Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A simple and effective 1,2,3-triazole based "*turn-on*" fluorescence sensor for the detection of anions

Debanjana Ghosh, Shannon Rhodes, Karena Hawkins, Domonique Winder, Austin Atkinson, Weihua Ming, Clifford Padgett[a], Jeffrey Orvis, Karelle Aiken, Shainaz Landge*

[*]Department of Chemistry, Georgia Southern University,
250, Forest Drive, Statesboro, Georgia-30460, USA.
Email: slandge@georgiasouthern.edu

[a]Department of Chemistry and Physics, Armstrong Atlantic State University,
11935 Abercon Street, Savannah, GA 31419, USA.

Supporting Information
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General Considerations:

All chemicals and reactants were obtained from commercial sources and used without further purification.

NMR spectra were recorded on a Agilent MR400DD2 spectrometer, with a multinuclear probe with two RF channels and variable temperature capability (^{1}H-NMR: 400 MHz , ^{13}C-NMR: 100 MHz). The solvent used was CD_3CN with TMS as an internal standard set at 0 *ppm* in both ^{1}H-NMR and ^{13}C NMR spectra. The NMR signals are reported in parts per million (*ppm*) relative to the residual in the solvent. Signals are described with multiplicity, singlet (*s*), doublet (*d*), triplet (*t*), triplet of doublet (*td*), quartet (*q*) and multiplet (*m*); coupling constants (*J*; *Hz*) and integration.

All reactions were monitored by thin–layer chromatography (TLC) using Merck silica gel plates 60 F 254; visualization was accomplished with UV light and/or staining with appropriate stains (Iodine, Vanillin).

Column Chromatography was performed with Selecto Scientific Silica-gel (particle size 100–200 microns).

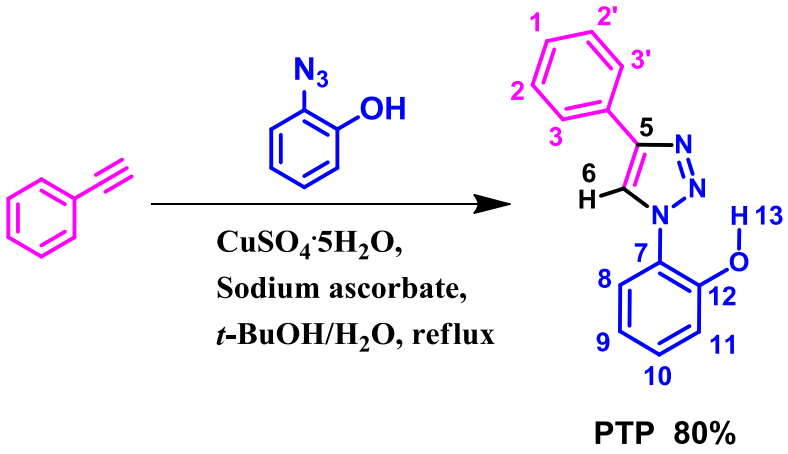
Melting points were measured with Vernier Melt Station using Vernier LabQuest 2 and are uncorrected.

Room temperature absorption and steady state fluorescence measurements are performed using a Shimadzu UV-2450 spectrophotometer and PerkinElmer LS55 with well plate reader fluorimeter respectively. Concentration of **PTP** is kept at ~5.0×10^{-5} mol dm^{-3} in acetonitrile to avoid any possible intermolecular effect. The solvents used are of HPLC grade and Millipore water has been used for the experiment.

The Electrospray Ionization mass spectrometry (ESI-MS) has been conducted using Shimadzu LCMS-2020 Single Quad respectively. All the experiments are performed at ambient temperature (27 ^{0}C) with air-equilibrated solutions.

High Resolution MS (HRMS) analyses were performed using MALDI, Q-TOF micro, 3200API, LCMS, GCMS EI(DI).

Synthetic Procedure:



PTP 80%

Synthesis of PTP: 2-azidophenol[1] (438 mg, 3.24 mmol) and phenylacetylene (0.36 mL, 3.24 mmol) were suspended in *tert*-butanol/water (65 mL; 1:1, v/v) in a round bottom flask. An aqueous solution of copper (II) sulfate pentahydrate (8.10 mg, 0.03 mmol in 4 mL of water) was added dropwise, followed by sodium ascorbate (64.0 mg, 0.32 mmol). The reaction was vigorously stirred while refluxing for 24 hours. Upon cooling to room temperature, the resulting mixture was placed in an ice bath and diluted with water (30 mL) to induce precipitation. The crude, solid product was collected with vacuum filtration and purified by flash column chromatography (40% ethyl acetate in hexanes, followed by 50% ethyl acetate in hexanes) to yield off-white/ beige powder 0.71 g (80%).

Charaterization of probe PTP:

M.P. 193.3-193.7 °C

^{1}H-NMR [400 mHz, CD_3CN] δ 8.68 (*s*, HO), 8.65 (*s*, 1-H), 7.96 (*dd*, 2-H, 1.3, 7.5Hz), 7.68 (*dd*, 1-H, 1.6, 8.0Hz), 7.50 (*t*, 2-H, 7.4Hz), 7.41 (*t*, 1-H, 7.5Hz), 7.39 (*dd*, 1-H, 1.6, 7.4Hz), 7.17 (*dd*, 1-H, 1.3, 8.3Hz), 7.09 (*td*, 1-H, 1.3, 7.4Hz);

^{13}C-NMR [100 mHz, CD_3CN] δ 149.1, 146.9, 130.4, 130.1, 128.9, 128.3, 125.6, 124.0, 123.3, 121.1, 120.5, 117.8

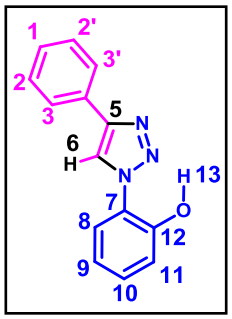
ESI-MS for **PTP**: *m/z* = 238.05 $[M+H]^+$; *calculated* value for $C_{14}H_{11}N_3O$ = 237, *found* from experiment 238.05.

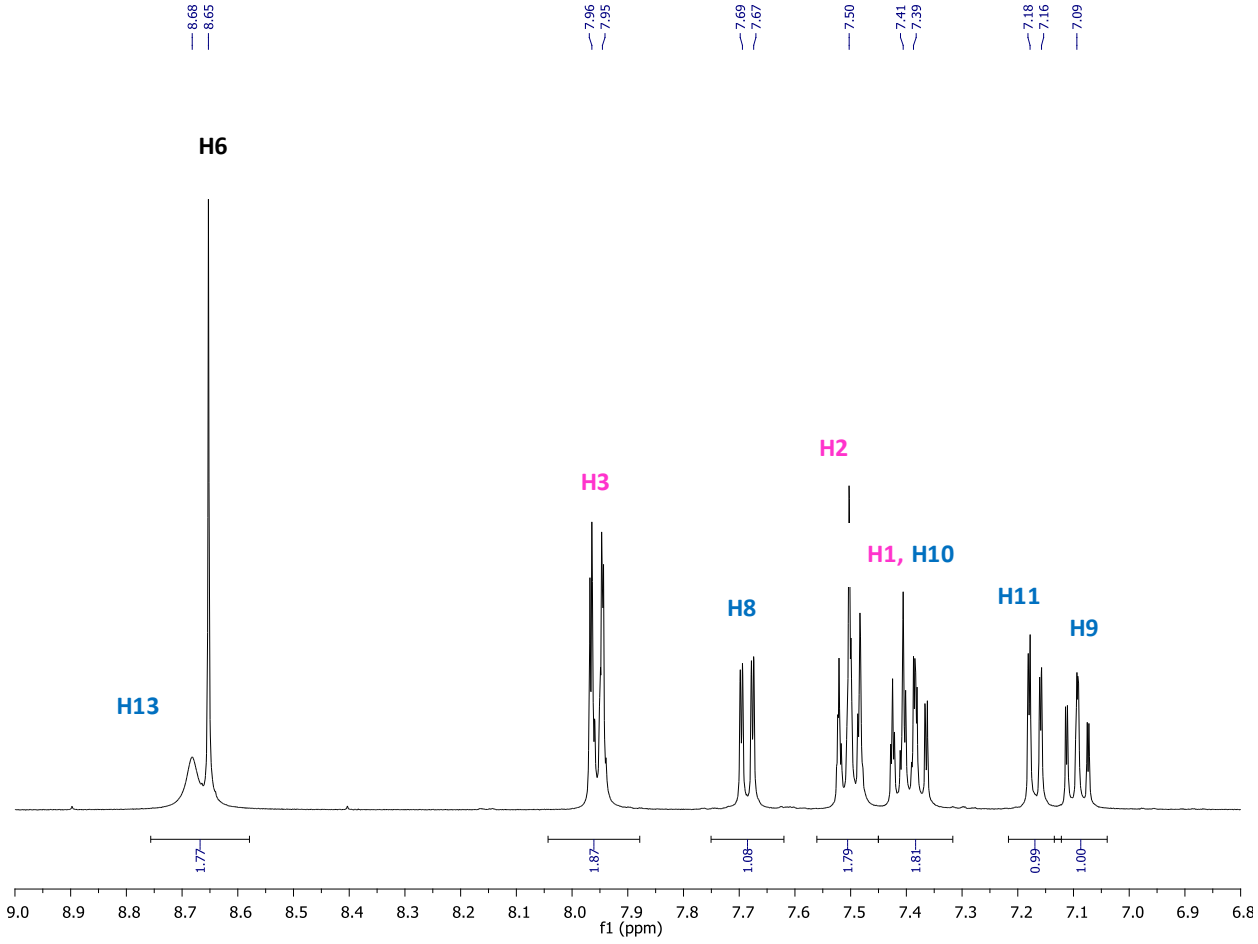
HRMS $(M + H)^+$ *calculated* for $C_{14}H_{11}N_3O$ = 238.0975, *found* = 238.0965.

Nuclear Magnetic Resonance Spectroscopy Characterization of PTP:

PTP, ^{1}H NMR Spectrum

(a)





(b)

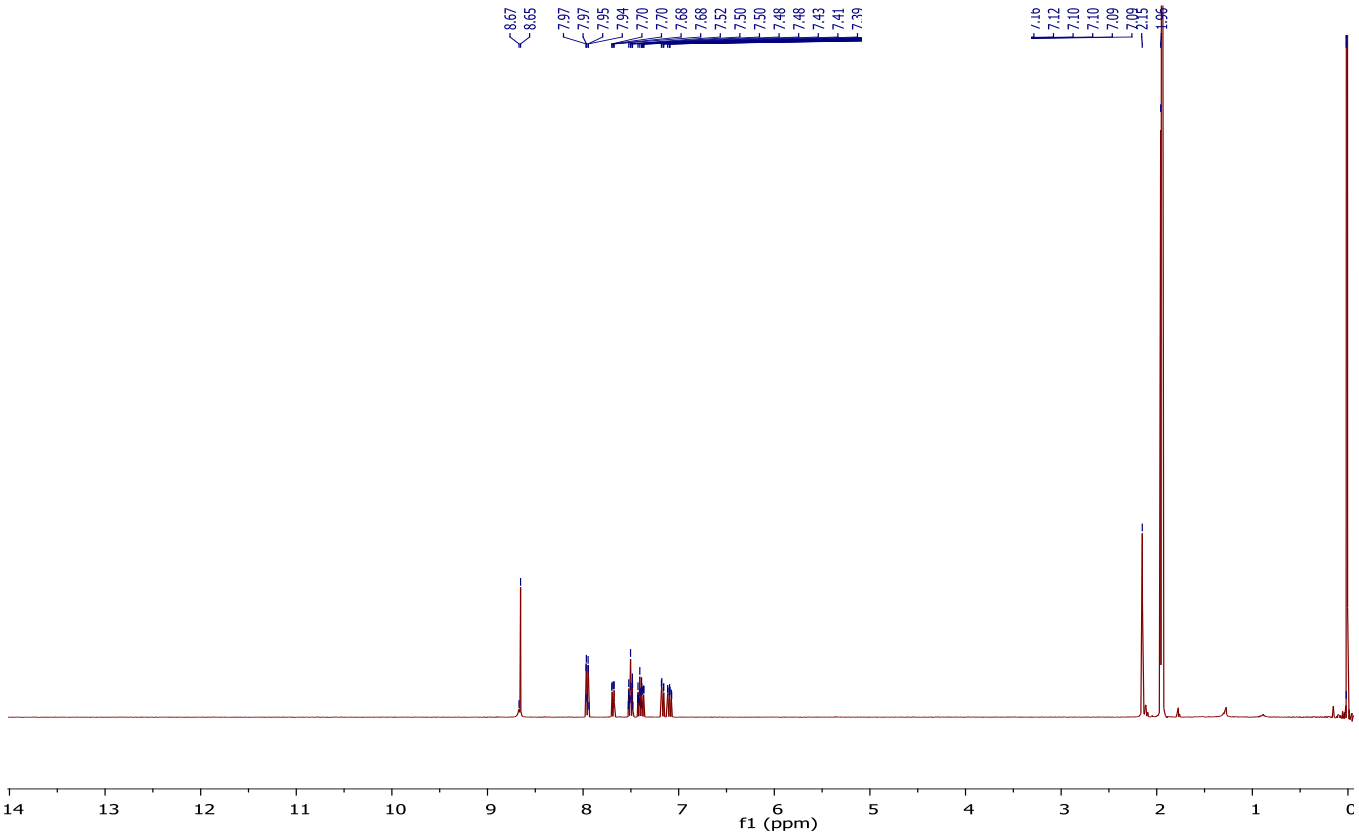
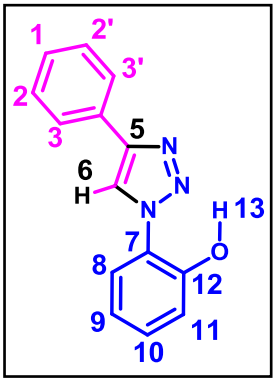
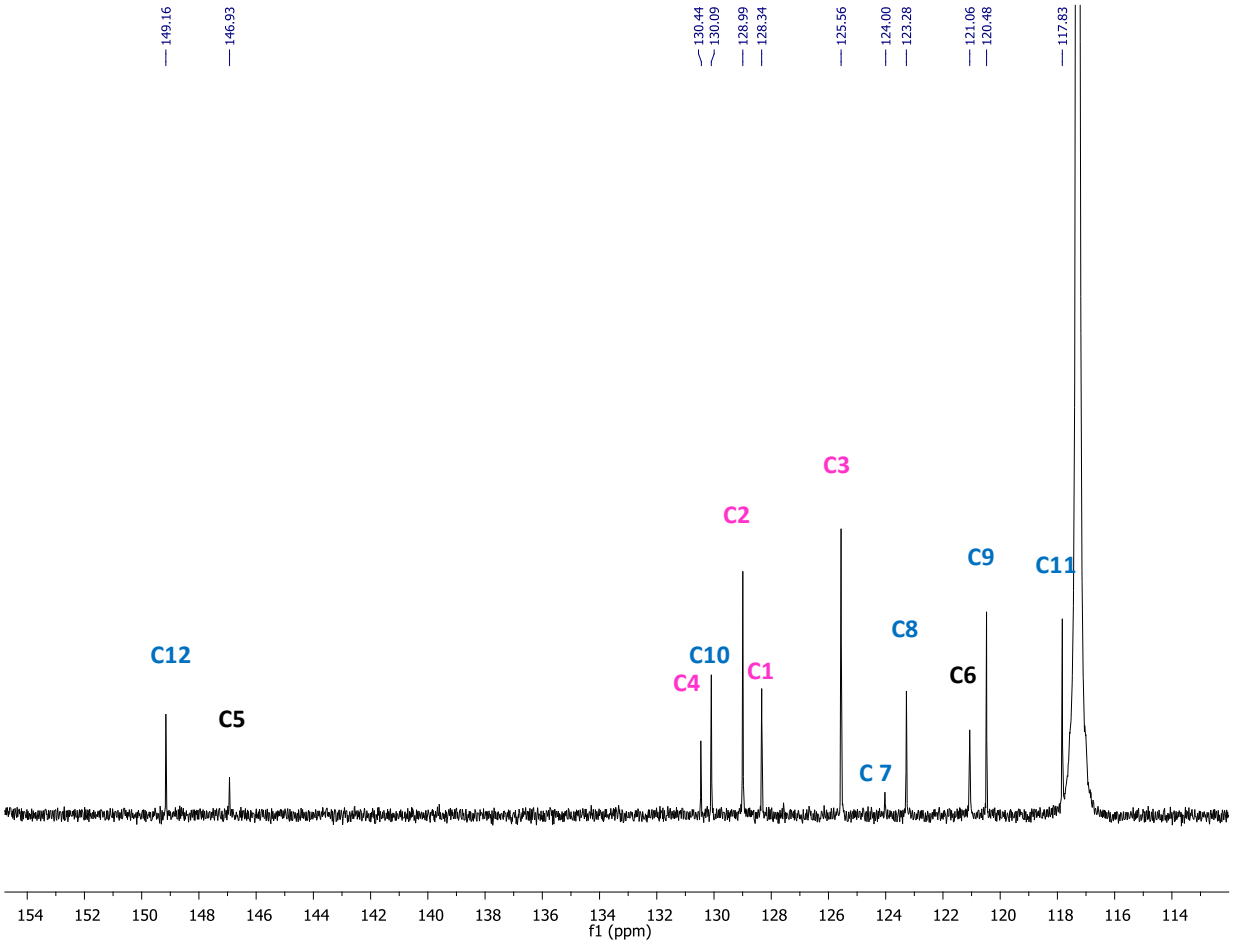


Figure S1: NMR spectra (^{1}H = 400 MHz, CD_3CN, RT) of **PTP**. (a) ^{1}H-NMR spectrum showing the expansion of aromatic region from 6.80 to 9.00 *ppm*. (b) Full ^{1}H-NMR spectrum of **PTP**.

PTP, ^{13}C NMR Spectrum



(a)



(b)

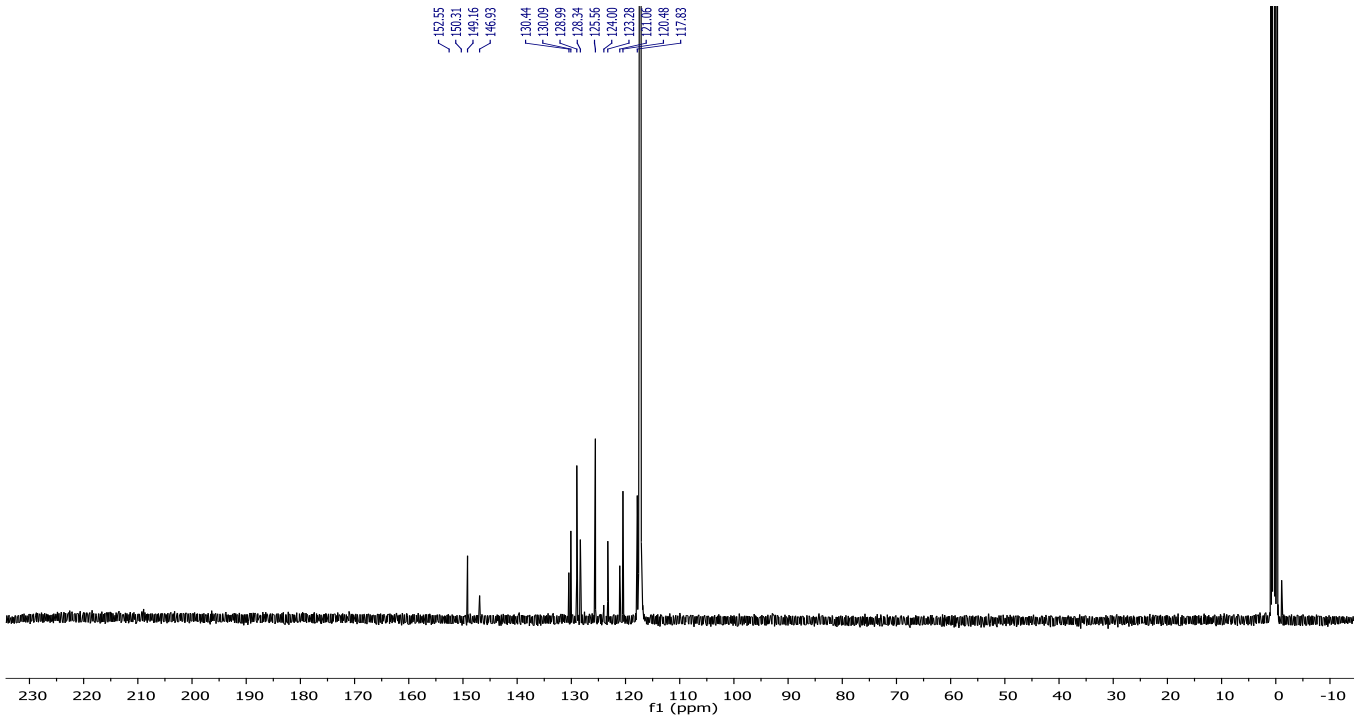


Figure S2: NMR spectra (^{13}C = 100 MHz, CD_3CN, RT) of **PTP**. (a) ^{13}C-NMR spectrum showing the expansion from 112-155 *ppm*. (b) Full ^{13}C-NMR spectrum of **PTP**.

2D g^{1}H-^{1}H COSY spectrum of PTP.

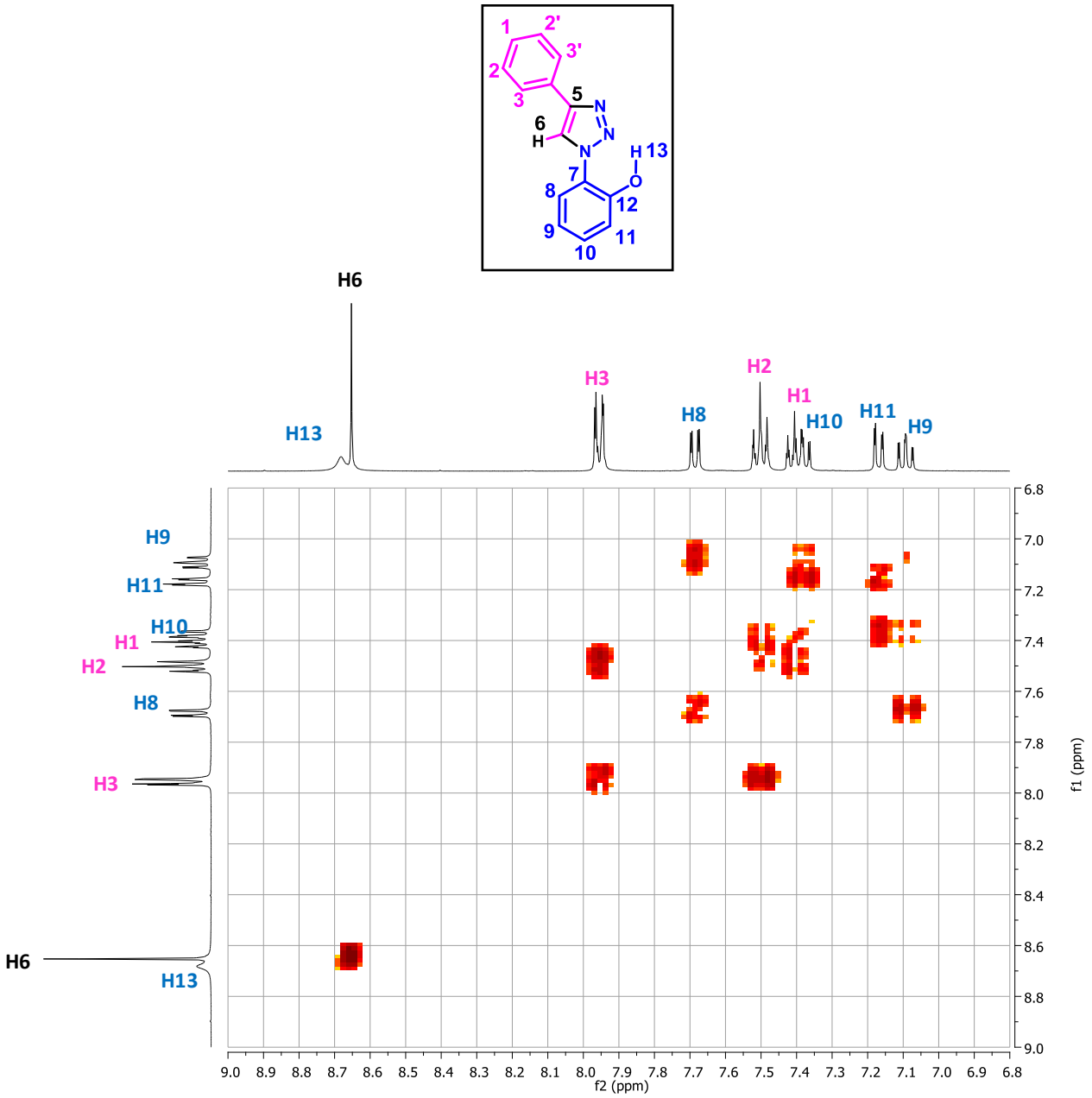
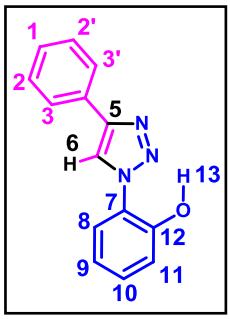


Figure S3: The 2D COSY spectrum (400 MHz, CD_3CN, RT) of **PTP**, The correlation, with all aromatic protons is seen.

1D DEPT90 spectrum of PTP.



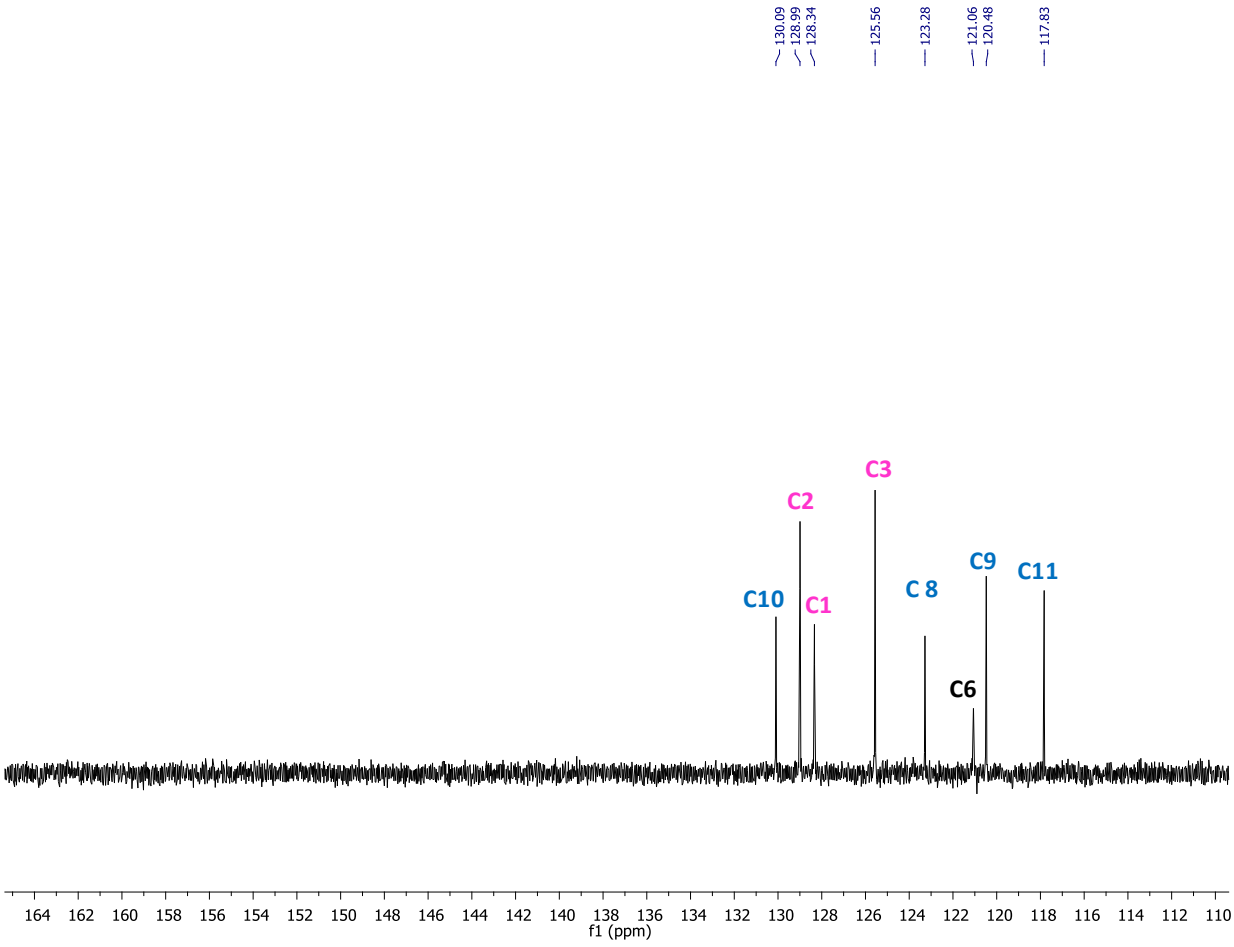


Figure S4: The 1D DEPT 90 spectrum (400 MHz, CD_3CN, RT) of **PTP**, Only C-H signals are visible. The quaternary carbons (4, 5, 7, 12) are missing.

2D HSQC spectrum of PTP.

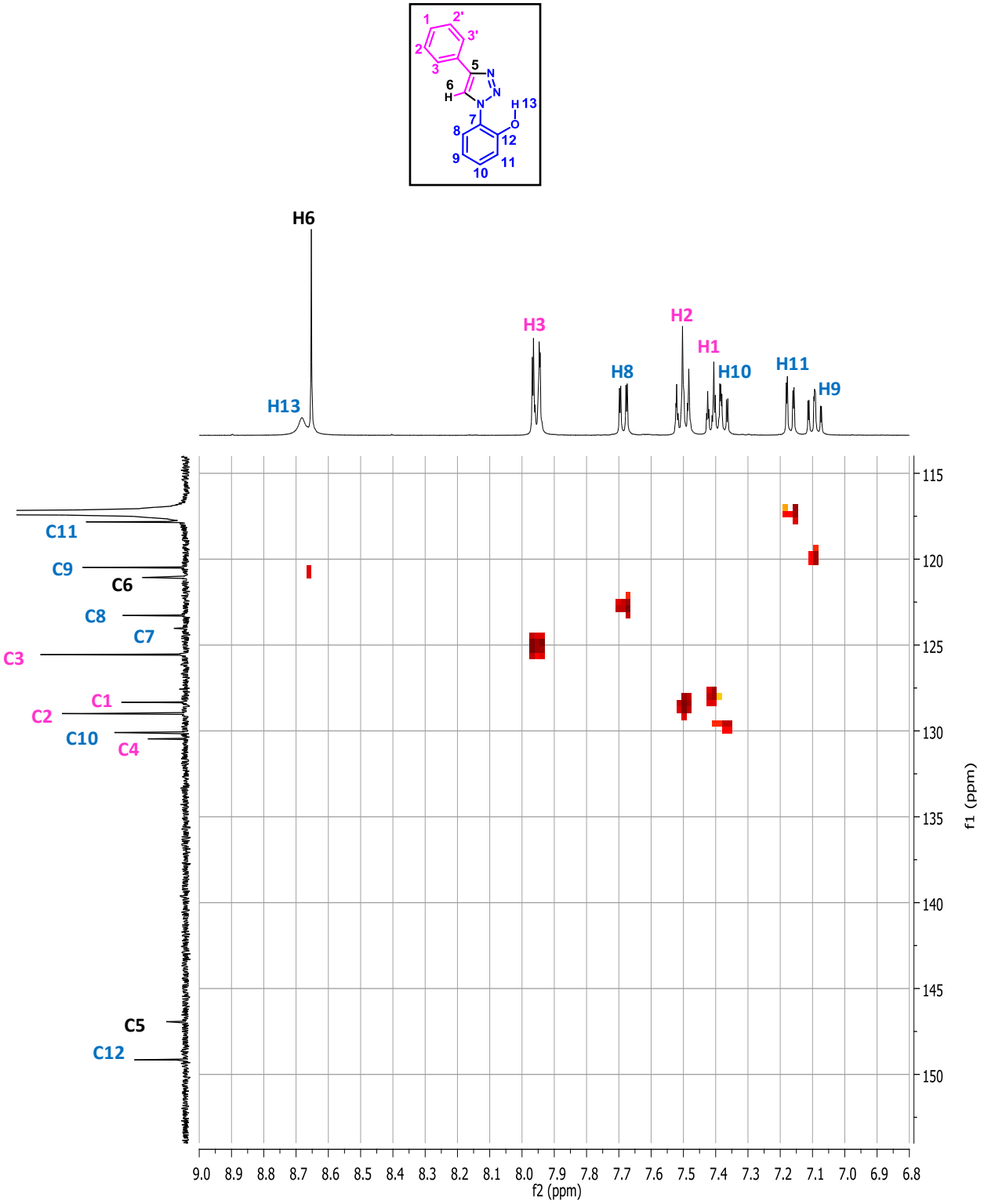


Figure S5: The 2D HSQC spectrum of **PTP**, showing single bond carbon hydrogen correlation.

2D HMBC spectrum of PTP.

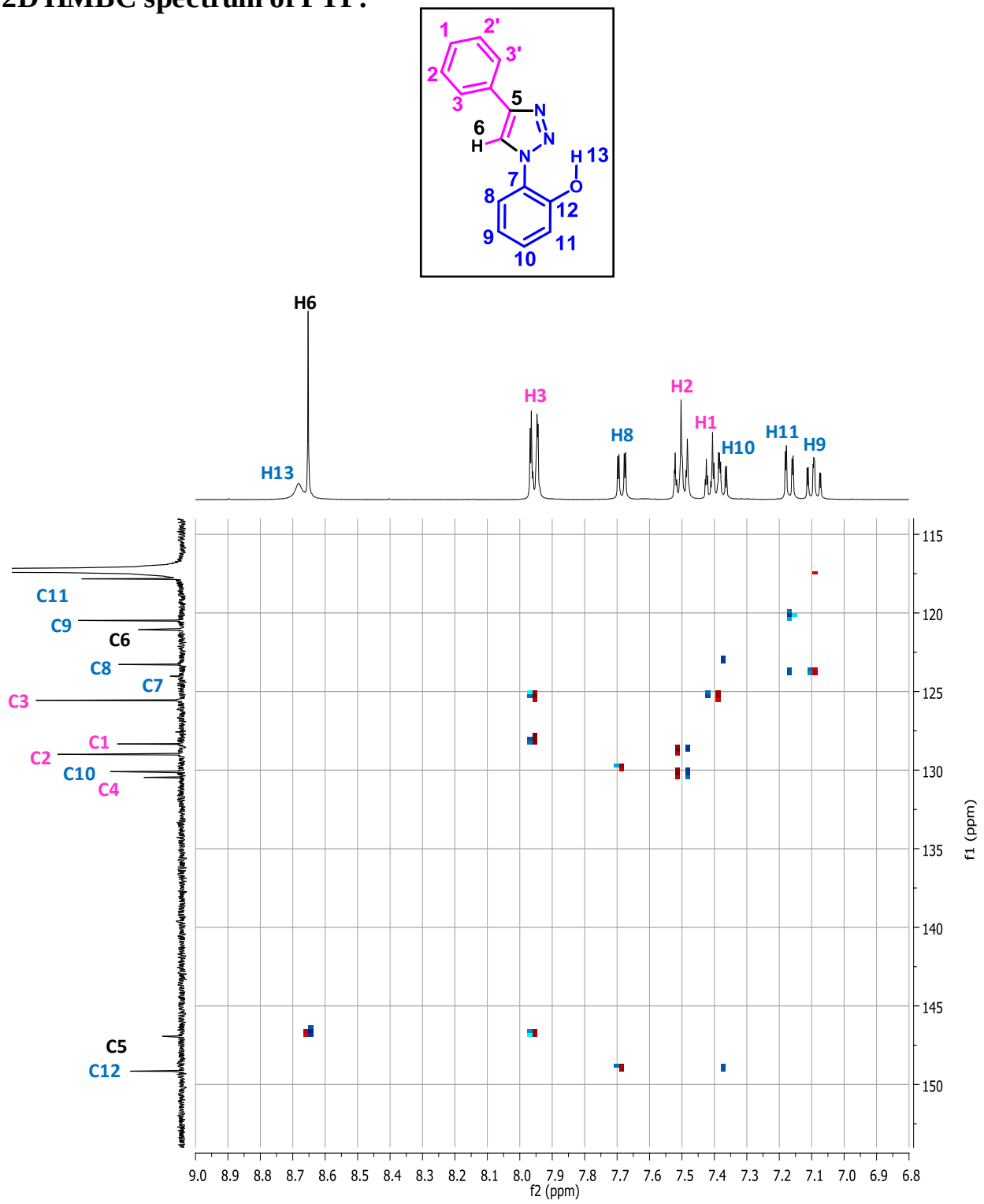


Figure S6: The 2D HMBC spectrum of **PTP**, showing multiple bond carbon hydrogen correlation.

2D NOESY spectrum of PTP.

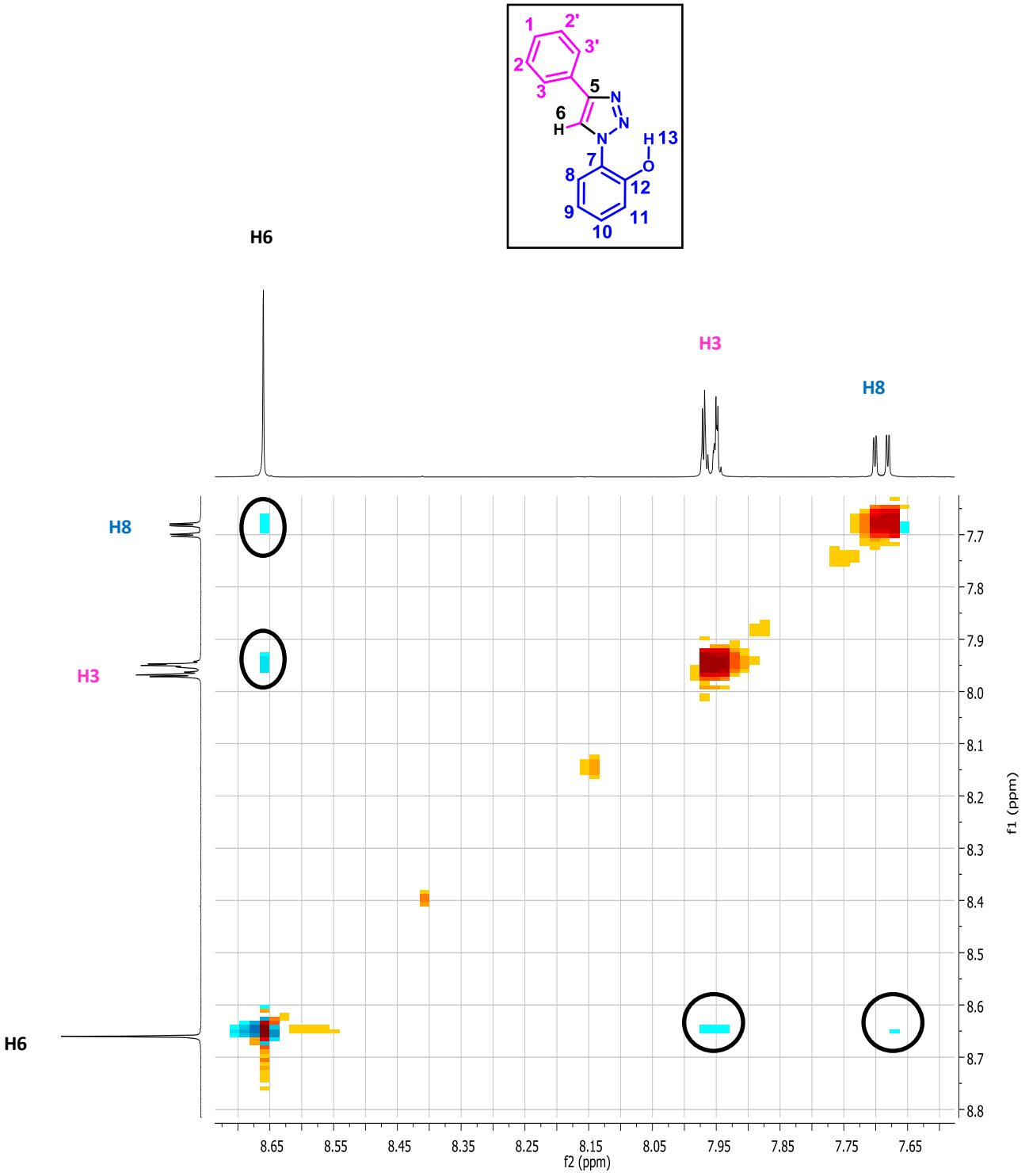


Figure S7: The 2D NOESY spectrum of **PTP** in CD_3CN showing the correlation between the H6 proton and H3 and H8 protons.

2D NOESY spectrum of PTP + 1 equivalence of TBAF.

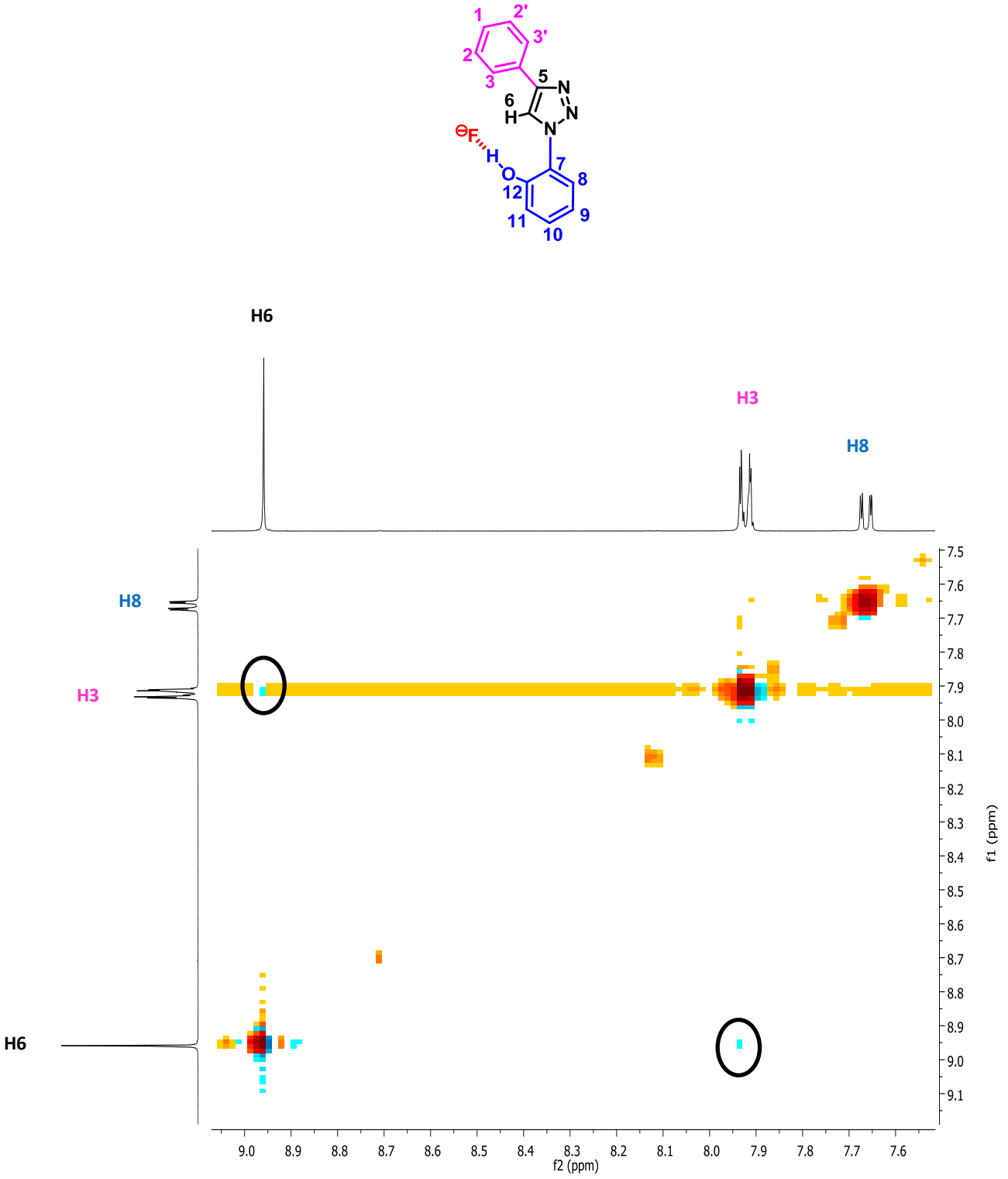


Figure S8: The 2D NOESY spectrum of **PTP** with 1 equivalence of TBAF in CD_3CN showing the correlation between the H6 proton and H3 proton.

No formation of HF_2^- peaks.

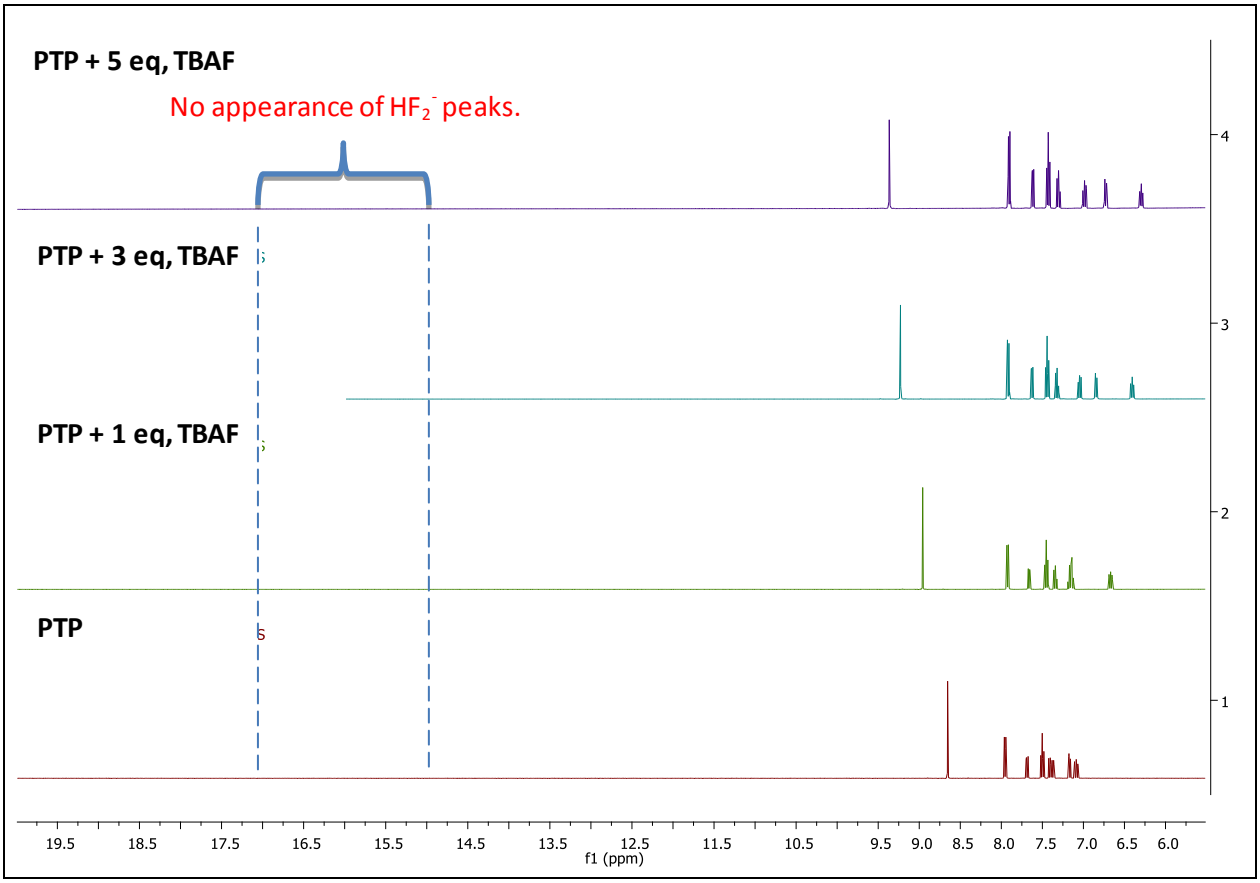


Figure S9: The ^1H NMR spectra's of PTP with various equivalence of TBAF (0-5 eq.) with extended range from (6.0 to 20 *ppm*); showing no formation of HF_2^- triplet peaks.

Absorption and fluorescence studies:

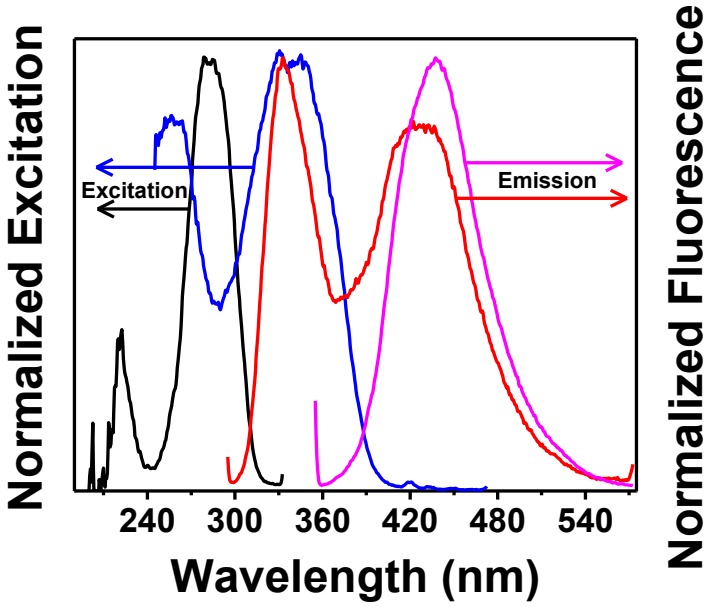


Figure S10. Normalized emission (red and magenta) and fluorescence excitation (black and blue) spectra of **PTP** (~5 × 10^{-5} mol dm^{-3}) upon addition of 4 × 10^{-6} mol dm^{-3} of TBAF in acetonitrile. For emissions, the excitation wavelengths are 290 nm (red) and 350 nm (magenta); for excitation the monitoring wavelengths are 340 nm (black) and 480 nm (blue).

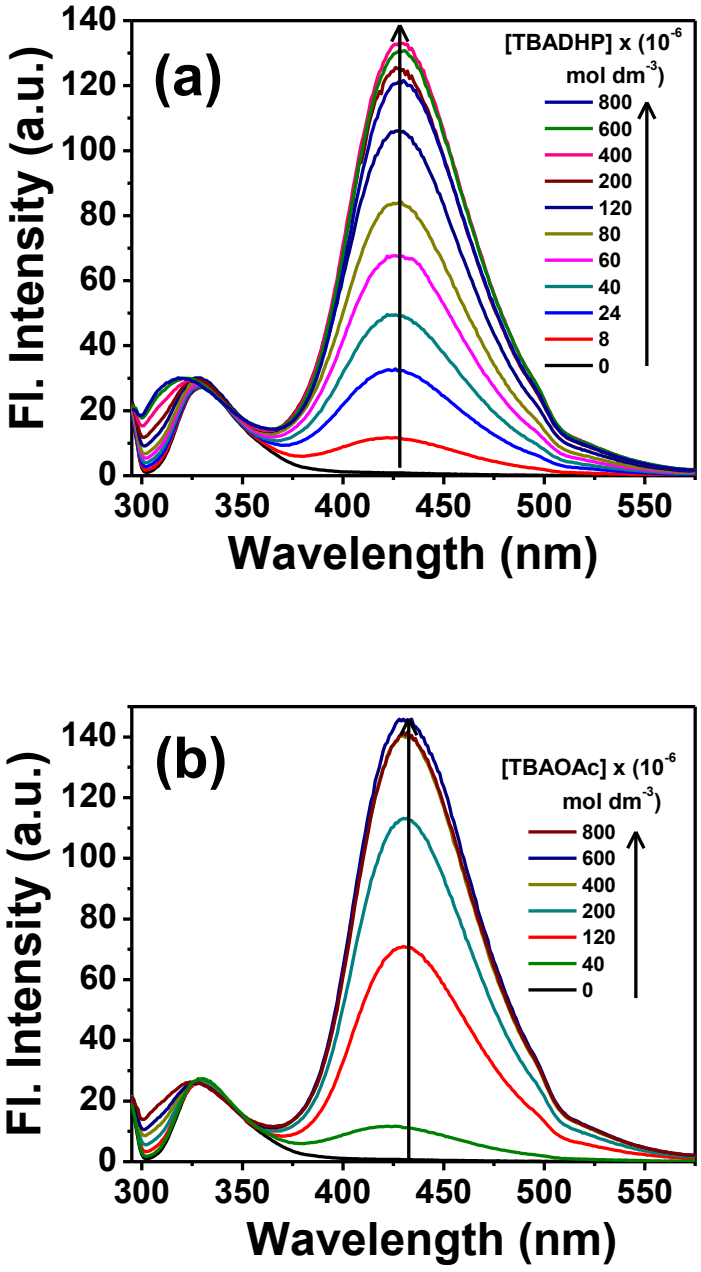


Figure S11. Fluorescence spectral variation of **PTP** (~5 × 10^{-5} mol dm^{-3}) in with the addition of (a) TBADHP and (b) TBAOAc in acetonitrile. Concentrations of TBADHP and TBAOAc are provided in the legends. λ_{exc} = 290 nm.

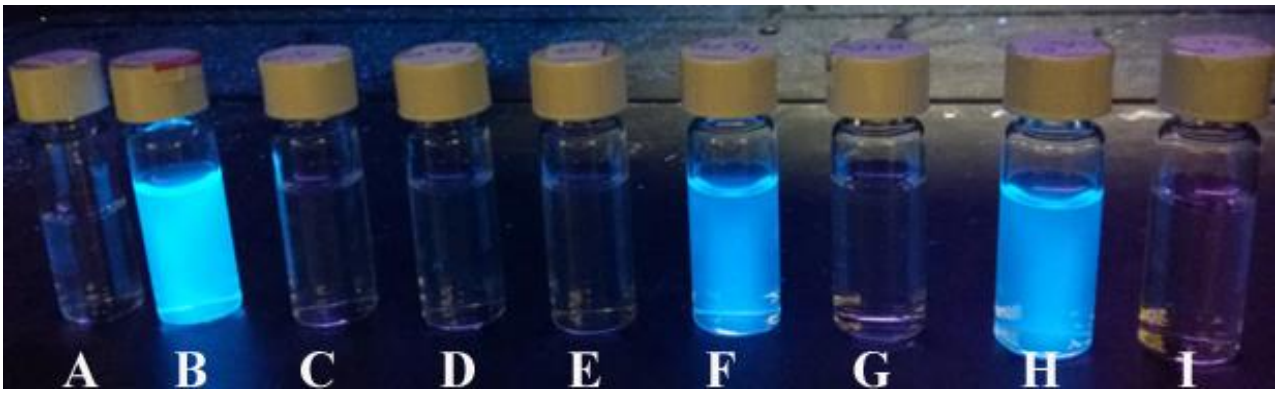


Figure S12. Color changes of **PTP** under UV lamp of long wavelength 365 nm upon addition of ~2 × 10^{-4} mol dm^{-3} of anions in acetonitrile (from A to I: free, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, ClO_4^-, OAc^-, BF_4^-).

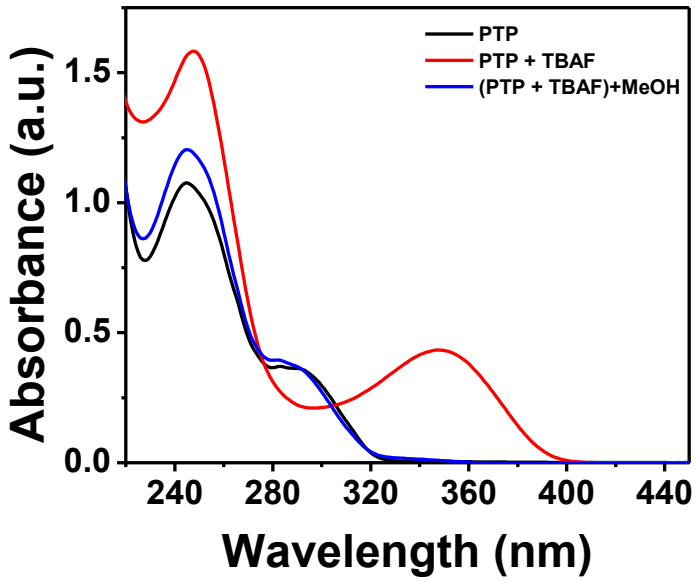


Figure S13. Absorption spectra of **PTP** (~5 × 10^{-5} mol dm^{-3}) with the addition of 200μM TBAF and MeOH to **PTP**+TBAF in acetonitrile.

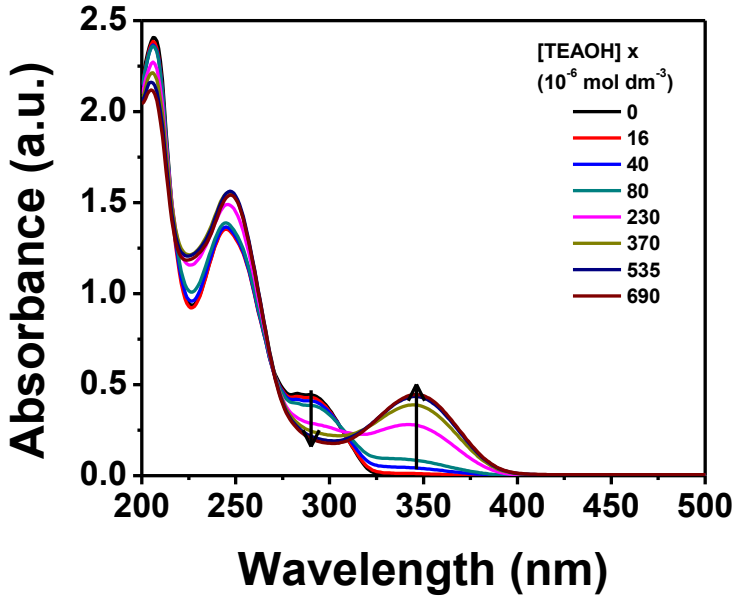


Figure S14. Absorption spectral variation of **PTP** (~5 × 10^{-5} mol dm^{-3}) with the addition of TEAOH in acetonitrile.

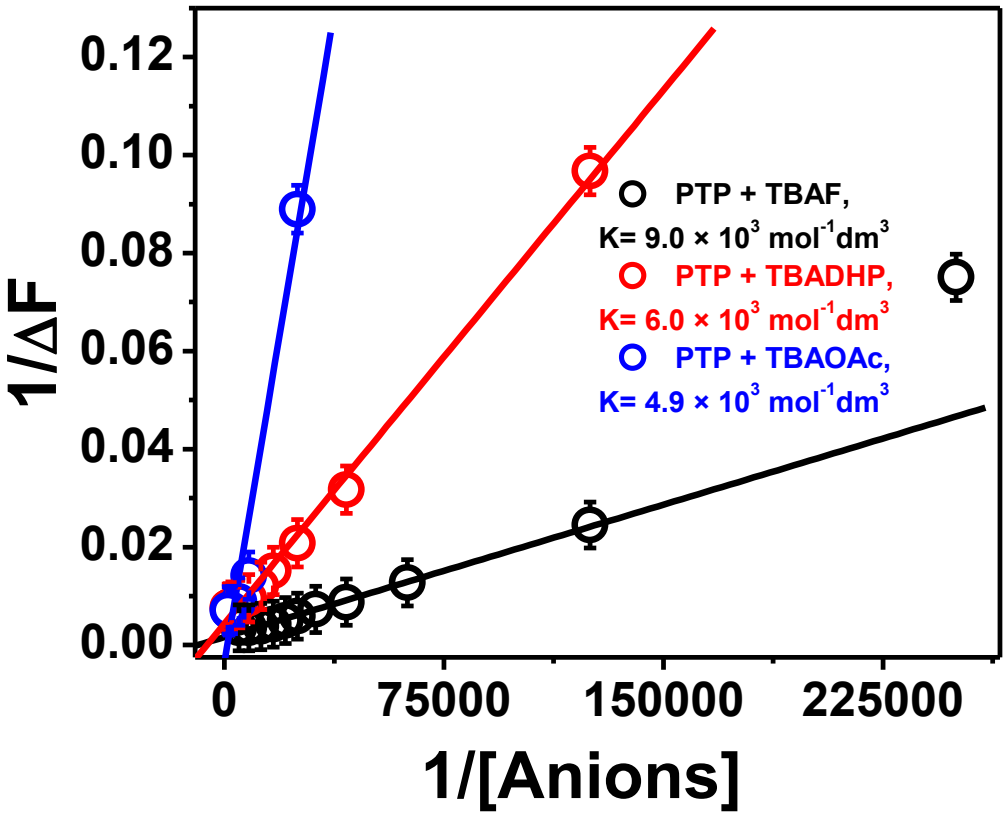


Figure S15: Benesi-Hildebrand plot of **PTP** with addition TBAF (black), TBADHP (red) and TBAOAc (blue).

Job's plot of PTP through NMR.

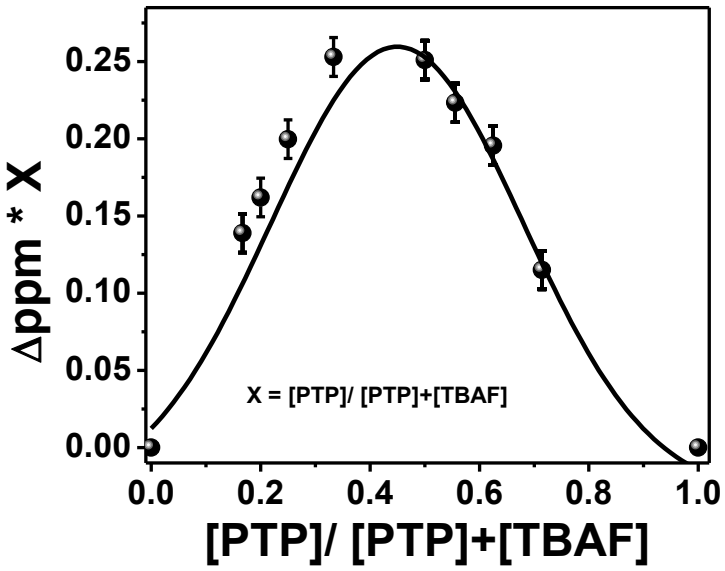


Figure S16: The Job's plot of **PTP** with TBAF in deuterated acetonitrile from ^{1}H NMR titrations.

ESI-MS spectrum of PTP.

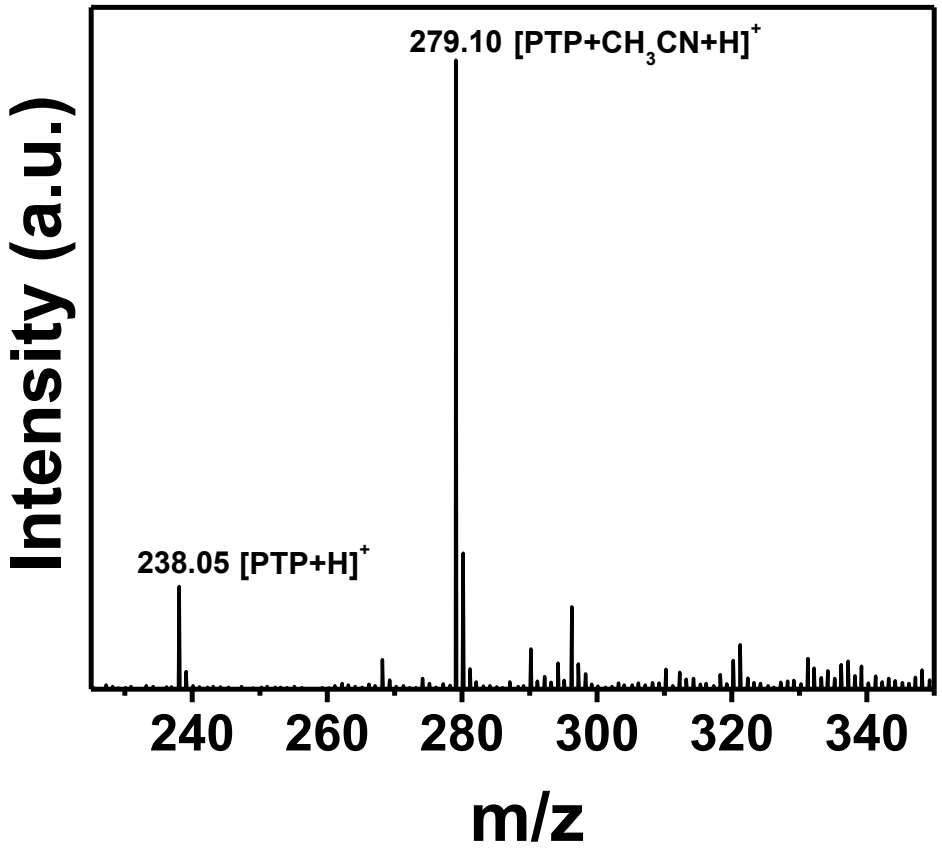


Figure S17: The ESI-MS spectrum of **PTP** showing the *m/z* of 238 [**PTP** +H]$^+$.

Single Crystal X-ray spectroscopic study.

Data Collection : A colorless prism crystal of $C_{30}H_{46}FN_4O$ having approximate dimensions of 0.200 x 0.050 x 0.050 mm was mounted on a glass fiber. All measurements were made on a Rigaku[1] XtaLAB mini diffractometer using graphite monochromated Mo-Kα radiation. The crystal-to-detector distance was 50.09 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 9.575(9) Å

b = 20.50(2) Å β = 105.413(11)°

c = 15.88(2) Å

V = 3006(5) Å^3

For Z = 4 and F.W. = 497.72, the calculated density is 1.100 g/cm^3. The reflection conditions of: h0l: l = 2n and 0k0: k = 2n

Uniquely determine the space group to be: $P2_1/c$ (#14)

The data were collected at a temperature of -100 ± 1°C to a maximum 2θ value of 55.1°. A total of 540 oscillation images were collected. A sweep of data was done using ω oscillations from -60.0 to 120.0° in 1.0° steps. The exposure rate was 40.0 [sec./°]. The detector swing angle was 29.80°. A second sweep was performed using ω oscillations from -60.0 to 120.0° in 1.0° steps. The exposure rate was 40.0 [sec./°]. The detector swing angle was 29.80°. Another sweep was performed using ω oscillations from -60.0 to 120.0° in 1.0° steps. The exposure rate was 40.0 [sec./°]. The detector swing angle was 29.80°. The crystal-to-detector distance was 50.09 mm. Readout was performed in the 0.146 mm pixel mode.

Data Reduction: Of the 31516 reflections that were collected, 6862 were unique (R_{int} = 0.0585). Data were collected and processed using CrystalClear (Rigaku). The linear absorption coefficient, μ, for Mo-Kα radiation is 0.713 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.878 to 0.986. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement The structure was solved by direct methods[3] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares

refinement[4] on F^2 was based on 6862 observed reflections and 325 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \; ||Fo| - |Fc|| \; / \; \Sigma \; |Fo| = 0.0649$$

$$wR2 = [\; \Sigma \; (\; w \; (Fo^2 - Fc^2)^2 \;) / \; \Sigma \; w(Fo^2)^2]^{1/2} = 0.2092$$

The standard deviation of an observation of unit weight[5] was 1.06. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.45 and -0.29 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in Fcalc;[7] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[8] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[9] All calculations were performed using the CrystalStructure[10] crystallographic software package except for refinement, which was performed using SHELXL-97. [11]

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{30}H_{46}FN_4O$
Formula Weight	497.72
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.200 X 0.050 X 0.050 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.575(9) Å
	b = 20.50(2) Å
	c = 15.88(2) Å
	β = 105.413(11) °
	V = 3006(5) $Å^3$
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.100 g/cm^3
F_{000}	1084.00
μ(MoKα)	0.713 cm^{-1}

B. Intensity Measurements

Diffractometer	XtaLAB mini
Radiation	MoKα (λ = 0.71075 Å)
	graphite monochromated
Voltage, Current	50kV, 12mA

Temperature	-100.0°C
Detector Aperture	75 mm (diameter)
Data Images	540 exposures
ω oscillation Range	-60.0 - 120.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	29.80°
ω oscillation Range	-60.0 - 120.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	29.80°
ω oscillation Range	-60.0 - 120.0°
Exposure Rate	40.0 sec./°
Detector Swing Angle	29.80°
Detector Position	50.09 mm
Pixel Size	0.146 mm
$2\theta_{max}$	55.1°
No. of Reflections Measured	Total: 31516
Unique: 6862 (R_{int} = 0.0585)	
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.878 - 0.986)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\, w\,(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/[\,\sigma^2(Fo^2) + (0.0926 \cdot P)^2 + 0.8665 \cdot P\,]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	55.1^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	6862
No. Variables	325
Reflection/Parameter Ratio	21.11
Residuals: R1 ($I>2.00\sigma(I)$)	0.0649
Residuals: R (All reflections)	0.0881
Residuals: wR2 (All reflections)	0.2092
Goodness of Fit Indicator	1.058
Max Shift/Error in Final Cycle	0.005
Maximum peak in Final Diff. Map	$0.45\ e^-/Å^3$
Minimum peak in Final Diff. Map	$-0.29\ e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
F1	0.9928(2)	0.18352(9)	0.04384(11)	6.06(4)
O1	0.7255(2)	0.23010(7)	-0.03910(10)	3.84(3)
N1	0.4257(2)	0.23675(8)	-0.04625(10)	3.25(3)
N2	0.2868(2)	0.24302(10)	-0.04160(12)	3.97(4)
N3	0.2305(2)	0.18412(10)	-0.04855(12)	4.01(4)
N4	0.8495(2)	0.28693(8)	0.24289(10)	2.95(3)
C1	0.6754(4)	0.4064(2)	-0.0338(2)	6.24(7)
C2	0.5320(4)	0.4107(2)	-0.0345(3)	6.92(9)
C3	0.4520(3)	0.35459(13)	-0.0378(2)	5.37(6)
C4	0.5154(3)	0.29360(10)	-0.04049(12)	3.46(4)
C5	0.6637(3)	0.28626(10)	-0.03809(12)	3.43(4)
C6	0.7405(3)	0.34619(12)	-0.0351(2)	4.53(5)
C7	0.4562(2)	0.17316(10)	-0.05677(13)	3.28(4)
C8	0.3307(2)	0.13954(11)	-0.05839(12)	3.37(4)
C9	0.2989(3)	0.06898(11)	-0.06776(13)	3.54(4)
C10	0.1809(3)	0.04250(13)	-0.0456(2)	4.59(5)
C11	0.1550(3)	-0.0237(2)	-0.0523(2)	5.04(6)
C12	0.2458(3)	-0.06542(13)	-0.0801(2)	4.64(5)
C13	0.3626(4)	-0.0398(2)	-0.1038(2)	5.54(6)
C14	0.3892(3)	0.02712(13)	-0.0981(2)	4.85(5)
C15	0.7043(2)	0.26234(10)	0.18834(12)	3.09(4)
C16	0.5992(2)	0.23957(10)	0.23955(12)	3.18(4)
C17	0.4561(3)	0.21907(11)	0.17661(13)	3.45(4)

C18	0.3453(3)	0.19844(12)	0.2243(2)	4.07(4)
C19	0.9297(2)	0.23469(9)	0.30625(13)	3.19(4)
C20	0.9365(3)	0.16718(11)	0.2675(2)	3.75(4)
C21	1.0398(3)	0.12356(12)	0.3346(2)	4.59(5)
C22	1.0163(4)	0.0516(2)	0.3147(3)	6.94(8)
C23	0.9348(3)	0.30658(11)	0.17790(13)	3.35(4)
C24	1.0748(3)	0.34364(11)	0.2148(2)	3.71(4)
C25	1.1461(3)	0.35845(13)	0.1412(2)	4.28(5)
C26	1.2885(3)	0.3944(2)	0.1737(2)	5.40(6)
C27	0.8304(3)	0.34448(9)	0.29968(12)	3.16(4)
C28	0.7475(3)	0.40247(10)	0.2509(2)	3.86(4)
C29	0.7440(3)	0.45727(11)	0.3149(2)	4.68(5)
C30	0.6531(4)	0.5152(2)	0.2737(3)	6.46(8)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F1	0.0688(10)	0.0974(13)	0.0662(10)	0.0072(9)	0.0216(8)	0.0007(9)
O1	0.0397(8)	0.0561(9)	0.0531(9)	0.0018(7)	0.0173(7)	-0.0022(7)
N1	0.0376(9)	0.0542(10)	0.0296(8)	0.0096(7)	0.0052(7)	-0.0009(7)
N2	0.0415(10)	0.0643(12)	0.0437(10)	0.0155(9)	0.0092(8)	0.0008(8)
N3	0.0370(9)	0.0686(13)	0.0457(10)	0.0093(8)	0.0093(8)	0.0030(9)
N4	0.0344(8)	0.0475(9)	0.0294(8)	0.0006(7)	0.0070(6)	-0.0029(6)
C1	0.105(3)	0.055(2)	0.064(2)	-0.017(2)	-0.002(2)	-0.0091(12)
C2	0.093(3)	0.050(2)	0.098(3)	0.010(2)	-0.013(2)	-0.021(2)
C3	0.062(2)	0.060(2)	0.069(2)	0.0132(12)	-0.0063(13)	-0.0203(13)
C4	0.0466(11)	0.0493(12)	0.0308(10)	0.0071(9)	0.0020(8)	-0.0045(8)
C5	0.0514(12)	0.0521(12)	0.0260(9)	-0.0023(9)	0.0086(8)	-0.0024(8)
C6	0.069(2)	0.064(2)	0.0362(11)	-0.0154(12)	0.0096(11)	-0.0044(10)
C7	0.0376(10)	0.0521(12)	0.0358(10)	0.0059(8)	0.0109(8)	-0.0030(8)
C8	0.0339(9)	0.0614(13)	0.0320(9)	0.0055(9)	0.0074(8)	-0.0007(8)
C9	0.0383(10)	0.0598(13)	0.0346(10)	-0.0023(9)	0.0065(8)	-0.0015(9)
C10	0.0479(13)	0.072(2)	0.060(2)	-0.0004(11)	0.0240(11)	0.0019(12)
C11	0.059(2)	0.073(2)	0.064(2)	-0.0137(13)	0.0230(13)	0.0014(13)
C12	0.063(2)	0.060(2)	0.0515(13)	-0.0139(11)	0.0115(11)	-0.0066(11)
C13	0.069(2)	0.065(2)	0.083(2)	-0.0075(13)	0.033(2)	-0.019(2)
C14	0.0527(13)	0.064(2)	0.075(2)	-0.0081(11)	0.0297(13)	-0.0112(13)
C15	0.0322(9)	0.0541(12)	0.0285(9)	-0.0000(8)	0.0038(7)	-0.0034(8)
C16	0.0354(10)	0.0549(12)	0.0284(9)	-0.0011(8)	0.0047(8)	-0.0008(8)
C17	0.0406(11)	0.0528(12)	0.0346(10)	-0.0009(9)	0.0045(8)	-0.0036(8)

C18	0.0446(12)	0.061(2)	0.0465(12)	-0.0068(10)	0.0086(10)	0.0004(10)
C19	0.0361(10)	0.0477(11)	0.0343(10)	-0.0002(8)	0.0038(8)	0.0001(8)
C20	0.0418(11)	0.0523(12)	0.0474(12)	0.0015(9)	0.0102(9)	-0.0051(9)
C21	0.0530(13)	0.063(2)	0.058(2)	0.0108(11)	0.0139(11)	0.0014(11)
C22	0.089(3)	0.064(2)	0.107(3)	0.021(2)	0.019(2)	0.005(2)
C23	0.0400(10)	0.0560(12)	0.0332(10)	0.0002(9)	0.0131(8)	0.0001(8)
C24	0.0386(11)	0.0616(13)	0.0421(11)	-0.0022(9)	0.0132(9)	-0.0048(9)
C25	0.0493(12)	0.067(2)	0.0511(13)	-0.0050(11)	0.0213(10)	-0.0006(11)
C26	0.055(2)	0.082(2)	0.075(2)	-0.0162(13)	0.0296(13)	-0.007(2)
C27	0.0436(11)	0.0444(11)	0.0334(10)	-0.0004(8)	0.0123(8)	-0.0027(8)
C28	0.0526(13)	0.0503(12)	0.0464(12)	0.0024(10)	0.0181(10)	0.0040(9)
C29	0.065(2)	0.0496(13)	0.069(2)	0.0031(11)	0.0280(13)	-0.0015(11)
C30	0.097(3)	0.055(2)	0.109(3)	0.019(2)	0.054(2)	0.012(2)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

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4. Least Squares function minimized: (SHELXL97)

   $\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.
5. Standard deviation of an observation of unit weight:

   $[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_O = number of observations

N_V = number of variables

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