

Supplementary Information

## **Reactivity of molybdenum-nitride complex bearing pyridine-based PNP-type pincer ligand toward various carbon-centered electrophiles**

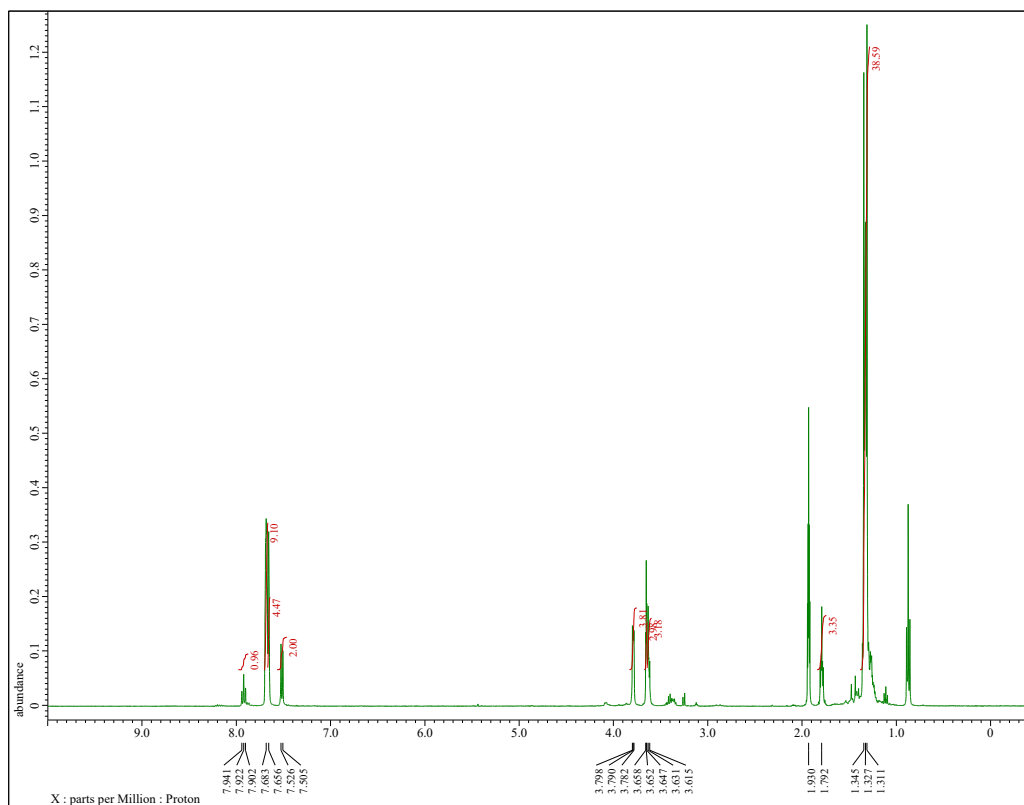
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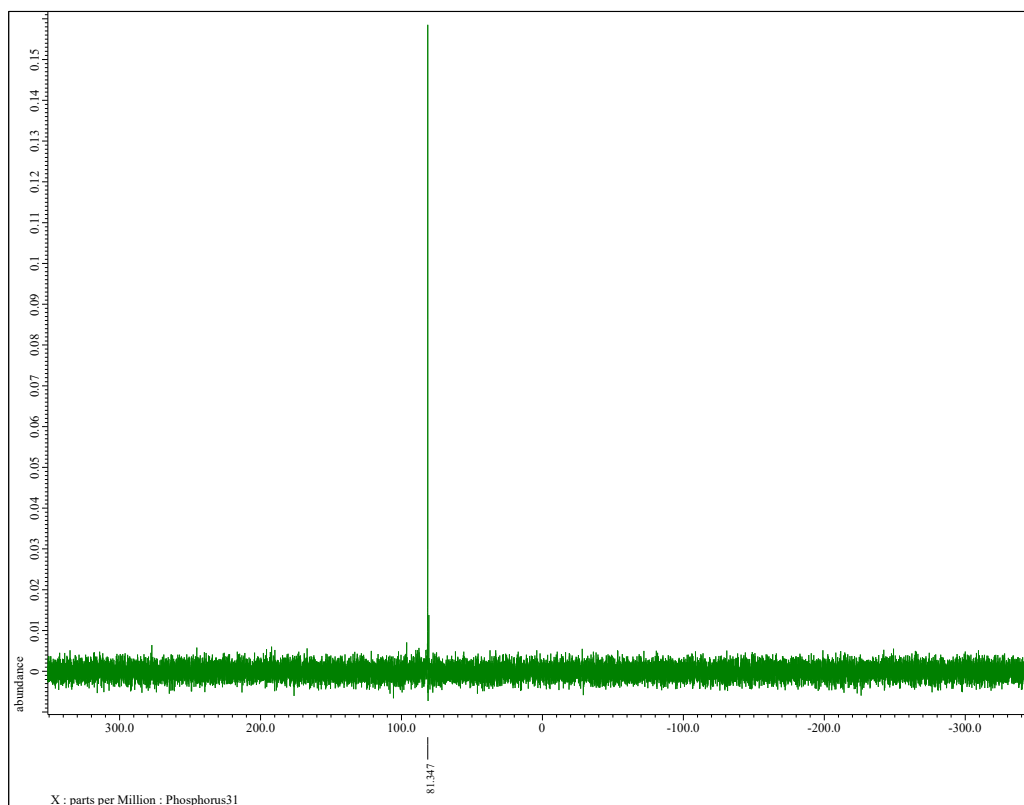
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## NMR spectra



**Fig. S1**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$



**Fig. S2**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$

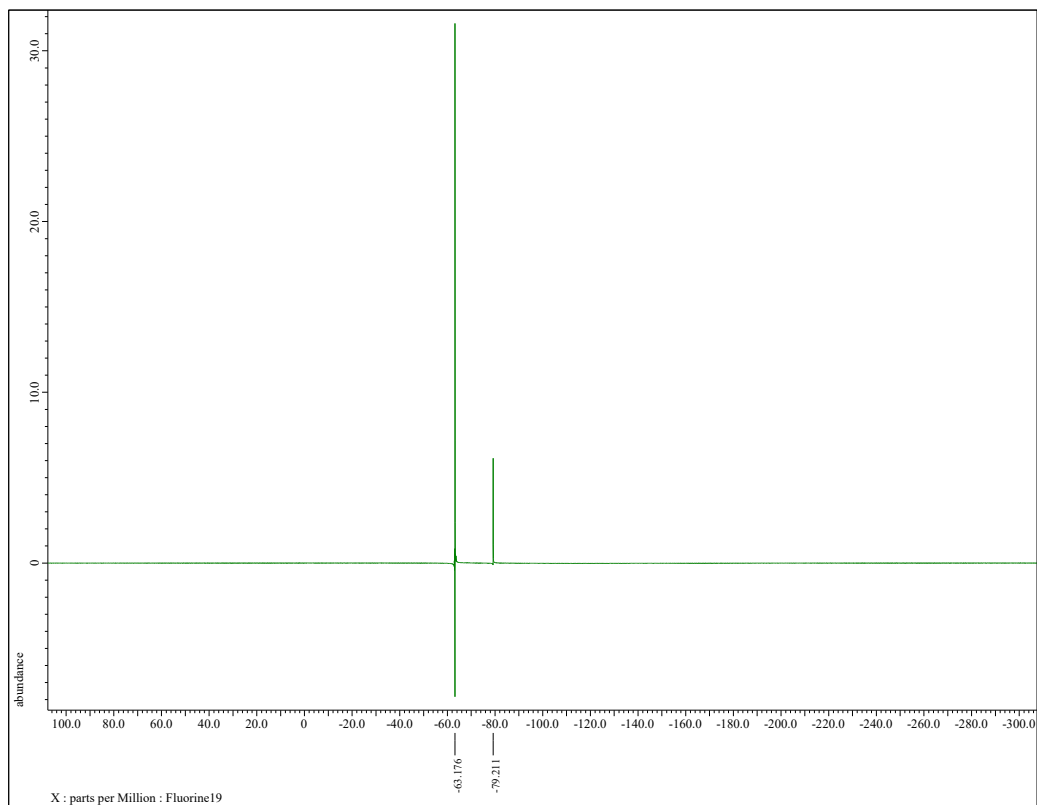


Fig. S3  $^{19}\text{F}$  NMR spectrum of **2** in  $\text{CD}_3\text{CN}$

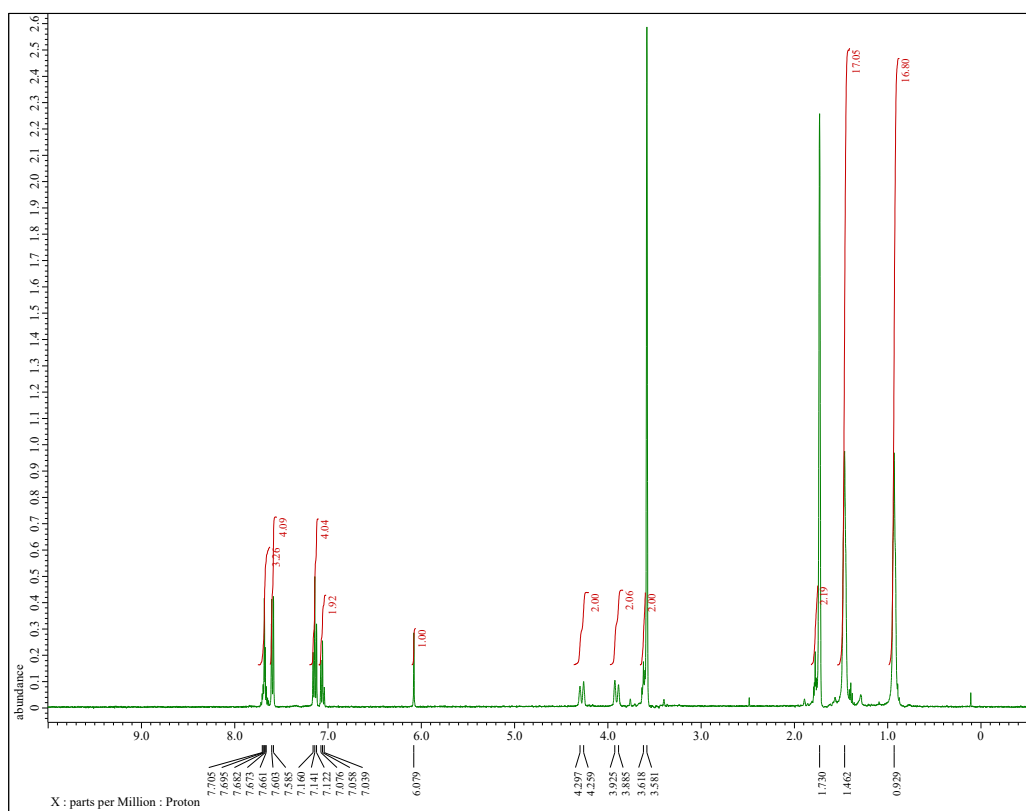


Fig. S4  $^1\text{H}$  NMR spectrum of **3** in  $\text{THF-}d_8$

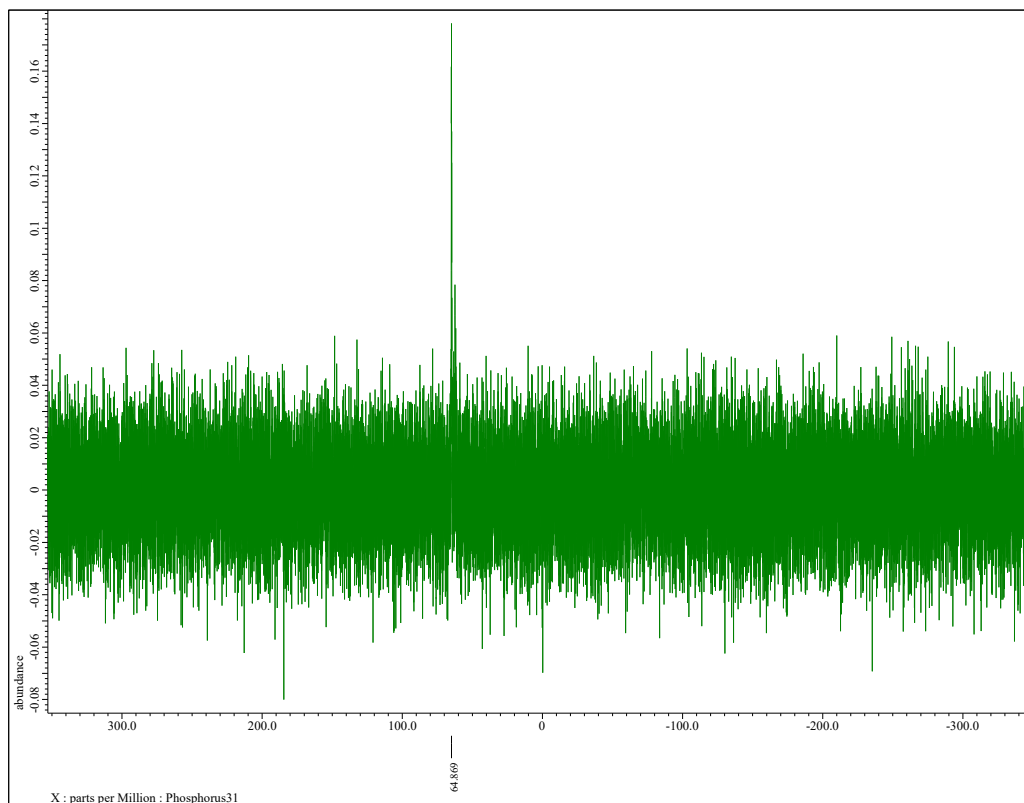


Fig. S5  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{THF-}d_8$

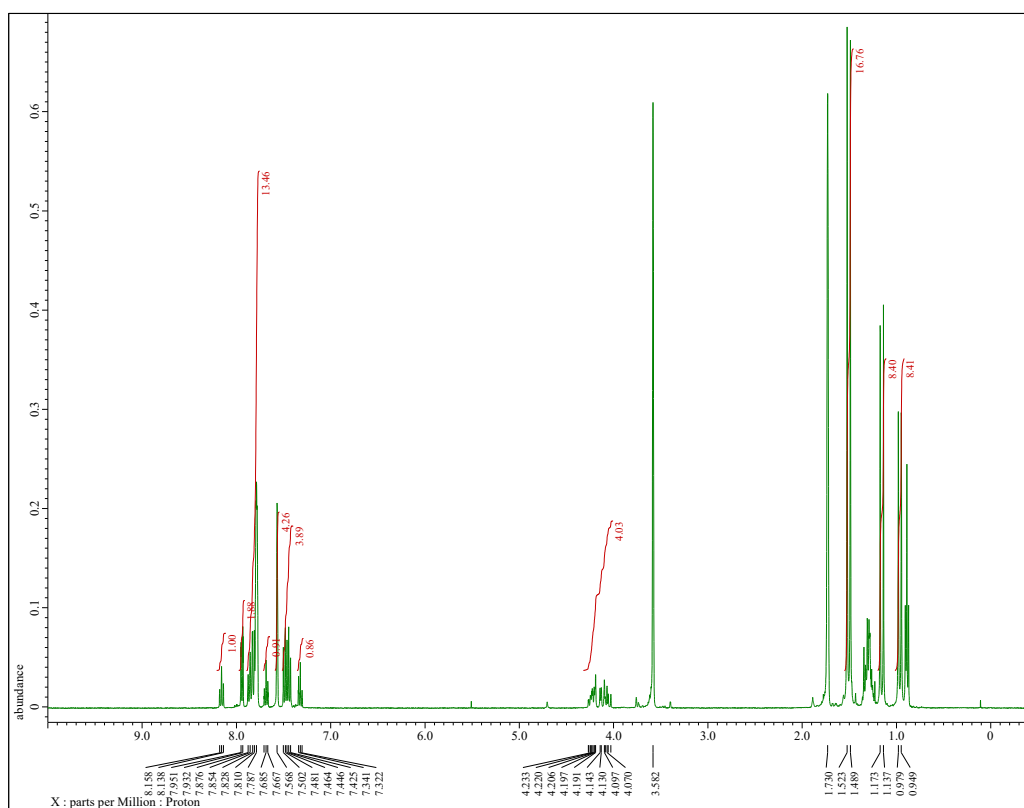


Fig. S6  $^1\text{H}$  NMR spectrum of **4** in  $\text{THF-}d_8$

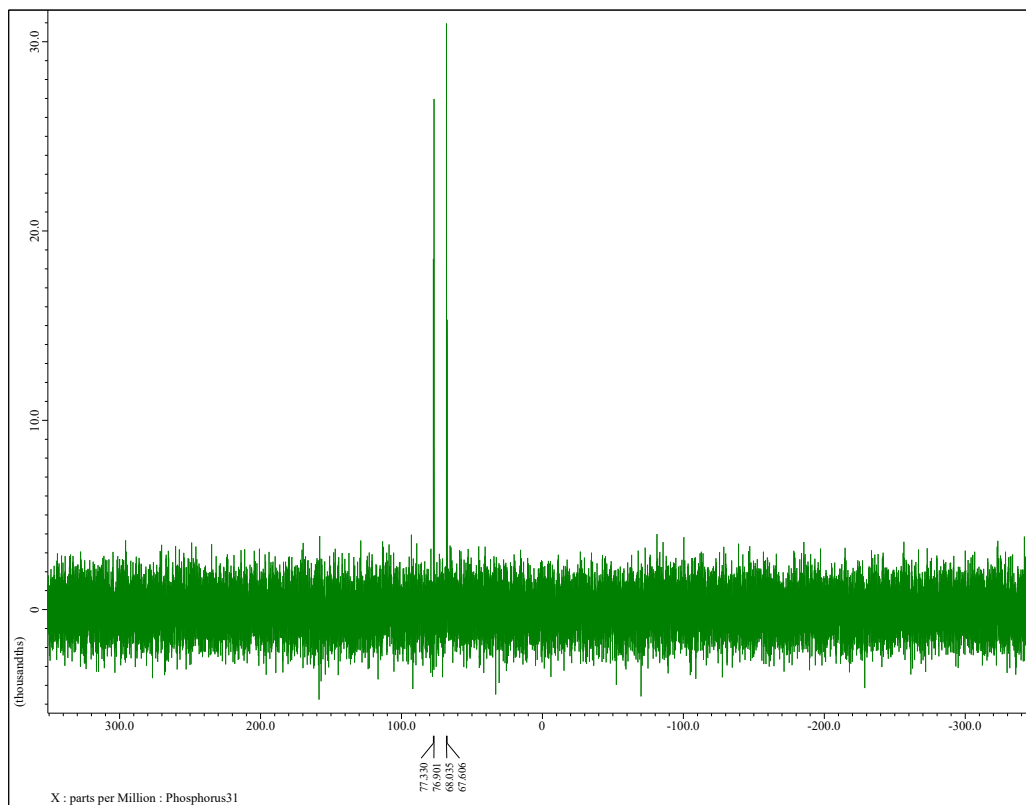


Fig. S7  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** in  $\text{THF-}d_8$

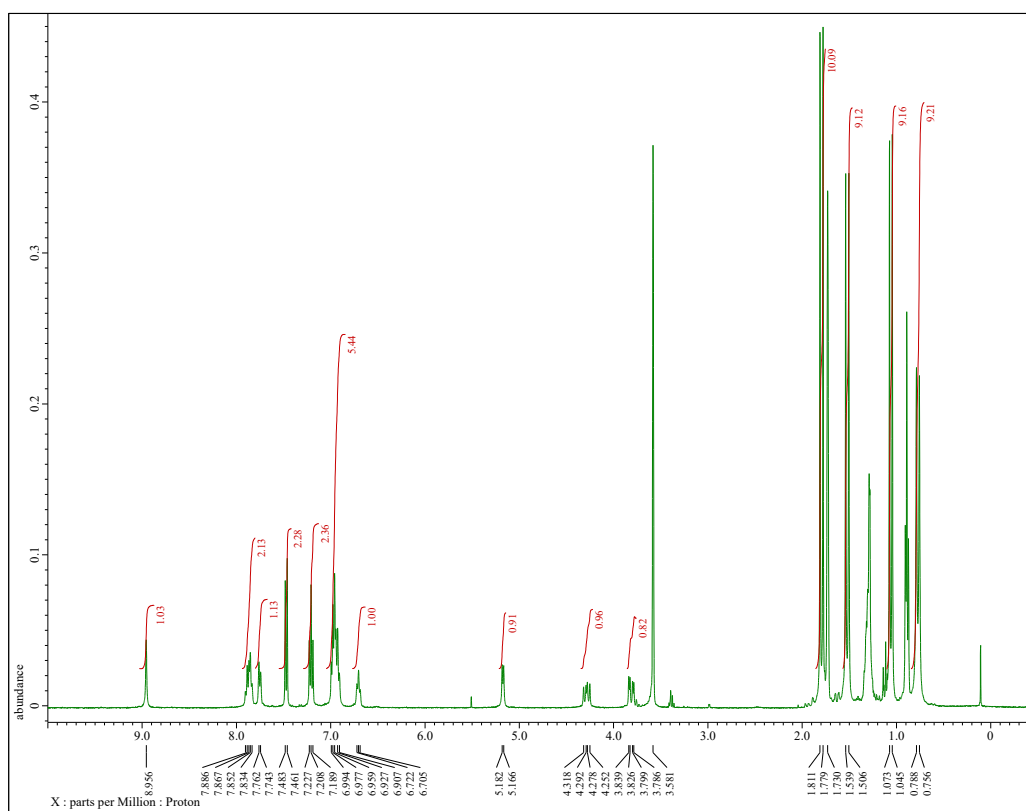


Fig. S8  $^1\text{H}$  NMR spectrum of **5** in  $\text{THF-}d_8$

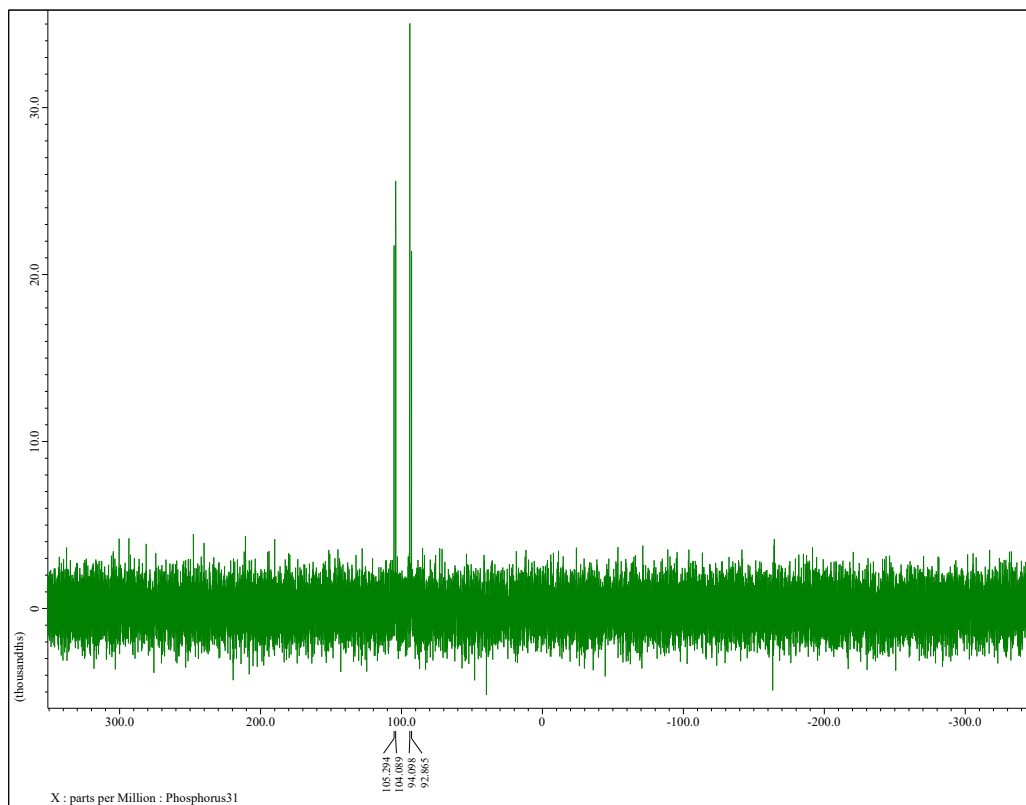


Fig. S9  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **5** in  $\text{THF-d}_8$

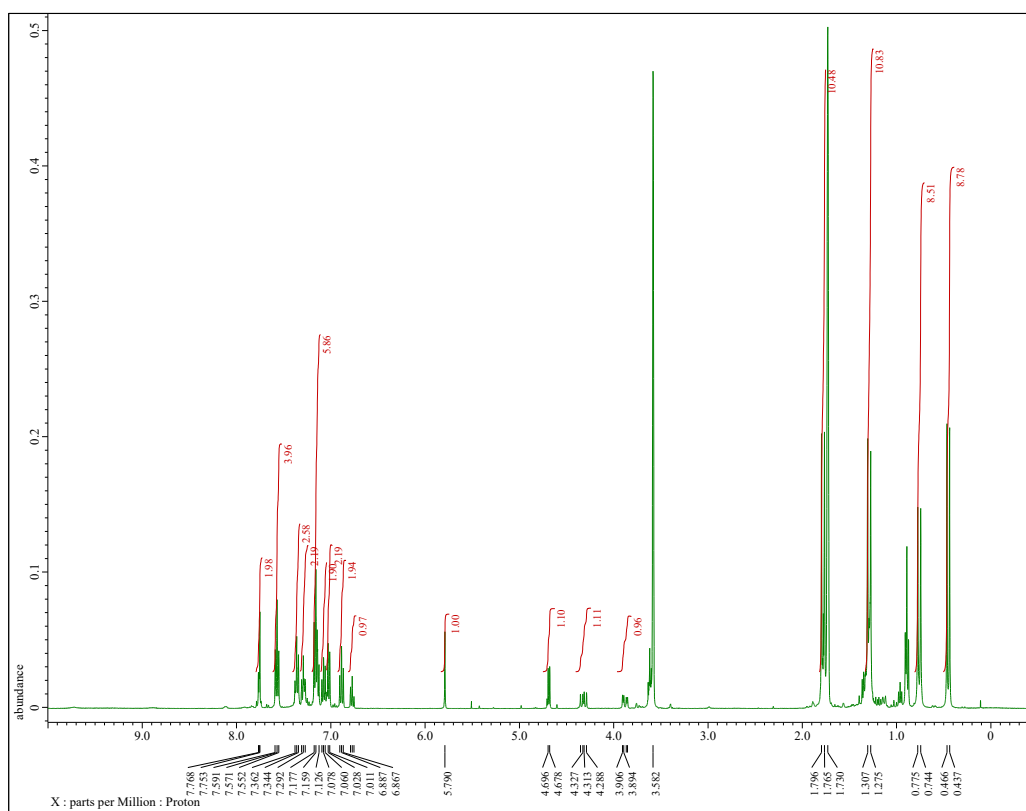


Fig. S10  $^1\text{H}$  NMR spectrum of **6** in  $\text{THF-d}_8$

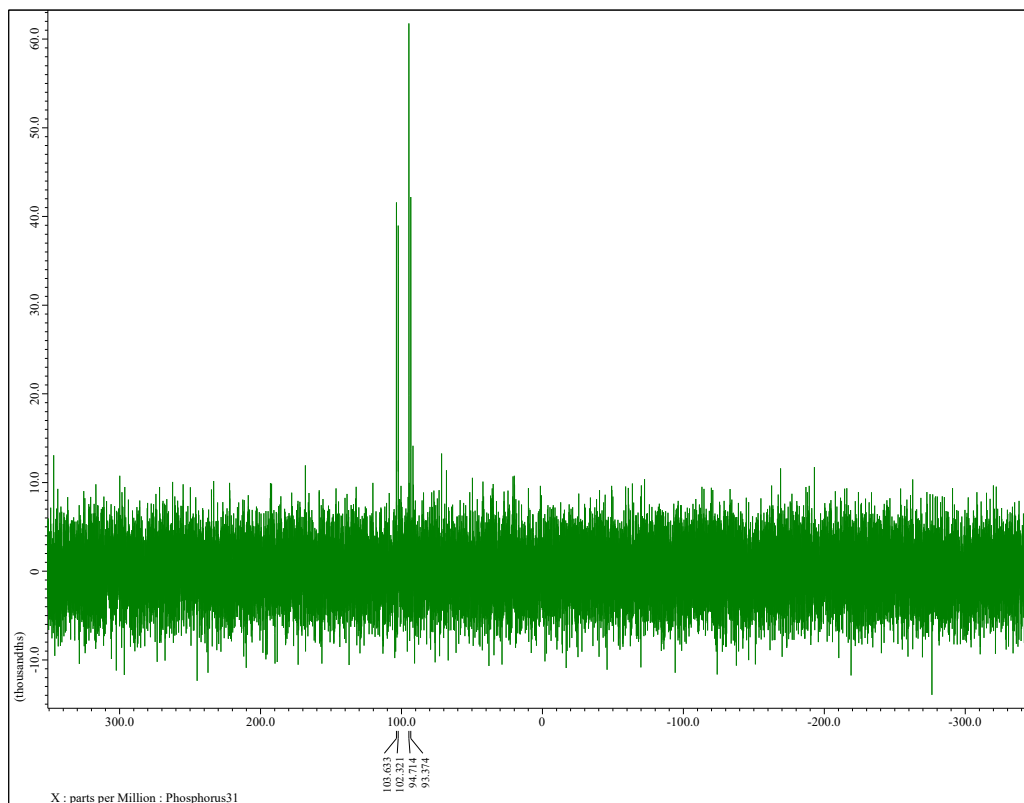


Fig. S11  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{THF-}d_8$

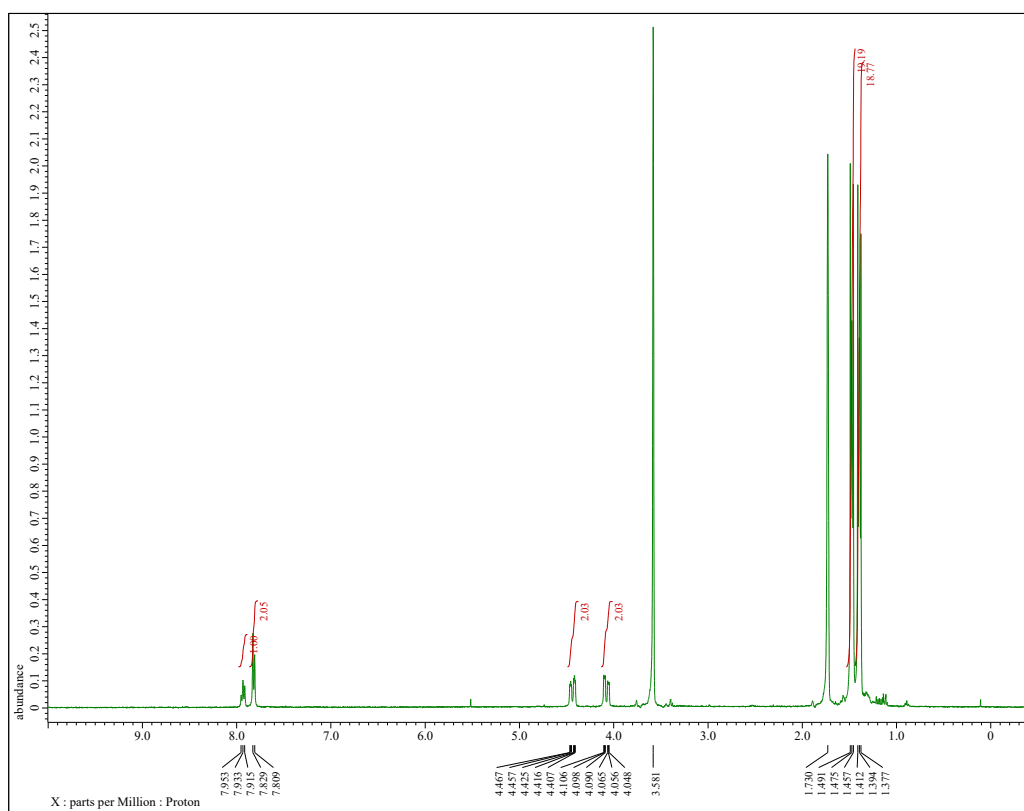


Fig. S12  $^1\text{H}$  NMR spectrum of **7** in  $\text{THF-}d_8$

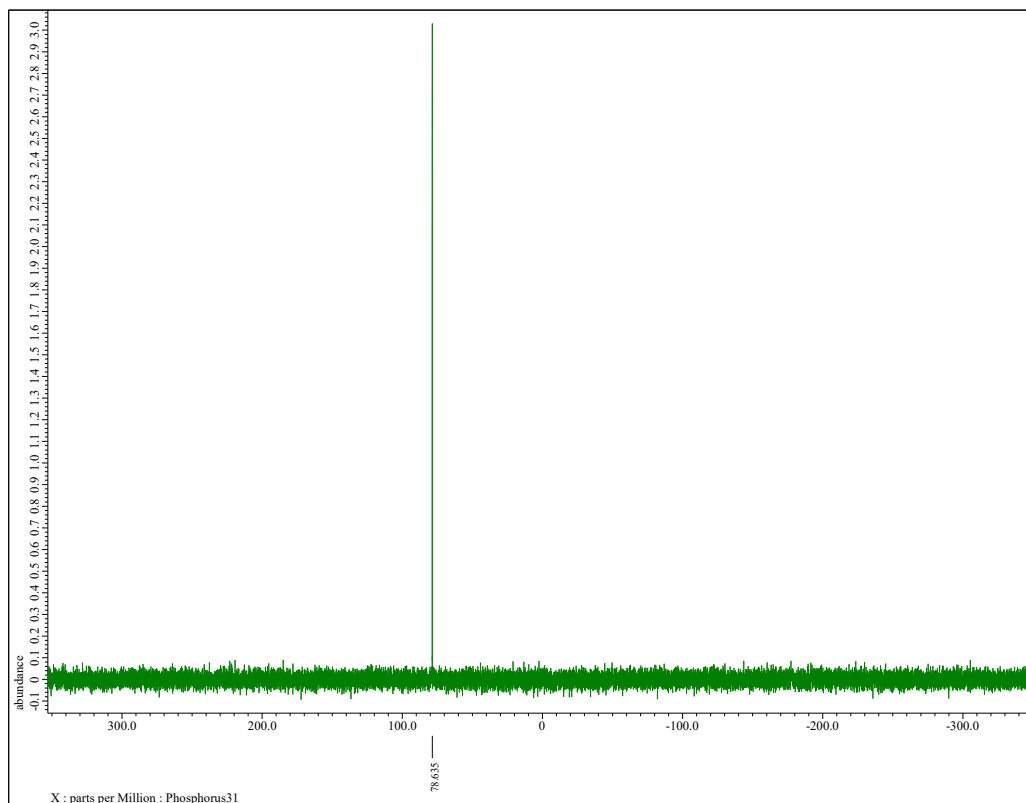


Fig. S13  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** in  $\text{THF-}d_8$

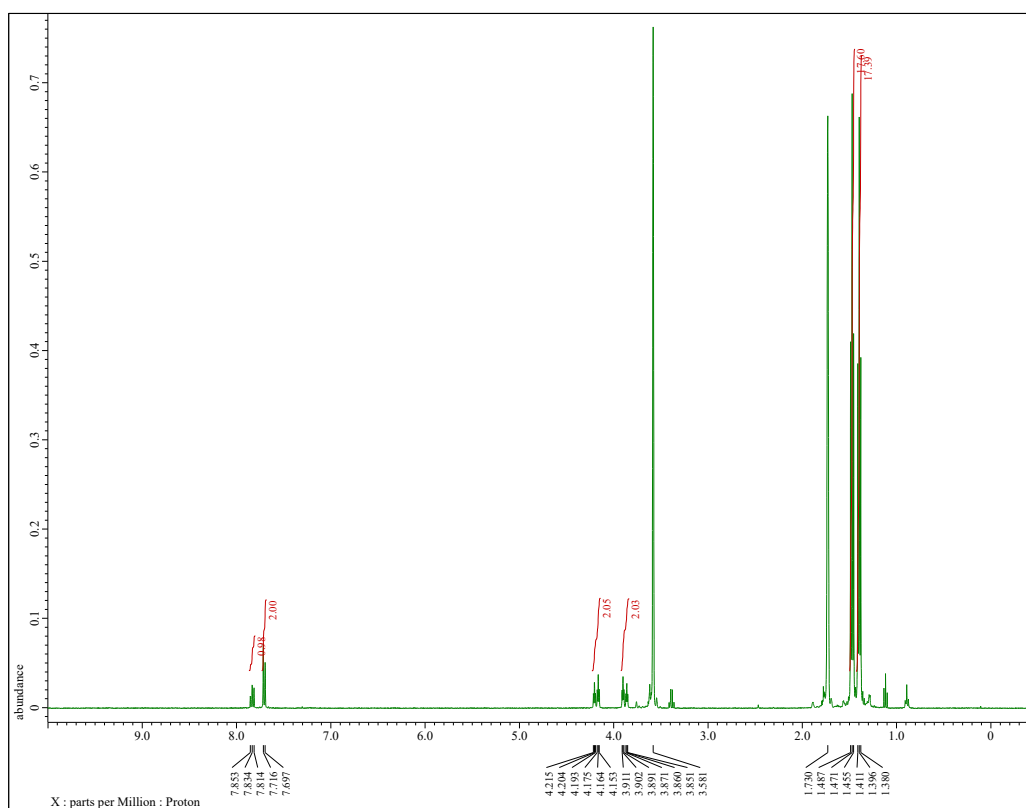


Fig. S14  $^1\text{H}$  NMR spectrum of **8** in  $\text{THF-}d_8$



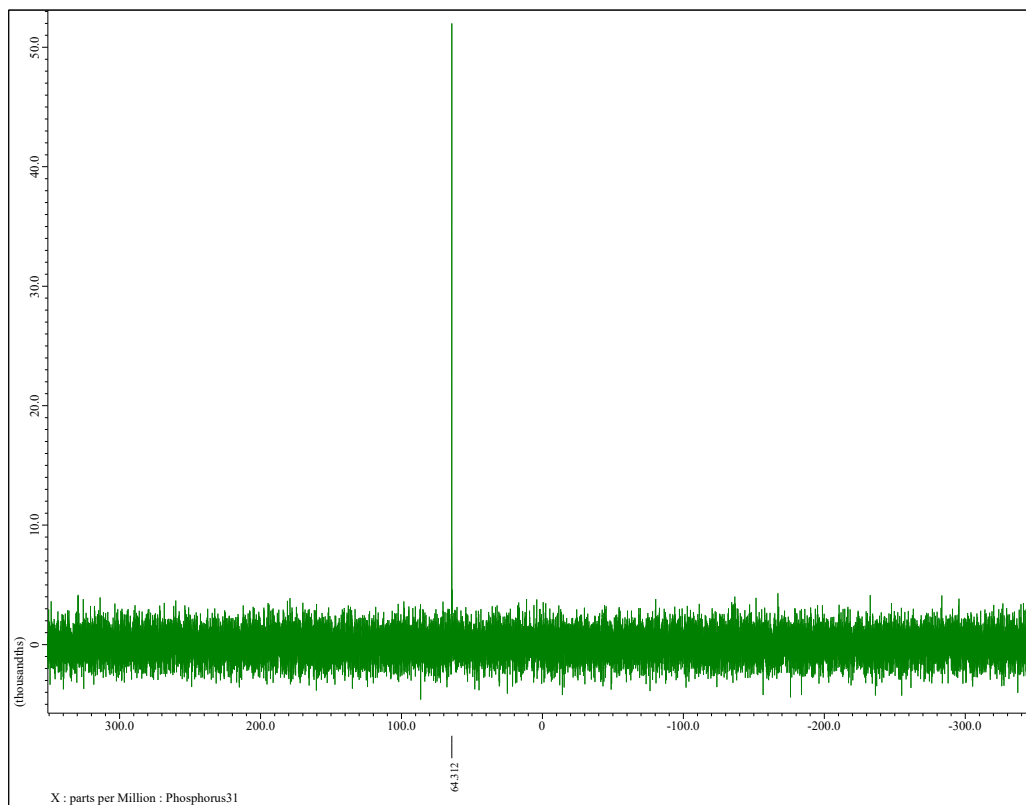


Fig. S15  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8** in  $\text{THF-}d_8$

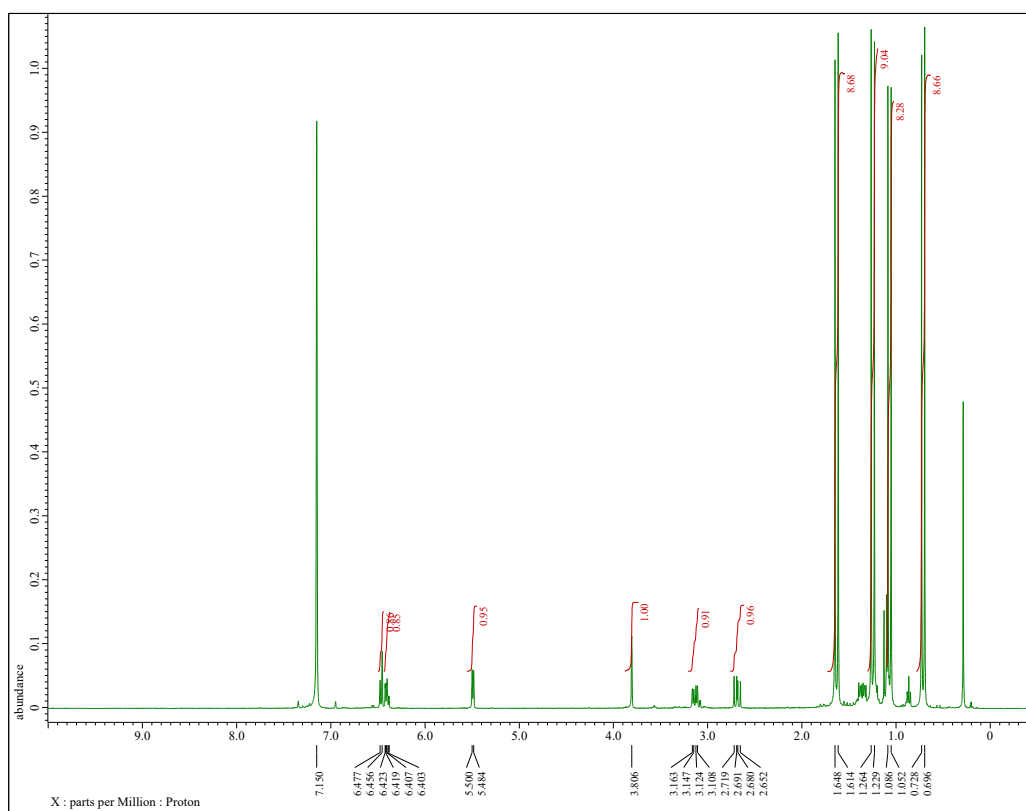
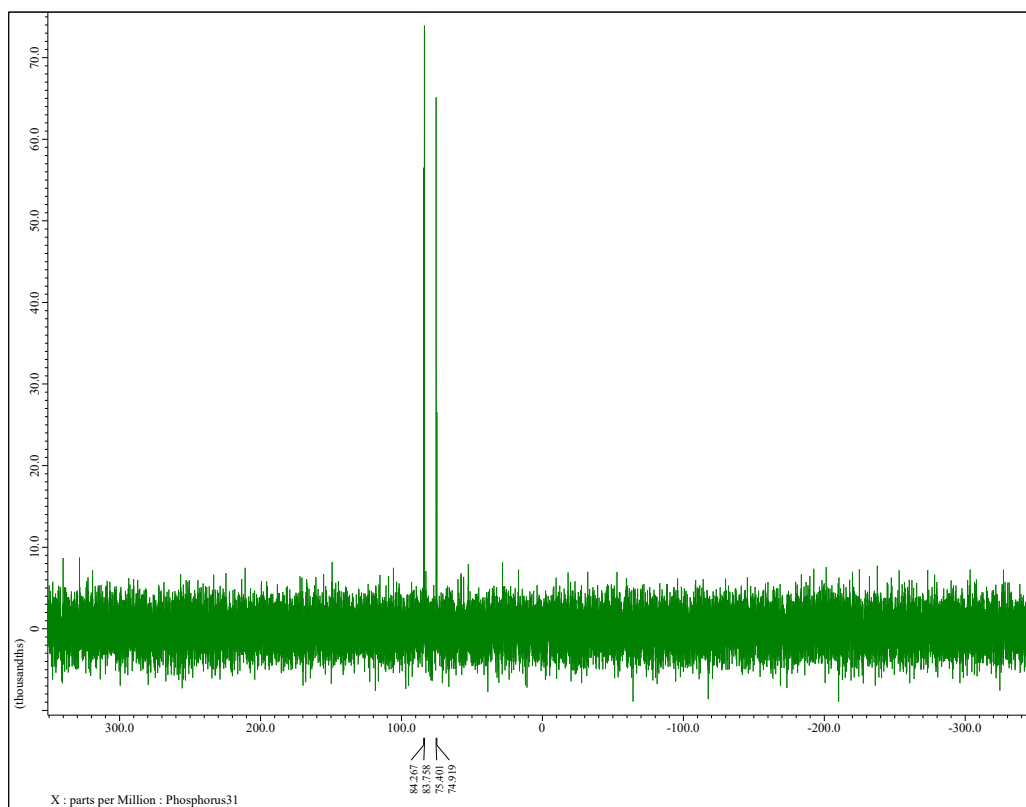
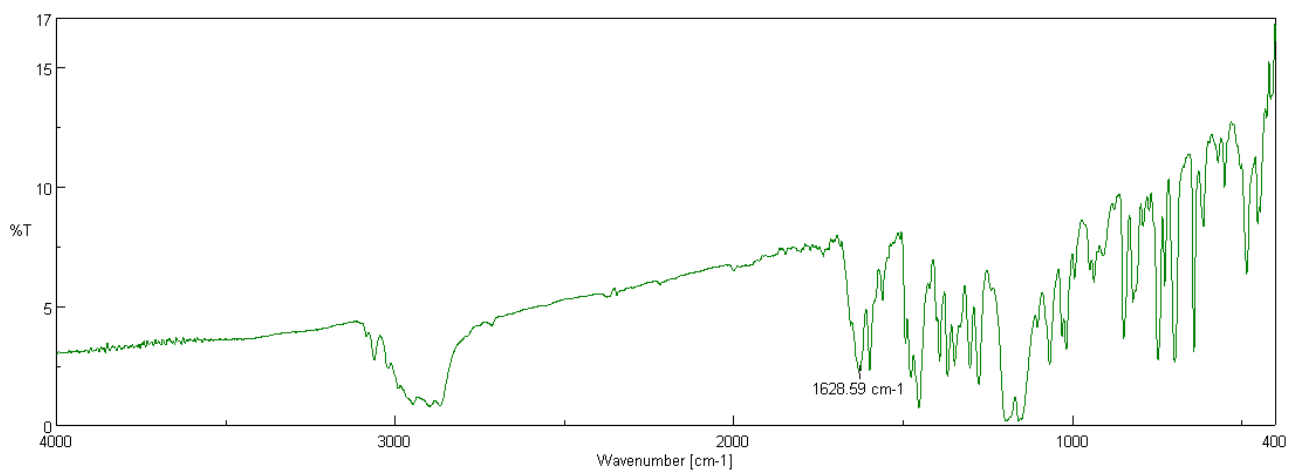


Fig. S16  $^1\text{H}$  NMR spectrum of **9** in  $\text{C}_6\text{D}_6$

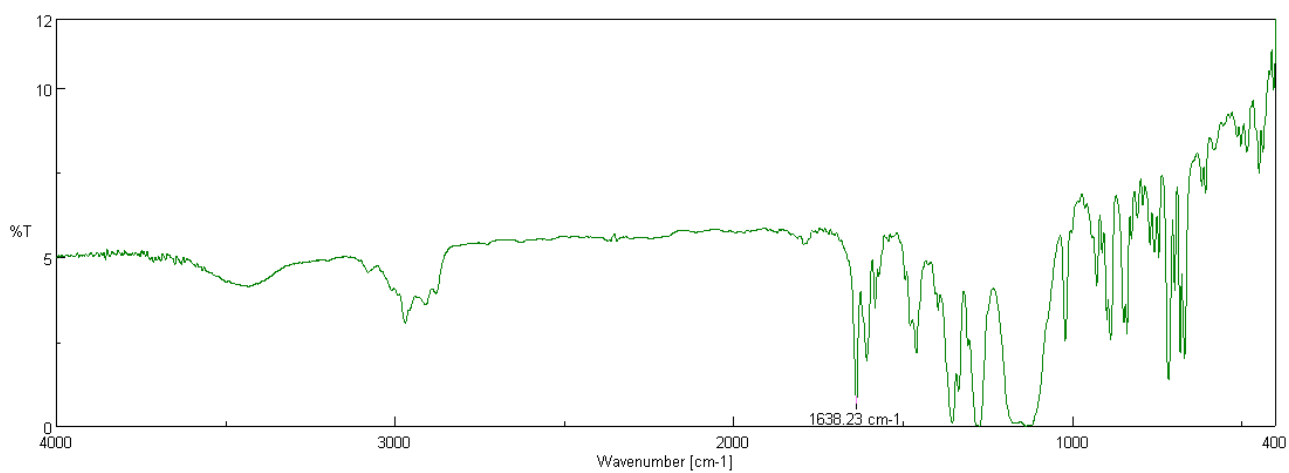


**Fig. S17**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **9** in  $\text{C}_6\text{D}_6$

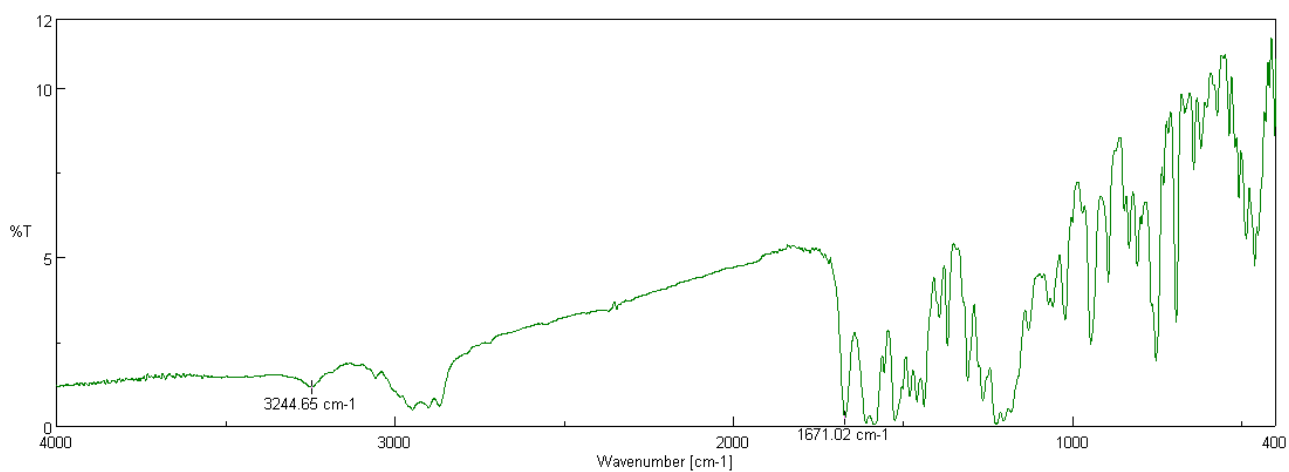
## IR spectra



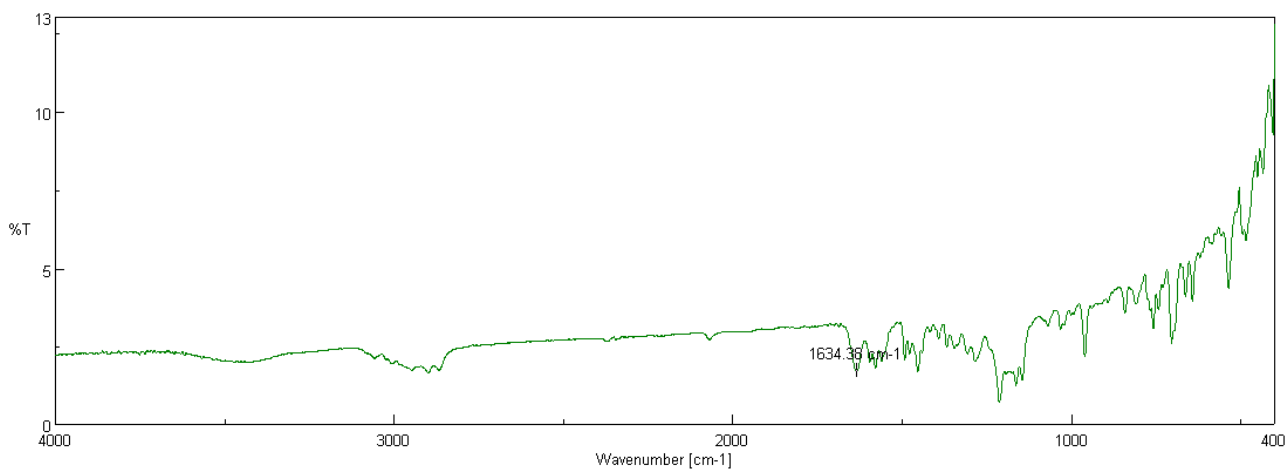
**Fig. S18** IR spectrum of **3** in KBr



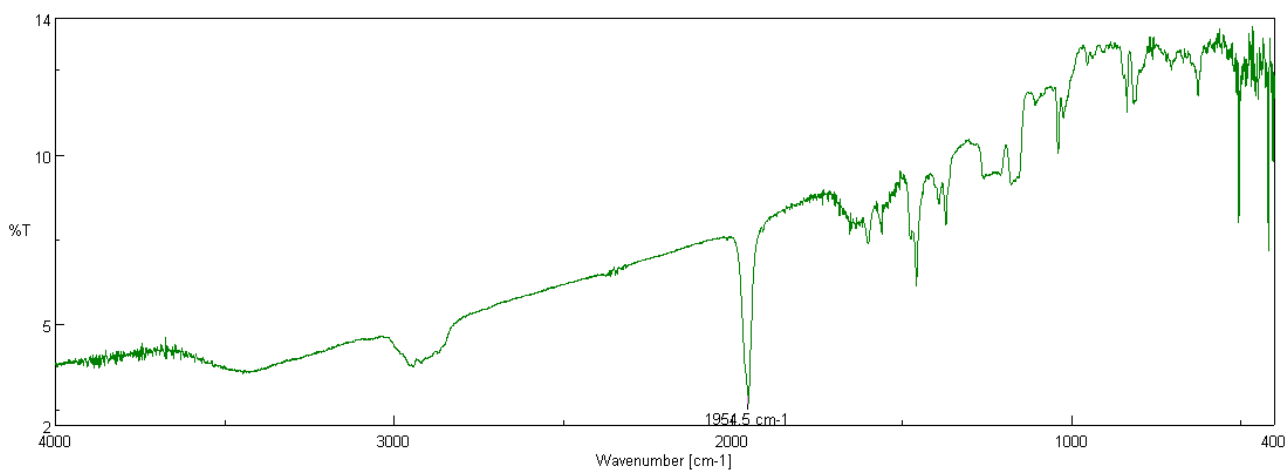
**Fig. S19** IR spectrum of **4** in KBr



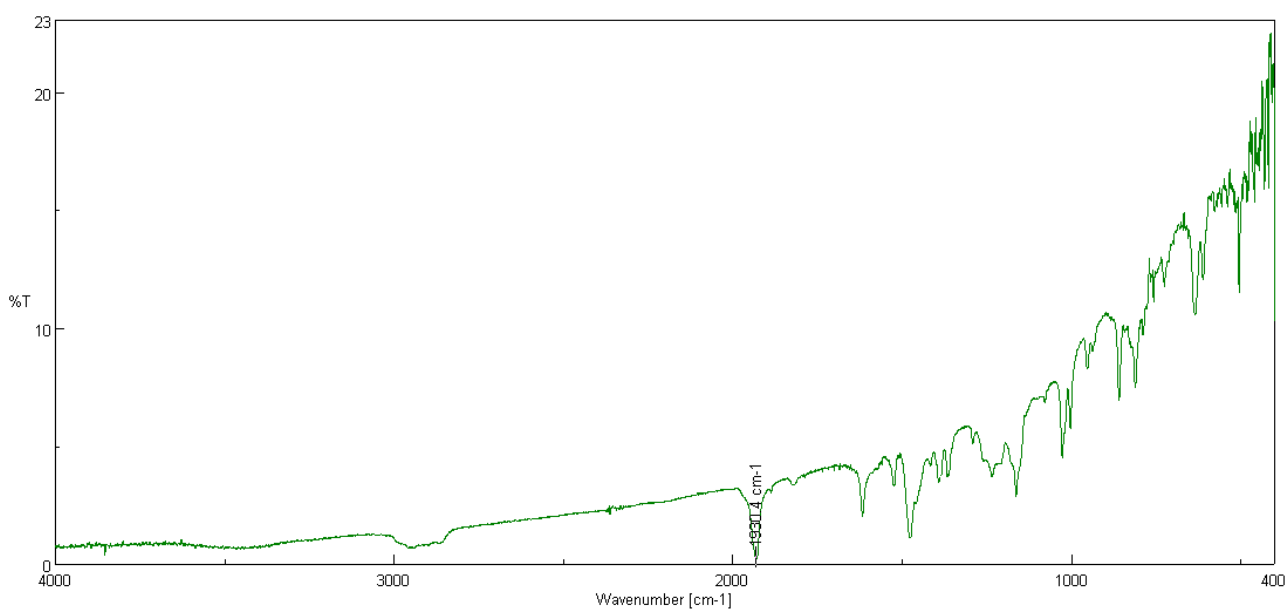
**Fig. S20** IR spectrum of **5** in KBr



**Fig. S21** IR spectrum of **6** in KBr



**Fig. S22** IR spectrum of **7** in KBr



**Fig. S23** IR spectrum of **9** in KBr

### X-ray crystallography.

Diffraction data for **2**, **3**, **4**, **5**·THF **6**, **7**, **8**, and **9** were collected for the  $2\theta$  range of  $4^\circ$  to  $63^\circ$  at  $-180^\circ\text{C}$  on a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and VariMax optics using multi-layer mirror monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (CrysAlisPro),<sup>S1</sup> whereas structure solutions and refinements were carried out by using the *CrystalStructure* crystallographic software package.<sup>S2</sup> Positions of non-hydrogen atoms were determined by direct methods (SHELXS Version 2013/1 for **2**, **3**, **4**, **5**·THF, **6**, **7**, and **8**; SHELXT Version 2014/5 for **9**)<sup>S3,S4</sup> and subsequent Fourier syntheses (SHELXL Version 2016/6),<sup>S5</sup> and were refined on  $F_o^2$  using all unique reflections by full-matrix least-squares with anisotropic thermal parameters. All the hydrogen atoms except for the H(H3N) atom in **5**·THF were placed at the calculated positions with fixed isotropic parameters. The position of the H(H3N) atom in **5**·THF was determined on the peak in the difference Fourier maps and further refined isotropically. Anomalous dispersion effects were included in  $F_o$ ,<sup>S6</sup> and mass attenuation coefficients, values for  $\Delta f'$  and  $\Delta f''$ , and neutral atom scattering factors were taken from references.<sup>S7–S9</sup> Details of the crystal and data collection parameters are summarized in [Tables S1–S3](#), and ORTEP drawings of molecular structures are shown in [Fig. S24–S31](#).

For **2**, the trifluoromethyl group (F10, F11A, F11B, F12, C44) in  $\text{BAr}^{\text{F}_4}$  anion were disordered, thus these non-hydrogen atoms were solved isotropically. In addition, **2** was solved as a pair of two enantiomeric twins (BASF = 0.12493) with the Flack parameter fixed at 0.

For **4**, the trifluoromethyl groups (F15, F16, F17, F18, F23, F24, C60, C61) in  $\text{BAr}^{\text{F}_4}$  anion were disordered, thus these non-hydrogen atoms were solved isotropically.

The unit cells of **3** and **6** contain solvent accessible voids of 349 and  $543 \text{ \AA}^3$ , respectively. The difference Fourier maps suggested that voids of **3** were occupied by half a THF molecule per asymmetric unit, which could not be located appropriately because of heavy disorders. The difference Fourier maps suggested that voids of **6** were occupied by a THF molecule per asymmetric unit, which could not be located appropriately because of heavy disorders. The electron density associated with these solvent molecules was removed by the SQUEEZE routine of PLATON<sup>S10</sup> for crystal data of **3** and **6**.

**Table S1** X-ray crystallographic data for 2, 3, 4

	<b>2</b>	<b>3</b>	<b>4</b>
chemical formula	C <sub>61</sub> H <sub>66</sub> BF <sub>27</sub> MoN <sub>2</sub> O <sub>3</sub> P <sub>2</sub> S	C <sub>37</sub> H <sub>55</sub> ClIMoN <sub>2</sub> OP <sub>2</sub>	C <sub>69</sub> H <sub>65</sub> BF <sub>24</sub> MoN <sub>2</sub> O <sub>3</sub> P <sub>2</sub>
CCDC number	2123058	2123059	2123060
formula weight	1588.92	864.10	1594.94
dimensions of crystals, mm <sup>3</sup>	0.184 × 0.138 × 0.060	0.823 × 0.460 × 0.288	0.590 × 0.380 × 0.239
crystal color, habit	green, block	brown, block	brown, block
crystal system	Monoclinic	monoclinic	orthorhombic
space group	<i>Cc</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>
<i>a</i> , Å	19.6528(4)	11.3993(3)	13.3884(3)
<i>b</i> , Å	18.6233(3)	24.5388(4)	14.0757(4)
<i>c</i> , Å	19.0075(4)	15.2165(3)	37.3799(8)
<i>α</i> , deg	90	90	90
<i>β</i> , deg	95.4900(18)	106.053(2)	90
<i>γ</i> , deg	90	90	90
<i>V</i> , Å <sup>3</sup>	6924.8(2)	4090.46(16)	7044.3(3)
<i>Z</i>	4	4	4
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.524	1.403	1.504
<i>F</i> (000)	3224	1764	3240
$\mu$ , cm <sup>-1</sup>	3.824	12.474	3.421
temperature, °C	-180	-180	-180
trans. factors range	0.961 – 1.000	0.200 – 0.698	0.255 – 0.921
no. reflections measured	22733	33248	39708
no. unique reflections	13444 ( <i>R</i> <sub>int</sub> = 0.0299)	10849 ( <i>R</i> <sub>int</sub> = 0.0853)	17770 ( <i>R</i> <sub>int</sub> = 0.0673)
no. parameters refined	890	418	891
<i>R</i> 1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0630	0.0589	0.0764
<i>wR</i> 2 (all data) <sup>b</sup>	0.1670	0.1739	0.2002
GOF (all data) <sup>c</sup>	1.033	1.112	0.987
max diff peak / hole, e Å <sup>-3</sup>	+1.78 / -0.58	+1.95 / - 1.90	+1.69 / -0.86
Flack parameter	0		-0.05(2)

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ ,  $w = 1 / [\sigma^2(F_o^2) + (qP)^2 + rP]$ ,  $P = (\text{Max}(F_o^2, 0) + 2 F_c^2) / 3$  [ $q = 0.1242$  (**2**), 0.0889 (**3**), 0.1174 (**4**);  $r = 5.4329$  (**2**), 0.6266 (**3**), 0 (**4**)]. <sup>c</sup>  $GOF = [\sum w(F_o^2 - F_c^2)^2 / (N_o - N_{\text{params}})]^{1/2}$ .

**Table S2** X-ray crystallographic data for 5·THF, 6, 7

	5·THF	6	7
chemical formula	C <sub>41</sub> H <sub>61</sub> IMoN <sub>4</sub> O <sub>3</sub> P <sub>2</sub>	C <sub>51</sub> H <sub>63</sub> IMoN <sub>2</sub> O <sub>2</sub> P <sub>2</sub>	C <sub>24</sub> H <sub>43</sub> IMoN <sub>2</sub> OP <sub>2</sub>
CCDC number	2123061	2123062	2123063
formula weight	942.75	1020.86	660.41
dimensions of crystals, mm <sup>3</sup>	0.959 × 0.720 × 0.422	0.824 × 0.685 × 0.497	0.143 × 0.127 × 0.037
crystal color, habit	green, block	brown, block	pink, plate
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	14.8514(3)	12.6123(5)	15.8268(6)
<i>b</i> , Å	14.5855(3)	17.4852(5)	15.8794(5)
<i>c</i> , Å	20.1014(5)	23.5748(8)	12.0854(4)
<i>α</i> , deg	90	90	90
<i>β</i> , deg	102.659(2)	102.857(4)	104.863(4)
<i>γ</i> , deg	90	90	90
<i>V</i> , Å <sup>3</sup>	4248.42(17)	5068.6(3)	2935.68(18)
<i>Z</i>	4	4	4
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.474	1.338	1.494
<i>F</i> (000)	1936	2096	1336
$\mu$ , cm <sup>-1</sup>	11.517	9.689	16.244
temperature, °C	-180	-180	-180
trans. factors range	0.124 – 0.615	0.144 – 0.618	0.196 – 0.942
no. reflections measured	37035	50196	25593
no. unique reflections	11329 ( <i>R</i> <sub>int</sub> = 0.0920)	14095 ( <i>R</i> <sub>int</sub> = 0.0951)	7934 ( <i>R</i> <sub>int</sub> = 0.0836)
no. parameters refined	481	544	292
<i>R</i> 1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0546	0.0607	0.0509
<i>wR</i> 2 (all data) <sup>b</sup>	0.1430	0.1780	0.1361
GOF (all data) <sup>c</sup>	0.992	1.041	1.082
max diff peak / hole, e Å <sup>-3</sup>	+ 1.62 / - 1.30	+1.72 / -1.45	+ 1.89 / - 1.53

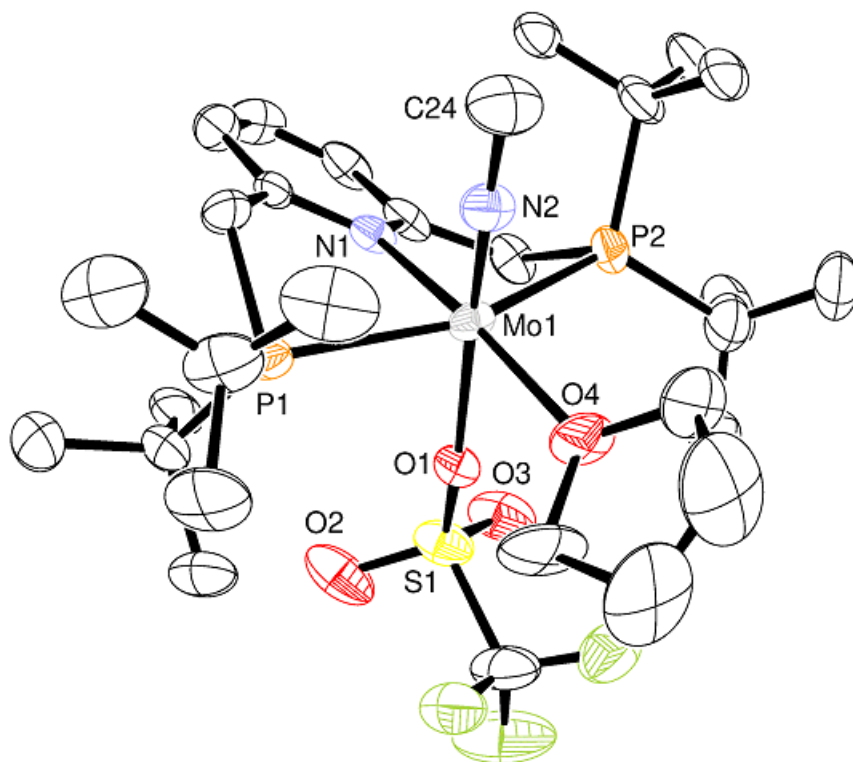
<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = 1 / [\sigma^2(F_o^2) + (qP)^2 + rP]$ ,  $P = (\text{Max}(F_o^2, 0) + 2 F_c^2) / 3$  [ $q = 0.0784$  (5·THF) 0.0981 (6) 0.0527 (7)];  $r = 0$  (5·THF, 6), 1.8678 (7)]. <sup>c</sup>  $GOF = [\sum w(F_o^2 - F_c^2)^2 / (N_o - N_{\text{params}})]^{1/2}$ .

**Table S3** X-ray crystallographic data for **8**, **9**

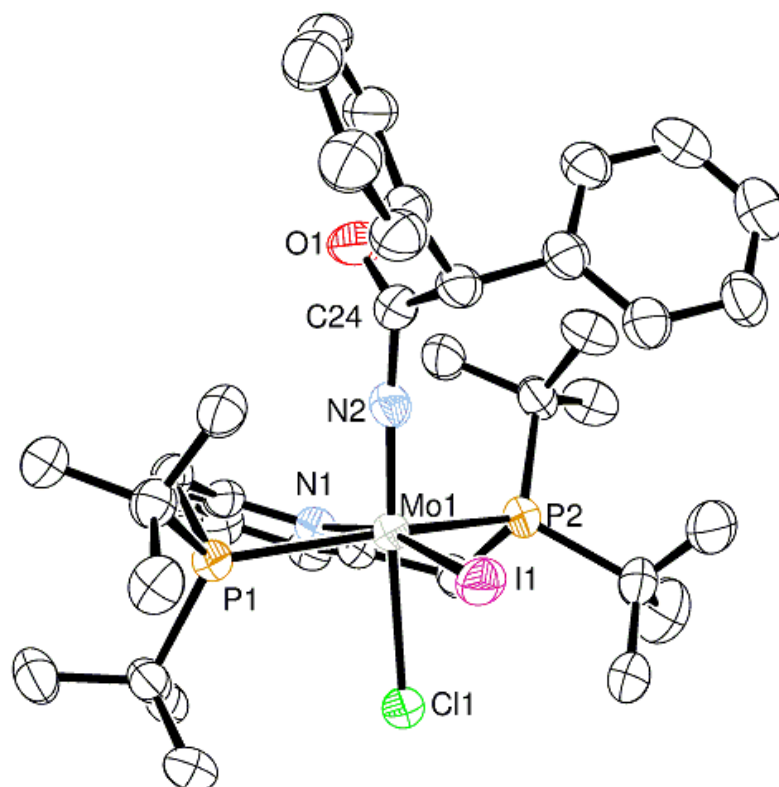
	<b>8</b>	<b>9</b>
chemical formula	C <sub>23</sub> H <sub>43</sub> ClIMoNOP <sub>2</sub>	C <sub>24</sub> H <sub>42</sub> MoN <sub>2</sub> OP <sub>2</sub>
CCDC number	2123064	2123065
formula weight	669.84	532.50
dimensions of crystals, mm <sup>3</sup>	0.305 × 0.213 × 0.111	0.994 × 0.254 × 0.151
crystal color, habit	green, block	red, plate
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> , Å	13.0791(5)	16.1322(4)
<i>b</i> , Å	15.0104(4)	10.9355(4)
<i>c</i> , Å	15.3134(5)	15.4225(5)
<i>α</i> , deg	90	90
<i>β</i> , deg	106.185(4)	98.881(3)
<i>γ</i> , deg	90	90
<i>V</i> , Å <sup>3</sup>	2887.21(17)	2688.12(15)
<i>Z</i>	4	4
$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	1.541	1.316
<i>F</i> (000)	1352	1120
$\mu$ , cm <sup>-1</sup>	17.41	6.232
temperature, °C	-180	-180
trans. factors range	0.568 – 1.000	0.222 – 0.910
no. reflections measured	25111	27342
no. unique reflections	7237 ( <i>R</i> <sub>int</sub> = 0.0583)	7443 ( <i>R</i> <sub>int</sub> = 0.1024)
no. parameters refined	283	283
<i>R</i> 1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0516	0.0766
<i>wR</i> 2 (all data) <sup>b</sup>	0.1412	0.2131
GOF (all data) <sup>c</sup>	1.070	1.091
max diff peak / hole, e Å <sup>-3</sup>	+ 1.30 / - 1.42	+1.96 / -1.70

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = 1 / [\sigma^2(F_o^2) + (qP)^2 + rP]$ ,  $P = (\text{Max}(F_o^2, 0) + 2 F_c^2) / 3$  [ $q = 0.0624$  (**8**),  $0.1091$  (**9**);  $r = 4.1602$  (**8**),  $3.2213$  (**9**)]. <sup>c</sup>  $\text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (N_o - N_{\text{params}})]^{1/2}$ .

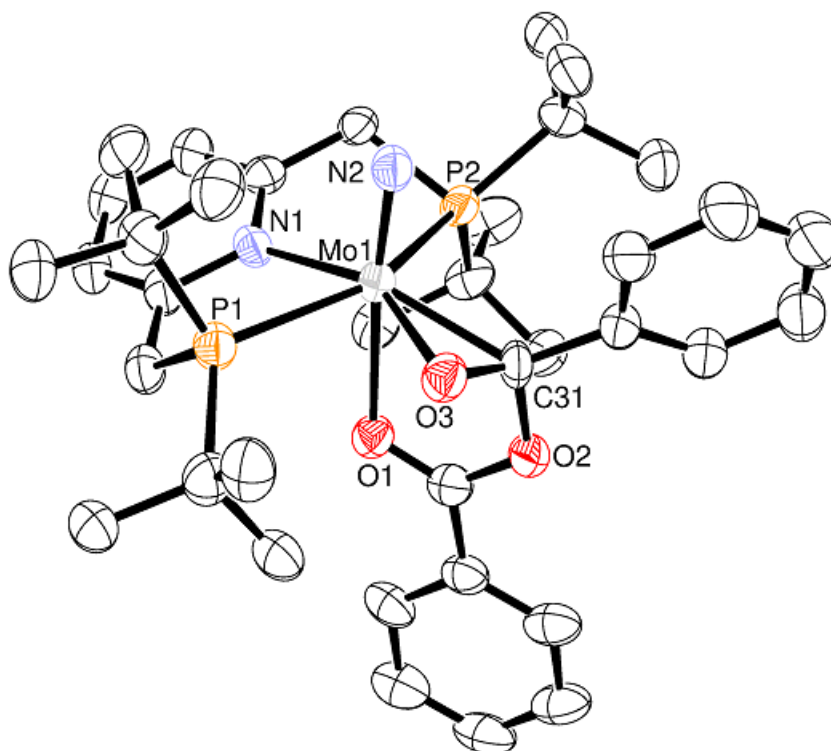




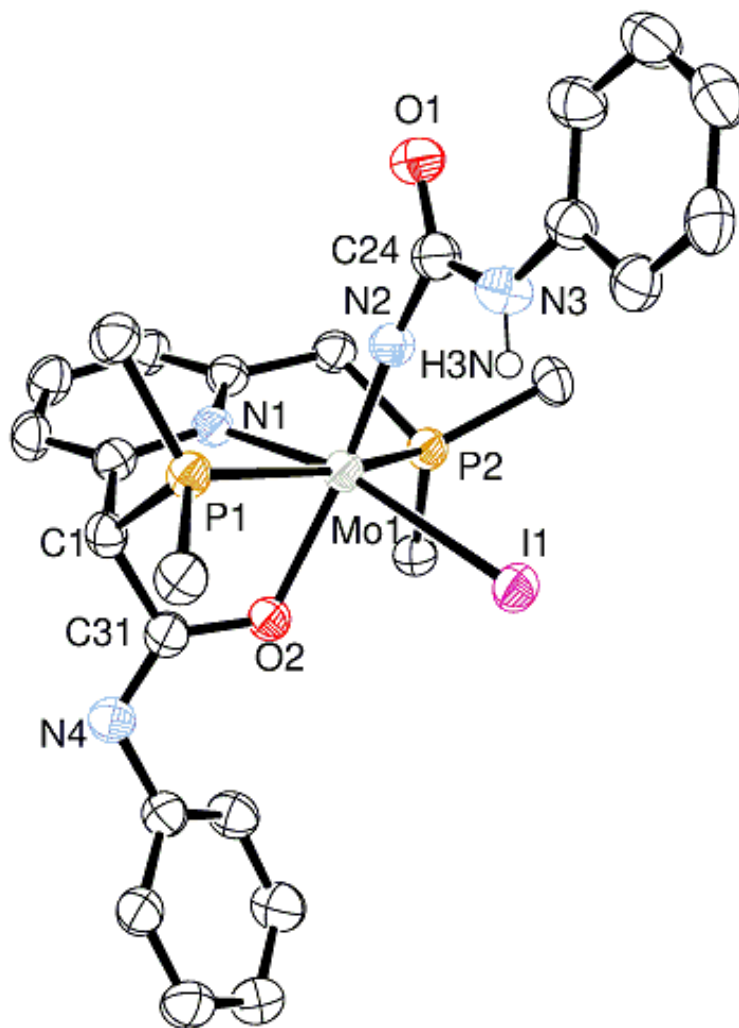
**Fig. S24** Molecular structure of the cationic part of **2**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.151(4), Mo1–N2 1.721(6), Mo1–O1 2.223(4), Mo1–O4 2.189(4), Mo1–P1 2.5974(17), Mo1–P2 2.5575(18), N2–C24 1.445(11); P1–Mo1–P2 155.33(6), Mo1–N2–C24 179.2(7).



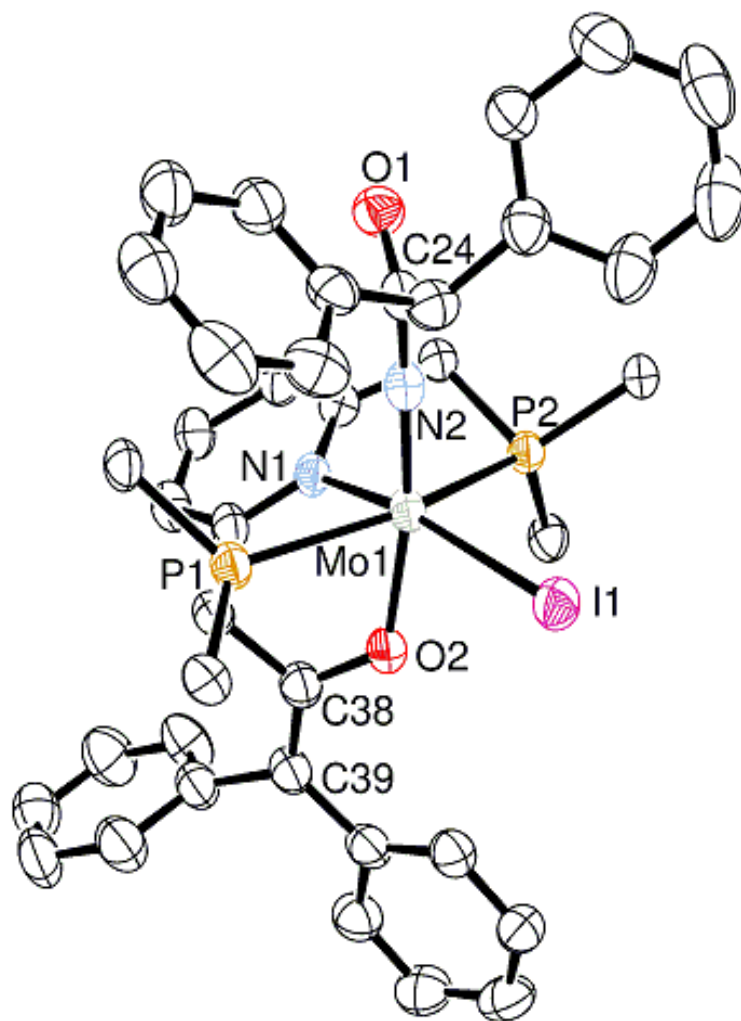
**Fig. S25** Molecular structure of **3**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.181(3), Mo1–N2 1.768(3), Mo1–P1 2.5606(10), Mo1–P2 2.5584(10), Mo1–I1 2.8472(4), Mo1–Cl1 2.4784(9), N2–C24 1.381(5), O1–C24 1.209(5); P1–Mo1–P2 154.45(3), Mo1–N2–C24 172.7(3), N2–C24–O1 121.4(4), N2–C24–C25 115.3(3), O1–C24–C25 123.4(4).



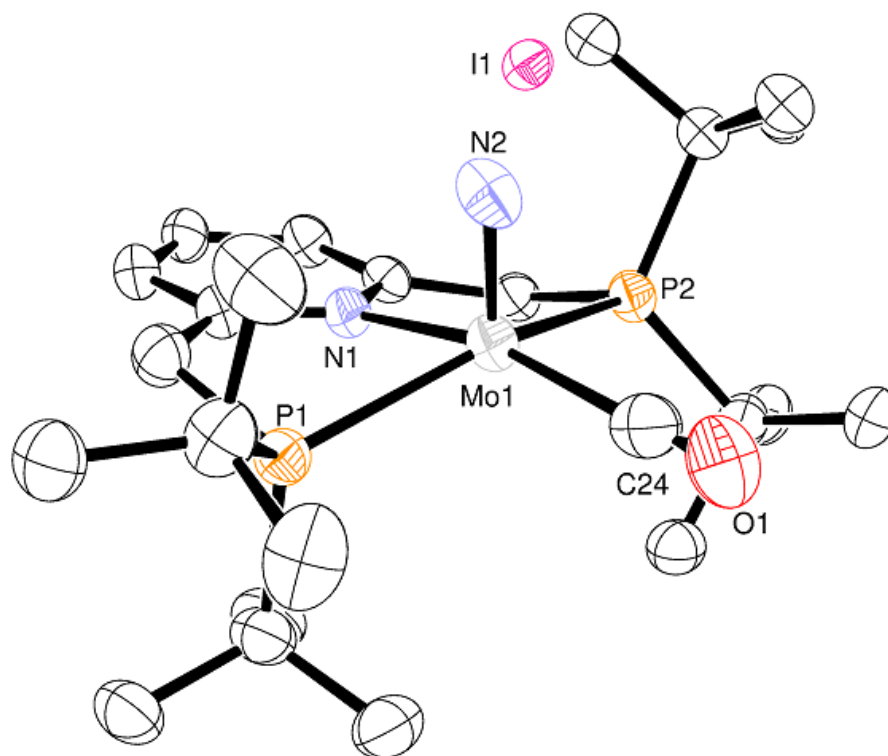
**Fig. S26** Molecular structure of the cationic part of **4**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.247(6), Mo1–N2 1.654(5), Mo1–O1 2.379(5), Mo1–O3 2.058(5), Mo1–C31 2.187(7), Mo1–P1 2.573(2), Mo1–P2 2.6256(18), O3–C31 1.319(9); P1–Mo1–P2 152.09(6), N1–Mo1–N2 99.6(2), O3–Mo1–C31 36.0(2).



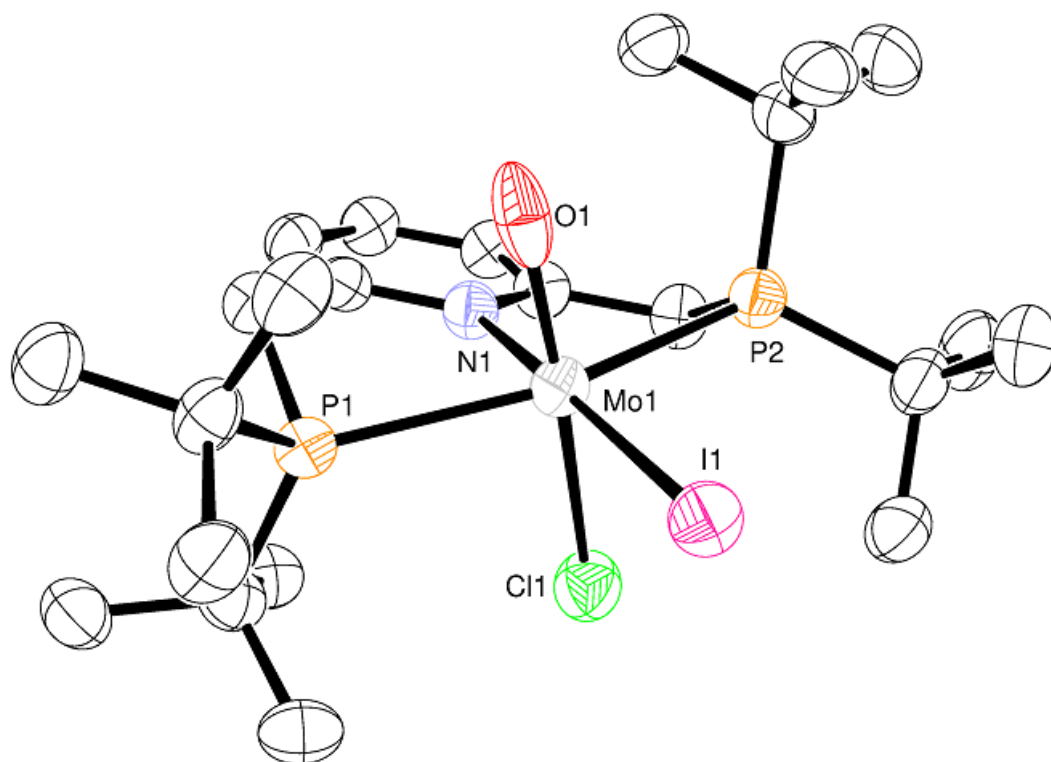
**Fig. S27** Molecular structure of **5**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms except for H3N as well as solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.165(3), Mo1–N2 1.755(3), Mo1–O2 2.115(2), Mo1–P1 2.5068(9), Mo1–P2 2.5255(9), Mo1–I1 2.8373(3), N2–C24 1.394(4), O1–C24 1.226(4), N3–C24 1.352(4), O2–C31 1.317(4), N4–C31 1.283(4), C1–C31 1.532(4); P1–Mo1–P2 156.98(3), Mo1–N2–C24 164.9(2), N2–C24–O1 122.5(3), O1–C24–N3 126.0(3), N2–C24–N3 111.5(3), O2–C31–N4 128.9(3), O2–C31–C1 113.4(3), N4–C31–C1 117.7(3).



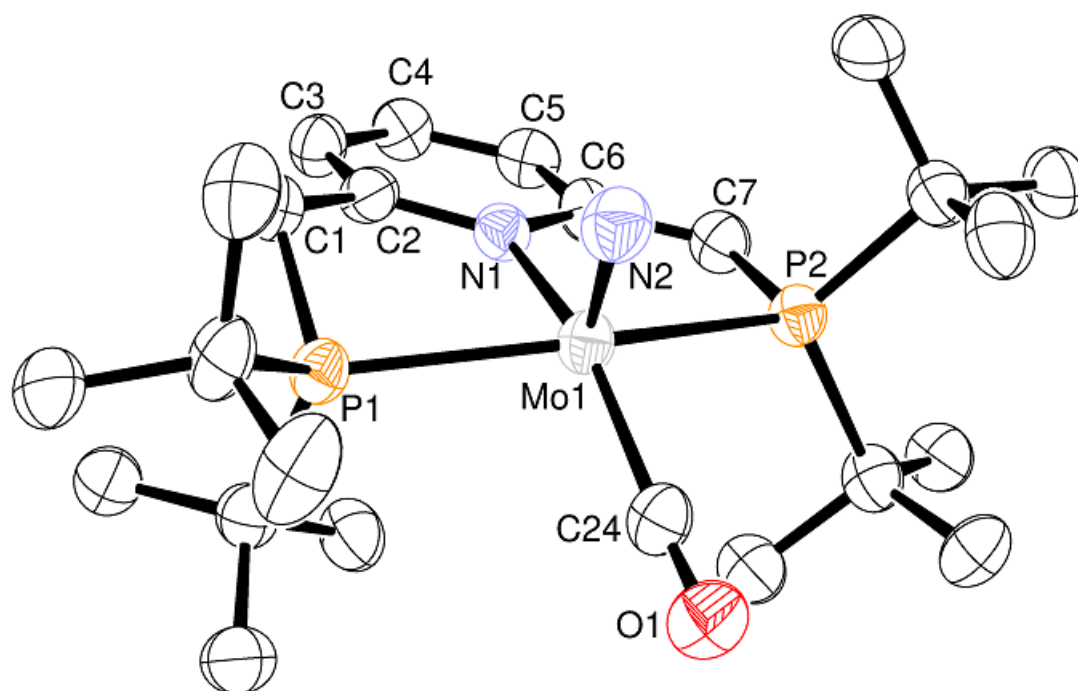
**Fig. S28** Molecular structure of **6**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.172(3), Mo1–N2 1.796(3), Mo1–O2 2.040(2), Mo1–P1 2.5329(9), Mo1–P2 2.5208(9), Mo1–I1 2.8413(4), N2–C24 1.364(5), O1–C24 1.224(4), O2–C38 1.328(4), C38–C39 1.357(5); P1–Mo1–P2 153.29(3), Mo1–N2–C24 172.6(3), N2–C24–O1 123.1(3), O1–C24–C25 121.6(3), N2–C24–C25 115.2(3), O2–C38–C39 125.0(3), O2–C38–C1 111.4(3), C1–C38–C39 123.6(3).



**Fig. S29** Molecular structure of **7**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.237(4), Mo1–N2 1.634(4), Mo1–P1 2.4880(12), Mo1–P2 2.4953(12), Mo1–C24 2.111(7), O1–C24 0.981(6); P1–Mo1–P2 150.38(4), N1–Mo1–C24 165.63(17), N2–Mo1–C24 92.3(2), N1–Mo1–N2 102.00(18).  $\tau = 0.254$



**Fig. S30** Molecular structure of **8**. Thermal ellipsoids are shown at the 50% probability level as well as hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.190(4), Mo1–O1 1.870(5), Mo1–P1 2.5272(13), Mo1–P2 2.5619(13), Mo1–I1 2.8247(5), Mo1–Cl1 2.4549(14); P1–Mo1–P2 158.23(4).



**Fig. S31** Molecular structure of **9**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo1–N1 2.219(4), Mo1–N2 1.660(4), Mo1–P1 2.4977(12), Mo1–P2 2.5150(11), Mo1–C24 2.027(5), O1–C24 1.136(6), N1–C2 1.362(6), N1–C6 1.405(5), C1–C2 1.504(6), C2–C3 1.376(6), C3–C4 1.408(7), C4–C5 1.348(7), C5–C6 1.447(7), C6–C7 1.386(7); P1–Mo1–P2 152.13(4), N1–Mo1–C24 156.42(17), N2–Mo1–C24 93.1(2), N1–Mo1–N2 110.48(18). Selected torsion angles (deg): P1–C1–C2–N1 –37.7(5), N1–C6–C7–P2 0.5(7).  $\tau = 0.0715$



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