Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Synthesis, Characterization and Aggregation Induced Enhanced Emission Properties of Tetraaryl Pyrazole Decorated Cyclophosphazenes

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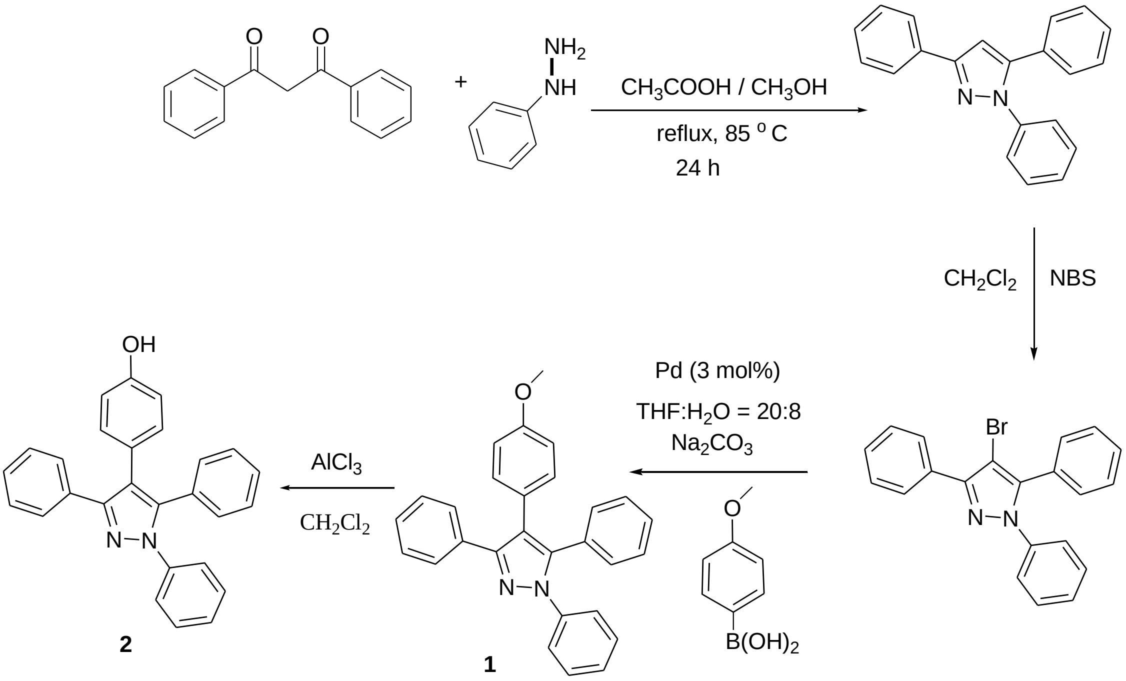
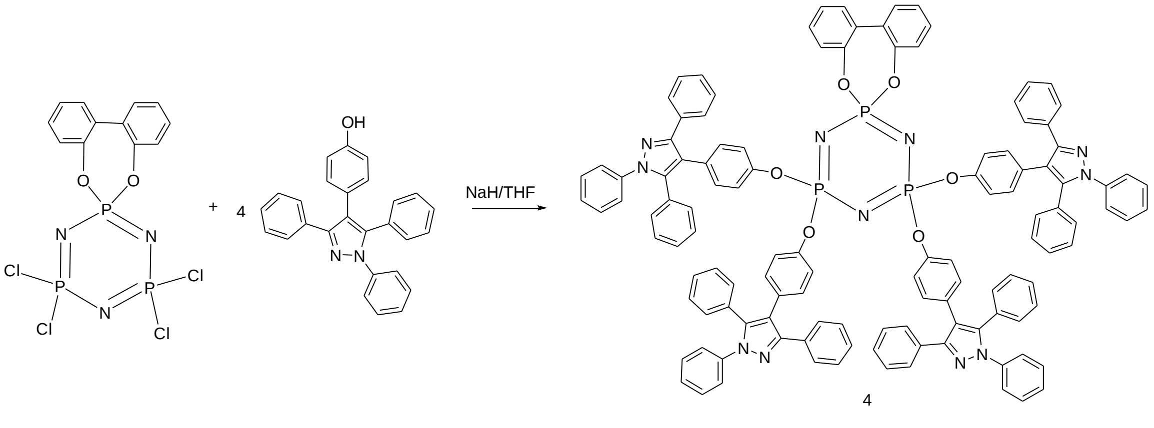
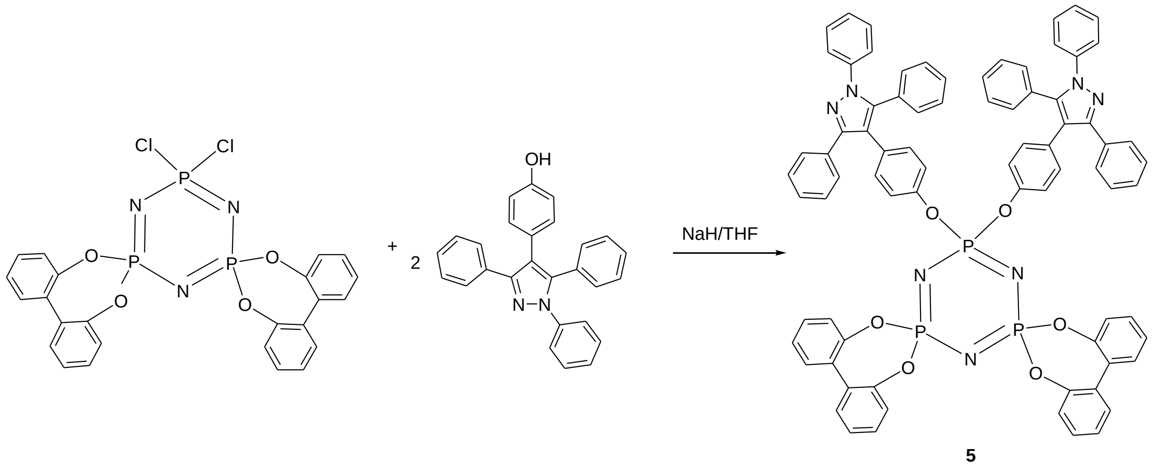


Scheme S1. Synthetic pathway for compound **1**



Scheme S2. Synthetic pathway for compound **4**



Scheme S3. Synthetic pathway for compound **5**

Experimental Section:

General

Reagents and starting materials were purchased from Alfa-Aesar, Sigma-Aldrich and Spectrochem chemical companies and used as received unless otherwise noted. Dichloromethane was distilled from CaH_2. THF was distilled from Na/benzophenone prior to use. 1,3,5-triphenyl-1*H*-pyrazole was prepared according to literature procedure.[1] All 400 MHz ^1H, 100 MHz ^{13}C NMR and 81 MHz ^{31}P spectra were recorded on a Bruker ARX 400 spectrometer operating at 400 MHz. ^1H & ^{13}C NMR spectra were referenced internally to solvent signals and ^{31}P spectrum was referenced externally to H_3PO_4 in D_2O ($\delta = 0$) . All NMR spectra were recorded at ambient temperature. ESI mass spectra were recorded on Bruker, micrOTOF-QII mass spectrometer. The absorbance spectra are recorded on a Perkin Elmer Lambda 750 UV–visible spectrometer. The fluorescence spectra are recorded on a Perkin Elmer LS-55 fluorescence spectrometer. The fluorescence spectra are corrected for the instrumental response. The quantum yield was calculated by measuring the integrated area under the emission curves and by using the following equation. $\Phi_{\text{sample}} = \Phi_{\text{standard}}$ X ($I_{\text{sample}}/I_{\text{standard}}$) X ($OD_{\text{standard}}/OD_{\text{sample}}$) X ($\eta^2_{\text{sample}}/\eta^2_{\text{standard}}$) where, '$\Phi$' is the quantum yield, 'I' the integrated emission intensity, 'OD' the optical density at the excitation wavelength, and 'η' the refractive index of the solvent. The subscripts "standard" and "sample" refer to the fluorophore of reference and unknown respectively. In this case unknown is **3**, **4**, **5** & **7**, reference is *p*-terphenyl (quantum yield of *p*-terphenyl in cyclohexane is 0.82). Optically matched solutions with very similar optical densities of the "sample" and "standard" at a given absorbing wavelength were used for quantum yield calculations. A time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh, OB920) with a light emitting diode (LED) source (λ_{exc} = 280 nm) was used for all time-resolved measurements. A micro channelplate (MCP) photomultiplier (Hamamatsu R3809U-50) was used as the detector for all time resolved measurements. The instrument response function (IRF) was recorded by scatterer (dilute ludox solution in water) in place of the sample. Decay curves were analyzed using the nonlinear least-squares interation process using F900 decay analysis software. The quality of the fit was judged using the chi square (χ^2) values. Elemental analyses were carried out by using a Thermo quest CE instrument model EA/110 CHNS-O elemental analyzer. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II diffractometer equipped with an Oxford instruments low-temperature attachment. The data were collected at 296 K using, Mo-Kα radiation (0.71073 Å). Crystallographic data for **1** and **5,** details of X-ray diffraction experiments and crystal structure refinements are given in Table S1. SADABS absorption corrections were applied in both cases.[2]The structures were solved and refined with SHELX suite of programs.[3] 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 the structure **1** & **5** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1419099, 1440235. 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 Gaussian03 program.[4] The structures were optimized using 6-31G(d) (B3LYP) as the basis set. The input files were generated using X-ray data (for compound 1 and 5). Excitation data were determined using TD-DFT (B3LYP) calculations.

Reference:

1. R. Mamidala, V. Mukundam, K. Dhanunjayarao, K. Venkatasubbaiah, *Dalton Trans.* **2014**, *44*, 5805
2. G. M. Sheldrick, SADABS Program for Correction of Area Detector Data; University of Gottingen: Gottingen, Germany, 1999.
3. SHELXTL, Package v. 6.10, BrukerAXS, Madison and WI.
4. 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.

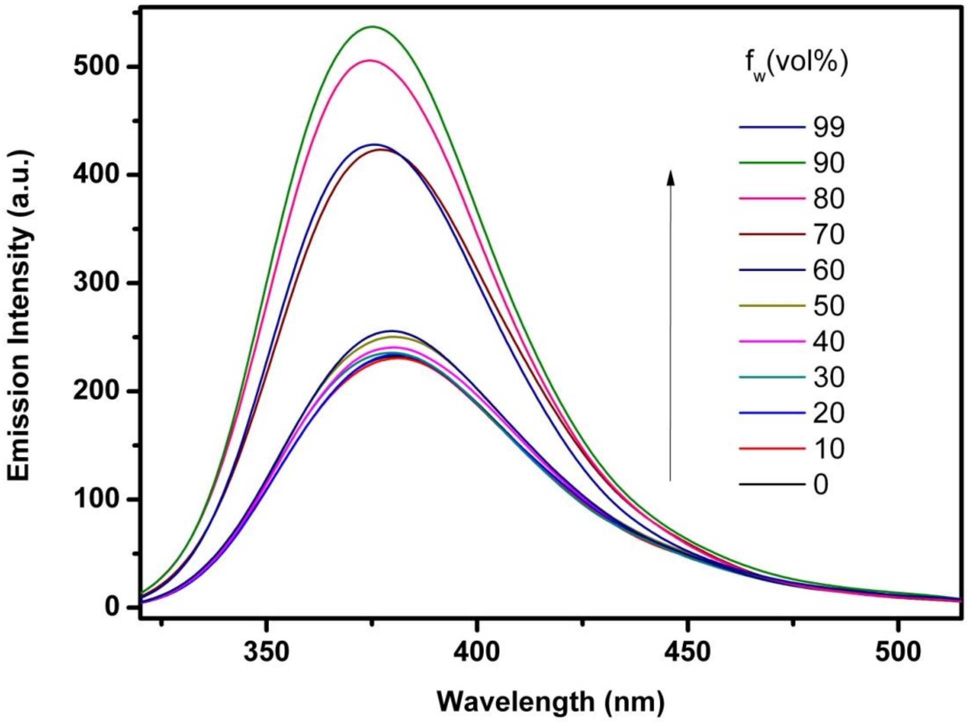


Figure S1. Fluorescence spectra of compound **4** (4.8×10^{-6} M; excited at 280 nm) in THF/H_2O mixture with different water fraction (f_w)

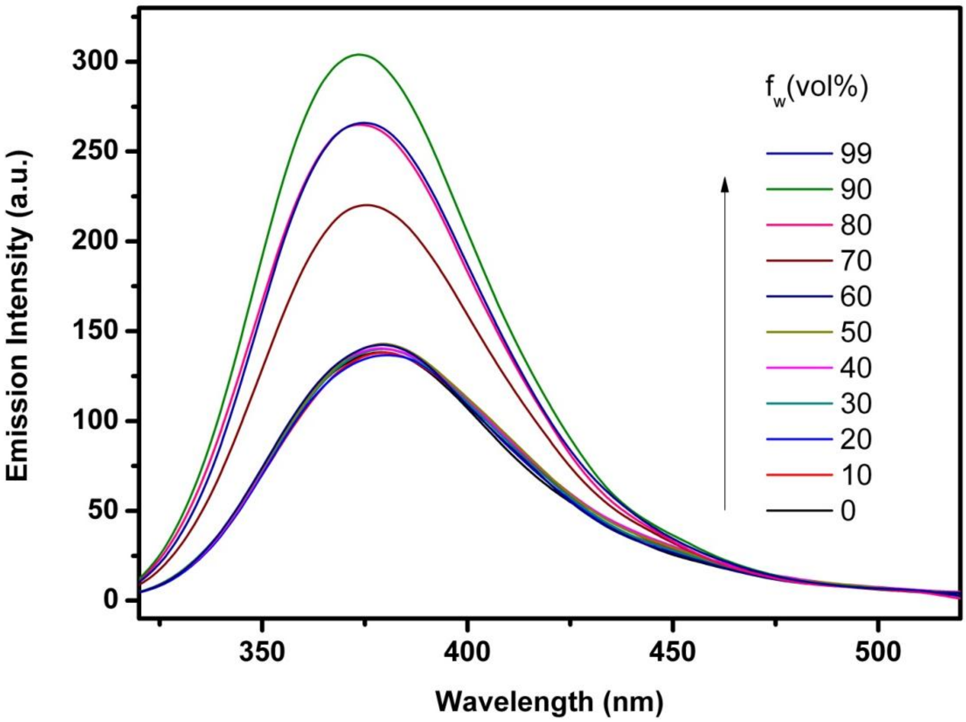


Figure S2. Fluorescence spectra of compound **5** (4.8×10^{-6} M; excited at 280 nm) in THF/H_2O mixture with different water fraction (f_w)

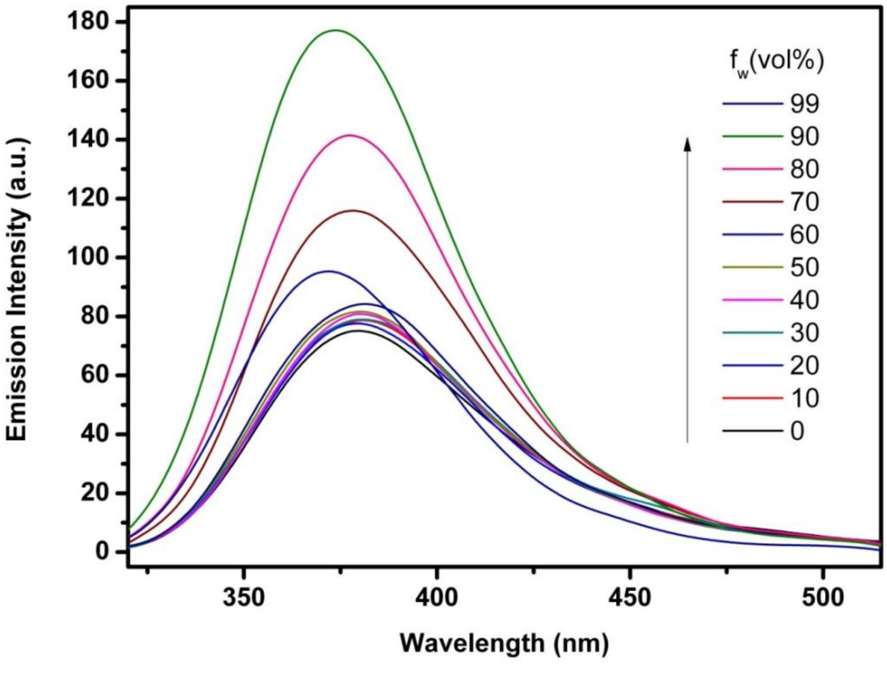


Figure S3. Fluorescence spectra of compound **7** (4.8×10^{-6} M; excited at 280 nm) in THF/H_2O mixture with different water fraction (f_w)

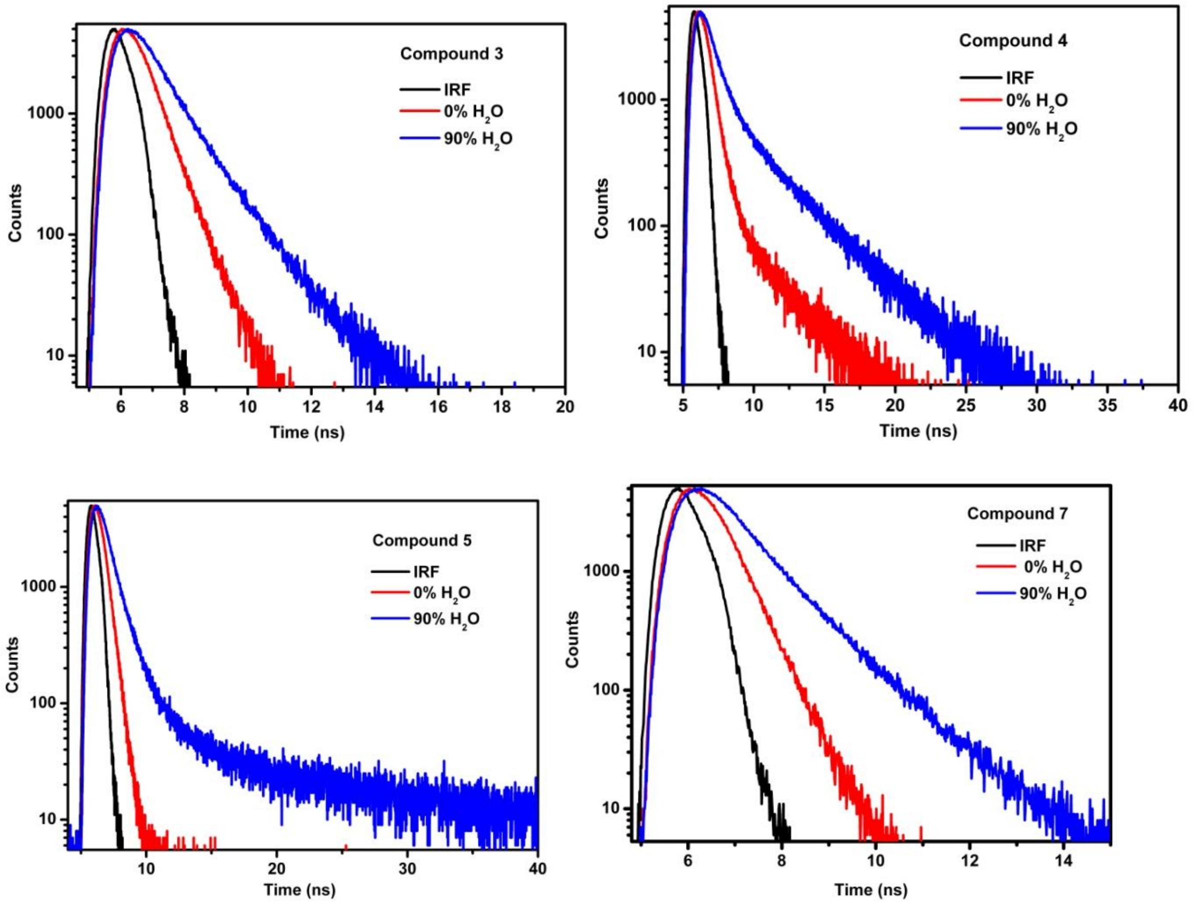


Figure S4. Fluoresce decay of compound **3**, **4**, **5** & **7** in THF (red) solution and THF:H_2O (10:90; blue) aggregates. (2.28 x 10^{-5} M; excited at 280 nm)

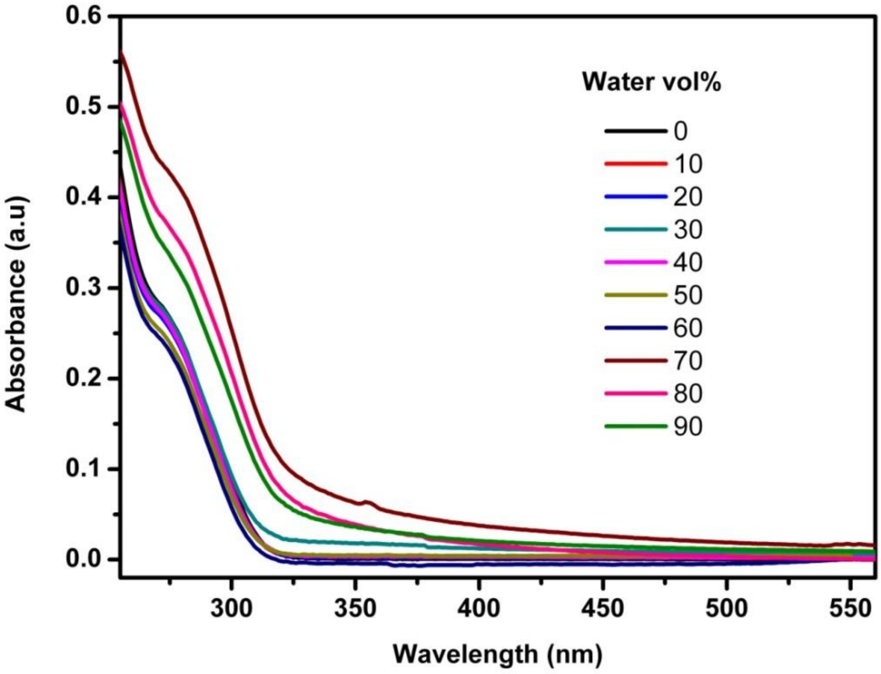


Figure S5. UV absorption spectra of compound **5 (**4.8 X 10 $^{-6}$ M) in H_2O/THF mixtures with different volume fractions of water

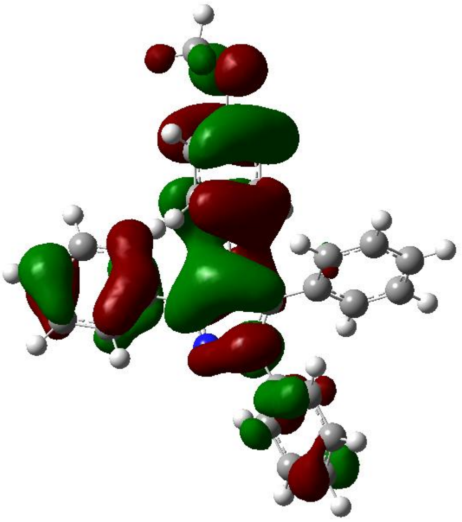
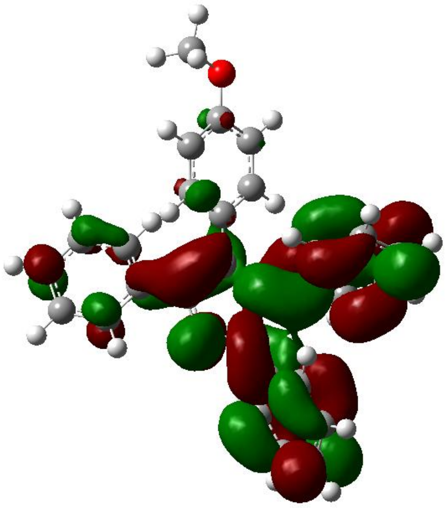
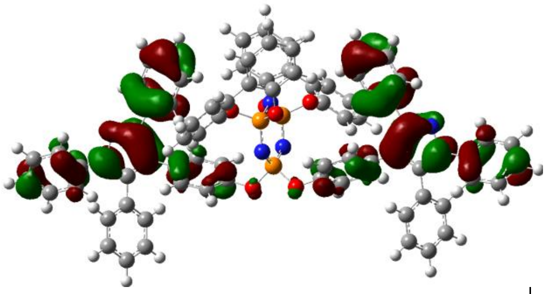
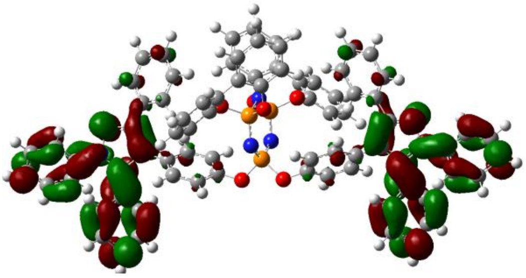
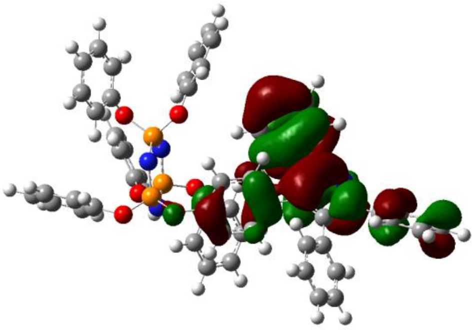
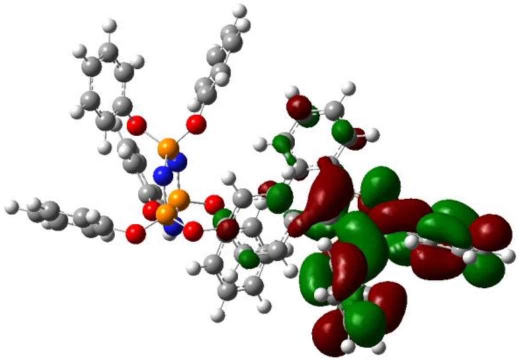
Compound	HOMO	LUMO
1	 - 5.414 eV	 -0.789 eV
5	 -5.659	 -0.843
7	 -5.550	 -0.789

Figure S6. Computed orbitals for compound **1, 5 & 7**

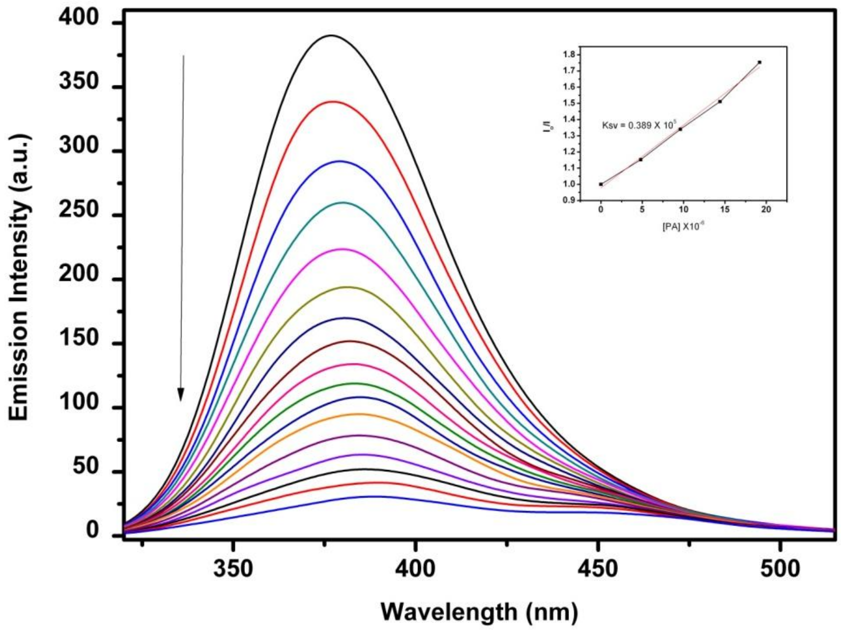


Figure S7. Fluorescence quenching of Compound **4** (4.8 x 10^{-6} M; excited at 280 nm) in THF/water mixture (30:70) with various concentrations of picric acid (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 13.0, 15.0, 17.0, 19.0 & 21.0 equiv).

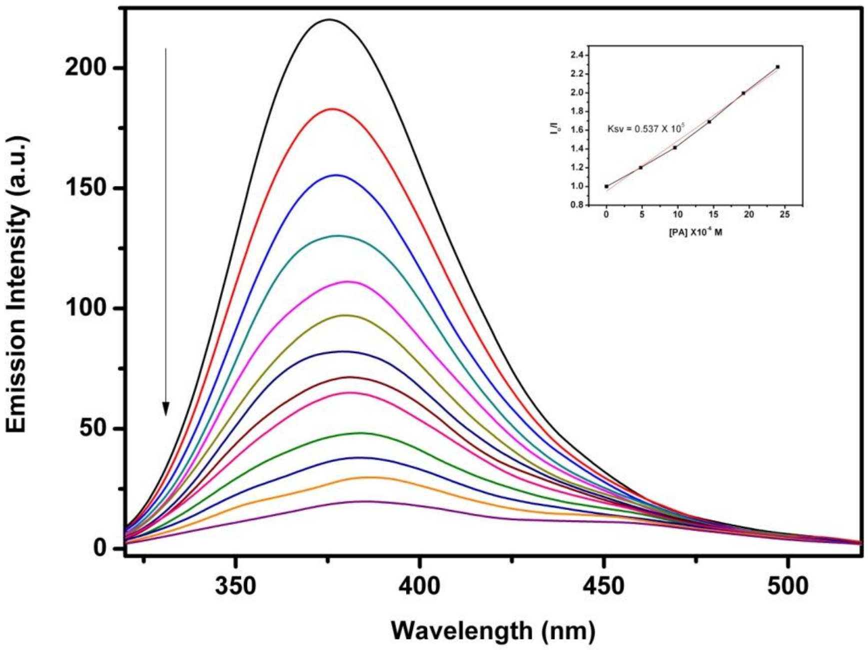


Figure S8. Fluorescence quenching of Compound **5**(4.8 x 10^{-6} M; excited at 280 nm) in THF/water mixture (30:70) with various concentrations of picric acid (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 13.0, 15.0, 17.0, 19.0 & 21.0 equiv).

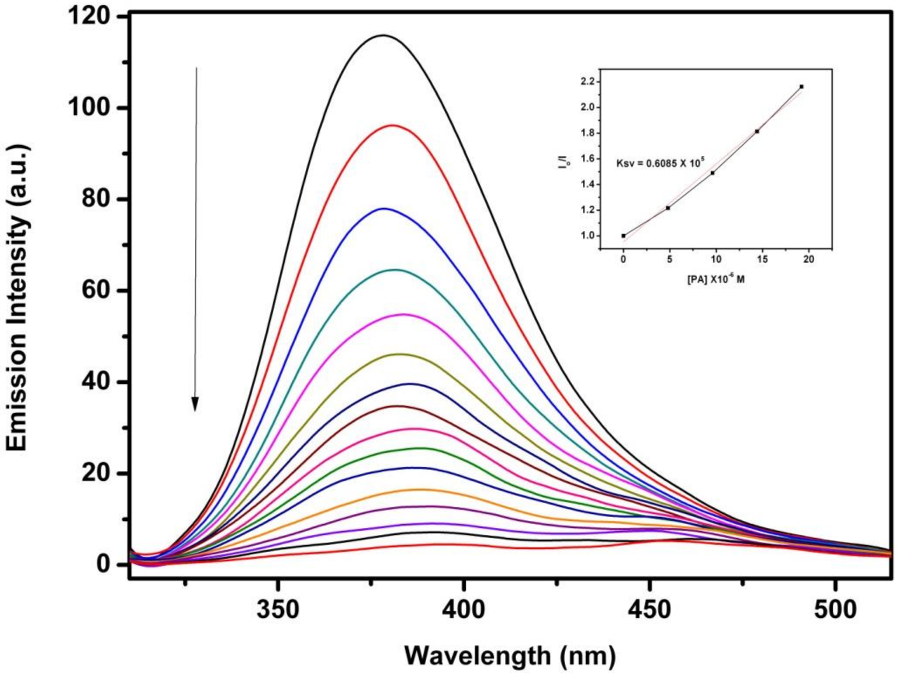


Figure S9. Fluorescence quenching of Compound **7** (4.8 x 10^{-6} M; excited at 280 nm) in THF/water mixture (30:70) with various concentrations of picric acid (0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 13.0, 15.0, 17.0, 19.0 & 21.0 equiv).

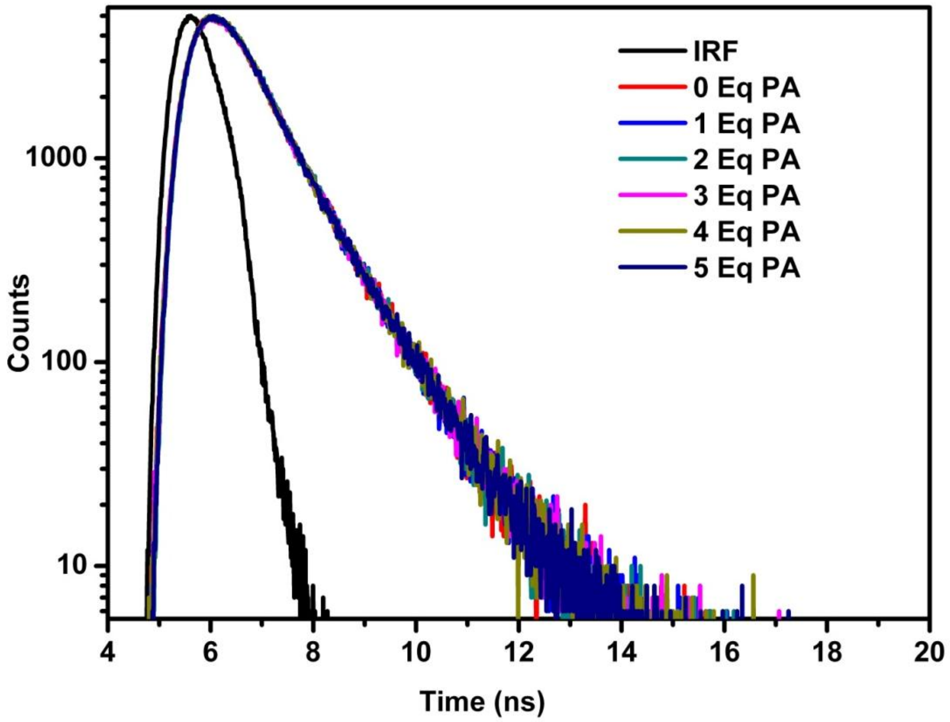


Figure S10. Life time decay profile for compound 3 in THF/water mixture (30:70) (4.8 x 10^{-6} M ; λ_{ex} = 280 nm).

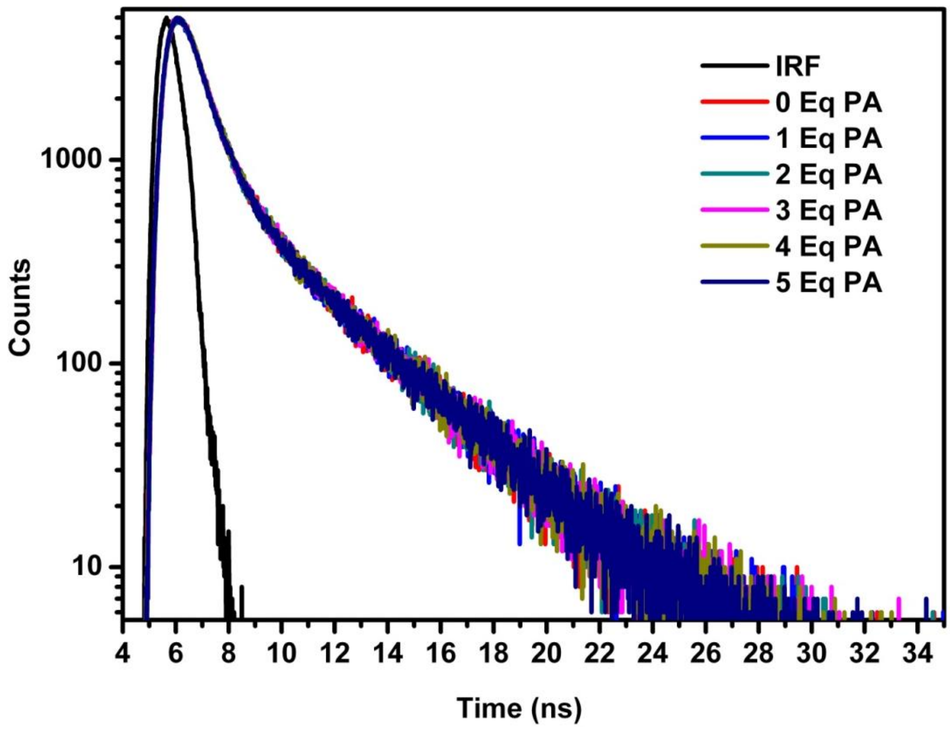


Figure S11. Life time decay profile for compound 4 in THF/water mixture (30:70) (4.8×10^{-6} M ; λ_{ex} = 280 nm).

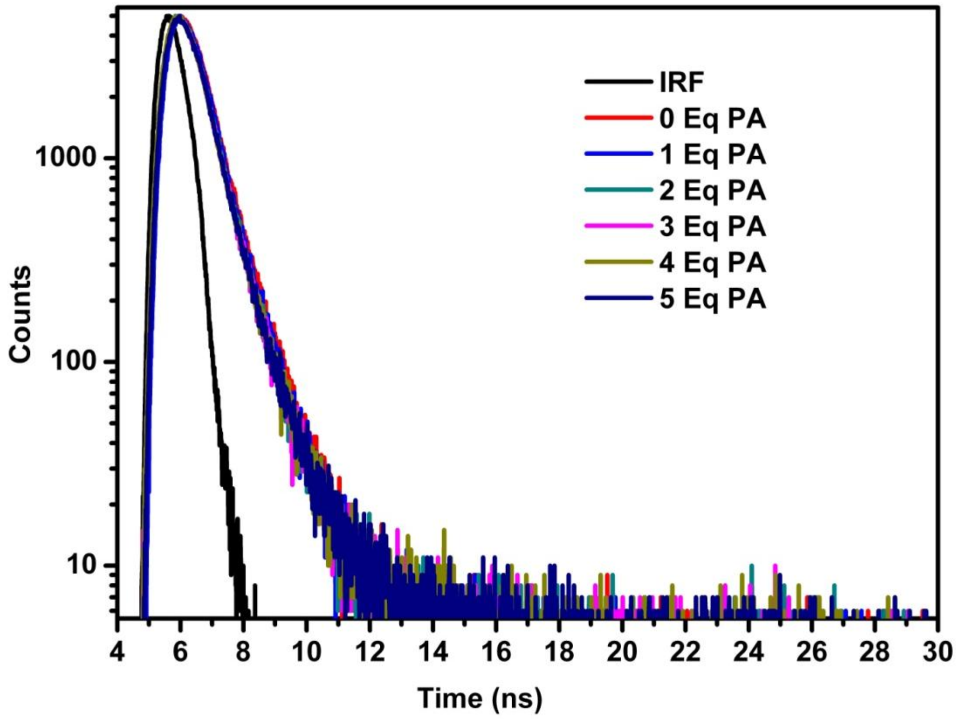


Figure S12. Life time decay profile for compound 5 in THF/water mixture (30:70) (4.8×10^{-6} M ; λ_{ex} = 280 nm)

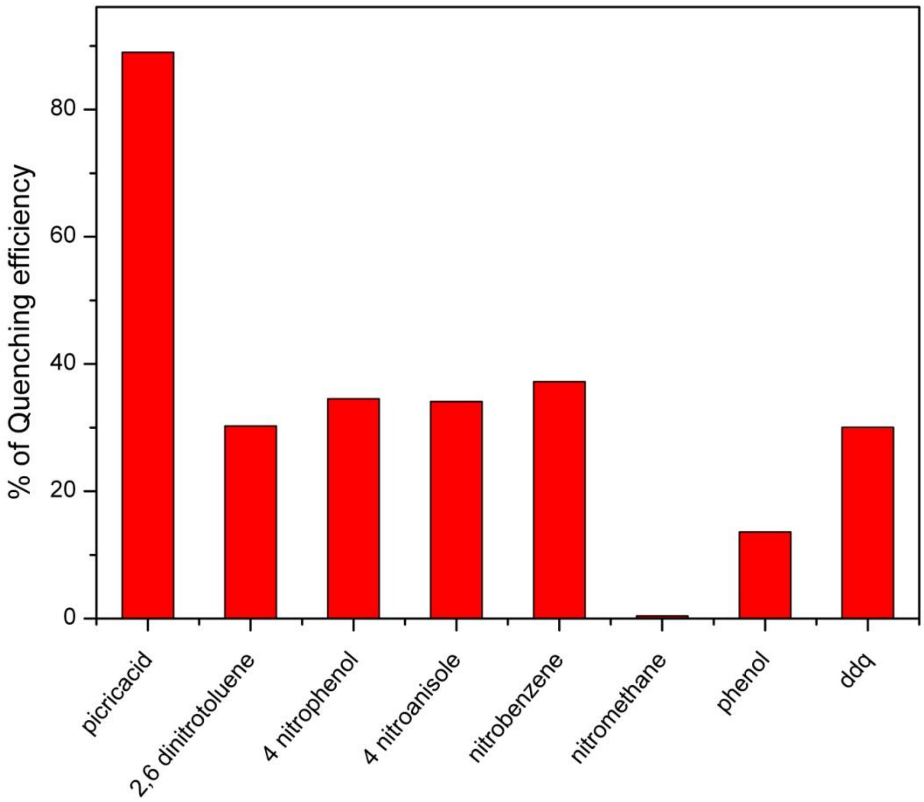
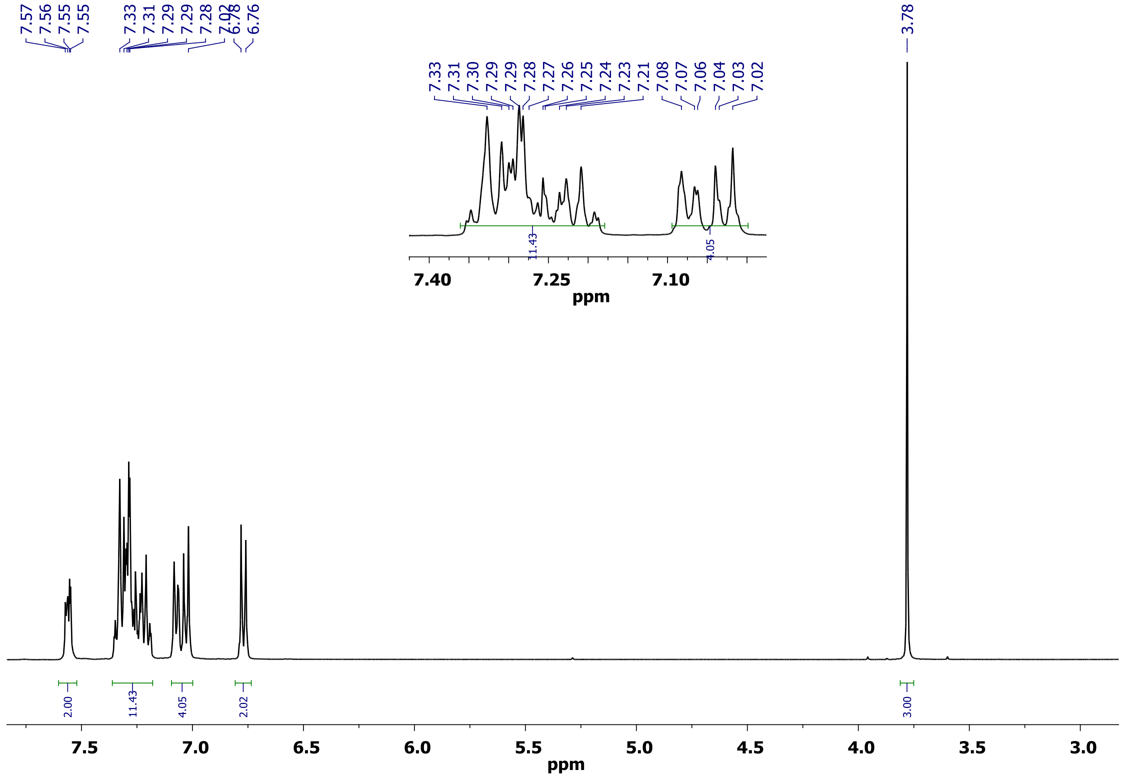
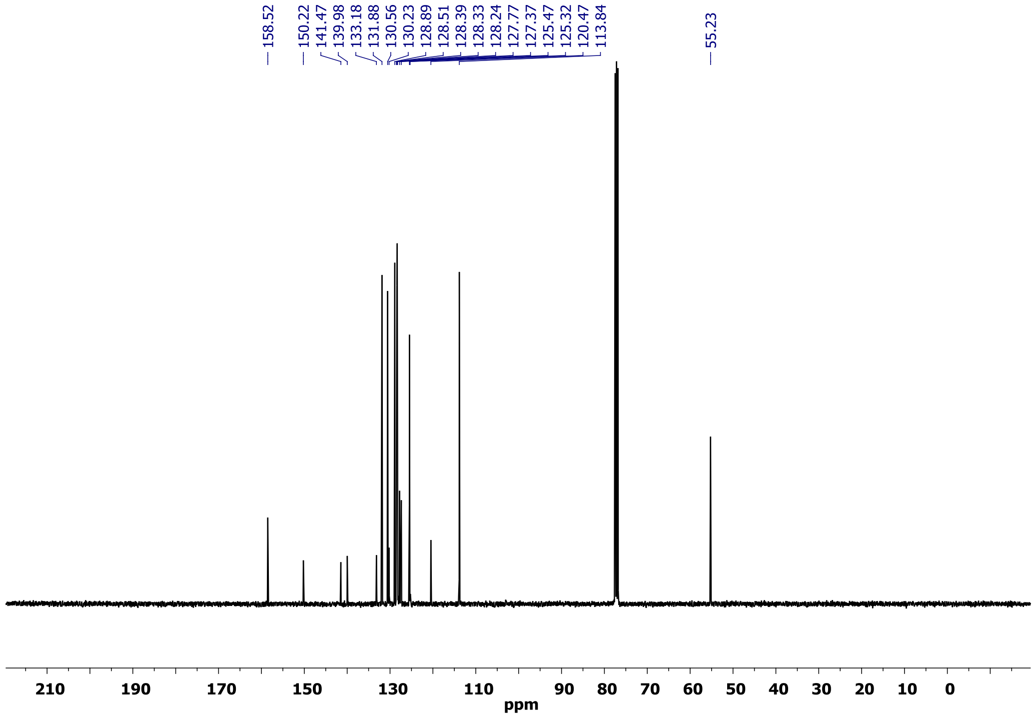


Figure S13. Fluorescence quenching efficiencies of compound **3** in THF:H_2O (30:70) mixture (4.8 x 10^{-6} M; excited at 280 nm) toward different analytes (12 eq). (DDQ= 2,3-dichloro-5,6-dicyano-1,4-benzoquinone)

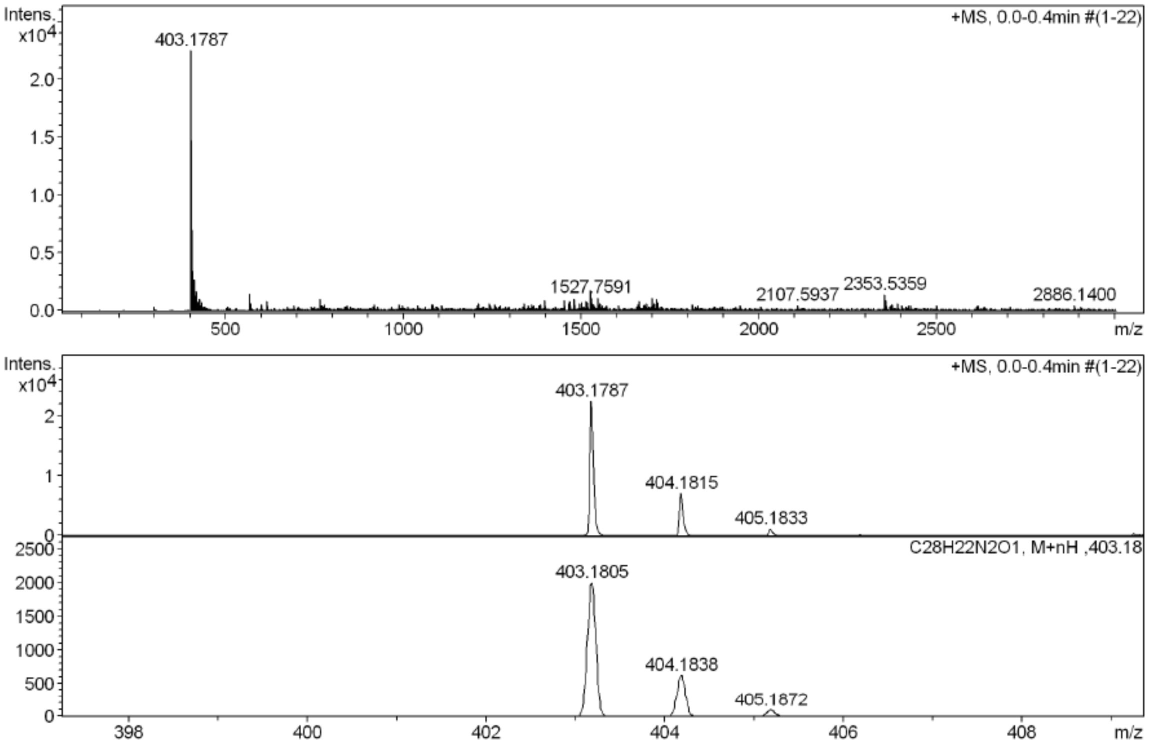
Compound **1** ^{1}H NMR



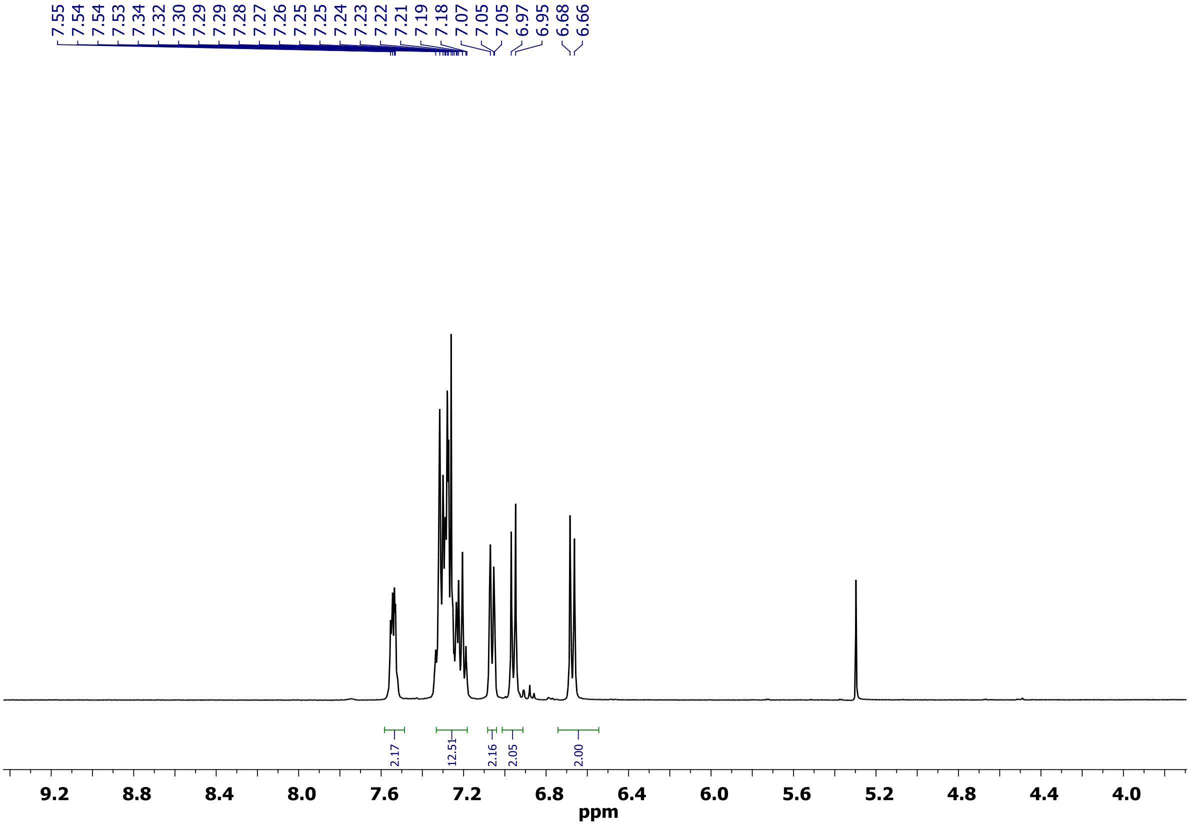
Compound **1** ^{13}C NMR



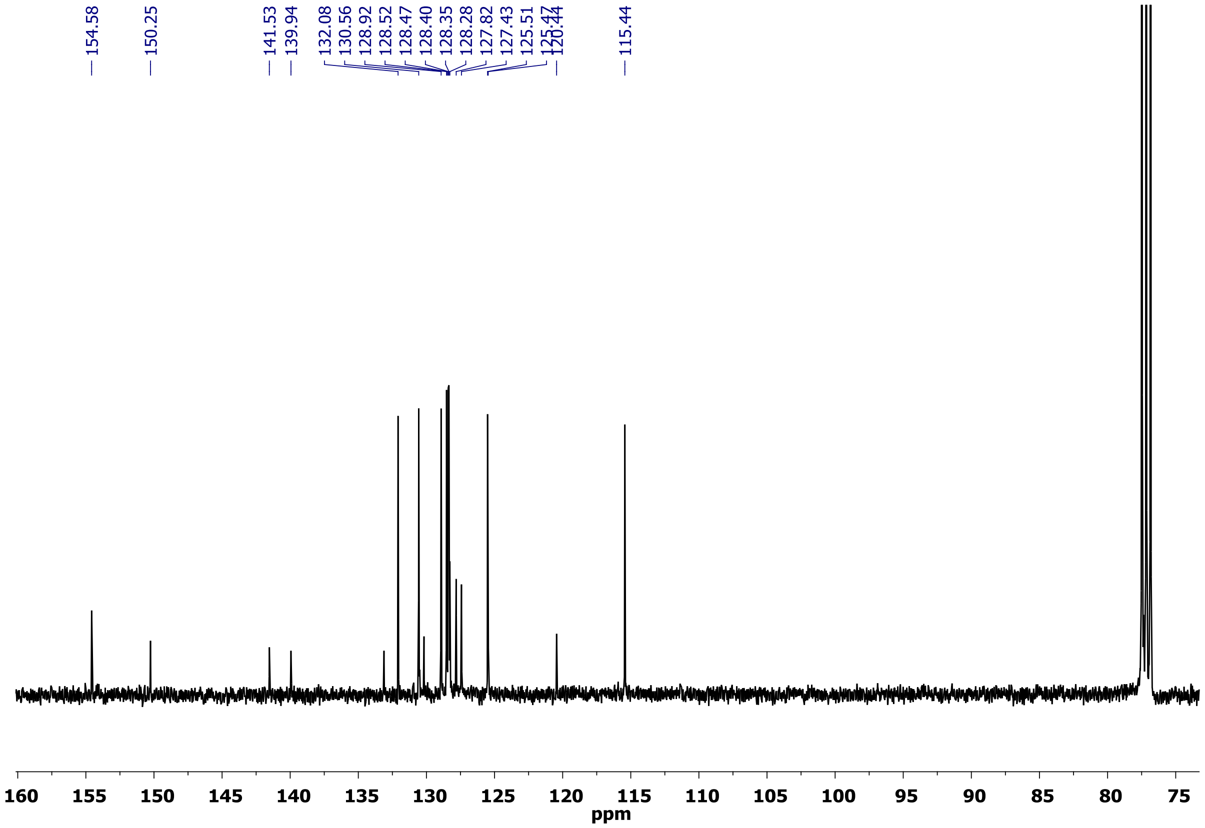
Compound **1** HRMS



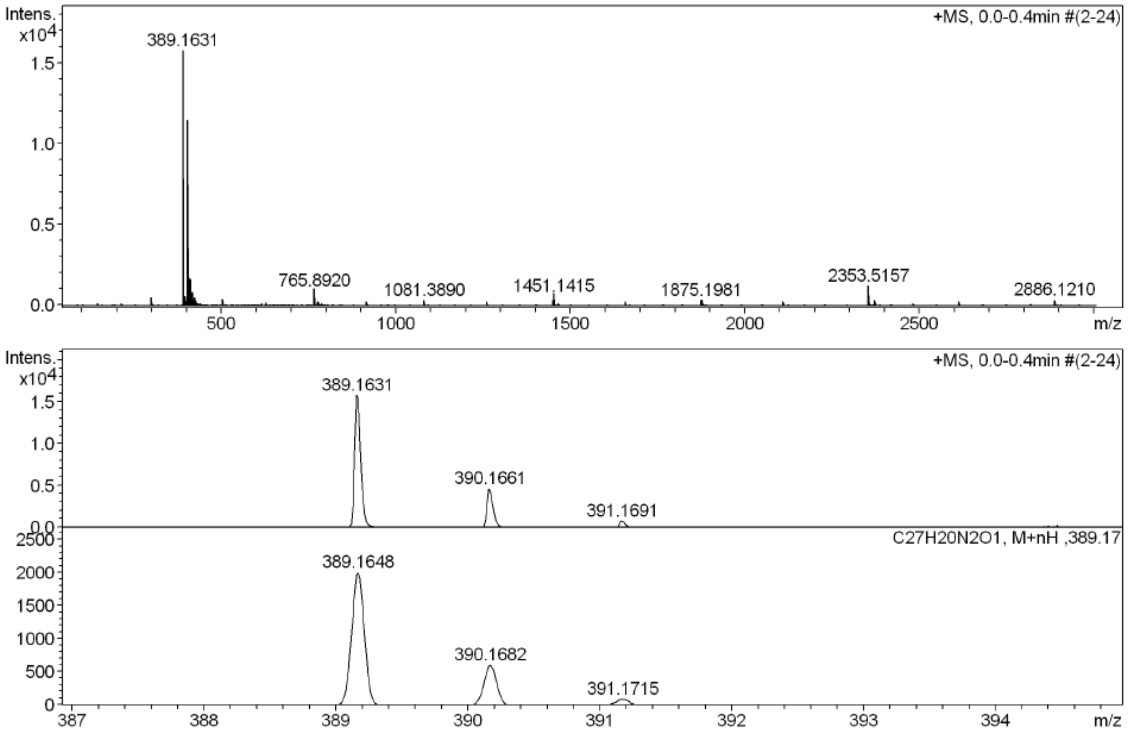
Compound **2** ^{1}H NMR



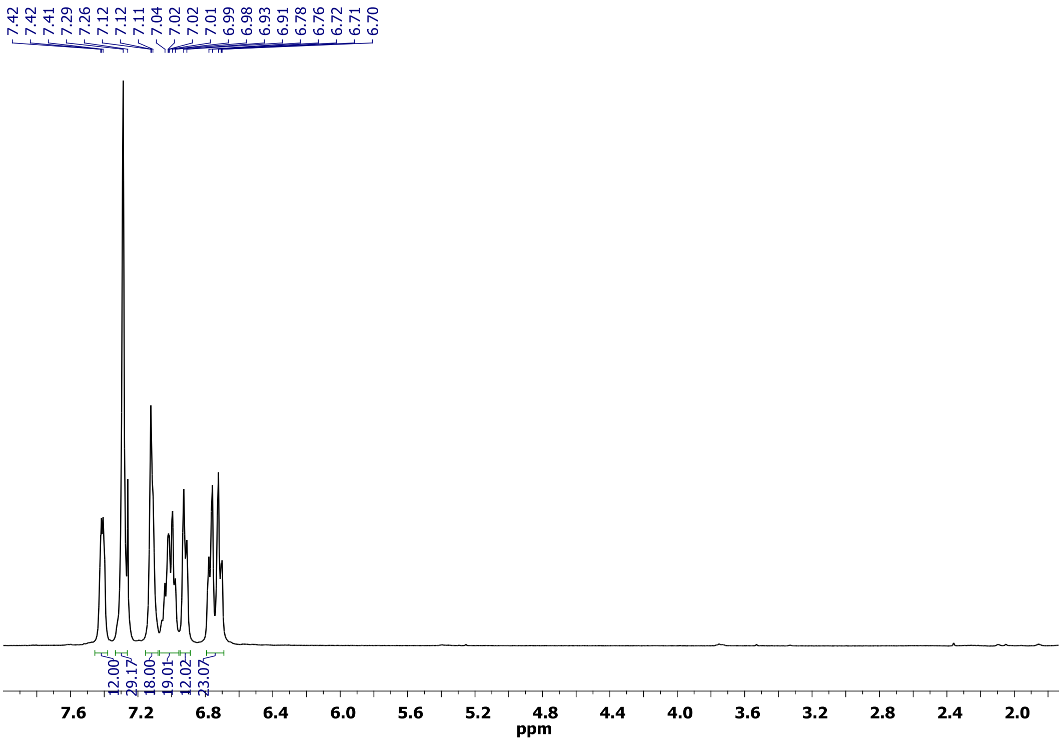
Compound **2** ^{13}C NMR



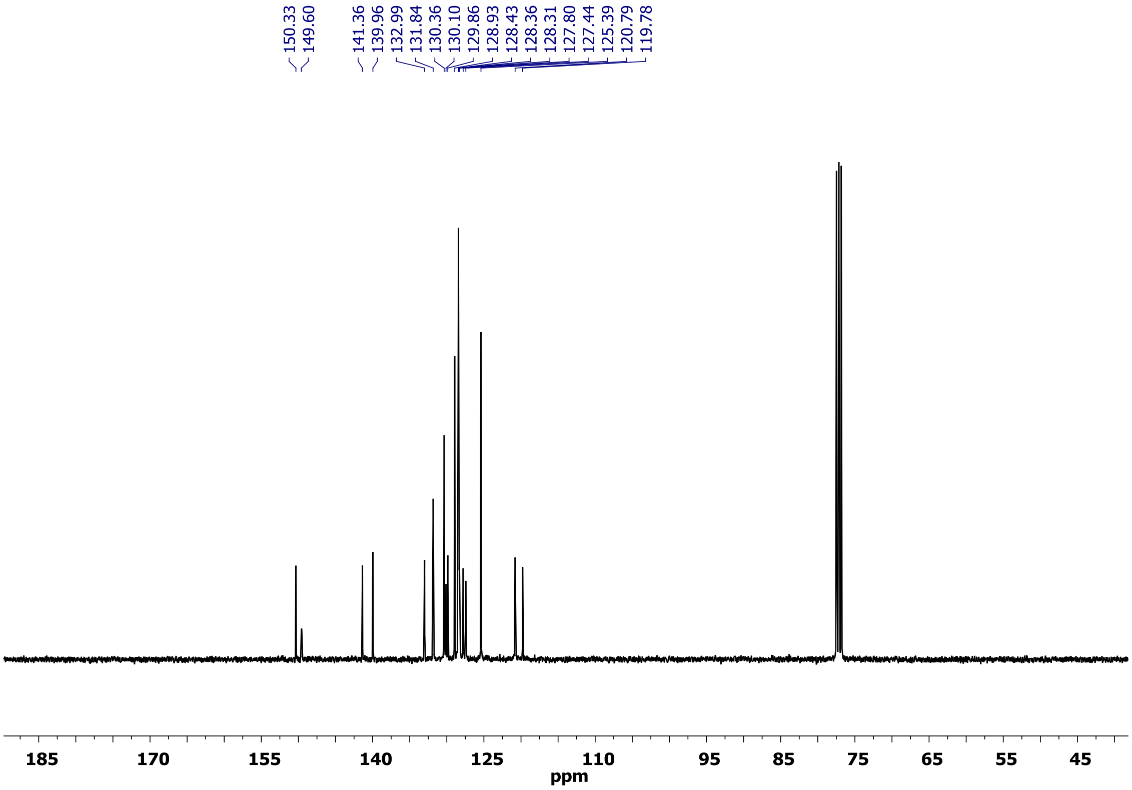
Compound **2** HRMS



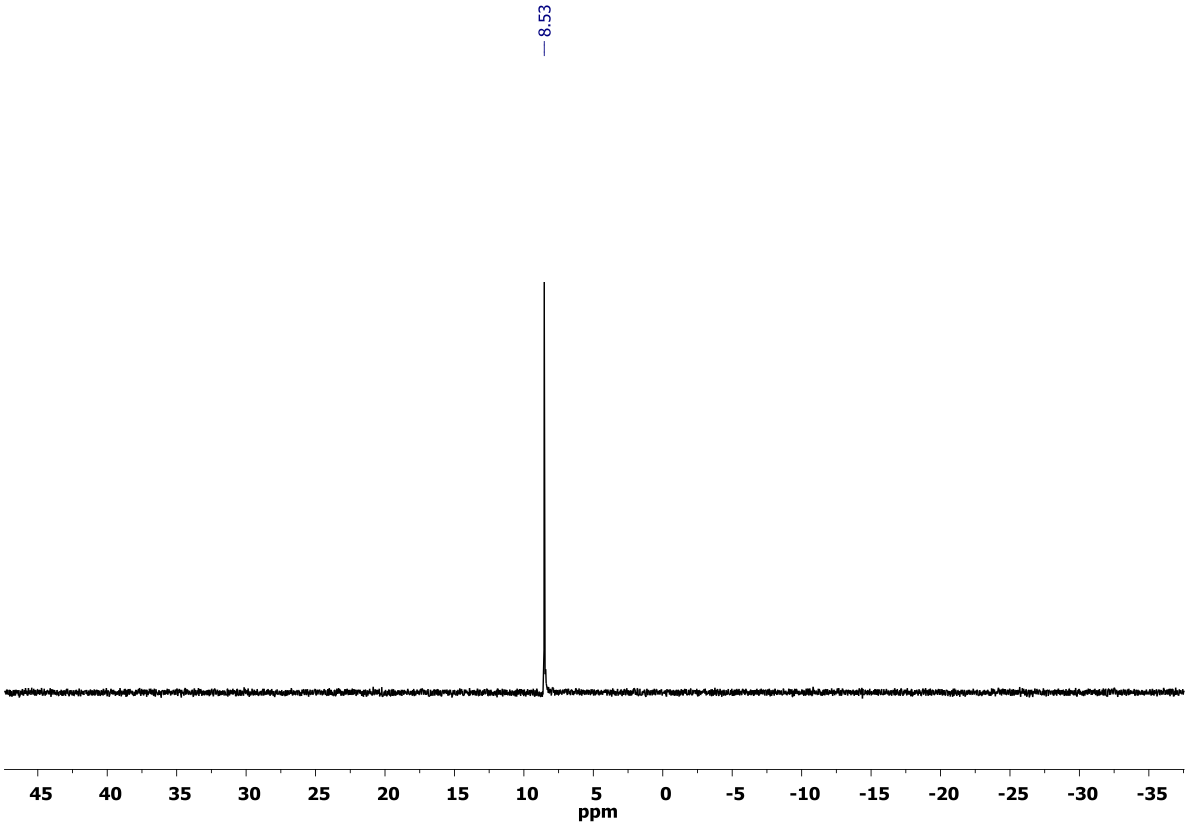
Compound **3** ^{1}H NMR



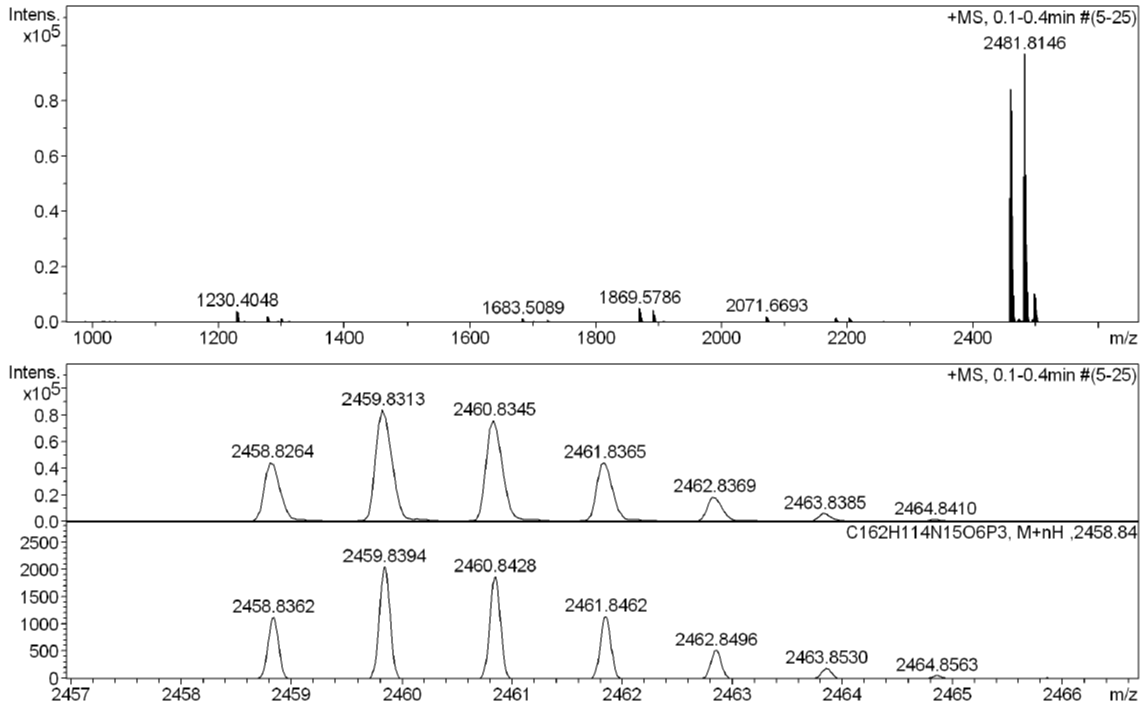
Compound **3** ^{13}C NMR



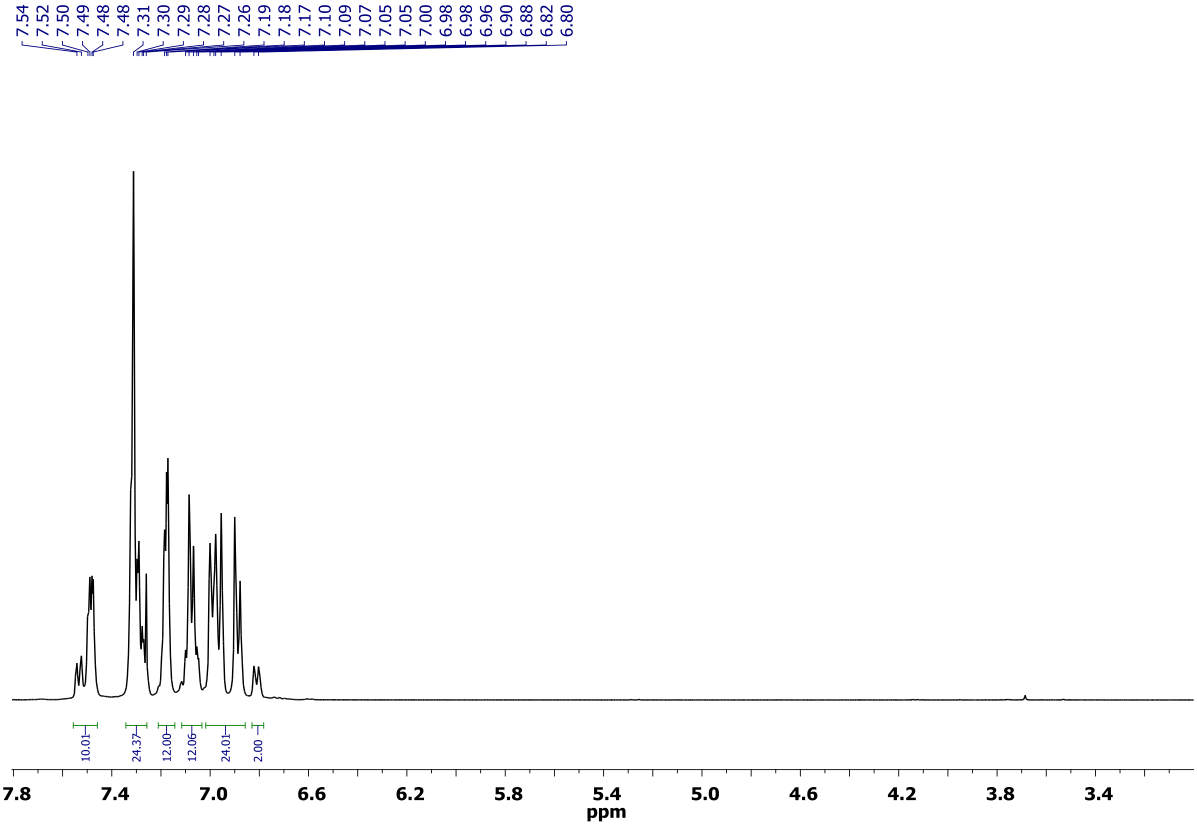
Compound **3** ^{31}P NMR



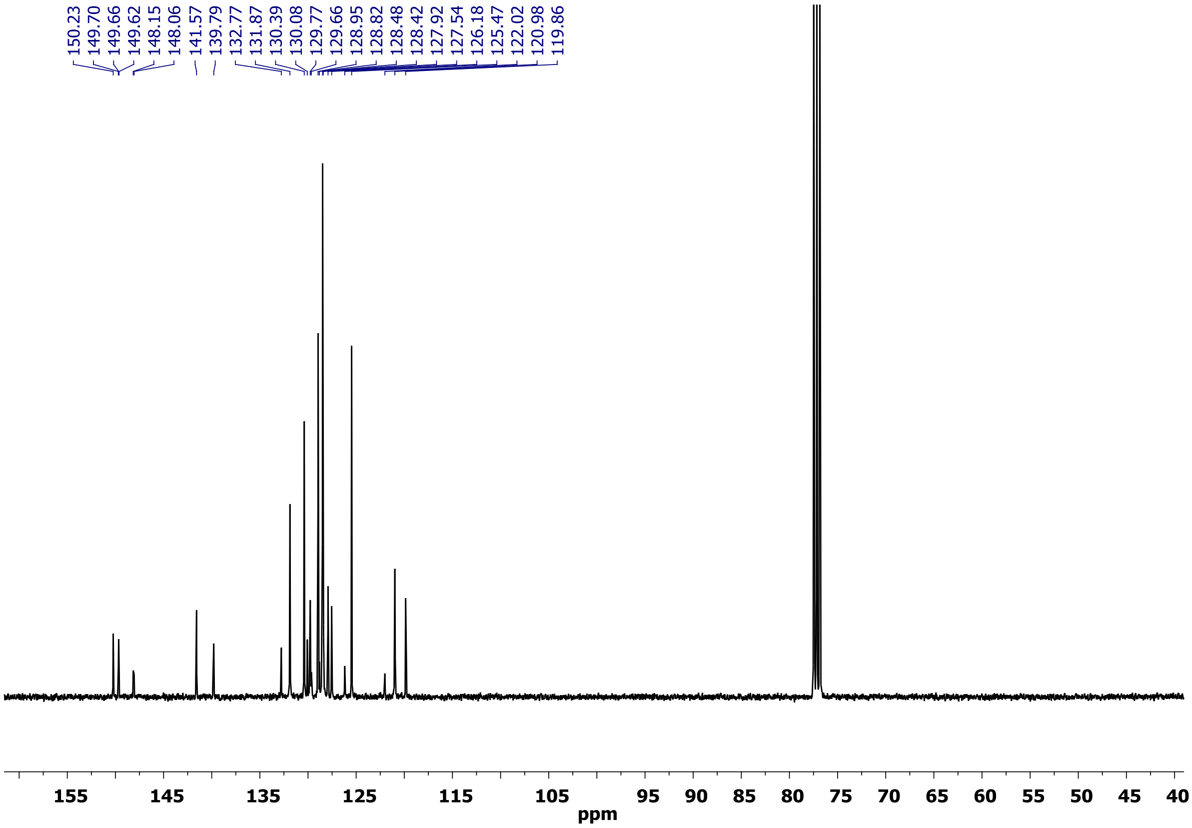
Compound **3** HRMS



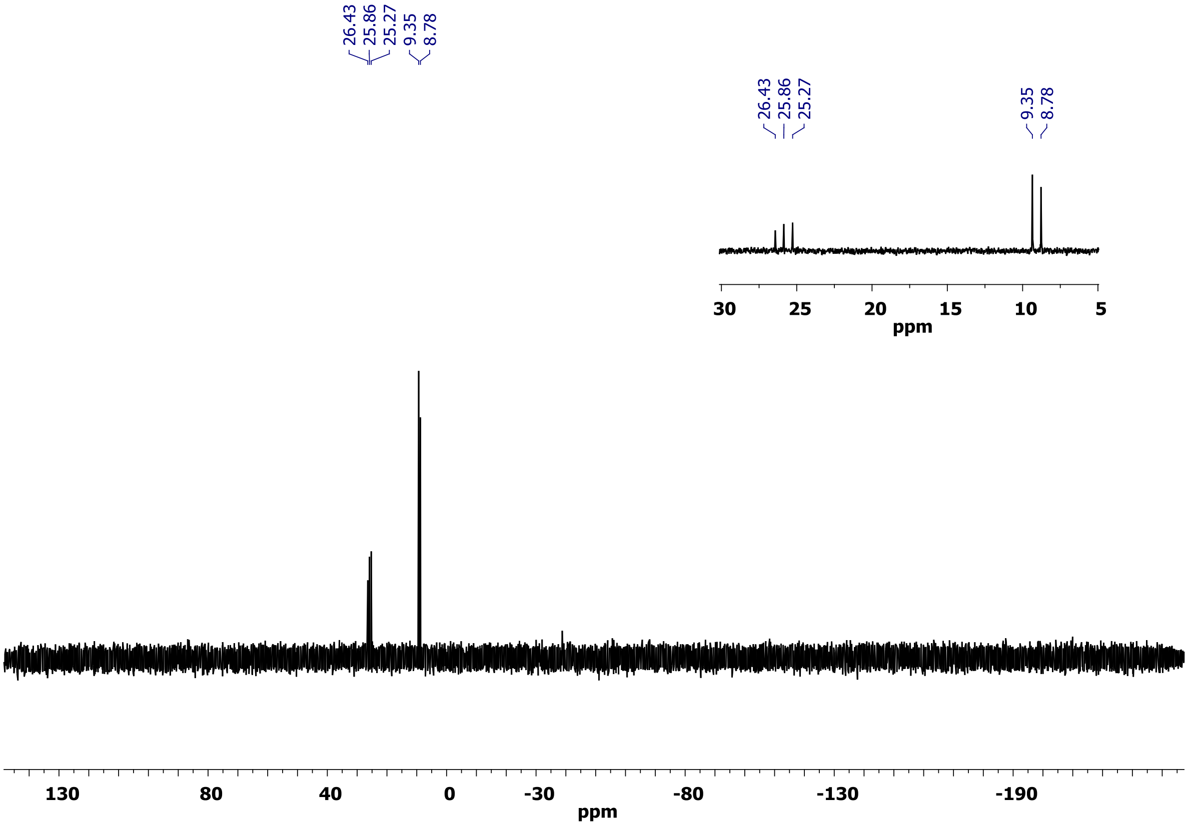
Compound **4** ^{1}H NMR



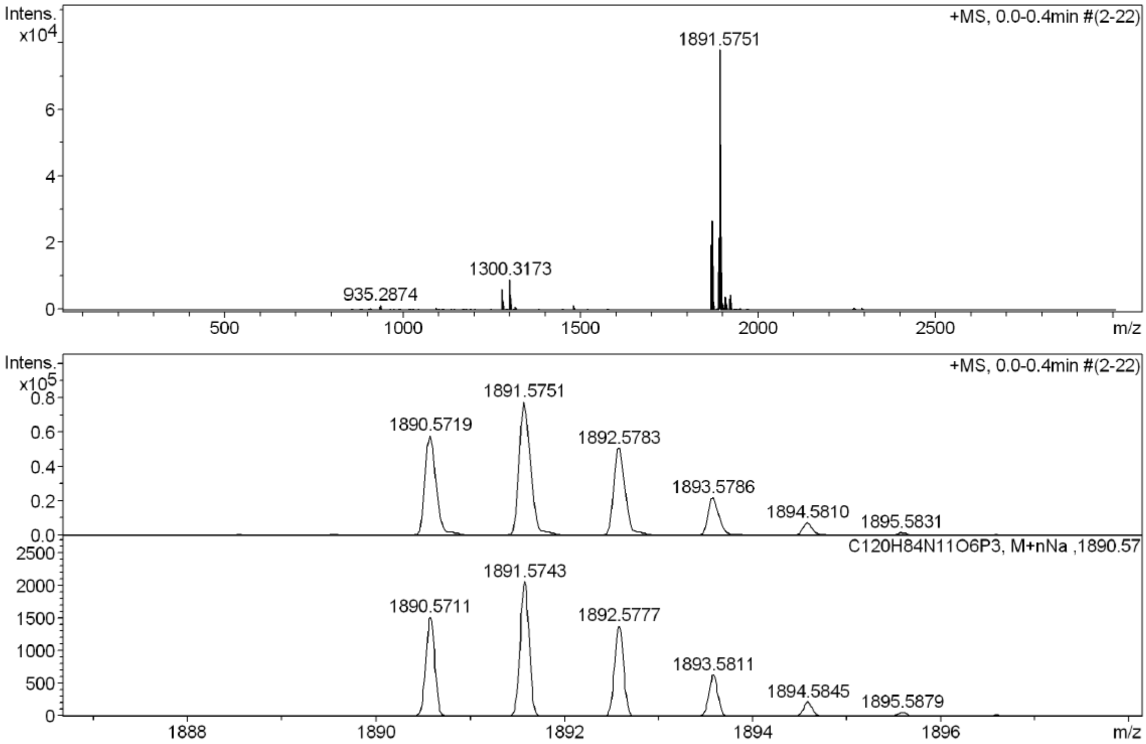
Compound **4** ^{13}C NMR



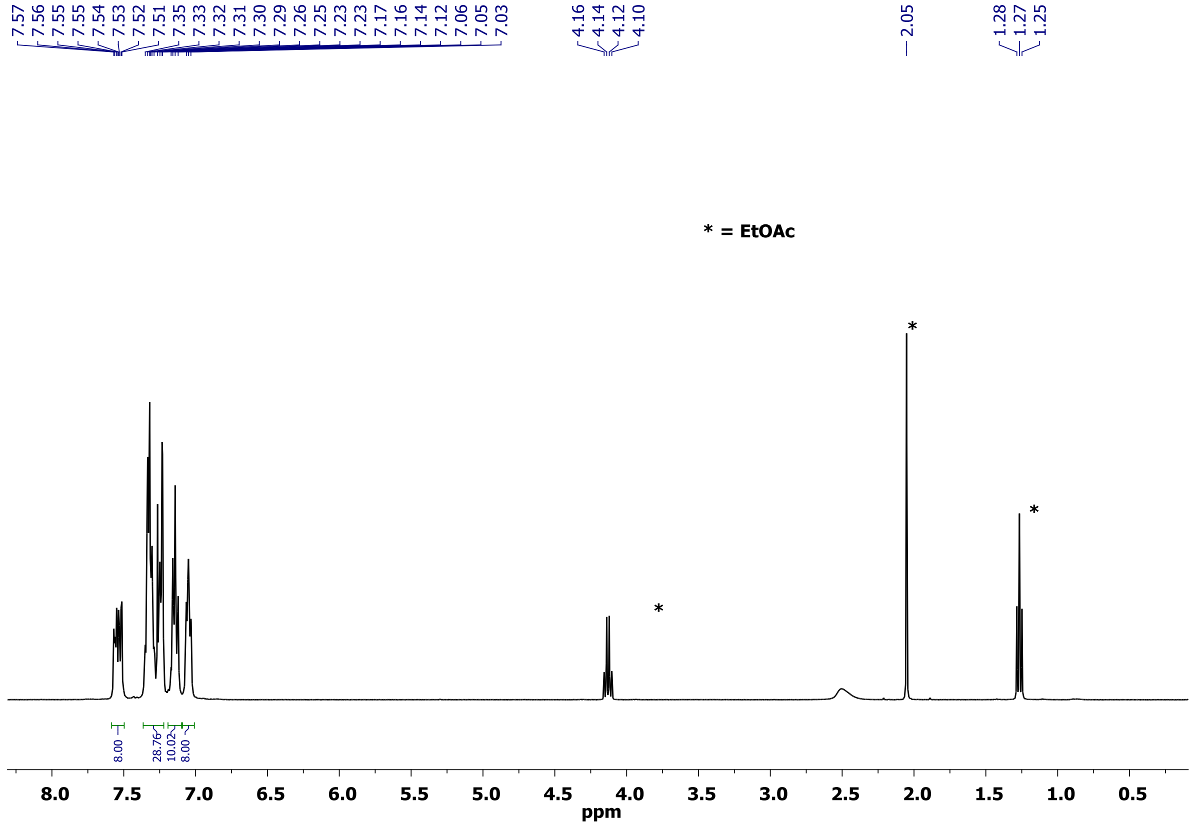
Compound **4** ^{31}P NMR



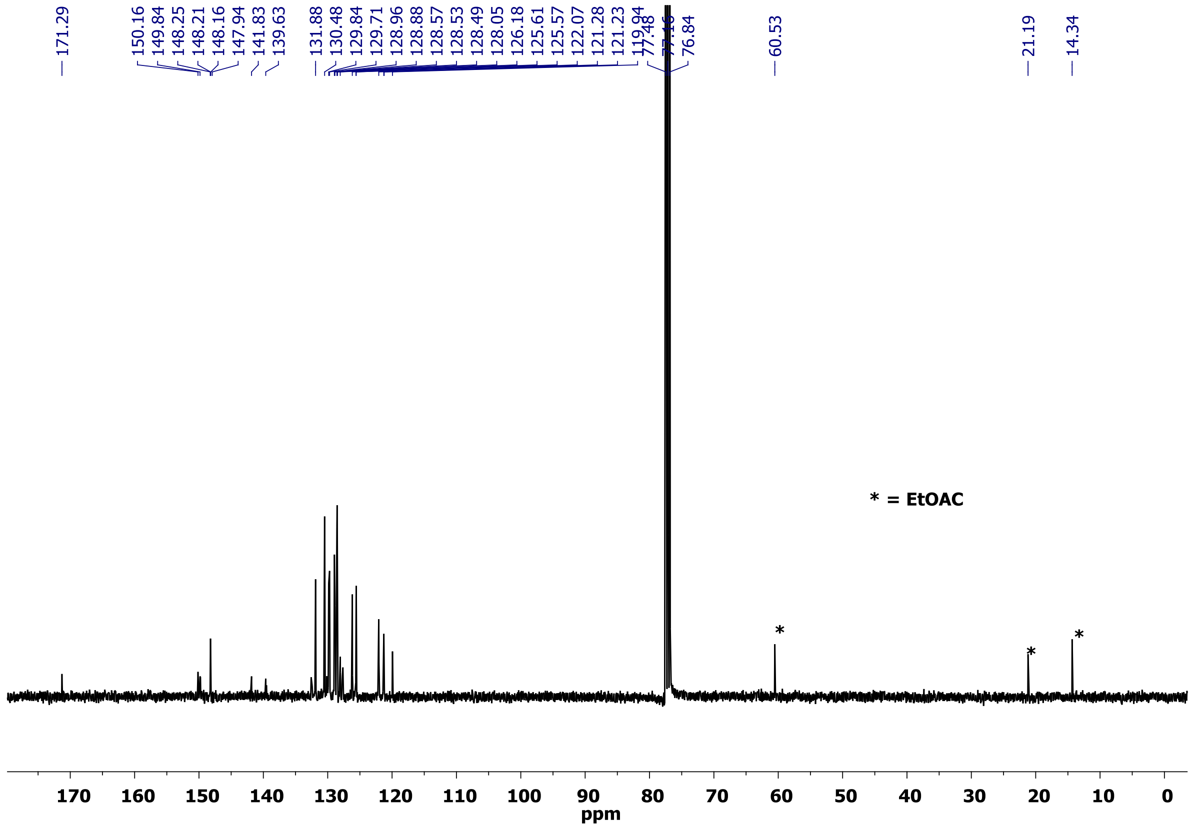
Compound **4** HRMS +sodium



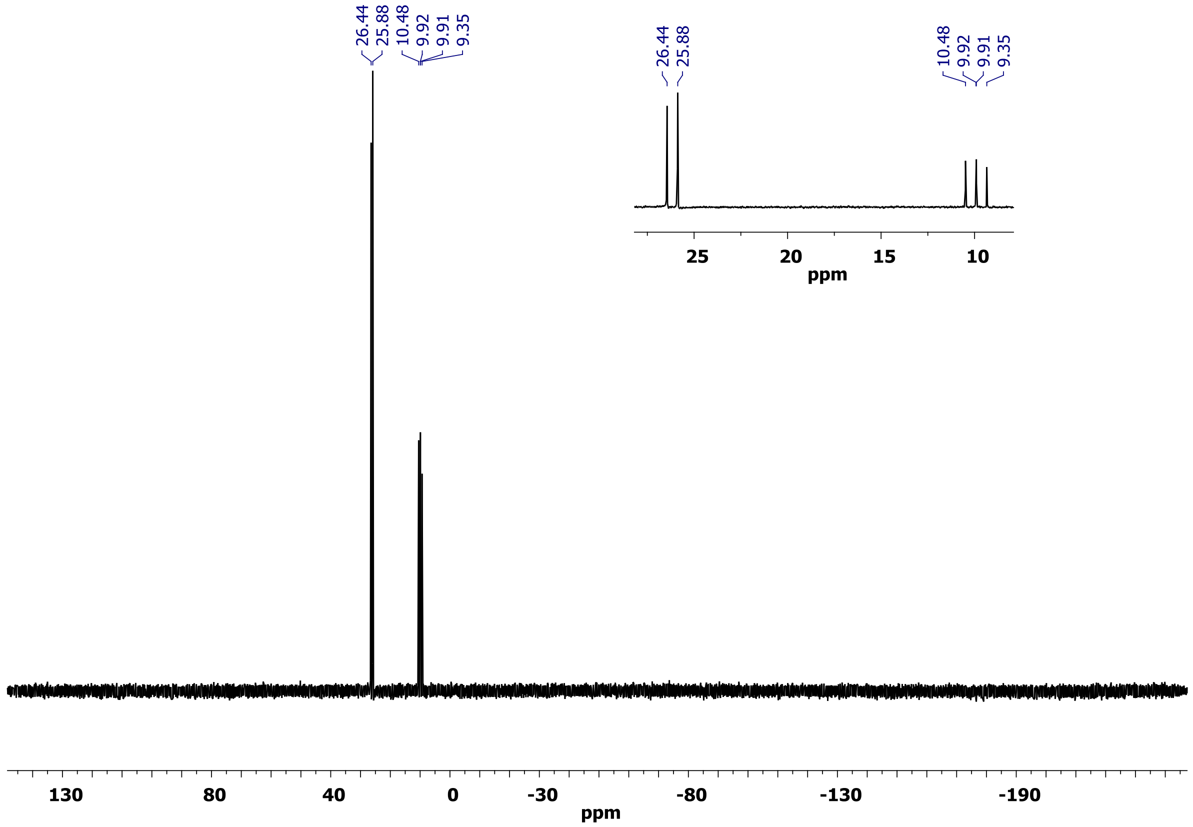
Compound **5** ^{1}H NMR



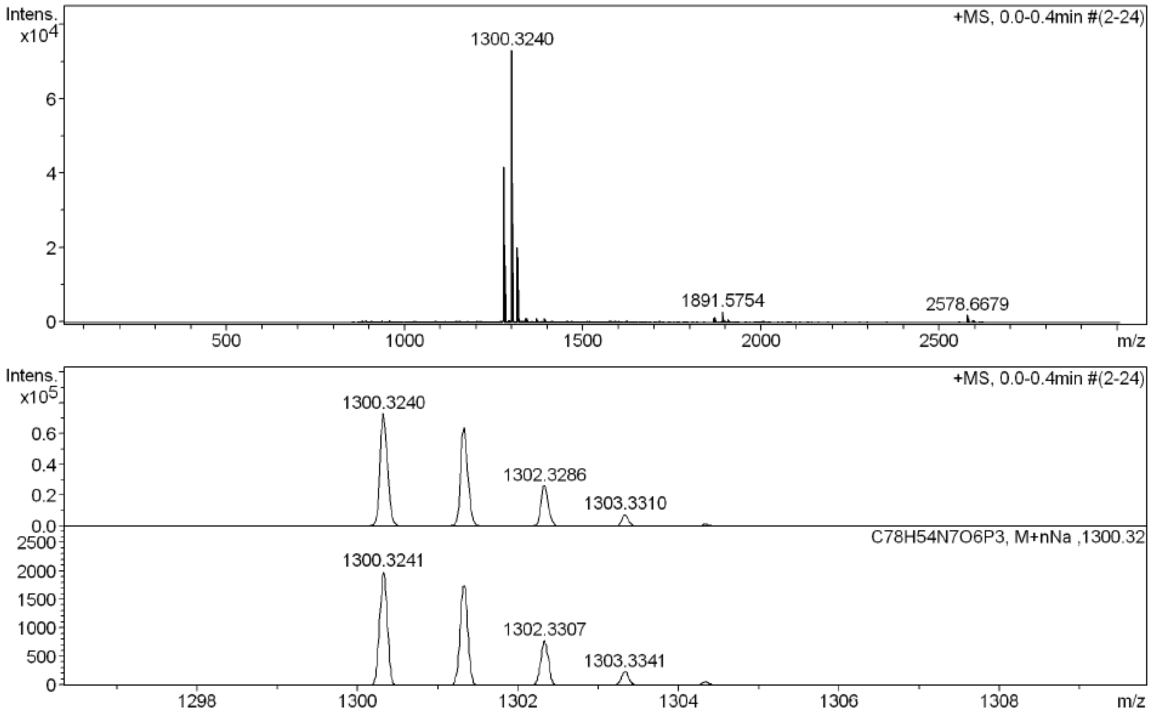
Compound **5** ^{13}C NMR



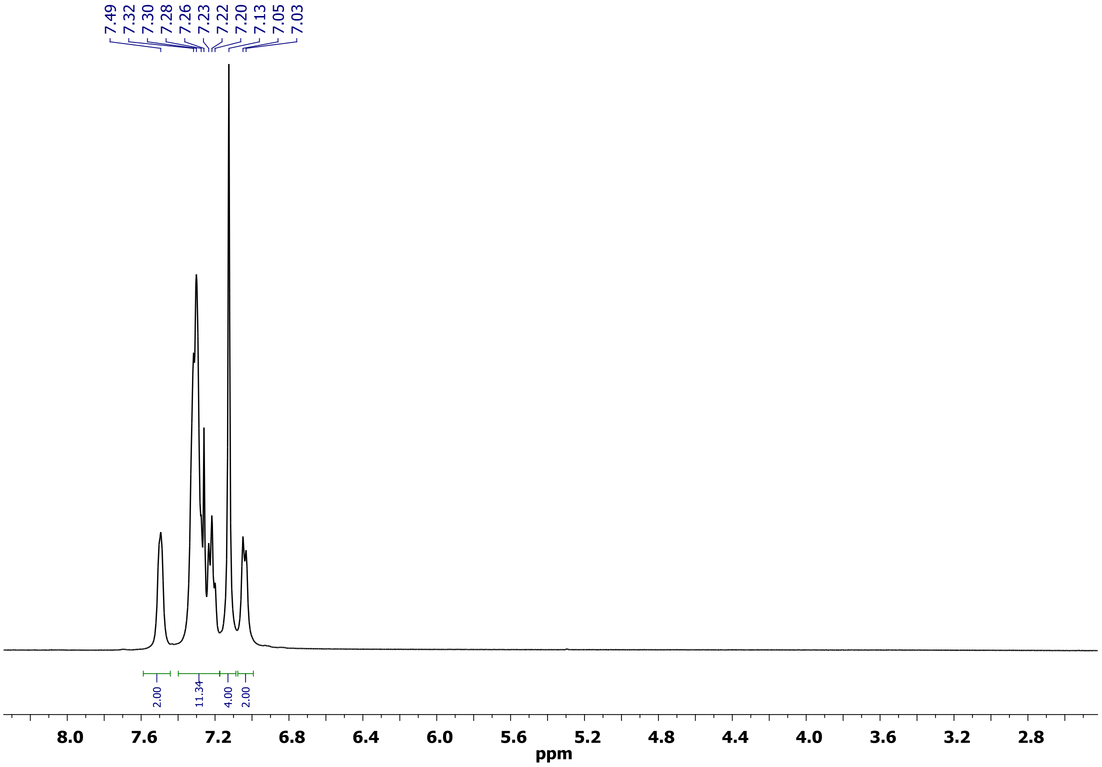
Compound **5** ^{31}P NMR



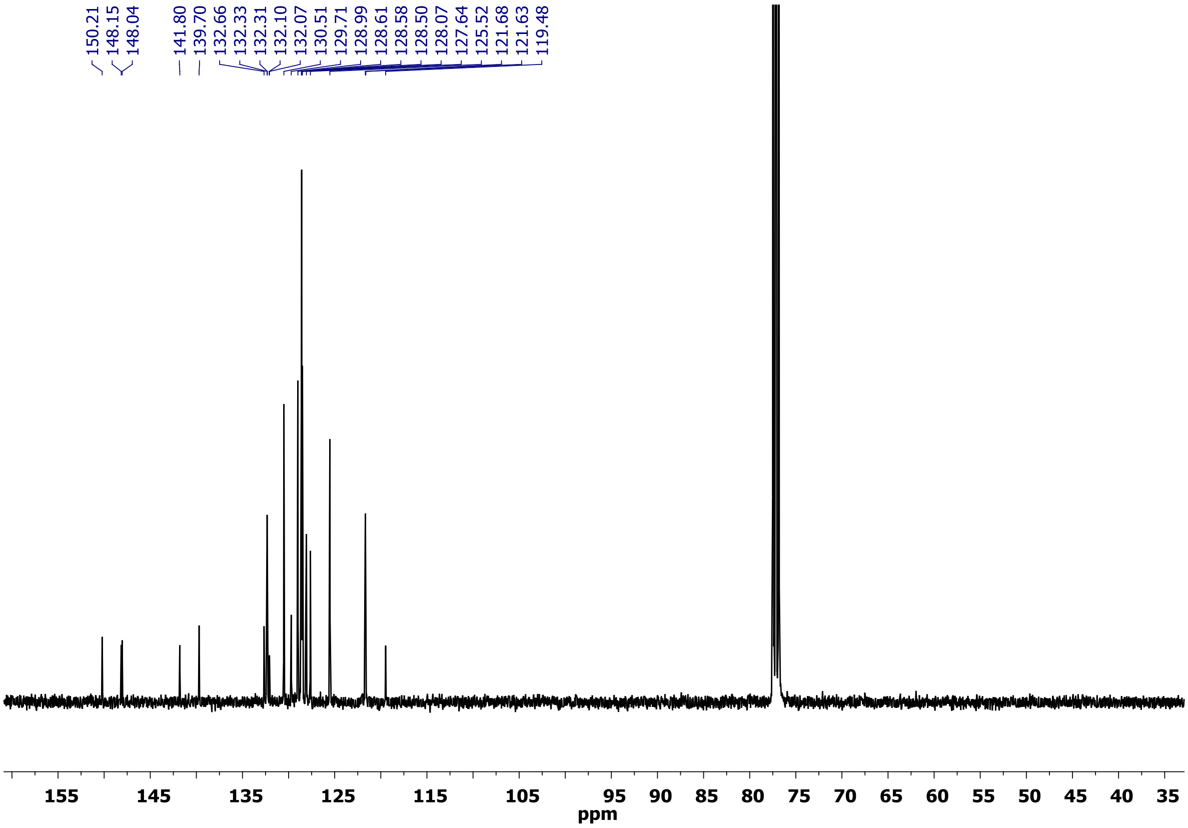
Compound **5** HRMS +sodium



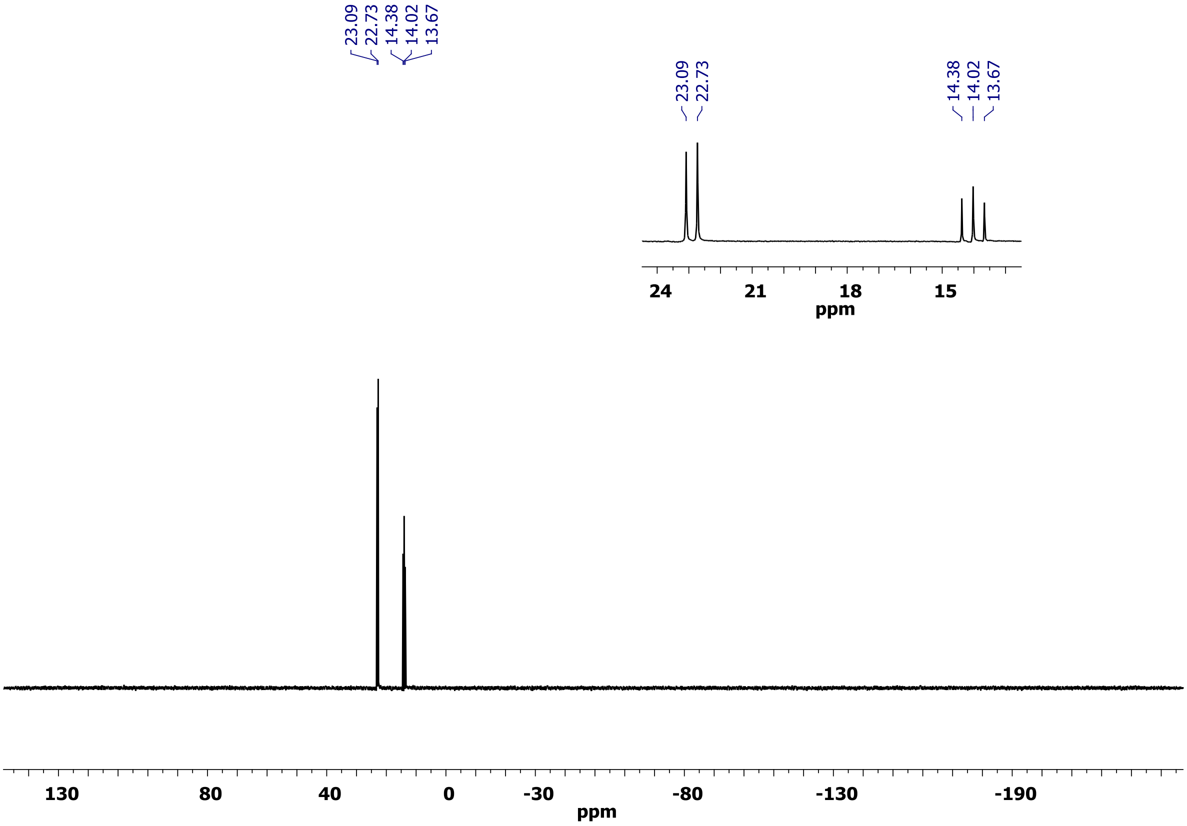
Compound **6** ^{1}H NMR



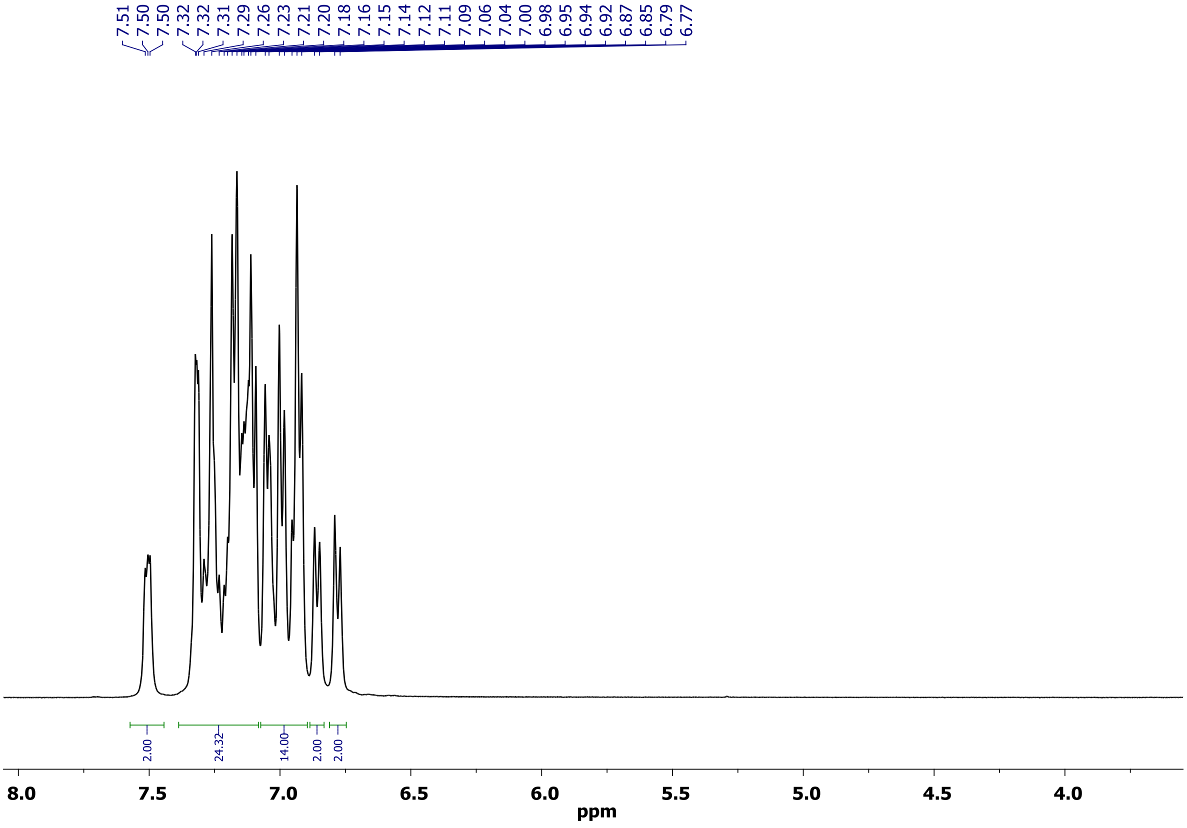
Compound **6** ^{13}C NMR



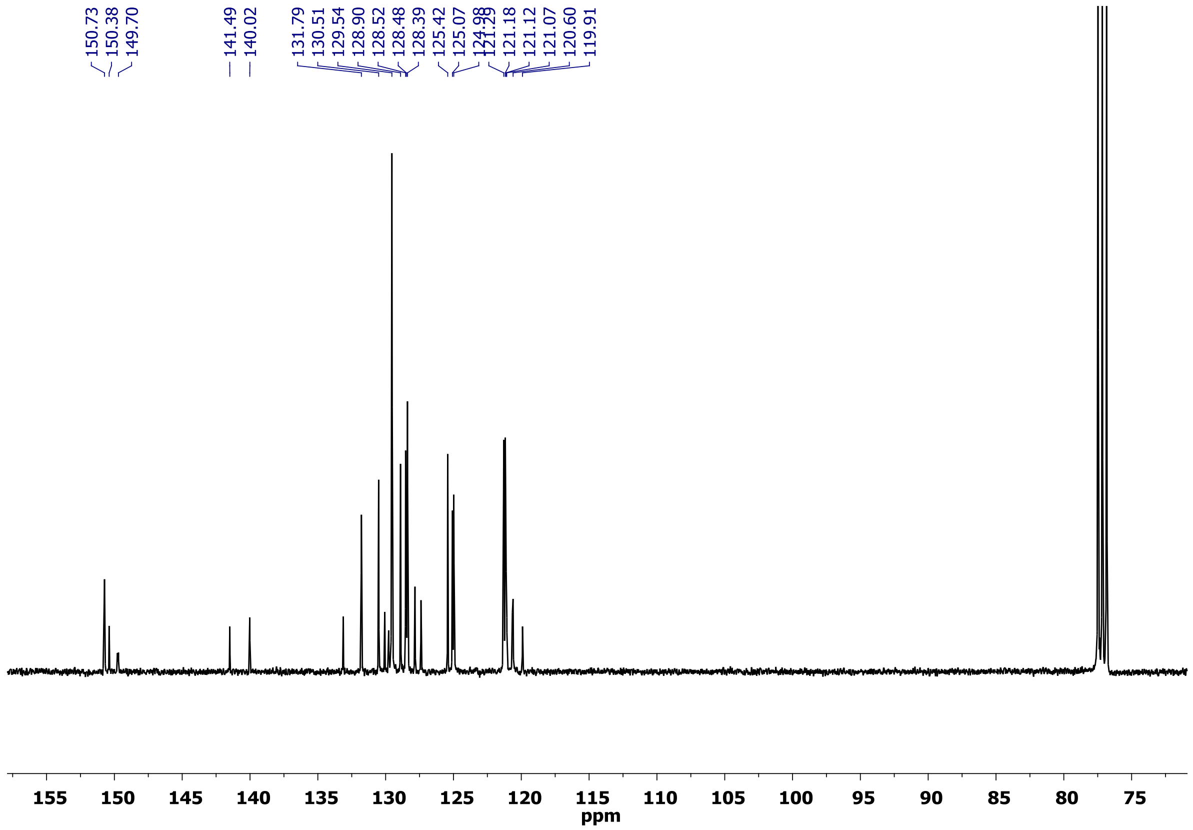
Compound **6** ^{31}P NMR



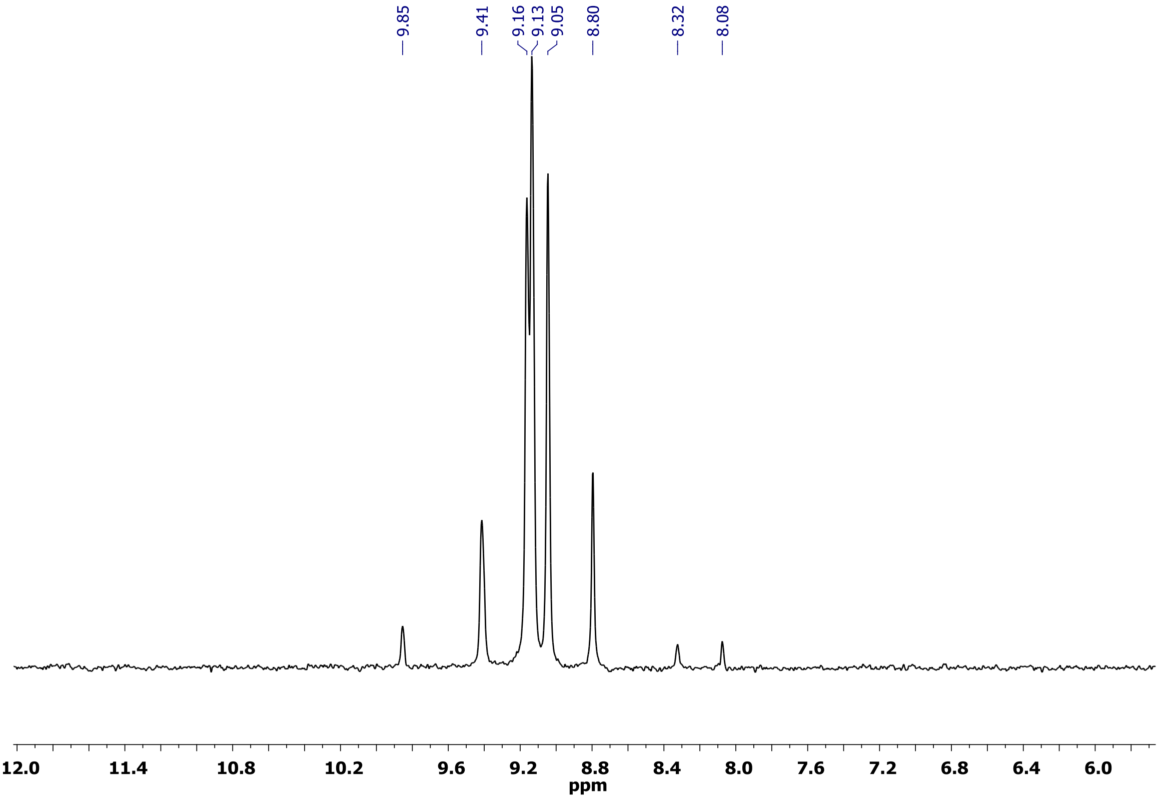
Compound **7** ^{1}H NMR



Compound **7** ^{13}C NMR



Compound **7** ^{31}P NMR



Compound **7** HRMS

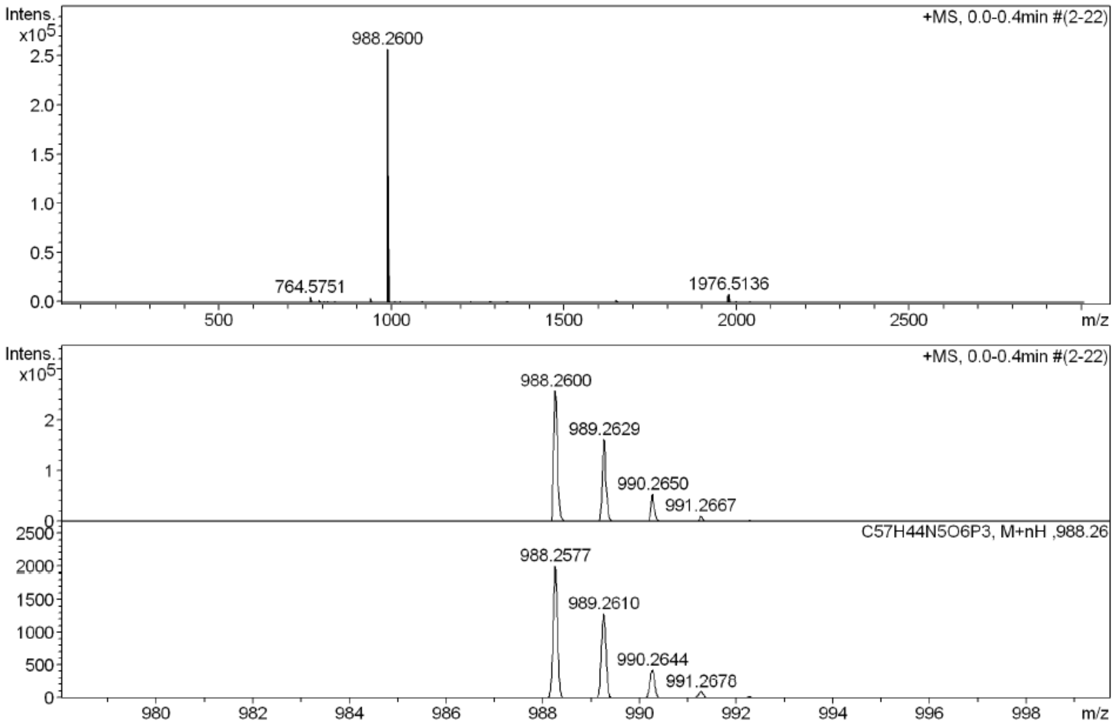


Table S1. Details of X-ray crystal structure analyses of compound **1 & 5**.

	Compound **1**	Compound **5**
Empirical formula	$C_{28}H_{22}N_2O$	$C_{164}H_{124}N_{14}O_{17}P_6$
M_r	402.48	2748.59
T [K]	296(2)	296(2)
wavelength, Å	0.71073 Å	0.71073 Å
crystal system	Orthorhombic	Triclinic
space group	$P2_12_12_1$	*P-1*
a [*Å*]	9.4128(2)	12.6054(3)
b [*Å*]	10.2247(2)	17.2285(4)
c [*Å*]	22.8025(6)	18.9581(5)
α [°]	90	64.2940(10)
β [°]	90	89.5010(10)
γ [°]	90	80.5230(10)
V [Å^3]	2194.58(9)	3649.95(15)
Z	4	1
ρ_{calc} [g cm^{-3}]	1.218	1.250
μ (MoKα) [mm^{-1}]	0.074	0.144
F (000)	848	1432
Crystal size [mm]	0.28 x 0.26 x 0.22	0.28x0.25x0.20
θ range [°]	1.79 – 28.33	1.64 – 26.05
limiting indices	-12<=h<=12	-15<=h<=13

	-13<=k<=13	-21<=k<=21
	-30<=l<=30	-23<=l<=23
reflns collected	35656	46528
independent reflns	5470	14371
	[*R*(int) = 0.0741]	[*R*(int) = 0.0471]
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	5470 / 0 / 282	14371 / 0 / 909
Goodness-of-fit on F^2	1.011	1.045
final R indices	$R_1 = 0.0502$	$R_1 = 0.0705$
[I >2σ(I)] [a]	$wR_2 = 0.1024$	$wR_2 = 0.2206$
R indices (all data) [a]	$R_1 = 0.1002$	$R_1 = 0.1145$
	$wR_2 = 0.1294$	$wR_2 = 0.2620$
$\text{peak}_{\text{max}}/\text{hole}_{\text{min}}$ [e $Å^{-3}$]	0.333 and -0.365	1.359 and -0.357

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