

Electronic Supplementary Information for New Journal of Chemistry

Azine based AIEgens with multi-stimuli response towards picric acid

Munusamy Sathiyaraj^a, Kumaravelu Pavithra^a and Viruthachalam Thiagarajan^{a*}

^aSchool of Chemistry, Bharathidasan University, Tiruchirappalli-620 024, India

E-mail: v.thiagarajan@bdu.ac.in; vthiags@gmail.com

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Table S1. Photophysical data of different azine derivatives in various solvents

Compound	BA			DMBA			DEBA			DPBA			DAPA		
	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stoke's shift (cm^{-1})
Toluene	302	-	-	386	466	4447	391	486	4999	394	470	4104	406	483	3927
DCM	301	-	-	388	479	4897	397	473	4047	399	476	4054	407	500	4570
THF	300	-	-	384	467	4628	390	471	4410	392	473	4369	402	482	4129
MeOH	304	-	-	392	483	4807	401	486	4361	403	476	3805	406	524	5547
ACN	298	-	-	387	477	4875	393	476	4437	396	488	4761	400	510	5393
DMF	303	-	-	392	465	4005	398	479	4249	400	481	4210	406	504	4789
DMSO	304	-	-	395	477	4352	401	482	4191	404	483	4049	408	510	4902

Aggregation Induced Emission studies:

Table S2. Photophysical data of azine derivatives in the aggregated form (THF-water mixture)

Compounds	$\lambda_{\text{abs max}}$ (nm)	$\lambda_{\text{em max}}$ (nm)	$\Phi_{\text{F}}^{\text{a}}$ In AIE form	Fluorescence enhancement due to AIE (fold)
DMBA	401	496	0.0525	1923
DEBA	410	494	0.0729	1082
DPBA	410	487	0.0497	461
DABA	411	525	0.0327	77

^a Quantum yield measured at THF-water mixture having maximum fluorescence enhancement

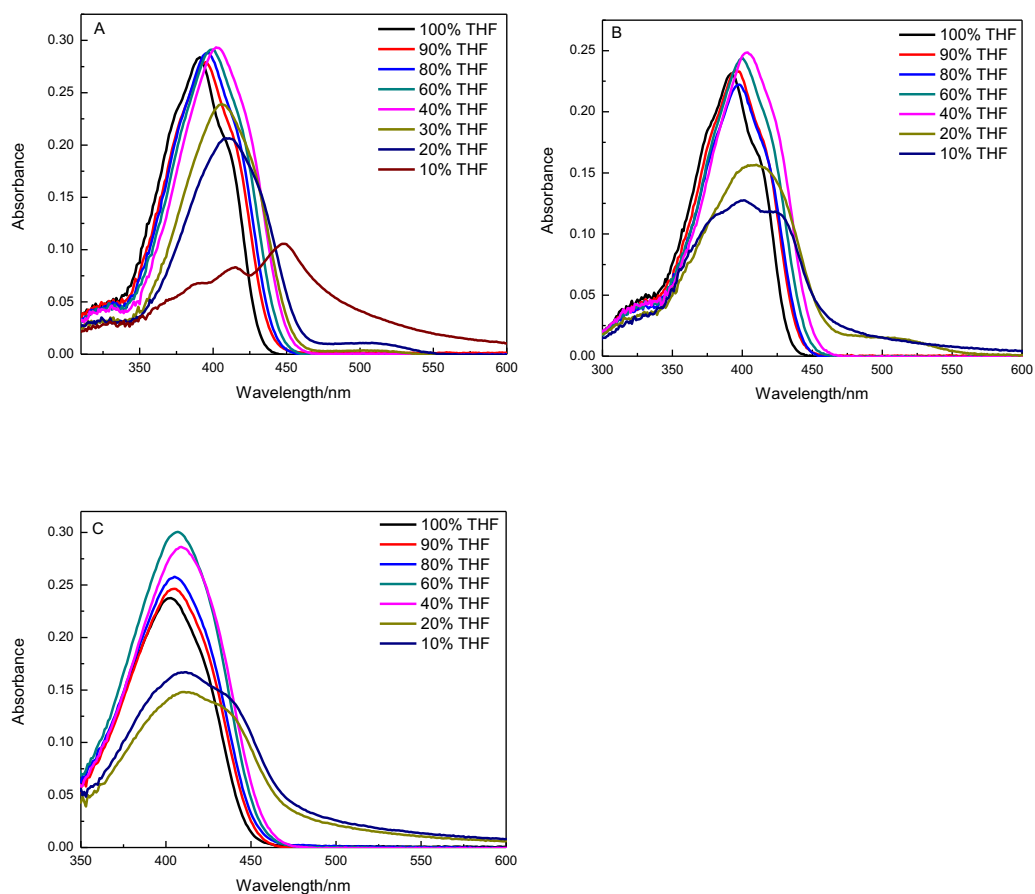


Figure S1. Absorption spectra of azine derivatives (5 μM) in different fraction of THF- water mixture. (A) DEBA; (B) DPBA and (C) DABA

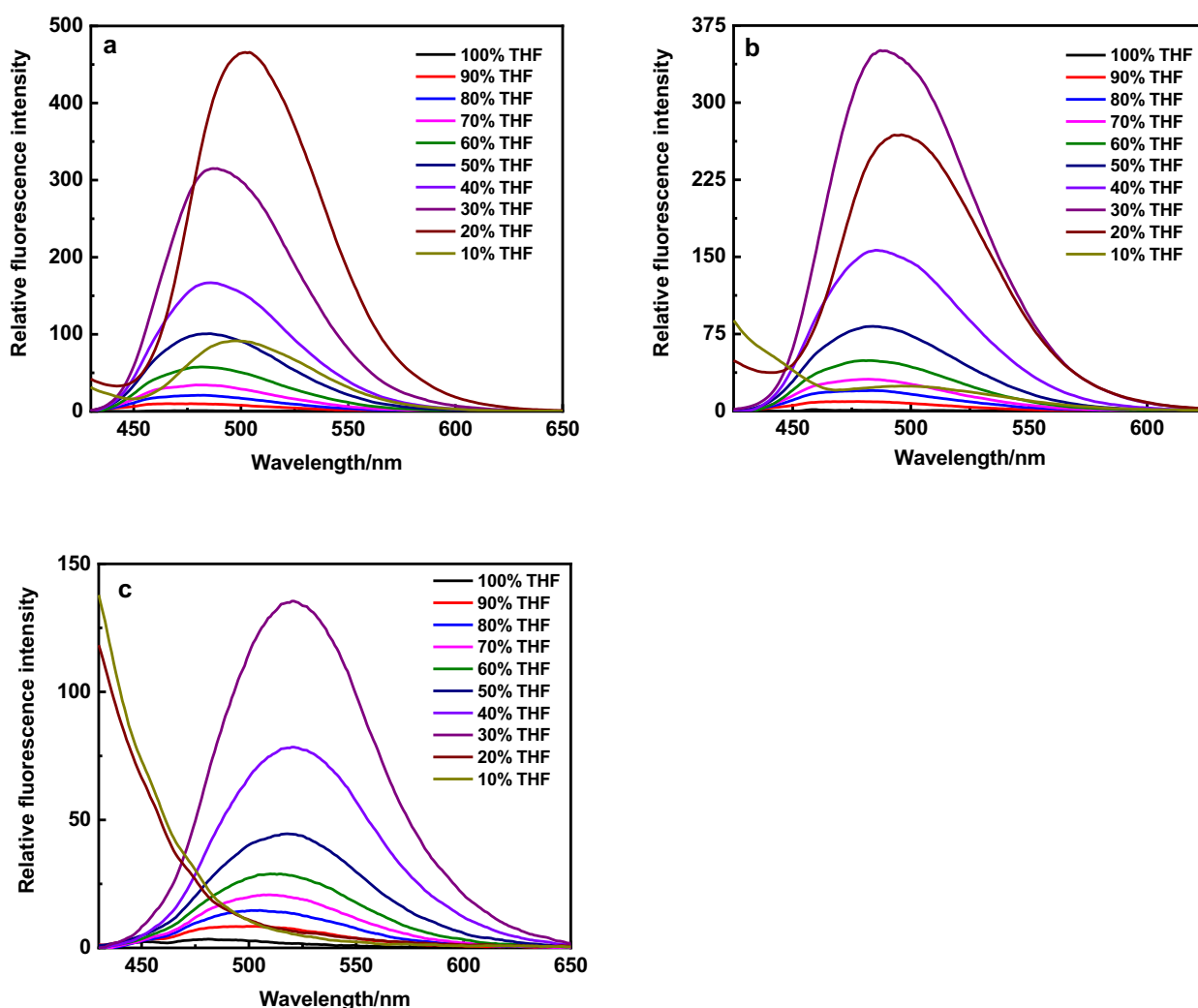


Figure S2. Emission spectra of azine derivatives (5 μ M) in different fraction of THF- water mixture. (a) DEBA($\lambda_{exc} = 392$ nm); (b) DPBA($\lambda_{exc} = 392$ nm) and (c) DABA($\lambda_{exc} = 403$ nm)

Restricted intramolecular rotation mechanism

To analyse the influence of viscosity on the azine derivatives, the fluorescence studies were carried out in methanol containing varying percentages of glycerol (Figure S3). The absorption spectrum shows a decrease in absorbance at the 390 nm band along with the formation of a new band at 500 nm with a clear isosbestic point at 427 nm on increasing the glycerol percentage. The new absorption band at 500 nm is very similar to the protonated species. The emission spectra given in Figure S3 clearly shows the increase in the emission intensity along with a red shift as the percentage of glycerol increases. The increase in viscosity restricts the intramolecular rotations and this induces the radiative process which leads to the strong emission around 500 nm similar to one in the aggregated state. Increase in viscosity restricts

both the intramolecular rotation as well as aggregate formation which results in less fluorescence enhancement compared to enhancement with the 85% water fraction. In addition to that, self-quenching by protonated species may also decrease the fluorescence intensity. With viscosity studies, we can confirm that the restriction of intramolecular rotation leads to increase in fluorescence enhancement via a decrease in non-radiative deactivation pathways.

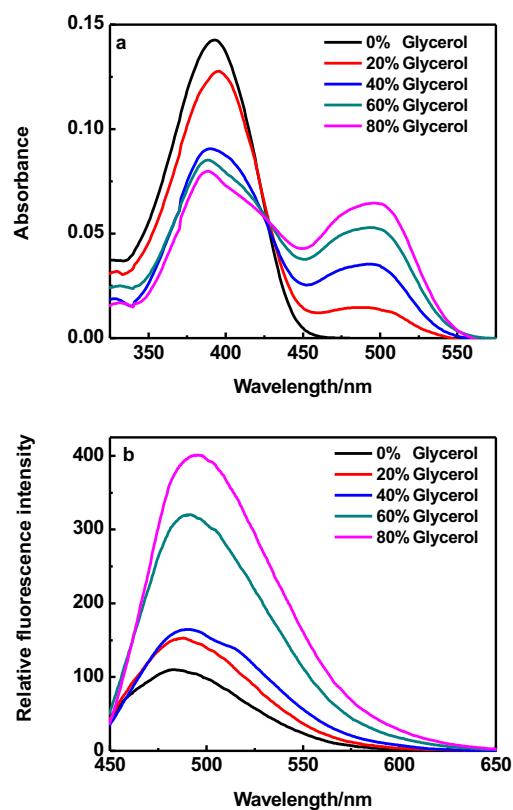


Figure S3. (a) Absorption and (b) emission spectrum of DMBA (10 μ M) λ_{exc} = 425 nm in methanol with varying percentage of glycerol.

Picric acid detection in THF

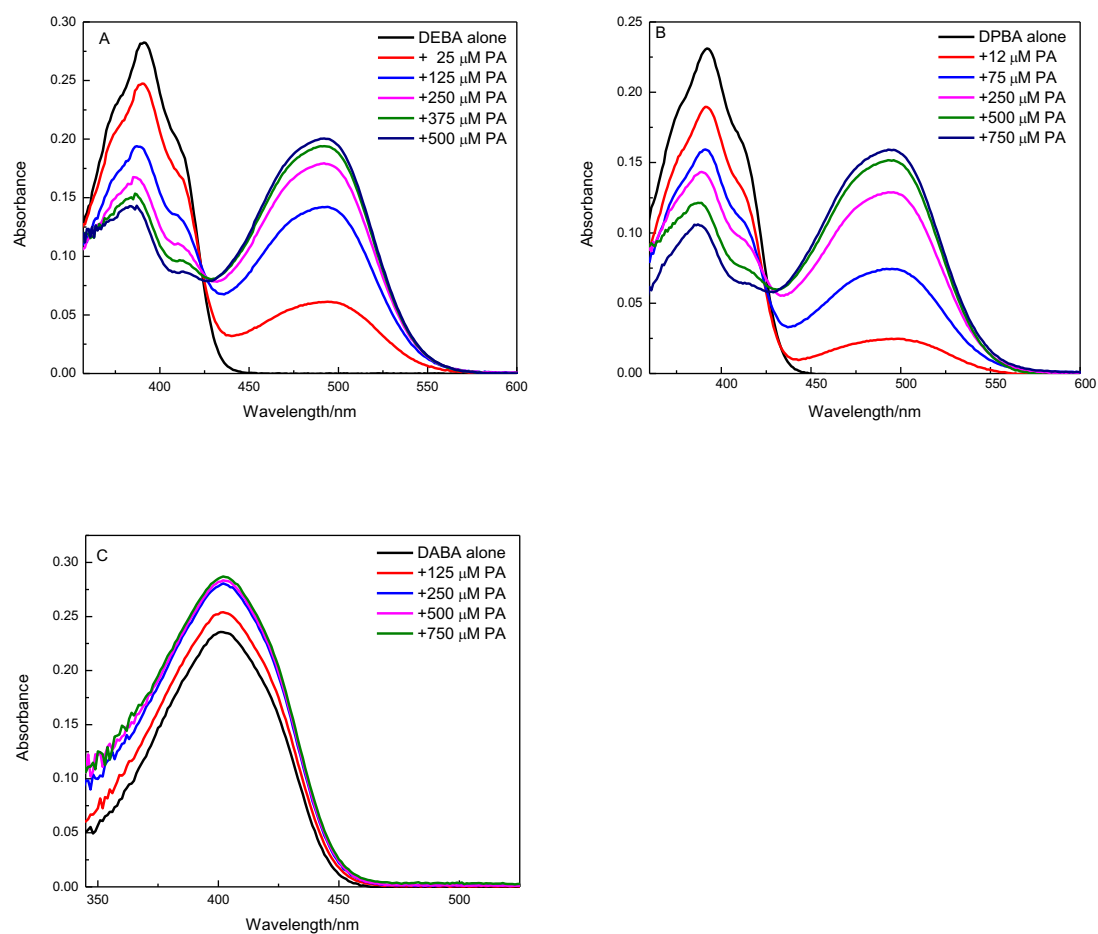


Figure S4. Absorption spectra of azine derivatives (5 μM) in the presence and absence of picric acid in pure THF. (A) DEBA; (B) DPBA and (C) DABA

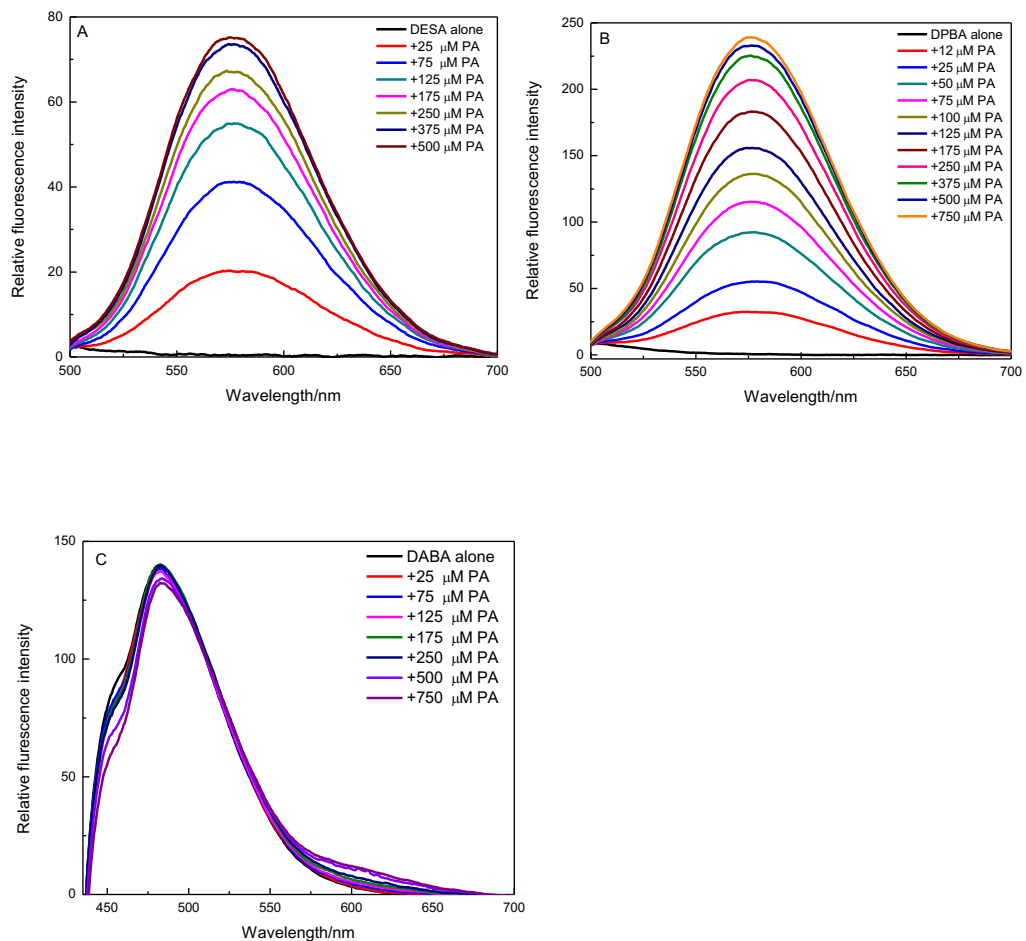


Figure S5. Emission spectra of azine derivatives (5 μM) in the presence and absence of picric acid in pure THF. (A) DEBA ($\lambda_{\text{exc}} = 425 \text{ nm}$); (B) DPBA ($\lambda_{\text{exc}} = 425 \text{ nm}$) and (C) DABA ($\lambda_{\text{exc}} = 401 \text{ nm}$).

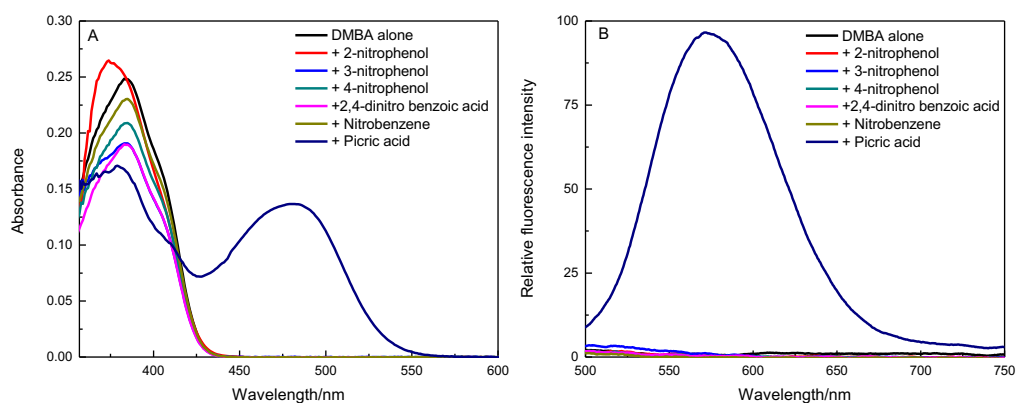


Figure S6 . Absorption (A) and emission (B) spectrum of DMBA (5 μM) in the absence and presence of 125 equivalents of different explosive compounds (625 μM) in THF, $\lambda_{\text{exc}} = 415 \text{ nm}$.

Table S3. Photophysical data of azine derivatives in the presence and absence of picric acid in THF.

Compounds	λ_{absmax} (nm)	λ_{emmax} (nm)	Fluorescence enhancement in the presence of PA	Detection limit of PA
DMBA	384, 480	467, 574	133	26 μM
DEBA	390, 491	471, 576	171	44 μM
DPBA	392, 493	473, 577	478	49 μM
DABA	402	482	-	0.6 mM

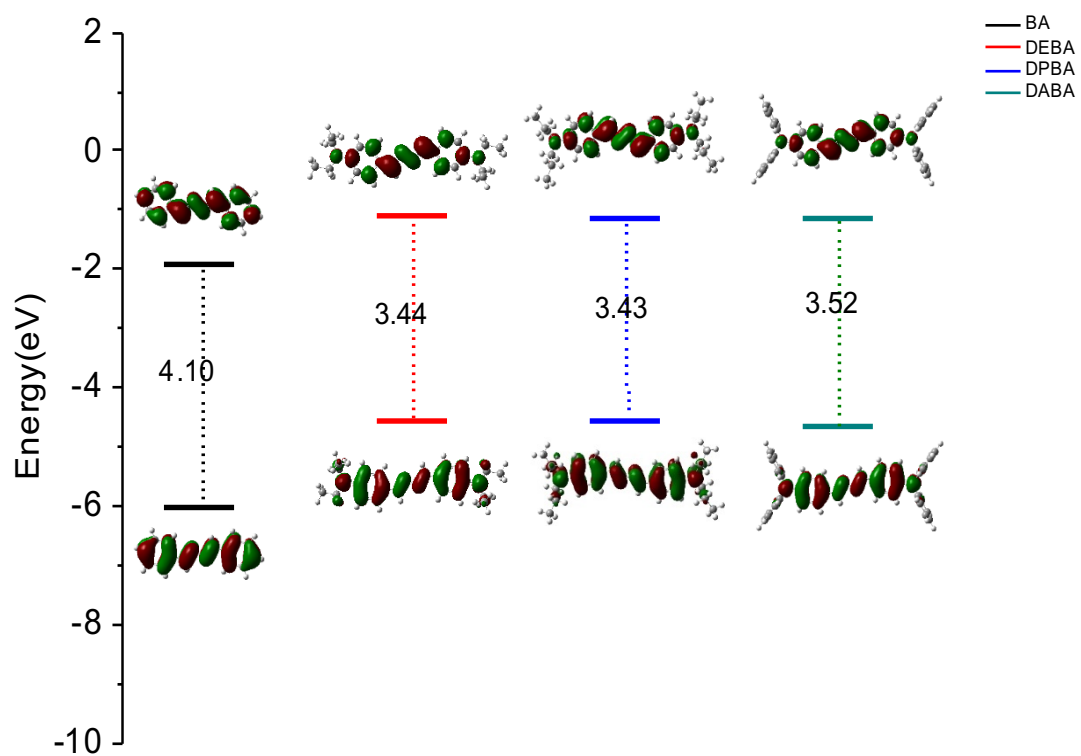


Figure S7. HOMO-LUMO gap and orbital distribution of the HOMO and LUMO for azine derivatives

Table S4. Theoretical band gap data of DMBA in vacuum and THF in comparison with the experimental values

Azine molecule	Experimental band gap obtained from absorption spectrum (eV)	Theoretical band gap without counterion in vacuum (eV)	Theoretical band gap without counterion in THF (eV)	Theoretical band gap energy with chloride counterion in THF (eV)
DMBA	3.23	3.45	3.30	-
DMBA-H ⁺	2.57	2.49	2.97	3.14 (DMBA-H ⁺ Cl ⁻)
⁺ H-DMBA-H ⁺	-	4.14	4.15	5.61 (Cl ⁻ H ⁺ -DMBA- H ⁺ Cl ⁻)

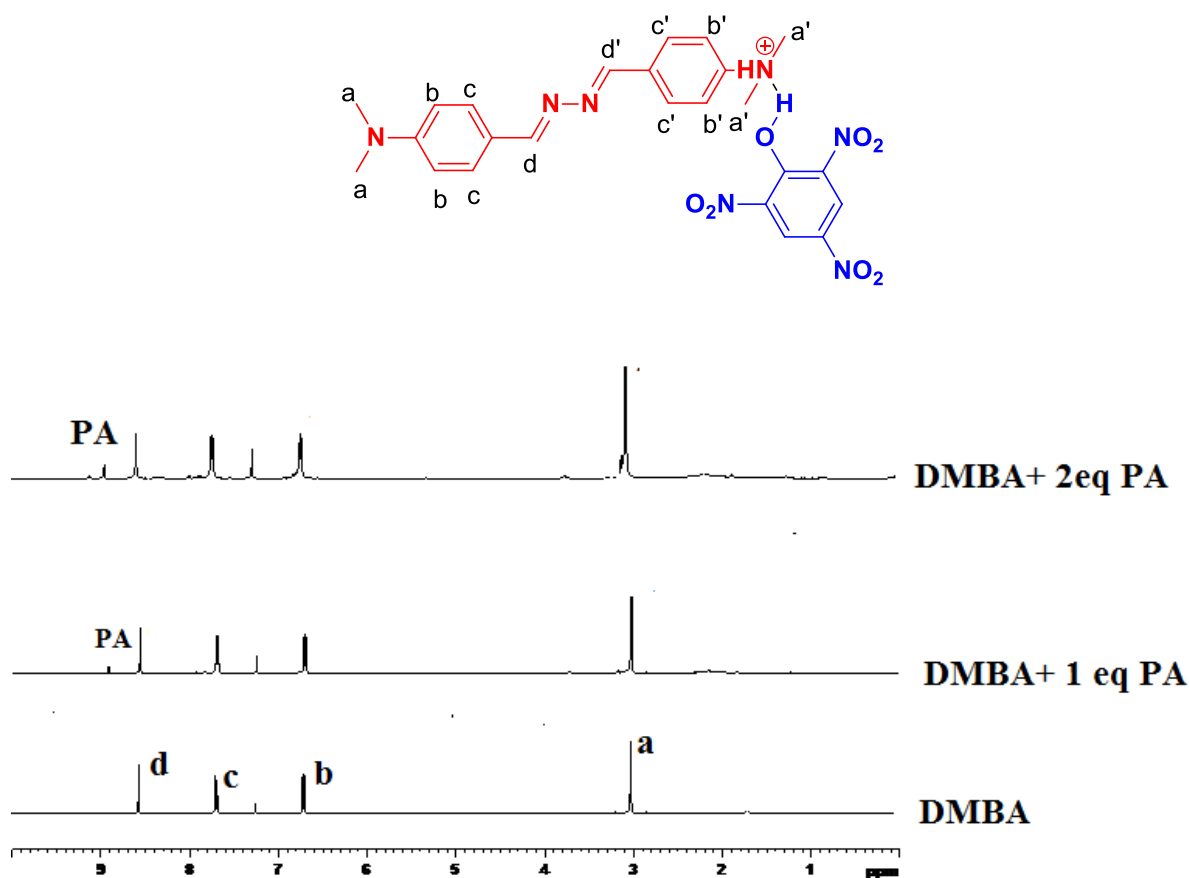


Figure S8. ¹H NMR spectra of DMBA before and after addition of picric acid

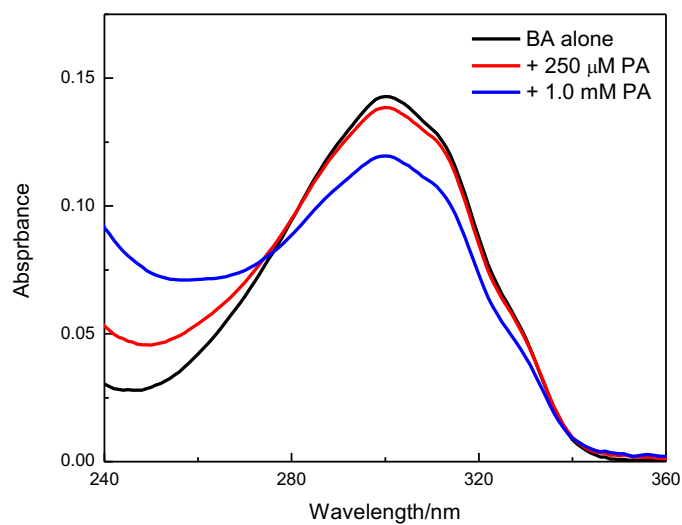


Figure S9. Absorption spectrum of BA (5 μM) in the presence and absence of picric acid in THF.

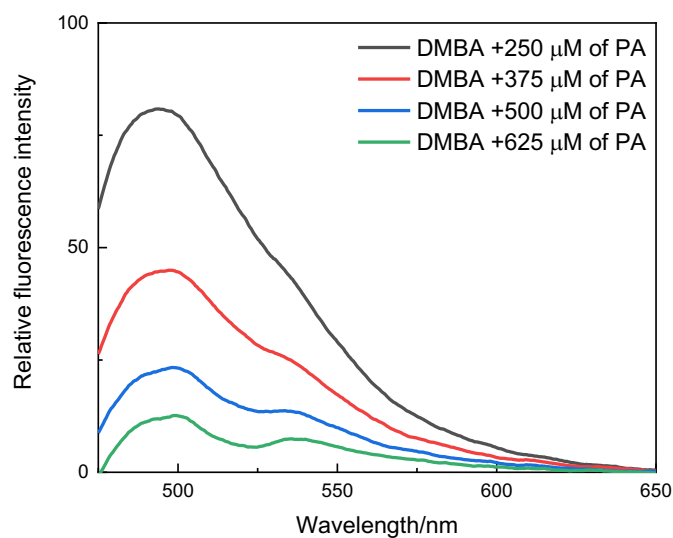


Figure S10. Emission spectrum of DMBA (5 μM) in the presence of higher concentration of picric acid in THF/water (3:7) mixture.

PA detection in aqueous mixture:

Table S5. Photophysical data of azine derivatives in the presence and absence of picric acid in THF/water (3:7) mixture.

Compounds	λ_{absmax} (nm)	λ_{emmax} (nm)	Detection limit of PA
DMBA	400, 495	496	38 μM
DEBA	405, 500	494	76 μM
DPBA	407, 504	487	46 μM
DABA	415	525	138 μM

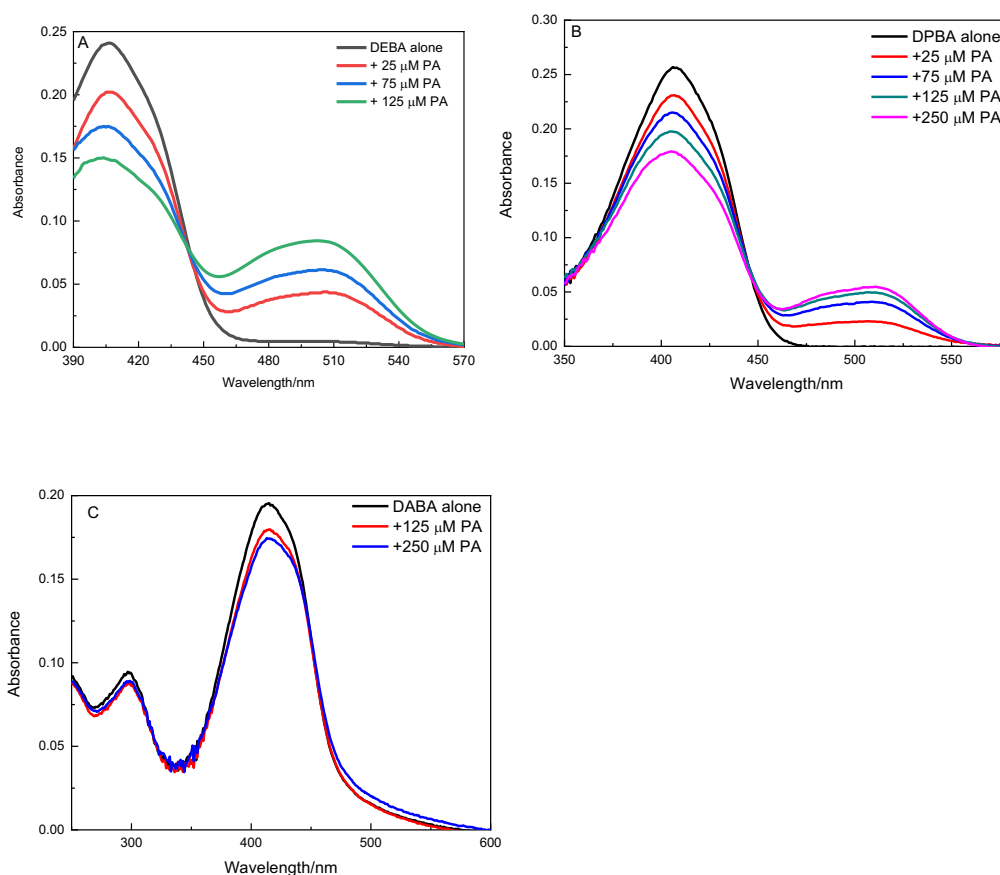


Figure S11. Absorption spectra of azine derivatives (5 μM) in the presence and absence of picric acid in THF/water (3:7) mixture. (A) DEBA; (B) DPBA and (C) DABA

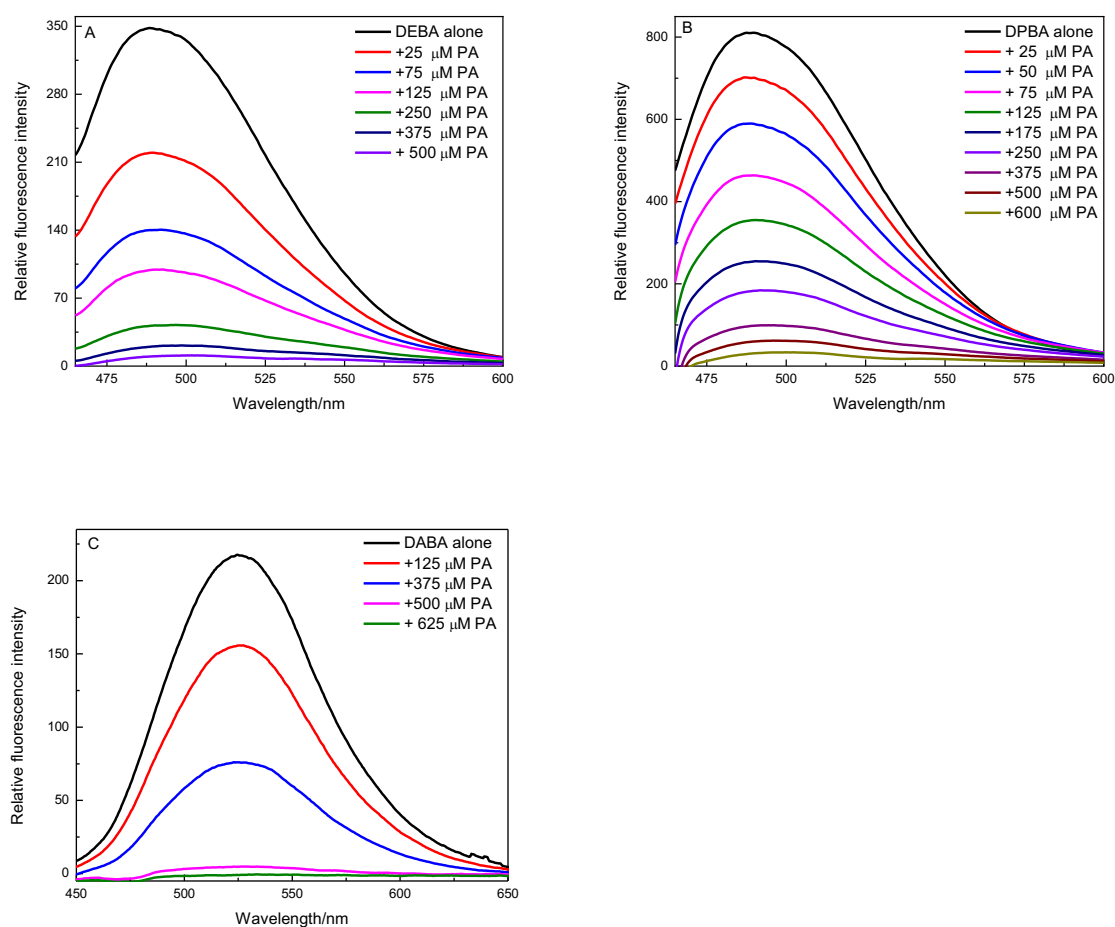


Figure S12. Emission spectra of azine derivatives (5 μM) in the presence and absence of picric acid in THF/water (3:7) mixture. (A) DEBA ($\lambda_{\text{exc}} = 425 \text{ nm}$); (B) DPBA ($\lambda_{\text{exc}} = 446 \text{ nm}$) and (C) DABA ($\lambda_{\text{exc}} = 456 \text{ nm}$)

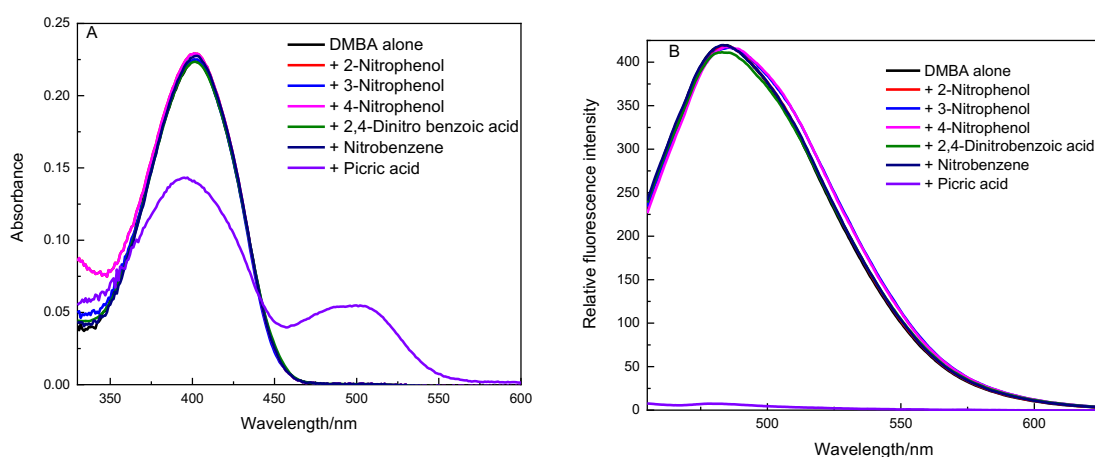


Figure S13. (A) Absorption and (B) emission spectrum of DMBA (5 μM) in the absence and presence of 125 equivalents of different explosive compounds (625 μM) in THF/water (3:7) mixture, $\lambda_{\text{exc}} = 443 \text{ nm}$.

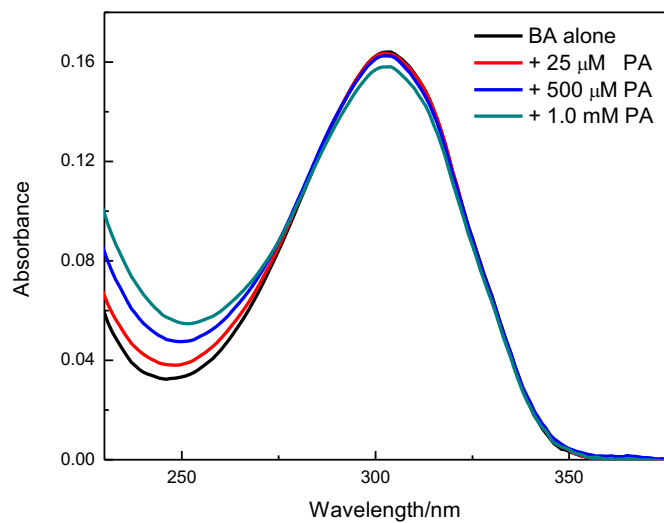


Figure S14. Absorption spectrum of BA (5 μM) in the presence and absence of picric acid in THF/water (3:7) mixture.

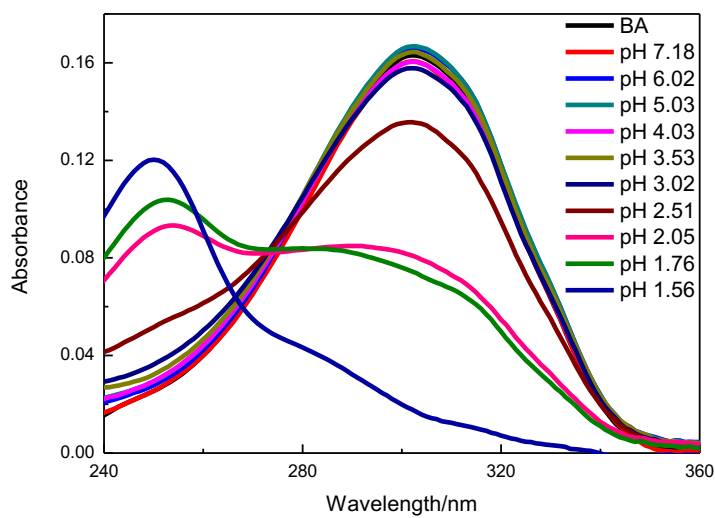


Figure S15. Absorption spectrum of BA (5 μM) in different pH in THF/water (3:7) mixture.

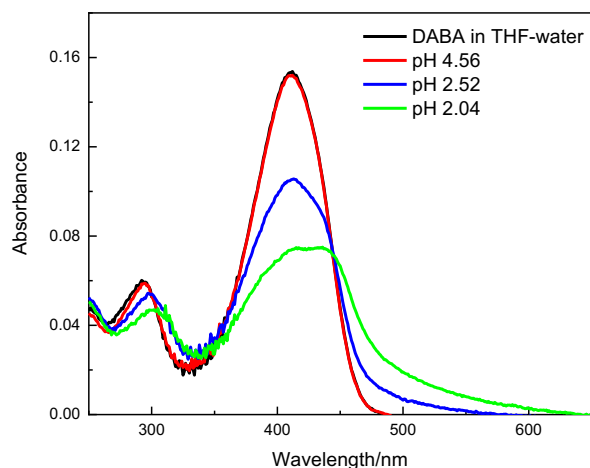


Figure S16. Absorption spectrum of DABA in different pH in THF/water (3:7) mixture.

Determination of Fluorescent quantum yield

Fluorescence quantum yields were obtained from the corrected fluorescence spectra using the expression,

$$\Phi_f = (A_s/A_r) (a_s/a_r) (n_s / n_r)^2 \times 0.54$$

Where, A_s and A_r are the area under the corrected fluorescence spectrum, a_s and a_r are the absorbances at the wavelength of excitation, and n_s and n_r are the refractive indices of the solvent for the sample and reference, respectively. Quinine sulphate in 0.1 N sulphuric acid was used as the reference for the quantum yield determination (Φ_f of quinine sulphate is 0.546).

Limit of detection:

The limit of detection (LOD) of PA for azine molecules were calculated from a fluorescence titration using the earlier literature. To determine the S/N ratio, the fluorescence intensity of azine molecules without PA was measured ten times and the standard deviation of blank measurements was determined. The fluorescence intensity plot $[I/I_0-1]$ varies linearly vs. the concentration of PA. The limit of detection was then calculated from the following equation,

$$\text{LOD} = 3\sigma/k$$

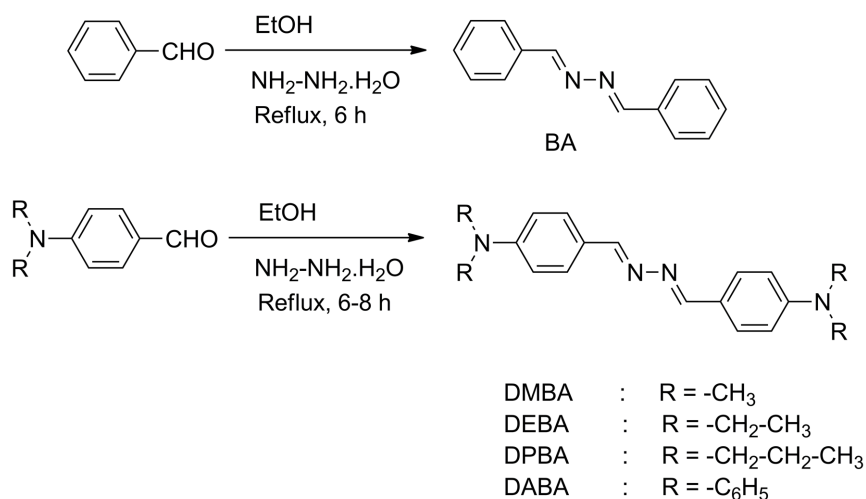
Where σ is the standard deviation of blank measurements, k is the slope obtained from the plot of $[I/I_0-1]$ versus PA concentration.

Fluorescence lifetime:

The fluorescence lifetime of azine derivatives were measured in pure THF and found to be in the order of 0.2 ns [DMBA(0.25), DEBA(0.28), DPBA(0.23) and DABA (0.24)]. The lifetime of azine derivatives in THF-water mixture and in the presence of picric acid were found to be shorter than the instrument response of our TCSPC instrument (> 150 ps).

Synthesis and characterization of azine derivatives:

Two equivalents of the corresponding aldehyde dissolved in 5mL of ethanol and then one equivalent of hydrazine monohydrate in ethanol was added dropwise along with stirring. The above reaction mixture was stirred for 6 h at 80 °C and then the formed product was filtered, washed several times with ethanol and dried. The final dried product was recrystallized using dichloromethane- ethanol mixture.



BA

¹H NMR (400 MHz, CDCl₃) δ : 8.67(s, 2H), 7.86(m, 4H), 7.46(m, 6H); ¹³C NMR (400MHz, CDCl₃) δ : 162.13, 134.11, 131.25, 128.83, 128.60. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for C₁₄H₁₃N₂ 209.1073; found: 209.1074.

DMBA

^1H NMR (400 MHz, CDCl_3) δ : 8.57(s, 2H), 7.71(d, 4H), 6.72(d, 4H), 3.02(s, 12H); ^{13}C NMR (400MHz, CDCl_3) δ : 160.80, 152.12, 129.88, 122.25, 111.75, 40.20. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_4$ 295.1917; found: 295.1917.

DEBA

^1H NMR (400 MHz, CDCl_3) δ : 8.56(s, 2H), 7.68(d, 4H), 6.68(d, 4H), 3.43(q, 4H), 1.21(t, 6H); ^{13}C NMR (400MHz, CDCl_3) δ : 160.58, 149.64, 130.14, 121.39, 111.13, 44.49, 12.65. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{30}\text{N}_4$ 350.2470; found: 350.2531.

DPBA

^1H NMR (400 MHz, CDCl_3) δ : 8.54(s, 2H), 7.66(d, 4H), 6.65(d, 4H), 3.30(t, 8H), 1.68(m, 8H), 0.96(t, 12H); ^{13}C NMR (400MHz, CDCl_3) δ : 160.54, 150.08, 130.04, 121.30, 111.22, 52.82, 20.48, 11.45. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{39}\text{N}_4$, 407.3169; found: 401.3163.

DAPA

^1H NMR (400 MHz, CDCl_3) δ : 8.59(s, 2H), 7.68(d, 4H), 7.32(m, 8H), 7.16(m, 16H); ^{13}C NMR (400MHz, CDCl_3) δ : 160.97, 150.50, 146.99, 129.58, 129.51, 127.27, 125.44, 124.01, 121.68. HRMS (ESI-TOF) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{38}\text{H}_{31}\text{N}_4$, 543.2543; found: 543.2543.

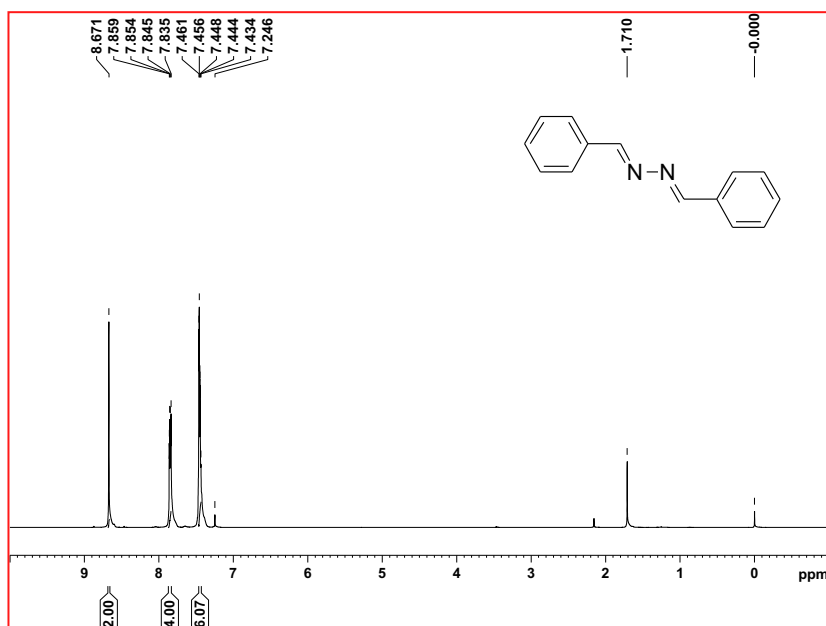


Figure S17. ^1H NMR Spectrum of BA in CDCl_3

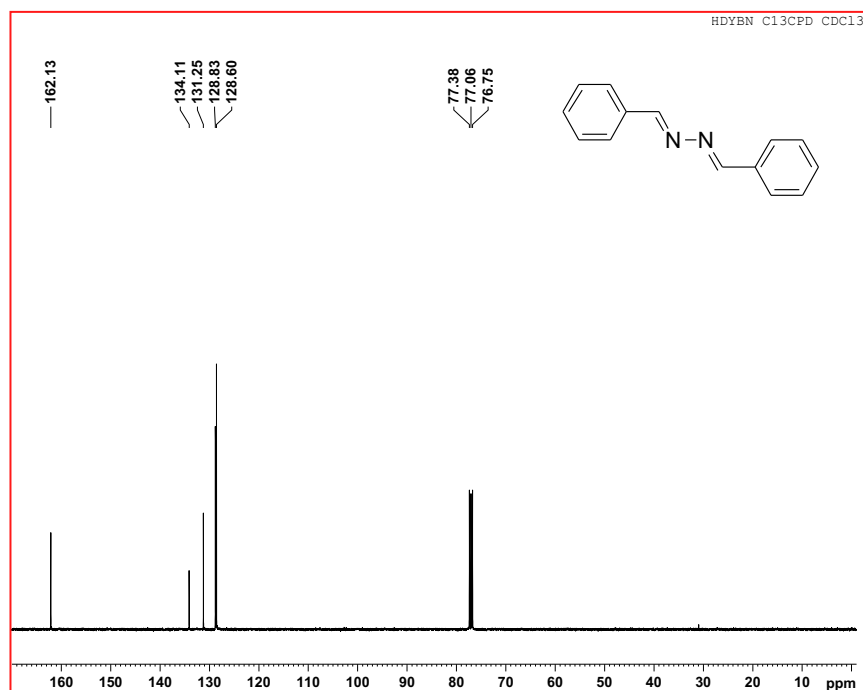


Figure S18. ^{13}C NMR Spectrum of BA in CDCl_3

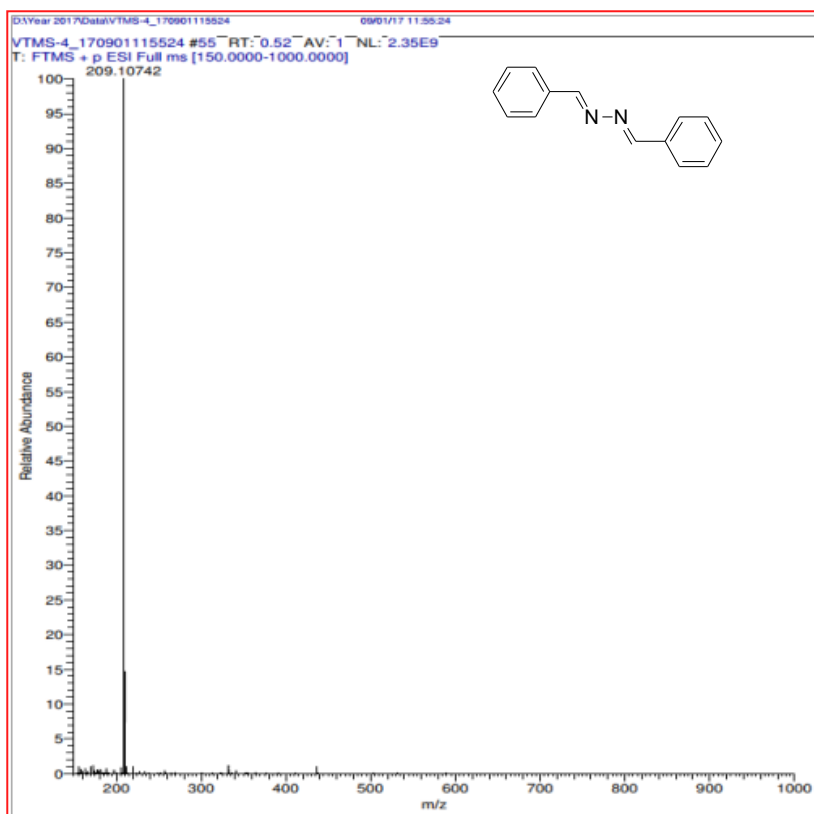


Figure S19. Mass Spectrum of BA

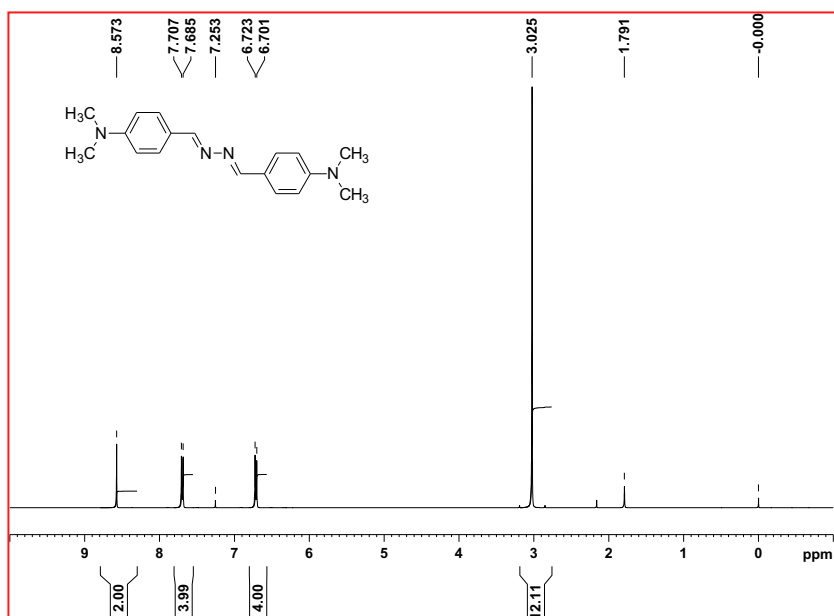


Figure S20. ^1H NMR Spectrum of DMBA in CDCl_3

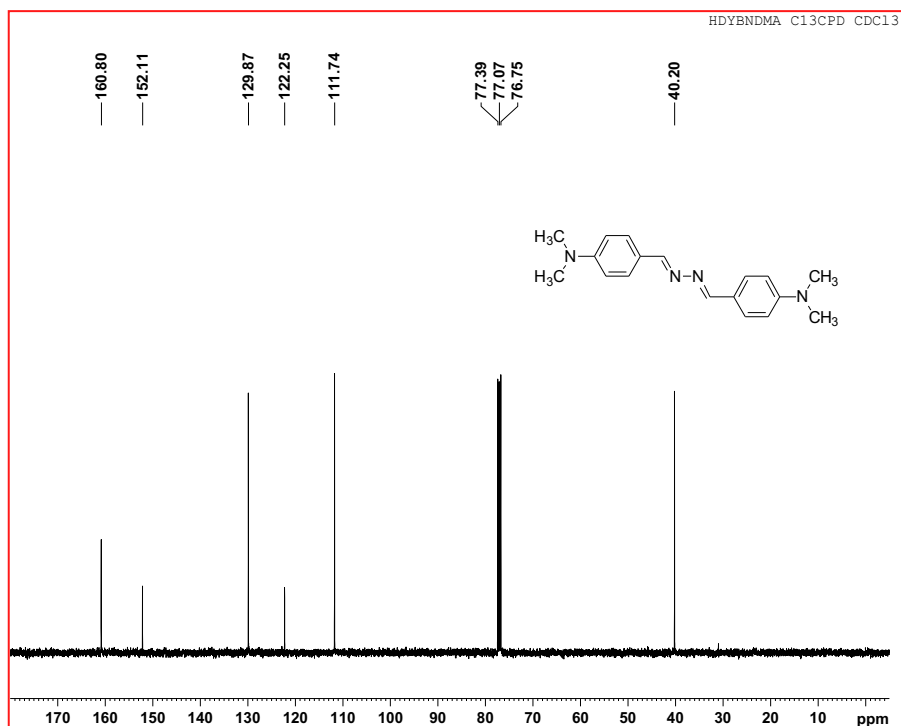


Figure S21. ^{13}C NMR Spectrum of DMBA in CDCl_3

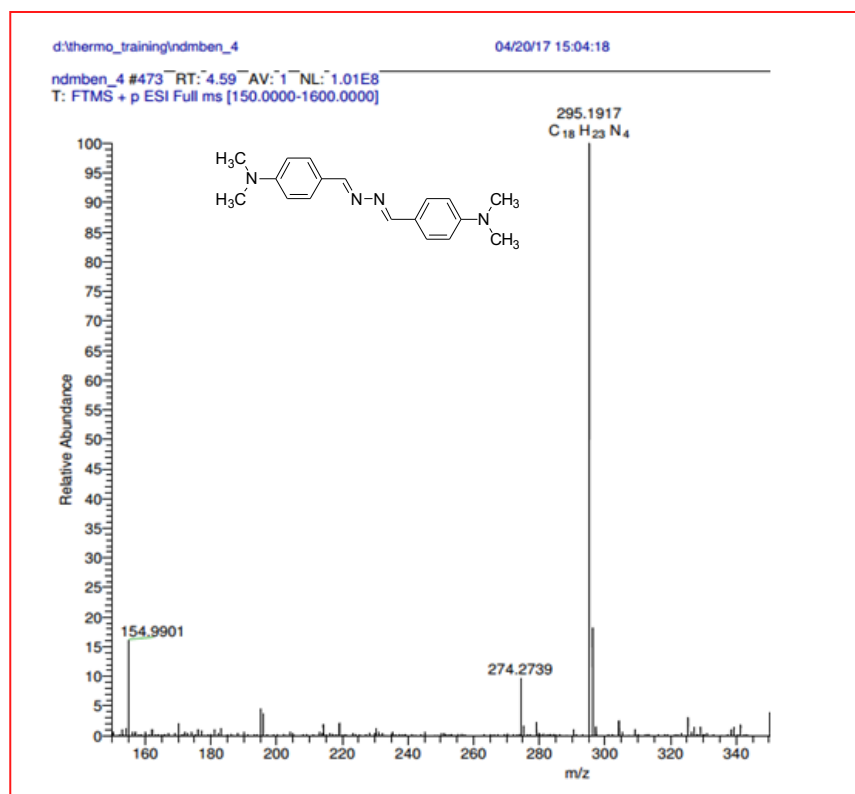


Figure S22. Mass Spectrum of DMBA

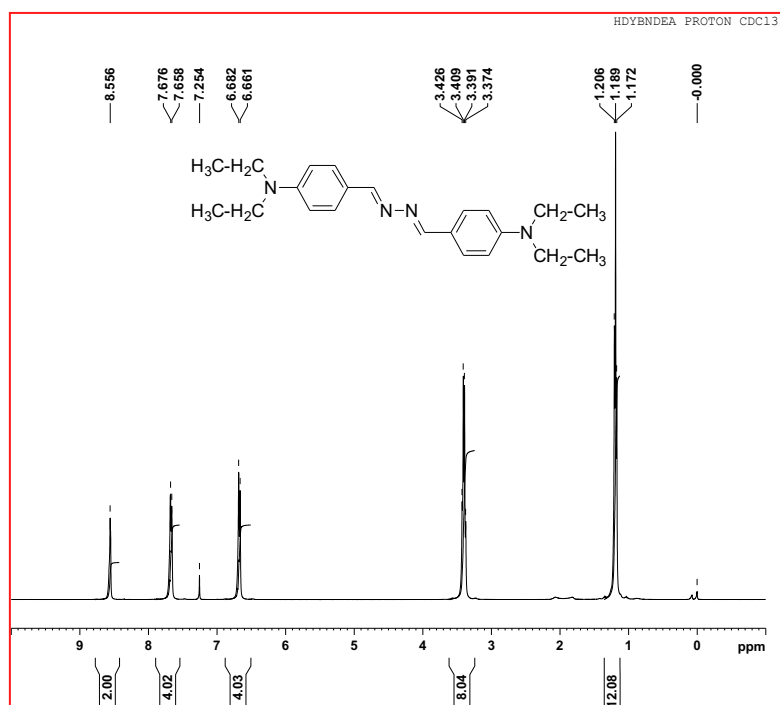


Figure S23. ^1H NMR Spectrum of DEBA in CDCl_3

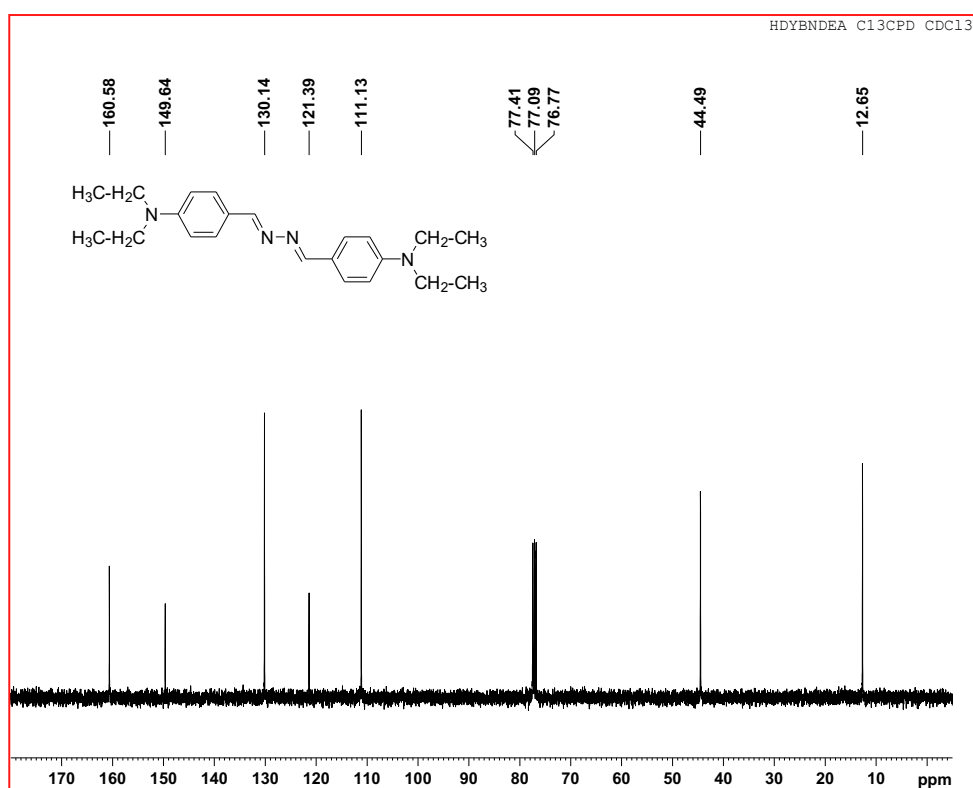


Figure S24. ^{13}C NMR Spectrum of DEBA in CDCl_3

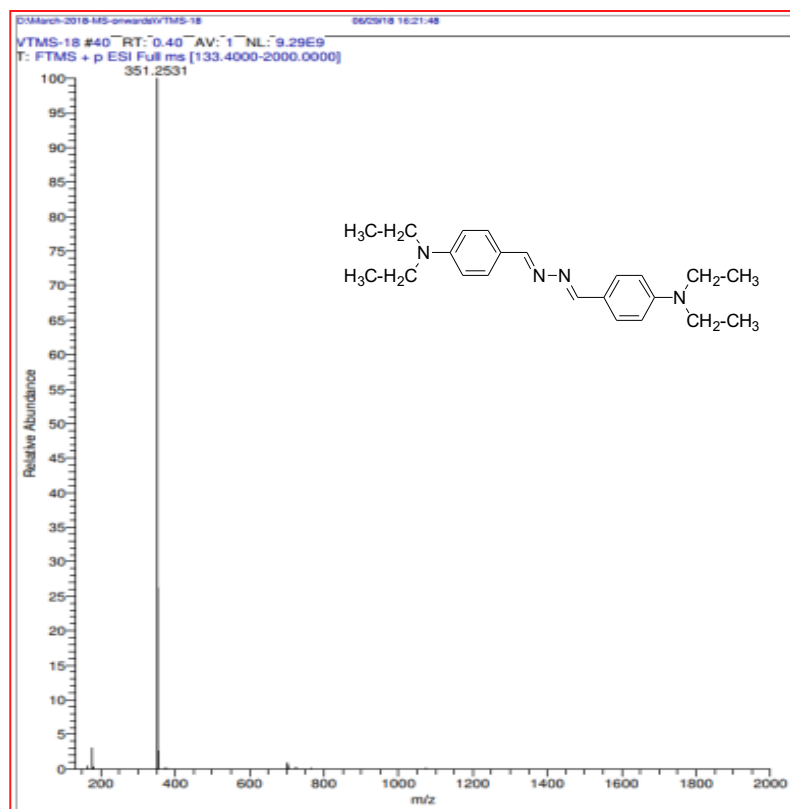


Figure S25. Mass Spectrum of DEBA

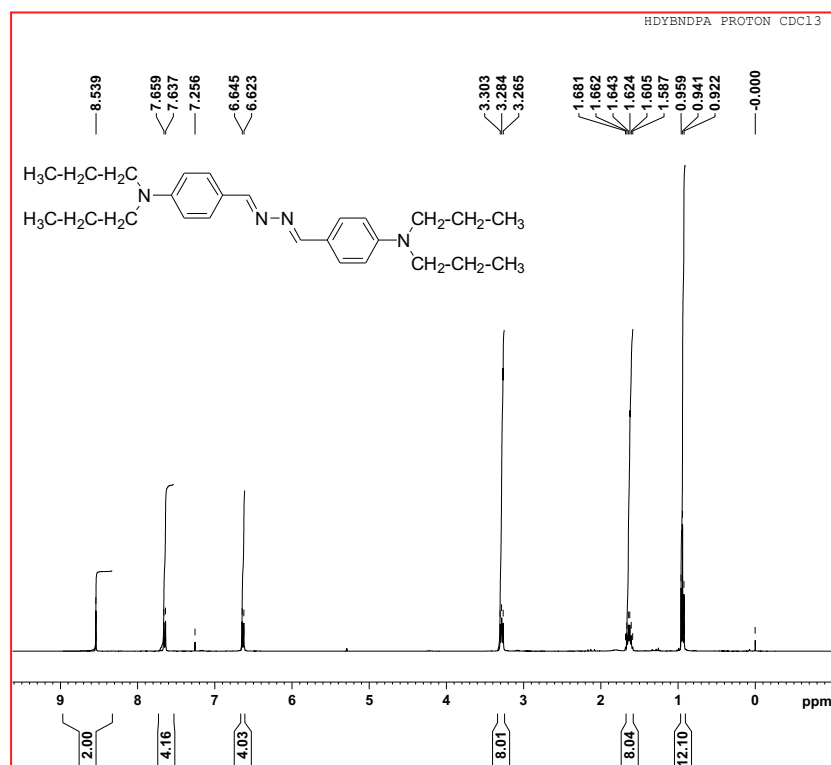


Figure S26. ¹H NMR Spectrum of DPBA in CDCl₃

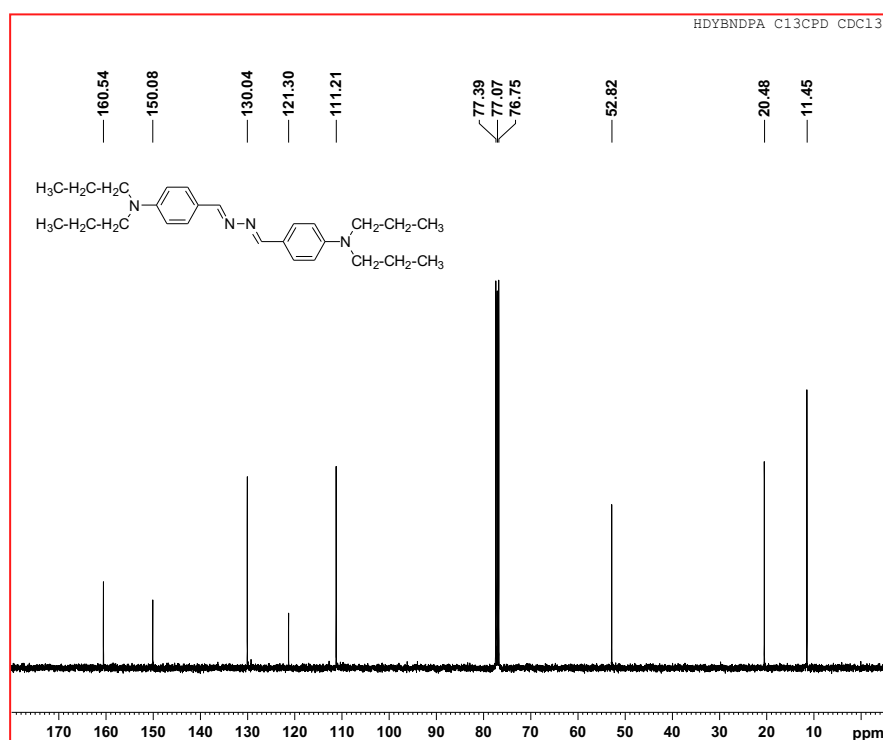


Figure S27. ¹³C NMR Spectrum of DPBA in CDCl₃

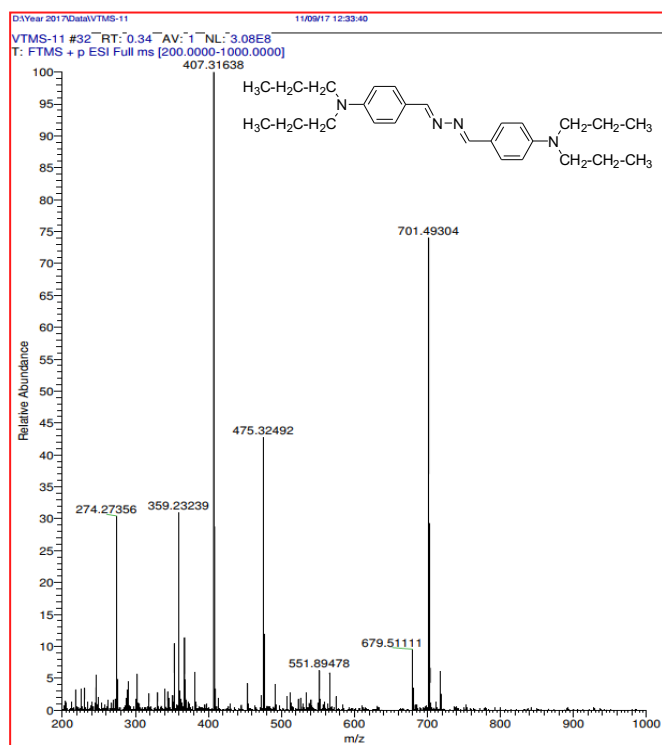


Figure S28. Mass Spectrum of DPBA

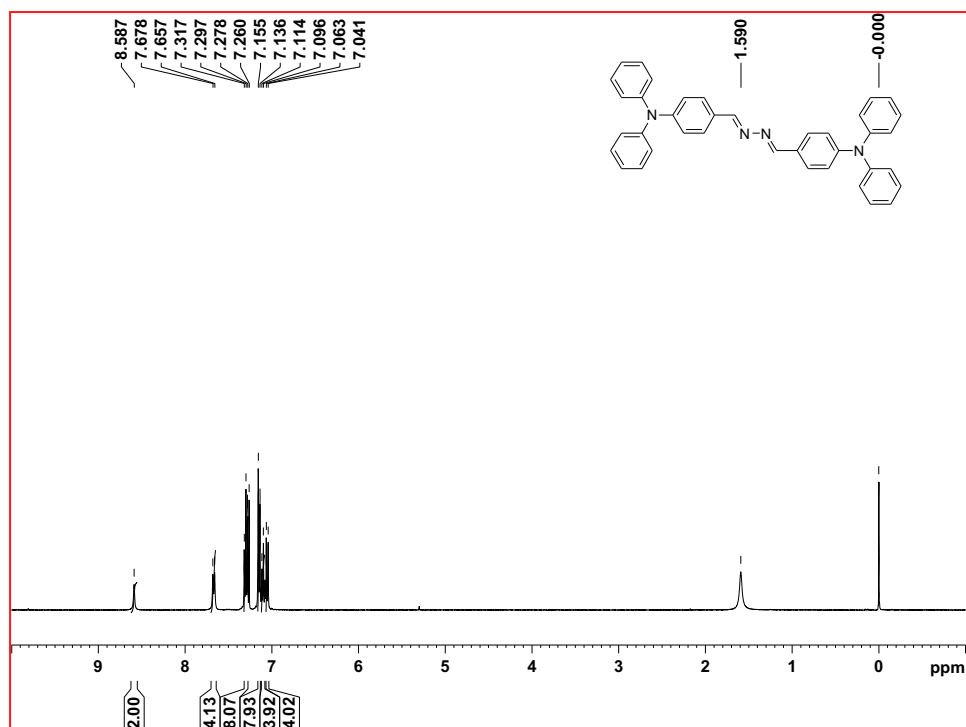


Figure S29. ¹H NMR Spectrum of DAPA in CDCl₃

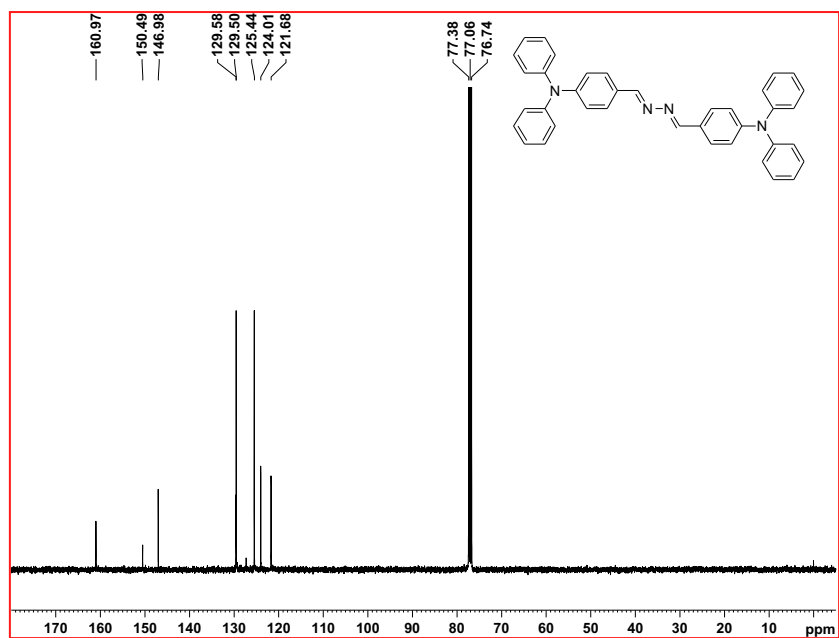


Figure S30. ¹³C NMR Spectrum of DAPA in CDCl₃

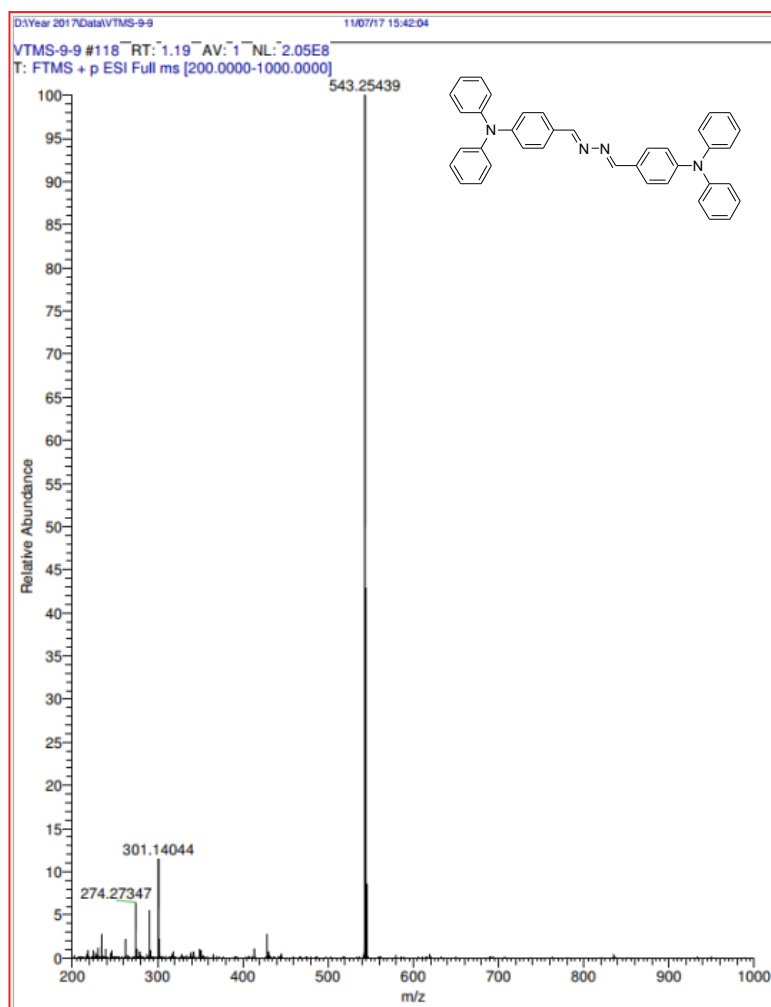


Figure S31. Mass Spectrum of DAPA