energy bands, and an emission band around 570- 645 nm region in chloroform. Similarly, the neutral compounds **n-H1, n-H2** showed absorption band around 420-431 nm and emission band around 505-523 nm in chloroform. The cationic compounds showed large Stokes shift (126 – 162 nm; 4979 cm^{-1} to 5200 cm^{-1}) in various solvents; the flexibility of the helicenic core and significant structural changes between the ground state and excited state were accountable for considerable Stokes shift values. The neutral heterohelicenes exhibited relatively higher fluorescence quantum yield values in the range of φ = 0.34 – 0.28 in chloroform and the excited-state lifetime values in the range of 9.3– 7.8 ns in chloroform.

Table S4A. Solvent-dependent photophysical properties of **c-H1**

Entry	Solvent	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Φ (%)	τ (ns)
1	THF	425	568	9.9	5.66
2	$CHCl_3$	437	576	9.3	4.91
3	ACN	439	572	17.5	6.20
4	MeOH	427	578	10.7	7.14
5	EtOH	431	579	12.2	6.90
6	H_2O	423	572	8.4	6.0
7	DMSO	427	578	15.5	7.24

Table S4B. Solvent-dependent photophysical properties of **c-H2**

Entry	Solvent	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Φ (%)	τ (ns)
1	THF	463	645	4.4	2.34
2	$CHCl_3$	482	646	6.2	2.43
3	ACN	471	672	2.9	2.20
4	MeOH	477	673	2.0	1.43
5	EtOH	478	672	2.6	1.63
6	H_2O	465	668	1.0	0.72
7	DMSO	464	672	2.8	1.79

Table S4C. Solvent-dependent photophysical properties of **c-H3**

Entry	Solvent	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Φ (%)	τ (ns)
1	Toluene	450	588	2.17	0.96
2	THF	441	559	1.82	0.82
3	$CHCl_3$	446	584	1.24	0.62
4	ACN	450	578	0.18	1.04
5	MeOH	452	546	0.27	2.13
6	EtOH	456	565	1.73	0.11
7	H_2O	455	608	0.325	0.21
8	DMSO	449	593	0.19	0.94

Table S4D: Solvent-dependent photophysical properties of **n-H1**

Entry	Solvent	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Φ (%)	τ (ns)
1	Hexane	386, 422, 444	476, 501	28.8	9.13
2	Toluene	387, 422	483, 506	36.6	8.73
3	THF	420, 443	505	39.9	9.54
4	$CHCl_3$	418	506	34.4	9.32
5	ACN	418	508	33.0	9.48
6	MeOH	415	512	28.8	7.38
7	EtOH	417	511	26.7	10.14
8	DMSO	416	512	36.6	10.33

Table S4E: Solvent-dependent photophysical properties of **n-H2**

Entry	Solvent	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Φ (%)	τ (ns)
1	Hexane	438	495, 521	25.9	7.33
2	Toluene	435	509	25.4	7.84
3	THF	432	522	29.0	8.85
4	$CHCl_3$	440	523	21.8	7.94
5	ACN	431	534	18	4.94
6	MeOH	428	536	18.9	2.9
7	EtOH	430	534	18.5	9.72
8	DMSO	431	540	26.1	4.86

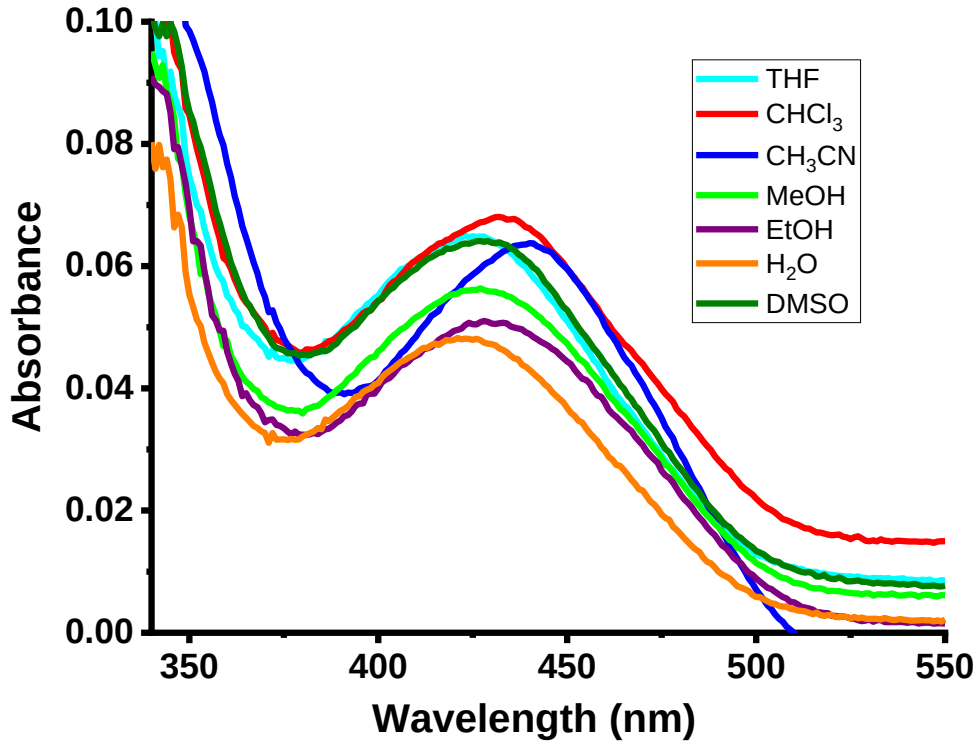


Figure S14a. Absorption spectra of **c-H1** (4 μM) in different solvents.

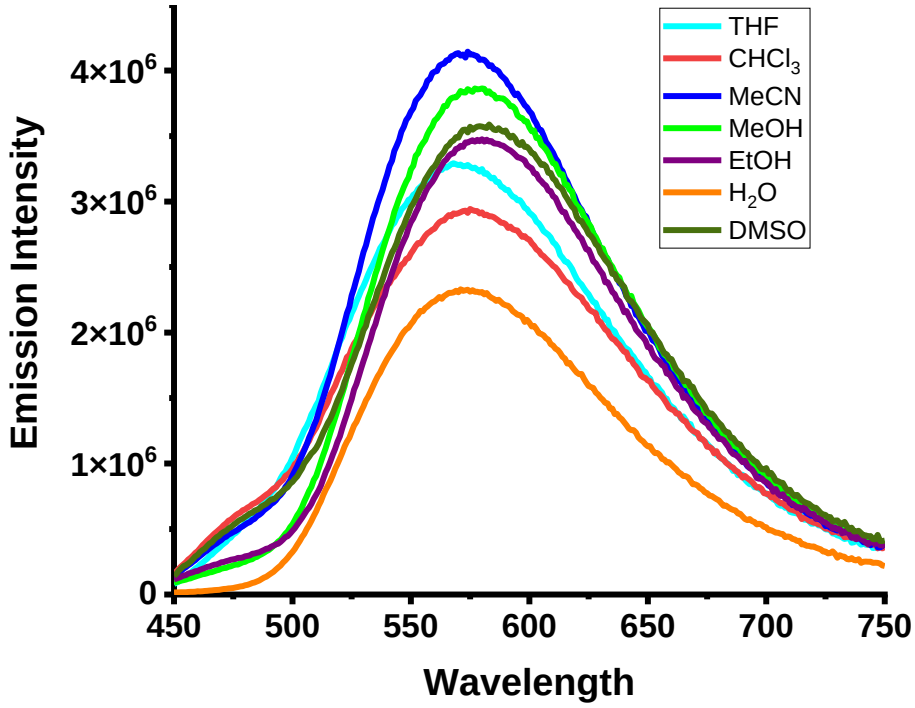


Figure S14b. Emission spectra of **c-H1** (4 μM) in different solvents (λ_{ex} = 430 nm).

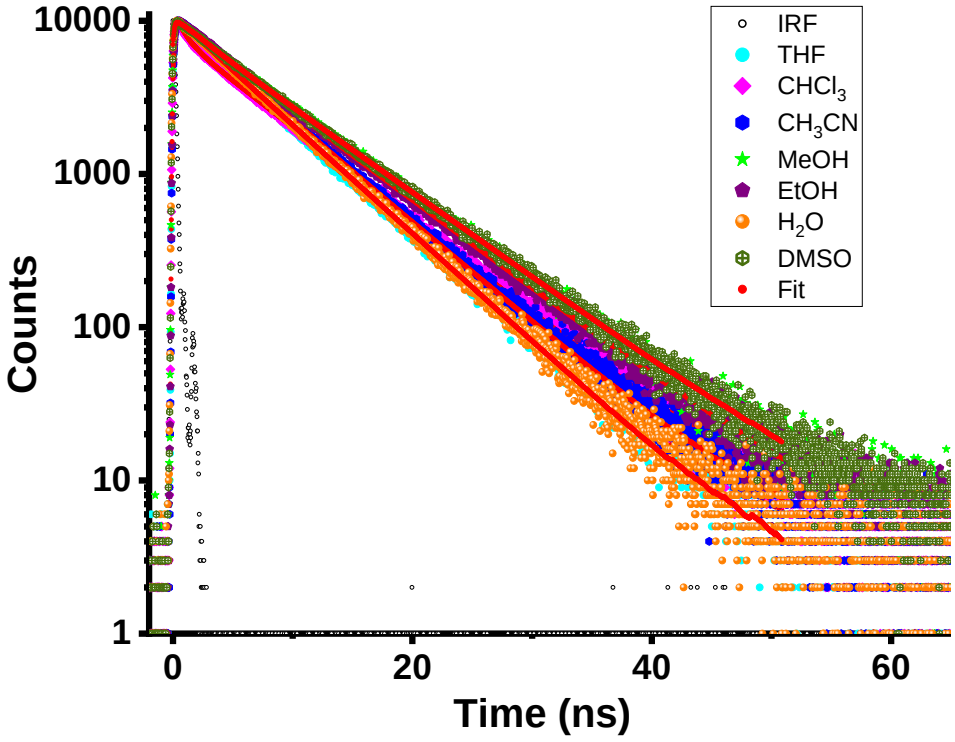


Figure S14c. Fluorescence lifetime of **c-H2** (4 μM) in different solvents.

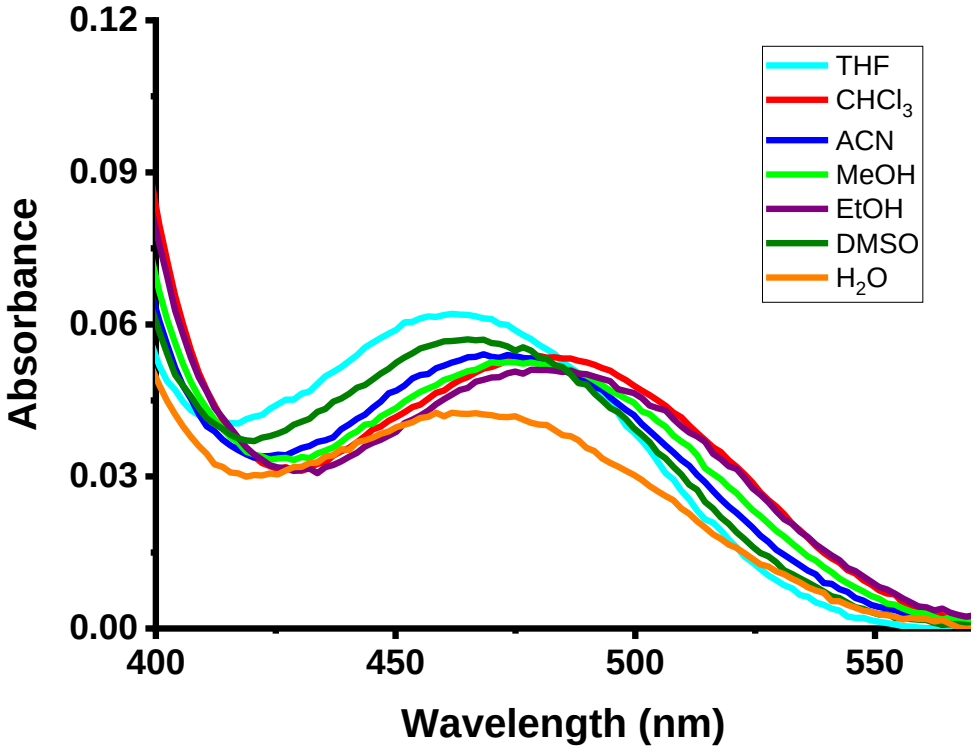


Figure S15a. Absorption spectra of **c-H2** (8 μM) in different solvents.

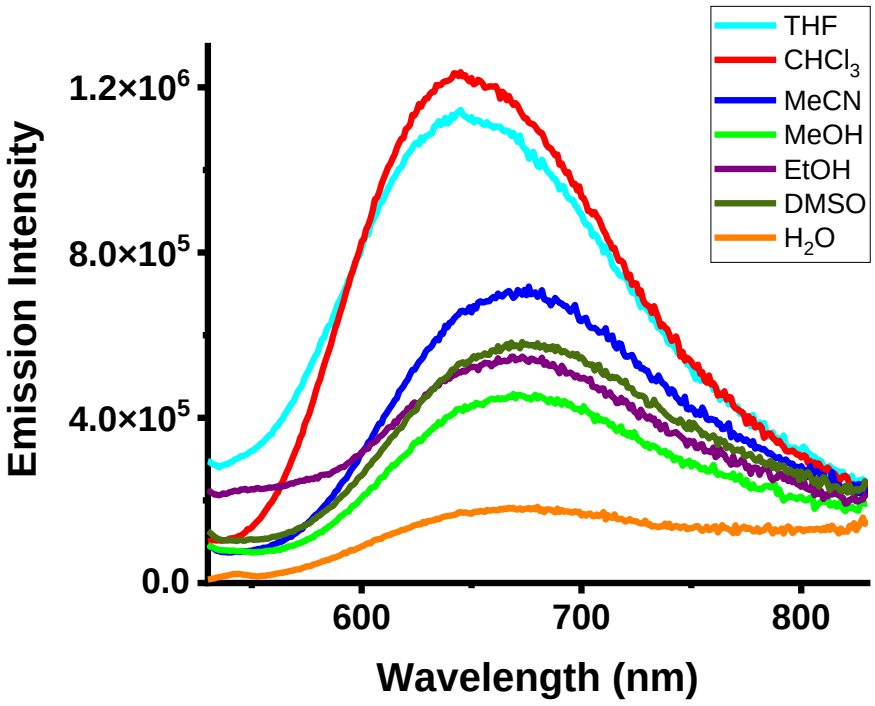


Figure S15b. Emission spectra of **c-H2** (8 μM) in different solvents (λ_{ex} = 455 nm).

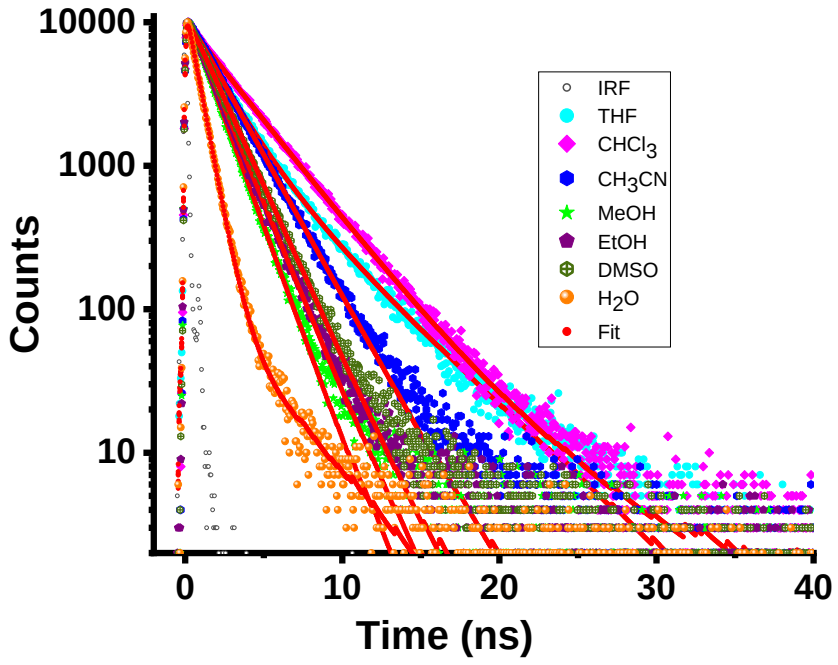


Figure S15c. Fluorescence lifetime of **c-H2** (8 μM) in different solvents.

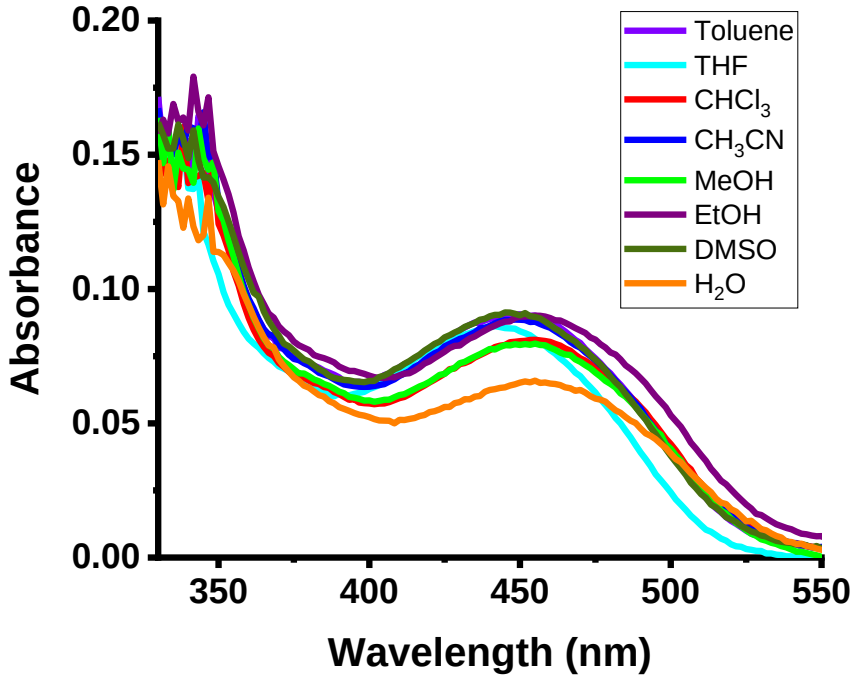


Figure S16a. Absorption spectra of **c-H3** (4 μM) in different solvents.

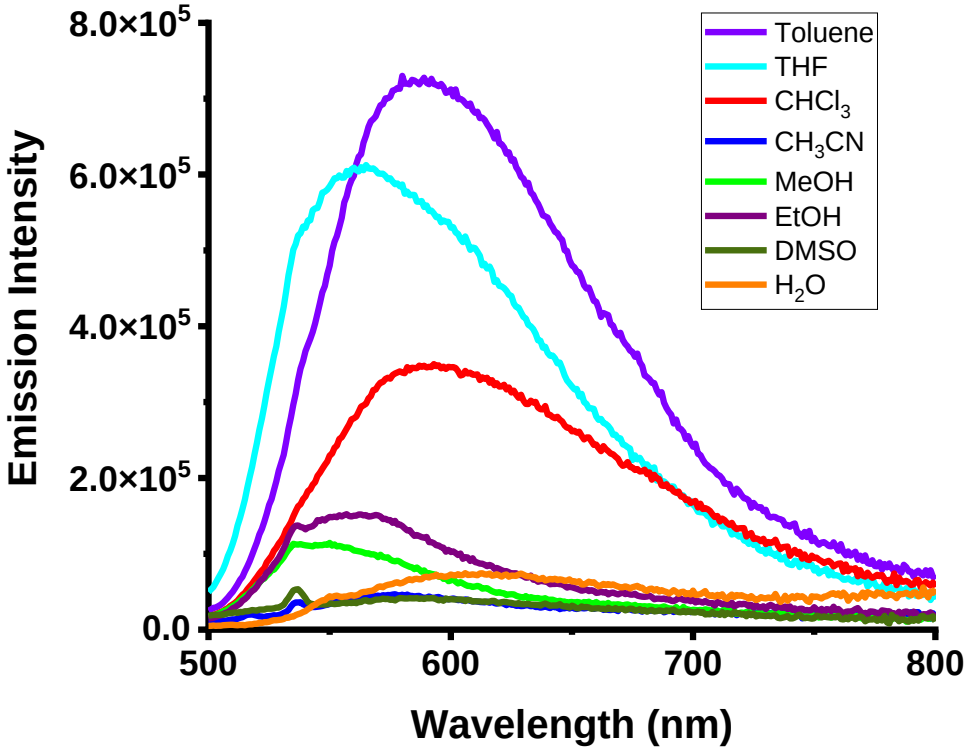


Figure S16b. Emission spectra of **c-H3** (4 μM) in different solvents (λ_{ex} = 460 nm).

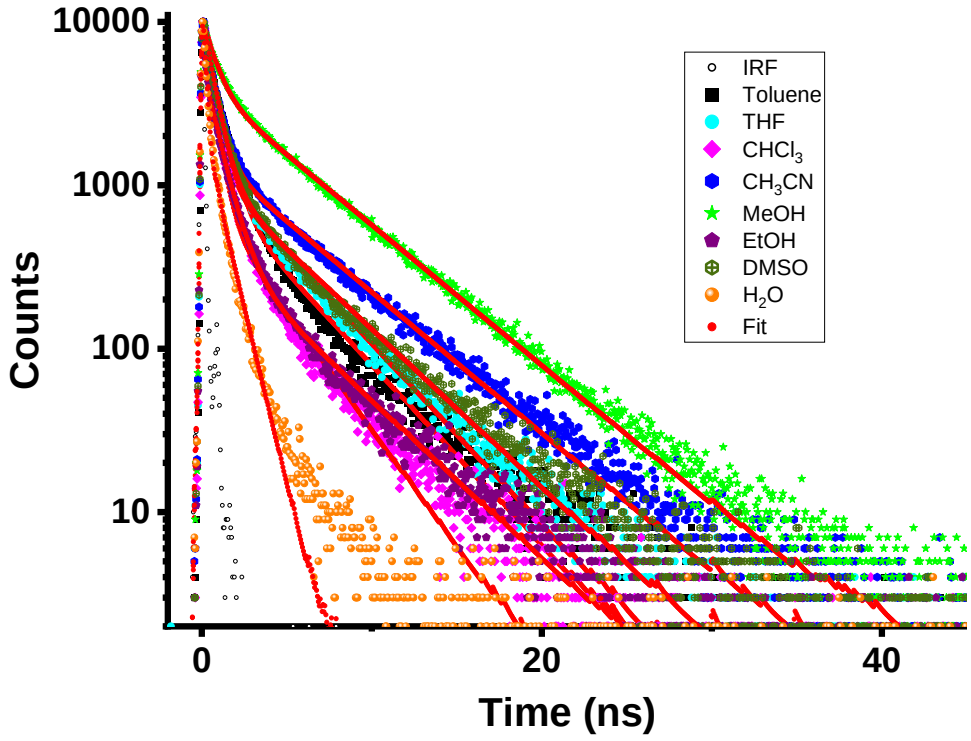


Figure S16c. Fluorescence lifetime of **c-H3** (8 μM) in different solvents.

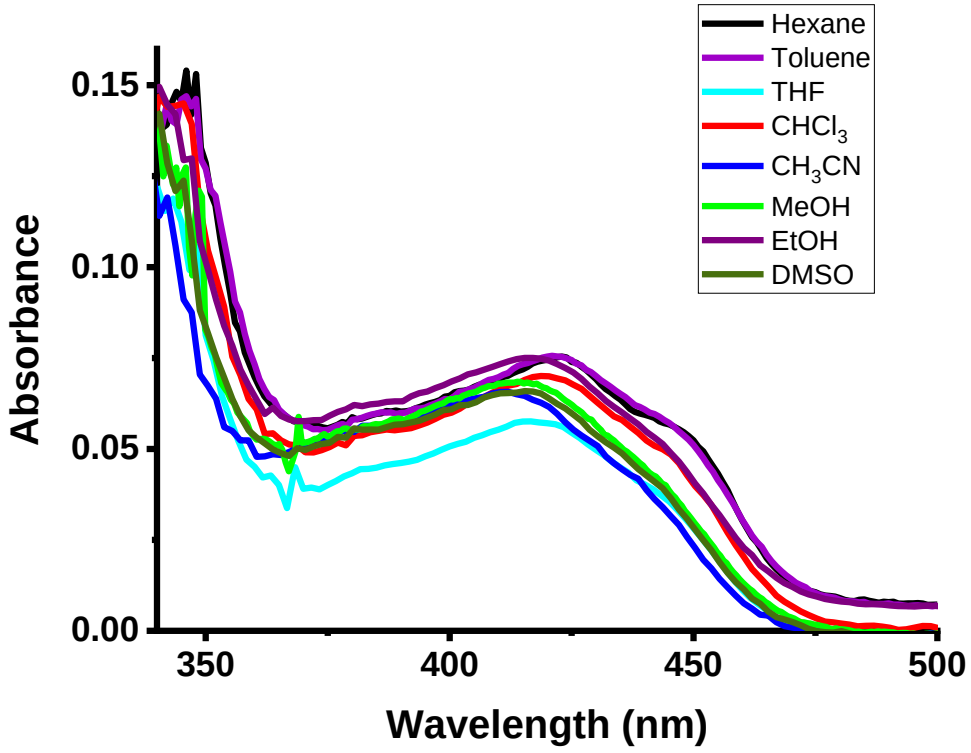


Figure S17a. Absorption spectra of **n-H1** (4 μM) in different solvents.

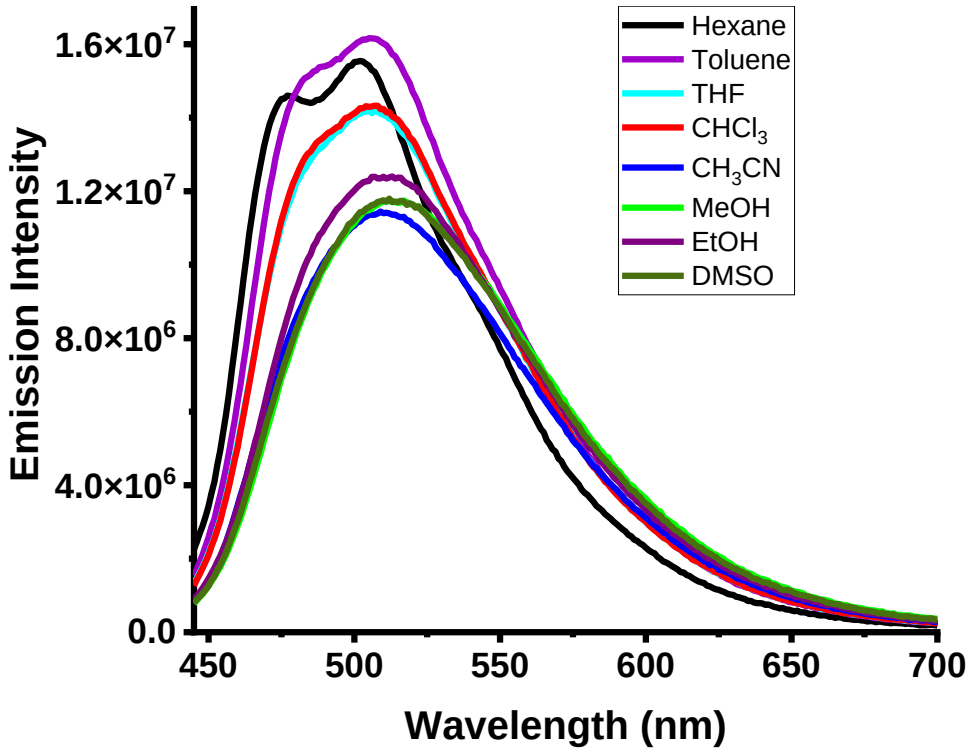


Figure S17b. Emission spectra of **n-H1** (4 μM) in different solvents (λ_{ex} = 430 nm).

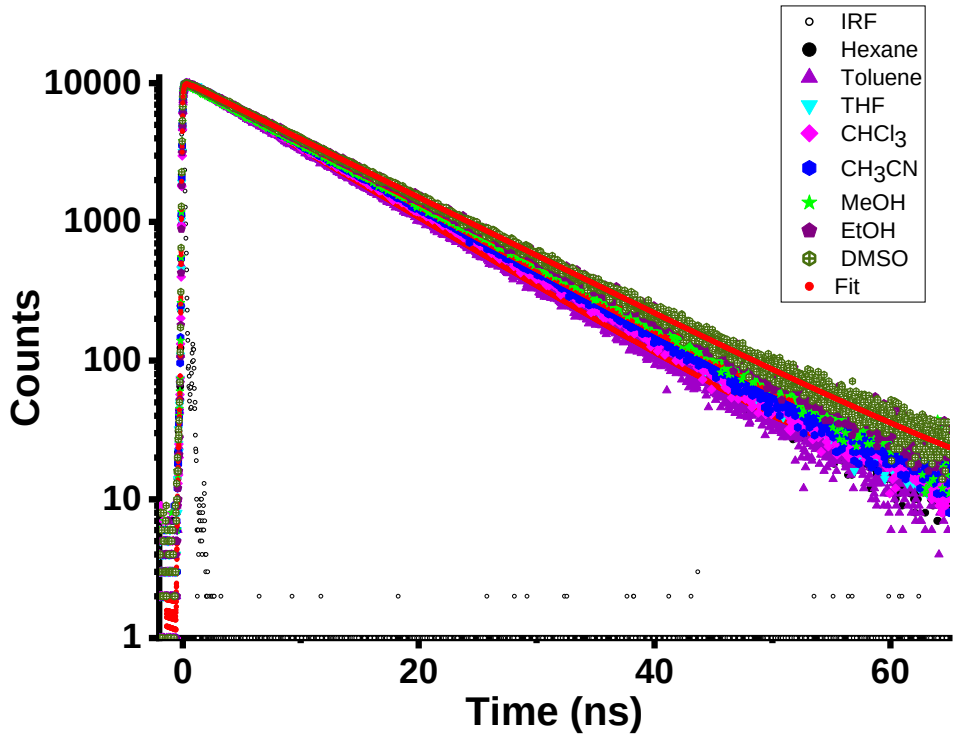


Figure S17c. Fluorescence lifetime of **n-H1** (4 μM) in different solvents.

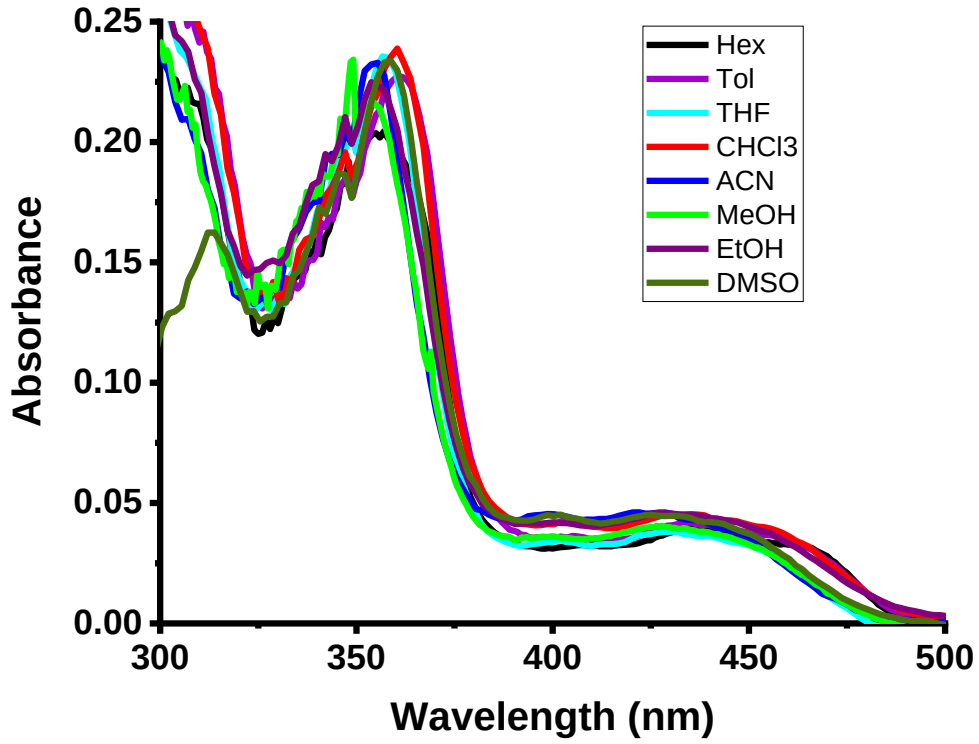


Figure S18a. Absorption spectra of **n-H2** (4 μM) in different solvents.

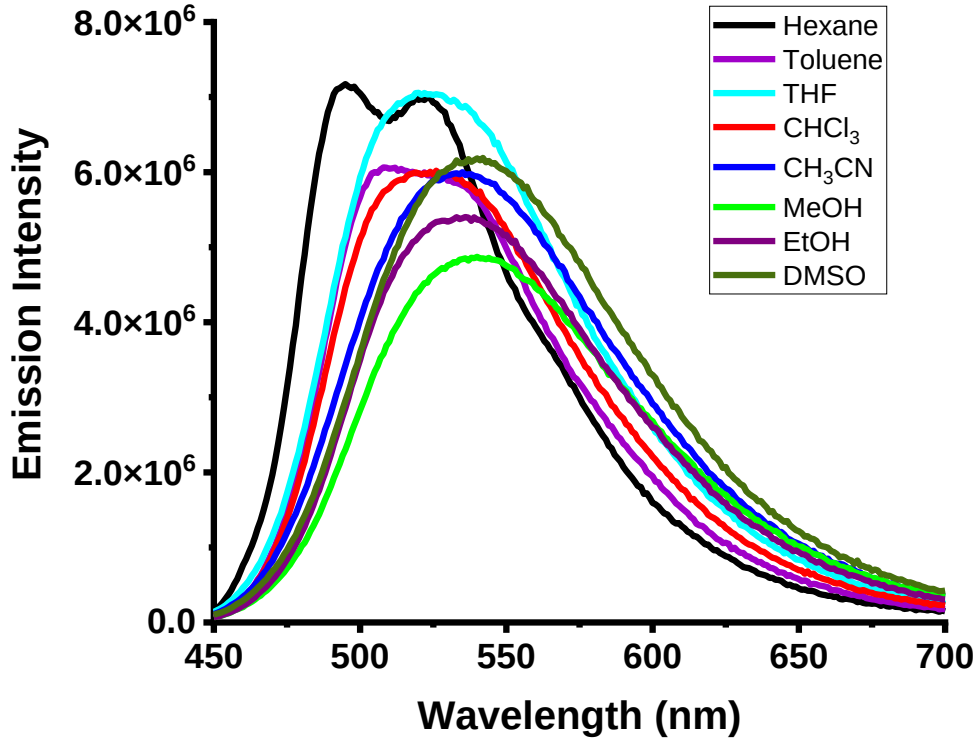


Figure S18b. Emission spectra of **n-H2** (4 μM) in different solvents (λ_{ex} = 431 nm).

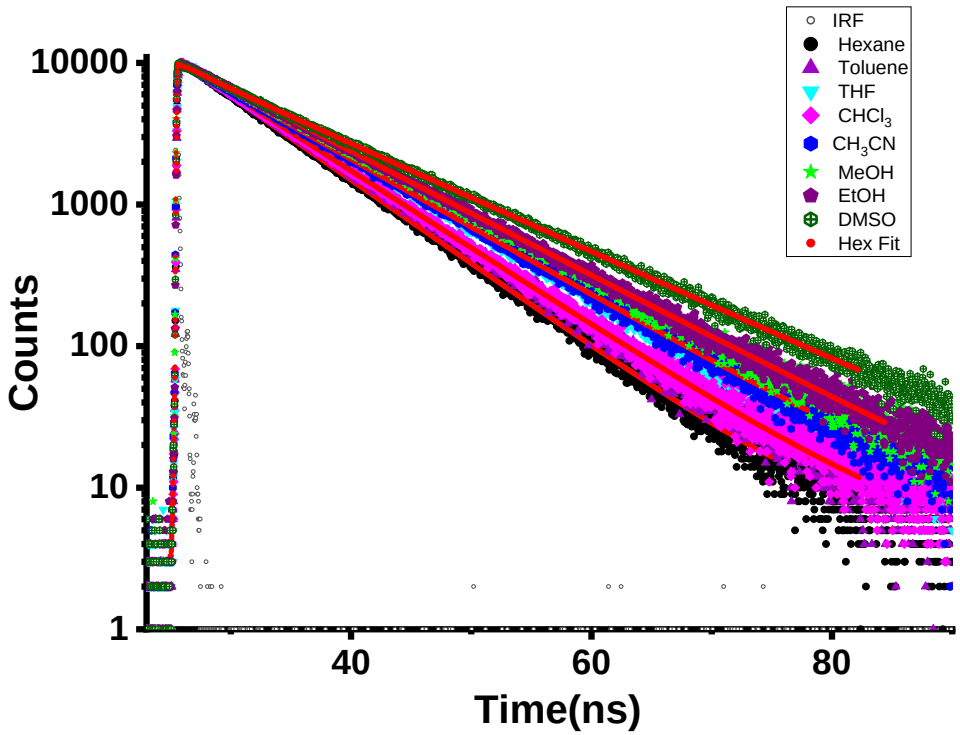


Figure S18c. Fluorescence lifetime of **n-H2** (4 μM) in different solvents.

11. FMO analysis

Gaussian 09 software was used to carry out all the theoretical studies.[S6] For bandgap calculations the geometry optimization were performed at 6-31G (d,p) level of theory in dichloromethane using CPCM model at 298.15 K and 1 atm. Frequency calculations were carried out to check the true minima of the optimized structures. For ground-state optimized geometries, it showed zero imaginary frequency. The effect of counter anions was not considered during geometry optimizations of cationic helicenes**.** Later, images of HOMO and LUMO were obtained from optimized geometry to check electronic distributions and the energy gap in between. Time-dependent (TD)-DFT calculations were carried out on the optimized structure using B3LYP/6-31g(d,p) as a basis set and CH_2Cl_2 was used as a solvent for calculations (CPCM model). The excited state energies along with the corresponding oscillator strengths (*f*) are listed in **Tables Sa-5b** and. The UV/Vis spectra (**Figure S19g**) were simulated using the GaussView5 visualization software package.

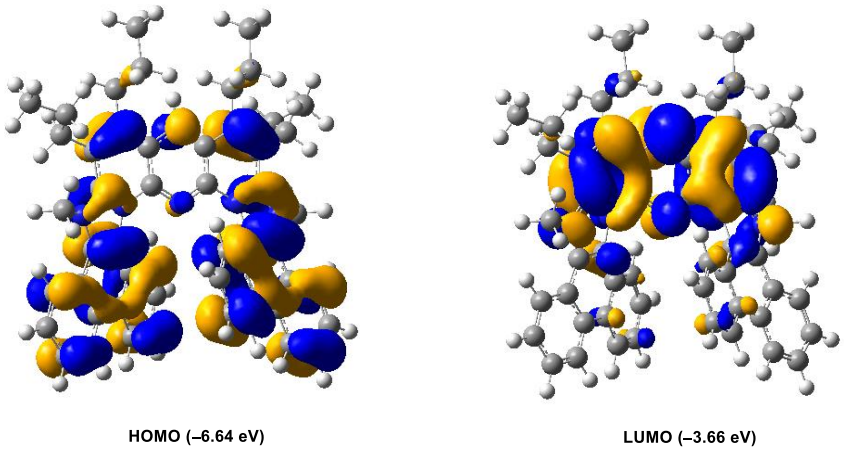


Figure S19a. Kohn-Sham frontier orbital representation and MO energies of **c-H1.**

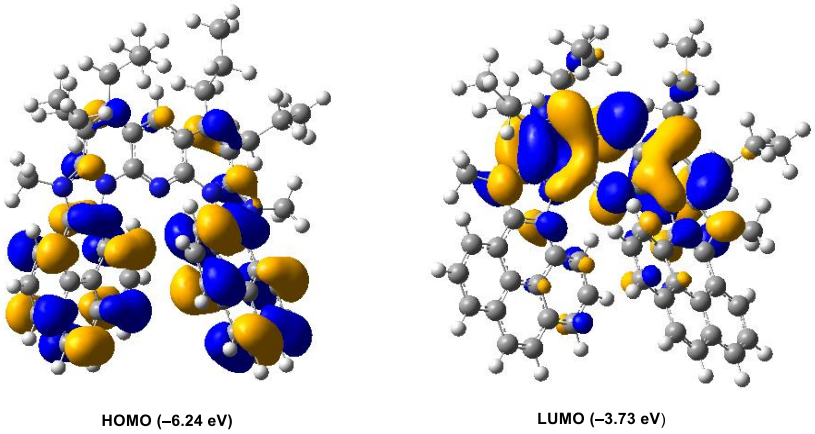


Figure S19b. Kohn-Sham frontier orbital representation and MO energies of **c-H2.**

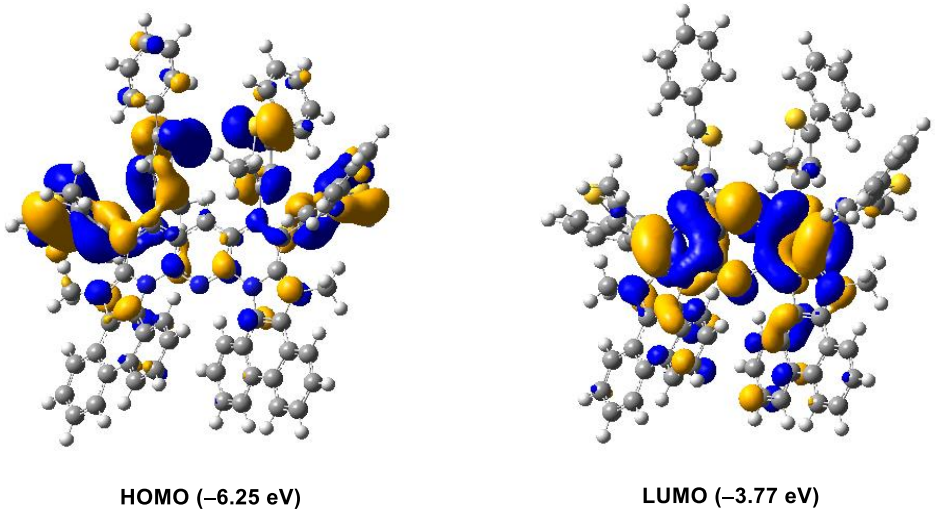


Figure S19c. Kohn-Sham frontier orbital representation and MO energies of **c-H3.**

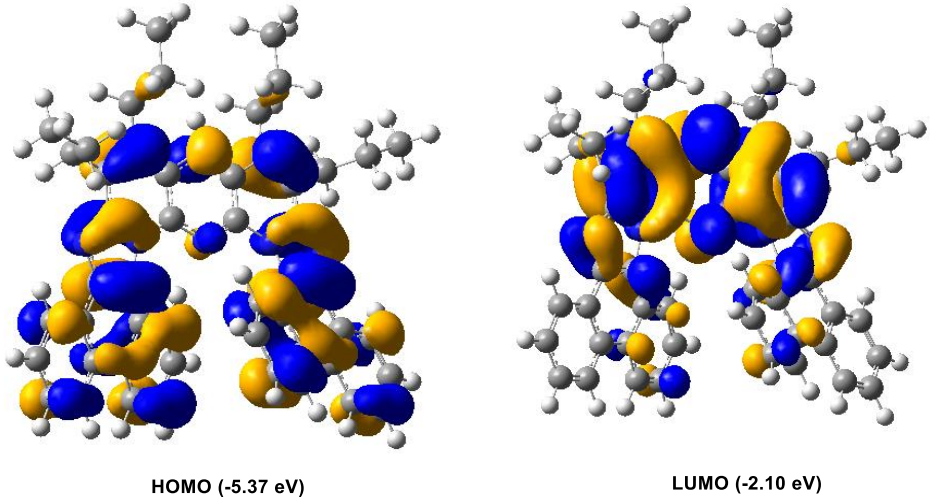


Figure S19d. Kohn-Sham frontier orbital representation and MO energies of **n-H1.**

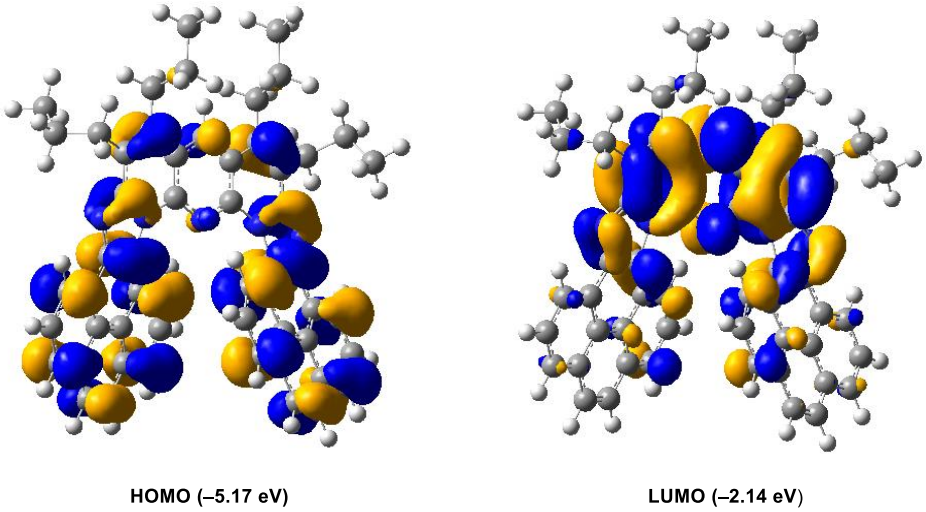


Figure S19e. Kohn-Sham frontier orbital representation and MO energies of **n-H2.**

Comparison of FMO between cationic and neutral sub-expanded helicenes

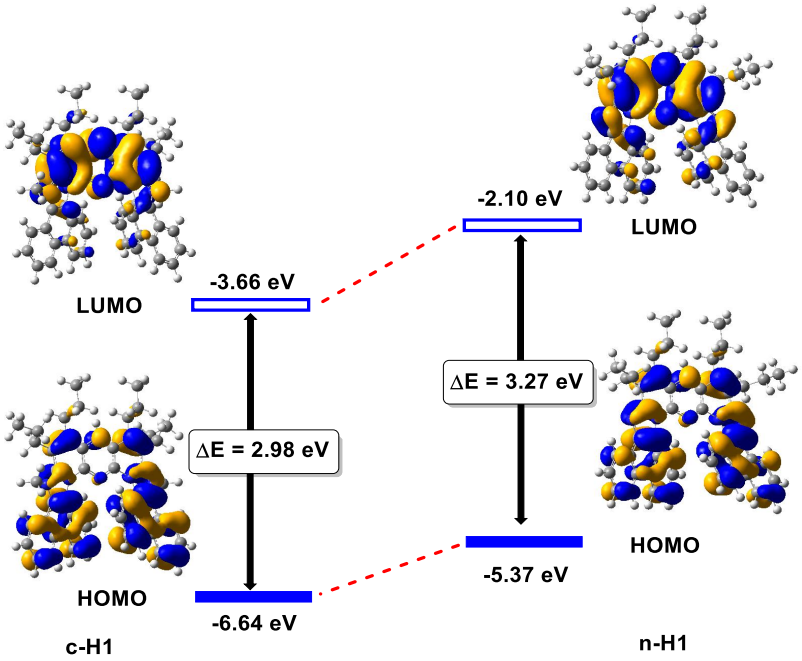


Figure S19f. FMO images of **c-H1** and **n-H1.**

We noticed that for cationic helicene HOMO is mostly delocalized over the phenanthrene or pyrene unit, where LUMO is localized on the cationic aza anthracene part of the helicene. But HOMO and LUMO are delocalized over the entire helical backbone of neutral helicenes. Interestingly, LUMO is more destabilized for neutral helicene (say **n-H1**) than corresponding cationic helicene **c-H1** (Figure S19a-d), resulting in higher bandgap values. Thus the cationic helicenes showed a red-shifted absorption spectrum compared to their corresponding neutral analogue.

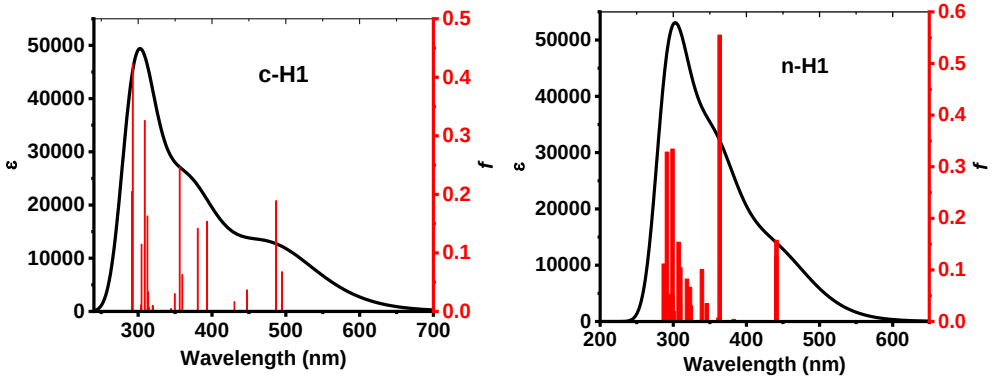


Figure S19g. TD-DFT-calculated UV/Vis absorption spectra of **c-H1** and **n-H1** calculated at B3LYP/6-31g(d,p), CPCM-CH_2Cl_2 level of theory.

Table S5a: TD-DFT-calculated UV/Vis absorption data for **c-H1** at the B3LYP/6-31g(d,p) (solvent CPCM-CH_2Cl_2) level of theory.

Calcd. λ [nm]	***f***	**Composition**	**Coefficient**	**Contribution (%)**
495.06	0.0677	HOMO-1 -> LUMO	0.69575	96.81
486.96	0.1890	HOMO -> LUMO	0.69580	96.82
447.32	0.0367	HOMO-2 -> LUMO	0.70030	98.08
430.38	0.0165	HOMO-3 -> LUMO	0.69837	97.54
393.43	0.1539	HOMO -> LUMO+1	0.69306	96.1
380.68	0.1419	HOMO-1 -> LUMO+1	0.69338	96.15
359.78	0.0631	HOMO-2 -> LUMO+1	0.69200	95.77
356.17	0.2468	HOMO-4 -> LUMO HOMO-3 -> LUMO+1 HOMO -> LUMO+3	0.65539 0.16822 -0.11748	85.90 5.61 2.76
349.49	0.0302	HOMO-4 -> LUMO HOMO-3 -> LUMO+1	-0.14564 0.67033	4.24 89.8
344.65	0.0048	HOMO-5 -> LUMO	0.69667	97.06
319.86	0.0100	HOMO-7 -> LUMO HOMO-6 -> LUMO HOMO-1 -> LUMO+2 HOMO -> LUMO+2 - HOMO -> LUMO+3 HOMO -> LUMO+4	0.37196 0.33931 0.22204 0.25116 0.24720 0.10028	27.67 23.02 9.86 12.61 12.22 2.01
319.54	0.0090	HOMO-7 -> LUMO HOMO-6 -> LUMO HOMO-4 -> LUMO+1 HOMO-1 -> LUMO+2 HOMO -> LUMO+2	-0.26729 0.48431 0.10813 -0.19309 -0.20398	14.28 46.91 2.33 7.45 8.32

		HOMO -> LUMO+3	0.23694	11.22
314.37	0.0077	HOMO-7 -> LUMO HOMO-3 -> LUMO+3 HOMO-2 -> LUMO+2 HOMO-1 -> LUMO+2 HOMO-1 -> LUMO+5 HOMO -> LUMO+4	0.46643 -0.11578 0.19051 -0.39954 0.10076 -0.13118	43.51 2.68 7.25 31.92 2.03 3.44
313.74	0.0333	HOMO-6 -> LUMO HOMO-2 -> LUMO+3 HOMO-1 -> LUMO+3 HOMO -> LUMO+2 HOMO -> LUMO+5	0.34767 0.17332 -0.25995 0.46586 -0.10293	24.17 6.00 13.51 43.40 2.11
312.54	0.1629	HOMO-4 -> LUMO+1 HOMO-3 -> LUMO+2 HOMO-2 -> LUMO+1 HOMO-2 -> LUMO+3 HOMO-1 -> LUMO+3 HOMO-1 -> LUMO+4 HOMO -> LUMO+2 HOMO -> LUMO+5	0.18219 -0.19528 0.10173 0.17245 0.53684 0.14771 0.13967 -0.16691	6.63 7.62 2.06 5.94 57.63 4.36 3.90 5.57
308.84	0.3259	HOMO-7 -> LUMO HOMO-4 -> LUMO HOMO-2 -> LUMO+2 HOMO-2 -> LUMO+5 HOMO-1 -> LUMO+2 HOMO -> LUMO+3	-0.14741 0.10208 -0.21581 0.10079 -0.37937 0.46475	4.34 2.08 9.31 2.03 28.78 43.19
304.54	0.1147	HOMO-4 -> LUMO+1 HOMO-3 -> LUMO+2 HOMO-2 -> LUMO+3 HOMO-2 -> LUMO+6 HOMO-1 -> LUMO+3 HOMO-1 -> LUMO+4 HOMO -> LUMO+2 HOMO -> LUMO+5	0.15087 0.30660 -0.14956 -0.11401 0.20914 0.31240 0.33273 0.25942	4.55 18.80 4.47 2.59 8.74 19.51 22.14 13.45
303.85	0.0109	HOMO-5 -> LUMO+1 HOMO-2 -> LUMO+2 HOMO-1 -> LUMO+2 HOMO-1 -> LUMO+5 HOMO -> LUMO+3 HOMO -> LUMO+4	-0.18387 0.39256 0.21129 0.18802 0.29507 -0.28487	6.76 30.82 8.92 7.07 17.41 16.23

292.58	0.4232	HOMO-6 -> LUMO HOMO-5 -> LUMO+1 HOMO-4 -> LUMO+1 HOMO-2 -> LUMO+3 HOMO-1 -> LUMO+3	-0.10905 0.12886 0.57671 0.20184 0.22962	2.37 3.32 66.51 8.14 10.54
291.73	0.2048	HOMO-8 -> LUMO HOMO-5 -> LUMO+1 HOMO-4 -> LUMO+1 HOMO-1 -> LUMO+5	0.18782 0.61073 -0.10608 0.15390	7.05 74.59 2.25 4.73

Table S5b: TD-DFT-calculated UV/Vis absorption data for **n-H1** at the B3LYP/6-31g(d,p) (solvent CPCM-CH_2Cl_2) level of theory.

Calcd. λ [nm]	***f***	**Composition**	**Coefficient**	**Contribution (%)**
441.10	0.1574	HOMO -> LUMO	0.69931	97.80
440.81	0.1256	HOMO-1 -> LUMO	0.70304	98.85
382.72	0.0041	HOMO-2 -> LUMO HOMO -> LUMO-1	-0.47437 0.50968	45.00 51.95
363.40	0.5551	HOMO-2 -> LUMO HOMO -> LUMO-1	0.50735 0.47110	51.41 44.38
361.86	0.0071	HOMO-3 -> LUMO HOMO-1 -> LUMO-1	0.28955 0.61928	16.76 76.70
345.82	0.0348	HOMO-3 -> LUMO HOMO-1 -> LUMO-1 HOMO -> LUMO+3	0.61308 -0.30524 -0.12258	75.17 18.63 3.00
339.16	0.1009	HOMO-4 -> LUMO HOMO-1 -> LUMO+3 HOMO -> LUMO+2	0.60922 0.17001 0.27360	74.23 5.78 14.97
324.04	0.0305	HOMO-3 -> LUMO HOMO-2 -> LUMO-1 HOMO-1 -> LUMO+2 HOMO -> LUMO+3 HOMO -> LUMO+5	0.11222 -0.32346 0.39781 0.39594 -0.16772	2.51 20.92 31.65 31.35 5.67

322.74	0.0664	HOMO-4 -> LUMO HOMO-3 -> LUMO-1 HOMO-2 -> LUMO+5 HOMO-1 -> LUMO+3 HOMO -> LUMO+2 HOMO -> LUMO+4	-0.31986 0.14634 0.12618 0.32215 0.46630 -0.11681	20.46 4.28 3.18 20.75 43.48 2.72
318.68	0.0823	HOMO-3 -> LUMO HOMO-2 -> LUMO-1 HOMO-2 -> LUMO+2 HOMO-1 -> LUMO+2 HOMO-1 -> LUMO+4 HOMO -> LUMO+3 HOMO -> LUMO+5	0.14438 0.35911 -0.12794 -0.21930 -0.25082 0.42878 0.11066	4.16 25.79 3.27 9.61 12.58 36.77 2.44
309.65	0.1045	HOMO-6 -> LUMO HOMO-2 -> LUMO-1 HOMO-1 -> LUMO+2 HOMO-1 -> LUMO+3 HOMO-1 -> LUMO+4 HOMO -> LUMO+3 HOMO -> LUMO+4 HOMO -> LUMO+5	-0.11660 0.36471 0.40184 -0.10243 -0.23609 -0.21867 -0.19905 -0.13978	2.71 26.60 32.29 2.09 11.14 9.56 7.92 3.90
309.06	0.0405	HOMO-3 -> LUMO-1 HOMO-2 -> LUMO-1 HOMO-1 -> LUMO+2 HOMO-1 -> LUMO+3 HOMO -> LUMO+4	0.10284 0.13517 0.13363 0.23924 0.58444	2.11 3.65 3.51 11.44 68.31
307.34	0.1538	HOMO-1 -> LUMO+3 HOMO -> LUMO+2 HOMO -> LUMO+4	0.51733 -0.39740 -0.19521	53.52 31.58 7.62
300.81	0.0192	HOMO-6 -> LUMO HOMO-5 -> LUMO HOMO-1 -> LUMO+2 HOMO -> LUMO+5	0.24107 -0.16679 0.26399 0.55915	11.62 5.56 13.93 62.52
298.96	0.3342	HOMO-5 -> LUMO HOMO-2 -> LUMO-1 HOMO-2 -> LUMO+2 HOMO-1 -> LUMO+2 HOMO-1 -> LUMO+4 HOMO-1 -> LUMO+5 HOMO -> LUMO+3	-0.27861 0.22954 0.11648 0.11933 0.48473 0.57661 0.17287	15.52 10.53 2.71 2.84 46.99 66.49 5.97
298.85	0.0516	HOMO-5 -> LUMO HOMO-3 -> LUMO-1 HOMO-2 -> LUMO+3	0.10970 -0.23603 -0.11306	2.40 11.14 2.55

		HOMO-1 -> LUMO+4 HOMO-1 -> LUMO+5 HOMO -> LUMO+4	-0.16097 0.57661 0.14596	5.18 66.49 4.26
297.22	0.0200	HOMO-6 -> LUMO HOMO-5 -> LUMO HOMO-4 -> LUMO-1 HOMO-2 -> LUMO-1 HOMO -> LUMO+5	0.53745 0.32834 0.19961 0.14589 -0.15281	57.77 21.56 7.96 4.25 4.67
296.39	0.0525	HOMO-3 -> LUMO-1 HOMO-2 -> LUMO+3 HOMO-1 -> LUMO+5 HOMO -> LUMO+2	0.60696 -0.15598 0.22164 -0.13789	73.68 4.86 9.82 3.80
291.30	0.3283	HOMO-6 -> LUMO HOMO-5 -> LUMO HOMO-4 -> LUMO-1 HOMO-2 -> LUMO-1 HOMO-1 -> LUMO+4 HOMO -> LUMO+3 HOMO -> LUMO+5 HOMO -> LUMO+6	-0.32283 0.46317 0.15009 0.10479 0.22315 0.10341 0.22979 -0.10272	20.84 42.90 4.50 2.19 9.95 2.13 10.56 2.11
287.00	0.1115	HOMO-6 -> LUMO HOMO-5 -> LUMO HOMO-4 -> LUMO-1 HOMO-2 -> LUMO+2 HOMO-1 -> LUMO+4	-0.11644 -0.14923 0.57799 0.22457 -0.17017	2.71 4.45 66.81 10.08 5.79

12. Reversible Acid Base Switching and Contraction-Expansion of the Neutral Heterohelicenes

For the evaluation of effects of acid, triflic acid (2.5 equiv. or 5.0 equiv.) was added to a 20 μM solution of **n-H1** or **n-H2** in $CHCl_3$ (2 mL). Further, to recover (for deprotonation) the original compound Et_3N (5.0 equiv.) was added to the protonated solution of **n-H1** or **n-H2** in $CHCl_3$.

(A)

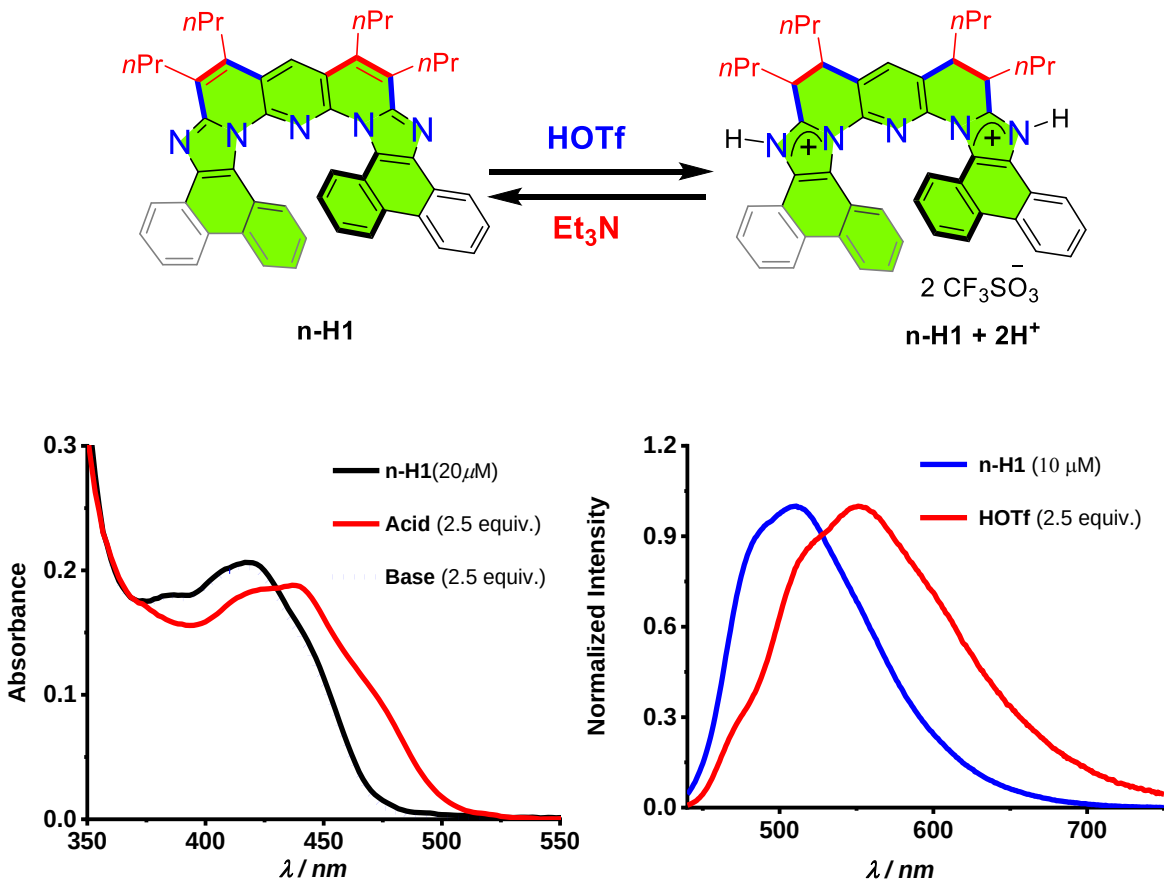


Figure S20. Absorption spectra (left) and Emission spectra (right) of **n-H1** in $CHCl_3$ upon addition of 5.0 equiv. Triflic acid (HOTf), followed by 5.0 equiv. Triethylamine (Et_3N). Excitation wavelength = 420 nm.

(B)

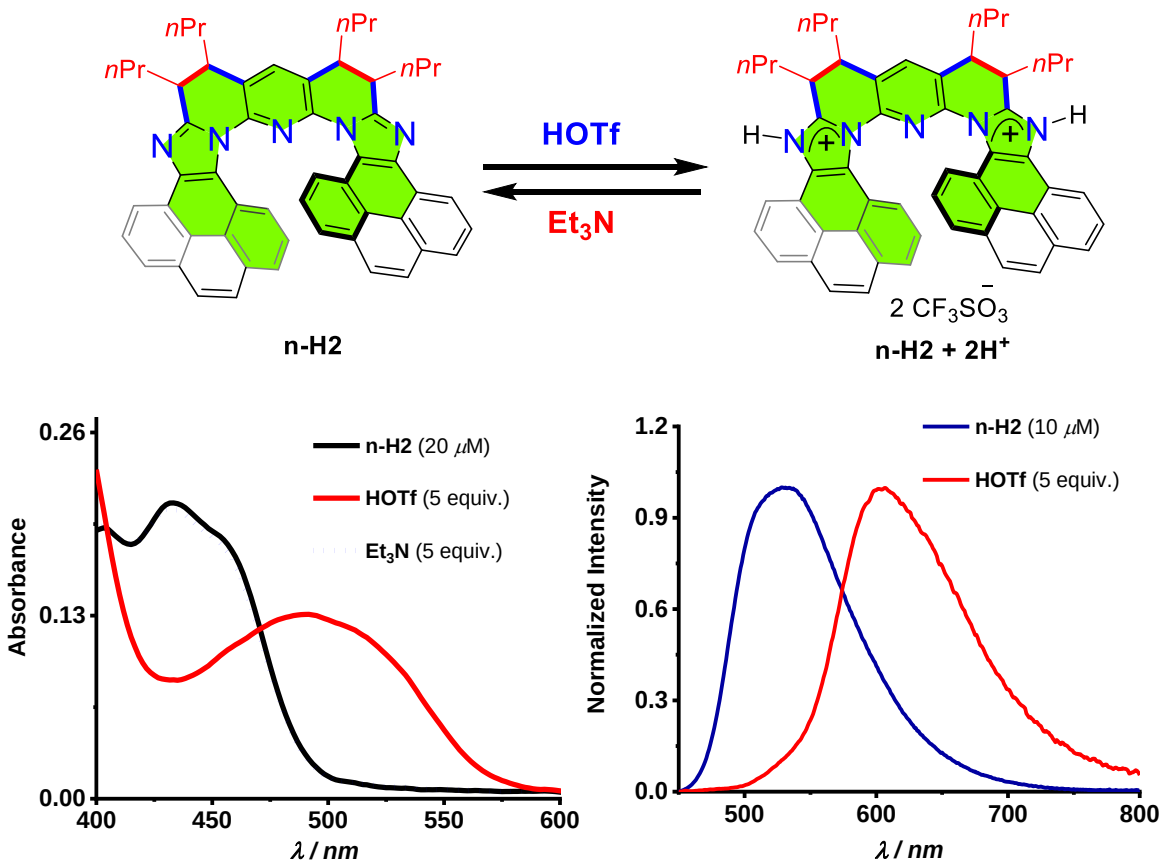


Figure S21. Absorption spectra (left) and Emission spectra (right) of **n-H2** in $CHCl_3$ upon addition of 5.0 equiv. Triflic acid (HOTf), followed by 5.0 equiv. Triethylamine (Et_3N). Excitation wavelength = 440 nm.

(C) Computational Studies for Contraction-Expansion of the Helical Pitch upon protonation/deprotonation

The geometry optimization were performed at 6-31G (d,p) level of theory in dichloromethane using CPCM model at 298.15 K and 1 atm. Frequency calculations were carried out to check the true minima of the optimized structures. For ground-state optimized geometries, it showed zero imaginary frequency. The distance shown below is the helical pitch i.e., centroid-to centroid distance). The results suggest that upon protonation there is construction of helical pitch.

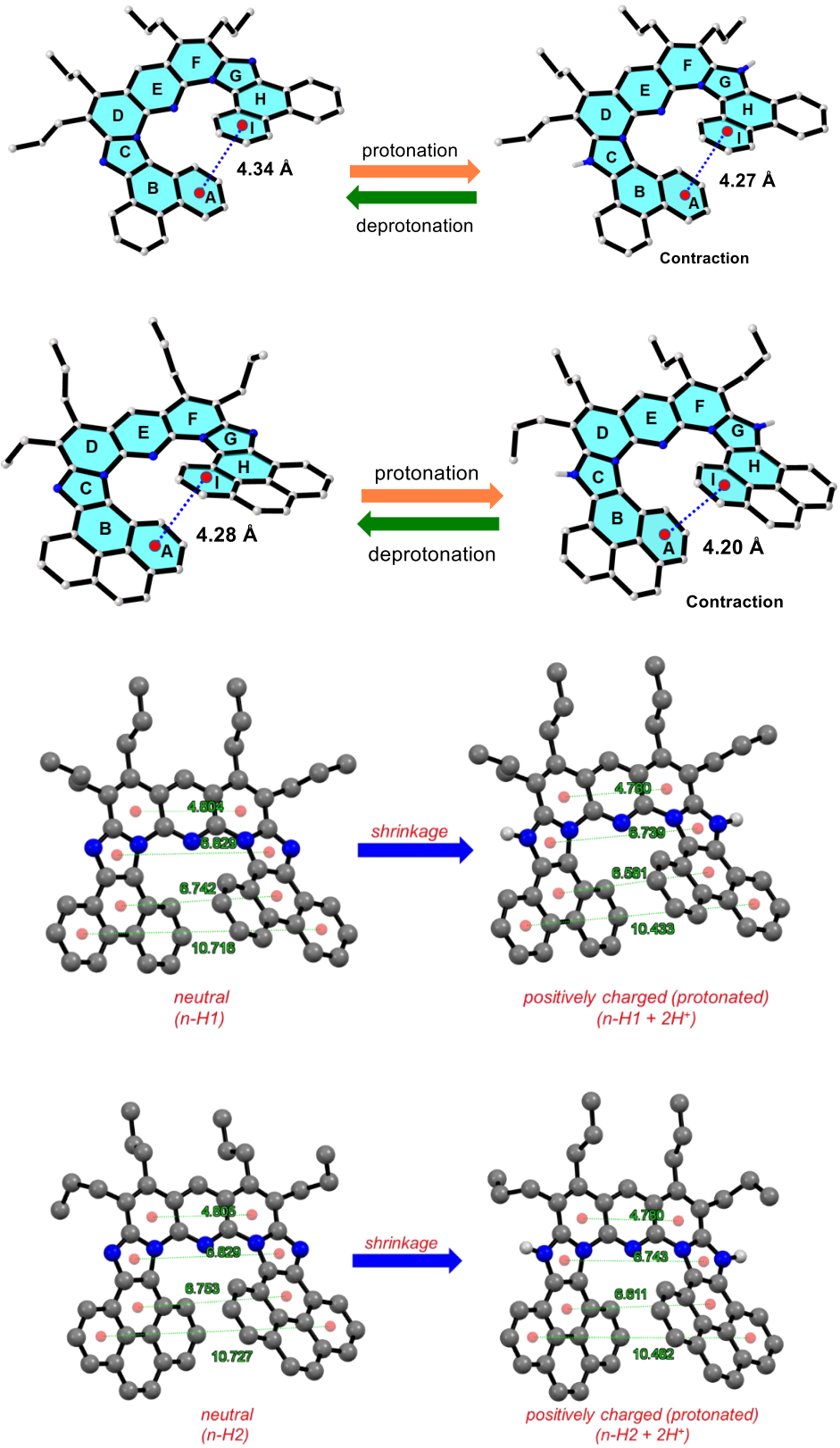


Figure S22. Optimized geometry calculated at 6-31G (d,p) level of theory in dichloromethane using CPCM model.

13. Reversible Photochromic Properties

For photochromic studies, a 1.0 mM stock solution of **c-H3** was prepared in acetonitrile under dark conditions. From the freshly prepared 1.0 mM stock solution of **c-H3**, a particular amount (60 µL or 20 µL) stock was used in 2 mL acetonitrile in a quartz cuvette for different UV-vis studies. Absorption spectra of **c-H3** were recorded in the dark, and the same solution was subjected to blue light (blue LED, 2.25 mW/cm^2) irradiation for 5-10 min with stirring and spectra were recorded without disturbing the solutions. Similarly, for reverse photoreaction, red LED (1.55 mW/cm^2) was used for irradiation of solution (green) for a relatively long time (40-50 min). All the experiments were carried out in a quartz cuvette at room temperature (25°C).

For reversibility experiments (see **Figure S23f**), 20 µL of 1.0 mM **c-H3** was added to 2 mL acetonitrile to make a 10 µM solution in a quartz cuvette. The same solution (10 µM) was irradiated with blue LED light (2.25 mW/cm^2) for 3 min, and red LED light (1.55 mW/cm^2) for 45 min respectively with stirring in every cycle (i.e., photocyclization/photoreversion reactions). The absorption spectra were recorded without disturbing the solution. The temperature was maintained at 25 °C throughout the experiments. Monitoring wavelength = 654 nm.

(a) Photochromism of c-H3 in acetonitrile

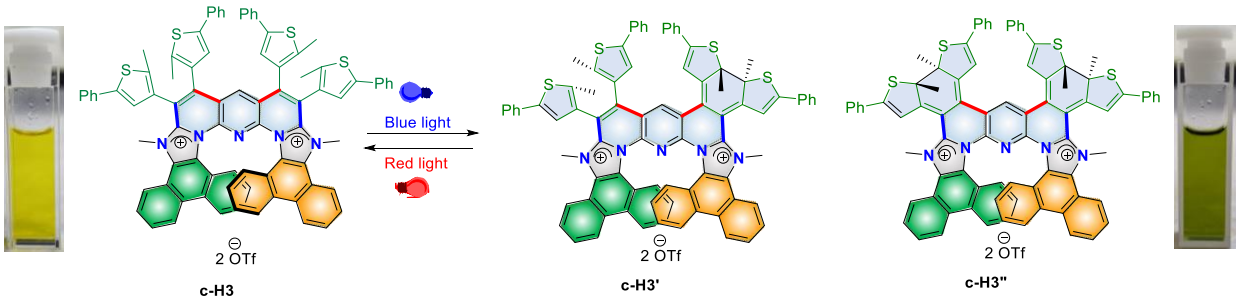


Figure S23a. Reversible ring-closing/ring-opening of **c-H3.**

(b) UV-Vis studies in acetonitrile upon blue light irradiation

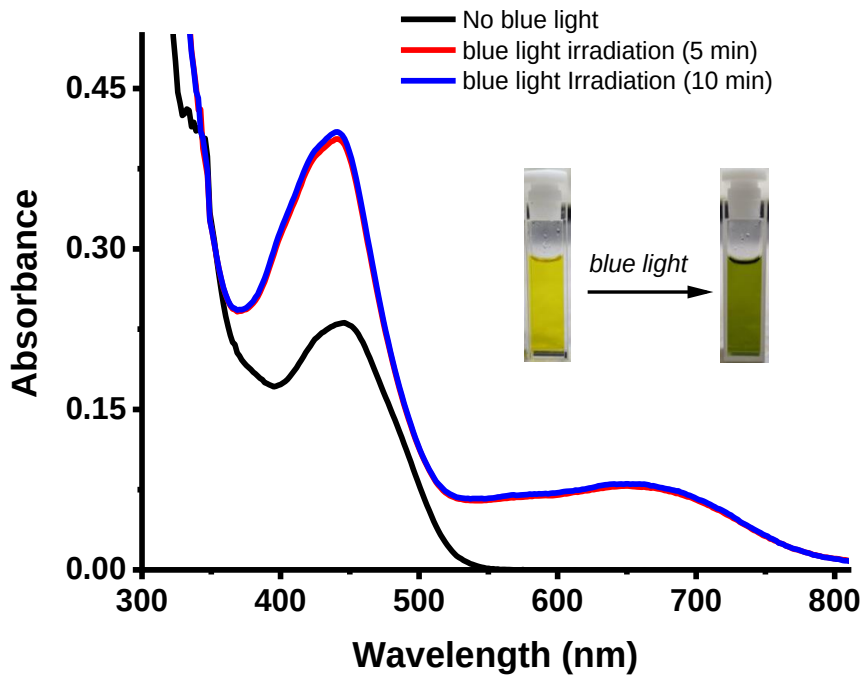


Figure S23b. Absorption spectra of **c-H3** (10 μM)) in CH_3CN before and after LED blue light (2.25 mW/cm^2) irradiation.

(c) Emission studies in acetonitrile upon blue light irradiation

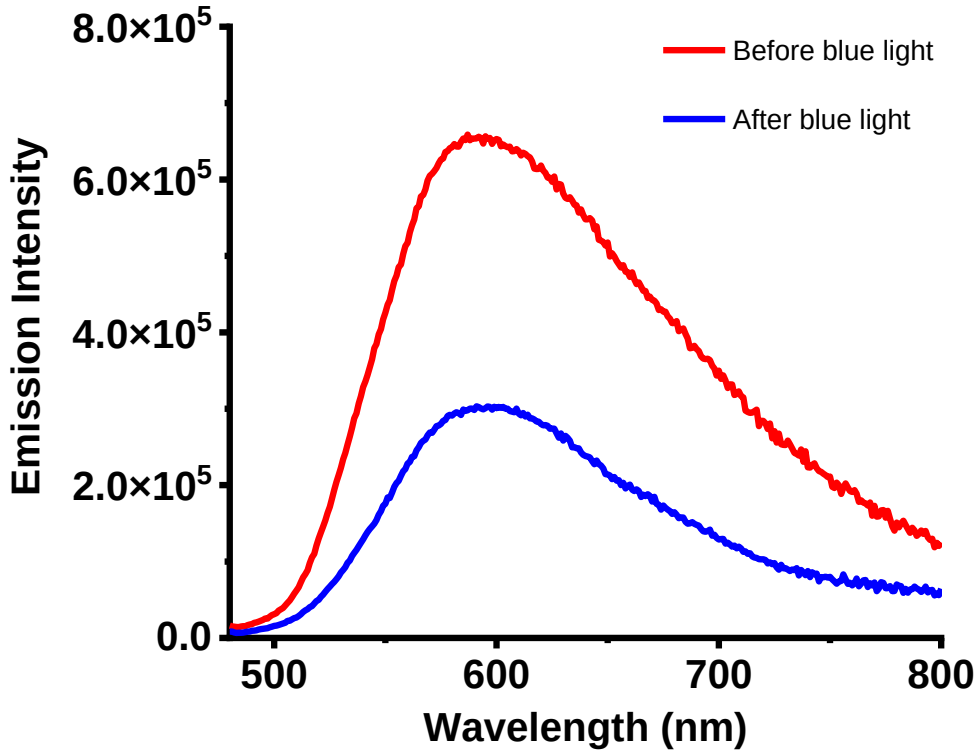


Figure S23c. Emission spectra of **c-H3** (10 μM) in $CHCl_3$ before and after blue light (2.25 mW/cm^2) irradiation for 2 min. Excitation wavelength = 440 nm.

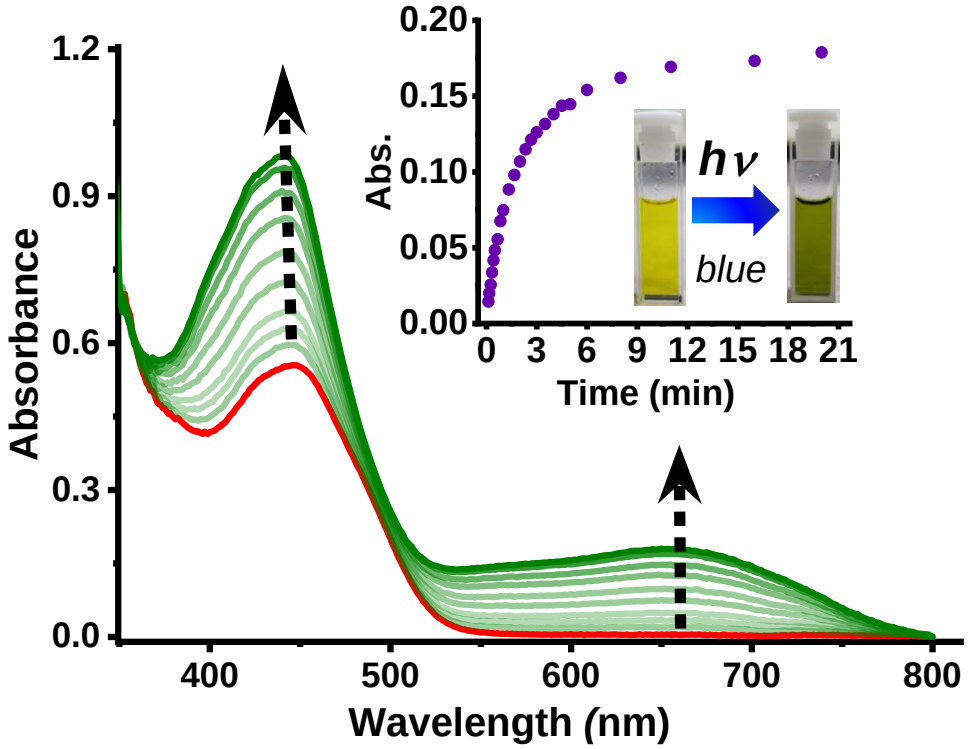


Figure S23d. UV-vis spectra of **c-H3 (**30 μM) upon irradiation of blue light (2.25 mW/cm^2) for a time period of 20 min in CH_3CN.

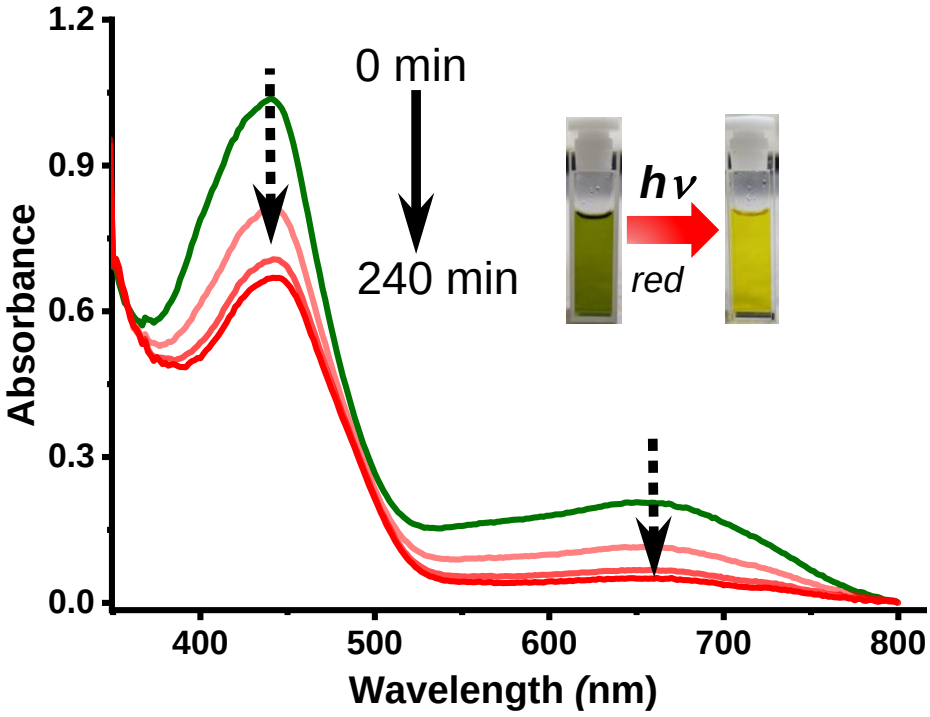


Figure S23e. UV-vis spectra of **c-H3'** (30 μM) upon irradiation of red light (1.55 mW/cm^2) for a time period of 0 to 240 min in CH_3CN.

(d) UV-Vis studies in acetonitrile for reversibility

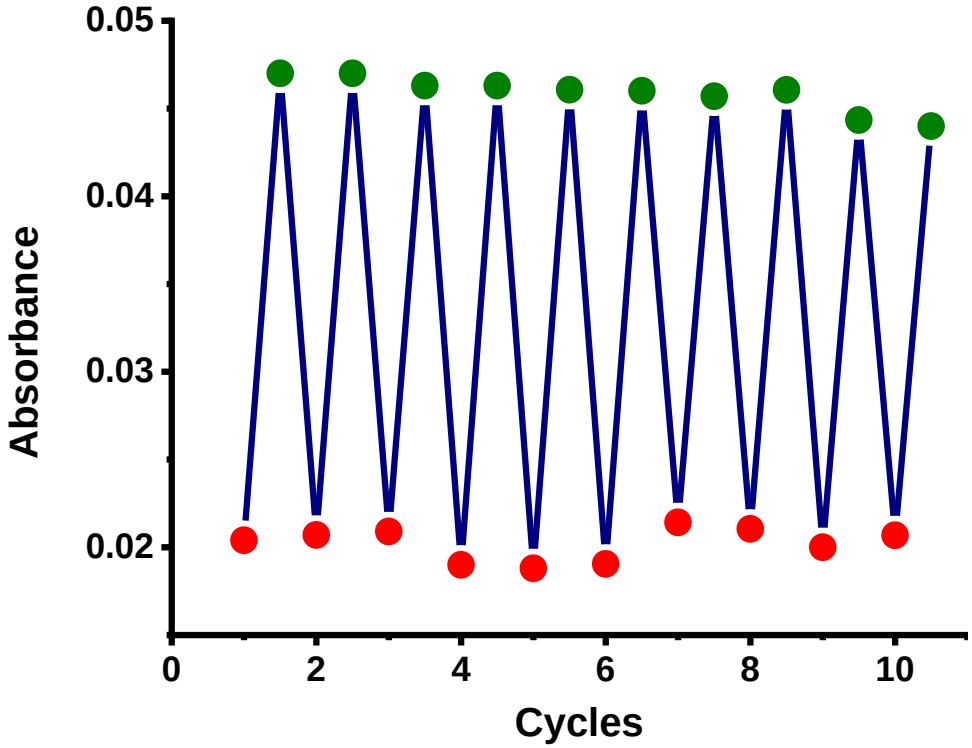


Figure S23f. Reversibility plot of **c-H3** (10 μM) upon alternative irradiation of blue light (2.25 mW/cm^2) for a time period of 3 min and red light (1.55 mW/cm^2) for 45 min in CH_3CN. Monitoring wavelength = 654 nm.

(e) Photochromism in PMMA gel

1.2 mg **c-H3** and 52 mg poly(methyl methacrylate) (PMMA) (2.3 wt.%) was dissolved in a mixture of acetonitrile (0.5 mL) and propylene carbonate (0.5 mL) and coated on a flexible PET surface (3 cm × 1.5 cm), dried at 60 °C for overnight under dark. A schematic diagram of the device is shown below

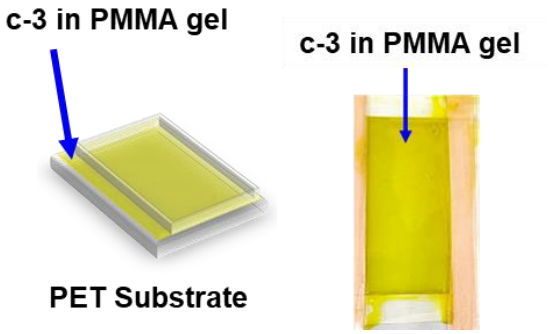


Figure S23g. Schematic representation of the device.

(f) UV-Vis and emission studies in PMMA gel

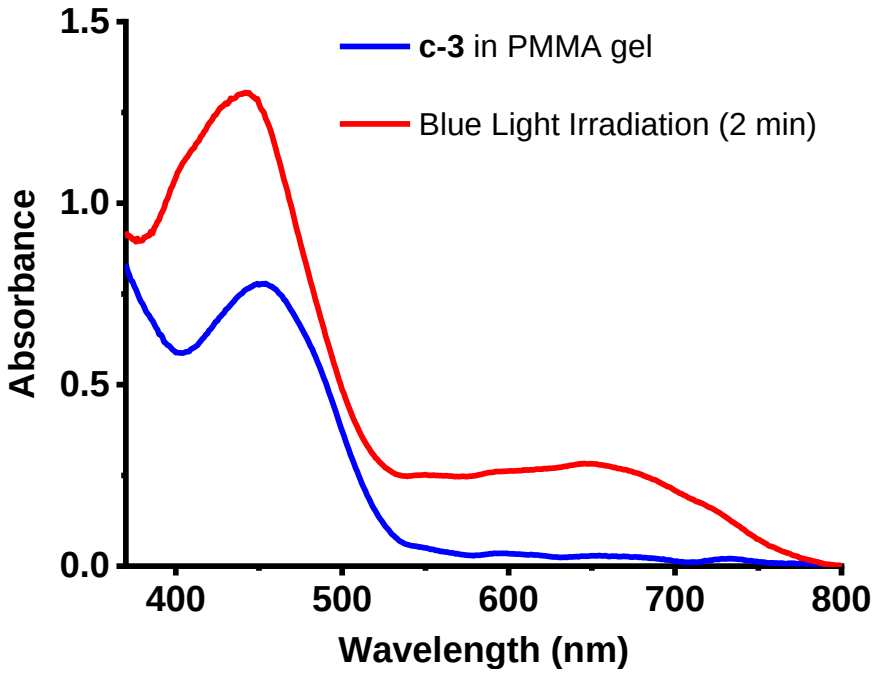


Figure S23h. Absorption spectra of **c-H3** in PMMA gel upon blue light (5.10 mW/cm^2) irradiation for 2.0 min.

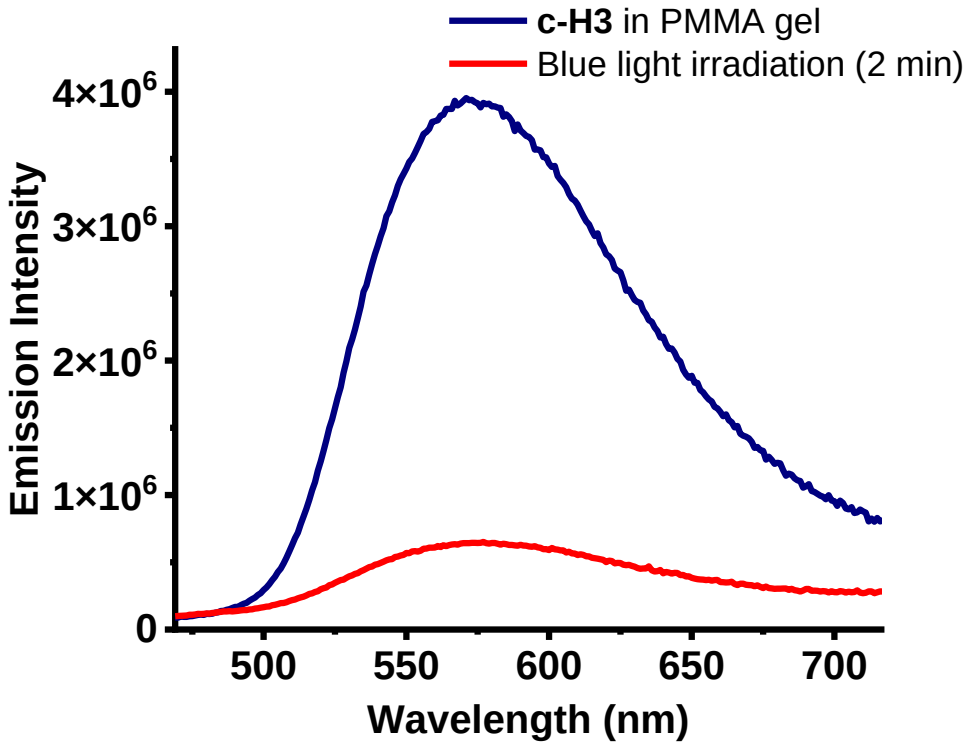


Figure S23i. Emission spectra of **c-H3** in PMMA gel upon blue light (5.10 mW/cm^2) irradiation for 2.0 min. Excitation wavelength = 440 nm.

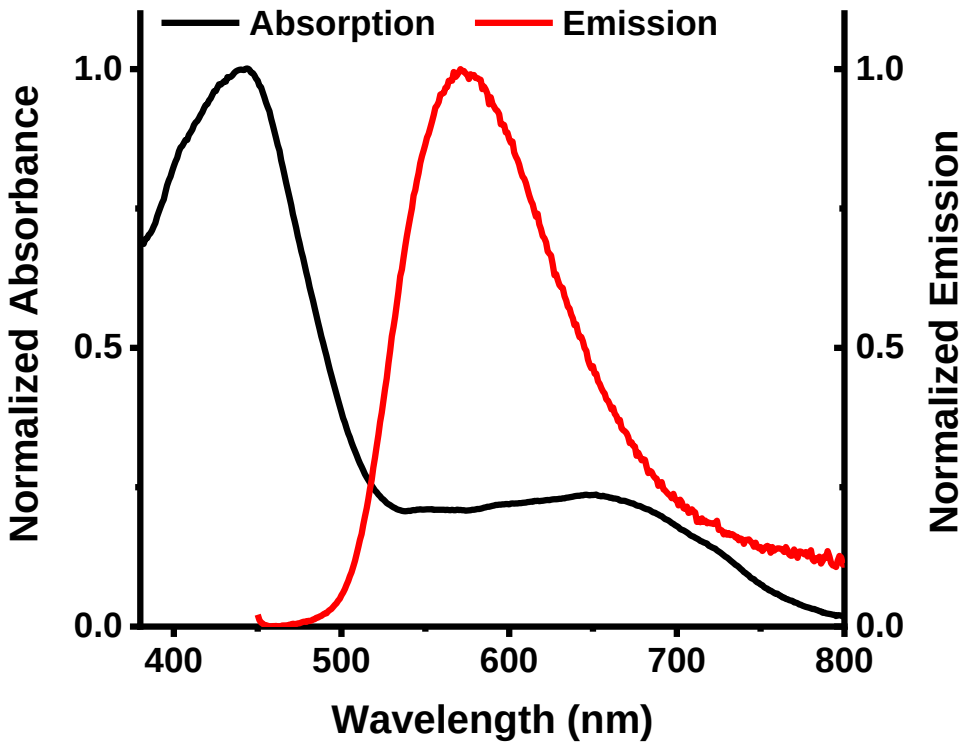


Figure S23j. Absorption and Emission spectral overlap of **c-H3** in PMMA gel.

(g) UV-Vis studies in PMMA gel for reversibility

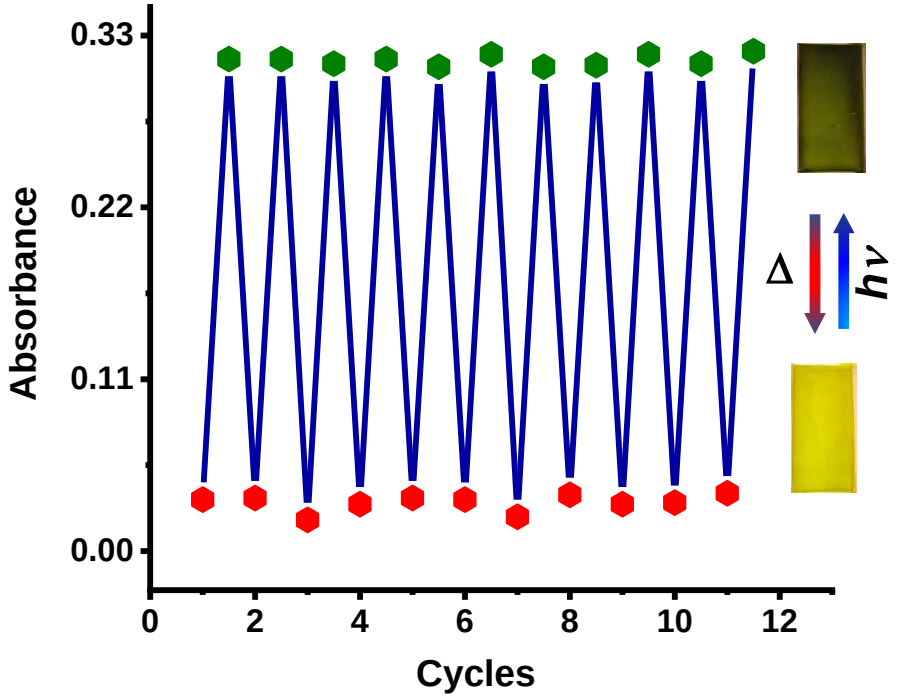


Figure S23k. Reversibility plot of **c-H3** in PMMA gel upon alternative irradiation of blue light (5.10 mW/cm^2) for a time period of 2.5 min and heating with hot air flow (~100 °C) for 3 min. Monitoring wavelength = 654 nm.

14. Visible Light-Triggered Soft Molecular Spring-Like Motion

Initially, geometry optimizations were carried out at B3LYP/6-31g(d,p) for **c-H3/c-H3'** level of theory in the gas phase to reduce the computational cost. The distance between the two carbon atoms at the end of the molecule was r = 5.39 and 5.60 Å for **c-H3, c-H3',** respectively. A relaxed potential energy surface was scanned with 10 steps in 0.2 Å increments. Where molecular geometry was optimized in each step with a fixed distance between the two carbon atoms (r). The change of potential energy upon elongation of the distance between two carbon atoms is plotted and fitted based on the following equation

$$y = Ax^2 \ldots\ldots\ldots (1)$$

where the coefficient A has the unit of kJ·mol^{-1}·Å^{-2}. By comparing the equation 1 with $\Delta E=(1/2)\cdot k\cdot(\Delta r^2)$, where E = relative energy, k = force constant, and r = the elongation of the distance between the two carbon atoms at the edge of the molecule, the force constant k (N·m^{-1}) was calculated from A (kJ·mol^{-1}·Å^{-2}) as follows: $k=(2\times10^{23}\cdot N_A^{-1})\cdot A$, where N_A is the Avogadro constant. From this result, the force constant of the molecular spring was determined.

(A) Effect of light on molecular spring **c-H3**

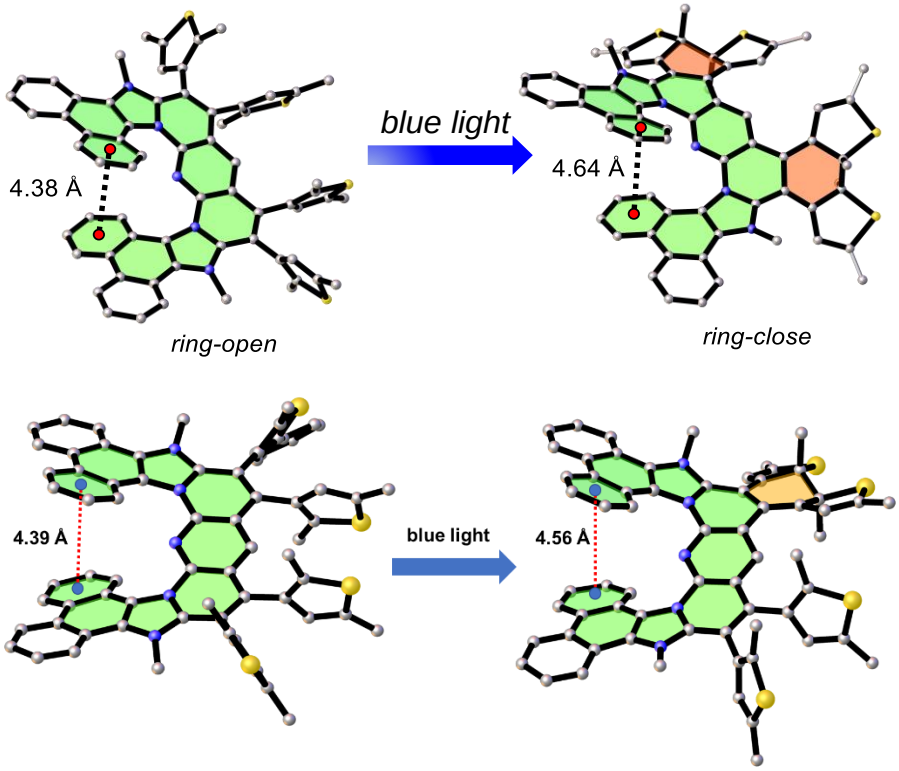


Figure S24a.Optimized geometry of ring-open and ring-close isomer of **c-H3** at B3LYP/6-31g(d,p) CPCM-CH_3CN level of theory. The distance shown is centroid to centroid distance between two terminal rings. Ph-groups are not shown here for clarity.

(i) Spring constant at B3LYP/6-31g(d,p) level of theory for **c-H3**

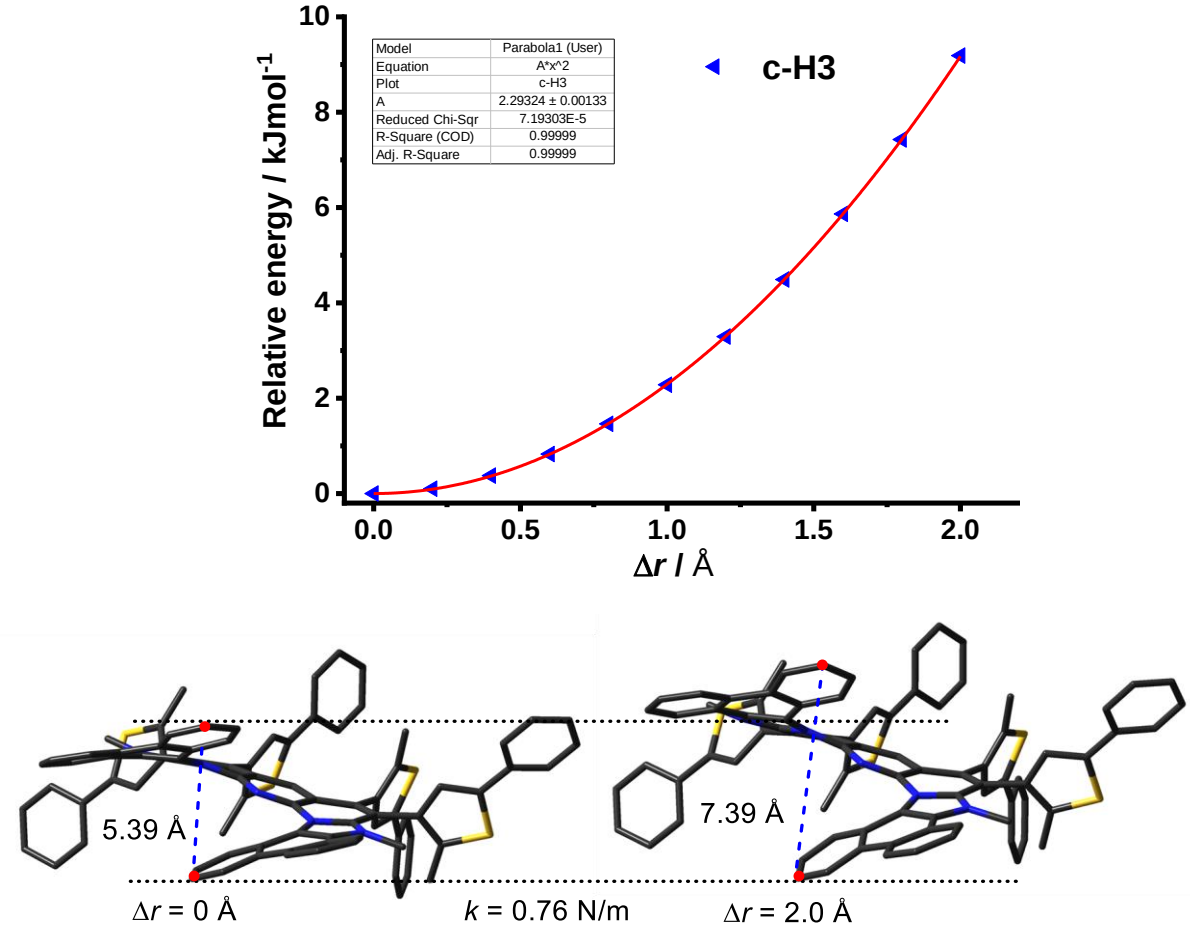
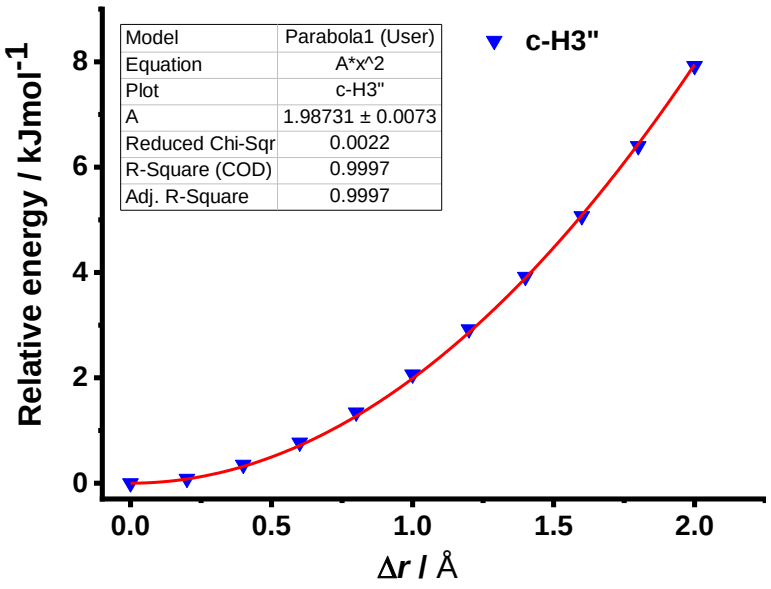


Figure S24c. Spring constant at B3LYP/6-31g(d,p) level of theory for **c-H3**

(ii) Spring constant at B3LYP/6-31g(d,p) level of theory for **c-H3''**



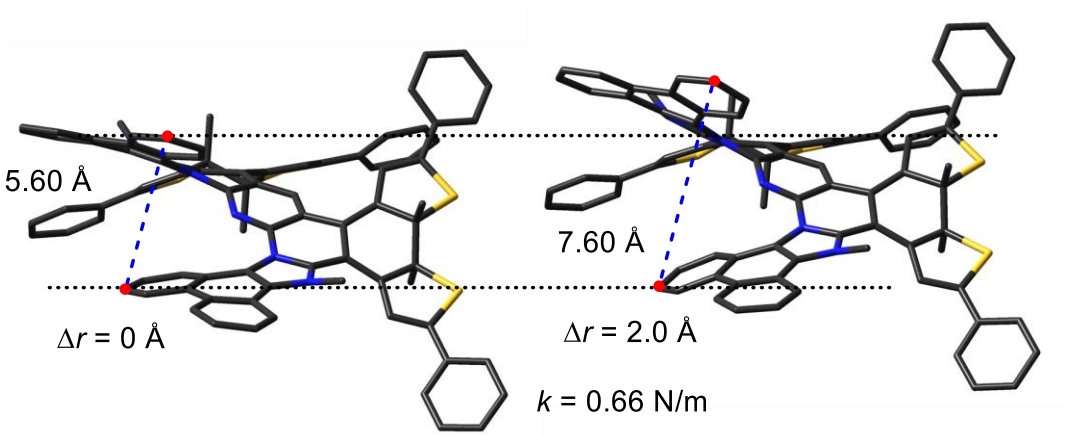


Figure S24d. Spring constant at B3LYP/6-31g(d,p) level of theory for **c-H3''**

Spectroscopic Ellipsometry

Thin film preparation

Thin-film was prepared by spin coating at 35 °C (angular speed 400-700 rpm) on a silicon substrates using a solution of 12 wt% **c-H3** (0.7 mg) in PMMA (~6 mg) in 1.0 mL acetonitrile. The solution was stirred for 2 h under dark condition before spin-coating. For spin-casting 20-30 μL of the solution was taken and spin casted. The spin-casting procedure was 400 rpm for initial 5 min and then 700 rpm for additional 25 min.

Spectroscopic ellipsometry measurements

Spectroscopic ellipsometry data were recorded using a J. A. Woollam (Lincoln, USA) model M-2000V variable angle Spectroscopic Ellipsometer (SE) with the Complete EASE software in the 370–1000 nm wavelength range. Initially, the ellipsometer was calibrated using ellipsometry standards silicon wafers (thermally grown silicon dioxide). The samples were coated on blank Si-wafer substrate. We performed the measurements in a dark room at room temperature varying the angles of incidence (55°,60°, 65°). The spot size on the sample was on the order of a few mm^2. The sample position was kept fixed strictly throughout the experiments, i.e., during the *in situ* blue light irradiation or heating the sample. The data analysis has been carried out using the CompleteEASE software. The data were fitted with a suitable model (B-Spline) for absorbing film and verified by Mean Squared Error (MSE) values.

The Mean Squared Error (MSE) function is defined as

$$\mathrm{MSE}^2 = \frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{exp}-\Psi_i^{calc}}{\sigma_{\Psi,i}^{exp}}\right)^2 + \left(\frac{\Delta_i^{exp}-\Delta_i^{calc}}{\sigma_{\Delta,i}^{exp}}\right)^2\right] = \frac{1}{2N-M}\chi^2$$

where N is the number of wavelengths, M the number of free parameters and $\sigma_{\Psi,i}^{exp}$ and $\sigma_{\Delta,i}^{exp}$ are the standard deviations of the experimental data point.[7]

(a) SE spectra of thin film (sample 1) of **c-H3** (thickness ~125.08 nm)

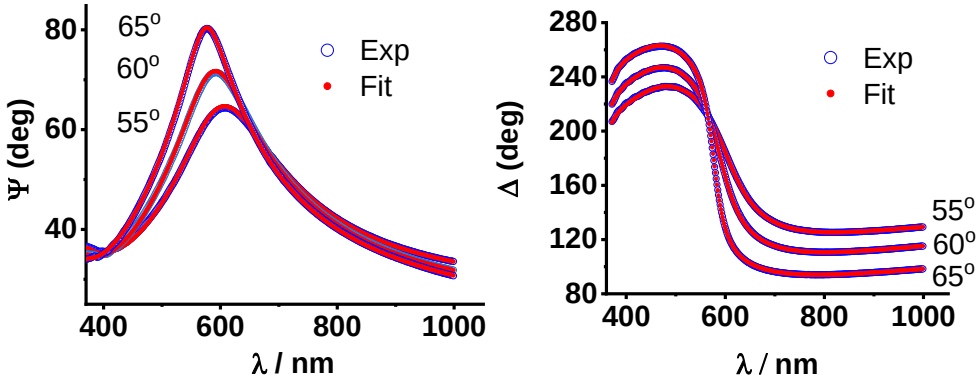


Figure S25a. Comparison between experimental and simulated (best-fit) SE spectra of a PMMA thin film of **c-H3.**

(b) SE spectra of thin film (sample 1)of **c-H3** after blue light irradiation

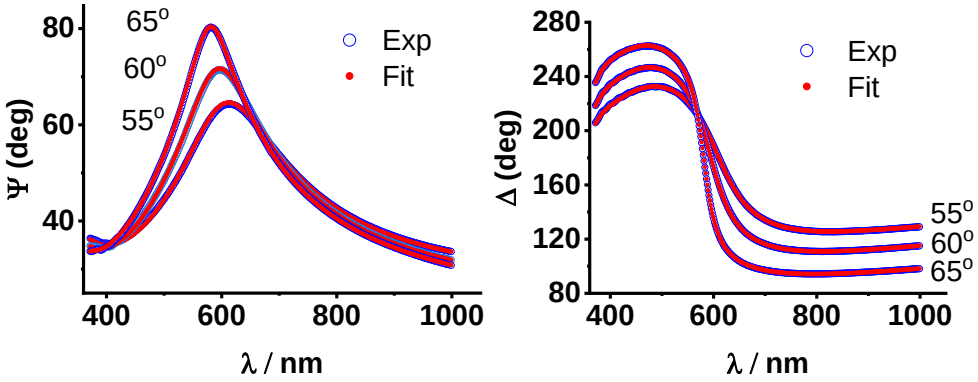


Figure S25b. Comparison between experimental and simulated (best-fit) SE spectra of a PMMA thin film of **c-H3** upon 6 min blue light (5.10 mW/cm^2) irradiation.

(c) SE spectra of thin film (sample 1) of after heating the light irradiated thin film

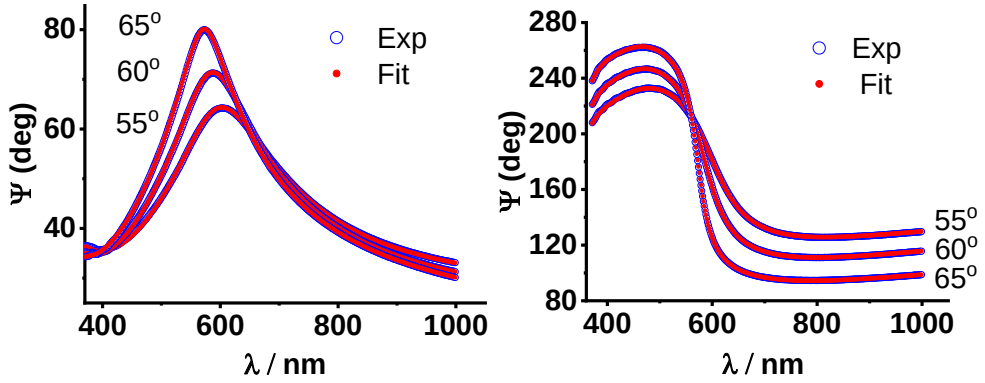


Figure S25c. Comparison between experimental and simulated (best-fit) SE spectra of a PMMA thin film of **c-H3** upon 6 min blue light (5.10 mW/cm^2) irradiation, followed by heating (~80 ^{o}C for 3 min).

Table S6: Summary of thickness changes

Sample 1	**Value**	**MSE**	**Δn**	**Δk**
Initial thickness, d_i (nm)	125.08	3.49	0.00635	0.00267
After blue light, d_f (nm)	127.25	3.34		
Change, $d_f - d_i$ (Å)	(+) 21.70	-		
After heat, $d_{i'}$ (nm)	124.83	3.14		

Sample 2	**Value**	**MSE**	**Δn**	**Δk**
Initial thickness, d_i (nm)	107.42	8.25	0.00634	0.00314
After blue light, d_f (nm)	108.97	8.44		
Change, $d_f - d_i$ (Å)	(+) 15.5	-		
After heat, $d_{i'}$ (nm)	107.96	8.17		
Sample 3	**Value**	**MSE**	**Δn**	**Δk**
Initial thickness, d_i (nm)	257.06	8.77	0.0042	0.0011
After blue light, d_f (nm)	259.94	9.39		
Change, $d_f - d_i$ (Å)	(+) 28.8	-		
After heat, $d_{i'}$ (nm)	255.83	16.36		

15. ^{1}H, $^{13}C\{^{1}H\}$, & ^{19}F NMR and ESI Mass Spectra

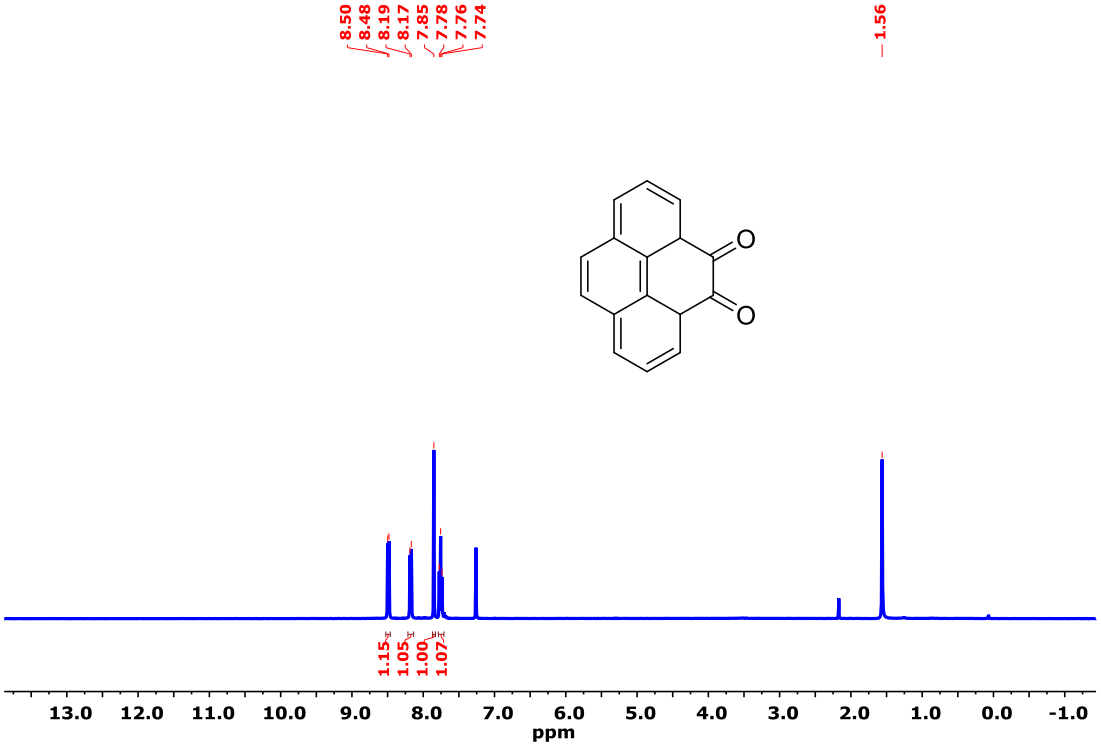


Figure S26.1. ^{1}H NMR spectrum of **1a** (500 MHz, DMSO-d_6, 298 K)

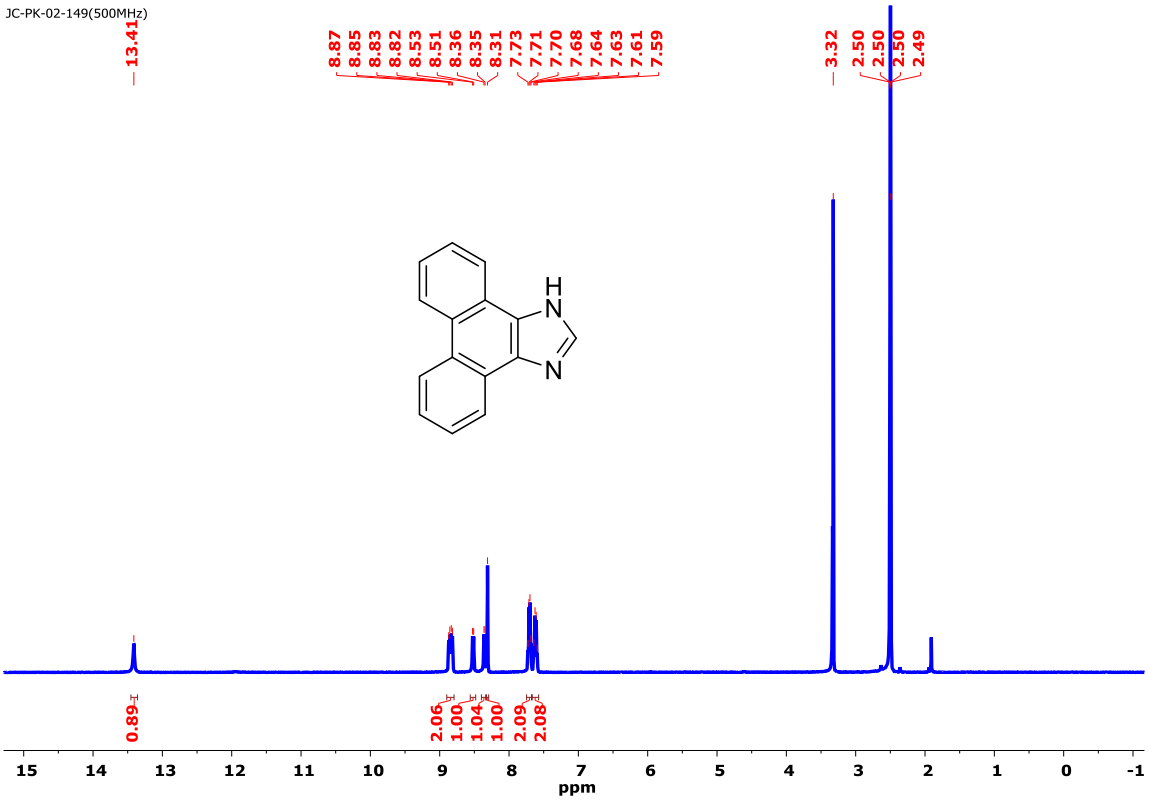


Figure S26.2. ^{1}H NMR spectrum of **2a** (500 MHz, DMSO-d_6, 298 K)

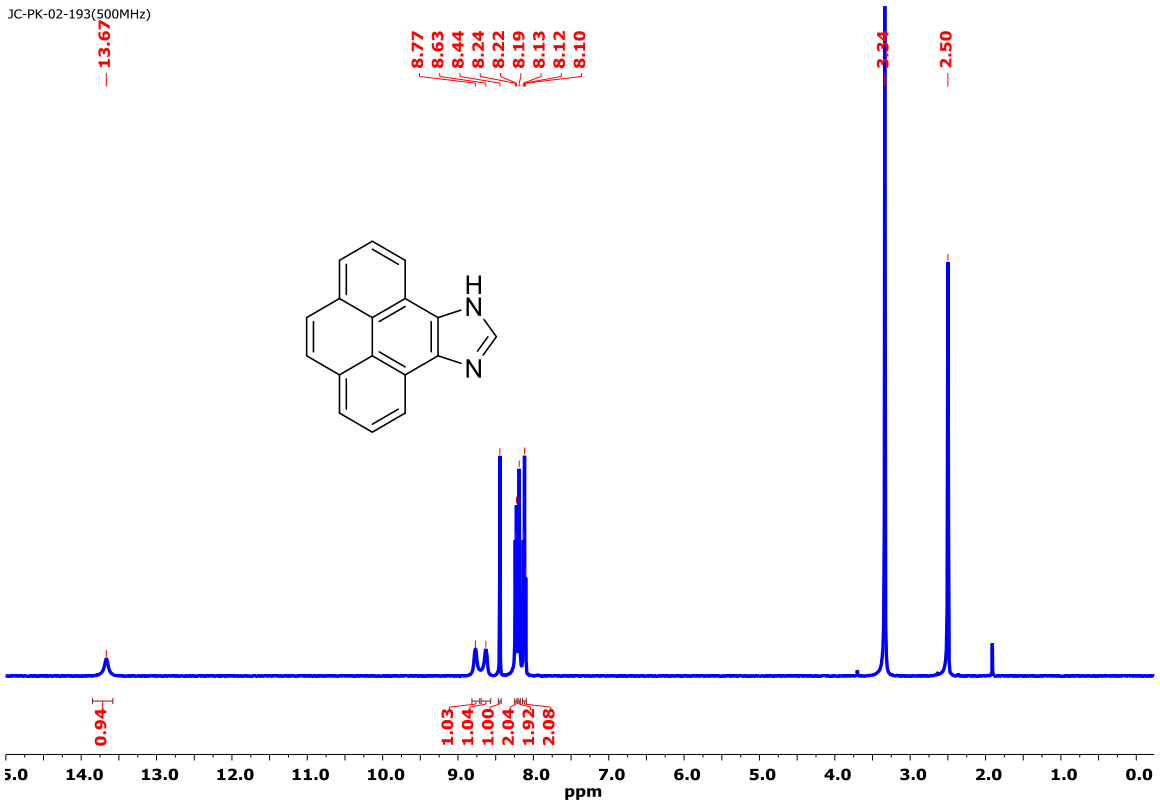


Figure S26.3. ^{1}H NMR spectrum of **2b** (500 MHz, DMSO-d_6, 298 K)

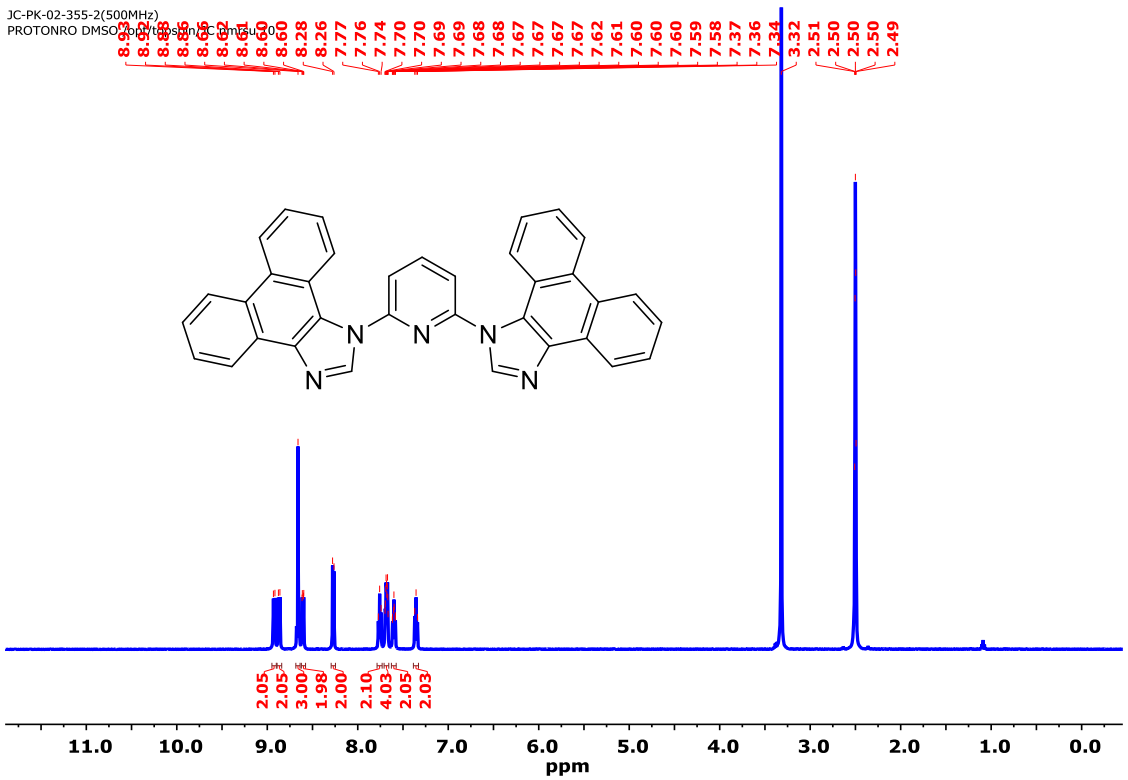


Figure S26.4. ^{1}H NMR spectrum of **n-Pybim1** (500 MHz, DMSO-d_6, 298 K)

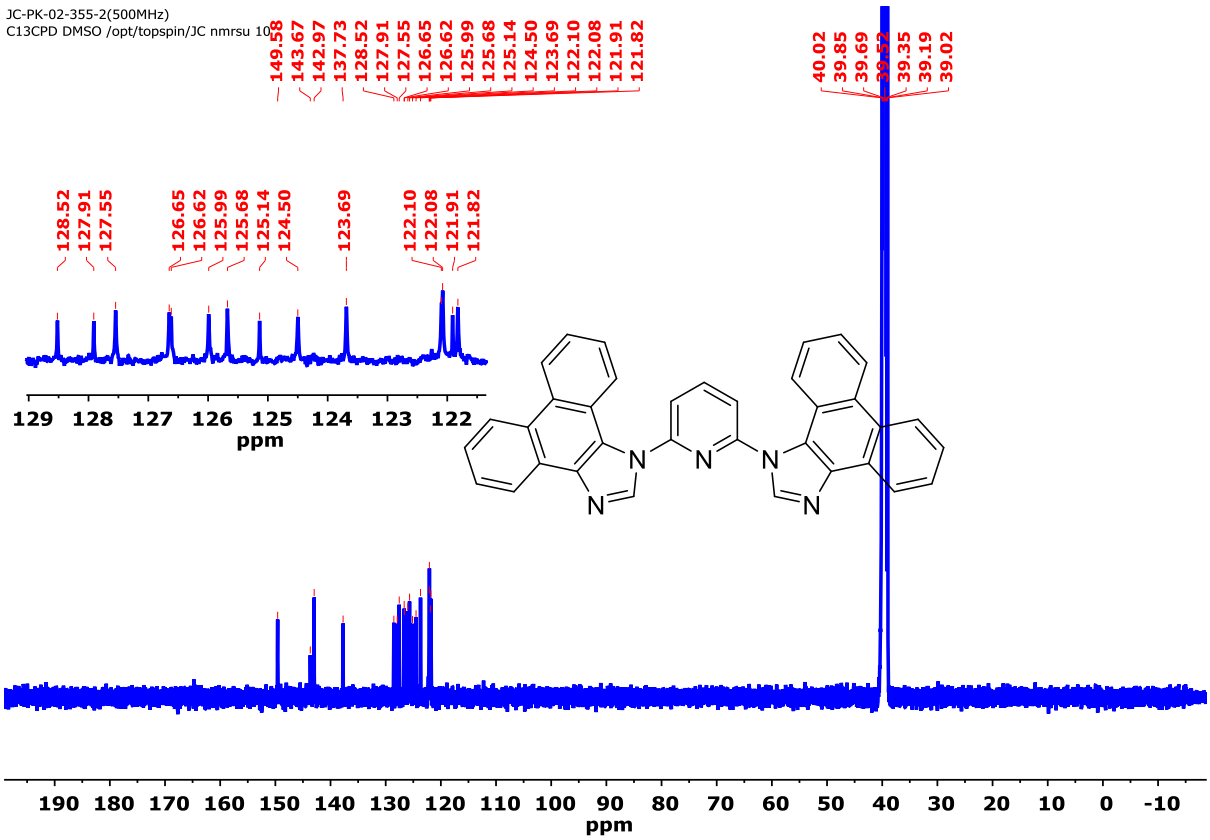


Figure S26.5. $^{13}C\{^{1}H\}$ NMR spectrum of **n-Pybim1** (126 MHz, DMSO-d_6, 298 K).

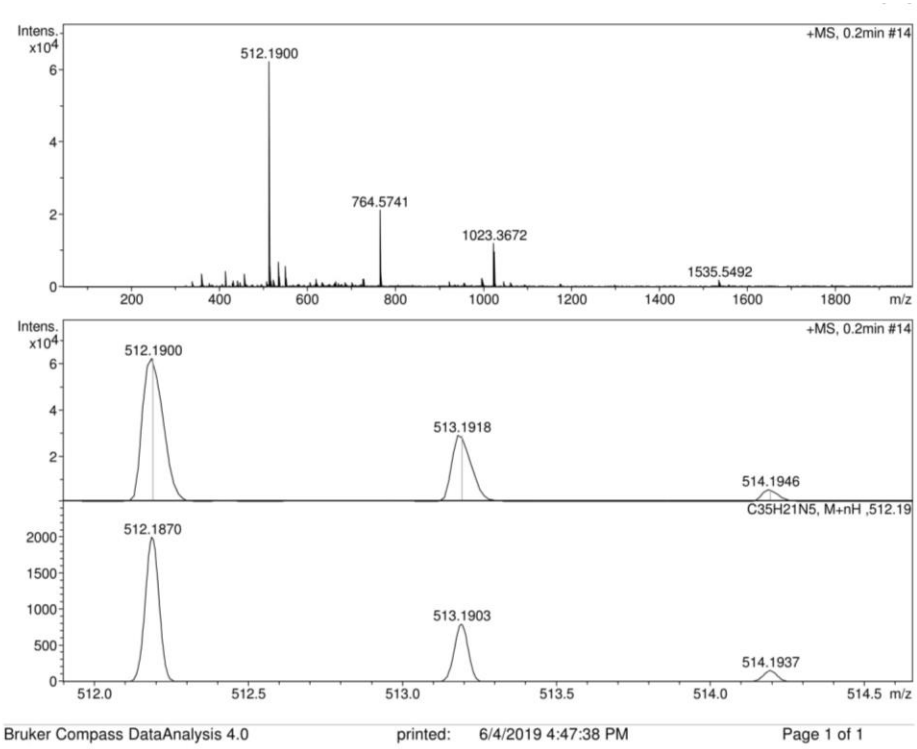


Figure S26.6. ESI-HRMS (positive ion mode) spectrum of **n-Pybim1.**

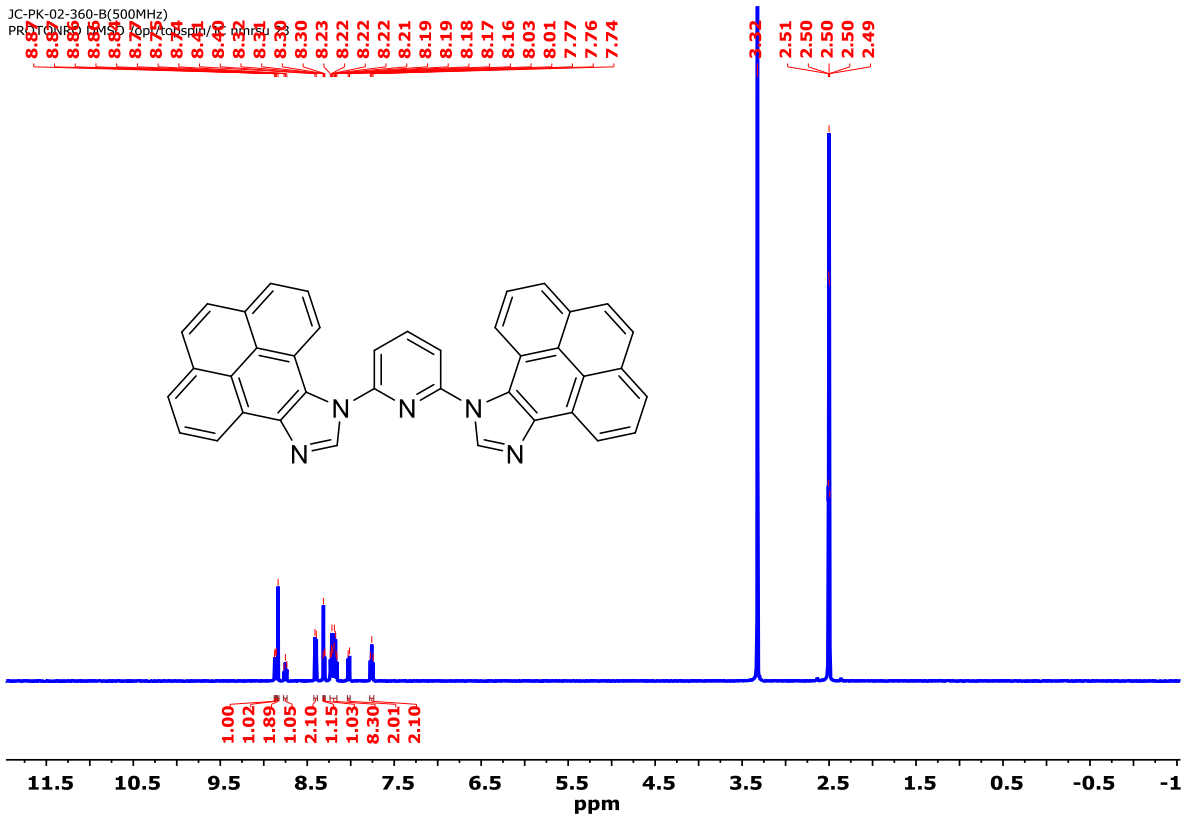


Figure S26.7. ^{1}H NMR spectrum of **n-Pybim2** (500 MHz, DMSO-d_6, 298 K)

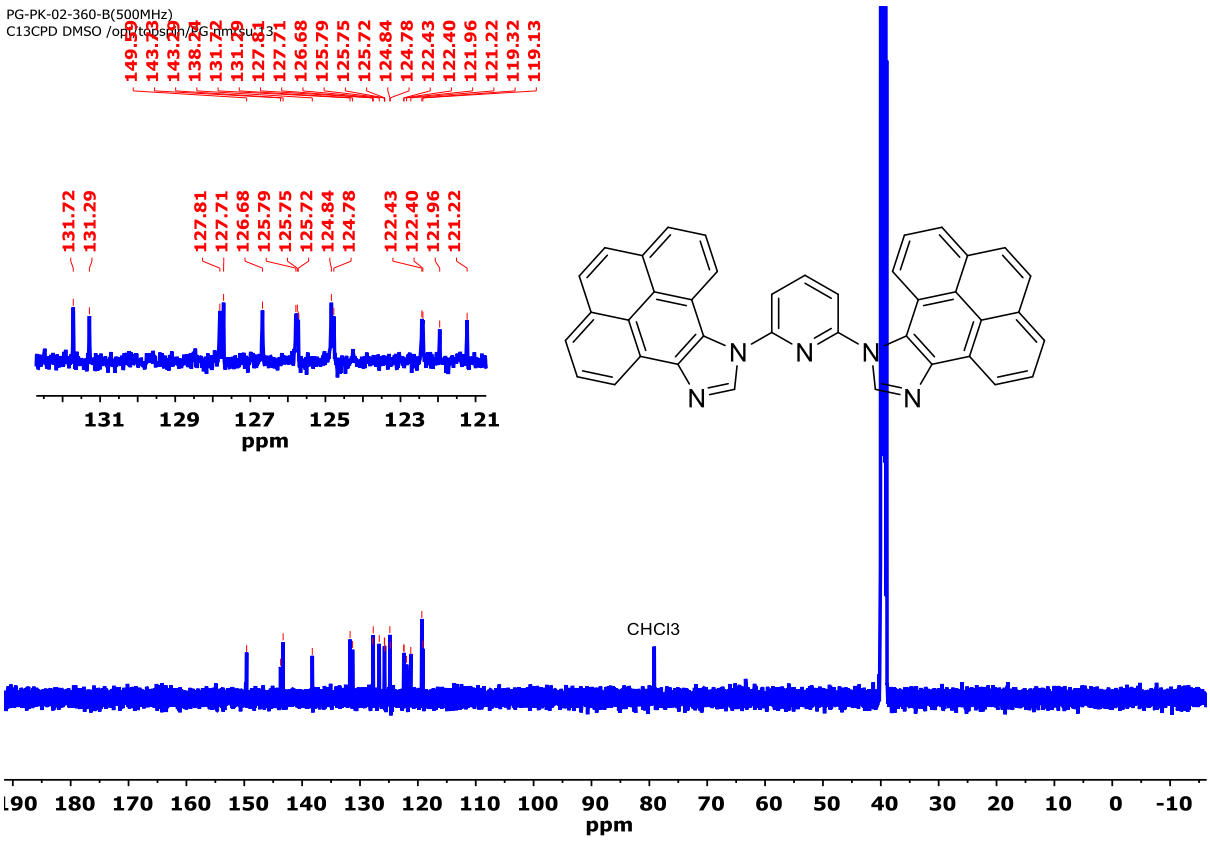


Figure S26.8. ^{13}C{^{1}H} NMR spectrum of **n-Pybim2** (126 MHz, DMSO-d_6, 298 K).

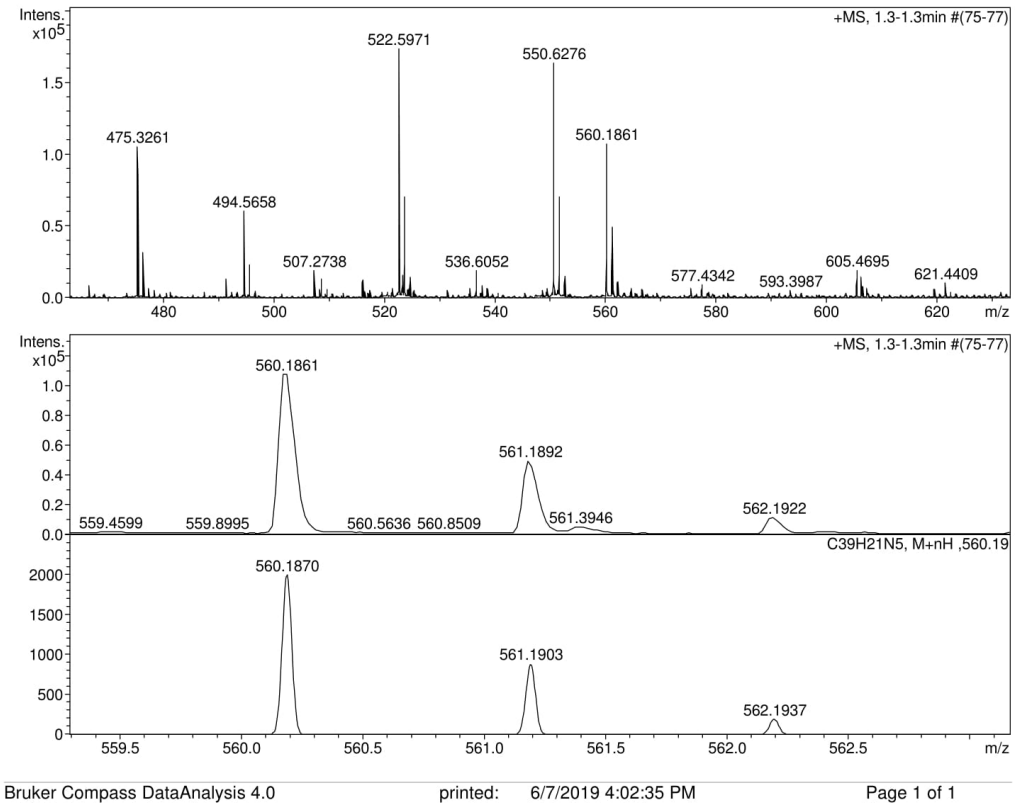


Figure S26.9. ESI-HRMS (positive ion mode) spectrum of **n-Pybim2.**

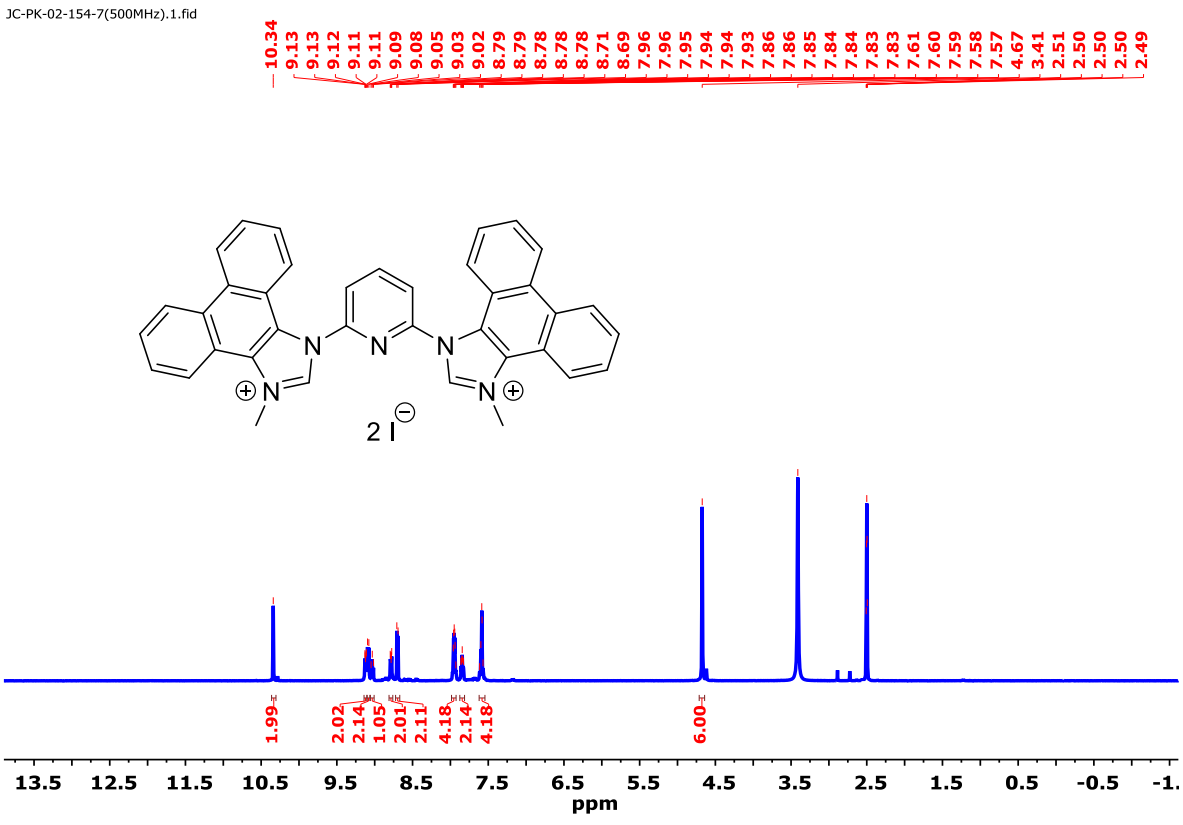


Figure S26.10. ^{1}H NMR spectrum of **c-Pybim1** (500 MHz, DMSO-d_6, 298 K)

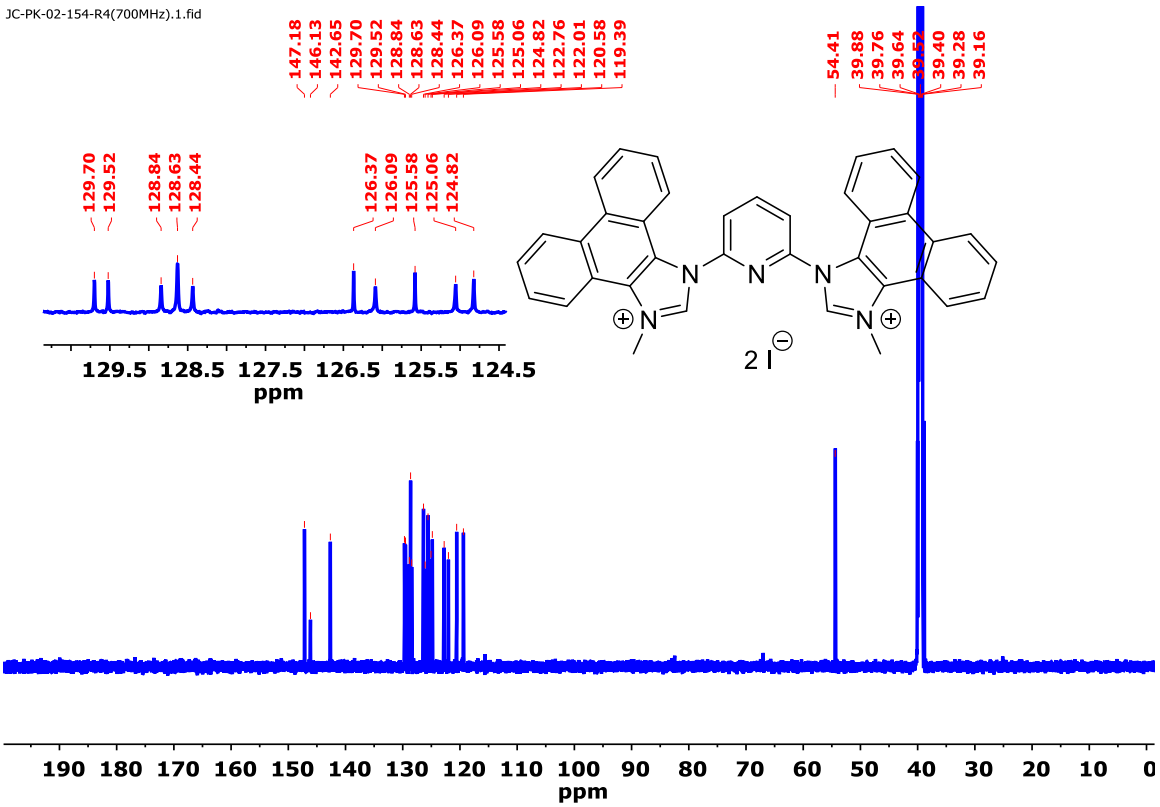


Figure S26.11. $^{13}C\{^{1}H\}$ NMR spectrum of **c-Pybim1** (176 MHz, DMSO-d_6, 298 K).

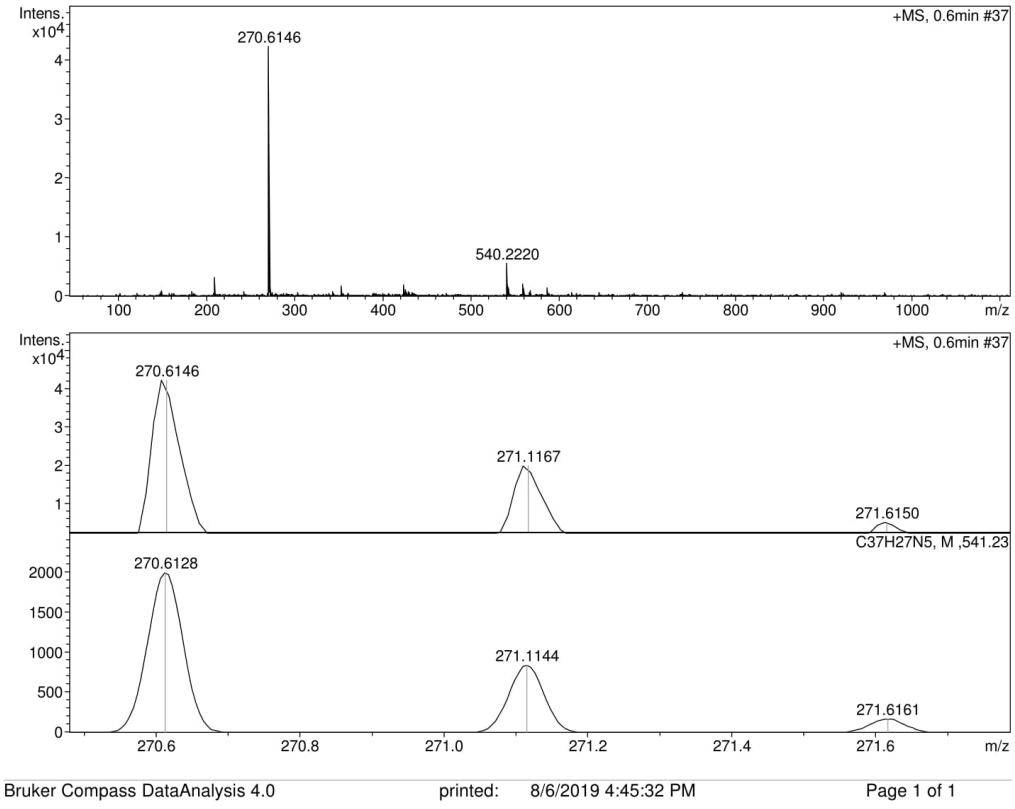


Figure S26.12. ESI-HRMS (positive ion mode) spectrum of **c-Pybim1.**

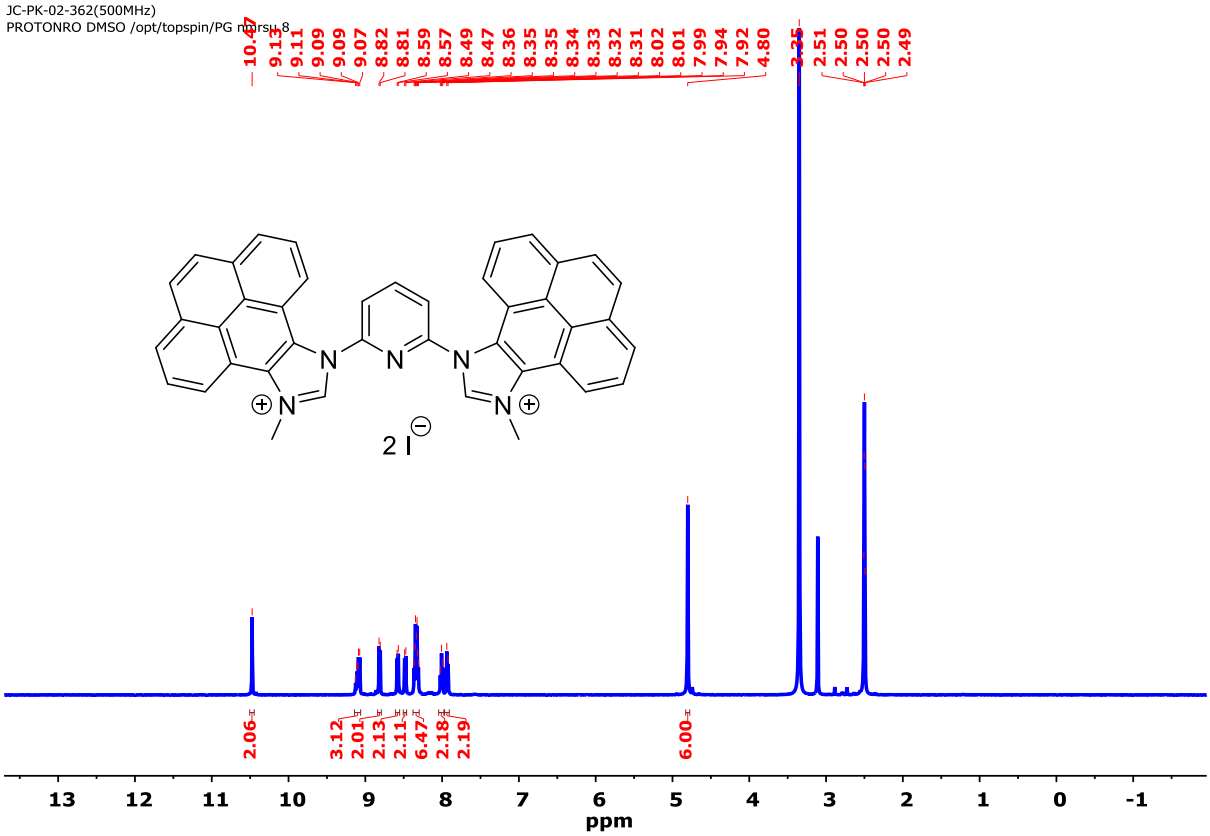


Figure S26.13. ^{1}H NMR spectrum of **c-Pybim2** (500 MHz, DMSO-d_6, 298 K)

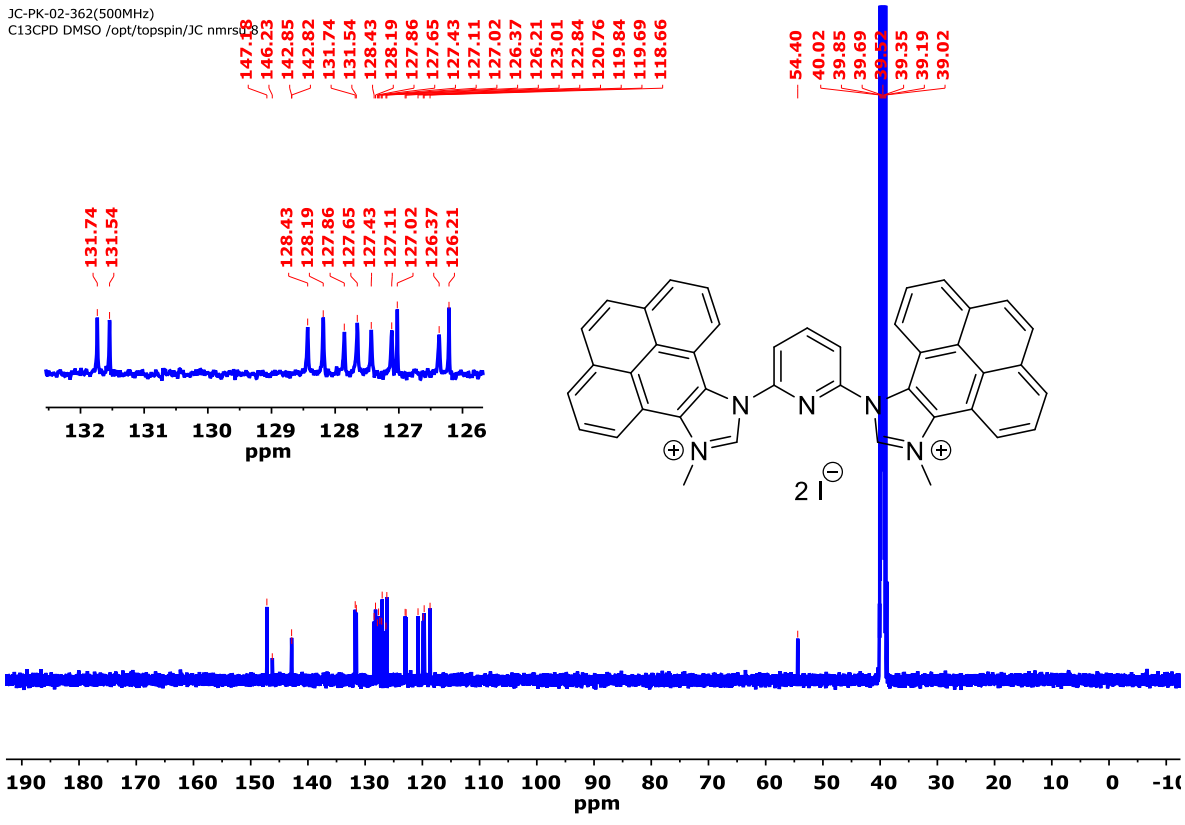


Figure S26.14. ^{13}C{^{1}H} NMR spectrum of **c-Pybim2** (126 MHz, DMSO-d_6, 298 K).

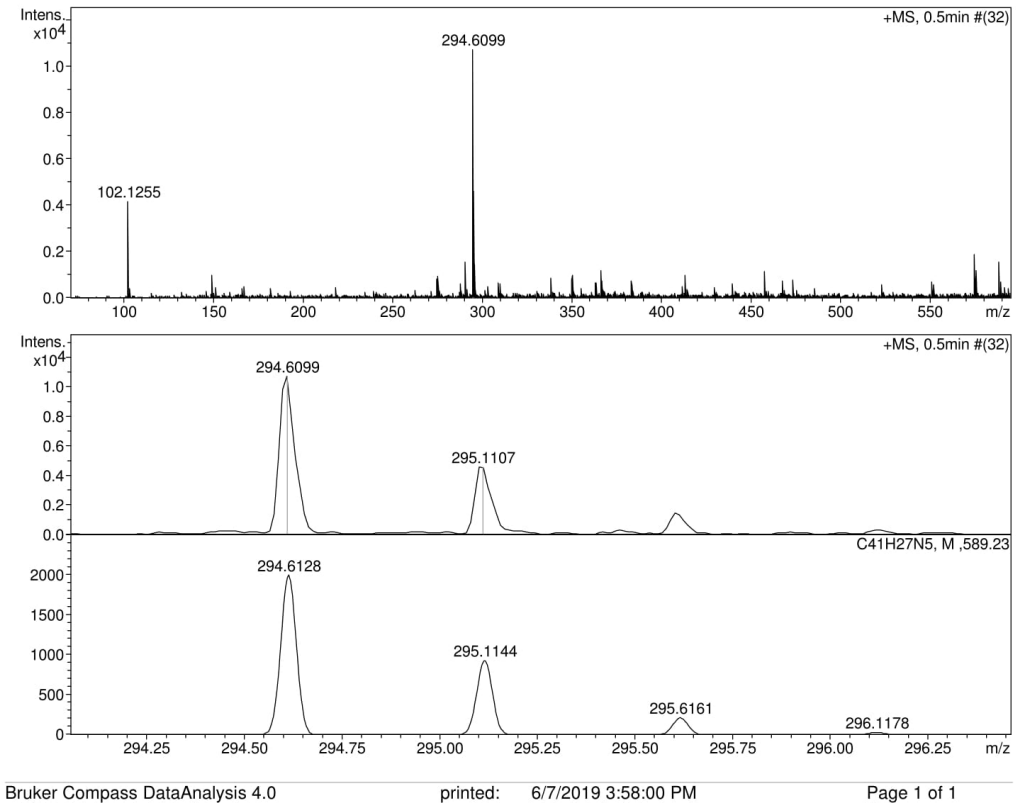


Figure S26.15. ESI-HRMS (positive ion mode) spectrum of **c-Pybim2.**

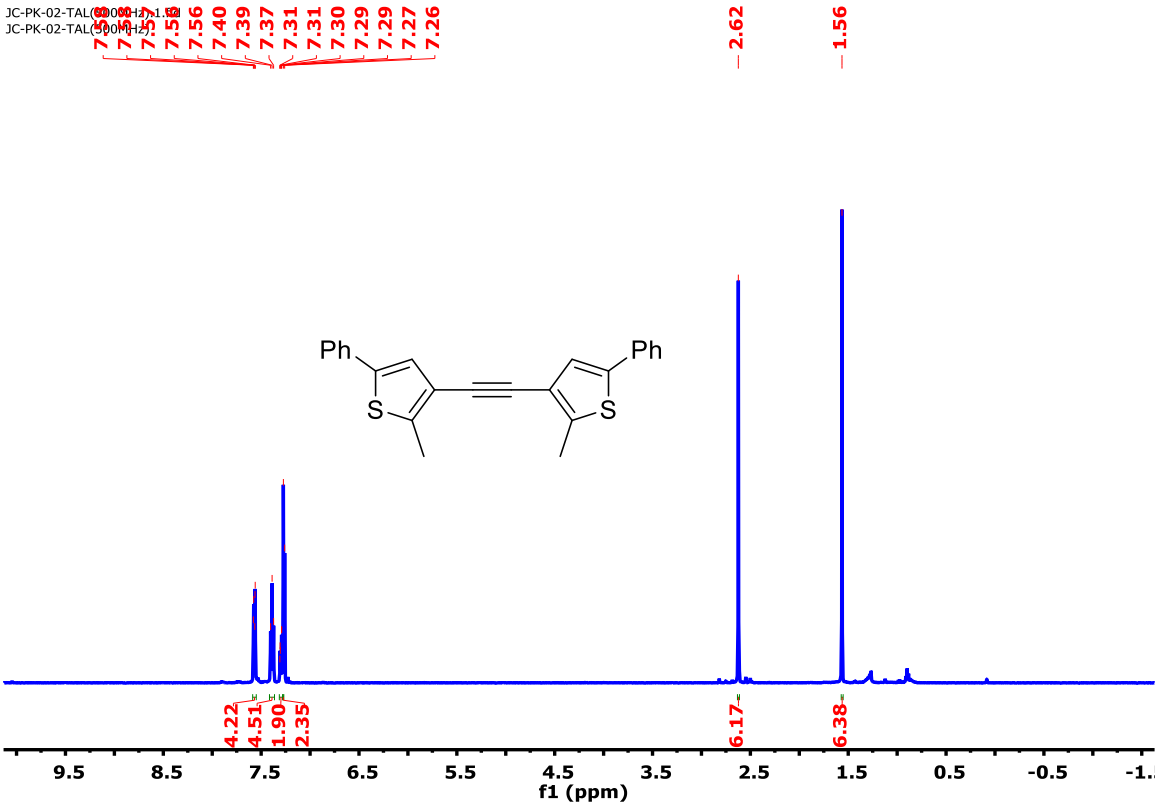


Figure S26.16. ^{1}H NMR spectrum of **Ph-thiophene** alkyne (500 MHz, $CDCl_3$, 298 K)

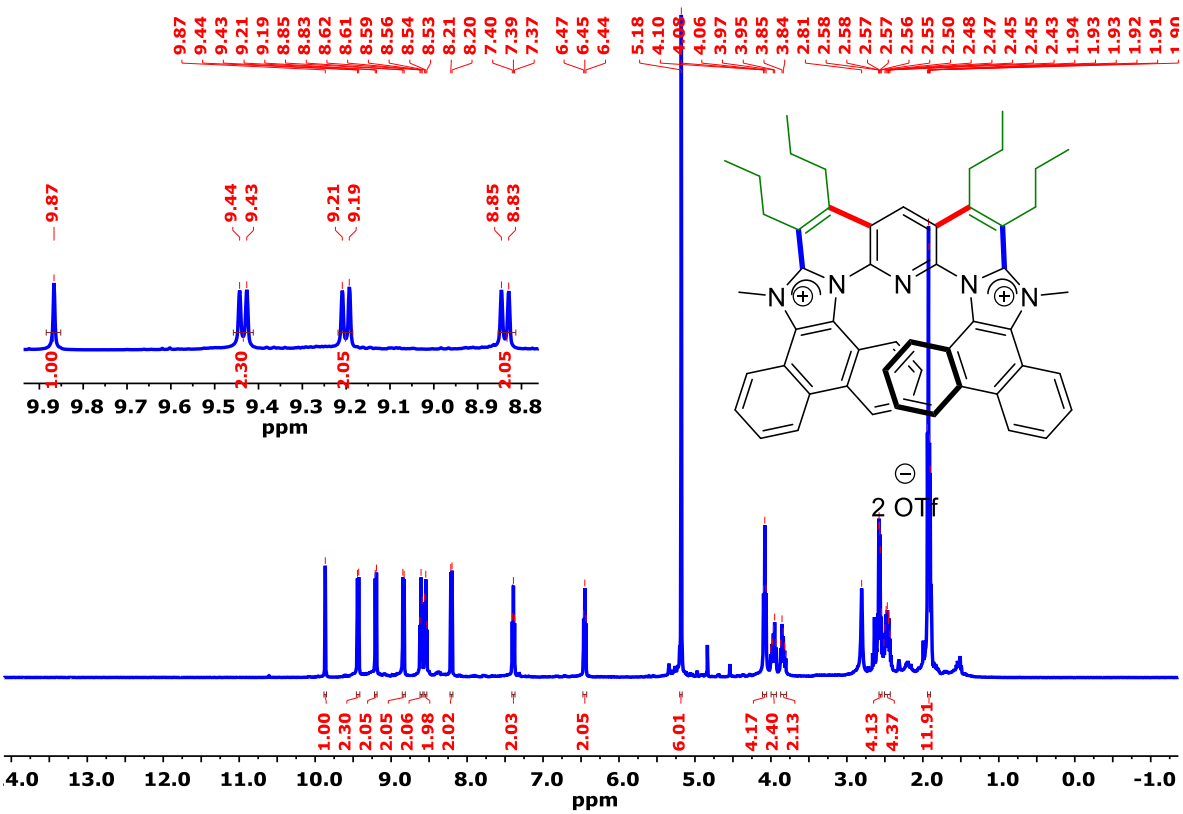


Figure S26.17. ^{1}H NMR spectrum of **c-H1** (500 MHz, CD_3CN, 298 K)

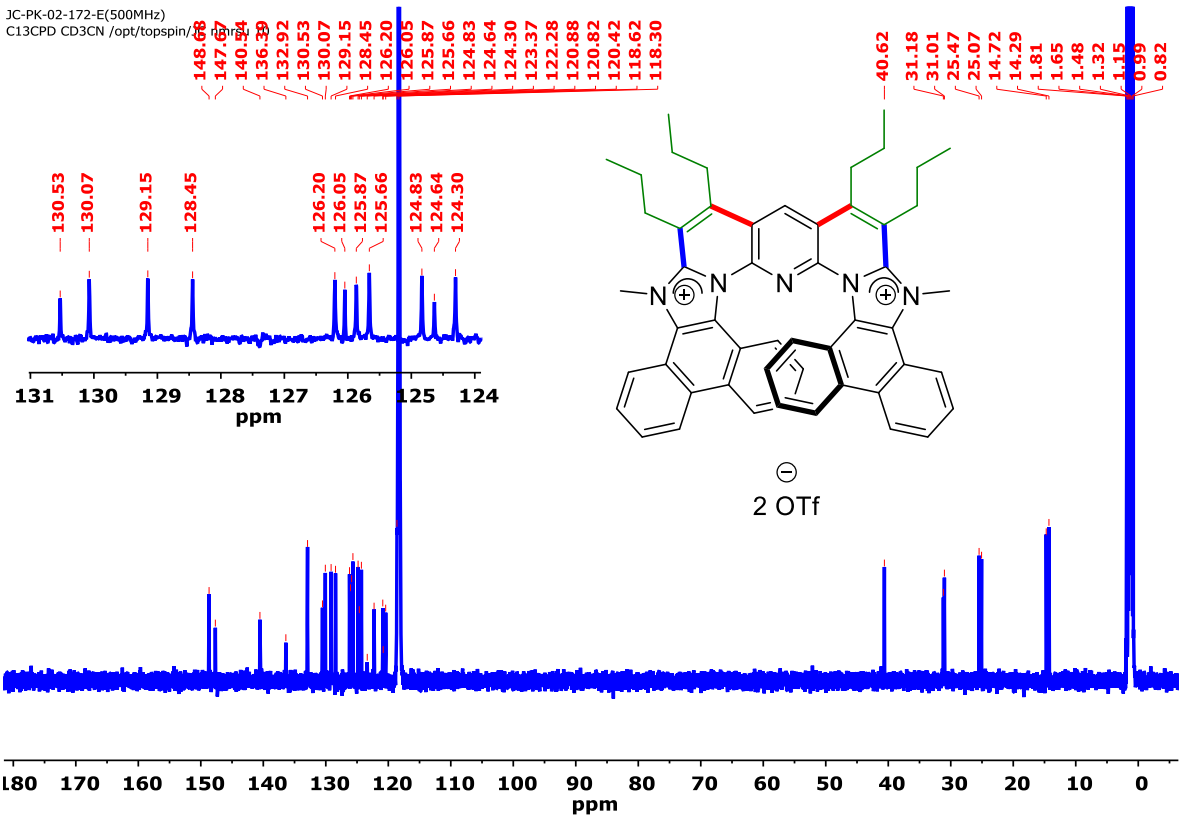


Figure S26.18. $^{13}C\{^{1}H\}$ NMR spectrum of **c-H1** (126 MHz, CD_3CN, 298 K).

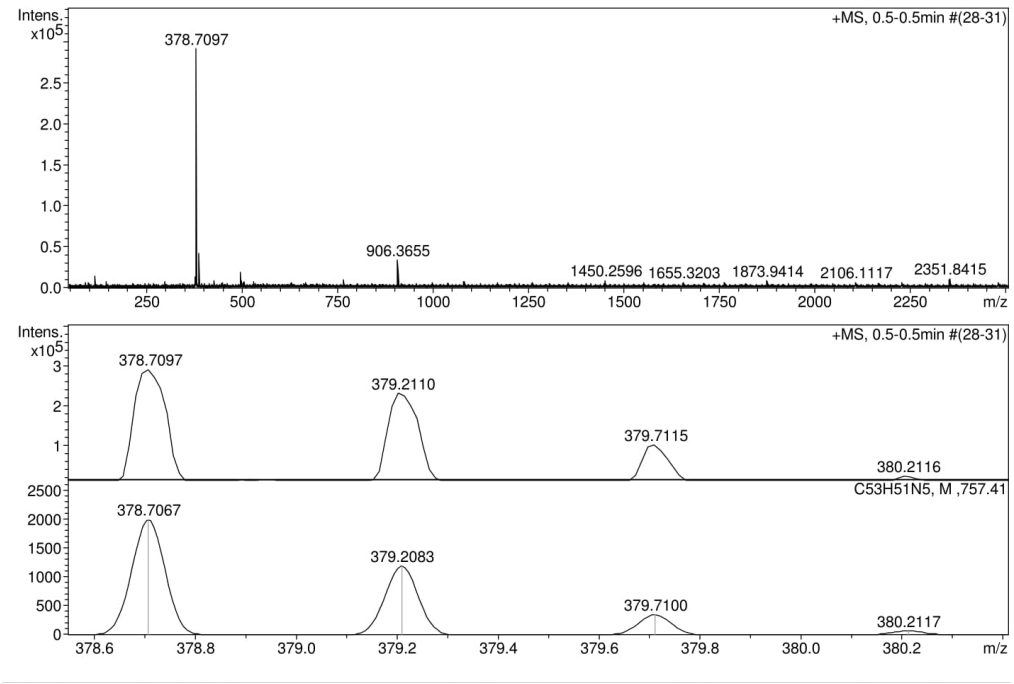


Figure S26.19. ESI-HRMS (positive ion mode) spectrum of **c-H1.**

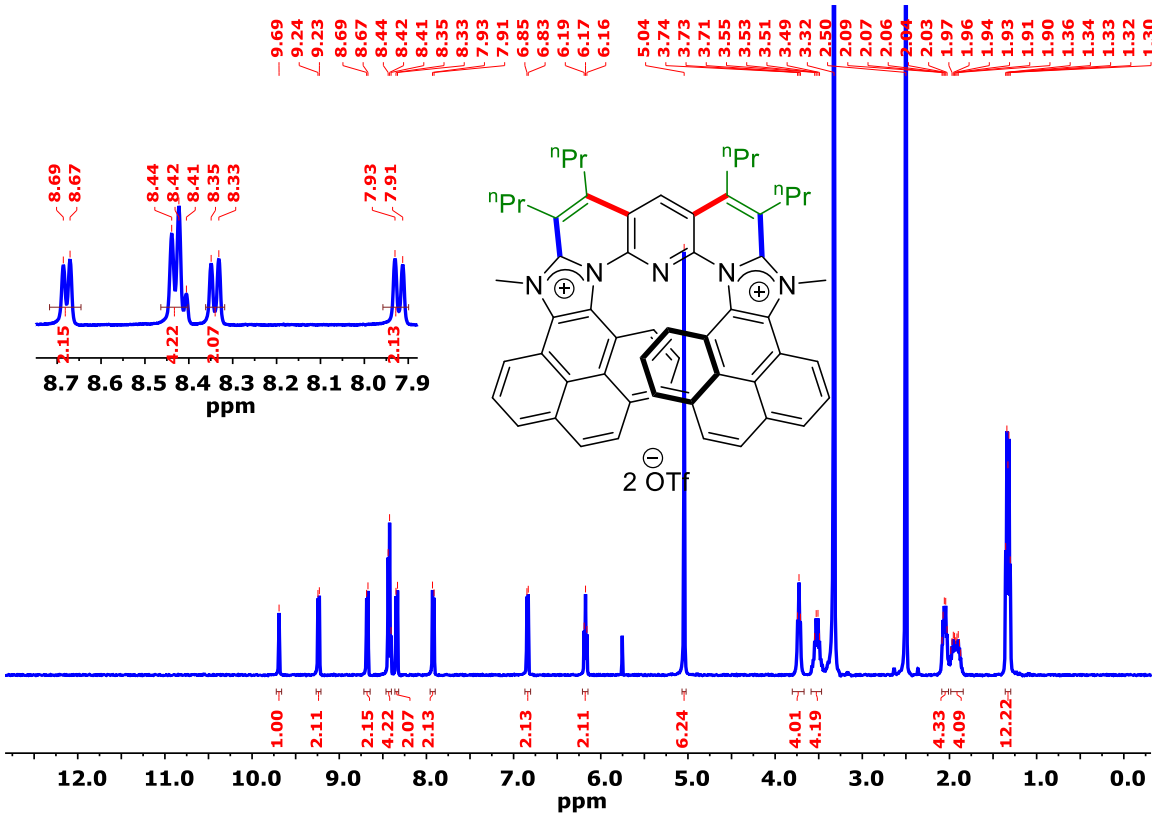


Figure S26.20. ^{1}H NMR spectrum of **c-H2** (500 MHz, DMSO-d_6, 298 K)

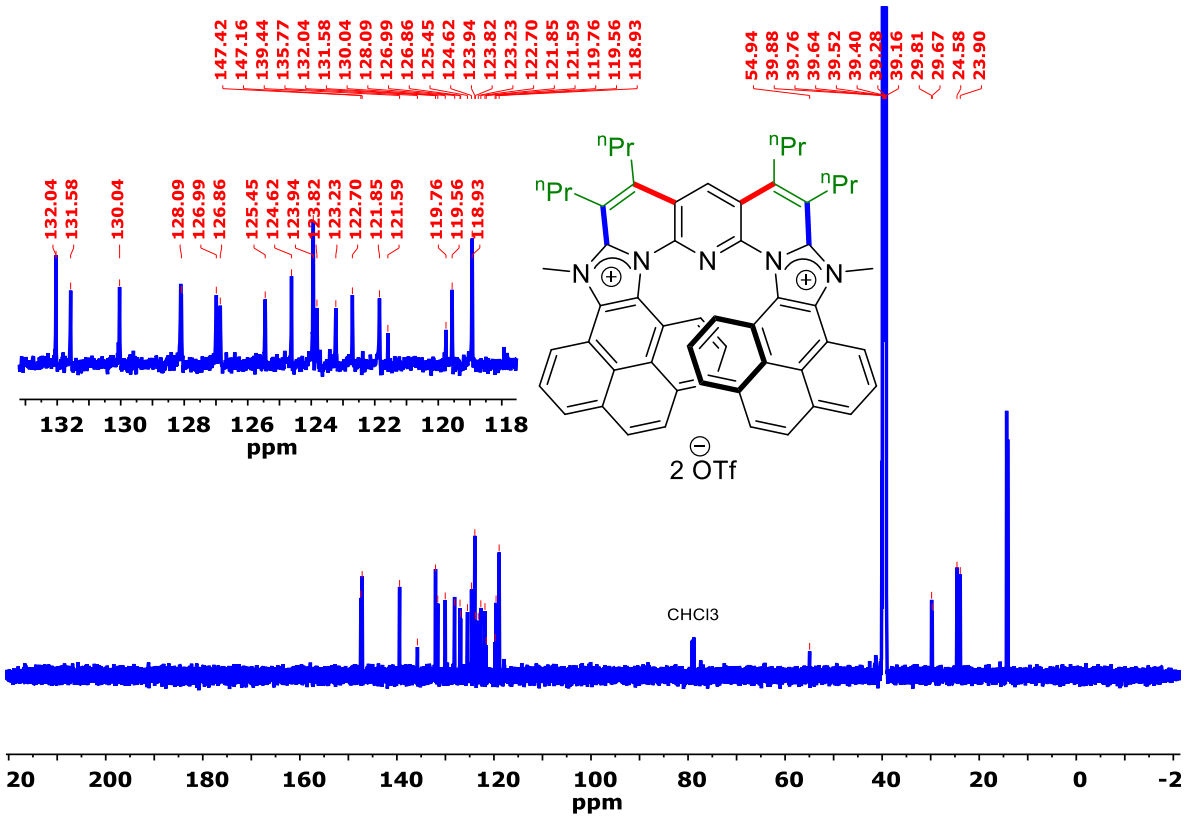


Figure S26.21. $^{13}C\{^{1}H\}$ NMR spectrum of **c-H2** (176 MHz, DMSO-d_6, 298 K).

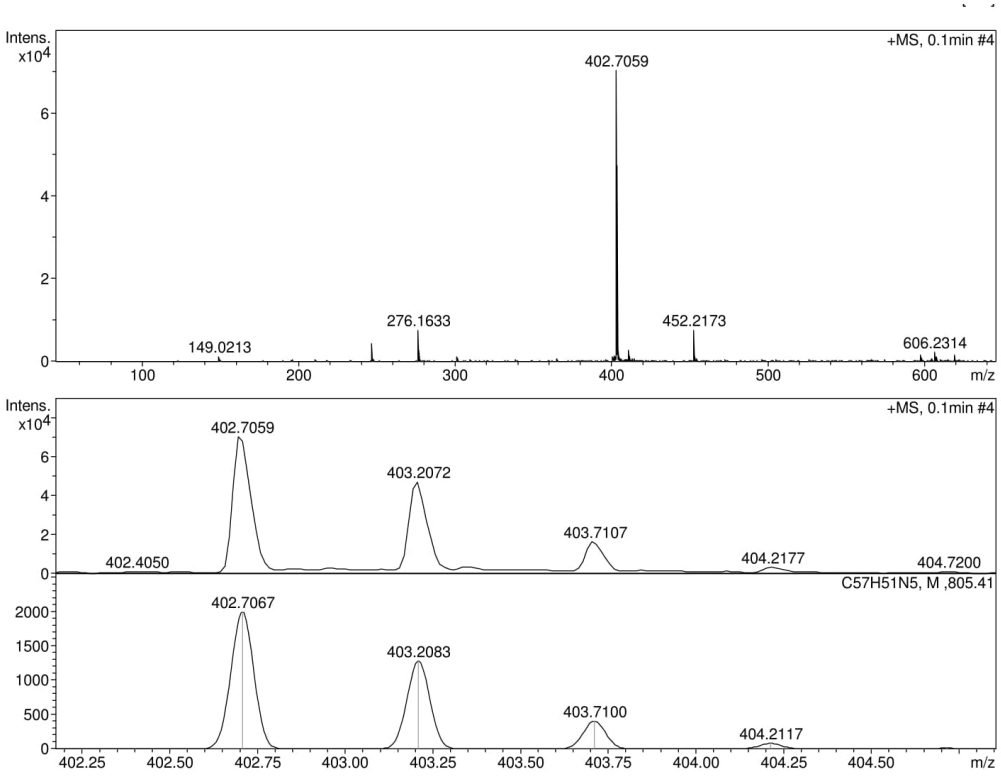


Figure S26.22. ESI-HRMS (positive ion mode) spectrum of **c-H2.**

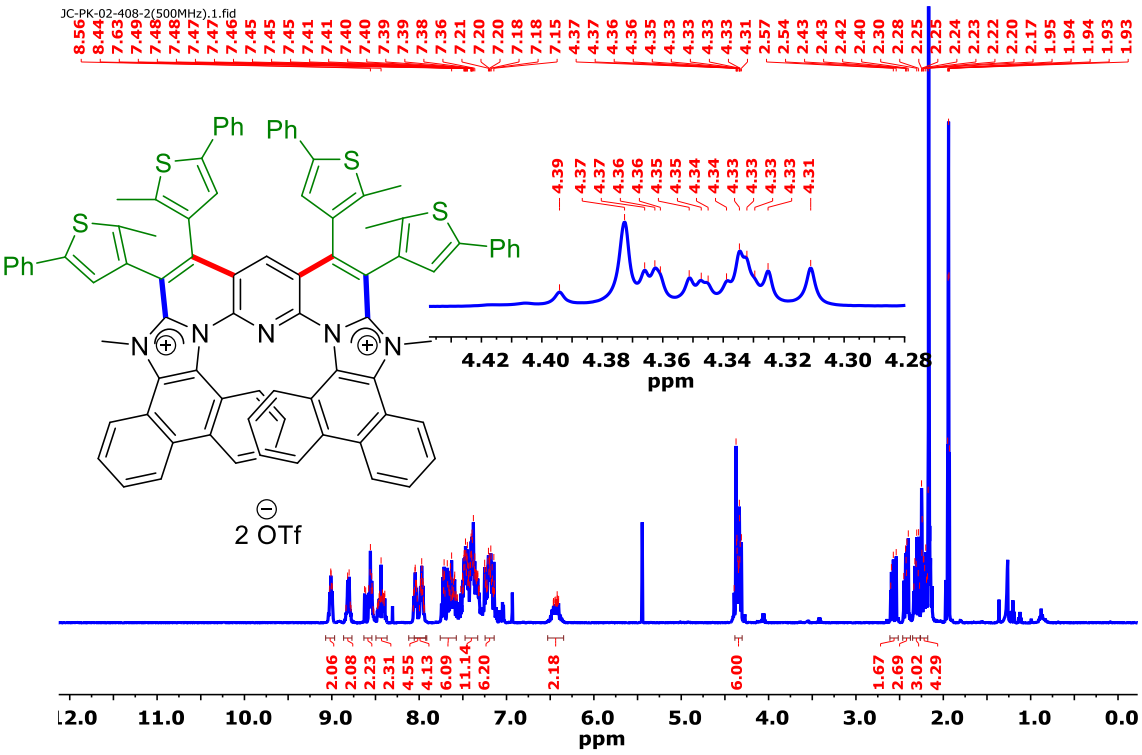


Figure S26.23. ^{1}H NMR spectrum of **c-H3** (mixture of all isomer) (500 MHz, CD_3CN, 298 K).

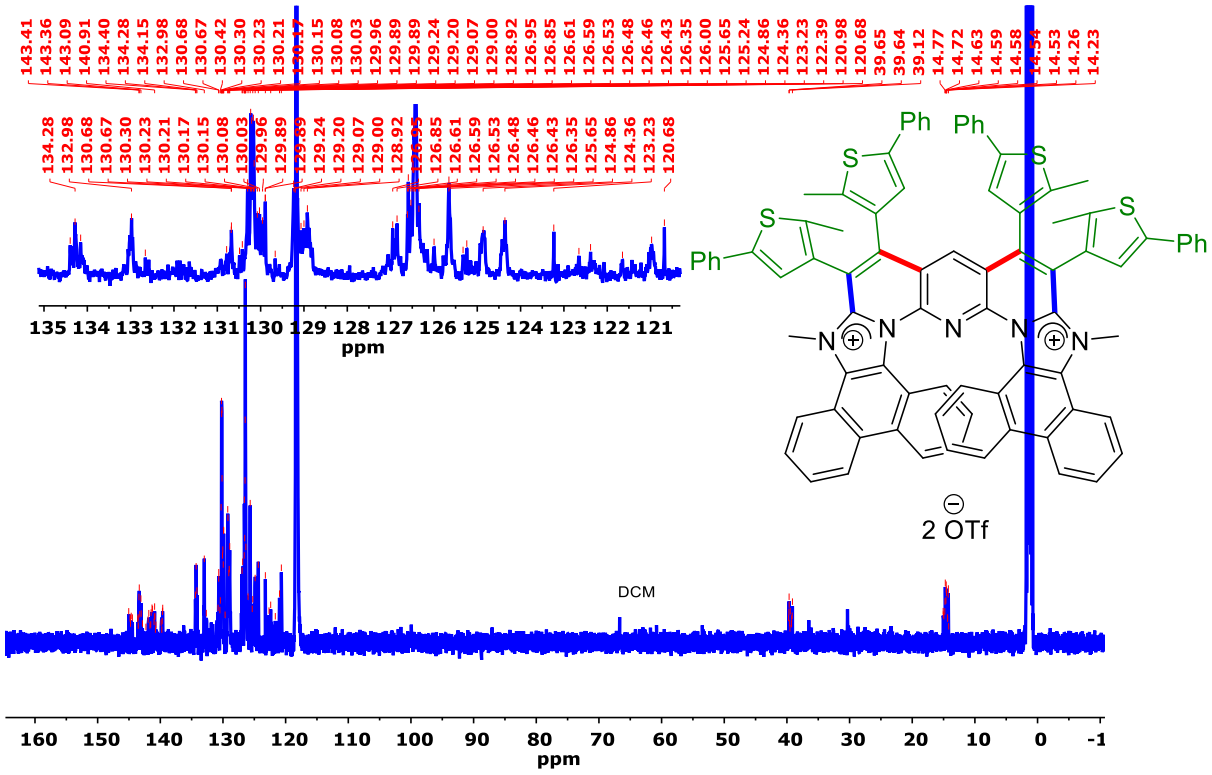


Figure S26.24. $^{13}C\{^{1}H\}$ NMR spectrum of **c-H3** (mixture of all isomers) (126 MHz, CD_3CN, 298 K).

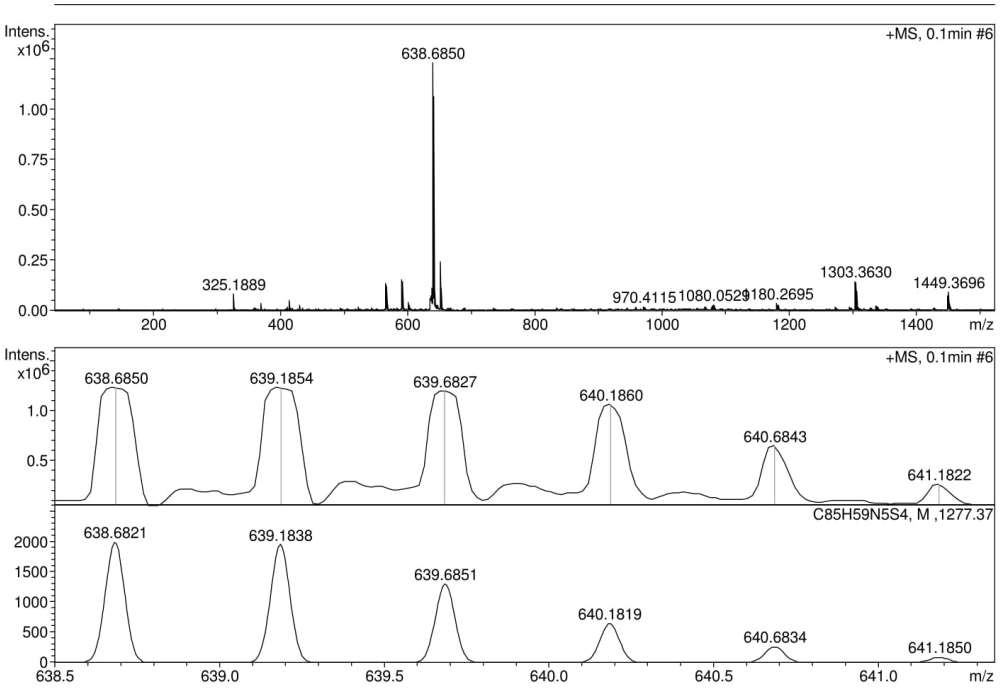


Figure S26.25. ESI-HRMS (positive ion mode) spectrum of **c-H3.**

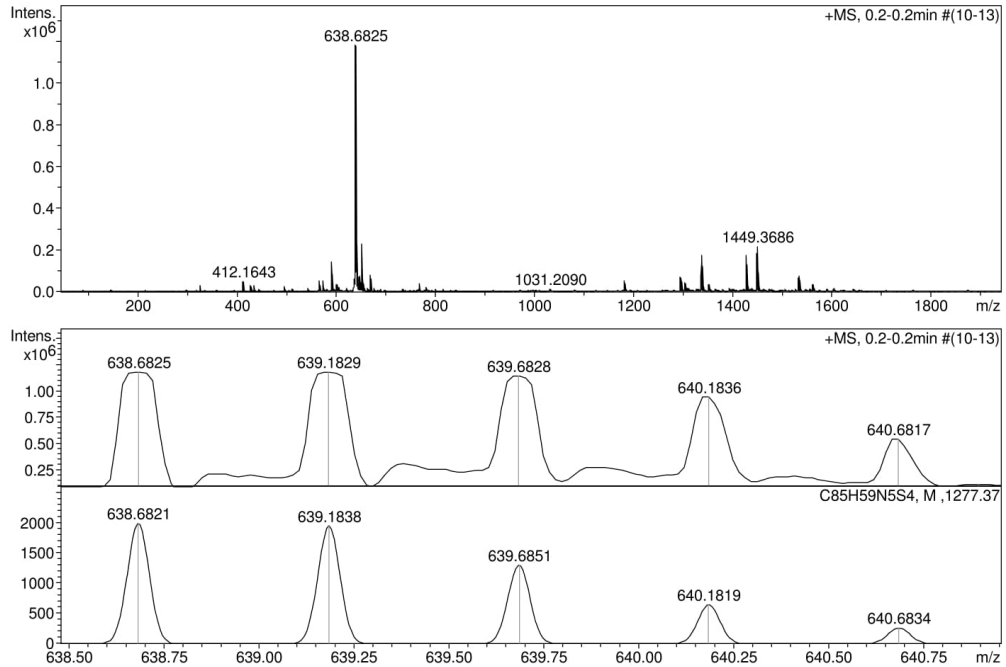


Figure S26.26. ESI-HRMS (positive ion mode) spectrum of **c-H3** in photostationary state after blue light irradiation (5.10 mW/cm^2) in acetonitrile.

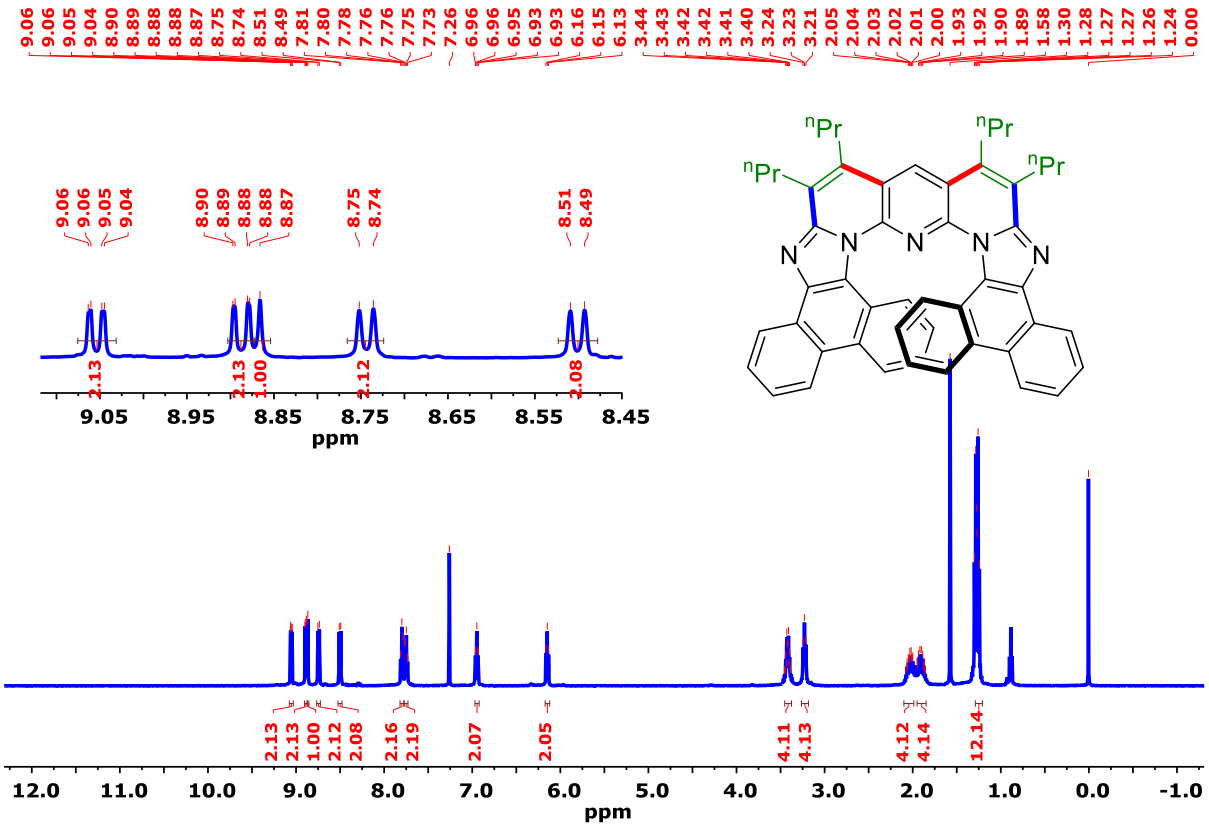


Figure S26.27. ^{1}H NMR spectrum of **n-H1** (500 MHz, $CDCl_3$, 298 K)

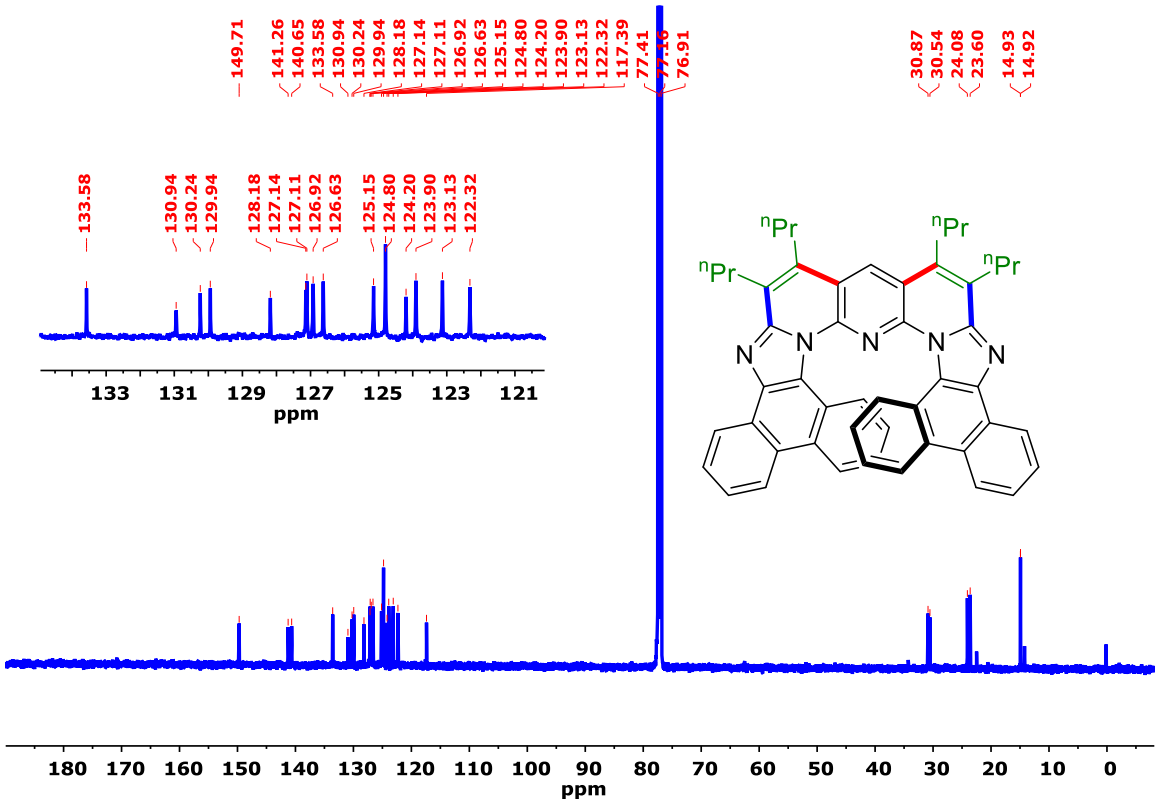


Figure S26.28. $^{13}C\{^{1}H\}$ NMR spectrum of **n-H1** (126 MHz, $CDCl_3$, 298 K).

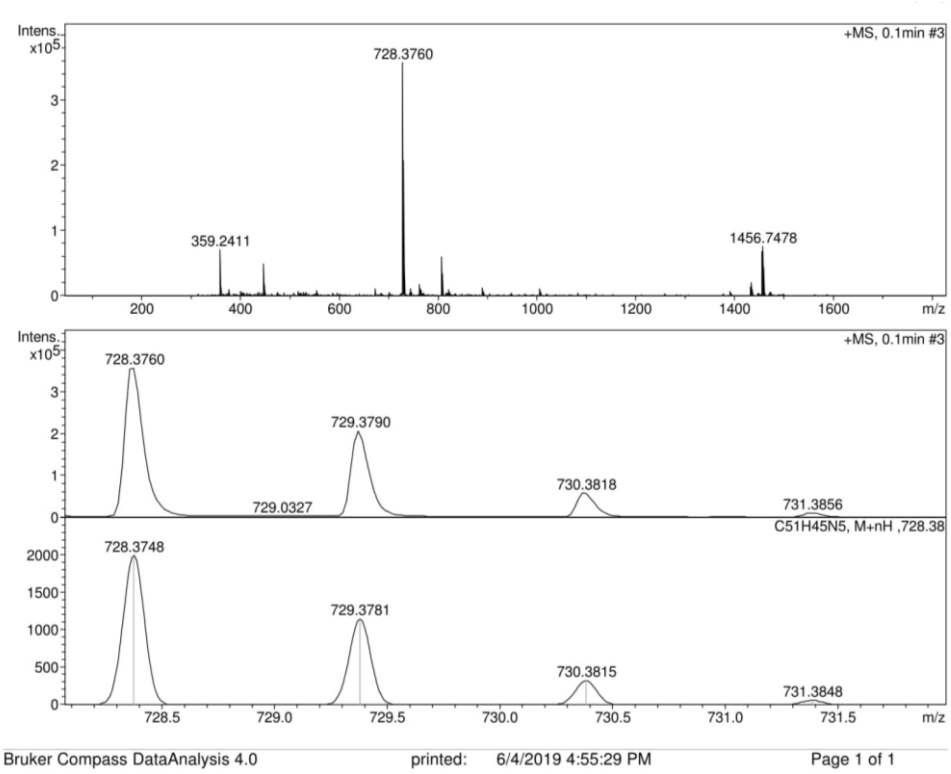


Figure S26.29. ESI-HRMS (positive ion mode) spectrum of **n-H1.**

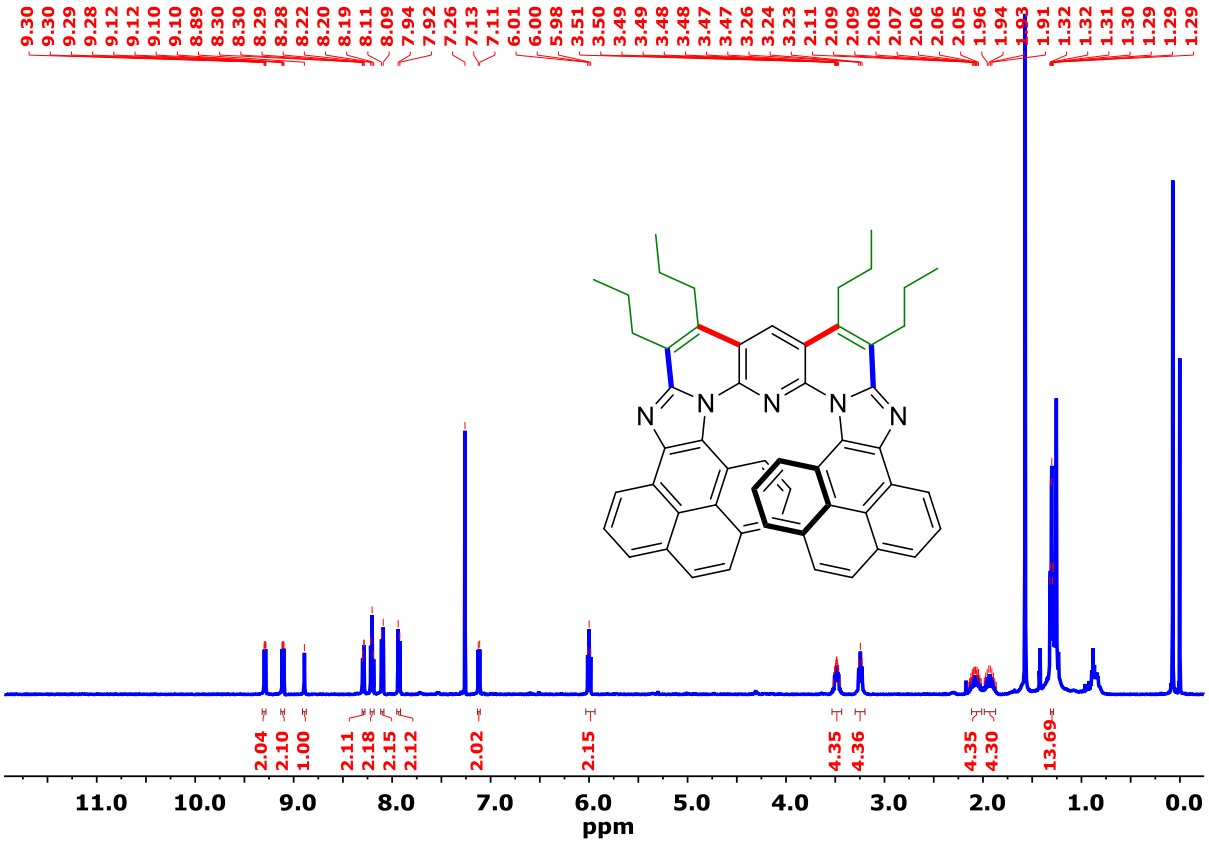


Figure S26.30. ^{1}H NMR spectrum of **n-H2** (500 MHz, $CDCl_3$, 298 K)

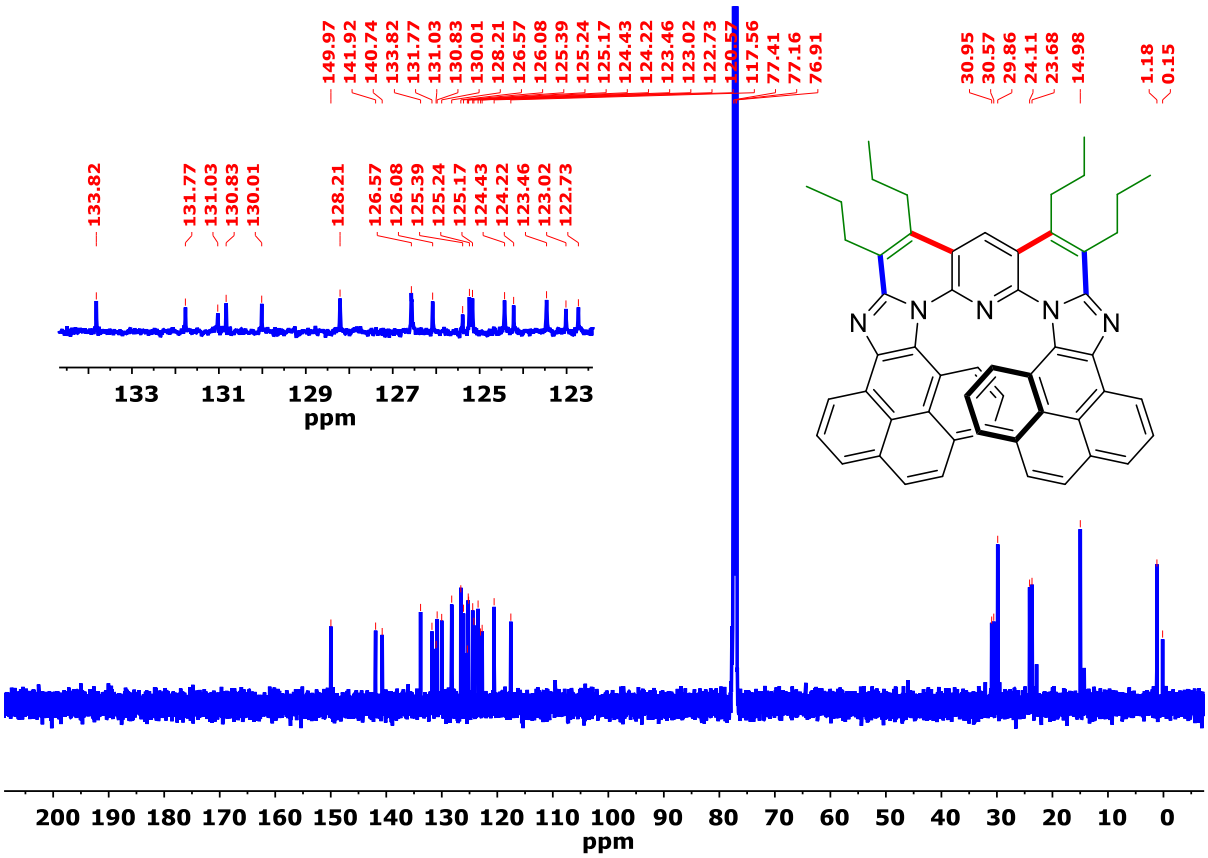


Figure S26.31. $^{13}C\{^{1}H\}$ NMR spectrum of **n-H2** (126 MHz, $CDCl_3$, 298 K).

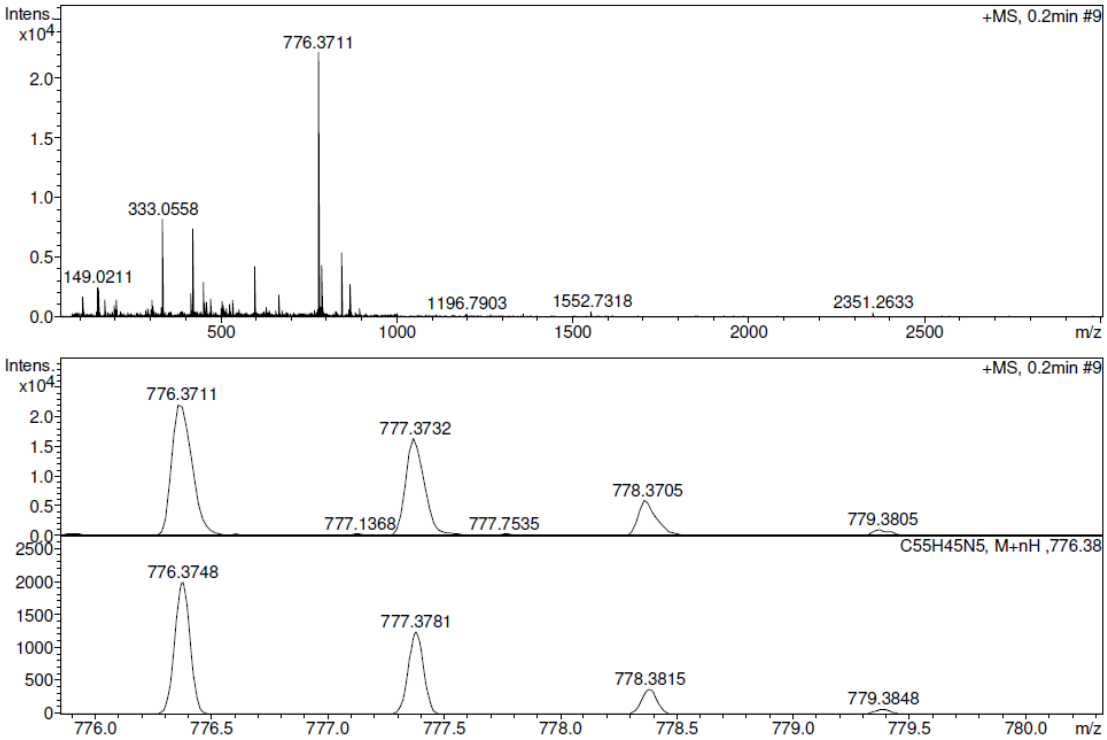


Figure S26.32. ESI-HRMS (positive ion mode) spectrum of **n-H2.**

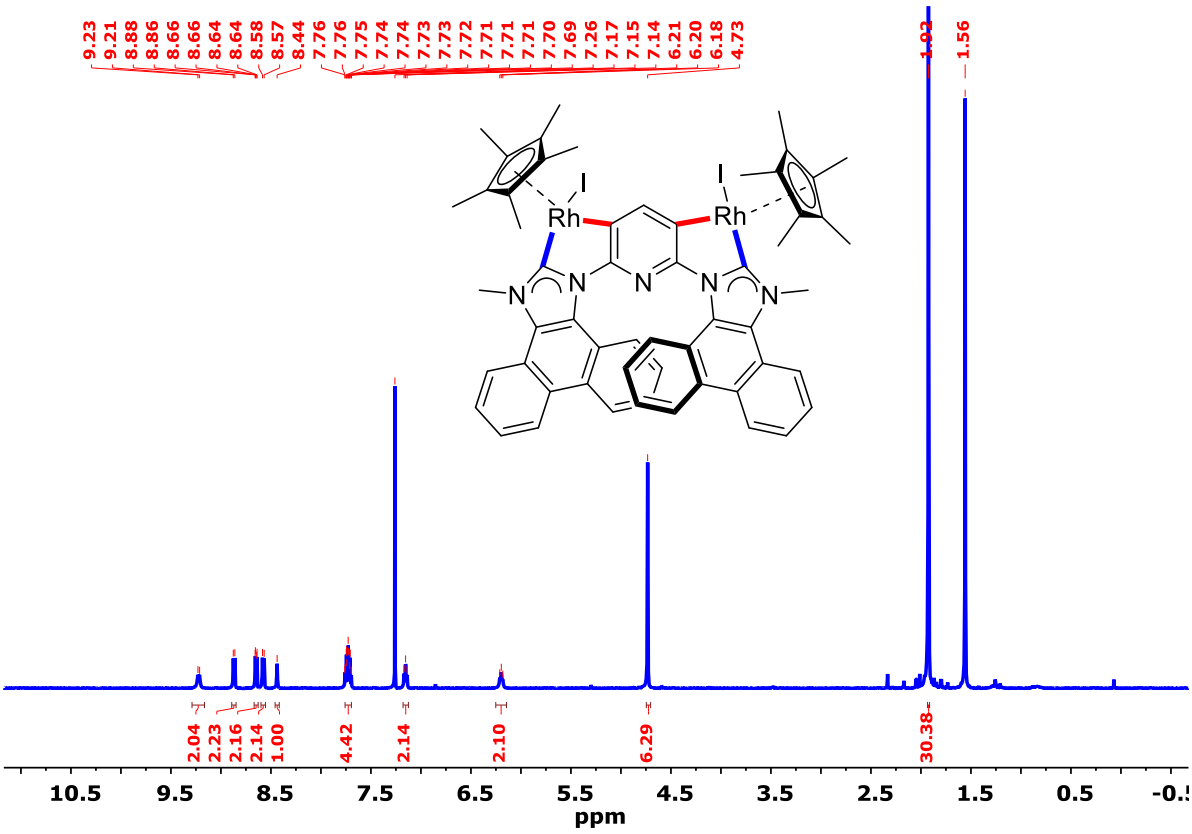


Figure S26.33. ^{1}H NMR spectrum of **Rh-H1** (500 MHz, $CDCl_3$, 298 K)

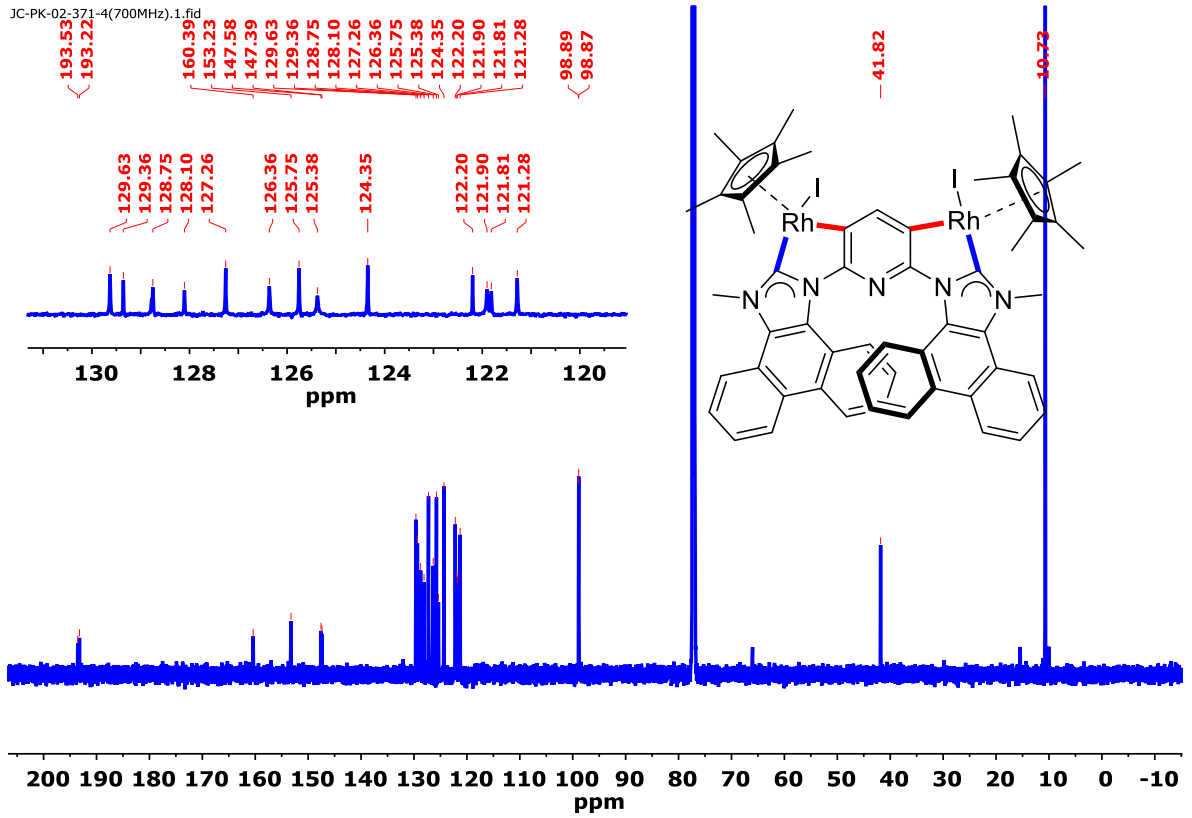


Figure S26.34. ^{13}C{^{1}H} NMR spectrum of **Rh-H1** (176 MHz, $CDCl_3$, 298 K).

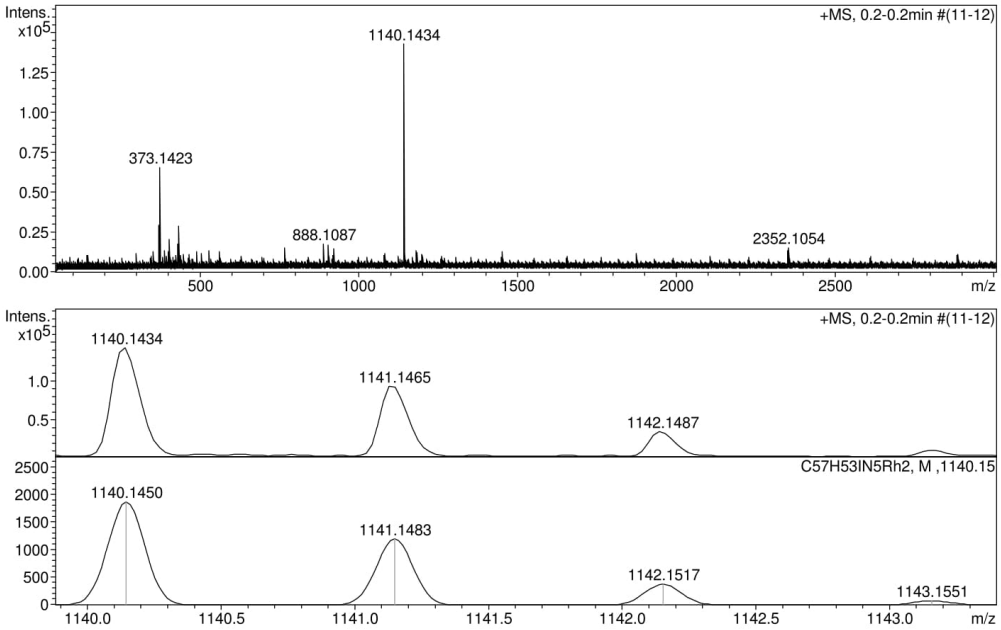


Figure S26.35. ESI-HRMS (positive ion mode) spectrum of **Rh-H1.**

16. Cartesian Coordinates

Using B3LYP/6-31g(d,p), CH_2Cl_2, CPCM model

c-H1

Total energy of the optimized structure E = -2323.9872 Hartree

N	-2.296408000	0.245000000	-0.522550000
N	0.001739000	0.337837000	-0.123530000
N	2.304163000	0.335930000	0.262307000
N	4.423832000	-0.087969000	-0.160387000
C	-5.283454000	-5.362817000	-0.248871000
H	-5.618124000	-6.390962000	-0.157620000
C	-3.957915000	-5.095002000	-0.539513000
H	-3.283566000	-5.930575000	-0.675071000
C	-3.474757000	-3.773690000	-0.667577000
C	-4.388952000	-2.701922000	-0.414618000
C	-3.824193000	-1.375969000	-0.413946000
C	-2.490646000	-1.136825000	-0.706491000
C	-1.127993000	0.993642000	-0.330715000
C	1.117217000	1.035613000	0.010531000
C	2.523450000	-1.004191000	0.624314000
C	3.849447000	-1.269651000	0.320821000
C	4.431171000	-2.577997000	0.490920000
C	5.790249000	-2.897294000	0.257056000
H	6.505832000	-2.126110000	0.019327000

C	6.244373000	-4.200109000	0.348557000
H	7.290360000	-4.418290000	0.160997000
C	5.352056000	-5.229578000	0.677973000
H	5.695694000	-6.257782000	0.723747000
C	-6.194700000	-4.307656000	-0.103092000
H	-7.245203000	-4.509605000	0.077245000
C	-5.753451000	-2.999786000	-0.184855000
H	-6.482187000	-2.210629000	-0.085891000
C	-2.116014000	-3.500242000	-1.143664000
C	-1.624556000	-2.161422000	-1.232770000
C	3.500847000	0.908013000	-0.115677000
C	3.642336000	2.330014000	-0.278549000
C	5.014856000	2.978298000	-0.374500000
H	5.773463000	2.325632000	0.061285000
H	5.010325000	3.862394000	0.269337000
C	5.441752000	3.407178000	-1.796124000
H	5.429744000	2.546073000	-2.475390000
H	4.700011000	4.103219000	-2.202815000
C	6.827485000	4.057177000	-1.806807000
H	6.851398000	4.947666000	-1.169568000
H	7.105868000	4.362482000	-2.819566000
H	7.594459000	3.365207000	-1.442592000
C	2.493302000	3.098408000	-0.228953000
C	1.203549000	2.441102000	-0.159713000

C	-0.026235000	3.102315000	-0.273752000
H	-0.036705000	4.179373000	-0.344427000
C	-1.243250000	2.407976000	-0.311284000
C	-2.541604000	3.051503000	-0.350252000
C	-3.683627000	2.271894000	-0.300604000
C	-3.512306000	0.844125000	-0.273003000
N	-4.427153000	-0.147812000	-0.122600000
C	-5.728282000	0.013903000	0.544396000
H	-5.739362000	0.954002000	1.083271000
H	-5.834065000	-0.787548000	1.273393000
H	-6.550613000	-0.017665000	-0.171593000
C	-5.077231000	2.866075000	-0.452614000
H	-5.760938000	2.099966000	-0.823138000
H	-5.030526000	3.602443000	-1.261413000
C	-5.688601000	3.548054000	0.789753000
H	-5.651473000	2.875950000	1.655700000
H	-5.079780000	4.414068000	1.065472000
C	-7.130993000	3.996517000	0.538939000
H	-7.186963000	4.692388000	-0.305058000
H	-7.538709000	4.503650000	1.418113000
H	-7.780404000	3.143973000	0.312464000
C	-2.592632000	4.560799000	-0.415095000
H	-3.564736000	4.887415000	-0.788538000
H	-1.859501000	4.915006000	-1.148811000

C	-2.329307000	5.260757000	0.941879000
H	-3.057828000	4.905502000	1.678262000
H	-1.347050000	4.970774000	1.330707000
C	-2.408308000	6.784341000	0.819823000
H	-1.664425000	7.165481000	0.111707000
H	-2.225609000	7.261255000	1.787231000
H	-3.396077000	7.103072000	0.469963000
C	2.536667000	4.609558000	-0.219214000
H	1.742790000	5.007631000	-0.859498000
H	3.466522000	4.968816000	-0.659298000
C	2.395076000	5.202137000	1.203446000
H	1.466734000	4.843021000	1.662898000
H	3.211074000	4.822991000	1.829932000
C	2.412704000	6.732518000	1.191621000
H	3.345478000	7.114817000	0.763564000
H	2.322418000	7.129755000	2.206917000
H	1.583528000	7.134274000	0.599089000
C	5.712063000	-0.007011000	-0.864416000
H	5.705051000	0.848394000	-1.528517000
H	5.816062000	-0.899667000	-1.478326000
H	6.544849000	0.068359000	-0.163744000
C	4.034248000	-4.931662000	0.974157000
H	3.375375000	-5.744057000	1.251648000
C	3.539425000	-3.609337000	0.928149000

C	2.193083000	-3.282463000	1.406065000
C	1.686272000	-1.950035000	1.316538000
C	0.486232000	-1.617925000	1.983890000
H	0.143798000	-0.594636000	1.996954000
C	-0.248736000	-2.581347000	2.647738000
H	-1.162991000	-2.302200000	3.161228000
C	0.196195000	-3.911946000	2.665845000
H	-0.382219000	-4.675271000	3.176129000
C	1.398038000	-4.245668000	2.069410000
H	1.745400000	-5.266898000	2.154727000
C	-0.409897000	-1.913407000	-1.910429000
H	-0.077575000	-0.898187000	-2.062016000
C	0.353306000	-2.952614000	-2.407100000
H	1.278092000	-2.738076000	-2.932679000
C	-0.075544000	-4.278027000	-2.240221000
H	0.525861000	-5.099262000	-2.616416000
C	-1.290832000	-4.538411000	-1.634635000
H	-1.625073000	-5.566013000	-1.578617000

c-H2

Total energy of the optimized structure E = -2476.4547 Hartree

C	-0.397671000	3.045901000	-0.457247000
C	-0.700206000	1.658166000	-0.428668000

N	0.201147000	0.710489000	-0.236243000
C	1.477775000	1.052721000	-0.186226000
C	1.957454000	2.358929000	-0.461298000
C	0.968597000	3.349043000	-0.543743000
N	-2.037517000	1.282787000	-0.584965000
N	2.419882000	0.054439000	0.076664000
C	-3.027549000	2.224723000	-0.383113000
N	-4.220412000	1.574117000	-0.421198000
C	-3.982891000	0.206374000	-0.574428000
C	-2.629537000	0.014398000	-0.788942000
C	2.238993000	-1.276563000	0.506525000
C	3.430654000	-1.919987000	0.222932000
N	4.355654000	-0.963640000	-0.203610000
C	3.733589000	0.239821000	-0.315604000
C	4.232008000	1.511932000	-0.758012000
C	3.361904000	2.590270000	-0.726579000
C	-5.515268000	2.193488000	-0.774096000
C	5.810434000	-1.193764000	-0.159515000
C	-4.926351000	-0.875547000	-0.497598000
C	-4.425253000	-2.155824000	-0.893579000
C	-3.071751000	-2.319751000	-1.339027000
C	-2.126443000	-1.235629000	-1.319895000
C	1.199492000	-1.914399000	1.282996000
C	1.376145000	-3.323165000	1.503186000

C	2.523641000	-4.029281000	1.010283000
C	3.596223000	-3.344532000	0.351745000
C	-6.231747000	-0.763520000	0.005663000
C	-7.065298000	-1.880403000	0.065843000
C	-6.617419000	-3.118143000	-0.376110000
C	-5.305629000	-3.281418000	-0.854321000
C	-2.657512000	-3.596781000	-1.833748000
C	-1.368117000	-3.751260000	-2.368473000
C	-0.501781000	-2.669904000	-2.432404000
C	-0.870010000	-1.429961000	-1.910897000
C	0.133372000	-1.259473000	1.915770000
C	-0.794540000	-1.967391000	2.678673000
C	-0.691069000	-3.343747000	2.821084000
C	0.387879000	-4.038634000	2.250600000
C	2.616227000	-5.444844000	1.189740000
C	3.723134000	-6.138947000	0.671727000
C	4.722441000	-5.467715000	-0.018939000
C	4.666042000	-4.083122000	-0.178328000
C	-4.834182000	-4.558182000	-1.309365000
C	-3.572643000	-4.703032000	-1.792472000
C	0.520244000	-5.458292000	2.420979000
C	1.577706000	-6.134379000	1.901220000
H	1.267698000	4.376634000	-0.681883000
H	-5.340201000	3.009721000	-1.470171000

H	-6.114131000	1.444034000	-1.283661000
H	-6.047226000	2.550100000	0.107628000
H	6.002054000	-1.987320000	0.558820000
H	6.196889000	-1.479661000	-1.138687000
H	6.307345000	-0.297401000	0.194143000
H	-6.597672000	0.178541000	0.391478000
H	-8.068969000	-1.775072000	0.463997000
H	-7.276455000	-3.980531000	-0.345021000
H	-1.066371000	-4.722534000	-2.748691000
H	0.477753000	-2.783088000	-2.885465000
H	-0.172423000	-0.611855000	-1.978594000
H	0.025355000	-0.190504000	1.828383000
H	-1.606294000	-1.429923000	3.157949000
H	-1.431738000	-3.895820000	3.391710000
H	3.781059000	-7.214393000	0.809588000
H	5.556097000	-6.017890000	-0.442362000
H	5.444260000	-3.599947000	-0.751538000
H	-5.515503000	-5.402792000	-1.273590000
H	-3.227660000	-5.665853000	-2.157290000
H	-0.251709000	-5.981270000	2.977439000
H	1.665576000	-7.209191000	2.027343000
C	-2.752727000	3.616859000	-0.165156000
C	-3.856730000	4.536755000	0.328761000
H	-3.474261000	5.555523000	0.362004000

H	-4.698325000	4.570834000	-0.365706000
C	-4.366969000	4.177544000	1.744232000
H	-4.749558000	3.151512000	1.768981000
H	-3.523040000	4.197678000	2.441188000
C	-5.454145000	5.146105000	2.217605000
H	-5.796095000	4.883702000	3.222972000
H	-5.081416000	6.175482000	2.248625000
H	-6.324319000	5.127642000	1.552242000
C	-1.442174000	4.042197000	-0.322272000
C	-1.032138000	5.502303000	-0.319206000
H	-1.898645000	6.130389000	-0.530420000
H	-0.362212000	5.648829000	-1.174556000
C	-0.320824000	6.038051000	0.950189000
H	0.573671000	5.441481000	1.159302000
H	0.034547000	7.045507000	0.706920000
C	-1.181558000	6.095430000	2.213159000
H	-1.495286000	5.097749000	2.534879000
H	-0.614911000	6.540360000	3.036658000
H	-2.078433000	6.705729000	2.063254000
C	3.808937000	4.000637000	-1.033560000
H	3.090966000	4.478981000	-1.708640000
H	4.756746000	3.991169000	-1.572735000
C	3.977712000	4.873563000	0.234829000
H	4.700693000	4.395416000	0.904992000

H	3.034429000	4.914090000	0.791486000
C	4.438098000	6.292583000	-0.106830000
H	3.715505000	6.799328000	-0.755595000
H	4.551931000	6.892190000	0.801064000
H	5.403007000	6.282350000	-0.624846000
C	5.637436000	1.651315000	-1.324005000
H	5.577713000	2.304300000	-2.199590000
H	5.971186000	0.692965000	-1.723277000
C	6.705060000	2.219820000	-0.364320000
H	6.744472000	1.629114000	0.559013000
H	6.411397000	3.227209000	-0.052735000
C	8.090428000	2.265762000	-1.014413000
H	8.827617000	2.692908000	-0.328538000
H	8.433750000	1.263810000	-1.293857000
H	8.080900000	2.879836000	-1.921259000

c-H3

Total energy of the optimized structure E = -5140.9838 Hartree

C	-1.174442000	-0.120801000	-0.309562000
C	-1.080928000	1.293075000	-0.379151000
N	-0.018782000	1.983692000	0.004349000
C	1.057770000	1.315226000	0.386829000
C	1.180987000	-0.096255000	0.316024000

C	0.010440000	-0.796413000	0.003338000
N	-2.206581000	1.998492000	-0.823502000
N	2.168681000	2.043620000	0.831260000
C	-3.444986000	1.382031000	-0.823696000
N	-4.378464000	2.347713000	-1.006156000
C	-3.740692000	3.586772000	-1.091936000
C	-2.373223000	3.370018000	-1.095230000
C	2.306337000	3.417790000	1.105203000
C	3.668779000	3.664230000	1.098355000
N	4.332993000	2.439371000	1.007879000
C	3.420015000	1.453941000	0.827181000
C	-2.447263000	-0.787731000	-0.467288000
C	-3.591276000	-0.038281000	-0.663787000
C	3.595884000	0.036944000	0.667154000
C	2.467642000	-0.736363000	0.472461000
C	-5.795740000	2.132789000	-1.350499000
C	5.756749000	2.254676000	1.342217000
C	-4.309715000	4.909481000	-1.119802000
C	-3.399042000	5.977680000	-1.385686000
C	-1.996831000	5.698369000	-1.707920000
C	-1.452381000	4.385013000	-1.550528000
C	1.364640000	4.411284000	1.565107000
C	1.880964000	5.735489000	1.726266000
C	3.276055000	6.046120000	1.401794000

C	4.208826000	4.999000000	1.128464000
C	-5.654114000	5.201508000	-0.793281000
C	-6.108232000	6.507668000	-0.761207000
C	-5.226070000	7.560935000	-1.039912000
C	0.147685000	6.441935000	-2.610818000
C	0.654265000	5.138575000	-2.507971000
C	-0.134308000	4.128477000	-1.988754000
C	0.052610000	4.125114000	2.003252000
C	-0.756977000	5.116333000	2.526409000
C	-0.278029000	6.429718000	2.633924000
C	5.067508000	7.669982000	1.057431000
C	5.971121000	6.637303000	0.770561000
C	5.545270000	5.321556000	0.798165000
H	0.021977000	-1.878648000	0.003163000
H	-5.897928000	1.175314000	-1.849042000
H	-6.096256000	2.921145000	-2.036404000
H	-6.419412000	2.145503000	-0.456052000
H	6.045002000	3.047800000	2.027885000
H	6.373428000	2.283405000	0.443253000
H	5.883741000	1.298397000	1.837302000
H	-6.337193000	4.411452000	-0.517154000
H	-7.140825000	6.711660000	-0.498529000
H	-5.574709000	8.587888000	-1.004201000
H	0.762879000	7.238254000	-3.016969000

H	1.659545000	4.913092000	-2.848661000
H	0.260586000	3.125803000	-1.945312000
H	-0.321025000	3.114516000	1.955847000
H	-1.757141000	4.868398000	2.866553000
H	-0.909708000	7.211249000	3.043500000
H	5.393759000	8.704390000	1.025475000
H	6.998106000	6.864670000	0.505086000
H	6.244012000	4.547643000	0.515641000
C	-3.899708000	7.296675000	-1.334709000
H	-3.233648000	8.133040000	-1.504185000
C	-1.154932000	6.706260000	-2.227950000
H	-1.540899000	7.707264000	-2.371388000
C	1.018328000	6.723214000	2.250986000
H	1.382806000	7.731809000	2.397565000
C	3.748139000	7.375775000	1.355182000
H	3.064823000	8.196888000	1.530299000
C	-2.480822000	-2.270081000	-0.324375000
C	-2.086762000	-3.153060000	-1.383152000
C	-2.806487000	-2.928342000	0.841398000
C	-2.131505000	-4.483384000	-1.044056000
H	-1.761162000	-2.800130000	-2.354462000
S	-2.661537000	-4.652119000	0.620519000
C	-4.937701000	-0.678798000	-0.652058000
C	-5.817089000	-0.591840000	0.476447000

C	-5.458116000	-1.412607000	-1.696565000
C	-7.006024000	-1.257686000	0.307078000
H	-5.572981000	-0.032778000	1.372054000
S	-7.041543000	-2.010703000	-1.278200000
C	-1.811291000	-5.651879000	-1.875228000
C	-1.409474000	-6.872768000	-1.302544000
C	-1.898780000	-5.569029000	-3.277868000
C	-1.104125000	-7.970936000	-2.105024000
H	-1.316257000	-6.959243000	-0.224053000
C	-1.581638000	-6.665222000	-4.077001000
H	-2.233887000	-4.647304000	-3.742509000
C	-1.184855000	-7.872113000	-3.495656000
H	-0.796146000	-8.903295000	-1.641581000
H	-1.657179000	-6.579771000	-5.156853000
H	-0.944824000	-8.727182000	-4.119846000
C	-3.227414000	-2.367829000	2.166691000
H	-4.280849000	-2.581041000	2.377072000
H	-3.096962000	-1.283448000	2.180773000
H	-2.634874000	-2.789561000	2.984381000
C	-4.867034000	-1.711478000	-3.041397000
H	-5.575390000	-1.493257000	-3.846413000
H	-4.581532000	-2.765148000	-3.127373000
H	-3.971947000	-1.107625000	-3.206636000
C	-8.127081000	-1.388071000	1.248009000

C	-9.433933000	-1.653990000	0.800272000
C	-7.911096000	-1.242268000	2.631591000
C	-10.488080000	-1.769178000	1.704532000
H	-9.631525000	-1.754915000	-0.262972000
C	-8.969091000	-1.347506000	3.531545000
H	-6.907507000	-1.063906000	3.004266000
C	-10.262206000	-1.613036000	3.073625000
H	-11.488909000	-1.973370000	1.336557000
H	-8.780452000	-1.233434000	4.594763000
H	-11.084254000	-1.700592000	3.777128000
C	4.955874000	-0.574223000	0.651761000
C	5.820709000	-0.486825000	-0.487966000
C	5.496029000	-1.295068000	1.695178000
H	5.540071000	0.020506000	-1.403368000
C	2.531878000	-2.217742000	0.329557000
C	2.858536000	-2.868621000	-0.840117000
C	2.167393000	-3.108964000	1.391911000
S	2.750660000	-4.595072000	-0.618951000
C	2.235395000	-4.437946000	1.051294000
C	3.256831000	-2.298505000	-2.168480000
H	3.070012000	-1.222417000	-2.193007000
H	4.321213000	-2.457684000	-2.371336000
H	2.691584000	-2.757413000	-2.985239000
H	1.844133000	-2.763411000	2.366662000

C	1.946287000	-5.613034000	1.884611000
C	2.050300000	-5.530580000	3.286143000
C	1.557756000	-6.839745000	1.315190000
C	1.762020000	-6.633078000	4.087565000
H	2.375493000	-4.603832000	3.747854000
C	1.281370000	-7.943999000	2.119803000
H	1.451422000	-6.926131000	0.237898000
C	1.378352000	-7.845739000	3.509444000
H	1.849876000	-6.547815000	5.166503000
H	0.983039000	-8.880749000	1.658901000
H	1.160817000	-8.705593000	4.135308000
S	7.087542000	-1.865801000	1.268581000
C	7.018576000	-1.138548000	-0.327232000
C	8.130212000	-1.261519000	-1.280019000
C	8.314474000	-0.288493000	-2.280723000
C	9.028573000	-2.342586000	-1.225055000
C	9.354486000	-0.402359000	-3.200314000
H	7.651247000	0.569543000	-2.325649000
C	10.074822000	-2.447075000	-2.139868000
H	8.897900000	-3.116499000	-0.474286000
C	10.240939000	-1.480400000	-3.133747000
H	9.479867000	0.359625000	-3.963664000
H	10.755559000	-3.290756000	-2.080370000
H	11.054429000	-1.564175000	-3.847588000

C	4.921375000	-1.594508000	3.046944000
H	4.661297000	-2.653664000	3.144789000
H	5.629774000	-1.352552000	3.845286000
H	4.013840000	-1.009752000	3.212788000

n-H1

Total energy of the optimized structure E = -2244.5155 Hartree

N	2.328162000	0.141670000	0.003796000
N	0.003812000	0.329649000	-0.251469000
N	-4.556582000	0.383671000	-0.148545000
N	4.511023000	-0.307397000	-0.376739000
N	-2.325798000	0.422872000	-0.515462000
C	1.191792000	0.921840000	-0.224449000
C	-1.088512000	1.065011000	-0.421580000
C	2.532424000	-1.202280000	0.374563000
C	-2.089356000	-2.130386000	-1.100316000
C	3.877078000	-1.431957000	0.081095000
C	-2.727196000	-0.924757000	-0.621794000
C	1.380427000	2.311688000	-0.475010000
C	-1.074088000	2.489580000	-0.468828000
C	2.339520000	-3.469803000	1.283001000
C	-4.095274000	-0.890201000	-0.346942000
C	4.486410000	-2.722214000	0.246304000
C	5.207199000	2.415287000	-1.042591000
H	5.680299000	1.581794000	-1.570564000
H	5.223434000	3.271464000	-1.723058000
C	0.201305000	3.064784000	-0.539384000
H	0.279155000	4.136654000	-0.649923000

C	1.742509000	-2.176013000	1.091647000
C	-3.496101000	1.162807000	-0.270497000
C	2.705733000	2.873990000	-0.695812000
C	-2.303028000	3.268731000	-0.410285000
C	3.693889000	-3.764581000	0.799546000
C	-3.491778000	2.600929000	-0.240898000
C	3.581930000	0.632690000	-0.400532000
C	3.780980000	2.019579000	-0.728140000
C	-0.803040000	-2.185092000	-1.684281000
H	-0.215487000	-1.282026000	-1.736985000
C	2.839916000	4.364992000	-0.916028000
H	3.778189000	4.581439000	-1.431988000
H	2.047488000	4.715437000	-1.588467000
C	-4.895001000	-2.081641000	-0.282265000
C	-2.878662000	-3.331898000	-1.062543000
C	5.816604000	-2.963389000	-0.154378000
H	6.389952000	-2.139324000	-0.565368000
C	-4.840643000	3.252304000	-0.033840000
H	-5.582001000	2.709536000	-0.630017000
H	-4.826237000	4.281619000	-0.401191000
C	0.490296000	-1.912055000	1.692429000
H	0.050852000	-0.933438000	1.576834000
C	1.607378000	-4.436334000	2.008352000
H	2.033909000	-5.419029000	2.169002000

C	-0.184789000	-2.880433000	2.413283000
H	-1.143197000	-2.642677000	2.864876000
C	-4.267370000	-3.319479000	-0.587591000
C	4.282796000	-5.047635000	0.891843000
H	3.712649000	-5.882867000	1.280836000
C	0.368803000	-4.160322000	2.560220000
H	-0.158494000	-4.927394000	3.119025000
C	7.503284000	3.080010000	-0.144181000
H	7.559734000	3.953460000	-0.803754000
H	8.085416000	3.303737000	0.755529000
H	7.990887000	2.244094000	-0.658220000
C	2.799174000	5.192998000	0.387999000
H	3.614462000	4.864082000	1.042931000
H	1.871078000	4.983766000	0.933467000
C	-0.279993000	-3.367647000	-2.175593000
H	0.710208000	-3.371956000	-2.621120000
C	-2.215590000	4.779270000	-0.471245000
H	-1.448864000	5.071529000	-1.198054000
H	-3.151819000	5.186150000	-0.861963000
C	6.052191000	2.741114000	0.206830000
H	6.025244000	1.880885000	0.885284000
H	5.596820000	3.579621000	0.747284000
C	6.365379000	-4.227486000	-0.037709000
H	7.387837000	-4.411643000	-0.353275000

C	5.586243000	-5.276355000	0.481785000
H	6.005707000	-6.274606000	0.563350000
C	-6.251404000	-2.036004000	0.100257000
H	-6.694743000	-1.070168000	0.317631000
C	-2.299466000	-4.521973000	-1.557037000
H	-2.873803000	-5.440347000	-1.543618000
C	-1.911126000	5.456225000	0.882909000
H	-2.707162000	5.205780000	1.593688000
H	-0.987160000	5.041487000	1.303816000
C	-6.681464000	3.906462000	1.608748000
H	-6.668120000	4.951247000	1.278115000
H	-7.445058000	3.382718000	1.022675000
H	-6.997779000	3.892511000	2.656700000
C	-1.786182000	6.976934000	0.758997000
H	-0.974033000	7.253745000	0.077151000
H	-2.710247000	7.420339000	0.371525000
H	-1.577388000	7.435832000	1.730450000
C	-6.988421000	-3.201249000	0.208375000
H	-8.030995000	-3.163721000	0.509280000
C	-1.026705000	-4.551741000	-2.099063000
H	-0.620280000	-5.484678000	-2.477467000
C	-5.046725000	-4.492471000	-0.452457000
H	-4.607937000	-5.464133000	-0.645487000
C	2.916445000	6.696885000	0.127270000

H	3.853966000	6.938336000	-0.385844000
H	2.092779000	7.056582000	-0.499812000
H	2.893652000	7.261654000	1.064486000
C	-5.308473000	3.251133000	1.437712000
H	-4.568297000	3.773802000	2.055714000
H	-5.342540000	2.216910000	1.796272000
C	-6.374881000	-4.437173000	-0.062174000
H	-6.943013000	-5.357471000	0.034846000

n-H2

Total energy of the optimized structure E = -2396.9837 Hartree

N	-0.024052000	0.706194000	0.158360000
N	4.493996000	0.754395000	-0.448208000
N	2.320605000	0.817835000	0.172656000
N	-4.492504000	0.071751000	0.761708000
N	-2.362445000	0.503997000	0.142401000
C	4.275656000	-2.902584000	0.275203000
C	4.065732000	-0.505315000	-0.126779000
C	1.074868000	1.451416000	0.170295000
C	-1.212920000	1.295047000	0.212190000
C	-1.384267000	2.696656000	0.399430000
C	2.151647000	-1.702876000	0.903397000
C	-2.595505000	-0.855228000	-0.146264000

C	2.955480000	-2.899634000	0.842114000
C	4.867222000	-1.696276000	-0.199031000
C	3.452596000	1.541895000	-0.243164000
C	-3.905204000	-1.070551000	0.290297000
C	-2.499920000	-3.156963000	-0.966914000
C	-3.572780000	1.014843000	0.646204000
C	1.054433000	2.876195000	0.128952000
C	6.169342000	-1.699881000	-0.711904000
H	6.597983000	-0.767146000	-1.062014000
C	2.736978000	-0.523012000	0.305051000
C	-1.866968000	-1.863243000	-0.884126000
C	2.444008000	-4.116854000	1.392883000
C	-4.536473000	-2.360177000	0.219532000
C	-3.796603000	-3.408089000	-0.401087000
C	-0.210111000	3.453734000	0.300011000
H	-0.283189000	4.529967000	0.358863000
C	-1.838404000	-4.217251000	-1.662920000
C	-0.661556000	-1.666648000	-1.575068000
H	-0.187686000	-0.698022000	-1.546890000
C	6.338182000	-4.080495000	-0.321027000
H	6.908874000	-5.003927000	-0.366078000
C	2.264097000	3.649659000	-0.110712000
C	3.435119000	2.975862000	-0.355717000
C	-3.745209000	2.417949000	0.916718000

C	-0.612357000	-3.973523000	-2.305109000
H	-0.121387000	-4.784978000	-2.834818000
C	6.895712000	-2.889805000	-0.777311000
H	7.902549000	-2.885025000	-1.183981000
C	4.752808000	3.623168000	-0.729469000
H	4.581174000	4.634194000	-1.106873000
H	5.180917000	3.048105000	-1.556883000
C	2.170034000	5.159855000	-0.180640000
H	3.137375000	5.601333000	0.067594000
H	1.481277000	5.525067000	0.589596000
C	-4.387454000	-4.707264000	-0.488992000
C	5.038375000	-4.110729000	0.216238000
C	-5.668794000	-4.920115000	0.051472000
H	-6.108704000	-5.911360000	-0.014965000
C	1.195442000	-4.121858000	2.037666000
H	0.819143000	-5.050828000	2.456554000
C	4.461875000	-5.321971000	0.727925000
H	5.042380000	-6.238393000	0.668094000
C	3.226991000	-5.319314000	1.297243000
H	2.805462000	-6.235045000	1.702710000
C	-5.815885000	-2.603826000	0.731596000
H	-6.360001000	-1.787748000	1.194578000
C	-2.682428000	3.267741000	0.725475000
C	0.464563000	-2.947731000	2.152058000

H	-0.487657000	-2.949225000	2.673908000
C	0.930042000	-1.757779000	1.591622000
H	0.328205000	-0.866252000	1.672452000
C	-0.049310000	-2.705409000	-2.276913000
H	0.884941000	-2.514401000	-2.796281000
C	-6.373208000	-3.880940000	0.652086000
H	-7.363357000	-4.063196000	1.058948000
C	1.719828000	5.691144000	-1.559331000
H	2.439173000	5.361105000	-2.318694000
H	0.760116000	5.237160000	-1.833821000
C	5.798318000	3.667096000	0.410048000
H	5.989495000	2.643121000	0.746538000
H	6.739113000	4.034139000	-0.018278000
C	-5.119944000	2.844707000	1.395243000
H	-5.008569000	3.552622000	2.223628000
H	-5.618514000	1.961268000	1.801240000
C	-3.662146000	-5.757571000	-1.146559000
H	-4.112075000	-6.745151000	-1.198061000
C	-2.449587000	-5.517874000	-1.713532000
H	-1.915906000	-6.311639000	-2.229032000
C	-6.037958000	3.479358000	0.325388000
H	-6.979886000	3.745392000	0.821092000
H	-5.602290000	4.423162000	-0.022227000
C	-6.333262000	2.580422000	-0.878249000

H	-5.420827000	2.345663000	-1.436191000
H	-7.026942000	3.072564000	-1.567762000
H	-6.780411000	1.632002000	-0.564807000
C	-2.801265000	4.766924000	0.892836000
H	-1.962265000	5.141363000	1.492747000
H	-3.701465000	5.003905000	1.465216000
C	1.599243000	7.217031000	-1.585834000
H	2.554398000	7.693520000	-1.338244000
H	0.855589000	7.569021000	-0.861902000
H	1.295569000	7.571917000	-2.575651000
C	-2.850768000	5.545509000	-0.441573000
H	-1.957812000	5.322268000	-1.037145000
H	-3.702055000	5.187456000	-1.032029000
C	5.409214000	4.543954000	1.603364000
H	6.183079000	4.511947000	2.377236000
H	4.471454000	4.209604000	2.059654000
H	5.282967000	5.591672000	1.307281000
C	-2.963068000	7.057282000	-0.228472000
H	-2.105810000	7.443125000	0.334808000
H	-3.869724000	7.312503000	0.331317000
H	-3.000602000	7.587975000	-1.184901000

n-H1 + 2H^{+}

Total energy of the optimized structure E = -2245.3969 Hartree

N	2.320705000	0.143490000	0.010811000
N	0.007468000	0.353777000	-0.259915000
N	-4.472371000	0.373802000	-0.183369000
N	4.422420000	-0.370106000	-0.325242000
N	-2.312642000	0.462398000	-0.535587000
C	1.191621000	0.941643000	-0.219746000
C	-1.068525000	1.101315000	-0.440685000
C	2.482653000	-1.212003000	0.403479000
C	-2.026712000	-2.083436000	-1.150636000
C	3.804365000	-1.518385000	0.127754000
C	-2.696424000	-0.900157000	-0.661203000
C	1.398888000	2.328594000	-0.466108000
C	-1.048676000	2.524680000	-0.488915000
C	2.182092000	-3.468393000	1.291239000
C	-4.051730000	-0.926670000	-0.378197000
C	4.379069000	-2.816870000	0.281965000
C	5.230835000	2.384946000	-1.016939000
H	5.700142000	1.579758000	-1.595608000
H	5.243350000	3.250180000	-1.682930000
C	0.229416000	3.095451000	-0.546017000
H	0.317075000	4.165792000	-0.658380000
C	1.645147000	-2.148184000	1.116568000
C	-3.436290000	1.221314000	-0.304783000
C	2.727977000	2.877649000	-0.673771000

C	-2.270385000	3.309240000	-0.439748000
C	3.522890000	-3.822318000	0.813120000
C	-3.467137000	2.644027000	-0.265668000
C	3.543034000	0.645604000	-0.371588000
C	3.797837000	2.006332000	-0.705630000
C	-0.762736000	-2.088938000	-1.779876000
H	-0.218701000	-1.164403000	-1.887269000
C	2.888047000	4.364321000	-0.877704000
H	3.831034000	4.571463000	-1.386540000
H	2.104387000	4.733492000	-1.548130000
C	-4.833181000	-2.119133000	-0.290359000
C	-2.777139000	-3.306038000	-1.084488000
C	5.701976000	-3.118585000	-0.104047000
H	6.347547000	-2.344042000	-0.505797000
C	-4.814055000	3.298192000	-0.046144000
H	-5.570423000	2.792399000	-0.660394000
H	-4.786675000	4.325579000	-0.412922000
C	0.419265000	-1.818668000	1.734802000
H	0.039405000	-0.812260000	1.659187000
C	1.404234000	-4.405655000	2.006796000
H	1.778850000	-5.410082000	2.156185000
C	-0.299461000	-2.759935000	2.448110000
H	-1.234983000	-2.476688000	2.919345000
C	-4.157021000	-3.335419000	-0.588564000

C	4.044879000	-5.132952000	0.896527000
H	3.428412000	-5.942341000	1.266227000
C	0.185261000	-4.069951000	2.567245000
H	-0.378329000	-4.815160000	3.119141000
C	7.538043000	3.022993000	-0.137131000
H	7.588461000	3.901291000	-0.789407000
H	8.126651000	3.237476000	0.759531000
H	8.017404000	2.189018000	-0.661222000
C	2.855175000	5.169920000	0.443863000
H	3.658307000	4.813389000	1.098400000
H	1.918665000	4.972943000	0.978715000
C	-0.212735000	-3.257067000	-2.274337000
H	0.756907000	-3.229386000	-2.760698000
C	-2.184653000	4.815455000	-0.509822000
H	-1.406972000	5.100042000	-1.226028000
H	-3.114670000	5.216156000	-0.919098000
C	6.090510000	2.688867000	0.230696000
H	6.069522000	1.831053000	0.913992000
H	5.641749000	3.525050000	0.777839000
C	6.181424000	-4.409748000	0.008613000
H	7.197112000	-4.641271000	-0.293778000
C	5.340773000	-5.421219000	0.503243000
H	5.707884000	-6.439588000	0.578608000
C	-6.185336000	-2.119240000	0.111575000

H	-6.689957000	-1.186225000	0.340951000
C	-2.168327000	-4.480415000	-1.579918000
H	-2.706753000	-5.418727000	-1.544517000
C	-1.902102000	5.496718000	0.849966000
H	-2.708187000	5.249519000	1.549426000
H	-0.984100000	5.085762000	1.286344000
C	-6.647167000	3.962957000	1.596397000
H	-6.634455000	5.001440000	1.249148000
H	-7.413704000	3.428190000	1.025123000
H	-6.952202000	3.964372000	2.646816000
C	-1.778917000	7.016055000	0.713659000
H	-0.956530000	7.288967000	0.043340000
H	-2.698254000	7.453865000	0.310424000
H	-1.586208000	7.478549000	1.686111000
C	-6.872253000	-3.311450000	0.239819000
H	-7.910278000	-3.310112000	0.554715000
C	-0.910627000	-4.466812000	-2.154925000
H	-0.480450000	-5.388076000	-2.534106000
C	-4.888863000	-4.533808000	-0.429572000
H	-4.415757000	-5.489500000	-0.615529000
C	3.007467000	6.673113000	0.200456000
H	3.954692000	6.899860000	-0.300240000
H	2.196561000	7.058027000	-0.427488000
H	2.988654000	7.222394000	1.146292000

C	-5.273665000	3.308220000	1.430879000
H	-4.529121000	3.841581000	2.031909000
H	-5.302349000	2.285075000	1.825449000
C	-6.213030000	-4.523732000	-0.025163000
H	-6.743878000	-5.463257000	0.089127000
H	5.403446000	-0.278521000	-0.546961000
H	-5.426708000	0.668897000	-0.032711000

n-H2 + 2H^{+}

Total energy of the optimized structure E = -2397.8647 Hartree

N	0.007198000	0.732258000	-0.165985000
N	-4.436732000	0.640461000	0.395481000
N	-2.332237000	0.800541000	-0.190044000
N	4.407970000	0.123110000	-0.709273000
N	2.341800000	0.564874000	-0.137916000
C	-4.107946000	-3.018315000	-0.290032000
C	-4.017006000	-0.637345000	0.086808000
C	-1.095684000	1.462352000	-0.186440000
C	1.178988000	1.344802000	-0.205705000
C	1.333872000	2.748291000	-0.384851000
C	-2.057345000	-1.709991000	-0.947802000
C	2.572507000	-0.802482000	0.174570000
C	-2.795323000	-2.945301000	-0.865580000

C	-4.773914000	-1.846418000	0.177563000
C	-3.439246000	1.519493000	0.199575000
C	3.868052000	-1.058300000	-0.246251000
C	2.441364000	-3.097883000	0.990393000
C	3.508924000	1.118300000	-0.616558000
C	-1.104731000	2.886292000	-0.140028000
C	-6.071964000	-1.919821000	0.697266000
H	-6.576800000	-1.029127000	1.056712000
C	-2.700925000	-0.564675000	-0.342137000
C	1.826314000	-1.796439000	0.914879000
C	-2.222702000	-4.135329000	-1.414895000
C	4.501937000	-2.337894000	-0.187349000
C	3.733702000	-3.370182000	0.428652000
C	0.149315000	3.490270000	-0.295002000
H	0.205322000	4.567064000	-0.350690000
C	1.762416000	-4.148430000	1.683871000
C	0.634742000	-1.572798000	1.617861000
H	0.187300000	-0.592201000	1.618279000
C	-6.095751000	-4.306901000	0.323406000
H	-6.611101000	-5.261039000	0.378353000
C	-2.326226000	3.636442000	0.091187000
C	-3.490770000	2.936349000	0.326812000
C	3.698939000	2.500556000	-0.901201000
C	0.544629000	-3.881543000	2.331253000

H	0.040342000	-4.685085000	2.859478000
C	-6.723834000	-3.150167000	0.772560000
H	-7.726555000	-3.201468000	1.183356000
C	-4.828401000	3.552025000	0.687872000
H	-4.671547000	4.560362000	1.074041000
H	-5.254492000	2.989278000	1.527697000
C	-2.268997000	5.143761000	0.170792000
H	-3.241673000	5.562504000	-0.091915000
H	-1.575707000	5.527637000	-0.584400000
C	4.299963000	-4.679308000	0.515855000
C	-4.798476000	-4.267264000	-0.217749000
C	5.579109000	-4.913264000	-0.019576000
H	6.000360000	-5.911878000	0.046738000
C	-0.988122000	-4.069520000	-2.081664000
H	-0.564917000	-4.977694000	-2.500114000
C	-4.158222000	-5.448991000	-0.720826000
H	-4.685832000	-6.395100000	-0.647333000
C	-2.931193000	-5.380727000	-1.301222000
H	-2.461328000	-6.273102000	-1.703807000
C	5.777909000	-2.602863000	-0.699438000
H	6.359197000	-1.819205000	-1.174920000
C	2.620919000	3.340014000	-0.701408000
C	-0.332841000	-2.855465000	-2.228975000
H	0.600656000	-2.804921000	-2.779911000

C	-0.855046000	-1.690575000	-1.667406000
H	-0.317888000	-0.764128000	-1.790484000
C	0.007659000	-2.602415000	2.318907000
H	-0.913970000	-2.394553000	2.852672000
C	6.307484000	-3.890237000	-0.617353000
H	7.293607000	-4.091279000	-1.022322000
C	-1.855329000	5.668313000	1.566555000
H	-2.576826000	5.310511000	2.310379000
H	-0.887741000	5.238472000	1.850870000
C	-5.860828000	3.601350000	-0.466617000
H	-6.039177000	2.591773000	-0.856496000
H	-6.811618000	3.931475000	-0.034362000
C	5.061861000	2.954941000	-1.391987000
H	4.912061000	3.704484000	-2.173667000
H	5.564843000	2.124788000	-1.900184000
C	3.555945000	-5.719724000	1.166716000
H	3.989258000	-6.714038000	1.215326000
C	2.347498000	-5.460229000	1.731991000
H	1.798856000	-6.244356000	2.245145000
C	6.005756000	3.537817000	-0.314876000
H	6.898557000	3.902347000	-0.834896000
H	5.535304000	4.417018000	0.137690000
C	6.420580000	2.557057000	0.784784000
H	5.559343000	2.186605000	1.351013000

H	7.091730000	3.045406000	1.497213000
H	6.958204000	1.694096000	0.374434000
C	2.727152000	4.838610000	-0.846063000
H	1.886129000	5.212988000	-1.440721000
H	3.625532000	5.094583000	-1.410664000
C	-1.779511000	7.196351000	1.604781000
H	-2.744662000	7.647040000	1.349962000
H	-1.035885000	7.575116000	0.895154000
H	-1.499374000	7.546452000	2.602625000
C	2.767921000	5.587321000	0.508959000
H	1.873052000	5.349400000	1.095416000
H	3.617979000	5.220932000	1.095159000
C	-5.475697000	4.525863000	-1.624268000
H	-6.245094000	4.504410000	-2.401612000
H	-4.530386000	4.225457000	-2.088042000
H	-5.375169000	5.563399000	-1.288045000
C	2.875704000	7.102139000	0.319712000
H	2.019746000	7.494110000	-0.240423000
H	3.785104000	7.369829000	-0.228669000
H	2.905593000	7.612125000	1.287007000
H	-5.371577000	0.900505000	0.676597000
H	5.364457000	0.252813000	-1.005389000

TS c-H1

Total energy of the optimized structure E = -2323.9616 Hartree

C	-0.958870000	2.519677000	-0.033205000
C	-1.013230000	1.108930000	0.127018000
C	0.311742000	3.088619000	0.032589000
C	-2.138769000	3.287363000	-0.401478000
N	0.049353000	0.321702000	0.279233000
N	-2.278550000	0.516883000	-0.079976000
C	1.463768000	2.295954000	0.077984000
H	0.413374000	4.157082000	-0.082234000
C	-3.216089000	2.615493000	-0.941065000
C	-2.109556000	4.786743000	-0.223244000
C	1.250792000	0.898851000	0.198588000
C	-3.152632000	1.178462000	-0.918315000
C	-2.714038000	-0.809402000	0.048539000
C	-4.501928000	3.322133000	-1.340239000
H	-1.245724000	5.201892000	-0.757781000
H	-2.985398000	5.237321000	-0.690108000
C	-2.049594000	5.234454000	1.256314000
N	2.390553000	0.083684000	0.059905000
C	-3.709397000	-0.995613000	-0.895495000
C	-2.527398000	-1.715196000	1.144746000
C	3.759772000	1.997508000	-0.684903000

H	-4.262206000	4.247393000	-1.871148000
H	-5.084395000	2.728211000	-2.040147000
C	-5.407384000	3.632545000	-0.126076000
H	-1.158257000	4.816596000	1.737935000
H	-2.909151000	4.816091000	1.792493000
C	-2.042127000	6.759155000	1.390474000
C	2.508439000	-1.315949000	0.137797000
C	3.505524000	0.587996000	-0.598624000
C	-4.343697000	-2.277448000	-1.085172000
C	-3.173389000	-2.980193000	1.028608000
C	-1.963418000	-1.315936000	2.373557000
C	5.042957000	2.547423000	-1.284302000
H	-5.636226000	2.696187000	0.396676000
H	-4.865062000	4.260468000	0.588820000
C	-6.704983000	4.327573000	-0.545841000
H	-2.000068000	7.055944000	2.442580000
H	-1.175872000	7.197779000	0.883216000
H	-2.944085000	7.201138000	0.953841000
C	3.576711000	-1.654627000	-0.665870000
C	1.999723000	-2.251453000	1.108400000
C	-3.960401000	-3.305826000	-0.163175000
C	-5.278644000	-2.582285000	-2.101792000
C	-3.151731000	-3.833569000	2.153907000
C	-2.024404000	-2.151471000	3.472876000

H	-1.530915000	-0.327609000	2.471114000
H	5.399975000	1.892567000	-2.078731000
H	4.807889000	3.484986000	-1.793319000
C	6.168876000	2.806186000	-0.260264000
H	-7.330991000	4.540314000	0.325714000
H	-6.500251000	5.277488000	-1.051482000
H	-7.287212000	3.702537000	-1.231604000
C	3.874332000	-3.024414000	-0.999561000
C	2.421999000	-3.608327000	0.957043000
C	1.353236000	-1.848582000	2.292585000
C	-4.449247000	-4.610956000	-0.382979000
C	-5.760036000	-3.869081000	-2.265804000
H	-5.635543000	-1.817521000	-2.774040000
C	-2.595642000	-3.427940000	3.354764000
H	-3.641563000	-4.798318000	2.108819000
H	-1.640736000	-1.813403000	4.429313000
H	6.409225000	1.880840000	0.278177000
H	5.803757000	3.501397000	0.504183000
C	7.429055000	3.372086000	-0.919544000
C	3.226376000	-4.012685000	-0.198106000
C	4.647771000	-3.422267000	-2.113032000
C	2.120491000	-4.516365000	1.992459000
C	1.129357000	-2.756826000	3.312387000
H	1.078250000	-0.810557000	2.427467000

C	-5.321849000	-4.896229000	-1.418533000
H	-4.130848000	-5.416651000	0.267191000
H	-6.468606000	-4.078347000	-3.060201000
H	-2.634042000	-4.088100000	4.215116000
H	8.209264000	3.554930000	-0.175098000
H	7.833744000	2.680233000	-1.666182000
H	7.218103000	4.320917000	-1.424308000
C	3.411168000	-5.367751000	-0.541502000
C	4.812640000	-4.763394000	-2.414639000
H	5.076494000	-2.682399000	-2.776056000
C	1.492803000	-4.100976000	3.154675000
H	2.441344000	-5.547873000	1.911806000
H	0.681575000	-2.422306000	4.240364000
H	-5.674262000	-5.912149000	-1.563722000
C	4.195396000	-5.740650000	-1.620860000
H	2.907973000	-6.138901000	0.029280000
H	5.398936000	-5.051613000	-3.280742000
H	1.310009000	-4.812371000	3.953396000
H	4.310797000	-6.791791000	-1.864419000
C	2.774771000	2.844837000	-0.212198000
C	2.977817000	4.335233000	-0.066072000
H	2.213614000	4.882632000	-0.630353000
H	3.930874000	4.636361000	-0.498446000
C	2.949425000	4.793929000	1.411886000

H	1.994843000	4.514118000	1.871773000
H	3.725879000	4.252809000	1.965241000
C	3.167815000	6.302943000	1.544642000
H	4.131661000	6.603056000	1.119785000
H	2.384009000	6.865020000	1.025268000
H	3.156627000	6.605474000	2.595893000
C	5.610511000	-0.475533000	-1.546467000
H	6.192879000	0.271273000	-1.017415000
H	5.638572000	-0.293795000	-2.621774000
H	6.044317000	-1.446991000	-1.327113000
N	4.225059000	-0.476951000	-1.043844000
C	-4.676389000	0.457676000	-2.763950000
H	-4.432538000	-0.363516000	-3.435218000
H	-4.326221000	1.372663000	-3.231645000
H	-5.753358000	0.502822000	-2.595682000
N	-3.942272000	0.244787000	-1.505844000

B3LYP/6-31g(d,p), CPCM-CH_2Cl_2

# of imaginary frequencies = 1

-------Thermochemistry-------

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction = 0.922422 (Hartree/Particle)

Thermal correction to Energy = 0.971161

Thermal correction to Enthalpy = 0.972105

Thermal correction to Gibbs Free Energy = 0.841408

Sum of electronic and zero-point Energies = -2323.039146

Sum of electronic and thermal Energies = -2322.990407

Sum of electronic and thermal Enthalpies = -2322.989463

Sum of electronic and thermal Free Energies = -2323.120160

TS c-H2

Total energy of the optimized structure E = -2476.4284 Hartree

C	-1.216186000	2.772410000	0.006503000
C	-1.137557000	1.358113000	0.115872000
C	0.000028000	3.455415000	0.034408000
C	-2.471704000	3.447013000	-0.284251000
N	0.000007000	0.669782000	0.223603000
N	-2.346603000	0.656777000	-0.102805000
C	1.216232000	2.772392000	0.006504000
H	0.000036000	4.531765000	-0.054876000
C	-3.498895000	2.704778000	-0.826035000
C	-2.574441000	4.930957000	-0.024115000
C	1.137582000	1.358096000	0.115874000
C	-3.296061000	1.282817000	-0.887149000
C	-2.659434000	-0.712423000	-0.051761000
C	-4.861291000	3.300250000	-1.143896000
H	-1.771650000	5.453441000	-0.559186000

H	-3.503301000	5.321965000	-0.439655000
C	-2.505074000	5.300226000	1.476174000
N	2.346617000	0.656742000	-0.102800000
N	-4.007190000	0.319818000	-1.521653000
C	-3.654477000	-0.927859000	-0.991905000
C	-2.342719000	-1.679608000	0.959685000
C	3.498943000	2.704727000	-0.826025000
H	-4.733491000	4.276957000	-1.618390000
H	-5.403529000	2.695411000	-1.866539000
C	-5.752216000	3.438114000	0.111722000
H	-1.565113000	4.936850000	1.906784000
H	-3.306608000	4.777703000	2.010846000
C	-2.626526000	6.809566000	1.699481000
C	2.659427000	-0.712463000	-0.051757000
C	3.296089000	1.282769000	-0.887138000
C	-4.208827000	-2.236138000	-1.241834000
C	-2.904821000	-2.981991000	0.763606000
C	-1.707595000	-1.369619000	2.167294000
C	4.861348000	3.300179000	-1.143883000
H	-5.870915000	2.451727000	0.575980000
H	-5.250944000	4.069408000	0.853190000
C	-7.125621000	4.024558000	-0.224827000
H	-2.578098000	7.048944000	2.765854000
H	-1.817942000	7.351690000	1.197081000

H	-3.576746000	7.193606000	1.313257000
C	3.654471000	-0.927913000	-0.991897000
C	2.342689000	-1.679647000	0.959682000
N	4.007206000	0.319760000	-1.521640000
C	-3.760791000	-3.270650000	-0.350198000
C	-5.142175000	-2.555547000	-2.241324000
C	-2.674444000	-3.986756000	1.753507000
C	-1.593887000	-2.335118000	3.166661000
H	-1.337993000	-0.367656000	2.345252000
H	5.403586000	2.695323000	-1.866512000
H	4.733563000	4.276881000	-1.618393000
C	5.752265000	3.438052000	0.111740000
H	-7.742486000	4.109344000	0.674674000
H	-7.034016000	5.024094000	-0.663414000
H	-7.662779000	3.393068000	-0.940828000
C	4.208802000	-2.236200000	-1.241827000
C	2.904770000	-2.982039000	0.763601000
C	1.707561000	-1.369653000	2.167288000
C	-4.263760000	-4.598750000	-0.517336000
C	-5.589070000	-3.865696000	-2.411643000
H	-5.536773000	-1.799391000	-2.901547000
C	-2.027397000	-3.636510000	2.950127000
H	-1.154719000	-2.065434000	4.119836000
H	5.870949000	2.451670000	0.576014000

H	5.250996000	4.069363000	0.853195000
C	7.125680000	4.024474000	-0.224807000
C	3.760742000	-3.270708000	-0.350199000
C	5.142153000	-2.555619000	-2.241311000
C	2.674369000	-3.986804000	1.753496000
C	1.593830000	-2.335155000	3.166650000
H	1.337975000	-0.367685000	2.345248000
C	-5.151087000	-4.878084000	-1.570006000
H	-6.295937000	-4.084735000	-3.204980000
H	-1.895138000	-4.392160000	3.718527000
H	7.742539000	4.109266000	0.674697000
H	7.662835000	3.392967000	-0.940795000
H	7.034090000	5.024005000	-0.663410000
C	4.263691000	-4.598815000	-0.517338000
C	5.589028000	-3.865775000	-2.411632000
H	5.536770000	-1.799466000	-2.901527000
C	2.027320000	-3.636553000	2.950113000
H	1.154659000	-2.065468000	4.119823000
H	-5.515561000	-5.892871000	-1.697699000
C	5.151022000	-4.878159000	-1.570003000
H	6.295898000	-4.084822000	-3.204964000
H	1.895042000	-4.392205000	3.718509000
H	5.515480000	-5.892952000	-1.697697000
C	2.471759000	3.446977000	-0.284249000

C	2.574513000	4.930922000	-0.024124000
H	1.771730000	5.453411000	-0.559203000
H	3.503379000	5.321915000	-0.439665000
C	2.505146000	5.300206000	1.476161000
H	1.565178000	4.936851000	1.906771000
H	3.306669000	4.777676000	2.010842000
C	2.626622000	6.809546000	1.699454000
H	3.576850000	7.193567000	1.313231000
H	1.818050000	7.351679000	1.197044000
H	2.578193000	7.048936000	2.765824000
C	3.157712000	-5.319555000	1.527263000
C	3.896839000	-5.617480000	0.426590000
H	2.930904000	-6.082418000	2.265928000
H	4.266715000	-6.625215000	0.263751000
C	-3.896932000	-5.617417000	0.426599000
C	-3.157808000	-5.319500000	1.527277000
H	-4.266823000	-6.625146000	0.263762000
H	-2.931018000	-6.082363000	2.265946000
C	-4.778900000	0.540394000	-2.755651000
H	-5.852580000	0.475363000	-2.573166000
H	-4.521793000	1.510637000	-3.169524000
H	-4.471642000	-0.212938000	-3.478824000
C	4.778923000	0.540327000	-2.755636000
H	4.521830000	1.510573000	-3.169509000

H 5.852602000 0.475281000 -2.573148000

H 4.471657000 -0.213001000 -3.478810000

B3LYP/6-31g(d,p), CPCM-CH_2Cl_2

# of imaginary frequencies = 1

-------Thermochemistry -------

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction = 0.947086 (Hartree/Particle)

Thermal correction to Energy = 0.997527

Thermal correction to Enthalpy= 0.998471

Thermal correction to Gibbs Free Energy = 0.863628

Sum of electronic and zero-point Energies = -2475.481289

Sum of electronic and thermal Energies = -2475.430848

Sum of electronic and thermal Enthalpies = -2475.429904

Sum of electronic and thermal Free Energies = -2475.564747

TS n-H1

Total energy of the optimized structure E = -2244.4883 Hartree

C -1.221678000 2.392954000 0.056128000

C -1.147177000 0.972341000 0.154778000

C -0.000001000 3.066816000 0.091382000

C -2.458914000 3.088636000 -0.287658000

N 0.000000000 0.289151000 0.251171000

N	-2.362269000	0.281392000	-0.017170000
C	1.221677000	2.392955000	0.056130000
H	-0.000001000	4.143918000	0.011012000
C	-3.484476000	2.345476000	-0.809790000
C	-2.530444000	4.591991000	-0.140730000
C	1.147177000	0.972342000	0.154778000
C	-3.380979000	0.912137000	-0.762942000
C	-2.714910000	-1.078074000	0.020268000
C	-4.765697000	2.901667000	-1.391248000
H	-1.688572000	5.070056000	-0.658073000
H	-3.428978000	4.967803000	-0.634631000
C	-2.550001000	5.061347000	1.330524000
N	2.362270000	0.281394000	-0.017171000
N	-4.238815000	0.044588000	-1.270315000
C	-3.825124000	-1.180474000	-0.814169000
C	-2.408650000	-2.125018000	0.958579000
C	3.484476000	2.345480000	-0.809785000
H	-4.572830000	3.857363000	-1.888314000
H	-5.116429000	2.208972000	-2.161677000
C	-5.885613000	3.083257000	-0.345810000
H	-1.658843000	4.690442000	1.850640000
H	-3.409682000	4.604316000	1.835671000
C	-2.623286000	6.585434000	1.454175000
C	2.714910000	-1.078072000	0.020264000

C	3.380980000	0.912140000	-0.762941000
C	-4.433713000	-2.449744000	-1.106597000
C	-3.062247000	-3.385545000	0.754558000
C	-1.698182000	-1.900833000	2.155565000
C	4.765699000	2.901671000	-1.391238000
H	-6.069505000	2.120805000	0.145953000
H	-5.544387000	3.771725000	0.437234000
C	-7.183670000	3.606484000	-0.966144000
H	-2.648777000	6.894819000	2.503724000
H	-1.755517000	7.063633000	0.985894000
H	-3.522235000	6.979878000	0.967457000
C	3.825123000	-1.180470000	-0.814174000
C	2.408651000	-2.125017000	0.958574000
N	4.238815000	0.044592000	-1.270317000
C	-3.981015000	-3.581475000	-0.372699000
C	-5.417476000	-2.590219000	-2.105564000
C	-2.901591000	-4.381458000	1.741193000
C	-1.624807000	-2.880298000	3.130499000
H	-1.247058000	-0.931064000	2.326483000
H	5.116429000	2.208980000	-2.161673000
H	4.572836000	3.857371000	-1.888298000
C	5.885616000	3.083250000	-0.345799000
H	-7.964392000	3.726028000	-0.208174000
H	-7.030568000	4.580717000	-1.444261000

H	-7.561942000	2.918044000	-1.730085000
C	4.433711000	-2.449741000	-1.106605000
C	3.062247000	-3.385544000	0.754550000
C	1.698185000	-1.900833000	2.155562000
C	-4.508971000	-4.843420000	-0.725521000
C	-5.928204000	-3.839184000	-2.414239000
H	-5.747586000	-1.703664000	-2.636871000
C	-2.204779000	-4.138197000	2.913182000
H	-3.389898000	-5.341049000	1.615925000
H	-1.128241000	-2.668621000	4.070480000
H	6.069504000	2.120794000	0.145957000
H	5.544392000	3.771714000	0.437249000
C	7.183675000	3.606476000	-0.966130000
C	3.981014000	-3.581472000	-0.372708000
C	5.417473000	-2.590214000	-2.105573000
C	2.901594000	-4.381458000	1.741185000
C	1.624813000	-2.880299000	3.130495000
H	1.247062000	-0.931065000	2.326481000
C	-5.458935000	-4.972262000	-1.727070000
H	-4.161482000	-5.736712000	-0.218650000
H	-6.677323000	-3.945693000	-3.192932000
H	-2.136103000	-4.910750000	3.672732000
H	7.964397000	3.726011000	-0.208159000
H	7.561944000	2.918039000	-1.730075000

H	7.030577000	4.580712000	-1.444240000
C	4.508969000	-4.843417000	-0.725533000
C	5.928200000	-3.839179000	-2.414251000
H	5.747583000	-1.703659000	-2.636880000
C	2.204784000	-4.138198000	2.913175000
H	3.389902000	-5.341049000	1.615915000
H	1.128249000	-2.668623000	4.070477000
H	-5.840962000	-5.956597000	-1.980439000
C	5.458933000	-4.972257000	-1.727083000
H	4.161482000	-5.736710000	-0.218663000
H	6.677319000	-3.945686000	-3.192945000
H	2.136111000	-4.910751000	3.672726000
H	5.840960000	-5.956592000	-1.980454000
C	2.458914000	3.088638000	-0.287652000
C	2.530443000	4.591993000	-0.140721000
H	1.688573000	5.070059000	-0.658066000
H	3.428979000	4.967807000	-0.634618000
C	2.549994000	5.061347000	1.330533000
H	1.658834000	4.690441000	1.850645000
H	3.409673000	4.604314000	1.835683000
C	2.623279000	6.585433000	1.454187000
H	3.522231000	6.979878000	0.967475000
H	1.755513000	7.063634000	0.985902000
H	2.648764000	6.894816000	2.503737000

B3LYP/6-31g(d,p), CPCM-CH_2Cl_2

# of imaginary frequencies = 1

-------Thermochemistry -------

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.837618 (Hartree/Particle)

Thermal correction to Energy= 0.883513

Thermal correction to Enthalpy= 0.884457

Thermal correction to Gibbs Free Energy= 0.757935

Sum of electronic and zero-point Energies= -2243.650672

Sum of electronic and thermal Energies= -2243.604777

Sum of electronic and thermal Enthalpies= -2243.603832

Sum of electronic and thermal Free Energies= -2243.730354

TS n-H2

Total energy of the optimized structure E = -2396.9566 Hartree

C	-1.220880000	2.744927000	0.117007000
C	-1.147318000	1.321390000	0.155211000
C	0.000000000	3.416946000	0.185646000
C	-2.452676000	3.456497000	-0.214614000
N	0.000000000	0.634165000	0.225051000
N	-2.364245000	0.641966000	-0.056626000
C	1.220880000	2.744927000	0.117007000

H	0.000000000	4.496540000	0.151725000
C	-3.464491000	2.738175000	-0.794117000
C	-2.529749000	4.950653000	0.004291000
C	1.147318000	1.321390000	0.155211000
C	-3.361934000	1.303762000	-0.803916000
C	-2.730882000	-0.714701000	-0.064257000
C	-4.731316000	3.319259000	-1.382495000
H	-1.683409000	5.455936000	-0.478787000
H	-3.423741000	5.347783000	-0.481038000
C	-2.567842000	5.345351000	1.496819000
N	2.364245000	0.641966000	-0.056626000
N	-4.213380000	0.459855000	-1.358709000
C	-3.823455000	-0.781825000	-0.928308000
C	-2.438833000	-1.793568000	0.842597000
C	3.464491000	2.738175000	-0.794117000
H	-4.528681000	4.300011000	-1.823531000
H	-5.055494000	2.666269000	-2.198025000
C	-5.883257000	3.442044000	-0.363606000
H	-1.680618000	4.952740000	2.007710000
H	-3.430862000	4.859686000	1.968408000
C	-2.649547000	6.860923000	1.697047000
C	2.730882000	-0.714701000	-0.064257000
C	3.361934000	1.303763000	-0.803916000
C	-4.465649000	-2.028573000	-1.247145000

C	-3.121445000	-3.034388000	0.585569000
C	-1.706211000	-1.656701000	2.027768000
C	4.731316000	3.319259000	-1.382495000
H	-6.077847000	2.454457000	0.070745000
H	-5.569735000	4.089301000	0.464905000
C	-7.164088000	3.993493000	-0.995257000
H	-2.686766000	7.116153000	2.760731000
H	-1.779247000	7.365876000	1.262771000
H	-3.545390000	7.276380000	1.222226000
C	3.823455000	-0.781825000	-0.928308000
C	2.438833000	-1.793568000	0.842597000
N	4.213380000	0.459855000	-1.358709000
C	-4.068047000	-3.166707000	-0.485459000
C	-5.444779000	-2.151373000	-2.238908000
C	-2.919272000	-4.139375000	1.467207000
C	-1.615244000	-2.715902000	2.932530000
H	-1.237456000	-0.708123000	2.258786000
H	5.055493000	2.666269000	-2.198026000
H	4.528681000	4.300011000	-1.823531000
C	5.883257000	3.442044000	-0.363606000
H	-7.967758000	4.071554000	-0.256107000
H	-7.000654000	4.991612000	-1.417392000
H	-7.516401000	3.344639000	-1.804901000
C	4.465649000	-2.028572000	-1.247146000

C	3.121445000	-3.034388000	0.585569000
C	1.706211000	-1.656701000	2.027768000
C	-4.695636000	-4.424091000	-0.742638000
C	-6.019954000	-3.395170000	-2.507533000
H	-5.740354000	-1.270576000	-2.798950000
C	-2.171000000	-3.954881000	2.642645000
H	-1.098495000	-2.567845000	3.873413000
H	6.077847000	2.454457000	0.070745000
H	5.569735000	4.089301000	0.464905000
C	7.164088000	3.993493000	-0.995257000
C	4.068047000	-3.166707000	-0.485459000
C	5.444779000	-2.151373000	-2.238908000
C	2.919272000	-4.139375000	1.467207000
C	1.615244000	-2.715902000	2.932530000
H	1.237456000	-0.708123000	2.258786000
C	-5.651219000	-4.517447000	-1.771177000
H	-6.766980000	-3.484632000	-3.290480000
H	-2.057507000	-4.784334000	3.334697000
H	7.967758000	4.071554000	-0.256107000
H	7.516401000	3.344639000	-1.804901000
H	7.000654000	4.991612000	-1.417392000
C	4.695636000	-4.424091000	-0.742638000
C	6.019954000	-3.395170000	-2.507534000
H	5.740354000	-1.270576000	-2.798950000

C	2.171000000	-3.954880000	2.642645000
H	1.098495000	-2.567845000	3.873413000
H	-6.116795000	-5.478624000	-1.970744000
C	5.651219000	-4.517447000	-1.771177000
H	6.766979000	-3.484632000	-3.290480000
H	2.057507000	-4.784334000	3.334697000
H	6.116795000	-5.478624000	-1.970744000
C	2.452676000	3.456497000	-0.214613000
C	2.529749000	4.950653000	0.004291000
H	1.683409000	5.455936000	-0.478787000
H	3.423741000	5.347783000	-0.481038000
C	2.567842000	5.345351000	1.496819000
H	1.680618000	4.952740000	2.007710000
H	3.430862000	4.859686000	1.968408000
C	2.649547000	6.860923000	1.697047000
H	3.545390000	7.276380000	1.222226000
H	1.779247000	7.365876000	1.262771000
H	2.686766000	7.116153000	2.760731000
C	3.535692000	-5.402199000	1.160477000
C	4.365643000	-5.546268000	0.091823000
H	3.331337000	-6.243774000	1.816677000
H	4.827645000	-6.505750000	-0.123608000
C	-4.365643000	-5.546268000	0.091823000
C	-3.535692000	-5.402199000	1.160477000

H -4.827645000 -6.505750000 -0.123608000

H -3.331337000 -6.243774000 1.816677000

B3LYP/6-31g(d,p), CPCM-CH_2Cl_2

# of imaginary frequencies = 1

-------Thermochemistry -------

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.863021 (Hartree/Particle)

Thermal correction to Energy= 0.910265

Thermal correction to Enthalpy= 0.911209

Thermal correction to Gibbs Free Energy= 0.781998

Sum of electronic and zero-point Energies= -2396.093570

Sum of electronic and thermal Energies= -2396.046326

Sum of electronic and thermal Enthalpies= -2396.045381

Sum of electronic and thermal Free Energies= -2396.174592

Optimized geometry for calculation of spring constants for c-H1 and c-H3

Cartesian coordinates (Å) of gas phase optimized structure of **c-H1** at B3LYP/6-311g(2d,p) level of theory. Similarly, the geometry of ring-open isomer **c-H3** and ring-close isomer **c-H3'** in the ground state (S_0) were optimized at the B3LYP/6-31g(d,p) level of theory to reduce the computational cost.

c-H1

Total energy of the optimized structure E = -2324.3445 Hartree at B3LYP/6-311g(2d,p) level

N	2.297359000	0.229696000	-0.514146000
N	-0.000345000	0.333658000	-0.121633000
N	-2.303000000	0.335780000	0.257439000
N	-4.419092000	-0.072224000	-0.175132000
C	5.275833000	-5.364187000	-0.243595000
H	5.609579000	-6.390117000	-0.153796000
C	3.958801000	-5.095261000	-0.544232000
H	3.287059000	-5.928132000	-0.688993000
C	3.479124000	-3.778321000	-0.673021000
C	4.387991000	-2.711682000	-0.406057000
C	3.822852000	-1.390889000	-0.403426000
C	2.494320000	-1.151214000	-0.703090000
C	1.131140000	0.980171000	-0.324750000
C	-1.112494000	1.029624000	0.012957000
C	-2.535184000	-1.001095000	0.622890000
C	-3.857258000	-1.258809000	0.310326000
C	-4.448691000	-2.557981000	0.480472000

C	-5.802033000	-2.874071000	0.231393000
H	-6.513096000	-2.105519000	-0.017846000
C	-6.260601000	-4.168780000	0.324279000
H	-7.302830000	-4.385717000	0.128677000
C	-5.378754000	-5.196071000	0.666840000
H	-5.727526000	-6.219903000	0.712445000
C	6.184356000	-4.314794000	-0.087820000
H	7.230819000	-4.520876000	0.096555000
C	5.746283000	-3.012118000	-0.166000000
H	6.475445000	-2.227496000	-0.058773000
C	2.132143000	-3.502201000	-1.168676000
C	1.637762000	-2.169171000	-1.244767000
C	-3.491616000	0.915742000	-0.127876000
C	-3.622927000	2.335583000	-0.288952000
C	-4.988904000	2.989902000	-0.398741000
H	-5.752567000	2.346394000	0.036202000
H	-4.986235000	3.876324000	0.237315000
C	-5.405040000	3.410911000	-1.823730000
H	-5.379302000	2.549538000	-2.499108000
H	-4.663456000	4.106184000	-2.225283000
C	-6.791241000	4.053744000	-1.854113000
H	-6.829497000	4.945104000	-1.223754000
H	-7.057910000	4.353694000	-2.868112000
H	-7.561534000	3.364770000	-1.498824000

C	-2.475122000	3.096427000	-0.225385000
C	-1.191925000	2.433092000	-0.153018000
C	0.038017000	3.086145000	-0.261830000
H	0.053376000	4.161582000	-0.324222000
C	1.249966000	2.391454000	-0.301178000
C	2.546420000	3.032464000	-0.341027000
C	3.682686000	2.252788000	-0.288246000
C	3.510329000	0.828546000	-0.258674000
N	4.422804000	-0.161616000	-0.108676000
C	5.722863000	-0.002770000	0.557182000
H	5.742487000	0.939976000	1.087346000
H	5.827047000	-0.802301000	1.285656000
H	6.544389000	-0.044567000	-0.156129000
C	5.075862000	2.842923000	-0.438350000
H	5.756243000	2.077495000	-0.809780000
H	5.032974000	3.578386000	-1.244762000
C	5.691587000	3.520654000	0.801716000
H	5.647376000	2.851196000	1.666957000
H	5.088734000	4.387536000	1.077329000
C	7.134956000	3.959633000	0.554329000
H	7.199194000	4.656733000	-0.284271000
H	7.544894000	4.459699000	1.432491000
H	7.781056000	3.108200000	0.326262000
C	2.602570000	4.538399000	-0.421231000

H	3.573103000	4.855874000	-0.798759000
H	1.874707000	4.887076000	-1.160042000
C	2.344855000	5.262755000	0.921875000
H	3.054513000	4.899336000	1.668763000
H	1.354342000	5.002783000	1.305225000
C	2.465411000	6.779981000	0.782952000
H	1.747855000	7.175041000	0.059491000
H	2.281131000	7.273229000	1.738264000
H	3.463848000	7.070269000	0.448097000
C	-2.513887000	4.604824000	-0.208395000
H	-1.715620000	5.005639000	-0.838020000
H	-3.435452000	4.968069000	-0.656300000
C	-2.385716000	5.192074000	1.215786000
H	-1.459243000	4.838584000	1.678465000
H	-3.198032000	4.802210000	1.836136000
C	-2.419781000	6.719962000	1.215016000
H	-3.354109000	7.096835000	0.793197000
H	-2.334758000	7.109980000	2.230115000
H	-1.598850000	7.138466000	0.627360000
C	-5.707341000	0.015749000	-0.874605000
H	-5.705559000	0.877154000	-1.527553000
H	-5.816021000	-0.872138000	-1.491199000
H	-6.537212000	0.082269000	-0.172607000
C	-4.069527000	-4.902651000	0.978203000

H	-3.418925000	-5.714347000	1.267368000
C	-3.570812000	-3.587304000	0.935246000
C	-2.237023000	-3.262836000	1.437584000
C	-1.716628000	-1.942329000	1.333596000
C	-0.534489000	-1.609284000	2.022165000
H	-0.182469000	-0.591196000	2.022960000
C	0.163901000	-2.557584000	2.732657000
H	1.057540000	-2.276886000	3.275859000
C	-0.296054000	-3.877275000	2.772097000
H	0.251318000	-4.628735000	3.326980000
C	-1.475552000	-4.212868000	2.147095000
H	-1.839613000	-5.223541000	2.253578000
C	0.440165000	-1.916483000	-1.941063000
H	0.106947000	-0.902229000	-2.082870000
C	-0.297940000	-2.944360000	-2.479946000
H	-1.202832000	-2.727779000	-3.033776000
C	0.134458000	-4.265478000	-2.331387000
H	-0.446048000	-5.079041000	-2.747721000
C	1.328399000	-4.530400000	-1.700053000
H	1.669578000	-5.553837000	-1.662095000

n-H1

Total energy of the optimized structure E = -2245.0094 Hartree at B3LYP/6-311g(2d,p) level

N	-2.321473000	0.155613000	0.018254000

N	-0.002372000	0.333815000	-0.248265000
N	4.545044000	0.363151000	-0.151115000
N	-4.501568000	-0.270761000	-0.364387000
N	2.321888000	0.408865000	-0.521423000
C	-1.184391000	0.927180000	-0.211907000
C	1.092356000	1.056357000	-0.422872000
C	-2.538209000	-1.189310000	0.372842000
C	2.079871000	-2.140968000	-1.088660000
C	-3.879464000	-1.404898000	0.077581000
C	2.719592000	-0.938897000	-0.616525000
C	-1.363842000	2.315725000	-0.457633000
C	1.085257000	2.477664000	-0.466708000
C	-2.364205000	-3.460237000	1.254572000
C	4.081880000	-0.909020000	-0.338595000
C	-4.497926000	-2.687599000	0.228716000
C	-5.183175000	2.443940000	-1.009008000
H	-5.653254000	1.615105000	-1.541344000
H	-5.199294000	3.304748000	-1.680117000
C	-0.183310000	3.057063000	-0.527243000
H	-0.254751000	4.127801000	-0.632709000
C	-1.758823000	-2.174623000	1.077348000
C	3.494853000	1.142468000	-0.279880000
C	-2.683564000	2.885436000	-0.669472000
C	2.316713000	3.246800000	-0.416330000

C	-3.716359000	-3.738128000	0.766639000
C	3.497995000	2.576416000	-0.255054000
C	-3.571311000	0.657649000	-0.379319000
C	-3.760892000	2.043511000	-0.697771000
C	0.803201000	-2.191780000	-1.681199000
H	0.221084000	-1.289038000	-1.745530000
C	-2.810334000	4.374299000	-0.891819000
H	-3.742924000	4.591539000	-1.412690000
H	-2.015891000	4.720733000	-1.560622000
C	4.873524000	-2.100081000	-0.263396000
C	2.859191000	-3.341473000	-1.037582000
C	-5.824795000	-2.912424000	-0.175424000
H	-6.387613000	-2.078495000	-0.574336000
C	4.851881000	3.215705000	-0.066749000
H	5.578806000	2.655630000	-0.659593000
H	4.846355000	4.238837000	-0.445453000
C	-0.509863000	-1.928125000	1.679846000
H	-0.060765000	-0.955645000	1.574165000
C	-1.643934000	-4.434099000	1.971271000
H	-2.079529000	-5.411451000	2.123546000
C	0.153516000	-2.903620000	2.389795000
H	1.113185000	-2.680286000	2.840097000
C	4.241204000	-3.332167000	-0.555031000
C	-4.312390000	-5.013662000	0.839366000

H	-3.748115000	-5.855957000	1.214560000
C	-0.409510000	-4.174315000	2.524599000
H	0.110887000	-4.948737000	3.075223000
C	-7.478170000	3.092627000	-0.109428000
H	-7.537993000	3.971520000	-0.757863000
H	-8.062135000	3.303531000	0.789217000
H	-7.960382000	2.262406000	-0.631784000
C	-2.773875000	5.206549000	0.405407000
H	-3.584188000	4.875663000	1.060569000
H	-1.847451000	5.003284000	0.950502000
C	0.279571000	-3.368416000	-2.168375000
H	-0.705878000	-3.370920000	-2.618323000
C	2.241244000	4.755396000	-0.484412000
H	1.472045000	5.050119000	-1.204608000
H	3.174982000	5.150299000	-0.886509000
C	-6.029368000	2.753393000	0.239936000
H	-6.003231000	1.885666000	0.903357000
H	-5.578303000	3.583850000	0.791566000
C	-6.379404000	-4.168694000	-0.077171000
H	-7.400585000	-4.341825000	-0.395440000
C	-5.610917000	-5.226263000	0.426162000
H	-6.037026000	-6.220546000	0.491895000
C	6.224556000	-2.058440000	0.120748000
H	6.670639000	-1.093637000	0.324029000

C	2.279334000	-4.525635000	-1.529815000
H	2.849064000	-5.443851000	-1.509047000
C	1.956903000	5.446251000	0.863264000
H	2.751259000	5.188659000	1.568747000
H	1.033082000	5.048376000	1.293465000
C	6.713164000	3.864339000	1.547435000
H	6.709797000	4.904564000	1.209250000
H	7.462192000	3.327657000	0.959399000
H	7.040855000	3.855753000	2.589365000
C	1.855309000	6.965923000	0.732653000
H	1.047648000	7.254079000	0.053972000
H	2.782260000	7.392611000	0.340220000
H	1.658341000	7.433944000	1.699419000
C	6.949177000	-3.222334000	0.246529000
H	7.989137000	-3.188817000	0.548923000
C	1.016578000	-4.550909000	-2.079474000
H	0.607521000	-5.481370000	-2.454542000
C	5.008909000	-4.504356000	-0.399830000
H	4.562953000	-5.472795000	-0.578418000
C	-2.900390000	6.707171000	0.143057000
H	-3.840509000	6.943031000	-0.362606000
H	-2.086392000	7.071345000	-0.489975000
H	-2.874217000	7.274761000	1.075578000
C	5.334011000	3.222858000	1.396916000

H	4.607726000	3.755829000	2.018265000
H	5.362846000	2.193479000	1.759616000
C	6.329787000	-4.453008000	-0.006592000
H	6.890201000	-5.373658000	0.106679000

Optimized geometry of different isomers of photochromic compound c-H3

The geometry of different ring-opened and ring-closed isomers of **c-H3** in the ground state (S_0) were optimized at the B3LYP/6-31g(d,p), CH_3CN-CPCM model level of theory to reduce the computational cost.

Ring-open isomer **c-H3** (antiparallel-antiparallel)

Total energy of the optimized structure E = -5140.9993 Hartree

(CH_3CN-CPCM model level of theory)

C	-1.175230000	-0.111928000	-0.307444000
C	-1.077915000	1.301398000	-0.377664000
N	-0.014006000	1.989253000	0.005213000
C	1.060713000	1.317734000	0.386825000
C	1.180236000	-0.093780000	0.315067000
C	0.007813000	-0.790926000	0.003863000
N	-2.201584000	2.009529000	-0.822014000
N	2.173515000	2.042812000	0.831201000
C	-3.441641000	1.397205000	-0.822611000
N	-4.372248000	2.365733000	-1.002667000
C	-3.730694000	3.602564000	-1.087616000
C	-2.364136000	3.381387000	-1.092235000
C	2.314406000	3.416415000	1.104098000

C	3.677149000	3.659995000	1.095893000
N	4.338594000	2.433975000	1.005705000
C	3.423299000	1.450709000	0.827010000
C	-2.449770000	-0.774586000	-0.465342000
C	-3.591422000	-0.022819000	-0.663743000
C	3.595240000	0.033269000	0.667076000
C	2.465260000	-0.736405000	0.470907000
C	-5.791530000	2.155508000	-1.340131000
C	5.763092000	2.246402000	1.333985000
C	-4.294742000	4.927625000	-1.112511000
C	-3.380552000	5.993106000	-1.377267000
C	-1.979523000	5.709512000	-1.700996000
C	-1.440117000	4.393779000	-1.546802000
C	1.374976000	4.412077000	1.563858000
C	1.893310000	5.735757000	1.722194000
C	3.288715000	6.043348000	1.396057000
C	4.219315000	4.994110000	1.123471000
C	-5.637605000	5.223993000	-0.783806000
C	-6.087023000	6.531775000	-0.748835000
C	-5.201487000	7.582472000	-1.026657000
C	0.167655000	6.446948000	-2.602631000
C	0.669057000	5.141234000	-2.503393000
C	-0.123417000	4.132844000	-1.986639000
C	0.063057000	4.128317000	2.003958000

C	-0.744922000	5.121849000	2.525390000
C	-0.264201000	6.434928000	2.629625000
C	5.082500000	7.663735000	1.046907000
C	5.983899000	6.628928000	0.760612000
C	5.555824000	5.313891000	0.790936000
H	0.016375000	-1.873062000	0.003524000
H	-5.899059000	1.199227000	-1.839610000
H	-6.093234000	2.944807000	-2.024305000
H	-6.410310000	2.169959000	-0.442334000
H	6.056205000	3.038932000	2.018154000
H	6.375564000	2.273467000	0.432116000
H	5.889961000	1.290719000	1.830056000
H	-6.323036000	4.435866000	-0.508295000
H	-7.118611000	6.738708000	-0.484407000
H	-5.546257000	8.610693000	-0.988541000
H	0.786123000	7.241998000	-3.006398000
H	1.673476000	4.912329000	-2.844285000
H	0.267655000	3.128590000	-1.946075000
H	-0.312084000	3.118182000	1.959262000
H	-1.745321000	4.875658000	2.866062000
H	-0.894821000	7.218326000	3.037368000
H	5.410364000	8.697608000	1.012673000
H	7.010973000	6.853816000	0.493274000
H	6.252740000	4.538285000	0.508795000

C	-3.876396000	7.313903000	-1.323436000
H	-3.207360000	8.148094000	-1.492068000
C	-1.133905000	6.715523000	-2.218832000
H	-1.515867000	7.718536000	-2.359178000
C	1.032418000	6.725921000	2.245384000
H	1.398282000	7.734452000	2.389159000
C	3.762980000	7.372225000	1.346819000
H	3.081127000	8.194697000	1.521436000
C	-2.488058000	-2.256898000	-0.319744000
C	-2.109187000	-3.144465000	-1.380106000
C	-2.802740000	-2.909993000	0.851751000
C	-2.153705000	-4.473432000	-1.036195000
H	-1.792187000	-2.795075000	-2.355486000
S	-2.665348000	-4.635440000	0.635220000
C	-4.938231000	-0.663106000	-0.654586000
C	-5.814577000	-0.588739000	0.477121000
C	-5.459266000	-1.388797000	-1.704186000
C	-7.002083000	-1.256213000	0.305214000
H	-5.568775000	-0.036525000	1.376425000
S	-7.040372000	-1.994955000	-1.287192000
C	-1.844132000	-5.645251000	-1.866672000
C	-1.438719000	-6.865304000	-1.294366000
C	-1.944740000	-5.566756000	-3.268847000
C	-1.142943000	-7.966625000	-2.096296000

H	-1.334510000	-6.948542000	-0.216624000
C	-1.637076000	-6.666077000	-4.067539000
H	-2.281602000	-4.645583000	-3.733161000
C	-1.236911000	-7.872119000	-3.486476000
H	-0.831476000	-8.897791000	-1.632674000
H	-1.722304000	-6.583336000	-5.146916000
H	-1.003995000	-8.729438000	-4.110366000
C	-3.207164000	-2.343170000	2.179392000
H	-4.258987000	-2.552045000	2.401962000
H	-3.072605000	-1.259332000	2.187811000
H	-2.606957000	-2.763884000	2.991930000
C	-4.872241000	-1.670781000	-3.054301000
H	-5.576537000	-1.424216000	-3.854795000
H	-4.604623000	-2.727110000	-3.161957000
H	-3.967553000	-1.078302000	-3.206778000
C	-8.119932000	-1.397971000	1.248258000
C	-9.425687000	-1.674431000	0.803246000
C	-7.902592000	-1.252924000	2.631895000
C	-10.476952000	-1.800682000	1.709557000
H	-9.624917000	-1.774923000	-0.259729000
C	-8.957783000	-1.369138000	3.533894000
H	-6.900178000	-1.065390000	3.003009000
C	-10.249715000	-1.645246000	3.078576000
H	-11.476757000	-2.012741000	1.343042000

H	-8.767532000	-1.254829000	4.596835000
H	-11.069477000	-1.741132000	3.783746000
C	4.952700000	-0.583949000	0.652479000
C	5.815573000	-0.508157000	-0.489508000
C	5.490439000	-1.302087000	1.698784000
H	5.536163000	-0.002387000	-1.406093000
C	2.526386000	-2.217928000	0.324837000
C	2.839995000	-2.865373000	-0.850126000
C	2.171277000	-3.111751000	1.388032000
S	2.730832000	-4.592785000	-0.633625000
C	2.232760000	-4.439702000	1.042623000
C	3.226240000	-2.291100000	-2.180162000
H	3.035609000	-1.215689000	-2.200640000
H	4.289619000	-2.446530000	-2.391291000
H	2.656038000	-2.749969000	-2.993400000
H	1.857331000	-2.767955000	2.366388000
C	1.947615000	-5.616566000	1.874732000
C	2.060836000	-5.538098000	3.275951000
C	1.553086000	-6.841422000	1.305067000
C	1.775961000	-6.642299000	4.076383000
H	2.389499000	-4.612823000	3.738002000
C	1.280148000	-7.947442000	2.108611000
H	1.438911000	-6.924902000	0.228347000
C	1.386552000	-7.853095000	3.497908000

H	1.870578000	-6.559470000	5.154971000
H	0.976615000	-8.882228000	1.647013000
H	1.171397000	-8.714117000	4.123076000
S	7.077538000	-1.885911000	1.271923000
C	7.009665000	-1.166163000	-0.327765000
C	8.118673000	-1.299551000	-1.282162000
C	8.302531000	-0.334965000	-2.291297000
C	9.015401000	-2.381792000	-1.220975000
C	9.340097000	-0.458322000	-3.212534000
H	7.640693000	0.523736000	-2.341734000
C	10.059326000	-2.495689000	-2.137520000
H	8.885392000	-3.149208000	-0.463427000
C	10.224933000	-1.537420000	-3.139715000
H	9.464587000	0.297366000	-3.982306000
H	10.738590000	-3.340260000	-2.072714000
H	11.036482000	-1.628466000	-3.854961000
C	4.918014000	-1.587125000	3.054468000
H	4.668699000	-2.647198000	3.168696000
H	5.623780000	-1.325668000	3.849069000
H	4.005031000	-1.008552000	3.210795000

Ring-close isomer **c-H3”**

Total energy of the optimized structure E = -5140.9264 Hartree

(CH_3CN-CPCM model level of theory)

C	-1.163536000	0.650030000	0.493629000
C	-1.325916000	-0.751569000	0.628866000
N	-0.388190000	-1.638290000	0.353259000
C	0.840050000	-1.224070000	0.107860000
C	1.241350000	0.115812000	0.318731000
C	0.185446000	1.040402000	0.405937000
N	-2.597393000	-1.252637000	0.998253000
N	1.794608000	-2.198317000	-0.300069000
C	-3.708196000	-0.543990000	0.639233000
N	-4.799904000	-1.247648000	1.045842000
C	-4.363386000	-2.459311000	1.596948000
C	-2.981675000	-2.437204000	1.652484000
C	1.677155000	-3.596826000	-0.455144000
C	2.965179000	-4.102784000	-0.374799000
N	3.843094000	-3.017470000	-0.253208000
C	3.125402000	-1.869999000	-0.291312000
C	-2.342720000	1.488873000	0.218830000
C	-3.620686000	0.753242000	0.043862000
C	3.576312000	-0.503413000	-0.285595000
C	2.659591000	0.465212000	0.349824000
C	-6.101021000	-0.642539000	1.379813000
C	5.222371000	-3.092131000	0.254060000
C	-5.144756000	-3.587903000	2.016682000
C	-4.433686000	-4.642623000	2.665419000

C	-3.000354000	-4.511707000	2.939679000
C	-2.245706000	-3.406103000	2.429309000
C	0.554406000	-4.440102000	-0.785001000
C	0.779661000	-5.849645000	-0.693203000
C	2.115536000	-6.383901000	-0.417927000
C	3.250046000	-5.513803000	-0.377401000
C	-6.524194000	-3.734164000	1.741793000
C	-7.203518000	-4.877686000	2.118815000
C	-6.517930000	-5.913353000	2.771629000
C	-5.162972000	-5.797156000	3.028394000
C	-2.325640000	-5.455158000	3.747219000
C	-0.987522000	-5.319207000	4.068545000
C	-0.268722000	-4.208376000	3.604573000
C	-0.889609000	-3.268931000	2.802442000
C	2.344325000	-7.771335000	-0.279536000
C	3.620930000	-8.293187000	-0.172761000
C	4.732618000	-7.440159000	-0.226701000
C	4.548758000	-6.073379000	-0.326287000
C	-2.299186000	2.828043000	-0.152371000
C	-4.695493000	1.323446000	-0.641597000
C	3.202813000	1.594664000	0.921383000
C	4.768350000	-0.060567000	-0.833562000
C	-0.679254000	-3.971664000	-1.292234000
C	-1.703765000	-4.846542000	-1.598635000

C	-1.525608000	-6.225942000	-1.412864000
C	-0.303228000	-6.710840000	-0.986455000
C	-4.750430000	2.846036000	-0.744625000
S	-6.079854000	3.206624000	-2.003719000
C	-6.556438000	1.510430000	-2.084305000
C	-5.755562000	0.685297000	-1.321785000
C	-1.351657000	3.849213000	0.138913000
C	-1.666712000	5.111210000	-0.308038000
S	-3.207044000	5.187744000	-1.167226000
C	-3.355839000	3.335775000	-1.160148000
C	4.716440000	1.810849000	0.789420000
S	4.966152000	3.625011000	1.174528000
C	3.393546000	3.691992000	2.004289000
C	2.601030000	2.609156000	1.728836000
C	5.738066000	-0.744215000	-1.616470000
C	6.923345000	-0.073541000	-1.795367000
S	6.959712000	1.499468000	-0.983189000
C	5.118110000	1.416192000	-0.647750000
C	-5.231463000	3.405416000	0.618743000
C	-2.909954000	2.829843000	-2.558558000
C	5.455076000	1.021275000	1.899891000
C	4.427924000	2.256207000	-1.754759000
C	-7.677253000	1.102849000	-2.928628000
C	-8.261867000	-0.173533000	-2.784485000

C	-9.322789000	-0.562889000	-3.594688000
C	-9.828928000	0.310502000	-4.562257000
C	-9.264877000	1.579456000	-4.713392000
C	-8.201703000	1.972792000	-3.906278000
C	-0.897935000	6.342070000	-0.113104000
C	0.021964000	6.458406000	0.948196000
C	0.744605000	7.633094000	1.133652000
C	0.567825000	8.715631000	0.266717000
C	-0.342989000	8.616140000	-0.786932000
C	-1.071348000	7.444249000	-0.974341000
C	3.093441000	4.810180000	2.901603000
C	3.906200000	5.960163000	2.924308000
C	3.638667000	7.008773000	3.801716000
C	2.551406000	6.933781000	4.675106000
C	1.733766000	5.798978000	4.664192000
C	2.001176000	4.747609000	3.792962000
C	8.085590000	-0.534743000	-2.554966000
C	9.351883000	0.053239000	-2.368463000
C	10.457235000	-0.394631000	-3.086748000
C	10.320328000	-1.434774000	-4.008619000
C	9.068297000	-2.024495000	-4.208569000
C	7.961552000	-1.581816000	-3.491935000
H	0.438989000	2.084842000	0.330364000
H	-6.850144000	-0.822284000	0.609654000

H	-5.962589000	0.429389000	1.501772000
H	-6.436106000	-1.066348000	2.324970000
H	5.926316000	-3.365593000	-0.531254000
H	5.247662000	-3.830368000	1.054406000
H	5.498215000	-2.123995000	0.660948000
H	-7.056753000	-2.966708000	1.197215000
H	-8.259985000	-4.976648000	1.892311000
H	-7.044287000	-6.816914000	3.061801000
H	-4.658355000	-6.628935000	3.503013000
H	-2.868515000	-6.297135000	4.156867000
H	-0.505522000	-6.060355000	4.697931000
H	0.771815000	-4.073505000	3.881548000
H	-0.327605000	-2.408350000	2.478172000
H	1.506485000	-8.456214000	-0.257310000
H	3.758256000	-9.364347000	-0.066431000
H	5.738287000	-7.845086000	-0.184834000
H	5.422613000	-5.442174000	-0.374674000
H	-0.819187000	-2.915389000	-1.458917000
H	-2.638952000	-4.462553000	-1.993081000
H	-2.330628000	-6.917684000	-1.639370000
H	-0.172953000	-7.783054000	-0.919053000
H	-5.855551000	-0.391409000	-1.359547000
H	-0.473377000	3.695793000	0.748802000
H	1.606024000	2.507886000	2.141641000

H	5.564831000	-1.724774000	-2.038173000
H	-6.194598000	2.961463000	0.877868000
H	-4.509736000	3.160573000	1.402589000
H	-5.350422000	4.488787000	0.579092000
H	-3.562312000	3.214508000	-3.343398000
H	-1.890591000	3.167616000	-2.754427000
H	-2.921447000	1.737150000	-2.593432000
H	5.094026000	1.356140000	2.874051000
H	5.260705000	-0.050100000	1.819047000
H	6.532382000	1.185985000	1.848740000
H	4.721499000	3.304469000	-1.685287000
H	4.723598000	1.871699000	-2.732695000
H	3.341170000	2.192615000	-1.672080000
H	-7.898498000	-0.857336000	-2.025839000
H	-9.761582000	-1.547136000	-3.465988000
H	-10.659072000	0.004645000	-5.191080000
H	-9.650830000	2.262765000	-5.462954000
H	-7.765201000	2.956570000	-4.048027000
H	0.151882000	5.640333000	1.647744000
H	1.440839000	7.705969000	1.962339000
H	1.132897000	9.630594000	0.415099000
H	-0.485771000	9.450332000	-1.466648000
H	-1.762093000	7.373722000	-1.808550000
H	4.752840000	6.040038000	2.249412000

H	4.280507000	7.884034000	3.802456000
H	2.344739000	7.748659000	5.361636000
H	0.892139000	5.727626000	5.345908000
H	1.372550000	3.864327000	3.822553000
H	9.477895000	0.853133000	-1.645111000
H	11.425809000	0.067219000	-2.924370000
H	11.181827000	-1.782264000	-4.570091000
H	8.952952000	-2.826744000	-4.930440000
H	6.993492000	-2.034207000	-3.677161000

Ring-open isomer **c-H3** (Parallel-antiparallel)

(CH_3CN-CPCM model level of theory)

Total energy of the optimized structure E = -5140.9991 Hartree

C	1.139059000	0.338974000	-0.132437000
C	0.648301000	1.663420000	0.008017000
N	-0.610103000	2.010031000	-0.208741000
C	-1.486085000	1.054642000	-0.476365000
C	-1.182839000	-0.331209000	-0.442054000
C	0.171152000	-0.655711000	-0.308705000
N	1.567723000	2.663487000	0.347480000
N	-2.809488000	1.425280000	-0.745689000
C	2.919784000	2.433876000	0.171641000
N	3.560881000	3.615951000	0.336879000

C	2.614602000	4.613460000	0.576450000
C	1.371498000	4.014744000	0.696265000
C	-3.376722000	2.698946000	-0.942230000
C	-4.738890000	2.531722000	-0.759524000
N	-4.998828000	1.165310000	-0.641302000
C	-3.822324000	0.493444000	-0.611318000
C	2.557522000	0.076920000	-0.183658000
C	3.446500000	1.132242000	-0.122164000
C	-3.556017000	-0.912595000	-0.479290000
C	-2.236578000	-1.320647000	-0.452601000
C	5.006123000	3.784935000	0.581194000
C	-6.335687000	0.569415000	-0.818518000
C	2.795212000	6.039681000	0.645459000
C	1.658132000	6.796734000	1.061196000
C	0.430767000	6.120426000	1.489521000
C	0.259549000	4.711947000	1.301663000
C	-2.833815000	3.931604000	-1.463863000
C	-3.729972000	5.046334000	-1.495078000
C	-5.101681000	4.926323000	-0.993323000
C	-5.644713000	3.647204000	-0.662130000
C	3.967312000	6.709424000	0.224761000
C	4.038421000	8.090615000	0.240684000
C	2.932202000	8.841795000	0.662430000
C	-1.730331000	6.199979000	2.626516000

C	-1.862934000	4.811007000	2.490868000
C	-0.883183000	4.081663000	1.842639000
C	-1.563166000	4.052976000	-2.069175000
C	-1.151086000	5.247307000	-2.631018000
C	-2.000929000	6.362276000	-2.611778000
C	-7.229878000	5.943542000	-0.360109000
C	-7.747727000	4.686508000	-0.017863000
C	-6.963348000	3.556036000	-0.159774000
H	0.478398000	-1.692746000	-0.344962000
H	5.407133000	2.870078000	1.004919000
H	5.128433000	4.588146000	1.304211000
H	5.534871000	4.024333000	-0.341722000
H	-6.925446000	1.248676000	-1.429178000
H	-6.818908000	0.403893000	0.144948000
H	-6.236436000	-0.375447000	-1.341154000
H	4.810397000	6.153483000	-0.159248000
H	4.943019000	8.586523000	-0.094965000
H	2.978063000	9.925974000	0.663894000
H	-2.496914000	6.777155000	3.133300000
H	-2.725498000	4.299435000	2.905262000
H	-0.989064000	3.010958000	1.774456000
H	-0.907924000	3.197933000	-2.120287000
H	-0.173881000	5.310744000	-3.098463000
H	-1.681615000	7.302299000	-3.049970000

H	-7.837169000	6.834704000	-0.239361000
H	-8.753476000	4.596707000	0.378777000
H	-7.363616000	2.606877000	0.165514000
C	1.767303000	8.204303000	1.053180000
H	0.917451000	8.812814000	1.334289000
C	-0.598777000	6.832408000	2.144090000
H	-0.493057000	7.896568000	2.311607000
C	-3.266522000	6.253162000	-2.064448000
H	-3.923820000	7.111708000	-2.113191000
C	-5.931757000	6.056249000	-0.827065000
H	-5.546752000	7.044661000	-1.042670000
C	3.010954000	-1.329343000	-0.373471000
C	3.172842000	-2.229450000	0.730739000
C	3.256054000	-1.913863000	-1.595907000
C	3.552731000	-3.496594000	0.362599000
H	2.985554000	-1.939877000	1.758072000
S	3.716209000	-3.583257000	-1.382873000
C	4.900040000	0.921525000	-0.372854000
C	5.762373000	0.255718000	0.558237000
C	5.540503000	1.313173000	-1.528917000
C	7.061444000	0.144657000	0.129295000
H	5.411876000	-0.141688000	1.502788000
S	7.226248000	0.871555000	-1.460631000
C	3.814088000	-4.660020000	1.220979000

C	3.668874000	-5.974990000	0.741339000
C	4.215562000	-4.476939000	2.557904000
C	3.915206000	-7.067914000	1.570896000
H	3.341287000	-6.145062000	-0.280180000
C	4.448974000	-5.571780000	3.387245000
H	4.363300000	-3.472502000	2.941469000
C	4.302652000	-6.872523000	2.898311000
H	3.795807000	-8.073924000	1.180127000
H	4.758692000	-5.407757000	4.415034000
H	4.491749000	-7.724309000	3.544229000
C	3.179279000	-1.316416000	-2.968408000
H	4.167264000	-1.259395000	-3.437597000
H	2.771237000	-0.304676000	-2.920739000
H	2.535849000	-1.907577000	-3.627535000
C	4.993318000	2.029832000	-2.728056000
H	5.243933000	1.505768000	-3.655241000
H	5.393877000	3.046466000	-2.810933000
H	3.904967000	2.102509000	-2.669915000
C	8.204900000	-0.466343000	0.820763000
C	9.303039000	-0.983868000	0.110001000
C	8.218093000	-0.549805000	2.226113000
C	10.376639000	-1.566228000	0.781585000
H	9.309929000	-0.947428000	-0.975493000
C	9.287714000	-1.142690000	2.893211000

H	7.395369000	-0.131239000	2.796826000
C	10.373055000	-1.652070000	2.175402000
H	11.213046000	-1.961085000	0.212883000
H	9.278474000	-1.195911000	3.977730000
H	11.208395000	-2.108264000	2.697503000
C	-4.666452000	-1.894445000	-0.319421000
C	-5.385947000	-2.043539000	0.911087000
C	-5.085703000	-2.760159000	-1.306814000
H	-5.165593000	-1.459076000	1.796247000
C	-1.846650000	-2.753862000	-0.341276000
C	-1.844901000	-3.464015000	0.839555000
C	-1.339796000	-3.502797000	-1.454369000
S	-1.248907000	-5.080870000	0.569258000
C	-0.970667000	-4.787430000	-1.138543000
C	-2.248871000	-3.026984000	2.215762000
H	-2.392015000	-1.944597000	2.244975000
H	-3.186911000	-3.497388000	2.528892000
H	-1.485070000	-3.285560000	2.955310000
H	-1.233083000	-3.083038000	-2.447555000
C	-0.421162000	-5.826310000	-2.020187000
C	-0.690377000	-5.799815000	-3.401763000
C	0.387204000	-6.862727000	-1.517193000
C	-0.157289000	-6.768604000	-4.249527000
H	-1.334116000	-5.026807000	-3.809075000

C	0.909262000	-7.836777000	-2.366900000
H	0.624885000	-6.896842000	-0.457991000
C	0.643246000	-7.792809000	-3.737248000
H	-0.378531000	-6.729790000	-5.311922000
H	1.531015000	-8.626991000	-1.957038000
H	1.052402000	-8.550256000	-4.398566000
S	-6.382474000	-3.764042000	-0.713320000
C	-6.351682000	-3.018671000	0.875826000
C	-7.266596000	-3.440577000	1.945178000
C	-7.606082000	-2.546716000	2.978792000
C	-7.820188000	-4.733599000	1.971545000
C	-8.458819000	-2.939825000	4.007734000
H	-7.213848000	-1.534854000	2.965069000
C	-8.682109000	-5.119584000	2.996692000
H	-7.561366000	-5.448061000	1.195538000
C	-9.002887000	-4.226891000	4.021499000
H	-8.708177000	-2.234379000	4.794672000
H	-9.096296000	-6.123264000	2.998019000
H	-9.671899000	-4.529408000	4.821122000
C	-4.601555000	-2.905433000	-2.717874000
H	-4.040342000	-3.835977000	-2.853405000
H	-5.434651000	-2.914081000	-3.427337000
H	-3.942455000	-2.075229000	-2.981209000

Ring-Close isomer **c-H3'** (Parallel-antiparallel)

(CH_3CN-CPCM model level of theory)

Total energy of the optimized structure E = -5140.9618 Hartree

C	-1.219544000	-0.535932000	-0.791439000
C	-1.512364000	0.854563000	-0.710721000
N	-0.635287000	1.800299000	-0.448190000
C	0.646291000	1.469158000	-0.346703000
C	1.127253000	0.165591000	-0.595233000
C	0.144333000	-0.833451000	-0.745566000
N	-2.858518000	1.254927000	-0.856044000
N	1.565366000	2.473833000	-0.015534000
C	-3.859587000	0.389348000	-0.481482000
N	-5.035408000	1.073086000	-0.545239000
C	-4.758269000	2.406144000	-0.883457000
C	-3.412203000	2.510963000	-1.171032000
C	1.375733000	3.812337000	0.372414000
C	2.598440000	4.443366000	0.184081000
N	3.519685000	3.479417000	-0.228098000
C	2.902346000	2.270810000	-0.282003000
C	-2.305534000	-1.520504000	-0.690010000
C	-3.606880000	-0.989829000	-0.222982000
C	3.437955000	0.958349000	-0.501358000
C	2.547924000	-0.095412000	-0.627782000
C	-6.348514000	0.457472000	-0.806275000
C	4.875317000	3.750803000	-0.727022000
C	-5.651568000	3.528785000	-0.911196000
C	-5.118124000	4.746762000	-1.432505000
C	-3.760981000	4.785364000	-1.982373000
C	-2.878594000	3.664270000	-1.854107000
C	0.258100000	4.478381000	0.995419000

C	0.357481000	5.899322000	1.100878000
C	1.585776000	6.598402000	0.712708000
C	2.766058000	5.865534000	0.368016000
C	-6.958775000	3.505862000	-0.371987000
C	-7.740851000	4.645836000	-0.366313000
C	-7.231896000	5.844467000	-0.889522000
C	-5.946977000	5.890490000	-1.401563000
C	-3.295412000	5.914969000	-2.692908000
C	-2.043882000	5.943401000	-3.280342000
C	-1.207668000	4.820394000	-3.195941000
C	-1.620509000	3.701299000	-2.497287000
C	1.672187000	8.007458000	0.757012000
C	2.865468000	8.673676000	0.543655000
C	4.037086000	7.944894000	0.299531000
C	3.986470000	6.565536000	0.212084000
C	-2.128493000	-2.891109000	-0.771207000
C	-4.541552000	-1.848720000	0.369492000
C	-0.836493000	3.816912000	1.596253000
C	-1.859013000	4.528627000	2.194352000
C	-1.817331000	5.930621000	2.214817000
C	-0.722155000	6.594323000	1.693257000
C	-4.491370000	-3.330127000	-0.015601000
S	-5.635828000	-4.182418000	1.183990000
C	-6.218005000	-2.650131000	1.825831000
C	-5.552184000	-1.556552000	1.301941000
C	-1.142348000	-3.646083000	-1.466943000
C	-1.330428000	-5.005513000	-1.482003000
S	-2.763510000	-5.528011000	-0.587540000
C	-3.032091000	-3.807907000	0.077666000
C	-5.101781000	-3.470573000	-1.434093000

C	-2.460483000	-3.770951000	1.519939000
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C	-7.569070000	-1.442432000	3.543791000
C	-8.573556000	-1.424082000	4.504481000
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C	-9.029990000	-3.761001000	4.085343000
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C	0.212250000	-5.640908000	-3.337458000
C	1.001079000	-6.577911000	-3.998238000
C	1.085535000	-7.889738000	-3.521913000
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C	-0.425458000	-7.325807000	-1.718767000
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H	5.554673000	3.967065000	0.098261000
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H	4.908878000	6.037777000	0.031743000
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C	3.984273000	-3.490422000	0.055751000
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C	2.408637000	-1.891055000	-3.252080000
H	1.610599000	-2.563083000	-3.583199000
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H	4.827775000	-7.857149000	1.434759000
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C	5.713503000	0.367470000	-1.495282000
C	5.619493000	0.822776000	0.807390000
S	7.358742000	0.155283000	-0.958187000
C	6.958851000	0.539659000	0.707647000
H	5.131896000	1.061877000	1.745138000
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H	6.032974000	0.782170000	-3.584160000

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