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# Supplementary Information for:

## Aryl group transfer and C-P bond formation in the reaction of organonickel σ-complexes with sodium 3,4,5-triphenyl-1,2-diphospholide

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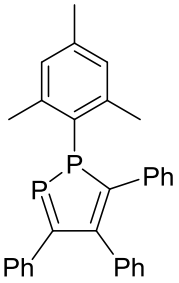


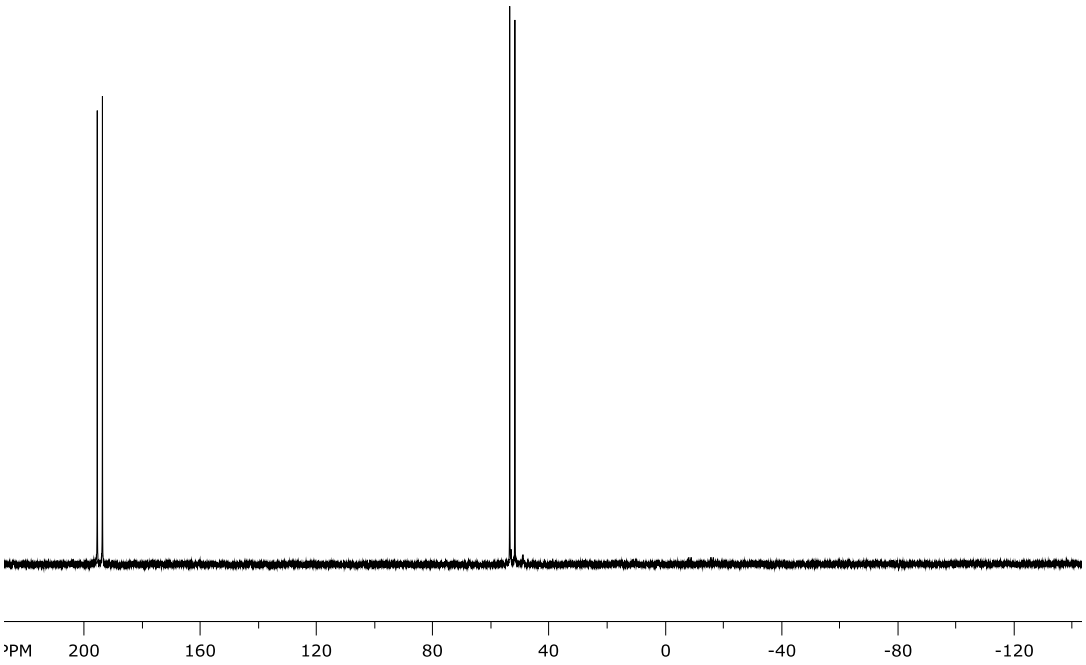




**Figure S1.** $^{31}P\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

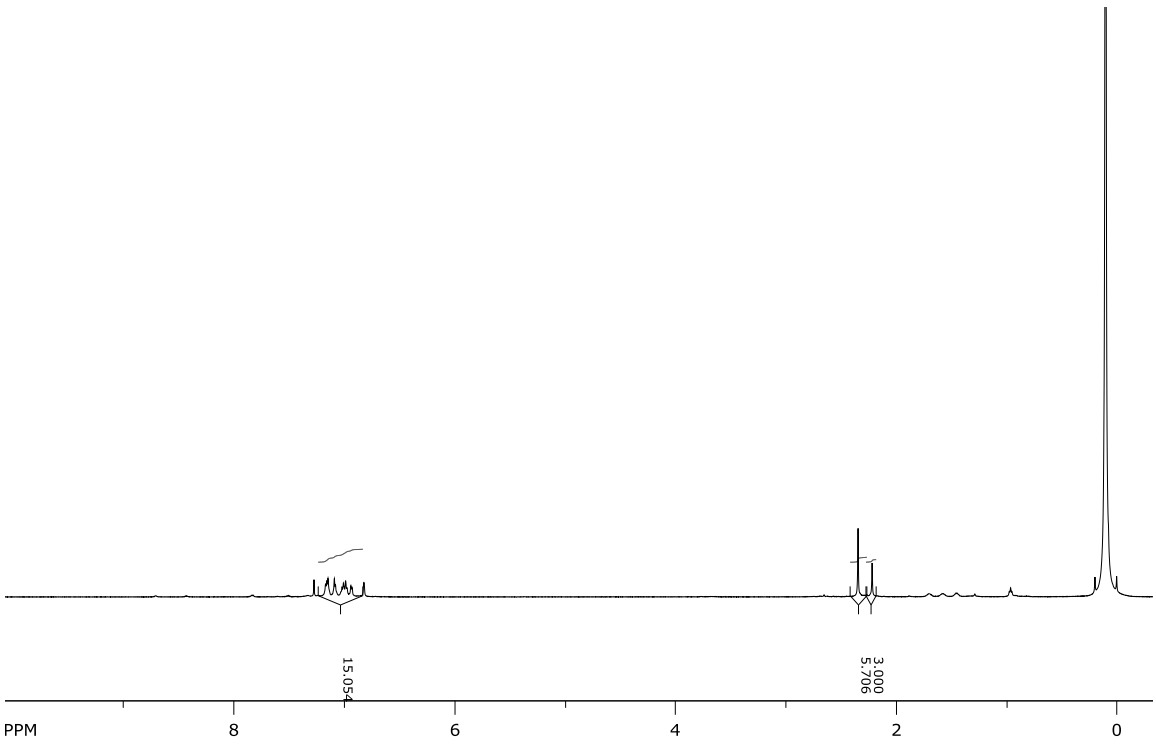



**Figure S2.** $^{1}H$ NMR spectrum of **4** in $CDCl_3$.

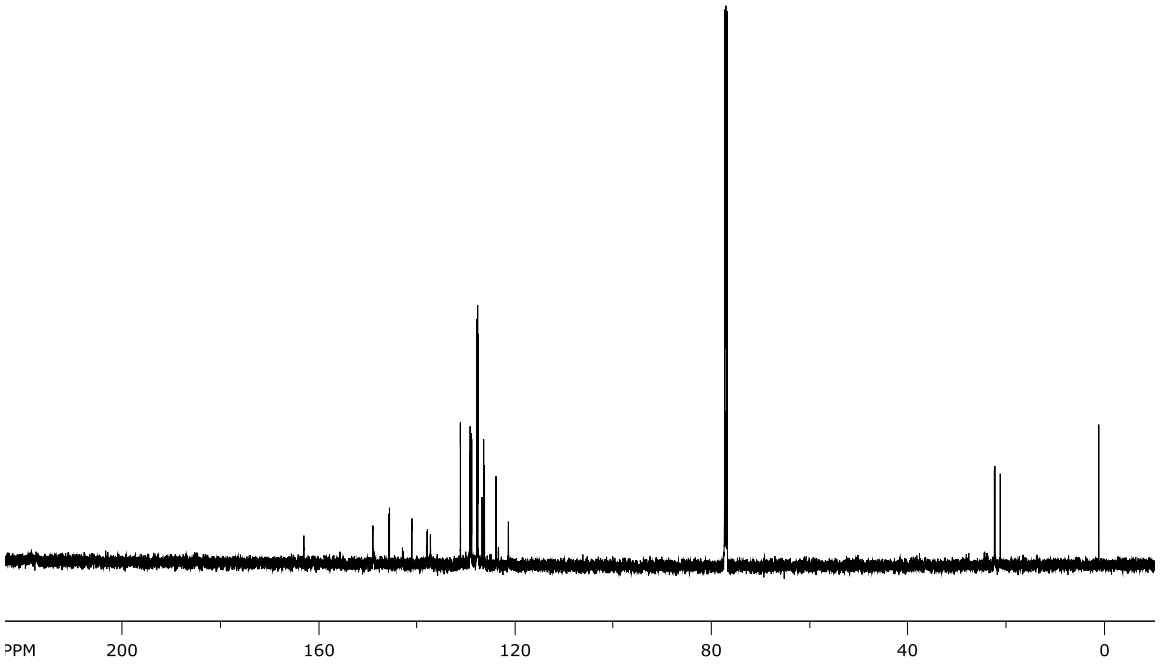
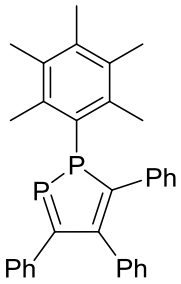



**Figure S3.** $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$.

## 2. Experimental $^{31}P$, $^{1}H$, $^{13}C$ NMR spectra for 5.



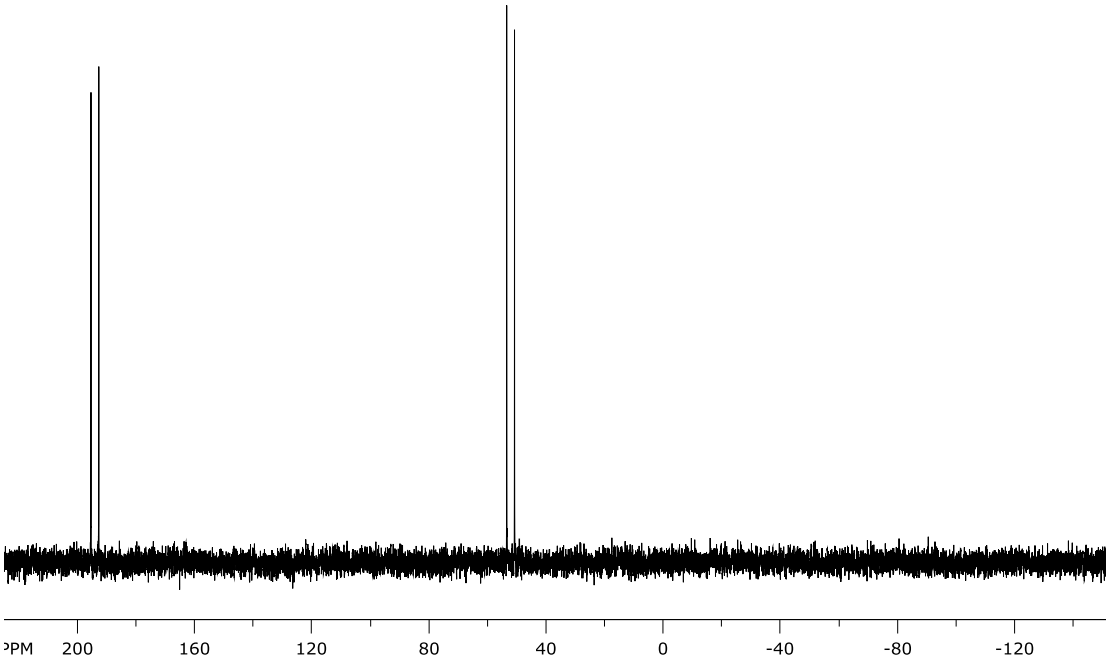




**Figure S4.** $^{31}P\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

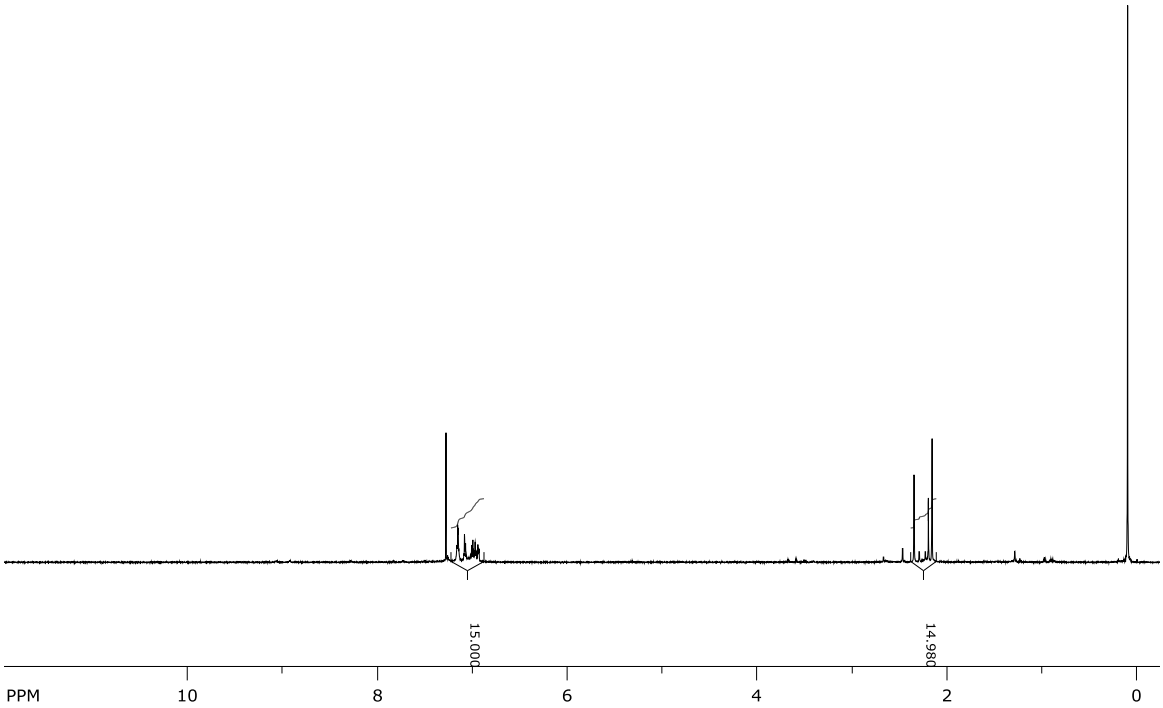



**Figure S5.** $^{1}H$ NMR spectrum of **5** in $CDCl_3$.

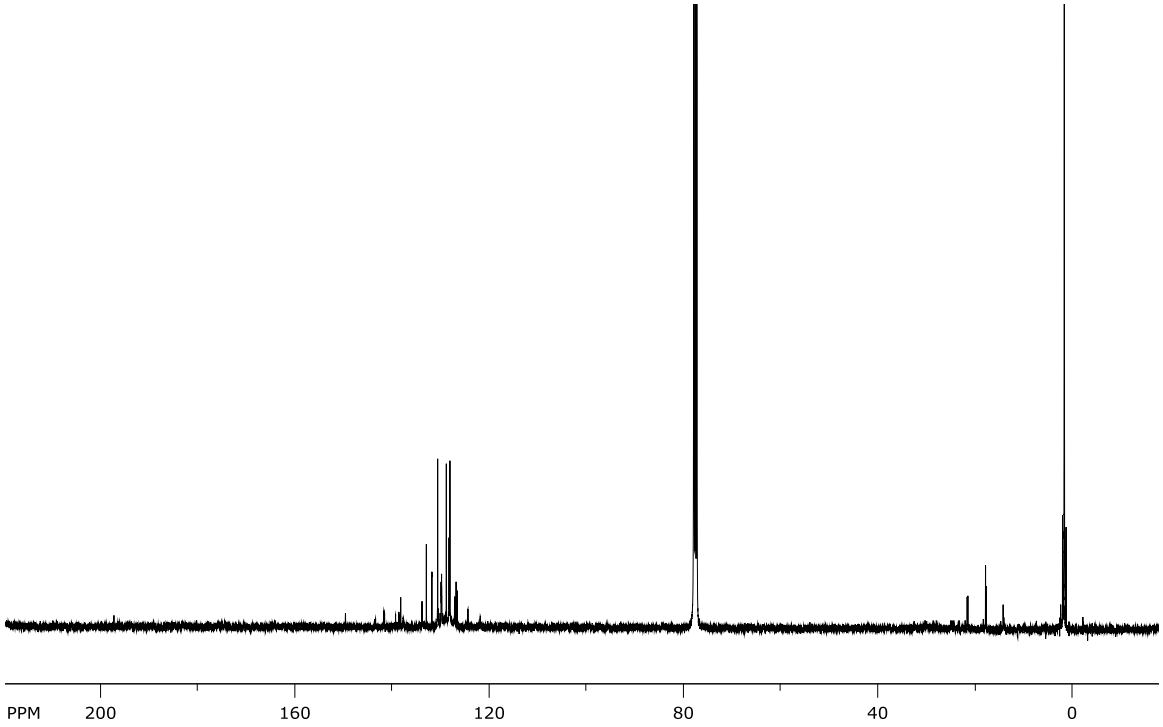
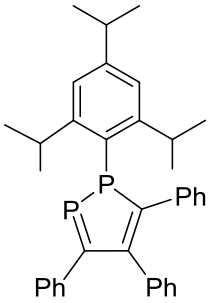



**Figure S6.** $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$.

## 3. Experimental $^{31}P$, $^{1}H$, $^{13}C$ NMR spectra for 6.



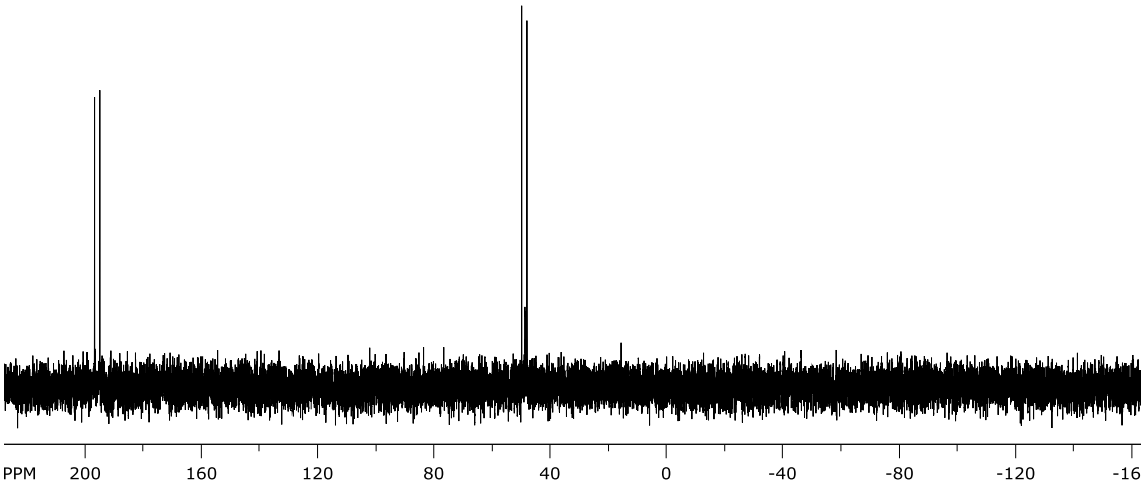




**Figure S7.** $^{31}P\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

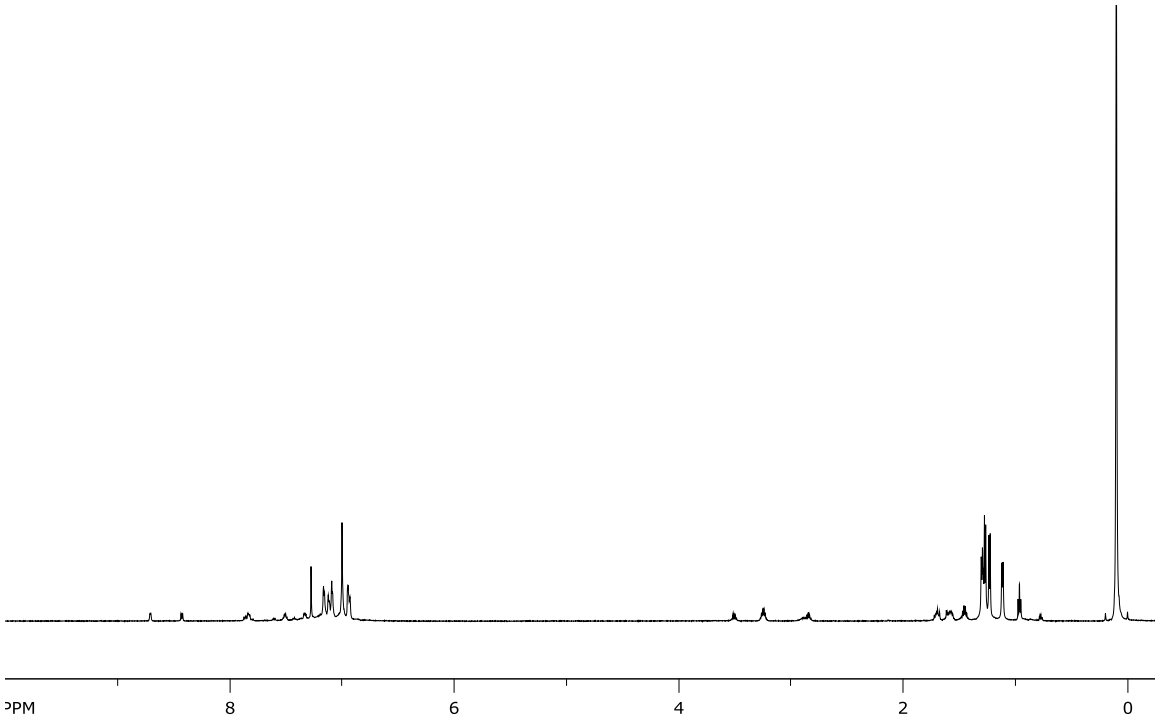



**Figure S8.** $^{1}H$ NMR spectrum of **6** in $CDCl_3$.

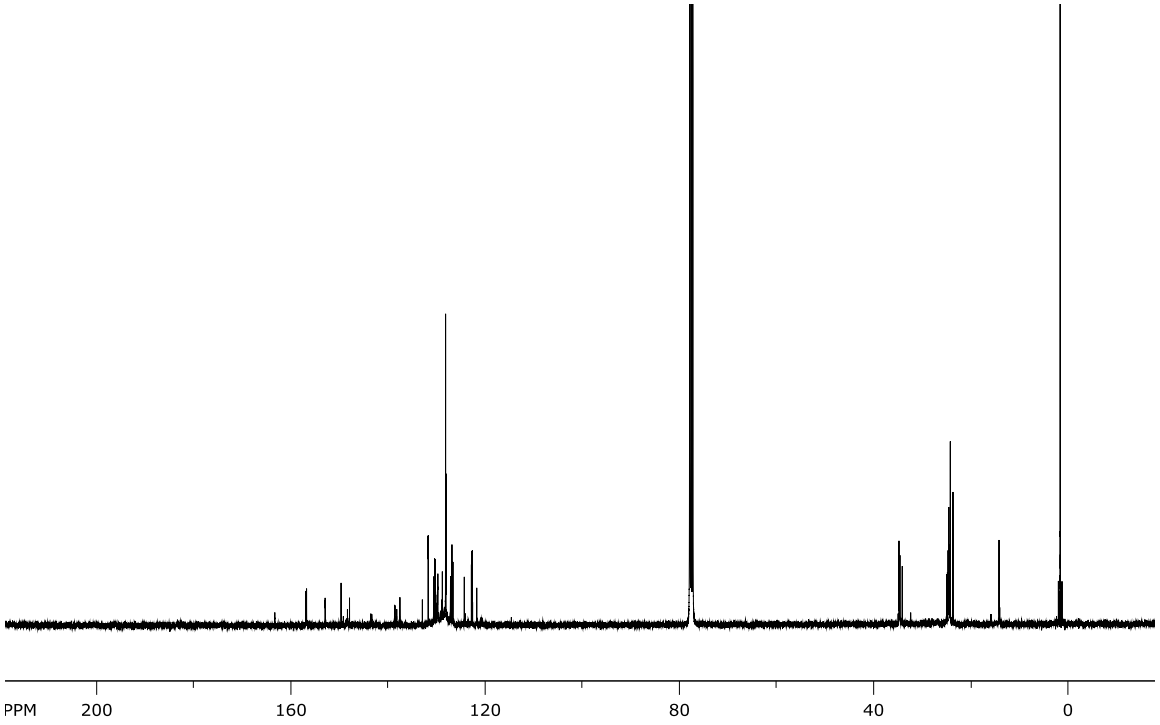
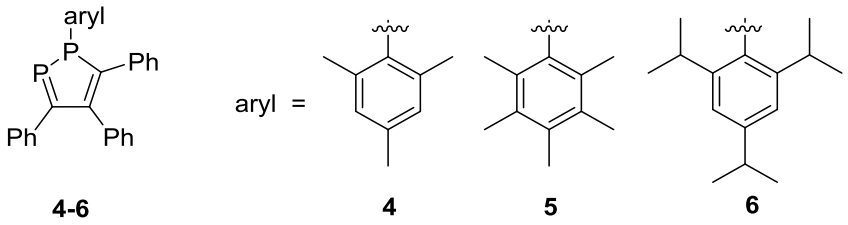



**Figure S9.** $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$.

## 4. Gas chromatography mass spectrometry (GC/MS) for 4-6.

GC/MS proves the formation of **4-6** in each case. The signals of molecular ions with *m/z* 448 (**4**), *m/z* 476 (**5**) and *m/z* 532 (**6**) were detected in the electron ionization (EI) mass spectra.




**4-6** **4** **5** **6**

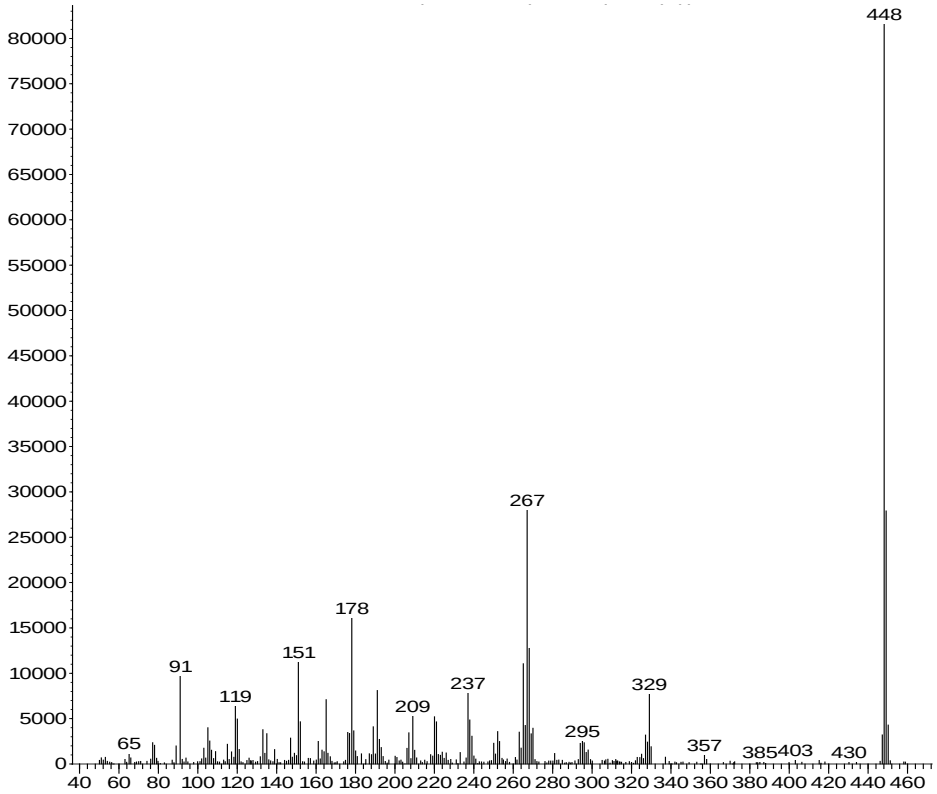



**Figure S10.** EI mass spectra of compound **4**.

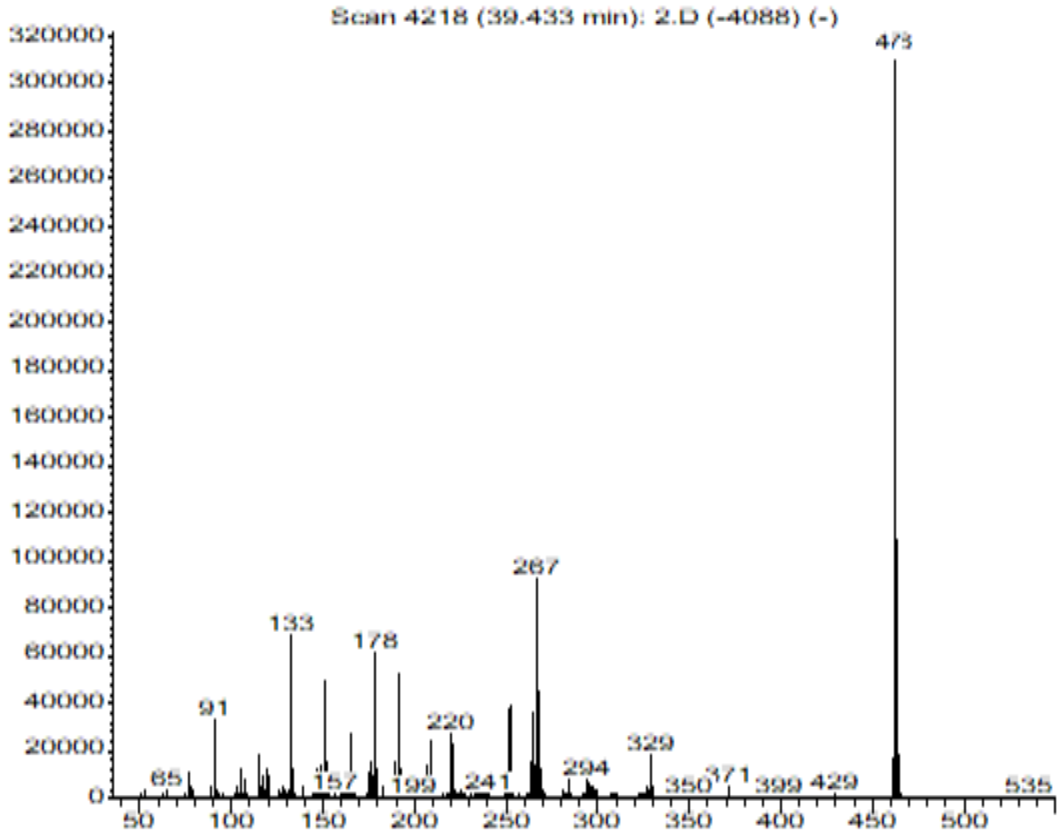



**Figure S11.** EI mass spectra of compound **5**.

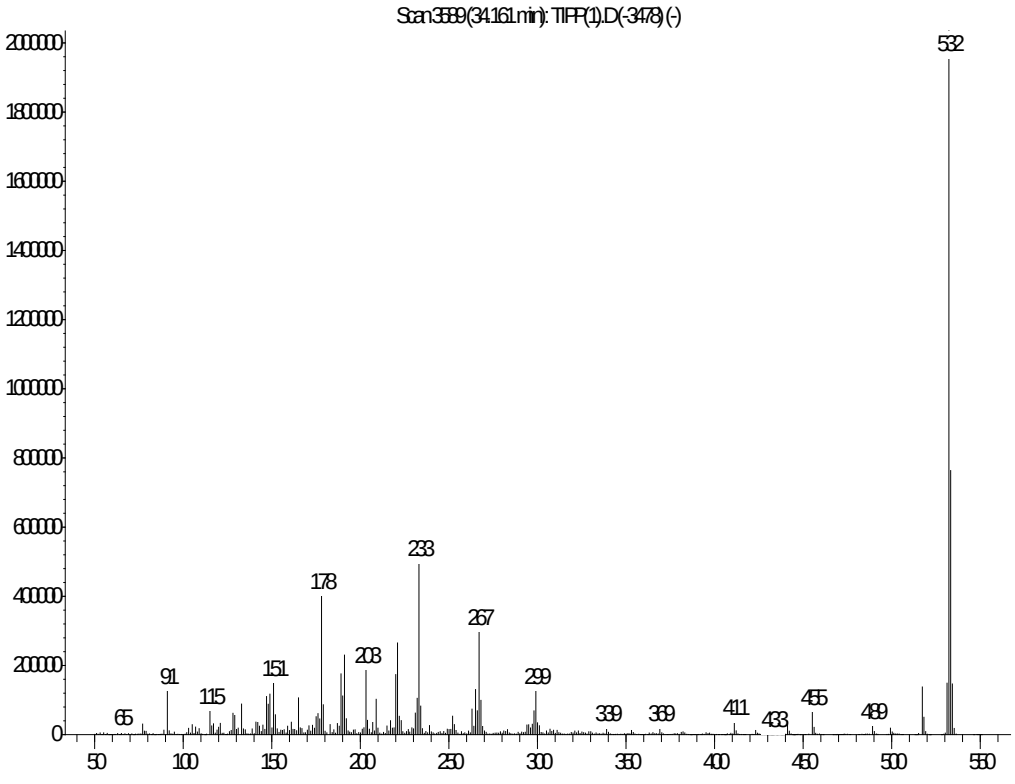
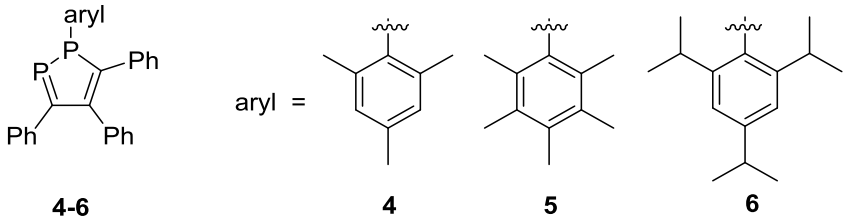



**Figure S12.** EI mass spectra of compound **6**.

# 5. Experimental IR spectra for 4-6.



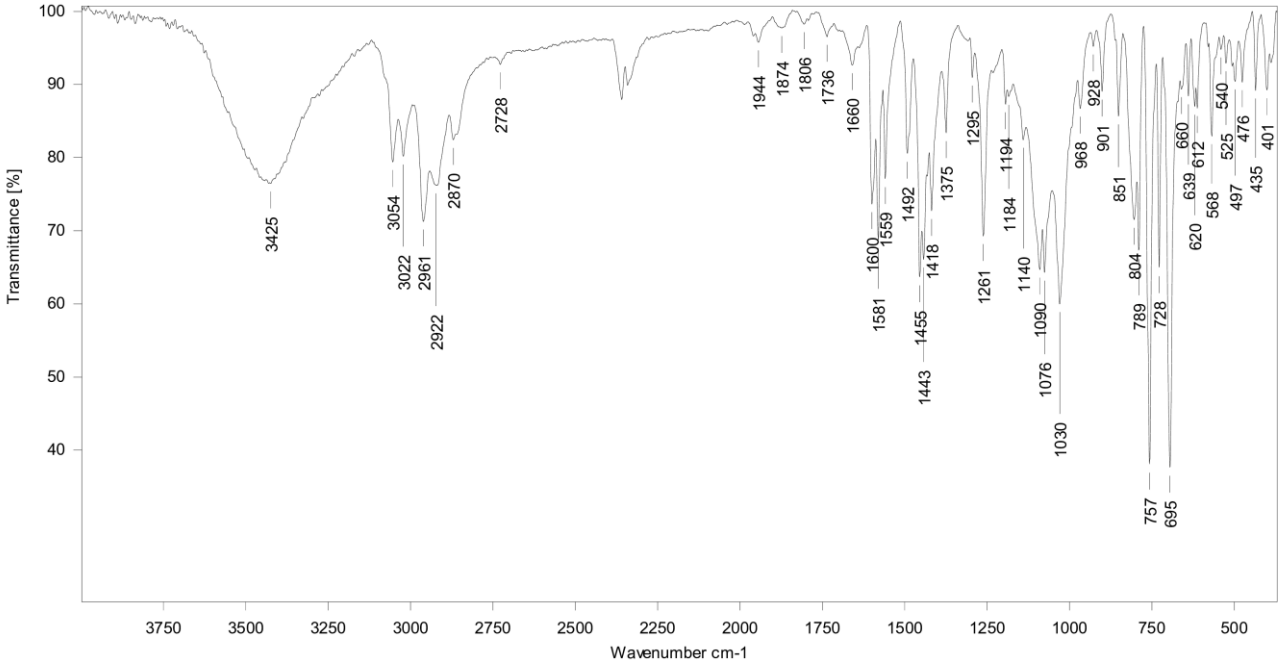




**Figure S13.** IR spectrum of compound **4**.

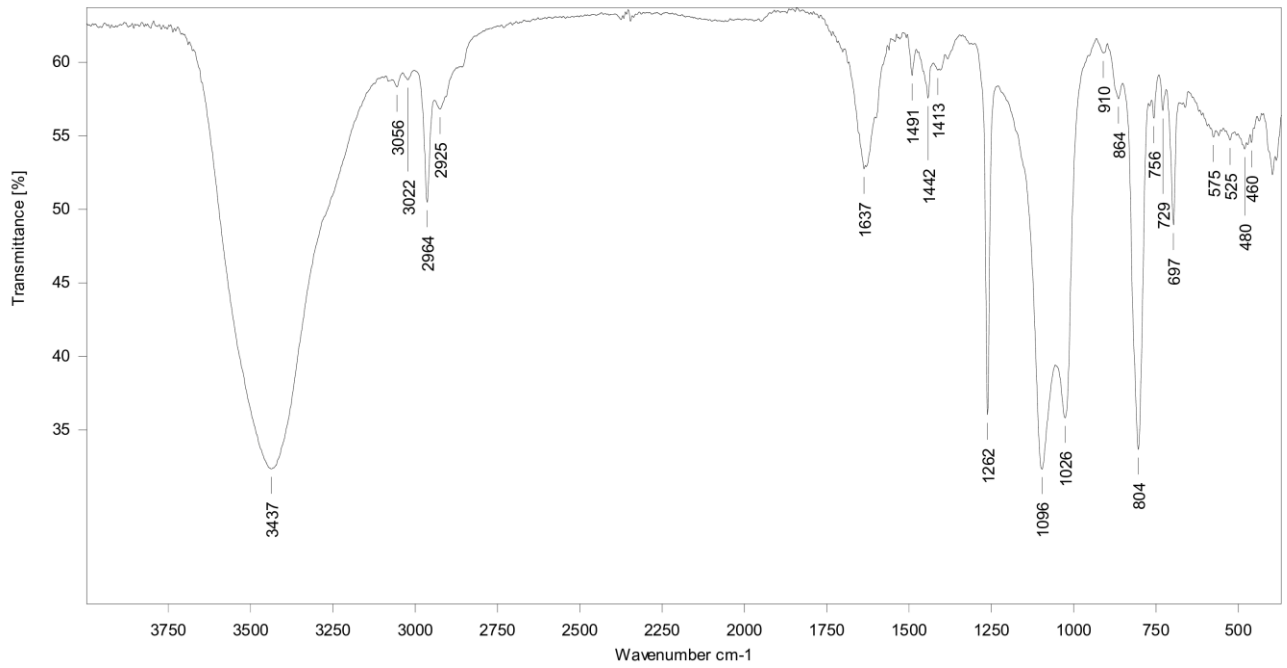



**Figure S14.** IR spectrum of compound **5**.

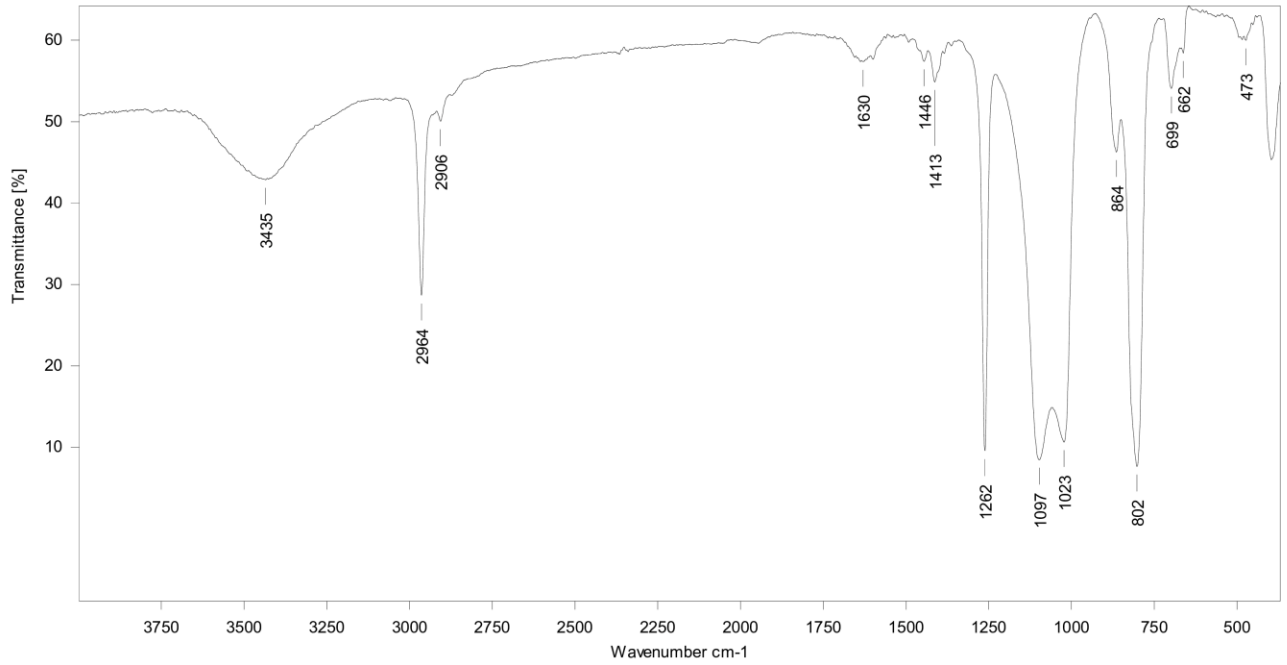



**Figure S15.** IR spectrum of compound **6**.

## 6. X-ray diffraction experiment and molecular structure for 4.

**Table S1.** Crystal parameters of compound **4** and conditions of X-ray diffraction experiment.

| Parameter | **4** |
|---|---|
| Color, habit | Yellow, formless |
| Crystal dimensions, mm | 0.40 × 0.20 × 0.15 |
| Moiety Formula<br>Sum Formula | $C_{30}H_{26}P_2$, 0.5($C_{10}H_8N_2$)<br>$C_{35}H_{30}NP_2$ |
| Molecular mass | 471.75 |
| Crystal System | monoclinic |
| Space group | C2/c (№ 15) |
| Cell parameters, Å, angles, deg | *a* = 24.2770(8),<br>*b* = 15.3360(6),<br>*c* = 17.4979(11),<br>α = 90,<br>β = 119.683(1),<br>γ = 90 |
| Cell volume, $Å^3$ | 5659.8(5) |
| *Z* | 8 |
| D(calc) [$g/cm^3$] | 1.236 |
| μ(MoKa) [ /mm ] | 0.178 |
| Absorption correction | multi-scan |
| Radiation (λ, Å) | $MoK_\alpha$, 0.71073 |
| F(000) | 2216 |
| Reflections measured | 100232 |
| Independent reflections | 7592 |
| R(int) | 0.076 |
| Observed reflections I > 2σ(I) | 6325 |

| | |
|---|---|
| R-factors, I > 2σ(I) | $R^1$ = 0.0385,<br>$wR^2$ = 0.0986 |
| R-factors, total | $R^1$ = 0.0489,<br>$wR^2$ = 0.1043 |
| goodness of fit | 0.994 |
| refine_ls_number_parameters | 346 |
| Index range | $-33 \le h \le 33$,<br>$-21 \le k \le 20$,<br>$-23 \le l \le 23$ |
| Theta Min-Max [Deg] | 1.9, 29.1 |
| Min. and Max. Resd. Dens. [e·Å$^{-3}$] | –1.57, 1.9 |
| CCDC No | 2255352 |

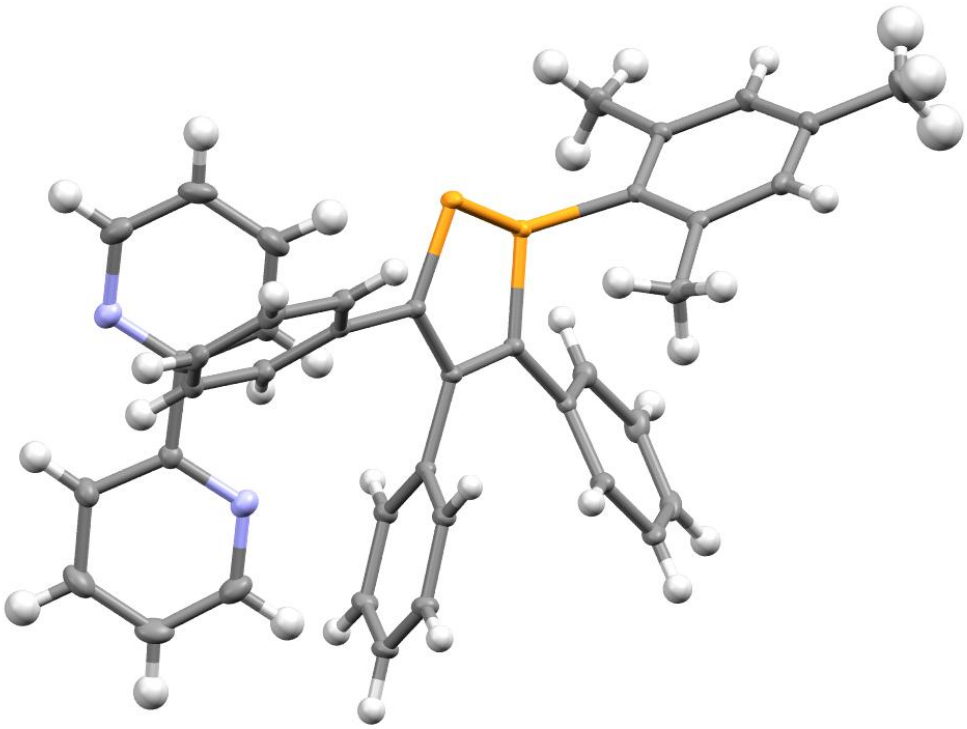
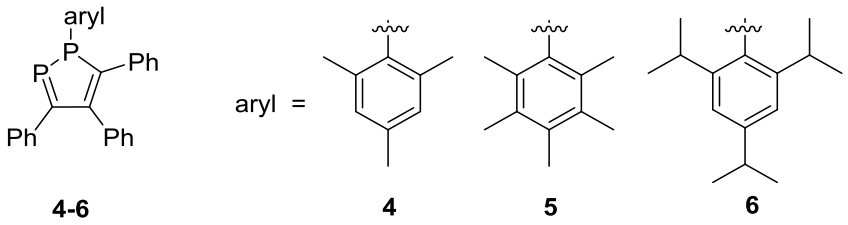


**Figure S16.** Geometry of the asymmetric part of the crystal of **4**. Ellipsoids of anisotropic displacements are shown with a probability 50%.

## 7. Solid-state excitation and emission spectra of compounds 4-6.



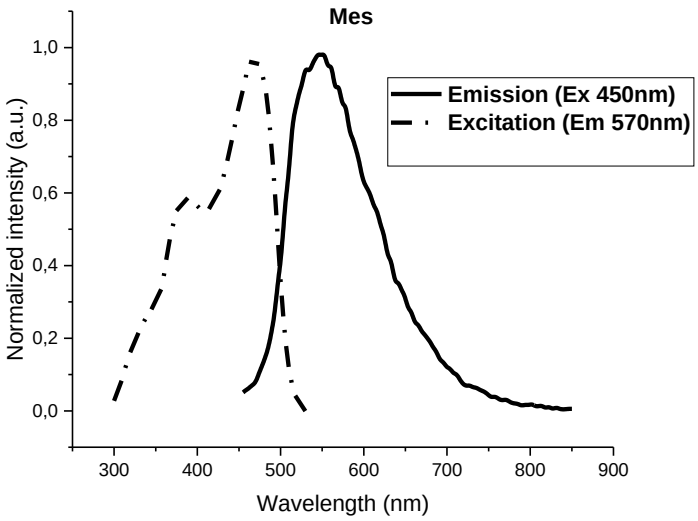




**Figure S17**. Solid-state excitation and emission spectra of compound **4**.

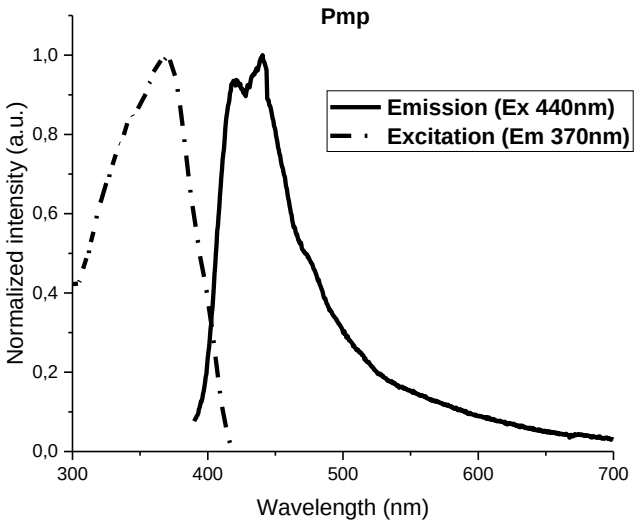



**Figure S18**. Solid-state excitation and emission spectra of compound **5**.

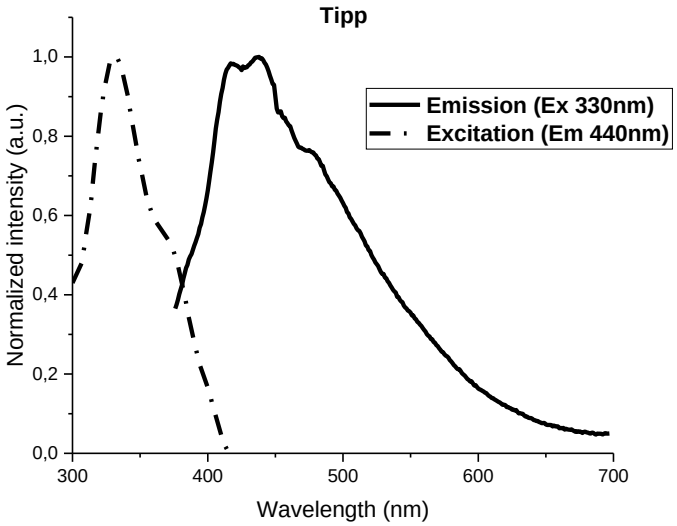



**Figure S19**. Solid-state excitation and emission spectra of compound **6**.

## 8. ESR spectra of obtained in the reaction Ni(0)-species.

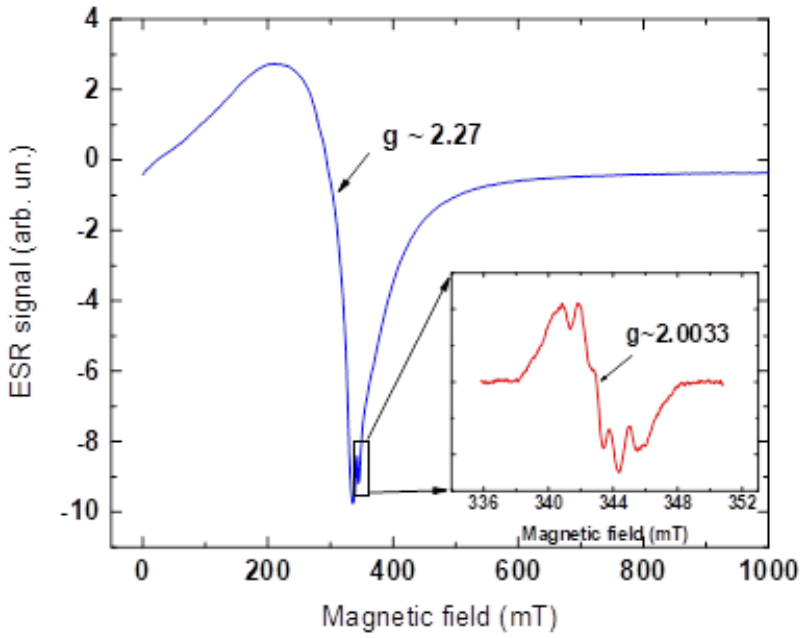
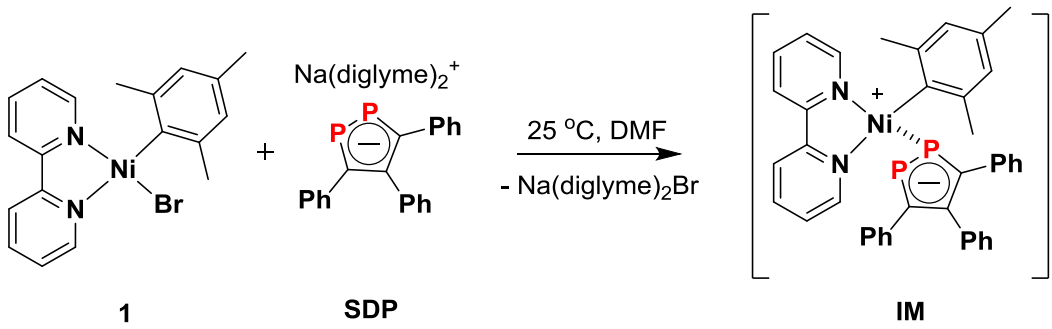



**Figure S20.** ESR spectrum recorded at ambient temperature. In the inset, another low intensity spectrum is shown.

## 9. ESI-MS of reaction intermediate (IM).



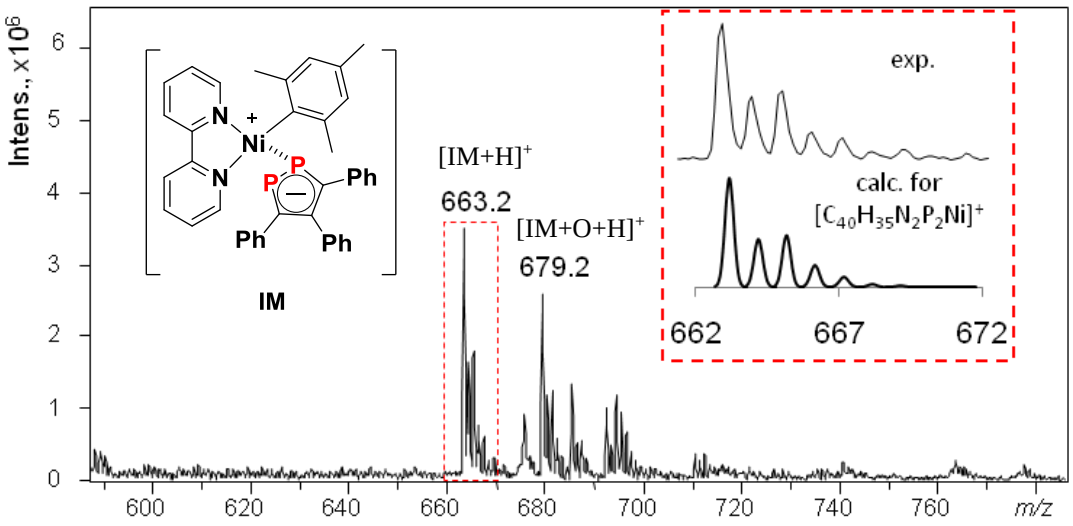




**Figure S21.** ESI mass spectrum of the reaction mixture (the mass range of 590-780).

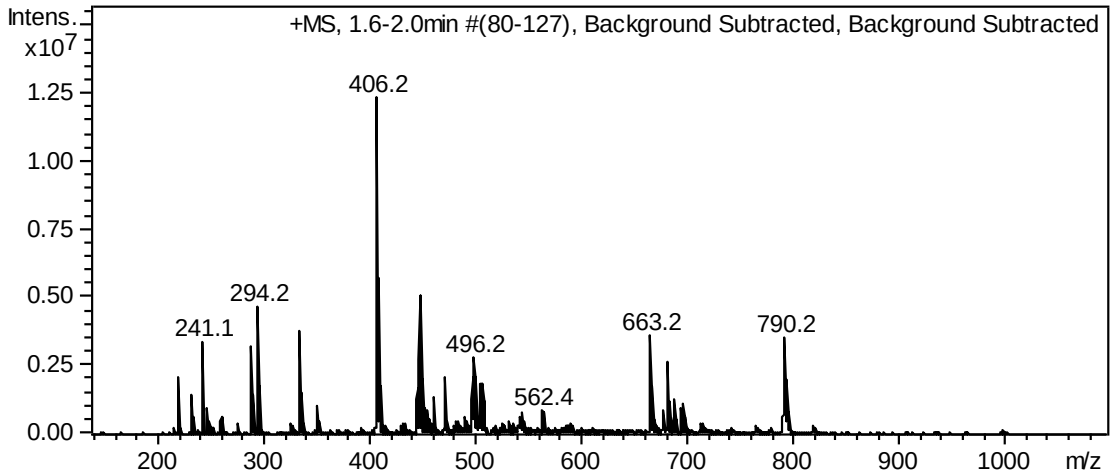
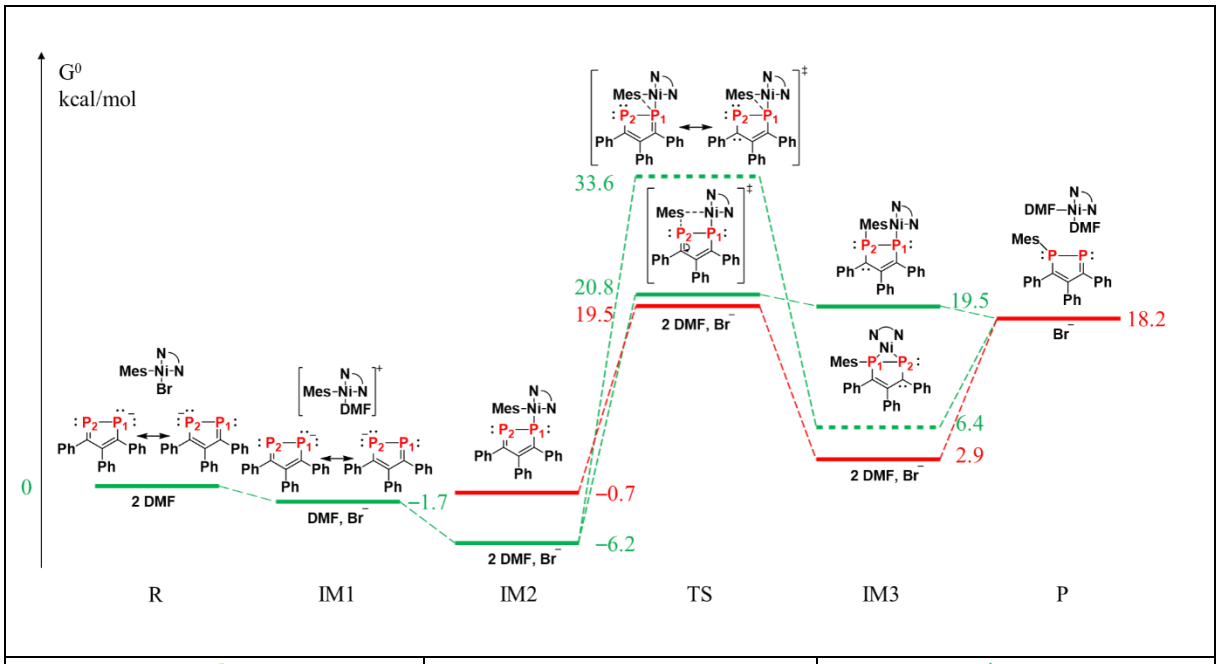


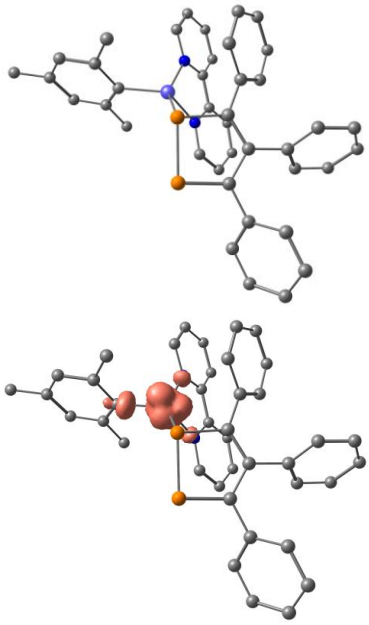
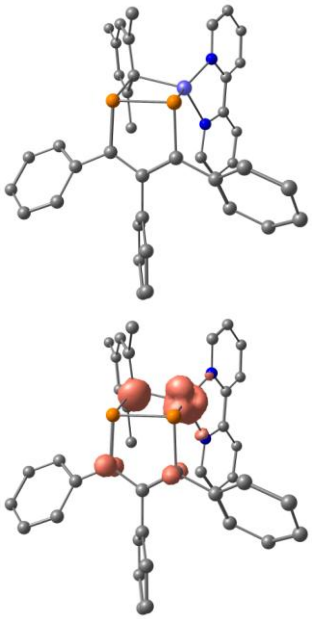
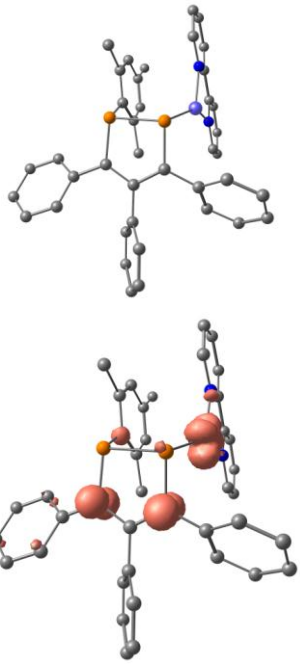
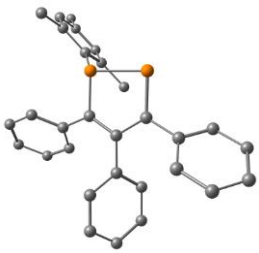
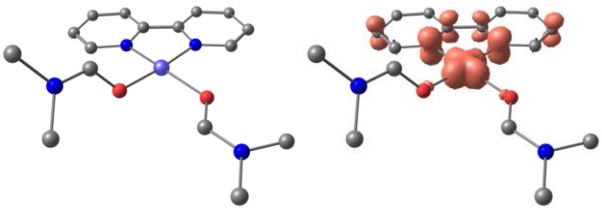

**Figure S22.** ESI mass spectrum of the reaction mixture (the mass range of 150-1100).

## 10. Quantum-chemical calculations.

**Table S2.** Computed free-energy profile and optimized structures of reactants (R), intermediates (IM) and transition states (TS) involved in the formation of 1-(2,4,6-trimethylphenyl)-3,4,5-triphenyl-1,2-diphosphole (**4**), along with spin-density distributions for triplet-state structures. Singlet-state paths and structures are marked in green, triplet-state ones – in red.




| | | |
|---|---|---|
| complex **1** | DP | $^1$IM1 |
| $^1$IM2 | $^1$TS (path 1) | $^1$IM3 (path 1) |
| $^1$IM2 | $^1$TS (path 2) | $^1$IM3 (path 2) |

| | | |
|---|---|---|
| $^3$IM2 | $^3$TS (path 2) | $^3$IM3 (path 2) |
|  |  |  |
| product **4** | $^3$[Ni(bpy)(DMF)$_2$] | |
|  |  | |

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