Styrylpyrimidine chromophores with bulky electron-donating substituents: experimental and theoretical investigation

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Supporting Information

Table S1: Angles within the **1-3** series for the ground and first singlet/triplet excited states, characterizing the twist between the styrylpyrimidine and acridine groups computed at the SCS-CC2/def2-TZVP level in gas phase. For *Qeq*, we considered the dihedral angle $1\hat{2}34$ called θ and for *Qax* the angle $2\hat{3}X$ called ϕ. Atom numbering is defined in Figure S8.

	1			**2**			**3**		
	S_0	S_1	T_1	S_0	S_1	T_1	S_0	S_1	T_1
$1\hat{2}34$ (θ, *Qeq*)	89°	90°	89°	73°	93°	73°	81°	91°	74°
$2\hat{3}X$ (ϕ, *Qax*)	125°	136°	125°	115°	143°	115°	98°	136°	98°

Table S2: ωB97X-D/6-311+G(d,p) TD-DFT calculations of vertical excitation and de-excitation for both conformers in gas phase.

Conformer	Cmpd	E_{abs} (eV)	λ_{abs} (nm)	f_{abs}	$State_{abs}$	E_{em} (eV)	λ_{em} (nm)	f_{em}
Qeq	1	4.41	281	1.51	S_3	3.30	375	0.20
	2	4.42	280	1.44	S_4	3.00	413	0
	3	4.42	281	1.49	S_3	3.01	411	0
Qax	1	3.83	319	1.54	S_1	3.43	361	1.73
	2	3.98	311	1.50	S_1	3.44	361	1.69
	3	3.98	311	1.50	S_1	3.46	358	1.69

Table S3: M06-2X/6-311+G(d,p) TD-DFT calculations of vertical excitation and de-excitation for both conformers in gas phase.

Conformer	Cmpd	E_{abs} (eV)	λ_{abs} (nm)	f_{abs}	$State_{abs}$	E_{em} (eV)	λ_{em} (nm)	f_{em}
Qeq	1	4.40	282	1.52	S_4	2.93	423	0
	2	4.41	281	1.46	S_4	2.60	476	0
	3	4.41	281	1.51	S_4	2.55	486	0
Qax	1	3.78	328	1.52	S_1	3.38	367	1.73
	2	3.89	319	1.46	S_1	3.37	368	1.65
	3	3.92	316	1.47	S_1	3.41	364	1.67

Table S4: B3LYP/6-311+G(d,p) TD-DFT calculations of vertical excitation and de-excitation for both conformers in gas phase.

Conformer	Cmpd	E_{abs} (eV)	λ_{abs} (nm)	f_{abs}	$State_{abs}$	E_{em} (eV)	λ_{em} (nm)	f_{em}
Qeq	1	4.01	309	1.49	S_7	1.88	660	0
	2	4.00	310	1.34	S_8	1.52	818	0
	3	4.00	310	1.23	S7	1.46	849	0
Qax	1	3.24	383	1.33	S_1	/ [a]	/[a]	/ [a]
	2	3.27	379	1.16	S_1	/[a]	/[a]	/[a]
	3	3.32	374	1.22	S_1	3.25	382	0.16

[a] No stable Qax conformer found

Table S5: ωB97X-D/6-311+G(d,p) TD-DFT calculations of excitation and de-excitation for both conformers in toluene.

Conformer	Cmpd	E_{abs} (eV)	λ_{abs} (nm)	f_{abs}	$State_{abs}$	E_{em} (eV)	λ_{em} (nm)	f_{em}
Qeq	1	4.24	292	1.58	S_2	3.16	392	0.95
	2	4.27	292	1.54	S_4	3.02	410	0.67
	3	4.25	292	1.56	S_3	3.09	401	0.00
Qax	1	3.71	334	1.65	S_1	3.14	395	1.84
	2	3.81	325	1.60	S_1	3.15	394	1.82
	3	3.80	326	1.61	S_1	3.17	391	1.82

Table S6: M06-2X/6-311+G(d,p) TD-DFT calculations of vertical excitation and de-excitation for both conformers in toluene.

Conformer	Cmpd	E_{abs} (eV)	λ_{abs} (nm)	f_{abs}	$State_{abs}$	E_{em} (eV)	λ_{em} (nm)	f_{em}
Qeq	1	4.23	293	1.61	S_2	2.97	418	0.28
	2	4.25	292	1.57	S_3	2.70	460	0.00
	3	4.24	292	1.61	S_3	2.65	467	0.00
Qax	1	3.60	344	1.64	S_1	3.09	401	1.88
	2	3.71	334	1.58	S_1	3.10	400	1.84
	3	3.73	332	1.58	S_1	3.13	396	1.84

Table S7: B3LYP/6-311+G(d,p) TD-DFT calculations of vertical excitation and de-excitation for both conformers in toluene.

Conformer	Cmpd	E_{abs} (eV)	λ_{abs} (nm)	f_{abs}	$State_{abs}$	E_{em} (eV)	λ_{em} (nm)	f_{em}
Qeq	1	3.82	324	1.59	S_5	1.93	642	0.00
	2	3.84	323	1.54	S_7	1.61	770	0.00
	3	3.82	324	1.56	S_5	1.56	794	0.00
Qax	1	3.03	409	1.46	S_1	2.82	440	1.54
	2	3.08	402	1.31	S_1	/[a]	/[a]	/[a]
	3	3.12	397	1.38	S_1	/[a]	/[a]	/[a]

[a] no stable Qax conformer found

Table S8: Transition energies, oscillator strengths and corresponding states involved for different dihedral angles between the styrylpyrimidine and the acridine groups of the *Qeq* conformer. The dihedral angle is $1\hat{2}34$, with atom numbering defined in Figure S8. Values are computed at the SCS-CC2/def2-TZVP level in gas phase.

	Dihedral Angle $1\hat{2}34$ (°)	**E (eV)**	***f***	**States**
1	75	3.05	0.11	$S_0 \rightarrow S_1$
		4.10	0.12	$S_0 \rightarrow S_3$
		4.21	1.16	$S_0 \rightarrow S_4$
		4.39	0.25	$S_0 \rightarrow S_5$
	105	3.05	0.08	$S_0 \rightarrow S_1$
		4.10	0.11	$S_0 \rightarrow S_3$
		4.20	1.20	$S_0 \rightarrow S_4$
		4.39	0.53	$S_0 \rightarrow S_5$
2	75	3.10	0.17	$S_0 \rightarrow S_1$
		4.13	0.11	$S_0 \rightarrow S_4$
		4.24	1.13	$S_0 \rightarrow S_5$
	105	3.10	0.07	$S_0 \rightarrow S_1$
		4.16	0.13	$S_0 \rightarrow S_4$
		4.21	1.15	$S_0 \rightarrow S_5$
3	75	3.28	0.01	$S_0 \rightarrow S_1$
		4.17	0.23	$S_0 \rightarrow S_4$
	105	3.28	0.01	$S_0 \rightarrow S_1$
		4.17	0.28	$S_0 \rightarrow S_4$

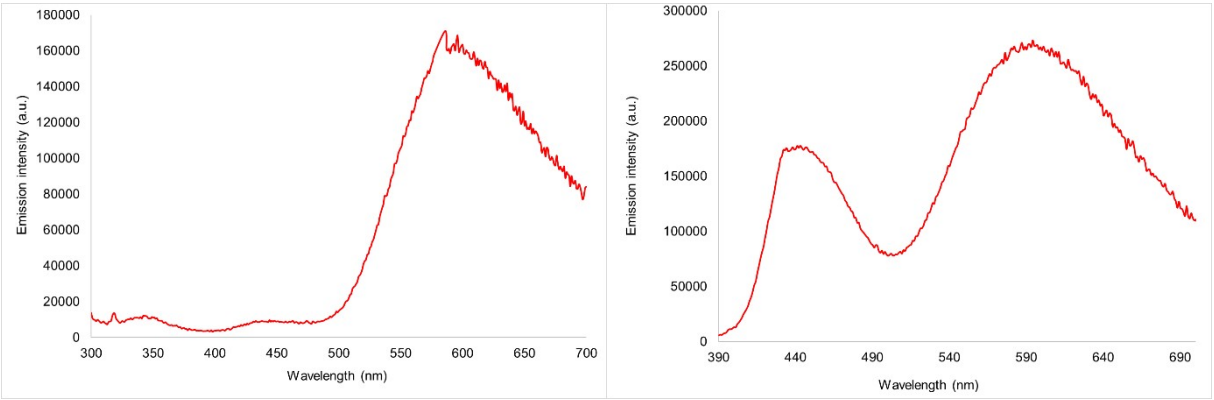

Figure S1: Emission spectra of compound **3** in toluene (c = 1 × 10^{-5} M) after excitation at 290 nm (left) and 380 nm (right)

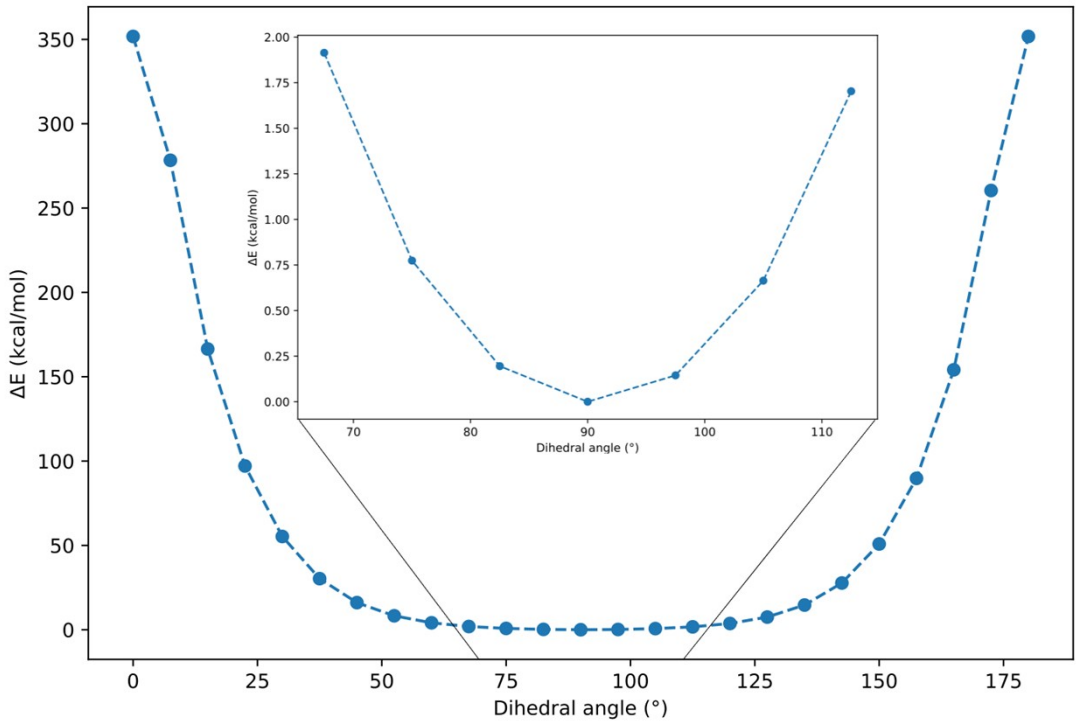

Figure S2: Rigid scan of the ground state of compound **1** along the donor-acceptor θ angle (Figure S8), at the DFT level (ωB97X-D/6-311+G(d,p) (PCM: CH_2Cl_2).

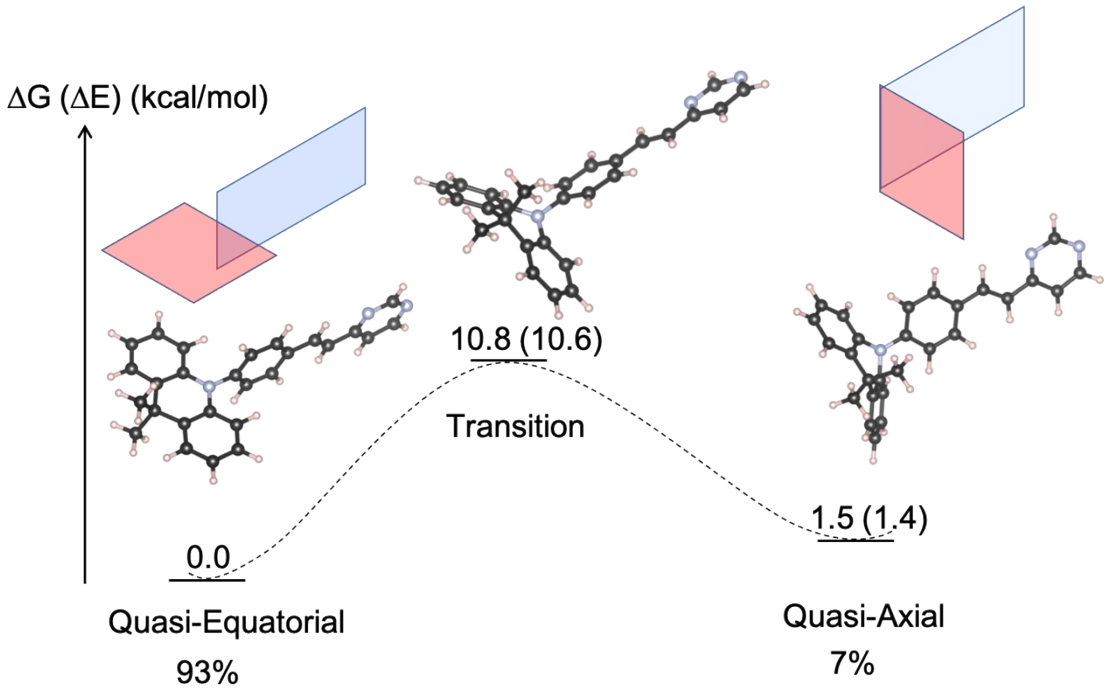

Figure S3: Relative total Gibbs free energies (total electronic energies in parenthesis) of the *Qeq* and *Qax* conformers and of the transition state, obtained at the ωB97X-D/6-311+G(d,p) level of theory for compound **1**. Boltzmann relative populations obtained with ΔG are also presented.

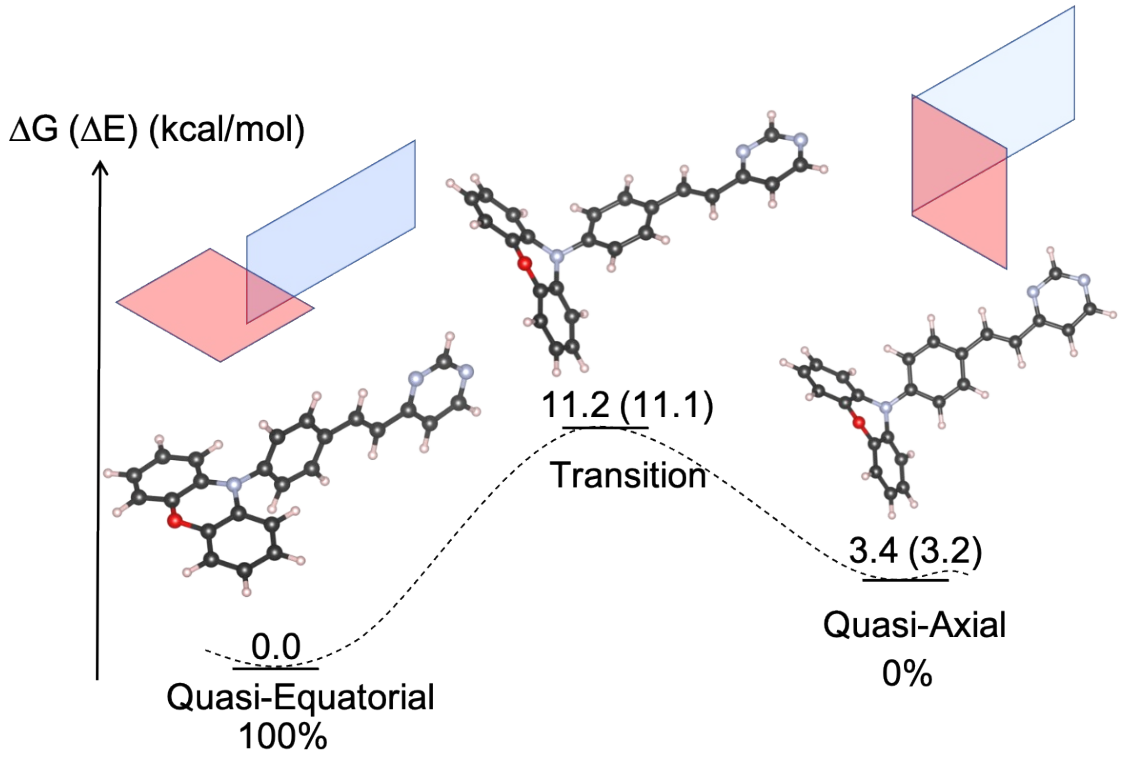

Figure S4: Relative total Gibbs free energies (total electronic energies in parenthesis) of the *Qeq* and *Qax* conformers and of the transition state, obtained at the ωB97X-D/6-311+G(d,p) level of theory for compound **2**. Boltzmann relative populations obtained with ΔG are also presented.

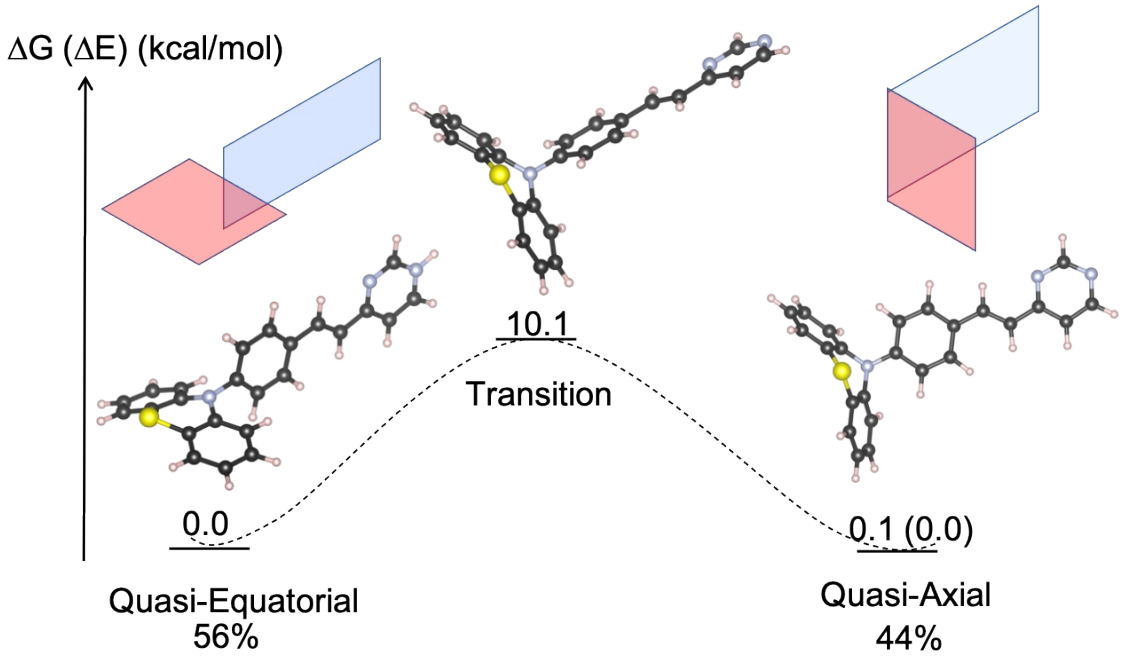

Figure S5: Relative total Gibbs free energies (total electronic energies in parenthesis) of the *Qeq* and *Qax* conformers and of the transition state, obtained at the ωB97X-D/6-311+G(d,p) level of theory for compound **3**. Boltzmann relative populations obtained with ΔG are also presented

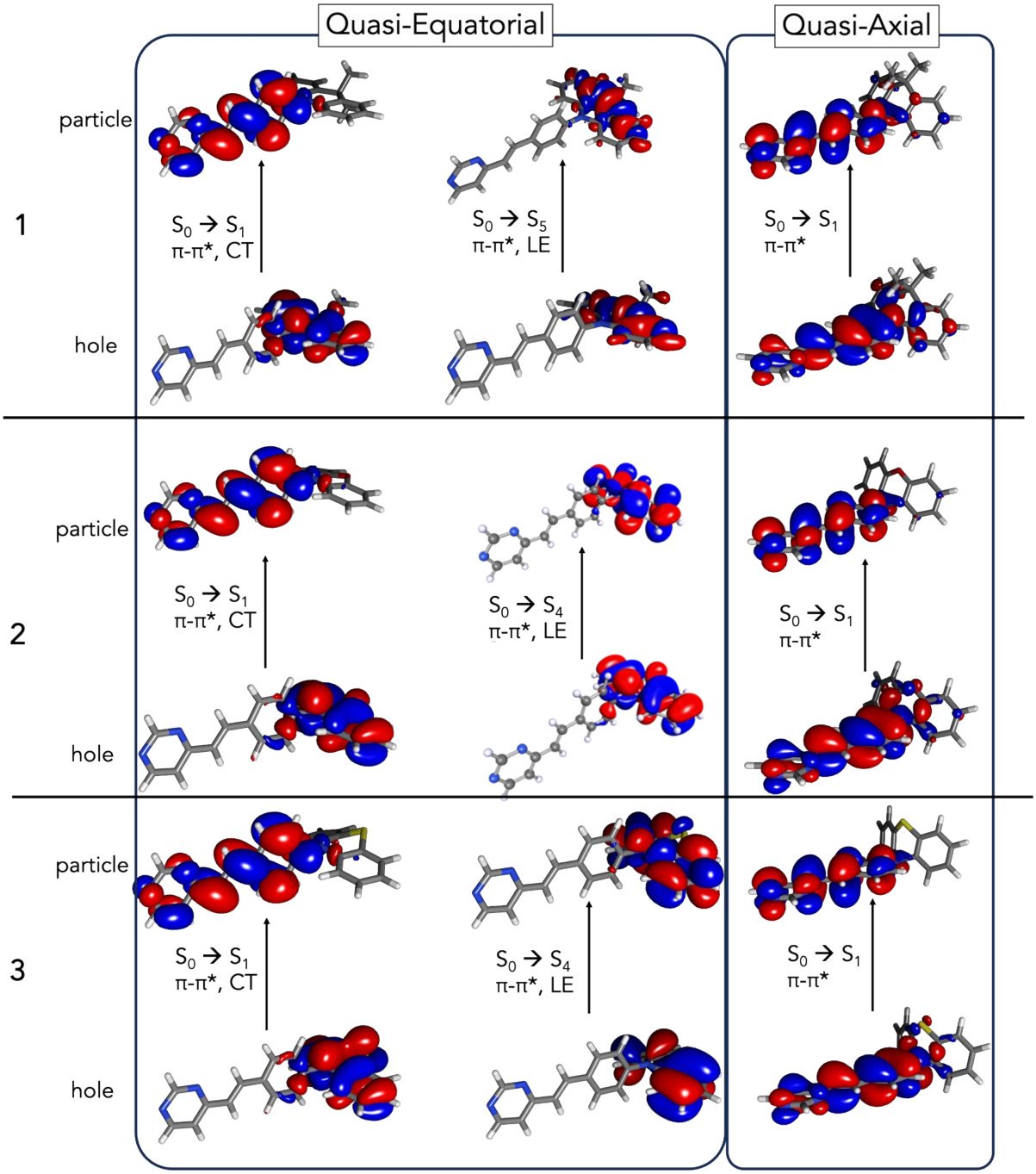

Figure S6: NTOs relevant to absorption of compounds **1-3**, computed at the SCS-CC2/def2-TZVP level in gas phase. (Isovalue = 0.02 $e^-/Å^3$)

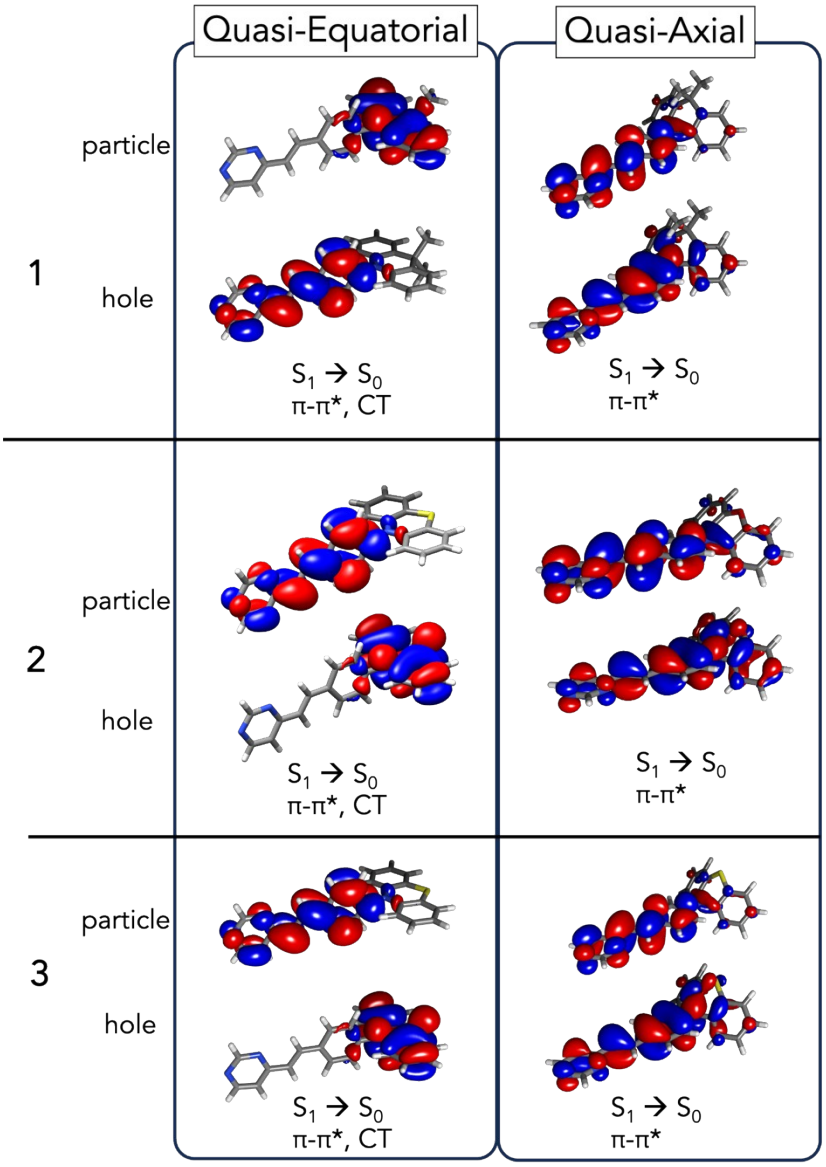

Figure S7: NTOs relevant to the emission of compounds **1-3**, computed at the SCS-CC2/def2-TZVP level in gas phase. (Isovalue = 0.02 $e^-/Å^3$)

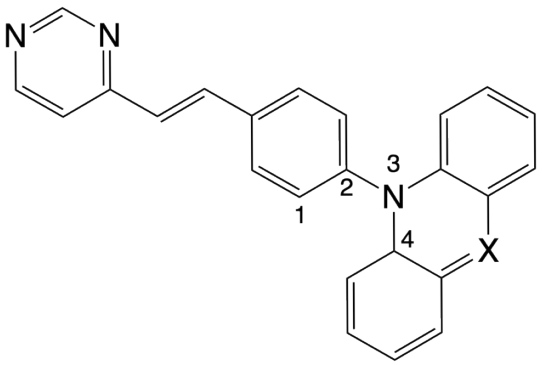

Figure S8: Atom numbering used in Table S1 to characterize the twist angle between the donor and acceptor in each of two conformers.

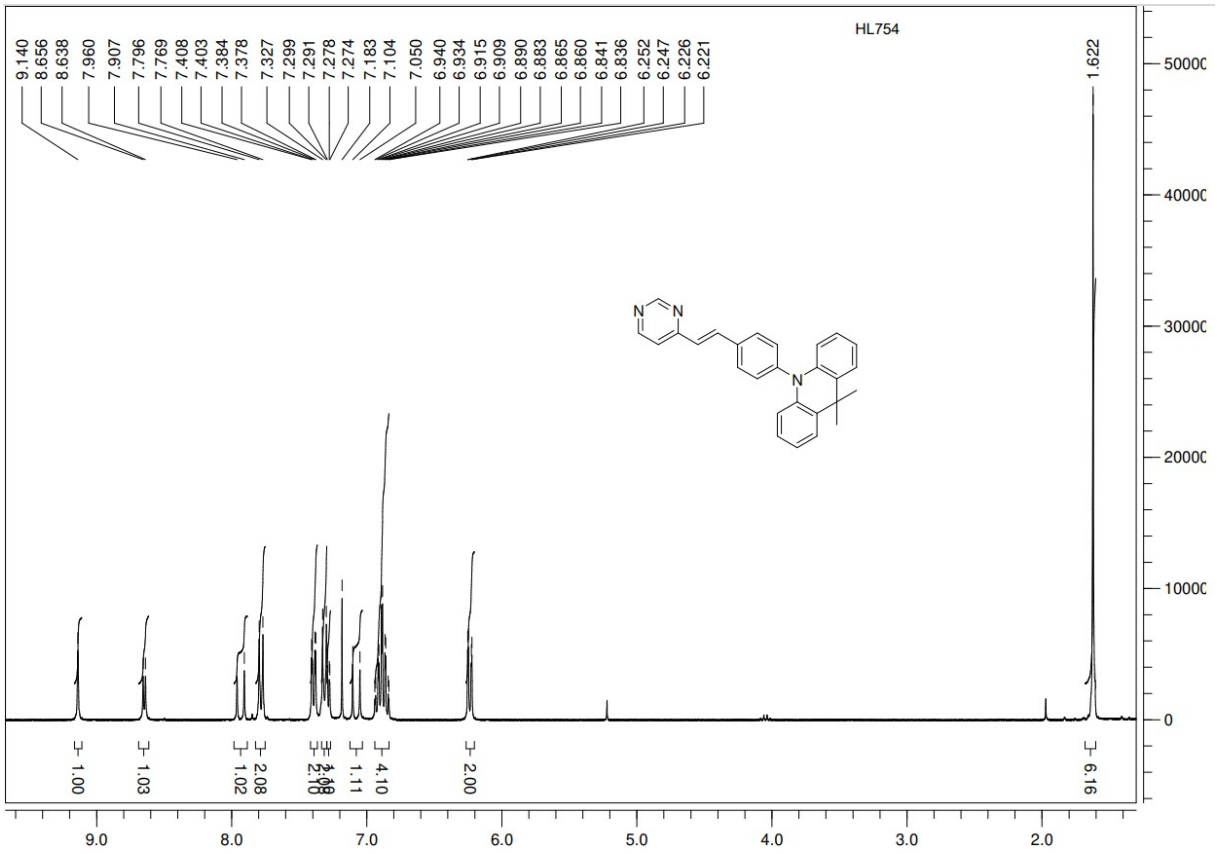

Figure S9: ^{1}H nmr spectrum (300 MHz) of **1** in $CDCl_3$

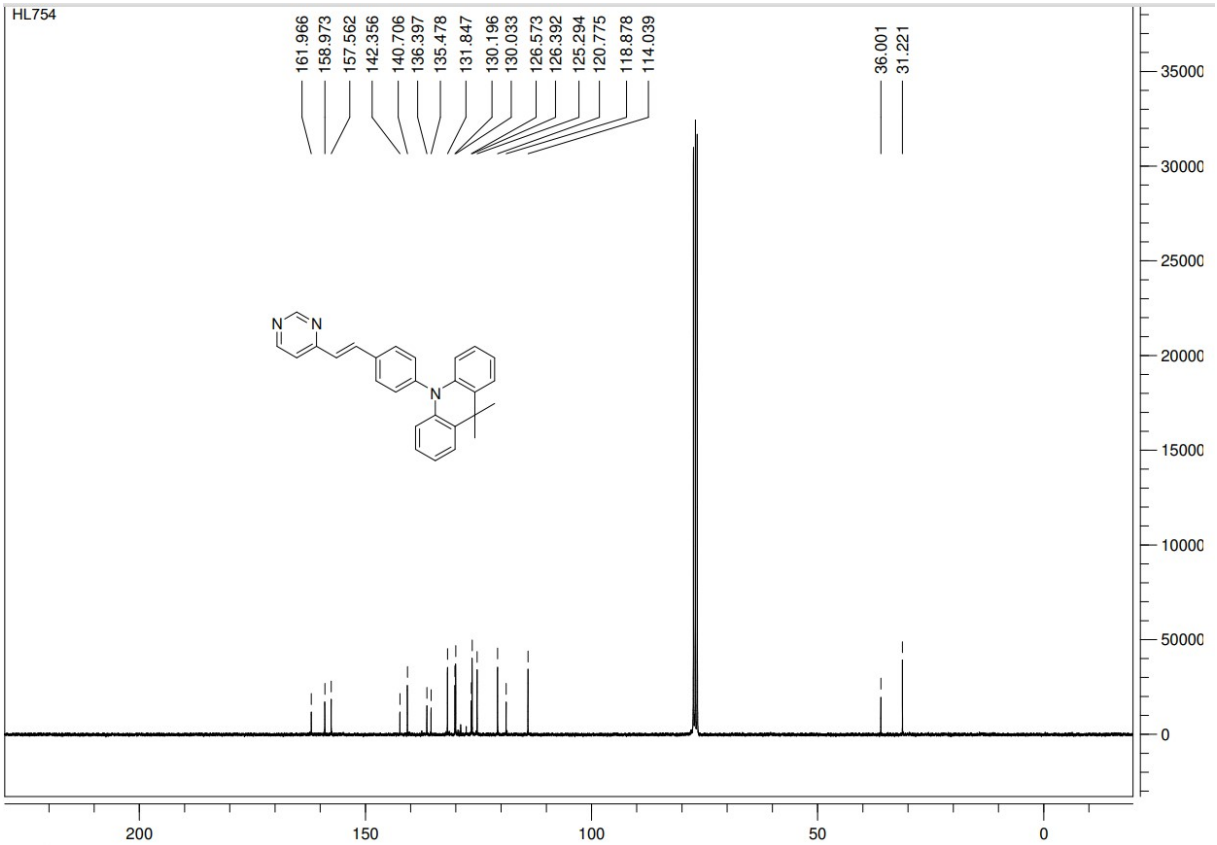

Figure S10: ^{13}C nmr spectrum (75 MHz) of **1** in $CDCl_3$

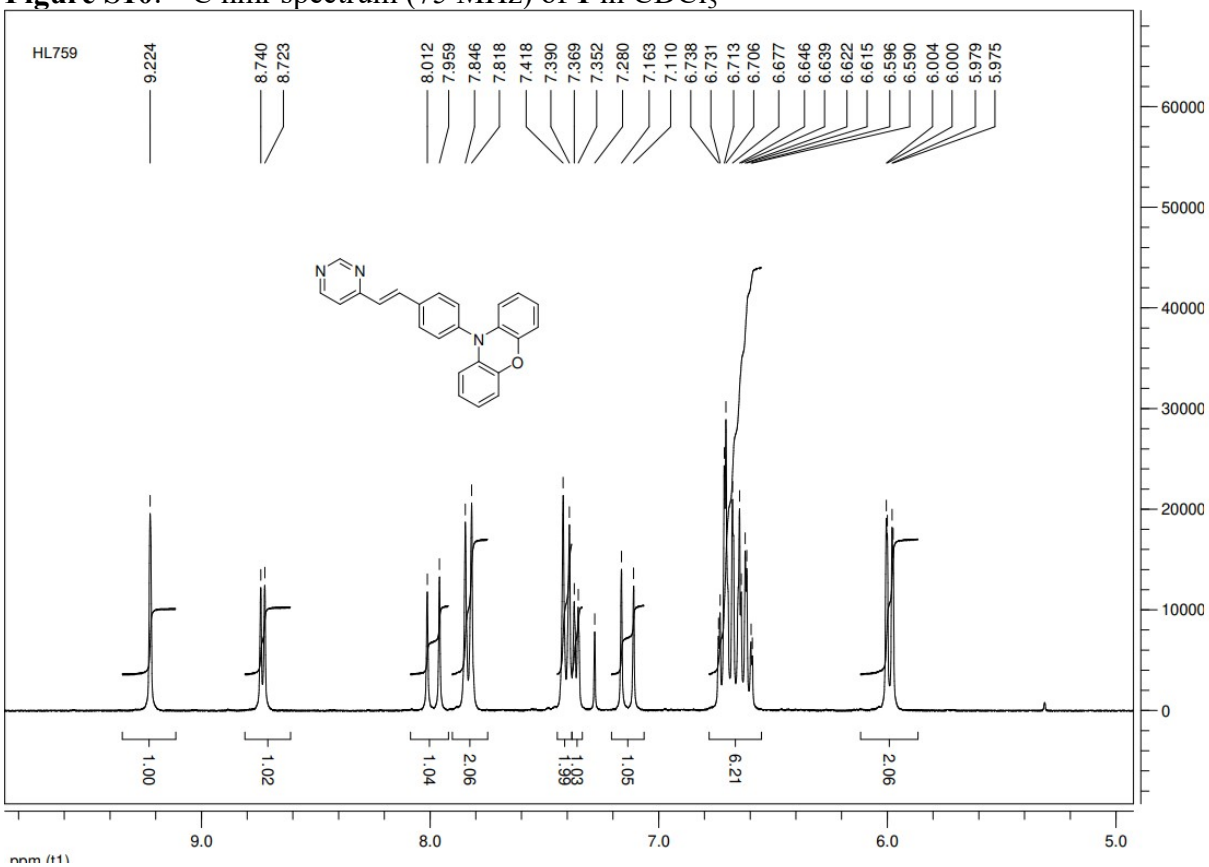

Figure S12: ^{1}H nmr spectrum (300 MHz) of **2** in $CDCl_3$

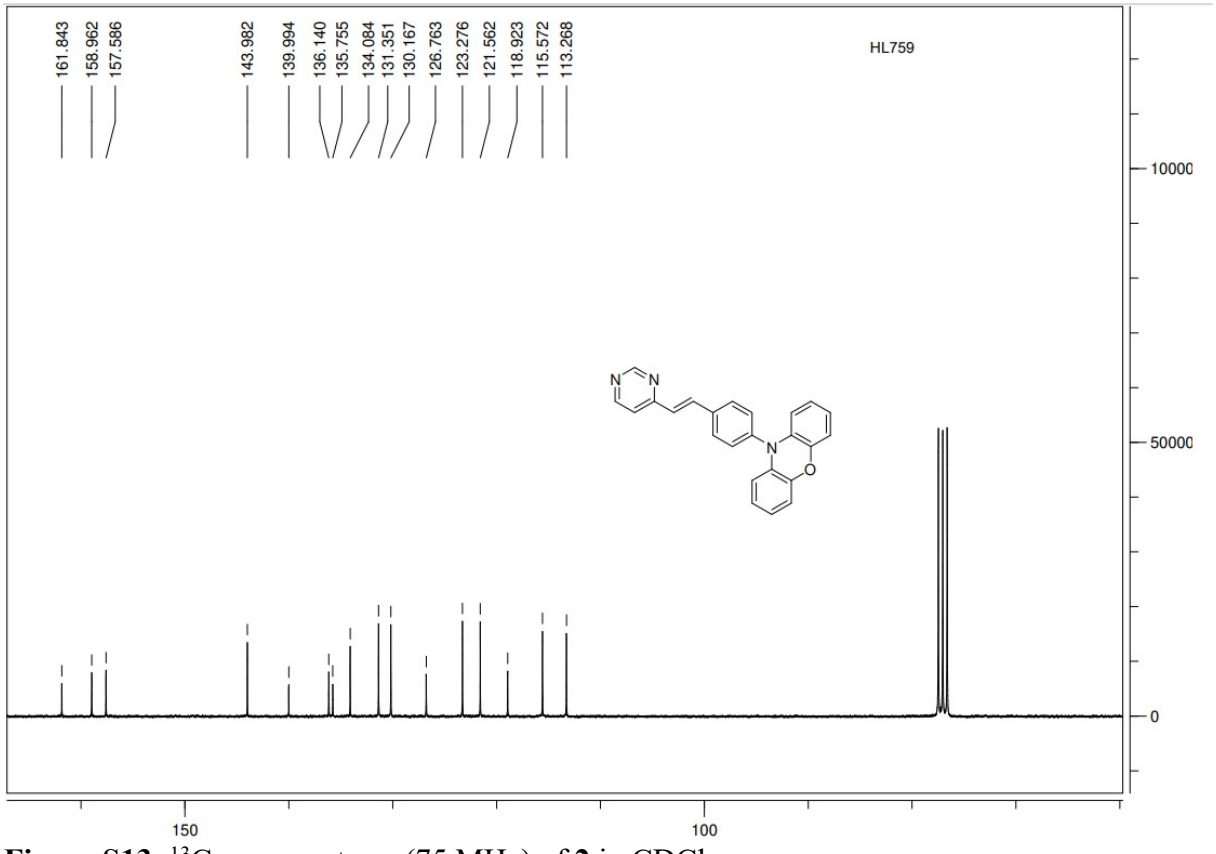

Figure S13: ^{13}C nmr spectrum (75 MHz) of **2** in $CDCl_3$

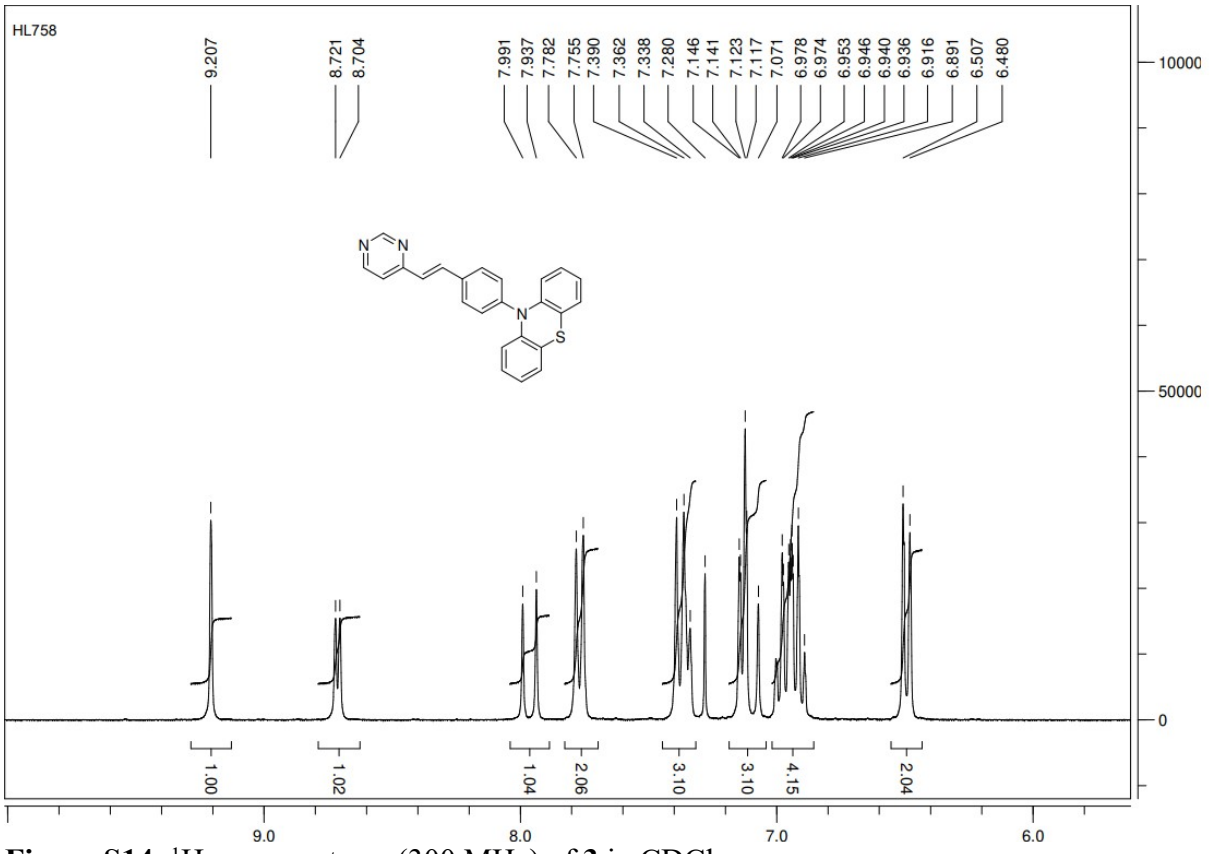

Figure S14: ^{1}H nmr spectrum (300 MHz) of **3** in $CDCl_3$

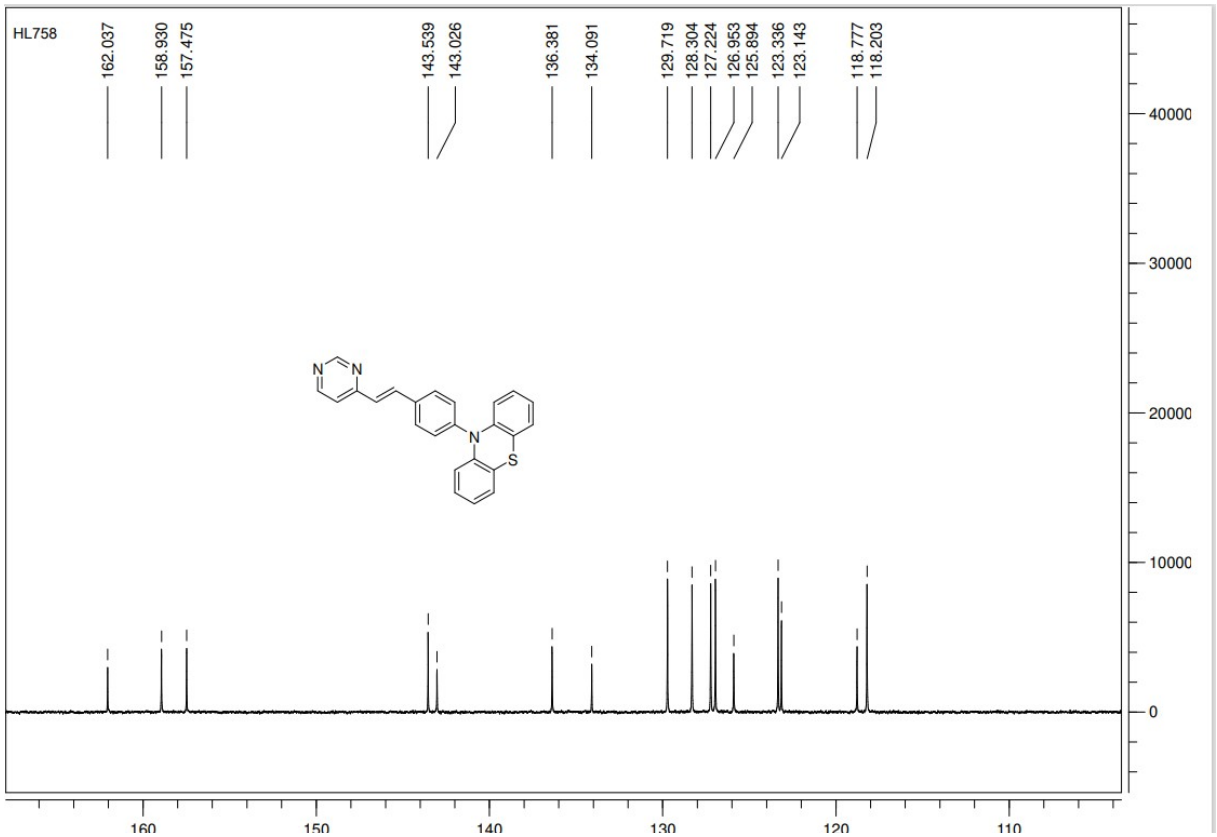

Figure S15: ^{13}C nmr spectrum (75 MHz) of **3** in $CDCl_3$