Supporting Information

Non-Photoisomerizable Butterfly Shaped Tetrasubstituted Azobenzenes: Synthesis and Photophysical Studies

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Materials and analytical methods:

Solvents and starting materials were purchased from Sigma Aldrich. Other chemicals were of analytical reagent grade and were used without further any purification except when specified. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates (Merck 60F-254) using UV light for visualization. Silica gel (Merck 60, particle size 60-12 mesh) was used for column chromatography. Absorption spectra was measured in Shimadzu UV-1800 and fluorescence spectra was recorded on Cary Eclipse fluorescence spectrophotometer using quartz cuvettes at room temperature. Differential scanning calorimetry (DSC) was performed using a DSC 204 F1 Phoenix unit at heating and cooling rates of 10 °C min^{-1}. The low-temperature phosphorescence spectra of the carbazole, phenothiazine and phenyl hybrids were obtained using Hitachi F-4500 Fluorescence Spectrophotometer coupled with a liquid nitrogen-cooled charge-coupled device Optistat DN_2 Variable Temperature Liquid Nitrogen Cryostat. Irradiation experiments were performed using UVGL-25 compact 4 watt 365 nm UV lamp. NMR spectra were recorded on a Bruker 400 MHz (101 MHz for ^{13}C) spectrometer using residual protonated solvent signals as the internal standard. Mass spectra were measured using a Bruker autoflex MALDITOF mass spectrometer.

Femtosecond Transient Absorption Spectroscopy: The basic seed laser pulses were obtained from Ti:sapphire laser (Mai Tai HP, Spectra Physics, USA) pumped by 14 W frequency doubled Nd:YVO_4 (532 nm). It was centered at 800 nm (80 MHz repetition rate) with pulse width of < 110 fs and an average power of 2.5W. A part of (25%) fundamental pulsed laser beam was amplified

at 1 kHz using a Ti:sapphire regenerative amplifier (Spitfire Ace, Spectra Physics) pumped by the second harmonic (527 nm, 30 W) from intercavity-doubled, diode-pumped Q switched Nd:YLF laser (Empower-30 Spectra Physics). The amplified laser output with energy of 4 mJ centered at 800 nm having pulse width of < 120 fs was split (75:25%) into two beams, in which high energy beam is converted to desired excitation wavelengths (pump 325 nm) by coupling it into a TOPAZ (Prime, Light Conversion). The pump beam was then passed through a computer-controlled optical chopper and focused (3 μm) on the sample cell. The another part of amplified beam (200 mW) was focused on a 1 mm thick sapphire plate to generate a white light continuum (350-1000 nm), which finally spilt into two for sample and reference probe beams. The sample cell is a 0.4 mm optical path quartz cylindrical cell placed in a variable speed rotating holder. After passing through the sample cell, the white light continuum is coupled into a 100 μm optical fiber connected to imaging spectrometer. The pump probe spectrophotometer setup was based on an ExciPro spectrometer (CDP Systems Corp). Typically, the time-resolved absorption spectra were acquired by averaging over 2000 excitation pulses at all spectral delay time. The polarization of the pump pulse was set at the magic angle (54.7°) relative to the probe pulse to recover the isotropic absorption spectrum. The effective time resolution of the ultrafast spectrometer is determined to be about ≤ 120 fs.

SYNTHESIS DETAILS

1. Synthesis of 2,6-dibromo-4-nitroaniline (5):

To a solution of 4-nitroaniline (1 g, 7.24 mmol) in acetonitrile (20 mL), NBS (2.7 g, 15.2 mmol) was added at room temperature. The mixture was stirred overnight, and then diluted with water and chloroform. The organic and aqueous phases were separated and the organic phase was dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by column chromatography (Ethyl acetate/hexanes: 30%/70%) to give 6 as a yellow solid (2 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 2H), 5.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.52, 2C 128.00 and 106.46 ppm.

2. Synthesis of 1,3-dibromo-5-nitrobenzene (6):

To a stirred, boiling mixture of 2,6-dibromo-4-nitroaniline (1g, 3.37mmol), 7 ml. of ethanol and 2 ml. of concentrated sulfuric acid, 0.72 g of sodium nitrite was added in slowly. Boiling was

continued for a half-hour after the sodium nitrite addition was completed. The mixture was allowed to cool, and the solids were collected by filtration, washed with water and dried in a vacuum. Yield of the product is 0.8 g. (85%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 8.00 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.07, 125.599 and 123.489 ppm.

3. a) Synthesis of 9,9'-(5-nitro-1,3-phenylene)bis(9H-carbazole) by Buchwald coupling (7):

A DMF solution mixture of **6** (0.5g, 1.77 mmol), carbazole (0.59g, 3.54 mmol), K_2CO_3 (0.49g, 3.54 mmol), 1, 10-phenanthroline (127 mg, 0.708 mmol) and CuI (134 mg, 0.708 mmol) was refluxed under stirring for 48 h. After cooling down to room temperature, 50 mL of ice-water was added into the reaction mixture and the solid was collected through celite. The filtrate was extracted with chloroform and concentrated. The crude solid was purified by column chromatography (Ethyl acetate/hexane: 2/8) to give the yellow solid. Yield: 0.6 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 2H), 8.21 (s, 1H), 8.17 (d, J = 7.7 Hz, 4H), 7.55 (d, J = 8.1 Hz, 4H), 7.48 (t, J = 7.6 Hz, 4H), 7.37 (t, J = 7.4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.46, 140.69, 139.96, 130.27, 126.66, 124.10, 121.34, 120.78, 119.90, 109.31.

b) Synthesis of 10, 10'-(5-nitro-1, 3-phenylene)bis(10H-phenothiazine) by Buchwald coupling (8):

A DMF solution mixture of **6** (1g, 3.55 mmol), Phenothiazine (1.55g, 7.81 mmol), K_2CO_3 (1.07g, 7.81 mmol), 1, 10- phenanthroline (0.25 g, 1.42 mmol) and CuI (0.27 g, 1.42 mmol) was refluxed under stirring for 48 h. After cooling down to room temperature, 50 mL of ice-water was added into the reaction mixture and the solid was collected through celite. The filtrate was extracted with chloroform and concentrated. The crude solid was purified by column chromatography (Ethyl acetate/hexane: 2/8) to give the yellow solid. Yield: 1.3 g (68%). ^{1}H NMR (400 MHz, CDCl3) δ 7.69 (s, 2H), 7.31 (d, J = 7.6 Hz, 4H), 7.16 (d, J = 8.0 Hz, 5H), 7.09 (t, J = 7.3 Hz, 4H), 6.95 (d, J = 7.8 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.52, 146.61, 141.75, 129.63, 128.36, 127.46, 125.40, 123.08, 118.05, 110.25.

c) Synthesis of 5'-nitro-1, 1':3',1''-terphenyl by Suzuki coupling (9):

A 250 ml three necked round bottom flask was charged with **6** (0.5g, 1.77 mmol), phenyl boronic acid (0.47 g, 3.89 mmol), palladium acetate (17.4 mg, 0.07 mmol), tri(o-tolyl) phosphine (47 mg,

0.155 mmol), toluene (12 ml) and 2 M aqueous sodium carbonate (6 ml). The reaction mixture was heated under reflux overnight, cooled to room temperature, then quenched by adding 50 ml of 2 M aqueous NaOH. The two layers were separated, and the organic layer was concentrated to dryness. The crude residue was purified by column chromotography on silica using 20:80 mixture percentage of ethyl acetate and hexane as the eluent. Yield: 0.41 g, 74 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 2H), 8.11 (s, 1H), 7.68 (d, J = 7.5 Hz, 4H), 7.51 (t, J = 7.4 Hz, 4H), 7.45 (t, J = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.32, 143.37, 138.82, 131.71, 129.22, 128.65, 127.28, 120.60.

4. a) Synthesis of (E)-1,2-bis(3,5-di(9H-carbazol-9-yl)phenyl)diazene (1):

To a stirred and boiling suspension of 0.3 g of zinc dust and 0.40 g of **7** in 5 ml of ethanol, 1 ml. of 30 % aqueous sodium hydroxide was added as rapidly. After completion of the reaction, the ethanol was concentrated then made a slurry with chloroform and purified by column chromotography on silica using (ethyl acetate/ hexane: 1/9). Yield: 0.011 g, 3%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 2H), 8.51 (s, 2H), 8.15 (dd, J = 7.3, 3.5 Hz, 8H), 8.10 (s, 1H), 7.90 (s, 1H), 7.61 (t, J = 7.7 Hz, 8H), 7.46 (dd, J = 13.9, 7.0 Hz, 8H), 7.33 (dd, J = 16.6, 7.9 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.51, 146.02, 140.43, 140.23, 140.19, 139.66, 128.31, 126.53, 126.34, 126.09, 123.96, 123.77, 122.60, 121.01, 120.66, 120.61, 120.51, 119.54, 109.68, 109.48.

b) Synthesis of (E)-1,2-bis(3,5-di(10H-phenothiazin-10-yl)phenyl)diazene (2) :

To a stirred, boiling suspension of 0.4 g of zinc dust in a solution of 0.5 g of **8** in 5 ml. of ethanol, 1 ml. of 30 % aqueous sodium hydroxide was added as rapidly as foaming would permit (about ten minutes). After completion of the reaction, the ethanol was concentrated then made slurry with chloroform and purified by column chromotography on silica using (ethyl acetate/ hexane: 1/9). Yield: 0.015 g, 4%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.99 (s, 2H), 7.29 (s, 1H), 7.23 (d, J = 7.2 Hz, 4H), 7.10 (dd, J = 12.4, 7.4 Hz, 9H), 7.00 (dd, J = 15.7, 7.8 Hz, 8H), 6.91 (t, J = 7.3 Hz, 4H), 6.81 (d, J = 8.0 Hz, 4H), 6.59 (d, J = 7.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.79, 146.85, 145.55, 144.37, 143.28, 142.43, 127.93, 127.38, 127.34, 127.15, 126.95, 124.61, 123.74, 123.59, 122.78, 122.00, 121.03, 119.53, 118.55, 114.02.

c) Synthesis of (E)-1,2-di([1,1':3',1''-terphenyl]-5'-yl)diazene (3) :

To a stirred, boiling suspension of 0.4 g of zinc dust in a solution of 0.5 g of **9** in 5 ml of ethanol, 1 ml. of 30 % aqueous sodium hydroxide was added as rapidly as foaming would permit (about ten minutes). After completion of the reaction, the ethanol was concentrated then made slurry with chloroform and purified by column chromatography on silica using (ethyl acetate/ hexane: 1/9). Yield: 0.015 g, 4%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.57 (s, 1H), 8.45 (s, 1H), 8.20 (s, 2H), 7.99 (d, J = 19.3 Hz, 2H), 7.80 – 7.71 (m, 8H), 7.50 (d, J = 6.9 Hz, 8H), 7.42 (t, J = 7.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.54, 142.77, 142.33, 140.52, 140.41, 139.73, 129.06, 128.95, 128.91, 128.55, 128.22, 127.86, 127.77, 127.37, 127.34, 120.60.

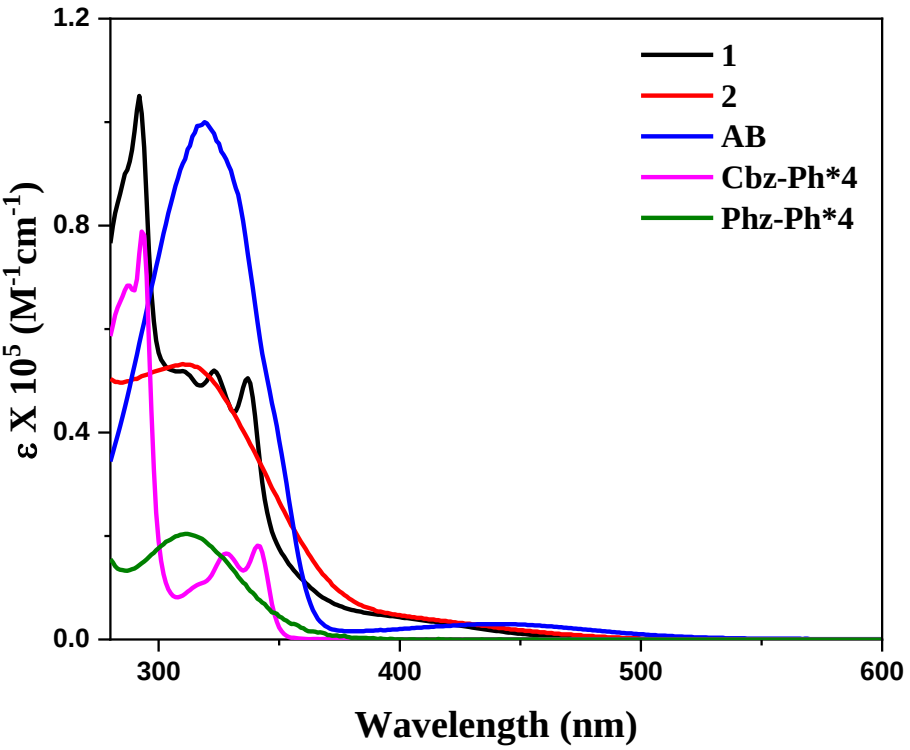


Figure S1: UV-visible absorption spectra of **1**, **2**, **AB** and *N*-phenyl carbazole (**Cbz-Ph)** and *N*-phenyl phenothiazine (**Phz-Ph)** in $CHCl_3$. The Epsilon (ε) values of **Cbz-Ph** and **Phz-Ph** are multiplied by four times as 4 units are substituted to the azobenzene.

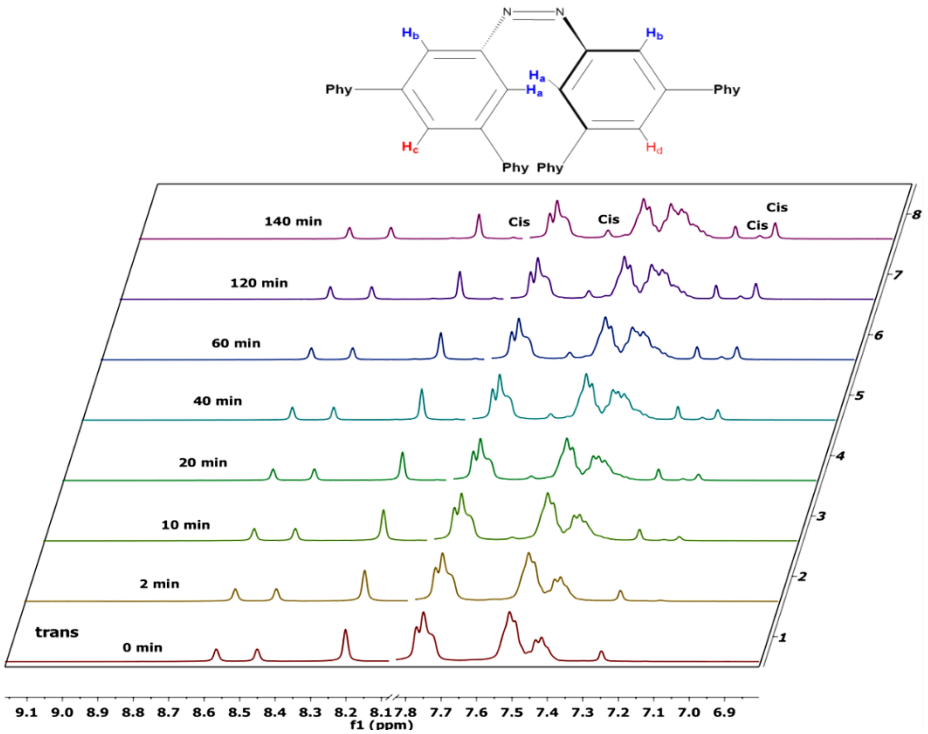


Figure S2. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of photoirradiation of **3** at 360 nm from 0 to 140 min.

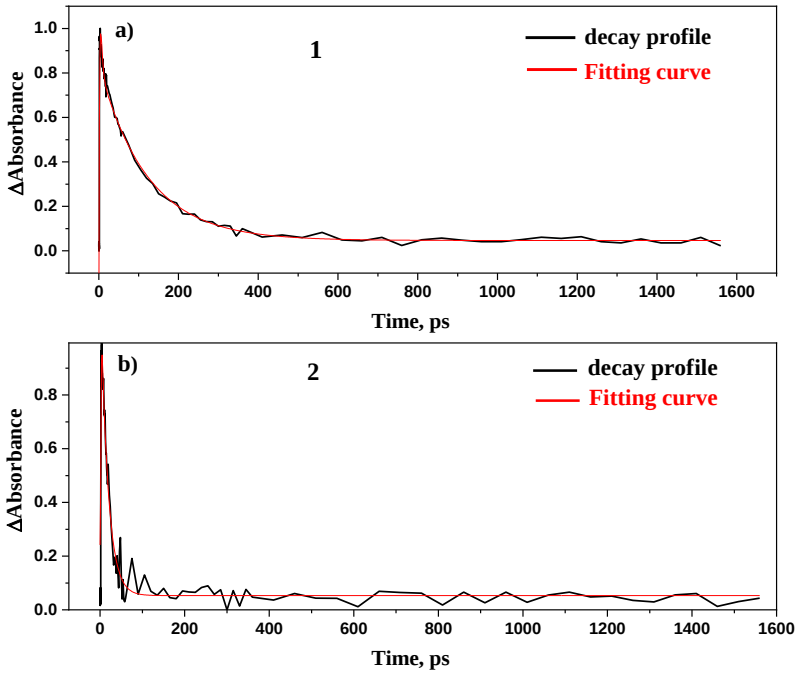


Figure S3. Kinetic profile at 515 nm obtained from femtosecond transient absorption spectra of a) **1** and b) **2** in chloroform obtained by exciting at 325 nm. .

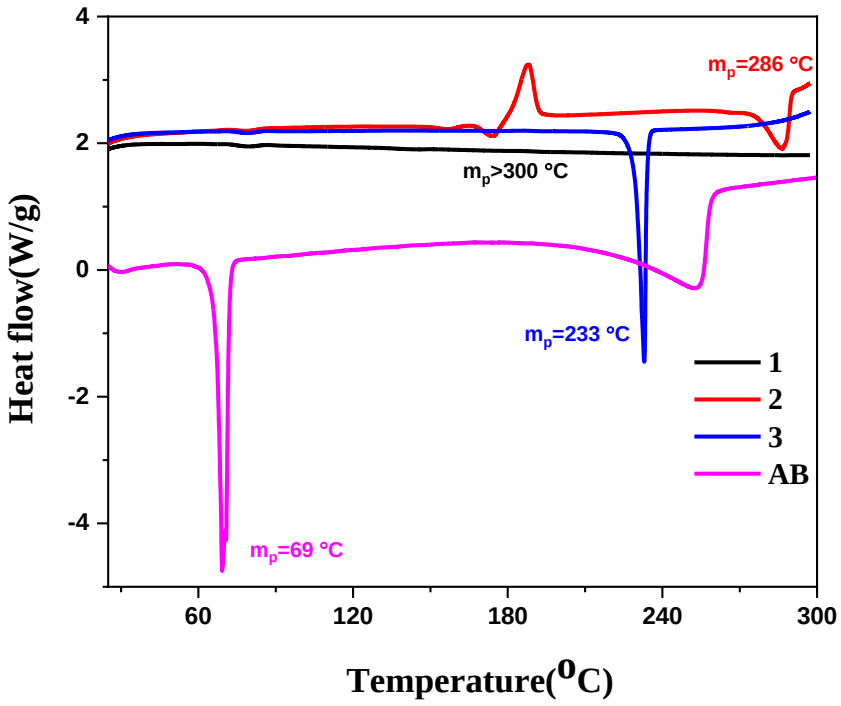


Figure S4: DSC curve of target **1**, **2**, **3** and **AB.**

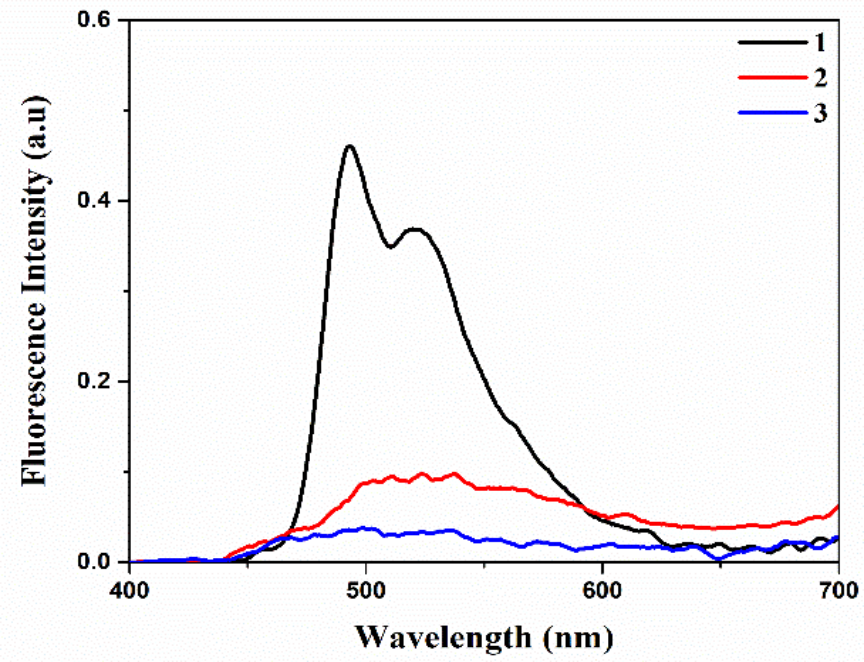


Figure S5: Phosphorescent spectra of **1**, **2** and **3** in 2-methyltetrahydrofuran at 77 K.

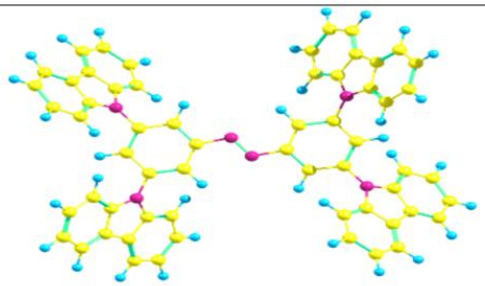
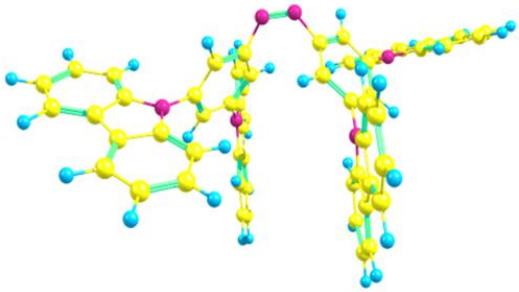
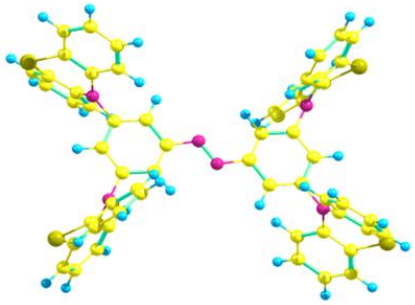
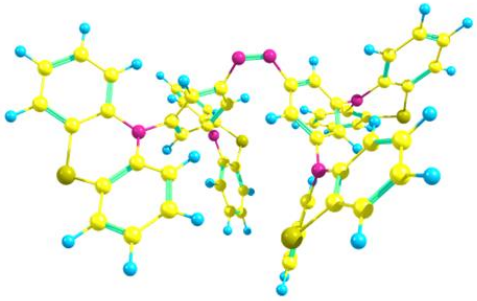
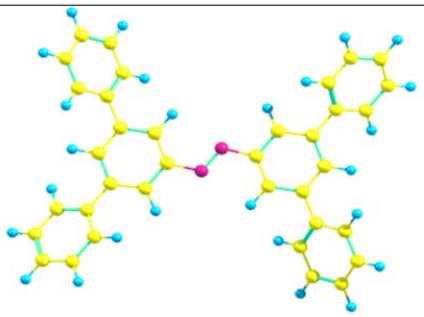
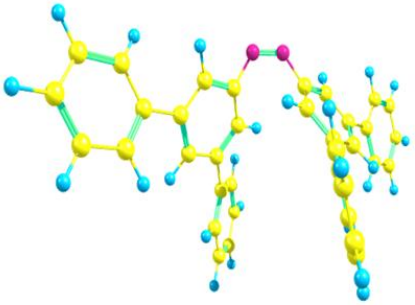
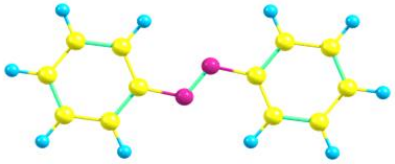
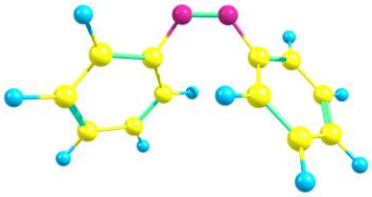
Target	trans	cis
1		
2		
3		
AB		

Figure S6: Optimized structure and Molecular orbital diagrams for trans/cis-**1**, **2**, **3** and **AB** at B3LYP/6-31G* level of theory.

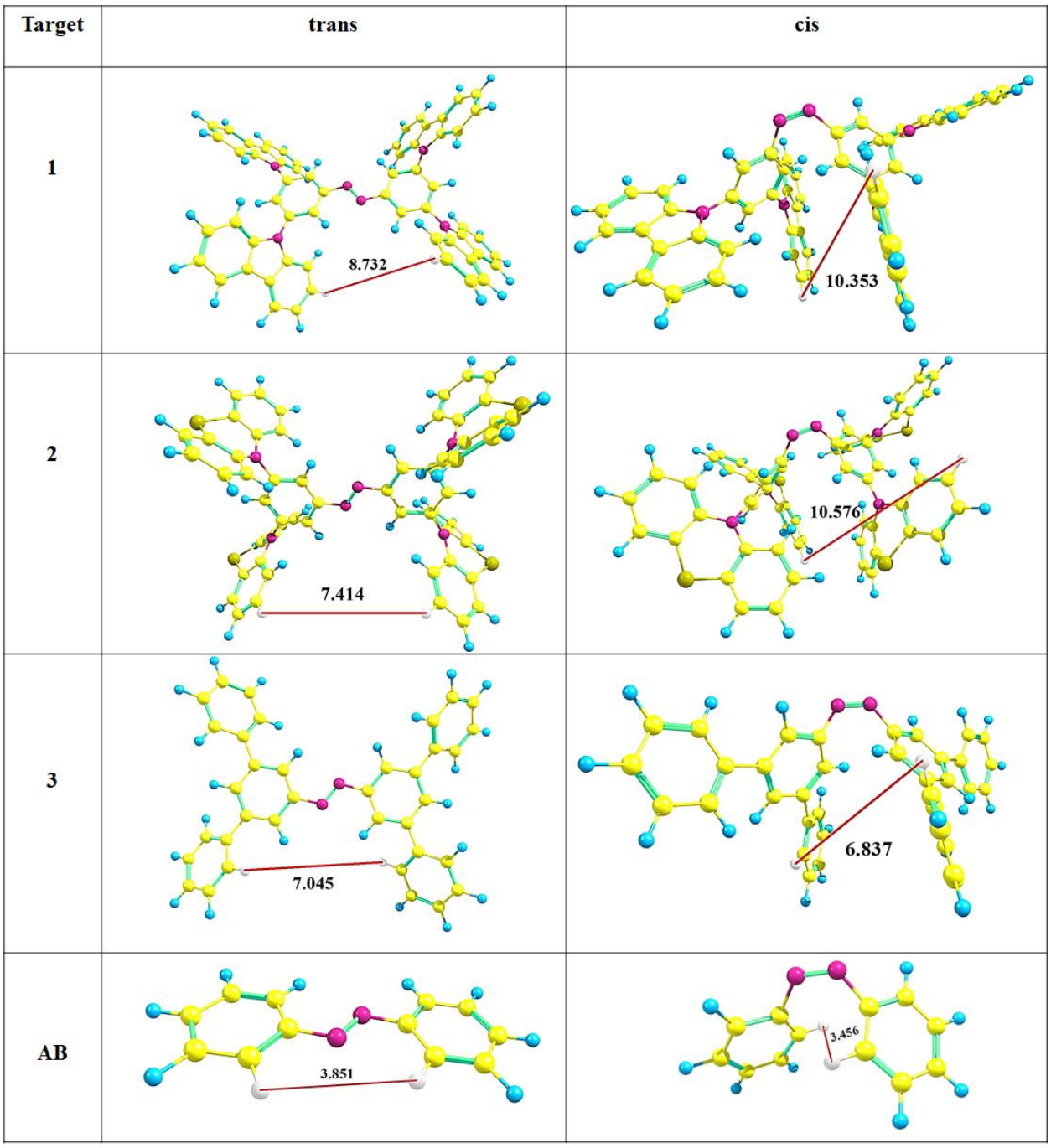


Figure S7: The calculated value of distance between closest hydrogens of trans/cis-**1**, **2**, **3** and **AB** at B3LYP/6-31G* level of theory.

Compound Name	$\Delta H_{trans\text{-}cis}$ (kcal/mol)	$\Delta G_{trans\text{-}cis}$ (kcal/mol)
1	15.45	16.34
2	14.561	17.75
3	15.63	15.27
AB	15.58	15.63

Table S1. Theoretically calculated value of enthalpy and free energy of formation of trans-cis isomer using Gaussian 03 at B3LYP/6-31G* level.

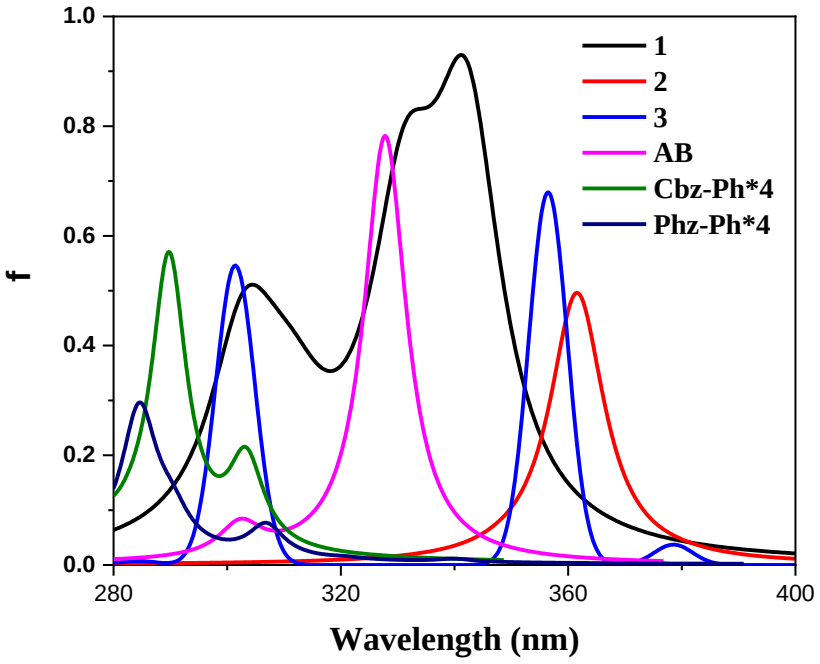


Figure S8. Computed UV-visible absorption spectra of **1**, **2**, **3**, **AB**, free carbazole and phenothiazine in terms of oscillator strengths.

S. No	Target molecules	ϵ x (10^5 M^{-1} cm^{-1})	
		π-π*	**n- π***
1	**1**	0.5 (336 nm)	0.036 (410 nm)
2	**2**	0.53 (313 nm)	0.037 (416 nm)
3	**3**	0.12 (335 nm)	0.003 (448 nm)
4	**AB**	1.0 (319 nm)	0.035 (448 nm)

Table S2. Molar absorptivity values of target molecules **1**, **2**, **3** and **AB** with absorbance maxima obtained from UV-vis absorption spectra (**Figure 2**) in $CHCl_3$.

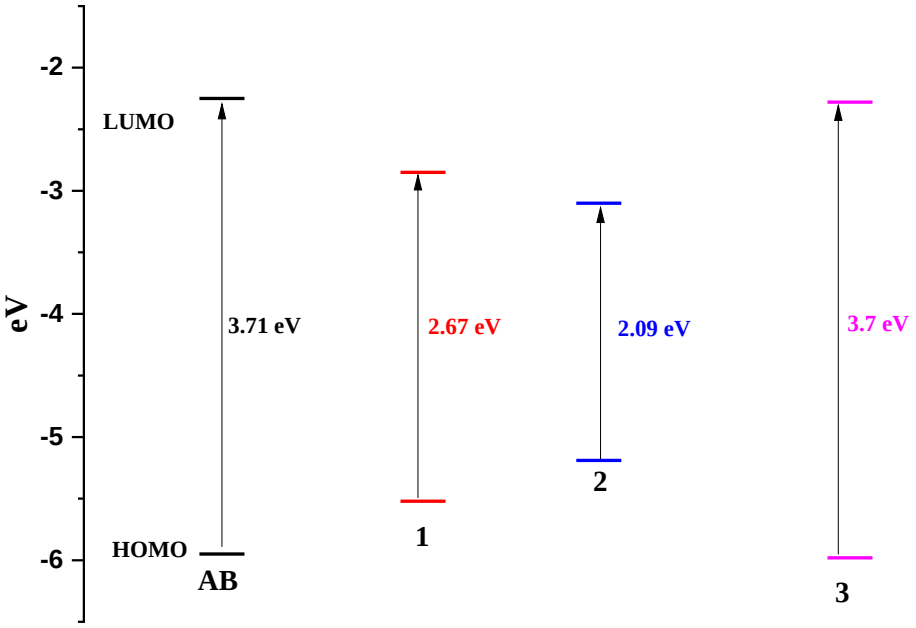


Figure S9. Calculated energy level of **1**, **2**, **3** and **AB.**

SPECTRAL CHARACTERIZATIONS

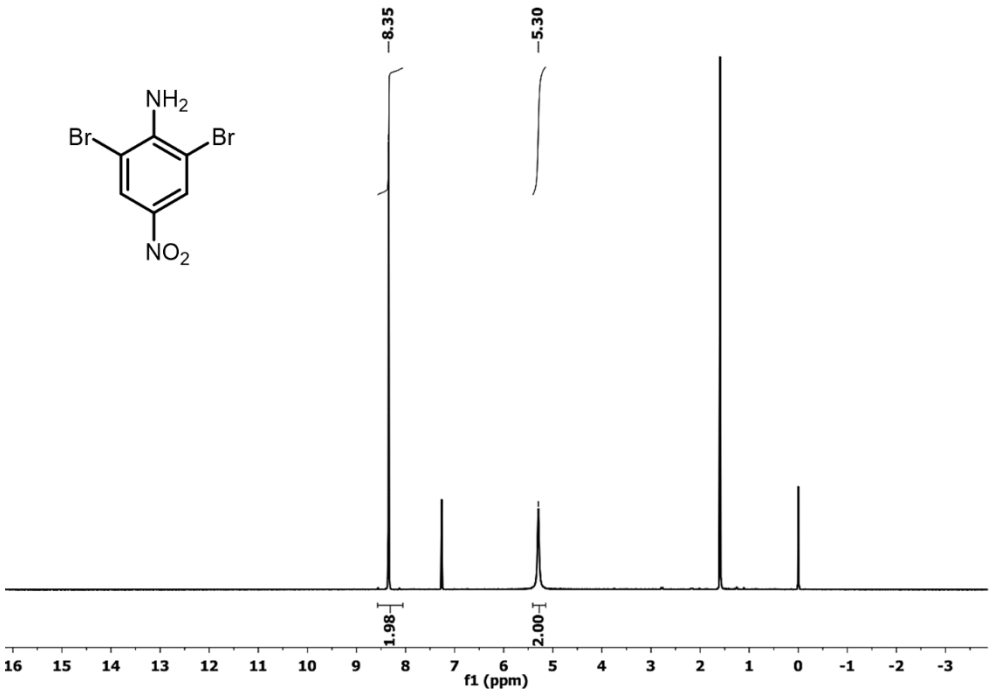


Figure S10. ^{1}H NMR spectrum of **5** in $CDCl_3$

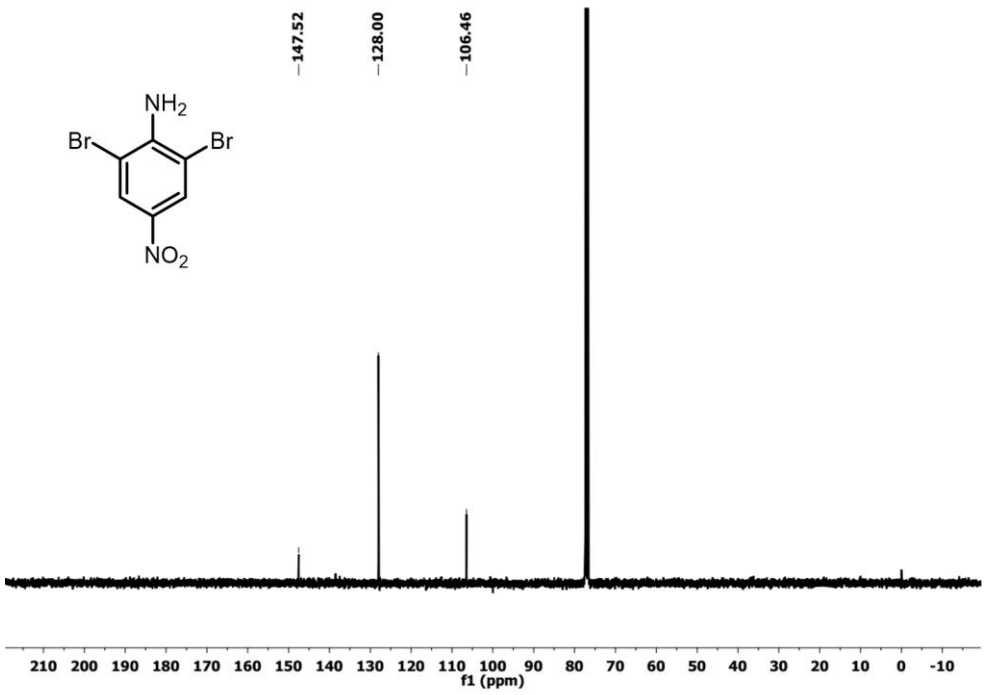


Figure S11. ^{13}C NMR spectrum of **5** in $CDCl_3$

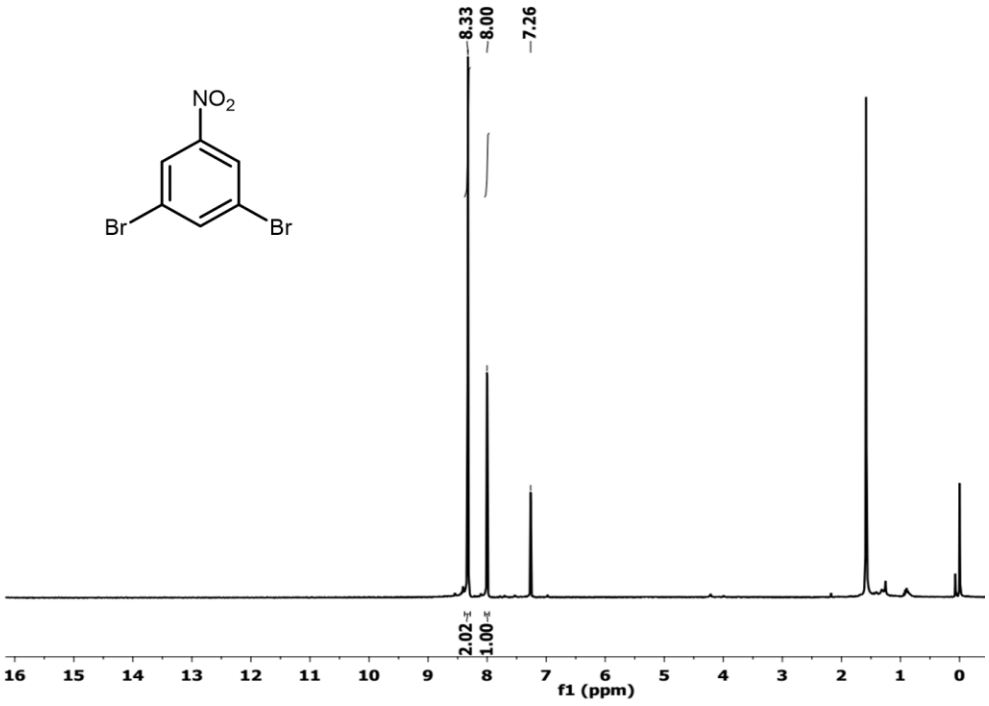


Figure S12. ^{1}H NMR spectrum of **6** in $CDCl_3$

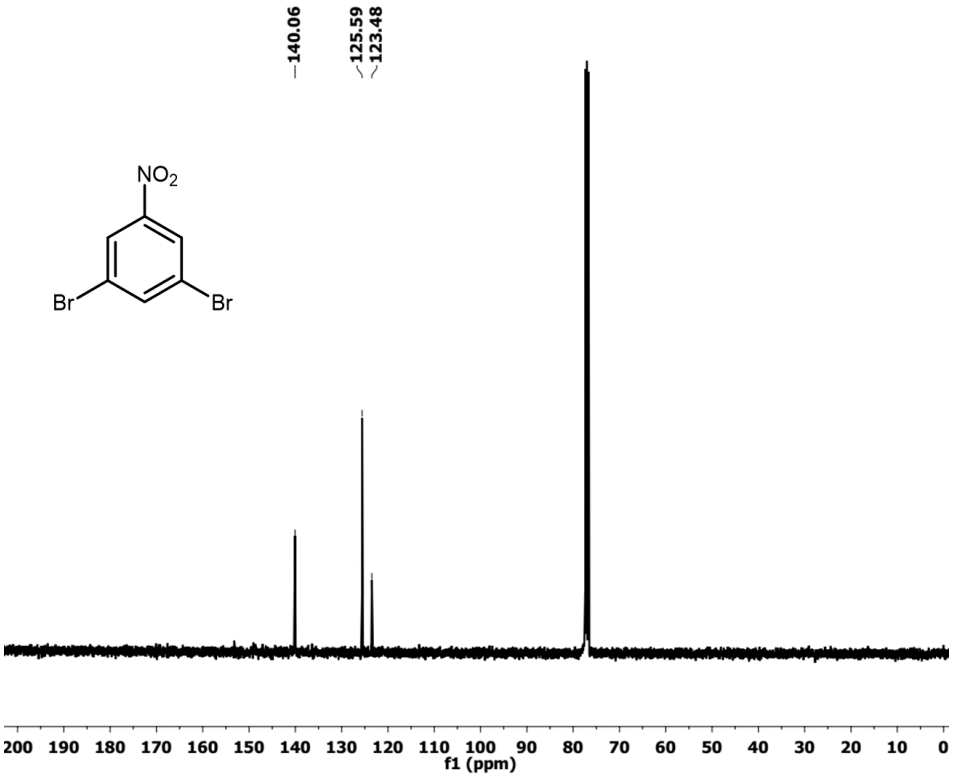


Figure S13. ^{13}C NMR spectrum of **6** in $CDCl_3$

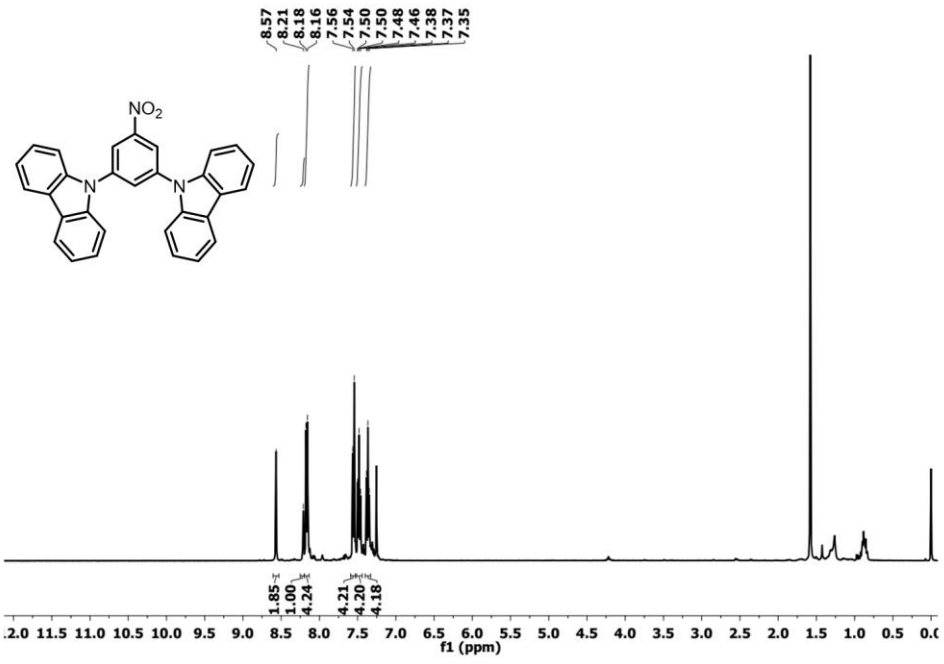


Figure S14. ^{1}H NMR spectrum of **7** in $CDCl_3$.

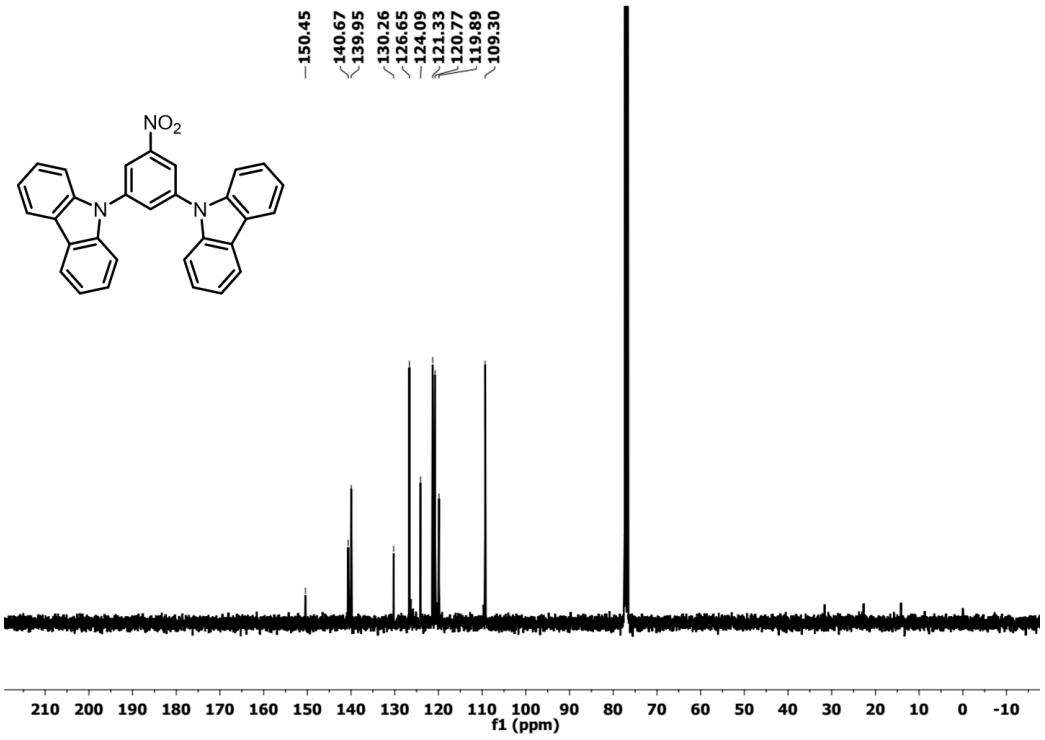


Figure S15. ^{13}C NMR spectrum of **7** in $CDCl_3$

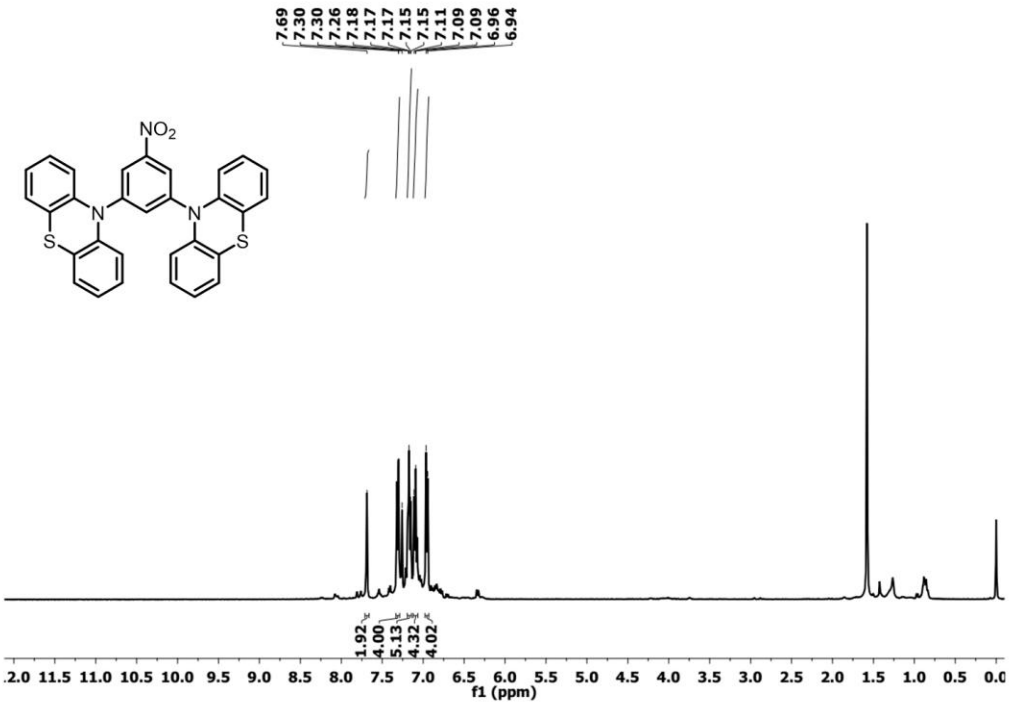


Figure S16. ^{1}H NMR spectrum of **8** in $CDCl_3$

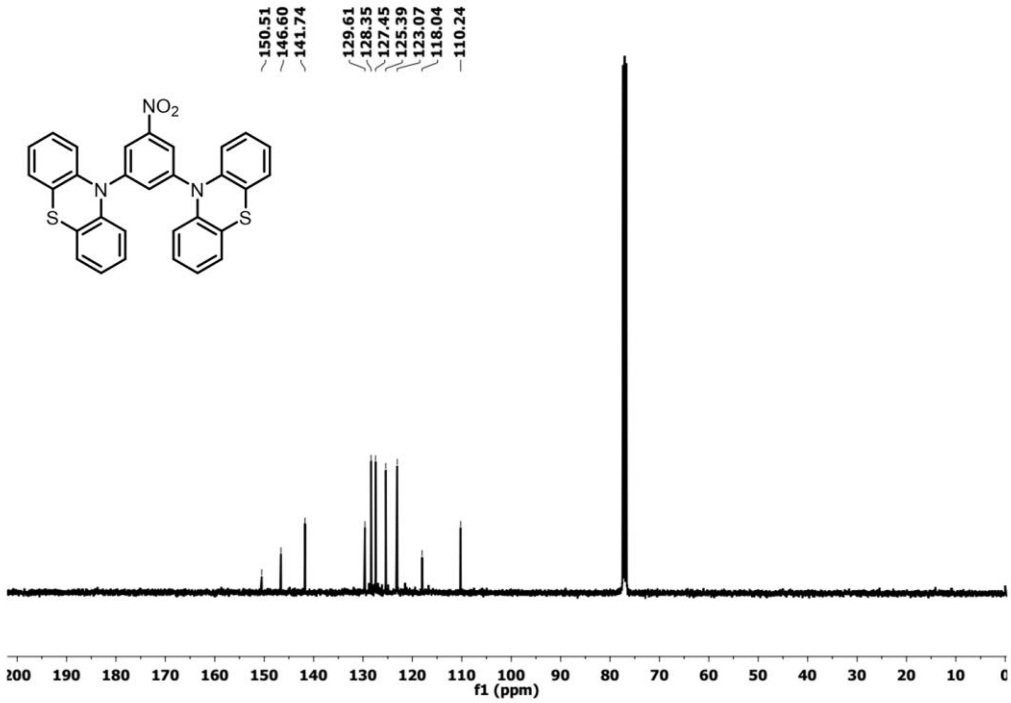


Figure S17. ^{13}C NMR spectrum of **8** in $CDCl_3$

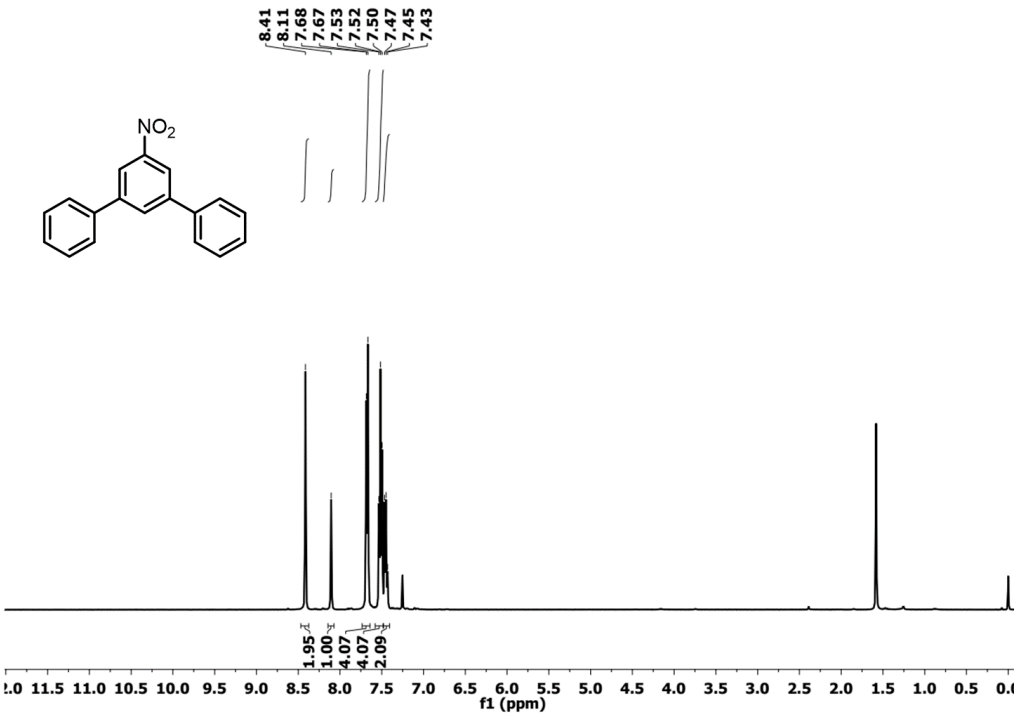


Figure S18. ^{1}H NMR spectrum of **9** in $CDCl_3$

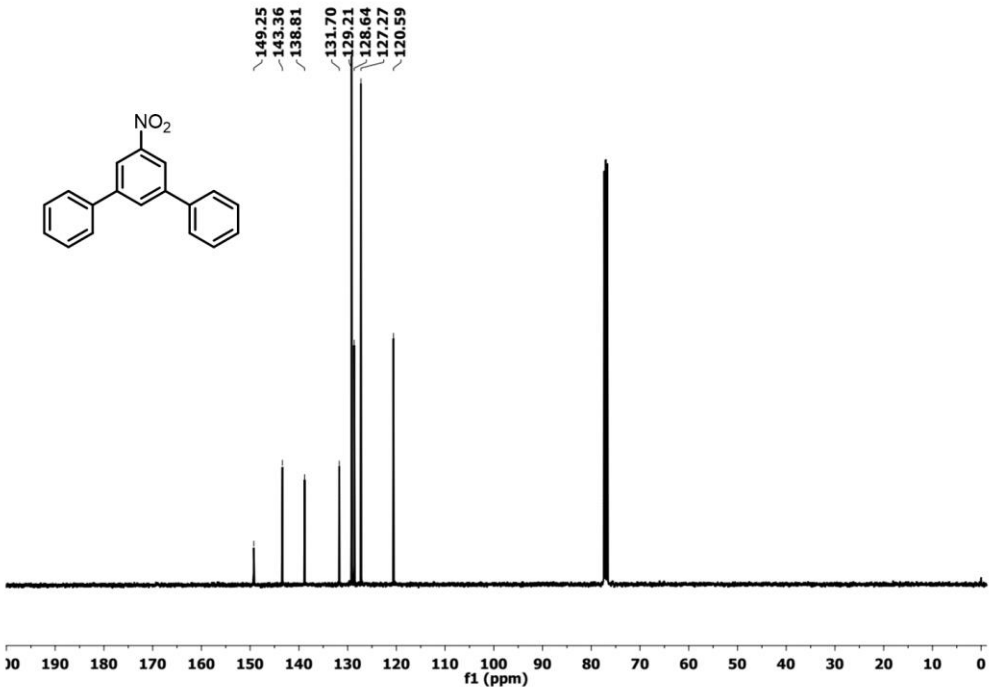


Figure S19. ^{13}C NMR spectrum of **9** in $CDCl_3$

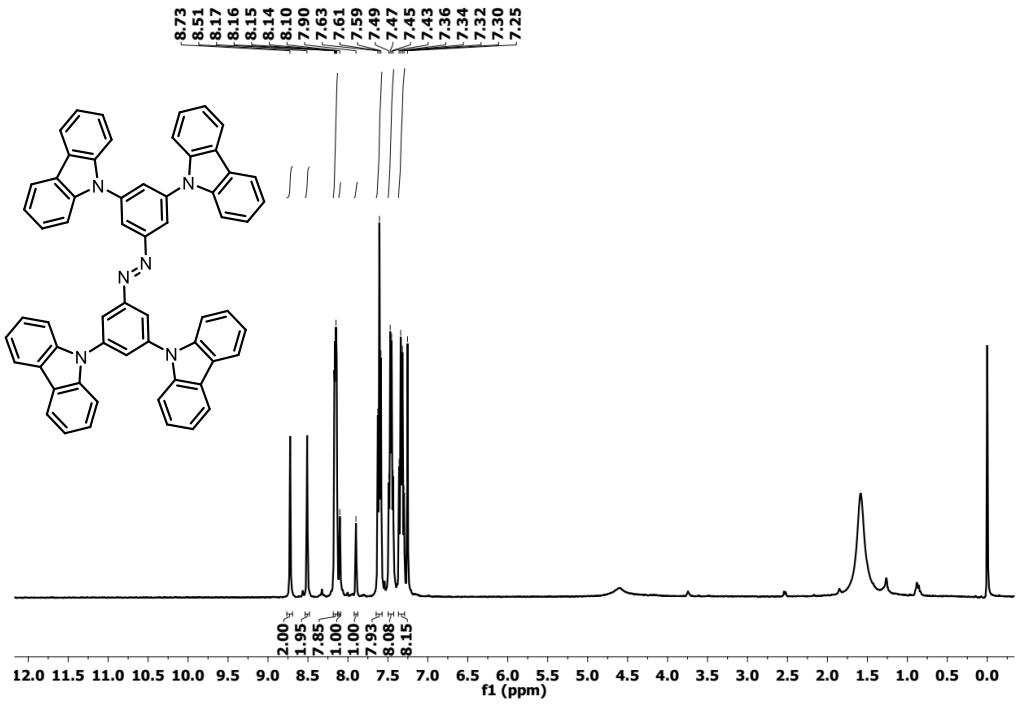


Figure S20. ^{1}H NMR spectrum of **1** in $CDCl_3$

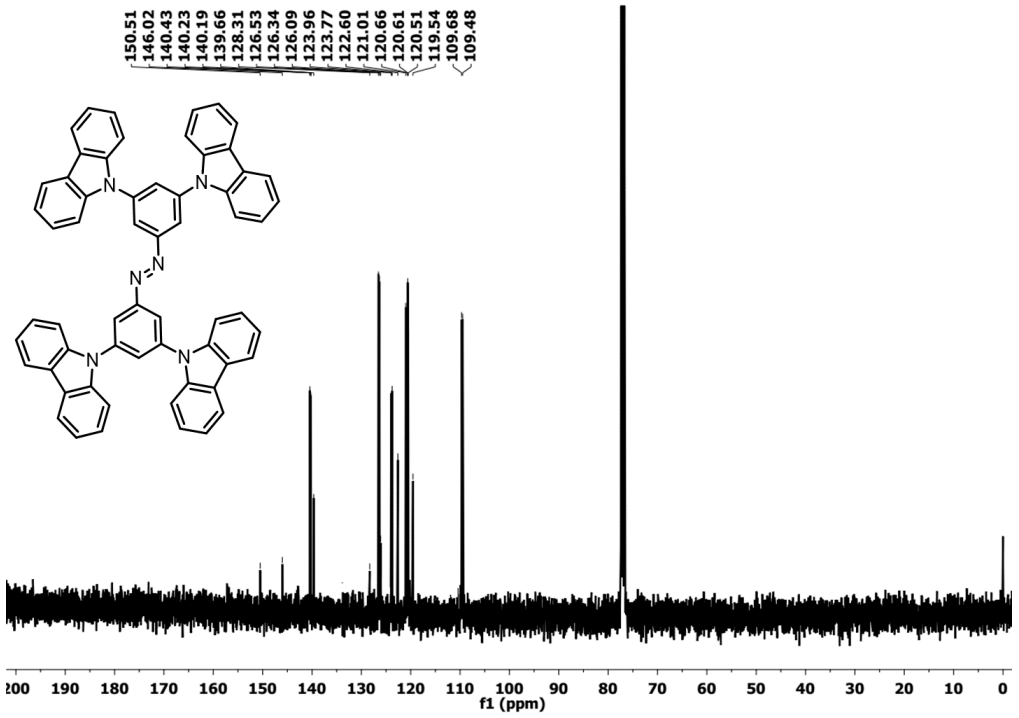


Figure S21. ^{13}C NMR spectrum of **1** in $CDCl_3$

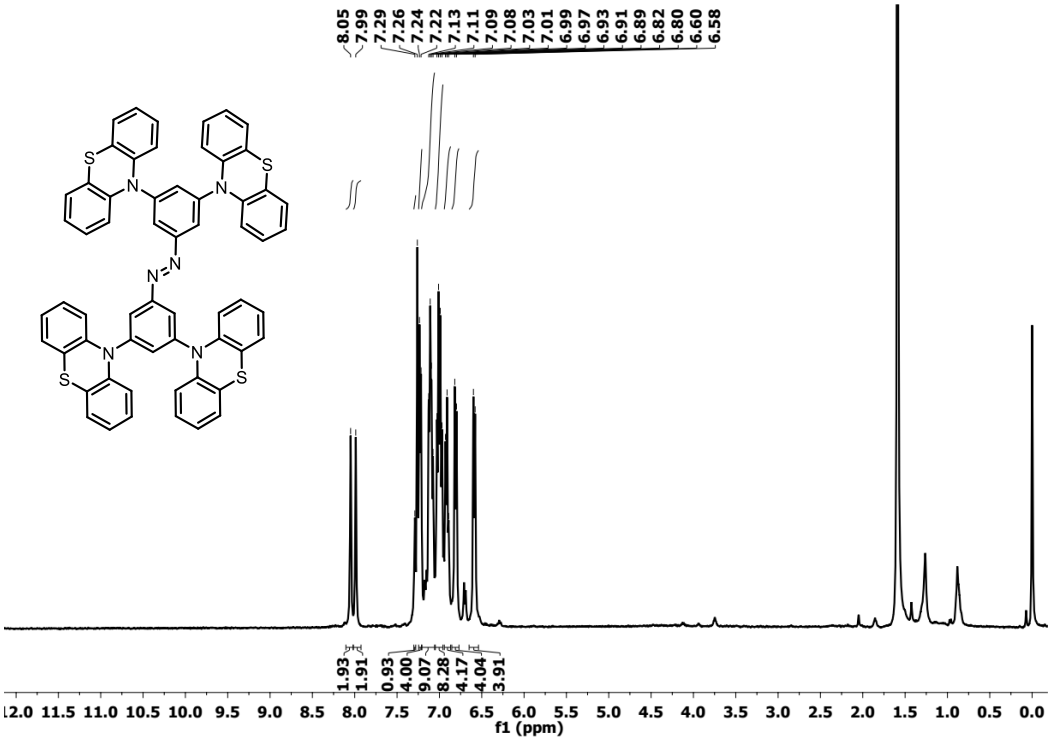


Figure S22. ^{13}H NMR spectrum of **2** in $CDCl_3$

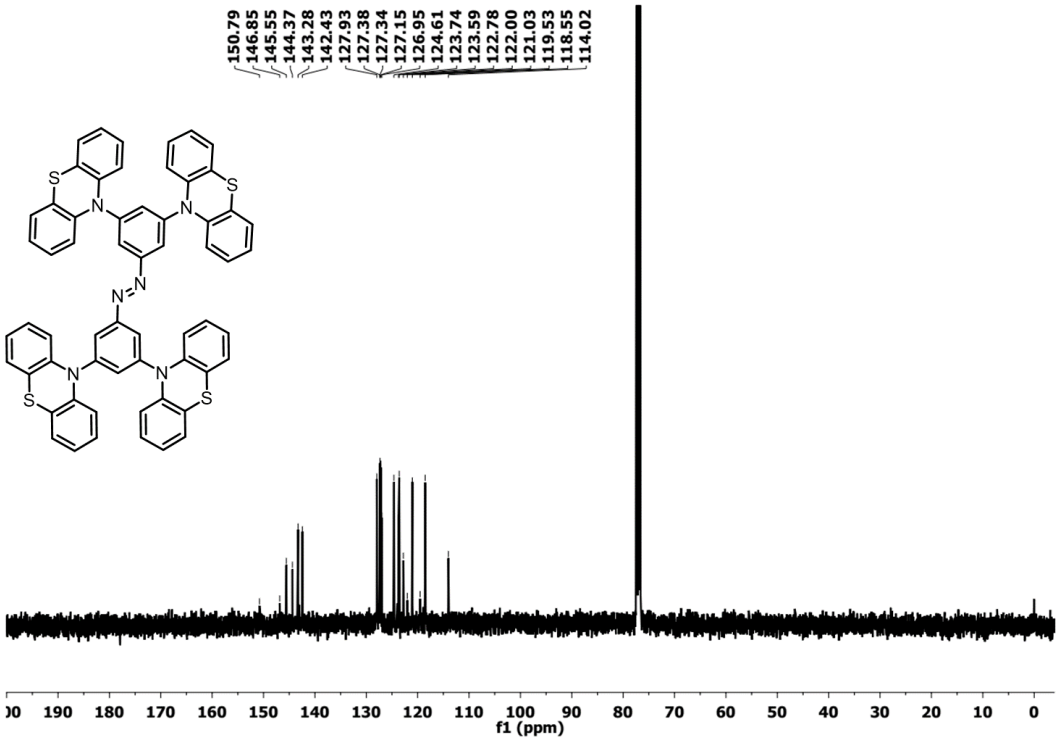


Figure S23. ^{13}C NMR spectrum of **2** in $CDCl_3$

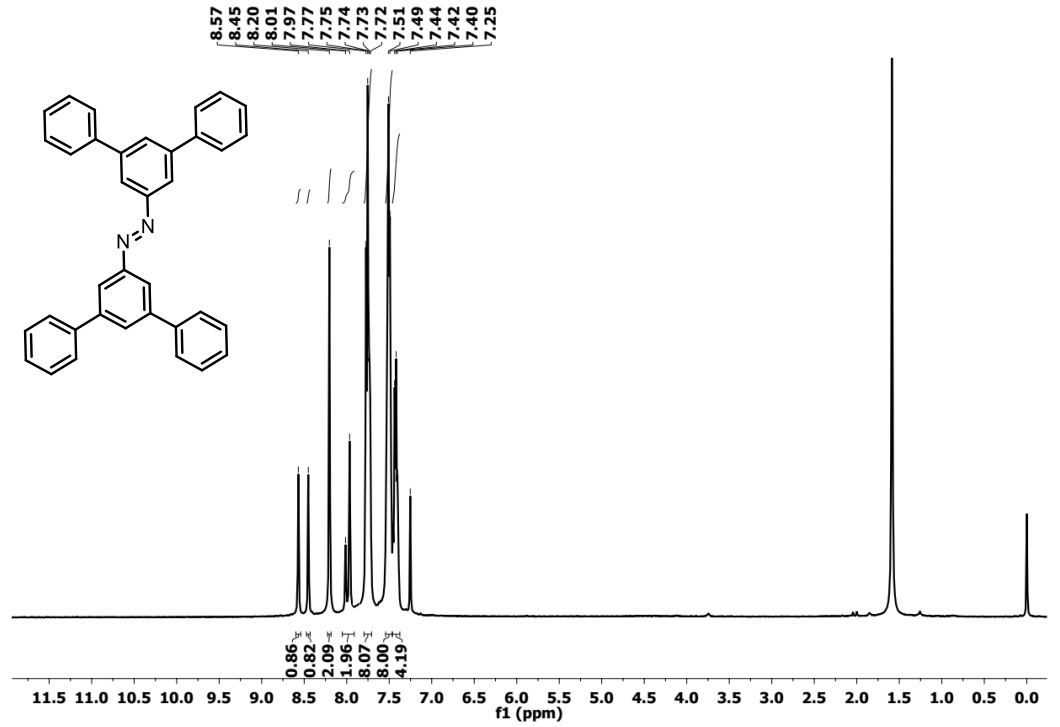


Figure S24. ^{1}H NMR spectrum of **3** in $CDCl_3$

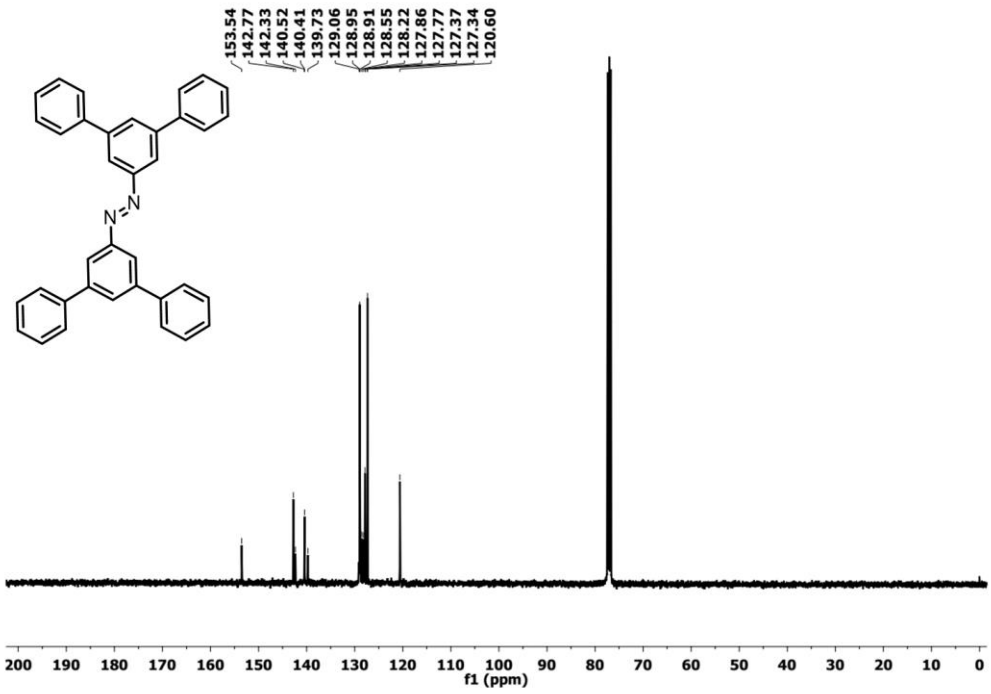


Figure S25. ^{13}C NMR spectrum of **3** in $CDCl_3$

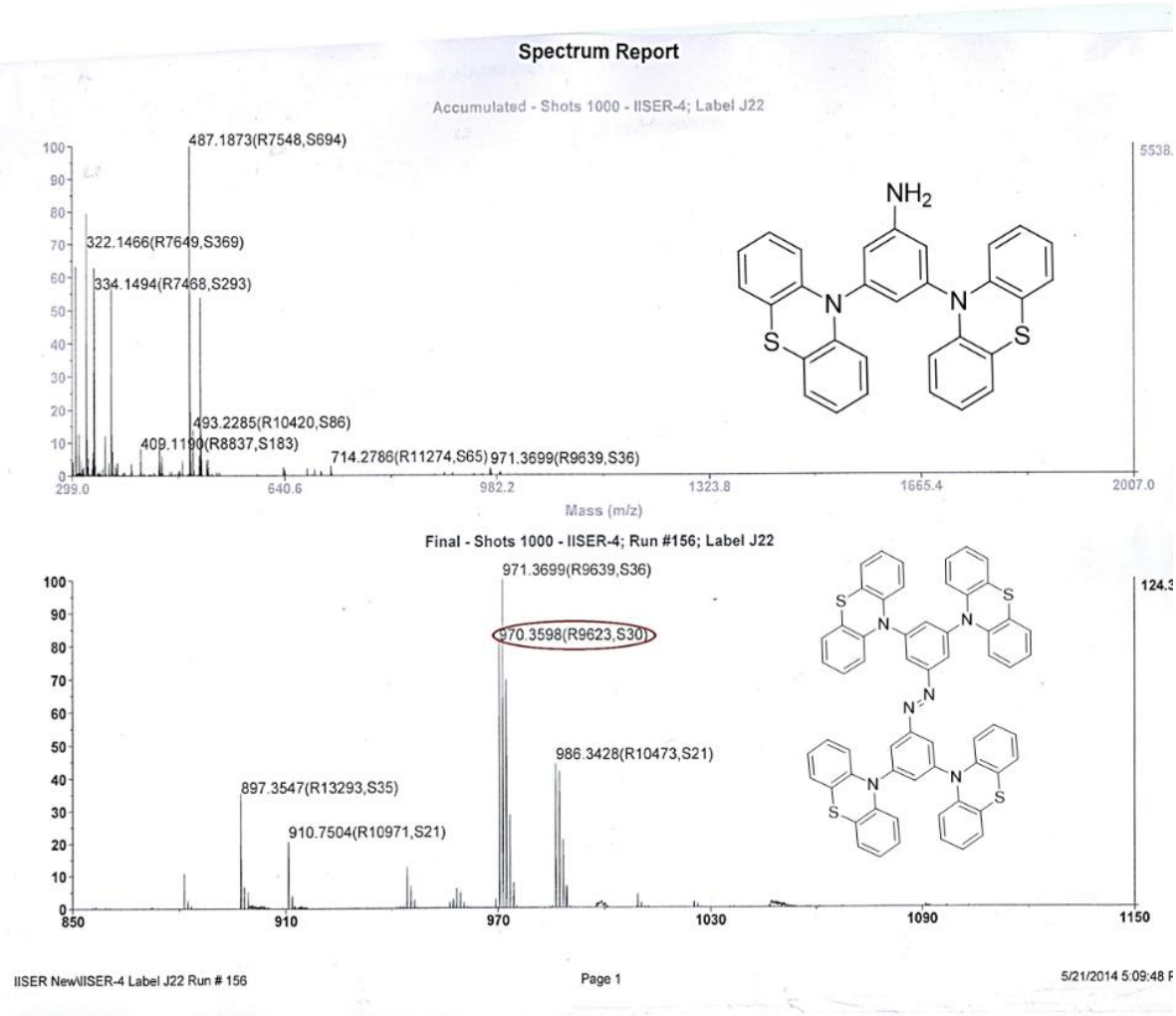


Figure S26. MALDI-TOF spectrum of **2**

Reference 31 with complete authors list:

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