# Synthesis and Properties of Nonaromatic Stable N-Methylated Triphyrin(2.*1*.1)s

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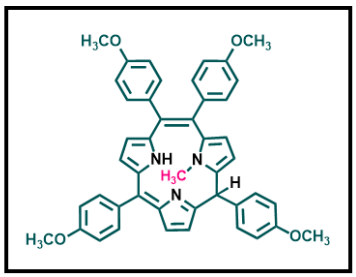
## General Experimental section

**Materials and Methods.** Chemicals such as pyrrole, trifluoroacetic acid (TFA), methyl iodide ($CH_3I$), triethylamine ($Et_3N$) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were used as obtained from Sigma-Aldrich. All other chemicals used for synthesis were reagent grade unless otherwise specified. The required 5,16-diphenyl-10,11-di(*p*-tolyl) triphyrin(2.1.1)[1] **1c** was prepared by following our recently reported method. Column chromatography was performed on basic alumina and silica gel (60–120 mesh size). The 1D, 2D and $^{13}C$ NMR spectra (δ in ppm) were recorded on 500 MHz and 400 MHz Bruker instruments using $CDCl_3$ as a deuterated solvent. The frequencies for the $^{1}H$ and $^{13}C$ nucleus for 400 MHz and 500 MHz instruments are 100.06 MHz and 125.77 MHz, respectively. Tetramethylsilane ($Si(CH_3)_4$) was used as an internal reference for recording $^{1}H$ and $^{13}C\{^{1}H\}$ NMR. Structural assignments were made using additional information from COSY, NOSEY and HSQC experiments for compounds **2-3**. Absorption spectra were obtained using a SHIMADZU-MPC-3100-UV-NIR spectrophotometer. UV−Vis stock solution ($10^{-5}$M) was prepared by using a HPLC-grade chloroform solvent. Cyclic voltammetry (CV) studies were carried out with BASi C3 Cell Stand electrochemical system (Manufacturer: Bioanalytical Systems. Inc.) utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel as reference electrode (the electrode is composed of $Hg/Hg_2Cl_2$/Saturated KCl solution). The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The initial and final potential was at 0 V, first switching potential at -2.0 V and second switching potential at 2.0 V. The high-resolution mass spectra were recorded with a Q-TOF micro mass spectrometer.

**Computational Details.** The geometry optimization of compounds **1a-b** and **2-4** was carried out by using Gaussian 09 quantum chemical software.[2] The density functional theory (DFT)[3] method with the B3LYP/6-31G(d,p)[4] basis set was used to optimize the structures of compounds **1a-b** and **2-4** in $S_0$ state. To obtain the oscillator strengths, identical basis and functional hybrid set were used whereas the vertical excitation energies were obtained with the help of TD-DFT techniques for $S_0 \rightarrow S_n$ transitions.[5] Under the Polarizable Continuum Model (PCM) in the toluene media all the computations were done using the Self-Consistent Reaction Field (SCRF). The electronic absorption spectra as well as the oscillator strengths were thoroughly examined using TD-DFT with PCM model[6] based on the optimized structures in the $S_0$ state.




**Compound Details**

**Cpd. 1: C45 H39 N3 O4**

| Formula | m/z | Observed M/Z | Difference_Da | Difference_PPM | Score |
|---|---|---|---|---|---|
| C45 H39 N3 O4 | 686.3021 | 686.302129490322 | 0.501327188203504 | 0.731550468388738 | 98.93 |

*Compound Spectra (Zoomed)*

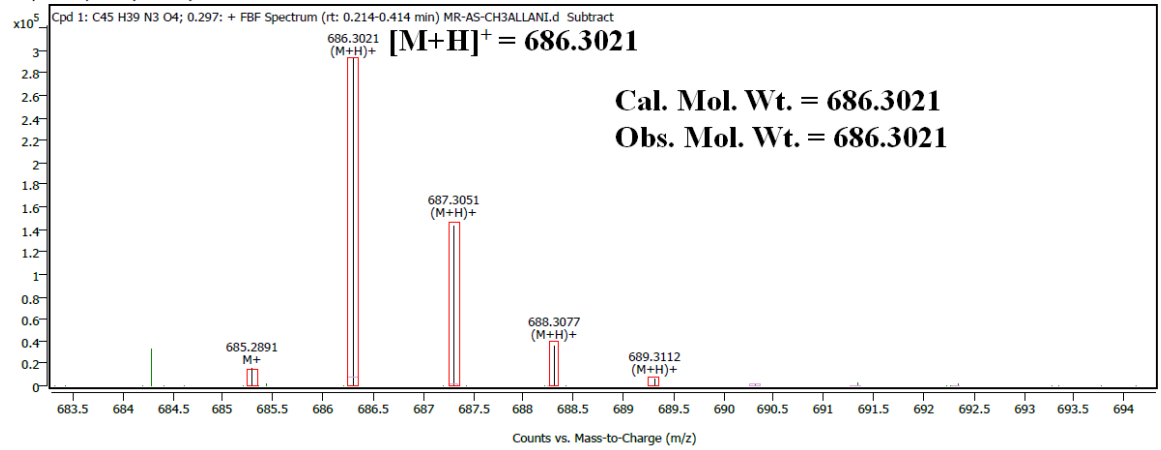



**Figure S1.** HR mass spectrum of the compound **2**.

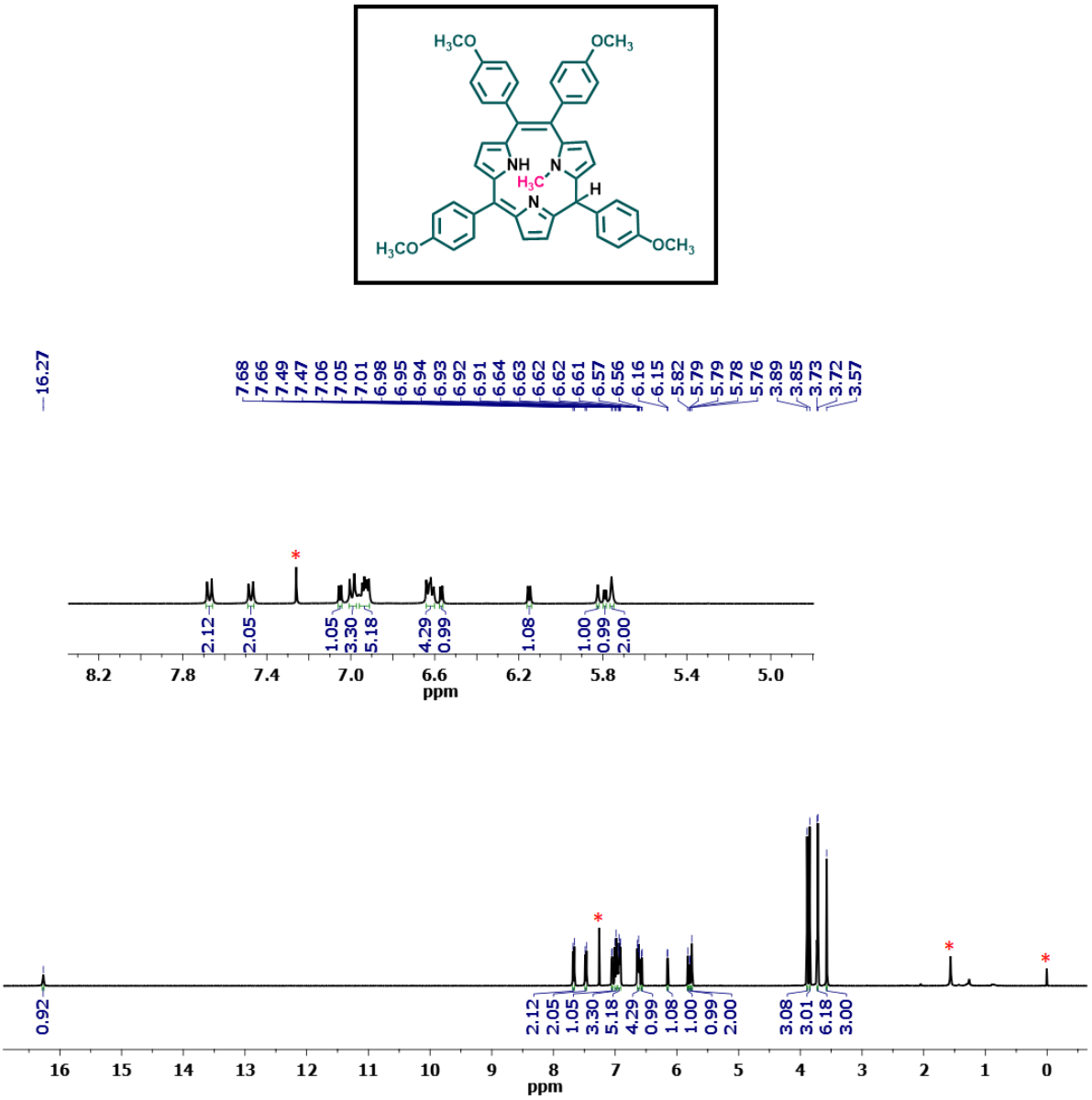



**Figure S2.** $^{1}H$ NMR spectrum of the compound **2** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

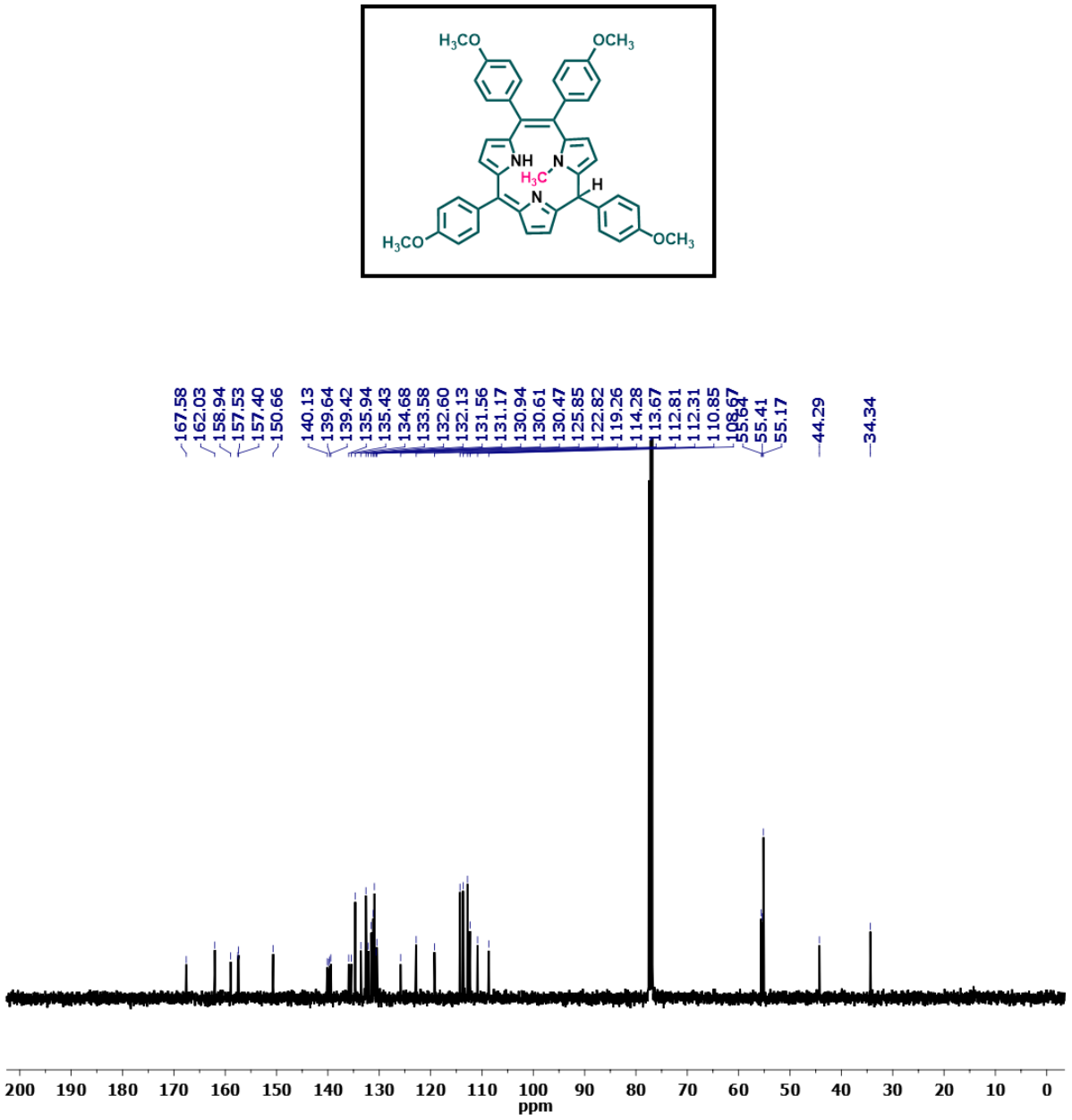



**Figure S3.** $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

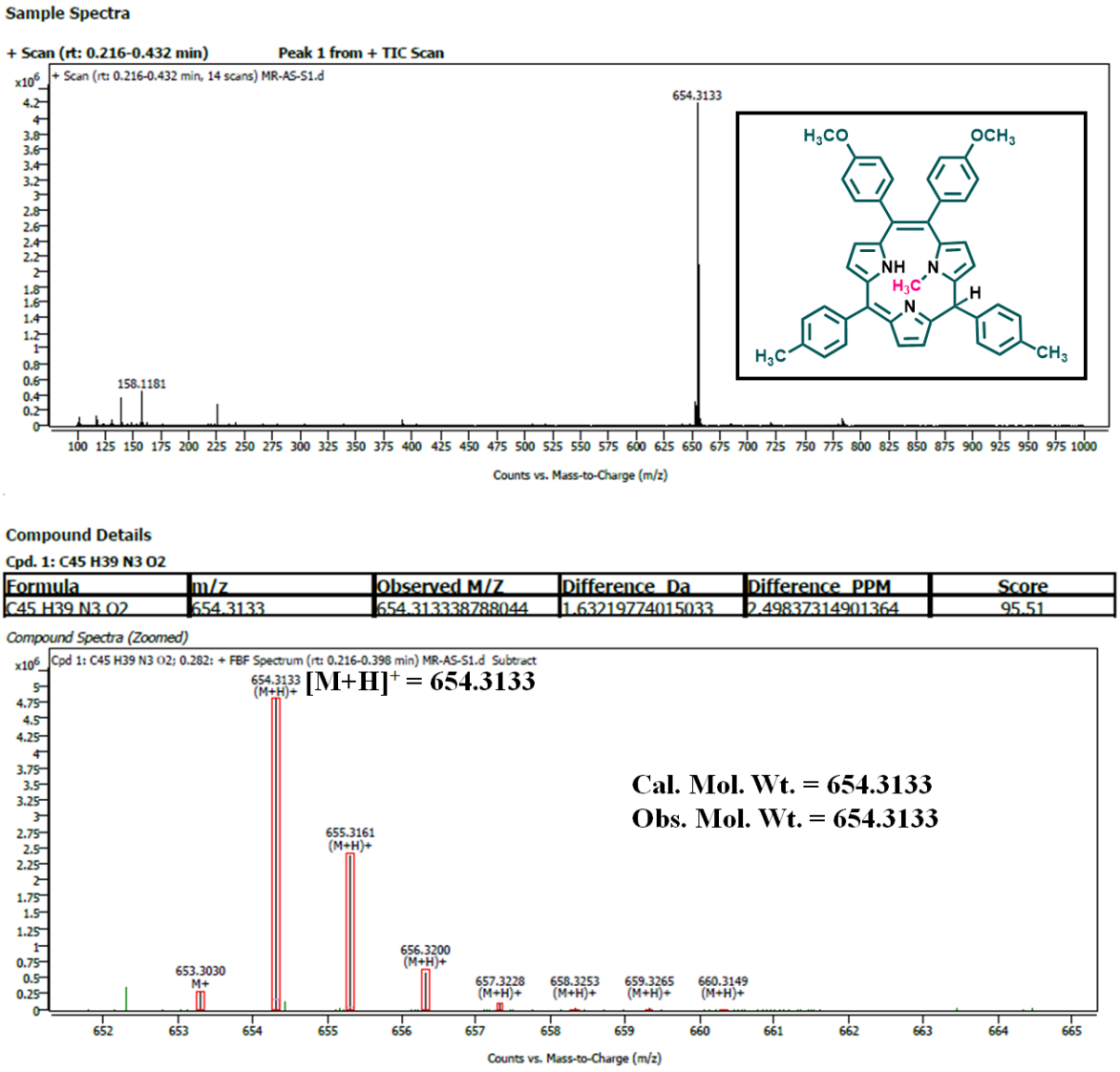



**Figure S4.** HR mass spectrum of the compound **3**.

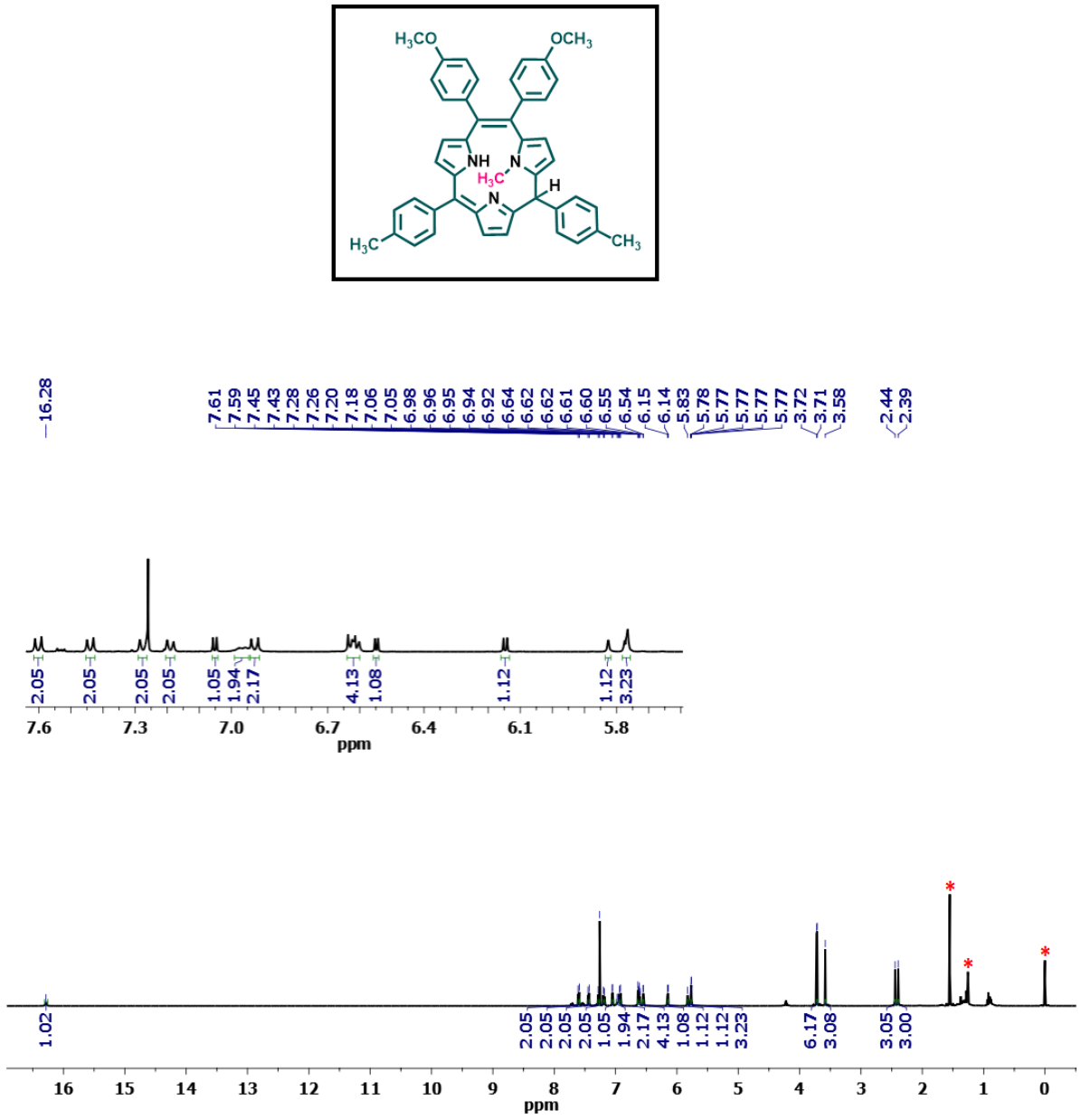



**Figure S5.** $^{1}H$ NMR spectrum of the compound **3** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

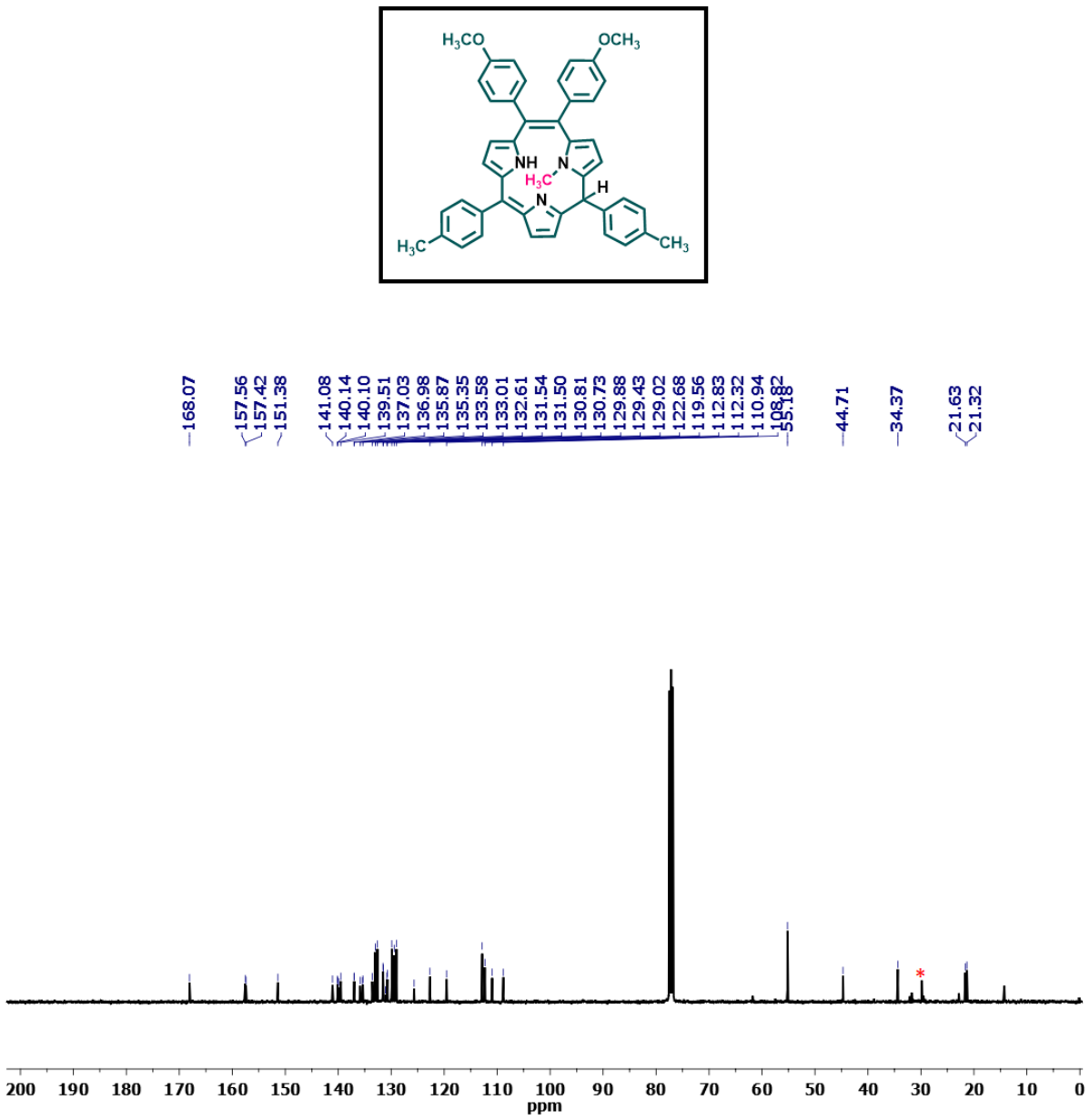



**Figure S6.** $^{13}C\{^{1}H\}$ NMR spectrum of the compound **3** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

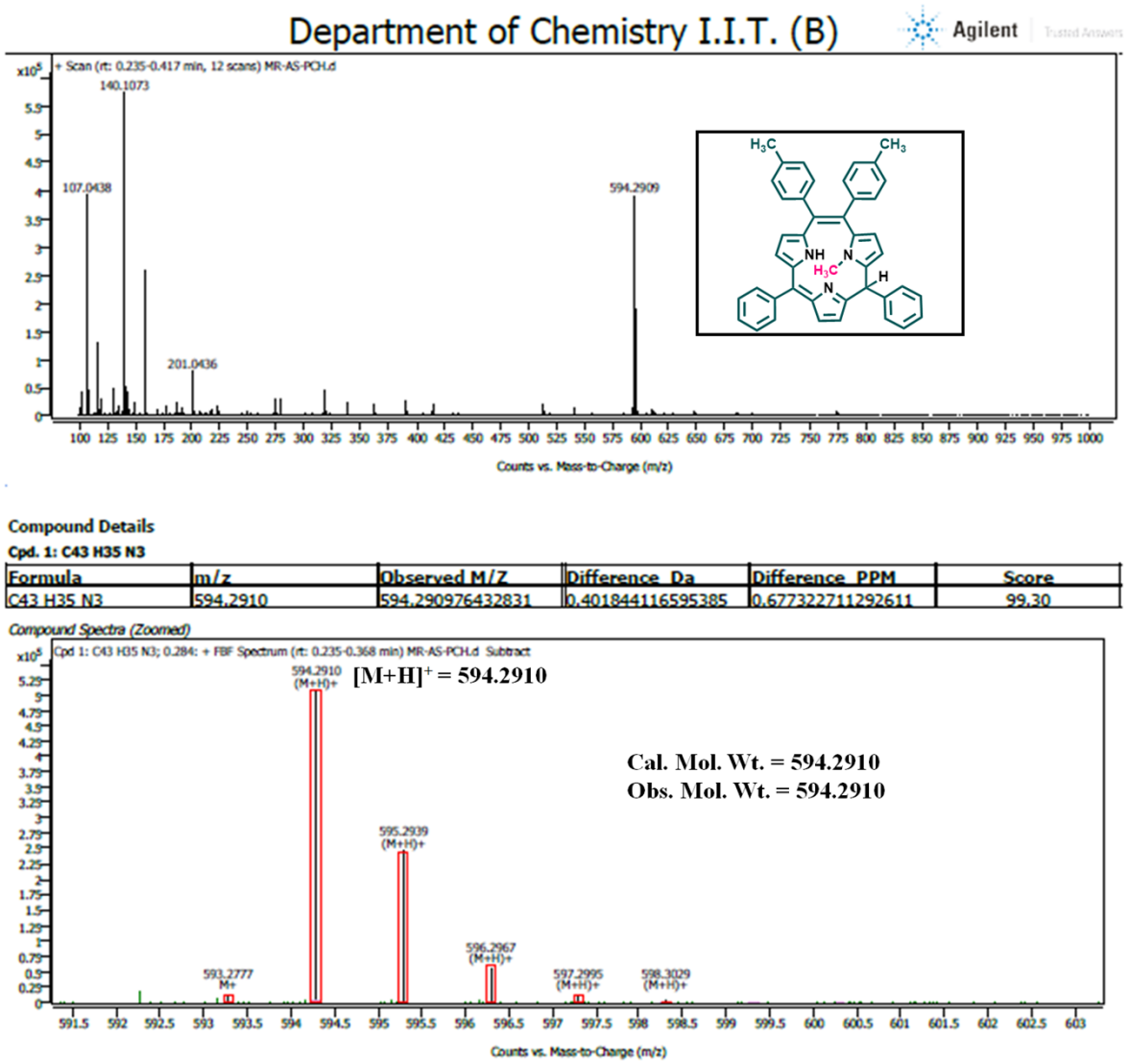



**Figure S7.** HR mass spectrum of the compound **4**.

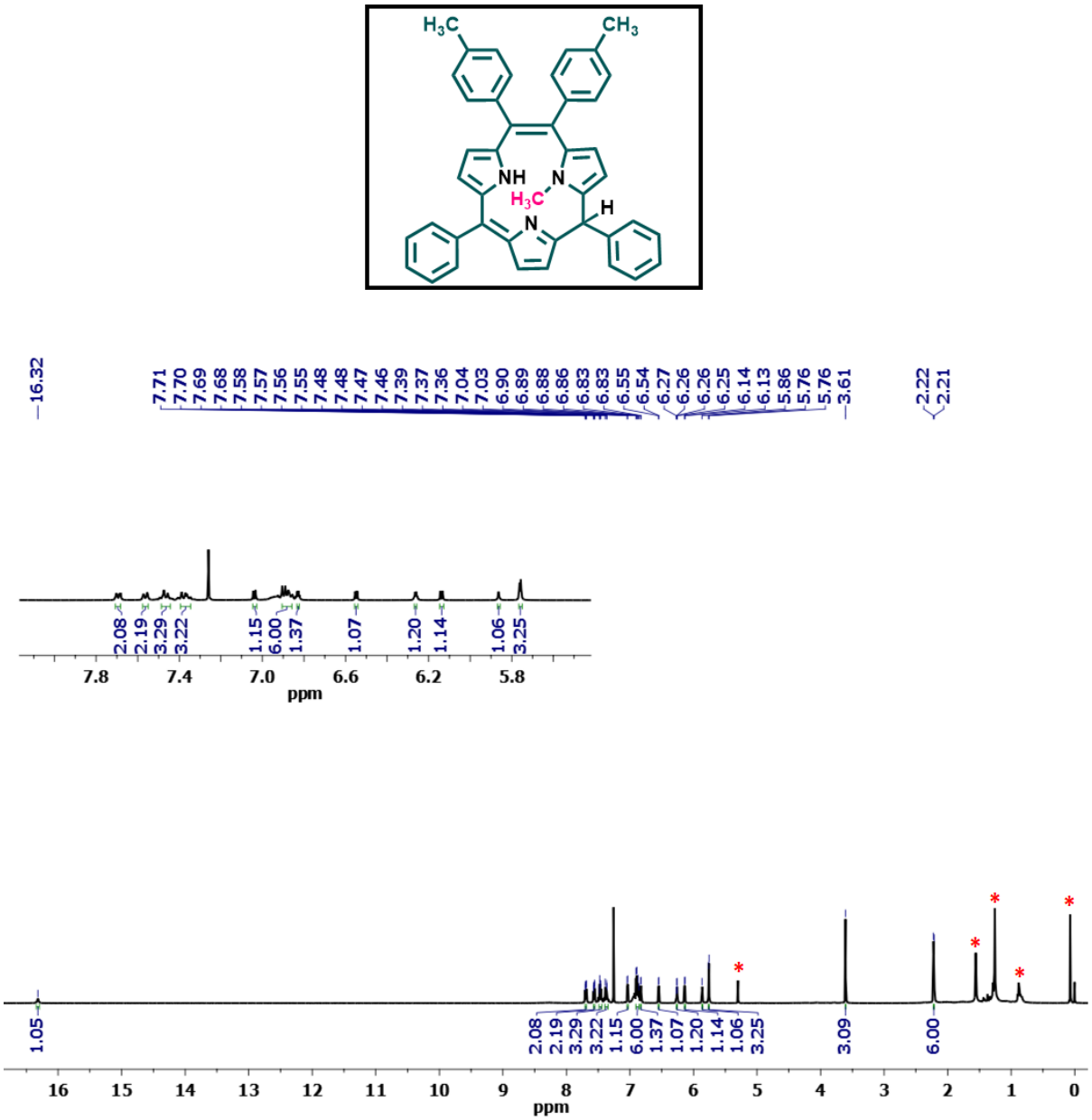



**Figure S8.** $^{1}H$ NMR spectrum of the compound **4** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

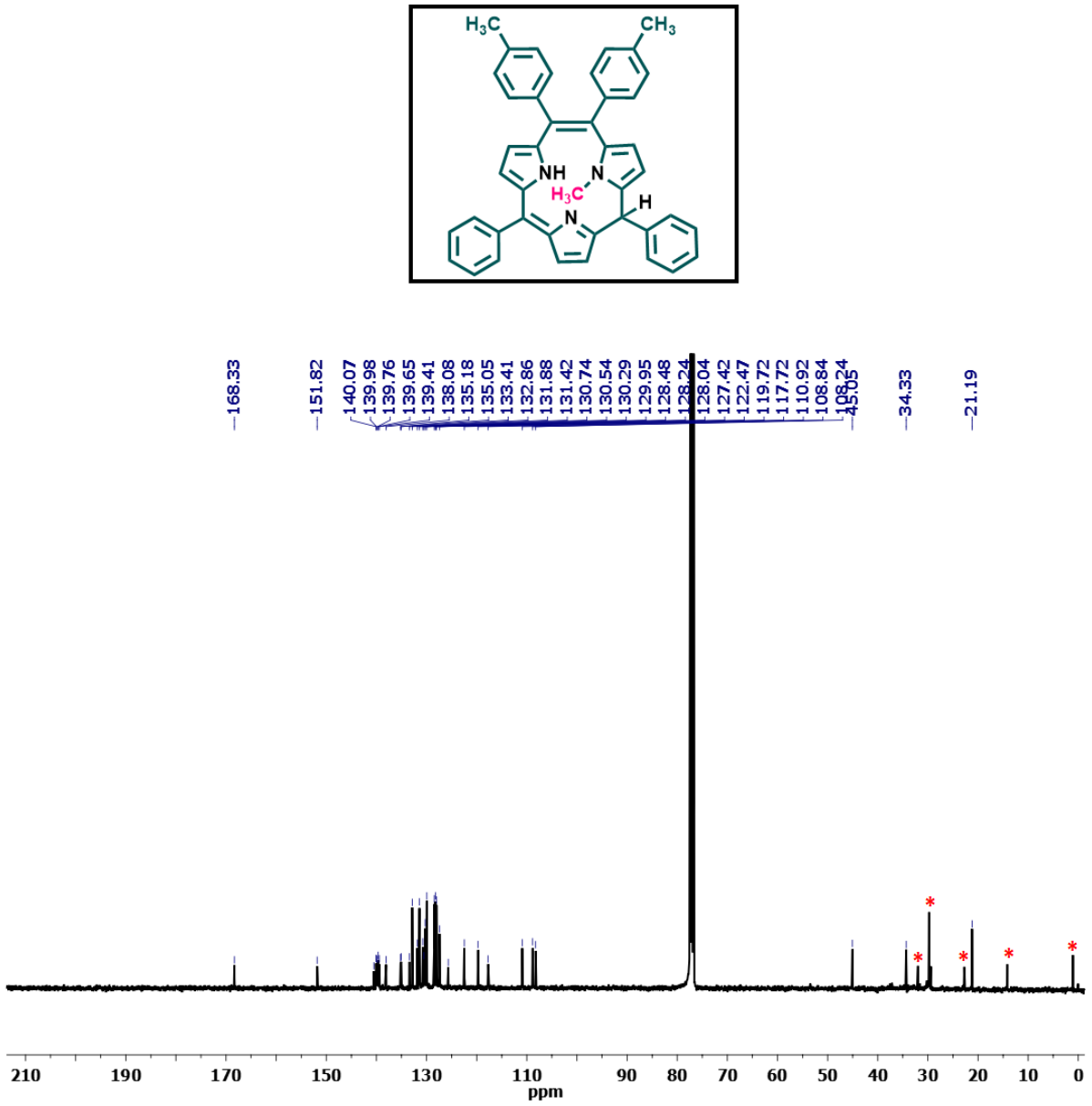



**Figure S9.** $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

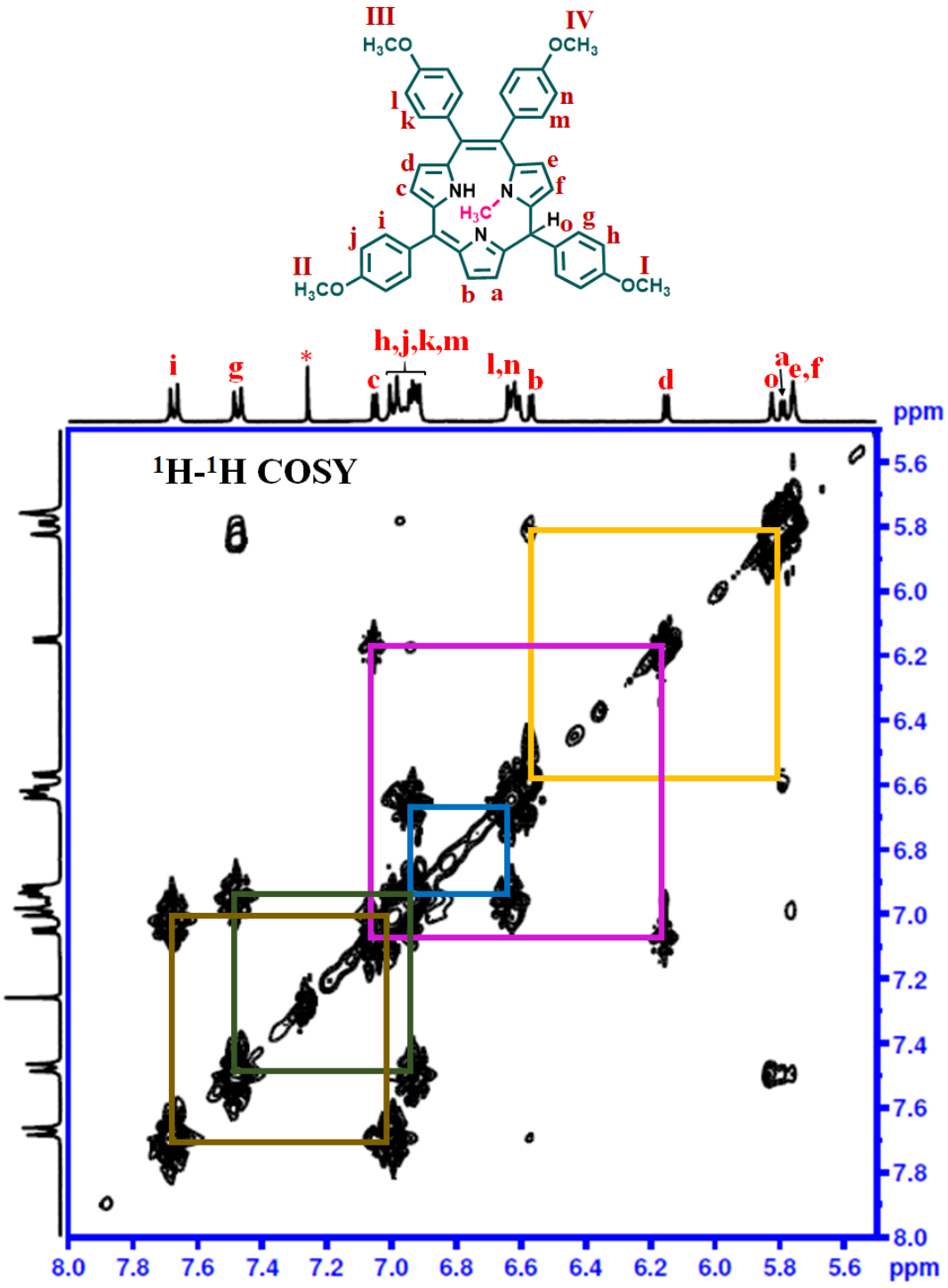



**Figure S10.** Partial $^{1}H$-$^{1}H$ COSY spectrum of compound **2** recorded in $CDCl_3$ at room temperature on 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

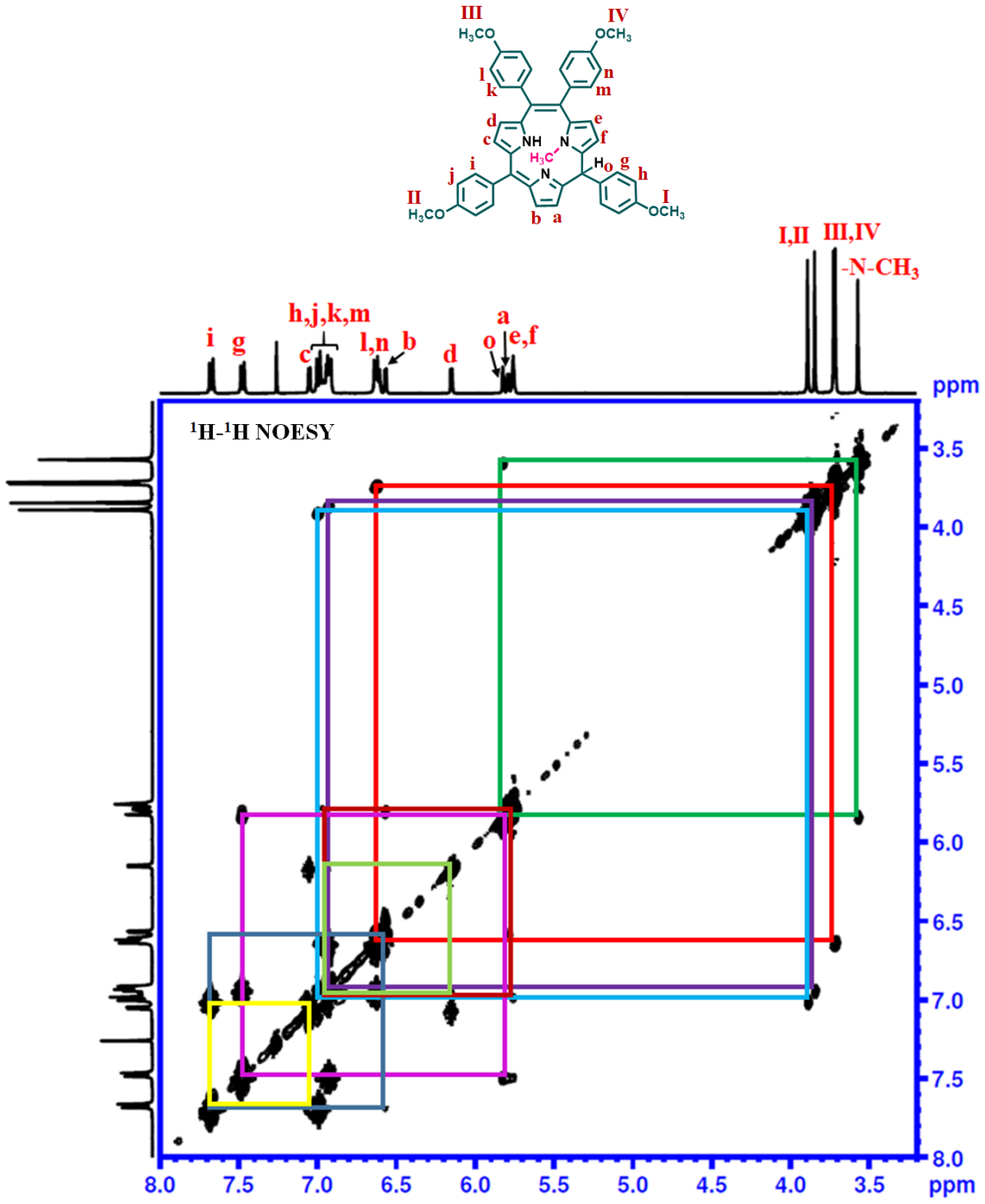



**Figure S11.** Partial $^{1}$H-$^{1}$H NOESY spectrum of compound **2** recorded in $CDCl_3$ at room temperature on 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

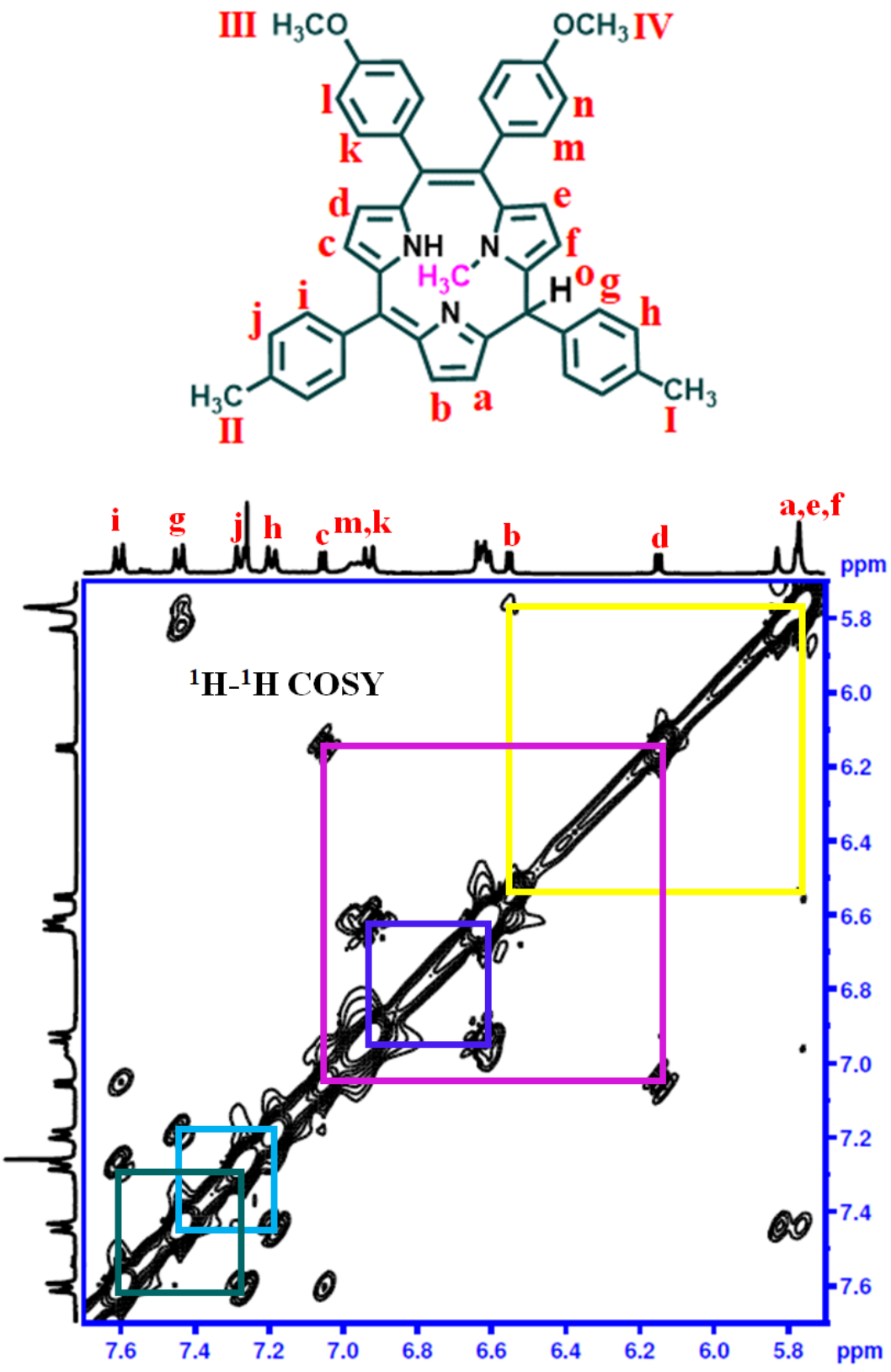



**Figure S12.** Partial $^{1}H$-$^{1}H$ COSY spectrum of compound **3** recorded in $CDCl_3$ at room temperature on 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

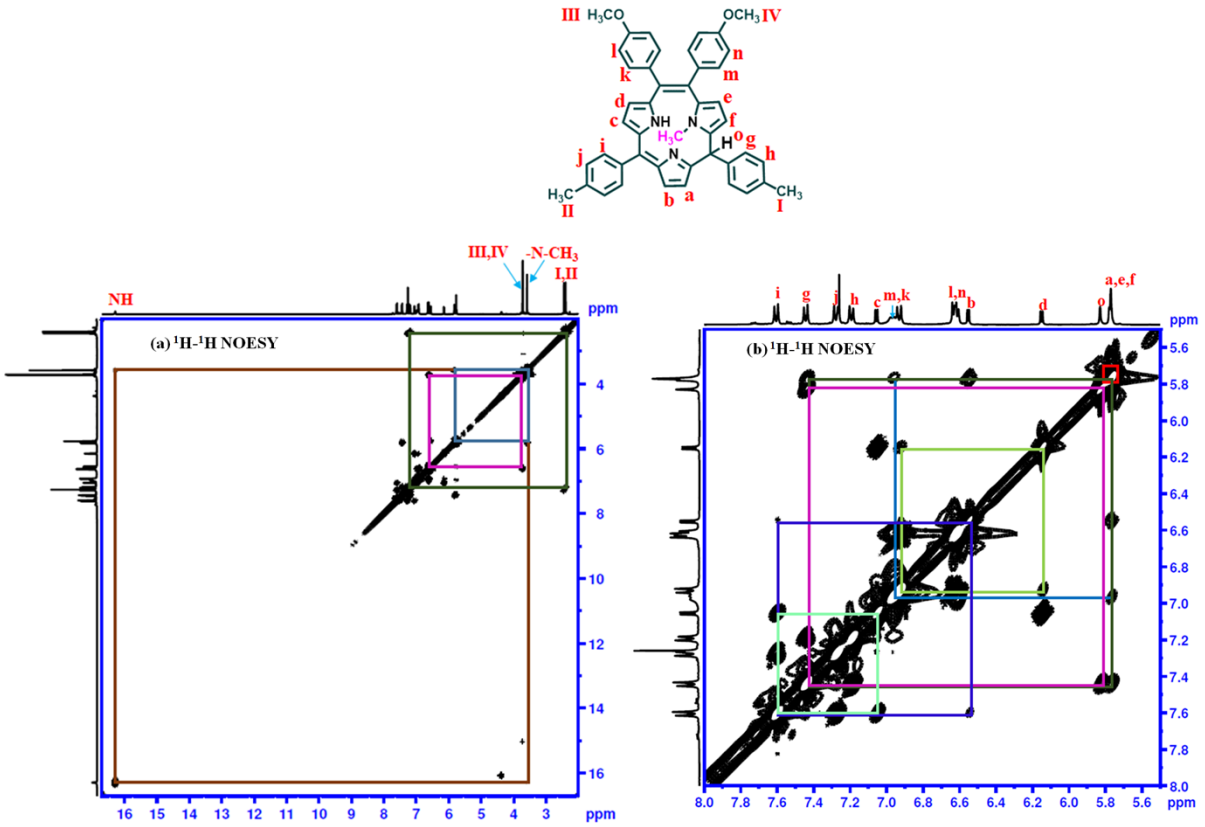



**Figure S13.** (a) $^{1}$H-$^{1}$H NOESY and (b) Partial $^{1}$H-$^{1}$H NOESY spectrum of compound **3** recorded in $CDCl_3$ at room temperature on 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

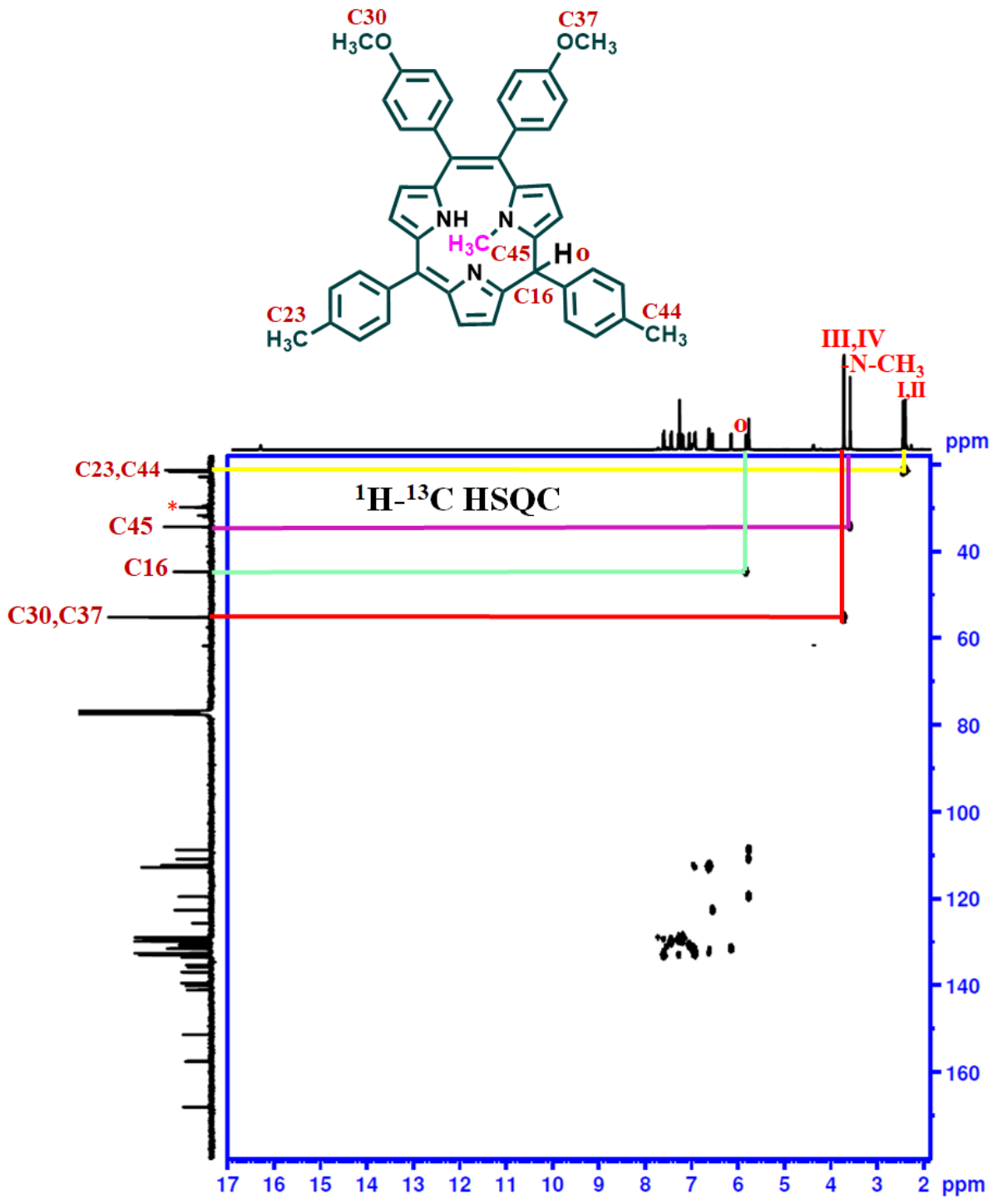



**Figure S14.** $^{1}H$-$^{13}C$ HSQC spectrum of compound **3** recorded in $CDCl_3$ at room temperature on 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

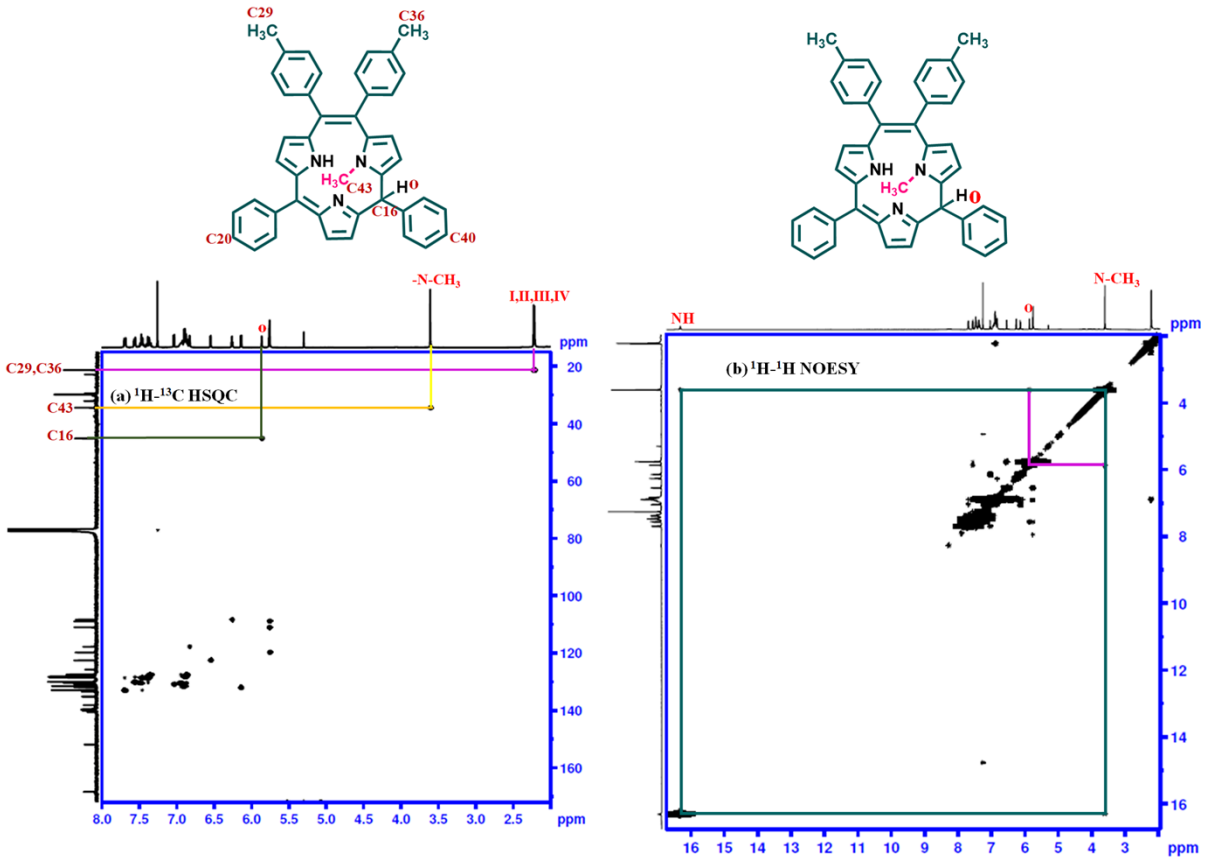



**Figure S15. (a)** $^{1}H$-$^{13}C$ HSQC and (b) $^{1}H$-$^{1}H$ NOESY spectrum of compound **4** recorded in $CDCl_3$ at room temperature on 400 MHz instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

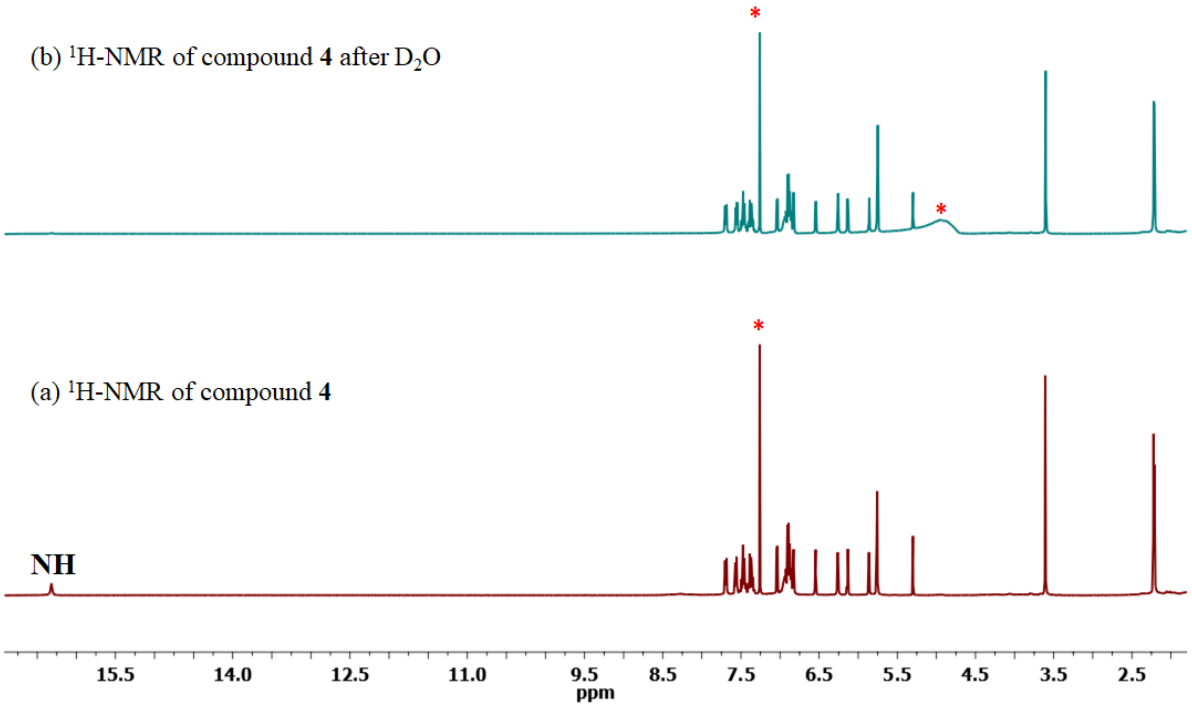
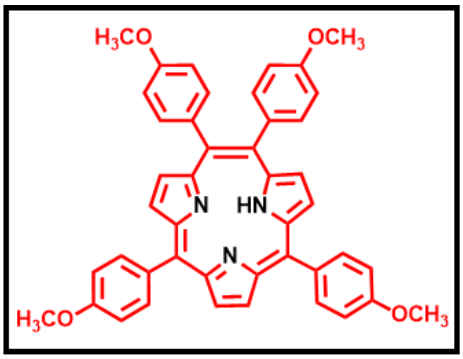
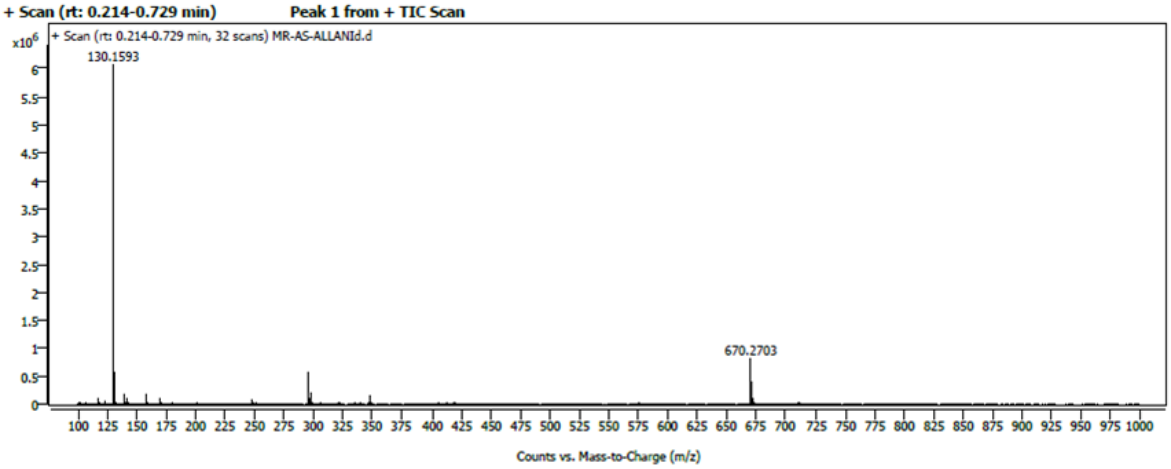



**Figure S16**. Comparison of partial $^{1}$H-NMR spectra of (a) compound **4** and (b) after addition of $D_2O$ to compound **4**. Note: Peaks marked with asterisk (*) are due to residual solvents.




**Sample Spectra**

**+ Scan (rt: 0.214-0.729 min)** **Peak 1 from + TIC Scan**




**Compound Details**

**Cpd. 1: C44 H35 N3 O4**

| Formula | m/z | Observed M/Z | Difference_Da | Difference_PPM | Score |
|---|---|---|---|---|---|
| C44 H35 N3 O4 | 670.2703 | 670.270328045084 | 0.401193769448582 | 0.59945629048598 | 99.58 |

*Compound Spectra (Zoomed)*

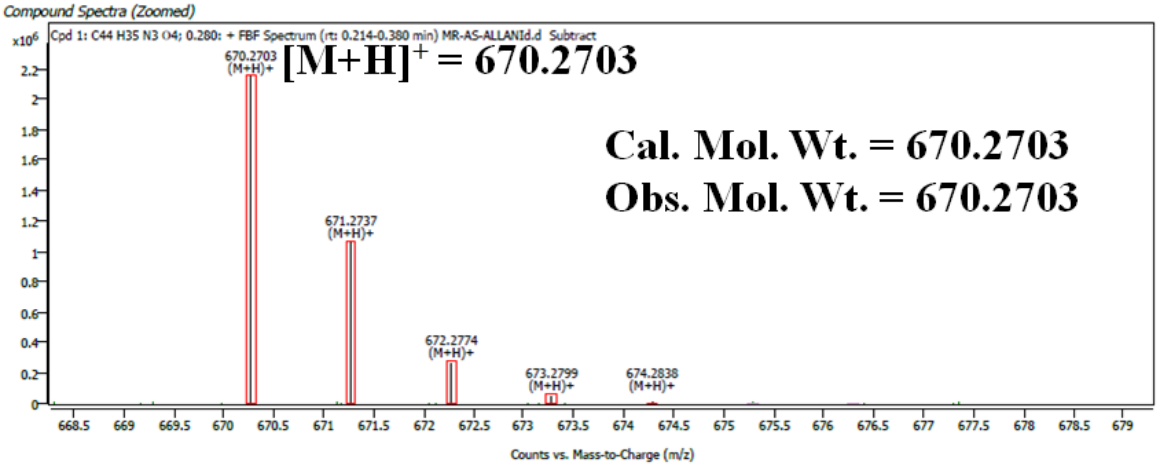



**Figure S17.** HR mass spectrum of the compound **1a**.

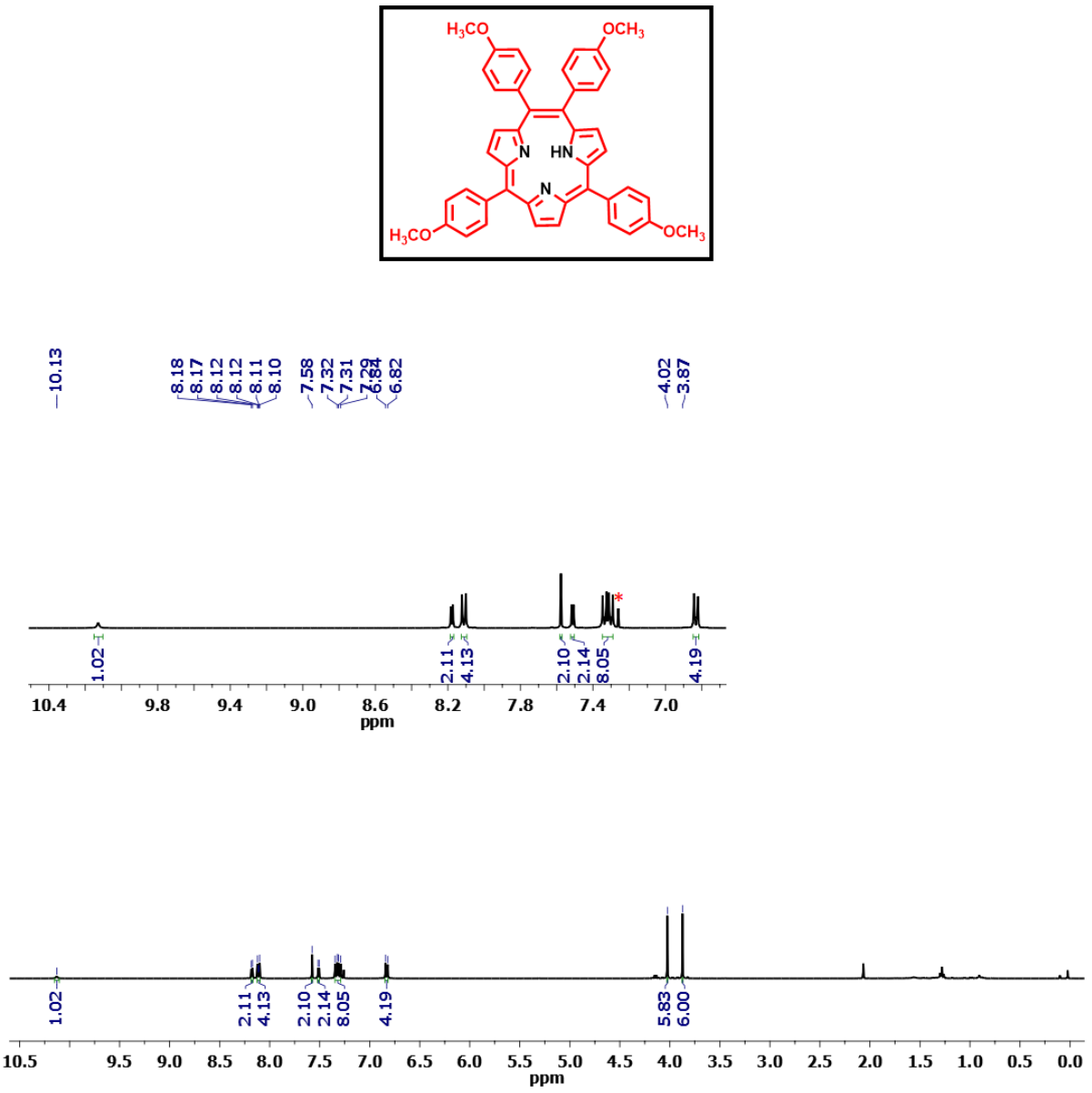



**Figure S18.** $^{1}$H NMR spectrum of the compound **1a** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

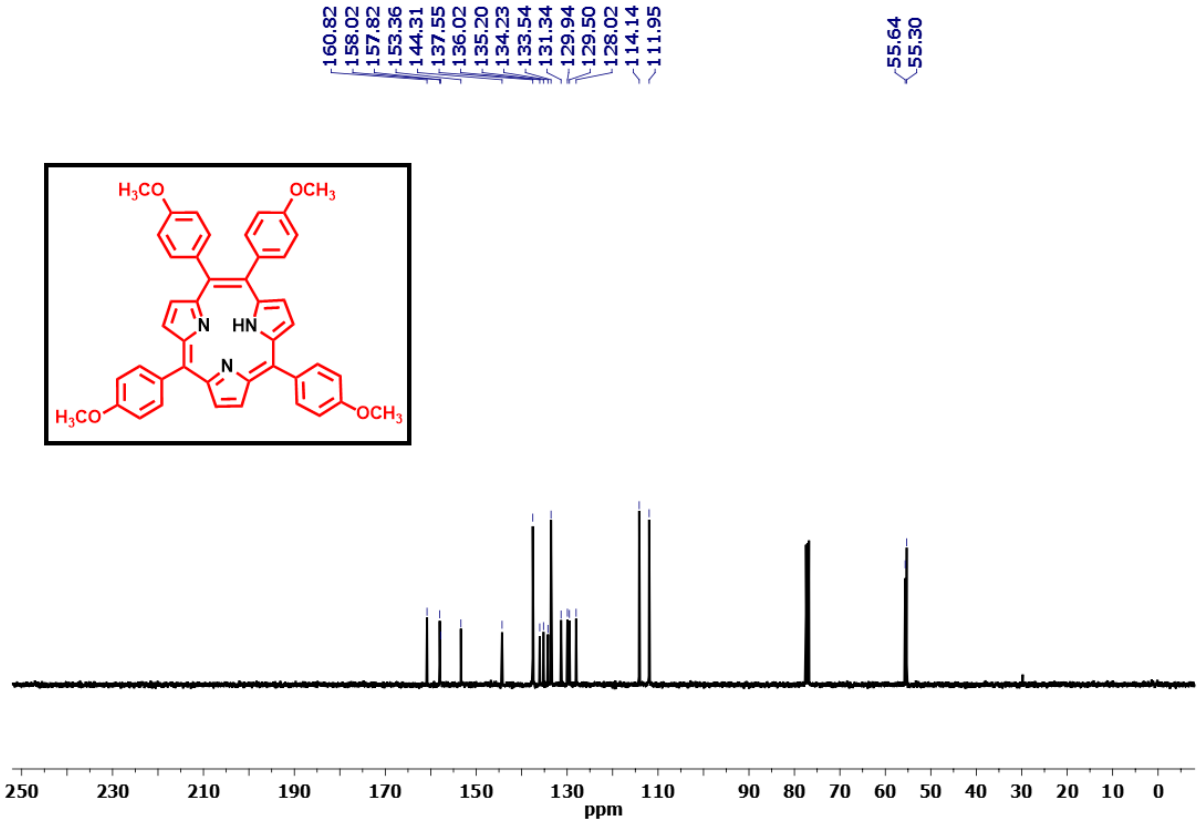
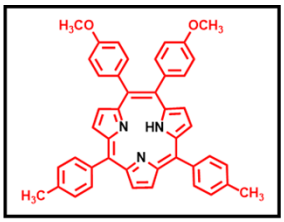



**Figure S19.** $^{13}C\{^{1}H\}$ NMR spectrum of the compound **1a** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.




**Compound Details**

**Cpd. 1: C44 H36 N3 O2**

| Formula | Theoretical Mass | Observed M/Z | Difference Da | Difference PPM | Score |
|---|---|---|---|---|---|
| C44 H36 N3 O2 | 638.2817 | 638.281043749702 | 0.962586678838306 | 1.50809291239938 | 97.52 |

*Compound Spectra (Zoomed)*

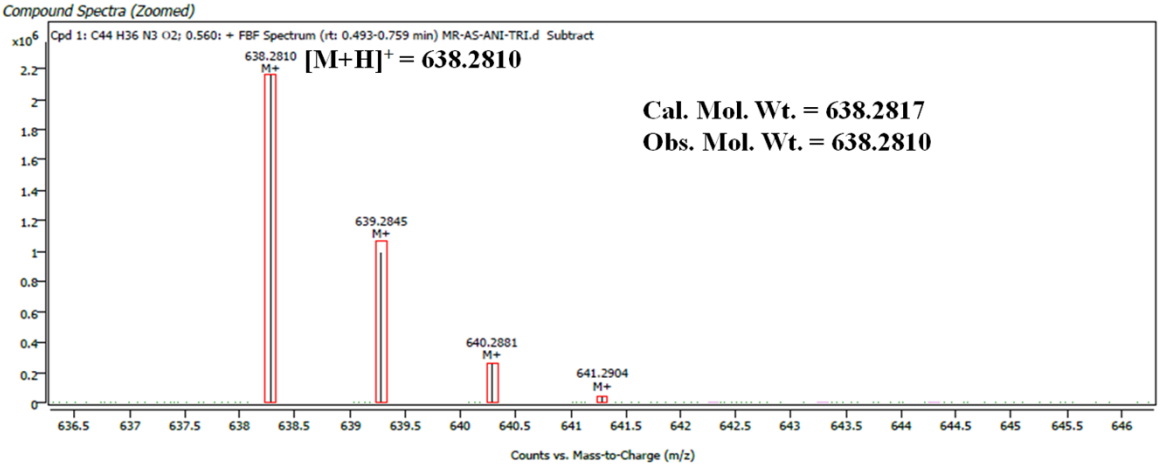



**Figure S20.** HR mass spectrum of the compound **1b**.

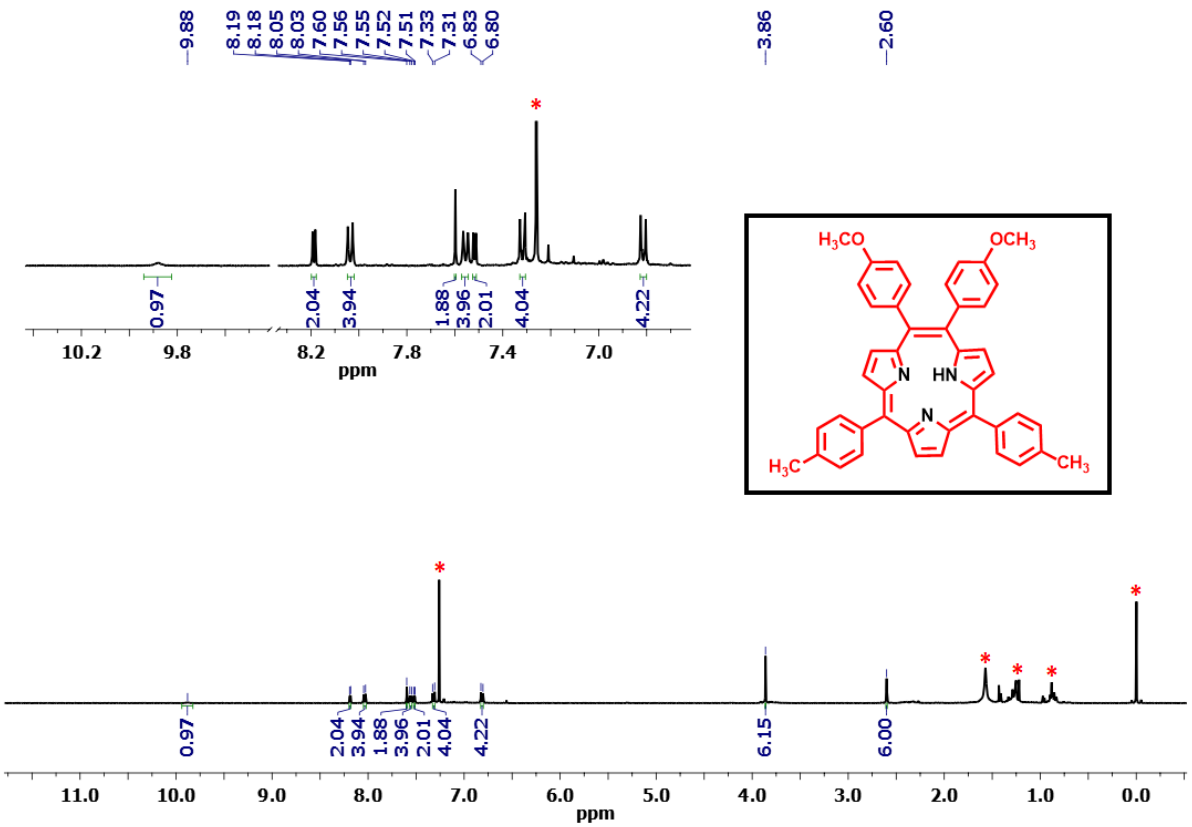



**Figure S21.** $^{1}H$ NMR spectrum of the compound **1b** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

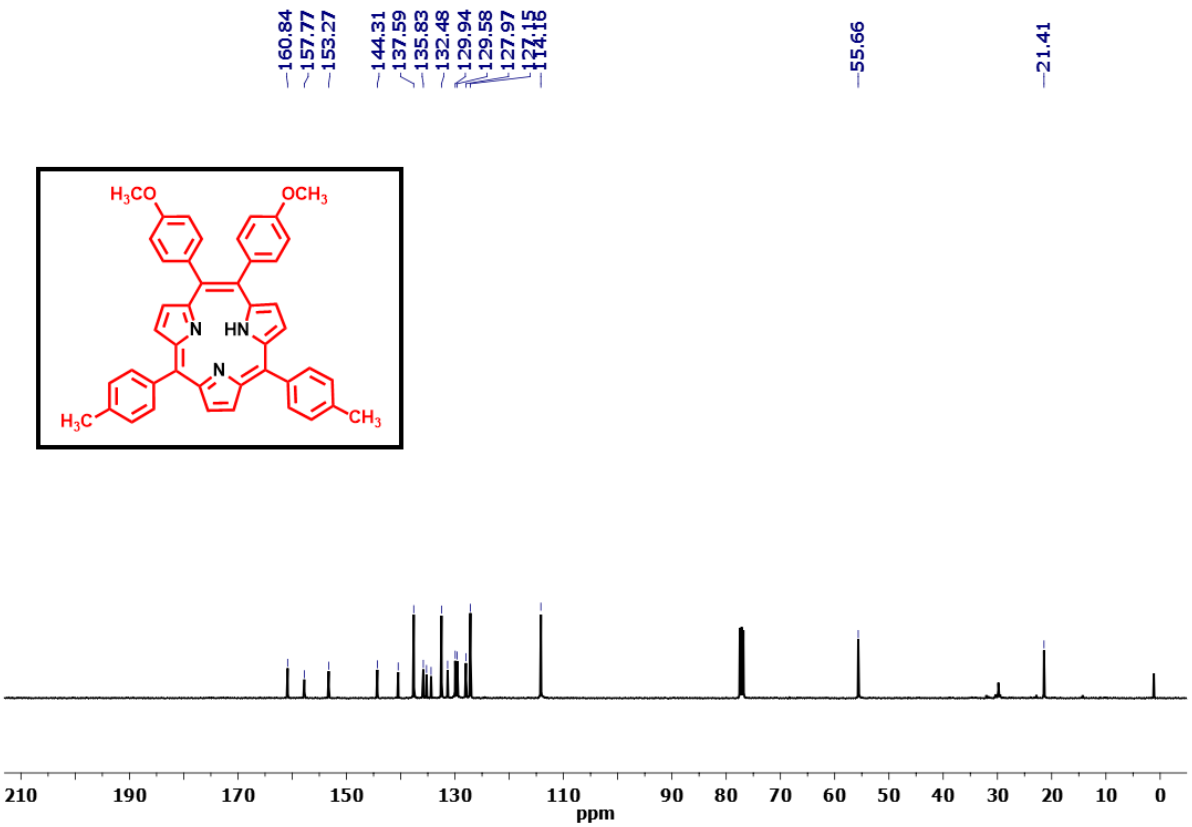
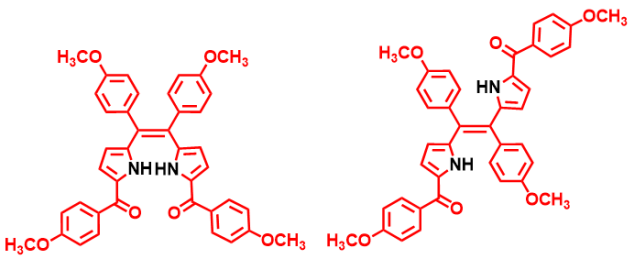



**Figure S22.** $^{13}C\{^{1}H\}$ NMR spectrum of the compound **1b** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.




**Compound Details**

**Cpd. 1: C40 H34 N2 O6**

| Formula | Theoretical Mass | Observed M/Z | Difference_Da | Difference_PPM | Score |
|---|---|---|---|---|---|
| C40 H34 N2 O6 | 638.2429 | 639.250278859377 | 1.16897562065787 | 1.83155635987685 | 97.15 |

*Compound Spectra (Zoomed)*

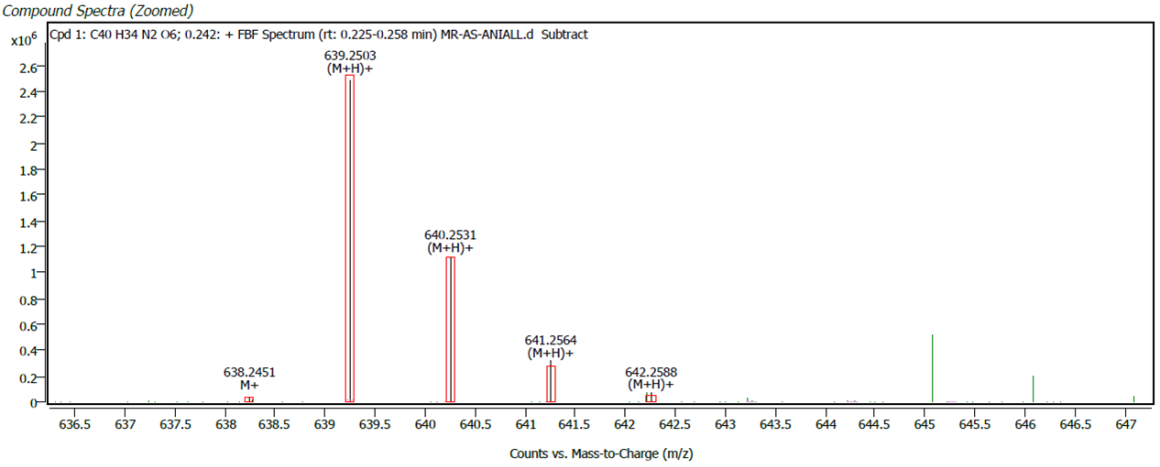



**Figure S23.** HR mass spectrum of the compound **5a**.

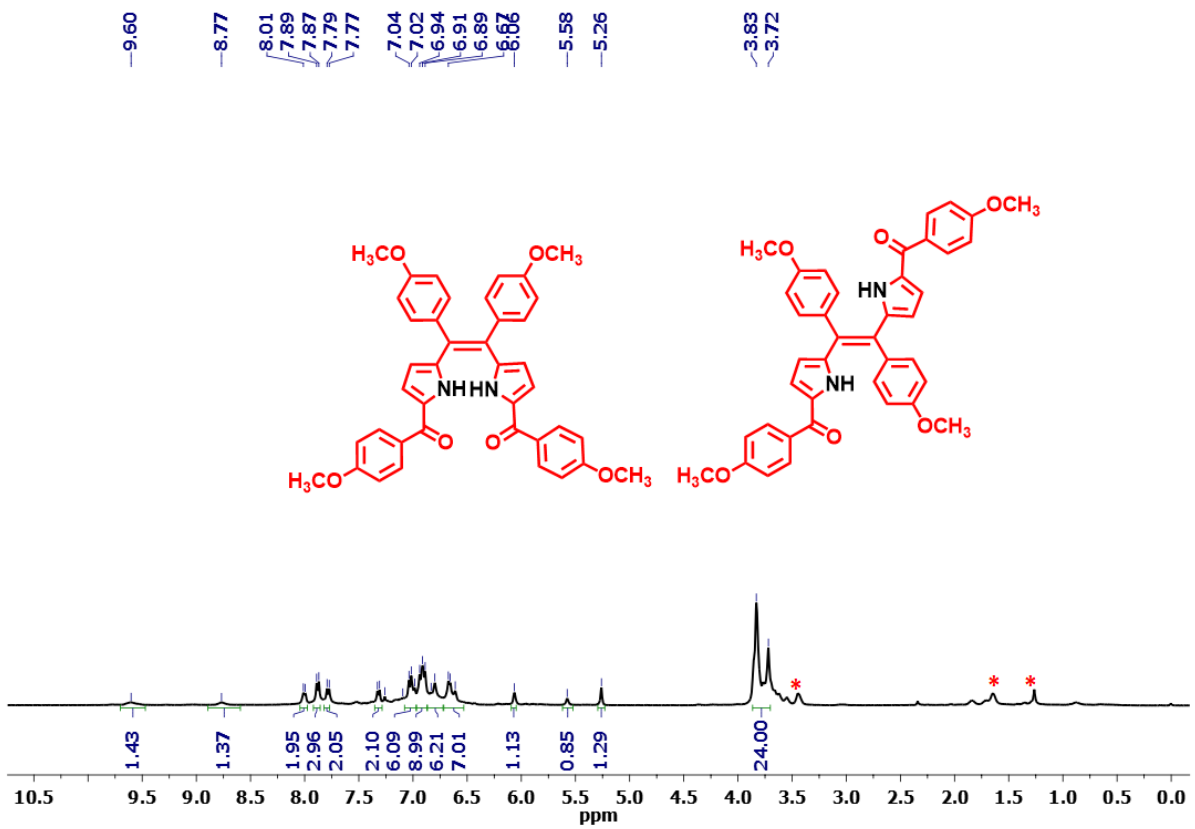



**Figure S24.** $^{1}$H NMR spectrum of the compound **5a (***E/Z* mixture**)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

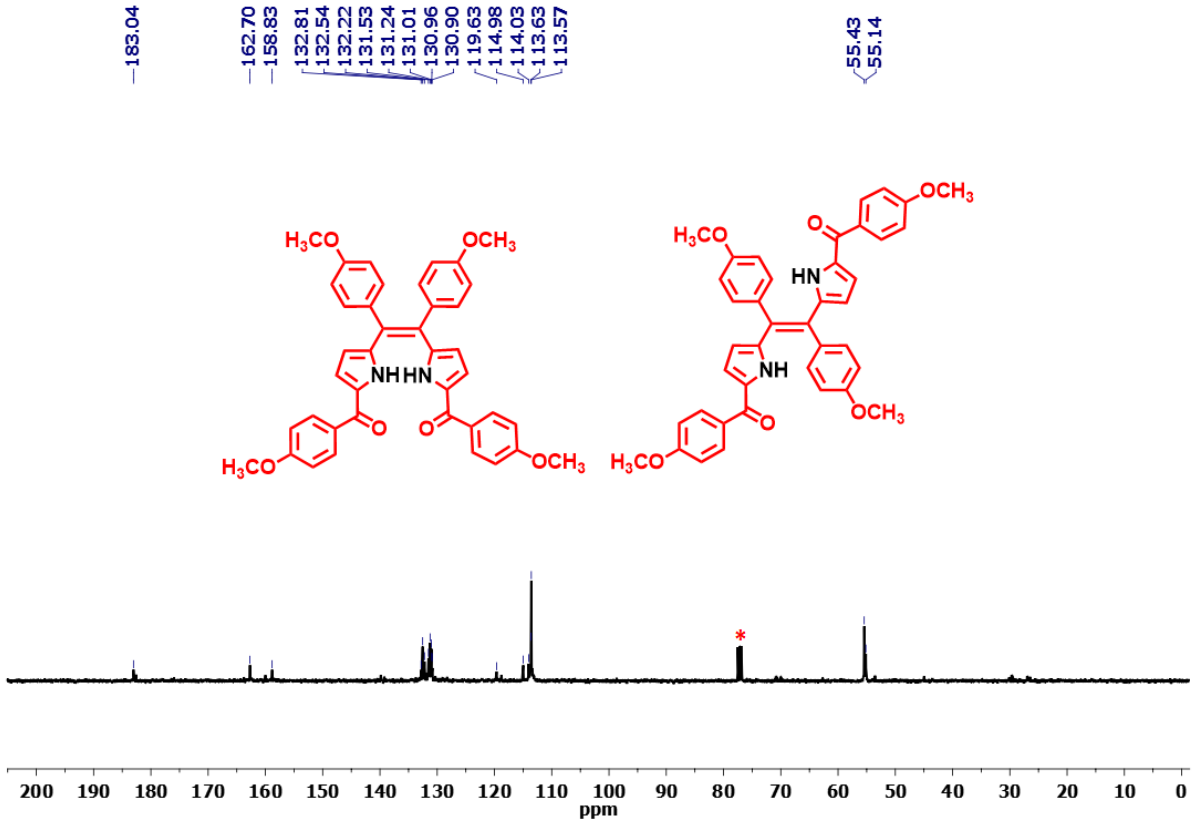
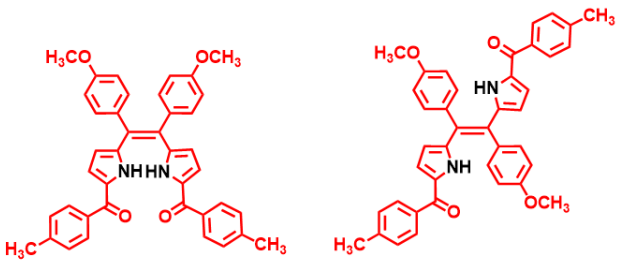



**Figure S25.** $^{13}C\{^{1}H\}$ NMR spectrum of the compound **5a (***E/Z* mixture**)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.




**Compound Details**

**Cpd. 1: C40 H34 N2 O4**

| Formula | Theoretical Mass | Observed M/Z | Difference_Da | Difference_PPM | Score |
|---|---|---|---|---|---|
| C40 H34 N2 O4 | 606.2531 | 607.259965727673 | 1.19844272910541 | 1.97680669197828 | 95.47 |

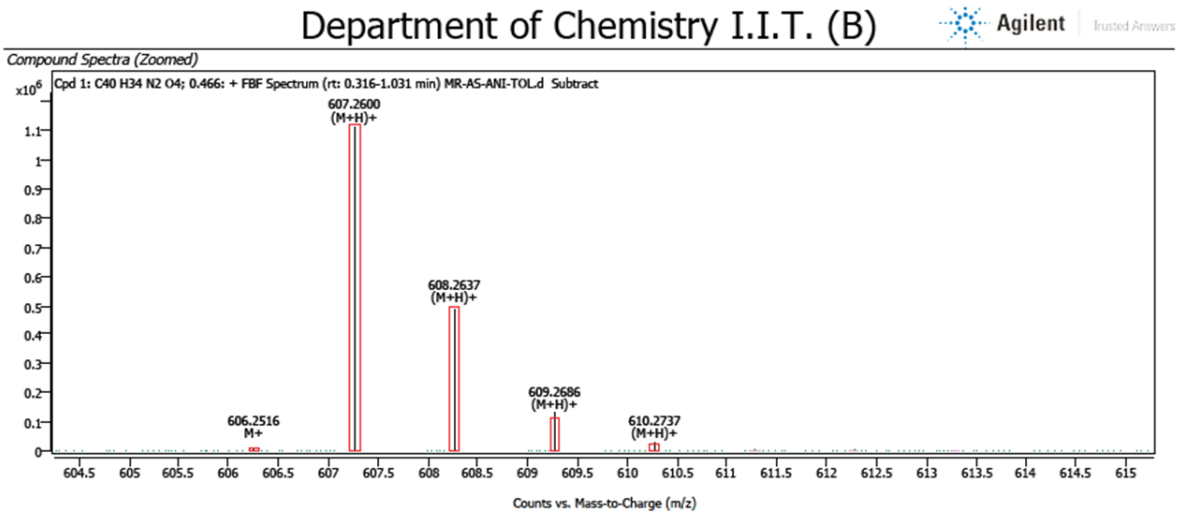



**Figure S26.** HR mass spectrum of the compound **5b**.

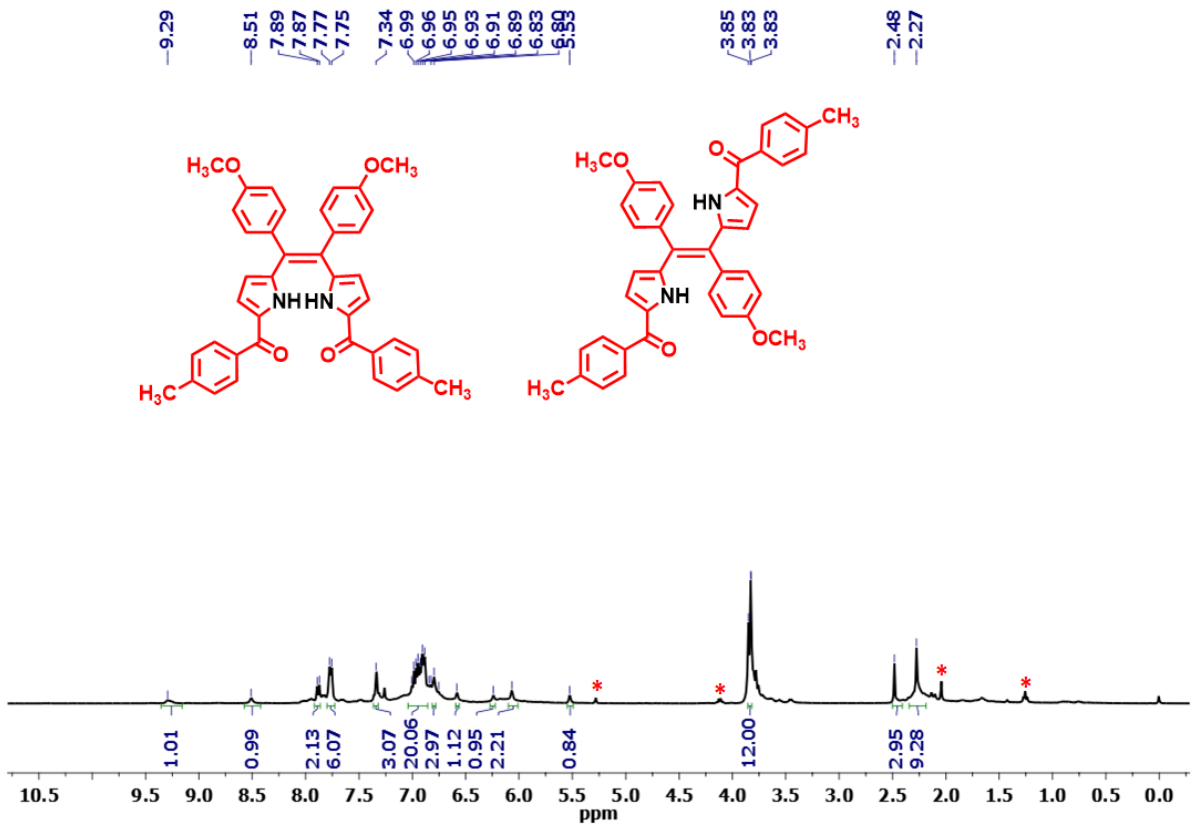



**Figure S27.** $^{1}$H NMR spectrum of the compound **5b (***E/Z* mixture**)** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

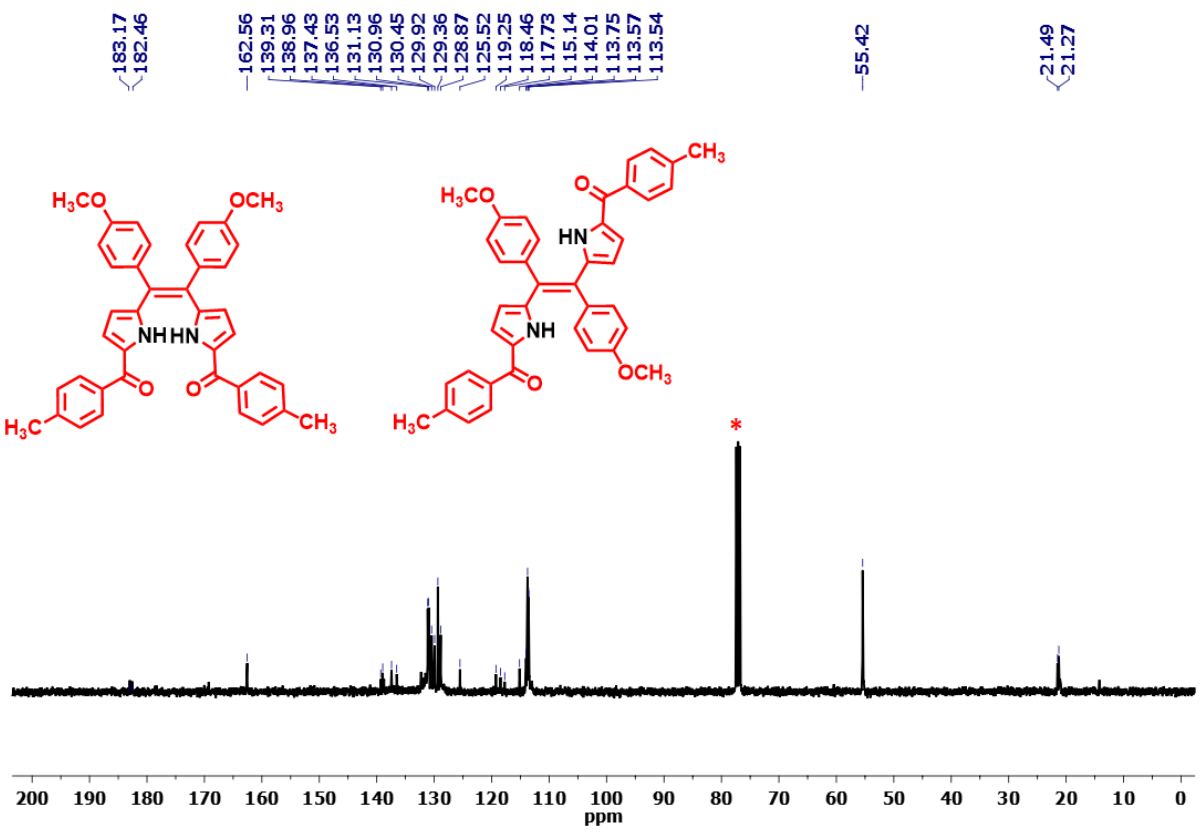



**Figure S28.** $^{13}C\{^{1}H\}$ NMR spectrum of the compound **5b** recorded in $CDCl_3$ on 400 MHz NMR instrument. Note: Peaks marked with asterisk (*) are due to residual solvents.

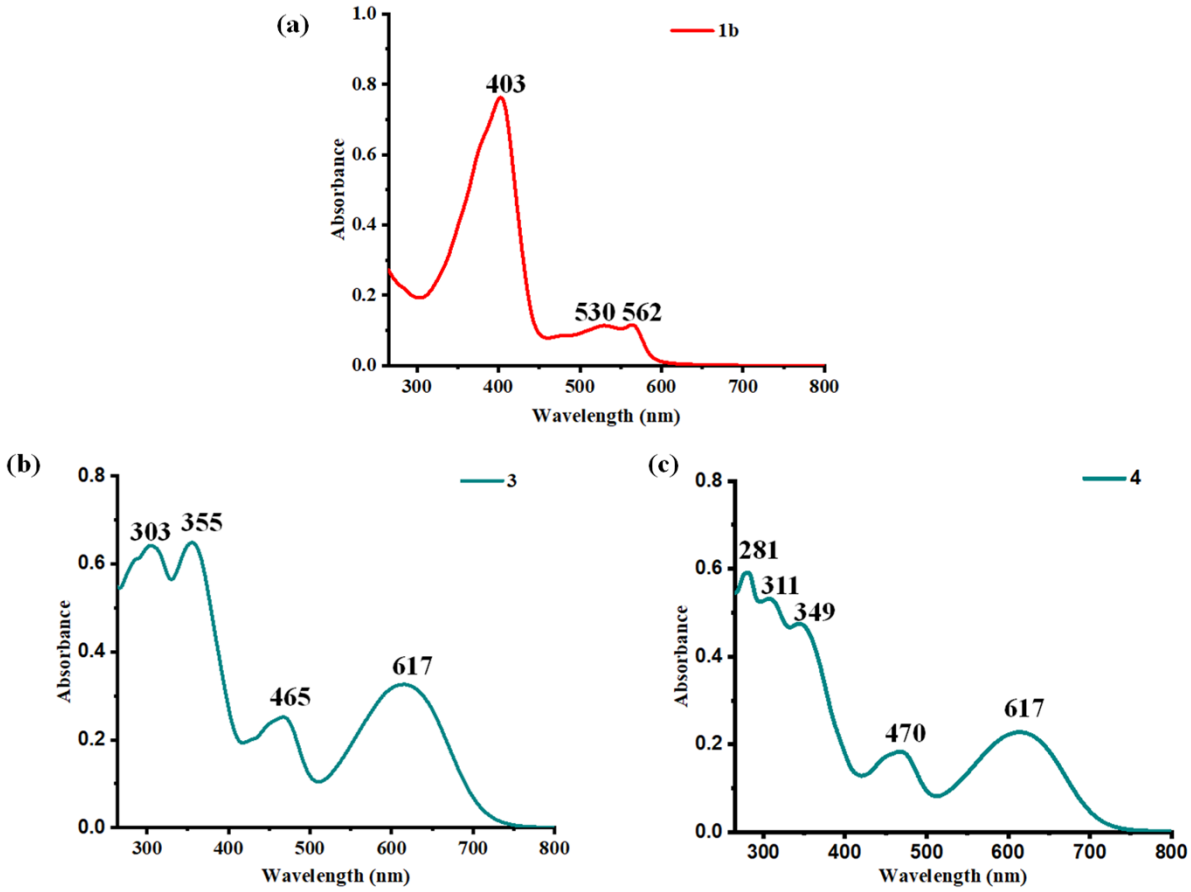



**Figure S29.** Absorption spectra of compounds**1b** (a), **3** (b), and **4** (c) ($10^{-5}$ M) recorded in chloroform at rt.

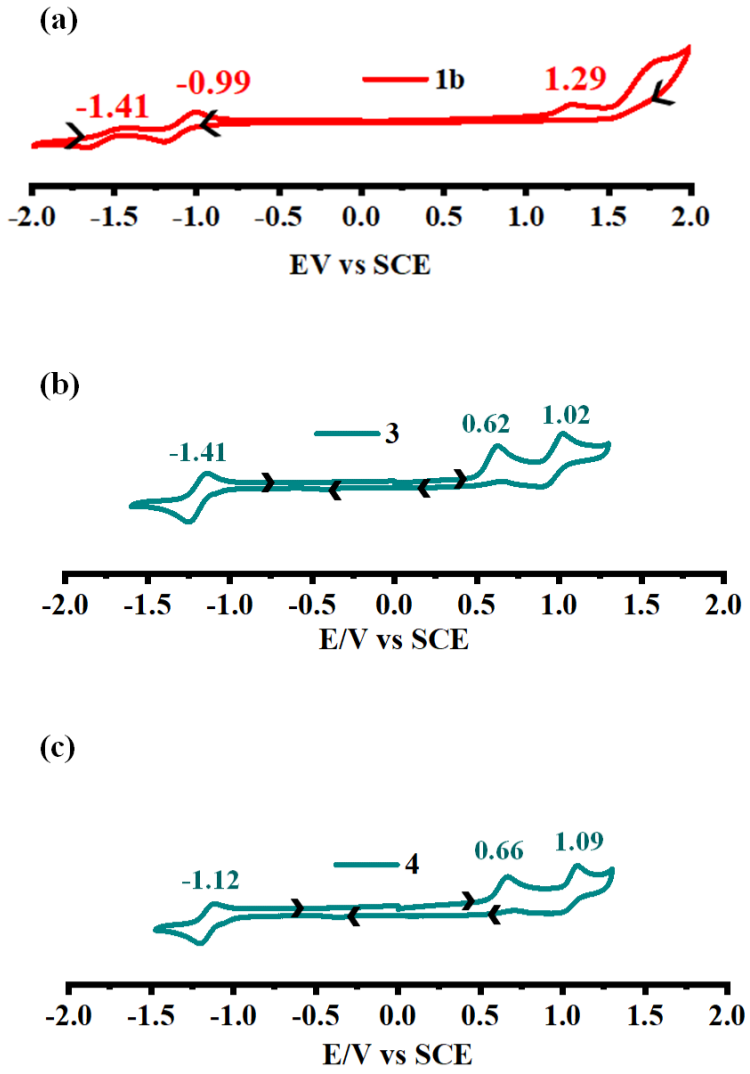



**Figure S30.** Comparison of cyclic voltammograms (red and green coloured solid line) of compounds **1b** (a), **3** (b) and **4** (c) recorded in dry $CH_2Cl_2$ with 0.1 M TBAP as the supporting electrolyte and a saturated calomel electrode (SCE) as the reference electrode at a scan rate of 50 $mVs^{-1}$. A saturated calomel electrode (SCE) was employed as the reference electrode, glassy carbon as the working electrode, and S34 platinum wire as the auxiliary electrode. (Note that polarographic convention has been followed for plotting CV starting at 0 V). All the potentials were calibrated using ferrocene as an external standard, taking E1/2 (Fc/Fc+) = 0.42 V versus SCE.

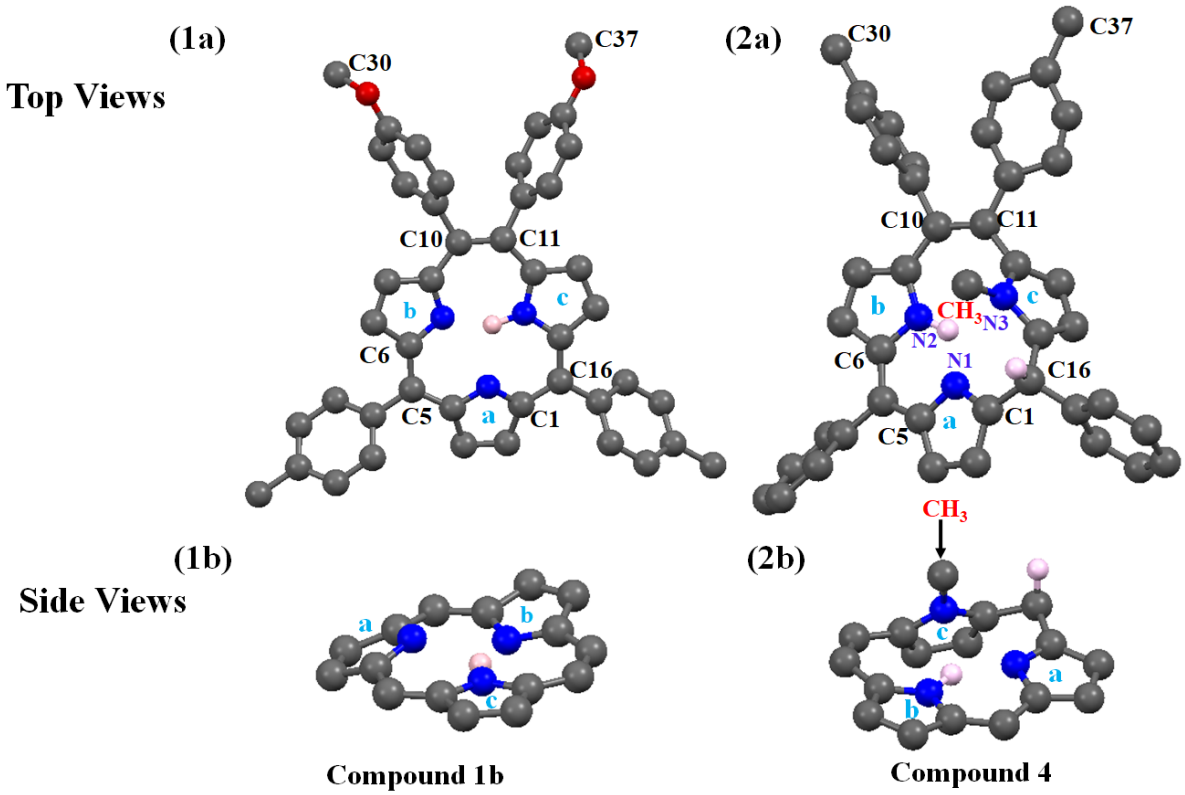
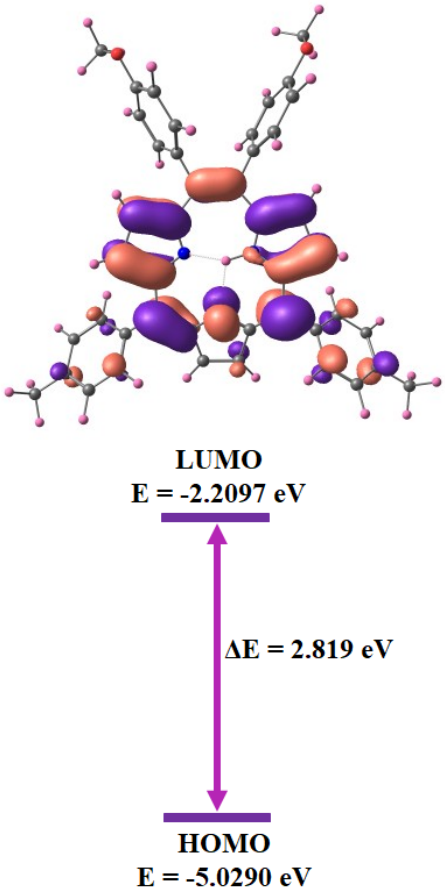



**Figure S31.** Ground state optimized structures with top views of compounds **1b** (1a) and **4** (2a) along with side views of compounds **1b** (1b) and **4** (2b). Hydrogen atoms were omitted for clarity in side views.




**Compound 1b**

**Figure S32.** Energy-level diagrams (selected FMOs) of compounds **1b** calculated by the B3LYP/6-3g (d, p) method.

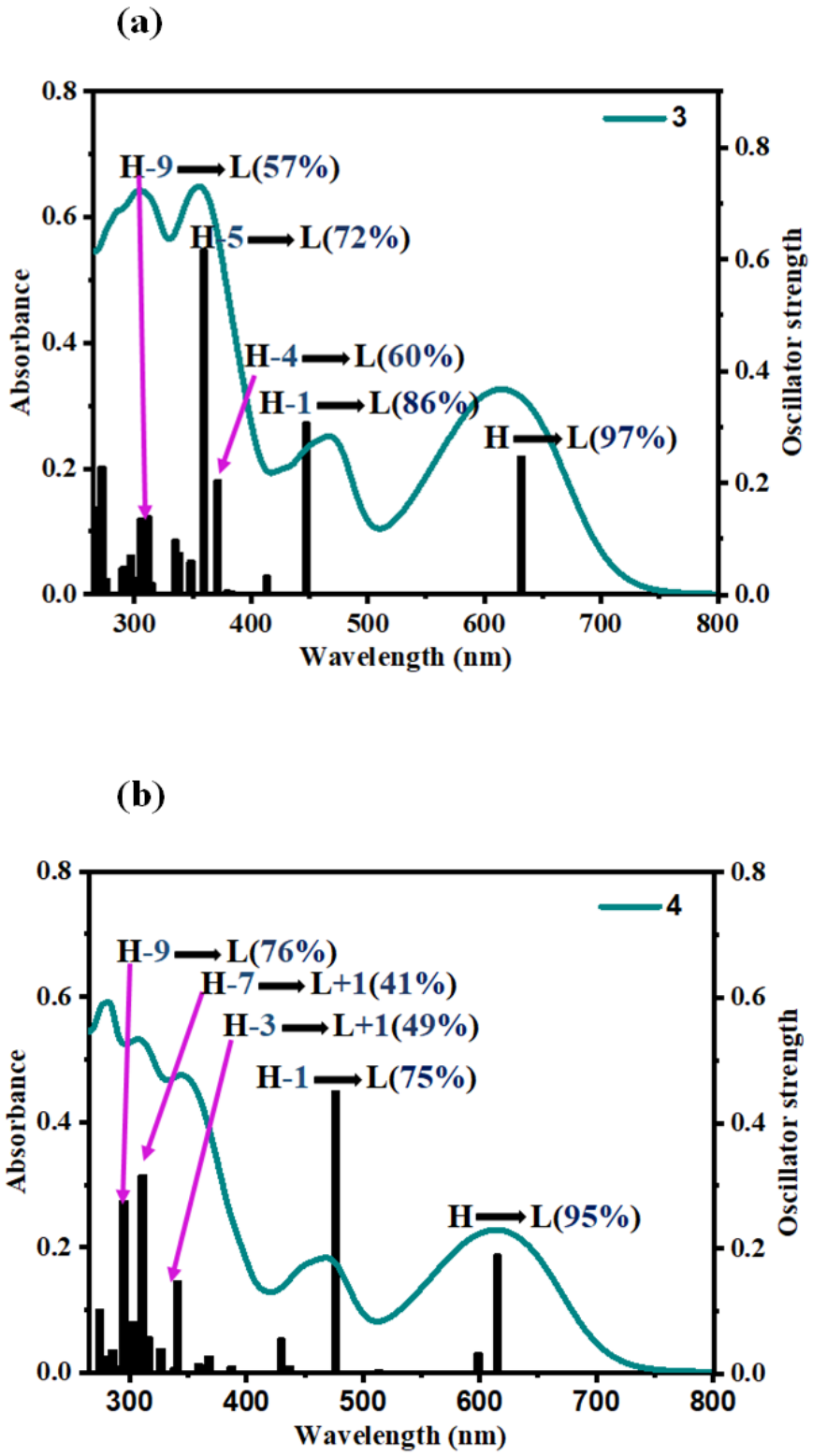



**Figure S33.** Calculated excitations (black vertical lines) and the experimental absorption spectrum (green line) for compounds **3** (a) and **4** (b).

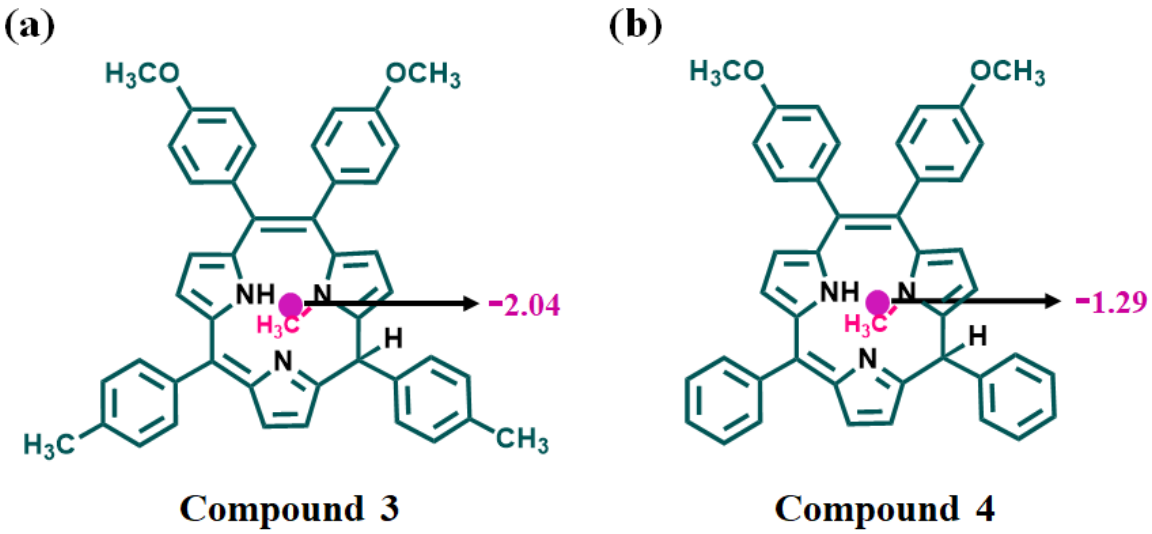



**Figure S34.** NICS(0) value for compounds **3** (a), and **4** (b) (pink circle denote the Bq atom).

**Table S1**. S0 optimized geometry of compound **2** at B3LYP/6-31g (d,p) level of theory.

# Sum of imaginary frequencies= 0

# Total Energy (hartree) = -2203.398151

| Atom | X | Y | Z | Atom | X | Y | Z |
|---|---|---|---|---|---|---|---|
| C | -2.18479 | -0.91016 | 0.020501 | H | 2.184655 | 2.482564 | 2.038409 |
| C | -2.21301 | 0.464202 | -0.16681 | C | -0.11828 | 0.953995 | 2.106827 |
| C | -1.04793 | 1.367029 | -0.21049 | H | -0.1503 | 1.773394 | 2.832795 |
| C | -1.00599 | -1.77752 | 0.058127 | H | -1.03262 | 0.369628 | 2.20322 |
| N | -0.03998 | 1.478628 | 0.749355 | H | 0.739054 | 0.31028 | 2.313252 |
| C | 0.936708 | 2.350806 | 0.291963 | C | -3.47709 | -1.65569 | 0.202623 |
| C | 0.5293 | 2.826204 | -0.94268 | C | -3.89745 | -2.64656 | -0.70378 |
| C | -0.71314 | 2.230453 | -1.2484 | C | -4.29983 | -1.39767 | 1.303791 |
| C | -0.96414 | -3.18419 | 0.255537 | C | -5.08913 | -3.33538 | -0.52251 |
| C | 0.36582 | -3.59463 | 0.196788 | H | -3.28081 | -2.87179 | -1.56892 |
| C | 1.163276 | -2.4465 | -0.01149 | C | -5.50058 | -2.08215 | 1.504691 |
| N | 0.286088 | -1.38408 | -0.12037 | H | -4.00128 | -0.63909 | 2.020862 |
| C | 2.593817 | -2.28304 | 0.040567 | C | -5.90207 | -3.0574 | 0.585985 |
| C | 2.312069 | 2.44088 | 0.946357 | H | -5.41598 | -4.09159 | -1.22877 |
| C | 3.163938 | -1.01913 | 0.246639 | H | -6.10507 | -1.84874 | 2.373029 |
| C | 4.528581 | -0.53368 | 0.244673 | C | -3.49046 | 1.176197 | -0.48115 |
| C | 4.459781 | 0.821166 | 0.487494 | C | -3.80552 | 2.37758 | 0.170345 |
| C | 3.052445 | 1.135745 | 0.630288 | C | -4.38092 | 0.731732 | -1.4783 |
| N | 2.323855 | 0.053052 | 0.483858 | C | -4.96935 | 3.092209 | -0.11457 |
| C | 3.44105 | -3.48817 | -0.08297 | H | -3.12458 | 2.764947 | 0.921996 |
| C | 3.069585 | 3.698948 | 0.546782 | C | -5.53357 | 1.438103 | -1.7871 |
| C | 3.114611 | 4.799019 | 1.40479 | H | -4.15627 | -0.17523 | -2.02729 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.779013 | 5.97925 | 1.060035 | C | -5.8435 | 2.621244 | -1.10073 |
| C | 4.421771 | 6.070005 | -0.17873 | H | -5.17556 | 4.008412 | 0.425837 |
| C | 4.390633 | 4.97407 | -1.05266 | H | -6.20939 | 1.097539 | -2.56467 |
| C | 3.724713 | 3.809829 | -0.69131 | O | -7.05258 | -3.78831 | 0.677057 |
| C | 4.53276 | -3.70659 | 0.78293 | O | -7.0037 | 3.238351 | -1.47264 |
| C | 5.335418 | -4.82971 | 0.659974 | C | -7.35516 | 4.450359 | -0.82529 |
| C | 5.076907 | -5.77715 | -0.34288 | H | -6.59991 | 5.23033 | -0.98626 |
| C | 3.997301 | -5.58249 | -1.21339 | H | -8.29894 | 4.767965 | -1.27113 |
| C | 3.192871 | -4.45203 | -1.07287 | H | -7.49663 | 4.308224 | 0.253953 |
| H | 0.738347 | -4.59898 | 0.334049 | C | -7.91906 | -3.53837 | 1.771813 |
| H | -1.82185 | -3.8153 | 0.42569 | H | -8.76616 | -4.21443 | 1.646532 |
| H | -1.29638 | 2.364631 | -2.14811 | H | -7.43067 | -3.74764 | 2.732379 |
| H | 1.092884 | 3.503908 | -1.56642 | H | -8.28168 | -2.50243 | 1.773825 |
| H | 5.420767 | -1.1155 | 0.057785 | O | 5.104376 | 7.16705 | -0.62439 |
| H | 5.285509 | 1.516409 | 0.555949 | O | 5.924433 | -6.84288 | -0.38267 |
| H | 6.165858 | -5.00478 | 1.335834 | C | 5.166209 | 8.304501 | 0.22 |
| H | 4.729127 | -2.99272 | 1.575513 | H | 5.669223 | 8.079119 | 1.169389 |
| H | 2.368374 | -4.30152 | -1.76179 | H | 5.745751 | 9.05264 | -0.32295 |
| H | 3.77965 | -6.29313 | -2.00153 | H | 4.167484 | 8.707492 | 0.432623 |
| H | 2.618516 | 4.742513 | 2.370765 | C | 5.707939 | -7.84084 | -1.36977 |
| H | 3.790237 | 6.807029 | 1.759028 | H | 5.794968 | -7.43168 | -2.38408 |
| H | 3.718466 | 2.968206 | -1.37695 | H | 6.487056 | -8.58853 | -1.21635 |
| H | 4.898444 | 5.058456 | -2.00788 | H | 4.724901 | -8.31483 | -1.25651 |
| H | 0.681456 | -0.43957 | -0.08174 | | | | |

**Table S2**. S0 optimized geometry of compound **3** at B3LYP/6-31g (d,p) level of theory.

# Sum of imaginary frequencies= 0

# Total Energy (hartree) = -2052.988749

| **Atom** | **X** | **Y** | **Z** | **Atom** | **X** | **Y** | **Z** |
|---|---|---|---|---|---|---|---|
| C | 1.940809 | 0.895204 | -0.02166 | H | -0.92581 | 0.425924 | -0.13405 |
| C | 1.966787 | -0.48492 | -0.162 | H | -2.45815 | -2.42304 | 2.060378 |
| C | 0.79913 | -1.38554 | -0.18945 | C | -0.1534 | -0.89788 | 2.104258 |
| C | 0.764008 | 1.76584 | -0.0268 | H | -0.13305 | -1.69268 | 2.857386 |
| N | -0.2174 | -1.4669 | 0.764208 | H | 0.761738 | -0.31344 | 2.192215 |
| C | -1.19194 | -2.34999 | 0.32352 | H | -1.01067 | -0.24478 | 2.279621 |
| C | -0.77491 | -2.86221 | -0.89293 | C | -6.16376 | 7.019562 | -0.72729 |
| C | 0.471811 | -2.27866 | -1.20439 | H | -5.74348 | 7.861617 | -0.16296 |
| C | 0.723448 | 3.179841 | 0.114566 | H | -7.18012 | 6.856295 | -0.35692 |
| C | -0.60471 | 3.589957 | 0.028809 | C | -5.41314 | -7.36786 | -0.41394 |
| C | -1.40302 | 2.435293 | -0.13924 | H | -6.45835 | -7.31949 | -0.08317 |
| N | -0.52709 | 1.367889 | -0.1987 | H | -4.9608 | -8.23942 | 0.068793 |
| C | -2.83272 | 2.275928 | -0.08833 | H | -5.42345 | -7.54633 | -1.49342 |
| C | -2.57374 | -2.41565 | 0.966217 | H | -6.22916 | 7.331701 | -1.7738 |
| C | -3.40948 | 1.021613 | 0.149898 | C | 3.233174 | 1.643192 | 0.149672 |
| C | -4.77774 | 0.546027 | 0.176173 | C | 3.667446 | 2.600966 | -0.78528 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.71586 | -0.80026 | 0.462589 | C | 4.041674 | 1.421164 | 1.269099 |
| C | -3.30878 | -1.12043 | 0.601964 | C | 4.858856 | 3.292617 | -0.61323 |
| N | -2.57449 | -0.04908 | 0.41097 | H | 3.062289 | 2.79769 | -1.66537 |
| C | -3.67717 | 3.482371 | -0.24673 | C | 5.241907 | 2.109066 | 1.460936 |
| C | -3.32579 | -3.6873 | 0.598498 | H | 3.732249 | 0.688526 | 2.008205 |
| C | -3.34964 | -4.77154 | 1.482764 | C | 5.657427 | 3.051026 | 0.514102 |
| C | -4.00756 | -5.95567 | 1.154354 | H | 5.196471 | 4.02316 | -1.34109 |
| C | -4.67018 | -6.09823 | -0.07097 | H | 5.835153 | 1.904197 | 2.344095 |
| C | -4.64446 | -5.01312 | -0.95584 | C | 3.245116 | -1.21091 | -0.43766 |
| C | -3.98679 | -3.82761 | -0.62892 | C | 3.547749 | -2.39166 | 0.256179 |
| C | -4.74752 | 3.740714 | 0.627456 | C | 4.148998 | -0.80211 | -1.43806 |
| C | -5.54636 | 4.869189 | 0.464894 | C | 4.71212 | -3.11912 | 0.008612 |
| C | -5.31319 | 5.782099 | -0.57223 | H | 2.856584 | -2.75217 | 1.011861 |
| C | -4.24742 | 5.523224 | -1.44444 | C | 5.302399 | -1.52215 | -1.70995 |
| C | -3.4395 | 4.400895 | -1.28455 | H | 3.9343 | 0.087152 | -2.01902 |
| H | -0.97632 | 4.599893 | 0.119974 | C | 5.599704 | -2.68341 | -0.98179 |
| H | 1.581134 | 3.815733 | 0.265792 | H | 4.908453 | -4.01797 | 0.580868 |
| H | 1.063296 | -2.44097 | -2.094 | H | 5.988635 | -1.20945 | -2.4901 |
| H | -1.33529 | -3.55609 | -1.50159 | O | 6.808813 | 3.781587 | 0.593944 |
| H | -5.66732 | 1.129504 | -0.01758 | O | 6.761774 | -3.31603 | -1.31952 |
| H | -5.54549 | -1.4869 | 0.563112 | C | 7.101404 | -4.50752 | -0.62894 |
| H | -6.3626 | 5.048201 | 1.160422 | H | 6.345507 | -5.29 | -0.77373 |
| H | -4.93524 | 3.05866 | 1.449894 | H | 8.049379 | -4.84216 | -1.05284 |
| H | -2.63012 | 4.213601 | -1.98254 | H | 7.230403 | -4.33075 | 0.446714 |
| H | -4.05089 | 6.207886 | -2.26577 | C | 7.661363 | 3.567493 | 1.707173 |
| H | -2.84115 | -4.6905 | 2.44061 | H | 8.511804 | 4.236758 | 1.568895 |
| H | -4.00731 | -6.78143 | 1.861872 | H | 7.161985 | 3.811044 | 2.653886 |
| H | -3.98941 | -3.00118 | -1.33308 | H | 8.020962 | 2.531364 | 1.749295 |
| H | -5.14747 | -5.09537 | -1.91644 | | | | |

**Table S3** S0 optimized geometry of compound **4** at B3LYP/6-31g (d,p) level of theory.

# Sum of imaginary frequencies= 0

# Total Energy (hartree) = -1821.247846

| **Atom** | **X** | **Y** | **Z** | **Atom** | **X** | **Y** | **Z** |
|---|---|---|---|---|---|---|---|
| C | 2.088041 | 0.469227 | 0.000521 | C | -4.7635 | 5.385319 | 0.64261 |
| C | 1.946402 | -0.90444 | -0.10674 | C | -4.45354 | 6.238839 | -0.4176 |
| C | 3.177508 | -1.68101 | -0.19477 | C | -3.47983 | 5.862848 | -1.34478 |
| C | 0.687037 | -1.65988 | -0.24512 | C | -2.81812 | 4.643516 | -1.21242 |
| C | 1.058651 | 1.492672 | -0.03082 | H | -0.27109 | 4.540419 | -0.00159 |
| C | 3.487861 | 1.01808 | 0.091304 | H | 2.168383 | 3.41998 | 0.058852 |
| C | 4.480118 | -1.12602 | -0.16941 | H | 0.860168 | -2.59684 | -2.21852 |
| C | 5.700138 | -1.51403 | -0.20567 | H | -1.68454 | -3.40891 | -1.75036 |
| C | 5.899189 | -2.91574 | -0.3288 | H | -5.39314 | 1.718371 | 0.066174 |
| C | 4.600481 | -3.43577 | -0.36697 | H | -5.62896 | -0.9197 | 0.49138 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.386005 | -3.07392 | -0.31172 | H | -5.51266 | 5.67452 | 1.373843 |
| C | 4.109442 | 1.225758 | 1.342749 | H | -4.33647 | 3.508436 | 1.608745 |
| C | 5.352997 | 1.837348 | 1.425981 | H | -2.07269 | 4.347197 | -1.94304 |
| C | 6.020104 | 2.280464 | 0.273658 | H | -3.23762 | 6.518018 | -2.17644 |
| C | 5.385076 | 2.121226 | -0.96651 | H | -3.4557 | -4.59077 | 2.062846 |
| C | 4.142158 | 1.508175 | -1.06102 | H | -4.90861 | -6.43848 | 1.296535 |
| N | -0.35391 | -1.65868 | 0.680663 | H | -4.23821 | -2.45417 | -1.57751 |
| C | -1.42949 | -2.36507 | 0.159928 | H | -5.68508 | -4.30265 | -2.35335 |
| C | -1.05296 | -2.84421 | -1.08094 | H | 5.818838 | 1.973657 | 2.398171 |
| C | 0.27369 | -2.41801 | -1.32917 | H | 3.605308 | 0.889609 | 2.243646 |
| C | 1.221785 | 2.903402 | 0.006784 | H | 5.876322 | 2.477291 | -1.8679 |
| C | -0.04375 | 3.485315 | -0.03623 | H | 3.662362 | 1.390034 | -2.02758 |
| C | -0.99737 | 2.440372 | -0.09174 | H | -0.8086 | 0.384682 | -0.02038 |
| N | -0.279 | 1.263471 | -0.10904 | H | -2.73256 | -2.39354 | 1.870836 |
| C | -2.43621 | 2.464554 | -0.01944 | C | -0.23622 | -1.21981 | 2.064732 |
| C | -2.82049 | -2.27824 | 0.780119 | H | -0.25328 | -2.07741 | 2.745617 |
| C | -3.16998 | 1.292724 | 0.194341 | H | 0.714431 | -0.70201 | 2.188884 |
| C | -4.59208 | 1.007383 | 0.21437 | H | -1.04647 | -0.53166 | 2.313983 |
| C | -4.71405 | -0.34708 | 0.422888 | C | 7.197502 | -3.66121 | -0.40574 |
| C | -3.36218 | -0.86736 | 0.522448 | H | 7.83077 | -3.42444 | 0.455948 |
| N | -2.48889 | 0.102724 | 0.388499 | H | 7.757321 | -3.37499 | -1.30352 |
| C | -3.12545 | 3.771351 | -0.15288 | C | 7.391172 | 2.901493 | 0.366421 |
| C | -3.73992 | -3.3926 | 0.297064 | H | 8.167634 | 2.12964 | 0.303472 |
| C | -3.94464 | -4.52536 | 1.093943 | H | 7.530497 | 3.427523 | 1.315406 |
| C | -4.76232 | -5.56944 | 0.661463 | H | 7.036339 | -4.74183 | -0.43213 |
| C | -5.3922 | -5.49538 | -0.58154 | H | 7.567575 | 3.609351 | -0.44854 |
| C | -5.19757 | -4.37107 | -1.38498 | H | -4.96582 | 7.190961 | -0.51973 |
| C | -4.37877 | -3.3283 | -0.94911 | H | -6.0315 | -6.30554 | -0.91998 |
| C | -4.10814 | 4.162309 | 0.773713 | | | | |

**Table S4**. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **2**.

| **Wavelength (nm)** | **Osc. Strength** | **Major contributions** |
|---|---|---|
| 625.235466527 | 0.2518 | HOMO->LUMO (97%) |
| 445.329524845 | 0.2951 | H-1->LUMO (86%) |
| 410.530091759 | 0.0808 | H-2->LUMO (94%) |
| 395.647933791 | 0.0692 | H-3->LUMO (87%) |
| 379.737191462 | 0.0978 | H-6->LUMO (12%), H-5->LUMO (44%), H-4->LUMO (35%) |
| 378.543012891 | 0.226 | H-7->LUMO (16%), H-5->LUMO (21%), H-4->LUMO (58%) |
| 374.145069142 | 0.0172 | H-7->LUMO (26%), H-6->LUMO (58%), H-3->LUMO (10%) |
| 368.277172852 | 0.4875 | HOMO->L+1 (79%) |
| 348.573738402 | 0.0375 | H-7->LUMO (46%), H-6->LUMO (18%), H-5->LUMO (22%) |
| 337.344415455 | 0.1037 | H-13->LUMO (12%), H-8->LUMO (68%) |
| 314.138524912 | 0.1105 | H-13->LUMO (15%), H-1->L+1 (69%) |
| 311.049154572 | 0.0038 | H-13->LUMO (11%), HOMO->L+2 (66%) |

| | | |
|---|---|---|
| 309.883011778 | 0.0404 | H-13->LUMO (18%), H-8->LUMO (11%), HOMO->L+2 (28%), HOMO->L+3 (13%) |
| 307.142450547 | 0.1026 | HOMO->L+3 (63%), HOMO->L+4 (15%) |
| 305.809123677 | 0.0592 | H-9->LUMO (24%), HOMO->L+5 (47%) |
| 301.716090361 | 0.0005 | H-10->LUMO (95%) |
| 300.087600475 | 0.0102 | H-11->LUMO (81%) |
| 299.247424725 | 0.0481 | H-9->LUMO (23%), HOMO->L+3 (13%), HOMO->L+4 (56%) |
| 298.304244189 | 0.0108 | H-12->LUMO (27%), H-9->LUMO (17%), HOMO->L+4 (18%), HOMO->L+5 (26%) |
| 297.831302727 | 0.0042 | H-13->LUMO (23%), H-12->LUMO (35%), H-9->LUMO (16%), HOMO->L+5 (10%) |
| 291.364164717 | 0.0137 | H-2->L+1 (87%) |
| 282.907456959 | 0.0178 | HOMO->L+6 (95%) |
| 277.972766433 | 0.0661 | HOMO->L+7 (39%), HOMO->L+8 (48%) |
| 275.845313396 | 0.1268 | H-14->LUMO (47%), HOMO->L+7 (28%) |
| 274.532113308 | 0.1509 | H-14->LUMO (21%), H-3->L+1 (22%), HOMO->L+7 (26%), HOMO->L+8 (17%) |
| 271.365521268 | 0.061 | H-3->L+1 (58%), HOMO->L+8 (18%) |
| 268.590786621 | 0.0674 | H-5->L+1 (72%) |
| 266.558151511 | 0.0211 | H-4->L+1 (64%) |
| 265.320335999 | 0.0444 | H-1->L+2 (71%), HOMO->L+9 (16%) |
| 265.036752912 | 0.1926 | H-1->L+2 (22%), HOMO->L+9 (53%) |
| 258.176692444 | 0.0163 | H-6->L+1 (62%), H-1->L+3 (14%) |
| 257.132591589 | 0.0117 | H-6->L+1 (10%), H-1->L+3 (71%), H-1->L+4 (10%) |
| 255.579544871 | 0.0089 | H-7->L+1 (54%), H-1->L+4 (24%) |
| 254.964615062 | 0.0274 | H-7->L+1 (25%), H-1->L+4 (58%) |
| 252.174659342 | 0.038 | H-1->L+5 (85%) |
| 247.197130976 | 0.0384 | H-8->L+1 (11%), H-2->L+3 (30%), H-2->L+4 (10%), H-2->L+5 (11%) |
| 245.634854903 | 0.0411 | H-3->L+3 (11%), H-3->L+4 (25%), H-2->L+4 (15%) |
| 245.018364911 | 0.0134 | H-9->L+1 (18%), H-2->L+3 (11%), H-2->L+5 (37%) |
| 243.383049374 | 0.0287 | H-8->L+1 (17%), H-1->L+6 (45%) |
| 242.64475999 | 0.0628 | H-8->L+1 (33%), H-4->L+2 (22%), H-3->L+2 (11%), H-2->L+2 (10%) |
| 241.981757348 | 0.0523 | H-8->L+1 (30%), H-1->L+6 (38%) |
| 239.277815756 | 0.0278 | H-15->LUMO (57%), H-1->L+7 (29%) |
| 238.577957613 | 0.0045 | H-15->LUMO (27%), H-1->L+7 (49%) |
| 238.133473566 | 0.0023 | H-3->L+2 (13%), H-2->L+2 (62%) |
| 234.427834314 | 0.0123 | H-11->L+1 (24%), H-9->L+1 (15%), H-2->L+3 (25%) |
| 233.522673445 | 0.0559 | H-1->L+8 (78%) |
| 232.746748662 | 0.0429 | H-11->L+1 (21%), H-9->L+1 (15%), H-2->L+4 (24%) |
| 232.480532921 | 0.0249 | H-9->L+1 (16%), H-2->L+4 (31%), H-2->L+5 (18%) |
| 231.949924255 | 0.0018 | H-4->L+2 (25%), H-3->L+2 (52%) |
| 230.964760366 | 0.0057 | H-1->L+8 (10%), H-1->L+9 (53%), HOMO->L+10 (23%) |
| 228.922069816 | 0.0176 | H-11->L+1 (32%), H-5->L+3 (11%), H-4->L+3 (16%) |
| 226.890279096 | 0.0031 | H-7->L+2 (25%), H-6->L+2 (58%), H-3->L+2 (12%) |
| 226.153608909 | 0.0025 | H-5->L+3 (17%), H-3->L+3 (49%), H-3->L+4 (14%) |
| 225.581661898 | 0.0149 | H-9->L+1 (15%), H-5->L+5 (14%), H-4->L+5 (15%), H-3->L+5 (19%) |

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|---|---|---|
| 224.755625067 | 0.0027 | H-13->L+1 (38%), H-10->L+1 (32%) |
| 224.324575741 | 0.0172 | H-5->L+4 (17%), H-3->L+5 (36%) |
| 223.874962554 | 0.0041 | H-10->L+1 (37%), H-3->L+5 (10%) |
| 223.411044061 | 0.0024 | H-13->L+1 (36%), H-10->L+1 (26%) |
| 223.197884772 | 0.0026 | H-5->L+2 (79%) |
| 222.981121544 | 0.2313 | H-2->L+6 (17%), H-1->L+9 (16%), HOMO->L+10 (24%) |
| 222.245671953 | 0.0279 | H-6->L+4 (13%), H-4->L+3 (14%), H-4->L+4 (15%), H-2->L+6 (13%) |
| 222.030753411 | 0.092 | H-2->L+6 (49%) |
| 221.080567415 | 0.0037 | H-7->L+5 (18%), H-6->L+5 (14%), H-5->L+5 (31%), H-4->L+5 (21%) |
| 220.785299901 | 0.0158 | H-5->L+3 (18%), H-5->L+4 (21%), H-4->L+3 (21%), H-4->L+4 (17%) |
| 220.00566589 | 0.0032 | H-7->L+3 (14%), H-7->L+4 (16%), H-6->L+4 (13%), H-4->L+4 (23%) |
| 219.336234034 | 0.0242 | H-2->L+7 (55%), H-2->L+8 (12%) |
| 218.786625866 | 0.003 | H-7->L+2 (48%), H-6->L+2 (26%) |
| 218.216718609 | 0.0111 | H-14->L+1 (29%), HOMO->L+11 (23%) |
| 218.109232144 | 0.0713 | H-3->L+6 (14%), H-2->L+7 (24%), H-2->L+8 (28%) |
| 217.810363144 | 0.092 | H-6->L+3 (12%), H-3->L+6 (30%), HOMO->L+11 (10%) |
| 216.964201614 | 0.0466 | H-7->L+3 (13%), H-6->L+3 (22%), H-3->L+6 (23%) |
| 215.872467549 | 0.0427 | H-7->L+5 (12%), H-6->L+5 (14%), H-4->L+5 (19%), H-2->L+9 (20%) |
| 215.587190075 | 0.0117 | H-13->L+1 (12%), H-12->L+1 (58%) |
| 215.321361234 | 0.0752 | H-4->L+6 (11%), H-2->L+9 (16%), HOMO->L+11 (21%) |
| 214.035239201 | 0.0557 | H-16->LUMO (36%), H-3->L+7 (35%) |
| 213.699529477 | 0.0083 | H-16->LUMO (42%), H-7->L+3 (22%) |
| 213.075192501 | 0.0089 | H-16->LUMO (11%), H-14->L+1 (10%), H-7->L+3 (14%), H-3->L+7 (13%) |
| 212.665854223 | 0.0046 | H-7->L+4 (26%), H-2->L+9 (11%) |
| 212.359881153 | 0.0097 | H-8->L+2 (90%) |
| 212.174540964 | 0.0001 | H-7->L+4 (19%), H-6->L+4 (11%), H-5->L+4 (13%) |
| 212.033028375 | 0.013 | H-17->LUMO (24%), H-14->L+1 (11%), H-4->L+6 (17%) |
| 211.634905456 | 0.034 | H-6->L+6 (20%), H-4->L+6 (27%) |
| 211.346299284 | 0.0081 | H-7->L+5 (20%), H-7->L+6 (11%), H-6->L+5 (17%) |
| 210.224652004 | 0.0088 | H-17->LUMO (49%) |
| 209.790678374 | 0.0012 | H-3->L+8 (39%), H-3->L+9 (15%) |
| 209.386778262 | 0.0181 | H-17->LUMO (10%), H-7->L+6 (15%), H-6->L+6 (20%), H-3->L+8 (11%) |
| 208.299776574 | 0.0317 | H-5->L+6 (34%), H-5->L+7 (21%) |
| 207.804024223 | 0.0186 | H-6->L+7 (14%), H-4->L+7 (46%) |
| 207.772682808 | 0.0146 | H-6->L+7 (13%), H-5->L+8 (16%), H-4->L+8 (15%), H-3->L+9 (15%) |
| 207.376508291 | 0.0044 | H-22->LUMO (17%), H-18->LUMO (48%) |
| 206.926570109 | 0.0101 | H-5->L+8 (13%), H-3->L+9 (28%), HOMO->L+12 (12%) |
| 206.733351695 | 0.0022 | H-18->LUMO (17%), H-7->L+7 (16%), H-6->L+7 (11%), H-3->L+8 (12%), H-3->L+9 (13%) |
| 206.258743012 | 0.0021 | H-7->L+7 (14%), H-4->L+7 (14%), H-4->L+8 (10%) |
| 205.871733881 | 0.015 | H-8->L+3 (63%), H-8->L+4 (14%) |

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|---|---|---|
| 205.731673463 | 0.0089 | H-22->LUMO (29%), H-19->LUMO (14%), H-18->LUMO (11%) |
| 204.922388993 | 0.009 | H-7->L+6 (25%), H-6->L+6 (11%), H-5->L+9 (13%), H-4->L+9 (16%) |
| 204.149695403 | 0.0103 | H-5->L+8 (24%), H-4->L+8 (18%), HOMO->L+12 (28%) |
| 203.469587285 | 0.012 | H-9->L+3 (39%), H-9->L+4 (15%) |
| 203.106272545 | 0.0064 | H-9->L+3 (10%), H-5->L+8 (10%), H-5->L+9 (20%) |
| 202.429782217 | 0.0005 | H-23->LUMO (32%), H-19->LUMO (41%) |

**Table S5**. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **3**.

| **Wavelength (nm)** | **Osc. Strength** | **Major contributions** |
|---|---|---|
| 631.573496063 | 0.2447 | HOMO->LUMO (97%) |
| 447.225022589 | 0.3056 | H-1->LUMO (86%) |
| 413.390880942 | 0.0321 | H-2->LUMO (94%) |
| 383.638198565 | 0.0033 | H-6->LUMO (11%), H-4->LUMO (60%), H-3->LUMO (13%) |
| 379.795353078 | 0.005 | H-5->LUMO (72%), H-3->LUMO (17%) |
| 371.588422383 | 0.2024 | H-3->LUMO (26%), HOMO->L+1 (54%) |
| 359.457825038 | 0.6151 | H-4->LUMO (23%), H-3->LUMO (35%), HOMO->L+1 (30%) |
| 348.583538608 | 0.0584 | H-6->LUMO (80%), H-5->LUMO (10%) |
| 338.77313791 | 0.073 | H-13->LUMO (11%), H-8->LUMO (48%), H-7->LUMO (24%) |
| 335.409692986 | 0.0954 | H-8->LUMO (19%), H-7->LUMO (73%) |
| 314.776563959 | 0.0192 | H-13->LUMO (37%), H-12->LUMO (14%), H-8->LUMO (12%), H-1->L+1 (16%) |
| 311.878535524 | 0.1378 | H-9->LUMO (31%), H-1->L+1 (51%) |
| 310.573865916 | 0.0322 | H-12->LUMO (14%), H-9->LUMO (57%), H-1->L+1 (12%) |
| 307.844054655 | 0.0174 | H-12->LUMO (53%), H-10->LUMO (18%), HOMO->L+3 (11%) |
| 306.747304516 | 0.0095 | H-10->LUMO (15%), HOMO->L+3 (35%), HOMO->L+4 (12%), HOMO->L+5 (18%) |
| 306.19429273 | 0.1338 | H-13->LUMO (19%), H-12->LUMO (12%), H-10->LUMO (13%), HOMO->L+3 (32%) |
| 303.2213872 | 0.0271 | HOMO->L+2 (87%) |
| 302.326732534 | 0.0016 | H-13->LUMO (11%), H-11->LUMO (78%) |
| 300.262019307 | 0.0267 | H-10->LUMO (33%), HOMO->L+4 (41%), HOMO->L+5 (11%) |
| 297.174547619 | 0.0676 | HOMO->L+4 (34%), HOMO->L+5 (53%) |
| 292.298354462 | 0.0078 | H-2->L+1 (29%), HOMO->L+6 (61%) |
| 291.954206825 | 0.0206 | H-2->L+1 (55%), HOMO->L+6 (30%), HOMO->L+7 (10%) |
| 290.333910201 | 0.0471 | H-2->L+1 (11%), HOMO->L+7 (80%) |
| 276.220186722 | 0.0254 | H-3->L+1 (11%), HOMO->L+8 (78%) |
| 272.265345453 | 0.2276 | H-14->LUMO (62%), HOMO->L+8 (10%), HOMO->L+9 (18%) |
| 268.742154573 | 0.0652 | H-4->L+1 (32%), H-3->L+1 (53%) |
| 265.41689254 | 0.1531 | H-14->LUMO (13%), HOMO->L+9 (64%) |
| 263.297570584 | 0.0976 | H-4->L+1 (41%), H-3->L+1 (29%) |
| 258.607498513 | 0.001 | H-1->L+2 (86%) |

| | | |
|---|---|---|
| 257.902801956 | 0.0038 | H-5->L+1 (70%), H-4->L+1 (10%) |
| 255.758799043 | 0.01 | H-1->L+3 (86%) |
| 253.61901774 | 0.0127 | H-1->L+4 (82%) |
| 252.354303825 | 0.0413 | H-1->L+5 (79%) |
| 250.235519834 | 0.0182 | H-6->L+1 (56%), H-1->L+6 (11%), H-1->L+7 (14%) |
| 250.129504947 | 0.0017 | H-1->L+6 (72%), H-1->L+7 (16%) |
| 247.968386024 | 0.0517 | H-6->L+1 (13%), H-1->L+7 (37%) |
| 246.093156174 | 0.0455 | H-8->L+1 (13%), H-2->L+3 (21%), H-2->L+5 (12%), H-1->L+7 (22%) |
| 245.028049431 | 0.0112 | H-10->L+1 (20%), H-2->L+3 (26%), H-2->L+5 (14%) |
| 242.616271084 | 0.0317 | H-8->L+1 (29%), H-7->L+1 (47%) |
| 241.421047224 | 0.0294 | H-8->L+1 (47%), H-7->L+1 (32%) |
| 236.755638963 | 0.0445 | H-15->LUMO (80%) |
| 234.667435765 | 0.0009 | H-2->L+2 (86%) |
| 234.259518974 | 0.0141 | H-11->L+1 (23%), H-10->L+1 (11%), H-2->L+3 (15%) |
| 233.628282071 | 0.0079 | H-10->L+1 (11%), H-2->L+4 (18%) |
| 232.856029697 | 0.0185 | H-11->L+1 (20%), H-10->L+1 (16%), H-2->L+5 (16%), H-1->L+8 (12%) |
| 232.803561996 | 0.0976 | H-1->L+8 (62%), H-1->L+9 (11%) |
| 232.245374192 | 0.0059 | H-12->L+1 (19%), H-7->L+2 (14%), H-4->L+2 (19%), H-3->L+2 (10%) |
| 230.94755148 | 0.0007 | H-2->L+4 (41%), H-2->L+5 (16%) |
| 230.359691227 | 0.0048 | H-1->L+8 (13%), H-1->L+9 (47%), HOMO->L+10 (22%) |
| 228.60971533 | 0.016 | H-11->L+1 (12%), H-3->L+3 (23%), H-2->L+6 (25%) |
| 228.580212408 | 0.0125 | H-9->L+1 (11%), H-3->L+3 (13%), H-2->L+6 (46%) |
| 228.197366216 | 0.004 | H-9->L+1 (82%) |
| 227.569092567 | 0.0046 | H-2->L+7 (68%) |
| 224.873842409 | 0.0199 | H-10->L+1 (21%), H-3->L+4 (10%), H-3->L+5 (33%) |
| 223.972023434 | 0.0028 | H-13->L+1 (39%), H-5->L+2 (27%) |
| 223.604445629 | 0.007 | H-13->L+1 (30%), H-6->L+2 (14%), H-5->L+2 (43%) |
| 222.0904113 | 0.2352 | H-2->L+8 (16%), H-1->L+9 (20%), HOMO->L+10 (25%) |
| 221.693296521 | 0.0664 | H-4->L+4 (30%), H-3->L+4 (13%) |
| 220.510427582 | 0.0055 | H-5->L+5 (10%), H-4->L+3 (12%), H-4->L+4 (13%), H-4->L+5 (29%) |
| 219.935417686 | 0.0225 | H-12->L+1 (19%), H-5->L+4 (27%), H-3->L+2 (17%) |
| 219.818436984 | 0.013 | H-5->L+4 (19%), H-3->L+2 (45%) |
| 219.592626791 | 0.0065 | H-5->L+6 (16%), H-4->L+6 (50%), H-3->L+6 (13%) |
| 219.146268757 | 0.0189 | H-12->L+1 (40%), H-4->L+2 (33%) |
| 218.543666735 | 0.0263 | H-3->L+4 (14%), H-2->L+8 (35%) |
| 218.189837062 | 0.0228 | H-4->L+3 (49%), H-4->L+5 (14%) |
| 217.56574835 | 0.014 | H-6->L+5 (10%), H-5->L+3 (29%), H-5->L+7 (14%) |
| 216.842774214 | 0.0151 | H-6->L+6 (10%), H-5->L+6 (38%), H-5->L+7 (17%), H-4->L+6 (13%) |
| 216.282935913 | 0.0659 | H-3->L+4 (17%), H-2->L+8 (10%), H-2->L+9 (25%), HOMO->L+11 (14%) |
| 215.906300413 | 0.034 | H-14->L+1 (17%), H-2->L+9 (10%), HOMO->L+11 (42%) |
| 214.892181455 | 0.0032 | H-4->L+7 (28%), H-3->L+7 (11%) |
| 214.813994165 | 0.0048 | H-6->L+2 (19%), H-5->L+2 (10%), H-4->L+2 (14%), H-3->L+2 (11%) |

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|---|---|---|
| 213.872786414 | 0.0036 | H-5->L+3 (31%), H-5->L+5 (10%), H-5->L+7 (11%) |
| 213.622207502 | 0.0557 | H-5->L+3 (11%), H-3->L+5 (15%), H-2->L+9 (18%) |
| 212.881291551 | 0.0092 | H-3->L+6 (20%), H-3->L+7 (10%), H-2->L+9 (10%) |
| 212.363518511 | 0.0017 | H-16->LUMO (76%), H-14->L+1 (14%) |
| 211.663809431 | 0.0002 | H-4->L+6 (11%), H-3->L+6 (42%), H-3->L+7 (12%) |
| 211.559070066 | 0.0001 | H-5->L+5 (22%), H-4->L+7 (11%), H-3->L+7 (13%) |
| 210.599594055 | 0.0065 | H-6->L+3 (53%) |
| 210.149823744 | 0.0065 | H-14->L+1 (18%), H-6->L+4 (20%) |
| 209.932767253 | 0.0025 | H-8->L+2 (14%), H-7->L+2 (34%), H-6->L+2 (31%) |
| 209.344352912 | 0.0585 | H-17->LUMO (11%), H-14->L+1 (12%), H-6->L+4 (25%) |
| 208.566081843 | 0.0 | H-17->LUMO (70%) |
| 208.415325543 | 0.0137 | H-8->L+2 (73%) |
| 208.142416123 | 0.0675 | H-6->L+5 (28%), H-6->L+6 (13%), H-3->L+8 (17%) |
| 207.751793784 | 0.0084 | H-6->L+7 (16%), H-3->L+8 (30%) |
| 207.272502821 | 0.0238 | H-7->L+4 (10%), H-6->L+7 (17%), H-3->L+8 (10%), HOMO->L+12 (21%) |
| 206.138717475 | 0.0199 | H-8->L+3 (13%), HOMO->L+12 (12%) |
| 205.707779752 | 0.008 | H-8->L+3 (34%), H-7->L+4 (15%) |
| 205.156357369 | 0.0046 | H-7->L+3 (17%), H-6->L+6 (10%), H-6->L+7 (25%) |
| 204.864826524 | 0.0067 | H-21->LUMO (11%), H-8->L+3 (22%), H-7->L+3 (17%), H-7->L+4 (16%) |
| 204.661923097 | 0.0086 | H-8->L+4 (37%), H-7->L+3 (18%) |
| 204.604506844 | 0.004 | H-21->LUMO (35%), H-20->LUMO (14%) |
| 204.176590824 | 0.0062 | H-7->L+5 (14%), H-3->L+9 (23%) |
| 203.713635786 | 0.0285 | H-8->L+4 (21%), H-3->L+9 (15%), HOMO->L+12 (13%) |
| 203.126237774 | 0.0018 | H-10->L+3 (19%), H-7->L+6 (29%) |
| 202.943369964 | 0.0212 | H-10->L+3 (25%), H-4->L+8 (24%), H-3->L+9 (14%), HOMO->L+12 (10%) |
| 202.664715518 | 0.0073 | H-10->L+3 (11%), H-7->L+5 (32%), H-7->L+6 (23%) |
| 202.106401415 | 0.0022 | H-18->LUMO (61%), H-7->L+7 (18%) |
| 201.862899727 | 0.0072 | H-18->LUMO (19%), H-7->L+7 (44%) |
| 201.175065735 | 0.0034 | H-19->LUMO (70%) |

**Table S6**. Selected TD-DFT calculated oscillator strengths and compositions of the major electronic transitions of **4**.

| **Wavelength (nm)** | **Osc. Strength** | **Major contributions** |
|---|---|---|
| 781.248853259 | 0.0036 | HOMO->LUMO (95%) |
| 626.594193219 | 0.1885 | HOMO->L+1 (79%) |
| 611.301612327 | 0.0316 | H-2->LUMO (11%), H-1->LUMO (75%), HOMO->L+1 (10%) |
| 531.641837881 | 0.0046 | H-2->LUMO (84%), H-1->LUMO (10%) |
| 497.289399215 | 0.4493 | H-1->L+1 (86%) |
| 460.086807972 | 0.0113 | H-7->LUMO (24%), H-6->LUMO (56%) |
| 453.622834085 | 0.055 | H-2->L+1 (81%) |
| 442.011383288 | 0.0005 | H-3->LUMO (76%) |
| 413.79098559 | 0.0103 | H-4->LUMO (94%) |

| | | |
|---|---|---|
| 405.110906755 | 0.0012 | H-4->L+1 (85%), H-3->L+1 (11%) |
| 395.748964257 | 0.0266 | H-3->L+1 (21%), HOMO->L+2 (66%) |
| 387.595951645 | 0.0151 | H-5->L+1 (93%) |
| 370.588812208 | 0.1469 | H-8->LUMO (12%), H-3->L+1 (49%), H-1->L+2 (12%), HOMO->L+2 (11%) |
| 367.556602076 | 0.0075 | H-5->LUMO (95%) |
| 357.385544253 | 0.0387 | H-8->LUMO (39%), H-1->L+2 (47%) |
| 347.207127089 | 0.0577 | H-7->LUMO (34%), H-6->LUMO (22%) |
| 345.745100424 | 0.0311 | H-13->L+1 (14%), H-11->L+1 (17%), H-6->L+1 (30%) |
| 342.497770752 | 0.3155 | H-7->L+1 (41%), H-1->L+2 (12%) |
| 339.366598271 | 0.0235 | HOMO->L+3 (79%) |
| 337.087607765 | 0.0405 | H-8->L+1 (52%), H-6->L+1 (27%) |
| 335.110527629 | 0.0818 | H-8->L+1 (20%), H-7->L+1 (12%), H-6->L+1 (33%) |
| 333.272923532 | 0.0119 | H-11->LUMO (52%), H-10->LUMO (27%) |
| 331.570596134 | 0.0774 | H-10->L+1 (15%), H-8->L+1 (11%), H-7->L+1 (17%), H-2->L+2 (17%) |
| 330.263426686 | 0.0136 | H-11->LUMO (15%), H-10->LUMO (35%), H-7->LUMO (16%), H-2->L+2 (11%) |
| 327.697087385 | 0.0372 | H-9->LUMO (76%) |
| 327.446104511 | 0.2748 | H-10->L+1 (16%), H-9->LUMO (12%), H-2->L+2 (35%) |
| 324.481007622 | 0.01 | H-9->L+1 (87%) |
| 319.645748717 | 0.0103 | H-13->L+1 (39%), H-10->L+1 (37%) |
| 318.43074022 | 0.0368 | H-12->L+1 (23%), H-11->L+1 (40%) |
| 317.891885063 | 0.0183 | H-14->LUMO (60%) |
| 312.901759066 | 0.0265 | H-13->L+1 (17%), H-12->L+1 (57%), H-11->L+1 (11%) |
| 308.257360613 | 0.1012 | HOMO->L+4 (84%) |
| 304.532196134 | 0.0001 | H-12->LUMO (94%) |
| 298.426305811 | 0.0052 | H-13->LUMO (87%) |
| 297.673988649 | 0.0411 | H-1->L+3 (88%) |
| 291.885474521 | 0.0065 | HOMO->L+5 (83%) |
| 290.926609128 | 0.031 | H-15->LUMO (47%), HOMO->L+5 (14%), HOMO->L+6 (19%) |
| 289.432483629 | 0.0119 | H-4->L+2 (89%) |
| 288.563499074 | 0.1008 | H-15->LUMO (13%), HOMO->L+6 (66%) |
| 283.599874222 | 0.0682 | HOMO->L+7 (10%), HOMO->L+8 (23%), HOMO->L+9 (52%) |
| 281.136919825 | 0.0249 | HOMO->L+7 (79%), HOMO->L+8 (10%) |
| 280.754948965 | 0.0184 | H-14->L+1 (53%), H-3->L+2 (22%) |
| 278.772777993 | 0.0019 | H-16->LUMO (30%), H-1->L+4 (42%) |
| 277.642854291 | 0.0207 | H-16->LUMO (17%), H-1->L+4 (21%), HOMO->L+8 (38%) |
| 277.016317028 | 0.0084 | H-16->LUMO (17%), H-3->L+2 (15%), HOMO->L+8 (20%), HOMO->L+9 (16%) |
| 275.165770811 | 0.0551 | H-3->L+2 (29%), H-2->L+3 (20%), HOMO->L+9 (11%) |
| 274.046666841 | 0.0482 | H-14->L+1 (13%), H-2->L+3 (58%) |
| 270.8971181 | 0.0023 | H-15->L+1 (68%), H-8->L+2 (18%) |
| 269.448848203 | 0.0004 | H-5->L+2 (92%) |
| 263.040613158 | 0.0366 | H-16->L+1 (11%), H-15->L+1 (12%), H-8->L+2 (37%), HOMO->L+10 (24%) |
| 262.283837897 | 0.043 | H-16->L+1 (13%), H-8->L+2 (30%), HOMO->L+10 (29%) |
| 260.854603434 | 0.011 | H-6->L+2 (14%), H-2->L+4 (52%) |

| | | |
|---|---|---|
| 259.979435966 | 0.0211 | H-7->L+2 (15%), H-6->L+2 (46%) |
| 258.645262459 | 0.0009 | H-1->L+5 (91%) |
| 257.159257902 | 0.0075 | H-1->L+6 (54%), H-1->L+7 (22%) |
| 256.012292247 | 0.0382 | H-3->L+3 (45%), H-1->L+9 (17%) |
| 255.106259156 | 0.0217 | H-7->L+3 (18%), H-6->L+3 (43%) |
| 254.430931689 | 0.006 | H-1->L+6 (15%), H-1->L+7 (55%), H-1->L+8 (12%) |
| 253.132284631 | 0.2399 | H-16->L+1 (35%), H-1->L+8 (20%), HOMO->L+10 (19%) |
| 252.215698385 | 0.0311 | H-16->L+1 (10%), H-7->L+2 (11%), H-3->L+3 (12%), H-1->L+8 (41%) |
| 251.61683006 | 0.0543 | H-11->L+2 (15%), H-10->L+2 (14%), H-7->L+2 (40%), H-6->L+2 (11%) |
| 248.604814349 | 0.0382 | H-3->L+3 (16%), H-1->L+9 (60%) |
| 247.715715994 | 0.0274 | H-11->L+2 (32%), H-10->L+2 (24%), H-7->L+2 (17%) |
| 245.522977172 | 0.0036 | H-4->L+3 (89%) |
| 243.674835424 | 0.0234 | H-11->L+2 (24%), H-10->L+2 (41%), H-1->L+10 (13%) |
| 242.953819196 | 0.0005 | H-9->L+2 (89%) |
| 240.989334886 | 0.004 | H-17->LUMO (76%), H-16->LUMO (10%) |
| 240.65721969 | 0.0417 | H-2->L+6 (12%), H-2->L+10 (15%), H-1->L+10 (24%) |
| 237.658749472 | 0.0004 | H-12->L+2 (57%), H-3->L+5 (11%), H-2->L+5 (11%) |
| 236.088416887 | 0.0023 | H-3->L+4 (17%), H-2->L+9 (43%) |
| 234.867478096 | 0.0006 | H-13->L+2 (68%), H-2->L+5 (20%) |
| 234.064929228 | 0.0027 | H-3->L+4 (20%), H-2->L+5 (17%), H-2->L+6 (25%), H-1->L+10 (11%) |
| 233.919198936 | 0.0012 | H-13->L+2 (10%), H-12->L+2 (11%), H-2->L+5 (46%), H-2->L+6 (13%) |
| 233.417160254 | 0.0421 | H-3->L+4 (44%), H-2->L+6 (18%), H-2->L+9 (13%) |
| 230.762717786 | 0.0011 | H-5->L+3 (18%), H-4->L+4 (47%) |
| 230.10317548 | 0.0023 | H-5->L+3 (13%), H-2->L+7 (59%) |
| 229.941010779 | 0.0045 | H-5->L+3 (62%), H-4->L+4 (25%) |
| 228.664526682 | 0.048 | H-17->L+1 (44%), H-2->L+8 (15%) |
| 227.995941545 | 0.0393 | H-17->L+1 (30%), H-2->L+8 (24%) |
| 227.673564486 | 0.0125 | H-14->L+2 (58%) |
| 227.50228084 | 0.0051 | H-9->L+7 (20%), H-7->L+8 (14%), H-2->L+7 (12%), H-2->L+8 (11%) |
| 227.302080835 | 0.0062 | H-12->L+2 (20%), H-3->L+5 (46%) |
| 227.014909846 | 0.0022 | H-8->L+3 (10%), H-8->L+4 (17%), H-4->L+4 (11%) |
| 226.50479194 | 0.0448 | H-2->L+6 (10%), H-2->L+8 (16%), H-2->L+10 (40%) |
| 225.110650566 | 0.0811 | H-14->L+2 (16%), H-8->L+3 (56%) |
| 222.209823307 | 0.0008 | H-4->L+6 (31%), H-4->L+7 (46%) |
| 221.998948974 | 0.0002 | H-15->L+2 (51%), H-3->L+9 (12%) |
| 221.836094135 | 0.003 | H-15->L+2 (36%), H-3->L+9 (18%) |
| 221.364768184 | 0.0267 | H-5->L+4 (11%), H-5->L+6 (13%), H-3->L+6 (42%) |
| 221.321301343 | 0.0016 | H-5->L+4 (22%), H-5->L+5 (61%) |
| 221.041152791 | 0.0455 | H-5->L+4 (24%), H-5->L+5 (28%), H-5->L+6 (15%), H-3->L+6 (17%) |
| 220.11893799 | 0.0041 | H-4->L+5 (49%), H-4->L+8 (23%) |
| 219.728836019 | 0.0014 | H-4->L+5 (36%), H-4->L+6 (10%), H-4->L+8 (33%) |
| 218.92956811 | 0.0144 | H-7->L+3 (36%), H-6->L+3 (13%), H-3->L+9 (15%) |

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| 217.998018448 | 0.0375 | H-6->L+4 (12%), H-4->L+6 (20%), H-4->L+7 (10%), HOMO->L+12 (18%) |
| 217.925215777 | 0.029 | H-4->L+6 (19%), H-4->L+7 (15%), H-4->L+8 (15%) |
| 217.009771957 | 0.0189 | H-11->L+3 (47%), H-10->L+3 (18%) |
| 216.937627751 | 0.0074 | H-5->L+4 (29%), H-5->L+6 (47%) |
| 216.377300196 | 0.0499 | H-7->L+4 (10%), H-6->L+4 (19%), HOMO->L+12 (12%) |
| 216.034209218 | 0.0431 | H-3->L+7 (42%), HOMO->L+11 (19%) |

**References:**


1. K. N. Panda, K. G. Thorat, and M. Ravikanth, *J. Org. Chem.* 2018, **83**, 12945-12950.

2. O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346–354.

3. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377.

4. C. Xiii, F. Component, L. Radom, W. J. Hehre and J. A. Pople, Orbital XIII., 1971, **4064**, 2371–2381.

5. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3093.