Supporting Information

for

Aggregation-induced emission and reversible mechanoresponsive behavior of boryl substituted phenothiazine

Weidong Zhang,* Juanfang Zhou, Chao Zhang, and Xinliang Liu*

School of Chemical Engineering, Qinghai University, Xining, 810016, China

E-mail address: zhangwd@qhu.edu.cn, and liuxl1219@163.com

Contents

1. The excitation and emission spectra

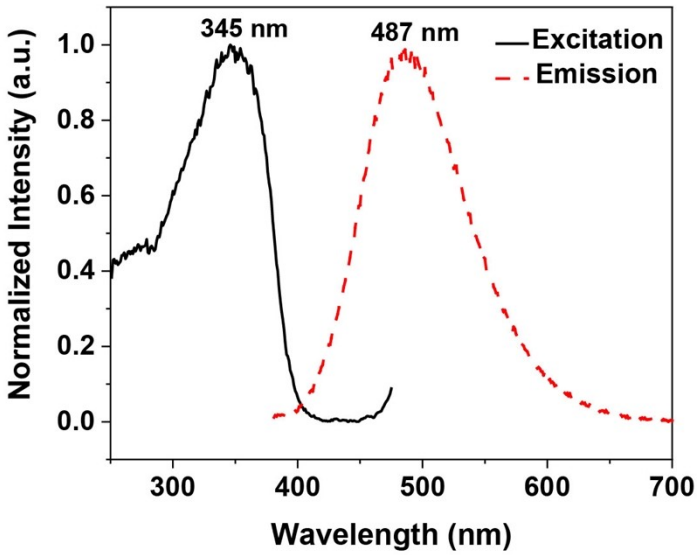


Figure S1. Fluorescence excitation (solid line) and emission spectra (dashed line) of **4a**.

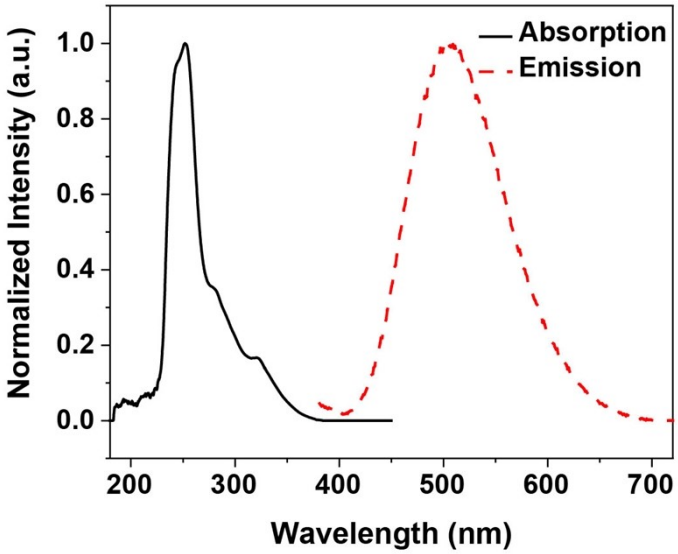


Figure S2. Fluorescence excitation (solid line) and emission spectra (dashed line) of **4b**.

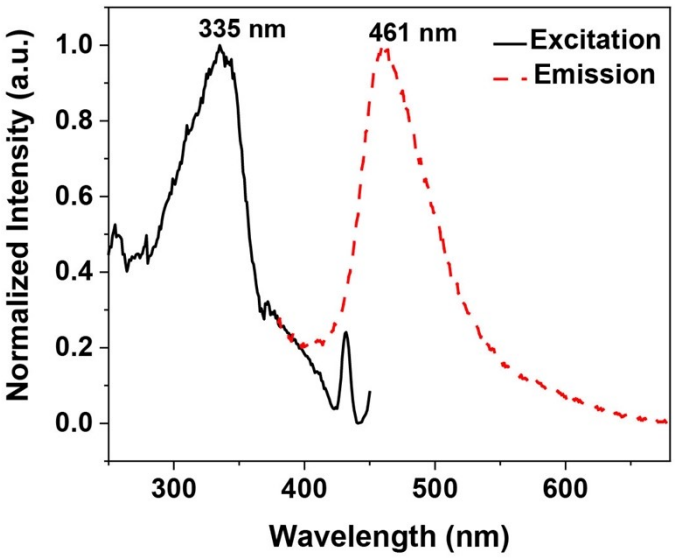


Figure S3. Fluorescence excitation (solid line) and emission spectra (dashed line) of **4c**.

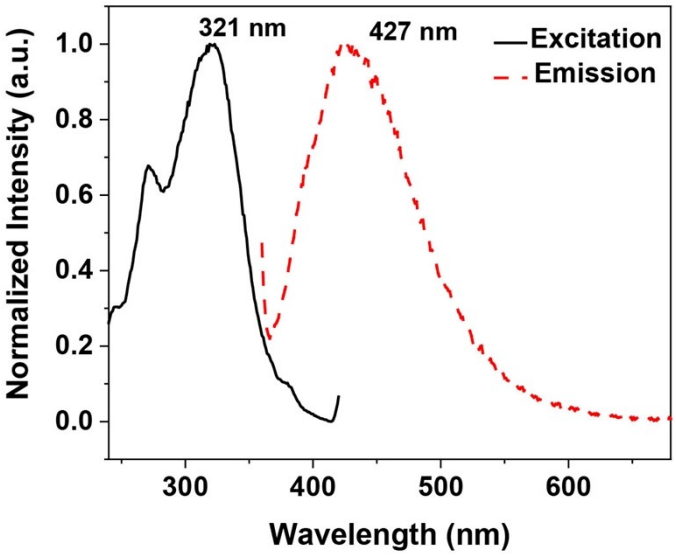


Figure S4. Fluorescence excitation (solid line) and emission spectra (dashed line) of **4d**.

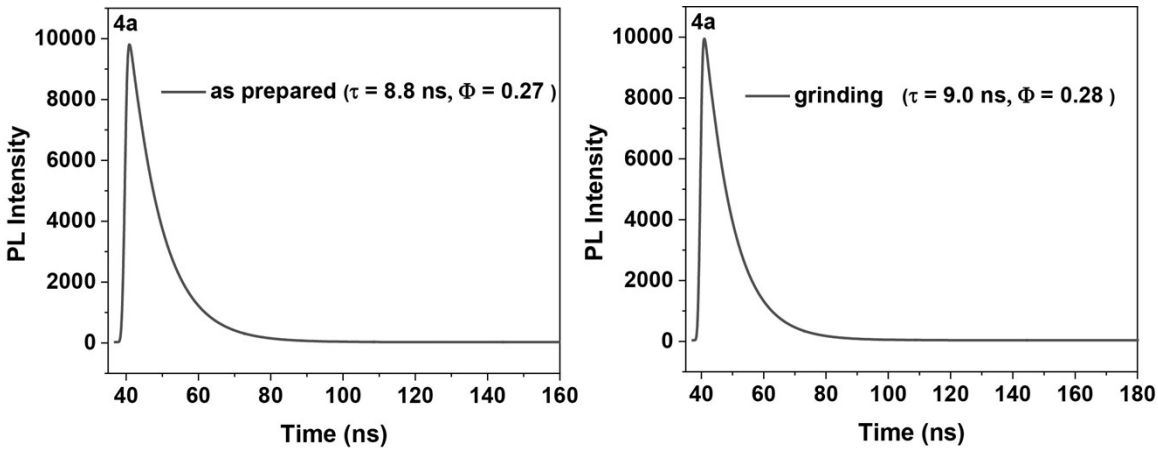


Figure S5. Time-resolved fluorescence spectra of as-prepared and gringding of **4a**.

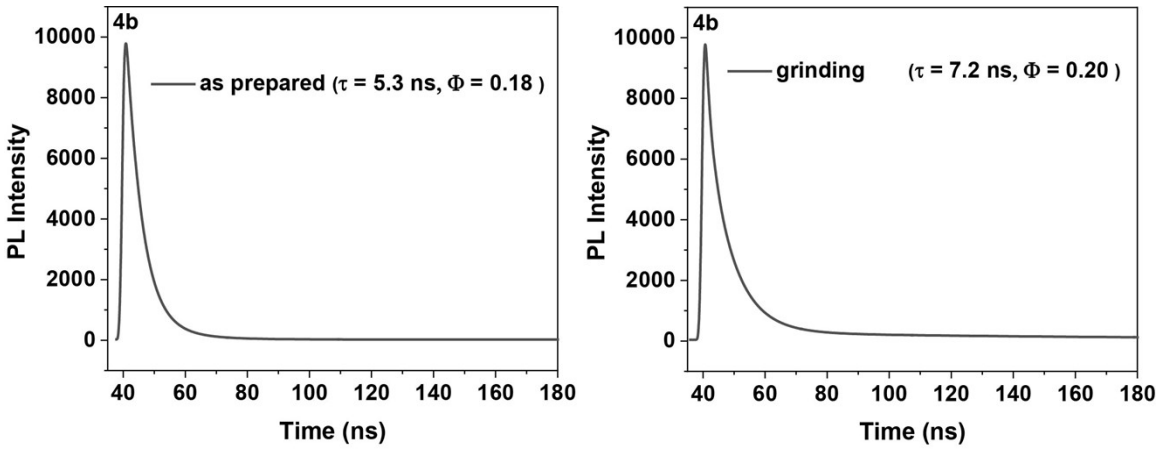


Figure S6. Time-resolved fluorescence spectra of as-prepared and gringding of **4b**.

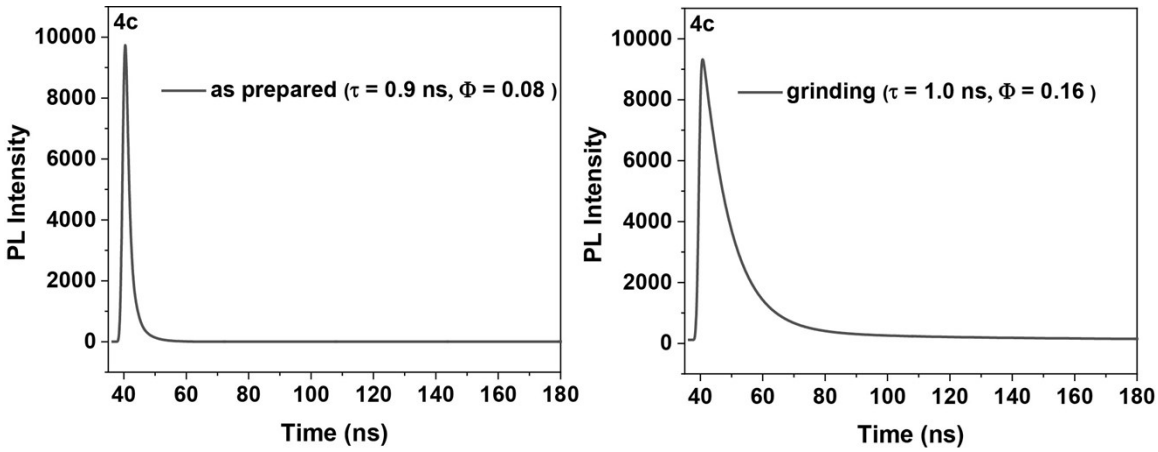


Figure S7. Time-resolved fluorescence spectra of as-prepared and gringding of **4c**.

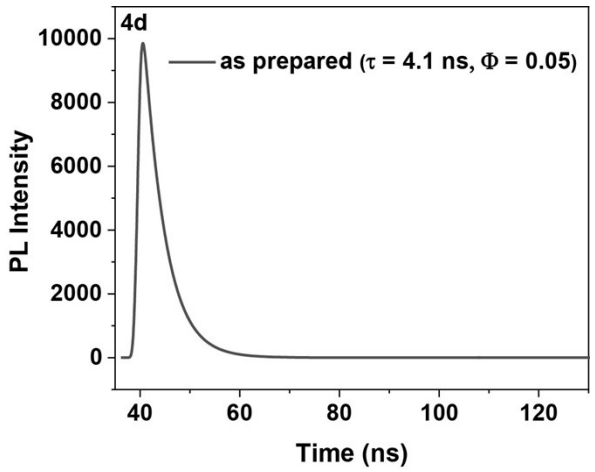


Figure S8. Time-resolved fluorescence spectra of as-prepared of **4d**.

2. Electrochemical properties

Cyclic voltammograms were recorded with a Metrohm PGSTAT204 electrochemical analyzer using DCM. The CV cell consisted of a gold electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. All measurements were performed using DCM solutions of samples with a concentration of 1 mM and 0.1 M $Bu_4N^+BF_6^-$ as a supporting electrolyte with a scan rate of 100 mVs^{-1}. Potentials are determined against a ferrocene/ferrocenyl ion couple (Fc/Fc^+).

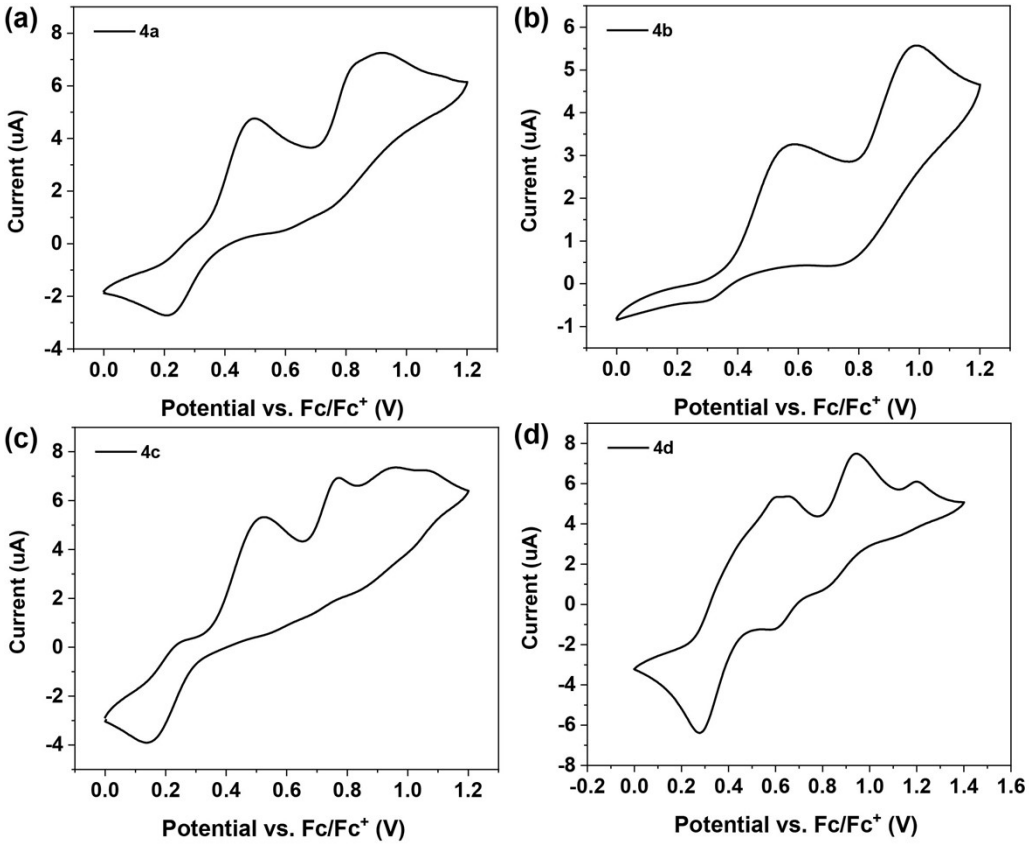


Figure S9. Cyclic voltammograms of **4a**, **4b**, **4c** and **4d** in DCM with $Bu_4N^+BF_6^-$ (0.1 M) as a supporting electrolyte, Fc = ferrocene.

3. Comparison of HOMO/LUMO plots

Table S1 Electronic properties of **4a**, **4b**, **4c** and **4d**

Entry	E_g[a](eV)	E_{OX}[b](V)	HOMO(eV) (Exp)[c]	LUMO(eV) (Exp)[d]	HOMO(eV) (Cal)[e]	LUMO(eV) (Cal)[e]	E_g (eV) (Cal)[e]
4a	3.85	0.37	-5.17	-1.32	-5.74	-0.96	4.78
4b	3.62	0.35	-5.15	-1.53	-5.56	-1.12	4.44
4c	3.82	0.36	-5.16	-1.34	-5.67	-1.24	4.43
4d	3.66,	0.27	-5.07	-1.41	-5.52	-0.84	4.68

[a] E_g estimated from the UV-Vis absorption spectra.

[b] Oxidation onset potentials measured by cyclic voltammetry.

[c] HOMO = -(E_{OX} + 4.8) eV.

[d] LUMO = HOMO + E_g.

[e]Theoretical calculations have been carried out by using the GAUSSIAN09 suite of programs in gas-phase at the B3LYP/6-31G(d) levele [1], respectively.

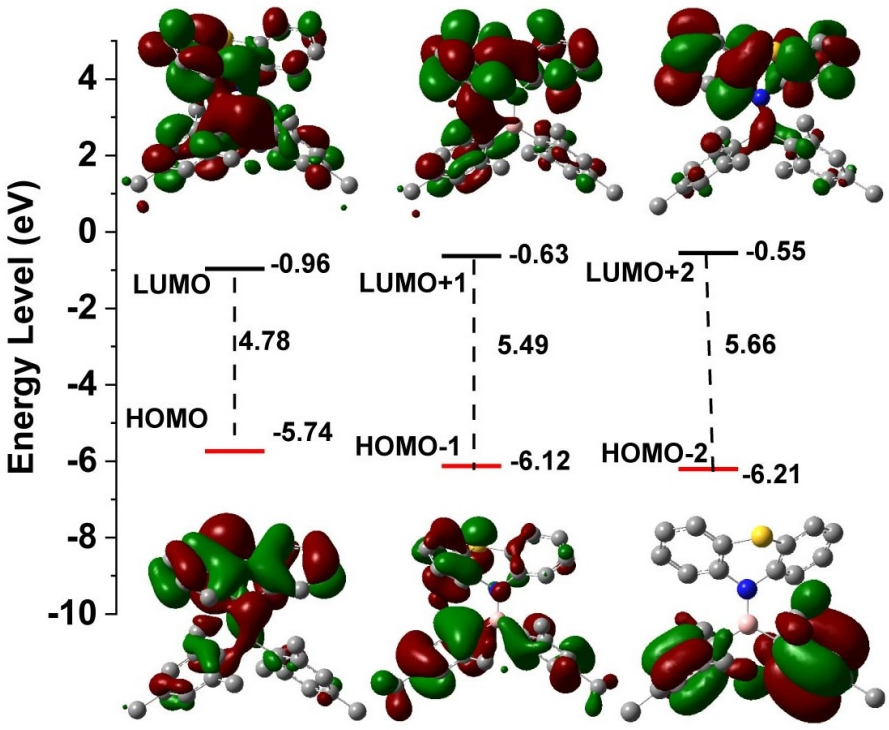


Figure S10. Computed molecular orbital plots for **4a**.

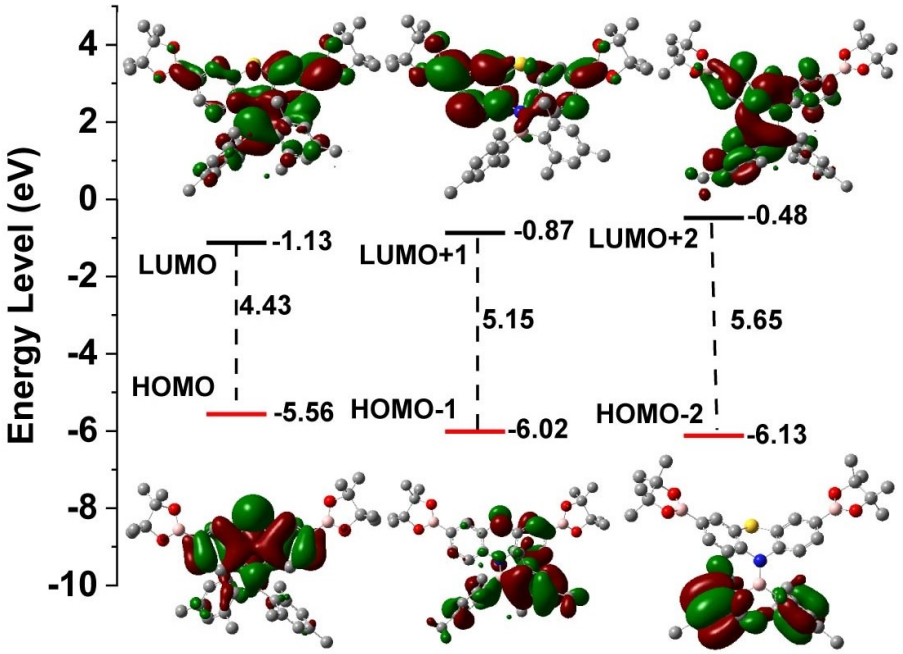


Figure S11. Computed molecular orbital plots for **4b**.

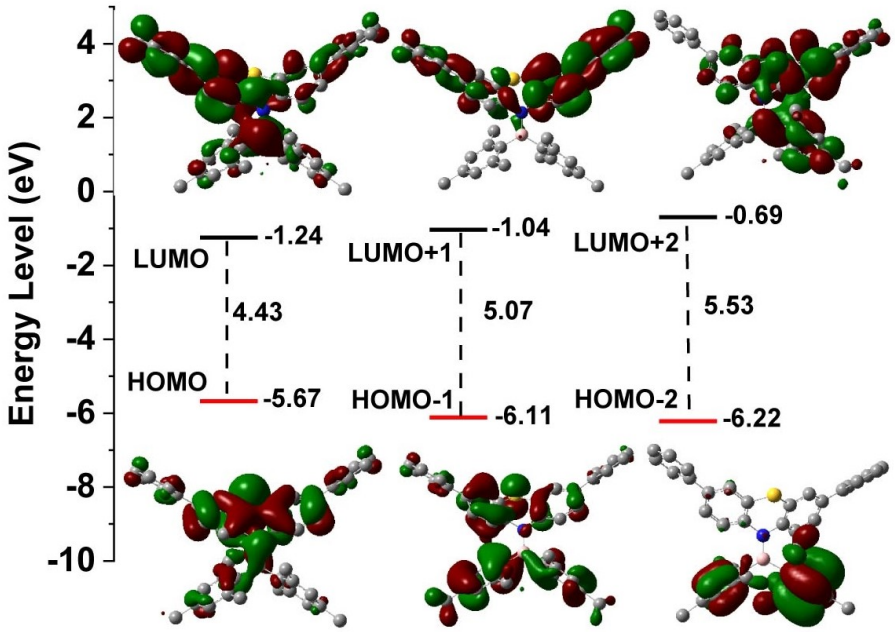


Figure S12. Computed molecular orbital plots for **4c**.

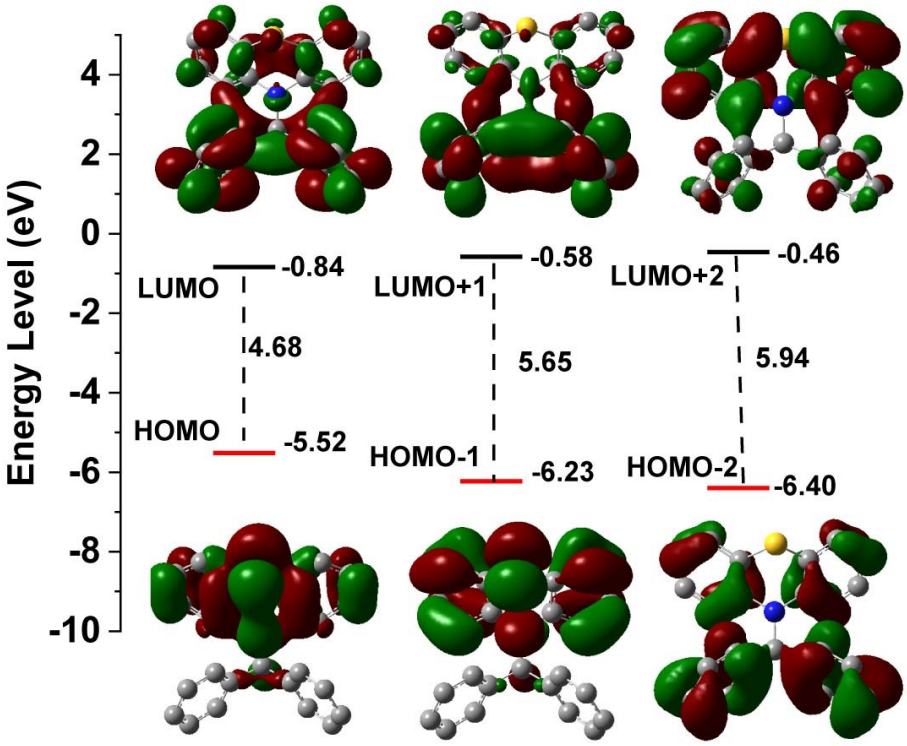


Figure S13. Computed molecular orbital plots for **4d**.

4. Single-crystal X-ray structure determination

X-ray Crystallography. Crystals of appropriate quality for X-ray diffraction studies were removed from a vial (in a glove box) and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a glass vial. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo/Cu Kα radiation. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods programs SHELXS-97, and refinements were completed using the program SHELXL-97.[8]

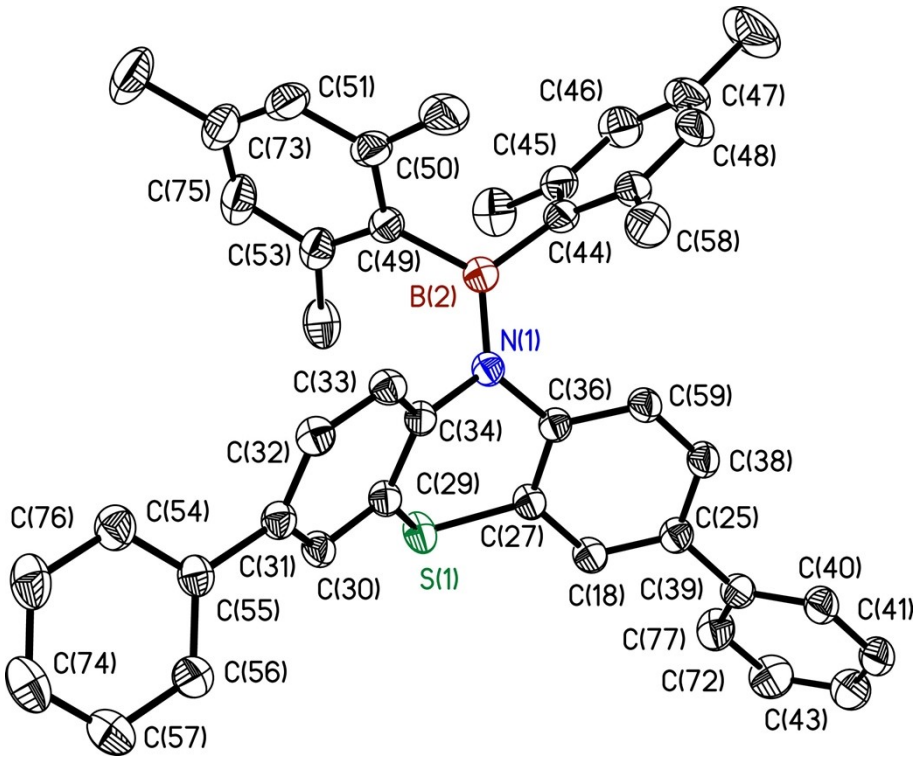


Figure S14. Molecular Structure of **4c** (CCDC 2195211) with thermal ellipsoids presented at a 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): C(34)—N(1), 1.445(2); C(36)—N(1), 1.450(2); N(1)—B(2), 1.431(3); C(49)—B(2), 1.605(3); C(44)—B(2), 1.598(3); C(27)—S(1), 1.761(2); C(29)—S(1), 1.760(2); C(31)—C(55), 1.491(3); C(25)—C(39), 1.486(3); Bond angles (deg): B(2)—N(1)—C(34), 120.64(16); B(2)—N(1)—C(36), 125.69(16); C(34)—N(1)—C(36), 113.60(15); C(44)—B(2)—C(49), 117.04(17); N(1)—B(2)—C(44), 122.80(18); N(1)—B(2)—C(49), 120.11(18); C(44)—B(2)—C(49), 117.04(17); C(29)—S(1)—C(27), 97.01(9).

Table S2. Crystallographic experimental details for compound **4c** (CCDC 2195211).

Empirical formula	$C_{42}H_{38}BNS$	
Formula weight	599.6	
Temperature	293(2) K	
Wavelength	1.54184 A	
Crystal system, space group	Monoclinic, P 21/n	
Unit cell dimensions	a = 13.5233(4) A	alpha = 90.000(2) deg.
	b = 16.5378(4) A	beta = 100.155(2) deg.
	c = 30.5504(7) A	gamma = 90.000(2) deg.
Volume	6725.5(3) A^3	
Z, Calculated density	8, 1.184 Mg/m^3	
Absorption coefficient	1.069 mm^-1	
F(000)	2544	
Crystal size	? x ? x ? mm	
Theta range for data collection	2.939 to 68.209 deg.	
Limiting indices	-16<=h<=16, -19<=k<=14, -36<=l<=36	
Reflections collected / unique	74535 / 12232 [R(int) = 0.0676]	
Completeness to theta = 67.684	99.90%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12232 / 0 / 812	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1687	
R indices (all data)	R1 = 0.0663, wR2 = 0.1825	
Extinction coefficient	0.00172(13)	
Largest diff. peak and hole	0.337 and -0.307 e.A^-3	

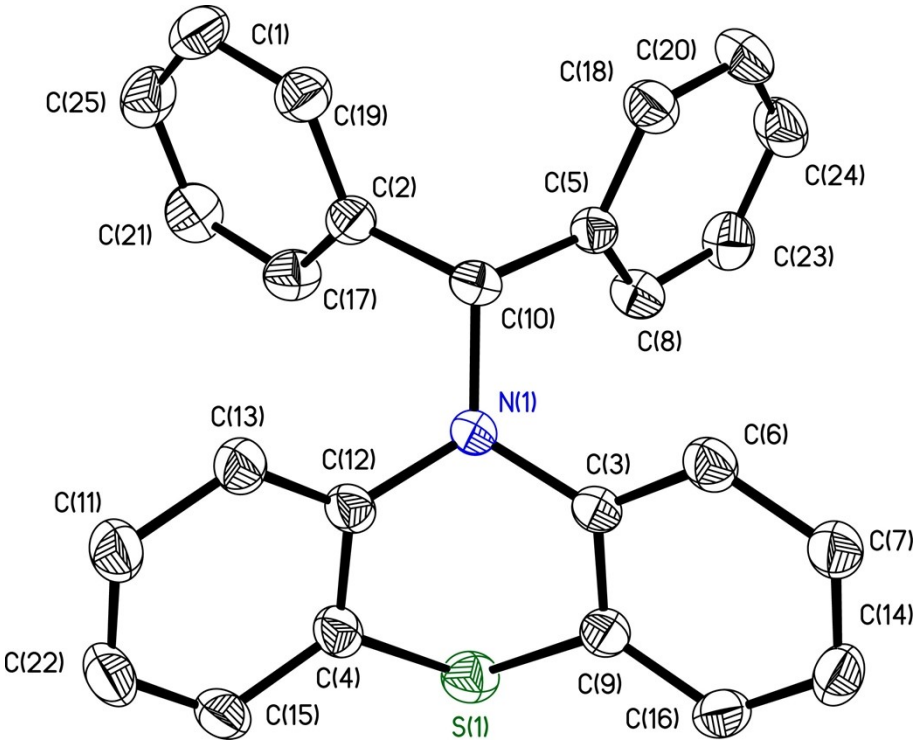
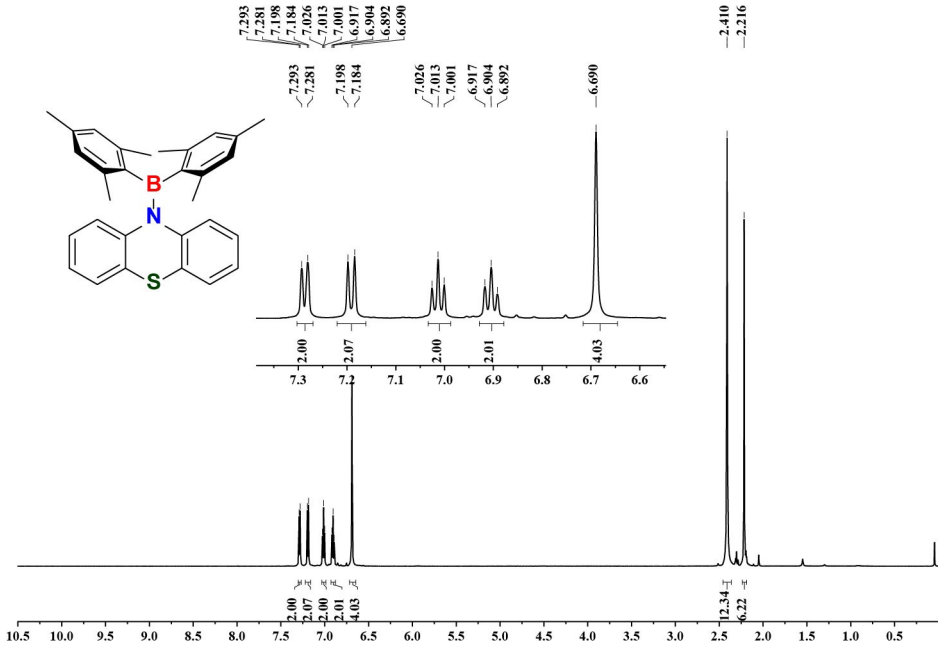


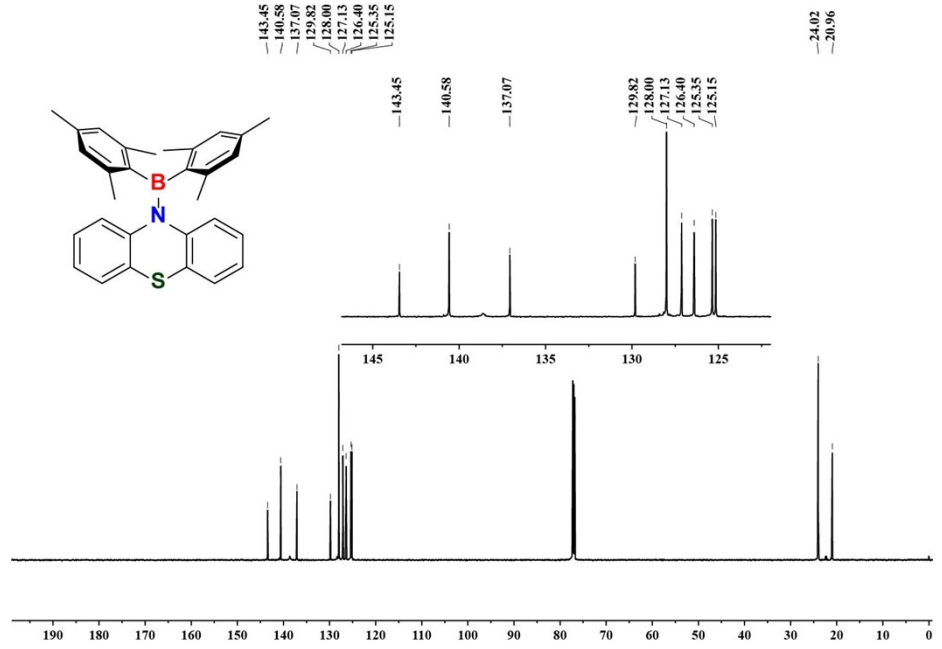
Figure S15. Molecular Structure of **4d** (CCDC 2194930) with thermal ellipsoids presented at a 50% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): S(1)—C(9), 1.766(5); S(1)—C(4), 1.769(5); N(1)—C(3), 1.431(5); N(1)—C(12), 1.434(5); N(1)—C(10), 1.468(5); C(2)—C(17), 1.378(6); C(2)—C(19), 1.386(6); C(2)—C(10), 1.518(6); C(3)—C(6), 1.388(6); C(3)—C(9), 1.395(6); Bond angles (deg): C(9)—S(1)—C(4), 97.3(2); C(3)—N(1)—C(12), 113.1(3); C(3)—N(1)—C(10), 119.6(3); C(12)—N(1)—C(10), 120.3(3); C(17)—C(2)—C(10), 122.6(4); C(19)—C(2)—C(10), 118.9(4); N(1)—C(10)—C(2), 113.2(3); N(1)—C(10)—C(5), 110.1(3); C(2)—C(10)—C(5), 107.1(3).

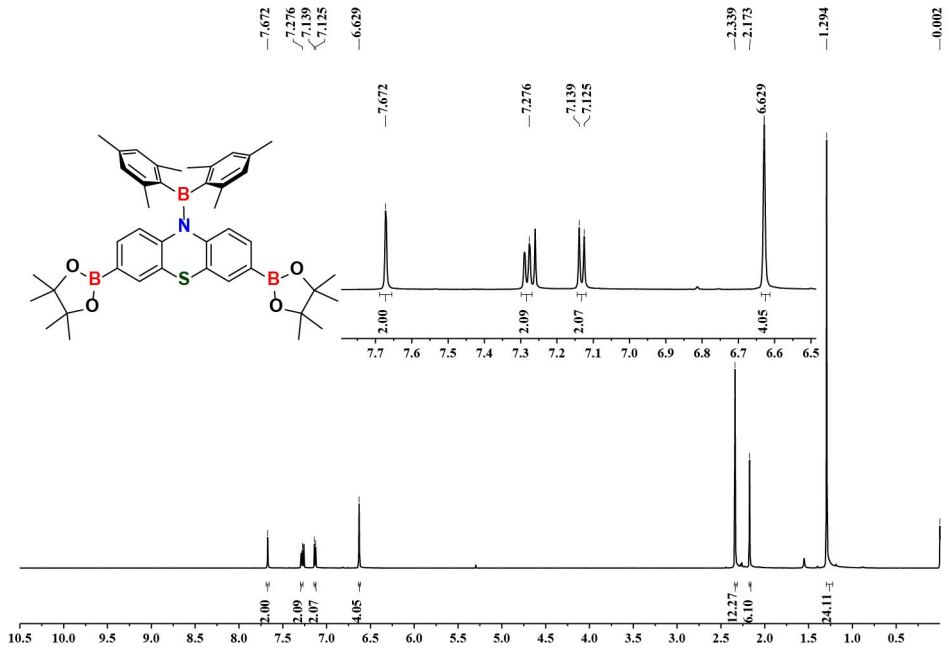
Table S3. Crystallographic experimental details for compound **4d** (CCDC 2194930).

Empirical formula	$C_{25}H_{19}NS$
Formula weight	365.47
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 19.024(12) A alpha = 90 deg.
	b = 6.265(4) A beta = 115.51(2) deg.
	c = 17.503(13) A gamma = 90 deg.
Volume	1883(2) A^3
Z, Calculated density	4, 1.289 Mg/m^3
Absorption coefficient	0.181 mm^-1
F(000)	768
Crystal size	? x ? x ? mm
Theta range for data collection	2.328 to 26.021 deg.
Limiting indices	-21<=h<=21, -7<=k<=7, -21<=l<=21
Reflections collected /unique	11447 / 3602 [R(int) = 0.1274]
Completeness to theta = 25.242	98.20%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / par	ameters 3602 / 0 / 245
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0854, wR2 = 0.1853
R indices (all data)	R1 = 0.1791, wR2 = 0.2595
Extinction coefficient	0.210(15)
Largest diff. peak and hole	0.874 and -0.939 e.A^-3

5. ^{1}H NMR and ^{13}C NMR spectra



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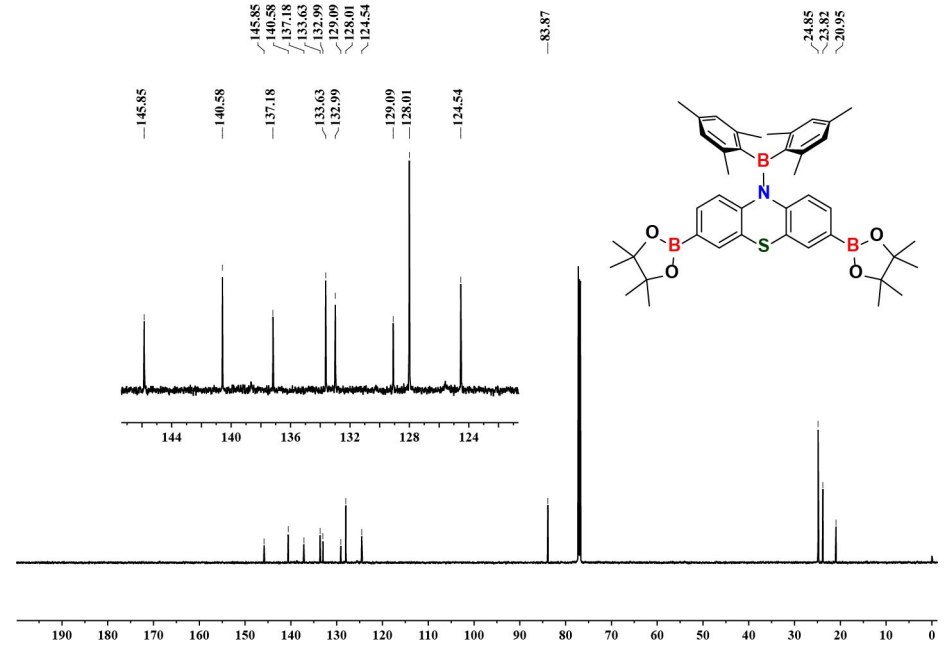
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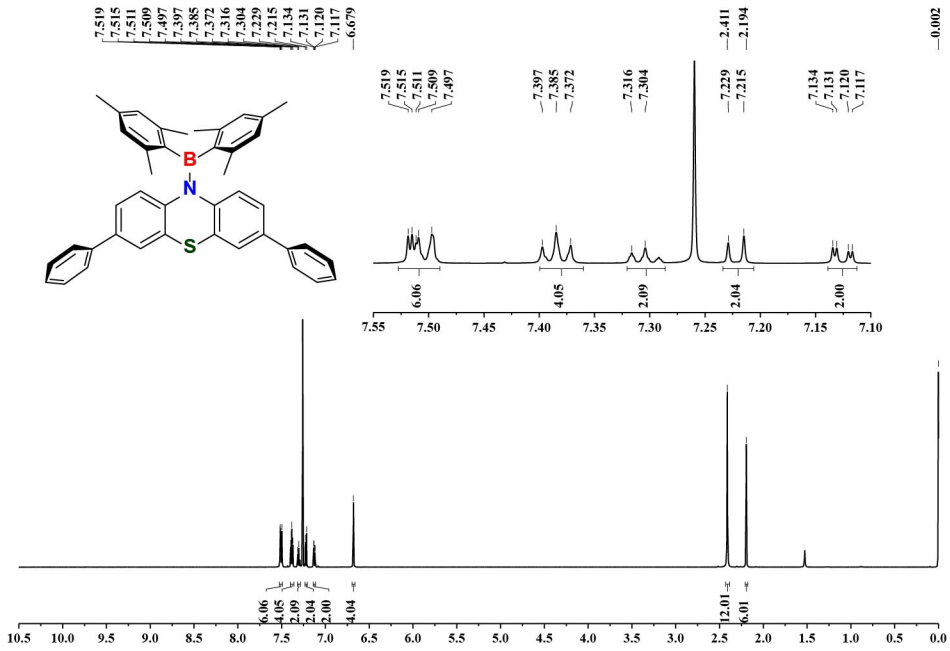
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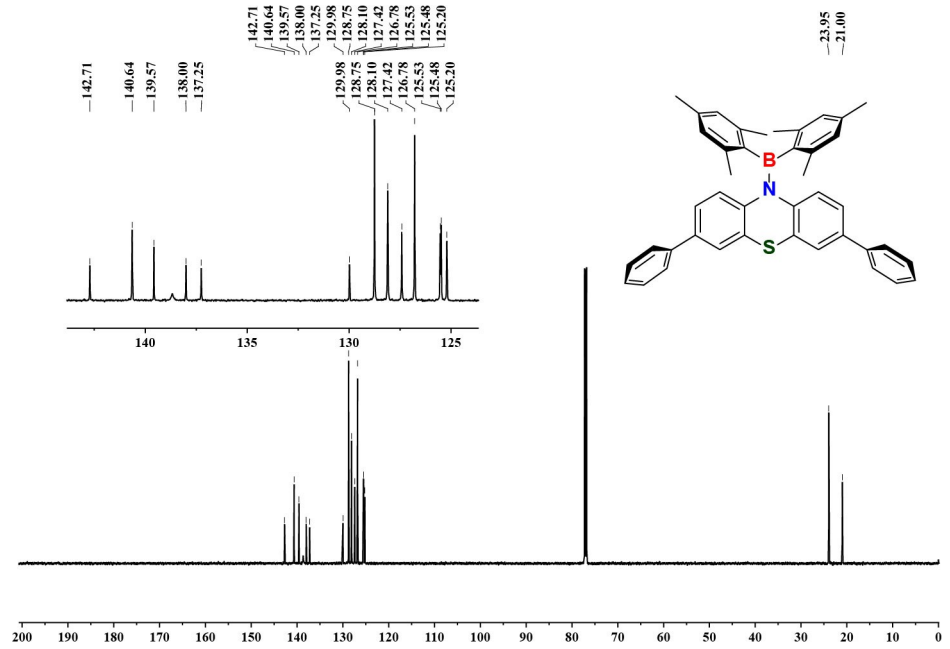
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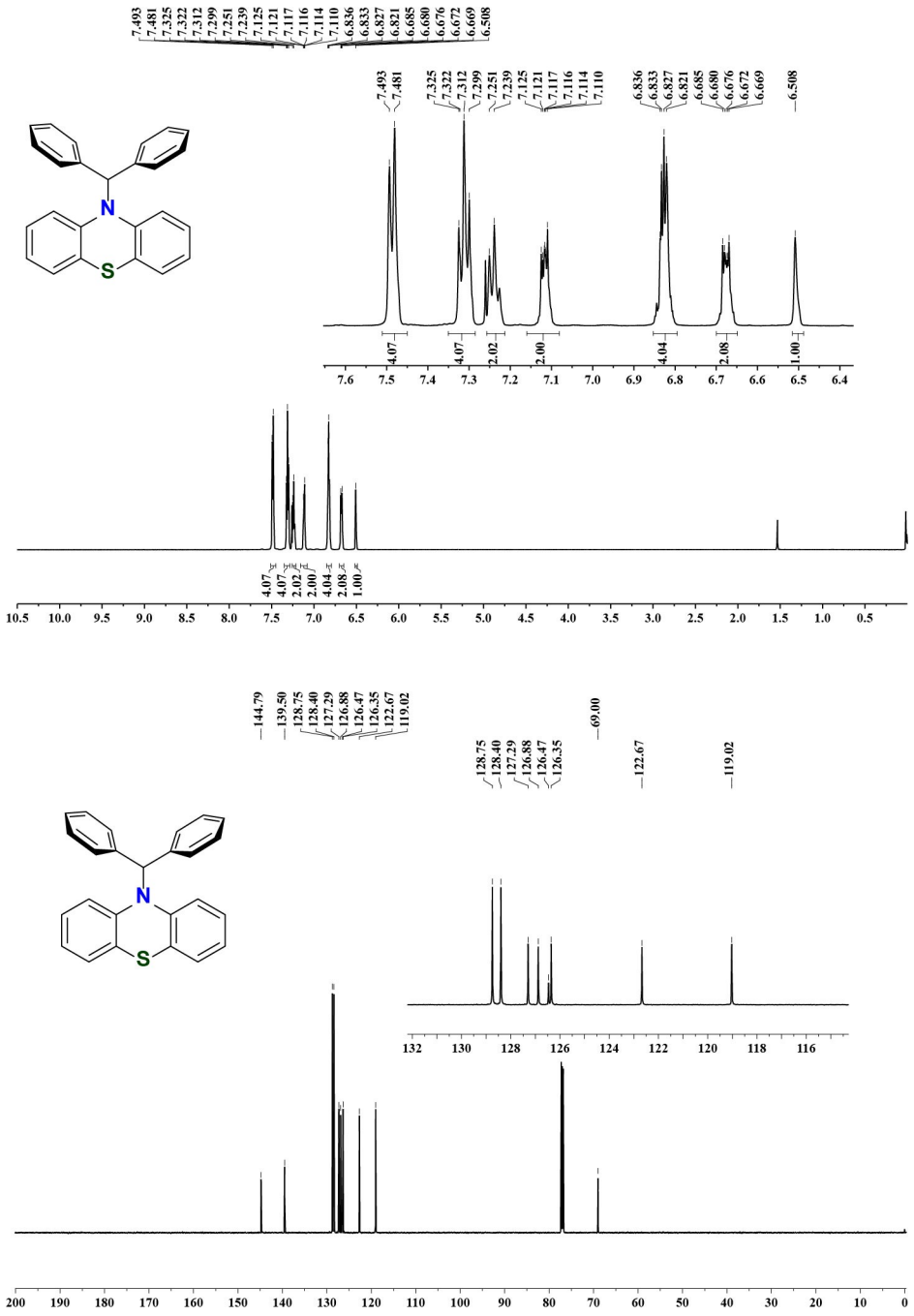

6. Reference

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B. Gaussian09, Revision A.01, Gaussian, Wallingford, Con, USA, **2009**.