Phosphorus Complexes of *Meso*-Triaryl-25-Oxasmaragdyrins

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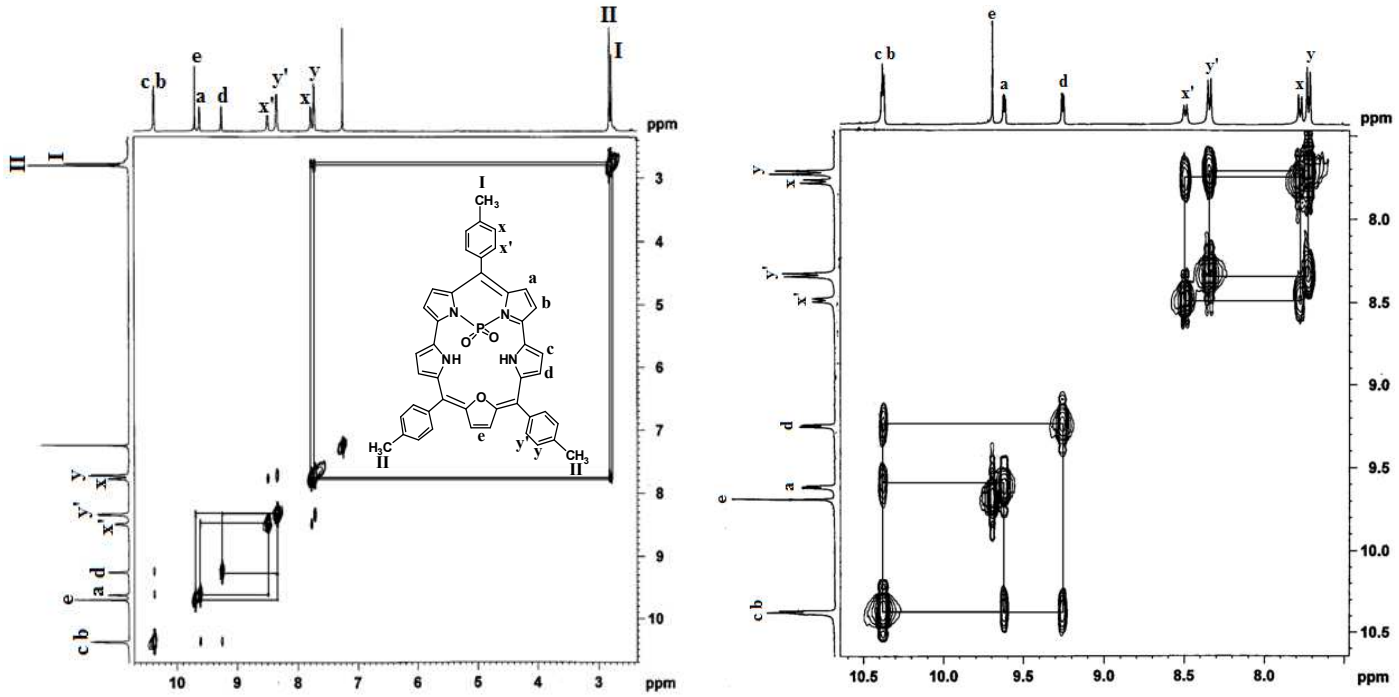
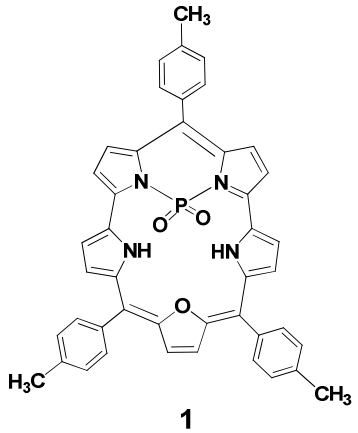
Structural Elucidation of compound 1 by COSY and NOESY NMR: The ^{1}H-^{1}H COSY and NOESY NMR spectra of complex **1** are shown in the Figure S2 along with the proton assignments. The assignments were made on the basis of resonance position and intensity data as well as the proton-to-proton connectivity revealed in the COSY and NOESY NMR spectra. Inspection of ^{1}H-NMR spectrum of complex **1** showed two singlets at 2.60 and 2.70 ppm corresponding to three and six protons respectively of *meso*-tolyl-CH_3 protons. The signal at 2.60 ppm was assigned to *type I* –CH_3 protons of *meso*-tolyl group and the signal at 2.70 ppm was assigned to *type II* –CH_3 protons of *meso*-tolyl group. The *type I* signal at 2.60 ppm showed NOE correlation with a doublet signal at 7.80 ppm which we assigned as *x-type* aryl protons of *meso*-tolyl group. The *x-type* protons signal at 7.80 ppm showed cross peak correlation with doublet signal at 8.50 ppm which we identified as *x'-type* aryl protons of *meso*-tolyl group. The signal at 8.50 ppm showed NOE correlation with a doublet at 9.60 ppm which we assigned as *a-type* pyrrole protons. The *a-type* pyrrole protons showed cross peak correlation with a signal at 10.40 ppm which was identified as *b-type* pyrrole protons. To identify the signals corresponding to other two *meso*-tolyl groups, furan protons and pyrrole protons *c* and *d*, we looked at NOE correlations observed for *type II*, –CH_3 protons. The *type II* –CH_3 protons at 2.80 ppm showed NOE correlation with a doublet at 7.72 ppm which was assigned to *y-type* protons of *meso*-tolyl group. The *y-type* signal showed cross peak correlation with a doublet at 8.38 ppm corresponding to *y'-type* aryl protons of *meso*-tolyl group. The singlet at 9.72 ppm was identified as *e-type* furan protons based on its NOE correlation with *y'-type* protons. The *y'-type* signal also showed NOE correlation with a signal at 9.27 ppm which was assigned as *d-type* pyrrole signal. The *d-type* signal showed a cross peak correlation with a multiplet at 10.38 ppm

which was assigned as *c-type* pyrrole signal. Furthermore, the two inner NH protons were observed at -1.70 ppm and this signal also showed cross peak correlation with *c* and *d-type* pyrrole protons in COSY spectrum. The complexes **2**, **3,** and **4** also showed similar NMR features. In ^{31}P NMR, the complexes **1-4** showed one sharp signal in the region of ~ -32 to -33 ppm (Figure S4, S7, S10, S13). Thus, 1D and 2D NMR specroscopy was very useful in deducing the molecular structure of the PO_2 complexes of 25-oxasmaragdyrins **1-4**.



(a) **(b)**

Figure S2: (a) Selected region of NOESY NMR spectrum of compound **1** (b) selected region of COSY NMR spectrum of compound **1** recorded in $CDCl_3$.



1

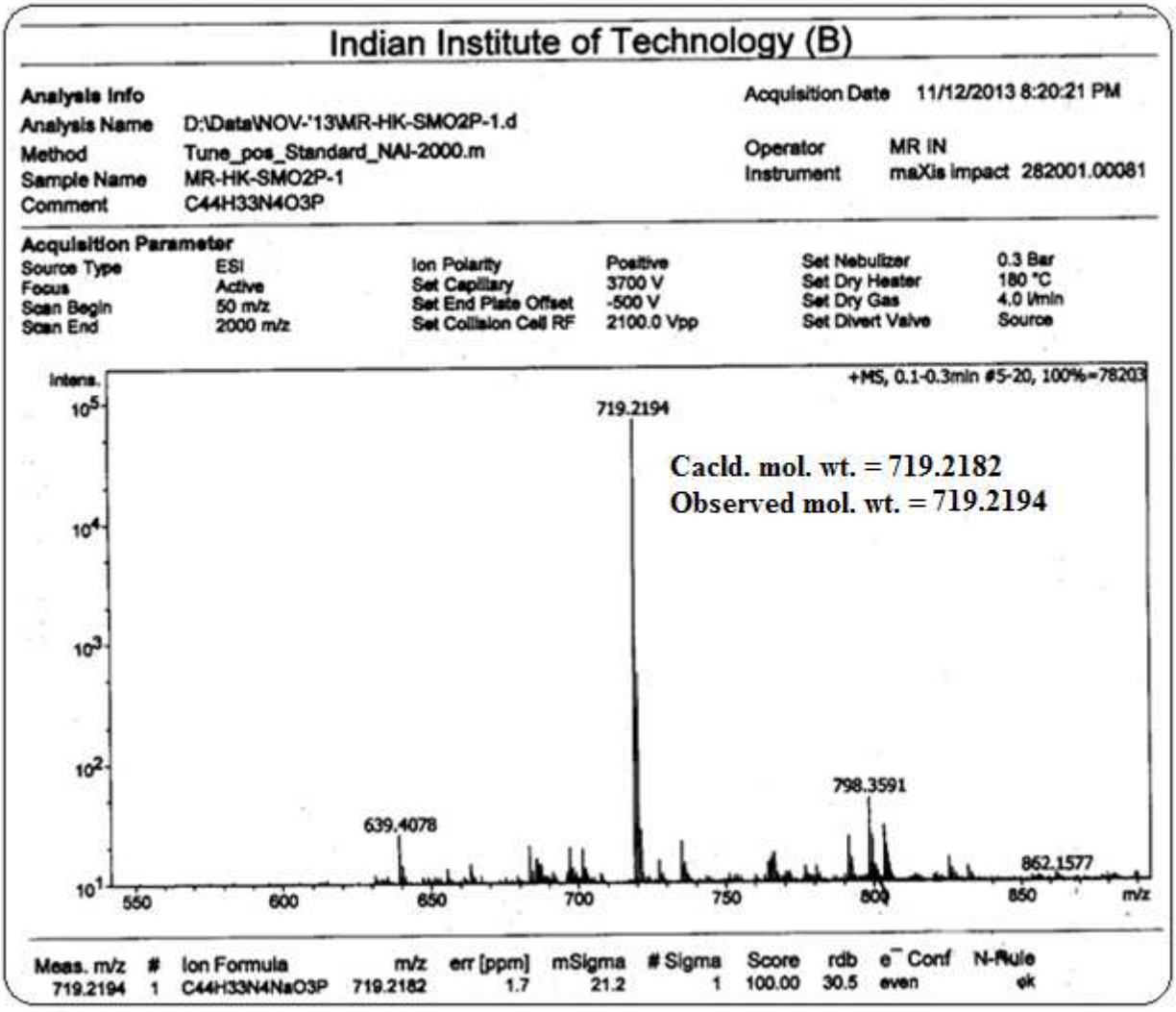


Figure S3. HR-MS spectrum of compound **1**.

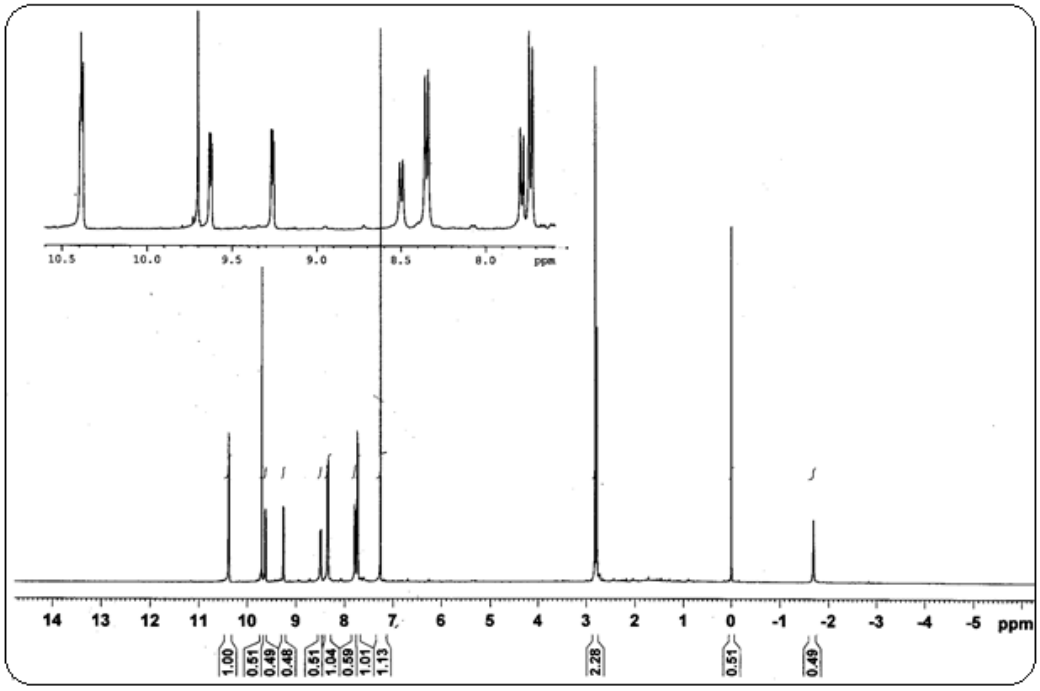


Figure S4. ^{1}H NMR spectrum of compound **1** recorded in $CDCl_3$**.** The inset shows the expansion.

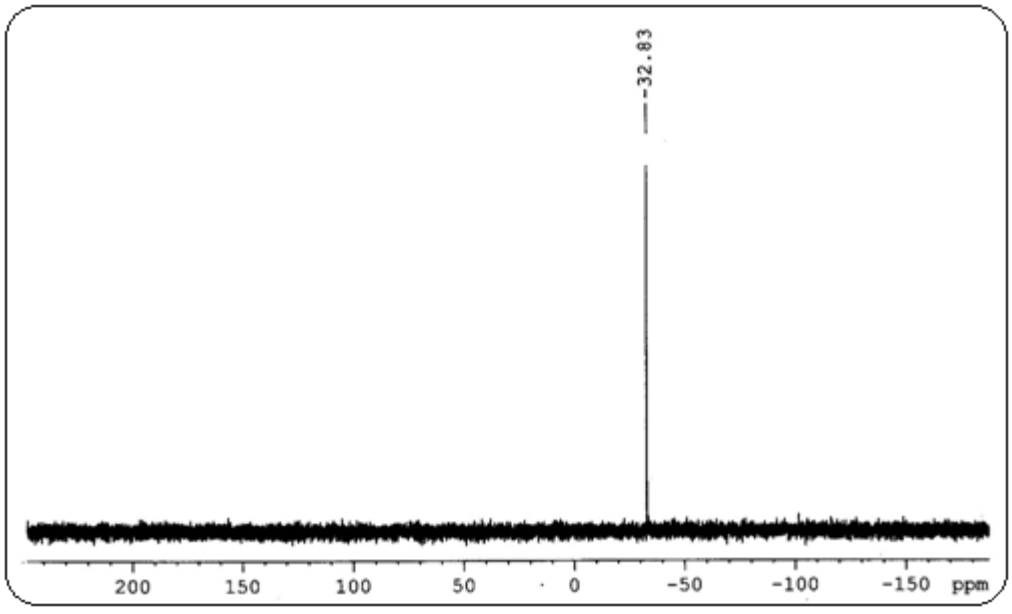


Figure S4. ^{31}P NMR spectrum of compound **1** recorded in $CDCl_3$**.**

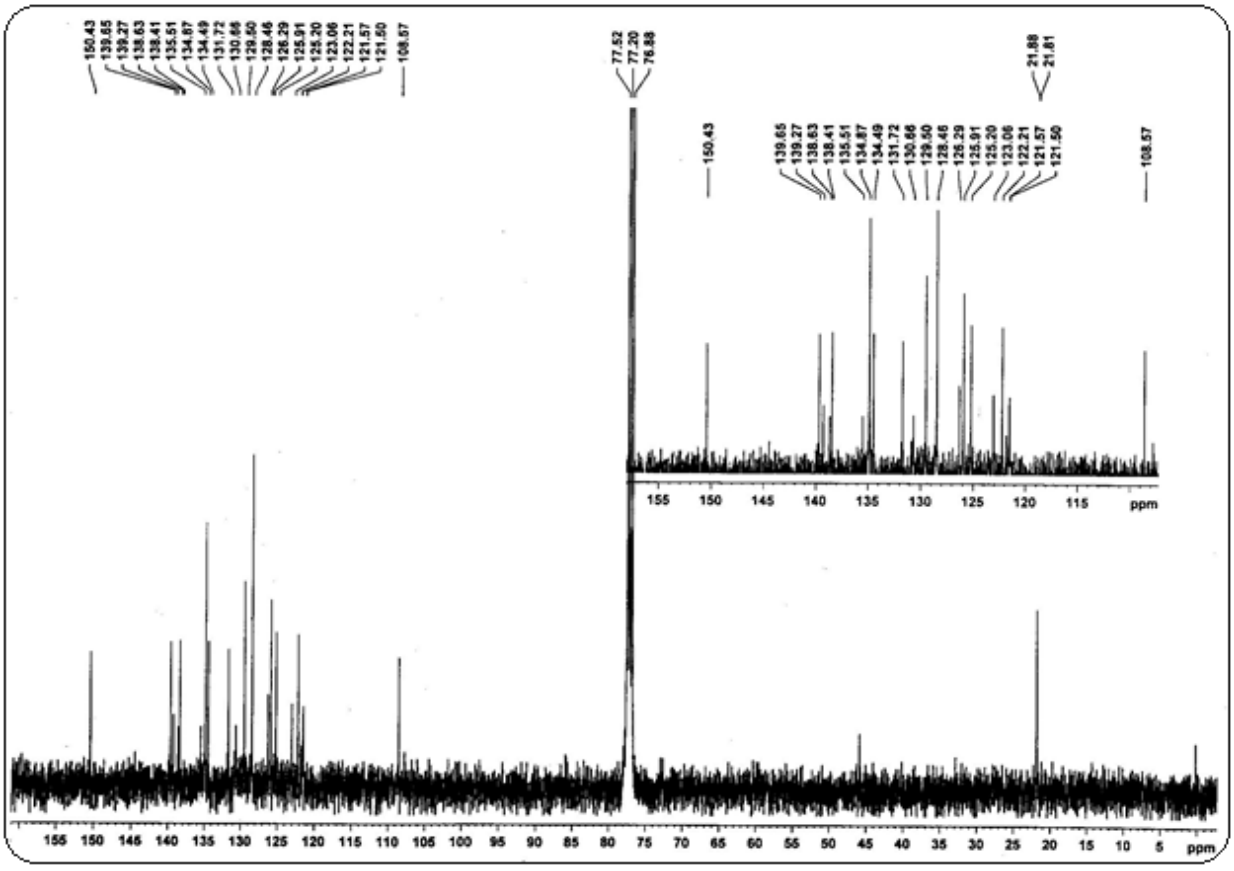
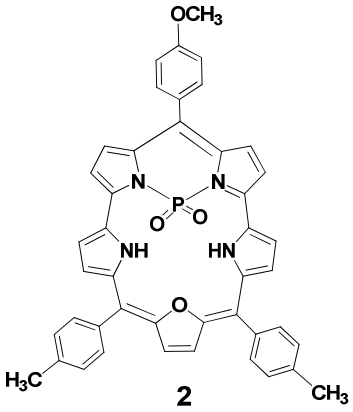


Figure S5. ^{13}C NMR spectrum of compound of **1** recorded in $CDCl_3$.



2

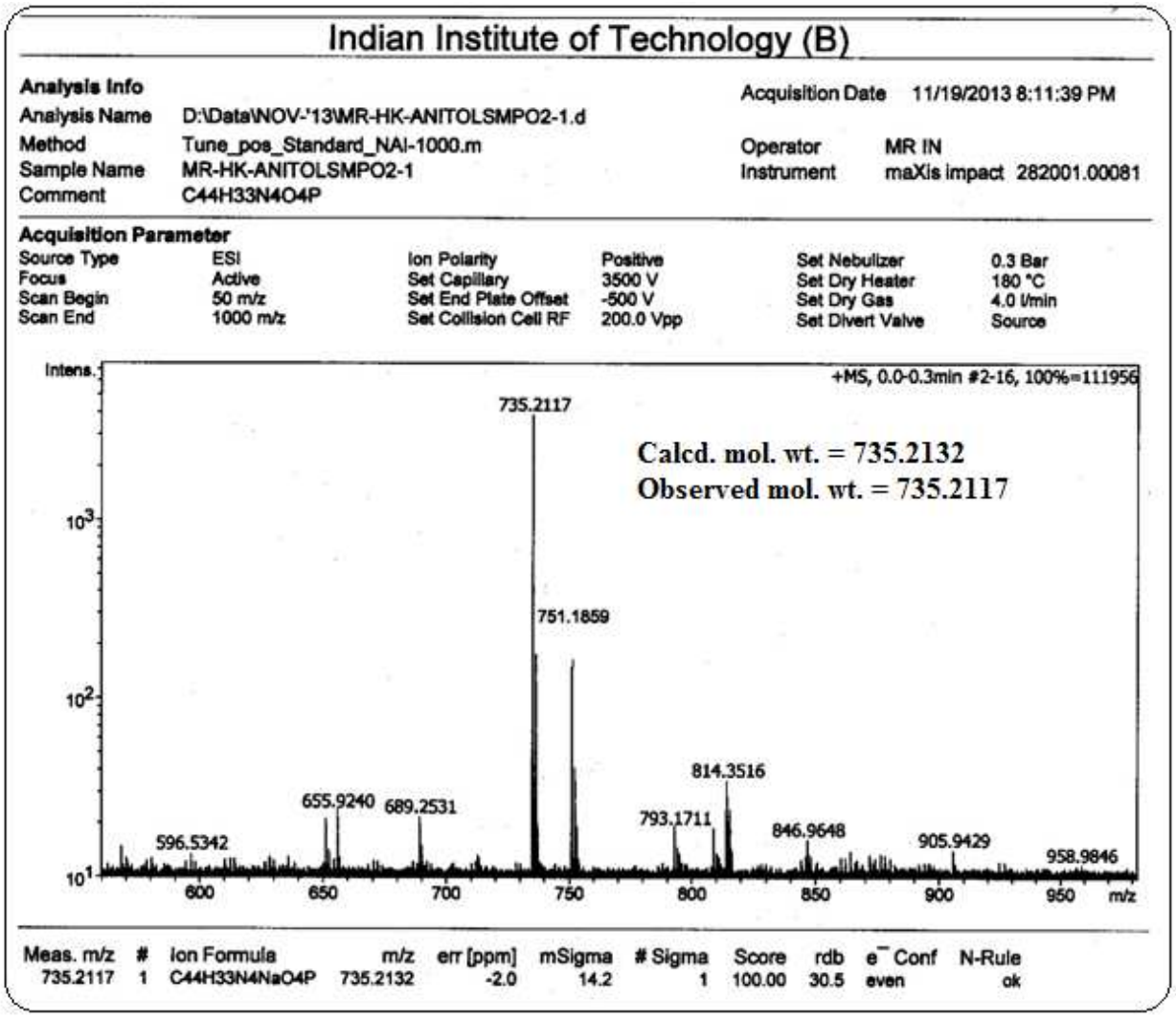


Figure S6. HR-MS spectrum of compound **2**.

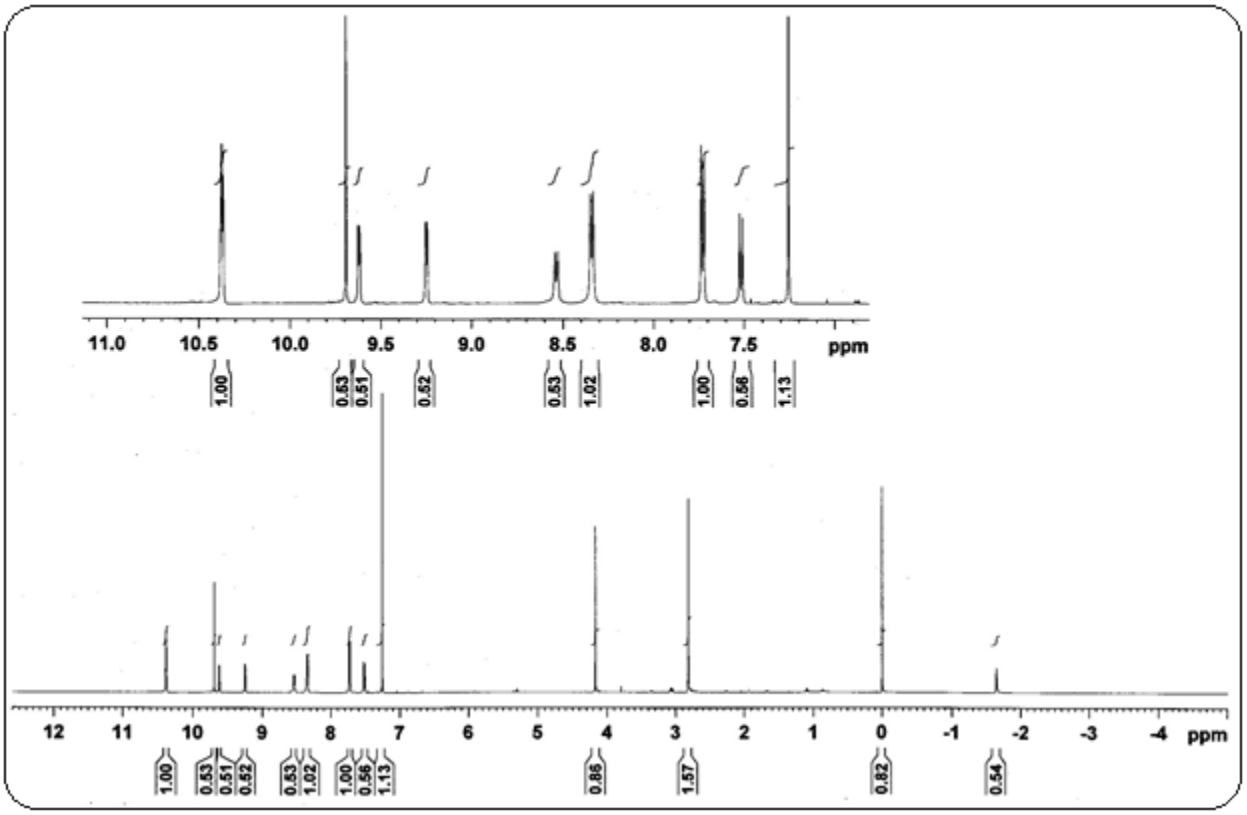


Figure S7. ^{1}H NMR spectrum of compound **2** recorded in $CDCl_3$**.** The inset shows the expansion.

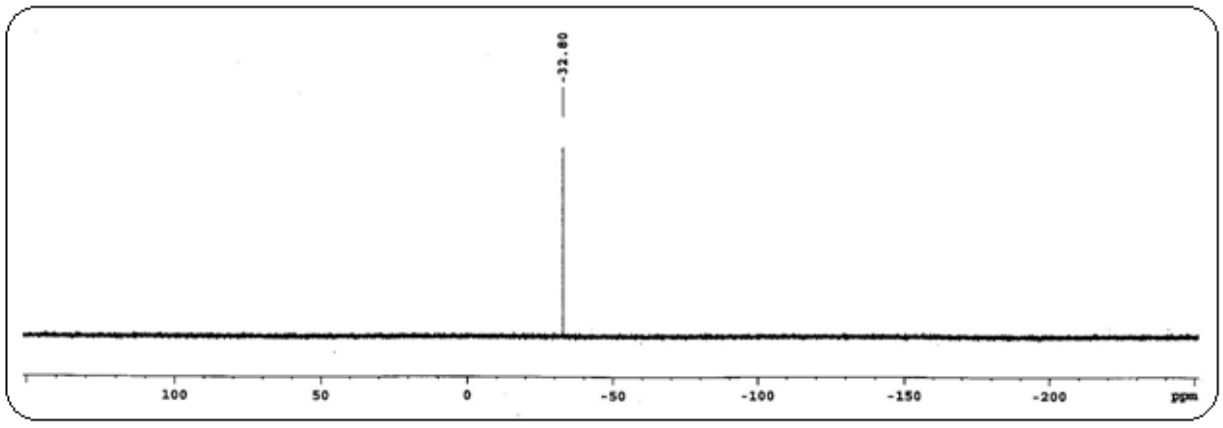


Figure S7. ^{31}P NMR spectrum of compound **2** recorded in $CDCl_3$**.**

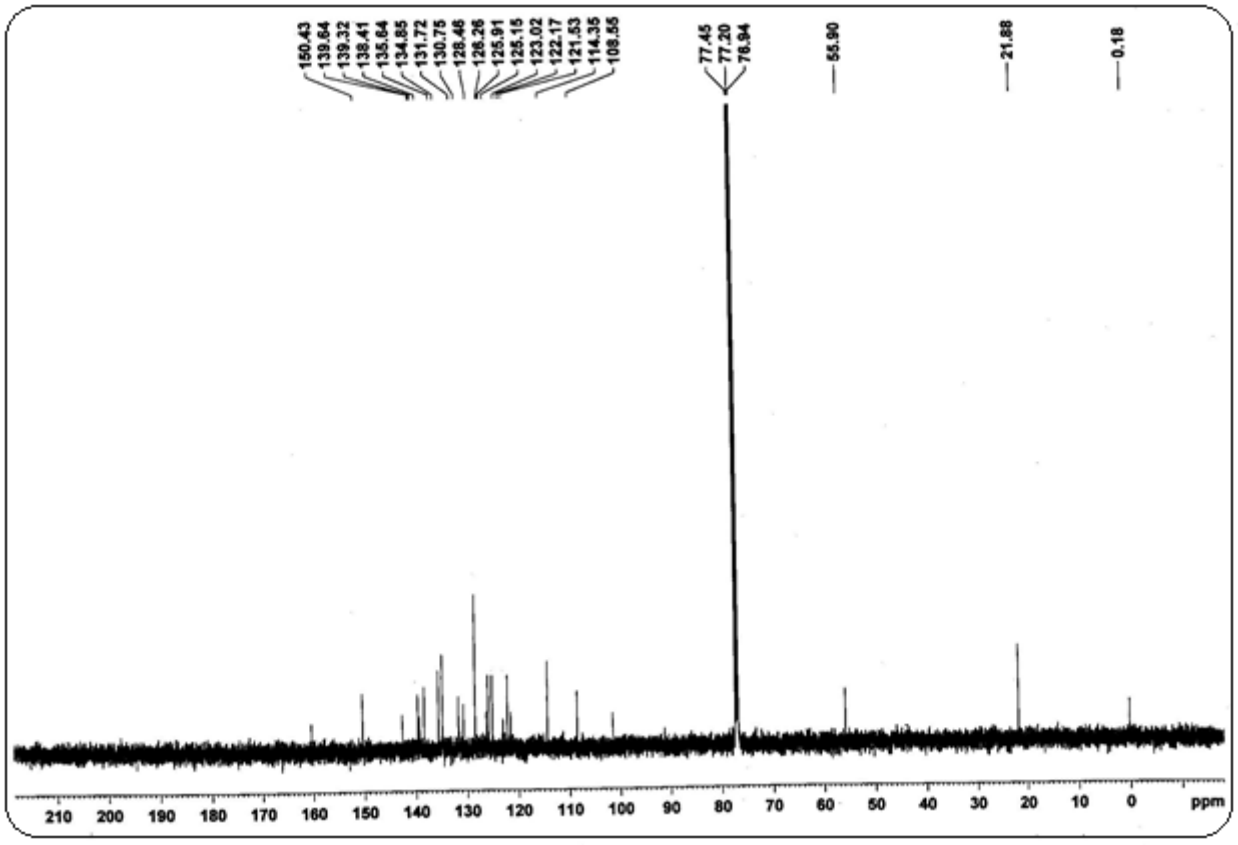
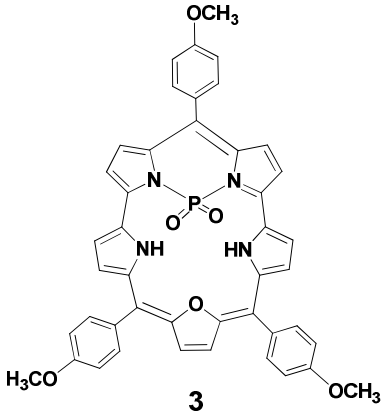


Figure S8. ^{13}C NMR spectrum of compound of **2** recorded in $CDCl_3$**.**



3

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Analysis Info

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Comment	C44H33N4O6P		

Acquisition Parameter

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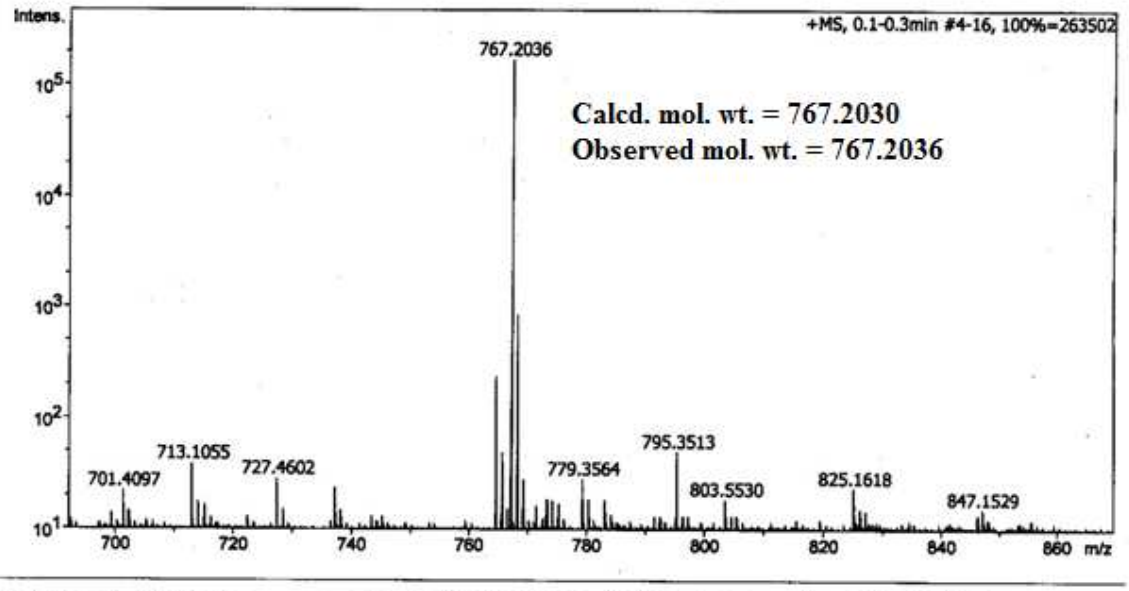

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
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Figure S9. HR-MS spectrum of compound **3**.

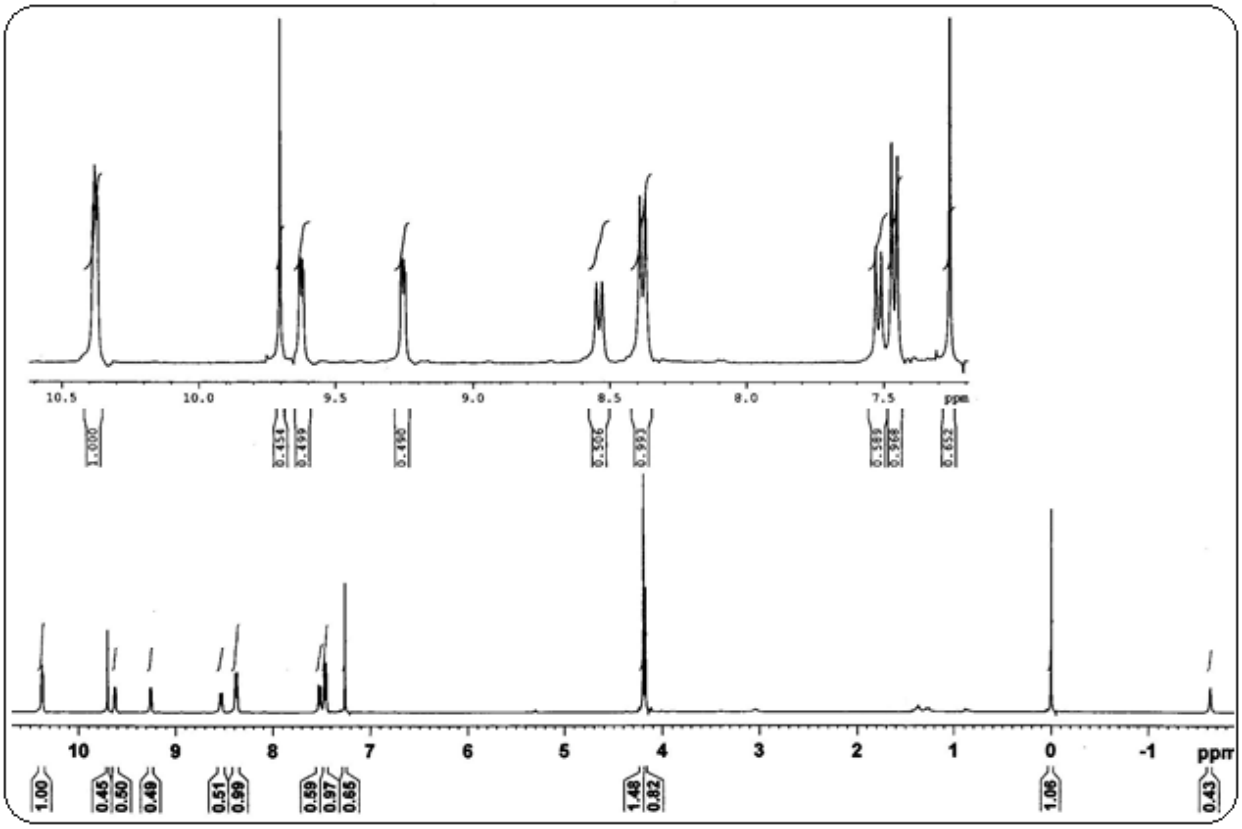


Figure S10. ^{1}H NMR spectrum of compound **3** recorded in $CDCl_3$**.** The inset shows the expansion.

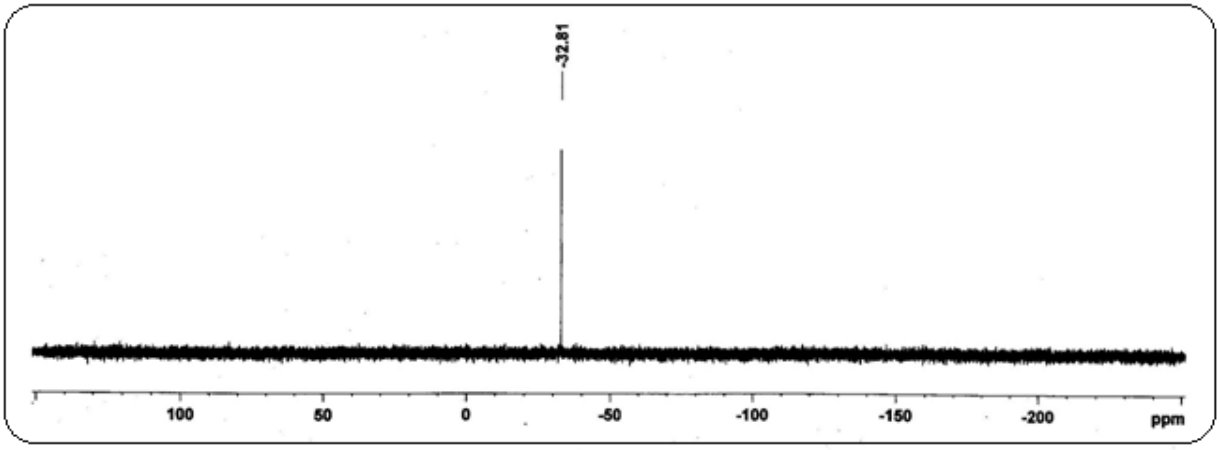


Figure S10. ^{31}P NMR spectrum of compound **3** recorded in $CDCl_3$**.**

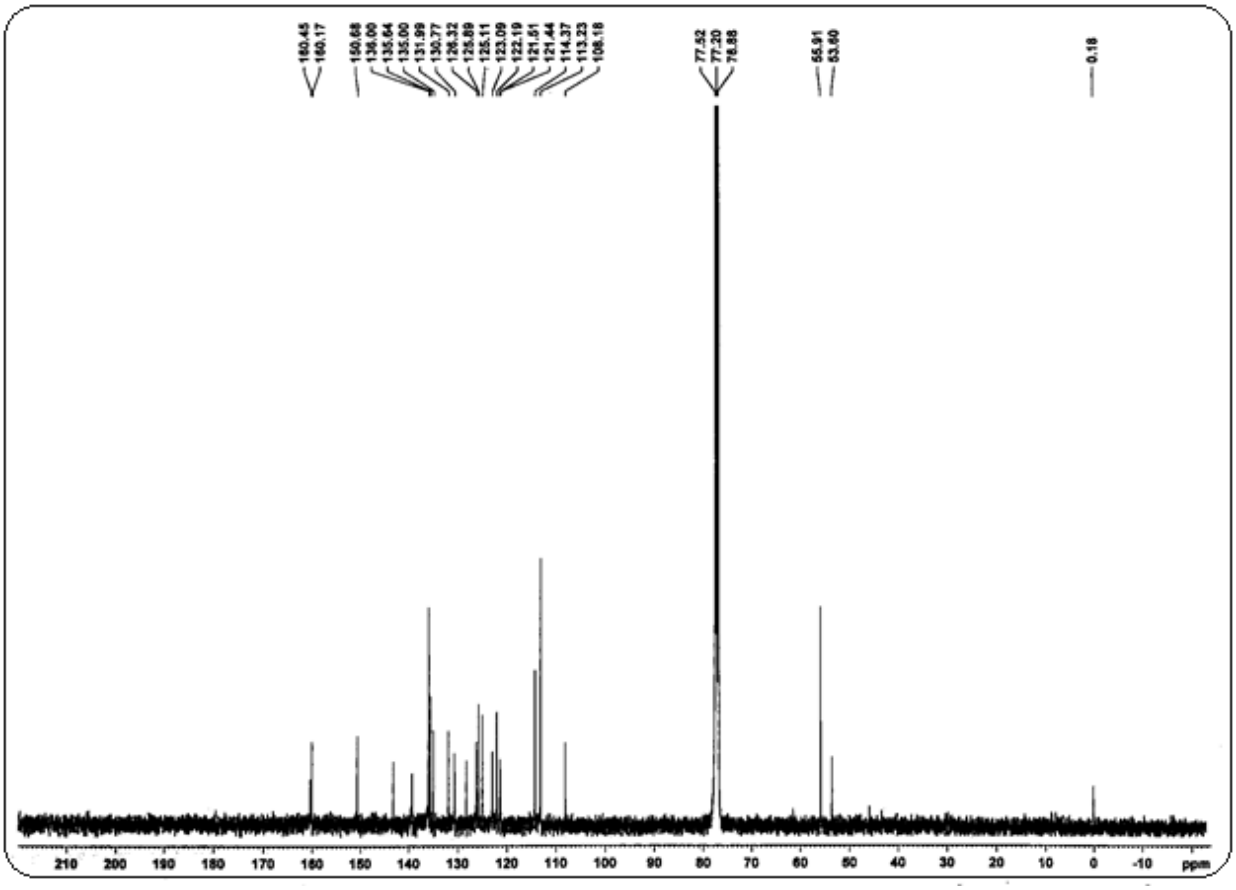
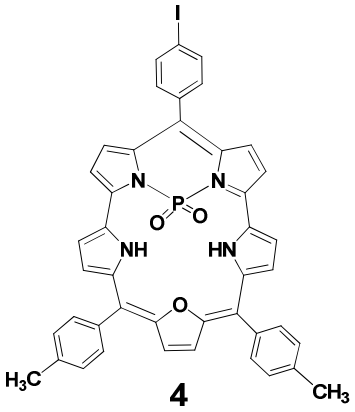


Figure S11. ^{13}C NMR spectrum of compound of **3** recorded in $CDCl_3$.



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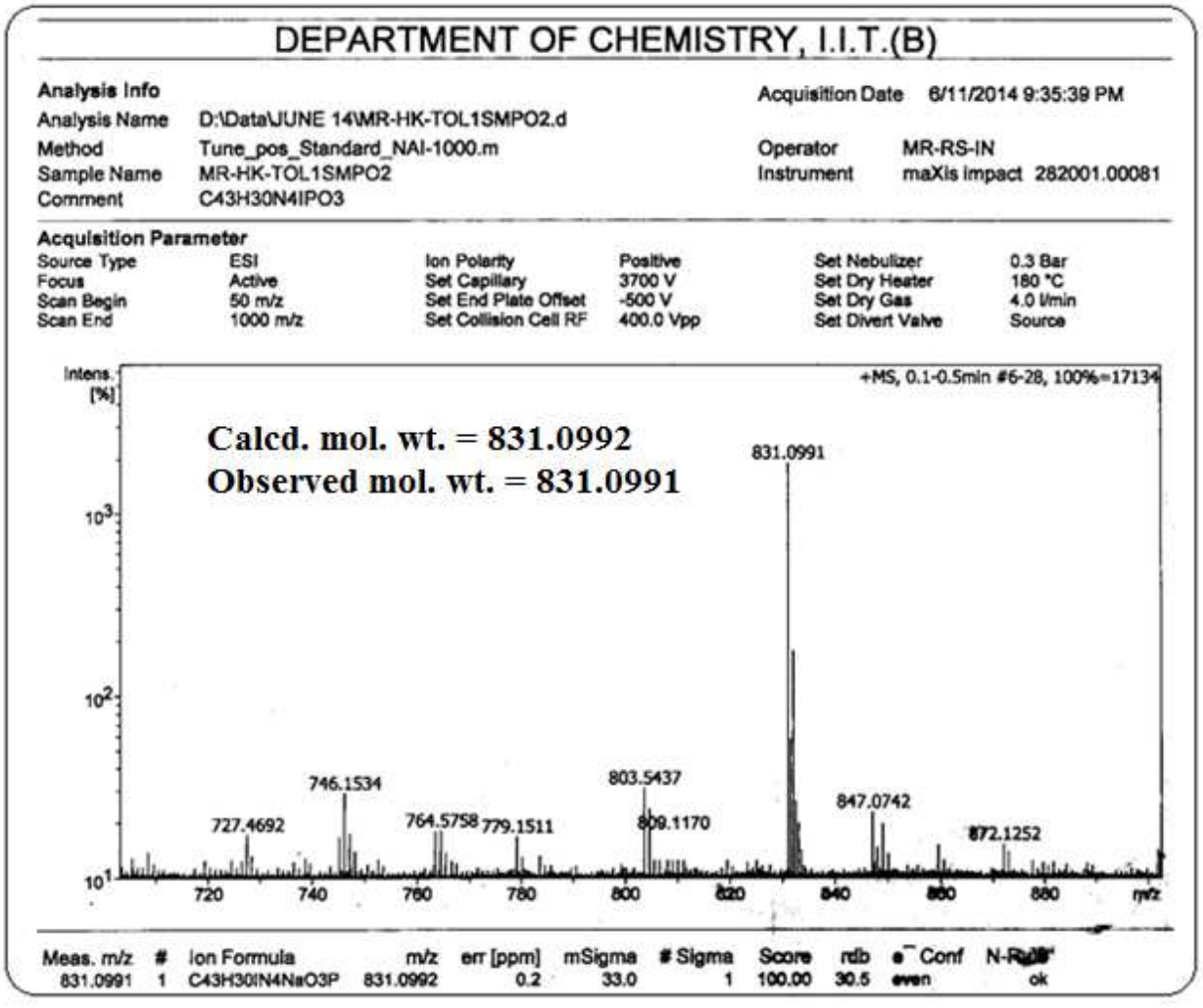


Figure S12. HR-MS spectrum of compound **4**.

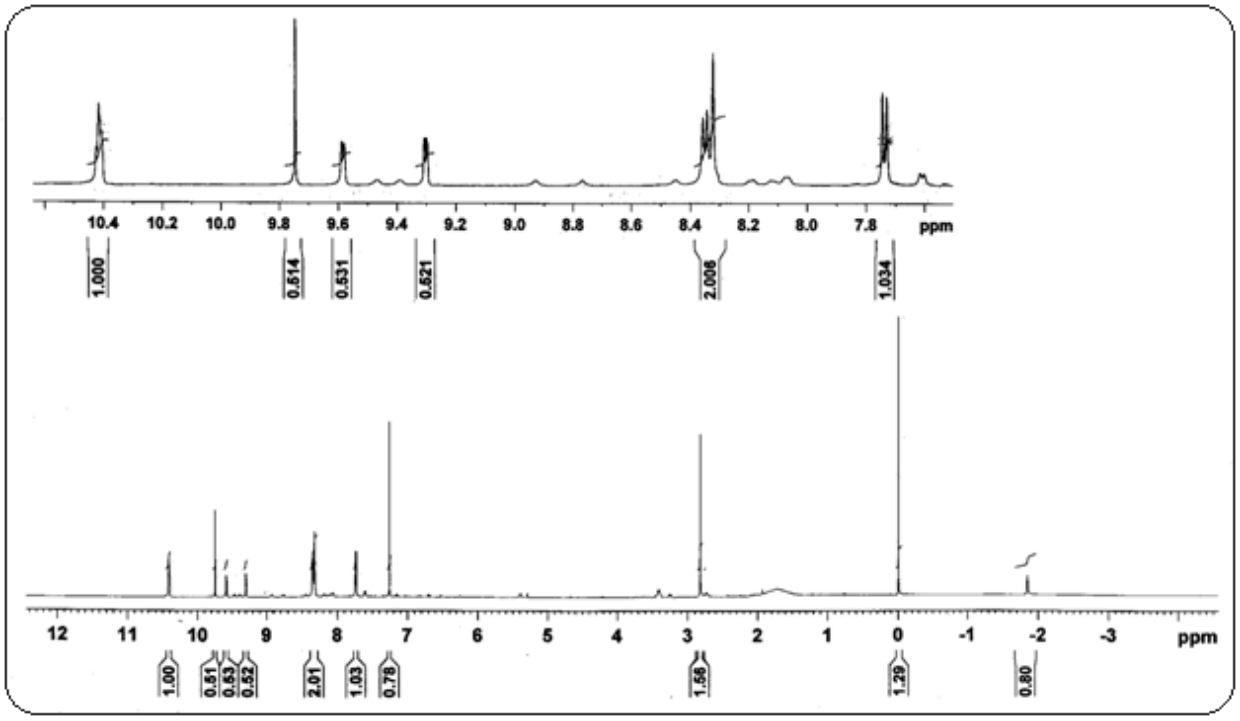


Figure S13. ^{1}H NMR spectrum of compound **4** recorded in $CDCl_3$**.** The inset shows the expansion.

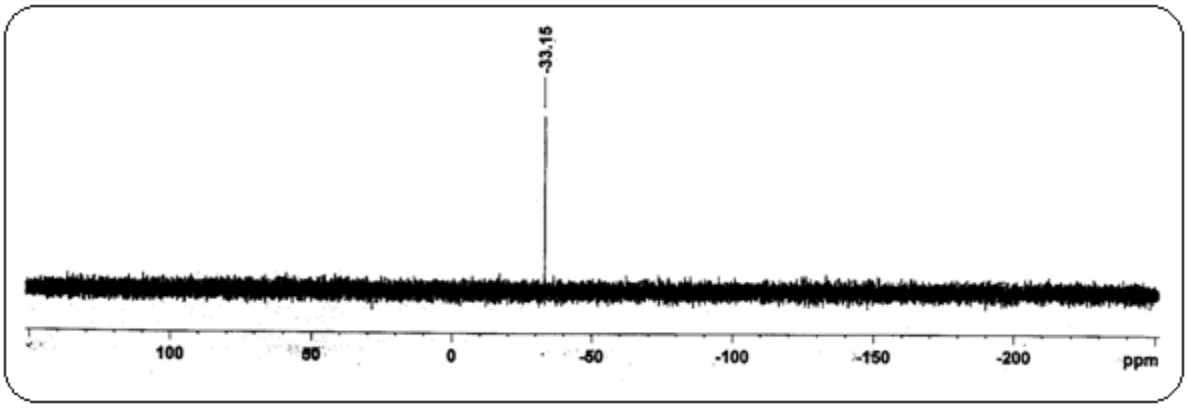


Figure S13. ^{31}P NMR spectrum of compound **4** recorded in $CDCl_3$.

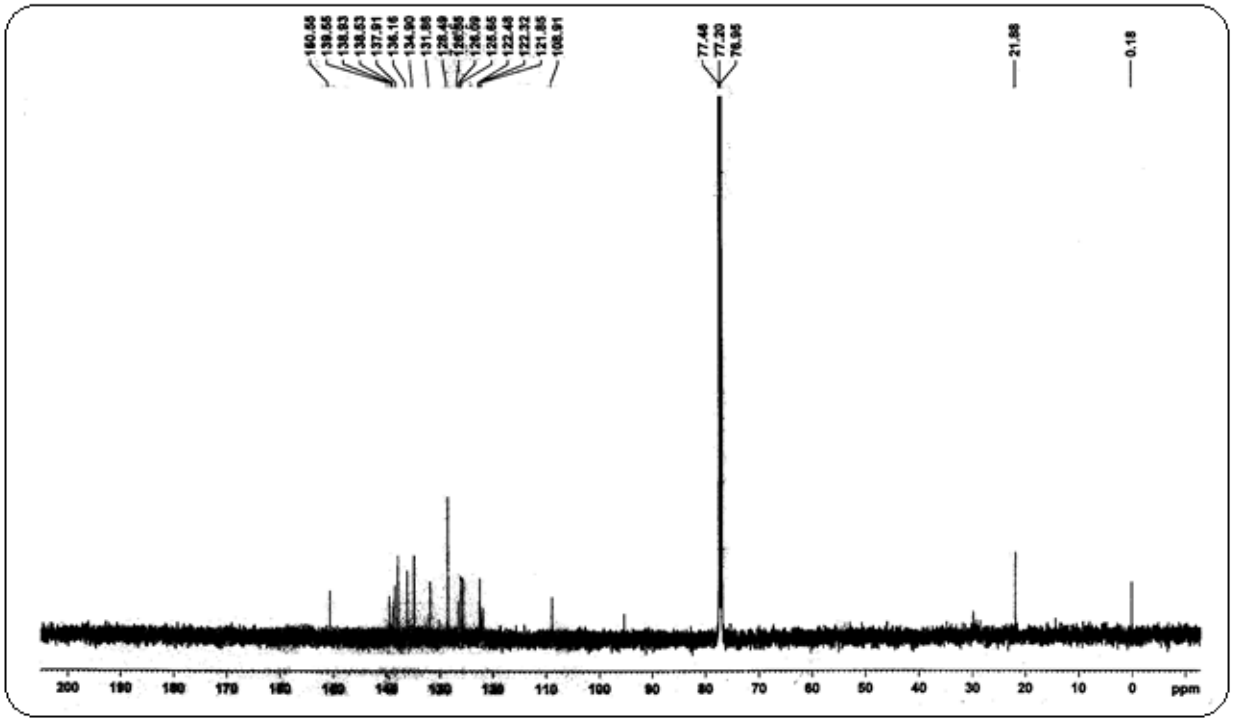
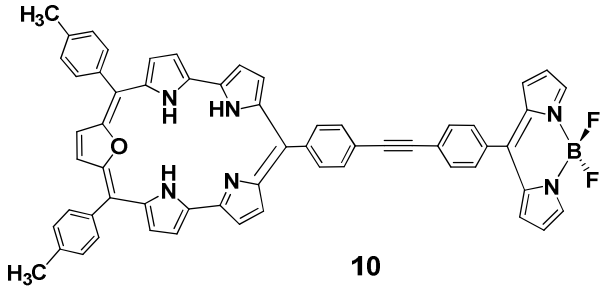


Figure S14. ^{13}C NMR spectrum of compound of **4** recorded in $CDCl_3$.



10

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Comment	C60H41BF2N6O		

Acquisition Parameter

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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Source

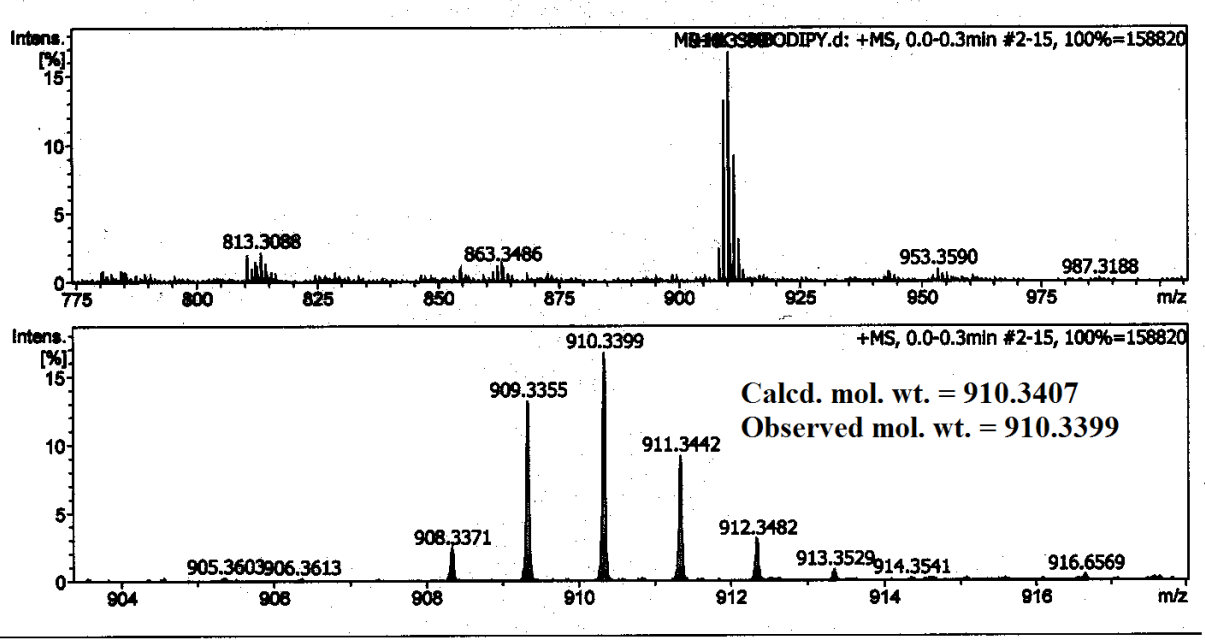

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Figure S15. HR-MS spectrum of compound **10**.

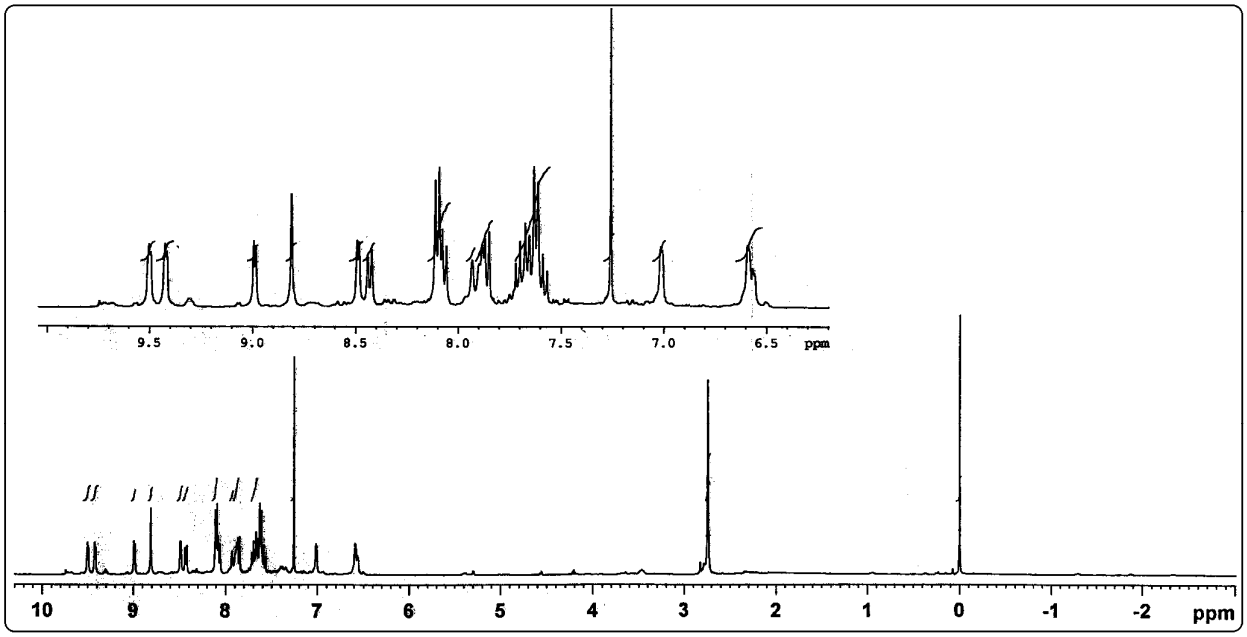
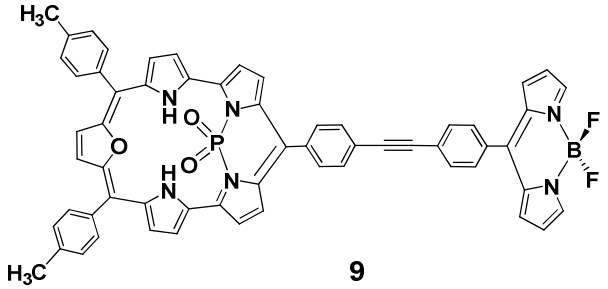


Figure S16. ^{1}H NMR spectrum of compound **10** recorded in $CDCl_3$. The inset shows the expansion.



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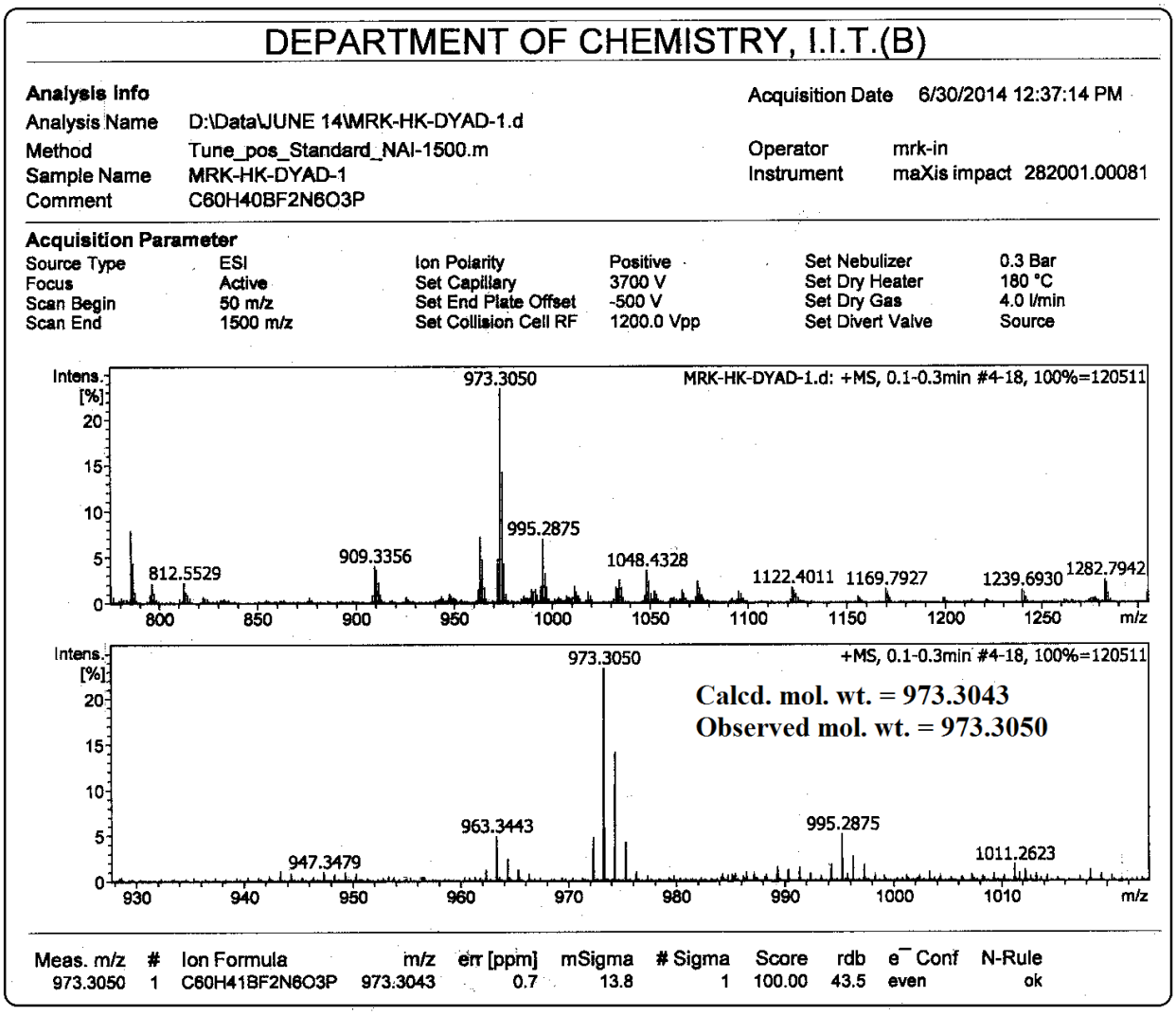

Figure S17. HR-MS spectrum of compound **9**.

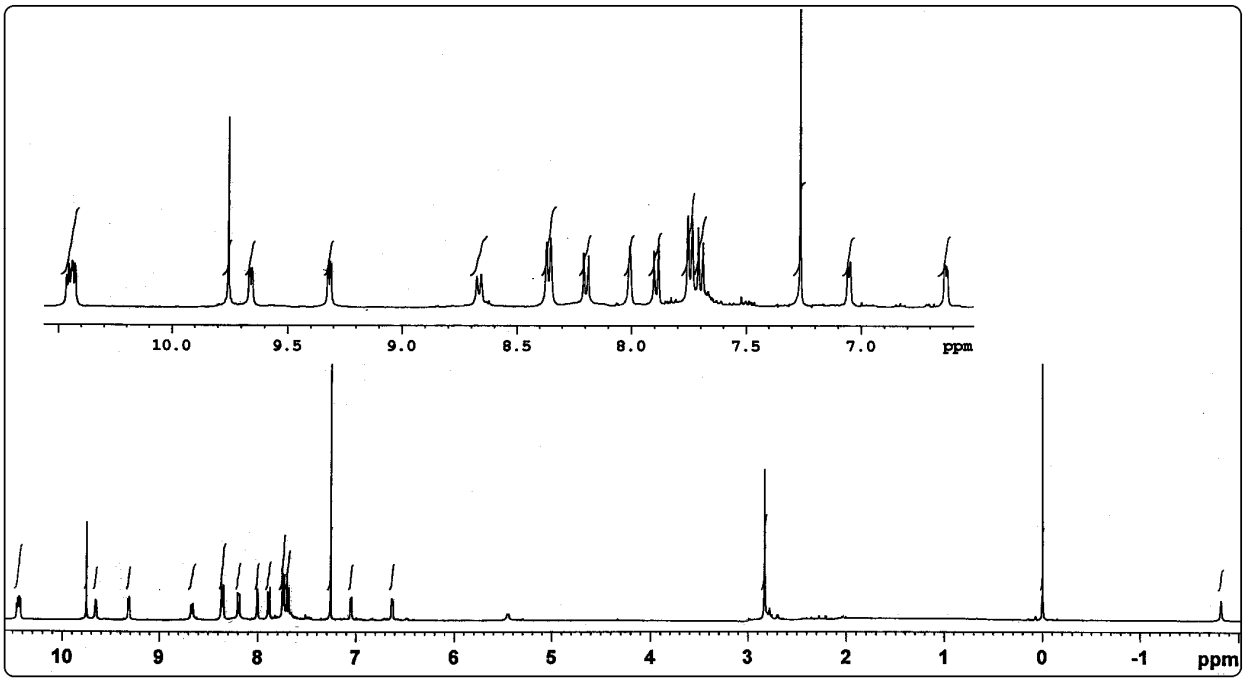

Figure S18. ^{1}H NMR spectrum of compound **9** recorded in $CDCl_3$. The inset shows the expansion.

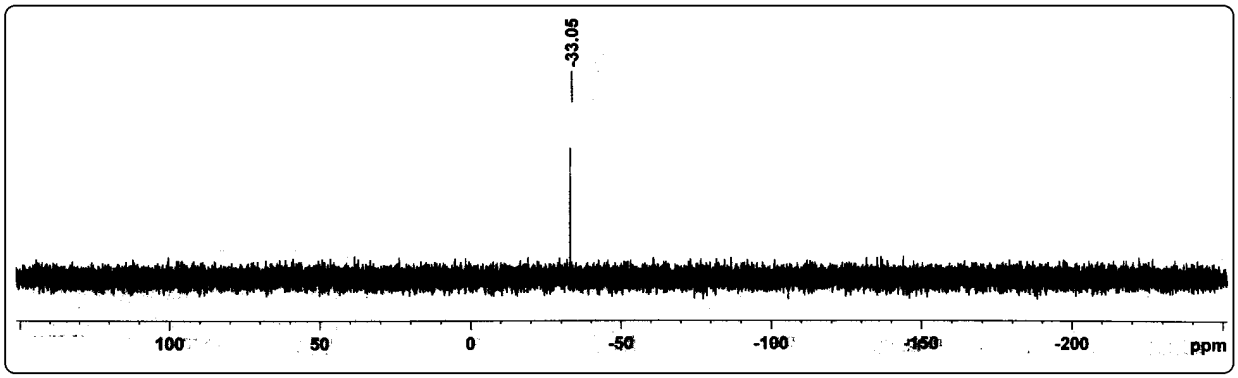

Figure S18. ^{31}P NMR spectrum of compound **9** recorded in $CDCl_3$.

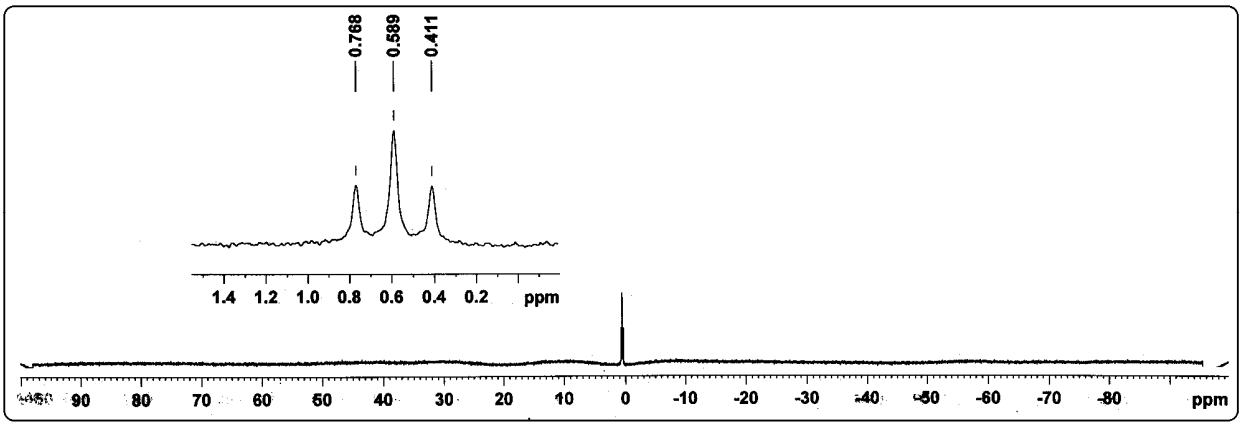

Figure S19. ^{11}B NMR spectrum of compound **9** recorded in $CDCl_3$**.** The inset shows the expansion.

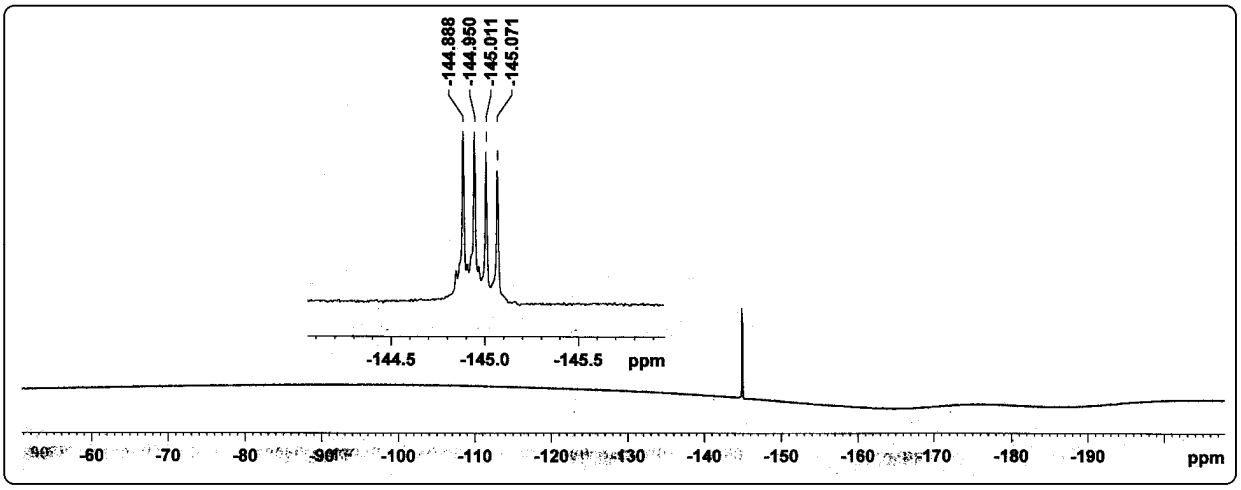

Figure S19. ^{19}F NMR spectrum of compound **9** recorded in $CDCl_3$. The inset shows the expansion.

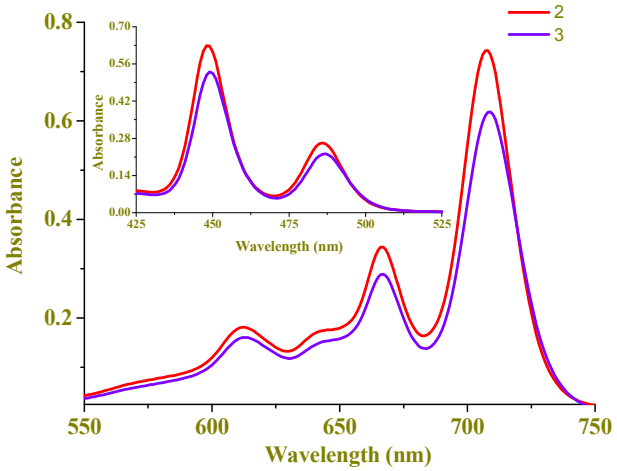

Figure S20. Q-bands absorption spectra of compounds of **2** and **3** recorded in $CHCl_3$. The inset shows the corresponding Soret bands. The concentrations were used 10^{-5} M and 10^{-6} M for Q and Soret bands respectively.

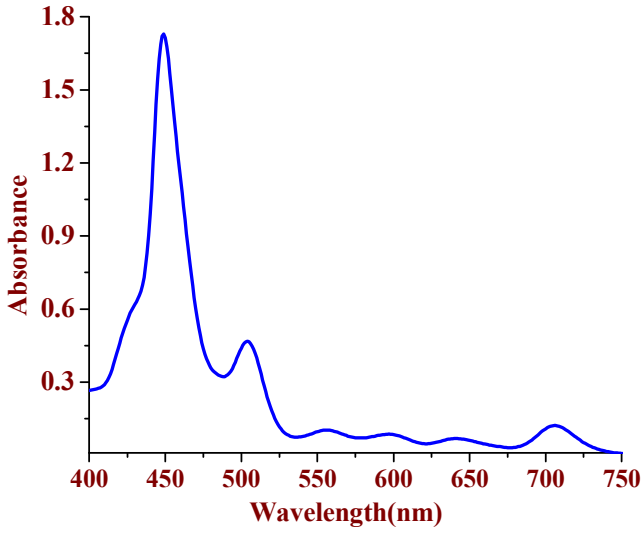

Figure S20. Absorption spectrum of compound **10** recorded in $CHCl_3$.

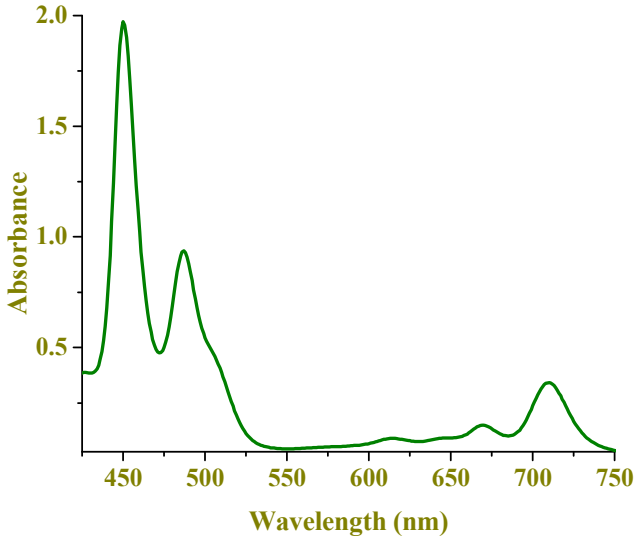

Figure S21. Absorption spectrum of compound **9** recorded in $CHCl_3$

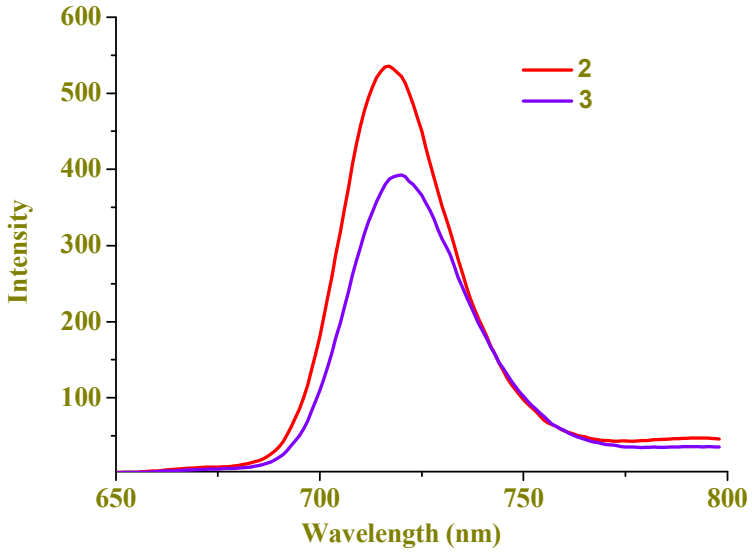

Figure S21. Emission spectra of compounds of **2** and **3** recorded in $CHCl_3$ by exciting at their corresponding absorption maxima.

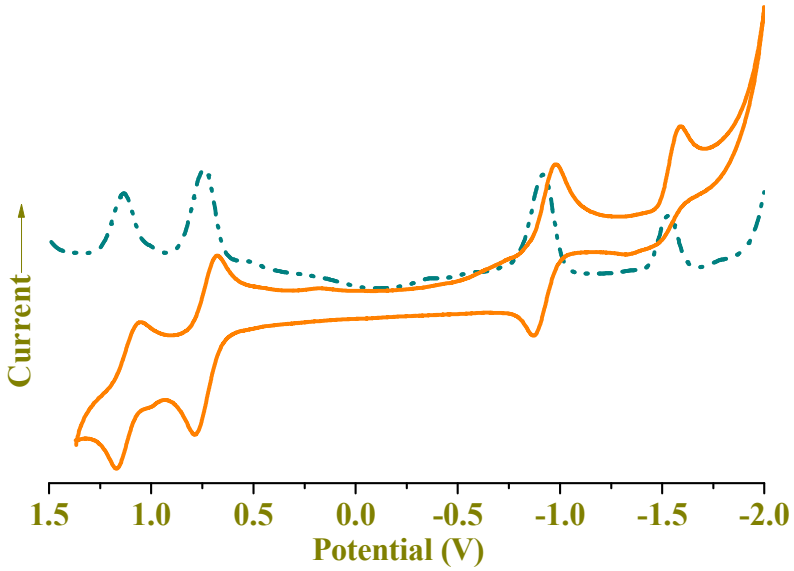

Figure S22. Cyclic voltammogram of compound of **2** recorded in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte recorded using scan rate of 50 mV/sec. The dotted line represents the DPV curve.

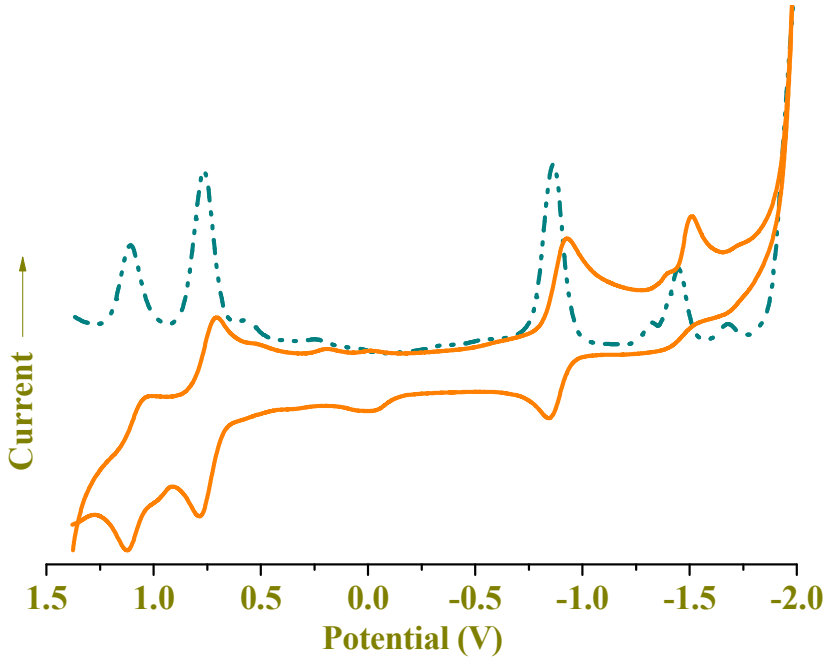

Figure S23. Cyclic voltammogram of compound of **3** recorded in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte recorded using scan rate of 50 mV/sec. The dotted line represents the DPV curve.

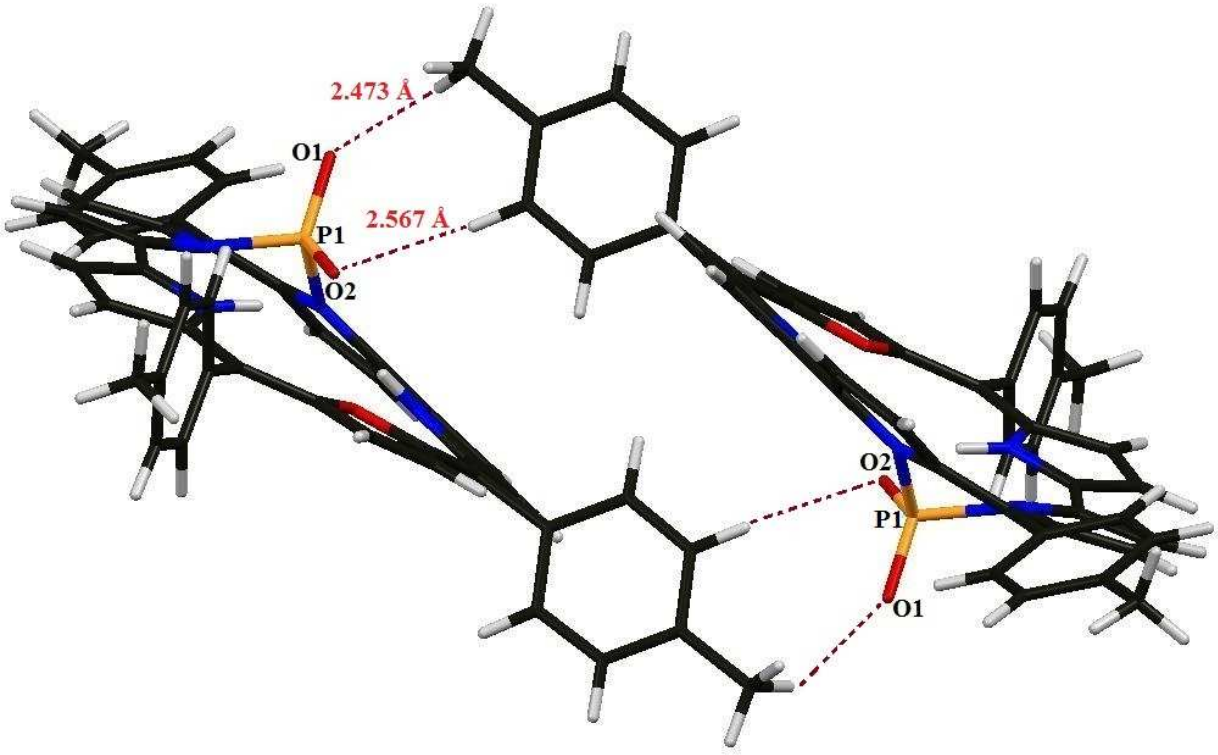

Figure S24. Solid state crystal packing structure of compound **1**. The dotted lines show the H-bonding interaction.

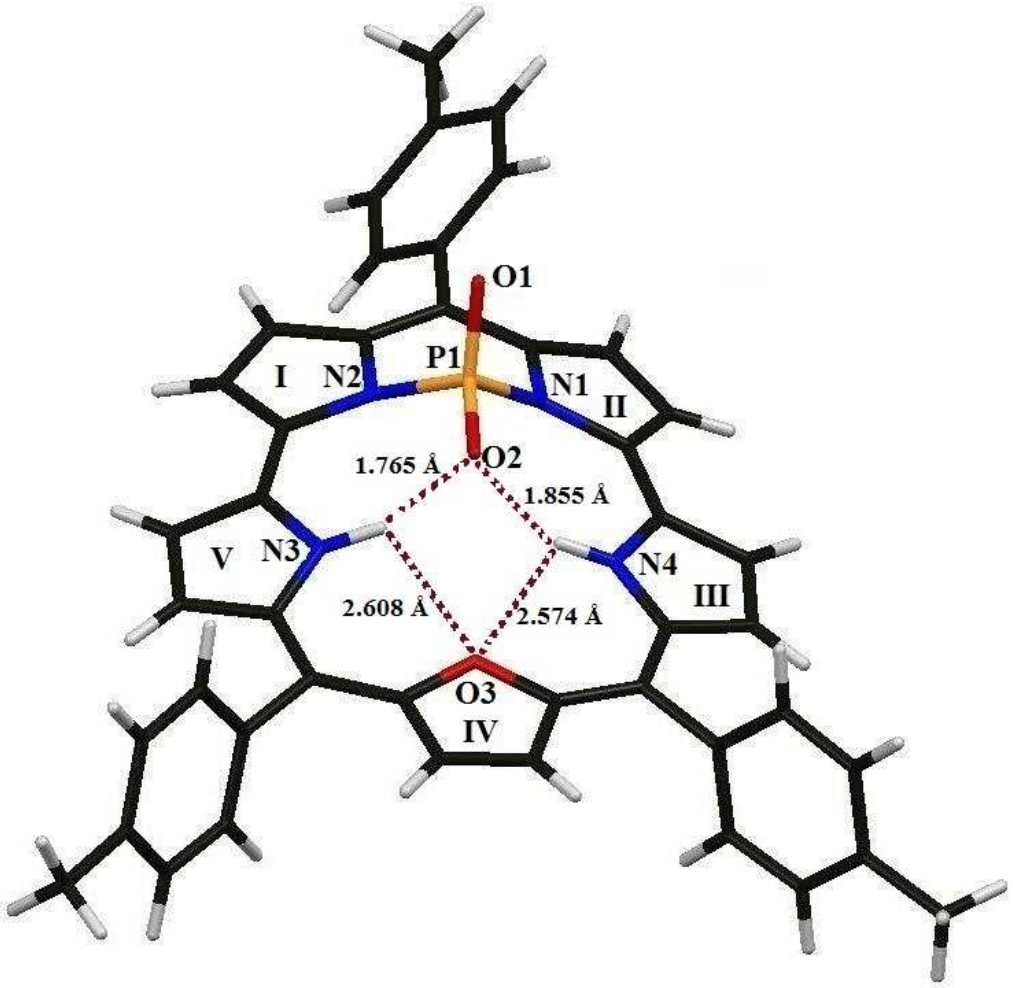

Figure S25. Solid state crystal structure of compound **1**. The dotted lines represent the intramolecular H-bonding interaction.