Electronic supplementary information

Intramolecular Locking and Coumarin Insertion: A Stepwise Approach for TADF Design

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1. Materials and methods

All reagents and chemicals were obtained from commercial sources and used without further purification. Dry solvents were obtained from an MBraun solvent purification system (MB SPS-800) equipped with alumina columns. Preparative (recycling) size exclusion chromatography (SEC) was performed on a JAI LC-9110 NEXT system equipped with JAIGEL 1H and 2H columns (eluent chloroform, flow rate 3.5 mL min^{-1}). Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were obtained on a Jeol spectrometer operating at 400 MHz for ^{1}H (100 MHz for ^{13}C). Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (δ = 7.26 ppm for ^{1}H NMR, δ = 77.16 ppm for ^{13}C NMR). Matrix-assisted laser desorption/ionization -time-of-flight (MALDI-ToF) mass spectra were recorded on a Bruker Daltonics UltrafleXtreme ToF/ToF. Approximately 10 µL of the matrix solution (25 mg mL^{-1} *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DTCB) in chloroform) was mixed with 3 µL of the analyte solution (10 mg mL^{-1} in chloroform), after which 0.5 µL of the resulting solution was spotted onto an MTP Anchorchip 600/384 MALDI plate.

Electronic absorption spectra of the small molecule chromophores in solution were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer from Agilent Technologies. Corrected steady-state excitation and emission spectra of the chromophore solutions were recorded on a Horiba-Jobin Yvon Fluorolog-3 spectrofluorometer equipped with a 450 W Xe lamp as the light source, with an excitation wavelength (λ_{exc}) depending on the fluorescence quantum yield standard used and a slit width of 2 nm. Freshly prepared samples in 1 cm quartz cells were used to perform all UV-Vis-NIR absorption and fluorescence measurements. The fluorescence measurements were done under a right-angle arrangement. The standard uncertainty (square root of the variance) on the absorption and emission maxima is approximately 1 nm. Spectroscopic measurements under normal atmosphere were done in non-degassed spectroscopic grade solvents at 20 °C. Inert atmosphere was created by three consecutive freeze-pump-thaw cycles.

For the determination of the relative fluorescence quantum yields (Φ_f) in toluene, dilute solutions with an absorbance around 0.1 at the excitation wavelength were used. Quinine (λ_{exc} = 347 nm, Φ_f = 0.58 in 0.1 M H_2SO_4 solution) was used as a standard to determine the fluorescence quantum yields.[1] The fluorescence quantum yield of the tested compound ($\Phi_{f,x}$) was calculated using Equation (1), in which $\Phi_{f,st}$ is the fluorescence quantum yield of the standard, F_x and F_{st} are the integrated fluorescence of the test compound and the standard, A_x and A_{st} are the absorbance of the test compound and the standard at the excitation wavelength, and n_x and n_{st} are the refractive indices of the solvents in which the test compound and the standard were dissolved, respectively.

$$\Phi_x = \Phi_{st}\frac{F_x\left(1-10^{-A_{st}}\right)n_x^{\,2}}{F_{st}\left(1-10^{-A_x}\right)n_{st}^{\,2}} \quad (1)$$

1,3-Diphenylisobenzofuran (1,3-DPBF) was used as a singlet oxygen ($^{1}O_2$) scavenger to determine the singlet oxygen quantum yields (Φ_Δ). The $^{1}O_2$ production was monitored by following the absorbance of 1,3-DPBF at 414 nm upon excitation of the respective chromophore at 325 nm using a single LED325W2 from Thorlabs (λ_{exc} = 325±5 nm, fwhm = 11 nm, P = 1.7 mW). To determine Φ_Δ, a relative method was used according to Equation (2). Here, *x* and *st* represent the sample and the standard, while Φ, A, m, and n represent the singlet oxygen quantum yield, the absorbance at the excitation wavelength (λ_{exc} = 325 nm), the slope of the decrease in absorbance of 1,3-DPBF over

2. F. Wilkinson, W. P. Helman and A. B. Ross, J. Phys. Chem. Ref. Data, 1993, 22, 113–262.
3. M. Trkovnik, V. Kalaj, D. Kitan, Org. Prep. Proced. Int., 1987, 19, 450–455.
4. T. Huang, D. Liu, J. Jiang and W. Jiang, Chem. Eur. J., 2019, 25, 10926–10937.

time, and the refractive index of the solvent used for the measurement, respectively. Optically matched solutions with an absorbance around 0.6 at 414 nm and 0.3 at 325 nm were used. Coronene was used as the standard (Φ_Δ = 0.90 in spectrograde toluene).[2] The solutions were continuously stirred during all measurements using a Cimarec magnetic stirrer.

$$\Phi_x = \Phi_{st}\left(\frac{1-10^{-A_{st}}}{1-10^{-A_x}}\right)\left(\frac{m_x}{m_{st}}\right)\left(\frac{n_x}{n_{st}}\right)^2 \quad (2)$$

Zeonex films were prepared via drop-casting using a mixture of the emitter and host (zeonex) in toluene at 1 w/w%. The initial solution concentrations were 100 mg mL^{-1} of zeonex and 1 mg mL^{-1} of emissive material, combined in equal volumes. The films were drop-casted onto a quartz substrate at 65 °C to facilitate evaporation of the solvent. Absorption and emission spectra of the films were collected using a UV-3600 double beam spectrophotometer (Shimadzu) and a Fluoromax fluorimeter (Jobin Yvon). Time-resolved photoluminescence spectra and decays were recorded using a nanosecond gated spectrograph-coupled iCCD (Stanford) camera (time resolution of 500 ps) using an Nd:YAG laser (EKSPLA) emitting at 355 nm with a pulse width of 200 ps under vacuum. Photoluminescence quantum yields in film were determined using a calibrated integrating sphere (Horiba Quanta-Phi) fibre-coupled to a spectrofluorometer (Horiba Fluorolog) as excitation source and as detection system. For the measurements in inert atmosphere, the sphere was flushed with a stream of dry nitrogen for at least 30 min to prevent oxygen quenching of triplets.

Materials synthesis

*Coumarin precursors (**1**) and (**2**) were synthesized according to literature procedures.*[3]

*2,3-bis(4-bromophenyl)quinoxaline (**3**)*[4]

General procedure 1: 1,2-Bis(4-bromophenyl)ethane-1,2-dione (0.500 g, 1.36 mmol) and benzene-1,2-diamine (150 µL, 1.36 mmol) were dissolved in glacial acetic acid (15 mL) and the mixture was stirred at 125 °C for 16 h. Afterwards, the mixture was cooled down to room temperature and poured into water. The formed precipitate was filtered off, washed with water, and dried under vacuum, yielding a white solid (0.571 g, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 – 8.13 (m, 2H), 7.83 – 7.77 (m, 2H), 7.51 (d, J = 8.5 Hz, 4H), 7.40 (d, J = 8.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 141.4, 137.8, 131.8, 131.6, 130.6, 129.3, 123.9. MS (MALDI-ToF) Calcd. for $C_{20}H_{12}Br_2N_2$ $[M]^+$: *m/z* 437.9, found: 438.0.

*2,3-bis(4-bromophenyl)benzo[f]quinoxaline (**4**)*

Synthesis according to general procedure 1: 1,2-bis(4-bromophenyl)ethane-1,2-dione (0.235 g, 0.63 mmol), naphthalene-1,2-diamine (0.100 g, 0.63 mmol), glacial acetic acid (10 mL); pale yellow solid (0.171 g, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.31 – 9.20 (m, 1H), 8.05 (d, J = 9.1 Hz, 1H), 7.98 (d, J = 9.1 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.79 – 7.72 (m, 2H), 7.54 – 7.50 (m, 6H), 7.46 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 149.8, 140.8, 139.7, 138.0, 133.6, 132.3, 131.9, 131.7, 131.6, 130.8, 129.2, 128.2, 127.8, 126.6, 124.8, 123.69, 123.65. MS (MALDI-ToF) Calcd. for $C_{24}H_{14}Br_2N_2$ $[M]^+$: *m/z* 488.0, found: 488.0.

*2,3-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)quinoxaline (**Qx-Ph-DMAC**)*

General procedure 2 (Buchwald-Hartwig cross-coupling): 2,3-Bis(4-bromophenyl)quinoxaline (0.118 g, 398 µmol), 9,9-dimethyl-9,10-dihydroacridine (79.2 mg, 432 µmol), palladium(II) acetate (8.9 mg, 40 µmol), tri-*tert*-butylphosphonium tetrafluoroborate (16.1 mg, 80 µmol), and sodium *tert*-butoxide (76.6 mg, 797 µmol) were dissolved in dry toluene (12 mL) under argon atmosphere. The mixture was heated to reflux for 16 h while stirring and then cooled down to room temperature and concentrated under reduced pressure. The crude product was purified by column chromatography (silica) with CH_2Cl_2/petroleum ether (v/v = 60/40) as the eluent. **Qx-Ph-DMAC** was further purified using preparative (recycling) SEC and was obtained as a yellow solid (0.116 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 – 8.27 (m, 2H), 7.92 – 7.87 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 4H), 7.45 (dd, *J* = 7.6, 1.7 Hz, 4H), 7.41 (d, *J* = 8.3 Hz, 4H), 6.92 – 6.81 (m, 8H), 6.34 (dd, *J* = 8.0, 1.4 Hz, 4H), 1.69 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 142.2, 141.6, 140.8, 138.9, 132.6, 131.5, 130.7, 130.3, 129.5, 126.7, 125.2, 120.9, 114.1, 36.1, 31.0. MS (MALDI-ToF) Calcd. for $C_{50}H_{40}N_4$ $[M]^+$: *m/z* 696.3, found: 696.4.

*2,3-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)benzo[f]quinoxaline (**BQx-Ph-DMAC**)*

Synthesis according to general procedure 2: 2,3-bis(4-bromophenyl)benzo[*f*]quinoxaline (0.220 g, 448 µmol), 9,9-dimethyl-9,10-dihydroacridine (0.205 g, 987 µmol), palladium(II) acetate (10 mg, 45 µmol), tri-*tert*-butylphosphonium tetrafluoroborate (26 mg, 90 µmol), sodium *tert*-butoxide (108 mg, 1.12 mmol), dry toluene (12 mL), eluent CH_2Cl_2/petroleum ether (v/v = 60/40); yellow solid (19 mg, 6%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 – 9.39 (m, 1H), 8.16 – 8.14 (m, 2H), 8.07 – 7.97 (m, 3H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.88 – 7.78 (m, 2H), 7.52 – 7.40 (m, 8H), 6.96 – 6.78 (m, 8H), 6.46 – 6.33 (m, 4H), 1.71 (2 x s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 150.9, 142.0, 141.0, 140.9, 140.8, 140.0, 139.2, 139.1, 133.7, 133.0, 132.7, 132.5, 131.6, 131.3, 130.9, 130.4, 130.3, 129.3, 128.3, 127.9, 126.7, 126.6, 125.2, 125.0, 120.92, 120.89, 114.2, 36.2, 31.1, 31.0. MS (MALDI-ToF) Calcd. for $C_{54}H_{42}N_4$ $[M]^+$: *m/z* 746.3, found: 746.4.

*2,3-bis(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)-5H-chromeno[3,4-b]pyrazin-5-one (**ChromPy-Ph-DMAC**)*

Synthesis according to general procedure 2: 2,3-bis(4-bromophenyl)-5*H*-chromeno[3,4-*b*]pyrazin-5-one (0.200 g, 395 µmol), 9,9-dimethyl-9,10-dihydroacridine (0.181 g, 866 µmol), palladium(II) acetate (9 mg, 40 µmol), tri-*tert*-butylphosphonium tetrafluoroborate (23 mg, 79 µmol), sodium *tert*-butoxide (95 mg, 988 mmol), dry toluene (12 mL), eluent CH_2Cl_2/petroleum ether (v/v = 70/30); orange solid (139 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.55 – 7.49 (m, 2H), 7.49 – 7.43 (m, 6H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.98 – 6.82 (m, 8H), 6.39 – 6.29 (m, 4H), 1.69 (2 x s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 157.5, 154.2, 152.8, 146.1, 143.6, 142.9, 140.7, 137.3, 137.1, 133.4, 132.8, 132.7, 131.7, 131.5, 131.4, 130.8, 130.4, 126.7, 125.5, 125.4, 125.3, 121.2, 121.0, 118.3, 117.7, 114.3, 114.2, 36.21, 36.15, 31.1, 31.0. MS (MALDI-TOF) Calcd. for $C_{53}H_{40}N_4O_2$ $[M]^+$: *m/z* 764.3, found: 764.5.

*10,13-bis(9,9-dimethylacridin-10(9H)-yl)-6H-dibenzo[f,h]chromeno[3,4-b]quinoxalin-6-one (**DBChromQx-DMAC**)*

Synthesis according to general procedure 2: 10,13-dibromo-6*H*-dibenzo[*f*,*h*]chromeno[3,4-*b*]quinoxalin-6-one (200 mg, 395 µmol), 9,9-dimethyl-9,10-dihydroacridine (186 mg, 869 µmol), palladium(II) acetate (9 mg, 40 µmol), tri-*tert*-butylphosphonium tetrafluoroborate (23 mg, 79 µmol), sodium *tert*-butoxide (95 mg, 988 mmol), dry toluene (12 mL), eluent CH_2Cl_2/petroleum ether (v/v = 70/30); red solid (178 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (d, *J* = 8.6 Hz, 1H), 9.72 (d, *J* = 8.6 Hz, 1H), 8.90 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.50 (d, *J* = 1.9 Hz, 1H), 8.46 (d, *J* = 1.9 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.73 – 7.65 (m, 1H), 7.57 – 7.48 (m, 2H), 7.48 – 7.41 (m, 4H), 6.95 – 6.82 (m, 8H), 6.33 – 6.18 (m, 4H), 1.70 (2 x s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 152.7, 146.4, 145.2, 145.0, 144.3, 142.8, 140.7, 140.6, 135.7, 134.0, 133.4, 133.1, 132.4, 132.0, 130.4, 130.34, 130.26, 130.0, 129.2, 128.8, 126.6, 126.3, 126.2, 125.8, 125.5, 125.4, 121.2, 121.1, 118.9, 117.8, 114.2, 114.1, 36.19, 36.15, 31.8, 31.7. MS (MALDI-ToF) Calcd. for $C_{53}H_{38}N_4O_2$ $[M]^+$: *m/z* 762.3, found: 762.3.

2. TDDFT calculations

Table S1: Charge-transfer distance (d_{CT}) and change in dipole moment ($\Delta\mu$, excited state dipole – ground state dipole) accompanying the $S_0 \rightarrow S_x$ and $S_0 \rightarrow T_x$ (x = 1,2) transitions in cyclohexane, as determined with TDDFT-TDA and a modified LC-BLYP (ω = 0.17 bohr^{-1}) exchange correlation functional.

Compound	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$		$S_0 \rightarrow T_1$		$S_0 \rightarrow T_2$	
	d_{CT} (Å)	$\Delta\mu$ (D)	d_{CT} (Å)	$\Delta\mu$ (D)	d_{CT} (Å)	$\Delta\mu$ (D)	d_{CT} (Å)	$\Delta\mu$ (D)
Qx-Ph-DMAC	3.54	20.00	3.37	18.68	0.01	0.03	1.23	2.46
BQx-Ph-DMAC	3.35	19.95	3.44	20.61	0.55	1.23	0.06	0.14
ChromPy-Ph-DMAC	3.51	21.84	3.53	21.64	0.07	0.18	0.60	1.63
DBChromQx-DMAC	3.95	24.51	4.24	26.40	0.15	0.34	1.73	6.19

Table S2: TDDFT results for the vertical first singlet excitation energy and the corresponding oscillator strength (f), and the first vertical triplet excitation energies, as determined with TDDFT-TDA and a modified LC-BLYP (ω = 0.17 bohr^{-1}) exchange correlation functional.

Compound	S_1 (eV)	f_{S_1}	T_1 (eV)	$\Delta E_{S_1-T_1}$ (eV)
Qx-Ph-DMAC	3.34	0.002	2.87	0.47
BQx-Ph-DMAC	3.37	0.004	2.97	0.40
ChromPy-Ph-DMAC	3.11	0.001	2.99	0.12
DBChromQx-DMAC	2.85	<0.001	2.77	0.08

Table S3: TDDFT results for the vertical excitation energy of S_2, S_3 and S_4, and the corresponding oscillator strength (f), and the vertical triplet excitation energies of T_2, T_3, T_4 and T_5, as determined with TDDFT-TDA and a modified LC-BLYP (ω = 0.17 bohr^{-1}) exchange correlation functional.

Compound	S_2 (eV)	f_{S_2}	S_3 (eV)	f_{S_3}	S_4 (eV)	f_{S_4}	T_2 (eV)	T_3 (eV)	T_4 (eV)	T_5 (eV)
Qx-Ph-DMAC	3.35	0.001	3.40	0.003	3.71	0.002	3.25	3.25	3.33	3.35
BQx-Ph-DMAC	3.38	0.001	3.54	0.007	3.67	0.448	3.04	3.25	3.33	3.35
ChromPy-Ph-DMAC	3.21	0.006	3.44	0.002	3.52	0.006	3.05	3.10	3.16	3.20
DBChromQx-DMAC	2.93	<0.001	3.24	>0.001	3.31	0.002	2.79	2.86	2.93	3.09

Table S4: Charge-transfer distance (d_{CT}) and change in dipole moment ($\Delta\mu$, excited state dipole – ground state dipole) accompanying the $S_0 \rightarrow T_x$ (x = 3,4,5) transitions in cyclohexane, as determined with TDDFT-TDA and a modified LC-BLYP (ω = 0.17 bohr^{-1}) exchange correlation functional.

Compound	$S_0 \rightarrow T_3$		$S_0 \rightarrow T_4$		$S_0 \rightarrow T_5$	
	d_{CT} (Å)	$\Delta\mu$ (D)	d_{CT} (Å)	$\Delta\mu$ (D)	d_{CT} (Å)	$\Delta\mu$ (D)
Qx-Ph-CTDO	1.632	3.784	3.397	16.543	3.273	16.263
BQx-Ph-CTDO	0.308	0.447	3.187	16.367	3.237	16.628
ChromPy-Ph-DMAC	3.403	19.177	2.402	7.046	3.082	13.372
DBChromQx-DMAC	3.613	18.506	4.151	24.423	1.270	1.765

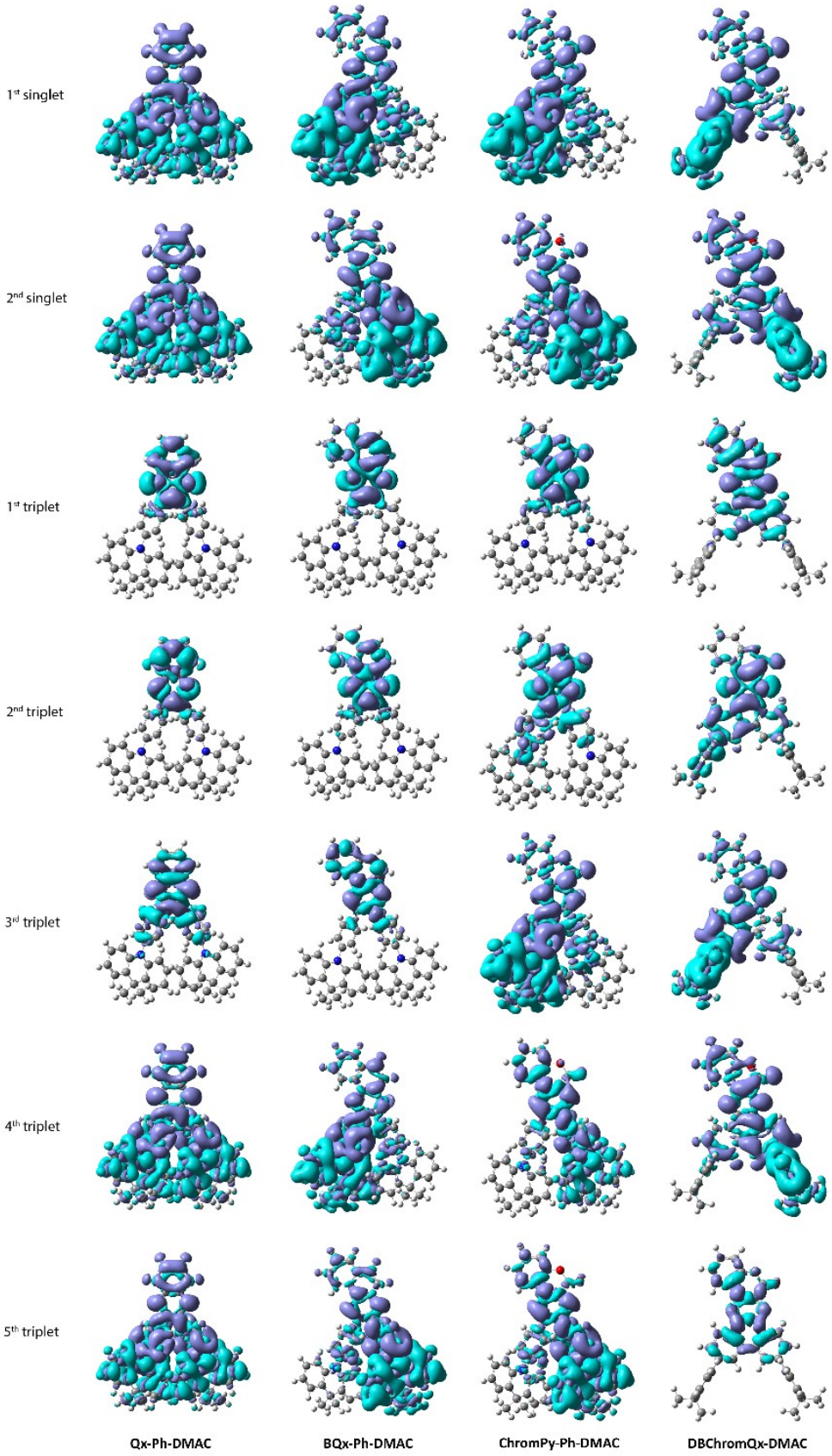

Figure S1: Ground – excited state electron density differences for the singlet and triplet excited states of **Qx-Ph-DMAC**, **BQx-Ph-DMAC**, **ChromPy-Ph-DMAC**, and **DBChromQx-DMAC**. Purple areas indicate increased electron density, while cyan areas point to decrease electron density (isosurface value = 0.0004 a.u. for all densities).

3. Simulated UV-Vis absorption spectra

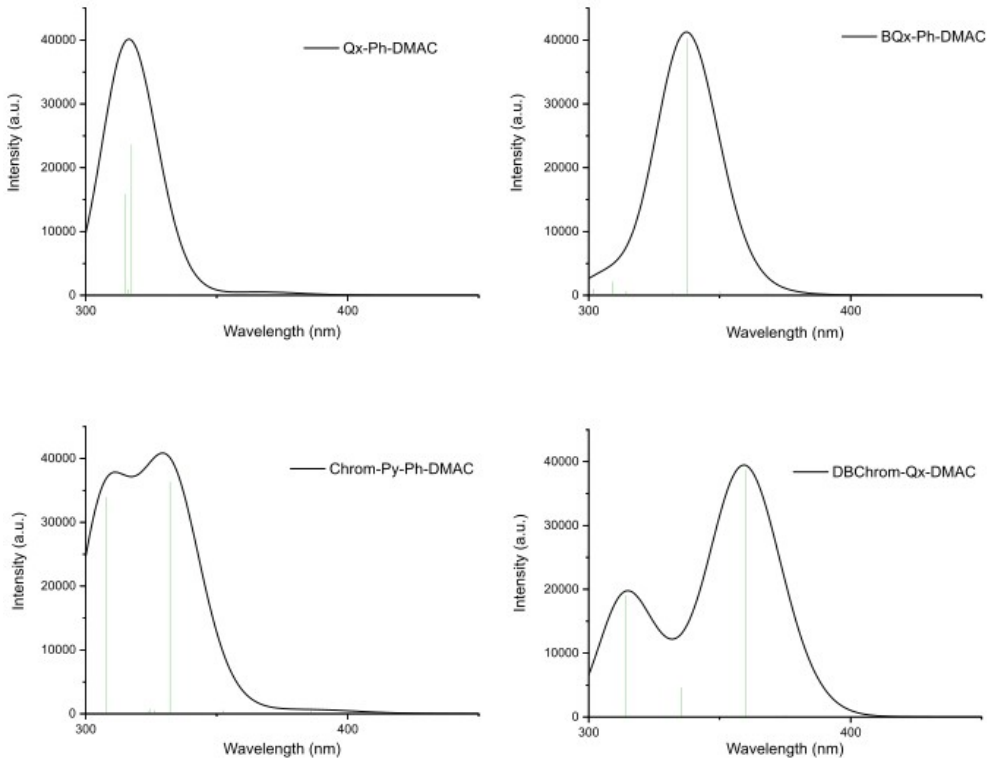

Figure S2: Simulated UV-Vis absorption spectra derived from the TD-DFT results for the optimized geometries by fitting the vertical excitation energies with a Gaussian fit and employing a full-width at half maximum of 0.3 eV for each excitation. The vertical lines indicate the specific excitation energies and their relative size is indicative of the oscillator strength accompanying the transition.

4. Photographs of the fluorescent dyes in zeonex

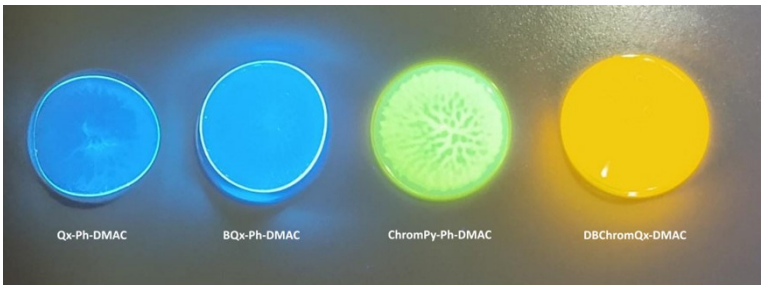

Figure S3: Photographs of the dyes doped in a 1 w/w% zeonex film upon UV-excitation (λ_{exc} = 365 nm).

5. Time-resolved emission spectra in zeonex

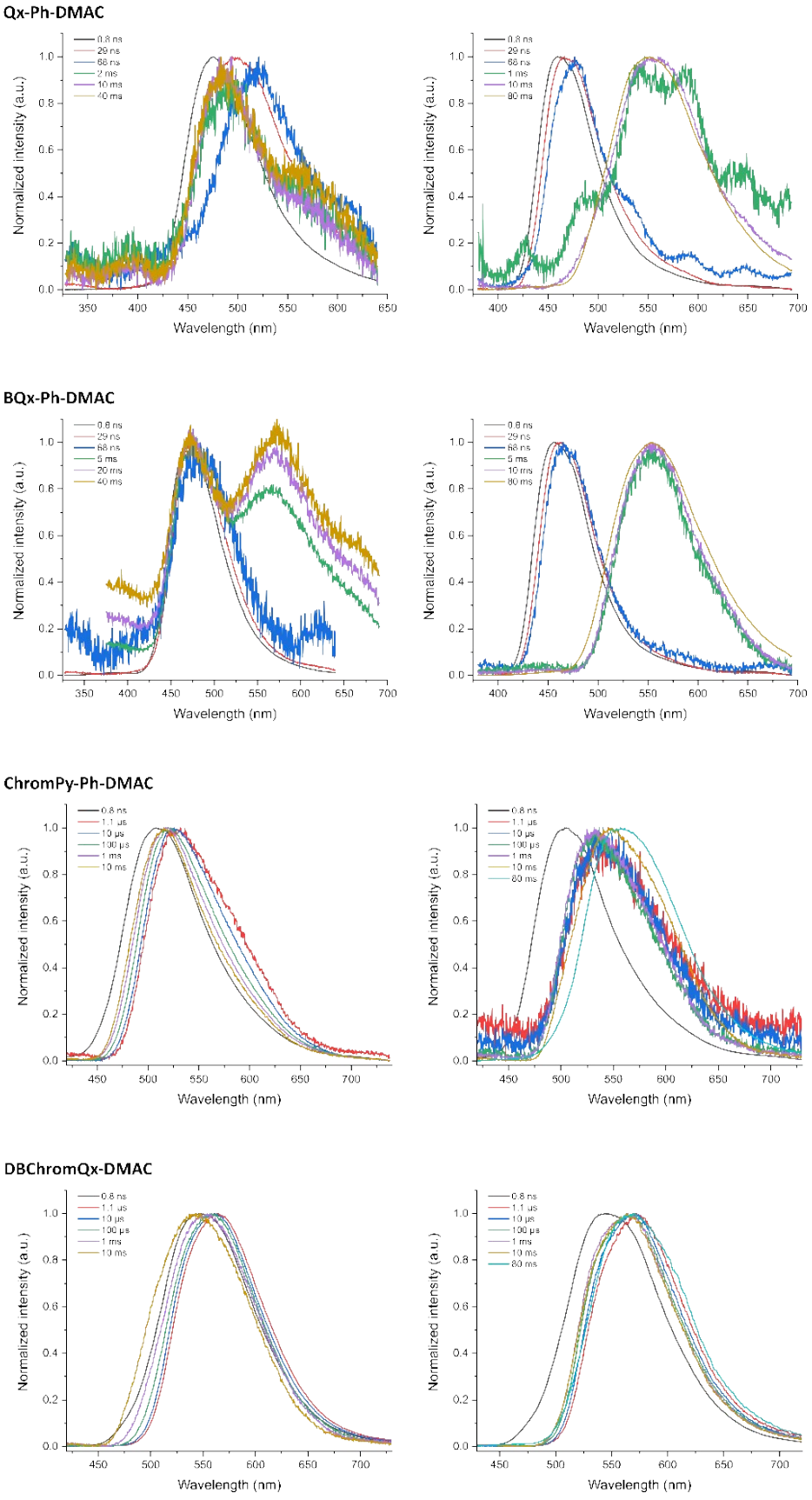

Figure S4: Snapshots of the emission at various time scales for **Qx-Ph-DMAC**, **BQx-Ph-DMAC**, **ChromPy-Ph-DMAC**, and **DBChromQx-DMAC** in zeonex at room temperature (left) and at 80 K (right).

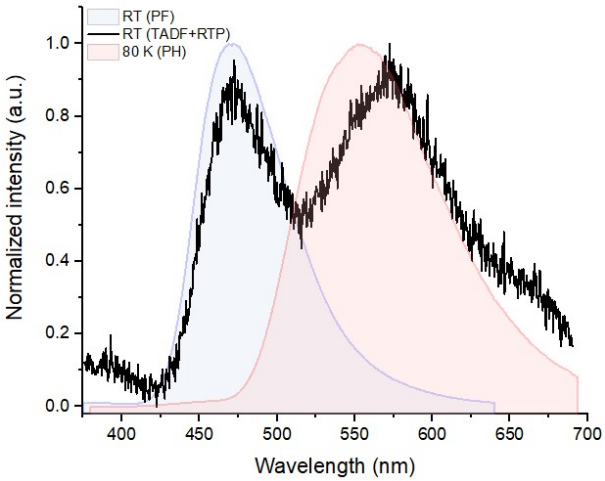

Figure S5: Snapshots of the emission at longer time scales for **BQx-Ph-DMAC** in zeonex at room temperature (blue, 0.8 ns delay time; black line; 40 ms delay time) and at 80 K (red; 80 ms delay time).

6. Singlet oxygen generation in toluene

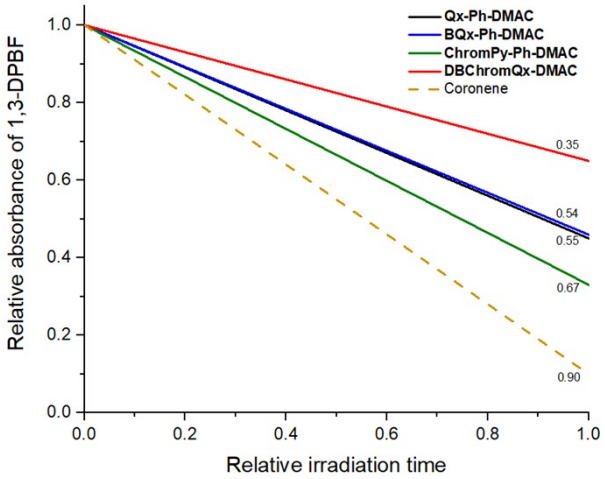

Figure S6: Relative decrease in absorbance of 1,3-DPBF at 414 nm under continuous irradiation using a single 325 nm LED in the presence of the respective dyad in toluene. Coronene was used as a standard (Φ_Δ = 0.90 in toluene).

7. Photoluminescence quantum yield in toluene

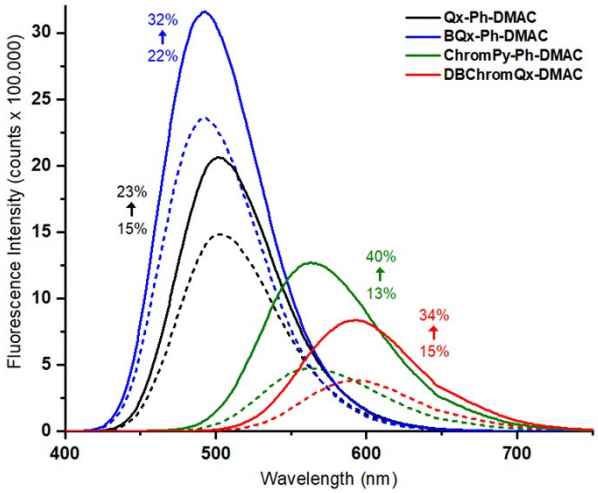

Figure S7: Emission spectra for **Qx-Ph-DMAC**, **BQx-Ph-DMAC**, **ChromPy-Ph-DMAC**, and **DBChromQx-DMAC** in air (dashed lines) and in inert atmosphere (solid lines).

8. Determination of krISC

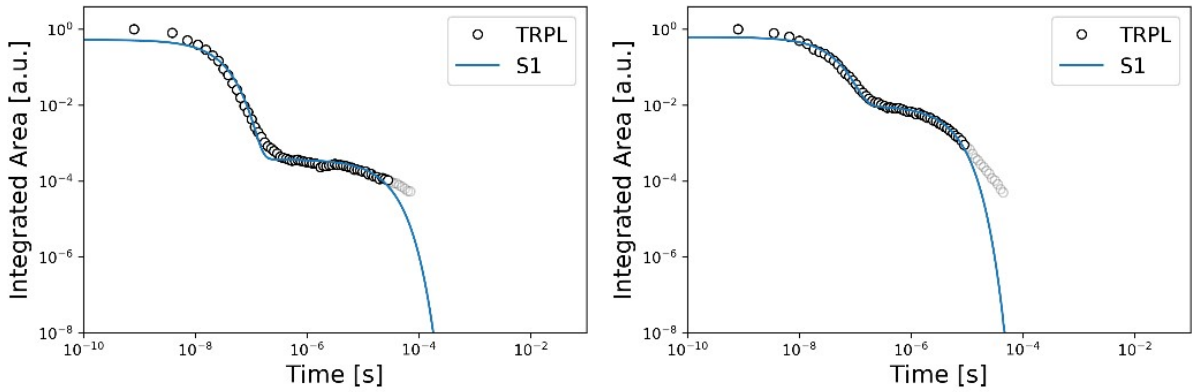

Figure S8: Experimental decay plot of the total emission of **ChromPy-Ph-DMAC** (left) and **DBChromQx-DMAC** (right) with the resulting theoretical fitting.

9. NMR spectra

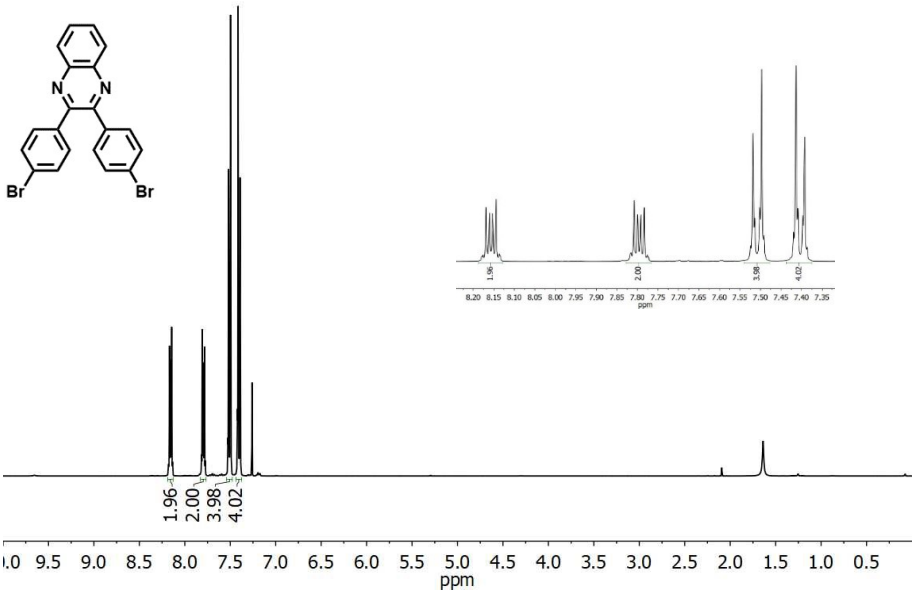

Figure S9: ^{1}H NMR spectrum of 2,3-bis(4-bromophenyl)quinoxaline (**3**) in $CDCl_3$.

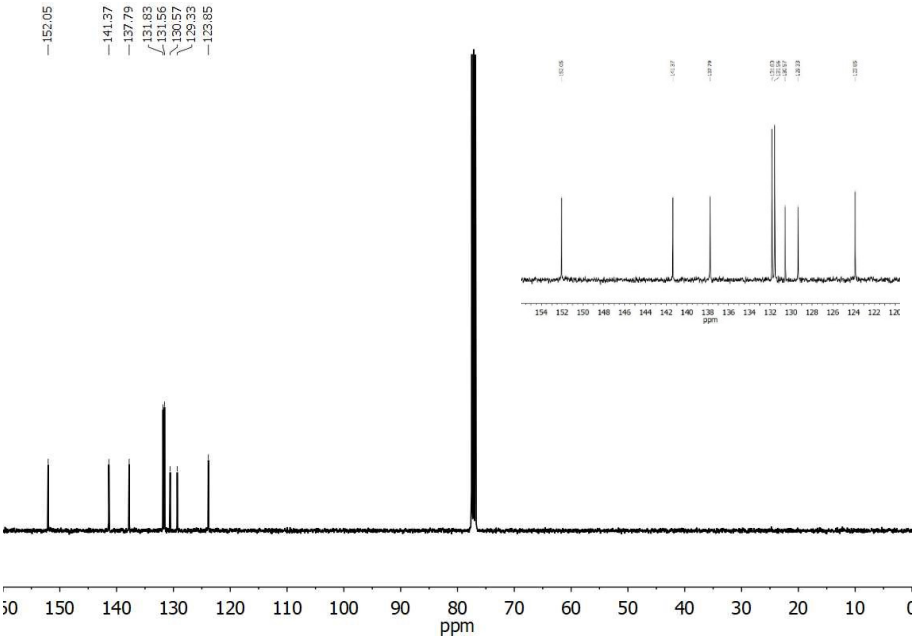

Figure S10: ^{13}C NMR spectrum of 2,3-bis(4-bromophenyl)quinoxaline (**3**) in $CDCl_3$.

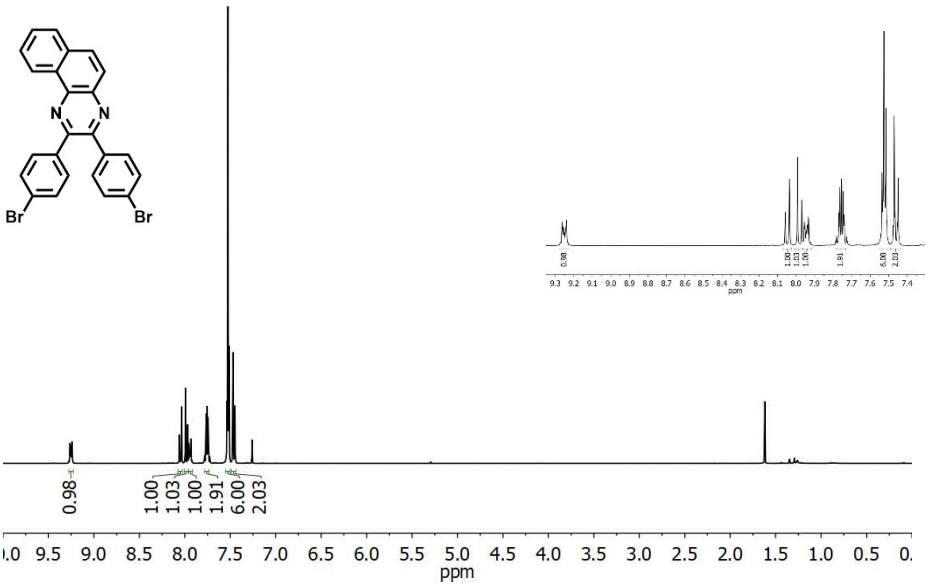

Figure S11: ^{1}H NMR spectrum of 2,3-bis(4-bromophenyl)benzo[*f*]quinoxaline (**4**) in $CDCl_3$.

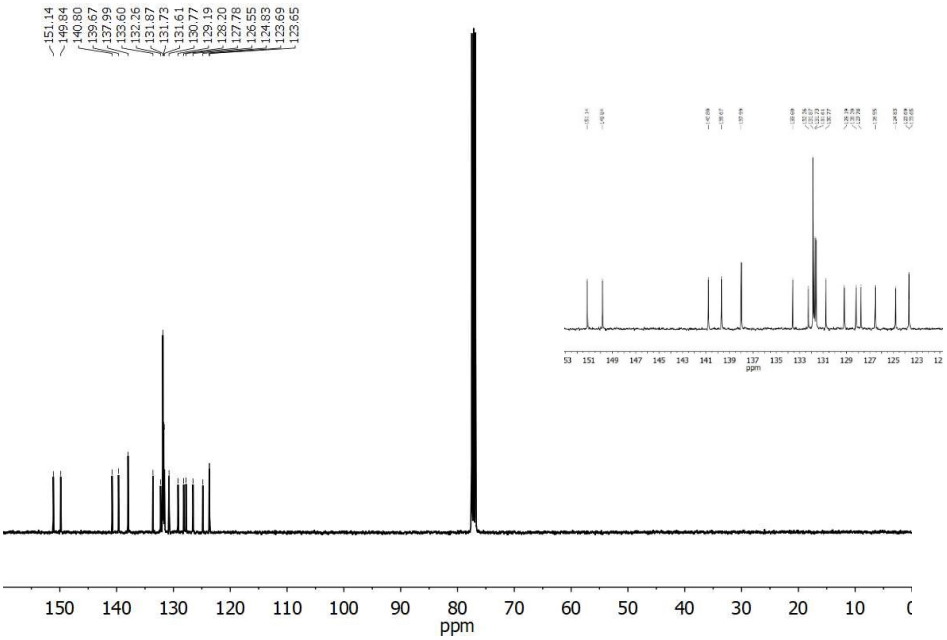

Figure S12: ^{13}C NMR spectrum of 2,3-bis(4-bromophenyl)benzo[*f*]quinoxaline (**4**) in $CDCl_3$.

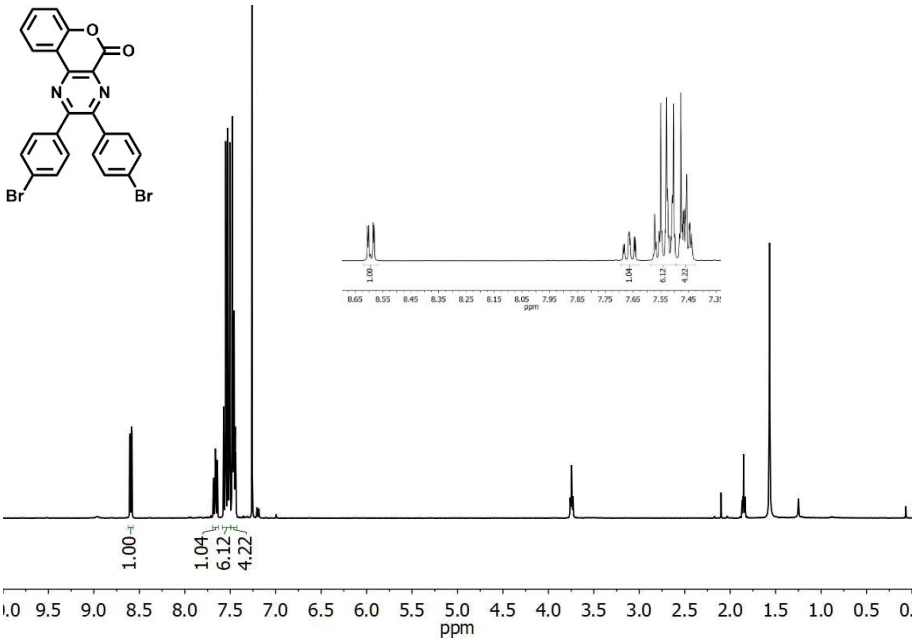

Figure S13: ^{1}H NMR spectrum of 2,3-bis(4-bromophenyl)-5*H*-chromeno[3,4-*b*]pyrazin-5-one (**5**) in $CDCl_3$.

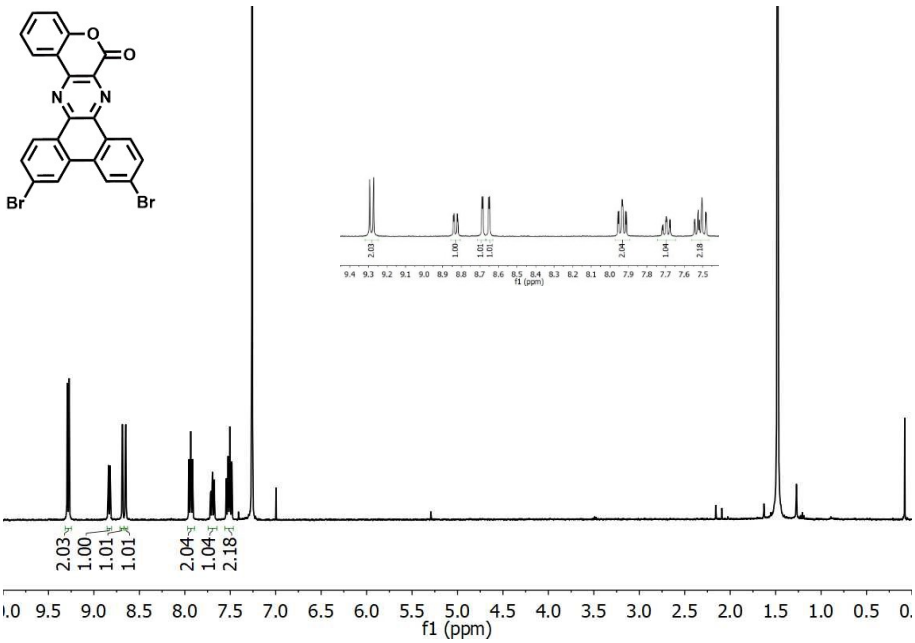

Figure S14: ^{1}H NMR spectrum 10,13-dibromo-6*H*-dibenzo[*f*,*h*]chromeno[3,4-*b*]quinoxalin-6-one (**6**) in $CDCl_3$.

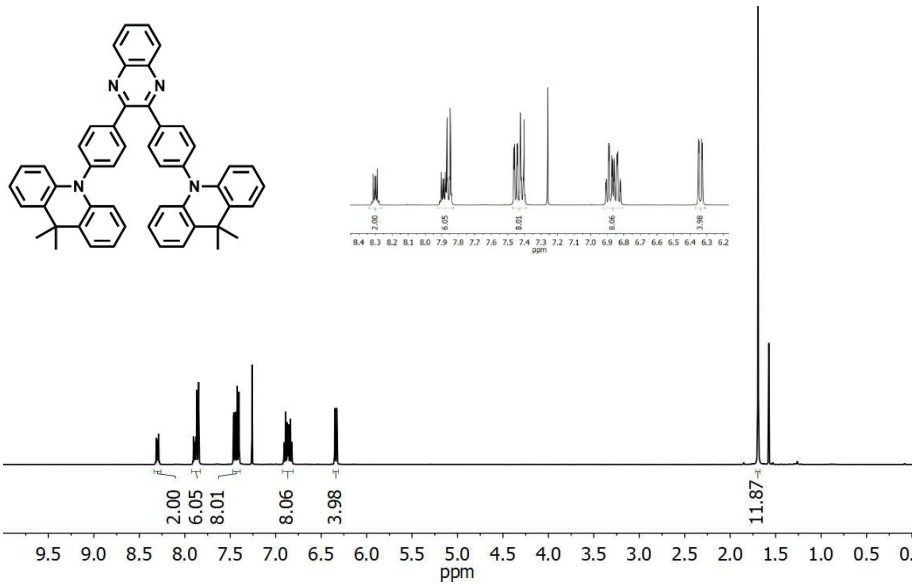

Figure S15: ^{1}H NMR spectrum of 2,3-bis(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)quinoxaline (**Qx-Ph-DMAC**) in $CDCl_3$.

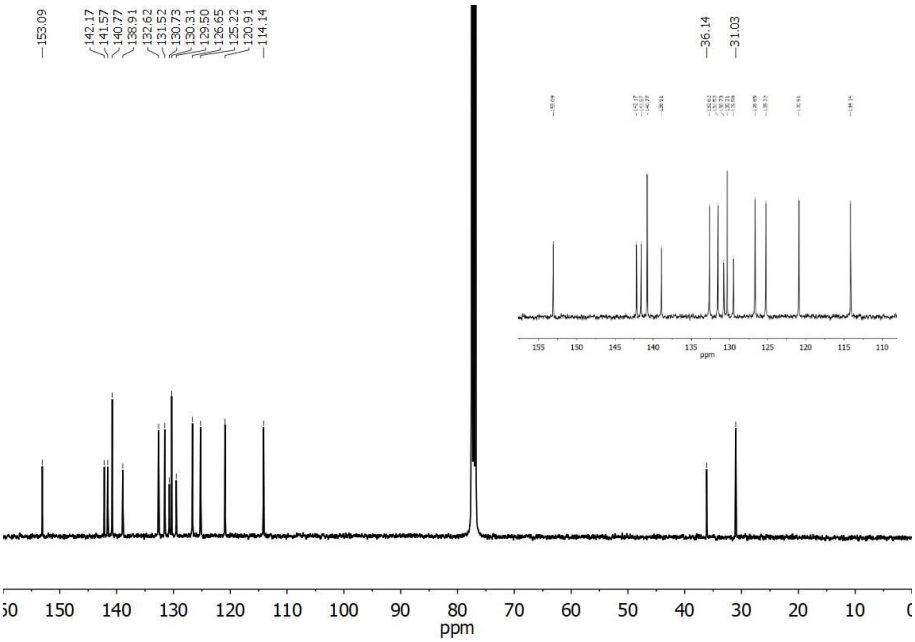

Figure S16: ^{13}C NMR spectrum of 2,3-bis(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)quinoxaline (**Qx-Ph-DMAC**) in $CDCl_3$.

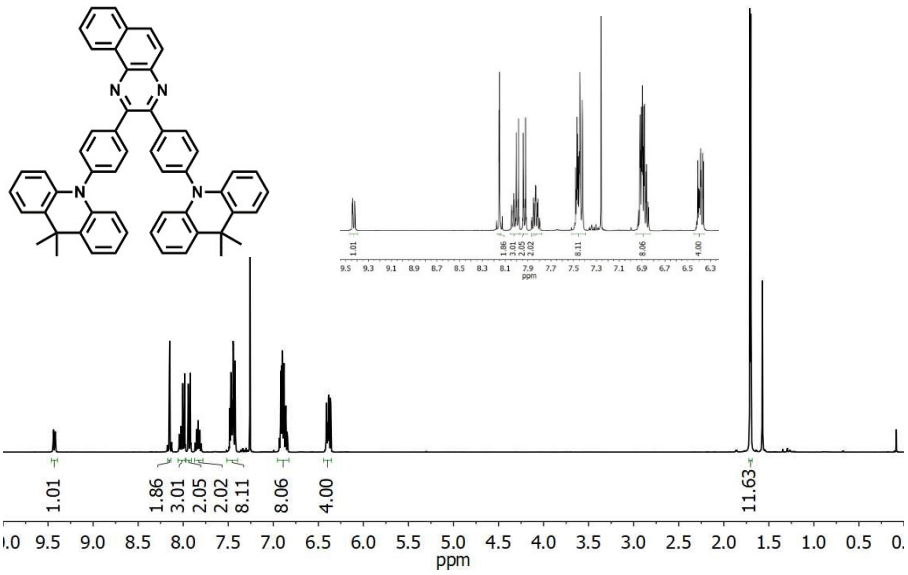

Figure S17: ^{1}H NMR spectrum of 2,3-bis(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)benzo[*f*]quinoxaline (**BQx-Ph-DMAC**) in $CDCl_3$.

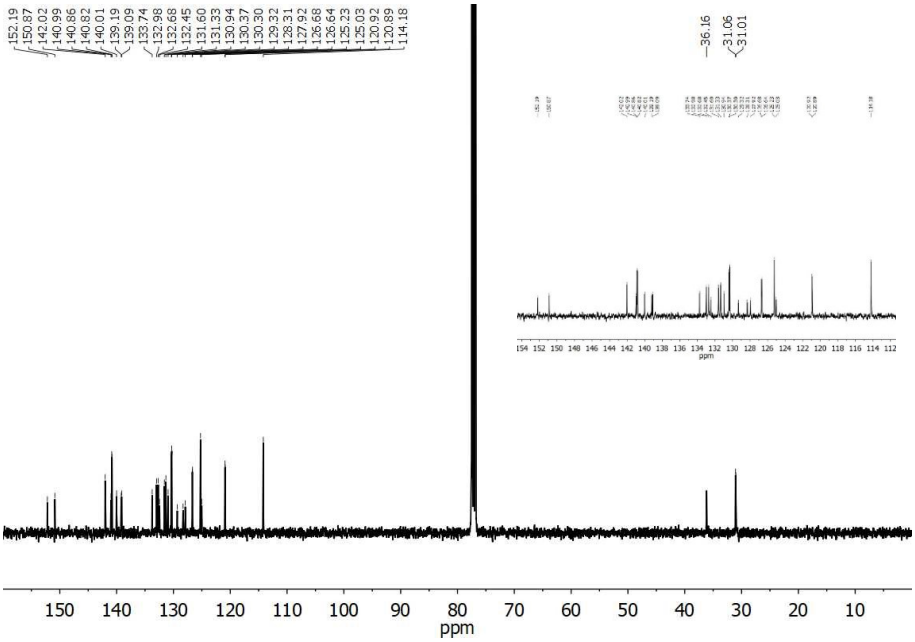

Figure S18: ^{13}C NMR spectrum of 2,3-bis(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)benzo[*f*]quinoxaline (**BQx-Ph-DMAC**) in $CDCl_3$.

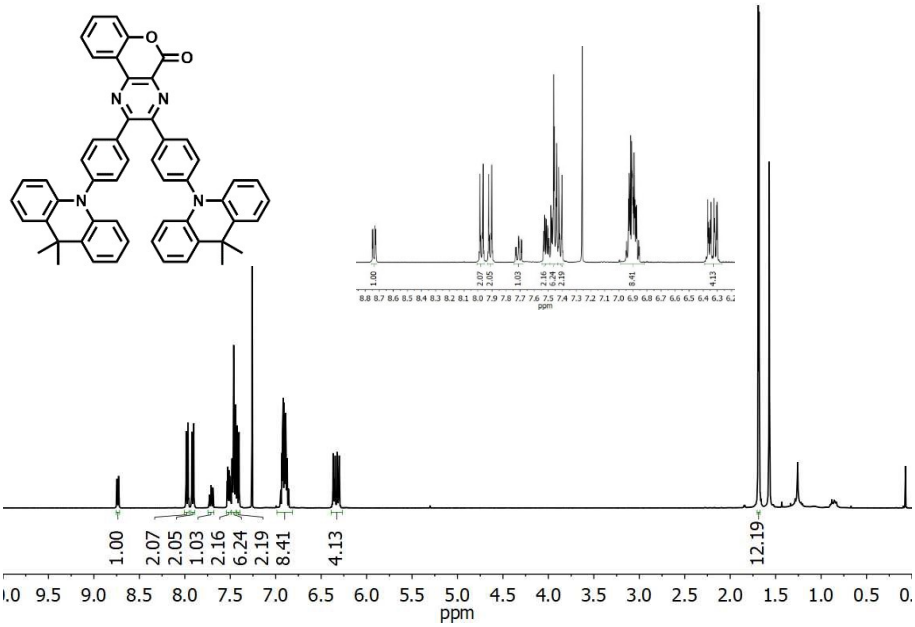

Figure S19: ^{1}H NMR spectrum of 2,3-bis(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)-5*H*-chromeno[3,4-*b*]pyrazin-5-one (**ChromPy-Ph-DMAC**) in $CDCl_3$.

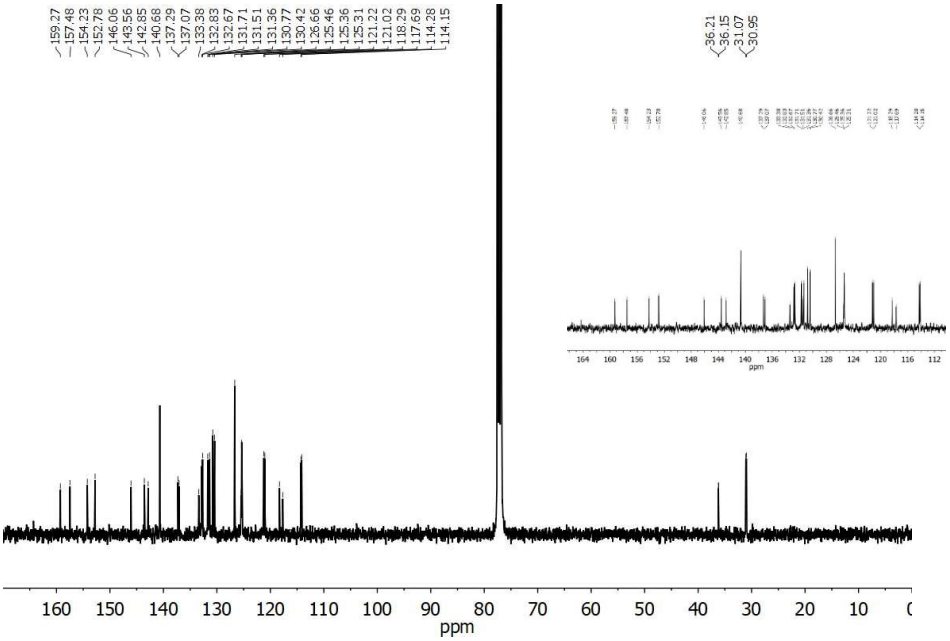

Figure S20: ^{13}C NMR spectrum of 2,3-bis(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)-5*H*-chromeno[3,4-*b*]pyrazin-5-one (**ChromPy-Ph-DMAC**) in $CDCl_3$.

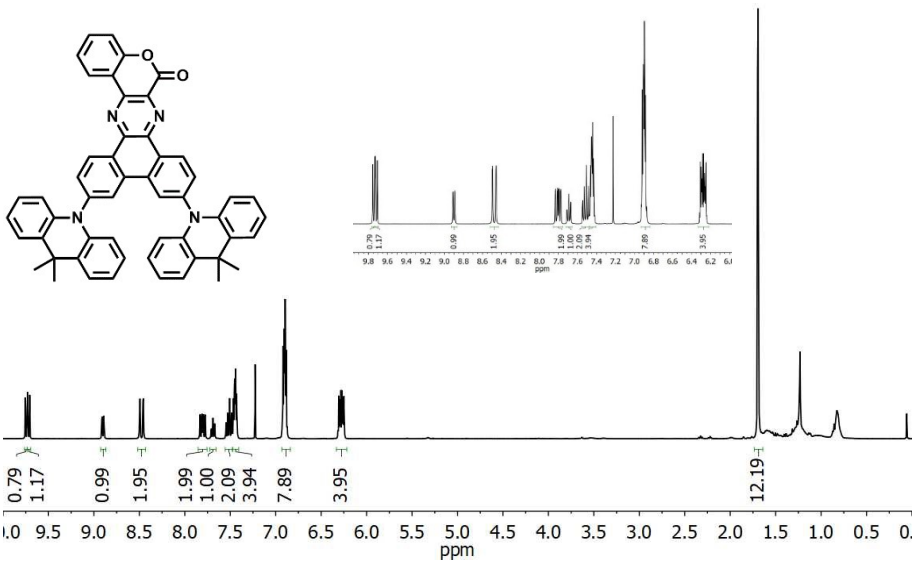

Figure S21: ^{1}H NMR spectrum of 10,13-bis(9,9-dimethylacridin-10(9*H*)-yl)-6*H*-dibenzo[*f*,*h*]chromeno[3,4-*b*]quinoxalin-6-one (**DBChromQx-DMAC**) in $CDCl_3$.

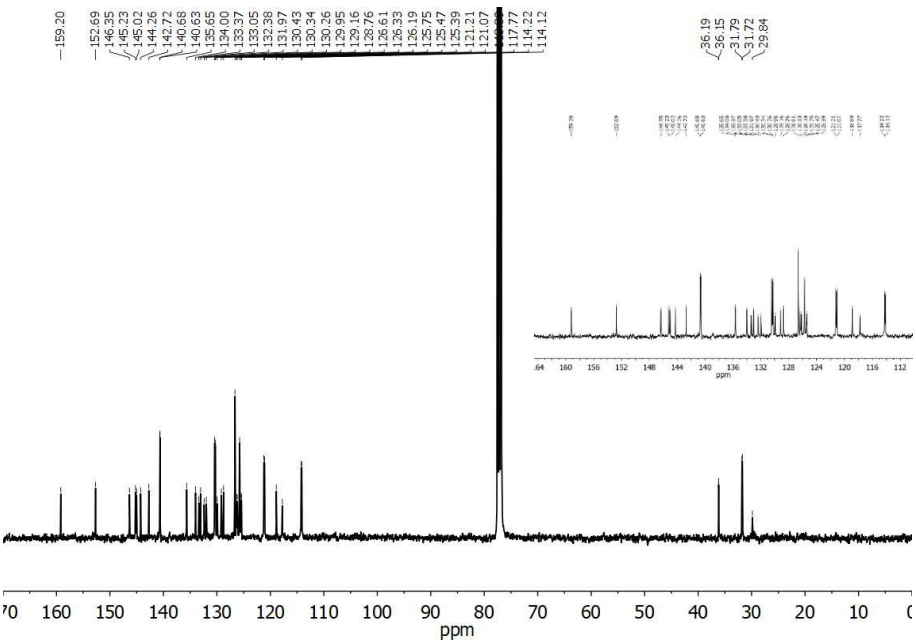

Figure S22: ^{13}C NMR spectrum of 10,13-bis(9,9-dimethylacridin-10(9*H*)-yl)-6H-dibenzo[*f*,*h*]chromeno[3,4-*b*]quinoxalin-6-one (**DBChromQx-DMAC**) in $CDCl_3$.

10. Coordinates of optimized geometries

Qx-Ph-DMAC

C	8.90695	-0.67387	0.20933
C	7.72928	-1.34124	0.41034
C	6.50126	-0.68018	0.19965
C	6.50126	0.68018	-0.19965
C	7.72928	1.34125	-0.41035
C	8.90695	0.67388	-0.20934
N	5.33799	-1.36188	0.33920
N	5.33799	1.36189	-0.33919
C	4.22288	-0.70854	0.13511
C	4.22288	0.70855	-0.13511
C	2.94837	-1.46264	0.16727
C	2.04072	-1.34584	-0.88562
C	2.61289	2.24540	-1.26809
C	2.94837	1.46264	-0.16727
C	2.61290	-2.24540	1.26809
C	1.35275	-2.81976	1.36040
C	0.43231	-2.64169	0.33642
C	0.79620	-1.94164	-0.80726
C	1.35274	2.81975	-1.36039
C	0.43231	2.64169	-0.33641
C	0.79620	1.94164	0.80727
C	2.04072	1.34584	0.88563
C	-3.24663	2.58793	-0.84117
C	-1.89241	2.23763	-0.90622
N	-0.90176	3.12663	-0.46159
C	-1.22220	4.39777	0.02566
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C	-3.72430	3.91831	-0.27664
C	-4.18481	1.65482	-1.27736
C	-3.82899	0.40893	-1.76238
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C	-1.52776	0.98365	-1.41329
C	-0.19872	5.26222	0.43606
C	-0.48560	6.52693	0.91159
C	-1.80061	6.95819	0.98979
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C	-4.55798	3.64287	0.98411
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C	-1.22220	-4.39777	-0.02567
N	-0.90176	-3.12664	0.46161
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C	-3.72430	-3.91831	0.27664
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H	7.69743	2.38327	-0.71896
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H	3.33598	-2.36331	2.07254
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H	1.05754	3.38918	-2.23952
H	0.07549	1.84374	1.61749
H	2.30463	0.76213	1.76590
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H	0.32910	7.17707	1.22251
H	-2.04096	7.95062	1.36238
H	-3.84020	6.43941	0.66243
H	-3.95249	3.13065	1.74185
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H	-5.42336	3.00806	0.76137
H	-5.45640	4.02081	-1.61010

H	-4.98040	5.58152	-0.94676
H	-4.01268	4.83716	-2.22964
H	-3.84020	-6.43940	-0.66247
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H	-2.17597	0.89592	2.20344
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H	-5.24232	-1.90669	1.22026
H	-4.01265	-4.83716	2.22965
H	-5.45639	-4.02083	1.61012
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H	-5.42337	-3.00806	-0.76134
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H	-4.93344	-4.57192	-1.42782

BQx-Ph-DMAC

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C	7.23617	-0.14459	-0.15355
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C	5.60893	-1.92325	0.38124
C	6.68949	-2.82426	0.61733
C	7.96865	-2.40945	0.46646
C	9.61188	-0.64539	-0.08853
C	9.89639	0.64657	-0.45943
C	8.85685	1.56082	-0.67776
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H	-6.55168	-4.67492	0.86265
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H	-4.61774	5.35376	1.45617

Chrom-Py-Ph-DMAC

C	-8.13852	-0.51457	0.02971
C	-7.07963	0.35973	0.27392
C	-5.73682	-0.13155	0.04992
C	-5.55459	-1.45381	-0.36321
C	-6.70794	-2.33456	-0.66848
O	-7.94531	-1.78517	-0.42321
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C	-8.66406	2.05547	0.92016
C	-7.36006	1.65468	0.71772
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C	-1.37552	1.06451	-0.96217
C	-1.08037	-1.57255	0.83992
C	-1.95396	-1.82924	-0.21718
C	-2.12237	1.93550	1.15205
C	-0.94905	2.66828	1.26157
C	0.01488	2.58726	0.26546
C	-0.22206	1.81851	-0.86780
C	0.22366	-2.02646	0.79627
C	0.67941	-2.72288	-0.31636
C	-0.20120	-3.04140	-1.34191
C	-1.51918	-2.61088	-1.28412
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C	2.50727	-4.29046	0.08425
C	3.87764	-4.55457	0.20817
C	4.94478	-3.51543	-0.10787
C	4.33961	-2.25587	-0.71196
C	2.95721	-2.06589	-0.83008
C	1.57606	-5.26925	0.45382
C	1.98947	-6.49825	0.93005
C	3.34177	-6.77729	1.05047
C	4.25841	-5.80439	0.69187
C	5.17852	-1.22400	-1.12783
C	4.69878	-0.03532	-1.64858
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C	2.46868	-0.87117	-1.37476
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C	2.36268	2.49255	0.86784
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C	3.97241	4.37632	0.20644
C	2.70226	5.12103	-0.18064
C	1.43039	4.53951	-0.09768
C	2.15468	1.21352	1.39985
C	3.21563	0.44483	1.83679
C	4.50827	0.93723	1.76285
C	4.70815	2.20752	1.25248
C	2.79365	6.41796	-0.68120
C	1.68715	7.13863	-1.09535
C	0.43621	6.54738	-1.01423
C	0.30840	5.26299	-0.52213
C	5.96323	-4.10978	-1.08924
C	5.65211	-3.13542	1.20209
C	4.82369	4.18047	-1.05750
C	4.75628	5.20522	1.23240
H	-10.24862	-0.82982	0.02965
H	-10.73835	1.47887	0.83653
H	-8.87694	3.06318	1.26651
H	-6.52514	2.32781	0.89334
H	-1.53573	0.42857	-1.83102
H	-1.42100	-0.99338	1.69652
H	-2.87441	1.97507	1.93729
H	-0.75392	3.29068	2.13251
H	0.53009	1.79340	-1.65441
H	0.91810	-1.81817	1.60844
H	0.16686	-3.60834	-2.19467
H	-2.21453	-2.84336	-2.08788
H	0.51345	-5.06205	0.36637
H	1.24445	-7.24018	1.20830
H	3.68130	-7.73978	1.42433
H	5.31848	-6.02403	0.80395
H	6.25512	-1.34850	-1.02582
H	5.38560	0.75381	-1.94528
H	2.92348	1.05779	-2.18029
H	1.39619	-0.71818	-1.46671
H	1.14829	0.80481	1.45059
H	3.02896	-0.55392	2.22922
H	5.35249	0.33463	2.08946
H	5.72641	2.58722	1.19010
H	3.77464	6.88263	-0.76046
H	1.80282	8.14816	-1.48121
H	-0.45208	7.08609	-1.33639
H	-0.67710	4.80971	-0.46512
H	5.47732	-4.38705	-2.03120
H	6.76263	-3.39834	-1.32061
H	6.44221	-5.00591	-0.68141
H	6.43296	-2.38495	1.03190
H	4.93522	-2.71823	1.91987
H	6.12303	-4.00749	1.67025
H	4.27360	3.59704	-1.80590
H	5.09047	5.14053	-1.51388
H	5.75543	3.64798	-0.83426
H	5.02262	6.19095	0.83679
H	4.16416	5.35646	2.14171
H	5.69090	4.71183	1.51877

DBChrom-Qx-DMAC

C	8.62798	1.40179	0.00001
C	9.57304	0.37611	0.00001
C	9.17386	-0.94678	0.00000
C	7.81882	-1.24639	0.00000
C	6.85792	-0.23538	0.00000
C	7.28317	1.09591	0.00001
O	7.49126	-2.57027	-0.00001
C	6.20083	-3.04023	-0.00002
C	5.14385	-1.99669	-0.00001
C	5.46232	-0.62650	0.00000
O	6.01431	-4.21355	-0.00003
N	3.89384	-2.42087	-0.00002
N	4.50215	0.29131	0.00000
C	3.23815	-0.12655	0.00000
C	2.92670	-1.50924	-0.00001
C	2.16753	0.85408	0.00000
C	0.82328	0.42554	0.00000
C	0.50540	-1.00118	-0.00001
C	1.54462	-1.95237	-0.00001

C	2.47104	2.22210	0.00001
C	1.47077	3.16456	0.00002
C	0.13753	2.74990	0.00001
C	-0.17634	1.40820	0.00000
C	-0.81443	-1.47188	-0.00001
C	-1.09130	-2.82206	-0.00001
C	-0.05407	-3.75665	-0.00002
C	1.25076	-3.32210	-0.00002
C	-2.34303	5.22458	-1.25895
C	-1.36306	4.22420	-1.22357
N	-0.90375	3.72095	0.00001
C	-1.36307	4.22418	1.22361
C	-2.34305	5.22455	1.25899
C	-2.96168	5.81599	0.00002
C	-2.76663	5.67705	-2.50649
C	-2.25633	5.18201	-3.69378
C	-1.28464	4.19540	-3.64295
C	-0.84258	3.72104	-2.42304
C	-0.84262	3.72099	2.42307
C	-1.28470	4.19532	3.64299
C	-2.25639	5.18192	3.69382
C	-2.76667	5.67699	2.50653
C	-4.46748	5.51607	0.00001
C	-2.73952	7.33503	0.00004
C	-4.42057	-3.91952	1.25893
C	-3.08648	-3.49327	1.22328
N	-2.44572	-3.26230	-0.00001
C	-3.08650	-3.49321	-1.22331
C	-4.42059	-3.91945	-1.25895
C	-5.24582	-4.14707	-0.00001
C	-5.00577	-4.12362	2.50644
C	-4.32231	-3.92731	3.69366
C	-3.00182	-3.51028	3.64264
C	-2.39021	-3.29480	2.42278
C	-2.39024	-3.29469	-2.42281
C	-3.00188	-3.51010	-3.64267
C	-4.32237	-3.92713	-3.69369
C	-5.00581	-4.12349	-2.50647
C	-6.42829	-3.16749	0.00002
C	-5.77250	-5.58896	-0.00004
H	8.95079	2.43937	0.00002
H	10.63381	0.61429	0.00001
H	9.88715	-1.76614	0.00000
H	6.52626	1.87565	0.00001
H	3.51660	2.51530	0.00001
H	1.69272	4.22953	0.00002
H	-1.23025	1.14372	0.00000
H	-1.66062	-0.79003	0.00000
H	-0.29843	-4.81673	-0.00003
H	2.07979	-4.02415	-0.00003
H	-3.53129	6.45017	-2.55278
H	-2.61524	5.56275	-4.64643
H	-0.86372	3.78571	-4.55831
H	-0.08252	2.94554	-2.39927
H	-0.08255	2.94549	2.39929
H	-0.86379	3.78560	4.55834
H	-2.61532	5.56264	4.64648
H	-3.53133	6.45011	2.55283
H	-4.64734	4.43513	-0.00001
H	-4.95960	5.93804	0.88331
H	-4.95959	5.93806	-0.88330
H	-3.18694	7.80697	0.88127
H	-1.66934	7.57031	0.00005
H	-3.18693	7.80699	-0.88119
H	-6.04360	-4.44825	2.55266
H	-4.81686	-4.09826	4.64633
H	-2.43685	-3.34873	4.55786
H	-1.35503	-2.96702	2.39871
H	-1.35507	-2.96691	-2.39874
H	-2.43692	-3.34852	-4.55789
H	-4.81693	-4.09802	-4.64636
H	-6.04364	-4.44812	-2.55269
H	-6.07277	-2.13088	0.00005
H	-7.06160	-3.30492	-0.88355
H	-7.06159	-3.30496	0.88360
H	-6.39077	-5.79135	-0.88104
H	-4.94298	-6.30478	-0.00007
H	-6.39076	-5.79140	0.88095