Supporting information

Feasibility of Multiple Excited-State Proton Transfer Processes in Hydroxyquinoline-containing Benzobisimidazole Dyes

Tatiana Munteanu,[a] Dancho Yordanov,[b,c] Gabriel Canard,[a] Olivier Siri,*[a] Denis Jacquemin,*[d,e] Anton Georgiev*[c] and Simon Pascal*[a,d]

[a] *Aix Marseille Univ, CNRS UMR 7325, Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), Campus de Luminy, case 913, Marseille cedex 09 13288, France.*

[b] *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev avenue, bldg. 9, Sofia 1113, Bulgaria.*

[c] *Department of Organic Chemistry, University of Chemical Technology and Metallurgy, 8 St. Kliment Ohridski blvd, 1756 Sofia, Bulgaria.*

[d] *Nantes Université, CEISAM UMR 6230, CNRS, Nantes F-44000, France.*

[e] *Institut Universitaire de France (IUF), Paris F-75005, France.*

TABLE OF CONTENT

I. GENERAL REMARKS AND ANALYSIS CONDITIONS

Reagents and solvents

All reagents and anhydrous solvents were purchased from Alfa Aesar or Sigma Aldrich and were used without further purification. Compound **6** was synthesized according to reported protocols.[1] Column chromatography were performed on silica gel 60 (230–400 mesh). When heating was required, oil bathes were used. Optical properties were recorded in spectroscopic grade solvents.

Analytical methods and apparatus

Melting points (M.P.) were measured in open capillary tubes with a STUART SMP30 melting points apparatus and are reported uncorrected in °C. ^{1}H NMR spectra were recorded at room temperature on a JEOL ECS400 spectrometer operating at 400 MHz or with a Bruker Avance NEO 600 MHz spectrometer. NMR chemical shifts are given in ppm (δ) relative to Me_4Si with residual solvent resonances used as internal standards ($CDCl_3$: 7.26; DMSO-d_6: 2.50 ppm; THF-d_8: 3.58 ppm). The 2D COSY ^{1}H NMR spectra and NOESY effect were carried out at similar frequency at room temperature. IR spectra were recorded on an Agilent Cary 630 FTIR equipped with an attenuated total reflectance (ATR) sampling. High resolution mass spectrometry (HRMS-ESI) analyses were performed on a QStar Elite (Applied Biosystems SCIEX) spectrometer or on a SYNAPT G2 HDMS (Waters) spectrometer by the *Spectropole* of Aix-Marseille University. These two instruments are equipped with an electrospray ionization (ESI) or a MALDI source and a TOF analyzer.

Electrochemistry

Cyclic voltammetry (CV) data were recorded using a BAS 100 (Bioanalytical Systems) potentiostat and the BAS100W software (v2.3). All the experiments were conducted under an argon atmosphere in a standard one-compartment using a three electrodes setup: a Pt working electrode (Ø = 1.6 mm), a Pt counter electrode and an Ag/AgCl reference electrode (filled with a 3 M NaCl solution). Tetra-*n*-butylammonium hexafluorophosphate ([TBA][PF_6]) was used as supporting electrolyte (10^{-1} M), with a concentration of the electro-active compound *ca*. 10^{-4} M for **4** and 10^{-5} M for **5**. The Ag/AgCl reference electrode was calibrated using ferrocene, with E°(Fc/Fc$^+$) = 0.46 V/SCE (in DCM)[2] or 0.435 V/SCE (in DMSO).[3] The solution was degassed using argon before recording each scan, and the working electrode (Pt) was polished before each scan recording.

Electronic absorption

Electronic absorption spectra were measured on a Varian Cary 50 UV-vis or on an Agilent Cary 5000 UV-vis-NIR or on a Perkin-Elmer Lambda EZ 210 UV-vis spectrophotometer, using 1 cm path quartz cuvettes.

Fluorescence

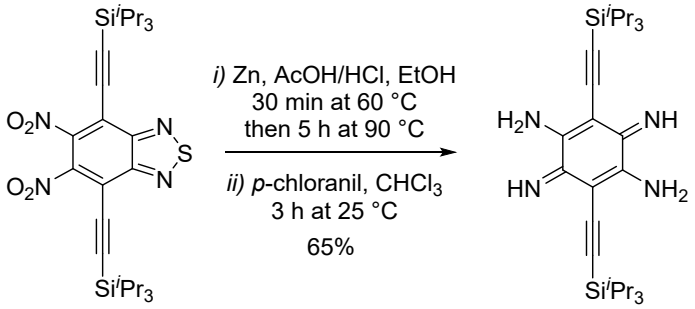
Emission spectra were measured using a Horiba-Jobin Yvon Fluorolog-3 spectrofluorimeter equipped with a three-slit double-grating excitation and a spectrograph emission mono-chromator with dispersions of 2.1 nm mm^{-1} (1200 grooves per mm). A 450 W xenon continuous wave lamp provided excitation. The luminescence of diluted solutions was detected at right angle using 10 mm quartz cuvettes. Alternatively, the emission spectra were measured on a FLS1000 (Edinburgh Instruments) spectrofluorometer in the range 200-900 nm with a resolution of 0.5 nm equipped with double-grating double grating Czerny-Turner monochromators was used to obtain the emission spectra. The concentration of the samples in solutions was kept ~ 2.7×10^{-6} mol L^{-1}. Solution fluorescence quantum yield (Φ) of compound **4** was measured in diluted solutions (5 different concentrations) with an optical density lower than 0.1 using the following equation:

$$\frac{\Phi_x}{\Phi_r} = \left(\frac{A_r(\lambda)}{A_x(\lambda)}\right)\left(\frac{n_x^2}{n_r^2}\right)\left(\frac{D_x}{D_r}\right) \quad (eq.1)$$

where A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated intensity. “r” and “x” stand for reference and sample. The fluorescence quantum yields were measured relative to Antracene in EtOH (Φ = 28%).[4] Excitation of reference and sample compounds was performed at the same wavelength (363 nm). The absolute fluorescence quantum yields (Φ_{fl}) of **5** were determined by using calibrated QYPro integrating sphere (Edinburgh Instruments) in dichloromethane or in solid-state. The fluorescence lifetimes were measured out on integrated TCC2 electronics module (Edinburgh Instruments) by using picosecond pulsed diode laser at 405 nm as excitation sources with wavelength near to the absorption maximum. The instrument response function (IRF) was obtained by using 2% water Ludox solution.

II. SYNTHETICS PROTOCOLS AND CHARACTERIZATION

Compound 8: 3,6-Diimino-2,5-bis((triisopropylsilyl)ethynyl)cyclohexa-1,4-diene-1,4-diamine

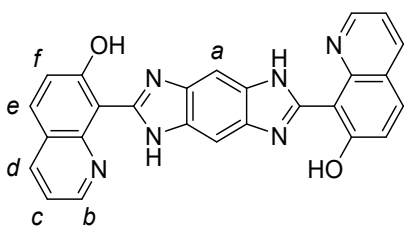


8

The synthesis of **8** was adapted from literature procedures,[5–7] with the addition of a supplementary oxidation step before final purification. Into a pressure tube containing the dinitrobenzothiadiazole precursor (906 mg, 1.543 mmol, 1 equiv.) and zinc powder (1.917 g, 23.330 mmol, 19 equiv.) were added ethanol (96%, 72 mL), glacial acetic acid (18 mL) and hydrochloric acid (1 M aqueous solution, 9 mL). The tube was closed with a Teflon® seal. The suspension was stirred for 30 min at 60 °C and then 5 h at 90 °C. The reaction mixture was cooled down to room temperature and poured into 180 mL of H_2O. The pH was adjusted to 6–7 using NaOH (10% aqueous solution), then the solution was extracted several times by Et_2O (total volume *ca*. 250 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The obtained dark-brown residue was then dissolved in 70 mL of anhydrous chloroform, degassed with argon bubbling for 10 minutes and oxidized with *p*-chloranil (414 mg, 1.683 mmol, 1.1 equiv.) for 3 h at 25 °C. After solvent evaporation, the solid was purified by silica gel column chromatography using dichloromethane/petroleum ether (8:2) as eluent to afford the product **8** as a brown-reddish powder (500 mg, 1.010 mmol, 65% yield). The ^{1}H NMR characterization was comparable to the previously reported results; however, the retardation factor and melting point were different although they were checked multiple times.

R_f = 0.65 (SiO_2, CH_2Cl_2/petroleum ether, 80:20). **M.P.:** 166–168 °C. **^{1}H NMR ($CDCl_3$, 298 K, 400 MHz):** δ = 9.59 (br s, 2H, NH), 5.63 (br s, 4H, NH_2), 1.14 (s, 42 H, $CH(CH_3)_2$). ^{13}C NMR: as already reported, all the signals could not be observed at room temperature due to very fast tautomerism within the molecule. **MS (ES+):** calculated for $[M]^{+\bullet}$: 497.3 ($C_{28}H_{49}N_4Si_2^{+\bullet}$), found: 497.3. **MS (ES-):** calculated for $[M]^{-\bullet}$: 495.3 ($C_{28}H_{47}N_4Si_2^{-\bullet}$), found: 495.3.

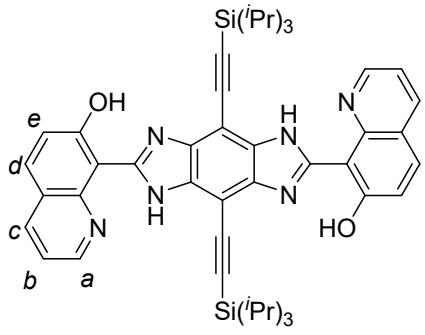
Compound 4: 8,8'-(1,5-dihydrobenzo[1,2-*d*:4,5-*d*']diimidazole-2,6-diyl)bis(quinolin-7-ol)



Tetraaminobenzene tetrahydrochloride **7** (24 mg, 0.085 mmol, 1 equiv.) and 7-hydroxyquinoline-8-carbaldehyde **6** (30 mg, 0.173 mmol, 2.05 equiv.) were dissolved in 3 mL of anhydrous dimethylsulfoxide. Piperidine (54 µL, 0.423 mmol, 5 equiv.) was added and the solution was stirred at 100 °C for 20 h. The reaction mixture was cooled down to room temperature and the orange precipitate was filtered on a sintered glass funnel (porosity 4). The orange powder was further purified with a Soxhlet using ethyl acetate (reflux, 20 h) and then with heptane (100 °C, 16 h). The final precipitate was collected and dried to afford 18 mg of the product as an orange powder (0.033 mmol, 39% yield).

M.P.: >400 °C (decomposition). **^{1}H NMR (DMSO-d_6, 363 K, 400 MHz):** δ = 9.11 (m, 2H, H^b or H^d), 8.43 (m, 2H, H^d or H^b), 8.17 (m, 2H, H^a), 8.02 (m, 2H, H^e or H^f), 7.55 (m, 2H, H^c), 7.43 (m, 2H, H^f or H^e). The compound was too insoluble to record a ^{13}C NMR spectrum. **IR (neat, cm^{-1}):** v = 3158, 1644, 1613, 1583, 1537, 1502, 1478, 1459, 1419, 1394, 1328, 1308, 1280, 1222, 1157, 1138, 1106, 1052, 993, 923, 869, 827, 803, 761, 732, 696, 668. **HRMS (MALDI-TOF)** calculated for $[M]^{+\bullet}$: 444.1329 ($C_{26}H_{16}N_6O_2^{+\bullet}$), found: 444.1321.

Compound 5: 8,8'-(4,8-bis((triisopropylsilyl)ethynyl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole-2,6-diyl)bis(quinolin-7-ol)



Quinone precursor **8** (25 mg, 0.05 mmol, 1 equiv.) and 7-hydroxyquinoline-8-carbaldehyde (18 mg, 0.1 mmol, 2.05 equiv.) were dissolved in 2 mL of anhydrous *N*,*N*-dimethylformamide. The solution was stirred at 100 °C for 22 h. The reaction mixture was cooled to room temperature, then the orange precipitate was filtered on a sintered glass funnel (porosity 4) and washed with water. The obtained solid was dried under vacuum to afford the product **5** as a yellow powder (16 mg, 0.019 mmol, 40% yield).

M.P.: >400 °C (decomposition). **^{1}H NMR ($CDCl_3$, 298 K, 400 MHz):** δ = 8.91 (m, 2H, H^a or H^c), 8.19 (d, ^3J = 8 Hz, 2H, H^a or H^c), 7.80 (d, ^3J = 8.8 Hz, 2H, H^d or H^e), 7.49 (d, ^3J = 8.8 Hz, 2H, H^d or H^e), 7.47 (m, 2H, H^b), 1.38–1.32 (m, 42H, Si(^{i}Pr)$_3$). **^{1}H NMR (THF-d_8, 298 K, 400 MHz):** δ = 14.02 (br d, 2H, NH), 8.97 (br s, 2H, H^a), 8.38 (d, ^3J = 8.3 Hz, 2H, H^c), 7.98 (d, ^3J = 8.8 Hz, 2H, H^d or H^e), 7.47 (m, 4H, H^d or H^e and H^b), 1.38–1.32 (m, 42H, Si(^{i}Pr)$_3$). The compound was too insoluble to record a ^{13}C NMR spectrum. **IR (neat, cm^{-1}):** v = 3203, 2936, 2922, 2859, 2418, 1612, 1583, 1518, 1460, 1418, 1317, 1281, 992, 875, 827, 803, 741, 671. **HRMS (ESI+)** calculated for $[M+H]^+$: 805.4076 ($C_{48}H_{57}N_6O_2Si_2^+$), found: 805.4084.

III. NMR SPECTRA

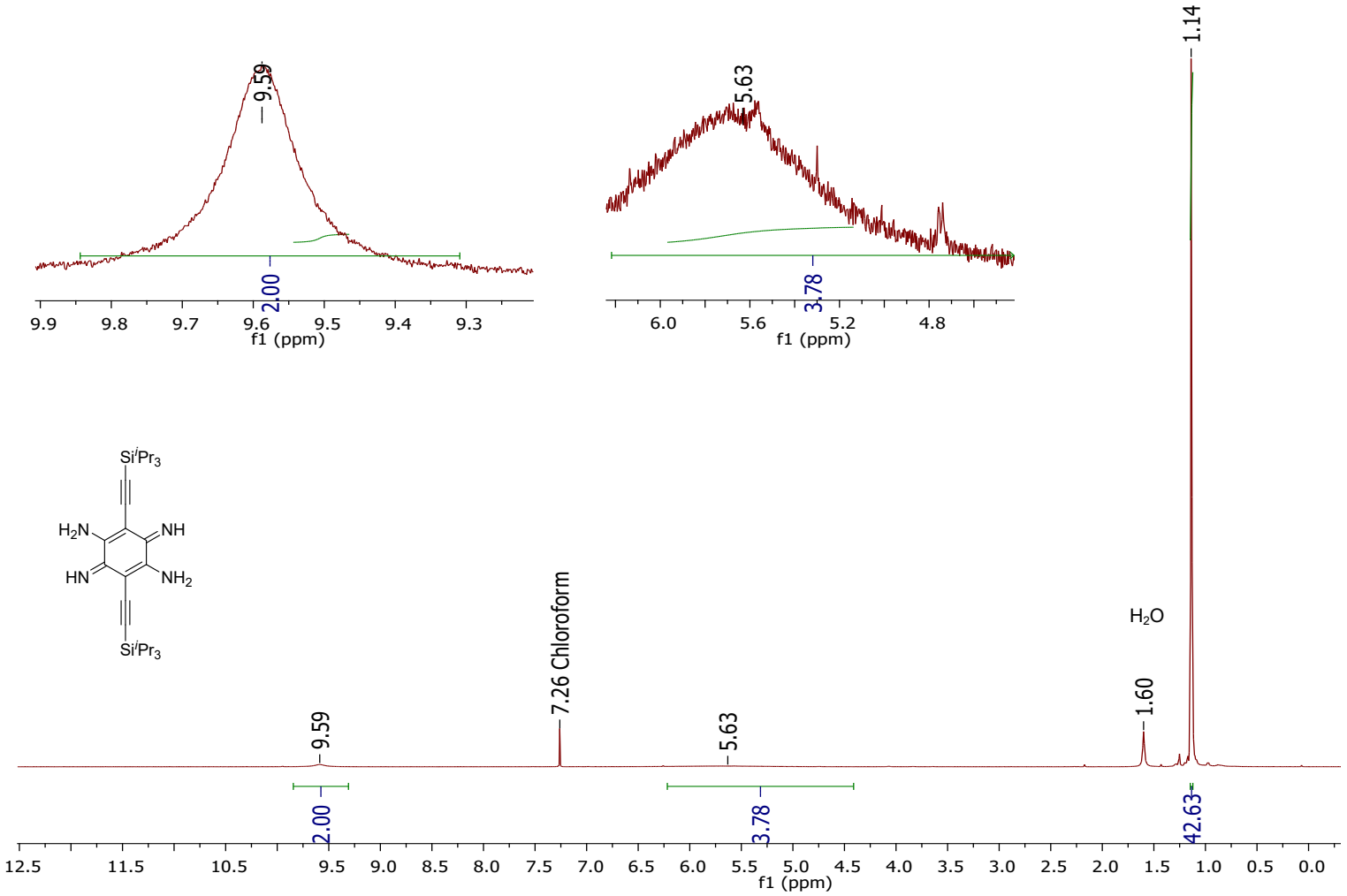


Figure S 1. ^{1}H NMR (298 K, 400 MHz, $CDCl_3$) of compound **8**.

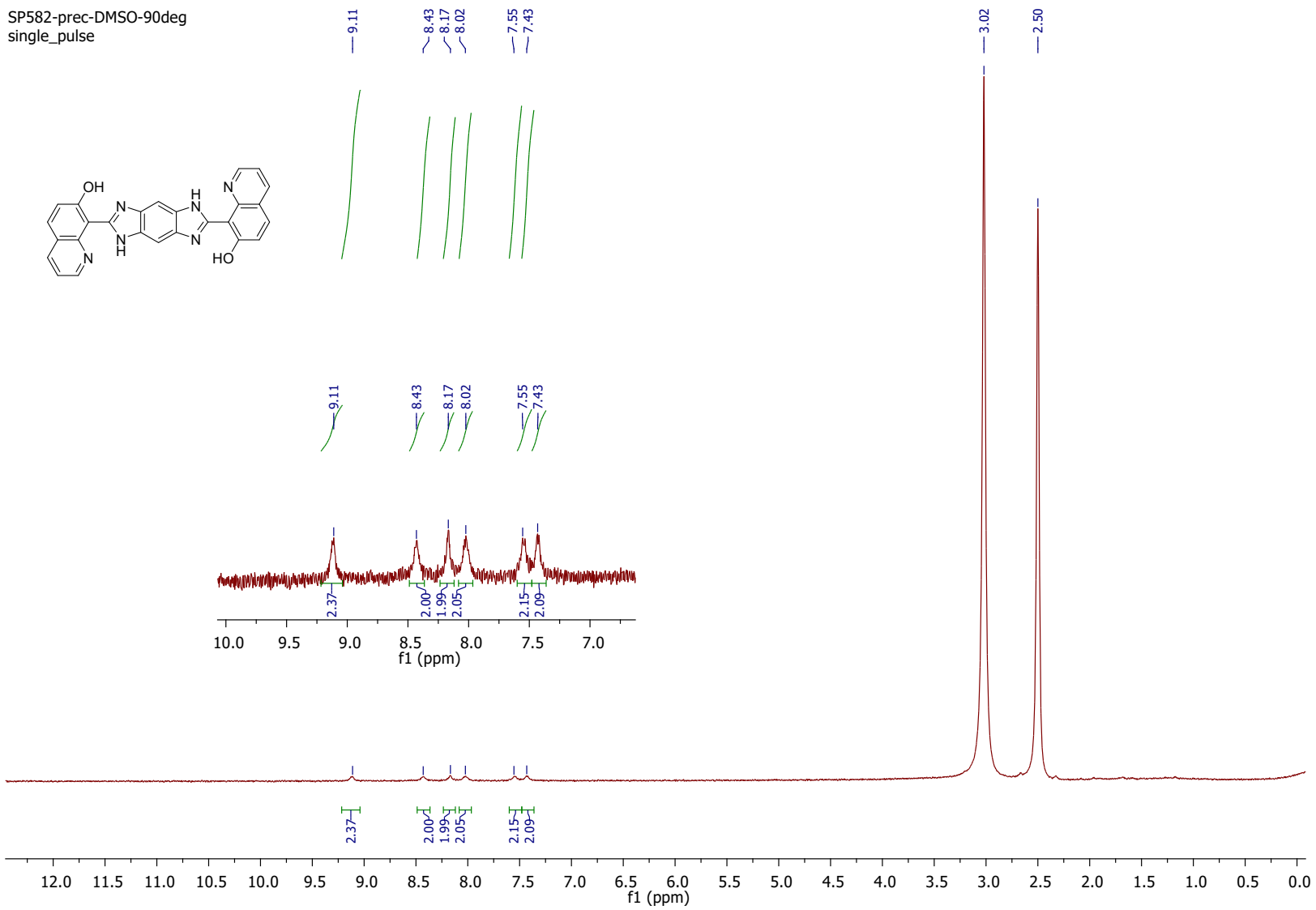


Figure S 2. ^{1}H NMR (400 MHz, 363 K, DMSO-d_6) of compound **4**.

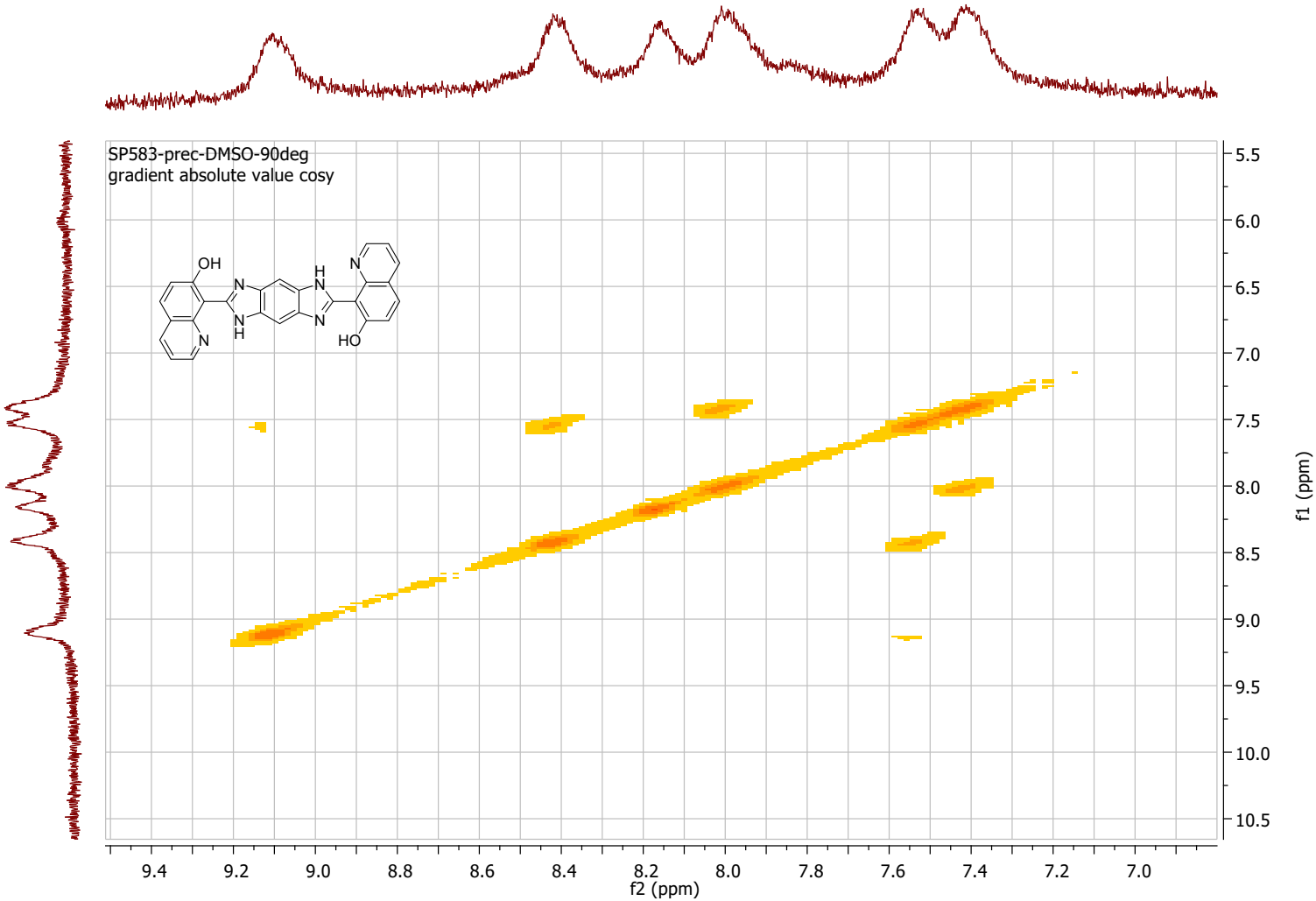


Figure S 3. COSY NMR (400 MHz, 363 K, DMSO-d_6) of compound **4**.

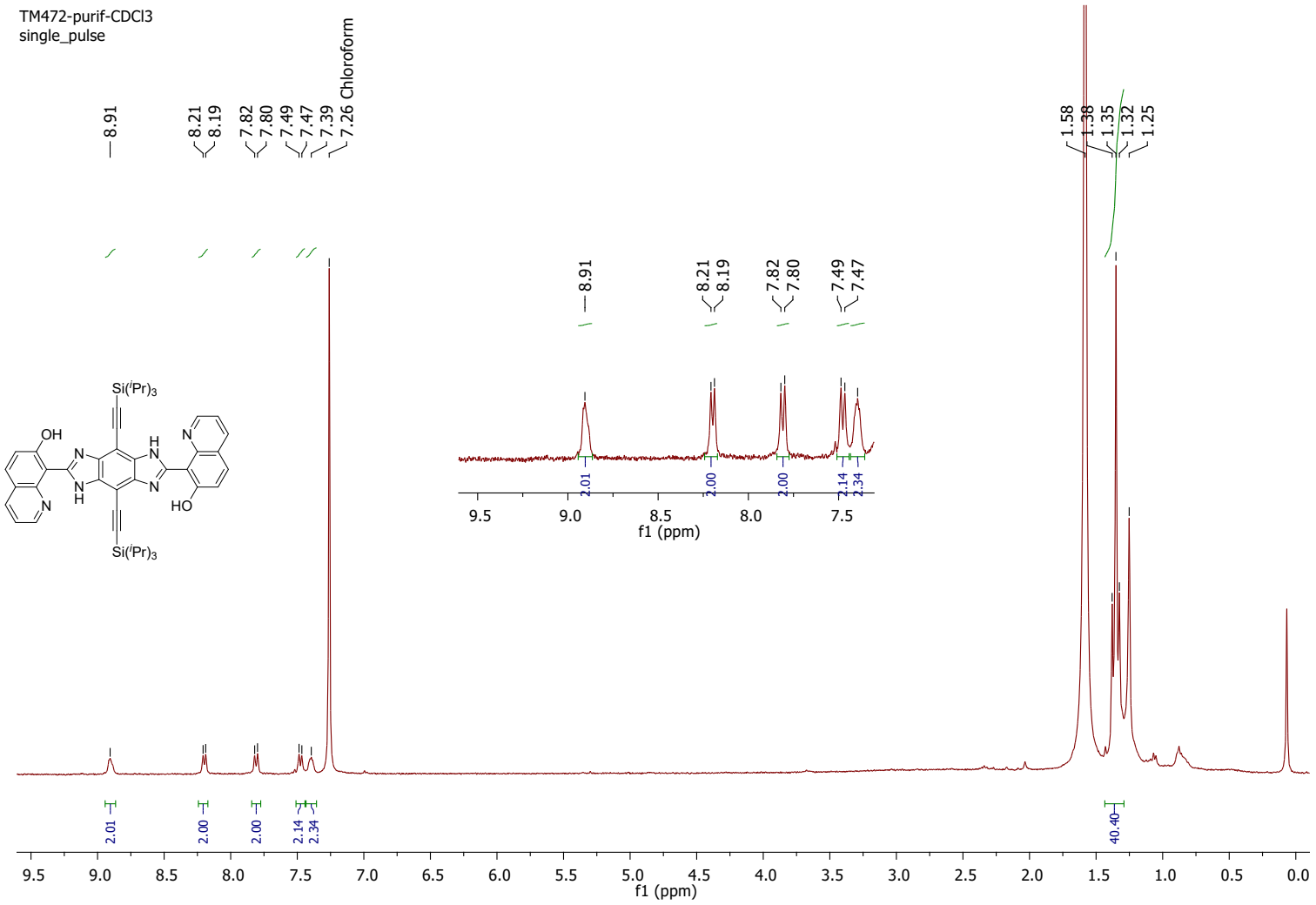


Figure S 4. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) of compound **5**.

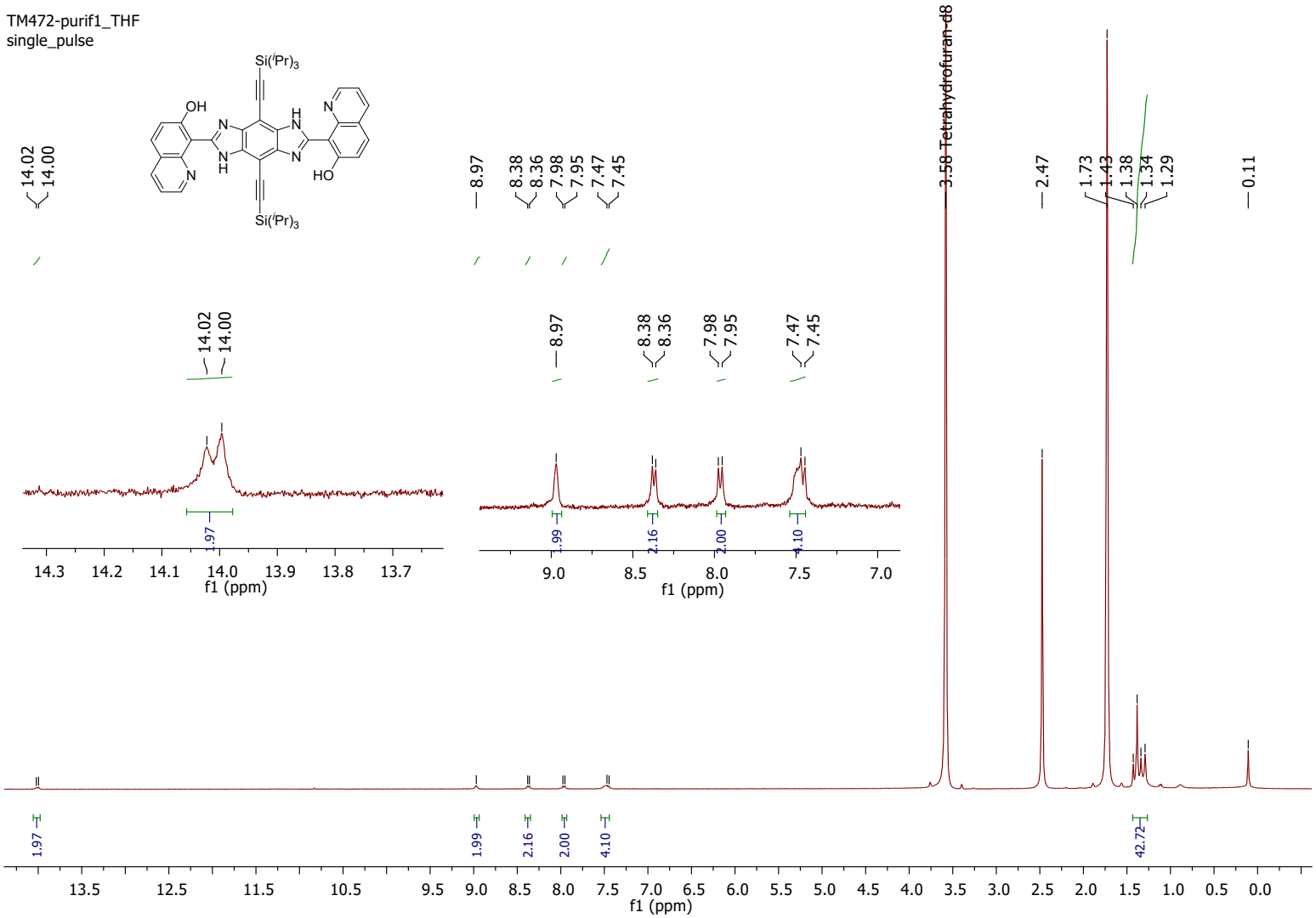


Figure S 5. ^{1}H NMR (400 MHz, 298 K, THF-d_8) of compound **5**.

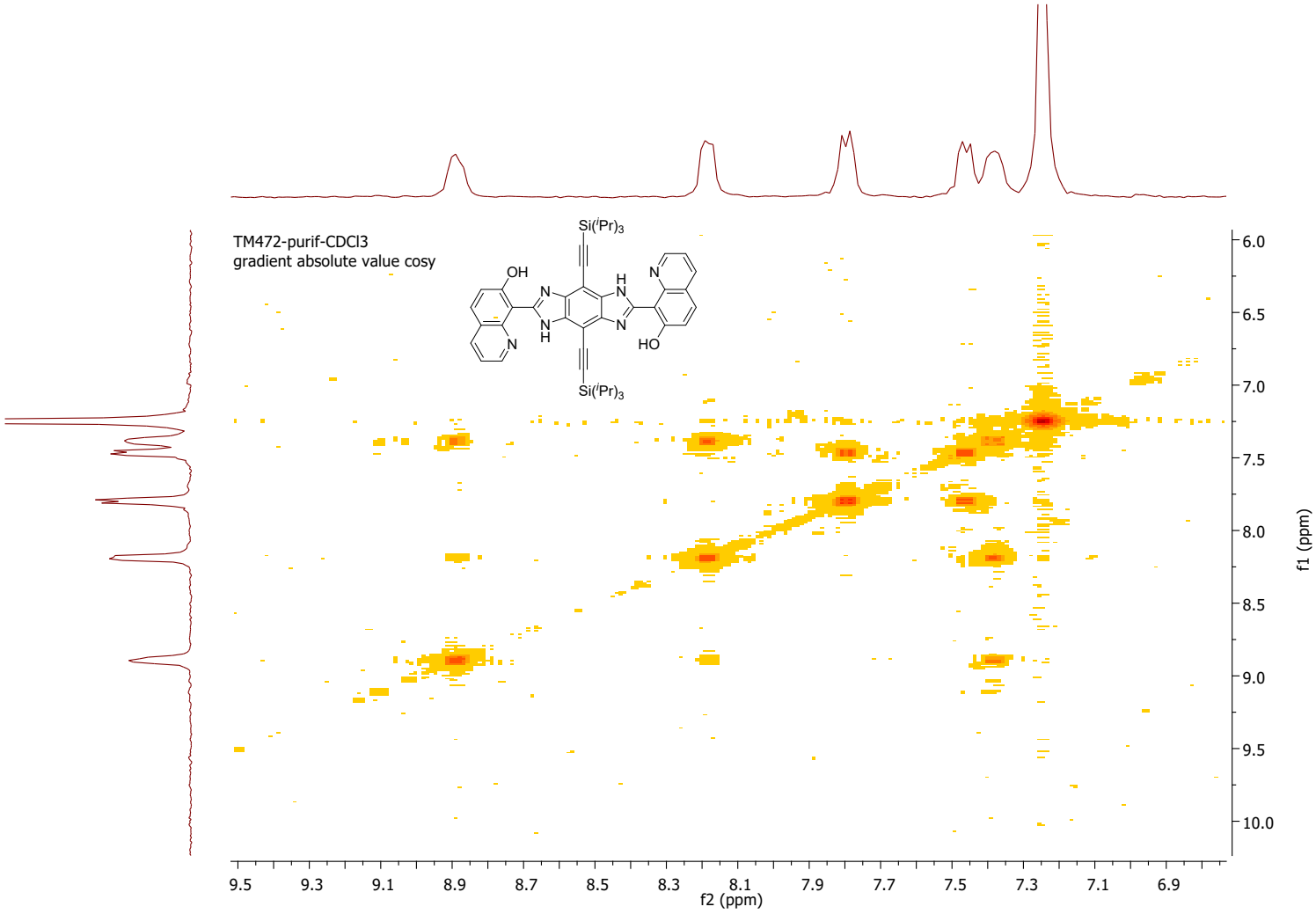


Figure S 6. COSY NMR (400 MHz, 298 K, $CDCl_3$) of compound **5**.

IV. MASS SPECTROMETRY

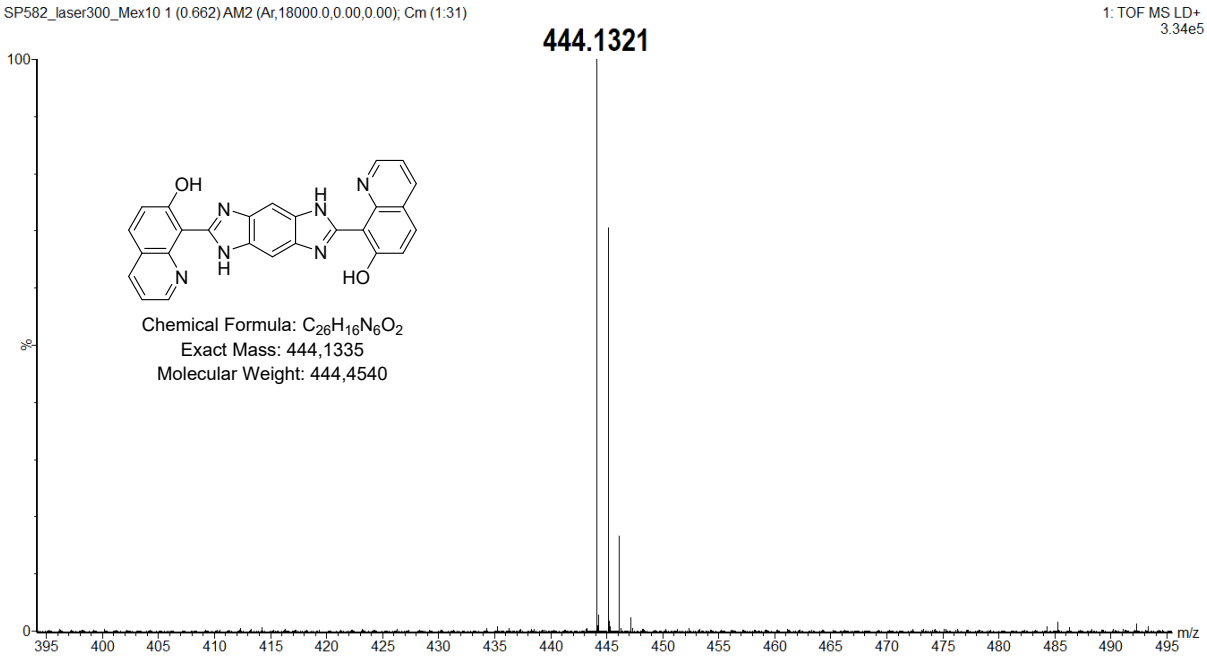


Figure S 7. HRMS spectrum of compound **4**.

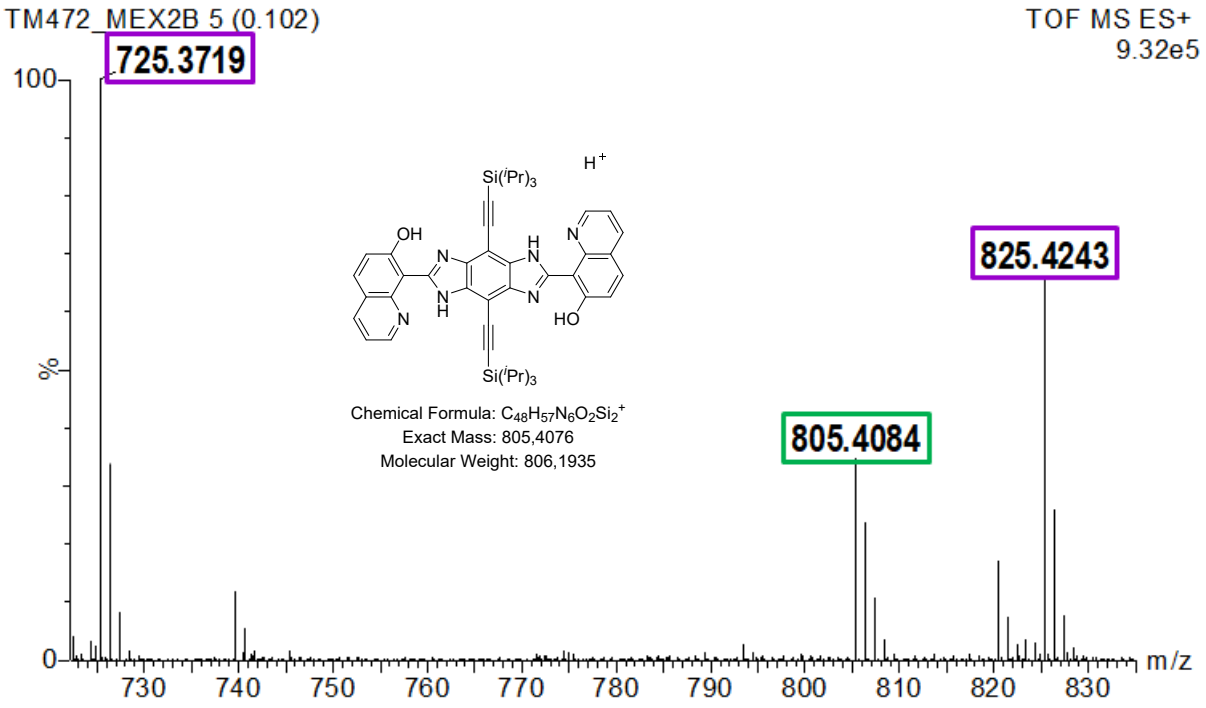


Figure S 8. HRMS spectrum of compound **5**. Target ion is detected at m/z 805.4084 and calibration peaks are observed at m/z 725.3719 and m/z 825.4243.

V. INFRARED SPECTRA

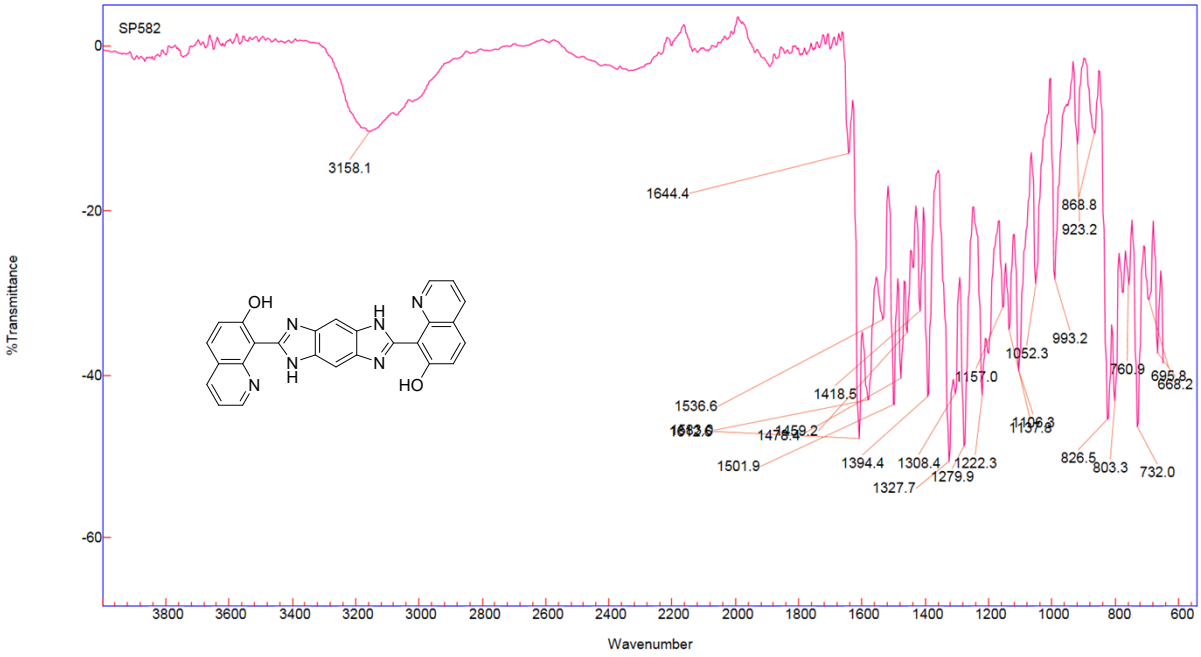


Figure S 9. Infrared spectrum of compound **4**.

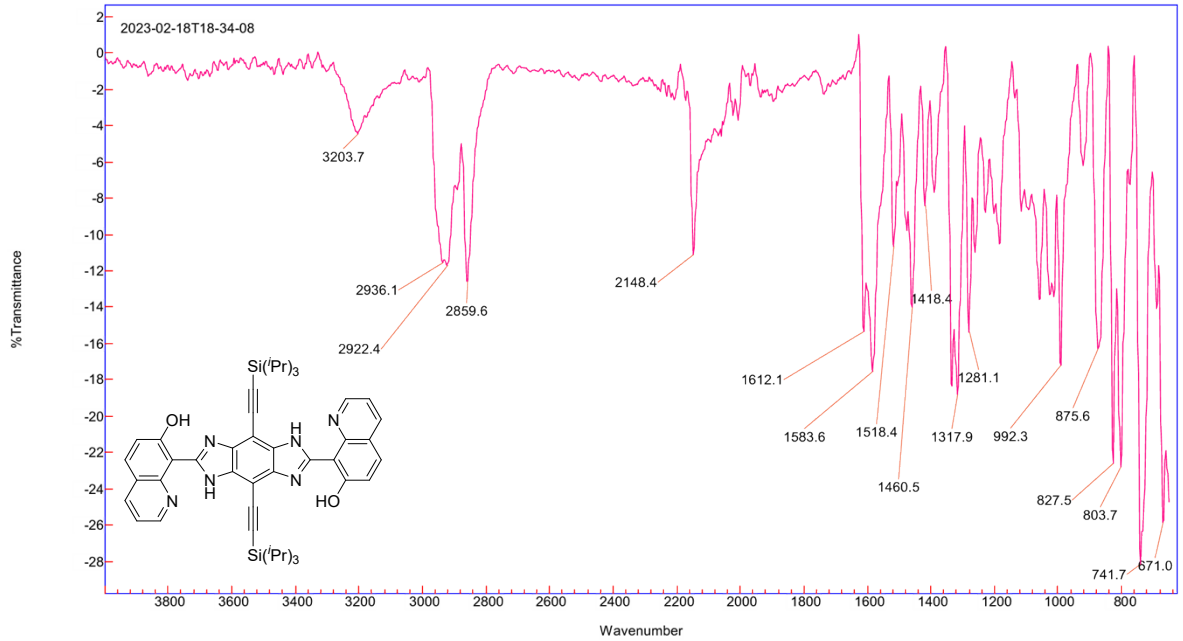


Figure S 10. Infrared spectrum of compound **5**.

VI. ELECTROCHEMICAL DATA

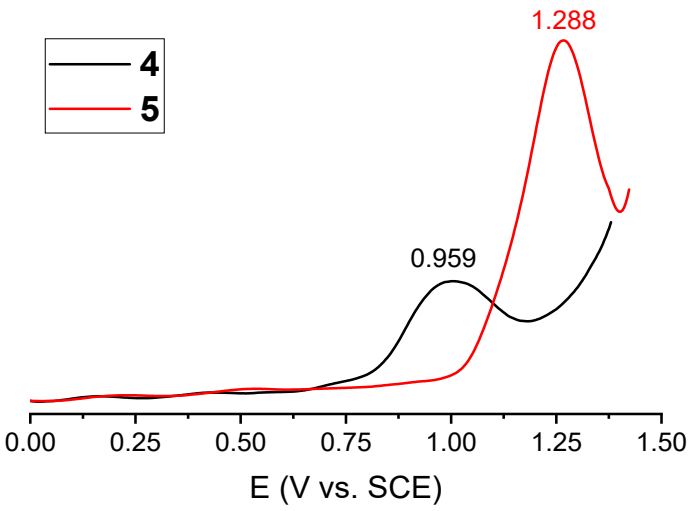


Figure S 11. Differential pulse voltammetry curves in oxidation for **4** (black) in DMSO and **5** (red) in DCM.

VII. PHOTOPHYSICAL DATA

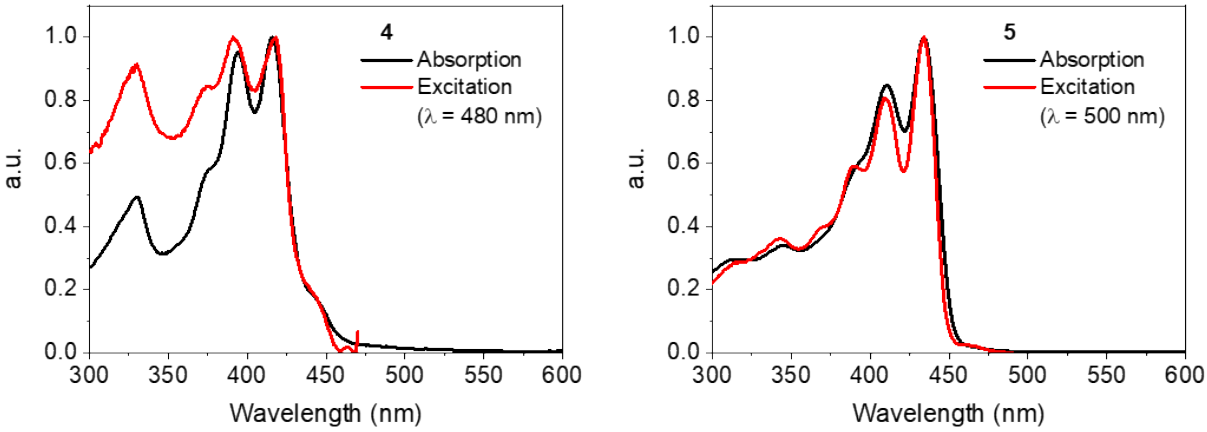


Figure S 12. Comparison between absorption and excitation spectra recorded for compounds **4** (left, in DMSO) and **5** (right, in DCM).

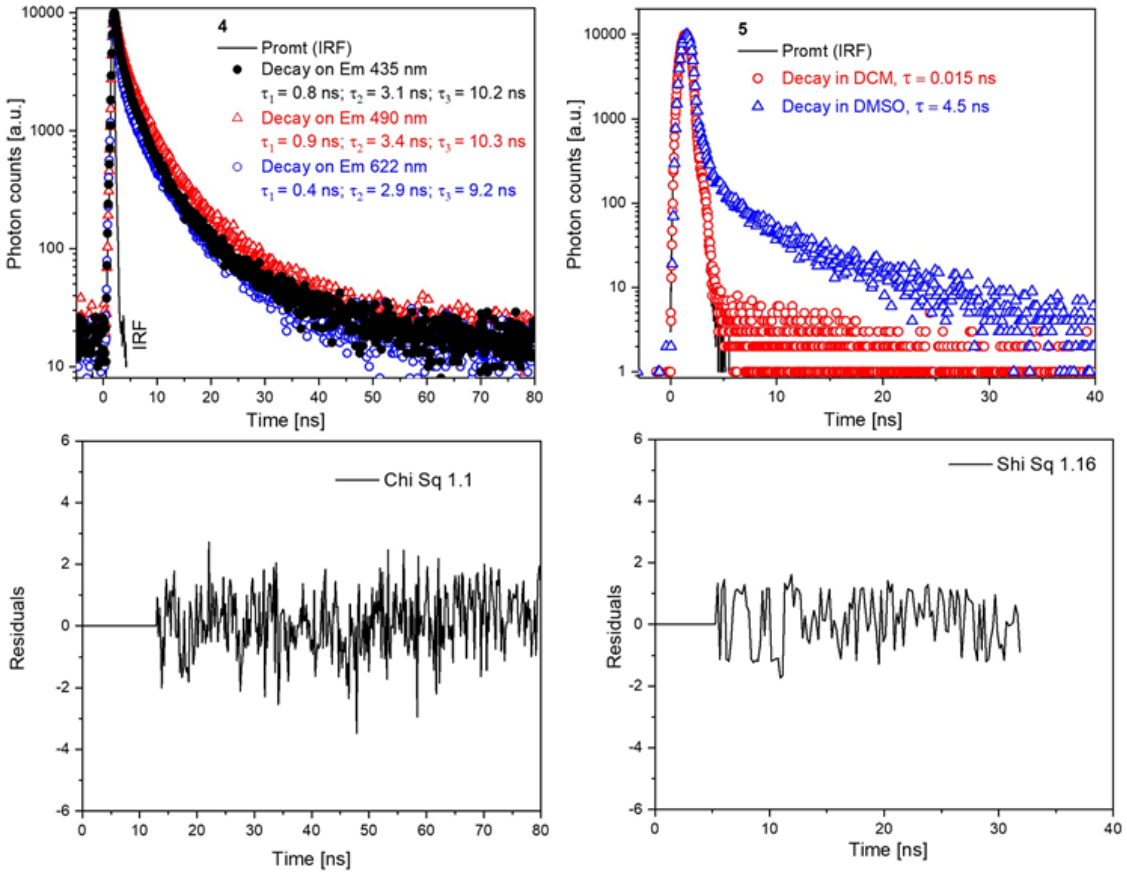


Figure S 13. Emission decay profiles of **4** (left) and **5** (right) upon excitation at 390 nm with a picosecond laser source, instrument response function (IRF) and fitting residuals.

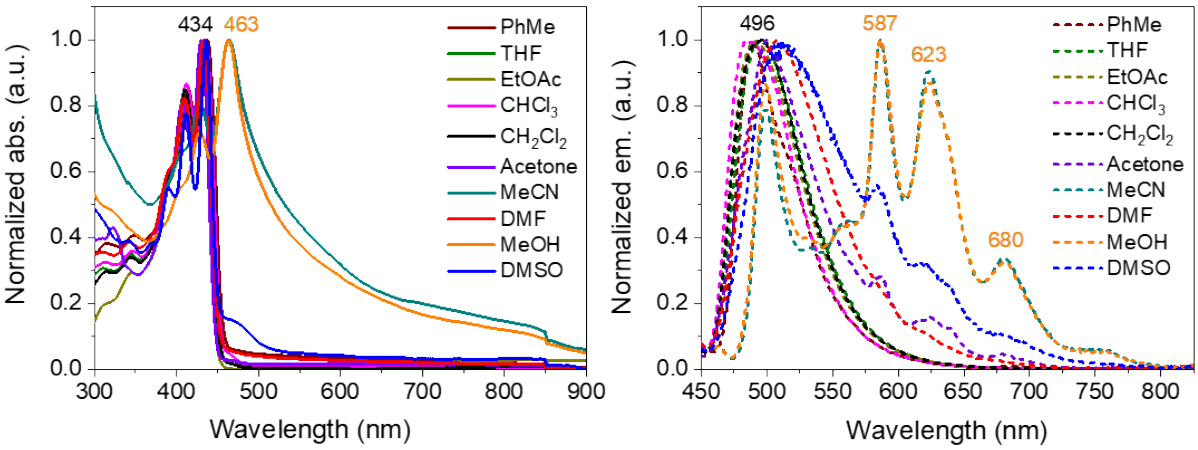


Figure S 14. Electronic absorption (left) and emission (right) solvatochromism of **5**.

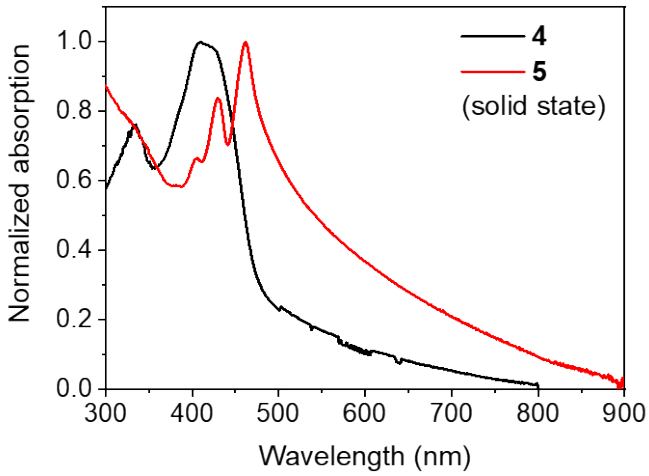


Figure S 15. Solid-state electronic absorption spectra of **4** (black) and **5** (red).

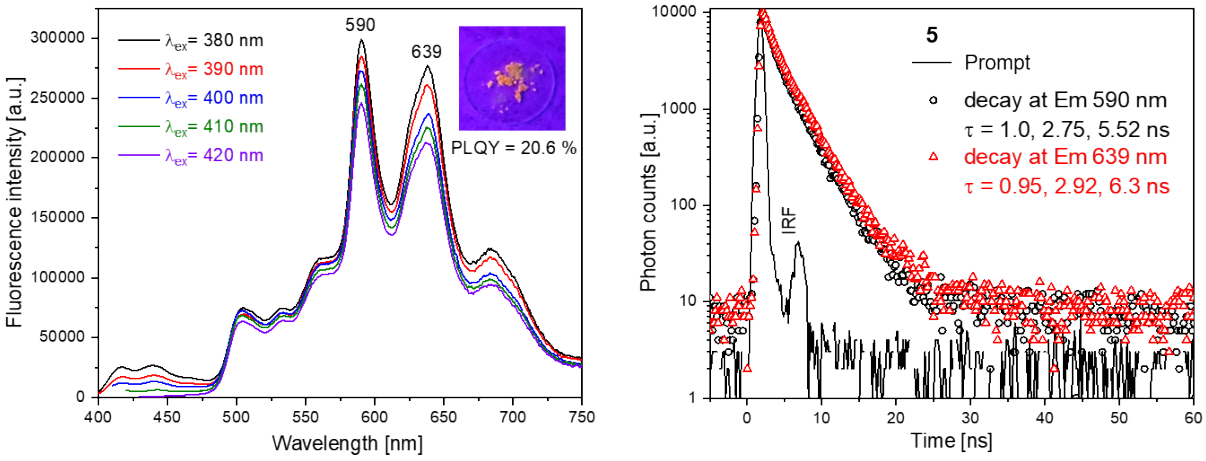


Figure S 16. Left: solid-state emission spectra of **5** measured as a crystalline powder on quartz substrate upon excitation at different wavelengths. Right: Emission decay profiles of **5** as a crystalline powder monitored at 590 and 639 nm.

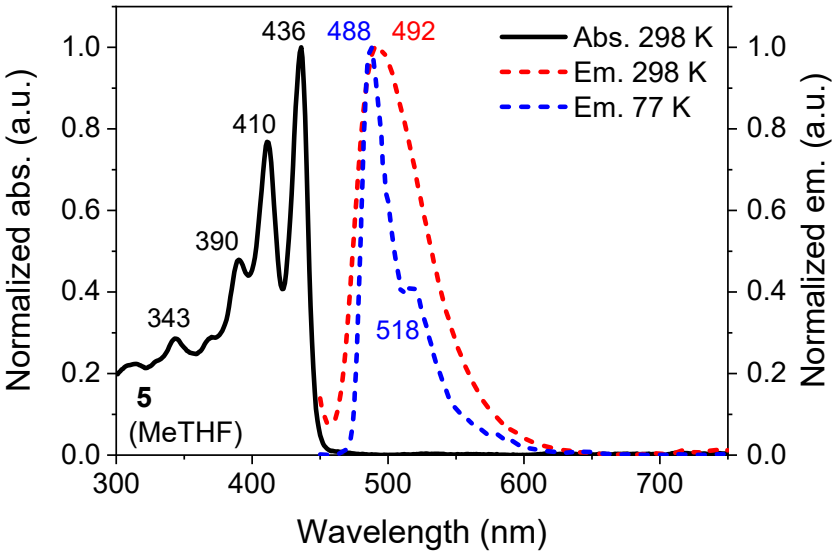


Figure S 17. Normalized electronic absorption (black plain line) and emission (dotted lines) spectra of **5** recorded in 2-methyltetrahydrofuran at 298 K (red) or 77 K (blue).

VIII. THEORETICAL CALCULATIONS

Methods

To model the dyes and the ESIPT, we have relied on both Time-Dependent Density Functional Theory (TD-DFT) and a wavefunction coupled-cluster-based approach, namely CC2. We have used exact dye structures but for the replacement of the TIPS by TMS moieties of **5** for obvious computational reasons. We have optimized and computed the vibrational frequencies of both **4** and **5** in their ground electronic state, and a large series of possible tautomers in their first excited state with TD-DFT. Symmetry was used, and it was (of course) lowered when necessary (presence at least one imaginary frequency) so as to obtain true minimum in all cases. The comparison between the free energies of the different tautomers allowed determining if a driving force exists for ESIPT to take place. The optimization and vibrational calculations were performed with the M06-2X functional[8] and the 6-31G(d) atomic basis set, including solvent effects (DMSO for **4** and DCM for **5** as in the experimental measurements displayed in Figure 3 of the main text) using the Polarizable Continuum Model (PCM), using the standard linear-response (LR) version of PCM for the TD-DFT part.[9] Next the vertical absorption and emission wavelengths have been respectively computed on both the optimal ground and excited state geometries. These calculations were done both in gas phase and in solution at the TD-M06-2X/6-311+G(2d,p) level, using the cLR^2 model[10,11] for the solution calculation, so as to simultaneously account for *linear-response* and *state-specific* solvent effects. For **4**, we have searched for the ESIPT transition state, by performing true TS search (not simple scans) on the basis of guess geometries and full Hessian calculations at each step. These calculations use the same level of theory as the standard optimizations and it has been checked that the final imaginary frequency corresponds to the actual ESIPT phenomenon. The All DFT and TD-DFT calculations were performed with Gaussian 16, using default algorithms but improved convergence thresholds for both ground state energies and residual forces.[12]

Secondly, we computed the vertical transition energies in gas-phase at the second-order coupled-cluster level, CC2,[13] with the *aug*-cc-pVTZ atomic basis set. These latter calculations were performed with the Turbomole package,[14] applying the RI approximation and freezing the core electrons. It was then possible to obtain theoretical best estimates of the vertical fluorescence energies using a combinatory approach

$$\Delta E^{fluo} = \Delta E_{Gas}^{CC2} + \left(\Delta E_{cLR^2-PCM}^{TD-DFT} - \Delta E_{Gas}^{TD-DFT}\right)$$

Therefore, the reported vertical transition wavelengths in the main text are CC2 values computed on TD-DFT geometries and corrected for solvation thanks to cLR^2-TD-M06-2X calculations. Such combination allows obtaining accurate estimates at a reasonable computational cost.

Additional results

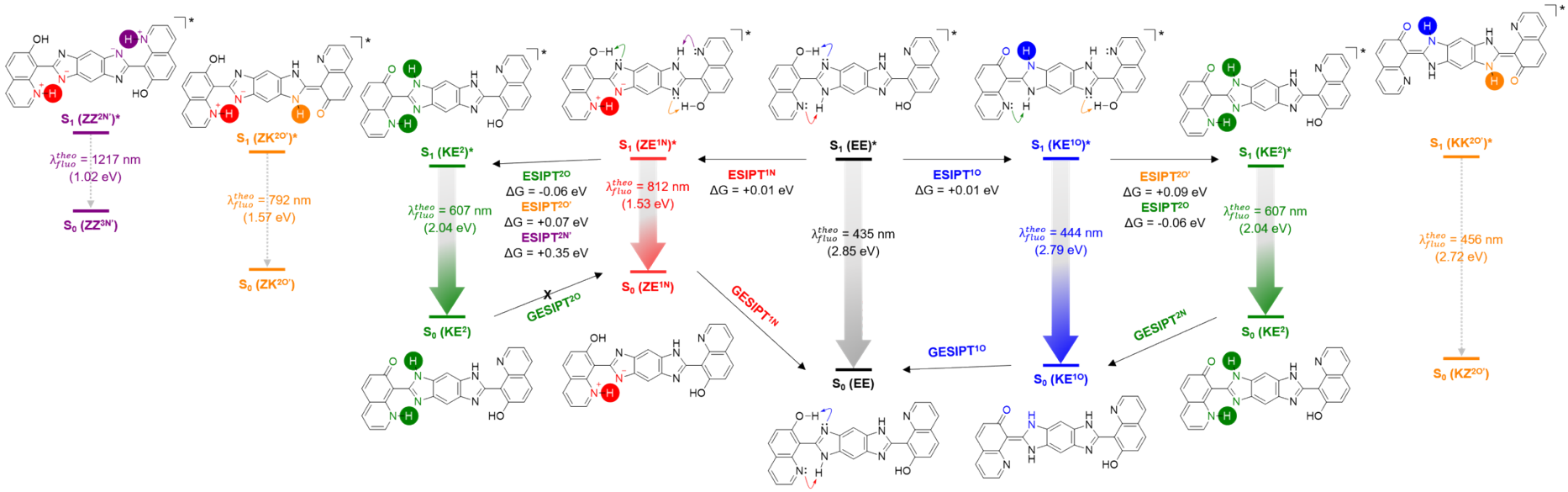


Figure S 18. Computed differences of free energies (ΔG) between tautomers of **4** at the first excited state and computed vertical emission wavelengths (λ_{fluo}^{theo}). The coloured circles identify the transferred proton(s) in each tautomer. K, E and Z stand for keto, enol and zwitterionic tautomers for the two sides of each molecule. The relative free energies are determined using LR-PCM(DMSO)-TD-M06-2X/6-31G(d), whereas the fluorescence wavelengths use a combinatory approach (see computational details).

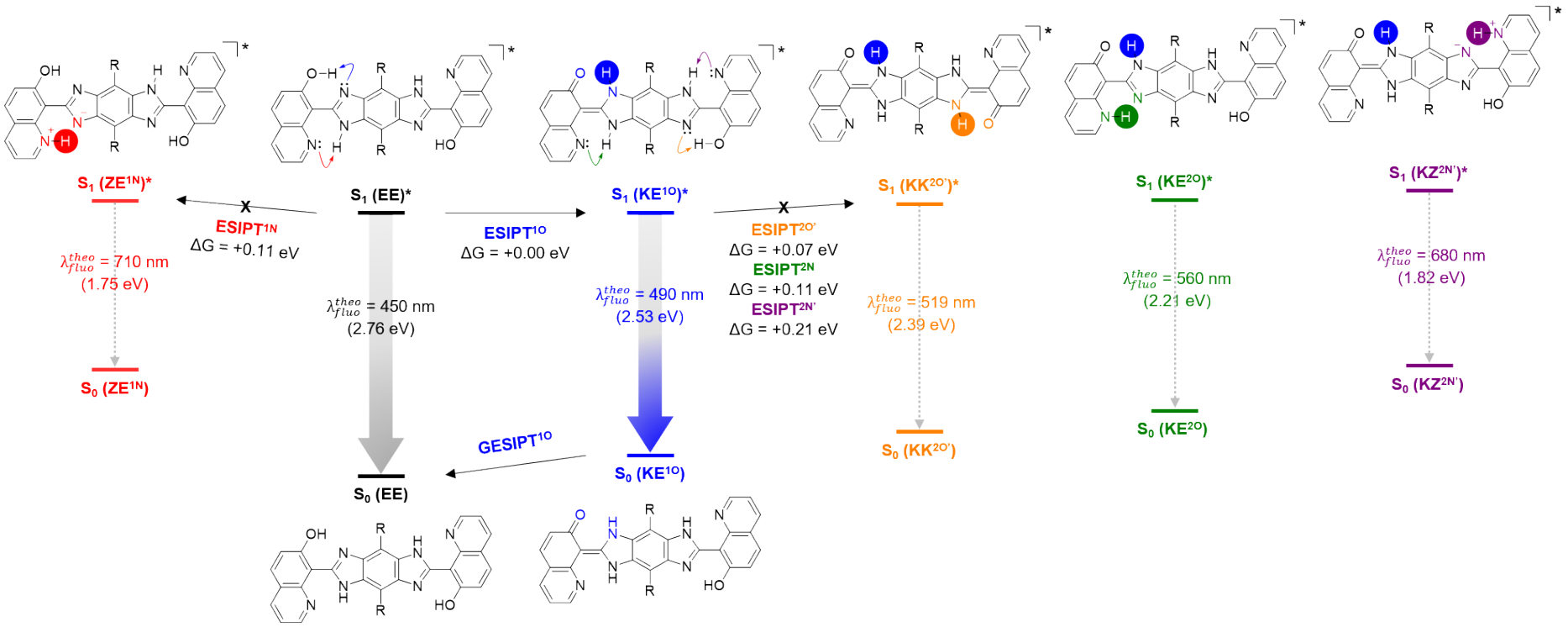


Figure S 19. Computed differences of free energies (ΔG) between tautomers of **5** (R = CCSi(^{i}Pr$_3$)) at the first excited state and computed vertical emissions (λ_{fluo}^{theo}). See caption of Figure S18 for more details.

Cartesian coordinates

Below we provide the Cartesian coordinates in Å for all identified excited-state minima.

4-EE

C	-0.8635890	1.0906040	0.0000000
C	0.5849560	1.2420610	0.0000000
C	1.4709900	0.1867720	0.0000000
C	0.8635890	-1.0906040	0.0000000
C	-0.5849560	-1.2420610	0.0000000
C	-1.4709900	-0.1867720	0.0000000
C	-0.4376190	3.2216770	0.0000000
H	2.5467700	0.3083670	0.0000000
H	-2.5467700	-0.3083670	0.0000000
H	1.6489660	3.1300810	0.0000000
N	0.7833140	2.5947910	0.0000000
N	-1.4417170	2.3006390	0.0000000
N	1.4417170	-2.3006390	0.0000000
N	-0.7833140	-2.5947910	0.0000000
H	-1.6489660	-3.1300810	0.0000000
C	0.4376190	-3.2216770	0.0000000
C	-0.6568410	4.6216400	0.0000000
C	-1.9969860	5.1191060	0.0000000
C	0.4288800	5.5848800	0.0000000
C	-2.2506000	6.5017340	0.0000000
C	0.1322920	6.9787470	0.0000000
C	-1.2188270	7.4122510	0.0000000
H	-3.2876290	6.8193840	0.0000000
C	1.2188270	7.8812960	0.0000000
C	2.6989140	6.0087260	0.0000000
H	-1.4274810	8.4779790	0.0000000
C	2.5083040	7.4001640	0.0000000
H	1.0182970	8.9492640	0.0000000
H	3.7028840	5.5924820	0.0000000
H	3.3632510	8.0664560	0.0000000
C	0.6568410	-4.6216400	0.0000000
C	1.9969860	-5.1191060	0.0000000
C	-0.4288800	-5.5848800	0.0000000
C	2.2506000	-6.5017340	0.0000000
C	-0.1322920	-6.9787470	0.0000000
C	1.2188270	-7.4122510	0.0000000
H	3.2876290	-6.8193840	0.0000000
C	-1.2188270	-7.8812960	0.0000000
C	-2.6989140	-6.0087260	0.0000000
H	1.4274810	-8.4779790	0.0000000
C	-2.5083040	-7.4001640	0.0000000
H	-1.0182970	-8.9492640	0.0000000
H	-3.7028840	-5.5924820	0.0000000
H	-3.3632510	-8.0664560	0.0000000
N	-1.7030990	-5.1333320	0.0000000
N	1.7030990	5.1333320	0.0000000
O	3.0602100	-4.3135300	0.0000000
H	2.7441720	-3.3639970	0.0000000
O	-3.0602100	4.3135300	0.0000000
H	-2.7441720	3.3639970	0.0000000

4-KE^{1O}

C	1.1959880	0.6717660	0.0000000
C	-0.0575520	1.3857460	0.0000000
C	-1.3061180	0.7707870	0.0000000
C	-1.2438870	-0.6239750	-0.0000000
C	0.0000000	-1.3533780	-0.0000000
C	1.2407290	-0.7319300	-0.0000000
C	1.6642670	2.7894600	0.0000000
H	-2.2410110	1.3158550	0.0000000
H	2.1731430	-1.2816370	-0.0000000
H	-0.2872910	3.5386540	0.0000000
N	0.2943050	2.7029580	0.0000000
N	2.2187050	1.5650490	0.0000000
N	-2.2296720	-1.5573390	-0.0000000
N	-0.3439780	-2.6751110	-0.0000000
H	0.2524770	-3.5022360	-0.0000000
C	-1.7080010	-2.8284660	-0.0000000
C	2.4230480	4.0072560	0.0000000
C	3.8355330	3.9298910	0.0000000

C	1.8087300	5.3136250	0.0000000
C	4.6245400	5.1029870	0.0000000
C	2.6277820	6.4774740	0.0000000
C	4.0421050	6.3423710	0.0000000
H	5.7021400	4.9796140	0.0000000
C	1.9890470	7.7369810	0.0000000
C	-0.1081040	6.5998850	0.0000000
H	4.6549330	7.2388780	0.0000000
C	0.6165750	7.8061470	0.0000000
H	2.5971810	8.6376130	0.0000000
H	-1.1951930	6.6178710	0.0000000
H	0.0932120	8.7550830	0.0000000
C	-2.4399930	-4.0278900	-0.0000000
C	-3.9198170	-3.9478190	-0.0000000
C	-1.7924710	-5.3189810	-0.0000000
C	-4.6456140	-5.1901630	-0.0000000
C	-2.5916250	-6.5037940	-0.0000000
C	-4.0154120	-6.4047930	-0.0000000
H	-5.7279760	-5.1125800	-0.0000000
C	-1.9182960	-7.7405340	-0.0000000
C	0.1607900	-6.5553000	-0.0000000
H	-4.5929880	-7.3253750	-0.0000000
C	-0.5404030	-7.7760030	-0.0000000
H	-2.4994860	-8.6590310	-0.0000000
H	1.2474550	-6.5453690	-0.0000000
H	0.0022540	-8.7144050	-0.0000000
N	-0.4381320	-5.3753420	-0.0000000
N	0.4542070	5.4042510	0.0000000
O	-4.5103090	-2.8403050	-0.0000000
O	4.4973730	2.7704740	0.0000000
H	3.8303090	2.0232630	0.0000000
H	-3.2447440	-1.4469020	-0.0000000

4-KE[2]

C	-0.1264700	-1.4247200	0.0000000
C	1.1402720	-0.7392600	-0.0000000
C	1.2138570	0.6626000	-0.0000000
C	0.0000000	1.3247310	-0.0000000
C	-1.2501990	0.6106850	0.0000000
C	-1.3569220	-0.7719970	0.0000000
C	1.5654370	-2.8587940	-0.0000000
H	2.1625630	1.1862710	-0.0000000
H	-2.3057390	-1.2939860	0.0000000
N	2.1490630	-1.6472150	-0.0000000
N	0.1948510	-2.7460710	-0.0000000
N	-0.2616880	2.6803090	0.0000000
N	-2.2091780	1.5890500	0.0000000
H	-3.2250920	1.5178860	0.0000000
C	-1.5801990	2.8040220	0.0000000
C	2.2492820	-4.1086560	-0.0000000
C	1.4508410	-5.3767310	-0.0000000
C	3.6872650	-4.1775710	-0.0000000
C	2.1835840	-6.6010900	-0.0000000
C	4.3472450	-5.4311550	-0.0000000
C	3.5606860	-6.6094600	-0.0000000
H	1.6086120	-7.5199010	-0.0000000
C	5.7834010	-5.4383040	-0.0000000
C	5.8065530	-3.0318580	-0.0000000
H	4.0899370	-7.5594580	-0.0000000
C	6.4844550	-4.2418300	-0.0000000
H	6.3033850	-6.3895990	-0.0000000
H	6.2745810	-2.0590680	-0.0000000
H	7.5687080	-4.2342880	-0.0000000
C	-2.2604590	4.0915940	0.0000000
C	-1.4814940	5.2559870	0.0000000
C	-3.6923710	4.2155700	0.0000000
C	-2.0956240	6.5400970	0.0000000
C	-4.2854240	5.5064170	0.0000000
C	-3.4522300	6.6607610	0.0000000
H	-1.4424980	7.4057690	0.0000000
C	-5.6936910	5.5956940	0.0000000
C	-5.7702210	3.2126880	0.0000000
H	-3.9185440	7.6416670	0.0000000
C	-6.4473030	4.4475250	0.0000000
H	-6.1610760	6.5767530	0.0000000
H	-6.3369500	2.2846250	0.0000000

H	-7.5304490	4.4735220	0.0000000
N	-4.4572030	3.0896730	0.0000000
N	4.4333180	-3.0456770	-0.0000000
O	-0.1484330	5.2504250	-0.0000000
H	0.1645150	4.2987230	-0.0000000
O	0.1988040	-5.3416820	0.0000000
H	3.9120190	-2.1621130	-0.0000000
H	-0.3927170	-3.5789040	0.0000000

4-KK$^{2o'}$

C	-0.8727190	1.0583630	0.0000000
C	0.5480740	1.2572500	0.0000000
C	1.4642820	0.2061350	0.0000000
C	0.8727190	-1.0583630	0.0000000
C	-0.5480740	-1.2572500	0.0000000
C	-1.4642820	-0.2061350	0.0000000
C	-0.4593250	3.2710000	0.0000000
H	2.5355350	0.3561230	0.0000000
H	-2.5355350	-0.3561230	0.0000000
H	1.6069730	3.1454610	0.0000000
N	0.7390930	2.6083440	0.0000000
N	-1.4271900	2.3026320	0.0000000
N	1.4271900	-2.3026320	0.0000000
N	-0.7390930	-2.6083440	0.0000000
H	-1.6069730	-3.1454610	0.0000000
C	0.4593250	-3.2710000	0.0000000
C	-0.6791580	4.6617420	0.0000000
C	-2.0660700	5.1406420	0.0000000
C	0.4132100	5.6035630	0.0000000
C	-2.2634110	6.5740940	0.0000000
C	0.1343920	7.0012490	0.0000000
C	-1.2239670	7.4533970	0.0000000
H	-3.2941380	6.9138650	0.0000000
C	1.2239670	7.8881210	0.0000000
C	2.6897540	6.0024440	0.0000000
H	-1.4065840	8.5249780	0.0000000
C	2.5130250	7.3963390	0.0000000
H	1.0349300	8.9585640	0.0000000
H	3.6904210	5.5775510	0.0000000
H	3.3735980	8.0550670	0.0000000
C	0.6791580	-4.6617420	0.0000000
C	2.0660700	-5.1406420	0.0000000
C	-0.4132100	-5.6035630	0.0000000
C	2.2634110	-6.5740940	0.0000000
C	-0.1343920	-7.0012490	0.0000000
C	1.2239670	-7.4533970	0.0000000
H	3.2941380	-6.9138650	0.0000000
C	-1.2239670	-7.8881210	0.0000000
C	-2.6897540	-6.0024440	0.0000000
H	1.4065840	-8.5249780	0.0000000
C	-2.5130250	-7.3963390	0.0000000
H	-1.0349300	-8.9585640	0.0000000
H	-3.6904210	-5.5775510	0.0000000
H	-3.3735980	-8.0550670	0.0000000
N	-1.6881360	-5.1375280	0.0000000
N	1.6881360	5.1375280	0.0000000
O	3.0448360	-4.3534250	0.0000000
O	-3.0448360	4.3534250	0.0000000
H	2.4063870	-2.5946710	0.0000000
H	-2.4063870	2.5946710	0.0000000

4-ZE^{1N}

C	-0.0487880	1.4346050	0.0000000
C	1.2125780	0.6766240	0.0000000
C	1.2358930	-0.7304750	-0.0000000
C	0.0000000	-1.3426050	-0.0000000
C	-1.2413800	-0.5766380	-0.0000000
C	-1.3061630	0.7963490	0.0000000
C	1.6262990	2.7742530	0.0000000
H	2.1615980	-1.2933920	-0.0000000
H	-2.2377730	1.3487410	0.0000000
N	2.2304320	1.5473760	0.0000000
N	0.2511580	2.7356200	0.0000000
N	-0.3099560	-2.6816880	-0.0000000
N	-2.2276260	-1.5292990	-0.0000000
H	-3.2409020	-1.4277890	-0.0000000

C	-1.6365390	-2.7630370	-0.0000000
C	2.3281990	4.0119590	0.0000000
C	1.5926370	5.2627110	0.0000000
C	3.7632370	4.0771330	0.0000000
C	2.2715450	6.4740370	0.0000000
C	4.4401360	5.3294960	0.0000000
C	3.6642290	6.5026320	0.0000000
H	1.6889010	7.3880160	0.0000000
C	5.8684880	5.3282510	0.0000000
C	5.8830750	2.9280000	0.0000000
H	4.1798080	7.4586080	0.0000000
C	6.5673080	4.1241140	0.0000000
H	6.3931680	6.2769170	0.0000000
H	6.3459340	1.9524400	0.0000000
H	7.6510240	4.1119720	0.0000000
C	-2.3516130	-4.0234530	-0.0000000
C	-1.6064940	-5.2141760	-0.0000000
C	-3.7892320	-4.1046560	-0.0000000
C	-2.2602340	-6.4782790	-0.0000000
C	-4.4191900	-5.3770130	-0.0000000
C	-3.6198870	-6.5562160	-0.0000000
H	-1.6343690	-7.3637000	-0.0000000
C	-5.8289010	-5.4255110	-0.0000000
C	-5.8361710	-3.0414550	-0.0000000
H	-4.1158450	-7.5224610	-0.0000000
C	-6.5486830	-4.2553260	-0.0000000
H	-6.3249080	-6.3923080	-0.0000000
H	-6.3745240	-2.0967950	-0.0000000
H	-7.6320980	-4.2499980	-0.0000000
N	-4.5192370	-2.9578210	-0.0000000
N	4.5086400	2.9426620	0.0000000
O	-0.2766830	-5.2491680	-0.0000000
H	0.0666960	-4.3067310	-0.0000000
O	0.2610030	5.2900600	0.0000000
H	-0.0783020	4.3419780	0.0000000
H	3.9810490	2.0614640	0.0000000

4-ZK$^{2O'}$

C	0.0149980	-1.4100830	-0.0000000
C	1.2571150	-0.6270530	-0.0000000
C	1.2509140	0.7838070	-0.0000000
C	0.0000000	1.3497480	0.0000000
C	-1.2262090	0.5747580	0.0000000
C	-1.2551260	-0.7994770	0.0000000
C	1.7163050	-2.7140780	-0.0000000
H	2.1625750	1.3681600	-0.0000000
H	-2.1756720	-1.3697620	0.0000000
N	2.2930980	-1.4713160	-0.0000000
N	0.3437280	-2.7052910	-0.0000000
N	-0.3957330	2.6673200	0.0000000
N	-2.2460720	1.4969810	0.0000000
H	-3.2580730	1.3571820	0.0000000
C	-1.7507230	2.7637460	0.0000000
C	2.4498560	-3.9346410	-0.0000000
C	1.7474310	-5.2023010	-0.0000000
C	3.8854920	-3.9651830	-0.0000000
C	2.4552300	-6.3966760	-0.0000000
C	4.5937030	-5.2018250	-0.0000000
C	3.8484780	-6.3937850	-0.0000000
H	1.8940070	-7.3240570	-0.0000000
C	6.0210650	-5.1637950	-0.0000000
C	5.9766100	-2.7651240	-0.0000000
H	4.3870040	-7.3368880	-0.0000000
C	6.6908600	-3.9444150	-0.0000000
H	6.5691100	-6.0993030	-0.0000000
H	6.4155690	-1.7785330	-0.0000000
H	7.7738780	-3.9058830	-0.0000000
C	-2.4794800	3.9676330	0.0000000
C	-1.7293620	5.2139240	0.0000000
C	-3.9253640	3.9739080	0.0000000
C	-2.5114590	6.4481700	0.0000000
C	-4.6143010	5.2135360	0.0000000
C	-3.8613720	6.4431040	0.0000000
H	-1.9432530	7.3725520	0.0000000
C	-6.0141110	5.1981240	0.0000000
C	-5.9251620	2.8176950	0.0000000

H	-4.4168510	7.3776630	0.0000000
C	-6.6874600	3.9902420	0.0000000
H	-6.5561010	6.1401690	0.0000000
H	-6.4144840	1.8468740	0.0000000
H	-7.7696970	3.9401680	0.0000000
N	-4.5982280	2.7982810	0.0000000
N	4.6049030	-2.8139560	-0.0000000
O	-0.4791910	5.2677570	0.0000000
O	0.4150910	-5.2636590	-0.0000000
H	4.0566410	-1.9453330	-0.0000000
H	0.0517680	-4.3266130	-0.0000000
H	0.1569250	3.5269250	0.0000000

4-ZZ$^{2N'}$

C	1.2577660	-0.6137060	0.0000000
C	0.0082360	-1.3858620	0.0000000
C	-1.2672950	-0.7615290	0.0000000
C	-1.2486740	0.6113730	0.0000000
C	-0.0000000	1.3803980	0.0000000
C	1.2658330	0.7690760	0.0000000
C	1.6914480	-2.7160520	0.0000000
H	-2.1836120	-1.3406770	0.0000000
H	2.1808010	1.3501200	0.0000000
N	0.3033870	-2.6827570	0.0000000
N	2.2863240	-1.5077450	0.0000000
N	-2.2863430	1.5167940	0.0000000
N	-0.3128100	2.6923010	0.0000000
C	-1.6776790	2.7051310	0.0000000
C	2.4442360	-3.9370910	0.0000000
C	3.8840300	-3.8776270	0.0000000
C	1.8250430	-5.2265140	0.0000000
C	4.6364070	-5.0464650	0.0000000
C	2.6094070	-6.4176250	0.0000000
C	4.0080930	-6.2889750	0.0000000
H	5.7172360	-4.9610080	0.0000000
C	1.9327560	-7.6776200	0.0000000
C	-0.1903770	-6.5597560	0.0000000
H	4.6078950	-7.1945390	0.0000000
C	0.5422900	-7.7269570	0.0000000
H	2.5227450	-8.5872270	0.0000000
H	-1.2690950	-6.5094780	0.0000000
H	0.0205420	-8.6769880	0.0000000
C	-2.4500250	3.9404570	0.0000000
C	-3.8541800	3.8910550	0.0000000
C	-1.8409700	5.2222490	0.0000000
C	-4.6275490	5.0889900	0.0000000
C	-2.6046330	6.4180420	0.0000000
C	-4.0258810	6.3113990	0.0000000
H	-5.7068460	4.9855790	0.0000000
C	-1.9276740	7.6497100	0.0000000
C	0.1626810	6.5042020	0.0000000
H	-4.6175820	7.2208940	0.0000000
C	-0.5451520	7.7017210	0.0000000
H	-2.5088640	8.5671330	0.0000000
H	1.2443430	6.4551140	0.0000000
H	-0.0093880	8.6414790	0.0000000
N	-0.4789240	5.3382450	0.0000000
N	0.4685660	-5.3533740	0.0000000
O	-4.5206740	2.7480470	0.0000000
H	-3.8430870	1.9900430	0.0000000
O	4.5349300	-2.7092890	0.0000000
H	3.8510220	-1.9691430	0.0000000
H	-0.0614130	-4.4763180	0.0000000
H	0.0310290	4.4225630	0.0000000

5-EE

C	-1.0942760	0.8627920	-0.0871350
C	0.2625740	1.3441360	-0.0687030
C	1.3987150	0.5409980	0.0166020
C	1.0942760	-0.8627920	0.0871350
C	-0.2625740	-1.3441360	0.0687030
C	-1.3987150	-0.5409980	-0.0166020
C	-1.1769260	3.0254940	-0.2149680
H	0.8758590	3.4136180	-0.1677630
N	0.1478880	2.7016730	-0.1511440
N	-1.9382120	1.8958420	-0.1755760

N	1.9382120	-1.8958420	0.1755760
N	-0.1478880	-2.7016730	0.1511440
H	-0.8758590	-3.4136180	0.1677630
C	1.1769260	-3.0254940	0.2149680
C	-1.7222370	4.3368010	-0.3092180
C	-3.1333360	4.4994620	-0.3650880
C	-0.8935110	5.5224470	-0.3509400
C	-3.7063950	5.7875530	-0.4587260
C	-1.5020440	6.8035600	-0.4458360
C	-2.9194430	6.9076630	-0.4982050
H	-4.7883810	5.8488280	-0.4976920
C	-0.6592150	7.9342720	-0.4846130
C	1.2129640	6.4622880	-0.3366400
H	-3.3696120	7.8934280	-0.5700120
C	0.7052370	7.7702030	-0.4302960
H	-1.1039030	8.9230730	-0.5572420
H	2.2862830	6.2947520	-0.2913510
H	1.3821110	8.6161030	-0.4578700
C	1.7222370	-4.3368010	0.3092180
C	3.1333360	-4.4994620	0.3650880
C	0.8935110	-5.5224470	0.3509400
C	3.7063950	-5.7875530	0.4587260
C	1.5020440	-6.8035600	0.4458360
C	2.9194430	-6.9076630	0.4982050
H	4.7883810	-5.8488280	0.4976920
C	0.6592150	-7.9342720	0.4846130
C	-1.2129640	-6.4622880	0.3366400
H	3.3696120	-7.8934280	0.5700120
C	-0.7052370	-7.7702030	0.4302960
H	1.1039030	-8.9230730	0.5572420
H	-2.2862830	-6.2947520	0.2913510
H	-1.3821110	-8.6161030	0.4578700
N	-0.4530380	-5.3807980	0.2981750
N	0.4530380	5.3807980	-0.2981750
O	3.9837810	-3.4766210	0.3333470
H	3.4677690	-2.6236420	0.2674490
O	-3.9837810	3.4766210	-0.3333470
H	-3.4677690	2.6236420	-0.2674490
C	-2.7072340	-1.0665990	-0.0312860
C	-3.8234730	-1.5668770	-0.0408770
C	2.7072340	1.0665990	0.0312860
C	3.8234730	1.5668770	0.0408770
Si	-5.4901850	-2.3568020	-0.0519470
Si	5.4901850	2.3568020	0.0519470
C	-6.4800760	-1.7255250	1.4145690
H	-5.9860010	-1.9699810	2.3597330
H	-6.6070430	-0.6396920	1.3669050
H	-7.4754450	-2.1829850	1.4227080
C	-6.3660890	-1.9245590	-1.6566670
H	-5.8049380	-2.2868380	-2.5233030
H	-7.3604630	-2.3837220	-1.6791320
H	-6.4907220	-0.8422550	-1.7591590
C	-5.2376100	-4.2149900	0.0773960
H	-4.6508460	-4.5912170	-0.7666140
H	-4.7141700	-4.4770230	1.0023450
H	-6.2033480	-4.7316640	0.0761450
C	5.2376100	4.2149900	-0.0773960
H	4.6508460	4.5912170	0.7666140
H	6.2033480	4.7316640	-0.0761450
H	4.7141700	4.4770230	-1.0023450
C	6.3660890	1.9245590	1.6566670
H	7.3604630	2.3837220	1.6791320
H	5.8049380	2.2868380	2.5233030
H	6.4907220	0.8422550	1.7591590
C	6.4800760	1.7255250	-1.4145690
H	6.6070430	0.6396920	-1.3669050
H	5.9860010	1.9699810	-2.3597330
H	7.4754450	2.1829850	-1.4227080

5-ZE^{1N}

C	-1.0626220	-0.8086540	0.0000000
C	-1.1760430	0.6327060	0.0000000
C	-0.1075580	1.5200160	0.0000000
C	1.1607470	0.8809690	0.0000000
C	1.2962090	-0.5812920	0.0000000
C	0.1758120	-1.4516410	0.0000000

C	-3.1705660	-0.3287290	0.0000000
H	-3.0241140	1.7603110	0.0000000
N	-2.5186220	0.8750160	0.0000000
N	-2.3166890	-1.3512630	0.0000000
N	2.3791150	1.4123190	0.0000000
N	2.5942520	-0.8859440	0.0000000
C	3.2273540	0.3273980	0.0000000
C	-4.6066250	-0.4921590	0.0000000
C	-5.1327800	-1.7956310	0.0000000
C	-5.5159950	0.6247230	0.0000000
C	-6.5398760	-2.0070470	0.0000000
C	-6.9154530	0.3880250	0.0000000
C	-7.4007110	-0.9515780	0.0000000
H	-6.8892560	-3.0334330	0.0000000
C	-7.7810680	1.5012900	0.0000000
C	-5.8546210	2.9060610	0.0000000
H	-8.4741670	-1.1173340	0.0000000
C	-7.2555090	2.7708520	0.0000000
H	-8.8550740	1.3363680	0.0000000
H	-5.4045050	3.8960180	0.0000000
H	-7.8869490	3.6513000	0.0000000
C	4.6376980	0.4882370	0.0000000
C	5.2183240	1.8169100	0.0000000
C	5.5351800	-0.6364330	0.0000000
C	6.5986700	1.9786580	0.0000000
C	6.9457090	-0.4468140	0.0000000
C	7.4400470	0.8702380	0.0000000
H	6.9942680	2.9876820	0.0000000
C	7.7825910	-1.6032250	0.0000000
C	5.8500900	-3.0233940	0.0000000
H	8.5165040	1.0143110	0.0000000
C	7.2220580	-2.8751530	0.0000000
H	8.8587060	-1.4701110	0.0000000
H	5.3320030	-3.9711760	0.0000000
H	7.8491670	-3.7588960	0.0000000
N	5.0575650	-1.9054790	0.0000000
N	-5.0149170	1.8881780	0.0000000
O	4.4622280	2.9115250	0.0000000
O	-4.3826040	-2.8929520	0.0000000
H	-3.4181320	-2.6269420	0.0000000
C	0.3201530	-2.8645430	0.0000000
C	0.4631280	-4.0753630	0.0000000
C	-0.2916910	2.9283210	0.0000000
C	-0.4993930	4.1298150	0.0000000
Si	0.7106610	-5.9072450	0.0000000
Si	-0.8438280	5.9479510	0.0000000
C	-0.0871290	-6.6205630	1.5426480
H	0.3620280	-6.2031470	2.4488510
H	-1.1605470	-6.4095300	1.5652120
H	0.0455120	-7.7075730	1.5673020
C	-0.0871290	-6.6205630	-1.5426480
H	0.3620280	-6.2031470	-2.4488510
H	0.0455120	-7.7075730	-1.5673020
H	-1.1605470	-6.4095300	-1.5652120
C	2.5602670	-6.2361150	0.0000000
H	3.0355030	-5.8058280	-0.8872000
H	3.0355030	-5.8058280	0.8872000
H	2.7550950	-7.3138810	0.0000000
C	-2.7097530	6.1660400	0.0000000
H	-3.1582400	5.7078480	0.8871920
H	-2.9687230	7.2301620	0.0000000
H	-3.1582400	5.7078480	-0.8871920
C	-0.0871290	6.7014450	1.5435470
H	-0.2791350	7.7795070	1.5693680
H	-0.5131590	6.2588040	2.4489230
H	0.9961810	6.5494360	1.5662430
C	-0.0871290	6.7014450	-1.5435470
H	0.9961810	6.5494360	-1.5662430
H	-0.5131590	6.2588040	-2.4489230
H	-0.2791350	7.7795070	-1.5693680
H	3.4960990	2.6411490	0.0000000
H	4.0336530	-1.9983380	0.0000000

5-KE^{1O}

C	-1.1635020	-0.8084650	0.0000000
C	-1.2554580	0.6218730	0.0000000

C	-0.1608480	1.5103270	0.0000000
C	1.0769240	0.8256200	0.0000000
C	1.1893840	-0.5974480	0.0000000
C	0.0924990	-1.4791630	0.0000000
C	-3.2680970	-0.3010280	0.0000000
H	-3.0721580	1.7847540	0.0000000
N	-2.5867290	0.8888710	0.0000000
N	-2.4090170	-1.3359020	0.0000000
N	2.3433130	1.3077730	0.0000000
N	2.5228150	-0.8682660	0.0000000
H	2.9958110	-1.7734100	0.0000000
C	3.2543990	0.2858480	0.0000000
C	-4.6954310	-0.4460360	0.0000000
C	-5.2468300	-1.7466820	0.0000000
C	-5.5948150	0.6818880	0.0000000
C	-6.6507690	-1.9364530	0.0000000
C	-6.9990050	0.4625310	0.0000000
C	-7.5027410	-0.8676980	0.0000000
H	-7.0150070	-2.9579440	0.0000000
C	-7.8468440	1.5905480	0.0000000
C	-5.8998890	2.9688520	0.0000000
H	-8.5780140	-1.0203740	0.0000000
C	-7.3026820	2.8524270	0.0000000
H	-8.9234030	1.4423480	0.0000000
H	-5.4350580	3.9520700	0.0000000
H	-7.9223280	3.7414320	0.0000000
C	4.6573990	0.4218860	0.0000000
C	5.2209260	1.7821980	0.0000000
C	5.5324010	-0.7220320	0.0000000
C	6.6680660	1.8968040	0.0000000
C	6.9413090	-0.5243870	0.0000000
C	7.4774370	0.8085850	0.0000000
H	7.0652930	2.9063240	0.0000000
C	7.7637280	-1.6607170	0.0000000
C	5.7945360	-3.0156900	0.0000000
H	8.5582120	0.9228480	0.0000000
C	7.1966660	-2.9193200	0.0000000
H	8.8431310	-1.5344870	0.0000000
H	5.3130990	-3.9903960	0.0000000
H	7.8042580	-3.8166110	0.0000000
N	4.9898340	-1.9671850	0.0000000
N	-5.0762280	1.9372460	0.0000000
O	4.4944740	2.7980920	0.0000000
O	-4.5034020	-2.8520260	0.0000000
H	-3.5372830	-2.5931660	0.0000000
C	0.2672940	-2.8784650	0.0000000
C	0.4810580	-4.0828890	0.0000000
C	-0.2907100	2.9149090	0.0000000
C	-0.4285950	4.1301010	0.0000000
Si	0.8374760	-5.8909010	0.0000000
Si	-0.6907600	5.9572150	0.0000000
C	0.0946360	-6.6701820	1.5396250
H	0.5188710	-6.2318420	2.4480170
H	-0.9903050	-6.5303190	1.5684810
H	0.2979090	-7.7465470	1.5543360
C	0.0946360	-6.6701820	-1.5396250
H	0.5188710	-6.2318420	-2.4480170
H	0.2979090	-7.7465470	-1.5543360
H	-0.9903050	-6.5303190	-1.5684810
C	2.7064780	-6.0967840	0.0000000
H	3.1510320	-5.6346950	-0.8873470
H	3.1510320	-5.6346950	0.8873470
H	2.9746620	-7.1586670	0.0000000
C	-2.5461230	6.2568910	0.0000000
H	-3.0150720	5.8190440	0.8868320
H	-2.7576170	7.3315330	0.0000000
H	-3.0150720	5.8190440	-0.8868320
C	0.0946360	6.6907980	1.5403390
H	-0.0501470	7.7765070	1.5570410
H	-0.3523120	6.2745530	2.4481930
H	1.1705070	6.4928250	1.5679300
C	0.0946360	6.6907980	-1.5403390
H	1.1705070	6.4928250	-1.5679300
H	-0.3523120	6.2745530	-2.4481930
H	-0.0501470	7.7765070	-1.5570410
H	2.6746570	2.2744410	0.0000000

5-KK^{2O}

C	-1.0995530	-0.8235810	0.0000000
C	-1.2332660	0.5911920	0.0000000
C	-0.1454630	1.4944660	0.0000000
C	1.0995640	0.8235830	0.0000000
C	1.2332770	-0.5911910	0.0000000
C	0.1454750	-1.4944650	0.0000000
C	-3.2843610	-0.3153720	0.0000000
N	-2.5697620	0.8471420	0.0000000
N	-2.3646210	-1.3243320	0.0000000
N	2.3646330	1.3243330	0.0000000
N	2.5697740	-0.8471410	0.0000000
C	3.2843730	0.3153730	0.0000000
C	-4.6862240	-0.4690110	0.0000000
C	-5.2239330	-1.8293170	0.0000000
C	-5.5712480	0.6669210	0.0000000
C	-6.6733710	-1.9609920	0.0000000
C	-6.9768470	0.4567060	0.0000000
C	-7.4951670	-0.8848420	0.0000000
H	-7.0590300	-2.9751770	0.0000000
C	-7.8126690	1.5816870	0.0000000
C	-5.8622170	2.9579410	0.0000000
H	-8.5745820	-1.0133180	0.0000000
C	-7.2609190	2.8482160	0.0000000
H	-8.8905470	1.4419560	0.0000000
H	-5.3905020	3.9376850	0.0000000
H	-7.8784200	3.7386210	0.0000000
C	4.6862360	0.4690130	0.0000000
C	5.2239460	1.8293180	0.0000000
C	5.5712600	-0.6669200	0.0000000
C	6.6733840	1.9609930	0.0000000
C	6.9768600	-0.4567040	0.0000000
C	7.4951800	0.8848430	0.0000000
H	7.0590450	2.9751780	0.0000000
C	7.8126810	-1.5816860	0.0000000
C	5.8622300	-2.9579400	0.0000000
H	8.5745950	1.0133200	0.0000000
C	7.2609320	-2.8482150	0.0000000
H	8.8905590	-1.4419550	0.0000000
H	5.3905150	-3.9376830	0.0000000
H	7.8784330	-3.7386190	0.0000000
N	5.0434960	-1.9183640	0.0000000
N	-5.0434830	1.9183650	0.0000000
O	4.4904230	2.8425520	0.0000000
O	-4.4904090	-2.8425500	0.0000000
C	0.3036560	-2.8943990	0.0000000
C	0.4705170	-4.1063080	0.0000000
C	-0.3036510	2.8943990	0.0000000
C	-0.4705230	4.1063070	0.0000000
Si	0.7695980	-5.9276640	0.0000000
Si	-0.7696220	5.9276590	0.0000000
C	-0.0000220	-6.6775550	1.5403850
H	0.4386620	-6.2523990	2.4481430
H	-1.0796990	-6.5016110	1.5684240
H	0.1669570	-7.7600810	1.5567960
C	-0.0000220	-6.6775550	-1.5403850
H	0.4386620	-6.2523990	-2.4481430
H	0.1669570	-7.7600810	-1.5567960
H	-1.0796990	-6.5016110	-1.5684240
C	2.6308870	-6.1883450	0.0000000
H	3.0902780	-5.7408170	-0.8870430
H	3.0902780	-5.7408170	0.8870430
H	2.8650200	-7.2582620	0.0000000
C	-2.6309160	6.1883130	0.0000000
H	-3.0903000	5.7407790	0.8870430
H	-2.8650620	7.2582270	0.0000000
H	-3.0903000	5.7407790	-0.8870430
C	-0.0000220	6.6775670	1.5403860
H	-0.1670420	7.7600860	1.5568050
H	-0.4386900	6.2523890	2.4481430
H	1.0796620	6.5016630	1.5684230
C	-0.0000220	6.6775670	-1.5403860
H	1.0796620	6.5016630	-1.5684230
H	-0.4386900	6.2523890	-2.4481430
H	-0.1670420	7.7600860	-1.5568050
H	-3.0602650	1.7439000	0.0000000

H	3.0602790	-1.7438980	0.0000000
H	2.6898780	2.2936770	0.0000000
H	-2.6898660	-2.2936760	0.0000000

5-KE^{2O}

C	-1.0839670	-0.7931260	0.0000000
C	-1.2107750	0.6314520	0.0000000
C	-0.1366910	1.5312100	0.0000000
C	1.1102750	0.8900660	0.0000000
C	1.2768310	-0.5371440	0.0000000
C	0.1671020	-1.4198550	0.0000000
C	-3.1963040	-0.3409980	0.0000000
N	-2.5523890	0.8679340	0.0000000
N	-2.3367520	-1.3529170	0.0000000
N	2.3682020	1.3910510	0.0000000
N	2.5911370	-0.8406880	0.0000000
C	3.2526140	0.3350440	0.0000000
C	-4.6378320	-0.5111320	0.0000000
C	-5.1574100	-1.8134980	0.0000000
C	-5.5501970	0.6003180	0.0000000
C	-6.5633260	-2.0318930	0.0000000
C	-6.9498670	0.3592730	0.0000000
C	-7.4302470	-0.9808890	0.0000000
H	-6.9076720	-3.0601170	0.0000000
C	-7.8187380	1.4707230	0.0000000
C	-5.8966950	2.8815440	0.0000000
H	-8.5029570	-1.1514470	0.0000000
C	-7.2977900	2.7416970	0.0000000
H	-8.8922750	1.3022710	0.0000000
H	-5.4501520	3.8732980	0.0000000
H	-7.9320660	3.6201470	0.0000000
C	4.6624410	0.4852950	0.0000000
C	5.2503040	1.8609840	0.0000000
C	5.5398820	-0.6585530	0.0000000
C	6.6749960	1.9562720	0.0000000
C	6.9493260	-0.4843930	0.0000000
C	7.4706850	0.8320460	0.0000000
H	7.0995520	2.9535230	0.0000000
C	7.7656250	-1.6603480	0.0000000
C	5.8031990	-3.0463470	0.0000000
H	8.5525750	0.9393740	0.0000000
C	7.1875180	-2.9170800	0.0000000
H	8.8444510	-1.5472520	0.0000000
H	5.2691940	-3.9849200	0.0000000
H	7.7993270	-3.8117430	0.0000000
N	5.0398970	-1.9150350	0.0000000
N	-5.0538040	1.8672730	0.0000000
O	4.5052490	2.8666090	0.0000000
O	-4.4001180	-2.9096450	0.0000000
H	-3.4386260	-2.6381470	0.0000000
C	0.3321950	-2.8291260	0.0000000
C	0.4903960	-4.0383220	0.0000000
C	-0.3111060	2.9412330	0.0000000
C	-0.4894530	4.1472160	0.0000000
Si	0.7556490	-5.8689370	0.0000000
Si	-0.8053900	5.9731770	0.0000000
C	-0.0356700	-6.5870410	1.5433560
H	0.4097590	-6.1646690	2.4490680
H	-1.1108800	-6.3854830	1.5654020
H	0.1067420	-7.6727750	1.5690180
C	-0.0356700	-6.5870410	-1.5433560
H	0.4097590	-6.1646690	-2.4490680
H	0.1067420	-7.6727750	-1.5690180
H	-1.1108800	-6.3854830	-1.5654020
C	2.6086890	-6.1772970	0.0000000
H	3.0785960	-5.7418140	-0.8875800
H	3.0785960	-5.7418140	0.8875800
H	2.8158520	-7.2527210	0.0000000
C	-2.6678560	6.2146620	0.0000000
H	-3.1225700	5.7626210	0.8870780
H	-2.9121690	7.2822290	0.0000000
H	-3.1225700	5.7626210	-0.8870780
C	-0.0356700	6.7105000	1.5443010
H	-0.2104430	7.7914010	1.5720950
H	-0.4684870	6.2731770	2.4490150
H	1.0451310	6.5415230	1.5660640

C	-0.0356700	6.7105000	-1.5443010
H	1.0451310	6.5415230	-1.5660640
H	-0.4684870	6.2731770	-2.4490150
H	-0.2104430	7.7914010	-1.5720950
H	2.7055660	2.3540130	0.0000000
H	-3.0656790	1.7490160	0.0000000
H	4.0138320	-1.9896050	0.0000000

5-KZ$^{2N'}$

C	-1.1729310	-0.8671810	0.0000000
C	-1.3190760	0.5910990	0.0000000
C	-0.2031900	1.4715040	0.0000000
C	1.0251630	0.8212870	0.0000000
C	1.1668130	-0.6071360	0.0000000
C	0.0979150	-1.4985500	0.0000000
C	-3.2432940	-0.3305210	0.0000000
N	-2.6166250	0.8885180	0.0000000
N	-2.3908300	-1.4064900	0.0000000
N	2.2974610	1.3250770	0.0000000
N	2.5115870	-0.8522680	0.0000000
H	3.0119820	-1.7440130	0.0000000
C	3.2126990	0.3164470	0.0000000
C	-4.6556580	-0.4939900	0.0000000
C	-5.2354660	-1.8173760	0.0000000
C	-5.5553160	0.6268640	0.0000000
C	-6.6169010	-1.9818700	0.0000000
C	-6.9681830	0.4369830	0.0000000
C	-7.4642180	-0.8790250	0.0000000
H	-7.0080290	-2.9928420	0.0000000
C	-7.8007310	1.5937270	0.0000000
C	-5.8693170	3.0108710	0.0000000
H	-8.5401270	-1.0250770	0.0000000
C	-7.2439050	2.8649690	0.0000000
H	-8.8773010	1.4611180	0.0000000
H	-5.3513270	3.9591730	0.0000000
H	-7.8707690	3.7485980	0.0000000
C	4.6077530	0.4768330	0.0000000
C	5.1341500	1.8368850	0.0000000
C	5.4986380	-0.6615590	0.0000000
C	6.5885750	1.9752700	0.0000000
C	6.8998520	-0.4445260	0.0000000
C	7.4104690	0.9044960	0.0000000
H	6.9700940	2.9908920	0.0000000
C	7.7448300	-1.5604230	0.0000000
C	5.8081520	-2.9496240	0.0000000
H	8.4895370	1.0370360	0.0000000
C	7.2023240	-2.8325380	0.0000000
H	8.8214730	-1.4119030	0.0000000
H	5.3410490	-3.9314280	0.0000000
H	7.8260560	-3.7184400	0.0000000
N	4.9803650	-1.9131310	0.0000000
N	-5.0813050	1.8976240	0.0000000
O	4.4065200	2.8518150	0.0000000
O	-4.4778810	-2.9139300	0.0000000
H	-3.5135130	-2.6433600	0.0000000
C	0.2969760	-2.9038580	0.0000000
C	0.5203630	-4.1026890	0.0000000
C	-0.3317520	2.8847400	0.0000000
C	-0.4413600	4.0992160	0.0000000
Si	0.8851890	-5.9169850	0.0000000
Si	-0.6673810	5.9362340	0.0000000
C	0.1376110	-6.6792200	1.5436240
H	0.5590770	-6.2320020	2.4488830
H	-0.9473300	-6.5394130	1.5668020
H	0.3417400	-7.7550610	1.5690870
C	0.1376110	-6.6792200	-1.5436240
H	0.5590770	-6.2320020	-2.4488830
H	0.3417400	-7.7550610	-1.5690870
H	-0.9473300	-6.5394130	-1.5668020
C	2.7536630	-6.1116310	0.0000000
H	3.1956870	-5.6474820	-0.8874100
H	3.1956870	-5.6474820	0.8874100
H	3.0267060	-7.1721920	0.0000000
C	-2.5149060	6.2749980	0.0000000
H	-2.9926680	5.8474400	0.8871160
H	-2.7031890	7.3538880	0.0000000

H	-2.9926680	5.8474400	-0.8871160
C	0.1376110	6.6385150	1.5432760
H	0.0163940	7.7268100	1.5687620
H	-0.3163190	6.2250760	2.4488960
H	1.2088100	6.4165500	1.5657730
C	0.1376110	6.6385150	-1.5432760
H	1.2088100	6.4165500	-1.5657730
H	-0.3163190	6.2250760	-2.4488960
H	0.0163940	7.7268100	-1.5687620
H	2.6232200	2.2943350	0.0000000
H	-4.0550740	1.9887950	0.0000000

Below we provide the Cartesian coordinates in Å for all identified excited-state transition states.

4-EE – **4**-KE[10]

C	1.2669140	0.6436570	0.0000000
C	0.0000000	1.3520940	0.0000000
C	-1.2375930	0.7300860	0.0000000
C	-1.1750960	-0.6731320	0.0000000
C	0.0887530	-1.3911030	0.0000000
C	1.3206930	-0.7656550	0.0000000
C	1.7171510	2.7681640	0.0000000
H	-2.1769200	1.2675510	0.0000000
H	2.2592700	-1.3048910	0.0000000
H	-0.2404030	3.5030870	0.0000000
N	0.3459030	2.6708980	0.0000000
N	2.2777070	1.5339110	0.0000000
N	-2.1641100	-1.5893500	0.0000000
N	-0.2494000	-2.7188810	0.0000000
H	0.3494910	-3.5397100	0.0000000
C	-1.6129980	-2.8382190	0.0000000
C	2.4664860	3.9765230	0.0000000
C	3.8903060	3.9080520	0.0000000
C	1.8456770	5.2858280	0.0000000
C	4.6681010	5.0813800	0.0000000
C	2.6635690	6.4522580	0.0000000
C	4.0770300	6.3221210	0.0000000
H	5.7465600	4.9658400	0.0000000
C	2.0180930	7.7086610	0.0000000
C	-0.0766680	6.5649270	0.0000000
H	4.6866390	7.2207510	0.0000000
C	0.6439110	7.7714790	0.0000000
H	2.6213180	8.6125510	0.0000000
H	-1.1635530	6.5765300	0.0000000
H	0.1180400	8.7192100	0.0000000
C	-2.4195310	-3.9843490	0.0000000
C	-3.8583160	-3.7718980	0.0000000
C	-1.8866110	-5.3236470	0.0000000
C	-4.7071740	-4.9137950	0.0000000
C	-2.7866530	-6.4259510	0.0000000
C	-4.1935230	-6.1866940	0.0000000
H	-5.7770710	-4.7351050	0.0000000
C	-2.2271290	-7.7189360	0.0000000
C	-0.0536000	-6.7155750	0.0000000
H	-4.8608930	-7.0441200	0.0000000
C	-0.8563530	-7.8695460	0.0000000
H	-2.8851610	-8.5838980	0.0000000
H	1.0297670	-6.8026190	0.0000000
H	-0.3954050	-8.8506560	0.0000000
N	-0.5438530	-5.4833370	0.0000000
N	0.4946710	5.3700920	0.0000000
O	-4.3547610	-2.5790410	0.0000000
H	-3.3634860	-1.7762150	0.0000000
O	4.5527920	2.7499730	0.0000000
H	3.8885060	2.0005410	0.0000000

4-EE – **4**-ZE[1N]

C	1.0148920	0.7929390	-0.0000010
C	1.2117920	-0.6483140	-0.0000020
C	0.1894330	-1.5666010	-0.0000030
C	-1.1081170	-1.0011830	-0.0000030
C	-1.3124540	0.4567960	-0.0000020
C	-0.2619450	1.3636420	-0.0000010
C	3.1528940	0.4329690	-0.0000000
H	0.3469440	-2.6380580	-0.0000030
H	-0.4101770	2.4364710	-0.0000010
H	3.1389370	-1.6519050	-0.0000010
N	2.5754920	-0.8041510	-0.0000010
N	2.2262860	1.4059890	-0.0000000
N	-2.2936130	-1.6168100	-0.0000030
N	-2.6545620	0.6473260	-0.0000020
H	-3.6089330	1.4614040	-0.0000010
C	-3.2141630	-0.5997270	-0.0000020
C	4.5673170	0.6950090	-0.0000000
C	5.0090410	2.0353710	-0.0000000
C	5.5552610	-0.3567840	0.0000010
C	6.3945310	2.3403870	0.0000000
C	6.9363160	-0.0230820	0.0000010

C	7.3289680	1.3449870	0.0000010
H	6.6745240	3.3879840	0.0000000
C	7.8756350	-1.0759330	0.0000020
C	6.0497510	-2.6099750	0.0000020
H	8.3882420	1.5849180	0.0000010
C	7.4376710	-2.3785720	0.0000030
H	8.9359800	-0.8386140	0.0000020
H	5.6682780	-3.6280750	0.0000030
H	8.1283430	-3.2134570	0.0000030
C	-4.6094190	-0.7724920	-0.0000010
C	-5.2105950	-2.0790390	-0.0000000
C	-5.4708730	0.3886360	0.0000010
C	-6.5935940	-2.2096790	0.0000020
C	-6.8882590	0.2264200	0.0000020
C	-7.4176550	-1.0813440	0.0000030
H	-7.0146020	-3.2090330	0.0000030
C	-7.6681000	1.4124880	0.0000030
C	-5.6593990	2.7302020	0.0000000
H	-8.4964370	-1.2049130	0.0000050
C	-7.0483570	2.6534070	0.0000020
H	-8.7509080	1.3336410	0.0000040
H	-5.1246580	3.6719790	-0.0000000
H	-7.6336550	3.5659120	0.0000020
N	-4.9049700	1.6118600	-0.0000000
N	5.1423820	-1.6501350	0.0000010
O	-4.4545190	-3.1845510	-0.0000020
H	-3.4963940	-2.9245040	-0.0000020
O	4.1814190	3.0779220	-0.0000000
H	3.2387670	2.7375750	-0.0000000

4- KE^{10-} to **4-** KE^{2}

C	-1.0145380	0.7639770	-0.0000040
C	-1.2259580	-0.6585290	-0.0000040
C	-0.2008850	-1.5985680	-0.0000040
C	1.0733590	-1.0375350	-0.0000040
C	1.3115760	0.3877660	-0.0000040
C	0.2667630	1.3122990	-0.0000040
C	-3.1558590	0.4355890	-0.0000020
H	-0.3738120	-2.6673760	-0.0000040
H	0.4397380	2.3814280	-0.0000040
H	-3.1541150	-1.6530200	-0.0000030
N	-2.5849620	-0.8088260	-0.0000030
N	-2.2311910	1.3953920	-0.0000030
N	2.3071850	-1.6189580	-0.0000030
N	2.6602000	0.5781960	-0.0000040
H	3.5824630	1.4162490	-0.0000040
C	3.2633390	-0.6381930	-0.0000030
C	-4.5794460	0.6997580	-0.0000000
C	-5.0143440	2.0365430	0.0000010
C	-5.5678080	-0.3467360	0.0000010
C	-6.3993920	2.3486370	0.0000040
C	-6.9490110	-0.0101360	0.0000030
C	-7.3382090	1.3580300	0.0000050
H	-6.6744990	3.3976750	0.0000050
C	-7.8910690	-1.0612810	0.0000040
C	-6.0687780	-2.5994130	-0.0000000
H	-8.3966870	1.6015140	0.0000070
C	-7.4571840	-2.3645010	0.0000030
H	-8.9507980	-0.8208170	0.0000060
H	-5.6910720	-3.6191110	-0.0000020
H	-8.1497610	-3.1978200	0.0000030
C	4.6600190	-0.7843110	-0.0000010
C	5.2747550	-2.1350760	0.0000010
C	5.4851200	0.3961200	0.0000000
C	6.7034380	-2.1888440	0.0000060
C	6.9064780	0.2616470	0.0000040
C	7.4741000	-1.0398580	0.0000070
H	7.1600450	-3.1727280	0.0000080
C	7.6544760	1.4679820	0.0000050
C	5.6076500	2.7377430	-0.0000020
H	8.5582930	-1.1171700	0.0000100
C	7.0087120	2.6904120	0.0000020
H	8.7393940	1.4176960	0.0000080
H	5.0536510	3.6682510	-0.0000040
H	7.5720860	3.6166710	0.0000030
N	4.8884360	1.6068350	-0.0000020

N	-5.1588450	-1.6438330	-0.0000010
O	4.5325450	-3.1456230	0.0000000
O	-4.1798990	3.0775670	0.0000010
H	-3.2400430	2.7302570	-0.0000010
H	2.5743570	-2.6000140	-0.0000020

IX. REFERENCES

1 K.-C. Tang, C.-L. Chen, H.-H. Chuang, J.-L. Chen, Y.-J. Chen, Y.-C. Lin, J.-Y. Shen, W.-P. Hu and P.-T. Chou, *J. Phys. Chem. Lett.*, 2011, **2**, 3063–3068.

2 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.

3 J. R. Aranzaes, M.-C. Daniel and D. Astruc, *Can. J. Chem.*, 2006, **84**, 288–299.

4 A. M. Brouwer, *Pure Appl. Chem.* 2011, **83**, 2213–2228.

5 C. An, S. Zhou and M. Baumgarten, *Cryst. Growth Des.*, 2015, **15**, 1934–1938.

6 C. Wagner, O. Hübner, E. Kaifer and H.-J. Himmel, *Chem. – Eur. J.*, 2019, **25**, 3781–3785.

7 T. L. Tam, H. Li, F. Wei, K. J. Tan, C. Kloc, Y. M. Lam, S. G. Mhaisalkar and A. C. Grimsdale, *Org. Lett.*, 2010, **12**, 3340–3343.

8 Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

9 R. Cammi and B. Mennucci, *J. Chem. Phys.*, 1999, **110**, 9877–9886.

10 M. Caricato, B. Mennucci, J. Tomasi, F. Ingrosso, R. Cammi, S. Corni and G. Scalmani, *J. Chem. Phys.*, 2006, **124**, 124520.

11 C. A. Guido, A. Chrayteh, G. Scalmani, B. Mennucci and D. Jacquemin, *J. Chem. Theory Comput.*, 2021, **17**, 5155–5164.

12 M. J. Frisch. et al., Gaussian 16A.03, Gaussian Inc., Wallingford, USA, 2016.

13 O. Christiansen, H. Koch and P. Jørgensen, *Chem. Phys. Lett.*, 1995, **243**, 409–418.

14 TURBOMOLE, V7.3 2018, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989−2007, TURBOMOLE GmbH, since 2007. http://www.turbomole.com.