ELECTRONIC SUPPLEMENTARY INFORMATION

Photophysical characterization of Tröger's base molecular scaffolds: A combined theoretical and experimental study

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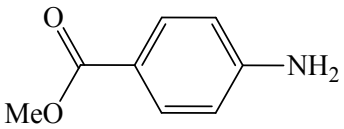
Summary

1. Synthesis



methyl 4-aminobenzoate

Precursor 1c. 4-aminobenzoic acid (2.0 g, 14.58 mmol) was dissolved in methanol (30 ml). Concentrated sulfuric acid (1.4 ml) was added dropwise. The mixture was heated to reflux for 36 h. Methanol was removed in a rotary evaporator and water (10 ml) was added to the mixture. The pH was adjusted to 3 with a 2M NaOH solution. The precipitated formed was filtered and washed with distilled water. **(1c)**: Isolated yield: 1.87 g (85%). FTIR (KBr, cm^{-1}): 3420, 3351, 3227, 2975, 2938, 1688, 1637, 1600, 1516, 1435, 1289, 1176, 1120. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.85 (d, J = 8.79 Hz, 2H), 6.63 (d, J = 8.79 Hz, 2H), 3.85 (s, 3H).

2. Spectroscopic characterization

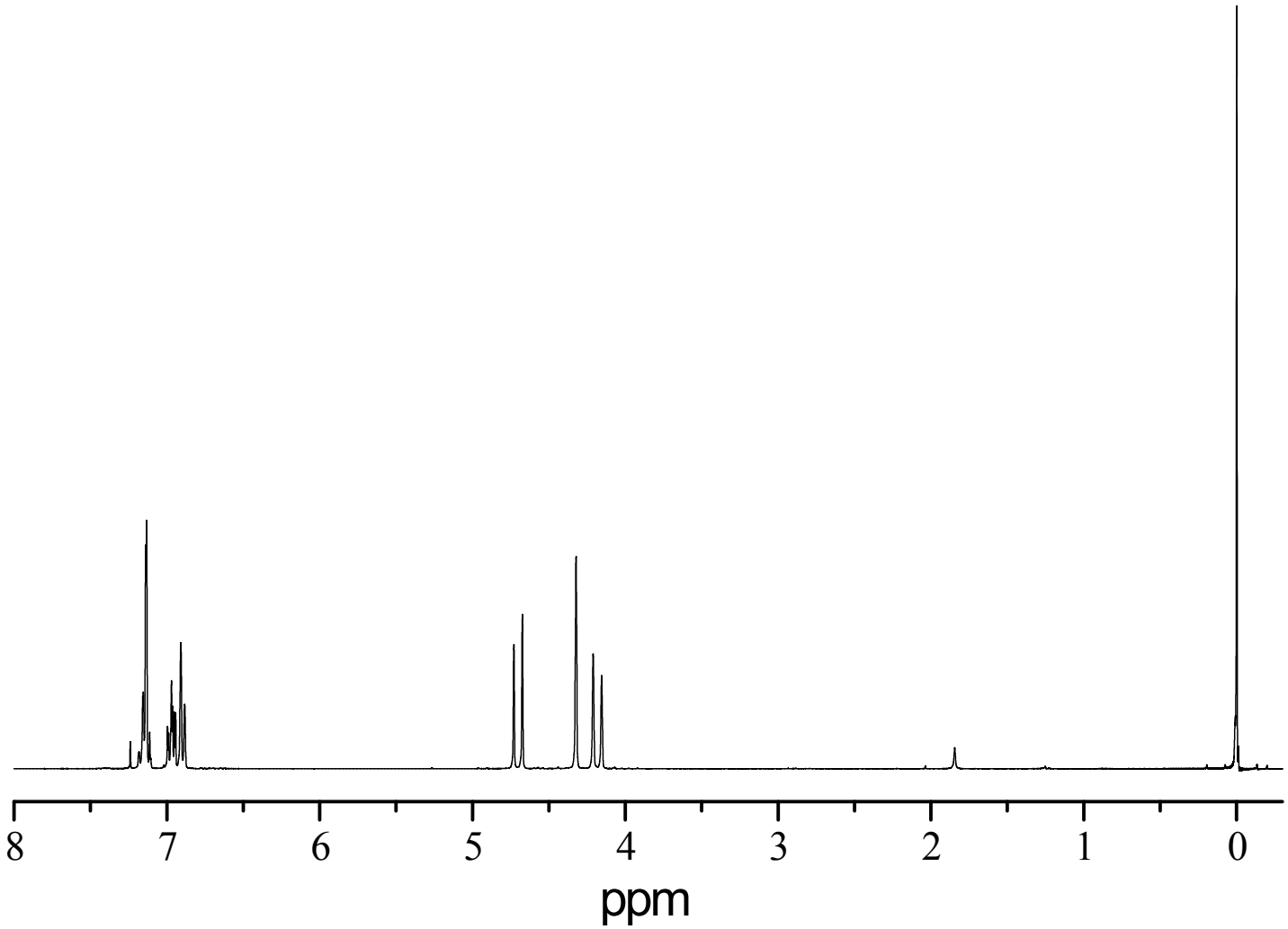


Fig. ESI1 ^{1}H NMR spectra of **2a** in $CDCl_3$.

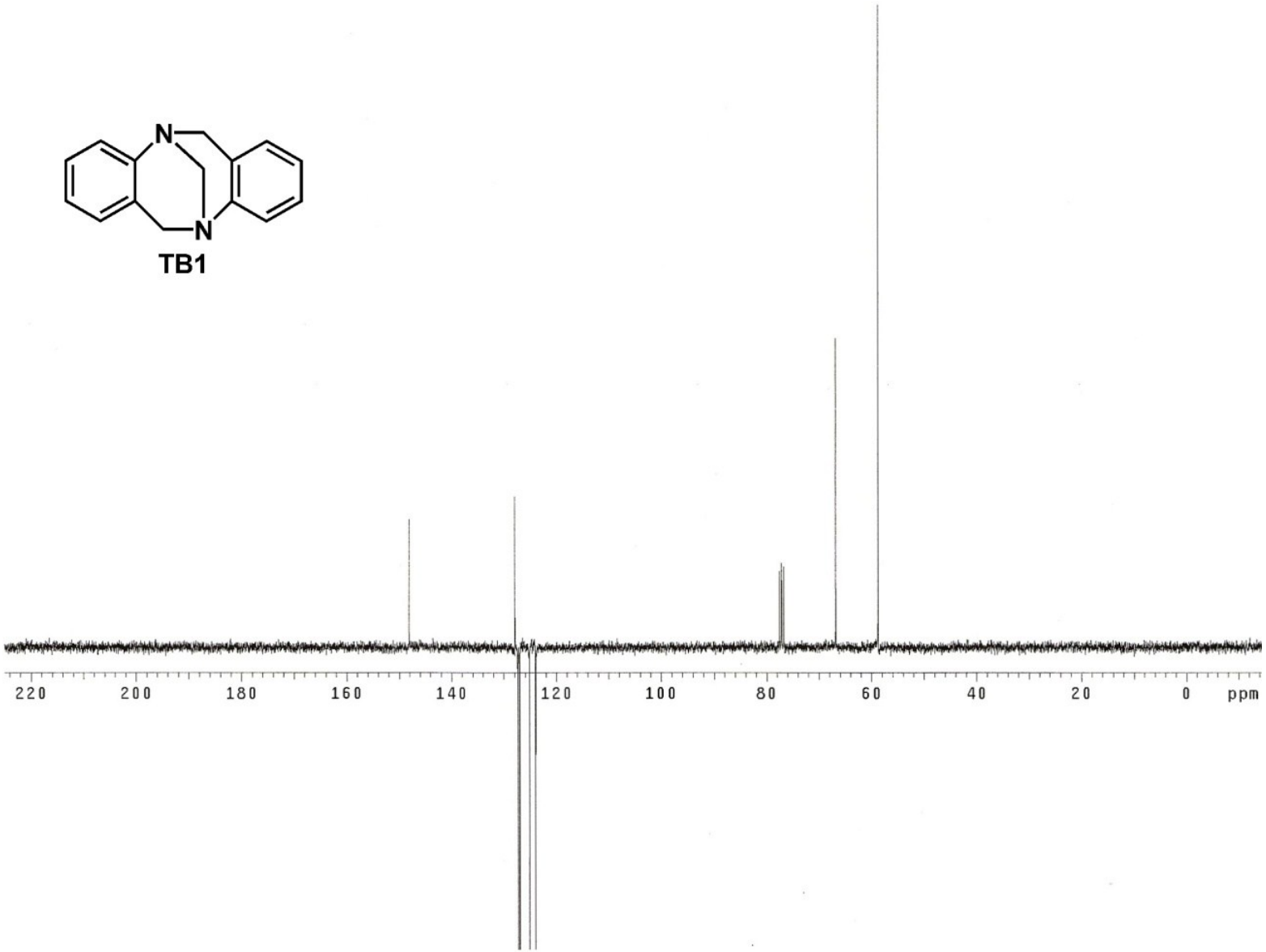


Fig. ESI2 ^{13}C NMR (APT) spectra of **2a** in $CDCl_3$.

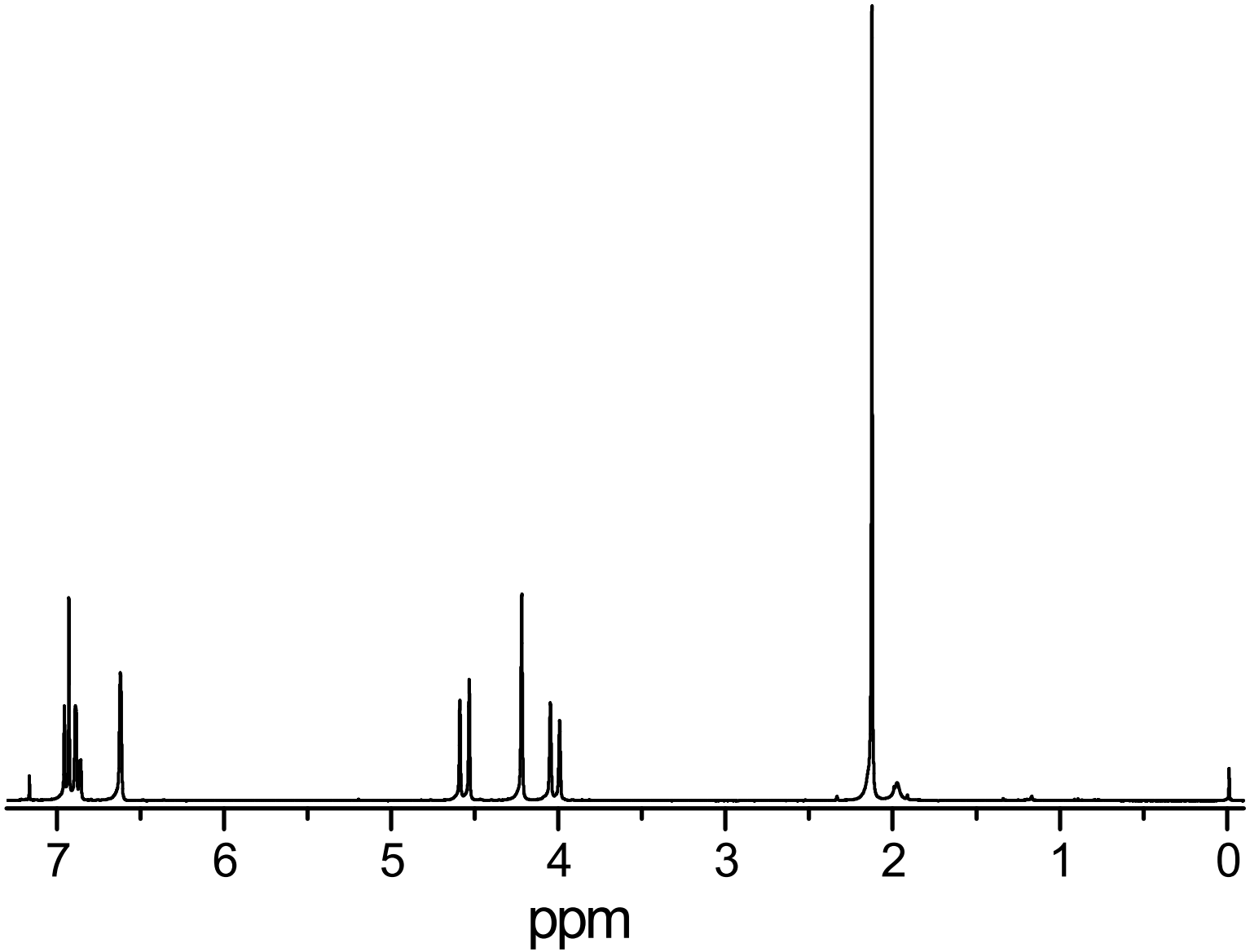


Fig. ESI3 ^{1}H NMR spectra of **2b** in $CDCl_3$.

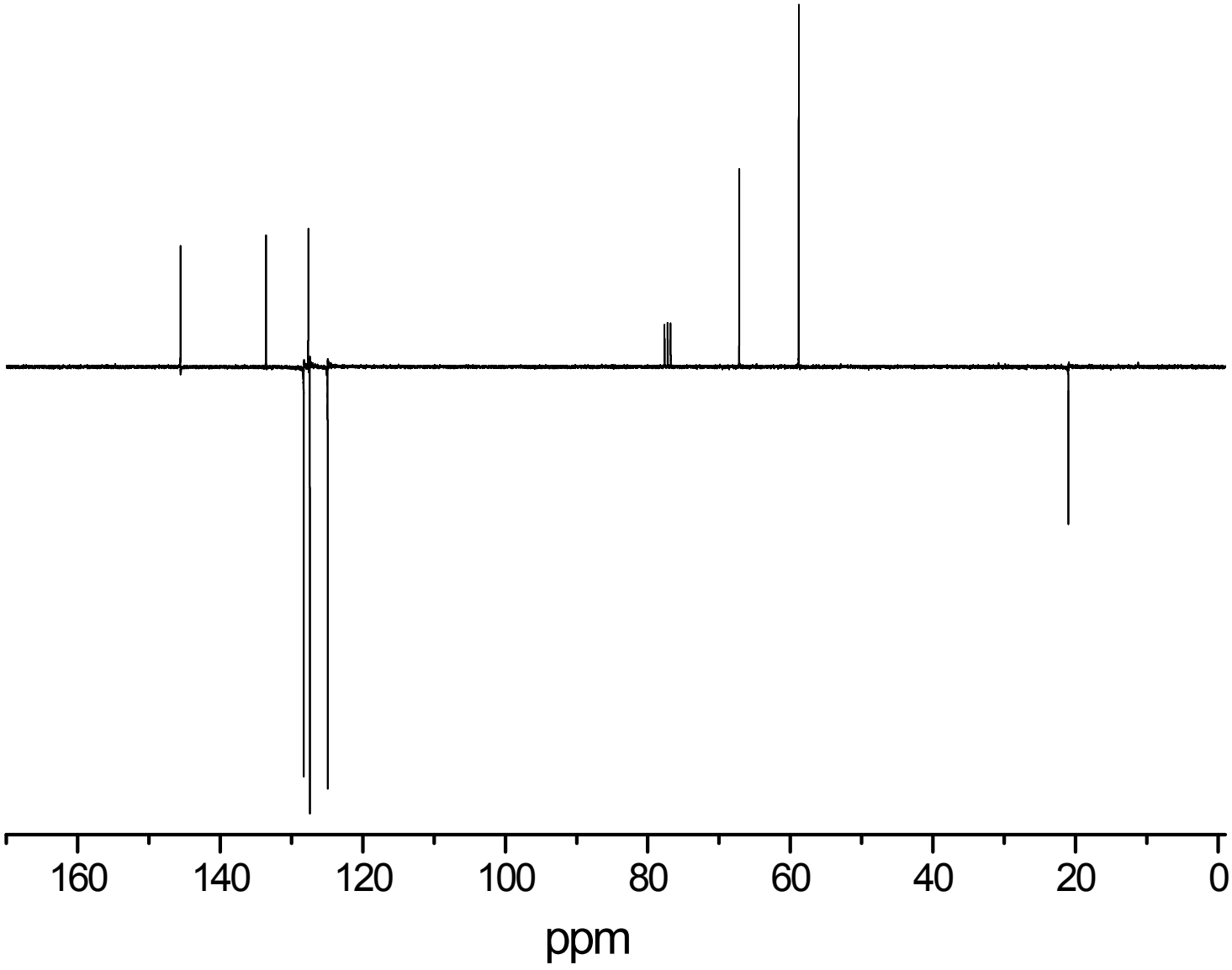


Fig. ESI4 ^{13}C NMR (APT) spectra of **2b** in $CDCl_3$.

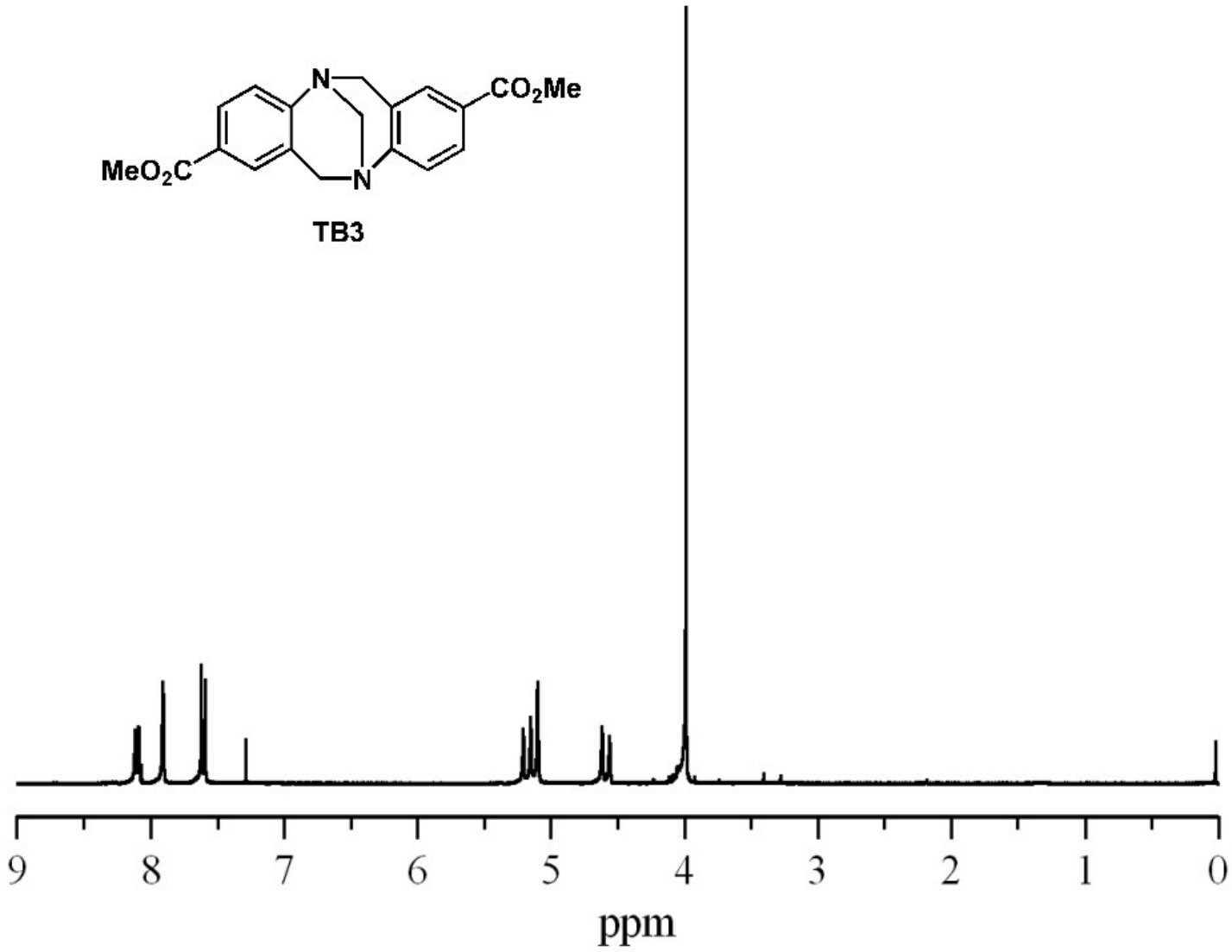


Fig. ESI5 ^{1}H NMR spectra of **2c** in $CDCl_3$.

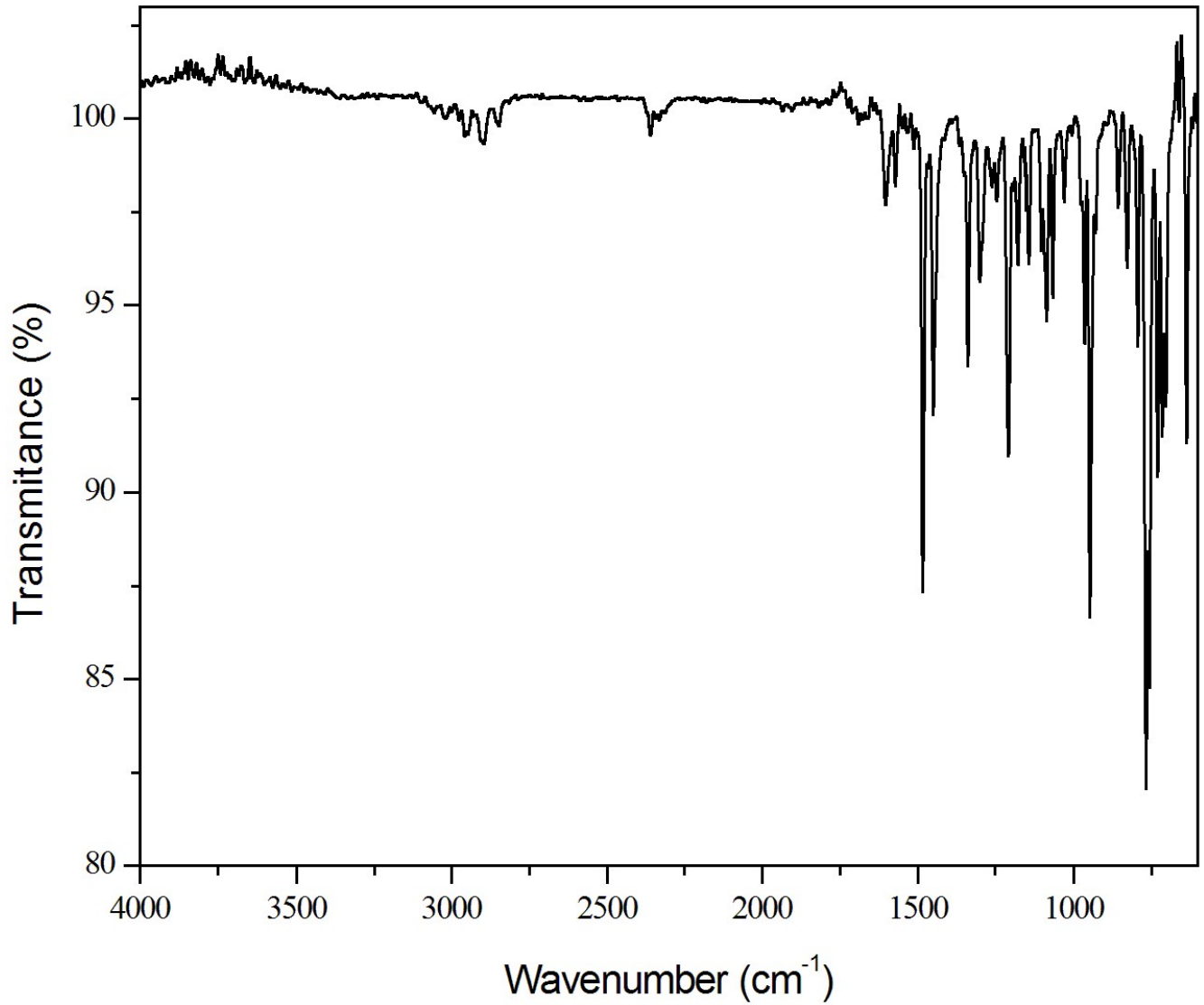


Fig. ESI6 FTIR spectra of **2a**.

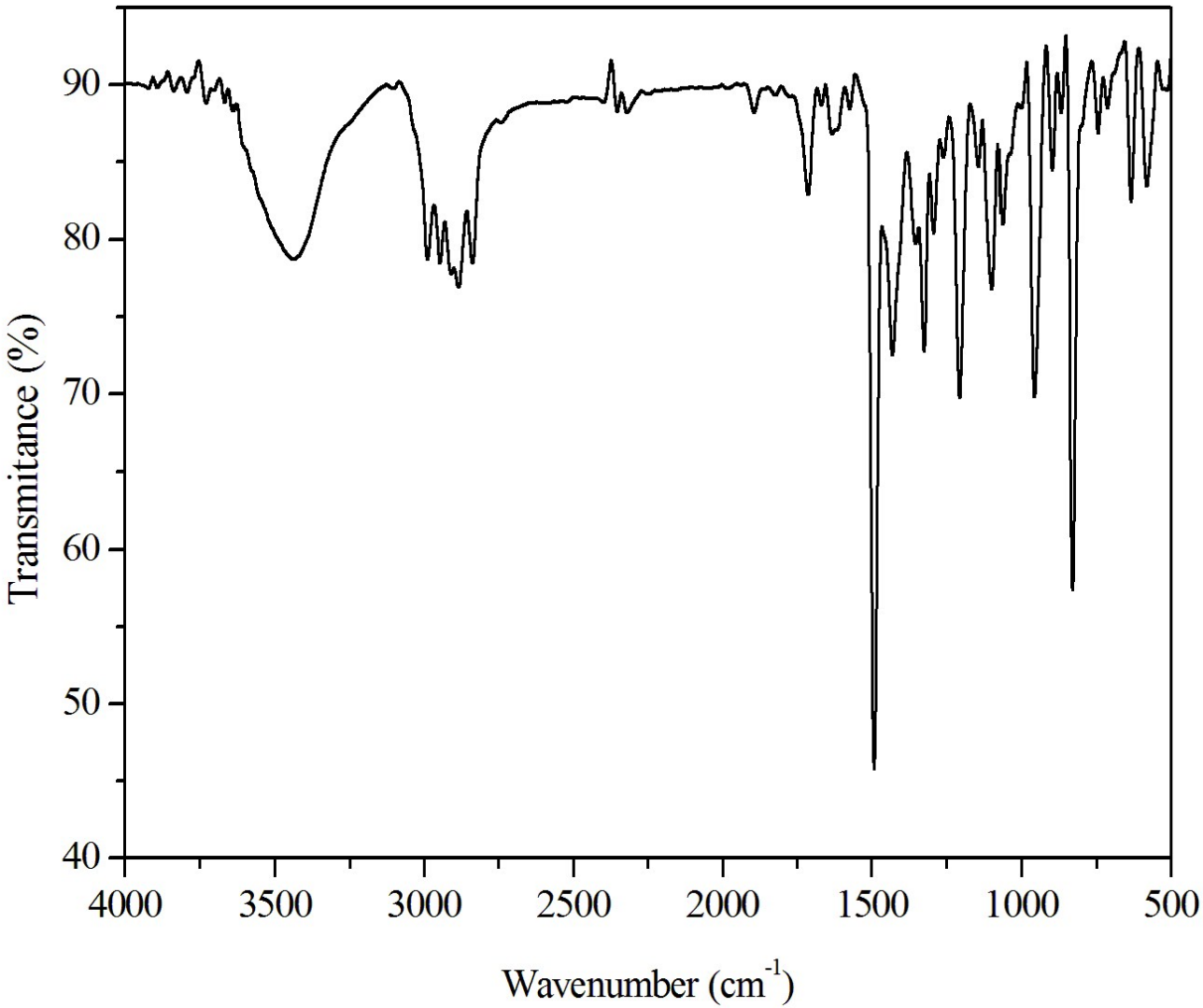


Fig. ESI7 FTIR spectra of **2b**.

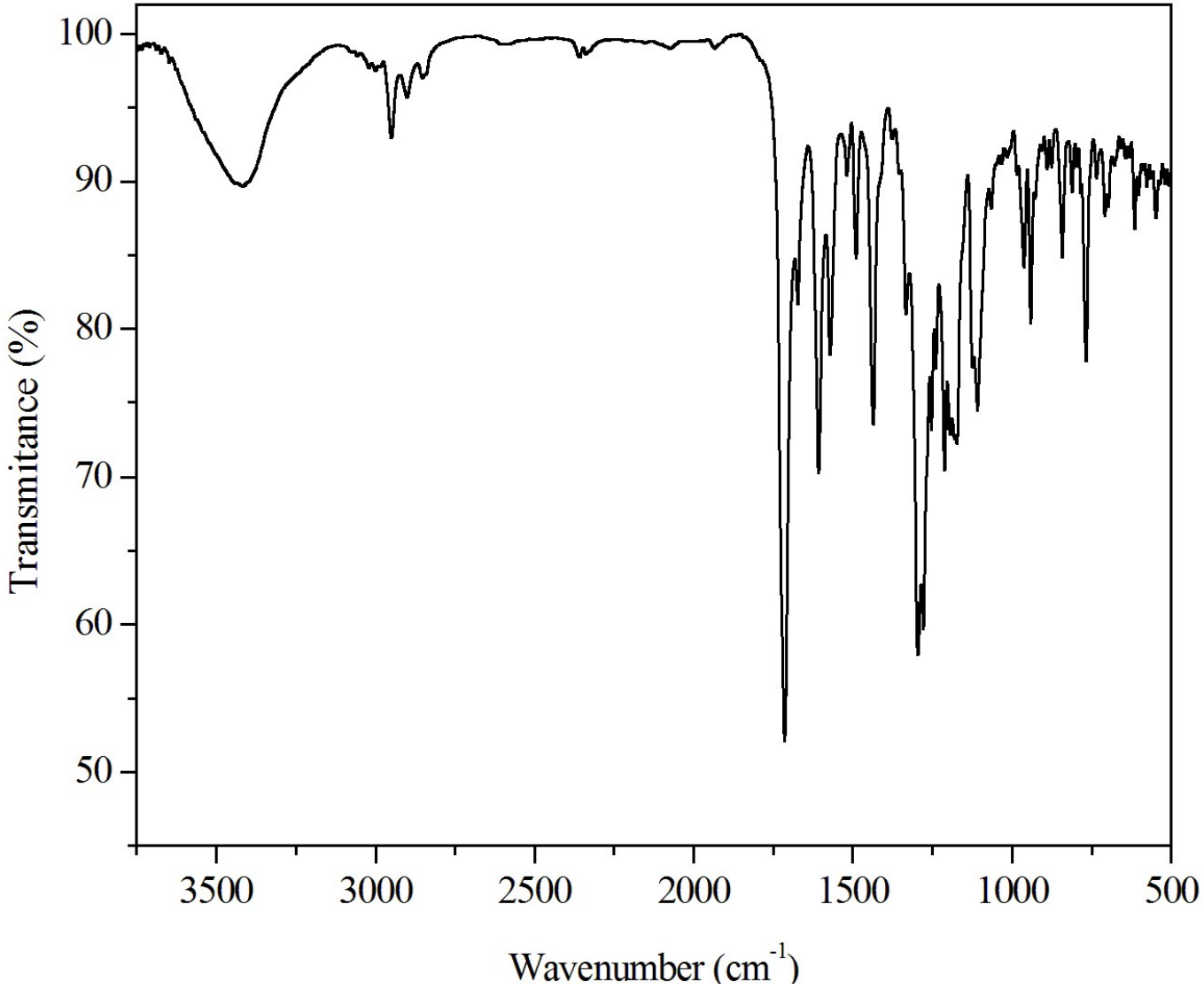


Fig. ESI8 FTIR spectra of **2c**.

3. Fluorescence lifetime data

Table ESI1. Relevant data from the time resolved fluorescence spectroscopy from TBs **2a-c**, where λ_{em} is the analyzed emission wavelength, EPLED is the excitation source in nanometers, A is the offset, B is the pre-exponential factor, τ is the fluorescence lifetime, Rel. is relative contribution and χ^2 is the chi-square of the fit.

TB	Solvent	λ_{em} (nm)	EPLED (nm)	A	B_1	Std. Dev.	τ_1 (ns)	Std. Dev.	Rel. %	χ^2
2a	1,4-dioxane	345	310	33.68	1778	12.08	1.467	8.678E-12	100	1.187
	Acetonitrile	349		49.17	2924	15.24	1.508	6.780E-12	100	1.151
2b	1,4-dioxane	344		47.38	700.7	7.417	1.804	1.836E-11	100	1.178
	Acetonitrile	345		43.09	665.6	9.025	1.152	1.443E-11	100	1.223
2c	1,4-dioxane	432		87.46	1775	12.75	1.420	9.260E-12	100	1.065
	Acetonitrile	450		118.7	384.4	6.398	1.868	3.548E-11	100	1.033

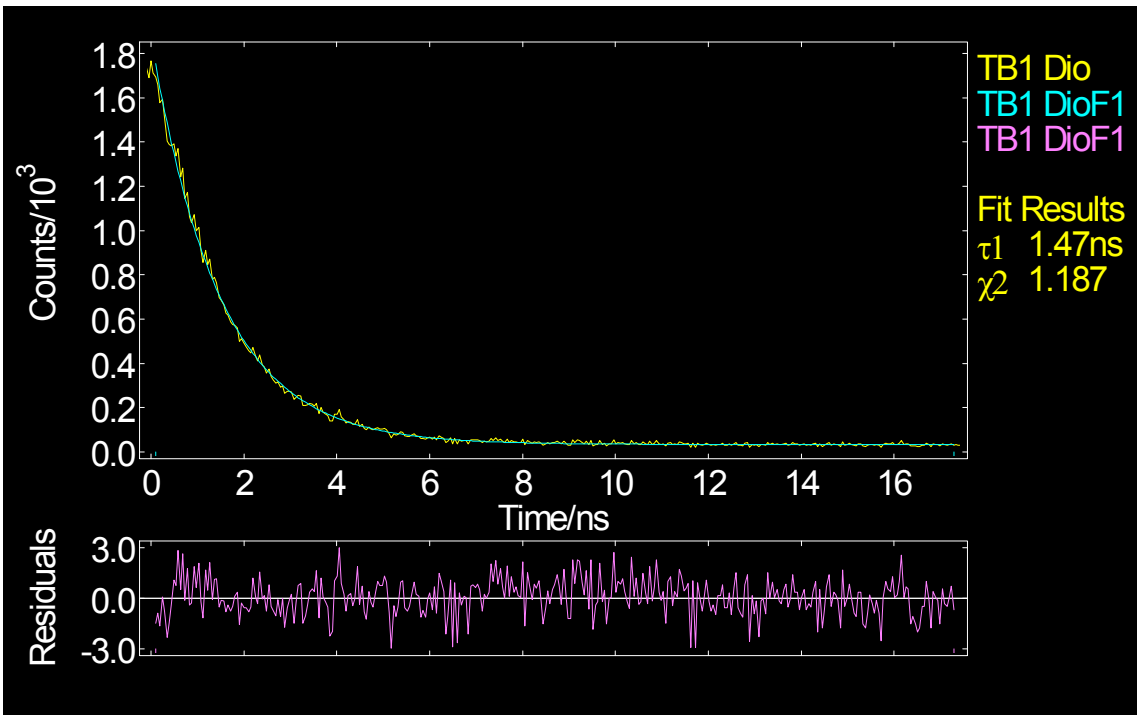


Fig. ESI9 Fit results of the TB **2a** in 1,4-dioxane @345 nm EPLED 310 nm. Fluorescence decay curves (yellow) and the single exponential function fits (cyan). The residuals are also presented (magenta).

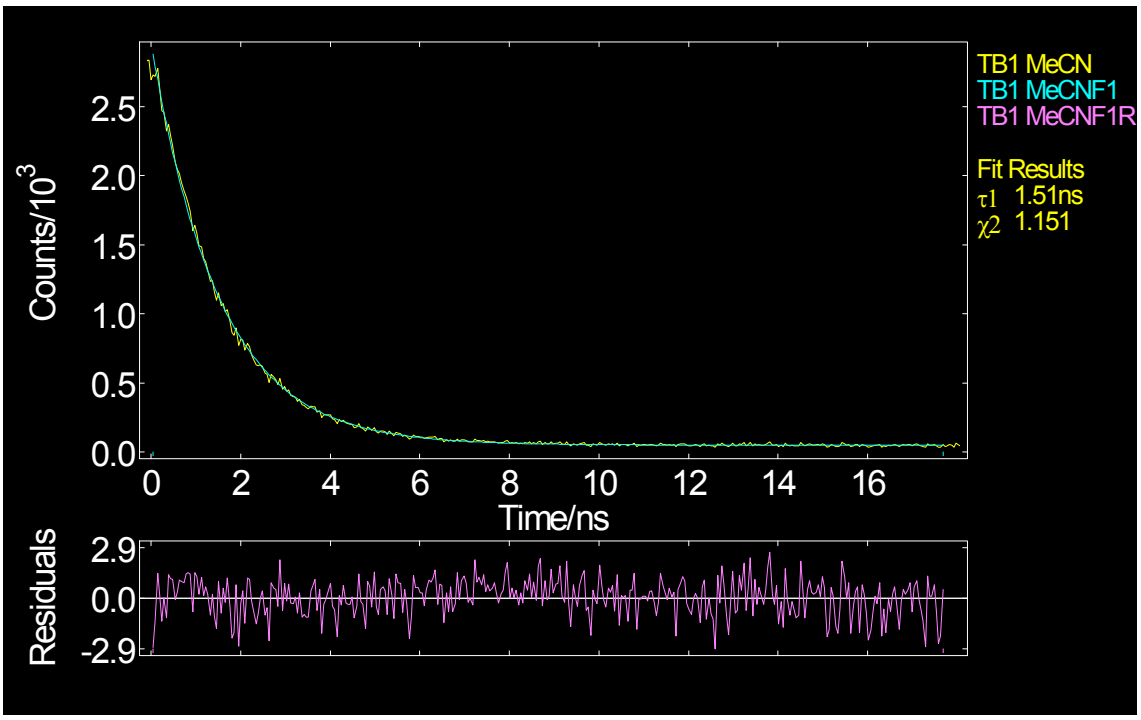


Fig. ESI10 Fit results of the TB **2a** in acetonitrile @349 nm EPLED 310 nm. Fluorescence decay curves (yellow) and the single exponential function fits (cyan). The residuals are also presented (magenta).

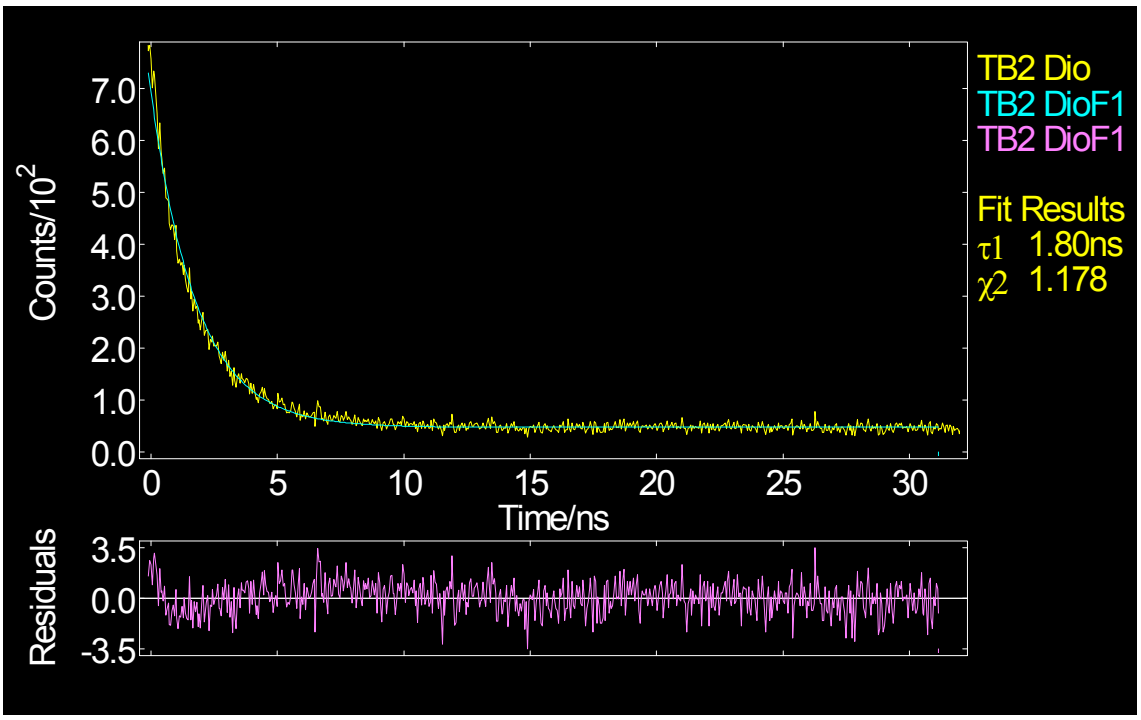


Fig. ESI11 Fit results of the TB **2b** in 1,4-dioxane @344 nm EPLED 310 nm. Fluorescence decay curves (yellow) and the single exponential function fits (cyan). The residuals are also presented (magenta).

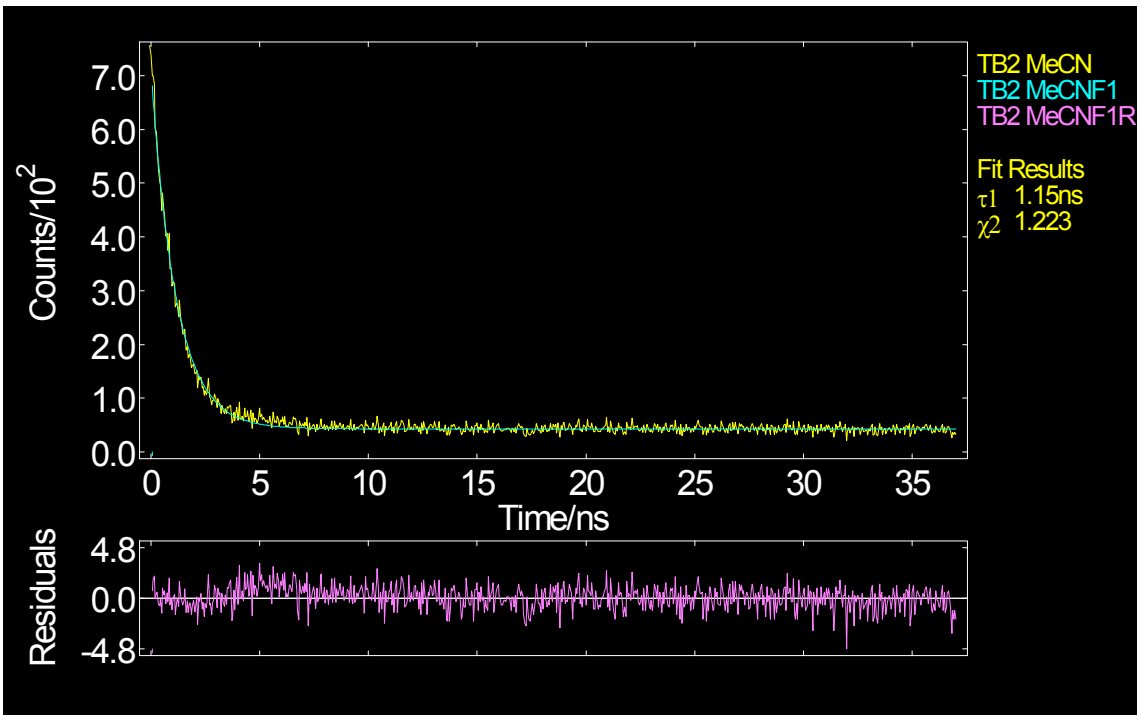


Fig. ESI12 Fit results of the TB **2b** in acetonitrile @345 nm EPLED 310 nm. Fluorescence decay curves (yellow) and the single exponential function fits (cyan). The residuals are also presented (magenta).

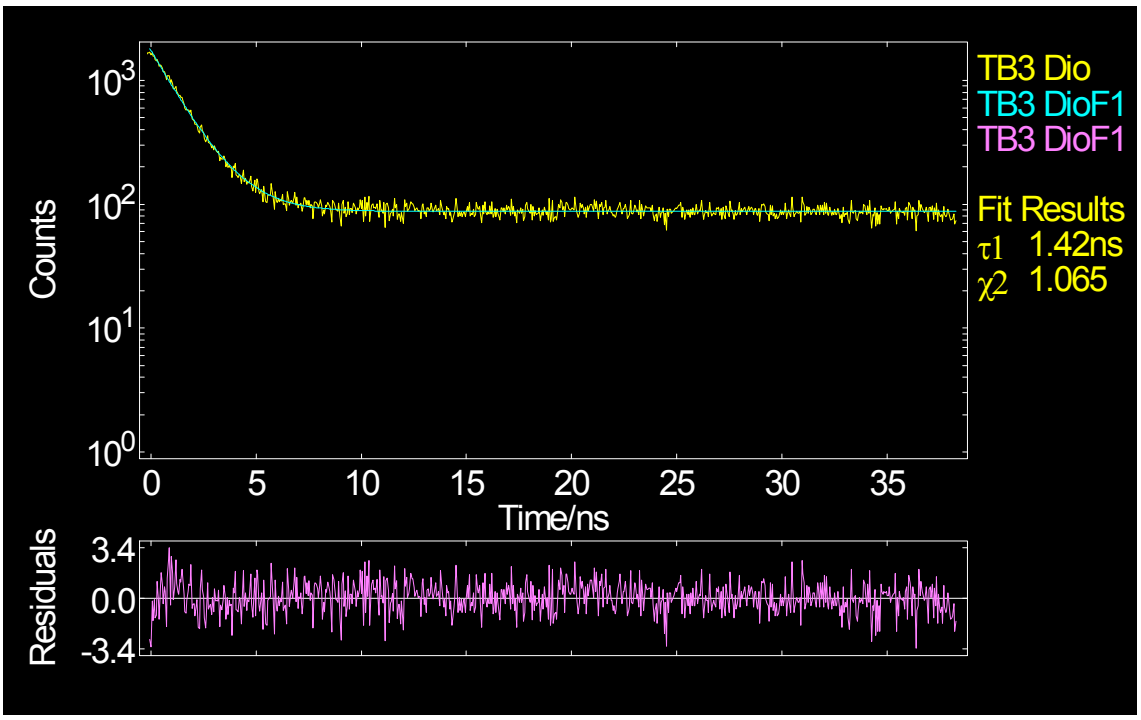


Fig. ESI13 Fit results of the TB **2c** in 1,4-dioxane @432 nm EPLED 310 nm. Fluorescence decay curves (yellow) and the single exponential function fits (cyan). The residuals are also presented (magenta).

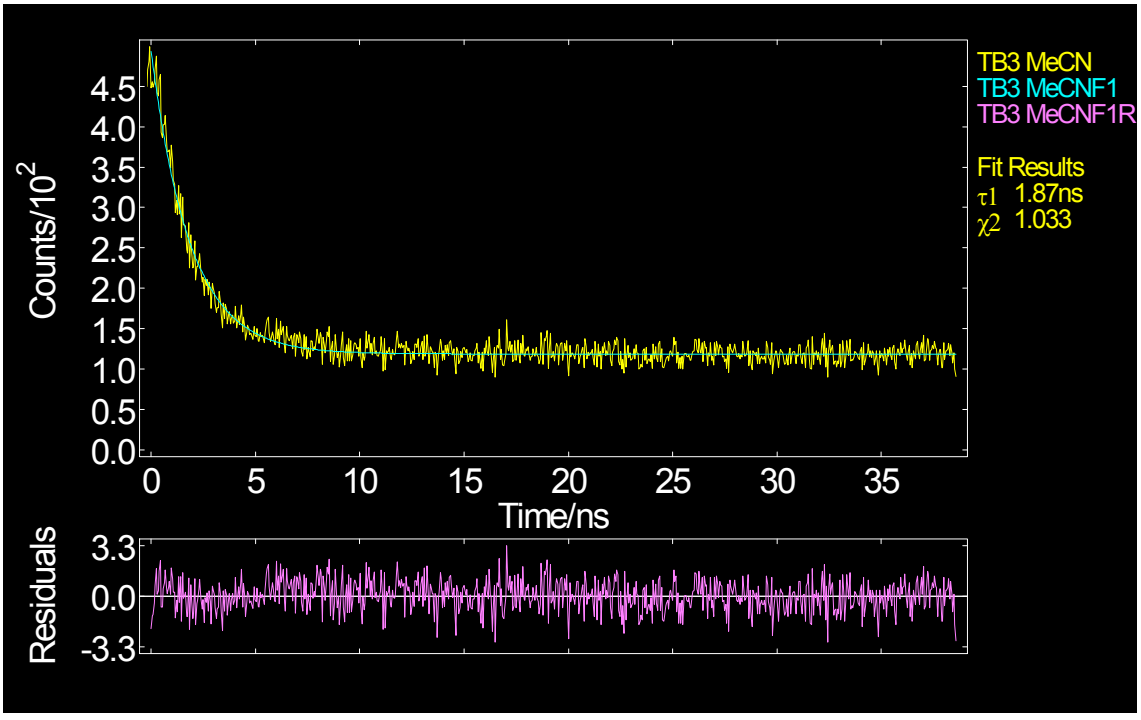


Fig. ESI14 Fit results of the TB **2c** in acetonitrile @450 nm EPLED 310 nm. Fluorescence decay curves (yellow) and the single exponential function fits (cyan). The residuals are also presented (magenta).

4. Lippert-Mataga Data

Table ESI2. Parameters for the linear regression (Y = A + BX) from the *Lippert-Mataga* plot.

TB	Plot	Parameters				
		A	*Error*	*B*	*Error*	*R*
1	ν_A vs. Δf	34413.520	127.41513	2281.599	475.23538	0.876
	ν_F vs. Δf	29358.861	109.67582	-2635.320	409.07095	-0.925
	ν_A-ν_F vs. Δf	5054.670	133.122	4916.885	496.521	0.966
2	ν_A vs. Δf	34673.253	94.545	-929.570	357.8315	-0.676
	ν_F vs. Δf	29178.850	227.128	-2037.706	859.622	-0.642
	ν_A-ν_F vs. Δf	5494.399	291.596	1108.136	1103.617	0.334
3	ν_A vs. Δf	26769.075	152.81729	198.451	596.56222	0.117
	ν_F vs. Δf	25726.031	81.68957	-10316.436	318.89658	-0.997
	ν_A-ν_F vs. Δf	1043.045	179.963	10514.887	702.534	0.983

Table ESI3. Calculated Onsager's radio to the TB's **2a-c**.

	Gas phase (S_0)		
Tröger's base	**TB1**	**TB2**	**TB3**
Onsager cavity radius (Å)	4.94	5.14	5.41

5. Theoretical calculations

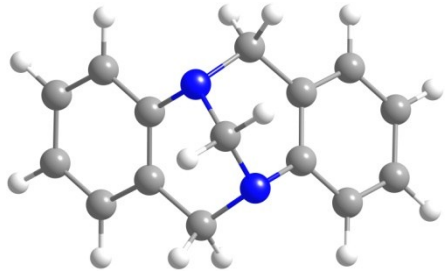
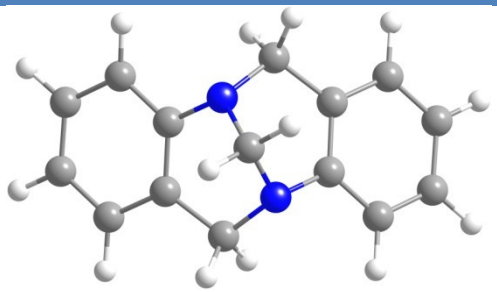
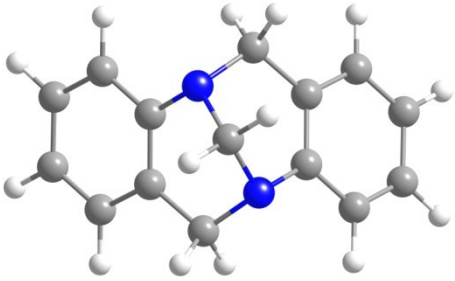
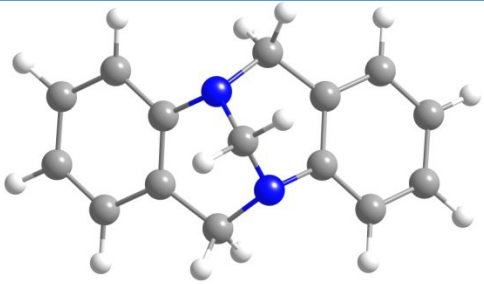
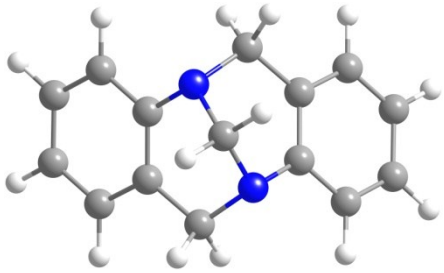
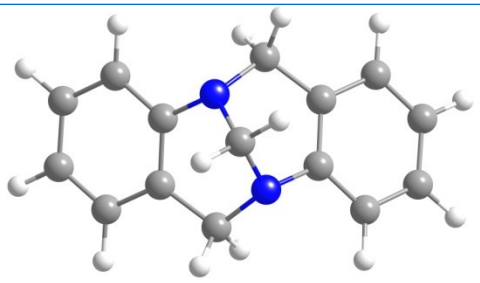
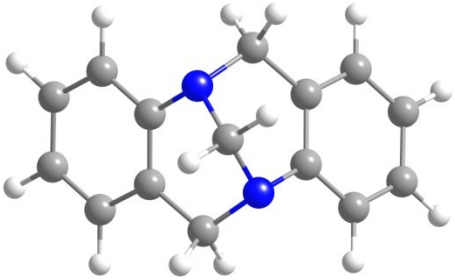
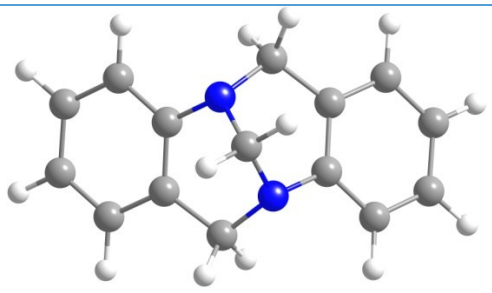
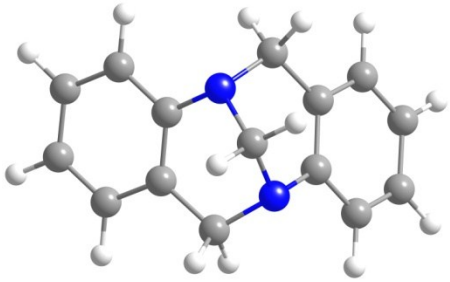
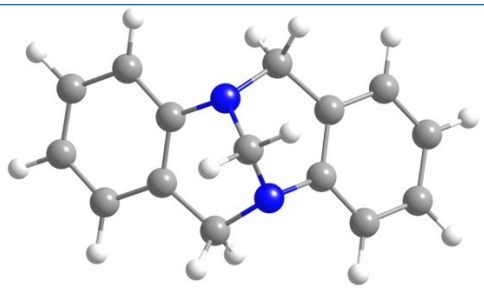
Solvent	Ground state	Excited state
Acetonitrile		
Dichloromethane		
1,4-Dioxane		
Ethyl acetate		
Ethanol		

Fig. ESI15 Representative equilibrium structures (front view) of **2a** in different organic solvents in the ground (left) and excited state (right).

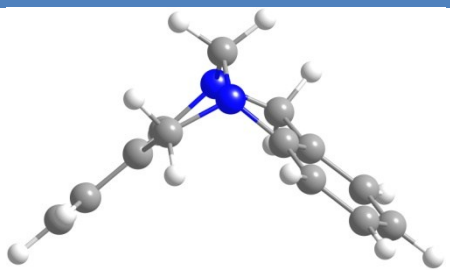
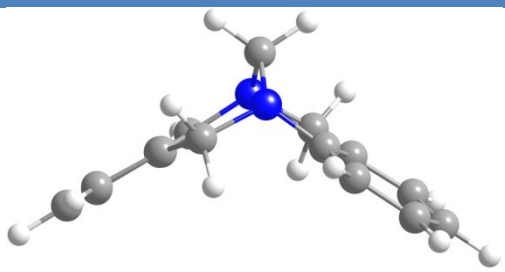
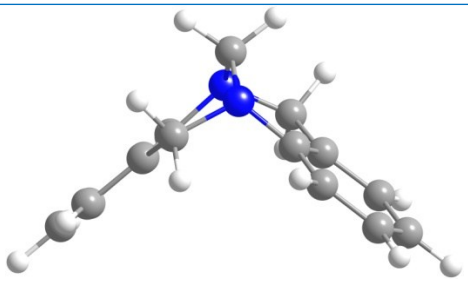
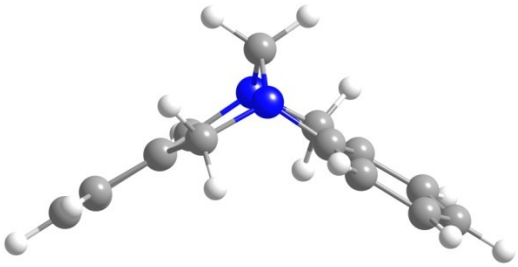
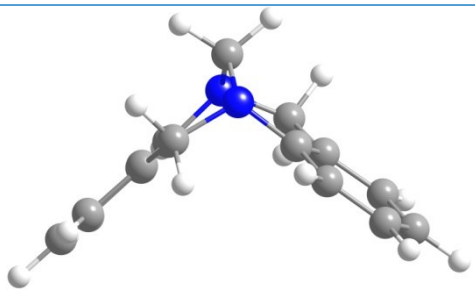
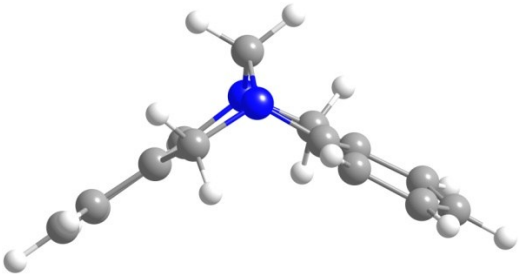
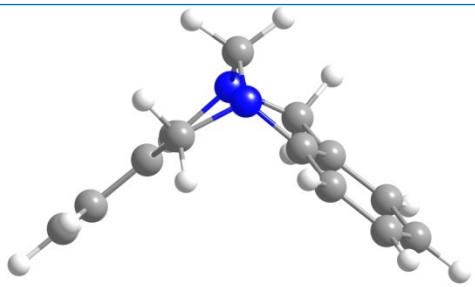
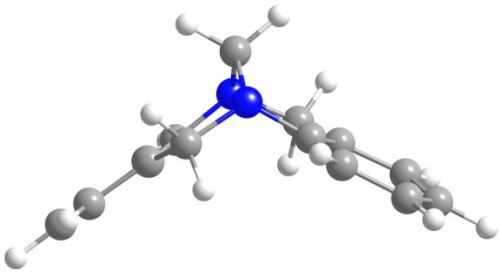
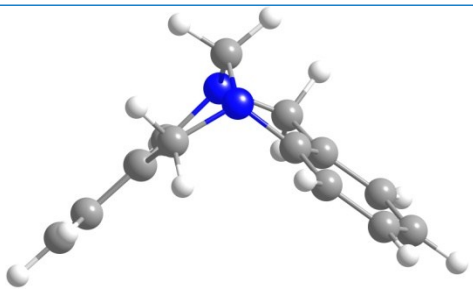
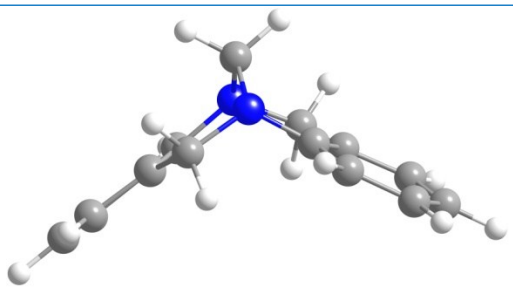
Solvent	Ground state	Excited state
Acetonitrile		
Dichloromethane		
1,4-Dioxane		
Ethyl acetate		
Ethanol		

Fig. ESI16 Representative equilibrium structures (lateral view) of **2a** in different organic solvents in the ground (left) and excited state (right).

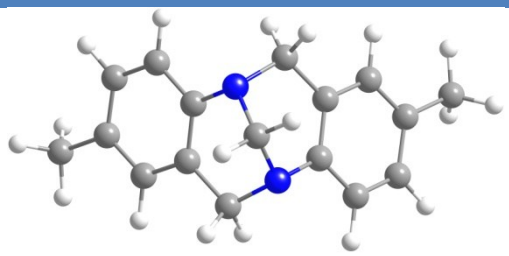
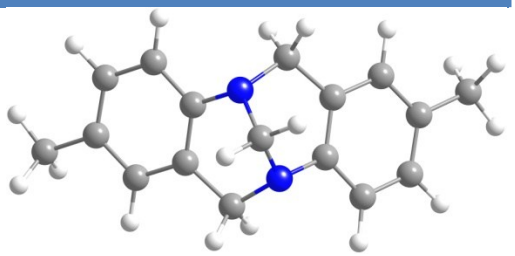
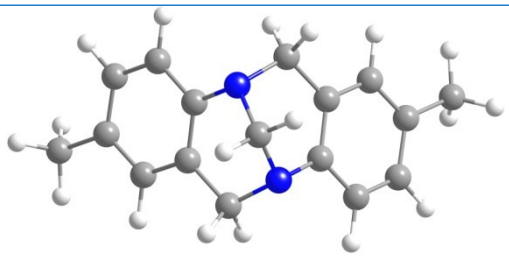
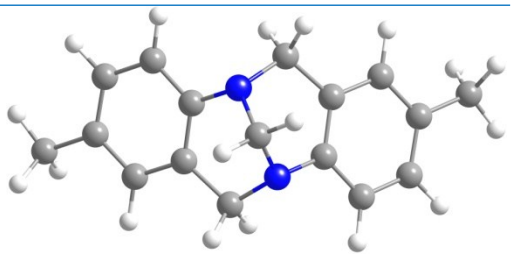
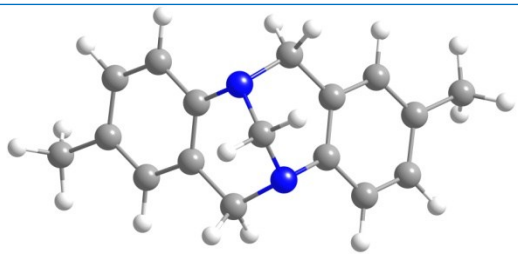
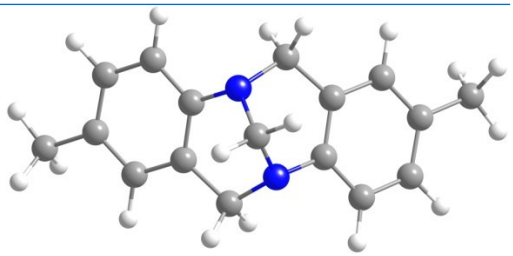
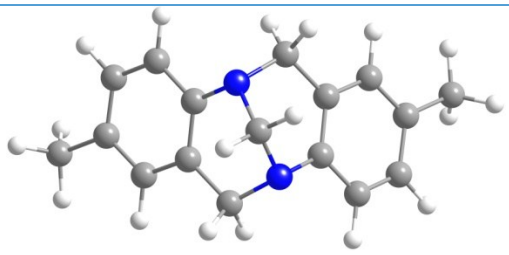
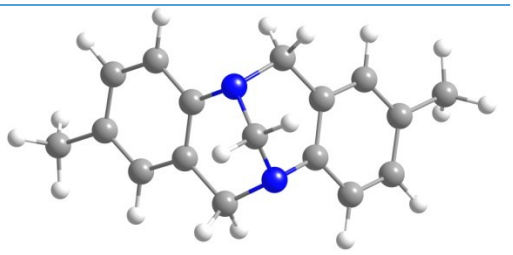
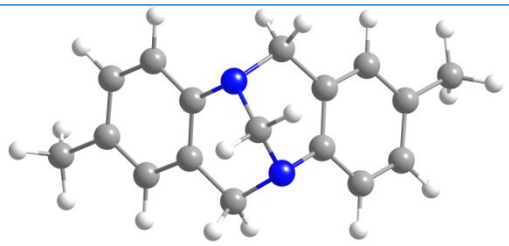
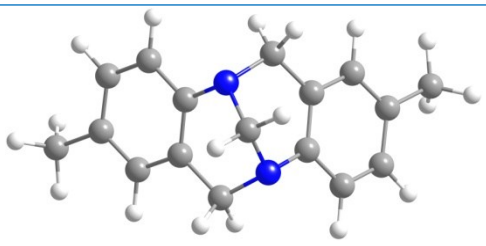
Solvent	Ground state	Excited state
Acetonitrile		
Dichloromethane		
1,4-Dioxane		
Ethyl acetate		
Ethanol		

Fig. ESI17 Representative equilibrium structures (front view) of **2b** in different organic solvents in the ground (left) and excited state (right).

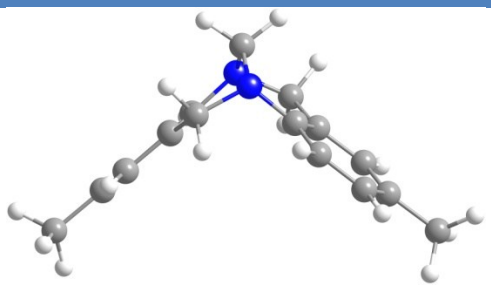
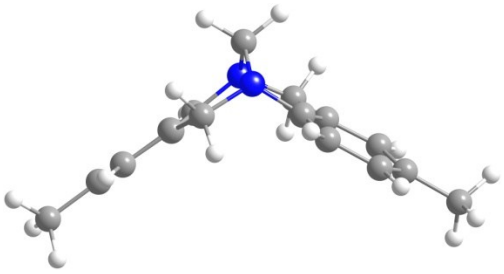
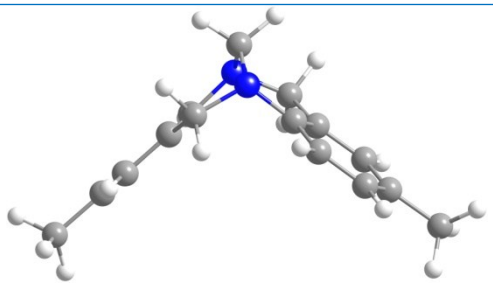
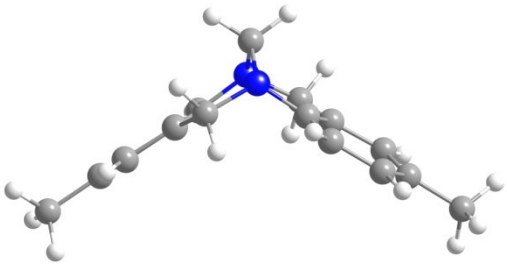
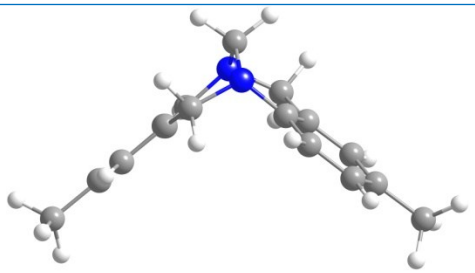
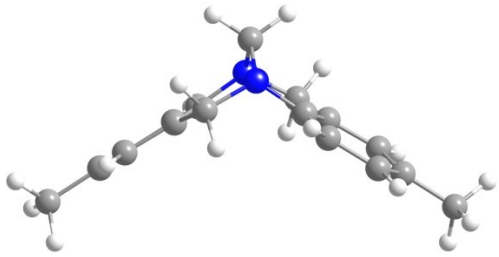
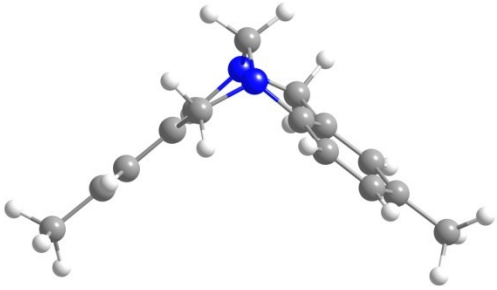
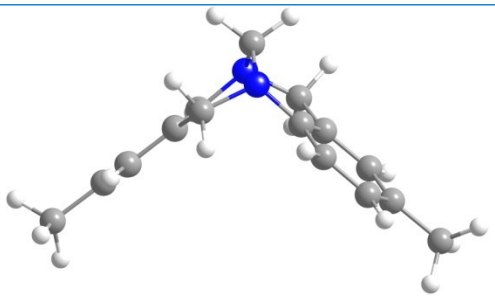
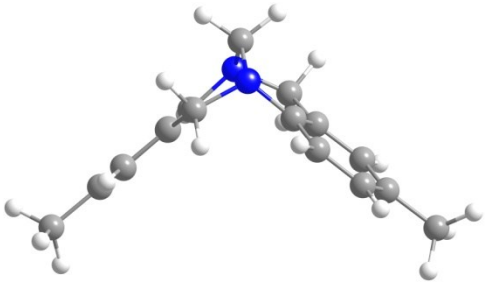
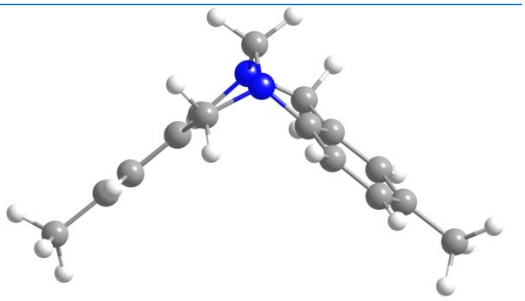
Solvent	Ground state	Excited state
Acetonitrile		
Dichloromethane		
1,4-Dioxane		
Ethyl acetate		
Ethanol		

Fig. ESI18 Representative equilibrium structures (lateral view) of **2b** in different organic solvents in the ground (left) and excited state (right).

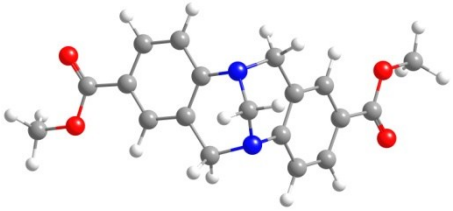
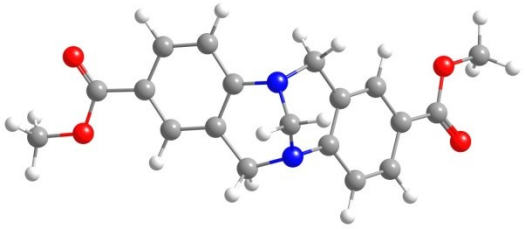
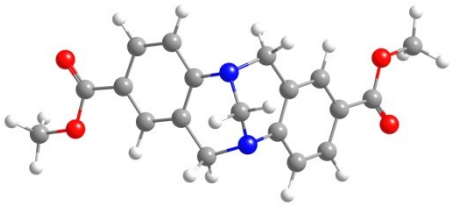
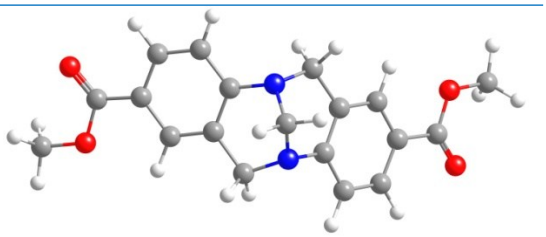
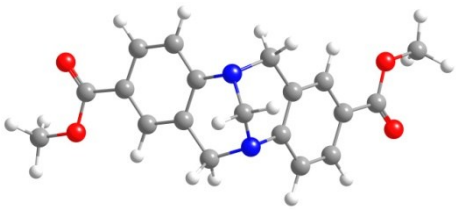
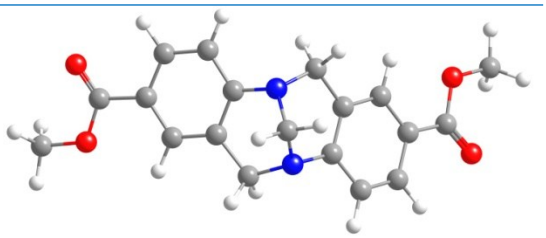
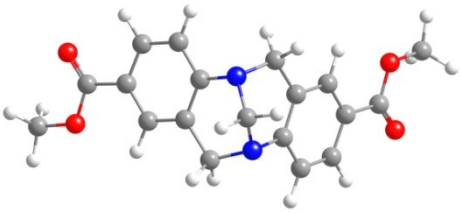
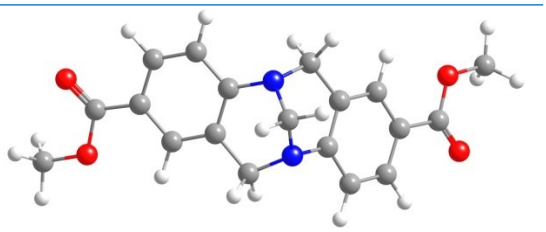
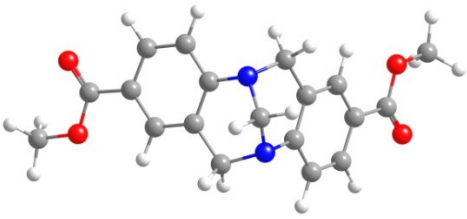
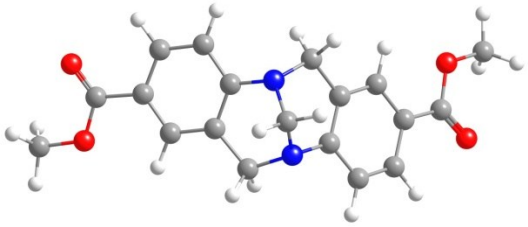
Solvent	Ground state	Excited state
Acetonitrile		
Dichloromethane		
1,4-Dioxane		
Ethyl acetate		
Ethanol		

Fig. ESI19 Representative equilibrium structures (front view) of **2c** in different organic solvents in the ground (left) and excited state (right).

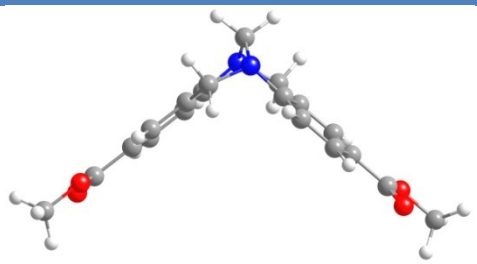
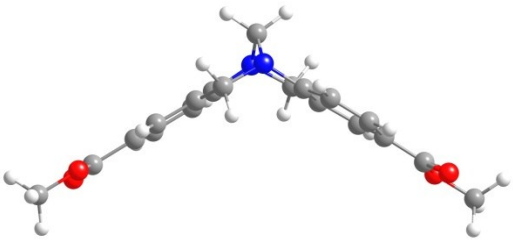
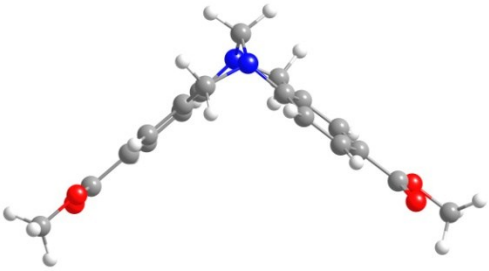
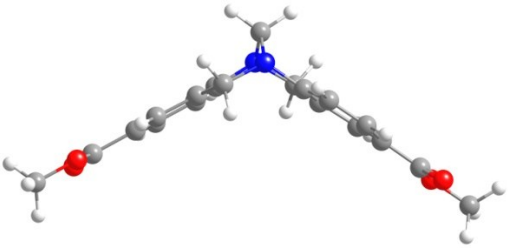
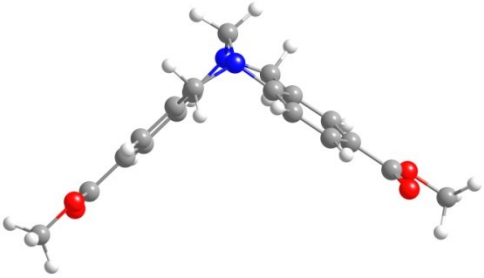
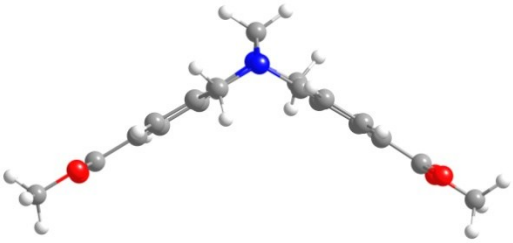
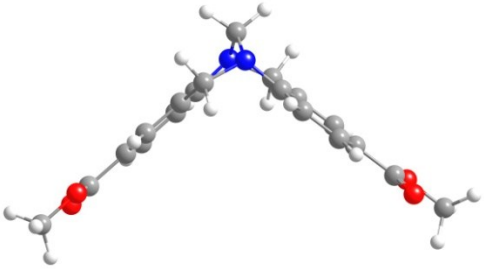
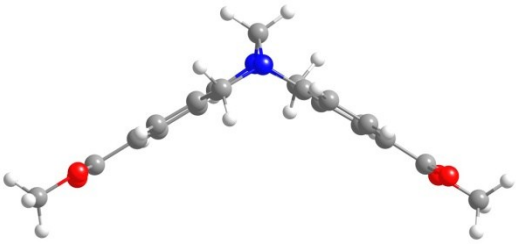
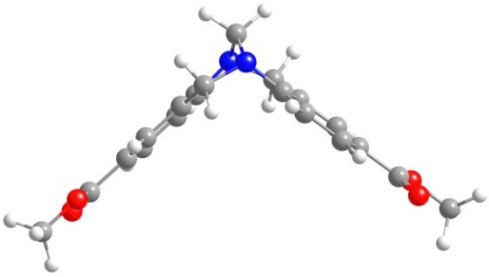
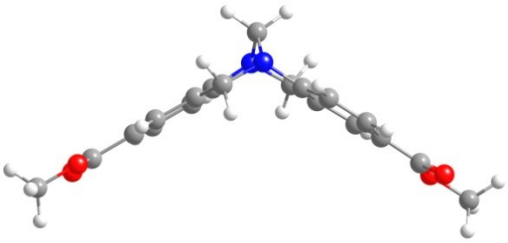
Solvent	Ground state	Excited state
Acetonitrile		
Dichloromethane		
1,4-Dioxane		
Ethyl acetate		
Ethanol		

Fig. ESI20 Representative equilibrium structures (lateral view) of **2c** in different organic solvents in the ground (left) and excited state (right).

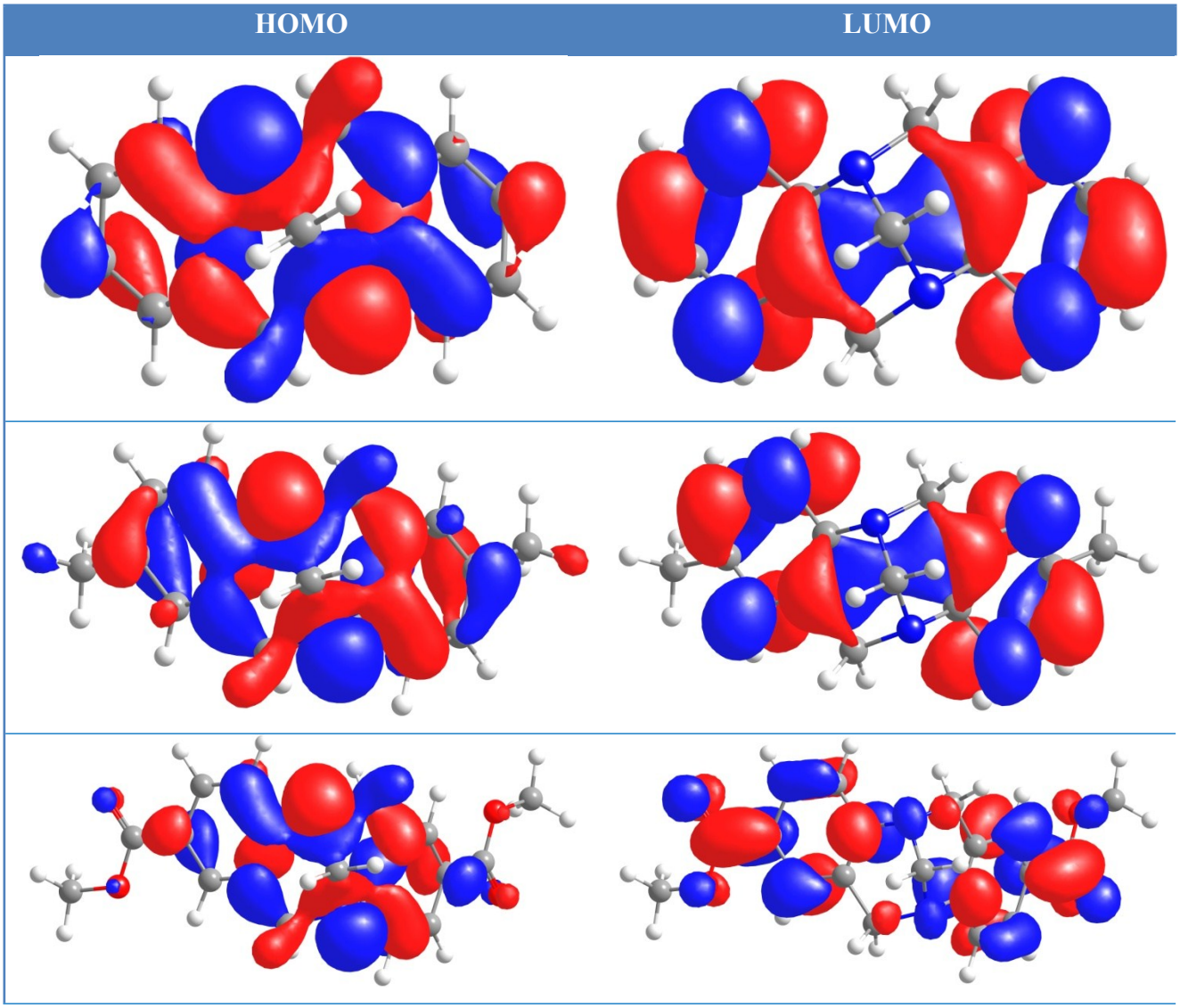


Fig. ESI21 Frontier orbitals of **2a** (top), **2b** (middle) and **2c** (bottom) calculated in ethyl acetate at PBE0/aug-cc-pVDZ//PBE0/cc-pVDZ level of theory.

Table ESI4. Populational analysis of **2a-c** HOMO and LUMO orbitals in gas phase.

TB	Orbital	Populational analysis
1	HOMO	+ 9.2% *5PZ(N5)* + 9.2% *5PZ(N11)* + 4.7% *6PZ(N5)* + 4.7% *6PZ(N11)* + 3.4% *5PX(N5)* + 3.4% *5PX(N11)*
	LUMO	+ 4.2% *5PY(C7)* + 4.2% *5PY(C1)* + 4.1% *6PY(C7)* + 4.1% *6PY(C1)* + 4.0% *5PY(C10)* + 4.0% *5PY(C4)*
2	HOMO	+ 8.6% 5PZ(N11) + 8.6% 5PZ(N5) + 4.5% 6PZ(N11) + 4.5% 6PZ(N5) + 3.2% 5PX(N5) + 3.2% 5PX(N11)
	LUMO	+ 4.4% 6PY(C7) + 4.4% 6PY(C1) + 4.2% 7PY(C7) + 4.2% 7PY(C1) + 4.1% 4S(C13) + 3.8% 5PY(C10)
3	HOMO	+ 11.1% 5PZ(N5) + 11.1% 5PZ(N11) + 5.4% 6PZ(N5) + 5.4% 6PZ(N11) - 2.7% 5PY(N5) + 2.7% 5PY(N11)
	LUMO	- 3.4% 5PY(C16) - 3.4% 5PY(C15) - 2.9% 5PY(C18) - 2.9% 5PY(C19) + 2.7% 5PY(C1) + 2.7% 5PY(C7)

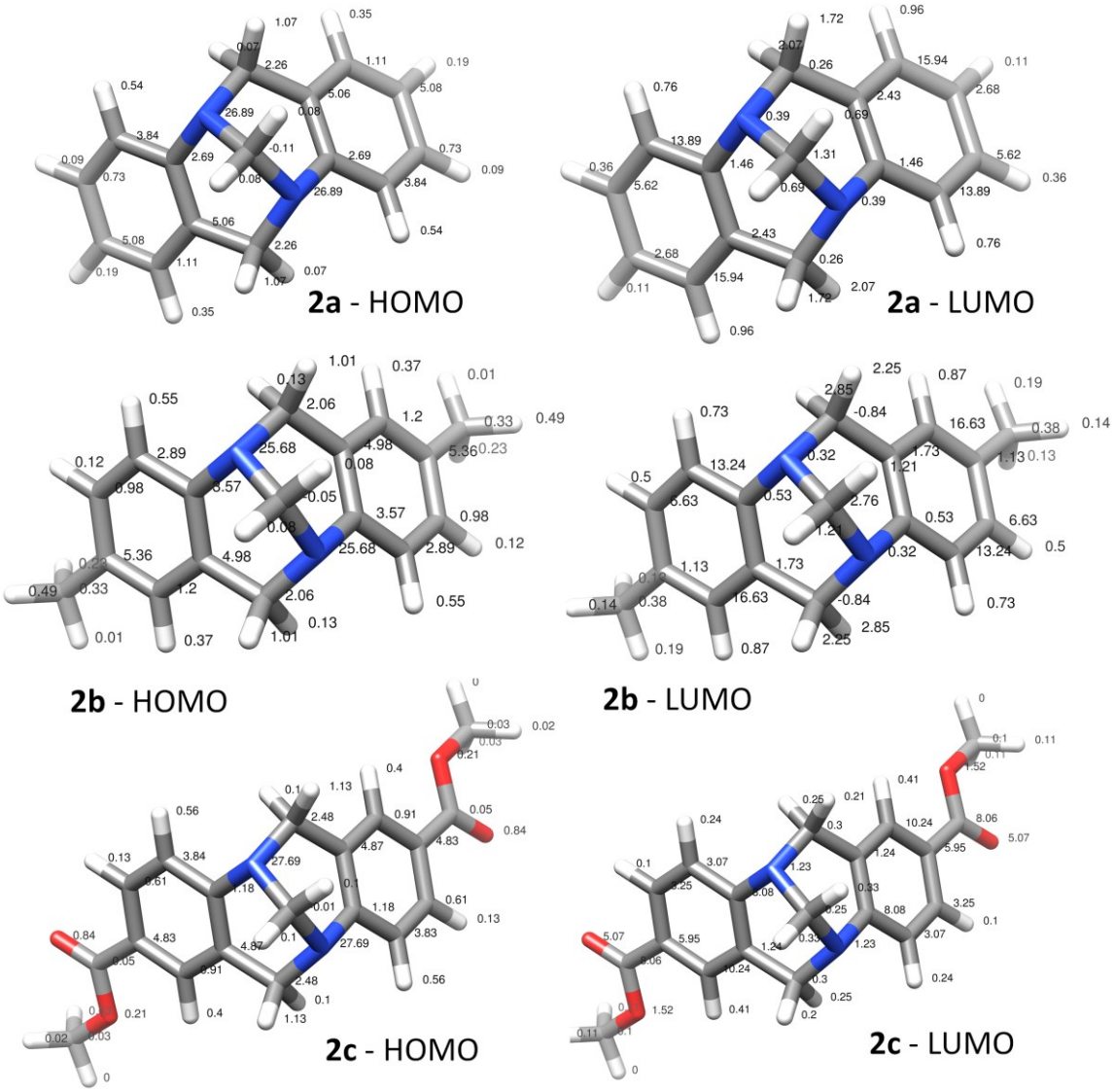


Fig. ESI22 Populational analysis of **2a-c** in gas phase calculated at PBE1PBE/aug-cc-pVDZ//PBE1PBE/cc-pVDZ level of theory.

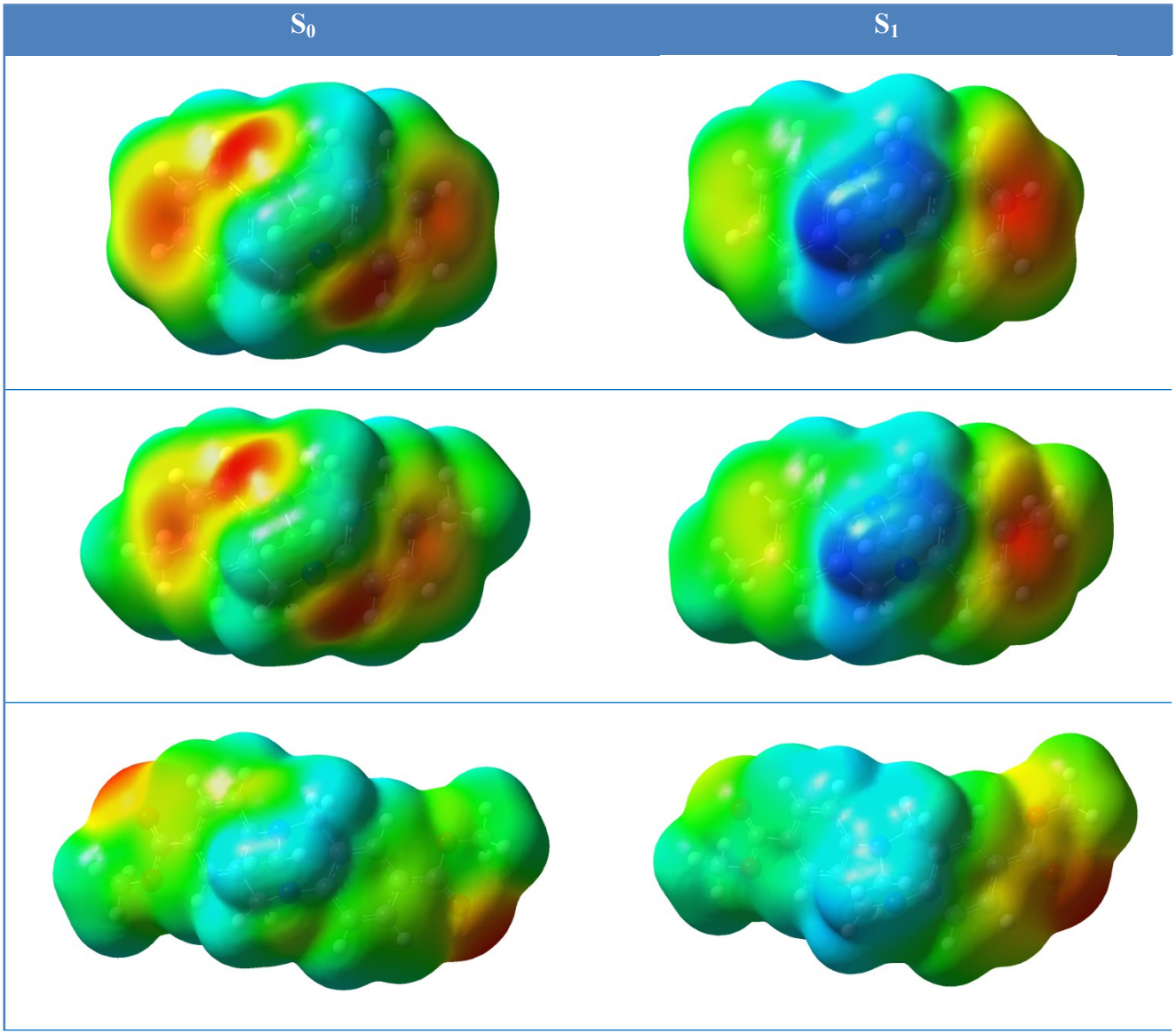


Fig. ESI23 Electrostatic potential surface of Tröger's base **2a** (top), **2b** (middle) and **2c** (bottom) in 1,4-dioxane in the ground electronic state (left) and first electronic excited state (right). The highest electron density potential is represented in red and the lowest electron density is represented in blue.