Supporting information for

Impact of 2,6-connectivity in Azulene: Optical Properties and Stimuli Responsive Behavior

Michael Koch, Olivier Blacque and Koushik Venkatesan*

Institute of Inorganic Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057

Zurich, Switzerland.

venkatesan.koushik@aci.uzh.ch

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Experimental Section

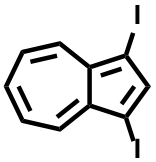
Materials and instruments

Unless otherwise stated, all other reagents used were purchased from commercial sources and used without further purification. All glassware used during the reaction was dried for at least 18 h at 160 °C. THF and Et_2O were dried over Na/ benzophenone; CH_2Cl_2 and NEt_3 were dried over CaH_2; DMF was dried over P_2O_5; toluene and pentane were machine dried. TMS-acetylene was dried over molecular sieve. ^{1}H- and ^{13}C- NMR were recorded with Bruker 500 MHz and Varian 300 MHz. The chemical shifts (δ) were reported in parts per million (ppm) relative to tetramethylsilane (external standard) calibrated on residual solvent peaks.[1, 2] Absorption spectra were recorded with Varian Cary UV500 Scan and Varian Cary 100 Bio; emission spectra were recorded with Varian Cary Eclipse Fluorescence Spectrometer. Column chromatography was conducted over silica gel (mesh 63–200 nm). If not indicated otherwise all reactions were performed under N_2-atmosphere.

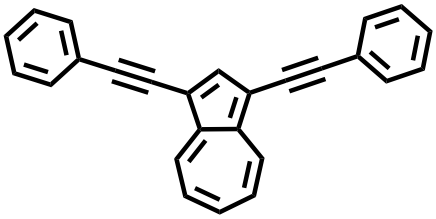
Theoretical Methods

All calculations were performed with the Gaussian 09 program package[3] using the hybrid functional PBE1PBE[4] in conjunction with the cc-pVDZ basis set.[5] Full geometry optimizations without symmetry constraints, were carried out in the gas phase for the singlet ground states (S_0). The optimized geometries were confirmed to be potential energy minima by vibrational frequency calculations at the same level of theory, as no imaginary frequency was found. The first twenty singlet-singlet transition energies were computed at the optimized S_0 geometries by using the time-dependent DFT (TD-DFT) methodology.[6-8] Solvent effects were taken into account using the conductor-like polarizable continuum model (CPCM)[9,10] with dichloromethane as solvent for the TD-DFT calculations on all optimized gas-phase geometries. The excited state structures were optimized by TD-DFT calculations, and the first four electronic transitions were computed taking into account the state-specific equilibrium solvation of each excited state at its equilibrium geometry.

Synthesis 1,3-disubstituted azulenes



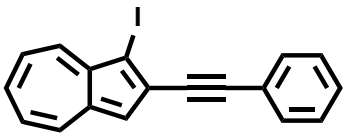
1,3- Diiodo-azulene (**6**).[11] To azulene (256.9 mg, 2 mmol) dissolved in dry CH_2Cl_2 (60 mL), N-Iodosuccinimide (900 mg, 4 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. Consequently the reaction mixture was concentrated under reduced pressure. The crude product was subjected to flash column chromatography using hexane as the eluent to obtain **6** as a blue powder. Yield: 98%, 744 mg, 1.96 mmol. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.18 (d, $^3J_{(H-H)}$ = 9.7 Hz, 2H, 4-, 8-H), 8.01 (s, 1H, 2-H), 7.69 (t, $^3J_{(H-H)}$ = 9.9 Hz, 1H, 6-H), 7.32 (t, $^3J_{(H-H)}$ = 9.9 Hz, 2H, 5-, 7-H). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 25 °C): δ (ppm) = 149.5 (s), 140.8 (s), 139.4 (s), 138.9 (s), 125.1 (s), 74.8 (s, *C*-I).



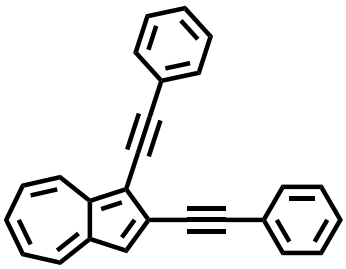
1,3- Diphenylethynyl-azulene (**1**).[12] To **6** (348 mg, 0.916 mmol) dissolved in dry toluene (20 mL), dry THF (20 mL) and dry NEt_3 (20 mL), CuI (17 mg, 0.09 mmol), PPh_3 (13 mg, 0.05 mmol), phenyl acetylene (357 mg, 3.5 mmol) and $Pd(PPh_3)_2Cl_2$ (32 mg, 0.046 mmol) were added. The reaction mixture was heated at 65 °C for 12 h. After, the mixture was poured into water (200 mL) and extracted with toluene (3 × 70 mL). The combined organic phases were dried over $MgSO_4$, filtered and consequently concentrated *in vacuo*. The crude product was subjected to column

chromatography using 20 % CH_2Cl_2 in hexane as the eluent to obtain **1** as a green powder. Yield: 90%,[13] 273 mg, 0.831 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.64 (d, $^3J_{(H-H)}$ = 11.8 Hz, 2H, 4-, 8-H), 8.13 (s, 1H, 2-H), 7.75 (t, $^3J_{(H-H)}$ = 9.8 Hz, 1H, 6-H), 7.64 (d, $^3J_{(H-H)}$ = 6.9 Hz, 4H, o-Ar-H), 7.43-7.36 (m, 2H, 5-, 7-H & m-, p-Ar-H). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 142.5 (s), 141.7 (s), 140.9 (s), 137.8 (s), 131.9 (s), 129.0 (s), 128.6 (s), 126.5 (s), 124.4 (s), 111.1 (s), 94.6 (s, C≡C), 85.3 (s, C≡C); elemental analysis (%) calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 94.91; H, 5.08.

Synthesis 1,2-disubstituted azulenes

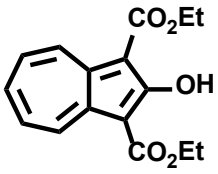


1-Iodo-2-phenylethynyl-azulene (**8**). 2-Phenylethynyl-azulene[14] (**7**) (114 mg, 0.5 mmol) was dissolved in dry toluene (50 mL) at 10 °C. To this N-Iodosuccinimide (112 mg, 0.5 mmol) was added. The reaction mixture was stirred for 2.5 h, filtered through a pad of silica and consequently concentrated under reduced pressure to a volume of 30 mL. Due to instability of **8** in the solid state, this compound was further used in the next step without purification. ^{1}H NMR[15] (300 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.26 (d, $^3J_{(H-H)}$ = 9.8 Hz, 1H, 4-H), 8.19 (d, $^3J_{(H-H)}$ = 9.6 Hz, 1H, 8-H), 7.73-7.69 (m, 2H, o-Ar-H), 7.64-7.57 (m, 2H, 6-H & p-Ar-H), 7.43-7.41 (m, 3H, 3-H & m-Ar-H), 7.36-7.22 (m, 2H, 5-, 7-H).

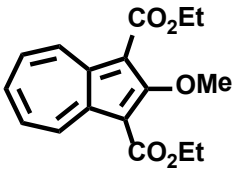


1,2- Diphenylethynyl-azulene (**2**). To the crude solution of 1-Iodo-2-phenylethynyl-azulene in toluene, dry NEt_3 (20 mL), PPh_3 (13 mg, 0.05 mmol), CuI (8 mg, 0.05 mmol), phenyl acetylene (153 mg, 1.5 mmol) and $Pd(PPh_3)_2Cl_2$ (17 mg, 0.025 mmol) were added. The reaction mixture was heated at 65 °C for 12 h. The mixture was poured into saturated NH_4Cl (100 mL) and then extracted with toluene (2 × 40 mL). The combined organic phases were dried over $MgSO_4$, filtered and consequently concentrated *in vacuo*. The crude product was subjected to column chromatography using 10 % ethyl acetate in hexane as the eluent to obtain **2** as a green powder. Yield: 91 %,[16] 149 mg, 0.455 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.59 (d, $^3J_{(H-H)}$ = 9.6 Hz, 1H, 4-H), 8.26 (d, $^3J_{(H-H)}$ = 9.6 Hz, 1H, 8-H), 7.68-7.62 (m, 5H, 6-H & o-Ar-H), 7.46-7.31 (m, 9H, 3-, 5-H & m-, p-Ar-H), 7.27 (t, $^3J_{(H-H)}$ = 9.6 Hz, 1H, 7-H). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 141.8 (s), 141.5 (s), 139.7 (s), 138.0 (s), 136.9 (s), 132.9 (s), 132.4 (s), 131.8 (s), 129.5 (s), 129.1 (s), 129.0 (s), 128.5 (s), 126.4 (s), 125.9 (s), 124.7 (s), 123.8 (s), 120.6 (s), 113.7 (s), 99.5 (s, C≡C), 97.3 (s, C≡C), 87.1 (s, C≡C), 85.1 (s, C≡C); elemental analysis (%) calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 94.82; H, 5.15.

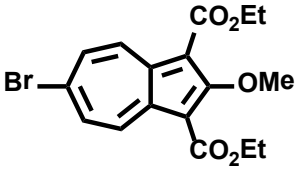
Synthesis 2,6-disubstituted azulenes



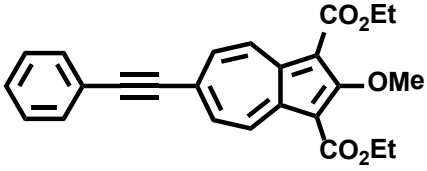
Diethyl 2-hydroxyazulene-1.3-dicarboxylate (**9**) was synthesized from α-tropolone according to literature.[8] α-tropolone was synthesized starting from dicyclopentadiene based on literature.[9]



Diethyl 2-methoxyazulene-1.3-dicarboxylate (**10**). To **9** (839 mg, 2.91 mmol) dissolved in acetone (150 mL), K_2CO_3 (6 g, 43.4 mmol) and CH_3I (4 mL, 9 g, 64 mmol) were added. The reaction mixture was then refluxed for 48 h. Following this the mixture was allowed to cool down and then filtered through a Celite plug and then concentrated *in vacuo*. Separation via column chromatography using 10 % EtOAc in CH_2Cl_2 as the eluent afforded **10** as a bright red powder. Yield: 82%, 722 mg, 2.39 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ^{o}C): δ (ppm) = 9.46 (d, $^3J_{(H-H)}$ = 10.4 Hz, 2H, 4-, 8-H), 7.81 (t, $^3J_{(H-H)}$ = 9.8 Hz, 1H, 6-H), 7.69 (t, $^3J_{(H-H)}$ = 10.0 Hz, 2H, 5-, 7-H), 4.45 (q, $^3J_{(H-H)}$ = 7.1 Hz, 4H, OCH_2), 4.13 (s, 3H, OCH_3), 1.45 (t, $^3J_{(H-H)}$ = 7.1 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 ^{o}C): δ (ppm) = 171.0 (s), 165.1 (s), 142.5 (s), 138.5 (s), 136.9 (s), 131.4 (s), 108.3 (s), 63.4 (s), 60.7 (s), 14.8 (s); elemental analysis (%) calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.77; H, 6.08.

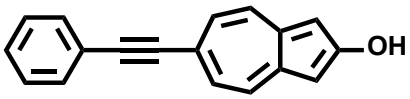


Diethyl 6-bromo-2-methoxyazulene-1.3-dicarboxylate (**11**). Diethyl 2-methoxyazulene-1.3-dicarboxylate (500 mg, 1.65 mmol) and NaOAc (164 mg, 2 mmol) was dissolved in dry DMF (50 mL) in the dark and cooled to 10°C. Under vigorous stirring Br_2 (291 mg, 1.82 mmol) in DMF (5 mL) was added over 20 minutes. The reaction was stirred at room temperature over night. The reaction mixture was then poured into water (100 mL). After separation of the phases, the aqueous layer was extracted with chloroform $CHCl_3$ (2 x 50 mL). The combined organic layer were washed with saturated $NaHCO_3$-solution (150 mL) and water (100 mL) and then dried over $MgSO_4$. After evaporation of the solvent *in vacuo*, the product was purified by column chromatography. (Eluent: 20 % EtOAc in hexane). Recrystallization from ethylacetate gave orange powder. Yield: 85%, 536 mg, 1.41 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ^{o}C): δ (ppm) = 9.50 (d, $^3J_{(H-H)}$ = 10.4 Hz, 2H, 4-, 8-H), 7.71 (t, $^3J_{(H-H)}$ = 10.1 Hz, 2H, 5-, 7-H), 4.49 (q, $^3J_{(H-H)}$ = 7.1 Hz, 4H, OCH_2), 4.17 (s, 3H, OCH_3), 1.49 (t, $^3J_{(H-H)}$ = 7.1 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 ^{o}C): δ (ppm) = 170.0 (s), 164.1 (s), 141.5(s), 137.5 (s), 130.4 (s), 117.2 (s), 107.3 (s), 62.4 (s), 59.7 (s), 13.8 (s); elemental analysis (%) calcd for $C_{17}H_{17}BrO_5$: C, 53.56; H, 4.49. Found: C, 53.29; H, 4.59.

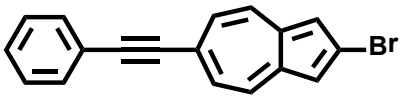


Diethyl 2-methoxy-6-phenylethynyl-azulene-1.3-dicarboxylate (**12**). **11** (500 mg, 1.31 mmol) was dissolved in dry toluene (20 mL), dry THF (20 mL) and dry NEt_3 (20 mL). To this mixture, CuI (25 mg, 0.13 mmol), PPh_3 (13 mg, 0.05 mmol), phenyl acetylene (357 mg, 3.5 mmol) and $Pd(PPh_3)_2Cl_2$) (45 mg, 0.065 mmol) were added. The reaction

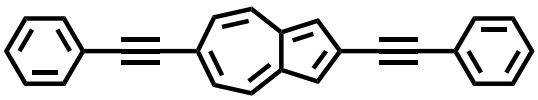
mixture was heated at 65 °C over night. The mixture was poured into water (200 mL) and then extracted with toluene (3 × 70 mL). The combined organic phases were dried over $MgSO_4$, filtered and consequently concentrated *in vacuo*. The crude product was subjected to column chromatography using 20 % EtOAc in CH_2Cl_2 as the eluent to obtain **1** as a red powder. Yield: 83 %, 438 mg, 1.09 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.42 (d, $^3J_{(H-H)}$ = 9.9 Hz, 2 H, 4-, 8-H), 7.76-7.67 (m, 3H, Ar-H), 7.54-7.35 (m, 2H, Ar-H), 7.61 (s, 2H, 1-,3-H), 7.35 (t, $^3J_{(H-H)}$ = 9.9 Hz, 2H, 5-, 7-H Az), 4.51 (q, $^3J_{(H-H)}$ = 7.1 Hz, 4H, OCH_2), 4.18 (s, 3H, OCH_3), 1.50 (t, $^3J_{(H-H)}$ = 7.1 Hz, 6H, CH_3). δ (ppm) = 170.0 (s), 164.1 (s), 141.5(s), 137.5 (s), 133.2 (s), 130.4 (s), 125.8 (s), 124.7 (s), 121.7 (s), 107.4 (s), 98.2 (s, C≡C), 90.1 (s, C≡C) 62.4 (s), 59.7 (s), 13.8 (s); elemental analysis (%) calcd for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51. Found: C, 74.69; H, 5.42.



2-Hydroxy-6-phenylethynyl-azulene (**13**). **12** (350 mg, 0.87 mmol) was dissolved in a mixture of DMF (50 mL) and water (10 mL). LiCl (932 mg, 22 mmol) was added and the reaction mixture was refluxed at 160 °C for 21 hours. The reaction mixture was allowed to cool down, and then poured into ice water and extracted with diethylether (3 × 100 mL). The combined organic phases was washed with water (2 × 150 mL), filtered and subsequently dried over $MgSO_4$. After evaporation of the solvent *in vacuo*, the product was purified by short column chromatography. (Eluent: 20 % EtOAc in CH_2Cl_2). Violet-red powder was obtained which decomposes quickly and was therefore directly used for the following reaction without further purification. Crude yield: 56%, 119 mg, 0.49 mmol. ^{1}H NMR (300 MHz, d6-acetone, 25 °C): δ = 8.37 (s, 1H, C-O*H*), 8.25 (d, 2H, $^3J_{(H-H)}$ = 9.6 Hz, 4-, 8-H), 7.74-7.65 (m, 3H, Ar-H), 7.31 (t, $^3J_{(H-H)}$ = 9.2 Hz , 2H, 5-,7-H), 7.56-7.43 (m, 2H, Ar-H), 7.11 (s, 2H, 1-,3-H).

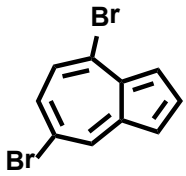


2-Bromo-6-phenylethynyl-azulene (**14**). **13** (100 mg, 0.41 mmol) was dissolved in dry toluene (60 mL) and dry pyridine (2 ml). PBr_3 (114 mg, 0.42 mmol) was then added drop wise. The solution was heated to 90 °C for 1 h. It was then poured into ice water (200 mL). After allowing to phase separate, the aqueous phase was extracted with toluene (2 × 100 mL). The combined organic phases were washed with water (100 mL), dried over $MgSO_4$ and then concentrated *in vacuo*. Separation after column chromatography using 10% CH_2Cl_2 in hexane as the eluent afforded **14** as a blue-violet powder. Yield: 68%, 86 mg, 0.28 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 8.40 (d, $^3J_{(H-H)}$ = 9.8 Hz, 2 H, 4-, 8-H), 7.74-7.66 (m, 3H, Ar-H), 7.52-7.33 (m, 2H, Ar-H), 7.59 (s, 2H, 1-, 3-H), 7.33 (t, $^3J_{(H-H)}$ = 9.9 Hz, 2H, 5-, 7-H Az). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 25 °C): δ (ppm) = 141.8 (s), 139.3 (s), 138.1 (s), 133.2 (s), 131.8 (s), 130.0 (s), 125.7 (s), 124.8 (s), 121.9 (s), 119.2 (s), 97.0 (s, C≡C), 89.2 (s, C≡C); elemental analysis (%) calcd for $C_{18}H_{11}Br$: C, 70.38; H, 3.61. Found: C, 70.52; H, 3.69.

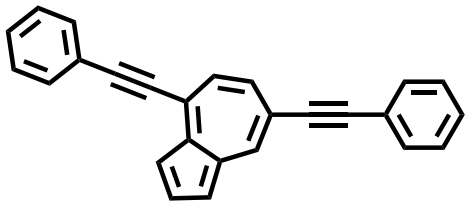


2,6-Diphenylethynyl-azulene (**3**). **14** (86 mg, 0.28 mmol) was dissolved in dry toluene (20 mL) and dry NEt_3 (20 mL). CuI (6 mg, 0.03 mmol), PPh_3 (13 mg, 0.05 mmol), phenyl acetylene (82 mg, 0.8 mmol) and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.015 mmol) were added. The reaction mixture was heated at 65 °C over night. The mixture was poured into water (100 mL) and then extracted with toluene (2 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and consequently concentrated *in vacuo*. The crude product was subjected to column chromatography using 20 % CH_2Cl_2 in hexane as the eluent to obtain **3** as a dark green powder. Yield: 96 %, 88 mg, 0.27 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.34 (d, $^3J_{(H-H)}$ = 10.1 Hz, 2H, 4-, 8-H), 7.66 (m, 7H, Ar-H),7.53 (s, 2H, 1-, 3-H) 7.44-7.22 (m, 3H, o-Ar-H), 7.29-7.25 (m, 2H, 5-,7-H & Ar-H). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 140.3 (s), 137.9 (s), 136.8 (s), 131.7 (s), 131.6 (s), 129.8(s), 128.6 (s), 128.5 (s), 124.2 (s), 123.3 (s), 122.9 (s), 120.4 (s), 95.1 (s, C≡C), 91.3 (s, C≡C), 89.6 (s, C≡C), 88.9 (s, C≡C); elemental analysis (%) calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 95.28; H, 4.70.

Synthesis 4,7 disubstituted azulenes



4,7-Dibromoazulene (**15**).[17] The blue-green powder was synthesized according to literature from 2,5-dibromo-S,S-dioxide and *N,N*-dimethylaminofulvene. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.59 (s, 1H, 8-H), 7.97 (s, 1H, 2-H), 7.71 (d, $^{3}J_{(H-H)}$ = 11.3 Hz, 1H, 6-H), 7.62 (s, 1H, 3-H), 7.45-7.39 (m, 2H, 1-, 5-H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 140.4 (s), 139.9 (s), 138.0 (s), 137.7 (s), 137.7 (s), 134.5 (s), 127.3 (s), 123.2 (s), 121.9 (s), 118.0 (s). The data is consistent with published results.[17]



4,7- Diphenylethynyl-azulene (**4**). **15** (71.6 mg, 0.25 mmol) was dissolved in dry toluene (10 mL) and dry NEt_3 (15 mL). PPh_3 (13 mg, 0.05 mmol), CuI (9.5 mg, 0.05 mmol), phenyl acetylene (102 mg, 1 mmol) and $Pd(PPh_3)_2Cl_2$ (18 mg, 0.025 mmol) were added. The reaction mixture was heated at 65 °C over night. The mixture was poured into water (100 mL) and then extracted with toluene (3 × 40 mL). The combined organic phases were dried over $MgSO_4$, filtered and consequently concentrated *in vacuo*. The crude product was subjected to column chromatography using 10% CH_2Cl_2 in hexane as the eluent to obtain **4** as a green powder. Yield: 93%, 77 mg, 0.234 mmol. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.59 (s, 1H, 8-H), 7.95 (t, $^{3}J_{(H-H)}$ = 3.7 Hz, 1H, 2-H), 7.83-7.81 (m, 2H, Ar-H), 7.73-7.71 (m, 2H, Ar-H), 7.61 (d, $^{3}J_{(H-H)}$ = 7.5 Hz, 2H, 6-H), 7.47-7.45 (m, 4H, 1-,3-H & Ar-H), 7.43-7.38 (m, 4H, 4-H & Ar-H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 140.2 (s), 139.5 (s), 139.4 (s), 138.7 (s), 138.7 (s), 132.6 (s), 132.1 (s), 130.7 (s), 130.0 (s), 129.2 (s), 129.1 (s), 129.0 (s), 126.4 (s), 123.8 (s), 123.1 (s), 121.8 (s), 120.9 (s), 118.3 (s), 97.8 (s, C≡C), 93.7 (s, C≡C), 91.3 (s, C≡C), 90.0 (s, C≡C); elemental analysis (%) calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 94.87; H, 4.72.

NMR-Spectra

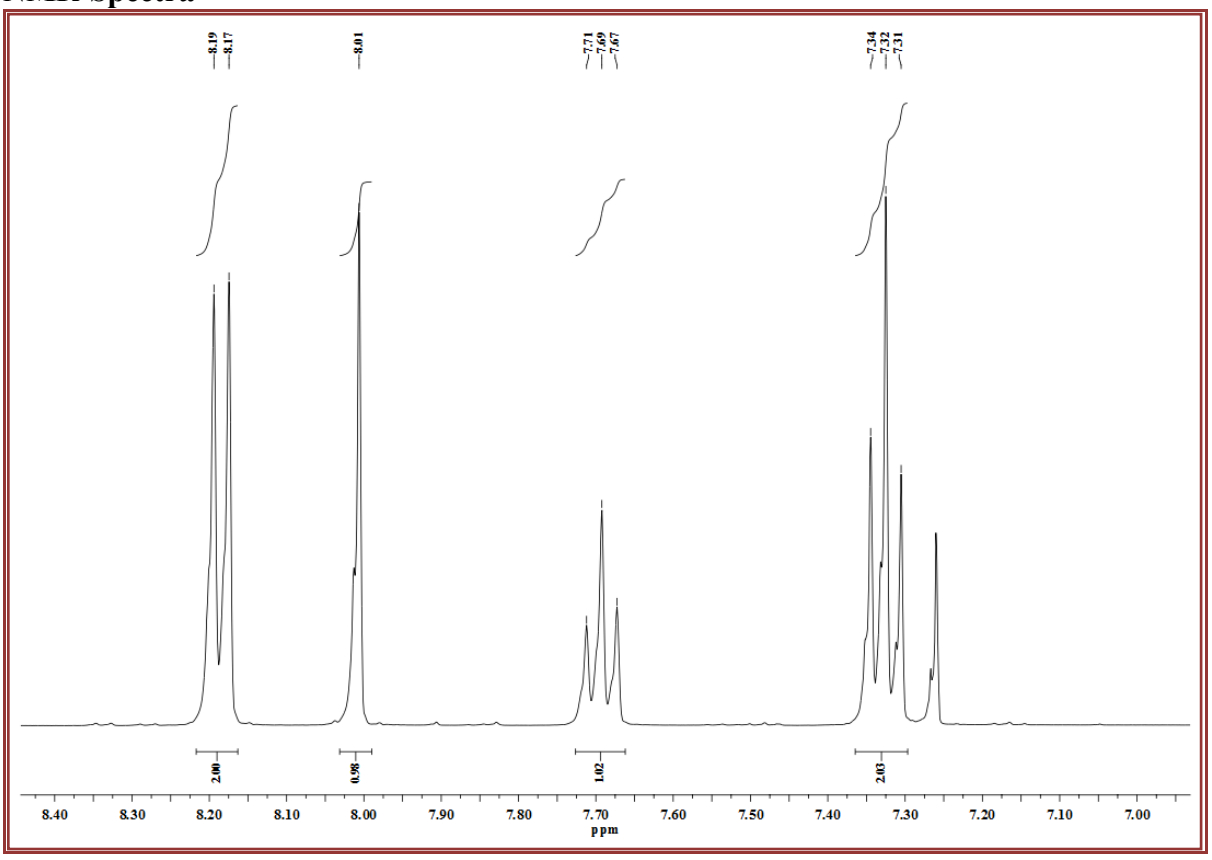


Figure S1. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **1**.

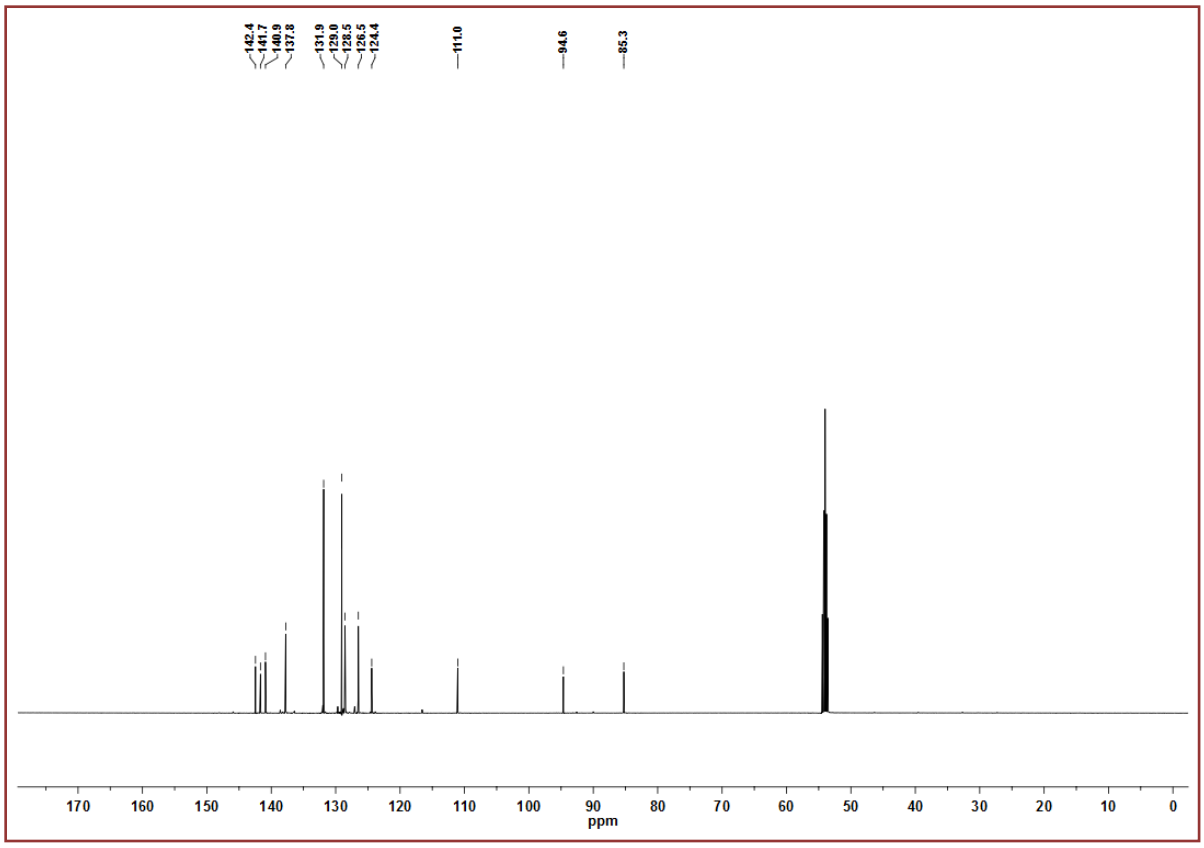


Figure S2. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 °C) of **1**.

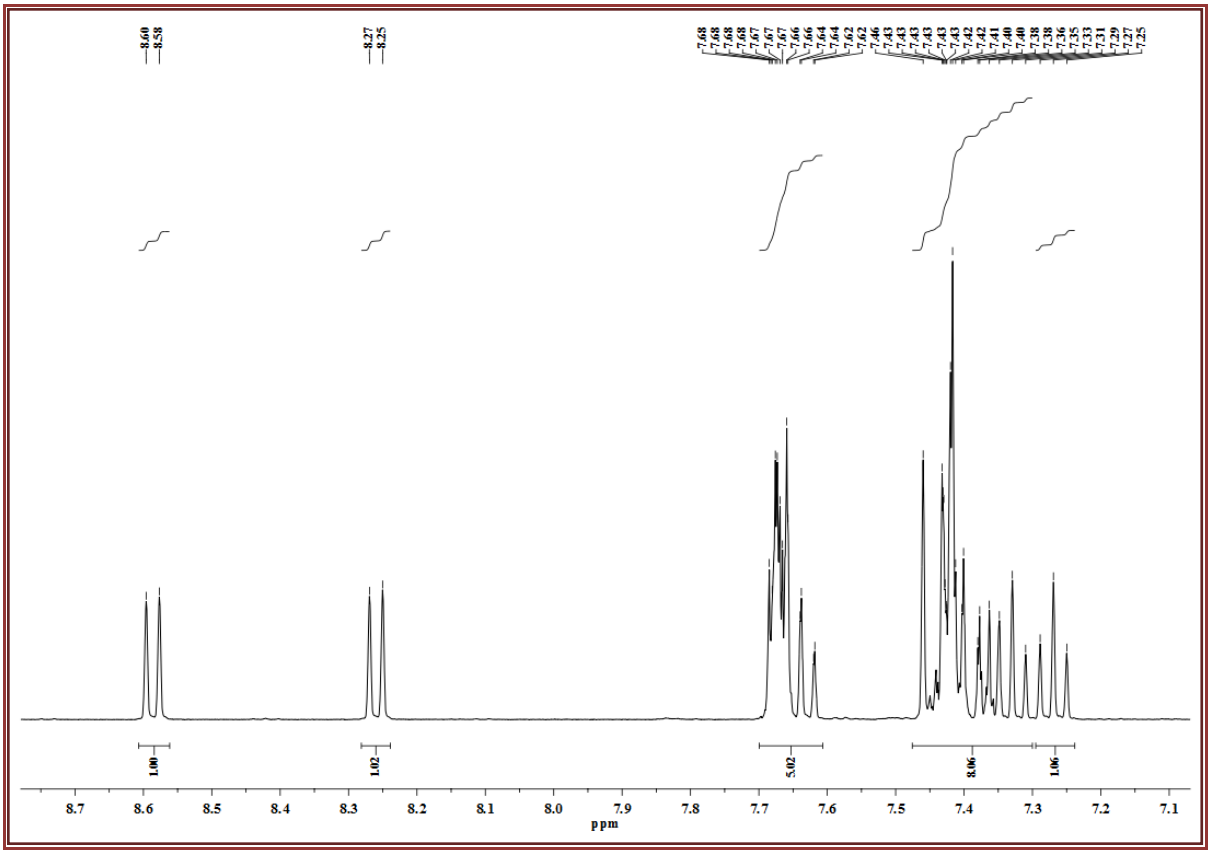


Figure S3. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **2**.

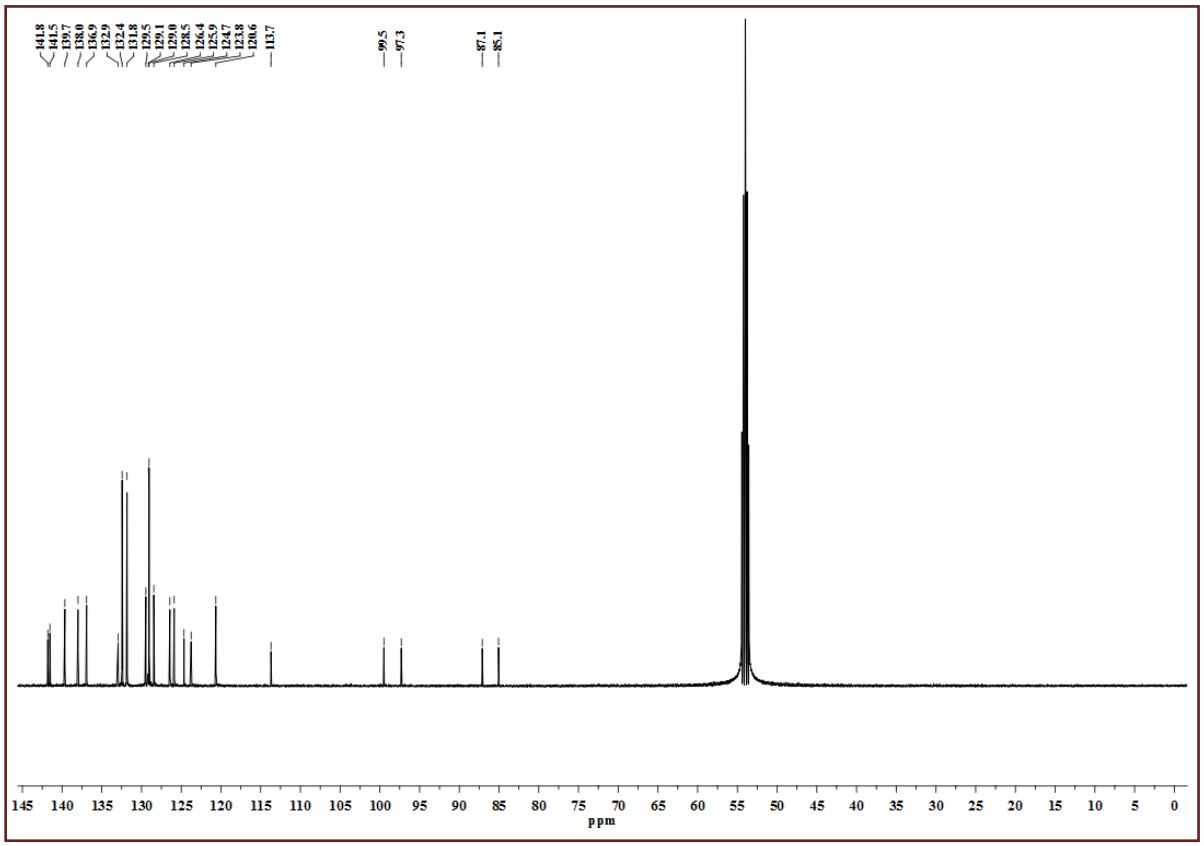


Figure S4. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C) of **2**.

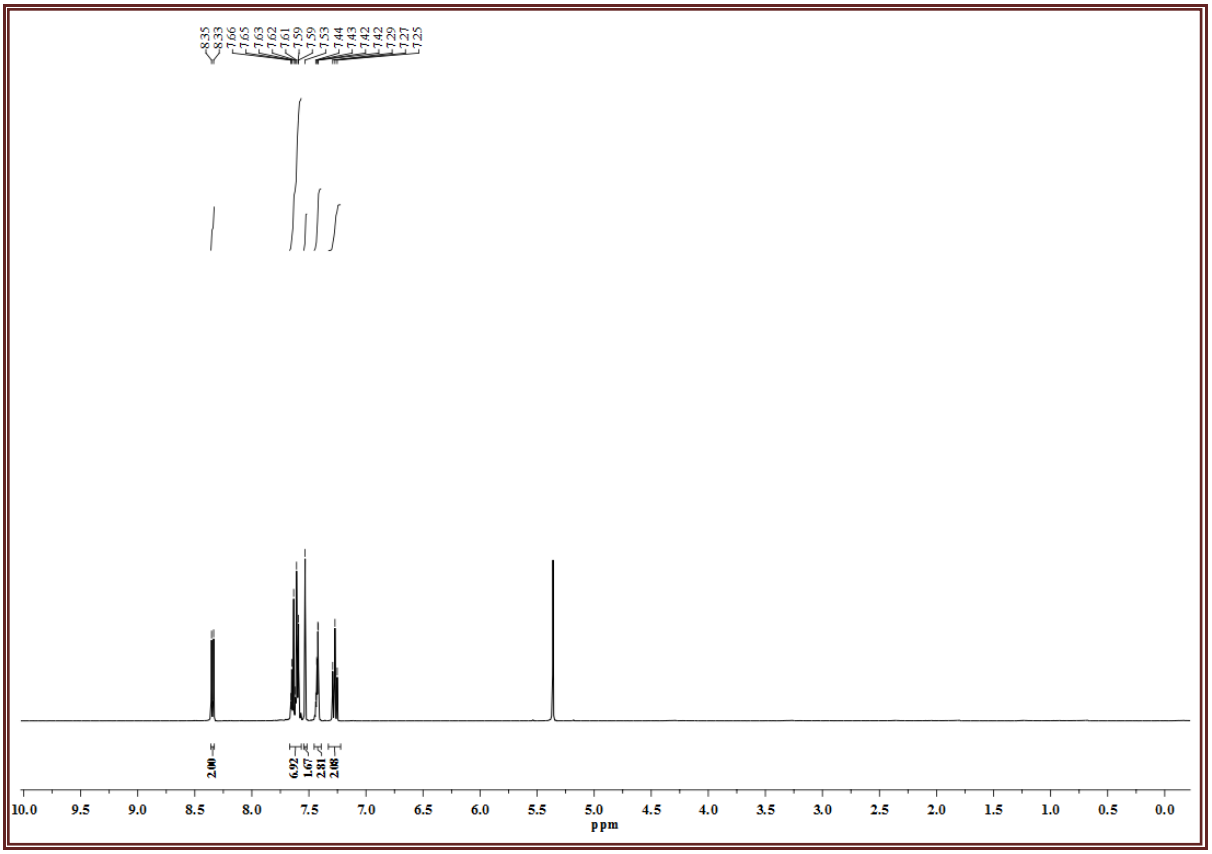


Figure S5. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **3**.

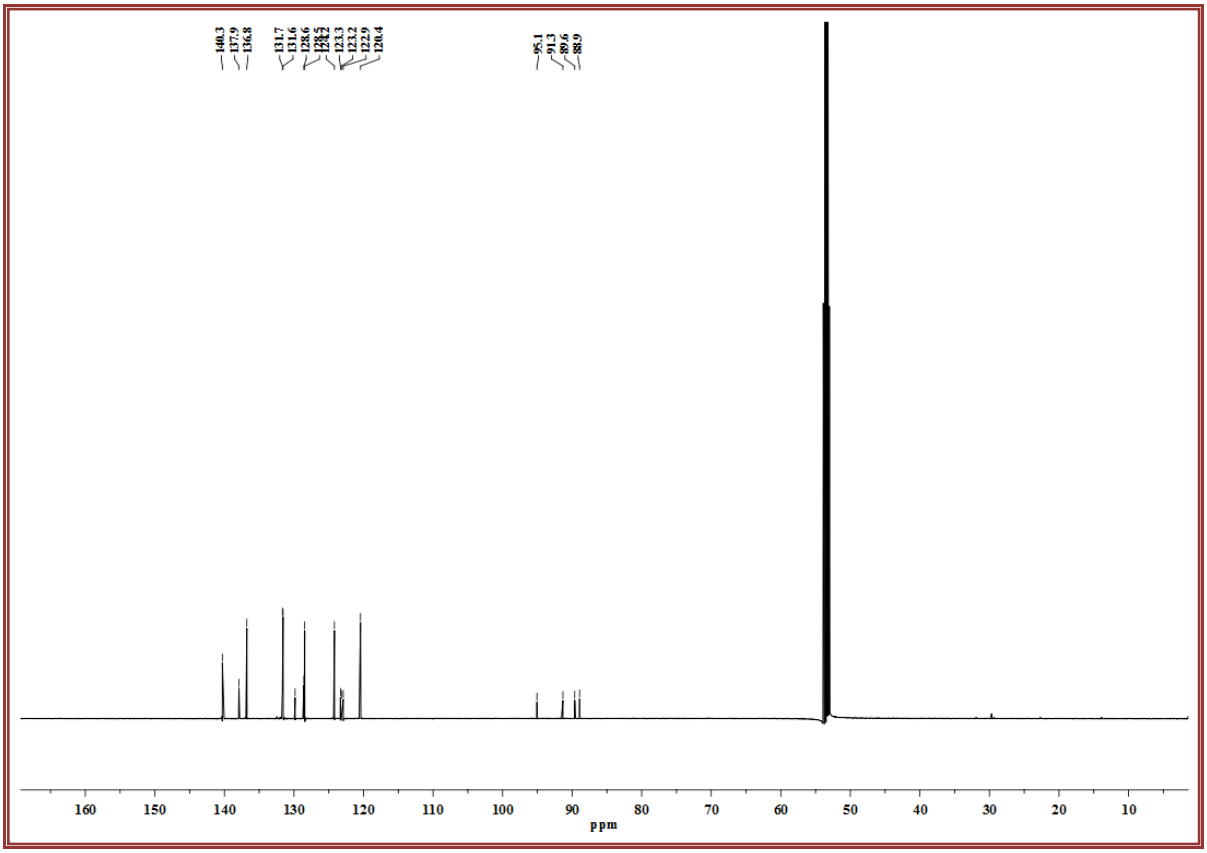


Figure S6. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 °C) of **3**.

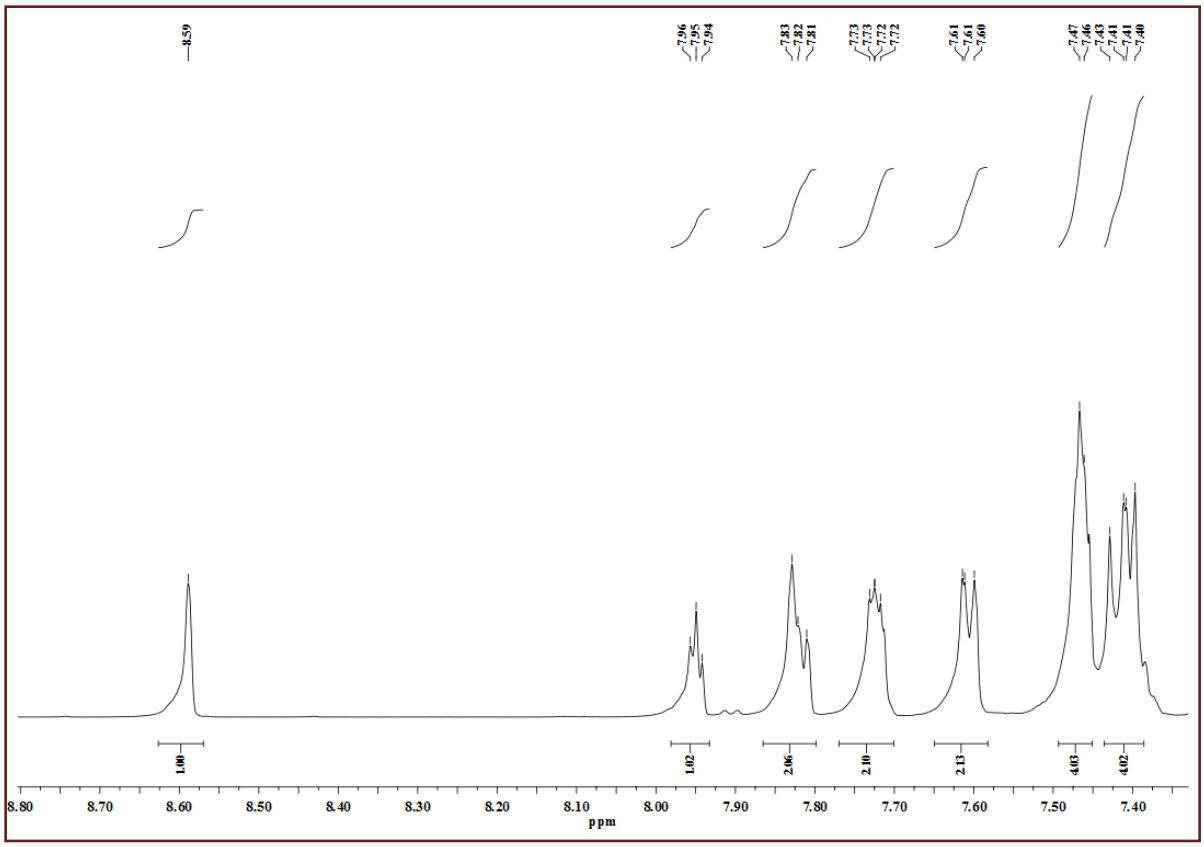


Figure S7. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **4**.

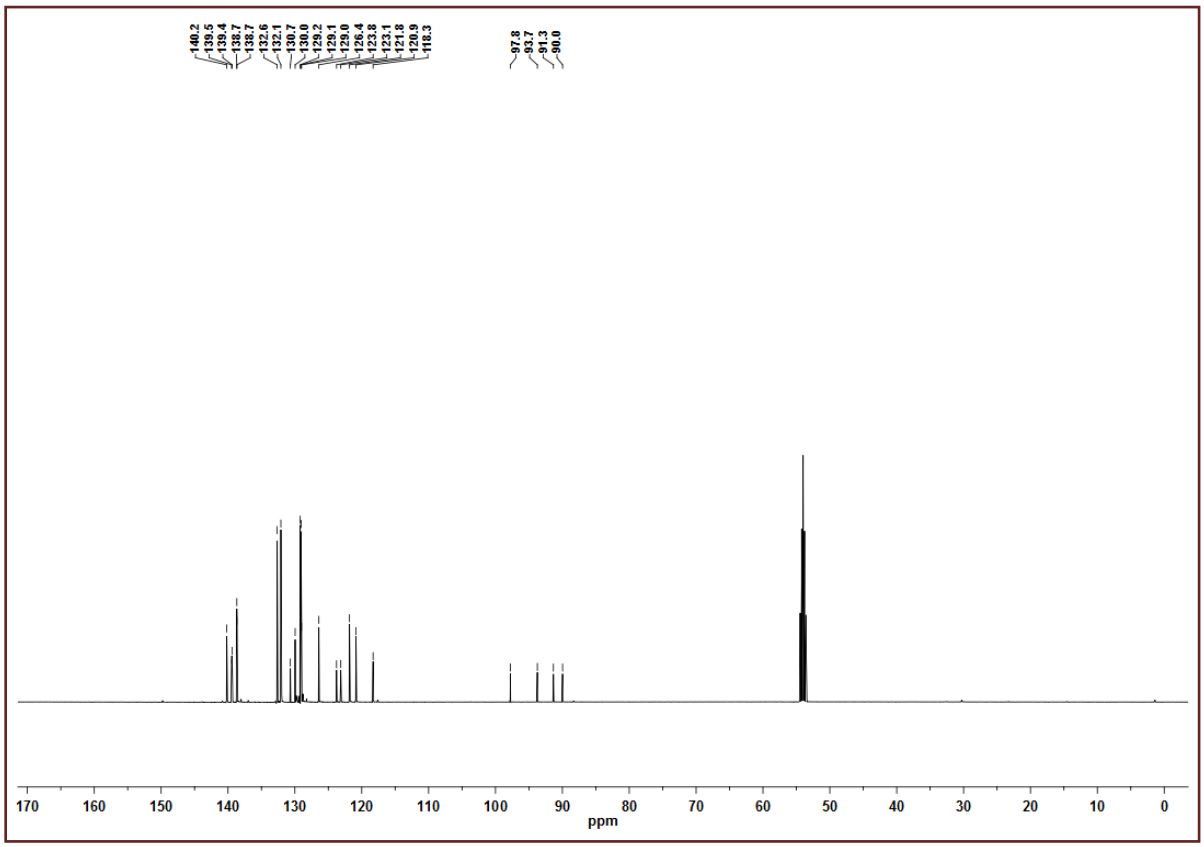


Figure S8. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 ^{o}C) of **4**.

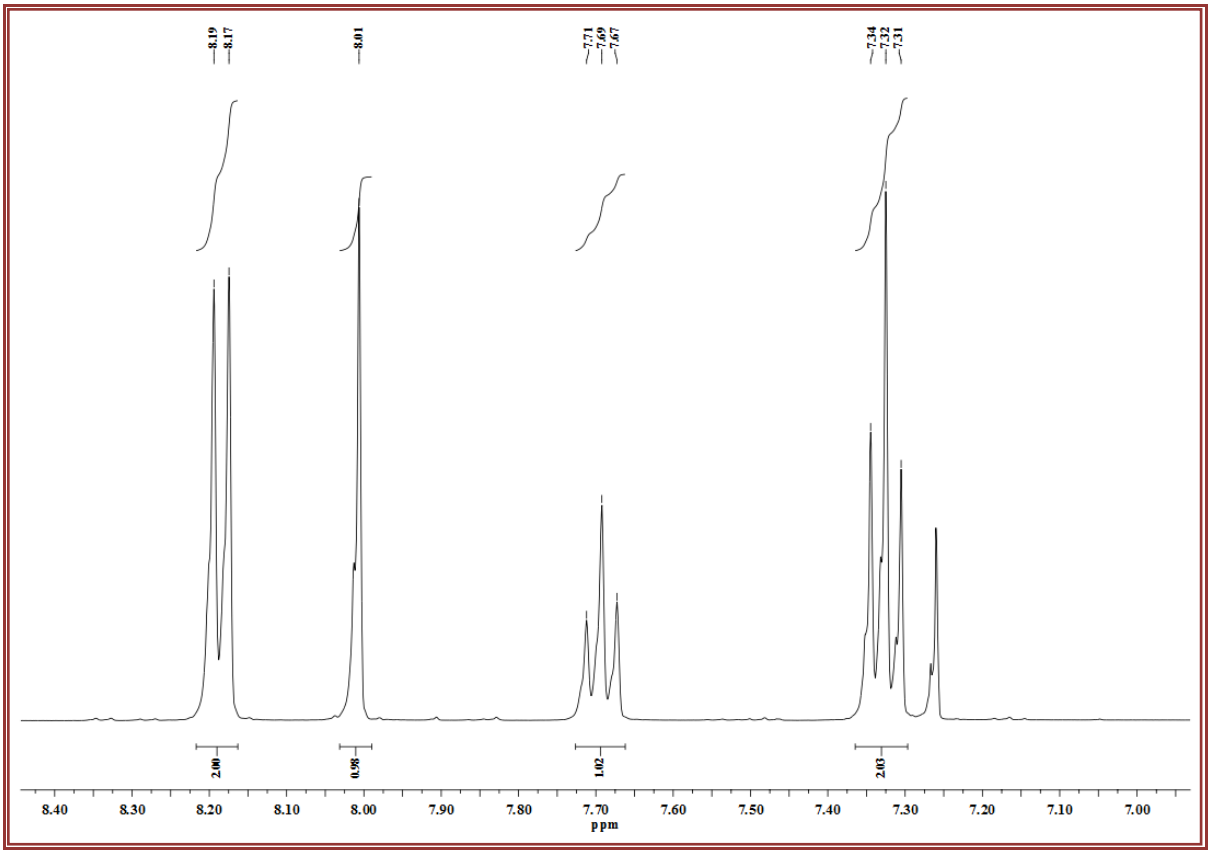


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) of **6**.

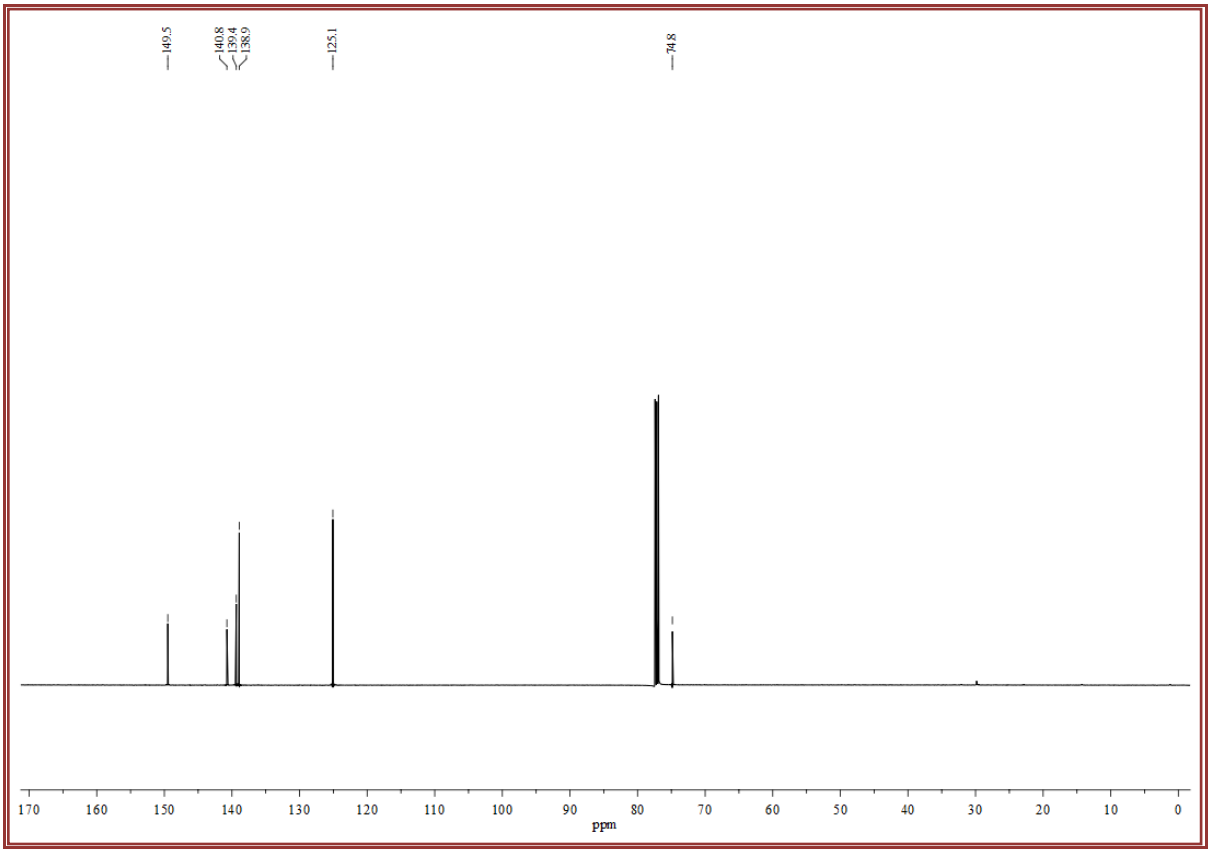


Figure S10. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25 ^{o}C) of **6**.

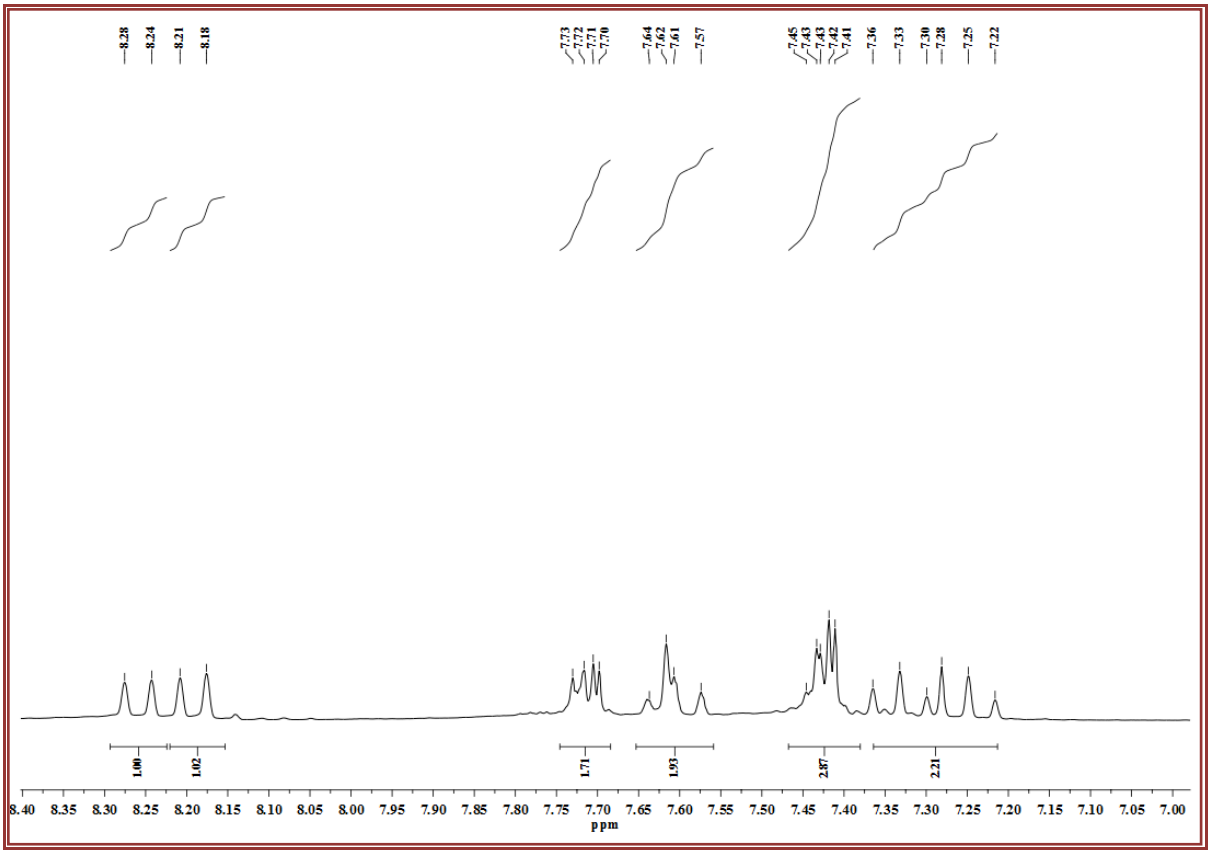


Figure S11. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **8**.

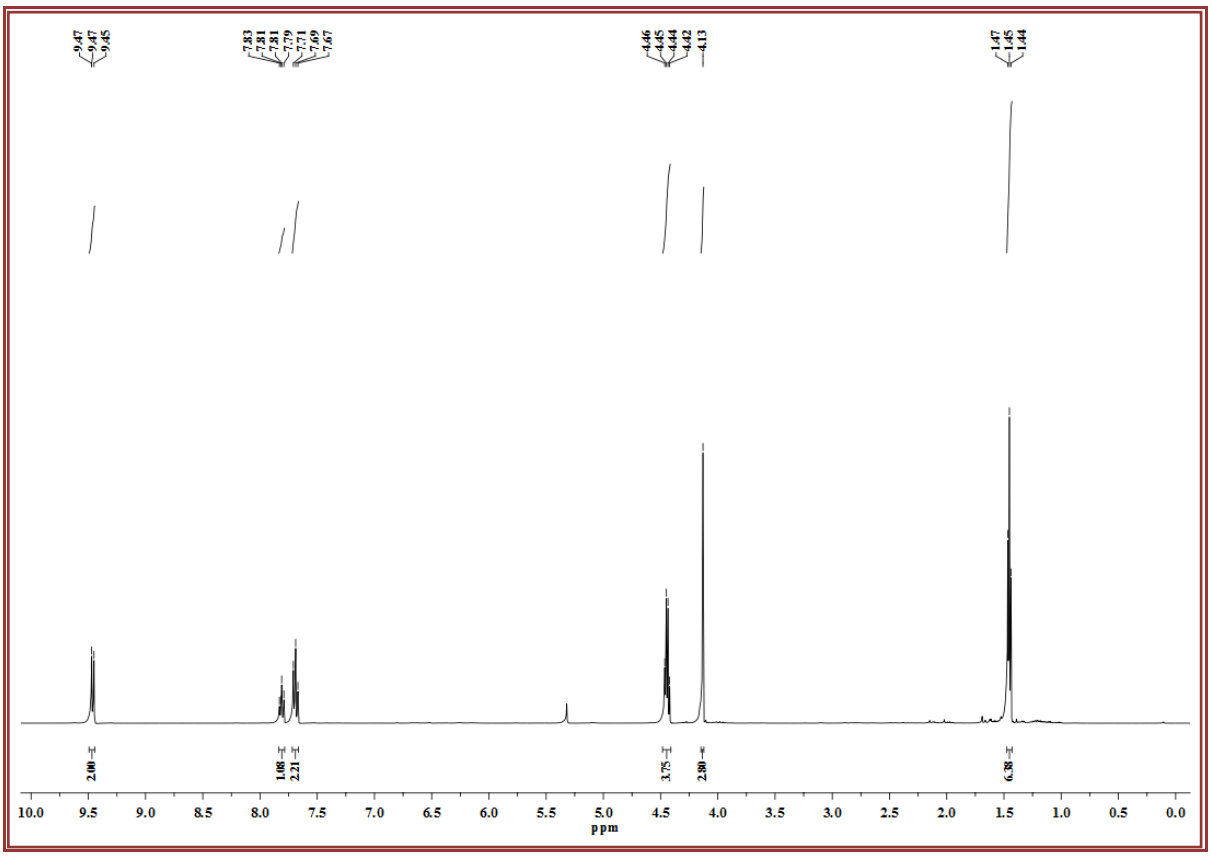


Figure S12. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **10**.

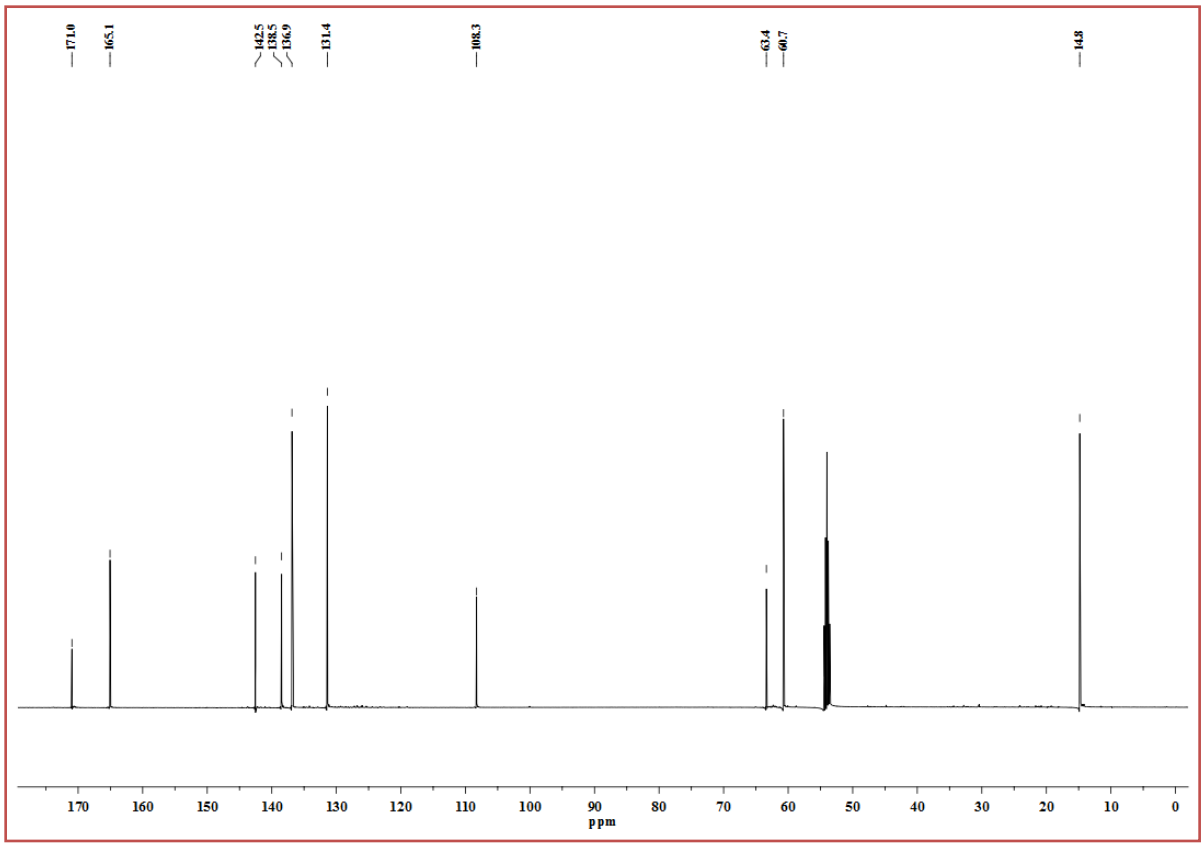


Figure S13. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 °C) of **10**.

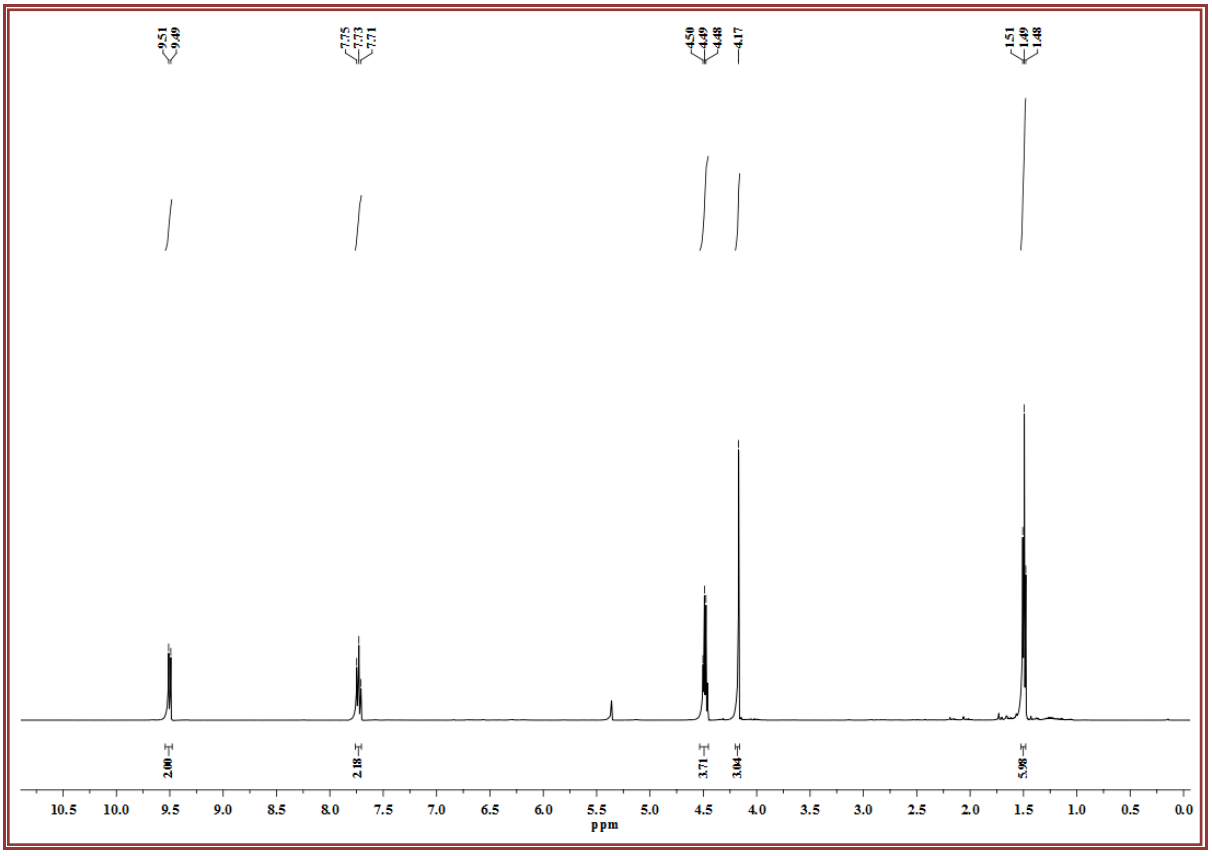


Figure S14. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **11**.

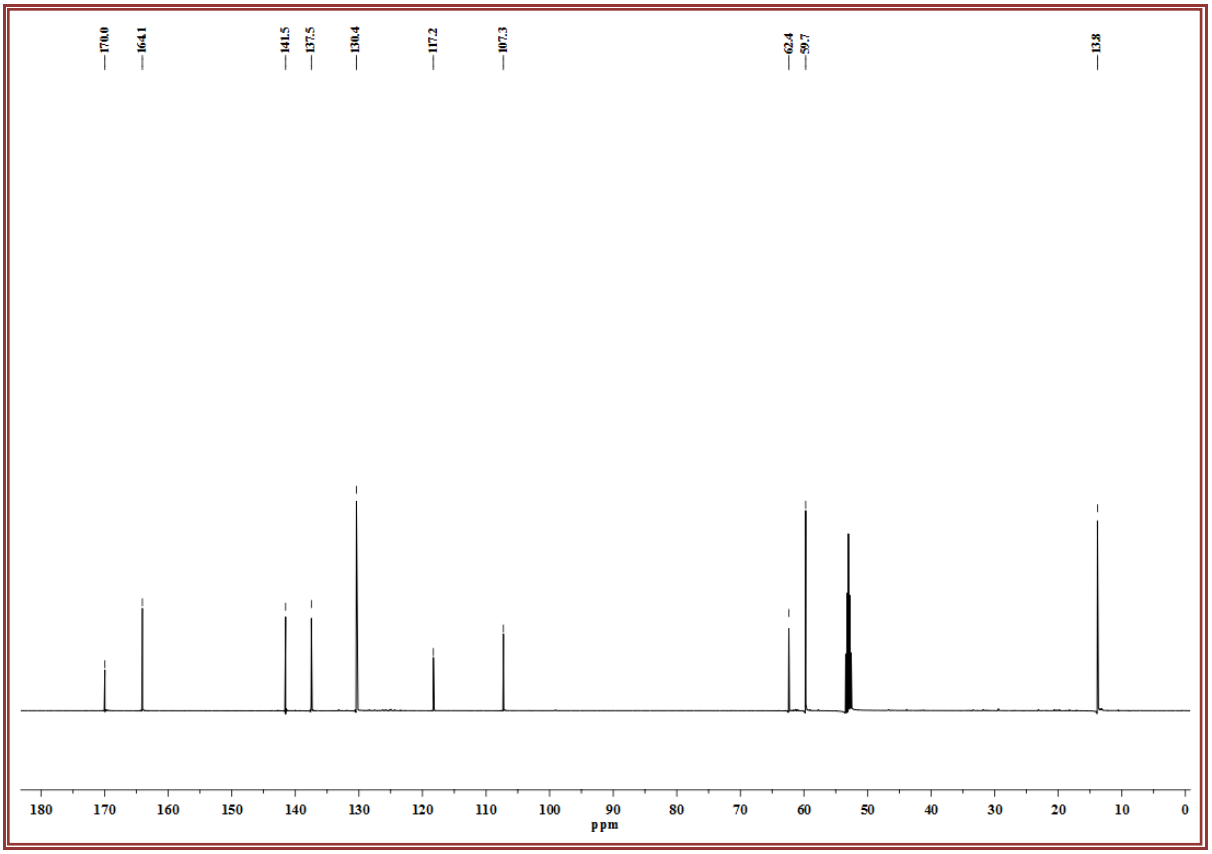


Figure S15. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 ^{o}C) of **11**.

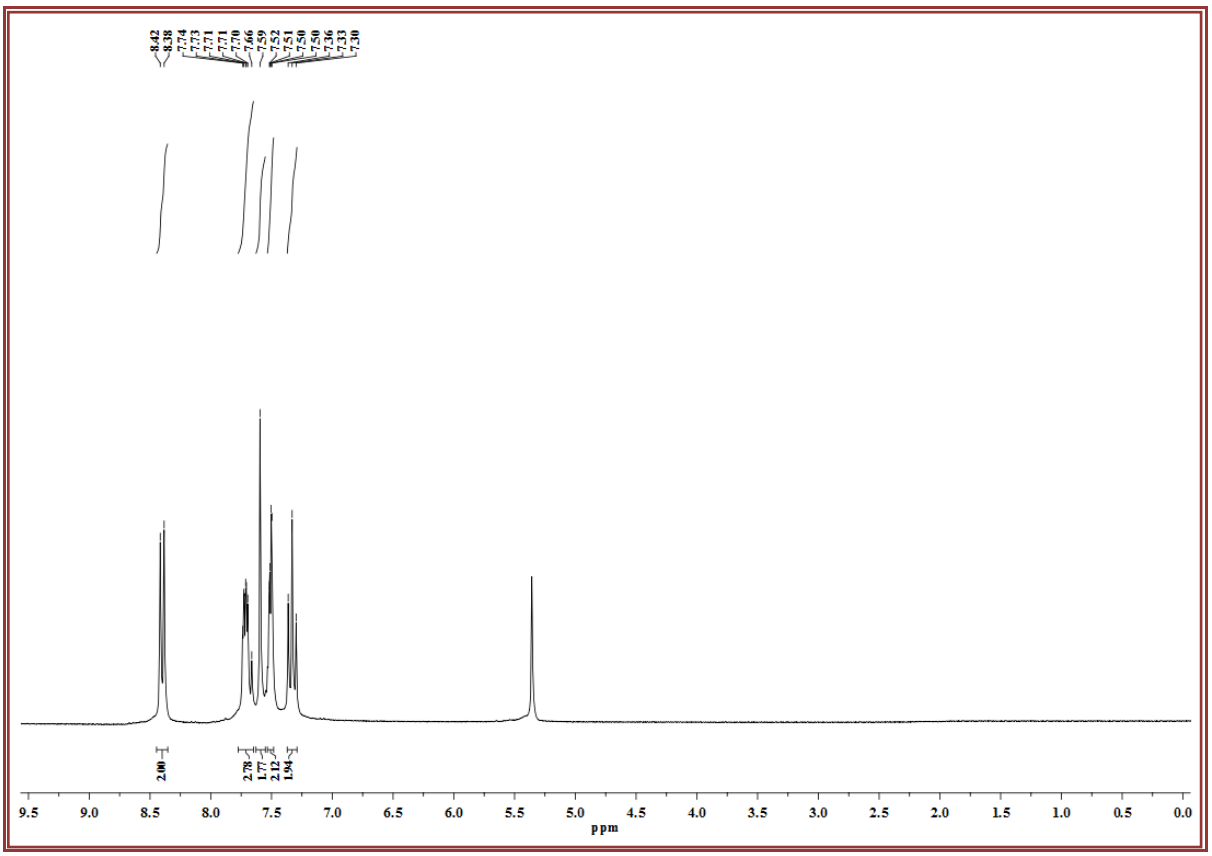


Figure S16. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2, 25 ^{o}C) of **14**.

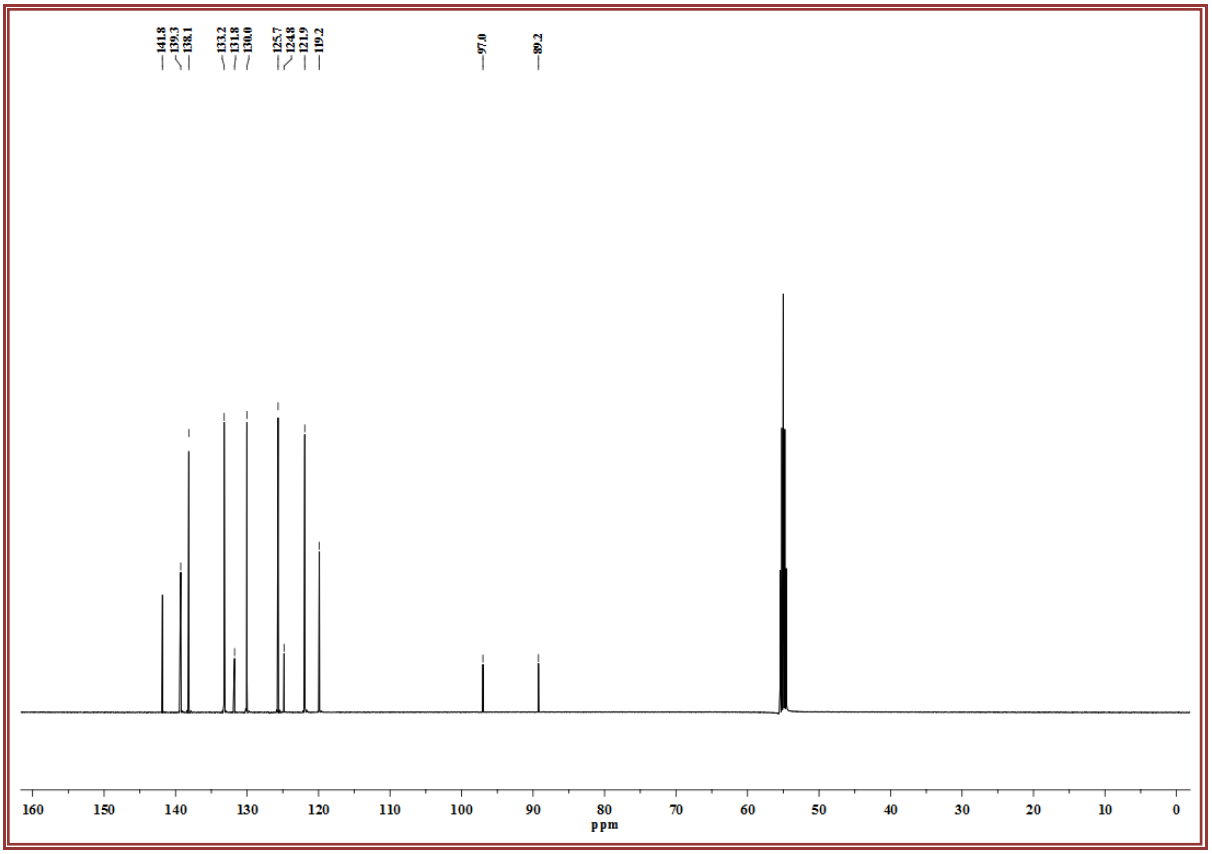


Figure S17. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **14**.

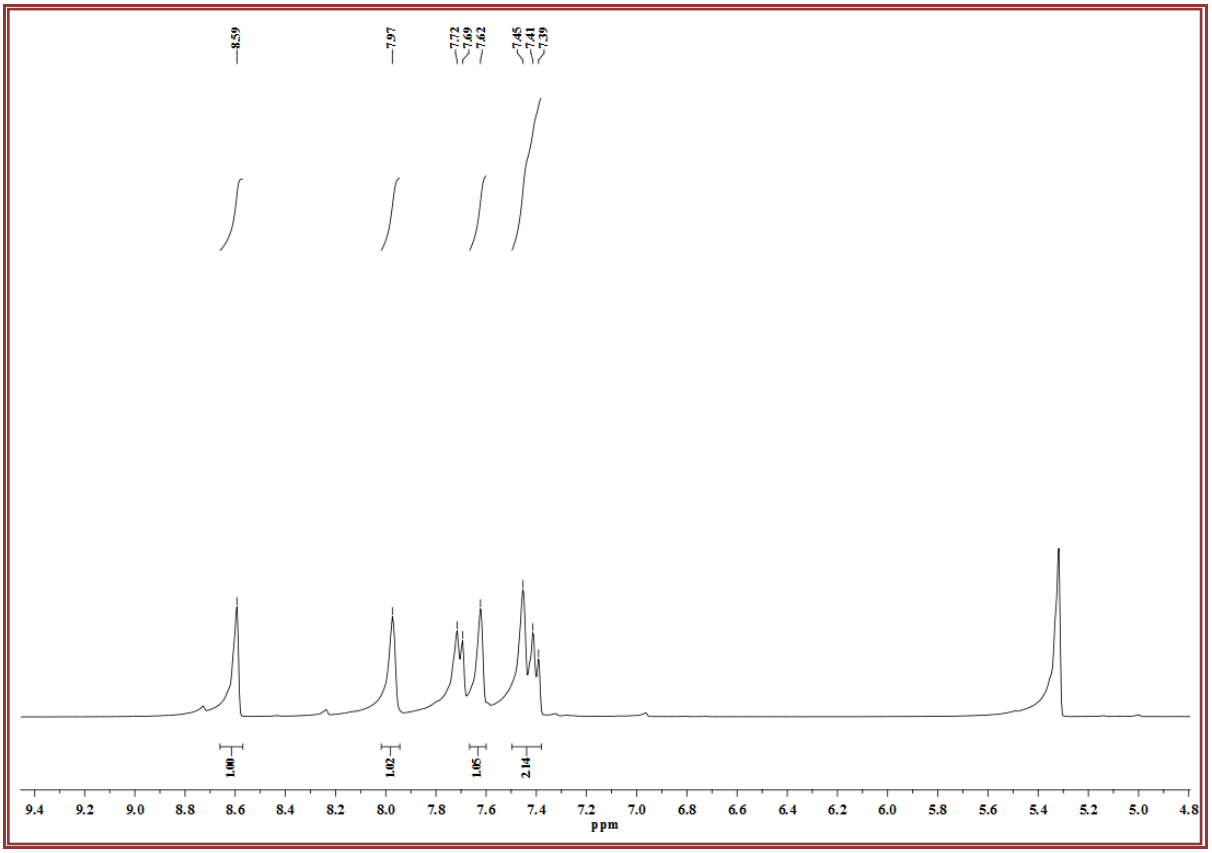


Figure S18. ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, 25 °C) of **15**.

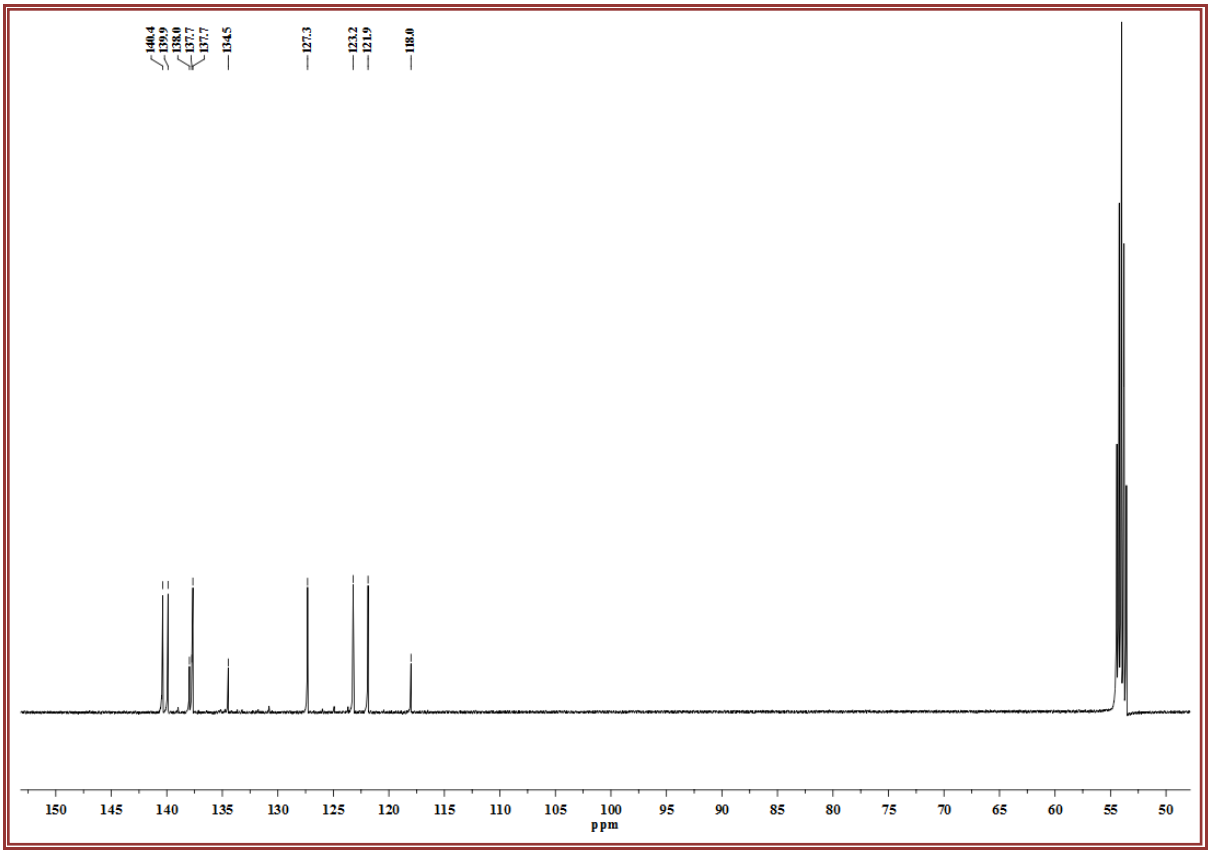


Figure S19. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) of **15**.

Energies and cartesian coordinates of the DFT optimized ground-state

Energies and cartesian coordinates of the DFT optimized ground-state structure of 1

C	-0.00030000	4.56120000	-0.00040000	C	-5.30940000	-2.48730000	0.00030000
C	1.26370000	3.96890000	-0.00040000	C	-6.06520000	-0.18590000	-0.00010000
C	1.58790000	2.61020000	-0.00030000	C	-6.63180000	-2.91550000	0.00040000
C	-1.26420000	3.96870000	-0.00030000	H	-4.49250000	-3.21030000	0.00050000
C	0.73670000	1.51420000	-0.00010000	C	-7.38430000	-0.62380000	0.00000000
C	-1.58820000	2.60990000	-0.00010000	H	-5.83700000	0.88110000	-0.00030000
C	-0.73680000	1.51400000	0.00000000	C	-7.67430000	-1.98840000	0.00020000
H	-0.00040000	5.65560000	-0.00050000	H	-6.85150000	-3.98510000	0.00060000
H	2.11140000	4.65860000	-0.00050000	H	-8.19520000	0.10750000	-0.00020000
H	2.65460000	2.36340000	-0.00030000	H	-8.71150000	-2.32900000	0.00020000
H	-2.11200000	4.65820000	-0.00030000	C	5.00670000	-1.11250000	0.00010000
H	-2.65490000	2.36300000	0.00000000	C	6.06570000	-0.18580000	0.00160000
C	1.15450000	0.15380000	0.00000000	C	5.30920000	-2.48690000	-0.00150000
H	0.00030000	-1.74000000	0.00030000	C	7.38470000	-0.62410000	0.00160000
C	0.00020000	-0.65130000	0.00010000	H	5.83780000	0.88130000	0.00290000
C	-1.15440000	0.15360000	0.00000000	C	6.63150000	-2.91550000	-0.00150000
C	2.49210000	-0.29320000	0.00010000	H	4.49200000	-3.20980000	-0.00270000
C	3.65540000	-0.66800000	0.00010000	C	7.67430000	-1.98870000	0.00010000
C	-2.49180000	-0.29370000	0.00000000	H	8.19580000	0.10700000	0.00280000
C	-3.65510000	-0.66870000	0.00000000	H	6.85090000	-3.98520000	-0.00270000
C	-5.00650000	-1.11290000	0.00010000	H	8.71140000	-2.32960000	0.00010000

Zero-point correction= 0.330587 (Hartree/Particle)
Thermal correction to Energy= 0.351273
Thermal correction to Enthalpy= 0.352218
Thermal correction to Gibbs Free Energy= 0.276144
Sum of electronic and zero-point Energies= -998.825560
Sum of electronic and thermal Energies= -998.804874
Sum of electronic and thermal Enthalpies= -998.803930
Sum of electronic and thermal Free Energies= -998.880004

Energies and cartesian coordinates of the DFT optimized ground-state structure of 2

C	6.00290000	-0.95920000	-0.00680000	C	-1.71150000	3.33430000	0.26290000
C	5.57590000	-2.29030000	0.00230000	C	0.39790000	4.43420000	-0.19280000
C	4.27410000	-2.78730000	0.01050000	C	-2.34650000	4.57050000	0.27920000
C	5.25320000	0.21760000	-0.01100000	H	-2.27580000	2.41730000	0.43950000
C	3.06810000	-2.08640000	0.00950000	C	-0.24590000	5.66600000	-0.17360000
C	3.86480000	0.36710000	-0.00850000	H	1.47130000	4.37410000	-0.37910000
C	2.88320000	-0.61660000	-0.00180000	C	-1.61900000	5.74100000	0.06130000
H	7.08820000	-0.81990000	-0.01070000	H	-3.42130000	4.62200000	0.46590000
H	6.36970000	-3.04150000	0.00430000	H	0.33000000	6.57790000	-0.34470000
H	4.17770000	-3.87780000	0.01900000	H	-2.12140000	6.71020000	0.07550000
H	5.82880000	1.14650000	-0.01690000	C	-3.19240000	-2.15030000	-0.02780000
H	3.48630000	1.39430000	-0.01230000	C	-3.76560000	-3.42260000	0.15090000
C	1.79310000	-2.66460000	0.01780000	C	-4.03740000	-1.04330000	-0.22830000
H	1.57640000	-3.73060000	0.02440000	C	-5.14670000	-3.57820000	0.13160000
C	0.82760000	-1.64060000	0.01010000	H	-3.11190000	-4.28210000	0.30600000
C	1.48960000	-0.37310000	0.00020000	C	-5.41720000	-1.20910000	-0.24760000
C	-0.56970000	-1.82480000	0.00470000	H	-3.59270000	-0.05760000	-0.37290000
C	-1.78070000	-1.98140000	-0.00770000	C	-5.97670000	-2.47450000	-0.06710000
C	0.86550000	0.88760000	0.00100000	H	-5.58040000	-4.57030000	0.27260000
C	0.32340000	1.98330000	0.00850000	H	-6.06310000	-0.34310000	-0.40560000
C	-0.32670000	3.24770000	0.02530000	H	-7.06110000	-2.60080000	-0.08210000

Zero-point correction= 0.330562 (Hartree/Particle)
Thermal correction to Energy= 0.351216
Thermal correction to Enthalpy= 0.352160
Thermal correction to Gibbs Free Energy= 0.276277
Sum of electronic and zero-point Energies= -998.824484
Sum of electronic and thermal Energies= -998.803829
Sum of electronic and thermal Enthalpies= -998.802885
Sum of electronic and thermal Free Energies= -998.878768

Energies and cartesian coordinates of the DFT optimized ground-state structure of 3

C	-2.57980000	0.00030000	0.00000000	H	6.88160000	2.15280000	0.00010000
C	-1.95870000	1.26860000	0.00000000	C	8.82320000	-1.20720000	0.00000000
C	-0.60730000	1.58660000	-0.00010000	H	6.88140000	-2.15320000	-0.00010000
C	-1.95870000	-1.26810000	0.00000000	C	9.52320000	-0.00030000	0.00010000
C	0.50610000	0.74390000	-0.00010000	H	9.36660000	2.15380000	0.00020000
C	-0.60730000	-1.58600000	0.00000000	H	9.36640000	-2.15440000	0.00000000
C	0.50610000	-0.74320000	0.00000000	H	10.61500000	-0.00040000	0.00020000
H	-2.64860000	2.11490000	0.00000000	H	2.19620000	-2.18110000	-0.00010000
H	-0.37850000	2.65730000	0.00000000	C	-4.00410000	0.00030000	0.00000000
H	-2.64850000	-2.11440000	0.00000000	C	-5.22530000	-0.00020000	0.00000000
H	-0.37850000	-2.65670000	0.00000000	C	-6.64780000	-0.00020000	0.00000000
C	1.84090000	1.15330000	0.00010000	C	-7.36150000	-1.21260000	0.00010000
H	2.19620000	2.18170000	0.00020000	C	-7.36160000	1.21210000	0.00000000
C	2.66300000	0.00030000	-0.00010000	C	-8.75140000	-1.20750000	0.00010000
C	1.84090000	-1.15270000	0.00000000	H	-6.81010000	-2.15390000	0.00010000
C	4.07460000	0.00030000	-0.00010000	C	-8.75140000	1.20700000	0.00000000
C	5.29630000	-0.00010000	-0.00010000	H	-6.81020000	2.15340000	-0.00010000
C	6.71840000	-0.00020000	0.00000000	C	-9.45070000	-0.00030000	0.00010000
C	7.43340000	1.21170000	0.00010000	H	-9.29480000	-2.15440000	0.00020000
C	7.43330000	-1.21210000	-0.00010000	H	-9.29490000	2.15390000	-0.00010000
C	8.82330000	1.20660000	0.00010000	H	-10.54250000	-0.00030000	0.00010000

Zero-point correction=	0.330024 (Hartree/Particle)
Thermal correction to Energy=	0.350725
Thermal correction to Enthalpy=	0.351669
Thermal correction to Gibbs Free Energy=	0.275854
Sum of electronic and zero-point Energies=	-998.819409
Sum of electronic and thermal Energies=	-998.798708
Sum of electronic and thermal Enthalpies=	-998.797764
Sum of electronic and thermal Free Energies=	-998.873580

Energies and cartesian coordinates of the DFT optimized ground-state structure of 4

C	-0.83740000	-0.78190000	-0.00010000	C	5.72770000	-2.24130000	0.00000000
C	-1.74820000	0.29590000	0.00000000	C	6.41130000	0.08540000	0.00010000
C	-1.41370000	1.66450000	0.00010000	C	7.06270000	-2.62790000	0.00010000
C	0.54810000	-0.80240000	-0.00030000	H	4.93310000	-2.98870000	-0.00010000
C	-0.16620000	2.26480000	0.00000000	C	7.74340000	-0.31070000	0.00020000
C	1.47980000	0.25970000	-0.00030000	H	6.14750000	1.14400000	0.00010000
C	1.18470000	1.63530000	-0.00020000	C	8.07360000	-1.66630000	0.00020000
H	-1.30990000	-1.76740000	-0.00020000	H	7.31770000	-3.68950000	0.00010000
H	-2.26500000	2.35150000	0.00000000	H	8.53170000	0.44450000	0.00020000
H	0.99800000	-1.79720000	-0.00030000	H	9.12110000	-1.97410000	0.00020000
C	0.04160000	3.65950000	-0.00030000	C	-5.70600000	-0.64710000	0.00010000
H	-0.75060000	4.40630000	-0.00060000	C	-6.11490000	-1.99340000	0.00000000
C	1.41790000	3.90140000	0.00010000	C	-6.68720000	0.36120000	0.00020000
H	1.88360000	4.88720000	0.00020000	C	-7.46660000	-2.31680000	0.00000000
C	2.11580000	2.67980000	0.00010000	H	-5.35710000	-2.77830000	-0.00010000
H	3.19550000	2.55110000	0.00020000	C	-8.03670000	0.02800000	0.00020000
C	2.85150000	-0.12290000	-0.00020000	H	-6.37430000	1.40640000	0.00020000
C	4.02050000	-0.47450000	-0.00010000	C	-8.43230000	-1.30990000	0.00010000
C	-3.13490000	-0.03090000	0.00000000	H	-7.77030000	-3.36560000	-0.00010000
C	-4.32290000	-0.31310000	0.00000000	H	-8.78790000	0.82040000	0.00030000
C	5.38520000	-0.87690000	0.00000000	H	-9.49310000	-1.56780000	0.00010000

Zero-point correction=	0.329875 (Hartree/Particle)
Thermal correction to Energy=	0.350556
Thermal correction to Enthalpy=	0.351501
Thermal correction to Gibbs Free Energy=	0.276038
Sum of electronic and zero-point Energies=	-998.813803
Sum of electronic and thermal Energies=	-998.793122
Sum of electronic and thermal Enthalpies=	-998.792178
Sum of electronic and thermal Free Energies=	-998.867641

Energies and cartesian coordinates of the DFT optimized ground-state structure of 1-H$^+$

C	0.14580000	4.46850000	0.76820000	C	4.77900000	-1.71570000	1.28060000
C	-1.08760000	3.80080000	0.83120000	C	7.02150000	-1.74920000	-0.38510000
C	-1.41940000	2.53290000	0.37810000	H	5.77560000	-0.75670000	-1.84250000
C	1.34630000	4.03050000	0.22310000	C	5.96890000	-2.27970000	1.72560000
C	-0.59040000	1.60340000	-0.26790000	H	3.89780000	-1.70120000	1.92370000
C	1.62780000	2.81280000	-0.41220000	C	7.09030000	-2.29710000	0.89590000
C	0.76820000	1.75260000	-0.63840000	H	7.89800000	-1.76490000	-1.03500000
H	0.16230000	5.46790000	1.21060000	H	6.02220000	-2.71050000	2.72690000
H	-1.89690000	4.35680000	1.31210000	H	8.02250000	-2.74170000	1.24910000
H	-2.44870000	2.20030000	0.54200000	C	-4.80240000	-1.10130000	-0.00810000
H	2.18440000	4.72870000	0.29500000	C	-5.78580000	-0.27860000	0.57010000
H	2.65490000	2.67210000	-0.76270000	C	-5.12410000	-2.42390000	-0.36380000
C	-1.04710000	0.27190000	-0.67010000	C	-7.06530000	-0.77360000	0.78630000
H	-0.03850000	-1.38870000	-1.67280000	H	-5.53710000	0.74750000	0.84530000
C	-0.00960000	-0.37500000	-1.27600000	C	-6.40700000	-2.90820000	-0.14190000
C	1.20540000	0.49480000	-1.36210000	H	-4.36020000	-3.06040000	-0.81220000
C	-2.35450000	-0.20440000	-0.43980000	C	-7.37780000	-2.08660000	0.43190000
C	-3.48950000	-0.60590000	-0.23430000	H	-7.82580000	-0.13210000	1.23460000
C	2.44400000	-0.09000000	-0.86520000	H	-6.65260000	-3.93470000	-0.41880000
C	3.48520000	-0.58140000	-0.47220000	H	-8.38450000	-2.47180000	0.60400000
C	4.70400000	-1.16140000	-0.00840000	H	1.35360000	0.77340000	-2.42980000
C	5.83640000	-1.18340000	-0.84030000				

Zero-point correction= 0.342658 (Hartree/Particle)
Thermal correction to Energy= 0.363712
Thermal correction to Enthalpy= 0.364656
Thermal correction to Gibbs Free Energy= 0.287256
Sum of electronic and zero-point Energies= -999.164956
Sum of electronic and thermal Energies= -999.143902
Sum of electronic and thermal Enthalpies= -999.142958
Sum of electronic and thermal Free Energies= -999.220358

Energies and cartesian coordinates of the DFT optimized ground-state structure of 2-H$^+$

C	5.88260000	-1.31480000	0.00080000	C	0.79250000	4.38890000	-0.37020000
C	5.38550000	-2.60390000	0.01590000	C	-1.84030000	4.85970000	0.43800000
C	4.04190000	-3.03130000	0.02960000	H	-1.97870000	2.72480000	0.73490000
C	5.17120000	-0.09520000	-0.00390000	C	0.29020000	5.68400000	-0.35570000
C	2.89880000	-2.25970000	0.02520000	H	1.81850000	4.19760000	-0.68810000
C	3.80890000	0.12040000	0.00020000	C	-1.02410000	5.92220000	0.04770000
C	2.77320000	-0.83960000	0.00960000	H	-2.86710000	5.04750000	0.75610000
H	6.97160000	-1.22300000	-0.00670000	H	0.92760000	6.51520000	-0.66150000
H	6.13070000	-3.40360000	0.01890000	H	-1.41430000	6.94150000	0.05860000
H	3.88970000	-4.11440000	0.04470000	C	-3.39840000	-1.93590000	-0.03310000
H	5.79110000	0.80530000	-0.01170000	C	-4.02550000	-3.19720000	0.03780000
H	3.47160000	1.16080000	-0.00330000	C	-4.18420000	-0.76900000	-0.13440000
C	1.52180000	-2.84780000	0.03920000	C	-5.40980000	-3.28220000	0.01000000
H	1.35960000	-3.47530000	0.93290000	H	-3.41330000	-4.09660000	0.11530000
C	0.61570000	-1.65700000	0.02320000	C	-5.56740000	-0.86860000	-0.16330000
C	1.37710000	-0.48610000	0.01070000	H	-3.69170000	0.20250000	-0.19410000
C	-0.76710000	-1.74320000	0.01360000	C	-6.18060000	-2.12160000	-0.09040000
C	-1.99110000	-1.83890000	-0.00600000	H	-5.89520000	-4.25780000	0.06590000
C	0.89120000	0.83370000	0.00580000	H	-6.17580000	0.03350000	-0.24370000
C	0.47760000	1.98340000	0.00870000	H	-7.26950000	-2.19440000	-0.11290000
C	-0.02490000	3.31280000	0.02010000	H	1.35140000	-3.50420000	-0.83170000
C	-1.34920000	3.56040000	0.42530000				

Zero-point correction= 0.342833 (Hartree/Particle)
Thermal correction to Energy= 0.363850
Thermal correction to Enthalpy= 0.364794
Thermal correction to Gibbs Free Energy= 0.288030
Sum of electronic and zero-point Energies= -999.192117
Sum of electronic and thermal Energies= -999.171099
Sum of electronic and thermal Enthalpies= -999.170155
Sum of electronic and thermal Free Energies= -999.246919

Energies and cartesian coordinates of the DFT optimized ground-state structure of 3-H$^+$

C	2.62650000	0.05510000	0.00000000	C	-8.82970000	1.15320000	0.00040000
C	1.97190000	-1.21880000	-0.00060000	H	-6.89730000	2.11570000	0.00000000
C	0.63580000	-1.52660000	-0.00080000	C	-9.51450000	-0.06390000	0.00070000
C	1.99310000	1.30980000	0.00050000	H	-9.35130000	-2.21830000	0.00090000
C	-0.48370000	-0.65370000	-0.00040000	H	-9.38430000	2.09270000	0.00040000
C	0.63130000	1.61820000	0.00060000	H	-10.60610000	-0.07220000	0.00090000
C	-0.46270000	0.76590000	0.00020000	H	-2.10280000	1.87100000	0.88310000
H	2.65500000	-2.07120000	-0.00090000	C	4.03470000	0.03500000	0.00000000
H	0.39630000	-2.59350000	-0.00120000	C	5.25920000	0.00630000	-0.00010000
H	2.67080000	2.16610000	0.00090000	C	6.67320000	-0.02420000	-0.00020000
H	0.39980000	2.68750000	0.00110000	C	7.40740000	1.17880000	-0.00030000
C	-1.83990000	-1.09870000	-0.00060000	C	7.35400000	-1.25820000	-0.00010000
H	-2.14950000	-2.14250000	-0.00110000	C	8.79450000	1.14140000	-0.00040000
C	-2.69270000	-0.01590000	-0.00020000	H	6.87640000	2.13160000	-0.00030000
C	-1.88120000	1.24670000	0.00040000	C	8.74140000	-1.28160000	-0.00030000
C	-4.08520000	-0.03730000	-0.00020000	H	6.78190000	-2.18690000	0.00000000
C	-5.31130000	-0.03340000	0.00000000	C	9.46190000	-0.08530000	-0.00040000
C	-6.72490000	-0.04260000	0.00020000	H	9.36240000	2.07300000	-0.00060000
C	-7.42350000	-1.26680000	0.00040000	H	9.26790000	-2.23710000	-0.00020000
C	-7.44220000	1.17070000	0.00020000	H	10.55320000	-0.10920000	-0.00050000
C	-8.81110000	-1.27030000	0.00070000	H	-2.10270000	1.87180000	-0.88180000
H	-6.86370000	-2.20290000	0.00040000				

Zero-point correction= 0.342449 (Hartree/Particle)
Thermal correction to Energy= 0.363469
Thermal correction to Enthalpy= 0.364413
Thermal correction to Gibbs Free Energy= 0.288274
Sum of electronic and zero-point Energies= -999.193703
Sum of electronic and thermal Energies= -999.172684
Sum of electronic and thermal Enthalpies= -999.171740
Sum of electronic and thermal Free Energies= -999.247879

Energies and cartesian coordinates of the DFT optimized ground-state structure of 4-H$^+$ (config. A)

C	-0.83920000	-0.82030000	-0.00070000	C	6.40370000	0.06390000	0.00070000
C	-1.75780000	0.26300000	0.00000000	C	7.01650000	-2.66640000	0.00020000
C	-1.40480000	1.63000000	0.00020000	H	4.88450000	-3.00330000	-0.00040000
C	0.53920000	-0.82720000	-0.00100000	C	7.72810000	-0.34980000	0.00090000
C	-0.14590000	2.20100000	0.00000000	H	6.15480000	1.12600000	0.00080000
C	1.48200000	0.23490000	-0.00080000	C	8.03590000	-1.71200000	0.00070000
C	1.14940000	1.61190000	-0.00050000	H	7.26240000	-3.72940000	0.00010000
H	-1.30710000	-1.80710000	-0.00090000	H	8.52840000	0.39170000	0.00130000
H	-2.24740000	2.32630000	0.00060000	H	9.07930000	-2.03250000	0.00090000
H	0.99330000	-1.82070000	-0.00140000	C	-5.69580000	-0.66850000	0.00010000
C	0.03280000	3.69440000	0.00020000	C	-6.09880000	-2.01910000	-0.00030000
H	-0.44710000	4.15730000	0.88150000	C	-6.66880000	0.35110000	0.00070000
C	1.50710000	3.87660000	-0.00020000	C	-7.44950000	-2.33670000	-0.00020000
H	1.99630000	4.85060000	-0.00020000	H	-5.34220000	-2.80480000	-0.00080000
C	2.13120000	2.67790000	-0.00050000	C	-8.01630000	0.01980000	0.00080000
H	3.20510000	2.50310000	-0.00080000	H	-6.35250000	1.39500000	0.00100000
C	2.84180000	-0.12980000	-0.00110000	C	-8.40760000	-1.32080000	0.00040000
C	4.01560000	-0.48110000	-0.00020000	H	-7.76100000	-3.38240000	-0.00050000
C	-3.12880000	-0.05550000	0.00030000	H	-8.76920000	0.80940000	0.00130000
C	-4.32060000	-0.33910000	0.00000000	H	-9.46890000	-1.57600000	0.00050000
C	5.36900000	-0.89280000	0.00010000	H	-0.44780000	4.15780000	-0.88050000
C	5.68800000	-2.26560000	0.00000000				

Zero-point correction= 0.342184 (Hartree/Particle)
Thermal correction to Energy= 0.363204
Thermal correction to Enthalpy= 0.364148
Thermal correction to Gibbs Free Energy= 0.288092
Sum of electronic and zero-point Energies= -999.188447
Sum of electronic and thermal Energies= -999.167427
Sum of electronic and thermal Enthalpies= -999.166483
Sum of electronic and thermal Free Energies= -999.242539

Energies and cartesian coordinates of the DFT optimized ground-state structure of 4-H$^+$ (config. B)

C	0.86449700	-0.80844700	-0.00055800	H	-4.87953500	-3.01708400	-0.00021000
C	1.77444000	0.29648000	-0.00032800	C	-7.70407600	-0.34277300	0.00047400
C	1.41442600	1.65003600	-0.00007000	H	-6.11903600	1.12095100	0.00032100
C	-0.50507300	-0.83516100	-0.00054400	C	-8.02151600	-1.70268000	0.00041900
C	0.13516100	2.21478500	-0.00002000	H	-7.26284600	-3.72553100	0.00013100
C	-1.46088600	0.23039100	-0.00035300	H	-8.49898900	0.40453100	0.00066300
C	-1.14448400	1.59216900	-0.00023200	H	-9.06725100	-2.01574500	0.00057000
H	1.35032100	-1.78661900	-0.00075500	C	5.71071000	-0.64486700	-0.00000800
H	2.24651900	2.35773100	0.00009500	C	6.10662000	-1.99743600	-0.00012300
H	-0.95226200	-1.83171200	-0.00070600	C	6.68856800	0.37003100	0.00033400
C	-0.07318400	3.65515100	0.00016900	C	7.45566800	-2.32188100	0.00010700
C	-1.39458600	3.92791700	0.00002300	H	5.34622800	-2.77942200	-0.00039400
H	-1.84201200	4.92172800	-0.00002200	C	8.03436100	0.03199200	0.00056300
C	-2.18569300	2.66802400	-0.00009300	H	6.37714400	1.41539000	0.00041600
C	-2.81961800	-0.14729800	-0.00029000	C	8.41877800	-1.31056600	0.00044900
C	-3.99309800	-0.49785400	-0.00015700	H	7.76210800	-3.36901700	0.00001700
C	3.14677500	-0.02003600	-0.00035800	H	8.79128400	0.81774700	0.00082700
C	4.33687400	-0.30945300	-0.00022600	H	9.47883200	-1.57118900	0.00063000
C	-5.34918000	-0.90327500	0.00003600	H	0.73960900	4.38075900	0.00033700
C	-5.67752800	-2.27351500	-0.00001800	H	-2.85194700	2.58392600	-0.87802800
C	-6.37658200	0.06094700	0.00028400	H	-2.85151900	2.58376800	0.87818800
C	-7.00914900	-2.66438300	0.00017400				

Zero-point correction= 0.342170 (Hartree/Particle)
Thermal correction to Energy= 0.363164
Thermal correction to Enthalpy= 0.364108
Thermal correction to Gibbs Free Energy= 0.288481
Sum of electronic and zero-point Energies= -999.188250
Sum of electronic and thermal Energies= -999.167256
Sum of electronic and thermal Enthalpies= -999.166311
Sum of electronic and thermal Free Energies= -999.241939

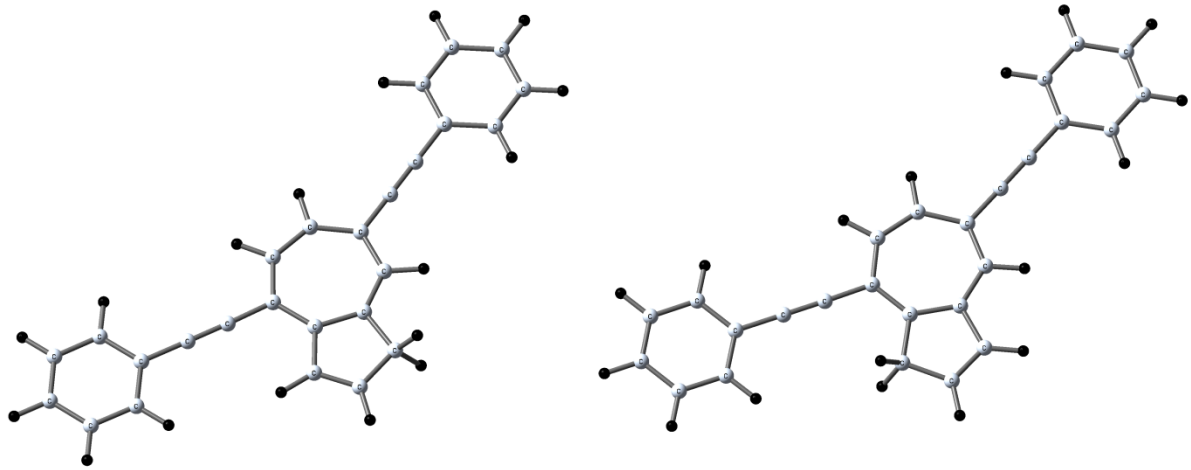


Figure S20. 4-H$^+$ (config. A) vs. **4-H$^+$** (config. B)

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S2 of 1

C	0.00010000	4.51720000	-0.00020000	C	-1.15160000	0.06370000	0.00000000
C	-1.26620000	3.92490000	-0.00010000	H	0.00000000	-1.83140000	0.00010000
C	-1.58820000	2.54990000	-0.00010000	C	0.00000000	-0.74280000	0.00000000
C	1.26640000	3.92480000	-0.00010000	C	1.15160000	0.06370000	0.00000000
C	-0.72230000	1.46330000	0.00000000	C	-2.47240000	-0.36440000	0.00000000
C	1.58830000	2.54980000	-0.00010000	C	-3.65730000	-0.70390000	0.00000000
C	0.72230000	1.46330000	0.00000000	C	2.47240000	-0.36450000	0.00000000
H	0.00010000	5.61180000	-0.00020000	C	3.65730000	-0.70410000	0.00000000
H	-2.11670000	4.61090000	-0.00020000	C	5.00860000	-1.10480000	0.00010000
H	-2.65290000	2.29830000	-0.00010000	C	5.35570000	-2.47500000	0.00010000
H	2.11690000	4.61080000	-0.00020000	C	6.04450000	-0.14290000	0.00000000
H	2.65300000	2.29820000	-0.00010000	C	6.68840000	-2.86030000	0.00010000

H	4.56060000	-3.22180000	0.00010000	C	-5.35570000	-2.47490000	0.00010000
C	7.37300000	-0.54230000	0.00000000	C	-7.37300000	-0.54230000	0.00000000
H	5.78310000	0.91630000	0.00000000	H	-5.78320000	0.91640000	0.00000000
C	7.70340000	-1.89990000	0.00010000	C	-6.68830000	-2.86030000	0.00010000
H	6.94230000	-3.92230000	0.00010000	H	-4.56050000	-3.22170000	0.00010000
H	8.16270000	0.21170000	0.00000000	C	-7.70340000	-1.89990000	0.00010000
H	8.75030000	-2.20910000	0.00010000	H	-8.16280000	0.21170000	0.00000000
C	-5.00860000	-1.10470000	0.00000000	H	-6.94220000	-3.92220000	0.00010000
C	-6.04450000	-0.14290000	0.00000000	H	-8.75030000	-2.20920000	0.00010000

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S2 of 2

C	6.02300000	-0.97520000	-0.00770000	C	-1.74650000	3.31890000	-0.02520000
C	5.58540000	-2.31130000	-0.00100000	C	0.40680000	4.44070000	-0.01960000
C	4.28040000	-2.79700000	0.00340000	C	-2.38260000	4.55250000	-0.03120000
C	5.27430000	0.21300000	-0.01190000	H	-2.32580000	2.39430000	-0.02550000
C	3.07320000	-2.05970000	0.00210000	C	-0.24090000	5.66810000	-0.02560000
C	3.88930000	0.38000000	-0.01050000	H	1.49650000	4.38860000	-0.01500000
C	2.89560000	-0.61910000	-0.00420000	C	-1.63640000	5.73310000	-0.03140000
H	7.10860000	-0.84140000	-0.01000000	H	-3.47380000	4.59680000	-0.03580000
H	6.37460000	-3.06750000	0.00120000	H	0.34800000	6.58770000	-0.02570000
H	4.16440000	-3.88460000	0.00840000	H	-2.14080000	6.70120000	-0.03610000
H	5.86060000	1.13570000	-0.01710000	C	-3.18610000	-2.14680000	0.02070000
H	3.51780000	1.40820000	-0.01470000	C	-3.76400000	-3.43910000	0.02600000
C	1.79220000	-2.65260000	0.00710000	C	-4.03970000	-1.01700000	0.02230000
H	1.58280000	-3.72060000	0.01250000	C	-5.14190000	-3.58750000	0.03270000
C	0.80880000	-1.63030000	0.00430000	H	-3.10830000	-4.31090000	0.02470000
C	1.48880000	-0.35770000	-0.00300000	C	-5.41580000	-1.18100000	0.02910000
C	-0.56800000	-1.82200000	0.00910000	H	-3.59400000	-0.02140000	0.01860000
C	-1.79100000	-1.98170000	0.01420000	C	-5.97370000	-2.46310000	0.03430000
C	0.86730000	0.88760000	-0.00820000	H	-5.57800000	-4.58830000	0.03680000
C	0.31290000	1.98570000	-0.01320000	H	-6.06530000	-0.30350000	0.03040000
C	-0.33620000	3.23950000	-0.01930000	H	-7.05840000	-2.58660000	0.03960000

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S2 of 3

C	-2.58580000	0.00000000	0.00000000	H	6.87340000	2.15910000	0.00010000
C	-1.95540000	1.28720000	0.00000000	C	8.81240000	-1.21090000	0.00010000
C	-0.61900000	1.60430000	0.00000000	H	6.87350000	-2.15920000	0.00000000
C	-1.95550000	-1.28720000	0.00000000	C	9.51220000	0.00000000	0.00010000
C	0.50790000	0.73250000	0.00000000	H	9.35850000	2.15630000	0.00010000
C	-0.61910000	-1.60430000	-0.00010000	H	9.35860000	-2.15620000	0.00010000
C	0.50780000	-0.73260000	-0.00010000	H	10.60400000	0.00000000	0.00010000
H	-2.65350000	2.12720000	0.00000000	H	2.18300000	-2.18810000	-0.00010000
H	-0.37940000	2.67180000	0.00000000	C	-3.98770000	0.00000000	0.00000000
H	-2.65360000	-2.12710000	0.00000000	C	-5.21990000	0.00010000	0.00000000
H	-0.37950000	-2.67190000	-0.00010000	C	-6.62780000	0.00000000	0.00000000
C	1.83430000	1.15720000	-0.00010000	C	-7.35020000	-1.21650000	0.00000000
H	2.18310000	2.18800000	-0.00010000	C	-7.35030000	1.21650000	0.00000000
C	2.67560000	-0.00010000	0.00000000	C	-8.73710000	-1.20890000	0.00010000
C	1.83420000	-1.15730000	-0.00010000	H	-6.79910000	-2.15810000	0.00000000
C	4.06620000	-0.00010000	0.00000000	C	-8.73720000	1.20880000	0.00010000
C	5.30090000	-0.00010000	0.00000000	H	-6.79920000	2.15810000	0.00000000
C	6.70470000	-0.00010000	0.00000000	C	-9.43890000	0.00000000	0.00010000
C	7.42660000	1.21890000	0.00010000	H	-9.28150000	-2.15550000	0.00010000
C	7.42670000	-1.21900000	0.00000000	H	-9.28160000	2.15550000	0.00010000
C	8.81230000	1.21090000	0.00010000	H	-10.53060000	-0.00010000	0.00010000

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S2 of 4

C	-0.85200000	-0.77940000	0.00000000	C	0.06850000	3.68070000	0.00010000
C	-1.76490000	0.31740000	0.00000000	H	-0.71650000	4.43490000	0.00020000
C	-1.42070000	1.69400000	0.00000000	C	1.45450000	3.91570000	0.00000000
C	0.53100000	-0.81330000	0.00000000	H	1.93170000	4.89530000	-0.00010000
C	-0.15440000	2.27630000	0.00000000	C	2.13070000	2.68220000	0.00000000
C	1.48090000	0.24970000	0.00010000	H	3.20800000	2.53460000	0.00000000
C	1.17570000	1.64320000	0.00000000	C	2.83570000	-0.12430000	0.00000000
H	-1.33700000	-1.75860000	0.00000000	C	4.01520000	-0.47300000	0.00000000
H	-2.26420000	2.38810000	0.00000000	C	-3.13200000	-0.01460000	0.00000000
H	0.97470000	-1.81080000	0.00000000	C	-4.32710000	-0.30860000	0.00000000

C	5.36800000	-0.87310000	0.00000000	C	-5.69510000	-0.64930000	0.00000000
C	5.71320000	-2.24380000	0.00000000	C	-6.10070000	-2.00420000	0.00000000
C	6.40380000	0.08870000	0.00000000	C	-6.69070000	0.35540000	0.00000000
C	7.04550000	-2.63040000	0.00000000	C	-7.44810000	-2.33340000	0.00000000
H	4.91730000	-2.99000000	0.00010000	H	-5.33800000	-2.78440000	0.00000000
C	7.73190000	-0.31150000	0.00000000	C	-8.03450000	0.01170000	0.00000000
H	6.14330000	1.14810000	0.00000000	H	-6.38470000	1.40270000	0.00000000
C	8.06060000	-1.66990000	0.00000000	C	-8.42250000	-1.33120000	0.00000000
H	7.29920000	-3.69240000	0.00000000	H	-7.74630000	-3.38390000	0.00000000
H	8.52250000	0.44140000	0.00000000	H	-8.79200000	0.79830000	0.00000000
H	9.10740000	-1.97980000	0.00000000	H	-9.48160000	-1.59600000	0.00000000

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S1 of 1-H$^+$

C	0.14780000	4.72860000	0.95730000	C	4.55990000	-1.18220000	1.35230000
C	-0.96180000	3.96030000	1.16390000	C	6.12490000	-2.79050000	-0.33310000
C	-1.26410000	2.65330000	0.62200000	H	4.89820000	-2.05850000	-1.94940000
C	1.31380000	4.46920000	0.16880000	C	5.58660000	-1.94130000	1.88410000
C	-0.48670000	1.90710000	-0.20720000	H	3.94130000	-0.54990000	1.98970000
C	1.58900000	3.32940000	-0.57730000	C	6.37070000	-2.74520000	1.04590000
C	0.81600000	2.19050000	-0.75600000	H	6.74210000	-3.41910000	-0.97630000
H	0.15240000	5.69350000	1.47250000	H	5.78740000	-1.91380000	2.95590000
H	-1.72820000	4.38040000	1.81780000	H	7.18080000	-3.34100000	1.47060000
H	-2.22490000	2.22530000	0.91400000	C	-4.41910000	-1.24710000	-0.04270000
H	2.07080000	5.25320000	0.15970000	C	-5.47520000	-0.56630000	0.61150000
H	2.55120000	3.33260000	-1.10040000	C	-4.60570000	-2.58540000	-0.46930000
C	-0.88290000	0.57310000	-0.73610000	C	-6.67960000	-1.21110000	0.82880000
H	0.05240000	-0.86950000	-2.08360000	H	-5.32580000	0.46400000	0.93550000
C	0.08470000	0.08230000	-1.55630000	C	-5.81600000	-3.21690000	-0.24570000
C	1.26170000	1.02210000	-1.61870000	H	-3.78800000	-3.10250000	-0.97220000
C	-2.11060000	-0.05710000	-0.48200000	C	-6.85330000	-2.53390000	0.40210000
C	-3.19190000	-0.60210000	-0.27250000	H	-7.49480000	-0.68900000	1.33150000
C	2.37840000	0.25760000	-1.06700000	H	-5.96280000	-4.24660000	-0.57410000
C	3.26060000	-0.44580000	-0.58950000	H	-7.80630000	-3.03710000	0.57570000
C	4.30240000	-1.22010000	-0.04020000	H	1.49260000	1.32310000	-2.65700000
C	5.10110000	-2.03680000	-0.87820000				

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S1 of 2-H$^+$

C	5.86850000	-1.29670000	-0.02580000	C	0.93770000	4.43350000	-0.01580000
C	5.33010000	-2.64330000	-0.01940000	C	-1.82230000	4.95010000	-0.00400000
C	4.01430000	-3.01850000	-0.01230000	H	-2.08890000	2.80880000	0.00200000
C	5.21450000	-0.10920000	-0.02590000	C	0.48210000	5.73870000	-0.01650000
C	2.85140000	-2.21440000	-0.00920000	H	2.00530000	4.21310000	-0.02040000
C	3.78800000	0.14410000	-0.01970000	C	-0.89420000	5.99980000	-0.01060000
C	2.79320000	-0.79070000	-0.01260000	H	-2.89090000	5.16840000	0.00060000
H	6.96040000	-1.24160000	-0.03130000	H	1.19370000	6.56520000	-0.02170000
H	6.06860000	-3.44620000	-0.02060000	H	-1.24760000	7.03260000	-0.01120000
H	3.83100000	-4.09840000	-0.00850000	C	-3.43470000	-1.96820000	0.02050000
H	5.84020000	0.78660000	-0.03140000	C	-3.99130000	-3.26730000	0.02850000
H	3.48710000	1.19220000	-0.02090000	C	-4.28930000	-0.84320000	0.02050000
C	1.46630000	-2.79030000	-0.00130000	C	-5.36770000	-3.42860000	0.03650000
H	1.26030000	-3.42050000	0.88320000	H	-3.32740000	-4.13250000	0.02850000
C	0.57070000	-1.58620000	-0.00020000	C	-5.66340000	-1.01890000	0.02840000
C	1.34310000	-0.42870000	-0.00670000	H	-3.85350000	0.15640000	0.01420000
C	-0.81480000	-1.66440000	0.00660000	C	-6.20410000	-2.30850000	0.03650000
C	-2.03680000	-1.80190000	0.01290000	H	-5.79730000	-4.43140000	0.04280000
C	0.86120000	0.87070000	-0.00760000	H	-6.32420000	-0.15070000	0.02840000
C	0.46260000	2.03860000	-0.00840000	H	-7.28760000	-2.44140000	0.04270000
C	0.00820000	3.36160000	-0.00910000	H	1.25200000	-3.42510000	-0.88040000
C	-1.38290000	3.63950000	-0.00320000				

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S1 of 3-H+

C	-2.58580000	0.00000000	0.00000000	C	0.50780000	-0.73260000	-0.00010000
C	-1.95540000	1.28720000	0.00000000	H	-2.65350000	2.12720000	0.00000000
C	-0.61900000	1.60430000	0.00000000	H	-0.37940000	2.67180000	0.00000000
C	-1.95550000	-1.28720000	0.00000000	H	-2.65360000	-2.12710000	0.00000000
C	0.50790000	0.73250000	0.00000000	H	-0.37950000	-2.67190000	-0.00010000
C	-0.61910000	-1.60430000	-0.00010000	C	1.83430000	1.15720000	-0.00010000

H	2.18310000	2.18800000	-0.00010000	H	10.60400000	0.00000000	0.00010000
C	2.67560000	-0.00010000	0.00000000	H	2.18300000	-2.18810000	-0.00010000
C	1.83420000	-1.15730000	-0.00010000	C	-3.98770000	0.00000000	0.00000000
C	4.06620000	-0.00010000	0.00000000	C	-5.21990000	0.00010000	0.00000000
C	5.30090000	-0.00010000	0.00000000	C	-6.62780000	0.00000000	0.00000000
C	6.70470000	-0.00010000	0.00000000	C	-7.35020000	-1.21650000	0.00000000
C	7.42660000	1.21890000	0.00010000	C	-7.35030000	1.21650000	0.00000000
C	7.42670000	-1.21900000	0.00000000	C	-8.73710000	-1.20890000	0.00010000
C	8.81230000	1.21090000	0.00010000	H	-6.79910000	-2.15810000	0.00000000
H	6.87340000	2.15910000	0.00010000	C	-8.73720000	1.20880000	0.00010000
C	8.81240000	-1.21090000	0.00010000	H	-6.79920000	2.15810000	0.00000000
H	6.87350000	-2.15920000	0.00000000	C	-9.43890000	0.00000000	0.00010000
C	9.51220000	0.00000000	0.00010000	H	-9.28150000	-2.15550000	0.00010000
H	9.35850000	2.15630000	0.00010000	H	-9.28160000	2.15550000	0.00010000
H	9.35860000	-2.15620000	0.00010000	H	-10.53060000	-0.00010000	0.00010000

Energies and cartesian coordinates of the TD-DFT optimized singlet excited-state S1 of 4-H$^+$ (A)

C	-0.84070400	-0.83993300	-0.00034000	C	6.38043000	0.06658500	0.00029900
C	-1.75924400	0.28219400	-0.00012400	C	7.01377100	-2.66627500	-0.00003200
C	-1.40385500	1.64644300	0.00003000	H	4.88654100	-3.02628300	-0.00033400
C	0.51902400	-0.85910900	-0.00036300	C	7.70491400	-0.33566500	0.00039500
C	-0.14553100	2.22343700	0.00004200	H	6.11785200	1.12526800	0.00042600
C	1.47641700	0.23028500	-0.00016800	C	8.02677700	-1.69890500	0.00023200
C	1.14873400	1.60818200	-0.00003600	H	7.27233400	-3.72631000	-0.00015800
H	-1.32713800	-1.81740300	-0.00050200	H	8.49935600	0.41220900	0.00059900
H	-2.24564400	2.34403600	0.00015000	H	9.07334600	-2.00925500	0.00031000
H	0.97686400	-1.85026200	-0.00054300	C	-5.68137400	-0.66097000	0.00002800
C	0.04519200	3.71368500	0.00019100	C	-6.08220500	-2.02225400	-0.00013700
H	-0.41778000	4.19822700	0.87988100	C	-6.67135100	0.35578300	0.00026600
C	1.51805400	3.87160900	0.00017100	C	-7.42801800	-2.34612300	-0.00006200
H	2.02444400	4.83697700	0.00024200	H	-5.31921300	-2.80160400	-0.00032100
C	2.13444300	2.65974900	0.00005200	C	-8.01270100	0.01363700	0.00033900
H	3.20878300	2.48467300	0.00001800	H	-6.36053500	1.40124300	0.00039100
C	2.82384900	-0.13840100	-0.00012300	C	-8.39608900	-1.33365800	0.00017800
C	4.00245400	-0.50435800	-0.00005300	H	-7.73435600	-3.39335900	-0.00018800
C	-3.12292300	-0.02965600	-0.00007700	H	-8.77263600	0.79658700	0.00052400
C	-4.32077000	-0.32635000	-0.00003500	H	-9.45569100	-1.59611500	0.00023800
C	5.34554500	-0.90411400	0.00003500	H	-0.41785200	4.19843600	-0.87934500
C	5.68380000	-2.28206400	-0.00013100				

Excitation energies and oscillator strengths from the ground-state structures (S_0) of 1 – 4 and 1-H^+ - 4-H^+

pbe1pbe/cc-pVDZ TD=(Nstates=20)

scrf=(cpcm,solvent=ch2cl2) …

1

Excited State 1: Singlet-A 2.0192 eV
614.01 nm f=0.0071
86 -> 87 0.68539
Excited State 2: Singlet-A 2.9564 eV
419.38 nm f=0.2919
85 -> 87 0.23604
86 -> 88 0.62013
Excited State 3: Singlet-A 3.5117 eV
353.06 nm f=1.3448
86 -> 89 0.67909
Excited State 4: Singlet-A 3.5436 eV
349.88 nm f=0.2943
85 -> 87 0.63488
86 -> 88 -0.18093
Excited State 5: Singlet-A 3.7955 eV
326.66 nm f=0.6449
81 -> 87 0.12177
85 -> 88 0.67647
***

2

Excited State 1: Singlet-A 2.0656 eV
600.23 nm f=0.0246
85 -> 87 -0.10929
86 -> 87 0.67099
Excited State 2: Singlet-A 2.9602 eV
418.84 nm f=0.3315
85 -> 87 0.53832
86 -> 87 0.10726
86 -> 88 0.39995
Excited State 3: Singlet-A 3.4542 eV
358.93 nm f=1.8054
85 -> 87 -0.35132
86 -> 88 0.50622
86 -> 89 0.10320
Excited State 4: Singlet-A 3.7376 eV
331.72 nm f=0.1081
84 -> 87 0.19917
85 -> 88 0.65286
Excited State 5: Singlet-A 3.9224 eV
316.10 nm f=0.2008
86 -> 89 0.66370
***

3

Excited State 1: Singlet-A 2.1578 eV
574.60 nm f=0.0119
85 -> 87 0.67574
86 -> 88 0.12908
Excited State 2: Singlet-A 2.6731 eV
463.82 nm f=1.8774
85 -> 88 -0.13679
86 -> 87 0.64563
Excited State 3: Singlet-A 3.5633 eV
347.95 nm f=0.1371
84 -> 87 0.67035
86 -> 89 0.10029
Excited State 4: Singlet-A 3.9986 eV
310.07 nm f=0.0566
77 -> 87 0.15345
86 -> 88 0.65718
Excited State 5: Singlet-A 4.0769 eV
304.12 nm f=0.0000
79 -> 87 0.22605
80 -> 87 0.65058
80 -> 89 0.10755
***

4

Excited State 1: Singlet-A 2.0539 eV
603.66 nm f=0.1593
85 -> 87 0.12730
86 -> 87 0.64090
86 -> 88 0.16854
Excited State 2: Singlet-A 2.9902 eV
414.63 nm f=0.9717
85 -> 87 0.46193
86 -> 87 -0.17817
86 -> 88 0.45765
Excited State 3: Singlet-A 3.4421 eV
360.20 nm f=0.4008
83 -> 87 0.32737
85 -> 87 0.42170
86 -> 88 -0.38761
Excited State 4: Singlet-A 3.7267 eV
332.69 nm f=0.0643
84 -> 87 0.67370
Excited State 5: Singlet-A 3.8796 eV
319.58 nm f=0.2424
85 -> 88 0.66994
***

1-H^+

Excited State 1: Singlet-A 2.5167 eV
492.65 nm f=0.0189
85 -> 87 -0.15183
86 -> 87 0.63470
86 -> 88 -0.22022
Excited State 2: Singlet-A 2.6101 eV
475.02 nm f=0.0265
85 -> 87 -0.11805
86 -> 87 0.19218
86 -> 88 0.65704
Excited State 3: Singlet-A 2.7816 eV
445.73 nm f=0.0234
85 -> 87 0.67121
86 -> 87 0.16186
Excited State 4: Singlet-A 2.9152 eV
425.30 nm f=0.0294
85 -> 88 0.70008
Excited State 5: Singlet-A 3.4636 eV
357.96 nm f=0.0000
84 -> 87 0.70701
***

2-H^+

Excited State 1: Singlet-A 2.3101 eV
536.70 nm f=0.6119
86 -> 87 0.63935
86 -> 88 0.11406
Excited State 2: Singlet-A 2.5081 eV
494.34 nm f=0.0392
86 -> 87 -0.10148
86 -> 88 0.68231
Excited State 3: Singlet-A 3.1408 eV
394.75 nm f=0.4815
85 -> 87 0.68036
Excited State 4: Singlet-A 3.4721 eV
357.09 nm f=0.0129
84 -> 87 0.69753
86 -> 89 0.10125
Excited State 5: Singlet-A 3.4924 eV
355.01 nm f=0.5403
83 -> 87 0.10402
84 -> 87 -0.10900
86 -> 89 0.64972
***

3-H^+

Excited State 1: Singlet-A 2.3919 eV
518.36 nm f=2.0692

```
      86 -> 87         0.65022
Excited State   2:   Singlet-A      2.7156 eV
456.56 nm  f=0.0225
      85 -> 87         0.10059
      86 -> 88         0.66347
Excited State   3:   Singlet-A      3.1118 eV
398.43 nm  f=0.0043
      85 -> 87         0.66049
Excited State   4:   Singlet-A      3.2940 eV
376.39 nm  f=0.3558
      85 -> 88         0.68178
Excited State   5:   Singlet-A      3.4716 eV
357.13 nm  f=0.0065
      83 -> 87         0.68708
      83 -> 88         0.11266
                     ***
```

4-H$^+$

```
Excited State   1:   Singlet-A      2.4524 eV
505.57 nm  f=1.4672
      86 -> 87         0.65236
Excited State   2:   Singlet-A      2.7643 eV
448.53 nm  f=0.1702
      86 -> 88         0.66107
Excited State   3:   Singlet-A      3.2117 eV
386.04 nm  f=0.0782
      85 -> 87         0.66768
Excited State   4:   Singlet-A      3.3397 eV
371.24 nm  f=0.3089
      85 -> 88         0.69386
Excited State   5:   Singlet-A      3.4406 eV
360.36 nm  f=0.0066
      84 -> 87         0.68871
      84 -> 88        -0.10196
```

Excitation energies and oscillator strengths from the excited-state structures (S_1) of 1-H$^+$ - 4-H$^+$

td=(nstates=4,root=1)/cc-pvdz

scrf=(cpcm,solvent=dichloromethane,ex

ternaliteration,read) nosymm pbe1pbe …

1-H$^+$

```
Excited State   1:      0.9411 eV 1317.48 nm
f=0.0042
      86 -> 87         0.70301
This state for optimization and/or second-
order correction.
Total Energy, E(TD-HF/TD-KS) =  -
999.504995398
Copying the excited state density for this
state as the 1-particle RhoCI density.
Excited State   2:      1.6430 eV  754.64 nm
f=0.0377
      86 -> 88         0.70346
                     ***
```

2-H$^+$

```
Excited State   1:      1.6221 eV  764.36 nm
f=0.1305
      84 -> 87         0.10672
      86 -> 87        -0.68318
      86 -> 88         0.15597
This state for optimization and/or second-
order correction.
Total Energy, E(TD-HF/TD-KS) =  -
999.518893816
Copying the excited state density for this
state as the 1-particle RhoCI density.
Excited State   2:      1.8303 eV  677.42 nm
f=0.0193
      86 -> 87         0.14859
      86 -> 88         0.68502
                     ***
```

3-H$^+$

```
Excited State   1:      2.2103 eV  560.93 nm
f=1.0057
      86 -> 87        -0.65979
      86 -> 88         0.24772
This state for optimization and/or second-
order correction.
Total Energy, E(TD-HF/TD-KS) =  -
999.499405617
Copying the excited state density for this
state as the 1-particle RhoCI density.
Excited State   2:      2.5274 eV  490.56 nm
f=0.9454
      85 -> 87         0.15136
      86 -> 87         0.25330
      86 -> 88         0.63802
                     ***
```

4-H$^+$

```
Excited State   1:      2.3980 eV  517.04 nm
f=1.2574
      86 -> 87        -0.70448
This state for optimization and/or second-
order correction.
Total Energy, E(TD-HF/TD-KS) =  -
999.487309197
Copying the excited state density for this
state as the 1-particle RhoCI density.
Excited State   2:      2.7520 eV  450.53 nm
f=0.0970
      85 -> 87         0.15141
      86 -> 88        -0.68200
                     ***
```

Excitation energies and oscillator strengths from the excited-state structures (S_2) of 1 - 4

td=(nstates=4,root=1)/cc-pvdz

scrf=(cpcm,solvent=dichloromethane,ex

ternaliteration,read) nosymm pbe1pbe …

1

```
Excited State   1:      1.7598 eV  704.53 nm
f=0.0025
      86 -> 87        -0.70258

Excited State   2:      2.6962 eV  459.84 nm
f=0.2219
      85 -> 87         0.22609
      86 -> 88         0.66580
 This state for optimization and/or second-
order correction.
 Total Energy, E(TD-HF/TD-KS) =  -
999.060104241
 Copying the excited state density for this
state as the 1-particle RhoCI density.
                     ***
```

2

```
Excited State   1:      1.8369 eV  674.96 nm
f=0.0115
      85 -> 87        -0.21890
      86 -> 87         0.66351
Excited State   2:      2.7096 eV  457.57 nm
f=0.4239
      85 -> 87         0.59924
```

```
      86 -> 87         0.21090
      86 -> 88         0.28417
This state for optimization and/or second-
order correction.
Total Energy, E(TD-HF/TD-KS) =  -
999.060104241
Copying the excited state density for this
state as the 1-particle RhoCI density.
                     ***

3
Excited State   1:      2.0398 eV  607.83 nm
f=0.0054
      85 -> 87        -0.69774
Excited State   2:      2.4478 eV  506.52 nm
f=1.6803
      85 -> 88        -0.12617
      86 -> 87         0.69831
This state for optimization and/or second-
order correction.
Total Energy, E(TD-HF/TD-KS) =  -
999.062629047
Copying the excited state density for this
state as the 1-particle RhoCI density.
                     ***
4
Excited State   1:      1.8633 eV  665.38 nm
f=0.2052
      85 -> 87         0.10613
      86 -> 87         0.67741
      86 -> 88         0.14172
Excited State   2:      2.7860 eV  445.02 nm
f=1.2444
      85 -> 87         0.48897
      86 -> 87        -0.17958
      86 -> 88         0.47085
 This state for optimization and/or second-
order correction.
 Total Energy, E(TD-HF/TD-KS) =  -
999.048103451
 Copying the excited state density for this
state as the 1-particle RhoCI density.
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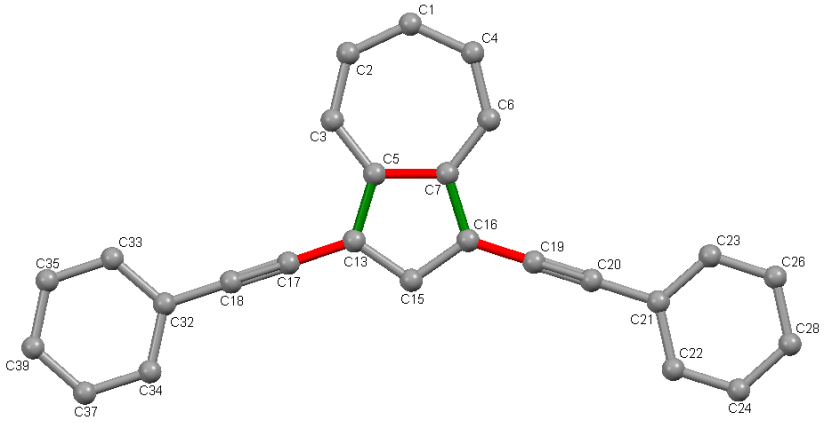

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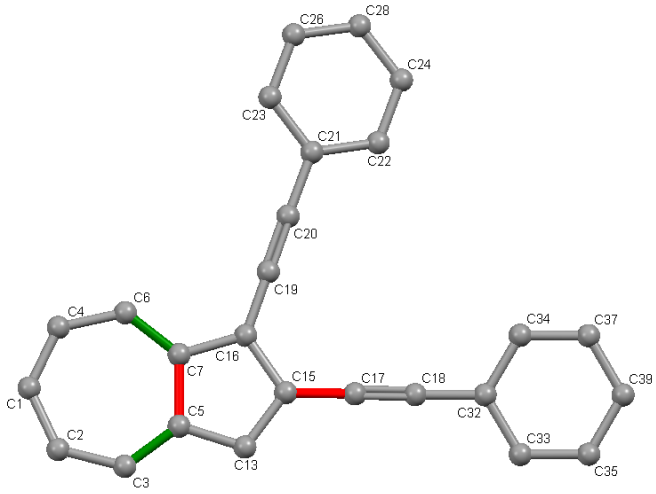
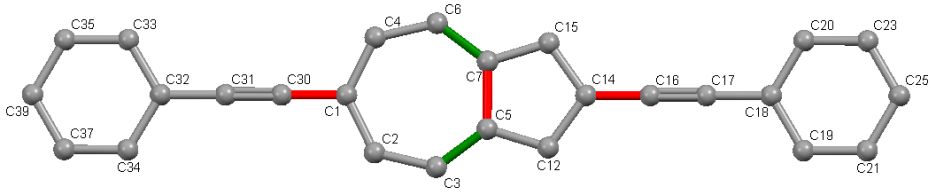
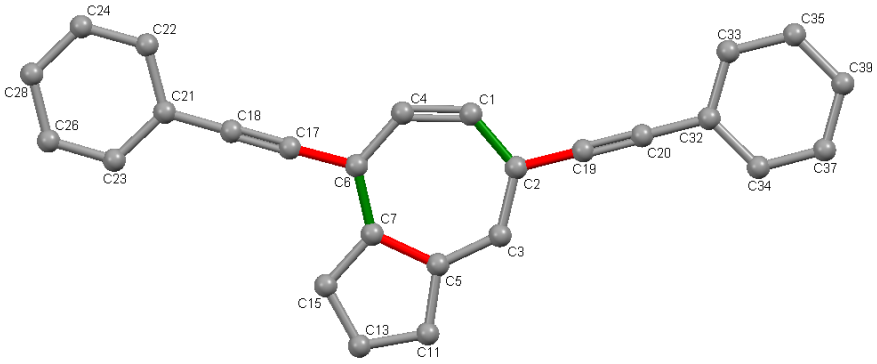


-0.030 / +0.020 Å

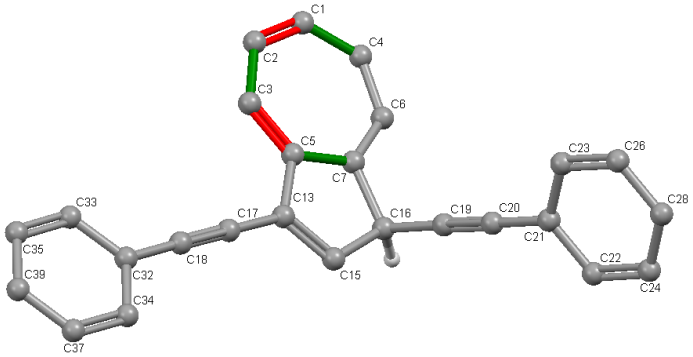


-0.022 / 0.028 Å

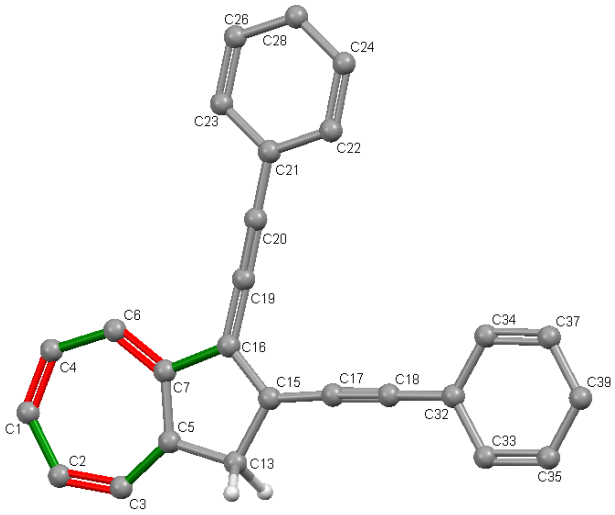


-0.019 / +0.020 Å

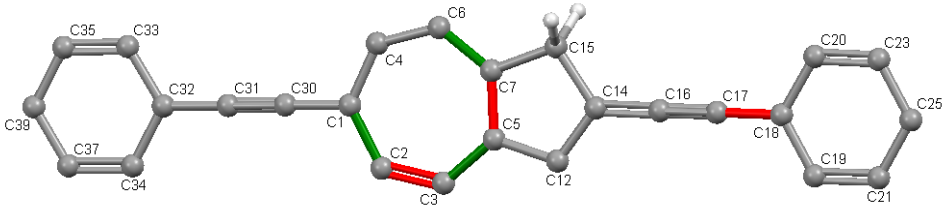
Figure S21. Most significant bond shortenings (red) and elongations (green) observed between the ground-state (S_0) and excited state (S_2) structures of **1** – **4** (reported on the TD-DFT optimized S_2 geometries).



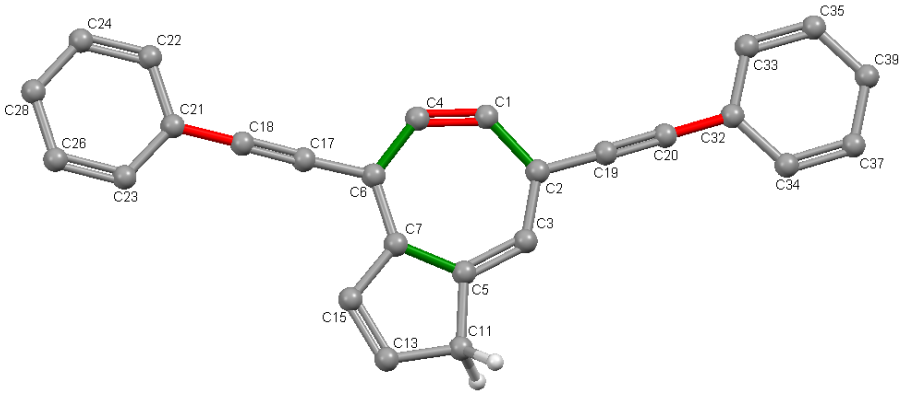
-0.043 / +0.060 Å



-0.056 / +0.070 Å



-0.015 / +0.022 Å



-0.019 / +0.030 Å

Figure S22. Most significant bond shortenings (red) and elongations (green) observed between the ground-state (S_0) and excited state (S_1) structures of **1-H$^+$** – **4-H$^+$** (reported on the TD-DFT optimized S_1 geometries).

Frontier orbitals of the ground-state of 1 - 4

1

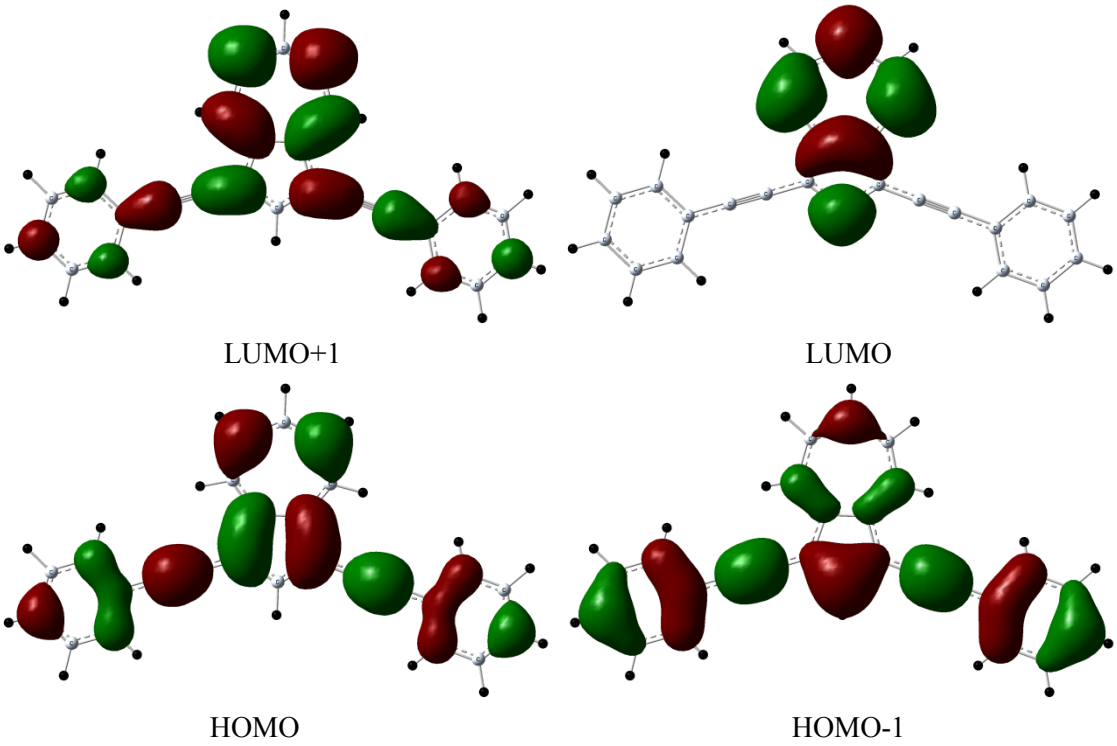


Figure S23. Frontier orbitals of the ground-state of **1**.

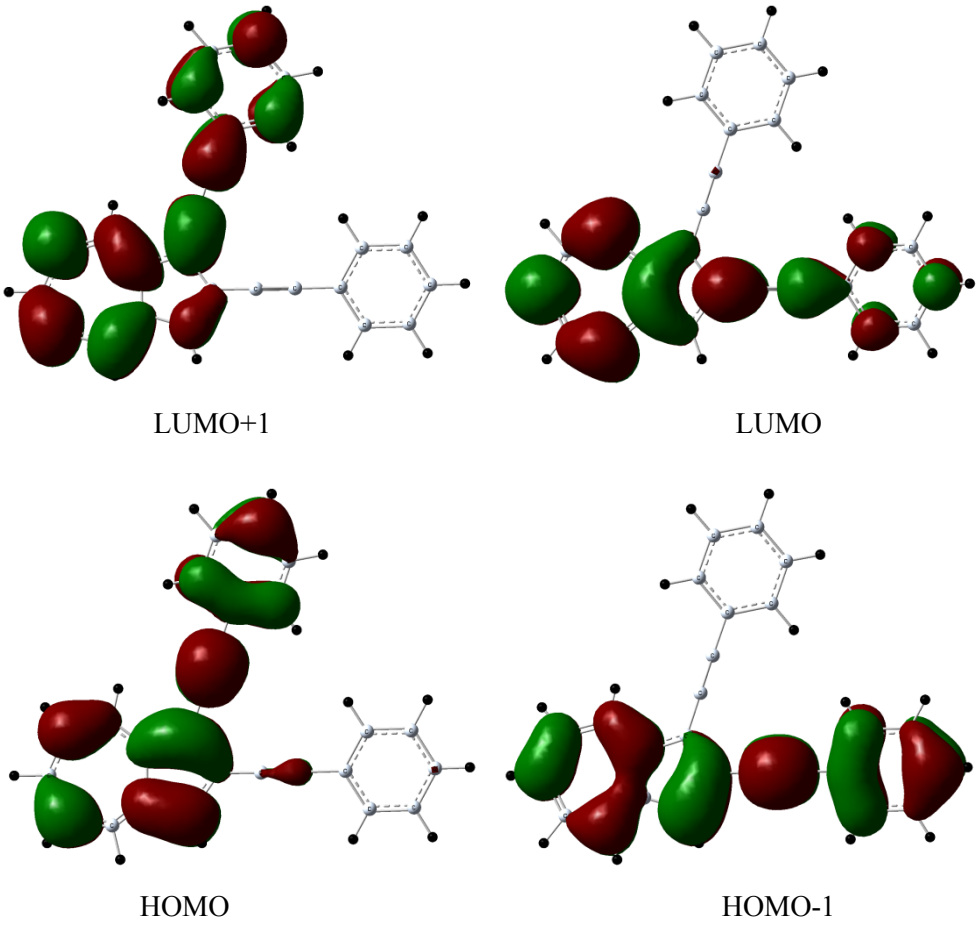


Figure S24. Frontier orbitals of the ground-state of **2**.

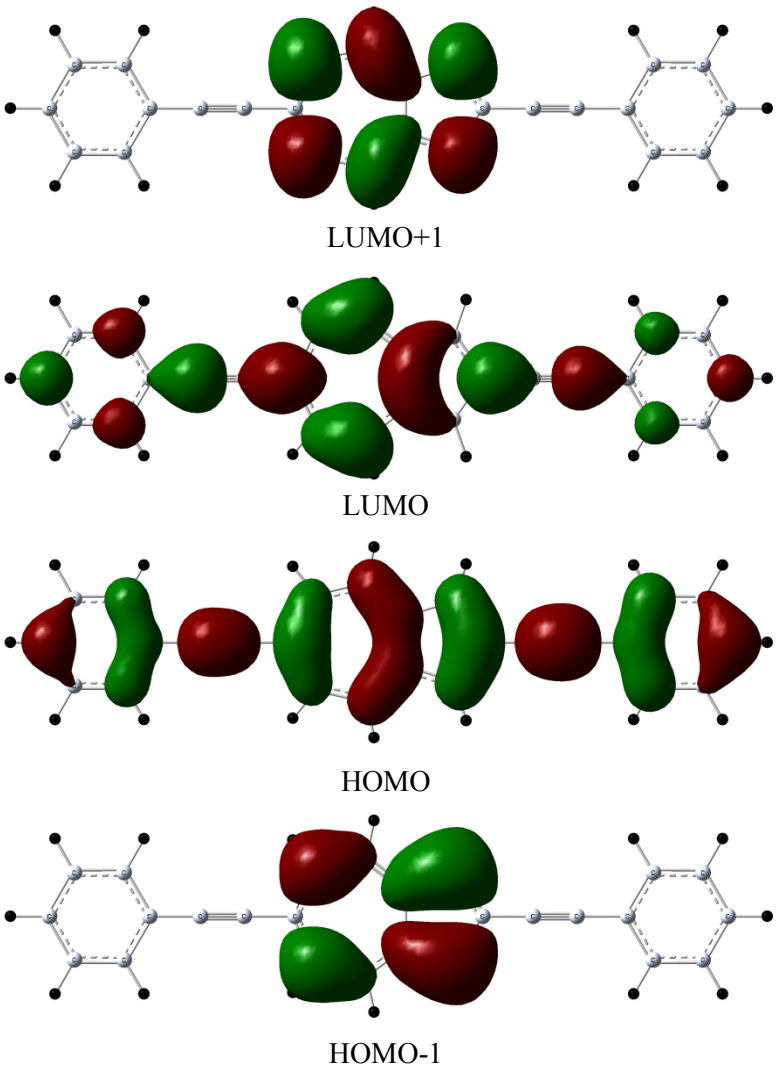


Figure S25. Frontier orbitals of the ground-state of **3**.

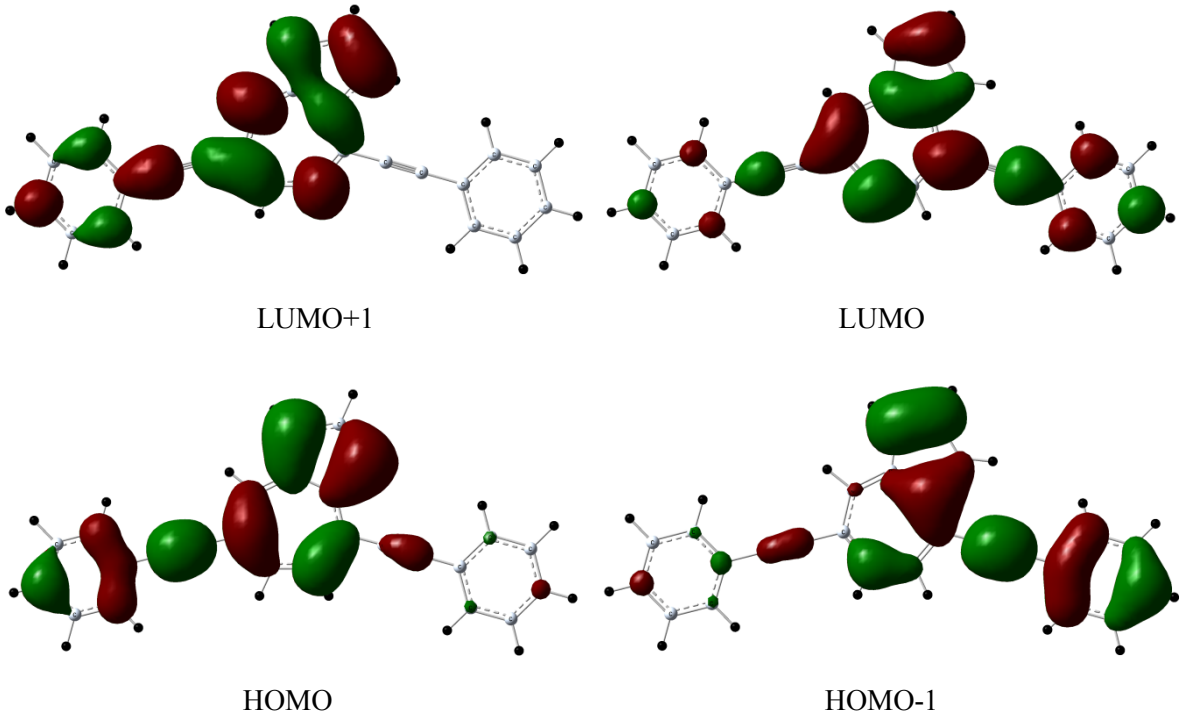


Figure S26. Frontier orbitals of the ground-state of **4**.

Frontier orbitals of the ground-state of 1-H$^+$ - 4-H$^+$

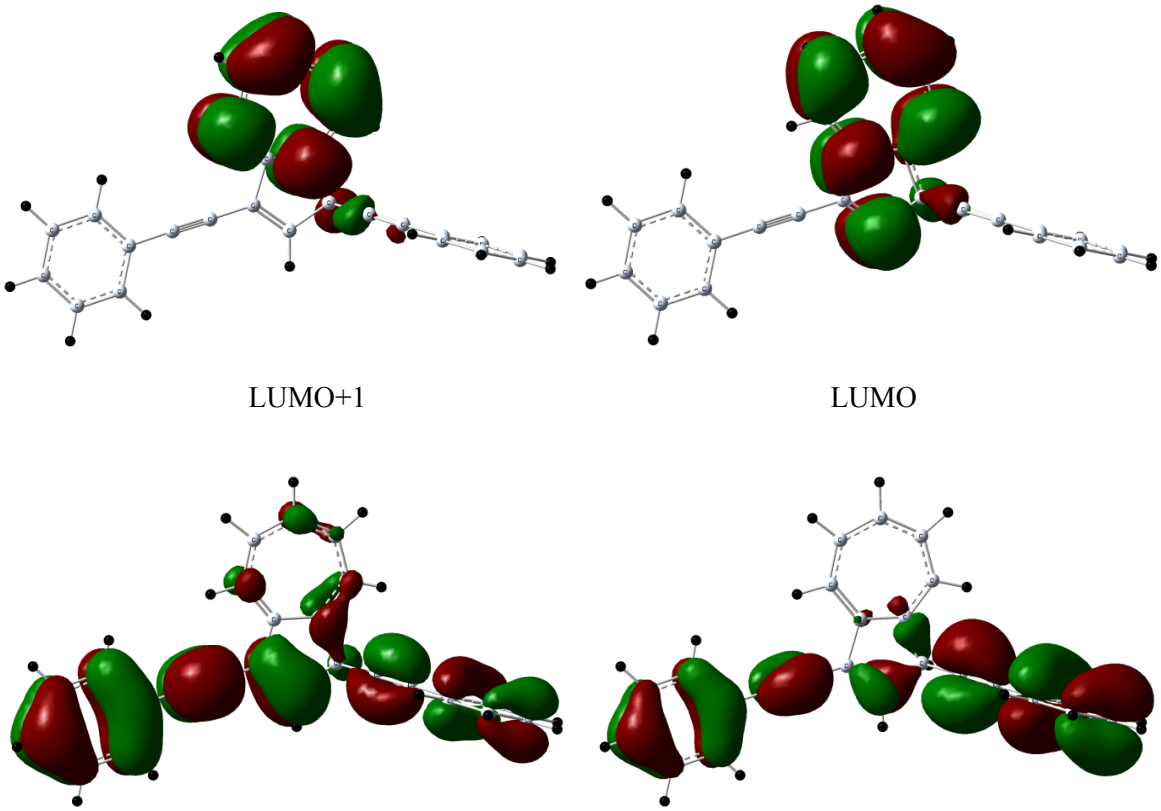


Figure S27. Frontier orbitals of the ground-state of **1-H$^+$**.

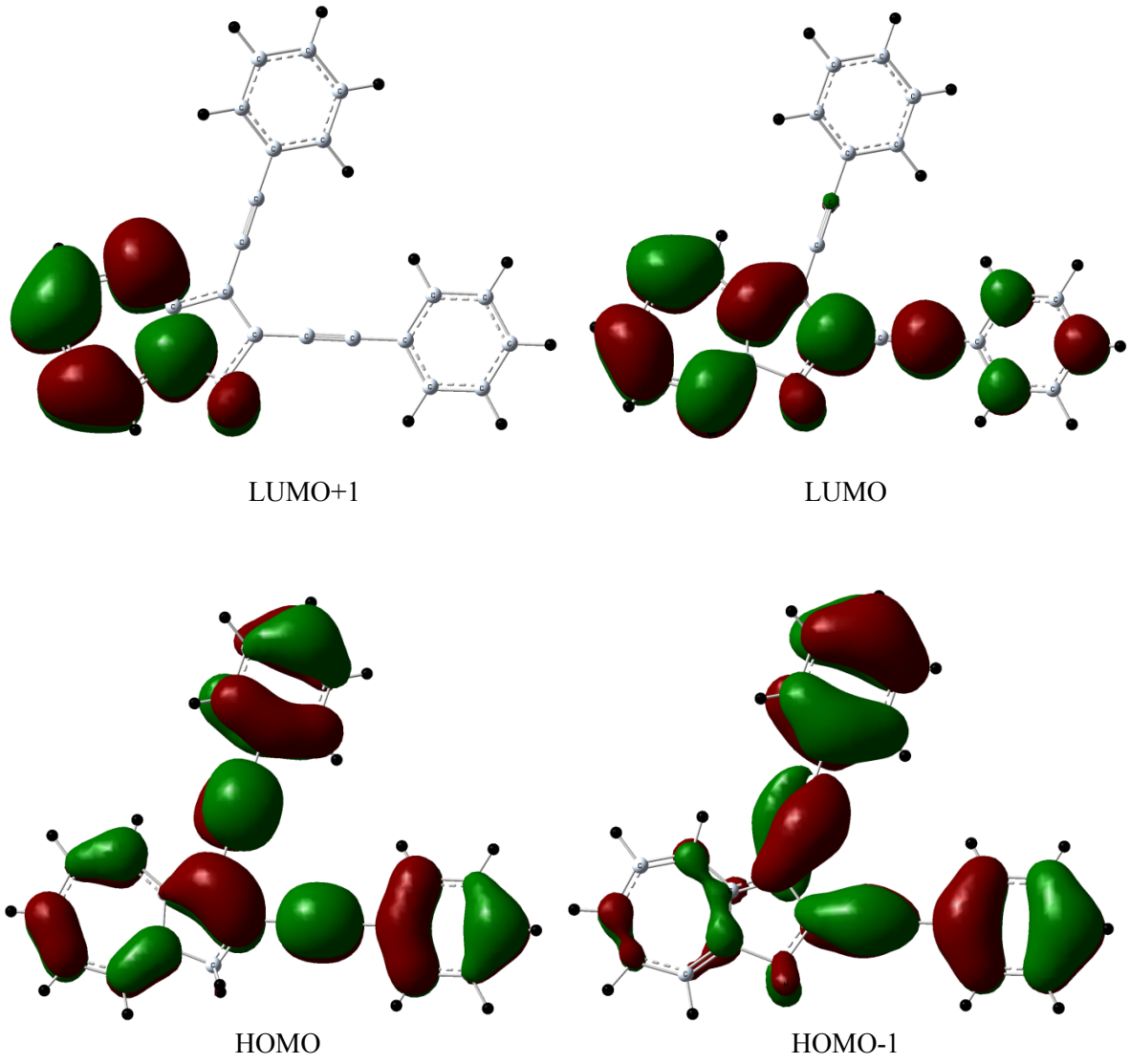
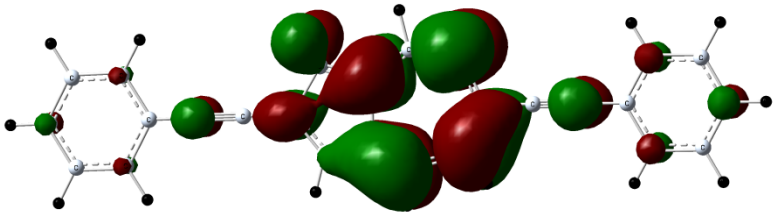
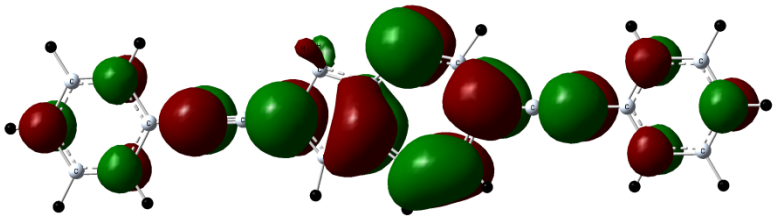


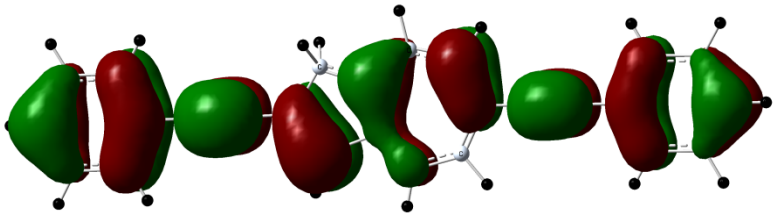
Figure S28. Frontier orbitals of the ground-state of **2-H+**.



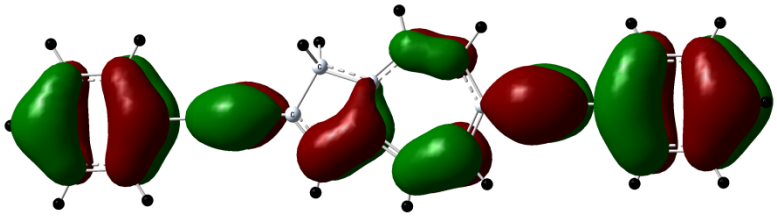
LUMO+1



LUMO

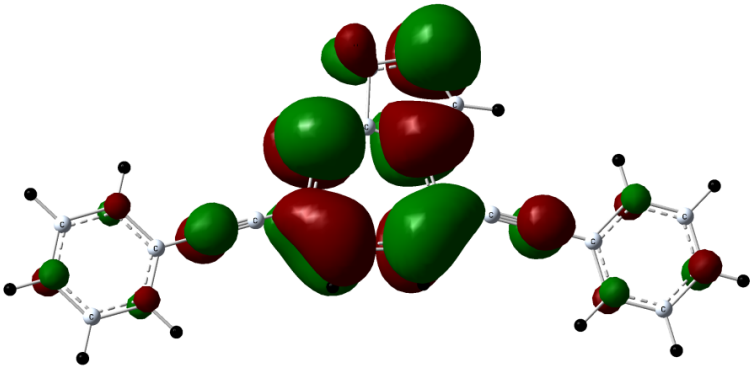


HOMO

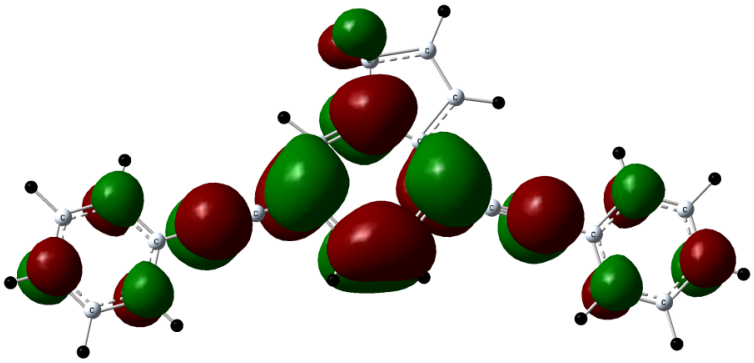


HOMO-1

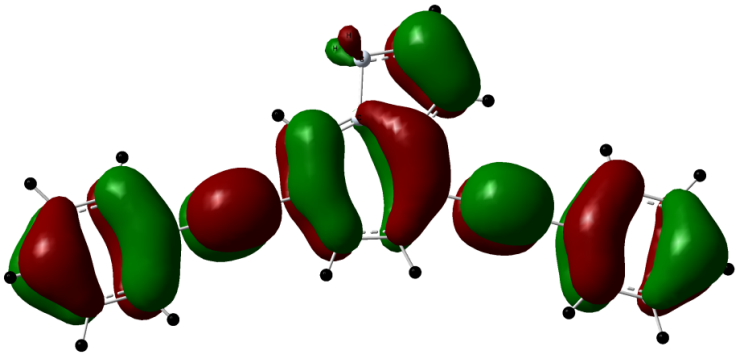
Figure S29. Frontier orbitals of the ground-state of **3-H+**.



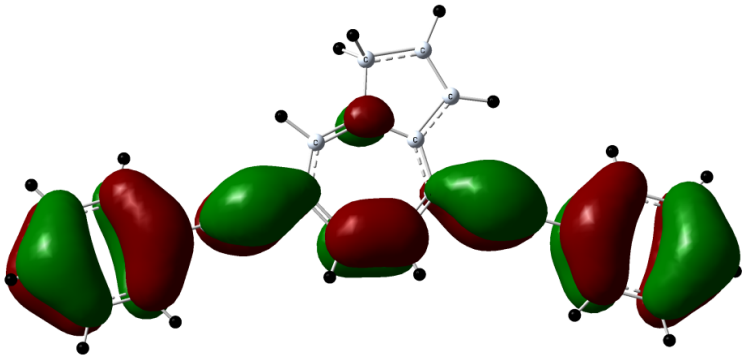
LUMO+1



LUMO



HOMO



HOMO-1

Figure S30. Frontier orbitals of the ground-state of **4-H+**.

TD-DFT UV-Vis spectra

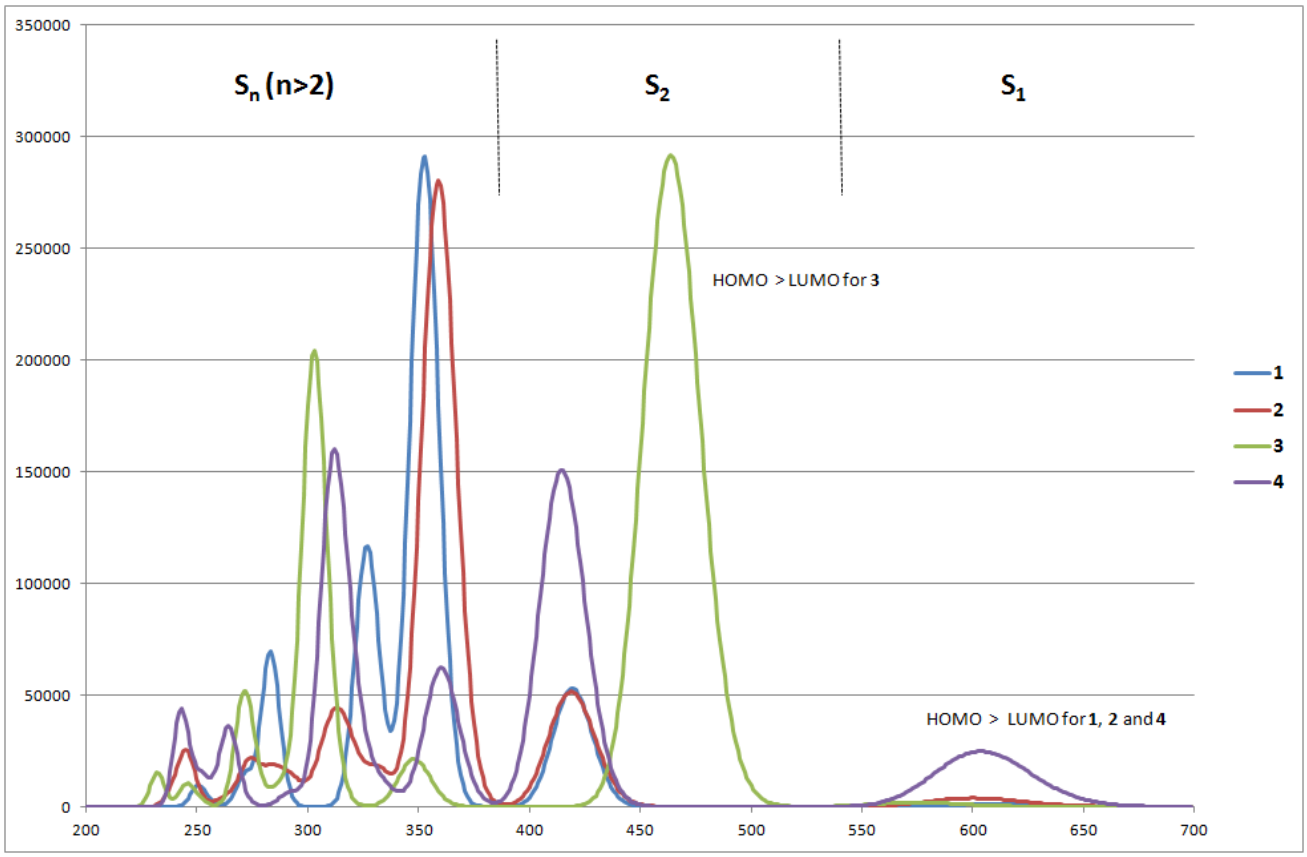


Figure S31. TD-DFT UV-Vis spectra produced by Gaussview (epsilon vs. nm) as calculated for **1**, **2**, **3** and **4** at the PBE1PBE/cc-pVDZ level.

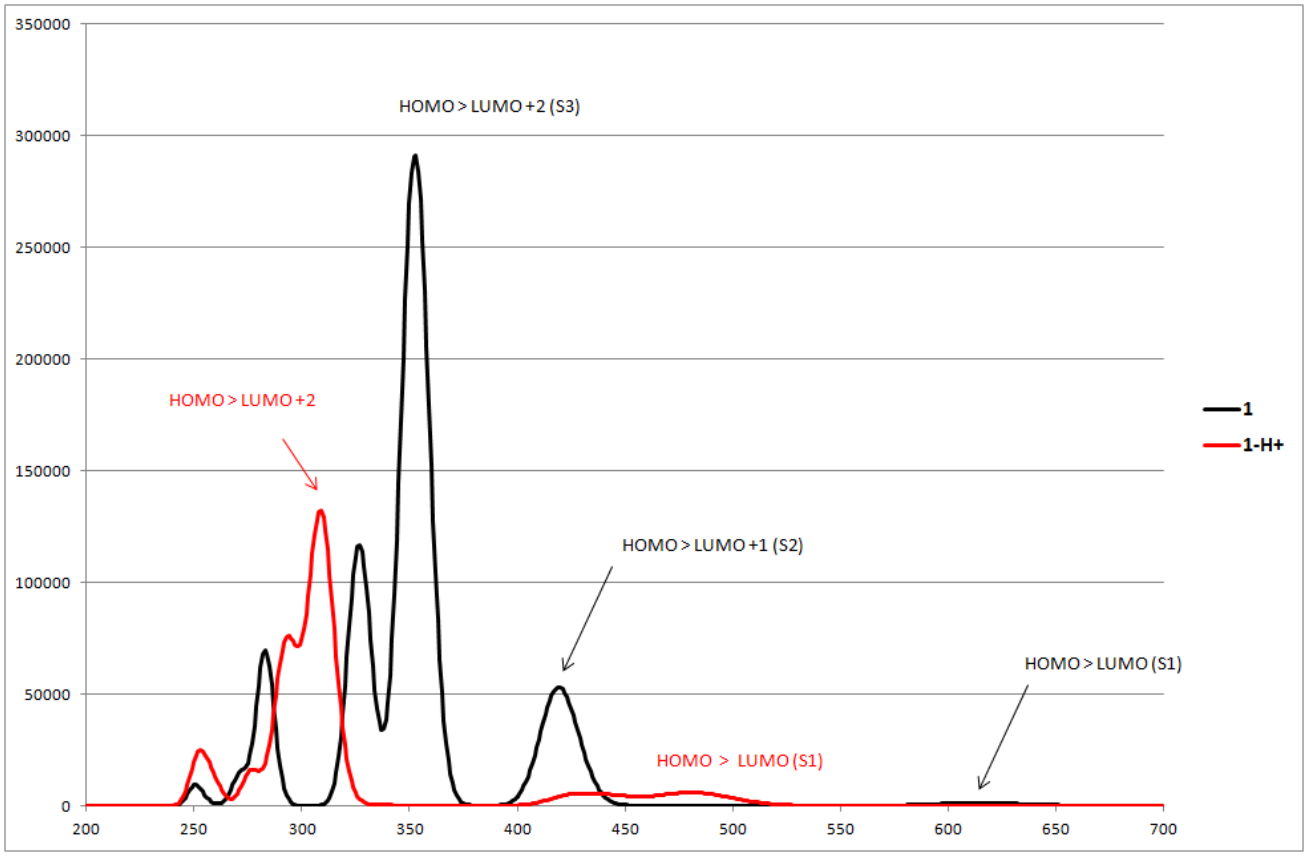


Figure S32. TD-DFT UV-Vis spectra produced by Gaussview (epsilon vs. nm) as calculated for **1** and **1-H**$^+$ at the PBE1PBE/cc-pVDZ level.

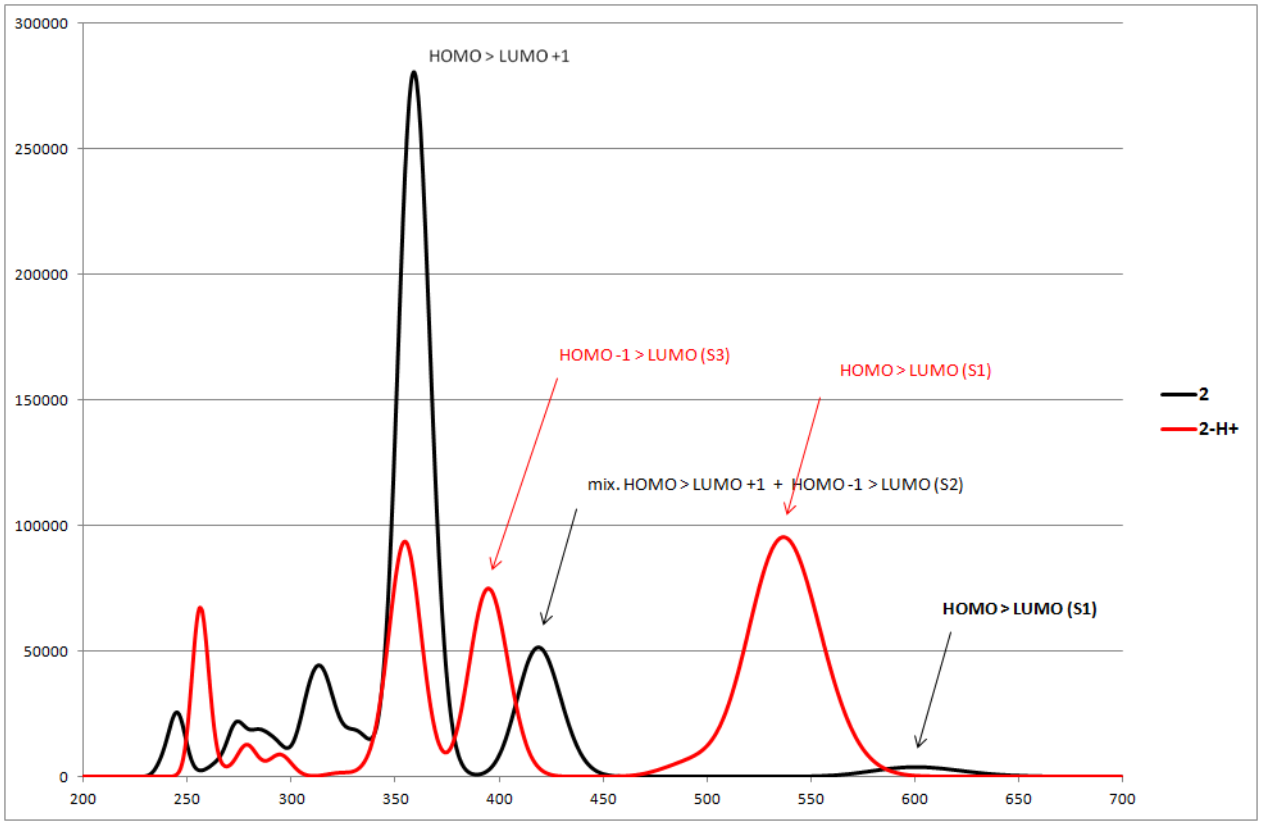


Figure S33. TD-DFT UV-Vis spectra produced by Gaussview (epsilon vs. nm) as calculated for **2** and **2-H**$^+$ at the PBE1PBE/cc-pVDZ level.

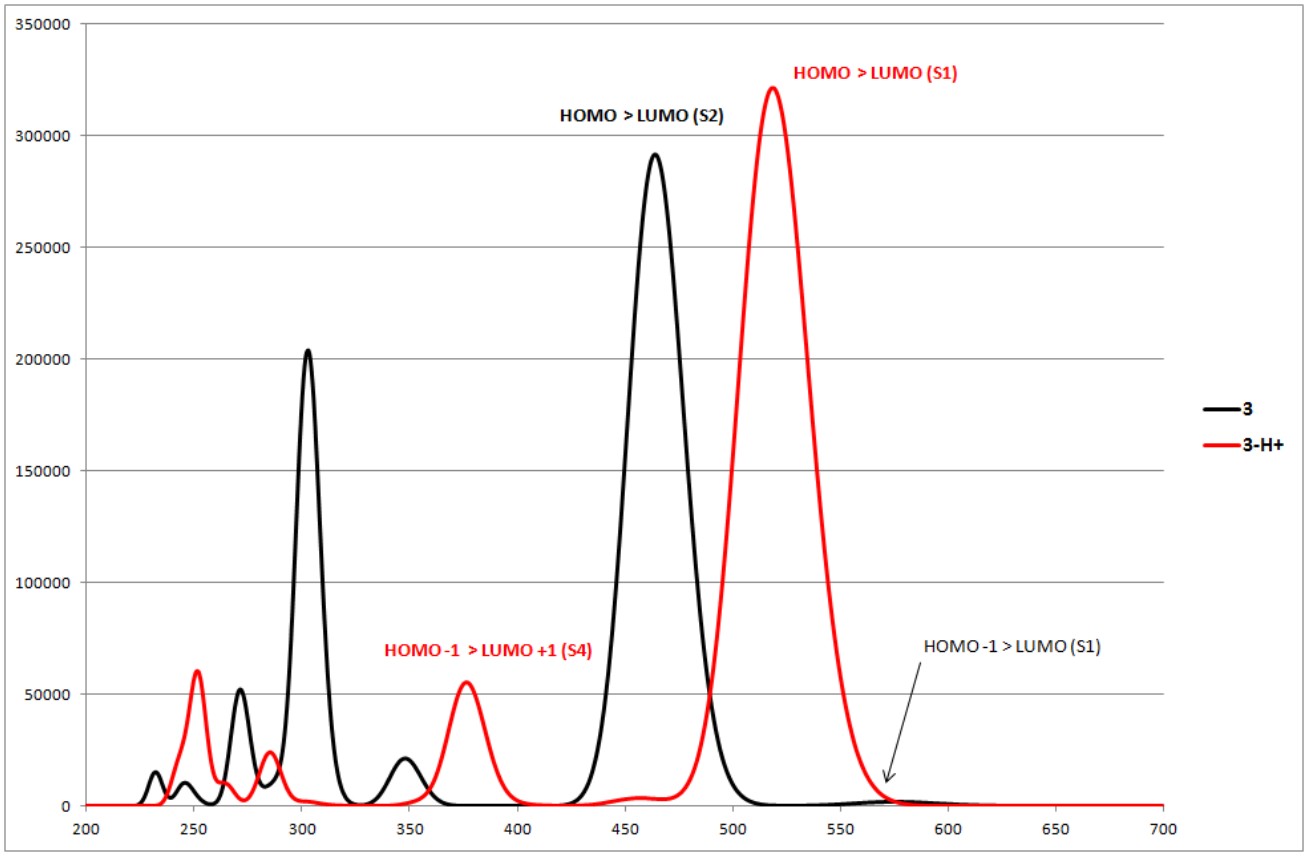


Figure S34. TD-DFT UV-Vis spectra produced by Gaussview (epsilon vs. nm) as calculated for **3** and **3-H**$^+$ at the PBE1PBE/cc-pVDZ level.

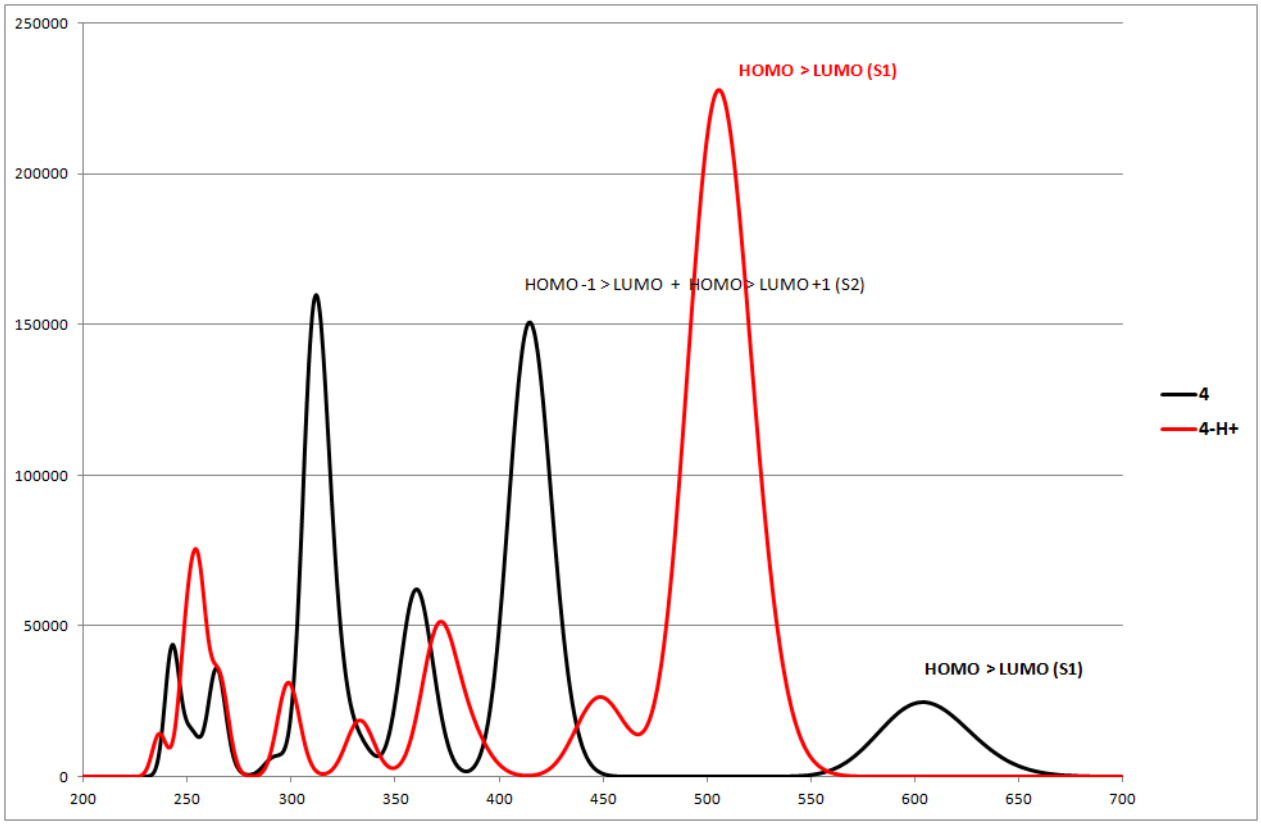


Figure S35. TD-DFT UV-Vis spectra produced by Gaussview (epsilon vs. nm) as calculated for **4** and **4-H**$^+$ at the PBE1PBE/cc-pVDZ level.

UV-Vis spectra

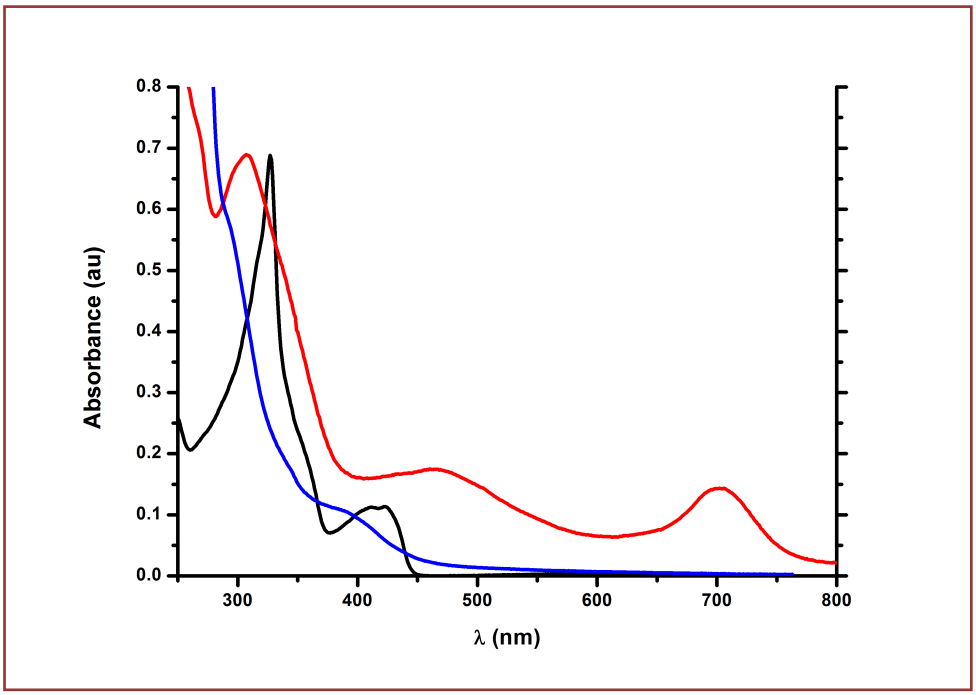


Figure S36. UV-Vis spectra of **1** in CH_2Cl_2 (black line), after treatment with $MeSO_3H$ (red line) followed by treatment with NEt_3 (blue line).

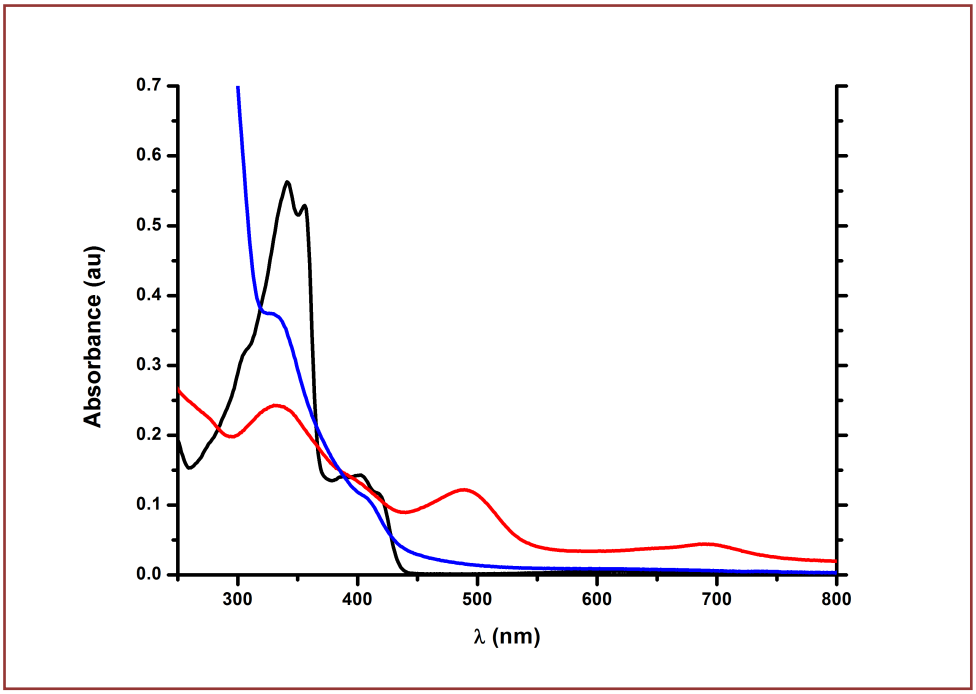


Figure S37. UV-Vis spectra of **2** in CH_2Cl_2 (black line), after treatment with $MeSO_3H$ (red line) followed by treatment with NEt_3 (blue line).

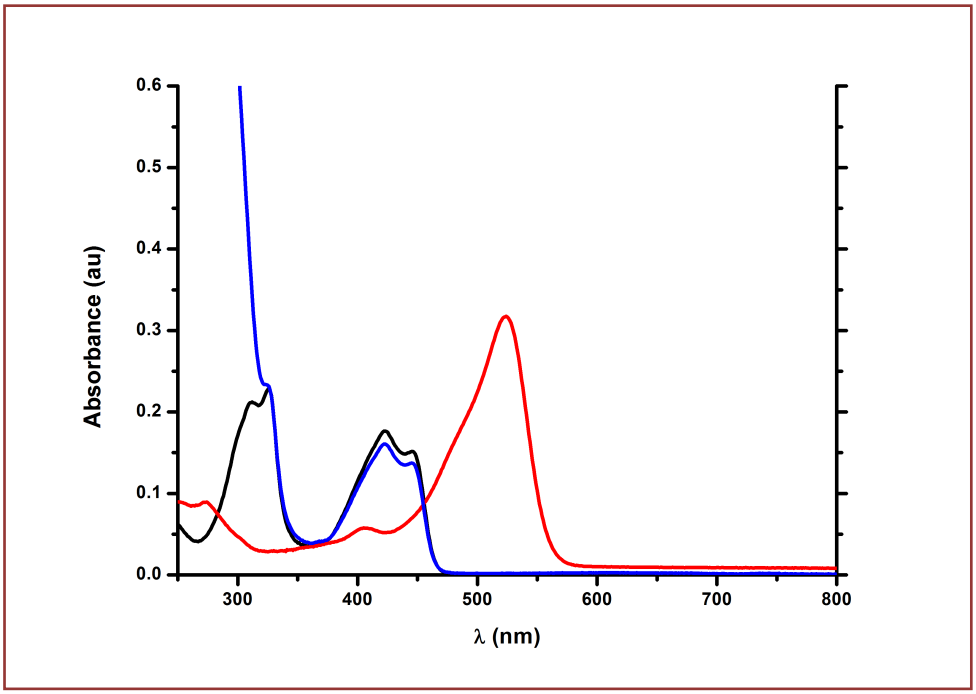


Figure S38. UV-Vis spectra of **3** in CH_2Cl_2 (black line), after treatment with $MeSO_3H$ (red line) followed by treatment with NEt_3 (blue line).

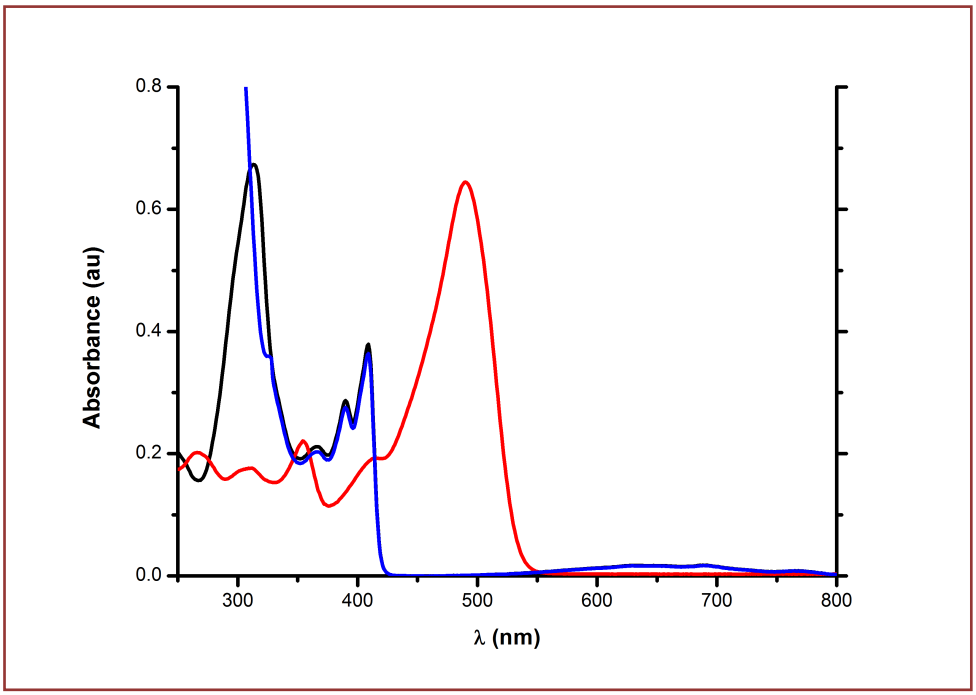


Figure S39. UV-Vis spectra of **4** in CH_2Cl_2 (black line), after treatment with $MeSO_3H$ (red line) followed by treatment with NEt_3 (blue line).

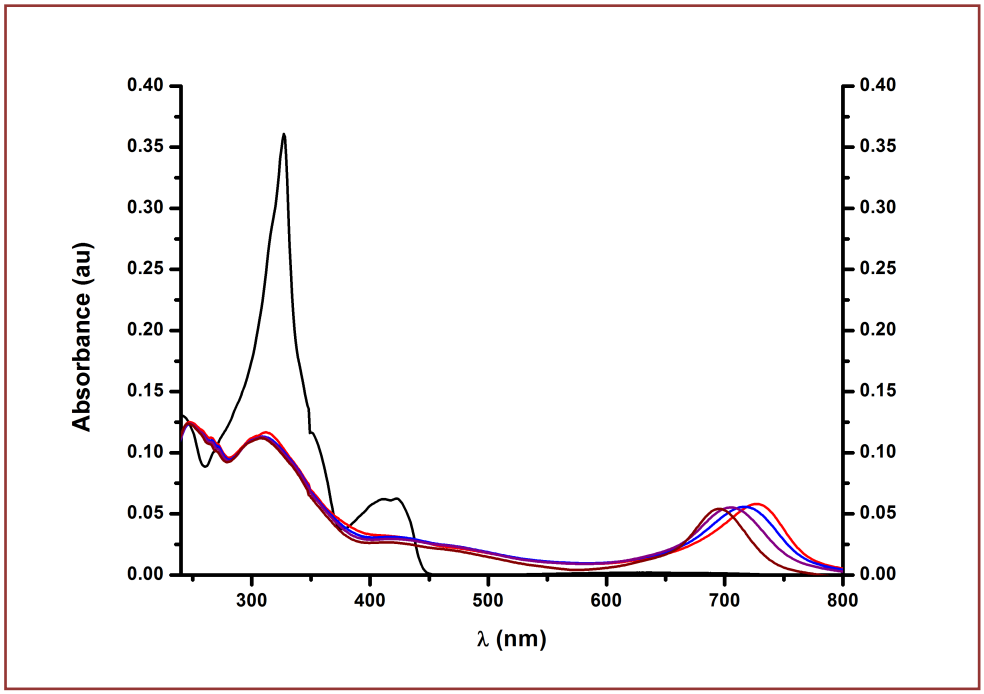


Figure S40. UV-Vis spectra of **1** in CH_2Cl_2 upon acid treatment.

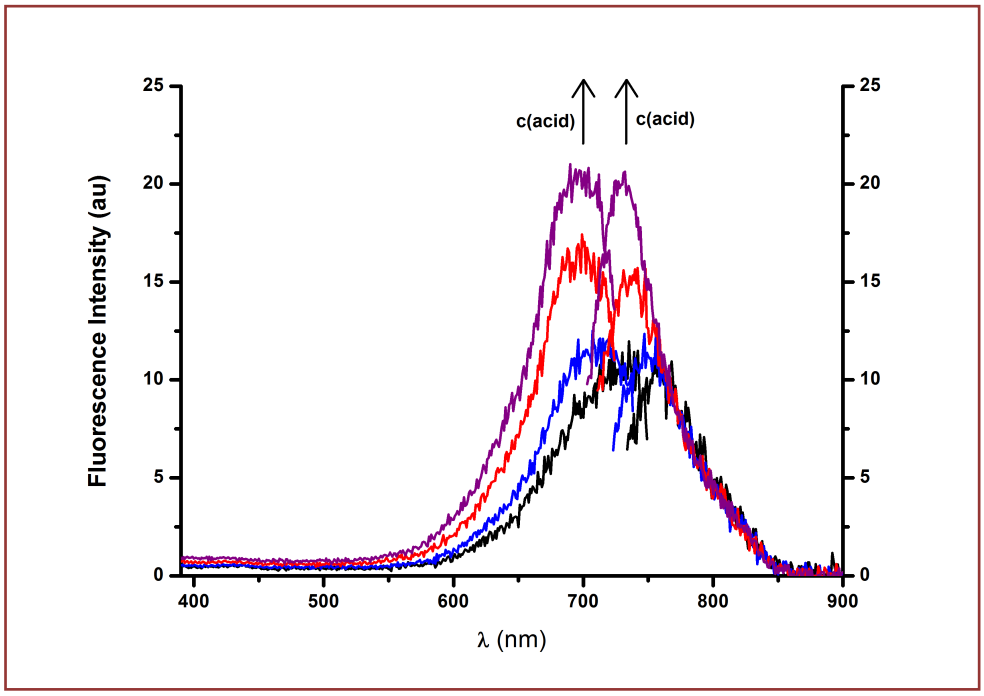


Figure S41. Excitation and emission spectra of **1** in CH_2Cl_2 upon acid treatment.

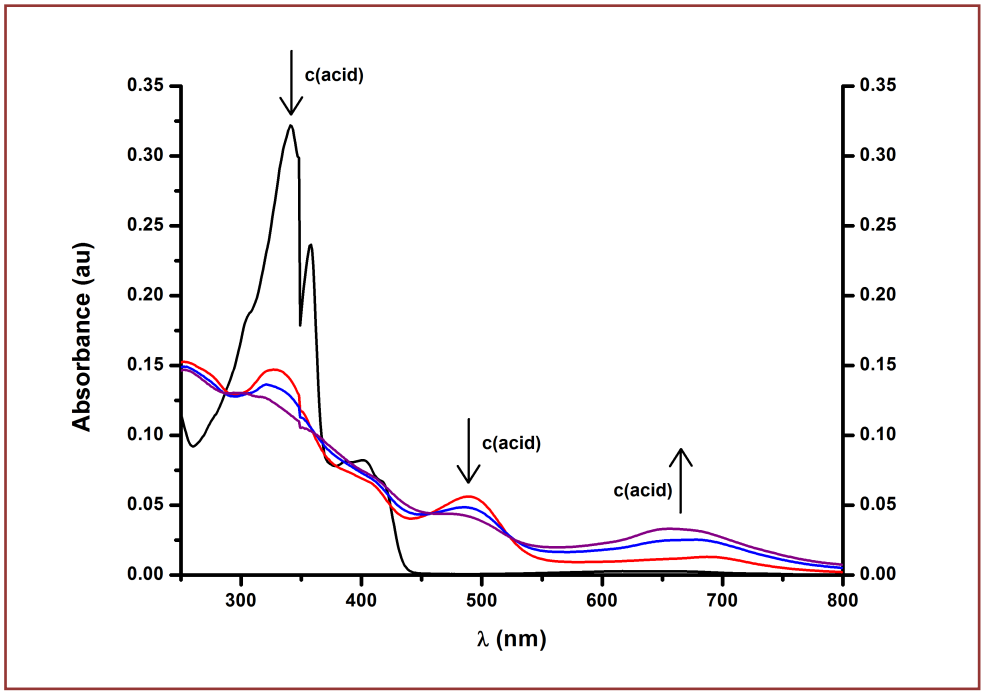


Figure S42. UV-Vis spectra of **2** in CH_2Cl_2 upon acid treatment.

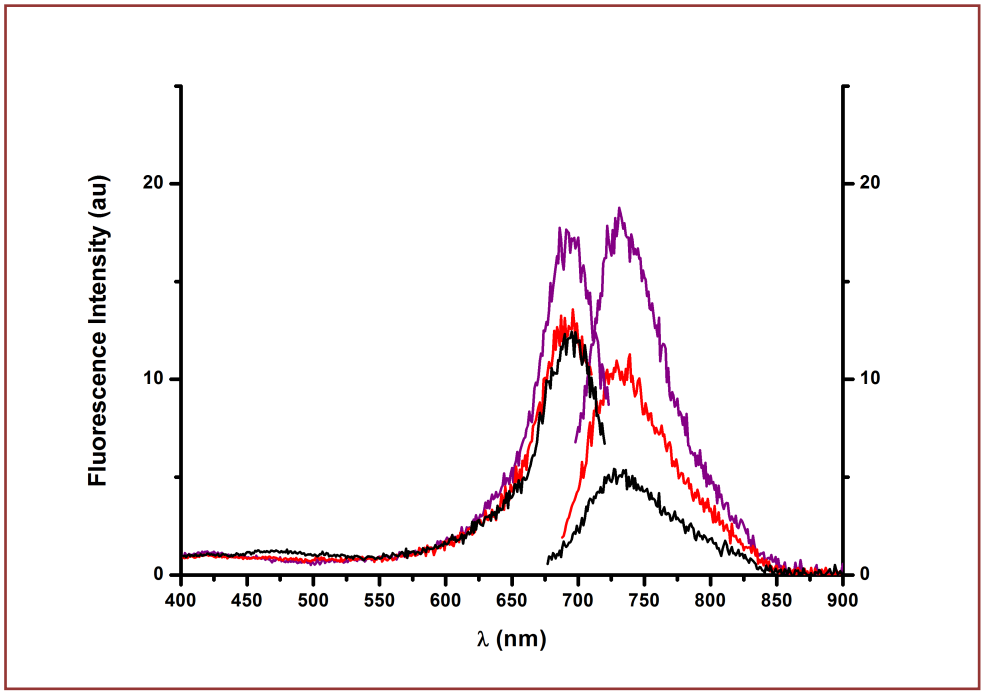


Figure S43. Excitation and emission spectra of **2** in CH_2Cl_2 upon acid treatment.

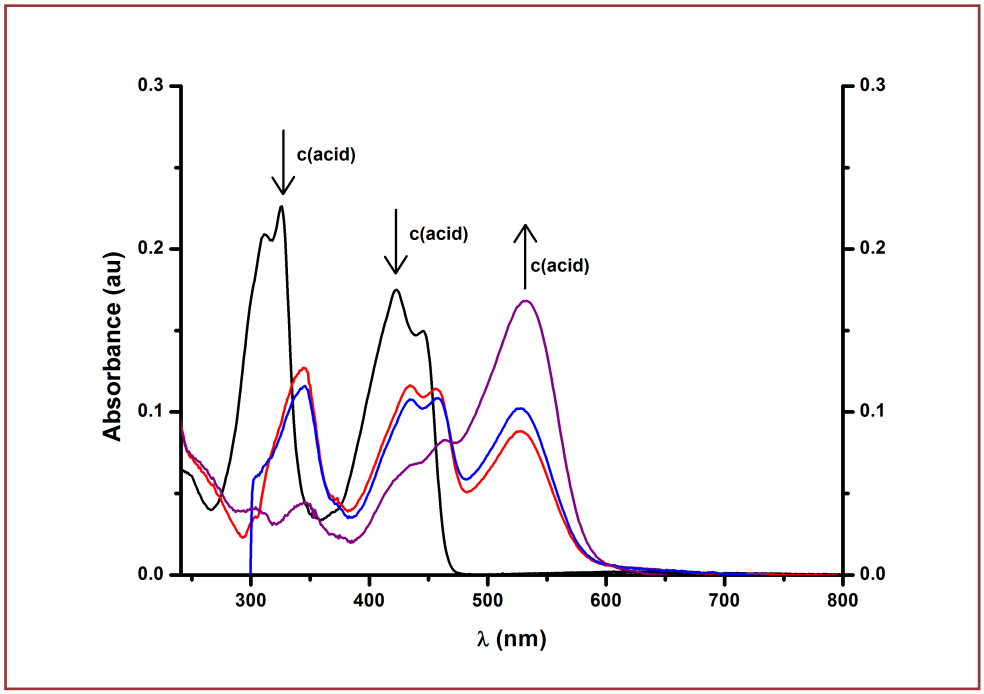


Figure S44. UV-Vis spectra of **3** in CH_2Cl_2 upon acid treatment (signal loss of the blue line at λ≤ 300 nm probably due to scattering).

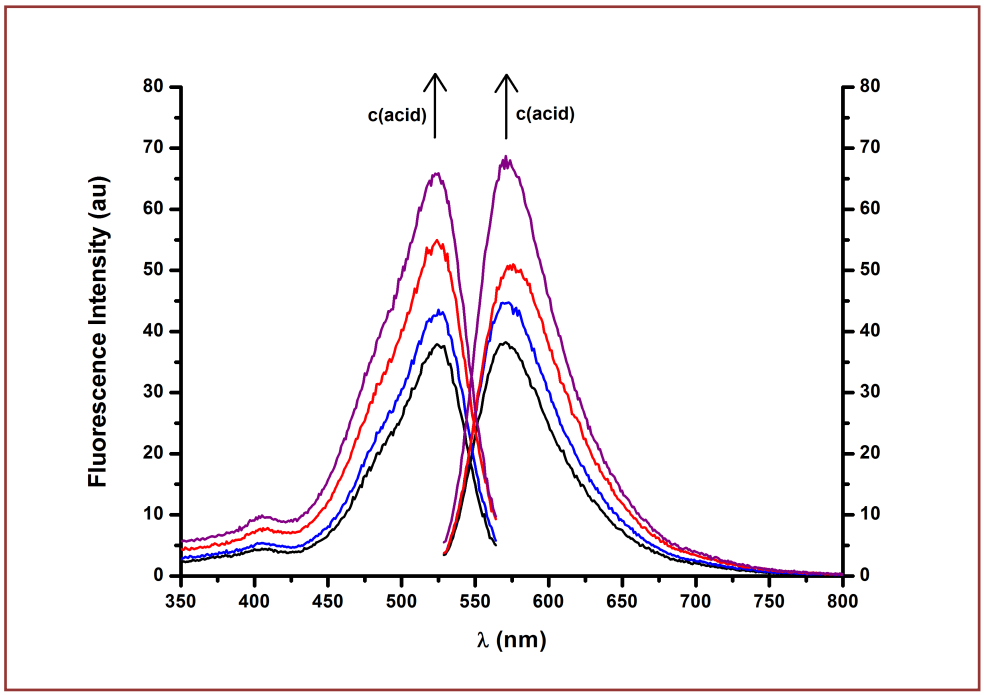


Figure S45. Excitation and emission spectra of **3** in CH_2Cl_2 upon acid treatment.

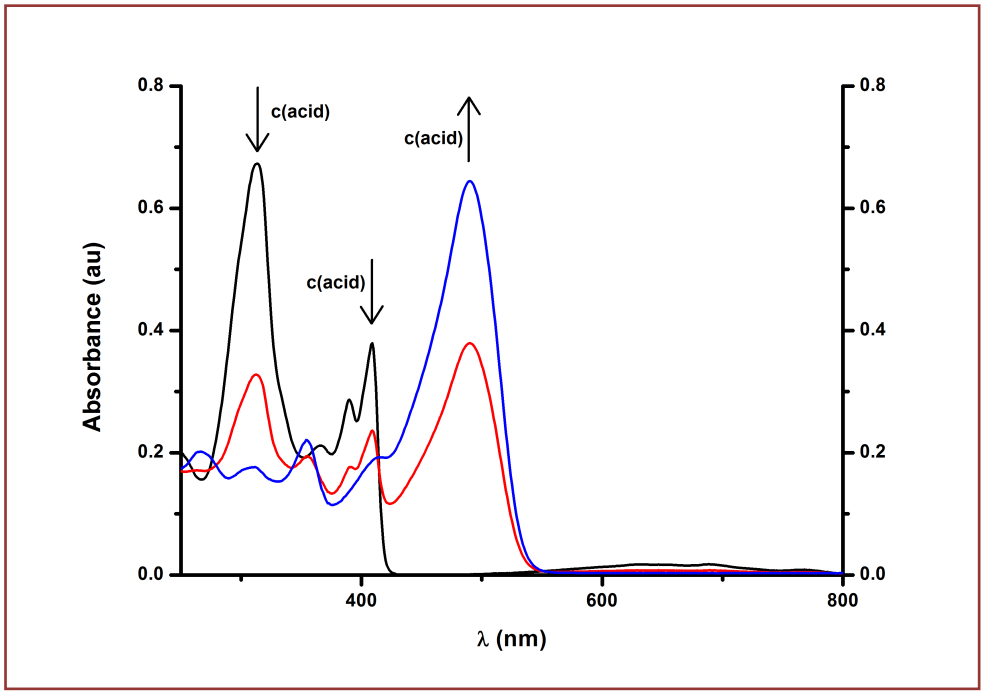


Figure S46. UV-Vis spectra of **4** in CH_2Cl_2 upon acid treatment.

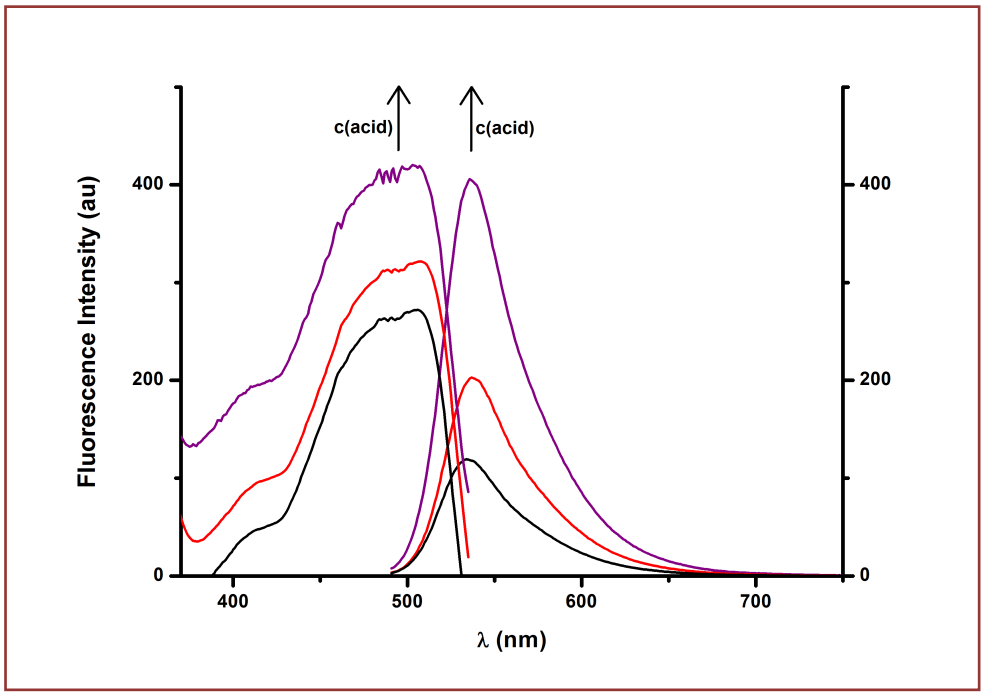


Figure S47. Excitation and emission spectra of **4** in CH_2Cl_2 upon acid treatment.

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