Electronic Supplementary Material (ESI) for Dalton Transactions.

The new diphosphanylphosphido complexes of Tungsten(VI) and Molybdenum(VI). Their synthesis, structures and properties.

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SUPPLEMENTARY MATERIALS

Part A. X-ray crystallographic analysis

Part B. DFT results

Part C. NMR data

Part D. References

Part A. X-ray crystallographic analysis

Diffraction data of ***t*Bu$_2$P-P(Li)-P(NEt$_2$)$_2$, 2W, 2Mo, 3W and 3Mo** was collected on diffractometer equipped with a STOE image plate detektor system IPDS2T using CuKα radiation with graphite monochromatization (λ = 1.54178 Å) for **2W** and MoKα radiation with graphite monochromatization (λ = 0.71073 Å) for ***t*Bu$_2$P-P(Li)-P(NEt$_2$)$_2$, 2Mo, 3W and 3Mo**. Good quality single-crystal specimens of ***t*Bu$_2$P-P(Li)-P(NEt$_2$)$_2$, 2Mo, 3W and 3Mo** were selected for the X-ray diffraction at 120 K. The structure were solved by direct methods and refined against F^2 using the Shelxs-97 and Shelxl-97 programs[1] run under WinGX.[2] Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were usually refined using the isotropic model with U_{iso}(H) values fixed to be 1.5 times U_{eq} of C atoms for $-CH_3$ or 1.2 times U_{eq} for $-CH$, $-CH_2$ groups and aromatic H.

Crystallographic data for the structures of ***t*Bu$_2$P-P(Li)-P(NEt$_2$)$_2$, 2Mo, 3W and 3Mo** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1838374-1838378. 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; E-mail: deposit@ccdc.cam.ac.uk).

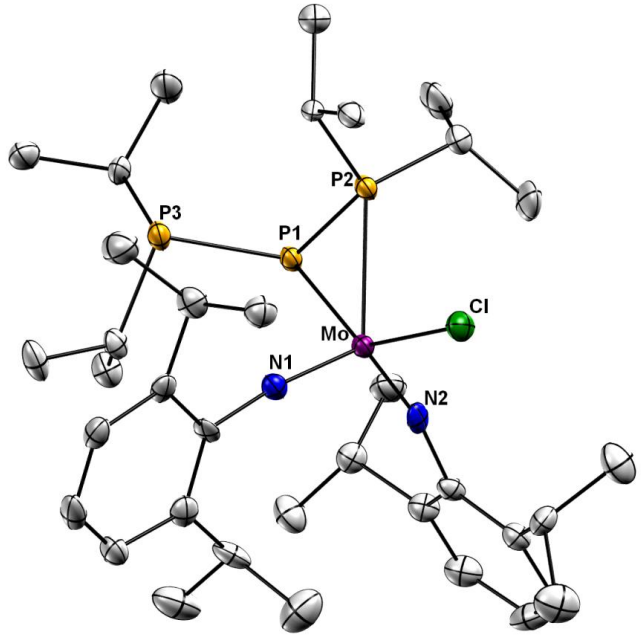


Figure S1. Molecular structure of **2Mo** (30% probability displacement ellipsoids), H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): P1-P2 2.153(4), P1-P3 2.240(3), P2-Mo1 2.549(3), P1-Mo1 2.564(2), Mo1-Cl1 2.407(2), Mo1-N1 1.764(7), Mo1-N2 1.768(9), P1-Mo1-P2 49.80(8), N1-Mo1-N2 116.2(4), C1-N1-Mo1 171.9(8), C13-N2-Mo1 168.3(6), P2-P1-P3 103.11(15), P2-P1-Mo1 64.74(9), P3-P1-Mo1 106.19(11). ΣP1 = 274.02, ΣP2 = 353.19, ΣP3 = 300.19.

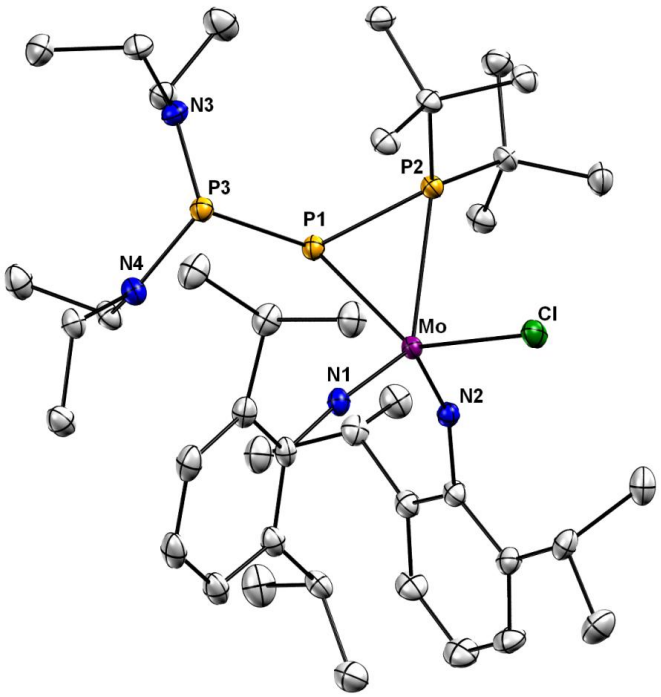


Figure S2. Molecular structure of **3Mo** (30% probability displacement ellipsoids), H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): P1-P2 2.1573(9), P1-P3 2.2394(9), P2-Mo1 2.5515(7), P1-Mo1 2.5208(7), Mo1-Cl1 2.3915(6), Mo1-N1 1.772(2), Mo1-N2 1.761(2), P1-Mo1-P2 50.34(2), N1-Mo1-N2 112.89(10), C1-N1-Mo1 174.5(2), C13-N2-Mo1 154.24(19), P2-P1-P3 109.78(4), P2-P1-Mo1 65.57(3), P3-P1-Mo1 107.72(3). ΣP1 = 283.05, ΣP2 = 345.45, ΣP3 = 307.76.

	***t*Bu$_2$P-P(Li)-P(NEt$_2$)$_2$**	**2W**	**2Mo**	**3W**	**3Mo**
Empirical formula	$C_{24}H_{54}LiN_2O_2P_3$	$C_{36}H_{62}WN_2P_3Cl$	$C_{36}H_{62}MoN_2P_3Cl$	$C_{40}H_{72}WN_4P_3Cl$	$C_{40}H_{72}MoN_4P_3Cl$
Formula weight	502.54	835.08	747.17	921.22	833.31
Temperature (K)	120	120	120	120	120
Wavelenght (Å) (Mo/Cu Kα)	0.71073	1.54186	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P 21/n*	*P 21*	*P 21*	*P-1*	*P-1*
***a* (Å)**	9.1291(5)	10.5090(5)	10.5885(16)	11.0041(4)	11.0012(10)
***b* (Å)**	17.0931(6)	20.8420(9)	20.9626(16)	20.8898(7)	20.8791(14)
***c* (Å)**	19.4531(10)	18.5788(8)	18.7533(17)	22.1047(7)	22.0534(14)
***α* (°)**	90	90	90	106.063(3)	105.878(5)
***β* (°)**	95.954(4)	98.817(4)	99.040(10)	102.935(3)	102.963(6)
***γ* (°)**	90	90	90	101.944(3)	102.300(7)
***V* (Å^3)**	3019.2(3)	4021.2(3)	4110.8(8)	4558.6(3)	4540.1(6)
Z	4	4	2	4	4
***D*$_{Calc}$ (Mg m^{-3})**	1.106	1.379	1.207	1.342	1.219
Crystal size (mm)	0.18x0.17x0.15	0.18x0.17x0.15	0.25x0.24x0.24	0.24x0.24x0.23	0.24x0.24x0.22
ϑ Range (°)	3.273- 26.999	3.208– 66.988	2.233– 26.999	3.227– 28	3.14– 27
Reflections collected/unique	6457/4893	13463/ 12932	11692/9020	21947/12693	19480/15043
Completness to ϑmax (%)	97.6	97.7	99.9	99.6	98.1
Refinement method	Full-matrix least –squares on F^2	Full-matrix least –squares on F^2	Full-matrix least –squares on F^2	Full-matrix least –squares on F^2	Full-matrix least –squares on F^2
Data/restraints /parameters	6457/0/289	13463/1/ 584	11692/1/775	21947/6/902	19480/1/883
Goodness-of-fit on F^2	1.051	1.16	1.01	0.924	1.023
Final R indices [I>2σ(I)] R indices (all data)	R1 = 0.0628 *wR2 = 0.1241* *R1 = 0.0439* *wR2 = 0.1132*	R1 = 0.0847 *wR2 = 0.223* *R1 = 0.0748* *wR2 = 0.1918*	*R1 = 0.0871* *wR2 = 0.1493* *R1 = 0.0623* *wR2 = 0.13*	*R1 = 0.1057* *wR2 = 0.1628* *R1 = 0.0551* *wR2 = 0.1295*	*R1 = 0.0562* *wR2 = 0.1031* *R1 = 0.0387* *wR2 = 0.0938*
Summary of Data CCDC	1838374	1838378	1838375	1838377	1838376

Table 1. Crystallographic data of ***t*Bu$_2$P-P(Li)-P(NEt$_2$)$_2$, 2W**, **2Mo**, **3W** and **3Mo**

Part B. DFT results

All calculations were performed using Amsterdam Density Functional (ADF) package (version 2016.101)[3]. Calculations were carried out with the General Gradient Approximation (GGA) functional BLYP (Becke[4] for the exchange part and Lee, Young, Parr[5] for the correlation part) with Grimme's dispersion correction with additional Becke and Johnson damping functions (-D3BJ)[6]. All atoms were described by a Slater-type triple-ζ quality basis set with two polarization functions, corresponding to TZ2P basis set[7] in the ADF package. Relativistic effects were included using scalar Zeroth Order Regular Approximation (scalar ZORA) model[8].

Starting geometries for all compounds were taken from experimental crystallographic data and optimized.

On optimized geometries series of other calculations were conducted – Natural Bonding Orbitals (NBO) analysis, Hirshfeld population analysis[9] and condensed Fukui function analysi[10].

Natural Bonding Orbitals (NBO, version 6.0)[11] analysis, was performed on all optimized geometries. Calculations included Natural Localized Molecular Orbitals (NLMO)[12] and Natural Population Analysis (NPA)[13].

In order to evaluate reactive centers in nucleophilic or electrophilic attack reactions we have used Fukui functions – f^+ for a nucleophilic attack and f^- for an electrophilic attack. Condensed Fukui functions were obtained (localized using Hirshfeld Population Analysis) to quantitatively assign properties to atoms. To further classify these reactive centers in the means of HSAB[14] theory local softness was calculated. The local softness is computed as overall softness (defined as the inverse of the HOMO-LUMO gap[15]), multiplied by condensed Fukui function for selected atom.

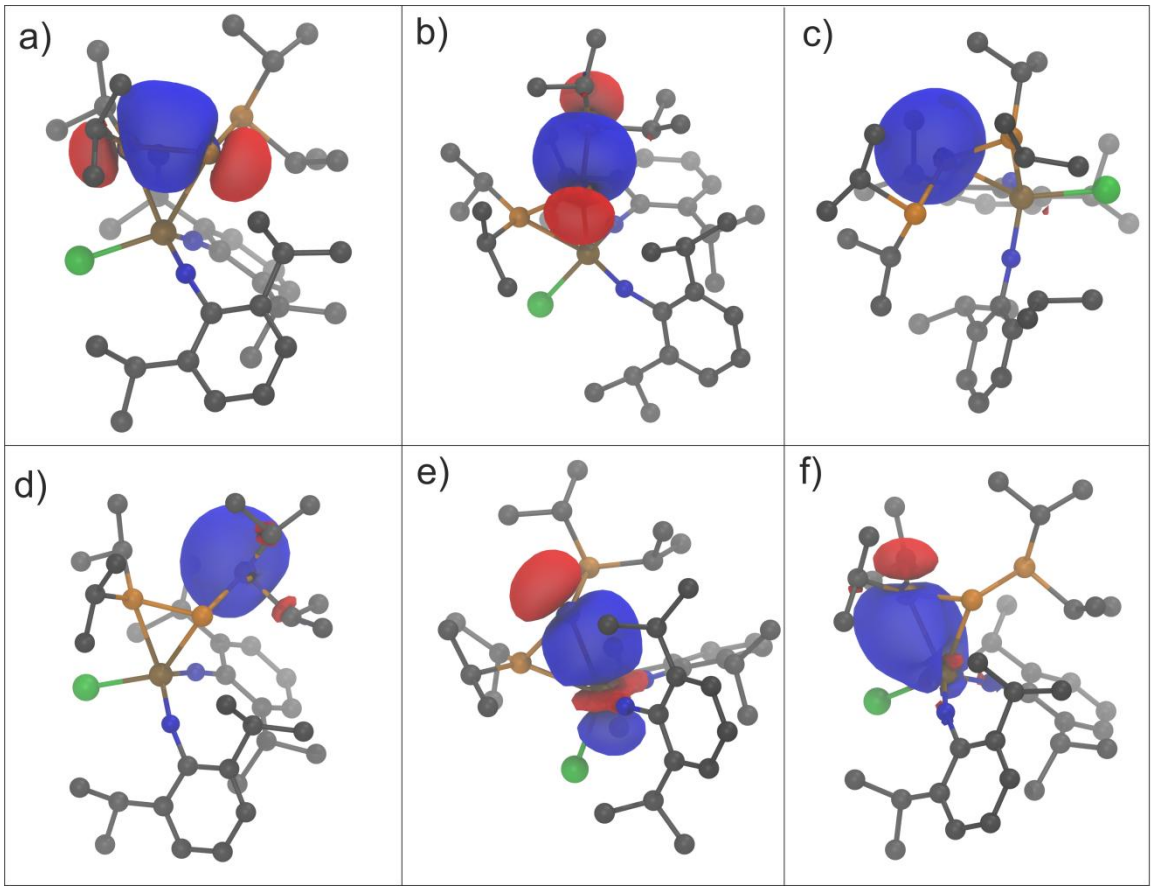


Figure S3. Graphical representation of the NBOs of **2W** associated to: a) σ(P1P2), b) σ(P2P3), c) P1 lone pair, d) P3 lone pair, e) σ(P1W), f) σ(P2W).

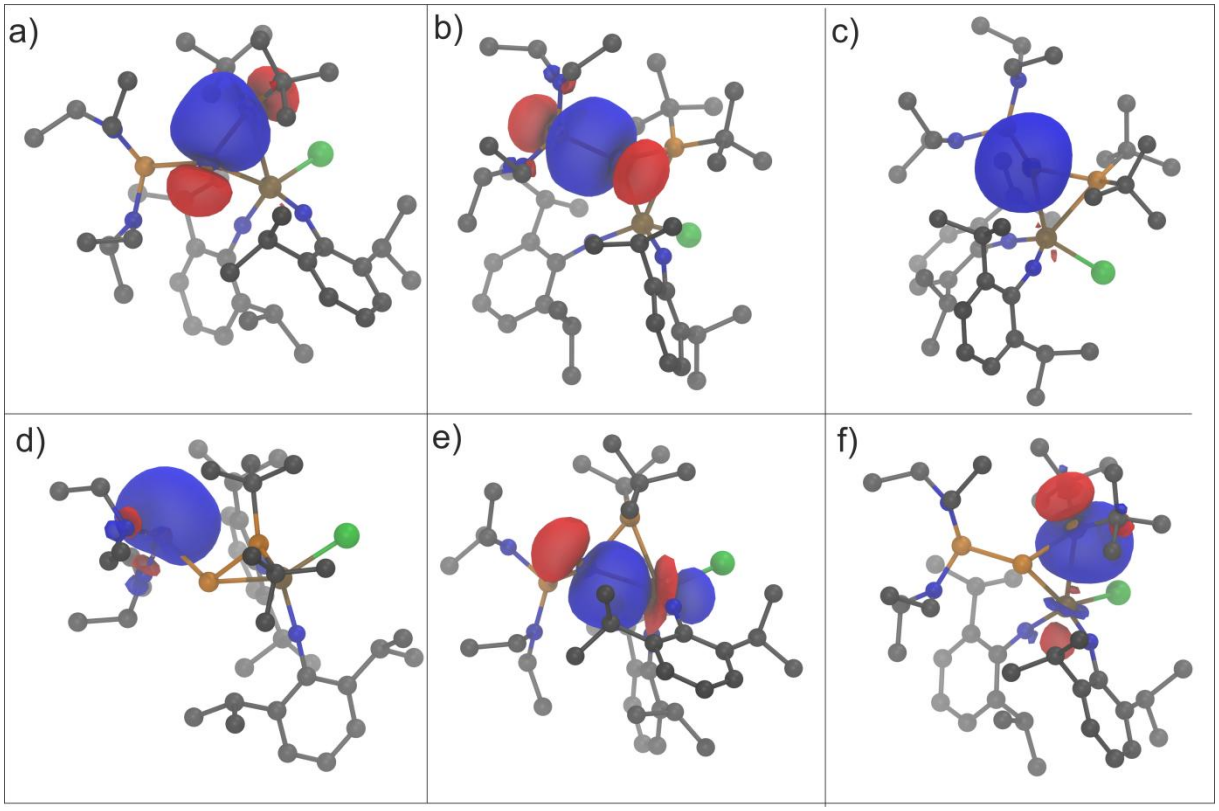
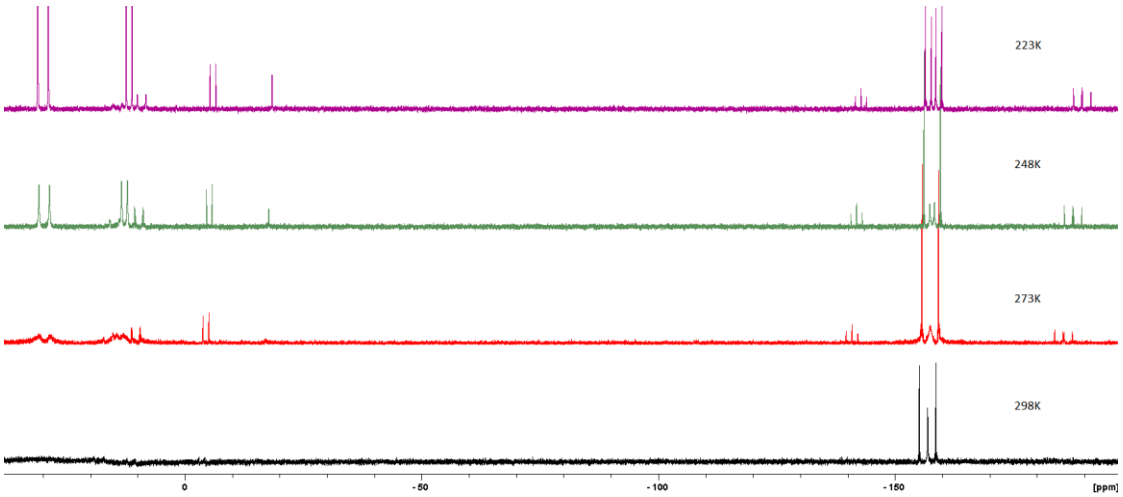


Figure S4. Graphical representation of the NBOs of **3W** associated to: a) σ(P1P2), b) σ(P2P3), c) P1 lone pair, d) P3 lone pair, e) σ(P1W), f) σ(P2W).

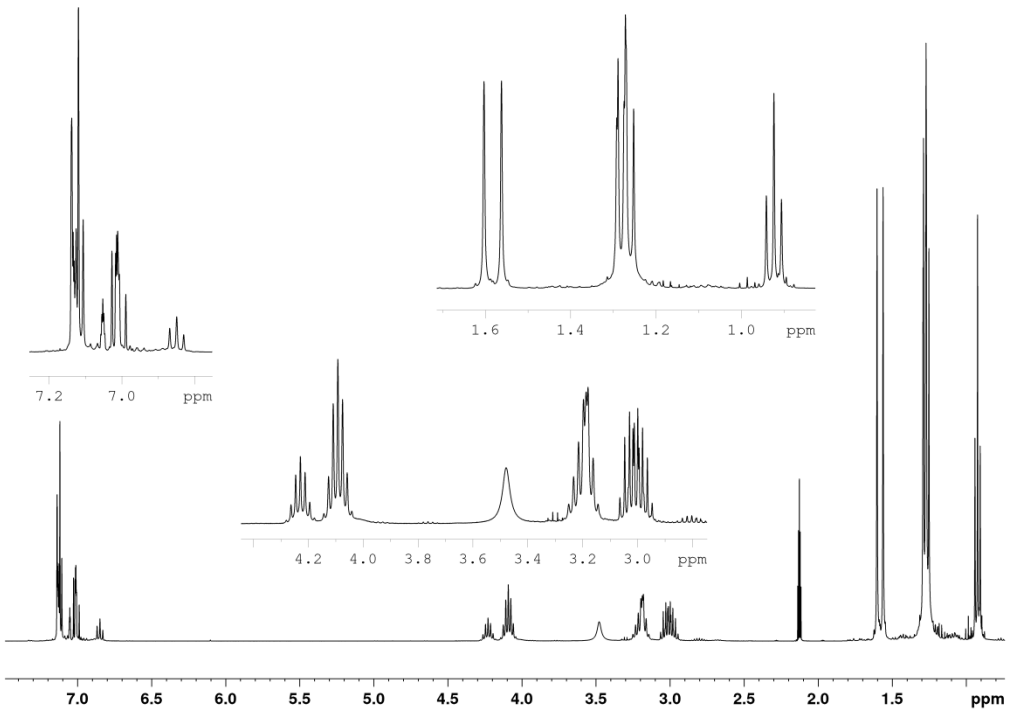
Part C. NMR data

1. *NMR data for **2W***

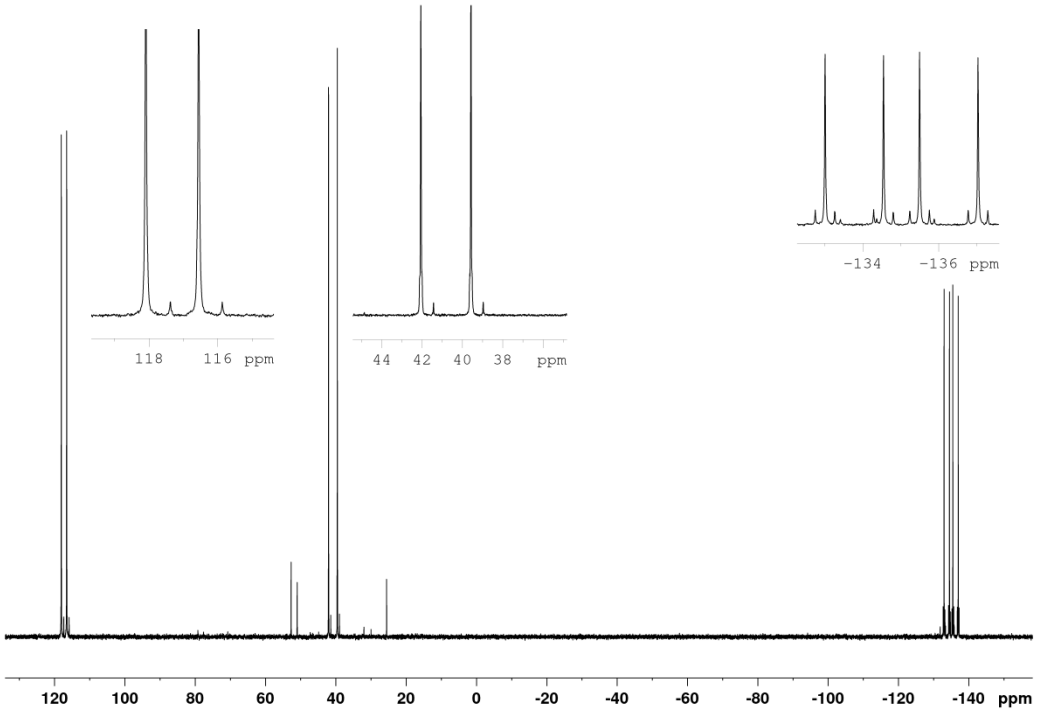


2. *NMR data for **3W***

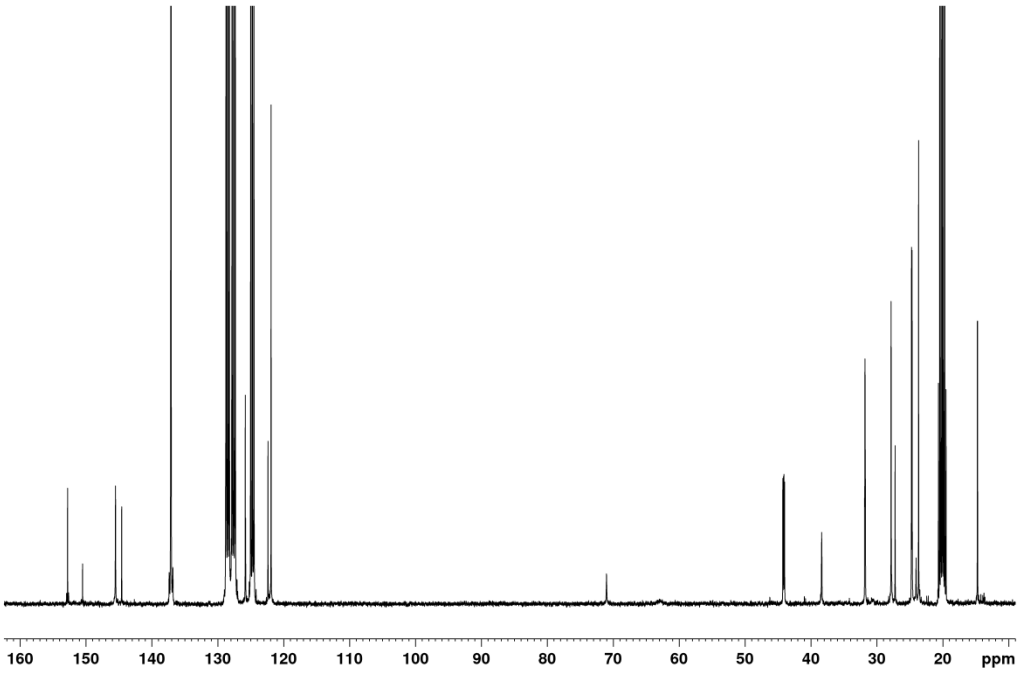
^{1}H NMR



$^{31}P\{^{1}H\}$ NMR

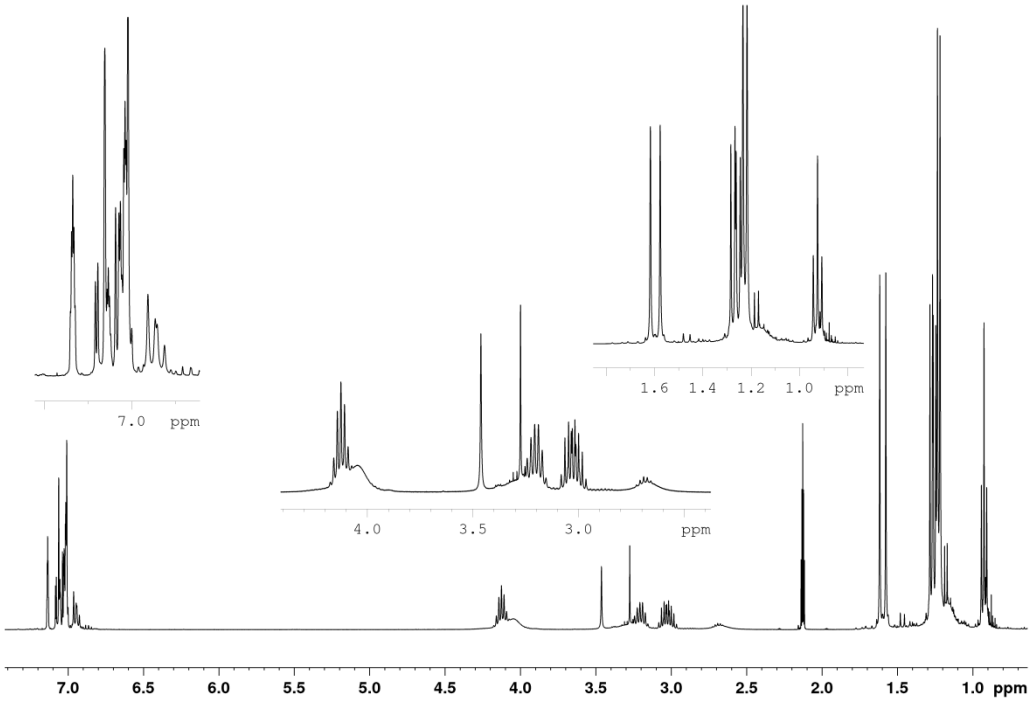


^{13}C NMR

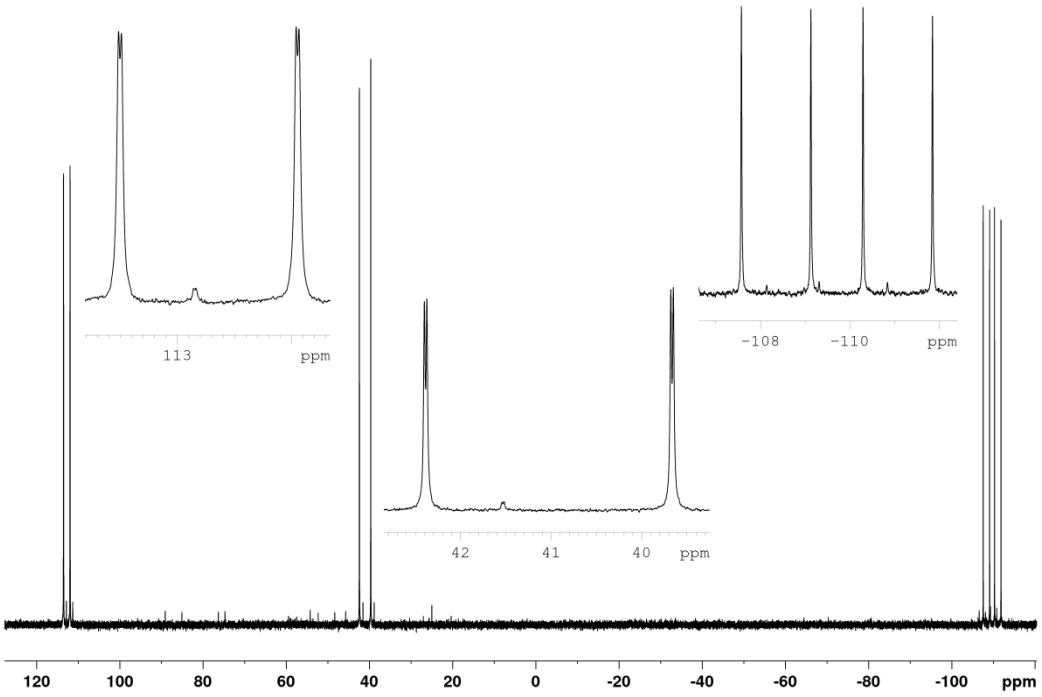


3. *NMR data for **3Mo***

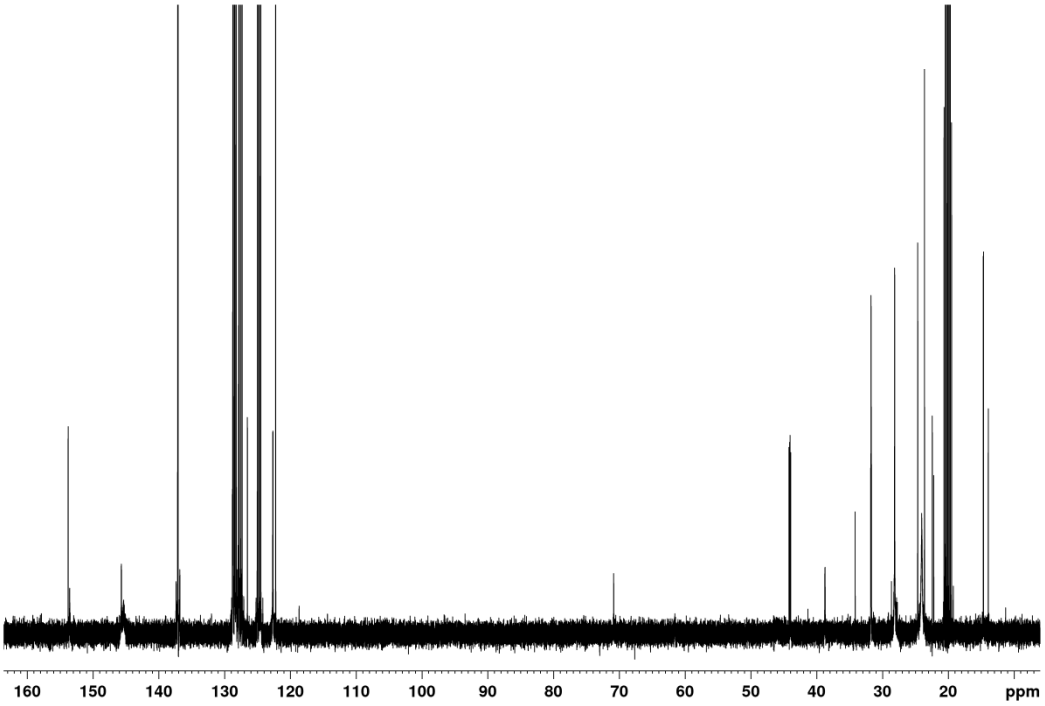
^{1}H NMR



^{31}P{^{1}H} NMR

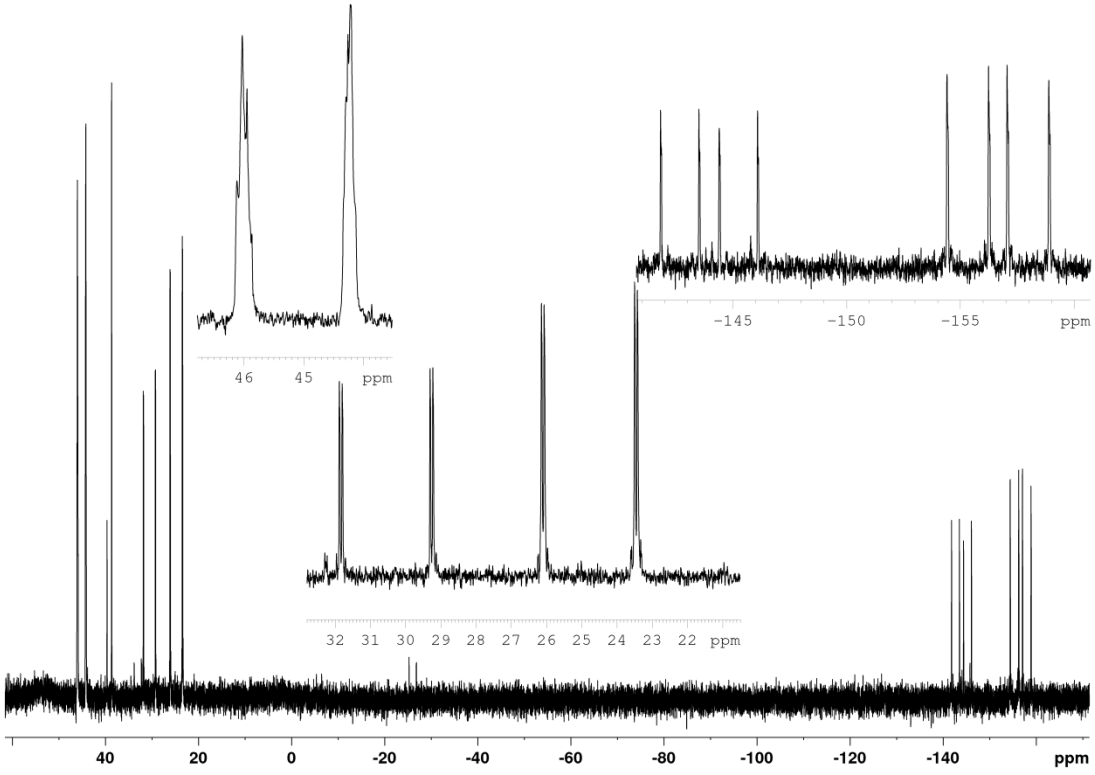


^{13}C NMR

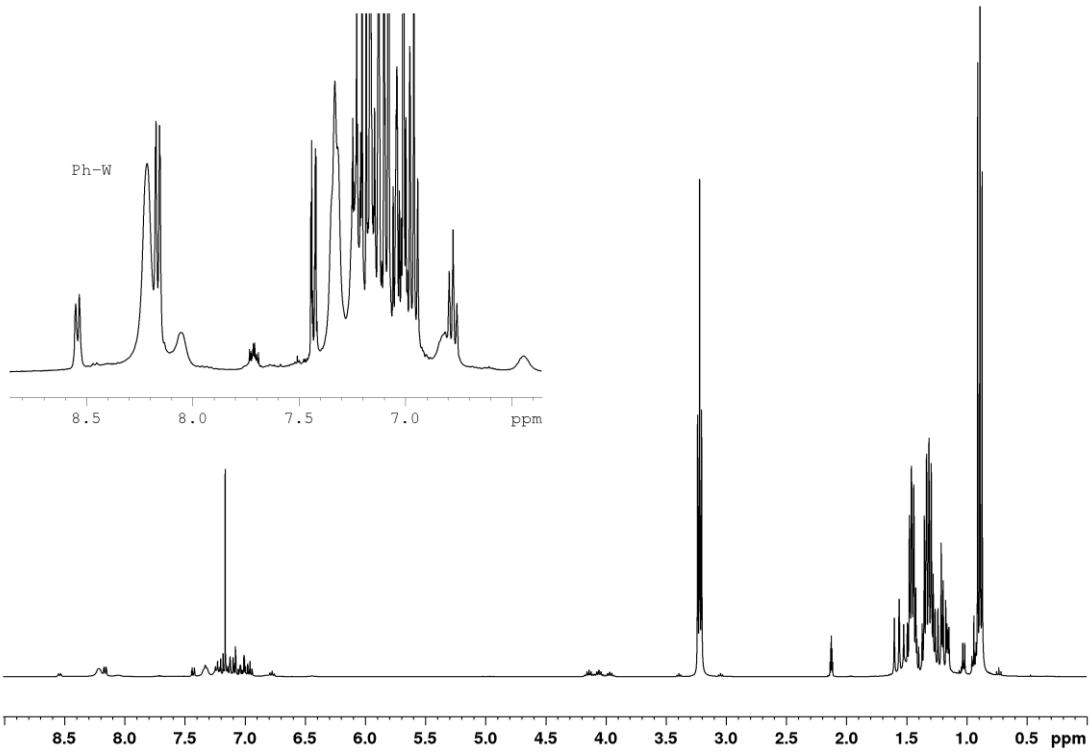


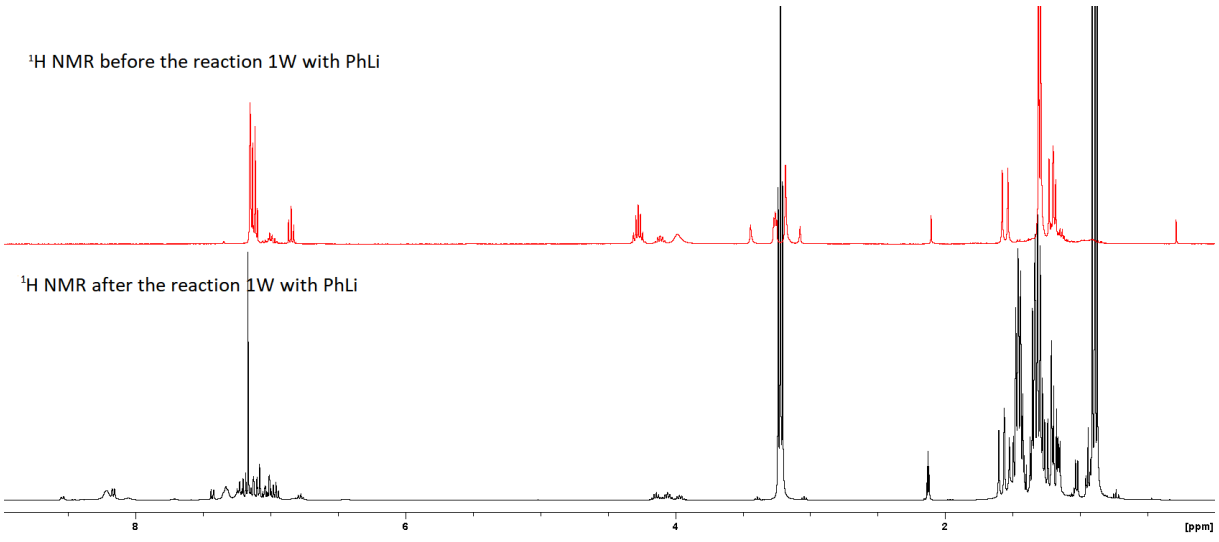
4. NMR spectra mixture of reaction (8)

$^{31}P\{^{1}H\}$ NMR

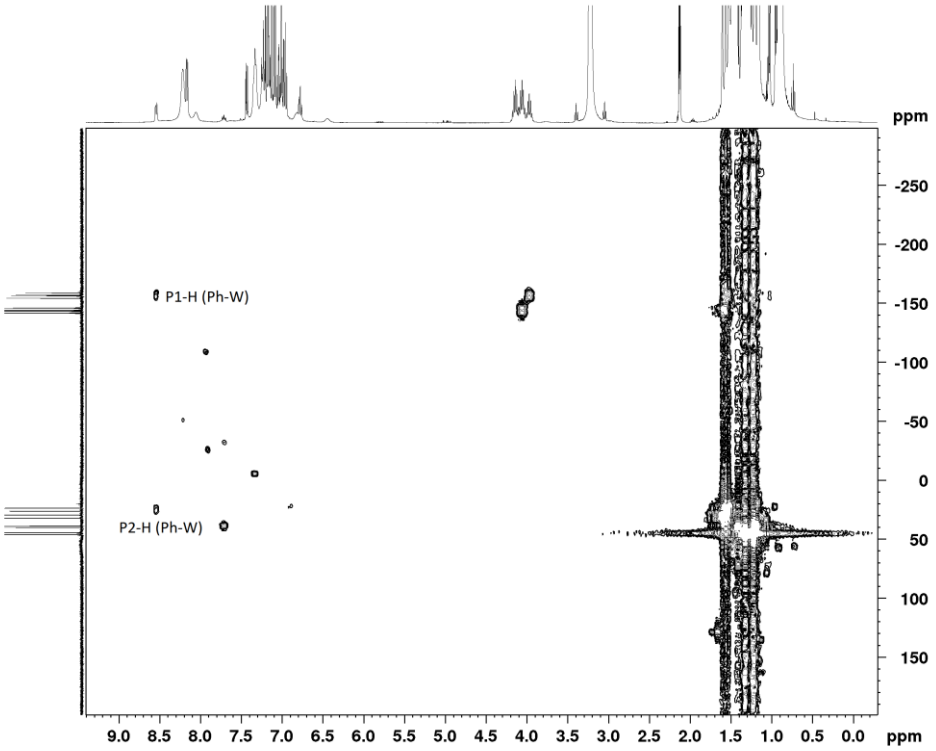


^{1}H NMR

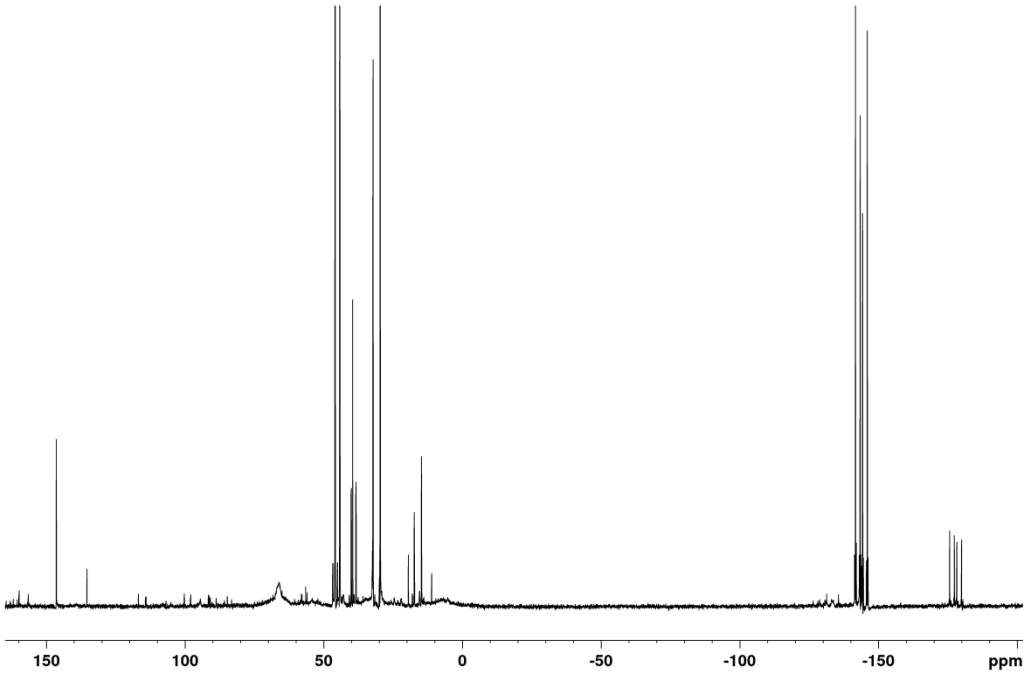

Ph-W
8.5
8.0
7.5
7.0
ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


^{1}H NMR before the reaction 1W with PhLi
^{1}H NMR after the reaction 1W with PhLi
8
6
4
2
[ppm]

^{1}H-^{31}P HMBC NMR



5. $^{31}P\{^{1}H\}$ NMR spectra mixture of reaction (9)



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