Synthesis of pyrazole anchored three-coordinated organoboranes and their application in the detection of picric acid

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Experimental Section

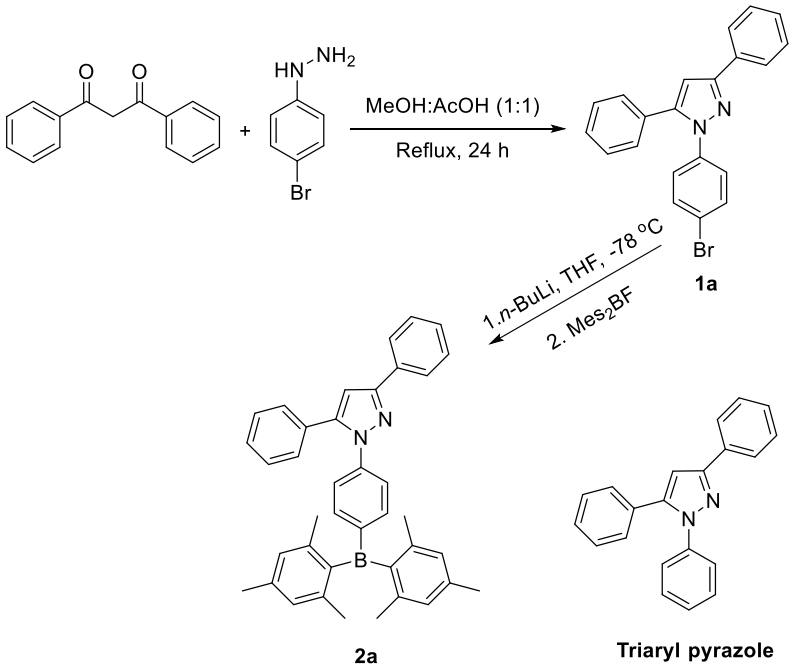
General Information

All reagents and starting materials were purchased from Sigma-Aldrich, Alfa-Aesar and Spectrochem chemical companies and used as received unless otherwise noted. Chlorinated solvents acetonitrile, and DMF were distilled from CaH_2. THF and toluene were distilled from Na/benzophenone prior to use. All 400 MHz ^1H, 100 MHz ^{13}C, NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400 MHz. All ^1H and ^{13}C NMR spectra were referenced internally to solvent signals. All NMR spectra were recorded at ambient temperature. ESI mass spectra were recorded on Bruker, micrOTOF-QII mass spectrometer. The absorbance spectra were recorded on a JASCO V-730 UV-Visible spectrometer. The fluorescence spectra were recorded using Edinburgh FS5 spectrofluorometer. Absolute fluorescence quantum yields of compounds **2a** and **2b** were measured by integrating sphere method using Edinburgh FS5 spectrofluorometer. The fluorescence spectra are corrected for the instrumental response. Cyclic voltammetry measurements were performed with a conventional three electrode cell using an electrochemical workstation (CH Instrument, Model: 1100A) The three-electrode system consisted of a Glassy carbon working electrode, a Pt wire as the secondary electrode, and a Ag wire as the reference electrode. The voltammograms were recorded with ca. 1.0 $x10^{-3}$ M solution in DMF containing Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The scans were referenced after the addition of a small amount of ferrocene as the internal standard. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II diffractometer using Mo-Kα radiation (0.71073 Å). SADABS absorption corrections were applied. The structures were solved and refined with SHELX suite of programs. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were placed at calculated positions and were refined as riding atoms. Crystallographic data for compounds **2a** & **2b** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC- 2063185-2063186. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk). DFT calculations were performed

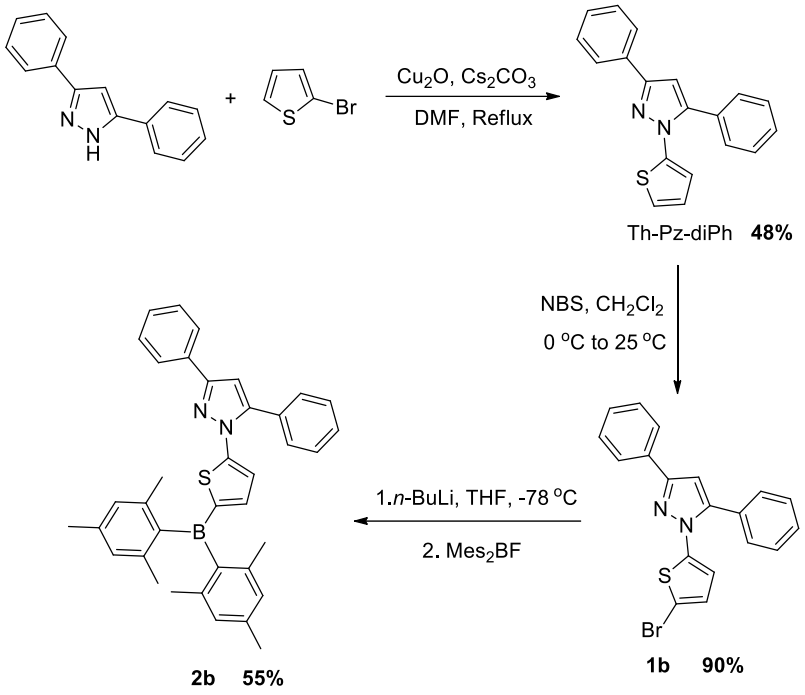
with the Gaussian09 program.[1] The structures were optimized using 6-31G(d,p) (B3LYP) as the basis set. Frequency calculations confirmed the optimized structures to be local minimum structures. Excitation data were determined using TD-DFT (B3LYP/631g(d,p))–calculations.

References:

1. Gaussian 09 (Rev. C.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, _. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.



Scheme S1: Synthetic pathway for compound **2a** and chemdraw of **Triaryl pyrazole**



Scheme S2: Synthetic pathway for compound **2b**.

Table S1: Photophysical data of compound **2a**, **2b** and **triaryl pyrazole**

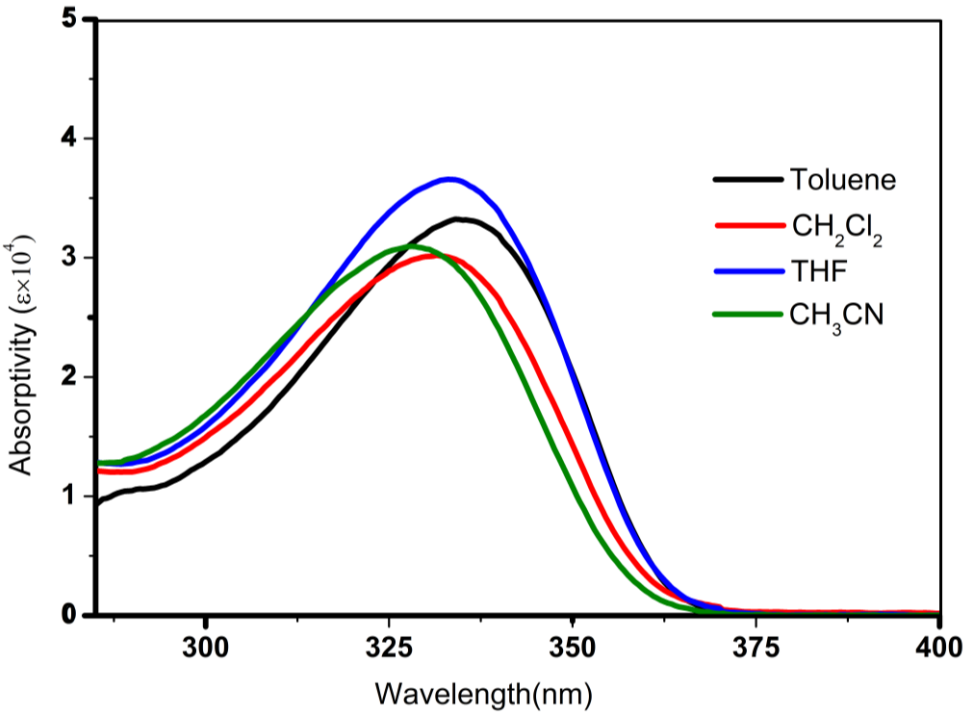
Compound	solvent	λ_{abs}[a] (nm)	ε_{max} (M^{-1} cm^{-1} × 10^3)	λ_{em}[a,b] (nm)	Φ_f[c]
2a	Toluene	334	33.19	370	0.30
	THF	333	36.55	377	0.23
	CH_2Cl_2	331	30.00	383	0.14
	CH_3CN	328	30.88	403	0.12
2b	Toluene	368	25.00	411	0.17
	THF	366	33.74	413	0.15
	CH_2Cl_2	361	27.61	413	0.14
	CH_3CN	358	29.61	415	0.12
Triaryl pyrazole	THF	258	21.3	365	0.08

[a]Absorption maximum (concentrations in solutions were 10^{-5} M). [b]Excited at absorption maximum. [c] Absolute fluorescence quantum yields were measured by integrating sphere method.

Table S2: Details of X-ray crystal structure analyses of compound **2a** and **2b**.

	2a	**2b**
formula	$C_{39}H_{37}BN_2$	$C_{37}H_{35}BN_2S$
M_r	544.51	550.54
T [K]	100	296.15
wavelength, Å	0.71073 Å	0.71073 Å
crystal system	Monoclinic	Monoclinic
space group	*P2₁/n*	*P2₁/c*
a [*Å*]	8.2587(4)	13.5234(3)
b [*Å*]	30.5396(17)	11.1663(3)
c [*Å*]	11.9793(7)	20.6115(5)
α [°]	90	90
β [°]	91.502(3)	93.494(2)
δ [°]	90	90
V [Å$^{3]}$	3020.3(3)	3106.68(13)
Z	4	4
ρ_{calc} [g cm^{-3}]	1.197	1.177
μ (MoKα) [mm^{-1}]	0.069	0.132
F (000)	1160.0	1168.0
Crystal size [mm]	0.22 × 0.2 × 0.15	0.23 × 0.21 × 0.2
θ range [°]	6.806 – 49.994	3.96 –55.868
limiting indices	$-9 \le h \le 9$	$-17 \le h \le 17$
	$-35 \le k \le 36$	$-14 \le k \le 13$
	$-13 \le l \le 14$	$-27 \le l \le 27$
reflns collected	24571	26106
independent reflns	5296	7413
	[*R*(int) = 0.0940]	[*R*(int) = 0.0385]
absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
refinement method	Full-matrix least square on F^2	Full-matrix least square on F^2
data / restraints / parameters	5296/0/385	7413/0/376
Goodness-of-fit on F^2	1.038	1.029
final R indices	R_1 = 0.0491	R_1 = 0.0474
[I >2σ(I)] [a]	wR_2 = 0.1150	wR_2 = 0.1215
R indices (all data) [a]	R_1 = 0.0675	R_1 = 0.0760
	wR_2 = 0.1252	wR_2 = 0.1380
$peak_{max}/hole_{min}$ [e Å^{-3}]	0.28 and -0.27	0.26 and -0.24

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.



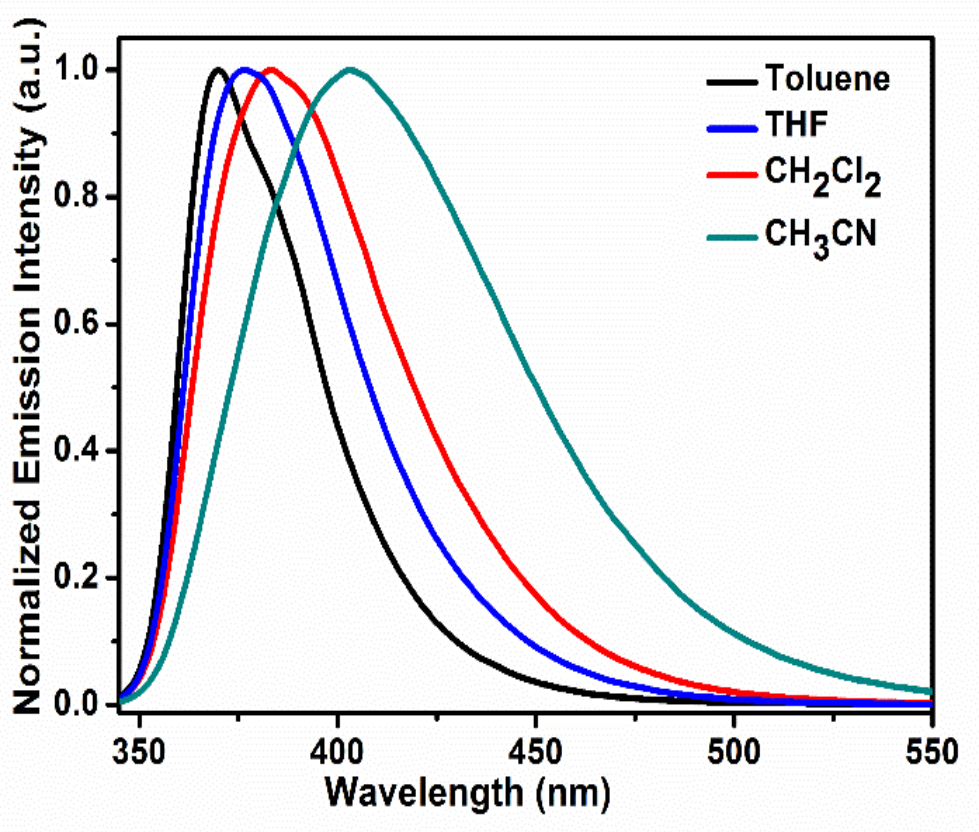
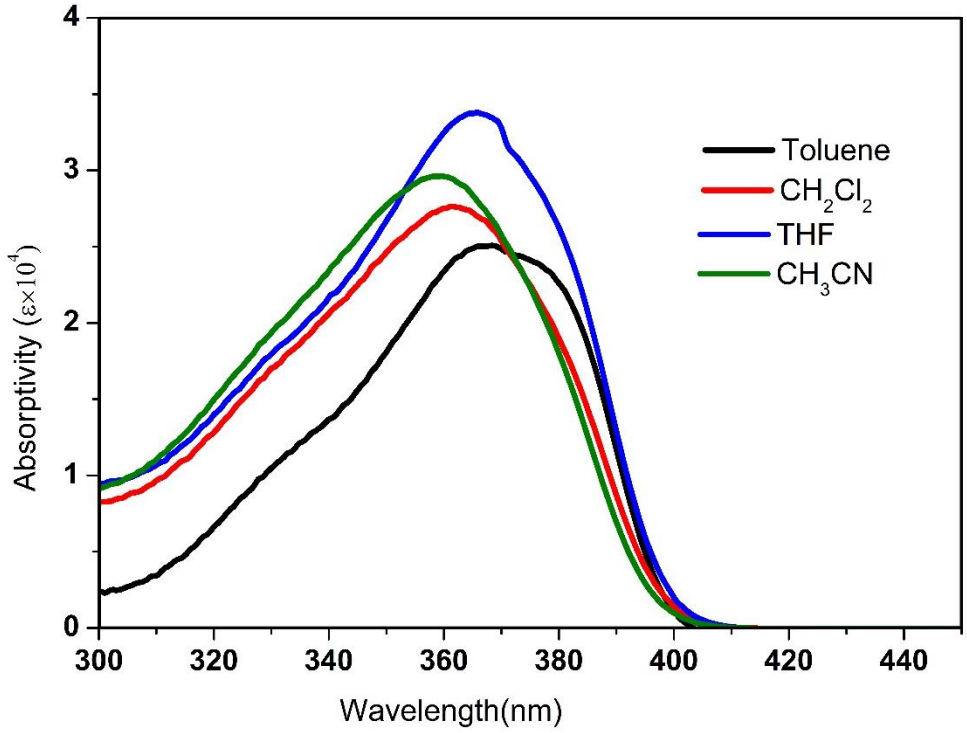


Figure S1. UV-Vis absorption (top) & Normalized fluorescence spectra (bottom) of compound **2a** in different solvents (Concentration = 10^{-5} M, excited at λ_{abs}).



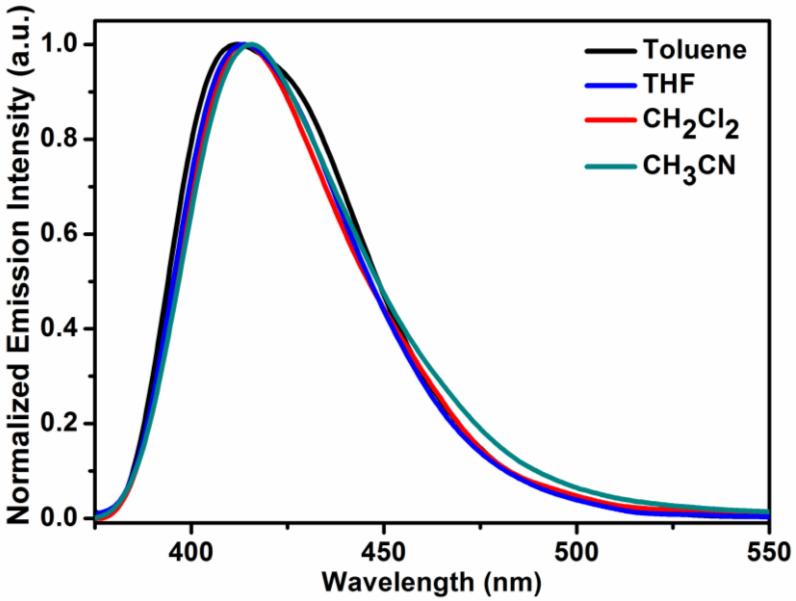


Figure S2: UV-Vis absorption (top) & Normalized emission spectra (bottom) of compound **2b** in different solvents (Concentration = 10^{-5} M, excited at $\lambda_{abs)}$.

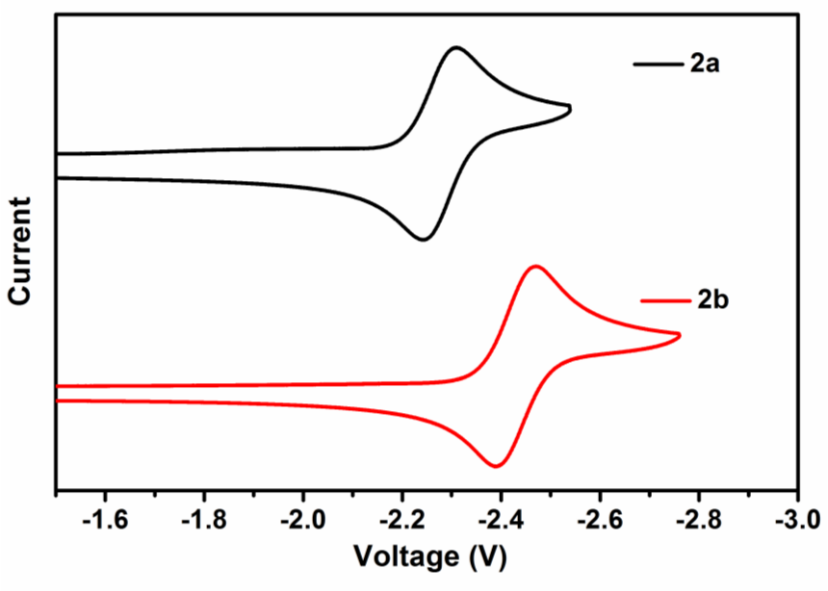


Figure S3: Cyclic voltammograms of compound **2a** & **2b** (*vs*. Ferrocene/Ferrocenium) with 0.1 M $^{n}Bu_4NPF_6$ in DMF as the supporting electrolyte (scan rate 100 mV/s).

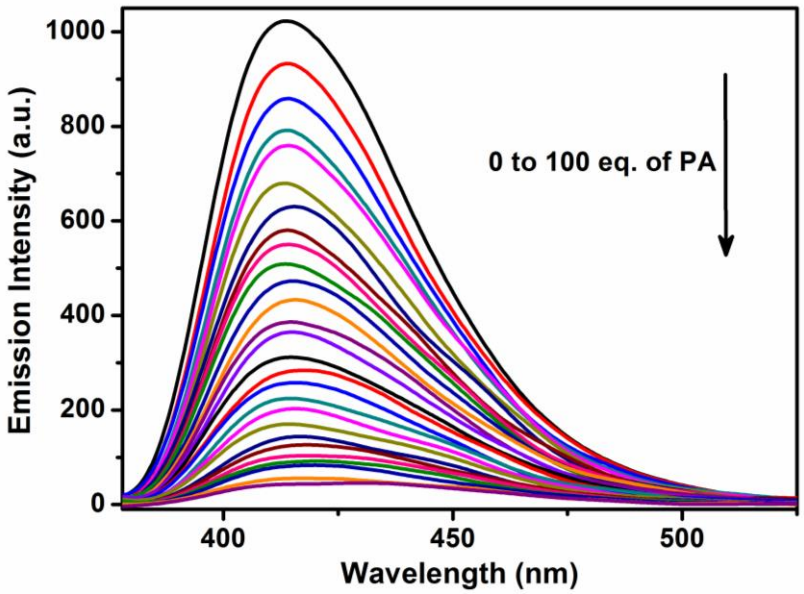


Figure S4: Fluorescence quenching of Compound **2b** with the addition of different concentrations of PA (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 23, 26, 29, 33, 37, 41, 45, 50, 55, 60, 65, 70, 75, 80, 90, and 100 equiv of PA) in THF (10^{-5} M; excited at 366 nm).

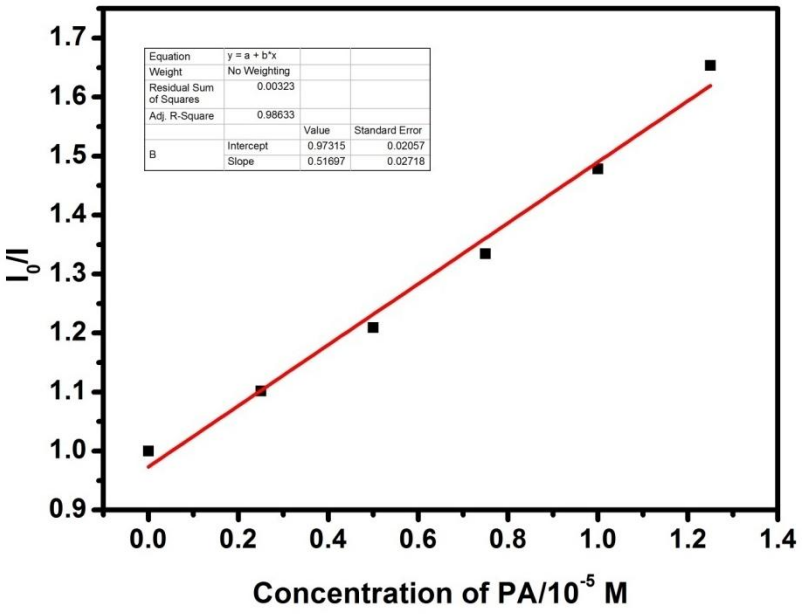


Figure S5: Stern-Volmer plot of compound **2a** (10^{-5}M) with addition of different concentration of PA in THF.

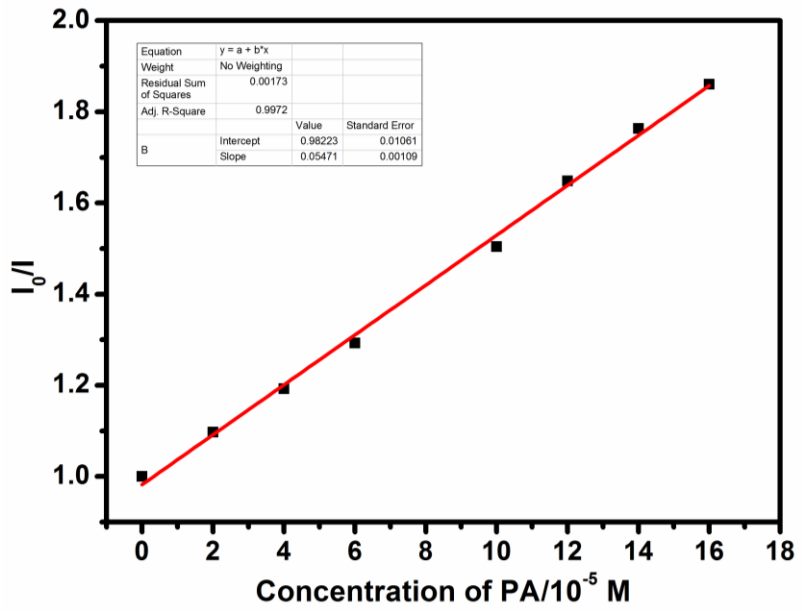


Figure S6: Stern-Volmer plot of compound **2b** (10^{-5}M) with addition of different concentration of PA in THF.

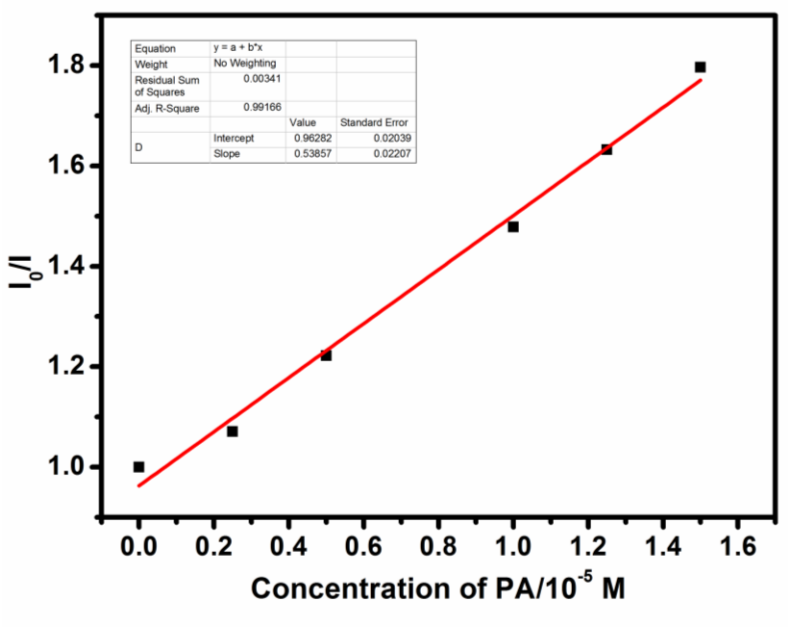


Figure S7: Stern-Volmer plot of compound **2a** (10^{-5}M) with addition of different concentration of PA in THF: H2O (70:30) mixture.

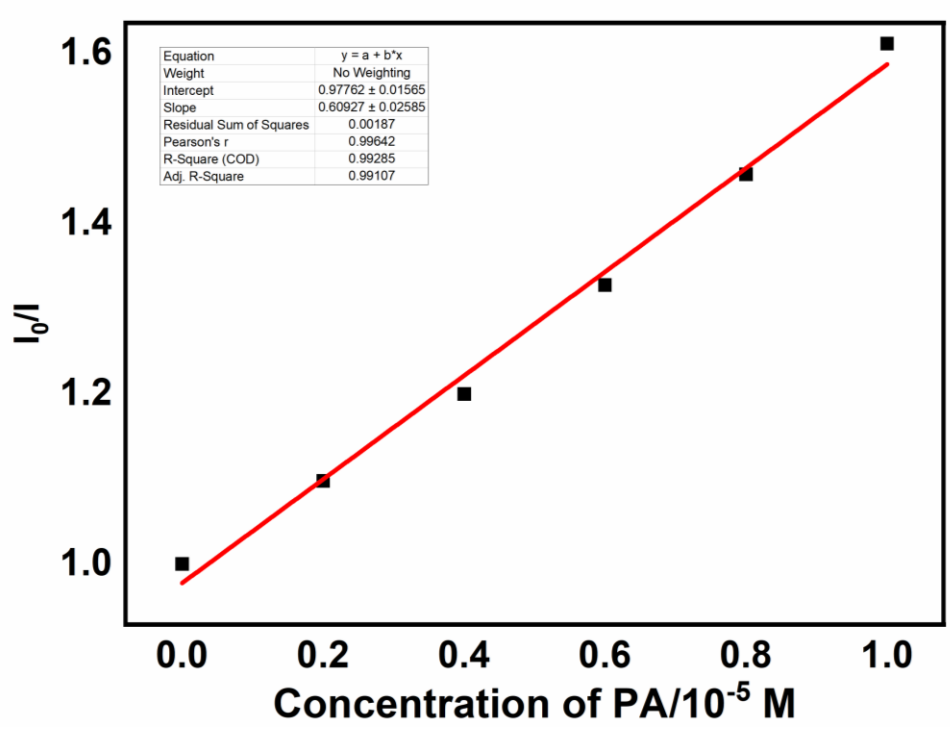


Figure S8: Stern-Volmer plot of compound **2b** (10^{-5}M) with addition of different concentration of PA in THF: H_2O (70:30) mixture.

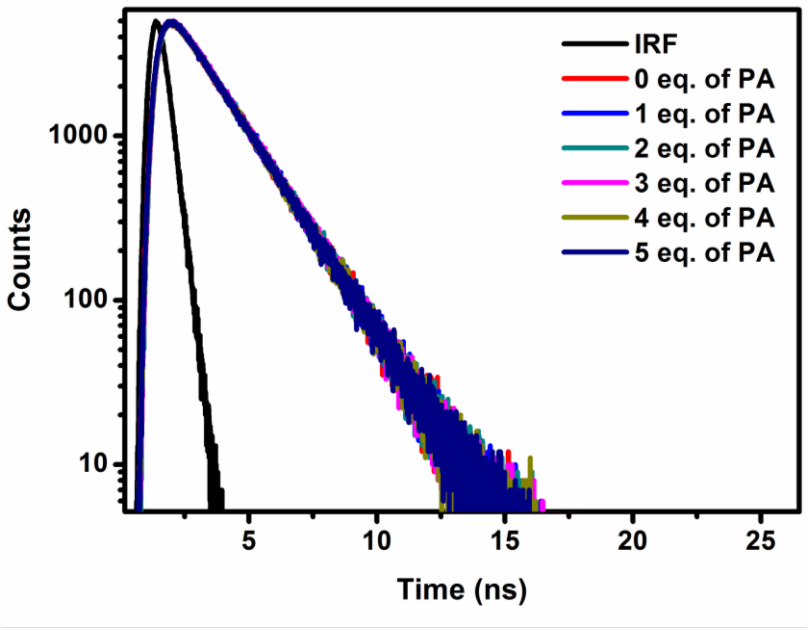


Figure S9: Fluorescence lifetime decay of compound **2a** after the addition of 0, 1, 2, 3, 4 and 5 equiv. of PA in THF (Concentration = 10^{-5} M).

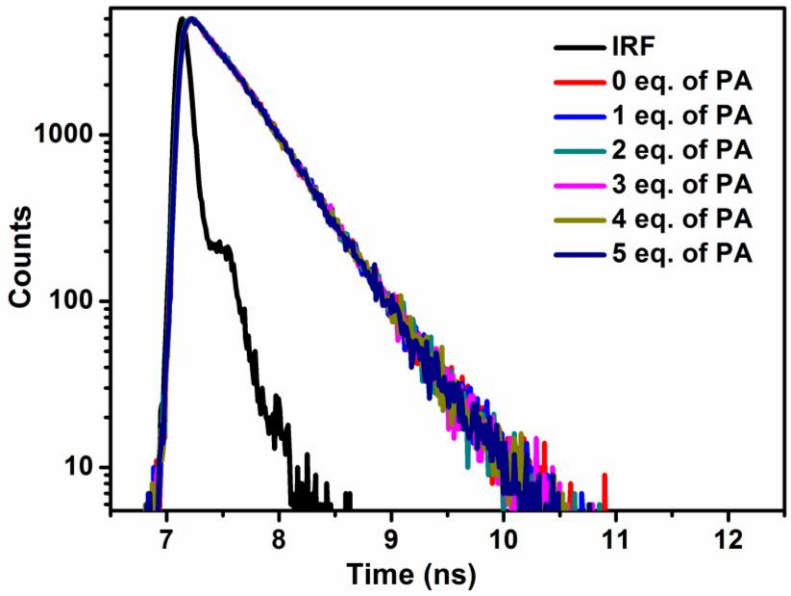


Figure S10: Fluorescence lifetime decay of compound **2b** after the addition of 0, 1, 2, 3, 4 and 5 equiv. of PA in THF (Concentration = 10^{-5} M).

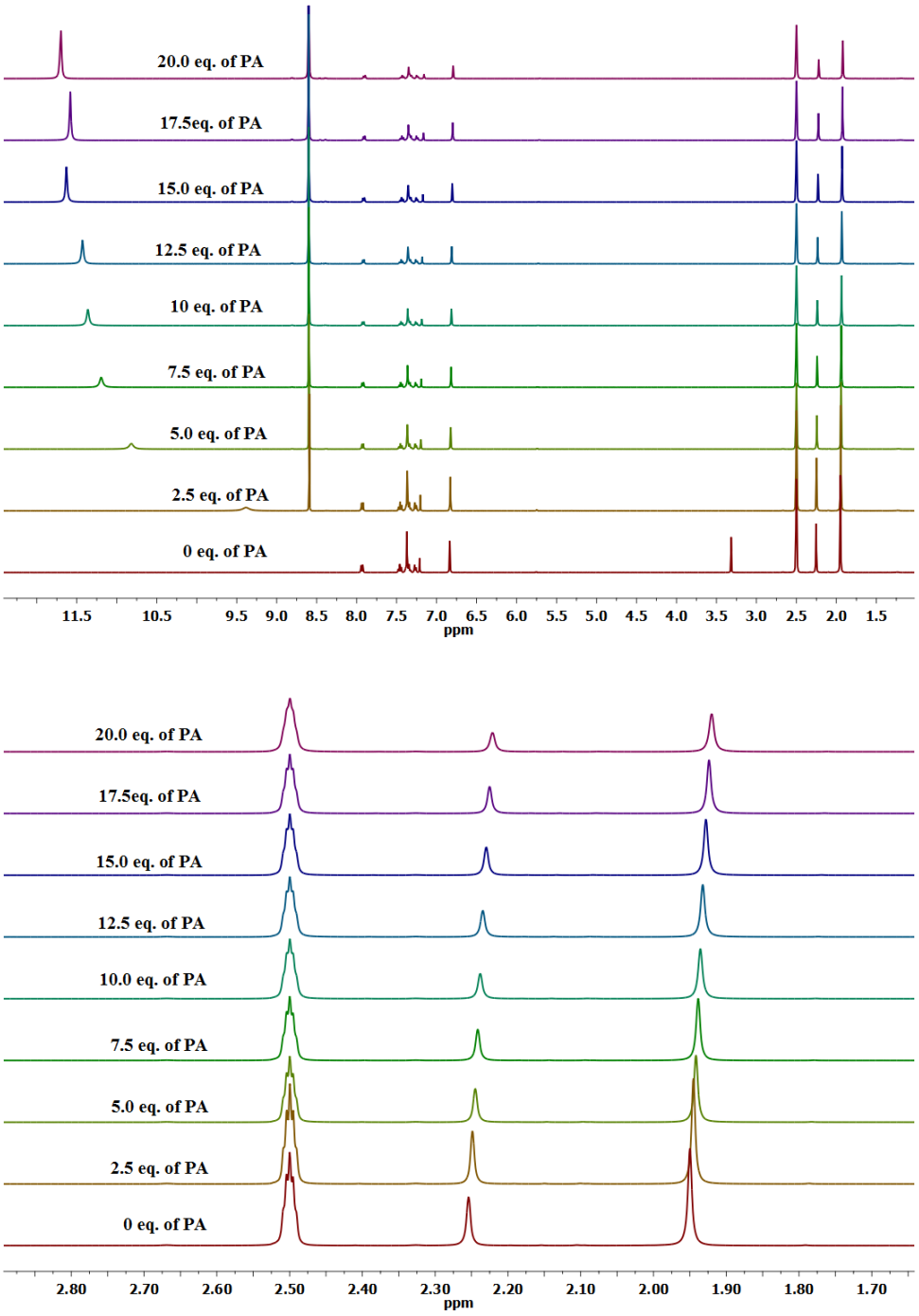
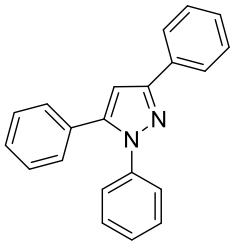


Figure S11: ^{1}H NMR titration of compound **2a** upon the addition of 0, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5 and 20.0 equiv. of PA in DMSO-d6.



Triphenyl pyrazole

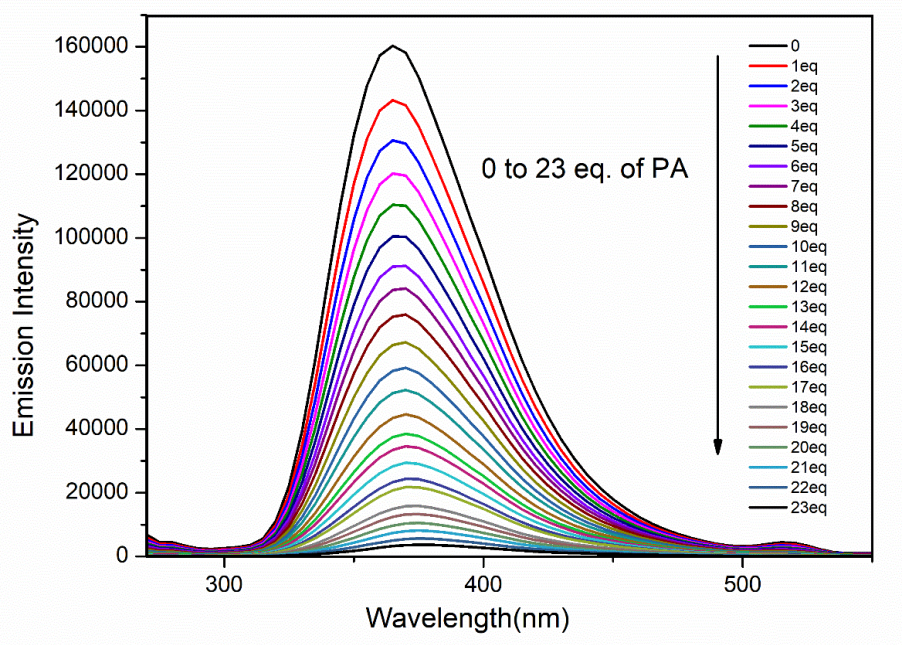


Figure **S12**: Fluorescence quenching of **triphenyl pyrazole** in 10^{-5} M THF with addition of 0 to 23 equiv. of PA.

Table S3: LOD data for Compound **2a-2b** and Ligand **2a-2b**

Probe	Detection Medium	Detection Limit
Compound **2a**	THF:H_2O(70:30)	1.63×10^{-7}M
Compound **2b**	THF:H_2O(70:30)	1.95×10^{-7}M
Compound **2a**	THF	1.28×10^{-7}M
Compound **2b**	THF	3.06×10^{-4}M
Triphenyl pyrazole	THF	8.41×10^{-7}M

The detection limits were calculated with the following equation:

$$\text{Detection limit} = 3\sigma/K$$

Where σ is the standard deviation of blank measurement and K is the slope between the emission counts vs picric acid concentration.

References: ***RSC Adv.***, 2015, **5**, 74924-74931.

Table S4: Comparison of detection limits of recently reported probes for PA in the literature with compound **2a** and compound **2b**

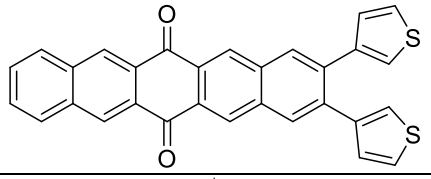
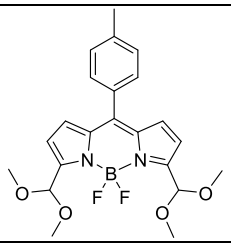
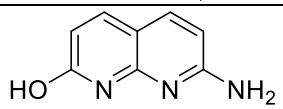
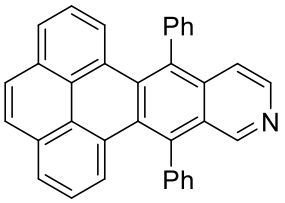
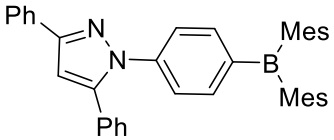
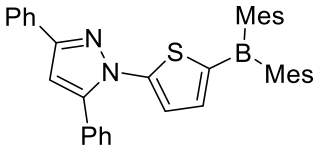
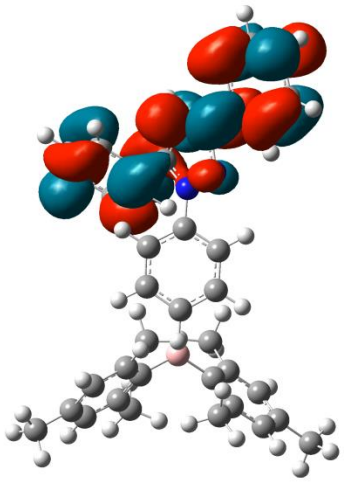
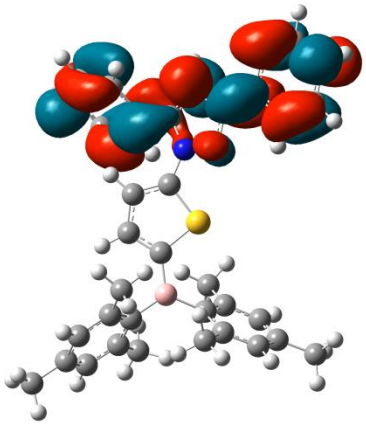
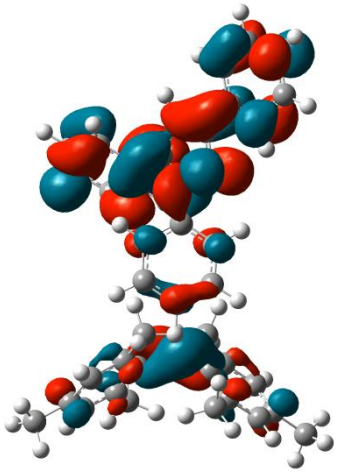
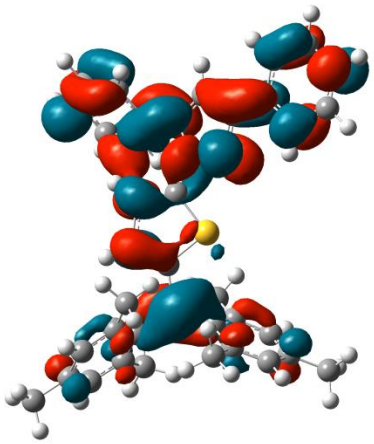
Probe	Detection Medium	Detection Limit(M)	References
	THF	1×10^{-6}	*Org. Lett*., 2012, **14**, 1312-1315
	$CH_3CN:H_2O$ (9:1)	7.27×10^{-7}	*RSC Adv.*, 2014, **4**, 7120–7123
	$H_2O:CH_3OH$ (8:2)	4.3×10^{-6}	*Anal. Methods*, 2015, **7**, 10272
	CH_3CN	2.42×10^{-6}	*Talanta*, 2017, **174**, 462–467
	$THF:H_2O$ (70:30)	1.63×10^{-7}M	This work
	$THF:H_2O$ (70:30)	1.95×10^{-7}M	This work

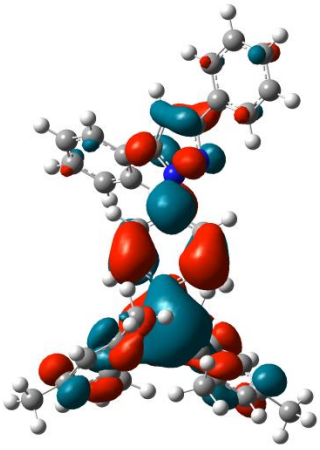
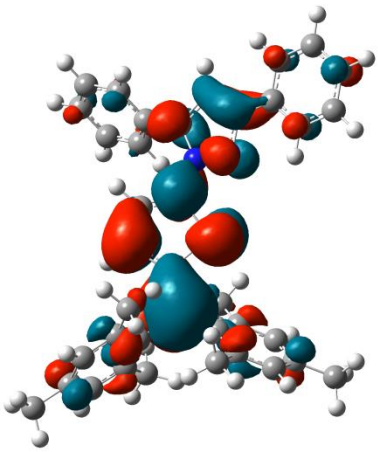
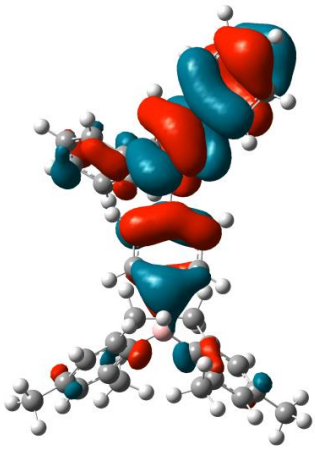
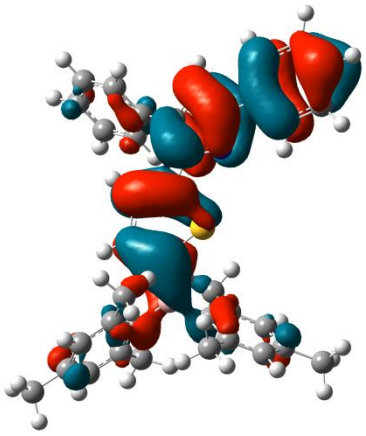
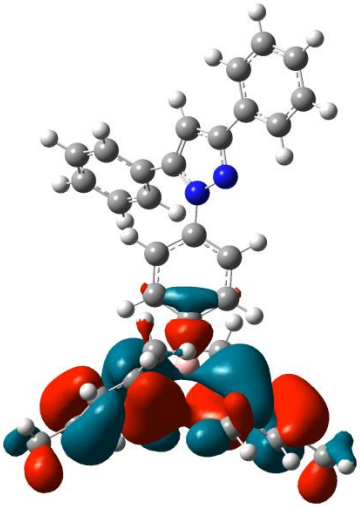
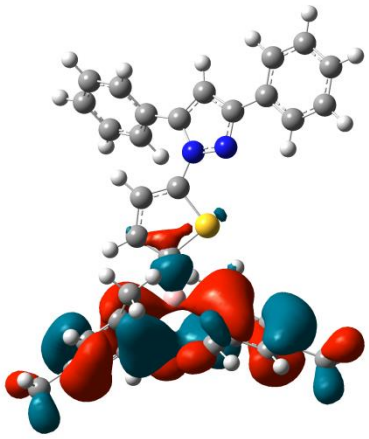
Table S5. Calculated electronic transitions for compound **2a** & **2b** from TD-DFT (B3LYP/631g(d,p))–PCM solvation (THF))) calculations

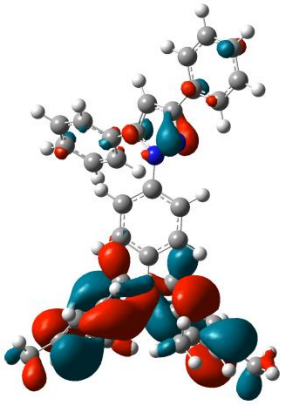
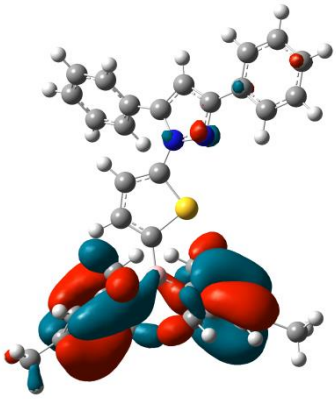
Compound	Transition	MO contributions	Energy gap eV (nm)	Oscillator strength/f
2a	$S_0 \rightarrow S_1$	HOMO-2→LUMO HOMO→LUMO	3.42 (361)	0.5599
	$S_0 \rightarrow S_2$	HOMO-1→LUMO	3.47 (357)	0.1042
	$S_0 \rightarrow S_3$	HOMO-3→LUMO HOMO-2→LUMO HOMO→LUMO	3.37 (337)	0.0266
2b	$S_0 \rightarrow S_1$	HOMO-3→LUMO HOMO→LUMO	3.24 (382)	0.7038
	$S_0 \rightarrow S_2$	HOMO-1→LUMO	3.46 (358)	0.0870
	$S_0 \rightarrow S_3$	HOMO-3→LUMO HOMO-2→LUMO	3.59 (345)	0.0084
2a-PA	S0→S1	HOMO-3→LUMO HOMO-1→LUMO HOMO→LUMO	2.28 (541)	0.0027
	S0→S2	HOMO-1→LUMO HOMO→LUMO	2.43 (508)	0.0000
	S0→S3	HOMO-3→LUMO HOMO-2→LUMO	2.55 (484)	0.0002
2b-PA	S0→S1	HOMO→LUMO	2.07 (597)	0.0005
	S0→S2	HOMO-3→LUMO	2.36 (524)	0.0000

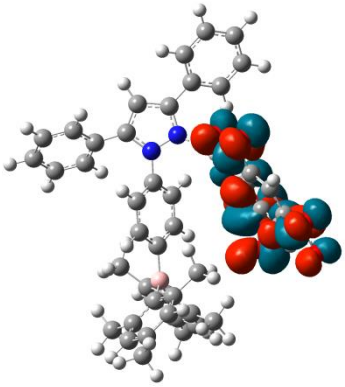
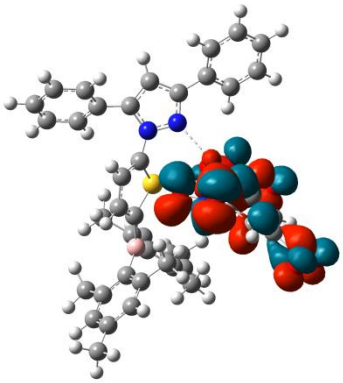
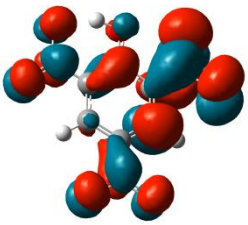
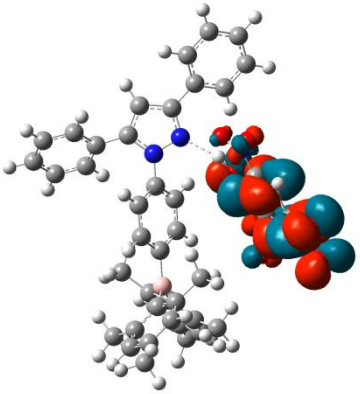
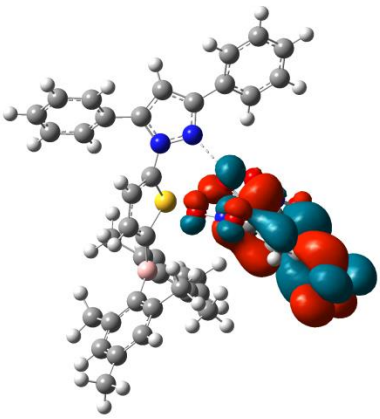
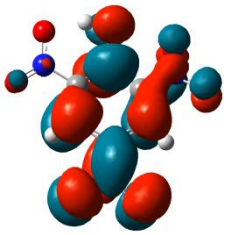
	S0→S3	HOMO-1→LUMO HOMO-2→LUMO	2.41 (513)	0.0001
Picric acid	S0→S1	HOMO→LUMO	3.62 (341)	0.1196
	S0→S2	HOMO-9→LUMO+2 HOMO-6→LUMO+2 HOMO-5→LUMO HOMO-4→LUMO HOMO-4→LUMO+2 HOMO-2→LUMO HOMO-2→LUMO+1 HOMO-2→LUMO+2 HOMO→LUMO HOMO→LUMO+2	3.85 (321)	0.0068
	S0→S3	HOMO-3→LUMO+1 HOMO-3→LUMO+2	3.93 (314)	0.0001

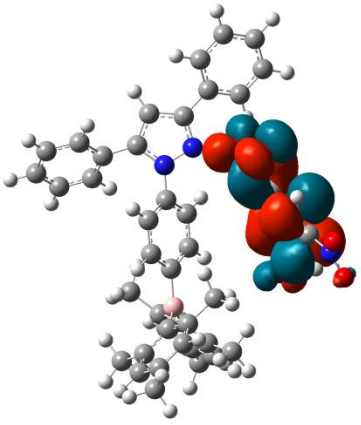
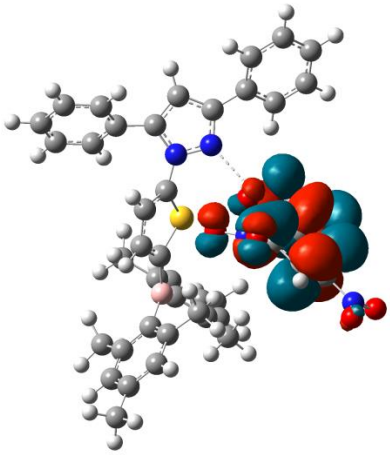
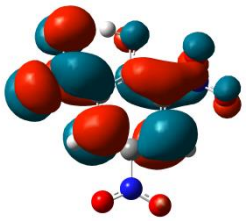
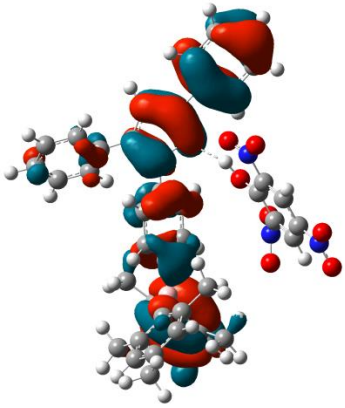
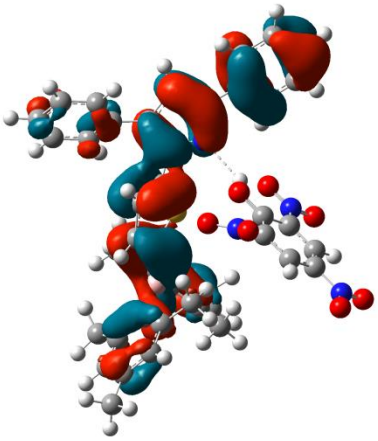
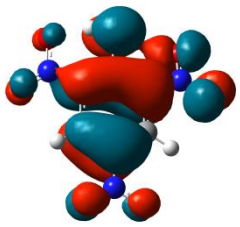
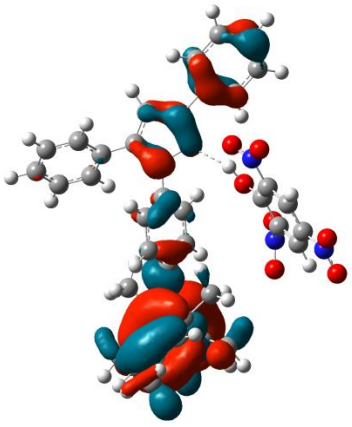
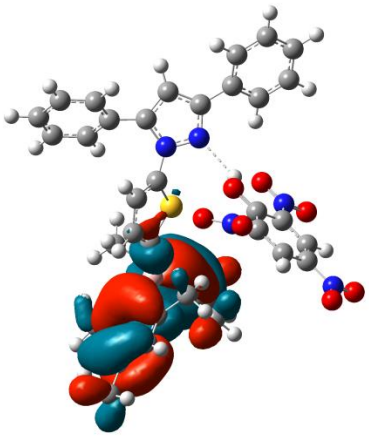
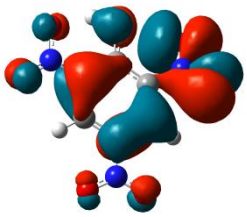
Table S6. Computed orbitals for compounds **2a, 2b, 2a-PA, 2b-PA, & picric acid**

Compound	**2a**	**2b**
LUMO+2	 -0531(eV)	 -0.581(eV)
LUMO+1	 -0.853(eV)	 -0.936(eV)

LUMO	 -1.822(eV)	 -1.921(eV)
HOMO	 -5.794(eV)	 -5.707(eV)
HOMO-1	 -6.052(eV)	 -6.096(eV)

HOMO-2	 -6.158(eV)	 -6.139(eV)

Compound	**2a-PA**	**2b-PA**	**Picric acid**
LUMO+2	 -2.593(eV)	 -2.618 (eV)	 -2.952 (eV)
LUMO+1	 -2.928(eV)	 -2.965 (eV)	 -3.303 (eV)

LUMO	 -3.245(eV)	 -3.358 (eV)	 -3.913 (eV)
HOMO	 -6.016 (eV)	 -5.910 (eV)	 -8.227 (eV)
HOMO-1	 -6.047(eV)	 -6.126 (eV)	 -8.586 (eV)

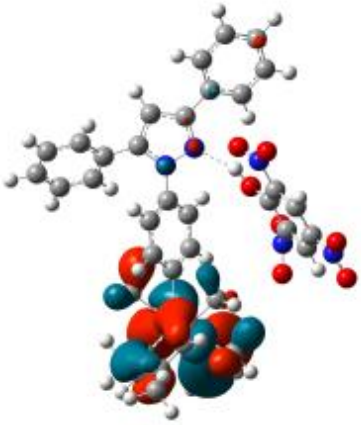
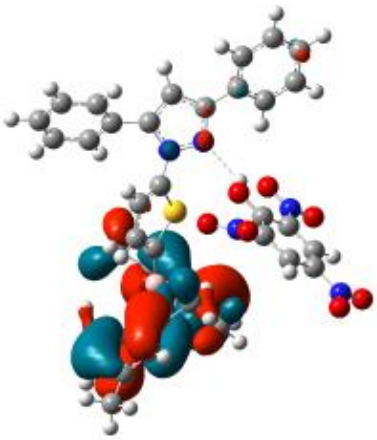
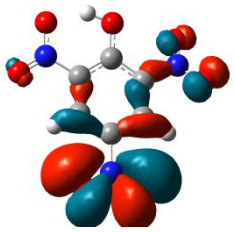
HOMO-2	 -6.156(eV)	 -6.189 (eV)	 -8.768 (eV)

Table S7: Calculated energy for compounds **2a, 2b, 2a-PA, 2b-PA** and **picric acid**.

Compound	HOMO (eV)	LUMO (eV)
2a	-5.794	-1.822
2b	-5.707	-1.921
2a-PA	-6.016	-3.245
2b-PA	-5.910	-3.358
Picric acid	-8.227	-3.913

Table S8: Comparison of optical nonlinearity coefficients of similar molecules

Compound	Laser Parameters	n_2 (cm^2W^{-1})	β (cm W^{-1})	TPAC (GM)	Reference
BPI* (crystal)	He-Ne Laser	$-4.27x10^{-8}$	$3.37x10^{-3}$		*J. Opt.*, 2017, **46**, 382–390
PP* (crystal)	532nm, CW Nd-Yag	$-7.35x10^{-8}$	$-0.10x10^{-4}$		*J. Mol. Struct*., 2019, **1190**, 1-10.
45-1	735 nm	-	-	22	*Chem. Sci*., 2017, **8**, 846–863
N2TFABDP*	1200nm,45fs, 1kHz	-	-	9	*Dyes Pigm*., 2013, **99**, 979 - 985
N2TFABDP*	1200nm,45fs, 1kHz	-	-	9	*Dyes Pigm*., 2013, **99**, 979 - 985
3TFABDP*	1200nm,45fs, 1kHz	-	-	8	*Dyes Pigm*., 2013, **99**, 979 - 985
TVBVT*	800nm, 100fs, 82MHz	-9.72×10^{-10}	-	-	*Dyes Pigm*., 2019, **162**, 776-785
HEAP*	He-Ne	$-9.2 x10^{-5}$	14.0		*Mater. Chem. Phys*., 2012, **134**, 736-746

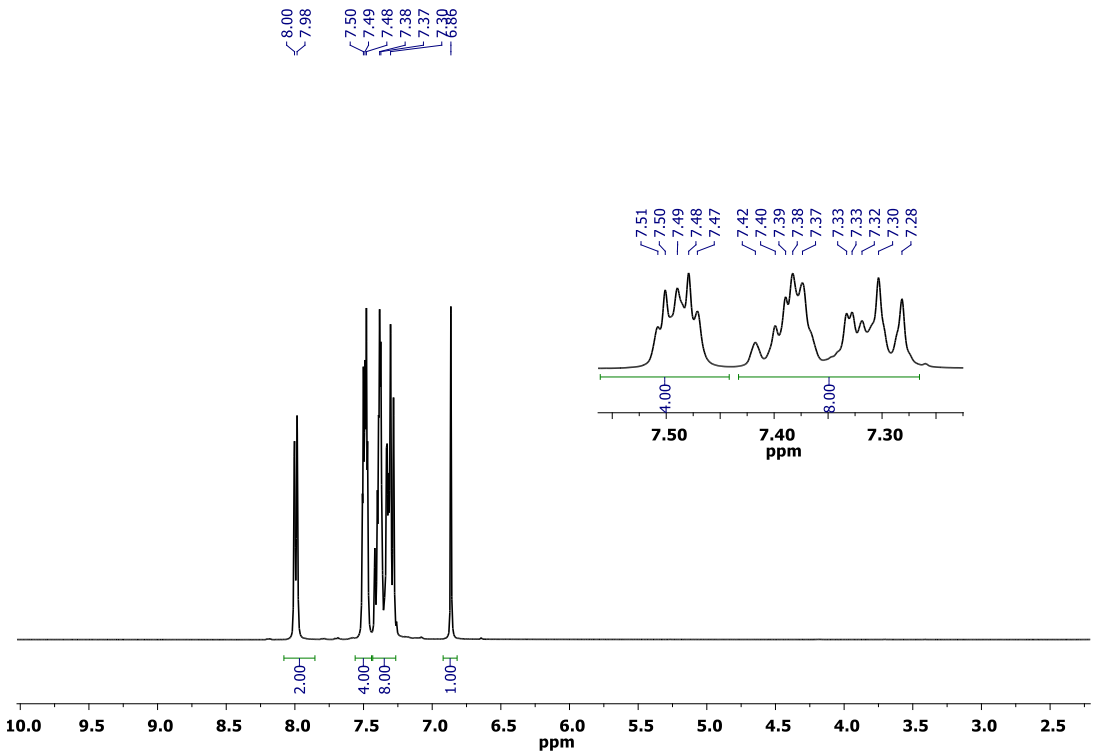


Figure S13: ^{1}H NMR of compound **1a.**

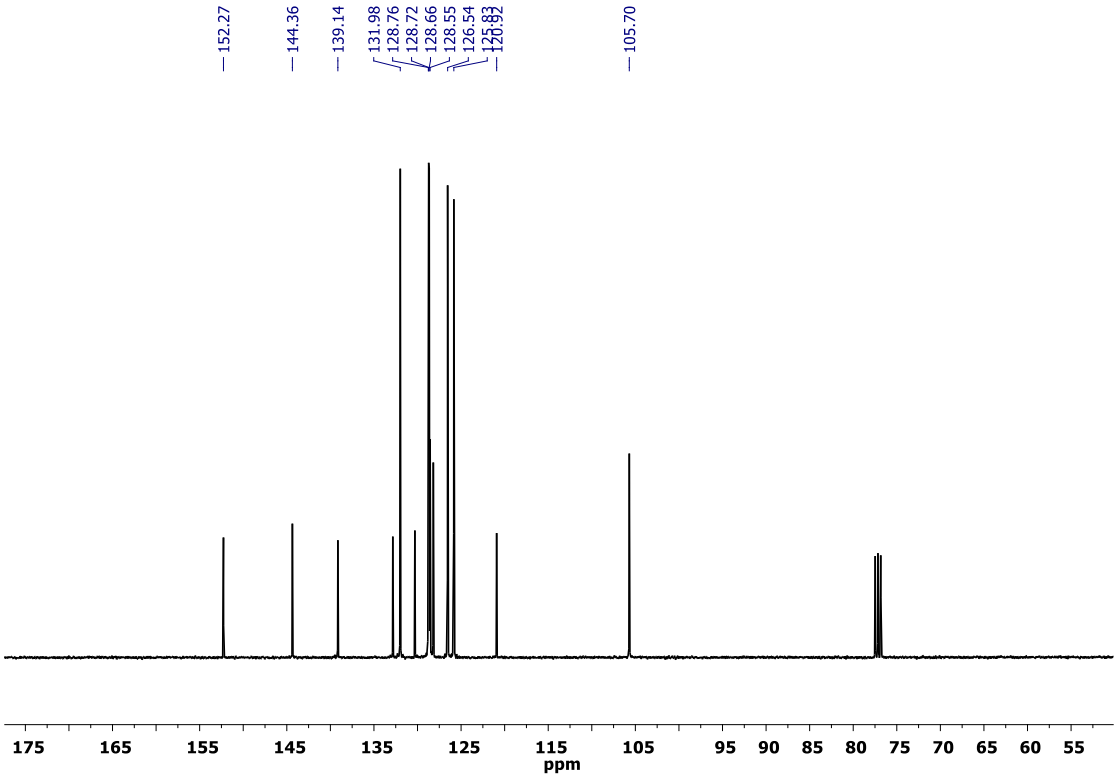


Figure S14: ^{13}C NMR of compound **1a**.

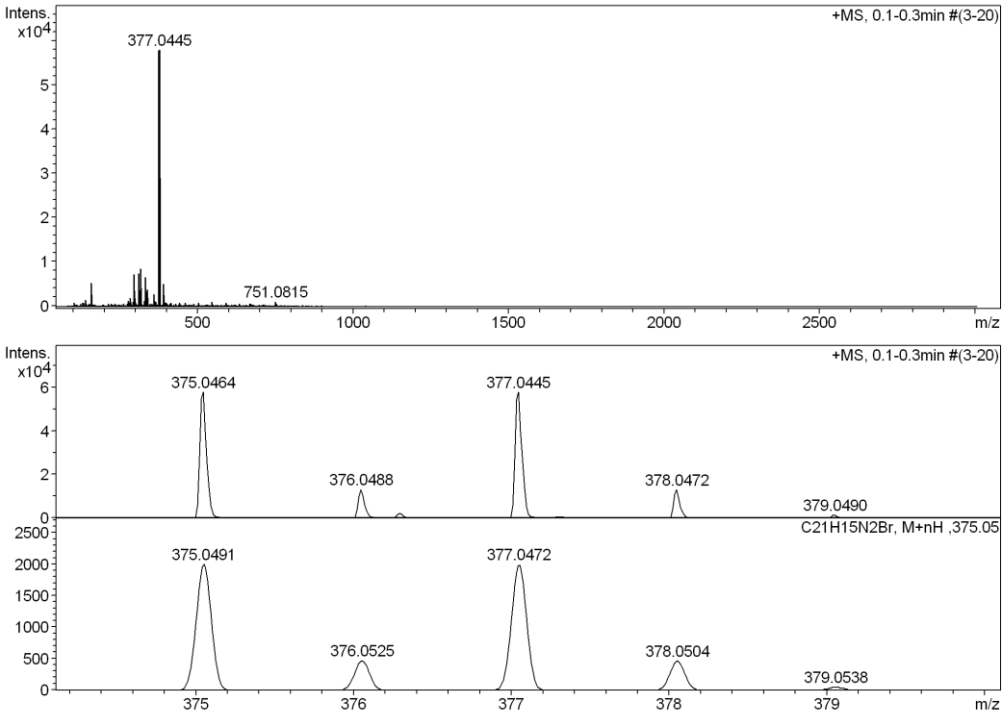


Figure S15: HRMS of compound **1a**.

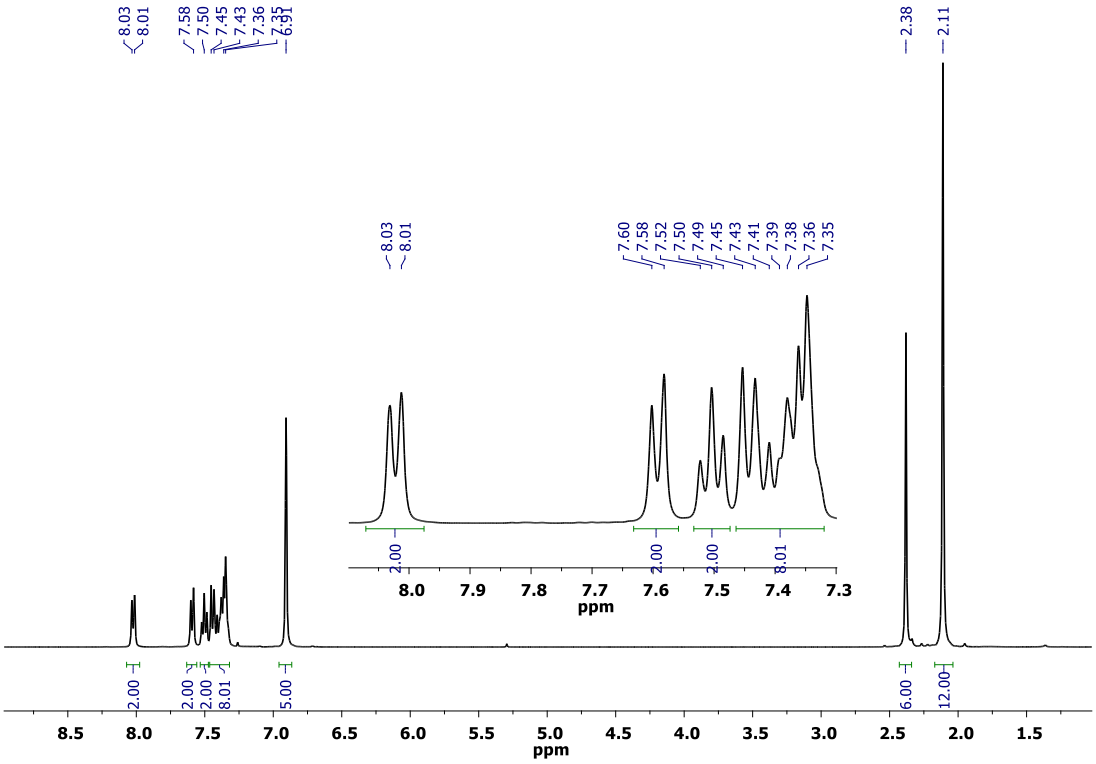


Figure S16: ^{1}H NMR of compound **2a.**

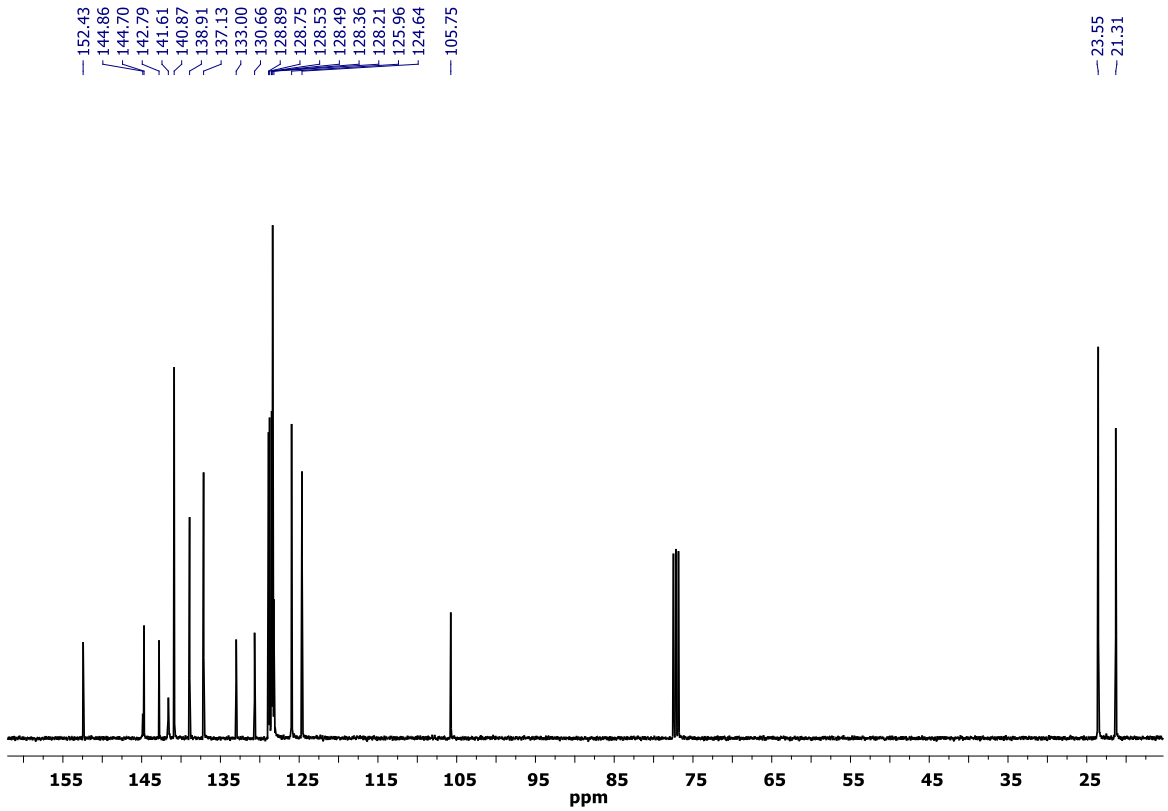


Figure S17: ^{13}C NMR of compound **2a**.

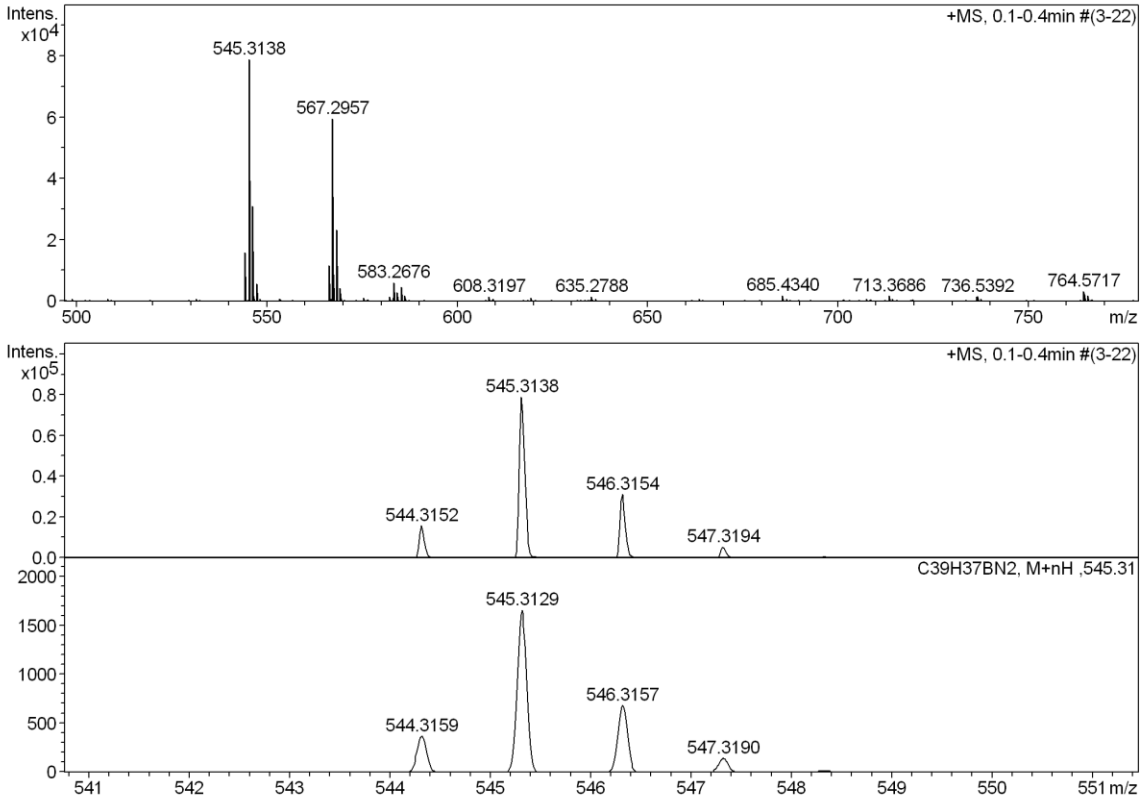


Figure S18: HRMS of compound **2a**.

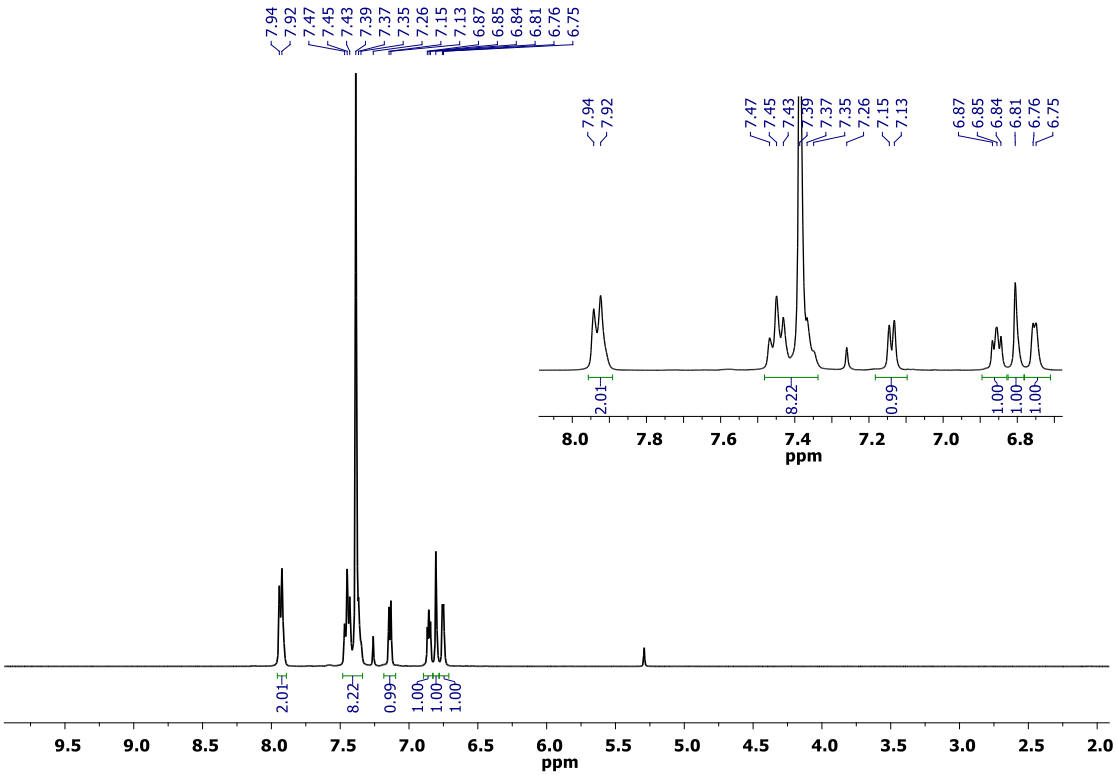


Figure S19: ^{1}H NMR of compound **Th-Pz-diPh.**

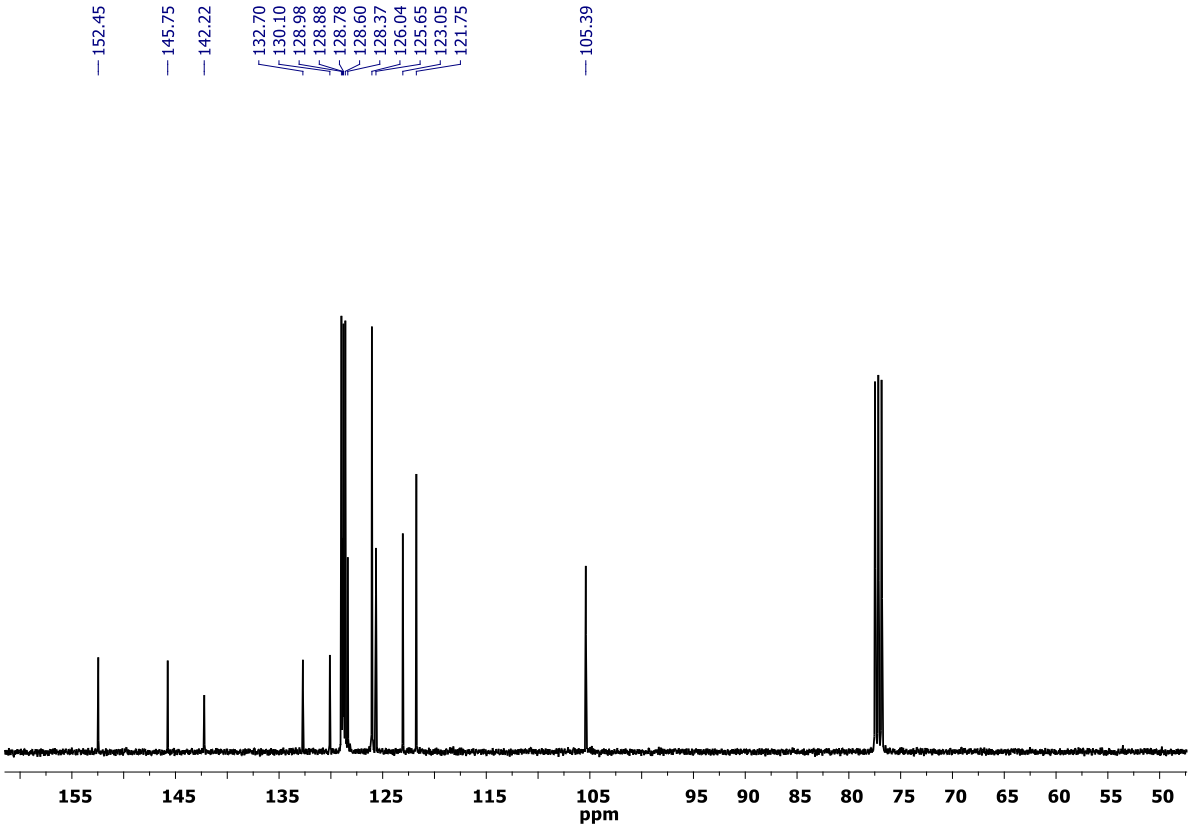


Figure S20: ^{13}C NMR of **Th-Pz-diPh**.

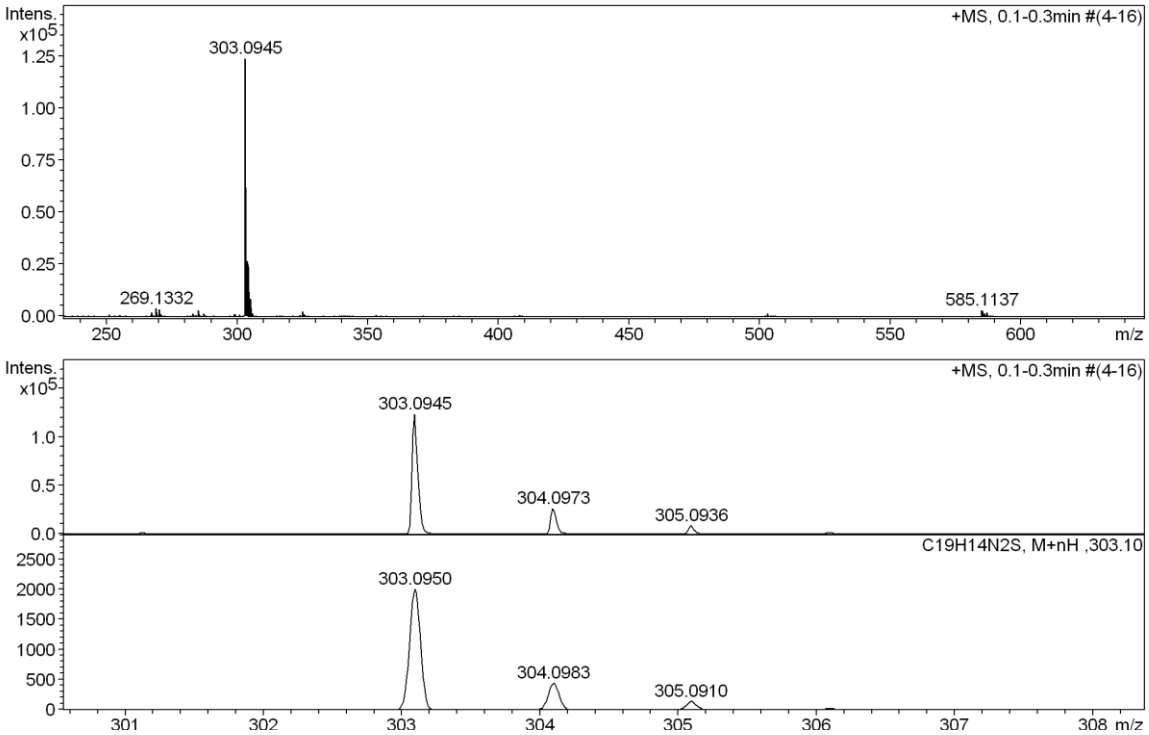


Figure S21: HRMS of **Th-Pz-diPh**.

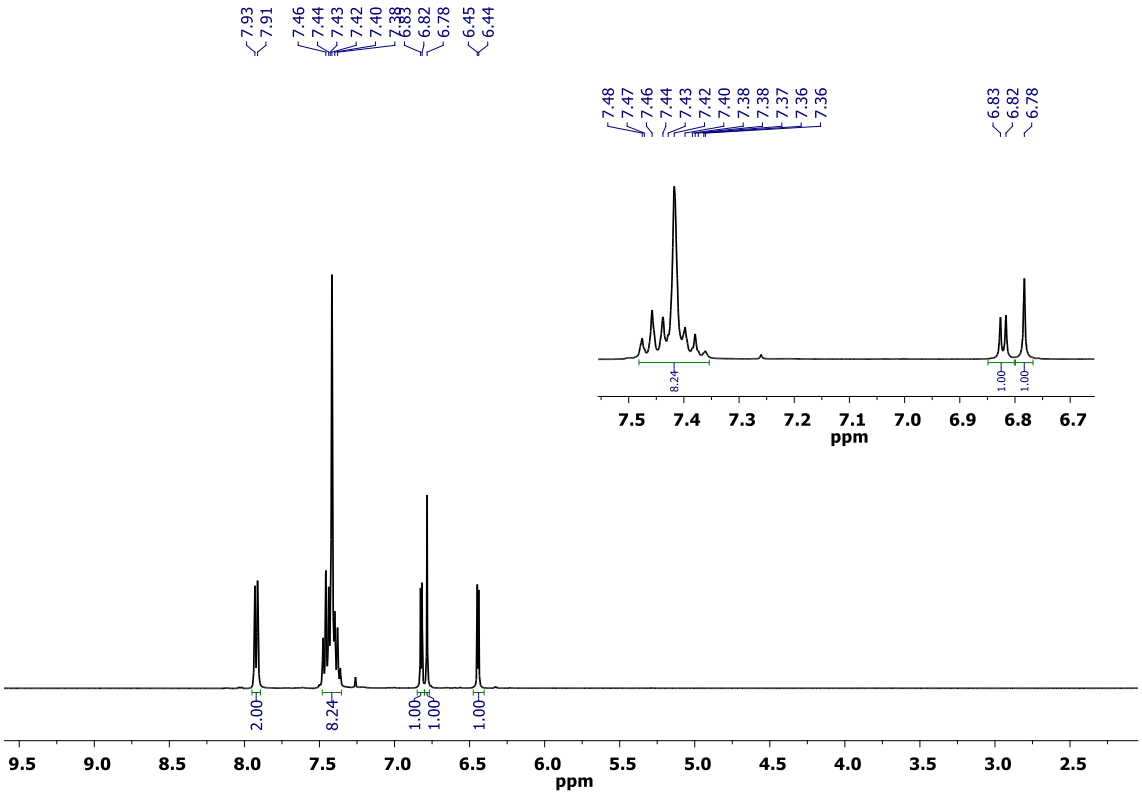


Figure S22: ^{1}H NMR of compound **1b**.

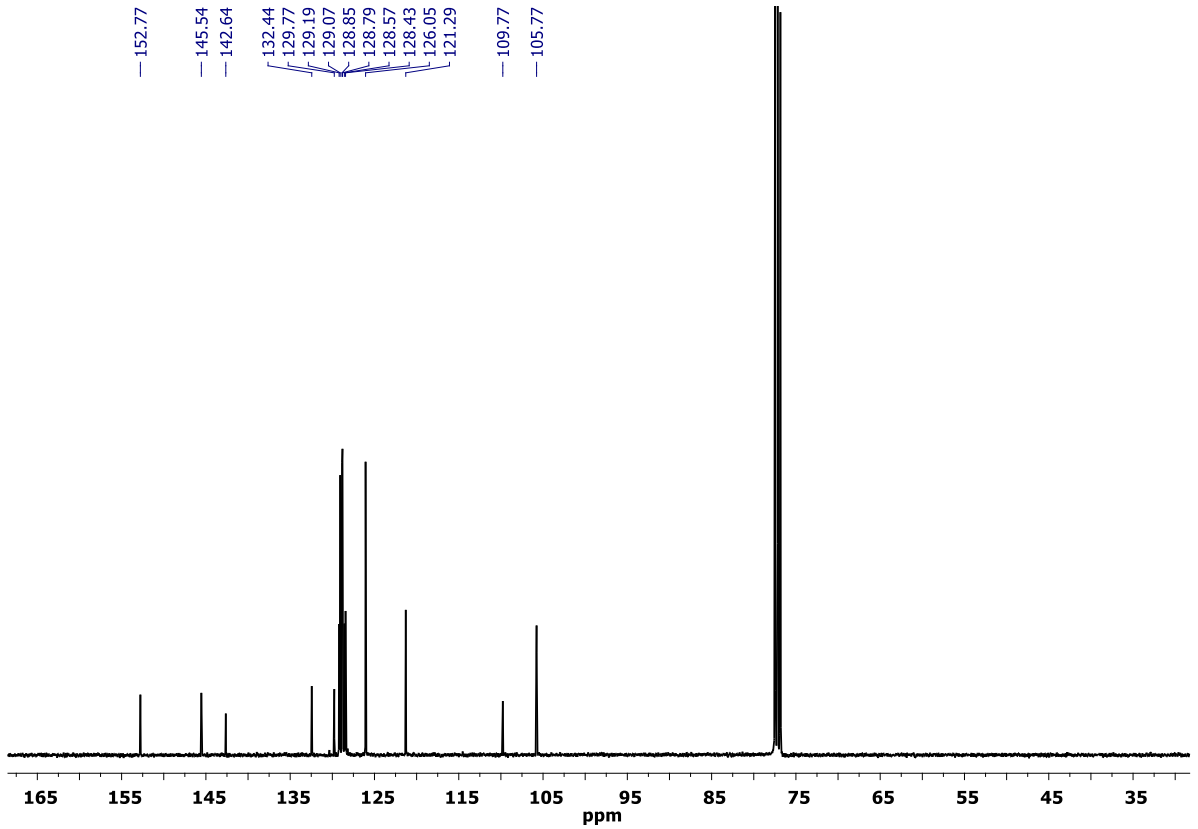


Figure S23: ^{13}C NMR of compound **1b**.

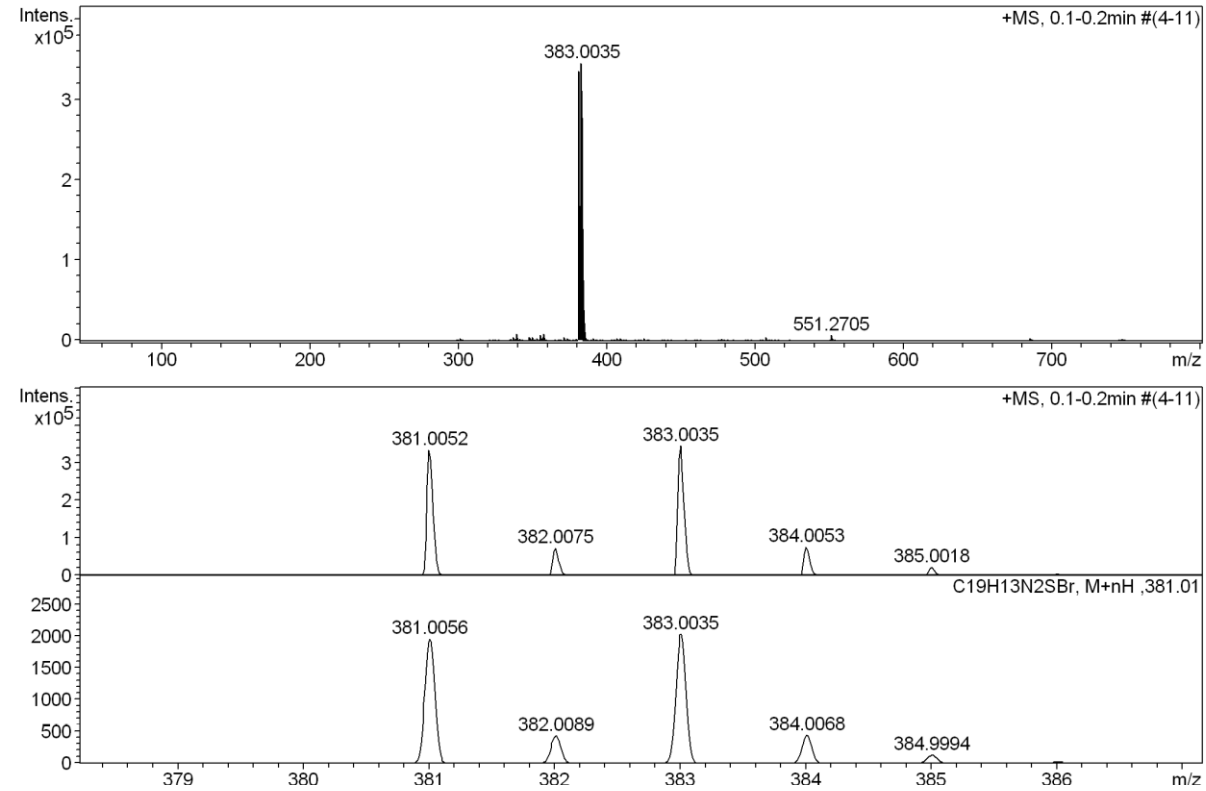


Figure S24: HRMS of compound **1b**.

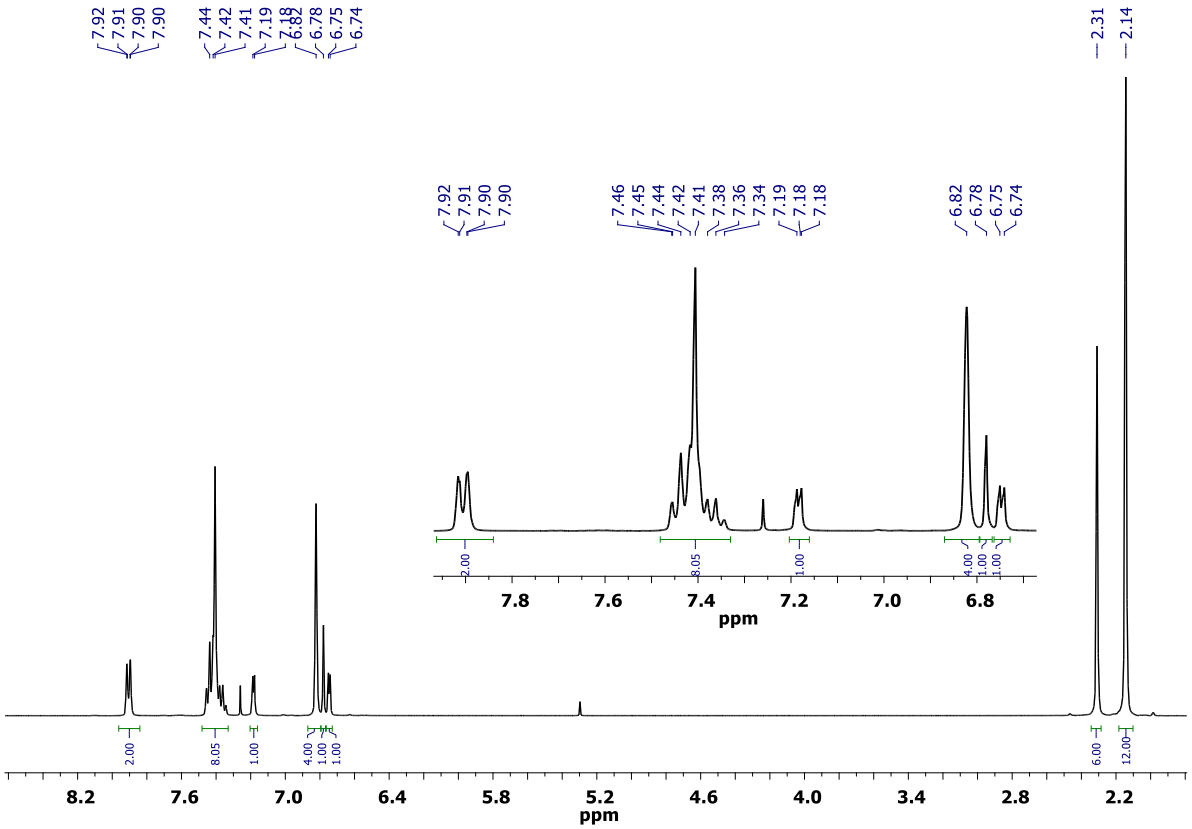


Figure S25: ^{1}H NMR of compound **2b**.

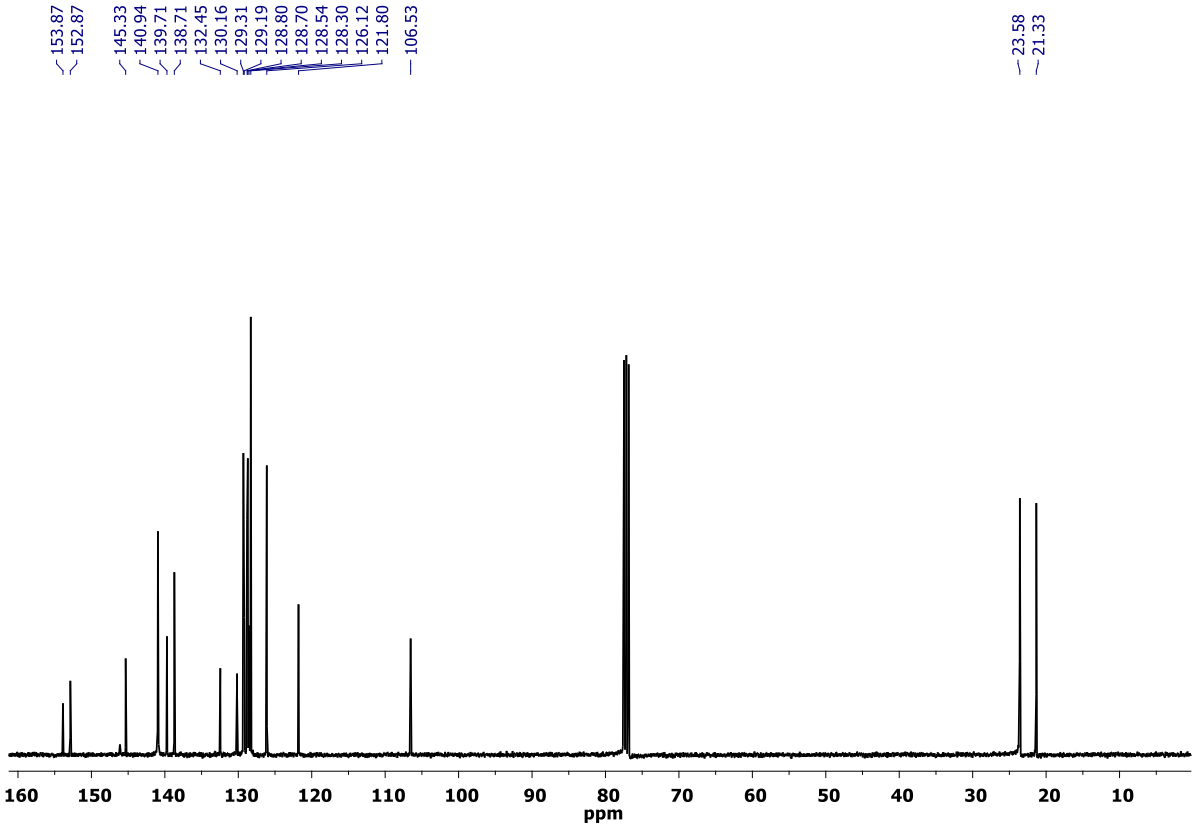


Figure S26: ^{13}C NMR of compound **2b**.

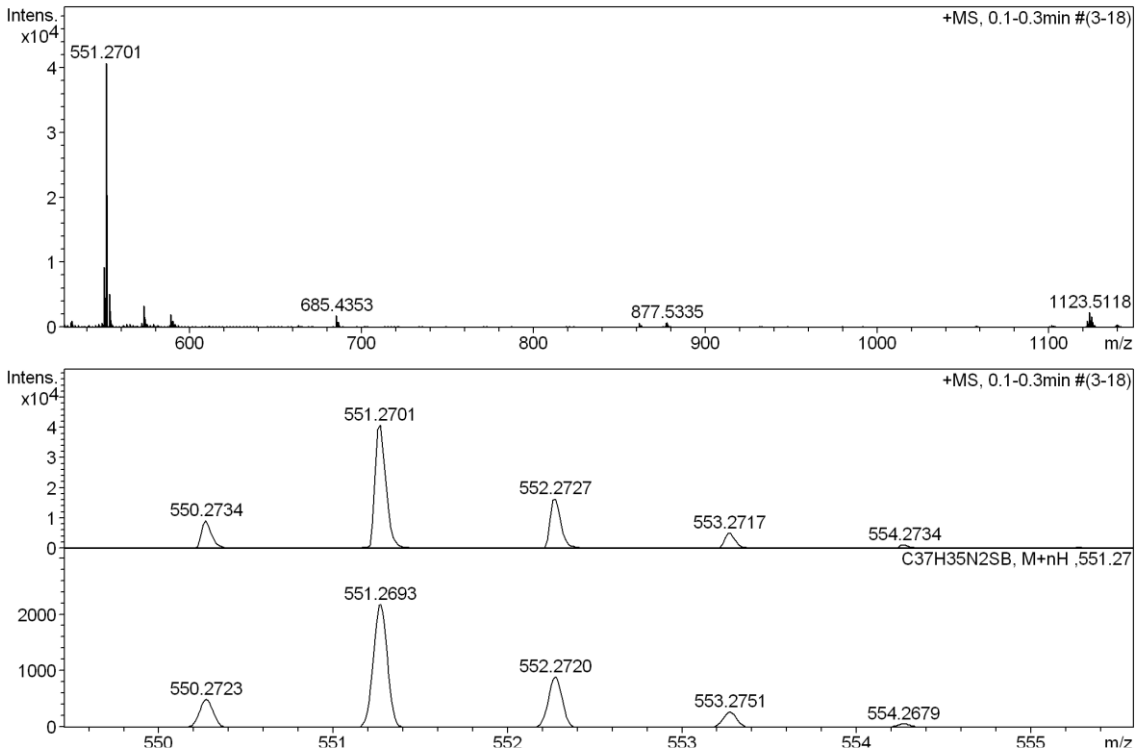


Figure S27: HRMS of compound **2b**.

Optimized x,y,z coordinates for compounds **2a, 2b, 2a-PA, 2b-PA & picric acid** calculated on Gaussian 03 at the B3LYP//6-31g(d,p) level

Compound **2a**

Center	Atomic	Atomic Coordinates (Angstroms)		
	Type	X	Y	Z
N		-3.747454	-0.869950	-0.467018
N		-3.030624	0.123968	0.119907
C		0.389760	-1.290888	0.145811
H		0.858588	-2.260825	0.285994
C		3.574035	0.813966	-0.997415
C		3.280588	1.072607	-2.362911
C		5.003201	2.804800	-2.464355
C		3.486021	-1.486768	0.556077

C	4.328997	-2.388495	-0.149358
C	4.931391	-3.458426	0.519339
H	5.557842	-4.144630	-0.046843
C	4.760843	-3.668041	1.889452
C	3.943464	-2.775187	2.583744
H	3.800313	-2.911260	3.654142
C	3.298847	-1.709215	1.947002
C	4.604066	1.580441	-0.385578
C	5.280930	2.560134	-1.117152
H	6.053225	3.145184	-0.621715
C	2.208810	0.318046	-3.128632
H	1.227347	0.792088	-3.017694
H	2.444188	0.298923	-4.196987
H	2.095434	-0.715653	-2.795023
C	-8.141699	-3.024042	-1.889760
H	-8.929533	-3.662339	-2.278855
C	-8.451160	-1.774226	-1.352101
H	-9.482185	-1.433611	-1.322111
C	-7.439828	-0.955073	-0.852932
H	-7.695532	0.017749	-0.444235
C	-6.100126	-1.372075	-0.880189
C	-0.995500	-1.198963	0.213935
H	-1.613431	-2.072545	0.384699
C	4.002111	2.043393	-3.067362
H	3.772431	2.207870	-4.118421
C	5.783685	3.833860	-3.246268
H	6.730541	3.418254	-3.613636
H	5.222599	4.185184	-4.117162
H	6.032101	4.702632	-2.628503

C	2.426121	-0.815641	2.809859
H	1.379915	-1.140472	2.792064
H	2.761003	-0.844738	3.851135
H	2.435751	0.227696	2.486718
C	5.463487	-4.799523	2.600386
H	6.449910	-4.486326	2.965389
H	4.891906	-5.144076	3.467514
H	5.621076	-5.653890	1.935226
C	-3.632338	4.650752	1.927518
H	-4.078852	5.617203	1.712934
C	-2.711142	4.519442	2.967389
H	-2.439321	5.382047	3.568395
C	-2.141994	3.271994	3.232787
H	-1.431456	3.160104	4.046426
C	-2.489042	2.162457	2.465400
H	-2.055334	1.193368	2.688863
C	-5.799159	-2.631910	-1.424914
H	-4.764773	-2.956682	-1.449482
C	-6.810583	-3.447336	-1.924329
H	-6.559947	-4.418558	-2.341518
C	-5.028259	-0.512424	-0.351250
C	-1.612162	0.048496	0.056549
C	1.205420	-0.165203	-0.100230
B	2.768611	-0.281104	-0.181893
C	-5.138494	0.733063	0.318949
H	-6.033987	1.259797	0.611053
C	-3.846583	1.120050	0.621009
C	4.576545	-2.260652	-1.638807
H	5.276463	-3.027825	-1.981079

H	3.653792	-2.384345	-2.217352
H	4.990155	-1.283569	-1.901569
C	4.980826	1.402801	1.071295
H	5.810169	2.063100	1.339242
H	4.146763	1.643947	1.740523
H	5.281150	0.375321	1.292530
C	0.545474	1.068954	-0.276230
H	1.134992	1.956181	-0.488903
C	-0.838504	1.187591	-0.196527
H	-1.317768	2.147473	-0.347846
C	-3.409612	2.285406	1.410803
C	-3.978101	3.543541	1.153925
H	-4.684060	3.648395	0.335752

Compound **2b**

Center Atomic Atomic Coordinates (Angstroms)

Type X Y Z

C	-3.089443	4.323054	1.568153
C	-2.576032	3.301536	2.361282
H	-2.285535	3.520327	3.387356
C	-2.422503	1.992148	1.882473
C	-2.803260	1.666807	0.556443
B	-2.601543	0.210361	-0.039040
C	-1.176532	-0.386126	-0.106095
S	0.268448	0.601297	0.104685
C	1.303965	-0.773171	-0.127675

N	2.693986	-0.603182	-0.089331
N	3.198485	0.599071	-0.478593
C	4.524429	0.470486	-0.428113
C	5.403696	1.596834	-0.780102
C	6.798102	1.441985	-0.810236
H	7.241685	0.478849	-0.577062
C	7.625618	2.513249	-1.142478
H	8.702754	2.374545	-1.160648
C	7.073972	3.756994	-1.451896
H	7.718782	4.591632	-1.710848
C	4.881459	-0.837978	-0.004484
H	5.867469	-1.237827	0.175623
C	3.696187	-1.507520	0.221017
C	0.592764	-1.934398	-0.354132
H	1.053664	-2.895699	-0.535025
C	-0.800258	-1.701774	-0.338973
H	-1.535398	-2.481016	-0.506028
C	-3.796063	-0.687384	-0.576374
C	-4.856137	-1.074668	0.293838
C	-5.875360	-1.908585	-0.164834
H	-6.663962	-2.201297	0.525699
C	-5.914632	-2.379280	-1.482705
C	-7.040025	-3.268824	-1.953660
H	-8.001427	-2.741992	-1.928158
H	-7.144193	-4.153290	-1.315012
H	-6.876207	-3.612010	-2.978894
C	-4.888886	-1.987077	-2.337063
H	-4.900208	-2.327188	-3.371215
C	-3.838115	-1.159997	-1.912100

C	-2.825880	-0.762215	-2.970601
H	-2.411837	-1.645957	-3.469130
H	-1.990035	-0.189797	-2.570969
H	-3.305934	-0.155438	-3.747930
C	-4.898997	-0.636316	1.742995
H	-5.809755	-0.996465	2.229432
H	-4.872124	0.452667	1.837953
H	-4.048626	-1.028885	2.312038
C	-3.471257	3.999814	0.260566
H	-3.876996	4.780319	-0.380213
C	-3.348323	2.707907	-0.249271
C	-3.774002	2.465698	-1.682320
H	-2.927309	2.172531	-2.313335
H	-4.204226	3.372272	-2.116692
H	-4.519453	1.668884	-1.754817
C	-1.909519	0.965348	2.875103
H	-0.975966	1.302203	3.338602
H	-1.721064	-0.008413	2.422944
H	-2.635517	0.820234	3.684488
C	3.503489	-2.865957	0.761628
C	2.686122	-3.104741	1.879251
H	2.147956	-2.280627	2.335923
C	2.572862	-4.388205	2.408430
H	1.939626	-4.557546	3.274205
C	3.276995	-5.450894	1.837179
H	3.187328	-6.450041	2.252900
C	4.097835	-5.222265	0.732401
H	4.648214	-6.043089	0.282238
C	4.210152	-3.939330	0.196952

H	4.839548	-3.761750	-0.669677
C	4.857784	2.853128	-1.093849
H	3.780536	2.975927	-1.071763
C	5.686528	3.920553	-1.426547
H	5.248448	4.885252	-1.666010
C	-3.224737	5.734508	2.086606
H	-2.503522	6.405324	1.603967
H	-3.051021	5.783456	3.165154
H	-4.222431	6.140059	1.885763

Compound 2a-PA

Center	Atomic	Atomic Coordinates (Angstroms)		
	Type	X	Y	Z
N		2.339500	-2.097182	-0.029198
C		-0.979114	-0.939842	1.152030
H		-1.429362	-0.594144	2.078027
C		-3.954224	-0.071663	-1.320143
C		-3.405798	1.058241	-1.986882
C		-5.111367	0.925071	-3.733650
C		-4.106949	-0.826135	1.354404
C		-4.802433	0.253067	1.966610
C		-5.494183	0.052665	3.164599
H		-6.004018	0.898011	3.622106
C		-5.555428	-1.195891	3.787183
C		-4.880489	-2.256013	3.180682
H		-4.919600	-3.241122	3.641541
C		-4.152104	-2.092504	1.997764

C	-5.098291	-0.688281	-1.895908
C	-5.639673	-0.193663	-3.086674
H	-6.505537	-0.693939	-3.515561
C	-2.195164	1.808172	-1.461395
H	-1.262377	1.305151	-1.739242
H	-2.163005	2.817539	-1.882419
H	-2.193747	1.906411	-0.372844
C	8.005714	0.097662	1.788610
H	8.911040	0.569735	2.158469
C	8.076312	-0.855550	0.771511
H	9.036901	-1.123879	0.341656
C	6.914672	-1.461043	0.296800
H	6.976794	-2.185946	-0.509166
C	5.662110	-1.125597	0.833416
C	0.369201	-1.284804	1.148362
H	0.971920	-1.197559	2.044727
C	-3.996261	1.538448	-3.160029
H	-3.572023	2.418450	-3.639548
C	-5.745671	1.473894	-4.988828
H	-6.525659	2.207611	-4.749171
H	-5.009844	1.978856	-5.621872
H	-6.216748	0.682038	-5.578968
C	-3.450349	-3.319312	1.443509
H	-2.399379	-3.352094	1.751460
H	-3.928797	-4.231853	1.811384
H	-3.460031	-3.358348	0.351493
C	-6.349868	-1.395376	5.055359
H	-7.419891	-1.507572	4.839550
H	-6.028837	-2.292781	5.592059

H	-6.246451	-0.540154	5.730750
C	2.242925	-6.146350	-2.788226
H	2.669654	-6.600053	-3.677773
C	1.113768	-6.705607	-2.188440
H	0.659133	-7.598575	-2.606747
C	0.572438	-6.112685	-1.045992
H	-0.300490	-6.547592	-0.568495
C	1.152388	-4.967247	-0.504974
H	0.735106	-4.523543	0.392644
C	5.601827	-0.167636	1.859022
H	4.639983	0.085727	2.292500
C	6.763875	0.439542	2.328498
H	6.701172	1.175535	3.124874
C	4.440201	-1.780178	0.339766
C	0.956101	-1.746966	-0.034308
C	-1.771973	-1.020326	-0.011397
B	-3.297750	-0.629202	0.008818
C	4.316875	-3.027728	-0.314058
H	5.096171	-3.743056	-0.527129
C	2.962556	-3.215538	-0.533638
C	-4.772402	1.655360	1.395907
H	-5.489267	2.298661	1.913569
H	-3.783096	2.111801	1.517836
H	-5.012474	1.669211	0.330302
C	-5.748697	-1.911770	-1.282659
H	-6.642618	-2.195894	-1.844555
H	-5.075846	-2.777403	-1.287841
H	-6.040732	-1.740221	-0.243836
C	-1.139122	-1.469666	-1.188942

H	-1.713219	-1.524564	-2.109576
C	0.203107	-1.839709	-1.209427
H	0.671014	-2.182726	-2.125704
C	2.284964	-4.392527	-1.105570
C	2.823912	-4.998363	-2.252381
H	3.693693	-4.555197	-2.727647
N	3.235722	-1.219172	0.501059
H	2.798737	0.712735	0.575671
C	2.603073	3.111779	-0.500522
C	1.898790	2.464772	0.557836
C	0.787397	3.191027	1.078743
C	0.400985	4.425772	0.594083
C	1.149177	5.015186	-0.422075
C	2.242584	4.369302	-0.973417
H	-0.472561	4.922137	0.995815
H	2.815334	4.826341	-1.769236
N	-0.037062	2.620584	2.157948
N	3.751244	2.475685	-1.145859
N	0.760905	6.335836	-0.927796
O	2.155188	1.286550	1.071476
O	-1.246271	2.858451	2.105577
O	0.521023	1.983570	3.041388
O	4.380740	3.122299	-1.976021
O	4.018775	1.313468	-0.820734
O	1.432568	6.812777	-1.840403
O	-0.211624	6.876144	-0.403438

Compoun2b-PA

Center	Atomic Type	Atomic Coordinates (Angstroms) X	Y	Z
C	-3.474960	-0.915039	4.805510
C	-2.997357	-2.087330	4.227227
H	-2.777379	-2.942086	4.864312
C	-2.795373	-2.207805	2.845027
C	-3.085547	-1.120209	1.982133
B	-2.823010	-1.209660	0.422012
C	-1.387162	-1.496155	-0.085411
S	0.031529	-1.304109	0.940683
C	1.093423	-1.766183	-0.355670
N	2.484432	-1.791567	-0.165156
N	3.086720	-0.732604	0.450898
C	4.397943	-0.988505	0.405316
C	5.383290	-0.069812	0.998627
C	6.709593	-0.062452	0.538082
H	6.999840	-0.721188	-0.274970
C	7.651160	0.798450	1.098353
H	8.672084	0.793983	0.727826
C	7.281984	1.667768	2.126201
H	8.015529	2.338765	2.563379
C	4.642262	-2.217614	-0.256765
H	5.588815	-2.717316	-0.394017
C	3.404091	-2.722715	-0.604389
C	0.408045	-2.074576	-1.509089
H	0.893477	-2.373935	-2.428716
C	-0.986969	-1.917844	-1.344880

H	-1.704173	-2.095917	-2.138152
C	-3.950580	-1.019974	-0.676518
C	-5.096393	-1.863419	-0.698449
C	-6.059564	-1.715022	-1.697771
H	-6.920382	-2.380820	-1.699423
C	-5.956899	-0.731855	-2.687336
C	-7.015220	-0.593800	-3.755132
H	-8.019671	-0.553938	-3.319633
H	-6.998768	-1.447622	-4.443366
H	-6.868544	0.312502	-4.348933
C	-4.846753	0.109648	-2.650061
H	-4.754372	0.897285	-3.395330
C	-3.844575	-0.022599	-1.679890
C	-2.692108	0.964220	-1.745861
H	-1.898777	0.624186	-2.420520
H	-2.226258	1.130495	-0.773060
H	-3.045503	1.931711	-2.117757
C	-5.301152	-2.958228	0.328057
H	-6.232888	-3.497898	0.137686
H	-5.345296	-2.556322	1.344321
H	-4.488731	-3.692901	0.308808
C	-3.772157	0.154473	3.952726
H	-4.151655	1.080936	4.379073
C	-3.597978	0.071963	2.571610
C	-3.928574	1.296373	1.743980
H	-3.024629	1.764170	1.334942
H	-4.432049	2.051455	2.353807
H	-4.576913	1.055814	0.897876
C	-2.342535	-3.567559	2.345995

H	-1.445578	-3.901349	2.878994
H	-2.117884	-3.579829	1.279386
H	-3.121118	-4.318174	2.528805
C	3.080139	-4.011501	-1.240295
C	2.089896	-4.864746	-0.725431
H	1.521490	-4.564046	0.148410
C	1.846934	-6.100738	-1.319997
H	1.081351	-6.751984	-0.909035
C	2.588613	-6.506759	-2.431648
H	2.396269	-7.471021	-2.892377
C	3.578875	-5.669021	-2.945911
H	4.158729	-5.976369	-3.811049
C	3.823152	-4.429798	-2.355838
H	4.583279	-3.771232	-2.764679
C	5.021094	0.805847	2.035627
H	4.002761	0.798768	2.407213
C	5.964614	1.668068	2.590026
H	5.671211	2.337118	3.393830
C	-3.662124	-0.789193	6.298104
H	-2.919318	-0.110480	6.734546
H	-3.559903	-1.756456	6.797753
H	-4.649484	-0.383562	6.544344
O	1.781834	1.481878	-0.793529
O	-1.156586	6.852111	-2.038410
O	1.101123	3.170236	-4.245173
O	-1.004380	7.037284	0.133055
O	0.736725	1.261767	-3.248486
N	-0.822365	6.443428	-0.927821
N	0.870332	2.480211	-3.253248

C	1.141125	2.625463	-0.753117
C	0.876003	3.398876	0.415857
C	0.234869	4.632817	0.362347
H	0.052287	5.185018	1.274515
C	-0.152252	5.140016	-0.865704
C	0.697298	3.200567	-1.978311
C	0.085303	4.437066	-2.045560
H	-0.206156	4.849630	-3.002644
N	1.280336	2.924022	1.735470
O	1.045637	3.629212	2.708381
O	1.843208	1.819912	1.799383
H	2.061391	1.156033	0.099466

Picric acid

Center Atomic Atomic Coordinates (Angstroms)

Type	X	Y	Z
O	-3.520040	-1.273437	0.052320
O	0.704891	-3.481285	0.001043
O	-3.625068	0.909315	0.045979
O	2.570235	-2.368937	-0.085900
N	-3.011511	-0.154953	0.040644
N	1.321514	-2.429284	-0.032118
C	1.273957	0.070664	-0.018850
C	0.459219	1.234293	-0.005844
C	-0.921838	1.164107	-0.004036
H	-1.508906	2.073302	-0.022038
C	-1.543750	-0.083415	0.018990
C	0.578866	-1.175454	-0.009918

C	-0.810075	-1.256543	0.017218
H	-1.301395	-2.220519	0.029954
N	1.059098	2.582335	0.011981
O	0.391741	3.483806	-0.492668
O	2.152043	2.713932	0.547713
O	2.585209	0.166781	-0.073027
H	2.936236	-0.762782	-0.100497