Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of compounds with C-P-P and C=P-P bond systems based on the phospha-Wittig reaction

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Titanium complexes, phosphanylphosphido ligand, phospha-Wittig reaction, coordination chemistry, X-ray analysis, DFT calculations, NMR spectroscopy analysis.

PART A. NMR DATA

1. *NMR spectra of reaction mixture after reaction of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-PtBu$_2$}] (**1**) with Ph$_2$C=O.*

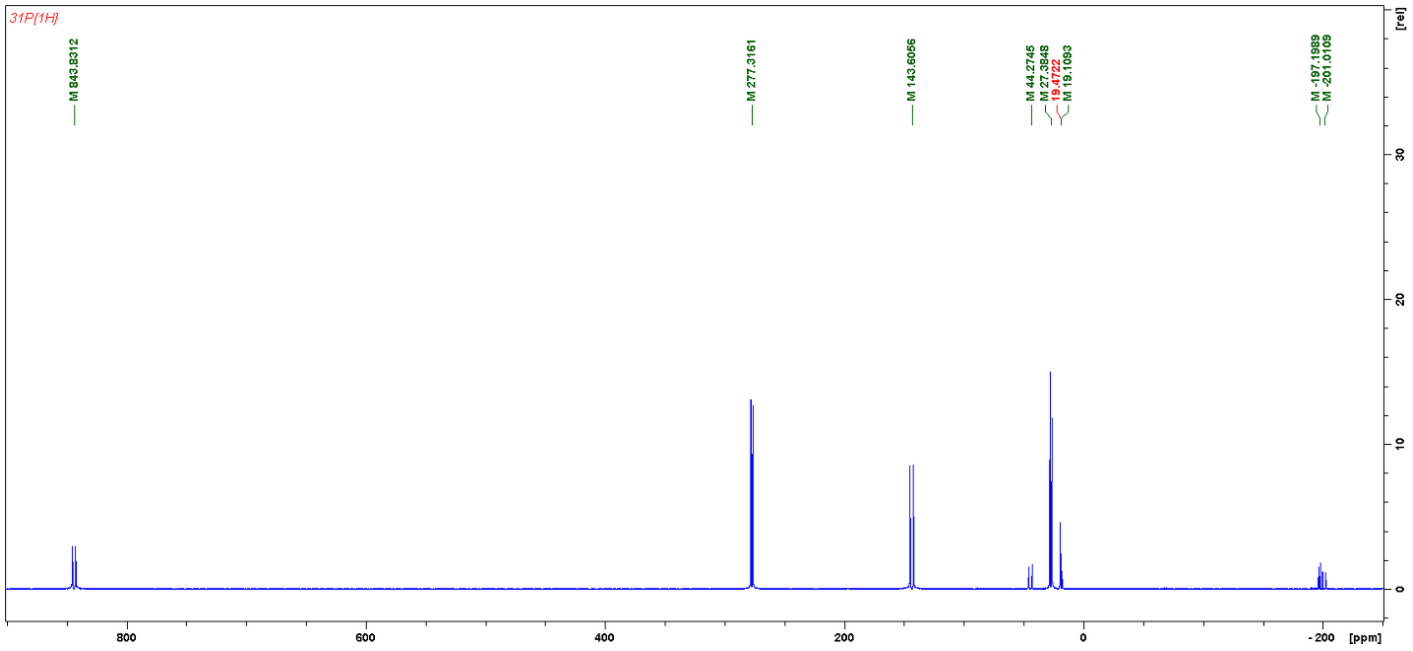

Figure S1. ^{31}P{^{1}H}-NMR spectrum of reaction mixture after reaction of [^{Me}NacNacTi(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] (**1**) with Ph$_2$C=O.

- 843.83 ppm, (d), J_{PP} = 450.5 Hz, [^{Me}NacNacTi(Cl)(η^2-**P**-P*t*Bu$_2$}];
- 277.32 ppm, (d), J_{PP} = 232.5 Hz, Ph$_2$C=**P**-P*t*Bu$_2$;
- 143.60 ppm, (d), J_{PP} = 450.5 Hz, [^{Me}NacNacTi(Cl)(η^2-P-**P***t*Bu$_2$}];
- 44.27 ppm, (d), J_{PP} = 399.6 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)$_2$;
- 27.38 ppm, (d), J_{PP} = 232.5 Hz, Ph$_2$C=P-**P***t*Bu$_2$;
- 19.47 ppm, (s), *t*Bu$_2$**P**H;
- 19.11 ppm, (d), J_{PP} = 196.2 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H;
- -197.20 ppm, (d), J_{PP} = 196.2 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H;
- -201.01 ppm, (d), J_{PP} = 399.6 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)$_2$;

2. *NMR spectra of reaction mixture after reaction of **1** with 9-fluorenone.*

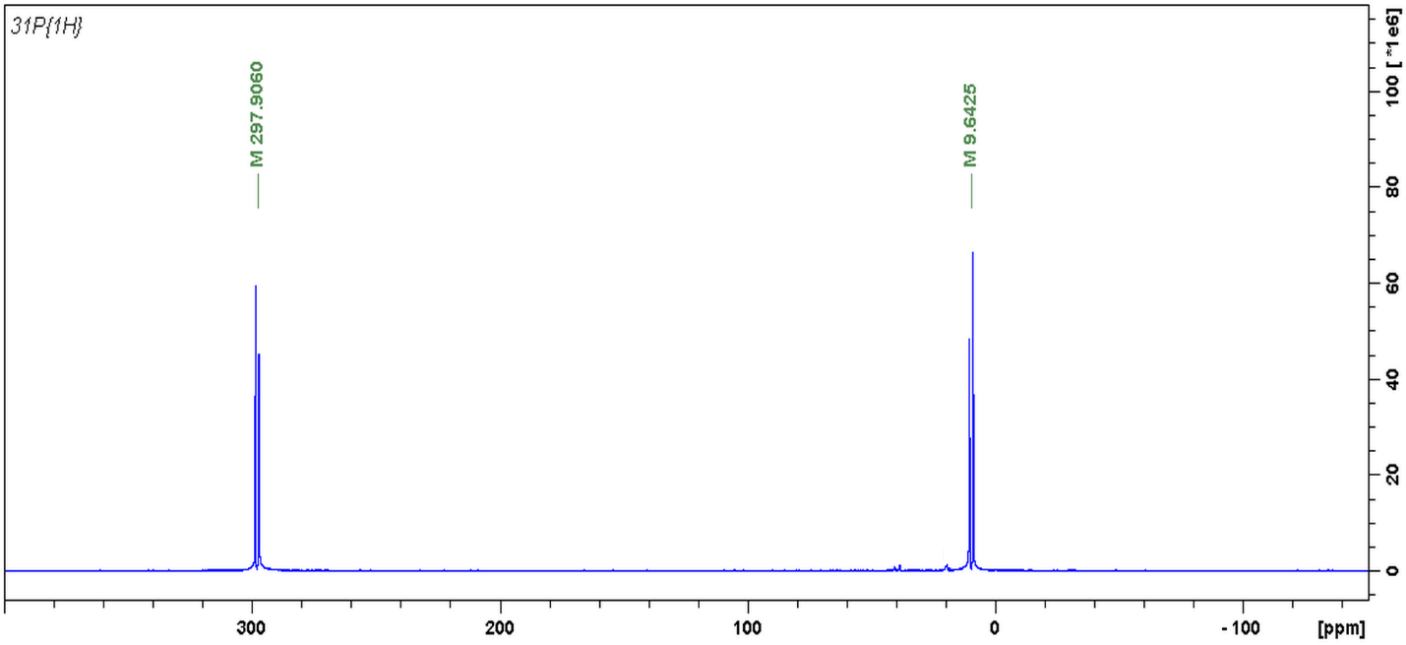

Figure S2. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture after reaction of **1** with 9-fluorenone.

- 297.91 ppm, (d), J_{PP} = 232.5 Hz, (fluorenyl)C=**P**-P*t*Bu$_2$;
- 9.64 ppm, (d), J_{PP} = 232.5 Hz, (fluorenyl)C=P-**P***t*Bu$_2$;

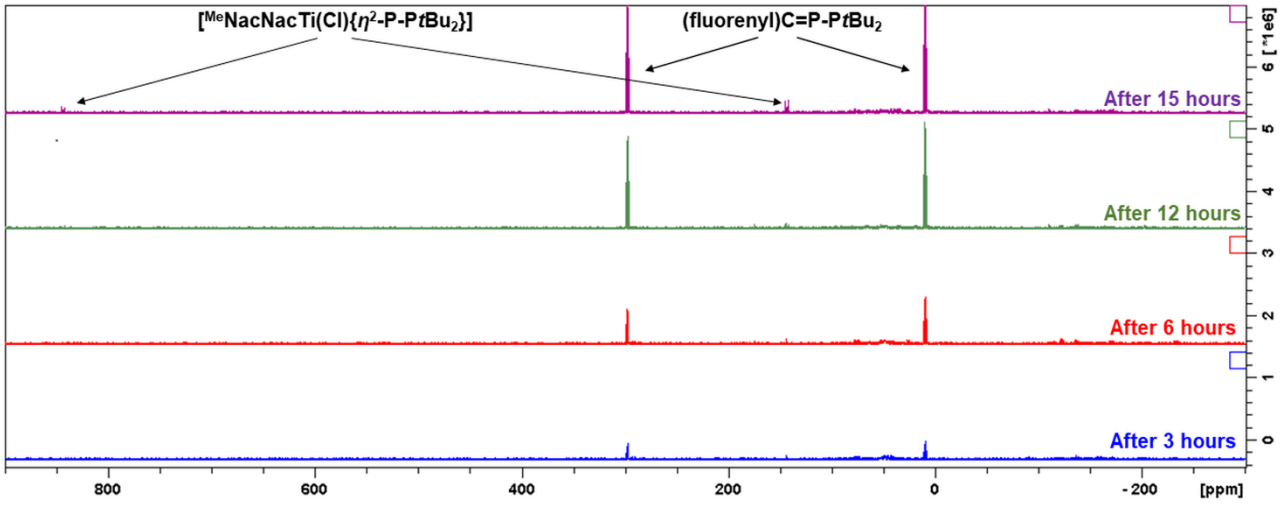

Figure S3. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture after reaction of **1** with 9-fluorenone (molar ratio 1:1) measured after 3, 6, 12 and 15 hours.

3. *NMR spectra of reaction mixture of reaction of **1** with (Ph)MeC=O and of isolated phosphanylphosphaalkene (Ph)MeC=P-PtBu$_2$.*

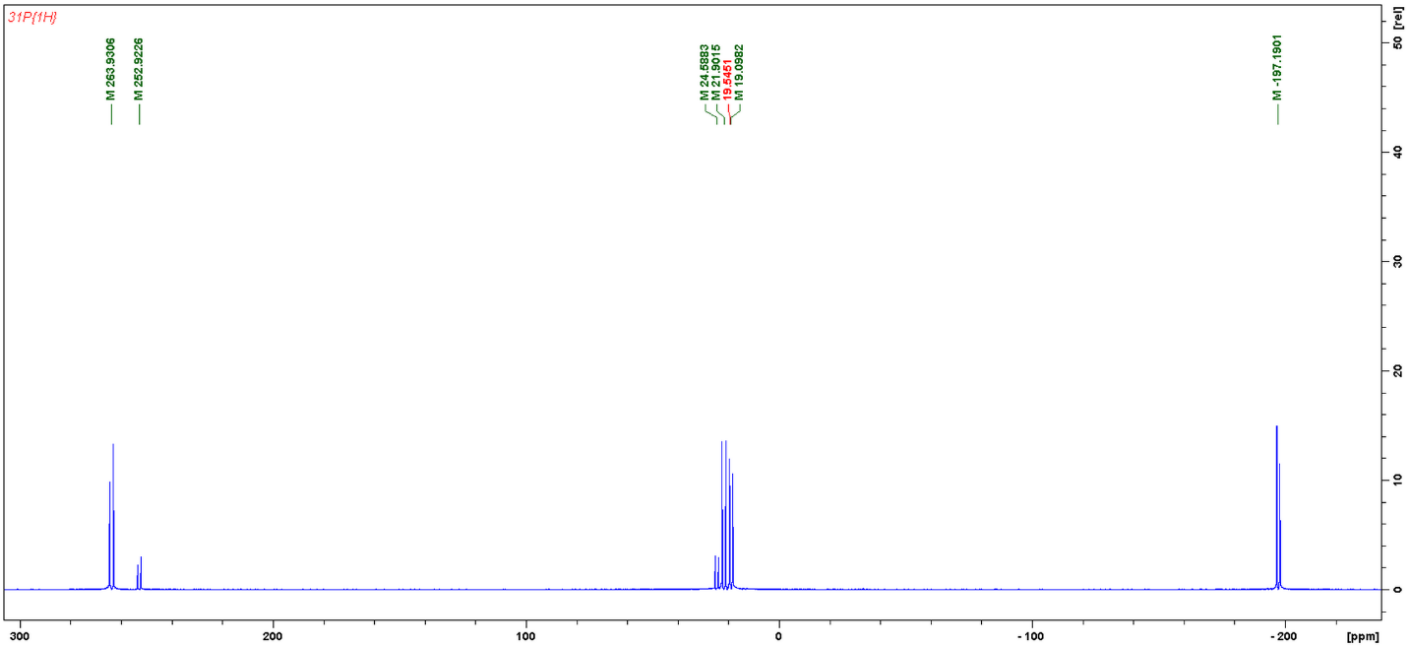

Figure S4. $^{31}P\{^{1}H\}$-NMR spectrum of the reaction mixture of **1** with acetophenone.

E - isomer:

- 263.93 ppm, (d), J_{PP} = 234.9 Hz, (Ph)MeC=**P**-P*t*Bu$_2$;
- 21.90 ppm, (d), J_{PP} = 234.9 Hz, (Ph)MeC=P-**P***t*Bu$_2$;

Z - isomer:

- 252.92 ppm, (d), J_{PP} = 222.8 Hz, (Ph)MeC=**P**-P*t*Bu$_2$;
- 24.59 ppm, (d), J_{PP} = 222.8 Hz, (Ph)MeC=P-**P***t*Bu$_2$;

Another signals:

- 19.54 ppm, s, *t*Bu$_2$PH;
- 19.09 ppm, d, 190.7 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H;
- -197.19 ppm, d, 190.7 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H;

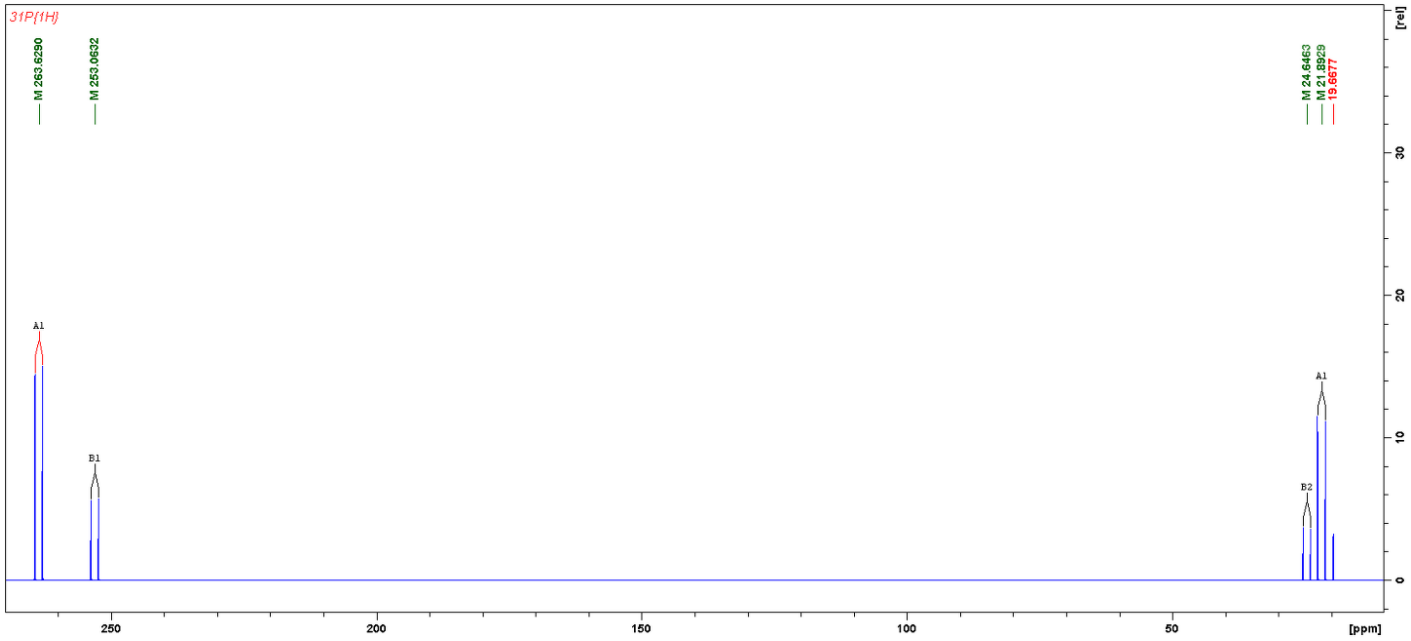

Figure S5. $^{31}P\{^{1}H\}$-NMR spectrum of isolated phosphanylphosphaalkene (Ph)MeC=P-P*t*Bu$_2$.

E - isomer:

- 263.63 ppm, (d), J_{PP} = 234.9 Hz, (Ph)MeC=**P**-P*t*Bu$_2$;
- 21.89 ppm, (d), J_{PP} = 234.9 Hz, (Ph)MeC=P-**P***t*Bu$_2$;

Z - isomer:

- 253.06 ppm, (d), J_{PP} = 222.8 Hz, (Ph)MeC=**P**-P*t*Bu$_2$;
- 24.65 ppm, (d), J_{PP} = 222.8 Hz, (Ph)MeC=P-**P***t*Bu$_2$;

19.67 ppm, s, *t*Bu$_2$PH;

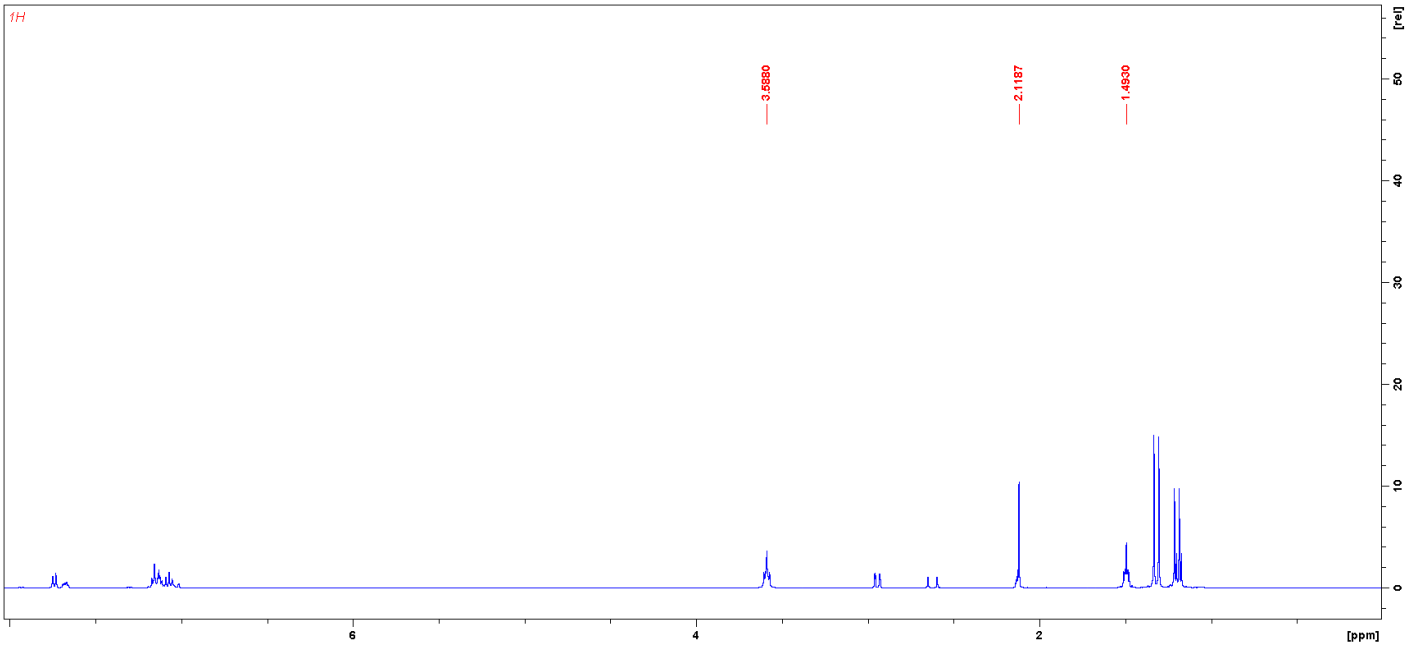

Figure S6. ^{1}H-NMR spectrum of isolated phosphanylphosphaalkene (Ph)MeC=P-P*t*Bu$_2$.

- 3.59 ppm and 1.45 ppm, pent., protons of THF;
- 2.12 ppm, tol-d$_8$ protons;
- From 8.00 ppm to 7.00 ppm, aromatic protons of phenyl groups from the phosphanylphosphaalkene isomers and toluene-d$_8$;

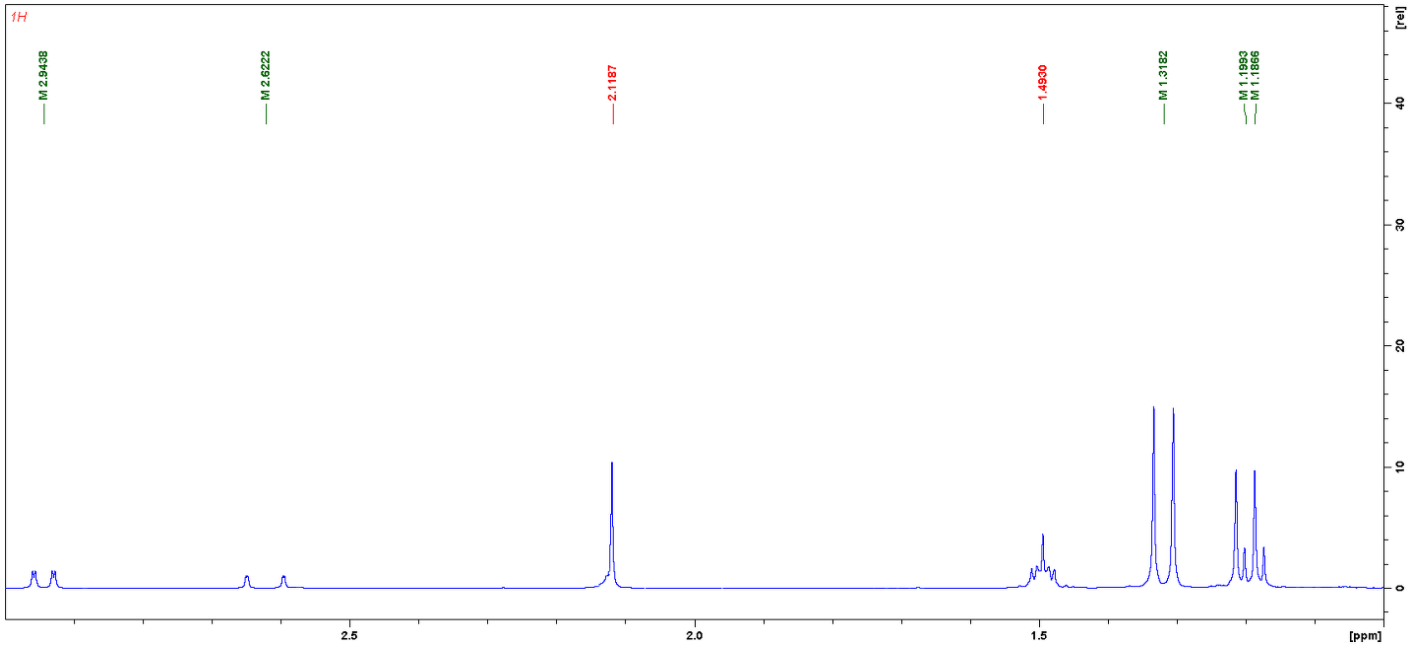

Figure S7. ^{1}H-NMR spectrum of isolated phosphanylphosphaalkene (Ph)MeC=P-P*t*Bu$_2$ in the range from 3.00 ppm to 1.00 ppm.

E - isomer:

- 2.94 ppm, (dd), J_{PH} = 11.4 Hz and J_{PH} = 1.6 Hz, (Ph)**Me**C=P-P*t*Bu$_2$;
- 1.32 ppm, (d), J_{PH} = 11.4 Hz, (Ph)MeC=P-P***t*Bu**$_2$;

Z - isomer:

- 2.62 ppm, (dd), J_{PH} = 21.4 Hz and J_{PH} = 0.9 Hz, (Ph)**Me**C=P-P*t*Bu$_2$;
- 1.19 ppm, (d), J_{PH} = 10.9 Hz, (Ph)MeC=P-P***t*Bu**$_2$;

1.18 ppm, (d), J_{PH} = 11.1 Hz, *t*Bu$_2$PH;

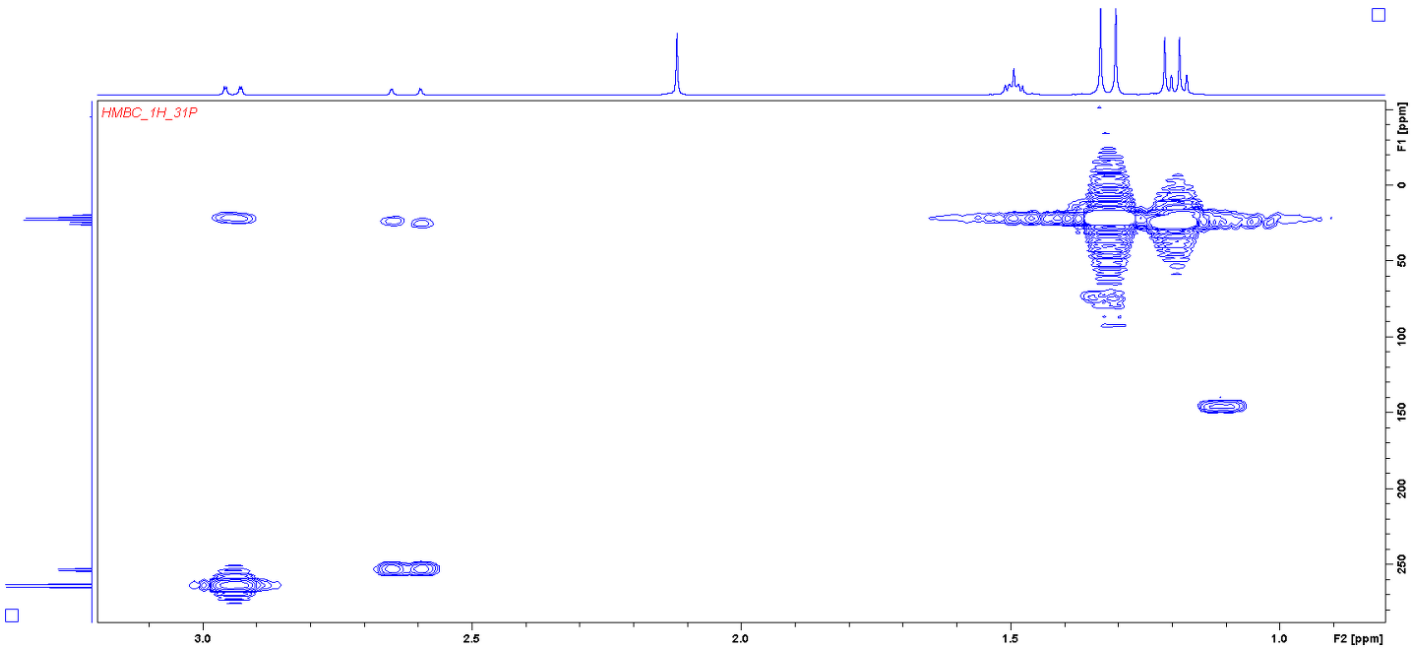

Figure S8. ^{1}H/^{31}P-HMBC correlation spectrum of isolated phosphanylphosphaalkene (Ph)MeC=P-P*t*Bu$_2$. Correlation between phosphorus atoms and *tert*-butyl and methyl groups.

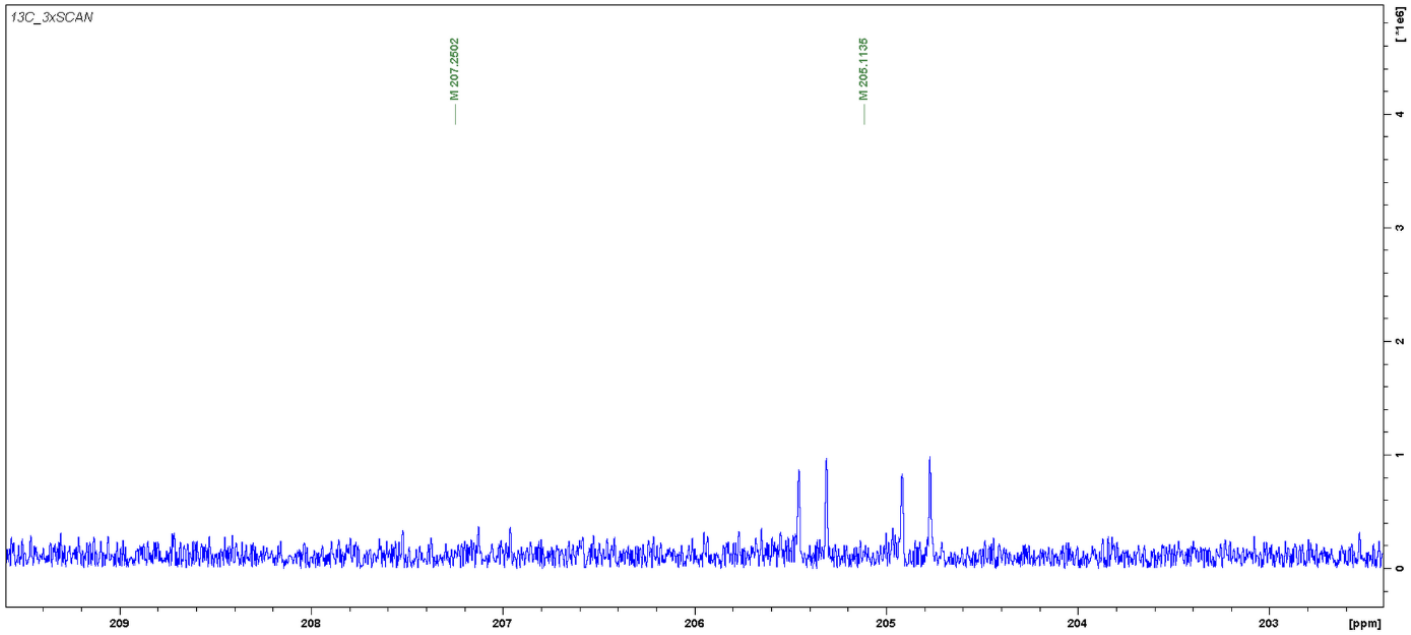

Figure S9. $^{13}C\{^{1}H\}$-NMR spectrum of isolated phosphanylphosphaalkene (Ph)MeC=P-P*t*Bu$_2$ in the range from 210 ppm to 202 ppm.

E - isomer:

- 205.11 ppm, (dd), J_{PC} = 53.6 Hz and J_{PC} = 14.53 Hz, (Ph)Me**C**=P-P*t*Bu$_2$;

Z - isomer:

- 207.25 ppm, (dd), J_{PC} = 39.7 Hz and J_{PC} = 14.9 Hz, (Ph)MeC=P-P*t*Bu$_2$;

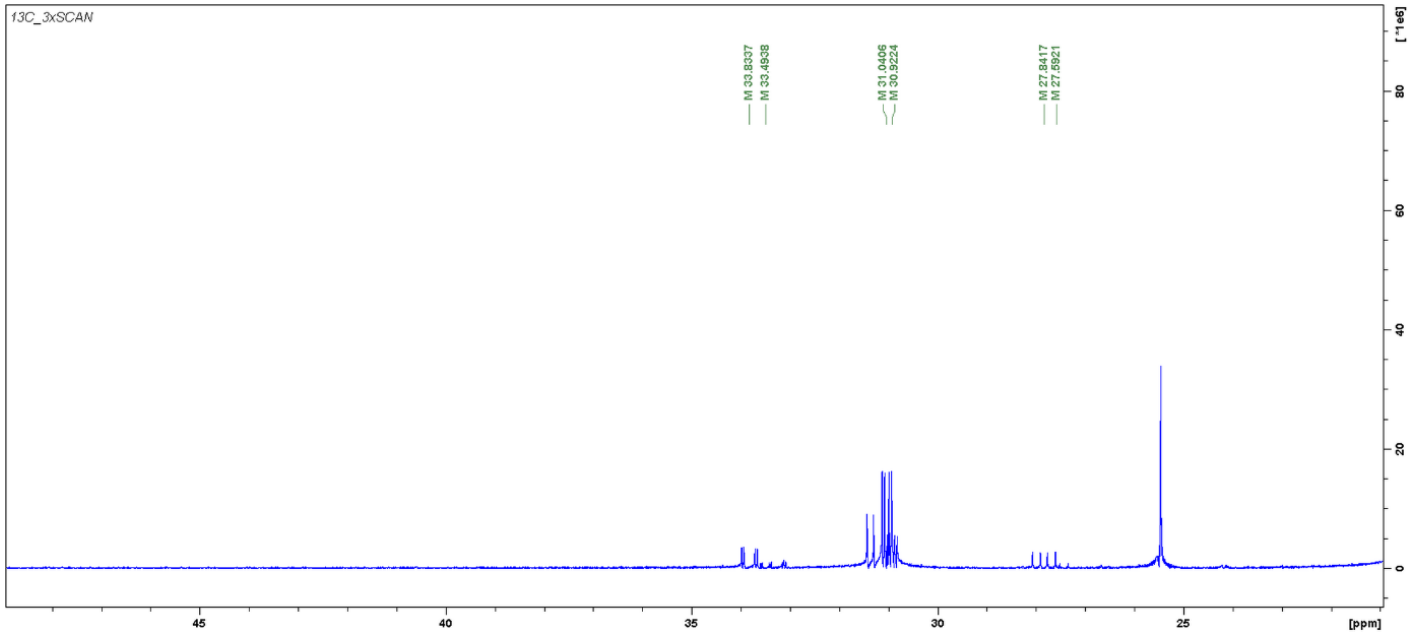

Figure S10. $^{13}C\{^{1}H\}$-NMR spectrum of isolated phosphanylphosphaalkene (Ph)MeC=P-P*t*Bu$_2$ in the range from 50 ppm to 20 ppm.

E - isomer:

- 33.83 ppm, (dd), J_{PC} = 27.2 Hz and J_{PC} = 4.2 Hz, (Ph)MeC=P-P***t*Bu**$_2$;
- 31.04 ppm, (dd), J_{PC} = 13.6 Hz and J_{PC} = 5.4 Hz, (Ph)MeC=P-P***t*Bu**$_2$;
- 27.84 ppm, (dd), J_{PC} = 29.9 Hz and J_{PC} = 16.3 Hz, (Ph)**Me**C=P-P*t*Bu$_2$;

Z - isomer:

- 33.49 ppm, (dd), J_{PC} = 17.6 Hz and J_{PC} = 3.7 Hz, (Ph)MeC=P-P***t*Bu**$_2$;
- 30.92 ppm, (dd), J_{PC} = 14.9 Hz and J_{PC} = 5.4 Hz, (Ph)MeC=P-P***t*Bu**$_2$;
- 27.59 ppm, (dd), J_{PC} = 27.4 Hz and J_{PC} = 16.0 Hz, (Ph)**Me**C=P-P*t*Bu$_2$;

4. *NMR spectra of dissolved complex **10** in THF and of isolated phosphanylphosphaalkene $(CH_2)_4C$=P-PtBu_2.*

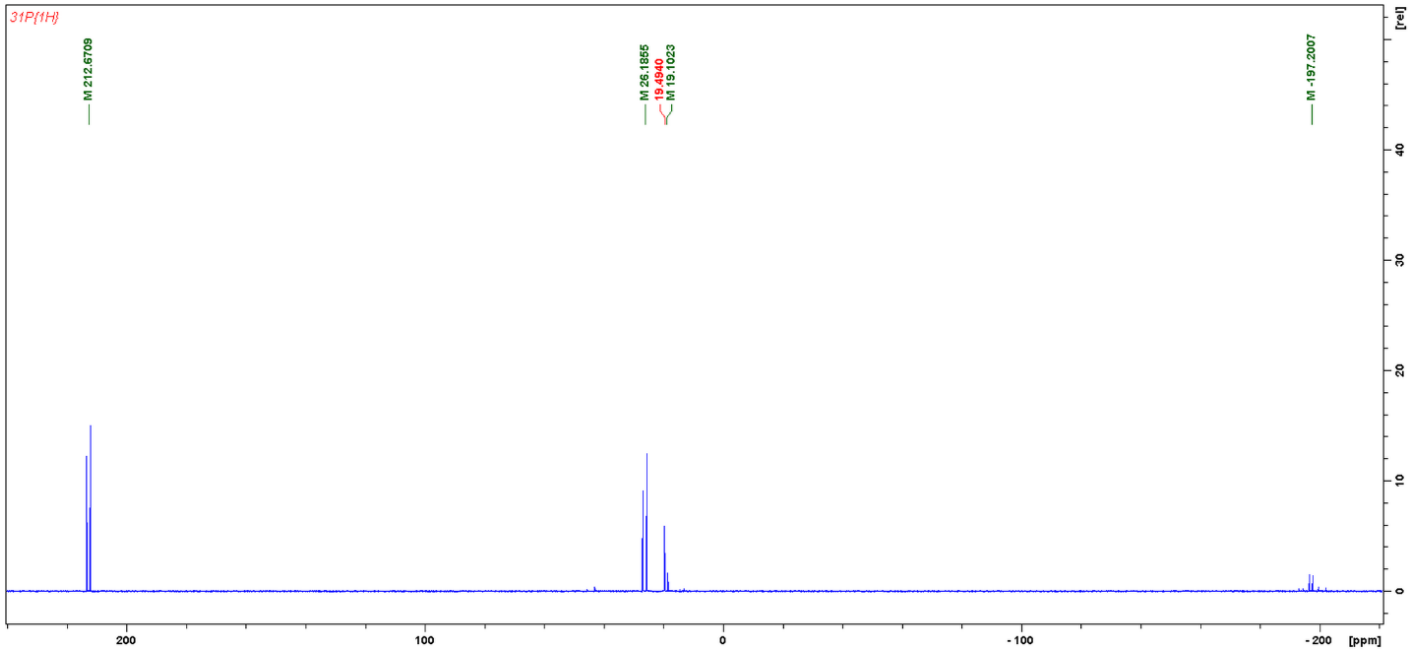

Figure S11. $^{31}P\{^{1}H\}$-NMR spectrum of dissolved complex **10** in THF.

- 212.67 ppm, (d), J_{PP} = 220.1 Hz, $(CH_2)_4C$=**P**-PtBu$_2$;
- 26.18 ppm, (d), J_{PP} = 220.1 Hz, $(CH_2)_4C$=P-**P**tBu$_2$;
- 19.49 ppm, (s), tBu$_2$PH;
- 19.10 ppm, (d), J_{PP} = 190.7 Hz, tBu$_2$**P**-P(SiMe$_3$)H;
- 19.10 ppm, (d), J_{PP} = 190.7 Hz, tBu$_2$P-**P**(SiMe$_3$)H;

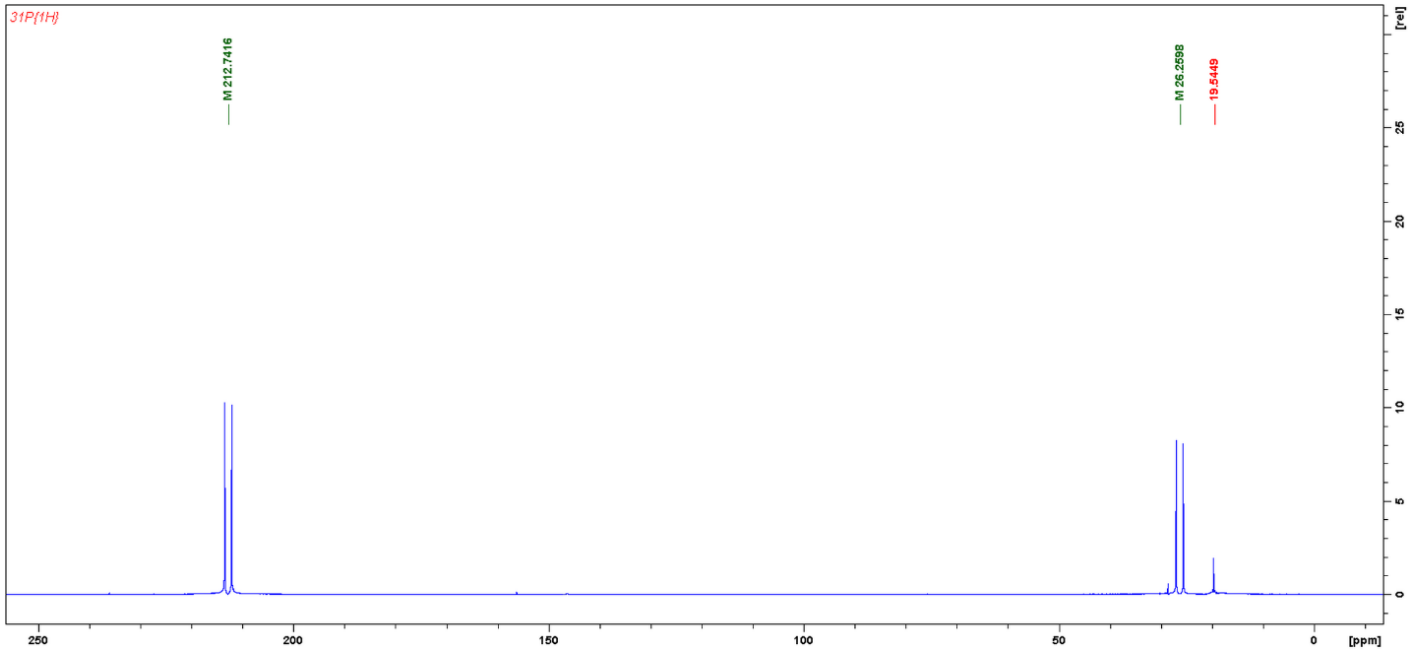

Figure S12. $^{31}P\{^{1}H\}$-NMR spectrum of isolated phosphanylphosphaalkene $(CH_2)_4C$=P-P*t*Bu_2.

- 212.74 ppm, (d), J_{PP} = 220.1 Hz, $(CH_2)_4C$=**P**-P*t*Bu_2;
- 26.26 ppm, (d), J_{PP} = 220.1 Hz, $(CH_2)_4C$=P-**P***t*Bu_2;
- 19.54 ppm, (s), *t*Bu_2PH;

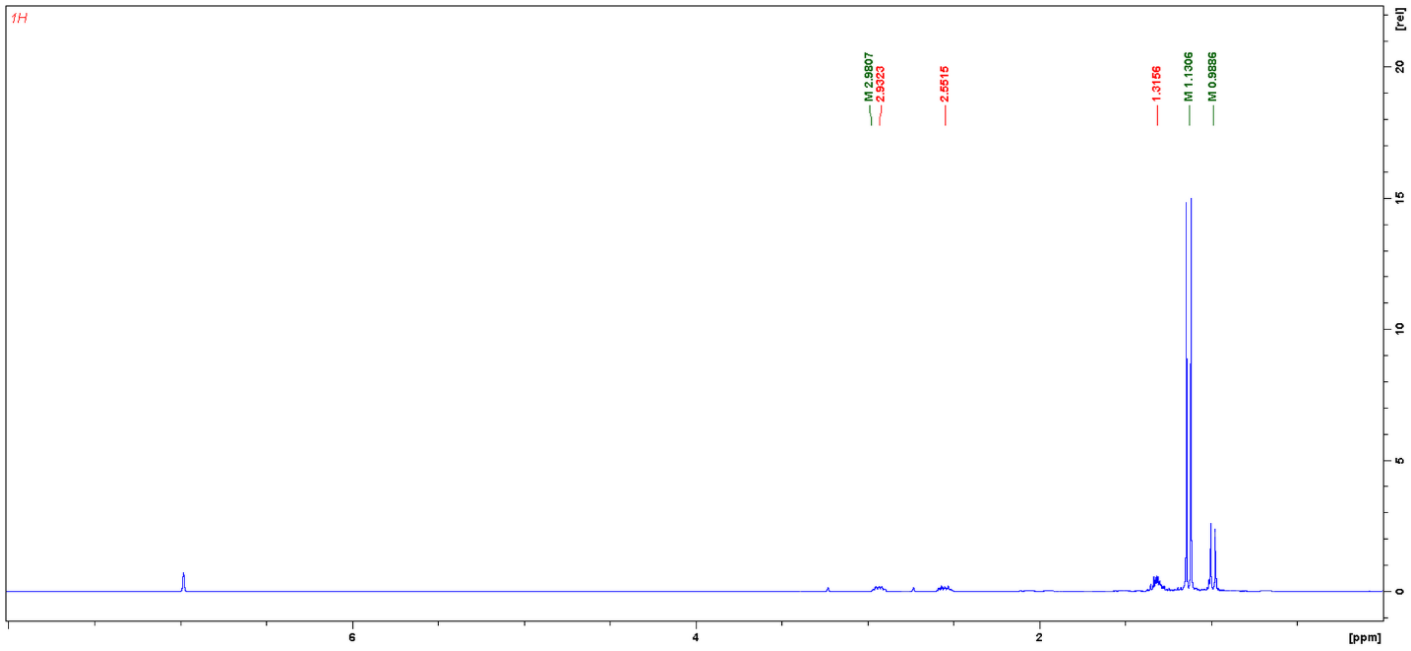

Figure S13. ^{1}H-NMR spectrum of isolated phosphanylphosphaalkene $(CH_2)_4C$=P-P*t*Bu_2.

- 2.98 ppm, (d), J_{PH} = 198.2 Hz, *t*Bu_2P**H**;
- 2. 93 ppm, (br. m.), $(CH_2)_4C$=P-P*t*Bu_2;
- 2.55 ppm, (br. m.), $(CH_2)_4C$=P-P*t*Bu_2;
- 1.31 ppm, (br. m.), $(CH_2)_4C$=P-P*t*Bu_2;
- 1.13 ppm, (d), J_{PP} = 11.1 Hz, $(CH_2)_4C$=P-P***t*Bu**$_2$;
- 0.99 ppm, (d), J_{PP} = 11.1 Hz; ***t*Bu**$_2$PH;

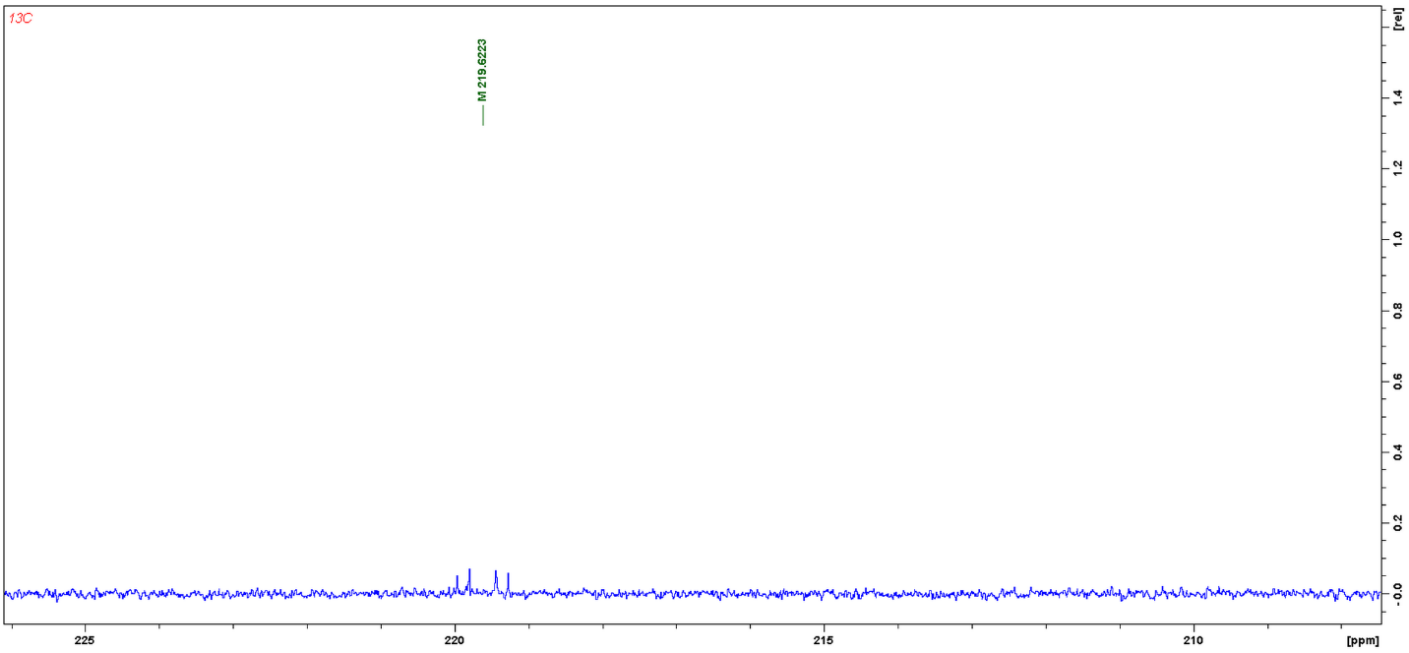

Figure S14. $^{31}C\{^{1}H\}$-NMR spectrum of isolated phosphanylphosphaalkene $(CH_2)_4C$=P-P*t*Bu$_2$ in the range from 225 ppm to 210 ppm.

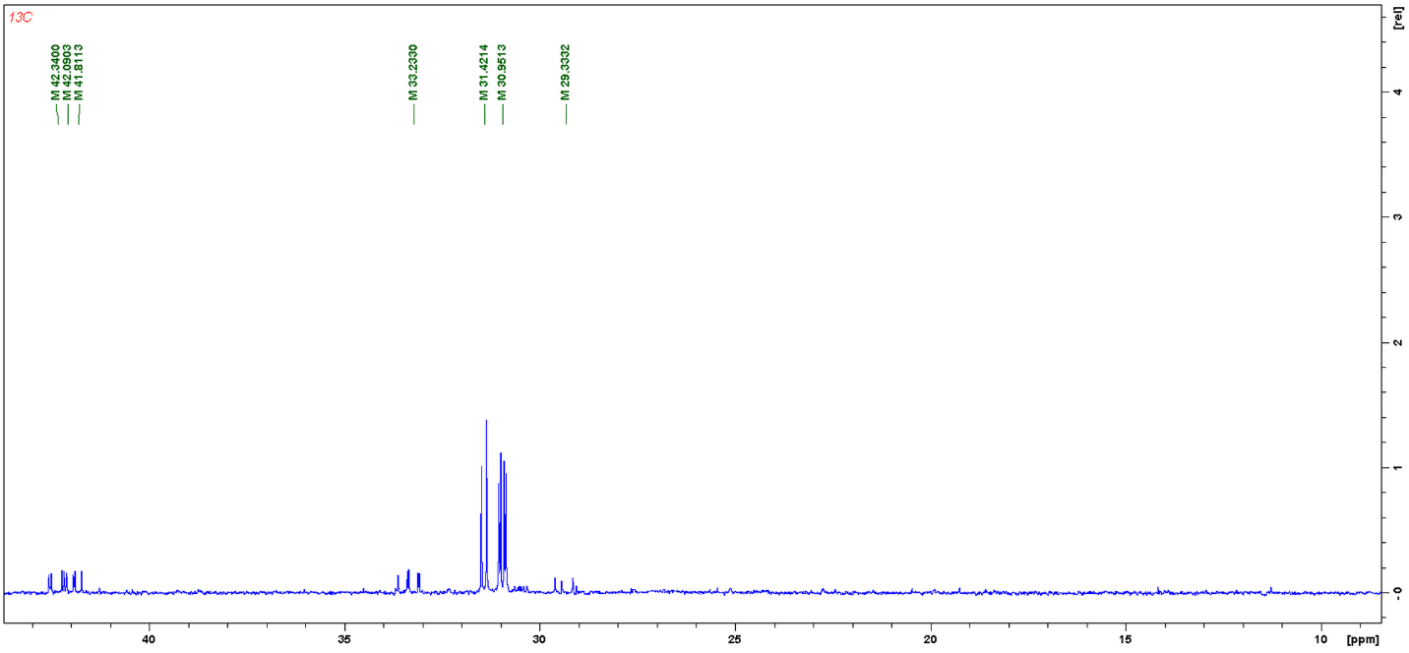

Figure S15. $^{31}C\{^{1}H\}$-NMR spectrum of isolated phosphanylphosphaalkene $(CH_2)_4C$=P-P*t*Bu$_2$ in the range from 45 ppm to 10 ppm.

5. *NMR spectra of dissolved complex **11** in THF and of isolated phosphanylphosphaalkene $(CH_2)_5C$=P-PtBu_2.*

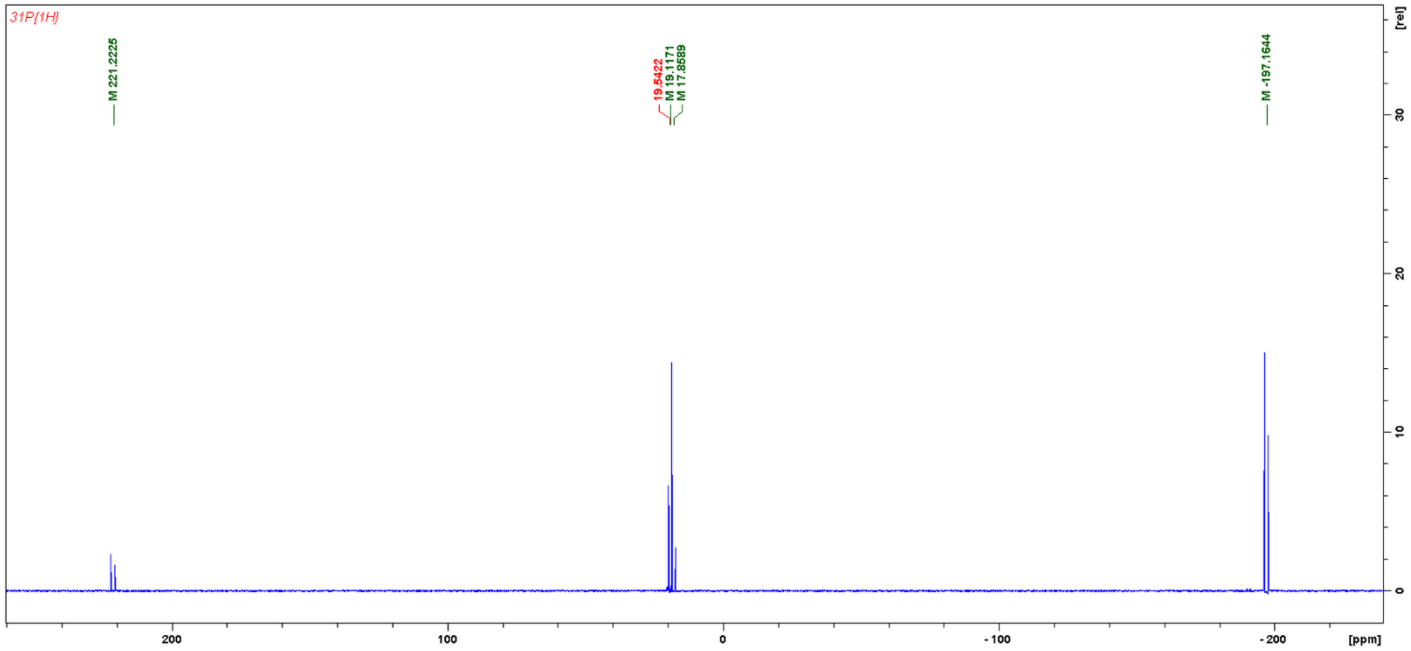

Figure S16. $^{31}P\{^1H\}$-NMR spectrum of dissolved complex **11** in THF.

- 221.22 ppm, (d), J_{PP} = 228.9 Hz, $(CH_2)_5C$=**P**-PtBu$_2$.
- 19.54 ppm, (s), tBu$_2$PH;
- 19.11 ppm, (d), J_{PP} = 192.7 Hz, tBu$_2$**P**-P(SiMe$_3$)H.
- 17.86 ppm, (d), J_{PP} = 228.9 Hz, $(CH_2)_5C$=P-**P**tBu$_2$.
- -197.16 ppm, (d), J_{PP} = 192.7 Hz, tBu$_2$P-**P**(SiMe$_3$)H.

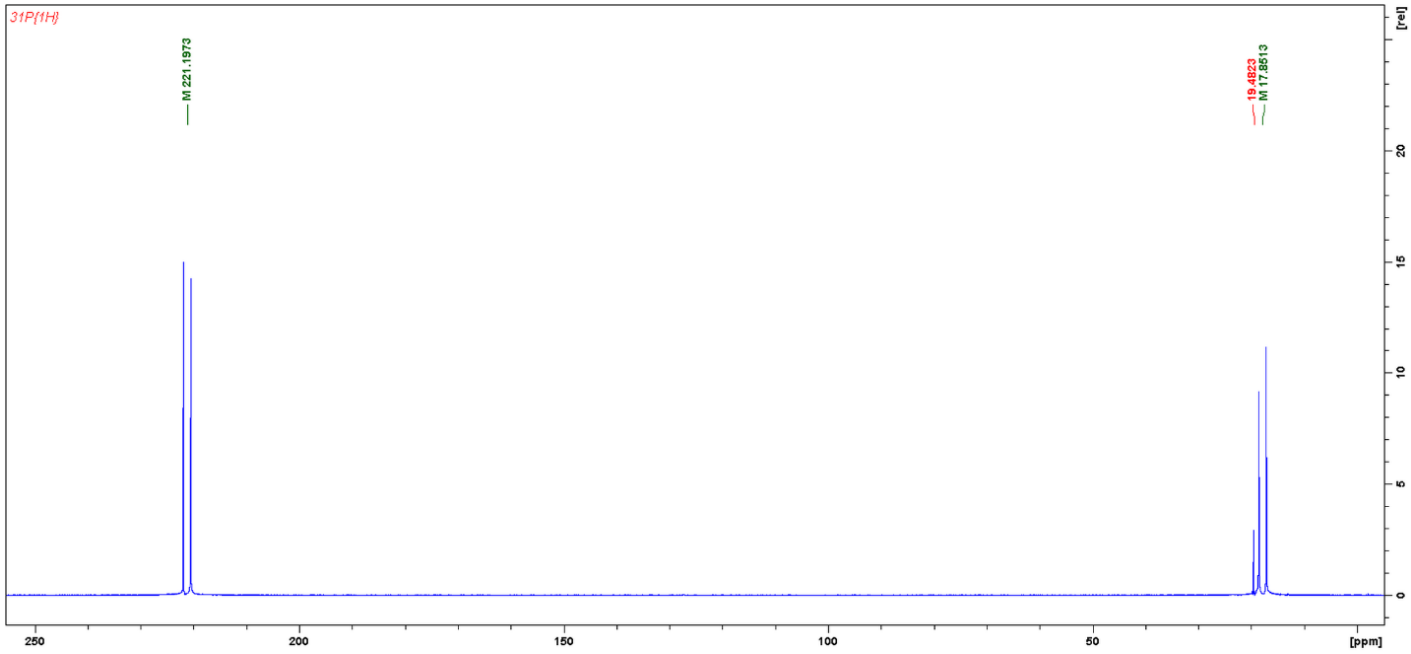

Figure S17. $^{31}P\{^{1}H\}$-NMR spectrum of the isolated phosphanylphosphaalkene $(CH_2)_5C{=}P\text{-}PtBu_2$.

- 221.19 ppm, (d), J_{PP} = 228.9 Hz, $(CH_2)_5C{=}P\text{-}PtBu_2$;
- 19.48 ppm, (s), tBu_2PH;
- 17.85 ppm, (d), J_{PP} = 228.9 Hz, $(CH_2)_5C{=}P\text{-}\mathbf{P}tBu_2$;

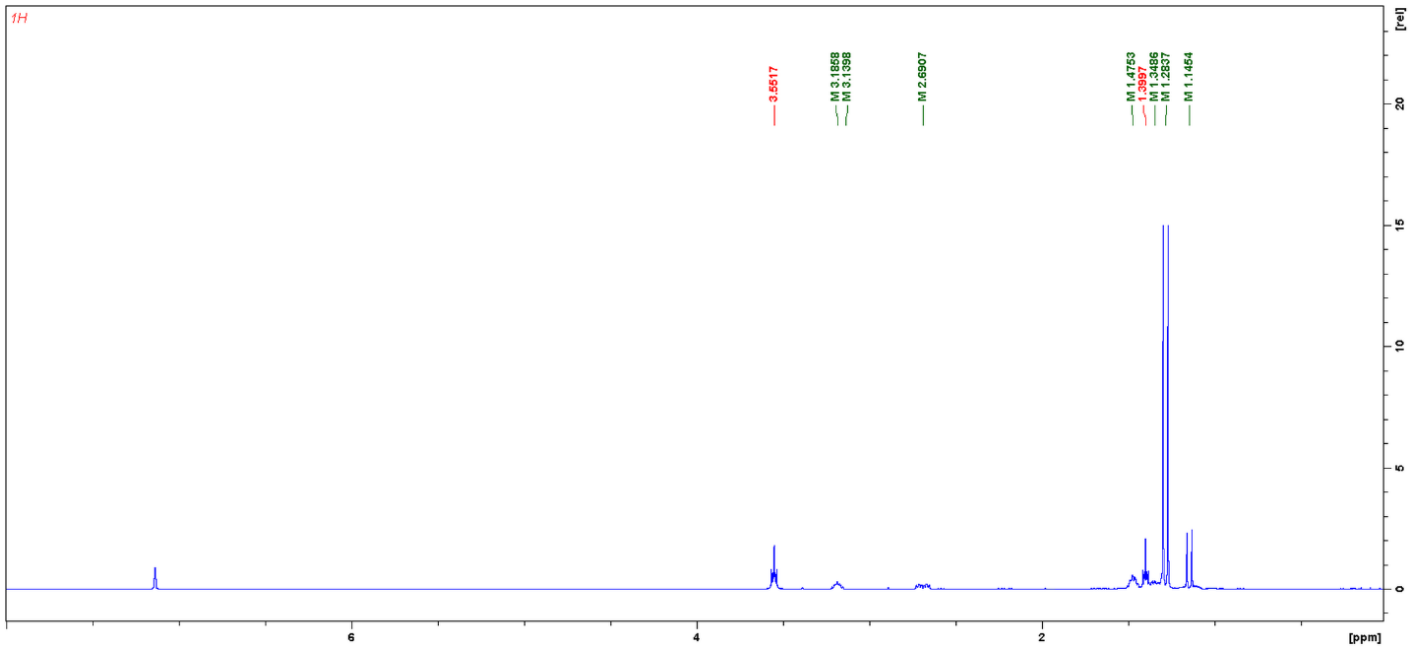

Figure S18. ^{1}H-NMR spectrum of the isolated phosphanylphosphaalkene $(CH_2)_5C$=P-P*t*Bu$_2$.

- 3.55 ppm, (m), THF protons;
- 3.18 ppm, (br. m), (C**H**$_2$)$_5$C=P-P*t*Bu$_2$;
- 3.14 ppm, (d), J_{PH} = 11.49 Hz, *t*Bu$_2$P**H**;
- 2.69 ppm, (br. m.), (C**H**$_2$)$_5$C=P-P*t*Bu$_2$;
- 1.47 ppm, (br. m.), (C**H**$_2$)$_5$C=P-P*t*Bu$_2$;
- 1.40 ppm, (m), THF protons;
- 1.35 ppm, (br. m.), (C**H**$_2$)$_5$C=P-P*t*Bu$_2$;
- 1.28 ppm, (d), J_{PP} = 11.2 Hz, $(CH_2)_5$C=P-P***t*Bu**$_2$;
- 1.14 ppm, (d), J_{PP} = 11.5 Hz, *t*Bu$_2$P**H**;

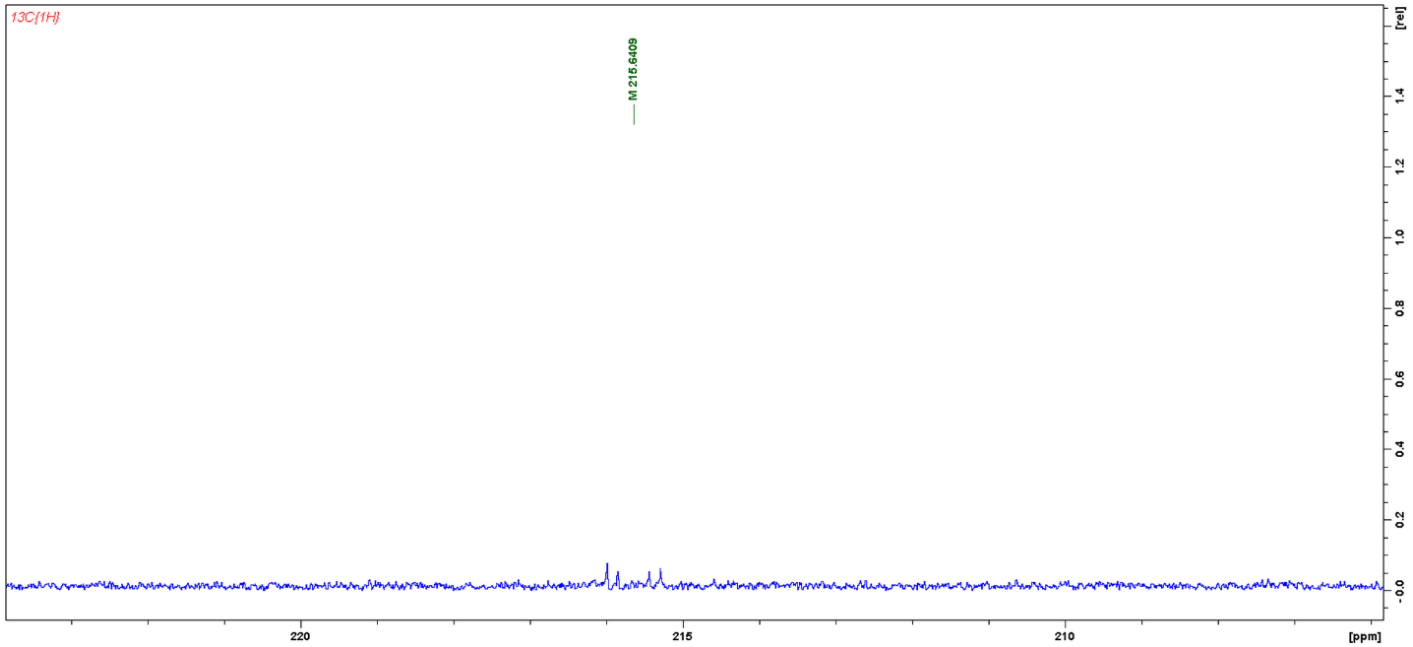

Figure S19. ^{31}C{^{1}H}-NMR spectrum of isolated phosphanylphosphaalkene $(CH_2)_5C$=P-P*t*Bu$_2$ in the range from 225 ppm to 205 ppm.

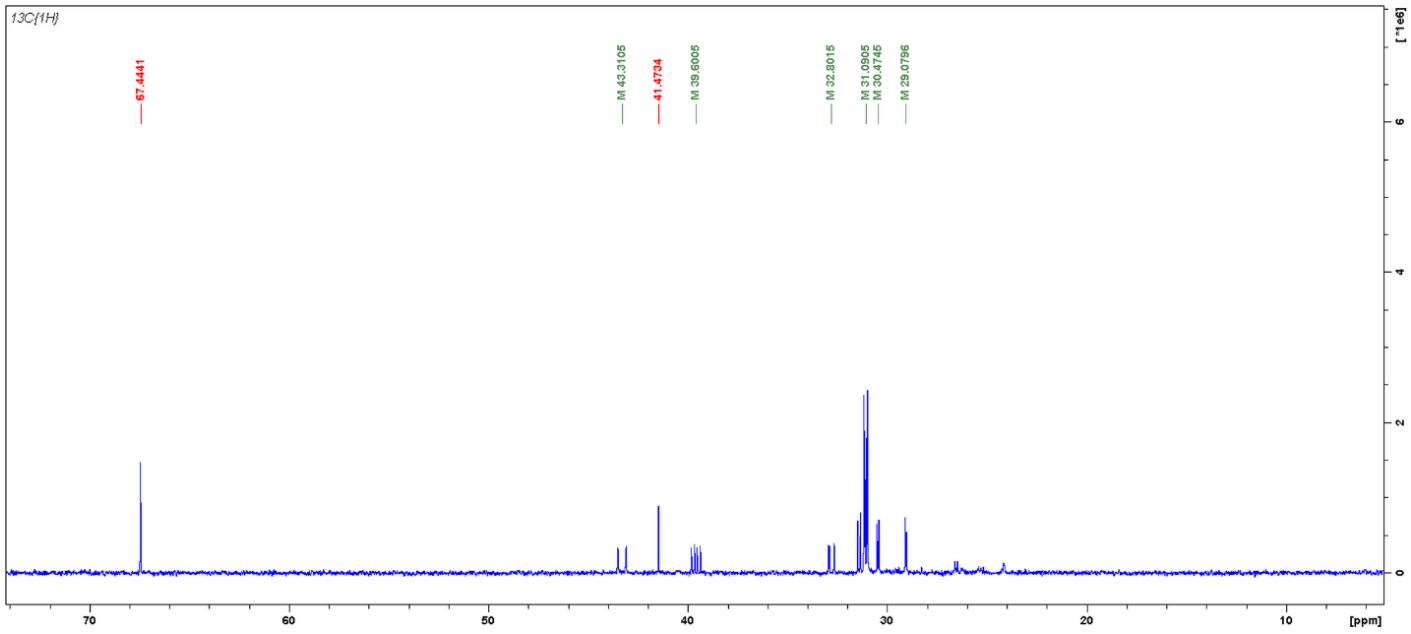

Figure S20. $^{31}C\{^{1}H\}$-NMR spectrum of isolated phosphanylphosphaalkene $(CH_2)_5C{=}P\text{-}PtBu_2$ in the range from 70 ppm to 5 ppm.

*6. NMR spectra of reaction mixture of **1** with cycloheptanone.*

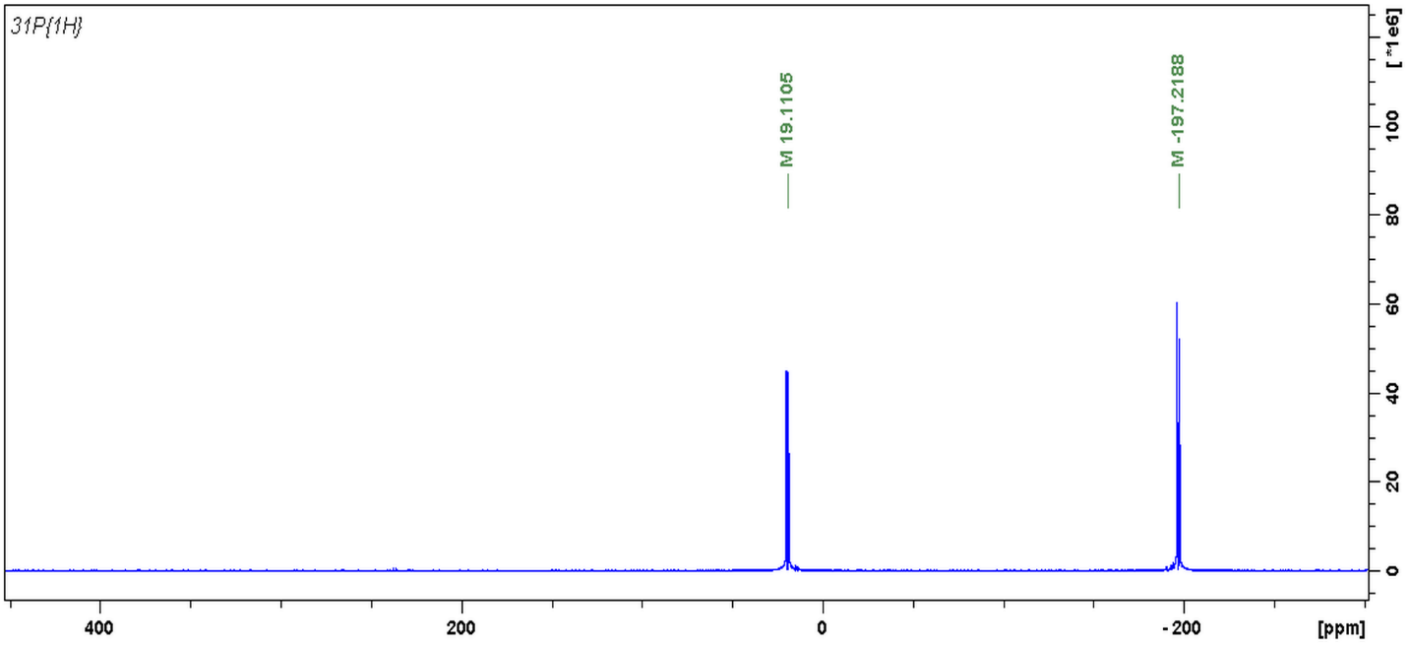

Figure 21. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture after reaction of **1** with cycloheptanone.

- 19.11 ppm, (d), J_{PP} = 196.2 Hz, tBu$_2$**P**-P(SiMe$_3$)H;
- -197.22 ppm, (d), J_{PP} = 196.2 Hz, tBu$_2$P-**P**(SiMe$_3$)H;

*7. NMR spectra of isolated crystals of **3**.*

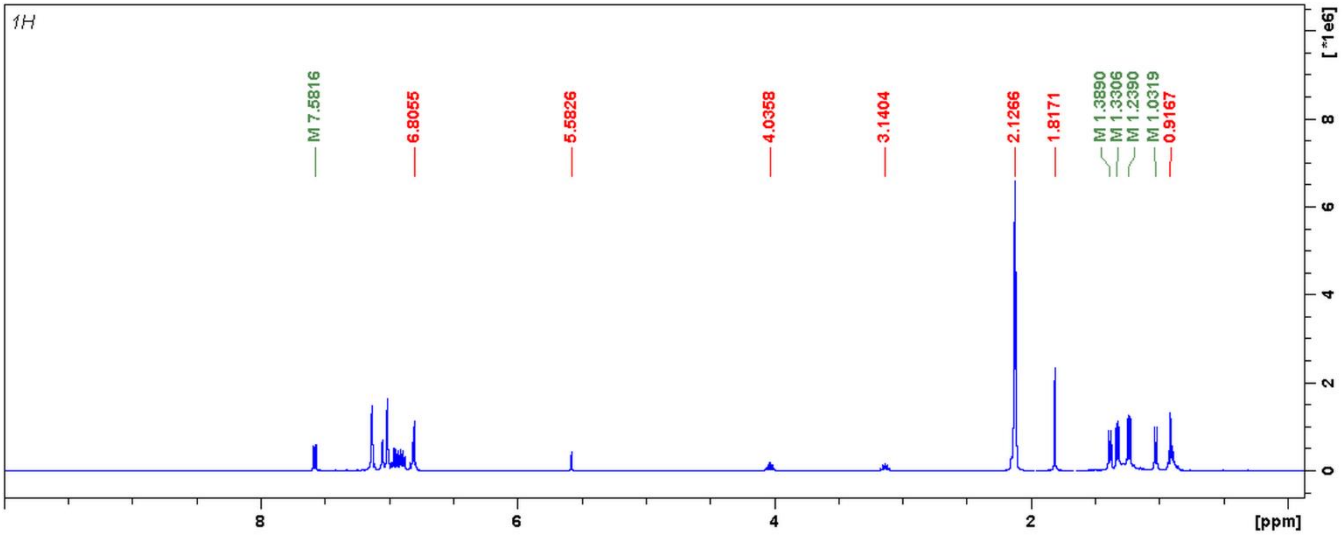

Figure S22. ^{1}H-NMR spectrum of isolated crystals of **3**.

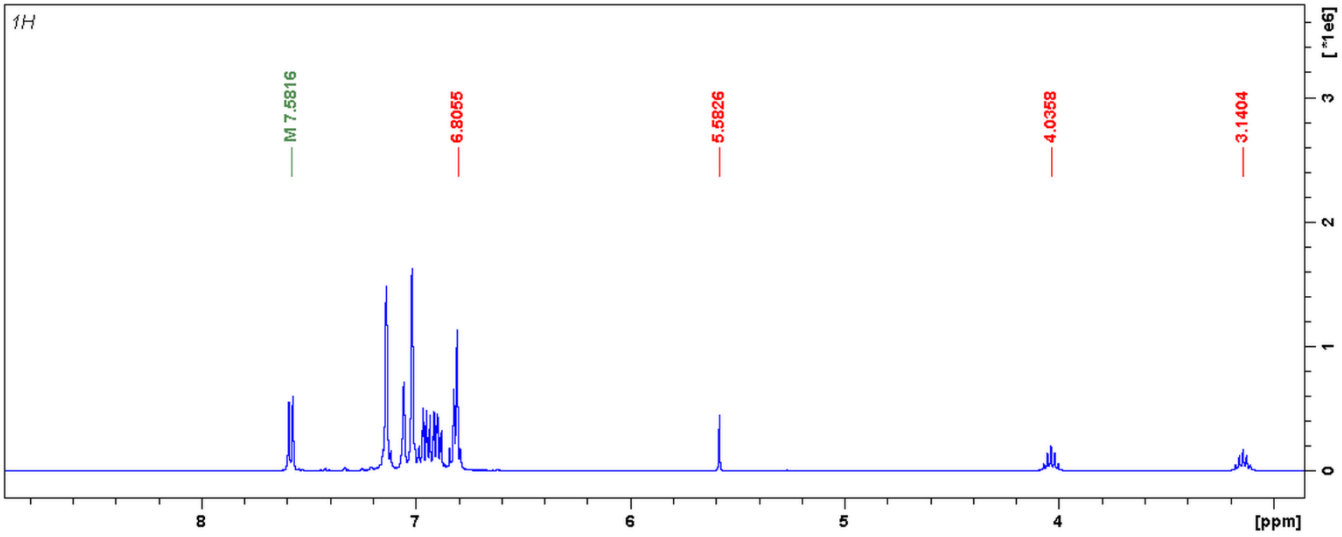

Figure S23. ^{1}H-NMR spectrum of isolated crystals of **3** in the range from 9 ppm to 3 ppm.

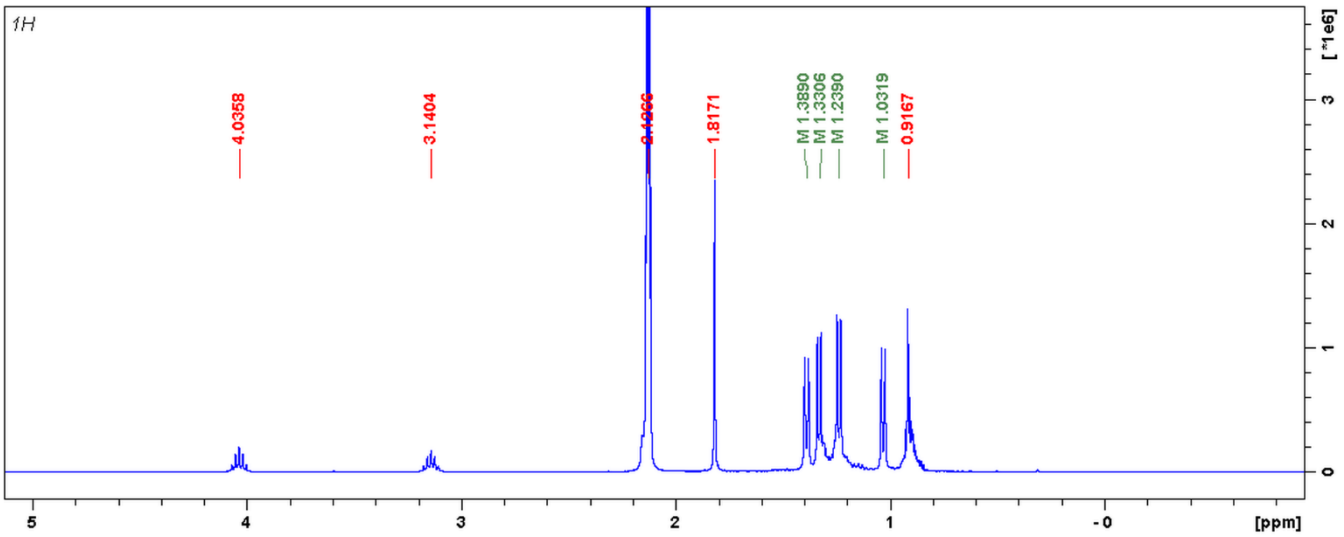

Figure S24. ^{1}H-NMR spectrum of isolated crystals of **3** in the range from 5 ppm to -1 ppm.

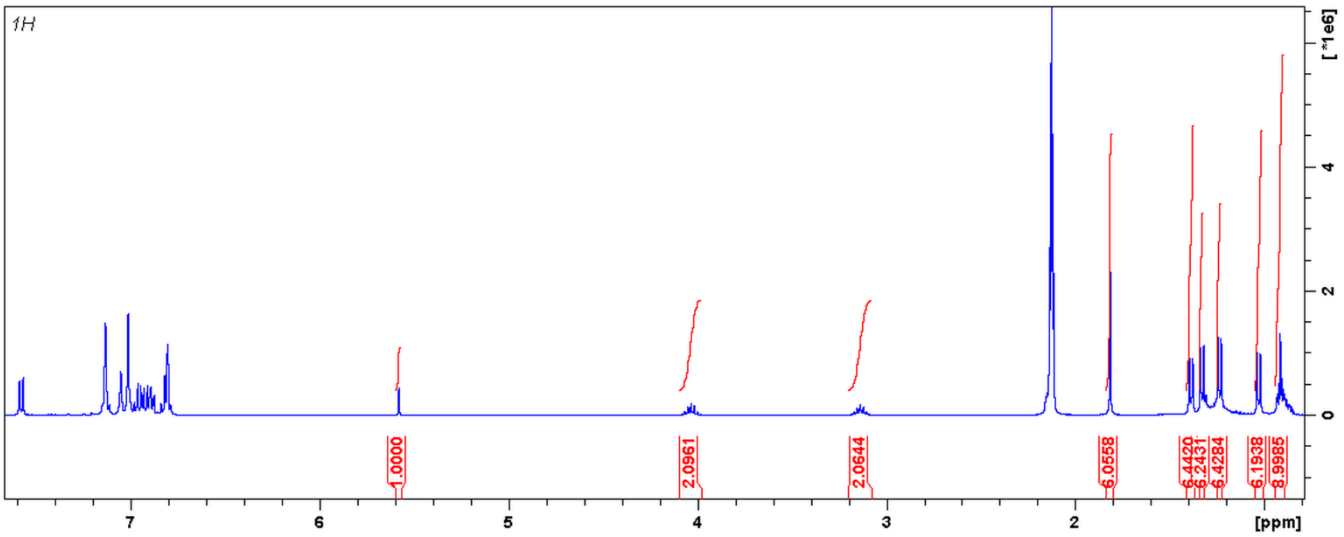

Figure S25. ^{1}H-NMR spectrum of isolated crystals of **3** with integration.

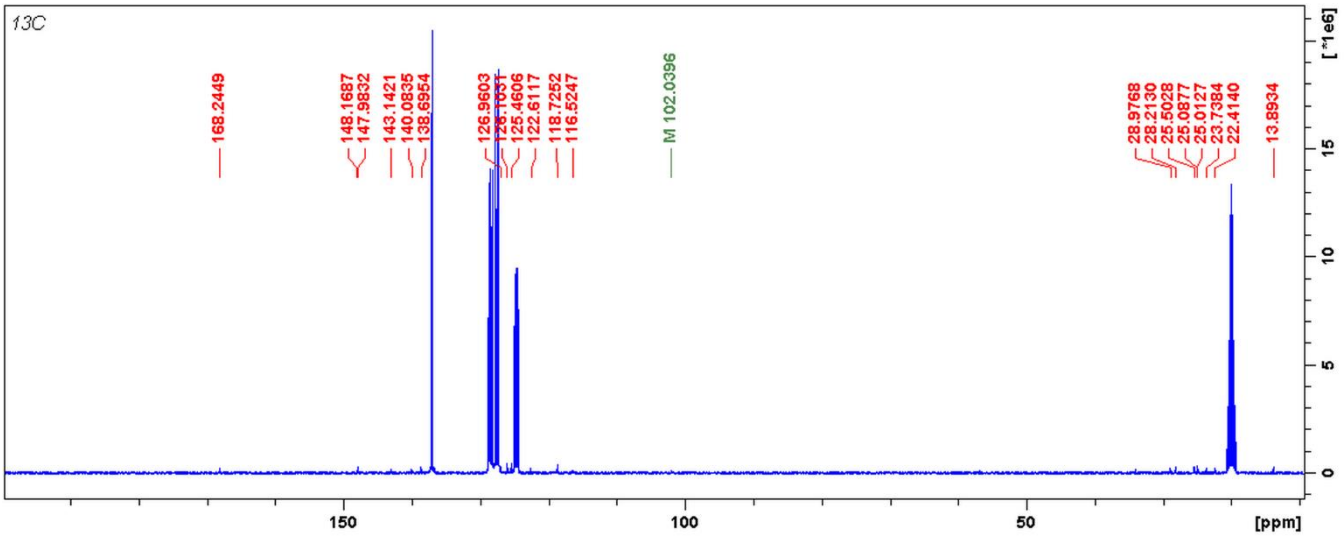

Figure S26. ^{13}C{^{1}H}-NMR spectrum of isolated crystals of **3**.

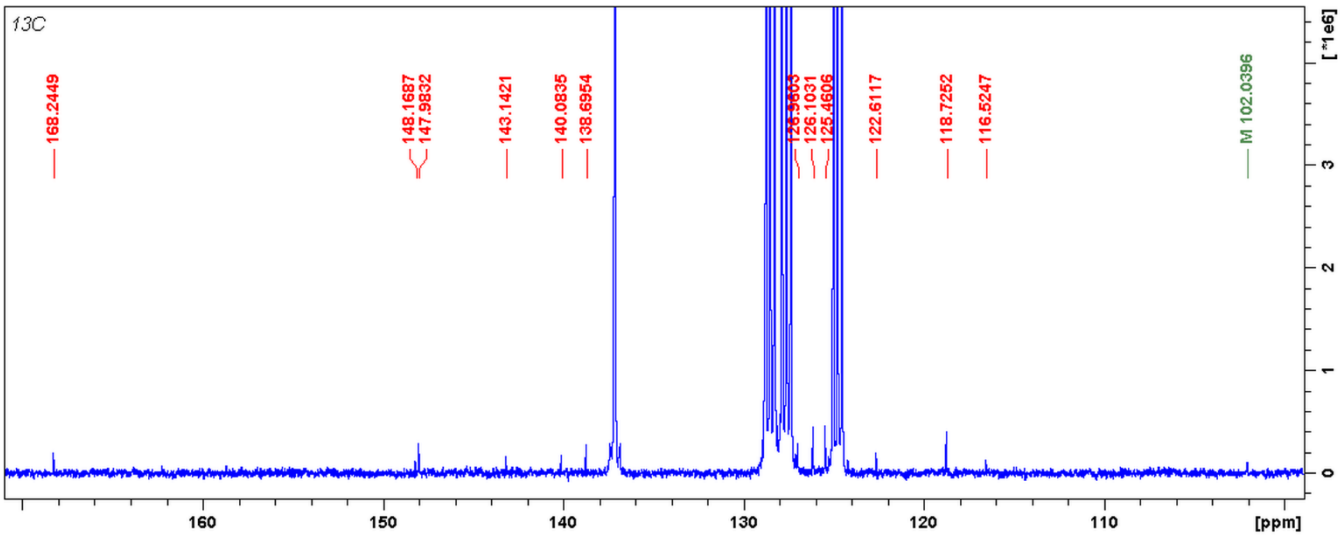

Figure S27. $^{13}C\{^{1}H\}$-NMR spectrum of isolated crystals of **3** in the range from 170 ppm to 100 ppm.

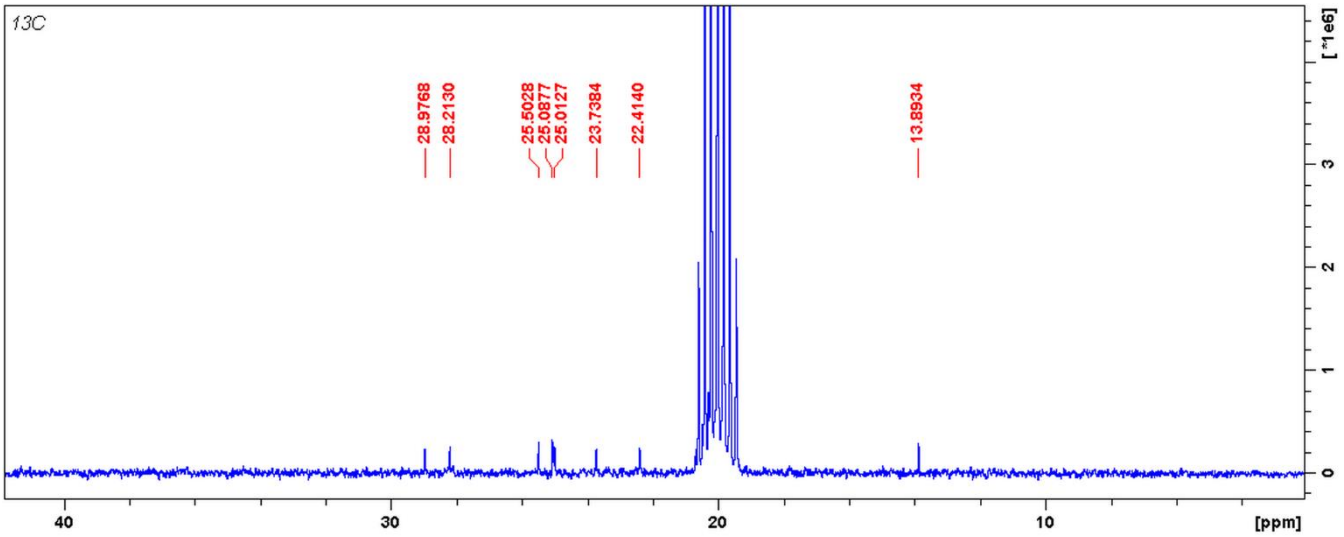

Figure S28. $^{13}C\{^{1}H\}$-NMR spectrum of isolated crystals of **3** in the range from 40 ppm to 0 ppm.

*8. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture of [^{Me}NacNacTi(Cl){η^2-P-PtBu$_2$}] (**4**) with 9-fluorenone.*

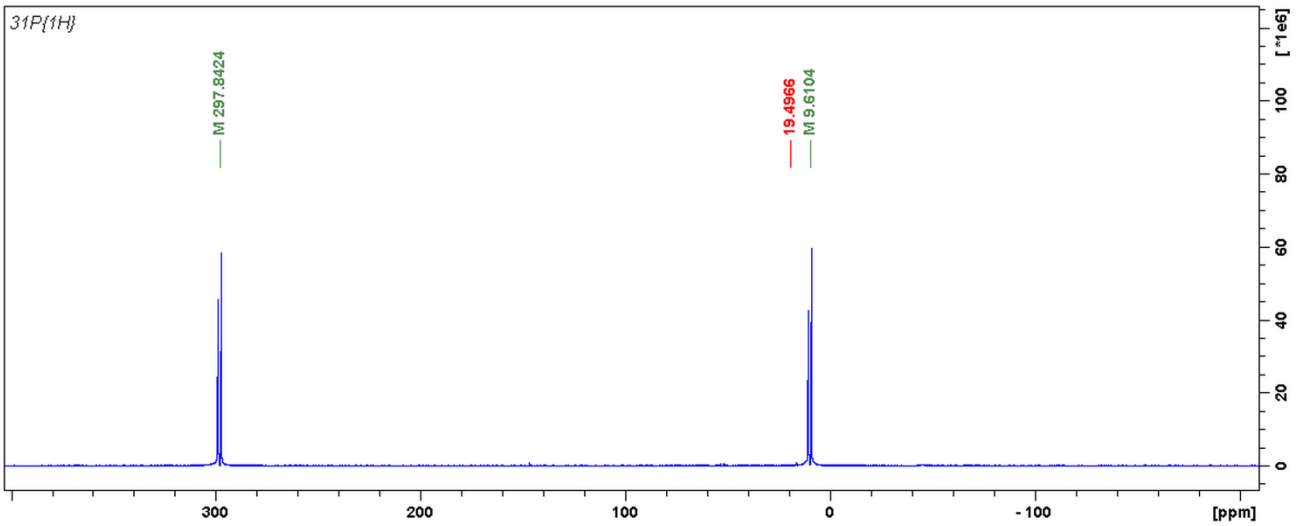

Figure S29. $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture of [^{Me}NacNacTi(Cl){η^2-P-PtBu$_2$}] (**4**) with 9-fluorenone.

- 297.84 ppm, (d), J_{PP} = 232.7 Hz, (fluorenyl)C=**P**-PtBu$_2$;
- 19.50 ppm, s, tBu$_2$PH;
- 9.61 ppm, (d), J_{PP} = 232.7 Hz, (fluorenyl)C=P-**P**tBu$_2$;

*9. $^{31}P\{^1H\}$-NMR spectrum of reaction mixture of [^{Me}NacNacTi(Cl){η^2-P-PtBu$_2$}] (**4**) with acetophenone.*

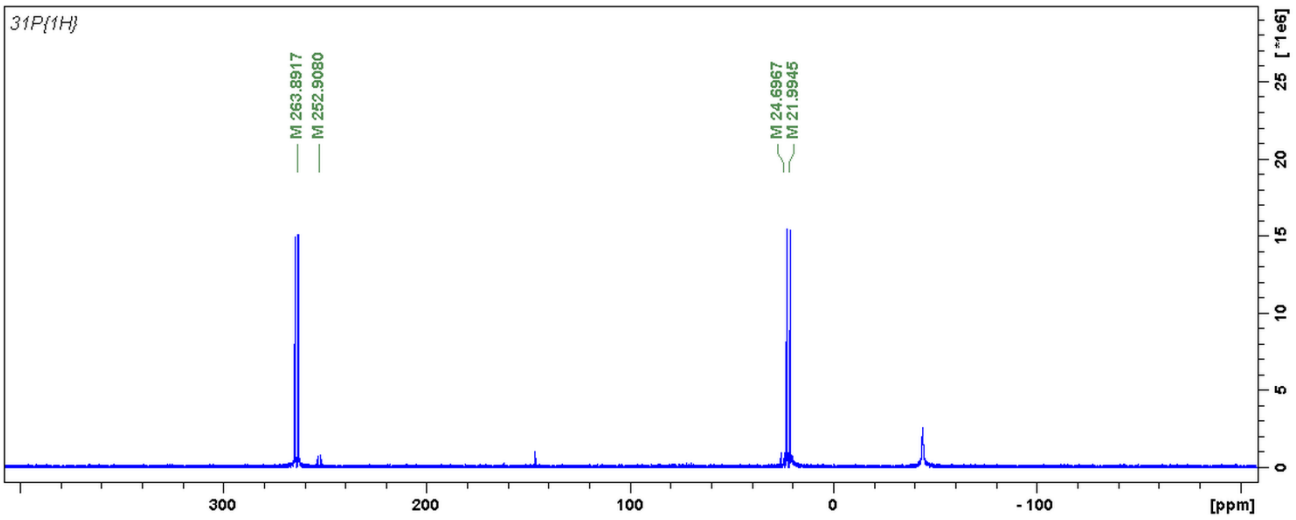

Figure S30. $^{31}P\{^1H\}$-NMR spectrum of reaction mixture of [^{Me}NacNacTi(Cl){η^2-P-PtBu$_2$}] (**4**) with acetophenone.

E - isomer:

- 263.89 ppm, (d), J_{PP} = 234.9 Hz, (Ph)MeC=**P**-PtBu$_2$;
- 21.99 ppm, (d), J_{PP} = 234.9 Hz, (Ph)MeC=P-**P**tBu$_2$;

Small amount of Z - isomer:

- 252.90 ppm, (d), J_{PP} = 222.8 Hz, (Ph)MeC=**P**-PtBu$_2$;
- 24.69 ppm, (d), J_{PP} = 222.8 Hz, (Ph)MeC=P-**P**tBu$_2$;

PART B. X-RAY CRYSTALLOGRAPHIC DATA

Diffraction data of **3, 5, 8, 10, 11, 11b,** and **12** were collected an a diffractometer IPDS2T equipped with a STOE image plate detector system IPDS2T and micro-focus X-ray sources providing *K*α radiation by the high-grade multilayer X-ray mirror optics for Mo (λ = 0.71073 Å) wavelengths. Good quality single-crystal specimens of **3, 5, 8, 10, 11, 11b,** and **12** were selected for the X-ray diffraction experiments at 120 K. The structures were solved by direct methods and refined against F^2 using the Shelxs-2008 and Shelxl-2008 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 at 1.5 *U*eq of the C atoms for CH_3 and 1.2 *U*eq for CH, CH_2 and aromatic H. The voids in the crystal structure of **3** contain disordered solvent. A satisfactory disorder model for the solvent was not found, and therefore the PLATON/SQUEEZE program was used to mask out the disordered density. The voids in **3** contain two molecules of pentane disordered over at least two positions and also partially absent. A satisfactory refinement of the partial occupancy solvent density as a disorder was not found.

Crystallographic data for the structures of **3, 5, 8, 10, 11, 11b,** and **12** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 2004562-2004568. 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).

Table S1. Crystallographic data for **3**, **5** and **8**.

	3	**5**	**8**
Empirical formula	$C_{58}H_{66}N_2O_3SiTi$ [+ solvent; 2 molecules of pentane]	$C_{64}H_{100}Cl_2N_4O_2Si_2Ti_2$	$C_{45}H_{56}Cl_1N_2O_2Ti$
Mw ($g \cdot mol^{-1}$)	987.26	1180.35	740.26
T[*K*]	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal System	triclinic	monoclinic	monoclinic
Space group	*P*-1	*C*2/*c*	$P2_1/n$
a [Å]	11.8988(4)	21.982(2)	17.3918(7)
b [Å]	22.2268(8)	14.2942(8)	10.7850(3)
c [Å]	22.0748(7)	22.987(2)	21.7583(9)
α [°]	88.458(3)	90	90
β [°]	84.520(3)	114.710(7)	100.543(3)
γ [°]	74.716(3)	90	90
V [$Å^3$]	5605.9(3)	6561.6(10)	4012.3(3)
Z	4	4	4
ρ [$g \cdot cm^{-1}$]	1.170	1.195	1.225
μ [mm^{-1}]	0.220	0.405	0.318
F(000)	2120	2536	1580
Θ range data collection (º)	1.85-25.73	2.93-28.56	2.34-29.41
Index ranges	$-15 \le h \le 15$ $-29 \le k \le 29$ $-29 \le l \le 29$	$-28 \le h \le 28$ $-18 \le k \le 16$ $-30 \le l \le 23$	$-22 \le h \le 22$ $-14 \le k \le 12$ $-28 \le l \le 21$
Reflection collected	60887	16971	20254
Independent reflections	27045 [$R_{int} = 0.1352$]	8705 [$R_{int} = 0.0920$]	9557 [$R_{int} = 0.0843$]
Data/restrains/parameters	27045/0/1179	8705/0/343	9557/1/481
GooF an F^2	0.961	1.027	1.015
Final R indices	$R_1 = 0.0915$	$R_1 = 0.0602$	$R_1 = 0.0621$
[$I>2\sigma(I)$]	$wR_2 = 0.2241$	$wR_2 = 0.1612$	$wR_2 = 0.1451$
R indices (all data)	$R_1 = 0.2188$ $wR_2 = 0.2846$	$R_1 = 0.1655$ $wR_2 = 0.1988$	$R_1 = 0.1209$ $wR_2 = 0.1453$
Largest diff. peak and hole [$e \cdot Å^{-3}$]	0.493 and -0.716	0.533 and -0.463	0.351 and -0.439
CCDC	2004565	2004562	2004567

Table S2. Crystallographic data for **10**, **11** and **11b**.

	10	**11**	**11b**
Empirical formula	$C_{50}H_{84}Cl_1N_2O_2P_2Si_1Ti_1$	$C_{55}H_{95}Cl_1N_2O_2P_2Si_1Ti_1$	$C_{41}H_{60}Cl_1N_2O_2Ti$
Mw ($g \cdot mol^{-1}$)	918.57	989.70	696.26
T[*K*]	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal System	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	*P*-1	$P2_1/c$
a [Å]	9.7360(2)	9.9454(4)	16.9626(9)
b [Å]	27.4049(6)	10.3200(5)	11.7424(6)
c [Å]	19.8324(3)	27.9616(10)	19.4368(10)
α [°]	90	100.356(3)	90
β [°]	96.6120(10)	91.107(3)	98.640(4)
γ [°]	90	95.680(3)	90
V [$Å^3$]	5256.37(18)	2807.2(2)	3827.5(3)
Z	4	2	4
ρ [$g \cdot cm^{-1}$]	1.161	1.171	1.208
μ [mm^{-1}]	0.335	0.318	0.330
F(000)	1988	1076	1500
Θ range data collection (º)	2.20-29.55	2.22-29.58	2.03-29.29
Index ranges	$-11 \leq h \leq 13$ $-37 \leq k \leq 37$ $-27 \leq l \leq 27$	$-11 \leq h \leq 13$ $-13 \leq k \leq 13$ $-36 \leq l \leq 36$	$-23 \leq h \leq 23$ $-16 \leq k \leq 16$ $-26 \leq l \leq 22$
Reflection collected	41202	26152	25621
Independent reflections	14122 [$R_{int} = 0.0702$]	13376 [$R_{int} = 0.0814$]	10254 [$R_{int} = 0.0843$]
Data/restrains/parameters	14122/0/551	13376/0/598	10254/0/424
GooF an F^2	1.025	1.043	1.009
Final R indices	$R_1 = 0.0560$	$R_1 = 0.0963$	$R_1 = 0.0548$
[$I>2\sigma(I)$]	$wR_2 = 0.0973$	$wR_2 = 0.1363$	$wR_2 = 0.1222$
R indices (all data)	$R_1 = 0.1329$ $wR_2 = 0.1560$	$R_1 = 0.2533$ $wR_2 = 0.2881$	$R_1 = 0.1194$ $wR_2 = 0.1383$
Largest diff. peak and hole [$e \cdot Å^{-3}$]	0.91 and -0.553	-1.268 and -1.204	0.381 and -0.435
CCDC	2004563	2004564	2004566

Table S3. Crystallographic data for **12**.

	12
Empirical formula	$C_{43}H_{64}Cl_1N_2O_2Ti_1$
Mw ($g \cdot mol^{-1}$)	724.31
T[*K*]	120(2)
Wavelength (Å)	0.71073
Crystal System	monoclinic
Space group	*C*2/*c*
a [Å]	23.6443(16)
b [Å]	18.6688(7)
c [Å]	19.2429(10)
α [°]	90
β [°]	109.089(5)
γ [°]	90
V [$Å^3$]	8026.9(8)
Z	8
ρ [$g \cdot cm^{-1}$]	1.199
μ [mm^{-1}]	0.317
F(000)	3128
Θ range data collection (º)	2.83-28.75
Index ranges	$-32 \leq h \leq 32$ $-25 \leq k \leq 21$ $-24 \leq l \leq 26$
Reflection collected	27717
Independent reflections	10746 [$R_{int} = 0.0503$]
Data/restrains/parameters	10746/123/464
GooF an F^2	1.066
Final R indices	$R_1 = 0.0709$
[$I>2\sigma(I)$]	$wR_2 = 0.1299$
R indices (all data)	$R_1 = 0.1875$ $wR_2 = 0.2140$
Largest diff. peak and hole [$e \cdot Å^{-3}$]	0.717 and -0.620
CCDC	2004568

Molecular structure of [^{Me}NacNacTi(Cl){OC(CH$_2$)$_4$}CH(C=O)(CH$_2$)$_5$] (**11b**)

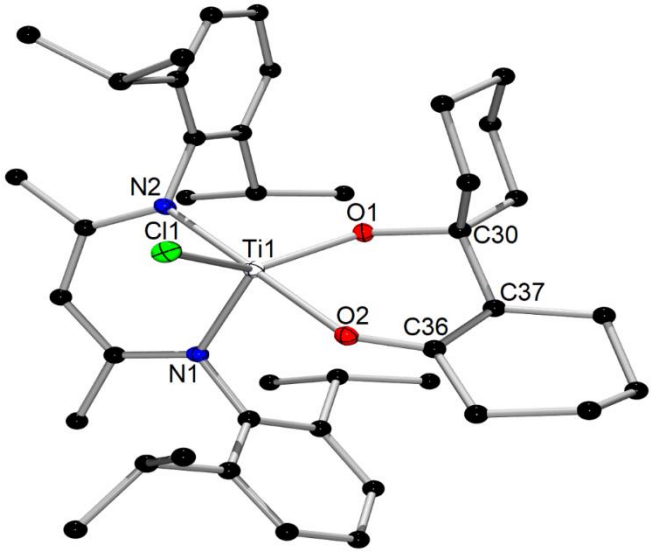

Figure S31. The molecular structures of [^{Me}NacNacTi(Cl){OC(CH$_2$)$_4$}CH(C=O)(CH$_2$)$_5$] (**11b**) (ellipsoids 50%, hydrogen atoms have been omitted for clarity). Important bond lengths (Å) and bond angles (°): Ti1-Cl1 2.3243(7). Ti-N1 2.0733(19), Ti1-N2 2.1238(19), Ti1-O1 1.8302(16), Ti1-O2 2.1068(16), O1-C30 1.434(3), O2-C36 1.230(3); O1-Ti1-N1 118.22(8), O1-Ti1-O2 84.11(7), N1-Ti1-O2 92.53(7), O1-Ti1-N2 96.06(7), N1-Ti1-N2 87.06(7), O2-Ti1-N2 179.58(7), O1-Ti1-Cl1 132.37(6), N1-Ti1-Cl1 108.45(6), O2-Ti1-Cl1 84.95(5), N2-Ti1-Cl1 95.21(6).

Molecular structure of [^{Me}NacNacTi(Cl){OC(CH$_2$)$_6$}CH(C=O)(CH$_2$)$_5$] (**12**)

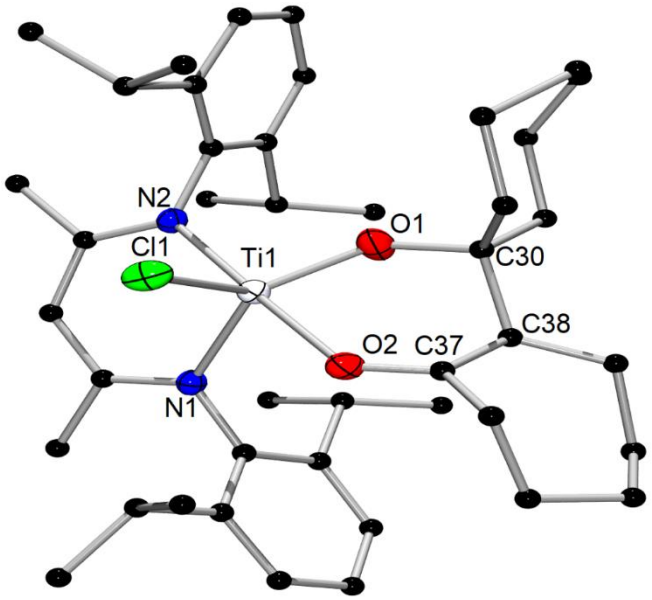

Figure S32. The molecular structures of [^{Me}NacNacTi(Cl){OC(CH$_2$)$_6$}CH(C=O)(CH$_2$)$_5$] (**12**) (ellipsoids 50%, hydrogen atoms have been omitted for clarity). The second disorder component of the {OC(CH$_2$)$_5$}CH(C=O)(CH$_2$)$_6$ ligand (site-occupancy factor = 0.242) and of selected methyl of *iso*-propyl groups (site-occupancy factor = 0.528) have been omitted. Important bond lengths (Å) and bond angles (°): Ti1-Cl1 2.3304(10), Ti1-N1 2.078(2), Ti1-N2 2.115(2), Ti1-O1 1.840(5), Ti1-O2 2.146(5), O1-C30 1.399(11), O2-C37 1.167(8); O1-Ti1-N1 131.02(15), O1-Ti1-N2 95.08(15), N1-Ti1-N2 88.00(9), O1-Ti1-O2 83.40(2), N1-Ti1-O2 92.74(19), N2-Ti1-O2 178.47(18), O1-Ti1-Cl1 122.75(14), N1-Ti1-Cl1 105.05(7), N2-Ti1-Cl1 97.77(7), O2-Ti1-Cl1 83.33(14), O1-C30-C31 109.30(6), O1-C30-C36 112.80(6).

PART C. DFT CALCULATIONS DATA

Molecular geometries of compounds **2**, **6**, **9_*E***, **9_*Z***, **10a**, **11a** were optimized using density functional theory at the ωB97XD functional by Head-Gordon[3, 4] with 6-31+G(d,p) basis set. The ωB97XD exchange-correlation functional has been chosen as it has good overall performance for the description of main-group element compounds, and it also accounts well for long-range and dispersion interactions. Molecular geometries were energy optimized and the most stable (the lowest energy) conformer was identified during the potential energy surface scanning of the C-**P-P**-C dihedral**.** Nature of the final gas phase geometries as a local minima (no imaginary frequencies on the potential energy surface were then validated by harmonic frequency calculations at the same level of theory. Theoretical ^{31}P NMR shift were determined by calculating NMR shielding tensors using Gauge-Independent Atomic Orbital (GIAO)[5] method at the mn12sx/cc-pvdz level of theory including presence of a solvent (benzene) using the CPCM polarizable conductor calculation model.[6] All calculations presented in the paper were performed using the Gaussian 09[7] program package.

Table S4. Selected computational parameters obtained for considered systems (in atomic units [A.U.]): ε_0 - electronic energy; $\varepsilon_{0+\dots}$ - sum of electronic and: E_{zpe} - zero-point energies, E_{therm} - thermal energies, H – thermal enthalpies, G - thermal free energies calculated at ωB97XD//6-31+G(d,p)

Compound	Imaginary frequencies	E_{electr} [A.U.]	$\varepsilon_0 + E_{ZPE}$ [A.U.]	$\varepsilon_0 + E_{therm}$ [A.U.]	ε_0 + H [A.U.]	ε_0 + G [A.U.]
Ph_2C=P-P*t*Bu_2 (**2**)	0	-1499.560716	-1499.120101	-1499.095741	-1499.094797	-1499.174031
(fluorene)C=P-P*t*Bu_2 (**6**)	0	-1498.365059	-1497.946382	-1497.923113	-1497.922169	-1497.998378
Z-(Ph)MeC=P-P*t*Bu_2 (**9_*Z***)	0	-1307.878866	-1307.491823	-1307.470664	-1307.469720	-1307.540584
E-(Ph)MeC=P-P*t*Bu_2 (**9_*E***)	0	-1307.877987	-1307.491965	-1307.470475	-1307.469531	-1307.541486
$(CH_2)_4$C=P-P*t*Bu_2 (**10a**)	0	-1193.601933	-1193.232083	-1193.213097	-1193.212153	-1193.277902
$(CH_2)_5$C=P-P*t*Bu_2 (**11a**)	0	-1232.915393	-1232.515647	-1232.495768	-1232.494824	-1232.562558

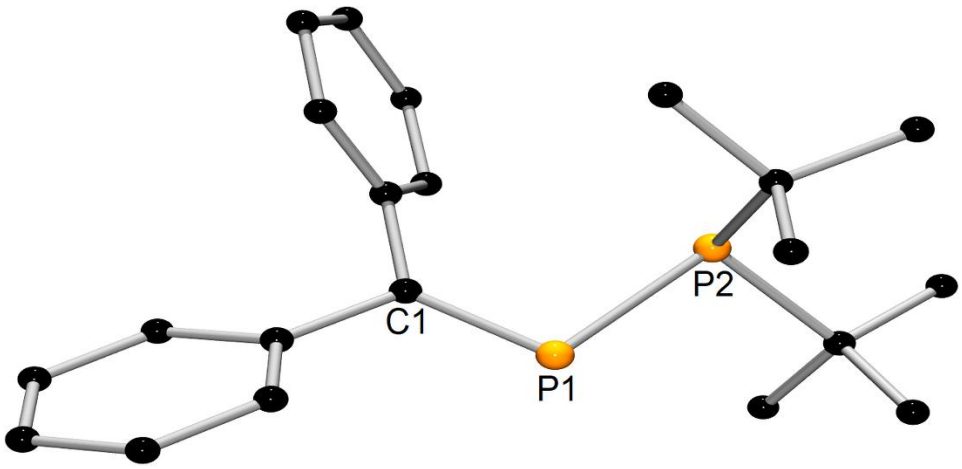

Figure S33. Optimized geometry of Ph_2C=P-P*t*Bu_2 (**2**) (hydrogen atoms have been omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.228, C1-P1 1.697; C1-P1-P2 104.88.

Below are presented xyz coordinates for optimized geometry of **2**:

C	-0.81400	3.36500	-1.36500
C	-0.74700	1.97500	-1.33600
C	-1.27700	1.26000	-0.25800
C	-1.89300	1.96700	0.78200
C	-1.94300	3.35700	0.76400
C	-1.40300	4.06100	-0.31200
H	-0.40100	3.90400	-2.21200
H	-2.41000	3.88900	1.58700
C	-1.23100	-0.22600	-0.21100
P	0.13700	-1.22600	-0.30400
P	1.87200	0.16800	-0.20900
C	2.26500	0.09300	1.66200
C	1.26400	1.07500	2.29900
C	2.11700	-1.26700	2.36000
C	3.68600	0.62800	1.89000
H	1.31800	2.06700	1.84100
H	0.23500	0.71600	2.20100
H	1.48000	1.17600	3.37000
H	2.81300	-2.01400	1.97600
H	2.31900	-1.14300	3.43200
H	1.10300	-1.66800	2.26300
H	3.84200	0.79900	2.96300
H	4.44700	-0.08500	1.56100
H	3.85200	1.57900	1.37200
C	3.14100	-0.85800	-1.19700
C	4.37700	0.03100	-1.43000
C	3.58000	-2.19600	-0.59200
C	2.49600	-1.11500	-2.57300
H	4.10200	0.97800	-1.90500
H	4.90800	0.26200	-0.50400
H	5.08000	-0.48900	-2.09200
H	2.72700	-2.84000	-0.35600

H	4.21600	-2.73300	-1.30700
H	4.16600	-2.05400	0.32000
H	3.25100	-1.51700	-3.25900
H	1.68000	-1.84200	-2.51800
H	2.10300	-0.19100	-3.01400
H	-0.28500	1.43600	-2.15600
H	-2.32600	1.42000	1.61500
H	-1.45000	5.14500	-0.33200
C	-2.55400	-0.89700	-0.08700
C	-2.72100	-2.07300	0.65900
C	-3.67600	-0.35700	-0.73700
C	-3.96000	-2.70300	0.73000
H	-1.87500	-2.48300	1.20100
C	-4.91200	-0.98800	-0.66600
H	-3.57100	0.56100	-1.30700
C	-5.06000	-2.16500	0.06600
H	-4.06800	-3.61000	1.31600
H	-5.76500	-0.55700	-1.18200
H	-6.02800	-2.65200	0.12800

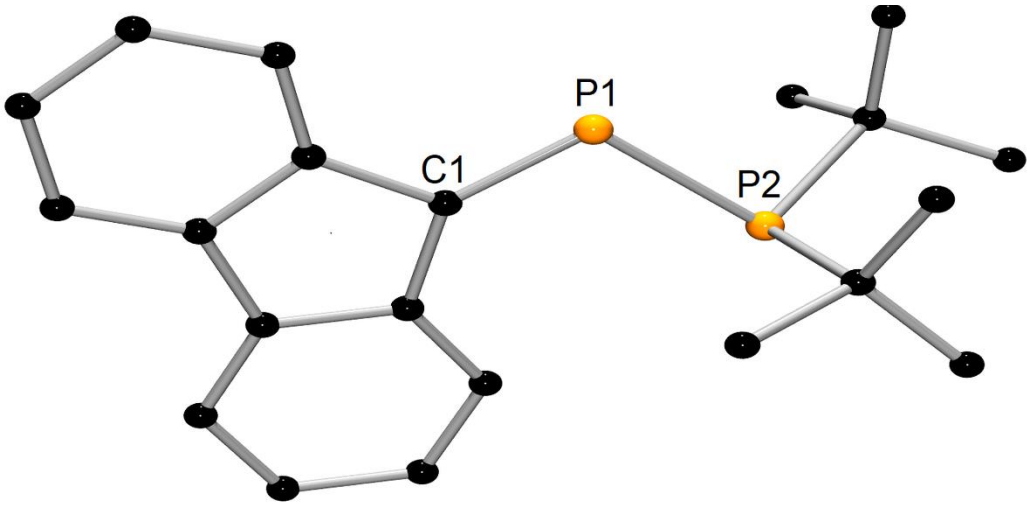

Figure S34. Optimized geometry of (fluorenyl)C=P-P*t*Bu$_2$ (**6**) (hydrogen atoms have been omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.219, C1-P1 1.691; C1-P1-P2 107.67.

Below are presented xyz coordinates for optimized geometry of **6**:

P	0.40900	-1.19300	0.04000
P	2.02300	0.30800	0.30000
C	2.53000	0.65800	-1.51100
C	1.26300	1.11600	-2.25600
C	3.51000	1.84600	-1.48400
C	3.16000	-0.51100	-2.27700
H	0.55400	0.29800	-2.40600
H	0.74300	1.92300	-1.73100
H	1.54900	1.49300	-3.24600
H	4.44700	1.60600	-0.97600
H	3.75700	2.13600	-2.51300
H	3.06800	2.71400	-0.98500
H	3.31500	-0.21800	-3.32300
H	4.13600	-0.78800	-1.87000
H	2.51800	-1.39800	-2.27000
C	3.31000	-0.80800	1.15800
C	3.46800	-2.24800	0.64400
C	4.67700	-0.10700	1.11900
C	2.83300	-0.86500	2.62200
H	2.53800	-2.81600	0.71900
H	3.80600	-2.28900	-0.39300
H	4.21800	-2.76300	1.25700
H	4.60800	0.94100	1.42800
H	5.36400	-0.61500	1.80800
H	5.12700	-0.14700	0.12300
H	3.54200	-1.45600	3.21600
H	2.76500	0.13400	3.06300
H	1.85100	-1.34300	2.71200
C	-1.06900	-0.37600	0.11900
C	-2.32300	-1.15900	-0.08100

C	-1.52700	1.01900	0.34000
C	-2.51000	-2.51700	-0.32400
C	-3.43200	-0.29800	-0.00300
C	-0.82400	2.19000	0.61600
C	-2.93700	1.05800	0.26200
C	-3.80900	-3.00100	-0.48100
H	-1.66300	-3.19200	-0.39100
C	-4.72500	-0.78000	-0.16300
C	-1.52900	3.38100	0.79800
H	0.25600	2.18000	0.70100
C	-3.63500	2.24400	0.43900
C	-4.90700	-2.14200	-0.40300
H	-3.96600	-4.05900	-0.66800
H	-5.58000	-0.11300	-0.10300
C	-2.92000	3.41200	0.70500
H	-0.98300	4.29400	1.01600
H	-4.71900	2.26500	0.37500
H	-5.90900	-2.53700	-0.53000
H	-3.45000	4.34900	0.84500

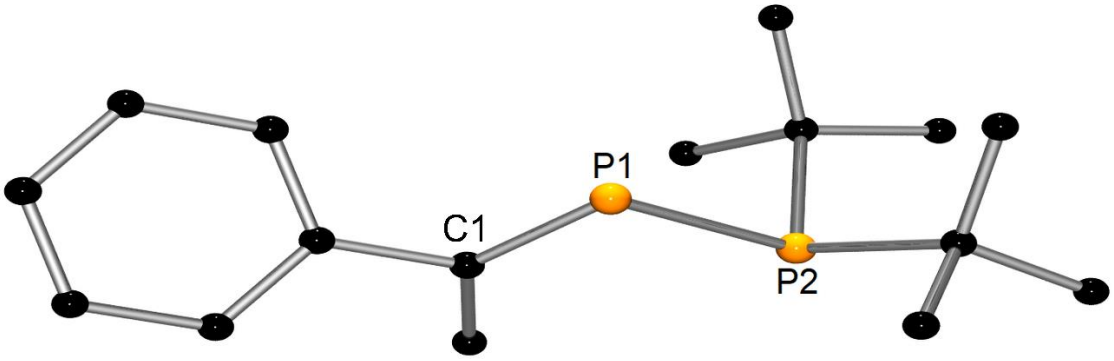

Figure S35. Optimized geometry for *Z*-isomer of (Ph)MeC=P-P*t*Bu$_2$ (**9**) (hydrogen atoms have been omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.223, C1-P1 1.682; C1-P1-P2 103.80.

Below are presented xyz coordinates for optimized geometry for *Z*-isomer of **9**:

C	4.51900	0.50400	-1.46000
C	3.20600	0.55000	-0.99800
C	2.84600	-0.06000	0.21200
C	3.84800	-0.70700	0.95100
C	5.15700	-0.75900	0.48600
C	5.50000	-0.15200	-0.72100
H	4.77400	0.98900	-2.39700
H	5.91200	-1.27900	1.06800
C	1.43500	-0.02500	0.69500
P	0.25900	-0.46200	-0.44000
P	-1.66100	-0.11400	0.62500
C	-2.11000	1.62800	-0.02800
C	-1.27100	2.58800	0.83700
C	-1.80200	1.91800	-1.50500
C	-3.59700	1.90200	0.24300
H	-1.47000	2.45000	1.90400
H	-0.19800	2.44600	0.66700
H	-1.51200	3.62600	0.57500
H	-2.37300	1.28300	-2.18400
H	-2.06000	2.96200	-1.72800
H	-0.74000	1.78600	-1.73200
H	-3.80700	2.96500	0.07200
H	-4.24400	1.33000	-0.42800
H	-3.87300	1.66600	1.27600
C	-2.75100	-1.43900	-0.20300
C	-4.08800	-1.48900	0.55900
C	-3.01900	-1.27100	-1.70300
C	-2.03600	-2.78400	0.03200
H	-3.92800	-1.65200	1.63000
H	-4.67200	-0.57300	0.44100
H	-4.69500	-2.31900	0.17600
H	-2.09100	-1.17000	-2.27500
H	-3.55100	-2.15300	-2.08100
H	-3.64800	-0.40000	-1.90800

H	-2.70200	-3.60300	-0.26600
H	-1.11800	-2.87400	-0.55800
H	-1.78000	-2.92700	1.08700
H	2.44900	1.07700	-1.57000
H	3.59800	-1.20100	1.88500
H	6.52300	-0.18800	-1.08000
C	1.25500	0.40000	2.12700
H	1.91100	-0.17900	2.78600
H	1.54700	1.45100	2.24000
H	0.22600	0.28300	2.46700

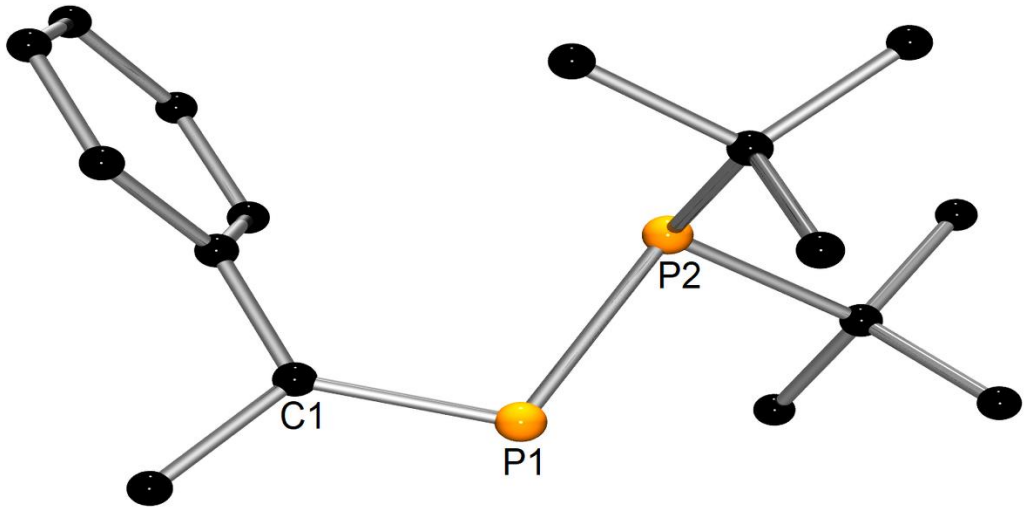

Figure S36. Optimized geometry for *E*-isomer of (Ph)MeC=P-P*t*Bu$_2$ (**9**) (hydrogen atoms have been omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.229, C1-P1 1.687; C1-P1-P2 104.64.

Below are presented xyz coordinates for optimized geometry for *E*-isomer of **9**:

C	-3.07700	-0.40800	-2.10300
C	-2.26600	-0.95400	-1.11400
C	-2.30300	-0.45700	0.19400
C	-3.17900	0.59500	0.48700
C	-3.97800	1.15300	-0.50600
C	-3.93200	0.65100	-1.80500
H	-3.03500	-0.80800	-3.11100
H	-4.64000	1.97900	-0.26300
C	-1.46300	-1.05300	1.26600
P	0.21900	-1.08600	1.38700
P	0.93400	0.05700	-0.38800
C	1.34700	1.73200	0.43600
C	-0.00900	2.45700	0.51700
C	1.95600	1.68900	1.84500
C	2.27400	2.53200	-0.49100
H	-0.48000	2.55100	-0.46600
H	-0.70800	1.92700	1.17200
H	0.13800	3.46300	0.93000
H	2.92000	1.17800	1.87200
H	2.11400	2.71600	2.20000
H	1.29200	1.19500	2.56100
H	2.32700	3.57200	-0.14300
H	3.29400	2.13600	-0.48600
H	1.91000	2.54300	-1.52300
C	2.53300	-0.91500	-0.76000
C	3.10200	-0.39100	-2.09100
C	3.62900	-0.89000	0.31200
C	2.09200	-2.37400	-0.99200

H	2.34600	-0.41700	-2.88300
H	3.47400	0.63300	-2.01300
H	3.94200	-1.02400	-2.40300
H	3.25400	-1.20800	1.28900
H	4.43800	-1.57400	0.02500
H	4.06900	0.10600	0.41800
H	2.93900	-2.95000	-1.38500
H	1.76300	-2.86000	-0.06900
H	1.27800	-2.43700	-1.72300
H	-1.59200	-1.77100	-1.35100
H	-3.21800	0.99800	1.49600
H	-4.55900	1.08100	-2.57900
C	-2.25000	-1.70100	2.38200
H	-1.60000	-2.13400	3.14600
H	-2.90800	-0.96700	2.86300
H	-2.89800	-2.48600	1.97500

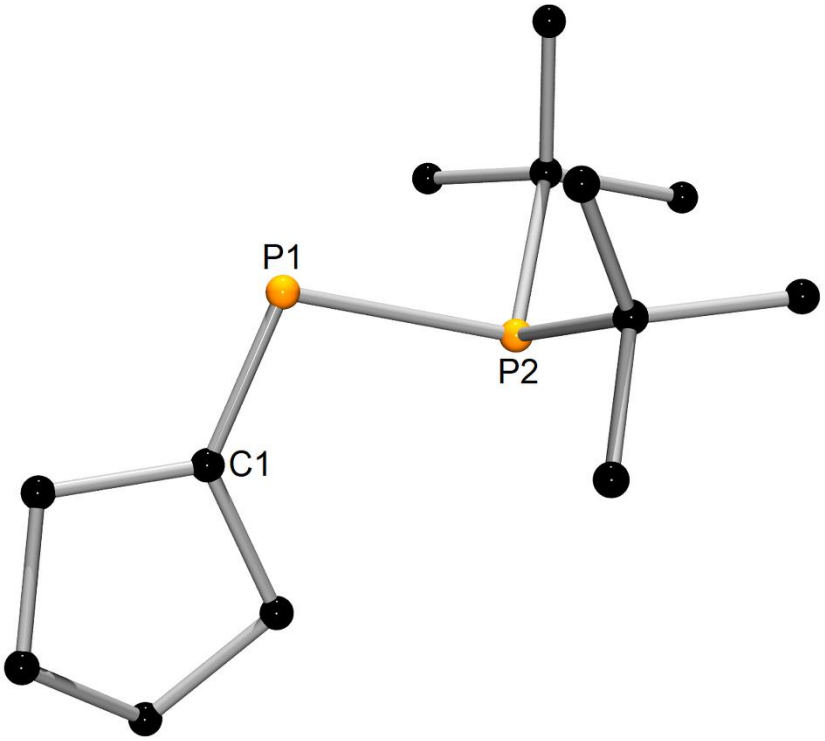

Figure S37. Optimized geometry of $(CH_2)_4C{=}P\text{-}PtBu_2$ (**10a**) (hydrogen atoms have been omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.226, C1-P1 1.683; C1-P1-P2 102.00.

Below are presented xyz coordinates for optimized geometry for **10a**:

P	-0.77032	-0.04353	-0.51760
P	0.68785	-0.52530	1.09427
C	-2.12253	-1.34119	-0.17030
C	-3.12946	-1.29719	-1.33456
C	-2.87160	-1.21701	1.16152
H	-2.62632	-1.42111	-2.29877
H	-3.85263	-2.11503	-1.22181
H	-3.69418	-0.36284	-1.36602
H	-2.18704	-1.18661	2.01517
H	-3.50140	-0.32337	1.19076
H	-3.53181	-2.08408	1.29322
C	-1.35502	1.68853	0.04010
C	-2.65957	2.04473	-0.68795
C	-0.24713	2.63946	-0.45144
H	-3.51325	1.49257	-0.28461
H	-2.87094	3.11321	-0.55504
H	-2.59522	1.84670	-1.76331
H	0.70644	2.43273	0.04734
H	-0.09671	2.55892	-1.53290
H	-0.52186	3.67616	-0.22008
C	-1.41747	-2.70998	-0.22201
H	-0.81609	-2.82107	-1.13125
H	-0.76333	-2.86974	0.64064
H	-2.17197	-3.50623	-0.21896
C	-1.54104	1.91094	1.54848

H	-1.84529	2.95102	1.72450
H	-2.30966	1.26530	1.97630
H	-0.61261	1.74146	2.10187
C	2.16090	-0.32649	0.30443
C	2.49111	0.09990	-1.11463
C	3.47829	-0.57630	1.02917
C	4.00045	-0.14411	-1.27146
H	2.27181	1.17031	-1.22144
H	1.87009	-0.41151	-1.85436
C	4.54542	0.08205	0.14311
H	3.65271	-1.66056	1.06574
H	3.47123	-0.21883	2.06204
H	4.18326	-1.18124	-1.57750
H	4.45633	0.50780	-2.02150
H	5.54293	-0.33828	0.29740
H	4.59847	1.15681	0.35555

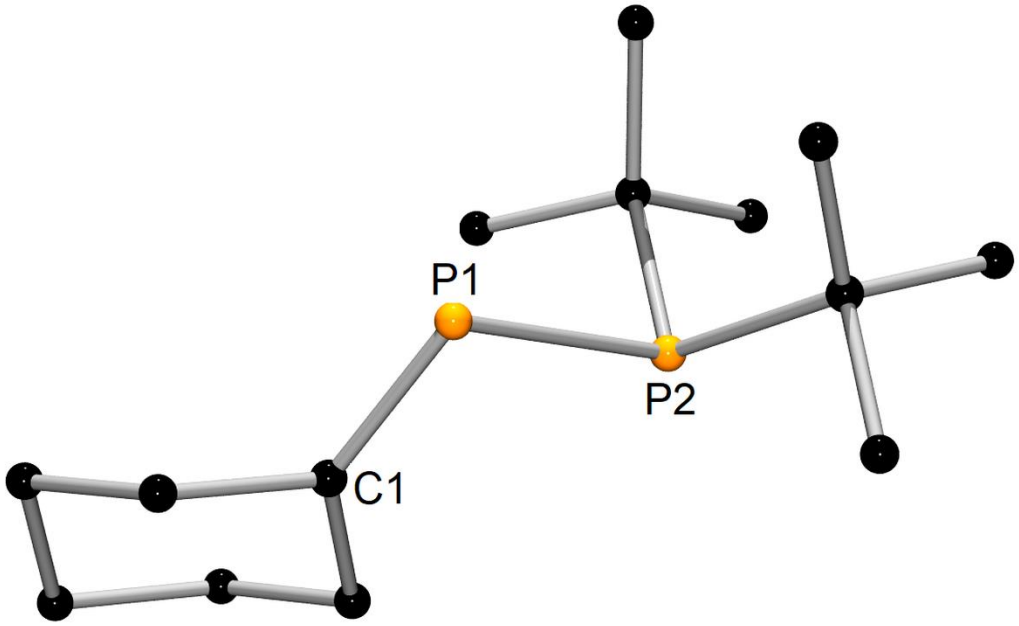

Figure S38. Optimized geometry of $(CH_2)_5C{=}P\text{-}PtBu_2$ (**11a**) (hydrogen atoms have been omitted for clarity). Important bond lengths (Å), bond angles (deg.): P1-P2 2.228, C1-P1 1.687; C1-P1-P2 104.12.

Below are presented xyz coordinates for optimized geometry for **11a**:

P	1.04648	0.01363	-0.55093
P	-0.41358	-0.90958	0.85661
C	1.35484	1.72085	0.24662
C	2.23853	2.53991	-0.71227
C	1.97911	1.71840	1.64646
H	1.80382	2.58032	-1.71611
H	2.32455	3.56828	-0.33851
H	3.24985	2.13749	-0.79811
H	1.40958	1.09965	2.34724
H	3.01159	1.35855	1.62834
H	1.99855	2.74223	2.04223
C	2.53323	-1.14422	-0.24531
C	3.80859	-0.49577	-0.80407
C	2.21242	-2.39214	-1.09089
H	4.16920	0.31127	-0.15968
H	4.60484	-1.24864	-0.85859
H	3.65686	-0.09466	-1.81192
H	1.29438	-2.88591	-0.75305
H	2.09244	-2.14024	-2.14929
H	3.03083	-3.11738	-1.00086
C	-1.88475	-0.82680	0.03604
C	-2.22055	-0.22120	-1.30081
C	-3.10307	-1.37393	0.74770
C	-3.28748	0.87847	-1.14410
H	-2.63439	-1.01768	-1.93784
H	-1.33073	0.16693	-1.80017
C	-4.17424	-0.28140	0.91434

H	-3.52208	-2.18824	0.13754
H	-2.83523	-1.79981	1.71968
C	-4.53479	0.35393	-0.42976
H	-3.54721	1.27355	-2.13219
H	-2.85995	1.70933	-0.56876
H	-5.06374	-0.71016	1.38857
H	-3.78744	0.48949	1.59349
H	-5.25595	1.16549	-0.28320
H	-5.02651	-0.39653	-1.06428
C	-0.01762	2.41569	0.31008
H	-0.51737	2.40674	-0.66510
H	-0.68483	1.94680	1.03919
H	0.11967	3.46301	0.60563
C	2.79351	-1.59407	1.20090
H	3.66462	-2.26193	1.21670
H	3.00743	-0.75707	1.86786
H	1.94746	-2.14806	1.61649

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